Supporting Information (S1)

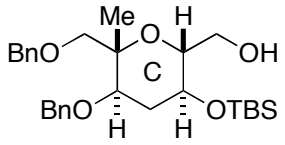
Synthetic Studies on Maitotoxin. 3. Stereoselective Synthesis of the BCDE-Ring System

Masanori Satoh,[†] Hiroyuki Koshino,[‡] and Tadashi Nakata*[,†]

Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan, and RIKEN (The Institute of Physical and Chemical Research), 1-2 Hirosawa, Wako-shi, Saitama 351-0198 , Japan

nakata@rs.kagu.tus.ac.jp

General: All melting points were measured by Yanaco MP-500 and are uncorrected. Optical rotations were measured with JASCO P-1010 polarimeter. IR spectra were recorded on JASCO FT/IR-460 Plus spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on JEOL JNM-AL300, JEOL JNM-LA500, and JEOL JNM-α-spectrometer. MASS spectra were recorded on BRUKER DALTONICS micrOTOF-NR and JEOL JMS-SX102A spectrometer. Flash column chromatography was performed on Silica Gel 60N (spherical, neutral; Kanto).



Dibenzyl ether 3

To a solution of **2** (5.12 g, 18.3 mmol) in THF (65 mL) were added NaH (60% in oil, 2.44 g, 61.0 mmol), BnBr (6.50 mL, 54.7 mmol), and *n*-Bu_4NI (0.517 g, 1.40 mmol) at 0 °C under argon atmosphere. After stirring at rt for 13 h, sat. NH_4Cl solution (5 mL) was added at 0 °C and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 7:1→6:1→3:1) to give benzyl ether (8.13 g, 96% yield).

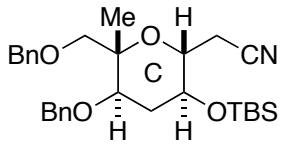
To a solution of the benzyl ether (291 mg, 0.632 mmol) in CH_2Cl_2 (3 mL)–MeOH (3.5 mL) was added CSA (35.3 mg, 0.152 mmol) at 0 °C under argon atmosphere. After stirring at rt for 15 h, additional CSA (19.9 mg) was added. After stirring for additional 24 h, Et_3N was added at 0 °C and the mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 1:3→EtOAc) to give diol (218.5 mg, 93% yield).

To a solution of the diol (0.853 g, 2.29 mmol) in CH_2Cl_2 (12 mL) were added 2,6-lutidine (1.35 mL, 11.6 mmol) and TBSOTf (1.35 mL, 5.88 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 30 min, sat. $NaHCO_3$ solution was added and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc =

8:1) to give di-TBS ether (1.49 g).

To a solution of the di-TBS ether (1.49 g) in CH_2Cl_2 (8 mL)–MeOH (4 mL) was added CSA (109.1 mg, 0.470 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 1 h, Et_3N was added and the mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 6:1→3:1→2:1) to give alcohol **3** (1.08 g, 97% yield, 2 steps).

3: $[\alpha]^{21}_D$ +13.3 (*c* 1.08, $CHCl_3$); IR (neat) 3448, 3030, 2928, 2857, 1497, 1454, 1362, 1251, 1090, 863, 837, 777, 736, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 10H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 12.5 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 3.76 (dd, *J* = 11.3, 2.7 Hz, 1H), 3.67 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.59 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.54-3.49 (m, 1H), 3.53 (d, *J* = 10.4 Hz, 1H), 3.43 (d, *J* = 10.4 Hz, 1H), 3.43-3.39 (m, 1H), 2.15 (ddd, *J* = 11.9, 4.6, 4.6 Hz, 1H), 1.59 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.17 (s, 3H), 0.87 (s, 9H), 0.049 (s, 3H), 0.043 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.3, 128.34 (2C), 128.28 (2C), 127.68 (2C), 127.59, 127.54 (2C), 77.1, 74.8, 74.6, 73.52, 73.49, 71.4, 66.8, 62.7, 34.3, 25.7 (3C), 17.9, 13.7, -4.2, -4.9; HRMS (ESI) calcd for $C_{28}H_{42}O_5SiNa$ 509.2694, found 509.2694.



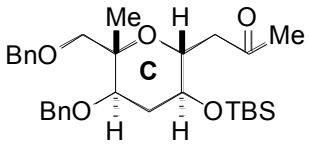
Nitrile 4

To a solution of **3** (36.9 mg, 0.0758 mmol) in CH_2Cl_2 (0.5 mL) were added Et_3N (31.0 μL, 0.222 mmol) and MsCl (9.0 μL, 0.116 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 40 min, sat. $NaHCO_3$ solution was added and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give crude methanesulfonyl ester (43.6 mg), which was used for the next reaction without purification.

To a solution of the above residue in DMSO (2 mL) were added powdered MS 4A (18.8 mg) and NaCN (63.9 mg, 1.30 mmol) at rt. After stirring at 80 °C for 2 h, H_2O was added at 0 °C and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 6:1) to give nitrile **4** (36.0 mg, 96% yield, 2 steps) as a colorless oil.

4: $[\alpha]^{25}_D$ +20.9 (*c* 1.00, $CHCl_3$); IR (neat) 3030, 2951, 2252, 1605, 1496, 1455, 1361, 1254, 1091, 1027, 837, 778, 736, 698, 673 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.24 (m, 10H), 4.67 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 12.5 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.46 (d, *J* = 11.9

Hz, 1H), 3.73 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.57 (d, *J* = 11.0 Hz, 1H), 3.53 (ddd, *J* = 9.8, 6.4, 3.7 Hz, 1H), 3.47 (d, *J* = 11.0 Hz, 1H), 3.40 (ddd, *J* = 11.3, 9.5, 4.6 Hz, 1H), 2.68 (dd, *J* = 16.5, 3.7 Hz, 1H), 2.53 (dd, *J* = 16.5, 6.1 Hz, 1H), 2.15 (ddd, *J* = 12.2, 4.9, 4.6 Hz, 1H), 1.57 (ddd, *J* = 12.2, 12.2, 12.2 Hz, 1H), 1.18 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.4, 128.29 (2C), 128.27 (2C), 127.62 (2C), 127.57 (3C), 127.4, 117.5, 78.3, 74.2, 73.6, 73.2, 71.7, 70.9, 69.5, 34.3, 25.6 (3C), 21.4, 17.8, 13.3, -4.1, -4.9; HRMS (EI) calcd for $C_{29}H_{41}O_4NSi$ 495.2805, found 495.2804.



Ketone 5

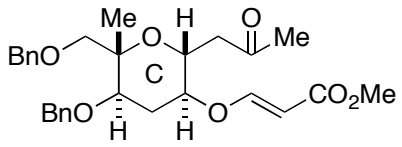
To a solution of **4** (2.81 g, 5.66 mmol) in toluene (50 mL) was added DIBALH (0.94 M in *n*-hexane, 12.0 mL, 11.2 mmol) dropwise at −78 °C under argon atmosphere. After stirring at 0 °C for 1 h, *i*-PrOH and H_2O were added and the mixture was warmed to rt. After addition of SiO_2 and EtOAc, the mixture was stirred at rt for 1 h. $MgSO_4$ was added and the mixture was filtered through a Celite® pad and the filtrate was concentrated i*n vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 5:1) to give aldehyde (2.68 g, 95% yield).

To a solution of the aldehyde (1.84 g, 3.69 mmol) in THF (30 mL) was added MeMgBr (0.84 M in THF, 6.6 mL, 5.54 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 1.25 h, sat. NH_4Cl solution was added and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 5:1→4:1) to give alcohol (1.76 g, 93% yield).

To a solution of the alcohol (2.67 g, 5.18 mmol) and powdered MS 4A (777.2 mg) in CH_2Cl_2 (35 mL) was added NMO (945.8 mg, 7.83 mmol) at rt under argon atmosphere and stirred for 40 min. After addition of TPAP (94.0 mg, 0.267 mmol), the mixture was stirred at rt for 1 h and directly purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 5:1) to give ketone **5** (2.58 g, 97% yield) as a colorless oil.

5: $[\alpha]^{23}_{D}$ +32.5 (*c* 1.09, $CHCl_3$); IR (neat) 3063, 3030, 2951, 2857, 1717, 1605, 1496, 1455, 1359, 1307, 1253, 1207, 1185, 1089, 1028, 1004, 862, 837, 777, 736, 698, 673 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.23 (m, 10H), 4.57 (d, *J* = 12.5 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 3.82 (ddd, *J* = 9.5, 9.5, 2.7 Hz, 1H), 3.71 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.50 (d, *J* = 10.7 Hz, 1H), 3.37 (d, *J* = 10.4 Hz, 1H), 3.29 (ddd, *J* =

11.0, 9.2, 4.6 Hz, 1H), 2.71 (dd, *J* = 15.0, 2.7 Hz, 1H), 2.45 (dd, *J* = 15.0, 9.5 Hz, 1H), 2.17 (s, 3H), 2.15 (ddd, *J* = 11.9, 4.6, 4.6 Hz, 1H), 1.59 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.16 (s, 3H), 0.86 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.8, 138.5 (2C), 128.2 (4C), 127.57 (3C), 127.52 (2C), 127.4, 77.35, 74.3, 73.44, 73.41, 71.9, 71.4, 70.4, 46.6, 34.7, 30.7, 25.7 (3C), 17.8, 13.4, -4.1, -4.7; HRMS (EI) calcd for $C_{30}H_{44}O_5Si$ 512.2958, found 512.2961.

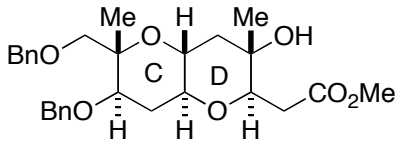


α,β-Unsaturated ester 6.

To a solution of **5** (1.57 g, 3.06 mmol) in THF (20 mL) was added TBAF (1.0 M in THF, 4.6 mL, 4.60 mmol) at 0 °C under argon atmosphere. After stirring at rt for 1 h, H_2O was added and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give crude alcohol, which was used for the next reaction without purification.

To a solution of the crude alcohol in CH_2Cl_2 (20 mL) were added *N*-methylmorpholine (1.35 mL, 12.2 mmol) and methyl propiolate (0.515 mL, 6.13 mmol) at 0 °C under argon atmosphere. After stirring at rt for 1.5 h, H_2O was added and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 3:1→2:1) to give β-alkoxyacrylate **6** (1.47 g, 100% yield, 2 steps).

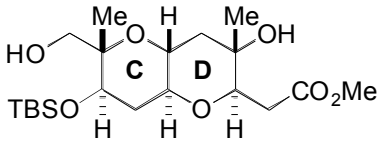
6: $[\alpha]^{19}_D$ +28.0 (*c* 0.86, $CHCl_3$); IR (neat) 2949, 1716, 1644, 1497, 1455, 1360, 1202, 1139, 1028, 835, 739, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 12.2 Hz, 1H), 7.33-7.22 (m, 10H), 5.29 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 2H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 4.06 (ddd, *J* = 9.2, 9.2, 3.1 Hz, 1H), 3.79 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.71 (s, 3H), 3.69-3.65 (m, 1H), 3.51 (d, *J* = 10.7 Hz, 1H), 3.39 (d, *J* = 10.7 Hz, 1H), 2.64 (dd, *J* = 15.6, 3.1 Hz, 1H), 2.56 (dd, *J* = 15.6, 8.8 Hz, 1H), 2.45 (ddd, *J* = 11.9, 4.6, 4.6 Hz, 1H), 2.17 (s, 3H), 1.69 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 167.9, 160.8, 138.3, 138.1, 128.30 (2C), 128.27 (2C), 127.63, 127.55 (2C), 127.50, 127.46 (2C), 98.3, 79.2, 77.7, 74.0, 73.4, 72.9, 71.4, 68.7, 51.1, 45.6, 31.1, 30.6, 13.3; HRMS (ESI) calcd for $C_{28}H_{34}O_7Na$ 505.2197, found 505.2244.



CD-ring 7

To a solution of **6** (306.4 mg, 0.635 mmol) in THF (6.3 mL)–MeOH (0.1mL, 2.47 mmol) was added SmI_2 (0.1 M in THF, 21.6 mL, 2.16 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 10 min, sat. $Na_2S_2O_3$ solution was added, and the mixture was extracted with EtOAc. The organic layer was washed with sat. $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 2:1→1:1) to give CD-ring **7** (324.8 mg, 100% yield) as a colorless oil.

7: $[\alpha]^{24}_{D}$ +0.301 (*c* 1.04, $CHCl_3$); IR (neat) 3450, 3029, 2946, 1740, 1604, 1496, 1454, 1366, 1298, 1201, 1092, 1046, 737, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.19 (m, 10H), 4.59 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 3.73-3.68 (m, 2H), 3.69 (s, 3H), 3.50 (d, *J* = 10.4 Hz, 1H), 3.43 (d, *J* = 10.4 Hz, 1H), 3.29 (ddd, *J* = 11.6, 9.5, 4.3 Hz, 1H), 3.04 (ddd, *J* = 11.9, 9.5, 4.0 Hz, 1H), 2.72 (dd, *J* = 15.6, 3.4 Hz, 1H), 2.39-2.35 (m, 2H), 2.38 (dd, *J* = 15.6, 9.5 Hz, 1H), 2.11 (dd, *J* = 11.6, 4.3 Hz, 1H), 1.61 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.57 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.21 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 138.36, 138.31, 128.2 (4C), 127.65 (2C), 127.44 (2C), 127.37 (2C), 81.1, 77.78, 77.73, 74.37, 74.21, 73.4, 70.97, 70.51, 68.9, 51.8, 45.9, 34.5, 30.4, 21.4, 13.8; HRMS (EI) calcd for $C_{28}H_{36}O_7$ 484.2461, found 484.2460.



Diol 8.

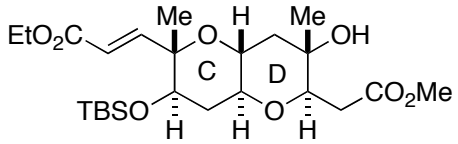
A solution of **7** (1.02 g, 2.10 mmol) and 20% $Pd(OH)_2/C$ (225.6 mg) in EtOAc (20 mL) was stirred under H_2 atmosphere at rt for 3 h. The mixture was filtrated through a Celite® pad and the filtrate was concentrated *in vacuo* to give crude triol (632 mg).

To a solution of the crude triol (203.3 mg, 0.668 mmol) in CH_2Cl_2 (7 mL) were added 2,6-lutidine (0.465 mL, 4.01 mmol) and TBSOTf (0.430 mL, 1.87 mmol) at −78 °C under argon atmosphere. After stirring at the same temperature for 20 min, sat. $NaHCO_3$ solution was added and the mixture was extracted with EtOAc. The organic layer was washed with sat. $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 7:1→13:2) to give di-TBS ether **47**

(286.1mg, 80% yield, 2 steps).

To a solution of the TBS ether (75.8 mg, 0.142 mmol) in MeOH (1.4 mL) was added CSA (8.7 mg, 0.0375 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 3.5 h, Et_3N was added and the mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 1:1→1:2) to give diol **8** (57.7 mg, 97% yield) as colorless crystals.

8: mp 117-118 °C (*n*-hexane); $[\alpha]^{22}_{D}$ +15.4 (*c* 1.06, $CHCl_3$); IR (KBr); 3523, 2952, 1747, 1373, 1095, 836, 774, 679 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.88 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.72 (s, 3H), 3.69 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.48 (dd, *J* = 11.3, 9.2 Hz, 1H), 3.43 (dd, *J* = 11.3, 4.0 Hz, 1H), 3.27 (ddd, *J* = 11.6, 9.2, 4.3 Hz, 1H), 2.99 (ddd, *J* = 11.9, 9.2, 4.3 Hz, 1H), 2.72 (dd, *J* = 15.9, 3.7 Hz, 1H), 2.40 (dd, *J* = 15.9, 9.2 Hz, 1H), 2.10-2.05 (m, 2H), 1.99 (m, 1H), 1.62 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.53 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.20 (s, 3H), 1.09 (s, 3H), 0.86 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 81.1, 78.2, 77.8, 70.5, 68.7, 67.0, 66.9, 51.9, 45.8, 34.51,34.47, 25.6 (3C), 21.4, 17.7, 13.4, −4.2, −5.2; HRMS (FAB) calcd for $C_{20}H_{39}O_7Si$ ($M+H^+$) 419.2465, found 419.2464.



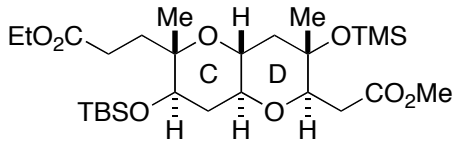
α,β-Unsaturated ester 9.

To a solution of **8** (572.4 mg, 1.37 mmol) and powdered MS 4A (229.1 mg) in CH_2Cl_2 (8 mL) was added NMO (250.7 mg, 2.07 mmol) at rt under argon atmosphere. After stirring for 30 min, TPAP (26 mg, 0.0739 mmol) was added and the mixture was stirred at rt for 30 min. The mixture was directly purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 1:1) to give aldehyde (569.8 mg).

To a solution of the aldehyde (569.8 mg, 1.37 mmol) in toluene (13 mL) was added (carbethoxymethylene)triphenylphosphorane (666.4 mg, 1.81 mmol). After stirring at 100 °C for 1 h, the mixture was evaporated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 2:1) to give α,β-unsaturated ester **9** (628.2 mg, 94% yield, 2 steps).

9: $[\alpha]^{20}_{D}$ +26.5 (*c* 1.08, $CHCl_3$); IR (neat) 3480, 2953, 1717, 1660, 1463, 1367, 1281, 1095, 1043, 867, 838, 777 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J* = 15.9 Hz, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 4.25-4.13 (m, 2H), 3.72 (s, 3H), 3.70 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.52 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.29 (ddd, *J* = 11.3, 9.5, 4.0 Hz, 1H), 3.02 (ddd, *J* = 11.9, 9.5, 4.3 Hz, 1H), 2.72 (dd, *J* = 15.9, 3.4 Hz, 1H), 2.40 (dd, *J* = 15.9, 9.2 Hz, 1H), 2.10 (dd, *J* = 11.9, 4.3 Hz, 1H), 2.07 (ddd, *J* = 11.9, 4.3, 4.3 Hz, 1H), 1.75 (s, 3H), 1.66 (ddd, *J* = 11.6, 11.6, 11.6 Hz, 1H), 1.57 (dd,

J = 11.6, 11.6 Hz, 1H), 1.29 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 1H), 1.24 (s, 3H), 0.88 (s, 9H), 0.046 (s, 3H), 0.039 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 166.7, 151.7, 119.0, 81.1, 77.7, 72.1, 70.6, 68.7, 60.2, 51.9, 45.9, 34.8, 34.6, 25.6 (3C), 21.5, 17.8, 15.1, 14.2, -4.3, -5.1; HRMS (ESI) calcd for $C_{24}H_{42}O_8SiNa$ 509.2541, found 509.2527.

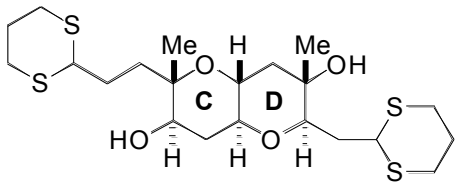


Diester 10.

A solution of **9** (628.2 mg, 1.29 mmol) and 10% Pd/C (135.8 mg) in EtOAc (10 mL) was stirred under H_2 atmosphere at rt for 19 h. The mixture was filtrated through Celite® pad and the filtrate was concentrated *in vacuo* to give crude ester (659 mg).

To a solution of the crude ester (659 mg) in CH_2Cl_2 (10 mL) were added 2,6-lutidine (0.613 mL, 5.15 mmol) and TMSOTf (0.365 mL, 1.94 mmol) at −78 °C under argon atmosphere. After stirring at the same temperature for 15 min, sat. $NaHCO_3$ solution was added and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 10:1) to give diester **10** (694.3 mg, 96% yield, 2 steps) as a colorless oil.

10: $[\alpha]^{24}_D$ +12.1 (*c* 1.02, $CHCl_3$); IR (neat) 2953, 2892, 2857, 1741, 1463, 1437, 1376, 1307, 1252, 1142, 1097, 1059, 932, 898, 862, 839, 776, 674, 626 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.11 (q, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 3.66 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.51 (dd, *J* = 11.3, 4.9, Hz, 1H), 3.13 (ddd, *J* = 11.6, 9.5, 4.3 Hz, 1H), 2.97 (ddd, *J* = 11.9, 9.5, 4.0 Hz, 1H), 2.67 (dd, *J* = 15.6, 2.7 Hz, 1H), 2.38 (dd, *J* = 7.9, 7.9 Hz, 2H), 2.29 (dd, *J* = 15.6, 9.8 Hz, 1H), 2.05-2.01 (m, 1H), 2.02 (dd, *J* = 11.6, 4.3, Hz, 1H), 1.97 (ddd, *J* = 14.3, 7.9, 7.9 Hz, 1H), 1.75 (ddd, *J* = 14.3, 7.9, 7.9 Hz, 1H), 1.59 (ddd, *J* = 11.6, 11.6, 11.6 Hz, 1H), 1.57 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.21 (s, 3H), 1.12 (s, 3H), 0.86 (s, 9H), 0.12 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 172.6, 81.3, 77.8, 76.7, 73.2, 71.8, 68.3, 60.1, 51.7, 45.7, 34.8, 34.3, 28.2, 25.6 (3C), 22.5, 17.8, 15.6, 14.2, 2.5 (3C), −4.0, −5.0; HRMS (EI) calcd for $C_{27}H_{52}O_8Si_2$ 560.3201, found 560.3203.

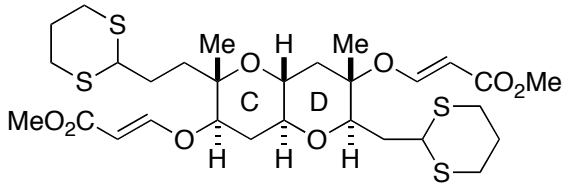


Bis(thioacetal) 11

To a solution of **10** (161.6 mg, 0.288 mmol) in CH_2Cl_2 (3 mL) was added DIBALH (0.94 M in *n*-hexane, 0.680 mL, 0.639 mmol) at −78 °C under argon atmosphere. After stirring at the same temperature for 50 min, *i*-PrOH and H_2O were added the mixture was warmed to rt. After addition of SiO_2 and EtOAc, the mixture was stirred at rt for 50 min. After addition of $MgSO_4$, the mixture was filtered through Celite® pad and the filtrate was concentrated i*n vacuo* to give crude aldehyde (149 mg), which was used for the next reaction without purification.

To a solution of the crude aldehyde (149 mg) in CH_2Cl_2 (2.8 mL) were added $BF_3{\cdot}OEt_2$ (40 μL, 0.301 mmol) and 1,3-propanedithiol (140 μL, 1.32 mmol) at 0 °C under argon atmosphere. After stirring at rt for 13 h, the mixture was diluted with EtOAc. The organic layer was washed with 3N NaOH solution, sat. NaS_2O_3 solution, sat. NH_4Cl solution, and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 1:1) to give bis(thioacetal) **11** (94.9 mg, 67% yield, 2 steps) as colorless oil.

11: $[\alpha]^{23}_D$ +27.4 (*c* 1.05, $CHCl_3$); IR (neat) 3433, 2941, 2898, 1724, 1630, 1461, 1422, 1377, 1276, 1243, 1109, 1066, 1021, 946, 924, 908, 895, 868, 753, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.20 (dd, *J* = 10.7, 3.7 Hz, 1H), 4.02 (dd, *J* = 7.0, 6.1 Hz, 1H), 3.57 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.44 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.15 (ddd, *J* = 11.6, 9.5, 4.3 Hz, 1H), 2.96 (ddd, *J* = 11.6, 9.5, 4.3 Hz, 1H), 2.93-2.78 (m, 8H), 2.20-2.08 (m, 4H), 2.02 (dd, *J* = 11.6, 4.3 Hz, 1H), 1.95-1.82 (m, 5H), 1.77 (ddd, *J* = 14.3, 10.1, 4.0 Hz, 1H), 1.68 (m, 1H), 1.62 (ddd, *J* = 11.6, 11.6, 11.6 Hz, 1H), 1.48 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.20 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 80.8, 77.9, 76.6, 71.2, 70.7, 68.6, 48.0, 46.0, 43.8, 36.8, 34.65, 34.22, 30.33, 30.28, 29.87, 29.31, 28.6, 25.9, 21.4, 15.4; HRMS (EI) calcd for $C_{21}H_{36}O_4S_4$ 480.1496, found 480.1498.

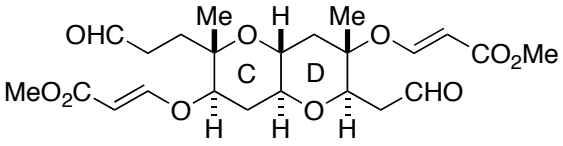


bis(β-alkoxyacryltate) 12

To a solution of **11** (321.3 mg, 0.668 mmol) in toluene (7 mL) were added methyl 3-methoxyacrylate (0.435 mL, 4.01 mmol) and PPTS (11.8 mg, 0.0460 mmol) at rt under argon atmosphere. After stirring at 140 °C for 29 h, the mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 3:1→2:1) to give bis(β-alkoxyacryltate) **12** (249.2 mg, 58% yield).

12: $[\alpha]^{20}_D$ +37.2 (*c* 0.97, $CHCl_3$); IR (neat) 2950, 2359, 1712, 1640, 1436, 1290, 1139, 910, 838, 731, 647 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 12.2 Hz, 1H), 7.46 (d, *J* = 12.5 Hz, 1H), 5.38 (d, *J* = 11.9 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 4.17 (dd, *J* = 10.7, 3.7 Hz, 1H), 3.95

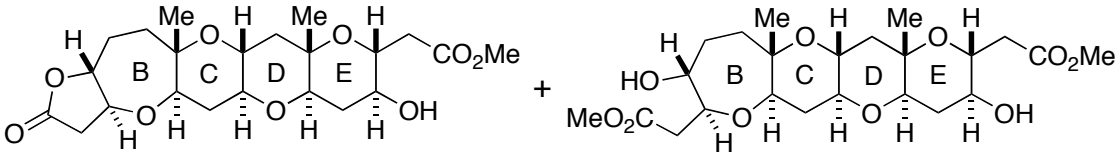
(dd, *J* = 6.4, 6.4 Hz, 1H), 3.79 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 3.69 (m. 1H), 3.21 (m, 1H), 3.02 (m, 1H), 2.93-2.81 (m, 8H), 2.36 (ddd, *J* = 11.9, 4.3, 4.3 Hz, 1H), 2.24 (dd, *J* = 11.6, 4.3 Hz, 1H), 2.14-2.04 (m, 3H), 1.95-1.72 (m, 6H), 1.69-1.60 (m, 3H), 1.36 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.98, 167.91, 161.0, 155.8, 100.4, 98.3, 81.4, 79.6, 78.6, 77.2, 75.6, 68.4, 51.2, 51.0, 47.6, 43.5, 41.9, 36.9, 34.4, 30.8, 30.2, 30.0, 29.4, 28.6, 25.94, 25.89, 19.2, 16.0; HRMS (ESI) calcd for $C_{29}H_{44}O_8S_4Na$ 671.1811, found 671.1816.



bis(aldehyde) 13.

To a solution of **12** (111.3 mg, 0.172 mmol) in MeCN (1.6 mL)–H_2O (0.4 mL) were added $NaHCO_3$ (47.1 mg, 0.555 mmol) and MeI (0.53 mL, 8.47 mmol) at rt. After stirring at rt for 13 h, the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 1:1) to give bis(aldehyde) **13** (71.2 mg, 89% yield).

13: $[\alpha]^{20}_D$ +35.6 (*c* 1.375, $CHCl_3$); IR (neat) 2951, 1716, 1645, 1437, 1386, 1334, 1291, 1191, 1140, 956, 839, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (dd, *J* = 2.4, 1.5 Hz, 1H), 9.70 (dd, *J* = 1.8, 1.5 Hz, 1H), 7.58 (d, *J* = 12.2 Hz, 1H), 7.44 (d, *J* = 12.5 Hz, 1H), 5.37 (d, *J* = 12.2 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 3.97 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.80 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.23 (ddd, *J* = 11.6, 9.5, 4.3 Hz, 1H), 3.09 (ddd, *J* = 11.9, 9.5, 4.3 Hz, 1H), 2.64 (ddd, *J* = 16.8, 2.7, 1.2 Hz, 1H), 2.55-2.44 (m, 3H), 2.34 (ddd, *J* = 11.9, 4.6, 4.3 Hz, 1H), 2.29 (dd, *J* = 11.6, 4.3 Hz, 1H), 2.00 (tt, *J* = 7.3, 7.3 Hz, 1H), 1.83 (tt, *J* = 7.3, 7.3 Hz, 1H), 1.72-1.63 (m, 2H), 1.39 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.7, 199.4, 167.8, 167.7, 160.7, 155.3, 100.9, 98.6, 81.2, 79.2, 77.3, 77.2, 75.5, 68.3, 51.2, 51.1, 42.9, 41.6, 37.7, 32.3, 30.7, 19.2, 16.0; HRMS (ESI) calcd for $C_{23}H_{32}O_{10}Na$ 491.1888, found 491.1912.



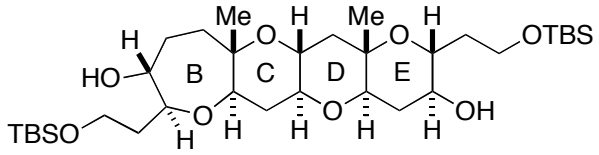
Lactone-ester 14. **Diester 15.**

To a solution of **13** (33.1 mg, 0.0707 mmol) in THF (1 mL)–MeOH (23 μL, 0.567 mmol) was added SmI_2 (0.1 M in THF, 8.5 mL, 0.85 mmol) at rt under argon atmosphere. After stirring

for 1 h, sat. $Na_2S_2O_3$ solution was added at 0 °C and the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 1:2→1:3→1:6) to give lactone-ester **14** (18.8 mg, 60% yield) as a colorless solid and diester **15** (9.8 mg, 29% yield).

14: mp 226-227 °C; $[\alpha]^{24}_D$ +62.9 (*c* 1.01, $CHCl_3$); IR (KBr) 3531, 2950, 1773, 1066, 869, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.36 (ddd, *J* = 8.8, 8.8, 8.8 Hz, 1H), 4.03 (ddd, *J* = 10.7, 9.2, 7.6 Hz, 1H), 3.87 (ddd, *J* = 9.5, 7.0, 4.9 Hz, 1H), 3.69 (s, 3H), 3.53-3.46 (m, 1H), 3.38 (ddd, *J* = 11.6, 9.8, 4.3 Hz, 1H), 3.25 (dd, *J* = 11.9, 4.0 Hz, 1H), 3.12 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.05 (ddd, *J* = 11.9, 9.8, 4.3 Hz, 1H), 2.82 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.74 (dd, *J* = 15.6, 4.9 Hz, 1H), 2.65 (dd, *J* = 16.8, 10.7 Hz, 1H), 2.51 (dd, *J* = 15.6, 7.0 Hz, 1H), 2.39-2.32 (m, 2H), 2.22-2.14 (m, 2H), 1.98-1.79 (m, 4H), 1.67-1.60 (m, 2H), 1.39 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.29 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.66, 172.48, 84.53, 82.0, 79.62, 79.20, 78.8, 77.7, 73.2, 70.84, 70.54, 68.7, 51.8, 43.1, 38.2, 36.58, 36.23, 33.7, 32.2, 24.2, 16.0, 15.3; HRMS (EI) calcd for $C_{22}H_{32}O_9$ 440.2046, found 440.2041.

15: $[\alpha]^{19}_D$ +39.5 (*c* 0.20, $CHCl_3$); IR (neat) 3461, 2951, 1734, 1438, 1275, 1196, 1102, 1064, 756, 667, 444 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.96 (ddd, *J* = 7.0, 7.0, 3.4 Hz, 1H), 3.89-3.83 (m, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.53-3.46 (m, 2H), 3.39 (ddd, *J* = 11.6, 9.8, 4.6 Hz, 1H), 3.10 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.01 (ddd, *J* = 11.9, 9.5, 4.0 Hz, 1H), 2.74 (dd, *J* = 15.6, 4.9 Hz, 1H), 2.54-2.50 (m, 3H), 2.25 (d, *J* = 5.8 Hz, 1H), 2.18 (ddd, *J* = 11.6, 4.3, 4.3 Hz, 1H), 2.06 (ddd, *J* = 11.6, 4.3, 4.3 Hz, 1H), 1.98-1.90 (m, 3H), 1.84-1.79 (m, 2H), 1.66-1.53 (m, 2H), 1.39 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.27 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 171.8, 82.5, 79.7, 79.5, 79.1, 77.1, 74.0, 73.2, 70.8, 68.7, 51.8, 51.7, 43.4, 39.6, 38.4, 34.9, 33.9, 32.8, 27.3, 16.06, 16.02; HRMS (ESI) calcd for $C_{23}H_{36}O_{10}Na$ 495.2201, found 495.2201.



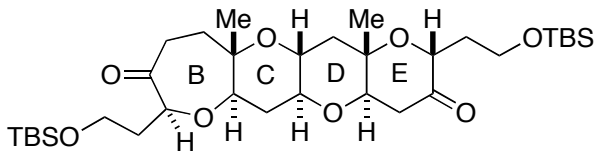
Diol 16

(a) To a solution of **14** (89.0 mg, 0.202 mmol) in THF (8 mL) was added $LiAlH_4$ (42 mg, 1.02 mmol) at 0 °C under argon atmosphere. After stirring at 0 °C for 30 min, the mixture was warmed to rt and stirred for 4 h. After addition of H_2O, 12% NaOH solution, and H_2O at 0 °C, the mixture was diluted with EtOAc, $CHCl_3$, and MeOH. After stirring at rt for 1 h, $MgSO_4$ was added, and the mixture was filtrated through a Celite® pad and the filtrate was concentrated *in vacuo* to give crude tetraol. To a solution of the crude tetraol in pyridine (2.5 mL) was added

TBSCl (94.5 mg, 0.614 mmol) at 0 °C under argon atmosphere. After stirring at rt for 3.5 h, TBSCl (103.6 mg) was added. After stirring at rt for 11 h, TBSCl (98.3 mg) was added. After stirring for additional 6 h, the mixture was evaporated with toluene azeotropically. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 2:1→1:1→1:2) to give diol **16** (102.1 mg, 78% yield, 2 steps).

(b) To a solution of **15** (37.0 mg, 0.0783 mmol) in THF (3.5 mL) was added $LiAlH_4$ (17.6 mg, 0.426 mmol) at 0 °C under argon atmosphere. After stirring at 0 ° C for 30 min, the mixture was warmed to rt and stirred for 1 h. After addition of H_2O, 12% NaOH solution, and H_2O at 0 °C, the mixture was diluted with EtOAc, $CHCl_3$, and MeOH. After stirring at rt for 1 h, $MgSO_4$ was added, and the mixture was filtrated through a Celite® pad and the filtrate was concentrated *in vacuo* to give crude tetraol. To a solution of the crude tetraol in pyridine (1.5 mL) was added TBSCl (40.2 mg, 0.261 mmol) at 0 °C under argon atmosphere. After stirring at rt for 1.5 h, TBSCl (38.7 mg) was added. After stirring for 16 h, TBSCl (42.1 mg) was added. After stirring for additional 10.5 h, the mixture was evaporated with toluene azeotropically. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 1:2) to give diol **16** (39.4 mg, 78% yield, 2 steps).

16: $[\alpha]^{19}_{D}$ +24.1 (*c* 1.085, $CHCl_3$); IR (neat) 3419, 2953, 1471, 1256, 1099, 909, 837, 777, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.47 (d, *J* = 2.1 Hz, 1H), 3.85-3.81 (m, 2H), 3.76-3.68 (m, 3H), 3.64 (ddd, *J* = 6.4, 6.4, 3.4 Hz, 1H), 3.51 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.49-3.39 (m, 3H), 3.12 (dd, *J* = 12.5, 3.7 Hz, 1H), 3.02 (ddd, *J* = 11.9, 9.5, 4.0 Hz, 1H), 2.22 (d, *J* = 3.1 Hz, 1H), 2.16 (ddd, *J* = 11.6, 4.3, 4.3 Hz, 1H), 2.08 (ddd, *J* = 11.6, 4.3, 4.3 Hz, 1H), 1.98-1.91 (m, 2H), 1.84-1.79 (m, 4H), 1.69-1.65 (m, 2H), 1.63-1.56 (m, 3H), 1.40 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.26 (s, 3H), 1.22 (s, 3H), 0.91 (s, 9H), 0.89 (s, 9H), 0.099 (s, 3H), 0.091 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.7, 79.7, 79.5, 78.6, 77.3, 74.6, 73.8, 72.8, 71.0, 68.8, 60.7, 59.9, 43.7, 38.1, 37.9, 35.1, 33.1, 32.7, 27.2, 25.9 (3C), 25.8 (3C), 18.3, 18.2, 16.3, 16.2, -5.36, -5.38, -5.46, -5.54; HRMS (ESI) calcd for $C_{33}H_{64}O_8Si_2Na$ 667.4032, found 667.4030.

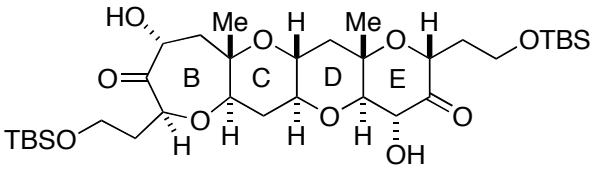


Diketone 17

To a solution of **16** (102.1 mg, 0.102 mmol) and powdered MS 4A (90.3 mg) in CH_2Cl_2 (2.5 mL) was added NMO (123.1 mg, 1.02 mmol) at rt under argon atmosphere. After stirring for 45 min, TPAP (3.6 mg, 0.0102 mmol) was added and the mixture was stirred at rt for 40 min. The mixture was directly purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 6:1) to

give diketone **17** (69.3 mg, 69% yield).

17: $[\alpha]^{19}_{D}$ –26.7 (*c* 0.415, $CHCl_3$); IR (neat) 2953, 2857, 1719, 1472, 1380, 1256, 1096, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.16 (dd, *J* = 5.5, 5.2 Hz, 1H), 4.00 (dd, *J* = 7.9, 4.6 Hz, 1H), 3.78-3.65 (m, 4H), 3.58 (dd, *J* = 12.5, 5.8 Hz, 1H), 3.49 (ddd, *J* = 11.6, 9.5, 4.3 Hz, 1H), 3.10 (dd, *J* = 11.6, 4.3 Hz, 1H), 3.04 (ddd, *J* = 11.9, 9.5, 4.3 Hz, 1H), 2.90 (ddd, *J* = 14.3, 10.9, 2.7 Hz, 1H), 2.79 (ddd, *J* = 17.7, 5.8, <1 Hz, 1H), 2.41 (dd, *J* = 17.4, 12.5 Hz, 1H), 2.33 (ddd, *J* = 12.5, 6.4, 1.8 Hz, 1H), 2.16 (ddd, *J* = 11.9, 4.3, 4.3 Hz, 1H), 2.10 (dd, *J* = 11.6, 4.3 Hz, 1H), 2.06-2.00 (m, 1H), 1.93-1.86 (m, 2H), 1.82-1.75 (m, 2H), 1.72 (ddd, *J* = 11.6, 11.6, 11.6 Hz, 1H), 1.65-1.53 (m, 2H), 1.39 (s, 3H), 1.32 (s, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.037 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.2, 208.0, 84.3, 81.8, 78.8, 77.6, 73.8, 72.4, 68.6, 58.35, 58.33, 43.2, 40.8, 38.3, 36.7, 36.1, 34.3, 32.8, 25.93 (3C), 25.88 (3C), 18.4, 18.3, 15.7, 15.1, -5.41 (2C), -5.47 (2C); HRMS (ESI) calcd for $C_{33}H_{60}O_8Si_2Na$ 663.3719, found 663.3741.



Bis(α-hydroxyketone) 19.

To a solution of **17** (88.3 mg, 0.138 mmol) in THF (3 mL) were added Et_3N (0.764 mL, 5.48 mmol), TMSCl (0.706 mL, 5.48 mmol) and LiHMDS (1.0 M in THF, 1.37 mL, 1.37 mmol) at –78 °C under argon atmosphere. After stirring at the same temperature for 30 min, phosphate pH buffer (pH = 6.86) (4 mL) was added. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give crude TMS enol ether **18**, which was immediately used for the next reaction without purification.

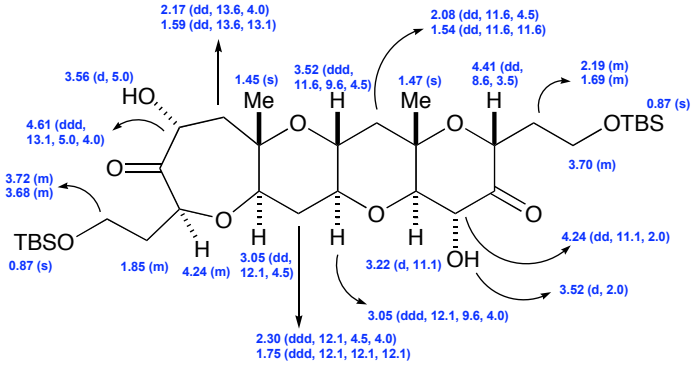
To a solution of **18** in THF (1.5 mL)–H_2O (0.5 mL) were added NMO (170.9 mg, 1.42 mmol) and OsO_4 (2.5 wt% in *t*-BuOH, 86 μL, 6.85 μmol) at 0 °C under argon atmosphere. After stirring at rt for 9.5 h, the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; *n*-hexane:EtOAc = 4:1→3:1→2:1) to give bis(hydroxyketone) **19** as a colorless oil (38.8 mg, 42% yield, 2 steps).

19: $[\alpha]^{26}_{D}$ +18.5 (*c* 1.11, $CHCl_3$); IR (neat) 3480, 2954, 2857, 1725, 1471, 1383, 1361, 1323, 1255, 1090, 1015, 949, 836, 777, 665 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.61 (ddd, *J* = 13.1, 5.0, 4.0 Hz, 1H), 4.41 (dd, *J* = 8.6, 3.5 Hz, 1H), 4.24 (dd, *J* = 11.1, 2.0 Hz, 1H), 4.24 (m, 1H), 3.72 (m, 1H), 3.70 (m, 2H), 3.68 (m, 1H), 3.56 (d, *J* = 5.0 Hz, 1H), 3.52 (ddd, *J* = 11.6, 9.6, 4.5 Hz, 1H), 3.52 (d, *J* = 2.0 Hz, 1H), 3.22 (d, *J* = 11.1 Hz, 1H), 3.05 (dd, *J* = 12.1, 4.5 Hz, 1H),

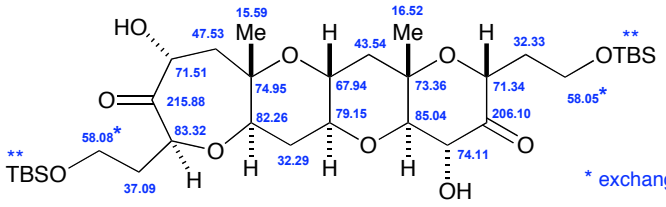
3.04 (ddd, J = 12.1, 9.6, 4.0 Hz, 1H), 2.30 (ddd, J = 12.1, 4.5, 4.0 Hz, 1H), 2.19 (m, 1H), 2.17 (dd, J = 13.6, 4.0 Hz, 1H), 2.08 (dd, J = 11.6, 4.5 Hz, 1H), 1.85 (m, 2H), 1.75 (ddd, J = 12.1, 12.1, 12.1 Hz, 1H), 1.69 (m, 1H), 1.59 (dd, J = 13.6, 13.1 Hz, 1H), 1.54 (dd, J = 11.6, 11.6 Hz, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 0.87 (s, 18H), 0.04 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.9, 206.1, 85.0, 83.3, 82.3, 79.2, 75.0, 74.1, 73.4, 71.5, 71.3, 67.9, 58.08, 58.05, 47.5, 43.5, 37.1, 32.33, 32.29, 25.9 (6C), 18.3 (2C), 16.5, 15.6, −5.4 (2C), −5.5 (2C); HRMS (EI) calcd for $C_{33}H_{60}O_{10}Si_2$ 672.3725, found 672.3721.

NMR analysis of 19.

^{1}H-NMR (600MHz, $CDCl_3$)



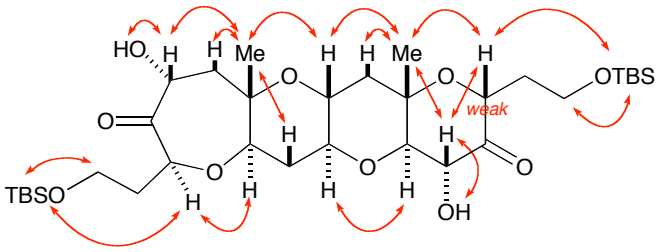
^{13}C-NMR (150MHz, $CDCl_3$)



* exchangeable

**
t-Bu: 25.88 (Mex6)
18.30 (Cx2)
SiMe: –5.37 (x2)
–5.46 (x2)

PFG-NOESY (400ms, 600 MHz)



PFG-HMBC (62.5ms, 600 MHz)