Regioselective Synthesis of Medium-Sized Bicyclic Butenolides
by Lewis Acid catalyzed Cyclization of
cyclic 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with Oxalyl Chloride

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Supplementary Material

General Comments. All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere (nitrogen) using glassware dried with a heat-gun in vacuo. THF and pentane was freshly distilled from Na, CH₂Cl₂ from CaH₂. For the ¹H and ¹³C NMR spectra (¹H NMR: 250 MHz, ¹³C NMR: 62.5 MHz) the deuterated solvents indicated were used. The multiplicity of the ¹³C NMR signals were determined with the DEPT 135 technique. Yields refer to analytically pure samples. Isomer ratios were derived from suitable ¹H NMR integrals. Mass spectral data (MS) were obtained using the electron ionization (70 eV) or the chemical ionization technique (CI, H₂O). For preparative scale chromatography, silica gel (Merck, 60-200 mesh) was used. For column chromatography, ether (E) and petroleum ether (b. p. 40-70 °C) were used.
Melting points were measured on a Dr. Tottoli apparatus (Büchi) and are uncorrected. Elemental analyses were performed at the microanalytical laboratory of the University of Göttingen.

Representative experimental procedure for the synthesis of bis-silyl enol ethers (3a-i). To a THF-solution (30 mL) of LDA, prepared by addition of n-BuLi (23.8 mL, 36.5 mmol, solution in n-hexane) to a THF-solution of diisopropylamine (4.2 mL, 32 mmol), was added dropwise ethyl cycloheptanone-2-carboxylate (1f) (2.69 g, 14.6 mmol) at 0 °C. After stirring of the yellow solution for 1.5 h at 0 °C (for 3i: stirring for 2 h at −78 °C), trimethylchlorosilane (5.5 mL, 43.8 mmol, 3 equiv.) was added (for 3i: addition of 5 equiv. of trimethylchlorosilane). After stirring for 3 h at 0 °C (for 3i: warming to 0 °C within 1 h and stirring for 3 h at 0 °C), the solvent was removed in vacuo. To the residue was added pentane and the suspension obtained was filtered under nitrogen. The solvent of the filtrate was removed in vacuo to give essentially pure 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3f in 95% crude yield. All bis-silyl enol ethers reported were used without further purification (90-95 % purity, 5-10 % mono-silyl enol ether) and were stored at −30 °C under nitrogen. Due to their instability, all bis-silyl enol ethers were characterized only by NMR and by high-resolution mass spectroscopy.

3a: Starting with ethyl cyclohexanone-2-carboxylate 1a (1.02 g, 6.00 mmol), 3a was isolated as a light yellow oil (1.73 g, 92 %). 1H NMR (CDCl₃, 250 MHz): 0.14, 0.21 (2 x s, 2 x 9 H, Me₃Si), 1.22 (t, J = 8 Hz, 3 H, CH₃), 1.58 (m, 2 H, CH₂), 2.06, 2.31 (2 x m, 2 x 2 H, CH₂), 3.79 (q, J = 8 Hz, 2 H, OCH₂), 4.78 (t, J = 6 Hz, 1 H, CH). 13C NMR (CDCl₃, 62.5 MHz): δ 0.61, 0.66, 14.80, 23.38, 24.88, 25.62, 63.84, 97.19, 107.25, 147.46, 147.92. MS (EI, 70 eV): 314 (M⁺, 60), 73 (100). HRMS calcd. for C₁₅H₃₀O₃Si₂ 314.1734, found 314.1730.
3b: Starting with *iso*-propyl cyclohexanone-2-carboxylate 1b (1.012 g, 5.50 mmol), 3b was isolated as a light yellow oil (1.73 g, 96 %). $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 0.18, 0.21 (2 x s, 2 x 9 H, Me$_3$Si), 1.20 (d, $J = 8$ Hz, 6 H, CH$_3$), 1.60 (m, 2 H, CH$_2$), 2.11, 2.32 (2 x m, 2 x 2 H, CH$_2$), 4.30 (hept, $J = 8$ Hz, 1 H, OCH), 4.80 (t, $J = 6$ Hz, 1 H, CH). $^{13}$C NMR (CDCl$_3$, 62.5 MHz): $\delta$ 0.22, 0.23, 21.87, 23.44, 24.98, 25.98, 69.30, 98.48, 107.55, 146.61, 147.62. MS (EI, 70 eV): 328 (M$^+$, 52), 73 (100). HRMS calcd. for C$_{16}$H$_{32}$O$_3$Si$_2$ 328.1890, found 328.1886.

3c: Starting with methoxyethyl cyclohexanone-2-carboxylate 1c (1.20 g, 6.00 mmol), 3c was isolated as a light yellow oil (1.96 g, 95 %). $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 0.11, 0.20 (2 x s, 2 x 9 H, Me$_3$Si), 1.58 (m, 2 H, CH$_2$), 2.08, 2.32 (2 x m, 2 x 2 H, CH$_2$), 3.36 (s, 3 H, OCH$_3$), 3.55, 3.89 (2 x m, 2 x 2 H, OCH$_2$), 4.80 (t, $J = 6$ Hz, 1 H, CH). $^{13}$C NMR (CDCl$_3$, 62.5 MHz): $\delta$ 0.11, 0.17, 23.27, 24.82, 25.37, 58.81, 67.08, 71.06, 97.45, 107.54, 147.25, 147.60. MS (EI, 70 eV): 344 (M$^+$, 62), 73 (100). HRMS calcd. for C$_{16}$H$_{32}$O$_4$Si$_2$ 344.1839, found 344.1840.

3d: Starting with 2-benzoylcyclohexanone 1e (1.21 g, 6.00 mmol), 3e was isolated as a light yellow oil (1.97 g, 95 %). $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 0.12, 0.20 (2 x s, 2 x 9 H, Me$_3$Si), 1.40-1.70 (2 x m, 2 H, CH$_2$), 1.90-2.20 (m, 4 H, CH$_2$), 4.90 (t, $J = 6$ Hz, 1 H, CH), 7.10-7.50 (m, 5 H, Ph). MS (EI, 70 eV): 346 (M$^+$, 22), 73 (100). HRMS calcd. for C$_{19}$H$_{30}$O$_2$Si$_2$ 346.1784, found 346.1782.

3e: Starting with ethyl cyclopentanone-2-carboxylate 1e (1.02 g, 6.54 mmol), 3e was isolated as a deep yellow oil as a 2:1 mixture with the respective mono-silyl enol ether. Since no purification was possible, the crude material (1.5 equiv.) was used in the cyclization reaction with oxalyl chloride. $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 0.21, 0.23 (2 x s, 2 x 9 H,
Me₂Si), 1.21 (t, J = 8 Hz, 3 H, CH₃), 1.20-1.30 (m, 2 x H, CH₂), 2.24 (m, 2 H, CH₂), 3.80 (q, J = 8 Hz, 2 H, OCH₂CH₃), 4.71 (t, J = 5 Hz, 1 H, CH). MS (EI, 70 eV): 300 (M⁺, 12), 73 (100).

3f: Starting with ethyl cycloheptanone-2-carboxylate 1f (2.69 g, 14.60 mmol), 3f was isolated as a light yellow oil (4.55 g, 95 %). ¹H NMR (CDCl₃, 250 MHz): δ 0.10, 0.21 (2 x s, 2 x 9 H, Me₂Si), 1.22 (t, J = 7 Hz, 3 H, CH₃), 1.45-1.65 (2 x m, 2 x H, CH₂), 1.95, 2.18 (2 x m, 2 x 2 H, CH₂), 3.82 (q, J = 7 Hz, 2 H, OCH₂CH₃), 4.94 (t, J = 6.5 Hz, 1 H, CH). ¹³C NMR (CDCl₃, 62.5 MHz): δ 0.30, 0.34, 15.04, 25.64, 26.84, 27.57, 30.38, 63.52, 98.75, 109.35, 150.66, 152.22. MS (EI, 70 eV): 328 (M⁺, 62), 199 (25), 73 (100). HRMS calcd. for C₁₆H₃₂O₃Si₂ 328.1890, found 328.1886.

3g: Starting with 2-pivaloylcycloheptanone 1g (1.76 g, 9.00 mmol), 3g was isolated as a light yellow oil (2.94 g, 96 %). ¹H NMR (CDCl₃, 250 MHz): δ 0.10, 0.19 (2 x s, 2 x 9 H, Me₂Si), 1.18 (s, 9 H, CH₃), 1.35-1.75 (m, 6 H, CH₂), 1.98 (m, 2 H, CH₂), 4.90 (t, J = 6.5 Hz, 1 H, CH). ¹³C NMR (CDCl₃, 62.5 MHz): δ 0.56, 1.26, 25.78, 26.90, 29.17, 30.32, 31.70, 37.26, 109.25, 117.10, 154.81, 155.69. MS (EI, 70 eV): 340 (M⁺, 56), 283 (36), 215 (57), 73 (100). HRMS calcd. for C₁₈H₃₆O₂Si₂ 340.2254, found 340.2256.

3h: Starting with ethyl cyclooctanone-2-carboxylate 1h (1.98 g, 10.00 mmol), 3h was isolated as a light yellow oil (3.25 g, 95 %). ¹H NMR (CDCl₃, 250 MHz): δ 0.17, 0.20 (2 x s, 2 x 9 H, Me₂Si), 1.25 (t, J = 7 Hz, 3 H, CH₃), 1.45-1.55 (m, 6 H, CH₂), 1.95, 2.18 (2 x m, 2 x 2 H, CH₂), 3.82 (q, J = 7 Hz, 2 H, OCH₂CH₃), 4.75 (t, J = 7 Hz, 1 H, CH). ¹³C NMR (CDCl₃, 62.5 MHz): δ 0.92, 1.32, 15.74, 26.42, 27.34, 28.30, 30.02, 30.22, 64.82, 99.36, 107.68, 149.88, 150.66. MS (EI, 70 eV): 342 (M⁺, 80), 317 (32), 73 (100). HRMS calcd. for C₁₇H₃₄O₃Si₂ 342.2047, found 342.2044.
3i: Starting with ethyl cyclohexanone-2-carboxylate 1a (1.00 g, 4.71 mmol), 3a was isolated as a light yellow oil (1.58 g, 94%). $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 0.10, 0.18 (2 x s, 2 x 9 H, Me$_3$Si), 1.20-1.45 (m, 10 H, CH$_2$), 2.00, 2.10 (2 x m, 2 x 2 H, CH$_2$), 3.48 (s, 3 H, OCH$_3$), 4.74 (t, $J = 8$ Hz, 1 H, CH). $^{13}$C NMR (CDCl$_3$, 62.5 MHz): $\delta$ 0.32, 0.50, 24.48, 24.55, 24.60, 25.34, 25.64, 26.94, 28.20, 56.24, 101.64, 115.02, 145.48, 149.96. MS (EI, 70 eV): 356 (M$^+$, 92), 341 (62), 73 (100). HRMS calcd. for C$_{18}$H$_{36}$O$_3$Si 356.2203, found 356.2186.

Synthesis of silyl enol ether (5): To a THF-solution (20 mL) of methyl cyclododecanone-2-carboxylate (3.15 g, 14.67 mmol) was added NEt$_3$ (2.22 g, 22 mmol) and TMSCl (2.40 g, 22 mmol) at 20 °C. After stirring of the suspension for 24 h the solvent was removed in vacuo. To the residue was added petroleum ether, the suspension was filtered under nitrogen and the solvent of the filtrate was removed in vacuo. The residue was distilled using a kugelrohr apparatus (ot: 110 °C, 0.1 Torr) to give 5 as a colourless oil (3.88 g, 90%). $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 0.18, (s, 9 H, Me$_3$Si), 1.05-1.50 (m, 14 H, CH$_2$), 1.55-1.65 (m, 2 H, CH$_2$), 1.80, 2.22, 2.46, 3.52 (4 x m, 4 x 1 H, CH$_2$), 3.72 (s, 3 H, OCH$_3$). $^{13}$C NMR (CDCl$_3$, 62.5 MHz): $\delta$ 0.68, 24.10, 24.75, 24.83, 24.85, 25.13, 25.40, 25.52, 25.72, 25.80, 33.50, 50.62, 115.12, 165.52, 169.98. MS (EI, 70 eV): 312 (M$^+$, 62), 297 (100), 73 (80). HRMS calcd. for C$_{17}$H$_{32}$O$_3$Si 312.2121, found 312.2108.

Synthesis of bis-silyl enol ether (3j): To a THF-solution of LDA, prepared by addition of n-BuLi (4.4 mmol, 2.35 M solution in n-hexane) to a THF-solution (7 mL) of diisopropylamine (4.4 mmol) at 0 °C, was added a THF-solution (1.5 mL) of silyl enol ether 5 (1.18 g, 3.8 mmol) at −78 °C. After stirring for 1.5 h at −78 °C, TMSCl (0.52 g, 4.8 mmol) was added. The temperature of the solution was allowed to rise to 0 °C during 1 h and the solution was stirred for 4 h. The solvent was removed in vacuo and pentane was added to the residue. The precipitated lithium chloride was removed by filtration under nitrogen and the solvent of the filtrate was removed in vacuo to give 3j as a light yellow oil (1.38 g, 95 %,
4:1-mixture of E/Z-isomers. $^1$H NMR (CDCl₃, 250 MHz, major isomer): δ 0.14, 0.18 (2 x s, 2 x 9 H, Me₃Si), 1.20-1.40 (m, 14 H, CH₂), 2.00-2.10 (m, 4 H, CH₂), 3.48 (s, 3 H, OCH₃), 4.54 (t, J = 7 Hz, 1 H, CH). $^{13}$C NMR (CDCl₃, 62.5 MHz): δ 0.26, 0.35, 24.33, 24.75, 25.79, 26.15, 26.25, 26.15, 26.25, 26.60, 26.84, 56.40, 101.26, 113.78, 146.07, 151.15. MS (EI, 70 eV): 384 (M⁺, 56), 369 (40), 353 (92), 73 (100). HRMS calcd. for C₁₈H₃₆O₃Si₂ 384.2616, found 384.2610.

**Alternative procedure for the preparation of 1,3-bis(trimethylsilyloxy)-1,3-butadiene (3d):** To an ether-solution (20 mL) of 1d (10 mmol) and triethylamine (2.84 mL, 20.40 mmol), trimethylsilyl trifluoromethanesulfonate (TMSOTf, 3.54 mL, 19.6 mmol) was slowly added at 0 °C. After stirring of the suspension for 2 h the organic layer was separated from the salt using a syringe. The solvent was removed and in vacuo to give 3d as a light yellow oil (3.14 g, 91 %).

**General procedure for the synthesis of butenolides (4).** To a CH₂Cl₂-solution (60 mL) of oxalyl chloride (3.94 mmol, 0.34 mL) and 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3f (3.28 mmol, 1.08 g) was added a CH₂Cl₂-solution (7 mL) of Me₃SiOTf (0.18 mL, 0.3 equiv.) at −78 °C. The temperature of the reaction mixture was allowed to rise to 20 °C during 12 h. After stirring for 2 h at 20 °C a saturated solution of NaCl was added, the organic layer was separated and the aqueous layer was repeatedly extracted with ether. The combined organic extracts were dried (MgSO₄), filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by column chromatography (silica gel, ether / petrol ether = 1:10 → 1:1) to give 4f as a colourless solid (781 mg, 84 %).

**4a:** Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3a (566 mg, 1.80 mmol), 4a was isolated as a light yellow oil (305 mg, 76 %). $^1$H NMR (acetone-d₆, 250 MHz): δ 1.28 (t, J = 6 Hz, 3 H, CH₃), 1.80 (quintet, J = 5 Hz, 2 H, CH₂), 2.52 (t, J = 5 Hz, 2 H, CH₂), 2.58 (t, J = 5 Hz, 2 H,
CH₂), 4.18 (q, J = 6 Hz, 2 H, OCH₂). ¹³C NMR (acetone-d₆, 75 MHz): δ 14.57 (CH₃), 21.16, 22.53, 25.14 (CH₂), 60.99 (OCH₂), 107.91, 123.13, 139.97, 152.72 (C), 165.08, 165.37 (CO). MS (EI, 70 eV): 224 (M⁺, 35), 178 (100), 150 (61). Anal.: calcd. for C₁₁H₁₂O₅: C 58.93, H 5.39. Found: C 58.76, H 5.50.

4b: Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3b (590 mg, 1.80 mmol), 4b was isolated as a light yellow oil (318 mg, 74 %). ¹H NMR (acetone-d₆, 250 MHz): δ 1.24 (d, J = 6 Hz, 6 H, CH₃), 1.76 (quintet, J = 6 Hz, 2 H, CH₂), H, CH₂2.46 (t, J = 6 Hz, 2 ), 2.54 (t, J = 6 Hz, 2 H, CH₂), 4.99 (hept, J = 6 Hz, 2 H, OCH). ¹³C NMR (acetone-d₆, 75 MHz): δ 20.99 (CH₂), 21.98 (CH₃), 22.34, 24.98 (CH₂), 68.46 (OCH), 108.23, 123.09, 139.64, 152.43, 164.47, 165.20 (C). MS (EI, 70 eV): 238 (M⁺, 42). Anal.: calcd. for C₁₂H₁₄O₅: C 60.50, H 5.92. Found: C 60.13, H 6.22.

4c: Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3c (1.032 g, 3.00 mmol), 4c was isolated as a light yellow oil (572 mg, 75 %). ¹H NMR (MeOH-d₄, 250 MHz): δ 1.78 (quintet, J = 7 Hz, 2 H, CH₂), 2.50 (q, J = 7 Hz, 4 H, CH₂), 3.38 (s, 3 H, CH₃), 3.62, 4.27 (2 x t, J = 5 Hz, 2 x 2 H, OCH₂). ¹³C NMR (MeOH-d₄, 62.5 MHz): δ 21.39, 22.88, 25.35 (CH₂), 59.22 (OCH₃), 64.90, 71.46 (OCH₂), 107.57, 122.98, 140.90, 154.25, 166.14, 166.27 (C). MS (EI, 70 eV): 254 (M⁺, 40). Anal.: calcd. for C₁₂H₁₄O₆: C 56.69, H 5.55. Found: C 56.48, H 5.67.

4d: Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3d (622 mg, 1.80 mmol), 4d was isolated as a light yellow oil (312 mg, 68 %). ¹H NMR (acetone-d₆, 250 MHz): δ 1.90 (quintet, J = 5 Hz, 2 H, CH₂), 2.66 (m, J = 5 Hz, 4 H, CH₂), 5.80 (br, OH), 7.40-7.85 (m, 5 H, Ph). ¹³C NMR (acetone-d₆, 75 MHz): δ 19.23 (CH₃), 20.74, 21.33, 22.77 (CH₂), 115.34, 122.51 (C), 128.93, 129.93, 133.43 (CH, Ph), 139.54, 149.96 (C), 164.79, 194.14 (CO). MS (EI, 70 eV): 256 (M⁺, 100), 227 (46), 105 (58), 77 (56). Anal.: calcd. for C₁₅H₁₂O₄: C 70.31, H 4.72. Found: C 70.18, H 4.90.
4e: Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3e (540 mg, 1.80 mmol), 4e was isolated as a colourless solid (208 mg, 55 %). $^1$H NMR (CDCl$_3$, 250 MHz): $\delta = 1.35$ (t, $J = 6$ Hz, 3 H, CH$_3$), 2.78, 3.02 (2 x m, 2 x 2 H, CH$_2$), 4.28 (q, $J = 6$ Hz, 2 H, OCH$_2$), 5.30 (br, 1 H, OH). $^{13}$C NMR (acetone-d$_6$, 62.5 MHz): $\delta$ 13.75 (CH$_3$), 20.35, 31.79 (CH$_2$), 60.00 (OCH$_2$CH$_3$), 108.19, 132.80, 135.91, 156.49, 162.39, 168.34 (C). MS (EI, 70 eV): 210 (M$,^+$, 18). Anal.: calcd. for C$_{10}$H$_{10}$O$_5$: C 57.14, H 4.80. Found: C 57.50, H 4.92.

4f: Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3f (1.08 g, 3.28 mmol), 4f was isolated as a colourless solid (781 mg, 84 %), m. p. 78 °C. $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 1.28 (t, $J = 6$ Hz, 3 H, CH$_3$), 1.65-1.90 (m, 4 H, CH$_2$), 2.64 (m, 4 H, CH$_2$), 4.25 (q, $J = 6$ Hz, 2 H, OCH$_2$CH$_3$), 8.00 (br, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 62.5 MHz): $\delta$ 13.91 (CH$_3$), 23.88, 24.01, 26.59, 28.53 (CH$_2$), 61.55 (OCH$_2$CH$_3$), 117.21, 126.85, 141.60, 148.68, 164.82, 167.18 (C). MS (EI, 70 eV): 238 (M$,^+$, 100). Anal.: calcd. for C$_{12}$H$_{14}$O$_5$: C 60.50, H 5.92. Found: C 60.28, H 5.75.

4g: Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3g (1.088 g, 3.20 mmol), 4g was isolated as a colourless solid (600 mg, 75 %), m. p. 84 °C. $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 1.15 (s, 9 H, CH$_3$), 1.65-1.90 (m, 4 H, CH$_2$), 2.42, 2.59 (2 x t, $J = 5$ Hz, 2 x 2 H, CH$_2$), 7.90 (br, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 62.5 MHz): $\delta$ 24.64, 24.75 (CH$_2$), 27.07 (CH$_3$), 27.15, 30.91 (CH$_2$), 44.18 (C(CH$_3$)$_3$), 126.38, 127.24, 140.14, 141.54, 164.85, 213.56 (C). MS (EI, 70 eV): 250 (M$,^+$, 58). Anal.: calcd. for C$_{14}$H$_{18}$O$_4$: C 67.18, H 7.25. Found: C 67.02, H 7.37.

4h: Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 3h (1.094 g, 3.20 mmol), 4h was isolated as a colourless solid (596 mg, 74 %), m. p. 92 °C. $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ 1.27 (t, $J = 7$ Hz, 3 H, CH$_2$CH$_3$), 1.48 (m, 2 H, CH$_2$), 1.72 (m, 4 H, CH$_2$), 2.75, 2.80 (2 x t, $J = 6$ Hz, 2 x 2 H, CH$_2$), 4.24 (q, $J = 7$ Hz, 2 H, OCH$_2$), 8.00 (br, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 62.5 MHz): $\delta$ 14.02 (CH$_3$), 21.35, 22.38, 25.33, 26.41 (CH$_2$), 61.36 (OCH$_2$), 111.73, 125.80, 142.75, 153.06, 165.26,
Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene \(3i\) (1.032 g, 2.90 mmol), \(4i\) was isolated as a colourless oil (564 mg, 73 %). \(^1\)H NMR (CDCl\(_3\), 250 MHz): \(\delta\) 1.50 (m, 6 H, CH\(_2\)), 1.68 (m, 4 H, CH\(_2\)), 2.72 (m, 4 H, CH\(_2\)), 3.79 (s, 3 H, OCH\(_3\)), 7.90 (br, 1 H, OH). \(^{13}\)C NMR (CDCl\(_3\), 62.5 MHz): \(\delta\) 20.75, 21.59, 22.95, 24.62, 25.45, 26.41, 27.05 (CH\(_2\)), 52.39 (OCH\(_3\)), 117.70, 127.38, 143.39, 148.75, 164.81, 167.49 (C). MS (EI, 70 eV): 266 (M\(^+\), 60). Anal.: calcd. for C\(_{14}\)H\(_{18}\)O\(_5\): C 63.15, H 6.81. Found: C 62.92, H 6.95.

Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene \(3j\) (1.152 g, 3.00 mmol), \(4j\) was isolated as a colourless solid (615 mg, 70 %, \(E:Z = 1:4\)), m. p. 82 °C. \(^1\)H NMR (CDCl\(_3\), 250 MHz): \(\delta\) 1.20-1.60 (m, 14 H, CH\(_2\)), 2.32-2.55 (m, 4 H, CH\(_2\)), 3.78 (s, 3 H, OCH\(_3\)), 8.00 (br, 1 H, OH). \(^{13}\)C NMR (CDCl\(_3\), 62.5 MHz): \(Z\)-isomer: \(\delta\) 20.30, 20.42, 23.22, 23.27, 24.61, 24.89, 25.39, 25.54, 25.65 (CH\(_2\)), 52.33 (OCH\(_3\)), 117.69, 126.33, 142.75, 146.60, 164.04, 167.61 (C). \(E\)-Isomer: \(\delta\) 20.40, 22.63, 23.01, 23.22, 23.97, 24.45, 25.07, 25.23, 26.67, 29.28 (CH\(_2\)), 52.00 (OCH\(_3\)), 118.06, 126.83, 145.48, 154.16, 164.16, 168.30 (C). MS (EI, 70 eV): 294 (M\(^+\), 40), 263 (58), 249 (39), 234 (79). Anal.: calcd. for C\(_{16}\)H\(_{22}\)O\(_5\): C 65.29, H 7.53. Found: C 65.18, H 7.68.

**Synthesis of triflate (6):** To a CH\(_2\)Cl\(_2\) solution (7 mL) of butenolide \(4h\) (0.75 mmol, 190 mg) was added pyridine (1.88 mmol, 0.15 mL) and trifluoromethane sulfonic anhydride (0.90 mmol, 255 mg) at –78 °C. The temperature of the solution was warmed to 20 °C within 4 h and the mixture was stirred at 20 °C for 1 h. The reaction mixture was purified by chromatography (silica gel, CH\(_2\)Cl\(_2\)) to give 6 as a light yellow oil (225 mg, 78 %). \(^1\)H NMR (CDCl\(_3\), 250 MHz): \(\delta\) 1.26 (t, \(J = 7\) Hz, 3 H, CH\(_3\)), 1.47 (m, 2 H, CH\(_2\)), 1.65-1.80 (m, 4 H, CH\(_2\)), 2.71, 2.87 (2 x t, \(J = 7\) Hz, 2 x 2 H, CH\(_2\)), 4.21 (q, \(J = 7\) Hz, 2 H, OCH\(_2\)). \(^{13}\)C NMR (CDCl\(_3\), 62.5 MHz): \(\delta\) 13.74 (CH\(_3\)), 20.80, 23.94, 24.20, 24.93, 25.81 (CH\(_2\)), 61.65 (OCH\(_2\)), 119.42 (C), 120.71 (CF\(_3\)), \(q, J = 113.9\) Hz), 135.27,
146.02, 148.11, 159.72, 165.33. MS (EI, 70 eV): 384 (M⁺, 24). Anal.: calcd. for C₁₄H₁₅O₇SF₃: C 43.75, H 3.93. Found: C 43.68, H 3.75.

Synthesis of butenolide (7a): To a THF solution (3 mL) of triflate 6 (0.30 mmol, 115 mg) was added Pd₂dba₃·CHCl₃ (5 mol-%, 16 mg), P(2-furyl)₃ (10 mol-%, 14 mg) and LiCl (0.90 mmol, 39 mg). After stirring for 5 min trimethylphenylstannane (0.36 mmol, 0.086 mL) was added. After stirring for 24 h at 20 °C water (100 mL) was added. The aqueous layer was extracted with ether (4 x 100 mL) and the organic layer was dried (MgSO₄), filtrated and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography to give 14a as a yellow solid (63 mg, 68 %). ¹H NMR (CDCl₃, 250 MHz): δ 1.24 (t, J = 7 Hz, 3 H, CH₃), 1.48 (m, 2 H, CH₂), 1.62-1.84 (m, 4 H, CH₂), 2.68, 2.85 (2 x t, J = 7 Hz, 2 x 2 H, CH₂), 4.20 (q, J = 7 Hz, 2 H, OCH₂), 7.10-7.30 (m, 5 H, Ph). ¹³C NMR (CDCl₃, 62.5 MHz): δC 13.70 (CH₃), 20.78, 23.91, 24.24, 24.92, 25.75 (CH₂), 61.58 (OCH₂), 119.40 (C), 126.28, 126.92, 128.02, 133.08, 135.27, 132.08, 148.11, 159.72, 165.33. MS (70 eV, EI), m/z (%): 312 (40) [M⁺], 229 (26), 201 (24). Anal.: calcd. for C₁₉H₂₀O₄: C 73.06, H 6.45; found: C 72.78; H 6.72.

Synthesis of butenolide (7b): To a THF solution (5 mL) of triflate 6 (0.46 mmol, 176 mg) was added Pd₂dba₃·CHCl₃ (10 mol-%, 48 mg), P(2-furyl)₃ (20 mol-%, 43 mg) and LiCl (1.38 mmol, 59 mg). After stirring for 5 min tetramethylstannane (0.55 mmol, 0.080 mL) was added. After stirring for 24 h at 55 °C water (100 mL) was added. The aqueous layer was extracted with ether (4 x 100 mL) and the organic layer was dried (MgSO₄), filtrated and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography to give 7b as a yellow solid (74 mg, 64 %). ¹H NMR (CDCl₃, 250 MHz): δ 1.24 (t, J = 7 Hz, 3 H, CH₃), 1.50 (m, 2 H, CH₂), 1.62-1.82 (m, 4 H, CH₂), 2.15 (s, 3 H, CH₃), 2.70, 2.85 (2 x t, J = 7 Hz, 2 x 2 H, CH₂), 4.22 (q, J = 7 Hz, 2 H, OCH₂). ¹³C NMR (CDCl₃, 62.5 MHz): δC 8.10, 13.74 (CH₃), 20.82, 23.91, 24.25, 24.90, 25.84 (CH₂), 61.64 (OCH₂), 119.46, 132.14, 135.26, 148.14, 159.70, 165.31. MS (70 eV, EI), m/z (%): 250 (12) [M⁺]. Anal.: calcd. for C₁₄H₁₈O₄: C 67.18, H 7.25; found: C 66.90, H 7.48.
Synthesis of 1,3-Bis(trimethylsilyloxy)-1,3-butadiene (8). Diene 8 was prepared according to the procedure given for the synthesis of diene 3a. The dianion of cyclooctane-1,3-dione was generated in the presence of HMPA (2 equiv.). Starting with cyclooctane-1,3-dione (840 mg, 6.00 mmol), 8 was isolated as a light yellow oil (1.30 g, 76%). The crude material was used for the cyclization reaction with oxalyl chloride. \(^1\)H NMR (CDCl\(_3\), 250 MHz): \(\delta\) 0.12, 0.22 (2 x s, 2 x 9 H, Me\(_3\)Si), 1.40-1.70 (m, 4 H, CH\(_2\)), 1.98, 2.24 (2 x m, 2 x 2 H, CH\(_2\)), 4.90 (t, \(J = 11\) Hz, 1 H, CH), 4.98 (s, 1 H, CH). MS (EI, 70 eV): 284 (M\(^+\), 12), 73 (100). HRMS calcd. for C\(_{14}\)H\(_{28}\)O\(_2\)Si\(_2\): 284.1628, found 284.1626.

Synthesis of Butenolide (9): Butenolide 9 was prepared according to the procedure given for the synthesis of butenolides 4a-j. Starting with 1,3-bis(trimethylsilyloxy)-1,3-butadiene 8 (425 mg, 1.50 mmol), 9 was isolated as a light yellow oil (178 mg, 61%). \(^1\)H NMR (CDCl\(_3\), 250 MHz): \(\delta\) 1.72, 1.95 (2 x m, 2 x 2 H, CH\(_2\)), 2.57 (m, 4 H, CH\(_2\)), 5.79 (s, 1 H, CH), 7.40 (br, 1 H, OH). \(^{13}\)C NMR (CDCl\(_3\), 62.5 MHz): \(\delta\) 19.68, 21.81, 25.67, 41.75 (CH\(_2\)), 108.02 (CH), 122.78, 144.44, 157.08, 164.48 (C), 204.71 (CO). MS (EI, 70 eV): 194 (M\(^+\), 28). Anal.: calcd. for C\(_{10}\)H\(_{16}\)O\(_4\): C 61.85, H 5.19. Found: C 61.60, H 5.42.