SUPPORTING INFORMATION

µ-Oxo-Bridged Iron(III) Complexes for Selective Reduction of Aromatic Ketones Catalyzed through Base Promoted In-situ Nanoparticles Formation

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Table S1 shows X-ray crystal structure refinement data of the complex 1
Table S2 shows TH of various aromatic ketones using KOH
Figure S1. ESI-MS mass spectra of the ligands A) L₁ and B) L₂.
**Figure S2.** IR spectra of the complexes 1 and 2 were recorded using KBr pellet.

**Figure S3.** The Raman spectra of the complexes 1 (top) and 2 (bottom).
Figure S4. MALDI-TOF mass spectra of the complexes A) 1 and B) 2.
Figure S5. UV-visible spectra of the complexes (A) 1, ([c] = 1.7 x 10^{-5} M) and (B) 2, ([c] = 2.0 x 10^{-5}) in different solvents. (C, D) UV-Visible spectra of complexes 1 and 2 at temperature 25°C and 80°C (in MeOH). (E) Time dependent UV-Visible study of complex 1 at 80°C (in MeOH) monitored for 4 h with 15 min interval.
Figure S6. Cyclic voltammograms of a $10^{-3}$ M solution of 1 and 2 in DMF, in presence of 0.1 M tetrabutylammonium perchlorate (TBAP), using working electrode: glassy-carbon (0.07 cm$^2$); reference electrode: Ag/AgCl; auxiliary electrode: platinum wire, scan rate 75 mV/s.
Figure S7. GC-MS spectra (A-H) of selected alcohol products obtained from the transformation of the corresponding ketones in presence of the complex 1 (2 mol%) with KOH and i-PrOH.
A)

B)

C)

D)

E)

F)

G)
Figure S8. GC-MS spectra (A-H) of selected alcohol products obtained from the transformation of the corresponding ketones in presence of the complex 2 (2 mol%) with NaOH and i-PrOH.
Figure S9. $^1$H NMR spectra of few selected alcohols A) 1-phenylethanol B) 1-(4-chlorophenyl)ethanol C) (4-bromophenyl)(phenyl)methanol D) diphenylmethanol in CD$_3$CN.
**Figure S10.** FESEM images of the A, B) complexes 1 and 2 in i-PrOH respectively. C, D) complex 1 and 2 + base in i-PrOH.
Figure S11. Time dependent DLS studies of catalytic mixture of complex 1 in i-PrOH after every 2 h interval.
**Figure S12.** Energy dispersive X-ray (EDX) analysis showing the presence of iron and other elements (inset) in catalytic mixture, in presence of complex 2. (Presence of gold and palladium is due to Au/Pd coating to sample using Quorum Q150T sputter unit)

**Figure S13.** FESEM image of the iron oxide alone.
**Figure S14.** A) Recyclability of the catalysts (1 and 2) using acetophenone as a substrate. B, C) FESEM image and IR spectrum of catalytic mixture after 4\textsuperscript{th} cycle, using complex 1.
Figure S15. A) UV-Visible spectra of the complex 1 in i-PrOH (black, $[\text{Complex } 1] = 40 \mu M$) in presence of base (red, $[\text{Base}] = 40 \text{ mM}$) B) ATR-IR spectra of complex 1 in DCM and i-PrOH, C) ATR-IR spectra of catalytic reaction mixture in presence of complex 1 at time $t = 1$ h and 12 h (benzophenone (0.1 mmol), base (0.2 mM) in 2-propanol (1 mL) and catalyst (2 mol%), respectively.
Table S1. X-ray crystal structure refinement data of the complex 1.

<p>| | | | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Formula weight (gmol⁻¹)</td>
<td>1950.94</td>
<td>β (°)</td>
<td>68.4270(10)</td>
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<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>γ (°)</td>
<td>66.3200(10)</td>
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<tr>
<td>Space group</td>
<td>P̅V</td>
<td>V (Å³)</td>
<td>2391.33(15)</td>
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<tr>
<td>λ (Å) (Mo-Kα)</td>
<td>0.71073</td>
<td>Z</td>
<td>1</td>
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<tr>
<td>Crystal size (mm)</td>
<td>0.25x0.15x0.10</td>
<td>θ range (deg)</td>
<td>1.4-26.5</td>
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<td>a (Å)</td>
<td>13.4221(5)</td>
<td>F (000)</td>
<td>1025</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.5676(5)</td>
<td>R₁[a] [I &gt;2σ(I)]</td>
<td>0.0469</td>
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<tr>
<td>c (Å)</td>
<td>15.5152(5)</td>
<td>wR₂[b] [I &gt;2σ(I)]</td>
<td>0.1301</td>
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<tr>
<td>α (°)</td>
<td>86.9640(10)</td>
<td>GOF</td>
<td>1.089</td>
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</tbody>
</table>

[a] $R_I = (\sum |F_o| - |F_c|)/(|F_o|)$.  
[b] $wR_2 = (\sum w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2)^{1/2}$.
Table S2. Complexes 1 and 2 catalyzed TH of various aromatic ketones using KOH.\textsuperscript{[a, b]}

<table>
<thead>
<tr>
<th>Si.No</th>
<th>Substrate</th>
<th>Complex 1 Conversion yield (%)\textsuperscript{[b]} (TOF, h\textsuperscript{-1})</th>
<th>Complex 2 Conversion yield (%)\textsuperscript{[b]} (TOF, h\textsuperscript{-1})</th>
</tr>
</thead>
</table>
| 1     | \[
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{O} \\
\end{array}
\text{CH}_3
\] | 92 (3.83) | 90 (3.75) |
| 2     | \[
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{O} \\
\end{array}
\text{F}
\] | 100 (4.16) | 88 (3.67) |
| 3     | \[
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{O} \\
\text{Cl} \\
\end{array}
\text{CH}_3
\] | 98 (4.08) | 100 (4.16) |
| 4     | \[
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{O} \\
\text{I}
\end{array}
\] | 100 (4.16) | 51 (2.13) |
| 5     | \[
\begin{array}{c}
\text{S}
\end{array}
\] | 89 (3.71) | 94 (3.92) |
| 6     | \[
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{O}
\end{array}
\] | 87 (3.63) | 79 (3.29) |
| 7     | \[
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{O} \\
\text{Cl}
\end{array}
\text{CH}_3
\] | 30 (1.25) | 12 (50) |
| 8     | \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{C} \\
\text{H}_3
\end{array}
\text{O} \\
\text{C} \\
\text{H}_3 \\
\text{H}_3\text{C}
\] | 5 (0.21) | 47 (1.95) |
| 9     | \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{C} \\
\text{H}_3
\end{array}
\text{O} \\
\text{C} \\
\text{H}_3 \\
\text{H}_3\text{C}
\] | 41 (1.70) | 40 (1.66) |
| 10    | \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{C} \\
\text{H}_3
\end{array}
\text{O} \\
\text{C} \\
\text{H}_3 \\
\text{H}_3\text{C}
\] | 44 (1.83) | 13 (0.54) |
| 11    | \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{C} \\
\text{H}_3
\end{array}
\text{O} \\
\text{C} \\
\text{H}_3 \\
\text{H}_3\text{C}
\] | 15 (0.63) | 9 (0.38) |

\textsuperscript{[a]}Data represent the mean (SD ± 1\% ) of three independent experiments. Reaction conditions: acetophenone (0.1 mM), complexes 1 or 2 (2 mol\%), base (KOH, 0.2 mM), solvent (\textit{i}-PrOH, 1 mL), temperature (80-85 °C), time 12 h, argon atmosphere.

\textsuperscript{[b]}Conversions determined by GC-MS analysis. TOF = TON/time in h, and TON was calculated using moles of catalyst.