A mercury-catalyzed transetherification cyclization leading to fused cyclic polyethers

Derek S. Tan and Stuart L. Schreiber

Howard Hughes Medical Institute, Department of Chemistry and Chemical Biology,
Institute of Chemistry and Cell Biology, Harvard University, 12 Oxford St., Cambridge, MA 02138, USA

Supplementary Material

I. General Experimental Methods S1
II. Synthesis of Cyclization Substrates S2
III. Cyclization Reactions S13
IV. References S18

I. General Experimental Methods

Sources. Reagents were obtained from Aldrich Chemical (Milwaukee, WI) or Fluka (Milwaukee, WI) and used without further purification. Solvents were obtained from Fisher Scientific (Pittsburgh, PA), degassed with Ar, and purified on a solvent drying system as described in Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518-1520. Tetrahydrofuran (THF), diethyl ether (Et₂O), acetonitrile (CH₃CN), and methylene chloride (CH₂Cl₂) were passed over two alumina columns. Hexane, benzene (PhH) and toluene (tol) were passed over one alumina column and one supported copper redox catalyst (Q5 reactant) column. Dimethylformamide (DMF) was passed over two activated molecular sieve columns.

Reaction Methods. Reactions were performed in oven- or flame-dried glassware under positive N₂ or Ar pressure. Flash chromatography was performed on E. Merck 60 230-400 mesh silica gel. TLC was performed on 0.25 mm E. Merck silica gel 60 F₂₅₄ plates and visualized by UV (254 nm) and cerium ammonium molybdenate (CAM). IR spectra were recorded on a Nicolet 5PC FT-IR Spectrometer with peaks reported in cm⁻¹. NMR spectra were recorded on Varian 600 and 500 MHz Unity Inova and 400 MHz Mercury instruments. Chemical shifts are expressed in ppm relative to TMS (0.00 ppm) or residual solvent signals (CDCl₃ 7.26 ppm/77.0 ppm). Peak assignments were made based on two-dimensional gradient COSY, TOCSY, NOESY, HMQC, HSQC, and HMBC experiments. Coupling constant determination was assisted by application of “resolv” processing parameters when necessary. Mass spectra were obtained on JEOL AX-505H or SX-102A mass spectrometers by electron impact ionization (EI), chemical ionization (CI) with ammonia (NH₃), or fast atom bombardment ionization (FAB) with glycerol or 3-nitrobenzyl alcohol/sodium iodide (NBA/NaI) matrices. Time-of-flight electrospray ionization (TOF-ESI) data were obtained on a Micromass LCT mass spectrometer.
**Structure Notation.** Atom numbers shown in structures below refer only to NMR peak assignments and not to CAS or trivial nomenclature.

## II. Synthesis of Cyclization Substrates

![Structure Image](image)

### 6-O-Triisopropylsilyl-D-glucal, 1

In a 250 mL round bottom flask, D-glucal (4.38 g, 30 mmol, 1.0 equiv) was dissolved in 75 mL DMF. Imidazole (5.62 g, 82.5 mmol, 2.75 equiv) was added, followed by triisopropyl chloride (7.06 mL, 33 mmol, 1.1 equiv), and the reaction was stirred at rt. After 3 h, the reaction was poured into 150 mL H₂O and extracted 5 × 90 mL Et₂O. The combined organic extracts were washed 5 × 75 mL H₂O, 1 × 75 mL brine, dried (MgSO₄), filtered, and evaporated to yield 11.27 g of the crude product as a clear liquid. Purification by silica flash chromatography (2:1 hexane/EtOAc then 1:1 hexane/EtOAc) yielded 6-O-triisopropylsilyl-D-glucal as a clear liquid (7.99 g, 88.1%).

TLC: \( R_f \) 0.17 (2:1 hexane/EtOAc); \( R_f \) 0.32 (1:1 hexane/EtOAc); \( R_f \) 0.63 (EtOAc). IR (film): 3355, 2942, 2866, 1652, 1646, 1457, 1234, 1108, 1054, 1031, 882. \(^1\)H-NMR (500 MHz, CDCl₃): \( \delta \) 6.31 (dd, 1H, \( J = 5.96, 1.19 \), C1-H), 4.74 (dd, 1H, \( J = 5.96, 2.11 \), C2-H), 4.29 (m, 1H, C3-H), 4.09 (dd, 1H, \( J = 10.92, 2.90 \), C6-H\(_a\)), 3.99 (dd, 1H, \( J = 10.52, 4.99 \), C6-H\(_b\)), 3.83 (m, 2H, C4-H, C5-H), 3.34 (d, 1H, \( J = 1.07 \), OH), 2.32 (d, 1H, \( J = 5.32 \), OH), 1.25-1.00 (m, 21H, iPr₃Si). FAB-MS (NBA/NaI) \( m/z \) (rel int): 325 ([M+Na]+, 100).

### 3,4-Di-O-benzyl-6-O-triisopropylsilyl-D-glucal, 6, 1

In a 250 mL round bottom flask, 6-O-triisopropylsilyl-D-glucal (7.99 g, 26.42 mmol, 1.0 equiv) was dissolved in 60 mL DMF and cooled to 0 °C under Ar. Benzyl bromide (6.91 mL, 58.11 mmol, 2.2 equiv) was added with stirring, followed by sodium hydride (60% suspension in mineral oil, 3.2 g, 79.24 mmol, 3.0 equiv). The reaction became homogeneous and was allowed to warm slowly to rt. After 2 h, the
reaction was poured into 120 mL cold H$_2$O and extracted 5 × 40 mL Et$_2$O. The combined organic extracts were washed 5 × 20 mL H$_2$O, 1 × 20 mL brine, dried (MgSO$_4$), filtered, and evaporated to yield 15.8 g of the crude product as a wet, white solid. Purification by silica flash chromatography (49:1 hexane/EtOAc) yielded 6 as a clear oil (9.6142 g, 75.3%). Repurification of mixed fractions yielded additional pure product (1.728 g, 13.5%; 88.8% overall).

TLC: \( R_f 0.31 \) (19:1 hexane/EtOAc); \( R_f 0.23 \) (24:1 hexane/EtOAc). IR (film): 2941, 2865, 1647, 1454, 1239, 1101, 1066, 882. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.25 (m, 10H, Ar-H), 6.39 (dd, 1H, $J = 6.14, 1.35$, C1-H), 4.86 (d, 1H, $J = 11.43$, C14-H$_a$), 4.83 (dd, 1H, $J = 6.16, 2.67$, C2-H), 4.76 (d, 1H, $J = 11.72$, C9-H$_a$), 4.58 (d, 1H, $J = 11.72$, C9-H$_b$), 4.20 (m, 1H, C3-H), 4.04 (dd, 1H, $J = 11.16, 3.58$, C6-H$_a$), 3.99 (dd, 1H, $J = 11.16, 2.40$, C6-H$_b$), 3.89-3.96 (m, 2H, C4-H, C5-H), $\delta$ 1.15-1.00 (m, 21H, iPr$_3$Si).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 144.767, 138.446, 138.431, 128.384, 128.369, 127.915, 127.763, 127.679, 127.588, 99.566, 78.101, 75.665, 74.011, 73.814, 70.619, 61.923, 17.975, 17.937, 11.973. FAB-MS (NBA/NaI) m/z (rel int): 505 ([M+H]$^+$, 100). HRMS (NBA/NaI) m/z calcd for C$_{29}$H$_{42}$NaO$_4$Si 505.2750; found 505.2753.

(1S,2R)-3,4-Di-O-benzyl-6-O-trisopropylsilyl-D-glucal-1,2-oxirane, 7. In a 250 mL round bottom flask, 3,4-di-O-benzyl-6-O-trisopropylsilyl-D-glucal, 6, (1.415 mg, 2.931 mmol, 1.0 equiv) was dissolved in 50 mL CH$_2$Cl$_2$ and cooled to 0 °C. Dimethyldioxirane$^4$ (0.038M in acetone, 31.4 mL, 1.19 mmol, 1.2 equiv) was added via syringe and the reaction was stirred at 0 °C for 90 min. The solvent was evaporated under a stream of dry N$_2$ to yield 7 as a clear oil (1.462 g, 100%) that was used immediately without further purification. The diastereomeric ratio was 94:6 as determined by integration of the C2-H NMR peaks ($\beta$-epoxide diastereomer: C1-H, $\delta$ 4.95; C2-H $\delta$ 3.32).

TLC: \( R_f 0.05 \) (19:1 hexane/EtOAc); \( R_f 0.37 \) (1:1 hexane/EtOAc). IR (film): 2941, 2865, 1456, 1164, 1102, 1013, 884. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.45-7.25 (m, 10H, Ar-H), 4.93 (app d, 1H, $J = 1.82$, C1-H), 4.84 (d, 1H, $J = 10.90$, C14-H$_a$), 4.81 (d, 1H, $J = 11.53$, C9-H$_a$), 4.75 (d, $J = 10.88$, C14-H$_b$), 4.71 (d, 1H, $J = 11.49$, C9-H$_b$), 4.02 (dd, 1H, $J = 11.34$, 2.79, C6-H$_a$), 3.97 (dd, 1H, $J = 8.12$, 0.92, C3-H), 3.90 (dd, 1H, $J = 11.32, 1.64$, C6-H$_b$), 3.69 (dd, 1H, $J = 10.03, 8.20$, C4-H), 3.56 (dt, 1H, $J = 9.97, 2.08$, C5-H), 3.07 (d, 1H, $J = 2.35$, C2-H), 1.20-1.05 (m, 21H, iPr$_3$Si). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 138.519, 137.564, 128.564, 128.342, 127.995,
127.972, 127.792, 127.639, 79.099, (77.469), (77.203), 74.702, 74.110, 72.481, 70.813, 61.766, 52.900, 18.015, 17.961, 12.025. CI-MS (NH$_3$) m/z (rel int): 516 ([M+NH$_4$]$^+$, 28). FAB-MS (NBA/NaI) m/z (rel int): 521 ([M+Na]$^+$, 100). HRMS (NBA/NaI) m/z calcd for C$_{29}$H$_{42}$NaO$_5$Si 521.2699; found 521.2692.

(1$S$)-1- Allyl-3,4-di-O-benzyl-1-deoxy-6-O-triisopropylsilyl-D-glucose, 8a and (1$R$)-1- Allyl-3,4-di-O-benzyl-1-deoxy-6-O-triisopropylsilyl-D-glucose, 8b. In a 100 mL round bottom flask, freshly prepared (1$S$,2$R$)-3,4-di-O-benzyl-6-O-triisopropylsilyl-D-glucal-1,2-oxirane, 7 (486.3 mg, 975.1 µmol, 1.0 equiv), was dissolved in 10 mL THF and cooled to 0 °C. Allyl magnesium chloride (2.0M in THF, 585 µl, 1.170 mmol, 1.2 equiv) was added dropwise via syringe with stirring. When the addition was complete, the reaction was allowed to warm slowly to rt. After 90 min, the reaction was poured into 10 mL satd NH$_4$Cl and extracted 5 $\times$ 10 mL Et$_2$O. The combined organic extracts were washed 3 $\times$ 10 mL H$_2$O, 1 $\times$ 10 mL brine, dried (MgSO$_4$), filtered, and evaporated to yield 532.7 mg of the crude product as a clear oil. The diastereomeric ratio was 93:7 as determined by integration of the C19-H$_a$ and C19-H$_b$ NMR peaks. Purification by silica flash chromatography (9:1 hexane/EtOAc) yielded 8a (428.4 mg, 80%) and 8b (21.2 mg, 4%) as clear oils.

8a: TLC: $R_f$ 0.70 (1:1 hexane/EtOAc); $R_f$ 0.50 (3:1 hexane/EtOAc); $R_f$ 0.12 (9:1 hexane/EtOAc). IR (film): 3455 br, 2942, 2866, 1455, 1383, 1148, 1099, 1044, 915, 883. $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.40-7.25 (m, 10H, Ar-H), 5.88 (ddt, 1H, $J$ = 17.19, 10.15, 7.04, C19-H), 5.08 (app dd, 1H, $J$ = 17.19, 1.75, C21-H$_Z$), 5.03 (app d, 1H, $J$ = 10.10, C21-H$_E$), 4.99 (d, 1H, $J$ = 11.50, C9-H$_a$), 4.84 (d, 1H, $J$ = 10.74, C14-H$_a$), 4.80 (d, 1H, $J$ = 10.76, C14-H$_b$), 4.73 (d, 1H, $J$ = 11.54, C9-H$_b$), 3.98 (d, 2H, $J$ = 2.27, C6-H$_2$), 3.75 (t, 1H, $J$ = 9.37, C4-H), 3.48 (t, 1H, $J$ = 8.95, C3-H), 3.31 (td, 1H, $J$ = 9.03, 2.55, C2-H), 3.25 (obs dt, 1H, $J$ = 9.31, 2.29, C5-H), 3.22 (obs m, 1H, C1-H), 2.53 (ddm, 1H, $J$ = 14.50, 6.67, C19-H$_b$), 2.22 (app quint, 1H, $J$ = 7.32, C19-H$_a$), 2.05 (d, 1H, $J$ = 2.52, C2-OH), 1.20-1.00 (m, 21H, iPr$_3$Si). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 138.643, 138.439, 128.711, 128.498, 127.989, 127.968, 127.778, 116.904, 86.680, 79.901, 78.540, 77.933, 77.202, 75.293, 74.762, 73.487, 73.487, 72.378, 36.390, 18.020, 17.975, 12.018. FAB-MS (NBA/NaI) m/z (rel int): 563 ([M+Na]$^+$, 100). HRMS (NBA/NaI) m/z calcd for C$_{32}$H$_{48}$NaO$_5$Si 563.3169; found 563.3187.
8b: TLC: \( R_f 0.46 \) (3:1 hexane/EtOAc); \( R_f 0.05 \) (9:1 hexane/EtOAc). IR (film): 3472 br, 2941, 2865, 1455, 1099, 1070, 883. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.40-7.28 (m, 10H, Ar-H), 5.82 (ddt, 1H, \( J = 17.07,10.20, 6.88 \), C20-H), 5.06 (dd, 1H, \( J = 17.00, 1.70 \), C21-H\(_Z\)), 5.04 (dd, 1H, \( J = 10.13, 1.81 \), C21-H\(_E\)), 4.74 (d, 1H, \( J = 11.44 \), C14-H\(_a\)), 4.67 (d, 1H, \( J = 11.50 \), C9-H\(_a\)), 4.66 (d, 1H, \( J = 11.41 \), C14-H\(_b\)), 4.56 (d, 1H, \( J = 11.50 \), C9-H\(_b\)), 3.97 (dd, 1H, \( J = 10.42, 4.74 \), C6-H\(_a\)), 3.89 (t, 1H, \( J = 6.49 \), C4-H), 3.86 (obs m, 1H, C6-H\(_b\)), 3.82 (m, 2H, C1-H, C2-H), 3.78 (m, 1H, C3-H), 3.69 (dt, 1H, \( J = 5.50, 5.63 \), C5-H), 2.35 (obs m, 1H, C19-H\(_a\)), 2.34 (obs m, 1H, C19-H\(_b\)), 1.15-1.00 (m, 21H, iPr\(_3\)Si). FAB-MS (NBA/NaI) \( m/z \) (rel int): 563 ([M+Na]\(^+\), 100). HRMS (NBA/NaI) \( m/z \) calcd for C\(_{32}\)H\(_{48}\)NaO\(_5\)Si 563.3169; found 563.3185.

(1S)-1- Allyl-3,4-di-O-benzyl-1-deoxy-2-keto-6-O-triisopropylsilyl-D-glucose. In a 5 mL conical flask, Dess-Martin periodinane\(^{5,6} \) (16.0 mg, 37.0 \( \mu \)mol, 2.0 equiv) was suspended in 100 \( \mu \)L CH\(_2\)Cl\(_2\). (1S)-1-Allyl-3,4-di-O-benzyl-1-deoxy-6-O-triisopropylsilyl-D-glucose, 8a (10.0 mg, 18.5 \( \mu \)mol, 1.0 equiv), was dissolved in 100 \( \mu \)L CH\(_2\)Cl\(_2\) and added to the stirring mixture. After 4 h, the CH\(_2\)Cl\(_2\) was evaporated and the residue taken up in 5 mL Et\(_2\)O. 2 mL of 1N NaOH was added to the mixture and stirred for 10 min. The layers were separated and the Et\(_2\)O layer washed \( 1 \times 2 \) mL 1N NaOH, \( 1 \times 2 \) mL H\(_2\)O, dried (MgSO\(_4\)), filtered, and evaporated to yield 6.8 mg of the crude product. Purification by silica flash chromatography (19:1 hexane/EtOAc) yielded (1S)-1-allyl-3,4-di-O-benzyl-1-deoxy-2-keto-6-O-triisopropylsilyl-D-glucose (1.6 mg, 16%) as a clear oil.

TLC: \( R_f 0.61 \) (3:1 hexane/EtOAc); \( R_f 0.27 \) (9:1 hexane/EtOAc). IR (film): 2941, 2865, 1734, 1456, 1104, 1067, 1028, 883. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.42 (app d, 2H, \( J = 7.08 \), C11-H, C11'-H), 7.36-7.28 (m, 8H, Ar-H), 5.85 (ddt, 1H, \( J = 17.21, 10.19, 6.96 \), C20-H), 5.14 (app dd, 1H, \( J = 17.09, 1.47 \), C21-H\(_Z\)), 5.06 (app d, 1H, \( J = 10.25 \), C21-H\(_E\)), 5.00 (d, 1H, \( J = 11.47 \), C9-H\(_b\)), 4.89 (d, 1H, \( J = 10.50 \), C14-H\(_b\)), 4.71 (d, 1H, \( J = 10.74 \), C14-H\(_a\)), 4.62 (d, 1H, \( J = 11.23 \), C9-H\(_a\)), 4.19 (d, 1H, \( J = 9.28 \), C3-H), 4.01 (m, 3H, C4-H, C6-H\(_2\)), 3.79 (dd, 1H, \( J = 8.18, 4.27 \), C1-H), 3.60 (app dt, 1H, \( J = 9.44, 2.62 \), C5-H), 2.59 (app ddd, 1H, \( J = 14.95, 7.14, 4.58 \), C19-H\(_a\)), 2.34 (ddd, 1H, \( J = 14.89, 8.06, 6.84 \), C19-H\(_b\)), 1.15-0.91 (m, 21H, iPr\(_3\)Si). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 202.098 (C2), 137.930 (C15), 137.429 (C10), 133.690 (C20), 128.306 (Ar), 128.290 (Ar), 128.017 (Ar), 127.979 (Ar), 127.775 (Ar), 127.706 (Ar), 117.316 (C21), 86.639 (C3), 80.367 (C1), 80.018 (C5), 79.685 (C4), 75.157 (C14), 73.815 (C9), 62.317 (C6), 33.089 (C19), 20.028 (C19-H).
18.095 (C8'), 18.073 (C8), 12.074 (C7). TOF-ESI-MS m/z (rel int): 539 ([M+H]+, 46); 561 ([M+Na]+, 60); 577 ([M+K]+, 100).

(1S)-1-Allyl-3,4-di-O-benzyl-1-deoxy-6-O-triisopropylsilyl-D-mannose, 8c. In a 5 mL conical flask, (1S)-1-allyl-3,4-di-O-benzyl-1-deoxy-2-keto-6-O-triisopropylsilyl-D-glucose (2.0 mg, 3.71 µmol, 1.0 equiv) is dissolved in 100 µL THF and cooled to 0 °C. L-Selectride (1.0M in THF, 11.1 µL, 11.1 µmol, 3.0 equiv) was added via syringe and the solution allowed to warm slowly to rt. After 1 h, the reaction mixture was poured into 5 mL satd NH₄Cl and the reaction flask rinsed several more times with 1 mL CH₂Cl₂. The layers were separated and the aqueous layer extracted 2 x 2 mL CH₂Cl₂. The combined organic extracts were dried (MgSO₄), filtered, and evaporated to yield the crude product as a cloudy oil. Purification by silica flash chromatography (9:1 hexane/EtOAc) yielded 8c (1.7 mg, 85%) as a clear oil.

TLC: Rf 0.55 (3:1 hexane/EtOAc); Rf 0.09 (9:1 hexane/EtOAc). IR (film): 3444 br, 2939, 2865, 1456, 1099, 1016, 916, 882. ¹H-NMR (500 MHz, CDCl₃): δ 7.39 (app d, 2H, J = 7.74, C11-H, C11'-H), 7.36-7.28 (m, 8H, Ar-H), 5.84 (dddd, 1H, J = 17.25, 10.16, 7.58, 6.61, C20-H), 5.13 (app dd, 1H, J = 17.09, 1.29, C21-H₂), 5.05 (app d, 1H, J = 10.32, C21-H₃), 4.89 (d, 1H, J = 10.64, C14-H₃), 4.77 (d, 1H, J = 11.61, C9-H₃), 4.69 (obs d, 1H, J = 10.44, C14-H₄), 4.68 (obs d, 1H, J = 12.48, C9-H₄), 3.96-3.90 (m, 3H, C2-H, C6-H₂), 3.89 (obs t, 1H, J = 9.67, C4-H), 3.58 (dd, 1H, J = 9.35, 3.22, C3-H), 3.34 (app t, 1H, J = 6.93, C1-H), 3.22 (ddd, 1H, J = 9.67, 3.22, 1.93, C5-H), 2.49 (app quint, 1H, J = 7.09, C19-H₂), 2.36 (app quint, 1H, J = 7.01, C19-H₃), 2.18 (d, 1H, J = 4.52, C2-OH), 1.15-1.00 (m, 21H, iPr₃Si). ¹³C-NMR (100 MHz, CDCl₃): δ 138.469 (C15), 137.901 (C10), 134.601 (C20), 128.416 (Ar), 128.321 (Ar), 128.001 (Ar), 127.790 (Ar), 127.615 (Ar), 117.103 (C21), 83.432 (C3), 80.278 (C5), 77.525 (C1), 75.295 (C14), 74.239 (C4), 71.580 (C9), 68.040 (C2), 62.817 (C6), 35.499 (C19), 18.095 (C8), 18.052 (C8'), 12.114 (C7). TOF-ESI-MS m/z (rel int): 541 ([M+H]+, 100).
(1S)-3,4-Di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropysilyl-D-glucose, 9a. In a 50 mL round bottom flask, (1S)-1-allyl-3,4-di-O-benzyl-1-deoxy-6-O-triisopropysilyl-D-glucose, 8a (425 mg, 785.8 µmol, 1.0 equiv), was dissolved in 10 mL CH₂Cl₂ and cooled to –78 °C. Ozone was bubbled through the reaction with stirring until the solution was a light blue color. Nitrogen was then bubbled through the reaction until the solution was clear. Triphenylphosphine (420 mg, 1.60 mmol, 2.0 equiv) was dissolved in 4 mL CH₂Cl₂ and added via syringe at –78 °C and the reaction was allowed to warm slowly to rt. After 5 h, the solvent was evaporated and the crude product was purified by silica flash chromatography (3:1 hexane/EtOAc) to yield 9a as a clear oil (355.3 mg, 83.3%).

TLC: Rf 0.19 (3:1 hexane/EtOAc). IR (film): 3455 br, 2941, 2865, 1727, 1456, 1151, 1095, 883. ¹H-NMR (400 MHz, CDCl₃): δ 9.77 (dd, 1H, J = 2.64, 1.84, C19-H), 7.43-7.30 (m, 10H, Ar-H), 5.02 (d, 1H, J = 11.53, C9-Ha), 4.86 (d, 1H, J = 10.77, C14-Ha), 4.82 (d, 1H, J = 10.78, C14-Hb), 4.73 (d, 1H, J = 11.54, C9-Hb), 3.99 (obs dd, 1H, J = 11.48, 2.73, C6-Ha), 3.96 (obs dd, 1H, J = 11.48, 1.91, C6-Hb), 3.79 (obs t, 1H, J = 9.46, C4-H), 3.76 (obs ddd, 1H, J = 9.38, 8.39, 3.78, C1-H), 3.52 (t, 1H, J = 9.05, C3-H), 3.34 (obs app dt, 1H, J = 9.58, 2.30, C5-H), 3.32 (obs td, 1H, J = 9.18, 2.67, C2-H), 2.80 (ddd, 1H, J = 16.37, 3.73, 1.84, C19-Hb), 2.55 (ddd, 1H, J = 16.40, 8.35, 2.72, C19-Ha), 2.16 (d, 1H, J = 2.68, C2-OH), 1.20-1.00 (m, 21H, iPr₃Si). ¹³C-NMR (100 MHz, CDCl₃): δ 200.706, 138.435, 138.236, 128.783, 128.533, 128.125, 127.964, 127.866, 86.311, 80.167, 77.719, 77.202, 75.347, 74.854, 74.363, 73.558, 62.152, 46.252, 17.970, 17.907, 11.972. FAB-MS (NBA/NaI) m/z (rel int): 565 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcd for C₃₁H₄₀NaO₆Si 565.2961; found 565.2990.
(1R)-3,4-Di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropylsilyl-D-glucose, 9b. In a 50 mL round bottom flask, (1R)-1-allyl-3,4-di-O-benzyl-1-deoxy-6-O-triisopropylsilyl-D-glucose, 8b (18 mg, 33.3 µmol, 1.0 equiv), was dissolved in 4 mL CH₂Cl₂ and cooled to –78 °C. Ozone was bubbled through the reaction with stirring until the solution was a light blue color. Nitrogen was then bubbled through the reaction until the solution was clear. Triphenylphosphine (17.5 mg, 66.6 µmol, 2.0 equiv) was dissolved in 1 mL CH₂Cl₂ and added via syringe at –78 °C and the reaction was allowed to warm slowly to rt. After 5 h, the solvent was evaporated and the crude product was purified by silica flash chromatography (3:1 hexane/EtOAc) to yield 9b as a clear oil (15.9 mg, 88.0%).

TLC: Rf 0.13 (3:1 hexane/EtOAc). IR (film): 3438 br, 2942, 2865, 1726, 1462, 1454, 1106, 1066, 883. 1H-NMR (500 MHz, CDCl₃): δ 9.78 (app t, 1H, J = 2.12, C₂₀-H), 7.38-7.28 (m, 10H, Ar-H), 4.66 (obs d, 1H, J = 11.35, C₉-Ha), 4.65 (obs d, 1H, J = 11.99, C₁₄-H₂), 4.58 (d, 1H, J = 11.97, C₁₄-H₂), 4.42 (d, 1H, J = 11.37, C₉-H₂), 4.21 (td, 1H, J = 8.31, 4.43, C₁-H), 4.15 (app t, 1H, J = 4.04, C₃-H), 3.97 (app dd, 1H, J = 6.45, 3.44, C₂-H), 3.86 (m, 2H, C₅-H, C₆-H), 3.80 (app t, 1H, J = 4.04, C₃-H), 3.72 (app td, 1H, J = 6.45, 3.44, C₂-H), 2.75 (ddd, 1H, J = 16.36, 4.43, 1.73, C₁₉-H), 2.64 (ddd, 1H, J = 16.35, 8.53, 2.57, C₁₉-H₂), 2.27 (d, 1H, J = 9.19, C₂-OH), 1.15-0.97 (m, 21H, iPr₃Si). FAB-MS (NBA/NaI) m/z (rel int): 565 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcd for C₃₁H₄₆NaO₆Si 565.2961; found 565.2957.

TLC: Rf 0.13 (3:1 hexane/EtOAc). IR (film): 3438 br, 2942, 2865, 1726, 1462, 1454, 1106, 1066, 883. 1H-NMR (500 MHz, CDCl₃): δ 9.78 (app t, 1H, J = 2.12, C₂₀-H), 7.38-7.28 (m, 10H, Ar-H), 4.66 (obs d, 1H, J = 11.35, C₉-Ha), 4.65 (obs d, 1H, J = 11.99, C₁₄-H₂), 4.58 (d, 1H, J = 11.97, C₁₄-H₂), 4.42 (d, 1H, J = 11.37, C₉-H₂), 4.21 (td, 1H, J = 8.31, 4.43, C₁-H), 4.15 (app t, 1H, J = 4.04, C₃-H), 3.97 (app dd, 1H, J = 6.45, 3.44, C₂-H), 3.86 (m, 2H, C₅-H, C₆-H), 3.80 (app t, 1H, J = 4.04, C₃-H), 3.72 (app td, 1H, J = 6.45, 3.44, C₂-H), 2.75 (ddd, 1H, J = 16.36, 4.43, 1.73, C₁₉-H), 2.64 (ddd, 1H, J = 16.35, 8.53, 2.57, C₁₉-H₂), 2.27 (d, 1H, J = 9.19, C₂-OH), 1.15-0.97 (m, 21H, iPr₃Si). FAB-MS (NBA/NaI) m/z (rel int): 565 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcd for C₃₁H₄₆NaO₆Si 565.2961; found 565.2957.

(1S)-3,4-Di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropylsilyl-D-mannose (S)-hemiacetal, 9cS and (1S)-3,4-Di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropylsilyl-D-mannose (R)-hemiacetal, 9cR. In a 25 mL round bottom flask, (1S)-1-allyl-3,4-di-O-benzyl-1-deoxy-6-O-triisopropylsilyl-D-mannose, 8c (8.8 mg, 16.3 µmol, 1.0 equiv), was dissolved in 4 mL CH₂Cl₂ and cooled to –78 °C. Ozone was bubbled through the reaction with stirring until the solution was a light blue color. Oxygen was then bubbled through the reaction until the solution was clear. Triphenylphosphine (8.5 mg, 32.5 µmol, 2.0 equiv) was dissolved in 0.5 mL CH₂Cl₂ and added via syringe at –78 °C and the reaction was allowed to warm slowly to rt. After 39 h, the solvent was evaporated and the crude product was purified by silica flash chromatography (5:1 hexane/EtOAc) to yield 9c as a clear oil (6.0 mg, 68.0%). Stereochemistry at the hemiacetal carbon was tentatively assigned based on NOESY data. Initial NMR analysis indicated a 31:69 mixture of 9cS:9cR which equilibrated to a 75:25 mixture upon standing for 2 d in CDCl₃.
TLC: \( R_f \) 0.25 (3:1 hexane/EtOAc); \( R_f \) 0.06 (6:1 hexane/EtOAc). IR (film): 3489 br, 2958, 2923, 2853, 1457, 1109, 999, 883. 9cS: \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.40 (app d, 2H, \( J = 7.57 \), C11-H, C11’-H), 7.36-7.27 (m, 8H, Ar-H), 5.43 (dd, 1H, \( J = 12.94 \), 5.13, C20-H), 5.03 (d, 1H, \( J = 10.74 \), C14-H\(_2\)), 4.84 (d, 1H, \( J = 12.21 \), C9-H\(_b\)), 4.75 (obs d, 1H, \( J = 12.21 \), C9-H\(_a\)), 4.74 (obs d, 1H, \( J = 10.74 \), C14-H\(_b\)), 4.19-4.15 (m, 3H, C1-H, C2-H, C4-H), 4.08 (obs d, 1H, \( J = 10.86 \), C6-H\(_a\)), 3.9 (obs dd, 1H, \( J = 10.74 \), 2.20, C6-H\(_b\)), 3.76 (obs dd, 1H, \( J = 9.28 \), 3.42, C3-H), 3.28 (dt, 1H, \( J = 9.60 \), 2.14, C5-H), 2.15 (app d, 1H, \( J = 13.67 \), C19-H\(_a\)), 2.08 (ddd, 1H, \( J = 13.67 \), 5.37, 3.17, C19-H\(_b\)), 1.59 (s, 1H, C20-OH, H\(_2\)O), 1.16-0.94 (m, 21H, iPr\(_3\)Si).

13C-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 138.385 (C15), 138.043 (C11), 128.237 (Ar), 128.002 (Ar), 127.775 (Ar), 127.532 (Ar), 127.502 (Ar), 79.965 (C3), 79.025 (C2), 78.577 (C5), 76.211 (C1), 75.225 (C14), 73.163 (C4), 71.577 (C9), 61.642 (C6), 41.325 (C19), 18.141 (C8), 18.057 (C8’), 12.036 (C7).

9cR: \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.40 (app d, 2H, \( J = 7.24 \), C11-H, C11’-H), 7.36-7.27 (m, 8H, Ar-H), 5.76 (td, 1H, \( J = 5.14 \), 2.91, C20-H), 4.93 (d, 1H, \( J = 10.54 \), C14-H\(_b\)), 4.85 (d, 1H, \( J = 12.18 \), C9-H\(_a\)), 4.83 (d, 1H, \( J = 5.14 \), C9-H\(_b\)), 4.0 (obs d, 1H, \( J = 12.18 \), C14-H\(_b\)), 4.43 (dd, 1H, \( J = 3.87 \), 1.73, C2-H), 4.1 (obs dd, 1H, \( J = 4.36 \), 1.73, C1-H), 4.0 (obs t, 1H, \( J = 9.38 \), C4-H), 3.97 (obs dd, 1H, \( J = 11.19 \), 3.62, C6-H\(_a\)), 3.89 (obs dd, 1H, \( J = 11.28 \), 3.62, C6-H\(_b\)), 3.74 (obs dd, 1H, \( J = 9.22 \), 3.79, C3-H), 3.16 (ddd, 1H, \( J = 9.547 \), 3.46, 1.646, C5-H), 2.80 (d, 1H, \( J = 2.96 \), C20-OH), 2.36 (ddd, 1H, \( J = 14.24 \), 5.68, C19-H\(_1\)), 1.94 (dt, 1H, \( J = 14.16 \), 4.61, C19-H\(_2\)), 1.16-0.93 (m, 21H, iPr\(_3\)Si).

13C-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 138.536 (C15), 138.013 (C11), 128.237 (Ar), 128.002 (Ar), 127.775 (Ar), 127.532 (Ar), 127.502 (Ar), 99.335 (C20), 79.965 (C3), 79.025 (C2), 78.577 (C5), 76.211 (C1), 75.225 (C14), 73.163 (C4), 71.577 (C9), 62.644 (C6), 41.325 (C19), 18.141 (C8), 18.057 (C8’), 12.036 (C7).

TOF-ESI-MS \( m/z \) (rel int): 565 ([M+Na]\(^{+}\), 100).

(1S)-3,4-Di-O-benzyl-1-deoxy-1-(E-\( \gamma \)-methoxyallyl)-6-O-triisopropylsilyl-D-glucose, \( E \)-10a and (1S)-3,4-Di-O-benzyl-1-deoxy-1-(Z-\( \gamma \)-methoxyallyl)-6-O-triisopropylsilyl-D-glucose, \( Z \)-10a\(^\dagger\). In a 5 mL conical flask, methoxymethyltriphenylphosphonium chloride (38 mg, 110.5 \( \mu \)mol, 3.0 equiv) was suspended in 500 \( \mu \)L THF and cooled to 0 °C. Sodium hexamethyldisilazide (1.0M in THF, 92.1 \( \mu \)L, 92.1 \( \mu \)mol, 2.5 equiv) was added slowly via syringe and the bright orange mixture was stirred at 0 °C for 1 h. (1S)-3,4-Di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropylsilyl-D-glucose, 9a (20 mg, 36.85 \( \mu \)mol, 1.0 equiv) was dried azeotropically by evaporation of benzene three times, then dissolved in 200 \( \mu \)L THF and added to the phosphorane solution via syringe at 0 °C. The reaction was allowed to warm slowly to rt.
After 12 h, the mixture was diluted with 5 mL THF, poured into 5 mL satd NH₄Cl, and extracted 3×5 mL Et₂O. The combined organic extracts were washed 1×5 mL H₂O, 1×5 mL brine, dried (MgSO₄), filtered, and evaporated to yield 37.1 mg of the crude product as a translucent oil. The E/Z ratio was 71:29 as determined by integration of the C21-H NMR peaks.

Purification by silica flash chromatography (9:1 hexane/EtOAc) yielded 10a as clear oil that was a mixture of E and Z isomers (12.7 mg, 60.2%). The E/Z ratio was 72:28 as determined by integration of the C21-H NMR peaks.

**TLC:** Rf 0.14 (3:1 hexane/EtOAc). **E-10a:** ¹H-NMR (600 MHz, CDCl₃): δ 7.40-7.30 (m, 10H, Ar-H), 5.97 (d, 1H, J = 11.23, C9-Hₙ), 4.89 (d, 1H, J = 11.72, C9-Hₙ), 3.99 (d, 2H, J = 2.44, C6-H₂), 3.75 (t, 1H, J = 9.40, C4-H), 3.49 (s, 3H, C22-H₃), 3.48 (t, 1H, J = 9.03, C3-H), 3.33 (td, 1H, J = 9.28, 3.17, C2-H), 2.38 (obs m, 1H, C19-Hₙ), 1.18-1.00 (m, 21H, iPr₃Si). ¹³C-NMR (100 MHz, CDCl₃): δ 148.493 (C21), 138.513 (C10), 138.309 (C15), 128.613 (Ar), 127.877 (Ar), 127.680 (Ar), 127.564 (Ar), 127.401 (Ar), 127.321 (Ar), 127.877 (Ar), 127.680 (Ar), 127.564 (Ar), 127.401 (Ar), 127.321 (Ar), 127.043 (Ar), 126.744 (C20), 86.711 (C3), 79.848 (C5), 79.792 (C9), 74.734 (C14), 72.972 (C2), 62.372 (C6), 55.670 (C22), 30.173 (C19), 18.095 (C8), 18.044 (C8'), 12.107 (C7). FAB-MS (NBA/NaI) m/z (rel int): 593 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcd for C₃₃H₅ₐNO₂S₃ 593.3274; found 593.3270.

**Z-10a:** ¹H-NMR (600 MHz, CDCl₃): δ 7.40-7.30 (m, 10H, Ar-H), 5.97 (d, 1H, J = 11.23, C9-Hₙ), 4.89 (d, 1H, J = 11.72, C9-Hₙ), 3.99 (d, 1H, J = 11.23, C9-Hₙ), 4.86 (d, 1H, J = 10.74, C14-Hₙ), 4.50 (dt, 1H, J = 8.38, 6.65, C20-H), 3.96 (d, 1H, J = 2.93, C6-H₂), 3.70 (t, 1H, J = 9.28, C4-H), 3.61 (s, 3H, C22-H₃), 3.55 (t, 1H, J = 9.03, C3-H), 3.42 (td, 1H, J = 9.28, 3.17, C2-H), 3.26 (obs m, 1H, C5-H), 3.24 (obs m, 1H, C1-H), 2.73 (d, 1H, J = 2.93, C2-OH), 2.49 (ddd, 1H, J = 14.53, 9.04, 5.49, C19-Hₙ), 2.38 (obs m, 1H, C19-Hₙ), 1.18-1.00 (m, 21H, iPr₃Si). ¹³C-NMR (100 MHz, CDCl₃): δ 147.320 (C21), 138.513 (C10), 138.309 (C15), 128.613 (Ar), 127.877 (Ar), 127.680 (Ar), 127.564 (Ar), 127.546 (C9), 79.944 (C20), 86.711 (C3), 79.848 (C5), 79.792 (C9), 74.734 (C14), 72.972 (C2), 62.372 (C6), 55.670 (C22), 30.173 (C19), 18.095 (C8), 18.044 (C8'), 12.107 (C7). FAB-MS (NBA/NaI) m/z (rel int): 593 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcd for C₃₃H₅ₐNO₂S₃ 593.3274; found 593.3270.

(1R)-3,4-Di-O-benzyl-1-deoxy-1-(E-γ-methoxyallyl)-6-O-triisopropylsilyl-D-glucose, E-10b

(1R)-3,4-Di-O-benzyl-1-deoxy-1-(Z-γ-methoxyallyl)-6-O-triisopropylsilyl-D-glucose, Z-
10b. In a 5 mL conical flask, methoxymethyltriphenylphosphonium chloride (28 mg, 82.91 µmol, 3.0 equiv) was suspended in 375 µL THF and cooled to 0 °C. Sodium hexamethyldisilazide (1.0M in THF, 69.1 µL, 69.1 µmol, 2.5 equiv) was added slowly via syringe and the bright orange mixture was stirred at 0 °C for 1 h. (1R)-3,4-Di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropylsilyl-D-glucose, 9b (15 mg, 27.63 µmol, 1.0 equiv) was dried azeotropically by evaporation of benzene three times, then dissolved in 200 µL THF and added to the phosphorane solution via syringe at 0 °C. The reaction was allowed to warm slowly to rt. After 12 h, the mixture was diluted with 5 mL THF, poured into 5 mL satd NH₄Cl, and extracted 3 × 5 mL Et₂O. The combined organic extracts were washed 1 × 5 mL H₂O, 1 × 5 mL brine, dried (MgSO₄), filtered, and evaporated. TLC indicated approximately 40% conversion. The entire process was repeated once more to yield 36 mg of the crude product as a translucent oil. NMR analysis indicated complete conversion. The E/Z ratio was 65:35 as determined by integration of the C21-H NMR peaks. Purification by silica flash chromatography (5:1 hexane/EtOAc) yielded 10b as clear oil that was a mixture of E and Z isomers (2.6 mg, 16.5%). The E/Z ratio was 68:32 as determined by integration of the C21-H NMR peaks.

TLC: Rf 0.24 (3:1 hexane/EtOAc); Rf 0.17 (5:1 hexane/EtOAc). ¹H-NMR (400 MHz, CDCl₃): E-10b and Z-10b: δ 7.38-7.28 (m, 20H, E-ArH, Z-ArH), 6.30 (d, 1H, J = 12.71, E-C21-H), 5.95 (dt, 1H, J = 6.20, Z-C21-H), 4.77 (d, 1H, J = 10.77, Z-C9-Hₐ), 4.74 (d, 1H, J = 11.22, E-C9-Hₐ), 4.71 (obs dt, 1H, E-C20-H), 4.68 (d, 1H, J = 11.09, Z-C14-Hₐ), 4.65 (d, 1H, J = 10.80, E-C9-Hₐ), 4.56 (obs m, 3H, Z-C19-H, Z-C9-Hb), 4.43 (dt, 1H, J = 8.02, Z-C20-H), 3.97 (dd, 2H, J = 10.40, 4.60, C6-H₂), 3.91 (obs m, 1H, E-C2-H), 3.89 (m, 7H C1-6-H), 3.77 (dd, 1H, J = 6.85, 3.47, Z-C4-H), 3.72 (obs m, 1H, E-C19-H), 3.68 (m, 7H C1-6-H), 3.56 (s, 3H, Z-C22-H₃), 3.50 (s, 3H, E-C22-H₃), 3.49 (obs m, 1H, Z-C19-H), 2.45 (d, 1H, J = 4.91, Z-C2-OH), 2.30 (d, 1H, J = 6.35, E-C2-OH), 2.28 (obs m, 1H, Z-C19-H), 2.21 (app t, 2H, J = 7.06, E-C19-H), 1.15 (m, 42H, E-iPr₃Si, Z-iPr₃Si). FAB-MS (NBA/NaI) m/z (rel int): 593 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcd for C₃₃H₅₀O₆NaO₆Si 593.3274; found 593.3273.

(1S)-3,4-Di-O-benzyl-1-deoxy-1-(E-γ-methoxyallyl)-6-O-triisopropylsilyl-D-mannose, E-10c and (1S)-3,4-Di-O-benzyl-1-deoxy-1-(Z-γ-methoxyallyl)-6-O-triisopropylsilyl-D-mannose, Z-10c. In a 5 mL conical flask, methoxymethyltriphenylphosphonium chloride (16.5 mg, 48.1 µmol, 3.0 equiv) was suspended in 300 µL THF and cooled to 0 °C. Sodium hexamethyldisilazide (1.0M in THF, 40.1 µL, 40.1 µmol, 2.5 equiv) was added slowly via
syringe and the bright orange mixture was stirred at 0 °C for 30 min. (15)-3,4-Di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropylsilyl-D-mannose (S)-hemiacetal, 9cS and (15)-3,4-di-O-benzyl-1-deoxy-1-formylmethyl-6-O-triisopropylsilyl-D-mannose (R)-hemiacetal, 9cR (8.7 mg, 16.0 µmol, 1.0 equiv) were dried azeotropically by evaporation of benzene three times, then dissolved in 200 µL THF and added to the phosphorane solution via syringe at 0 °C. The reaction was allowed to warm slowly to rt. After 16 h, the mixture was diluted with 3 mL Et2O, poured into 5 mL satd NH4Cl, and extracted 5 × 3 mL Et2O. The combined organic extracts were washed 1 × 5 mL H2O, 1 × 5 mL brine, dried (MgSO4), filtered, and evaporated. NMR analysis indicated approximately 40% conversion with the unreacted material consisting primarily of 9cR. The entire process was repeated once more, however, the reaction did not proceed any further. The E/Z ratio was 72:28 as determined by integration of the C21-H NMR peaks. Purification by silica flash chromatography (7:1 hexane/EtOAc) yielded 10c as clear oil that was an mixture of E and Z isomers (2.1 mg, 22.9%). The E/Z ratio was 74:26 as determined by integration of the C21-H NMR peaks. TLC: Rf 0.45 (3:1 hexane/EtOAc); Rf 0.15 (7:1 hexane/EtOAc). IR (film): 3457 br, 2939, 2864, 1653, 1457, 1429, 1319, 1208, 1093, 1035, 1015, 935, 883. E-10c: 1H-NMR (500 MHz, CDCl3): δ 7.39 (d, 2H, J = 6.84, C11-H, C11’-H), 7.37-7.27 (m, 8H, Ar-H), 6.37 (dt, 1H, J = 12.70, 1.22, C21-H), 4.89 (d, 1H, J = 10.74, C14-Ha), 4.77 (d, 1H, J = 11.72, C9-Ha), 4.72 (ddd, 1H, J = 13.67, 6.99, 5.25, C20-H), 4.69 (d, 1H, J = 11.72, C9-Hb), 4.68 (d, 1H, J = 10.74, C14-Hb), 3.93 (m, 3H, C2-H, C6-H2), 3.87 (t, 1H, J = 9.52, C4-H), 3.57 (dd, 1H, J = 9.40, 3.30, C3-H), 3.51 (t, 3H, C22-H3), 3.22 (m, 2H, C1-H, C5-H), 2.33 (obs m, 1H, C19-Ha), 2.24 (dddd, 1H, J = 14.79, 7.69, 6.53, 1.10, C19-Hb), 1.15-0.95 (m, 21H, iPr3Si). 13C-NMR (100 MHz, CDCl3): δ 148.857 (C21), 138.447 (C15), 137.937 (C10), 128.409 (Ar), 128.321 (Ar), 128.100 (Ar), 128.015 (Ar), 127.790 (Ar), 127.622 (Ar), 98.352 (C20), 83.564 (C3), 80.278 (C5), 78.501 (C1), 75.295 (C14), 74.334 (C4), 71.617 (C9), 67.654 (C2), 62.875 (C6), 55.991 (C22), 29.554 (C19), 18.088 (C8), 18.044 (C8’), 12.114 (C7). Z-10c: 1H-NMR (500 MHz, CDCl3): δ 7.39 (d, 2H, J = 6.84, C11-H, C11’-H), 7.37-7.27 (m, 8H, Ar-H), 5.95 (dt, 1H, J = 6.27, 1.28, C21-H), 4.91 (d, 1H, J = 10.74, C14-Ha), 4.78 (d, 1H, J = 11.72, C9-Ha), 4.69 (d, 1H, J = 11.72, C9-Hb), 4.68 (d, 1H, J = 10.74, C14-Hb), 4.42 (td, 1H, J = 8.38, 6.59, C20-H), 3.97-3.85 (obs m, 4H, C2-H, C4-H, C6-H2), 3.60 (t, 3H, C22-H3), 3.56 (obs dd, 1H, J = 9.52, 3.17, C3-H), 3.29 (td, 1H, J = 7.33, 0.98, C1-H), 3.22 (obs m, 1H, C5-H), 2.46 (dddd, 1H, J = 15.14, 7.81, 6.65, 1.28, C19-Ha), 2.38 (app quint d, 1H, J = 14.16, 7.08, 1.46, C19-Hb), 2.34 (obs, 1H, C2-OH), 1.15-0.95 (m, 21H, iPr3Si). 13C-NMR (100 MHz, CDCl3): δ 147.553 (C21), 138.556 (C15), 138.097 (C10), 128.321 (Ar), 128.100 (Ar), 127.970 (Ar), 127.622 (Ar), 98.352 (C20), 83.564 (C3), 80.278 (C5), 78.501 (C1), 75.295 (C14), 74.334 (C4), 71.617 (C9), 67.654 (C2), 62.875 (C6), 55.991 (C22), 29.554 (C19), 18.088 (C8), 18.044 (C8’), 12.114 (C7). FAB-MS (NBA/NaI) m/z (rel int): 593 ([M+Na]+, 100).
III. Cyclization Reactions

![Diagram of cyclization reactions]

(1S,2S,1’S,2’S'R)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury acetate tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11aS and (1S,2S,1’R,2’S'R)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury acetate tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11aR. In a 5 mL conical flask, (1S)-3,4-di-O-benzyl-1-deoxy-1-(γ-methoxyallyl)-6-O-triisopropylsilyl-D-glucose, 10a (3.9 mg, 6.83 µmol, 1.0 equiv), was dried azeotropically by evaporation of benzene three times and placed under a condenser under Ar. Mercuric acetate (3.0 mg, 9.31 µmol, 1.36 equiv) was added, then 680 µL THF. The reaction was heated to reflux for 11 h, then the solvent was evaporated to yield the crude product as a 58:42 mixture of two stereoisomers. Extensive analysis of COSY, TOCSY, NOESY, HSQC, HMQC, and HMBC NMR experiments allowed assignment of the majority of the proton resonances. Stereochemistry at C20 and C21 in the minor product, 11aR, was assigned based upon the large C20-H, C21-H coupling constant. Tentative stereochemistry in the major product, 11aS, was then assigned based upon NOESY data and mechanistic considerations. The diagnostic C20-H and C21-H peaks are identified as follows: ¹H-NMR (400 MHz, CDCl₃) 11aS: δ 4.77 (C21-H), 2.76 (C20-H); 11aR: δ 4.58 (C21-H), 2.61 (C20-H). Also, a characteristic acetate peak was observed at δ 2.05.

TLC: Rf 0.34 (3:1 hexane/EtOAc); Rf 0.15 (17:3 hexane/EtOAc). 11aS: ¹H-NMR (600 MHz, CDCl₃): δ 7.37 (d, 2H, J = 7.69, C11-H, C11'-H), 7.35-7.27 (m, 8H, Ar-H), 4.94 (d, 1H, J = 11.00, C9-Hₙ), 4.88 (d, 1H, J = 10.62, C14-Hₙ), 4.79 (d, 1H, J = 10.80, C9-H₂), 4.77 (d, 1H, J = 3.30, C21-H), 4.70 (d, 1H, J = 10.62, C14-H₂), 3.93 (m, 2H, C6-H₂), 3.70 (obs m, 1H, C4-H), 3.61 (obs t, 1H, J = 6.04, C2-H/C3-H), 3.60 (obs t, 1H, J = 6.96, C2-H/C3-H), 3.41 (s, 3H, C22-H₃), 3.30 (obs m, 1H, C5-H), 3.13 (obs m, 1H, C1-H), 2.75 (app td, 1H, J = 9.29, 3.48, C20-H), 2.17 (m, 2H, C19-H₂), 2.05 (s, 3H, OAc), 1.13-0.95 (m, 21H, iPr₃Si). 11aR: ¹H-NMR (600 MHz, CDCl₃): δ 7.37 (d, 2H, J = 7.69, C11-H, C11'-H), 7.35-7.27 (m, 8H, Ar-H), 4.97 (d, 1H, J = 10.98, C9-Hₙ), 4.89 (d, 1H, J = 10.62, C14-Hₙ), 4.81 (obs d, 1H, C9-H₂), 4.70 (d, 1H, J = 10.62, C14-H₂), 4.59 (d, 1H, J = 9.70, C21-H), 3.93 (m, 2H, C6-H₂), 3.72 (obs m, 2H, C3-H, C4-H), 3.53 (s, 3H, C22-H₃), 3.30 (obs m, 1H, C2-H), 3.11 (obs m, 1H, C1-H), 2.61 (ddd, 1H, J = 14.05, 9.93, 3.07, C20-H), 2.39 (dt, 1H, J = 12.63, 4.16, C19-H₂), 2.05 (s, 3H, OAc), 1.93 (m, 1H, C19-H₂), 1.13-0.95 (m, 21H, iPr₃Si). FAB-MS (NBA/NaI) m/z (rel int): 853 ([M+Na]+, not detected), 919 (88), 921 (100).
(1S,2S,1'S,2'R)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury trifluoroacetate tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11bS and (1S,2S,1'R,2'R)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury trifluoroacetate tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11bR. The crude products 11bS and 11bR were prepared as 11aS and 11aR above with mercuric trifluoroacetate. The diagnostic C20-H peaks were identified by analogy to 11aS and 11aR as follows: 1H-NMR (400 MHz, CDCl₃): 11bS: δ 2.97 (C20-H); 11bR: δ 2.83 (C20-H).

(1S,2S,1'S,2'R)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury chloride tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11cS and (1S,2S,1'R,2'R)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury chloride tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11cR. The organomercury acetates 11aS and 11aR above were converted to organomercury chlorides for comparison. In a 5 mL conical flask, (1S,2S,1'S,2'R)-3,4-di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury acetate tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11aS and (1S,2S,1'R,2'R)-3,4-di-O-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury acetate tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 11aR, were dissolved in 1 mL THF. 1 mL brine was added and the mixture stirred for 18 h. The mixture was diluted with 3 mL THF and extracted 3 × 5 mL Et₂O. The combined organic extracts were washed 3 × 5 mL brine, dried (MgSO₄), filtered, and evaporated to yield crude 11cS and 11cR. The diagnostic C20-H peaks were identified by analogy to 11aS and 11aR as follows: 1H-NMR (400 MHz, CDCl₃): 11cS: δ 2.74 (C20-H); 11cR: δ 2.59 (C20-H). Also, the characteristic acetate peak was no longer observed.
(1S,2S)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(Δ1',2'-dihydropyrano)-6-O-triisopropylsilyl-D-glucose, 12a, (1S,2S,1'S)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-((1'-methoxy-tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 13aS, and (1S,2S,1'R)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-((1'-methoxy-tetrahydropyrano)-6-O-triisopropylsilyl-D-glucose, 13aR. In a 5 mL conical flask, (1S)-3,4-di-O-benzyl-1-deoxy-1-((γ-methoxyallyl)-6-O-triisopropylsilyl-D-glucose, 10a (8.5 mg, 14.89 µmol, 1.0 equiv), was dried azeotropically by evaporation of benzene three times. Mercuric trifluoroacetate (0.3 mg, 0.703 µmol, 0.047 equiv) was added as a solid, then the flask was placed under a condenser under Ar. 300 µL THF was added and the reaction heated to reflux for 24 h. The reaction was then diluted with 5 mL THF, poured into 5 mL satd NaHCO3, and extracted 3 × 5 mL Et2O. The combined organic extracts were washed 1 × 5 mL H2O, 1 × 5 mL brine, dried (MgSO4), filtered, and evaporated to yield 8.2 mg of crude product as a clear residue. NMR analysis indicated an 80:10:10 mixture of 12a, 13aS, and 13aR along with trace 11b. Purification by silica flash chromatography (19:1 hexane/EtOAc) yielded 12a (5.7 mg, 71.0%), 13aS (0.4 mg, 4.7%), and 13aR (0.4 mg, 4.7%) as clear oils. Stereochemistry at C1' was assigned based on NOESY and coupling constant data.

12a: TLC: Rf 0.39 (9:1 hexane/EtOAc); Rf 0.15 (19:1 hexane/EtOAc). IR (film): 2941, 2865, 1651, 1455, 1237, 1157, 1108, 1067, 1052, 882. 1H-NMR (500 MHz, CDCl3): δ 7.40 (d, 2H, J = 7.03, C11-H, C11'-H), 7.34-7.25 (m, 8H, Ar-H), 6.38 (app dt, 1H, J = 5.90, 1.89, C21-H), 4.97 (d, 1H, J = 11.14, C9-Ha), 4.90 (d, 1H, J = 10.69, C14-Ha), 4.81 (d, 1H, J = 11.12, C9-Hb), 4.72 (d, 1H, J = 10.71, C14-Hb), 4.69 (ddt, 1H, J = 5.72, 2.10, C20-H), 3.97 (app d, 2H, J = 2.57, C6-H2), 3.78 (t, 1H, J = 9.14, C4-H), 3.73 (t, 1H, J = 8.78, C3-H), 3.54 (t, 1H, J = 9.04, C2-H), 3.47 (td, 1H, J = 9.47, 6.01, C1-H), 3.36 (dt, 1H, J = 9.31, 2.56, C5-H), 2.29 (dtd, 1H, J = 16.41, 5.71, 1.32, C19-Ha), 2.06 (ddt, 1H, J = 16.39, 9.48, 2.35, C19-Hb), 1.26-0.98 (m, 21H, iPr3Si). 13C-NMR (100 MHz, CDCl3): δ 142.969 (C21), 138.848 (C10), 138.575 (C15), 128.393 (ArH), 128.318 (ArH), 127.989 (ArH), 127.664 (ArH), 127.535 (ArH), 98.414 (C20), 84.231 (C3), 79.982 (C5), 79.322 (C2), 77.205 (C4), 75.270 (C14), 75.065 (C9), 71.856 (C1), 62.637 (C6), 26.784 (C19), 17.990 (C8), 17.929 (C8'), 12.019 (C7). FAB-MS (NBA/NaI) m/z (rel int): 561 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcld for C32H46NaO5Si 561.3012; found 561.3011.

13aS: TLC: Rf 0.30 (9:1 hexane/EtOAc); Rf 0.12 (19:1 hexane/EtOAc). 1H-NMR (600 MHz, CDCl3): δ 7.39 (d, 2H, J = 6.96, Ar-H), 7.34-7.27 (m, 8H, Ar-H), 4.98 (d, 1H, J = 10.98, C9-H), 4.92 (d, 1H, J = 10.69, C14-H), 4.77 (d, 1H, J = 11.14, C9-H), 4.72 (d, 1H, J = 10.71, C14-H), 4.69 (ddt, 1H, J = 5.72, 2.10, C20-H), 3.97 (app d, 2H, J = 2.57, C6-H2), 3.78 (t, 1H, J = 9.14, C4-H), 3.73 (t, 1H, J = 8.78, C3-H), 3.54 (t, 1H, J = 9.04, C2-H), 3.47 (td, 1H, J = 9.47, 6.01, C1-H), 3.36 (dt, 1H, J = 9.31, 2.56, C5-H), 2.29 (dtd, 1H, J = 16.41, 5.71, 1.32, C19-Ha), 2.06 (ddt, 1H, J = 16.39, 9.48, 2.35, C19-Hb), 1.26-0.98 (m, 21H, iPr3Si). 13C-NMR (100 MHz, CDCl3): δ 142.969 (C21), 138.848 (C10), 138.575 (C15), 128.393 (ArH), 128.318 (ArH), 127.989 (ArH), 127.664 (ArH), 127.535 (ArH), 98.414 (C20), 84.231 (C3), 79.982 (C5), 79.322 (C2), 77.205 (C4), 75.270 (C14), 75.065 (C9), 71.856 (C1), 62.637 (C6), 26.784 (C19), 17.990 (C8), 17.929 (C8'), 12.019 (C7). FAB-MS (NBA/NaI) m/z (rel int): 561 ([M+Na]+, 100). HRMS (NBA/NaI) m/z calcld for C32H46NaO5Si 561.3012; found 561.3011.
4.89 (d, 1H, J = 10.62, C14-H_a), 4.80 (d, 1H, J = 10.98, C9-H_b), 4.72 (obs d, 1H), 4.70 (d, 1H, J = 10.62, C14-H_b), 3.94 (app d, 2H, J = 2.56, C6-H_2), 3.70 (t, 1H, J = 9.153, C4-H), 3.63 (t, 1H, J = 8.97, C3-H), 3.53 (t, 1H, J = 9.52, C2-H), 3.41 (app dt, 1H, J = 9.70, 2.79, C5-H), 3.14 (app td, 1H, J = 9.98, 4.03, C1-H), 1.89-1.83 (m, 2H, C19-H_a, C20-H_ax), 1.82-1.74 (m, 2H, C19-H_b, C20-H_eq), 1.13-1.00 (m, 21H, iPr_3Si). FAB-MS (NBA/NaI) m/z (rel int): 593 ([M+Na]^+, 100). HRMS (NBA/NaI) m/z calcd for C_{33}H_{50}NaO_6Si 593.3274; found 593.3284.

13aR: TLC: Rf 0.25 (9:1 hexane/EtOAc); Rf 0.08 (19:1 hexane/EtOAc). ^H-NMR (600 MHz, CDCl_3): δ 7.39 (d, 2H, J = 7.32, C11_a-H, C11_b-H), 7.35-7.28 (m, 8H, Ar-H), 5.01 (d, 1H, J = 10.98, C9-H_a), 4.90 (d, 1H, J = 10.62, C14-H_b), 4.81 (d, 1H, J = 10.98, C9-H_b), 4.70 (d, 1H, J = 10.62, C14-H_b), 4.45 (d, 1H, J = 9.15, C21-H), 3.94 (app d, 2H, J = 2.56, C6-H_2), 3.74 (t, 1H, J = 8.97, C3-H), 3.71 (t, 1H, J = 8.77, C4-H), 3.54 (s, 3H, C22-H_3), 3.33 (app dt, 1H, J = 9.15, 2.44, C5-H), 3.24 (t, 1H, J = 8.97, C2-H), 3.15 (app td, 1H, J = 9.70, 3.91, C1-H), 2.05 (m, 1H), 1.93 (m, 1H), 1.55 (obs m, 2H), 1.13-0.99 (m, 21H). FAB-MS (NBA/NaI) m/z (rel int): 593 ([M+Na]^+, 100). HRMS (NBA/NaI) m/z calcd for C_{33}H_{50}NaO_6Si 593.3274; found 593.3284.

(1R,2S)-3,4-Di-O-benzyl-1,2-dideoxy-1,2-(Δ^1',2'-dihydropyrano)-6-O-triisopropylsilyl-D-glucose, 12b. In a 5 mL conical flask, (1R)-3,4-di-O-benzyl-1-deoxy-1-(γ-methoxyallyl)-6-O-triisopropylsilyl-D-glucose, 10b (2.5 mg, 4.38 µmol, 1.0 equiv), was dried azeotropically by evaporation of benzene three times. Mercuric trifluoroacetate (0.1 mg, 0.219 µmol, 0.05 equiv) was added as a solid, then the flask was placed under a condenser under Ar. 1.5 mL THF was added and the reaction heated to reflux for 72 h. The reaction was then diluted with 5 mL THF, poured into 5 mL satd NaHCO_3, and extracted 2×5 mL Et_2O. The combined organic extracts were washed 1×5 mL H_2O, 1×5 mL brine, dried (MgSO_4), filtered, and evaporated to yield the crude product as a clear residue. Purification by silica flash chromatography (19:1 hexane/EtOAc) yielded a trace amount of partially purified 12b. TLC: Rf 0.43 (9:1 hexane/EtOAc). ^H-NMR (600 MHz, CDCl_3): δ 7.34-7.25 (m, 10H, Ar-H), 6.37 (d, 1H, J = 5.86, C21-H), 4.71 (d, 1H, J = 12.21, C9/14-H_a*), 4.64 (dd, 1H, J = 5.68, 2.11, C20-H), 4.58 (d, 1H, J = 12.21, C9/14-H_b*), 4.55 (d, 1H, J = 12.452, C14/9-H_a*), 4.47 (d, 1H, J = 12.452, C14/9-H_b*), 4.17 (t, 1H, J = 9.03, C4-H*), 4.08 (m, 1H, C1-H), 4.02 (app t, 1H, J = 7.447, C3-H*), 3.98-3.93 (obs m, 2H, C6-H_2*), 3.94 (obs dd, 1H, J = 9.64, 6.23, C5-H*), 3.90 (d, 1H, J = 2.69, C2-H*), 2.27 (dt, 1H, J = 16.20, 5.86, C19-H_a), 2.10 (ddt, 1H, J = 16.40, 9.32, 2.41, C19-H_b),
1.09-0.98 (m, 23H, iPr\textsubscript{3}Si). (*tentative assignment) FAB-MS (NBA/NaI) \text{m/z (rel int)}: 561 ([M+Na]+). HRMS (NBA/NaI) \text{m/z} calcd for C\textsubscript{33}H\textsubscript{50}NaO\textsubscript{6}Si 561.3012; found 561.3023.

(1S,2R)-3,4-Di-\textit{O}-benzyl-1,2-dideoxy-1,2-(\Delta-1',2'-dihydropyran)-6-\textit{O}-triisopropylsilyl-D-mannose, 12c, (1S,2R,1'S)-3,4-Di-\textit{O}-benzyl-1,2-dideoxy-1,2-(1'-methoxy-tetrahydropyran)-6-\textit{O}-triisopropylsilyl-D-mannose, 13c\textsubscript{S}, and (1S,2R,1'R)-3,4-Di-\textit{O}-benzyl-1,2-dideoxy-1,2-(1'-methoxy-tetrahydropyran)-6-\textit{O}-triisopropylsilyl-D-mannose, 13c\textsubscript{R}. In a 25 mL conical flask, (1S)-3,4-di-\textit{O}-benzyl-1-deoxy-1-(\gamma-methoxyallyl)-6-\textit{O}-triisopropylsilyl-D-mannose, 10c (2.1 mg, 3.68 \textmu mol, 1.0 equiv), was dried azeotropically by evaporation of benzene three times. Mercuric trifluoroacetate (0.1 mg, 0.234 \textmu mol, 0.06 equiv) was added as a solid, then the flask was placed under a condenser under Ar. 400 \mu L THF was added via syringe and the reaction heated to reflux for 48 h with addition of THF as necessary to maintain volume. The reaction was then diluted with 20 mL Et\textsubscript{2}O, poured into 5 mL satd NaHCO\textsubscript{3}, and extracted 4 \times 5 mL Et\textsubscript{2}O. The combined organic extracts were washed 1 \times 5 mL H\textsubscript{2}O, 1 \times 5 mL brine, dried (MgSO\textsubscript{4}), filtered, and evaporated to yield the crude product as a clear residue. NMR analysis indicated a 10:38:52 mixture of 12c, 13c\textsubscript{S}, and 13c\textsubscript{R}. Purification by silica flash chromatography (19:1 hexane/EtOAc) yielded 12c (0.4 mg) and 13c\textsubscript{S} (0.3 mg) as white solids, and 13c\textsubscript{R} (0.5 mg) as a clear oil. Stereochemistry at C1’ was assigned based on NOESY and coupling constant data.

12c: TLC: \textit{Rf} 0.35 (7:1 hexane/EtOAc); 0.12 (19:1 hexane/EtOAc). \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}): \delta 7.40 (d, 2H, \textit{J} = 6.72, C11-H, C11'-H), 7.38-7.28 (m, 8H, Ar-H), 6.40 (app d, 1H, \textit{J} = 5.88, C21-H), 4.96 (d, 1H, \textit{J} = 10.63, C14-H\textsubscript{a}), 4.82 (d, 1H, \textit{J} = 12.03, C9-H\textsubscript{a}), 4.73 (obs d, 1H, \textit{J} = 10.63, C14-H\textsubscript{b}), 4.61 (app t, 1H, \textit{J} = 5.32, C20-H), 4.06 (obs d, 1H, \textit{J} = 3.36, C2-H), 4.05 (obs t, 1H, \textit{J} = 9.37, C4-H), 3.99 (dd, 1H, \textit{J} = 11.19, 3.64, C6-H\textsubscript{a}), 3.94 (dd, 1H, \textit{J} = 11.19, 1.96, C6-H\textsubscript{b}), 3.64 (obs d, 1H, \textit{J} = 5.32, C1-H), 3.62 (obs dd, 1H, \textit{J} = 9.23, 2.94, C3-H), 3.29 (ddd, 1H, \textit{J} = 9.58, 3.71, 1.75, C5-H), 2.30 (dm, 1H, \textit{J} = 18.19, C19-H\textsubscript{a}), 2.06 (ddq, 1H, \textit{J} = 17.98, 5.11, 1.47, C19-H\textsubscript{b}), 1.13-0.98 (m, 21H, iPr\textsubscript{3}Si). TOF ESI MS \text{m/z (rel int)}: 539 ([M+H]+), 56.

13c\textsubscript{S}: TLC: \textit{Rf} 0.31 (7:1 hexane/EtOAc); 0.07 (19:1 hexane/EtOAc). IR (film): 2941, 2864, 1457, 1363, 1110, 1043, 1018, 883. \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}): \delta 7.39 (d, 2H, \textit{J} = 6.65, C11-H, C11'-H), 7.37-7.28 (m, 8H, Ar-H), 4.98 (d, 1H, \textit{J} = 10.47, C14-H\textsubscript{a}), 4.83 (obs app s, 1H, C21-H), 4.82 (obs d, 1H, \textit{J} = 12.13, C9-H\textsubscript{b}), 4.720 (obs d, 1H, \textit{J} = 11.97, C9-H\textsubscript{b}), 4.716 (obs d, 1H, \textit{J} = 12.13, C9-H\textsubscript{b}).
\[ S18 \]

\[ \text{13cR: TLC: Rf 0.25 (7:1 hexane/EtOAc); 0.05 (19:1 hexane/EtOAc). IR (film): 2941, 2864, 1462, 1390, 1200, 1151, 1101, 1049, 1020, 916, 883.} \]

\[ \text{\textsuperscript{1}H-NMR (500 MHz, CDCl}_3): \delta 7.41 (d, 2H, J = 7.11, C11-H, C11'-H), 7.35-7.27 (m, 8H, Ar-H), 4.95 (d, 1H, J = 10.83, C14-H\textsubscript{a}), 4.73 (d, 1H, J = 12.01, C9-H\textsubscript{a}), 4.66 (obs d, 1H, J = 12.01, C9-H\textsubscript{b}), 4.65 (obs d, 1H, J = 10.66, C14-H\textsubscript{b}), 4.28 (dd, 1H, J = 9.90, 1.95, C21-H), 3.97 (dd, 1H, J = 11.08, 1.95, C6-H\textsubscript{a}), 3.94 (obs m, 1H, C6-H\textsubscript{b}), 3.93 (obs t, 1H, J = 9.39, C4-H), 3.77 (dd, 1H, J = 3.55, 0.85, C2-H), 3.63 (dd, 1H, J = 9.31, 3.72, C3-H), 3.54 (s, 3H, C22-H\textsubscript{3}), 3.29 (obs app s, 1H, C1-H), 3.29 (obs ddd, 1H, J = 9.65, 4.82, 1.86, C5-H), 2.02 (app dquint, 1H, J = 13.88, 2.27, C19-H\textsubscript{a}), 1.86 (m, 1H, C20-H\textsubscript{a}), 1.62 (obs ddd, 1H, J = 13.88, 4.65, 3.13, C19-H\textsubscript{b}), 1.55 (obs dqunt, J = 12.39, 2.26, 1H, C20-H\textsubscript{b}), 1.15-0.98 (m, 21H, iPr\textsubscript{3}Si). TOF ESI-MS m/z (rel int): 593 ([M+Na]\textsuperscript{+}, 100), 609 ([M+K]\textsuperscript{+}, 47).} \]

\[ \text{IV. References} \]


S18