Supporting Information

Synthesis of Pyrazines and Quinoxalines via Acceptorless Dehydrogenative Coupling Routes Catalyzed by Manganese Pincer Complexes

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1. General Procedure

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques under argon atmosphere. All solvents were reagent grade or better. Non-deuterated solvents were dried over sodium/benzophenoneketyl (tetrahydrofuran, n-pentane, 1,4-dioxane, and toluene), and distilled under argon atmosphere. All solvents were degassed with argon and kept in the glove box over activated 4Å molecular sieves. Deuterated solvents were purchased from Aldrich, purged with argon and stored over activated 4Å molecular sieves in the glove box. $^1$H, and $^{13}$C NMR spectra were recorded using Bruker AMX-300 and 500 NMR spectrometer. All spectra were recorded at 298 K, unless otherwise noted. $^1$H NMR and $^{13}$C{H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual signals of an appropriate deuterated solvent. $^{31}$P{H} NMR chemical shifts are reported in ppm downfield from $\text{H}_3\text{PO}_4$ and referenced to an external 85% solution of phosphoric acid in $\text{D}_2\text{O}$. NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; m, multiplet. GCMS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. Most of the commercially available reagents were used as received. Elemental analyses were performed on a Thermo Finnigan Italia S.p.A-FlashEA 1112 CHN Elemental Analyzer. IR spectra were recorded on Thermo Nicolet 6700 FT-IR.

Ligand Acr-PNP$^\text{Ph}$ and the Manganese complexes 3, 4, 5 were prepared according to literature procedures.$^{1-4}$

2. Experimental

a) Synthesis of complex Mn(Acr-PNP$^{\text{Ph}}$)(CO)$_2$Br (1)

To a solution of the Acr-PNP$^{\text{Ph}}$ ligand (140 mg, 0.26 mmol) in 5 mL THF was added under $\text{N}_2$ atmosphere an orange solution of Mn(CO)$_3$Br (72 mg, 0.26 mmol) in 10 mL THF and the reaction mixture was kept stirring at 65°C for 12 h (Note: The $\text{N}_2$ atmosphere need to be removed occasionally in vacuo). The solvent was concentrated in
vacuo. The solid residue was washed with pentane (10 mL), which on drying gives a green solid in 92% (176 mg) yield. A green single crystal was obtained by slow evaporation of the dilute THF solution. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 7.31$ (m, 6H, PPh$_2$), 7.45 (m, 10H, PPh$_2$), 7.80 (t, $J = 7.4$ Hz, 2H, Acr), 8.42 (m, 4H, PPh$_2$), 8.26 (d, $J = 8$ Hz, 2H, Acr), 8.42 (m, 2H, Acr), 9.02 (s, AcrC=H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 125 MHz): $\delta = 126.5, 128.0, 128.2, 129.1, 129.7, 130.0, 131.3, 131.8, 132.2, 132.6$ (t), 133.0, 135.2, 136.9 (t), 138.3 (t), 139.2, 140.8, 154.8 (t), 227 (CO), 230 (CO). $^{31}$P{$^1$H} NMR (CDCl$_3$, 202.4 MHz): $\delta = 67.6$ (s). IR (thin film, NaCl) = 1928 cm$^{-1}$($\nu$CO), 1859 cm$^{-1}$($\nu$CO).

HRMS: m/z 658 (1-Br), 686 (1-Br+CO); Anal Calcd for C$_{39}$H$_{27}$MnNO$_2$P$_2$ 0.5C$_4$H$_8$O: C: 63.58; H: 4.03; N: 1.81. Found: C: 62.72; H: 3.86; N: 1.78.

b) Synthesis of complex Mn(HAcr-PNP$^{Ph}$)(CO)$_2$(BH$_3$) (2)

147 mg (0.20 mmol) of Mn(Acr-PNP$^{Ph}$)(CO)$_2$Br (complex 1) was taken in 10 mL THF under N$_2$ atmosphere and 0.74 mg (2 mmol) NaBH$_4$ was added and stirred for 48h at room temperature, and the green solution turned orange. The THF was evaporated in vacuo and the residue was extracted with 20 ml benzene and filtered through a small pad of Celite. The benzene was evaporated and the residue was washed with pentane to obtain an orange solid. The orange crude product was dissolved in THF (5 mL), layered with pentane and kept in the refrigerator to obtain orange crystals in 80% (107 mg) yield. $^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = -7.40$ (b, 1H, BH$_3$-H$^a$), 2.11 (b, 2H, BH$_3$-H$^b$), 3.42 (d, $J = 19.2$Hz, 1H, Acr-C$^9$-H$_2$), 3.75 (d, $J = 19.2$Hz, 1H, Acr-C$^9$-H$_2$), 6.82 (m, 4H, Ph), 6.95-7.07 (m, 11H, Ph, Acr), 7.40 (b, 2H, Acr), 7.58 (b, 4H, Ph), 7.86 (b, 1H, Acr) 8.21 (b, 4H, Ph). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 125 MHz): $\delta = 31.2$ (AcrC$^9$), 117.5, 124.2, 129.1, 129.5, 129.8, 130.7, 131.3, 131.8, 132.0, 134.0, 136.8 (t), 160.6 (t), 224.5 (CO), 230.1 (CO); $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 202 MHz): $\delta = 79.5$ (s); IR (thin film, NaCl) = 1868 cm$^{-1}$($\nu$CO), 1904 cm$^{-1}$($\nu$CO), 2347 cm$^{-1}$, 2424cm$^{-1}$ ($\nu$B-H). HRMS: m/z 602 (2-BH$_3$-2CO), 643 (2-CO). Anal Calcd for C$_{39}$H$_{31}$MnBNO$_2$P$_2$ 0.5C$_4$H$_8$O: C: 69.41; H: 4.97; N: 1.97. Found: C: 64.38; H: 4.79; N: 1.79.
c) General procedure for the catalytic reactions:

For Table 1: 0.01 mmol of the catalyst (2, or, 3, 4, 5, 1 for entry 12, 13, 14, 15 in table 1) in 2 mL dry toluene (THF or 1,4 dioxane for entry 2 and 3) were placed in a 50 ml Teflon Schlenk tube and 0.5 mmol of 2-phenylglycinol was added under N₂ atmosphere. The mentioned amount of base (KH, or tBuOK, NaOMe and NaOEt for entries 8, 9 and 10, Table 1) was added to the reaction mixture and the tube was closed and heated at 150 ºC (or 125 ºC, Table 1, entry 4) with stirring for 24 h (12h in entry 5). The reaction mixture was then cooled down in an ice bath and the formed H₂ was vented off. The reaction products were analyzed by GC-MS and ¹H NMR. The formation of 2,5-diphenylpyrazine was determined by GCMS and the isolated yield of the product was determined after column chromatography.

Substrate scope (for Table 2): 0.01 mmol of the catalyst (2) and 3mol% KH in 2 mL dry toluene were placed in a 50 ml Teflon Schlenk tube and 0.5 mmol of the 2-amino alcohol derivative was added under N₂ atmosphere. The closed tube was heated at 150 ºC with stirring for 24 h. The reaction mixture was then cooled down in an ice bath and the formed H₂ was vented off. The reaction products were analyzed by GC-MS and ¹H NMR, and the pyrazines were isolated after column chromatography.

Substrate scope (for Table 3): 0.01 mmol of the catalyst (2) and 3mol% KH in 2 mL dry toluene were placed in a 50 ml Teflon Schlenk tube and 0.5 mmol of 1,2-diaminobenzene and 0.5 mmol of 1,2-diol derivative were added under N₂ atmosphere. The closed tube was heated at 150 ºC with stirring for 36 h. The reaction mixture was then cooled down in an ice bath and the formed H₂ was vented off. The reaction products were analyzed by GC-MS and ¹H NMR. The formed quinoxalines were isolated after column chromatography.
Table S1. Optimization Table$^a$

![Chemical structures](image)

| Entry | Catalyst (2 mol%) | Base (3 mol%) | Yield$^b$ (%) |
|-------|-------------------|---------------|---------------|
| 1     | 2                 | KH            | 99            |
| 2$^c$ | 2                 | KH            | 90            |
| 3$^d$ | 2                 | KH            | 95            |
| 4$^e$ | 2                 | KH            | 99            |
| 5$^f$ | 2                 | KH            | 99            |
| 6$^g$ | 2                 | KH            | 92            |
| 7     | 2                 | -             | 05            |
| 8     | 2                 | tBuOK         | 15            |
| 9     | 2                 | NaOMe         | 10            |
| 10    | 2                 | NaOEt         | 81            |
| 11$^h$| 2                 | KH            | 99            |
| 12    | 3                 | KH            | 24            |
| 13    | 4                 | KH            | 23$^i$        |
| 14    | 5                 | KH            | 64            |
| 15    | 1                 | KH            | 95            |

$^a$Reaction conditions: catalyst [Mn] (2 mol%), substrate (0.5 mmol), base (3 mol%), 150°C, 24h, solvent (2 ml), $^b$GC-MS yield with mesitylene as internal standard, $^c$solvent THF, $^d$solvent 1,4-dioxane, $^e$reaction temperature 125°C, reaction time 24h, $^f$reaction time 12h, $^g$open system under N$_2$ flow at 125°C, $^h$in presence of 300 eq. of Hg, $^i$other unidentified products formed, total conversion 40%.
Table S2. Synthesis of pyrazines from β-amino alcohols catalyzed by complex 2\textsuperscript{a}

\[
\begin{array}{ccccccc}
\text{Entry} & \text{Substrate} & \text{Product} & \text{GC-Mass} & \text{GC-MS-t\textsubscript{r}} & \text{Conv.} & \text{Yield\textsuperscript{b}}
\hline
1 & \text{Ph} \text{-} \text{NH}_{2} & \text{Ph} \text{-} \text{N} & 260 & 20.3 & 99 & 95 \\
2 & \text{NH}_{2} & \text{N} & 164 & 11.8 & 99 & 86 \\
3 & \text{NH}_{2} & \text{N} & 192 & 13.6 & 99 & 80 \\
4 & \text{NH}_{2} & \text{N} & 192 & 14.6 & 99 & 65 \\
5 & \text{NH}_{2} & \text{N} & 164 & 12.7 & 99 & 95 \\
6 & \text{NH}_{2} & \text{N} & 136 & 10.3 & 99 & 40 \\
7 & \text{NH}_{2} & \text{N} & 108 & 8.2 & 99 & 45 \\
8\textsuperscript{c} & \text{H} & \text{N} & 164 & 16.8 & 65 & 30 \\
\end{array}
\]

\textsuperscript{a}Optimized reaction conditions: catalyst 2 (2 mol%), β-amino alcohol (0.5mmol), KH (3mol%), 150°C, 24h, toluene. \textsuperscript{b}Isolated yield. \textsuperscript{c}reaction time 48h.

GC-MS data of the benzimidazole products was obtained using an HP 6890 GC chromatograph equipped with flame ionization and thermal conductivity detectors, and a HP 5973 (MS detector) instruments, equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas with a flow rate of 1 ml/min.
Table S3. Synthesis of pyrazines from 1,2-diaminobenzene and 1,2 diols

| Entry | Alcohols | Products | GC-Mass | GC-MS-\(t_r\) | Conv. (%) | Yield (%)\(^b\) |
|-------|----------|----------|---------|---------------|-----------|---------------|
| 1     |          | ![Structure](image) | 158     | 13.9          | 99        | 95            |
| 2     |          | ![Structure](image) | 186     | 15.6          | 45        | 40 (5)        |
| 3     |          | ![Structure](image) | 242     | 18.6          | 98        | 49 (24)       |
| 4     |          | ![Structure](image) | 298     | 21.16         | 99        | 65 (35)       |
| 5\(^c\) |          | ![Structure](image) | 312     | 21.77         | 99        | 85%           |
| 6\(^c\) |          | ![Structure](image) | 256     | 19.34         | 94        | 74 (17)       |
| 7\(^d\) |          | ![Structure](image) | 144     | 13.14         | 85        | 80            |
| 8\(^d\) |          | ![Structure](image) | 130     | 12.28         | 70        | 35            |
| 9\(^c,d\) |          | ![Structure](image) | 158     | 14.19         | 80        | 78%           |
| 10\(^c,d\) |          | ![Structure](image) | 172     | 14.96         | 85        | 82%           |
| 11\(^c,d\) |          | ![Structure](image) | 200     | 16.5          | 99        | 80 (20)       |
| 12\(^d\) |          | ![Structure](image) | 206     | 18.56         | 85        | 75 (8)        |

\(^a\)Optimized reaction conditions: catalyst 2 (2 mol%), KH (3 mol%), 1,2-diaminobenzenes (0.5 mmol), 1,2-diols (0.5 mmol), 150°C, 36h, toluene, \(^b\)Isolated yield (In parenthesis hydrogenated product). \(^c\)4-methyl-1,2-diaminobenzene. \(^d\)Base (KH) used 0.5 mmol,
a) Reaction of benzyl alcohol catalyzed by 2: 0.5 mmol of benzyl alcohol was placed in the closed pressure tube (50ml) and 0.01 mmol catalyst 2 and 3mol% KH were added and heated in the closed tube for 24h at 150°C. The reaction vessel was then cooled down and analyzed by GC-MS using mesitylene as internal standard. Benzylbenzoate in 99% yield was the only observed product.

\[
\text{Cat 2 (2 mol%)} \quad \text{KH (3 mol%)} \\
\text{Toluene, 150°C, 24h}
\]

b) Reaction of benzyl alcohol with 1-hexylamine: 0.5 mmol of benzyl alcohol and 0.05 mmol of 1-hexyl amine were placed in a 50ml Fischer-Porter pressure tube. 0.01 mmol of catalyst 2 and 3mol% KH were added and the closed tube was heated for 24h at 150°C. The tube was then cooled down and the solution analyzed by GC-MS with mesitylene as internal standard. N-benzylidenehexylamine was found as the only product.

\[
\text{Cat 2 (2 mol%)} \quad \text{KH (3 mol%)} \\
\text{Toluene, 150°C, 24h}
\]

c) Reaction of 1,2-hexanediol with aniline: 0.5 mmol of 1,2-hexanediol, 0.5mmol of aniline and 0.01 mmol of catalyst 2 were place in a pressure tube in presence of 3 mol% KH as base in toluene and heated at 150°C for 24h under closed system. The reaction mixture was cooled down and analyzed by GC-MS with mesitylene as internal standard. 1-(phenylamino)hexane-2-ol (mass 193) was found in 10% yield as the only product with unreacted starting materials.

\[
\text{Cat 2 (2 mol%)} \quad \text{KH (3 mol%)} \\
\text{Toluene, 150°C, 24h}
\]

1-(phenylamino)hexan-2-ol
4. X-ray Crystal structure determination:

Crystal data were measured at 100 K on a Rigaku XtaLab Pro diffractometer equipped with [λ(Cu-Kα) = 1.54184 Å] radiation, Pilaus 200 detector. The data were processed with CrysAlis PRO programs. Structures were solved by the SHELXT program and refined with full-matrix least-squares refinement based on F^2 with SHELXL-2014/7. Full details can be found in the CIF files.

![Molecular structure of complex 1](image)

**Figure S1.** Molecular structure of complex 1. Thermal ellipsoids are drawn at 50% probability level. Selected hydrogen atoms are omitted for clarity.
Table S4: Selected bond lengths and bond angles of 1.

| Bond lengths [Å] | Bond Angles [°] |
|------------------|-----------------|
| Br1 Mn1 2.5339(9) | O2 C39 Mn1 179.3(5) |
| C39 Mn1 1.759(6)  | C39 Mn1 C38 88.7(2) |
| Mn1 C38 1.786(4)  | C39 Mn1 N1 93.26(18) |
| Mn1 N1 2.077(3)   | C39 Mn1 N1 177.81(13) |
| Mn1 P1 2.2491(9)  | C39 Mn1 P1 91.62(14) |
| Mn1 P2 2.2527(9)  | C38 Mn1 P1 95.49(11) |
| P1 C1 1.817(3)    | N1 Mn1 P1 83.53(8) |
| P2 C12 1.825(4)   | N1 Mn1 P2 83.92(8) |
| O1 C38 1.153(5)   | N1 Mn1 P2 97.08(11) |
| C39 O2 1.193(8)   | P1 Mn1 P2 167.42(4) |
|                  | C39 Mn1 Br1 177.06(15) |
|                  | P2 Mn1 Br1 93.97(3) |
|                  | P1 Mn1 Br1 85.77(3) |
|                  | C38 Mn1 Br1 92.88(11) |
|                  | N1 Mn1 Br1 85.10(7) |
Figure S2. Molecular structure of complex 2. Thermal ellipsoids are drawn at 50% probability level. Selected hydrogen atoms are omitted for clarity.

Table S5: Selected bond lengths and bond angles of 2.

| Bond lengths [Å] | Bond Angles [°] |
|------------------|-----------------|
| Mn1 C39 1.769(3) | C39 Mn1 C38 94.09(15) |
| Mn1 C38 1.775(3) | C39 Mn1 N1 100.52(13) |
| Mn1 N1 2.077(2)  | C38 Mn1 N1 165.36(12) |
| Mn1 P2 2.2269(7) | C38 Mn1 N1A 159.1(5)  |
| Mn1 P1 2.2319(7) | C38 Mn1 P2 96.34(8)   |
| Mn1 B1 2.309(3)  | C39 Mn1 P2 88.27(11)  |
| Mn1 H1A 1.71(4)  | N1 Mn1 P2 85.16(6)   |
| P1 C26 1.678(7)  | C39 Mn1 P1 88.53(11)  |
| P1 C1 1.811(3)   | C38 Mn1 P1 95.41(8)   |
| P1 C32 1.875(6)  | N1 Mn1 P1 84.07(6)    |
| P2 C13 1.820(3)  | P2 Mn1 P1 168.01(3)   |
| P2 C14 1.821(3)  | C39 Mn1 B1 142.26(14) |
| P2 C20 1.835(3)  | C38 Mn1 B1 123.64(13) |
| O1 C38 1.162(3)  | N1 Mn1 B1 41.75(10)   |
|                  | P2 Mn1 B1 88.13(8)    |
|                  | B1 Mn1 H1A 31.6(12)   |
|                  | P1 Mn1 B1 87.34(8)    |
5. NMR Spectra of compounds 1 and 2

**Figure S3.** $^{31}$P-$^1$H NMR of complex 1 in CDCl$_3$

**Figure S4.** $^1$H NMR of complex 1 in CDCl$_3$
Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR of complex 1 in CDCl$_3$.

Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR of complex 2 in C$_6$D$_6$. 
Figure S7. $^1$H NMR of complex 2 in C$_6$D$_6$

Figure S8. $^{13}$C{$^1$H} NMR of complex 2 in C$_6$D$_6$
Figure S9. IR spectrum of complex 1

Figure S10. IR spectrum of complex 2
Figure S11. HRMS of complex 1

Figure S12. HRMS of complex 2
6. Synthesis of complex Mn(HAcr-PNPPh\textsubscript{Ph})(CO)\textsubscript{2}(BnNH\textsubscript{2}) (6)

3.5 mg (0.005 mmol) of Mn(HAcr-PNP\textsubscript{Ph})(CO)\textsubscript{2}(BH\textsubscript{3}) (complex 2) was taken in J young NR tube and dissolved in 0.5 mL C\textsubscript{6}D\textsubscript{6} under N\textsubscript{2} atmosphere. 2 equivalent of benzyl amine was added to the NMR tube and heated at 80°c for 2h.

![Figure S13. \textsuperscript{31}P{\textsuperscript{1}H} NMR of complex 6 in C\textsubscript{6}D\textsubscript{6}](image)

![Figure S14. \textsuperscript{1}H NMR of complex 6 in C\textsubscript{6}D\textsubscript{6}](image)
7. Synthesis of complex Mn(HAcr-PNP$^\text{Ph}$)(CO)$_2$(NH$_3$) (7)

67 mg (0.10 mmol) of Mn(Acr-PNP$^\text{Ph}$)(CO)$_2$(BH$_3$) (complex 2) was placed in a 50 ml J young Schleck flask and dissolved in 10 mL C$_6$H$_6$ under N$_2$ atmosphere. The gas was removed by freeze pump thaw and charged with 1 bar of NH$_3$ and heated at 80°c for 4h. The solution was filtered through a small pad of Celite and the orange solution was evaporated in vacuum and the residue was washed with 10 mL of pentane to obtain a yellow orange solid (63 mg, 95% yield). The solid product was dissolved in THF (5 mL), layered with pentane and kept in the refrigerator to obtain orange crystals. $^1$H NMR (C$_6$D$_6$, 500 MHz): δ = -0.58 (s, 3H, NH$_3$), 4.20 (d, $J = 20.2$ Hz, 1H, AcrCH$_2$), 4.36 (d, $J = 20.2$ Hz, 1H, AcrCH$_2$), 6.62 (t, $J = 7.08$ Hz, 1H), 6.69 (t, $J = 7.08$ Hz, 2H), 6.83 (d, $J = 5.6$ Hz, 1H), 6.92-7.09 (m, 10H), 7.26 (s, b, 2H), 7.60 (b, 4H), 7.86 (b, 2H), 8.09 (b, 4H); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 125 MHz): δ = 32.8 (AcrC$^9$), 116.9 (t), 117.4, 117.5, 123.0, 124.4, 128.1, 128.3, 128.6, 128.7, 129.4, 130.7, 131.8, 132.0, 132.1, 132.4, 133.1, 160.1 (t), 226.6, 228.8; $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 202 MHz): δ = 80.1. IR (thin film, NaCl) = 1918 cm$^{-1}$ (νCO), 1839 cm$^{-1}$ (νCO), 3356cm$^{-1}$ (νNH$_3$).

![Figure S15](image-url)  
**Figure S15.** Molecular structure of complex 7. Thermal ellipsoids are drawn at 50% probability level. Selected hydrogen atoms are omitted for clarity.
Table S6: Selected bond lengths and bond angles of 7.

| Bond lengths [Å] | Bond Angles [°] |
|------------------|-----------------|
| Mn1 C39 1.775(2) | C39 Mn1 C38 89.60(11) |
| Mn1 C38 1.778(2) | C39 Mn1 N1 92.55(10) |
| Mn1 N1 2.0713(19) | C38 Mn1 N1 177.12(9) |
| Mn1 N2 2.134(2)  | C39 Mn1 N2 176.57(10) |
| Mn1 P1 2.2436(6) | C39 Mn1 P1 90.94(7) |
| Mn1 P2 2.2559(6) | C39 Mn1 P1 95.60(7) |
| P1 C1 1.803(2)   | N1 Mn1 N2 84.16(8) |
| O1 C38 1.163(3)  | N1 Mn1 P1 82.46(6) |
| O2 C39 1.161(3)  | N2 Mn1 P1 89.58(6) |
| N1 C13 1.383(3)  | C39 Mn1 P2 90.10(7) |
| N1 C6  1.389(3)  | C38 Mn1 P2 98.51(7) |
|                 | N1 Mn1 P2 83.40(6) |
|                 | N2 Mn1 P2 88.57(6) |
|                 | P1 Mn1 P2 165.86(3) |
|                 | C1 P1 Mn1 102.22(8) |
|                 | C20 P1 Mn1 123.12(8) |
|                 | C14 P1 Mn1 114.88(8) |
|                 | C26 P2 Mn1 122.02(8) |
|                 | C32 P2 Mn1 116.25(8) |
|                 | C13 N1 Mn1 120.27(16) |
|                 | C6 N1 Mn1 119.75(15) |
|                 | C12 P2 Mn1 101.84(8) |
Table S7. Crystallographic data.

| Species          | Complex 1                                      | Complex 2                                      | Complex 7                                      |
|------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| **Formula**      | $C_{39}H_{27}BrMnNO_2P_2+2C_4H_8O$            | $C_{39}H_{31}BMnNO_2P_2$                      | $C_{39}H_{31}MnN_2O_2P_2$                     |
| **Formula weight** | 882.61                                        | 673.34                                        | 676.54                                        |
| **Crystal system** | Triclinic                                     | Triclinic                                     | Trigonal                                      |
| **Space group**   | $P -1$                                        | $P -1$                                        | $R-3$                                         |
| **Crystal size (mm)** | 0.226×0.179×0.016                          | 0.107×0.088×0.046                            | 0.092×0.044×0.030                            |
| **Crystal color and shape** | Brown plate                                 | Yellow plate                                 | Orange needle                                |
| **Temperature (K)** | 100                                          | 100                                          | 100                                          |
| **Wavelength (Å)**  | 1.54184                                       | 1.54184                                       | 1.54184                                       |
| **a (Å)**         | 12.0659(3)                                    | 10.0379(1)                                   | 37.5012(5)                                   |
| **b (Å)**         | 12.6901(2)                                    | 11.3687(1)                                   | 37.5012(5)                                   |
| **c (Å)**         | 13.3087(3)                                    | 15.6568 (2)                                  | 11.9805(2)                                   |
| **α (°)**         | 94.2850(10)                                   | 73.9700(10)                                  | 90                                           |
| **β (°)**         | 102.738(2)                                    | 77.5420(10)                                  | 90                                           |
| **γ (°)**         | 90.704(2)                                     | 72.8200(10)                                  | 120                                          |
| **Volume (Å$^3$)** | 1981.22(8)                                    | 1623.02(3)                                   | 14591.4(4)                                   |
| **Z**             | 2                                             | 2                                             | 18                                           |
| **ρ$_{calc.}$ (g cm$^{-1}$)** | 1.480                                        | 1.378                                        | 1.386                                        |
| **μ (mm$^{-1}$)**  | 5.027                                         | 4.524                                        | 4.545                                        |
| **No. of reflection (unique)** | 32011(8038)                                 | 47243(6903)                                  | 27956(6825)                                  |
| **R$_{int}$**     | 0.0677                                        | 0.0400                                        | 0.0350                                        |
| **Completeness to θ (%)** | 99.8                                         | 99.1                                         | 99.9                                         |
| **Data / restraints / parameters** | 8038 / 13 / 536                             | 6903 / 1 / 535                               | 6825 / 0 / 416                               |
| **Goodness-of-fit on $F^2$** | 1.030                                        | 1.038                                        | 1.072                                        |
| **Final $R_1$ and w$R_2$ indices [I > 2σ(I)]** | 0.0612, 0.1610                             | 0.0490, 0.1158                               | 0.0501, 0.1434                               |
| **$R_1$ and w$R_2$ indices (all data)** | 0.0643, 0.1637                             | 0.0505, 0.1167                               | 0.0540, 0.1473                               |
| **Largest diff. peak and hole (e$^-$ Å$^3$)** | 1.338 and -1.438                           | 0.542 and -0.486                            | 0.887 and -0.330                             |

S20
Figure S16. $^{31}\text{P} \{^1\text{H}\}$ NMR of complex 7 in $\text{C}_6\text{D}_6$

Figure S17. $^1\text{H}$ NMR of complex 7 in $\text{C}_6\text{D}_6$
**Figure S19.** IR spectrum of complex 7
8. Synthesis of complex Mn(HAcr-PNP^Ph)(CO)_2(2-amino-1-propanol) (8)

3.5 mg (0.005 mmol) of Mn(Acr-PNP^Ph)(CO)_2(BH_3) (2) was placed in a J young NR tube and dissolved in 0.5 mL C_6D_6 under N_2 atmosphere. Two equivalent of 2-amino-1-propanol was added to the NMR tube and it was heated at 80°C for 2h.

**Figure S20.** \(^{11}\)B NMR of after the reaction of complex 2 with NH_3

**Figure S21.** \(^{31}\)P{\(^1\)H} NMR of reaction complex 2 and 2-amino-1-propanol and formation of complex 8
9. Reaction of complex 1 with NaH and benzyl alcohol:
Sodium hydride (10 equiv) was added to a stirred solution of 1 (0.05 mmol) and benzyl alcohol (3.3 equiv) in THF (5 mL). The reaction mixture was stirred for 2 h at RT and then filtered through a Celite plug. The resulting orange solution was evaporated to dryness, and the solid residue was washed with pentane several times to remove benzyl benzoate and excess benzyl alcohol. The resulting orange powder was dried under high vacuum for several hours. A tricarbonyl Mn complex with amido acridine ligand was observed as product.

![Figure S22. 31P{1H} NMR of reaction complex 1 and NaH in presence of BnOH in THF](image_url)

![Figure S23. The product IR of the reaction complex 1 and NaH in presence of BnOH in THF](image_url)
10. Reaction of complex 1 with NaBEt$_3$H:

Complex 1 was treated with an equivalent amount of NaBEt$_3$H solution in THF afforded a unstable Mn-H complex which was decomposed and formed a NMR silent complex after 5 min room temperature stirring.

After 5 min.

Figure S24. $^{31}$P{$^1$H} NMR of reaction complex 1 and NaBEt$_3$H

Figure S25. $^1$H NMR of reaction complex 1 and NaBEt$_3$H
11. Proposed mechanism for alcohol dehydrogenation:
12. $^1$H and $^{13}$C NMR data of isolated pyrazines and quinoxaline:

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.50-7.58 (m, 3H), 8.10 (d, 2H, $J = 7.43$Hz), 9.11 (s, 1H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 126.8, 129.1, 129.8, 136.3, 141.2, 150.7

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 4.15 (s, 1H), 7.25-7.33 (m, 5H), 8.41 (s, 1H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 41.4, 126.7, 128.7, 129.0, 138.3, 143.7, 153.7.

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.957 (d, $J = 6.88$Hz, 6H), 2.10 (h, $J = 6.74$, 1H), 2.66 (d, $J=7.35$, 2H), 8.35 (s, 1H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 22.3, 29.0, 44.0, 143.9, 153.4.

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.33 (d, $J = 7.03$ Hz, 6H), 3.09 (h, $J = 7.05$, 1H), 8.39 (s, 1H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 22.3, 33.5, 141.8, 159.3.

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.96 (t, $J = 7.44$ Hz, 3H), 1.37-1.43 (m, 2H), 1.70-1.74 (m, 2H), 2.74 (t, $J = 7.80$ Hz, 2H), 8.36 (s, 1H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 13.8, 22.4, 31.4, 32.6, 143.3, 154.6.

S27
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.99 (t, J = 7.53 Hz, 3H), 1.75-1.80 (m, 2H), 2.76 (t, J = 7.34 Hz, 2H), 8.36 (s, 1H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 13.7, 22.7, 37.0, 143.4, 154.5.

![Diagram of molecule 1](image1)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.54 (t, J= 7.81Hz, 3H), 3.16 (q, J=7.2Hz, 2H), 7.77-7.84 (m, 2H), 8.14-8.19 (m, 2H), 8.86 (s, 1H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): 13.4, 29.6, 128.8, 129.1, 129.9, 141.2, 142.0, 145.5, 158.4.

![Diagram of molecule 2](image2)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.90 (t, J= 7.30Hz, 3H), 1.28 (b, 14H), 1.38 (m, 2H), 1.45 (m, 2H), 1.87 (p, J=7.7Hz, 2H), 3.04 (t, J=7.9, 2H), 7.71-7.78 (m, 2H), 8.08 (dd, J=16.8, J=7.2, 2H), 8.77 (s, 1H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 14.1, 22.7, 29.34, 29.43, 29.46, 29.52, 29.58, 29.61, 29.62, 29.64, 29.67, 31.9, 36.5, 128.8, 128.9, 129.1, 129.9, 141.2, 142.2, 145.8, 157.7.

![Diagram of molecule 3](image3)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.06(t, J= 7.30Hz, 3H), 1.52-1.57 (m, 2H), 1.87-1.95 (m, 2H), 2.64, 2.67 (s, 3H), 3.08 (t, J=7.8, 2H), 7.60-7.67 (m, 1H), 7.91 (d, J=8.9Hz, 1H), 8.03 (dd, J=8.44Hz, J=12.4Hz, 1H), 8.76, 8.78 (s, 1H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): 13.9, 21.7, 21.8, 22.5, 31.6, 31.7, 36.1, 36.2, 127.3, 127.7, 127.9, 128.0, 128.3, 128.6, 131.1, 132.2, 139.3, 139.6, 140.4, 140.6, 141.2, 142.2, 144.9, 145.7, 156.7, 157.5.

![Diagram of molecule 4](image4)
$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.52 (t, $J= 7.80$Hz, 3H), 2.64, 2.67 (s, 3H), 3.12 (q, $J=7.3$, 2H), 7.61-7.67 (m, 1H), 7.92 (d, $J=7.7$Hz, 1H), 8.03 (dd, $J=8.44$Hz, $J=10.7$Hz, 1H), 8.78, 8.80 (s, 1H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): 13.45, 13.49, 21.7, 21.8, 29.5, 29.6, 127.7, 128.0, 128.3, 128.6, 131.1, 132.2, 139.3, 139.7, 140.4, 140.6, 141.3, 142.2, 144.6, 145.4, 157.5, 158.3.

![Chemical Structure 1](image1)

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.59, 2.61 (s, 3H), 2.75, 2.78 (s, 3H), 7.52-7.60 (m, 1H), 7.81-7.86 (d, 1H), 7.92-7.98 (dd, 1H), 8.70, 8.72 (s, 1H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): 21.7, 21.8, 22.4, 22.5, 119.0, 120.5, 127.5, 128.0, 128.1, 128.6, 131.2, 132.3, 139.3, 140.5, 145.1, 145.9, 152.8, 153.6

![Chemical Structure 2](image2)

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.89 (t, $J= 7.14$Hz, 3H), 1.26-1.31 (m, 6H), 1.34-1.38 (m, 2H), 1.44 (m, 2H), 1.84-1.88 (m, 2H), 2.61 (s, 3H), 3.04 (t, $J=8.1$, 2H), 7.56-7.61 (m, 1H), 7.88 (d, $J=8.1$Hz, 1H), 7.99 (dd, $J=5.14$Hz, $J=8.3$Hz, 1H), 8.71, 8.73 (s, 1H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): 18.1, 21.7, 21.8, 22.6, 29.1, 29.3, 29.4, 29.6, 29.7, 31.8, 36.2, 36.3, 127.3, 127.9, 128.1, 128.9, 131.4, 132.4, 139.6, 139.7, 140.9, 141.1, 144.8, 145.5, 156.5, 157.2

![Chemical Structure 3](image3)

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.90 (t, $J= 7.14$Hz, 3H), 1.27 (m, 14H), 1.36-1.38 (m, 2H), 1.43-1.45 (m, 2H), 1.84-1.88 (m, 2H), 2.62 (s, 3H), 3.06 (t, $J=7.7$, 2H), 7.58-7.63 (m, 1H), 7.89-7.93 (d, 1H), 8.00-8.02 (dd, 1H), 8.73, 8.74 (s, 1H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): 18.1, 21.7, 21.8, 22.6, 29.1, 29.3, 29.4, 29.6, 29.7, 31.8, 36.2, 36.3, 127.3, 127.9, 128.1, 128.9, 131.4, 132.4, 139.6, 139.7, 140.9, 141.1, 144.8, 145.5, 156.5, 157.2

![Chemical Structure 4](image4)
MHz, CDCl$_3$): 14.1, 21.7, 21.9, 22.6, 29.3, 29.4, 29.6, 29.7, 31.9, 35.9, 36.1, 126.9, 128.7, 128.9, 128.6, 131.7, 132.7, 139.7, 141.0, 141.3, 144.8, 145.5, 156.4, 157.0.

![Chemical Structure](image)

$^1$H NMR (400 MHz, CDCl$_3$): 7.64-7.71 (m, 3H), 7.86-7.94 (m, 2H), 8.27-8.32 (m, 4H), 9.45 (s, 1H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): 126.6, 128.6, 129.2, 129.6, 129.9, 130.4, 130.7, 136.7, 140.7, 142.4, 142.6, 151.9
13. $^1$H and $^{13}$C NMR spectra of isolated pyrazines and quinoxaline:

**Figure S26.** $^1$H NMR of 2,5-diphenylpyrazine

**Figure S27.** $^{13}$C{$^1$H} NMR of 2,5-diphenylpyrazine
Figure S28. $^1$H NMR of 2,5-dibenzylpyrazine

Figure S29. $^{13}$C{$^1$H} NMR of 2,5-dibenzylpyrazine
Figure S30. $^1$H NMR of 2,5-diisobutylpyrazine

Figure S31. $^{13}$C$^{{}^1}$H NMR of 2,5-diisobutylpyrazine
**Figure S32.** $^1$H NMR of 2,5-diisopropylpyrazine

**Figure S33.** $^{13}$C{$^1$H} NMR of 2,5-diisopropylpyrazine
Figure S34. $^1$H NMR of 2,5-dibutylpyrazine

Figure S35. $^{13}$C{$^1$H} NMR of 2,5-diisobutylpyrazine
Figure S36. $^1$H NMR of 2,5-dipropylpyrazine

Figure S37. $^{13}$C{$^1$H} NMR of 2,5-dipropylpyrazine
Figure S38. $^1$H NMR of 2-ethylquinoxaline

Figure S39. $^{13}$C\{$^1$H\} NMR of 2-ethylquinoxaline
Figure S40. $^1$H NMR of 2-dodecylquinoxaline

Figure S41. $^{13}$C{$^1$H} NMR of 2-dodecylquinoxaline
Figure S42. $^1$H NMR of 2-butyl-6-methylquinoxaline

Figure S43. $^{13}$C${}^1$H NMR of 2-butyl-6-methylquinoxaline
Figure S44. $^1$H NMR of 2-ethyl-6-methylquinoxaline

Figure S45. $^{13}$C{$^1$H} NMR of 2-ethyl-6-methylquinoxaline
Figure S46. $^1$H NMR of 2-methyl-6-methylquinoxaline

Figure S47. $^{13}$C{$^1$H} NMR of 2-methyl-6-methylquinoxaline
Figure S48. $^1$H NMR of 2-octyl-6-methylquinoxaline

Figure S49. $^{13}$C{$^1$H} NMR of 2-octyl-6-methylquinoxaline
Figure S50. $^1$H NMR of 2-dodecyl-6-methylquinoxaline

Figure S51. $^{13}$C{$^1$H} NMR of 2-butyl-6-methylquinoxaline
Figure S52. $^1$H NMR of 2-phenylquinoxaline

Figure S53. $^{13}$C{$^1$H} NMR of 2-phenylquinoxaline
14. References

(1) Srimani, D.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. Iron Pincer Complex Catalyzed, Environmentally Benign, E-Selective Semi-Hydrogenation of Alkynes. *Angew. Chem. Int. Ed.* **2013**, *52*, 14131 –14134.

(2) Mukherjee, A.; Nerush, A.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Espinosa Jalapa, N. A.; Milstein, D. Manganese-Catalyzed Environmentally Benign Dehydrogenative Coupling of Alcohols and Amines to Form Aldimines and H$_2$: A Catalytic and Mechanistic Study. *J. Am. Chem. Soc.* **2016**, *138*, 4298-4301.

(3) Kumar, A.; Espinosa-Jalapa, N. A.; Leitus, G.; Diskin-Posner, Y.; Avram, L.; Milstein, D. Direct Synthesis of Amides by Dehydrogenative Coupling of Amines with either Alcohols or Esters: Manganese Pincer Complex as Catalyst. *Angew. Chem. Int. Ed.* **2017**, *56*, 14992 –14996.

(4) Chakraborty, S.; Gellrich, U.; Diskin-Posner, Y.; Leitus, G.; Avram, L.; Milstein, D. Manganese-Catalyzed N-Formylation of Amines by Methanol Liberating H$_2$: A Catalytic and Mechanistic Study. *Angew. Chem. Int. Ed.* **2017**, *56*, 4229-4233.