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SOME UNEXPECTED REACTIVITY OF PROPARGYL 2,3-DIDEOXY-2-EN-α-D-GLUCOPYRANOSIDE DERIVATIVES

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Abstract: The formation of (2*R*) 1-[(*t*-butyldiphenylsilyl)oxy]-2-furanylethanol (**4**) and anhydro sugar **13** from propargyl 6-*O*-*t*-butyldiphenylsilyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (**1**) and propargyl 4-*O*-allyl-6-*O*-*t*-butyldiphenylsilyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside **10**, respectively, is described.

In the course of our current work on the synthesis of annulated sugars *via* free radical strategies[1] or the Pauson-Khand reaction[2] we were interested in the preparation of the disaccharide **3** (Scheme 1) in order to test these protocols in new, more complex oligosaccharide substrates. A simple entry to this compound was devised based on the very efficient methodology proposed by Koreeda for glycoside synthesis.[3] In fact, in our hands this method has proven[4] to be the most reliable and high yielding version of the well known Ferrier glycosylation reaction.[5]

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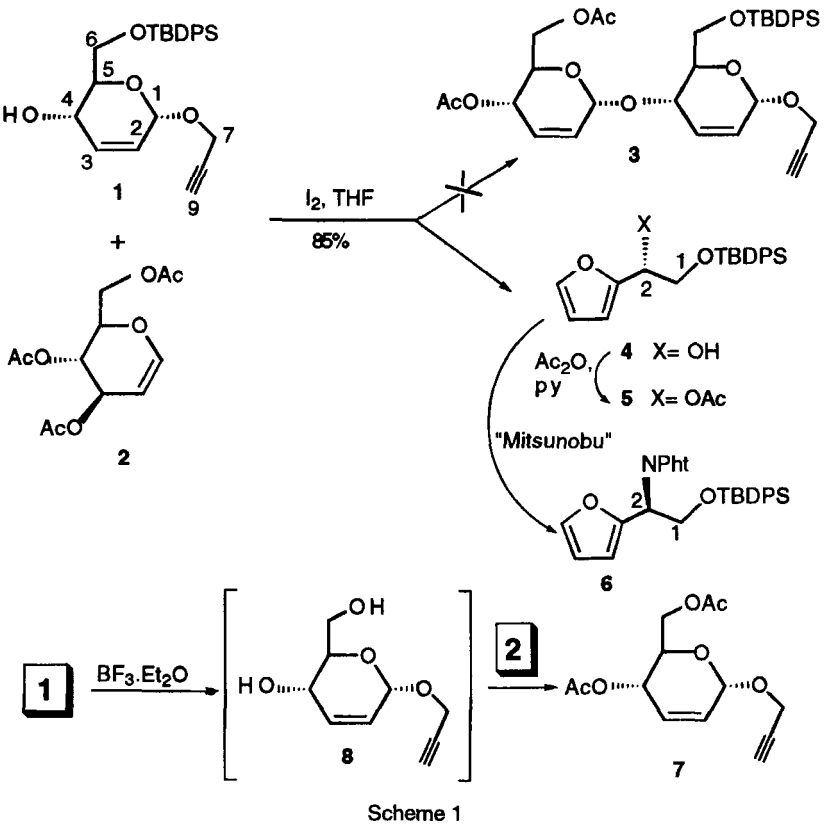
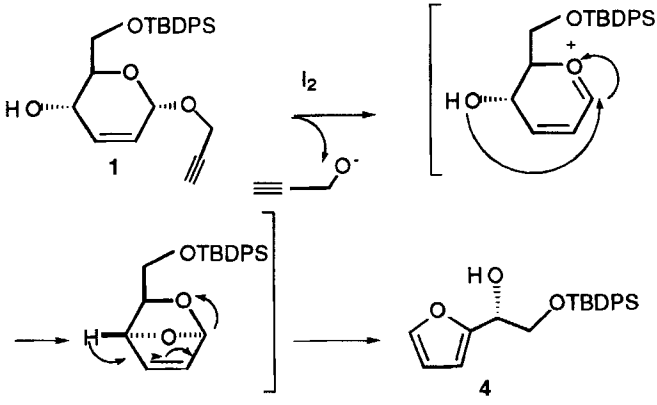
In the standard conditions (iodine, THF, room temperature; see **Experimental**),[3] when we treated propargyl 6-*O*-*t*-butyldiphenylsilyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside **1**[6] with tri-*O*-acetyl-D-glucal **2**, we obtained, instead of the desired glycoside **3**, a new compound whose analytical and spectroscopic data were in full agreement with (2*R*) 1-[(*t*-butyldiphenylsilyl)oxy]-2-furanylethanol (**4**)[7] (Scheme 1). In fact, this product showed in the IR spectrum no carbonyl absorption, but bands for hydroxyl (3.500-3.100 cm^{-1}) and olefinic CH bonds (3.100-3.000 cm^{-1}). In the ^1H NMR spectrum, in addition to the aromatic and the *t*-butyldiphenylsilyl signals, we found a typical pattern for aromatic protons in a α-substituted furan ring[8] (7.34 ppm, m, 1 H; 6.32 ppm, dd, 1 H and 6.28 ppm, d, 1 H); finally, we detected also three protons (4.82 ppm. dd, 1 H; 3.88-3.96, m, 2 H) in a ABX system. All these data strongly supported structure **4**. In agreement with this, in the ^{13}C NMR spectrum, signals for a furan ring (155.65 ppm, quaternary; 141.97, 110.16 and 107.03 ppm, 3xCH) and for the *C*HO-*C*H_2O grouping (68.40 and 66.41 ppm, respectively) were analyzed. Acetylation under standard conditions gave the acetate **5** in quantitative yield. This compound showed analytical and spectroscopic data [IR (film) υ 3.080, 3.060, 1.740 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.60-7.45 (m, 11 H, aromatic, furanyl proton), 6.34 (dd, *J*= 0.6 Hz, *J*= 3.2 Hz, 1 H, furanyl proton), 6.31 (dd, *J*=1.8 Hz, *J*= 3.2 Hz, 1 H, furanyl proton), 6.04 (dd, *J*= 5.2 Hz, *J*= 7.4 Hz, 1 H, H-2), 4.07 (dd, *J*= 10.7 Hz, *J*= 7.4 Hz, 1 H, H-1), 3.95 (dd, *J*= 5.2 Hz, *J*= 10.7 Hz, 1 H, H-1'), 2.05 (s, 3 H, $OCOCH_3$), 1.01 (s, 9 H, *t*-$SiPh_2C(CH_3)_3$] in good agreement with this structure. A careful analysis of the literature has shown that compounds **4** and **5** have been already described by Wong et al.[9] Product **4** has been obtained, as an unexpected result, in 69% yield, in the attempted glycosylation of a glycosyl phosphite with 6-*O*-*t*-butyldiphenylsilyl-D-glucal; acetate **5** was obtained by simple acetylation. The



Scheme 1

recorded spectroscopic values for these compounds are in good accord with the data observed by us. Based on Wong's report,[9] in Scheme 2 we show a hypothetical mechanism for the obtention of compound **4** from glycoside **1**: iodine promoted elimination of the propargyloxy anion followed by intramolecular cyclization and 1,4-elimination.

Our result compares very favourably in terms of chemical yield with the reported by Wong:[9] furan **4** can be obtained in simple, mild reaction conditions, in multigram quantities and in an increased chemical yield. It is important to remember that these compounds are very useful in organic synthesis. In fact, the

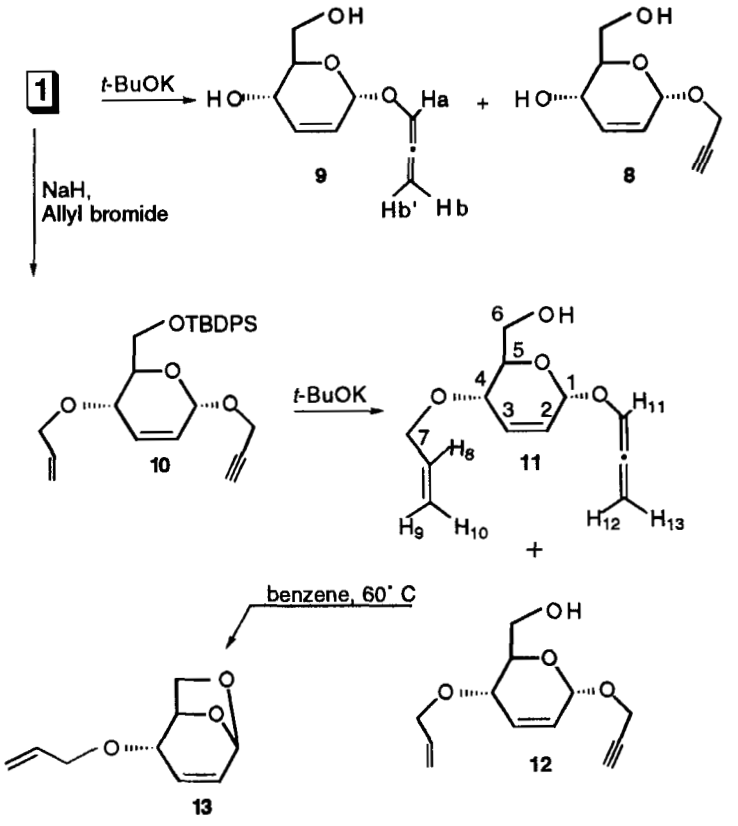


Scheme 2

oxidation of 2-furfurylalcohols to dihydropyrones is a very well known and exploited method for the synthesis of sugars from furans.[10] Our method allows us to obtain these key intermediates in a more convenient process. In addition, it has been shown, for instance, that the Achmatowicz transformation can be also achieved with furylamides.[11] In line with this we have also prepared the imide **6** (Scheme 1) by simple Mitsunobu inversion[12] of compound **4**.

In view of the unexpected problems found in the synthesis of glycoside **3**, we tested the typical Ferrier conditions.[5] When we repeated the reaction using boron trifluoride etherate as catalyst, again instead of the desired product, we obtained a different compound. A simple spectroscopic analysis and comparison with an authentic sample,[3] showed that the new sugar was propargyl 4,6-di-*O*-acetyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside **7**.[13] Apparently, in our reaction conditions, traces of water promote the Lewis acid hydrolysis of the silyl group and the tri-*O*-acetyl-D-glucal serves as substrate for the acid catalyzed transacetylation reaction of the free diol (**8**) obtained from **1** (Scheme 1).

In another current project in our laboratoty,[2,4] we were interested in the allenyl glycoside **9** or **11** (Scheme 3). These chiral *O*-alkoxyallenes are potential u-



Scheme 3

seful intermediates in asymmetric reactions.[14] A simple synthesis of compound **9** from **1** (Scheme 1) would implicate base promoted isomerization of a *O*-propargyl derivative; this is usally performed with potassium *t*-butoxide in *t*-butanol, THF or benzene.[15]

When compound **1** was submitted to these conditions we obtained compounds **9** and **8** (Scheme 3), in 2:1 ratio, in 48% yield, as a mixture that we were unable to separate. Compound **8** was identical (tlc mobility in different solvents) to the product obtained in the basic hydrolysis of the Ferrier reaction

product obtained in the coupling of tri-*O*-acetyl-D-glucal and propargyl alcohol (see **Experimental**). Compound **9** was present in the reaction mixture as we could deduce by inspection of the ^{1}H NMR spectrum of the mixture: a triplet (J= 6.0 Hz, 1H) at 6.66 ppm corresponding to H-a and a multiplet at 5.45-5.35 ppm, corresponding to H-b and H-b' in the allenyl moiety. Note that the silyl group was very unstable in these basic conditions. Further efforts in order to improve this transformation were unsuccessful: only mixtures of the *O*-propargyl and *O*-alkoxyallene products were obtained.

Similar experiments with the 4-*O*-allyl ether **10** (Schem 3) gave desilylated compounds **11** {$[\alpha]_D^{25}$ +8 (c 1.3, $CHCl_3$)} and **12** {$[\alpha]_D^{25}$+143 (c 0.9, $CHCl_3$)}, in a combined 40% yield, that we could separate and isolate by flash chromatography. Without separation, when this mixture was warmed at 60 °C in benzene, we finally obtained the anhydro sugar **13** in 40% yield. This type of anhydro sugars are synthetically important intermediates; they have been used, for instance, in the synthesis of the Cerny epoxides.[16]

It is interesting to note that no Cope or other related isomerization took place in substrates **9** or **11**, as it has been oberved in analogous non-sugars substrates.[17]

In summary, we have described an easy entry to (2*R*) 1-[(*t*-butyldiphenylsilyl)oxy]-2-furanylethanol derivatives (**4**, **5**) in enantiomerically pure form from propargyl 6-*O*-*t*-butyldiphenylsilyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (**1**). We have also observed and described some unexpected results in the base isomerization of this propargyl glycoside.

Experimental

Reactions were monitored by TLC using precoated silica gel aluminium plates containing a fluorescent indicator (Merck, 5539). Detection was done by UV

(254 nm) followed by charring with sulfuric-acetic acid spray, 1% aqueous potassium permanganate solution or 0.5% phosphomolybdic acid in 95% EtOH. Anhydrous Na_2SO_4 was used to dry organic solutions during workups and the removal of solvents was carried out under vacuum with a rotary evaporator. Flash column chromatography was performed using Kieselgel 60 (230-400 mesh, Merck) and hexane-ethyl acetate mixtures as eluent. Optical rotations were determined with a Perkin-Elmer 257 instrument. ^1H and ^{13}C NMR spectra were recorded with a Varian VXR-300S spectrometer, using tetramethylsilane as internal standard.

Propargyl 6-*O* - *t*-butyldiphenylsilyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (1)

This compound was obtained according to the method described by Koreeda:[3] Tri-*O*-acetyl-D-glucal (2.72 g, 10 mmol) was dissolved in dry THF (16 mL) and propargyl alcohol (0.58 mL, 10 mmol, 1 equiv) and iodine (508 mg, 2 mmol) were added at room temperature (rt). The reaction was stirred for 5 h. The solvent was removed and the residue diluted with ethyl acetate, washed with 5% aqueous sodium thiosulfate solution and brine. The organic layer was dried (Na_2SO_4), filtered and evaporated. The crude residue was submitted to basic hydrolysis with sodium methoxide in methanol at rt. After 3 h the reaction was complete. The solvent was evaporated and the residue purified by flash chromatography, eluting with 10% methylene chloride/methanol. The resulting diol (**8**) (1.90 g, 10 mmol, 100% yield from tri-*O*-acetyl-D-glucal) was dissolved in dry DMF (15 mL) and treated with *t*-butyldiphenylsilyl chloride (3.2 mL, 12, 5 mmol, 1.25 equiv) and imidazole (1.5 g, 23 mmol, 2.3 equiv) at 0 °C and at rt for 3 h. This mixture was diluted with methylene chloride and washed with brine, dried (Na_2SO_4), filtered and submitted to flash chromatography, eluting with 20%

hexane/ethyl acetate, to give compound **1** (3.4 g, 82% yield) as an oil: $[\alpha]_D^{25}$ +37.6 (*c* 3.8, $CHCl_3$); IR (film) υ 3.600–3.100, 3.300, 3.080, 3.060, 2.940, 1.590, 1.430, 1.110, 1.040 cm^{-1} ^1H NMR (200 MHz, $CDCl_3$) δ 7.73-7.37 (m, 10 H, aromatic), 5.98 (dt, $J_{2,4}=J_{1,2}=$ 1.3 Hz, $J_{2,3}=$ 10.2 Hz, 1 H, H-2), 5.74 (dt, $J_{3,4}=J_{3,5}=$ 2.4 Hz, 1 H, H-3), 5.15 (t, $J_{1,4}=$ 1.3 Hz, 1 H, H-1), 4.27 (m, 1 H, H-4), 4.23 (d, $J=$ 2.4 Hz, 2 H, 2H-7), 3.90 (m, 1 H, H-5), 3.89 (dd, $J_{6,6'}=$ 15.2 Hz, $J_{6,5}=$ 3.0 Hz, 1 H, H-6), 3.78 (dd, $J_{5,6'}=$ 5.1 Hz, 1 H, H-6'), 2.54 (d,$J_{4,OH}=$ 4.7 Hz, 1 H, OH), 2.35 (t, 1 H, H-9), 1.08 [s, 9 H, OSi*t*-C(C*H*$_3$)Ph$_2$]. Anal. Calcd. for $C_{25}H_{30}O_4Si$: C, 71.05; H, 7.15. Found: C, 70.89; H, 7.27.

(2*R*) 1-[(*t*-Butyldiphenylsilyl)oxy]-2-furanylethanol (4)

Compound **1** (386 mg, 0.91 mmol) was dissolved in dry THF (10 mL) and treated with iodine (46 mg, 0.18 mmol) and tri-*O*-acetyl-D-glucal (272 mg, 1 mmol) according to Koreeda.[3] After 2 h the reaction was complete, the solvent was removed and the residue diluted in ethyl acetate and washed with 5% aqueous sodium thiosulfate solution and brine. The organic layer was dried, filtered, evaporated and submitted to flash chromatography. Elution with hexane/ethyl acetate 5% gave pure **4** {$[\alpha]_D^{25}$ +3.6 (*c* 2.4, $CHCl_3$), 294 mg, 85% yield} as an oil whose spectroscopic data (see Text) were in full agreement with the values reported in the literature for this compound.[9] Simple acetylation of alcohol **4** (Ac_2O, pyridine, rt, 4 h) gave **5**[9] (see Text) as an oil {$[\alpha]_D^{25}$ +51 (*c* 2.9, $CHCl_3$)}in quantitative yield, after flash chromatography (hexane/ethyl acetate 5%).

Mitsunobu reaction of compound 1

Compound **1** (170 mg, 0.46 mmol) was dissolved in dry THF (6 mL), mixed with triphenylphosphine (305 mg, 1.16 mmol), and phtalimide (171 mg, 1.16 mmol) and cooled at 0 °C, under argon. To this solution diethyldiazodicarboxylate

(190 µl, 1.21 mmol) was slowly added in 40 min. The reaction was warmed at rt for 3 h. The solvent was removed and the the residue was submitted to chromatography (hexane/ethyl acetate 10%) to give compound **6** (134 mg, 60% yield) as an oil: $[\alpha]_D^{25}$ -2.5 (*c* 2.9, $CHCl_3$); IR (film) υ 3.080, 3060, 2.940, 1.770, 1.710, 1.610, 1.590, 1.470, 1.430, 1.380, 1.360, 1.110, 960 cm;$^{-1}$ ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80-7.20 (m, 15 H, aromatic, furanyl proton), 6.31 (d, *J*= 3.4 Hz, 1 H, furanyl proton), 6.27 (dd, *J*= 3.4 Hz, *J*= 1.8 Hz, 1 H, furanyl proton), 5.65 (dd, *J*= 5.6 Hz, *J*= 10.0 Hz, 1 H, H-2), 4.58 (t, *J*= 10.0 Hz, 1 H, H-1), 4.18 (dd, *J*= 5.6 Hz, *J*= 10.0 Hz, 1 H, H-1'), 0.89 [s, 9 H, *t*-$SiPh_2C(CH_3)_3$]. Anal. Calcd. for $C_{30}H_{29}NO_4Si$: C, 72.69; H, 5.89; N, 2.82. Found: C, 72.55; H, 5.73; N, 2.67.

Propargyl 4,6-di-*O*-acetyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (7)

6-*O*-*t*-Butyldiphenylsilyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (**1**) (387 mg, 0.91 mmol) was dissolved in dry toluene (10 mL), cooled at 0 °C, under argon and mixed with tri-*O*-acetyl-D-glucal (272 mg, 1.0 mmol). Then, boron trifluoride etherate (50 µl, 0.45 mmol)) was added and the mixture was warmed at rt; after 1 h the reaction was complete and Na_2CO_3 was added, the solvent evaporated and the residue diluted with methylene chloride, washed with brine, and the organic layer dried, filtered and evaporated. The residue was submitted to flash chromatography (hexane/ethyl acetate 20%) to give glycoside **7** (208 mg, 84% yield). This compound was identical in the spectroscopic values to an authentic sample obtained as described by Koreeda.[3]

Propargyl 4-*O*-allyl, 6-*O*-*t*-butyldiphenylsilyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (10)

Compound **1** (925 mg, 2.1 mmol) was dissolved in dry THF (15 mL) and cooled at 0 °C. Sodium hydride (166 mg, 42.2 mmol, 60% dispersion in oil) was

added and the suspension stirred at rt for 30 min. The mixture was cooled again in a ice-water bath, and tetrabutylammonium iodide (cat) and allyl bromide (0.36 mL, 4.2 mmol) were added. The reaction was stirred for 4 h (complete reaction). Silica gel was added and the solvent was evaporated. The absorbed crude reaction was submitted to flash chromatography, eluting with hexane/ethyl acetate 10%, giving **10** (729 mg, 71% yield) as an oil: $[\alpha]_D^{25}$ +80 (*c* 4.8, $CHCl_3$); IR (film) υ 3.300, 3.080, 3060, 2.940, 1.590, 1.430, 1.110, 1.040 cm;$^{-1}$ ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75-7.40 (m, 10 H, aromatic), 6.10 (d, $J_{2,3}$= 10.4 Hz, 1 H, H-2), 5.86 (ddt, $J_{8,10}$= 10.4 Hz, $J_{8,9}$= 15.2 Hz, $J_{7,8}$= 5.4 Hz, 1 H, H-8), 5.80 (dt, $J_{3,4}$= $J_{3,5}$= 2.4 Hz, 1 H, H-3), 5.26 (br s, 1 H, H-1), 5.23 (dq, $J_{9,7}$= $J_{9,10}$= 1.5 Hz, 1 H, H-9), 5.16 (dq, $J_{10,7}$= 1.5 Hz, 1 H, H-10), 4.31 (d, *J*= 2.4 Hz, 2 H, 2 H-11), 4.17-3.80 (m, 4 H, H-4, H-5, 2 H-6), 3.91 (d, $J_{7,8}$= 5.4 Hz, 2 H, 2 H-7, 2.44 (t, 1 H, H-12), 1.08 [s, 9 H, OSi*t*-C(C*H*$_3$)Ph$_2$]. Anal. Calcd. for $C_{28}H_{34}O_4Si$: C, 72.68; H, 7.40. Found: C, 72.55; H, 7.33.

General method for the attempted isomerization alkyne/allene in glycosides 1 and 10

The compound (**1** or **10**) was treated with potassium *t*-butoxide (2 equiv), 18-crown ether (cat) in THF at reflux for 24 h. The solvent was removed and the residue dissolved in ethyl acetate and washed with water. The organic phase was dried, filtered and evaporated.

Compound **1** (396 mg, 0.93 mmol) gave, after flash chromatography eluting with hexane/ethyl acetate 50%, 84 mg (48% yield) of an inseparable mixture of allenyl 2,3-dideoxyhex-2-en-α-D-glucopyranoside (**9**) and propargyl 2,3-dideoxyhex-2-en-α-D-glucopyranoside (**8**) (see Text). This last compound was identical in the tlc behaviour to the product obtained (see above) in the basic

hydrolysis of the Ferrier product obtained from propargyl alcohol and tri-*O*-acetyl-D-glucal.

Compound **10** (284 mg, 0.61 mmol) gave, after flash chromatography eluting with hexane/ethyl acetate 20%, compounds **11+12** (58 mg, 40% yield).

Allenyl 4-*O*-allyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (**11**): oil; $[\alpha]_D^{25}$ +8 (*c* 1.3, $CHCl_3$); IR (film) υ 3.600–3.100, 3.080, 3060, 2.920, 1.625, 1.400, 1.200-1.000 cm;$^{-1}$ ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.66 (t, $J_{11,12}= J_{11,13}=$ 6.1 Hz, 1 H, H-11), 6.13 (dt, $J_{2,3}=$ 10.7 Hz, $J_{2,1}= J_{2,4}=$ 1.3 Hz, 1 H, H-2), 5.90 (ddt, $J_{8,10}=$ 10.5 Hz, $J_{8,9}=$ 14.1 Hz, $J_{7,8}=$ 5.6 Hz, 1 H, H-8), 5.81 (ddd, $J_{3,4}=$ 4.7 Hz, $J_{3,5}=$ 2.0 Hz, 1 H, H-3), 5.43 (dd,$J_{12,13}=$ 8.9 Hz, 1 H, H-12), 5.36 (dd, 1 H, H-13), 5.29 (dq, $J_{9,10}=J_{7,9}=$ 1.6 Hz, 1 H, H-9), 5.26 (d, 1 H, H-1), 5.20 (dq, $J_{10,7}=$ 1.5 Hz, 1 H, H-10), 4.20-3.70 (m, 6 H, H-4, H-5, 2 H-6, 2 H-7), 2.00 (br s, 1 H, OH). Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.40; H, 7.33.

Propargyl 4-*O*-allyl-2,3-dideoxyhex-2-en-α-D-glucopyranoside (**12**): oil; $[\alpha]_D^{25}$ +143 (*c* 0.9, $CHCl_3$); IR (film) υ 3.500-3.100, 3.300, 3.080, 2.940, 1.640, 1.400, 1.200-1.040 cm;$^{-1}$ ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.09 (dt, $J_{2,3}=$ 10.3 Hz, $J_{2,1}= J_{2,4}=$ 1.4 Hz, 1 H, H-2), 5.90 (ddt, $J_{8,10}=$ 10.4 Hz, $J_{8,9}=$ 17.2 Hz, $J_{7,8}=$ 5.6 Hz, 1 H, H-8), 5.76 (ddd, $J_{3,4}=$ 2.7 Hz, $J_{3,5}=$ 2.0 Hz, 1 H, H-3), 5.28 (dq, $J_{9,10}=$ $J_{7,9}=$ 2.6 Hz, 1 H, H-9), 5.22-5.15 (m, 2 H, H-1, H-10), 4.31 (dd, $J_{11,11'}=$ 18.0 Hz, $J_{11,13}=$ 2.4 Hz, 1 H, H-11), 4.28 (dd,$J_{11',13}=$ 2.4 Hz, 1 H, H-11'), 4.20-3.70 (m, 6 H, H-4, H-5, 2 H-6, 2 H-7), 2.43 (t, 1 H, H-13). Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.34; H, 7.23}.

Only for analytical purposes these compounds were separated. This mixture (**11+12**) was heated in benzene for 2 days. Evaporation of the solvent and flash chromatography (hexane/ethyl acetate 25%) gave product **13** (17 mg, 40% yield), as an oil: $[\alpha]_D^{25}$ +130 (*c* 1.7, $CHCl_3$); IR (film) υ 3.080, 3.060, 2.990, 2.900, 1.650, 1.390, 1.180, 1.100, 1.070, 1.040 cm;$^{-1}$ ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.10

(ddd, $J_{2,3}$= 9.7 Hz, $J_{2,1}$= 3.4 Hz, $J_{2,4}$= 1.0 Hz, 1 H, H-2), 5.88 (ddt, $J_{8,10}$= 10.3 Hz, $J_{8,9}$= 17.3 H z, $J_{7,8}$= 5.6 Hz, 1 H, H-8), 5.83 (m, 1 H, H-3), 5.53 (d, 1 H, H-1), 5.28 (dq, $J_{9,10}$=$J_{7,9}$= 1.4 Hz, 1 H, H-9), 5.18 (dq, $J_{10,7}$= 1.4 Hz, 1H, H-10), 4.74 (ddd, $J_{5,6}$= 6.6 Hz, $J_{5,6'}$= 2.1 Hz, $J_{5,4}$= 1.1 Hz, 1 H, H-5), 4.13 (dt, 2 H, 2H-7), 3.90 (dd, $J_{6,6'}$= 7.8 Hz, 1 H, H-6), 3.46 (dt, $J_{3,4}$= 4.2 Hz, $J_{2,4}$= 1.0 Hz, 1 H, H-4), 3.39 (dd, 1 H, H-6'). Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.39; H, 7.32.

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6. Compound **1** has been prepared from tri-*O*-acetyl-D-glucal *via*: a) Ferrier reaction with propargyl alcohol, b) basic hydrolysis, c) silylation with *t*-butyldiphenylsilyl chloride (see **Experimental**).
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