Stereoselective total synthesis of sporiolide B and attempted synthesis of sporiolide A

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SUPPORTING INFORMATION

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GENERAL PROCEDURES

Solvents were dried over standard drying agents and freshly distilled prior to use. All commercially available chemicals were used without further purification. All reactions were performed under Nitrogen. ^1H NMR and ^{13}C NMR spectra were measured with Varian Gemini FT 200 MHz spectrometer, Bruker Avance 300 MHz, Unity 400 MHz and Inova 500 MHz with tetramethylsilane as internal standard for solutions in CDCl_3 . J values are given in Hz. Chemical shifts were reported in ppm relative to solvent signal. All column chromatographic separations were performed using silica gel (Acme's, 60-120 mesh). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40 °C in *vacuo*. IR-spectra were recorded on FT IR (Perkin-Elmer IR-683) spectrophotometer with NaCl optics. JASCO DIP 300 digital polarimeter was used for measurement of optical rotations at 25 °C. Mass spectra were recorded on direct inlet system or LC by MSD trap SL (Agilent Technologies), the HRMS data were obtained using Q-TOF mass spectrometry.

(R)-(2-(Benzyloxy)-3-(4-methoxybenzyloxy)propoxy)(tert.-butyl)dimethylsilane (14):

To an ice cooled suspension of NaH (3.53 g, 147.23 mmol) in THF (120 mL), alcohol **12** (12 g, 36.80 mmol) was added, stirred for 30 min and treated with a solution of BnBr (5.25 mL, 44.17 mmol) in THF (30 mL) and stirred at 35 °C temperature for 6 h. The reaction mixture was quenched with sat. NH_4Cl solution (20 mL) and extracted with ethyl acetate (2 x 100 mL). The organic layers were washed with water (2 x 50 mL), brine (100 mL) and dried (Na_2SO_4). Solvent was evaporated under reduced pressure and purified the residue by column chromatography (60-120 mesh silica gel, 8% ethyl acetate in pet. ether) to furnish **14** (13.1 g, 85%) as a yellow liquid with 100% diastereoselectivity. $[\alpha]_{\text{D}}^{25} = +4.8$ (c 0.5, CHCl_3); IR (neat): 3018, 2930, 2857, 1612, 1513, 1466, 1249, 1214, 1175, 1094, 1035, 928, 837, 743, 667 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 7.35-7.27 (m, 5H, ArH-Bn), 7.22 (d, 2H, J = 8.6 Hz, ArH-PMB), 6.83 (d, 2H, J = 8.6 Hz, ArH-PMB), 4.65 (s, 2H, benzylic), 4.44 (s, 2H,

benzylic), 3.75 (s, 3H, -OCH₃), 3.68 (d, 2H, *J* = 4.8 Hz, -OCH₂), 3.64-3.55 (m, 2H, -OCH₂), 3.52-3.48 (m, 1H, -OCH), 0.90 (s, 9H, 3 x -CH₃), 0.06 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 158.9, 138.7, 129.0, 128.0, 127.4, 127.2, 113.5, 78.7, 72.8, 72.0, 69.6, 62.9, 54.9, 25.7, 18.1, -5.4; HRMS (ESI): *m/z* calculated for C₂₄H₄₀O₄NSi [M+NH₄]⁺ 434.2714, found 434.2721.

(*S*)-2-(Benzyloxy)-3-(4-methoxybenzyloxy)propan-1-ol (15):

To a solution of **14** (11.5 g, 27.64 mmol) in THF (115 mL) at 0 °C, 1M TBAF in THF (33 mL) was added and stirred for 1 h. It was diluted with water (50 mL) and extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with water (2 x 50 mL), brine (50 mL), dried (Na₂SO₄), evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 13% ethyl acetate in pet. ether) to give **15** (7.1 g, 85%) as a yellow liquid with 100% diastereoselectivity. [α]_D²⁵ = +28.3 (*c* 0.5, CHCl₃); IR (neat): 3447, 2930, 1719, 1636, 1454, 1268, 1217, 1102, 1035, 916, 771 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.35-7.28 (m, 5H, ArH-Bn), 7.24 (d, 2H, *J* = 8.5 Hz, ArH-PMB), 6.87 (d, 2H, *J* = 8.6 Hz, ArH-PMB), 4.65 (dd, 2H, *J* = 11.7, 46.0 Hz, benzylic), 4.46 (d, *J* = 11.7 Hz, 2H, benzylic), 3.80 (s, 3H, -OCH₃), 3.76-3.72 (m, 1H, -OCH), 3.69-3.64 (m, 2H, 2 x -OCH), 3.62-3.55 (m, 2H, -OCH₂); ¹³C NMR (CDCl₃, 75 MHz): δ 159.1, 138.2, 128.4, 128.2, 127.7, 127.5, 126.3, 117.4, 96.1, 81.0, 79.3, 73.5, 60.4, 55.8; HRMS (ESI): *m/z* calculated for C₁₈H₂₂O₄Na [M+Na]⁺ 325.1402, found 325.1409.

(*S,E*)-Ethyl 4-(benzyloxy)-5-(4-methoxybenzyloxy)pent-2-enoate (16):

To a solution of oxalyl chloride (2.98 mL, 34.72 mmol) in dry CH₂Cl₂ (30 mL) at -78 °C, dry DMSO (9.48 mL, 69.53 mmol) was added dropwise and stirred for 20 min. A solution of **15** (7 g, 23.17 mmol) in dry CH₂Cl₂ (70 mL) was added and stirred for 2 h at -78 °C. It was quenched with Et₃N (19.34 mL, 139.0 mmol) and diluted with CH₂Cl₂ (80 mL).

The reaction mixture was washed with water (80 mL), brine (38 mL), dried (Na₂SO₄) and evaporated to furnish the corresponding aldehyde **15a**.

Aldehyde **15a** (7 g, 23.33 mmol) was dissolved in benzene (70 mL) and treated with (ethoxycarbonylmethylene)triphenyl phosphorane (11.69 g, 35.0 mmol) at reflux for 2 h. Solvent was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 10% ethyl acetate in pet. ether) to furnish **16** (7.5 g, 87%) as a yellow liquid. **The diastereoselectivity of E and Z isomers are 98:2.** $[\alpha]_D^{25} = +63.8$ (c 0.5, CHCl₃); IR (neat): 3063, 3031, 2979, 2923, 2856, 1716, 1657, 1611, 1586, 1512, 1455, 1390, 1366, 1346, 1246, 1174, 1092, 1033, 982, 820, 737, 698 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.36-7.23 (m, 7H, ArH-Bn, ArH-PMB), 6.94-6.86 (m, 3H, ArH-PMB, olefinic), 6.11 (d, 1H, *J* = 15.86 Hz, olefinic), 4.67-4.49 (m, 4H, benzylic), 4.25-4.17 (m, 3H, -OCH₂, -OCH), 3.80 (s, 3H, -OCH₃), 3.62-3.50 (m, 2H, -OCH₂), 1.30 (t, 3H, *J* = 7.17 Hz, -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 166.1, 159.2, 145.2, 137.9, 129.9, 129.3, 128.3, 127.6, 123.0, 113.7, 73.1, 71.8, 71.5, 60.5, 55.2, 14.2; HRMS (ESI): *m/z* calculated for C₂₂H₃₀O₅N [M+NH₄]⁺ 388.2120, found 388.2118.

(*S,E*)-4-(Benzyloxy)-5-(4-methoxybenzyloxy)pent-2-en-1-ol (17):

To a stirred solution of **16** (7.3 g, 19.73 mmol) in dry CH₂Cl₂ (70 mL), DIBAL-H (22.4 mL, 39.43 mmol, 20% solution in hexane) was added at 0 °C and for 2 h. Methanol (30 mL) was added to the reaction mixture at this temperature and stirred for 10 min. The reaction mixture was diluted with EtOAc (50 mL), aq. potassium sodium tartrate (10 mL) and stirred vigorously at 35 °C temperature for an additional 1 h. It was filtered through celite and the filtrate dried (Na₂SO₄). Solvent was evaporated and the residue purified by column chromatography (60-120 mesh silica gel, 13% ethyl acetate in pet. ether) to furnish **17** (5.6 g, 86%) as colorless syrup **with 100% diastereoselectivity.** $[\alpha]_D^{25} = +119.3$ (c 0.5, CHCl₃); IR

(neat): 3453, 2860, 1636, 1513, 1456, 1248, 1217, 1175, 1093, 1033, 760, 671 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.37-7.29 (m, 5H, ArH-Bn), 7.25 (d, 2H, J = 8.93 Hz, ArH-PMB), 6.86 (d, 2H, J = 8.69 Hz, ArH-PMB), 5.93-5.88 (m, 1H, olefinic), 5.70-5.64 (m, 1H, olefinic), 4.64-4.46 (m, 4H, benzylic), 4.16 (d, 2H, J = 5.34 Hz, $-\text{OCH}_2$), 4.08-4.04 (m, 1H, $-\text{OCH}$), 3.80 (s, 3H, $-\text{OCH}_3$), 3.58-3.49 (m, 2H, $-\text{OCH}_2$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 159.1, 138.4, 133.1, 130.2, 129.2, 128.7, 128.3, 127.6, 127.4, 113.7, 78.3, 72.9, 72.6, 70.6, 62.8, 55.2; HRMS (ESI): m/z calculated for $\text{C}_{20}\text{H}_{28}\text{NO}_4$ $[\text{M}+\text{NH}_4]^+$ 346.2009, found 346.2012.

((2*S*,3*R*)-3-((*R*)-1-(Benzyloxy)-2-(4-methoxybenzyloxy)ethyl)oxiran-2-yl)methanol (18**):**

To a stirred solution of (+)-DIPT (0.78 g, 3.35 mmol) in CH_2Cl_2 (30 mL) at $-20\text{ }^\circ\text{C}$ containing MS 4 Å (3 g), $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.49 mL, 1.67 mmol) and cumene hydroperoxide (3.76 mL, 25.15 mmol) were added sequentially and stirred for 20 min. A solution of allylic alcohol **17** (5.5 g, 16.76 mmol) in CH_2Cl_2 (30 mL) was added and stirred at $-20\text{ }^\circ\text{C}$ for 5 h. The reaction mixture was quenched with 10% NaOH solution (5.5 g in 55 mL brine) and stirred for 3 h. It was filtered through a pad of celite and washed with CH_2Cl_2 (60 mL). The organic layer was dried (Na_2SO_4), evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 15% ethyl acetate in pet. ether) to furnish **18** (4.9 g, 85%) as a yellow oil with 100% diastereoselectivity. $[\alpha]_D^{25} = +107.1$ (c 0.5, CHCl_3); IR (neat): 3447, 2908, 2865, 1720, 1611, 1585, 1513, 1457, 1364, 1301, 1248, 1093, 1032, 899, 699 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 7.37-7.27 (m, 5H, ArH-Bn), 7.23 (d, 2H, J = 8.69 Hz, ArH-PMB), 6.87 (d, 2H, J = 8.54 Hz, ArH-PMB), 4.79-4.61 (m, 2H, benzylic), 4.50-4.43 (m, 2H, benzylic), 3.94-3.83 (m, 1H, $-\text{OCH}$), 3.80 (s, 3H, $-\text{OCH}_3$), 3.65-3.53 (m, 3H, 3 x $-\text{OCH}$), 3.43-3.40 (m, 1H, $-\text{OCH}$), 3.18-3.02 (m, 2H, epoxy), 3.58-3.49 (m, 2H, $-\text{OCH}_2$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 159.1, 138.0, 129.8, 129.2, 128.3, 127.7, 127.6, 113.7, 78.0, 73.1, 72.0, 69.8, 61.2, 56.6, 55.2; HRMS (ESI): m/z calculated for $\text{C}_{20}\text{H}_{28}\text{NO}_5$ $[\text{M}+\text{NH}_4]^+$ 362.1963, found 362.1969.

(3R,4R)-4-(Benzyloxy)-5-(4-methoxybenzyloxy)pentane-1,3-diol (19**):**

To a stirred solution of epoxide **18** (4.8 g, 13.95 mmol) in dry THF (50 mL), Red-Al (5.5 mL, 27.87 mmol, 70% w/w in toluene) was added at 0 °C. After 4 h, the reaction mixture was quenched with sat. NH₄Cl solution (15 mL) and filtered through a pad of celite and washed with EtOAc (2 x 100 mL). Organic layers were dried (Na₂SO₄), evaporated solvent and purified the residue by column chromatography (60-120 mesh silica gel, 25% ethyl acetate in pet. ether) to afford **19** (4.1 g, 85%) as a colorless oil with 100% diastereoselectivity. $[\alpha]_D^{25} = +119.4$ (*c* 0.5, CHCl₃); IR (neat): 3401, 2984, 2940, 2878, 1715, 1651, 1419, 1373, 1217, 1159, 1055, 862 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.36-7.29 (m, 5H, ArH-Bn), 7.25 (d, 2H, *J* = 8.69 Hz, ArH-PMB), 6.88 (d, 2H, *J* = 8.54 Hz, ArH-PMB), 4.72 (dd, 1H, *J* = 11.59, 23.95 Hz, benzylic), 4.59-4.45 (m, 3H, benzylic), 3.99 (m, 1H, -OCH), 3.81 (s, 3H, -OCH₃), 3.80 (m, 1H, -OCH), 3.71-3.65 (m, 2H, 2 x -OCH), 3.60-3.48 (m, 2H, 2 x -OCH), 1.82-1.65 (m, 2H, -CH₂); ¹³C NMR (CDCl₃, 75 MHz): δ 163.4, 142.4, 133.6, 132.5, 132.1, 132.0, 131.9, 118.0, 84.7, 81.4, 74.9, 73.8, 64.6, 59.4, 39.1; HRMS (ESI): *m/z* calculated for C₂₀H₂₆O₅Na [M+Na]⁺ 369.1669, found 369.1672.

(2R,3R)-2-(Benzyloxy)-5-(tert.-butyldimethylsilyloxy)-1-(4-methoxybenzyloxy)pentan-3-ol (11**):**

To a cooled (0 °C) solution of **19** (4 g, 11.56 mmol) in CH₂Cl₂ (40 mL), imidazole (2.35 g, 34.68 mmol), dibutyltin oxide (0.005 g, 0.02 mmol) was added. After 30 min TBDMS-Cl (1.73 g, 11.56 mmol) was added and stirred at 35 °C temperature for 2 h. The reaction mixture was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 11% EtOAc in pet. ether) to afford **11** (4.8 g, 90%) as a colorless liquid with 100% diastereoselectivity. $[\alpha]_D^{25} = +98.4$ (*c* 0.5, CHCl₃); IR (neat): 3455, 2953, 2930, 2857, 1718, 1610, 1513, 1464, 1390, 1251, 1092, 1034, 773 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.34-7.24 (m, 7H, ArH-Bn, ArH-PMB), 6.87 (d, 2H, *J* = 8.54 Hz, ArH-PMB), 4.75 (dd, 1H, *J*

= 9.3, 11.59 Hz, benzylic), 4.59 (t, 1H, J = 11.59 Hz, benzylic), 4.51-4.44 (m, 2H, benzylic), 3.97-3.83 (m, 2H, -OCH₂), 3.80 (s, 3H, -OCH₃), 3.77-3.61 (m, 3H, -OCH₂, -OCH), 3.54-3.51 (m, 1H, -OCH), 1.87-1.65 (m, 2H, -CH₂), 0.89 (s, 9H, 3 x -CH₃), 0.06 (d, 6H, J = 4.12 Hz, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 158.8, 138.2, 130.0, 129.9, 129.1, 128.7, 115.6, 80.8, 74.2, 73.1, 71.9, 70.0, 61.2, 55.6, 34.6, 25.2, 17.9, -5.7; HRMS (ESI): m/z calculated for C₂₆H₄₀O₅NaSi [M+Na]⁺ 483.1603, found 483.1618.

((3*R*,4*R*)-4-(Benzyloxy)-3-methoxy-5-(4-methoxybenzyloxy)pentyloxy)(*tert*.-butyl)dimethylsilane (9):

To an ice cooled suspension of NaH (0.73 g, 30.65 mmol) in THF (50 mL), alcohol **11** (4.7 g, 10.21 mmol) was added, stirred for 30 min and treated with a solution of CH₃I (0.82 mL, 13.28 mmol) in THF (25 mL) and stirred at 35 °C temperature for 6 h. Work up as described for **14** and purification of the residue by column chromatography (60-120 mesh silica gel, 8% EtOAc in pet. ether) to furnish **9** (4.1 g, 85%) as a yellow liquid **with 100% diastereoselectivity**. [α]_D²⁵ = +91.8 (c 0.5, CHCl₃); IR (neat): 3451, 2929, 2857, 1612, 1513, 1463, 1362, 1301, 1249, 1175, 1092, 1035, 835, 774, 698 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.37-7.28 (m, 5H, ArH-Bn), 7.25 (d, 2H, J = 8.30 Hz, ArH-PMB), 6.87 (d, 2H, J = 8.30 Hz, ArH-PMB), 4.75-4.60 (m, 2H, benzylic), 4.50-4.44 (m, 2H, benzylic), 3.80 (s, 3H, -OCH₃), 3.75-3.48 (m, 6H, 2 x -OCH₂, 2 x -OCH), 3.38 (s, 3H, -OCH₃), 1.82-1.56 (m, 2H, -CH₂), 0.88 (s, 9H, 3 x -CH₃), 0.04 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 159.1, 138.7, 129.0, 128.1, 127.8, 127.5, 127.3, 113.6, 79.0, 77.8, 76.9, 72.9, 70.0, 59.4, 58.6, 55.1, 33.3, 25.8, 18.1, -5.4; HRMS (ESI): m/z calculated for C₂₇H₄₂O₅NaSi [M+Na]⁺ 497.1836, found 497.1842.

(2*R*,3*R*)-2-(Benzyloxy)-5-(*tert*.-butyldimethylsilyloxy)-3-methoxypentan-1-ol (20):

To a solution of **9** (4 g, 8.43 mmol) in aq. CH₂Cl₂ (40 mL, 19:1), DDQ (2.87 g, 12.65 mmol) was added and stirred at 35 °C temperature for 1 h. The reaction mixture was quenched with sat. NaHCO₃ solution (25 mL), filtered, washed with CH₂Cl₂ (40 mL). The filtrate was washed with water (40 mL), brine (40 mL), dried (Na₂SO₄) and evaporated under reduced pressure. The residue was purified by column chromatography (60-120 mesh silica gel, 14% EtOAc in pet. ether) to furnish **20** (2.6 g, 87%) as a yellow liquid with 100% diastereoselectivity. $[\alpha]_D^{25} = +100.5$ (*c* 0.5, CHCl₃); IR (neat): 3418, 2926, 1713, 1607, 1454, 1375, 1273, 1174, 1065, 769, 710 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.39-7.29 (m, 5H, ArH-Bn), 4.91-4.75 (m, 2H, benzylic), 4.08-3.90 (m, 2H, -OCH₂), 3.87 (s, 3H, -OCH₃), 3.83-3.68 (m, 4H, -OCH₂, 2 x -OCH), 2.22-1.95 (m, 2H, -CH₂), 0.95 (s, 9H, 3 x -CH₃), 0.08 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 137.9, 128.5, 128.0, 127.9, 127.8, 127.7, 80.6, 79.4, 72.9, 61.6, 60.5, 58.6, 40.3, 29.6, 14.3, -3.6; HRMS (ESI): *m/z* calculated for C₁₉H₃₄O₄NaSi [M+Na]⁺ 377.1228, found 377.1236.

(5*S*,6*S*,7*R*)-5-Allyl-6-(benzyloxy)-7-methoxy-11,11,12,12-tetramethyl-2,4,10-trioxa-11-silatridecane (22**):**

To a cooled (0 °C) solution of **21** (2.1 g, 5.32 mmol) in CH₂Cl₂ (20 mL), DIPEA (4.6 mL, 26.64 mmol) and MOM-Cl (0.5 mL, 6.39 mmol) were added sequentially and stirred at 35 °C temperature for 6 h. The reaction mixture was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 6% EtOAc in pet. ether) to afford **22** (2 g, 86%) as a yellow liquid with 100% diastereoselectivity. $[\alpha]_D^{25} = +75.6$ (*c* 0.5, CHCl₃); IR (neat): 3447, 3070, 2929, 2855, 1723, 1604, 1451, 1375, 1314, 1272, 1152, 1102, 1033, 918, 837, 775 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.39-7.27 (m, 5H, ArH-Bn), 5.94-5.85 (m, 1H, olefinic), 5.14-5.07 (m, 2H, olefinic), 4.75-4.63 (m, 4H, benzylic, -OCH₂), 3.77-3.69 (m, 3H, -OCH₂, -OCH), 3.66-3.54 (m, 2H, 2 x -OCH), 3.39 (s, 3H, -OCH₃), 3.20 (s, 3H, -OCH₃), 2.52-2.45 (m, 2H, -CH₂), 1.87-1.73 (m, 2H, -CH₂), 0.91 (s, 9H, 3 x -CH₃), 0.06 (s, 6H, 2 x -

CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 138.7, 135.1, 128.2, 127.6, 127.4, 126.6, 117.1, 96.3, 80.4, 78.3, 73.4, 59.6, 59.4, 57.7, 56.6, 55.8, 41.3, 35.4, 33.4, 25.9, 18.3, -5.3; HRMS (ESI): *m/z* calculated for C₂₄H₄₂O₅NaSi [M+Na]⁺ 461.1827, found 461.1832.

(3*R*,4*S*,5*S*)-4-(Benzyloxy)-3-methoxy-5-(methoxymethoxy)oct-7-en-1-ol (23):

To a solution of **22** (1.9 g, 4.33 mmol) in THF (20 mL) at 0 °C, 1 M solution of TBAF in THF (5.2 mL, 5.2 mmol) was added and stirred for 1 h. Work up as described for **15** and purification of the residue by column chromatography (60-120 mesh silica gel, 14% EtOAc in pet. ether) to give **23** (1.25 g, 89%) as a yellow liquid with 100% diastereoselectivity. [α]_D²⁵ = +116.2 (*c* 0.5, CHCl₃); IR (neat): 3448, 3070, 2929, 1723, 1640, 1452, 1271, 1211, 1102, 1034, 916, 739 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.36-7.27 (m, 5H, ArH-Bn), 5.95-5.81 (m, 1H, olefinic), 5.16-5.07 (m, 2H, olefinic), 4.80-4.69 (m, 2H, benzylic), 4.67 (s, 2H, -OCH₂), 3.82-3.65 (m, 5H, -OCH₂, 3 x -OCH), 3.41 (s, 3H, -OCH₃), 3.38 (s, 3H, -OCH₃), 2.70-2.38 (m, 2H, -CH₂), 1.98-1.75 (m, 2H, -CH₂); ¹³C NMR (CDCl₃, 75 MHz): δ 138.3, 134.2, 128.4, 128.3, 127.9, 127.8, 127.6, 117.7, 96.9, 81.0, 79.7, 74.4, 60.4, 57.1, 55.8, 36.2, 32.0, 29.7; HRMS (ESI): *m/z* calculated for C₁₈H₂₈O₅Na [M+Na]⁺ 347.0812, found 347.0820.

(3*R*,4*S*,5*S*)-4-(Benzyloxy)-3-methoxy-5-(methoxymethoxy)oct-7-enoic acid (5):

To a stirred solution of **23** (1.0 g, 3.08 mmol) in CH₂Cl₂:H₂O (1:1, 10 mL), TEMPO (0.14 g, 0.92 mmol) and BAIB (2.98 g, 9.25 mmol) were added at 0 °C and stirred for 2 h. The reaction mixture was diluted with water (10 mL) and extracted with CH₂Cl₂ (2 x 20 mL). Organic layers were washed with sat. aq. hypo (15 mL), brine (20 mL) and dried (Na₂SO₄). Solvent was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 26% EtOAc in pet. ether) to give acid **5** (0.84 g, 81%) as a colorless gummy oil with 100% diastereoselectivity. [α]_D²⁵ = +126.9 (*c* 0.5, CHCl₃); IR (neat): 3451, 2927, 2854, 1726, 1638, 1457, 1380, 1270, 1211, 1153, 1101, 1034, 917, 768, 701 cm⁻¹; ¹H NMR

(CDCl₃, 300 MHz): δ 7.34-7.27 (m, 5H, ArH-Bn), 5.89-5.81 (m, 1H, olefinic), 5.14 -5.08 (m, 2H, olefinic), 4.74-4.68 (m, 2H, benzylic), 4.67 (s, 2H, -OCH₂), 3.96-3.91 (m, 1H, -OCH), 3.80-3.77 (m, 1H, -OCH), 3.40 (s, 3H, -OCH₃), 3.38 (s, 3H, -OCH₃), 2.75-2.66 (m, 2H, -CH₂), 2.46-2.43 (m, 2H, -CH₂); ¹³C NMR (CDCl₃, 75 MHz): δ 177.1, 138.2, 134.6, 128.2, 127.8, 127.5, 117.4, 96.0, 79.6, 78.2, 73.4, 57.7, 55.9, 35.8, 35.4; HRMS (ESI): m/z calculated for C₁₈H₂₆O₆Na [M+Na]⁺ 361.0948, found 361.0941.

(4*R*,5*R*,6*S*,12*S*)-5-Hydroxy-4-methoxy-6-(methoxymethoxy)-12-methyloxacyclododecan-2-one (25):

To a stirred solution of **24** (0.2 g, 0.51 mmol) in MeOH (10 mL), 10% Pd-C was added and stirred under H₂ atmosphere for 12 h. The reaction mixture was filtered through celite, concentrated the filtrate and purified the residue by column chromatography (60-120 mesh silica gel, 18% EtOAc in pet. ether) to afford **25** (0.12 g, 77%) as colorless syrup **with 100% diastereoselectivity**. $[\alpha]_D^{25} = +41.6$ (c 0.5, CHCl₃); IR (neat): 3453, 2928, 2856, 1786, 1717, 1633, 1461, 1370, 1275, 1168, 1104, 1034, 920, 836, 757, 713 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 4.71-4.60 (m, 3H, -OCH₂, -OCH), 4.50-4.39 (m, 1H, -OCH), 4.21-4.07 (m, 1H, -OCH), 3.90-3.71 (m, 1H, -OCH), 3.35 (s, 6H, 2 x -OCH₃), 2.89-2.70 (m, 1H, -CH), 2.51-2.48 (m, 1H, -CH), 1.79-1.30 (m, 7H, 7 x -CH), 1.20 (d, 3H, J = 6.3 Hz, -CH₃), 0.99-0.77 (m, 3H, 3 x -CH); ¹³C NMR (75 MHz, CHCl₃): δ 175.5, 96.5, 86.4, 76.2, 67.9, 56.4, 55.9, 39.0, 35.3, 30.6, 29.6, 29.5, 25.5, 25.3, 23.5; HRMS (ESI): m/z calculated for C₁₅H₂₈O₆Na [M+Na]⁺ 327.0649, found 327.0655.

(4*R*,6*S*,12*S*)-4-Methoxy-6-(methoxymethoxy)-12-methyloxacyclododecane-2,5-dione(26):

To a stirred solution of alcohol **25** (0.07 g, 0.23 mmol) in dry CH₂Cl₂ (10 mL), Dess-Martin periodinane (0.11 g, 0.27 mmol) was added at 0 °C, and stirred at 35 °C temperature for 4 h. The reaction mixture was quenched with a 1:1 mixture of saturated solutions of

Na₂S₂O₃ and NaHCO₃ (20 mL), and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layers were washed with water (20 mL), brine (20 mL) and dried (Na₂SO₄), solvent was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 15% EtOAc in pet. ether) to afford **26** (0.055 g, 80%) as a yellow liquid with 100% diastereoselectivity. $[\alpha]^{25}_{\text{D}} = -5.8$ (*c* 0.5, CHCl₃); IR (neat): 3451, 2923, 2853, 1781, 1710, 1636, 1459, 1364, 1169, 1096, 1037, 918, 768 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 4.79-4.71 (m, 3H, -OCH₂, -OCH), 4.53 (d, 1H, *J* = 8.9 Hz, -OCH), 4.27 (d, 1H, *J* = 5.9 Hz, -OCH), 3.49 (s, 3H, -OCH₃), 3.47 (s, 3H, -OCH₃), 2.97-2.90 (m, 1H, -CH), 2.63 (dd, 1H, *J* = 8.5 Hz, 13.6 Hz, -CH), 2.10-2.01 (m, 1H, -CH), 1.69-1.58 (m, 2H, 2 x -CH), 1.57-1.48 (m, 2H, 2 x -CH), 1.47-1.38 (m, 2H, 2 x -CH), 1.36-1.25 (m, 2H, 2 x -CH), 1.23 (d, 3H, *J* = 6.4 Hz, -CH₃), 1.09-1.07 (m, 1H, -CH); ¹³C NMR (75 MHz, CHCl₃): δ 208.8, 170.6, 76.1, 74.4, 73.3, 58.4, 41.4, 33.4, 30.0, 26.5, 23.8, 22.2, 20.8; HRMS (ESI): *m/z* calculated for C₁₅H₂₆O₆Na [M+Na]⁺ 325.1319, found 325.1327.

(2*R*,3*R*)-2-(Benzyloxy)-5-(*tert*.-butyldimethylsilyloxy)pentane-1,3-diol(11a**):**

To a solution of **11** (0.6 g, 1.30 mmol) in aq. CH₂Cl₂ (6 mL, 19:1), DDQ (0.44 g, 1.95 mmol) was added and stirred at 35 °C temperature for 1 h. Work up as described for **20** and purification of the residue by column chromatography (60-120 mesh silica gel, 24% EtOAc in pet. ether) furnished **11a** (0.38 g, 85%) as a colorless liquid with 100% diastereoselectivity. $[\alpha]^{25}_{\text{D}} = +80.1$ (*c* 0.5, CHCl₃); IR (neat): 3460, 3420, 3065, 2938, 1715, 1640, 1470, 1375, 1310, 1173, 1095, 1020, 919, 757 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.37-7.27 (m, 5H, ArH-Bn), 4.67 (s, 2H, benzylic), 4.24-4.16 (m, 1H, -OCH), 3.87-3.65 (m, 4H, 2 x -OCH, -OCH₂), 3.62-3.56 (m, 1H, -OCH), 2.03-1.77 (m, 2H, -CH₂), 0.93 (s, 9H, 3 x -CH₃), 0.12 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 134.7, 128.4, 127.8, 127.6, 83.2, 74.3, 71.1, 59.0, 55.9, 35.2, 25.8, 17.9, -4.3, -4.7; HRMS (ESI): *m/z* calculated for C₁₈H₃₂O₄NaSi [M+Na]⁺ 363.2071, found 363.2079.

(3*R*,4*R*,5*S*)-4-(Benzyloxy)-1-(*tert*.-butyldimethylsilyloxy)oct-7-ene-3,5-diol (28):

To a solution of alcohol **11a** (0.3 g, 0.88 mmol) in CH₂Cl₂ (10 mL), P^H 8.6 buffer (2 mL) (aq. solutions of 0.5 M NaHCO₃, 0.05 M K₂CO₃), TEMPO (13 mg, 0.1 mmol), TBACl (24 mg, 0.08 mmol), *N*-Chlorosuccinimide (0.11 g, 0.879 mmol) were added, stirred at 35 °C temperature for 1 h. After completion of the reaction, it was diluted with water (3 mL) and extracted with CH₂Cl₂ (2 x 5 mL). Organic layers were washed with brine (5 mL), dried (Na₂SO₄), evaporated to furnish the corresponding aldehyde **27**.

To a solution of the aldehyde **27** (0.25 g, 0.74 mmol) in CH₂Cl₂ (3 mL), MgBr₂·OEt₂ (0.38 g, 1.47 mmol) was added at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 45 min. Allyltributyltin (0.3 mL, 1.11 mmol) was added to the reaction mixture dropwise, and stirred at -78 °C for 4 h. Work up as described for **21** and purification of the residue by column chromatography (60-120 mesh silica gel, 16% EtOAc in pet. ether) to furnish **28** (0.22 g, 79%) as a colorless syrup. *The diastereoselectivity of syn and anti alcohols are 96:4.* [α]_D²⁵ = +81.6 (c 0.5, CHCl₃); IR (neat): 3420, 3060, 2935, 1710, 1642, 1450, 1376, 1316, 1250, 1176, 1099, 1026, 919, 758 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.48-7.28 (m, 5H, ArH-Bn), 6.06-5.90 (m, 1H, olefinic), 5.26 -5.17 (m, 2H, olefinic), 4.74 (s, 2H, benzylic), 4.33-4.25 (m, 1H, -OCH), 3.92-3.76 (m, 3H, -OCH, -OCH₂), 3.71-3.68 (m, 1H, -OCH), 2.72-2.47 (m, 2H, -CH₂), 2.13-1.85 (m, 2H, -CH₂), 1.10 (s, 9H, 3 x -CH₃), 0.21 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 138.0, 134.4, 128.1, 127.6, 127.5, 117.2, 83.4, 74.6, 70.1, 60.0, 59.7, 36.3, 35.4, 26.4, -5.7, -5.4; HRMS (ESI): *m/z* calculated for C₂₁H₃₆O₄NaSi [M+Na]⁺ 403.2476, found 403.2482.

(2-((4*R*,5*R*,6*S*)-6-Allyl-5-(benzyloxy)-2,2-dimethyl-1,3-dioxan-4-yl)ethoxy)(*tert*.-butyl)dimethylsilane (29):

To a cooled (0 °C) solution of **28** (0.15 g, 0.39 mmol) in dry CH₂Cl₂ (3 mL), 2, 2-dimethoxy propane (0.1 mL, 0.78 mmol), PTSA (cat.) were added and stirred at 35 °C temperature for 1 h. The reaction mixture was neutralised with Et₃N (1 mL) and extracted with CH₂Cl₂ (2 x 3 mL). The organic layers were washed with water (3 mL), brine (3 mL) and dried (Na₂SO₄). Solvent was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 11% EtOAc in pet. ether) to furnish **29** (0.12 g, 73%) as a yellow liquid with 100% diastereoselectivity. $[\alpha]_D^{25} = +86.9$ (c 0.5, CHCl₃); IR (neat): 3340, 2943, 2861, 1682, 1520, 1374, 1250, 1105, 1020, 825, 775 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.39-7.28 (m, 5H, ArH-Bn), 6.08-5.98 (m, 1H, Olefinic), 5.30-5.22 (m, 2H, Olefinic), 4.80-4.74 (m, 2H, benzylic), 4.30-4.24 (m, 1H, -OCH), 3.97-3.80 (m, 3H, -OCH, -OCH₂), 3.71-3.68 (m, 1H, -OCH), 2.69-2.41 (m, 2H, -CH₂), 2.10-1.93 (m, 2H, -CH₂), 1.54 (s, 3H, -CH₃), 1.28 (s, 3H, -CH₃), 1.07 (s, 9H, 3 x -CH₃), 0.20 (s, 6H, 2 x -CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 139.1, 135.4, 128.6, 127.2, 127.0, 117.1, 96.4, 80.7, 78.1, 73.5, 59.7, 41.6, 35.3, 33.4, 30.2, 26.5, 19.7, 18.2, -5.4; HRMS (ESI): *m/z* calculated for C₂₄H₄₀O₄NaSi [M+Na]⁺ 443.1685, found 443.1690.

(R)-5-((R)-1-(Benzyloxy)-2-(4-methoxybenzyloxy)ethyl)-2,2,3,3,9,9,10,10-octamethyl-4,8-dioxa-3,9-disilaundecane (10):

To a cooled (0 °C) solution of **11** (4 g, 8.69 mmol) in CH₂Cl₂ (40 mL), imidazole (1.77 g, 26.02 mmol) was added. After 30 min TBDMS-Cl (1.3 g, 8.66 mmol) was added and stirred at 35 °C temperature for 2 h. The reaction mixture was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 8% EtOAc in pet. ether) to afford **10** (4.2 g, 84%) as a yellow liquid with 100% diastereoselectivity. $[\alpha]_D^{25} = +113.6$ (c 0.5, CHCl₃); IR (neat): 2952, 2925, 2857, 1716, 1610, 1512, 1470, 1390, 1261, 1097, 1034, 771 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.40-7.33 (m, 5H, ArH-Bn), 7.28 (d, 2H, *J* = 8.8 Hz, ArH-PMB), 6.90 (d, 2H, *J* = 8.5 Hz, ArH-PMB), 4.78-4.67 (m, 2H, benzylic), 4.55-4.45

(m, 2H, benzylic), 4.10-4.01 (m, 1H, -OCH), 3.85 (s, 3H, -OCH₃), 3.79-3.57 (m, 5H, 2 x -OCH₂, -OCH), 1.96-1.67 (m, 2H, -CH₂), 0.93-0.91 (m, 18H, 6 x -CH₃), 0.09 (d, 6H, $J = 3.3$ Hz, 2 x -CH₃), 0.07 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 159.0, 138.9, 130.6, 129.1, 128.1, 127.7, 127.6, 127.3, 113.6, 82.1, 72.9, 72.3, 70.3, 68.1, 59.6, 55.2, 34.7, 25.9, 18.2, 17.9, -4.6, -5.3; HRMS (ESI): m/z calculated for C₃₂H₅₄O₅NaSi₂ [M+Na]⁺ 597.2429, found 597.2436.

(2*R*,3*R*)-2-(Benzyloxy)-3,5-bis(*tert*.-butyldimethylsilyloxy)pentan-1-ol (30):

To a solution of **10** (4 g, 6.96 mmol) in aq. CH₂Cl₂ (40 mL, 19:1), DDQ (2.37 g, 10.45 mmol) was added and stirred at 35 °C temperature for 1 h. Work up as described for **20** and purification of the residue by column chromatography (60-120 mesh silica gel, 13% EtOAc in pet. ether) to furnish **30** (2.5 g, 79%) as a yellow liquid with 100% diastereoselectivity. $[\alpha]_D^{25} = +101.4$ (c 0.5, CHCl₃); IR (neat): 3449, 3065, 3031, 2954, 2930, 2887, 2857, 1725, 1609, 1467, 1388, 1361, 1254, 1095, 936, 776, 698 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.37-7.29 (m, 5H, ArH-Bn), 4.76-4.53 (m, 2H, benzylic), 4.16-4.05 (m, 1H, -OCH), 3.84-3.47 (m, 5H, 2 x -OCH₂, -OCH), 2.37-2.24 (m, 1H, -CH), 1.82-1.67 (m, 1H, -CH), 0.94-0.85 (m, 18H, 6 x -CH₃), 0.11-0.02 (m, 12H, 4 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 138.3, 132.2, 128.4, 127.8, 127.6, 114.3, 80.7, 72.2, 68.3, 59.4, 59.2, 37.0, 25.9, 18.2, 17.9, -4.5, -4.9, -5.3; HRMS (ESI): m/z calculated for C₂₄H₄₆O₄NaSi₂ [M+Na]⁺ 477.2129, found 477.2135.

(4*S*,5*R*,6*R*)-5-(Benzyloxy)-6,8-bis(*tert*.-butyldimethylsilyloxy)oct-1-en-4-ol (31):

To a solution of oxalyl chloride (0.7 mL, 7.59 mmol) in dry CH₂Cl₂ (10 mL) at -78 °C, dry DMSO (2.1 mL, 15.13 mmol) was added dropwise and stirred for 20 min. A solution of **30** (2.3 g, 5.06 mmol) in dry CH₂Cl₂ (20 mL) was added and stirred for 2 h at -78 °C. Work up as described for **15a** furnish the corresponding aldehyde **30a**.

To a solution of the aldehyde **30a** (2.3 g, 5.08 mmol) in dry CH₂Cl₂ (25 mL), MgBr₂·OEt₂ (2.62 g, 10.17 mmol) was added at -78 °C. The reaction mixture was stirred at -78 °C for 45 min, then allyltributyltin (2.3 mL, 7.63 mmol) was added to the reaction mixture dropwise, and the whole was stirred for 4 h at -78 °C. Work up as described for **21** and purification of the residue by column chromatography (60-120 mesh silica gel, 8% EtOAc in pet. ether) to furnish **31** (1.9 g, 76%) as a yellow syrup. The diastereo selectivity of *syn* and *anti* alcohols are 96:4. $[\alpha]_D^{25} = +84.2$ (c 0.5, CHCl₃); IR (neat): 3448, 3070, 2955, 2929, 2856, 1725, 1640, 1463, 1383, 1254, 1091, 914, 775, 698 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.40-7.29 (m, 5H, ArH-Bn), 5.90-5.71 (m, 1H, olefinic), 5.09-4.97 (m, 2H, olefinic), 4.90-4.52 (m, 2H, benzylic), 4.33-4.09 (m, 1H, -OCH), 3.93-3.62 (m, 3H, -OCH₂, -OCH), 3.39-3.27 (m, 1H, -OCH), 2.46-2.18 (m, 2H, -CH₂), 1.72-1.58 (m, 2H, -CH₂), 0.97-0.85 (m, 18H, 6 x -CH₃), 0.13-0.03 (m, 12H, 4 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 138.0, 135.3, 128.3, 127.9, 127.6, 116.9, 81.4, 72.9, 70.3, 69.0, 67.7, 59.3, 39.9, 35.2, 27.8, 25.8, 17.5, 13.5, -4.3, -4.8, -5.3; HRMS (ESI): *m/z* calculated for C₂₇H₅₀O₄NaSi₂ [M+Na]⁺ 517.2048, found 517.2055.

(5*S*,6*R*,7*R*)-5-Allyl-6-(benzyloxy)-7-(*tert*.-butyldimethylsilyloxy)-11,11,12,12-tetramethyl-2,4,10-trioxa-11-silatridecane (32**):**

To a cooled (0 °C) solution of **31** (1.8 g, 3.64 mmol) in CH₂Cl₂ (20 mL), DIPEA (3.1 mL, 18.21 mmol) and MOM-Cl (0.3 mL, 4.37 mmol) were added sequentially and stirred at 35 °C temperature for 6 h. The reaction mixture was evaporated and purified the residue by column chromatography (60-120 mesh silica gel, 5% EtOAc in pet. ether) to afford **32** (1.5 g, 76%) as a colorless liquid with 100% diastereoselectivity. $[\alpha]_D^{25} = +81.1$ (c 0.5, CHCl₃); IR (neat): 3450, 2927, 2856, 1741, 1636, 1464, 1377, 1248, 1092, 836, 773, 696 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.50-7.44 (m, 5H, ArH-Bn), 6.10-6.01 (m, 1H, olefinic), 5.28-5.21 (m, 2H, olefinic), 4.99 (d, 1H, *J* = 11.3 Hz, benzylic), 4.84 (d, 1H, *J* = 6.7 Hz, -OCH), 4.79 (d,

1H, $J = 6.7$ Hz, -OCH), 4.74 (d, 1H, $J = 11.3$ Hz, benzylic), 4.30-4.26 (m, 1H, -OCH), 3.94-3.83 (m, 3H, -OCH₂, -OCH), 3.70-3.68 (m, 1H, -OCH), 3.53 (s, 3H, -OCH₃), 2.67-2.58 (m, 2H, -CH₂), 2.07-1.88 (m, 2H, -CH₂), 1.07-1.04 (m, 18H, 6 x -CH₃), 0.24 (d, 6H, $J = 6.2$ Hz, 2 x -CH₃), 0.09 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 138.9, 133.3, 128.3, 127.9, 127.3, 117.9, 83.8, 80.0, 74.4, 73.3, 69.7, 59.1, 36.2, 35.4, 25.9, 21.1, 17.9, -3.6, -4.9, -5.3; HRMS (ESI): m/z calculated for C₂₉H₅₅O₅Si₂ [M+H]⁺ 539.2425, found 539.2418.

(3*R*,4*R*,5*S*)-4-(Benzyloxy)-3-(*tert*.-butyldimethylsilyloxy)-5-(methoxymethoxy)oct-7-en-1-ol (33):

To a cooled (0 °C) solution of **32** (1.3 g, 2.41 mmol) in MeOH (15 mL), catalytic amount of PPTS was added and stirred at 35 °C temperature for 1 h. The reaction mixture was quenched with sat. NaHCO₃ solution (10 mL) and MeOH was evaporated. H₂O (10 mL) was added and the mixture was extracted with EtOAc (2 x 10 mL). The organic extracts were washed with brine (15 mL), dried (Na₂SO₄) and evaporated. The residue was purified by column chromatography (60-120 mesh silica gel, 13% EtOAc in pet. ether) to give **33** (0.8 g, 78%) as a yellow liquid **with 100% diastereoselectivity**. $[\alpha]_D^{25} = +85.8$ (c 0.5, CHCl₃); IR (neat): 3031, 2954, 2930, 2886, 2856, 1612, 1585, 1513, 1466, 1387, 1361, 1301, 1094, 1040, 937, 776, 698 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.39-7.28 (m, 5H, ArH-Bn), 5.97-5.83 (m, 1H, olefinic), 5.19-5.09 (m, 2H, olefinic), 4.91 (d, 1H, $J = 11.1$ Hz, benzylic), 4.68 (s, 2H, -OCH₂), 4.67 (d, 1H, $J = 10.9$ Hz, benzylic), 4.26-4.18 (m, 1H, -OCH), 3.87-3.69 (m, 3H, -OCH₂, -OCH), 3.64-3.59 (m, 1H, -OCH), 3.40 (s, 3H, -OCH₃), 2.67-2.28 (m, 2H, -CH₂), 2.06-1.81 (m, 2H, -CH₂), 0.96 (s, 9H, 3 x -CH₃), 0.14 (s, 6H, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 138.3, 134.6, 128.3, 127.8, 127.6, 117.4, 96.2, 83.4, 77.2, 74.4, 71.1, 59.2, 55.9, 35.2, 34.7, 25.8, 17.9, -4.3, -4.7; HRMS (ESI): m/z calculated for C₂₃H₄₀O₅NaSi [M+Na]⁺ 447.1589, found 447.1592.

(3*R*,4*R*,5*S*)-4-(Benzyloxy)-3-(*tert*.-butyldimethylsilyloxy)-5-(methoxymethoxy)oct-7-enoic acid (7):

To a stirred solution of **33** (0.6 g, 1.41 mmol) in CH₂Cl₂:H₂O (1:1, 13 mL) TEMPO (0.06 g, 0.42 mmol) and BAIB (1.36 g, 4.24 mmol) were added at 0 °C and stirred for 2 h. Work up as described for **5** and purification of the residue by column chromatography (60-120 mesh silica gel, 20-24% EtOAc in pet. ether) to give acid **7** (0.45 g, 72%) as a colorless gummy oil with 100% diastereoselectivity. $[\alpha]_D^{25} = +54.4$ (*c* 0.5, CHCl₃); IR (neat): 3460, 3161, 2931, 2858, 1712, 1641, 1397, 1257, 1098, 917, 771, 699 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.36-7.27 (m, 5H, ArH-Bn), 5.95-5.79 (m, 1H, olefinic), 5.15-5.07 (m, 2H, olefinic), 4.84 (d, 1H, *J* = 11.3 Hz, benzylic), 4.66 (s, 2H, -OCH₂), 4.63 (d, 1H, *J* = 11.3 Hz, benzylic), 4.48-4.42 (m, 1H, -OCH), 3.79-3.72 (m, 1H, -OCH), 3.59-3.55 (m, 1H, -OCH), 3.39 (s, 3H, -OCH₃), 2.69 (d, 2H, *J* = 5.6 Hz, -CH₂), 2.48-2.41 (m, 2H, -CH₂), 0.89 (s, 9H, 3 x -CH₃), 0.10 (d, 6H, *J* = 6.6 Hz, 2 x -CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 176.9, 138.3, 137.4, 134.5, 130.2, 128.3, 127.7, 127.6, 117.5, 95.9, 83.3, 76.5, 73.9, 69.9, 55.9, 38.3, 35.1, 25.7, 17.9, -4.4, -4.9; HRMS (ESI): *m/z* calculated for C₂₃H₃₈O₆NaSi [M+Na]⁺ 461.3348, found 461.3359.

Spectrum 1: ^1H NMR Spectrum of **14** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **14** (75 MHz, CDCl_3).

Spectrum 2: ^1H NMR Spectrum of **15** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **15** (75 MHz, CDCl_3).

Spectrum 3: ^1H NMR Spectrum of **16** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **16** (75 MHz, CDCl_3).

Spectrum 4: ^1H NMR Spectrum of **17** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **17** (75 MHz, CDCl_3).

Spectrum 5: ^1H NMR Spectrum of **18** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **18** (75 MHz, CDCl_3).

Spectrum 6: ^1H NMR Spectrum of **19** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **19** (75 MHz, CDCl_3).

Spectrum 7: ^1H NMR Spectrum of **11** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **11** (75 MHz, CDCl_3).

Spectrum 8: ^1H NMR Spectrum of **9** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **9** (75 MHz, CDCl_3).

Spectrum 9: ^1H NMR Spectrum of **20** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **20** (75 MHz, CDCl_3).

Spectrum 10: ^1H NMR Spectrum of **21** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **21** (75 MHz, CDCl_3).

Spectrum 11: ^1H NMR Spectrum of **22** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **22** (75 MHz, CDCl_3).

Spectrum 12: ^1H NMR Spectrum of **23** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **23** (75 MHz, CDCl_3).

Spectrum 13: ^1H NMR Spectrum of **5** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **5** (75 MHz, CDCl_3).

Spectrum 14: ^1H NMR Spectrum of **3** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **3** (75 MHz, CDCl_3).

Spectrum 15: ^1H NMR Spectrum of **24** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **24** (75 MHz, CDCl_3).

Spectrum 16: ^1H NMR Spectrum of **25** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **25** (75 MHz, CDCl_3).

Spectrum 17: ^1H NMR Spectrum of **26** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **26** (75 MHz, CDCl_3).

Spectrum 18: ^1H NMR Spectrum of **1** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **1** (75 MHz, CDCl_3).

Spectrum 19: ^1H NMR Spectrum of **11a** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **11a** (75 MHz, CDCl_3).

Spectrum 20: ^1H NMR Spectrum of **28** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **28** (75 MHz, CDCl_3).

Spectrum 21: ^1H NMR Spectrum of **29** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **29** (75 MHz, CDCl_3).

Spectrum 22: ^1H NMR Spectrum of **10** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **10** (75 MHz, CDCl_3).

Spectrum 23: ^1H NMR Spectrum of **30** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **30** (75 MHz, CDCl_3).

Spectrum 24: ^1H NMR Spectrum of **31** (300 MHz, CDCl_3)

^{13}C NMR Spectrum of **31** (75 MHz, CDCl_3)

Spectrum 25: ^1H NMR Spectrum of **32** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **32** (75 MHz, CDCl_3).

Spectrum 26: ^1H NMR Spectrum of **33** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **33** (75 MHz, CDCl_3).

Spectrum 27: ^1H NMR Spectrum of **7** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **7** (75 MHz, CDCl_3).

Spectrum 28: ^1H NMR Spectrum of **4** (300 MHz, CDCl_3).

^{13}C NMR Spectrum of **4** (75 MHz, CDCl_3).