Palladium on Charcoal Catalyzed 3,4-Hydroperoxidation of α-Substituted Enals with Triethylsilane and Water

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1 General Information

1.1 Experimental methods

All reactions were carried out in screw cap glass vials or septum cap glass flasks under air atmosphere, unless otherwise noted. THF, Et₂O, DCM, ACN, and toluene were obtained by passing deoxygenated solvents through activated a mall pad of alumina (neutral) columns (MBraun SPS-800 Series solvent purification system). Other solvents and reagents were used as obtained from the supplier, unless otherwise noted. Pd/C was activated/dried using the previously published procedure.¹ Analytical TLC was performed using Merck silica gel F254 (230–400 mesh) plates and analyzed by UV light or by staining upon heating with vanillin solution (6 g of vanillin, 5 mL of conc. H₂SO₄, 3 mL of glacial acetic acid, 250 mL of EtOH) or KMnO₄ solution (1 g of KMnO₄, 6.7 g of K₂CO₃, 1.7 mL of 1 M NaOH, 100 mL of H₂O). For the 2-methyl-1,2-diols ⁵ and for the nitrile ⁷ silica gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230–400 mesh) and p.a. grade solvents unless otherwise noted. For the α-substituted acroleins, the silica gel chromatography, the Teledyne ISCO CombiFlash was used. A small pad of alumina (neutral) columns were prepared by filling plastic syringes (5–20 mL) with Sigma-Aldrich purum p.a. grade alumina. The ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on Bruker Advance 300 spectrometer. The chemical shifts are reported in ppm relative to residual CHCl₃ (δ 7.26) for ¹H NMR. For the ¹³C NMR spectra, the residual CDCl₃ (δ 77.16) was used as the internal standards. Melting point (mp) was determined in open capillary using Gallenkamp melting point apparatus. IR spectra were recorded on a Tensor27 FT-IR spectrometer. High-resolution mass spectrometric data were prepared using MicroMass LCT Premier Spectrometer.

1.2 Starting materials

The starting materials ¹a, ¹b, ¹c, ¹f, ¹g and ¹h used were prepared using the α-methylenation procedure described by Erkkilä and Pihko.² The starting material ¹e was purchased from commercial supplier and was used as received.

## Experimental Data

### 2.1 Optimization experiments

**Table S1. Screening of reaction conditions**

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Reaction Time</th>
<th>Conversion</th>
<th>Product selectivity 2a/3a/4a(^{a,b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>1 h 30 min</td>
<td>100 %</td>
<td>97:3:0</td>
</tr>
<tr>
<td>2</td>
<td>20 μL H₂SO₄</td>
<td>1 min</td>
<td>89 %</td>
<td>0:20:80</td>
</tr>
<tr>
<td>3</td>
<td>20 μL H₂SO₄</td>
<td>10 min</td>
<td>100 %</td>
<td>0:100:0</td>
</tr>
<tr>
<td>4</td>
<td>20 μL H₂O</td>
<td>2 min</td>
<td>100 %</td>
<td>0:11:89</td>
</tr>
</tbody>
</table>

Reaction conditions: 1a (44 mg, 0.30 mmol, 1.0 equiv), Pd/C (1 mg), triethylsilane (38 mg, 53 mml, 0.33 mmol, 1.1 equiv), EtOAc (1 mL), room temperature. For the procedure, see section 2.2. [a] Determined by \(^1\)H NMR analysis. [b] Identical selectivities were obtained with four different batches of Pd/C (5–10 wt %) from different sources (Sigma-Aldrich, Fluka and other suppliers).
Table S2. Solvent screening

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Reaction Time</th>
<th>Conversion</th>
<th>Product selectivity $3a/4a^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>4 min$^b$</td>
<td>100 %</td>
<td>31:69</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>2 h</td>
<td>37 %$^c$</td>
<td>30:70</td>
</tr>
<tr>
<td>3</td>
<td>Hexane</td>
<td>2 h</td>
<td>0 %</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>2 h</td>
<td>4 %</td>
<td>32:68</td>
</tr>
<tr>
<td>5</td>
<td>EtOAc</td>
<td>2 min$^b$</td>
<td>100 %</td>
<td>11:89</td>
</tr>
<tr>
<td>6</td>
<td>ACN</td>
<td>2 h</td>
<td>48 %</td>
<td>100:0</td>
</tr>
<tr>
<td>7</td>
<td>Ether$^d$</td>
<td>5 min$^b$</td>
<td>100 %</td>
<td>11:89</td>
</tr>
</tbody>
</table>

Reaction conditions: 1a (44 mg, 0.30 mmol, 1.0 equiv), Pd/C (1 mg), triethylsilane (38 mg, 53 mml, 0.33 mmol, 1.1 equiv), solvent (1 mL), room temperature. For the procedure, see section 2.2. [a] Determined by $^1$H NMR analysis. [b] Sample taken when the formation of hydrogen gas (as observed by bubbling of the reaction mixture) ended (see: background reaction section 2.8.1.1). [c] Including 9 % of corresponding enol silane, see ref 1. [d] Some of the α-substituted acroleins used in the substarete scope are not soluble in ether.
Table S3. Catalyst screening

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst loading</th>
<th>Reaction Time</th>
<th>Product selectivity 3a/4a&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 mg</td>
<td>20 min</td>
<td>11:89&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>1 mg</td>
<td>2 min&lt;sup&gt;c&lt;/sup&gt;</td>
<td>11:89</td>
</tr>
<tr>
<td>5</td>
<td>10 mg</td>
<td>1 min&lt;sup&gt;c&lt;/sup&gt;</td>
<td>51:49</td>
</tr>
</tbody>
</table>

Reaction conditions: 1a (44 mg, 0.30 mmol, 1.0 equiv), Pd/C, triethylsilane (38 mg, 53 mmol, 0.33 mmol, 1.1 equiv), EtOAc (1 mL), room temperature. For the procedure, see section 2.2. [a] Determined by <sup>1</sup>H NMR analysis. [b] Reaction stopped at 61 % conversion. [c] Sample taken when the formation of hydrogen gas (as observed by bubbling of the reaction mixture) ended (see: background reaction section 2.8.1.1).
Table S4. Triethylsilane screening

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Et₃SiH</th>
<th>Reaction Time</th>
<th>Conversion</th>
<th>Product selectivity 3a/4a&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5 equiv</td>
<td>1 min</td>
<td>21 %</td>
<td>15:85</td>
</tr>
<tr>
<td>2</td>
<td>0.5 equiv</td>
<td>5 min</td>
<td>37 %</td>
<td>18:82</td>
</tr>
<tr>
<td>3</td>
<td>0.5 equiv</td>
<td>10 min</td>
<td>36 %</td>
<td>22:78</td>
</tr>
<tr>
<td>4</td>
<td>1.0 equiv</td>
<td>1 min</td>
<td>47 %</td>
<td>26:74</td>
</tr>
<tr>
<td>5</td>
<td>1.0 equiv</td>
<td>5 min</td>
<td>100 %</td>
<td>21:79</td>
</tr>
<tr>
<td>6</td>
<td>1.1 equiv</td>
<td>2 min&lt;sup&gt;b&lt;/sup&gt;</td>
<td>100 %</td>
<td>11:89</td>
</tr>
<tr>
<td>7</td>
<td>1.5 equiv</td>
<td>1 min</td>
<td>87 %</td>
<td>19:81</td>
</tr>
<tr>
<td>8</td>
<td>1.5 equiv</td>
<td>5 min</td>
<td>100 %</td>
<td>20:80</td>
</tr>
<tr>
<td>9</td>
<td>2.0 equiv</td>
<td>1 min</td>
<td>100 %</td>
<td>23:77</td>
</tr>
<tr>
<td>10</td>
<td>2.0 equiv</td>
<td>5 min</td>
<td>100 %</td>
<td>18:82</td>
</tr>
</tbody>
</table>

Reaction conditions: 1a (44 mg, 0.30 mmol, 1.0 equiv), Pd/C (1 mg), triethylsilane, THF (1 mL), room temperature. For the procedure, see section 2.2. [a] Determined by ¹H NMR analysis. [b] Sample taken when the formation of hydrogen gas (as observed by bubbling of the reaction mixture) ended (see: background reaction section 2.8.1.1).
### Table S5. Effect of scale

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product selectivity 3a/4ab</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3 mmol</td>
<td>11:89</td>
</tr>
<tr>
<td>2</td>
<td>0.9 mmol</td>
<td>30:70</td>
</tr>
<tr>
<td>5</td>
<td>1.5 mmol</td>
<td>35:65</td>
</tr>
</tbody>
</table>

Reaction conditions: Entry 1: 1a (44 mg, 0.30 mmol, 1.0 equiv), Pd/C (1 mg), triethylsilane (38 mg, 53 mmol, 0.33 mmol, 1.1 equiv), EtOAc (1 mL), room temperature, 4 min; Entry 2: 1a (132 mg, 0.90 mmol, 1.0 equiv), Pd/C (3 mg), triethylsilane (115 mg, 158 mmol, 0.99 mmol, 1.1 equiv), EtOAc (3 mL), room temperature, 4 min; Entry 3: 1a (219 mg, 1.50 mmol, 1.0 equiv), Pd/C (5 mg), triethylsilane (192 mg, 264 mmol, 1.65 mmol, 1.1 equiv), EtOAc (5 mL), room temperature, 4 min. For the procedure, see section 2.2. [a] Determined by 1H NMR analysis.
Table S6. Autoxidation period after the reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time</th>
<th>Product selectivity 3a/4a&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOAc</td>
<td>0 h</td>
<td>35:65</td>
</tr>
<tr>
<td>2</td>
<td>EtOAc</td>
<td>1 h</td>
<td>24:76</td>
</tr>
<tr>
<td>3</td>
<td>EtOAc</td>
<td>2 h</td>
<td>14:86</td>
</tr>
<tr>
<td>4</td>
<td>EtOAc</td>
<td>3 h</td>
<td>12:88</td>
</tr>
<tr>
<td>5</td>
<td>EtOAc</td>
<td>4 h</td>
<td>11:89</td>
</tr>
<tr>
<td>6</td>
<td>EtOAc</td>
<td>6 h</td>
<td>10:90</td>
</tr>
<tr>
<td>7</td>
<td>EtOAc</td>
<td>8 h</td>
<td>10:90</td>
</tr>
<tr>
<td>8</td>
<td>EtOAc</td>
<td>12 h</td>
<td>10:90</td>
</tr>
</tbody>
</table>

Reaction conditions: 1a (44 mg, 0.30 mmol, 1.0 equiv), Pd/C (1 mg), triethylsilane (38 mg, 53 mmol, 0.33 mmol, 1.1 equiv), EtOAc (1 mL), room temperature. For the procedure, see section 2.2. [a] Determined by <sup>1</sup>H NMR analysis. 3a observed is most likely to be formed by tautomerization of enol 6 during the <sup>1</sup>H NMR sample preparation.
2.2 Preparation of 2-hydroperoxy-2-methyl-3-phenylpropanal

To a suspension of α-substituted acrolein \(1a\) (44 mg, 0.30 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 1 mg) in EtOAc (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv). After 4 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (10 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion. Isolation of the product was unsuccessful. Product \(4a\) decomposes/polymerizes when concentrated. Characterization was carried out from the crude filtrate containing EtOAc and triethylsilanol 7.

IR (film cm\(^{-1}\)): 3379, 2955, 2877, 1734, 1455, 823, 728, 701, 681; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 9.71\) (s, 1H), 8.40 (br.s, 1H), 7.44 – 7.08 (m, 5H), 3.19 (d, 1H, \(J = 14.3\) Hz), 2.88 (d, 1H, \(J = 14.3\) Hz), 1.22 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): = 203.0, 134.5, 130.7, 128.5, 127.2, 89.0, 38.5, 17.1; HRMS (ESI\(^+\)): m/z \([M+MeOH+Na]\) calcd for \([C_{11}H_{16}O_4Na]\) 235.0941, found 235.0945, \(\Delta = -0.4\) mDa.
2.3 Identification and characterization of the enol intermediate

2.3.1 First observation of the enol intermediate

To a suspension of α-substituted acrolein 1a (44 mg, 0.30 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 1 mg) in THF (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv) under argon atmosphere. After 4 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with DCM (10 mL). The $^1$H NMR sample was taken immediately from the filtrate, see spectral data.

2.3.2 Characterization of the enol intermediate in the presence of enol silane 2a

To the suspension of α-substituted acrolein 1a (44 mg, 0.30 mmol, 1.0 equiv), enol silane 2a (79 mg, 0.3 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 1 mg) in EtOAc (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv) under argon atmosphere. After 4 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (5 mL). The $^1$H NMR sample was taken immediately from the filtrate. The $^1$H NMR spectra showed the presence of a mixture of enol 6, enol silane 2a and α-hydroxyperoxide 4a.$^{3,4}$

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.36 – 7.15$ (m, 5H), 6.34 (br.dd, 1H, $J = 1.4$, 5.9 Hz), 3.42 (s, 1H), 1.51 (d, 3H, $J = 1.5$ Hz).

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2.4 **General procedure for the preparation of 2-methyl-1,2-diols**

To a suspension of α-substituted acrolein (1.50 mmol, 1.0 equiv), water (100 µL) and Pd/C (5 wt %, 5 mg) in EtOAc (5 mL) was added triethylsilane (1.65 mmol, 1.1 equiv). After 10 min of stirring (Note 1 and 2) the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (15 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion (Note 3).

To the filtrate was added MeOH (20 mL) and NaBH₄ (9.00 mmol, 6.0 equiv). After 3 h of stirring, 40 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x20 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 80:20 to 50:50) to afford products.

**Notes:**

1. With substrates 1a, 1b, 1e and 1f formation of hydrogen gas (as observed by bubbling of the reaction mixture) was used as an indicator of the full conversion. The identity of the gas was deduced from the control experiment without substrate (see: background reaction section 2.8.1 and Table S4). However, bubbling was not observed with all reactants. Presumably, the functional groups present in these substrates (e.g. C=C-bond) covers the Pd-surface and prevents the rapid formation of triethylsilanol 9 and H₂.

2. The starting materials should be of high purity since even small amounts of impurities (polymer, grease etc.) tend to slow or even prevent the reaction (see: section 2.4.7 and 2.4.8). Since the α-substituted acroleins tend to contain impurities and polymers (especially after prolonged storage), they should be purified immediately before use. α-Substituted acroleins prepared by the α-methylation method require silica gel chromatography and/or distillation even if they appear clean after the reaction.

3. After the filtration, a mixture of the saturated aldehyde 3 and α-hydroperoxy aldehyde 4 were observed in ¹H NMR. The scale, amount of Et₃SiH, reaction time and the catalyst loading used in the reaction varied the product ratio from 11:89 to 91:9 respectively (see: section 2.1). However, the filtrate mixture slowly converted towards the α-hydroperoxy aldehyde product when stirred under aerobic conditions.
2.4.1 2-methyl-3-phenylpropane-1,2-diol

To a suspension of α-substituted acrolein 1a (88 mg, 0.60 mmol, 1.0 equiv), water (40 µL) and Pd/C (5 wt %, 2 mg) in EtOAc (2 mL) was added triethylsilane (77 mg, 105 µL, 0.66 mmol, 1.1 equiv). After 3 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (10 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion.

To the filtrate was added MeOH (10 mL) and NaBH₄ (136 mg, 3.60 mmol, 6.0 equiv). After 3 h of stirring, 20 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x10 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 80:20 to 50:50) to afford product 5a as a white powder (74 mg, 0.45 mmol, 74 %).

Rₙ (n-hexane/EtOAc 50:50) = 0.30; m.p. 50.6 – 52.1; IR (film cm⁻¹): 3410, 3347, 2938, 1046, 730, 702, 625; ¹H NMR (300 MHz, CDCl₃): δ 7.35 – 7.22 (m, 5H), 3.47 (ABq, 2H, Δδ_AB = 0.06, J_AB = 10.9 Hz), 3.82 (ABq, 2H, Δδ_AB = 0.06, J_AB = 13.3 Hz), 1.95 (br.s, 2H), 1.15 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 137.1, 130.6, 128.5, 126.8, 73.1, 69.5, 44.8, 23.8; HRMS (ESI⁻): m/z [M-H] calcd for [C₁₀H₁₃O₂] 165.0921, found 165.0926, Δ = -0.5 mDa.
2.4.2 2-methyldecano-1,2-diol

To a suspension of α-substituted acrolein \(1b\) (101 mg, 0.60 mmol, 1.0 equiv), water (40 µL) and Pd/C (5 wt %, 2 mg) in EtOAc (2 mL) was added triethylsilane (77 mg, 105 µL, 0.66 mmol, 1.1 equiv). After 1 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (10 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion.

To the filtrate was added MeOH (10 mL) and NaBH\(_4\) (136 mg, 3.60 mmol, 6.0 equiv). After 3 h of stirring, 20 mL NH\(_4\)Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x10 mL). Organic phases were combined, dried with NaSO\(_4\) and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, \(n\)-hexane/EtOAc gradient from 80:20 to 50:50) to afford product \(5b\) as a colorless sticky oil (61 mg, 0.32 mmol, 54 %).

\[ R_f (n\text{-hexane/EtOAc 50:50}) = 0.38; \quad \text{IR (film cm}^{-1}) \text{: 3361, 2923, 2854, 1465, 1049;} \]
\[ ^1H \text{ NMR (300 MHz, CDCl}_3): 3.44 (ABq, 2H, } \Delta \delta_{AB} = 0.06, J_{AB} = 10.9 \text{ Hz), 1.89 (br.s, 2H), 1.51 - 1.44 (m), 1.38 - 1.25 (m), 1.17 (s), 0.88 (t, } J = 6.7 \text{ Hz); } ^{13}C \text{ NMR (75 MHz, CDCl}_3): } \delta 73.1, 70.0, 38.9, 32.0, 30.4, 29.7, 29.4, 23.9, 23.4, 22.8, 14.2; \text{ HRMS (ESI\textsuperscript{-}): } m/z [\text{M-H}] \text{ calcd for } [C_{11}H_{13}O_2] 187.1704, \text{ found } 187.1727, \Delta = -2.3 \text{ mDa.} \]
2.4.3 2,3,7-trimethyloct-6-ene-1,2-diol

To a suspension of α-substituted acrolein 1c (249 mg, 1.50 mmol, 1.0 equiv), water (100 µL) and Pd/C (5 wt %, 5 mg) in EtOAc (5 mL) was added triethylsilane (192 mg, 264 µL, 1.65 mmol, 1.1 equiv). After 10 min of stirring the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (20 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion.

To the filtrate was added MeOH (20 mL) and NaBH₄ (340 mg, 9.00 mmol, 6.0 equiv). After 3 h of stirring, 40 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x20 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 80:20 to 50:50) to afford product 5c as a colorless sticky oil (185 mg, 1.00 mmol, 67 %, as a mixture of diastereomers, dr 3:1).

Data for major diastereomer: Rᵣ (n-hexane/EtOAc 50:50) = 0.26; IR (film cm⁻¹): 3377, 2966, 2924, 1440, 1377, 1045, 1022; ¹H NMR (300 MHz, CDCl₃): δ 5.17 – 5.01 (m, 1H), 3.51 (ABq, 2H, Δδ_AB = 0.12, J_AB = 10.9 Hz), 2.17 – 2.01 (m, 1H), 1.98 – 1.86 (m, 1H), 1.78 (br.s, 2H), 1.69 (s, 3H), 1.67 – 1.53 (m, obstructed, 1H), 1.61 (s, 3H), 1.52 – 1.35 (m, 1H), 1.32 – 1.11 (m, 1H), 1.08 (s, 3H), 0.97 (d, 3H, J = 6.8 Hz), for the minor diastereomer, the following diagnostic signals were observed: 3.49 (ABq, 2H, Δδ_AB = 0.12, J_AB = 10.8 Hz), 1.06 (s, 3H), 0.88 (d, 3H, J = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 132.0, 124.5, 75.3, 68.5, 39.5, 31.9, 26.5, 25.9, 19.8, 17.9, 13.4, for the minor diastereomer, the following diagnostic signals were observed: δ 131.8, 124.7, 75.5, 68.9, 30.9, 26.6, 19.3, 14.6; HRMS (ESI): m/z [M-H] calcd for [C₁₁H₂₁O₂] 185.1547, found 185.1564, Δ = -1.7 mDa.
2.4.4 (Z)-2-methylundec-8-ene-1,2-diol

\[
\begin{align*}
\text{H} & \quad \text{Pd/C} \\
\text{EtOAc, H}_2\text{O} & \quad \text{EtOAc, MeOH} \\
\end{align*}
\]

To a suspension of \(\alpha\)-substituted acrolein 1d (270 mg, 1.50 mmol, 1.0 equiv), water (100 µL) and Pd/C (5 wt %, 5 mg) in EtOAc (5 mL) was added triethylsilane (192 mg, 264 µL, 1.65 mmol, 1.1 equiv). After 10 min of stirring the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (20 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion.

To the filtrate was added MeOH (20 mL) and NaBH\(_4\) (340 mg, 9.00 mmol, 6.0 equiv). After 3 h of stirring, 40 mL NH\(_4\)Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x20 mL). Organic phases were combined, dried with NaSO\(_4\) and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, \(n\)-hexane/EtOAc gradient from 80:20 to 50:50) to afford product 5d as a colorless sticky oil (239 mg, 1.19 mmol, 80 %).

\(R_f (n\text{-hexane/EtOAc} 50:50) = 0.33; \) IR (film cm\(^{-1}\)): 3363, 2932, 2856, 1462, 1053, 1031; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 5.41 – 5.26 (m, 2H), 3.44 (ABq, 2H, \(\Delta \delta_{AB} = 0.06, J_{AB} = 10.9 \) Hz), 2.09 – 1.97 (m, 4H), 1.78 (br.s, 2H), 1.52 – 1.45 (m, 2H), 1.42 – 1.31 (m, 6H), 1.17 (s, 3H), 0.95 (t, 3H, \(J = 7.5 \) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta \) 131.9, 129.2, 73.1, 70.0, 38.9, 30.0, 29.8, 27.2, 23.8, 23.4, 20.7, 14.5; HRMS (ES\(^+\)): m/z [M-H] calcd for [C\(_{12}\)H\(_{23}\)O\(_2\)] 199.1704, found 199.1721, \(\Delta = -1.7 \) mDa.
2.4.5 2-ethylhexane-1,2-diol

To a suspension of α-substituted acrolein 1e (189 mg, 1.50 mmol, 1.0 equiv), water (100 µL) and Pd/C (5 wt %, 5 mg) in EtOAc (5 mL) was added triethylsilane (192 mg, 264 µL, 1.65 mmol, 1.1 equiv). After 10 min of stirring the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (20 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion.

To the filtrate was added MeOH (20 mL) and NaBH₄ (340 mg, 9.00 mmol, 6.0 equiv). After 3 h of stirring, 40 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x20 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 80:20 to 50:50) to afford product 5e as a colorless sticky oil (132 mg, 0.90 mmol, 60 %).

Rᵢ (n-hexane/EtOAc 50:50) = 0.26; IR (film cm⁻¹): 3370, 2957, 2934, 2872, 1460, 1045; ¹H NMR (300 MHz, CDCl₃): δ 3.46 (s, 1H), 1.84 (br.s, 2H), 1.59 – 1.40 (m, 2H), 1.39 – 1.19 (m, 2H), 0.91 (t, obstructed, 3H, J = 6.9 Hz), 0.88 (t, obstructed, 3H, J = 7.6 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 75.0, 67.9, 35.2, 28.4, 25.7, 23.5, 14.2, 7.9; HRMS (ESI⁺): m/z [M-H] calcd for [C₈H₁₇O₂] 145.1234, found 145.1234, Δ = -0.0 mDa.
2.4.6 4-(5,5-dimethyl-1,3-dioxan-2-yl)-2-methylbutane-1,2-diol

To a suspension of α-substituted acrolein 1f (59 mg, 0.30 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 1 mg) in EtOAc (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv). After 2 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (10 mL). The filtrate was left to autoxidize for 2 h to allow the reaction to proceed to completion.

To the filtrate was added MeOH (10 mL) and NaBH₄ (68 mg, 1.80 mmol, 6.0 equiv). After 3 h of stirring, 10 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x10 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 50:50 to 0:100) to afford product 5f as a colorless sticky oil (44 mg, 0.20 mmol, 67 %).

Rᶠ (n-hexane/EtOAc 50:50) = 0.11; IR (film cm⁻¹): 3401, 2954, 2850, 1469, 1394, 1120, 1015, 735; ¹H NMR (300 MHz, CDCl₃): δ = 4.51 – 4.42 (m, 1H), 3.61 (d, 2H, J = 11.2 Hz), 3.45 (d, obstructed, 2H, J = 11.2 Hz), 3.42 (ABq, obstructed, 2H, ΔδAB = 0.03, JAB = 10.7 Hz), 2.69 (br.s, 1H), 2.29 (br.s, 1H), 1.86 – 1.53 (m, 4H), 1.18 (s, 3H), 1.15 (s, 3H), 0.72 (s, 3H); δ; ¹³C NMR (75 MHz, CDCl₃): δ = 102.3, 77.4, 72.3, 70.1, 32.2, 30.3, 29.0, 23.5, 23.1, 21.9; HRMS (ESI⁺): m/z [M+Na] calcd for [C₁₁H₂₂O₄Na] 241.1410, found 241.1392, Δ = 1.8 mDa.
2.4.7 2-methyl-3-(5-methylfuran-2-yl)butane-1,2-diol

To a suspension of α-substituted acrolein 1g (49 mg, 0.30 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 51 mg) in EtOAc (1 mL) was added triethylsilane (52 mg, 72 µL, 0.45 mmol, 1.5 equiv). After 3 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (10 mL). To the filtrate was added water (100 µL) and the autoxidation was allowed to proceed for further 2 h to allow the reaction to go to completion (75:25 ratio of saturated aldehyde 3g : α-hydroperoxide 4g, for more information, see Table S7).

To the filtrate was added MeOH (10 mL) and NaBH₄ (68 mg, 1.80 mmol, 6.0 equiv). After 3 h of stirring, 20 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x10 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 80:20 to 30:70) to afford product 5g as a colorless oil (10 mg, 0.05 mmol, 18 %, as a mixture of diastereomers, dr 3:2).

Data for major diastereomer: Rₜ (n-hexane/EtOAc 30:70) = 0.14; IR (film cm⁻¹): 3400, 2975, 2925, 1562, 1049, 1021, 784; ¹H NMR (300 MHz, CDCl₃): δ 6.01 – 5.81 (m, 2H), 3.57 – 3.30 (m, 2H), 3.01 (q, 1H, J = 7.3 Hz), 2.26 (s, 3H), 2.00 (br.s, 1H), 1.58 (br.s, 1H), 1.30 (d, 3H, J = 7.3 Hz), 1.11 (s, 3H), for the minor diastereomer, the following diagnostic signals were observed: 3.08 (q, 1H, J = 7.3 Hz), 2.27 (s, 3H), 1.24 (d, J = 7.2 Hz, 3H), 1.08 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 155.1, 155.0, 151.4, 150.9, 107.8, 107.2, 106.2, 106.2, 74.8, 68.8, 68.7, 40.4, 39.5, 29.9, 20.7, 20.4, 13.9, 13.7, 13.7, 13.3; HRMS (ESI⁺): m/z [M+Na] calcd for [C₁₀H₁₆O₃Na] 207.0992, found 207.0991, Δ = 0.1 mDa.

Substrate 1g appears to rapidly accumulate polymeric impurities that inhibit the reaction. Unless 1g was freshly purified, it did not react at all. Even a short storage in the freezer was not tolerated. Apparently, the α-hydroperoxide 4g polymerizes as well, see Table S7, entries 1 and 2.
Table S7. Optimization of reaction conditions for the preparation of 2-hydroperoxy-2-methyl-3-(5-methylfuran-2-yl)butanal

![Chemical structure of 1g, 3g, and 4g]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Modification</th>
<th>Conversion</th>
<th>NMR yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Oxidation Time</th>
<th>Product selectivity 3g/4g&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1 equiv Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>90 %</td>
<td>19 %</td>
<td>Over night</td>
<td>50:50</td>
</tr>
<tr>
<td>2</td>
<td>1.5 equiv Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>100 %</td>
<td>18 %</td>
<td>Over night</td>
<td>50:50</td>
</tr>
<tr>
<td>3</td>
<td>1.5 equiv Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>100 %</td>
<td>Quant.</td>
<td>0 h</td>
<td>97:3</td>
</tr>
<tr>
<td>4</td>
<td>1.5 equiv Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>100 %</td>
<td>Quant.</td>
<td>4 h</td>
<td>83:17</td>
</tr>
<tr>
<td>5</td>
<td>1.5 equiv Et&lt;sub&gt;3&lt;/sub&gt;SiH, 0 °C</td>
<td>100 %</td>
<td>Quant.</td>
<td>4 h</td>
<td>86:14</td>
</tr>
<tr>
<td>6</td>
<td>1.5 equiv Et&lt;sub&gt;3&lt;/sub&gt;SiH, H&lt;sub&gt;2&lt;/sub&gt;O (100 μL to filtrate)</td>
<td>100 %</td>
<td>Quant.</td>
<td>2 h</td>
<td>75:25</td>
</tr>
</tbody>
</table>

Reaction conditions: 1g (49 mg, 0.30 mmol, 1.0 equiv), Pd/C (1 mg), triethylsilane (38 mg, 53 mml, 0.33 mmol, 1.1 equiv), EtOAc (1 mL), room temperature. For the procedure, see section 2.2. [a] Integrals of the carbonyl protons were compared to the integrals of the protons in the double bond region. [b] Determined by <sup>1</sup>H NMR analysis.
2.4.8 *tert*-butyl 4-(1,2-dihydroxypropan-2-yl)piperidine-1-carboxylate

To the suspension of α-substituted acrolein 1h (72 mg, 0.30 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 1 mg) in EtOAc (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv). After 3 h of stirring, no conversion of the starting material 1h was observed by $^1$H NMR.\(^6\)

---

\(^6\) Substrate 1h also appears to accumulate polymeric impurities even when frozen. See the previous section for a similar observation.
2.5 2-hydroperoxy-2-methyl-3-phenylpropanal in presence of 1-Boc-4-piperidone

To the suspension of α-substituted acrolein 1a (44 mg, 0.30 mmol, 1.0 equiv), 1-Boc-4-piperidone 8 (60 mg, 0.30 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 1 mg) in EtOAc (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv). After 3 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (10 mL). The filtrate was left to autoxidize 2 h to allow the reaction to proceed to completion.

To the filtrate was added MeOH (10 mL) and NaBH₄ (68 mg, 1.80 mmol, 6.0 equiv). After 3 h of stirring, 10 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3x10 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 80:20 to 50:50) to afford product 5a as a white powder (29 mg, 0.19 mmol, 65 %).

The ¹H and ¹³C NMR data correspond to previously prepared compound 5a.
2.6 Preparation of (2E,10Z)-4-hydroxy-4-methyltrideca-2,10-dienenitrile

To the suspension of α-substituted acrolein 1d (270 mg, 1.50 mmol, 1.0 equiv), water (100 µL) and Pd/C (5 wt %, 5 mg) in EtOAc (5 mL) was added triethylsilane (192 mg, 264 µL, 1.65 mmol, 1.1 equiv). After 10 min of stirring the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (20 mL). The filtrate was left to autoxidize overnight to allow the reaction to proceed to completion.

Most of the EtOAc was removed carefully in rotary evaporator. To the crude mixture was added DCM (40 mL) and (triphenylphosphoranylidene)acetonitrile (723 mg, 2.40 mmol, 1.6 equiv). After 2 h of stirring, 40 mL NH₄Cl (aq) was added to quench the reaction. The reaction mixture was extracted with DCM (3x20 mL). Organic phases were combined, dried with NaSO₄ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 100:00 to 85:15) to afford product 9 as a colorless oil (189 mg, 0.85 mmol, 57 %, as a mixture of stereomers, 9:1).

Data for major stereomer: Rᵥ (n-hexane/EtOAc 85:15) = 0.19; IR (film cm⁻¹): 3466, 2932, 2856, 2225, 1462, 1146, 969, 724; ¹H NMR (300 MHz, CDCl₃): δ = 6.72 (d, 1H, J = 16.2 Hz), 5.66 (d, 1H, J = 16.2 Hz), 5.42 – 5.25 (m, 2H), 2.02 (q, 4H, J = 7.0 Hz), 1.56 – 1.49 (m, 2H), 1.49 (br.s, 1H), 1.39 – 1.24 (m, 6H), 1.32 (s, obstructed, 3H), 0.95 (t, 3H, J = 7.5 Hz), for the minor stereomer, the following diagnostic signals were observed: 6.56 (d, 1H, J = 16.5 Hz), 5.55 (d, 1H, J = 16.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ = 160.5, 132.0, 129.0, 117.7, 98.0, 73.7, 42.0, 29.7, 29.5, 27.9, 27.1, 23.7, 20.7, 14.5; HRMS (ESI⁺): m/z [M+Na] calcd for [C₁₄H₂₃N¹⁸ONa] 244.1672, found 244.1668, Δ = 0.4 mDa.
2.7 Preparation of α-substituted acroleins

2.7.1 (Z)-2-methyleneundec-8-enal

 Prepared using the α-methylenation procedure A described by Erkkilä and Pihko using aldehyde S1 (3.38 g, 4.0 mL, 20.10 mmol, 1.0 equiv), formaldehyde (37 % formaldehyde in water, 1.5 mL, 20.10 mmol, 1.0 equiv), pyrrolidine (143 mg, 168 µL, 2.00 mmol, 0.1 equiv), p-dimethylaminobenzoic acid (664 mg, 4.00 mmol, 0.2 equiv) and DCM (30 mL). Crude product was purified by flash chromatography (silica gel, n-hexane/EtOAc 95:05) to afford product 1d as a colorless oil (2.89 g, 16.0 mmol, 80 %).

Rf (n-hexane/EtOAc 95:05) = 0.59; IR (film cm⁻¹): 2929, 2856, 1693, 1461, 941, 726; ¹H NMR (300 MHz, CDCl₃): δ 9.54 (s, 1H), 6.24 (dd, 1H, J = 2.2, 1.3 Hz), 5.98 (d, 1H, J = 0.7 Hz), 5.44 – 5.24 (m, 2H), 2.29 – 2.20 (m, 2H), 2.11 – 1.96 (m, 4H), 1.51 – 1.23 (m, 6H), 0.95 (t, 3H, J = 7.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 194.9, 150.6, 134.0, 131.9, 129.2, 29.6, 29.0, 27.9, 27.8, 27.1, 20.7, 14.5; HRMS (ESI⁺): m/z [M+Na] calcd for [C₁₂H₂₀ONa] 203.1406, found 203.1399, Δ = 0.7 mDa.
2.7.2 4-(5,5-dimethyl-1,3-dioxan-2-yl)-2-methylenebutanal

Prepared using the α-methylation procedure A described by Erkkilä and Pihko\(^2\) using aldehyde S2 (250 mg, 1.34 mmol, 1.0 equiv), formaldehyde (37 % formaldehyde in water, 42 mg, 105 µL, 1.41 mmol, 1.05 equiv), pyrrolidine (10 mg, 11 µL, 0.13 mmol, 0.1 equiv), p-dimethylaminobenzoic acid (44 mg, 0.27 mmol, 0.2 equiv) and DCM (20 mL). Crude product was purified by flash chromatography (silica gel, n-hexane/EtOAc 80:20) to afford product 1f as a colorless oil (159 mg, 0.80 mmol, 60 %).\(^7\)

\(R_f\) (n-hexane/EtOAc 80:20) = 0.39; IR (film cm\(^{-1}\)): 3391, 2964, 2878, 1742, 1510, 1229, 733; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 9.54\) (s, 1H), 6.27 (app. s, 1H), 6.00 (app. s, 1H), 4.43 (t, 1H, \(J = 5.0\) Hz), 3.60 (d, 2H, \(J = 11.2\) Hz), 3.41 (d, 2H, \(J = 11.0\) Hz), 2.38 (app. t, 2H, \(J = 8.5\) Hz), 1.83 – 1.76 (m, 2H), 1.18 (s, 3H), 0.71 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 194.6, 149.8, 134.1, 101.6, 77.4, 32.8, 30.3, 23.2, 22.6, 22.0\); HRMS (ESI\(^+\)): m/z [M+Na\(^+\)] calcd for [C\(_{11}\)H\(_{18}\)O\(_3\)Na] 221.1148, found 221.1138, \(\Delta = 1.0\) mDa.

---

\(^7\) Part of the product was lost due the CombiFlash malfunction.
2.7.3 tert-butyl 4-(3-oxoprop-1-en-2-yl)piperidine-1-carboxylate

\[
\begin{align*}
\text{S3} & \\
\text{DCM reflux, 6 h} & \\
\text{1h}
\end{align*}
\]

Prepared using the α-methylenation procedure A described by Erkkilä and Pihko using aldehyde S3 (600 mg, 2.64 mmol, 1.0 equiv), formaldehyde (37% formaldehyde in water, 79 mg, 197 μL, 2.64 mmol, 1.0 equiv), pyrrolidine (19 mg, 22 μL, 0.26 mmol, 0.1 equiv), p-dimethylaminobenzoic acid (87 mg, 0.53 mmol, 0.2 equiv) and DCM (10 mL). Crude product was purified by flash chromatography (silica gel, n-hexane/EtOAc 80:20) to afford product 1h as a colorless oil (545 mg, 2.28 mmol, 86%).

Rf (n-hexane/EtOAc 80:20) = 0.34; IR (film cm⁻¹): 2930, 1684, 1418, 1365, 1249, 1162, 1121, 899; ¹H NMR (300 MHz, CDCl₃): δ = 9.53 (s, 1H), 6.23 (d, 1H, J = 1.0 Hz), 6.01 (s, 1H), 4.18 (dt, 2H, J = 13.4, 1.8 Hz), 2.76 (td, 2H, J = 13.1, 2.4 Hz), 2.63 (tt, 1H, J = 12.3, 3.2 Hz), 1.72 (dt, 2H, J = 13.0, 1.9 Hz), 1.58 – 1.56 (m, 1H), 1.46 (s, 9H), 1.33 (qd, 2H, J = 12.6, 4.3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ = 194.4, 154.9, 153.8, 133.5, 79.6, 44.2, 34.3, 30.9, 28.6; HRMS (ESI⁺): m/z [M+Na] calcd for [C₁₃H₂₁NO₃Na] 262.1414, found 262.1407, Δ = 0.7 mDa.
2.8 Control experiments

2.8.1 Background reactions

2.8.1.1 Triethylsilanol

\[
\text{Et}_3\text{SiH} \xrightarrow{\text{Pd/C}} \text{EtOAc, H}_2 \xrightarrow{\text{7}} \text{Et}_3\text{SiOH} + \text{H}_2
\]

To the suspension of Pd/C (5 wt %, 10 mg), water (465 µL, 25.8 mmol, 3.0 equiv) and EtOAc (10 mL) was added triethylsilane (1.0 g, 1.37 mL, 8.60 mmol, 1.0 equiv). Immediately after the addition of triethylsilane H\textsubscript{2}-formation\textsuperscript{8} was observed. After the bubbling ended, the reaction mixture was filtered through a small pad of alumina (neutral) column eluted with EtOAc (20 mL). The filtrate was concentrated in vacuum to afford product 7 as a colorless oil (1.15 g, 8.6 mmol, Quant).

\[R_f(\text{n-hexane/EtOAc 95:05}) = 0.25; \ IR (\text{film cm}^{-1}): 3268, 2954, 2817, 1015, 1004, 822, 724; \ ^1\text{H NMR (300 MHz, CDCl}_3): \delta 1.54 (\text{br.s, 1H}), 0.97 (t, 9H, \text{J} = 7.9 \text{Hz}), 0.59 (q, 6H, \text{J} = 7.9 \text{Hz}); \ ^{13}\text{C NMR (75 MHz, CDCl}_3): \delta 6.7, 5.9; \ HRMS (ESI-): m/z [M-H] calcd for [C\textsubscript{6}H\textsubscript{15}OSi] 131.0898, found 131.0891, \Delta = 0.7 \text{mDa.}\]

2.8.1.2 Conversion of α-hydroperoxy aldehyde 4a to 2a or 3a

Table S8. Screening of the conversion of α-hydroperoxy aldehyde 4a to 2a or 3a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conditions</th>
<th>Desired Product</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{a}</td>
<td><img src="image" alt="4a" /></td>
<td>Pd/C Et\textsubscript{3}SiH EtOAc</td>
<td><img src="image" alt="2a" /></td>
<td>No</td>
</tr>
<tr>
<td>2\textsuperscript{b}</td>
<td><img src="image" alt="4a" /></td>
<td>Pd/C H\textsubscript{2}SO\textsubscript{4} (1 M) EtOAc</td>
<td><img src="image" alt="3a" /></td>
<td>Yes</td>
</tr>
</tbody>
</table>

\[\text{[a]} \text{ Following the procedure in section 2.4 and after which the EtOAc was dried with NaSO}_4 \text{ and concentrated to 1 mL in vacuum. Pd/C (1 mg) and triethylsilane (38 mg, 53 mmol, 0.33 mmol, 1.1 equiv), were added to the mixture. After 2 h, no formation of the desired product 2a was observed in } ^1\text{H NMR. [b]} \text{ Following the procedure in section 2.4 and after which H}_2\text{SO}_4 \text{ (20 } \mu\text{L) was added to the mixture. After 16 h, substrate 4a was converted to the desired product 3a, determined with } ^1\text{H NMR.}\]

\textsuperscript{8} For the usage of H\textsubscript{2}-formation in reaction, see Table S4.
2.8.1.3 Formation of α-hydroperoxy aldehyde

Table S9. Screening of the formation of α-hydroperoxy aldehyde

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Silyl</th>
<th>Desired Product&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="1a" /></td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="1a" /></td>
<td>–</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="1a" /></td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;SiOH</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="3a" /></td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="3a" /></td>
<td>–</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="3a" /></td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;SiOH</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="3a" /></td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;SiH, Et&lt;sub&gt;3&lt;/sub&gt;SiOH</td>
<td>No</td>
</tr>
</tbody>
</table>

Reaction conditions: Substrate (0.30 mmol, 1.0 equiv), Pd/C (1 mg), silyl (1.1 equiv), EtOAc (1 mL), room temperature. For the procedure, see section 2.4. <sup>a</sup>Determined by 1H NMR analysis.
2.8.1.4 Formation of (Z)-2-methylundec-8-ene-1,2-diol with 3a

To a suspension of α-substituted acrolein 1d (54 mg, 0.30 mmol, 1.0 equiv), water (20 µL) and Pd/C (5 wt %, 1 mg) in EtOAc (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv). After 10 min of stirring the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (20 mL). 3a was added to the filtrate. After 4 h autoxidation period the ¹H NMR sample was taken from the filtrate. The ¹H NMR spectra showed the presence of a mixture of 3d and 4d in 10:90 ratio in addition of 3a.
2.8.2 Labeling experiments

2.8.2.1 Deuterium-2-hydroperoxy-2-methyl-3-phenylpropanal

![Chemical structure]

To a suspension of α-substituted acrolein 1a (44 mg, 0.30 mmol, 1.0 equiv), D$_2$O (20 µL) and Pd/C (5 wt %, 1 mg) in EtOAc (1 mL) was added triethylsilane (38 mg, 53 µL, 0.33 mmol, 1.1 equiv). After 4 min of stirring, gas formation was observed and the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (10 mL). The H/D ratio 21:79 was determined by $^1$H NMR analysis.

2.8.2.2 O$^{18}$-(2E,10Z)-4-hydroxy-4-methyltrideca-2,10-dienitrile

![Chemical structure]

The reaction was carried out under argon atmosphere. To a suspension of α-substituted acrolein 1a (216 mg, 1.20 mmol, 1.0 equiv), water-O$^{18}$ (100 µL) and Pd/C (5 wt %, 4 mg) in EtOAc (4 mL, flushed with argon) was added triethylsilane (153 mg, 211 µL, 1.32 mmol, 1.1 equiv). After 15 min of stirring the reaction mixture was filtered through a small pad of neutral alumina column. The column was eluted with EtOAc (20 mL). The filtrate was left to oxidize 2 h to allow the reaction to proceed to completion. Most of the EtOAc was removed carefully in rotary evaporator. To the crude mixture was added DCM (40 mL) and (triphenylphosphoranylidene)acetonitrile (795 mg, 2.64 mmol, 2.2 equiv). After 3 h of stirring, 40 mL NH$_4$Cl (aq) was added to quench the reaction. The reaction mixture was extracted with DCM (3x20 mL). Organic phases were combined, dried with Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, n-hexane/EtOAc gradient from 100:00 to 85:15) to afford product 9 as a colorless oil (136 mg, 0.61 mmol, 51 %).

The $^1$H and $^{13}$C NMR data correspond to previously prepared compounds 9, 7 and commercially available triphenylphosphine oxide (10). MS experiment did not involve any O$^{18}$ labeled product 9 or triphenylphosphine oxide (10). For Et$_3$SiOH (7), O$^{16}$/O$^{18}$ ratio 32:68 was determined by MS experiment; HRMS (ESI$^-$): m/z [M-H] calcd for [C$_6$H$_{15}$O$^{18}$Si]$^-$ 133.0940, found 133.0932, Δ = 0.8, mDa.
2.9   Possible mechanism of the entire reaction

Scheme 1. Proposed reaction mechanism
3 Spectral Data
This is where $E$-enol silane would be.