Supporting Information

Catalytic Oxidation of Aromatic Hydrocarbons by a Molecular Iron-NHC Complex

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1. Gas chromatography parameters

Table S4: Experimental parameters of gas chromatography analyses-

<table>
<thead>
<tr>
<th>Oven Temperature / °C</th>
<th>Ramp / °C/min</th>
<th>Hold / min</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p-Xylene Oxidation (GC-FID)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP-Chirasil-Dex CB (0.25 µm; 25 m x 0.25 mm), He flow: 1.0 mL/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>150</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td><strong>TMB Oxidation (GC-FID)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optima 5-Amine (1.50 µm; 30 m x 0.32 mm), He flow: 1.5 mL/min</td>
<td></td>
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</tr>
<tr>
<td>60</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>250</td>
<td>8</td>
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<td>320</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td><strong>GC-MS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VF-200ms (1.50 µm; 30 m x 0.32 mm), He flow: 2.0 psi/min, Saturn 2200 ion trap, 70 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>250</td>
<td>8</td>
<td>-</td>
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<tr>
<td>260</td>
<td>20</td>
<td>6</td>
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</table>
2. Catalytic data of \( p \)-xylene oxidation

Table S1. Catalytic oxidation of \( p \)-xylene with \( 1 \) and \( \text{H}_2\text{O}_2 \).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat. / pXy / ( \text{H}_2\text{O}_2 )</th>
<th>( c(pXy) / \text{M} )</th>
<th>( T / ^\circ \text{C} )</th>
<th>C(pXy) / %(^a)</th>
<th>Yield / %(^a)</th>
<th>2,5-DMP</th>
<th>2,4-DMP</th>
<th>DMBQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/100/10</td>
<td>0.5</td>
<td>0</td>
<td>5.3</td>
<td>2.8</td>
<td>2.5</td>
<td>2.5</td>
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<tr>
<td>2</td>
<td>1/100/50</td>
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<td>0</td>
<td>16.7</td>
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<td>6.6</td>
<td>3.8</td>
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<td>0</td>
<td>28.1</td>
<td>9.1</td>
<td>10.6</td>
<td>8.4</td>
<td></td>
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</tbody>
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\( ^a \) Conversion and yield were determined after 60 min by GC-FID analysis (wt.%)

Table S2. Influence of acid and base additives on the catalytic oxidation of \( p \)-xylene with \( 1 \) and hydrogen peroxide. Reaction conditions: pXy (0.5 mmol), \( 1 \) (0.005 mmol, 1 mol%), \( \text{H}_2\text{O}_2 \) (50 wt% in \( \text{H}_2\text{O} \), 0.125 mmol, 0.25 equiv.), additive (0.5 mmol, 1.0 equiv.), \( \text{CH}_3\text{CN} \) (1 mL), 0 ^\circ \text{C}, 60 min.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>C(pXy) / %(^a)</th>
<th>Yield / %(^a)</th>
<th>Ratio 2,5-DMP/2,4-DMP</th>
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</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>1</td>
<td>-</td>
<td>11.6</td>
<td>4.9</td>
<td>4.9</td>
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<tr>
<td>2</td>
<td>acetic acid</td>
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<td>4.4</td>
<td>4.4</td>
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<tr>
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<td>benzoic acid</td>
<td>10.2</td>
<td>4.5</td>
<td>3.9</td>
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<tr>
<td>4</td>
<td>propionic acid</td>
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<td>4.4</td>
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<tr>
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<td>pyridine</td>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>DMAP</td>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>NEt(_3)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>KO'Bu</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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</table>

\( ^a \) Conversion and yield were determined after 60 min by GC-FID analysis (wt.%)

S3
3. **Catalytic data of pseudocumene oxidation**

Table S3. Catalytic oxidation of TMB catalyzed by 1 and H$_2$O$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>Cat/Substrate/H$_2$O$_2$</th>
<th>c(Substrate) / M</th>
<th>T / °C</th>
<th>C(TMB) / %$^a$</th>
<th>Y(TMBQ) / %$^a$</th>
<th>S(TMBQ) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>TMB</td>
<td>1/100/50</td>
<td>0.5</td>
<td>0</td>
<td>29.2</td>
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<tr>
<td>2</td>
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<td>TMB</td>
<td>1/100/130</td>
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<td>0</td>
<td>63.1</td>
<td>8.9</td>
<td>14.1</td>
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<tr>
<td>3</td>
<td>1</td>
<td>TMB</td>
<td>1/100/150</td>
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<tr>
<td>6</td>
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<td>34.9</td>
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<td>7</td>
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<td>0</td>
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<td>8</td>
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<td>1.5/100/100</td>
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<td>0</td>
<td>53.7</td>
<td>6.8</td>
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<td>0.5</td>
<td>0</td>
<td>54.6</td>
<td>6.6</td>
<td>12.1</td>
</tr>
<tr>
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<td>TMB</td>
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<td>0</td>
<td>56.7</td>
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<td>11.9</td>
</tr>
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<td>FeCl$_2$</td>
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<td>FeCl$_3$</td>
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<td>0</td>
<td>1.8</td>
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<td>11.1</td>
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<td>13</td>
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<tr>
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<td>0</td>
<td>72.9</td>
<td>35.0</td>
<td>35.3</td>
</tr>
</tbody>
</table>

$^a$ Conversion and yield were determined after 120 min by GC-FID analysis (wt.%)
Figure S1. Reaction kinetics of the catalytic oxidation of TMB by 1 at -10 °C. Conversion of TMB (black ●), yield of TMBQ (red □) and 2,4,5-TMP (blue ◆) and selectivity for TMBQ (green ■). Reaction conditions: TMB (2 mmo), 1 (0.02 mmol, 1 mol%), H₂O₂ (50 wt% aqueous solution, 2 mmol, 1.0 equiv.), acetonitrile (4 mL).
4. NMR spectra of 3,3',5,5',6,6'-hexamethylbiphenyl-2,2'-diol (3,5,6-HMBD)

Figure S2. $^1$H NMR spectrum of 3,3',5,5',6,6'-hexamethylbiphenyl-2,2'-diol as received from catalytic oxidation of TMB.

Figure S3. $^{13}$C NMR spectrum of 3,3',5,5',6,6'-hexamethylbiphenyl-2,2'-diol as received from catalytic oxidation of TMB.