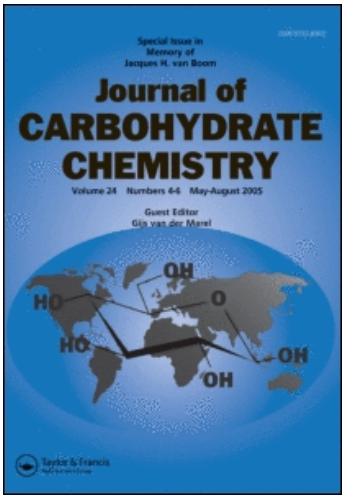

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Syntheses of Branched Non-1-ynitols by Chemoselective Addition of (Trimethylsilyl)-propargylmagnesium Bromide at the Anomeric Center of Side Chain Halogeno Functionalized Carbohydrates

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A convenient method for the syntheses of non-1-ynitols **8a**–**8d**, by chemoselective addition of (trimethylsilyl)-propargylmagnesium bromide at the anomeric center of a 1-unprotected sugar, in the presence of 3-*C*′-halide and 3-*C*′-silyl functions in the side chain is described. In addition, an efficient method for the synthesis of 3-*C*′-hydroxymethyl sugar **3** via the addition of C_1 silyl Grignard reagents to ulose **1** and subsequent oxidation by the Fleming-Tamao method in excellent yields is reported. Also, a suitable acid-catalyzed isomerization of the 1,2-*O*-isopropylidene group to the 2,3-*O*-isopropylidene group (**5a**–**5f**), to get access to the anomeric center, in good to excellent yields has been depicted.

Keywords Alkynes, Carbohydrates, Isomerizations, Grignard reaction

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INTRODUCTION

The known syntheses of glyco-1-ynitols involve the addition of acetylene to the aldehyde function of a sugar.[1] The resulting alkyne functional group is of high synthetic value because of its manageable susceptibility to electrophilic,[2] nucleophilic,[3] and radical attack.[4] Horton et al.[5] and Buchanan et al.[6] described the first syntheses of ynitols, where Buchanan demonstrated as a general procedure that ethynylmagnesium bromide can be added to a variety of sugar hemiacetals to obtain open-chain ynitols.

Here we report a very short-route synthesis of non-1-ynitols with the synthetic complication of a functionalized branched chain, which is susceptible to the C-C coupling reaction conditions. Such expositions are useful for further synthetic manipulations, here intended for the construction of branched, highly functionalized carbocycles after the removal of all the protecting groups, as is indicated by structural correlation in Figure 1. The desired ynitols were synthesized from 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose **1** in only five steps, by the Grignard addition of TMS-propargylmagnesium bromide to the hemiacetal function of the 1-unprotected sugar with a variety of functional groups in the side chain (Fig. 1). Surprisingly, despite of their great synthetic potential, there are no synthetic reports on such open-chain non-1-ynitols to be found in the literature.

RESULTS AND DISCUSSION

Synthesis

For the development of the synthetic route, two different starting points can be considered: In the first case a primary halide is present in the side chain before the addition of TMS-propargylmagnesium bromide to the unprotected hemiacetal function of the protected sugar derivative. In the second case, TMS-propargylmagnesium bromide is added first to the unprotected hemiacetal function of the protected sugar derivative, which then could be followed by an appropriate functionalization of the side chain in the presence of the acetylenic moiety. Considering the latter case, the protection of the

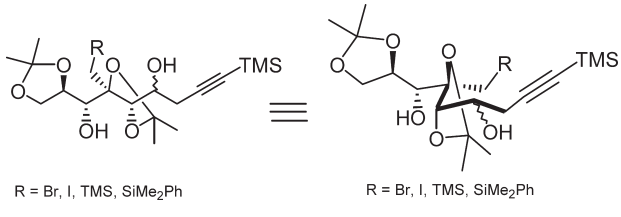
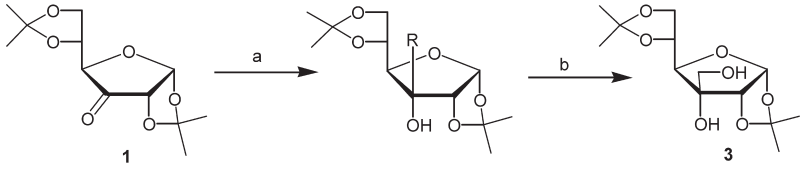


Figure 1: Non-1-ynitol.

side chain primary hydroxyl function has to be chosen carefully before the addition of TMS-propargylmagnesium bromide, because the TMS-protected acetylenic moiety in the non-1-ynitol is probably not compatible with deprotection by hydrogenolysis (benzyl ethers), fluoride sources (silyl ethers), or Lewis acids (acetal-type protecting groups). Therefore, to overcome the problem of selective protection of the side chain hydroxyl function in the precursor compound of the TMS-propargylmagnesium bromide addition reaction, compounds **2a**,[7] **2b**, and **2c**, with a 3-*C*′-silane side chain as a masked hydroxymethyl group equivalent, have been synthesized. The transformation of the C-Si bond to the hydroxymethyl group is possible by the mildly oxidative Fleming-Tamao method,[8] which is even feasible in the presence of an alkyne group.[9]

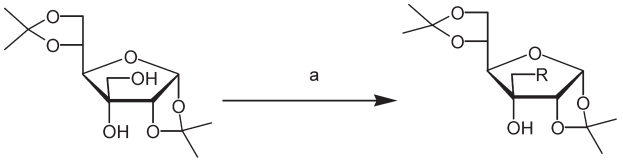
For the synthesis of compounds **2a**–**2c**, 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranosyl-3-ulose **1**[10] was added to four equivalents of the Grignard reagent prepared from the corresponding halogeno-silanes and refluxed under an argon atmosphere for 3 h. This gave solely the *allo*-configured 3-*C*′-silyl sugar derivatives in good yields between 78% and 92% (Sch. 1). On applying the Fleming-Tamao oxidation in a 1:1 mixture of THF and methanol with $KHCO_3$, KF, H_2O_2 or NaOAc, KBr, CH_3CO_3H, CH_3CO_2H (see experimental part), as expected the 3-*C*′-trimethylsilyl branched compound **2a** was inert, or decomposed under more vigorous conditions, but compounds **2b** and **2c** gave the *allo*-configured 3-*C*′-hydroxymethyl sugar **3** in excellent 92% and 93% yield, respectively. The described synthetic sequence is a high-yielding alternative to other known procedures[11] for the synthesis of compound **3** with the benefit that the hydroxymethyl group is present during the synthesis in a masked form.

The subsequent substitution reactions in the side chain of compound **3** (Sch. 2) to a halogen or tosylate turned out to be less easy than expected. A plausible reason could be that the unprotected tertiary hydroxyl function at the adjacent quaternary center takes part in the reaction. Epoxide formation



2a: R = CH_2TMS (92%)[a] –[b]
2b: R = CH_2SiMe_2Ph (88%)[a] 92%[a]
2c: R = CH_2SiMe_2(*i*Pr-O) (78%)[a] 93%[a]

Scheme 1: Reagents and conditions: (a) RMgX (X = Cl or Br), THF, 0 → reflux, 3 h; (b) NaOAc, KBr, CH_3CO_3H 35%, CH_3CO_2H or $KHCO_3$, KF, H_2O_2 30%, THF/MeOH. [a] Yields of isolated products. [b]No reaction, decomposition on applying vigorous conditions.



4a: R= Cl (68%)[a, b]
4b: R = Br (83%)[a]
4c: R = I (97%)[a]
4d: R = OTs (78%)[a, b, c]

Scheme 2: Reagents and conditions: (a) reagent (PPh_3-CCl_4: R = Cl; PPh_3Br_2: R = Br; PPh_3I_2: R = I; TsCl: R = OTs), imidazole, CH_3CN:pyridine (1:1), 60°C. [a]Yields of isolated products. [b]Reaction performed at rt and without the addition of imidazole and CH_3CN. [c]Reaction performed in pyridine:CH_2Cl_2 (1:3).

and even a substitution reaction from *O*-6 have been observed in some cases mentioned below.

The most efficient methods for the syntheses of compounds **4a**–**4d** are depicted in Scheme 2. The 3-*C*′-chloro derivative **4a** was obtained by reacting **3** with PPh_3-CCl_4 in pyridine at rt, in 68% yield. The 3-*C*′-bromo derivative **4b** and the 3-*C*′-iodo derivative **4c** were obtained by reacting **3** with PPh_3Br_2 and PPh_3I_2 in the presence of imidazole in a 1:1 mixture of pyridine and acetonitrile at 60°C, in 83% and 97% yields, respectively. The 3-C′-*O*-tosyl derivative **4d** was obtained by reacting **3** with tosyl chloride in the presence of pyridine in CH_2Cl_2, in 78% yield. The bromo derivative **4b** was recrystallized from an EtOAc-pentane mixture and the structure was confirmed by single crystal X-ray analysis (Fig. 2).

In order to access the anomeric center of compounds **2a**, **2b**, and **4a**–**4c**, the 1,2-*O*-isopropylidene protection was isomerized to the thermodynamically more stable 2,3-*O*-isopropylidene protection, which is possible because of the *cis* orientation of the 2,3-*O*-functions. To achieve optimal reaction conditions,

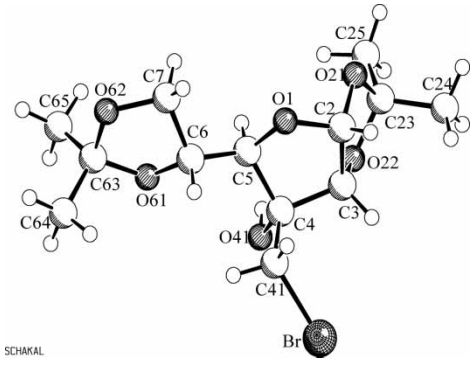
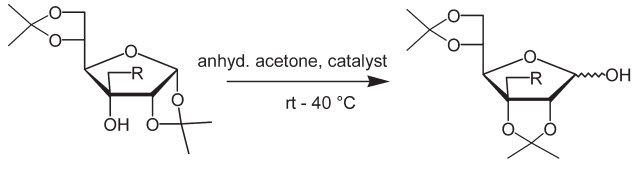


Figure 2: X-ray crystal structure of **4b**.

various acid-catalyzed reactions were tested for the substrates **2a**, **2b**, and **4a**–**4d** as depicted in Scheme 3. The isomerization of the acetonide group depends strongly on the substituent present at the C′-3 position. In anhydrous acetone the substrates with halide functional groups **4a**–**4c** isomerized in the presence of 1% H_2SO_4 in good yields. For compounds **4a**–**4c**, the yields were drastically enhanced by the addition of anhydrous $CuSO_4$ and powdered molecular sieve (4 Å). Use of HCl destroyed the starting material and $Zn(OTf)_2$ catalysis did not initiate any reaction. The isomerization of the tosyl derivative **4d** works with a catalytic amount of HCl or H_2SO_4; however, in the presence of H_2SO_4 the isomerized product **5d** decomposed in a few minutes. Compounds **2a** and **2b** with silyl functional groups isomerized in the presence of $Zn(OTf)_2$, but underwent decomposition with HCl and H_2SO_4.

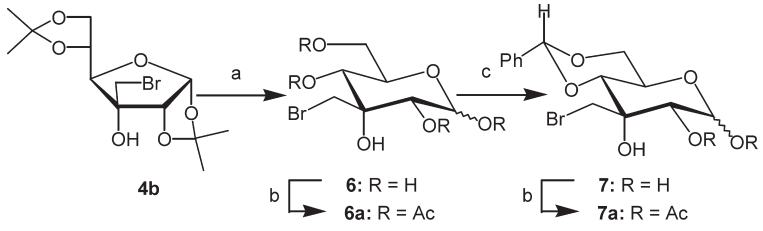
Additionally, compound **4b** was chosen for a transformation to a pyranose-type sugar to be able to study the addition of TMS-propargylmagnesium bromide in comparison to the furanose-type compound. Compound **4b** carrying a bromomethylene group is prone to the acidic conditions necessary for the cleavage of both isopropylidene groups. The best result was obtained by the treatment of compound **4b** with 0.1 N HCl to furnish unprotected compound **6** (Sch. 4). Cleavage was complete in 30 min at 70°C (monitored by TLC). Without further neutralization the reaction mixture was concentrated under reduced pressure. Some decomposition could be observed here. The crude product **6** was subjected to acylation with Ac_2O in pyridine; purification by column chromatography resulted in pure **6a** in 35% yield over both steps.

For the ongoing synthesis the 4,6-OH functions of crude compound **6** were subjected to benzaldehyde dimethyl acetal protection in the presence of a catalytic amount of PTSA · H_2O in DMF at 60°C, resulting in the 4,6-*O*-benzylidene acetal **7**, which was isolated by column chromatography in 32% yield (two steps) as a mixture of anomers (Sch. 4). For analytical reasons compound **7** was acetylated with Ac_2O in pyridine and afforded **7a** as a solid,



catalyst	
H_2SO_4	**5a:** R= Cl (57%)[a, b]
H_2SO_4	**5b:** R = Br (87%)[a, b]
H_2SO_4	**5c:** R = I (70%)[a, b]
HCl	**5d:** R = OTs (48%)[a]
$Zn(OTf)_2$	**5e:** R = TMS (58%)[a]
$Zn(OTf)_2$	**5f:** R = $SiMe_2Ph$ (89%)[a]

Scheme 3: Isomerization of the 1,2-*O*-isopropylidene group. [a]Yields of isolated products. [b]4 Å molecular sieves and $CuSO_4$ were added, reaction performed at 40°C.



Scheme 4: Reagents and conditions: (a) 0.1 N HCl, 70°C, 30 min; (b) Ac_2O, pyridine, rt, 2 h; (c) $PhCH(OMe)_2$, PTSA.H_2O, DMF, 60°C, 4 h, 32% (two steps).

which was further recrystallized from the EtOAc-pentane mixture to furnish the α-anomer in pure form. Under these conditions the tertiary 3-hydroxyl group was not acetylated. Single crystal X-ray analysis confirmed the pyranose ring structure of compound **7a** (Fig. 3).

The addition of (trimethylsilyl)-propargylmagnesium bromide to the 1-unprotected position of the above-described compounds is the focus of this study. As it is generally known, the success of such reactions depends on the amount of free aldehyde, which is in equilibrium with the corresponding hemiacetal form under the given experimental conditions. The furanoses **5b** ($R = CH_2Br$), **5c** ($R = CH_2I$), **5e** ($R = CH_2SiMe_3$), and **5f** ($R = CH_2SiMe_2Ph$) and the pyranose **7** ($R = CH_2Br$) were chosen for the addition reaction. (Trimethylsilyl)-propargylmagnesium bromide was prepared by the Groth[12] procedure, with anhydrous $CeCl_3$ as an additive. When the Grignard reagent is prepared without $CeCl_3$, a major side product is formed, involving the migration of the silyl group. Predominantly allenylic alcohols instead of propargyl alcohols were observed. The Grignard reagent was prepared in diethyl ether and the magnesium was activated by adding dibromomethane, which was added to a solution of anhydrous $CeCl_3$ (excess) in THF. Then the reaction mixture was stirred for 2 h at 0°C. After 2 h the fully protected anomeric free furanose (**5b**, **5c**, **5e**, and **5f**) was added to the Grignard reagent at −78°C, slowly warmed to rt, and then stirred for 12 h (Sch. 5).

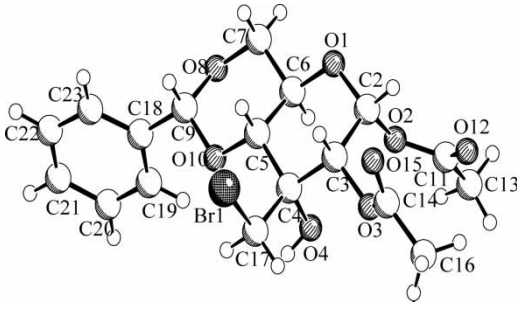
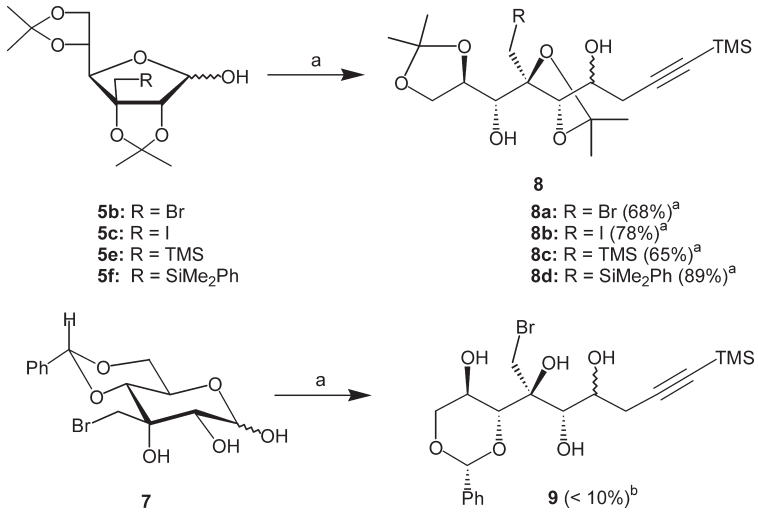


Figure 3: X-ray crystal structure of **7a**.



Scheme 5: Reagents and conditions: (a) Mg, TMSC ≡ CCH_2Br, ether, 0°C → 10°C, $CeCl_3$/THF, −78°C → rt. [a]Yields of isolated products. [b]Not isolated.

The reaction was monitored by TLC and hydrolyzed by adding NH_4Cl. Workup and column chromatography furnished a diastereomeric mixture of (D-*allo*/D-*altro*) non-1-ynitols of type **8** in good to excellent yields. The non-1-ynitols were characterized by ^1H NMR spectroscopy. The addition of the Grignard reagent was chemoselective at the aldehyde function in the presence of a halide group. Even though the primary halide should be susceptible to displacement by the Grignard reagent, we did not observe any halide substituted product.

On the other hand, the partially protected anomeric free pyranose **7**, when treated with an excess of Grignard reagent, gave a diastereomeric mixture of (D-*allo*/D-*altro*) non-1-ynitol **9** in low yield (less than 10%, estimated by TLC). The major side products were compounds, in which the bromide was substituted by oxygen. The yield of **9** could not be improved, indicating that the structural requirements are not comparable to those of the furanose derivatives **5**. The crude product **9** was confirmed by HRMS analysis.

In conclusion, this paper describes a concise method for the synthesis of open-chain non-1-ynitols (**8a**, **8b**, **8c**, **8d**) by the addition of (trimethylsilyl)-propargylmagnesium bromide to anomeric unprotected branched chain hexofuranose derivatives **5b**, **5c**, **5e**, and **5f** in good to excellent yields. All non-1-ynitols feature a functional group in the side chain, such as **5b** ($R = CH_2Br$), **5c** ($R = CH_2I$), **5e** ($R = CH_2SiMe_3$), and **5f** ($R = CH_2SiMe_2Ph$), which can be used as a potential entity in further functional group transformations. Compounds of type **5** are easily obtained by specific acid-catalyzed isomerization from the corresponding 1,2-*O*-isopropylidene derivatives of types **2** or **4**. The methyl-silyl branched compounds **2a**–**c** were obtained by a *Grignard*-type

addition of the corresponding halogeno-silyl compounds to 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose **1** in very good yields and **2b** and **2c** were converted to hydroxymethyl compound **3** by the mild Fleming-Tamao oxidation. Furthermore, only a few methods worked for the synthesis of the side chain halogenated compounds of type **4** in good yields.

EXPERIMENTAL

General

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with 0.2% ethanolic solution of naphthoresorcinol and 2 N H_2SO_4 (v/v 1:1) followed by heating. Flash chromatography was performed using silica gel Merck 60 (particle size 230–400 mesh). Nuclear magnetic resonance spectra were recorded on a Bruker ARX300 spectrometer. The chemical shift is specified as δ in ppm and the signal of the solvent was used as the internal standard ($CDCl_3$ ^1H: $\delta = 7.24$ ppm, ^{13}C: $\delta = 77.0$ ppm, C_6D_6 ^1H: $\delta = 7.16$ ppm, ^{13}C: $\delta = 128.0$ ppm). Optical rotations were recorded on a Perkin Elmer 341 Polarimeter (d = 589 nm, 1 dm cell). Elemental analyses were carried out with a CHN-RAPID of Heraeus. Electrospray ionization mass (MS-ESI) spectra were recorded on a Quattro LCZ (Waters-Micromass, Manchester, UK) with nanospray inlet.

General Procedure for *O*-Acetylation

The compound with free hydroxyls is dissolved in a mixture of dry pyridine and acetic anhydride (v/v 2:1). The reaction mixture is stirred at rt until the compound is completely converted, which can take hours to 1 day (monitored by TLC). The reaction may be accelerated by the addition of a catalytic amount of *N*,*N*-dimethyl aminopyridine (DMAP). The solvent is then evaporated under reduced pressure and traces of pyridine are removed by coevaporation with toluene. The crude product is purified by extraction from water with CH_2Cl_2 and, if necessary, by column chromatography.

General Procedure 1 for Synthesis of 3-*C*-silyl derivatives (2a–2c)

To a suspension of magnesium turnings (4.1 equiv) in dry THF (1.5 M) was added the appropriate silyl chloride (4.0 equiv) in dry THF (1.5 M). The Grignard reaction was initiated by adding a small amount of iodine. The

reaction mixture was refluxed for 1 h under argon atmosphere and then cooled to rt to furnish the Grignard reagent. Ulose (1.0 equiv) dissolved in dry THF (1 M) was added slowly to the mixture at rt. Then the reaction mixture was refluxed until the reaction was complete (usually 2–3 h; the progress of the reaction was monitored by TLC). The reaction was stopped by adding saturated aqueous solution of NH_4Cl (5–20 mL). The THF was removed under reduced pressure and the crude reaction mixture was back-extracted three times with CH_2Cl_2 (30 mL). The combined organic phases were washed with water and brine, dried over $MgSO_4$, filtered, and concentrated to yield crude product. The crude product was purified by flash column chromatography (cyclohexane-EtOAc) to provide the desired product.

1,2;5,6-Di-*O*-isopropylidene-3-*C*-(trimethylsilyl)methyl-α-D-*allo*-furanose (2a)

This was prepared as described in general procedure 1 from ulose **1** (3.0 g, 11.7 mmol). Purification on silica gel (cyclohexane-EtOAc; 4:1) afforded pure **2a** (3.7 g, 10.7 mmol, 92%) as a white solid; mp 103°C; $[\alpha]_D^{20}$ +23.3 (c = 1.00, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9H, TMS), 0.65 (d, J = 14.8 Hz, 1H, C<u>H</u>TMS), 1.10 (d, J = 14.8 Hz, 1H, C<u>H</u>TMS), 1.34, 1.36, 1.44, 1.57 (4 × s, 4 × 3H, 4 × C<u>H</u>$_3$-^{i}Pr), 2.80 (s, 1H, OH), 3.75 (d, J = 7.4 Hz, 1H, 4-H), 3.90 (dd, J = 5.5 Hz, J = 8.0 Hz, 1H, 6′-H), 4.10 (dd, J = 6.0 Hz, J = 8.0 Hz, 1H, 6-H), 4.15 (ddd, J = 5.5 Hz, J = 6.0 Hz, J = 7.4 Hz, 1H, 5-H), 4.25 (d, J = 3.7 Hz, 1H, 2-H), 5.69 (d, J = 3.7 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.4 (3 × C, TMS), 20.5 (C, <u>C</u>H$_2$TMS), 25.2, 26.3, 26.5, 26.5 (4 × C, C(<u>C</u>H$_3$)-^{i}Pr), 67.3 (C-6), 73.5 (C-5), 82.9 (C-2), 83.2 (C-4), 93.7 (C-3), 103.6 (C-1), 109.1, 112.5 (2 × C, C$_q$-^{i}Pr).

MS (EI): m/z = 346 (2) [M^+], 331 (2) [M^+ – CH_3], 273 (2) [375 – C_3H_6O], 215 (28) [M^+ – $C_6H_{12}O_2$], 101 (36) [$C_5H_9O_3^+$], 73 [$SiMe_3$], 59 (28) [$C_3H_7O^+$].

Anal. Calcd. for $C_{16}H_{30}O_6S_i$: C, 55.46; H, 8.73. Found: C, 55.54; H, 9.00.

1,2;5,6-Di-*O*-isopropylidene-3-*C*-(dimethylphenylsilyl) methyl-α-D-*allo*-furanose (2b)

This was prepared as described in general procedure 1 from ulose **1** (0.875 g, 3.4 mmol). Purification on silica gel (cyclohexane-EtOAc; 5:1) afforded pure **2b** (1.22 g, 3.0 mmol, 88%) as a colorless oil; $[\alpha]_D^{20}$ +10.9 (c = 1.00, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.37, 0.44 (2 × s, 2 × 3H, 2 × SiMe), 0.85 (d, J = 14.0 Hz, 1H, C<u>H</u>SiMe$_2$Ph), 1.15, 1.33 (2 × s, 2 × 3H, 2 × C<u>H</u>$_3$-^{i}Pr), 1.35 (d, J = 14.0 Hz, 1H, C<u>H</u>SiMe$_2$Ph), 1.39, 1.50 (2 × s, 2 × 3H, 2 × C<u>H</u>$_3$-^{i}Pr), 2.57 (s, 1H, OH), 3.71 (d, J = 7.2 Hz, 1H, 4-H), 3.90 (dd,

$J = 6.2$ Hz, $J = 8.0$ Hz, 1H, 6′-H), 4.02 (d, $J = 3.6$ Hz, 1H, 2-H), 4.06 (dd, $J = 5.6$ Hz, $J = 8.0$ Hz, 1H, 6-H), 4.14 (ddd, $J = 5.6$ Hz, $J = 6.2$ Hz, $J = 7.2$ Hz, 1H, 5-H), 5.46 (d, $J = 3.6$ Hz, 1H, 1-H), 7.28–7.36 (m, 3H, Ar), 7.50–7.57 (m, 2H, Ar).

^{13}C NMR ($CDCl_3$, 75 MHz) δ –1.64 (C, $SiCH_3$), –1.05 (C, $SiCH_3$), 26.1, 26.5, 27.0, 27.5, (4 × C, C($\underline{C}H_3$)-^{i}Pr), 29.5 (C, $\underline{C}H_2SiMe_2Ph$), 64.0 (C-6), 73.1 (C-5), 81.2 (C-3), 82.6, 83.1 (C-2, C-4), 103.6 (C-1), 109.9, 112.6 (2 × C, C_q-^{i}Pr), 127–140 (6 × C, Ar).

Anal. Calcd. for $C_{21}H_{32}O_6S_i$: C, 61.73; H, 7.89. Found: C, 62.02; H, 8.01.

1,2;5,6-Di-*O*-isopropylidene-3-*C*-(isopropoxydimethylsilyl) methyl-α-D-*allo*-furanose (2c)

This was prepared as described in general procedure 1 from ulose **1** (0.125 g, 0.49 mmol). Purification on silica gel (cyclohexane-EtOAc; 6:1) afforded pure **2c** (0.149 g, 0.38 mmol, 78%) as a yellow oil; $[\alpha]_D^{20}$ +32.6 (c = 1.00, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.16, 0.25 (2 × s, 2 × 3H, 2 × SiMe), 0.73 (d, $J = 15.2$ Hz, 1H, C$\underline{H}$SiMe$_2$O-^{i}Pr), 1.07 (d, $J = 15.2$ Hz, 1H, C$\underline{H}$SiMe$_2$O-^{i}Pr), 1.11 (d, $J = 2.4$ Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.14 (d, $J = 2.4$ Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.30, 1.32, 1.40, 1.54 (4 × s, 4 × 3H, 4 × C$\underline{H}_3$-^{i}Pr), 2.78 (s, 1H, OH), 3.74 (d, $J = 7.6$ Hz, 1H, 4-H), 3.90 (dd, $J = 5.6$ Hz, $J = 8.0$ Hz, 1H, 6′-H), 4.30 (m, 2H, SiOC$\underline{H}$(CH$_3$)$_2$, 6-H), 4.09 (ddd, $J = 5.6$ Hz, $J = 6.0$ Hz, $J = 7.6$ Hz, 1H, 5-H), 4.53 (d, $J = 3.6$ Hz, 1H, 2-H), 5.65 (d, $J = 3.6$ Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.4 (C, $SiCH_3$), 0.87 (C, $SiCH_3$), 21.0 (C, $\underline{C}H_2SiMe_2O$-^{i}Pr), 25.3, 25.7, 25.9, 26.0, 26.4, 26.6 (6 × C, C($\underline{C}H_3$)-^{i}Pr, CH($\underline{C}H_3$)$_2$), 65.2(C, SiO$\underline{C}$H(CH$_3$)$_2$), 67.6 (C-6), 73.7 (C-5), 79.4(C-3), 82.7, 83.2 (C-2, C-4), 103.6 (C-1), 109.2, 112.4 (2 × C, C_q-^{i}Pr).

MS (EI): m/z = 375 (8) [$M^+ - CH_3$], 317 (1) [375 – C_3H_6O], 259 (40) [$M^+ - C_6H_{12}O_2$], 201 (10) [259 – C_3H_6O], 117 (89) [$SiMe_2O^iPr^+$], 59 (30) [$C_3H_7O^+$].

Anal. Calcd. for $C_{18}H_{34}O_7S_i$: C, 55.36; H, 8.77. Found: C, 55.41; H, 8.98.

1,2;5,6-Di-*O*-isopropylidene-3-*C*-hydroxymethyl-α-D-*allo*-furanose (3)

To a solution of **2b** (0.10 g, 0.24 mmol) in acetic acid (1.5 mL) was added NaOAc (0.052 g, 0.72 mmol) and KBr (0.034 g, 0.28 mmol) and the mixture was cooled to 0°C. Then slowly dropwise 35% solution of CH_3CO_3H in acetic acid (0.29 mL, 1.4 mmol) was added and after 10 min again 35% solution of CH_3CO_3H in acetic acid (0.9 mL, 4.3 mmol) and NaOAc (0.018 g, 2.2 mmol) were added. The orange-colored solution was slowly warmed to rt and stirred for 90 min; TLC analysis showed completion of reaction. The reaction was quenched by adding a saturated aqueous solution of $Na_2S_2O_3$.

The organic solvents were removed under reduced pressure and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL); the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude product. The crude product was purified by flash column chromatography (cyclohexane-EtOAc; 2:1) and afforded pure **3** (0.065 g, 0.22 mmol, 92%) as a colorless oil; $[\alpha]_D^{20}$ +47.5 (c = 0.80, CH_3OH).

To a solution of **2c** (0.80 g, 2.05 mmol) in THF-methanol (1:1; 20 mL) was added $KHCO_3$ (0.20 g, 2.05 mmol), KF (0.12 g, 2.05 mmol), and 30% solution of H_2O_2 in water (0.52 mL, 8.2 mmol), and the resulting reaction mixture was stirred at rt. The reaction monitoring by TLC showed completion in 1 h. The reaction mixture was cooled to 0°C and quenched by adding saturated aqueous solution of $Na_2S_2O_3$. The organic solvents were removed under reduced pressure and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL); the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to give the crude product. The crude product was purified by flash column chromatography (cyclohexane-EtOAc; 3:2) and furnished **3** (0.553 g, 1.9 mmol, 93%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33, 1.34, 1.44, 1.56 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 2.88 (s, 1H, OH), 3.53 (d, J = 12.0 Hz, 1H, C$\underline{H}'$-OH), 3.82 (d, J = 8.4 Hz, 1H, 4-H), 3.87 (d, J = 12.0 Hz, 1H, C$\underline{H}$-OH), 3.92 (dd, J = 6.4 Hz, J = 8.4 Hz, 1H, 6′-H), 4.06 (dd, J = 6.0 Hz, J = 8.4 Hz, 1H, 6-H), 4.15 (ddd, J = 6.0 Hz, J = 6.4 Hz, J = 8.4 Hz, 1H, 5-H), 4.54 (d, J = 4.0 Hz, 1H, 2-H), 5.75 (d, J =4.0 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.9, 26.4, 26.4, 26.5 (4 × C, C($\underline{C}H_3$)$_2$-^{i}Pr), 62.3 (C, CH_2OH), 67.2 (C-6), 73.04 (C-5), 79.5 (C-3), 80.5 (C-2), 81.1 (C-4), 103.6 (C-1), 109.7 (C_q-^{i}Pr), 112.5 (C_q-^{i}Pr).

HRMS-ESI(+): m/z calcd for $C_{13}H_{22}O_7Na$ $[M + Na]^+$ 313.1263. Found: 313.1265.

Anal. Calcd for $C_{13}H_{22}O_7$: C, 53.78; H, 7.64. Found: C, 53.91; H, 7.69.

3-*C*-Chloromethyl-1,2;5,6-di-*O*-isopropylidene-α-D-*allo*-furanose (4a)

To a solution of compound **3** (1.0 g, 3.4 mmol) in dry pyridine (30 mL) was added PPh_3 (1.78 g, 6.8 mmol), which was followed by dropwise addition of CCl_4 (0.58 mL, 3.75 mmol) and stirred under argon atmosphere at rt for 24 h. After 24 h, TLC analysis showed presence of starting material. The reaction was continued by adding one more equivalent of PPh_3 and CCl_4; after 48 h TLC analysis showed complete consumption of starting material. The reaction was stopped by adding CH_3OH; solvents were concentrated under reduced pressure and coevaporated with toluene. The crude reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic phases were washed with brine, dried over

$MgSO_4$, filtered, and concentrated to give a yellow oil, which was further purified by flash column chromatography (cyclohexane-EtOAc; 5:1) and furnished **4a** (0.71 g, 2.3 mmol, 68%) as a white solid; mp 106°C; $[\alpha]_D^{20}$ −11.0 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32, 1.36, 1.42, 1.57 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 2.96 (s, 1H, OH), 3.57 (d, J = 12.0 Hz, 1H, C$\underline{H}'$-Cl), 3.82 (d, J = 8.2 Hz, 1H, 4-H), 3.90 (d, J = 12.0 Hz, 1H, C$\underline{H}$-Cl), 3.92 (dd, J = 4.0 Hz, J = 7.8 Hz, 1H, 6′-H), 4.07 (ddd, J = 3.6 Hz, J = 4.0 Hz, J = 8.2 Hz, 1H, 5-H), 4.15 (dd, J = 3.6 Hz, J = 7.8 Hz, 1H, 6-H), 4.60 (d, J = 4.0 Hz, 1H, 2-H), 5.77 (d, J = 4.0 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.2, 27.5, 27.8, 27.9 (4 × C, C($\underline{C}H_3$)$_2$-^{i}Pr), 51.2 (C, $\underline{C}H_2Cl$) 65.3 (C-6), 75.5 (C-5), 76.8 (C-3), 81.5, 81.9 (2 × C, C-2, C-4), 104.9 (C-1), 110.9 (C_q-^{i}Pr), 114.5 (C_q-^{i}Pr).

MS (EI): m/z = 257 [M^+ − CH_3-HCl].

3-*C*-Bromomethyl-1,2;5,6-di-*O*-isopropylidene-α-D-*allo*-furanose (4b)

To a solution of compound **3** (4.2 g, 14.5 mmol) and imidazole (3.95 g, 58.0 mmol) in dry pyridine-CH_3CN (1:1, 750 mL) was added PPh_3Br_2 (12.4 g, 29.0 mmol) in small portions under argon atmosphere with vigorous stirring. The reaction mixture was heated at 60°C for 5 h. After the completion of the reaction, solvents were evaporated under reduced pressure and codistilled with toluene. The crude reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a yellow oil, which was further purified by normal pressure column chromatography (cyclohexane-EtOAc; 4:1) and afforded pure **4b** (4.25 g, 12.1 mmol, 83%) as a white solid; for single crystal X-ray analysis **4b** was recrystalized from EtOAc-pentane mixture; mp 112°C; $[\alpha]_D^{20}$ −13.2 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32, 1.36, 1.42, 1.57 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 2.96 (s, 1H, OH), 3.40 (d, J = 12.0 Hz, 1H, C$\underline{H}'$-Br), 3.78 (d, J = 8.2 Hz, 1H, 4-H), 3.82 (d, J = 12.0 Hz, 1H, C$\underline{H}$-Br), 3.85 (dd, J = 4.0 Hz, J = 7.8 Hz, 1H, 6′-H), 4.05 (ddd, J = 3.6 Hz, J = 4.0 Hz, J = 8.2 Hz, 1H, 5-H), 4.15 (dd, J = 3.6 Hz, J = 7.8 Hz, 1H, 6-H), 4.60 (d, J = 4.0 Hz, 1H, 2-H), 5.75 (d, J = 4.0 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.2, 27.6, 27.8, 27.9 (4 × C, C($\underline{C}H_3$)$_2$-^{i}Pr), 31.2 (C, CH_2Br), 65.3 (C-6), 75.5 (C-5), 76.8 (C-3), 80.5 (C-2), 81.9 (C-4), 104.6 (C-1), 110.7 (C_q-^{i}Pr), 114.5 (C_q-^{i}Pr).

MS-ESI(+): m/z 375.1 [M + Na]$^+$.

Anal. Calcd. for $C_{13}H_{21}Br\ O_6$: C, 44.37; H, 5.99. Found: C, 44.37; H, 6.01.

3-*C*-Iodomethyl-1,2;5,6-di-*O*-isopropylidene-α-D-*allo*-furanose (4c)

It was prepared in the same manner as **4b**, from **3** (3.8 g, 13.1 mmol) and the halogenating reagent PPh_3I_2 (13.5 g, 26.0 mmol); purification by flash column chromatography (cyclohexane-EtOAc; 2:1), afforded pure **4c** (5.04 g, 12.6 mmol, 97%) as a white solid; mp 119°C; $[\alpha]_D^{20}$ −15.8 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29, 1.32, 1.38, 1.53 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 2.93 (s, 1H, OH), 3.11 (d, J = 11.2 Hz, 1H, C$\underline{H}'$-I), 3.63 (d, J = 11.2 Hz, 1H, C$\underline{H}$-I), 3.83 (d, J = 8.0 Hz, 1H, 4-H), 3.87 (dd, J = 4.0 Hz, J = 7.8 Hz, 1H, 6′-H), 4.05 (ddd, J = 3.6 Hz, J = 4.0 Hz, J = 8.0 Hz, 1H, 5-H), 4.06 (dd, J = 3.6 Hz, J = 7.8 Hz, 1H, 6-H), 4.42 (d, J = 4.0 Hz, 1H, 2-H), 5.71 (d, J = 4.0 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4 (C, $\underline{C}H_2$I), 25.6, 27.0, 27.1, 32.1 (4 × C, C($\underline{C}H_3$)$_2$-^{i}Pr), 68.3 (C-6), 73.3 (C-5), 73.7 (C-3), 83.1, 84.8 (2 × C, C-2, C-4), 103.9 (C-1), 110.4 (C_q-^{i}Pr), 113.3 (C_q-^{i}Pr).

Anal. Calcd. for $C_{13}H_{21}I\,O_6$: C, 39.01; H, 5.29. Found: C, 39.36; H, 4.83.

1,2;5,6-Di-*O*-isopropylidene-3-*C*-tosyloxymethyl-α-D-*allo*-furanose (4d)

To a cooled solution of hydroxy compound **3** (0.43 g, 1.49 mmol) in dry CH_2Cl_2 (18 mL) and dry pyridine (6 mL) was added *p*-TsCl (0.57 g, 2.98 mmol) at 0°C; the resulting mixture was stirred at rt for 48 h. Another portion of *p*-TsCl (0.43 g, 1.49 mmol) was added for complete consumption of starting material, which was stirred at rt for another 24 h. The reaction was quenched with water and pyridine was removed in vacuo; the residue was extracted with Et_2O (3 × 15 mL). Evaporation of the solvent under reduced pressure and purification by flash column chromatography (cyclohexane-EtOAc; 2:1) yielded pure **4d** (0.513 g, 1.16 mmol, 78%) as a white solid; mp 117°C; $[\alpha]_D^{20}$ +75.6 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25, 1.37, 1.38, 1.54 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 2.06 (s, 3H, Ts-CH_3), 3.80 (d, J = 8.0 Hz, 1H, 4-H), 3.87 (ddd, J = 5.6 Hz, J = 6.0 Hz, J = 8.0 Hz, 1H, 5-H), 3.97 (dd, J = 6.0 Hz, J = 10.4 Hz, 1H, 6′-H), 4.01 (dd, J = 5.6 Hz, J = 10.4 Hz, 1H, 6-H), 4.13 (d, J = 10.4 Hz, 1H, C$\underline{H}_2$-OTs), 4.29 (d, J = 10.4 Hz, 1H, C$\underline{H}_2$-OTs), 4.48 (d, J = 4.0 Hz, 1H, 2-H), 5.71 (d, J = 4.0 Hz, 1H, 1-H), 7.34 (d, J = 8.0 Hz, 2H, Ar), 7.80 (d, J = 8.0 Hz, 2H, Ar).

General Procedure 2 for the Synthesis of (5a–5c)

To a solution of anhydrous acetone (25 mL) containing conc. H_2SO_4 (5 μL) was added compound **4a**–**4c** (1 mmol) under argon atmosphere, which was followed by the addition of $CuSO_4$ (1.0 g) and 4° molecular sieves (1.0 g) at rt. The resulting reaction mixture was warmed to 40°C and stirred for 48 h. The

reaction mixture was quenched by adding NH_4OH; the white solid separated was filtered and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (cyclohexane-EtOAc), which provided the desired product.

3-*C*-Chloromethyl-2,3;5,6-di-*O*-isopropylidene-D-*allo*-furanose (5a)

This was prepared as described in general procedure 2 from **4a** (0.020 g, 0.065 mmol). Purification on silica gel (cyclohexane-EtOAc; 4:1) afforded pure **5a** (0.0113 g, 0.037 mmol, 57%) as a white solid; mp 112°C; $[\alpha]_D^{20}$ −14.5 (c = 0.5, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34, 1.42, 1.50, 1.57 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 3.50 (d, J = 12.0 Hz, 1H, C$\underline{H}'$-Cl), 3.54 (d, J = 12.0 Hz, 1H, C$\underline{H}$-Cl), 3.67 (dd, J = 5.2 Hz, J = 12.0 Hz, 1H, 6′-H), 3.88 (dd, J = 2.8 Hz, J = 12.0 Hz, 1H, 6-H), 3.98 (ddd, J = 2.8 Hz, J = 5.2 Hz, J = 8.4 Hz, 1H, 5-H), 4.06 (d, J = 8.4 Hz, 1H, 4-H), 4.42 (d, J = 4.0 Hz, 1H, 2-H), 5.48 (d, J = 4.0 Hz, 1H, 1-H).

Anal. Calcd. for $C_{13}H_{21}ClO_6$: C, 50.57; H, 6.86. Found: C, 50.21; H, 6.80.

3-*C*-Bromomethyl-2,3;5,6-di-*O*-isopropylidene-D-*allo*-furanose (5b)

This was prepared as described in general procedure 2 from **4b** (0.12 g, 0.34 mmol). Purification on silica gel (cyclohexane-EtOAc; 5:1) afforded pure **5b** (0.104 g, 0.3 mmol, 87%) as a white solid; mp 120°C; $[\alpha]_D^{20}$ −17.4 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31, 1.37, 1.46, 1.54 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 2.20 (s, 1H, OH), 3.33 (d, J = 20.4 Hz, 1H, C$\underline{H}'$-Br), 3.40 (d, J = 20.4 Hz, 1H, C$\underline{H}$-Br), 3.63 (dd, J = 9.2 Hz, J = 12.0 Hz, 1H, 6′-H), 3.82 (dd, J = 2.8 Hz, J = 12.0 Hz, 1H, 6-H), 3.94 (ddd, J = 2.8 Hz, J = 8.4 Hz, J = 9.2 Hz, 1H, 5-H), 4.04 (dd, J = 1.2 Hz, J = 8.4 Hz, 1H, 4-H), 4.43 (dd, J = 1.2 Hz, J = 4.0 Hz, 1H, 2-H), 5.45 (d, J = 4.0 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.3, 25.7, 26.7, 27.5 (4 × C, C(C$\underline{H}_3$)$_2$-^{i}Pr), 38.1 (CH_2, CH_2Br), 64.0 (C-6), 72.3 (C-5), 75.6 (C-3), 78.1, 80.3 (2 × C, C-2, C-4), 97.4 (C-1), 110.3 (C_q-^{i}Pr), 112.6 (C_q-^{i}Pr).

Anal. Calcd. for $C_{13}H_{21}Br\ O_6$: C, 44.37; H, 5.99. Found: C, 44.07; H, 5.78.

3-*C*-Iodomethyl-2,3;5,6-di-*O*-isopropylidene-D-*allo*-furanose (5c)

This was prepared as described in general procedure 2 from **4c** (0.157 g, 0.39 mmol). Purification on silica gel (cyclohexane-EtOAc; 5:1) afforded pure

5c (0.110 g, 0.27 mmol, 70%) as a white solid; mp 120°C; $[\alpha]_D^{20}$ −18.5 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30, 1.39, 1.49, 1.58 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 2.89 (s, 1H, OH), 3.65 (d, J = 12.0 Hz, 1H, C$\underline{H}'$-I), 3.87 (d, J = 12.0 Hz, 1H, C$\underline{H}$-I), 3.89 (dd, J = 5.2 Hz, J = 8.8 Hz, 1H, 6′-H), 4.05 (dd, J = 6.0 Hz, J = 8.8 Hz, 1H, 6-H), 4.09 (d, J = 10.0 Hz, 1H, 4-H), 4.20 (ddd, J = 5.2 Hz, J = 6.0 Hz, J = 10.0 Hz, 1H, 5-H), 4.40 (s, 1H, 2-H), 5.34 (d, J_{H1OH} = 3.6 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.0 ($\underline{C}H_2$, CH_2I), 25.9, 27.3, 28.4, 28.8 (4 × C, C($\underline{C}H_3)_2$-^{i}Pr), 68.5 (C-6), 76.0 (C-5), 91.7 (C-3), 88.1, 91.9 (2 × C, C-2, C-4), 101.6 (C-1), 110.7 (C_q-^{i}Pr), 114.6 (C_q-^{i}Pr).

MS (EI): m/z = 385 (92) [M^+ − CH_3], 327 (12) [385 − C_3H_6O], 267 (12) [385 − $C_6H_{12}O_2$], 141 (5) [CH_2I^+], 127 (20) [I^+], 101 (41) [$C_5H_9O_3^+$], 59 (100) [$C_3H_7O^+$].

Anal. Calcd. for $C_{13}H_{21}IO_6$: C, 39.01; H, 5.29. Found: C, 39.22; H, 5.43.

2,3;5,6-Di-*O*-isopropylidene-3-*C*-tosyloxymethyl-D-*allo*-furanose (5d)

To a solution of tosyl compound **4d** (0.083 g, 0.19 mmol) in anhydrous acetone (20 mL) was added 1% HCl in acetone (1 mL) and stirred at rt. After 12 h, one more portion of 1% HCl in acetone (1 mL) was added and the stirring was continued for 12 h more. The reaction was stopped by adding NH_4OH. The solvents were concentrated in vacuo, the crude product was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic extracts were washed with $NaHCO_3$, dried over $MgSO_4$, and filtered. Evaporation of the solvent in vacuo and purification by flash column chromatography (cyclohexane-EtOAc; 5:1) yielded pure **5d** (0.040 g, 0.09 mmol, 48%) as a white solid; mp 122°C; $[\alpha]_D^{20}$ +52.3 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21, 1.25, 1.41, 1.43 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 2.38 (s, 3H, Ts-CH_3), 3.68 (dd, J = 4.0 Hz, J = 12.4 Hz, 1H, 6-H), 3.80–4.01 (m, 3H, 4-H, 5-H, 6-H), 3.97 (d, J = 10.4 Hz, 1H, C$\underline{H}_2$-OTs), 3.99 (d, J = 10.4 Hz, 1H, C$\underline{H}_2$-OTs), 4.29 (d, J = 5.0 Hz, 1H, 2-H), 5.36 (d, J = 5.0 Hz, 1H, 1-H), 7.25 (d, J = 8.4 Hz, 2H, Ar), 7.75 (d, J = 8.4 Hz, 2H, Ar).

Anal. Calcd. for $C_{20}H_{28}O_9S$: C, 54.04; H, 6.35. Found: C, 54.22; H, 6.48.

The NMR data were recorded from the 1-*O*-acetyl derivative of **5d**, prepared by general acetylation procedure.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28, 1.31, 1.46, 1.56 (4 × s, 3 × 3H, C$\underline{H}_3$-^{i}Pr), 2.06 (s, 3H, OAc), 2.43 (s, 3H, Ts-CH_3), 3.82 (d, J = 7.6 Hz, 1H, 4-H), 3.84 (dd, J = 6.0 Hz, J = 14.0 Hz, 1H, 6-H), 3.91 (d, J = 10.4 Hz, 1H, C$\underline{H}_2$-OTs), 4.00 (d, J = 10.4 Hz, 1H, C$\underline{H}_2$-OTs), 4.15–4.26 (m, 2H, 2-H, 5-H), 4.29 (dd, J = 6.8 Hz, J = 14.0 Hz, 1H, 6′-H), 5.25 (d, J = 4.8 Hz, 1H, 1-H), 7.28–7.34 (m, 2H, Ar), 7.65–7.78 (m, 2H, Ar).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6 (C, Ts-$\underline{C}H_3$), 21.9 ($CO\underline{C}H_3$), 24.9, 26.0, 26.6, 26.9 (4 × C, $C(\underline{C}H_3)_2$-^{i}Pr), 64.4 (C, CH_2-OTs), 69.0 (C-6), 71.3 (C-5), 73.4 (C-3), 77.4, 79.5 (2 × C, C-2, C-4), 96.5 (C-1), 109.6 (C_q-^{i}Pr), 111.1 (C_q-^{i}Pr), 128.1–134.4 (6 × Ar), 169.2 (C, CO).

2,3;5,6-Di-*O*-isopropylidene-3-*C*-(trimethylsilyl)methyl-D-*allo*-furanose (5e)

To a solution of silyl derivative **2a** (1.0 g, 2.4 mmol) in anhydrous acetone (150 mL) was added $Zn(OTf)_2$ in small portions until the clear solution turned turbid and stirred at 40°C under argon atmosphere. After 48 h, TLC analysis showed presence of starting material; the reaction was continued by addition of one more portion of $Zn(OTf)_2$ at the same temperature for 48 h. The reaction mixture was quenched by adding NH_4OH; the white solid separated was filtered and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the crude product was purified by flash column chromatography (cyclohexane-EtOAc; 5:1) and yielded pure **5e** (0.58 g, 1.67 mmol, 58%) as a white solid; mp 103°C; $[\alpha]_D^{20}$ +27.2 (c = 1.00, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9H, TMS), 1.25 (d, J = 14.6 Hz, 1H, C$\underline{H}$TMS), 1.35, 1.41, 1.42, 1.45 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 1.55 (d, J = 14.6 Hz, 1H, C$\underline{H}$TMS), 2.80 (s, 1H, OH), 3.80 (dd, J = 4.5 Hz, J = 7.6 Hz, 1H, 6′-H), 4.10 (dd, J = 6.5 Hz, J = 7.6 Hz, 1H, 6-H), 4.15 (d, J = 7.6 Hz, 1H, 4-H), 4.20 (d, J = 4.4 Hz, 1H, 2-H), 4.25 (ddd, J = 4.5 Hz, J = 6.5 Hz, J = 7.6 Hz, 1H, 5-H), 5.70 (dd, J = 4.3 Hz, J = 4.4 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.4 (3 × C, TMS), 22.6 (C, $\underline{C}H_2$TMS), 25.2, 26.4, 26.9, 27.2 (4 × C, $C(\underline{C}H_3)$-^{i}Pr), 66.5 (C-6), 77.2 (C-5), 79.1, 79. 6 (2 × C, C-2, C-4), 89.8 (C-3), 104.4 (C-1), 109.9, 113.2 (2 × C, C_q-^{i}Pr).

Anal. Calcd. for $C_{16}H_{30}O_6Si$: C, 55.46; H, 8.73. Found: C, 55.78; H, 8.89.

2,3;5,6-Di-*O*-isopropylidene-3-*C*-(dimethylphenylsilyl) methyl-D-*allo*-furanose (5f)

It was prepared in the same manner as **5e**; from **2b** (1.0 g, 2.4 mmol), the reaction was stirred for 48 h at rt and then by adding one more portion of $Zn(OTf)_2$ the reaction was stirred at 40°C for 24 h. Purification by flash column chromatography (cyclohexane-EtOAc; 5:1) afforded pure **5f** (0.893 g, 2.2 mmol, 89%) as a colorless oil; $[\alpha]_D^{20}$ +9.8 (c = 1.00, CH_3OH).

^{1}H NMR (C_6D_6, 300 MHz) δ 0.37, 0.42 (2 × s, 2 × 3H, 2 × SiMe), 1.18, 1.25, 1.36, 1.38 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 1.56 (d, J = 14.0 Hz, 1H, C$\underline{H}$SiMe$_2$Ph), 1.78 (d, J = 14.0 Hz, 1H, C$\underline{H}$SiMe$_2$Ph), 2.55 (s, 1H, OH), 3.74 (dd, J = 7.2 Hz, J = 8.0 Hz, 1H, 6′-H), 4.05 (dd, J = 5.4 Hz, J = 8.0 Hz, 1H, 6-H), 4.11 (d, J = 9.2 Hz, 1H, 4-H), 4.20 (d, J = 2.8 Hz, 1H, 2-H), 4.23 (ddd, J = 5.4 Hz, J = 7.2 Hz, J = 9.2 Hz, 1H, 5-H), 5.23 (d, J = 2.8 Hz, J = 3.6 Hz, 1H, 1-H), 7.28-7.35 (m, 3H, Ar), 7.54–7.60 (m, 2H, Ar).

^{13}C NMR (C_6D_6, 75 MHz) δ −1.1 (C, Si$\underline{C}H_3$), −1.0 (C, Si$\underline{C}H_3$), 24.6, 26.0, 26.7, 27.7, (4 × C, C($\underline{C}H_3$)-^{i}Pr), 29.5 (C, $\underline{C}H_2SiMe_2Ph$), 64.0 (C-6), 72.1 (C-5), 76.0 (C-3), 79.7, 81.3 (2 × C, C-2, C-4), 96.7 (C-1), 109.1, 110.4 (2 × C, C_q-^{i}Pr), 121–140 (6 × C, Ar).

Anal. Calcd. for $C_{21}H_{32}O_6Si$: C, 61.73; H, 7.89. Found: C, 62.01; H, 7.99.

3-*C*-Bromomethyl-D-allose (6)

The bromo compound **4b** (2.0 g, 5.6 mmol) was suspended in 0.1 N HCl (20 mL) and heated at 70 to 80°C for 30 min. As the reaction progressed the suspension dissolved and formed a clear solution. The reaction was followed by TLC and showed complete consumption of starting material. The reaction mixture was cooled to rt and then concentrated to dryness under reduced pressure at rt, which furnished crude product **6** as a brown oil. Without further purification the crude product was subjected for the next reaction.

The crude compound **6** was *O*-acetylated by the general procedure for spectroscopic characterization to give a semisolid, which was crystallized from ethyl acetate-pentane mixture and yielded pure **6a** (0.872 g, 1.98 mmol, 35%, over two steps) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.14 (s, 3H, OAc), 3.29 (d, J = 11.5 Hz, 1H, C$\underline{H}'$-Br), 3.34 (d, J = 11.5 Hz, 1H, C$\underline{H}$-Br), 4.07 (dd, J = 2.6 Hz, J = 12.0 Hz, 1H, 6-H), 4.19 (ddd, J = 2.6 Hz, J = 4.3 Hz, J = 6.2 Hz, 1H, 5-H), 4.26 (dd, J = 4.3 Hz, J = 12.0 Hz, 1H, 6′-H), 5.26 (d, J = 8.3 Hz, 1H, 2-H), 5.29 (d, J = 6.2 Hz, 1H, 4-H), 5.99 (d, J = 8.3 Hz, 1H, 1-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.6, 22.7, 22.7, 22.8 (4 × C, CO$\underline{C}H_3$), 34.3 ($\underline{C}H_2Br$), 63.9 (C-6), 69.6 (C-4), 69.9 (C-2), 71.9 (C-5), 73.3 (C-3), 93.0 (C-1), 170.7, 171.0, 172.6 (4 × C, $\underline{C}OCH_3$).

MS-ESI(+): m/z 463.1 $[M + Na]^+$.

Anal. Calcd. for $C_{15}H_{21}BrO_{10}$: C, 40.83; H, 4.80. Found: C, 40.65; H, 4.56.

4,6-*O*-Benzylidene-3-*C*-bromomethyl-D-*allo*-pyranose (7)

To a solution of crude compound **6** (1.5 g, 5.4 mmol) in dry DMF (20 mL) was added catalytic amount of PTSA.H_2O (20 mg), which was followed by addition of benzaldehyde dimethyl acetal (1.25 g, 8.24 mmol). The resulting mixture was heated at 60°C with vigorous stirring under argon atmosphere. After 4 h, the reaction mixture was cooled to rt and stopped by adding Et_3N (0.3 mL). Solvents were evaporated under reduced pressure, which resulted in dark yellow compound. The residue was extracted with EtOAc (3 × 25 mL); the combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered; and solvents were evaporated in vacuo. The crude product on purification by flash column chromatography (cyclohexane-EtOAc; 3:1) gave

mixture of product and side product. However, pure product was precipitated from a column fraction, and yielded **7** (0.49 g, 1.3 mmol, 32%, over two steps) as a white solid; mp 172°C; $[\alpha]_D^{20}$ −9.9 (c = 1.00, CH_3OH).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.01 (br, 3 × OH), 3.27–3.40 (m, 2H, CH_2-Br), 3.45–3.81 (m, 5H, 2-H, 3-H, 4-H, 5-H, 6-H), 4.18 (dd, J = 4.3 Hz, J = 9 Hz, 1H, 6′-H), 5.41 (d, J = 8.5 Hz, 1H, 1-H), 5.71 (s, 1H, C<u>H</u>C_6H_5), 7.15–7.46 (m, 4H, Ar), 7.69–7.72 (m, H, Ar).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.1 (C, CH_2Br), 64.2 (C-5), 69.1 (C-6), 70.2 (C-3), 77.4 (C-4), 73.3 (C-3), 75.1 (C-2), 96.5 (C-1), 101.7 (<u>C</u>HC_6H_5), 126.3, 127.2, 128.2, 128.9, 133.1, 138.8 (6 × C, Ar).

HRMS-ESI(+): m/z calcd for $C_{14}H_{17}BrO_6Na$ $[M + Na]^+$ 383.0106. Found: 383.0079.

Anal. Calcd. for $C_{14}H_{17}BrO_6$: C, 46.56; H, 4.74. Found: C, 46.41; H, 4.74.

The compound **7** was *O*-acetylated by the general procedure for spectroscopic characterization to give a semisolid, which was crystallized from EtOAc-pentane mixture to yield α-anomer **7a** as white crystalline compound.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.09 (s, 3H, OAc), 2.14 (s, 3H, OAc), 3.35 (d, J = 10.5 Hz, 1H, C<u>H</u>′-Br), 3.34 (d, J = 10.5 Hz, 1H, C<u>H</u>-Br), 3.79 (dd, J = 9.0 Hz, J = 12.0 Hz, 1H, 6-H), 3.99 (d, J = 8.4 Hz, 1H, 4-H), 4.01 (ddd, J = 4.3 Hz, J = 8.4 Hz, J = 9.0 Hz, 1H, 5-H), 4.43 (dd, J = 4.3 Hz, J = 12.0 Hz, 1H, 6′-H), 5.37 (d, J = 8.1 Hz, 1H, 2-H), 5.61 (s, 1H, C<u>H</u>C_6H_5), 6.01 (d, J = 8.1 Hz, 1H, 1-H), 7.37–7.63 (m, 4H, Ar), 7.86-7.89 (m, 1H, Ar).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 21.7, (2 × C, CO<u>C</u>H_3), 30.1 (C, CH_2Br), 65.3 (C-5), 69.0 (C-6), 69.6 (C-3), 74.2 (C-2), 77.8 (C-4), 92.1 (C-1), 102.3 (<u>C</u>HC_6H_5), 126.5, 128.7, 129.3, 129.7, 130.1, 136.8 (6 × C, Ar), 169.2, 169.4 (2 × C, CO).

HRMS-ESI(+): m/z calcd for $C_{18}H_{21}BrO_8Na$ $[M + Na]^+$ 467.0317. Found: 467.0310.

Anal. Calcd. for $C_{18}H_{21}BrO_8$: C, 48.55; H, 4.75. Found: C, 48.86; H, 4.39.

General Procedure 3 for Syntheses Non-1-ynitols (8a–8d, 9)

Magnesium turnings (5.0 equiv) were suspended in dry diethyl ether (0.1 g/5 mL) at rt and dibromomethane (0.01 mL) was added. The mixture was stirred for 30 min and then cooled to 10°C. To the cooled suspension at 10°C, dropwise (trimethylsilyl)-propargyl bromide (5.0 equiv) was added in 30 min and temperature was maintained between 10 and 15°C, and stirring was continued for an additional 1 h to afford the Grignard reagent.

Anhydrous $CeCl_3$ (1.0 g for 0.2 g of 1-unprotected sugar) was suspended in dry THF (100 mL) and stirred for 1 h at rt. The suspension was cooled to 0°C, and a solution of previously formed Grignard reagent was added in 20 min and stirred for an additional 2 h. Subsequently, the Grignard reaction mixture was cooled to −78°C and a solution of 1-unprotected sugar (**5b**, **5c**, **5e**, **5f**, **7** [1 equiv]) in dry THF (0.1 g in 5 mL) was added via syringe. The reaction

was slowly allowed to warm to rt in 12 h. The reaction was monitored by TLC (cyclohexane-EtOAc; 2:1) and stopped by adding saturated aqueous solution of NH_4Cl. The organic solvents were removed under reduced pressure and residue was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (cyclohexane-EtOAc) and gave the product as D-*allo* or D-*altro* diastereomer and a small amount of mixture of D-*allo*-/-D-*altro* diastereomers. Only the major diastereomer was characterized by NMR spectroscopy.

6-*C*-Bromomethyl-5,6;8,9-di-*O*-isopropylidene-1-trimethylsilyl-D-*allo*-/-D-*altro*-D-*glycero*-non-1-ynitol (8a)

This was prepared as described in general procedure 3 from **5b** (0.15 g, 0.42 mmol). Purification on silica gel (cyclohexane-EtOAc; 5:1) afforded pure **8a** (0.134 g, 0.29 mmol, 68%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (s, 9H, TMS), 1.35, 1.41, 1,41, 1.54 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 2.43 (dd, $J_{34} = 4.8$ Hz, $J_{33'} = 17.6$ Hz, 1H, 3-H), 2.65 (dd, $J_{3'4} = 3.6$ Hz, $J_{3'3} = 17.6$ Hz, 1H, 3′-H), 3.01 (s, 1H, OH), 3.32 (d, $J = 12.4$ Hz, 1H, C$\underline{H}'$-Br), 3.36 (d, $J_{54} = 4.8$ Hz, 1H, 5-H), 3.44 (d, $J = 12.4$ Hz, 1H, C$\underline{H}$-Br), 3.73 (ddd, $J_{43'} = 3.6$ Hz, $J_{43} = 4.8$ Hz, $J_{45} = 4.8$ Hz, 1H, 4-H), 3.85 (dd, $J_{9'8} = 6.4$ Hz, $J_{9'9} = 8.0$ Hz, 1H, 9′-H), 4.18 (d, $J_{78} = 9.2$ Hz, 1H, 7-H), 4.28 (dd, $J_{98} = 2.4$ Hz, $J_{99'} = 8.0$ Hz, 1H, 9-H), 4.47 (ddd, $J_{89} = 2.4$ Hz, $J_{89'} = 6.4$ Hz, $J_{87} = 9.2$ Hz, 1H, 8-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.04 (3 × C, TMS), 25.3 (C, C($\underline{C}H_3)_2$-^{i}Pr), 26.4 (C-3), 26.8, 26.9, 28.2, (3 × C, C($\underline{C}H_3)_2$-^{i}Pr), 34.9 (C, CH_2Br), 64.0 (C-4), 67.9 (C-1), 76.6 (C-9), 71.2, 82. 5, 82.7 (3 × C, C-5, C-7, C-8), 83.3 (C-6), 87.8 (C-2), 108.9 (C_q-^{i}Pr), 110.6 (C_q-^{i}Pr).

6-*C*-Iodomethyl-5,6;8,9-di-*O*-isopropylidene-1-trimethyl silyl-D-*allo*-/-D-*altro*-D-*glycero*-non-1-ynitol (8b)

This was prepared as described in general procedure 3 from **5c** (0.192 g, 0.48 mmol). Purification on silica gel (cyclohexane-EtOAc; 5:1) afforded pure **8b** (0.192 g, 0.37 mmol, 78%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9H, TMS), 1.33, 1.40, 1,40, 1.51 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 2.49 (dd, $J_{34} = 6.4$ Hz, $J_{33'} = 17.2$ Hz, 1H, 3-H), 2.68 (dd, $J_{3'4} = 3.2$ Hz, $J_{3'3} = 17.2$ Hz, 1H, 3′-H), 3.08 (s, 1H, OH), 3.15 (d, $J = 11.6$ Hz, 1H, C$\underline{H}'$-I), 3.36 (d, $J_{54} = 4.8$ Hz, 1H, 5-H), 3.64 (d, $J = 11.6$ Hz, 1H, C$\underline{H}$-I), 3.73–3.81 (m, 2H, 9′-H, 4-H), 3.83 (dd, $J_{98} = 6.4$ Hz, $J_{99'} = 7.6$ Hz, 1H, 9-H), 4.21 (d, $J_{78} = 7.6$ Hz, 1H, 7-H), 4.47 (ddd, $J_{89'} = 2.0$ Hz, $J_{89} = 6.4$ Hz, $J_{87} = 7.6$ Hz, 1H, 8-H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.0 (3 × C, TMS), 9.2 (C, CH_2I), 25.0, 26.0 (2 × C, C($\underline{C}H_3)_2$-^{i}Pr), 26.2 (C-3), 26.9, 28.2, (2 × C, C($\underline{C}H_3)_2$-^{i}Pr), 63.7 (C-4), 67.9 (C-1), 75.4 (C-9), 70.5, 81. 2, 82.9 (3 × C, C-5, C-7, C-8), 82.9 (C-6), 87.3 (C-2), 107.7 (C_q-^{i}Pr), 108.7 (C_q-^{i}Pr).

5,6;8,9-Di-*O*-isopropylidene-6-*C*-(trimethylsilyl)methyl-1-trimethylsilyl-D-*allo*-/-D-*altro*-D-*glycero*-non-1-ynitol (8c)

This was prepared as described in general procedure 3 from **5e** (0.56 g, 1.61 mmol). Purification on silica gel (cyclohexane-EtOAc; 8:1) afforded both D-*allo* and D-*altro* diastereomers **8c** in pure form.

Diastereomer 1 (0.31 g, 0.68 mmol, 42%) as a colorless oil; $[\alpha]_D^{20}$ +31.6 (c = 0.50, $CHCl_3$):

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9H, TMS), 0. 17 (s, 9H, TMS), 0.75 (d, J = 15.6 Hz, 1H, C$\underline{H}$TMS), 1.22 (d, J = 15.6 Hz, 1H, C$\underline{H}$TMS), 1.23, 1.35, 1.37, 1,40 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 2.54 (dd, J_{34} = 6.6 Hz, $J_{33'}$ = 16.8 Hz, 1H, 3-H), 2.71 (dd, $J_{3'4}$ = 3.6 Hz, $J_{3'3}$ = 16.8 Hz, 1H, 3′-H), 2.80 (s, 1H, OH), 3.55 (d, J = 2.4 Hz, 1H, OH), 3.82 (d, J_{54} = 9.2 Hz, 1H, 5-H), 3.91 (dddd, J_{4HO} = 2.4 Hz, $J_{43'}$ = 3.6 Hz, J_{43} = 6.6 Hz, J_{45} = 9.2 Hz, 1H, 4-H), 3.96 (dd, J_{98} = 6.0 Hz, $J_{99'}$ = 7.8 Hz, 1H, 9-H), 4.00 (dd, $J_{9'8}$ = 7.8 Hz, $J_{9'9}$ = 7.8 Hz, 1H, 9′-H), 4.25 (d, J_{78} = 10.0 Hz, 1H, 7-H), 4.43 (ddd, J_{89} = 6.0 Hz, $J_{89'}$ = 7.8 Hz, J_{87} = 10.0 Hz, 1H, 8-H).

Anal. Calcd. for $C_{22}H_{42}O_6Si_2$: C, 57.60; H, 9.23. Found: C, 57.64; H, 9.19.

Diastereomer 2 (0.17 g, 0.37 mmol, 23%) as a colorless oil; $[\alpha]_D^{20}$ +42.3 (c = 0.50, $CHCl_3$):

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.14 (s, 9H, TMS), 0.16 (s, 9H, TMS), 0.85 (d, J = 15.8 Hz, 1H, C$\underline{H}$TMS), 0.87 (d, J = 15.8 Hz, 1H, C$\underline{H}$TMS), 1.25, 1.37, 1.40, 1,45 (4 × s, 4 × 3H, C$\underline{H}_3$-^{i}Pr), 2.63 (dd, J_{34} = 7.4 Hz, $J_{33'}$ = 17.4 Hz, 1H, 3-H), 2.71 (dd, $J_{3'4}$ = 6.3 Hz, $J_{3'3}$ = 17.4 Hz, 1H, 3′-H), 3.05 (s, 1H, OH), 3.35 (d, J = 2.5 Hz, 1H, OH), 3.87 (d, J_{54} = 2.0 Hz, 1H, 5-H), 3.95 (dd, J_{98} = 6.3 Hz, $J_{99'}$ = 7.9 Hz, 1H, 9-H), 4.00 (dd, $J_{9'8}$ = 7.9 Hz, $J_{9'9}$ = 7.9 Hz, 1H, 9′-H), 4.10 (dddd, J_{45} = 2.0 Hz, J_{4HO} = 2.5 Hz, $J_{43'}$ = 6.3 Hz, J_{43} = 7.4 Hz, 1H, 4-H), 4.24 (d, J_{78} = 1.6 Hz, 1H, 7-H), 4.43 (ddd, J_{87} = 1.6 Hz, J_{89} = 6.3 Hz, $J_{89'}$ = 7.9 Hz, 1H, 8-H).

Anal. Calcd. for $C_{22}H_{42}O_6Si_2$: C, 57.60; H, 9.23. Found: C, 57.58; H, 9.21.

5,6;8,9-Di-*O*-isopropylidene-6-*C*-(dimethylphenylsilyl) methyl-1-trimethylsilyl-D-*allo*-/-D-*altro*-D-*glycero*-non-1-ynitol (8d)

This was prepared as described in general procedure 3 from **5f** (0.2 g, 0.49 mmol). Purification on silica gel (cyclohexane-EtOAc; 9:1) afforded pure **8d** (0.23 g, 0.43 mmol, 89%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 9H, TMS), 0.35, 0.45 (2 × s, 2 × 3H, 2 × SiMe), 0.99 (d, $J = 16.0$ Hz, 1H, C<u>H</u>SiMe$_2$Ph), 1.16, 1.35, 1.40, 1,43 (4 × s, 4 × 3H, C<u>H</u>$_3$-^{i}Pr), 1.57 (d, $J = 16.0$ Hz, 1H, C<u>H</u>SiMe$_2$Ph), 2.40 (dd, $J_{34} = 7.2$ Hz, $J_{33'} = 17.6$ Hz, 1H, 3-H), 2.65 (dd, $J_{3'4} = 3.0$ Hz, $J_{3'3} = 17.6$ Hz, 1H, 3′-H), 2.95 (s, 1H, OH), 3.62 (d, $J = 3.2$ Hz, 1H, OH), 3.72 (d, $J_{54} = 9.2$ Hz, 1H, 5-H), 3.81 (br, 1H, 9-H), 3.89 (dd, $J_{9'8} = 7.6$ Hz, $J_{9'9} = 8.0$ Hz, 1H, 9′-H), 3.92 (ddd, $J_{43'} = 3.0$ Hz, $J_{43} = 7.2$ Hz, $J_{45} = 9.2$ Hz, 1H, 4-H), 4.24 (dd, $J_{78} = 1.6$ Hz, $J_{7OH} = 3.2$ Hz, 1H, 7-H), 4.41 (ddd, $J_{87} = 1.6$ Hz, $J_{89} = 6.0$ Hz, $J_{89'} = 7.6$ Hz, 1H, 8-H), 7.32–7.35 (m, 3H, Ar), 7.55–7.56 (m, 2H, Ar).

Anal. Calcd. for $C_{27}H_{44}O_6Si_2$: C, 62.27; H, 8.52. Found: C, 62.82; H, 9.10.

The compound **8d** was *O*-acetylated by general procedure for spectroscopic characterization to give a semisolid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 9H, TMS), 0.44, 0.47 (2 × s, 2 × 3H, 2 × SiMe), 0.92 (d, $J = 16.0$ Hz, 1H, C<u>H</u>SiMe$_2$Ph), 1.26, 1.33, 1.36, 1,40 (4 × s, 4 × 3H, C<u>H</u>$_3$-^{i}Pr), 1.49 (d, $J = 16.0$ Hz, 1H, C<u>H</u>SiMe$_2$Ph), 2.04 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.65 (dd, $J_{34} = 4.0$ Hz, $J_{33'} = 18.0$ Hz, 1H, 3-H), 2.82 (dd, $J_{3'4} = 3.8$ Hz, $J_{3'3} = 18.0$ Hz, 1H, 3′-H), 3.88 (dd, $J_{9'8} = 6.2$ Hz, $J_{9'9} = 7.6$ Hz, 1H, 9′-H), 3.95 (dd, $J_{98} = 7.6$ Hz, $J_{99'} = 7.6$ Hz, 1H, 9-H), 4.13 (d, $J_{78} = 1.6$ Hz, 1H, 7-H), 4.22 (d, $J_{54} = 9.6$ Hz, 1H, 5-H), 4.40 (ddd, $J_{87} = 1.6$ Hz, $J_{89'} = 6.2$ Hz, $J_{89} = 7.6$ Hz, 1H, 8-H), 5.06 (ddd, $J_{43'} = 3.8$ Hz, $J_{43} = 4.0$ Hz, $J_{45} = 9.6$ Hz, 1H, 4-H), 7.32–7.35 (m, 3H, Ar), 7.52–7.54 (m, 2H, Ar).

8,9-*O*-Benzylidene-6-*C*-bromomethyl-1-trimethylsilyl-D-*allo*-/-D-*altro*-D-*glycero*-non-1-ynitol (9)

This was prepared as described in general procedure 3 from **7** (0.2 g, 0.5 mmol); the compound was not isolated, and mass analysis of reaction mixture showed formation of the product **9** (<10%, by TLC estimation) as a mixture of D-*allo*-/-D-*altro* diastereomers.

HRMS-ESI(+): m/z calcd for $C_{20}H_{29}BrO_6SiNa$ $[M + Na]^+$ 495.0814. Found: 495.0792.

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