SUPPORTING INFORMATION FOR:

Divergent Titanium-Mediated Allylations via Modulation by Nickel or Palladium

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General: For the reactions employing titanocene all solvents and additives were rigorously deoxygenated prior to use. The following known compounds were isolated as pure samples and showed NMR spectra identical to reported data: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, Z-22, 24, 25, 26, and 32.

General procedure for Pd⁰-TiIII allylation of carbonyl compounds with allyl carbonates.

Protocol A. Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp₂TiCl₂ (2.0 mmol), PdCl₂ (0.2 mmol), PPh₃ (0.4 mmol) and Mn dust (8.0 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of carbonyl compound (1.0 mmol) and allyl carbonate (4.0 mmol) in THF (2 mL) was then added. The mixture was stirred for 6 h and then diluted with AcOEt, washed with brine, dried over anhydrous MgSO₄ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products.

Protocol B. Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp₂TiCl₂ (0.4 mmol), PdCl₂ (0.2 mmol), PPh₃ (0.4 mmol) and Mn dust (8.0 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of carbonyl compound (1.0 mmol), allyl carbonate (4.0 mmol), 2,4,6-collidine (7.0 mmol) and Me₃SiCl (4.0 mmol) in THF (2 mL) was then added. The mixture was stirred for 16 h and then diluted with AcOEt, washed with 10% aqueous HCl solution and washed with brine, dried over anhydrous MgSO₄ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products.

General procedure for Ni⁰-TiIII-promoted allylation of alkenes with allyl carbonates.

Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp₂TiCl₂ (2.0 mmol), NiCl₂(PPh₃)₂ (0.2 mmol) and Mn dust (8.0 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark brownish (about 15 min). A solution of allyl carbonate (1.0 mmol) in THF (2 mL) was then added. The mixture was stirred for 16 h and then diluted with EtOAc, washed with brine, dried over anhydrous MgSO₄ and the solvent was removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products.

Influence of the allylic derivative in the Pd0-Ti III-promoted allylation of carbonyl compounds

\[
\text{O} \quad \text{H} + \underbrace{\text{OCOR}}_{8} \xrightarrow{\text{Cp}_2\text{TiCl}} \quad \text{OH} \quad \text{R}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>Yield</th>
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<tbody>
<tr>
<td>CH₃</td>
<td>30 %</td>
</tr>
<tr>
<td>Ph</td>
<td>40 %</td>
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<tr>
<td>OEt</td>
<td>77 %</td>
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<tr>
<td>OCH₂CCl₃</td>
<td>10 %</td>
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Influence of the palladium complex in the Pd0-Ti III-promoted allylation of carbonyl compounds

\[
\text{O} \quad \text{H} + \underbrace{\text{OCO}_2\text{Et}}_{\text{[Pd]}} \xrightarrow{\text{Cp}_2\text{TiCl}} \quad \text{OH} \quad \text{[Pd]}
\]

<table>
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<th>[Pd]</th>
<th>Yield</th>
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<td>PdCl₂</td>
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<td>Na₂PdCl₄</td>
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<tr>
<td>PdCl₂/2PPh₃</td>
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<td>Pd(PPh₃)₂Cl₂</td>
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<td>Pd(PPh₃)₄</td>
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<td>Pd₂(dba)₃dba</td>
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<tr>
<td>Pd(OAc)₂</td>
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<tr>
<td>Pd(OAc)₂ + 2 PPh₃</td>
<td>-</td>
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<tr>
<td>Pd(MeCN)₂Cl₂</td>
<td>46 %</td>
</tr>
<tr>
<td>Pd(MeCN)₂Cl₂ + 2 PPh₃</td>
<td>46 %</td>
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Influence of the nickel complex and the titanium:nickel molar relationship in the Ni0-Ti III-promoted allylation of alkenes.

\[
\text{MeO₂C} - \text{O} - \text{CO}_2\text{Et} \xrightarrow{\text{[Ni]} \quad \text{Cp}_2\text{TiCl/Mn}} \quad \text{MeO₂C} + \text{MeO₂C} - \text{O} - \text{CO}_2\text{Et}
\]

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<tr>
<th>Cp₂TiCl₂ (mol %)</th>
<th>Ni complex</th>
<th>(mol %)</th>
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<th>Yield</th>
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<tr>
<td>400</td>
<td>Ni(PPh₃)₂Cl₂</td>
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<td>(97:3)</td>
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<td>Ni(PPh₃)₂Cl₂</td>
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<td>200</td>
<td>Ni(PPh₃)₂Cl₂</td>
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<td>(80:20)</td>
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<tr>
<td>100</td>
<td>Ni(PPh₃)₂Cl₂</td>
<td>20</td>
<td>(65:35)</td>
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<tr>
<td>40</td>
<td>Ni(PPh₃)₂Cl₂</td>
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<td>(60:40)</td>
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<tr>
<td>10</td>
<td>Ni(PPh₃)₂Cl₂</td>
<td>20</td>
<td>(30:70)</td>
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<tr>
<td>200</td>
<td>Ni(dppe)Cl₂</td>
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<td>-</td>
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<tr>
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<td>NiCl₂.7H₂O</td>
<td>20</td>
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<tr>
<td>200</td>
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<td>20</td>
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<td>51</td>
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Complete experimental data for the Pd\textsuperscript{II}-Ti\textsuperscript{III}-promoted allylation of carbonyl compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allyl carbonate</th>
<th>Carbonyl compound</th>
<th>Product (Protocol, Yield, %)</th>
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<tr>
<td>1</td>
<td>(\text{EtOCO}_2)</td>
<td>decanal</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(\text{EtOCO}_2)</td>
<td>3-phenyl propanal</td>
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<tr>
<td>3</td>
<td>(\text{EtOCO}_2)</td>
<td>citronelal</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(\text{EtOCO}_2)</td>
<td>2-decanone</td>
<td></td>
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<tr>
<td>5</td>
<td>(\text{EtOCO}_2)</td>
<td>adamantanone</td>
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</tr>
<tr>
<td>6</td>
<td>(\text{EtOCO}_2)</td>
<td>acetophenone</td>
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</tr>
<tr>
<td>7</td>
<td>(\text{EtOCO}_2)</td>
<td>tetralone</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(\text{EtOCO}_2)</td>
<td>acetyl ferrocene</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(\text{EtOCO}_2)</td>
<td>cyclododecanone</td>
<td></td>
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<td>(\text{EtOCO}_2)</td>
<td>(\text{t-Butyl-cyclohexanone})</td>
<td>A, 54; B, 78</td>
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<tr>
<td>11</td>
<td>(\text{EtOCO}_2)</td>
<td>decanal</td>
<td>A 61; B, 65\textsuperscript{d}</td>
</tr>
<tr>
<td>12</td>
<td>(\text{EtOCO}_2)</td>
<td>2-decanone</td>
<td>A 65; B, 58\textsuperscript{d}</td>
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<td>13</td>
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<td>2-decanone</td>
<td>A, 65; B, 75\textsuperscript{d}</td>
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<td>(\text{t-Butyl-cyclohexanone})</td>
<td>A 61; B, 55</td>
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<tr>
<td>14</td>
<td>ZCO ( \text{Et} )</td>
<td>decanal</td>
<td>2</td>
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<tr>
<td>----</td>
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<td>---------</td>
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<tr>
<td></td>
<td>( Z = \text{C}(\text{CO}_2\text{Me})_2 )</td>
<td></td>
<td>A, 59; B 52</td>
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<tr>
<td>15</td>
<td>Z-1 Z = C(CO(_2)Me(_2))</td>
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<td>19</td>
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<td>A, 63[f]</td>
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<tr>
<td>16</td>
<td>ZCO ( \text{EtO} )</td>
<td></td>
<td>21</td>
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<td>( Z = \text{C}(\text{CO}_2\text{Me})_2 )</td>
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<td>A, 73[h]</td>
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<tr>
<td>17</td>
<td>ZCO ( \text{EtO} )</td>
<td></td>
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</tr>
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<td>( Z = \text{C}(\text{CO}_2\text{Me})_2 )</td>
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<td>A, 74[h]</td>
</tr>
<tr>
<td>18</td>
<td>ZCO ( \text{EtO} )</td>
<td></td>
<td>23</td>
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<td>( Z = \text{C}(\text{CO}_2\text{Me})_2 )</td>
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<td>A, 98; B 95</td>
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<td>19</td>
<td>ZCO ( \text{EtO} )</td>
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<tr>
<td></td>
<td>( Z = \text{C}(\text{CO}_2\text{Me})_2 )</td>
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<td>A, 70; B 92</td>
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Synthesis of starting materials (E-1, Z-1, 18, E-20, Z-20, E-22, 27, 29, 31, 33, 35, 37, 39)

General procedure for the synthesis of allyl carbonates from alcohols. Ethylchloroformiate (1.0 mmol) was slowly added to a mixture of DMAP (0.2 mmol), pyridine (2.0 mmol) and allyl alcohol (1 mmol) in CH$_2$Cl$_2$ (25-30 mL). The reaction was stirred for 4 h and then subsequently washed with 10% aqueous HCl, 10% aqueous NaOH and brine, dried over anhydrous MgSO$_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding allyl carbonate.

Synthesis of carbonate E-1.

![Diagram](image)

Synthesis of alcohol I. 1,3-butadiene monoxide (81 mg, 1.1 mmol) was added to a solution of dimethyl allylmalonate (200 mg, 1.1 mmol), Pd$_2$(dba)$_3$·dba (10 mg, 0.05 mmol) and dppe (23 mg, 0.05 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 4 h and then reduced in volume to 0.5 mL. The residue was submitted to flash chromatography (EtOAc/Hexane,2/3) to give 1 (275 mg, 98 %) as a colourless oil. Its spectroscopic data were identical to the reported compound.$^{13}$

**Carbonate E-1.** It was prepared from I according to previously described general procedure. The compound was purified by flash chromatography (EtOAc/Hexane, 15/85) to give E-1 in a 84 % yield as a colourless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 5.69-5.57 (m, 3H), 5.11-5.08 (m, 2H), 4.53 (d, $J$ = 13.7, 1.8 Hz, 2H), 4.69 (d, $J$ = 6.6 Hz, 2H), 4.22 (q, $J$ = 7.2 Hz, 2H), 3.75 (s, 6H), 2.73 (d, $J$ = 7.7 Hz, 2H), 2.67 (d, $J$ = 7.5 Hz, 2H), 1.33 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (755 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 171.5 (C), 155.5 (C), 132.6 (CH), 130.5 (CH), 128.6 (CH), 120.0 (CH$_2$), 68.2 (CH$_2$), 64.5 (CH$_3$), 58.1 (C), 52.9 (CH$_2$), 37.7 (CH$_2$), 36.0 (CH$_2$), 14.8 (CH$_3$); ESHRMS calcd. for C$_{15}$H$_{20}$O$_2$Na m/z 337.1257, found m/z 337.1258.

Synthesis of carbonate Z-1.

![Diagram](image)

A sample of (Z)-BrCH$_2$CH=CHCH$_2$OCO$_2$Et$^{14}$ (777 mg, 3.4 mmol) was added to a mixture of NaH (84 mg, 3.4 mmol) and dimethyl allylmalonate (300 mg, 1.7 mmol) in DMF (25 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et$_2$O, washed with 10% aqueous HCl and dried with anhydrous Na$_2$SO$_4$, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,15/85) to give Z-1 (530 mg, 97 %) as a colourless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 5.76-5.61 (m, 2H), 4.18 (q, $J$ = 7.1 Hz, 2H), 3.71 (s, 6H), 2.64-2.61 (m, 4H), 1.29 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 171.5 (C), 155.5 (C), 132.6 (CH), 130.5 (CH), 128.6 (CH), 120.0 (CH$_2$), 68.2 (CH$_2$), 64.5 (CH$_3$), 58.1 (C), 52.9 (CH$_2$), 37.7 (CH$_2$), 36.0 (CH$_2$), 14.8 (CH$_3$); ESHRMS calcd. for C$_{15}$H$_{20}$O$_2$Na m/z 337.1257, found m/z 337.1258.

Synthesis of allyl carbonate 18.

![Diagram](image)

**Synthesis of carbonate II.** It was prepared from dimethyl (E)-2-(4-hydroxy-2-butenyl)malonate$^{14}$ according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane,15/85) to give II in a 85 % yield as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.76-5.61 (m, 2H), 4.54 (d, $J$ = 5.6 Hz, 2H), 4.18 (q, $J$ = 7.2 Hz, 2H), 3.73 (s, 6H), 3.44 (t, $J$ = 7.6 Hz, 1H), 2.65 (t, $J$ = 7.2 Hz, 2H), 1.30 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 171.2 (C), 155.3 (C), 132.2 (CH), 128.5 (CH), 127.1 (CH), 119.7 (CH$_2$), 64.2 (CH$_2$), 63.4 (CH$_2$), 57.6 (C), 52.8 (CH$_2$), 37.4 (CH$_3$), 30.8 (CH$_2$), 14.5 (CH$_3$); ESHRMS calcd. for C$_{15}$H$_{20}$O$_2$Na m/z 337.1257, found m/z 337.1258.

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DEPT) δ (ppm): 166.6 (C), 152.5 (C), 129.0 (CH), 124.4 (CH), 65.2 (CH₂), 61.6 (CH₂), 50.2 (CH₃), 48.8 (CH), 29.0 (CH₂), 11.8 (CH₃); ESHRMS calc'd. for C₁₅H₂₉O₅Na m/z 297.0944, found m/z 297.0949.

**Carbonate 18.** A sample of 3-chloro-2-methylpropene (600 mg, 6.6 mmol) was added to a mixture of NaH (159 mg, 6.6 mmol) and compound II (908 mg, 3.3 mmol) in DMF (30mL). This solution was stirred at room temperature for 4 h and then diluted with Et₂O, washed with 10% aqueous HCl and dried with anhydrous Na₂SO₄, and the solvent was removed. The residue was submitted to flash chromatography (EtOAc/Hexane:3/7) to give 18 (902 mg, 83 %) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.67 (m, 2H), 4.87 (s, 1H), 4.73 (s, 1H), 4.53 (d, J = 4.4 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.71 (s, 6H), 2.71-2.66 (m, 4H), 1.64 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃; DEPT) δ (ppm): 169.0 (C), 152.6 (C), 137.9 (C), 128.1 (CH), 125.6 (C), 113.6 (CH₂), 65.3 (CH₂), 61.6 (CH₂), 54.8 (C), 50.0 (CH₃), 38.2 (CH₂), 33.2 (CH₂), 20.7 (CH₃), 11.9 (CH₃); ESHRMS calc'd. for C₁₆H₂₉O₅Na m/z 351.1414, found m/z 351.1389.

**Synthesis of aldehyde E-20.**

**Synthesis of compound III.** A sample of I(CH₃)₂OTHP¹⁵ (271 mg, 1.0 mmol) was added to a mixture of NaH (33 mg, 1.4 mmol) and compound II (250 mg, 1.0 mmol) in DMF (25 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et₂O, washed with 10% aqueous HCl and dried with anhydrous Na₂SO₄, and the solvent was removed. The residue was submitted to flash chromatography (EtOAc/Hexane:1/4) to give III (315 mg, 83 %) as a colourless oil; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 5.66-5.64 (m, 2H), 4.54 (d, J = 2.8, 1H), 4.55-4.50 (m, 3H), 4.17 (q, J = 7.2 Hz, 2H), 3.82 (t, J = 10.4 Hz, 1H), 3.72-3.68 (m, 1H), 3.70 (s, 6H), 3.48 (dt, J = 11.1, 4.6 Hz, 1H), 3.35-3.32 (m, 1H), 2.64 (d, J = 5.4 Hz, 2H), 1.90-1.89 (m, 2H), 1.82-1.72 (m, 1H), 1.71-1.66 (m, 1H), 1.56-1.44 (m, 6H), 1.28 (t, J = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃; DEPT) δ (ppm): 173.9 (C), 157.4 (C), 132.6 (CH), 130.4 (CH), 101.3 (CH), 70.2 (CH₂), 69.6 (CH₂), 66.5 (CH₂), 64.8 (CH₂), 59.9 (C), 55.0 (CH₃), 38.2 (CH₂), 33.2 (CH₂), 31.9 (CH₃), 28.0 (CH₂), 27.1 (CH₂), 22.1 (CH₃), 16.8 (CH₃); ESHRMS calc'd. for C₂₀H₂₉O₄Na m/z 439.1938, found m/z 439.1931.

**Synthesis of compound IV.** p-Toluenesulfonic acid (16 mg, 0.09 mmol) was added to a solution of THP-derivative III (359 mg, 0.99 mmol) in MeOH (20 mL). The resulting mixture was stirred for 14 h and then diluted with Et₂O, washed with brine, dried over anhydrous Na₂SO₄ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane:3/7) to give IV (267 mg, 93 %) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.67-5.64 (m, 2H), 4.54 (d, J = 7.0 Hz), 4.17 (q, J = 7.2 Hz, 2H), 3.71 (s, 6H), 3.61 (t, J = 6.4 Hz, 2H), 2.65 (d, J = 5.2 Hz, 2H), 1.97-1.83 (m, 2H), 1.49-1.42 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃; DEPT) δ (ppm): 171.7 (C), 155.2 (C), 130.2 (CH), 128.2 (CH), 69.3 (CH₂), 67.7 (CH₂), 62.8 (CH₂), 57.5 (C), 52.8 (CH₃), 39.3 (CH₃), 36.1 (CH₂), 29.3 (CH₂), 14.5 (CH₃); ESHRMS calc'd. for C₁₉H₂₇O₄Na m/z 355.1363, found m/z 355.1368.

**Aldehyde E-20.** Dess-Martin Periodinane (DMP) (607 mg, 1.4 mmol) was added to a solution of IV (238 mg, 0.7 mmol) in CH₂Cl₂ (30 mL). The resulting mixture was stirring for 2 h at room temperature and then washed with saturated aqueous solution of NaHCO₃ and NaClO₃ in 1:1 proportion, dried over anhydrous Na₂SO₄ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane:3/7) to give E-20 (185 mg, 78 %) as a colourless oil; ¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.70 (s, 1H), 5.71-5.60 (m, 2H), 4.52 (d, J = 4.7 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.70 (s, 6H), 2.63 (d, J = 5.8 Hz, 2H), 2.46 (t, J = 7.5 Hz, 2H), 2.19-2.14 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃; DEPT) δ (ppm): 200.0 (CH), 170.9 (C), 154.8 (C), 129.4 (CH), 128.3 (CH), 67.4 (CH₂), 64.0 (CH₂), 56.4 (C), 52.6 (CH₃), 39.0 (CH₂), 36.6 (CH₂), 25.2 (CH₂), 14.2 (CH₃); ESHRMS calc'd. for C₁₃H₂₀O₄Na m/z 369.1156, found m/z 369.1152.

**Synthesis of aldehyde Z-20.**

¹⁵ It was prepared from OH(CH₂)₃OTHP according to known procedure: J. Garegg, B. Samuelsson. J. Chem. Soc. Perkin I. 1980, 2866-2869. I(CH₃)₂OTHP was isolated as pure sample and showed NMR spectra identical to those reported: G. G. Cox, C. Moody. J. Tetrahedron, 1993, 49, 5109-5126.
Synthesis of compound V. A sample of I(CH₂)₂OThP⁶ (271 mg, 1.0 mmol) was added to a mixture of NaH (33 mg, 1.4 mmol) and dimethyl (Z)-2-(4-ethoxy-2-butenyloxy)malonate⁹ (250 mg, 0.9 mmol) in DMF (25 mL). This solution was stirred at room temperature for 4 h and then diluted with Et₂O, washed with 10% aqueous HCl and dried with anhydrous Na₂SO₄, and the solvent was removed. The residue was submitted to flash chromatography (EtOAc/Hexane,1/4) to give V (367 mg, 96%) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.75 (s, 1H), 5.79-5.70 (m, 1H), 5.59-5.50 (m, 1H), 4.66 (d, J = 6.8 Hz, 2H), 4.19 (q, J = 6.8 Hz, 2H), 3.61 (t, J = 6.0 Hz, 2H), 2.71 (d, J = 7.6 Hz, 2H), 1.96-1.91 (m, 2H), 1.49-1.43 (m, 2H), 1.28 (t, J = 7.6 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃; DEPT) δ (ppm): 200.5 (C), 171.0 (C), 155.1 (C), 128.2 (CH), 127.3 (CH), 64.1 (CH₂), 63.0 (CH₂), 56.6 (C), 52.7 (CH₂), 39.2 (CH₃), 31.7 (CH₂), 25.3 (CH₃), 14.3 (CH₃); ESHRMS calcd. for C₁₉H₂₀OₙNa m/z 439.1938, found m/z 439.1925.

Synthesis of compound VI. p-Toluenesulfonic acid (7 mg, 0.03 mmol) was added to a solution of ether V (152 mg, 0.3 mmol) in MeOH (15 mL). The resulting mixture was stirred for 14 h and then diluted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,1/1) to give VI (687 mg, 96%) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.07 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H), 3.61 (t, J = 6.0 Hz, 2H), 1.96-1.91 (m, 2H), 1.49-1.43 (m, 2H), 1.28 (t, J = 7.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃; DEPT) δ (ppm): 172.0 (C), 157.9 (C), 129.1 (CH), 127.5 (CH), 64.7 (CH₂), 63.2 (CH₂), 57.7 (C), 53.1 (CH₃), 31.6 (CH₂), 29.7 (CH₂), 28.1 (CH₃), 14.8 (CH₃); ESHRMS calcd. for C₁₅H₂₂O₃Na m/z 355.1363, found m/z 355.1347.

Aldehyde Z-20. Dess-Martin Periodinane (DMP) (1.7 g, 4.1 mmol) was added to a solution of IV (687 mg, 2.1 mmol) in CH₂Cl₂ (30 mL). The resulting mixture was stirring for 2 h at room temperature and then washed with saturated aqueous solution of Na₂SO₄ and NaHCO₃ in 1:1 proportion, dried over anhydrous Na₂SO₄ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,3/7) to give Z-20 (505 mg, 74%) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.72 (d, J = 7.6 Hz, 2H), 2.50 (t, J = 7.6 Hz, 2H), 2.20 (t, J = 8.0 Hz, 2H), 1.30 (t, J = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃; DEPT) δ (ppm): 200.5 (C), 171.0 (C), 155.1 (C), 128.2 (CH), 127.3 (CH), 64.1 (CH₂), 63.0 (CH₂), 56.6 (C), 52.7 (CH₂), 39.2 (CH₃), 31.7 (CH₂), 25.3 (CH₃), 14.3 (CH₃); Compound Z-20 is an air-sensitive compound and only a good quality HRMS was obtained for the closely related acid derivative ESHRMS calcd. for C₁₆H₂₀OₙNa m/z 369.1156, found m/z 369.1156.

Synthesis of ketone E-22.

It was prepared from compound VII⁹ according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane,3/7) to give E-22 in a 95% yield as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.66 (m, 2H), 4.53 (d, J = 4.0 Hz, 2H), 4.18 (q, J = 6.4 Hz, 3H), 3.71 (s, 6H), 2.63 (d, J = 5.2 Hz, 2H), 2.45 (t, J = 7.2 Hz, 2H), 2.16-2.10 (m, 2H), 2.12 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃; DEPT) δ (ppm): 207.1 (C), 171.3 (C), 155.1 (C), 129.9 (CH), 128.5 (CH), 67.7 (CH₂), 64.2 (CH₂), 57.0 (C), 52.8 (CH₂), 38.7 (CH₃), 37.0 (CH₃), 30.1 (CH₂), 26.9 (CH₃), 14.4 (CH₃); ESHRMS calcd. for C₁₈H₂₀O₄Na m/z 367.1363, found m/z 367.1356.

Synthesis of carbonate 27.
A sample of (Z)-BrCH=CH=CHCH$_2$CO$_2$Et$^{13}$ (81 mg, 0.3 mmol) was added to a mixture of NaH (11 mg, 0.4 mmol) and N-allylbenzenesulphonamide$^{16}$ (48 mg, 0.2 mmol) in DMF (8 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et$_2$O, washed with 10% aqueous HCl and dried with anhydrous Na$_2$SO$_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane, 2/8) to give 27 (65 mg, 79 %) as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.82 (d, $J = 8.4$ Hz, 2H), 7.60-7.49 (m, 3H), 5.71-5.48 (m, 3H), 5.19-5.14 (m, 2H), 4.61 (d, $J = 6.8$ Hz, 2H), 4.18 (q, $J = 7.2$ Hz, 2H), 3.90 (d, $J = 6.8$ Hz, 2H), 3.81 (d, $J = 6.0$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H); ESHRMS calcd. for C$_{10}$H$_{17}$NO$_2$S m/z 339.1140, found m/z 340.1211.

**Synthesis of carbonate 29.**

A sample of (Z)-BrCH=CH=CHCH$_2$CO$_2$Et$^{13}$ (158 mg, 0.7 mmol) was added to a mixture of NaH (22 mg, 0.9 mmol) and N-(2-methyl-allyl)-benzenesulphonamide$^{16}$ (100 mg, 0.4 mmol) in DMF (15 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et$_2$O, washed with 10% aqueous HCl and dried with anhydrous Na$_2$SO$_4$, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane, 2/8) to give 29 (80 mg, 48 %) as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.82 (d, $J = 7.8$ Hz, 2H), 7.59-7.49 (m, 3H), 5.65-5.59 (m, 1H), 5.46-5.40 (m, 1H), 4.92 (s, 1H), 4.85 (s, 1H), 4.59 (d, $J = 6.8$ Hz, 2H), 4.18 (q, $6.8$ Hz, 2H), 3.87 (d, $J = 6.8$ Hz, 2H), 3.71 (s, 2H), 1.70 (s, 3H), 1.29 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 155.1 (C), 142.9 (C), 138.9 (C), 136.9 (C), 132.8 (CH), 129.5 (CH), 129.3 (CH), 127.4 (CH), 127.0 (CH), 114.9 (CH$_2$), 62.8 (CH$_3$), 53.8 (CH$_2$), 43.8 (CH$_2$), 29.9 (CH$_3$), 19.9 (CH$_3$), 14.4 (CH$_3$); ESHRMS calcd. for C$_{21}$H$_{20}$NO$_2$SNa m/z 376.1189, found m/z 376.1186.

**Synthesis of allyl carbonate 31.**

**Synthesis of alcohol VIII.** Isoprene monoxide (40 mg, 0.4 mmol) was added to a solution of N-allyl-$p$-toluenesulphonamide$^{17}$ (100 mg, 0.4 mmol), Pd$_2$(dba)$_3$/dba (4 mg, 0.05 mmol) and dpppe (9 mg, 0.05 mmol) in THF (15 mL). The resulting mixture was stirred at room temperature for 24 h and then reduced in volume to 0.5 mL. The residue was submitted to flash chromatography (EtOAc/Hexane, 3/7) to give VIII (60 mg, 43 %) as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.68 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 5.70-5.60 (m, 2H), 5.29-5.11 (m, 2H), 4.08 (s, 2H), 3.83-3.77 (m, 4H), 2.42 (s, 3H), 1.77 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 142.9 (C), 138.9 (C), 136.9 (C), 132.8 (CH), 129.3 (CH), 126.9 (CH), 121.8 (CH), 118.4 (CH$_2$), 60.8 (CH$_3$), 49.8 (CH$_2$), 43.5 (CH$_2$), 21.2 (CH$_3$), 21.1 (CH$_3$); ESHRMS calcd. for C$_{13}$H$_{21}$NO$_2$S m/z 296.1314, found m/z 296.1312.

**Carbonate 31.** Ethyl carbonate 31 was prepared from allyl alcohol VIII according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane, 1/4) to give 31 in a 79 % yield as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.72 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 7.9$ Hz, 2H), 5.70-5.58 (m, 1H), 5.35-5.29 (m, 1H), 5.16 (d, $J = 16.3$ Hz, 1H), 5.15 (d, $J = 10.5$ Hz, 1H), 4.58 (s, 2H), 4.21 (q, $J = 7.2$ Hz, 2H), 3.88 (d, $J = 7.0$ Hz, 2H), 3.81 (d, $J = 6.0$ Hz, 2H), 2.45 (s, 3H), 1.78 (s, 3H), 1.32 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 152.7 (C),

140.9 (C), 136.7 (C), 134.9 (C), 130.7 (CH), 127.3 (CH), 124.8 (CH), 123.3 (CH), 116.4 (CH₂), 63.2 (CH₂), 61.8 (CH₂), 47.5 (CH₃), 41.6 (CH₂), 19.1 (CH₃), 18.9 (CH₃), 11.9 (CH₃); ESHRMS calcd for C₁₃H₁₂NO₅S m/z 368.1526, found m/z 368.1543.

**Synthesis of acetate 33.**

A sample of *trans*-4-acetoxy-1-bromo-2-methyl-2-butenone (541 mg, 2.6 mmol) was added to a mixture of NaH (60 mg, 2.6 mmol) and dimethyl allylmalonate (300 mg, 1.7 mmol) in DMF (20 mL). This solution was stirred at room temperature for 4 h and then diluted with Et₂O, washed with 10% aqueous HCl and dried with anhydrous Na₂SO₄, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane, 2/8) to give 33 (453 mg, 90%) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.82 (d, J = 8.4 Hz, 2H), 7.59-7.48 (m, 3H), 5.55-5.43 (m, 2H), 5.08 (d, J = 9.6 Hz, 1H), 5.06 (d, J = 16.8 Hz, 1H), 4.58 (d, J = 6.8 Hz, 2H), 3.75 (d, J = 6.8 Hz, 2H), 3.72 (s, 2H), 2.03 (s, 3H), 1.67 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 168.5 (C), 137.9 (C), 133.5 (C), 130.3 (CH), 129.8 (CH), 126.7 (CH), 124.8 (CH), 122.8 (CH), 117.0 (CH₂), 58.4 (CH₂), 51.7 (CH₃), 47.4 (CH₃), 18.5 (CH₃), 12.0 (CH₃); ESHRMS calcd for C₁₃H₁₂NO₅SNa m/z 346.1083, found m/z 346.1098.

**Synthesis of allyl carbonate 37.**

**Synthesis of sulfonamide IX.** Vinylmagnesium chloride (2.65 mL, 1.0 M in THF) was slowly added to a solution of N-benzylidenbenzenesulfonamide (500 mg, 2.0 mmol) in 1:1 mixture of THF:Et₂O (20 mL) at rt and continued stirring for 15 h. The reaction mixture was quenched with saturated NH₄Cl and extracted with ether. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄ and the solvent removed. The resulting solution was stirred at room temperature for 4 h and then diluted with Et₂O, washed with 10% aqueous HCl and dried with anhydrous Na₂SO₄, and the solvent removed. The

**Carbonate 37.** A sample of (Z)-BrCH₂CH=CHCH₂OCOEt (183 mg, 0.8 mmol) was added to a mixture of NaH (25 mg, 1.1 mmol) and sulfonamide IX (149 mg, 0.5 mmol) in DMF (10 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et₂O, washed with 10% aqueous HCl and dried with anhydrous Na₂SO₄, and the solvent removed. The

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residue was submitted to flash chromatography (EtOAc/Hexane:2/8) to give 37 (145 mg, 64 %) as a colourless oil: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 7.85 (d, $J = 6.9$ Hz, 2H), 7.59-7.48 (m, 3H), 7.32-7.24 (m, 5H), 6.04 (ddd, $J = 17.2$, 10.3, 6.7 Hz, 1H), 5.72 (d, $J = 6.7$ Hz, 1H), 5.43-5.40 (m, 2H), 5.31 (dd, $J = 9.2$, 1.2 Hz, 1H), 5.15 (dd, $J = 17.2$, 1.2 Hz, 1H), 4.37 (d, $J = 3.7$ Hz, 2H), 4.21 (q, $J = 7.2$ Hz, 2H), 3.81 (d, $J = 3.4$ Hz, 2H), 1.33 (t, $J = 7.2$Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 155.1 (C), 141.1 (C), 138.3 (C), 134.4 (CH), 132.6 (CH), 131.9 (CH), 129.0 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 127.7 (CH), 126.6 (CH), 119.5 (CH), 67.2 (CH$_2$), 64.2 (CH$_2$), 63.5 (CH), 46.6 (CH$_2$), 14.5 (CH$_3$); ESHRMS calcd. for C$_{22}$H$_{25}$NO$_3$Na $m/z$ 438.4924, found $m/z$ 438.1354.

**Synthesis of carbonate 39.**

![Diagram of carbonate 39 synthesis](image)

**Synthesis of compound X.** A sample of (Z)-ICh$_3$CH=CHCH$_2$OTHP$^{19}$ (356 mg, 1.2 mmol) was added to a mixture of NaH (33 mg, 1.4 mmol) and dodec-1-en-3-ol$^{20}$ (250 mg, 1.2 mmol) in DMF (15 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with EtO, washed with 10% aqueous HCl, dried over anhydrous Na$_2$SO$_4$ and the solvent removed. The residue was submitted to flash chromatography (5:95, EtOAc/Hexane,1/9) to give X (275 mg, 65 %) as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.85-5.81 (m, 2H), 5.66 (ddd, $J = 16.4$, 10.8, 7.6, 1H), 5.16 (d, $J = 10.8$ Hz, 1H), 5.15 (d, $J = 16.4$ Hz, 1H), 4.64 (t, $J = 3.6$ Hz, 1H), 4.24 (bd, $J = 11.2$ Hz, 1H), 4.05-3.96 (m, 2H), 3.89-3.81 (m, 2H), 3.65 (q, $J = 6.8$ Hz, 1H), 3.51-3.48 (m, 1H), 1.87-1.81 (m, 1H), 1.74-1.69 (m, 1H), 1.61-1.24 (m, 20H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 139.4 (CH), 129.9 (CH), 129.0 (CH), 98.1 (CH$_3$), 81.2 (CH), 81.1 (CH), 68.4 (CH$_2$), 67.3 (CH$_3$), 62.3 (CH$_3$), 35.6 (CH$_2$), 32.1 (CH$_2$), 30.8 (CH$_3$), 29.8 (CH$_2$), 29.5 (CH$_2$), 25.7 (CH$_2$), 25.5 (CH$_2$), 22.9 (CH$_3$), 19.6 (CH$_3$), 14.3 (CH$_3$), (one carbon signal was not observed); ESHRMS calcd. for C$_{21}$H$_{23}$O$_3$Na $m/z$ 361.2713, found $m/z$ 361.2707.

**Synthesis of alcohol XI.** $p$-Toluenesulfonic acid (8 mg, 0.04 mmol) was added to a solution of ether X (139 mg, 0.4 mmol) in MeOH (25 mL). The resulting mixture was stirred for 14 h and then diluted with EtOAc, washed with brine, dried over anhydrous Na$_2$SO$_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,2/8) to give XI (88 mg, 84 %) as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.86 (dt, $J = 15.6$, 4.8 Hz, 1H), 5.70 (dt, $J = 15.6$, 4.8 Hz, 1H), 5.65 (ddd, $J = 17.2$, 10.0, 7.6 Hz, 1H), 5.16 (d, $J = 10.0$ Hz, 1H), 5.15 (d, $J = 17.6$ Hz, 1H), 4.13 (d, $J = 4.8$ Hz, 2H), 4.02 (dd, $J = 12.8$, 5.2 Hz, 1H), 3.82 (dd, $J = 12.8$, 5.6 Hz, 1H), 3.65 (q, $J = 6.8$ Hz, 1H), 1.25 (m, 16H), 0.86 (t, $J = 6.4$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 139.3 (CH), 131.9 (CH), 128.6 (CH), 117.0 (CH$_3$), 81.3 (CH), 68.3 (CH$_3$), 63.3 (CH$_3$), 35.6 (CH$_2$), 32.1 (CH$_2$), 29.8 (CH$_3$), 29.5 (CH$_2$), 25.5 (CH$_2$), 22.9 (CH$_3$), 14.3 (CH$_3$), (one carbon signal was not observed); ESHRMS calcd. for C$_{19}$H$_{23}$O$_3$Na $m/z$ 277.2143, found $m/z$ 277.2134.

**Carbonate 39.** It was prepared from allyl alcohol XI according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane, ) to give 39 in a 96 % yield as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.90-5.76 (m, 2H), 5.64 (ddd, $J = 17.6$, 10.8, 7.6 Hz, 1H), 5.15 (d, $J = 9.2$ Hz, 1H), 5.14 (d, $J = 18.0$ Hz, 1H), 4.61 (d, $J = 5.2$ Hz, 2H), 4.18 (q, $J = 7.2$ Hz, 2H), 4.03 (dd, $J = 12.8$, 4.4 Hz, 1H), 3.83 (dd, $J = 12.8$, 4.5 Hz, 1H), 3.64 (q, $J = 6.8$ Hz, 1H), 1.31-1.25 (m, 19H), 0.87 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 153.9 (C), 138.0 (CH), 131.3 (CH), 124.3 (CH), 115.8 (CH), 80.0 (CH), 66.6 (CH$_2$), 62.9 (CH$_2$), 62.7 (CH$_2$), 34.4 (CH$_3$), 30.8 (CH$_3$), 28.5 (CH$_3$), 28.3 (CH$_2$), 24.3 (CH$_3$), 21.6 (CH$_2$), 13.2 (CH$_3$), 13.0 (CH$_3$), (two carbon signals were not observed); ESHRMS calcd. for C$_{15}$H$_{16}$O$_3$Na $m/z$ 349.2349, found $m/z$ 349.2322.

$^{19}$It was prepared from (Z)-OHCH$_3$CH=CHCH$_2$OTHP according to known procedure: J. Garegg, B. Samuelsson. J. Chem. Soc. Perkin I. 1980, 2866-2869. (Z)-ICh$_3$CH=CHCH$_2$OTHP was isolated as a pure sample and showed NMR spectra identical to those reported: R. A. Holton, J. R. Zoeller. J. Am. Chem. Soc. 1985, 107, 2124-2126.

Allylation Products

Compound 2.

\[
\begin{align*}
\text{MeO} &\quad \text{MeO} \\
\text{OH} &
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.65-5.50 (m, 2H), 5.10 (d, $J = 10.2$ Hz, 1H), 5.08 (d, $J = 17.0$ Hz, 1H), 5.07 (d, $J = 10.5$ Hz, 1H), 5.01 (d, $J = 17.2$ Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.42-3.39 (m, 1H), 2.71 (dd, $J = 14.2$, 7.0 Hz, 1H), 2.62 (dd, $J = 14.2$, 7.2 Hz, 1H), 2.03-1.97 (m, 1H), 1.42-1.37 (m, 1H), 1.34-1.19 (m, 14H), 0.86 (t, $J = 6.6$ Hz, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 171.8 (C), 171.7 (C), 138.0 (CH), 132.6 (CH), 119.3 (CH$_2$), 118.2 (CH$_2$), 74.6 (CH), 57.0 (C), 52.5 (CH$_3$), 52.2 (CH$_3$), 45.8 (CH$_2$), 37.8 (CH), 34.4 (CH$_2$), 33.8 (CH$_2$), 32.0 (CH$_2$), 29.9 (CH$_2$), 29.8 (CH$_2$), 29.7 (CH$_2$), 29.5 (CH$_2$), 26.1 (CH$_2$), 22.8 (CH$_2$), 14.3 (CH$_3$); ES-HRMS calcd. for C$_{22}$H$_{38}$O$_5$Na $m/z$ 405.2611, found $m/z$ 405.2596.

Compound 7.

\[
\begin{align*}
\text{OH} &
\end{align*}
\]

Compound 7 was obtained as a 1:1 mixture of diastereomers. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.79 (ddt, $J =$ 16.5, 10.7, 7.4 Hz, 1H), 5.13 (bd, $J =$ 16.5 Hz, 1H), 5.06 (bd, $J =$ 6.5 Hz, 1H), 3.75-3.70 (m, 1H), 2.30-1.94 (m, 4H), 1.66 (s, 3H), 1.58 (s, 3H), 1.50-1.17 (m, 5H), 0.88 (d, $J =$ 6.2 Hz, 3H, one diastereoisomer), 0.84 (d, $J =$ 6.2 Hz, 3H, other diastereoisomer);

$^{13}$C NMR (100 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 134.9 (CH), 131.5 (C), 124.8 (CH), 118.1 (CH$_2$), 68.7 (CH), 44.3 (CH$_2$), 42.2 (CH$_2$), 37.9 (CH$_2$), 28.9 (CH), 25.7 (CH$_2$), 25.4 (CH$_2$), 20.2 (CH$_2$), 17.7 (CH$_3$); FAB-HRMS calcd. for C$_{13}$H$_{24}$ONa $m/z$ 219.1724, found $m/z$ 219.1718.

Compound 8.

\[
\begin{align*}
\text{OH} &
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.85 (ddt, $J =$ 17.2, 10.0, 7.2 Hz, 1H), 5.14 (d, $J =$ 7.6 Hz, 1H), 5.11 (d, $J =$ 16.0 Hz, 1H), 2.22 (d, $J =$ 7.6 Hz, 2H), 1.45-1.26 (m, 14H), 1.16 (s, 3H), 0.88 (t, $J =$ 7.2 Hz, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 134.1 (CH), 118.4 (CH$_2$), 72.1 (C), 46.2 (CH$_2$), 41.8 (CH$_2$), 31.8 (CH$_2$), 30.1 (CH$_2$), 29.5 (CH$_2$), 29.2 (CH$_3$), 26.6 (CH$_3$), 23.8 (CH$_3$), 22.6 (CH$_2$), 14.0 (CH$_3$); ESH-RMS calcd. for C$_{13}$H$_{26}$ONa $m/z$ 221.1875, found $m/z$ 221.1867.

Compound 9.

\[
\begin{align*}
\text{OH} &
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 5.85 (ddt, $J =$ 17.1, 10.2, 7.5 Hz, 1H), 5.12 (dd, $J =$ 10.2, 2.4 Hz, 1H), 5.10 (dd, $J =$ 17.1, 2.4 Hz, 1H), 2.40 (d, $J =$ 7.5 Hz, 2H), 2.15 (bd, $J =$ 12.4 Hz, 2H), 1.85-1.49 (m, 10H);

$^{13}$C NMR (100 MHz, CDCl$_3$; DEPT) $\delta$ (ppm): 133.8 (CH), 118.9 (CH$_2$), 74.5 (C), 42.8 (CH$_2$), 38.4 (CH$_2$), 37.1 (CH), 34.5 (CH$_2$), 33.0 (CH$_2$), 27.5 (CH), 27.4 (CH), (some carbon signals were not observed); ESH-RMS calcd. for C$_{13}$H$_{20}$ONa $m/z$ 215.1406, found $m/z$ 215.1415.

Compound 16.
Compound 16 was obtained as a 3:2 mixture of diastereomers; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.82 (dd, J = 16.9, 10.6, 6.9 Hz, 1H), 5.10 (dd, J = 10.6, 1.7 Hz, 1H), 5.07 (dd, J = 16.9, 1.7 Hz, 1H), 2.24 (quint, J = 6.9 Hz, 1H), 1.49-1.27 (m, 14H), 1.11 (s, 3H, minor stereoisomer), 1.09 (s, 3H, major stereoisomer), 1.03 (d, J = 6.9 Hz, 3H, minor stereoisomer), 1.00 (d, J = 6.9 Hz, 3H, major stereoisomer), 0.88 (t, J = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$; DEPT) δ(ppm): 140.7 (CH), 140.5 (CH), 116.4 (CH$_2$), 115.9 (CH$_3$), 73.8 (C), 47.9 (CH), 47.2 (CH), 40.1 (CH$_2$), 39.6 (CH$_2$), 31.9 (CH$_3$), 30.4 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 24.2 (CH$_3$), 23.7 (CH$_3$), 23.4 (CH$_3$), 22.3 (CH$_3$), 22.8 (CH$_2$), 14.6 (CH$_3$), 14.2 (CH$_3$), (some carbon signals were not observed); FABHRMS calcd. for C$_{14}$H$_{26}$O$_2$ m/z 265.1046, found m/z 265.1049.

**Compound 17.**

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 6.04 (dd, J = 17.5, 10.9 Hz, 1H), 5.08 (d, J = 10.9 Hz, 1H), 5.05 (d, J = 17.5 Hz, 1H), 1.47-1.41 (m, 2H), 1.32-1.20 (m, 12H), 1.11 (s, 6H), 0.88 (t, J = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$; DEPT) δ(ppm): 145.6 (CH), 113.4 (CH$_2$), 75.7 (C), 44.6 (C), 36.6 (CH$_2$), 31.9 (CH$_3$), 30.6 (CH$_2$), 29.8 (CH$_2$), 23.9 (CH$_3$), 22.8 (CH$_3$), 22.3 (CH$_3$), 22.2 (CH$_3$), 21.1 (CH$_3$), 14.2 (CH$_3$), (one carbon signal was not observed); FABHRMS calcd. for C$_{13}$H$_{20}$O$_2$ m/z 249.2194, found m/z 249.2200.

**Compound 19.**

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.54 (dd, J = 17.4, 10.3, 9.1 Hz, 1H), 5.10 (dd, J = 10.3, 1.9 Hz, 1H), 5.00 (dd, J = 17.2, 1.9 Hz, 1H), 4.85 (s, 1H), 4.73 (s, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.45-3.43 (m, 1H), 2.74 (s, 2H), 2.20-2.14 (m, 2H), 2.07-2.01 (m, 1H), 1.63 (s, 3H), 1.42-1.32 (m, 2H), 1.30-1.24 (m, 14H), 0.87 (t, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$; DEPT) δ(ppm): 172.1 (C), 171.8 (C), 140.7 (C), 137.6 (CH), 117.8 (CH$_2$), 74.7 (CH$_2$), 56.1 (C), 52.2 (CH$_3$), 52.0 (CH$_3$), 45.5 (CH$_2$), 41.4 (CH$_3$), 34.3 (CH$_3$), 34.1 (CH$_3$), 31.9 (CH$_3$), 29.6 (CH$_2$), 29.5 (CH$_3$), 29.4 (CH$_2$), 29.3 (CH$_3$), 25.9 (CH$_2$), 23.0 (CH$_3$), 22.6 (CH$_3$), 14.1 (CH$_3$); ESHRMS calcd. for C$_{13}$H$_{20}$O$_2$Na m/z 419.2767, found m/z 419.2745.

**Compound 21.**

Compound 21 was obtained as a 1:1 mixture of diastereomers.

Diastereomer 21a: $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.87 (dd, J = 16.8, 10.8, 5.6 Hz, 1H), 5.19 (dd, J = 16.8, 1.2 Hz, 1H), 5.16 (dd, J = 10.8, 1.2 Hz, 1H), 3.89 (bs, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.36-2.32 (m, 1H), 2.19-2.02 (m, 4H), 1.91 (dq, J = 14.4, 3.0 Hz, 1H), 1.70-1.61 (m, 1H), 1.25 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) δ(ppm): 172.5 (C), 171.6 (C), 139.4 (CH), 116.3 (CH$_2$), 67.0 (CH), 54.8 (C), 52.8 (CH$_2$), 52.6 (CH$_3$), 41.4 (CH), 29.0 (CH$_2$), 28.6 (CH$_3$), 24.5 (CH$_2$); ESHRMS calcd. for C$_{15}$H$_{26}$O$_2$Na m/z 265.1046, found m/z 265.1049.

Diastereomer 21b: $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.74 (dd, J = 17.2, 10.0, 8.4Hz, 1H), 5.24-5.17 (m, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.29 (td, J = 10.4, 4.4 Hz, 1H), 2.45-2.37 (m, 2H), 2.13-1.98 (m, 2H), 1.77 (td, J = 13.6, 3.6 Hz, 1H), 1.62 (t, J = 13.2 Hz, 1H), 1.39 (qd, J = 14.0, 3.6 Hz, 1H); NOE-diff. experiment: proton irradiated, (NOE observed): H-6, (H-7), H-7, (H-6); $^{13}$C NMR (125 MHz, CDCl$_3$; DEPT) δ(ppm): 172.3 (C), 171.1 (C), 139.0 (CH), 118.1 (CH$_2$), 71.8 (CH$_3$), 54.5 (C), 52.8 (CH$_2$), 52.7 (CH$_3$), 47.2 (CH), 35.5 (CH$_2$), 30.3 (CH$_3$), 29.9 (CH$_2$); ESHRMS calcd. for C$_{15}$H$_{26}$O$_2$Na m/z 265.1046, found m/z 265.1049.

**Compound 23.**
\[ ^1\text{H NMR (400 MHz, CDCl}_3 \delta \text{ (ppm): } 5.91 \text{ (ddd, } J = 17.1, 10.2, 7.2 \text{ Hz, 1H), 5.21 (ddd, } J = 17.1, 0.9 \text{ Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 2.40-1.98 \text{ (m, 5H), 1.73 (dt, } J = 14.1, 3.3 \text{ Hz, 1H), 1.54 (td, } J = 14.1, 4.5 \text{ Hz, 1H), 1.20 (s, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-7, (H-2, H-6); 13\text{C NMR (75 MHz, CDCl}_3; DEPT) } \delta \text{ (ppm): } 174.2 (C), 173.6 (C), 142.5 (CH), 113.3 (CH}_3; \text{ ESHRMS calcd. for C}_{19}H_{20}O_4Na m/z 279.1202, found m/z 279.1192. \]

The stereochemistry of 23 was confirmed based on NOE-diff. experiments of closely related acetylated derivative 23ac:

![Diagram of 23ac structure]

\[ ^1\text{H NMR (400 MHz, CDCl}_3 \delta \text{ (ppm): } 5.83-5.68 \text{ (m, 1H), 5.22-5.10 \text{ (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 3.02 (dt, } J = 6.7 \text{ Hz, 1H), 0.75 (d, } J = 7 \text{ Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-6\beta, (H-9, H-2, H-6\alpha), H_2-9, (H-2, H-6\alpha, H-6\beta), H_2-6\alpha, (H-6\beta, H_2-9); 13\text{C NMR (125 MHz, CDCl}_3; DEPT) } \delta \text{ (ppm): } 172.3 (C), 171.6 (C), 167.3 (C), 137.0 (CH), 118.1 (CH}_3, 83.2 (C), 54.4 (C), 52.9 (CH)_3, 49.2 (CH), 32.7 (CH)_2, 31.3 (CH)_2, 26.7 (CH)_2, 25.6(CH)_3, 24.2(CH)_3. \]

**Cyclization Products**

### Compound 28.

![Diagram of Compound 28 structure]

### Compound 30.

![Diagram of Compound 30 structure]

### Compound 34.

![Diagram of Compound 34 structure]

### Compound 36.
Compound 38.

Mayor diastereomer 38 was obtained as a 9:1 mixture of epimers at C-2. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.75 (d, \(J = 8.4\) Hz, 2H), 7.57-7.44 (m, 3H), 7.30-7.22 (m, 5H), 5.42 (ddd, \(J = 11.0\) Hz, 1H), 5.00 (d, \(J = 7.2\) Hz, 1H), 4.38 (d, \(J = 4.4\) Hz, 1H), 3.74 (dd, \(J = 10.0, 6.8\) Hz, 1H), 3.43 (dd, \(J = 10.0, 7.2\) Hz, 1H), 2.86 (quint, \(J = 6.8\) Hz, 1H), 2.18 (sext., \(J = 6.0\) Hz, 1H), 0.64 (d, \(J = 7.2\) Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-1 (H-5, H-8), H-2 (H-3, H-5, H-7), H-3 (H-4, H-5, H-7, H-8), H-4 (H-3, H-5, H-7, H-8), H-5 (H-3, H-7, H-8), H-7 (H-1, H-2, H-4, H-5, H-7, H-8), H-8 (H-5, H-7, H-8); \(^1^3\)C NMR (125 MHz, CDCl\(_3\); DEPT) \(\delta\) (ppm): 137.6 (CH), 135.9 (C), 131.0 (CH), 127.5 (CH), 125.7 (CH), 112.6 (CH\(_2\)), 56.7 (CH\(_3\)), 51.9 (CH\(_3\)), 44.7 (C), 41.5 (CH), 24.7 (CH\(_3\)), 14.0 (CH\(_3\)); ESHRMS calcd. for \(\text{C}_1\text{H}_{19}\text{NO}_3\text{SNa} m/z 288.1028, \text{found m/z 288.1030.}

Compound 40.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 5.69 (dt, \(J = 17.0, 10.0\) Hz, 1H), 4.99 (d, \(J = 10.0\) Hz, 1H), 4.97 (d, \(J = 17.0\) Hz, 1H), 3.90 (dd, \(J = 8.5, 7.0\) Hz, 1H), 3.53 (dd, \(J = 8.5, 5.6\) Hz, 1H), 3.37 (dt, \(J = 7.4, 3.6\) Hz, 1H), 2.74 (quint, \(J = 6.9\) Hz, 1H), 1.85 (sext., \(J = 7.2\) Hz, 1H), 1.45-1.36 (m, 2H), 1.21-1.19 (m, 14H), 0.84 (d, \(J = 7.0\) Hz, 3H), 0.81 (t, \(J = 6.9\) Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-1 (H-2, H-3), H-2 (H-1, H-3, H-5, H-7, -5), H-3 (H-1, H-2, H-4, H-7), H-4 (H-1, H-3, H-5, H-7), H-5 (H-1, H-2, H-4, H-7), H-6 (H-1, H-2, H-4, H-7); \(^1^3\)C NMR (125 MHz, CDCl\(_3\); DEPT) \(\delta\) (ppm): 135.8 (CH), 115.1 (CH\(_2\)), 84.4 (CH), 70.6 (CH\(_2\)), 46.7 (CH), 41.2 (CH), 33.8 (CH\(_2\)), 30.8 (CH\(_2\)), 28.8 (CH\(_3\)), 28.6 (CH\(_2\)), 28.5 (CH\(_2\)), 28.3 (CH\(_2\)), 25.4 (CH\(_2\)), 21.6 (CH\(_2\)), 13.0 (CH\(_3\)), 12.5 (CH\(_3\)); ESHRMS calcd. for \(\text{C}_{10}\text{H}_{22}\text{O}_2\text{S} m/z 328.1365, \text{found m/z 328.1371.}

Wurtz-type coupling of farnesyl ethyl carbonate

\[ \text{Cp}_2\text{TiCl}_2 / 2\text{PPH}_3 \text{(cat)} \]

\[ \text{Farnesyl ethyl carbonate} \]

\[ \text{squalene} \]

(60%)
Synthesis of farnesyl ethyl carbonate. It was prepared from farnesyl alcohol according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane, 5/95) to give farnesyl ethyl carbonate in a 92 % yield as colourless oil and the spectroscopic data were identical to the reported compound.\textsuperscript{21}

Synthesis of squalene. Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp\textsubscript{2}TiCl\textsubscript{2} (11 mg, 0.04 mmol), PdCl\textsubscript{2} (15 mg, 0.08 mmol), PPh\textsubscript{3} (44 mg, 0.17 mmol) and Mn dust (186 mg, 3.3 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of farnesyl ethyl carbonate (125 mg, 0.4 mmol), 2,4,6-collidine (358 mg, 2.9 mmol) and Me\textsubscript{3}SiCl (184 mg, 1.6 mmol) in THF (2 mL) was then added. The mixture was stirred for 16 h and then diluted with AcOEt, washed with brine, dried over anhydrous MgSO\textsubscript{4} and the solvent removed. The residue was submitted to flash chromatography (Hexane) to give squalene (53 mg, 60 %) as colourless oil. Its spectroscopic data were identical to the reported compound.\textsuperscript{22}


\textsuperscript{22} Pure samples of squalene for comparison were obtained from a commercial source.