Supporting Information

Highly Selective, Efficient Deoxygenative Hydrogenation of Amides Catalyzed by a Manganese Pincer Complex via Metal–Ligand Cooperation

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1. General Information

All experiments were carried out in M-BRAUN Unilab 1200/780 glovebox under inert atmosphere of purified nitrogen or using standard Schlenk techniques. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. Analytical TLC was performed on Merck silica gel 60 F\textsubscript{254} plates. The TLC plates were visualized by either ultraviolet light or treatment with a potassium permanganate (KMnO\textsubscript{4}) stain followed by gentle heating. Purification of products was accomplished by flash column chromatography on silica gel 60 (Merck, particle diameter 40-63 μm). All solvents were purified according to standard procedures under an argon atmosphere, and stored over 4 Å molecular sieves (MS). The [Mn(P\textsubscript{tPr}NP\textsubscript{tPr})(CO)\textsubscript{2}Br] (Mn-I), [Mn(P\textsubscript{tBu}NN\textsubscript{tBu}H)(CO)\textsubscript{2}Br] (Mn-II)\textsuperscript{2} and [Mn(P\textsubscript{Ph}NN\textsubscript{tBu}H)(CO)\textsubscript{2}Br] (Mn-III)\textsuperscript{3} complexes were prepared according to the literature procedures.

NMR spectra were recorded at room temperature either on a Bruker AMX-300 or an AMX-500. Chemical shifts of the NMR spectra are reported relative to CDCl\textsubscript{3} (\textsuperscript{1}H NMR: δ = 7.26 ppm, \textsuperscript{13}C NMR: δ = 77.16 ppm) or benzene-\textsubscript{d}\textsubscript{6} (\textsuperscript{1}H NMR: δ = 7.16 ppm, \textsuperscript{13}C NMR: δ = 128.06 ppm).\textsuperscript{4} Data for \textsuperscript{1}H NMR spectra were reported as follows: chemical shift (ppm), peak shape (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, vt = virtual triplet, brs: broad singlet), coupling constant (Hz), and integration. Data for \textsuperscript{13}C NMR were reported in terms of chemical shift (ppm). GC analysis was carried out on HP 6890 with Hp-5 column, flame ionization detector, and helium as carrier gas.
2. Synthetic Procedures of Hydrogenation and GC Analysis

2.1 General Procedure for the Deoxygenative Hydrogenation of Amides

In a glovebox, a 25 mL stainless steel autoclave with a Teflon tube containing a magnetic stirring bar was charged with amide 2a (39.4 mg, 0.2 mmol) and B(C₆F₅)₃ (153.6 mg, 0.3 mmol). Complex Mn-I (5.3 mg, 0.01 mmol) and 'BuOK (1.3 mg, 0.012 mmol) were suspended in THF (1.0 mL) in a 5.0 mL vial and stirred at room temperature for 10 min, followed by solvent removal in vacuo. The residue was dissolved in dry and degassed m-xylene (2 × 0.5 mL) and the solution was transferred into the Teflon tube of the autoclave. The autoclave was taken out of the glovebox and purged five times with hydrogen and finally pressurized to 50 bar. The reaction mixture was stirred at 150 °C (oil bath temperature) for 72 hours, and then was cooled to room temperature in an ice bath. After releasing the pressure, biphenyl was added as an internal standard and the mixture was transferred into a 20 mL vial. The Teflon tube was washed with CH₂Cl₂ (3 × 1.0 mL) and the washing solutions were combined. The mixture was passed through a short Celite column and then submitted to GC analysis. Finally, the mixture was dried in vacuo and the residue was purified by flash column chromatography (eluted with pentane/ethyl acetate 40:1 to 20:1) to afford N-benzylaniline 3a as a yellowish oil (32.7 mg, 89% yield).
2.2 GC Analysis of the Crude Reaction Mixture

Figure S1. GC spectra of aniline.

Figure S2. GC spectra of benzyl alcohol.

Figure S3. GC spectra of the crude reaction mixture (Table 1, entry 11).
3. Mechanistic Studies

3.1 Synthesis of Complexes 1 and 4 and Characterization Data

Synthesis of Complex 1 and Characterization Data

In a glovebox, Mn-I (106.1 mg, 0.2 mmol) and \(^7\)BuOK (26.9 mg, 0.24 mmol) were suspended in THF (5.0 mL) in a 20.0 mL vial. After stirring at room temperature for 30 min, the resulting solution was dried in vacuo to remove THF. Then pentane (10 mL) was added to the residue and the solution was filtered through a Teflon syringe filter. The solution was then kept in freezer (−38 °C) for 48 hours to give red crystals. The crystals were collected by decantation and dried under vacuum (52.3 mg, 56% yield based on the N\(_2\)-bridged dinuclear manganese complex 5). \(^7\)

\(^1\)H NMR (500 MHz, Benzene-\(d_6\), 298 K) δ (ppm) = 6.31 (m, 1H, Py-H), 6.23 (t, \(^3\)J\(_{HH}\) = 7.7 Hz, 1H, Py-H), 5.31 (d, \(^3\)J\(_{HH}\) = 6.2 Hz, 1H, Py-H), 3.59 (s, 1H, P–CHPy), 2.60 (d, \(J = 9.8\) Hz, 2H, P–CH\(_3\)Py), 2.51 (m, 2H, P–CH(CH\(_3\))\(_2\)), 1.87 (m, 2H, P–CH(CH\(_3\))\(_2\)), 1.21–1.13 (m, 12H, P–CH(CH\(_3\))\(_2\)), 0.98 (dd, \(^3\)J\(_{PH}\) = 15.0, \(^4\)J\(_{HH}\) = 7.1 Hz, 6H, P–CH(CH\(_3\))\(_2\)), 0.82 (dd, \(^3\)J\(_{PH}\) = 14.3, \(^4\)J\(_{HH}\) = 7.1 Hz, 6H, P–CH(CH\(_3\))\(_2\)).

\(^13\)C{\(^1\)H} NMR (126 MHz, Benzene-\(d_6\), 298 K) δ (ppm) = 238.94 – 238.66 (m, Mn–(CO)\(_2\)), 175.30 – 175.06 (m, P–CHPy), 160.45 – 160.33 (m, P–CHPy), 132.35 (s, P–CHPy), 118.23 (d, \(^3\)J\(_{PC}\) = 18.2 Hz, P–CHPy), 98.95 (d, \(^3\)J\(_{PC}\) = 10.6 Hz, P–CHPy), 70.36 (d, \(^1\)J\(_{PC}\) = 43.1 Hz, CHP), 35.88 (d, \(^1\)J\(_{PC}\) = 16.7 Hz, CH\(_2\)P), 26.52 (d, \(^1\)J\(_{PC}\) = 21.4 Hz, P–CH(CH\(_3\))\(_2\)), 25.79 (d, \(^1\)J\(_{PC}\) = 29.0 Hz, P–CH(CH\(_3\))\(_2\)), 19.15 (s, P–CH(CH\(_3\))\(_2\)), 18.71 (s, P–CH(CH\(_3\))\(_2\)), 18.19 (s, P–CH(CH\(_3\))\(_2\)), 18.03 (s, P–CH(CH\(_3\))\(_2\)).

\(^31\)P{\(^1\)H} NMR (202 MHz, Benzene-\(d_6\), 298 K) δ (ppm) \(^8\) = 86.84 (d, \(^2\)J\(_{PP}\) = 72.7 Hz), 69.17 (d, \(^2\)J\(_{PP}\) = 72.7 Hz).

IR (NaCl, plates): \(\nu\) (cm\(^{-1}\)) = 1816.6 (\(\nu_{\text{sym}}\), CO), 1900.4 (\(\nu_{\text{asym}}\), CO).
Figure S4. $^1$H NMR spectrum of complex 1 at room temperature in benzene-$d_6$.  

Figure S5. $^{13}$C($^1$H) NMR spectrum of complex 1 at room temperature in benzene-$d_6$.  

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Figure S6. Phase sensitive HSQC NMR spectrum of complex 1 at room temperature in benzene-$d_6$.

Figure S7. $^{31}\text{P}$\{$^1\text{H}$\} NMR spectrum of complex 1 at room temperature in benzene-$d_6$. 
Synthesis of Complex 4 and Characterization Data

In a glovebox, Mn-I (106.1 mg, 0.2 mmol) and NaH (24.0 mg, 1.0 mmol) were suspended in THF (4.0 mL) in a 20.0 mL vial. After stirring at room temperature for 12 hours, the resulting solution was dried in vacuo to remove THF. Then pentane (10 mL) was added to the residue and the solution was filtered through a Teflon syringe filter. The solution was dried in vacuo to afford the desired product 4 as a yellow solid (43.3 mg, 48% yield).

$^1$H NMR (500 MHz, Benzene-d$_6$, 298 K) δ (ppm) = 6.61 (m, 1H, Py-H), 6.35 (d, $^3$J$_{HH}$ = 7.7 Hz, 2H, Py-H), 2.92 (m, 4H, P–CH$_2$Py), 2.26 (m, 2H, P–CH(CH$_3$)$_2$), 2.04 (m, 2H, P–CH(CH$_3$)$_2$), 1.35 – 1.30 (m, 12H, P–CH(CH$_3$)$_2$), 1.25 (m, 6H, P–CH(CH$_3$)$_2$), 0.95 (m, 6H, P–CH(CH$_3$)$_2$), –4.27 (t, $^2$J$_{PH}$ = 48.1 Hz, 1H, Mn-H).

$^{13}$C{^1}H NMR (126 MHz, Benzene-d$_6$, 298 K) δ (ppm) = 163.30 – 163.19 (vt, $^3$J$_{PC}$ = 6.9 Hz, 2C, Py-C), 133.12 (s, Py-CH), 118.48 – 118.41 (vt, $^3$J$_{PC}$ = 4.4 Hz, 2C, Py-CH), 40.98–40.88 (vt, $^3$J$_{PC}$ = 6.3 Hz, 2C, P–CH$_2$Py), 29.28-29.14 (vt, $^3$J$_{PC}$ = 8.8 Hz, 2C, P–CH(CH$_3$)$_2$), 26.91-26.74 (vt, $^3$J$_{PC}$ = 10.7 Hz, 2C, P–CH(CH$_3$)$_2$), 19.36 (s, P–CH(CH$_3$)$_2$), 19.06 (s, P–CH(CH$_3$)$_2$), 19.02 (s, P–CH(CH$_3$)$_2$), 18.20 (s, P–CH(CH$_3$)$_2$). The two CO resonances are not observed.

$^{31}$P{^1}H NMR (202 MHz, Benzene-d$_6$, 298 K) δ (ppm) = 110.92 (s, 2P).

IR (NaCl, plates): $\tilde{\nu}$ (cm$^{-1}$) = 1804.0 ($\nu_{sym}$, CO), 1878.4 ($\nu_{asym}$, CO).
Figure S8. $^1$H NMR spectrum of complex 4 at room temperature in benzene-$d_6$.

Figure S9. $^{13}$C($^1$H) NMR spectrum of complex 4 at room temperature in benzene-$d_6$. 
**Figure S10.** Phase sensitive HSQC NMR spectrum of complex 4 at room temperature in benzene-$d_6$.

**Figure S11.** $\text{\textsuperscript{31}P}\{^1\text{H}\}$ NMR spectrum of complex 4 at room temperature in benzene-$d_6$.  

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3.2 NMR Studies of Dearomatization and Aromatization starting with Mn-I

In a glovebox, Mn-I (5.3 mg, 0.01 mmol) and tBuOK (1.3 mg, 0.012 mmol) were suspended in THF (0.5 mL) in a 5.0 mL vial. After stirring at room temperature for 10 min, the resulting solution was transferred into a J. Young valve NMR tube and the $^{31}\text{P}\{^1\text{H}\}$ NMR measured directly. The $^{31}\text{P}\{^1\text{H}\}$NMR (121 MHz, THF) spectrum is as follows:

The above mixture in the J. Young valve NMR tube was frozen by liquid nitrogen and then carefully placed under vacuum. Then the NMR tube was warmed to room temperature and charged with 1 atm of dihydrogen. After shaking for 1 min, the NMR was measured directly. The spectra of $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF) and $^1\text{H}$ NMR (300 MHz, THF) are as follows:
The $^{31}$P\{\textsuperscript{1}H\} NMR (121 MHz, THF) spectrum of Mn-I is as follows:

Combined $^{31}$P\{\textsuperscript{1}H\} NMR spectra (121 MHz, THF):
3.3 Deoxygenative Hydrogenation Catalyzed by Complex 4

In a glovebox, a 25 mL stainless steel autoclave with a Teflon tube containing a magnetic stir bar was charged with 2a (39.4 mg, 0.2 mmol), 4 (4.5 mg, 0.01 mmol), B(C$_6$F$_5$)$_3$ (153.6 mg, 0.3 mmol) and degassed m-xylene (1.0 mL). The autoclave was taken out of the glovebox and purged five times with hydrogen and finally pressurized to 50 bar. The reaction mixture was stirred at 150 ºC (oil bath temperature) for 72 hours, and then was cooled to room temperature in an ice bath. After releasing the pressure, biphenyl was added as an internal standard and the mixture was transferred into a 20 mL vial. The Teflon tube was washed with CH$_2$Cl$_2$ (3 × 1.0 mL), combined the solution. The mixture was passed through a short Celite column and then submitted to analysis by GC. Finally, the mixture was dried in vacuo and the residue was purified by flash column chromatography (eluted with pentane/ethyl acetate 40:1 to 20:1) to afford N-benzyylaniline (3a) as a yellowish oil (33.4 mg, 91% yield).

3.4 Hydrogenation of Imine 6 Catalyzed by Complex Mn-I

**Synthesis of Imine 6 and Characterization Data**

Benzaldehyde (1.0 mL, 10 mmol), aniline (911 µL, 10 mmol) and magnesium sulfate (601.9 mg, 5 mmol) were mixed in THF (20 mL) under argon. The mixture was stirred at room temperature for 10 hours. After filtration, the mixture was dried in vacuo and the residue was purified by flash column chromatography using deactivated silica (eluted with pentane) to afford N-benzyldieneaniline 6 as a yellowish solid (1.6 g, 88% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$) δ (ppm) = 8.62 (s, 1H), 7.96 – 7.93 (m, 2H), 7.57 – 7.49 (m, 3H), 7.42 (dd, J = 8.4, 7.1 Hz, 2H), 7.30 – 7.22 (m, 3H).

$^{13}$C NMR (126 MHz, DMSO) δ (ppm) = 160.67, 151.45, 135.99, 131.45, 129.18, 128.79, 128.65, 125.95, 120.95.
Procedure for the Hydrogenation of Imine 6

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{Ph} \\
6 & \quad \xrightarrow{\text{Mn-I (5 mol%), } \text{H}_2 (50 \text{ bar}) , \text{B(C}_6\text{F}_5)_3 (\text{x eq.})} & \quad \text{Ph} & \quad \text{N} & \quad \text{Ph} \\
\text{m-xylene, 150 °C, t (h)} & \quad \xrightarrow{\text{B(C}_6\text{F}_5)_3 (\text{x eq.})} & \quad \text{Ph} & \quad \text{N} & \quad \text{Ph} \\
& & & & 3a
\end{align*}
\]

In a glovebox, a 25 mL stainless steel autoclave with a Teflon tube containing a magnetic stirring bar was charged with 6 (36.2 mg, 0.2 mmol) and B(C₆F₅)₃ (0–0.5 eq.). In a 5.0 mL vial, Mn-I (5.3 mg, 0.01 mmol) and t-BuOK (1.3 mg, 0.012 mmol) were suspended in THF (1.0 mL). After stirring at room temperature for 10 min, the resulting solution was dried in vacuo to remove THF. Then the catalyst vessel was extracted with dry and degassed m-xylene (2 × 0.5 mL) and the solution was transferred into the Teflon tube of the autoclave. The autoclave was taken out of the glovebox and purged five times with hydrogen and finally pressurized to 50 bar. The reaction mixture was stirred at 150 °C (oil bath temperature) for the specified hours, and then was cooled to room temperature in an ice bath. After releasing the pressure, biphenyl was added as an internal standard and the mixture was transferred into a 20 mL vial. The Teflon tube was washed with CH₂Cl₂ (3 × 1.0 mL) and the washings were combined. The mixture was passed through a short Celite column and then analyzed by GC. Finally, the mixture was dried in vacuo and the residue was purified by flash column chromatography (eluted with pentane/ethyl acetate 40:1 to 20:1) to afford N-benzylaniline 3a.
4. X-ray Crystal Structures of Complexes 4 and 5

Single crystal XRD were measured by fine-focus sealed tube dual source Rigaku XtaLAB PRO dual source equipped with Pilatus 200K for complex 4 (Cu radiation) and sealed tube diffractometers Bruker Kappa Apex-II CCD with Mo radiation for complex 5. Data collection was performed in low temperature under LN. Data were processed with APEX-2 package program (APEX) or CrysAlisPRO (Rigaku). Structures were solved using SHELXT and for complex 4 and SHELXS for complex 5. Refinement performed based on $F^2$ with SHELXL with full matrix least-squares. Hydrogens were calculated and refined in riding mode. Hydride was located in the electron density map. Full details can be found in the CIF files and Tables S1-S3.

**Figure S12.** X-ray crystal structure of complex 4. Atoms are presented as thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity except the hydride.

**Figure S13.** X-ray crystal structure of complex 5. Atoms are presented as thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity except H7 and H28 (dearomatized side arms).
Table S1. Selected bond lengths [Å] and bond angles [˚] of 4.

| Bond Lengths [Å] | Bond Angles [˚] |
|------------------|-----------------|
| Mn(1)-C(20)     | 1.7689(19)      | C(20)-Mn(1)-C(21) | 92.76(8) |
| Mn(1)-C(21)     | 1.796(2)        | C(20)-Mn(1)-N(1) | 171.38(8) |
| Mn(1)-N(1)      | 2.0983(14)      | C(21)-Mn(1)-N(1) | 95.35(7)  |
| Mn(1)-P(2)      | 2.2264(5)       | C(20)-Mn(1)-P(2) | 94.73(6)  |
| Mn(1)-P(1)      | 2.2373(5)       | C(21)-Mn(1)-P(2) | 90.08(6)  |
| Mn(1)-H         | 1.58(3)         | N(1)-Mn(1)-P(2)  | 82.34(4)  |
| P(1)-C(1)       | 1.8458(18)      | C(20)-Mn(1)-H    | 98.87(6)  |
| P(1)-C(11)      | 1.862(2)        | C(21)-Mn(1)-P(1) | 99.11(6)  |
| P(1)-C(8)       | 1.8619(19)      | N(1)-Mn(1)-P(1)  | 82.76(4)  |
| P(2)-C(7)       | 1.8403(18)      | P(2)-Mn(1)-P(1)  | 163.14(2) |
| P(2)-C(14)      | 1.8578(19)      | C(20)-Mn(1)-H    | 84.4(10)  |
| P(2)-C(17)      | 1.8582(2)       | C(21)-Mn(1)-H    | 177.1(10) |
| C(1)-C(2)       | 1.497(2)        | N(1)-Mn(1)-H     | 87.6(10)  |
| C(6)-C(7)       | 1.499(2)        | P(2)-Mn(1)-H     | 90.7(12)  |
| O(1)-C(20)      | 1.163(2)        | P(1)-Mn(1)-H     | 80.9(12)  |
| O(2)-C(21)      | 1.163(3)        | C(1)-P(1)-Mn(1)  | 101.62(6) |
|                 |                 | C(7)-P(2)-Mn(1)  | 100.00(6) |

Table S2. Selected bond lengths [Å] and bond angles [˚] of 5.

| Bond Lengths [Å] | Bond Angles [˚] |
|------------------|-----------------|
| Mn(1)-C(20)     | 1.7922(18)      | C(20)-Mn(1)-C(21) | 89.40(8) |
| Mn(1)-C(21)     | 1.7941(18)      | C(20)-Mn(1)-N(3) | 176.02(7) |
| Mn(1)-N(3)      | 1.9393(14)      | C(21)-Mn(1)-N(3) | 94.16(7)  |
| Mn(1)-N(1)      | 2.0845(14)      | C(20)-Mn(1)-N(1) | 92.65(7)  |
| Mn(1)-P(1)      | 2.3022(5)       | C(21)-Mn(1)-N(1) | 177.93(7) |
| Mn(1)-P(2)      | 2.3091(5)       | N(3)-Mn(1)-N(1)  | 83.78(5)  |
| P(1)-C(1)       | 1.8299(18)      | C(20)-Mn(1)-P(1) | 88.49(6)  |
| P(1)-C(11)      | 1.8541(18)      | C(21)-Mn(1)-P(1) | 98.99(6)  |
| P(1)-C(8)       | 1.8579(17)      | N(3)-Mn(1)-P(1)  | 92.71(4)  |
| P(2)-C(7)       | 1.7509(18)      | N(1)-Mn(1)-P(1)  | 81.34(4)  |
| P(2)-C(14)      | 1.8546(17)      | C(20)-Mn(1)-P(2) | 87.17(6)  |
| P(2)-C(17)      | 1.8740(18)      | C(21)-Mn(1)-P(2) | 97.24(6)  |
| C(1)-C(2)       | 1.506(3)        | N(3)-Mn(1)-P(2)  | 90.60(4)  |
| C(6)-C(7)       | 1.385(2)        | N(1)-Mn(1)-P(2)  | 82.60(4)  |
| C(7)-H(7)       | 0.9500          | P(1)-Mn(1)-P(2)  | 163.14(8) |
| C(20)-O(1)      | 1.153(2)        | O(1)-C(20)-Mn(1) | 178.42(16)|
| C(21)-O(2)      | 1.155(2)        | C(42)-Mn(2)-C(41)| 89.25(8) |
| Mn(2)-C(42)     | 1.7908(17)      | C(42)-Mn(2)-N(4) | 91.47(7) |
Table S3. Crystal data, data collection and structure refinement of 4 and 5.

|                      | Complex 4                                      | Complex 5                                      |
|----------------------|-----------------------------------------------|-----------------------------------------------|
| Diffractometer       | Rigaku XtaLAB PRO                             | Bruker APEX-II Kappa CCD                       |
| Empirical formula    | C$_{21}$H$_{36}$MnNO$_2$P$_2$                 | C$_{42}$H$_{68}$Mn$_2$N$_4$O$_4$P$_4$         |
| Crystal description  | Yellow chunk                                  | Orange chunk                                  |
| Formula weight (g/mol)| 451.39                                        | 926.76                                        |
| Temperature (K)      | 100                                           | 100                                           |
| Wavelength (Å)       | 1.54184                                       | 0.71073                                       |
| Crystal system       | Monoclinic                                    | Monoclinic                                    |
| Space group          | C2/c                                          | P21/c                                         |
| a (Å)                | 18.6272(2)                                    | 11.6109(2)                                    |
| b (Å)                | 10.6230(1)                                    | 18.5885(2)                                    |
| c (Å)                | 23.1001(3)                                    | 21.5322(3)                                    |
| α (°)                | 90                                            | 90                                            |
| β (°)                | 101.1920(10)                                  | 99.2180(10)                                   |
| γ (°)                | 90                                            | 90                                            |
| Volume (Å$^3$)       | 4484.04(9)                                    | 4587.26(11)                                   |
| Z                    | 8                                             | 4                                             |
| Density calculated (Mg/m$^3$) | 1.337                                        | 1.342                                         |
| Absorption coefficient (mm$^{-1}$) | 6.254                                        | 0.734                                         |
| F(000)               | 1920                                          | 1960                                          |
| Crystal size (mm$^3$) | 0.046 x 0.023 x 0.019 | 0.447 x 0.259 x 0.184 |
|----------------------|-------------------------|------------------------|
| Theta range for data collection (°) | 4.815 to 80.065 | 1.455 to 27.513 |
| Reflection collected (Unique) | 24184(4854) | 39322(10493) |
| R int | 0.0324 | 0.0345 |
| Completeness | 99.9% | 99.7% |
| Data/restraints/parameters | 4854 \ 0 \ 256 | 10493 \ 0 \ 521 |
| Goodness-of-fit on F$^2$ | 1.100 | 1.033 |
| Final R [I>2σ(I)] | R1=0.0391, wR2=0.1116 | R1=0.0309, wR2=0.0710 |
| R (all data) | R1=0.0414, wR2=0.1133 | R1=0.0426, wR2=0.0773 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.430 and -0.471 | 0.369 and -0.259 |

5. Deoxygenative Hydrogenation of Formamides Catalyzed by Complex Mn-I

We also examined the reactivity of the above two formamides. Under our optimal condition, full conversions were observed. However, the isolated yields of the desired amines were low, due to formation of some byproducts.
6. Characterization Data of Amine Products

N-Benzylaniline (3a)

![N-Benzylaniline (3a)](image)

**Yield:** 89% (yellowish oil, 32.7 mg).

**TLC:** $R_f = 0.75$ (pentane/ethyl acetate 20:1) [UV].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.39 (m, 4H), 7.31 (m, 1H), 7.22 (t, $J = 7.7$ Hz, 2H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.69 (d, $J = 7.9$ Hz, 2H), 4.36 (s, 2H), 3.85 (brs, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ (ppm) = 148.06, 139.41, 129.38, 128.74, 127.67, 127.36, 117.84, 113.12, 48.54.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^9,10$

N-Benzyl-4-methylaniline (3b)

![N-Benzyl-4-methylaniline (3b)](image)

**Yield:** 81% (yellowish oil, 32.1 mg).

**TLC:** $R_f = 0.72$ (pentane/ethyl acetate 20:1) [UV].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.45 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.62 (d, $J = 8.4$ Hz, 2H), 4.34 (s, 2H), 2.28 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ (ppm) = 145.48, 139.39, 129.87, 128.71, 127.74, 127.34, 113.53, 49.04, 20.54.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^9$
**N-Benzyl-4-methoxyaniline (3c)**

![Chemical structure of N-Benzyl-4-methoxyaniline (3c)](attachment:image)

**Yield:** 69% (colorless oil, 29.4 mg).

**TLC:** $R_f = 0.50$ (pentane/ethyl acetate 20:1) [UV].

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.41 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 6.79 (d, $J = 8.9$ Hz, 2H), 6.64 (d, $J = 8.9$ Hz, 2H), 4.29 (s, 2H), 3.75 (s, 3H).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ (ppm) = 152.56, 142.09, 139.49, 128.73, 127.79, 127.37, 115.04, 114.59, 55.94, 49.60.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^9$

**N-Benzyl-4-fluoroaniline (3d)**

![Chemical structure of N-Benzyl-4-fluoroaniline (3d)](attachment:image)

**Yield:** 86% (yellowish oil, 34.5 mg).

**TLC:** $R_f = 0.52$ (pentane/ethyl acetate 20:1) [UV].

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.41 – 7.34 (m, 4H), 7.31 (m, 1H), 6.90 (t, $J = 8.7$ Hz, 2H), 6.61 – 6.58 (m, 2H), 4.31 (s, 2H), 3.92 (brs, 1H).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ (ppm) = 157.04, 155.17, 144.39, 144.37, 139.20, 128.78, 127.85, 127.46, 115.88, 115.71, 113.98, 113.92, 49.15.

**$^{19}$F NMR** (282 MHz, CDCl$_3$) $\delta$ (ppm) = -128.62.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{11}$
**N-Benzyl-4-chloroaniline (3e)**

![Chemical structure of N-Benzyl-4-chloroaniline (3e)](attachment:image)

**Yield:** 87% (colorless oil, 38.0 mg).

**TLC:** $R_f = 0.75$ (pentane/ethyl acetate 20:1) [UV].

$^1\text{H NMR}$ (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.37 – 7.35 (m, 4H), 7.34 – 7.28 (m, 1H), 7.13 (d, $J = 8.8$ Hz, 2H), 6.57 (d, $J = 8.9$ Hz, 2H), 4.32 (s, 2H).

$^{13}\text{C NMR}$ (126 MHz, CDCl$_3$) $\delta$ (ppm) = 146.54, 138.89, 129.19, 128.82, 127.58, 127.52, 122.41, 114.21, 48.57.

The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra are consistent with those reported in the literature.$^9$

**N-Benzyl-4-bromoaniline (3f)**

![Chemical structure of N-Benzyl-4-bromoaniline (3f)](attachment:image)

**Yield:** 76% (colorless oil, 39.7 mg).

**TLC:** $R_f = 0.60$ (pentane/ethyl acetate 20:1) [UV].

$^1\text{H NMR}$ (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.37 (m, 4H), 7.31 (m, 1H), 7.27 (d, $J = 8.9$ Hz, 2H), 6.53 (d, $J = 8.8$ Hz, 2H), 4.32 (s, 2H).

$^{13}\text{C NMR}$ (126 MHz, CDCl$_3$) $\delta$ (ppm) = 147.04, 138.89, 132.04, 128.81, 127.52, 127.50, 114.62, 109.32, 48.39.

The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra are consistent with those reported in the literature.$^9,^{12}$
Dibenzylamine (3g)

![Dibenzylamine structure]

**Yield:** 83% (yellowish oil, 32.7 mg).

**TLC:** $R_f = 0.58$ (pentane/ethyl acetate 1:1) [UV, KMnO₄].

$^1$H NMR (500 MHz, CDCl₃) $\delta$ (ppm) = 7.40 – 7.33 (m, 8H), 7.31 – 7.25 (m, 2H), 3.84 (s, 4H), 1.90 (brs, 2H).

$^{13}$C NMR (126 MHz, CDCl₃) $\delta$ (ppm) = 140.27, 128.52, 128.29, 127.09, 53.22.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{13}$

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$N$-Benzycyclohexanamine (3h)

![$N$-Benzycyclohexanamine structure]

**Yield:** 71% (yellowish oil, 26.9 mg).

**TLC:** $R_f = 0.15$ (pentane/ethyl acetate 1:1) [KMnO₄].

$^1$H NMR (500 MHz, CDCl₃) $\delta$ (ppm) = 7.39 – 7.27 (m, 4H), 7.24 (m, 1H), 3.82 (s, 2H), 2.49 (, 1H), 1.94 – 1.90 (m, 2H), 1.76 – 1.73 (m, 2H), 1.62 (m, 1H), 1.27 – 1.13 (m, 5H).

$^{13}$C NMR (126 MHz, CDCl₃) $\delta$ (ppm) = 140.90, 128.50, 128.23, 126.91, 56.28, 51.09, 33.60, 26.29, 25.12.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{13}$
**N-Benzylhexan-1-amine (3i)**

Yield: 68% (yellowish oil, 26.0 mg).

TLC: $R_t = 0.20$ (pentane/ethyl acetate 1:1) [KMnO$_4$].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.33 (m, 4H), 7.28 – 7.22 (m, 1H), 3.80 (s, 2H), 2.63 (d, $J = 7.3$ Hz, 2H), 1.66 (brs, 1H), 1.55 – 1.49 (m, 2H), 1.33 – 1.28 (m, 6H), 0.89 (t, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ (ppm) = 140.54, 128.48, 128.25, 126.99, 54.17, 49.61, 31.91, 30.15, 27.16, 22.75, 14.17.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{14}$

**N-Ethylaniline (3j)**

Yield: 52% (colorless oil, 12.5 mg).

TLC: $R_t = 0.68$ (pentane/ethyl acetate 20:1) [UV].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.19 (m, 2H), 6.72 (m, 1H), 6.65 – 6.62 (m, 2H), 3.17 (q, $J = 7.1$ Hz, 2H), 1.26 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ (ppm) = 148.31, 129.36, 117.59, 113.09, 38.78, 14.95.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{15}$
**N-Propylaniline (3k)**

![N-Propylaniline](image)

**Yield:** 70% (colorless oil, 19.0 mg).

**TLC:** $R_t = 0.63$ (pentane/ethyl acetate 20:1) [UV].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.21 (m, 2H), 6.82 − 6.74 (m, 3H), 3.12 − 3.09 (m, 2H), 1.68 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ (ppm) = 146.60, 129.48, 119.15, 114.53, 47.31, 22.30, 11.69.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{16}$

**N-Isobutylaniline (3l)**

![N-Isobutylaniline](image)

**Yield:** 55% (colorless oil, 16.4 mg).

**TLC:** $R_t = 0.83$ (pentane/ethyl acetate 20:1) [UV].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.21 − 7.16 (m, 2H), 6.74 (m, 1H), 6.72 − 6.68 (m, 2H), 2.95 (d, $J = 6.8$ Hz, 2H), 1.91 (m, 1H), 0.99 (d, $J = 6.7$ Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ (ppm) = 147.53, 129.42, 118.23, 113.80, 52.77, 27.93, 20.65.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{16}$
N-Benzyl-N-ethylethanamine (3o)

![Chemical Structure](image)

**Yield:** 21% (colorless oil, 7.0 mg).

**TLC:** $R_f = 0.30$ (dichloromethane/methanol 20:1) [KMnO$_4$].

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ (ppm) = 7.36 – 7.29 (m, 4H), 7.27 – 7.23 (m, 1H), 3.59 (s, 2H), 2.55 (q, $J = 7.1$ Hz, 4H), 1.07 (t, $J = 7.1$ Hz, 6H).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ (ppm) = 139.77, 129.10, 128.27, 126.87, 57.60, 46.81, 11.78.

The $^1$H and $^{13}$C NMR spectra are consistent with those reported in the literature.$^{13}$
7. $^1$H and $^{13}$C NMR Spectra of the Synthesized Compounds
Ph=N^Ph
6

Ph=N^Ph
6
8. Infrared Spectra of Complexes 1 and 4

![Infrared Spectra of Complexes 1 and 4](image-url)
9. References

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(5) It is very important to wash the Teflon tube with dichloromethane, which will dissolve all components of the reaction mixture including some of the unreacted starting material amides.

(6) From GC spectra of the crude reaction mixture, only trace amount of aniline and benzyl alcohol were observed.

(7) In solution the manganese complex 1 exists as a monomer, and in the solid state it exists as a N$_2$-bridged dinuclear manganese complex 5.

(8) AB system.

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