Oxidation of Alkenes with H2O2 by an In-Situ Prepared Mn(II)/Pyridine-2-carboxylic Acid Catalyst and the Role of Ketones in Activating H2O2

Dong, Jia Jia; Saisaha, Pattama; Meinds, Tim G.; Alsters, Paul L.; Ijpeij, Edwin G.; van Summeren, Ruben P.; Mao, Bin; Fananas-Mastral, Martin; de Boer, Johannes W.; Hage, Ronald

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Oxidation of alkenes with $\text{H}_2\text{O}_2$ by an in situ prepared Mn(II)/pyridine-2-carboxylic acid catalyst and the role of ketones in activating $\text{H}_2\text{O}_2$.

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Caution. The drying or concentration of solutions that potentially contain H\(_2\)O\(_2\) should be avoided. Prior to drying or concentrating, the presence of H\(_2\)O\(_2\) should be tested for using peroxide test strips followed by neutralization on solid NaHSO\(_3\) or another suitable reducing agent. When working with H\(_2\)O\(_2\), suitable protective safeguards should be in place at all times.

Caution. Butanedione has been linked with lung disease upon exposure to vapors. It should be handled in a properly ventilated fumehood and exposure to vapors should be avoided.

All reagents are of commercial grade and used as received unless stated otherwise. Hydrogen peroxide was used as received as a 50 wt. % solution in water; note that the grade of H\(_2\)O\(_2\) employed can affect the outcome of the reaction where sequestrants are present as stabilizers. \(^1\)H NMR (400.0 MHz) and \(^{13}\)C NMR (100.6 MHz) spectra were recorded on a Varian Avance400. Chemical shifts are relative to \(^1\)H NMR CDCl\(_3\) (7.26 ppm), DMSO-d\(_6\) (2.5 ppm), CD\(_3\)CN (1.94 ppm), \(^{13}\)C NMR CDCl\(_3\) (77 ppm).
1. Optimization of conditions for catalytic oxidation of cyclooctene, \( \alpha \)-pinene and diethyl fumarate

**Table S1a. Optimization of conditions for the epoxidation of cyclooctene**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mn(ClO(_4))(_2) ( \cdot ) 6H(_2)O (mol %)</th>
<th>Pyridine-2-carboxylic acid (mol %)</th>
<th>Butanedione (equiv.)</th>
<th>Conversion (%)</th>
<th>Yield(^{b,c}) (isolated yield) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
<td>95</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.5</td>
<td>1.5</td>
<td>95</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>0.01</td>
<td>0.5</td>
<td>0.5</td>
<td>95</td>
<td>80 (73)</td>
</tr>
<tr>
<td>4</td>
<td>0.01</td>
<td>0.1</td>
<td>0.5</td>
<td>93</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>0.1</td>
<td>3.0</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by \(^{1}\)H NMR and Raman spectroscopy. \(^{b}\) Yields determined by \(^{1}\)H NMR using 1,2-dichlorobenzene as internal standard. \(^{c}\) The side products were the corresponding cis-diol and \( \alpha \)-hydroxyl ketone products.

**Table S1b. Optimization of conditions for the epoxidation of \( \alpha \)-pinene**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mn(ClO(_4))(_2) ( \cdot ) 6H(_2)O (mol %)</th>
<th>Pyridine-2-carboxylic acid (mol %)</th>
<th>Butanedione (equiv.)</th>
<th>Conversion (%)</th>
<th>Yield(^{b,c}) (isolated yield) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
<td>86</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.5</td>
<td>1.5</td>
<td>85</td>
<td>45 (43)</td>
</tr>
<tr>
<td>3</td>
<td>0.01</td>
<td>0.5</td>
<td>0.5</td>
<td>95</td>
<td>80 (73)</td>
</tr>
<tr>
<td>4</td>
<td>0.01</td>
<td>0.1</td>
<td>0.5</td>
<td>80</td>
<td>47</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>0.1</td>
<td>3.0</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>0.5</td>
<td>3.0</td>
<td>28</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by \(^{1}\)H NMR and Raman spectroscopy. \(^{b}\) Yields determined by \(^{1}\)H NMR using 1,2-dichlorobenzene as internal standard. \(^{c}\) The side products were the corresponding cis-diol and \( \alpha \)-hydroxyl ketone products and rearrangements.
Table S2. Optimization of conditions for the cis-dihydroxylation of diethyl fumarate

Mn(II), butanedione
H$_2$O$_2$ 1.5 equiv.
NaOAc 1.0 mol %
PCA 0.5 mol %
CH$_3$CN
(0.5 M substrate)
r.t. overnight

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mn(ClO$_4$)$_2$·6H$_2$O (mol %)</th>
<th>butanedione (equiv.)</th>
<th>Conversion$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>0.5</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>1.0</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>0.01</td>
<td>1.5</td>
<td>full</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.5</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>1.0</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>1.5</td>
<td>89</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR and Raman spectroscopy. Only the cis-diol product was formed.
2. Main products and side products for schemes 1, 2, 5-7 and 9

Table S3. Scope for epoxidation of electron rich alkenes; products and side products

Mn(ClO$_4$)$_2$·6H$_2$O 0.01 mol %  
PCA 0.5 mol %  
H$_2$O$_2$ 1.5 equiv.  
NaOAc(aq) 1.0 mol %  
butanedione 0.5 equiv.  
CH$_3$CN (0.5 M)  
0 °C to r.t.  2 h

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Main product</th>
<th>Conversion</th>
<th>Yield (isolated yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scheme 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Substrate" /></td>
<td><img src="image2.png" alt="Main product" /></td>
<td>Full</td>
<td>90% epoxide 5% cis-diol 2% α-hydroxylketone</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Substrate" /></td>
<td><img src="image4.png" alt="Main product" /></td>
<td>95%</td>
<td>80% (73%) epoxide (single enantiomer)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Substrate" /></td>
<td><img src="image6.png" alt="Main product" /></td>
<td>95%</td>
<td>79% (73%) epoxide Trace of benzyaldehyde</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Substrate" /></td>
<td><img src="image8.png" alt="Main product" /></td>
<td>80%</td>
<td>75% (68%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scheme 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><img src="image9.png" alt="Substrate" /></td>
<td><img src="image10.png" alt="Main product" /></td>
<td>95%</td>
<td>80% (73%) epoxide 10% cis-diol 5% α-hydroxylketone</td>
</tr>
<tr>
<td>6</td>
<td><img src="image11.png" alt="Substrate" /></td>
<td><img src="image12.png" alt="Main product" /></td>
<td>Full</td>
<td>72% epoxide 12% cis-diol 5% α-hydroxylketone</td>
</tr>
<tr>
<td></td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>Percent</td>
<td>Products</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
| 7 | ![Chemical Structure](image3) | ![Chemical Structure](image4) | 95% | 70% epoxide  
15% cis-diol  
5% α-hydroxylketone |
| 8 | ![Chemical Structure](image5) | ![Chemical Structure](image6) | Full | 55% epoxide  
7% cis-diol |
| 9 | ![Chemical Structure](image7) | ![Chemical Structure](image8) | Full | 68% epoxide  
13% diol |
| 10 | ![Chemical Structure](image9) | ![Chemical Structure](image10) | Full | 83% epoxide  
12% diol |
| 11 | ![Chemical Structure](image11) | ![Chemical Structure](image12) | Full | 78% epoxide |
| 12 | ![Chemical Structure](image13) | ![Chemical Structure](image14) | 60% | 44% (41%) epoxide |
| 12b | ![Chemical Structure](image15) | ![Chemical Structure](image16) | 90% | 60% epoxide  
20% ketone,  
10% diol  
N.B. substrate concentration 0.25 M |
| 13 | ![Chemical Structure](image17) | ![Chemical Structure](image18) | 95% | 80% (72%) epoxide  
10% diol |
| 14 | ![Chemical Structure](image19) | ![Chemical Structure](image20) | 62% | 60% epoxide |
| 15 | ![Chemical Structure](image21) | ![Chemical Structure](image22) | Full | 72% epoxide  
18% anti-diol |
| 16 | ![Chemical Structure](image23) | ![Chemical Structure](image24) | 50% | 46% epoxide  
2% diol |
| 16b | ![Chemical Structure](image25) | ![Chemical Structure](image26) | 85% | 68% epoxide  
17% α-hydroxyketone  
N.B. substrate concentration 0.25 M |
| 17 | ![Chemical Structure](image27) | ![Chemical Structure](image28) | 73% | 61% epoxide  
10% diol |
<p>| 18 | <img src="image29" alt="Chemical Structure" /> | <img src="image30" alt="Chemical Structure" /> | 92% | 62% epoxide |</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions and Yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>20</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td><strong>Scheme 5</strong></td>
</tr>
<tr>
<td>21</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>22</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td><strong>Scheme 6</strong></td>
</tr>
<tr>
<td>23</td>
<td><img src="image9" alt="Structure" /></td>
</tr>
<tr>
<td>24</td>
<td><img src="image11" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td><strong>Scheme 7</strong></td>
</tr>
<tr>
<td>25</td>
<td><img src="image13" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td><strong>Scheme 9</strong></td>
</tr>
<tr>
<td>26</td>
<td><img src="image15" alt="Structure" /></td>
</tr>
</tbody>
</table>
| 27 | ![structure1](image1.png) | ![structure2](image2.png) | 85% | 54% (45% E, 9% Z) epoxide  
27% anti-diol  
4% α-hydroxylketone |
| 28 | ![structure3](image3.png) | ![structure4](image4.png) | 40% | 30% epoxide (20% anti and 10% syn),  
8% diol |
| 29 | ![structure5](image5.png) | ![structure6](image6.png) | full | 80% epoxide (only anti), 20% diol |
| 30 | ![structure7](image7.png) | ![structure8](image8.png) | 40% | 12% syn-epoxide, 28% anti-epoxide  
13% cis-diol |

**Other examples**

| 31 | ![structure9](image9.png) | ![structure10](image10.png) | 80% | 35% epoxide  
Mixture of and diol |
| 32 | ![structure11](image11.png) | ![structure12](image12.png) | 10% | 6% epoxide |
| 33 | ![structure13](image13.png) | ![structure14](image14.png) | 0% | 0% |

See section 5 for details. Conversion and yield were determined by Raman and \(^1\)H NMR spectroscopy. Isolated yields are shown in parentheses for selected examples.
3. Solvent scope for the oxidation of cyclooctene

Table S4. Solvent scope for the epoxidation of cyclooctene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Butanediol (0.5 equiv.)</th>
<th>Conversion(^a) (%)</th>
<th>Yield(^b,c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone</td>
<td>yes</td>
<td>90</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>Butanone</td>
<td>yes</td>
<td>85</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>tert-BuOH</td>
<td>yes</td>
<td>65</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>CH(_3)CN</td>
<td>yes</td>
<td>95</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>Methanol</td>
<td>yes</td>
<td>90</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>Ethanol</td>
<td>yes</td>
<td>70</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>Diethyl carbonate</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>THF</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>H(_2)O</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>EtOAc</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>MTBE</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>CH(_3)CN</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>DCM</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>DCE</td>
<td>yes</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>Acetone</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>Butanone</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>tert-BuOH</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>CH(_3)CN</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>Methanol</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>Ethanol</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Determined by \(^1\)H NMR and Raman spectroscopy. \(^b\) Yields determined by \(^1\)H NMR using 1,2-dichlorobenzene as internal standard. \(^c\) The side products were the \textit{cis}-diol and \(\alpha\)-hydroxyl ketone products.
4. Main products and side products for α,β-unsaturated carbonyl compounds

Table S5. Catalytic oxidation of α,β-unsaturated carbonyl alkenes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Conversion</th>
<th>Yield (isolated yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Substrate 1" /></td>
<td><img src="image2" alt="Product 1" /></td>
<td>35%</td>
<td>20% 15% diol</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Substrate 2" /></td>
<td><img src="image4" alt="Product 2" /></td>
<td>50%</td>
<td>18%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="Substrate 3" /></td>
<td><img src="image6" alt="Product 3" /></td>
<td>45%</td>
<td>8% 35% diol</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7" alt="Substrate 4" /></td>
<td><img src="image8" alt="Product 4" /></td>
<td>95%</td>
<td>31% 60% diol</td>
</tr>
</tbody>
</table>
5. Procedures for catalytic oxidation of alkenes described in schemes 1, 2, 4-7 and 9 and characterization of products

**General procedure:** To a solution of Mn(ClO₄)₂·6H₂O (0.01 mol %, 0.0361 mg) and pyridine-2-carboxylic acid (0.5 mol %, 0.123 mg) in acetonitrile was added the alke ne (1 mmol) to give a final concentration of the substrate of 0.5 M, NaOAc (aq. 0.6 M, 1 mol %, 16.7µl) and 2,3-butenedione (0.5 equiv. 43.5 µl) to give a final volume of 2 ml. The solution was stirring in an ice/water bath before addition of H₂O₂ (50 wt. %, 1.5 equiv., 85 µl). The solution was stirred for 1 h.

After 1 h, brine (10 ml) was added and the reaction was extracted with dichloromethane. The combined organic layers were washed with brine. The product was dried over Na₂SO₄ (anhyd.), filtered, and the dichloromethane was removed in vacuo. 1,2-Dichlorobenzene was employed as internal standard for Raman and ¹H NMR spectroscopy. The products were isolated by flash column chromatography on silica gel 230-400 or neutral aluminum oxide 70-230.

**Note:** For some reactions CD₃CN was used as solvent with analysis after the reaction carried out by ¹H NMR spectroscopy directly.

![Diagram of manganese(VII) oxide catalytic oxidation](image)

**Cyclooctene oxide** Isolated by flash column chromatography on neutral aluminum oxide 70-230 (pentane/ether = 9:1, Rf = 0.6). The title compound was obtained as colorless solid (91.5mg, 0.73mmol, 73 %)

At 1.1 gram (10 mmol) scale, the oxidation of cyclooctene using the same procedure provided cyclooctene oxide as a colorless solid (881 mg, 7.0 mmol, 70 %)

At 5.5 gram (50 mmol) scale, the oxidation of cyclooctene using the same procedure provided full conversion with cyclooctene oxide obtained as a colorless solid (4.23 g, 33.5 mmol, 67 %). (side products: 15% diol, 7% alpha-hydroxyl ketone) ¹H NMR (400 MHz, CDCl₃) δ 2.87-2.81 (m, 2H), 2.12-2.06 (m, 2H), 1.60-1.30 (m, 8H), 1.25 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 55.5, 26.5, 26.3, 25.5.
$^1$H and $^{13}$C NMR spectra in CDCl$_3$ of the product cyclooctene oxide
Scheme 1

Entry 1 from Table S3

\[ \text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}\ 0.01 \text{ mol %} \]
\[ \text{PCA 0.5 mol%} \]
\[ \text{butanedione 0.5 equiv.} \]
\[ \text{H}_2\text{O}_2 \ 1.5 \text{ equiv.} \]
\[ \text{NaOAc(aq.)} \ 1 \text{ mol %} \]
\[ \text{CH}_3\text{CN (0.5 M)} \]
\[ 0 \ ^\circ \text{C to r.t.} \ 1 \text{ h} \]

\( ^1\text{H NMR spectrum in CD}_3\text{CN with 1,2-dcb internal standard of the reaction mixture obtained by oxidation of 1-methyl-cyclohexene} \)
Entry 2 from Table S3

\[
\text{Mn(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \quad 0.01 \text{ mol %} \\
\text{PCA} \quad 0.5 \text{ mol %} \\
\text{butanedione} \quad 0.5 \text{ equiv.} \\
\text{H}_2\text{O}_2 \quad 1.5 \text{ equiv.} \\
\text{NaOAc(aq.)} \quad 1 \text{ mol %} \\
\text{CH}_3\text{CN} \quad (0.5 \text{ M}) \\
0 \text{ °C to r.t.} \quad 1 \text{ h}
\]

α-pinene oxide  The procedure used was as for the catalyzed oxidation of cyclooctene.

The product was isolated by flash column chromatography over neutral aluminum oxide (pentane/ether = 99:1, Rf = 0.6). The title compound was obtained as colorless oil (111 mg, 0.73 mmol, 73%).

On a 680 mg (5 mmol) scale α-pinene was converted to α-pinene oxide to yield a colorless oil (540 mg, 3.55 mmol, 71%).

\(^1\text{H NMR (400 MHz, CDCl}_3) \ \delta 3.04 \text{ (dd, } J=4.1, 1.1, 1\text{H}), 2.02-1.86 \text{ (m, 4H), 1.73-1.68 \text{ (m, 1H), 1.60 \text{ (d, } J=9.4, 1\text{H), 1.33 \text{ (s, 3H), 1.28 \text{ (s, 3H), 0.93(s, 3H); } ^{13}\text{C NMR (101 MHz, CDCl}_3) \ \delta 60.3, 56.8, 45.0, 40.5, 39.7, 27.6, 26.6, 25.8, 22.3, 20.1; HRMS (ESI+) calc. for C}_{10}\text{H}_{17}\text{O (M+H)}^+ \ 153.1265, \text{ found 153.1274;}}\]
$^1$H and $^{13}$C NMR spectra in CDCl$_3$ of the isolated product $\alpha$-pinene oxide
Entry 3 from Table S3

\[
\begin{align*}
\text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \hspace{1cm} 0.01 \text{ mol } \% \\
\text{PCA} \hspace{0.5cm} 0.5 \text{ mol } \% \\
\text{butanedione} \hspace{0.5cm} 0.5 \text{ equiv.} \\
\text{H}_2\text{O}_2 \hspace{0.5cm} 1.5 \text{ equiv.} \\
\text{NaOAc(aq.)} \hspace{0.5cm} 1 \text{ mol } \% \\
\text{CH}_3\text{CN (0.5 M)} \\
0 \degree C \text{ to r.t.} \hspace{0.5cm} 1 \text{ h}
\end{align*}
\]

**Styrene oxide.** The procedure used was as for the catalyzed oxidation of cyclooctene. The product was isolated by flash column chromatography over neutral aluminum oxide (pentane/ether = 85:15, Rf = 0.5). The title compound was obtained as colorless oil (87.5mg, 0.73mmol, 73%).

\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.41-7.28 \text{ (m, 5H), 3.87 (t, } J = 2.7, 1\text{H), 3.15 (dd, } J = 5.5, 4.1, 1\text{H), 2.81 (dd, } J = 5.5, 2.5, 1\text{H); } ^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 137.61, 128.99, 128.50, 128.18, 127.97, 125.49, 52.35, 51.1.\)
$^1$H and $^{13}$C NMR spectra in CDCl$_3$ of the isolated product styrene oxide
Entry 4 from Table S3

\[
\text{Mn(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \ 0.01 \text{ mol %} \\
\text{PCA} \ 0.5 \text{ mol %} \\
\text{butanedione} \ 0.5 \text{ equiv.} \\
\text{H}_2\text{O}_2 \ 1.5 \text{ equiv.} \\
\text{NaOAc(aq.)} \ 1 \text{ mol %} \\
\text{CH}_3\text{CN (0.5 M)} \\
0 \ ^{\circ}\text{C to r.t.} \ 1 \text{ h}
\]

**Citronellol epoxide** The procedure used was as for the catalyzed oxidation of cyclooctene. The product was isolated by flash column chromatography over neutral aluminum oxide (pentane/ether = 30:70, Rf = 0.5). The title compound was obtained as colorless oil (117 mg, 0.68 mmol, 68%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.65 (m, 2H), 2.68 (t, $J=6.3$, 3H), 1.74-1.36 (m, 7H), 1.28 (s, 3H), 1.24 (s, 3H), 0.89 (d, $J=6.5$, 3H), $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 64.6, 64.6, 60.8, 58.4, 58.3, 39.7, 39.5, 33.7, 33.6, 29.3, 29.1, 26.4, 26.1, 24.8, 19.6, 19.4, 18.6, 18.6; HRMS (ESI+) calc. for C$_{10}$H$_{21}$O$_2$ (M+H)$^+$ 173.1536, found 173.1527.
$^1$H and $^{13}$C NMR spectra in CDCl$_3$ of the isolated product citronellol epoxide
Scheme 2

Entry 6 from Table S3

\[
\begin{align*}
\text{Mn(ClO}_4\text{)}_2 \cdot \text{H}_2\text{O} & \text{  0.01 mol } \% \\
\text{PCA} & \text{  0.5 mol } \% \\
\text{butanedione} & \text{  0.5 equiv.} \\
\text{H}_2\text{O}_2 & \text{  1.5 equiv.} \\
\text{NaOAc(aq.)} & \text{  1 mol } \% \\
\text{CH}_3\text{CN} & \text{  (0.5 M)} \\
0 \text{ °C to r.t.} & \text{  1 h}
\end{align*}
\]

\[\begin{aligned}
\text{H} & \text{NMR spectrum in CDCl}_3 \text{ of the crude product obtained by oxidation of cycloheptene}
\end{aligned}\]
Entry 7 from Table S3

Mn(ClO4)2·6H2O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H2O2 1.5 equiv.
NaOAc(aq.) 1 mol %
CH3CN (0.5 M)
0 °C to r.t. 1 h

1H NMR spectrum in CD3CN with 1,2-dcb internal standard of the reaction mixture obtained by oxidation of cyclohexene
Entry 8 from Table S3

Mn(ClO$_4$)$_2$·6H$_2$O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc(aq.) 1 mol %
CH$_3$CN (0.5 M)
0 °C to r.t. 1 h

$^1$H NMR spectrum in CD$_3$CN with 1,2-dcb internal standard of the reaction mixture obtained by oxidation of cyclopentene
Entry 9 from Table S3

\[
\text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \quad 0.01 \text{ mol \%} \\
\text{PCA} \quad 0.5 \text{ mol \%} \\
\text{butanedione} \quad 0.5 \text{ equiv.} \\
\text{H}_2\text{O}_2 \quad 1.5 \text{ equiv.} \\
\text{NaOAc(aq.)} \quad 1 \text{ mol \%} \\
\text{CH}_3\text{CN} \quad (0.5 \text{ M}) \\
0 \, ^\circ\text{C} \text{ to r.t.} \quad 1 \text{ h}
\]

\[\text{O} \]

\[\text{HNMR spectrum in CD}_3\text{CN with 1,2-dcb internal standard of the reaction mixture obtained by oxidation of 1-methyl cyclopentene}\]
Entry 10 from Table S3

\[
\text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O 0.01 mol }% \\
\text{PCA 0.5 mol }% \\
\text{butanedione 0.5 equiv.} \\
\text{H}_2\text{O}_2 1.5 \text{equiv.} \\
\text{NaOAc(aq.) 1 mol }% \\
\text{CH}_3\text{CN (0.5 M)} \\
0^\circ\text{C to r.t. 1 h}
\]

1H NMR spectrum in CD$_3$CN with 1,2-dcb internal standard of the reaction mixture obtained by oxidation of 2-methyl 2-pentene
Entry 11 from Table S3

Mn(ClO₄)₂·6H₂O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc (aq.) 1 mol %
CH₃CN (0.5 M)
0 °C to r.t. 1 h

¹H NMR spectrum in CD₃CN with 1,2-dcb internal standard of the reaction mixture obtained by oxidation of 2,3-dimethyl-2-butene
Entry 12 from Table S3

Mn(ClO$_4$)$_2$: 6H$_2$O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc (aq.) 1 mol %
CH$_3$CN (0.5 M)
0 °C to r.t. 1 h

1,2-Epoxyoctane The procedure used was as for the catalyzed oxidation of cyclooctene. The product was isolated by flash column chromatography over neutral aluminum oxide (pentane/ether = 98:2, Rf = 0.5). The title compound was obtained as colorless oil (52.5mg, 0.41 mmol, 41%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.89 (m, 1H), 2.74 (q, 1H), 2.45 (q, 1H), 1.53- 1.27 (m, 10H), 0.88(t, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 52.3, 47.1, 32.4, 31.7, 29.0, 25.9, 22.5, 14.
$^1$H and $^{13}$C NMR spectra in CDCl$_3$ of the isolated product 1,2-epoxyoctane
Entry 13 from Table S3

Mn(ClO$_4$)$_2$·6H$_2$O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc(aq.) 1 mol %
CH$_3$CN (0.5 M)
0 °C to r.t. 1 h

2-Methyl-2-(2-methylpentyl)oxirane The procedure used was the same as for the catalyzed oxidation of cyclooctene. The product was isolated by flash column chromatography over silica gel (pentane/ether = 97:3, Rf = 0.5). The title compound was obtained as a colorless oil (102 mg, 0.72 mmol, 72%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.52-2.45 (m, 2H), 1.73-1.40 (m, 2H), 1.26-1.18 (m, 7H), 1.09-0.97 (m, 1H), 0.88-0.79 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 56.0, 55.9, 54.3, 53.7, 44.2, 44.1, 39.7, 39.1, 30.0, 29.8, 20.7, 20.6, 20.0, 19.8, 19.5, 14.1; HRMS (ESI+) calc. for C$_9$H$_{19}$O (M+H)$^+$ 143.1425, found 143.1430;
$^1$H and $^{13}$C NMR spectra in CDCl$_3$ of the isolated product 2-methyl-2-(2-methylpentyl)oxirane
Entry 14 from Table S3

Mn(ClO$_4$)$_2$·6H$_2$O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc(aq.) 1 mol %
CH$_3$CN (0.5 M)
0°C to r.t. 1 h

$^1$H NMR spectrum in CDCl$_3$ of the crude product obtained upon oxidation of 1-phenyl cyclohexene
Entry 15 from Table S3

\[
\text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O 0.01 mol \%}
\]
\[
\text{PCA 0.5 mol \%}
\]
\[
2, 3\text{-butanedione 0.5 equiv.}
\]
\[
\text{H}_2\text{O}_2 1.5 equiv.
\]
\[
\text{NaOAc(aq.) 1 mol \%}
\]
\[
\text{CH}_3\text{CN (0.5 M)}
\]
\[
0^\circ\text{C to r.t. 1 h}
\]

\[
\text{1H NMR spectrum in CDCl}_3 \text{ of the crude product obtained upon oxidation of trans-stilbene}
\]
At 9 gram (50 mmol) scale, the oxidation of cyclooctene using the same procedure provided 85% conversion with stilbene oxide obtained as a colorless solid (6.24 g, 31 mmol, 63.5 %). (side products: 15% diol, 3% alpha-hydroxyl ketone).
$^1$H NMR spectrum in CDCl$_3$ of the purified product obtained by multi-gram oxidation of trans-stilbene
\(^{13}\)C NMR spectrum in CDCl\(_3\) of the purified product obtained by multi-gram oxidation of trans-stilbene

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49, 7.49, 7.49, 7.47, 7.47, 7.46, 7.45, 7.45, 7.44, 7.44, 7.43, 7.43, 7.42, 7.42, 7.41, 7.40, 7.40, 7.26, 3.96.

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.25, 128.66, 128.41, 125.63, 77.52, 77.20, 76.88, 62.91.
Entry 16 from Table S3

\[
\text{Mn(ClO}_4\text{)}_2\cdot 6\text{H}_2\text{O} \ 0.01 \text{ mol} \%
\]

PCA 0.5 mol %
butanedione 0.5 equiv.
H\textsubscript{2}O\textsubscript{2} 1.5 equiv.

\[
\text{NaOAc(aq.)} \ 1 \text{ mol} \%
\]

CH\textsubscript{3}CN (0.5 M)
0 °C to r.t. 1 h

\( ^1\text{H NMR spectrum in CDCl}_3 \) of the crude product obtained by oxidation of phenanthrene
Entry 17 from Table S3

Mn(ClO4)2·6H2O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H2O2 1.5 equiv.
NaOAc(aq.) 1 mol %
CH3CN (0.5 M)
0 °C to r.t. 1 h

1H NMR spectrum in CD3CN of the crude product obtained upon oxidation of 4-vinylanisole
Entry 18 from Table S3

\[
\text{Mn(ClO}_3\text{)}_2 \cdot \text{H}_2\text{O} 0.01 \text{ mol}\% \\
\text{PCA 0.5 mol}\% \\
\text{butanedione 0.5 equiv.} \\
\text{H}_2\text{O}_2 1.5 \text{ equiv.} \\
\text{NaOAc (aq.) 1 mol}\% \\
\text{CH}_3\text{CN (0.5 M)} \\
0 ^\circ \text{C to r.t. 1 h}
\]

\[\begin{array}{c}
\text{F}_3\text{C} \\
\text{H} \\
\text{C} \\
\text{C} \\
\end{array}\]

\[\begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\text{C} \\
\end{array}\]

$^1$H NMR spectrum in CDCl$_3$ of the crude product obtained upon oxidation of 4-(trifluoromethyl) styrene
Entry 19 from Table S3

\[
\text{Mn(ClO}_4\text{)}_{2} \cdot 6\text{H}_2\text{O} \ 0.01 \text{ mol \%} \\
\text{PCA} 0.5 \text{ mol \%} \\
\text{butanedione} 0.5 \text{ equiv.} \\
\text{H}_2\text{O}_2 \ 1.5 \text{ equiv.} \\
\text{NaOAc(aq.)} \ 1 \text{ mol \%} \\
\text{CH}_3\text{CN (0.5 M)} \\
0 \ ^\circ \text{C to r.t.} \ 1 \text{ h}
\]

\[\text{H NMR spectrum in CD}_3\text{CN with 1,2-dcb internal standard of the reaction mixture obtained by oxidation of 2-carene}\]
**3-carene oxide** The procedure used was as for the catalyzed oxidation of cyclooctene. The product was isolated by flash column chromatography over neutral aluminum oxide (pentane/ether = 96:4, Rf = 0.5). The title compound was obtained as colorless oil (68 mg, 0.45 mmol, 45%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.82 (s, 1H), 2.30 (m, 1H), 2.13 (dd, $J$=9.0, 7.2), 1.55 (m, 2H), 1.24 (s, 3H), 0.99 (s, 3H), 0.71 (s, 3H), 0.50 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 58.1, 55.8, 27.7, 23.3, 23.0, 19.1, 15.9, 14.5, 13.8.
$^1$H NMR and $^{13}$C NMR spectra in CDCl$_3$ of the isolated product 3-carene oxide
Scheme 5

Entry 21 from Table S3

Mn(ClO₄)₂ 6H₂O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc(aq.) 1 mol %
CH₃CN (0.5 M)
0 °C to r.t.  1 h

HO \( \rightarrow \) n-hept

\( \text{O} \)

\(^{1}H\) NMR spectrum in CDCl₃ with 1,2-DCB internal standard of the crude product obtained upon oxidation of dec-2-en-1-ol
3-(Oxiran-2-yl)benzaldehyde  The procedure used was as for the catalyzed oxidation of cyclooctene. The product was isolated by flash column chromatography over neutral aluminum oxide (pentane/ether = 81:19, Rf = 0.6). The title compound was obtained as colorless oil (90 mg, 0.61 mmol, 61%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.02 (s, 1H), 7.83 (m, 2H), 7.54 (m, 2H), 3.95 (t, $J$ =2.6, 1H), 3.20 (dd, $J$ =5.3, 4.1, 1H), 2.82 (dd, $J$ =5.4, 2.5, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.9, 139.0, 131.3, 129.5, 129.2, 126.6, 51.7, 51.2; HRMS (ESI+) calc. for C$_9$H$_9$O$_2$ (M+H)$^+$ 149.05971, found 149.05980.
$^1$H and $^{13}$C NMR spectrum in CDCl$_3$ of product 3-(oxiran-2-yl)benzaldehyde
Scheme 6

Entry 23 from Table S3

Ma(ClO$_4$)$_2$:H$_2$O 0.01 mol%
PCA 0.5 mol%
butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc (aq.) 1 mol%
CH$_3$CN (0.5 M)
0 °C to r.t. 1 h

$^1$H NMR spectrum in CDCl$_3$ with 1,2-DCB internal standard of the reaction mixture obtained upon oxidation of tert-butyl (4-phenylbut-3-en-2-yl) carbonate.
Scheme 7

For Entry 24 from Table S3 see section 9 below

Entry 25 from Table S3

\[
\text{(1aS*,2S*,7bR*)-3-Benzoyl-1a,2,3,7b-tetrahydrooxireno[2,3-c]quinoline-2-carbonitrile.}
\]

The reactions procedure was the same as for the oxidation of cyclooctene. The product was isolated by flash column chromatography over silica gel (Dichloromethane, RF = 0.5). The title compound was obtained as white solid (180 mg, 0.65 mmol, 65%).

\[
\begin{align*}
\text{1H NMR} &\ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.53-7.51 (\text{dd}, J=7.5, 1.1, 1\text{H}), 7.4-7.34 (\text{m}, 3\text{H}), 7.27-7.23 (\text{m}, 2\text{H}), 7.19-7.16 (\text{t}, J=7.5, 1\text{H}), 7.08-7.03 (\text{t}, J=7.6, 1\text{H}), 6.54-6.52 (\text{d}, J=8.0, 1\text{H}), 6.27 (\text{d}, J=2.4, 1\text{H}), 4.29-4.27 (\text{dd}, J=3.8, 2.6, 1\text{H}), 4.15 (\text{d}, J=4.0, 1\text{H}) \ ; \\
\text{13C NMR} &\ (101 \text{ MHz, CDCl}_3) \ \delta \ 170.12, 135.23, 133.68, 131.38, 130.16, 129.12, 128.32, 126.80, 126.47, 124.00, 114.83, 59.43, 51.09, 41.59; \\
\text{HRMS} &\ (\text{ESI}^+) \ \text{calc. for C}_{17}\text{H}_{12}\text{N}_2\text{O}_2 (\text{M+Na})^+ \ 299.07910, \ \text{found} 299.07887; \\
\text{The stereochemistry of 1-Benzoyl-1,2-dihydro-2-quinolinecarbonitrile oxide was determined by 1H-NMR spectroscopic analysis. The coupling constants of protons H_a, H_b and H_c (see Scheme) indicate that the CN group is trans to the epoxide moiety.}
\end{align*}
\]
$^1$H and $^{13}$C NMR spectra in CDCl$_3$ of the isolated product from the oxidation of 1-Benzoyl-1,2-dihydro-2-quinolinecarbonitrile. Only one diastereoisomer pair formed.
Entry 26 from Table S3

Mn(ClO₄)₂·6H₂O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc(aq.) 1 mol %
CH₃CN (0.5 M)
0 °C to r.t. 1 h

¹H NMR spectrum in CDCl₃ with 1,2-DCB internal standard of the crude product obtained upon oxidation of cis-heptene
Entry 27 from Table S3

Mn(ClO$_4$)$_2$·6H$_2$O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc(aq.) 1 mol %
CH$_3$CN (0.5 M)
0 °C to r.t. 1 h

$^1$H NMR spectrum in CDCl$_3$ with 1,2-DCB internal standard of the crude product obtained upon oxidation of trans-heptene
**Entry 28 from Table S3**

Mn(ClO₄)₂·H₂O 0.01 mol%  
PCA 0.5 mol%  
butanedione 0.5 equiv.  
H₂O₂ 1.5 equiv.  
NaOAc (aq.) 1 mol%  
CH₃CN (0.5 M)  
0 °C to r.t. 1 h

\[ \text{cis-1-methylstyrene} \]

\[ \text{1H NMR spectrum in CDCl}_3 \text{ of the reaction mixture obtained upon oxidation of cis-1-methylstyrene} \]
Entry 29 from Table S3

Mn(ClO₄)₂·H₂O 0.01 mol%
PCA 0.5 mol%
butanedione 0.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc (aq.) 1 mol%
CH₃CN (0.5 M)
0 °C to r.t. 1 h

¹H NMR spectrum in CDCl₃ of the reaction mixture obtained upon oxidation of trans-1-methylstyrene
Scheme 9

Entry 30 from Table S3

Mn(ClO$_4$)$_2$·6H$_2$O 0.01 mol %
PCA 0.5 mol %
2, 3-butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc(aq.) 1 mol %
CH$_3$CN (0.5 M)
0 °C to r.t. 1 h

$^1$H NMR spectrum in CDCl$_3$ of the crude product obtained by oxidation of cis-stilbene
Other examples

Entry 31 from Table S3

\[
\text{Mn(ClO}_4\text{)}_2\cdot 6\text{H}_2\text{O} \quad 0.01 \text{ mol \%}
\]
\[
\text{PCA} \quad 0.5 \text{ mol\%}
\]
\[
\text{butanedione} \quad 0.5 \text{ equiv.}
\]
\[
\text{H}_2\text{O}_2 \quad 1.5 \text{ equiv.}
\]
\[
\text{NaOAc(aq.)} \quad 1 \text{ mol \%}
\]
\[
\text{CH}_3\text{CN (0.5 M)}
\]
\[
0 \, ^\circ\text{C to r.t.} \quad 1 \text{ h}
\]

\[
\text{\textsuperscript{1}H NMR spectrum in CDCl}_3\text{ of the crude product obtained upon oxidation of 1(4-}
\text{methoxyphenyl)}\text{but-3-en-1-ol}
\]
Oxidation of conjugated and non-conjugated dienes – Scheme 4

Mn(ClO₄)₂·6H₂O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc (aq.) 1 mol %
CH₃CN (0.5 M)
0 °C to r.t. 1 h

¹H NMR spectrum in CD₃CN of the reaction mixture obtained after oxidation of isoprene
\[
\text{Mn(ClO}_4\text{)}_2 \cdot \text{6H}_2\text{O} \quad 0.01 \text{ mol } \%
\]
\[
\text{PCA} \quad 0.5 \text{ mol } \%
\]
\[
\text{butanedione} \quad 0.5 \text{ equiv.}
\]
\[
\text{H}_2\text{O}_2 \quad 1.5 \text{ equiv.}
\]
\[
\text{NaOAc(aq.)} \quad 1 \text{ mol } \%
\]
\[
\text{CH}_3\text{CN} \quad (0.5 \text{ M})
\]
\[
0 ^\circ \text{C to r.t.} \quad 1 \text{ h}
\]

\[
\begin{align*}
&\text{1H NMR spectrum in CDCl}_3 \text{ with 1,2-DCB internal standard of the crude product obtained upon}
\\&\text{oxidation of limonene}
\end{align*}
\]
Mn(ClO$_4$)$_2$·6H$_2$O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.
NaOAc (aq.) 1 mol %
CH$_3$CN (0.5 M)
0 °C to r.t. 1 h

$^1$H NMR spectrum in CD$_3$CN with 1,2-DCB internal standard of the reaction mixture obtained upon oxidation of citral
Entry 1 from Table S5

\[ \text{Mn(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \ 0.01 \text{ mol} \% \]
\[ \text{PCA} \ 0.5 \text{ mol} \% \]
\[ \text{butanedione} \ 0.5 \text{ equiv.} \]
\[ \text{H}_2\text{O}_2 \ 1.5 \text{ equiv.} \]
\[ \text{NaOAc(aq.)} \ 1 \text{ mol} \% \]
\[ \text{CH}_3\text{CN} \ (0.5 \text{ M}) \]
\[ 0 \ ^\circ\text{C} \text{ to r.t.} \ 1 \text{ h} \]

\[ ^1\text{H NMR spectrum in CD}_3\text{CN with 1,2-DCB internal standard of the reaction mixture obtained upon oxidation of 3-methyl 2-cyclohexene-1-one} \]
Entry 2 from Table S5

Mn(ClO₄)₂·6H₂O 0.01 mol %
PCA 0.5 mol %
butanedione 0.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc (aq.) 1 mol %
CH₃CN (0.5 M)
0 °C to r.t. 1 h

¹H NMR spectrum in CDCl₃ with 1,2-DCB internal standard of the crude product obtained upon oxidation of 5-methyl-2-one-3-hexene
Entry 3 from Table S5

Mn(ClO$_4$)$_2$: 6H$_2$O 0.01 mol %
PCA 0.5 mol %
butanediol 0.5 equiv.
H$_2$O$_2$ 1.5 equiv.

NaOAc (aq.) 1 mol %
CH$_3$CN (0.5 M)
0 ºC to r.t. 1 h

$^1$H NMR spectrum in CDCl$_3$ with 1,2-DCB internal standard of the crude product obtained upon oxidation of trans-3-nonen-2-one
Entry 4 from Table S5

\[
\text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \text{ 0.01 mol %} \\
\text{PCA 0.5 mol %} \\
\text{butanedione 0.5 equiv.} \\
\text{H}_2\text{O}_2 \text{ 1.5 equiv.} \\
\text{NaOAc (aq.) 1 mol %} \\
\text{CH}_3\text{CN (0.5 M)} \\
\text{0 °C to r.t. 1 h}
\]

\[\text{O} \quad \text{O} \quad \text{O} \]

\[^1\text{H NMR spectrum in CD}_3\text{CN with 1,2-DCB internal standard of the reaction mixture obtained upon oxidation of 1-acetyl-pentene}\]
6. Procedure for catalytic oxidation of α-pinene followed by in situ isomerization and product characterization

**Procedure:** After epoxidation of α-pinene (1 mmol, 158µl) by the procedure described for cyclooctene, silica gel 230-400 (150g) was added to the reaction mixture, which was then stirred at 40°C for 1 h. The silica gel was removed by filtration and the solvent was removed *in vacuo*. Campholenic aldehyde was obtained (30 mg, 0.2 mmol, 20%)
$^1$H and $^{13}$C NMR in spectrum in CDCl$_3$ of the product campholenic aldehyde obtained from $\alpha$-pinene
7. Procedures for the catalytic oxidation of electron deficient alkenes and product characterization

Oxidation of electron deficient alkenes to their cis-diol products. In all cases only a single product was formed.

The alkene (1 mmol, final conc. 0.5 M), aqueous NaOAc (0.6 M, 16.7 µl, final conc. 5 mM) and 2,3-butanedione (130.5 µl, final conc. 0.75 M) were added to a solution of Mn(ClO₄)₂ (final conc. 0.05 mM) and pyridine-2-carboxylic acid (2.5 mM) in CH₃CN to give a final volume of 2ml. The solution was stirred in an ice water bath and H₂O₂ (50 wt. %, 1.5 equiv. 85 µl) was added as a single portion and the solution stirred for 1 h. After 1 h, brine (10 ml) was added and the reaction was extracted with dichloromethane. The combined organic layers were washed with brine. The product was dried over Na₂SO₄(anhyd.), filtered, and the dichloromethane was removed in vacuo.
\[ \text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \ 0.01 \text{ mol}\% \]
\[ \text{PCA} \ 0.5 \text{ mol}\% \]
\[ \text{butanedione 1.5 equiv.} \]
\[ \text{H}_2\text{O}_2 \ 1.5 \text{ equiv.} \]
\[ \text{NaOAc (aq.) 1 mol}\% \]
\[ \text{CH}_3\text{CN (0.5 M)} \]
\[ 0 ^\circ\text{C to r.t. 1 h} \]

\[ \text{EtO} \]
\[ \text{OEt} \]
\[ \text{O} \]
\[ \text{OOH} \]
\[ \text{OH} \]

\(^1\text{H NMR spectrum in CDCl}_3\) of the crude product obtained by the oxidation of diethyl fumarate
\[ \text{Mn(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \text{ 0.01 mol \%} \]
\[ \text{PCA 0.5 mol \%} \]
\[ \text{butanedione 1.5 equiv.} \]
\[ \text{H}_2\text{O}_2 \text{ 1.5 equiv.} \]
\[ \text{NaOAc (aq.) 1 mol \%} \]
\[ \text{CH}_3\text{CN (0.5 M)} \]
\[ 0 \degree \text{C to r.t. 1 h} \]

\[ \text{EtO} \quad \text{OEt} \quad \text{O} \quad \text{O} \]
\[ \text{HO} \quad \text{OH} \]

\[ ^1\text{H NMR spectrum in CDCl}_3 \text{ of the crude product obtained by the oxidation of diethyl maleate} \]
Mn(ClO₄)₂·6H₂O 0.01 mol %
PCA 0.5 mol %
butanedione 1.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc (aq.) 1 mol %
CH₃CN (0.5 M)
0 °C to r.t. 1 h

¹H NMR spectrum in DMSO-d₆ of the crude product obtained by the oxidation of maleimide with 1,2-dichlorobenzene internal standard.
Mn(ClO₄)₂·6H₂O 0.01 mol %
PCA 0.5 mol %
butanedione 1.5 equiv.
H₂O₂ 1.5 equiv.
NaOAc (aq.) 1 mol %
CH₃CN (0.5 M)
0 °C to r.t. 1 h

¹H NMR spectrum in DMSO-d₆ of the crude product obtained by the oxidation of 1-benzyl-1H-pyrrole-2,5-dione
8. Identification of acetic acid formation in reaction mixture by $^{13}$C NMR spectroscopy

The $^{13}$C NMR spectrum of the reaction mixture allowed for the identification of acetic acid formation during the reaction. The reaction mixture excluding the alkene was stirred for 40 min. The $^{13}$C NMR spectrum showed the appearance of acetic acid, which was confirmed by spiking with additional acetic acid.

$^{13}$C NMR spectrum of the reaction mixture after 40 min showing the presence of acetic acid and butanedione (in CD$_3$CN).
$^{13}$C NMR spectrum of the reaction mixture after 40 min showing the presence of acetic acid and butanedione (in CD$_3$CN) spiked with additional acetic acid.

\[
\text{Mn(ClO}_4\text{)}_2 \cdot \text{H}_2\text{O} \ 0.01 \text{ mol}\% \\
\text{PCA} \ 0.5 \text{ mol}\% \\
\text{butanedione} \ 0.5 \text{ equiv.} \\
\text{H}_2\text{O}_2 \ 1.5 \text{ equiv.} \\
\text{NaOAc (aq.)} \ 1 \text{ mol}\% \\
\text{CH}_3\text{CN (0.5 M)} \\
0 \ ^\circ \text{C to r.t.} \ 1 \text{ h}
\]

$^1H$ NMR spectrum in CDCl$_3$ of the crude product obtained by the oxidation of (S)-4-phenylbut-3-en-2-yl acetate
HPLC chromatogram of the product obtained by the oxidation of racemic 4-phenylbut-3-en-2-yl acetate (together with 4-phenylbut-3-en-2-yl acetate) also showing all four stereoisomers.

(2) For proton couplings in cyclohexane, see: Garbisch Jr., E. W.; Griffith, M. G. *J. Am. Chem. Soc.* **1968**, *90*, 6543