Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

The Leiodolide B Puzzle**

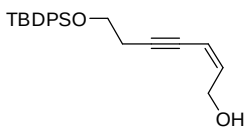
*Alexandre Larivée, John B. Unger, Mikaël Thomas, Conny Wirtz, Christophe Dubost, Shinya Handa, and Alois Fürstner**

anie_201005850_sm_miscellaneous_information.pdf

General: Unless otherwise noted, all reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg·anthracene), CH_2Cl_2, Et_3N, CH_3CN, DMSO (CaH_2), hexane, toluene (Na/K), DMF (Desmodur 15, dibutyl tin dilaurate), MeOH, EtOH (Mg). Flash chromatography (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on a Bruker DPX 300, AMX 300, AV 400, DMX 600 or AVIII 600 spectrometer in the solvents indicated; chemical shifts (*d*) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $d_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $d_H \equiv 7.26$ ppm; CD_2Cl_2: $d_C \equiv 53.8$ ppm; residual ^{1}H: $d_H \equiv 5.32$ ppm; CD_3OD $d_C \equiv 49.0$ ppm; residual ^{1}H: $d_H \equiv 3.30$ ppm; [D_8]acetone: $d_C \equiv 29.8$ ppm; residual ^{1}H: $d_H \equiv 2.05$ ppm; C_6D_6: $d_C \equiv 128.0$ ppm; residual ^{1}H: $d_H \equiv 7.15$ ppm). Where indicated, the signal assignments are unambiguous; the numbering scheme is arbitrary and shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygpqf* and *cosydqtp*); HSQC (*hsqcedetgpsisp2.2*) optimized for $^1J_{C,H}$ = 145 Hz; HMBC (*hmbcetgpl3nd*) for correlations via $^nJ_{C,H}$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms; NOESY (noesygpph). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers (ν) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Melting points: Büchi melting point apparatus B-540 (corrected). Unless stated otherwise, all commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

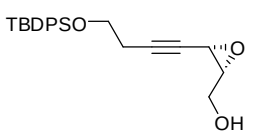
Tetrahydrofuran Sector.

Compound 6. CuI (1.09 g, 5.74 mmol, 15 mol%) was added in one portion to a solution of bromide **4**



(6.25 g, 45.6 mmol)[1] in distilled and degassed Et_2NH (150 mL). After stirring for 10 min, the mixture became pale blue and $Pd(PPh_3)_4$ (953.4 mg, 0.825 mmol, 2.2 mol%) was introduced. A solution of alkyne **5** (11.7 g, 37.93 mmol) in Et_2NH (20 mL) was added dropwise over 20 min and the resulting dark green suspension was stirred for 24 h before the mixture was concentrated to a total volume of about 40 mL. Sat. aq. NH_4Cl was added, the layers were separated and the aqueous phase extracted with *tert*-butyl methyl ether (3 x 100 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (10:1, hexanes/EtOAc) to give product **6** as a colorless oil (13.83 g, quant.). ^{1}H NMR (300 MHz, C_6D_6): d = 7.77-7.73 (m, 4H), 7.25-7.19 (m, 6H), 5.75 (dt, J = 10.9, 4.8 Hz, 1H), 5.41 (dqn, J = 10.8, 2.4 Hz, 1H), 4.25 (td, J = 6.1, 1.5 Hz, 2H), 3.69 (t, ^3J = 6.4 Hz, 2H), 2.41 (td, J = 6.9, 2.3 Hz, 2H), 1.16 (s, 9H), 0.85 (br s, 1H); ^{13}C NMR (100 MHz, C_6D_6): d = 141.8, 136.0, 134.0, 130.1, 128.2, 110.4, 93.6, 78.2, 62.8, 27.1, 24.0, 19.5; HRMS (ESI+): *m*/*z*: calcd for $C_{23}H_{28}O_2SiNa$ [M+Na]$^+$: 387.17508; found: 387.17480.

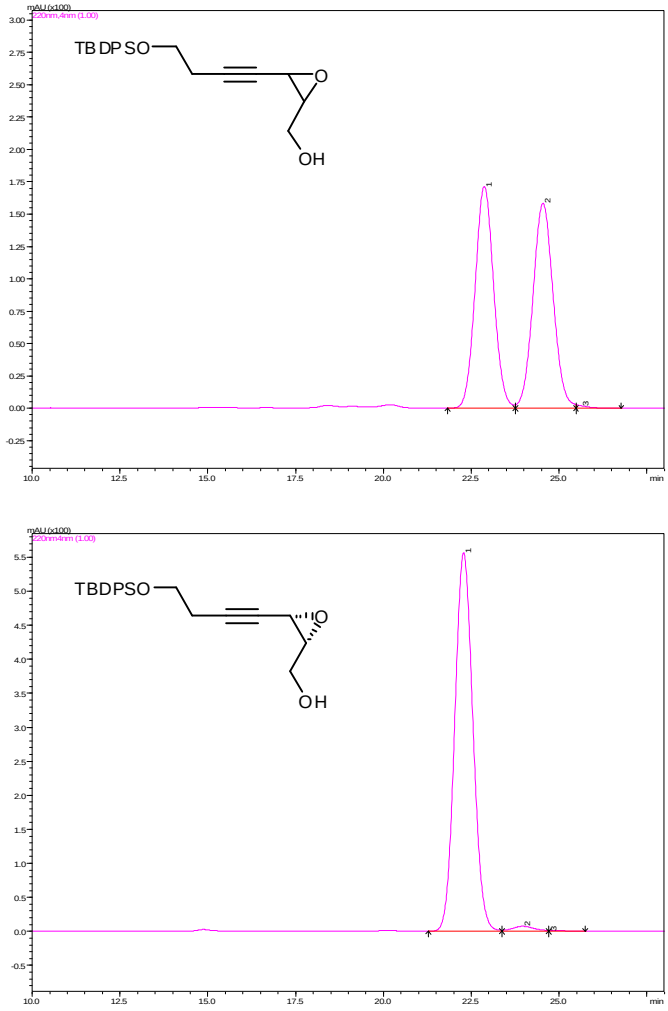
Compound S1: A bright yellow solution of salan **8** (439.6 mg, 0.92 mmol, 12 mol%) and Ti(O*i*Pr)$_4$



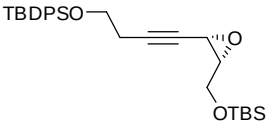
(224 μL, 0.77 mmol, 10 mol%) in CH_2Cl_2 (3.6 mL) was stirred for 1 h before phosphate buffer (2.5 mL, pH 7.4, 67 mM) was added followed by addition of a solution of alcohol **6** (2.80 g, 7.68 mmol) in CH_2Cl_2 (25.8 mL) and H_2O_2 (30 % *w*/*w*, 23.8 mL). The thick glass vessel was sealed and then warmed to 40 °C.

[1] (a) S. Ma, X. Lu, Z. Li, *J. Org. Chem.* **1992**, *57*, 709-713; (b) X. Wei, R. J. K. Taylor, *J. Org. Chem.* **1999**, *65*, 616-620.

After stirring for 7 h, the mixture was cooled to 0 °C and the reaction quenched with aq. sat. $Na_2S_2O_3$. The aqueous layer was extracted with *tert*-butyl methyl ether, the combined organic extracts were washed with aq. sat. $Na_2S_2O_3$ and brine, dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (6:1→2:1, hexanes/EtOAc) to give product **S1** as a yellow oil (2.88 g, 99 %, 97 % *ee*). The *ee* was determined by HPLC analysis (Chiralcel OD-R 250 x 4.6 mm, 40 % H_2O in MeCN, 0.5 mLmin^{-1}, 308 K isotherm, 7.4 MPa, DAD 220 nm) (+)-**S1**: t_r = 22.87 min, (–)-**S1**: t_r = 24.54 min. $[a]_D^{20}$ = +18.7 (c = 1.32 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): d = 7.77-7.69 (m, 4H), 7.27-7.20 (m, 6H), 3.75-3.64 (m, 2H), 3.61 (t, ^3J = 6.0 Hz, 2H), 3.14 (dt, ^3J = 4.4, 1.7 Hz, 1H), 2.83 (ddd, ^3J = 6.1, 4.5, 4.0 Hz, 1H), 2.20 (td, J = 6.6, 1.8 Hz, 2H), 1.57 (br s, 1H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): d = 136.0, 133.9, 130.1, 128.2, 84.1, 76.5, 62.5, 62.4, 57.4, 44.4, 27.1, 23.1, 19.5; IR: 3420, 2914, 2864, 1612, 1512, 1463, 1362, 1174, 1092, 1030 cm^{-1}; HRMS (ESI+): *m/z*: calcd for $C_{23}H_{28}O_3SiNa$ $[M+Na]^+$: 403.16999; found: 403.16993.

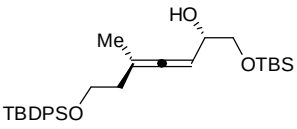


Product 7: Imidazole (474.5 mg, 6.97 mmol), DMAP (15.3 mg, 0.125 mmol) and TBSCl (565.7 mg, 3.75 mmol) were successively added to a solution of epoxy alcohol **S1** (1.29 g, 3.40 mmol) in CH_2Cl_2 (34 mL) at 0 °C and the mixture was stirred at ambient temperature for 95 min. The reaction was quenched with aq. sat. NH_4Cl, the aqueous phase was extracted with CH_2Cl_2 (3 x), the combined organic extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash



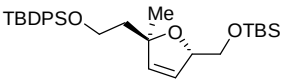
chromatography (10:1, hexanes/EtOAc) to give product **7** as a colorless oil (1.59 g, 95 %). $[a]_D^{20}$ = +3.3 (*c* = 1.5 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.77-7.71 (m, 4H), 7.26-7.21 (m, 6H), 3.96-3.87 (m, 2H), 3.65 (t, ^3J = 6.4 Hz, 2H), 3.17 (dt, ^3J = 3.8, 1.8 Hz, 1H), 2.96 (td, ^3J = 5.4, 4.0 Hz, 1H), 2.25 (td, ^3J = 6.7, 1.8 Hz, 2H), 1.16 (s, 9H), 0.97 (s, 9H), 0.08 (d, *J* = 8.3 Hz, 6H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 136.0, 133.9, 130.1, 128.4, 128.2, 128.1, 127.7, 83.8, 76.8, 63.3, 62.6, 57.6, 44.5, 27.1, 26.1, 23.2, 19.4, 18.5, –5.0, –5.1; HRMS (ESI+): *m*/*z*: calcd for $C_{29}H_{42}O_3Si_2Na$ $[M+Na]^+$: 517.25647; found: 517. 25617.

Allenol 9: $(PhO)_3P$ (0.54 mL, 2.07 mmol) was added to a suspension of CuCN (187 mg, 2.09 mmol) in



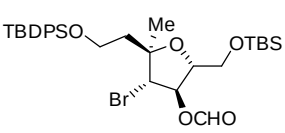
THF (40 mL) and the suspension was stirred until a clear solution had formed (ca. 10 min). The mixture was then cooled to –40 °C before a solution of MeMgBr (2.6 M in THF, 1.66 mL, 4.32 mmol) was added. After stirring for 30 min at this temperature, a solution of epoxide **7** (855 mg, 1.73 mmol) in THF (18 mL) was added over 15 min. The temperature was maintained at –40 °C for 2 h before the mixture was allowed to slowly warm to 10 °C overnight. The reaction was quenched with aq. sat. NH_4Cl and diluted with *tert*-butyl methyl ether. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined extracts were washed with brine, dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (20:1→10:1, hexanes/EtOAc) to give product **9** as a pale yellow oil (892 mg, 99 %). $[a]_D^{20}$ = –16.1 (*c* = 1.4 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.74-7.71 (m, 4H), 7.46-7.40 (m, 6H), 5.07 (m, 1H), 4.09 (m, 1H), 3.75 (t, *J* = 6.8 Hz, 2H), 3.58 (dd, *J* = 4.0, 9.9 Hz, 1H), 3.46 (dd, *J* = 7.0, 9.9 Hz, 1H), 2.24 (m, 2H), 1.67 (s, 3H), 1.52 (brs, 1H), 1.06 (s, 9H), 0.91 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 201.09, 135.52, 133.87, 133.85, 129.57, 127.60, 99.33, 90.84, 70.47, 67.34, 62.44, 36.95, 26.82, 25.86, 19.18, 19.14, 18.28, -5.35; IR (neat): 2930, 2858, 1472, 1428, 1365, 1228, 1217, 1111 cm^{-1}; MS (EI): *m*/*z* (%): 453 (M-*t*Bu), 321, 199; HRMS (ESI+): *m*/*z*: calcd for $C_{30}H_{46}O_3Si_2Na$ $[M+Na]^+$: 533.2877; found: 533.2878.

Compound 10. $AgNO_3$ (1.79 g, 10.53 mmol) and $CaCO_3$ (1.92 g, 19.16 mmol) were successively



added to a solution of compound **9** (4.88 g, 9.55 mmol) in acetone (128 mL) and H_2O (32 mL). After stirring in the dark for 4 h, TLC analysis showed complete conversion. Brine (100 mL) was added followed by *tert*-butyl methyl ether (100 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash chromatography (50:1, hexanes/EtOAc) to give product **10** as a colorless oil (4.44 g, 91 %). $[a]_D^{20}$ = –71.2 (*c* = 2.0 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.79-7.76 (m, 4H), 7.23-7.21 (m, 6H), 5.51-5.50 (bs, 2H), 4.70 (td, *J* = 0.8, 5.7 Hz, 1H), 3.94-3.81 (m, 2H), 3.60 (dd, *J* = 4.9, 10.1 Hz, 1H), 3.48 (dd, *J* = 5.8, 10.1 Hz, 1H), 2.05 (dt, *J* = 6.2, 7.8 Hz, 1H), 1.91 (dt, *J* = 6.0, 7.8 Hz, 1H), 1.26 (s, 3H), 1.17 (s, 9H), 0.93 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 136.1, 135.5, 134.4, 130.0, 126.9, 89.1, 86.9, 67.5, 61.1, 44.4, 28.4, 27.2, 26.2, 19.5, 18.7, -5.0, -5.2; IR: 2929, 2857, 1472, 1428, 1361, 1255, 1087, 1006 cm^{-1}; MS (EI): *m*/*z* (%): 453 (M-*t*Bu), 365, 321, 197; HRMS (ESI+): *m*/*z*: calcd for $C_{30}H_{46}O_3Si_2Na$ $[M+Na]^+$: 533.2877; found: 533.2872.

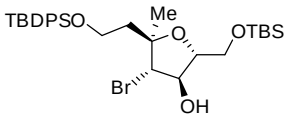
Compound 11. NBS (6.18 g, 34.72 mmol) was added in 4 portions, one every 12 h, to a solution of



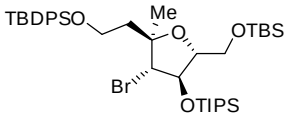
compound **10** (4.44 g, 8.69 mmol) in DMF (86.9 mL) and H_2O (5.8 mL) at 10 °C in the dark. After 48 h, the mixture was diluted with H_2O and *tert*-butyl methyl ether. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined organic phases were washed with H_2O and brine before

being dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (30:1, hexanes/EtOAc) to give compound **11** as a colorless oil (3.54 g, 64 %). $[a]_D^{20}$ = +2.0 (*c* = 1.0 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.79-7.76 (m, 4H), 7.41 (s, 1H), 7.23-7.21 (m, 6H), 5.85 (td, *J* = 0.8, 6.6 Hz, 1H), 4.62 (d, *J* = 6.6 Hz, 1H), 3.97-3.90 (m, 1H), 3.77 (m, 2H), 3.69 (dd, *J* = 4.2, 10.8 Hz, 1H), 3.61 (dd, *J* = 4.2, 10.8 Hz, 1H), 1.92 (dt, *J* = 6.8, 14.4 Hz, 1H), 1.74 (dt, *J* = 5.8, 14.4 Hz, 1H), 1.36 (s, 3H), 1.18 (s, 9H), 0.94 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 159.6, 136.5, 134.5, 134.3, 130.6, 128.8, 83.6, 81.8, 79.9, 64.3, 60.8, 57.6, 41.3, 27.6, 26.6, 19.8, 19.0, –4.8, –4.9; IR: 2955, 2930, 2857, 1737, 1472, 1428, 1256, 1152, 1111, 837 cm^{-1}; MS (EI): *m*/*z* (%): 579-577 (M-*t*Bu), 269; HRMS (ESI+): *m*/*z*: calcd for $C_{31}H_{47}O_5Si_2BrNa$ $[M+Na]^+$: 657.2037; found: 657.2042.

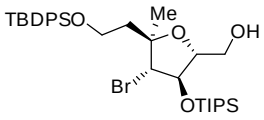
Alcohol S2. Solid $NaHCO_3$ (929 mg, 11.06 mmol) was added to a solution of formate ester **11** (1.40 g, 2.21 mmol) in MeOH (44 mL) and H_2O (2.9 mL) and the resulting mixture was stirred until TLC showed complete conversion. For work up, the mixture was diluted with brine and *tert*-butyl methyl ether, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (10:1→4:1, hexanes/EtOAc) to give alcohol **S2** as a colorless oil (1.14 g, 85 %). $[a]_D^{20}$ = –1.97 (*c* = 1.2 in C_6H_6). ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.72-7.66 (m, 4H), 7.42-7.36 (m, 6H), 4.40 (d, *J* = 8.7 Hz, 1H), 4.33 (bt, *J* = 7.2 Hz, 1H), 3.88 (m, 1H), 3.77 (m, 2H), 3.64 (m, 2H), 2.24 (bs, 1H), 1.97 (dt, *J* = 6.3, 14.3 Hz, 1H), 1.74 (dt, *J* = 5.7, 14.3 Hz, 1H), 1.29 (s, 3H), 1.05 (s, 9H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 135.6, 134.8, 133.6, 129.6, 127.7, 127.7, 82.0, 80.6, 78.8, 63.8, 59.8, 59.5, 41.7, 26.8, 26.6, 25.9, 19.1, 18.2, –5.4, –5.5; IR: 3435, 3071, 2929, 2857, 1472, 1427, 1361, 1254, 1083, 834 cm^{-1} MS (EI): *m*/*z* (%): 551-549 (M-*t*Bu), 269; HRMS (ESI+): calcd for $C_{30}H_{47}O_4Si_2BrNa$ $[M+Na]^+$: 629.2088; found: 629.2087.



Compound 12. 2,6-Lutidine (2.19 mL, 18.82 mmol) and TIPSOTf (2.53 mL, 9.41 mmol) were added to a solution of alcohol **S2** (1.43 g, 2.35 mmol) in CH_2Cl_2 (34 mL) at 0 °C and the resulting mixture was stirred at ambient temperature for 5 h. The reaction was quenched with aq. sat. NH_4Cl, the aqueous phase was extracted with CH_2Cl_2 (3 x), the combined extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (50:1→30:1, hexanes/EtOAc) to give product **12** as a colorless oil (1.67 g, 93 %). $[a]_D^{20}$ = +0.47 (*c* = 1.5 in C_6H_6). ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.69-7.66 (m, 4H), 7.44-7.37 (m, 6H), 4.67 (m, 1H), 4.40 (d, *J* = 5.3 Hz, 1H), 3.89-3.71 (m, 5H), 2.14 (dt, *J* = 6.5, 14.2 Hz, 1H), 1.90 (dt, *J* = 6.2, 14.2 Hz, 1H), 1.31 (s, 3H), 1.12-1.04 (m, 22H), 1.04 (s, 9H), 0.89 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* =135.6, 135.6, 133.7, 129.6, 129.6, 127.6, 84.3, 82.5, 79.7, 62.9, 62.5, 60.2, 40.9, 26.8, 26.6, 26.0, 19.1, 18.5, 18.2, 12.5, –5.2, –5.4; IR: 2930, 2863, 1463, 1255, 1096, 835, 700 cm^{-1}; MS (EI): *m*/*z* (%): 705 (M-*t*Bu), 303, 269; HRMS (ESI+): *m*/*z*: calcd for $C_{39}H_{68}O_4Si_3BrNa$ $[M+Na]^+$: 763.3603; found: 763.3607.

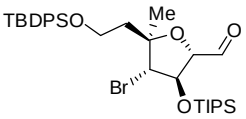


Alcohol S3. An aq. solution of trichloroacetic acid (2.1 g·mL^{-1}, 5.5 mL) was added to a solution of silylether **12** (1.66 g, 2.17 mmol) in THF (22 mL) and the resulting mixture stirred overnight. The reaction was quenched with aq. sat. $NaHCO_3$, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined organic extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (20:1→6:1, hexanes/EtOAc) to give product **S3** as a colorless oil (1.21 g, 86 %). $[a]_D^{20}$ = +0.85 (*c* = 1.1 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): *d* = 7.69-7.65 (m, 4H),

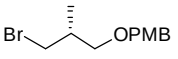


7.42-7.36 (m, 6H), 4.57 (dd, *J* = 4.4, 5.3 Hz, 1H), 4.34 (d, *J* = 4.4 Hz, 1H), 3.82-3.75 (m, 4H), 3.63 (dd, *J* = 4.7, 12.4 Hz, 1H), 2.17 (dt, *J* = 6.3, 14.3 Hz, 1H), 1.74 (dt, *J* = 6.4, 14.3 Hz, 1H), 1.64 (bs, 1H), 1.33 (s, 3H), 1.09-1.04 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): *d* = 135.60, 135.58, 135.69, 133.55, 129.65, 129.62, 127.72, 127.66, 84.20, 82.99, 80.62, 63.15, 62.15, 60.04, 40.25, 26.82, 26.27, 19.06, 18.04, 12.34; IR: 3464, 2942, 2866, 1463, 1428, 1089, 701 cm^{-1}; MS (EI): *m*/*z* (%): 647, 593-591 (M-*t*Bu), 427, 269; HRMS (ESI+): *m*/*z*: calcd for $C_{30}H_{47}O_4Si_2BrNa$ [M+Na]$^+$: 671.2558; found: 671.2558.

Aldehyde 13. Dess-Martin periodinane (327 mg, 0.773 mmol) and pyridine (242 µl, 3.09 mmol) were added to a solution of alcohol **S3** (335 mg, 0.515 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After 4 h, aq. sat. $Na_2S_2O_3$/$NaHCO_3$ (1:1) was introduced at 0 °C, the aqueous phase was extracted with CH_2Cl_2 (3 x), the combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography on a short silica gel column (10:1, hexanes/EtOAc) to give aldehyde **13** as a colorless oil (303 mg, 90 %). $[a]_D^{20}$ = –8.4 (*c* = 1.1 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 9.55 (d, *J* = 1.2 Hz, 1H), 7.79-7.75 (m, 4H), 7.24-7.23 (m, 6H), 4.90 (t, *J* = 2.9 Hz, 1H), 4.39 (d, *J* = 2.9 Hz, 1H), 4.09 (dd, *J* = 1.3 Hz, 1H), 3.89 (dt, *J* = 6.3, 10.5 Hz, 1H), 3.78 (dt, *J* = 6.8, 10.5 Hz, 1H), 2.22 (dt, *J* = 6.0, 14.1 Hz, 1H), 1.74 (dt, *J* = 6.8, 14.1 Hz, 1H), 1.30 (s, 3H), 1.17 (m, 10H), 1.07 (m, 20H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 200.1, 136.1, 136.0, 133.9, 130.2, 130.1, 128.2, 89.4, 85.9, 84.6, 63.0, 60.7, 40.7, 27.1, 25.7, 19.4, 18.0, 12.3; IR: 2943, 2866, 1735, 1463, 1428, 1111 cm^{-1}; MS (EI): *m*/*z* (%): 591-589 (M-*t*Bu), 509, 397, 321, 269; HRMS (ESI+): *m*/*z*: calcd for $C_{33}H_{51}O_4Si_2BrNa$ [M+Na]$^+$: 669.2401; found: 669.2398.



Alkyl Bromide *R*-14.[2] Pyridinium *p*-toluenesulfonate (98.4 mg, 0.39 mmol) was added to a solution of (*R*)-3-bromo-2-methyl-1-propanol (2.19 g, 14.32 mmol) and 4-methoxybenzoyl trichloroacetimidate (5.10 g, 18.04 mmol)[3] in CH_2Cl_2 (100 mL). The mixture was stirred overnight before the reaction was quenched with sat. aq. $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (3 x) and the combined organic extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (30:1, hexane/EtOAc) to give product *R*-**14** as a colorless oil (2.82 g, 72 %). $[a]_D^{20}$ = –10.7 (*c* = 1.6 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.17 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.7, 2H), 4.25 (s, 2H), 3.31 (s, 3H), 3.23 (d, *J* = 5.3 Hz, 2H), 3.15 (d, *J* = 5.6 Hz, 2H), 1.83 (d, *J* = 6.9 Hz, 1H), 0.81 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 159.8, 131.1, 129.4, 114.1, 73.0, 72.4, 54.9, 38.2, 36.1, 15.8; IR: 2961, 2857, 1611, 1511, 1461, 1244, 1087, 1034, 816 cm^{-1}; HRMS (EI): *m*/*z*: calcd for $C_{12}H_{17}BrO_2$: 272.04121; found: 272.04099.

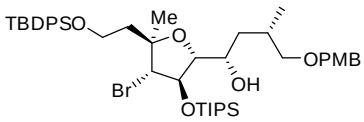


Alcohols 15 and 16. Anhydrous LiBr (21.0 g, 241.8 mmol) was added to a solution of aldehyde **13** (368.7 mg, 0.569 mmol) in CH_2Cl_2 (57 mL). After vigorous stirring for 10 min, the resulting suspension was cooled to –78 °C. In a separate Schlenk flask, *t*BuLi (1.7 M in pentane, 4.5 mL, 7.72 mmol) was added in one portion to a solution of *R*-**14** (1.17 g, 4.29 mmol) in Et_2O (14.3 mL) at –78 °C. The resulting yellow solution was stirred for 5 min at –78 °C before a freshly prepared solution of $MgBr_2$ in Et_2O/toluene (2:1) (0.66 M, 6.5 mL, 4.29 mL) was added dropwise over 5 min. Stirring was continued for 20 min at –78 °C before the mixture was added via canula to the suspension of the aldehyde and LiBr at –78 °C. The resulting mixture was vigourously stirred at this temperature for 14 h before aq. sat. NH_4Cl was introduced and the mixture allowed to reach ambient temperature. After dilution with *tert*-butyl methyl ether, the layers were separated and the aqueous phase was extracted with *tert*-butyl

[2] S. D. Meyer, T. Miwa, M. Nakatsuka, S. L. Schreiber, *J. Org. Chem*. **1992**, *57*, 5058-5060.
[3] M. G. Organ, J. Wang, *J. Org. Chem.* **2003**, 68, 5568-5574.

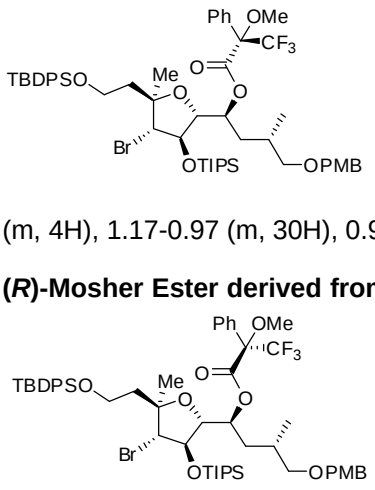
methyl ether (3 x). The combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (2→15 %, Et_2O in hexanes) to give the diastereomeric alcohols as colorless oils each (350.8 mg, 73 % combined yield, dr = 4:1).

Compound 16. $[a]_D^{20}$ = –2.6 (*c* = 0.3 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.84-7.76 (m, 4H), 7.31-7.19 (m, 8H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.93 (t, ^3J = 6.3 Hz, 1H), 4.57 (d, *J* = 6.1 Hz, 1H), 4.33 (s, 2H), 4.04-3.91 (m, 2H), 3.81 (dt, *J* = 10.3, 6.4 Hz, 1H), 3.72 (dd, *J* = 6.6, 1.7 Hz, 1H), 3.31 (s, 3H), 3.22 (d, *J* = 6.0 Hz, 2H), 2.25-2.08 (m, 3H), 1.92 (ddd, *J* = 14.6, 10.3, 4.5 Hz, 1H), 1.79 (dt, *J* = 14.6, 6.1 Hz, 1H), 1.32 (s, 3H), 1.23-1.14 (m, 30H), 1.02 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 159.9, 136.1, 134.1, 131.2, 130.1, 129.5, 128.2, 114.2, 86.8, 82.5, 80.5, 76.2, 73.0, 67.7, 63.1, 60.4, 54.8, 41.1, 40.1, 31.2, 29.6, 29.4, 27.5, 27.2, 26.7, 19.4, 18.5, 17.2, 13.0; IR: 3562, 2942, 2865, 1513, 1463, 1247, 1089 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{45}H_{69}BrO_6Si_2Na$ [M+Na]$^+$: 863.37084; found: 863.37115.

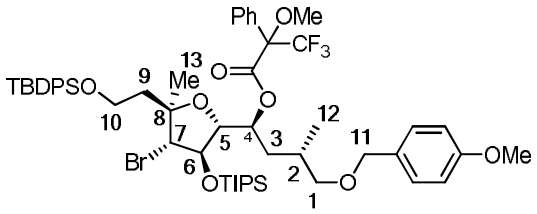


Compound 15. $[a]_D^{20}$ = +2.7 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (300 MHz, C_6D_6): *d* = 7.85-7.76 (m, 4H), 7.31-7.18 (m, 8H), 6.84 (d, *J* = 8.1 Hz, 2H), 5.15 (br dd, ^3J = 3.2, 1.8 Hz, 1H), 4.36 (br d, ^3J = 1.8 Hz, 1H), 4.22 (s, 2H), 4.07-3.83 (m, 4H), 3.33 (s, 3H), 3.22-3.04 (m, 3H), 2.51 (dt, *J* = 14.0, 7.0 Hz, 1H), 2.15-1.99 (m, 2H), 1.83 (ddd, *J* = 14.4, 9.4, 2.9 Hz, 1H),1.61 (ddd, *J* = 14.0, 9.5, 4.0 Hz, 1H) 1.42 (s, 3H), 1.27-1.14 (m, 30H), 0.87 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 159.9, 136.1, 134.2, 134.1, 130.5, 130.0, 129.8, 129.3, 128.4, 128.1, 114.2, 89.4, 84.8, 83.9, 75.8, 73.2, 71.1, 65.4, 60.9, 54.8, 40.4, 40.2, 30.3, 27.2, 26.2, 19.4, 18.5, 18.4, 12.8; IR: 3443, 2942, 2865, 1514, 1248, 1113 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{45}H_{69}BrO_6Si_2Na$ [M+Na]$^+$: 863.37084; found: 863.37165.

(*S*)-Mosher Ester derived from 16. ^{1}H NMR (300 MHz, $CDCl_3$): *d* = 7.66-7.54 (m, 6H), 7.43-7.24 (m, 9H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.45 (ddd, *J* = 10.2, 7.3, 2.7 Hz, 1H), 4.48 (t, ^3J = 4.2 Hz, 1H), 4.26 (s, 2H), 4.23 (d, *J* = 3.7 Hz, 1H), 3.78-3.69 (m, 6H), 3.46 (s, 3H), 3.11 (d, *J* = 5.8 Hz, 2H), 2.16 (dt, *J* = 14.0, 6.9 Hz, 1H), 1.89 (dt, *J* = 14.0, 6.9 Hz, 1H), 1.72 (ddd, *J* = 14.0, 10.3, 3.1 Hz, 1H), 1.61-1.45 (m, 1H), 1.37-1.21 (m, 4H), 1.17-0.97 (m, 30H), 0.90 (d, *J* = 6.6 Hz, 3H).

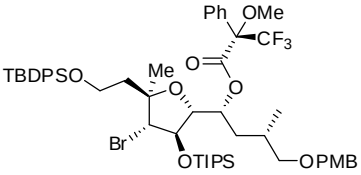


(*R*)-Mosher Ester derived from 16. ^{1}H NMR (300 MHz, $CDCl_3$): *d* = 7.64-7.49 (m, 7H), 7.44-7.19 (m, 6H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.38 (ddd, *J* = 9.4, 5.5, 4.0 Hz, 1H), 4.39 (m, 3H), 4.18 (d, *J* = 3.9 Hz, 1H), 3.77 (s, 3H), 3.71-3.65 (m, 3H), 3.36 (m, 3H), 3.22 (d, *J* = 6.0 Hz, 2H), 2.10 (dt, *J* = 14.5, 6.6 Hz, 1H), 1.96-1.69 (m, 3H), 1.40 (ddd, *J* = 13.6, 9.4, 4.2 Hz, 1H), 1.17 (s, 3H), 1.07-0.97 (m, 30H), 0.94 (d, *J* = 6.6 Hz, 3H).

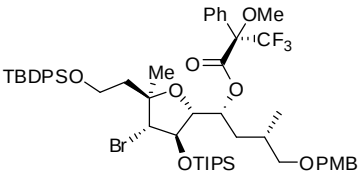


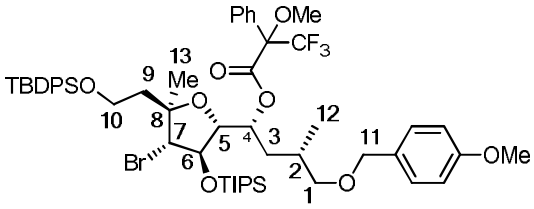
H	1	2	3a	3b	5	6	7	9a	9b	10	11	12	13
d_S - d_R	-0.11	-0.21	-0.17	-0.08	0.05	0.11	0.04	0.06	0.08	0.05	-0.11	-0.04	0.09

(*S*)-Mosher Ester derived from 15. ^{1}H NMR (300 MHz, $CDCl_3$): d = 7.65-7.57 (m, 4H), 7.52-7.46 (m, 2H), 7.41-7.25 (m, 9H), 7.21 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 9.1 Hz, 2H), 5.42 (dt, J = 8.4, 3.9 Hz, 1H), 4.44 (dd, ^3J = 4.9, 3.0 Hz, 1H), 4.38 (s, 2H), 4.18 (d, J = 3.0 Hz, 1H), 3.81 (dd, J = 4.9, 3.5 Hz, 1H), 3.77 (s, 3H), 3.66 (t, J = 6.7 Hz, 2H), 3.47 (s, 3H), 3.33-3.22 (m, 2H), 2.03 (dt, J = 14.1, 6.1 Hz, 1H;CH_{2a}), 1.94-1.77 (m, 2H), 1.77-1.63 (m, 2H), 1.19 (s, 3H), 1.04-0.97 (m, 30H), 0.94 (d, J = 6.7 Hz, 3H).



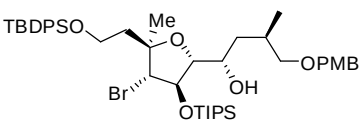
(*R*)-Mosher Ester derived from 15. ^{1}H NMR (300 MHz, $CDCl_3$): d = 7.68-7.56 (m, 4H), 7.55-7.49 (m, 2H), 7.43-7.25 (m, 9H), 7.21 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 5.41 (br m, 1H), 4.52 (dd, ^3J = 5.9, 3.4 Hz, 1H), 4.36 (s, 2H), 4.22 (d, J = 3.5 Hz, 1H), 3.93 (dd, J = 5.9, 2.2 Hz, 1H), 3.77 (s, 3H), 3.73 (t, J = 6.6 Hz, 2H), 3.45 (s, 3H), 3.24-3.14 (m, 2H), 2.11 (dt, J = 14.1, 6.3 Hz, 1H), 1.91 (dt, J = 14.1, 6.7 Hz, 1H), 1.73-1.54 (m, 3H), 1.29 (s, 3H) 1.09-0.98 (m, 30H), 0.81 (d, J = 6.1 Hz, 3H).



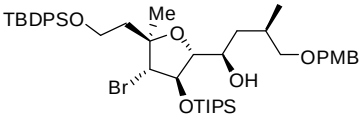


H	1	2	3a	3b	5	6	7	9a	9b	10	11	12	13
d_S - d_R	0.09	0.06	0.18	0.06	-0.12	-0.08	-0.05	-0.08	-0.03	-0.07	0.02	0.13	-0.10

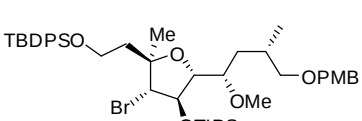
Compound 21. Prepared analogously as a colorless oil using *S*-**14**. $[a]_D^{20}$ = –2.7 (c = 0.6 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): d = 7.81-7.78 (m, 4H), 7.28-7.21 (m, 8H), 6.81 (d, J = 8.6 Hz, 2H), 4.93 (t, J = 6.4 Hz, 1H), 4.57 (d, J = 5.7 Hz, 1H), 4.36 (d, J = 11.8 Hz, 1H), 4.31 (d, J = 11.8 Hz, 1H), 4.01-3.95 (m, 2H), 3.81 (dt, J = 11.8, 5.8 Hz, 1H), 3.74 (dd, J = 6.4, 1.9 Hz, 1H), 3.31-3.28 (m, 5H), 2.20-2.09 (m, 2H), 2.05 (d, J = 9.3 Hz, 1H), 1.82-1.76 (dt, J = 14.2, 6.0 Hz, 1H), 1.71-1.58 (m, 2H), 1.34 (s, 3H), 1.20-1.15 (m, 30H), 1.02 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): d = 159.7, 136.1, 134.0, 131.2, 130.1, 129.3, 128.9, 114.1, 86.4, 82.5, 80.6, 75.0, 73.0, 67.5, 63.2, 60.4, 54.8, 41.0, 39.7, 30.8, 27.2, 26.7, 19.4, 18.5, 18.4, 13.0; IR: 3564, 2944, 2865, 1613, 1513, 1463, 1247, 1111, 1088, 822, 702 cm^{-1}; HRMS (ESI+): *m/z*: calcd for $C_{45}H_{69}BrO_6Si_2Na$ $[M+Na]^+$: 863.37084; found: 863.37084.



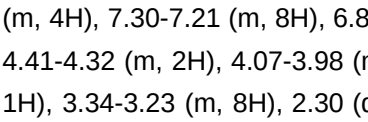
Compound 20. $[a]_D^{20}$ = +5.5 (*c* = 0.2 in $CHCl_3$). ^{1}H NMR (300 MHz, C_6D_6): *d* = 7.85-7.76 (m, 4H), 7.29-7.18 (m, 8H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.16 (br dd, *J* = 3.2, 1.8 Hz, 1H), 4.36 (br d, *J* = 1.7 Hz, 1H), 4.24 (d, *J* = 11.4 Hz, 1H), 4.19 (d, *J* = 11.4 Hz, 1H), 4.02-3.83 (m, 3H), 3.82 (dd, *J* = 7.2, 3.2 Hz, 1H), 3,51 (d, *J* = 3.0 Hz, 1H), 3.33 (s, 3H), 3.17 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.06 (t, *J* = 8.4 Hz, 1H), 2.51 (ddd, *J* = 13.5, 6.4 Hz, 1H), 2.09-1.99 (ddd, *J* = 14.6, 7.4 Hz, 1H), 1.99 (m, 2H), 1.51-1.42 (m, 4H), 1.24-1.16 (m, 30H), 0.87 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 160.0, 136.1, 134.3, 134.2, 130.4, 130.0, 129.7, 128.1, 127.9, 114.2, 89.5, 84.4, 83.9, 76.7, 73.1, 72.7, 65.4, 60.9, 54.8, 40.8, 40.5, 32.2, 30.2, 27.2, 26.2, 19.4, 18.6, 18.2, 12.9.



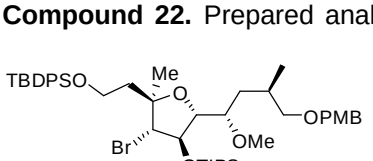
Methyl Ether 17. LiHMDS (0.5 M in THF, 0.73 mL, 0.364 mmol) was added dropwise to a solution of alcohol **16** (278.4 mg, 0.331 mmol) in THF (1.65 mL) at −78 °C and the resulting mixture stirred at this temperature for 35 min before a solution of MeOTf in CH_2Cl_2 (1.0 M, 0.35 mL, 0.35 mmol) was slowly added. Stirring was continued at −78 °C for 5 min before the cooling bath was removed and the mixture allowed to reach ambient temperature over the course of 65 min. The reaction was quenched with aq. sat. $NaHCO_3$, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (20:1→10:1, hexanes/EtOAc) to give product **17** as a colorless oil (247 mg, 87 %). $[a]_D^{20}$ = +2.2 (*c* = 0.6 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.85-7.77 (m, 4H), 7.30-7.21 (m, 8H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.99 (t, ^{3}*J* = 5.8 Hz, 1H), 4.51 (d, *J* = 5.0 Hz, 1H), 4.41-4.32 (m, 2H), 4.07-3.98 (m, 2H), 3.87 (dt, *J* = 10.6, 6.2 Hz, 1H), 3.59 (ddd, ^{3}*J* = 8.9, 5.6, 3.8 Hz, 1H), 3.34-3.23 (m, 8H), 2.30 (dt, *J* = 14.1, 6.5 Hz, 1H), 2.14-1.96 (m, 2H), 1.87 (dt, *J* = 14.3, 6.1 Hz, 1H), 1.63 (ddd, *J* = 13.3, 7.7, 5.6 Hz, 1H), 1.44 (s, 3H), 1.23-1.15 (m, 30H), 1.06 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 159.7, 136.1, 134.1 (2), 131.5, 130.0, 129.3, 128.1, 127.9, 114.1, 85.7, 82.7, 81.4, 77.4, 75.6, 73.0, 64.1, 60.6, 57.3, 54.8, 40.8, 34.5, 31.0, 27.2, 26.4, 19.4, 18.5 (2), 18.0, 13.1; IR: 2942, 2865, 1513, 1462, 1247, 1088, 702 cm^{-1}; HRMS (ESI+): *m/z*: calcd for $C_{46}H_{71}BrO_6Si_2Na$ [M+Na]$^+$: 877.38649; found: 877.38722.



Compound 22. Prepared analogously as a colorless oil (383.1 mg, 77 %). $[a]_D^{20}$ = +1.3 (*c* = 1.1 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.83-7.77 (m, 4H), 7.30-7.21 (m, 8H), 6.83-6.78 (m, 2H), 5.00 (t, *J* = 5.7 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 4.33 (s, 2H), 4.08-3.98 (m, 2H), 3.84 (dt, *J* = 10.6, 6.1 Hz, 1H), 3.56 (td, *J* = 6.6, 3.2 Hz, 1H), 3.33-3.28 (m, 4H), 3.27-3.20 (m, 4H), 2.25 (dt, *J* = 13.9, 6.8 Hz, 1H), 2.11-1.95 (m, 2H), 1.82 (dt, *J* = 14.1, 6.1 Hz, 1H), 1.62 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.46 (s, 3H), 1.25-1.15 (m, 30H), 1.08 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 159.7, 136.1, 134.1, 134.0, 131.4, 130.0, 129.3, 128.1, 114.1, 84.9, 82.5, 80.8, 77.4, 75.7, 72.9, 63.7, 60.6, 56.9, 54.8, 40.8, 33.9, 30.9, 27.2, 26.5, 19.4, 18.5 (2), 18.1, 13.1; IR: 2932, 2867, 1513, 1463, 1248, 1088, 702 cm^{-1}; HRMS (ESI+): *m/z*: calcd for $C_{46}H_{71}BrO_6Si_2Na$ [M+Na]$^+$: 877.38649; found: 877.38655.

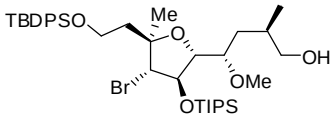


Compound 18. DDQ (43.4 mg, 0.191 mmol) was added to a solution of compound **17** (109.1 mg, 0.127 mmol) in CH_2Cl_2 (4.25 mL) and H_2O (0.21 mL) at 0 °C and the resulting mixture stirred at ambient temperature for 30 min. The reaction was quenched with aq. sat. $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2 (3 x), the combined extracts were dried over Na_2SO_4,

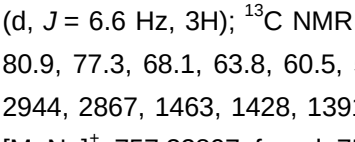


filtered and evaporated, and the residue was purified by flash chromatography (15:1→6:1 hexanes/EtOAc) to give product **18** as a colorless oil (93.3 mg, 99 %). $[a]_D^{20}$ = –4.3 (*c* = 0. 9 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.83-7.78 (m, 4H), 7.30-7.22 (m, 6H), 4.94 (dd, ^3J = 5.9, 4.2 Hz, 1H), 4.46 (d, *J* = 4.4 Hz, 1H), 4.04-3.97 (m, 2H), 3.87 (dt, *J* = 10.4, 6.5 Hz 1H), 3.52 (dt, ^3J = 8.2, 4.2 Hz, 1H), 3.33-3.27 (m, 5H), 2.32 (dt, *J* = 14.5, 6.5 Hz, 1H), 1.94-1.72 (m, 3H), 1.58 (ddd, *J* = 13.9, 7.1, 5.2 Hz, 1H), 1.43 (s, 3H), 1.22-1.14 (m, 30H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.44 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 136.1, 134.1, 134.0, 130.0, 128.7, 127.9, 85.9, 82.8, 81.8, 78.1, 68.1, 64.3, 60.6, 57.4, 40.6, 34.4, 33.5, 27.2, 26.3, 19.4, 18.5, 17.7, 13.0; IR: 3396, 2941, 2868, 1462, 1428, 1381, 1111, 702 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{38}H_{63}BrO_5Si_2Na$ $[M+Na]^+$: 757.32898; found: 757.32821.

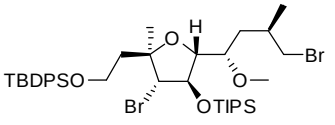
Compound 23. Prepared analogously as a colorless oil (306.2 mg, 93 %). $[a]_D^{20}$ = +3.0 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.81-7.77 (m, 4H), 7.30-7.22 (m, 6H), 4.97 (dd, *J* = 5.8, 5.3 Hz, 1H), 4.54 (d, *J* = 5.1 Hz, 1H), 4.05-3.95 (m, 2H), 3.84 (dt, *J* = 11.2, 5.9 Hz 1H), 3.49 (td, *J* = 6.5, 3.2 Hz, 1H), 3.34-3.26 (m, 2H), 3.21 (s, 3H), 2.25 (dt, *J* = 14.1, 6.9 Hz, 1H), 1.91-1.70 (m, 3H), 1.54 (ddd, *J* = 13.8, 6.9 Hz, 1H), 1.43 (s, 3H), 1.29 (br t, 1H), 1.23-1.13 (m, 30H), 0.91 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 136.1, 134.1, 134.0, 130.0 (2), 128.2, 84.7, 82.7, 80.9, 77.3, 68.1, 63.8, 60.5, 56.8, 40.8, 33.5, 33.1, 27.2, 26.4, 19.4, 18.5 (2), 17.4, 13.0; IR: 3454, 2944, 2867, 1463, 1428, 1391, 1110, 1084, 702 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{38}H_{63}BrO_5Si_2Na$ $[M+Na]^+$: 757.32897; found: 757.32862.



Iodide 19. A mixture of PPh_3 (118.2 mg, 0.451 mmol) and iodine (114.1 mg, 0.450 mmol) in CH_2Cl_2 (10 mL) was added to a solution of alcohol **18** (163.0 mg, 0.221 mmol) and imidazole (108.5 mg, 1.594 mmol) in CH_2Cl_2 (12 mL). After stirring for 2 h, the reaction was quenched with aq. sat. $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2 (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (30:1→20:1, hexanes/EtOAc) to give product **19** as a colorless oil (172.9 mg, 92 %). $[a]_D^{20}$ = +4.7 (*c* = 1.1 in $CHCl_3$). ^{1}H NMR (300 MHz, C_6D_6): *d* = 7.84-7.76 (m, 4H), 7.30-7.22 (m, 6H), 4.94 (dd, ^3J = 5.7, 4.6 Hz, 1H), 4.48 (d, *J* = 4.5 Hz, 1H), 3.99 (dt, ^3J = 10.5, 6.3 Hz, 1H), 3.93-3.76 (m, 2H), 3.39 (ddd, ^3J = 9.2, 5.7, 3.5 Hz 1H), 3.25 (s, 3H), 2.92 (d, *J* = 4.7 Hz, 2H), 2.29 (dt, *J* = 14.2, 6.6 Hz 1H), 1.91-1.65 (m, 2H), 1.61-1.40 (m, 5H), 1.24-1.15 (m, 30H), 0.85 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 136.1, 134.0, 130.0, 102.6, 85.4, 82.9, 81.3, 77.2, 64.0, 60.6, 57.5, 46.3, 40.7, 37.0, 31.3, 27.2, 26.3, 21.1, 19.5, 18.5, 18.2 , 13.0; IR: 2943, 2866, 1462, 1428, 1380, 1110 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{38}H_{62}BrIO_4Si_2Na$ $[M+Na]^+$: 845.24877; found: 845.24974.

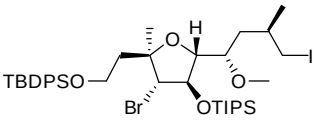


Bromide 24. A 25 mL round bottom flask was charged with alcohol **23** (403 mg, 0.548 mmol) and benzene (5.0 mL). A mixture of PPh_3 (646 mg, 2.46 mmol) and CBr_4 (908 mg, 2.74 mmol) in benzene (5.0 mL) was then transferred to this flask and the resulting mixture was stirred at 50 °C for 30 min. The opaque solution was diluted with hexanes (10 mL) and the suspension filtered through a short pad of Celite. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 30:1 → 10:1) to yield product **24** as a colorless oil (433 mg, 97 %). $[a]_D^{20}$ = –4.5 (*c* = 2.2 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.81–7.77 (m, 4H), 7.29-7.21 (m, 6H), 4.92 (dd, *J* = 5.8, 5.1 Hz, 1H), 4.48 (d, *J* = 5.1 Hz, 1H), 3.99 (dt, *J* = 10.4, 6.6 Hz, 1H), 3.89-3.83 (m, 2H), 3.37 (dt, *J* = 6.1, 3.3 Hz, 1H), 3.17 (s, 3H), 3.14 (dd, *J* = 9.9, 4.0 Hz, 1H), 3.10 (dd, *J* = 9.9, 5.4



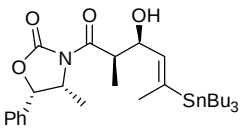
Hz, 1H), 2.24 (dt, *J* = 14.3, 6.6 Hz, 1H), 1.89-1.78 (m, 3 H), 1.52 (t, 6.6 Hz, 1H), 1.41 (s, 3H), 1.20-1.14 (m, 30H), 0.92 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 136.1, 134.0, 130.1, 128.2, 85.1, 82.8, 81.1, 77.2, 63.7, 60.6, 57.1, 41.7, 40.8, 35.1, 32.0, 27.2, 26.3, 19.4, 19.2, 18.5, 13.0; IR (film): 2942, 2866, 1462, 1428, 1380, 1110, 1083, 882, 823, 738, 684 cm^{-1}; HRMS (ESI+): calcd for $C_{38}H_{62}O_4Br_2Si_2Na$ [M+Na]$^+$: 819.24459, found: 819.24523.

Iodide 25. A 25 mL round bottom flask was charged with bromide **24** (100 mg, 0.125 mmol) and acetone (4 mL). NaI (75 mg, 0.50 mmol) was added and the suspension stirred for 60 h. For work up, the mixture was diluted with hexanes (10 mL) and filtered through a short pad of silica to yield iodide **25** as a colorless oil that was taken on without further purification (93 mg, 88 %). $[a]_D^{20}$ = –4.2 (*c* = 0.8 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.82-7.78 (m, 4H), 7.30-7.22 (m, 6H), 4.93 (apparent t, *J* = 5.3 Hz, 1H), 4.49 (d, *J* = 5.0 Hz, 1H), 4.01 (dt, *J* = 10.5, 6.5 Hz, 1H), 3.91-3.83 (m, 2H), 3.35 (dt, 6.5, 3.4 Hz, 1H), 3.18 (s, 3H), 2.96 (dd, *J* = 9.7, 4.0 Hz, 1H), 2.91 (dd, *J* = 9.7, 5.4 Hz, 1H), 2.26 (dt, *J* = 14.2, 6.5 Hz, 1H), 1.86 (dt, *J* = 14.2, 6.5 Hz, 1H), 1.75 (dt, *J* = 13.5, 6.2 Hz, 1H), 1.55-1.44 (m, 2H), 1.43 (s, 3H), 1.21-1.14 (m, 30H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 136.1, 134.0, 130.1, 128.2, 85.3, 82.8, 81.1, 77.2, 63.8, 60.6, 57.2, 40.8, 36.7, 31.4, 27.2, 26.3, 21.2, 19.4, 18.5, 18.0, 13.1; IR: 2942, 2866, 1462, 1428, 1380, 1110, 1084, 882, 824, 738, 701, 685 cm^{-1}.

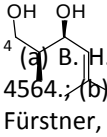


Oxazole Sector.

Compound 36. Freshly distilled Bu_2BOTf (10.66 g, 38.91 mmol) was added to a solution of compound **35** (8.38 g, 35.92 mmol) in CH_2Cl_2 (150 mL) at –10 °C, followed by Et_3N (6.03 g, 59.8 mmol). The resulting mixture was stirred at –10 °C for 1 h before it was cooled to –50 °C and a solution of aldehyde **34** (10.75 g, 29.9 mmol)[4] in CH_2Cl_2 (50 mL) was slowly introduced. The resulting mixture was stirred –50 °C for 5 h before the reaction was quenched with pH 7 phosphate buffer (30 mL) and MeOH (100 mL). After reaching 0 °C, a mixture of aq. H_2O_2 (30 % *w*/*w*) and MeOH (1:1, 100 mL) was added and all volatile materials were evaporated. The residue was diluted with H_2O and *tert*-butyl methyl ether, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined extracts were dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 10/1) to give product **36** as a colorless oil (16.81 g, 95 %). $[a]_D^{20}$ = +8.0 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.43-7.37 (m, 3H), 7.31-7.29 (m, 2H), 5.66 (d, *J* = 7.2 Hz, 1H), 5.60 (dq, *J* = 7.8, 1.8 Hz, 1H), 4.88 (dd, *J* = 7.8, 4.1 Hz, 1H), 4.77 (dq, *J* = 7.2, 6.6 Hz, 1H), 3.80 (dq, *J* = 6.9, 4.1 Hz, 1H), 2.70 (bs, 1H), 1.92 (d, *J* = 1.8 Hz, 3H), 1.51-1.46 (m, 6 H), 1.36-1.27 (m, 9H), 0.93-0.87 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 176.4, 152.7, 143.5, 139.3, 133.2, 128.8, 128.7, 125.7, 78.9, 67.8, 54.8, 42.9, 29.1, 27.3, 19.9, 14.4, 13.7, 11.4, 9.2; IR (neat): 3384, 2956, 2924, 1754, 1456, 1417, 1376, 1337, 1255, 1000 cm^{-1}; MS (EI): *m*/*z* : 592, 536 (M-Bu); HRMS (ESI+): *m*/*z*: calcd for $C_{29}H_{47}O_4SnNa$ [M+Na]+: 616.2418; found: 616.2420.



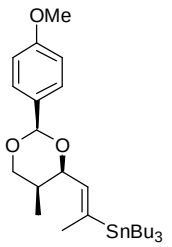
Diol S4. MeOH (566 µL, 14 mmol) and $LiBH_4$ (2 M in THF, 7 mL, 14 mmol) were successively added to



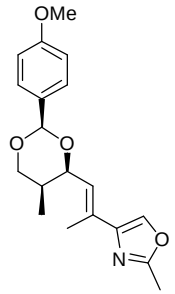
[4] (a) B. H. Lipshutz, G. C. Clososki, W. Chrisman, D. W. Chung, D. B. Ball, J. Howell, *Org. Lett.* **2005**, *7*, 4561-4564.; (b) J. F. Betzer, F. Delaloge, B. Muller, A. Pancrazi, J. Prunet, *J. Org. Chem.* **1997**, *62*, 7768-7780.; (c) A. Fürstner, C. Nevado, M. Waser, M. Tremblay, C. Chevrier, F. Teplý, C. Aïssa, E. Moulin, O. Müller, *J. Am. Chem. Soc.* **2007**, *129*, 9150-9161.

a solution of oxazolidinone **36** (2.1 g, 3.54 mmol) in THF (25 mL) at 0 °C, and the resulting mixture was stirred at ambient temperature for 3 h before the reaction was carefully quenched with aq. sat. NH_4Cl and *tert*-butyl methyl ether. HCl (1 % *w*/*w*) was added until the evolution of gas had ceased, the layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x), and the combined extracts were dried over $MgSO_4$ and evaporated. The residue was triturated with hexane, the hexane phase evaporated and the residue purified by flash chromatography (1:1, hexanes/EtOAc) to give diol **S4** as a colorless oil (1.43 g, 97 %). $[a]_D^{20}$ = +2.0 (*c* = 1.9 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 5.65 (dq, *J* = 8.3, 1.8 Hz, 1H), 4.71 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.72 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.62 (dd, *J* = 10.7, 4.5 Hz, 1H), 2.20 (bs, 2H), 1.90 (d, *J* = 1.8 Hz, 3H), 1.50-1.45 (m, 6H), 1.36-1.26 (m, 7H), 0.93-0.87 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 143.0, 140.4, 70.4, 66.4, 40.4, 29.1, 27.3, 19.8, 13.7, 11.6, 9.2; IR (neat): 3337, 2956, 2923, 1457, 1417, 1376, 1290, 1072, 1028 cm^{-1}; MS (EI): *m*/*z* (%): 363 (M-Bu); HRMS (ESI+): *m*/*z*: calcd for $C_{19}H_{40}O_2SnNa$ $[M+Na]^+$: 443.19418; found: 443.19435.

Acetal 37. 4-Methoxybenzaldehyde dimethylacetal (1.08 g, 1.01 mL, 5.96 mmol) and camphor sulphonic acid (13.8 mg, 0.059 mmol) were added to a solution of diol **S4** (500 mg, 1.19 mmol) in DMF (10 mL). After stirring for 2 h, the reaction was quenched with aq. sat. $NaHCO_3$ and *tert*-butyl methyl ether, the layers were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 x). The combined extracts were washed with water, dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (40:1, hexanes/EtOAc) to give product **37** as a colorless oil (562 mg, 88 %). $[a]_D^{20}$ = –6.44 (*c* = 1.0 in C_6H_6). ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 7.63 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.96 (dd, *J* = 6.5, 1.7 Hz, 1H), 5.52 (s, 1H), 4.82 (d, *J* = 5.5 Hz, 1H), 3.80 (bs, 2H), 3.23 (s, 3H), 1.94 (d, *J* = 1.7 Hz, 3H), 1.65-1.52 (m, 6H), 1.42 (m, 10H), 1.04-0.88 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): *d* = 160.6, 141.3, 140.1, 132.7, 114.1, 102.3, 77.5, 73.3, 54.9, 52.1, 33.5, 29.9, 28.0, 20.6, 14.2, 12.3, 9.8; IR (neat): 2955, 2954, 2847, 1615, 1517, 1462, 1247, 1113, 1034, 999, 825 cm^{-1}; MS (EI): *m*/*z* (%): 537, 481; HRMS (ESI+): *m*/*z*: calcd for $C_{27}H_{46}O_3SnNa$: 561.23633; found : 561.23604.



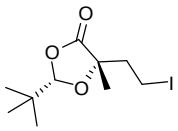
Oxazole 39. A solution of oxazolyl triflate **38** (101 mg, 0.44 mmol)[5] and stannane **37** (233 mg, 0.43 mmol) in DMF (6 mL) was added to a Schlenk tube containing flame-dried $[Bu_4N]^+[Ph_2POO]^-$ (296 mg, 0.65 mmol). $Pd(PPh_3)_4$ (348 mg, 0.30 mmol) was then introduced followed by copper thiophenecarboxylate (CuTC, 298 mg, 0.65 mmol), and the resulting mixture was stirred for 45 min before the reaction was quenched with water. The aqueous phase was extracted with *tert*-butyl methyl ether (4 x), the combined organic layers were dried over Na_2SO_4 and evaporated. The crude product was purified by flash chromatography (4:1→2:1, hexanes/EtOAc) to afford product **39** as a yellow oil (127 mg, 90 %). $[a]_D^{20}$ = –21.5 (*c* = 1.0 in C_6H_6). ^{1}H NMR (300 MHz, C_6D_6): *d* = 7.68-7.62 (m, 2H), 7.02 (s, 1H), 6.90 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.86-6.81 (m, 2H), 5.54 (s, 1H), 4.71 (dd, *J* = 7.7, 2.2 Hz, 1H), 3.79 (br s, 2H), 3.28 (s, 3H), 1.97 (s, 3H), 1.78 (d, *J* = 1.3 Hz, 3H), 1.35-1.29 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 161.2, 160.4, 143.4, 133.3, 132.5, 127.3, 126.8, 113.8, 102.0, 77.7, 73.3, 54.8, 33.5, 14.6, 13.5, 12.1; IR: 2963, 2855, 1615, 1518, 1248, 1106, 1033, 829 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{19}H_{23}NO_4Na$: 352.15193; found : 352.15220.



[5] A. B. Smith, K. P. Minbiole, P. R. Verhoest, M. Schelhaas, *J. Am. Chem. Soc.* **2001**, *123*, 10942-10953.

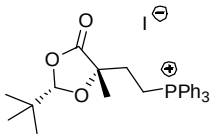
Side Chain Sector.

Iodide 30. Borane-dimethyl sulfide (132 µL, 1.40 mmol) was added over 15 min to a solution of acid



28 (200.0 mg, 0.93 mmol)[6] in THF (4.62 mL) at –20 °C. Once the evolution of H_2 had ceased, the mixture was stirred at ambient temperature for 18 h before the excess borane was destroyed upon addition of MeOH. The solvents were evaporated and the residue dissolved in CH_2Cl_2 (7 mL). Imidazole (380 mg, 5.58 mmol) was added before a premixed solution of triphenylphosphine (488 mg, 1.86 mmol) and iodine (472 mg, 1.86 mmol) in CH_2Cl_2 (7 mL) was slowly added. The resulting mixture was stirred for 3 h before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with *tert*-butyl methyl ether, the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (9:1→4:1, hexanes/EtOAc) to give iodide **30** as a colorless oil (120 mg, 41 % over 2 steps). $[a]_D^{20}$ = +14.0 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 5.14 (s, 1H); 3.24 (m, 1H); 3.00 (m, 1H); 2.40 (m, 2H); 1.38 (s, 3H); 0.96 (s, 9H) ^{13}C NMR (100 MHz, $CHCl_3$): *d* = 174.3, 107.4, 80.8, 42.2, 34.4, 23.7, 19.4, -4.3; IR: *n* = 2964, 2875, 1796, 1199, 1170, 974 cm^{-1};

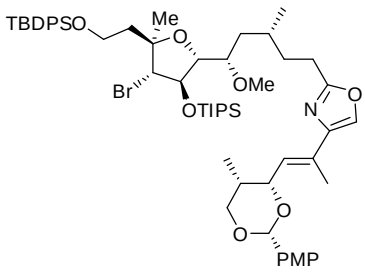
Phosphonium Salt 31. A solution of iodide **30** (100 mg, 0.32 mmol) and triphenylphosphine (419 mg,



1.6 mmol) was heated in a sealed tube in a microwave oven to 150 °C for 2.5 h, giving rise to an internal pressure in the tube of 6-7 bars. The tube was cooled before it was opened and the solution was evaporated to dryness. Purification of the residue by flash chromatography (5 % → 10 %, MeOH in CH_2Cl_2) gave salt **31** as a white solid (183 mg, quant.) ^{1}H NMR (400 MHz, $CDCl_3$,): *d* = 7.80-7.68 (m, 15H); 5.17 (s, 1H); 4.21-4.09 (m, 1H); 3.28-3.15 (m, 1H); 2.17-2.08 (m, 1H); 2.02-1.92 (m, 1H); 1.64 (s, 3H); 0.86 (s, 9H) ^{13}C NMR (100 MHz, $CD.Cl_3$): *d* = 135.5, 133.7, 133.6. 132.0, 130.9, 130.7, 128.6, 128.5, 107.6, 29.7, 23.4, 19.4, 18.7, 18.2; IR: 2965, 2926, 2873, 1785, 1438, 1204, 1113, 690 cm^{-1}.

Fragment Coupling.

Compound 40. A solution of Et_2NLi (0.6 M in THF, 0.43 mL, 0.256 mmol) was added dropwise at

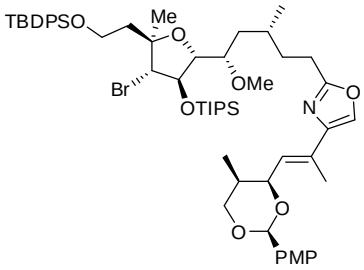


–78 °C to a solution of oxazole **39** (88.7 mg, 0.269 mmol) in THF (1.35 mL) and the resulting mixture was stirred for 35 min at this temperature before a solution of iodide **19** (154.0 mg, 0.182 mmol) in THF (0.70 mL) was slowly introduced. Stirring was continued for 2.5 h before the reaction was quenched with aq. sat. $NaHCO_3$ at –78 °C. After reaching ambient temperature, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined organic extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (10:1→2:1, hexanes/EtOAc) to give product **40** as a beige foam (149.9 mg, 79 %). $[a]_D^{20}$ = –4.9 (*c* = 2.9 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.83-7.78 (m, 4H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.29-7.23 (m, 6H), 7.09 (s, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 5.54 (s, 1H), 4.95 (t, ^{3}*J* = 4.8 Hz, 1H), 4.72 (d, *J* = 7.3 Hz, 1H), 4.49 (d, *J* = 4.8 Hz, 1H), 4.01 (dt, ^{3}*J* = 10.4, 6.6 Hz, 1H), 3.95 (dd, *J* = 5.7, 3.4 Hz, 1H), 3.87 (dt, *J* = 10.5, 6.3 Hz, 1H), 3.79 (s, 2H), 3.49 (br m, 1H), 3.29 (s, 3H), 3.25 (s, 3H), 2.71-2.54 (m, 2H), 2.29 (dt, *J* = 14.3, 6.6 Hz, 1H), 1.93-1.47 (m, 10H), 1.43 (s, 3H), 1.22-1.15 (m, 33H), 0.85 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 165.0, 160.5, 143.4, 136.1, 134.2, 133.3, 132.5, 130.2, 128.7, 127.3, 126.8, 113.9, 102.1, 85.7, 82.7, 81.4, 77.8, 77.2, 76.7,

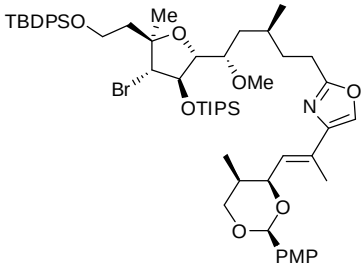
[6] D. Seebach, R. Naef, G. Calderari, *Tetrahedron* **1984**, *40,* 1313-1324.

73.3, 64.2, 60.7, 57.2, 54.9, 40.8, 37.3, 34.6, 33.6, 29.7, 27.2, 26.4, 26.0, 20.2, 19.7, 19.4, 18.6, 14.6, 13.1, 12.2; IR: 2938, 2865, 1518, 1462, 1248, 1108, 825, 702 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{57}H_{85}BrNO_8Si_2$ $[M+H]^+$: 1046.49918; found: 1046.50002.

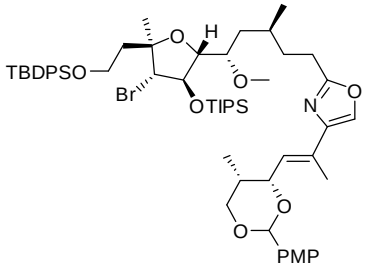
Isomeric Acetal S5: Prepared analogously as a yellow foam (177 mg, 69 %). $[a]_D^{20}$ = +5.8 (*c* = 1.2 in C_6H_6). ^1H NMR (400 MHz, C_6D_6): *d* = 7.83-7.78 (m, 4H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.29-7.23 (m, 6H), 7.09 (s, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 5.54 (s, 1H), 4.95 (t, ^3J = 4.8 Hz, 1H), 4.72 (d, *J* = 7.3 Hz, 1H), 4.49 (d, *J* = 4.8 Hz, 1H), 4.01 (dt, ^3J = 10.4, 6.6 Hz, 1H), 3.95 (dd, *J* = 5.7, 3.4 Hz, 1H), 3.87 (dt, *J* = 10.5, 6.3 Hz, 1H), 3.79 (s, 2H), 3.49 (br m, 1H), 3.29 (s, 3H), 3.25 (s, 3H), 2.71-2.54 (m, 2H), 2.29 (dt, *J* = 14.3, 6.6 Hz 1H), 1.93-1.47 (m, 10H), 1.43 (s, 3H), 1.22-1.15 (m, 33H), 0.85 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 165.0, 160.5, 143.2, 136.1, 134.1, 133.2, 132.5, 130.1, 128.7, 127.3, 126.8, 113.8, 102.1, 85.6, 82.7, 81.3, 77.7, 77.1, 76.7, 73.3, 64.0, 60.6, 57.2, 54.8, 40.8, 37.3, 34.6, 33.5, 29.7, 27.2, 26.4, 26.0, 20.2, 19.7, 19.4, 18.5, 14.6, 13.1, 12.1; IR: 2942, 2866, 1518, 1462, 1248, 1111, 826, 702 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{57}H_{84}BrNO_8Si_2Na$ $[M+Na]^+$: 1068.48112; found: 1068.48144.



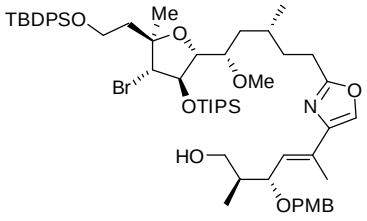
Isomeric Acetal S6. Prepared according to the procedure described above (153 mg, 73 %). $[a]_D^{20}$ = +16.7 (*c* = 1.0 in $CHCl_3$). ^1H NMR (400 MHz, C_6D_6): *d* = 7.81-7.78 (m, 4H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.30-7.23 (m, 6H), 7.08 (s, 1H), 6.91 (br d, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.54 (s, 1H), 4.98 (t, *J* = 5.8 Hz, 1H), 4.71 (d, *J* = 7.3 Hz, 1H), 4.54 (d, *J* = 5.4 Hz, 1H), 4.01 (dt, *J* = 10.4, 6.4 Hz, 1H), 3.93-3.83 (m, 3H), 3.79 (s, 2H), 3.44 (dt, *J* = 6.6, 2.8 Hz, 1H), 3.28 (s, 3H), 3.20 (s, 3H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.25 (dt, *J* = 14.0, 6.6 Hz, 1H), 1.88-1.77 (m, 6H), 1.62-1.53 (m, 3H), 1.51-1.43 (m, 4H), 1.22-1.15 (m, 30H), 0.92 (t, *J* = 7.1 Hz, 2H), 0.84 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 165.0, 160.4, 143.2, 136.1, 134.1, 133.2, 132.4, 130.0, 128.2, 127.2, 126.8, 113.8, 102.0, 84.4, 82.5, 80.6, 77.7, 77.0, 73.2, 63.7, 60.6, 56.8, 54.8, 40.9, 36.5, 34.6, 33.5, 29.6, 27.2, 26.4, 26.0, 20.6, 19.9, 19.4, 18.5, 14.6, 13.1, 12.1; IR: 2934, 2867, 1519, 1462, 1248, 1110, 826, 702 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{57}H_{84}BrNO_8Si_2Na$ $[M+Na]^+$: 1068.48112; found: 1068.48203.



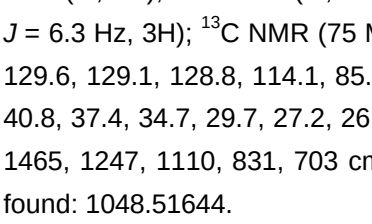
Isomeric Acetal S7. $[a]_D^{20}$ = –4.8 (*c* = 1.0 in C_6H_6); ^1H NMR (400 MHz, C_6D_6): *d* = 7.82-7.78 (m, 4H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.31-7.23 (m, 6H), 7.07 (s, 1H), 6.91 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.53 (s, 1H), 4.98 (apparent t, *J* = 5.8 Hz, 1H), 4.71 (br d, 7.4 Hz, 1H), 4.57 (d, *J* = 5.5 Hz, 1H), 4.00 (dt, *J* = 10.4, 6.5 Hz, 1H), 3.92 (dd, *J* = 5.9, 2.6 Hz, 1H), 3.85 (dt, *J* = 10.5, 6.1 Hz, 1H), 3.79 (apparent s, 2H), 3.44 (dt, *J* = 6.6, 2.6 Hz, 1H), 3.28 (s, 3H), 3.20 (s, 3H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.23 (dt, *J* = 14.4, 6.6 Hz, 1H), 1.88-1.73 (m, 2H), 1.77 (d, *J* = 0.9 Hz, 3H), 1.63-1.53 (m, 2H), 1.51-1.40 (m, 4H), 1.35-1.27 (m, 4H) 1.22-1.45 (m, 30H), 0.84 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 165.0, 160.4, 136.1, 134.0, 133.2, 132.4, 130.1, 128.2, 127.2, 126.8, 113.8, 102.0, 84.3, 82.4, 80.5, 77.7, 76.9, 73.2, 63.7, 60.6, 56.8, 54.8, 40.9, 36.5, 34.6, 33.5, 29.6, 27.2, 26.4, 26.0, 19.9, 18.5, 14.6, 13.1, 12.1; IR (film): 2942, 2865, 1462, 1248, 1111, 824, 739, 704 cm^{-1}; HRMS (ESI+): calcd for $C_{57}H_{84}BrNO_8Si_2Na$ $[M+Na]^+$: 1068.48112; found: 1068.48077.



Compound 41. Dibal-H (1 M in toluene, 0.72 mL, 0.715 mmol) was slowly added to a solution of compound **40** (149.9 mg, 0.143 mmol) in toluene (0.72 mL) at –40 °C. After stirring for 2.5 h, the reaction was quenched with sat. aq. Rochelle's salt at –40 °C and the mixture allowed to warm to ambient temperature. At this point, two drops of NaOH (1 M) were added and the mixture was vigorously stirred for 30 min to reach a clean separation of the phases. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (4:1→2:1, hexanes/EtOAc) to give product **41** as a colorless oil (111.8 mg, 75 %). $[a]_D^{20}$ = +23.1 (*c* = 1.8 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.83-7.78 (m, 4H), 7.30-7.23 (m, 6H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.09 (s, 1H), 6.86 (dd, *J* = 9.6, 1.2 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 4.95 (t, ^3J = 5.1 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 6.6 Hz, 1H), 4.41 (dd, *J* = 9.4, 4.8 Hz, 1H), 4.24 (d, *J* = 11.6 Hz, 1H), 4.01 (dt, ^3J = 10.6, 6.3 Hz, 1H), 3.96 (dd, *J* = 5.6, 3.4 Hz, 1H), 3.88 (dt, *J* = 10.4, 6.5 Hz, 1H), 3.73 (dd, *J* = 10.7, 7.0 1H), 3.54-3.47 (m, 2H), 3.31 (s, 1H), 3.30 (s, 3H), 3.26 (s, 3H), 2.74-2.57 (m, 2H), 2.30 (dt, *J* = 14.5, 6.3 Hz, 1H), 1.99 (m, 1H), 1.93-1.47 (m, 10H), 1.43 (s, 3H), 1.22-1.16 (m, 30H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 165.0, 159.7, 143.1, 136.1, 134.2, 133.2, 131.4, 130.1, 129.6, 129.1, 128.8, 114.1, 85.7, 82.8, 81.5, 77.2, 76.9, 73.5, 70.1, 65.9, 64.1, 60.6, 57.2, 54.8, 41.4, 40.8, 37.4, 34.7, 29.7, 27.2, 26.3, 26.1, 19.7, 19.5, 18.5, 14.4, 13.1, 12.5; IR: 3711, 2942, 2861, 1514, 1465, 1247, 1110, 831, 703 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{57}H_{87}BrNO_8Si_2$ $[M+H]^+$: 1048.51483; found: 1048.51644.



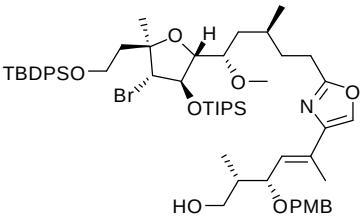
Isomer S8. Prepared analogously (106 mg, 60 %). $[a]_D^{20}$ = –27.1 (*c* = 1.1 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.83-7.77 (m, 4H), 7.30-7.23 (m, 6H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 1H), 6.86 (dd, *J* = 9.7, 1.12 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.95 (t, ^3J = 5.1 Hz, 1H), 4.59 (d, ^2J = 11.6 Hz, 1H), 4.49 (d, *J* = 6.6 Hz, 1H), 4.41 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.24 (d, ^2J = 11.4 Hz, 1H), 4.01 (dt, *J* = 10.6, 6.3 Hz, 1H), 3.96 (dd, *J* = 5.6, 3.4 Hz, 1H), 3.88 (dt, *J* = 10.4, 6.5 Hz, 1H), 3.73 (ddd, *J* = 10.9, 6.6, 4.5, 1H), 3.54-3.47 (m, 2H), 3.31 (s, 1H), 3.30 (s, 3H), 3.26 (s, 3H), 2.74-2.57 (m, 2H), 2.30 (dt, *J* = 14.5, 6.3 Hz 1H), 1.99 (m, 1H), 1.93-1.47 (m, 9H), 1.43 (s, 3H), 1.22-1.16 (m, 30H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 165.0, 159.7, 143.1, 136.1, 134.1, 133.2, 131.3, 130.1, 129.6, 128.2, 128.0, 127.5, 114.1, 85.7, 82.7, 81.4, 77.1, 76.9, 70.1, 65.8, 64.1, 60.6, 57.2, 54.8, 41.4, 40.8, 39.7 37.3, 34.7, 29.7, 27.2, 26.4, 26.1, 19.7, 19.4, 18.5, 14.4, 13.0, 12.5; IR: 3443, 2943, 2866, 1513, 1464, 1247, 1110, 823, 703 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{57}H_{86}BrNO_8Si_2Na$ $[M+Na]^+$: 1070.49677; found: 1070.49645.



Isomer S9. Prepared analogously (143 mg, 94 %). $[a]_D^{20}$ = +12.1 (*c* = 0.8 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.82-7.79 (m, 4H), 7.30-7.254 (m, 6H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.08 (s, 1H), 6.86 (br d, *J* = 9.6 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 2H), 4.95 (t, *J* = 5.8 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 5.3 Hz, 1H), 4.41 (dd, *J* = 9.7, 4.8 Hz, 1H), 4.24 (d, *J* = 11.3 Hz, 1H), 4.02 (dt, *J* = 10.4, 6.7 Hz, 1H), 3.93 (dd, *J* = 5.9, 2.9 Hz, 1H), 3.87 (dt, *J* = 10.4, 5.9 Hz, 1H), 3.73 (dd, *J* = 10.8, 7.3 1H), 3.54-3.43 (m, 2H), 3.30 (s, 3H), 3.21 (s, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.26 (dt, *J* = 13.8, 6.6 Hz, 1H), 1.99 (m, 1H), 1.88-

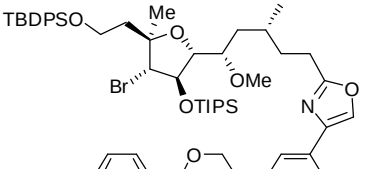
1.74 (m, 7H), 1.65-1.55 (m, 2H), 1.51-1.44 (m, 4H), 1.22-1.16 (m, 30H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 5.7 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 165.0, 159.7, 143.1, 136.1, 134.1, 134.0, 133.2, 131.3, 130.1, 129.6, 129.4, 129.0, 128.9, 114.1, 84.4, 82.4, 80.5, 77.0, 76.8, 72.3, 70.1, 65.7, 63.7, 60.5, 56.8, 54.8, 49.2, 41.4, 40.9, 36.4, 34.7, 29.7, 27.2, 26.4, 26.1, 19.9, 19.4, 18.5, 14.4, 13.1, 12.5; IR: 3711, 2934, 2866, 1513, 1463, 1247, 1111, 823, 702 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{57}H_{86}BrNO_8Si_2Na$ [M+Na]$^+$: 1070.49677; found: 1070.49742.

Isomer S10. $[a]_D^{20}$ = +24.9 (*c* = 1.8 in C_6H_6); ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.82-7.78 (m, 4H), 7.30-7.23 (m, 6H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.06 (s, 1H), 6.86 (dd, *J* = 9.6, 1.3 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.98 (t, *J* = 5.8 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 5.5 Hz, 1H), 4.40 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.23 (d, *J* = 11.6 Hz, 1H), 4.01 (dt, *J* = 10.5, 6.5 Hz, 1H), 3.93 (dd, *J* = 6.0, 3.0 Hz, 1H), 3.86 (dt, *J* = 10.4, 6.1 Hz, 1H), 3.73 (dd, *J* = 10.7, 6.9 Hz, 1H), 3.51 (dd, *J* = 10.7, 4.8 Hz, 1H), 3.44 (dt, *J* = 6.7, 2.9 Hz, 1H), 3.29 (s, 3H), 3.20 (s, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.25 (dt, *J* = 14.2, 6.6 Hz, 1H), 1.98 (tt, *J* = 9.6, 6.9, 4.7 Hz, 1H), 1.88-1.75 (m, 3H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.63-1.54 (m, 2H), 1.51-1.42 (m, 4H), 1.22-1.15 (m, 30H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.0 Hz, 3H), 0.60 (bs, 1H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 165.1, 159.7, 143.1, 136.1, 134.0, 133.2, 131.3, 130.1, 129.6, 128.6, 128.2, 114.1, 84.4, 82.5, 80.6, 77.0, 76.9, 70.1, 65.8, 63.7, 60.6, 56.8, 54.8, 41.4, 36.5, 34.7, 29.7, 27.2, 26.4, 26.1, 19.9, 19.4, 18.5 (2), 14.4, 13.1, 12.5; IR (film): 3472, 2933, 2866, 1612, 1587, 1513, 1462, 1428, 1380, 1247, 1110, 1083, 1038, 883, 823, 740, 702, 685 cm^{-1}; HRMS (ESI+): calcd for $C_{57}H_{86}BrNO_8Si_2Na$ [M+Na]$^+$: 1070.49677, found: 1070.49668.



Benzoate 42. Hünigs base (66 μL, 0.384 mmol), benzoyl chloride (22 μL, 0.192 mmol) and DMAP (6.0 mg, 0.048 mmol) were successively added to a solution of alcohol **41** (50.6 mg, 0.048 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C and the resulting mixture was allowed to reach ambient temperarure. After 16h, the reaction was quenched with aq. sat. $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2 (3 x), the combined extracts were washed (2 x) with aqueous $CuSO_4$ (0.1 M) and then dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash chromatography (1:0→2:1, hexanes/EtOAc) to give product **42** as a yellow oil (44.3 mg, 80 %). $[a]_D^{20}$ = +10.4 (*c* = 1.1 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.11 (d, *J* = 6.8 Hz, 2H), 7.83-7.77 (m, 4H), 7.29-7.17 (m, 8H), 7.15-7.05 (m, 3H), 7.08 (s, 1H), 6.85 (dd, *J* = 9.3, 1.3 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.95 (t, ^3J = 5.2 Hz, 1H), 4.64 (d, ^2J = 11.6 Hz, 1H), 4.53-4.45 (m, 2H), 4.42 (dd, *J* = 9.3, 5.3 Hz, 1H), 4.32 (dd, *J* = 10.9, 5.8 Hz, 1H), 4.27 (d, ^2J = 11.6 Hz, 1H), 4.01 (dt, *J* = 11.6, 5.8 Hz, 1H), 3.96 (dd, *J* = 5.7, 3.4 Hz, 1H), 3.87 (dt, *J* = 11.6, 5.8 Hz, 1H), 3.50 (m, 1H), 3.27 (s, 3H), 3.26 (s, 3H), 2.74-2.55 (m, 2H), 2.30 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.17 (h, *J* = 6.4 Hz, 1H), 1.93-1.47 (m, 9H), 1.43 (s, 3H), 1.23-1.13 (m, 33H), 0.86 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 166.2, 165.0, 159.7, 142.9, 136.1, 134.1, 134.0, 133.3, 132.7, 131.4, 130.1, 130.0, 129.8, 129.0, 128.5, 128.1, 127.9, 114.0, 85.6, 82.7, 81.4, 77.1, 74.5, 69.9, 67.1, 64.1, 60.5, 57.2, 54.7, 40.8, 39.1, 37.7, 34.7, 30.3, 29.7, 27.2, 26.4, 26.1, 19.7, 19.4, 18.5, 14.3, 13.0, 12.6; IR: 2934, 2867, 1721, 1462, 1273, 1111, 677 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{64}H_{90}BrNO_9Si_2Na$ [M+Na]$^+$: 1174.52299; found: 1174.52376.

Isomeric Benzoate S11. Prepared analogously (103.1 mg, 88 %). $[a]_D^{20}$ = –18.6 (*c* = 1.0 in C_6H_6). ^{1}H NMR (300 MHz, C_6D_6): *d* = 8.13-8.08 (m, 2H), 7.83-7.76 (m, 4H),



7.30-7.18 (m, 8H), 7.15-7.02 (m, 4H), 6.85 (dd, *J* = 9.5, 1.2 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.95 (dd, *J* = 5.7, 4.9 Hz, 1H), 4.65 (d, ^{2}J = 11.9 Hz, 1H), 4.52-4.38 (m, 3H), 4.36-4.24 (m, 2H), 4.07-3.93 (m, 2H), 3.87 (ddd, *J* = 10.5, 6.3 Hz, 1H), 3.50 (m, 1H), 3.27 (s, 3H), 3.26 (s, 3H), 2.76-2.54 (m, 2H), 2.29 (ddd, *J* = 13.9, 6.8 Hz, 1H), 2.17 (h, *J* = 6.4 Hz, 1H), 1.94-1.46 (m, 9H), 1.43 (s, 3H), 1.27-1.11 (m, 33H), 0.86 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): *d* = 166.2, 164.9, 159.6, 142.9, 136.1, 134.1, 134.0, 133.3, 132.7, 131.3 (2), 130.1, 129.9, 129.7, 129.0, 128.5, 128.2, 127.9, 114.0, 85.6, 82.7, 81.3, 77.1, 74.5, 69.9, 67.1, 64.1, 60.6, 57.2, 54.7, 40.7, 39.0, 37.3, 34.6, 29.7, 27.2, 26.4, 26.1, 19.7, 19.4, 18.5 (2), 14.3, 13.0, 12.6; IR: 2941, 2865, 1720, 1463, 1272, 1109, 709 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{64}H_{90}BrNO_9Si_2Na$ [M+Na]$^+$: 1174.52299; found: 1174.52218.

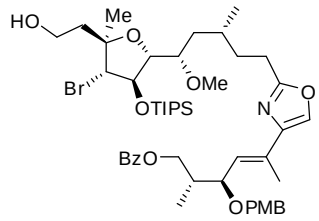
Isomeric Benzoate S12. Prepared analogously (150 mg, 96 %) $[a]_D^{20}$ = +4.4 (*c* = 0.6 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.11 (d, *J* = 8.1 Hz, 2H), 7.82-7.79 (m, 4H), 7.29-7.24 (m, 6H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.13-7.06 (m, 3H), 7.04 (s, 1H), 6.85 (dd, *J* = 9.6, 1.3 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 4.98 (t, ^{3}J = 5.7 Hz, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 5.4 Hz, 1H), 4.51-4.47 (dd, *J* = 11.4, 6.8 Hz, 1H), 4.42 (dd, *J* = 9.7, 5.2 Hz, 1H), 4.32 (dd, *J* = 10.8, 6.2 Hz, 1H), 4.28 (d, *J* = 11.7 Hz, 1H), 4.02 (dt, *J* = 10.3, 6.5 Hz, 1H), 3.94 (dd, *J* = 6.0, 2.9 Hz, 1H), 3.87 (dt, *J* = 10.7, 6.1 Hz, 1H), 3.42 (m, 1H), 3.30 (s, 3H), 3.21 (s, 3H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.26 (dt, *J* = 14.3, 6.8 Hz, 1H), 2.17 (h, *J* = 6.4 Hz, 1H), 1.89-1.75 (m, 3H), 1.72 (d, *J* = 1.1 Hz, 3H), 1.65-4.46 (m, 3H) 1.44 (s, 3H), 1.23-1.15 (m, 33H), 0.86 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 166.2, 165.0, 159.7, 143.0, 136.1, 134.1, 134.0, 133.2, 132.7, 131.4, 131.3, 130.1, 129.9, 129.8, 129.0, 128.5, 128.2, 127.9, 114.0, 84.5, 82.5, 80.6, 77.1, 74.6, 70.0, 67.1, 63.7, 60.6, 56.8, 54.7, 40.9, 39.1, 36.5, 34.6, 30.2, 29.7, 27.2, 26.4, 26.1, 19.7, 19.4, 18.5, 14.3, 13.1, 12.6; IR: 2931, 2866, 1720, 1462, 1272, 1111, 706; 677 cm^{-1}.

Isomeric Benzoate S13. $[a]_D^{20}$ = +19.1 (*c* = 0.7 in C_6H_6); ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.10 (d, *J* = 7 Hz, 2H), 7.82-7.78 (m, 4H), 7.31-7.23 (m, 6H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.13-7.05 (m, 3H), 7.03 (s, 1H), 6.84 (dd, *J* = 9.5, 1.0 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.98 (t, *J* = 5.7 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 5.4 Hz, 1H), 4.48 (dd, *J* = 10.8, 6.6 Hz, 1H), 4.41 (dd, *J* = 9.4, 5.3 Hz, 1H), 4.32 (dd, *J* = 10.8, 5.7 Hz, 1H), 4.27 (d, *J* = 11.7 Hz, 1H), 4.01 (dt, *J* = 10.5, 6.4 Hz, 1H), 3.93 (dd, *J* = 6.1, 2.9 Hz, 1H), 3.86 (dt, *J* = 10.4, 6.2 Hz, 1H), 3.45 (dt, *J* = 6.8, 2.6 Hz, 1H), 3.27 (s, 3H), 3.21 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.25 (dt, *J* = 14.2, 6.6 Hz, 1H), 2.16 (pent., *J* = 6.3 Hz, 1H), 1.90-1.74 (m, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.65-1.54 (m, 2H), 1.52-1.45 (m, 1H), 1.43 (s, 3H), 1.23-1.12 (m, 33H), 0.85 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 166.2, 165.0, 159.6, 142.9, 136.1, 134.1, 134.0, 133.3, 132.7, 131.3, 130.1, 129.9, 129.8, 129.0, 128.5, 128.2, 114.0, 84.4, 82.5, 80.6, 77.0, 74.5, 69.9, 67.1, 63.7, 60.6, 56.8, 54.7, 40.9, 39.0, 36.5, 34.6, 29.7, 27.2, 26.4, 26.1, 20.0, 19.4, 18.5 (2), 14.3, 13.1, 12.6; IR (film): 2940, 2866, 1720, 1586, 1513, 1463, 1382, 1272, 1111, 823, 708 cm^{-1}; HRMS (ESI+): calcd for $C_{64}H_{90}BrNO_9Si_2Na$ [M+Na]$^+$: 1174.52298, found: 1174.52369.

Alcohol 43. HF·pyridine (70 % *w*/*w*, 1.59 mL) was added to a solution of silylether **42** (44.0 mg, 38.2 µmol) in THF (6.4 mL) and pyridine (1.34 mL) at 0 °C. After stirring at 0 °C for 3.5 h, the mixture was transferred via canula to a mixture of aq. sat. $NaHCO_3$ (80 mL) and *tert*-butyl methyl ether (25 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 x), the combined

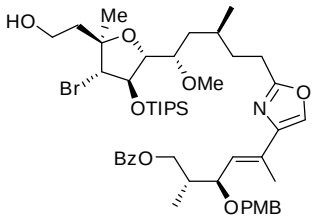
extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (6:1→2:1 hexanes/EtOAc) to give product **43** as a colorless oil (25.1 mg, 72 %). $[a]_D^{20}$ = +22.5 (*c* = 1.3 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.14-8.07 (m, 2H), 7.24-7.18 (m, 2H), 7.16-7.03 (m, 4H), 6.84 (d, *J* = 9.2 Hz, 1H), 6.78-6.72 (m, 2H), 4.91 (t, *J* = 5.8 Hz, 1H), 4.64 (d, ^2J = 11.6 Hz, 1H), 4.49 (dd, *J* = 10.6, 6.6 Hz, 1H), 4.41 (dd, *J* = 8.5, 5.3 Hz, 1H), 4.32 (dd, *J* = 10.7, 5.7 Hz, 1H), 4.28 (d, ^2J = 11.6 Hz, 1H), 4.22 (d, *J* = 5.6 Hz, 1H), 3.93 (dd, *J* = 5.7, 2.7 Hz, 1H), 3.70 (ddd, *J* = 11.3, 8.4, 4.7 Hz, 1H), 3.58 (dt, *J* = 11.1, 5.6 Hz, 1H), 3.48-3.41 (m, 1H), 3.27 (s, 3H), 3.22 (s, 3H), 2.71-2.52 (m, 2H), 2.18 (h, *J* = 6.2 Hz, 1H), 2.07-1.96 (m, 2H), 1.89-1.78 (m, 1H), 1.75-1.45 (m, 6H), 1.42 (s, 3H), 1.38-1.25 (m, 2H), 1.25-1.11 (m, 24H), 0.84 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 166.2, 164.9, 159.7, 143.0, 133.3, 132.7, 131.3 (2), 129.9, 129.8, 129.4, 129.0, 128.5, 114.0, 85.4, 84.0, 80.5, 76.9, 74.5, 70.0, 67.1, 63.7, 59.2, 57.2, 54.7, 40.3, 39.1, 37.2, 34.4, 29.6, 26.0, 25.5, 19.7, 18.5, 14.3, 13.1, 12.6; IR: 3446, 2942, 2867, 1721, 1513, 1457, 1275, 1109 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{48}H_{72}NBrO_9SiNa$ [M+Na]$^+$: 936.40521; found: 936.40500.

Isomeric Alcohol S14. Prepared analogously (61.0 mg, 75 %). $[a]_D^{20}$ = –26.5 (*c* = 1.1 in C_6H_6). ^{1}H



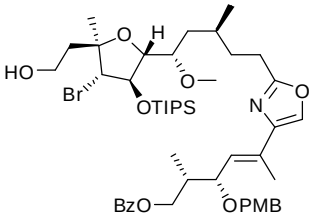
NMR (400 MHz, C_6D_6): *d* = 8.12-8.08 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.15-7.05 (m, 4H), 6.82 (d, *J* = 9.2, 1.3 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 4.91 (t, *J* = 5.7 Hz, 1H), 4.64 (d, ^2J = 11.7 Hz, 1H), 4.48 (dd, *J* = 10.5, 6.7 Hz, 1H), 4.41 (dd, *J* = 9.4, 5.3 Hz, 1H), 4.35-4.25 (m, 2H), 4.22 (d, *J* = 5.4 Hz, 1H), 3.93 (dd, *J* = 6.0, 3.3 Hz, 1H), 3.71 (ddd, *J* = 11.1, 7.7, 4.8 Hz, 1H), 3.59 (dt, *J* = 11.2, 5.6 Hz, 1H), 3.48-3.41 (m, 1H), 3.28 (s, 3H), 3.22 (s, 3H), 2.71-2.53 (m, 2H), 2.23-1.95 (m, 3H), 1.89-1.78 (m, 1H), 1.75-1.45 (m, 8H), 1.42 (s, 3H), 1.20-1.11 (m, 24H), 0.85 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 166.2, 164.9, 159.7, 143.0, 133.3, 132.7, 131.4 (2), 129.9, 129.7, 129.0, 128.8, 128.5, 128.1, 114.0, 85.4, 84.0, 80.6, 77.0, 74.6, 70.0, 67.1, 63.7, 59.2, 57.2, 54.8, 40.4, 39.0, 37.2, 34.4, 29.6, 26.0, 25.5, 19.7, 18.5, 14.3, 13.1, 12.6; IR: 3537, 2942, 2867, 1720, 1513, 1463, 1272, 1109 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{48}H_{72}NBrO_9SiNa$ [M+Na]$^+$: 936.40521; found: 936.40496.

Isomeric Alcohol S15. Prepared analogously (93 mg, 78 %). $[a]_D^{20}$ = + 6.5 (*c* = 0.4 in $CHCl_3$). ^{1}H



NMR (400 MHz, C_6D_6): *d* = 8.11 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.16-7.04 (m, 4H), 6.84 (dd, *J* = 9.3, 1.1 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 4.95 (t, *J* = 6.4 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.49 (dd, *J* = 10.7, 6.4 Hz, 1H), 4.41 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.31 (dd, *J* = 10.8, 5.7 Hz, 1H), 4.28 (d, *J* = 11.7Hz, 1H), 4.23(d, *J* = 6.3 Hz, 1H), 3.90 (dd, *J* = 6.3, 2.7 Hz, 1H), 3.76-3.70 (m, 1H), 3.64-3.58 (m, 1H), 3.42-3.38 (m, 1H), 3.28 (s, 3H), 3.18 (s, 3H), 2.71-2.66 (m, 2H), 2.27-2.15 (m, 2H), 2.00-1.95 (m, 1H), 1.83-1.64 (m, 7H), 1.43 (s, 4H), 1.38-1.25 (m, 1H), 1.25-1.11 (m, 24H), 0.81 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 166.2, 164.9, 159.7, 143.0, 133.4, 132.7, 131.4, 131.3, 129.9, 129.8, 129.4, 129.0, 128.6, 128.5, 114.0, 84.0, 83.8, 80.0, 76.8, 74.6, 70.0, 67.1, 63.4, 59.1, 56.7, 54.7, 40.6, 39.0, 36.2, 34.8, 29.5, 26.0, 25.4, 19.9, 18.5, 14.3, 13.1, 12.6; IR: 3446, 2944, 2865, 1721, 1513, 1457, 1273, 1111, 828, 712 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{48}H_{72}NBrO_9SiNa$ [M+Na]$^+$: 936.40521; found: 936.40431.

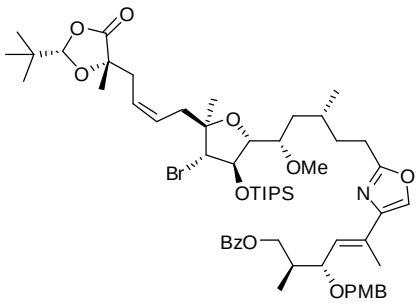
Isomeric Alcohol S16. $[a]_D^{20}$ = +21.0 (*c* = 0.8 in C_6H_6); ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.13-8.07 (m,



2H), 7.25-7.19 (m, 2H), 7.14-7.05 (m, 4H), 6.83 (dd, *J* = 9.6, 1.2 Hz, 1H), 6.78-6.73 (m, 2H), 4.95 (t, *J* = 6.4 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.47 (dd, *J* = 10.8, 6.5 Hz, 1H), 4.40 (dd, *J* = 9.4, 5.4 Hz, 1H), 4.32 (dd, *J* =

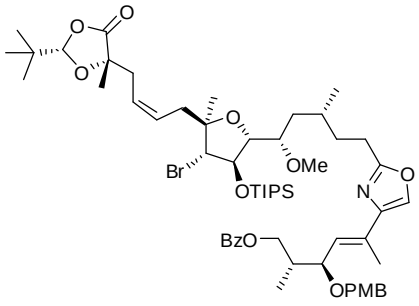
10.8, 5.7 Hz, 1H), 4.28 (d, *J* = 11.6 Hz, 1H), 4.23 (d, *J* = 6.1 Hz, 1H), 3.92-3.87 (m, 1H), 3.78-3.69 (m, 1H), 3.66-3.58 (m, 1H), 3.42-3.36 (m, 1H), 3.28 (s, 3H), 3.18 (s, 3H), 2.73-2.64 (m, 2H), 2.27 (br s, 1H), 2.17 (pent., *J* = 6.3 Hz, 1H), 2.01-1.93 (m, 1H), 1.84-1.75 (m, 2H), 1.72 (d, *J* = 1.1 Hz, 3H), 1.61-1.54 (m, 2H), 1.43 (s, 3H), 1.21-1.14 (m, 26H), 0.81 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 166.3, 165.0, 159.8, 143.0, 133.6, 132.8, 131.4 (2), 130.0, 129.9, 129.1, 128.6, 128.4, 114.1, 84.0, 83.9, 76.9, 74.7, 70.1, 67.2, 63.5, 59.2, 56.8, 54.9, 40.7, 39.1, 36.3, 34.8, 29.5, 26.1, 25.6, 20.0, 18.6, 14.4, 13.2, 12.7; HRMS (ESI+): calcd for $C_{48}H_{72}BrNO_9SiNa$ $[M+Na]^+$: 936.40521, found: 936.40476.

Alkene 45. Dess-Martin periodinane (39.5 mg, 93.13 μmol) was added to a solution of alcohol **43** (57.5 mg, 62.84 μmol) in CH_2Cl_2 (6.3 mL) at 0 °C and the resulting mixture stirred at this temperature for 90 min. Stirring was then continued for 30 min at ambient temperature before the reaction was quenched with sat. aq. $NaHCO_3$ (6 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue quickly passed through a short column of silica (6:1→4:1, hexanes/EtOAc) to give aldehyde **44** as a colorless oil, which was used immediately in the next step.



Phosphonium salt **31** (49.5 mg, 86.17 μmol) was lyophilized in benzene before it was dissolved in THF (575 μL) and the solution cooled to –78 °C. *n*BuLi (0.53 M in THF/hexane (2:1), 148 μL, 78.55 μmol) was added over 2 min and stirring continued at –78 °C for 15 min before a solution of aldehyde **44** in THF (650 μL) was slowly added. The resulting mixture was stirred at –78 °C for 2 h before the cooling-bath was removed and stirring continued for 90 min. The mixture was then transferred with EtOAc to a round bottom flask containing silica and the suspension concentrated. The loaded silica was added on top of a silica column and the product eluted with hexanes/EtOAc (6:1→4:1) to give olefin **45** as a colorless oil (48.0 mg, 71 % over 2 steps). $[a]_D^{20}$ = +26.9 (*c* = 1.0 in C_6H_6). ^{1}H NMR (600 MHz, C_6D_6): *d* = 8.14-8.10 (m, 2H), 7.23-7.19 (m, 2H), 7.16-7.11 (m, 1H), 7.10-7.06 (m, 2H), 7.04 (s, 1H), 6.87 (dd, *J* = 9.4, 1.0 Hz, 1H), 6.77-6.73 (m, 2H), 5.79-5.71 (m, 2H), 4.97 (dd, *J* = 5.5, 4.5 Hz, 1H), 4.80 (s, 1H), 4.65 (d, ^2J = 11.7 Hz, 1H), 4.49 (dd, *J* = 10.6, 6.6 Hz, 1H), 4.43 (dd, *J* = 9.5, 5.3 Hz, 1H), 4.33 (dd, *J* = 10.8, 5.8 Hz, 1H), 4.28 (d, ^2J = 11.7 Hz, 1H), 4.20 (d, *J* = 4.4 Hz, 1H), 3.99 (dd, *J* = 5.6, 3.4 Hz, 1H), 3.55-3.50 (m, 1H), 3.28 (s, 3H), 3.26 (s, 3H), 2.78-2.50 (m, 5H), 2.37 (dd, *J* = 14.9, 5.3 Hz, 1H), 2.17 (m, 1H), 1.93-1.85 (m, 1H), 1.82-1.68 (m, 5H), 1.67-1.56 (m, 2H), 1.48 (s, 3H), 1.25-1.13 (m, 24H), 1.11 (s, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.85 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 174.4, 166.2, 164.9, 159.6, 142.9, 133.3, 132.7, 131.3 (2), 129.9, 129.8, 129.0, 128.7, 128.6, 128.5, 128.4, 125.9, 114.0, 107.0, 85.6, 83.6, 81.5, 79.6, 77.2, 74.4, 69.9, 67.1, 63.3, 57.3, 54.7, 39.0, 37.3, 36.1, 35.7, 34.6, 34.3, 29.6, 26.0 (2), 23.6, 19.7, 19.5, 18.5, 18.3, 14.2, 13.0, 12.5; IR: 2963, 2868, 1798, 1721, 1513, 1452, 1272, 1111 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{58}H_{86}BrNO_{11}SiNa$ $[M+Na]^+$: 1102.50458; found: 1102.50349.

Isomeric Alkene S17. Prepared analogously (42.8 mg, 59 % over 2 steps). $[a]_D^{20}$ = –17.7 (*c* = 1.1 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.13-8.07 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.15-7.04 (m, 4H), 6.83 (dd, *J* = 9.5, 1.1 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.78-5.68 (m, 2H), 4.95 (dd, *J* = 5.4, 4.7 Hz, 1H), 4.81 (s, 1H), 4.64 (d, ^2J = 11.6 Hz, 1H), 4.48 (dd, *J* = 10.6, 6.6 Hz, 1H), 4.41 (dd, *J* = 9.5, 5.2 Hz, 1H), 4.35-4.25 (m,



2H), 4.19 (d, *J* = 4.5 Hz, 1H), 3.97 (dd, *J* = 5.7, 3.4 Hz, 1H), 3.55-3.48 (m, 1H), 3.30-3.26 (m, 6H), 2.79-2.48 (m, 5H), 2.37 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.16 (h, *J* = 6.4 Hz, 1H), 1.96-1.52 (m, 8H), 1.46 (s, 3H), 1.24-1.08 (m, 27H), 0.89 (d, *J* = 6.3 Hz, 3H), 0.84 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 174.4, 166.2, 164.9, 159.7, 143.0, 133.3, 132.7, 131.3 (2), 129.9, 129.8, 129.0, 128.7, 128.5 (2), 128.4, 125.9, 114.0, 107.1, 85.7, 83.7, 81.6, 79.6, 77.3, 74.6, 69.9, 67.1, 63.3, 57.4, 54.8, 39.0, 37.4, 36.3, 35.8, 34.6, 34.4, 29.7, 26.1, 26.0, 23.7, 19.7, 19.5, 18.5, 18.3, 14.3, 13.0, 12.6; IR: 2941, 2868, 1799, 1721, 1513, 1452, 1272, 1112, 713 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{58}H_{86}BrNO_{11}SiNa$ [M+Na]$^+$: 1102.50459; found: 1102.50403.

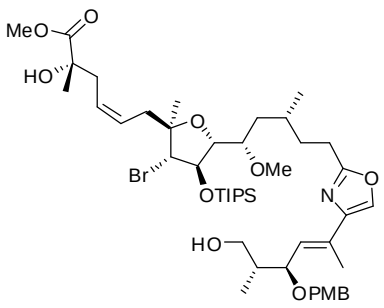
Isomeric Alkene S18. Prepared analogously (60 mg, 56 % over two steps). $[a]_D^{20}$ = +14.6 (*c* = 0.4 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.11 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.13-7.11 (m, 4H), 6.87 (dd, *J* = 9.4, 1.4 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 5.79-5.71 (m, 2H), 4.99 (t, *J* = 5.4 Hz, 1H), 4.81 (s, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.49 (dd, *J* = 10.8, 6.6 Hz, 1H), 4.43 (dd, *J* = 9.3, 5.2 Hz, 1H), 4.33 (dd, *J* = 10.8, 5.8 Hz, 1H), 4.28 (d, *J* = 11.7 Hz, 1H), 4.20 (d, *J* = 5.4 Hz, 1H), 3.95 (dd, *J* = 5.9, 3.0 Hz, 1H), 3.50-3.45 (dd, *J* = 6.6, 3.1 Hz, 1H), 3.28 (s, 3H), 3.24 (s, 3H), 2.72-2.67 (m, 3H), 2.55 (d, *J* = 5.6 Hz, 2H), 2.37 (dd, *J* = 14.7, 5.1 Hz, 1H), 2.17 (h, *J* = 6.0 Hz, 1H), 1.93-1.82 (m, 2H), 1.75 (d, *J* = 1.2 Hz, 3H), 1.69-1.59 (m, 2H), 1.55-1.47 (m, 4H), 1.22-1.16 (m, 24H), 1.12 (s, 3H), 0.89-0.84 (m, 12H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 174.4, 166.2, 165.0, 159.7, 143.0, 133.3, 132.7, 131.4, 131.3, 129.9, 129.8, 129.0, 128.7, 128.6, 128.5, 128.2, 127.9, 125.9, 114.0, 107.1, 84.6, 83.5, 81.0, 79.7, 77.3, 74.6, 70.0, 67.1, 63.0, 57.0, 54.7, 39.1, 36.7, 36.4, 35.7, 34.6, 34.4, 29.7, 26.1, 25.9, 23.7, 19.9, 19.5, 18.5, 14.3, HRMS (ESI+): *m*/*z*: calcd for $C_{58}H_{86}BrNO_{11}SiNa$ [M+Na]$^+$: 1102.50459; found: 1102.50285.

Isomeric Alkene S19. $[a]_D^{20}$ = +22.9 (*c* = 0.5 in C_6H_6); ^{1}H NMR (400 MHz, C_6D_6): *d* = 8.13-8.09 (m, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.13-7.04 (m, 4H), 6.85 (dd, *J* = 9.4, 1.0 Hz, 1H), 6.78-6.71 (m, 2H), 5.80-5.69 (m, 2H), 4.99 (dd, *J* = 5.8, 5.2 Hz, 1H), 4.81 (s, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.49 (dd, *J* = 10.8, 6.6 Hz, 1H), 4.42 (dd, *J* = 9.4, 5.2 Hz, 1H), 4.32 (dd, *J* = 10.8, 5.7 Hz, 1H), 4.28 (d, *J* = 11.7 Hz, 1H), 4.20 (d, *J* = 5.0 Hz, 1H), 3.95 (dd, *J* = 5.9, 3.1 Hz, 1H), 3.47 (dt, *J* = 6.6, 2.9 Hz, 1H), 3.27 (s, 3H), 3.24 (s, 3H), 2.74-2.64 (m, 3H), 2.55 (d, *J* = 5.3 Hz, 2H), 2.43-2.32 (m, 1H), 2.17 (pent., *J* = 6.2 Hz, 1H), 1.94-1.79 (m, 2H), 1.74 (d, *J* = 1.2 Hz, 3H), 1.70-1.57 (m, 2H), 1.56-1.47 (m, 1H), 1.47 (s, 3H), 1.22-1.13 (m, 24H), 1.12 (s, 3H), 0.89-0.82 (m, 12H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 174.4, 166.2, 165.0, 159.6, 143.0, 133.3, 132.7, 131.3 (2), 129.9, 129.8, 129.0, 128.7, 128.6, 128.5, 125.9, 114.0, 107.1, 84.6, 83.4, 80.9, 79.6, 77.2, 74.5, 69.9, 67.1, 63.0, 57.0, 54.7, 39.0, 36.7, 36.4, 35.7, 34.6, 34.4, 29.6, 26.1, 25.9, 23.7, 19.9, 19.5, 18.5, 14.3, 13.0, 12.6; IR (film): 2943, 2868, 1799, 1720, 1585, 1513, 1452, 1378, 1273, 1248, 1183, 1113, 975, 883, 825, 712, 682 cm^{-1}; HRMS (ESI+): calcd for $C_{58}H_{86}BrNO_{11}SiNa$ [M+Na]$^+$: 1102.50459; found: 1102.50353.

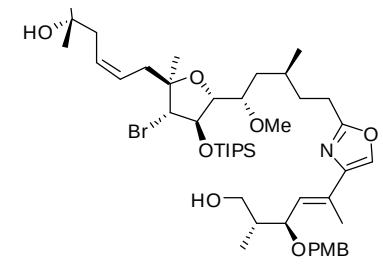
Compound 46. A freshly prepared solution of MeONa (1.0 M in MeOH, 0.45 mL, 0.45 mmol) was added at 0 °C to a solution of compound **45** (48.0 mg, 44.39 μmol) in MeOH (1.5 mL) and the resulting mixture was stirred at this temperature for 30 min and for 8 h at ambient temperature. The reaction was quenched with aq. sat. NH_4Cl (5 mL), the aqueous

phase was extracted with EtOAc (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (4:1→1:1, hexanes/EtOAc) to give product **46** as a colorless oil (30.8 mg, 75 %). $[a]_D^{20}$ = +38.7 (*c* = 1.2 in C_6H_6). ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.21-7.17 (m, 2H), 7.07 (s, 1H), 6.87 (d, *J* = 9.6 Hz, 1H), 6.79-6.75 (m, 2H), 5.75-5.64 (m, 2H), 4.95 (dd, ^3J = 5.7, 5.0 Hz, 1H), 4.58 (d, ^2J = 11.6 Hz, 1H), 4.40 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.25-4.19 (m, 2H), 3.96 (dd, *J* = 5.8, 3.3 Hz, 1H), 3.74 (dd, *J* = 10.6, 6.9 Hz, 1H), 3.54-3.48 (m, 2H), 3.35 (br s, 1H), 3.29-3.27 (m, 6H), 3.26 (s, 3H), 2.73-2.59 (m, 3H), 2.54-2.43 (m, 2H), 2.36 (dd, *J* = 14.9, 6.8 Hz, 1H), 2.03-1.97 (m, 1H), 1.93-1.84 (m, 2H), 1.81-1.70 (m, 5H), 1.65-1.56 (m, 2H), 1.46 (s, 3H), 1.38 (s, 3H), 1.22-1.11 (m, 21H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.0, 165.0, 159.6, 143.0, 133.2, 131.2, 129.6, 129.0, 127.8, 127.3, 126.8, 114.0, 85.5, 83.6, 81.1, 77.0, 76.8, 74.5, 70.0, 65.7, 62.9, 57.1, 54.7, 52.1, 41.3, 38.6, 37.2, 36.1, 34.5, 29.6, 26.0 (2), 25.7, 19.6, 18.4 (2), 14.3, 12.9, 12.5; IR: 3727, 3510, 2933, 2867, 1735, 1513, 1462, 1247, 1104 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{47}H_{76}BrNO_{10}SiNa$ $[M+Na]^+$: 944.43142; found: 944.43228.

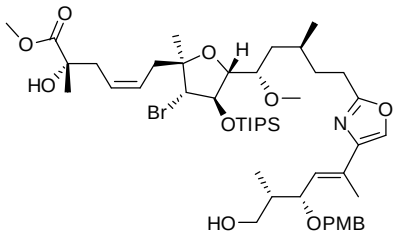
Isomer S20. Prepared analogously (21.0 mg, 57 %). $[a]_D^{20}$ = –29.6 (*c* = 1.1 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.22-7.18 (m, 2H), 7.10 (s, 1H), 6.86 (d, *J* = 9.5, 1.3 Hz, 1H), 6.80-6.77 (m, 2H), 5.76-5.62 (m, 2H), 4.95 (dd, ^3J = 5.9, 4.9 Hz, 1H), 4.59 (d, ^2J = 11.6 Hz, 1H), 4.41 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.24 (d, ^2J = 11.6 Hz, 1H), 4.21 (d, *J* = 4.6 Hz, 1H), 3.96 (dd, *J* = 5.8, 3.3 Hz, 1H), 3.73 (br t, *J* = 8.7 Hz, 1H), 3.55-3.47 (m, 2H), 3.32-3.26 (m, 10H), 2.76-2.58 (m, 3H), 2.56-2.44 (m, 2H), 2.37 (dd, *J* = 14.5, 6.4 Hz, 1H), 2.04-1.71 (m, 8H), 1.68-1.54 (m, 2H), 1.47 (s, 3H), 1.39 (s, 3H), 1.22-1.12 (m, 21H), 1.02 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.1, 165.0, 159.7, 143.1, 133.2, 131.4, 129.6, 129.1, 128.0, 127.5, 126.9, 114.1, 85.7, 83.7, 81.3, 77.2, 76.9, 74.6, 70.1, 65.8, 63.0, 57.3, 54.8, 52.2, 41.4, 38.7, 37.3, 36.3, 34.6, 29.7, 26.1 (2), 25.8, 19.7, 18.5 (2), 14.4, 13.0, 12.5; IR: 3506, 3432, 2943, 2868, 1734, 1513, 1460, 1247, 1108 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{47}H_{76}BrNO_{10}SiNa$ $[M+Na]^+$: 944.43142; found: 944.43140.



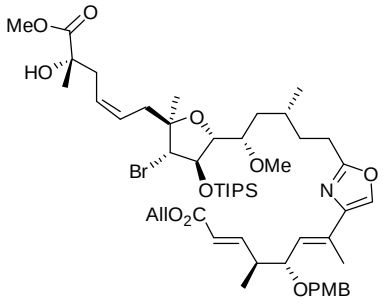
Isomer S21. Prepared analogously (36 mg, 52 %). $[a]_D^{20}$ = +18.4 (*c* = 0.4 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.20 (d, *J* = 8.5 Hz, 2H), 7.12 (s, 1H), 6.87 (dd, *J* = 9.6, 1.2 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 5.76-5.64 (m, 2H), 5.00 (t, *J* = 5.8 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.40 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.26-4.22 (m, 2H), 3.93 (dd, *J* = 6.1, 2.8 Hz, 1H), 3.75 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.54 (dd, *J* = 10.4, 5.0 Hz, 1H), 3.48-3.44 (m, 2H), 3.31 (s, 3H), 3.30 (s, 3H), 3.22 (s, 3H), 2.73-2.59 (m, 3H), 2.53-2.50 (m, 2H), 2.37 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.04-1.94 (m, 1H), 1.93-1.81 (m, 3H), 1.76 (d, *J* = 1.0Hz, 3H), 1.68-1.48 (m, 6H), 1.41 (s, 3H), 1.19-1.13 (m, 21H), 1.03 (d, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.0, 165.1, 159.7, 143.1, 133.3, 131.3, 129.6, 129.0, 128.6, 127.9, 127.4, 127.0, 114.1, 84.3, 83.4, 80.5, 77.1, 76.9, 74.6, 70.1, 65.8, 62.5, 56.8, 54.8, 52.2, 41.4, 38.8, 36.5, 36.4, 34.7, 29.6, 26.1, 26.0, 25.7, 19.8, 18.5, 18.3, 14.4, 12.6; IR: 3510, 2925, 2866, 1732, 1513, 1462, 1247, 1108 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{47}H_{76}BrNO_{10}SiNa$ $[M+Na]^+$: 944.43142; found: 944.43042.



Isomer S22. $[a]_D^{20}$ = +13.5 (*c* = 0.7 in C_6H_6); ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.21 (d, *J* = 8.6 Hz, 2H), 7.12 (s, 1H), 6.85 (dd, *J* = 9.6, 1.1 Hz, 1H), 6.80-6.75 (m, 2H), 5.76-5.61 (m, 2H), 4.99 (t, *J* = 5.8 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.41 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.25 (d, *J* = 11.6 Hz, 1H), 4.21 (d, *J* = 5.6 Hz, 1H), 3.93 (dd, *J* = 6.0, 2.8 Hz, 1H), 3.75 (dd, *J* = 10.5, 6.8 Hz, 1H), 3.53 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.51-3.41 (m, 2H), 3.32 (s, 3H), 3.31 (s, 3H), 3.22 (s, 3H), 2.76-2.68 (m, 2H), 2.66-2.58 (m, 1H), 2.56-2.46 (m, 2H), 2.40-2.32 (m, 2H), 2.04-1.96 (m, 1H), 1.94-1.82 (m, 2H), 1.76 (d, *J* = 1.1 Hz, 3H), 1.71-1.58 (m, 2H), 1.54-1.45 (m, 1H), 1.47 (s, 3H), 1.40 (s, 3H), 1.21-1.12 (m, 21H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.0, 165.1, 159.7, 133.3, 131.4, 129.6, 129.4, 129.1, 128.0, 127.4, 127.0, 114.1, 84.3, 83.4, 80.4, 77.1, 76.9, 74.6, 70.1, 65.8, 62.5, 56.8, 54.8, 52.2, 41.4, 38.8, 36.4 (2), 34.7, 29.5, 26.1, 26.0, 25.7, 19.8, 18.5, 14.4, 13.1, 12.6; IR (film): 3487, 2943, 2867, 1738, 1613, 1586, 1513, 1462, 1378, 1248, 1110, 883, 820, 681 cm^{-1}; HRMS (ESI+): calcd for $C_{47}H_{76}BrNO_{10}SiNa$ $[M+Na]^+$: 944.43142; found: 944.43143.

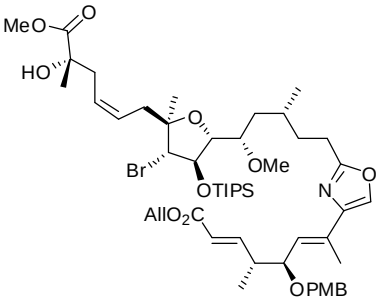


Compound 47. Pyridine (16 μL, 200.2 μmol) and Dess-Martin periodinane (20.5 mg, 48.33 μmol) were successively added to a solution of compound **46** (30.8 mg, 33.4 μmol) in CH_2Cl_2 (3.3 mL) at 0 °C. The reaction was stirred at ambient temperature for 2.5 h, before the reaction was quenched with sat. aq. $NaHCO_3$ (6 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue quickly passed through a short plug of silica (4:1→2:1, hexanes/EtOAc) to give the corresponding aldehyde as a colorless oil, which was immediately used in the next step without further characterization.

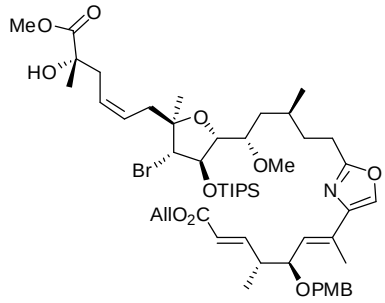


A freshly prepared solution of lithium allyl diethylphosphonoacetate (0.4 M in THF, 580 μL, 233.6 μmol) was added to a solution of this aldehyde in THF (2.0 mL) at 0 °C and the resulting mixture was stirred at 0 °C for 2 h and for 90 min at ambient temperature. Sat. aq. NH_4Cl (5 mL) was added, the aqueous phase was extracted with EtOAc (3 x), the combined extracts were washed with brine, dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (4:1→2:1, hexanes/EtOAc) to give product **47** as a colorless oil (24.1 mg, 72 % over 2 steps). $[a]_D^{20}$ = +17.4 (*c* = 0.8 in C_6H_6). ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.33 (dd, *J* = 15.8, 7.4 Hz, 1H), 7.22-7.17 (m, 2H), 7.04 (s, 1H), 6.82-6.78 (m, 2H), 6.72 (d, *J* = 9.6 Hz, 1H), 5.95 (d, *J* = 15.8 Hz, 1H), 5.75-5.64 (m, 3H), 5.09 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.97-4.91 (m, 2H), 4.59 (d, ^2J = 11.7 Hz, 1H), 4.53-4.41 (m, 2H), 4.23-4.19 (m, 2H), 4.09 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.96 (dd, *J* = 5.8, 3.3 Hz, 1H), 3.53-3.48 (m, 1H), 3.32 (s, 1H), 3.29 (s, 3H), 3.28 (s, 3H), 3.26 (s, 3H), 2.71-2.43 (m, 6H), 2.36 (dd, *J* = 14.8, 6.7 Hz, 1H), 1.88-1.67 (m, 6H), 1.64-1.54 (m, 2H), 1.46 (s, 3H), 1.38 (s, 3H), 1.23-1.12 (m, 21H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.0, 165.8, 164.9, 159.6, 151.3, 142.7, 133.3, 133.0, 131.2, 129.6 (2), 128.1, 127.1, 126.8, 121.4, 117.4, 114.0, 85.5, 83.6, 81.1, 77.0 (2), 74.5, 69.8, 64.7, 62.9, 57.2, 54.7, 52.1, 42.3, 38.6, 37.2, 36.1, 34.4, 29.6, 26.0, 25.9, 25.7, 19.6, 18.4 (2), 14.9, 14.4, 12.9; IR: 3727, 2939, 2867, 1735, 1723, 1513, 1456, 1248, 1109 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{52}H_{80}BrNO_{11}SiNa$ $[M+Na]^+$: 1024.45764; found: 1024.45793.

Isomer S23. Prepared analogously (19.7 mg, 86 %). $[a]_D^{20}$ = –5.1 (*c* = 1.0 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.33 (dd, *J* = 15.8, 7.5 Hz, 1H), 7.23-7.19 (m, 2H), 7.06 (s, 1H), 6.83-6.78 (m, 2H), 6.70 (dd, *J* = 9.7, 1.1 Hz, 1H), 5.95 (dd, *J* = 15.9, 1.3 Hz, 1H), 5.78-5.62 (m, 3H), 5.09 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.98-4.92 (m, 2H), 4.59 (d, ^2J = 11.9 Hz, 1H), 4.55-4.43 (m, 2H), 4.25-4.20 (m, 2H), 4.10 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.96 (dd, *J* = 5.7, 3.4 Hz, 1H), 3.55-3.49 (m, 1H), 3.32 (s, 3H), 3.31-3.26 (m, 7H), 2.73-2.44 (m, 6H), 2.38 (dd, *J* = 14.5, 6.4 Hz, 1H), 1.92-1.68 (m, 6H), 1.66-1.53 (m, 2H), 1.47 (s, 3H), 1.39 (s, 3H), 1.21-1.13 (m, 21H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.1, 165.9, 165.0, 159.7, 151.4, 142.9, 133.4, 133.1, 131.3, 129.6, 128.7, 128.0, 127.2, 126.9, 121.5, 117.5, 114.1, 85.7, 83.7, 81.4, 77.2 (2), 74.6, 69.9, 64.8, 63.1, 57.3, 54.8, 52.2, 42.3, 38.7, 37.3, 36.3, 34.5, 29.7, 26.1, 26.0, 25.8, 19.7, 18.5 (2), 15.0, 14.5, 13.0; IR: 3743, 2946, 2866, 1721, 1513, 1459, 1248, 1109 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{52}H_{80}BrNO_{11}SiNa$ [M+Na]$^+$: 1024.45764; found: 1024.45688.

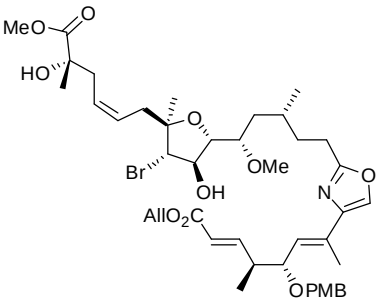


Isomer S24. Prepared analogously (36 mg, 52 %). $[a]_D^{20}$ = +11.4 (*c* = 0.3 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.33 (dd, *J* = 15.8, 7.4 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.08 (s, 1H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 9.7 Hz, 1H), 5.95 (d, *J* = 15.8 Hz, 1H), 5.77-5.64 (m, 3H), 5.09 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.00-4.93 (m, 2H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.50-4.47 (m, 2H), 4.24-4.21 (m, 2H), 4.10 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.93 (dd, *J* = 6.0, 2.8 Hz, 1H), 3.47-3.40 (m, 2H), 3.32 (s, 6H), 3.22 (s, 3H), 2.69-2.48 (m, 6H), 2.39 (dd, *J* = 14.7, 6.5 Hz, 1H), 1.91-1.82 (m, 2H), 1.71 (d, *J* = 0.9 Hz, 3H), 1.69-1.48 (m, 3H), 1.48 (s, 3H), 1.41 (s, 3H), 1.18-1.12 (m, 21H), 1.08 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.0, 165.9, 165.1, 159.7, 151.4, 142.8, 133.4, 133.1, 131.3, 129.6, 128.6, 128.1, 127.1, 127.0, 121.5, 117.4, 114.1, 84.3, 83.4, 80.5, 77.1 (2), 74.6, 69.9, 64.8, 62.6, 56.8, 54.8, 52.2, 42.3, 38.8, 36.4 (2), 34.7, 29.6, 26.1, 26.0, 25.7, 19.8, 18.5, 15.0, 14.5, 13.0; IR: 3727, 2939, 2867, 1735, 1723, 1513, 1456, 1248, 1109 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{52}H_{80}BrNO_{11}SiNa$ [M+Na]$^+$: 1024.45764; found: 1024.45793.

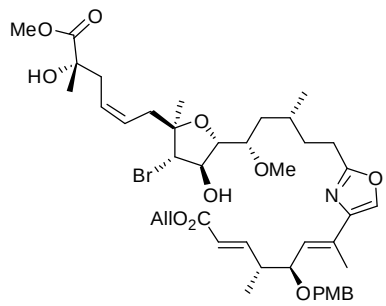


Isomer S25. $[a]_D^{20}$ = +18.3 (*c* = 0.3 in C_6H_6); ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.33 (dd, *J* = 15.8, 7.4 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.08 (s, 1H), 6.83-6.78 (m, 2H), 6.72 (dd, *J* = 9.6, 1.2 Hz, 1H), 5.95 (dd, *J* = 15.8, 1.2 Hz, 1H), 5.78-5.63 (m, 3H), 5.10 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.99 (t, *J* = 5.8 Hz, 1H), 4.95 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.54-4.43 (m, 2H), 4.23 (t, *J* = 5.5 Hz, 1H), 4.22 (s, 1H), 4.10 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.93 (dd, *J* = 6.1, 2.8 Hz, 1H), 3.45 (dt, *J* = 6.8, 2.9 Hz, 1H), 3.40 (br s, 1H), 3.31 (s, 6H), 3.22 (s, 3H), 2.73-2.46 (m, 6H), 2.37 (dd, *J* = 14.6, 6.0 Hz, 1H), 1.92-1.81 (m, 2H), 1.71 (d, *J* = 1.2 Hz, 3H), 1.70-1.55 (m, 2H), 1.54-1.45 (m, 1H), 1.48 (s, 3H), 1.41 (s, 3H), 1.22-1.13 (m, 21H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.85 (d *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.0, 165.9, 165.1, 159.7, 151.4, 142.8, 133.4, 133.1, 131.3, 129.6, 128.6, 127.1, 127.0, 121.5, 117.5, 114.1, 84.4, 83.4, 80.5, 77.1, 74.6, 69.9, 64.8, 62.6, 56.8, 54.8, 52.2, 42.3, 38.8, 36.5, 36.4, 34.7, 30.1, 29.6, 26.1, 26.0, 25.8, 19.8, 18.5, 15.0, 14.5, 13.1; IR (film): 3513, 2933, 2867, 1722, 1651, 1612, 1586, 1513, 1457, 1377, 1247, 1216, 1172, 1086, 1055, 988, 921, 882, 820, 746, 682 cm^{-1}; HRMS (ESI+): calcd for $C_{52}H_{80}BrNO_{11}SiNa$ [M+Na]$^+$: 1024.45764, found: 1024.45792.

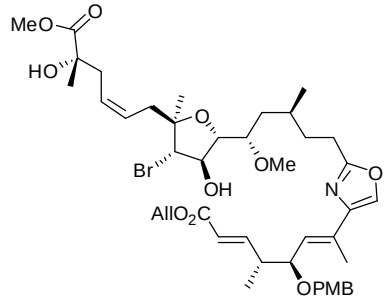
Compound S26. Pyridine (223 μL) and HF·pyridine (70 % *w*/*w*, 279 μL) were successively added to a solution of compound **47** (5.6 mg, 5.6 μmol) in THF (1.1 mL) at 0 °C and the resulting mixture was stirred at ambient temperature for 20 h. The mixture was carefully transferred via canula into sat. aq. $NaHCO_3$ (20 mL) and *tert*-butyl methyl ether (10 mL), the aqueous phase was extracted with EtOAc (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (4:1→1:1, hexanes/EtOAc) to give product **S26** as a white foam (3.6 mg, 76 %). $[a]_D^{20}$ = +19.0 (*c* = 1.1 in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.34 (dd, *J* = 15.8, 7.4 Hz, 1H), 7.23-7.18 (m, 2H), 7.05 (s, 1H), 6.82-6.75 (m, 2H), 6.72 (d, *J* = 9.6 Hz, 1H), 5.96 (dd, *J* = 15.6, 1.3 Hz, 1H), 5.82-5.60 (m, 3H), 5.10 (dq, *J* = 17.2, 1.2 Hz, 1H), 4.94 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.58 (d, ^2J = 11.9 Hz, 1H), 4.54-4.43 (m, 2H), 4.33 (br m, 1H), 4.23 (d, ^2J = 11.9 Hz, 1H), 4.16 (d, *J* = 7.6 Hz, 1H), 4.09 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.79 (dd, *J* = 7.5, 4.9 Hz, 1H), 3.42 (s, 1H), 3.38-3.29 (m, 7H), 3.28 (s, 3H), 2.68-2.34 (m, 7H), 1.87-1.49 (m, 7H), 1.42-1.33 (m, 7H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.1, 166.2, 165.2, 159.8, 151.5, 142.9, 133.5, 133.1, 131.3, 129.7 (2), 128.2, 127.5, 127.1, 121.6, 117.6, 114.2, 83.3, 82.9, 79.4, 78.7, 77.2, 74.6, 69.9, 64.9, 60.3, 58.7, 54.8, 52.2, 42.3, 38.5, 37.2 (2), 34.7, 29.3, 26.5, 26.0 (2), 19.6, 15.0, 14.5; IR: 3442, 2935, 1721, 1513, 1455, 1248, 1175, 1097 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{43}H_{60}BrNO_{11}Na$ $[M+Na]^+$: 868.32421; found: 868.32444.



Isomer S27. Prepared analogously (12.0 mg, 72 %, 98 % brsm). $[a]_D^{20}$ = –18.5 (*c* = 1.0 in C_6H_6). ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.35 (dd, *J* = 15.8, 7.4 Hz, 1H), 7.23-7.18 (m, 2H), 7.03 (s, 1H), 6.82-6.77 (m, 2H), 6.72 (dq, *J* = 9.7, 1.3 Hz, 1H), 5.94 (dd, *J* = 15.8, 1.3 Hz, 1H), 5.75-5.61 (m, 3H), 5.09 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.94 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.59 (d, ^2J = 11.8 Hz, 1H), 4.54-4.42 (m, 2H), 4.35 (br m, 1H), 4.23 (d, ^2J = 11.8 Hz, 1H), 4.18 (d, *J* = 7.7 Hz, 1H), 4.08 (dd, *J* = 9.7, 6.2 Hz, 1H), 3.82 (dd, *J* = 7.5, 4.9 Hz, 1H), 3.45 (s, 1H), 3.36 (ddd, *J* = 8.9, 4.5 Hz, 1H), 3.30 (s, 3H), 3.29 (s, 3H), 3.28 (s, 3H), 2.67 br d, *J* = 4.3 Hz, 1H), 2.64-2.36 (m, 7H), 1.83-1.65 (m, 5H), 1.64-1.49 (m, 2H), 1.42-1.33 (m, 7H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.0, 166.1, 165.1, 159.6, 151.4, 142.7, 133.4, 132.9, 131.1, 129.6 (2), 127.8, 127.3, 126.8, 121.5, 117.5, 114.0, 83.1, 82.8, 79.2, 78.5, 77.0, 74.5, 69.8, 64.8, 60.3, 58.6, 54.7, 52.2, 42.1, 38.4, 37.1 (2), 34.5, 29.1, 26.5, 25.9, 25.8, 19.5, 15.0, 14.4; IR: 3747, 3443, 2933, 1725, 1722, 1513, 1456, 1248, 1174, 1100 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{43}H_{60}BrNO_{11}Na$ $[M+Na]^+$: 868.32421; found: 868.32458.

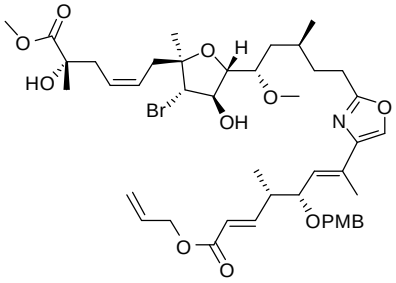


Isomer S28. Prepared analogously (16 mg, 52 %). $[a]_D^{20}$ = –4.6 (*c* = 0.2 in $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): *d* = 7.35 (dd, *J* = 15.8, 7.3 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.72 (dq, *J* = 9.7, 1.3 Hz, 1H), 5.95 (dd, *J* = 15.9, 1.3 Hz, 1H), 5.77-5.63 (m, 3H), 5.11 (dq, *J* = 17.1, 1.8 Hz, 1H), 4.95 (dq, *J* = 10.2, 1.0 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.49 (tt, *J* = 5.6, 1.3 Hz, 2H), 4.41 (t, *J* = 8.0 Hz, 1H), 4.20 (m, 2H), 4.09 (dd, *J* = 9.5, 6.1 Hz, 1H), 3.80 (dd, *J* = 7.7, 4.8 Hz, 1H), 3.46 (m, 1H), 3.30 (m, 10H), 3.00 (m, 1H), 2.72-2.37 (m, 7H),

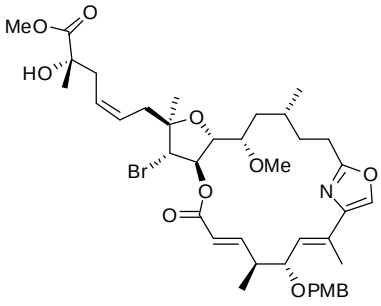


1.88-1.80 (m, 1H), 1.71 (d, *J* = 1.2 Hz, 3H), 1.67-1.58 (m, 2H), 1.48-1.33 (m, 8H), 1.03 (d, *J* = 7.3 Hz, 3H), 0.82 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): *d* = 177.1, 166.2, 165.3, 159.8, 151.5, 142.9, 133.5, 133.0, 131.2, 129.6 (2), 128.6, 127.4, 127.0, 121.6, 117.6, 114.1, 83.2, 82.8, 79.5, 78.4, 77.2, 74.6, 69.9, 64.9, 60.5, 58.6, 54.8, 52.2, 42.3, 38.6, 37.5, 37.2, 34.0, 29.5, 26.5, 26.1, 26.0, 25.8, 20.2, 15.1, 14.6; IR: 3587, 2933, 1730, 1680, 1513, 1470, 1264, 1089 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{43}H_{60}BrNO_{11}Na$ [M+Na]$^+$: 868.32421; found: 868.32367.

Isomer S29. $[a]_D^{20}$ = +2.6 (*c* = 0.6 in C_6H_6); ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.32 (dd, *J* = 15.7, 7.2 Hz, 1H), 7.24-7.20 (m, 2H), 7.04 (s, 1H), 6.82-6.78 (m, 2H), 6.67 (dd, *J* = 9.7, 1.3 Hz, 1H), 5.93 (dd, *J* = 15.7, 1.3 Hz, 1H), 5.75-5.62 (m, 3H), 5.10 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.94 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.52-4.44 (m, 2H), 4.41 (t, *J* = 7.7 Hz, 1H), 4.22 (d, *J* = 11.7 Hz, 1H), 4.21 (d, *J* = 7.7 Hz, 1H), 4.07 (dd, *J* = 9.7, 6.3 Hz, 1H), 3.80 (dd, *J* = 7.6, 4.7 Hz, 1H), 3.49 (br s, 1H), 3.36-3.31 (m, 7H), 3.30 (s, 3H), 3.10 (br s, 1H), 2.67-2.60 (m, 1H), 2.59-2.51 (m, 2H), 2.51-2.48 (m, 2H), 2.45-2.37 (m, 2H), 1.86-1.77 (m, 1H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.67-1.58 (m, 2H), 1.48-1.41 (m, 2H), 1.42 (s, 3H), 1.38 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.0, 166.1, 165.1, 159.6, 151.4, 142.6, 133.5, 132.9, 131.1, 129.5, 127.9, 127.3, 126.8, 121.5, 117.5, 114.0, 83.3, 82.7, 79.4, 78.4, 77.0, 74.5, 69.8, 64.9, 60.4, 58.6, 54.8, 52.2, 42.2, 38.5, 37.4, 37.0, 33.8, 29.4, 26.4, 25.9, 25.7, 20.2, 15.0, 14.4; IR (film): 3456, 2934, 1721, 1651, 1612, 1585, 1513, 1452, 1376, 1248, 1174, 1090, 1052, 988, 820, 751 cm^{-1}; HRMS (ESI+): calcd for $C_{43}H_{60}BrNO_{11}Na$ [M+Na]$^+$: 868.32421; found: 868.32398.



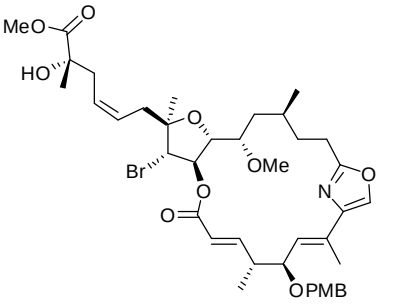
Macrolactone 49. $Pd(PPh_3)_4$ (5.5 mg, 4.8 μmol) was added in one portion to a solution of compound **S26** (9.1 mg, 10.8 μmol) in THF (1.25 mL) at 0 °C before the ice-bath was removed and a solution of sodium *p*-tosylsufinate monohydrate (10.6 mg, 59.3 μmol) in MeOH (250 μL) was introduced. After stirring for 2 h at ambient temperature, the mixture was diluted with EtOAc and aq. $KHSO_4$ (10 % *w*/*w*), the aqueous phase was extracted with EtOAc (2 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (2:1→1:2, hexanes/EtOAc containing 1 % of HOAc) to give acid **48** as a pale yellow oil, which contained residual Ph_3PO.



This *seco*-acid was immediately dissolved in toluene (625 μL). Et_3N (9 μL, 64.5 μmol) followed by a solution of 2,4,6-trichlobenzoyl chloride (0.1 M in toluene, 161 μL, 16.1 μmol) were added dropwise and the resulting mixture stirred at ambient temperature for 2.5 h before it was diluted with toluene (1.9 mL). The resulting solution was loaded into a syringe and added via syringe pump over 5 h to a solution of DMAP (26.1 mg, 213.6 μmol) in toluene (21.25 mL) at 45 °C. Once the addition was complete, stirring was continued for 9 h at 45 °C before the mixture was diluted with EtOAc and washed successively with aq. sat. $NaHCO_3$, $CuSO_4$ (0.1 M, 2x), aq. sat. $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (4:1→2:1, hexanes/EtOAc) to give macrolactone **49** as a pale yellow oil (5.8 mg, 68 % over 2 steps). $[a]_D^{20}$ = +69.6 (*c* = 0.7 in C_6H_6). ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.90 (dd, *J* = 16.1, 4.9 Hz, 1H), 7.13-7.09 (m, 2H), 6.99 (s, 1H), 6.80-6.75 (m, 2H), 6.66 (d, *J* = 10.6 Hz, 1H), 6.51 (dd, *J* =

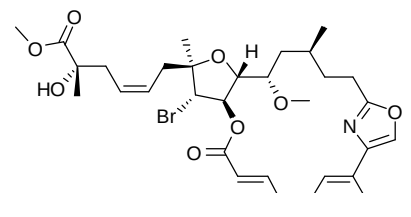
9.2, 7.3 Hz, 1H), 5.93 (dd, *J* = 16.1, 1.6 Hz, 1H), 5.81-5.66 (m, 2H), 4.50 (d, *J* = 9.2 Hz, 1H), 4.42 (d, ^2J = 11.8 Hz, 1H), 4.14-4.06 (m, 2H), 3.97 (dd, *J* = 7.3, 1.5 Hz, 1H), 3.46 (ddd, *J* = 10.9, 4.4, 1.4 Hz, 1H), 3.35 (s, 1H), 3.31 (s, 3H), 3.29 (s, 3H), 3.25 (s, 3H), 2.83 (br m, 1H), 2.57-2.42 (m, 4H), 2.35 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.28 (ddd, *J* = 13.6, 9.1, 4.5 Hz, 1H), 2.17 (ddd, *J* = 16.7, 8.4, 5.2 Hz, 1H), 1.88 (ddd, *J* = 13.2, 11.0, 3.7 Hz, 1H), 1.61 (s, 3H), 1.58-1.49 (m, 4H), 1.45 (ddd, *J* = 13.4, 9.7, 4.1 Hz, 1H), 1.35 (s, 3H), 1.14 (br m, 1H), 0.73 (d, *J* = 6.5 Hz, 3H), 0.70 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.0, 165.5, 164.9, 159.6, 152.4, 142.5, 133.0, 131.0, 129.6, 129.2, 127.6, 127.4, 126.8, 120.5, 114.0, 83.7, 80.5, 77.1 (2), 76.6, 74.3, 69.6, 57.4, 54.7, 54.5, 52.1, 41.3, 38.5, 36.6, 36.2, 31.6, 29.2, 25.8 (2), 25.5, 20.5, 13.8, 13.7; IR: 3727, 2938, 1733, 1513, 1456, 1248, 1170, 1081 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{40}H_{54}BrNO_{10}Na$ [M+Na]$^+$: 810.28234; found: 810.28231.

Macrolactone S30. Prepared analogously (4.5 mg, 48 % over 2 steps). $[a]_D^{20}$ = –44.7 (*c* = 0.6 in C_6H_6). ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.31 (dd, *J* = 15.9, 6.9 Hz, 1H), 7.20-7.16 (m, 2H), 6.99 (s, 1H), 6.83-6.78 (m, 2H), 6.46 (dd, *J* = 9.0, 7.5 Hz, 1H), 6.42 (dq, *J* = 9.3, 1.3 Hz, 1H), 5.89 (dd, *J* = 15.9, 1.4 Hz, 1H), 5.72-5.62 (m, 2H), 4.49 (d, ^2J = 11.7 Hz, 1H), 4.39 (d, *J* = 9.0 Hz, 1H), 4.18 (d, *J* = 11.7 Hz, 1H), 3.96 (dd, *J* = 7.5, 1.9 Hz, 1H), 3.92 (dd, *J* = 9.3, 6.3 Hz, 1H), 3.39 (s, 3H), 3.34 (s, 1H), 3.31 (s, 3H), 3.30 (s, 3H), 3.23 (ddd, *J* = 10.3, 1.9 Hz, 1H), 2.68 (m, 1H), 2.53-2.37 (m, 5H), 2.32 (dd, *J* = 14.7, 5.6 Hz, 1H), 1.94-1.84 (m, 2H), 1.70 (d, *J* = 1.3 Hz, 1H), 1.65-1.57 (m, 4H), 1.46 (ddd, *J* = 13.7, 8.6, 3.9 Hz, 1H), 1.36 (s, 3H), 1.22-1.11 (m, 1H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.1, 165.2, 165.0, 159.7, 151.4, 143.0, 132.7, 131.0, 129.5 (2), 127.6, 127.4, 126.8, 121.4, 114.0, 83.5, 80.6, 77.7, 77.4, 77.2, 74.4, 69.9, 57.4, 55.0, 54.7, 52.1, 42.6, 38.5, 36.9, 36.1, 33.4, 28.3, 25.8, 25.7, 24.8, 20.6, 15.5, 14.4; IR: 3728, 2935, 1732, 1513, 1456, 1247, 1093 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{40}H_{54}BrNO_{10}Na$ [M+Na]$^+$: 810.28234; found: 810.28266.



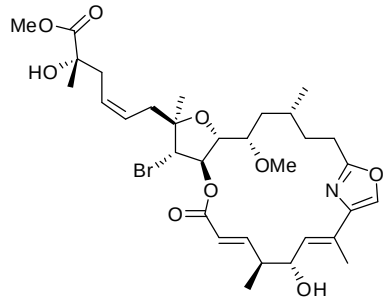
Macrolactone S31. $[a]_D^{20}$ = –40.6 (*c* = 0.5 in C_6H_6). ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.90 (dd, *J* = 15.8, 7.1 Hz, 1H), 7.13-7.09 (m, 2H), 6.96 (s, 1H), 6.81-6.74 (m, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.30 (dd, *J* = 8.7, 7.9 Hz, 1H), 5.93 (dd, *J* = 15.8, 1.4 Hz, 1H), 5.73-5.63 (m, 2H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 8.9 Hz, 1H), 4,20 (d, *J* = 11.7 Hz, 1H), 3.98 (dd, *J* = 10.1, 6.1 Hz, 1H), 3,92 (dd, *J* = 7.7, 1.9 Hz, 1H), 3.37 (s, 1H), 3.32 (s, 3H), 3.31 (s, 3H), 3.29 (s, 3H), 3.21 (m, 1H), 2.71 (br m, 1H), 2.60-2.55 (ddd, *J* = 15.7, 6.5, 5.8, 1H), 2.51-2.28 (m, 5H), 1.96-1.86 (m, 1H), 1.75 (m, 1H), 1.61 (m, 1H), 1.61 (d, *J* = 1.57 Hz, 3H), 1.56 (s, 3H), 1.46 (m, 1H), 1.37 (s, 3H), 1.28 (br m, 1H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.1, 165.3 (*2), 159.7, 151.4, 142.8, 133.0, 131.1, 129.6, 129.1, 128.0, 127.6, 127.4, 127.1, 121.3, 114.0, 83.8, 83.4, 78.8, 77.5, 77.3, 74.4, 69.6, 58.8, 55.1, 54.7, 52.2, 42.7, 38.9, 38.5, 37.1, 33.8, 30.9, 30.1, 26.0, 25.8, 25.4, 20.5, 15.8, 14.0; IR: 3727, 2938, 1733, 1513, 1456, 1248, 1170, 1081 cm^{-1}; HRMS (ESI+): *m*/*z*: calcd for $C_{40}H_{54}BrNO_{10}Na$ [M+Na]$^+$: 810.28234; found: 810.28222.

Macrolactone S32. $[a]_D^{20}$ = +11.0 (*c* = 0.1 in C_6H_6); ^{1}H NMR (600 MHz, C_6D_6): *d* = 7.73 (dd, *J* = 16.0, 5.6 Hz, 1H), 7.16-7.13 (m, 2H), 7.01 (s, 1H), 6.80-6.77 (m, 2H), 6.55 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.38 (dd, *J* = 8.9, 7.7 Hz, 1H),

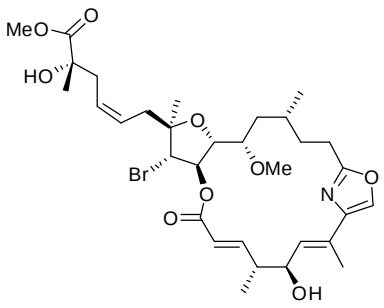


5.94 (dd, *J* = 16.0, 1.5 Hz, 1H), 5.80-5.66 (m, 2H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 9.0 Hz, 1H), 4.18 (d, *J* = 11.8 Hz, 1H), 4.08 (dd, *J* = 10.4, 4.5 Hz, 1H), 3.84 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.43-3.39 (m, 1H), 3.38 (s, 3H), 3.35 (br s, 1H), 3.30 (s, 3H), 3.28 (s, 3H), 2.81-2.74 (m, 1H), 2.49 (t, *J* = 6.8 Hz, 2H), 2.48-2.42 (m, 2H), 2.41-2.33 (m, 2H), 1.93-1.85 (m, 1H), 1.79-1.70 (m, 2H), 1.63 (d, *J* = 1.4 Hz, 3H), 1.59 (s, 3H), 1.57-1.50 (m, 2H), 1.36 (s, 3H), 0.77 (d, *J* = 6.9 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): *d* = 177.1, 165.4, 165.3, 159.7, 152.3, 142.9, 132.8, 131.1, 129.7, 129.6, 127.7, 127.6, 126.6, 120.8, 114.1, 83.8, 83.6, 77.6, 77.5, 77.2, 74.4, 69.7, 58.9, 54.8 (2), 52.2, 41.4, 38.5, 38.0, 36.9, 32.2, 29.8, 26.1, 25.9, 24.3, 20.0, 14.5, 14.0; IR (film): 2927, 1731, 1648, 1612, 1585, 1513, 1456, 1377, 1248, 1168, 1087, 1034, 802, 680 cm^{-1}; HRMS (ESI+): calcd for $C_{40}H_{54}BrNO_{10}Na$ $[M+Na]^+$: 810.28234; found: 810.28311.

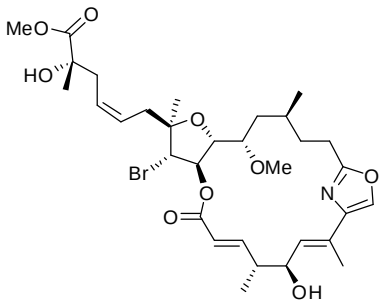
Ester 13*R*-50. DDQ (2.4 mg, 10.6 μmol) was added to a solution of compound **49** (5.8 mg, 7.4 μmol) in CH_2Cl_2 (250 μL) and H_2O (12 μL) at 0 °C and the resulting mixture stirred for 30 min at ambient temperature. The reaction was quenched with aq. sat. $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2 (3 x), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (4:1→1:2, hexanes/EtOAc) to give product 13*R*-**50** as a pale yellow oil (2.3 mg, 47 %). ^{1}H NMR (600 MHz, CD_3OD): *d* = 7.68 (s, 1H), 7.19 (dd, *J* = 16.0, 6.4 Hz, 1H), 6.11 (dd, *J* = 10.0, 1.3 Hz, 1H), 5.85-5.77 (m, 2H), 5.64-5.53 (m, 2H), 4.48 (dd, *J* = 10.0, 4.9 Hz, 1H), 4.26 (d, *J* = 8.2 Hz, 1H), 3.70 (s, 3H), 3.58 (dd, *J* = 7.4, 2.0 Hz, 1H), 3.44 (s, 3H), 3.18 (ddd, *J* = 10.3, 4.6, 1.9 Hz, 1H), 2.82 (ddd, *J* = 16.2, 6.8, 6.4 Hz, 1H), 2.75 (br m, 1H), 2.63 (ddd, *J* = 16.1, 7.9, 6.5 Hz, 1H), 2.50 (dd, *J* = 14.6, 6.7 Hz, 1H), 2.45-2.38 (m, 2H), 2.34 (dd, *J* = 15.2, 5.8 Hz, 1H), 2.06 (br m, 1H), 1.93 (d, *J* = 1.4 Hz, 3H), 1.59-1.46 (m, 2H), 1.42-1.28 (m, 8H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): *d* = 177.5, 166.7, 166.5, 153.2, 143.4, 135.2, 128.4, 128.3, 127.9, 121.5, 84.5, 80.9, 78.5, 77.9, 75.7, 72.0, 58.0, 55.9, 52.8, 44.7, 39.2, 37.3, 37.0, 33.9, 29.4, 25.9 (2), 25.8, 20.9, 15.5, 14.1; HRMS (ESI+): *m*/*z*: calcd for $C_{32}H_{46}BrNO_9Na$ $[M+Na]^+$: 690.22483; found: 690.22524.



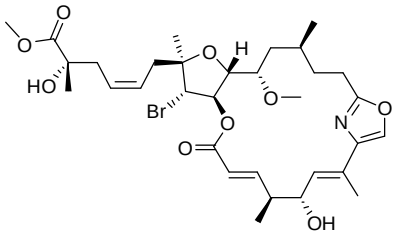
Ester 13*R*-51. ^{1}H NMR (600 MHz, CD_3OD): *d* = 7.69 (s, 1H), 7.05 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.08 (dq, *J* = 9.1, 1.3 Hz, 1H), 5.85 (dd, *J* = 15.8, 1.3 Hz, 1H), 5.76 (dd, *J* = 8.3, 7.6 Hz, 1H), 5.67-5.52 (m, 2H), 4.34 (dd, *J* = 9.1, 6.8 Hz, 1H), 4.30 (d, *J* = 8.4 Hz, 1H), 3.75-3.70 (m, 4H), 3.32 (s, 3H), 2.94 (m, 1H), 2.81 (m, 1H), 2.68 (m, 1H), 2.61 (m, 1H), 2.53 (m, 1H), 2.49-2.35 (m, 3H), 1.93 (d, *J* = 1.3 Hz, 3H), 1.89 (m, 1H), 1.59-1.46 (m, 4H), 1.37 (s, 3H), 1.35 (s, 3H), 1.15 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): *d* = 177.5, 166.6 (2), 153.3, 143.7, 134.8, 129.1, 128.9, 128.5, 127.9, 121.8, 84.4, 80.9, 78.3 (2), 75.8, 71.9, 58.0, 55.8, 52.8, 45.6, 39.2, 37.5, 36.7, 34.5, 29.2, 26.0, 25.9, 25.2, 20.9, 15.9, 14.4; HRMS (ESI+): *m*/*z*: calcd for $C_{32}H_{46}BrNO_9Na$ $[M+Na]^+$: 690.22483; found: 690.22551.



Ester 13*S*-51. ^{1}H NMR (600 MHz, CD_3OD): *d* = 7.70 (s, 1H), 6.84 (dd, *J* = 15.6, 8.9 Hz, 1H), 6.12 (dq, *J* = 9.6, 1.3 Hz, 1H), 5.93 (d, *J* = 15.6, 1H), 5.66-5.56 (m, 3H), 4.27 (dd, *J* = 9.6 Hz, 1H), 4.26 (d, *J* = 8.8 Hz, 1H), 3.72 (s, 3H), 3.66 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.12 (s, 3H), 2.82 (m, 2H), 2.71 (ddd, *J* = 15.4, 9.8, 4.2 Hz, 1H), 2.57-2.53 (m, 2H), 2.45-2.44 (m, 2H), 2.37 (m, 1H), 1.92 (d, *J* = 1.3 Hz, 3H), 1.83 (m, 1H), 1.54-1.48 (m, 2H), 1.40-1.27 (m, 8H), 1.20 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): *d* = 177.5, 167.1, 166.9, 153.5, 143.5, 135.5, 129.5, 128.5, 128.4, 127.8, 121.7, 84.2, 83.7, 79.6, 77.8, 75.7, 71.5, 59.9, 55.4, 52.8, 46.2, 39.9, 39.2, 37.8, 35.6, 31.5, 26.3, 26.0, 25.9, 21.1, 16.7, 14.3; HRMS (ESI+): *m*/*z*: calcd for $C_{32}H_{46}BrNO_9Na$ $[M+Na]^+$: 690.22553; found: 690.22482.



Ester 13*S*-50. A 10 mL conical flask was charged with macrolactone **S32** (2 mg, 0.00254 mmol), CH_2Cl_2 (0.5 mL), and H_2O (0.025 mL) and immersed in an ice bath. Freshly crystallized DDQ (1 mg, 0.00441 mmol) was added and the reaction was stirred in the ice bath until the starting material was consumed (*ca.* 30 min). The reaction was quenched with 3 drops of distilled Et_3N and immediately flashed through a short pad of silica using hexanes/EtOAc (3:1→1:2) to yield 13*S*-**50** as a yellow oil (1 mg, 60 %). ^{1}H NMR (600 MHz, CD_3OD): *d* = 7.69 (s, 1H), 7.17 (dd, *J* = 15.9, 6.5 Hz, 1H), 6.09 (dq, *J* = 9.8, 1.4 Hz, 1H), 5.85 (dd, *J* = 15.9, 1.5 Hz, 1H), 5.70 (dd, *J* = 7.6 Hz, 1H), 5.65-5.55 (m, 2H), 4.47 (dd, *J* = 9.8, 5.2 Hz, 1H), 4.24 (d, *J* = 7.8 Hz, 1H), 3.70 (s, 3H), 3.57 (dd, *J* = 7.4, 1.7 Hz, 1H), 3.45 (s, 3H), 3.20 (td, *J* = 6.1, 1.6 Hz, 1H), 2.77 (dt, *J* = 15.8, 6.4 Hz, 1H), 2.73-2.63 (m, 2H), 2.54-2.48 (m, 1H), 2.45-2.39 (m, 2H), 2.38-2.33 (m, 1H), 1.96 (d, *J* = 1.4 Hz, 3H), 1.93-1.86 (m, 1H), 1.71-1.52 (m, 3H), 1.40-1.37 (m, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): *d* = 177.5, 166.7, 166.5, 153.5, 143.5, 135.1, 129.2, 128.4, 128.0, 127.9, 121.5, 84.7, 83.7, 79.2, 79.0, 75.7, 72.0, 59.1, 56.0, 52.8, 44.5, 39.2, 38.7, 37.3, 34.0, 30.4, 26.1, 25.9, 25.1, 20.2, 15.6, 14.3.



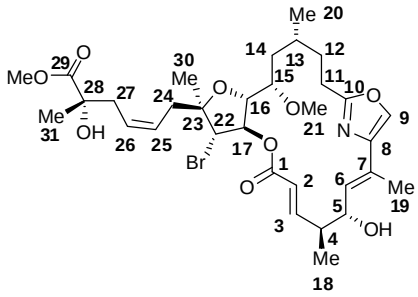


Table S-1: Comparison of the ^{1}H NMR data of acid 13*R*-**2**, its ester precursor 13*R*-**50**, and the diastereomeric ester 13*R*-**51** (600 MHz, [D_4]-MeOH) with the data of leiodolide B reported in the literature (500 MHz, [D_4]-MeOH).[7] Numbering scheme as shown for 13*R*-**50** in the Insert.

Pos.	Literature	13*R*-**2**	13*R*-**50**	13*R*-**51**
2	5.79 d (15.5)	5.82 dd (16.0, 1.2)	5.81 dd (16.0, 1.4)	5.85 dd (15.8, 1.3)
3	7.02 dd (15.5, 10.0)	7.18 dd (16.0, 6.4)	7.18 dd (16.0, 6.4)	7.05 dd (15.8, 7.3)
4	2.44 m	2.75 m	2.75 m	2.62 m
5	4.54 m	4.48 dd (10.0, 5.0)	4.48 dd (10.0, 4.9)	4.34 dd (9.1, 6.8)
6	6.22 dd (8.0, 0.5)	6.10 dq (10.0, 1.0)	6.11 dq (10.0, 1.3)	6.08 dq (9.1, 1.3)
9	7.64 s	7.67 s	7.68 s	7.69 s
11	2.61 m 2.79 m	2.63 m 2.82 m	2.63 ddd (16.1, 7.9, 6.5) 2.82 ddd (16.2, 6.8, 6.4)	2.68 m 2.81 m
12	1.41 m 2.06 m	1.38 m 2.05 m	1.37 m 2.06 m	1.53 m 1.89 m
13	1.27 m	1.32 m	1.32 m	1.52 m
14	1.50 m	1.55 m 1.50 m	1.55 m 1.51 m	1.52 m
15	3.09 m	3.18 m	3.18 ddd (10.3, 4.6, 1.9)	2.94 m
16	3.62 dd (8.0, 2.0)	3.57 dd (7.4, 1.8)	3.58 dd (7.4, 2.0)	3.73 dd (7.6, 2.0)
17	5.75 t (8.0)	5.78 dd (7.8, 7.8)	5.79 dd (8.1, 7.5)	5.76 dd (8.3, 7.6)
18	1.24 d (7.0)	1.07 d (6.9)	1.06 d (6.8)	1.15 d (6.7)
19	1.89 d (1.0)	1.93 d (1.0)	1.93 d (1.4)	1.93 d (1.3)
20	0.97 d (6.5)	0.96 d (6.3)	0.96 d (6.4)	0.94 d (5.6)
21	3.41 s	3.44 s	3.44 s	3.32 s
22	4.28 d (8.5)	4.27 d (8.2)	4.26 d (8.2)	4.30 d (8.2)
24	2.33 m 2.47 m	2.37 m 2.57 m	2.34 m 2.41 m	2.38 m 2.45 m
25	5.50 m	5.40 m	5.57 m	5.63 m
26	5.66 m	5.72 m	5.60 m	5.63 m
27	2.34 m 2.43 m	2.37 m 2.57 m	2.42 m 2.50 m	2.44 m 2.53 m
30	1.33 s	1.35 s	1.34 s	1.35 s
31	1.28 s	1.37 s	1.36 s	1.37 s

[7] J. S. Sandler, P. L. Colin, M. Kelly, W. Fenical, *J. Org. Chem*. **2006**, *71*, 7245-7251; correction: *J. Org. Chem*. **2006**, *71*, 8684.

Table S-2: Comparison of the ^{1}H NMR data of esters 13*S*-**50** and 13*S*-**51** (600 MHz, [D_4]-MeOH) with the data of leiodolide B reported in the literature (500 MHz, [D_4]-MeOH). Numbering scheme as shown in the Insert of Table S-1.

Pos.	Literature	13*S*-**50**	13*S*-**51**
2	5.79 d (15.5)	5.85 dd (15.9, 1.5)	5.93 d (15.6)
3	7.02 dd (15.5, 10.0)	7.17 dd(15.9, 6.5)	6.84 dd (15.6, 8.9)
4	2.44 m	2.71 m	2.57 m
5	4.54 m	4.47 dd (9.8, 5.2)	4.27 m
6	6.22 dd (8.0, 0.5)	6.09 dq (9.8, 1.4)	6.12 dd (9.6, 1,3)
9	7.64 s	7.69 s	7.70 s
11	2.61 m 2.79 m	2.67 m 2.77 dt (15.8, 6.4)	2.71 m 2.82 m
12	1.41 m 2.06 m	1.61 m 1.90 m	1.50 m 1.83 m
13	1.27 m	1.67 m	1.27 m
14	1.50 m	1.38 m 1.57 m	1.52 m 1.37 m
15	3.09 m	3.20 td (6.1, 1.6)	2.82 m
16	3.62 dd (8.0, 2.0)	3.57 dd (7.4, 1.7)	3.66 dd (8.2, 1.9)
17	5.75 t (8.0)	5.70 d (7.6)	5.62 dd (8.8, 8.2)
18	1.24 d (7.0)	1.09 d (6.9)	1.20 d (6.6)
19	1.89 d (1.0)	1.96 d (1.4)	1.92 d (1.3)
20	0.97 d (6.5)	0.97 d (6.6)	0.97 (6.6)
21	3.41 s	3.45 s	3.12 s
22	4.28 d (8.5)	4.24 d (7.8)	4.26 d (8.8)
24	2.33 m 2.47 m	2.35 m 2.41 m	2.37 m 2.44 m
25	5.50 m	5.58 m	5.56-5.66 m
26	5.66 m	5.61 m	5.56-5.66 m
27	2.34 m 2.43 m	2.43 m 2.51 m	2.45 m 2.53 m
30	1.33 s	1.35 s	1.34 s
31	1.28 s	1.37 s	1.38 s