Electronic Supplementary Information

Ti/Pd-Promoted Catalyzed intramolecular Michael-type addition of allylic carboxylates to activated alkenes

Alba Millán, Ana Martín-Lasanta, Delia Miguel, Luis Álvarez de Cienfuegos, Juan M. Cuerva

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Granada, Avda. Severo Ochoa s/n, 18071-Granada, Spain
jmcuerva@ugr.es, lac@ugr.es, dmalvarez@ugr.es

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**General Information**

All intramolecular cyclization reactions were assembled under argon atmosphere in oven-dried glassware with magnetic stirring. For the reactions employing titanocene all solvents and additives were rigorously deoxygenated prior to use. THF was previously distilled and dried over sodium. All commercially available reagents and solvents used in extraction and purification, ether, hexane and ethyl acetate, were obtained from standard chemical suppliers and used without further purification. TLC was performed on aluminium-backed plates coated with silica gel 60 (230-240 mesh) with F$_{254}$ indicator. The spots were visualized with UV light (254 nm) and/or staining with Ce/Mo reagent or phosphomolybdic acid solution and subsequent heating.

NMR Spectra were measured at room temperature. $^1$H NMR spectra were recorded at 300, 400 or 500 MHz. The ratio of isomers was determined by integration of the allylic proton in $^1$H-NMR spectra in C$_6$D$_6$ or CDCl$_3$. In case of mixture of isomers, the protons and carbons are assigned to the major or minor isomer when it is possible. When nothing is said the two isomers appear together and therefore the number of protons/carbons specified corresponds to both of them. Chemical shifts are reported in ppm using residual solvent peak as reference (CHCl$_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quint: quintuplet; m: multiplet, dd: doublet of doublets, dt: doublet of triplets, dq: doublet of quartets, td: triplet of doublets, bs: broad singlet), coupling constant (J in Hz) and integration. $^{13}$C-NMR spectra were recorded at 75, 100 or 126 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference (CDCl$_3$: δ 77.16). Carbon multiplicities were assigned by DEPT techniques. The stereochemistry of the cyclization products was assigned using the Beckwith-Houk rules for radical cyclizations and the described $^{13}$C NMR for the trans isomer of a very closely related derivative of 2.

High resolution mass spectra (HRMS) were recorded on a Micromass AutoSpec using EI at 70eV.

The following known compounds were isolated as pure samples and showed NMR spectra identical to reported data: (Z)-I 1, (E)-I 2, II 3, (Z)-BrCH=CH=CHCH$_2$CO$_2$Et 4, VII 5, IX 6, trans-4-acetoxy-1-bromo-2-methyl-2-butene 7, XV 8, carbonate XIX 9.

Optimization of the reaction conditions for the Pd\(^{0}\)-Ti\(^{III}\)-promoted Michael-type addition of allylic carboxylates to activated alkenes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ti catalyst (\text{mol}%)</th>
<th>Ligand (\text{mol}%)</th>
<th>Pd catalyst (\text{mol}%)</th>
<th>Mn (\text{mol}%)</th>
<th>TMSCl (\text{mol}%)</th>
<th>2,4,6-Collidine (\text{mol}%)</th>
<th>Yield ((\text{cis:trans}))</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>((t\text{BuCp})_2\text{TiCl}_2) (150)</td>
<td>PPh(_3) (40)</td>
<td>PdCl(_2) (20)</td>
<td>800</td>
<td>-</td>
<td>-</td>
<td>54 (4:1)</td>
</tr>
<tr>
<td>2</td>
<td>((t\text{BuCp})_2\text{TiCl}_2) (150)</td>
<td>PPh(_3) (40)</td>
<td>PdCl(_2) (20)</td>
<td>800</td>
<td>-</td>
<td>-</td>
<td>62 (4:1)</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>PPh(_3) (40)</td>
<td>PdCl(_2) (20)</td>
<td>800</td>
<td>400</td>
<td>-</td>
<td>62 (4:1)</td>
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<tr>
<td>4</td>
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<td>700</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>((t\text{BuCp})_2\text{TiCl}_2) (40)</td>
<td>PPh(_3) (40)</td>
<td>-</td>
<td>800</td>
<td>400</td>
<td>700</td>
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<td>6</td>
<td>((t\text{BuCp})_2\text{TiCl}_2) (40)</td>
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<td>PdCl(_2) (20)</td>
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<td>-</td>
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<td>0</td>
</tr>
<tr>
<td>8</td>
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<td>PPh(_3) (40)</td>
<td>PdCl(_2) (20)</td>
<td>800</td>
<td>400</td>
<td>-</td>
<td>71 (4:1)</td>
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<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>Pd(PPh(_3))^4 (20)</td>
<td>-</td>
<td>-</td>
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Influence of the phosphorous ligand and the palladium complex in the Pd\textsuperscript{0}-Ti\textsuperscript{III}-promoted Michael-type addition of allylic carboxylates to activated alkenes.

![Chemical Reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand (mol %)</th>
<th>Pd catalyst (mol %)</th>
<th>Yield, (2_{\text{cis}}:2_{\text{trans}})</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>PCy\textsubscript{3} (40)</td>
<td>PdCl\textsubscript{2} (20)</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>P(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (40)</td>
<td>PdCl\textsubscript{2} (20)</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>[Pd\textsubscript{2}(dba)\textsubscript{3}]dba (20)</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>4</td>
<td>dppm (40)</td>
<td>PdCl\textsubscript{2} (20)</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>o-Tolylphosphine (40)</td>
<td>PdCl\textsubscript{2} (20)</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>6</td>
<td>(2-MeOC\textsubscript{6}H\textsubscript{4})\textsubscript{3}PPh\textsubscript{3} (40)</td>
<td>PdCl\textsubscript{2} (20)</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>dppe (40)</td>
<td>PdCl\textsubscript{2} (20)</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>P(OPh)\textsubscript{3} (40)</td>
<td>PdCl\textsubscript{2} (20)</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>Pd(PPh\textsubscript{3})\textsubscript{4} (20)</td>
<td>51, (4:1)</td>
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</table>
Synthesis of compound (Z)-1:

Methyl 4-bromocrotonate (230mg, 1.1 mmol) was added to a mixture of NaH (44 mg, 1.1 mmol) and dimethylmalonate derivative (Z)-I (274 mg, 1 mmol) in DMF (10 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na₂SO₄. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give a 6:1 mixture (253 mg, 68 %) of the Z- and E-isomers of the carbonate as a colourless oil. Data of the major isomer (Z)-1:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 6.76 (dt, J = 15.4, 7.6 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.74 – 5.60 (m, 1H), 5.50 (ddd, J = 11.1, 8.5, 4.5 Hz, 1H), 4.63 (d, J = 6.8 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.72 (s, J = 3.3 Hz, 6H), 3.70 (s, J = 3.3 Hz, 3H), 2.76 (d, J = 7.7 Hz, 2H), 2.70 (d, J = 7.7 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C-NMR (126 MHz, CDCl₃): δ (ppm) = 170.5 (2xC), 166.2 (C), 155.1 (C), 142.4 (CH), 127.6 (CH), 125.1 (CH), 64.2 (CH₂), 63.1 (CH₂), 57.3 (C), 52.9 (2xCH₃), 51.7 (CH₃), 35.8 (CH₂), 31.3 (CH₂), 14.4 (CH₃).

HRMS (EI, 70 eV) m/z calcd. for C₁₇H₂₄O₉[M⁺]: 372.1420; found: 372.1403.

Synthesis of compound (E)-1:

Methyl 4-bromocrotonate (979mg, 5.5 mmol) was added to a mixture of NaH (219 mg, 5.5 mmol) and dimethylmalonate derivative (E)-I (1 g, 3.7 mmol) in DMF (25 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na₂SO₄. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give a 6:1 mixture (936 mg, 68%) of the E- and Z-isomers of the carbonate as a colourless oil. Data of the major isomer (E)-1:

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 6.75 (dt, J = 15.3, 7.6 Hz, 1H), 5.85 (d, J = 15.6 Hz, 1H), 5.72 – 5.52 (m, 2H), 4.53 (d, J = 4.9 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.72 (s, 6H), 3.70 (s, 3H), 2.79 - 2.67 (m, 2H), 2.64 (d, J = 5.9 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 170.4 (2xC), 166.2 (C), 154.9 (C), 142.4 (CH), 129.2 (CH), 128.7 (CH), 124.9 (CH), 67.5 (CH₂), 64.0 (CH₂), 57.3 (C), 52.7 (2xCH₃), 51.6 (CH₃), 36.0 (CH₂), 35.6 (CH₂), 14.3 (CH₃).
HRMS (EI, 70 eV) m/z calcd. for C_{17}H_{24}O_{9} [M]^+: 372.1420; found: 372.1418.

Synthesis of compound 3:

**Compound III:** AcO (102 mg, 1 mmol) was added to a solution of compound II (202 mg, 1 mmol) and DMAP (121 mg, 1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 1 h and then solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give III (232 mg, 95%) as a colourless oil.

^1H NMR (300 MHz, CDCl_3): δ (ppm) = 5.72 - 5.64 (m, 2H), 4.48 (d, J = 4.9 Hz, 2H), 3.73 (s, 6H), 3.44 (t, J = 7.5 Hz, 1H), 2.69 - 2.60 (m, 2H), 2.04 (s, 3H).

^13C NMR (75 MHz, CDCl_3): δ (ppm) = 169.2 (3xC), 130.8 (CH), 127.4 (CH), 64.6 (CH_2), 52.7 (2xCH_3), 51.4 (CH), 31.6 (CH_2), 21.1 (CH_3).

HRMS (EI, 70 eV) m/z calcd. for C_{11}H_{17}O_6 [M+1]^+: 245.1025; found: 245.1017

**Compound 3:** Methyl 4-bromocrotonate (220 mg, 1.23 mmol) was added to a mixture of NaH (49 mg, 1.23 mmol) and III (200 mg, 0.82 mmol) in DMF (15 mL) at 0°C. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 7:1 mixture (221 mg, 79%) of the E- and Z- isomers of the carbonate as a colourless oil. Data of the major isomer 3:

^1H NMR (300 MHz, CDCl_3): δ (ppm) = 6.73 (dt, J = 15.3, 7.6 Hz, 1H), 5.84 (d, J = 15.5 Hz, 1H), 5.68 - 5.49 (m, 2H), 4.46 (d, J = 4.2 Hz, 2H), 3.70 (bs, 9H), 2.72 (d, J = 7.2 Hz, 2H), 2.61 (d, J = 5.6 Hz, 2H), 2.02 (s, 3H).

^13C NMR (75 MHz, CDCl_3): δ (ppm) = 170.5 (3xC), 166.2 (C), 142.5 (CH), 129.3 (CH), 128.6 (CH), 125.0 (CH), 64.4 (CH_2), 57.3 (C), 52.7 (2xCH_3), 51.6 (CH_3), 36.0 (CH_2), 35.6 (CH_2), 20.9 (CH_3).

HRMS (EI, 70 eV) m/z calcd. for C_{16}H_{22}O_8 [M]^+: 342.1315; found: 342.1304

Synthesis of compound 4:

**Compound IV:** Benzoyl chloride (140 mg, 1 mmol) was added to a solution of compound II (202 mg, 1 mmol) and DMAP (122 mg, 1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 1 h and then...
solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give IV (281 mg, 92%) as a colourless oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 8.02 (d, $J$ = 8.4 Hz, 2H), 7.54 (t, $J$ = 7.4 Hz, 1H), 7.42 (t, $J$ = 7.6 Hz, 2H), 5.80 (m, 2H), 4.74 (d, $J$ = 4.0 Hz, 2H), 3.72 (s, 6H), 3.47 (t, $J$ = 7.5 Hz, 1H), 2.70-2.62 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 169.2 (2xC), 166.3 (C), 133.1 (CH), 130.9 (CH), 130.3 (C), 129.7 (2xCH), 128.5 (2xCH), 127.5 (CH), 65.0 (CH$_2$), 52.6 (2xCH$_3$), 51.4 (CH), 31.6 (CH$_2$).

HRMS (EI, 70eV) $m/z$ calcd. for C$_{16}$H$_{18}$O$_6$ [M]$: 306.1103$; found: $306.1103$.

**Compound 4:** Methyl 4-bromocrotonate (220 mg, 1.23 mmol) was added to a mixture of NaH (49 mg, 1.23 mmol) and IV (250 mg, 0.82 mmol) in DMF (15 mL) at 0°C. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na$_2$SO$_4$. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 12:1 mixture (248 mg, 75%) of the $E$- and $Z$- isomers in the carbonate as a colourless oil.

Data of the major isomer 4:

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 7.96 (d, $J$ = 8.4 Hz, 2H), 7.43 (t, $J$ = 7.4 Hz, 1H), 7.33 (t, $J$ = 7.6 Hz, 2H), 6.72 (dt, $J$ = 15.3, 7.6 Hz, 1H), 5.82 (d, $J$ = 15.5 Hz, 1H), 5.76 - 5.56 (m, 2H), 4.68 (d, $J$ = 4.2 Hz, 2H), 3.65 (bs, 9H), 2.72 (d, $J$ = 7.2 Hz, 2H), 2.62 (d, $J$ = 5.6 Hz, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 170.3 (3xC), 165.9 (C), 142.3 (CH), 132.8 (CH), 130.1 (C), 129.4 (2xCH), 129.1 (CH), 128.6 (CH), 128.3 (2xCH), 124.8 (CH), 64.7 (CH$_2$), 57.1 (C), 52.5 (2xCH$_3$), 51.3 (CH$_3$), 35.9 (CH$_2$), 35.5 (CH$_3$).

HRMS (EI, 70eV) $m/z$ calcd. for C$_{21}$H$_{24}$O$_8$ [M]$: 404.1471$; found: $404.1455$.

**Synthesis of compound 5:**

$\text{Type 1}$

**Compound V:** (R)-2-(6-Methoxynaphthalen-2-yl)propanoyl chloride (248 mg, 1mmol) was added to a solution of compound II (202 mg, 1 mmol) and DMAP (122 mg, 1 mmol) in CH$_2$Cl$_2$ (15mL). The
mixture was stirred for 3h and then solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give V (364 mg, 88%) as a colourless oil.

\[^{1}H\] NMR (300 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) = 7.68 (m, 2H), 7.41 (d, \(J = 1.7\) Hz, 1H), 7.38 (d, \(J = 1.7\) Hz, 1H), 7.15 (d, \(J = 2.4\) Hz, 1H), 7.12 (d, \(J = 3.8\) Hz, 1H), 5.59 (m, 2H), 4.55 - 4.40 (m, 2H), 3.90 (s, 3H), 3.84 (q, \(J = 7.1\) Hz, 1H), 3.68 (s, 6H), 3.36 (t, \(J = 7.6\) Hz, 1H), 2.63 - 2.54 (m, 2H), 1.57 (d, \(J = 7.2\) Hz, 3H).

\[^{13}C\] NMR (75 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) = 174.3 (C), 169.1 (2xC), 157.7 (C), 135.7 (C), 133.8 (C), 129.3 (CH), 129.0 (C), 127.3 (CH), 127.2 (CH), 126.3 (CH), 126.0 (CH), 119.1 (CH), 105.7 (CH), 64.8 (CH\(_{2}\)), 55.4 (CH\(_{3}\)), 52.5 (2xCH\(_{3}\)), 51.3 (CH), 45.8 (CH), 31.5 (CH\(_{2}\)), 18.6 (CH\(_{3}\)).

HRMS (EI, 70eV) m/z calcd. for C\(_{23}\)H\(_{26}\)O\(_{7}\) [M]\(^{+}\): 414.1679; found: 414.1681.

**Compound 5:** Methyl 4-bromocrotonate (193 mg, 1.08 mmol) was added to a mixture of NaH (43 mg, 1.08 mmol) and V (300 mg, 0.72 mmol) in DMF (15 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na\(_{2}\)SO\(_{4}\). The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give 5 (225 mg, 61%) as a colourless oil.

\[^{1}H\] NMR (300 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) = 7.66 (m, 2H), 7.41 (d, \(J = 1.8\) Hz, 1H), 7.38 (d, \(J = 1.8\) Hz, 1H), 7.14 (d, \(J = 2.4\) Hz, 1H), 7.11 (d, \(J = 2.2\) Hz, 1H), 6.71 (m, 1H), 5.78 (d, \(J = 15.5\) Hz, 1H), 5.66 - 5.41 (m, 2H), 4.50 (d, \(J = 5.7\) Hz, 2H), 3.90 (s, 3H), 3.85 (q, \(J = 7.1\) Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 2.63 (d, \(J = 6.9\) Hz, 2H), 2.58 (d, \(J = 6.8\) Hz, 2H), 1.57 (d, \(J = 7.2\) Hz, 3H).

\[^{13}C\] NMR (75 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) = 174.2 (C), 170.4 (2xC), 166.2 (C), 157.7 (C), 142.4 (CH), 135.6 (C), 133.7 (C), 129.3 (CH), 129.1 (CH), 128.9 (C), 128.3 (CH), 127.2 (CH), 126.3 (CH), 126.0 (CH), 119.1 (CH), 105.7 (CH), 64.6 (CH\(_{2}\)), 55.4 (CH\(_{3}\)), 52.5 (2xCH\(_{3}\)), 51.3 (CH), 45.8 (CH), 35.9 (CH\(_{2}\)), 35.4 (CH\(_{2}\)), 18.5 (CH\(_{3}\)).

HRMS (EI, 70eV) m/z calcd. for C\(_{28}\)H\(_{32}\)O\(_{9}\) [M]\(^{+}\): 512.2046; found: 512.2042.

**Synthesis of compound 6:**

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**Compound VI:** Tert-butylacrylate (0.192 g, 1.5 mmol) was added to a solution of Grubb's 2\(^{nd}\) generation catalyst (21 mg, 0.025 mmol) and allyldimethylmalonate (86 mg, 0.5 mmol) in CH\(_{2}\)Cl\(_{2}\) (5 ml) and the mixture was stirred under reflux for 24h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give VI (106 mg, 78 %) as a colourless oil.

\[^{1}H\]-NMR (400 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) = 6.71 (dt, \(J = 15.2, 7.1\) Hz, 1H), 5.77 (d, \(J = 15.6\) Hz, 1H), 3.71 (s, 6H), 3.47 (t, \(J = 7.4\) Hz, 1H), 2.73 (dd, \(J = 10.4, 4.0\) Hz, 2H), 1.43 (d, \(J = 6.3\) Hz, 9H).
\[ ^{13}C\text{-NMR} \ (101 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 168.8 \ (2\times C), \ 165.4 \ (C), \ 142.3 \ (\text{CH}), \ 125.7 \ (\text{CH}), \ 80.5 \ (C), \ 52.8 \ (2\times \text{CH}_3), \ 50.5 \ (\text{CH}), \ 31.0 \ (\text{CH}_2), \ 28.1 \ (3\times \text{CH}_3) \]

HRMS (EI, 70 eV) \( m/z \) calcd. for C\textsubscript{13}H\textsubscript{21}O\textsubscript{6} [M+1]\textsuperscript{+}: 273.1338; found: 273.1344.

**Compound 6:** A sample of (Z)-BrCH\textsubscript{2}CH=CHCH\textsubscript{2}CO\textsubscript{2}Et\textsuperscript{6} (120 mg, 0.54 mmol) was added to a mixture of NaH (22 mg, 0.54 mmol) and VI (98 mg, 0.36 mmol) in DMF (5 mL) at 0ºC. The resulting solution was stirred at room temperature for 16h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give 6 (132 mg, 89 %) as a colourless oil.

\[ ^{1}H\text{-NMR} \ (500 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 6.63 \ (\text{dtd, } J = 12.1, 7.7, 4.4 \text{ Hz, 1H}), \ 5.79 \ (\text{d, } J = 15.5 \text{ Hz, 1H}), \ 5.73 - 5.64 \ (\text{m, 1H}), \ 5.56 - 5.47 \ (\text{m, 1H}), \ 4.64 \ (\text{d, } J = 6.8 \text{ Hz, 2H}), \ 4.18 \ (\text{q, } J = 7.1 \text{ Hz, 2H}), \ 3.73 \ (\text{s, } J = 3.7 \text{ Hz, 6H}), \ 2.75 \ (\text{d, } J = 7.7 \text{ Hz, 2H}), \ 2.70 \ (\text{d, } J = 7.8 \text{ Hz, 2H}), \ 1.46 \ (\text{s, 9H}), \ 1.29 \ (\text{t, } J = 7.1 \text{ Hz, 3H}). \]

\[ ^{13}C\text{-NMR} \ (126 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 170.6 \ (2\times C), \ 165.2 \ (C), \ 155.2 \ (C), \ 140.7 \ (\text{CH}), \ 128.0 \ (\text{CH}), \ 127.5 \ (\text{CH}), \ 127.3 \ (\text{CH}), \ 80.6 \ (C), \ 64.2 \ (\text{CH}_2), \ 63.2 \ (\text{CH}_2), \ 57.3 \ (C), \ 52.9 \ (\text{CH}_3), \ 52.8 \ (\text{CH}_3), \ 35.7 \ (\text{CH}_2), \ 31.3 \ (\text{CH}_3), \ 28.2 \ (3\times \text{CH}_3), \ 14.4 \ (\text{CH}_3) \]

HRMS (EI, 70 eV) \( m/z \) calcd. for C\textsubscript{20}H\textsubscript{31}O\textsubscript{9} [M+1]\textsuperscript{+}: 415.1958; found: 415.1960.

**Synthesis of compound 7:**

Compound 7: Methyl vinyl ketone (0.43 g, 5.2 mmol) was added to a solution of the Grubb’s 2\textsuperscript{nd} generation catalyst ((210 mg, 0.25 mmol)) and the allyldimethylmalonate derivative VII (300 mg, 1.74 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL) and the mixture was stirred under reflux for 24h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give 7 (353 mg, 95 %) as a colourless oil.

\[ ^{1}H\text{-NMR} \ (500 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 6.68 - 6.58 \ (\text{m, 1H}), \ 6.09 \ (\text{d, } J = 15.9 \text{ Hz, 1H}), \ 5.73 - 5.59 \ (\text{m, 2H}), \ 4.55 \ (\text{d, } J = 5.6 \text{ Hz, 2H}), \ 4.19 \ (\text{q, } J = 7.1 \text{ Hz, 2H}), \ 3.73 \ (\text{s, 6H}), \ 2.75 \ (\text{dd, } J = 7.6, 0.9 \text{ Hz, 2H}), \ 2.66 \ (\text{d, } J = 6.6 \text{ Hz, 2H}), \ 2.23 \ (\text{s, 3H}), \ 1.30 \ (\text{t, } J = 7.1 \text{ Hz, 3H}). \]

\[ ^{13}C\text{-NMR} \ (126 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = 198.1 \ (C), \ 170.6 \ (2\times C), \ 155.1 \ (C), \ 141.4 \ (\text{CH}), \ 134.7 \ (\text{CH}), \ 129.3 \ (\text{CH}), \ 128.9 \ (\text{CH}), \ 67.6 \ (\text{CH}_2), \ 64.2 \ (\text{CH}_2), \ 57.5 \ (C), \ 52.9 \ (2\times \text{CH}_3), \ 36.4 \ (\text{CH}_2), \ 36.2 \ (\text{CH}_2), \ 27.2 \ (\text{CH}_3), \ 14.4 \ (\text{CH}_3) \]

HRMS (EI, 70 eV) \( m/z \) calcd. for C\textsubscript{14}H\textsubscript{18}O\textsubscript{5} [M-C\textsubscript{3}H\textsubscript{6}O\textsubscript{3}]\textsuperscript{+}: 266.1154; found: 266.1150.

**Synthesis of compound 8:**
Compound VIII: Butadiene monoxide (0.02 mL, 0.38 mmol) was added to a solution of the dimethylmalonate derivative I (100 mg, 0.38 mmol), Pd$_2$(dba)$_3$·dba (3 mg, 0.019 mmol) and dppe (8 mg, 0.019 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 16 h and then solvent was removed. The residue was filtered through a short silica pad to give VIII (71 mg, 54 %) as a colourless oil.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 5.77 – 5.49 (m, 4H), 4.54 (d, $J = 4.2$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 4.08 (d, $J = 5.6$ Hz, 2H), 3.71 (s, 6H), 2.64 (m, 4H), 1.30 (t, $J = 7.1$ Hz, 3H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ (ppm) = 171.2 (2xC), 155.2 (C), 134.6 (CH), 130.1 (CH), 128.4 (CH), 125.2 (CH), 67.8 (CH$_2$), 64.2 (CH$_2$), 63.1 (CH$_3$), 58.0 (C), 52.8 (CH$_2$), 52.7 (CH$_3$), 35.8 (CH$_2$), 35.7 (CH$_2$), 14.5 (CH$_3$).

HRMS (EI, 70 eV) $m/z$ calcd. for C$_{14}$H$_{21}$O$_6$ [M-CO$_2$Me]$^+$: 285.1338; found: 285.1341.

Compound 8: Dess-Martin periodinane (DMP) (148 mg, 0.35 mmol) was added to a solution of VIII (100 mg, 0.29 mmol) in CH$_2$Cl$_2$ (20 mL). The resulting mixture was stirred for 3 h at room temperature and then washed with saturated aqueous solution of Na$_2$S$_2$O$_3$ and NaHCO$_3$ in 1:1 proportion, dried over anhydrous Na$_2$SO$_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give a 8:1 mixture (84 mg, 85 %) of the Z- and E-isomers in the carbonate as a colourless oil. Data of the major isomer 8:

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 9.49 (d, $J = 7.8$ Hz, 1H), 6.77 – 6.65 (m, 1H), 6.13 (d, $J = 7.8$ Hz, 1H), 5.66 (dd, $J = 10.5$, 6.1 Hz, 2H), 4.54 (d, $J = 5.6$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.73 (s, 6H), 2.85 (d, $J = 7.4$ Hz, 2H), 2.67 (d, $J = 6.8$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) = 193.4 (C), 170.4 (2xC), 155.9 (C), 151.4 (CH), 136.1 (CH), 129.1 (CH), 129.0 (CH), 67.5 (CH$_2$), 64.2 (CH$_2$), 57.4 (C), 53.0 (CH$_3$), 52.9 (CH$_3$), 36.6 (CH$_2$), 36.3 (CH$_2$), 14.4 (CH$_3$).

HRMS (EI, 70 eV) $m/z$ calcd. for C$_{13}$H$_{17}$O$_5$ [M-OCO$_2$Et]$^+$: 253.1076; found: 253.1071.

Synthesis of compound 9:

In a round-bottom flask methyl 4-bromocrotonate (230 mg, 1.1 mmol), the tosyl amide derivative IX* (341 mg, 1 mmol), K$_2$CO$_3$ (152 mg, 1.1 mmol) and CH$_3$CN (10 mL) were placed. The resulting
mixture was stirred under reflux for 3 h. Then \( \text{K}_2\text{CO}_3 \) was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give 9 (298 mg, 68 %) as a colourless oil.

\(^1\text{H}-\text{NMR} \) (300 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.69 (dt, \( J = 8.3, 2.1 \) Hz, 2H), 7.30 (dd, \( J = 8.5, 2.5 \) Hz, 2H), 6.73 (dt, \( J = 15.6, 5.8 \) Hz, 1H), 5.93 (dt, \( J = 15.6, 1.7 \) Hz, 1H), 5.75 – 5.45 (m, 2H), 4.56 (dd, \( J = 7.0, 1.4 \) Hz, 2H), 4.23 – 4.12 (m, 2H), 3.91 (dd, \( J = 5.7, 1.7 \) Hz, 2H), 3.87 (d, \( J = 1.4 \) Hz, 2H), 3.71 (s, 3H), 2.42 (s, 3H), 1.28 (t, \( J = 7.1 \) Hz, 3H).

\(^{13}\text{C}-\text{NMR} \) (75 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 166.1 (C), 143.9 (C), 142.8 (C), 136.7 (C), 130.0 (2xCH), 129.9 (CH), 127.6 (CH), 127.4 (2xCH), 127.3 (CH), 123.7 (CH), 63.4 (CH\(_2\)), 62.5 (CH\(_2\)), 51.8 (CH\(_3\)), 48.2 (CH\(_2\)), 44.8 (CH\(_2\)), 21.6 (CH\(_3\)), 14.3 (CH\(_3\)).

HRMS (EI, 70 eV) \( m/z \) calcd. for C\(_{19}\)H\(_{26}\)NO\(_7\)S [M+1]: 412.1430; found: 412.1430.

**Synthesis of compound 10:**

**Compound X:** A sample of (Z)-BrCH\(_2\)CH=CHCH\(_2\)CO\(_2\)Et (1 g, 4.5 mmol) was added to a mixture of NaH (270 mg, 6.8 mmol) and N-Boc aniline (878 mg, 4.5 mmol) in DMF (20 mL) at 0\(^\circ\)C. The resulting solution was stirred at 60\(^\circ\)C for 15 h. Then the mixture was diluted with EtOAc, washed with HCl (10%), dried over anhydrous Na\(_2\)SO\(_4\), and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 1:9) to give X (1 g, 70 %) as a colorless oil.

\(^1\text{H}-\text{NMR} \) (300 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.34 – 7.28 (m, 2H), 7.24 – 7.16 (m, 3H), 5.99 – 5.85 (m, 1H), 5.80 – 5.64 (m, 1H), 4.62 (dd, \( J = 6.0, 1.0 \) Hz, 2H), 4.28 – 4.15 (m, 4H), 1.46 (s, 9H), 1.32 (t, \( J = 7.1 \) Hz, 3H).

\(^{13}\text{C}-\text{NMR} \) (75 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 155.2 (C), 154.6 (C), 142.9 (C), 131.7 (CH), 128.9 (3xCH), 126.7 (CH), 126.1 (CH), 125.9 (CH), 80.7 (C), 67.6 (CH\(_2\)), 64.2 (CH\(_2\)), 51.9 (CH\(_3\)), 28.5 (3xCH\(_3\)), 14.5 (CH\(_3\)).

HRMS (EI, 70 eV) \( m/z \) calcd. for C\(_{18}\)H\(_{25}\)NO\(_5\) [M]: 335.1733; found: 335.1733.

**Compound XI:** An excess of trifluoroacetic acid (TFA) was added to a solution of X (502 mg, 1.5 mmol) in CH\(_2\)Cl\(_2\) (15 mL). The resulting mixture was stirred at room temperature for 2h and then the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give XI (318 mg, 90%) as a colourless oil.
\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.21 – 7.15 (m, 2H), 6.72 (t, \(J = 7.3\) Hz, 1H), 6.61 (d, \(J = 7.8\) Hz, 2H), 5.98 – 5.90 (m, 1H), 5.89 – 5.80 (m, 1H), 4.62 (d, \(J = 5.9\) Hz, 2H), 4.20 (q, \(J = 7.1\) Hz, 2H), 3.79 (d, \(J = 5.1\) Hz, 2H), 1.31 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 155.1 (C), 132.8 (CH), 129.3 (2xCH), 128.8 (C), 125.3 (CH), 117.8 (CH), 113.1 (2xCH), 67.6 (CH\(_2\)), 64.1 (CH\(_2\)), 45.3 (CH\(_2\)), 14.4 (CH\(_3\)).

HRMS (EI, 70 eV) \(m/z\) calcd. for C\(_{13}\)H\(_{17}\)NO\(_3\) [M]\(^+\): 235.1208; found: 235.1210

**Compound 10:** Methyl 4-bromocrotonate (314mg, 1.5 mmol) was added to a mixture of NaH (60 mg, 1.5 mmol) and XI (235 mg, 1 mmol) in DMF (10 mL) at 0°C. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na\(_2\)SO\(_4\). The residue was submitted to flash chromatography (EtOAc: Hexane, 4:6) to give 10 (111 mg, 33 %) as a colourless oil.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.21 (t, \(J = 7.2\) Hz, 2H), 6.97 (d, \(J = 14.4\) Hz, 1H), 6.74 (t, \(J = 7.2\) Hz, 1H), 6.67 (d, \(J = 7.8\) Hz, 2H), 5.96 (d, \(J = 16.2\) Hz, 1H), 5.80 – 5.68 (m, 2H), 4.72 (d, \(J = 3.7\) Hz, 2H), 4.26 – 4.18 (m, 2H), 4.08 – 4.01 (m, 4H), 3.72 (s, 3H), 1.32 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 166.7 (C), 155.2 (C), 144.9 (C), 132.1 (CH), 129.5 (3xCH), 125.8 (CH), 121.9 (CH), 117.6 (CH), 112.9 (2xCH), 64.3 (CH\(_2\)), 63.0 (CH\(_2\)), 51.9 (CH\(_2\)), 51.7 (CH\(_2\)), 48.0 (CH\(_2\)), 14.4 (CH\(_3\)).

HRMS (EI, 70 eV) \(m/z\) calcd. for C\(_{18}\)H\(_{23}\)NO\(_5\) [M]\(^+\): 333.1576; found: 335.1575.

**Synthesis of compound 11:**

**Compound XII:** In a round-bottom flask methyl 4-bromocrotonate (230mg, 1.1 mmol), bis(phenylsulfonyl)methane (296 mg, 1 mmol), K\(_2\)CO\(_3\) (152 mg, 1.1 mmol) and CH\(_3\)CN (10 mL) were placed. The resulting mixture was stirred under reflux for 3 h. Then K\(_2\)CO\(_3\) was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 3:7) to give XII (276mg, 70 %) as a colourless oil.
$^1$H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.85 (d, $J = 7.4$ Hz, 4H), 7.61 (t, $J = 7.3$ Hz, 2H), 7.49 (t, $J = 7.5$ Hz, 4H), 6.71 (dt, $J = 14.3, 7.0$ Hz, 1H), 5.69 (d, $J = 15.5$ Hz, 1H), 4.53 (t, $J = 5.9$ Hz, 1H), 3.61 (s, 3H), 3.00 (t, $J = 6.4$ Hz, 2H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ (ppm) = 165.9 (C), 141.7 (CH), 137.6 (2xC), 134.9 (2xCH), 129.7 (4xCH), 129.3 (4xCH), 124.4 (CH), 82.3 (CH), 51.7 (CH$_3$), 28.3 (CH$_2$).

HRMS (EI, 70 eV) $m/z$ calcd. for C$_{18}$H$_{18}$O$_6$S$_2$ [M$^+$]: 394.0545; found: 394.0537.

**Compound XIII:** Butadiene monoxide (35mg, 0.5mmol) was added to a solution of XII (197mg, 0.5mmol), Pd$_2$(dba)$_3$·dba (4mg, 0.025mmol) and dppe (10mg, 0.025mmol) in THF (10mL). The resulting mixture was stirred at room temperature for 16 h and then solvent was removed. The residue was filtered through a short silica pad to give XIII (47mg, 63%) as a white foam.

$^1$H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.95 (d, $J = 7.8$ Hz, 4H), 7.64 (t, $J = 7.4$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 4H), 7.00 – 6.89 (m, 1H), 5.80 (d, $J = 15.7$ Hz, 1H), 5.74 (t, $J = 6.5$ Hz, 1H), 5.68 (dd, $J = 9.5, 4.7$ Hz, 1H), 4.00 (d, $J = 4.6$ Hz, 2H), 3.64 (s, 3H), 3.04 (d, $J = 6.9$ Hz, 2H), 2.94 (d, $J = 6.2$ Hz, 2H), 2.18 (s, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ (ppm) = 166.0 (C), 140.3 (CH), 136.4 (2xC), 136.2 (CH), 135.0 (2xCH), 131.5 (4xCH), 128.8 (4xCH), 125.5 (CH), 122.3 (CH), 89.6 (C), 62.8 (CH$_2$), 51.8 (CH$_3$), 32.9 (CH$_2$), 32.4 (CH$_2$).

HRMS (EI, 70 eV) $m/z$ calcd. for C$_{22}$H$_{25}$O$_7$S$_2$ [M$^+$]: 465.1042; found: 465.1044.

**Compound 11:** Ethyl chloroformiate (31 mg, 0.29 mmol) was added to a solution of XIII (122 mg, 0.26 mmol), dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol), pyridine (62 mg, 0.8 mmol) in CH$_2$Cl$_2$ (5 mL), and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH$_2$Cl$_2$, washed with HCl (10%), NaOH (10%) and brine and dried over anhydrous Na$_2$SO$_4$. The residue was submitted to flash chromatography (EtOAc: Hexane, 4:6) to give 11 (85 mg, 55%) as a colorless foam.

$^1$H-NMR (500 MHz, CDCl$_3$): δ (ppm) = 8.03 (d, $J = 8.3$ Hz, 4H), 7.72 (t, $J = 7.1$ Hz, 2H), 7.60 (t, $J = 7.8$ Hz, 4H), 7.05 – 6.95 (m, 1H), 5.98 – 5.90 (m, 1H), 5.88 (d, $J = 15.5$ Hz, 1H), 5.75 – 5.67 (m, 1H), 4.55 (d, $J = 6.1$ Hz, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.73 (s, 3H), 3.11 (d, $J = 6.9$ Hz, 2H), 3.02 (d, $J = 6.7$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ (ppm) = 165.8 (C), 155.0 (C), 139.9 (CH), 136.5 (2xC), 135.1 (2xCH), 131.7 (4xCH), 130.4 (CH), 128.9 (4xCH), 126.7 (CH), 125.9 (CH), 89.6 (C), 67.3 (CH$_2$), 64.3 (CH$_2$), 51.8 (CH$_3$), 33.1 (CH$_3$), 32.6 (CH$_2$), 14.4 (CH$_2$).

HRMS (EI, 70 eV) $m/z$ calcd. for C$_{25}$H$_{28}$O$_9$S$_2$ [M$^+$]: 536.1175; found: 536.1176.

_Synthesis of compound 12:_

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**Compound XIV:** Isoprene monoxide (191 mg, 2.27 mmol) was added to a solution dimethylmalonate (300 mg, 2.27 mmol), Pd$_2$(dba)$_3$-dba (20 mg, 0.11 mmol) and dppe (44 mg, 0.11 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 3 h and then solvent was removed. The residue was filtered through a short silica pad to give XIV (476 mg, 97%) as colourless oil. Its spectroscopic data were identical to the reported compound.

**Compound XV:** Ethyl chloroformiate (285 mg, 2.64 mmol) was added to a solution of II (476 mg, 2.20 mmol), dimethylaminopyridine (DMAP) (81 mg, 0.66 mmol), pyridine (521 mg, 6.6 mmol) in CH$_2$Cl$_2$, and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH$_2$Cl$_2$, washed with HCl (10%), NaOH (10%) and brine and dried over anhydrous Na$_2$SO$_4$. The residue was submitted to flash chromatography (EtOAc:Hexane, 4:6) to give XV (628 mg, 99%) as a colourless oil. Its spectroscopic data were identical to the reported compound.

**Compound 12:** Methyl 4-bromocrotonate (585 mg, 3.27 mmol) was added to a mixture of NaH (131 mg, 3.27 mmol) and XV (628 mg, 2.18 mmol) in DMF (15 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na$_2$SO$_4$. The residue was submitted to flash chromatography (EtOAc:Hexane, 4:6) to give 12 (513 mg, 61%, 3:2 mixture of isomers) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) = 6.81 - 6.73 (m, 2H), 5.87 (dd, $J$ = 3.9, 2.5 Hz, 1H, major isomer), 5.84 (dd, $J$ = 3.9, 2.5 Hz, 1H, minor isomer), 5.33 (dd, $J$ = 8.1, 6.8 Hz, 1H, minor isomer), 5.25 (dd, $J$ = 8.1, 6.8 Hz, 1H, major isomer), 4.59 (s, 2H, major isomer), 4.48 (s, 2H, minor isomer), 4.20 (q, $J$ = 7.1 Hz, 4H), 3.73 (s, 12H), 3.71 (s, 6H), 2.76 (d, $J$ = 7.7 Hz, 4H), 2.70 (d, $J$ = 7.8 Hz, 2H, major isomer), 2.66 (d, $J$ = 7.1 Hz, 2H, minor isomer), 1.78 (s, 3H, major isomer), 1.67 (s, 3H, minor isomer), 1.31 (t, $J$ = 7.1 Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ (ppm) = 170.8 (2xC), 166.3 (C), 155.3 (C), 142.7 (CH), 134.4 (C), 125.0 (CH), 123.6 (CH, major isomer), 122.5 (CH, minor isomer), 72.9 (CH$_2$), 65.9 (CH$_2$, major isomer), 64.2 (CH$_2$, minor isomer), 57.5 (C), 52.9 (2xCH$_3$), 51.7 (CH$_3$), 35.7(CH$_2$), 31.6 (CH$_3$), 21.7 (CH$_3$), 14.4 (CH$_3$).

HRMS (EI, 70eV) m/z calcd. for C$_{18}$H$_{26}$O$_9$ [M]: 386.1577; found: 386.1581.
Synthesis of compound 13:

**Compound XVI:** In a round-bottom flask dimethylmalonate (660 mg, 5 mmol), K$_2$CO$_3$ (760 mg, 5.5 mmol), trans-4-acetoxy-1-bromo-2-methyl-2-butene$^7$ (1.13 g, 5.5 mmol), and CH$_3$CN (15 mL) were placed. The resulting mixture was stirred under reflux for 16 h. Then K$_2$CO$_3$ was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give XVI (894 mg, 69%) as a colourless oil.

$^1$H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 5.34 (t, $J = 6.3$ Hz, 1H), 4.50 (d, $J = 6.9$ Hz, 2H), 3.69 (s, 6H), 3.55 (t, $J = 7.9$ Hz, 1H), 2.60 (d, $J = 7.7$ Hz, 2H), 1.99 (s, 3H), 1.68 (s, 3H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ (ppm) = 170.9 (C), 169.3 (2xC), 137.6 (C), 121.4 (CH), 60.9 (CH$_2$), 52.6 (2xCH$_3$), 50.3 (CH), 38.3 (CH$_2$), 21.0 (CH$_3$), 16.3 (CH$_3$).

A good quality mass spectra could not be obtained.

**Compound 13:** Methyl 4-bromocrotonate (107 mg, 0.6 mmol) was added to a mixture of NaH (30 mg, 0.75 mmol) and XVI (125 mg, 0.5 mmol) in DMF (5 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with aqueous NH$_4$Cl, dried over anhydrous Na$_2$SO$_4$, and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give 13 (90 mg, 50%) as a colourless oil.

$^1$H-NMR (500 MHz, CDCl$_3$): δ (ppm) = 6.78 (tt, $J = 15.4, 7.6$ Hz, 1H), 5.87 (t, $J = 15.9$ Hz, 1H), 5.43 – 5.33 (m, 1H), 4.55 (d, $J = 6.8$ Hz, 2H), 3.72 (s, 6H), 3.72 (s, 3H), 2.75 (dd, $J = 7.6, 1.2$ Hz, 2H), 2.72 (d, $J = 6.0$ Hz, 2H), 2.04 (s, 3H), 1.62 (s, 3H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ (ppm) = 171.0 (2xC), 166.3 (C), 142.9 (CH), 136.0 (C), 125.0 (CH), 124.9 (CH), 124.2 (C), 61.0 (CH$_2$), 57.3 (C), 52.8 (2xCH$_3$), 51.7 (CH$_3$), 42.8 (CH$_2$), 35.7 (CH$_2$), 21.0 (CH$_3$), 17.2 (CH$_3$).

HRMS (EI, 70 eV) m/z calcd. for C$_{17}$H$_{24}$O$_8$ [M]: 356.1471; found: 356.1462.
Synthesis of compound 14:

Compound XVII: Isoprene monoxide (0.04 mL, 0.38 mmol) was added to a solution of the dimethylmalonate derivative (Z)-I (100 mg, 0.038 mmol), Pd$_2$(dba)$_3$·dba (6 mg, 0.1 mmol) and dppe (16 mg, 0.038 mmol) in THF (10 mL) and the mixture was stirred at room temperature for 16 h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane) to give XVII (105 mg, 79%) as a colourless oil.

$^1$H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 5.74 – 5.58 (m, 2H), 5.11 (t, $J$ = 8.3 Hz, 1H), 4.53 (d, $J$ = 4.8 Hz, 2H), 4.17 (q, $J$ = 7.2 Hz, 2H), 4.07 (d, $J$ = 2.3 Hz, 2H), 3.71 (s, 6H), 2.68 – 2.56 (m, 4H), 1.79 (s, 3H), 1.30 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ (ppm) = 171.3 (C), 154.9 (C), 139 (C), 129.9 (CH), 128.1 (CH), 120.5 (CH), 120.4 (CH), 67.6 (CH$_2$), 64.0 (CH$_2$), 61.2 (CH$_3$), 57.8 (C), 52.6 (CH$_3$), 52.6 (CH$_3$), 35.8 (CH$_3$), 31.0 (CH$_2$), 21.7 (CH$_3$), 14.2 (CH$_3$).

HRMS (EI, 70 eV) m/z calcd. for C$_{14}$H$_{21}$O$_5$ [M-OCO$_2$Et]$^+$: 269.1389; found: 269.1361.

Compound XVIII: Dess-Martin periodinane (DMP) (77 mg, 0.17 mmol) was added to a solution of XVII (29 mg, 0.08 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting mixture was stirred for 3 h at room temperature and then washed with saturated aqueous solution of Na$_2$S$_2$O$_3$ and NaHCO$_3$ in 1:1 proportion, dried over anhydrous Na$_2$SO$_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane) to give XVIII (20 mg, 69%) as a colourless oil.

$^1$H-NMR (500 MHz, CDCl$_3$): δ (ppm) = 9.39 (s, 1H), 6.35 (t, $J$ = 7.3 Hz, 1H), 5.66 (m, 2H), 4.54 (d, $J$ = 4.7 Hz, 2H), 4.18 (q, $J$ = 7.1 Hz, 2H), 3.74 (s, 6H), 2.90 (d, $J$ = 5.8 Hz, 2H), 2.69 (d, $J$ = 5.8 Hz, 2H), 1.74 (s, 3H), 1.29 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ (ppm) = 193.4 (CH), 170.4 (2xC), 155.0 (C), 151.4 (CH), 136.1 (CH), 129.1 (CH), 129.0 (CH), 67.5 (CH$_3$), 64.2 (CH$_2$), 57.4 (C), 52.9 (2xCH$_3$), 36.6 (CH$_3$), 36.3 (CH$_3$), 29.8 (CH$_3$), 14.4 (CH$_3$).

HRMS (EI, 70 eV) m/z calcd. for C$_{15}$H$_{21}$O$_6$ [M-CO$_2$Me]$^+$: 297.1338; found: 297.1347.

S16
**Compound 14:** Sodium chlorite (660 mg, 7.25 mmol) and potassium dihydrogen phosphate (720 mg, 5.28 mmol) were added to a solution of XVIII (190 mg, 0.55 mmol) in water (4 mL) and t-butanol (10 mL). The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with diethyl ether, washed with water, dried over anhydrous Na$_2$SO$_4$, and the solvent removed. In a separated flask equipped with a magnetic stir bar, a solution of iodine (183 mg, 1.05 mmol) in dry CH$_2$Cl$_2$ (10 mL) and triphenylphosphine (275 mg, 1.5 mmol) was prepared. Then, imidazole (160 mg, 3.3 mmol) was added and a white solid appeared. Subsequently, the carboxylic acid without further purification (160 mg, 0.7 mmol) and dissolved in dry CH$_2$Cl$_2$ (5 mL) was added and then dry MeOH (1 mL). The resulting mixture was stirred at room temperature for 16 h. Then the mixture was diluted with CH$_2$Cl$_2$, washed with 2 N HCl, dried over anhydrous Na$_2$SO$_4$, and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane,) to give 14 (148 mg, 70%) as a colourless oil.

$^1$H-NMR (500 MHz, CDCl$_3$): δ (ppm) = 6.53 (t, J = 7.4 Hz, 1H), 5.70 – 5.62 (m, 1H), 5.51 – 5.43 (m, 1H), 4.58 (d, J = 6.8 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.68 (s, 6H), 3.67 (s, 3H), 2.73 (d, J = 7.5 Hz, 2H), 2.68 (d, J = 7.7 Hz, 2H), 1.78 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ (ppm) = 170.7 (2xC), 167.9 (C), 155.0 (C), 134.8 (CH), 131.1 (C), 128.0 (CH), 127.4 (CH), 64.0 (CH$_2$), 63.0 (CH$_2$), 57.1 (C), 52.8 (2xCH$_3$), 51.9 (CH$_3$), 32.0 (CH$_3$), 31.2 (CH$_3$), 14.3 (CH$_3$), 12.6 (CH$_3$).

HRMS (EI, 70 eV) m/z calcd. for C$_{18}$H$_{26}$O$_9$ [M]$^+$: 386.1577; found: 386.1575.

**Synthesis of compound 15:**

![Synthesis of compound 15](image)

**Compound XX:** Carbonate XIX (590 mg, 3.79 mmol) was added to a solution of dimethylmalonate (500 mg, 2.27 mmol), Pd$_2$(dba)$_3$·dba (33 mg, 0.19 mmol) and dppe (75 mg, 0.19 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 3 h and then solvent was removed. The
Residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give XX (549 mg, 73%) as a colourless oil.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta (ppm) = 6.34 - 6.20 (m, 1H), 6.17 - 6.01 (m, 1H), 5.62 (dt, J = 14.9, 7.3 Hz, 1H), 5.13 (dd, J = 16.7, 1.6 Hz, 1H), 5.02 (dd, J = 10.1, 1.6 Hz, 1H), 3.73 (s, 6H), 3.44 (t, \(J = 7.6\) Hz, 1H), 2.66 (dd, \(J = 13.8, 7.4\) Hz, 2H).

\(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta (ppm) = 169.7 (2\times C), 137.0 (CH), 134.3 (CH), 129.8 (CH), 117.1 (CH\(_2\)), 53.0 (2\times CH\(_3\)), 52.1 (CH), 32.3 (CH\(_2\)).

LRMS (EI, 70 eV) \(m/\text{z} \text{calcd. for } C_{6}H_{9}O_{4} [M-C_{4}H_{5}]^+: 145.05; \text{found: 145.03. A good HRMS could not be obtained.}

**Compound XXI:** Butadiene monoxide (176 mg, 2.52 mmol) was added to a solution of compound XX (500 mg, 2.52 mmol), Pd\(_2\)(dba)\(_3\)·dba (22 mg, 0.13 mmol) and dppe (50 mg, 0.13 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 16 h and then solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 4:6) to give XXI (506 mg, 75%) as a colourless oil.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta (ppm) = 6.26 (dt, J = 17.0, 10.3 Hz, 1H), 6.12 - 6.03 (m, 1H), 5.75 - 5.64 (m, 1H), 5.51 (ddt, J = 18.1, 15.2, 7.5 Hz, 2H), 5.12 (dd, J = 16.6, 4.5 Hz, 1H), 5.02 (dd, J = 9.9, 5.3 Hz, 1H), 4.07 (d, \(J = 5.4\) Hz, 2H), 3.70 (s, 6H), 2.64 (m, 4H).

\(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta (ppm) = 171.1 (2\times C), 136.5 (CH), 135.2 (CH), 134.0 (CH), 127.6 (CH), 125.8 (CH), 116.6 (CH\(_2\)), 63.2 (CH\(_2\)), 58.0 (C), 52.4 (2\times CH\(_3\)), 35.9 (CH\(_3\)), 35.6 (CH\(_3\)).

LRMS (EI, 70 eV) \(m/\text{z} \text{calcd. for } C_{6}H_{9}O_{4} [M-C_{6}H_{11}O]^+: 145.05; \text{found: 145.04. A good HRMS could not be obtained.}

**Compound XXII:** Ethyl chloroformiate (245 mg, 2.27 mmol) was added to a solution of XXI (506 mg, 1.89 mmol), dimethylaminopyridine (DMAP) (70 mg, 0.57 mmol) and pyridine (448 mg, 5.67 mmol) in CH\(_2\)Cl\(_2\), and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH\(_2\)Cl\(_2\), washed with HCl (10%), NaOH (10%) and brine and dried over anhydrous Na\(_2\)SO\(_4\). The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give XXII (513 mg, 80%) as a colourless oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta (ppm) = 6.23 (dt, J = 16.9, 10.2 Hz, 1H), 6.03 (dd, J = 14.6, 10.7 Hz, 1H), 5.65 - 5.58 (m, 2H), 5.44 (dt, J = 15.1, 7.6 Hz, 1H), 5.09 (d, J = 16.8 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.55 - 4.42 (m, 2H), 4.15 (q, \(J = 7.2\) Hz, 2H), 3.67 (s, 6H), 2.63 - 2.55 (m, 4H), 1.26 (t, \(J = 7.1\) Hz, 3H).

\(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta (ppm) = 171.5 (2\times C), 155.5 (C), 137.1 (CH), 135.9 (CH), 130.5 (CH), 128.8 (CH), 128.1 (CH), 117.2 (CH\(_2\)), 68.2 (CH\(_3\)), 64.6 (CH\(_3\)), 58.4 (C), 53.0 (2\times CH\(_3\)), 36.6 (CH\(_3\)), 36.3 (CH\(_3\)), 14.9 (CH\(_3\)).

HRMS (EI, 70eV) \(m/\text{z} \text{calcd. for } C_{17}H_{24}O_{7} [M]^+: 340.1522; \text{found: 340.1527}

S18
**Compound 15:** Methylacrilate (163 mg, 1.90 mmol) was added to a deoxygenated solution of Grubb's 2nd generation catalyst (11 mg, 0.03 mmol) and compound XXII (215 mg, 0.63 mmol) in dry CH$_2$Cl$_2$ (2 mL). The resulting mixture was refluxed for 16 hours and the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 10:1 mixture (120 mg, 48%) of the E- and Z-isomers in the carbonate as a colourless oil. Data of the major isomer 15:

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.20 (dd, $J$ = 15.4, 11.0 Hz, 1H), 6.24 - 6.10 (m, 1H), 5.98 - 5.86 (m, 1H), 5.81 (d, $J$ = 15.4 Hz, 1H), 5.70 - 5.57 (m, 2H), 4.53 (d, $J$ = 4.9 Hz, 2H), 4.18 (q, $J$ = 7.1 Hz, 2H), 3.72 (s, 3H), 3.70 (s, 6H), 2.72 - 2.68 (m, 2H), 2.67 - 2.54 (m, 2H), 1.29 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) = 170.8 (2xC), 167.5 (C), 155.1 (C), 144.1 (CH), 137.0 (CH), 132.4 (CH), 129.7 (CH), 128.7 (CH), 120.8 (CH), 67.7 (CH$_2$), 64.2 (CH$_2$), 57.8 (C), 52.8 (2xCH$_3$), 51.7 (CH$_3$), 36.7 (CH$_2$), 36.2 (CH$_2$), 14.5 (CH$_3$).

HRMS (EI, 70eV) $m/z$ calcd. for C$_{19}$H$_{26}$O$_9$ [M]: 398.1577; found: 398.1566.

**Synthesis of compound 16:**

![Chemical Structure](image)

**Compound 16:** Methylvinylketone (185 mg, 2.65 mmol) was added to a deoxygenated solution of Grubb's 2nd generation catalyst (15 mg, 0.05 mmol) and compound XXII (300 mg, 0.88 mmol) in dry CH$_2$Cl$_2$ (2 mL). The resulting mixture was refluxed for 16 hours and the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 5:1 mixture (100 mg, 30%) of the E- and Z-isomers in the carbonate as a colourless oil. Data of the major isomer 16:

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.02 (dd, $J$ = 15.7, 10.7 Hz, 1H), 6.25 - 6.12 (m, 1H), 6.03 (d, $J$ = 15.7 Hz, 1H), 6.03 - 5.91 (m, 1H), 5.65 - 5.59 (m, 2H), 4.52 (d, $J$ = 4.9 Hz, 2H), 4.16 (q, $J$ = 7.1 Hz, 2H), 3.69 (s, 6H), 2.74 - 2.65 (m, 2H), 2.65 - 2.57 (m, 2H), 2.23 (s, 3H), 1.27 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) = 198.9 (C), 171.0 (2xC), 155.3 (C), 143.0 (CH), 138.0 (CH), 133.1 (CH), 130.6 (CH), 129.8 (CH), 128.9 (CH), 67.9 (CH$_2$), 64.4 (CH$_2$), 58.0 (C), 53.0 (2xCH$_3$), 37.0 (CH$_3$), 36.4 (CH$_2$), 27.5 (CH$_3$), 14.7 (CH$_3$).

HRMS (EI, 70eV) $m/z$ calcd. for C$_{19}$H$_{26}$O$_8$ [M]: 382.1628; found: 382.1624.
**Synthesis of compound 17:**

![Chemical structure diagram](image)

**Compound XXIII and XXIV:** AlLiH₄ (489 mg, 13.23 mmol) was added to a solution of compound XXII (300 mg, 0.88 mmol) in THF (20 mL). The mixture was stirred at room temperature for 24 h. Then the mixture was diluted with EtOAc, washed with H₂O, dried over anhydrous Na₂SO₄, and the solvent removed. The mixture was filtered through a short silica pad. The crude was diluted in CH₂Cl₂ (15 mL) and DMAP (313 mg, 2.56 mmol) and benzoyl chloride (360 mg, 2.56 mmol) was added. The mixture was stirred at room temperature for 16 h and then the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give XXIV (113 mg, 25%) as a viscous liquid.

**¹H NMR** (500 MHz, CDCl₃): δ (ppm) = 8.04 - 7.98 (m, 6H), 7.57 - 7.49 (m, 3H), 7.46 - 7.37 (m, 6H), 6.30 (dt, J = 17.0, 10.2 Hz, 1H), 6.14 (ddd, J = 15.2, 12.3, 7.3 Hz, 1H), 6.02 - 5.88 (m, 1H), 5.88 - 5.68 (m, 2H), 5.08 (d, J = 16.9 Hz, 1H), 5.00 (d, J = 10.1 Hz, 1H), 4.76 (d, J = 6.1 Hz, 2H), 4.33 (s, 4H), 2.37 (d, J = 7.6 Hz, 4H).

**¹³C NMR** (126 MHz, CDCl₃): δ (ppm) = 166.3 (3xC), 136.6 (CH), 135.5 (CH), 133.3 (3xCH), 133.0 (CH), 130.7 (CH), 130.0 (3xC), 129.7 (6xCH), 128.6 (6xCH), 128.0 (CH), 116.6 (CH₂), 66.9 (2xCH₂), 65.2 (CH₂), 41.6 (C), 36.0 (CH₂), 35.8 (CH₂).

**HRMS** (EI, 70 eV) m/z calcd. for C₃₃H₃₂O₆ [M⁺]: 524.2199; found: 524.2188.

**Compound 17:** Methyacrylate (46 mg, 0.53 mmol) was added to a deoxygenated solution of Grubb’s 2nd generation catalyst (4 mg, 0.05 mmol) and compound XXIV (93 mg, 0.18 mmol) in dry CH₂Cl₂ (2 mL). The resulting mixture was refluxed for 24 hours and the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 5:1 mixture (43 mg, 42%) of the E- and Z- isomers in the benzoate as a colourless oil. Data of the major compound 17:

**¹H NMR** (300 MHz, CDCl₃): δ (ppm) = 8.01 (d, J = 7.1 Hz, 6H), 7.60 - 7.51 (m, 3H), 7.43 (t, J = 7.5 Hz, 6H), 7.28 - 7.18 (m, 1H), 6.25 - 6.17 (m, 2H), 5.95 - 5.87 (m, 1H), 5.86 - 5.79 (m, 1H), 5.76 (d, J = 15.5 Hz, 1H), 4.77 (d, J = 5.7 Hz, 2H), 4.35 (s, 4H), 3.73 (s, 3H), 2.45 (d, J = 6.6 Hz, 2H), 2.38 (d, J = 7.1 Hz, 2H).
Synthesis of compound 18:

Ethyl (2-bromomethyl)acrylate (212 mg, 1.1 mmol) was added to a mixture of NaH (44 mg, 1.1 mmol) and \((Z)\)-I (274 mg, 1 mmol) in DMF (10 mL) at 0°C. The resulting solution was stirred at room temperature for 24 h. Then the mixture was diluted with EtOAc, washed with aqueous NH\(_4\)Cl, dried over anhydrous \(\text{Na}_2\text{SO}_4\), and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give 18 (211 mg, 52%) as a colourless oil.

\(^1\text{H}-\text{NMR}\) (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 6.26 (d, \(J = 1.2\) Hz, 1H), 5.68 (dt, \(J = 13.4, 6.7\) Hz, 1H), 5.61 (s, 1H), 5.63 – 5.56 (m, 1H), 4.64 (d, \(J = 6.6\) Hz, 2H), 4.171 (q, \(J = 7.1\) Hz, 2H), 4.166 (q, \(J = 7.1\) Hz, 2H), 3.69 (s, 6H), 2.97 (d, \(J = 11.9\) Hz, 2H), 2.64 (d, \(J = 7.3\) Hz, 2H), 1.29 (t, \(J = 7.1\) Hz, 3H), 1.27 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\text{C}-\text{NMR}\) (126 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 170.9 (2xC), 166.9 (C), 155.2 (C), 136.1 (C), 129.1 (CH\(_2\)), 128.5 (CH), 127.0 (CH), 64.1 (CH\(_2\)), 63.3 (CH\(_2\)), 61.1 (CH\(_2\)), 57.8 (C), 52.6 (2xCH\(_2\)), 34.2 (CH\(_2\)), 31.1 (CH\(_2\)), 14.4 (CH\(_3\)), 14.3 (CH\(_3\)).

HRMS (EI, 70 eV) \(m/z\) calcd. for C\(_{18}\)H\(_{26}\)O\(_9\) [M]: 386.1577; found: 386.1577

Synthesis of compound 19:

\textbf{Compound XXV:} In a round-bottom flask ethyl (2-bromomethyl)acrylate (213 mg, 1.1 mmol), bis(phenylsulfonfyl)methane (296 mg, 1 mmol), K\(_2\text{CO}_3\) (152 mg, 1.1 mmol) and CH\(_3\)CN (10 mL) were
placed. The resulting mixture was stirred under reflux for 5 h. Then K₂CO₃ was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 3:7) to give XXV (320 mg, 79%) as a colourless oil.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.97 – 7.85 (m, 4H), 7.68 (t, J = 7.4 Hz, 2H), 7.55 (t, J = 7.6 Hz, 4H), 6.24 (s, 1H), 5.73 (s, 1H), 5.32 (t, J = 7.0 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.18 (d, J = 7.0 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 138.4 (C), 134.6 (2xCH), 134.1 (C), 132.0 (C), 129.70 (CH₂), 129.67 (4xCH), 129.2 (4xCH), 128.7 (C), 81.2 (CH), 61.2 (CH₂), 29.6 (CH₂), 14.2 (CH₃).

HRMS (EI, 70 eV) m/z calcd. for C₁₉H₂₀O₆S₂ [M⁺]: 408.0701; found: 408.0703.

Compound XXVI: Butadiene monoxide (53 mg, 0.75 mmol) was added to a solution of XXV (306 mg, 0.75 mmol), Pd₂(dba)₃ · dba (6 mg, 0.0375 mmol) and dppe (15 mg, 0.0375 mmol) in THF (10 mL) and the mixture was stirred at room temperature for 16 h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane, 4:6) to give XXVI (230 mg, 64%) as a colourless oil.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 6.26 (d, J = 1.2 Hz, 1H), 5.68 (dt, J = 13.4, 6.7 Hz, 1H), 5.61 (s, 1H), 5.63 – 5.56 (m, 1H), 4.64 (d, J = 6.6 Hz, 2H), 4.171 (q, J = 7.1 Hz, 2H), 4.166 (q, J = 7.1 Hz, 2H), 3.69 (s, 6H), 2.97 (d, J = 11.9 Hz, 2H), 2.64 (d, J = 7.3 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ (ppm) = 167.4 (C), 137.3 (2xC), 134.8 (2xCH), 133.7 (C), 132.7 (CH₂), 131.8 (4xCH), 128.8 (4xCH), 124.5 (CH), 90.8 (C), 63.2 (CH₂), 61.5 (CH), 33.7 (CH₂), 31.6 (CH₂), 14.1 (CH₃).

HRMS (EI, 70 eV) m/z calcd. for C₂₃H₂₆O₇S₂ [M⁺]: 478.1120; found: 478.1119.

Compound 19: Ethyl chloroformiate (52 mg, 0.48 mmol) was added to a solution of XXVI (208 mg, 0.44 mmol), dimethylaminopyridine (DMAP) (16 mg, 0.13 mmol), pyridine (103 mg, 1.3 mmol) in CH₂Cl₂ (10 mL), and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH₂Cl₂, washed with saturated NH₄Cl and dried over anhydrous Na₂SO₄. The residue was submitted to flash chromatography (EtOAc: Hexane, 3:7) to give 32 (110 mg, 49%) as a colourless oil.

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 8.04 (d, J = 7.9 Hz, 4H), 7.71 (t, J = 7.4 Hz, 2H), 7.58 (t, J = 7.8 Hz, 4H), 6.46 (s, 1H), 6.12 (s, 1H), 6.02 – 5.94 (m, 1H), 5.68 – 5.60 (m, 1H), 4.49 (d, J = 6.3 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.38 (s, 2H), 3.00 (d, J = 6.4 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H).

¹³C-NMR (126 MHz, CDCl₃): δ (ppm) = 167.1 (C), 155.1 (C), 137.4 (2xC), 134.8 (2xCH), 133.5 (C), 132.6 (CH₂), 131.9 (4xCH), 128.8 (4xCH), 128.7 (CH), 128.6 (CH), 90.7 (C), 67.7 (CH₂), 64.2 (CH₂), 61.4 (CH₂), 33.9 (CH₂), 31.9 (CH₂), 14.4 (CH₂), 14.2 (CH₃).

HRMS (EI, 70 eV) m/z calcd. for C₂₆H₃₀O₉S₂ [M⁺]: 550.1331; found: 550.1331.
General procedure for Pd⁰-Ti⁻³ catalyzed intramolecular Michael-type addition of allylic carboxylates to activated alkenes:

Rigorously deoxygenated THF (10 mL) was added to a mixture of Cp₂TiCl₂ (0.1 mmol), PdCl₂ (0.05 mmol), PPh₃ (0.1 mmol) and Mn dust (2 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of the activated alkene (0.25 mmol) and 2,4,6-collidine (1.75 mmol) in THF (2 mL) and Me₃SiCl (1 mmol) was then added. The mixture was stirred at room temperature for 21 h and then diluted with AcOEt, washed with HCl (10%), dried over anhydrous Na₂SO₄ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products 2, 20-33.

Colourless oil. Yield: 73%. Mixture of isomers ≈ 4:1 (cis-:trans-).

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.58 (ddt, J = 13.3, 8.3, 6.7 Hz, 1H, major isomer), 5.53-5.47 (m, 1H, minor isomer), 5.00 – 4.88 (m, 2H), 3.65 (s, 3H), 3.64 (s, 3H), 3.56 (s, 3H), 2.79 – 2.68 (m, 1H), 2.51 – 2.37 (m, 1H), 2.25 (dd, J = 16.0, 7.0 Hz, 2H), 2.17 – 2.09 (m, 2H), 1.99 – 1.91 (m, 2H).

¹³C-NMR (126 MHz, CDCl₃): δ (ppm) = 173.2 (2xC), 172.9 (C), 139.2 (CH, minor isomer), 137.4 (CH, major isomer), 116.5 (CH₂, major isomer), 116.4 (CH₂, minor isomer), 59.0 (C, major isomer), 58.5 (C, minor isomer), 52.94 (CH₃), 52.90 (CH₃), 51.6 (CH₃, major isomer), 50.2 (CH₃, minor isomer), 45.9 (CH, major isomer), 41.5 (CH, minor isomer), 40.5 (CH₂, minor isomer), 40.0 (CH₂, minor isomer), 39.2 (CH₂, major isomer), 39.1 (CH), 38.8 (CH₂, major isomer), 37.6 (CH₂, minor isomer), 35.3 (CH₂, major isomer).

HRMS (EI, 70 eV) m/z calcd. for C₁₄H₂₀O₆[M]+: 284.1260; found: 284.1265.

Colourless oil. Yield: 73%. Mixture of isomers ≈ 5:1 (cis-:trans-).

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.66 (ddd, J = 16.7, 10.6, 8.7 Hz, 1H, major isomer), 5.62 – 5.56 (m, 1H, minor isomer), 5.06 – 4.97 (m, 2H), 3.71 (s, 3H), 3.71 (s, 3H), 2.83 – 2.75 (m, 1H, major isomer), 2.66 – 2.60 (m, 1H, minor isomer), 2.52 (d, J = 7.4 Hz, 1H, minor isomer), 2.50 – 2.47 (m, 2H, major isomer), 2.45 (t, J = 6.5 Hz, 1H), 2.23 (dd, J = 15.9, 6.9 Hz, 1H), 2.17 (dd, J = 14.1, 6.3 Hz, 1H), 2.09 (dd, J = 16.0, 8.0 Hz, 1H), 2.06 – 1.97 (m, 1H), 1.42 (s, 9H, minor isomer), 1.41 (s, 9H, major isomer).

¹³C-NMR (126 MHz, CDCl₃): δ (ppm) = 173.1 (C, minor isomer) 173.01 (C, major isomer), 172.97 (C, major isomer), 172.9 (C, minor isomer), 172.1 (C, major isomer), 172.0 (C, minor isomer), 139.4 (CH, minor isomer), 137.6 (CH, major isomer), 116.4 (CH₂), 80.5 (C, minor isomer), 80.4 (C, major isomer), 62.9.
59.0 (C, major isomer), 58.5 (C, minor isomer), 52.92 (CH₃, major isomer), 52.87 (CH₃, major isomer), 52.85 (2xCH₃, minor isomer), 50.1 (CH₂, minor isomer), 45.9 (CH, major isomer), 41.7 (CH, minor isomer), 40.5 (CH₂, minor isomer), 39.9 (CH₂, minor isomer), 39.3 (CH, major isomer), 39.2 (CH₂, major isomer), 39.1 (CH₂, minor isomer), 38.9 (CH₂, major isomer), 36.8 (CH₂, major isomer), 28.23 (3xCH₃, minor isomer), 28.21 (3xCH₃, major isomer).

**HRMS** calcd for C₁₇H₂₇O₆ [M⁺+1]: 327.1808; found: 327.1806.

Colourless oil. Yield: 63%. Mixture of isomers ≈ 6:1 (cis-:trans-).

**¹H-NMR** (500 MHz, CDCl₃): δ (ppm) = 5.69 – 5.58 (m, 1H), 5.07 – 4.94 (m, 2H), 3.721 (s, 3H), 3.716 (s, 3H), 2.85 – 2.76 (m, 1H), 2.62 (ddd, J = 19.5, 10.2, 6.1 Hz, 1H), 2.55 (dd, J = 13.9, 7.2 Hz, 1H), 2.50 – 2.41 (m, 2H), 2.33 (dd, J = 17.4, 7.4 Hz, 1H), 2.13 (dd, J = 12.5, 4.9 Hz, 1H), 2.09 (s, 3H), 1.97 (dd, J = 13.7, 9.2 Hz, 1H).

**¹³C-NMR** (126 MHz, CDCl₃): δ (ppm) = 207.7 (C), 173.2 (C), 173.0 (C), 137.9 (CH), 116.3 (CH₂), 58.9 (C), 53.0 (CH₃), 52.9 (CH₂), 45.7 (CH₂), 44.5 (CH₂), 39.3 (CH₂), 38.89 (CH₂), 38.0 (CH₂), 30.6 (CH₃).

A good high resolution mass spectra could not be obtained.

Pale yellow oil. Yield: 26%. Mixture of isomers ≈ 3:2 (cis-:trans-).

**¹H-NMR** (500 MHz, CDCl₃): δ (ppm) = 9.75 (t, J = 2.0 Hz, 1H, minor isomer), 9.74 (t, J = 1.4 Hz, 1H, major isomer), 5.63 (ddddd, J = 18.2, 17.2, 10.2, 8.4 Hz, 1H, major isomer), 5.59–5.56 (m, 1H, minor isomer), 5.10 – 4.98 (m, 2H), 3.74 (s, 3H, major isomer), 3.73 (s, 3H, minor isomer), 3.73 (s, 3H), 2.88 – 2.80 (m, 1H, minor isomer), 2.70 – 2.60 (m, 2H), 2.56 (dd, J = 14.2, 7.4 Hz, 1H), 2.53 – 2.46 (m, 2H), 2.38 – 2.29 (m, 1H), 2.21 – 2.14 (m, 1H), 2.04 (dddd, J = 19.4, 13.6, 10.0 Hz, 1H, major isomer), 1.92–1.86 (m, 1H, minor isomer).

**¹³C-NMR** (126 MHz, CDCl₃): δ (ppm) = 201.5 (C, minor isomer), 201.4 (C, major isomer), 173.0 (2xC, major isomer), 172.9 (C, minor isomer), 172.8 (C, major isomer), 139.1 (CH, minor isomer), 137.6 (CH, major isomer), 116.9 (CH₂, minor isomer), 116.8 (CH₂, major isomer), 59.0 (C, major isomer), 58.7 (C, minor isomer), 53.03 (2xCH₃, minor isomer), 52.98 (2xCH₃, major isomer), 50.4 (CH, minor isomer), 47.5 (CH₂, minor isomer), 45.9 (CH, major isomer), 45.1 (CH₂, major isomer), 40.4 (CH₂, minor isomer), 28.23 (3xCH₃, minor isomer), 28.21 (3xCH₃, major isomer).
40.0 (CH₂, major isomer), 39.5 (CH, minor isomer), 39.3 (CH₂, minor isomer), 38.9 (CH₂, major isomer), 37.1 (CH, major isomer).

**HRMS (EI, 70 eV) m/z calcd. for C₁₃H₁₈O₅ [M⁺]:** 254.1154; found: 254.1155.

![Ts-N=\text{CO}_2\text{Me}]

Colourless oil. Yield: 67%. Mixture of isomers ≈ 3:2 (cis-:trans-).

**¹H-NMR (500 MHz, CDCl₃):** δ (ppm) = 7.71 (d, J = 8.1 Hz, 4H), 7.32 (d, J = 7.7 Hz, 4H), 5.45 (dt, J = 18.7, 9.6 Hz, 2H), 5.10 – 4.94 (m, 4H), 3.62 (s, 6H), 3.50 (ddd, J = 22.4, 10.0, 7.5 Hz, 1H), 3.38 (dd, J = 10.0, 6.6 Hz, 1H), 3.23 (dd, J = 10.0, 4.4 Hz, 1H), 3.03 (dd, J = 10.0, 7.8 Hz, 1H), 2.94 (dd, J = 18.6, 9.0 Hz, 2H), 2.80 (dt, J = 13.0, 6.5 Hz, 1H), 2.51 (tt, J = 14.3, 7.2 Hz, 1H), 2.43 (s, 6H), 2.31 – 2.22 (m, 2H), 2.15 – 2.03 (m, 2H).

**¹³C-NMR (126 MHz, CDCl₃):** δ (ppm) = 172.4 (C, major isomer), 172.2 (C, minor isomer), 143.64 (C, minor isomer), 143.62 (C, major isomer), 136.0 (CH, minor isomer), 134.5 (CH, major isomer), 134.0 (C, minor isomer), 134.1 (C, major isomer), 129.83 (2xC H, minor isomer), 129.82 (2xCH, major isomer), 127.63 (2xCH, minor isomer), 127.57 (2xCH, major isomer), 118.2 (CH₂, minor isomer), 118.1 (CH₂, major isomer), 53.0 (CH₂, minor isomer), 52.5 (CH₂, major isomer), 51.9 (CH₂, minor isomer), 51.81 (CH₂, minor isomer), 51.79 (CH₃, major isomer), 51.7 (CH₃, major isomer), 48.9 (CH, minor isomer), 45.1 (CH, major isomer), 40.5 (CH, minor isomer), 38.4 (CH, major isomer), 35.9 (CH₂, minor isomer), 33.2 (CH₂, major isomer), 21.64 (CH₃, minor isomer), 21.63 (CH₃, major isomer).

**HRMS (EI, 70 eV) m/z calcd. for C₁₆H₂₂NO₄S [M+1⁺]:** 324.1270; found: 324.1271.

Pale orange oil. Yield: 47%. Mixture of isomers ≈ 1:1 (cis-:trans-).

**¹H-NMR (500 MHz, CDCl₃):** δ (ppm) = 7.25 – 7.20 (m, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 7.3 Hz, 2H), 5.83 – 5.70 (m, 1H), 5.22 – 5.07 (m, 2H), 3.70 (s, 3H, one isomer), 3.69 (s, 3H, other isomer), 3.51 (dd, J = 12.1, 9.6, 4.5 Hz, 2H), 3.28 (dd, J = 9.4, 4.0 Hz, 1H, one isomer), 3.18 – 3.08 (m, 1H), 3.05 (t, J = 9.0 Hz, 1H), 2.83 (dt, J = 13.8, 6.9 Hz, 1H, one isomer), 2.63 (dt, J = 10.6, 5.3 Hz, 1H, other isomer), 2.56 (dt, J = 16.7, 8.4 Hz, 1H, one isomer), 2.53 – 2.44 (m, 1H), 2.41 – 2.28 (m, 1H).

**¹³C-NMR (126 MHz, CDCl₃):** δ (ppm) = 173.2 (C), 172.9 (C), 147.7 (C), 147.5 (C), 137.9 (CH), 136.3 (CH), 129.3 (4xCH), 117.5 (CH₃), 117.2 (CH₂), 116.0 (CH), 115.9 (CH), 111.6 (4xCH), 53.4 (CH₂), 53.0 (CH₂), 52.2 (CH₂), 52.0 (CH₂), 51.8 (2xCH₃), 49.2 (CH), 45.3 (CH), 40.7 (CH), 38.4 (CH), 36.6 (CH₂), 34.1 (CH₂).
**HRMS** (EI, 70 eV) *m/z* calcd. for C₁₅H₁₉NO₂ [M⁺]: 245.1416; found: 254.1410

Pale yellow solid. Yield: 50%. Mixture of isomers ≈3:2.

**¹H-NMR** (500 MHz, CDCl₃): δ (ppm) = 8.06 (dd, *J* = 13.3, 4.9 Hz, 4H), 7.75 – 7.68 (m, 2H), 7.60 (tdd, *J* = 10.7, 6.1, 4.5 Hz, 4H), 5.81 – 5.71 (m, 1H, minor isomer), 5.48 (dd, *J* = 17.0, 10.2, 8.5 Hz, 1H, major isomer), 5.09 – 4.98 (m, 2H), 3.65 (s, 3H, minor isomer), 3.64 (s, 3H, major isomer), 3.06–2.96 (m, 1H, minor isomer), 2.86 (dt, *J* = 21.8, 9.1 Hz, 1H, major isomer), 2.74 – 2.66 (m, 2H), 2.53 (dd, *J* = 14.3, 6.8, 4.2 Hz, 1H), 2.47 (dd, *J* = 15.8, 4.0 Hz, 1H), 2.40 (d, *J* = 11.4 Hz, 1H), 2.36 – 2.32 (m, 2H), 2.32 – 2.24 (m, 1H), 2.17 – 2.08 (m, 1H), 2.02 – 1.95 (m, 1H).

**¹³C-NMR** (126 MHz, CDCl₃): δ (ppm) = 172.9 (C), 172.3 (C), 137.6 (CH), 136.6 (CH), 136.3 (C), 136.1 (C), 134.8 (2xCH), 134.7 (CH), 134.6 (CH), 131.6 (2xCH), 131.5 (2xCH), 131.46 (2xCH), 131.45 (2xCH), 129.8 (C), 129.2 (C), 128.94 (2xCH), 128.89 (2xCH), 128.87 (2xCH), 128.8 (2xCH), 118.1 (CH₂), 117.3 (CH₂), 93.8 (C), 91.8 (C), 51.73 (CH₃), 51.71 (CH₃), 49.9 (CH), 46.5 (CH), 41.5 (CH), 39.1 (CH), 38.2 (CH₂), 37.9 (CH₂), 36.9 (CH₂), 36.8 (CH₂), 36.5 (CH₂), 35.0 (CH₂).

**HRMS** (EI, 70 eV) *m/z* calcd. for C₁₅H₂₁O₆S₂ [M⁺]: 448.1014; found: 448.1011.


**¹H NMR** (500 MHz, CDCl₃): δ (ppm) = 4.86 (s, 1H, major isomer), 4.79 (s, 1H, minor isomer), 4.76 (s, 1H, minor isomer), 4.69 (s, 1H, major isomer), 3.73 (s, 6H, minor isomer), 3.72 (s, 6H, major isomer), 3.64 (s, 3H, major isomer), 3.63 (s, 3H, minor isomer), 2.72 – 2.58 (m, 2H), 2.54 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.45 (dd, *J* = 15.4, 4.3 Hz, 1H, minor isomer). 2.39 (dd, *J* = 13.4, 6.1 Hz, 1H, major isomer), 2.25 – 2.18 (m, 1H), 2.17 (d, *J* = 4.4 Hz, 1H), 2.14 (d, *J* = 4.1 Hz, 1H), 2.04 (dd, *J* = 16.1, 10.4 Hz, 1H, major isomer), 1.97 – 1.89 (m, 1H, minor isomer), 1.71 (s, 3H, major isomer), 1.67 (s, 3H, minor isomer).

**¹³C NMR** (126 MHz, CDCl₃): δ (ppm) = 173.7 (C), 173.1 (2xC), 144.0 (C, minor isomer), 143.6 (C, major isomer), 112.9 (CH₂ minor isomer), 111.8 (CH₂ major isomer), 58.3 (C), 53.1 (CH₃, minor isomer), 53.0 (CH₃, major isomer), 48.9 (2xCH₃), 39.9 (CH₃, minor isomer), 39.4 (CH₃, major isomer), 38.9 (CH₃ minor isomer), 38.9 (CH₃ minor isomer), 37.9 (CH₃, major isomer), 37.1 (CH₃ major isomer), 36.1 (CH₂ major isomer), 34.4 (CH₂ major isomer), 23.2 (CH₃).

**HRMS** (EI, 70 eV) (EI, 70 eV) *m/z* calcd. for C₁₅H₂₂O₃S₂ [M⁺]: 298.1416; found: 298.1412.

$^1$H-NMR (500 MHz, CDCl$_3$): δ (ppm) = 5.73 (dd, $J = 17.4$, 10.8 Hz, 1H), 5.06 - 4.94 (m, 2H), 3.72 (s, 6H, minor isomer), 3.72 (s, 6H, major isomer), 3.65 (s, 3H, minor isomer), 3.63 (s, 3H, major isomer), 2.60 - 2.49 (m, 1H), 2.46 (d, $J = 14.3$ Hz, 1H, minor isomer), 2.35 (d, $J = 14.0$ Hz, 1H, major isomer), 2.28 (dt, $J = 9.0$, 3.8 Hz, 1H), 2.25 - 2.03 (m, 4H), 1.13 (s, 3H, minor isomer), 0.88 (s, 3H, major isomer).

$^{13}$C-NMR (126 MHz, CDCl$_3$): δ (ppm) = 173.5 (C), 173.3 (2xC), 173.2 (C), 173.04 (C), 172.97 (C), 145.7 (CH), 141.5 (CH), 113.8 (CH$_2$), 113.09 (CH$_2$), 57.9 (C), 57.8 (C), 53.1 (CH$_3$), 52.9 (CH$_3$), 51.69 (CH$_3$), 51.66 (CH$_3$), 47.6 (2xCH$_2$), 47.4 (C), 47.3 (C), 46.2 (CH$_2$), 46.11 (CH), 44.7 (2xCH), 39.4 (CH$_2$), 38.7 (CH$_2$), 34.8 (CH$_2$), 34.1 (CH$_2$), 24.1 (CH$_2$), 17.6 (CH$_2$).

HRMS (EI, 70 eV) $m/z$ calcd. for C$_{15}$H$_{22}$O$_6$ [M$^+$]: 298.1416; found:298.1420.

Colourless oil. Yield: 64%. Mixture of isomers >15:1. Only one isomer could be characterized and a C-3, C-7-cis stereochemistry was tentatively assigned. The stereochemistry at C-8 could not be determined.

$^1$H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 5.66 (dd, $J = 16.6$, 10.1 Hz, 1H), 5.04 (d, $J = 10.1$ Hz, 1H), 5.00 (s, 1H), 3.70 (s, 6H), 3.65 (s, 3H), 2.77 (m, 1H), 2.58 (dd, $J = 14.3$, 7.3 Hz, 1H), 2.36 - 2.09 (m, 5H), 1.12 (d, $J = 6.7$ Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): δ (ppm) = 176.6 (C), 173.0 (C), 172.98 (C), 137.0 (CH), 116.5 (CH$_2$), 58.8 (C), 53.0 (CH$_2$), 52.9 (CH$_2$), 51.6 (CH$_3$), 46.6 (CH), 45.2 (CH), 40.9 (CH), 39.9 (CH$_2$), 37.3 (CH$_2$), 16.0 (CH$_3$).

HRMS (EI, 70 eV) $m/z$ calcd. for C$_{15}$H$_{22}$O$_6$ [M$^+$]: 298.1416; found: 298.1415.


$^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) = 5.73 - 5.60 (m, 1H), 5.59 - 5.48 (m, 1H), 5.48 - 5.38 (m, 1H), 4.99 (m, 2H), 3.73 (s, 6H), 3.67 (s, 3H), 3.03 (d, $J = 6.4$ Hz, 2H), 2.82 - 2.71 (m, 1H), 2.59 - 2.52 (m, 1H), 2.48 (dd, $J = 13.8$, 6.8 Hz, 1H), 2.34 - 2.27 (m, 1H), 2.23 - 2.15 (m, 1H), 2.08 - 1.98 (m, 1H).
**\(^{13}\)C NMR** (125 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 173.2 (2xC), 173.0 (C), 139.2 (CH, minor isomer), 138.3 (CH, major isomer), 135.0 (CH, minor isomer), 134.3 (CH, major isomer), 123.1 (CH, minor isomer), 122.9 (CH, major isomer) 115.6 (CH\(_2\)), 59.2 (C), 53.0 (2xCH\(_3\)), 51.9 (CH\(_3\)), 49.8 (CH, minor isomer), 48.6 (CH, minor isomer), 47.3 (CH, major isomer), 46.1 (CH, minor isomer), 40.4 (CH\(_2\), minor isomer), 40.2 (CH\(_2\), major isomer), 39.2 (CH\(_2\), minor isomer), 39.1 (CH\(_2\), major isomer), 38.0 (CH\(_2\)).

**HRMS** (EI, 70 eV) \(m/z\) calcd. for C\(_{16}\)H\(_{22}\)O\(_6\) [M]: 310.1416; found: 310.1420.

*MeO\(_2\)C

Colourless oil. Yield: 47%. Mixture of isomers \(\approx\)2:1.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 5.74 - 5.57 (m, 1H), 5.60 - 5.47 (m, 1H), 5.48 – 5.35 (m, 1H), 4.99 (dd, \(J\) = 15.6, 5.5 Hz, 2H), 3.73 (s, 6H), 3.10 (d, \(J\) = 6.7 Hz, 2H), 2.78 (dt, \(J\) = 14.1, 7.0 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.39 – 2.23 (m, 1H), 2.25 – 2.14 (m, 1H), 2.13 (s, 3H), 2.07 – 1.97 (m, 1H).

**\(^{13}\)C NMR** (101 MHz, CDCl\(_3\)): \(\delta\) 207.3 (C), 172.9 (2xC), 139.2 (CH, minor isomer), 138.3 (CH, major isomer), 135.6 (CH, minor isomer), 134.7 (CH, major isomer), 123.4 (CH, minor isomer), 123.2 (CH, major isomer), 115.8 (CH\(_2\), minor isomer), 115.6 (CH\(_2\), major isomer), 59.1 (C, major isomer), 58.4 (C, minor isomer), 53.0 (2xCH\(_3\)), 49.9 (CH, minor isomer), 48.7 (CH, major isomer), 47.7(CH\(_2\)), 47.3 (CH, major isomer), 46.1 (CH, minor isomer), 40.4 (CH\(_2\), minor isomer), 40.2 (CH\(_2\), major isomer), 39.3 (CH\(_2\), major isomer), 38.9, (CH\(_2\), minor isomer) 29.8 (CH\(_2\), major isomer), 29.4 (CH\(_2\), minor isomer).

**HRMS** (EI, 70eV) calcd. for C\(_{16}\)H\(_{21}\)O\(_5\) [M-1]: 293.1389; found: 293.1390.

*\(\text{BzOH}_2\)C

Colourless oil. Yield: 53%. Mixture of isomers \(\approx\)1:1.

**\(^1\)H NMR** (500 MHz, CDCl\(_3\)): \(\delta\) (ppm)= 8.02 (d, \(J\) = 7.6 Hz, 4H), 7.56 (t, \(J\) = 7.2 Hz, 2H), 7.41 (t, \(J\) = 7.3 Hz, 4H), 5.84 – 5.57 (m, 1H), 5.60 – 5.35 (m, 1H), 4.41 (s, 4H, minor isomer), 4.34 (s, 4H, major isomer), 3.02 (d, \(J\) = 18.0 Hz, 2H), 2.93 - 2.83 (m, 1H), 2.47 – 2.31 (m, 1H), 2.05 (m, 1H), 2.00 – 1.90 (m, 1H), 1.79 – 1.69 (m, 1H), 1.64 – 1.47 (m, 1H).

**\(^{13}\)C NMR** (126 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 172.4 (C), 166.7 (2xC), 139.8 (CH, one isomer), 139.1 (CH, one isomer), 135.7 (CH, one isomer), 134.9 (CH, one isomer), 133.2 (2xCH), 130.1 (2xC), 129.7 (4xCH), 128.6 (4xCH), 122.8 (CH, one isomer), 122.7 (CH, one isomer), 115.4 (CH\(_2\)), 69.3 (CH\(_2\), one isomer), 68.8 (CH\(_2\), one isomer), 68.7 (CH\(_2\), one isomer), 68.1 (CH\(_2\), one isomer), 51.9 (CH\(_3\)), 49.6 (CH, one isomer), 48.3 (CH, one isomer), 47.2 (CH, one isomer), 45.9 (CH, one isomer), 44.6 (C), 39.2
(CH₂, one isomer), 39.0 (CH₂, other isomer), 38.0 (CH₂), 37.9 (CH₂, one isomer), 37.7 (CH₂, other isomer).

HRMS (El, 70 eV) m/z calcd. for C₃8H₆O₆[M⁺]: 462.2042; found: 462.2030.

MeO₂C
MeO₂C
CO₂Et

32

Colourless oil. Yield: 61%. Mixture of isomers ≈ 6:1. Data of the major isomer:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.72 (ddd, J = 23.4, 10.9, 5.7 Hz, 1H), 5.07 – 4.96 (m, 2H), 4.19 – 4.03 (m, 2H), 3.69 (s, 3H), 3.68 (s, J = 2.6 Hz, 3H), 2.89 (dq, J = 11.8, 6.0 Hz, 1H), 2.68 (dd, J = 4.1, 1.7 Hz, 1H), 2.34 – 2.24 (m, 3H), 1.95 – 1.87 (m, 1H), 1.74 (dt, J = 19.0, 9.6 Hz, 1H), 1.58 (ddd, J = 13.3, 8.3, 4.7 Hz, 1H), 1.25 (td, J = 7.1, 2.5 Hz, 3H).

¹³C-NMR (126 MHz, CDCl₃): δ (ppm) = 174.8 (C), 172.3 (C), 171.8 (C), 141.4 (CH), 114.0 (CH₂), 60.6 (CH₂), 52.8 (CH₃), 54.9 (C), 52.70 (CH₃), 52.66 (CH₃), 36.4 (CH), 35.7 (CH₂), 34.0 (CH), 31.7 (CH₂), 31.2 (CH₂), 14.3 (CH₃).

HRMS (El, 70 eV) m/z calcd. for C₃₆H₂₄O₆S₂[M-CH₂]⁺: 298.1416; found: 298.1408.

PhO₂S
PhO₂S
CO₂Et

33

Colourless oil. Yield: 60%. Mixture of isomers ≈ 9:1. Data of the major isomer:

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.05 (m, 4H), 7.77 – 7.67 (m, 2H), 7.65 – 7.52 (m, 4H), 5.70 (ddd, J = 16.7, 10.8, 7.0 Hz, 1H), 5.04 – 4.91 (m, 2H), 4.18 (qd, J = 7.1, 1.9 Hz, 2H), 3.15 – 3.02 (m, 2H), 2.71-2.47 (ddd, J = 20.9, 15.6, 7.4 Hz, 2H), 2.39-1.99 (m, 2H), 1.60-1.49 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 174.0 (C), 140.8 (CH), 136.2 (2xC), 134.8 (2xCH), 131.7 (2xCH), 131.5 (2xCH), 128.9 (2xCH), 128.8 (2xCH), 114.9 (CH₃), 87.1 (C), 61.1 (CH₂), 35.6 (CH), 33.2 (CH), 30.1 (CH₂), 29.6 (CH₂), 26.4 (CH₂), 14.3 (CH₃).

(EI, 70 eV) m/z calcd. for C₃₆H₂₄O₆S₂[M+1⁺]: 463.1249; found: 463.1241.
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