Supporting Information

Design, Total Synthesis and Evaluation of C13-C14 Cyclopropane Analogues of Discodermolide

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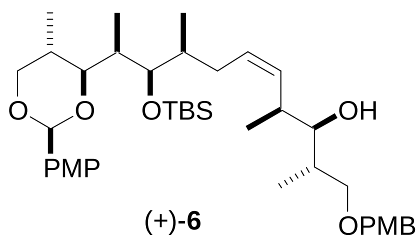
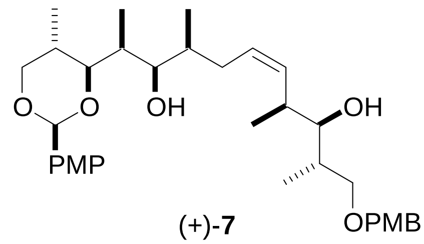
Materials and Methods: Reactions were carried out in oven or flame-dried glassware under an argon atmosphere, unless otherwise noted. All solvents were reagent grade. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were freshly distilled from sodium / benzophenone under argon. Reactions were magnetically 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. All melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 283B spectrophotometer or 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), acetonitrile (δ 1.94), or benzene (δ 7.15) for 1H NMR and chloroform (δ 77.0), acetonitrile (δ 1.32, 118.26), 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 on either a VG Micromass 70/70 H or VG ZAB-E spectrometer.

Experimental Procedures

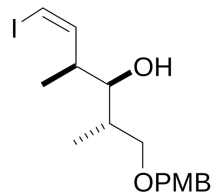


(+)-**6**



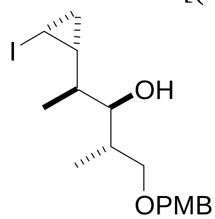
(+)-**7**

(+)-**6** and (+)-**7**: A solution of (+)-**5** (100 mg, 0.125 mmol) in THF (2 mL) was treated with TBAF (1.0 M in THF, 1 mmol). The mixture was stirred at r.t. for 8 h and then diluted with ether (70 mL), washed [aqueous NH_4Cl, water, brine], dried over Na_2SO_4, filtered and concentrated. Flash chromatography (20% to 30% ethyl acetate/hexanes) afford (+)-**6** (55 mg, 64% yield) and (+)-**7** (25 mg, 35%). (+)-**6**: $[\alpha]_D^{23}$ +56.5 (*c* 1.0, $CHCl_3$); IR 3498, 2930, 1515, 1248, 1034 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.42-5.37 (m, 1H), 5.40 (s, 1H), 5.30 (m, 1H), 4.41 (dd, *J* = 11.9, 20.0 Hz, 2H), 4.10 (dd, *J* = 4.8, 11.2 Hz, 1H), 3.80 (s, 6H), 3.68 (dd, *J* = 1.5, 7.4 Hz, 1H), 3.60 (dd, *J* = 4.1, 9.3 Hz, 1H), 3.53-3.47 (m, 2H), 3.40 (dd, *J* = 6.3, 8.9 Hz, 1H), 3.37-3.29 (m, 2H), 2.57 (m, 1H), 2.11-1.70 (m, 6H), 1.02 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.85 (d, *J* = 7.1 Hz, 3H), 0.74 (d, *J* = 7.1 Hz, 3H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.7, 159.2, 134.1, 131.4, 129.8, 129.2, 127.9, 127.2, 113.8, 113.4, 100.8, 82.9, 79.9, 77.2, 74.6, 73.3, 73.2, 55.2 (2C), 38.1, 36.3, 35.7, 35.4, 33.3, 30.7, 26.2, 18.4, 14.7, 14.5, 12.9, 12.1, 10.9, -3.4, -3.6; high resolution mass spectrum (ES^+) m/z 707.4301 $[(M+Na)^+$; calcd for $C_{40}H_{64}O_7SiNa$: 707.4319]. (+)-**7**: $[\alpha]_D^{23}$ +44.5 (*c* 1.0, $CHCl_3$); IR 3487, 2930, 1515, 1249, 1034 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.40 (s, 1H), 5.40 (app t, *J* = 10.4 Hz, 1H), 5.30 (m, 1H), 4.41 (dd, *J* = 11.0, 20.5 Hz, 2H), 4.11 (dd, *J* = 4.5, 11.2 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.61 (dd, *J* = 2.0, 10.0 Hz, 1H), 3.59-3.56 (m, 2H), 3.51 (app t, *J* = 11.2 Hz, 1H), 3.39 (dd, *J* = 6.7, 9.3 Hz, 1H), 3.33 (br s, 1H), 3.30 (app t, *J* = 5.9 Hz, 1H), 3.07 (br s, 1H), 2.56 (m, 1H), 2.13-1.83 (m, 5H), 1.70 (m, 1H), 1.04 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 6H), 0.76 (d, *J* = 7.1 Hz, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.9, 159.2, 134.4, 130.7, 129.7, 129.3, 127.2, 126.7, 113.8, 113.6, 101.1, 87.8, 80.1, 76.7, 74.3, 73.2, 73.1, 55.2 (2C), 35.8, 35.5, 35.4, 34.9, 31.2, 30.4, 15.2, 15.1, 14.8, 11.8, 6.8; high resolution mass spectrum (ES^+) m/z 593.3436 $[(M+Na)^+$; calcd for $C_{34}H_{50}O_7Na$: 593.3454].



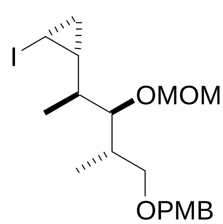
(+)-**S1**

(+)-**S1**: A solution of (+)-**11** (3.0 g, 5.95 mmol) in MeOH (40 mL)/THF (15 mL) was treated with 6N HCl (10 mL). The mixture was stirred at r.t. for 4 h and then diluted with ethyl acetate (500 mL), washed [aqueous $NaHCO_3$, water, brine], dried over Na_2SO_4, filtered and concentrated. Flash chromatography (10% ethyl acetate/hexanes) afford (+)-**S1** (2.2 g, 95% yield) as a colorless oil. $[\alpha]_D^{23}$ +73.5 (*c* 1.1, $CHCl_3$); IR 3479, 2963, 2868, 2361, 1513, 1248 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.17-6.12 (m, 2H), 4.44 (apparent s, 2H), 3.78 (s, 3H), 3.66 (dd, *J* = 3.8, 9.2 Hz, 1H), 3.58 (br s, 1H), 3.44 (app t, *J* = 6.3 Hz, 1H), 3.42 (dd, *J* = 6.9, 9.3 Hz, 1H), 2.64-2.61 (m, 1H), 1.89-1.85 (m, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.8, 145.1, 130.1, 129.8, 114.4, 81.2, 79.2, 75.5, 73.8, 55.7, 43.3, 36.2, 14.7, 13.3; high resolution mass spectrum (ES^+) m/z 413.0608 $[(M+Na)^+$; calcd for $C_{16}H_{23}IO_3Na$: 413.0590].



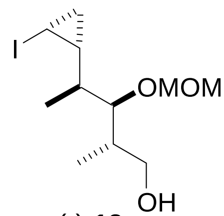
(+)-**12**

(+)-**12**: A stirred solution of Et_2Zn (3 mmol) in dry $ClCH_2CH_2Cl$ (6 mL) was cooled to 0 ^oC and $ClCH_2I$ (6 mmol) was added by use of a gas-tight syringe. After the mixture had been stirred at 0 ^oC for 5 min, a solution of (+)-**S1** (390 mg, 1 mmol) in dry $ClCH_2CH_2Cl$ (2 mL) was added (cannulation) and stirred at r.t. for 3 h. The reaction was quenched by sat. NH_4Cl (10 mL). The mixture was then diluted with ether (30 mL). The phases were separated and the aq. layer was extracted with ether. The combined organic extracts were washed (H_2O, brine), dried (Na_2SO_4), and concentrated. Flash chromatography (10% ethyl acetate/hexanes) afforded (+)-**12** (287 mg, 71% yield). $[\alpha]_D^{23}$ +21.4 (*c* 0.6, $CHCl_3$); IR 3482, 2963, 2929, 1612, 1513, 1246 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.44 (dd, *J* = 11.4, 15.5 Hz, 2H), 3.78 (s, 3H), 3.57 (dd, *J* = 3.9, 9.1 Hz, 1H), 3.54 (dd, *J* = 2.4, 9.1 Hz, 1H), 3.45 (app t, *J* = 9.0 Hz, 1H), 2.66 (dt, *J* = 4.8, 7.6 Hz, 1H), 1.97-1.95 (m, 1H), 1.34-1.30 (m, 1H), 1.17-1.13 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.67 (m, 1H), 0.48 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.8, 130.1, 129.8, 114.3, 79.9, 76.8, 73.7, 55.7, 42.5, 36.3, 20.4, 15.9, 13.8, 11.5, -5.4; high resolution mass spectrum (ES^+) m/z 427.0739 $[(M+Na)^+$; calcd for $C_{17}H_{25}IO_3Na$: 427.0746].



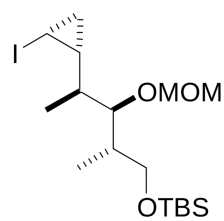
(-)-**S2**

(-)-**S2**: To a solution of (+)-**12** (1.0 g, 2.47 mmol) and *i*-Pr_2NEt (4.3 mL, 24.7 mmol) in CH_2Cl_2 (20 mL) was added MOMCl (1.13 mL, 14.8 mmol) at room temperature. After stirring for 24 h, the reaction was quenched with sat. NH_4Cl and extracted with ether. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (8% ethyl acetate/hexanes) afforded (-)-**S2** (1.05, 95% yield). $[\alpha]_D^{23}$ –11.0 (*c* 0.4, $CHCl_3$); IR 2932, 1612, 1512, 1246, 1035 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.62 (dd, *J* = 6.5, 9.9 Hz, 2H), 4.41 (dd, *J* = 11.6, 15.9 Hz, 2H), 3.78 (s, 3H), 3.49 (dd, *J* = 3.6, 8.9 Hz, 1H), 3.45-3.35 (m, 2H), 3.33 (s, 3H), 2.67 (dd, *J* = 7.5, 12.9 Hz, 1H), 1.97-1.93 (m, 1H), 1.29-1.24 (m, 2H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.56-0.50 (m, 2H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.5, 131.2, 129.7, 114.2, 98.8, 84.7, 73.2, 72.7, 56.5, 55.7, 42.0, 37.1, 20.9, 16.3, 15.3, 12.9, -5.4; high resolution mass spectrum (ES^+) m/z 471.0999 $[(M+Na)^+$; calcd for $C_{19}H_{29}IO_4Na$: 471.1008].



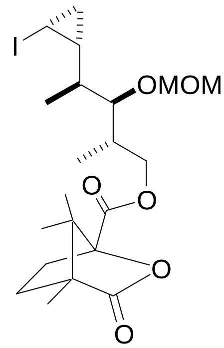
(-)-**13**

(-)-**13**: To a solution of (-)-**S2** (0.56 g, 1.25 mmol) in CH_2Cl_2 (12 mL) was added H_2O (0.3 mL) and DDQ (0.37 g, 1.6 mmol) at 0 ^{o}C. After stirring at 0 ^{o}C for 1 h and room temperature for 20 min, the reaction was quenched with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (25% ethyl acetate/hexanes) afforded (-)-**13** (370 mg, 90% yield). $[\alpha]_D^{23}$ –78.1 (*c* 0.6, $CHCl_3$); IR 3458, 2964, 1458, 1238, 1031 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.76 (d, *J* = 6.5 Hz, 1H), 4.65 (d, *J* = 6.5 Hz, 1H), 3.85 (dd, *J* = 3.3, 11.3 Hz, 1H), 3.52-3.48 (m, 2H), 3.43 (s, 3H), 2.82 (br s, 1H), 2.74-2.70 (m, 1H), 1.83-1.81 (m, 1H), 1.33-1.24 (m, 2H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.55-0.46 (m, 2H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 98.7, 85.5, 65.1, 56.3, 41.8, 37.5, 20.2, 15.7, 14.6, 12.0, -6.0; high resolution mass spectrum (ES^+) m/z 351.0436 $[(M+Na)^+$; calcd for $C_{11}H_{21}IO_3Na$: 351.0433].



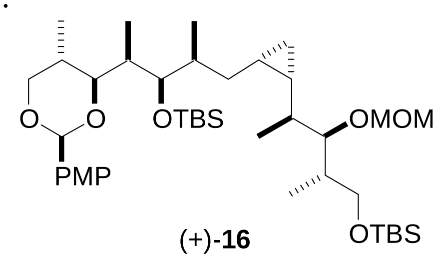
(-)-**14**

(-)-**14**: To a solution of (-)-**13** (0.6 g, 1.83 mmol) in CH_2Cl_2 (10 mL) was added 2,6-lutidine (0.38 mL, 3.3 mmol) and TBSOTf (0.46 mL, 2.0 mmol) at -30 ^{o}C. After stirring for 2 h, the reaction was quenched with sat. NH_4Cl and diluted with ether (60 mL). The organic layer was washed (1M $NaHSO_4$, brine), dried (Na_2SO_4), filtered, and concentrated. Flash chromatography (3% ethyl acetate/hexanes) afforded (-)-**14** (800 mg, 99% yield). $[\alpha]_D^{23}$ –7.7 (*c* 0.63, $CHCl_3$); IR 2959, 1466, 1251, 1090, 1036 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.68 (dd, *J* = 6.4, 8.6 Hz, 2H), 3.67-3.60 (m, 2H), 3.45 (dd, *J* = 2.0, 9.1 Hz, 1H), 3.38 (s, 3H), 2.73-2.70 (m, 1H), 1.82-1.80 (m, 1H), 1.35-1.30 (m, 2H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 9H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.59-0.52 (m, 2H), 0.03 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 98.4, 83.9, 64.9, 55.9, 41.5, 38.4, 25.9, 20.5, 18.3, 15.7, 14.3, 12.3, -5.46, -5.47, -5.5; high resolution mass spectrum (ES^+) m/z 465.1309 $[(M+Na)^+$; calcd for $C_{17}H_{35}IO_3SiNa$: 465.1298].



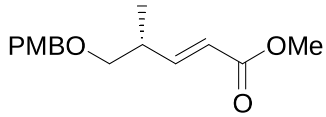
(-)-**15**

(-)-**15**: To a solution of (-)-**13** (40 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) was added DMAP (44 mg, 0.36 mmol) and (-)-camphanic acid chloride (53 mg, 0.24 mmol) at room temperature. After stirring at room temperature for 3 h, the reaction was diluted with ether (20 mL) and washed with sat. NH_4Cl and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (15% ethyl acetate/hexanes) afforded (-)-**15** (59 mg, 96% yield). $[\alpha]_D^{23}$ –38.9 (*c* 1.0, $CHCl_3$); m.p. 71-72 ^oC; IR 2967, 1789, 1750, 1271, 1030 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.69 (d, *J* = 6.7 Hz, 1H), 4.59 (d, *J* = 6.7 Hz, 1H), 4.38 (dd, *J* = 3.4, 10.8 Hz, 1H), 4.20 (dd, *J* = 6.4, 10.8 Hz, 1H), 3.41 (dd, *J* = 2.2, 9.0 Hz, 1H), 3.39 (s, 3H), 2.74-2.70 (m, 1H), 2.46-2.39 (m, 1H), 2.10-2.01 (m, 2H), 1.92 (ddd, *J* = 4.6, 10.8, 13.2 Hz, 1H), 1.69 (ddd, *J* = 4.2, 9.4, 13.4 Hz, 1H), 1.34-1.27 (m, 2H), 1.12 (s, 3H), 1.09 (s, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.98 (s, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.56-0.52 (m, 2H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 178.2, 167.5, 98.4, 91.2, 84.1, 68.1, 56.3, 54.8, 54.0, 41.8, 35.3, 30.7, 28.9, 20.1, 16.74, 16.68, 15.7, 14.6, 12.2, 9.7, -6.2; high resolution mass spectrum (ES^+) m/z 531.1216 [$(M+Na)^+$; calcd for $C_{21}H_{33}IO_6Na$: 531.1219].



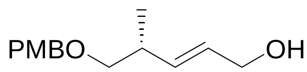
(+)-**16**

(+)-**16**: A solution of (-)-**14** (240 mg, 0.54 mmol) in THF (5 mL) was cooled to –78 ^oC. *t*-BuLi (1.7 M in pentane, 0.65 mL, 1.1 mmol) was added, and the resultant yellow solution was stirred at –78 ^oC for 30 min. To this mixture was added 2-ThCuCNLi (0.48 M in THF, 1.3 mL, 0.64 mmol). The resultant brown solution was stirred at –78 ^oC for 10 min and then warmed to –20 ^oC and allowed to stir for 20 min. The brown solution was then cooled to –40 ^oC. To this solution was transferred slowly via cannula a solution of (+)-**9** (880 mg, 1.6 mmol) in THF (5 mL). The mixture was then warmed to 0 ^oC over 3 h and allowed to stir at 0 ^oC for another 20 h. The reaction was quenched with sat. NH_4Cl (20 mL) and diluted with ether (100 mL). The organic layer was washed (H_2O, brine), dried (Na_2SO_4), filtered, and concentrated. Flash chromatography (3% ethyl acetate/hexanes) afforded (+)-**16** (240 mg, 61% yield). $[\alpha]_D^{23}$ +8.1 (*c* 0.6, $CHCl_3$); IR 2957, 1616, 1518, 1463, 1387, 1251, 1035 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.44 (s, 1H), 4.77 (d, *J* = 6.3 Hz, 1H), 4.71 (d, *J* = 6.3 Hz, 1H), 4.14 (dd, *J* = 4.6, 11.2 Hz, 1H), 3.84 (s, 3H), 3.76 (dd, *J* = 3.4, 9.7 Hz, 1H), 3.74 (app t, *J* = 7.5 Hz, 1H), 3.60-3.56 (m, 2H), 3.54 (app t, *J* = 11.0 Hz, 1H), 3.39 (s, 3H), 3.38 (dd, *J* = 1.8, 9.0 Hz, 1H), 2.13-2.08 (m, 1H), 1.93-1.81 (m, 3H), 1.58-1.53 (m, 1H), 1.17-1.14 (m, 1H), 1.08-1.03 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.94 (s, 18H), 0.93-0.89 (m, 1H), 0.88 (d, *J* = 6.7 Hz, 3H), 0.85-0.82 (m, 1H), 0.78 (d, *J* = 6.7 Hz, 3H), 0.62-0.59 (m, 1H), 0.08 (s, 3H), 0.07 (s, 3H), 0.05 (s, 6H), -0.21 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.7, 131.5, 127.3, 113.4, 100.9, 98.6, 84.6, 83.2, 77.4, 73.3, 65.2, 56.1, 55.2, 38.5, 37.9, 36.7, 35.1, 33.4, 30.7, 26.2, 25.9, 21.2, 18.5, 18.3, 15.3, 14.4, 13.84, 13.77, 12.1, 10.9, 10.7, -3.5, -3.7, -5.42, -5.46; high resolution mass spectrum (ES^+) m/z 759.5009 [$(M+Na)^+$; calcd for $C_{41}H_{76}O_7Si_2Na$: 759.5027].



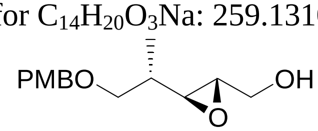
(+)-**S3**

(+)-**S3**: To a solution of (+)-**20** (5.0 g, 0.024 mol) in benzene (250 mL) was added $Ph_3P{=}CHCO_2Me$ (16 g, 0.048 mol) at room temperature. After stirring at room temperature for 20 h, the mixture was concentrated. Flash chromatography (5% ethyl acetate/hexanes) afforded (+)-**S3** (6.0, 95% yield). $[\alpha]_D^{23}$ +14.8 (*c* 1.3, $CHCl_3$); IR 2954, 2854, 1720, 1512, 1250 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.9 Hz, 2H), 6.93 (dd, *J* = 7.1, 15.6 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.86 (dd, *J* = 1.2, 15.6 Hz, 1H), 4.44 (s, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 3.38-3.35 (m, 2H), 2.66-2.61 (m, 1H), 1.07 (d, *J* = 7.1 Hz, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 167.0, 159.2, 151.5, 130.2, 129.1, 120.4, 113.7, 73.5, 72.7, 55.2, 51.4, 36.7, 16.0; high resolution mass spectrum (CI) m/z 264.1364 [M^+; calcd for $C_{15}H_{20}O_4$: 264.1362].



(+)-**S4**

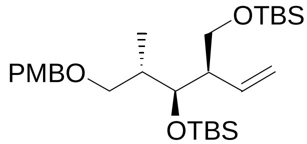
(+)-**S4**: To a solution of (+)-**S3** (2.0 g, 7.57 mmol) in CH_2Cl_2 (25 mL) was added DIBAL (1.5 M in toluene, 15 mL, 22.7 mmol) at –78 ^oC. The mixture was stirred 2 h at –78 ^oC and quenched via drop-wise addition of MeOH (4 mL). Saturated aqueous sodium potassium tartrate (100 mL) was added, and the resultant solution was vigorously stirred at ambient temperature. After 1 h, the mixture was diluted with CH_2Cl_2 (100 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL) and the combined organic layers were washed with water, brine, dried ($MgSO_4$) and concentrated. Flash chromatography (40% ethyl acetate/hexanes) afforded (+)-**S4** (1.7 g, 95% yield). $[\alpha]_D^{23}$ +7.0 (*c* 1.3, $CHCl_3$); IR 3394, 2862, 1612, 1512, 1458, 1246 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.68-5.65 (m, 2H), 4.44 (s, 2H), 4.09 (app d, *J* = 4.5 Hz, 2H), 3.80 (s, 3H), 3.34 (dd, *J* = 6.3, 8.9 Hz, 1H), 3.28 (dd, *J* = 6.3, 8.9 Hz, 1H), 2.52-2.46 (m, 1H), 1.52 (br s, 1H), 1.03 (d, *J* = 6.7 Hz, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.1, 135.3, 130.5, 129.1, 128.7, 113.7, 74.7, 72.6, 63.7, 55.2, 36.4, 16.9; high resolution mass spectrum (ES+) m/z 259.1305 [$(M+Na)^+$; calcd for $C_{14}H_{20}O_3Na$: 259.1310].



(-)-**21**

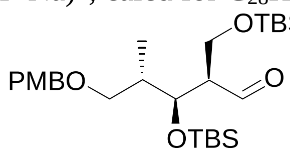
(-)-**21**: Ti(O-*i*Pr)$_4$ (1.68 mL, 6.1 mmol) was added to a stirred suspension of 3A MS (4.0 g) in CH_2Cl_2 (20 mL), containing diethyl (+)-tartrate (1.4 g, 6.78 mmol) at –30 ^oC under argon. After 30 min, a solution of (+)-**S4** (4.2 g, 17.8 mmol) in CH_2Cl_2 (10 mL) was added dropwise, and the stirring was continued for 30 min, then a 5.5 M *t*-BuOOH solution in decane (4.6 mL, 25.4 mmol) was added. The mixture was stirred for 20 h at –30 ^oC, and then poured into a cold solution of $FeSO_4{\cdot}7H_2O$ (5 g) and tartaric acid (1.5 g) in water (10 mL). Stirring was continued at r.t. for 30 min, and then 100 mL CH_2Cl_2 was added followed by 30% NaOH (6 mL). The mixture was stirred for 30 min, then extracted with CH_2Cl_2. The extracts were washed with brine, dried over Na_2SO_4 and concentrated. Flash chromatography (40% ethyl acetate/hexanes) afforded (-)-**21** (4.0 g, 90% yield). $[\alpha]_D^{23}$ –20.0 (*c* 0.4, $CHCl_3$); IR 3429, 2866, 1612, 1512, 1246, 1092 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3

Hz, 2H), 6.88 (d, J = 8.3 Hz, 2H), 4.45 (dd, J = 11.5, 13.8 Hz, 2H), 3.89 (dd, J = 2.5, 12.3 Hz, 1H), 3.80 (s, 3H), 3.61 (dd, J = 4.7, 12.5 Hz, 1H), 3.45-3.40 (m, 2H), 3.00-2.98 (m, 1H), 2.93 (dd, J = 2.2, 6.7 Hz, 1H), 1.82-1.77 (m, 1H), 1.76 (br s, 1H), 0.99 (d, J = 7.1 Hz, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.1, 130.4, 129.1, 113.7, 72.7, 72.1, 61.8, 57.7, 56.8, 55.2, 35.7, 13.3; high resolution mass spectrum (ES+) m/z 275.1255 [$(M+Na)^+$; calcd for $C_{14}H_{20}O_4Na$: 275.1259].



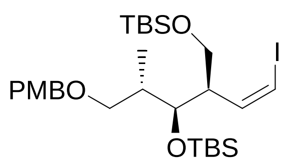
(-)-**S5**

(-)-**S5** was prepared from (-)-**21** employing the same procedure as reported in the literature.[1] $[\alpha]_D^{23}$ –9.8 (c 0.5, $CHCl_3$); IR 2930, 1513, 1469, 1251, 1098 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.71 (ddd, J = 8.9, 10.8, 19.7 Hz, 1H), 5.04 (d, J = 1.8 Hz, 1H), 5.01 (dd, J = 1.8, 10.1 Hz, 1H), 4.39 (s, 2H), 3.80 (s, 3H), 3.79 (dd, J = 3.7, 6.8 Hz, 1H), 3.70 (dd, J = 4.8, 9.7 Hz, 1H), 3.63 (dd, J = 6.3, 9.7 Hz, 1H), 3.57 (dd, J = 5.2, 9.7 Hz, 1H), 3.23 (app t, J = 8.9 Hz, 1H), 2.39 (m, 1H), 2.03 (m, 1H), 1.00 (d, J = 7.1 Hz, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H), 0.02 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 158.9, 138.5, 130.9, 129.1, 116.2, 113.6, 74.3, 72.4, 72.0, 63.7, 55.2, 50.8, 37.6, 26.0, 25.9, 18.22, 18.21, 15.0, -4.1, -4.3, -5.3, -5.4; high resolution mass spectrum (ES+) m/z 531.3296 [$(M+Na)^+$; calcd for $C_{28}H_{52}O_4Si_2Na$: 531.3302].



(+)-**S6**

(+)-**S6** was prepared from (-)-**S5** employing the same procedure as reported in the literature.[2] $[\alpha]_D^{23}$ +3.9 (c 1.0, $CHCl_3$); IR 2929, 1725, 1613, 1513, 1471, 1251, 1088 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 9.24 (d, J = 2.2 Hz, 1H), 7.23 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.35 (s, 2H), 4.23 (app t, J = 5.2 Hz, 1H), 4.04 (dd, J = 7.8, 10.4 Hz, 1H), 3.90 (dd, J = 5.9, 10.4 Hz, 1H), 3.80 (s, 3H), 3.40 (dd, J = 6.7, 9.3 Hz, 1H), 3.25 (dd, J = 6.0, 9.3 Hz, 1H), 2.70 (m, 1H), 2.04 (m, 1H), 0.96 (d, J = 6.7 Hz, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 6H), 0.03 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 204.1, 159.0, 130.4, 129.1, 113.7, 72.5, 71.3, 71.1, 59.8, 57.4, 55.2, 38.2, 25.8, 25.7, 18.1, 18.0, 14.0, -4.4, -4.6, -5.5, -5.6; high resolution mass spectrum (ES+) m/z 533.3092 [$(M+Na)^+$; calcd for $C_{27}H_{50}O_5Si_2Na$: 533.3095].

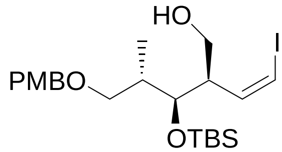


(-)-**22**

(-)-**22** was prepared from (-)-**S6** employing the same procedure as reported in the literature.[3] $[\alpha]_D^{23}$ –18.5 (c 0.9, $CHCl_3$); IR 2930, 1513, 1469, 1250, 1099 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.22 (d, J = 7.4 Hz, 1H), 6.11 (dd, J = 7.4, 9.3 Hz, 1H), 4.40 (dd, J = 11.9, 16.0 Hz, 2H), 3.95 (dd, J = 3.4, 7.1 Hz, 1H), 3.80 (s, 3H), 3.73 (d, J = 4.8 Hz, 2H), 3.51 (dd, J = 5.9, 9.7 Hz, 1H), 3.24 (app t, J = 8.2 Hz, 1H), 2.73 (m, 1H), 2.02 (m, 1H), 1.03 (d, J = 7.1 Hz, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}CNMR (125 MHz,

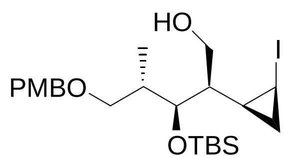
[1] Horita, K.; Tanaka, K.; Yonemitsu, O. *Chem. Pharm. Bull.* **1993**, *41*, 2044-2046.
[2] Smith, A. B., III.; Freeze, B. S.; Xian, M.; Hirose, T. *Org. Lett.* **2005**, *7*, 1825-1828.
[3] Chen, J.; Wang, T.; Zhao, K. *Tetrahedron Lett.* **1994**, *35*, 2827.

$CDCl_3$) δ 159.0, 141.9, 129.1, 128.4, 113.7, 82.7, 73.1, 72.5, 72.0, 62.4, 55.2, 50.8, 38.6, 26.0, 25.9, 18.3, 18.2, 14.5, -4.2, -4.3, -5.3, -5.5; high resolution mass spectrum (ES+) m/z 657.2271 $[(M+Na)^+$; calcd for $C_{28}H_{51}IO_4Si_2Na$: 657.2268].



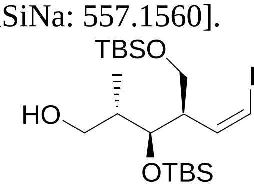
(+)-**23**

(+)-**23**: Vinyl iodide (-)-**22** (200 mg, 0.31 mmol) was dissolved in a 1.0% conc. HCl/EtOH solution (8 mL) and stirred for 30 min at r.t. The mixture was then neutralized with sat. $NaHCO_3$, extracted with $CHCl_3$, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (15% ethyl acetate/hexanes) afforded **23** (148 mg, 90% yield). $[\alpha]_D^{23}$ +36.8 (*c* 1.0, $CHCl_3$); IR 3436, 2929, 1513, 1249, 1038 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.30 (d, *J* = 7.4 Hz, 1H), 6.24 (dd, *J* = 7.4, 9.3 Hz, 1H), 4.39 (dd, *J* = 11.9, 22.0 Hz, 2H), 4.02 (app t, *J* = 5.6 Hz, 1H), 3.81 (s, 3H), 3.73 (d, *J* = 4.8 Hz, 2H), 3.43 (dd, *J* = 7.1, 9.3 Hz, 1H), 3.28 (dd, *J* = 6.7, 9.3 Hz, 1H), 2.82 (m, 1H), 2.47 (br s, 1H), 2.10 (m, 1H), 1.03 (d, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.1, 140.9, 130.6, 129.1, 113.7, 83.6, 75.5, 72.6, 71.8, 63.3, 55.2, 48.7, 39.5, 25.9, 18.1, 13.1, -4.3, -4.4; high resolution mass spectrum (ES+) m/z 543.1414 $[(M+Na)^+$; calcd for $C_{22}H_{37}IO_4SiNa$: 543.1404].



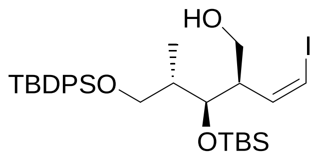
(+)-**24**

(+)-**24**: Employing the same procedure for converting (+)-**S1** to (+)-**12**, (+)-**24** can be obtained from (+)-**23** in 15% yield: $[\alpha]_D^{23}$ +10.0 (*c* 0.4, $CHCl_3$); IR 3501, 2929, 1512, 1248, 1056 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.44 (dd, *J* = 11.9, 18.6 Hz, 2H), 4.20 (dd, *J* = 3.0, 11.2 Hz, 1H), 4.10 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 3.72 (d, *J* = 11.5 Hz, 1H), 3.61 (dd, *J* = 4.1, 8.9 Hz, 1H), 3.31 (dd, *J* = 7.4, 8.9 Hz, 1H), 3.24 (br s, 1H), 2.66 (m, 1H), 2.20 (m, 1H), 1.50 (m, 1H), 1.27 (m, 1H), 1.10 (d, *J* = 7.1 Hz, 3H), 1.07 (m, 1H), 0.90 (s, 9H), 0.61 (m, 1H), 0.10 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.1, 130.6, 129.0, 113.7, 76.8, 72.7, 72.4, 63.7, 55.2, 47.3, 38.8, 26.0, 18.1, 16.4, 16.0, 14.6, -4.1, -4.2, -6.9; high resolution mass spectrum (ES+) m/z 557.1565 $[(M+Na)^+$; calcd for $C_{23}H_{39}IO_4SiNa$: 557.1560].



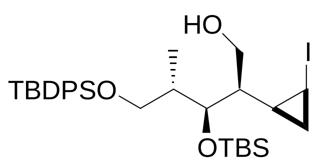
(-)-**S7**

(-)-**S7**: At 0 ^oC, a solution of (-)-**22** (1.0 g, 1.58 mmol) in CH_2Cl_2 (30 mL) was treated with water (0.8 mL) and DDQ (465 mg, 2.05 mmol) and stirred for 2 h. The reaction was quenched with sat. $NaHCO_3$ and the layers separated. The aqueous layer was then extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The resultant residue was dissolved in MeOH (22 mL) and treated with $NaBH_4$ (5 eq). After stirring at r.t. for 15 min, the reaction was diluted with ether (300 mL), washed (sat. NH_4Cl, water, brine), dried (Na_2SO_4), and concentrated. Flash chromatography (4% ethyl acetate/hexanes) afforded (-)-**S7** (0.80 g, 99% yield). $[\alpha]_D^{23}$ –42.2 (*c* 0.2, $CHCl_3$); IR 3402, 2928, 1472, 1255, 1098 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 7.5 Hz, 1H), 6.19 (dd, J = 7.5, 9.2 Hz, 1H), 3.98 (dd, J = 3.6, 7.0 Hz, 1H), 3.76-3.60 (m, 4H), 2.83 (m, 1H), 2.33 (app t, J = 5.7 Hz, 1H), 1.86 (m, 1H), 1.06 (d, J = 7.1 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.13 (s, 6H), 0.04, (s, 3H), 0.03 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 140.8, 83.8, 75.7, 63.3, 61.9, 52.2, 38.2, 26.0, 25.9, 18.2, 18.1, 15.8, -4.2, -4.3, -5.3; high resolution mass spectrum (ES+) m/z 537.1693 [(M+Na)$^+$; calcd for $C_{20}H_{43}IO_3Si_2Na$: 537.1693].



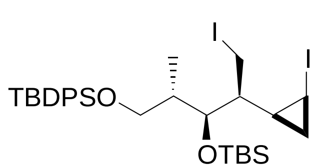
(+)-**25**

(+)-**25**: (-)-**S7** (800 mg, 1.56 mmol) was dissolved in dry DMF (20 mL). To this solution was then added imidazole (215 mg, 3.16 mmol) and TBDPSCl (0.43 mL, 1.66 mmol), and the mixture was stirred at r.t. for 20 h. The reaction was then diluted with ether (300 mL), washed (1M $NaHSO_4$, water, brine), dried ($MgSO_4$), and concentrated. The resultant residue was then dissolved in a 1.0% conc. HCl/EtOH solution (15 mL) and stirred for 30 min at r.t. The mixture was then neutralized with sat. $NaHCO_3$, extracted with $CHCl_3$, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (5% ethyl acetate/hexanes) afforded (+)-**25** (0.91 g, 90% yield): $[\alpha]_D^{23}$ +31.5 (c 0.5, $CHCl_3$); IR 3430, 2929, 1463, 1258, 1075 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.39 (m, 6H), 6.24-6.18 (m, 2H), 4.13 (app t, J = 5.6 Hz, 1H), 3.72 (d, J = 5.2 Hz, 2H), 3.63 (dd, J = 7.4, 10.4 Hz, 1H), 3.49 (dd, J = 7.1, 10.4 Hz, 1H), 2.80 (m, 1H), 2.49 (br s, 1H), 2.10 (m, 1H), 1.08 (s, 9H), 1.00 (d, J = 6.7 Hz, 3H), 0.87 (s, 9H), 0.10 (s, 3H), 0.04 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 140.9, 135.5, 133.6, 129.6, 127.6, 83.6, 75.1, 65.8, 63.4, 48.5, 42.1, 26.9, 25.9, 19.2, 18.0, 12.2, -4.36, -4.37; high resolution mass spectrum (ES+) m/z 661.2203 [(M+Na)$^+$; calcd for $C_{30}H_{47}IO_3Si_2Na$: 661.2187].



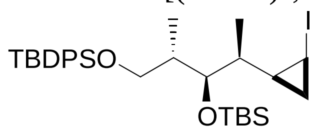
(+)-**26**

(+)-**26**: Employing the same procedure for converting (+)-**S1** to (+)-**12**, (+)-**26** can be obtained from (+)-**25** in 70% yield: $[\alpha]_D^{23}$ +16.0 (c 1.7, $CHCl_3$); IR 3448, 2935, 2862, 1465, 1253, 1103 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.40 (m, 6H), 4.22 (dd, J = 2.6, 11.2 Hz, 1H), 4.01 (d, J = 8.2 Hz, 1H), 3.86 (dd, J = 3.9, 9.7 Hz, 1H), 3.68 (app t, J = 8.8 Hz, 1H), 3.49 (dd, J = 7.8, 9.7 Hz, 1H), 3.25 (d, J = 9.4 Hz, 1H), 2.62 (m, 1H), 2.10 (m, 1H), 1.49 (m, 1H), 1.22 (m, 1H), 1.09 (s, 9H), 1.06 (d, J = 6.7 Hz, 3H), 1.05 (m, 1H), 0.78 (s, 9H), 0.58 (m, 1H), 0.03 (s, 3H), -0.12 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 135.7, 133.7, 129.5, 127.6, 76.7, 66.3, 63.9, 46.9, 40.9, 26.9, 25.9, 19.2, 18.0, 16.2, 16.0, 14.0, -4.0, -4.2, -6.8; high resolution mass spectrum (ES+) m/z 653.2375 [(M+H)$^+$; calcd for $C_{31}H_{50}IO_3Si_2$: 653.2343].



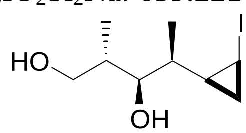
(+)-**S8**

(+)-**S8**: A solution of (+)-**26** (300 mg, 0.46 mmol), PPh_3 (217 mg, 0.83 mmol) and imidazole (56 mg, 0.83 mmol) in benzene/ether (1:2, 13 mL) was treated with iodine (175 mg, 0.69 mmol) at r.t. The reaction mixture was stirred for 1 h and then quenched with sat. $NaHCO_3$. The mixture was extracted with ether and the combined organics were washed (sat. $Na_2S_2O_3$, 5% H_2O_2, water, brine), dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (1% ethyl acetate/hexanes) afforded (+)-**S8** (333 mg, 95% yield): $[\alpha]_D^{23}$ +11.0 (*c* 1.0, $CHCl_3$); IR 2935, 2858, 1466, 1253, 1076 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.67 (m, 4H), 7.38 (m, 6H), 3.91 (dd, *J* = 2.2, 7.5 Hz, 1H), 3.85 (dd, *J* = 4.2, 9.8 Hz, 1H), 3.49 (dd, *J* = 7.8, 9.8 Hz, 1H), 3.45 (dd, *J* =3.3, 10.3 Hz, 1H), 3.27 (dd, *J* = 8.5, 10.3 Hz, 1H), 2.46 (m, 1H), 1.98 (m, 1H), 1.59-1.56 (m, 2H), 1.10 (s, 9H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.00 (m, 1H), 0.80 (s, 9H), 0.60 (m, 1H), 0.01 (s, 3H), -0.12 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 135.7, 129.53, 129.45, 127.5, 75.4, 66.3, 48.2, 40.9, 27.0, 26.0, 19.4, 19.0, 18.1, 17.9, 14.6, 6.4, -3.91, -3.95, -9.6; high resolution mass spectrum (ES+) m/z 785.1199 $[(M+Na)^+$; calcd for $C_{31}H_{48}I_2O_2Si_2Na$: 785.1180].



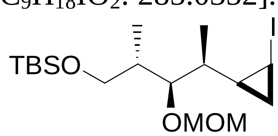
(+)-**27**

(+)-**27**: A solution of (+)-**S8** (730 mg, 0.96 mmol) and $NaCNBH_3$ (0.95 g, 14.4 mmol) in DMPU (7.5 mL) was warmed to 70 ^oC. The mixture was stirred at this temperature for 40 h and then diluted with water (20 mL) and extracted with ethyl acetate. The combined organics were then dried over $MgSO_4$, filtered through a short silica pad, and concentrated. Flash chromatography (2% ethyl acetate/hexanes) afforded (+)-**27** (580 mg, 95% yield): $[\alpha]_D^{23}$ +15.9 (*c* 1.3, $CHCl_3$); IR 2935, 1466, 1250, 1107, 833 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.67 (m, 4H), 7.39 (m, 6H), 3.87 (dd, *J* = 3.7, 9.7 Hz, 1H), 3.75 (dd, *J* = 1.5, 8.3 Hz, 1H), 3.43 (dd, *J* = 8.4, 9.6 Hz, 1H), 2.54 (m, 1H), 1.88 (m, 1H), 1.37-1.29 (m, 2H), 1.09 (s, 9H), 1.03 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.79 (s, 9H), 0.60 (m, 1H), 0.48 (m, 1H), -0.03 (s, 3H), -0.19 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 135.7, 134.1, 129.4, 127.5, 74.1, 66.9, 41.8, 40.6, 27.0, 26.1, 19.9, 19.3, 18.3, 15.9, 14.3, 12.1, -3.7, -3.9, -6.3; high resolution mass spectrum (ES+) m/z 659.2240 $[(M+Na)^+$; calcd for $C_{31}H_{49}IO_2Si_2Na$: 659.2214].



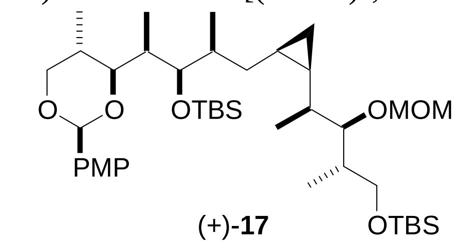
S9

S9: A solution of (+)-**27** (300 mg, 0.47 mmol) and acetic acid (0.11 mL, 1.89 mmol) in THF (10 mL) was treated with TBAF (1.0 M in THF, 5.64 mL, 5.64 mmol). The mixture was stirred at r.t. for 18 h and then quenched with sat. NH_4Cl and extracted with ethyl acetate. The combined organics were then washed (brine), dried ($MgSO_4$), filtered and concentrated. Flash chromatography (50% ethyl acetate/hexanes) afforded **S9** (121 mg, 90% yield): IR 3321, 2923, 1454, 1234, 1030 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 3.81 (d, *J* = 9.5 Hz, 1H), 3.77 (dd, *J* = 3.7, 10.5 Hz, 1H), 3.71 (dd, *J* = 8.6, 10.5 Hz, 1H), 3.27 (br s, 1H), 3.00 (br s, 1H), 2.66-2.63 (m, 1H), 1.90-1.86 (m, 1H), 1.40-1.34 (m, 2H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.73 (m, 1H), 0.54-0.50 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 78.0, 69.3, 40.9, 37.7, 18.5, 15.3, 13.4, 11.2, -6.6; high resolution mass spectrum (ES+) m/z 285.0342 $[(M+H)^+$; calcd for $C_9H_{18}IO_2$: 285.0352].



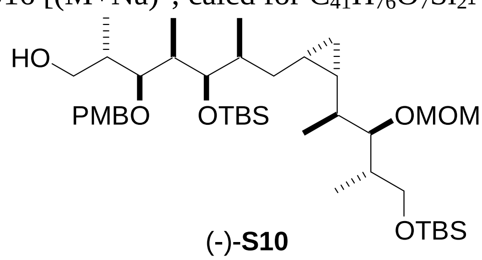
(+)-**18**

(+)-**18**: A solution of **S9** (610 mg, 2.15 mmol) and imidazole (219 mg, 3.22 mmol) in CH_2Cl_2 (30 mL) was treated with TBSCl (347 mg, 2.30 mmol) and stirred for 2 h at room temperature. The reaction was then diluted with ether (150 mL), washed (1M $NaHSO_4$, brine), dried ($MgSO_4$), filtered, and concentrated. The resultant residue was then diluted with ether (300 mL), washed (sat. NH_4Cl, water, brine), dried (Na_2SO_4), and concentrated. The resultant residue was then dissolved in CH_2Cl_2 (10 mL), and treated with *i*-Pr_2NEt (3.75 mL, 21.5 mmol) and MOMCl (0.98 mL, 12.9 mmol) at room temperature. After stirring for 24 h, the reaction was quenched with sat. NH_4Cl and extracted with ether. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (2% ethyl acetate/hexanes) afforded (+)-**18** (855 mg, 90% yield): $[\alpha]_D^{23}$ +53.5 (*c* 1.0, $CHCl_3$); IR 2930, 1463, 1251, 1088, 1035 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 4.77 (s, 2H), 3.73-3.70 (m, 3H), 3.43 (s, 3H), 2.69-2.65 (m, 1H), 1.85-1.82 (m, 1H), 1.46-1.38 (m, 2H), 1.09 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.93 (s, 9H), 0.78 (m, 1H), 0.55 (m, 1H), 0.03 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 99.1, 82.1, 64.9, 56.0, 40.6, 38.6, 25.9, 19.4, 18.3, 15.8, 14.5, 12.2, -5.4, -5.5, -6.8; high resolution mass spectrum (ES^+) m/z 465.1306 [$(M+Na)^+$; calcd for $C_{17}H_{35}IO_3SiNa$: 465.1298].



(+)-**17**

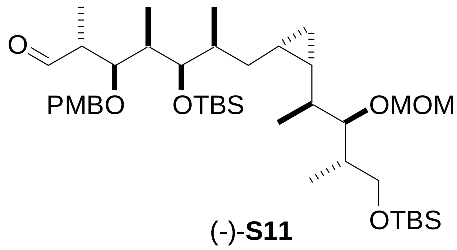
(+)-**17**: Employing the same procedure for converting (-)-**14** to (+)-**16**, (+)-**17** can be obtained from (+)-**18** in 63% yield: $[\alpha]_D^{23}$ +33.0 (*c* 1.0, $CHCl_3$); IR 2930, 1616, 1463, 1389, 1251, 1035 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.40 (s, 1H), 4.73 (d, *J* = 6.1 Hz, 1H), 4.69 (d, *J* = 6.1 Hz, 1H), 4.09 (dd, *J* = 4.6, 11.2 Hz, 1H), 3.80 (s, 3H), 3.74 (d, *J* = 7.3 Hz, 1H), 3.68 (dd, *J* = 3.0, 9.6 Hz, 1H), 3.59 (dd, *J* = 5.8, 9.6 Hz, 1H), 3.53 (d, *J* = 9.8 Hz, 1H), 3.49 (app t, *J* = 11.1 Hz, 1H), 3.39 (s, 3H), 3.36 (d, *J* = 9.6 Hz, 1H), 2.05 (m, 1H), 1.87 (m, 3H), 1.74 (m, 1H), 1.18 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.88 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H), 0.90-0.81 (m, 2H), 0.72 (d, *J* = 6.7 Hz, 3H), 0.70 (m, 1H), 0.62 (m, 1H), 0.02 (s, 6H), -0.01 (s, 6H), -0.25 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.6, 131.5, 127.2, 113.3, 100.8, 98.8, 83.7, 82.9, 76.0, 73.3, 65.1, 56.0, 55.2, 38.5, 38.2, 37.1, 35.4, 33.7, 30.7, 26.2, 25.9, 20.2, 18.4, 18.2, 15.8, 14.3, 13.9, 13.2, 12.2, 11.5, 10.8, -3.4, -3.8, -5.4, -5.5; high resolution mass spectrum (ES^+) m/z 759.5016 [$(M+Na)^+$; calcd for $C_{41}H_{76}O_7Si_2Na$: 759.5027].



(-)-**S10**

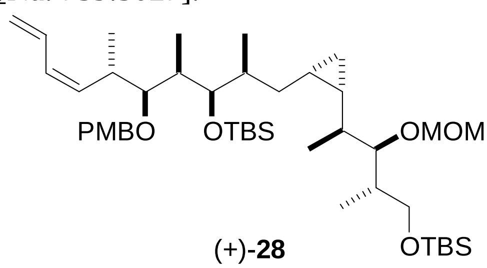
(-)-**S10**: Employing the same procedure in the literature starting from (+)-**17**.[4] $[\alpha]_D^{23}$ –14.6 (*c* 1.0, $CHCl_3$); IR 3472, 2956, 1513, 1465, 1251, 1036 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.74 (d, *J* = 6.3 Hz, 1H), 4.67 (d, *J* = 6.3 Hz, 1H), 4.50 (dd, *J* = 10.5, 21.5 Hz, 2H), 3.79 (s, 3H), 3.75-3.70 (m, 2H), 3.61-3.53 (m, 3H), 3.39 (s, 3H), 3.38-3.36 (m, 2H), 2.70 (br s, 1H), 1.95-1.77 (m, 4H), 1.56-1.51 (m, 1H), 1.15-1.10 (m, 1H), 1.10-1.05 (m, 1H), 1.04 (d, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.88-0.83 (m, 2H), 0.83 (d, *J* = 7.1 Hz, 3H), 0.63-0.59 (m, 1H), 0.07 (s, 3H), 0.04 (s, 6H), 0.03 (s, 3H), -0.24 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.3, 130.3, 129.2, 113.9, 98.6, 86.2, 84.5, 76.9, 75.1, 65.7, 65.1, 56.0, 55.2, 39.8, 38.4, 38.2, 37.6, 35.1, 32.8, 26.2, 25.9, 21.3, 18.5, 18.3, 15.6, 15.1, 14.4, 14.3, 13.8, 11.4, 10.8, -3.3, -3.6, -5.45, -5.46; high resolution mass spectrum (ES^+) m/z 761.5209 [$(M+Na)^+$; calcd for $C_{41}H_{78}O_7Si_2Na$: 761.5184].

[4] Smith, A. B., III; Freeze, B. S.; Brouard, I.; Hirose, T. *Org. Lett*. **2003**, *5*, 4405-4408.



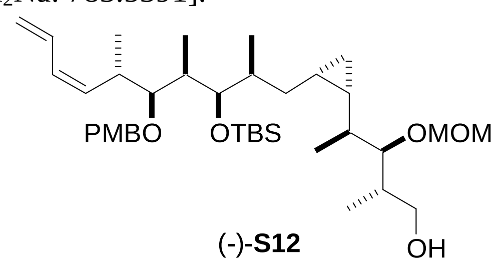
(-)-**S11**

(-)-**S11**: Employing the same procedure in the literature starting from (-)-**S10**.[2] $[\alpha]_D^{23}$ –58.5 (*c* 0.1, $CHCl_3$); IR 2958, 1724, 1515, 1251, 1037 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 9.80 (d, *J* = 2.5 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.73 (d, *J* = 6.4 Hz, 1H), 4.68 (d, *J* = 6.4 Hz, 1H), 4.46 (s, 2H), 3.79 (s, 3H), 3.72 (dd, *J* = 3.4, 9.7 Hz, 1H), 3.65 (dd, *J* = 2.2, 4.8 Hz, 1H), 3.61 (app t, *J* = 5.2 Hz, 1H), 3.55 (dd, *J* = 6.3, 9.3 Hz, 1H), 3.40 (s, 3H), 3.37 (d, *J* = 8.9 Hz, 1H), 2.77-2.72 (m, 1H), 1.94-1.80 (m, 3H), 1.56-1.52 (m, 1H), 1.15-1.13 (m, 1H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.04-1.03 (m, 1H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.87-0.82 (m, 2H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.63-0.59 (m, 1H), 0.06 (s, 3H), 0.04 (s, 6H), 0.03 (s, 3H), -0.25 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 204.6, 159.2, 130.3, 128.9, 113.7, 98.6, 84.5, 82.4, 76.7, 74.3, 65.2, 56.0, 55.2, 49.5, 40.0, 38.4, 38.0, 35.1, 32.8, 26.2, 25.9, 21.3, 18.5, 18.3, 15.1, 14.4, 14.2, 13.8, 12.1, 11.3, 10.7, -3.3, -3.6, -5.40, -5.44; high resolution mass spectrum (ES^+) m/z 759.4996 $[(M+Na)^+$; calcd for $C_{41}H_{76}O_7Si_2Na$: 759.5027].



(+)-**28**

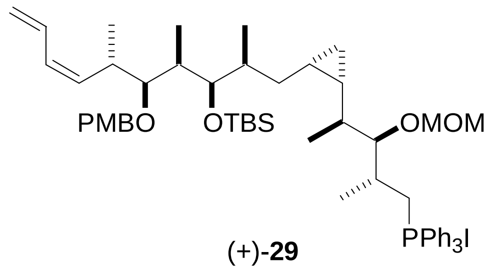
(+)-**28**: Employing the same procedure in the literature starting from (-)-**S11**.[5] $[\alpha]_D^{23}$ +9.7 (*c* 1.0, $CHCl_3$); IR 2957, 1464, 1251, 1037, 835 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H),6.59 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 6.00 (app t, *J* = 11.1 Hz, 1H), 5.57 (app t, *J* = 10.4 Hz, 1H), 5.18 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.73 (d, *J* = 6.3 Hz, 1H), 4.68 (d, *J* = 6.3 Hz, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 3.80 (s, 3H), 3.72 (dd, *J* = 3.4, 9.7 Hz, 1H), 3.56 (dd, *J* = 6.7, 10.0 Hz, 1H), 3.51 (app t, *J* = 4.4 Hz, 1H), 3.40 (s, 3H), 3.36 (dd, *J* = 1.9, 8.6 Hz, 1H), 3.25 (dd, *J* = 4.1, 7.1 Hz, 1H), 3.01-2.95 (m, 1H), 1.83-1.71 (m, 3H), 1.48-1.40 (m, 1H), 1.12-1.10 (m, 1H), 1.09 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.94 (s, 9H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.89-0.87 (m, 1H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.84-0.76 (m, 2H), 0.59-0.54 (m, 1H), 0.08 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), -0.30 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 158.9, 134.7, 132.3, 131.2, 129.0, 128.9, 117.3, 113.6, 98.6, 84.6, 84.5, 76.6, 74.9, 65.2, 56.0, 55.2, 39.9, 38.4, 35.5, 35.1, 32.2, 30.3, 26.3, 25.9, 21.3, 18.7, 18.5, 18.3, 15.1, 14.9, 14.4, 13.8, 10.8, 10.7, -3.3, -3.4, -5.40, -5.43; high resolution mass spectrum (ES^+) m/z 783.5359 $[(M+Na)^+$; calcd for $C_{44}H_{80}O_6Si_2Na$: 783.5391].



(-)-**S12**

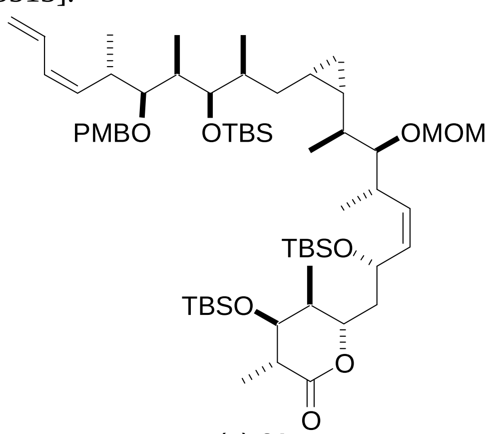
[5] Paterson, I.; Schlapbach, A. *Synlett* **1995**, 498.

(-)-**S12**: Employing the same procedure in the literature starting from (+)-**28**.[2] $[\alpha]_D^{23}$ –13.0 (*c* 0.5, $CHCl_3$); IR 3496, 2960, 1613, 1462, 1250, 1036 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.59 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 5.99 (app t, *J* = 11.1 Hz, 1H), 5.56 (app t, *J* = 10.8 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.85 (d, *J* = 6.7 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.54 (d, *J* = 10.4 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 3.88 (dd, *J* = 3.0, 11.1 Hz, 1H), 3.79 (s, 3H), 3.51-3.46 (m, 3H), 3.45 (s, 3H), 3.24 (dd, *J* = 4.1, 7.1 Hz, 1H), 3.01-2.95 (m, 1H), 1.83-1.66 (m, 3H), 1.45-1.39 (m, 1H), 1.13-1.10 (m, 1H), 1.08 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 7.1 Hz, 3H), 0.93 (s, 9H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.88-0.84 (m, 2H), 0.73-0.66 (m, 1H), 0.56-0.53 (m, 1H), 0.08 (s, 3H), 0.05 (s, 3H), -0.28 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 158.9, 134.7, 132.3, 131.1, 129.0, 128.9, 117.3, 113.6, 99.2, 86.3, 84.5, 76.6, 74.9, 65.3, 56.3, 55.2, 39.9, 38.4, 37.3, 35.4, 35.3, 32.0, 26.2, 21.1, 18.7, 18.5, 15.1, 15.0, 14.8, 13.6, 10.8, 10.7, -3.3, -3.5; high resolution mass spectrum (ES^+) m/z 669.4522 [$(M+Na)^+$; calcd for $C_{38}H_{66}O_6SiNa$: 669.4526].



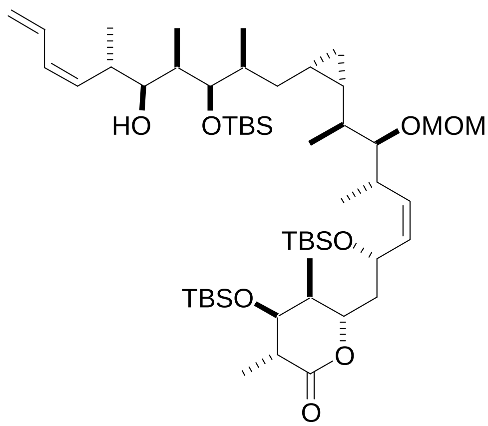
(+)-**29**

(+)-**29**: Employing the same procedure in the literature starting from (-)-**S12**.[2] $[\alpha]_D^{23}$ +6.7 (*c* 0.2, $CHCl_3$); IR 2932, 2358, 1513, 1439, 1249, 1030 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.89-7.43 (m, 15H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H),6.55 (ddd, *J* = 16.8, 10.7, 10.7 Hz, 1H), 5.93 (app t, *J* = 10.8 Hz, 1H), 5.52 (app t, *J* = 10.8 Hz, 1H), 5.12 (d, *J* = 6.8 Hz, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 4.81 (dd, *J* = 5.9, 7.8 Hz, 2H), 4.58 (d, *J* = 10.4 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 4.06 (app t, *J* = 15.3 Hz, 1H), 3.78 (s, 3H), 3.56-3.48 (m, 2H), 3.44 (app t, *J* = 4.5 Hz, 1H), 3.37 (s, 3H), 3.22-3.19 (m, 1H), 2.97-2.91 (m, 1H), 2.12-2.04 (m, 1H), 1.74-1.64 (m, 2H), 1.58 (d, *J* = 6.7 Hz, 1H), 1.49 (d, *J* = 6.7 Hz, 1H), 1.32 (app t, *J* = 10.0 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 9H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.85-0.81 (m, 1H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.67 (d, *J* = 6.7 Hz, 3H), 0.71-0.65 (m, 1H), 0.55-0.51 (m, 1H), 0.05 (s, 3H), 0.01 (s, 3H), -0.29 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 158.9, 135.1, 133.7, 132.3, 132.0, 130.6, 130.5, 129.0, 128.4, 119.1, 118.4, 117.3, 113.6, 99.7, 88.5, 88.4, 84.5, 74.9, 56.3, 55.3, 54.5, 39.9, 38.3, 35.4, 34.7, 31.9, 31.2, 26.2, 20.5, 18.7, 18.6, 17.8, 17.4, 15.2, 14.9, 13.0, 10.6, -3.3, -3.4; high resolution mass spectrum (ES^+) m/z 891.5514 [$(M-I)^+$; calcd for $C_{56}H_{80}O_5PSi$: 891.5513].



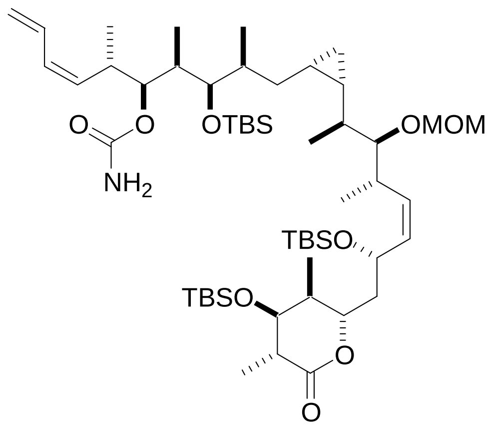
(+)-**31**

(+)-**31**: Employing the same procedure in the literature starting from (+)-**29** and (-)-**30**.[2] $[\alpha]_D^{23}$ +6.5 (*c* 0.2, $CHCl_3$); IR 2957, 1738, 1464, 1251, 1039 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.58 (ddd, *J* = 16.8, 10.7, 10.7 Hz, 1H), 5.99 (app t, *J* = 11.1 Hz, 1H), 5.56 (app t, *J* = 10.4 Hz, 1H), 5.37 (dd, *J* = 7.6, 11.2 Hz, 1H), 5.23 (app t, *J* = 10.4 Hz, 1H), 5.18 (d, *J* = 15.6 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.84 (app t, *J* = 8.2 Hz, 1H), 4.66 (d, *J* = 6.7 Hz, 1H), 4.57 (d, *J* = 6.7 Hz, 1H), 4.54 (d, *J* = 10.4 Hz, 1H), 4.51 (app t, *J* = 9.1 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.66 (app t, *J* = 3.0 Hz, 1H), 3.51 (app t, *J* = 4.1 Hz, 1H), 3.33 (s, 3H), 3.27-3.22 (m, 2H), 3.01-2.94 (m, 1H), 2.77-2.60 (m, 2H), 1.87-1.67 (m, 5H), 1.43-1.39 (m, 1H), 1.26-1.23 (m, 1H), 1.25 (d, *J* = 7.4 Hz, 3H), 1.14-1.09 (m, 1H), 1.07 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 7.1 Hz, 6H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.93 (s, 9H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.85-0.74 (m, 2H), 0.54-0.51 (m, 1H), 0.1-0.06 (m, 18H), -0.33 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 173.4, 158.9, 134.7, 133.7, 132.7, 132.3, 131.2, 129.0, 128.9, 117.3, 113.6, 97.9, 86.3, 84.5, 77.2, 76.5, 74.8, 74.5 64.8, 55.9, 55.2, 43.8, 42.3, 39.9, 38.5, 35.5, 35.4, 35.0, 34.4, 32.2, 30.3, 26.2, 25.8, 25.7, 21.5, 18.7, 18.5, 18.0, 17.9, 17.6, 16.2, 15.1, 15.0, 14.0, 13.9, 10.8, -3.3, -3.5, -4.4, -4.6, -4.90, -4.91; high resolution mass spectrum (ES^+) m/z 1079.7214 $[(M+Na)^+$; calcd for $C_{60}H_{108}O_9Si_3Na$: 1079.7199].



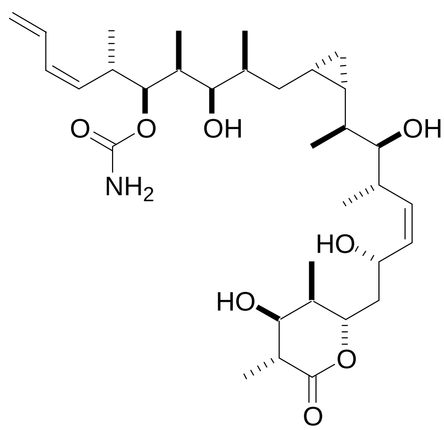
(-)-**S13**

(-)-**S13**: Employing the same procedure in the literature starting from (+)-**31**.[2] $[\alpha]_D^{23}$ –3.9 (*c* 0.7, $CHCl_3$); IR 3508, 2958, 1735, 1464, 1253, 1098 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 6.63 (ddd, *J* = 16.8, 10.7, 10.7 Hz, 1H), 6.14 (app t, *J* = 10.8 Hz, 1H), 5.38-5.20 (m, 4H), 5.14 (d, *J* = 10.1 Hz, 1H), 4.84 (app t, *J* = 8.5 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.58 (d, *J* = 6.7 Hz, 1H), 4.51 (app t, *J* = 10.1 Hz, 1H), 3.66 (app t, *J* = 2.6 Hz, 1H), 3.63 (dd, *J* = 2.6, 6.3 Hz, 1H), 3.35 (dd, *J* = 2.6, 6.3 Hz, 1H), 3.34 (s, 3H), 3.27 (d, *J* = 8.4 Hz, 1H), 2.82-2.59 (m, 3H), 1.88-1.68 (m, 5H), 1.58 (br s, 1H), 1.54-1.47 (m, 1H), 1.25 (d, *J* = 7.4 Hz, 3H), 1.24-1.12 (m, 2H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.87 (s, 9H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.88-0.76 (m, 2H), 0.57-0.53 (m, 1H), 0.08 (s, 3H), 0.07 (s, 6H), 0.06 (s, 6H), 0.04 (s, 3H), -0.26 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 173.4, 134.9, 133.7, 132.8, 132.1, 131.0, 118.3, 97.9, 86.3, 78.4, 77.2, 76.1, 74.5, 64.9, 56.0, 43.8, 42.3, 37.7, 37.6, 36.3, 35.5, 34.9, 34.4, 32.4, 26.2, 25.8, 25.6, 21.5, 18.4, 18.0, 17.9, 17.6, 17.1, 16.2, 15.1, 14.1, 13.9, 13.8, 10.6, 9.4, -3.3, -3.7, -4.4, -4.6, -4.91, -4.92; high resolution mass spectrum (ES^+) m/z 959.6638 $[(M+Na)^+$; calcd for $C_{52}H_{100}O_8Si_3Na$: 959.6624].



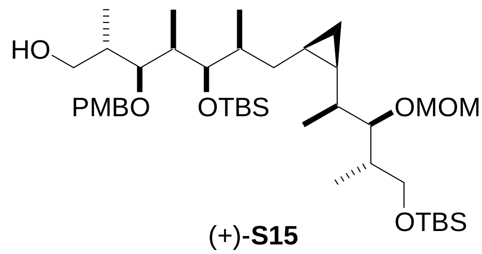
(+)-**S14**

(+)-**S14**: Employing the same procedure in the literature starting from (-)-**S13**.[2] $[\alpha]_D^{23}$ +10.8 (*c* 0.9, $CHCl_3$); IR 3359, 2957, 1730, 1381, 1037 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 6.59(ddd, *J* = 16.7, 10.7, 10.7 Hz, 1H), 6.01 (app t, *J* = 11.1 Hz, 1H), 5.37 (app t, *J* = 8.9 Hz, 2H), 5.24 (app t, *J* = 10.0 Hz, 1H), 5.20 (d, *J* = 16.7 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 4.84 (app t, *J* = 8.9 Hz, 1H), 4.70 (app t, *J* = 6.0 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.57 (d, *J* = 6.7 Hz, 1H), 4.50 (t, *J* = 9.7 Hz, 1H), 4.47 (br s, 2H), 3.66 (app t, *J* = 2.2 Hz, 1H), 3.44 (app t, *J* = 4.5 Hz, 1H), 3.34 (s, 3H), 3.28 (d, *J* = 8.6 Hz, 1H), 3.00-2.95 (m, 1H), 2.72-2.60 (m, 2H), 1.90-1.68 (m, 5H), 1.45-1.40 (m, 1H), 1.26-1.24 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.16-1.10 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 9H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.88 (s, 9H), 0.88 (d, *J* = 6.7 Hz, 3H), 0.87 (s, 9H), 0.84-0.74 (m, 2H), 0.56-0.52 (m, 1H), 0.08 (s, 6H), 0.07 (s, 3H), 0.06 (s, 6H), 0.04 (s, 3H), -0.25 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 173.4, 156.8, 133.8, 133.7, 132.8, 132.1, 129.7, 117.7, 97.9, 86.3, 78.7, 77.2, 76.4, 74.5, 64.9, 56.0, 43.8, 42.3, 38.3, 37.6, 35.5, 35.0, 34.5, 34.4, 31.8, 30.2, 26.2, 25.8, 25.6, 21.5, 18.5, 18.0, 17.9, 17.6, 17.5, 16.2, 14.9, 14.3, 13.9, 10.5, 10.2, -3.4, -3.8, -4.4, -4.6, -4.90, -4.91; high resolution mass spectrum (ES^+) m/z 1002.6672 [$(M+Na)^+$; calcd for $C_{53}H_{101}NO_9Si_3Na$: 1002.6682].



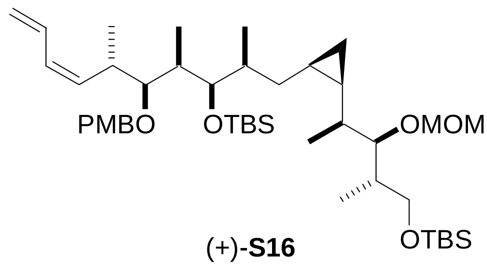
(+)-**1**

(+)-**1**: Employing the same procedure in the literature starting from (+)-**S14**.[2] $[\alpha]_D^{23}$ +3.7 (*c* 0.3, CH_3CN); IR 3422, 2969, 1712, 1386, 1040 cm^{-1}; ^{1}HNMR (500 MHz, CD_3CN) δ 6.66 (ddd, *J* = 16.7, 10.7, 10.7 Hz, 1H), 6.01 (app t, *J* = 11.1 Hz, 1H), 5.45-5.36 (m, 3H), 5.20 (d, *J* = 17.5 Hz, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 5.07 (br s, 2H), 4.70 (app t, *J* = 6.0 Hz, 1H), 4.63-4.58 (m, 1H), 4.48 (app t, *J* = 10.0 Hz, 1H), 3.65 (dd, *J* = 4.1, 8.2 Hz, 1H), 3.31 (br s, 1H), 3.23 (m, 1H), 3.08-3.02 (m, 1H), 2.95 (br s, 1H), 2.77-2.71 (m, 1H), 2.60-2.55 (m, 1H), 2.50 (br s, 1H), 2.10 (br s, 1H), 1.93-1.87 (m, 2H), 1.79-1.63 (m, 4H), 1.44-1.38 (m, 1H), 1.21 (d, *J* = 7.4 Hz, 3H), 1.07-1.02 (m, 1H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.83-0.80 (m, 1H), 0.76-0.67 (m, 2H), 0.57-0.53 (m, 1H), -0.25 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 173.7, 157.2, 134.0, 133.7, 132.9, 132.3, 129.3, 117.8, 78.1, 77.9, 77.1, 74.2, 72.1, 63.1, 43.0, 41.3, 37.3, 36.2, 35.7, 35.5, 35.2, 34.0, 31.4, 20.3, 17.6, 17.2, 14.7, 14.4, 13.3, 13.2, 12.0, 10.4, 8.4; high resolution mass spectrum (ES^+) m/z 616.3844 [$(M+Na)^+$; calcd for $C_{33}H_{55}NO_8Na$: 616.3826].



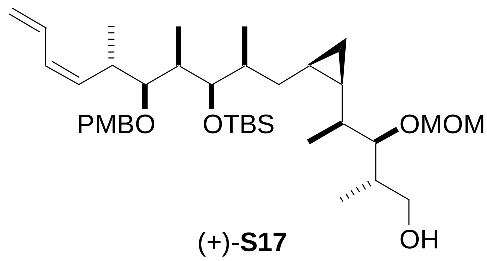
(+)-**S15**

(+)-**S15**: Employing the same procedure for converting (+)-**16** to (-)-**S10**, (+)-**S15** can be obtained from (+)-**17**: $[\alpha]_D^{23}$ +11.6 (*c* 1.0, $CHCl_3$); IR 3457, 2957, 1514, 1464, 1251, 1035 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.75 (d, *J* = 6.1 Hz, 1H), 4.71 (d, *J* = 6.1 Hz, 1H), 4.56 (d, *J* = 10.4 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.69 (m, 3H), 3.59 (m, 2H), 3.39 (s, 3H), 3.37 (m, 2H), 2.78 (br s, 1H), 1.98-1.85 (m, 4H), 1.74 (m, 1H), 1.20 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.93 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.88 (s, 9H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.87 (m, 1H), 0.71-0.68 (m, 3H), 0.06 (s, 6H), 0.04 (s, 6H), -0.18 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.3, 130.4, 129.2, 113.8, 98.8, 86.2, 83.8, 75.8, 74.9, 65.8, 65.1, 56.0, 55.2, 40.1, 38.8, 38.5, 37.8, 35.4, 32.9, 26.2, 25.9, 20.1, 18.5, 18.3, 16.0, 15.6, 14.7, 14.4, 13.2, 11.8, 11.6, -3.2, -3.6, -5.45, -5.5; high resolution mass spectrum (ES^+) m/z 761.5148 [$(M+Na)^+$; calcd for $C_{41}H_{78}O_7Si_2Na$: 761.5184].



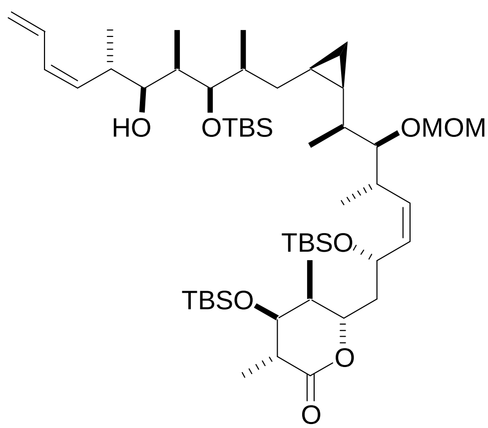
(+)-**S16**

(+)-**S16**: Employing the same procedure for converting (+)-**S10** to (+)-**28**, (+)-**S16** can be obtained from (+)-**S15**: $[\alpha]_D^{23}$ +33.5 (*c* 1.0, $CHCl_3$); IR 2954, 1608, 1462, 1250, 1038 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.60 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 5.99 (app t, *J* = 11.0 Hz, 1H), 5.55 (app t, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 4.74 (d, *J* = 6.3 Hz, 1H), 4.69 (d, *J* = 6.3 Hz, 1H), 4.53 (d, *J* = 10.6 Hz, 1H), 4.46 (d, *J* = 10.6 Hz, 1H), 3.80 (s, 3H), 3.72 (dd, *J* = 2.8, 9.6 Hz, 1H), 3.58 (m, 2H), 3.40 (s, 3H), 3.34 (d, *J* = 9.5 Hz, 1H), 3.23 (t, *J* = 4.5 Hz, 1H), 2.97 (m, 1H), 1.94 (m, 1H), 1.76 (m, 3H), 1.17 (m, 1H), 1.08 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 7.1 Hz, 3H), 0.94 (s, 9H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.83-0.76 (m, 1H), 0.70-0.60 (m, 3H), 0.08 (s, 6H), 0.04 (s, 6H), -0.23 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 158.9, 134.8, 132.4, 131.3, 129.0, 128.9, 117.1, 113.5, 98.8, 84.5, 83.9, 75.7, 74.6, 65.2, 56.0, 55.2, 40.1, 39.6, 38.5, 35.6, 35.4, 32.7, 26.2, 25.9, 19.8, 18.7, 18.5, 18.3, 16.2, 15.3, 14.4, 13.2, 11.9, 11.0, -3.3, -3.6, -5.44, -5.46; high resolution mass spectrum (ES^+) m/z 783.5413 [$(M+Na)^+$; calcd for $C_{44}H_{80}O_6Si_2Na$: 783.5391].



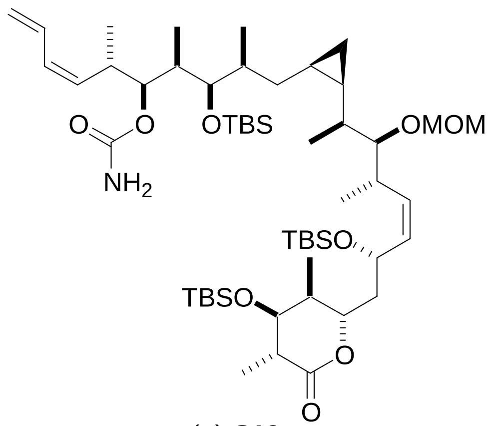
(+)-**S17**

(+)-**S17**: Employing the same procedure for converting (+)-**28** to (-)-**S12**, (+)-**S17** can be obtained from (+)-**S16**: $[\alpha]_D^{23}$ +17.4 (*c* 1.0, $CHCl_3$); IR 3495, 2958, 1462, 1250, 1033 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.60 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 6.00 (app t, *J* = 11.0 Hz, 1H), 5.55 (app t, *J* = 10.4 Hz, 1H), 5.16 (dd, *J* = 1.6, 16.7 Hz, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 4.85 (d, *J* = 6.3 Hz, 1H), 4.69 (d, *J* = 6.3 Hz, 1H), 4.54 (d, *J* = 10.6 Hz, 1H), 4.45 (d, *J* = 10.6 Hz, 1H), 3.81 (m, 1H), 3.80 (s, 3H), 3.58 (app t, *J* = 4.0 Hz, 1H), 3.47 (m, 1H), 3.44 (s, 3H), 3.22 (dd, *J* = 4.2, 6.4 Hz, 1H), 3.01-2.95 (m, 2H), 1.97 (m, 1H), 1.77 (m, 3H), 1.20 (m, 1H), 1.06 (d, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.94 (s, 9H), 0.88 (d, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 7.1 Hz, 3H), 0.87 (m, 1H), 0.75-0.60 (m, 4H), 0.07 (s, 3H), 0.03 (s, 3H), -0.19 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 158.9, 134.8, 132.4, 131.2, 129.0, 128.9, 117.2, 113.8, 99.3, 85.8, 84.6, 75.6, 74.7, 65.3, 56.2, 55.2, 40.0, 39.8, 37.6, 35.7, 35.5, 32.7, 26.1, 19.6, 18.7, 18.5, 16.3, 15.3, 14.7, 13.2, 12.2, 11.0, -3.4, -3.6; high resolution mass spectrum (ES^+) m/z 669.4533 [$(M+Na)^+$; calcd for $C_{38}H_{66}O_6SiNa$: 669.4526].



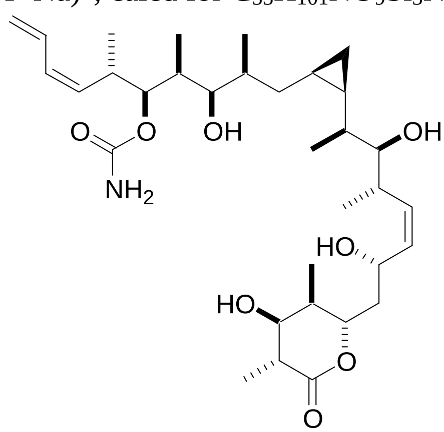
(+)-**S18**

(+)-**S18**: Employing the same procedure for converting (-)-**S12** to (+)-**31**, (+)-**S18** can be obtained from (-)-**30**: $[\alpha]_D^{23}$ +23.5 (*c* 0.8, $CHCl_3$); IR 3479, 2954, 1732, 1462, 1253, 1091 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 6.66(ddd, *J* = 16.8, 10.7, 10.7 Hz, 1H), 6.12 (app t, *J* = 10.8 Hz, 1H), 5.36-5.17 (m, 4H), 5.13 (d, *J* = 9.7 Hz, 1H), 4.83 (app t, *J* = 9.3 Hz, 1H), 4.75 (d, *J* = 6.7 Hz, 1H), 4.52 (d, *J* = 6.7 Hz, 1H), 4.49 (app t, *J* = 10.8 Hz, 1H), 3.66 (m, 2H), 3.34-3.29 (m, 2H), 3.32 (s, 3H), 2.78 (m, 1H), 2.63 (m, 2H), 2.21 (s, 1H), 1.86-1.60 (m, 7H), 1.24 (d, *J* = 7.1 Hz, 3H), 1.23-1.22 (m, 1H), 0.98 (d, *J* = 7.1 Hz, 6H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 7.1 Hz, 6H), 0.91 (s, 9H), 0.88 (s, 9H), 0.87 (s, 9H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.79-0.65 (m, 3H), 0.07-0.02 (m, 18H), -0.23 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 173.4, 135.5, 133.5, 133.1, 132.4, 130.6, 117.8, 97.9, 85.4, 78.9, 77.2, 75.7, 74.5, 64.9, 56.0, 44.8, 42.3, 37.8, 37.7, 36.5, 35.5, 35.4, 34.4, 33.7, 26.2, 25.8, 25.6, 20.4, 18.5, 18.3, 18.2, 17.7, 16.9, 16.2, 16.1, 13.9, 13.6, 13.1, 11.7, 9.5, -3.1, -3.7, -4.4, -4.6, -4.90, -4.94; high resolution mass spectrum (ES^+) m/z 959.6592 [$(M+Na)^+$; calcd for $C_{52}H_{100}O_8Si_3Na$: 959.6624].



(+)-**S19**

(+)-**S19**: Employing the same procedure for converting (-)-**S13** to (+)-**S14**, (+)-**S19** can be obtained from (+)-**S18:** $[\alpha]_D^{23}$ +34.3 (*c* 1.0, $CHCl_3$); IR 3359, 2958, 1728, 1377, 1253, 1037 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$) δ 6.60 (ddd, *J* = 16.8, 10.6, 10.6 Hz, 1H), 6.01 (app t, *J* = 10.8 Hz, 1H), 5.41-5.35 (m, 2H), 5.22-5.17 (m, 2H), 5.12 (d, *J* = 9.7 Hz, 1H), 4.84 (app t, *J* = 8.9 Hz, 1H), 4.71 (app t, *J* = 5.6 Hz, 1H), 4.68 (d, *J* = 6.3 Hz, 1H), 4.64 (s, 2H), 4.58 (d, *J* = 6.3 Hz, 1H), 4.50 (app t, *J* = 10.4 Hz, 1H), 3.66 (s, 1H), 3.49 (app t, *J* = 4.8 Hz, 1H), 3.33 (s, 3H), 3.28 (d, *J* = 8.6 Hz, 1H), 3.00-2.95 (m, 1H), 2.63 (m, 2H), 1.89-1.69 (m, 6H), 1.25 (d, *J* = 7.4 Hz, 3H), 1.18 (m, 1H), 0.99 (d, *J* = 7.1 Hz, 6H), 0.97 (d, *J* = 6.7 Hz, 6H), 0.92 (s, 9H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.77-0.70 (m, 2H), 0.60 (m, 2H), 0.08-0.05 (m, 18H), -0.23 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 173.4, 156.9, 133.8, 133.7, 132.8, 132.2, 129.7, 117.6, 98.0, 85.9, 78.7, 77.2, 76.0, 74.5, 64.9, 56.0, 43.8, 42.2, 39.3, 37.9, 35.8, 35.4, 34.5, 34.3, 32.8, 26.1, 25.8, 25.6, 19.9, 18.5, 18.0, 17.8, 17.6, 17.5, 16.2, 15.9, 14.7, 13.9, 13.4, 12.1, 10.4, -3.5, -3.8, -4.4, -4.6, -4.91, -4.93; high resolution mass spectrum (ES^+) m/z 1002.6634 $[(M+Na)^+$; calcd for $C_{53}H_{101}NO_9Si_3Na$: 1002.6682].



(+)-**2**

(+)-**2**: Employing the same procedure for converting (+)-**S14** to (+)-**1**, (+)-**2** can be obtained from (+)-**S19**: $[\alpha]_D^{23}$ +50.3 (*c* 0.5, CH_3CN); IR 3422, 2969, 1712, 1386, 1040 cm^{-1}; ^{1}HNMR (500 MHz, CD_3CN) δ 6.66 (ddd, *J* = 16.7, 10.7, 10.7 Hz, 1H), 6.01 (app t, *J* = 10.8 Hz, 1H), 5.46 (dd, *J* = 8.2, 10.4 Hz, 1H), 5.40 (app t, *J* = 10.8 Hz, 1H), 5.29 (app t, *J* = 10.4 Hz, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 5.08 (br, s, 2H), 4.69 (app t, *J* = 5.9 Hz, 1H), 4.60 (m, 1H), 4.47 (app t, *J* = 10.1 Hz, 1H), 3.65 (m, 1H), 3.33 (d, *J* = 4.5 Hz, 1H), 3.26 (m, 2H), 3.05 (m, 2H), 2.63-2.47 (m, 3H), 2.16 (app t, *J* = 6.3 Hz, 1H), 1.95-1.65 (m, 6H), 1.21 (d, *J* = 7.4 Hz, 3H), 1.19 (m, 1H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 7.1 Hz, 3H), 0.87 (m, 1H), 0.65 (m, 3H), -0.25 (m, 1H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 173.7, 157.2, 134.6, 133.9, 133.3, 132.4, 129.3, 117.2, 77.9, 77.2 (2C), 74.6, 72.1, 63.4, 43.0, 41.3, 37.3, 36.6, 36.4, 35.2, 34.6, 34.1, 32.0, 19.7, 17.1, 17.0, 14.7, 14.6, 14.3, 12.0, 11.8, 11.0, 8.5; high resolution mass spectrum (ES^+) m/z 616.3831 [$(M+Na)^+$; calcd for $C_{33}H_{55}NO_8Na$: 616.3826].