Supplementary Material (ESI) for Chemical Communications

Toward the Total Synthesis of Spirastrellolide A, Part 3: Intelligence gathering and preparation of a ring-expanded analogue

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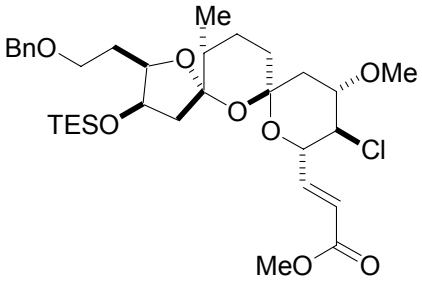
General: All reactions were carried out under Ar in flame-dried glassware. IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). The solvents used were purified by distillation over the drying agents indicated and were transferred under Argon: THF, Et_2O (Mg-anthracene), CH_2Cl_2, MeCN, Et_3N (CaH_2), DMF (Desmodur®, dibutyltin dilaurate), MeOH (Mg), toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. The solvent signals were used as references (CD_2Cl_2: $\delta_C \equiv 54.0$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm; C_6D_6: $\delta_C \equiv 128.0$ ppm; residual C_6H_6 in C_6D_6: $\delta_H \equiv 7.15$ ppm; $CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm). ***Where indicated, the signal assignments are unambiguous***; the numbering scheme is arbitrary and is 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 (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for $^1J(C,H) = 145$ Hz; HMBC (*inv4gslplrnd*) for correlations via $^nJ(C,H)$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

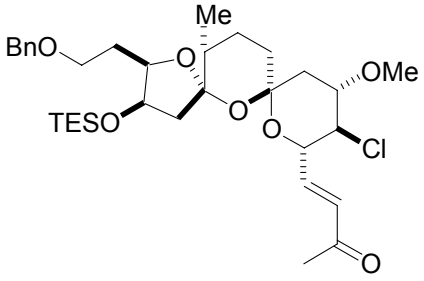
Ester 5b. To a solution of **3** (63 mg, 0.108 mmol) in acetone (1.2 mL) at room temperature was added N-methylmorpholine N-oxide (17 mg, 0.141 mmol) and the resulting mixture was stirred for 20 min. A 2.5% wt solution of OsO_4 in *tert*-butanol (22 μL, 2.16 μmol) was then added and the mixture was stirred for 12 h. The reaction was quenched with aq. $Na_2S_2O_3$ (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo* to yield an intermediate diol as a mixture of diastereomers that was used without further purification.



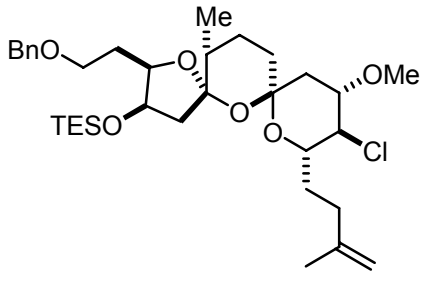
To a solution of the crude intermediate diol in CH_2Cl_2 (1.08 mL) at room temperature was added $Pb(OAc)_4$ (58 mg, 0.128 mmol) and the mixture was stirred for 30 min. The reaction was quenched with aq. $NaHCO_3$ (1.0 mL) and diluted with ethyl acetate (15 mL). The organic phase was washed with aq. $Na_2S_2O_3$ (10 mL), brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield aldehyde **4** that was used without further purification.

To a solution of crude aldehyde **4** in THF (1.1 mL) at 0°C was added methoxycarbonyl-triphenylphosphorane (43 mg, 0.128 mmol) and the mixture was stirred at room temperature for 1.5 h. The reaction was concentrated *in vacuo* and purified by flash chromatography (10/1 to 4/1 hexanes-ethyl acetate) on SiO_2 to yield **5b** (30 mg, 44% over 3 steps) as an oil. $[\alpha]_D^{20} = +5.0$ (*c* 0.5, CH_2Cl_2). IR (ATR) 2953, 2876, 1726, 1661, 1455, 1436, 1380, 1307, 1277, 1190, 1167, 1074, 1048, 1003, 976, 924, 861, 835, 789, 733 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.69 (dd, *J* = 15.6, 3.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.64 (dd, *J* = 15.7, 2.0 Hz, 1H), 4.65 (ddd, *J* = 10.7, 3.6, 2.0 Hz, 1H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.16 (dt, *J* = 8.8, 3.8 Hz, 1H), 3.92 (m, 2H), 3.86 (dd, *J* = 6.3, 4.6 Hz, 1H), 3.83 (dd, *J* = 9.5, 4.9 Hz, 1H), 3.52 (m, 1H), 3.39 (s, 3H), 3.27 (s, 3H), 2.14 (dd, *J* = 14.3, 6.2 Hz, 1H), 2.04 (dd, *J* = 12.7, 4.8 Hz, 1H), 1.99 (m, 1H), 1.62 (dt, *J* = 13.2, 3.1 Hz, 1H), 1.47 (m, 2H), 1.36 – 1.12 (m, 4H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.92 (m, 9H), 0.48 (m, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 166.8, 145.0, 139.8, 128.7, 128.0, 127.8, 122.8, 109.6, 98.3, 81.6, 79.7, 73.4, 72.9, 72,4, 68.6, 63.9, 57.8, 51.3, 50.0, 43.4, 38.4, 36.3, 30.4, 24.3, 16.8, 7.3, 5.3. HRMS (ESI+): Calcd for $C_{33}H_{51}O_8NaSiCl$ $(M + Na)^+$: 661.2927. Found 661.2934.

Ketone 5c. To a flask containing $Ba(OH)_2 \cdot 8H_2O$ (10 mg, 30.8 μmol) at room temperature (previously activated by heating at 120°C for 1.5 h), was added a solution of diethyl-methylphosphonate (6.5 μL, 37.0 μmol) in THF (250 μL) and the mixture was stirred for 30 min. The mixture was then cooled to 0°C and aldehyde **4** (18 mg, 30.8 μmol) was added as a solution in THF:H_2O (40:1, 250 μl). The reaction was stirred for 2 h, diluted with CH_2Cl_2 (10 mL), filtered through Celite, and concentrated *in vacuo*. Purification by flash chromatography (4/1 hexanes-ethyl acetate) on SiO_2 afforded **5c** (16 mg, 85%) as an oil. $[\alpha]_D^{20} =$ +7.1 (*c* 0.5, CH_2Cl_2). IR (ATR) 2928, 1774, 1709, 1457, 1351, 1292, 1258, 1178, 1096, 1007, 834, 802, 720 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.13 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.73 (dd, *J* = 15.9, 1.8 Hz, 1H), 4.65 (ddd, *J* = 10.6, 3.9, 1.8 Hz, 1H), 4.49 (d, *J* = 13.2 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.22 (m, 1H), 4.00 (m, 1H), 3.87 (m, 1H), 3.57 (dd, *J* = 12.9, 6.2 Hz, 1H), 3.56 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.48 (dd, *J* = 15.1, 8.5 Hz, 1H), 3.47 (m, 1H), 3.29 (s, 3H), 2.17 (dd, *J* = 14.3, 6.2 Hz, 1H), 2.09 (dd, *J* = 12.8, 5.0 Hz, 1H), 1.97 (m, 1H), 1.94 (dd, *J* = 14.2, 2.0 Hz, 1H), 1.88 (s, 3H), 1.67 (dt, *J* = 13.2, 3.1 Hz, 1H), 1.49 (m, 2H), 1.34 (m, 1H), 1.24 (m, 1H), 1.20 (dq, *J* = 12.9, 3.6 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.93 (m, 9H), 0.50 (m, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 197.0, 142.5, 139.6, 131.9, 128.8, 128.0, 127.8, 109.5, 98.3, 81.5, 79.8, 73.3, 72.8, 72.6, 68.2, 64.1, 57.9, 49.8, 43.5, 38.3, 36.3, 30.3, 27.3, 24.3, 16.8, 7.3, 5.3. HRMS (ESI+): Calcd for $C_{33}H_{51}O_7NaSiCl$ $(M + Na)^+$: 645.2987. Found 645.2984.

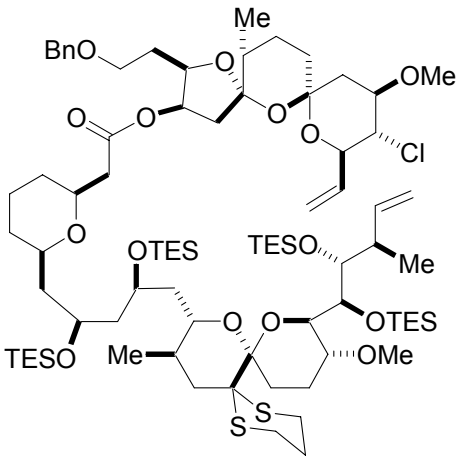


Compound 8. To a stirred solution of alkene **3** (10 mg, 17 μmol) in THF (500 μL) at room temperature was added 9-BBN (10 mg, 85 μmol) and the reaction was stirred for 3 h. To a separate flask containing 2-bromopropene (15 μL, 0.17 mmol) in DMF (700 μL) at room temperature was added Cs_2CO_3 (11 mg, 34 μmol), $(dppf)PdCl_2$ (1 mg, 1.7 μmol) and $AsPh_3$ (1 mg, 3.4 μmol). The mixture was stirred for 10 min before the dropwise addition of the intermediate alkylborane solution (followed by a 500 μL THF rinse). The resulting mixture was heated to 65 °C for 4 h and then cooled to room temperature. The reaction was



quenched with water (4 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (4/1 hexanes-ethyl acetate) on SiO_2 to afford **8** (4.3 mg, 41%) as an oil. $[\alpha]_D^{20} = -8.1$ (*c* 0.57, CH_2Cl_2). IR (film): 2989, 2873, 145, 1381, 1132, 1073, 977, 791 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.36 - 7.23 (m, 5H), 4.70 - 4.66 (m, 2H), 4.53 - 4.42 (m, 3H), 4.20 (dt, *J* = 7.5, 5.4 Hz, 1H), 3.74 (ddd, *J* = 10.2, 7.8, 2.4 Hz, 1H), 3.63 - 3.55 (m, 3H), 3.46 - 3.39 (m, 1H), 3.40 (s, 3H), 2.31 - 2.21 (m, 1H), 2.18 - 2.10 (m, 2H), 2.09 - 1.49 (m, 8H), 1.72 (s, 3H), 1.37 (ddd, *J* = 12.5, 7.0, 3.6 Hz, 1H), 1.30 (dd, *J* = 12.1, 10.9 Hz, 1H), 1.27 - 1.12 (m, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 - 0.84 (m, 1H), 0.60 (q, *J* = 7.7 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 147.2, 134.3, 129.1, 128.8, 128.1, 109.5, 108.7, 97.8, 80.5, 79.6, 73.3, 73.1, 72.2, 68.4, 64.8, 57.6, 47.7, 43.5, 37.6, 36.5, 32.9, 31.3, 30.2, 24.3, 23.1, 16.9, 7.2, 5.4. HRMS (ESI+): Calcd for $C_{34}H_{45}O_6NaSiCl$ $(M+Na)^+$: 645.3345. Found: 645.3349.

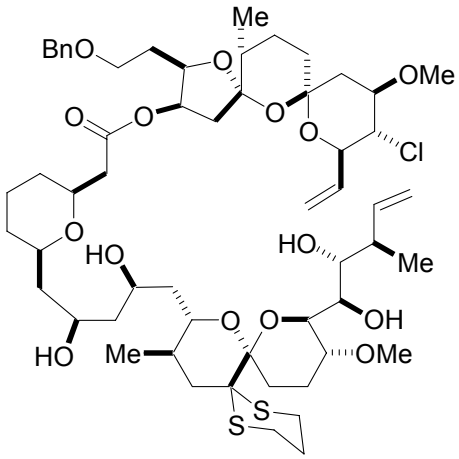
Diene 9a. To a solution of acid **2** (30 mg, 26.8 μmol) in toluene (1.34 mL) at 0 °C



were added triethylamine (11.2 μL, 67 μmol) and 2,4,6-trichlorobenzoyl chloride (6.3 μL, 40.2 μmol) and the reaction was stirred for 45 min. A solution of alcohol **3** (10 mg, 22.3 μmol) and DMAP (16 mg, 112 μmol) in toluene (1.34 mL) was then added and the mixture was warmed to room temperature for 2.0 h. The reaction was quenched with aq. $NaHCO_3$ (20 mL) and extracted with ethyl acetate (2 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography (10/1 to 4/1 hexanes-ethyl acetate) on SiO_2 afforded **9a** (26 mg, 76%) as an oil. $[\alpha]_D^{20} = -18$ (*c* 1.0, CH_2Cl_2). IR (ATR) 3071, 3029, 2951, 2911, 1739, 1641, 1457, 1240, 1112, 1018, 735 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.34 (m, 2H), 7.23 (m, 2H), 7.12 (m, 1H), 6.25 (m, 1H), 6.18 (m, 1H), 5.67 (dt, *J* = 17.2, 1.8 Hz, 1H), 5.34 – 5.27 (m, 2H), 5.20 (dt, *J* = 10.7, 1.8 Hz, 1H), 5.14 (dd, *J* = 10.3, 2.2 Hz, 1H), 4.54 (m, 1H), 4.42 (m, 1H), 4.38 (m, 2H),4.29 (m, 1H), 4.28 (m, 1H), 4.23 (m, 1H), 4.13 (m, 1H), 3.94 – 3.81 (m, 3H), 3.70 – 3.41 (m, 6H), 3.37 (s, 3H), 3.10 (m, 1H), 3.09 (s, 3H),

2.60 – 2.48 (m, 3H), 2.46 – 2.37 (m, 4H), 2.32 (dd, *J* = 15.3, 8.9 Hz, 1H), 2.26 – 2.01 (m, 8H), 2.00 – 1.91 (m, 2H), 1.91 – 1.78 (m, 2H), 1.70 (dt, *J* = 13.1, 3.2 Hz, 1H), 1.60 – 1.29 (m, 12H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.26 – 1.04 (m, 5H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.96 – 0.89 (m, 1H), 0.86 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 170.4, 139.6, 139.0, 135.6, 128.6, 128.1, 127.9, 127.8, 116.8, 116.3, 109.0, 99.6, 98.1, 80.0, 79.3, 75.6, 75.2, 74.5, 74.4, 73.9, 73.5, 73.2, 72.3, 71.8, 70.8, 68.2, 66.4, 65.4, 64.9, 58.0, 57.7, 56.2, 47.0, 43.8, 43.4, 43.0, 41.8, 40.8, 40.5, 39.7, 38.1, 36.3, 32.2, 31.3, 31.1, 29.7, 29.6, 25.8, 25.5, 24.9, 24.1, 23.6, 18.3, 17.4, 16.7. HRMS (ESI+): Calcd for $C_{81}H_{143}O_{15}NaS_2Si_4Cl$ $(M+Na)^+$: 1589.8527. Found: 1589.8522.

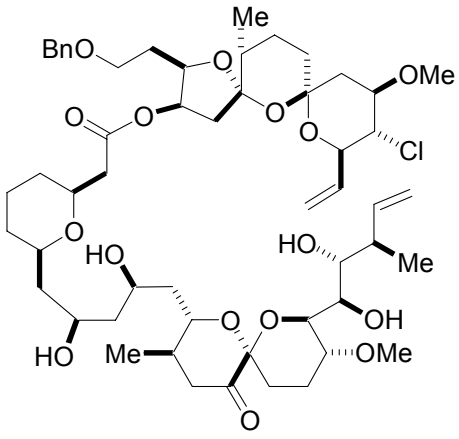
Diene 9b. To a stirred solution of **2** (20 mg, 12.7 μmol) in methanol (2.1 mL), diethyl ether (600 μL), and water (300 μL) at 0 °C was added PPTS (15 mg) and the mixture was allowed to stir at room temperature for 19 h. The reaction was quenched with aq. $NaHCO_3$ (20 mL), and extracted with ethyl acetate (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography (2/1 to 1/1 to 0/1 hexanes-ethyl acetate) afforded **9b** (13 mg, 90%) as an oil.



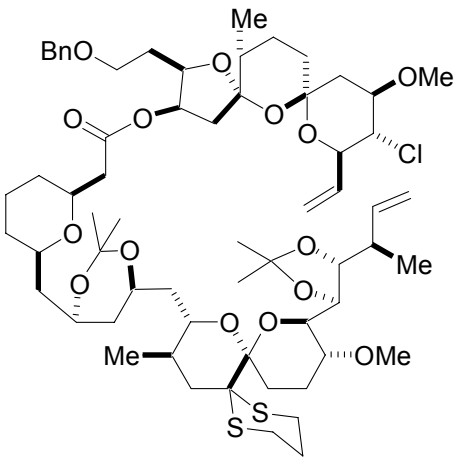
$[\alpha]_D^{20} = -71.1$ (*c* 1.0, CH_2Cl_2). IR (ATR) 3452, 2934, 2869, 1737, 1641, 1454, 1093, 928 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.34 (m, 2H), 7.23 (m, 2H), 7.12 (m, 1H), 6.25 (m, 1H), 6.18 (m, 1H), 5.67 (dt, *J* = 17.2, 1.8 Hz, 1H), 5.34 – 5.27 (m, 2H), 5.20 (dt, *J* = 10.7, 1.8 Hz, 1H), 5.14 (dd, *J* = 10.3, 2.2 Hz, 1H), 4.54 (m, 1H), 4.42 (m, 1H), 4.38 (m, 2H), 4.29 (m, 1H), 4.28 (m, 1H), 4.23 (m, 1H), 4.13 (m, 1H), 3.94 – 3.81 (m, 3H), 3.70 – 3.41 (m, 6H), 3.37 (s, 3H), 3.10 (m, 1H), 3.09 (s, 3H), 2.60 – 2.48 (m, 3H), 2.46 – 2.37 (m, 4H), 2.32 (dd, *J* = 15.3, 8.9 Hz, 1H), 2.26 – 2.01 (m, 8H), 2.00 – 1.91 (m, 2H), 1.91 – 1.78 (m, 2H), 1.70 (dt, *J* = 13.1, 3.2 Hz, 1H), 1.60 – 1.29 (m, 12H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.26 – 1.04 (m, 5H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.96 – 0.89 (m, 1H), 0.86 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 170.4, 139.6, 139.0, 135.6, 128.6, 128.1, 127.9, 127.8, 116.8, 116.3, 109.0, 99.6, 98.1, 80.0, 79.3, 75.6, 75.2, 74.5, 74.4, 73.9, 73.5, 73.2, 72.3, 71.8, 70.8, 68.2, 66.4, 65.4, 64.9, 58.0, 57.7, 56.2, 47.0, 43.8, 43.4, 43.0, 41.8, 40.8, 40.5, 39.7, 38.1, 36.3, 32.2, 31.3, 31.1, 29.7,

29.6, 25.8, 25.5, 24.9, 24.1, 23.6, 18.3, 17.4, 16.7. HRMS (ESI+): Calcd for $C_{57}H_{87}O_{15}NaClS_2$ $(M+Na)^+$: 1133.5067. Found: 1133.5077.

Diene 9c. To a vigorously stirred solution of N-chlorosuccinimide (7 mg, 53.6 μmol), 2,6-lutidine (13 μL, 107 μmol), and $AgNO_3$ (10 mg, 60.3 μmol) in 80% aq. acetonitrile (540 μL) was added a solution of **9b** (15 mg, 13.4 μmol) in THF (200 μL). The mixture was stirred for 20 min and was then quenched by the sequential addition of saturated aq. solutions of Na_2SO_3 (100 μL), $NaHCO_3$ (100 μL), and NaCl (100 μL) in 1 min intervals. The resulting mixture was then filtered through Celite with ethyl acetate, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography (1/1 to 0/1 hexanes-ethyl acetate) afforded **9c** (6 mg, 69%) as an oil. $[\alpha]_D^{20} = -56.1$ (*c* 0.5, CH_2Cl_2). IR (ATR) 3450, 2934, 2873, 1773, 1705, 1496, 1455, 1429, 1418, 1376, 1295, 1195, 1096, 1050, 1003, 975, 934, 851, 823, 737, 699, 641 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.34 (m, 2H), 7.22 (m, 2H), 7.13 (m, 1H), 6.25 (m, 1H), 6.19 (m, 1H), 5.66 (dt, *J* = 17.2, 1.8 Hz, 1H), 5.33 – 5.25 (m, 2H), 5.22 – 5.14 (m, 2H), 4.54 (m, 1H), 4.41 (m, 1H), 4.40 (m, 2H), 4.30 (m, 2H), 4.28 (m, 2H), 4.13 – 4.02 (m, 2H), 3.89 (m, 1H), 3.87 (m, 1H), 3.77 (m, 1H), 3.65 (m, 1H), 3.61 (m, 1H), 3.55 (m, 1H), 3.51 (m, 1H), 3.37 (s, 3H), 3.35 (m, 1H), 3.09 (s, 3H), 3.01 (m, 1H), 2.42 (bs, 1H), 2.37 (dd, *J* = 13.1, 8.8 Hz, 1H), 2.35 (m, 1H), 2.29 (dd, *J* =6.2, 4.0 Hz, 1H), 2.27 (m, 1H), 2.26 (m, 1H), 2.23 (m, 1H), 2.18 (m, 1H), 2.15 – 2.09 (m, 3H), 2.08 – 2.05 (m, 2H), 2.02 (m, 1H), 1.97 (m, 1H), 1.88 (m, 1H), 1.86 (m, 1H), 1.82 (m, 1H), 1.81 – 1.70 (m, 4H), 1.69 – 1.62 (m, 4H), 1.38 (m, 1H), 1.36 (d, *J* = 7.1 Hz, 3H), 1.34 (m, 1H), 1.25 – 1.13 (m, 2H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.94 – 0.82 (m, 2H), 0.64 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 202.0, 170.5, 139.4, 139.0, 135.5, 128.6, 128.1, 127.9, 116.7, 116.5, 109.0, 98.1, 97.6, 80.0, 79.3, 75.6, 74.7, 74.6, 74.4, 74.0, 73.5, 73.2, 71.9, 71.5, 70.4, 68.3, 66.1, 65.5, 64.9, 57.7, 56.3, 47.0, 44.2, 43.9, 43.4, 43.1, 41.8, 40.7, 39.8, 39.7, 38.1, 36.3, 31.3, 31.2, 29.8, 29.7, 27.9, 27.7, 27.6, 24.1, 23.6, 18.1, 16.7. HRMS (ESI+): Calcd for $C_{54}H_{81}O_{16}NaCl$ $(M + Na)^+$: 1043.5098. Found 1043.5105.

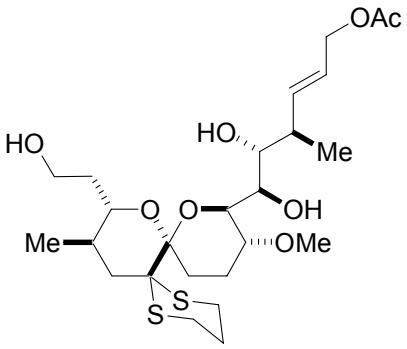


Diene 9d. To a solution of acid **2** (15 mg, 20.1 μmol) in toluene (1.0 mL) at 0 °C was

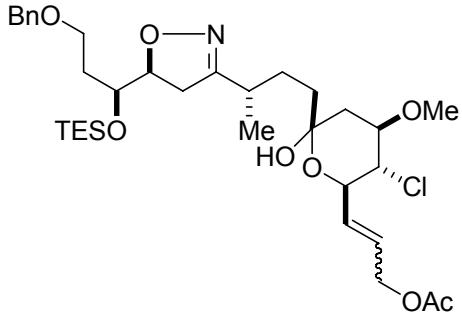


added triethylamine (6.0 μL, 50.3 μmol) and 2,4,6-trichlorobenzoyl chloride (4.0 μL, 30.1 μmol) and the reaction was stirred for 45 min. A solution of alcohol **3** (8 mg, 16.8 μmol) and DMAP (10 mg, 0.101 mmol) in toluene (1.0 mL) was then added and the mixture was warmed to room temperature for 2.0 h. The reaction was quenched with aq. $NaHCO_3$ (20 mL) and extracted with ethyl acetate (2 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography (4/1 to 2/1 hexanes-ethyl acetate) on SiO_2 afforded **9d** (16 mg, 80%) as an oil. $[\alpha]_D^{20} = -53.1$ (*c* 1.0, CH_2Cl_2). IR (ATR) 2979, 2935, 2871, 1738, 1644, 1580, 1547, 1496, 1455, 1379, 1343, 1261, 1249. 1219, 1190, 1169, 1093, 1027, 975, 927, 737, 699 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.33 (m, 2H), 7.21 (m, 2H), 7.11 (m, 1H), 6.33 (m, 1H), 6.25 (m, 1H), 5.69 (dt, *J* = 17.2, 1.8 Hz, 1H), 5.26 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.25 (dd, *J* = 6.0, 3.3 Hz, 1H), 5.21 (dt, *J* = 10.8, 1.8 Hz, 1H), 5.15 (dt, *J* = 10.6, 1.4 Hz, 1H), 4.61 (dd, *J* = 6.6, 1.5 Hz, 1H), 4.47 (m, 1H), 4.43 (qt, *J* = 5.9, 1.5 Hz, 1H), 4.36 (m, 2H), 4.29 (m, 1H), 4.23 (m, 1H), 4.00 (m, 2H), 3.88 (m, 1H), 3.79 (m, 2H), 3.69 (m, 1H), 3.61 (m, 1H), 3.58 (m, 1H), 3.49 (m, 2H), 3.38 (m, 1H), 3.37 (s, 3H), 3.16 (s, 3H), 2.64 – 2.50 (m, 4H), 2.45 (m, 1H), 2.44 – 2.22 (m, 6H), 2.17 – 2.03 (m, 6H), 2.01 – 1.87 (m, 4H), 1.94 (s, 3H), 1.71 (dt, *J* = 13.1, 3.2 Hz, 1H), 1.66 (s, 3H), 1.65 (m, 1H), 1.60 (m, 1H), 1.59 – 1.48 (m, 6H), 1.57 (s, 3H), 1.45 – 1.18 (m, 6H), 1.38 (s, 3H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.07 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.99 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 170.4, 142.6, 139.2, 135.6, 128.5, 128.1, 127.9, 127.6, 116.8, 113.4, 108.9, 107.9, 100.7, 100.6, 98.1, 81.5, 80.0, 79.3, 76.0, 74.8, 74.6, 74.4, 74.2, 73.6, 73.1, 71.1, 68.0, 64.9, 63.2, 62.5, 58.5, 57.7, 56.3, 47.2, 43.5, 43.2, 42.8, 41.8, 40.1, 38.7, 38.3, 36.4, 36.4, 33.3, 32.0, 31.3, 29.7, 29.3, 27.7, 26.3, 25.9, 25.8, 25.6, 25.2, 24.2, 23.8, 23.8, 17.5, 16.6, 16.5. HRMS (ESI+): Calcd for $C_{63}H_{95}O_{15}NaS_2Cl$ $(M + Na)^+$: 1213.5678. Found 1213.5693.

Allyl acetate 13. To a stirred solution of **11** (10 mg, 21.2 µmol) in CH_2Cl_2 (1 mL) was added **12** (37 mg, 212 µmol) and catalyst **10** (2 mg, 2.1 µmol). The resulting solution was refluxed for 16 h, cooled to room temperature, and directly submitted to flash chromatography. Purification over SiO_2 (1/1 to 1/2 hexanes-ethyl acetate) afforded **11** (5 mg, 49 %) and **13** (4 mg, 33 %, 65 % brsm) as a colorless oil. $[\alpha]_D^{20}$ = –50.2 (*c* 0.62, CH_2Cl_2). IR (kap.): 3433, 2930, 2828, 1737, 1671, 1456, 1239, 1094, 957, 736 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.86 (dd, *J* = 15.6, 7.5 Hz, 1H), 5.70 (dt, *J* = 15.2, 6.0 Hz, 1H), 4.56 (dd, *J* = 8.7, 6.4 Hz, 2H), 3.89 (dt, *J* = 10.6, 2.4 Hz, 1H), 3.75 (d, *J* = 9.6 Hz, 1H), 3.72 - 3.61 (m, 2H), 3.58 - 3.48 (m, 2H), 3.39 - 3.30 (m, 1H), 3.38 (s, 3H), 3.03 - 2.95 (m, 1H), 2.92 - 2.83 (m, 2H), 2.72 - 2.62 (m, 2H), 2.52 (dd, *J* = 12.8, 2.7 Hz, 1H), 2.36 - 2.23 (m, 2H), 2.21 - 2.12 (m, 2H), 2.06 (s, 3H), 2.02 - 1.52 (m, 9H), 1.16 (d, *J* = 7.1 Hz, 3H), 0.88 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 134.9, 126.4, 99.3, 74.9, 73.3, 72.4, 71.1, 70.0, 65.2, 58.9, 57.3, 56.4, 40.2, 37.1, 34.9, 31.7, 28.9, 25.8, 25.5, 25.1, 24.1, 21.0, 17.2, 17.2. HRMS (ESI+): Calcd for $C_{25}H_{42}O_8NaS_2$ $(M+Na)^+$: 557.2213. Found: 557.2214.

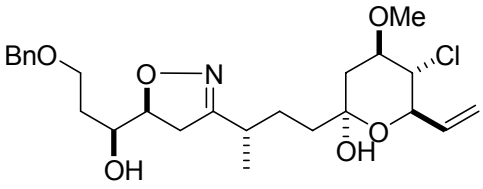


Allyl Acetate 15. To a solution of terminal alkene **14** (25 mg, 42.6 µmol) in toluene (5 mL) was added **12** (73 mg, 426 µmol) and catalyst **10** (4 mg, 4.3 µmol). The resulting mixture was heated to 80 °C for 90 min, cooled to room temperature and concentrated *in vacuo*. The crude product was purified by flash chromatography (2/1 hexanes-ethyl acetate) on SiO_2 to afford **15** (14 mg, 48%) as an oil. $[\alpha]_D^{20}$ = +42.5 (*c* 1.36, CH_2Cl_2). IR (kap.): 3399, 3030, 2955, 2876, 1741, 1622, 1232, 976, 741 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.30 - 7.26 (m, 2H), 7.21 - 7.16 (m, 2H), 7.12 - 7.07 (m, 1H), 6.03 - 5.95 (m, 2H), 4.56 - 4.42 (m, 3H), 4.39 - 4.27 (m, 2H), 3.97 (ddd, *J* = 8.4, 6.4, 3.6 Hz, 1H), 3.81 (ddd, *J* = 11.1, 9.6, 5.0 Hz, 1H), 3.58 - 3.51 (m, 3H), 3.28 - 3.23 (m, 1H), 3.26 (s, 3H), 2.82 - 2.74 (m, 1H), 2.49 - 2.29 (m, 3H), 2.16 (dd, *J* = 12.7, 5.0 Hz, 1H), 1.93 - 1.84 (m, 1H), 1.63 (s, 3H), 1.61 - 1.25 (m, 6H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.85 (d,



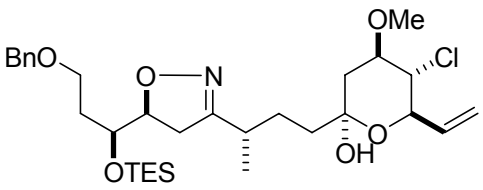
J = 7.1 Hz, 3H), 0.75 - 0.63 (m, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 169.8, 161.3, 138.9, 131.3, 128.6, 128.1, 127.9, 127.9, 98.1, 82.8, 79.4, 73.2, 73.0, 70.8, 66.7, 64.5, 64.2, 57.8, 39.9, 39.3, 36.1, 33.3, 33.0, 27.6, 20.4, 18.2, 7.3, 5.5. HRMS (ESI+): Calcd for $C_{34}H_{54}NO_8NaClSi$ $(M+Na)^+$: 690.3199. Found: 690.3203.

Compound 14. To a solution of **16** (474 mg, 0.486 mmol) in DMF (10 mL) at 0 °C



was added a solution of TAS-F (743 mg, 2.43 mmol) in DMF (5 mL) and water (175 µL 9.72 mmol) over 10 min. The reaction was stirred at 0 °C for 3 h and then quenched with pH = 7 buffer solution (30 mL). The mixture was extracted with ethyl acetate (3 x 30 mL) and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (1/1 hexanes-ethyl acetate) on SiO_2 to afford **14** (226 mg, 97%) as an oil. $[\alpha]_D^{20}$ = +58.2 (*c* 2.14, $CHCl_3$). IR (film): 3400, 2933, 1454, 1095 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.24 - 7.08 (m, 5H), 6.06 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1H), 5.45 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.16 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.60 (dd, *J* = 10.2, 6.0 Hz, 1H), 4.31 - 4.19 (m, 2H), 4.14 (ddd, *J* = 10.8, 6.4, 3.1 Hz, 1H), 3.88 (ddd, *J* = 11.1, 9.8, 5.0 Hz, 1H), 3.62 - 3.57 (m, 2H), 3.54 - 3.48 (m, 1H), 3.48 - 3.41 (m, 1H), 3.38 - 3.32 (m, 1H), 3.30 (s, 3H), 2.83 - 2.79 (m, 1H), 2.57 (dd, *J* = 17.0, 6.5 Hz, 1H), 2.33 (dd, *J* = 17.0, 10.9 Hz, 2H), 2.23 (dd, *J* = 12.7, 5.0 Hz, 1H), 1.78 - 1.70 (m, 1H), 1.67 - 1.46 (m, 3H), 1.43 - 1.27 (m, 3H), 0.97 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 161.7, 138.9, 135.8, 128.6, 127.9, 127.8, 117.8, 98.2, 82.0, 79.6, 74.1, 73.2, 71.8, 67.5, 64.6, 57.8, 39.6, 38.2, 37.7, 33.7, 32.8, 27.5, 17.3. HRMS (ESI+): Calcd for $C_{25}H_{36}NO_6NaCl$ $(M+Na)^+$: 504.2123. Found: 504.2125.

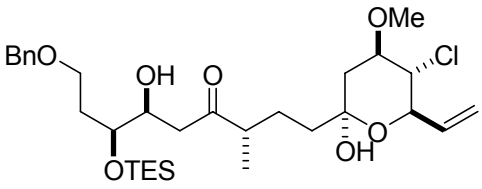
Compound 17. To a stirred solution of **14** (32 mg, 66.8 µmol) in CH_2Cl_2 (2 mL) at -78



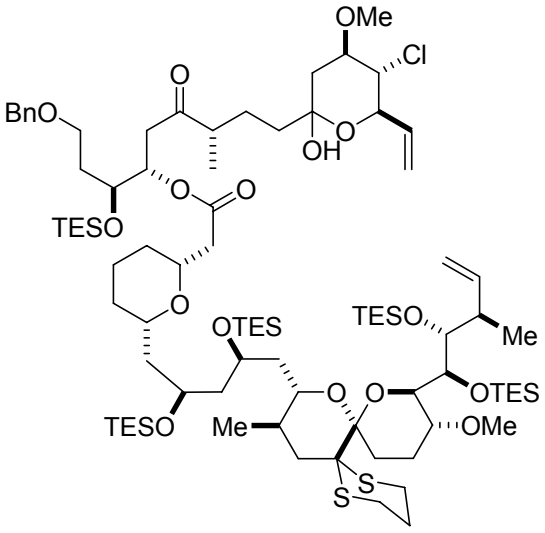
°C was added a premixed solution of 2,6-lutidine (11.7 µL, 0.10 mmol) and TESOTf (16.6 µL, 73.5 µmol) in CH_2Cl_2 (250 µL), and the mixture was stirred at -78 °C for 1 h. The reaction was quenched with NH_4Cl (saturated solution, 1 mL) and extracted with diethyl ether. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (2/1 hexanes-ethyl acetate) on SiO_2 to

afford **17** (52 mg, 76%) as an oil (inseparable mixture of 3 isomers). $[\alpha]_D^{20}$ = +53.2 (*c* 0.50, CH_2Cl_2). IR (kap.): 3383, 3063, 2954, 1646, 1455, 1101, 741 cm^{-1}. Major isomer: ^1H NMR (400 MHz, C_6D_6): δ 7.30 - 7.26 (m, 2H), 7.20 - 7.13 (m, 2H), 7.12 - 7.07 (m, 1H), 6.06 (ddd, *J* = 17.0, 10.6, 5.8 Hz, 1H), 5.48 - 5.41 (m, 1H), 5.20 - 5.14 (m, 1H), 4.54 - 4.43 (m, 2H), 4.39 - 4.29 (m, 2H), 3.98 (ddd, *J* = 8.3, 6.4, 3.6 Hz, 1H), 3.81 (ddd, *J* = 11.1, 9.7, 5.0 Hz, 1H), 3.60 - 3.49 (m, 3H), 3.26 (s, 3H), 2.46 (d, *J* = 8.3 Hz, 1H), 2.43 - 2.39 (m, 2H), 2.39 - 2.27 (m, 1H), 2.14 (dd, *J* = 12.7, 5.0 Hz, 1H), 1.87 (dddd, *J* = 13.9, 7.7, 6.3, 3.6 Hz, 1H), 1.63 - 1.53 (m, 1H), 1.52 - 1.44 (m, 2H), 1.43 - 1.35 (m, 2H), 1.29 (ddd, *J* = 12.8, 11.3, 2.4 Hz, 1H), 1.02 (t, *J* = 7.9 Hz, 9H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.69 (dd, *J* = 7.7, 15.5 Hz, 3H), 0.68 (dd, *J* = 16.2, 8.1 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 161.2, 135.7, 128.6, 128.1, 127.9, 117.6, 97.9, 82.8, 79.5, 74.0, 73.2, 70.8, 66.7, 64.5, 57.7, 39.8, 39.4, 36.1, 33.2, 33.0, 27.6, 18.2, 7.2, 5.5. HRMS (ESI+): Calcd for $C_{31}H_{50}NO_6NaSiCl$ $(M+Na)^+$: 618.2988. Found: 618.2985.

Compound 18. To a solution of **17** (52 mg, 86.8 μmol) in acetonitrile (7 mL) and water (1 mL) was added $Mo(CO)_6$ (23 mg, 86.8 μmol) and the resulting mixture was heated to 90 °C for 2 h. The reaction was cooled to room temperature, filtered through a plug of SiO_2 (2/1, hexanes-ethyl acetate, 5 mL) and concentrated *in vacuo*. The crude product was purified by flash chromatography (2/1 hexanes-ethyl acetate) on SiO_2 to afford **18** (48 mg, 92%) as an oil (inseparable mixture of 5 isomers). $[\alpha]_D^{20}$ = +25.7 (*c* 0.97, CH_2Cl_2). IR (kap.): 3410, 3088, 2955, 1708, 1455, 1232, 1097, 741 cm^{-1}. Characteristic data of the major isomer: ^1H NMR (400 MHz, C_6D_6): δ 6.06 (ddd, *J* = 17.0, 10.5, 5.9 Hz, 1H), 5.50 - 5.44 (m, 1H), 5.19 - 5.16 (m, 1H), 4.55 (dd, *J* = 10.2, 5.8 Hz, 1H), 3.55 (t, *J* = 9.9 Hz, 1H), 3.28 (s, 3H), 2.62 (dd, *J* = 16.3, 9.6 Hz, 1H), 2.43 (dd, *J* = 16.2, 2.7 Hz, 1H), 2.21 (dd, *J* = 12.7, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 213.4, 138.8, 135.8, 128.6, 127.9, 127.7, 117.7, 98.1, 79.6, 74.0, 73.2, 72.4, 70.9, 66.8, 64.6, 57.7, 46.7, 43.4, 39.7, 38.9, 33.4, 26.2, 15.9, 7.2, 5.4. HRMS (ESI+): Calcd for $C_{31}H_{51}O_7NaSiCl$ $(M+Na)^+$: 621.2985. Found: 621.2983.



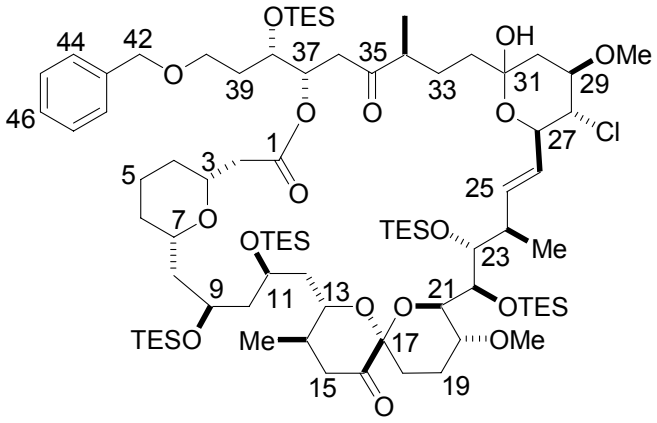
Diene 19. To a solution of **2** (30 mg, 26.4 μmol) in toluene (1 mL) at room temperature were added Et_3N (7.4 μL, 52.8 μmol) and 2,4,6-trichlorobenzoyl chloride (4.1 μl, 26.4 μmol) and the resulting solution was stirred for 1 h. A solution of **18** (19 mg, 31.4 μmol) and DMAP (3 mg, 26.4 μmol) in toluene (1.8 mL) was then added dropwise and the mixture was stirred for 2 h. The reaction was quenched with aq. $NaHCO_3$ (2 mL) and the aqueous phase was extracted with diethyl ether (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo.* The crude product was purified by flash chromatography (6/1 hexanes-ethyl acetate) on SiO_2 to afford **19** (23 mg, 50%) as an oil. $[\alpha]_D^{20}$ = –20.8 (*c* 1.16, CH_2Cl_2). IR (kap.): 3408, 2953, 2876, 1739, 1717, 1636, 1457, 1415, 1238, 1112, 1006, 929, 739 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.35 - 7.31 (m, 2H), 7.25 - 7.18 (m, 2H), 7.13 - 7.09 (m, 1H), 6.60 (ddd, *J* = 17.4, 10.5, 6.7 Hz, 1H), 6.09 (ddd, *J* = 16.8, 10.6, 5.7 Hz, 1 H) 5.63 (dt, *J* = 7.8, 3.6 Hz, 1 H), 5.54 - 5.47 (m, 1H), 5.32 - 5.25 (m, 1 H), 5.24 - 5-15 (m, 3 H), 4.52 (dd, *J* = 10.2, 5.8 Hz, 1 H), 4.44 - 4.33 (m, 5H), 4.30 - 4.22 (m, 1 H), 3.90 - 3.78 (m, 3 H), 3.72 - 3.52 (m, 5 H), 3.37 - 3.28 (m, 3H), 3.29 (s, 3H), 3.15 (s, 3 H), 2.85 (dd, *J* = 16.9, 3.4 Hz, 1 H), 2.77 - 2.55 (m, 3H), 2.52 - 2.29 (m, 9H), 2.28 - 1.92 (m, 11 H), 1.89 - 1.76 (m, 2 H), 1.75 - 1.57 (m, 5 H), 1.56 - 1.33 (m, 8H), 1.28 - 0.65 (m, 83H). ^{13}C NMR (100 MHz, C_6D_6): δ 210.1, 170.3, 143.2, 139.0, 135.7, 128.6, 127.9, 127.9, 117.7, 112.8, 100.1, 98.0, 80.7, 79.5, 77.3, 75.9, 75.4, 74.4, 74.1, 74.0, 73.6, 73.3, 72.3, 68.8, 68.4, 67.7, 66.9, 64.5, 58.4, 57.8, 54.6, 47.7, 46.4, 45.5, 43.3, 42.1, 39.9, 39.7, 39.6, 39.5, 39.3, 32.9, 32.6, 31.9, 31.5, 29.1, 26.3, 25.9, 25.5, 25.4, 23.8, 23.2, 20.2, 17.6, 16.3, 7.8, 7.6, 7.5, 7.4, 7.2, 6.5, 6.1, 5.9, 5.8, 5.4. HRMS (ESI+): Calcd for $C_{87}H_{159}O_{16}NaClS_2Si_5$ $(M+Na)^+$: 1721.9497. Found: 1721.9517.



Compound 21. To a solution of diene **19** (16 mg, 9.4 μmol) in toluene (6 mL) at 60 °C was added complex **10** (20 mg, 23.5 μmol) in several portions over 18 h. The reaction was cooled to room temperature, a drop of ethyl-vinyl ether was added and

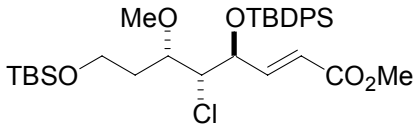
the solution was stirred for 1 h. The solvents were removed *in vacuo*, and the residue was filtered through a plug of silica (10/1 hexanes-ethyl acetate) yielding compound **20** (12 mg, 7.1 μmol) that was used without further purification.

To a vigorously stirred solution of N-chlorosuccinimide (4 mg, 28.4 μmol), 2,6-lutidine (6.5 μL, 56.8 μmol), and $AgNO_3$ (11 mg, 32.0 μmol) in 80% aq. acetonitrile (355 μL) was added **20** (12 mg, 7.1 μmol) as a solution in THF (355 μL). The mixture was stirred 30 min and was then quenched by the sequential addition of saturated aq. solutions of Na_2SO_3 (100 μL), $NaHCO_3$ (100 μL), and NaCl (100 μL), added in 1 min intervals. The mixture was filtered through Celite with ethyl acetate, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography (4/1 hexanes-ethyl acetate) afforded **21** (8 mg, 49% over 2 steps) as an oil. $[\alpha]_D^{20} = +14.2$ (*c* 0.3CH_2Cl_2). IR (ATR) 3378, 2932, 2875, 1740, 1670, 1458, 1414, 1289, 1243, 1185, 1094, 1004, 917, 807 cm^{-1}. ^1H NMR (600 MHz, C_6D_6): δ 7.31 (d, *J* = 7.3 Hz, 2H, H(43, 43')), 7.19 (t, *J* = 7.5 Hz, 2H, H(45, 45')), 7.09 (t, *J* = 7.4 Hz, 1H, H(46)), 6.63 (b, 1H, H(25)), 6.12 (b, 1H, H(26)), 5.70 (ddd, *J* = 10.8, 4.2, 1.0 Hz, 1H, H(37)), 4.85 (dd, *J* = 10.1, 1.4 Hz, 1H, H(27)), 4.49 (ddt, *J* = 9.5, 4.0, 2.7 Hz, 1H, H(38)), 4.44 (m, 1H), 4.38 (d, *J* = 11.9 Hz, 1H, H(41a)), 4.34 (d, *J* = 11.8 Hz, 1H, H(41b)), 4.25 (m, 1H), 4.06 (m, 1H) 3.98 (ddt, *J* = 10.8, 9.8, 5.0 Hz, 1H, H(29)), 3.86 (t, *J* = 9.6 Hz, 1H, H(28)), 3.81 (t, *J* = 10.8 Hz, 1H, H(3)), 3.73 (t, *J* = 10.3 Hz, 1H), 3.58 (m, 2H, H(40)), 3.33 (s, 3H, (29-O*Me*), 2.99 (bs, 3H, (20-O*Me*), 2.85 (dd, *J* = 17.4, 11.0 Hz, 1H, H(36a)), 2.57 (d, *J* = 16.6 Hz, 1H, H(36b)), 2.52 (dd, *J* = 14.3, 11.4 Hz, 1H, H(2a)), 2.43 – 2.34 (m, 3H, H(34, 15, 30a)), 2.19 (m, 1H), 2.10 (m, 1H), 2.03 (m, 1H, H(39a)), 1.89 – 1.73 (m, 5H), 1.74 (m, 1H, H(33a)), 1.70 (m, 1H), 1.65 (m, 2H, H(39b, 32b)), 1.57 (m, 1H), 1.52 (m, 1H, H(33b)), 1.43 (m, 1H H(30b)), 1.39 (m, 1H), 1.31 – 1.23 (m, 15H), 1.17 – 1.06 (m, 47H), 1.02 (m, 1H), 0.98 – 0.70 (m, 42H). ^{13}C NMR (150 MHz, C_6D_6): δ 207.77 (C35), 202.43 (C16), 170.23 (C1), 139.07 (C42), 135.7 (C25), 128.56 (C45), 127.80 (C43), 127.67 (C46), 124.6 (C26), 98.84 (C31), 96.97 (C17), 79.99 (C29), 77.86 (C7), 77.28 (C3), 73.11 (C41), 72.2 (C27), 72.08 (C37), 71.40 (C13), 68.99 (C9), 67.73 (C11), 67.44 (C38), 67.06 (C40),



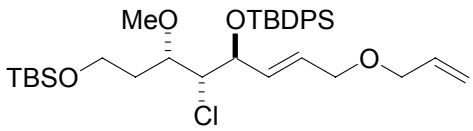
66.06 (C28), 57.75 (C29-*OMe*), 54.2 (C20-*OMe*), 46.60 (C10), 44.65, 44.38 (C34), 43.89 (C15), 40.64 (C2), 39.52 (C36), 39.0 (C30), 37.40 (C32), 37.2, 32.36 (C39), 30.73 (C4), 30.25, 30.16, 28.08, 27.2 (C19), 24.6 (C33), 23.74, 23.07, 22.35, 18.33, 18.29, 14.32, 13.01 (C34-*Me*), 7.75, 7.68, 7.54, 7.15, 7.10. HRMS (ESI+): Calcd for $C_{82}H_{153}NO_{17}Si_5Cl$ $(M + NH_4)^+$: 1598.9661. Found 1598.9668.

Ester 24. Ozone was bubbled through a solution of **22** (682 mg, 1.25 mmol) in CH_2Cl_2 (25 mL) at –78 °C for 10 min. The resulting blue solution was purged with argon (until the solution became colorless) and Ph_3P (818 mg, 3.12 mmol) was then added. The solution was warmed to room temperature for 1.0 h and concentrated *in vacuo* to yield the crude aldehyde **23** that was used without further purification.



The crude aldehyde **23** was dissolved in CH_2Cl_2 (6.2 mL) at 0 °C and methoxycarbonyl triphenylphosphorane (500 mg, 1.50 mmol) was added. The solution was allowed to warm to room temperature for 2 h and was then concentrated *in vacuo*. Purification by flash chromatography (10/1 hexanes-ethyl acetate) on SiO_2 afforded **24** (642 mg, 86% over 2 steps) as an oil. $[\alpha]_D^{20}$ = +52.0 (*c* 0.5, CH_2Cl_2). IR (ATR) 2954, 2928, 2856, 1730, 1663, 1471, 1463, 1362, 1112, 837, 611, 504 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.62 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.44 - 7.35 (m, 6H), 6.75 (dd, *J* = 15.6, 7.6 Hz, 1H), 5.69 (dd, *J* = 15.6, 0.8 Hz, 1H), 4.57 (td, *J* = 6.4, 0.8 Hz, 1H), 3.88 (dd, *J* = 6.4, 3.6 Hz, 1H), 3.75 (dt, *J* = 6.4, 3.6 Hz, 1H), 3.66 (s, 3H), 3.65 (m, 1H), 3.57 (m, 1H), 3.26 (s, 3H), 1.69 (dt, *J* = 12.4, 6.0 Hz, 2H), 1.08 (s, 9H), 1.07 (s, 9H), 0.06 (s, 6H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 145.4, 136.0, 135.9, 133.1, 130.0, 129.9, 127.8, 127.6, 123.7, 76.4, 73.2, 66.9, 59.2, 57.9, 51.4, 34.1, 27.0, 25.9, 19.4, 18.2, -5.37, -5.40. HRMS (ESI+): Calcd for $C_{32}H_{49}O_5NaSi_2Cl$ $(M + Na)^+$: 627.2693. Found 627.2699.

Compound 25. To a stirred solution of **24** (425 mg, 0.702 mmol) in CH_2Cl_2 (7.0 mL) at –78 °C was added a solution of DIBAL-H (1.0 M in hexanes, 1.54 mL, 1.54 mmol). The reaction was stirred for 5 min and then warmed to 0 °C for 0.5 h. The reaction was quenched with a 1.0 M solution of Rochelle's salt (25 mL) and stirred vigorously with ethyl acetate (25mL) for 45 min until 2 clear layers had



formed. The layers were separated and the aqueous phase re-extracted with ethyl acetate (25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield an intermediate allylic alcohol that could be used without further purification. $[\alpha]_D^{20} = -13.0$ (*c* 0.5, CH_2Cl_2). IR (ATR) 3451, 2954, 2928, 2856, 1589, 1471, 1463, 1428, 1389, 1361, 1105, 836, 703, 741, 703, 611, 505 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (m, 2H), 7.68 (m, 2H), 7.35 – 7.47 (m, 6H), 5.47 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.33 (dt, *J* = 15.2, 10, 5.2 Hz, 1H), 4.53 (t, *J* = 7.6 Hz, 1H), 3.98 (td, *J* = 6.4, 2.8 Hz, 1H), 3.90 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.74 (dt, *J* = 3.6, 1.6 Hz, 2H), 3.68 (m, 2H), 3.38 (s, 3H), 1.84 (m, 1H), 1.77 (m, 1H), 1.06 (s, 9H), 0.91 (s, 9H), 0.08 (s, 6H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 135.9, 134.6, 133.8, 133.4, 130.5, 129.8, 129.6, 127.7, 127.3, 76.0, 74.5, 67.4, 62.6, 59.4, 58.1, 34.2, 27.0, 25.9, 19.3, 18.2, -5.4. HRMS (ESI+): Calcd for $C_{31}H_{49}O_4NaSi_2Cl$ $(M + Na)^+$: 599.2751. Found 599.2750.

To a suspension of NaH (50 mg, 2.08 mmol) in THF (2.5 mL) and DMF (2.5 mL) at 0° C was added a solution of the crude allylic alcohol in THF (1.0 mL) and DMF (1.0 mL) and the resulting solution was stirred for 20 min. Allyl bromide (304 μL, 3.51 mmol) was then added and the mixture was allowed to warm to room temperature for 2.0 h. The reaction was quenched with ice water (30 mL) and extracted with ethyl acetate (2 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (10/1 hexanes-ethyl acetate) on SiO_2 to afford **25** (393 mg, 97% over 2 steps) as an oil. $[\alpha]_D^{20} = +5.0$ (*c* 0.5, CH_2Cl_2). IR (ATR) 3135, 3072, 3050, 2954, 2928, 2856, 1590, 1472, 1463, 1428, 1389, 1361, 1106, 835, 703, 611, 505 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, 2H), 7.65 (m, 2H), 7.32 – 7.45 (m, 6H), 5.82 (m, 1H), 5.76 (m, 1H), 5.57 (ddt, *J* = 15.6, 8.4, 1.2 Hz, 1H), 5.29 (dt, *J* = 15.4, 5.6 Hz, 1H), 5.15 (m, 2H), 4.47 (m, 1H), 3.86 (m, 2H), 3.70 (m, 4H), 3.65 (m, 2H), 3.33 (s, 3H), 1.74 (m, 2H), 1.05 (s, 9H), 0.90 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 135.9, 134.8, 134.0, 133.5, 131.6, 131.3, 129.8, 129.6, 127.6, 127.4, 116.5, 76.4, 74.4, 70.4, 69.5, 67.8, 59.4, 58.2, 34.4, 27.0, 25.9, 19.4, 18.2, -5.3, -5.4. . HRMS (ESI+): Calcd for $C_{34}H_{53}O_4NaSi_2Cl$ $(M + Na)^+$: 639.3062. Found 639.3063.

Compound 26. To a solution of **25** (393 mg, 0.681 mmol) in methanol (6.8 mL) at 0 °C was added PPTS (205 mg, 0.817 mmol) and the mixture was allowed to warm to

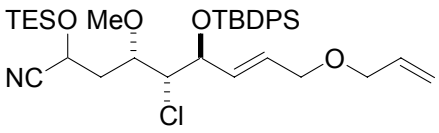
room temperature for 10 h. The reaction was quenched with aq. $NaHCO_3$ (35 mL) and extracted with CH_2Cl_2 (2 x 25 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo.* Purification by flash chromatography (10/1 to 4/1 hexanes-ethyl acetate) on SiO_2 afforded an intermediate primary alcohol (281 mg, 82%) as an oil. $[\alpha]_D^{20} = +33.0$ (*c* 0.5, CH_2Cl_2). IR (ATR) 3453, 2930, 2857, 1735, 1672, 1589, 1472, 1463, 1428, 1390, 1362, 1112, 1064, 926, 822, 742, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, 2H), 7.64 (m, 2H), 7.40 (m, 6H), 5.85 (m, 1H), 5.80 (m, 1H), 5.67 (ddt, *J* = 15.6, 8.0, 1.2 Hz, 1H), 5.39 (td, 1H, *J* = 15.5, 5.6 Hz) 5.18 (m, 2H), 4.44 (dd, *J* = 8.0, 5.6 Hz) 3.90 (dd, *J* = 5.6, 4.4 Hz), 3.78 (ddd, *J* = 5.1, 3.2, 1.5 Hz, 2H), 3.71 (m, 2H), 3.63 (m, 2H), 3.31 (s, 3H), 1.75 (m, 2H), 0.99 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 135.9, 134.8, 133.7, 133.5, 131.5, 130.8, 129.9, 129.7, 127.7, 127.5, 116.7, 78.5, 74.1, 70.6, 69.6, 67.6, 59.7, 58.3, 33.6, 27.0, 19.4. HRMS (ESI+): Calcd for $C_{28}H_{39}O_4NaSi_1Cl$ $(M + Na)^+$: 525.2193. Found 525.2198.

To a solution of oxalyl chloride (73 μL, 0.838 mmol) in CH_2Cl_2 (5.0 mL) at –78° C was added DMSO (79 μL, 1.12 mmol) and the resulting solution was stirred for 15 min. The intermediate primary alcohol (281 mg, 0.558 mmol) was then added dropwise as a solution in CH_2Cl_2 (580 μL) and the resulting reaction mixture was stirred for 15 min. Triethylamine was then added (389 μL, 2.792 mmol) and the reaction was warmed to room temperature for 1 h. The reaction was quenched with water (25 mL) and extracted with CH_2Cl_2 (2 x 25 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was used without further purification.

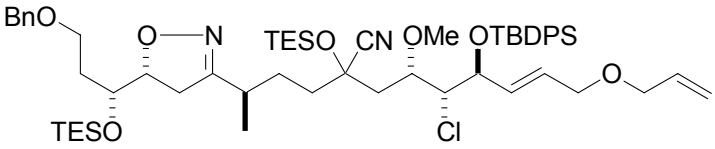
To a solution of the crude aldehyde in acetonitrile (5.6 mL) and water (5.6 mL) at 0 °C was added KCN (182 mg, 2.795 mmol) and Dowex® 50WX4 (50 mg). The resulting mixture was stirred for 1h, quenched with aq. $NaHCO_3$ (25 mL), and extracted with *tert*-butyl methyl ether (2 x 25 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*, to give a ca. 1:1 mixture of diastereomers that was used in the next step without further purification.

To a solution of crude cyanohydrin in CH_2Cl_2 (5.6 mL) at 0° C was added 2,6-lutidine (163 μL, 1.40 mmol) and TESOTf (152 μL, 0.670 mmol). The resulting reaction mixture was allowed to warm to room temperature for 1 h and was then quenched with aq. $NaHCO_3$ (25 mL). The mixture was extracted with CH_2Cl_2 (2 x 25mL) and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in*

vacuo. Purification by flash chromatography (10/1 to 4/1 hexanes-ethyl acetate) on SiO_2 afforded **26** (262 mg, 73 % over 3 steps) as an oil. IR (ATR) 2957, 2877, 1726, 1696, 1648, 1461, 1428, 1362, 1112, 1006, 937, 822, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (m, 4H), 7.57 (m, 4H), 7.39 – 7.26 (m, 12H), 5.72 (m, 2H), 5.53 (m, 2H), 5.24 (tt, *J* = 15.6, 5.5 Hz, 2H), 5.08 (m, 4H), 4.54 (dd, *J* = 7.2, 5.2 Hz, 1H), 4.46 (dd, *J* = 8.7, 4.4 Hz, 1H), 4.37 (ddd, *J* = 8.5, 6.1, 2.4 Hz, 2H), 3.92 (m, 1H), 3.85 (dd, *J* = 6.4, 3.6 Hz, 1H), 3.75 – 3.82 (m, 2H), 3.67 – 3.63 (m, 8H), 3.25 (s, 3H), 3.22 (s, 3H), 2.04 – 1.95 (m, 3H), 1.89 (m, 1H), 0.99 (s, 9H), 0.98 (s, 9H), 0.92 (t, *J* = 8.0 Hz, 12H), 0.67 – 0.58 (m, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 136.0, 135.9, 134.8, 134.7, 133.8, 133.7, 133.4, 133.3, 132.1, 132.1, 130.8, 130.7, 129.9, 129.9, 129.7, 129.7, 127.7, 127.7, 127.5, 127.5, 116.6, 116.6, 76.2, 75.6, 74.4, 74.3, 70.6, 70.6, 69.4, 67.1, 66.7, 59.5, 58.6, 58.3, 38.6, 38.1, 27.0, 19.4, 6.6, 6.5, 4.5, 4.4. HRMS (ESI+): Calcd for $C_{35}H_{52}N_1O_4NaSi_2Cl$ $(M + Na)^+$: 664.3013. Found 664.3016.

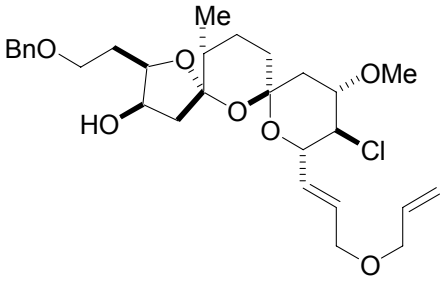


Compound 28. To a cold (-78°C) solution of compound **26** (129 mg, 0.201 μmol) in THF (4 mL) was added lithium diisopropylamide (650 μL, 0.3 M in THF 197 μmol). The mixture was stirred for 10 min before a cold (-78°C) solution of compound **27** (82 mg, 154 μmol) in THF (2.0 mL) was added over 1 min. The mixture was stirred for 2 h and quenched by the addition of aq. sat. NH_4Cl (4 mL). The layers were separated and the aqueous phase extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated *in vacuo*. The crude product was purified by flash chromatography (2/1 hexanes-ethyl acetate) on SiO_2 to afford **28** (77 mg, 48%) as an oil. $[\alpha]_D^{20} = -15.8$ (*c* 2.7, CH_2Cl_2). IR (kap.): 3071, 2956, 1687, 1646, 1589, 1457, 1240, 1111, 1007, 742, 702 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.85-7.72 (m, 4H), 7.31-7.16 (m, 10H), 7.13-7.07 (m, 1H), 5.89 (tdd, *J* = 1.4, 8.6, 15.4 Hz, 1H), 5.76 (tdd, *J* = 5.2, 10.4, 17.2 Hz, 1H), 5.36 (td, *J* = 5.3, 15.5 Hz, 1H), 5.24-5.17 (m, 1H), 5.02 (ddd, *J* = 1.5, 3.3, 10.5 Hz, 1H), 4.73 (dd, *J* = 5.3, 8.5 Hz, 1H), 4.53 (ddd, *J* = 6.3, 9.0, 10.0 Hz, 1H), 4.37-4.30 (m, 2H), 4.23 (dd, *J* = 3.7, 5.2 Hz, 1H), 4.05 (ddd, *J* = 3.6, 6.4, 8.4 Hz, 1H), 3.98 (td, *J* = 3.6, 7.1 Hz, 1H), 3.68-3.63 (m, 2H), 3.62-3.50 (m, 4H), 3.08 (s, 3H), 2.64-2.55



(m, 2H), 2.52-2.37 (m, 2H), 2.16 (dd, *J* = 7.2, 14.7 Hz, 1H), 1.96-1.71 (m, 4H), 1.70-1.54 (m, 2H), 1.19 (s, 9H), 1.10-0.84 (m, 2H), 1.03 (t, *J* = 7.9 Hz, 18 H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.81 (q, *J* = 7.5 Hz, 6H), 0.75-0.62 (m, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 160.7, 139.1, 136.4, 136.3, 135.5, 134.2, 133.9, 132.6, 130.9, 130.2, 130.0, 128.6, 128.1, 127.9, 127.9, 127.7, 121.8, 115.9, 83.0, 77.1, 74.8, 73.2, 71.9, 71.0, 70.9, 69.6, 66.9, 66.6, 57.3, 42.2, 38.8, 35.5, 33.2, 33.0, 29.3, 27.3, 19.7, 18.4, 7.2, 7.2, 6.2, 5.6. HRMS (ESI+): Calcd for $C_{58}H_{89}N_2O_7NaClSi_3$ $(M+Na)^+$: 1067.5558. Found: 1067.5563.

Compound 29. To a solution of **28** (77 mg, 76.1 μmol) in acetonitrile (3.5 mL) and water (3.5 mL) was added $Mo(CO)_6$ (20 mg, 76.1 μmol) and the mixture was heated to 90° C for 1 h. The reaction was cooled to room temperature, flushed through a plug of SiO_2 (4/1 hexanes ethyl acetate), and concentrated *in vacuo* to yield an intermediate ketone as a brown oil that was used without further purification.

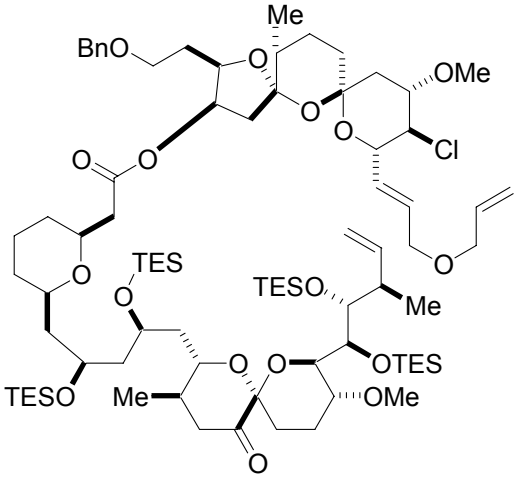


To a solution of the crude ketone in DMF (2.0 mL) and water (40 μL) at 0° C was added a solution of TASF (105 mg, 0.381 mmol) in DMF (1.8 mL). The reaction was allowed to warm to room temperature for 1.75 h, and was then quenched with a pH = 7.4 buffer solution (25 mL) and extracted with ethyl acetate (2 x 25 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield an intermediate *hemi*-ketal that was used without further purification.

To a solution of the crude *hemi*-ketal in CH_2Cl_2 (5.0 mL) and methanol (500 μL) at 0°C was added PPTS (7 mg, 22.8 μmol) and the mixture was warmed to room temperature for 45 min. The reaction was quenched with aq. $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (2 x 20 mL). Purification by flash chromatography (4/1 to 2/1 hexanes-ethyl acetate) afforded **29** (18.4 mg, 45% over 3 steps) as an oil. $[\alpha]_D^{20}$ = +13.8 (*c* 1.0, CH_2Cl_2). IR (ATR) 3480, 3030, 2932, 1646, 1454, 1381, 1191, 1170, 1095, 975, 923 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.14 (m, 5H), 6.17 (dtd, *J* = 15.5, 5.3, 1.0 Hz, 1H), 6.08 (ddt, *J* = 15.5, 5.3, 1.1 Hz, 1H), 5.82 (m, 1H), 5.78 (m, 1H), 5.21 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.99 (dq, *J* = 10.4, 1.5 Hz, 1H), 4.57 (ddd, *J* = 10.4, 5.4, 1.0 Hz, 1H), 4.13 (m, 1H), 4.09 (m, 2H), 3.89 (m, 1H), 3.87 (m, 2H), 3.80 (dt, *J* = 5.3, 1.5 Hz, 2H), 3.66 (t, *J* = 9.6 Hz, 1H), 3.29 (s, 3H), 3.26 (m, 1H), 3.13 (m, 1H),

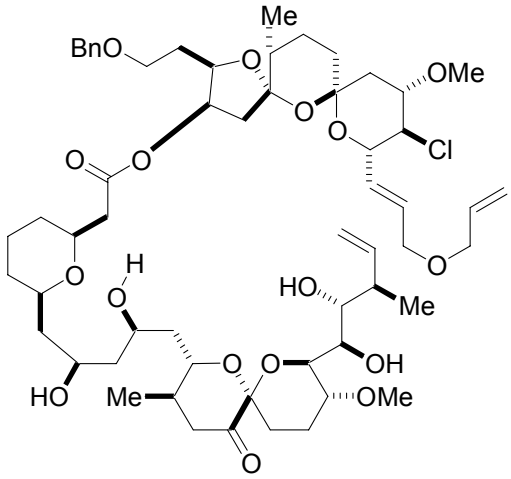
2.79 (d, *J* = 2.2 Hz, 1H), 2.34 (ddd, *J* = 14.7, 6.5, 0.9 Hz, 1H), 2.22 – 2.08 (m, 4H), 1.12 (m, 1H), 1.70 (dt, 13.1, 3.2 Hz, 1 H), 1.54 (m, 1H), 1.35 (m, 2H*), 1.22 (dq, *J* = 12.9, 3.4 Hz, 1H*), 1.15 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 135.5, 130.7, 129.6, 128.7, 128.1, 127.9, 116.1, 109.5, 98.1, 84.2, 79.6, 73.6, 73.5, 71.7, 71.1, 70.3, 67.5, 64.9, 57.5, 48.3, 43.6, 38.3, 36.3, 29.3, 24.3, 16.8. HRMS (ESI+): Calcd for $C_{29}H_{41}O_7NaCl$ $(M + Na)^+$: 559.2430. Found 559.2433.

Compound 30. To a solution of acid **2** (25 mg, 24.2 μmol) in toluene (1.0 mL) at 0 °C was added triethylamine (9.0 μL, 50.1 μmol) and 2,4,6-trichlorobenzoyl chloride (5.0 μL, 30.6 μmol) and the reaction was stirred for 1 h. A solution of alcohol **29** (11 mg, 20.4 μmol) and DMAP (13 mg, 0.102 mmol) in toluene (1.0 mL) was then added and the mixture was stirred at room temperature for 6 h. The reaction was quenched with aq. $NaHCO_3$ (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography (10/1 hexanes-ethyl acetate) on SiO_2 afforded **30** (24 mg, 82%) as an oil. $[\alpha]_D^{20} = -18.7$ (*c* 0.5, CH_2Cl_2). IR (ATR) 2953, 2876, 1738, 1580, 1456, 1416, 1380, 1240, 1190, 1070, 1004, 974, 924, 725 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.39 (m, 2H), 7.24 (m, 2H), 7.13 (m, 1H), 6.38 (m, 1H), 6.26 (dt, *J* = 15.6, 5.5 Hz, 1H), 6.19 (dd, *J* = 15.6, 4.4 Hz, 1H), 5.81 (m, 1H), 5.30 (m, 1H), 5.22 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.13 (m, 2H), 5.00 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.50 (m, 1H), 4.43 (m, 2H), 4.36 (m, 2H), 4.29 (m, 1H), 4.25 (dd, *J* = 3.7, 1.8 Hz, 1H), 4.07 (m, 1H), 3.91 – 3.80 (m, 7H), 3.63 (m, 2H), 3.56 (m, 2H), 3.31 (s, 3H), 3.16 (dd, *J* = 9.3, 4.3 Hz, 1H), 3.06 (s, 3H), 3.98 (m, 1H), 2.78 (t, *J* = 13.3 Hz, 1H), 2.66 (dd, *J* = 15.5, 5.9 Hz, 1H), 2.37 – 2.25 (m, 3H), 2.25 – 2.02 (m, 7H), 2.02 – 1.75 (m, 8H), 1.69 (m, 3H), 1.64 – 1.43 (m, 4H), 1.42 – 1.17 (m, 6H), 1.29 (d, *J* = 7.1 Hz, 3H), 1.10 (m, 36H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.85 – 0.70 (m, 27H). ^{13}C NMR (100 MHz, C_6D_6): δ 201.6, 170.1, 143.0, 139.3, 135.5, 129.9, 129.3, 128.5, 128.1, 127.9, 127.6, 116.2, 113.0, 108.9, 98.1, 97.3, 80.0, 79.8, 79.3, 77.5, 75.2, 74.7, 74.4, 74.3, 74.1, 73.3, 73.2, 73.1, 71.3, 70.3, 68.2, 67.9, 67.4, 65.0, 57.6, 54.7, 48.4, 47.0, 45.8, 43.4, 42.0, 41.9, 40.2, 39.8, 38.2, 36.3,

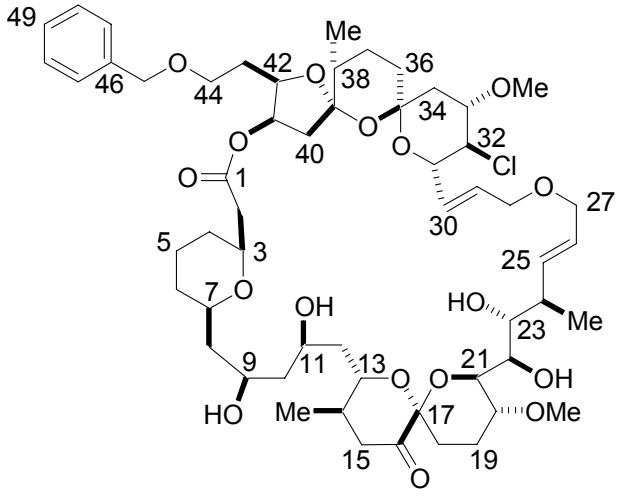


32.1, 31.6, 29.7, 26.9, 24.1, 23.8, 22.6, 19.1, 18.2, 16.7, 7.5, 7.5, 7.4, 6.3, 5.9, 5.8. HRMS (ESI+): Calcd for $C_{82}H_{143}O_{17}NaClSi_4$ $(M + Na)^+$: 1569.8966. Found 1569.8983.

Compound 31. To a solution of **30** (18 mg, 11.6 μmol) in methanol (1.4 mL), diethyl ether (400 μL) and water (200 μL) at 0 °C was added PPTS (10 mg) and the resulting mixture was stirred at room temperature for 12 h. The reaction was quenched with aq. $NaHCO_3$ (15 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash chromatography (1/1 to 0/1 hexanes-ethyl acetate) afforded **31** (8.1mg, 64%) as an oil. $[\alpha]_D^{20} = -52.0$ (*c* 0.3, CH_2Cl_2). IR (ATR) 2923, 2852, 1736, 1660, 1632, 1456, 1377, 1259, 1216, 1193, 1090, 975, 925, 878, 803 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.40 (m, 2H), 7.25 (m, 2H), 7.12 (m, 1H), 6.23 (m, 2H), 6.15 (m, 1H), 5.80 (m, 1H), 5.30 (m, 1H), 5.26 (m, 1H), 5.21 (ddd, *J* = 17.3, 3.4, 1.6 Hz, 1H), 5.13 (dd, *J* = 10.3, 1.9 Hz, 1H), 4.99 (ddd, *J* = 10.5, 2.7, 1.3 Hz, 1H), 4.51 (m, 1H), 4.48 (m, 1H), 4.46 (m, 2H), 4.31 (m, 1H), 4.23 (m, 1H), 4.08 (m, 2H), 3.94 (m, 1H), 3.86 (m, 1H), 3.81 dt (*J* = 5.4, 1.4 Hz, 2H), 3.75 (m, 1H), 3.66 – 3.53 (m, 4H), 3.43 (m, 1H), 3.36 (s, 3H), 3.35 (m, 1H), 3.09 (s, 3H), 2.99 (m, 1H), 2.38 (dd, *J* = 15.6, 6.5 Hz, 1H), 2.31 (dd, *J* = 14.4, 2.5 Hz, 1H), 2.26 (m, 1H), 2.20 (m, 1H), 2.15 (m, 1H), 2.14 – 2.07 (m, 3H), 2.05 (m, 1H), 2.03 (m, 1H), 2.00 (m, 1H), 1.98 (m, 1H), 1.88 (m, 1H), 1.84 (m, 1H), 1.83 – 1.64 (m, 4H), 1.57 (m, 1H), 1.53 (m, 2H), 1.48 (m, 1H), 1.44 (m, 2H), 1.43 (m, 2H), 1.38 (m, 2H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.31 (m, 2H), 1.25 – 1.02 (m, 4H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.95 – 0.81 (m, 4H), 0.62 (d, *J* = 6.6 Hz, 3H), 0.60 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 202.1, 170.5, 139.5, 139.0, 135.4, 129.6, 129.2, 128.6, 116.4, 116.3, 109.0, 98.1, 97.6, 80.0, 79.2, 75.5, 74.5, 74.4, 73.9, 73.2, 73.1, 71.8, 71.6, 71.3, 70.4, 70.3, 68.3, 66.3, 66.2, 65.4, 65.1, 57.6, 56.3, 47.0, 44.2, 43.4, 43.3, 42.6, 41.7, 40.4, 39.7, 38.1, 36.3, 31.1, 31.0, 29.7, 27.7, 24.1, 23.5, 18.2, 18.0, 16.6. HRMS (ESI+): Calcd for $C_{58}H_{87}O_{17}NaCl$ $(M + Na)^+$: 1091.5712. Found 1091.5705.



Compound 32. To a stirred solution of **31** (7 mg, 6.4 μmol) in CH_2Cl_2 (2.0 mL) was added complex **10** (1 mg, 1.3 μmol) and the mixture was heated to 40 °C for 15 h. The reaction was cooled to room temperature and concentrated *in vacuo*. Purification by flash chromatography (2/1 to 1/1 to 0/1 hexanes-ethyl acetate) afforded **32** (4.3 mg, 64%) as an oil. $[\alpha]_D^{20} = -10.1$ (*c* 0.2, CH_2Cl_2). IR (ATR) 2979, 2933, 1638, 1458, 1415, 1259, 1221, 1211, 1169, 1123, 1090, 1025, 987, 962, 911, 797 cm^{-1}. ^1H NMR (600 MHz, C_6D_6): δ 7.57 (d, *J* = 7.4 Hz, 2H, H(47, 47')), 7.25 (t, *J* = 7.6 Hz, 2H, H(48, 48')), 7.09 (m, 1H, H(49)), 6.31 (m, 1H, H(30)), 6.21 (dt, *J* = 15.6, 4.6 Hz, 1H, H(29)), 6.06 (dd, *J* = 15.4, 8.2 Hz, 1H, H(25)), 5.74 (dt, *J* = 15.6, 4.8 Hz, 1H, H(26)), 5.18 (dd, *J* = 6.1, 3.6 Hz, 1H, H(41)), 4.88 (d, *J* = 12.4 Hz, 1H, H(45a)), 4.69 (d, *J* = 12.4 Hz, 1H, H(45b)), 4.56 (m, 1H, H(7)), 4.44 (dd, *J* = 9.8, 3.6 Hz, 1H, H(31)), 4.34 (d, *J* = 9.6 Hz, 1H, H(21)), 4.29 (m, 1H, H9)), 4.10 – 4.00 (m, 3H, H(13, 42, 22)), 3.93 (dd, *J* = 12.9, 4.6 Hz, 1H, H(28a)), 3.91 (m, 1H (O*H*)), 3.87 (dd, *J* = 13.2, 5.5 Hz, 1H, H(28b)), 3.82 (m, 3H, H(33, 27a, 27b)), 3.67 (m, 1H, H(23)), 3.63 – 3.55 (m, 3H, H(3, 32, 11)), 3.31 (s, 3H, (30 O*Me*)), 3.27 (m, 1H, H(20)), 2.92 (s, 3H, (20 O*Me*)), 2.33 (m, 2H, H(15a, 2a)), 2.26 (dd, *J* = 14.2, 4.6 Hz, 1H, H(15b)), 2.20 (dd, *J* = 15.4, 6.5 Hz, 1H, H(40a)), 2.16 (dd, *J* = 14.0, 4.3 Hz, 1H), 2.11 (dd, *J* = 14.7, 2.6 Hz, 1H, H(2b)), 2.07 (dd, *J* = 12.7, 4.9 Hz, 1H, H(34a)), 2.03 (m, 2H, H(43)), 1.90 (d, *J* = 16.0 Hz, 1H, H(40b)), 1.78 (m, 1H, H(19a)), 1.75 (m, 1H, H(18b)), 1.71 (m, 1H), 1.69 (m, 1H, H(19b)), 1.66 (m, 1H, H(14)), 1.58 (m, 2H, H(10)), 1.53 (m, 1H, H(8a)), 1.50 (m, 1H), 1.48 – 1.39 (m, 3H, H(8b, 38, 24)), 1.38 – 1.15 (m, 6H), 1.32 (d, *J* = 7.2 Hz, 3H, (24-*Me*)), 1.14 – 1.05 (m, 3H, H(4, 12b)), 0.98 (m, 1H), 0.95 – 0.75 (m, 3H), 0.89 (d, *J* = 6.7 Hz, 3H, (38-*Me*)), 0.62 (d, *J* = 6.6 Hz, 3H, (14-*Me*)). ^{13}C NMR (150 MHz, C_6D_6): δ 201.9 (C16), 169.4 (C1), 138.9 (C46), 132.6 (C25), 129.2 (C29, C30), 129.1 (C26), 108.9 (C39), 98.0 (C35), 97.4 (C17), 79.8 (C42) , 79.3 (C33), 75.3 (C23), 74.9 (C11), 74.2 (C3), 74.1 (C41), 73.6 (C20), 73.3 (C45), 72.5 (C31), 71.8 (C13), 71.7 (C21), 70.3 (C22), 70.0 (C27), 69.6 (C28), 68.4 (C44), 65.4 (C32), 65.2 (C9), 65.1 (C7), 57.6 (C33-*OMe*), 55.9 (C20-*OMe*), 46.9 (C8, C40), 44.3 (C15), 44.2 (C10), 43.5 (C34), 43.0 (C2), 40.9, 39.8 (C14), 38.2



(C38), 38.1 (C24), 36.2, 31.8 (C12), 31.5 (C4), 30.2, 29.8 (C43), 27.6 (C18), 24.0, 23.9 (C19), 23.7, 23.1, 18.9 (C24-*Me*), 18.0 (C14-*Me*), 16.6 (C38- *Me*). HRMS (ESI+): Calcd for $C_{56}H_{82}O_{17}Cl$ $(M)^-$: 1061.5258. Found 1061.5246.