Supporting Information for

Use of Hindered Silyl Ethers as Protecting Groups for the Non-Aldol Aldol Process

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General

All reactions were carried out under argon with the exclusion of moisture. Solvents were purified as follow: dichloromethane, diisopropylethylamine (DIPEA), and triethylamine were distilled from calcium hydride and tetrahydrofuran (THF) and ether were from sodium/benzophenone ketyl radical. Commercial *t*-butylhydroperoxide (TBHP) was dried over 4 Å molecular sieves for 30 min. Flash chromatography was conducted on 400 mesh silica gel (SiO₂) or alumina, eluting with hexanes, ethyl acetate (EtOAc), and dichloromethane. Thin-layer chromatography was carried out using Silica gel 60 F254 plates (Merck).

¹H and ¹³C nuclear magnetic resonance (NMR) were recorded on a Bruker ARX400 at room temperature. Chemical shifts are given in ppm (δ) relative to tetrahydromethylsilane (TMS) as an external standard. Coupling constants (*J*) are in Hertz (Hz) and signals are designated as follow: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quint* (quintet), *m* (multiplet), br (broad). Diastereomeric purities were determined by integration of the appropriate ¹H signals of the compounds prepared. Other spectroscopic data were obtained as follow: IR spectra on Nicolet 510 FT-IR spectrometer, optical rotations on a Autopol IV Automatic Polarimeter, high resolution mass spectra (MS) were obtained at the Center for Molecular and Medical Science Mass Spectroscopy of UCLA.

(1'*R*,2*R*,3*R*)-2-[(Triethylsiloxy)methyl]-3-[2'-(diphenyl-*t*-butylsiloxy)-1'-methyl-ethyl]-2-methyloxirane (13a).

D-(-)-DIPT (9.4 mg, 0.04 mmol) and molecular sieves (50 mg) were weighed into a dry flask under Ar and dissolved in dichloromethane (4 ml). The solution was cooled to – 20 °C and treated with Ti(OiPr)₄ (8.7 µl, 0.03 mmol). The mixture was stirred for 15 min at – 20 °C and a 5-6 M solution of TBHP in decane (107 µl) was added. The reaction mixture was stirred for a

further 15 min and a solution of the corresponding allylic alcohol (100 mg, 0.26 mmol) in dichloromethane (2 ml) was added dropwise within 10 min. After stirring for 2 h at $-20\text{ }^{\circ}\text{C}$, the reaction mixture was quenched by adding 0.05 M pH 7.0 phosphate buffer (5 ml). The layers were separated, the aqueous phase extracted with dichloromethane ($3 \times 5\text{ ml}$), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO_4 . Removal of the solvent under vacuum gave the crude epoxide (colorless oil) which was used for the next reaction without any further purification. $R_f = 0.33$ (cyclohexane/EtOAc: 4/1).

A solution of the crude epoxy alcohol (104 mg, 0.27 mmol) in dichloromethane (5 ml) was treated with DMAP (5 mg) and triethylamine (57 μl , 0.40 mmol). The mixture was cooled to $0\text{ }^{\circ}\text{C}$ and TESC1 was added (59 μl , 0.35 mmol). After stirring for 1 h, the reaction was quenched by adding 0.05 M pH 7.0 phosphate buffer (5 ml). The layers were separated, the aqueous phase extracted with dichloromethane ($3 \times 10\text{ ml}$), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO_4 . Chromatography (Alumina VII, cyclohexane/EtOAc: 20/1 $\rightarrow$ 5/1) afforded 130 mg (0.26 mmol, 96% for two steps, de:96/4) of **13a** as a colorless oil.

$R_f = 0.66$ (cyclohexane/EtOAc: 8/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.69–7.66 (*m*, 4H); 7.41–7.26 (*m*, 6H); 3.76 (*dd*, $J = 3.8, 9.8\text{ Hz}$, 1H); 3.73 (*dd*, $J = 5.5, 9.8\text{ Hz}$, 1H); 3.59 (*s*, 2H); 2.84 (*d*, $J = 9.4\text{ Hz}$, 1H); 1.65–1.54 (*m*, 1H); 1.28 (*s*, 3H); 1.06 (*s*, 9H); 1.06 (*d*, $J = 7.0\text{ Hz}$, 3H); 0.94 (*t*, $J = 7.8\text{ Hz}$, 9H); 0.60 (*q*, $J = 7.8\text{ Hz}$, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 135.67; 133.82; 129.56; 127.62; 67.61; 66.35; 62.15; 60.56; 35.64; 26.89; 19.38; 14.16; 13.61; 6.76; 4.42. IR (thin film): 2952.5 (*s*), 2853.0 (*s*), 1456.4 (*m*), 1415.9 (*s*), 1386.9 (*m*), 1238.4 (*m*), 1107.2 (*s*), 1006.9 (*s*), 897.0 (*w*), 821.7 (*s*), 740.7 (*s*), 700.25 (*s*), 623.0 (*m*) cm^{-1} .

(2*S*,3*R*,4*R*)-2,4-Dimethyl-5-(diphenyl-*t*-butylsilyloxy)-3-trimethylsilyloxy-pentanal (14a).

The silyl epoxide **13a** (90 mg, 0.18 mmol) was dissolved in dichloromethane (6 ml) and treated successively with 50 mg of powdered 4 Å molecular sieves and DIPEA (157 μl , 0.90 mmol). The solution was cooled to $-45\text{ }^{\circ}\text{C}$ and treated with TMSOTf (163 μl , 0.90 mmol). After 1 h, the

solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (3 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane (3 × 10 ml), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine, dried over MgSO₄ and concentrated. The colorless oil thus obtained contained 97% (98:2 de) of **14a**.

¹H NMR (400 MHz, CDCl₃) δ: 9.67 (*d*, *J* = 0.9 Hz, 1H); 7.67–7.64 (*m*, 4H); 7.41–7.37 (*m*, 6H); 4.11 (*dd*, *J* = 3.4, 7.4 Hz, 1H); 3.74 (*dd*, *J* = 4.9, 9.9 Hz, 1H); 3.49 (*dd*, *J* = 6.8, 9.9 Hz, 1H); 2.55–2.49 (*m*, 1H); 1.90–1.83 (*m*, 1H); 1.06 (*s*, 9H); 1.06 (*d*, *J* = 6.5 Hz, 3H); 0.91 (*d*, *J* = 6.9 Hz, 3H); –0.03 (*s*, 9H). ¹³C NMR (100 MHz, CDCl₃) δ: 205.12; 135.73; 133.75; 133.78; 129.64; 129.11; 127.72; 127.63; 72.70; 65.74; 49.79; 40.05; 26.98; 19.28; 14.01; 7.66; 6.81; 6.42; 0.44.

(2*S*,3*R*,4*R*)-2,4-Dimethyl-5-(triisopropylsilyloxy)-3-trimethylsilyloxy-pentanal (14b).

The silyl epoxide **13b** (33 mg, 0.067 mmol) was dissolved in dichloromethane (3 ml) and treated successively with 20 mg of powdered 4 Å molecular sieves and DIPEA (59 µl, 0.34 mmol). The solution was cooled to – 45 °C and treated with TMSOTf (61 µl, 0.34 mmol). After 1 h, the solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (3 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane (3 × 10 ml), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine, dried over MgSO₄ and concentrated. The colorless oil thus obtained contained 95% (98:2 de) of **14b**.

¹H NMR (400 MHz, CDCl₃) δ: 9.70 (*d*, *J* = 1.0 Hz, 1H); 4.11 (*dd*, *J* = 3.5, 7.3 Hz, 1H); 3.81 (*dd*, *J* = 5.2, 9.6 Hz, 1H); 3.49 (*dd*, *J* = 7.1, 9.6 Hz, 1H); 2.59–2.53 (*m*, 1H); 1.90–1.83 (*m*, 1H); 1.08 (*d*, *J* = 7.0 Hz, 3H); 1.05 (*s*, 18H); 1.04 (*s*, 3H); 0.90 (*d*, *J* = 6.8 Hz, 3H); 0.05 (*s*, 9H). ¹³C NMR (100 MHz, CDCl₃) δ: 205.20; 72.78; 65.38; 53.82; 49.83; 42.09; 40.36; 18.04; 13.86; 12.09; 7.74; 0.54.

(2*R*,3*S*,4*R*,5*R*)-2,4-Dimethyl-5-(diphenyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (16a).

The silyl epoxide **15a** (45 mg, 0.08 mmol) was dissolved in dichloromethane (3 ml) and treated successively with 30 mg of powdered 4 Å molecular sieves and DIPEA (72 µl, 0.41 mmol). The

solution was cooled to $-45\text{ }^{\circ}\text{C}$ and treated with TMSOTf (75 μl , 0.41 mmol). After 1 h, the solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (2 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane ($3 \times 10\text{ ml}$), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO_4 . Chromatography (SiO_2 , hexane/EtOAc: 9/1) afforded 34 mg (0.07 mmol, 85%, 98:2 de) of **16a** as a colorless oil.

$R_f = 0.44$ (hexane/EtOAc: 9/1). ^1H NMR (400 MHz, CDCl_3) δ : 9.69 (br.s, 1H); 7.72–7.65 (*m*, 4H); 7.41–7.35 (*m*, 6H); 4.38 (*dd*, $J = 1.7, 8.8\text{ Hz}$, 1H); 4.01 (*ddd*, $J = 0.9, 3.6, 9.7\text{ Hz}$, 1H); 2.48 (*dq*, $J = 1.6, 6.8\text{ Hz}$, 1H); 1.62 (br *t*, $J = 7.2\text{ Hz}$, 1H); 1.47–1.35 (*m*, 3H); 1.06 (*d*, $J = 5.9\text{ Hz}$, 3H); 1.05 (*s*, 9H); 1.06–1.00 (*m*, 1H); 0.94 (*d*, $J = 7.0\text{ Hz}$, 3H); 0.63 (*t*, $J = 7.3\text{ Hz}$, 3H); -0.10 (*s*, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ : 205.30; 135.98; 135.89; 135.55; 134.39; 129.61; 129.40; 129.10; 127.58; 127.31; 73.15; 72.55; 50.31; 41.41; 37.78; 27.19; 19.52; 18.88; 13.72; 10.05; 6.15; 0.73. IR (thin film): 2957.2 (*s*), 2930 (*s*), 2856.9 (*s*), 1728.4 (*s*), 1462.2 (*m*), 1427.5 (*m*), 1251.9 (*s*), 1109.1 (*s*), 1005.0 (*s*), 841.0 (*m*), 702.2 (*s*) cm^{-1} . High resolution EI MS (m/z): 497.2907 calcd for $\text{C}_{29}\text{H}_{45}\text{O}_3\text{Si}_2$ 497.2885 ($\text{M}-\text{H}^+$).

(2R,3S,4R,5R)-2,4-Dimethyl-5-(triisopropylsilyloxy)-3-trimethylsilyloxyoctanal (16b).

The silyl epoxide **15b** (30 mg, 0.065 mmol) was dissolved in dichloromethane (2 ml) and treated successively with 20 mg of powdered 4 Å molecular sieves and DIPEA (57 μl , 0.32 mmol). The solution was cooled to $-45\text{ }^{\circ}\text{C}$ and treated with TMSOTf (59 μl , 0.32 mmol). After stirring for 1 h, the solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (2 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane ($3 \times 10\text{ ml}$), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO_4 . Chromatography (SiO_2 , hexane/EtOAc: 9/1) afforded 24 mg (0.06 mmol, 88%, 98:2 de) of **16b** as a colorless oil.

$R_f = 0.64$ (hexane/EtOAc: 9/1). ^1H NMR (400 MHz, CDCl_3) δ : 9.71 (br *s*, 1H); 4.34 (*dd*, $J = 1.7, 8.4\text{ Hz}$, 1H); 4.04 (*ddd*, $J = 1.3, 3.6, 10.0\text{ Hz}$, 1H); 2.48 (*dq*, $J = 1.7, 6.9\text{ Hz}$, 1H); 1.66–1.50 (*m*,

3H); 1.28–1.22 (*m*, 2H); 1.07 (*d*, $J = 6.7$ Hz, 3H); 1.07 (*s*, 21H); 0.91 (*t*, $J = 7.3$ Hz, 3H); 0.82 (*d*, $J = 7.0$ Hz, 3H); 0.06 (*s*, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ : 205.30; 72.64; 72.26; 50.31; 41.42; 38.03; 19.04; 18.47; 14.21; 13.29; 9.55; 6.38; 0.88. IR (thin film): 2958.5 (*s*), 2867.5 (*s*), 1730.9 (*s*), 1463.6 (*m*), 1384.0 (*m*), 1251.3 (*s*), 1103.5 (*s*), 1035.7 (*s*), 840.8 (*s*), 677.43 (*m*) cm^{-1} . High resolution CI MS (m/z): 415.3063 calcd for $\text{C}_{22}\text{H}_{47}\text{O}_3\text{Si}_2$ 415.3072 ($\text{M}-\text{H}^+$).

(2*R*,3*S*,4*R*,5*R*)-2,4-Dimethyl-5-(dimethyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (16c).

The silyl epoxide **15c** (30 mg, 0.07 mmol) was dissolved in dichloromethane (3 ml) and treated successively with 20 mg of powdered 4 Å molecular sieves and DIPEA (63 μl , 0.36 mmol). The solution was cooled to -45 °C and treated with TMSOTf (65 μl , 0.36 mmol). After 1 h, the solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (2 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane (3 $\times$ 10 ml), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO_4 . Chromatography (SiO_2 , hexane/EtOAc: 9/1) afforded 24 mg (0.064 mmol, 89%, 95:5 de) of **16c** as a colorless oil.

$R_f = 0.51$ (hexane/EtOAc: 9/1). ^1H NMR (400 MHz, CDCl_3) δ : 9.70 (br *s*, 1H); 4.26 (*dd*, $J = 1.6$, 8.3 Hz, 1H); 3.90 (br *t*, $J = 5.9$ Hz, 1H); 2.46 (*dq*, $J = 1.7$, 6.8 Hz, 1H); 1.62 (br *t*, $J = 7.0$ Hz, 1H); 1.51–1.46 (*m*, 2H); 1.29–1.21 (*m*, 2H); 1.07 (*d*, $J = 6.9$ Hz, 3H); 0.91 (*t*, $J = 7.2$ Hz, 3H); 0.89 (*s*, 9H); 0.78 (*d*, $J = 7.0$ Hz, 3H); 0.08 (*s*, 3H); 0.07 (*s*, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ : 205.26; 72.61; 71.77; 50.18; 41.42; 38.18; 26.04; 18.97; 18.34; 14.24; 9.77; 6.46; 0.92; -4.04 ; -4.61 . IR (thin film): 2957.7 (*s*), 2932.3 (*s*), 2858.3 (*m*), 1730.6.4 (*s*), 1463.4 (*m*), 1252.1 (*s*), 1102.0 (*m*), 1035.9 (*s*), 838.7 (*s*), 773.4 (*m*) cm^{-1} . High resolution CI MS (m/z): 373.2594 calcd for $\text{C}_{19}\text{H}_{41}\text{O}_3\text{Si}_2$ 373.2619 ($\text{M}-\text{H}^+$).

(2*S*,3*R*,4*R*,5*R*)-2,4-Dimethyl-5-(diphenyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (21a) and (2*R*,3*R*,4*R*,5*R*)-2,4-Dimethyl-5-(diphenyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (22a).

The silyl epoxide **20a** (30 mg, 0.055 mmol) was dissolved in dichloromethane (2 ml) and treated successively with 20 mg of powdered 4 Å molecular sieves and DIPEA (48 µl, 0.28 mmol). The solution was cooled to – 45 °C and treated with TMSOTf (50 µl, 0.28 mmol). After 1 h, the solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (2 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane (3 × 10 ml), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO₄. Chromatography (SiO₂, hexane/EtOAc: 20/1) afforded 26 mg (0.052 mmol, 95%, 76:24 de) of **21a** and **22a** as a colorless oil.

R_f = 0.45 (hexane/EtOAc: 9/1). ¹H NMR (400 MHz, CDCl₃) δ: 9.64 (*d*, *J* = 2.6 Hz, 1H_(22a)); 9.45 (*br s*, 1H_(21a)); 7.68–7.63 (*m*, 4H); 7.42–7.35 (*m*, 6H); 4.36 (*dd*, *J* = 1.9, 9.2 Hz, 1H_(21a)); 3.83 (*dd*, *J* = 2.6, 8.7 Hz, 1H_(22a)); 3.82 (*ddd*, *J* = 2.7, 4.3, 8.5 Hz, 1H_(22a)); 3.62 (*ddd*, *J* = 1.7, 4.4, 9.3 Hz, 1H_(21a)); 2.37–2.33 (*m*, 1H_(22a)); 2.13 (*dq*, *J* = 1.9, 6.8 Hz, 1H_(21a)); 1.82–1.78 (*m*, 1H_(22a)); 1.65–1.35 (*m*, 4H); 1.06 (*d*, *J* = 6.2 Hz, 3H_(22a)); 1.06 (*s*, 9H); 1.05 (*d*, *J* = 6.4 Hz, 3H_(21a)); 1.06–1.00 (*m*, 1H); 0.85 (*d*, *J* = 6.9 Hz, 3H); 0.63 (*t*, *J* = 7.2 Hz, 3H_(21a)); 0.60 (*t*, *J* = 7.3 Hz, 3H_(22a)); 0.10 (*s*, 9H_(22a)); 0.07 (*s*, 9H_(21a)). ¹³C NMR (100 MHz, CDCl₃) δ: 205.37 (_{22a}); 204.90 (_{21a}); 135.95; 135.90; 135.84; 134.73; 133.59; 129.89; 129.56; 129.10; 127.73; 127.35; 73.16; 73.07; 49.29; 39.49; 37.29; 27.11; 19.50; 18.72; 13.76; 9.95; 5.96; 0.84. IR (thin film): 2957.2 (*s*), 2930 (*s*), 2856.9 (*s*), 1728.4 (*s*), 1462.2 (*m*), 1427.5 (*m*), 1251.9 (*s*), 1109.1 (*s*), 1005.0 (*s*), 841.0 (*m*), 702.2 (*s*) cm^{–1}. High resolution EI MS (*m/z*): 497.2907 calcd for C₂₉H₄₅O₃Si₂ 497.2885 (M–H⁺).

(2*S*,3*R*,4*R*,5*R*)-2,4-Dimethyl-5-(diphenyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (21b), (2*R*,3*R*,4*R*,5*R*)-2,4-Dimethyl-5-(diphenyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (22b) and (2*S*,3*R*,4*S*,5*R*)-3-[(Trimethylsilyl)oxy]-2-[[triethylsilyl]oxy]methyl-2,4-dimethyl-5-propyltetrahydrofuran (23).

The silyl epoxide **20b** (30 mg, 0.065 mmol) was dissolved in dichloromethane (2 ml) and treated successively with 20 mg of powdered 4 Å molecular sieves molecular sieves and DIPEA (57 µl,

0.32 mmol). The solution was cooled to $-45\text{ }^{\circ}\text{C}$ and treated with TMSOTf (59 μl , 0.32 mmol). After stirring for 1 h, the solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (2 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane ($3 \times 10\text{ ml}$), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO_4 . Chromatography (SiO_2 , hexane/EtOAc: 9/1) afforded 22 mg (0.05 mmol, 82%) of **21b**, **22b** and **23** in a ratio of 38:12:50 as a colorless oil.

Data for **21b** and **22b**: ^1H NMR (400 MHz, CDCl_3) δ : 9.75 (*d*, $J = 2.6\text{ Hz}$, $1\text{H}_{(22b)}$); 9.72 (*s*, $1\text{H}_{(21b)}$); 4.37 (*dd*, $J = 2.2, 8.7\text{ Hz}$, 1H); 3.83 (*ddd*, $J = 2.3, 4.4, 9.3\text{ Hz}$, 1H); 2.66 (*dq*, $J = 2.2, 6.8\text{ Hz}$, 1H); 1.70–1.64 (*m*, 2H); 1.55–1.50 (*m*, 1H); 1.28–1.12 (*m*, 2H); 1.07 (*d*, $J = 6.2\text{ Hz}$, 3H); 1.06 (*s*, 21H); 0.92 (*t*, $J = 7.3\text{ Hz}$, 3H); 0.92 (*d*, $J = 6.9\text{ Hz}$, 3H); 0.07 (*s*, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ : 205.03; 73.00; 72.96; 49.83; 39.70; 37.39; 18.83; 18.39; 14.28; 13.24; 9.84; 6.62; 0.77. IR (thin film): 2959.2 (*s*), 2867.9 (*s*), 1728.9 (*s*), 1463.2 (*m*), 1251.6 (*s*), 1095.7 (*s*), 1032.4 (*s*), 882.5 (*m*), 840.1 (*s*) cm^{-1} . High resolution CI MS (m/z): 415.3063 calcd for $\text{C}_{22}\text{H}_{47}\text{O}_3\text{Si}_2$ 415.3072 ($\text{M}-\text{H}^+$).

Data for **23**: ^1H NMR (400 MHz, CDCl_3) δ : 3.95 (*ddd*, $J = 2.3, 4.3, 9.0\text{ Hz}$, 1H); 3.92 (*d*, $J = 6.0\text{ Hz}$, 1H); 3.45 (*d*, $J = 10.2\text{ Hz}$, 1H); 3.42 (*d*, $J = 10.2\text{ Hz}$, 1H); 2.16–2.08 (*m*, 1H); 1.47–1.24 (*m*, 4H); 1.04 (*s*, 3H); 0.96 (*t*, $J = 8.0\text{ Hz}$, 9H); 0.92 (*d*, $J = 7.2\text{ Hz}$, 3H); 0.90 (*t*, $J = 7.2\text{ Hz}$, 3H); 0.61 (*q*, $J = 8.3\text{ Hz}$, 6H); 0.10 (*s*, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ : 83.59; 79.19; 67.68; 43.73; 33.63; 19.62; 18.62; 14.22; 12.42; 6.79; 4.37; 0.27. IR (thin film): 2958.0 (*s*), 2876.1 (*s*), 1458.3 (*m*), 1376.7 (*m*), 1251.3 (*s*), 1100.9 (*s*), 1015.0 (*m*), 888.1 (*s*), 841.2 (*s*) cm^{-1} . High resolution EI MS (m/z): 373.2594 calcd for $\text{C}_{19}\text{H}_{41}\text{O}_3\text{Si}_2$ 373.2582 ($\text{M}-\text{H}^+$).

(2*S*,3*R*,4*R*,5*R*)-2,4-Dimethyl-5-(dimethyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (21c) and (2*R*,3*R*,4*R*,5*R*)-2,4-Dimethyl-5-(dimethyl-*t*-butylsilyloxy)-3-trimethylsilyloxyoctanal (22c).

The silyl epoxide **20c** (30 mg, 0.07 mmol) was dissolved in dichloromethane (2 ml) and treated successively with 20 mg of powdered 4 Å molecular sieves and DIPEA (63 μl , 0.36 mmol). The

solution was cooled to $-45\text{ }^{\circ}\text{C}$ and treated with TMSOTf (65 μl , 0.36 mmol). After 1 h, the solution was quenched by adding 0.05 M pH 7.0 phosphate buffer (2 ml) and was filtered through Celite. The layers were separated, the aqueous phase extracted with dichloromethane ($3 \times 10\text{ ml}$), the combined extracts were washed with 0.05 M pH 7.0 phosphate buffer, brine and dried over MgSO_4 . Chromatography (SiO_2 , hexane/EtOAc: 20/1) afforded 22 mg of a mixture of **21c**, **22c** and **23** in a ratio of 12/12/76 as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ : 9.75 (*d*, $J = 2.6\text{ Hz}$, $1\text{H}_{(22\text{c})}$); 9.72 (*br s*, $1\text{H}_{(21\text{c})}$); 4.26 (*dd*, $J = 2.5, 8.3\text{ Hz}$, $1\text{H}_{(21\text{c})}$); 3.83 (*dd*, $J = 3.5, 7.5\text{ Hz}$, $1\text{H}_{(22\text{c})}$); 3.75–3.71 (*m*, $1\text{H}_{(22\text{c})}$); 3.64–3.60 (*m*, $1\text{H}_{(21\text{c})}$); 2.70–2.62 (*m*, 1H); 1.84–1.78 (*m*, $1\text{H}_{(22\text{c})}$); 1.73–1.66 (*m*, $1\text{H}_{(21\text{c})}$); 1.55–1.20 (*m*, 4H); 1.08 (*d*, $J = 6.2\text{ Hz}$, $3\text{H}_{(21\text{c})}$); 1.07 (*d*, $J = 6.2\text{ Hz}$, $3\text{H}_{(21\text{c})}$); 1.06–0.87 (*m*, 32H); 0.12–0.03 (*m*, 27H).