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, CH_2Cl_2 from CaH_2. For the ^{1}H and ^{13}C NMR spectra (^{1}H NMR: 250 MHz, ^{13}C NMR: 62.5 MHz) the deuterated solvents indicated were used. The multiplicity of the ^{13}C NMR signals were determined with the DEPT 135 technique. Yields refer to analytically pure samples. Isomer ratios were derived from suitable ^{1}H NMR integrals. Mass spectral data (MS) were obtained using the electron ionization (70 eV) or the chemical ionization technique (CI, H_2O). 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 di*iso*propylamine (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 %). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.14, 0.21 (2 x s, 2 x 9 H, Me_3Si), 1.22 (t, *J* = 8 Hz, 3 H, CH_3), 1.58 (m, 2 H, CH_2), 2.06, 2.31 (2 x m, 2 x 2 H, CH_2), 3.79 (q, *J* = 8 Hz, 2 H, OCH_2), 4.78 (t, *J* = 6 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 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 $C_{15}H_{30}O_3Si_2$ 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): δ 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): δ 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 $C_{16}H_{32}O_3Si_2$ 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): δ 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): δ 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 $C_{16}H_{32}O_4Si_2$ 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): δ 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 $C_{19}H_{30}O_2Si_2$ 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): δ 0.21, 0.23 (2 x s, 2 x 9 H,

Me_3Si), 1.21 (t, J = 8 Hz, 3 H, CH_3), 1.20-1.30 (m, 2 x H, CH_2), 2.24 (m, 2 H, CH_2), 3.80 (q, J = 8 Hz, 2 H, OCH_2CH_3), 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 ($CDCl_3$, 250 MHz): δ 0.10, 0.21 (2 x s, 2 x 9 H, Me_3Si), 1.22 (t, J = 7 Hz, 3 H, CH_3), 1.45-1.65 (2 x m, 2 x H, CH_2), 1.95, 2.18 (2 x m, 2 x 2 H, CH_2), 3.82 (q, J = 7 Hz, 2 H, OCH_2CH_3), 4.94 (t, J = 6.5 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 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 $C_{16}H_{32}O_3Si_2$ 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 ($CDCl_3$, 250 MHz): δ 0.10, 0.19 (2 x s, 2 x 9 H, Me_3Si), 1.18 (s, 9 H, CH_3), 1.35-1.75 (m, 6 H, CH_2), 1.98 (m, 2 H, CH_2), 4.90 (t, J = 6.5 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 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 $C_{18}H_{36}O_2Si_2$ 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 ($CDCl_3$, 250 MHz): δ 0.17, 0.20 (2 x s, 2 x 9 H, Me_3Si), 1.25 (t, J = 7 Hz, 3 H, CH_3), 1.45-1.55 (m, 6 H, CH_2), 1.95, 2.18 (2 x m, 2 x 2 H, CH_2), 3.82 (q, J = 7 Hz, 2 H, OCH_2CH_3), 4.75 (t, J = 7 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 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 $C_{17}H_{34}O_3Si_2$ 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): δ 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): δ 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 $C_{18}H_{36}O_3Si_2$ 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): δ 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): δ 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 $C_{17}H_{32}O_3Si$ 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 di*iso*propylamine (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 ($CDCl_3$, 250 MHz, major isomer): δ 0.14, 0.18 (2 x s, 2 x 9 H, Me_3Si), 1.20-1.40 (m, 14 H, CH_2), 2.00-2.10 (m, 4 H, CH_2), 3.48 (s, 3 H, OCH_3), 4.54 (t, *J* = 7 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 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 $C_{18}H_{36}O_3Si_2$ 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 CH_2Cl_2-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 CH_2Cl_2-solution (7 mL) of Me_3SiOTf (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 ($MgSO_4$), 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-d_6, 250 MHz): δ 1.28 (t, *J* = 6 Hz, 3 H, CH_3), 1.80 (quintet, *J* = 5 Hz, 2 H, CH_2), 2.52 (t, *J* = 5 Hz, 2 H, CH_2), 2.58 (t, *J* = 5 Hz, 2 H,

CH_2), 4.18 (q, *J* = 6 Hz, 2 H, OCH_2). ^{13}C NMR (acetone-d_6, 75 MHz): δ 14.57 (CH_3), 21.16, 22.53, 25.14 (CH_2), 60.99 (OCH_2), 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 $C_{11}H_{12}O_5$: 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 %). ^{1}H NMR (acetone-d_6, 250 MHz): δ 1.24 (d, *J* = 6 Hz, 6 H, CH_3), 1.76 (quintet, *J* = 6 Hz, 2 H, CH_2), H, $CH_2$2.46 (t, *J* = 6 Hz, 2), 2.54 (t, *J* = 6 Hz, 2 H, CH_2), 4.99 (hept, *J* = 6 Hz, 2 H, OCH). ^{13}C NMR (acetone-d_6, 75 MHz): δ 20.99 (CH_2), 21.98 (CH_3), 22.34, 24.98 (CH_2), 68.46 (OCH), 108.23, 123.09, 139.64, 152.43, 164.47, 165.20 (C). MS (EI, 70 eV): 238 (M$^+$, 42). Anal.: calcd. for $C_{12}H_{14}O_5$: 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 %). ^{1}H NMR (MeOH-d_4, 250 MHz): δ 1.78 (quintet, *J* = 7 Hz, 2 H, CH_2), 2.50 (q, *J* = 7 Hz, 4 H, CH_2), 3.38 (s, 3 H, CH_3), 3.62, 4.27 (2 x t, *J* = 5 Hz, 2 x 2 H, OCH_2). ^{13}C NMR (MeOH-d_4, 62.5 MHz): δ 21.39, 22.88, 25.35 (CH_2), 59.22 (OCH_3), 64.90, 71.46 (OCH_2), 107.57, 122.98, 140.90, 154.25, 166.14, 166.27 (C). MS (EI, 70 eV): 254 (M$^+$, 40). Anal.: calcd. for $C_{12}H_{14}O_6$: 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 %). ^{1}H NMR (acetone-d_6, 250 MHz): δ 1.90 (quintet, *J* = 5 Hz, 2 H, CH_2), 2.66 (m, *J* = 5 Hz, 4 H, CH_2), 5.80 (br, OH), 7.40-7.85 (m, 5 H, Ph). ^{13}C NMR (acetone-d_6, 75 MHz): δ 19.23 (CH_3), 20.74, 21.33, 22.77 (CH_2), 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 $C_{15}H_{12}O_4$: 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): δ = 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): δ 13.75 (CH_3), 20.35, 31.79 (CH_2), 60.00 ($O\mathit{C}H_2CH_3$), 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): δ 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, $OC\mathit{H}_2CH_3$), 8.00 (br, 1 H, OH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.91 (CH_3), 23.88, 24.01, 26.59, 28.53 (CH_2), 61.55 ($O\mathit{C}H_2CH_3$), 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): δ 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): δ 24.64, 24.75 (CH_2), 27.07 (CH_3), 27.15, 30.91 (CH_2), 44.18 ($\mathit{C}(CH_3)_3$), 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): δ 1.27 (t, *J* = 7 Hz, 3 H, $CH_2C\mathit{H}_3$), 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): δ 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, 166.83 (C). MS (EI, 70 eV): 252 (M^+, 32). Anal.: calcd. for $C_{13}H_{16}O_5$: C 61.89, H 6.39. Found: C 61.62, H 6.60.

4i: 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): δ 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): δ 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.

4j: 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): δ 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: δ 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, 164.64, 167.61 (C). *E*-Isomer: δ 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_2Cl_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_2Cl_2) to give **6** as a light yellow oil (225 mg, 78 %). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 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): δ_C 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 $C_{14}H_{15}O_7SF_3$: 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 $Pd_2dba_3{\cdot}CHCl_3$ (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 ($MgSO_4$), 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 %). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.24 (t, *J* = 7 Hz, 3 H, CH_3), 1.48 (m, 2 H, CH_2), 1.62-1.84 (m, 4 H, CH_2), 2.68, 2.85 (2 x t, *J* = 7 Hz, 2 x 2 H, CH_2), 4.20 (q, *J* = 7 Hz, 2 H, OCH_2), 7.10-7.30 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ_C 13.70 (CH_3), 20.78, 23.92, 24.24, 24.92, 25.75 (CH_2), 61.58 (OCH_2), 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 $C_{19}H_{20}O_4$: 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 $Pd_2dba_3{\cdot}CHCl_3$ (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 ($MgSO_4$), 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 %). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.24 (t, *J* = 7 Hz, 3 H, CH_3), 1.50 (m, 2 H, CH_2), 1.62-1.82 (m, 4 H, CH_2), 2.15 (s, 3 H, CH_3), 2.70, 2.85 (2 x t, *J* = 7 Hz, 2 x 2 H, CH_2), 4.22 (q, *J* = 7 Hz, 2 H, OCH_2). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ_C 8.10, 13.74 (CH_3), 20.82, 23.91, 24.25, 24.90, 25.84 (CH_2), 61.64 (OCH_2), 119.46, 132.14, 135.26, 148.14, 159.70, 165.31. MS (70 eV, EI), m/z (%): 250 (12) [M^+]. Anal.: calcd. for $C_{14}H_{18}O_4$: 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): δ 0.12, 0.22 (2 x s, 2 x 9 H, Me_3Si), 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 $C_{14}H_{28}O_2Si_2$: 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-butdiene **8** (425 mg, 1.50 mmol), **9** was isolated as a light yellow oil (178 mg, 61 %). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 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): δ 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 $C_{10}H_{10}O_4$: C 61.85, H 5.19. Found: C 61.60, H 5.42.