Supporting Information

Desymmetrization of 1,4-Dien-3-ols and Related Compounds via Ueno-Stork Radical Cyclizations

Félix Villar, Olivier Equey and Philippe Renaud*
Université de Fribourg, Institut de Chimie Organique, Pérolles, CH-1700 Fribourg, Switzerland

General techniques. THF was freshly distilled from K under N_2; CH_2Cl_2 from CaH_2 under N_2. Et_3B soln. (1M) in hexane was freshly prepared from commercially available Et_3B (95%, *Aldrich*). Other reagents were obtained from commercial sources and used as received. Flash column chromatography (FC) and filtration: *Baker* silica gel (0.063-0.200 mm); AcOEt, Et_2O and hexane as eluents. Thin-layer chromatography (TLC): *Merck* silica gel 60 F_{254} analytical plates; detection either with UV or by spraying with a soln. of vanilin and subsequent heating. FT–IR: *Mattson Unicam 5000*. NMR: *Varian Gemini 200* (^{1}H = 200 MHz, ^{13}C = 50.3 MHz), *Bruker AM 360* (^{1}H = 360 MHz*), Bruker avance DRX 500* (^{1}H = 500.13 MHz, ^{13}C = 125.8 MHz); chemical shift δ in ppm relative to tetramethylsilane (= 0 ppm) or $CHCl_3$ (= 7.26 ppm) for ^{1}H and $CDCl_3$ (= 77.0 ppm) for ^{13}C. MS: *Vacuum Generators Micromass VG 70/70E* and *DS 11-250*; CI (CH_4), EI (70 eV); m/z (%). High resolution mass spectra (HRMS) were recorded on a FTICR mass spectrometer *Bruker 4.7 BioApex II*. Elementary analysis: Ilse Beetz, Microanalytisches Laboratorium, D-8640 Kronach (Germany).

Preparation of haloacetals

General procedure 1.[1] To a soln. of the dienol (10 mmol) and the enol ether (10 mmol) in CH_2Cl_2 (10 mL) cooled at –20°C was added in portions *N*-halosuccinimide (10 mmol). The resulting mixture was stirred for 2–3 h below –20 °C. Hexane was added and the precipitate was filtered off. The filtrate was washed successively with 5% aq. KOH, water and brine. After drying and evaporation of the solvents, the crude product was purified by FC (hexane/Et_2O).

3-(2-Bromo-1-ethoxy)-1,4-pentadiene (1). Prepared according to general procedure 1 from ethyl vinyl ether (0.72 g, 10 mmol), 1,4-pentadien-3-ol (840 mg, 10 mmol) and NBS (1.78 g, 10 mmol). FC (hexane/Et_2O 40:1) gave **1** (2.02 g, 86%) as a colorless oil. IR (KBr): 3029, 2978, 2883, 1420, 1115, 1028, 928 cm^{-1}. ^{1}H NMR (360 MHz): 5.92–5.71 (m, 2H, 2 C*H*=CH_2), 5.32–5.15 (m, 4H, 2 C*H*$_2$=CH), 4.77 (t, 1H, J = 5.2 Hz, OC*H*CH_2Br), 4.54 (tt, 1H, J = 1.2, 6.1 Hz, C*H*(CH=CH_2)$_2$, 3.65 (dq, 1H, J = 7.0, 9.2 Hz, CH_3C*H*H), 3.58 (dq, 1H, J = 7.0, 9.5 Hz, CH_3CH*H*), 3.39 (dd, 2H, J = 2.7, 5.2 Hz, C*H*$_2$Br), 1.23 (t, 3H, J = 7.0 Hz, CH_3). ^{13}C NMR (50 MHz): 137.4 (d), 136.9 (d), 117.5 (t), 116.3 (t), 99.5 (d), 78.8 (d), 62.0 (t), 32.1 (t), 15.2 (q). MS (EI) m/z (%):153 (M^+–84, 65), 151 (M^+–84, 65), 125 (36), 123 (37), 67 (100), 65 (20). Anal. Calcd for $C_9H_{15}O_2Br$ (235.12): C, 45.98; H, 6.43. Found: C, 46.00; H, 6.38.

3-(2-Bromo-1-ethoxy-2-methylpropoxy)-1,4-pentadiene (2). Prepared according to general procedure 1 from 1-ethoxy-2-methyl-1-propene[2] (1.00 g, 10 mmol), 1,4-pentadien-3-ol (840 mg, 10 mmol) and NBS (1.78 g, 10 mmol). FC (hexane/Et_2O 20:1) afforded **2** (1.12 g, 43%) as a colorless oil. IR (KBr): 3084, 2978, 2876, 1464, 1383, 1112, 1055, 927 cm^{-1}. ^{1}H NMR (360 MHz): 5.92–5.73 (m, 2H, 2 C*H*=CH_2), 5.32–5.15 (m, 4H, 2 C*H*$_2$=CH), 4.56 (tt, 1H, J = 0.9, 5.8 Hz, C*H*(CH=CH_2)$_2$), 4.54 (s, 1H, OC*H*CBrMe_2), 3.82 (dq, 1H, J = 7.0, 9.1 Hz,

CH_3CHH), 3.68 (dq, 1H, J = 7.0, 9.2 Hz, CH_3CHH), 1.74 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.23 (t, 3H, CH_3). ^{13}C NMR (50 MHz): 137.7 (d), 137.1 (d), 117.7 (t), 116.2 (t), 105.2 (d), 80.4 (d), 67.1 (t), 29.1 (q), 28.4 (q), 15.4 (q). MS (EI) m/z (%): 181 (M^+–84, 63), 179 (M^+–84, 65), 153 (9), 151 (9), 75 (20), 67 (100). Anal. Calcd. For $C_{11}H_{19}O_2Br$ (263.18): C, 50.20; H, 7.28. Found: C, 50.83; H, 7.46%.

Methyl 3-ethoxy-2-iodo-3-[(1-vinyl-2-propenyl)-oxy]propanoate (3). To a soln. of methyl (*E*)-3-ethoxy-2-propenoate[3] (1.69 g, 13 mmol) and 1,4-pentadien-3-ol (0.93 g, 11 mmol) in CH_2Cl_2 (10 mL) was added in portions NIS (2.92 g, 13 mmol) at 0 °C. The resulting mixture, protected from the light, was stirred at rt for 3 days. The precipitate was diluted in hexane and filtered off. The filtrate was washed with $Na_2S_2O_3$ (sat.) and brine. Drying and evaporation in vacuo afforded a yellow oil that was purified by flash chromatography (hexane/Et_2O 10:1) to furnished the iodoacetal **3** (2.24 g, 60%). IR (KBr): 3082, 2978, 2895, 1741, 1435, 1303, 1253, 1109, 1030, 929 cm^{-1}. ^{1}H NMR (360 MHz): 5.85–5.60 (m, 2H, 2 $CH{=}CH_2$), 5.30–5.15 (m, 4H, 2 $CH_2{=}CH$), 5.03 (d, 1H, J = 8.6 Hz, $CHICO_2Me$), 4.55 (dt, 1H, J = 1.2, J = 7.3 Hz, $CH(CH{=}CH_2)_2$), 4.46 (d, 1H, J = 8.5 Hz, $OCHCHICO_2Me$), 3.82–3.61 (m, 2H, OCH_2CH_3), 3.73 (s, 3H, CH_3O), 1.24 (t, 3H, J = 7.3 Hz, CH_3CH_2O). ^{13}C NMR (50 MHz): 169.9 (s), 137.2 (d), 136.4 (d), 117.7 (t), 116.4 (t), 100.2 (d), 79.7 (d), 61.6 (t), 52.8 (d), 21.4 (q), 14.9 (q). MS (EI) m/z (%): 257 (M^+–83, 56), 229 (17), 197 (17), 169 (19), 127 (12), 103 (19), 89 (34), 67 (100), 55 (16). Anal. Calcd. for $C_{11}H_{17}O_4I$ (340.16): C, 38.84; H, 5.04. Found: C, 39.10; H, 5.18.

3-(2-Bromo-1-ethoxy-3-methylbutoxy)-1,4-pentadiene (4). Prepared according to general procedure 1 from (*Z/E*)-1-ethoxy-3-methyl-1-butene[2] (1.14 g, 10 mmol), 1,4-pentadien-3-ol (840 mg, 10 mmol) and NBS (1.78 g, 10 mmol). FC (hexane/Et_2O 20:1) furnished **4** (0.47 g, 17%) as a colorless oil. Mixture of diastereomers. IR (KBr): 3084, 2968, 2877, 1464, 1386, 1109, 1035, 925 cm^{-1}. ^{1}H NMR (360 MHz): 5.95–5.65 (m, 2H, 2 $CH{=}CH_2$), 5.32–5.15 (m, 4H, 2 $CH_2{=}CH$), 4.70 (d, 1H, J = 7.0 Hz, $OCHCHBr$), 4.56 (t, 1H, J = 6.1 Hz, $CH(CH{=}CH_2)_2$), 4.03 (dd, 1H, J = 3.1, 7.3 Hz, $OCHCHBr$), 3.68–3.56 (m, 2H, CH_3CH_2O), 2.18–2.05 (m, 1H, $CH(CH_3)_2$), 1.20 (t, 3H, J = 7.0 Hz, CH_3CH_2O), 1.01 (d, 3H, J = 6.7 Hz, CH_3), 0.96 (d, 3H, J = 6.7 Hz, CH_3). ^{13}C NMR (50 MHz): 137.6 (d), 137.5 (d), 117.6 (t), 116.3 (t), 100.8 (d), 79.4 (d), 64.5 (d), 61.4 (t), 29.4 (d), 22.0 (q), 17.7 (q), 15.2 (q). MS (EI) m/z (%): 195 (M^+–84, 98), 193 (M^+–84, 100), 167 (8), 165 (8), 137 (26), 113 (84), 85 (57), 75 (31), 55 (62). HRMS (ESI) for $C_{12}H_{21}O_2BrNa$: calculated 299.06171; found 299.06128.

4-[1-(*tert*-Butoxy)-2-iodomethoxy[-4-methyl-2,5-cyclohexadien-1-one (5). Prepared according to the general procedure 1 from *tert*butyl vinyl ether (1.00 g, 10 mmol) and 4-hydroxy-4-methyl-2,5-cyclohexadien-1-one[4] (1,24 g, 10 mmol) in CH_2Cl_2 (10 mL) and NIS (2.25 g, 10 mmol). The resulting mixture was stirred at rt overnight protected from the light. After work up, FC (hexane/EtO_2 5:1) gave **5** (2.80 g, 80%) as a colorless oil. IR (KBr): 3043, 2978, 2931, 1668, 1631, 1338, 1091 cm^{-1}. ^{1}H NMR (360 MHz): 7.04 (dd, 1H, J = 3.1, 5.1 Hz, $CH{=}CH$), 7.01 (dd, 1H, J = 3.1, 5.1 Hz, $CH{=}CH$), 6.31 (dd, 1H, J = 3.1, 10.1 Hz, $CH{=}CH$), 6.22 (dd, 1H, J = 3.1, 10.1 Hz, $CH{=}CH$), 4.69 (dd, 1H, J = 4.0, 5.8 Hz, $OCHCH_2I$), 3.15 (dd, 2H, J = 4.0, 5.8 Hz, CH_2I), 1.48 (s, 3H, CH_3), 1.19 (s, 9H, *t*Bu). ^{13}C NMR (50 MHz): 185.0 (s), 152.5 (d), 151.2 (d), 129.6 (d), 128.0 (d), 95.0 (d), 75.4 (s), 72.5 (s), 29.1 (q), 27.5 (q), 10.0 (q). MS (EI) m/z (%): 351 (M^++1, 2), 153 (25), 125 (63), 124 (16), 109 (20), 108 (14), 107 (100), 77 (28), 57 (66), 53 (12). Anal.Calcd. for $C_{13}H_{19}O_3I$ (350.20): C, 44.59; H, 5.47. Found: C, 44.41; H, 5.45.

Radical Reactions

Method A[5]. A soln. of the haloacetal (2.1 mmol) and Bu_3SnH (735 mg, 2.5 mmol) in toluene (52 mL) was cooled at –78 ºC and a 1M soln. of Et_3B in hexane (2.9 mL, 2.9 mmol) was added followed by air (2.0 mL). The soln. was kept at –78 ºC for 3 h. A 1M NaOH soln. (30 mL) was added and the heterogeneus mixture was stirred for 2 h at rt. The organic layer was washed with H_2O, dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by FC (hexane/Et_2O).

Method B. A soln. of Bu_3SnH (735 mg, 2.52 mmol), AIBN (17 mg, 0.11 mmol) and the haloacetal (2.1 mmol) was heated under reflux in benzene (20 mL). The reaction was monitored by TLC. Then after cooling a 1M NaOH soln. (30 mL) was added and the heterogeneus mixture was stirred for 2 h at rt. The organic layer was washed with H_2O, dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by FC (hexane/Et_2O).

Method C. A soln. of the haloacetal (1 mmol) and $(Bu_3Sn)_2$ (58 mg, 0.1 mmol) in benzene (5 mL) was irradiated with a sun lamp for 2 h at 10 ºC. A KF aqueous soln. was added and the mixture was stirred for 2 h. The organic layer was washed with water, dried over $MgSO_4$ and evaporated. The crude product was purified by FC (hexane/Et_2O).

Method D. A soln. of 2-(methoxycarbonyl)propenyltributylstannane (1.55 g, 4 mmol), AIBN (4 mg, 0.025 mmol) and the haloacetal (0.5 mmol) in benzene (6 mL) was heated under reflux. The reaction was monitored by TLC until disappearance of the starting material. A KF aqueous soln. was added and the mixture was stirred at rt for 2 h. The organic layer was washed with H_2O, dried over $MgSO_4$ and evaporated. The crude product was purified by FC (hexane/Et_2O).

5-Ethoxy-3-methyl-2-vinyltetrahydrofuran (6). Prepared according to the Method A from **1** (0.49 g, 2.1 mmol), Bu_3SnH (735 mg, 2.5 mmol) and a 1M soln. of Et_3B in hexane (2.9 mL, 2.9 mmol). FC (hexane/Et_2O 10:1) gave **6** (0.21g, 65%) as a single diastereomer.
IR (KBr): 3082, 2974, 2876, 1448, 1375, 1107, 985, 923 cm^{-1}. ^1H NMR (360 MHz): 5.77 (ddd, 1H, J = 7.3, 10.4, 17.4 Hz, C*H*=CH_2), 5.32–5.16 (m, 2H, CH_2=CH), 5.15 (dd, 1H, J = 4.0, 5.8 Hz, OC*H*CH_2), 3.93 (t, 1H, J = 8.2 Hz, C*H*CH=CH_2), 3.79 (dq, 1H, J = 7.0, 9.5 Hz, CH_3C*H*H), 3.45 (dq, 1H, J = 7.0, 9.5 Hz, CH_3CH*H*), 2.40 (ddd, 1H, J = 5.8, 8.9, 13.4 Hz, OCHC*H*H), 1.91–1.77 (m, 1H, C*H*Me), 1.57 (ddd, 1H, J = 3.7, 9.2, 13.1 Hz, OCHCH*H*), 1.20 (t, 3H, J = 7.0 Hz, CH_3), 1.03 (d, 3H, J = 6.4 Hz, CH_3). ^{13}C NMR (50 MHz): 137.1 (d), 117.2 (t), 103.7 (d), 85.4 (d), 63.4 (t), 41.2 (t), 39.2 (d), 15.8 (q), 15.3 (q). MS (EI) m/z (%): 157 (M^++1, 5), 111 (69), 100 (100), 93.10 (71), 85 (74), 82 (27), 72 (38), 67 (76), 57 (74). HRMS (CI, isobutane) for $C_9H_{15}O_2$ ([M^+–1]): calculated 155.10665; found 155.10660.

2-Ethoxy-3,3,4-trimethyl-5-vinyltetrahydrofuran (7). Prepared according to the Method A from the bromoacetal **2** (0.55 g, 2.1 mmol), Bu_3SnH (735 mg, 2.5 mmol) and a 1M soln of Et_3B in hexane (2.9 mL, 2.9 mmol). FC (hexane/Et_2O 10:1) furnished **7** as a mixture of diastereomers (0.29g, 75%, 86% ds). According to the Method B from **2** (0.55 g, 2.1 mmol), Bu_3SnH (735 mg, 2.52 mmol) and AIBN (17 mg, 0.11 mmol). Compound **7** (0.34 g, 88%,. 74% ds) was obtained after FC.
Major diastereomer. IR (KBr): 3082, 2974, 2877, 1645, 1469, 1388, 1109, 1020, 922 cm^{-1}. ^1H NMR (360 MHz): 5.80 (ddd. 1H, J = 7.3, 10.1, 17.1, C*H*=CH_2), 5.23 (ddd, 1H, J = 0.9, 1.5, 17.1 Hz, CH*H*=CH), 5.13 (ddd, 1H, J = 0.9, 1.5, 10.1 Hz, C*H*H=CH), 4.69 (s, 1H,

OC*H*CMe$_2$), 4.00 (dd, 1H, J = 7.3, 8.2 Hz, C*H*CH=CH$_2$), 3.82 (dq, 1H, J = 7.0, 9.5 Hz, CH$_3$C*H*H), 3.48 (dq, 1H, J = 7.0, 9.8 Hz, CH$_3$CH*H*), 1.57 (dq, 1H, J = 7.0, 8.2 Hz, C*H*Me), 1.20 (t, 3H, J = 7.0 Hz, *CH*$_3$CH$_2$), 1.00 (s, 3H, CH$_3$), 0.87 (s, 3H, CH$_3$), 0.86 (d, 3H, J = 6.7 Hz, CHC*H*$_3$). ^{13}C NMR (50 MHz): 138.8 (d), 116.0 (t), 111.1 (d), 84.8 (d), 64.5 (t), 48.5 (d), 43.9 (s), 25.9 (q), 16.0 (q), 15.3 (q), 11.2 (q). Anal. Calcd. for $C_{11}H_{20}O_2$ (183.99): C, 71.70; H, 10.94. Found: C, 71.42; H, 10.93.

Methyl-2-ethoxy-4-iodomethyl-5-vinyltetrahydro-3-furancarboxylate (8). Prepared according to the Method C from the iodoacetal **3** (0.34 g, 1 mmol) and (Bu$_3$Sn)$_2$ (58 mg, 0.1 mmol). FC (hexane/Et$_2$O 5:1) afforded **8** as a mixture of diastereomers (0.24 g, 71%, 77% ds).

Major diastereomer. IR (KBr): 3082, 2978, 1739, 1437, 1199 cm^{-1}. ^{1}H NMR (360 MHz): 5.85 (ddd, 1H, J = 7.6, 10.2, 17.2 Hz, C*H*=CH$_2$), 5.39 (dt, 1H, J = 1.1, 17.1 Hz, C*H*H=CH), 5.33 (d, 1H, J = 2.5 Hz, OC*H*CHCO$_2$Me), 5.28 (ddd, 1H, J = 0.8, 1.4, 10.2 Hz, CH*H*=CH), 4.25 (t, 1H, J = 8.0 Hz, C*H*CH=CH$_2$), 3.77 (dq, 1H, J = 7.0, 9.7 Hz, CH$_3$C*H*H), 3.75 (s, 3H, CH$_3$), 3.49 (dq, 1H, J = 7.0, 9.4 Hz, CH$_3$CH*H*), 3.39 (dd, 1H, J = 4.9, 10.3 Hz, CHC*H*HI), 3.28 (dd, 1H, J = 6.3, 10.3 Hz, CHCH*H*I), 3.00 (dd, 1H, J = 2.5, 7.4 Hz, C*H*CO$_2$Me), 2.29 (m, 1H, CH), 1.22 (t, 3H, J = 7.2 Hz, C*H*$_3$CH$_2$). ^{13}C NMR (50 MHz): 171.7 (s), 135.7 (d), 118.9 (t), 104.5 (d), 84.2 (d), 63.5 (d), 57.7 (d), 52.5 (q), 48.7 (d), 15.1 (q), 6.0 (q). MS (EI) m/z (%): 341 (M$^+$+1, 4), 295 (100), 254 (7), 127 (4), 58 (6). Anal. Calcd. for $C_{11}H_{17}IO_4$ (340.16): C, 38.84; H, 5.04. Found: C, 38.74; H, 5.09.

2-Ethoxy-3-*iso*propyl-4-methyl-5-vinyltetrahydrofuran (9). Prepared according to the Method A from the bromoacetal **4** (0.58 g, 2.1 mmol), Bu$_3$SnH (735 mg, 2.5 mmol) and a 1M soln. of Et$_3$B in hexane (2.9 mL, 2.9 mmol). FC (hexane:Et$_2$O 40:1) gave *minor*-**9** (0.10 g) and *major*-**9** (0.17 g) in 66% yield and 63% ds.

Compound **9**-minor. ^{1}H NMR (360 MHz): 5.86 (ddd, 1H, J = 6.7, 10.4, 17.1 Hz, C*H*=CH$_2$), 5.20 (dt, 1H, J = 1.5, 17.1 Hz, C*H*H=CH), 5.04 (dt, 1H, J = 1.2, 10.4 Hz, CH*H*=CH), 4.97 (d, 1H, J = 4.6 Hz, OC*H*CH*i*–Pr), 4.21 (dquint, 1H, J = 1.2, 6.4 Hz, C*H*CH=CH$_2$), 3.76 (dq, 1H, J = 7.3, 9.8 Hz, CH$_3$C*H*H), 3.40 (dq, 1H, J = 7.2, 9.7 Hz, CH$_3$CH*H*), 2.04–1.94 (m, 1H, C*H*Me), 1.91-1.80 (m, 1H, C*H*Me$_2$), 1.72–1.65 (m, 1H, C*Hi*–Pr), 1.20–1.14 (m, 6H, C*H*$_3$CH$_2$, CH$_3$), 0.94 (d, 3H, J = 6.4 Hz, CH$_3$), 0.90 (d, 3H, J = 6.7 Hz, CH$_3$). ^{13}C NMR (50 MHz): 139.5 (d), 114.0 (t), 104.9 (d), 87.6 (d), 62.9 (t), 53.4 (d), 39.1 (d), 23.9 (d), 21.8 (q), 21.5 (q), 16.0 (q), 15.4 (q).

Compound **9**-major. ^{1}H NMR (500 MHz): 5.79 (ddd, 1H, J = 7.5, 10.3, 17.2 Hz, CH=CH$_2$), 5.27 (ddd, 1H, J = 1.0, 1.7, 17.2 Hz, C*H*H=CH), 5.17 (ddd, 1H, J = 0.8 , 1.7, 10.3 Hz, CH*H*=CH), 4.83 (d, 1H, J = 2.7 Hz, OC*H*CH*i*–Pr), 3.99 (t, 1H, J = 8.3 Hz, C*H*CH=CH$_2$), 3.77 (dq, 1H, J = 7.1, 9.7 Hz, CH$_3$C*H*H), 3.45 (dq, 1H, J = 7.0, 9.7 Hz, CH$_3$CH*H*), 1.73–1.68 (m, 1H, C*H*-Me$_2$), 1.59–1.55 (m, 1H, C*H*Me), 1.51-1.46 (m, 1H, C*Hi*–Pr), 1.20 (t, 3H, J = 7.1 Hz, C*H*$_3$CH$_2$), 1.1 (d, 3H, J = 6.4 Hz, CHC*H*$_3$), 0.95 (d, 3H, J = 2.7 Hz, CH$_3$), 0.93 (d, 3H, J = 2.7 Hz, CH$_3$). ^{13}C NMR (50 MHz): 137.2 (d), 117.2 (t), 107.1 (d), 85.9 (d), 63.1 (t), 60.3 (d), 42.9 (d), 29.8 (d), 20.7 (q), 20.5 (q), 16.0 (q), 15.3 (q).

Mixture of isomers of **9**. IR (KBr): 3082, 2960, 2876, 1465, 1377, 1093, 989, 922 cm^{-1}. HRMS (CI, isobutane) for $C_{12}H_{23}O_2$ ([M$^+$+1]): calculated 199.16925; found 199.17066.

2-(*tert*-Butoxy)-7a-methyl-2,3,3a,4,5,7a-hexahydrobenzo[b]furan-5-one (10). Prepared according to the Method A from the iodoacetal **5** (0.74 g, 2.1 mmol), Bu$_3$SnH (735 mg, 2.52 mmol) and a 1M soln of Et$_3$B in hexane (2.9 mL, 2.9 mmol). FC (hexane:Et$_2$O 5:1) afforded **10** (0.35 g, 74%, 98% ds).

Prepared according to the Method B from the iodoacetal **5** (0.18 g, 0.5 mmol), Bu$_3$SnH (174 mg, 0.60 mmol) and AIBN (4 mg, 0.025 mmol) to give **10** as a mixture of diastereomers (0.08 g, 71%, 89% ds).

Major diastereomer. IR (KBr): 3032, 2976, 2872, 1689, 1369, 1099 cm-1. ^{1}H NMR (360 MHz): 6.5 (dd, 1H, J = 1.8, 10.8 Hz, C*H*=CHCMe), 5.84 (d, 1H, J = 10.4 Hz,C*H*=CO), 5.29 (d, 1H, J = 5.2 Hz, OC*H*CH$_2$), 2.88–2.78 (m, 1H, C*H*CH$_2$CO), 2.64 (dd, 1H, J = 5.5, 17.0 Hz, CHC*H*HC=O), 2.54 (dd, 1H, J = 2.1, 16.8 Hz, CHCH*H*C=O), 1.96 (dd, 1H, J = 7.0, 12.5 Hz, C*H*HCH–O), 1.86 (dt, 1H, J = 5.2, 12.5 Hz, CH*H*CH–O), 1.52 (s, 3H, CH$_3$), 1.23 (s, 9H, *t*Bu). ^{13}C NMR (50 MHz): 197.6 (s), 151.8 (d), 126.0 (d), 97.1 (d), 79.3 (s), 74.1 (s), 41.6 (d), 39.7 (t), 39.4 (t), 29.1 (q), 25.6 (q). MS (CI, CH$_4$) m/z (%): 225 (M$^+$+1, 12), 197 (32), 169 (86), 152 (13), 150 (100), 122 (8), 57 (13). Anal.Calcd. for $C_{13}H_{20}O_3$ (224.30): C, 69.51; H, 8.97. Found: C, 69.61; H, 8.99.

Methyl-2-{[2-(tert-butoxy)-7a-methyl-5-oxo-2,3,3a,4,5,7a-hexahydro-1-benzofuran-4-yl]methyl}acrylate (11). Prepared according to the Method D from the iodoacetal **5** (0.18 g, 0.5 mmol), 2-(methoxycarbonyl)propenyltributylstannane (1.55g, 4 mmol) and AIBN (4 mg, 0.025 mmol). FC (hexane/Et$_2$O 2:1) gave **5** as a mixture of diastereomers (0.11 g, 68%, 81% ds).

Major diastereomer. IR (KBr): 3030, 2976, 1722, 1680, 1440, 1347, 1199, 1143 cm^{-1}. ^{1}H NMR (360 MHz): 6.50 (dd, 1H, J = 1.5, 10.1 Hz, C*H*=CHCMe), 6.26 (d, 1H, J = 1.2 Hz, C*H*H=CCO$_2$Me), 5.80 (d, 1H, J = 10.1 Hz, C*H*=CO), 5.56 (d, 1H, J = 1.2 Hz, CH*H*=CCO$_2$Me), 5.27 (d, 1H, J = 5.2 Hz, OCHCH$_2$), 3.76 (s, 3H, CH$_3$O), 2.75–2.72 (m, 2H, C*H*C=O, C*H*CHCO), 2.64–2.62 (m, 2H, C*H$_2$*C=CH$_2$), 2.03 (ddd, 1H, J = 0.9, 7.0, 12.8 Hz, C*H*HCHCHCO), 1.85 (dt, 1H, 5.2, 12.5 Hz, CH*H*CHCHCO), 1.59 (s, 3H, CH$_3$), 1.23 (s, 9H, *t*Bu). ^{13}C NMR (50 MHz): 199.8 (s), 166.9 (s), 149.8 (d), 137.5 (t), 127.4 (s), 124.9 (d), 96.9 (d), 78.3 (s), 74.1 (s), 51.8 (q), 47.9 (d), 46.0 (d), 41.1 (t), 35.1 (t), 29.1 (q), 28.8 (q). MS (CI, CH$_4$) m/z (%): 323 (M$^+$+1, 8), 267 (21), 235 (30), 217 (63), 169 (24), 151 (100), 136 (15), 57 (78). Anal. Calcd. for $C_{18}H_{26}O_5$ (322.46): C, 67.06; H, 8.13. Found: C, 67.10; H, 8.09.

(1*R*, 2*S*)-2-phenylcyclohexyl vinyl ether[6] (12). A solution of (1*R*,2*S*)-phenylcyclohexanol (3.0 g, 17.0 mmol) and Hg(OAc)$_2$ (102 mg, 0.32 mmol) in ethyl vinyl ether (10 mL) was heated at reflux for 2 days. Then the solution was cooled at rt. and an additional amount of K$_2$CO$_3$ was added. After filtration and evaporation of the solvent the crude was purified by FC (hexane:Et$_2$O 5 : 1) to furnish **12** (1.23 g, 88%) as a colorless oil and the chiral alcohol (1.78 g) recovered.

^{1}H NMR (200 MHz): 7.35–7.15 (m, 5 arom. H); 6.05 (dd, 1H, J = 6.1, 12.0 Hz, OC*H*=CH$_2$); 4.1 (d, 1H, J = 12.0, CH=C*H*H); 3.90–3.75 (m, 2H, CH=CH*H*, OC*H*CHPh); 2.72-2.50 (m, 1H, OCHC*H*Ph); 2.30–2.10 (m, 1H); 2.00–1.65 (m, 3H); 1.60–1.25 (m, 4H).

(1*S*)- and (1*R*)-2-Bromo-1-[(1*R*,2*S*)-(2-phenylcyclohexyl)oxy]ethyl 1-vinyl-2-propenyl ether (13). To a solution of **12** (0.72 g, 3.6 mmol) and 1,4-pentadien-3-ol (0.45 mL, 3.9 mmol) in CH$_2$Cl$_2$ (6 mL) cooled at –20 °C was added in portions NBS (0.73 g, 3.6 mmol). The resulting mixture was stirred at the same temperature for 2 h. Then hexane was added to precipitate the succinimide. After filtration, the organic phase was washed successively with KOH (5%), water and NaCl. Dried with MgSO$_4$ and the solvent removed under reduced pressure. Purification by FC (hexane/Et$_2$O 10:1) afforded a 1:1 mixture of the two diastereomers of **13** (0.98.g, 75%). In preliminary experiments, the diastereomers were separated by flash chromatography (hexane/Et$_2$O 80:1) to afford (*R*)-**13** and (*S*)-**13**. However, on larger scale, it was convenient to continue the synthesis with the mixture of diastereomers and to separate by flash chromatography after the radical cyclization step (see below).

(1*S*)-**13**: R$_f$ = 0.70 (hexane/Et$_2$O 5:1). ^{1}H NMR (360 MHz): 7.31–7.20 (m, 5 arom. H); 5.86–5.66 (m, 2H, C*H*=CH$_2$); 5.25–5.15 (m, 4H, C*H*$_2$=CH); 4.38 (t, 1H, J = 6.1 Hz, OC*H*(C=CH$_2$)$_2$); 4.25 (dd, 1H, J = 3.5, 6.7 Hz, OC*H*CH$_2$Br); 3.46 (dt, 1H, J = 4.5, 10.0 Hz, OC*H*CHPh); 2.75 (dd, 1H, J = 6.7, 10.7 Hz, OCHC*H*HBr); 2.58–2.53 (m, 1H, OCHC*H*Ph); 2.50 (dd, 1H, J = 3.5, 10.7 Hz, OCHCH*H*-Br); 2.19–2.11 (m, 1H); 1.91–1.82 (m, 2H); 1.77–1.71 (m, 1H); 1.61–1.27 (m, 4H). ^{13}C NMR (50 MHz): 144.5 (s); 138.1 (d); 137.8 (d); 128.8 (d); 128.6 (d); 127.0 (d); 117.7 (t); 116.6 (t); 101.0 (d); 82.1 (d); 79.1 (d); 51.8 (d); 34.6 (t); 33.8 (t); 32.8 (t); 26.2 (t); 25.7 (t).

(1*R*)-**13**: R$_f$ = 0.72 (hexane/Et$_2$O 5:1). ^{1}H NMR (360 MHz): 7.32–7.19 (m, 5 arom. H); 5.60–5.44 (m, 2H, 2 C*H*=CH$_2$); 5.12–4.91 (m, 4H, 2 CH=C*H*$_2$); 4.57 (dd, 1H, J = 7.0 Hz, OC*H*CH$_2$Br); 3.57–3.53 (m, 1H, OC*H*CHPh); 3.53–3.50 (m, 1H, OC*H*(CH=CH$_2$); 3.21 (dd, 1H, J = 7.0, 10.4 Hz, OCHC*H*HBr); 3.07 (dd, 1H, J = 3.7, 10.7 Hz, OCHCH*H*Br); 2.61–2.54 (m, 1H, OCHC*H*Ph); 2.13–1.32 (m, 8H, CH$_2$). ^{13}C NMR (50 MHz): 144.8 (s); 138.1 (d); 137.6 (d); 128.7 (d); 128.6 (d); 126.9 (d); 117.6 (t); 116.3 (t); 99.1 (d); 80.2 (d); 77.7 (d); 51.2 (d); 34.3 (t); 33.9 (t); 26.2 (t); 25.4 (t).

Mixture of diastereomers: IR (KBr): 3028, 2931, 2858, 1448, 1114, 1028 cm^{-1}.MS (CI–CH$_4$) m/z (%): 365 (1, M$^+$), 283 (6), 225 (14), 175 (16), 159 (100), 91 (11), 67 (51). Anal. Calcd. for C$_{19}$H$_{25}$O$_2$Br (365.31): C, 62.47; H, 6.90. Found: C, 62.43; H, 6.83.

(2*S*,4*S*,5*R*)- and (2*R*,4*R*,5*S*)-4-Methyl-5-vinyltetrahydro-2-furanyl (1*R*,2*S*)-2-phenylcyclohexyl ether [(2*S*,4*S*,5*R*)-14 and (2*R*,4*R*,5*S*)-14]. A soln. of **13** (1:1 mixture of diast., 0.98 g, 2.7 mmol) and Bu$_3$SnH (0.94 g, 3.24 mmol) in toluene (70 mL) was cooled at –78 °C and a 1M soln. of Et$_3$B in hexane (3.8 mL, 3.8 mmol) was added followed by air (3 mL). The soln. was kept at –78 °C for 2 h. Then a 1M NaOH soln. (50 mL) was added and the heterogeneous mixture was stirred for 2 h at rt. The organic layer was washed with water, dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography (hexane/Et$_2$O 30:1) to afford **14** (0.66 g, 85%). The two diasteroisomers were quantitatively separated by FC (hexane/Et$_2$O 30:1).

(2*S*,4*S*,5*R*)-**14**: $[\alpha]_D^{20}$ = +22.3° (c = 1.5, CH$_2$Cl$_2$). ^{1}H NMR (360 MHz): 7.30–7.15 (m, 5 arom. H); 5.67 (ddd, 1H, J = 7.4, 10.1, 17.1 Hz, C*H*=CH$_2$); 5.22 (ddd, 1H, J = 0.9, 1.5, 17.1 Hz, CH=C*H*H); 5.13 (ddd, 1H, J = 0.9, 1.8, 10.4 Hz, CH=CH*H*); 4.42 (dd, 1H, J = 3.5, 5.5 Hz, OC*H*CH$_2$); 3.85 (t, 1H, J = 8.2 Hz, OC*H*CH=CH$_2$); 3.55 (dt, 1H, J = 4.6, 10.4 Hz, OC*H*CHPh); 2.52–2.45 (m, 1H, OCHC*H*Ph); 2.20–2.13 (m, 1H, C*H*CH$_3$); 1.90–1.16 (m, 10H); 0.92 (d, 3H, J = 7.1 Hz, CH$_3$). ^{13}C NMR (50 MHz): 144.5 (s); 137.5 (d); 128.0 (d); 127.9 (d); 126.1 (d); 116.8 (t); 104.9 (d); 85.2 (d); 81.7 (d); 51.6 (d); 40.9 (t); 39.0 (d); 35.1 (t); 33.0 (t); 25.9 (t); 25.3 (t); 15.8 (q).

(2*R*,4*R*,5*S*)-**14**: $[\alpha]_D^{20}$ = –98.4° (c = 0.5, CH$_2$Cl$_2$). ^{1}H NMR (360 MHz): 7.30–7.23 (m, 5 arom. H); 5.56 (ddd, 1H, J = 7.6, 10.4, 18.0 Hz, C*H*=CH$_2$); 5.21 (dd, 1H, J = 1.8, 5.5 Hz, OC*H*CH$_2$); 5.05–4.93 (m, 2H, CH=C*H*$_2$); 3.80 (td, 1H, J = 4.0, 10.4 Hz, OC*H*CHPh); 2.60 (t, 1H, J = 7.2 Hz, OC*H*CH=); 2.54–2.46 (m, 1H, OCHC*H*Ph); 2.25–2.16 (m, 1H, C*H*CH$_3$); 1.91–1.22 (m, 10H, CH$_2$); 0.66 (d, 3H, J = 7.0 Hz, CH$_3$).

Mixture of diastereomers: IR (KBr): 3030, 2930, 2856, 1448, 1084, 987 cm^{-1}. MS (CI, CH$_4$) m/z (%): 287 (17, M$^+$+1), 187 (5), 159 (67), 111 (100), 93 (30), 91 (11). Anal. Calcd. for C$_{19}$H$_{26}$O$_2$ (286.42): C, 79.68; H, 9.15. Found: C, 79.78; H, 9.10.

(2*R*,4*S*,5*R*)-4-methyl-5-(3-methyl-2-butenyl)tetrahydro-2-furanyl-(1R,2S)-2-phenylcyclohexyl ether (15). A soln. of (2*S*,4*S*,5*R*)-**14** (540 mg, 2.0 mmol) in THF (1 mL) was added to a soln. of 9-BBN 0.5M in THF (4.1 mL, 2.1 mmol) under inert atmosphere. The soln. was heated at reflux for 3 h, cooled at 0 °C and a 3M NaOH soln. (2.3 mL) was added dropwise followed by 30% H$_2$O$_2$ (2.3 mL). The reaction mixture was stirred at rt for 1 h and extracted with Et_2O. The organic phases were washed with NaCl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by FC (hexane/Et_2O 2:1) afforded the alcohol (0.57 g, 93%). $[\alpha]_D^{20}$ = +50.0° (c = 1, CH_2Cl_2). IR (KBr): 3421, 2931, 2858, 1602, 1448, 1340, 1064, 993 cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$): 7.29-7.16 (m, 5 arom. H); 4.43 (dd, J = 3.4, 5.8 Hz, 1H, OC*H*CH$_2$); 3.77–3.72 (m, 2H, C*H$_2$*OH); 3.64 (dt, 1H, J = 3.1, 9.2 Hz, OC*H*CH$_2$CH$_2$OH), 3.48 (dt, 1H, J = 4.3, 10.1 Hz, OC*H*CHPh); 2.71 (t, 1H, J = 5.8 Hz, OH); 2.52–2.44 (m, 1H, OCHC*H*Ph); 2.13–2.10 (m, 1H, C*H*CH$_3$); 1.88–1.11 (m, 12H), 0.92 (d, 3H, *J* = 6.7 Hz, CHC*H$_3$*). ^{13}C NMR (50 MHz, $CDCl_3$): 144.9 (s); 128.5 (d); 128.5 (d); 126.5 (d); 105.3 (d); 84.0 (d); 82.5 (d); 62.2 (t); 51.9 (d); 41.0 (t); 38.9 (d); 35.6 (t); 35.5 (t); 33.4 (t); 26.4 (t); 25.8 (t); 16.7 (q). CI-MS: 305 (5, M$^+$+1), 257 (11), 159 (5), 129 (100), 111 (5), 85 (22). Anal. Calcd. for $C_{19}H_{28}O_3$ (344.43): C, 74.96; H, 9.27. Found: C, 74.83; H, 9.17.

A soln. of DMSO (0.29 mL, 4.0 mmol) in CH_2Cl_2 (2 mL) was added to a soln. of oxalyl chloride (0.18 mL, 2.1 mmol) in CH_2Cl_2 (13 mL) coolded at –78 °C. After 5 min, a soln. of the alcohol (0.54 g, 1.8 mmol) in CH_2Cl_2 (1 mL) was added slowly. The white mixture was stirred at –78 °C for 30 min and Et_3N (1.22 mL, 8.8 mmol) was added. The mixture was stirred at rt for 2 h and sat. NaCl (10 mL) was added. The mixture was extracted with CH_2Cl_2 and the org. phase was washed with sat. NaCl, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by FC (hexane/Et_2O 1:1) furnished the desired aldehyde (0.50 g, 95%). $[\alpha]_D^{20}$ = +23.3° (c = 0.3, CH_2Cl_2). IR (KBr): 2930, 2856, 1728, 1448, 1085, 989 cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$): 9.76 (dd, 1H, J = 2.1, 3.1 Hz, C*H*O); 7.29–7.18 (m, 5 arom. H); 4.42 (dd, 1H, J = 3.4, 5.8 Hz, OC*H*CH$_2$); 3.95 (dt, 1H, J = 3.7, 8.6 Hz, OC*H*CH$_2$CHO); 3.50 (dt, 1H, J = 4.3, 10.1 Hz, OC*H*CHPh); 2.56 (ddd, 1H, J = 2.1, 4.0, 16.2 Hz, C*H*HCHO); 2.50–2.47 (m, 1H, OCHC*H*Ph); 2.41 (ddd, 1H, J = 2.7, 8.2, 15.9 Hz, CH*H*CHO); 2.15–2.13 (m, 1H, C*H*CH$_3$); 1.90–1.17 (m, 10H); 0.97 (d, 3H, J = 6.4 Hz, CHC*H$_3$*). ^{13}C NMR (50 MHz, $CDCl_3$): 201.6 (d); 144.9 (s); 128.5 (d); 128.4 (d); 126.5 (d); 105.3 (d); 82.4 (d); 78.8 (d); 51.9 (d); 47.7 (t); 41.1 (t); 39.0 (d); 35.5 (t); 33.4 (t); 26.4 (t); 25.8 (t); 16.8 (q). MS–CI: 303 (2, M$^+$+1), 285 (22), 259 (5), 159 (27), 127 (100), 101 (4), 81 (11). HRMS (ESI–MS) for $C_{19}H_{26}O_3Na$ ([M$^+$+Na]): calculated 325.17741; found 325.17710.

To a suspension of isopropyltriphenylphosphonium iodide (0.37 g, 0.86 mmol) in THF (4 mL) was added dropwise BuLi (2.21M in hexane, 0.3 mL, 0.66 mmol). The red mixture was stirred at –30 °C for 20 min, cooled at –78 °C and a soln. of the aldehyde (0.19 g, 0.66 mmol) in THF (2 mL) was added. The mixture was stirred at the same temperature for 1 h, poured into water, extracted with Et_2O and the organic phases were washed with brine. After drying and evaporation of the solvent the crude product was purified by FC (hexane/Et_2O 40:1) to give **15** (0.11 g, 51%) as a colorless oil. $[\alpha]_D^{20}$ = +38.5° (c = 1, CH_2Cl_2). IR (KBr): 3030, 2930, 2856, 1448, 1377, 1066, 991 cm^{-1}. ^{1}H NMR (360 MHz): 7.22–7.15 (m, 5 arom. H); 5.16–5.12 (m, 1H, C*H*=CMe$_2$); 4.40 (dd, 1H, J = 3.1, 5.8 Hz, OC*H*CH$_2$); 3.56–3.50 (m, 2H, OC*H*CHPh , OC*H*CH$_2$CH=CMe$_2$); 2.51–2.44 (m, 1H, OCHC*H*Ph); 2.24–2.08 (m, 3H, C*H$_2$*CH=CMe$_2$, C*H*CH$_3$); 1.68 (s, 3H, CH$_3$); 1.58 (s, 3H, CH$_3$); 1.88–1.12 (m, 10H); 0.92 (d, 3H, J = 6.7 Hz, CHC*H$_3$*). ^{13}C–NMR (50 MHz): 145.1 (s); 133.5 (s); 128.5 (d); 128.4 (d); 126.4 (d); 120.8 (d); 105.0 (d); 84.0 (d); 81.8 (d); 52.0 (d); 41.5 (t); 38.0 (d); 35.5 (t); 33.5 (t); 32.6 (t); 26.4 (t); 26.2 (q); 25.8 (t); 18.4 (q); 17.7 (q). MS (CI, CH_4) m/z (%): 329 (M$^+$+1, 1), 259 (8), 159 (65), 153 (34), 117 (10), 109 (29), 91 (100), 69 (46). HRMS (CI, isobutane) for $C_{22}H_{33}O_2$ ([M$^+$+1]): calculated 329.24750; found 329.24887.

(4*S*,5*R*)-4-Methyl-5-(3-methyl-2-butenyl)dihydro-2(*3H*)-furanone [(+)-*Eldanolide*]. [7] A soln. of **15** (0.12 g, 0.36 mmol) in THF (1.3 mL) and 10% HCl (1 mL) was kept at rt for 30 min. After extraction with Et_2O, the organic phases were washed with sat. $NaHCO_3$ and H_2O, dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by

FC (pentane/Et_2O 6:1) to afford (1*R*,2*S*)-phenylcyclohexanol (40 mg, 62%) and the lactol (42 mg, 68%) as a mixture of diastereomers.
Mixture of diasteroisomers. ^{1}H NMR (360 MHz, $CDCl_3$): 5.52 (dt, 1H, J = 3.8, 5.7 Hz, OC*H*O, 1 diast.); 5.42 (t, 1H, J = 3.6 Hz, OC*H*O, 1 diast.); 5.27–5.18 (m, 2H, C*H*=CMe_2); 3.78–3.72 and 3.58–3.52 (m, 1H, OC*H*CH_2CH=CMe_2); 2.70–2.67 and 2.52–2.50 (m, 1H, OH); 2.42–2.03 (m, 8H); 1.92–1.78 (m,1H); 1.73 and 1.72 (2s, 3H, CH_3);1.53–1.46 (m, 1H); 1.09 and 1.08 (2d, 3H, J = 7.5 Hz, CHC*H$_3$*).
A soln. of the lactol (0.42 g, 0.25 mmol) in CH_2Cl_2 (4 mL) was added to a mixture of PCC (0.19 g, 0.9 mmol) and Al_2O_3 neutral (Woelm N, Activity Y, 0.35 g). The orange mixture was stirred overnight then diluted with Et_2O (6 mL) and filtrated through Florisil to afford the (+)-eldanolide (32 mg, 76%) as a colorless oil. The optical purity (>99% ee) was determined by GC (γ-cyclodextrine 65% diacetoxy, 140 °C). $[\alpha]_D^{20}$ = + 43.4° (c = 1, EtOH) [lit: $[\alpha]_D^{20}$ = + 51.5 ° (c = 1,15, MeOH)]. All spectral data are in accordance with literature data (see ref. [7]). ^{1}H NMR (360 MHz): 5.17 (broad t, 1H, C*H*=CMe_2); 4.06 (q, 1H, J = 7.0 Hz, OC*H*CH_2CH=CMe_2); 2.67 (dd, 1H, J = 7.6, 16.5 Hz, C*H*HCHCH_3); 2.46–2.22 (m, 3H, C*H*CH_3, CHC*H$_2$*CH=CMe_2); 2.17 (dd, 1H, J = 9.2, 16.8 Hz, CH*H*CHCH_3); 1.73 (s, 3H, CH_3); 1.64 (s, 3H, CH_3); 1.14 (d, 3H, *J* = 6.7 Hz, CHC*H$_3$*). ^{13}C-NMR (50 MHz): 176.4 (s); 135.4 (s); 118.0 (d); 87.0 (d); 37.1 (t); 35.1 (d); 32.2 (t); 25.8 (q); 17.9 (q); 17.7 (q). MS (CI, CH_4) m/z (%): 169 (100, M^++1), 151 (25), 123 (12), 109 (89), 99 (26), 84 (7), 69 (35).

4-(2-Bromo-1-*tert*-butoxyethoxy)-1,6-heptadiene (16). Prepared according to the general procedure 1 from 1,6-heptadien-3-ol (1.0 g, 8.9 mmol), *tert*-butyl vinyl ether (0.89 g, 8.9 mmol) and NBS (1.58 g, 8.9 mmol) to afford after flash chromatography (hexane/Et_2O 40:1) the bromoacetal **16** (1.74 g, 67%) as a colorless oil.
IR (KBr): 3076, 2978, 2935, 1641, 1367, 1033, 914 cm^{-1}. ^{1}H NMR (360 MHz): 5.91–5.78 (m, 2H, C*H*=CH_2), 5.12–5.02 (m, 4H, C*H$_2$*=CH), 4.87 (dd, 1H, J = 4.6, 6.1 Hz, OCHCH_2Br), 3.66 (m,1H, OC*H*(CH_2CH=CH_2)$_2$), 3.36 (dd, 1H, J = 6.1, 10.7 Hz, OCHC*H*HBr), 3.27 (dd, 1H, J = 4.3, 10.4 Hz, OCHCH*H*Br), 2.31 (t, 4H, 2 C*H$_2$*CH=CH_2), 1.27 (s, 9H, *t*Bu). ^{13}C NMR (50 MHz): 134.7 (d), 134.3 (d), 117.6 (t), 117.1 (t), 95.9 (d), 74.8 (s), 38.8 (t), 38.2 (t), 34.5 (t), 28.9 (q). MS (EI) m/z (%): 293 (M^++2, 4), 291 (M^+, 3), 219 (26), 217 (26), 201 (9), 199 (9), 169 (40), 127 (56), 95 (100), 81 (39), 57 (65). Anal. Cald. for $C_{13}H_{23}O_2Br$ (213.23): C, 53.62; H, 7.96. Found: C, 53.48; H, 8.13.

6-(3-Propenyl)-4-methyltetrahydro-*2H*-pyran-2-yl *tert*-butyl ether (17). Prepared according to the Method A from the bromoacetal **16** (0.61 g, 2.1 mmol), Bu_3SnH (735 mg, 2.5 mmol) and a 1M soln of Et_3B in hexane (2.9 mL, 2.9 mmol) to furnish the acetal **17** (0.19 g, 43%) as a single diastereomer.
IR (KBr): 3078, 2976, 2930, 2872, 1458, 1375, 1112, 1001 cm^{-1}. ^{1}H NMR (500 MHz): 5.82 (ddt, 1H, J = 7.0, 10.3, 17.0 Hz, C*H*=CH_2), 5.15 (dm, 1H, J= 3.3 Hz, *t*BuOC*H*CH_2), 5.05 (ddt,1H, J = 1.4, 2.1, 17.1 Hz, C*H*H=), 5.00 (ddt, 1H, J = 1.1, 2.1, 10.1 Hz, CH*H*=), 3.91 (dddd, 1H, J= 2.2, 5.6, 7.1, 11.6 Hz, OC*H*CH_2CH=CH_2), 2.20 (dtt, 1H, J = 1.3, 6.9, 14.1 Hz, C*H*HCH=CH_2), 2.12 (dddt, 1H, J = 1.0, 6.1, 7.3, 14.1 Hz, CH*H*CH=CH_2), 1.98 (tqt, 1H, J= 6.5 Hz, C*H*Me), 1.60 (ddt, 1H, J= 1.5, 3.8, 12.9 Hz, OCH(CH_2CH=CH_2)C*H*H), 1.54 (ddt, 1H, J = 1.5, 3.0, 12.9 Hz, *t*BuOCHC*H*H), 1.22 (s, 9H, *t*.Bu), 1.21 (ddd, 1H, J = 3.7, 12.3, 12.9 Hz, *t*BuOCHCH*H*) , 0.86 (d, 3H, J = 6.5 Hz, CH_3), 0.85 (ddd, 1H, J = 11.7, 11.7, 12.9 Hz, OCH(CH_2CH=CH_2)CH*H*). ^{13}C NMR (50 MHz): 135.5 (d), 116.2 (t), 91.8 (d), 73.7 (s), 67.8(d), 40.9 (t), 40.0 (t), 39.8 (t), 28.8 (q), 24.2 (d), 22.3 (q). MS (EI) m/z (%): 213 (M+1, 16), 171 (11), 157 (43), 139 (78), 115 (38), 95 (27), 69 (22), 57 (100). HRMS (ESI) for $C_{13}H_{24}O_2Na$: calculated 235.16685; found 235.16711.

References

[1] Ueno, Y.; Moriya, O.; Chino, K.; Watanabe, M.; Okawara, M. *J. Chem Soc. Perk. Trans. I*, **1986**, 1351-1356.

[2] Gosselin, P.; Rouessac, F.; Zamarlik, H. *Bull. Soc. Chim. Fr.* **1981**, 192-198.

[3] Weiguny, J.; Schäfer, H.F. *Liebigs Ann. Chem.* **1994**, 225-233.

[4] Aponick, A.; McKindley, J.; Raber, J. C.; Wigal, C. T. *J. Org. Chem.* **1998***, 8*, 2676-2678.

[5] Villar, F.; Renaud, P. *Tetrahedron Lett.* **1998**, *39*, 8655-8658.

[6] Denmark, S. E.; Hurd, A. R.; Sacha, H. J. *J. Org. Chem.* **1997**, *62*, 1668-1674.

[7] Suzuki, K.; Ohkuma, T.; Tsuchihashi, C.-I. *Tetrahedron Lett.* **1985**, *26*, 861-864.