Supporting Information

Direct Imines Formation by Oxidative Coupling of Alcohols and Amines using Supported Manganese oxide under Air atmosphere

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Table S1. Physical properties of various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( S_{\text{BET}} ) (m(^2)g(^{-1}))</th>
<th>Vol (cm(^3)g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAP-pure</td>
<td>37.9</td>
<td>0.14</td>
</tr>
<tr>
<td>MnO(_x)/HAP</td>
<td>36.3</td>
<td>0.13</td>
</tr>
<tr>
<td>MnO(_x)/(\text{TiO}_2)</td>
<td>46.4</td>
<td>0.32</td>
</tr>
<tr>
<td>MnO(_x)/MgO</td>
<td>107.4</td>
<td>0.45</td>
</tr>
<tr>
<td>MnO(_x)/(\text{Al}_2\text{O}_3)</td>
<td>148.0</td>
<td>0.27</td>
</tr>
<tr>
<td>MnO(_x)/SBA-15</td>
<td>369.2</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Figure S1. Time-on-stream course of conversion.
**Figure S2.** Time course of the reaction between benzaldehyde (1 mmol) and aniline (1 mmol) over various catalysts (125mg) at 80 °C under air balloon.

**Figure S3.** Hot filtration test for oxidative coupling of benzyl alcohol and aniline over MnOx/HAP in 3.5h
Characterization of Typical Products:

\[
\text{N-benzylideneaniline} \quad \text{Yellow solid.} \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.46 (s, 1H), 7.91 (d, \text{ } J = 4.8 \text{ Hz}, 2H), 7.48 (s, 3H), 7.39 (t, \text{ } J = 7.2 \text{ Hz}, 2H), 7.23 (t, \text{ } J = 9.2 \text{ Hz}, 3H); ^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 160.97 (s), 152.69 (s), 136.82 (s), 131.95 (s), 129.70 (s), 129.37 (d, \text{ } J = 3.9 \text{ Hz}, 126.51 (s), 121.44 (s).
\]

\[
\text{N-Benzylidencyclohexylamine} \quad \text{Yellow oil.} \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.31 (s, 1H), 7.81 – 7.67 (m, 2H), 7.37 (t, \text{ } J = 11.5 \text{ Hz}, 3H), 3.29 – 3.05 (m, 1H), 1.85 (d, \text{ } J = 12.7 \text{ Hz}, 2H), 1.79 – 1.50 (m, 5H), 1.47 – 1.19 (m, 3H); ^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 158.49 (s), 136.61 (s), 130.25 (s), 128.45 (s), 128.02 (s), 69.92 (s), 34.35 (s), 25.64 (s), 24.78 (s).
\]

\[
\text{N-(4-fluorophenyl)-1-phenylmethanimine} \quad \text{Brownish black solid.} \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.44 (s, 1H), 7.94 – 7.82 (m, 2H), 7.52 – 7.42 (m, 3H), 7.20 (ddd, \text{ } J = 10.1, 5.2, 2.7 \text{ Hz}, 2H), 7.13 – 7.02 (m, 2H); ^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 160.90 (s), 151.17 (s), 136.13 (s), 132.37 (s), 131.82 (s), 129.05 (d, \text{ } J = 7.9 \text{ Hz}, 122.80 (s), 119.50 (s).
\]
**N-(4-bromophenyl)-1-phenylmethanimine** Brownish black solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.41 (s, 1H), 7.95 – 7.83 (m, 2H), 7.48 (dd, $J = 14.4$, 7.0 Hz, 5H), 7.09 (d, $J = 8.6$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.90 (s), 151.17 (s), 136.13 (s), 132.37 (s), 131.82 (s), 129.05 (d, $J = 7.9$ Hz), 122.80 (s), 119.50 (s).

**N-hexyl-1-phenylmethanimine** Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.26 (s, 1H), 7.71 (dt, $J = 7.7$, 3.2 Hz, 2H), 7.43 – 7.35 (m, 3H), 3.60 (td, $J = 7.1$, 1.0 Hz, 2H), 1.74 – 1.62 (m, 2H), 1.42 – 1.22 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.92 (s), 136.63 (s), 130.64 (s), 128.79 (s), 128.24 (s), 62.05 (s), 31.91 (s), 31.13 (s), 27.27 (s), 22.85 (s), 14.30 (s).

**N-Benzylidenebenzylamine** Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 (s, 1H), 7.83 (dd, $J = 6.7$, 2.9 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.37 (dd, $J = 10.2$, 2.8 Hz, 4H), 7.30 (dt, $J = 8.8$, 4.4 Hz, 1H), 4.86 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.14 (s), 139.51 (s), 136.37 (s), 130.93 (s), 128.78 (s), 128.67 (s), 128.46 (s), 128.16 (s), 127.16 (s), 65.22 (s).
$^1$H NMR and $^{13}$C NMR Spectra of the Typical Products