# A mercury-catalyzed transetherification cyclization leading to fused cyclic polyethers

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## Supplementary Material



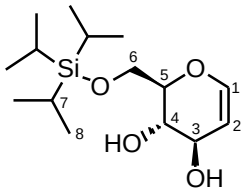
## I. General Experimental Methods

**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 ($Et_2O$), acetonitrile ($CH_3CN$), and methylene chloride ($CH_2Cl_2$) 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 $N_2$ 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 $F_{254}$ 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 ($CDCl_3$ 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 ($NH_3$), 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.

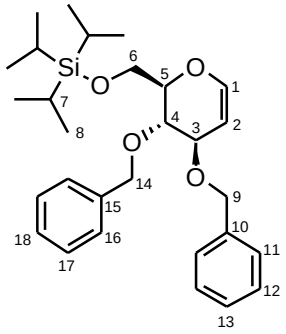
**Structure Notation.** Atom numbers shown in structures below refer only to NMR peak assignments and not to CAS or trivial nomenclature.

## II. Synthesis of Cyclization Substrates




**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 $H_2O$ and extracted 5 × 90 mL $Et_2O$. The combined organic extracts were washed 5 × 75 mL $H_2O$, 1 × 75 mL brine, dried ($MgSO_4$), 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%).

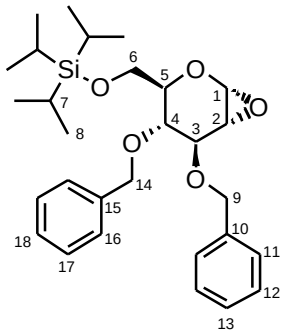
TLC: $R_f$ 0.17 (2:1 hexane/EtOAc); *Rf* 0.32 (1:1 hexane/EtOAc); *Rf* 0.63 (EtOAc). IR (film): 3355, 2942, 2866, 1652, 1646, 1457, 1234, 1108, 1054, 1031, 882. $^1$H-NMR (500 MHz, $CDCl_3$): δ 6.31 (dd, 1H, *J* = 5.96, 1.19, C1-H), 4.74 (dd, 1H, *J* = 5.96, 2.11, C2-H), 4.29 (m, 1H, C3-H), 4.09 (dd, 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, $iPr_3Si$). 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 $H_2O$ and extracted 5 × 40 mL $Et_2O$. The combined organic extracts were washed 5 × 20 mL $H_2O$, 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).

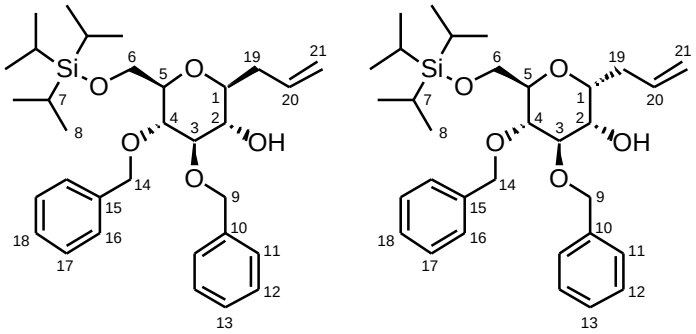
TLC: $R_f$ 0.31 (19:1 hexane/EtOAc); *Rf* 0.23 (24:1 hexane/EtOAc). IR (film): 2941, 2865, 1647, 1454, 1239, 1101, 1066, 882. $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 10H, Ar-H), 6.39 (dd, 1H, *J* = 6.14, 1.35, C1-H), 4.86 (d, 1H, *J* = 11.43, C14-$H_a$), 4.83 (dd, 1H, *J* = 6.16, 2.67, C2-H), 4.76 (d, 1H, *J* = 11.24, C14-$H_b$), 4.64 (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), δ 1.15-1.00 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 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 $C_{29}H_{42}NaO_4Si$ 505.2750; found 505.2753.




**(1*S*,2*R*)-3,4-Di-*O*-benzyl-6-*O*-triisopropylsilyl-D-glucal-1,2-oxirane, 7.**[1-3] In a 250 mL round bottom flask, 3,4-di-*O*-benzyl-6-*O*-triisopropylsilyl-D-glucal, **6**, (1.415 mg, 2.931 mmol, 1.0 equiv) was dissolved in 50 mL $CH_2Cl_2$ 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 (β-epoxide diastereomer: C1-H, δ 4.95; C2-H δ 3.32).

TLC: *Rf* 0.05 (19:1 hexane/EtOAc); *Rf* 0.37 (1:1 hexane/EtOAc). IR (film): 2941, 2865, 1456, 1164, 1102, 1013, 884. $^1$H-NMR (400 MHz, $CDCl_3$): δ 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, 1H, *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, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 138.519, 137.564, 128.564, 128.343, 127.995,

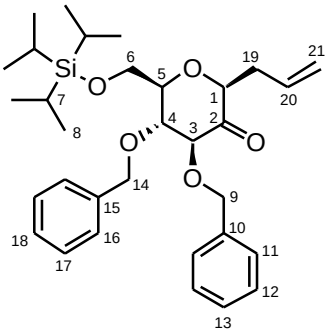
127.972, 127.792, 127.639, 79.099, (77.469), (77.203), 74.702, 74.110, 72.481, 70.813, 61.766, 52.900, 18.015, 17.961, 12.025. CI-MS ($NH_3$) *m/z* (rel int): 516 ($[M+NH_4]^+$, 28). FAB-MS (NBA/NaI) *m/z* (rel int): 521 ($[M+Na]^+$, 100). HRMS (NBA/NaI) *m/z* calcd for $C_{29}H_{42}NaO_5Si$ 521.2699; 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.**[3] 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 $NH_4Cl$ and extracted 5 × 10 mL $Et_2O$. The combined organic extracts were washed 3 × 10 mL $H_2O$, 1 × 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: *Rf* 0.70 (1:1 hexane/EtOAc); *Rf* 0.50 (3:1 hexane/EtOAc); *Rf* 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-$H_a$), 2.22 (app quint, 1H, *J* = 7.32, C19-$H_b$), 2.05 (d, 1H, *J* = 2.52, C2-OH), 1.20-1.00 (m, 21H, $iPr_3Si$). $^{13}$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, 62.378, 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 $C_{32}H_{48}NaO_5Si$ 563.3169; found 563.3187.

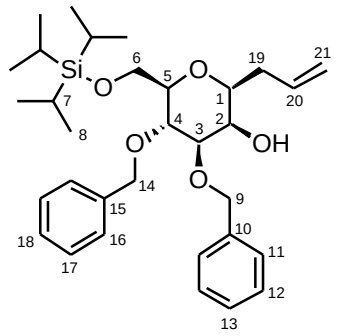
**8b**: TLC: *Rf* 0.46 (3:1 hexane/EtOAc); *Rf* 0.05 (9:1 hexane/EtOAc). IR (film): 3472 br, 2941, 2865, 1455, 1099, 1070, 883. $^1$H-NMR (500 MHz, $CDCl_3$): δ 7.40-7.28 (m, 10H, Ar-H), 5.82 (ddt, 1H, *J* = 17.07,10.20, 6.88, C20-H), 5.06 (dd, 1H, *J* = 17.00, 1.70, C21-$H_Z$), 5.04 (dd, 1H, *J* = 10.13, 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, $iPr_3Si$). FAB-MS (NBA/NaI) *m/z* (rel int): 563 ([M+Na]$^+$, 100). HRMS (NBA/NaI) *m/z* calcd for $C_{32}H_{48}NaO_5Si$ 563.3169; found 563.3185.




**(1*S*)-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 μmol, 2.0 equiv) was suspended in 100 μL $CH_2Cl_2$. (1*S*)-1-Allyl-3,4-di-*O*-benzyl-1-deoxy-6-*O*-triisopropylsilyl-D-glucose, **8a** (10.0 mg, 18.5 μmol, 1.0 equiv), was dissolved in 100 μL $CH_2Cl_2$ and added to the stirring mixture. After 4 h, the $CH_2Cl_2$ was evaporated and the residue taken up in 5 mL $Et_2O$. 2 mL of 1N NaOH was added to the mixture and stirred for 10 min. The layers were separated and the $Et_2O$ layer washed 1 × 2 mL 1N NaOH, 1 × 2 mL $H_2O$, 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 (1*S*)-1-allyl-3,4-di-*O*-benzyl-1-deoxy-2-keto-6-*O*-triisopropylsilyl-D-glucose (1.6 mg, 16%) as a clear oil.

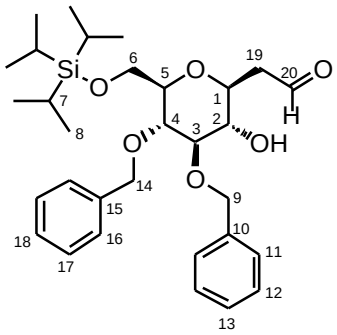
TLC: *Rf* 0.61 (3:1 hexane/EtOAc); *Rf* 0.27 (9:1 hexane/EtOAc). IR (film): 2941, 2865, 1734, 1456, 1104, 1067, 1028, 883. $^1$H-NMR (500 MHz, $CDCl_3$): δ 7.42 (app d, 2H, *J* = 7.08, C11-H, C11'-H), 7.36-7.28 (m, 8H, Ar-H), 5.85 (ddt, 1H, *J* = 17.21, 10.19, 6.96, C20-H), 5.14 (app dd, 1H, *J* = 17.09, 1.47, C21-$H_Z$), 5.06 (app d, 1H, *J* = 10.25, C21-$H_E$), 5.00 (d, 1H, *J* = 11.47, C9-$H_a$), 4.89 (d, 1H, *J* = 10.50, C14-$H_a$), 4.71 (d, 1H, *J* = 10.74, C14-$H_b$), 4.62 (d, 1H, *J* = 11.23, C9-$H_b$), 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* = 14.954, 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, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 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),

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).



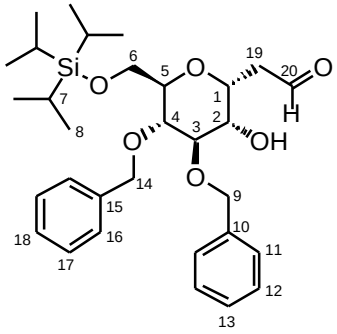

**(1*S*)-1-Allyl-3,4-di-*O*-benzyl-1-deoxy-6-*O*-triisopropylsilyl-D-mannose, 8c.** In a 5 mL conical flask, (1*S*)-1-allyl-3,4-di-*O*-benzyl-1-deoxy-2-keto-6-*O*-triisopropylsilyl-D-glucose (2.0 mg, 3.71 μmol, 1.0 equiv) is dissolved in 100 μL THF and cooled to 0 °C. L-Selectride (1.0M in THF, 11.1 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 $NH_4Cl$ and the reaction flask rinsed several more times with 1 mL $CH_2Cl_2$. The layers were separated and the aqueous layer extracted 2 × 2 mL $CH_2Cl_2$. The combined organic extracts were dried ($MgSO_4$), 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. $^1$H-NMR (500 MHz, $CDCl_3$): 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-$H_Z$), 5.05 (app d, 1H, *J* = 10.32, C21-$H_E$), 4.89 (d, 1H, *J* = 10.64, C14-$H_a$), 4.77 (d, 1H, *J* = 11.61, C9-$H_a$), 4.69 (obs d, 1H, *J* = 10.44, C14-$H_b$), 4.68 (obs d, 1H, *J* = 12.48, C9-$H_b$), 3.96-3.90 (m, 3H, C2-H, C6-$H_2$), 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-$H_a$), 2.36 (app quint, 1H, *J* = 7.01, C19-$H_b$), 2.18 (d, 1H, *J* = 4.52, C2-OH), 1.15-1.00 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 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).



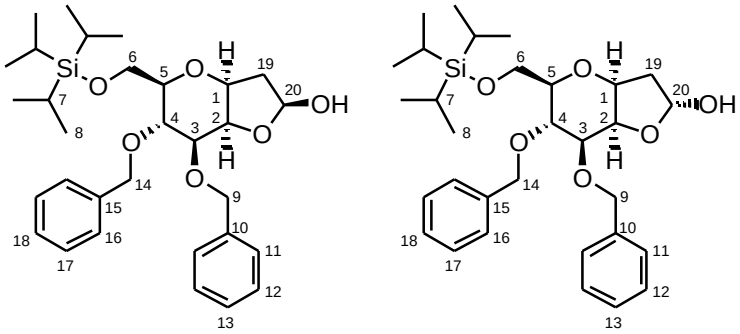
**(1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-formylmethyl-6-*O*-triisopropylsilyl-D-glucose, 9a.**[7] In a 50 mL round bottom flask, (1*S*)-1-allyl-3,4-di-*O*-benzyl-1-deoxy-6-*O*-triisopropylsilyl-D-glucose, **8a** (425 mg, 785.8 μmol, 1.0 equiv), was dissolved in 10 mL $CH_2Cl_2$ and cooled to –78 °C. Ozone 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 $CH_2Cl_2$ 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. $^1$H-NMR (400 MHz, $CDCl_3$): 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-$H_a$), 4.86 (d, 1H, *J* = 10.77, C14-$H_a$), 4.82 (d, 1H, *J* = 10.78, C14-$H_b$), 4.73 (d, 1H, *J* = 11.54, C9-$H_b$), 3.99 (obs dd, 1H, *J* = 11.48, 2.73, C6-$H_a$), 3.96 (obs dd, 1H, *J* = 11.48, 1.91, C6-$H_b$), 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-$H_a$), 2.55 (ddd, 1H, *J* = 16.40, 8.35, 2.72, C19-$H_b$), 2.16 (d, 1H, *J* = 2.68, C2-OH), 1.20-1.00 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 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 $C_{31}H_{46}NaO_6Si$ 565.2961; found 565.2990.



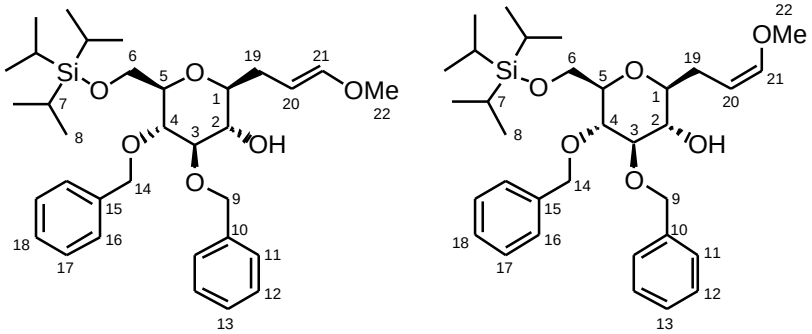
**(1*R*)-3,4-Di-*O*-benzyl-1-deoxy-1-formylmethyl-6-*O*-triisopropylsilyl-D-glucose, 9b.** In a 50 mL round bottom flask, (1*R*)-1-allyl-3,4-di-*O*-benzyl-1-deoxy-6-*O*-triisopropylsilyl-D-glucose, **8b** (18 mg, 33.3 μmol, 1.0 equiv), was dissolved in 4 mL $CH_2Cl_2$ and cooled to –78 °C. Ozone was 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 $CH_2Cl_2$ 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. $^1$H-NMR (500 MHz, $CDCl_3$): 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-$H_a$), 4.65 (obs d, 1H, J = 11.99, C14-$H_a$), 4.58 (d, 1H, J = 11.97, C14-$H_b$), 4.42 (d, 1H, J = 11.37, C9-$H_b$), 4.21 (td, 1H, J = 8.31, 4.43, C1-H), 4.07 (m, 1H, C6-$H_a$), 3.99 (dd, 1H, J = 4.45, 2.88, C4-H), 3.86 (m, 2H, C5-H, C6-$H_b$), 3.80 (app t, 1H, J = 4.04, C3-H), 3.72 (app td, 1H, J = 8.64, 3.44, C2-H), 2.75 (ddd, 1H, J = 16.36, 4.43, 1.73, C19-$H_a$), 2.64 (ddd, 1H, J = 16.35, 8.53, 2.57, C19-$H_b$), 2.27 (d, 1H, J = 9.19, C2-OH), 1.15-0.97 (m, 21H, $iPr_3Si$). FAB-MS (NBA/NaI) *m/z* (rel int): 565 ([M+Na]$^+$, 100). HRMS (NBA/NaI) *m/z* calcd for $C_{31}H_{46}NaO_6Si$ 565.2961; found 565.2957.



**(1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-formylmethyl-6-*O*-triisopropylsilyl-D-mannose (*S*)-hemiacetal, 9cS** and **(1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-formylmethyl-6-*O*-triisopropylsilyl-D-mannose (*R*)-hemiacetal, 9cR.** In a 25 mL round bottom flask, (1*S*)-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 $CH_2Cl_2$ 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 $CH_2Cl_2$ 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 $CDCl_3$.

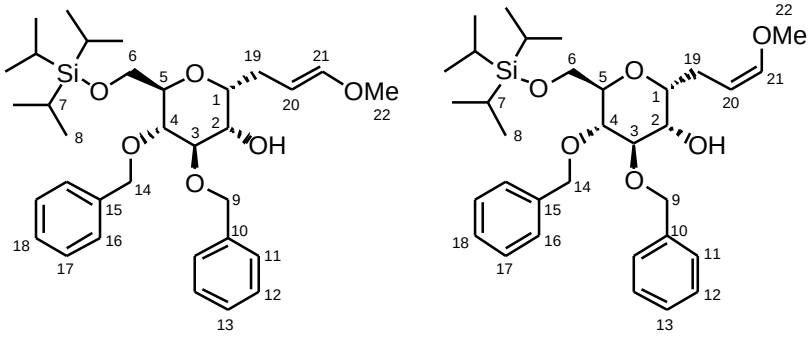
TLC: *Rf* 0.25 (3:1 hexane/EtOAc); *Rf* 0.06 (6:1 hexane/EtOAc). IR (film): 3489 br, 2958, 2923, 2853, 1457, 1109, 999, 883. **9cS**: $^{1}$H-NMR (500 MHz, $CDCl_3$): δ 7.40 (app d, 2H, *J* = 7.57, C11-H, C11'-H), 7.36-7.27 (m, 8H, Ar-H), 5.43 (dd, 1H, *J* = 12.94, 5.13, C20-H), 5.03 (d, 1H, *J* = 10.74, C14-$H_a$), 4.84 (d, 1H, *J* = 12.21, C9-$H_a$), 4.75 (obs d, 1H, *J* = 12.21, C9-$H_b$), 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 dd, 1H, *J* = 10.86, 2.08, C6-$H_a$), 3.86 (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, $H_2O$), 1.16-0.94 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 138.385 (C15), 138.043 (C11), 128.237 (Ar), 128.002 (Ar), 127.775 (Ar), 127.752 (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), 61.642 (C6), 41.325 (C19), 18.141 (C8), 18.057 (C8'), 12.036 (C7). **9cR**: $^{1}$H-NMR (500 MHz, $CDCl_3$): δ 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* = 10.53, C14-$H_a$), 4.85 (d, 1H, *J* = 12.18, C9-$H_a$), 4.75 (obs d, 1H, *J* = 12.18, C9-$H_b$), 4.74 (obs d, 1H, *J* = 10.54, C14-$H_b$), 4.43 (dd, 1H, *J* = 3.87, 1.73, C2-H), 4.10 (obs dd, 1H, *J* = 4.36, 1.73, C1-H), 4.00 (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, 1.73, 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 (dd, 1H, *J* = 14.24, 5.68, C19-$H_a$), 1.94 (dt, 1H, *J* = 14.16, 4.61, C19-$H_b$), 1.16-0.93 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 138.536 (C15), 138.013 (C11), 128.237 (Ar), 128.002 (Ar), 127.775 (Ar), 127.752 (Ar), 127.532 (Ar), 127.502 (Ar), 98.690 (C20), 79.836 (C3), 78.934 (C5), 77.387 (C1), 77.061 (C2), 75.263 (C14), 74.194 (C4), 71.577 (C9), 62.644 (C6), 41.818 (C19), 18.141 (C8), 18.057 (C8'), 12.157 (C7). TOF-ESI-MS *m/z* (rel int): 565 ($[M+Na]^+$, 100).




**(1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-(*E*-γ-methoxyallyl)-6-*O*-triisopropylsilyl-D-glucose, *E*-10a** and **(1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-(*Z*-γ-methoxyallyl)-6-*O*-triisopropylsilyl-D-glucose, *Z*-10a.**[7] In a 5 mL conical flask, methoxymethyltriphenylphosphonium chloride (38 mg, 110.5 μmol, 3.0 equiv) was suspended in 500 μL THF and cooled to 0 °C. Sodium hexamethyldisilazide (1.0M in THF, 92.1 μL, 92.1 μmol, 2.5 equiv) was added slowly via syringe and the bright orange mixture was stirred at 0 °C for 1 h. (1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-formylmethyl-6-*O*-triisopropylsilyl-D-glucose, **9a** (20 mg, 36.85 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 $NH_4Cl$, and extracted 3 × 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 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 an 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.

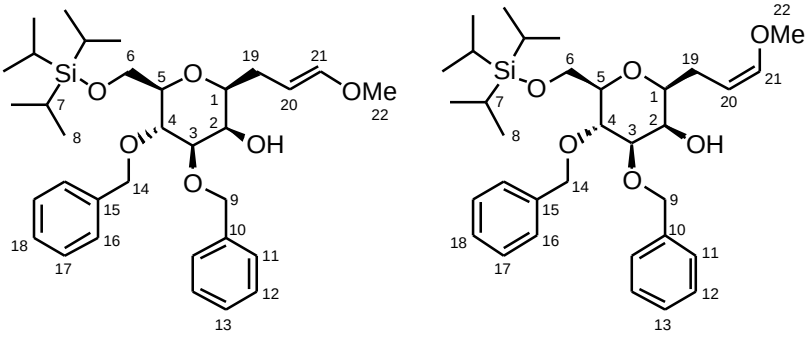
TLC: *Rf* 0.14 (3:1 hexane/EtOAc). ***E*-10a**: $^1$H-NMR (600 MHz, $CDCl_3$): δ 7.40-7.30 (m, 10H, Ar-H), 6.32 (d, 1H, *J* = 13.19, C21-H), 4.99 (d, 1H, *J* = 11.23, C9-$H_a$), 4.84 (d, 1H, *J* = 11.23, C14-$H_a$), 4.80 (d, 1H, *J* = 10.74, C14-$H_b$), 4.79 (quint, 1H, *J* = 6.67, C20-H), 4.72 (d, 1H, *J* = 11.72, C9-$H_a$), 3.99 (d, 2H, *J* = 2.44, C6-$H_2$), 3.75 (t, 1H, *J* = 9.40, C4-H), 3.49 (s, 3H, C22-$H_3$), 3.48 (t, 1H, *J* = 9.03, C3-H), 3.33 (td, 1H, *J* = 9.16, 2.60, C2-H), 3.25 (obs m, 1H, C5-H), 3.16 (ddd, 1H, *J* = 9.46, 6.78, 2.87, C1-H), 2.38 (obs m, 1H, C19-$H_a$), 2.11 (app quint, 1H, *J* = 7.32, C19-$H_b$), 2.04 (d, 1H, *J* = 2.44, C2-OH), 1.18-1.00 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 148.493 (C21), 138.513 (C10), 138.309 (C15), 128.613 (Ar), 128.401 (Ar), 128.321 (Ar), 127.877 (Ar), 127.680 (Ar), 127.564 (Ar), 97.944 (C20), 86.711 (C3), 79.848 (C5), 79.120 (C1), 77.954 (C4), 75.303 (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). ***Z*-10a**: $^1$H-NMR (600 MHz, $CDCl_3$): δ 7.40-7.30 (m, 10H, Ar-H), 5.97 (d, 1H, *J* = 6.348, C21-H), 4.91 (d, 1H, *J* = 11.23, C9-$H_a$), 4.89 (d, 1H, *J* = 11.72, C9-$H_b$), 4.86 (d, 1H, *J* = 11.23, C14-$H_a$), 4.75 (d, 1H, *J* = 10.74, C14-$H_b$), 4.50 (dt, 1H, *J* = 8.38, 6.65, C20-H), 3.96 (d, 2H, *J* = 2.93, C6-$H_2$), 3.70 (t, 1H, *J* = 9.28, C4-H), 3.61 (s, 3H, C22-$H_3$), 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-$H_a$), 2.38 (obs m, 1H, C19-$H_b$), 1.18-1.00 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 147.320 (C21), (138.513, C10), (138.309, C15), 128.613 (Ar), 128.401 (Ar), 128.321 (Ar), 127.877 (Ar), 127.680 (Ar), 127.564 (Ar), 101.943 (C20), 86.266 (C3), 79.965 (C5), 78.894 (C1), 77.707 (C4), 75.356 (C9), 74.887 (C14), 73.554 (C2), 62.591 (C6), 59.626 (C22), 25.970 (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 $C_{33}H_{50}NaO_6Si$ 593.3274; found 593.3270.




**(1*R*)-3,4-Di-*O*-benzyl-1-deoxy-1-(*E*-γ-methoxyallyl)-6-*O*-triisopropylsilyl-D-glucose, *E*-10b** and **(1*R*)-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. (1*R*)-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 $NH_4Cl$, and extracted 3 × 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. 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 an 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). $^1$H-NMR (400 MHz, $CDCl_3$): ***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-$H_a$), 4.74 (d, 1H, *J* = 11.22, *E*-C9-$H_a$), 4.71 (obs dt, 1H, *E*-C20-H), 4.68 (d, 1H, *J* = 11.09, *E*-C14-$H_a$), 4.65 (d, 1H, *J* = 10.80, *E*-C9-$H_b$), 4.65 (obs m, 3H, *Z*-C14-$H_2$, *Z*-C9-H*b*), 4.56 (d, 1H, *J* = 11.54, *E*-C14-$H_b$), 4.43 (dt, 1H, *J* = 8.02, *Z*-C20-H), 3.97 (dd, 2H, *J* = 10.40, 4.60, C6-$H_2$), 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, *Z*-C1-H), 3.68 (m, 2H C1-6-H), 3.56 (s, 3H, *Z*-C22-$H_3$), 3.50 (s, 3H, *E*-C22-$H_3$), 3.49 (obs m, 1H, *Z*-C19-$H_a$), 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-$H_b$), 2.21 (app t, 2H, *J* = 7.06, *E*-C19-$H_2$), 1.15 (m, 42H, *E*-i$Pr_3$Si, *Z*-i$Pr_3$Si). 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 593.3273.

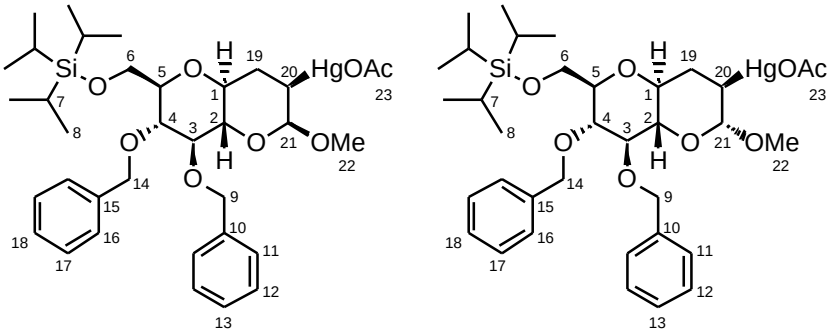



**(1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-(*E*-γ-methoxyallyl)-6-*O*-triisopropylsilyl-D-mannose, *E*-10c** and **(1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-(*Z*-γ-methoxyallyl)-6-*O*-triisopropylsilyl-D-mannose, *Z*-10c.** In a 5 mL conical flask, methoxymethyltriphenylphosphonium chloride (16.5 mg, 48.1 μmol, 3.0 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. (1*S*)-3,4-Di-*O*-benzyl-1-deoxy-1-formylmethyl-6-*O*-triisopropylsilyl-D-mannose (*S*)-hemiacetal, **9cS** and (1*S*)-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 $Et_2O$, poured into 5 mL satd $NH_4Cl$, and extracted 5 × 3 mL $Et_2O$. The combined organic extracts were washed 1 × 5 mL $H_2O$, 1 × 5 mL brine, dried ($MgSO_4$), 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.

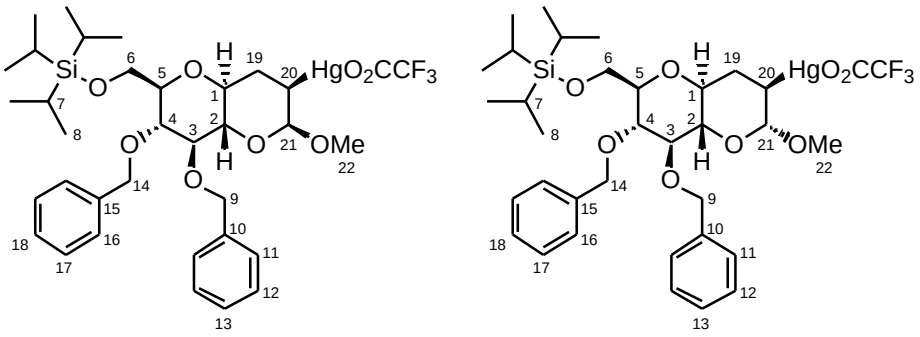
TLC: *Rf* 0.45 (3:1 hexane/EtOAc); *Rf* 0.15 (7:1 hexane/EtOAc). IR (film): 3457 br, 2939, 2864, 1653, 1457, 1429, 1319, 1208, 1093, 1035, 1015, 935, 883. ***E*-10c**: $^1$H-NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J* = 6.84, C11-H, C11'-H), 7.37-7.27 (m, 8H, Ar-H), 6.37 (dt, 1H, *J* = 12.70, 1.22, C21-H), 4.89 (d, 1H, *J* = 10.74, C14-$H_a$), 4.77 (d, 1H, *J* = 11.72, C9-$H_a$), 4.72 (ddd, 1H, *J* = 13.67, 6.99, 5.25, C20-H), 4.69 (d, 1H, *J* = 11.72, C9-$H_b$), 4.68 (d, 1H, *J* = 10.74, C14-$H_b$), 3.93 (m, 3H, C2-H, C6-$H_2$), 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-$H_3$), 3.22 (m, 2H, C1-H, C5-H), 2.33 (obs m, 1H, C19-$H_a$), 2.24 (dddd, 1H, *J* = 14.79, 7.69, 6.53, 1.10, C19-$H_b$), 2.17 (d, 1H, *J* = 4.39, C2-OH), 1.15-0.95 (m, 21H, i$Pr_3$Si). $^{13}$C-NMR (100 MHz, $CDCl_3$): 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**: $^1$H-NMR (500 MHz, $CDCl_3$): 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-$H_a$), 4.78 (d, 1H, *J* = 11.72, C9-$H_a$), 4.69 (d, 1H, *J* = 11.72, C9-$H_b$), 4.68 (d, 1H, *J* = 10.74, C14-$H_b$), 4.42 (td, 1H, *J* = 8.38, 6.59, C20-H), 3.97-3.85 (obs m, 4H, C2-H, C4-H, C6-$H_2$), 3.60 (t, 3H, C22-$H_3$), 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-$H_a$), 2.38 (app quint d, 1H, *J* = 14.16, 7.08, 1.46, C19-$H_b$), 2.34 (obs, 1H, C2-OH), 1.15-0.95 (m, 21H, i$Pr_3$Si). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 147.553 (C21), 138.556 (C15), 138.097 (C10), 128.409 (Ar), 128.321 (Ar), 128.100 (Ar), 128.015 (Ar), 127.790 (Ar), 127.622 (Ar), 102.009 (C20), 83.471 (C3), 79.151 (C5), 77.525 (C1), 75.273 (C14), 74.334 (C4), 71.427 (C9), 67.909 (C2), 62.940 (C6), 59.626 (C22), 25.642 (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

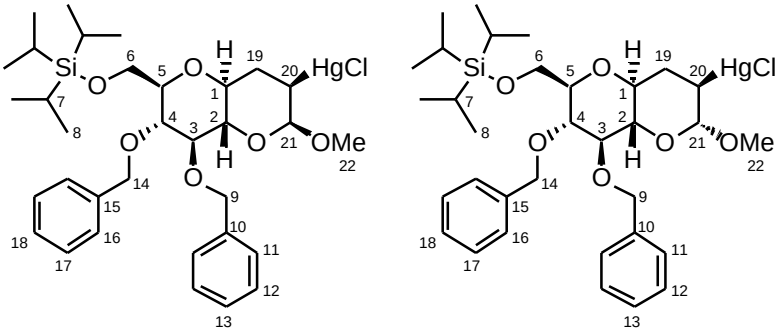


**(1*S*,2*S*,1′*S*,2′*R*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury acetate tetrahydropyrano)-6-*O*-triisopropylsilyl-D-glucose, 11aS** and **(1*S*,2*S*,1′*R*,2′*R*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(1'-methoxy-2'-mercury acetate tetrahydropyrano)-6-*O*-triisopropylsilyl-D-glucose, 11aR.** In a 5 mL conical flask, (1*S*)-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: $^1$H-NMR (400 MHz, $CDCl_3$) **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.

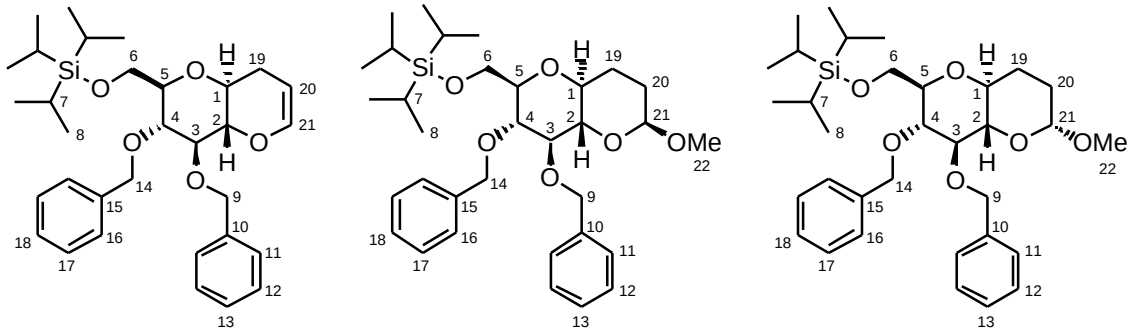
TLC: *Rf* 0.34 (3:1 hexane/EtOAc); *Rf* 0.15 (17:3 hexane/EtOAc). **11aS**: $^1$H-NMR (600 MHz, $CDCl_3$): δ 7.37 (d, 2H, *J* = 7.69, C11-H, C11'-H), 7.35-7.27 (m, 8H, Ar-H), 4.94 (d, 1H, *J* = 11.00, C9-$H_a$), 4.88 (d, 1H, *J* = 10.62, C14-$H_a$), 4.79 (d, 1H, *J* = 10.80, C9-$H_b$), 4.77 (d, 1H, *J* = 3.30, C21-H), 4.70 (d, 1H, *J* = 10.62, C14-$H_b$), 3.93 (m, 2H, C6-$H_2$), 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-$H_3$), 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-$H_2$), 2.05 (s, 3H, OAc), 1.13-0.95 (m, 21H, i$Pr_3$Si). **11aR**: $^1$H-NMR (600 MHz, $CDCl_3$): 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-$H_a$), 4.89 (d, 1H, *J* = 10.62, C14-$H_a$), 4.81 (obs d, 1H, C9-$H_b$), 4.70 (d, 1H, *J* = 10.62, C14-$H_b$), 4.59 (d, 1H, *J* = 9.70, C21-H), 3.93 (m, 2H, C6-$H_2$), 3.72 (obs m, 2H, C3-H, C4-H), 3.53 (s, 3H, C22-$H_3$), 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-$H_a$), 2.05 (s, 3H, OAc), 1.93 (m, 1H, C19-$H_b$), 1.13-0.95 (m, 211H, i$Pr_3$Si). FAB-MS (NBA/NaI) *m/z* (rel int): 853 ([M+Na]$^+$, not detected), 919 (88), 921 (100).



**(1*S*,2*S*,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 **(1*S*,2*S*,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: $^1$H-NMR (400 MHz, $CDCl_3$): **11bS**: δ 2.97 (C20-H); **11bR**: δ 2.83 (C20-H).



**(1*S*,2*S*,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 **(1*S*,2*S*,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, (1*S*,2*S*,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 (1*S*,2*S*,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 $Et_2O$. The combined organic extracts were washed 3 × 5 mL brine, dried ($MgSO_4$), filtered, and evaporated to yield crude **11cS** and **11cR**. The diagnostic C20-H peaks were identified by analogy to **11aS** and **11aR** as follows: $^1$H-NMR (400 MHz, $CDCl_3$): **11cS**: δ 2.74 (C20-H); **11cR**: δ 2.59 (C20-H). Also, the characteristic acetate peak was no longer observed.



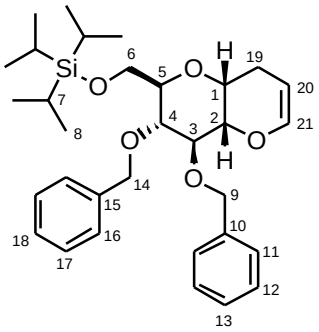
**(1*S*,2*S*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(Δ-1',2'-dihydropyrano)-6-*O*-triisopropylsilyl-D-glucose, 12a**, **(1*S*,2*S*,1′*S*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(1'-methoxy-tetrahydropyrano)-6-*O*-triisopropylsilyl-D-glucose, 13aS**, and **(1*S*,2*S*,1′*R*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(1'-methoxy-tetrahydropyrano)-6-*O*-triisopropylsilyl-D-glucose, 13aR.** In a 5 mL conical flask, (1*S*)-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 $NaHCO_3$, and extracted 3 × 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 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. $^1$H-NMR (500 MHz, $CDCl_3$): 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-$H_a$), 4.90 (d, 1H, *J* = 10.69, C14-$H_a$), 4.81 (d, 1H, *J* = 11.12, C9-$H_b$), 4.72 (d, 1H, *J* = 10.71, C14-$H_b$), 4.69 (td, 1H, *J* = 5.72, 2.10, C20-H), 3.97 (app d, 2H, *J* = 2.57, C6-$H_2$), 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-$H_a$), 2.06 (ddt, 1H, *J* = 16.39, 9.48, 2.35, C19-$H_b$), 1.18-0.98 (m, 21H, $iPr_3Si$). $^{13}$C-NMR (100 MHz, $CDCl_3$): 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* calcd for $C_{32}H_{46}NaO_5Si$ 561.3012; found 561.3011.

**13aS**: TLC: *Rf* 0.30 (9:1 hexane/EtOAc); *Rf* 0.12 (19:1 hexane/EtOAc). $^1$H-NMR (600 MHz, $CDCl_3$): 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-$H_a$),

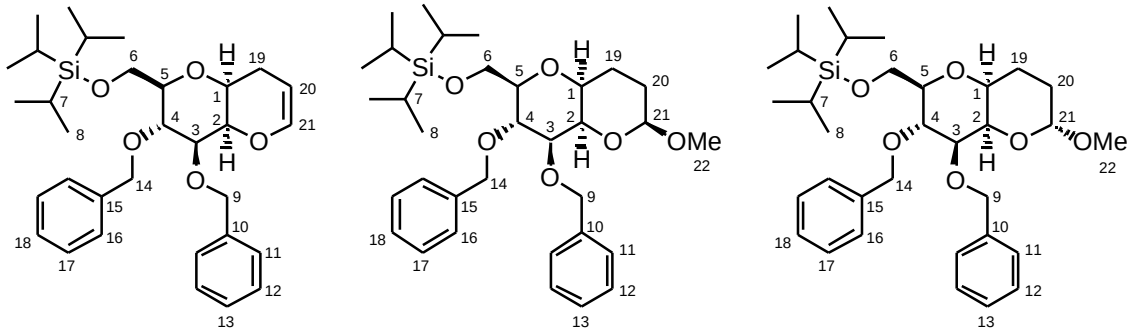
4.89 (d, 1H, *J* = 10.62, C14-$H_a$), 4.80 (d, 1H, *J* = 10.98, C9-$H_b$), 4.72 (obs d, 1H), 4.70 (d, 1H, *J* = 10.62, C14-$H_b$), 3.94 (app d, 2H, J = 2.56, C6-$H_2$), 3.70 (t, 1H, *J* = 9.153, C4-H), 3.63 (t, 1H, *J* = 8.97, C3-H), 3.53 (t, 1H, *J* = 9.52, C2-H), 3.41 (s, 3H, C22-$H_3$), 3.32 (app 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). $^1$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-$H_a$), 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.




**(1*R*,2*S*)-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, (1*R*)-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). $^1$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 (td, 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, $iPr_3Si$). (*tentative assignment) FAB-MS (NBA/NaI) *m/z* (rel int): 561 ($[M+Na]^+$, 15). HRMS (NBA/NaI) *m/z* calcd for $C_{33}H_{50}NaO_6Si$ 561.3012; found 561.3023.



**(1*S*,2*R*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(Δ-1',2'-dihydropyrano)-6-*O*-triisopropylsilyl-D-mannose, 12c**, **(1*S*,2*R*,1′*S*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(1'-methoxy-tetrahydropyrano)-6-*O*-triisopropylsilyl-D-mannose, 13cS**, and **(1*S*,2*R*,1′*R*)-3,4-Di-*O*-benzyl-1,2-dideoxy-1,2-(1'-methoxy-tetrahydropyrano)-6-*O*-triisopropylsilyl-D-mannose, 13cR.** In a 25 mL conical flask, (1*S*)-3,4-di-*O*-benzyl-1-deoxy-1-(γ-methoxyallyl)-6-*O*-triisopropylsilyl-D-mannose, **10c** (2.1 mg, 3.68 μmol, 1.0 equiv), was dried azeotropically by evaporation of benzene three times. Mercuric trifluoroacetate (0.1 mg, 0.234 μmol, 0.06 equiv) was added as a solid, then the flask was placed under a condenser under Ar. 400 μL 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 $Et_2O$, poured into 5 mL satd $NaHCO_3$, and extracted 4 × 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. NMR analysis indicated an 10:38:52 mixture of **12c**, **13cS**, and **13cR**. Purification by silica flash chromatography (19:1 hexane/EtOAc) yielded **12c** (0.4 mg) and **13cS** (0.3 mg) as white solids, and **13cR** (0.5 mg) as a clear oil. Stereochemistry at C1' was assigned based on NOESY and coupling constant data.

**12c**: TLC: *Rf* 0.35 (7:1 hexane/EtOAc); 0.12 (19:1 hexane/EtOAc). $^1$H-NMR (500 MHz, $CDCl_3$): δ 7.40 (d, 2H, *J* = 6.72, C11-H, C11'-H), 7.38-7.28 (m, 8H, Ar-H), 6.40 (app d, 1H, *J* = 5.88, C21-H), 4.96 (d, 1H, *J* = 10.63, C14-$H_a$), 4.82 (d, 1H, *J* = 12.03, C9-$H_a$), 4.73 (obs d, 1H, *J* = 12.03, C9-$H_b$), 4.72 (obs d, 1H, *J* = 10.63, C14-$H_b$), 4.61 (app t, 1H, *J* = 5.32, C20-H), 4.06 (obs d, 1H, *J* = 3.36, C2-H), 4.05 (obs t, 1H, *J* = 9.37, C4-H), 3.99 (dd, 1H, *J* = 11.19, 3.64, C6-$H_a$), 3.94 (dd, 1H, *J* = 11.19, 1.96, C6-$H_b$), 3.64 (obs d, 1H, *J* = 5.32, C1-H), 3.62 (obs dd, 1H, *J* = 9.23, 2.94, C3-H), 3.29 (ddd, 1H, *J* = 9.58, 3.71, 1.75, C5-H), 2.30 (dm, 1H, *J* = 18.19, C19-$H_a$), 2.06 (ddq, 1H, *J* = 17.98, 5.11, 1.47, C19-$H_b$), 1.13-0.98 (m, 21H, $iPr_3Si$). TOF ESI MS *m/z* (rel int): 539 ($[M+H]^+$, 56).

**13cS**: TLC: *Rf* 0.31 (7:1 hexane/EtOAc); 0.07 (19:1 hexane/EtOAc). IR (film): 2941, 2864, 1457, 1363, 1110, 1043, 1018, 883. $^1$H-NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J* = 6.65, C11-H, C11-H'), 7.37-7.28 (m, 8H, Ar-H), 4.98 (d, 1H, *J* = 10.47, C14-$H_a$), 4.83 (obs app s, 1H, C21-H), 4.82 (obs d, 1H, *J* = 12.13, C9-$H_a$), 4.720 (obs d, 1H, *J* = 11.97, C9-$H_b$), 4.716 (obs d, 1H, *J*

= 10.64, C14-$H_b$), 4.09 (obs d, 1H, *J* = 3.49, C2-H), 4.08 (obs t, 1H, *J* = 9.64, C4-H), 4.04 (dd, 1H, *J* = 11.14, 3.49, C6-$H_a$), 3.95 (dd, 1H, *J* = 11.05, 1.58, C6-$H_b$), 3.56 (dd, 1H, *J* = 9.56, 3.57, C3-H), 3.47 (s, 3H, C22-$H_3$), 3.37 (app t, 1H, *J* = 2.91, C1-H), 3.23 (ddd, 1H, *J* = 9.47, 3.49 ,1.66, C5-H), 2.09 (tdd, 1H, *J* = 13.63, 4.63, 3.63, C20-$H_a$), 1.92 (tdd, 1H, *J* = 13.79, 4.60, 2.88, C19-$H_a$), 1.75 (dquint, 1H, *J* = 13.63, 2.49, C19-$H_b$), 1.47 (dm, 1H, *J* = 13.63, C20-$H_b$), 1.15-0.95 (m, 21H, $iPr_3Si$). TOF ESI-MS *m/z* (rel int): 593 ($[M+Na]^+$, 100), 609 ($[M+K]^+$, 47).

**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. $^1$H-NMR (500 MHz, $CDCl_3$): δ 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-$H_a$), 4.73 (d, 1H, *J* = 12.01, C9-$H_a$), 4.66 (obs d, 1H, *J* = 12.01, C9-$H_b$), 4.65 (obs d, 1H, *J* = 10.66, C14-$H_b$), 4.28 (dd, 1H, *J* = 9.90, 1.95, C21-H), 3.97 (dd, 1H, *J* = 11.08, 1.95, C6-$H_a$), 3.94 (obs m, 1H, C6-$H_b$), 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-$H_3$), 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-$H_a$), 1.86 (m, 1H, C20-$H_a$), 1.62 (obs ddd, 1H, *J* = 13.88, 4.65, 3.13, C19-$H_b$), 1.55 (obs dquint, *J* = 12.39, 2.26, 1H, C20-$H_b$), 1.15-0.98 (m, 21H, $iPr_3Si$). TOF ESI-MS *m/z* (rel int): 593 ($[M+Na]^+$, 100), 609 ($[M+K]^+$, 47).

## IV. References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