

Supporting Information

Design, Synthesis, and Evaluation of Analogues of (+)-14-Normethyldiscodermolide

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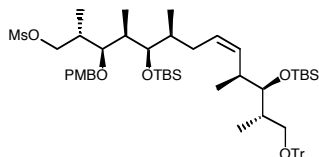
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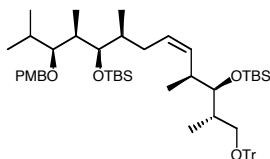
Materials and Methods. Reactions were carried out in oven or flame-dried glassware under an argon atmosphere, unless otherwise noted. All solvents were reagent grade. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone under argon. *n*-butyllithium and *t*-butyllithium were purchased from Aldrich. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Silicycle and Sorbent Technologies. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Infrared spectra were recorded on a Jasco Model FT/IR-480 Plus spectrometer. Proton and carbon-13 NMR spectra were recorded on a Bruker AMX-500 spectrometer. Chemical shifts are reported relative to chloroform (δ 7.26), methanol (δ 3.31), acetonitrile (δ 1.94), or benzene (δ 7.15) for ¹H-NMR and either chloroform (δ 77.0), methanol (δ 49.2), acetonitrile (δ 118.7), or benzene (δ 128.0) for ¹³C-NMR. Optical rotations were measured on a Perkin-Elmer model 241 polarimeter. High resolution mass spectra were measured at the University of Pennsylvania Mass Spectrometry Service Center.

Experimental Details



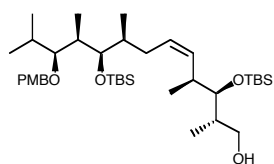
(+)-**S1**

Mesylate (+)-S1: To a room temperature solution (CH_2Cl_2 , 0.1 M) of alcohol (+)-**3** (30 mg, 0.032 mmol) was added triethylamine (7.0 μL , 0.048 mmol), then methanesulfonylchloride (4 μL , 0.048 mmol) dropwise via syringe. The reaction was then stirred for 1 h and quenched with 1 mL saturated NaHCO_3 solution. The mixture was then extracted (2x, CH_2Cl_2), washed with brine, dried (MgSO_4), filtered, and concentrated. The crude material was then purified by flash chromatography (25 % EtOAc/hexanes) to afford 29 mg (91%) of (+)-**S1** as a clear oil; $[\alpha]_{\text{D}}^{23} +10$ (c 0.54, CHCl_3); IR (film, NaCl) 2946, 2854, 1512, 1466, 1352, 1250, 1173, 1034, 957, 834, 772, 700 cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 7.59 (d, J = 7.3 Hz, 6H), 7.31 (d, J = 9.1 Hz, 2H), 7.15 (m, 6H), 7.05 (app t, J = 7.3 Hz, 3H), 6.82 (d, J = 8.6 Hz, 2H), 5.28 (app t, J = 10.5 Hz, 1H), 5.15 (ddd, J = 10.3, 10.3, 4.6 Hz, 1H), 4.51 (d, J = 3.1 Hz, 2H), 4.16 (d, J = 5.1 Hz, 2H), 3.71 (dd, J = 6.7, 2.6 Hz, 1H), 3.66 (dd, J = 6.7, 4.0 Hz, 1H), 3.46 (dd, J = 8.8, 6.2 Hz, 1H), 3.32 (dd, J = 6.8, 4.1 Hz, 1H), 3.30 (s, 3H), 3.07 (app t, J = 8.7 Hz, 1H), 2.76 (m, 1H), 2.40 (m, 1H), 2.17 (s, 3H), 2.04 (m, 1H), 1.97 (m, 1H), 1.92 (m, 1H), 1.80 (m, 1H), 1.33 (m, 1H), 1.17 (d, J = 6.9 Hz, 3H), 1.12 (d, J = 6.9 Hz, 6H), 1.03 (s, 9H), 0.96 (d, J = 6.8 Hz, 3H), 0.94 (s, 9H), 0.92 (d, J = 6.9 Hz, 3H), 0.14 (s, 3H), 0.12 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.9, 145.1, 135.0, 131.1, 129.4, 129.2, 128.3, 127.9, 127.1, 114.2, 86.9, 82.2, 78.3, 77.0, 75.1, 72.0, 66.6, 54.8, 40.5, 39.8, 38.0, 37.0, 36.5, 35.9, 33.0, 26.5, 26.3, 18.8, 18.5, 18.0, 15.0, 14.2, 13.9, 11.4, -3.1, -3.2, -3.7, -3.7; high resolution mass spectrum (ES^+) m/z 1023.5636 [($\text{M}+\text{Na}$) $^+$; calcd for $\text{C}_{58}\text{H}_{88}\text{O}_8\text{NaSi}_2\text{S}$: 1023.5703].



(+)-**S2**

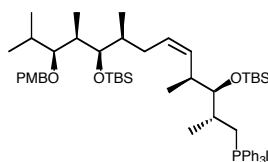
Trityl ether (+)-S2: To a 0° C ethereal solution (0.1 M) of mesylate (+)-**S1** (27 mg, 0.0269 mmol) was added LiAlH₄ (s, 1 mg, 0.0263 mmol). After 1 h the reaction was warmed to ambient temperature and another aliquot of LiAlH₄ was added. The reaction was quenched with Rochelle's solution and the resultant mixture extracted (2 x, Et₂O, 2 x CH₂Cl₂). The combined organic extracts were washed with brine, dried (MgSO₄), filtered, and concentrated. The crude material was then purified by flash chromatography (10% EtOAc/hexanes) to furnish 19 mg (+)-**S2** (80%) as a yellow oil. $[\alpha]_D^{23} +20$ (c 0.60, CHCl₃); IR (film, NaCl) 2930, 1454, 1614, 1251, 1037, 834, 760 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 8.2 Hz, 6H), 7.52 (m, 8H), 7.46 (app dt, *J* = 7.6, 1.1 Hz, 3H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.32 (app t, *J* = 10.5 Hz, 1H), 5.18 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1H), 4.74 (ABq, *J* = 10.8, $\Delta\nu$ = 24.6, 2H), 4.04 (s, 3H), 3.74 (m, 2H), 3.43 (dd, *J* = 8.8, 6.3 Hz, 1H), 3.31 (app t, *J* = 5.4 Hz, 1H), 3.06 (app t, *J* = 8.7 Hz, 1H), 2.73 (m, 1H), 2.40 (m, 1H), 2.10 (m, 4H), 1.85 (m, 1H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 6H), 1.18 (s, 9H), 1.13 (d, *J* = 6.6 Hz, 3H), 1.08 (s, 9H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.32 (s, 3H), 0.28 (s, 3H), 0.26 (s, 3H), 0.21 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.0, 144.6, 134.5, 131.5, 128.9, 128.8, 127.6, 127.2, 126.7, 113.7, 86.3, 85.8, 77.7, 76.6, 74.8, 66.3, 55.3, 40.0, 39.4, 38.0, 35.2, 32.3, 31.0, 26.3, 26.1, 20.5, 18.6, 18.2, 17.7, 17.5, 14.3, 13.7, 11.2, -3.4, -3.4, -3.9, -4.0; high resolution mass spectrum (ES⁺) *m/z* 929.5887 [(M+Na)⁺; calcd for C₅₇H₈₆O₅NaSi₂: 929.5912].



(+)-S3

Alcohol (+)-S3: Anhydrous MeOH (32 μ L) was added to a cold (0 °C) solution of chlorocatecholborane (199 mg, 1.288 mmol) in 2.0 mL of CH₂Cl₂. The resulting solution was added in 0.25 mL (0.161 mmol) aliquots at 10 min intervals to a 0.1 M solution (CH₂Cl₂) of trityl ether (+)-**S2** (146 mg, 0.161 mmol) at 0 °C until TLC (20% EtOAc/hexanes) indicated ca. 90% reaction completion, at which point the reaction was quenched via dropwise addition of 5 mL of saturated NaHCO₃. The resulting mixture was stirred for

15 min, diluted with 10 mL Et₂O, stirred an additional 30 min, and the layers were separated. The aqueous layer was extracted (3 × Et₂O), and the resulting organic layers were combined, washed (water and saturated brine solution), dried (MgSO₄), filtered, added to 3 g of SiO₂ and concentrated. Flash chromatography (gradient elution: 2% EtOAc/hexanes → 10% EtOAc/) provided (+)-**S3** (82 mg, 77%) as a colorless oil. $[\alpha]_D^{23} +18$ (*c* 0.58 CHCl₃); IR (film, NaCl) 3476, 2953, 1512, 1461, 1247, 1033, 832, 767 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.25 (d, *J* = 9.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.23 (m, 2H), 4.47 (ABq, *J* = 10.8, Δ*ν* = 40, 2H), 3.78 (s, 3H), 3.67 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.54 (app t, *J* = 5.4 Hz, 1H), 3.51 (dd, *J* = 4.9, 3.2 Hz, 1H), 3.44 (dd, *J* = 6.7, 3.7 Hz, 1H), 3.06 (app t, *J* = 5.4 Hz, 1H), 2.65 (m, 1H), 2.30 (br s, 1H), 1.99 (m, 1H), 1.94 (m, 1H), 1.90 (m, 1H), 1.84 (m, 2H), 1.66 (m, 1H), 0.98 (d, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 6H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 18H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) 159.0, 134.1, 131.5, 129.0, 128.5, 113.8, 85.8, 81.3, 77.0, 74.8, 65.3, 55.3, 39.3, 38.4, 38.0, 36.9, 32.5, 31.0, 26.3, 26.2, 20.8, 18.6, 18.3, 17.8, 17.4, 15.9, 14.2, 11.3, -3.4, -3.5, -3.6, -3.8; high resolution mass spectrum (ES⁺) *m/z* 687.4804 [(M+Na)⁺; calcd for C₃₈H₇₂O₅NaSi₂: 687.4816].

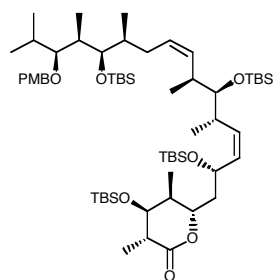


(+)-4

Phosphonium Salt (+)-4: To a 0 °C solution (benzene/Et₂O, 1:1, 0.1 M) of alcohol (+)-**S3** (75 mg, 0.1128 mmol) was added triphenylphosphine (86 mg, 0.327 mmol), imidazole (21 mg, 0.3146 mmol), and I₂ (80 mg, 0.315 mmol). The resultant yellow suspension was stirred 5 min at 0 °C, then warmed to ambient temperature. The reaction was then poured into 10 mL of saturated Na₂S₂O₃ and diluted with Et₂O. The layers were separated, and the organic layer was washed (saturated NaHCO₃, brine), dried (MgSO₄), added to SiO₂ and concentrated. The crude material was then purified by flash

chromatography (10% EtOAc/hexanes, 1% Et₃N) to afford the corresponding iodide (contaminated with ca. 20% PPh₃) which was taken onto the next step without further purification.

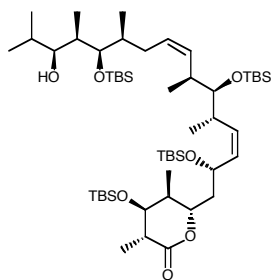
To a mixture of the iodide and diisopropylethylamine (0.2 mL, 1.14 mmol) was added triphenylphosphine (100 mg, 0.381 mmol). The resulting mixture was heated to 100° C for 6 h, cooled, and chromatographed (CH₂Cl₂ load, then CH₂Cl₂ □ 20% CH₃CN/CH₂Cl₂) to provide (+)-**4** as a light yellow solid (92 mg, 80% yield from alcohol (+)-**S3**. $[\alpha]_D^{23} + 14$ (c 0.4, CHCl₃) ; IR (film, NaCl) 2922, 2044, 1433, 1250, 1111, 830 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) □ 7.81 (m, 9H), 7.69 (ddd, *J* = 7.7, 7.7, 3.4 Hz, 6H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.56 (app t, *J* = 10.7 Hz, 1H), 5.25 (ddd, *J* = 10.5, 10.5, 4.7 Hz, 1H), 4.46 (ABq, *J* = 10.8, $\Delta\nu$ = 28.8, 2H), 3.79 (m, 2H), 3.76 (s, 3H), 3.50 (app t, *J* = 4.4 Hz, 1H), 3.32 (ddd, *J* = 15.5, 11.2, 11.2 Hz, 1H), 3.06 (app t, *J* = 5.4 Hz, 1H), 2.55 (m, 1H), 2.33 (app t, *J* = 7.5 Hz, 1H), 1.94 (m, 3H), 1.81 (dd, *J* = 11.9, 6.3 Hz, 1H), 1.60 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.84 (s, 9H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H), 0.10 (s, 3H), 0.04 (s, 3H), -0.02 (s, 3H), -0.05 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) □ 195.0, 135.2, 135.1, 134.2, 133.7, 133.6, 132.1, 132.0, 131.9, 131.4, 130.7, 130.6, 129.0, 128.5, 128.4, 128.2, 118.9, 118.1, 113.8, 85.7, 77.0, 76.6, 74.9, 55.3, 39.2, 38.1, 35.7, 34.1, 32.2, 30.8, 29.3, 26.2, 26.0, 20.6, 18.5, 18.3, 17.4, 17.2, 16.8, 14.6, 11.2, -3.3, -3.4, -3.9 (2); high resolution mass spectrum (ES⁺) *m/z* 909.5813 [(M-I)⁺; calcd for C₅₆H₈₆O₄PSi₂: 909.5813].



(+)-**6**

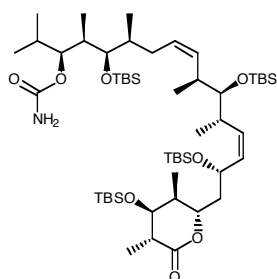
Diene (+)-6: Phosphonium salt (+)-**4** (70 mg, 0.0675 mmol), was azeotropically dried with benzene (3 □ 1.0 mL) using a double manifold and further dried by heating to 50 °C under vacuum (0.2 torr) for 12 h. The salt was back-filled with argon, dissolved in 300 μ L of freshly distilled THF, sparged with argon for 15

min, and cooled to $-20\text{ }^{\circ}\text{C}$. The resultant solution was treated with sodium bis(trimethylsilyl)amide (1.0 M in THF, 64 μL), stirred 15 min, warmed to $0\text{ }^{\circ}\text{C}$, stirred 30 min, and re-cooled to $-20\text{ }^{\circ}\text{C}$. To this orange/red solution was transferred via cannula a degassed solution of aldehyde (–)-**5** (30 mg, 0.0675 mmol) in THF (300 μL) over 1 min. The orange solution was allowed to slowly warm to $-8\text{ }^{\circ}\text{C}$ over 3.0 h. The resulting light yellow solution was quenched with saturated NH_4Cl and diluted ($\text{Et}_2\text{O}/\text{H}_2\text{O}$). The layers were separated, and the aqueous layer was extracted (3 \times Et_2O). The combined organic layers were dried (Na_2SO_4), concentrated, and chromatographed (gradient elution: 2% $\text{EtOAc}/\text{hexanes}$ \rightarrow 50% $\text{EtOAc}/\text{hexanes}$; then 40% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$) to afford *cis* isomer (+)-**6** (22 mg, 43%), and phosphonium salt (+)-**4** (30 mg, 43%). $[\alpha]_{\text{D}}^{23} +26$ (*c* 0.50 CHCl_3); IR (film, NaCl) 2929, 2851, 1738, 1458, 1246, 1045, 832, 776 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J = 9.4\text{ Hz}$, 2H), 6.85 (d, $J = 8.5\text{ Hz}$, 2H), 5.31 (m, 2H), 5.22 (app t, $J = 10.5\text{ Hz}$, 1H), 5.15 (ddd, $J = 10.9, 8.9, 5.5\text{ Hz}$, 1H), 4.78 (app t, $J = 9.0\text{ Hz}$, 1H), 4.49 (app t, $J = 10.7\text{ Hz}$, 1H), 4.47 (ABq, $J = 10.8$, $\Delta\nu = 14.1$, 2H), 3.78 (s, 3H), 3.60 (app t, $J = 2.3\text{ Hz}$, 1H), 3.52 (app t, $J = 4.5\text{ Hz}$, 1H), 3.28 (app t, $J = 5.1\text{ Hz}$, 1H), 3.06 (app t, $J = 5.3\text{ Hz}$, 1H), 2.60 (m, 3H), 1.97 (m, 2H), 1.90 (dd, $J = 12.4, 6.6\text{ Hz}$, 1H), 1.85 (dd, $J = 12.4, 5.8\text{ Hz}$, 1H), 1.77 (ddd, $J = 9.7, 6.7, 2.3\text{ Hz}$, 1H), 1.72 (app t, $J = 12.9\text{ Hz}$, 1H), 1.67 (m, 1H), 1.56 (m, 1H), 1.20 (d, $J = 7.6\text{ Hz}$, 3H), 0.96 (d, $J = 6.4\text{ Hz}$, 3H), 0.95 (d, $J = 6.8\text{ Hz}$, 6H), 0.93 (d, $J = 6.8\text{ Hz}$, 6H), 0.92 (s, 9H), 0.90 (d, $J = 7.1\text{ Hz}$, 3H), 0.88 (s, 9H), 0.86 (s, 9H), 0.85 (s, 9H), 0.81 (d, $J = 6.7\text{ Hz}$, 3H), 0.05 (s, 6H), 0.04 (s, 6H), 0.03 (s, 6H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.2, 158.2, 135.5, 133.6, 132.5, 131.5, 129.0, 127.1, 113.8, 85.8, 80.0, 77.0, 76.8, 74.9, 74.8, 64.6, 55.3, 44.1, 42.9, 39.4, 38.1, 37.5, 35.0, 34.2, 32.5, 31.0, 30.4, 29.7, 26.3, 26.2, 25.9, 25.7, 20.5, 18.6, 18.4, 18.1, 18.0, 17.7, 17.2, 16.4, 16.0, 14.3, 14.1, 11.2, -3.1, -3.4, -4.2, -4.3, -4.5, -4.8; high resolution mass spectrum (ES^+) m/z 1097.7469 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{60}\text{H}_{114}\text{O}_8\text{Si}_4\text{Na}$: 1097.7489].



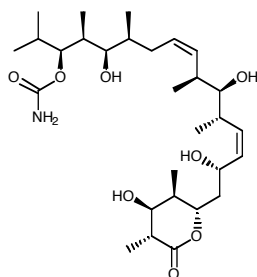
(+)-S4

Alcohol (+)-S4 To a room temperature solution of PMB ether (+)-6 (20 mg, 0.0186 mmol) in CH₂Cl₂ (2.0 mL) was treated with H₂O (100 μ L) and DDQ (5.1 mg, 0.0223 mmol). The mixture was stirred for 30 min and quenched with 5.0 mL saturated NaHCO₃, diluted with CH₂Cl₂, and washed with H₂O and saturated brine solution. The combined organic layers were dried (MgSO₄), filtered and concentrated. Flash chromatography (5% EtOAc/hexanes) provided (+)-S4 (14.0 mg, 78%) and recovered starting material (+)-6 (4.0 mg, 22%). $[\alpha]_D^{23}$ +26 (*c* 0.43, CHCl₃); IR (film, NaCl) 3522, 2920, 2851, 1727, 1458, 1251, 1044, 832, 771 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.36 (app t, *J* = 10.2 Hz, 1H), 5.31 (dd, *J* = 11.1, 7.7 Hz, 1H), 5.24 (app t, *J* = 10.7 Hz, 1H), 6.16 (ddd, *J* = 9.9, 9.9, 5.1 Hz, 1H), 4.80 (app t, *J* = 9.0, 1H), 4.51 (app t, *J* = 10.0 Hz, 1H), 3.66 (app t, *J* = 4.2 Hz, 1H), 3.64 (app t, *J* = 2.4 Hz, 1H), 3.32 (dd, *J* = 5.6, 4.5 Hz, 1H), 3.20 (m, 1H), 2.62 (m, 3H), 2.08 (m, 1H), 1.98 (m, 1H), 1.81 (m, 2H), 1.72 (m, 4H), 1.59 (ddd, *J* = 13.8, 11.2, 2.0 Hz, 1H), 1.22 (d, *J* = 7.6 Hz, 3H), 0.98 (d, *J* = 5.8 Hz, 3H), 0.97 (d, *J* = 6.4 Hz, 6H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 9H), 0.83 (d, *J* = 6.9 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (app s, 6H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 135.7, 133.6, 132.5, 127.3, 80.0, 79.9, 79.0, 77.1, 74.9, 64.7, 44.1, 42.9, 38.8, 37.5, 35.1, 34.2, 31.6, 31.3, 30.3, 29.3, 26.3, 26.2, 25.9, 25.7, 19.3, 18.8, 18.4, 18.1, 18.0, 17.3, 16.4, 15.8, 14.6, 14.1, 8.8, -3.1, -3.3, -4.0, -4.2, -4.3, -4.5, -4.9; high resolution mass spectrum (ES⁺) *m/z* 977.6865 [(M+Na)⁺; calcd for C₅₂H₁₀₆O₇Si₄Na: 977.6913]



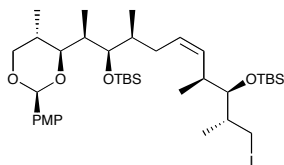
(+)-S5

Carbamate (+)-S5. A solution of alcohol (+)-S4 (13 mg, 0.0136 mmol) in CH₂Cl₂ (1.0 mL) was treated with Cl₃CCON=C=O (100 μ L, 1 M solution) at room temperature for 30 min. The solution was loaded directly onto neutral Al₂O₃ plug. After 4 h, the material was flushed from the Al₂O₃ (EtOAc, 50 mL), concentrated, and purified by flash chromatography (10% ethyl acetate/hexanes) providing 10 mg of (+)-S5 (71%). $[\alpha]_D^{23}$ +21 (*c* 0.075, CHCl₃); IR (film, NaCl) 3362, 2922, 2857, 1732, 1250, 1045, 836 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.33 (app t, *J* = 11.1 Hz, 1H), 5.23 (m, 1H), 5.17 (m, 1H), 4.79 (app t, *J* = 9.0 Hz, 1H), 4.56 (app t, *J* = 9.0 Hz, 1H), 4.49 (m, 4H), 3.63 (app t, *J* = 2.2 Hz, 1H), 3.46 (dd, *J* = 5.3, 3.5 Hz, 1H), 3.29 (app t, *J* = 5.1 Hz, 1H), 2.62 (m, 1H), 2.59 (dd, *J* = 8.1, 2.8 Hz, 1H), 2.57 (m, 1H), 1.97 (m, 2H), 1.89 (m, 2H), 1.80 (m, 1H), 1.72 (m, 2H), 1.56 (ddd, *J* = 13.6, 10.0, 1.7 Hz, 1H), 1.21 (d, *J* = 7.6 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 6H), 0.92 (s, 9H), 0.92 (d, obscured, 3H), 0.90 (s, 9H), 0.89 (d, *J* = 7.9 Hz, 3H), 0.88 (s, 9H), 0.88 (d, *J* = 5.4 Hz, 6H), 0.87 (s, 9H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.06 (s, 3H), 0.05 (s, 6H), 0.04 (s, 3H), 0.04 (s, 6H), 0.03 (s, 3H), 0.00 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.3, 157.1, 135.4, 133.6, 132.5, 127.1, 80.4, 80.0, 77.1, 76.4, 74.9, 64.7, 44.1, 42.9, 38.0, 37.8, 37.6, 35.0, 34.2, 32.3, 30.0, 26.3, 26.2, 25.9, 25.7, 19.5, 18.5, 18.4, 18.1, 18.0, 17.6, 17.2, 16.4, 15.9, 14.1, 13.9, 10.5, -3.1, -3.5, -3.7, -4.2, -4.3, -4.5, -4.9; high resolution mass spectrum (ES⁺) *m/z* 1020.6937 [(M+Na)⁺; calcd for C₅₃H₁₀₇NO₈Si₄Na: 1020.6972].



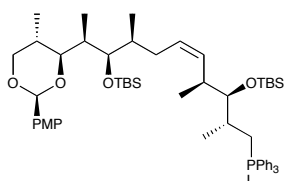
(+)-7

Tetra-ol (+)-7. Carbamate (+)-S5 (9.0 mg, 0.009 mmol) was dissolved in MeOH (2.0 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (3N, 5.0 mL) was added in 200–400 μ L portions over 4 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 2 mL of 3 N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 2.0 mL of MeOH. After 12 h the solution was quenched with NaHCO_3 (s), diluted with 30 mL of water and extracted 3 x with EtOAc. The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Flash chromatography using washed SiO_2 (hexanes then 10% MeOH/ CH_2Cl_2 then 5% MeOH/ CH_2Cl_2) via gradient elution (2% MeOH/ CH_2Cl_2 \rightarrow 10% MeOH/ CH_2Cl_2) gave (+)-7 (3.0 mg, 61% yield). $[\alpha]_D^{23} +50$ (c 0.08, MeCN); IR (film, NaCl) 3354, 2928, 1704, 1381, 1030 cm^{-1} ; ^1H NMR (500 MHz, CD_3CN) δ 5.45 (app t, J = 10.4 Hz, 1H), 5.39 (dd, J = 11.1, 8.1 Hz, 1H), 5.30 (m, 2H), 5.07 (br s, 2H), 4.54 (app t, J = 8.3 Hz, 1H), 4.50 (dd, J = 6.6, 5.1 Hz, 1H), 4.46 (dd, J = 10.0, 2.0 Hz, 1H), 3.65 (br s, 1H), 3.58 (br s, 1H), 3.32 (br s, 1H), 3.22 (dd, J = 11.1, 5.5 Hz, 1H), 3.17 (dd, J = 10.2, 5.4 Hz, 1H), 2.84 (br s, 1H), 2.65 (m, 2H), 2.57 (dd, J = 7.3, 4.7 Hz, 1H), 2.56 (m, 1H), 2.51 (dddd, J = 13.4, 8.6, 6.7, 6.7, 1H), 2.02 (ddd, J = 14.2, 4.2, 4.2 Hz, 1H), 1.87 (m, 3H), 1.75 (dd, J = 12.3, 2.1 Hz, 1H), 1.72 (dd, J = 10.2, 2.2 Hz, 1H), 1.59 (ddd, J = 14.4, 10.5, 2.7 Hz, 1H), 1.21 (d, J = 7.4 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.7 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 174.5, 158.3, 134.9, 133.8, 133.5, 128.1, 80.2, 79.1, 77.9, 75.9, 72.9, 63.8, 43.8, 42.2, 37.8, 36.5, 36.3, 36.1, 36.0, 32.4, 30.6, 19.5, 18.8, 17.6, 16.2, 15.5, 14.5, 12.8, 9.3; high resolution mass spectrum (ES^+) m/z 564.3505 [$(\text{M}+\text{Na})^+$; calcd for $\text{C}_{29}\text{H}_{51}\text{NO}_8\text{Na}$: 564.3512].



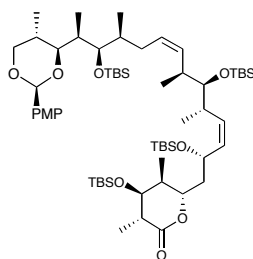
(+)-S7

Iodide (+)-S7: To a 0° C solution (benzene/Et₂O, 1:1, 40 mL) of alcohol (+)-8 (1.39 g, 2.05 mmol) was added triphenylphosphine (1.39 g, 5.30 mmol), imidazole (0.350 g, 5.14 mmol), and I₂ (1.09 g, 4.29 mmol). The resultant canary yellow suspension was stirred 45 min at 0 °C, then warmed to ambient temperature. The reaction was then poured into 75 mL of water and diluted with CH₂Cl₂. The layers were separated, and the organic layer was extracted with CH₂Cl₂ (3 x 25 mL), and then washed (2 x saturated Na₂S₂O₃, 1 x saturated NaHCO₃, 1 x brine), dried (MgSO₄), and concentrated. Flash chromatography (6% ether / hexanes) afforded iodide (+)-S7 (1.45 g, 90%). $[\alpha]_D^{23} +46.7$ (c 1, CHCl₃); IR (film, NaCl) 2957, 2940, 2856, 1617, 1462, 1387, 1250, 1169, 1085, 1032, 836, 773 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.46-5.36 (m, 2H), 5.40 (s, 1H), 3.94 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.87 (dd, *J* = 7.1, 1.5 Hz, 1H), 3.51-3.45 (m, 1H), 3.50 (d, *J* = 10.8 Hz, 1H), 3.34, (dd, *J* = 9.7, 4.8 Hz, 1H), 3.26 (s, 3H), 3.25 (d, *J* = 10.8 Hz, 1H), 3.04 (dd, *J* = 9.7, 7.8 Hz, 1H), 2.75 (dddd, *J* = 8.9, 6.7, 6.7, 6.7 Hz, 1H), 2.35-2.27 (m, 1H), 2.19 (m, 1H), 2.01-1.88 (m, 3H), 1.89-1.82 (m, 1H), 1.15 (d, *J* = 7.1 Hz, 3H), 1.055 (d, *J* = 6.7 Hz, 3H), 1.050 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H), 1.02 (s, 9H), 0.95 (s, 9H), 0.42 (d, *J* = 6.7 Hz, 3H), 0.13 (s, 3H), 0.09 (s, 3H), 0.086 (s, 3H), 0.080 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.4, 134.4, 132.2, 128.8, 127.9, 113.8, 101.6, 83.3, 79.5, 77.8, 73.3, 54.7, 41.6, 38.7, 36.9, 36.0, 33.8, 31.0, 26.5, 26.3, 18.8, 18.6, 17.8, 17.4, 13.6, 13.2, 12.0, 11.3, -3.4, -3.7, -3.5, -3.7; high resolution mass spectrum (ES⁺) *m/z* 789.3832 [(M+H)⁺; calcd for C₃₈H₇₀O₅Si₂Na: 789.3807]



(+)-S8

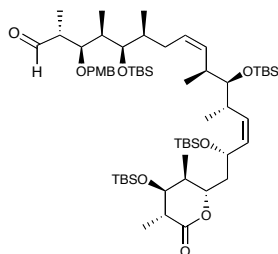
Phosphonium salt (+)-S8: To a mixture of iodide (+)-S7 (1.45 g, 1.84 mmol) and diisopropylethylamine (3.5 mL, 20.1 mmol) was added triphenylphosphine (5.5 g, 20.9 mmol). The resulting mixture was heated to 100° C for 36 h, cooled, and chromatographed (CH₂Cl₂ load, then 100% CH₂Cl₂ to 40% CH₃CN/CH₂Cl₂) to provide (+)-S8 as a white foam (1.58 g, 82% yield): $[\alpha]_D^{23} +32.0$ (*c* 1.0, CHCl₃); IR (film, NaCl) 2954, 2855, 1614, 1516, 1438, 1249, 1111, 1073, 1029, 834, 751 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.82-7.76 (m, 9H), 7.72-7.67 (m, 6H), 7.37-7.34 (m, 2H), 6.86-6.82 (m, 2H), 5.54 (dd, *J* = 10.8, 10.8 Hz, 1H), 5.37 (s, 1H), 5.28 (ddd, *J* = 10.8, 10.8, 3.7 Hz, 1H), 4.07 (dd, *J* = 11.7, 4.8 Hz, 1H), 3.76 (s, 3H), 3.76-3.72 (m, 2H), 3.61 (dd, *J* = 7.4, 1.5 Hz, 1H), 3.50-3.45 (m, 2H), 3.27, (ddd, *J* = 15.6, 11.2, 11.2 Hz, 1H), 2.59-2.51 (m, 1H), 2.12-1.98 (m, 3H), 1.84 (dddd, *J* = 7.4, 7.1, 7.1, 7.1, 1.1 Hz, 1H), 1.80-1.66 (m, 2H), 0.98 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 9H), 0.84 (s, 9H), 0.78 (d, *J* = 6.7 Hz, 3H), 0.72 (app d, *J* = 7.1 Hz, 6H), 0.09 (s, 3H), 0.01 (s, 3H), -0.05 (s, 3H), -0.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.7, 135.2 (d), 133.9, 133.6 (d), 131.4, 130.6 (d), 128.3, 127.3, 118.8 (d), 113.4, 100.8, 82.9, 79.5 (d), 77.2 (d), 73.2, 55.3, 37.99, 36.3, 35.8, 35.9 (2), 33.2, 26.1, 26.0, 25.6 (d), 18.4, 18.2, 17.0 (d), 13.1, 12.1, 10.9, -3.4, -3.6 (2), -3.9; high resolution mass spectrum (ES⁺) *m/z* 923.5591 [(M-I)⁺; calcd for C₅₆H₈₄O₅PSi: 923.5595



(+)-9

Diene (+)-9: Phosphonium salt (+)-S8 (1.40 g, 1.33 mmol), was azeotropically dried with benzene (3 \times 1.0 mL) using a double manifold and further dried by heating to 50 °C under vacuum (0.2 torr) for 12 h. The salt was back-filled with argon, dissolved in 6 mL of freshly distilled THF, sparged with argon for 15 min, and cooled to -20 °C. The resultant solution was treated with sodium bis(trimethylsilyl)amide (1.0 M in THF, 666 μ L), stirred 15 min, warmed to 0 °C, stirred 30 min, and re-cooled to -20 °C. To this orange/red solution was transferred via cannula a degassed solution of aldehyde (-)-5 (712 mg, 1.60

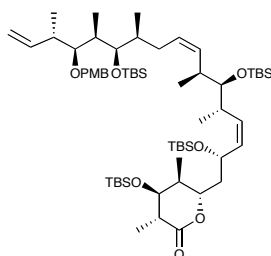
mmol) in THF (1 mL) over 1 min. The orange solution was allowed to slowly warm to $-8\text{ }^{\circ}\text{C}$ over 3.0 h. The resulting light yellow solution was quenched with saturated NH_4Cl and diluted ($\text{Et}_2\text{O}/\text{H}_2\text{O}$). The layers were separated, and the aqueous layer was extracted with Et_2O (3 \times 30 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and chromatographed (gradient elution: 2% $\text{EtOAc}/\text{hexanes}$ \rightarrow 50% $\text{EtOAc}/\text{hexanes}$; then 30% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$) to afford *cis* isomer (+)-**9** (420 mg, 31%), and phosphonium salt (+)-**S8** (750 mg, 54%). $[\alpha]_{\text{D}}^{23} +37.6$ (*c* 1, CHCl_3); IR (film, NaCl) 2956, 2929, 2886, 2856, 1734, 1471, 1250, 1045, 835, 775 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, $J = 8.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 5.39 (s, 1H), 5.36-5.28 (m, 2H), 5.21 (dd, $J = 10.4$, 10.4 Hz, 1H), 5.21-5.16 (m, 1H), 4.79 (dd, $J = 9.3$, 9.3 Hz, 1H), 4.50 (dd, $J = 10.4$, 10.4 Hz, 1H), 4.09 (dd, $J = 11.1$, 4.8 Hz, 1H), 3.80 (s, 3H), 3.67 (dd, $J = 7.1$, 1.5 Hz, 1H), 3.61 (dd, $J = 2.6$, 2.6 Hz, 1H), 3.50 (dd, $J = 10.0$, 1.5 Hz, 1H), 3.48 (dd, $J = 10.8$, 10.8 Hz, 1H), 3.28 (dd, $J = 4.8$, 4.8 Hz, 1H), 2.67-2.55 (m, 3H), 2.11-2.02 (m, 2H), 1.95-1.84 (m, 2H), 1.82-1.70 (m, 3H), 1.59 (ddd, $J = 13.8$, 11.2, 2.2 Hz, 1H), 1.20 (d, $J = 7.8$ Hz, 3H), 1.01 (d, $J = 6.7$ Hz, 3H), 0.96 (d, $J = 6.7$ Hz, 3H), 0.95 (d, $J = 6.7$ Hz, 3H), 0.92-0.89 (d, obscured, 3H), 0.91 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.83 (d, $J = 6.7$ Hz, 3H), 0.74 (d, $J = 6.7$ Hz, 3H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (app s, 6H), 0.044 (s, 3H), 0.036 (s, 3H), 0.022 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.2, 156.7, 135.3, 133.6, 132.4, 131.4, 127.2, 127.1, 113.4, 100.8, 83.0, 79.9, 77.1, 76.9, 74.8, 73.2, 64.6, 55.2, 44.1, 42.8, 28.0, 37.4, 36.5, 34.9, 34.0, 33.1, 30.7, 26.2, 26.1, 25.8, 25.6, 18.42, 18.36, 18.0, 17.8, 17.1, 16.3, 15.8, 14.0, 13.1, 12.1, 10.8, -3.1, -3.6, -3.7, -4.2, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES^+) m/z 1111.7260 [$(\text{M}+\text{Na})^+$; calcd for $\text{C}_{60}\text{H}_{112}\text{O}_9\text{Si}_4\text{Na}$: 1111.7281]



(+)-**10**

Aldehyde (+)-10: To a $0\text{ }^{\circ}\text{C}$ solution of acetal (+)-**9** (370 mg, 0.34 mmol) in CH_2Cl_2 (15 mL) was added DIBAL-H (0.61 mL, 3.40 mmol). The resulting solution was warmed to room temperature and stirred for

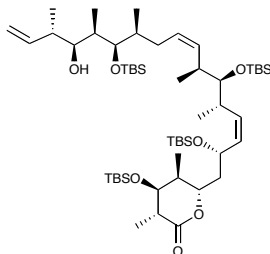
20 min. The reaction was quenched via dropwise addition of saturated aqueous Rochelle's salt (20 mL), diluted with ether (40 mL), the aqueous layer extracted with ether (4 x 30 mL), and the layers separated. The organic layer was washed with H₂O (15 mL) and brine (15 mL), dried (MgSO₄), filtered, and concentrated. Flash chromatography (10% EtOAc/hexanes) provided the corresponding diol as a mixture of epimers at the lactol stereocenter, which was taken directly to the next step. To a 0 °C solution of the diol in CH₂Cl₂ (11 mL) were added Dess-Martin periodinane (297 mg, 0.702 mmol) and NaHCO₃ (145 mg, 2.00 mmol). The resulting solution was stirred for 2.5 h and quenched with saturated Na₂S₂O₃ solution (15 mL) and saturated NaHCO₃ solution (15 mL). The mixture was then extracted with Et₂O (3 x 30 mL) and the layers separated. The organic solution was then washed with H₂O, dried (MgSO₄), filtered, and concentrated. Flash chromatography (5% ethyl acetate / hexanes) yielded aldehyde (+)-**10** (145 mg, 66%). $[\alpha]_D^{23}$ +18.8 (*c* 1, CHCl₃); IR (film, NaCl) 2956, 2929, 2884, 2856, 1739, 1732, 1514, 1472, 1464, 1360, 1250, 1047, 833, 775 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 9.73 (d, *J* = 2.2 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.66-5.58 (m, 2H), 5.51 (dd, *J* = 10.4, 10.4 Hz, 1H), 5.34 (ddd, *J* = 10.4, 10.0, 4.8 Hz, 1H), 5.16 (dd, *J* = 9.7, 9.7 Hz, 1H), 4.70 (dd, *J* = 10.4, 10.4 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.35 (d, *J* = 11.2 Hz, 1H), 3.71 (dd, *J* = 6.0, 3.0 Hz, 1H), 3.55 (dd, *J* = 10.8, 5.6 Hz, 2H), 3.38 (dd, *J* = 2.6, 2.6 Hz, 1H), 3.33 (s, 3H), 3.20-2.95 (m, 1H), 2.90-2.82 (m, 1H), 2.66 (dddd, *J* = 7.8, 7.4, 7.4, 3.0 Hz, 1H), 2.57 (dddd, *J* = 13.8, 6.7, 6.7, 2.2 Hz, 1H), 2.28 (ddd, *J* = 14.1, 9.7, 9.7 Hz, 1H), 2.12 (d, *J* = 14.9 Hz, 1H), 2.00-1.87 (m, 2H), 1.85-1.77 (m, 1H), 1.73 (ddd, *J* = 13.4, 11.2, 1.9 Hz, 1H), 1.70-1.64 (m, 1H), 1.218 (d, *J* = 6.7 Hz, 3H), 1.216 (d, *J* = 6.7 Hz, 3H), 1.12 (d, *J* = 7.4 Hz, 3H), 1.12 (d, *J* = 7.4 Hz, 3H), 1.07 (s, 9H), 1.04 (s, 9H), 1.03 (s, 9H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.92 (s, 9H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.31 (s, 3H), 0.29 (s, 3H), 0.23 (s, 3H), 0.22 (s, 3H), 0.14 (s, 3H), 0.10 (s, 3H), 0.06 (app s, 6H); ¹³C NMR (125 MHz, C₆D₆) δ 203.1, 171.7, 159.8, 137.0, 134.2, 132.9, 130.8, 129.4, 127.3, 114.1, 82.40, 80.39, 76.9, 76.5, 75.3, 74.4, 65.0, 54.8, 49.6, 44.5, 43.6, 40.4, 38.7, 38.1, 35.8, 34.8, 33.1, 26.5 (2), 26.2, 25.9, 18.8, 18.7, 18.4, 18.1, 17.2, 16.9, 16.4, 14.1 (2), 12.0, 11.7, -3.0, -3.1, -3.3, -4.0, -4.1, -4.5, -4.6, -4.8; high resolution mass spectrum (ES⁺) *m/z* 1111.7394 [(M+Na)⁺; calcd for C₆₀H₁₁₂O₉Si₄Na: 1111.7281]



(+)-**S9**

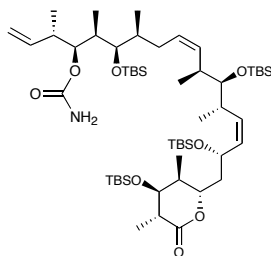
Triene (+)-S9: Methyltriphenylphosphonium bromide (262 mg, 0.733 mmol) was suspended in THF (3 mL) and cooled to -78 °C. *n*-BuLi (2.5 M, 0.264 mL) was added dropwise via syringe, and the resulting orange/red solution was warmed to room temperature and stirred for 40 min. In a separate flask, aldehyde (+)-**10** (40 mg, 0.037 mmol) was dissolved in THF (1.0 mL) and cooled to -78 °C. The orange ylide solution was added to the clear aldehyde solution by syringe until the orange color persisted. The reaction was then warmed to 0 °C, stirred for 30 min, and quenched with saturated NH₄Cl solution (10 mL). The mixture was then diluted with CH₂Cl₂ (10 mL) and the layers separated. The aqueous layer was extracted (3 × CH₂Cl₂), and the combined organic layers were dried (MgSO₄), concentrated, and chromatographed (3% EtOAc/hexanes) to afford *cis* isomer (+)-**S9** (37 mg, 68%). $[\alpha]_D^{23} +31.8$ (*c* 1, CHCl₃); IR (film, NaCl) 2956, 2929, 2886, 2856, 1739, 1514, 1471, 1360, 1250, 1047, 835 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.90 (dddd, *J* = 9.3, 9.3, 8.6, 8.6 Hz, 1H), 5.37-5.20 (m, 3H), 5.14 (ddd, *J* = 10.8, 8.9, 5.6 Hz, 1H), 5.04 (d, *J* = 4.0 Hz, 1H), 5.01 (s, 1H), 4.80 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.53 (d, *J* = 10.4 Hz, 1H), 4.51 (dd, *J* = 10.4, 10.4 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.62 (dd, *J* = 2.2, 2.2 Hz, 1H), 3.54 (dd, *J* = 4.5, 4.5 Hz, 1H), 3.29 (dd, *J* = 5.2, 5.2 Hz, 1H), 3.20 (dd, *J* = 6.3, 4.8 Hz, 1H), 2.70-2.60 (m, 2H), 2.56 (ddd, *J* = 10.8, 5.2, 5.2 Hz, 1H), 2.50 (dddd, *J* = 11.9, 7.1, 7.1, 7.1 Hz, 1H), 1.98-1.88 (m, 2H), 1.88-1.82 (m, 1H), 1.79 (ddd, *J* = 10.0, 6.7, 2.2 Hz, 1H), 1.74 (dd, *J* = 12.6, 12.6 Hz, 1H), 1.65-1.54 (m, 2H), 1.22 (d, *J* = 7.4 Hz, 3H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.965 (d, *J* = 7.4 Hz, 3H), 0.955 (d, *J* = 7.4 Hz, 3H), 0.93 (s, 9H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.064 (app s, 6H), 0.062 (s, 3H), 0.052 (s, 3H), 0.047 (s, 3H), 0.019 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 158.9, 140.9, 135.3, 133.5, 132.4, 131.2, 129.0, 127.1, 114.7, 113.6, 84.3, 79.9, 77.0, 76.4, 74.8, 74.6,

64.5, 55.2, 44.1, 42.8, 41.4, 39.7, 38.2, 37.4, 34.9, 34.1, 32.1, 26.20, 26.19, 25.8, 25.6, 18.5, 18.4, 18.05, 18.03, 17.9, 17.1, 16.3, 15.9, 14.7, 14.0, 10.7, -3.2, -3.4, -3.5, -4.3, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) m/z 1109.7530 [(M+Na)⁺; calcd for C₆₁H₁₁₄O₈Si₄Na: 1109.7489]



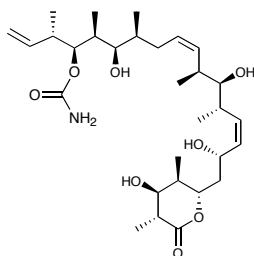
(+)-**S10**

Alcohol (+)-S10: A room temperature solution of PMB ether (+)-**S9** (26 mg, 0.024 mmol) in CH₂Cl₂ (2.0 mL) was treated with H₂O (100 μ L) and DDQ (10 mg, 0.044 mmol). The mixture was stirred for 30 min and quenched with 5.0 mL saturated NaHCO₃, diluted with CH₂Cl₂, and washed with H₂O and saturated brine solution. The combined organic layers were dried (MgSO₄), filtered and concentrated. Preparative TLC (15% EtOAc/hexanes) provided (+)-**S10** (20 mg, 87%). $[\alpha]_D^{23}$ +26.4 (*c* 1, CHCl₃); IR (film, NaCl) 2972, 2929, 2857, 1734, 1471, 1360, 1252, 1047, 836, 774 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.90 (ddd, *J* = 16.4, 11.2, 8.9 Hz, 1H), 5.38-5.12 (m, 5H), 5.11 (s, 1H), 4.80 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.51 (ddd, *J* = 10.4, 10.4, 1.1 Hz, 1H), 3.67 (dd, *J* = 6.0, 3.0 Hz, 1H), 3.64 (dd, *J* = 2.6, 2.3 Hz, 1H), 3.31 (m, 2H), 2.69-2.53 (m, 3H), 2.28 (dddd, *J* = 15.3, 7.4, 7.4, 7.4 Hz, 1H), 2.01 (m, 2H), 1.84-1.69 (m, 4H), 1.60 (ddd, *J* = 13.4, 11.2, 2.2 Hz, 1H), 1.22 (d, *J* = 7.4 Hz, 3H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.975 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 3H), 0.918 (d, *J* = 6.7 Hz, 3H), 0.912 (d, *J* = 6.7 Hz, 3H), 0.91 (s, 9H), 0.90 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.82 (d, *J* = 7.1 Hz, 3H), 0.086 (s, 3H), 0.078 (s, 3H), 0.074 (s, 3H), 0.069 (s, 3H), 0.059 (s, 3H), 0.056 (s, 3H), 0.047 (s, 3H), 0.020 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 141.3, 135.4, 133.5, 132.3, 127.3, 116.3, 80.0, 78.3, 76.9, 75.5, 74.8, 64.6, 44.0, 42.8, 42.4, 37.7, 37.5, 37.4, 35.0, 34.1, 32.2, 26.2, 26.1, 25.8, 25.6, 18.4, 18.37, 18.03, 17.9, 17.2, 16.6, 16.3, 15.8, 14.0, 13.7, 9.2, -3.2, -3.4, -3.8, -4.3, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) m/z 989.6887 [(M+Na)⁺; calcd for C₅₃H₁₀₆O₇Si₄Na: 989.6913]



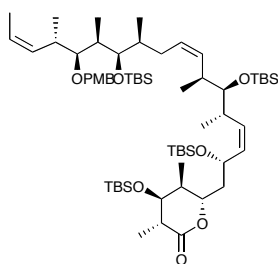
(+)-**S11**

Carbamate (+)-S11: A solution of alcohol (+)-**S10** (7.0 mg, 0.0073 mmol) in CH₂Cl₂ (0.5 mL) was treated with Cl₃CCON=C=O (29 μ L, 1 M solution) at room temperature for 30 min. The solution was loaded directly onto a neutral Al₂O₃ plug. After 4 h, the material was flushed from the Al₂O₃ (EtOAc, 50 mL), concentrated, and purified by flash chromatography (8% ethyl acetate/hexanes) providing 7.0 mg (+)-**S11** (96%). $[\alpha]_D^{23}$ +25.0 (*c* 0.5, CHCl₃); IR (film, NaCl) 2957, 2928, 2857, 1732, 1603, 1472, 1381, 1253, 1099, 1047 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.74 (ddd, *J* = 16.4, 11.2, 8.9 Hz, 1H), 5.40-5.21 (m, 3H), 5.17 (ddd, *J* = 14.9, 5.2, 5.2 Hz, 1H), 5.03 (d, *J* = 5.2 Hz, 1H), 5.01 (s, 1H), 4.80 (dd, *J* = 9.3, 8.9 Hz, 1H), 4.70 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.51 (ddd, *J* = 10.4, 10.4, 1.1 Hz, 1H), 4.51 (br s, 2H), 3.64 (dd, *J* = 2.6, 2.3 Hz, 1H), 3.50 (dd, *J* = 4.5, 4.1 Hz, 1H), 3.30 (dd, *J* = 5.2, 4.8 Hz, 1H), 2.70-2.52 (m, 3H), 2.52-2.44 (m, 1H), 2.06-1.85 (m, 3H), 1.85-1.65 (m, 3H), 1.60 (ddd, *J* = 13.4, 11.2, 2.2 Hz, 1H), 1.22 (d, *J* = 7.4 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.955 (d, *J* = 6.7 Hz, 3H), 0.92 (s, 9H), 0.91-0.87 (obscured, 6H), 0.90 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.09 (s, 3H), 0.070 (s, 3H), 0.069 (s, 3H), 0.063 (s, 3H), 0.059 (s, 3H), 0.055 (s, 3H), 0.046 (s, 3H), 0.018 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.3, 156.8, 139.8, 135.3, 133.5, 132.4, 127.0, 115.5, 79.9, 78.5, 76.9, 76.0, 74.8, 64.6, 44.1, 42.8, 40.7, 38.2, 37.8, 37.5, 34.9, 34.0, 32.0, 26.2, 26.1, 25.8, 25.6, 18.5, 18.4, 18.0, 17.9, 17.5, 17.1, 16.3, 15.8, 14.3, 14.0, 10.2, -3.2, -3.6, -3.8, -4.3, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) *m/z* 1032.6962 [(M+Na)⁺; calcd for C₅₄H₁₀₇NO₈Si₄Na: 1032.6972]



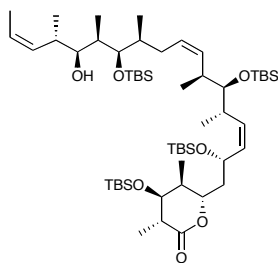
(+)-11

Tetra-ol (+)-11: Carbamate (+)-**S11** (7.0 mg, 0.007 mmol) was dissolved in MeOH (3.0 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (4N, 3.0 mL) was added in 200–400 μ L portions over 3 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 1 mL of 4N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 1.0 mL of MeOH. After 7 h the solution was diluted with EtOAc (25 mL) and H₂O (10 mL), and quenched with NaHCO₃ (s) until gas evolution ceased. The layers were separated and the aqueous layer extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried (MgSO₄), filtered, and concentrated. Flash chromatography gradient elution (2% MeOH/CH₂Cl₂ \rightarrow 10% MeOH/CH₂Cl₂) gave (+)-**11** (1.9 mg, 50% yield). $[\alpha]_D^{23} +24.0$ (*c* 0.33, MeOH); IR (film, NaCl) 3382, 2967, 2925, 1708, 1603, 1387, 1324, 1242, 1100, 1034, 970 cm⁻¹; ¹H NMR (500 MHz, CD₃OD) δ 5.79 (ddd, *J* = 17.5, 10.4, 9.3 Hz, 1H), 5.53 (dd, *J* = 10.4, 10.4 Hz, 1H), 5.39 (dd, *J* = 10.8, 8.6 Hz, 1H), 5.32-5.27 (m, 2H), 5.08-5.01 (m, 2H), 4.75 (dd, *J* = 7.1, 4.8 Hz, 1H), 4.65 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.58 (ddd, *J* = 10.8, 9.3, 1.9 Hz, 1H), 3.66 (dd, *J* = 4.1, 4.1 Hz, 1H), 3.19 (dd, *J* = 7.8, 4.1 Hz, 1H), 2.77-2.66 (m, 1H), 2.64 (ddd, *J* = 14.9, 7.4, 4.4 Hz, 1H), 2.63-2.53 (m, 1H), 2.46 (dddd, *J* = 14.9, 7.2, 7.2, 7.2 Hz, 1H), 1.97 (ddd, *J* = 13.8, 4.5, 4.5 Hz, 1H), 1.92-1.74 (m, 4H), 1.69 (m, 1H), 1.62 (ddd, *J* = 13.4, 11.2, 2.6 Hz, 1H), 1.29 (br s, 1H), 1.27 (d, *J* = 7.4 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 175.5, 158.8, 139.7, 133.7, 132.4, 132.2, 127.1, 114.6, 78.8, 77.9, 77.5, 74.7, 72.1, 62.6, 43.0, 41.3, 40.0, 37.1, 35.7, 35.6 (2), 35.2, 31.3, 17.8, 16.7, 15.8, 14.5, 14.1, 11.8, 8.3; high resolution mass spectrum (ES⁺) *m/z* 576.3502 [(M+Na)⁺; calcd for C₃₀H₅₁NO₈Na: 576.3512]



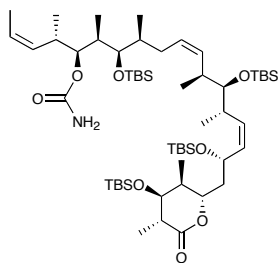
(+)-**S12**

Triene (+)-S12: Ethyltriphenylphosphonium bromide (273 mg, 0.735 mmol) was suspended in THF (3 mL) and cooled to -78 °C. *n*-BuLi (2.5 M, 0.264 mL) was added dropwise via syringe, and the resulting orange/red solution warmed to room temperature and stirred for 40 min. In a separate flask, aldehyde (+)-**10** (37 mg, 0.034 mmol) was dissolved in THF (1.0 mL) and cooled to -78 °C. The orange ylide solution was added to the clear aldehyde solution by syringe until the orange color persisted. The reaction was then warmed to 0 °C, stirred for 30 min, and quenched with saturated NH₄Cl solution (10 mL). The mixture was then diluted with CH₂Cl₂ (10 mL) and the layers separated. The aqueous layer was extracted (3 × CH₂Cl₂), and the combined organic layers were dried (MgSO₄), concentrated, and chromatographed (3% EtOAc/hexanes) to afford *cis* isomer (+)-**S12** (28 mg, 75%). $[\alpha]_D^{23} +35.4$ (*c* 1, CHCl₃); IR (film, NaCl) 2957, 2928, 2856, 1734, 1514, 1471, 1464, 1250, 1096, 1047, 835, 775 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 7.41 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.79 (dddd, *J* = 11.2, 9.7, 3.4, 1.5 Hz, 1H), 5.73-5.67 (m, 2H), 5.65-5.57 (m, 2H), 5.46 (ddd, *J* = 10.8, 7.1, 7.1 Hz, 1H), 5.26 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.80 (dd, *J* = 10.8, 10.8 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 3.80 (dd, *J* = 4.8, 4.8 Hz, 1H), 3.64 (dd, *J* = 4.8, 4.8, 1H), 3.47 (dd, *J* = 2.6, 2.2 Hz, 1H), 3.46-3.41 (m, 1H), 3.44 (s, 3H), 3.14-3.02 (m, 2H), 2.95 (dddd, *J* = 13.3, 7.4, 7.4, 7.4 Hz, 1H), 2.76 (dddd, *J* = 7.8, 7.4, 7.4, 3.0 Hz, 1H), 2.29 (m, 2H), 2.13 (dddd, *J* = 13.4, 6.7, 6.7, 4.8 Hz, 1H), 2.01 (ddd, *J* = 13.8, 10.8, 1.9 Hz, 1H), 1.95-1.85 (m, 1H), 1.87-1.74 (m, 2H), 1.73 (dd, *J* = 6.7, 1.5 Hz, 3H), 1.36 (d, *J* = 6.7 Hz, 3H), 1.31 (app d, *J* = 6.7 Hz, 6H), 1.23 (d, *J* = 7.4 Hz, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.17 (app s, 18H), 1.15 (s, 9H), 1.14 (d, *J* = 6.7 Hz, 3H), 1.02 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.41 (s, 3H), 0.40 (s, 3H), 0.34 (app s, 6H), 0.32 (s, 3H), 0.28 (s, 3H), 0.037 (s, 3H), 0.035 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 158.9, 135.2, 133.5, 132.8, 132.3, 131.4, 128.9, 127.1, 123.4, 113.6, 84.5, 79.9, 76.9, 76.6, 74.8, 74.7, 64.5, 55.2, 44.1, 42.8, 40.0, 38.1, 37.4, 34.9, 34.5, 34.1, 32.0, 26.22, 26.18, 25.83, 25.65, 18.5, 18.4, 18.3, 18.0, 17.9, 17.0, 16.3, 15.9, 14.9, 14.0, 13.1, 10.7, -3.1, -3.4 (2), -4.3, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) *m/z* 1123.7645 [(M+Na)⁺; calcd for C₆₂H₁₁₆O₈Si₄Na: 1123.7656]



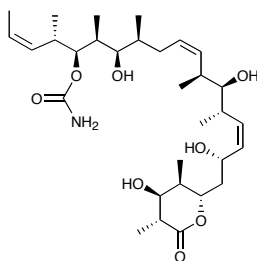
(+)-S13

Alcohol (+)-S13: A room temperature solution of PMB ether (+)-S12 (28 mg, 0.025 mmol) in CH₂Cl₂ (2.0 mL) was treated with H₂O (100 μ L) and DDQ (14 mg, 0.061 mmol). The mixture was stirred for 30 min and quenched with 5.0 mL saturated NaHCO₃, diluted with CH₂Cl₂, and washed with H₂O and saturated brine solution. The combined organic layers were dried (MgSO₄), filtered and concentrated. Preparative TLC (15% EtOAc/hexanes) provided (+)-S13 (21 mg, 84%) [α]_D²³ +24.0 (*c* 1, CHCl₃); IR (film, NaCl) 2957, 2901, 2840, 1734, 1471, 1354, 1252, 1098, 1047, 836, 775 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.64 (dddd, *J* = 10.8, 6.7, 6.7, 6.7 Hz, 1H), 5.37-5.16 (m, 5H), 4.80 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.51 (dd, *J* = 10.4, 10.4 Hz, 1H), 3.67-3.63 (m, 2H), 3.31 (dd, *J* = 5.2, 5.2 Hz, 1H), 3.28 (br d, *J* = 7.8 Hz, 1H), 2.70-2.54 (m, 4H), 2.07-1.95 (m, 2H), 1.85-1.70 (m, 4H), 1.66 (dd, *J* = 7.0, 1.9 Hz, 2H), 1.63-1.52 (m, 2H), 1.22 (d, *J* = 7.4 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.92 (s, 9H), 0.91 (d, obscured, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 9H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.074 (s, 3H), 0.070 (s, 3H), 0.059 (s, 3H), 0.057 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 135.3, 133.5, 133.3, 132.3, 127.3, 126.3, 79.9, 78.3, 77.0, 75.9, 74.8, 64.6, 44.0, 42.8, 37.8, 37.4, 37.1, 35.3, 35.0, 34.1, 32.5, 26.2 (2), 25.8, 25.7, 18.5, 18.4, 18.0, 17.9, 17.2, 16.8, 16.3, 15.9, 14.0, 13.4, 13.2, 9.4, -3.1, -3.3, -3.6, -4.3, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) *m/z* 1003.7054 [(M+Na)⁺; calcd for C₅₄H₁₀₈O₇Si₄Na: 1003.7069]



(+)-**S14**

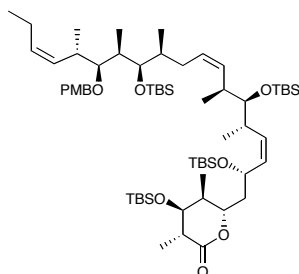
Carbamate (+)-S14: A solution of alcohol (+)-**S13** (10 mg, 0.010 mmol) in CH₂Cl₂ (1.0 mL) was treated with Cl₃CCON=C=O (31 μ L, 1 M solution in toluene) at room temperature for 30 min. The solution was loaded directly onto a neutral Al₂O₃ plug. After 4 h, the material was flushed from the Al₂O₃ (EtOAc, 50 mL), concentrated, and purified by flash chromatography (10% ethyl acetate/hexanes) providing 9.2 mg (+)-**S14** (86%). $[\alpha]_D^{23}$ +31.2 (*c* 0.5, CHCl₃); IR (film, NaCl) 2957, 2929, 2886, 2858, 1732, 1472, 1360, 1252 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.48 (dddd, *J* = 10.8, 6.7, 6.7, 6.7 Hz, 1H), 5.37-5.21 (m, 4H), 5.16 (ddd, *J* = 10.8, 9.3, 4.8 Hz, 1H), 4.80 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.71 (dd, *J* = 5.9, 5.9 Hz, 1H), 4.51 (dd, *J* = 10.8, 10.8 Hz, 1H), 4.49 (br s, 2H), 3.64 (dd, *J* = 2.2, 2.2 Hz, 1H), 3.45 (dd, *J* = 4.5, 4.5 Hz, 1H), 3.29 (dd, *J* = 5.2, 4.8 Hz, 1H), 2.83 (dddd, *J* = 10.0, 6.7, 6.7, 6.7, 6.7 Hz, 1H), 2.68-2.59 (m, 2H), 2.55 (dddd, *J* = 13.8, 7.1, 7.1, 6.7 Hz, 1H), 2.02-1.85 (m, 3H), 1.81 (ddd, *J* = 10.0, 7.1, 2.2 Hz, 1H), 1.74 (ddd, *J* = 12.5, 12.5, 1.1 Hz, 1H), 1.70-1.64 (m, 1H), 1.63 (dd, *J* = 6.7, 1.5 Hz, 3H), 1.57 (m, 1H), 1.23 (d, *J* = 7.4 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.93 (s, 9H), 0.91-0.87 (obscured, 6H), 0.90 (s, 9H), 0.88 (s, 9H), 0.87 (s, 9H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.10 (s, 3H), 0.073 (s, 3H), 0.069 (s, 3H), 0.066 (s, 3H), 0.061 (s, 3H), 0.056 (s, 3H), 0.045 (s, 3H), 0.018 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.3, 156.9, 135.2, 133.5, 132.4, 131.8, 127.0, 124.3, 79.9, 79.1, 76.9, 76.2, 74.8, 64.6, 44.1, 42.8, 38.1, 38.0, 37.5, 34.9, 34.0, 33.4, 31.9, 26.2, 26.1, 25.8, 25.6, 18.5, 18.4, 18.0, 17.9, 17.5, 17.1, 16.3, 15.8, 14.3, 14.0, 12.9, 10.2, -3.2, -3.6, -3.7, -4.3, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) *m/z* 1046.7147 [(M+Na)⁺; calcd for C₅₅H₁₀₉NO₈Si₄Na: 1046.7128]



(+)-**12**

Tetra-ol (+)-12: Carbamate (+)-**S14** (9.0 mg, 0.0092 mmol) was dissolved in MeOH (2.5 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (4N, 3.0 mL) was added in 200–400 μ L

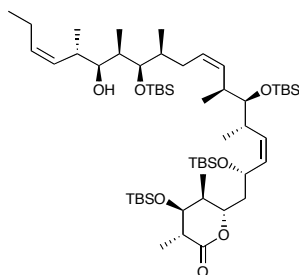
portions over 3 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 1 mL of 4N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 1.0 mL of MeOH. After 7 h the solution was diluted with EtOAc (25 mL) and H₂O (10 mL), and quenched with NaHCO₃ (s) until gas evolution ceased. The layers were separated and the aqueous layer extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried (MgSO₄), filtered, and concentrated. Flash chromatography gradient elution (2% MeOH/CH₂Cl₂ → 10% MeOH/CH₂Cl₂) gave (+)-**12** (3.7 mg, 70% yield). $[\alpha]_D^{23}$ +17.4 (*c* 0.33, CHCl₃); IR (film, NaCl) 3364, 2964, 2921, 1699, 1600, 1456, 1386, 1323, 1030, 967 cm⁻¹; ¹H NMR (500 MHz, CD₃CN) δ 5.50-5.43 (m, 2H), 5.41-5.22 (m, 4H), 5.07 (br s, 2H), 4.66 (dd, *J* = 6.7, 5.2 Hz, 1H), 4.53 (dddd, *J* = 10.4, 7.8, 5.2, 2.6 Hz, 1H), 4.46 (ddd, *J* = 10.4, 10.4, 1.9 Hz, 1H), 3.65 (dd, *J* = 8.2, 4.5 Hz, 1H), 3.34 (d, *J* = 4.8 Hz, 1H), 3.21-3.14 (m, 2H), 2.93-2.85 (m, 1H), 2.86 (d, *J* = 5.2 Hz, 1H), 2.69 (d, *J* = 5.2 Hz, 1H), 2.64 (m, 1H), 2.61 (d, *J* = 6.3 Hz, 1H), 2.58 (ddd, *J* = 14.5, 7.4, 4.5 Hz, 1H), 2.45 (dddd, *J* = 15.6, 6.7, 6.7, 6.7 Hz, 1H), 1.98-1.88 (m, 2H), 1.87 (dddd, *J* = 16.7, 7.1, 7.1, 3.7 Hz, 1H), 1.84-1.69 (m, 3H), 1.63 (dd, *J* = 7.1, 1.9 Hz, 3H), 1.57 (ddd, *J* = 13.4, 10.8, 2.6 Hz, 1H), 1.21 (d, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CD₃CN) δ 173.7, 159.4, 134.0, 133.0, 132.5, 131.8, 127.3, 124.0, 78.2 (2), 76.9, 74.7, 72.1, 62.8, 42.9, 41.3, 37.4, 35.7, 35.6, 35.3 (2), 33.0, 31.3, 18.1, 17.0, 15.5, 14.7, 14.4, 12.3, 12.0, 8.4; high resolution mass spectrum (ES⁺) *m/z* 590.3668 [(M+Na)⁺; calcd for C₃₁H₅₃NO₈Na: 590.3669].



(+)-**S15**

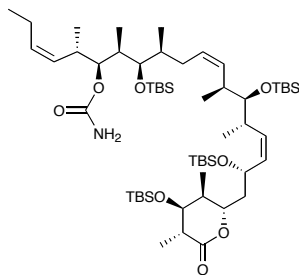
Triene (+)-S15: Propyltriphenylphosphonium bromide (389 mg, 1.01 mmol) was suspended in THF (5 mL) and cooled to -78 °C. *n*-BuLi (2.5 M, 0.364 mL) was added dropwise via syringe, and the resulting orange/red solution warmed to room temperature and stirred for 40 min. In a separate flask, aldehyde

(+)-**10** (55 mg, 0.050 mmol) was dissolved in THF (2.0 mL) and cooled to -78 °C. The orange ylide solution was added to the clear aldehyde solution by syringe until the orange color persisted. The reaction was then warmed to 0 °C, stirred for 30 min, and quenched with saturated NH₄Cl solution (10 mL). The mixture was then diluted with CH₂Cl₂ (10 mL) and the layers separated. The aqueous layer was extracted (3 × CH₂Cl₂), and the combined organic layers were dried (MgSO₄), concentrated, and chromatographed (3% EtOAc/hexanes) to afford *cis* isomer (+)-**S15** (41 mg, 73%). $[\alpha]_D^{23} +39.2$ (*c* 1, CHCl₃); IR (film, NaCl) 2956, 2929, 2856, 1740, 1514, 1462, 1359, 1250, 1096, 1046, 836, 775 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.44 (dd, *J* = 10.1, 9.7 Hz, 1H), 5.37 (dd, *J* = 7.1, 7.1 Hz, 1H), 5.35 (dd, *J* = 7.1, 7.1 Hz, 1H), 5.34-5.20 (m, 2H), 5.12 (ddd, *J* = 10.4, 9.3, 5.2 Hz, 1H), 4.80 (dd, *J* = 9.3, 8.9 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 4.51 (dd, *J* = 10.4, 10.4 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 3.79 (s, 3H), 3.62 (dd, *J* = 2.2, 2.2 Hz, 1H), 3.48 (dd, *J* = 4.5, 4.5 Hz, 1H), 3.29 (dd, *J* = 5.2, 5.2 Hz, 1H), 3.19 (dd, *J* = 6.3, 4.5 Hz, 1H), 2.84-2.76 (m, 1H), 2.63-2.59 (m, 2H), 2.59-2.50 (m, 1H), 2.08 (dddd, *J* = 14.9, 7.4, 7.4, 7.4, 7.4 Hz, 1H), 2.05-1.94 (m, 1H), 1.98-1.70 (m, 5H), 1.66-1.54 (m, 2H), 1.22 (d, *J* = 7.4 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H), 1.00-0.96 (obscured, 9H), 0.94 (s, 9H), 0.92-0.88 (obscured, 6H), 0.90 (s, 9H), 0.88 (s, 9H), 0.87 (s, 9H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.066 (app s, 9H), 0.050 (s, 3H), 0.047 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 158.9, 135.2, 133.5, 132.3, 131.4, 131.2, 129.0, 128.9, 127.1, 113.6, 84.4, 79.9, 77.0, 76.6, 74.8, 74.7, 64.5, 55.2, 44.1, 42.8, 39.9, 38.0, 37.4, 34.9 (2), 34.1, 32.0, 26.22, 26.18, 25.8, 25.7, 20.9, 18.8, 18.5, 18.4, 18.0, 17.9, 17.0, 16.3, 16.0, 14.8, 14.4, 14.0, 10.7, -3.2, -3.4 (2), -4.3, -4.4, -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) *m/z* 1137.7826 [(M+Na)⁺; calcd for C₆₃H₁₁₈O₈Si₄Na: 1137.7802]



(+)-**S16**

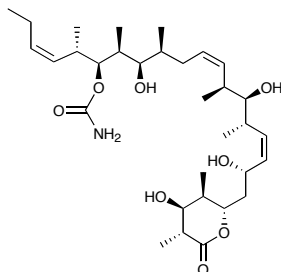
Alcohol (+)-S16: A room temperature solution of PMB ether (+)-S15 (40 mg, 0.036 mmol) in CH₂Cl₂ (3.0 mL) was treated with H₂O (150 μ L) and DDQ (16 mg, 0.070 mmol). The mixture was stirred for 30 min and quenched with 5.0 mL saturated NaHCO₃, diluted with CH₂Cl₂, and washed with H₂O and saturated brine solution. The combined organic layers were dried (MgSO₄), filtered and concentrated. Flash chromatography (5% EtOAc/hexanes) provided (+)-S16 (37 mg, 100%) [α]_D²³ +29.2 (*c* 1, CHCl₃); IR (film, NaCl) 2958, 2929, 2857, 1739, 1473, 1464, 1360, 1252, 1098, 1048, 984, 836, 775 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.56 (ddd, *J* = 10.8, 7.4, 7.4 Hz, 1H), 5.38-5.24 (m, 3H), 5.23-5.14 (m, 2H), 4.80 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.50 (ddd, *J* = 10.8, 10.8, 1.1 Hz, 1H), 3.67-3.62 (m, 2H), 3.30 (dd, *J* = 5.6, 4.8 Hz, 1H), 3.26 (ddd, *J* = 8.6, 2.6, 2.2 Hz, 1H), 2.69-2.53 (m, 4H), 2.15-1.95 (m, 4H), 1.85-1.69 (m, 4H), 1.64-1.56 (m, 1H), 1.22 (d, *J* = 7.4 Hz, 3H), 1.00-0.95 (m, 9H), 0.93 (d, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.92-0.89 (obscured, 6H), 0.89 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.09 (s, 3H), 0.072 (app s, 6H), 0.068 (s, 3H), 0.060 (s, 3H), 0.055 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 135.2, 134.2, 133.5, 132.3, 131.7, 127.3, 80.0, 78.4, 77.0, 75.6, 74.8, 64.6, 44.0, 42.8, 37.8, 37.4, 37.0, 35.8, 35.0, 34.0, 32.6, 26.2 (2), 25.8, 25.6, 21.0, 18.5, 18.4, 18.0, 17.9, 17.2, 17.0, 16.3, 15.9, 14.3, 14.0, 13.3, 9.5, -3.1, -3.3, -3.6, -4.3 (2), -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) *m/z* 1017.7211 [(M+Na)⁺; calcd for C₅₅H₁₁₀O₇Si₄Na: 1017.7226]



(+)-S17

Carbamate (+)-S17: A solution of alcohol (+)-S16 (17 mg, 0.017 mmol) in CH₂Cl₂ (1.0 mL) was treated with Cl₃CCON=C=O (68 μ L, 1 M solution in toluene) at room temperature for 30 min. The solution was loaded directly onto a neutral Al₂O₃ plug. After 4 h, the material was flushed from the Al₂O₃ (EtOAc, 50 mL), concentrated, and purified by flash chromatography (10% ethyl acetate/hexanes) providing 13 mg

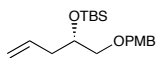
(+)-**S17** (77%). (71%). $[\alpha]_D^{23} +47.8$ (*c* 1.0, CHCl₃); IR (film, NaCl) 2958, 2929, 2857, 1733, 1473, 1464, 1361, 1253, 1097, 1047, 836 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.45-5.22 (m, 5H), 5.16 (ddd, *J* = 10.8, 9.3, 5.2 Hz, 1H), 4.80 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.69 (dd, *J* = 5.9, 5.9 Hz, 1H), 4.55-4.47 (m, 3H), 3.64 (dd, *J* = 2.6, 2.2 Hz, 1H), 3.45 (dd, *J* = 4.5, 4.5 Hz, 1H), 3.29 (dd, *J* = 5.6, 4.8 Hz, 1H), 2.80 (dddd, *J* = 16.0, 6.7, 6.7, 6.7 Hz, 1H), 2.68-2.59 (m, 1H), 2.63 (dd, *J* = 7.4, 3.0 Hz, 1H), 2.59-2.50 (m, 1H), 2.15-1.85 (m, 5H), 1.81 (dddd, *J* = 10.0, 6.7, 6.7, 6.7, 2.2 Hz, 1H), 1.74 (ddd, *J* = 14.1, 11.2, 1.5 Hz, 1H), 1.67 (dddd, *J* = 13.0, 6.7, 6.7, 2.2 Hz, 1H), 1.59 (dddd, *J* = 11.5, 11.5, 2.6, 2.6 Hz, 1H), 1.23 (d, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.98-0.94 (m, 9H), 0.92 (s, 9H), 0.93-0.89 (m, 6H), 0.89 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.09 (s, 3H), 0.071 (s, 3H), 0.068 (s, 3H), 0.062 (s, 3H), 0.059 (s, 3H), 0.054 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 156.9, 135.2, 133.5, 132.4, 132.0, 130.2, 127.0, 79.9, 78.9, 77.0, 76.2, 74.8, 64.6, 44.1, 42.8, 38.0, 37.5, 34.9, 34.0 (2), 33.9, 32.0, 26.2, 26.1, 25.8, 25.6, 20.7, 18.5, 18.4, 18.0, 17.9 (2), 17.1, 16.6, 15.9, 14.4, 14.3, 14.0, 10.2, -3.2, -3.6, -3.7, -4.3 (2), -4.6, -4.9 (2); high resolution mass spectrum (ES⁺) *m/z* 1060.7257 [(M+Na)⁺; calcd for C₅₆H₁₁₁NO₈Si₄Na: 1060.7285]



(+)-**13**

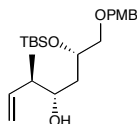
Tetra-ol (+)-13: Carbamate (+)-**S17** (13 mg, 0.012 mmol) was dissolved in MeOH (3.5 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (4N, 4.0 mL) was added in 200–400 μ L portions over 3 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 1 mL of 4N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 1.0 mL of MeOH. After 7 h the solution was diluted with EtOAc (25 mL) and H₂O (10 mL), and quenched with NaHCO₃ (s) until gas evolution ceases. The layers were separated and the aqueous layer extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried (MgSO₄), filtered, and concentrated.

Flash chromatography gradient elution (2% MeOH/CH₂Cl₂ → 10% MeOH/CH₂Cl₂) gave (+)-**13** (7.3 mg, 97% yield). $[\alpha]_D^{23} +38.2$ (*c* 0.5, MeOH); IR (film, NaCl) 3362, 2967, 2923, 2871, 1700, 1456, 1390, 1323, 1235, 1097, 1041, 974 cm⁻¹; ¹H NMR (500 MHz, CD₃OD) δ 5.54 (dd, *J* = 10.8, 10.8 Hz, 1H), 5.44-5.33 (m, 3H), 5.32-5.23 (m, 2H), 4.76 (dd, *J* = 7.4, 4.8 Hz, 1H), 4.65 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.58 (ddd, *J* = 10.8, 10.8, 1.9 Hz, 1H), 3.66 (dd, *J* = 4.1, 4.1 Hz, 1H), 3.23 (dd, *J* = 7.1, 4.1 Hz, 1H), 3.18 (dd, *J* = 7.8, 4.1 Hz, 1H), 2.93 (dddd, *J* = 16.0, 6.7, 6.7, 4.8 Hz, 1H), 2.71 (ddd, *J* = 16.4, 10.8, 6.7 Hz, 1H), 2.64 (dddd, *J* = 7.4, 7.4, 7.4, 4.5 Hz, 1H), 2.45 (dddd, *J* = 14.5, 8.19, 6.7, 6.7 Hz, 1H), 2.15-2.05 (m, 2H), 1.95 (ddd, *J* = 14.1, 3.7, 3.7 Hz, 1H), 1.90-1.73 (m, 4H), 1.70-1.58 (m, 2H), 1.27 (d, *J* = 7.4 Hz, 3H), 1.063 (d, *J* = 6.7 Hz, 3H), 1.055 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 7.4 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 176.9, 160.4, 135.2, 133.9, 133.7, 133.1, 131.1, 128.6, 80.2, 80.0, 78.9, 76.2, 73.6, 64.0, 44.5, 42.8, 38.9, 37.2, 37.1, 37.0, 36.7, 34.6, 32.7, 21.8, 19.3, 18.6, 17.3, 16.0, 15.9, 14.9, 13.2, 9.7; high resolution mass spectrum (ES⁺) *m/z* 604.3853 [(M+Na)⁺; calcd for C₃₂H₅₅NO₈Na: 604.3825]



(-)-**S18**

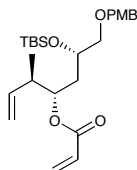
Alkene (-)-S18: A solution of alcohol (-)-**16** (0.768 g, 4 mmol) and imidazole (0.544 g, 8.0 mmol) in CH₂Cl₂ (40 mL) was cooled to 0 °C and treated with *tert*-butyldimethylsilyl chloride (900 mg, 6 mmol). The resultant solution was stirred 12 h at ambient temperature, diluted with ether (75 mL), washed with H₂O (2 x 100 mL) and saturated brine (100 mL), dried over MgSO₄, and concentrated. Flash chromatography (5% ethyl acetate/hexanes) afforded alkene (-)-**S18** (1.18 g, 95%) as a colorless oil. $[\alpha]_D^{23} -25$ (*c* 0.48, CHCl₃); IR (neat) 2954, 2928, 2897, 2856, 1613, 1514, 1472, 1249, 1105, 1038, 835 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.83 (dddd, *J* = 17.0, 10.2, 7.2, 7.2 Hz, 1H), 5.06 (d, *J* = 17.0 Hz, 1H), 5.03 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.88 (ddd, *J* = 11.2, 5.8, 5.6 Hz, 1H), 3.81 (s, 3H), 3.38 (dd, *J* = 9.6, 5.6 Hz, 1H), 3.36 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.24 (ddd, *J* = 13.4, 6.3, 6.3 Hz, 1H), 2.21 (ddd, *J* = 13.4, 6.3, 6.3 Hz, 1H), 0.90 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H); (ES⁺) *m/z* 335.2029 [(M+Na)⁺; calcd for C₁₉H₃₂NaO₃Si: 335.2042]



(-)-17

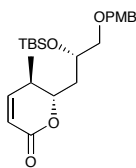
Alcohol (-)-17. Alkene (-)-**S18** (1.7 g, 5.5 mmol) was dissolved in CH_2Cl_2 (55 mL) and bubbled O_3 at -78°C for 20 minutes, then the solution was degassed with argon and PPh_3 (excess) was added. After 1 hour the mixture was evaporated and filtered quickly to provide the intermediate aldehyde. In an other flask, $n\text{-BuLi}$ (2.4 M in hexanes, 3.3 mL) was added dropwise to a cloudy solution of potassium *tert*-butoxide (925.8 mg, 8.25 mmol) and *trans*-2-butene (excess, 1 mL) in THF (12 mL) at -78°C . The resulting yellow mixture was stirred at -45°C for 20 min. The reaction mixture was recooled to -78°C and a solution of (+)- α -methoxydiisopinocampheylborane (2.96 g, 9.35 mmol) in THF (5 mL) was added. The resulting colorless reaction mixture was stirred at -78°C for 35 min. $\text{BF}_3\cdot\text{Et}_2\text{O}$ (1.4 mL, 11 mmol) was added rapidly followed immediately by a solution of the above aldehyde (1.7 g, 5.5 mmol) in 2.5 mL of THF. The resulting cloudy reaction mixture was stirred at -78°C for 4 h. The reaction was then quenched by addition of 3 N aqueous NaOH (5 mL) followed by 30% aqueous H_2O_2 (5 mL). The reaction mixture was warmed to 25°C and stirred overnight. The mixture was diluted with ethyl acetate and saturated aqueous NaCl. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were dried (MgSO_4) and then concentrated in vacuo. The homoallylic alcohols were purified by a very careful column chromatography on silica gel to obtain alcohol (-)-**17** (1.21 g, 75% yield). $[\alpha]_{\text{D}}^{23} -12.2$ (c 0.36, CHCl_3); IR (neat) 3474, 2957, 2929, 2856, 1514, 1472, 1250, 1172, 1089, 1036, 836 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.24 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 5.79 (ddd, $J = 16.5, 11.2, 7.8$ Hz, 1H), 5.07 (d, $J = 0.7$ Hz, 1H), 5.05-5.03 (m, 1H), 4.47 (d, $J = 11.6$ Hz, 1H), 4.42 (d, $J = 11.6$ Hz, 1H), 4.11 (brddd, $J = 11.9, 5.6, 5.2$ Hz, 1H), 3.80 (s, 3H), 3.70 (ddd, $J = 10.3, 5.4, 2.1$ Hz, 1H), 3.45 (dd, $J = 9.4, 5.6$ Hz, 1H), 3.42 (dd, $J = 9.4, 6.6$ Hz, 1H), 2.19 (brddd, $J = 13.7, 6.9, 6.7$ Hz, 2H), 1.67 (ddd, $J = 14.4, 5.4, 2.2$ Hz, 1H), 1.60 (ddd, $J = 14.4, 10.3, 4.1$ Hz, 1H), 1.01 (d, $J = 6.8$ Hz, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.005 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.1, 140.5, 130.1, 129.2, 115.2,

113.6, 73.1, 72.9, 71.3, 70.1, 55.2, 44.1, 37.6, 25.8, 17.9, 15.7, -4.6, -5.0; (ES⁺) *m/z* 417.2430 [(M+Na)⁺; calcd for C₂₂H₃₈NaO₄Si: 417.2437]



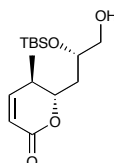
(-)-S19

Diene (-)-S19: To a stirred solution of (-)-17 (0.70 g, 1.77 mmol) in dry CH₂Cl₂ (25 mL), a catalytic amount of DMAP (~15 mg) was added at room temperature. The reaction mixture was cooled to -78°C. Et₃N (0.61 mL, 4.42 mmol) was added dropwise, immediately followed by acryloyl chloride (0.29 mL, 3.55 mmol). After 2 h of stirring at -78°C, the reaction mixture was diluted with CH₂Cl₂ (20 mL), quenched with brine (30 mL) and warmed rapidly to room temperature. The aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL). The organic layer was dried over MgSO₄, filtered and concentrated in vacuo. Flash chromatography (AcOEt/Hexanes 5%) provided diene (-)-S19 in 80% (640 mg). $[\alpha]_D^{23}$ -32 (*c* 1, CHCl₃); IR (film, CHCl₃) 2959, 2928, 2895, 1723, 1513, 1249, 1193, 1101 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.37 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.10 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.78 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.74 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.09 (ddd, *J* = 9.9, 4.5, 2.5 Hz, 1H), 5.06 (d, *J* = 9.0 Hz, 1H), 5.03 (brs, 1H), 4.43 (s, 2H), 3.85-3.76 (m, 1H), 3.80 (s, 3H), 3.36 (dd, *J* = 9.7, 5.2 Hz, 1H), 3.29 (dd, *J* = 9.7, 5.8 Hz, 1H), 2.58-2.52 (m, 1H), 1.79 (ddd, *J* = 14.5, 9.9, 3.0 Hz, 1H), 1.58 (ddd, *J* = 14.5, 9.2, 2.3 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.01 (s, 3H), -0.001 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.5, 159.1, 139.2, 130.3, 130.1, 129.1, 128.9, 115.4, 113.5, 74.6, 74.1, 72.8, 68.4, 55.1, 41.4, 36.1, 25.8, 18.0, 14.7, -4.2, -5.0; (ES⁺) *m/z* 471.2533 [(M+Na)⁺; calcd for C₂₅H₄₀NaO₅Si: 471.2542]



(-)-18

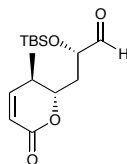
Lactone (-)-18: (4,5-DihydroIMES)(PCy₃)Cl₂Ru=CHPh (8.0 mg, 9.5 x 10⁻³ mmol) was added in one portion at room temperature to a stirred solution of (-)-**S19** (0.042 g, 0.095 mmol) in dry CH₂Cl₂ (10 mL). The reaction mixture was heated at reflux for 3 h (oil bath temperature: 58 °C), cooled to room temperature, concentrated in vacuo and purified by flash chromatography (AcOEt/Hexanes 20%). Lactone (-)-**18** was isolated in 75% yield (37 mg) [α]_D²³ -46.5 (*c* 0.5, CHCl₃); IR (film, CHCl₃) 2959, 2927, 2855, 1732, 1513, 1248, 1098, 823 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.63 (dd, *J* = 9.7, 2.4 Hz, 1H), 5.97 (dd, *J* = 9.7, 2.4 Hz, 1H), 4.46 (d, *J* = 11.8 Hz, 1H), 4.43 (d, *J* = 11.8 Hz, 1H), 4.24 (ddd, *J* = 10.6, 10.2, 2.0 Hz, 1H), 4.20 (ddd, *J* = 10.1, 5.1, 2.2 Hz, 1H), 3.80 (s, 3H), 3.40 (dd, *J* = 9.7, 4.8 Hz, 1H), 3.34 (dd, *J* = 9.7, 5.4 Hz, 1H), 2.47-2.40 (m, 1H), 1.87 (ddd, *J* = 14.2, 10.6, 2.3 Hz, 1H), 1.77 (ddd, *J* = 14.2, 10.2, 2.2 Hz, 1H), 1.11 (d, *J* = 7.2 Hz, 3H), 0.86 (s, 9H), 0.066 (s, 3H), 0.060 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 163.7, 159.1, 151.5, 130.3, 129.1, 120.1, 113.6, 79.8, 74.4, 72.8, 66.7, 55.2, 38.2, 33.6, 25.8, 17.9, 16.4, -4.3, -4.9; (ES⁺) *m/z* 443.2224 [(M+Na)⁺; calcd for C₂₃H₃₆NaO₅Si: 443.2229]



(-)-S20

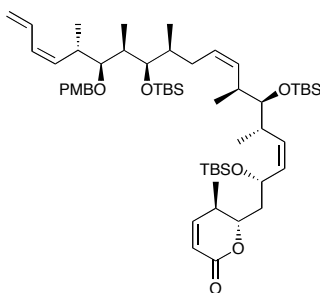
Alcohol (-)-S20: At 0 °C, a solution of PMB ether (-)-**18** (240 mg, 0.57 mmol) in CH₂Cl₂ (5.7 mL) was treated with H₂O (0.25 mL) and DDQ (143 mg, 0.63 mmol) and stirred for 3 h. The mixture was quenched with 10 mL of saturated NaHCO₃, washed with H₂O (2 x 10 mL) and separated. The aqueous layer was then extracted with CH₂Cl₂ (3 x 15 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated from hexanes to provide a colorless oil. Purification using flash chromatography (AcOEt/Hexanes 30%) afforded 150 mg of alcohol (-)-**S20** (89%); [α]_D²³ -65.6 (*c* 0.32, CHCl₃); IR (film, CHCl₃) 3446, 2953, 2928, 2895, 2856, 1697, 1465, 1389, 1257, 1085, 1014, 837 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.33 (dd, *J* = 9.7, 2.3 Hz, 1H), 5.93 (dd, *J* = 9.7, 2.4 Hz, 1H), 4.16 (ddd, *J* = 10.4, 10.4, 1.8 Hz, 1H), 4.12 (dd, *J* = 6.5, 3.5 Hz, 1H), 3.62 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.45 (dd, *J* = 11.3, 3.3 Hz, 1H), 2.44

(m, 1H), 1.96 (ddd, $J = 14.4, 10.1, 1.9$ Hz, 1H), 1.90 (brs, 1H), 1.74 (ddd, $J = 14.4, 10.7, 2.5$ Hz, 1H), 1.11 (d, $J = 7.2$ Hz, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.6, 151.6, 120.0, 80.1, 68.1, 66.8, 37.4, 33.6, 25.7, 17.9, 16.3, -4.4, -4.9; (ES $^+$) m/z 323.1645 [(M+Na) $^+$; calcd for $\text{C}_{15}\text{H}_{28}\text{NaO}_4\text{Si}$: 323.1654]



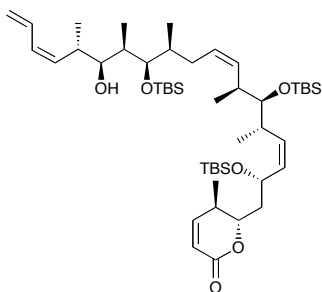
(-)-19

Aldehyde (-)-19: To a 0 °C solution of alcohol (-)-**S20** (28 mg, 0.094mmol) in CH_2Cl_2 (1 mL) were added Dess-Martin periodinane (39.7 mg, 0.103 mmol) and NaHCO_3 (24 mg, 0.28 mmol). The resulting solution was stirred for 2.5 h and quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (15 mL) and saturated NaHCO_3 solution (15 mL). The mixture was then extracted with Et_2O (3 x 10 mL) and separated. The organic solution was then washed with H_2O , dried (MgSO_4), filtered, and concentrated. The resulting aldehyde (-)-**19** (26 mg, 85%) was used without further purification: $[\alpha]_{\text{D}}^{23}$ -62.2 (c 1.05, CHCl_3); IR (film, CHCl_3) 2959, 2929, 2856, 1735, 1464, 1388, 1252, 1118, 1084, 1009 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.66 (d, $J = 0.7$ Hz, 1H), 6.67 (dd, $J = 9.7, 2.4$ Hz, 1H), 5.97 (dd, $J = 9.7, 2.4$ Hz, 1H), 4.44 (dd, $J = 10.6, 2.3$ Hz, 1H), 4.22 (ddd, $J = 10.4, 10.4, 2.1$ Hz, 1H), 2.51 (dddd, $J = 9.8, 7.3, 2.5, 2.5$ Hz, 1H), 2.05 (ddd, $J = 14.1, 10.6, 2.5$ Hz, 1H), 1.81 (ddd, $J = 14.1, 10.7, 2.1$ Hz, 1H), 1.13 (d, $J = 7.2$ Hz, 3H), 0.92 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.7, 163.1, 151.3, 120.1, 78.7, 73.3, 35.4, 33.5, 25.5, 18.0, 16.2, -4.6, -5.2; (ES $^+$) m/z [(M+Na) $^+$; calcd for $\text{C}_{15}\text{H}_{26}\text{NaO}_4\text{Si}$:].



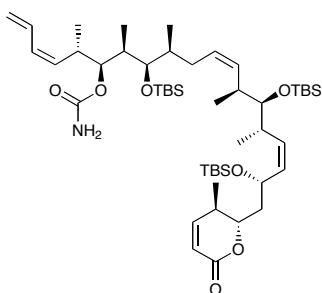
(+)-S21

PMB ether (+)-S21: Phosphonium salt (+)-**20** (220 mg, 0.22 mmol), was azeotropically dried with benzene (3 × 1.0 mL) using a double manifold and further dried by heating to 50 °C under vacuum (0.2 torr) for 12 h. The salt was back-filled with argon, dissolved in 1 mL of freshly distilled THF, sparged with argon for 15 min, and cooled to –78 °C. The resultant solution was treated with methyl lithium/lithium bromide complex (2.2 M in Et₂O, 0.11 mL), stirred 15 min, warmed to 0 °C, stirred 30 min, and re-cooled to –20 °C. To this orange/red solution was transferred via cannula a degassed solution of aldehyde (–)-**19** (70 mg, 0.24 mmol) in THF (500 μL) over 1 min. The orange solution was allowed to slowly warm to –8 °C over 3.0 h. The resulting light yellow solution was quenched with saturated NH₄Cl and diluted (Et₂O/H₂O). The layers were separated, and the aqueous layer was extracted (3 × Et₂O). The combined organic layers were dried (Na₂SO₄), concentrated, and chromatographed (gradient elution: 2% EtOAc/hexanes → 50% EtOAc/hexanes; then 40% CH₃CN/CH₂Cl₂) to afford *cis* isomer (+)-**S21** (65 mg, 31%), and phosphonium salt (+)-**20** (120 mg, 38%). $[\alpha]_D^{23} +52.8$ (c 0.7, CHCl₃); IR (film, NaCl) 2956, 1738, 1250, 1060 cm^{–1}; ¹H NMR (500 MHz, CDCl₃) 7.26 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.62–6.55 (m, 2H), 6.02 (app t, *J* = 11.0 Hz, 1H), 5.92 (dd, *J* = 2.3, 9.7 Hz, 1H), 5.56 (app t, *J* = 10.5 Hz, 1H), 5.30–5.28 (m, 3H), 5.19 (d, *J* = 16.8 Hz, 1H), 5.13–5.09 (m, 2H), 4.79–4.75 (m, 1H), 4.54 (d, *J* = 10.5 Hz, 1H), 4.45 (d, *J* = 10.5 Hz, 1H), 4.26–4.23 (m, 1H), 3.80 (s, 3H), 3.47 (app t, *J* = 4.2 Hz, 1H), 3.29 (app t, *J* = 5.1 Hz, 1H), 3.24 (dd, *J* = 3.9, 7.2 Hz, 1H), 3.00–2.97 (m, 1H), 2.64–2.60 (m, 1H), 2.51–2.49 (m, 1H), 2.37–2.35 (m, 1H), 1.92–1.73 (m, 5H), 1.61–1.57 (m, 1H), 1.10 (d, *J* = 7.0 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 6H), 0.94 (s, 9H), 0.91 (s, 9H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.78 (d, *J* = 7.0 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) 163.6, 158.9, 151.4, 134.9, 134.4, 133.0, 132.5, 132.2, 131.2, 129.2, 129.0, 127.3, 120.2, 117.4, 113.6, 84.4, 80.0, 79.7, 76.4, 74.9, 64.4, 55.2, 41.9, 40.1, 38.1, 37.4, 35.4, 35.2, 33.6, 31.8, 30.3, 26.2, 26.1, 25.8, 18.7, 18.6, 18.4, 18.0, 17.3, 16.4, 15.2, 10.6, –3.2, –3.4, –3.5, –4.1, –4.3, –4.9; high resolution mass spectrum (ES⁺) *m/z* 989.6524. [(M+Na)⁺; calcd for C₅₆H₉₈O₇Si₃Na: 989.6518.



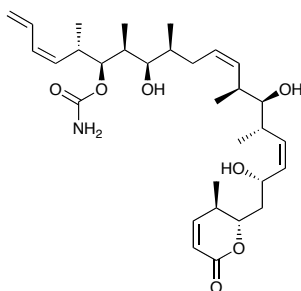
(+)-S22

Alcohol (+)-S22: To a room temperature solution of PMB ether (+)-S21 (59 mg, 0.061 mmol) in CH₂Cl₂ (3.0 mL) was treated with H₂O (50 μ L) and DDQ (20 mg, 0.087 mmol). The mixture was stirred for 30 min and quenched with 5.0 mL saturated NaHCO₃, diluted with CH₂Cl₂, and washed with H₂O and saturated brine solution. The combined organic layers were dried (MgSO₄), filtered and concentrated. Flash chromatography (5% EtOAc/hexanes) provided (+)-S22 (47 mg, 90%). $[\alpha]_D^{23}$ +41.5 (c 0.2, CHCl₃); IR (film, NaCl) 2960, 1737, 1259, 1093, 799 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.65-6.59 (m, 2H), 6.15 (app t, J = 10.9 Hz, 1H), 5.94 (dd, J = 2.3, 9.7 Hz, 1H), 5.34-5.15 (m, 7H), 4.79-4.75 (m, 1H), 4.28-4.24 (m, 1H), 3.64 (dd, J = 2.9, 6.2 Hz, 1H), 3.34-3.31 (m, 2H), 2.81-2.77 (m, 1H), 2.63-2.52 (m, 2H), 2.40-2.36 (m, 1H), 2.02-1.95 (m, 2H), 1.80-1.70 (m, 4H), 1.58 (d, J = 2.7 Hz, 1H), 1.11 (d, J = 7.0 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.93 (d, J = 7.0 Hz, 3H), 0.92 (s, 9H), 0.90 (s, 9H), 0.86 (s, 9H), 0.81 (d, J = 7.0 Hz, 3H), 0.09 (s, 3H), 0.07 (s, 6H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 163.7, 151.4, 135.1, 134.7, 133.1, 132.5, 132.0, 131.0, 127.5, 120.3, 118.4, 80.0, 79.7, 78.2, 76.0, 64.5, 41.9, 37.9, 37.3, 37.2, 36.3, 35.3, 33.6, 32.4, 26.2, 26.1, 25.8, 18.5, 18.4, 18.0, 17.4, 17.0, 16.5, 16.2, 13.6, 9.4, -3.2, -3.3, -3.6, -4.1, -4.3, -4.9; high resolution mass spectrum (ES⁺) m/z 869.5944. [(M+Na)⁺; calcd for C₄₈H₉₀O₆Si₃Na: 869.5943.



(+)-S23

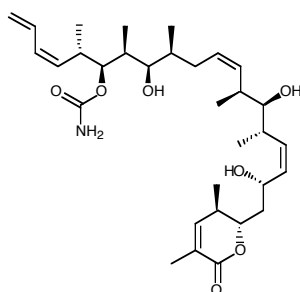
Carbamate (+)-23: A solution of alcohol (+)-**S22** (40 mg, 0.047 mmol) in CH₂Cl₂ (4.0 mL) was treated with Cl₃CCON=C=O (100 μ L, 1 M solution) at room temperature for 30 min. The solution was loaded directly onto a neutral Al₂O₃ plug. After 4 h, the material was flushed from the Al₂O₃ (EtOAc, 50 mL), concentrated, and purified by flash chromatography (10% ethyl acetate/hexanes) providing 42 mg (+)-**S23** (99%). $[\alpha]_D^{23}$ +51.3 (c 0.6, CHCl₃); IR (film, NaCl) 3364, 2959, 1731, 1386, 1259 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.65-6.58 (m, 2H), 6.03 (app t, *J* = 10.9 Hz, 1H), 5.94 (dd, *J* = 2.0, 9.7 Hz, 1H), 5.37 (app t, *J* = 10.4 Hz, 1H), 5.32-5.27 (m, 3H), 5.26-5.12 (m, 3H), 4.79-4.76 (m, 1H), 4.69 (app t, *J* = 6.1 Hz, 1H), 4.52 (br s, 2H), 4.27-4.24 (m, 1H), 3.45 (app t, *J* = 3.7 Hz, 1H), 3.31 (app t, *J* = 4.9 Hz, 1H), 2.99-2.96 (m, 1H), 2.62-2.37 (m, 3H), 1.94-1.87 (m, 3H), 1.76-1.62 (m, 3H), 1.11 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.93 (s, 9H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.86 (s, 9H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.059 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 163.7, 156.8, 151.4, 135.0, 133.5, 133.0, 132.5, 132.0, 129.8, 127.2, 120.2, 117.8, 80.0, 79.7, 78.7, 76.2, 64.4, 41.8, 37.9, 37.4, 35.2, 34.4, 33.6, 32.0, 30.3, 26.2, 26.1, 25.8, 18.5, 18.4, 18.0, 17.5, 17.3, 16.5, 16.3, 14.1, 10.2, -3.2, -3.5, -3.7, -4.2, -4.4, -4.9; high resolution mass spectrum (ES⁺) *m/z* 912.6019. [(M+Na)⁺; calcd for C₄₉H₉₁NO₇Si₃Na: 912.6001.



(+)-21

Triol (+)-21: Carbamate (+)-**S23** (42 mg, 0.047 mmol) was dissolved in MeOH (18 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (4N, 6.0 mL) was added in 200–400 μ L portions over 4 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 4 mL of 4N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 2.0 mL of MeOH. After 12 h the solution was quenched with NaHCO₃ (s), diluted with 30 mL of water and

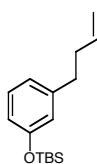
extracted 3 x with EtOAc. The combined organic extracts were dried (Na₂SO₄), filtered, and concentrated. Flash chromatography using washed SiO₂ (hexanes then 10% MeOH/CH₂Cl₂ then 5% MeOH/CH₂Cl₂) via gradient elution (2% MeOH/CH₂Cl₂ → 10% MeOH/CH₂Cl₂) gave (+)-**21** (23 mg, 92% yield). $[\alpha]_D^{23}$ +51.1 (c 0.367, MeOH); IR (film, NaCl) 3419, 2965, 1706, 1396 cm⁻¹; ¹H NMR (500 MHz, CD₃OD) δ 6.84 (dd, *J* = 2.7, 9.8 Hz, 1H), 6.67 (ddd, *J* = 16.9, 10.7, 10.7 Hz, 1H), 6.06 (app t, *J* = 11.0 Hz, 1H), 5.94 (dd, *J* = 2.3, 9.8 Hz, 1H), 5.58 (app t, *J* = 10.1 Hz, 1H), 5.45 (app t, *J* = 10.4 Hz, 1H), 5.39 (dd, *J* = 8.8, 19.6 Hz, 1H), 5.25-5.21 (m, 3H), 5.15 (d, *J* = 10.1 Hz, 1H), 4.82 (br s, 2H), 4.64 (dd, *J* = 4.0, 8.2 Hz, 1H), 4.39-4.37 (m, 1H), 3.23 (dd, *J* = 3.6, 7.8 Hz, 1H), 3.17 (dd, *J* = 3.5, 8.2 Hz, 1H), 3.15-3.12 (m, 1H), 2.73-2.70 (m, 1H), 2.48-2.37 (m, 2H), 1.95-1.80 (m, 2H), 1.77-1.60 (m, 5H), 1.16 (d, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 164.8, 158.8, 152.8, 133.4, 132.7, 132.6, 132.0, 131.9, 129.5, 127.4, 118.9, 117.0, 80.2, 78.8, 78.7, 74.5, 62.2, 40.9, 37.6, 35.77, 35.78, 35.5, 33.6, 33.5, 30.97, 18.0, 16.8, 16.1, 15.4, 14.7, 8.1; high resolution mass spectrum (ES⁺) *m/z* 570.3396. [(M+Na)⁺; calcd for C₃₁H₄₉NO₇Na: 570.3407.



(+)-**22**

Triol (+)-22: NaHMDS (1.0 M in THF, 27.8 mL, 27.8 mmol) was added to a solution of tetra-TBS carbamate (not shown) (4.8 mg, 4.64 μ mol) in THF (0.46 mL) over 10 min at rt. The mixture was stirred for 15 min further, then quenched with H₂O (2 mL), and diluted with CH₂Cl₂ (4 mL) and aq HCl (3 N, 2 mL). The resulting layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and concentrated to give tri-TBS α,β -unsaturated lactone as a oil which was used without further purification. Tri-TBS α,β -unsaturated lactone

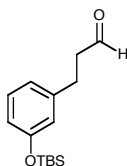
was dissolved in MeOH (2.0 mL). Aqueous HCl (3 N, 2.0 mL) was added dropwise over 4 hr at rt. The reaction mixture was stirred for 1 h further, diluted with H₂O (6 mL) and EtOAc (10 mL). The resulting mixture was neutralized by solid NaHCO₃, and separated. The aqueous layer was extracted with EtOAc (2 x 8 mL). The combined organic extracts were washed with saturated aq brine solution (1 x 10 mL), dried over Na₂SO₄, filtered, and concentrated. Preparative TLC (9% MeOH/CH₂Cl₂) furnished 1.0 mg α,β -unsaturated lactone (+)-**22** (39%, 2 steps) as a colorless solid. $[\alpha]_D^{23}$ +57 (*c* 0.08, MeOH); IR (film, NaCl) 3374, 2927, 1700, 1388, 1038 cm⁻¹; ¹H NMR (500 MHz, CD₃CN) δ 6.66 (ddd, *J* = 16.9, 10.7, 10.7 Hz, 1H), 6.44 (s, 1H), 6.04 (app t, *J* = 11.0 Hz, 1H), 5.46 (ddd, *J* = 10.3, 10.3, 10.3 Hz, 1H), 5.40 (m, 2H), 5.22 (m, 3H), 5.13 (d, *J* = 10.1 Hz, 1H), 5.04 (br s, 2H), 4.69 (dd, *J* = 7.4, 4.6 Hz, 1H), 4.51 (m, 1H), 4.26 (ddd, *J* = 9.7, 9.7, 2.8 Hz, 1H), 3.18 (m, 1H), 3.13 (m, 1H), 3.05 (m, 1H), 2.80 (d, *J* = 5.1 Hz, 1H), 2.62 (m, 1H), 2.55 (d, *J* = 6.4 Hz, 1H), 2.40 (m, 2H), 1.90 (app t, *J* = 3.4 Hz, 1H), 1.82 (s, 3H), 1.77 (m, 1H), 1.67 (m, 2H), 1.56 (m, 1H), 1.07 (d, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CD₃CN) δ 166.1, 158.1, 146.9, 134.8, 134.5, 133.8, 133.7, 133.3, 130.5, 128.6, 127.5, 118.8, 80.8, 79.3, 79.2, 75.5, 63.5, 41.8, 38.5, 36.9, 36.5, 36.4, 34.9, 34.7, 32.0, 19.2, 18.2, 17.0, 16.9, 16.7, 15.7, 9.2; high resolution mass spectrum (ES⁺) *m/z* 562.3769 [(MH)⁺; calcd for C₃₂H₅₂NO₇: 562.3744].



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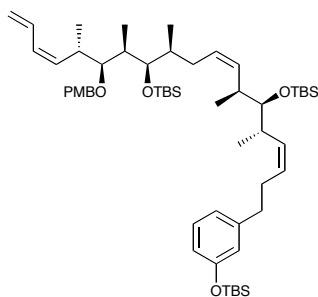
Olefin 24: To a 0° C solution of benzyl bromide **23** (1.18 g, 3.95 mmol) in THF (40 mL, 0.1 M) was added 11.84 mL of allylmagnesium bromide (1 M solution in Et₂O). Reaction was stirred for 3.5 h and quenched with ammonium chloride (saturated aqueous solution). Mixture was diluted with Et₂O, washed with H₂O, sodium bicarbonate (saturated aqueous solution), and brine (saturated aqueous solution). Organic layer was dried (MgSO₄), filtered, and concentrated directly onto SiO₂. Flash chromatography (hexanes) provided **24**, 842 mg (81%) of a clear oil: IR (film, NaCl) 2919, 2049, 1584, 1484, 1276, 1155, 844, 779

cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.15 (app t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.70 (m, 2H), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.06 (ddt, *J* = 17.1, 1.7, 1.7 Hz, 1H), 5.00 (m, 1H), 2.68 (app t, *J* = 7.8 Hz, 2H), 2.38 (m, 2H) 1.02 (s, 9H), 0.22 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 155.6, 143.4, 138.1, 129.0, 121.5, 120.2, 117.5, 114.9, 35.4, 35.3, 25.8, 18.7, -4.4.



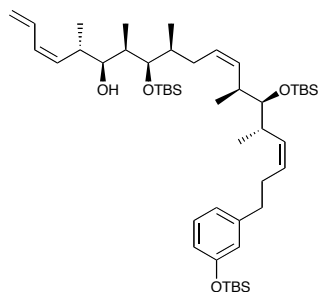
25

Aldehyde 25: A solution of olefin **24** (660 mg, 2.52 mmol) in CH₂Cl₂ (25.2 mL, 0.1 M) was cooled to -78 °C and treated with a stream of ozone and oxygen until the colorless solution became steel-blue in appearance. The reaction mixture was purged with a stream of argon for 10 min, followed by the cautious addition of triphenylphosphine (727 mg, 2.77 mmol). The cooling bath was removed, and the solution was stirred at ambient temperature for 1 h, concentrated, and chromatographed (0 to 5% ethyl acetate/hexanes, gradient elution) to afford **25** (518 mg, 78%) as a colorless oil: IR (film, NaCl) 2934, 2860, 1725, 1583, 1486, 1280, 1156, 836 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.80 (s, 1H), 7.12 (app t, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.3 Hz, 1H), 6.65 (s, 1H), 2.88 (app t, *J* = 7.5 Hz, 2H), 2.73 (app t, *J* = 7.4 Hz, 2H), 0.96 (s, 9H), 0.17 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 201.3, 155.8, 141.8, 129.4, 121.2, 120.1, 117.9, 45.1, 28.0, 25.7, 18.2, -4.4; high resolution mass spectrum (ES⁺) *m/z* 287.1450 [(M+Na)⁺; calcd for C₁₅H₂₄O₂NaSi: 287.1443]



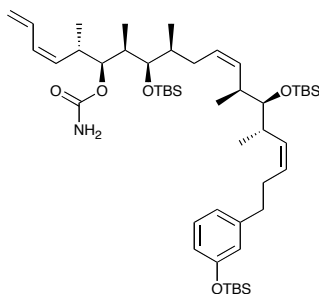
(+)-S24

Tetraene (+)-S24: Phosphonium salt (+)-**20** (140 mg, 0.120 mmol; 6:1 *Z/E* ratio of diene isomers), was azeotropically dried with benzene (3 x 1.5 mL) using a double manifold and further dried by heating to 50 °C under vacuum (0.2 torr) for 12 h. The salt was back-filled with argon, dissolved in 1.0 mL of freshly distilled THF, sparged with argon for 15 min, and cooled to –20 °C. The resultant solution was treated with methyl lithium/lithium bromide complex (2.2 M in ether, 55 μ L), stirred 15 min, warmed to 0 °C, stirred 30 min, and re-cooled to –20 °C. To this orange/red solution was transferred via cannula a degassed solution of aldehyde **25** (32 mg, 0.120 mmol) in THF (0.5 mL + 1 x 0.5 mL rinse) over 15 min. The orange solution was allowed to slowly warm to –8 °C over 3 h. The resulting light yellow solution was quenched with saturated NH₄Cl and diluted (Et₂O/H₂O). The layers were separated, and the aqueous layer was extracted (3 x Et₂O, 3 x CH₂Cl₂). The combined organic layers were dried (MgSO₄), concentrated, and chromatographed (gradient elution: 2% EtOAc/hexanes to 5% EtOAc/hexanes) to afford (+)-**S24** (61 mg, 55%; clear oil, 6:1 ratio of *Z/E* diene isomers. $[\alpha]_D^{23} +54.3^\circ$ (*c* 1.0, CHCl₃); IR (film, NaCl) 2954, 2857, 1604, 1511, 1465, 1369, 1253, 1157, 1041, 968, 836, 775, 424 cm^{–1}; ¹H NMR (500 MHz, CDCl₃, major diastereomer) δ 7.28-7.25 (m, 2H), 7.13-7.09 (m, 1H), 6.89-6.85 (m, 2H), 6.78-6.75 (m, 1H), 6.68-6.63 (m, 2H), 6.60 (ddd, *J* = 16.7, 10.8, 10.8 Hz, 1H), 6.02 (dd, *J* = 11.2, 11.2 Hz, 1H), 5.57 (dd, *J* = 10.4, 10.4 Hz, 1H), 5.45 (dd, *J* = 10.8, 10.8 Hz, 1H), 5.38-5.31 (m, 1H), 5.26-5.08 (m, 4H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.45 (d, *J* = 10.4 Hz, 1H), 3.80 (s, 3H), 3.49 (dd, *J* = 4.5, 4.5 Hz, 1H), 3.30 (dd, *J* = 7.1, 4.1 Hz, 1H), 3.23 (dd, *J* = 7.1, 4.1 Hz, 1H), 2.99 (dddd, *J* = 10.8, 6.7, 6.7, 6.7, 4.1 Hz, 1H), 2.66-2.44 (m, 4H), 2.37-2.19 (m, 2H), 1.98-1.77 (m, 3H), 1.66-1.57 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.99 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.94 (s, 9H), 0.92 (s, 9H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H), 0.19 (app s, 6H), 0.09 (s, 3H), 0.08 (s, 3H), 0.050 (s, 3H), 0.048 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, major diastereomer) δ 158.9, 155.5, 143.7, 134.7, 134.6, 132.9, 132.3, 131.2, 129.07, 129.03, 129.00, 128.2, 127.5, 121.4, 120.2, 117.4, 117.3, 113.6, 84.5, 80.3, 76.4, 74.9, 55.2, 40.0, 38.2, 36.6, 36.3, 36.0, 35.4, 31.9, 29.5, 26.22, 26.16, 25.7, 18.67, 18.56, 18.4, 18.1, 17.7, 17.5, 15.0, 10.6, –3.41, –3.45 (2), –3.68, –4.4 (2); high resolution mass spectrum (ES⁺) *m/z* 955.6489 [(M+Na)⁺; calcd for C₅₆H₉₆O₅NaSi₃: 955.6463].



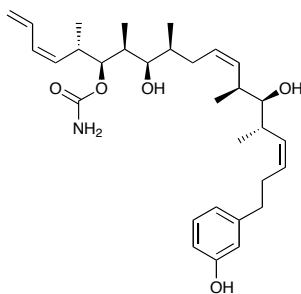
(+)-S25

Alcohol (+)-S25: At 0 °C, a solution of PMB ether (+)-S24 (51 mg, 0.054 mmol, 6:1 mixture of *Z/E* diene isomers) in CH₂Cl₂ (5 mL) was treated with H₂O (600 μL) and DDQ (19 mg, 0.084 mmol). The mixture was stirred for 10 min at 0 °C, warmed to rt and stirred an additional 15 min. The mixture was quenched with saturated NaHCO₃, diluted with CH₂Cl₂ (30 mL), washed with H₂O (1 x 10 mL) and saturated brine solution (1 x 10 mL). The combined organic layers were dried (MgSO₄), filtered and concentrated. Flash chromatography (5% EtOAc/hexanes) provided (+)-S25 (36 mg, 80%) as a clear oil. $[\alpha]_D^{23} +57$ (*c* 1, CHCl₃); IR (film, NaCl) 3580, 2958, 2930, 2889, 2857, 1605, 1584, 1473, 1257, 1158, 1099, 966, 837, 773 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.12 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.67-6.58 (m, 3H), 6.14 (dd, *J* = 10.8, 10.8 Hz, 1H), 5.46 (dd, *J* = 10.8, 10.0 Hz, 1H), 5.40-5.13 (m, 6H), 3.70-3.63 (m, 1H), 3.35-3.28 (m, 2H), 2.80 (dddd, *J* = 8.9, 8.9, 6.7, 6.7, 6.7 Hz, 1H), 2.66-2.48 (m, 4H), 2.38-2.19 (m, 2H), 2.07-1.93 (m, 2H), 1.79 (dddd, *J* = 6.7, 6.7, 6.7, 6.3, 3.5 Hz, 1H), 1.75-1.67 (m, 1H), 0.99 (s, 9H), 0.955 (d, *J* = 6.7 Hz, 3H), 0.951 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.3 Hz, 3H), 0.92 (app s, 18H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.19 (app s, 6H), 0.09 (s, 3H), 0.08 (s, 3H), 0.05 (app s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 155.5, 143.7, 134.8, 134.7, 132.9, 132.0, 130.9, 129.0, 128.2, 127.6, 121.4, 120.2, 118.3, 117.3, 80.3, 78.3, 76.1, 37.9, 37.3, 36.6, 36.4, 36.3, 35.9, 32.4, 29.4, 26.18, 26.15, 25.6, 18.5, 18.45, 18.38, 17.85, 17.4, 17.0, 13.7, 9.3, -3.5 (2), -3.65, -3.68, -4.5 (2); high resolution mass spectrum (ES⁺) *m/z* 835.5910 [(M+Na)⁺; calcd for C₄₈H₈₈O₄NaSi₃: 835.5888]



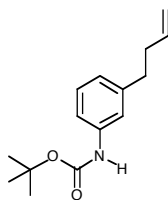
(+)-S26

Carbamate (+)-S26 A solution of alcohol (+)-S25 (30 mg, 0.036 mmol) in CH₂Cl₂ (2.0 mL) was treated with Cl₃CCON=C=O (55 μ L, 1 M solution in toluene) at room temperature for 30 min. The solution was loaded directly onto a neutral Al₂O₃ plug. After 4 h, the material was flushed from the Al₂O₃ (EtOAc, 100 mL), concentrated, and purified by flash chromatography (10% ethyl acetate/hexanes) providing 22 mg (+)-S26 (78%) as a clear oil: $[\alpha]_D^{23} + 63.6$ (*c* 0.5, CHCl₃); IR (film, NaCl) 3509, 3340, 3264, 2957, 2929, 2857, 1730, 1652, 1472, 1326, 1257, 1037, 837, 773 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.12 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 1H), 6.68-6.63 (m, 2H), 6.59 (ddd, *J* = 16.8, 10.4, 10.4 Hz, 1H), 6.02 (dd, *J* = 11.2, 11.2 Hz, 1H), 5.37-5.30 (m, 1H), 5.25-5.15 (m, 3H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.72 (dd, *J* = 5.6, 5.6 Hz, 1H), 4.44 (br s, 2H), 3.45 (dd, *J* = 4.1, 4.1 Hz, 1H), 3.31 (dd, *J* = 6.7, 3.4 Hz, 1H), 3.04-2.94 (m, 1H), 2.65-2.45 (m, 4H), 2.36-2.18 (m, 2H), 1.95-1.85 (m, 3H), 1.71-1.63 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.98 (s, 9H), 0.92 (d, obscured, 3H), 0.919 (s, 9H), 0.916 (s, 9H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H), 0.19 (app s, 6H), 0.10 (s, 3H), 0.06 (s, 3H), 0.05 (app s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.8, 155.6, 143.8, 134.7, 133.6, 133.0, 132.1, 129.8, 129.0, 128.2, 127.6, 121.4, 120.3, 117.8, 117.4, 80.4, 78.9, 76.3, 38.1, 38.0, 36.7, 36.4, 36.0, 34.5, 32.0, 29.4, 26.21, 26.20, 25.7, 18.53, 18.49, 18.45, 18.20, 17.6, 17.5, 14.4, 10.2, -3.4, -3.55, -3.61, -3.63, -4.4 (2); high resolution mass spectrum (ES⁺) *m/z* 878.5943 [(M+Na)⁺; calcd for C₄₉H₈₉NO₅NaSi₃: 878.5946].



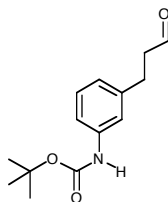
(+)-**32**

Triol (+)-32: Carbamate (+)-**S26** (11 mg, 0.013 mmol) was dissolved in MeOH (3 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (3N) was added in 100–200 μ L portions over 4 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 1.0 mL of 3 N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 2 mL of MeOH. After stirring for 12 h, the reaction was quenched by addition of NaHCO₃ (s), until gas evolution stopped. The mixture was then diluted with 20 mL of water and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated. Flash chromatography (5% MeOH/CH₂Cl₂) gave (+)-**32** (5.7 mg, 82% yield) as a clear oil. $[\alpha]_D^{23} +56.0$ (c 0.5, CHCl₃); IR (film, NaCl) 3348, 2964, 2921, 2872, 1700, 1588, 1456, 1393, 1327, 1152, 1044, 970 cm⁻¹; ¹H NMR (500 MHz, CD₃OD) δ 7.06 (dd, J = 7.4, 7.4 Hz, 1H), 6.70-6.56 (m, 3H), 6.02 (dd, J = 10.8, 10.8 Hz, 1H), 5.46-5.35 (m, 3H), 5.26-5.15 (m, 4H), 5.12 (d, J = 10.0 Hz, 1H), 4.82-4.77 (m, 1H), 3.23 (dd, J = 7.8, 4.1 Hz, 1H), 3.13 (dd, J = 8.6, 3.4 Hz, 1H), 3.12-3.07 (m, 1H), 2.63-2.48 (m, 3H), 2.42 (dddd, J = 15.3, 8.6, 6.7, 6.7 Hz, 1H), 2.36-2.25 (m, 1H), 2.25-2.16 (m, 1H), 1.89 (ddd, J = 14.1, 3.4, 3.4 Hz, 1H), 1.82 (ddd, J = 7.8, 7.1, 3.7 Hz, 1H), 1.79-1.70 (m, 1H), 1.70-1.58 (m, 1H), 0.99 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H), 0.90 (d, J = 7.1 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H), 0.87 (d, J = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 158.4, 156.9, 143.5, 133.8, 132.7, 132.0, 130.98, 129.4, 128.8, 128.7, 127.1, 119.3, 116.9, 115.9, 112.3, 79.4, 78.6, 74.6, 37.5, 35.9, 35.8, 35.7, 34.9, 33.7, 31.0, 29.3, 17.9, 16.8, 16.2, 14.6, 8.0; high resolution mass spectrum (ES⁺) m/z 536.3330 [(M+Na)⁺; calcd for C₃₁H₄₇NO₅Na: 536.3352].



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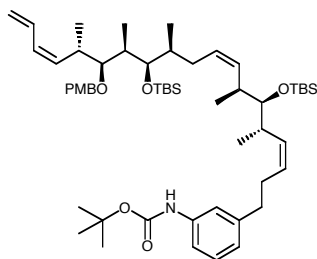
Olefin 27: To a solution of benzyl bromide **26** (247 mg, 0.8666 mmol in 9 mL THF) was added allyl magnesium bromide (2.60 mL, 1 M solution in Et₂O). The reaction was stirred for 3 h and added to a saturated aq NH₄Cl solution. The mixture was diluted (Et₂O) and separated. The organic layer was washed (saturated NaHCO₃, brine), dried (MgSO₄), filtered, and concentrated. The crude residue was then purified by flash chromatography (10% EtOAc/hexanes) to afford 192 mg of **27** (90%). IR (film, NaCl) 3333, 2978, 1699, 1541, 1237, 1161 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.25 (br s, 1H), 7.17 (app t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.54 (br s, 1H), 5.84 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 2.66 (app t, *J* = 7.8 Hz, 2H), 2.35 (app dt, *J* = 7.1, 7.1 Hz, 2H), 1.51 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 152.8, 142.8, 138.3, 137.9, 128.8, 123.0, 118.5, 116.0, 114.9, 80.3, 35.4, 35.3, 28.3; high resolution mass spectrum (CI) *m/z* 247.1565 [(M+Na)⁺; calcd for C₁₅H₂₁NO₂: 247.1572].



28

Aldehyde 28: A solution of olefin **27** (192 mg, 0.777 mmol) in CH₂Cl₂ (8.0 mL, 0.1 M) was cooled to -78 °C and treated with a stream of ozone and oxygen until the colorless solution became steel-blue in appearance. The reaction mixture was purged with a stream of argon for 10 min, followed by the cautious addition of triphenylphosphine (224 mg, 0.855 mmol). The cooling bath was removed, and the solution was stirred at ambient temperature for 1 h, concentrated, and chromatographed (20% ethyl acetate/hexanes, gradient elution) to afford **28** (87 mg, 66%) as a white solid. Melting point: 80-83 °C; IR

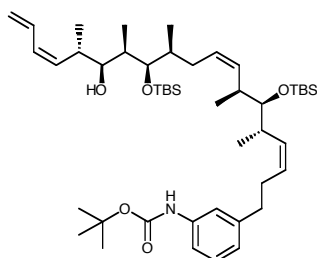
(film, NaCl) 3336, 2978, 1719, 1541, 1236, 1158 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.80 (s, 1H), 7.31 (s, 1H), 7.19 (app t, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 8.2$ Hz, 1H), 6.86 (d, $J = 7.4$ Hz, 1H), 6.53 (br s, 1H), 2.92 (app t, $J = 7.5$ Hz, 2H), 2.76 (app t, $J = 7.5$ Hz, 2H), 1.51 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.4, 152.7, 141.3, 138.6, 129.0, 122.9, 118.3, 116.5, 80.5, 45.1, 28.3, 28.1; high resolution mass spectrum (CI) m/z 249.1364 [$(\text{M})^+$; calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$: 249.1365]



(+)-**S27**

Tetraene (+)-S27: Phosphonium salt (+)-**20** (259 mg, 0.241 mmol; 12:1 *Z/E* ratio of diene isomers), was azeotropically dried with benzene (3 x 1.5 mL) using a double manifold and further dried by heating to 50 °C under vacuum (0.2 torr) for 12 h. The salt was back-filled with argon, dissolved in 3 mL of freshly distilled THF, sparged with argon for 15 min, and cooled to -78 °C. The resultant solution was treated with methyl lithium•lithium bromide (2.2 M in THF, 108 μL), stirred 15 min, and warmed to -20 °C. To this orange/red solution was transferred via cannula a degassed solution of aldehyde **28** (63 mg, 0.253 mmol) in THF (0.5 mL + 1 x 0.5 mL rinse) over 5 min. The orange solution was allowed to slowly warm to -8 °C over 3 h. The resulting light yellow solution was quenched with saturated NH_4Cl and diluted ($\text{Et}_2\text{O}/\text{H}_2\text{O}$). The layers were separated, and the aqueous layer was extracted (3 x Et_2O , 3 x CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), concentrated, and chromatographed (gradient elution: 2% EtOAc /hexanes to 50% EtOAc /hexanes; then 40% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$) to afford (+)-**S27** (44 mg, 10%, 12:1 ratio of *Z/E* diene isomers. $[\alpha]_{\text{D}}^{23} +54$ (c 0.38, CHCl_3); IR (film, NaCl) 3342, 2928, 1734, 1249, 836 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , major diastereomer) δ 7.24 (d, $J = 6.3$ Hz, 2H), 7.15 (d, $J = 5.3$ Hz, 2H), 7.13 (m, 1H), 6.83 (d, $J = 8.7$ Hz, 1H), 6.83 (m, 2H), 6.57 (ddd, $J = 17.1, 10.6, 10.6$ Hz, 1H), 6.38 (br s, 1H), 5.99 (app t, $J = 11.0$ Hz, 1H), 5.53 (app t, $J = 10.5$ Hz, 1H), 5.41 (ddd, $J = 10.5, 10.5, 10.5$ Hz, 1H), 5.31

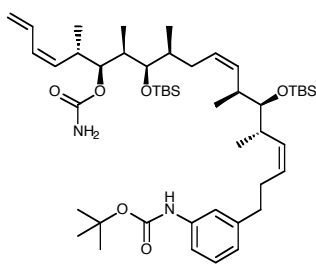
(m, 1H), 5.06-5.19 (m, 3H), 4.47 (ABq, $J = 10.6$, $\Delta\nu = 45.9$ Hz, 2H), 3.77 (s, 3H), 3.46 (app t, $J = 4.4$ Hz, 1H), 3.27 (dd, $J = 6.8, 3.3$ Hz, 1H), 3.21 (dd, $J = 6.8, 4.1$ Hz, 1H), 2.96 (m, 1H), 2.59 (m, 3H), 2.45 (app dq, $J = 6.9, 16.6$ Hz, 1H), 2.25 (m, 3H), 1.85 (m, 3H), 1.58 (m, 1H), 1.50 (s, 9H), 1.06 (d, $J = 6.8$ Hz, 3H), 0.96 (d, $J = 6.7$ Hz, 3H), 0.91 (s, 9H), 0.89 (s, 9H), 0.86 (d, $J = 6.6$ Hz, 3H), 0.84 (d, $J = 7.0$ Hz, 3H), 0.76 (d, $J = 6.7$ Hz, 3H), 0.062 (s, 3H), 0.045 (s, 3H), 0.023 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , major diastereomer) δ 143.2, 138.3, 134.7, 134.6, 133.0, 132.3, 131.3, 129.2, 129.1, 129.1, 128.8, 128.8, 128.1, 127.6, 123.2, 118.6, 117.4, 116.1, 113.7, 84.6, 80.6, 80.4, 76.3, 74.8, 55.3, 40.1, 38.2, 36.7, 36.4, 36.1, 35.5, 32.0, 29.4, 28.4, 26.3, 26.2, 18.7, 18.7, 18.5, 18.4, 17.5, 15.0, 10.6, -3.4 (2), -3.6 (2); high resolution mass spectrum (ES^+) m/z 940.6243 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{55}\text{H}_{91}\text{NO}_6\text{NaSi}_2$: 940.6283].



(+)-**S28**

Alcohol (+)-S28: At 0 °C, a solution of PMB ether (+)-**S27** (15 mg, 0.0164 mmol, 12:1 mixture of *Z/E* diene isomers) in CH_2Cl_2 (1 mL) was treated with H_2O (100 μL) and DDQ (4.1 mg, 0.0180 mmol). The mixture was stirred for 10 min at 0 °C, warmed to rt and stirred an additional 5 min. The mixture was quenched with saturated NaHCO_3 , diluted with CH_2Cl_2 (30 mL), and washed with H_2O and saturated brine solution. The combined organic layers were dried (MgSO_4), filtered and concentrated. Flash chromatography (10% EtOAc/hexanes) provided (+)-**S28** (12 mg, 90%) as a yellow oil. $[\alpha]_{\text{D}}^{23} +54$ (c 0.20, CHCl_3); IR (film, NaCl) 3342, 2928, 1734, 1251, 1161, 772 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.16 (m, 3H), 6.84 (m, 1H), 6.61 (ddd, $J = 16.8, 10.8, 10.8$ Hz, 1H), 6.52 (br s, 1H), 6.12 (app t, $J = 11.0$ Hz, 1H), 5.44 (app t, $J = 10.2$ Hz, 1H), 5.30 (m, 2H), 5.19 (m, 3H), 5.13 (d, $J = 10.1$ Hz, 1H), 3.77 (d, $J = 2.7$ Hz, 1H), 3.61 (dd, $J = 6.2, 2.9$ Hz, 1H), 3.30 (dddd, $J = 18.9, 8.6, 8.6, 3.7$ Hz, 2H), 2.77 (m, 1H), 2.58 (m, 3H), 2.46 (m, 1H), 2.30 (m, 1H), 2.25 (m, 1H), 1.96 (m, 1H), 1.88 (ddd, $J = 14.6, 3.8, 3.8$ Hz, 1H), 1.76 (dddd, J

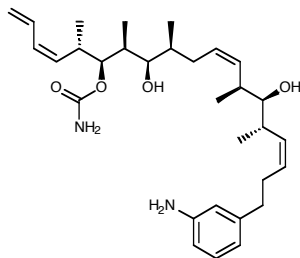
= 13.3, 6.8, 6.8, 3.2 Hz, 1H), 1.68 (m, 1H), 1.50 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H), 0.89 (s, 9H), 0.89 (s, 9H), 0.87 (d, J = 7.3 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H), 0.78 (d, J = 6.8 Hz, 3H), 0.059 (s, 3H), 0.034 (s, 3H), 0.027 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.1, 138.3, 134.8, 134.7, 133.7, 132.8, 132.1, 131.1, 128.8, 128.1, 127.8, 123.2, 118.6, 118.4, 116.1, 80.5, 78.3, 77.3, 76.2, 38.0, 37.1, 36.6, 36.6, 36.3, 36.1, 32.6, 29.3, 28.4, 26.2, 26.2, 18.7, 18.5, 17.9, 17.6, 17.1, 13.6, 9.5, -3.4, -3.5, -3.6 (2); high resolution mass spectrum (ES^+) m/z 820.5835 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{47}\text{H}_{83}\text{NO}_5\text{NaSi}_2$: 820.5708]



(+)-**S29**

Carbamate (+)-S29. A solution of alcohol (+)-**S28** (12.0 mg, 0.015 mmol) in CH_2Cl_2 (3.0 mL) was treated with $\text{Cl}_3\text{CCON}=\text{C}=\text{O}$ (100 μL , 1 M solution) at room temperature for 30 min. The solution was loaded directly onto a neutral Al_2O_3 plug. After 4 h, the material was flushed from the Al_2O_3 (EtOAc , 100 mL), concentrated, and purified by flash chromatography (10% ethyl acetate/hexanes) providing 9.0 mg (+)-**S29** (72%) as a clear oil: $[\alpha]_{\text{D}}^{23} + 70$ (c 0.26, CHCl_3); IR (film, NaCl) 3328, 2929, 1716, 1161, 836, 772 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.25 (br s, 1H), 7.17 (app t, J = 7.8 Hz, 1H), 7.09 (br s, 1H), 6.83 (d, J = 7.3 Hz, 1H), 6.80 (br s, 1H), 6.58 (ddd, J = 17.0, 10.5, 10.5 Hz, 1H), 6.00 (app t, J = 11.0 Hz, 1H), 5.47 (app t, J = 10.2 Hz, 1H), 5.35 (app t, J = 10.0 Hz, 1H), 5.30 (m, 1H), 5.16 (m, 2H), 5.10 (d, J = 10.0 Hz, 1H), 4.69 (app t, J = 5.9 Hz, 1H), 4.52 (br s, 2H), 3.43 (dd, J = 5.0, 3.8 Hz, 1H), 3.27 (dd, J = 7.4, 2.8 Hz, 1H), 2.96 (ddd, J = 9.8, 6.8, 6.8 Hz, 1H), 2.57 (m, 3H), 2.44 (app dq, J = 15.0, 7.5 Hz, 1H), 2.25 (m, 3H), 1.96 (m, 1H), 1.88 (m, 2H), 1.68 (m, 1H), 1.50 (s, 9H), 0.97 (d, J = 6.8 Hz, 3H), 0.90 (s, 18H), 0.90 (m, 3H), 0.87 (d, J = 7.3 Hz, 3H), 0.86 (d, J = 7.3 Hz, 3H), 0.76 (d, J = 6.7 Hz, 3H), 0.070 (s, 3H), 0.040 (s, 3H), 0.029 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.1, 152.9, 143.1, 138.4, 134.5, 133.7, 132.6, 132.2,

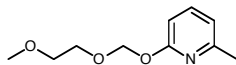
129.8, 128.8, 128.2, 127.8, 123.1, 118.6, 117.8, 116.1, 80.6, 78.8, 77.3, 76.5, 38.1, 37.8, 36.7, 36.5, 36.1, 34.6, 32.5, 29.3, 28.4, 26.2 (2), 18.9, 18.5, 18.2, 17.8, 17.5, 13.8, 10.3, -3.4, -3.5, -3.6 (2); high resolution mass spectrum (ES⁺) m/z 863.5781 [(M+Na)⁺; calcd for C₄₈H₈₄N₂O₆NaSi₂: 863.5766].



(+)-**33**

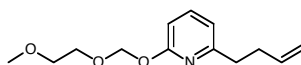
Aniline (+)-33: Carbamate (+)-**S29** (9.0 mg, 0.011 mmol) was dissolved in MeOH (1 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (3N) was added in 100–200 μ L portions over 4 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 1.0 mL of 3 N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 2 mL of MeOH. After stirring for 12 h, the reaction was quenched by addition of NaHCO₃ (s), until gas evolution stopped. The mixture was then diluted with 20 mL of water and extracted with EtOAc (3x). The combined organic layers were dried (Na₂SO₄), filtered, and concentrated. Preparative TLC (80% EtOAc/hexanes) gave (+)-**33** (3.0 mg, 58% yield) as a white amorphous solid. $[\alpha]_D^{23} +51$ (c 0.13, MeOH); IR (film, NaCl) 3348, 2926, 1712, 1388, 1042, 973 cm⁻¹; ¹H NMR (500 MHz, CD₃CN) δ 6.99 (app t, J = 7.9 Hz, 1H), 6.67 (ddd, J = 16.8, 10.6, 10.6 Hz, 1H), 6.50 (m, 2H), 6.46 (d, J = 8.0 Hz, 1H), 6.05 (app t, J = 11.1 Hz, 1H), 5.40 (m, 3H), 5.23 (m, 3H), 5.13 (d, J = 10.2 Hz, 1H), 5.06 (br s, 2H), 4.70 (dd, J = 7.0, 4.9 Hz, 1H), 4.03 (br s, 1H), 3.20 (m, 1H), 3.12 (m, 1H), 3.05 (m, 1H), 2.55 (m, 3H), 2.47 (d, J = 5.2 Hz, 1H), 2.40 (m, 1H), 2.25 (m, 3H), 1.91 (app dt, J = 13.9, 4.0 Hz, 1H), 1.75 (m, 3H), 1.62 (m, 1H), 0.96 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CD₃CN) δ 158.2, 148.3, 144.2, 135.1, 134.6, 133.3, 132.6, 130.4, 130.1, 129.9, 128.2, 119–117 (2 carbons, obscured by solvent), 115.5, 113.0, 79.8, 79.1, 75.6, 38.4, 36.8, 36.7, 36.6, 36.0,

34.9, 32.1, 30.2, 19.1, 18.1, 16.9, 15.5, 9.2; high resolution mass spectrum (ES^+) m/z 535.3501 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{31}\text{H}_{48}\text{N}_2\text{O}_4\text{Na}$: 535.3512].



S30

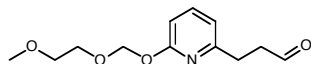
Pyridine S30: To a solution of pyridol **29** (1 g, 9.17 mmol in 90 mL CH_2Cl_2) was added Hunig's base (3.37 mL, 19.248 mmol) followed by MEMCI (2.085 mL, 18.331 mmol). The reaction was stirred for 30 min. and poured into a saturated NaHCO_3 aq. solution. The mixture was extracted (3 x CH_2Cl_2) and the combined organic extracts were dried (MgSO_4), filtered, and concentrated onto SiO_2 . Flash chromatography (50% EtOAc/hexanes) furnished 1.74 g of **S30** (96%); IR (film, NaCl) 2925, 1599, 1579, 1452, 1113, 975 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.46 (app t, $J = 7.4$ Hz, 1H), 6.73 (d, $J = 7.2$ Hz, 1H), 6.59 (d, $J = 8.2$ Hz, 1H), 5.57 (d, $J = 0.7$ Hz, 2H), 3.85 (app tt, $J = 4.6, 0.6$ Hz, 2H), 3.55 (tq, $J = 3.2, 0.9$ Hz, 2H), 3.36 (d, $J = 0.9$ Hz, 3H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 161.9, 156.2, 138.9, 116.5, 107.2, 90.7, 71.5, 68.5, 58.7, 23.8; high resolution mass spectrum (CI^+) m/z 198.1126 $[(\text{MH})^+]$; calcd for $\text{C}_{10}\text{H}_{16}\text{NO}_3$: 198.1130].



30

Olefin 30: To a -78°C THF solution of pyridine **S30** (188 mg, 0.954 mmol in 9.5 mL) was added 1.049 mL (1.049 mmol) NaHMDS (1 M in THF). The cooling bath was removed, the solution was warmed to ambient temperature and stirred for 20 min. Allyl bromide (124 μL , 1.431 mmol) was added to the solution and the mixture was stirred an additional 1.5 h. The resulting cloudy suspension was poured into a saturated NaHCO_3 aq. solution and extracted (2 x CH_2Cl_2 , 2 x Et_2O). The combined organic extracts were dried (MgSO_4), filtered, and concentrated. Flash chromatography (gradient elution: 10% EtOAc/hexanes to 20% EtOAc/hexanes) afforded 60 mg **30** (37%); IR (film, NaCl) 2926, 1597, 1579, 1456, 1115, 981 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.46 (app t, $J = 7.7$ Hz, 1H), 6.72 (d, $J = 7.3$ Hz, 1H),

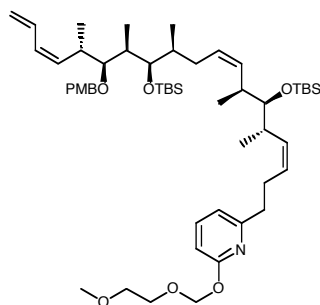
6.59 (d, $J = 8.2$ Hz, 1H), 5.83 (ddt, $J = 16.9, 10.3, 6.6$ Hz, 1H), 5.58 (s, 2H), 5.01 (dd, $J = 17.2, 1.6$ Hz, 1H), 4.93 (dd, $J = 9.5, 0.7$ Hz, 1H), 3.84 (app t, $J = 4.7$ Hz, 2H), 3.54 (app t, $J = 4.7$ Hz, 2H), 3.35 (s, 3H), 2.74 (app t, $J = 7.7$ Hz, 2H), 2.44 (app dt, $J = 15.1, 6.8$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.2, 159.4, 139.0, 138.0, 116.2, 114.8, 107.8, 90.8, 71.6, 68.7, 58.9, 37.0, 33.2; high resolution mass spectrum (Cl^+) m/z 238.1452 $[(\text{MH})^+]$; calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_3$: 238.1443].



31

Aldehyde 31: To a solution of olefin **30** (135 mg, 0.5696 mmol) in acetone/ H_2O (8:1, 5.7 mL) was added NMO (134 mg, 1.139 mmol) and 175 μL OsO_4 (4% wt. in H_2O). The reaction was stirred for 2 h, quenched by adding 1 mL saturated $\text{Na}_2\text{S}_2\text{O}_3$ and stirred for an additional 5 min. The mixture was poured into a saturated NaHCO_3 aq. solution and extracted (2 x CH_2Cl_2 , 2 x Et_2O). The combined organic extracts were dried (MgSO_4), filtered, and concentrated. The resulting crude diol material was taken on with no additional purification.

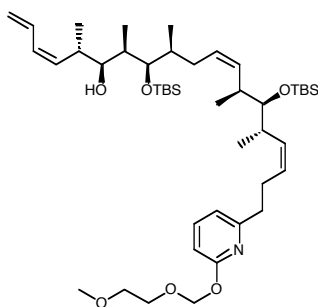
To a 0°C solution of crude diol 34 mg (0.1254 mmol) in THF (1.25 mL) was added $\text{Pb}(\text{OAc})_4$. The reaction was stirred for 30 min., then 100 μL of ethylene glycol was added and the mixture was stirred an additional 5 min. The mixture was poured into a saturated NaHCO_3 aq. solution and extracted (2 x CH_2Cl_2 , 2 x Et_2O). The combined organic extracts were dried (MgSO_4), filtered, and concentrated. Flash chromatography (gradient elution: 33% to 50% EtOAc /hexanes) furnished 23 mg (77%) aldehyde **31**. IR (film, NaCl) 2926, 1723, 1597, 1579, 1456, 1115, 981 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.86 (app t, $J = 1.4$ Hz, 1H), 7.49 (app t, $J = 7.7$ Hz, 1H), 6.78 (d, $J = 7.4$ Hz, 1H), 6.61 (d, $J = 8.2$ Hz, 1H), 5.55 (s, 2H), 3.83 (app t, $J = 4.8$ Hz, 2H), 3.55 (app t, $J = 4.8$ Hz, 2H), 3.36 (s, 3H), 3.03 (app t, $J = 7.1$ Hz, 2H), 2.85 (app dt, $J = 1.4, 7.1$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 178.9, 162.3, 157.5, 139.3, 116.3, 108.4, 91.0, 71.7, 68.7, 59.0, 42.2, 29.9; high resolution mass spectrum (Cl^+) m/z 240.1245 $[(\text{MH})^+]$; calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_4$: 240.1236].



(+)-**S31**

Tetraene(+)-S31: Phosphonium salt (+)-**20** (333 mg, 0.3096 mmol; 12:1 *Z/E* ratio of diene isomers), was azeotropically dried with benzene (3 x 1.5 mL) using a double manifold and further dried by heating to 50 °C under vacuum (0.2 torr) for 12 h. The salt was back-filled with argon, dissolved in 3 mL of freshly distilled THF, sparged with argon for 15 min, and cooled to –20 °C. The resultant solution was treated with methyllithium lithium bromide complex (1.5 M in Et₂O, 217 μ L), and stirred 30 min. To this orange/red solution was transferred via cannula a degassed solution of aldehyde **31** (74 mg, 0.03096 mmol) in THF (0.5 mL + 1 x 0.5 mL rinse) over 5 min. The orange solution was allowed to slowly warm to –8 °C over 3 h. The resulting light yellow solution was quenched with saturated NH₄Cl and diluted (Et₂O/H₂O). The layers were separated, and the aqueous layer was extracted (3 x Et₂O, 3 x CH₂Cl₂). The combined organic layers were dried (Na₂SO₄), concentrated, and chromatographed (gradient elution: 2% EtOAc/hexanes to 50% EtOAc/hexanes; then 40% CH₃CN/CH₂Cl₂) to afford (+)-**S31** (131 mg, 47%; yellow oil, 12:1 ratio of *Z/E* diene isomers) and phosphonium salt (+)-**20** (153 mg, 46%). $[\alpha]_D^{23} +62$ (*c* 0.65, CHCl₃); IR (film, NaCl) 2929, 1513, 1455, 1249, 835 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, major diastereomer) δ 7.46 (app t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.60 (ddd, *J* = 16.6, 10.6, 10.6 Hz, 1H), 6.02 (app t, *J* = 11.0 Hz, 1H), 5.61 (ABq, *J* = 6.2 Hz, $\Delta\nu$ = 6.8 Hz, 2H), 5.56 (app t, *J* = 10.6 Hz, 1H), 5.44 (app t, *J* = 10.3 Hz, 1H), 5.35 (m, 1H), 5.26-5.13 (m, 3H), 5.10 (d, *J* = 10.1 Hz, 1H), 4.50 (ABq, *J* = 10.6, $\Delta\nu$ = 45.3 Hz, 2H), 3.87 (app t, *J* = 4.7 Hz, 2H), 3.79 (s, 3H), 3.57 (app t, *J* = 4.7 Hz, 2H), 3.49 (app t, *J* = 4.3 Hz, 1H), 3.38 (s, 3H), 3.31 (dd, *J* = 6.7, 3.4 Hz, 1H), 3.24 (dd, *J* = 6.7, 4.2 Hz, 1H), 2.99 (dddd, *J* = 6.8, 6.8, 4.0, 4.0, 1H), 2.76-2.60 (m, 3H), 2.49 (m, 1H), 2.32 (m, 1H), 1.94-1.79 (m, 4H), 1.59 (m, 1H), 1.09 (d, *J* = 6.8 Hz,

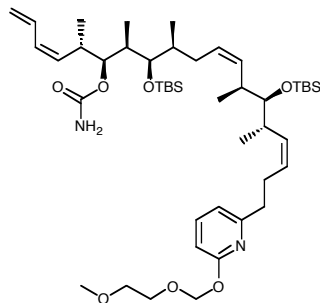
3H), 0.99 (d, $J = 6.7$ Hz, 3H), 0.94 (s, 9H), 0.92 (s, 9H), 0.90 (d, $J = 7.0$ Hz, 3H), 0.86 (d, $J = 7.0$ Hz, 3H), 0.79 (d, $J = 6.7$ Hz, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3 , major diastereomer) δ 162.2, 159.7, 159.0, 139.0, 134.7, 134.6, 133.0, 132.3, 131.2, 129.2, 129.1, 128.1, 127.6, 117.4, 116.2, 113.6, 107.8, 90.9, 84.5, 80.3, 76.4, 74.9, 71.7, 68.7, 59.0, 55.2, 40.1, 38.2, 37.9, 36.6, 36.3, 35.5, 31.9, 27.4, 26.2, 26.17, 18.7, 18.6, 18.5, 18.4, 17.4, 15.0, 10.7, -3.40, -3.44, -3.68 (2); high resolution mass spectrum (ES^+) m/z 930.6075 [$(\text{M}+\text{Na})^+$; calcd for $\text{C}_{53}\text{H}_{89}\text{NO}_7\text{NaSi}_2$: 930.6065].



(+)-**S32**

Alcohol (+)-S32: At 0 °C, a solution of PMB ether (+)-**S31** (23 mg, 0.0253 mmol, 12:1 mixture of *Z/E* diene isomers) in CH_2Cl_2 (1 mL) was treated with H_2O (100 μL) and DDQ (6.3 mg, 0.0278 mmol). The mixture was stirred for 10 min at 0 °C, warmed to rt and stirred an additional 5 min. The mixture was quenched with saturated NaHCO_3 , diluted with Et_2O (30 mL), and washed with H_2O and saturated brine solution. The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The crude residue was then dissolved in EtOAc/MeOH (1:1, 1 mL) cooled to 0 °C, treated with NaBH_4 (1 mg, 0.0253 mmol) and the mixture was allowed to warm to rt. To the solution was added 1 mL of saturated NaHCO_3 . The mixture was concentrated, diluted with H_2O , and extracted (3 x CH_2Cl_2 , 3 x Et_2O). The combined organic extracts were dried (Na_2SO_4) and concentrated. Flash chromatography (gradient elution: 10% $\text{EtOAc}/\text{hexanes}$ to 20% $\text{EtOAc}/\text{hexanes}$) provided (+)-**S32** (15.0 mg, 75%) as a clear oil: $[\alpha]_{\text{D}}^{23} +58$ (c 0.30, CHCl_3); IR (film, NaCl) 2929, 1455, 1251, 1105, 836, 773 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.46 (app t, $J = 7.8$ Hz, 1H), 6.71 (d, $J = 7.3$ Hz, 1H), 6.61 (ddd, $J = 17.0, 10.4, 10.4$ Hz, 1H), 6.59 (d, $J = 8.1$ Hz, 1H), 6.11 (app t, $J = 11.0$ Hz, 1H), 5.58 (ABq, $J = 6.3$, $\Delta\nu = 5.6$ Hz, 2H), 5.43 (app t, $J = 10.2$ Hz, 1H),

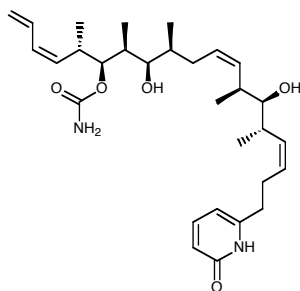
5.36–5.19 (m, 4H), 5.13 (d, $J = 10.2$ Hz, 1H), 3.85 (app t, $J = 4.8$ Hz, 2H), 3.62 (dd, $J = 6.0, 2.9$ Hz, 1H), 3.55 (app t, $J = 4.7$ Hz, 2H), 3.36 (s, 3H), 3.30 (m, 2H), 2.80–2.58 (m, 4H), 2.52–2.41 (m, 3H), 2.10–1.91 (m, 3H), 1.76 (m, 1H), 1.69 (dddd, $J = 6.8, 6.8, 3.5, 3.5$ Hz, 1H), 1.58 (d, $J = 2.4$ Hz, 1H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.92 (d, $J = 7.0$ Hz, 3H), 0.90 (d, $J = 4.1$ Hz, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.84 (d, $J = 6.9$ Hz, 3H), 0.78 (d, $J = 6.9$ Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.02 (app s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.3, 159.8, 139.0, 134.83, 134.80, 132.9, 132.1, 131.0, 128.2, 127.8, 118.4, 116.2, 107.8, 91.0, 80.4, 78.3, 76.2, 71.7, 68.8, 59.0, 38.0, 37.9, 37.3, 36.6, 36.5, 36.3, 32.5, 27.4, 26.24, 26.21, 18.7, 18.5, 18.4, 17.4, 17.1, 13.7, 9.4, -3.4, -3.57, -3.62 (2); high resolution mass spectrum (ES^+) m/z 810.5479 [(M+Na) $^+$]; calcd for $\text{C}_{45}\text{H}_{81}\text{NO}_6\text{NaSi}_2$: 810.5500]



(+)-**S33**

Carbamate (+)-S33: A solution of alcohol (+)-**S32** (15.0 mg, 0.019 mmol) in CH_2Cl_2 (3.0 mL) was treated with $\text{Cl}_3\text{CCON}=\text{C}=\text{O}$ (100 μL , 1 M solution) at room temperature for 30 min. The solution was loaded directly onto a neutral Al_2O_3 plug. After 4 h, the material was flushed from the Al_2O_3 (EtOAc , 100 mL), concentrated, and purified by flash chromatography (gradient elution: 10% to 20% EtOAc /hexanes) providing 7.0 mg (+)-**S33** (50%) as a clear oil: $[\alpha]_{\text{D}}^{25} +64$ (c 0.16, CHCl_3); IR (film, NaCl) 2928, 1734, 1457, 1252, 1035 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.48 (app t, $J = 7.7$ Hz, 1H), 6.73 (d, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 7.9$ Hz, 1H), 6.57 (ddd, $J = 16.6, 10.4, 10.4$ Hz, 1H), 6.01 (app t, $J = 11.0$ Hz, 1H), 5.58 (ABq, $J = 6.3$, $\Delta = 3.7$ Hz, 2H), 5.44 (m, 1H), 5.33 (m, 2H), 5.18 (m, 3H), 5.10 (d, $J = 10.1$ Hz, 1H), 4.70 (app t, $J = 6.0$ Hz, 1H), 4.52 (br s, 2H), 3.85 (app t, $J = 4.7$ Hz, 2H), 3.55 (app t, $J = 4.7$ Hz, 2H), 3.42 (app t, $J = 4.5$ Hz, 1H), 3.36 (s, 3H), 3.29 (dd, $J = 7.0, 3.3$ Hz, 1H), 2.96 (ddd, $J = 10.1, 6.6, 6.6$ Hz, 1H), 2.74–2.58 (m, 3H), 2.48–2.40 (m, 2H), 2.30 (m, 1H), 1.86 (m, 3H), 1.65 (m, 1H), 0.98 (d, $J = 6.8$ Hz, 3H), 0.91

(d, $J = 4.9$ Hz, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.88 (d, $J = 6.7$ Hz, 3H), 0.85 (d, $J = 7.1$ Hz, 3H), 0.77 (d, $J = 6.8$ Hz, 3H), 0.08 (s, 3H), 0.04 (s, 3H), 0.03 (app s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.8, 156.9, 139.1, 134.6 (2), 133.6, 132.9, 132.1, 129.8, 128.2, 127.7, 117.8, 116.3, 107.8, 91.0, 80.5, 78.7, 76.4, 71.7, 68.7, 59.0, 38.1, 38.0, 37.9, 36.6, 36.5, 36.3, 34.5, 32.1, 27.3, 26.2, 18.7, 18.6, 18.5, 18.4, 17.5, 14.3, 10.2, -3.4 (2), -3.60, -3.61; high resolution mass spectrum (ES^+) m/z 853.5541 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{46}\text{H}_{82}\text{N}_2\text{O}_7\text{NaSi}_2$: 853.5558].

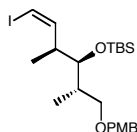


(+)-34

Pyridone (+)-34: Carbamate (+)-**S33** (5.0 mg, 0.006 mmol) was dissolved in MeOH (1 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (3N) was added in 100–200 μL portions over 4 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 1.0 mL of 3 N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 2 mL of MeOH. After stirring for 12 h, the reaction was quenched by addition of NaHCO_3 (s), until gas evolution stopped. The mixture was then diluted with 20 mL of water and extracted with EtOAc (3x). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. Preparative TLC (80% EtOAc/ CH_2Cl_2) gave (+)-**34** (2.1 mg, 70% yield) as a white amorphous solid: $[\alpha]_{\text{D}}^{23} +70$ (c 0.10, MeOH); IR (film, NaCl) 3397, 2961, 1700, 1653, 1617, 1457, 1040 cm^{-1} ; ^1H NMR (500 MHz, CD_3CN) δ 7.35 (dd, $J = 9.2, 6.8$ Hz, 1H), 6.65 (dddd, $J = 16.8, 11.1, 11.1, 1.0$ Hz, 1H), 6.22 (d, $J = 9.2$ Hz, 1H), 6.00 (m, 2H), 5.50–5.31 (m, 4H), 5.23–5.18 (m, 3H), 5.12 (dd, $J = 10.1, 2.1$ Hz, 1H), 4.67 (app t, $J = 5.9$ Hz, 1H), 3.16 (m, 1H), 3.12 (dd, $J = 8.0, 3.5$ Hz, 1H), 3.03 (ddd, $J = 16.1, 11.1, 5.1$ Hz, 1H), 2.57 (ddd, $J = 10.1, 6.8, 3.3$ Hz, 1H), 2.55 (d, $J = 5.0$ Hz, 1H), 2.52 (app t, $J = 7.5$ Hz, 2H), 2.34 (m, 2H), 2.26 (m, 1H), 1.84 (ddd, $J = 14.2, 3.5, 3.5$ Hz, 1H), 1.71 (m, 2H), 1.59 (m, 1H), 0.94 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.9$ Hz, 3H), 0.90 (d, $J = 6.7$ Hz,

3H), 0.80 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (125 MHz, CD_3CN) δ 164.4, 158.7, 150.1, 142.5, 135.1, 134.7, 133.7, 133.4, 130.4, 128.6, 128.2, 126.3, 117.9, 105.0, 79.9, 78.8, 75.5, 38.4, 36.9, 36.0, 35.0, 33.6, 32.4, 30.6, 26.9, 19.3, 18.1, 17.1, 15.1, 9.4; high resolution mass spectrum (ES^+) m/z 537.3279 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{30}\text{H}_{46}\text{N}_2\text{O}_5\text{Na}$: 537.3304].

Synthesis of the Previously Reported (+)-14-Normethyldiscodermolide

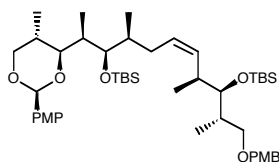


(+)-**N1**

Vinyl iodide (+)-N1: Iodomethyltriphenylphosphonium iodide (1.38 g, 2.61 mmol) was heated (50° C) in vacuo for 12 h, cooled, backfilled with Ar, then suspended in 6.0 mL of THF. 2.5 mL NaHMDS was added (1.0 M THF, 2.51 mmol) at rt and the mixture was stirred for 10 minutes. The red/brown suspension was cooled to –60° C, 750 μL of HMPA (freshly distilled) was added, and the orange suspension was cooled to –78° C. The substrate aldehyde **N2**¹ (795 mg) was added as a solution in THF (1.0 mL) via cannula and the cold bath was removed. After stirring for 30 minutes the brown suspension was diluted with hexanes and poured into NH_4Cl solution. The organic layer was washed (H_2O , brine), dried (Na_2SO_4), filtered and concentrated. Flash chromatography (gradient elution: 15% CH_2Cl_2 /hexane to 2% EtOAc/hexanes to 5% EtOAc/hexane) furnished vinyl iodide (+)-**N1** as a 7:1 *Z/E* mixture of olefin isomers (811 mg, 77% 2 steps). $[\alpha]_{\text{D}}^{23} +27$ (c 0.60, CHCl_3); IR (CHCl_3) 2928, 2855, 1512, 1248, 1078, 837, 774 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.26 (d, $J = 8.3$ Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 6.09 (d, $J = 7.3$ Hz, 1H), 6.07 (dd, $J = 8.7, 7.4$ Hz, 1H), 4.42 (ABq, $J = 11.6, \Delta\nu = 14.4$ Hz, 2H), 3.81 (s, 3H), 3.65 (app t, $J = 5.3$ Hz, 1H), 3.52 (dd, $J = 9.1, 5.5$ Hz, 1H), 3.26 (app t, $J = 8.5$ Hz, 1H), 2.70 (dq, $J = 13.4, 6.6$ Hz, 1H), 2.00 (m, 1H), 1.01 (m, 1H), 0.97 (d, $J = 6.8$ Hz, 3H), 0.89 (s, 1H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR

¹ Structure **19**, Smith, A. B., III; Beauchamp, T. J.; LaMarche, M. J.; Kaufman, M. D.; Qiu, Y.; Arimoto, H.; Jones, D. R.; Kobayashi, K. *J. Am. Chem. Soc.* **2000**, *122* (36), 8654-8664.

(125 MHz, CDCl₃) δ 159.0, 145.1, 130.9, 129.4, 113.7, 80.6, 76.2, 72.6, 72.3, 55.2, 42.7, 38.8, 26.1, 18.3, 14.8, 14.4, -3.8, -4.0; high resolution mass spectrum (ES⁺) m/z 527.1473 [(M+Na)⁺; calcd for C₂₂H₃₇O₃SiNa: 527.1454].

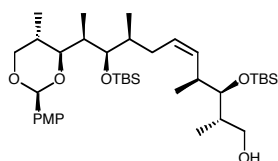


(+)-N3

PMP Acetal (+)-N3: A 1.0 M solution of anhydrous ZnCl₂ (1.10 mL, 1.10 mmol) was added via syringe to a solution of alkyl iodide (+)-**A**² (602 mg, 1.10 mmol) in dry Et₂O (4.0 mL), and the resulting solution was cooled to -78 °C and degassed 2 x (freeze-pump thaw). *t*-BuLi (1.7 M in pentane, 1.94 mL, 3.30 mmol) was added via cannula over 5 min. The resultant solution was stirred 5 min further, evacuated (1 \times 0.1 Torr) and back-filled with argon. The -78 °C bath was removed, and the reaction was stirred at ambient temperature for 1 h. The resulting cloudy suspension was transferred by cannula into an intimate mixture of vinyl iodide (+)-**N1** (410 mg, 0.826 mmol; 7:1 *Z/E*) and Pd(PPh₃)₄ (48 mg, 0.0413 mmol). The reaction mixture was stirred overnight in the absence of light, and quenched via slow addition of the reaction mixture to water (200 mL). The mixture was diluted with Et₂O, and the layers were separated. The water layer was extracted (3 \times Et₂O), and the combined organic layers were washed (saturated aqueous NaHCO₃, brine), dried (MgSO₄), filtered and concentrated. Flash chromatography (gradient elution: 2% EtOAc/hexanes \rightarrow 5% EtOAc/hexanes) furnished (+)-**N3** [397 mg, 60% yield]; [α]_D²³ +34 (*c* 1.0, CHCl₃); IR (CHCl₃) 2956, 2855, 1614, 1515, 1462, 1389, 1249, 1037, 835, 773 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 11.2 Hz, 2H), 7.21 (d, *J* = 11.6 Hz, 2H), 6.84 (app t, *J* = 9.0 Hz, 4H), 5.37 (s, 1H), 5.22 (m, 2H), 4.35 (s, 2H), 4.07 (dd, *J* = 4.6, 11.1 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.65 (d, *J* = 7.3 Hz, 1H), 3.45 (m, 3H), 3.20 (app t, *J* = 8.6 Hz, 1H), 2.57 (app ddq, *J* = 6.6, 9.0, 6.6 Hz, 1H), 2.06 (m, 3H), 1.95 (app t, *J*

² See structure **A**, Smith, A. B., III; Beauchamp, T. J.; LaMarche, M. J.; Kaufman, M. D.; Qiu, Y.; Arimoto, H.; Jones, D. R.; Kobayashi, K. *J. Am. Chem. Soc.* **2000**, *122* (36), 8654-8664.

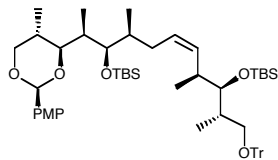
= 4.8 Hz, 1H), 1.92 (app t, J = 4.4 Hz, 1H), 1.88 (app t, J = 7.1 Hz, 1H), 1.74 (m, 1H), 0.99 (d, J = 7.1 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H), 0.89 (s, 9H), 0.89 (d, J = 6.5 Hz, 3H), 0.86 (s, 9H), 0.81 (d, J = 6.7 Hz, 3H), 0.03 (m, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.7, 159.0, 134.9, 131.5, 131.0, 129.0, 127.6, 127.3, 113.7, 113.5, 100.9, 83.1, 78.1, 77.2, 73.3, 72.6, 72.5, 55.2, 38.7, 38.2, 36.6, 35.4, 33.2, 30.8, 26.2, 26.1, 18.5, 18.4, 16.8, 14.6, 13.2, 12.2, 10.9, -3.6, -3.7, -3.8, -3.9; high resolution mass spectrum (ES^+) m/z 821.5222 [$(\text{M}+\text{Na})^+$; calcd for $\text{C}_{46}\text{H}_{78}\text{O}_7\text{Si}_2\text{Na}$: 821.5184].



(+)-**8**

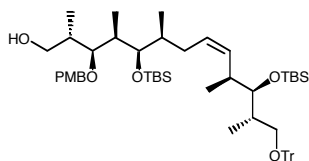
Alcohol (+)-8: At 0 °C, a solution of PMB ether (+)-**N3** (358 mg, 0.448 mmol) in CH_2Cl_2 (5 mL) was treated with H_2O (200 μL) and DDQ (111 mg, 0.490 mmol) and stirred for 60 min. The mixture was quenched with 20 mL of saturated NaHCO_3 , washed with H_2O (4 \times) and separated. The aqueous layer was then extracted with CH_2Cl_2 (2 \times). The combined organic extracts were dried (MgSO_4), filtered, concentrated, dissolved in MeOH (20 mL) and then treated with NaBH_4 (2.24 mmol). The reaction mixture was concentrated, diluted with CH_2Cl_2 , washed with aqueous saturated ammonium chloride and brine. The organic layer was dried over NaSO_4 , decanted, concentrated and chromatographed (10% EtOAc/hexanes) to provide 244 mg of (+)-**8** (80%); $[\alpha]_{\text{D}}^{23} + 41$ (c 1.0, CHCl_3); IR (film, NaCl) 3476, 2957, 2856, 1614, 1518, 1462, 1250, 1026, 835 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.38 (s, 1H), 5.25 (m, 2H), 4.08 (dd, J = 11.2, 4.7 Hz, 1H), 3.78 (s, 3H), 3.69 (dd, J = 7.3, 1.6 Hz, 1H), 3.65 (app t, J = 5.1 Hz, 1H), 3.55 (app t, J = 5.6 Hz, 1H), 3.52 (m, 1H), 3.50 (app t, J = 11.4, 1H), 3.46 (dd, J = 6.2, 4.3 Hz, 1H), 2.67 (app ddq, J = 6.7, 9.0, 6.7 Hz, 1H), 2.34 (app t, J = 5.5 Hz, 1H), 2.10 (m, 2H), 1.98 (ddd, J = 4.3, 4.3, 14 Hz, 1H), 1.87 (ddd, J = 1.4, 7.2, 7.2 Hz, 1H), 1.80 (m, 1H), 1.78 (m, 1H), 1.02 (d, J = 7.1 Hz, 3H), 0.99 (d, J = 7.1 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H), 0.93 (s, 9H), 0.92 (s, 9H), 0.85 (d, J = 6.7 Hz, 3H), 0.70 (d, J = 7.1 Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.7, 133.9, 131.5, 128.4, 127.3, 113.4, 100.9, 83.0, 81.2,

76.7, 73.3, 65.3, 55.2, 38.4, 38.2, 36.8, 36.5, 33.2, 30.7, 26.2, 26.1, 18.5, 18.3, 17.3, 15.7, 13.3, 12.1, 10.9, -3.6, -3.7, -3.8 (2); high resolution mass spectrum (ES⁺) m/z 701.4582 [(M+Na)⁺; calcd for C₃₈H₇₀O₆NaSi₂: 701.4609].



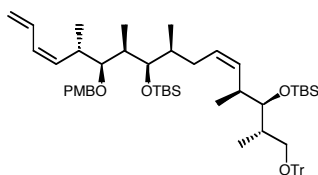
(+)-N4

Trityl protected acetal (+)-N4: To a solution of alcohol (+)-8 (229 mg, 0.337 mmol) in pyridine (3.4 mL) was added trityl chloride (112.8 mg, 0.405 mmol) and DMAP (49.4 mg, 0.405 mmol). The mixture was then refluxed for 18 h, cooled to ambient temperature, and added to a solution of 1M citric acid (50 mL). The mixture was extracted with CH₂Cl₂, washed with 1 M citric acid, H₂O (100 mL) and saturated NaHCO₃ solution. The organic layers were separated, dried (NaSO₄), filtered, and concentrated *in vacuo*. Flash chromatography (5% EtOAc/hexanes) provided (+)-N4 (271 mg, 87%) as a white foam; $[\alpha]_D^{23} + 36$ (*c* 1.0, CH₂Cl₂); IR (CHCl₃) 2929, 2855, 1615, 1461, 1250, 1036, 835, 773, 706 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 7.61 (d, *J* = 8.7 Hz, 2H), 7.59 (app d, *J* = 7.4 Hz, 6H), 7.16 (m, 6H), 7.05 (app t, *J* = 7.4 Hz, 3H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.41 (s, 1H) 5.30 (app t, *J* = 10.3 Hz, 1H), 5.25 (ddd, *J* = 10.9, 9.2, 4.1 Hz, 1H), 3.96 (dd, *J* = 11.1, 4.6 Hz, 1H), 3.83 (d, *J* = 7.4 Hz, 1H), 3.65 (dd, *J* = 6.8, 4.0 Hz, 1H), 3.48 (m, 2H), 3.28 (m, 1H), 3.24 (s, 3H), 3.07 (app t, *J* = 8.8 Hz, 1H), 2.77 (app ddq, *J* = 6.7, 9.4, 6.7 Hz, 1H), 2.41 (m, 1H), 2.26 (ddd, *J* = 14.1, 9.2, 9.2 Hz, 1H), 1.93 (m, 4H), 1.18 (app t, *J* = 6.8 Hz, 6H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.03 (s, 9H), 0.95 (s, 9H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.12 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ¹³C NMR (125 MHz, C₆D₆) δ 160.4, 145.1, 134.8, 132.3, 129.2 (2), 128.3, 127.9, 127.1, 113.8, 101.7, 86.9, 83.3, 78.5, 77.7, 73.3, 66.5, 54.7, 40.4, 38.6, 36.9, 36.0, 33.7, 30.9, 26.5, 26.3, 18.8, 18.5, 18.0, 14.4, 13.6, 12.0, 11.3, -3.3, -3.4, -3.7, -3.7; high resolution mass spectrum (ES⁺) m/z 943.5720 [(M+Na)⁺; calcd for C₅₇H₈₄O₆Si₂Na: 943.5704].



(+)-**3**

Trityl protected alcohol (+)-3: To a 0 °C solution of trityl ether (+)-**N4** (267 mg, 0.289 mmol) in CH₂Cl₂ (4.0 mL) was added DIBAL-H (1M in Toluene, 0.87 mL, 0.868 mmol). The resulting solution was stirred for 4.5 h, quenched via drop-wise addition of pH 7.0 buffer (20 mL), then diluted with CH₂Cl₂. The mixture was then added to saturated sodium potassium tartrate solution, extracted with CH₂Cl₂, and separated. The organic layer was washed with H₂O, dried (MgSO₄), filtered, and concentrated. Flash chromatography (20% EtOAc/hexanes) provided (+)-**3** (257 mg, 96%) as a white glass; $[\alpha]_D^{23} +18$ (*c* 1.0, CHCl₃); IR (film, NaCl) 2930, 2855, 1613, 1513, 1250, 1036, 836, 772, 706 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.58 (app d, *J* = 8.5 Hz, 6H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.16 (m, 6H), 7.05 (app t, *J* = 7.3 Hz, 3H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.27 (app t, *J* = 10.5 Hz, 1H), 5.14 (ddd, *J* = 10.3, 10.2, 4.7 Hz, 1H), 4.53 (ABq, *J* = 10.8, $\Delta\nu$ = 13.1 Hz, 2H), 3.70 (ddd, *J* = 10.1, 5.1, 4.8 Hz, 1H), 3.65 (m, 2H), 3.55 (ddd, *J* = 10.4, 5.1, 4.9 Hz, 1H), 3.46 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.40 (dd, *J* = 6.5, 4.2 Hz, 1H), 3.31 (s, 3H), 3.06 (app t, *J* = 8.7 Hz, 1H), 2.76 (app ddq, *J* = 6.7, 9.4, 6.7 Hz, 1H), 2.38 (m, 1H), 2.16 (ddd, *J* = 14.1, 9.8, 9.8 Hz, 1H), 2.04 (app t, *J* = 5.2 Hz, 1H), 1.94 (m, 3H), 1.80 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.04 (s, 9H), 0.95 (d, *J* = 6.6 Hz, 6H), 0.95 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 144.9, 134.7, 131.0, 129.2, 129.1, 128.3 (2), 126.9, 114.0, 86.7, 84.6, 78.0, 76.9, 74.9, 66.4, 65.1, 54.6, 40.3, 39.9, 38.3, 37.9, 35.7, 32.9, 26.4, 26.2, 18.6, 18.3, 17.8, 15.3, 14.1, 13.8, 11.6, -3.3, -3.4, -3.8, -3.9; high resolution mass spectrum (ES⁺) *m/z* 945.5843 [(M+Na)⁺; calcd for C₅₇H₈₆O₆Si₂Na: 945.5861].



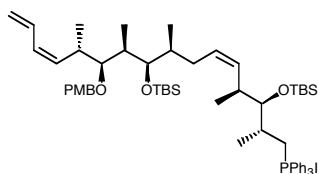
N5

Trityl Protected Triene N5: To a 0 °C solution of alcohol (+)-**3** (225 mg, 0.241 mmol) in CH₂Cl₂ (3.0 mL) were added Dess-Martin periodinane (307 mg, 0.724 mmol) and NaHCO₃ (315 mg, 4.34 mmol). The resulting solution was stirred for 2.5 h and quenched with saturated Na₂S₂O₃ solution and saturated NaHCO₃ solution. The mixture was then extracted with Et₂O (3 x) and separated. The organic solution was then washed with H₂O, dried (MgSO₄), filtered, and concentrated. The resulting white foam aldehyde **N6** was used without further purification:

Aldehyde [N6]: ¹H NMR (500 MHz, C₆D₆) δ 9.73 (d, J = 2.3 Hz, 1H), 7.59 (app d, J = 7.4 Hz, 6H), 7.22 (d, J = 8.6 Hz, 2H), 7.16 (m, 6H), 7.06 (app t, J = 7.3 Hz, 3H), 6.79 (d, J = 8.6 Hz, 2H), 5.28 (app t, J = 10.5 Hz, 1H), 5.12 (ddd, J = 10.3, 10.1, 4.6 Hz, 1H), 4.40 (ABq, J = 10.9, $\Delta\nu$ = 22.7 Hz, 2H), 3.66 (m, 2H), 3.55 (app t, J = 4.7 Hz, 1H), 3.47 (dd, J = 8.7, 6.2 Hz, 1H), 3.31 (s, 3H), 3.06 (app t, J = 8.7 Hz, 1H), 2.74 (app ddq, J = 6.7, 9.5, 6.7 Hz, 1H), 2.57 (m, 1H), 2.39 (m, 1H), 2.13 (ddd, J = 14.1, 9.7, 9.7 Hz, 1H), 1.91 (m, 2H), 1.74 (m, 1H), 1.17 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.6 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 1.02 (s, 9H), 0.95 (s, 9H), 0.93 (d, J = 7.0 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.13 (s, 3H), 0.09 (s, 3H), 0.07 (s, 6H); ¹³C NMR (125 MHz, C₆D₆) δ 202.8, 159.7, 144.9, 134.9, 130.6, 129.1, 129.0, 128.3, 128.3, 127.4, 126.9, 114.0, 86.7, 82.2, 78.2, 76.7, 74.2, 66.4, 54.6, 49.5, 40.3, 37.8, 35.7, 32.8, 26.2, 26.1, 18.6, 18.3, 17.7, 14.1, 13.9, 11.9, 11.5, -3.4, -3.5, -3.8, -3.9.

To a -78 °C solution of freshly distilled allyldiphenylphosphine (104 μ L, 0.482 mmol) in THF (1.0 mL, degassed) was added 283 μ L of *t*-butyllithium (1.7M in pentane, 0.482 mmol) and stirred for 5 min. The solution was warmed to 0 °C, stirred for 30 min and cooled to -78 °C. The solution was treated with freshly distilled Ti(*i*-OPr)₄ (142 μ L, 0.482 mmol) and stirred for 30 min. A precooled (-78 °C) solution of aldehyde **N6** (0.241 mmol) in THF (1.0 mL) was added via cannula (rinse 1 x 1.0 mL) and stirred for 1 h, then warmed to 0 °C. Iodomethane (225 μ L, 3.62 mmol) was added, and the solution was warmed to ambient temperature and stirred for 16 h. The solution was quenched with pH 7.0 buffer and extracted with CH₂Cl₂ (3 x 10 mL) and Et₂O (3 x 10 mL). The combined organic layers were washed with saturated brine solution, dried (MgSO₄), filtered, and concentrated. Flash chromatography (5% EtOAc/hexanes) provided **N5** (144 mg, 63% from (+)-**3**, 10:1 mixture of diastereomers) as a white foam:

IR (CHCl₃) 2956, 2855, 1613 cm⁻¹; ¹H NMR (500 MHz, C₆D₆, major diastereomer) δ 7.60 (m, 6H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.16 (m, 6H), 7.06 (m, 3H), 6.82 (d, *J* = 8.6 Hz, 2H) 6.70 (ddd, *J* = 16.8, 10.7, 10.7 Hz, 1H) 6.05 (app t, *J* = 11.0 Hz, 1H), 5.65 (app t, *J* = 10.5 Hz, 1H), 5.25 (app t, *J* = 10.2 Hz, 1H), 5.18 (dd, *J* = 16.7, 1.6 Hz, 1H), 5.10 (ddd, *J* = 10.1, 10.1, 4.9 Hz, 1H), 5.07 (d, *J* = 10.3 Hz, 1H), 4.55 (ABq, *J* = 10.7, $\Delta\nu$ = 48.6 Hz, 2H), 3.65 (m, 2H), 3.46 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.32 (s, 3H), 3.06 (m, 2H), 2.71 (m, 1H), 2.41 (m, 1H), 1.97 (m, 4H), 1.74 (m, 1H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.06 (s, 9H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 9H), 0.17 (s, 3H), 0.13 (s, 6H), 0.07 (s, 3H); ¹³C NMR (125 MHz, C₆D₆, major diastereomer) δ 159.5, 144.9, 134.7, 134.5, 132.6, 131.4, 129.4, 129.2, 129.0, 128.3, 127.8, 126.9, 117.5, 113.9, 86.7, 84.6, 78.2, 76.9, 75.1, 66.4, 54.6, 40.4, 40.3, 38.3, 35.8, 35.6, 32.3, 26.4, 26.2, 18.7, 18.6, 18.3, 17.7, 15.1, 14.0, 11.1, -3.3, -3.4, -3.8, -3.9; high resolution mass spectrum (ES⁺) *m/z* 967.6086 [(M+Na)⁺; calcd for C₆₀H₈₈O₅Si₂Na: 967.6068].



(+)-20

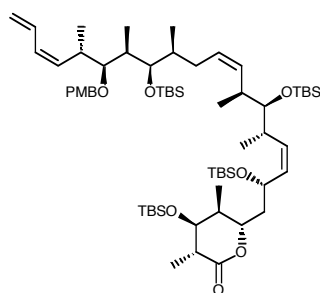
Triene Alcohol N7: Anhydrous MeOH (50 μ L) was added to a cold (0 °C) solution of chlorocatecholborane (0.769 g, 4.97 mmol) in 1.5 mL of CH₂Cl₂ (3.2 M). The resulting solution was added in 48 μ L (0.153 mmol) aliquots at 10 min intervals to a 0.07 M solution (CH₂Cl₂) of trityl ether **N5** (144 mg, 0.153 mmol, 10:1 dr) at 0 ° until TLC (20% EtOAc/hexanes) indicated ca. 90% reaction completion (total = 8 equivalents), at which point the reaction was quenched via drop-wise addition of 20 mL of saturated NaHCO₃. The resulting mixture was stirred for 15 min, diluted with Et₂O, stirred an additional 30 min, and the layers were separated. The aqueous layer was extracted (3 x Et₂O), and the resulting organic layers were combined, washed (water and saturated brine solution), dried (MgSO₄), filtered, added to SiO₂ and concentrated. Flash chromatography (gradient elution: 5% EtOAc/hexanes to 10% EtOAc/hexanes; 2nd column: 100% CH₂Cl₂; then 20% EtOAc/hexanes) provided **N7** (85 mg, 79%, 10:1 dr) as a white foam and starting ether **N5** (8% starting material): NMR (500 MHz, CDCl₃, major

diastereomer) δ 7.25 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.60 (ddd, J = 16.8, 10.6, 10.6, 1H), 6.03 (app t, J = 10.9 Hz, 1H), 5.57 (app t, J = 10.5 Hz, 1H), 5.21 (m, 1H), 5.20 (d, J = 16.9 Hz, 1H), 5.19 (m, 1H), 5.10 (d, J = 10.2 Hz, 1H), 4.50 (ABq, J = 10.7, $\Delta\nu$ = 52.4 Hz, 2H), 3.80 (s, 3H), 3.68 (ddd, J = 10.3, 4.7, 4.7 Hz, 1H), 3.54 (ddd, J = 11.2, 5.8, 5.8 Hz, 1H), 3.49 (app t, J = 4.4 Hz, 1H), 3.45 (dd, J = 6.9, 3.7 Hz, 1H), 3.23 (dd, J = 6.8, 4.2 Hz, 1H), 2.99 (app ddq, J = 6.8, 7.3, 6.8 Hz, 1H), 2.62 (m, 1H), 2.34 (app t, J = 5.6 Hz, 1H), 1.92 (m, 2H), 1.83 (m, 2H), 1.60 (m, 1H), 1.09 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 7.1 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H), 0.95 (m, 3H), 0.95 (s, 9H), 0.92 (s, 9H), 0.80 (d, J = 6.7 Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , major diastereomer) δ 159.1, 134.7, 134.0, 132.4, 131.3, 129.2, 129.0, 128.5, 117.4, 113.6, 84.5, 81.3, 76.4, 74.9, 65.3, 55.3, 40.2, 38.4, 38.2, 36.8, 35.5, 32.1, 26.3, 26.2, 18.7, 18.6, 18.4, 17.5, 15.8, 15.0, 10.8, -3.3, -3.4, -3.6, -3.8.

Phosphonium Salt (+)-20: A solution of iodine (138 mg, 0.545 mmol) in 1.0 mL of Et_2O was added drop-wise to a vigorously stirred solution of alcohol **N7** (38 mg, 0.054 mmol; 10:1 mix of *cis/trans* diene isomers), PPh_3 (142 mg, 0.54 mmol) and imidazole (44 mg, 0.648 mmol) in benzene/ether (1:1, 1.4 mL) at 0 °C. The resultant canary yellow suspension was stirred 30 min at 0 °C and poured into 1:1 water/hexanes. The layers were separated, and the aqueous layer was extracted with hexanes. The combined organic layers were washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2x), water and brine. The clear, colorless organic layer was dried over MgSO_4 , filtered and concentrated. The resulting white slurry was loaded onto a plug of SiO_2 with a minimal amount of CH_2Cl_2 and rapidly eluted off the column (0.05% Et_3N /2% Et_2O /hexanes) to afford iodide **N8** as colorless oil (10:1 mixture of diene isomers; contaminated with ca. 20% PPh_3) which was taken on to the next step without further purification. ^1H NMR (500 MHz, C_6D_6 , major diastereomer) δ 7.30 (dd, J = 8.4, 1.3 Hz, 2H), 6.83 (dd, J = 8.5, 1.5 Hz, 2H), 6.72 (ddd, J = 16.8, 10.5, 10.5 Hz, 1H), 6.09 (app t, J = 10.9 Hz, 1H), 5.70 (app t, J = 10.5 Hz, 1H), 5.33 (m, 2H), 5.18 (d, J = 16.8 Hz, 1H), 5.08 (d, J = 10.2 Hz, 1H), 4.55 (ABq, J = 10.7, $\Delta\nu$ = 51 Hz, 2H), 3.67 (m, 1H), 3.46 (m, 1H), 3.35 (m, 1H), 3.34 (s, 3H), 3.10 (m, 1H), 3.05 (ddd, J = 9.5, 9.5, 1.3 Hz, 1H), 2.72 (m, 1H), 2.13 (m, 2H), 2.00 (ddd, J = 12.0, 12.0, 6.7 Hz, 1H), 1.88 (m, 2H), 1.77 (m, 1H), 1.22 (d, J = 6.8 Hz, 3H), 1.11

(d, $J = 6.8$ Hz, 3H), 1.06 (s, 9H), 1.03 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.7$ Hz, 3H), 0.96 (s, 9H), 0.85 (d, $J = 6.7$ Hz, 3H), 0.17 (s, 3H), 0.16 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H).

To an intimate mixture of crude iodide **N8** (0.054 mmol) and triphenylphosphine (28 mg, 0.108 mmol) was added diisopropylethylamine (100 μ L). The resulting mixture was heated (95° C) for 8 h, cooled and diluted with CH₂Cl₂. Flash chromatography (gradient elution, CH₂Cl₂ \rightarrow 20% MeCN/CH₂Cl₂) furnished (+)-**20** as a white solid [55 mg, 95% yield from alcohol **N7**]: $[\alpha]_D^{23} +18$ (c 1.0, CHCl₃); IR (CHCl₃) 2928, 1513, 1438, 1249, 1070, 837 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, major diastereomer) δ 7.75 (m, 15H), 7.23 (d, $J = 8.3$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 6.53 (ddd, $J = 16.8, 10.6, 10.6$ Hz, 1H), 5.90 (app t, $J = 11.0$ Hz, 1H), 5.52 (app t, $J = 10.8$ Hz, 1H), 5.50 (app t, $J = 10.7$ Hz, 1H), 5.16 (dd, $J = 9.8, 5.1$ Hz, 1H), 5.10 (d, $J = 16.4$ Hz, 1H), 5.05 (d, $J = 10.1$ Hz, 1H), 4.24 (ABq, $J = 10.5$, $\Delta\nu = 56$ Hz, 2H), 3.75 (s, 3H), 3.74 (m, 2H), 3.43 (m, 1H), 3.20 (m, 2H), 2.94 (app ddq, $J = 6.7, 6.8, 6.7$ Hz, 1H), 2.49 (m, 1H), 2.01 (m, 1H), 1.80 (m, 2H), 1.72 (m, 1H), 1.55 (m, 1H), 1.07 (d, $J = 6.8$ Hz, 3H), 0.92 (d, $J = 6.9$ Hz, 3H), 0.88 (s, 9H), 0.86 (d, $J = 7.2$ Hz, 3H), 0.82 (s, 9H), 0.73 (d, $J = 6.7$ Hz, 3H), 0.69 (d, $J = 6.8$ Hz, 3H), 0.07 (s, 3H), 0.06 (s, 3H), 0.01 (s, 3H), -0.08 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, major diastereomer) δ 159.1, 135.3, 135.2, 134.5, 134.0, 13.7, 133.6, 132.2, 131.2, 130.8, 130.7, 129.2, 129.1, 129.0, 128.2, 118.8, 118.1, 117.6, 113.8, 84.5, 79.6, 79.5, 76.4, 75.1, 40.0, 38.2, 35.8, 35.4, 34.2, 34.1, 31.7, 26.3, 26.1, 26.0, 25.6, 18.8, 18.6, 18.3, 16.8, 15.5, 10.9, -3.2, -3.3, -3.4, -3.8; high resolution mass spectrum (ES⁺) m/z 947.5959 [(M-I)⁺; calcd for C₅₉H₈₈O₄PSi₂: 947.5950].



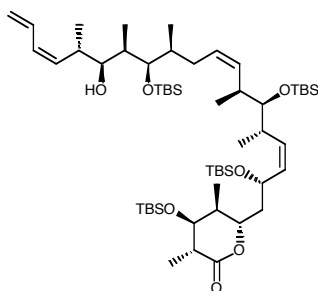
(+)-**N9**

Tetraene (+)-N9: Phosphonium salt (+)-**20** (80 mg, 0.074 mmol; 10:1 ratio of diene isomers), was azeotropically dried with benzene (3 x 1.5 mL) using a double manifold and further dried by heating to 50

°C under vacuum (0.2 torr) for 12 h. The salt was back-filled with argon, dissolved in 540 μ L of freshly distilled THF, sparged with argon for 15 min, and cooled to –20 °C. The resultant solution was treated with sodium bis(trimethylsilyl)amide (1.0 M in THF, 70 μ L), stirred 15 min, warmed to 0 °C, stirred 30 min, and re-cooled to –24 °C. To this orange/red solution was transferred via cannula a degassed solution of aldehyde (–)-**C**³ (29 mg, 0.066 mmol) in THF (0.5 mL + 1 x 0.2 mL rinse) over 7 min. The orange solution was allowed to slowly warm to –8 °C over 3.25 h. The resulting light yellow solution was quenched with saturated NH₄Cl and diluted (Et₂O/H₂O). The layers were separated, and the aqueous layer was extracted (3 x Et₂O). The combined organic layers were dried (Na₂SO₄), concentrated, and chromatographed (gradient elution: 2% EtOAc/hexanes to 50% EtOAc/hexanes; then 40% CH₃CN/CH₂Cl₂) to afford *cis* isomer (+)-**N9** (27 mg, 36%, 10:1 ratio of diene isomers) and phosphonium salt (+)-**20** (28 mg, 35%; 10:1 ratio of diene isomers); $[\alpha]_D^{23}$ +31 (*c* 1.0, CHCl₃); IR (CHCl₃) 2928, 2856, 1738, 1462, 1250, 1044, 836, 775 cm^{–1}; ¹H NMR (500 MHz, CDCl₃, major diastereomer) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.58 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 6.00 (app t, *J* = 11.0 Hz, 1H), 5.56 (app t, *J* = 10.5 Hz, 1H), 5.30 (dd, *J* = 11.0, 8.0 Hz, 1H), 5.29 (m, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.19 (dd, *J* = 16.8, 1.5 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.79 (app t, *J* = 9.2 Hz, 1H), 4.51 (app t, *J* = 10.2 Hz, 1H), 4.50 (ABq, *J* = 10.6, $\Delta\nu$ = 45 Hz, 2H), 3.79 (s, 3H), 3.62 (app t, *J* = 2.5 Hz, 1H), 3.48 (app t, *J* = 4.4 Hz, 1H), 3.28 (app t, *J* = 5.2 Hz, 1H), 3.23 (dd, *J* = 7.1, 4.0 Hz, 1H), 2.98 (app ddq, *J* = 6.8, 7.1, 6.8 Hz, 1H), 2.62 (m, 2H), 2.52 (m, 1H), 1.83 (m, 6H), 1.58 (m, 1H), 1.57 (dd, *J* = 11.2, 2.2 Hz, 1H), 1.21 (d, *J* = 7.6 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 9H), 0.90 (s, 9H), 0.88 (d, *J* = 6.1 Hz, 3H), 0.87 (s, 9H), 0.86 (s, 9H), 0.79 (d, *J* = 6.7 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 6H), 0.05 (s, 3H), 0.04 (s, 3H), 0.01 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, major diastereomer) δ 173.2, 159.1, 135.2, 134.5, 133.6, 132.4, 132.3, 131.2, 129.1, 127.1, 117.5, 113.7, 84.5, 80.1, 77.0, 76.5, 75.1, 75.0, 64.6, 55.3, 44.1, 42.9, 40.2, 38.3, 37.6, 35.5, 35.0, 34.2, 31.9, 26.3, 26.2, 26.0, 25.7, 18.7, 18.6, 18.4, 18.1, 18.0, 17.1, 16.4, 16.2, 15.2, 14.1,

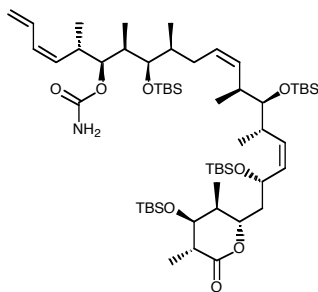
³ See structure **C**, Smith, A. B., III; Beauchamp, T. J.; LaMarche, M. J.; Kaufman, M. D.; Qiu, Y.; Arimoto, H.; Jones, D. R.; Kobayashi, K. *J. Am. Chem. Soc.* **2000**, *122* (36), 8654-8664.

10.7, -3.1, -3.3, -3.4, -4.2, -4.3, -4.5, -4.8 (2); high resolution mass spectrum (ES⁺) m/z 1113.7826 [(MH)⁺; calcd for C₆₃H₁₁₇O₈Si₄Na: 1113.7916].



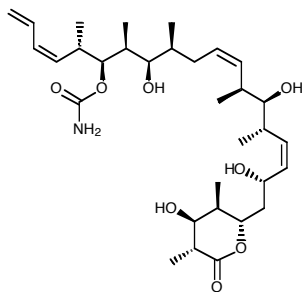
(+)-N10

Alcohol (+)-N10: At 0 °C, a solution of PMB ether (+)-N9 (24 mg, 0.0211 mmol, 10:1 mixture of *cis/trans* diene isomers) in CH₂Cl₂ (2 mL) was treated with H₂O (100 μL) and DDQ (72 mg, 0.0313 mmol). The mixture was stirred for 10 min at 0 °C, warmed to rt and stirred an additional 5 min. The mixture was quenched with saturated NaHCO₃, diluted with CH₂Cl₂, and washed with H₂O and saturated brine solution. The combined organic layers were dried (MgSO₄), filtered and concentrated. Flash chromatography (gradient elution; 5% EtOAc to 10% EtOAc/hexanes) furnished (+)-N10 (21 mg, 95%); $[\alpha]_D^{23}$ +44 (*c* 1.0 CH₂Cl₂) IR (film, NaCl) 2928, 2856, 2356, 1731, 1462, 1253, 1047, 836, 775 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.54 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 6.06 (app t, *J* = 10.9 Hz, 1H), 5.16 (m, 6H), 4.72 (app t, *J* = 8.7 Hz, 1H), 4.43 (app t, *J* = 10.2 Hz, 1H), 3.55 (m, 2H), 3.24 (m, 2H), 2.71 (m, 1H), 2.52 (m 3H), 1.91 (m, 2H), 1.69 (m, 4H), 1.51 (ddd, *J* = 13.3, 11.1, 1.9 Hz, 1H), 1.47 (d, *J* = 2.8 Hz, 1H), 1.13 (d, *J* = 7.6 Hz, 3H), 0.88 (m, 12H), 0.83 (s, 9H), 0.83 (d, obscured, 3H), 0.82 (s, 9H), 0.81 (s, 9H), 0.78 (s, 9H), 0.73 (d, *J* = 6.8 Hz, 3H), 0.08 (s, 3H), 0.076 (s, 3H), 0.070 (s, 3H), 0.066 (s, 3H), 0.058 (s, 3H), 0.053 (s, 3H), 0.043 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 135.4, 134.8, 133.6, 132.4, 132.1, 131.1, 127.3, 118.4, 80.1, 78.3, 77.1, 76.1, 74.9, 64.7, 44.1, 42.9, 38.0, 37.5, 37.4, 36.4, 35.1, 34.2, 32.4, 26.3 (2), 25.9, 25.7, 18.5, 18.4, 18.1, 18.0, 17.3, 17.1, 16.4, 16.0, 14.1, 13.8, 9.4, -3.1, -3.3, -3.6, -4.2, -4.3, -4.5, -4.8 (2); high resolution mass spectrum (ES⁺) m/z 1015.7070 [(M+Na)⁺; calcd for C₅₅H₁₀₈O₇Si₄Na: 1015.7090].



(+)-**N11**

Carbamate (+)-N11. A solution of alcohol (+)-**N10** (48 mg, 0.0479 mmol) in CH₂Cl₂ (1.6 mL) was treated with a solution (1 M, PhH) Cl₃CCON=C=O (144 μ L, 0.144 mmol) at room temperature for 30 min. Solution was loaded directly onto neutral Al₂O₃. After 4 h, the material was flushed from the Al₂O₃ (EtOAc), concentrated, and purified by flash chromatography (10% ethyl acetate/hexanes) providing 50 mg (+)-**N11** (99%); $[\alpha]_D^{23}$ +31 (*c* 1.0, CH₂Cl₂); IR (film, NaCl) 3362, 2929, 2856, 1732, 1595, 1462, 1360, 1253, 1098, 836, 775 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.59 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 6.02 (app t, *J* = 11.0 Hz, 1H), 5.37 (app t, *J* = 10.4 Hz, 1H), 5.30 (m, 2H), 5.20 (d, *J* = 16.7 Hz, 1H), 5.13 (m, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.80 (app t, *J* = 8.9 Hz, 1H), 4.71 (app t, *J* = 6.0 Hz, 1H), 4.50 (app t, *J* = 10.6 Hz, 1H), 4.46 (br s, 2H), 3.64 (app t, *J* = 2.3 Hz, 1H), 3.46 (app t, *J* = 4.5 Hz, 1H), 3.29 (app t, *J* = 5.1 Hz, 1H), 2.98 (app ddq, *J* = 6.7, 10.0, 6.7 Hz, 1H), 2.62 (m, 2H), 2.54 (app ddq, *J* = 6.6, 8.2, 6.6 Hz, 1H), 1.90 (m, 3H), 1.80 (ddd, *J* = 9.6, 6.7, 2.4 Hz, 1H), 1.73 (m, 1H), 1.67 (m, 1H), 1.57 (m, 1H), 1.24 (m, 1H), 1.22 (d, *J* = 7.6 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 6H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.88 (d, *J* = 5.2 Hz, 3H), 0.87 (s, 9H), 0.86 (s, 9H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 6H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.3, 156.9, 135.2, 133.6, 133.5, 132.5, 132.1, 129.9, 127.1, 117.9, 80.0, 78.8, 77.0, 76.3, 74.9, 64.7, 44.2, 42.9, 38.1, 38.0, 37.6, 35.0, 34.5, 34.2, 32.0, 26.3, 26.2, 25.9, 25.7, 18.6, 18.4, 18.1, 18.0, 17.6, 17.2, 16.4, 16.1, 14.3, 14.1, 10.3, -3.1, -3.5, -3.6, -4.2, -4.3, -4.5, -4.8 (2); high resolution mass spectrum (ES⁺) *m/z* 1058.7114 [(M+Na)⁺; calcd for C₅₆H₁₀₉NO₈Si₄Na: 1058.7128].



(+)-14-normethyldiscodermolide

(+)-14-normethyldiscodermolide: Carbamate (+)-**N11** (11 mg, 0.0105 mmol) was dissolved in MeOH (3.7 mL) and stirred for 15 min at room temperature. Aqueous hydrochloric acid (3N, 2.2 mL) was added in 100 μ L portions over 4 hours at a rate which minimized precipitation (ca. 10 to 15 min intervals). An additional 500 μ L of 3 N aq HCl was added over 1 h at 15 min intervals, and the sides of the flask/stir bar were rinsed with 2 mL of MeOH. After 12 h the solution was quenched with NaHCO₃ (s), diluted with 30 mL of water and extracted 3 x with EtOAc. The combined organic extracts were dried (Na₂SO₄), filtered, and concentrated. Flash chromatography (10% MeOH/CH₂Cl₂) using washed SiO₂ (10% MeOH/CH₂Cl₂ then 5% MeOH/CH₂Cl₂) furnished a white amorphous solid (+)-**14-normethyldiscodermolide** (5.5 mg, 90% yield). $[\alpha]_D^{23}$ +19 (*c* 1.0, CD₃CN); IR (film, NaCl) 3390, 2926, 1704, 1391, 1030 cm⁻¹; ¹H NMR (500 MHz, CD₃CN) δ 6.67 (dddd, *J* = 16.8, 11.1, 10.1, 0.8 Hz, 1H), 6.05 (app t, *J* = 10.9 Hz, 1H), 5.46 (app t, *J* = 10.4 Hz, 1H), 5.42 (app t, *J* = 12.1 Hz, 1H), 5.39 (dd, *J* = 11.2, 8.2 Hz, 1H), 5.25 (m, 3H), 5.13 (d, *J* = 10.1 Hz, 1H), 5.05 (br s, 2H), 4.69 (dd, *J* = 7.1, 4.9 Hz, 1H), 4.52 (dddd, *J* = 12.9, 5.2, 5.1, 2.3 Hz, 1H), 4.46 (ddd, *J* = 10.4, 10.4, 2.0 Hz, 1H), 3.64 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.28 (d, *J* = 4.6 Hz, 1H), 3.19 (ddd, *J* = 6.7, 6.7, 4.2 Hz, 1H), 3.14 (ddd, *J* = 6.7, 5.1, 5.1 Hz, 1H), 3.06 (app ddq, *J* = 6.7, 8.7, 6.7 Hz, 1H), 2.81 (d, *J* = 5.2 Hz, 1H), 2.64 (m, 1H), 2.63 (d, *J* = 5.4 Hz, 1H), 2.58 (m, 1H), 2.56 (d, *J* = 6.3 Hz, 1H), 2.42 (app ddq, *J* = 9.0, 6.7, 6.7 Hz, 1H), 1.90 (m, 1H), 1.86 (m, 1H), 1.79 (ddd, *J* = 4.2, 6.9, 6.9 Hz, 1H), 1.72 (m, 2H), 1.61 (m, 1H), 1.56 (ddd, *J* = 2.5, 10.7, 14.1 Hz, 1H), 1.20 (d, *J* = 7.3 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (125 MHz, CD₃CN) δ 174.5, 158.3, 135.0, 134.5, 134.0, 133.6, 133.4, 130.4, 128.3, 118.5, 79.3, 79.1, 77.9, 75.5, 73.1, 63.8, 44.0, 42.3, 38.5, 36.8, 36.6, 36.3, 36.2, 35.0, 32.1,

19.1, 18.2, 16.6, 15.7, 15.6, 13.0, 9.4; high resolution mass spectrum (ES⁺) m/z 602.3651 [(M+Na)⁺;
calcd for C₃₂H₅₃NO₈Na: 602.3669].