C−C Bond Formation with Acetylated 1-Chloroglycopyranos-1-yl Radicals, 2[+]

Stereocontrolled Access to Higher Sugars (Non-1-en-4-ulopyranosyl Derivatives) and Glycomimetics [3-(β-D-Glycopyranosyl)-1-propenes and (3*Z*)-4,8-Anhydro-nona-1,3-dienitols]

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Peracetylated 1-bromo-β-D-glycopyranosyl chlorides react with allyltributyltin under photolytic conditions to afford the corresponding acetylated α-D-non-1-en-4-ulopyranosyl chlorides. Yields vary, depending mainly on the parent sugar configuration (D-*gluco*: 86%; D-*galacto*: 51%; D-*manno*: 31%). The corresponding acetylated α-D-non-1-en-4-ulopyranoses resulting from hydrolysis were obtained as by-products (8–23% yield). Radical reduction of the acetylated α-D-non-1-en-4-ulopyranosyl chlorides, mediated by *n*Bu_3SnH, led to glycopyranos-1-yl radicals, the diastereoselective quenching of which produced acetylated 3-(β-D-glycopyranosyl)-1-propenes in good overall yield (50–57% yield). This approach, which combines C–C and C–H bond forming reactions involving glycopyranosyl radicals, constitutes a more efficient route to acetylated 3-(β-D-glycopyranosyl)-1-propenes. No traces of the 3-(α-D-glycopyranosyl)-1-propene epimers could be detected, so the diastereoselectivity of the radical-mediated reduction controlling the product structure was ascertained to be >95:5. On treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the acetylated 4-ulopyranosyl chlorides underwent stereoselective dehydrochlorination to afford new (3Z)-4,8-anhydrononona-1,3-dienitols (42–63% yield), which could be deacetylated. Since these syntheses can be carried out by one-pot procedures, this work opens up easy access to unsaturated *C*-glycopyranosyl compounds which are otherwise difficult to prepare or are completely unknown.

Introduction

C-Glycosides[1−3] constitute a broad class of well studied glycomimetics with a *C*-glycosidic bond resistant to hydrolysis. Hence they are substrate analogues of sugar-processing enzymes, of potential biological interest.[4,5] Among this class, 3-(glycosyl)-1-propenes (frequently erroneously termed *C*-allyl glycosides) constitute a group of synthetically useful compounds which has been thoroughly investigated. The first route to 3-(β-D-glucopyranosyl)-1-propenes involved treatment of tetra-*O*-acetyl-α-D-glucopyranosyl bromide with an ethereal solution of the Grignard reagent prepared from allyl bromide.[6] A more efficient route to 3-(β-D-glycopyranosyl)-1-propene is represented by nucleophilic attack by allylmagnesium bromide or allyllithium on benzylated glyconolactones, followed by Lewis acid-catalyzed reduction of the resulting intermediate hemiacetal with triethylsilane.[7,8] Recently, allylmetal addition to 1,2-anhydro-3,4,6-tri-*O*-benzyl-α-D-glucopyranose was proposed as a new route to 3-(β-D-glucopyranosyl)-1-propene.[8,9] Under these conditions, the Grignard reagent was found to be more effective than allyllithium and allyl cuprate.[9] Interestingly, these methods are highly stereoselective, affording predominantly 3-(β-D-glycopyranosyl)-1-propene, due either to S_N2 attack[6,8,9] or to stereoselective reduction of intermediate glycopyranosyl ions.[7,8] However, because of the basic conditions applied, these methods are restricted to suitably protected substrates, such as benzylated sugar derivatives.

The use of allyltrimethylsilane opened various possibilities for the Lewis acid-catalyzed synthesis of 3-(D-glycopyranosyl)-1-propenes. A large array of sugar precursors, diversely protected with acyl, isopropylidene or silyl groups, has been treated with allyltrimethylsilane in the presence of a Lewis acid, boron trifluoride−diethyl ether being used most frequently. These conditions have been applied to functionalized sugars possessing the following substituents at the anomeric position (all cleaved by the action of $BF_3{\cdot}OEt_2$, unless otherwise indicated): hydroxy,[7] methoxy (TMSOTf, TMSI),[10−15] formyloxy,[16] acetoxy[16] [sugar configuration: D-*gluco*,[13,16] D-*manno*,[16,17] D-*galacto*,[16,18−20] lactose,[16,20,21] D-*ribo* ($BF_3{\cdot}OEt_2$, TMSOTf, $ZnBr_2$),[22−24] and other[16,23−25]], benzoyloxy,[23,24,26] 2,4,6-trimethylbenzoyloxy,[16] 4-nitrobenzoyloxy,[7,24] nitrate,[27] bromide,[13] chloride,[10,12] and fluoride.[28] 3-Glycosyl-1-propenes could also be prepared using allyltrimethylsilane by Lewis acid-catalyzed opening of anhydro sugars (1,2-,[9] 1,4-,[29] and 1,6-anhydro sugars[7])

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and sugar lactones.[15,30] Allylation can be achieved with free *O*-methyl glycosides containing silyl ethers as temporary protective groups.[11] Zinc chloride was also found to be an effective Lewis acid.[19] Notwithstanding one example for which the alleged β-configuration of the obtained 3-(D-galactopyranosyl)-1-propene was not proved convincingly,[18] these methods lead with good stereoselectivity, in the D-pyranosyl series, to α-configured products. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(tetrachlorophthalimido)-α-D-glucopyranosyl fluoride represents the sole exception to the general trend, yielding the corresponding *C*-allyl compound by a β-selective reaction.[28] Not unexpectedly, lower selectivities were observed for the preparation of 3-(glycofuranosyl)-1-propenes.[22−24]

Allyltri-*n*-butyltin has also frequently been used to prepare 3-(glycosyl)-1-propenes by radical-mediated reactions[31] applied to monosaccharide,[32−35] *N*-acetylneuraminic acid,[36−38] and furanose[39] derivatives. As a consequence of the α-stereoselective quenching of D-glycopyranosyl radicals,[31,40] 3-(α-D-glycopyranosyl)-1-propenes are formed predominantly, as demonstrated when free radical allylation was applied, in particular, to D-glucosamine and D-galactosamine derivatives.[34,35] However, the presence at C-2 of a bulky substituent (*N*-phthalimido, *N*-tetrachlorophthalimido) permits the preparation of *C*-glycosyl compounds of the opposite β-configuration.[34,35] The use of allylic sulfides and allylic sulfones instead of allyltributyltin permits the stereoselective preparation, by radical routes, of 3-(α-D-glycopyranosyl)-1-propenes, from peracetylated α-D-galactopyranosyl bromide[41] and glycosyl dithiocarbonates.[42] In the 2-deoxy series, a 3-(β-D-glycopyranosyl)-1-propene was obtained as a result of stereoselective quenching[40] of an intermediate anomeric radical, produced by the Barton *O*-acyl thiohydroxamate protocol, with a thiol as the hydrogen atom donor.[43,44]

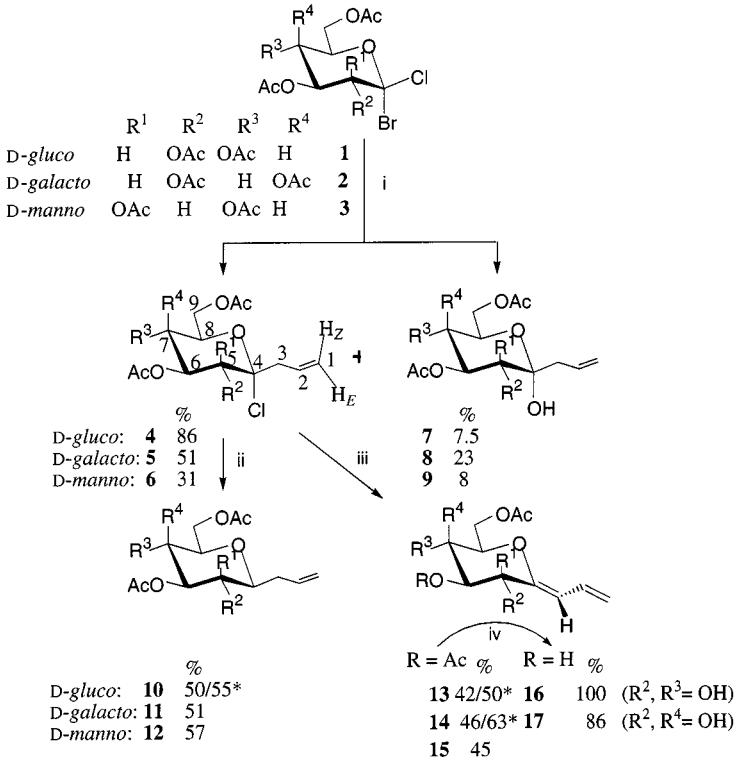
3-(Glycosyl)-1-propenes lend themselves to many synthetic applications, such as reduction,[18] double bond isomerisation,[45] oxidative ozonolysis,[22,46] reductive ozonolysis and related cleavages,[19,22,46−49] epoxidation,[6,8,50] hydroboration,[51] asymmetric dihydroxylation,[52] formation of bicyclic compounds,[53,54] and olefin metathesis.[55−57] Consequently, we wanted to explore another potentially stereocontrolled and smooth route[58] to 3-(β-D-glycopyranosyl)-1-propenes, with peracetylated glycopyranosylidene dihalides[59,60] serving as readily accessible substrates. After a preliminary communication,[58] our complete results on the synthesis of 3-(β-D-glycopyranosyl)-1-propenes and new glycopyranosylidenedienes are reported here in full.

Results and Discussion

Radical-mediated allylation has been shown to proceed under both thermal and photoinduced conditions.[32] A previous investigation showed that the peracetylated glucopyranosylidene dihalide **1** undergoes radical-mediated addition to acrylonitrile, in boiling solvents, to give mixtures of products.[61] Therefore, in order to enhance the selectivities of radical-mediated allylation of **1**−**3**,[59,60] we found it preferable to resort to photolytic conditions, where the temperature of the reaction mixture was maintained below ca. 35 °C. Bromine-containing compounds can be detected easily and with high sensitivity by TLC (see Experimental Section), and monitoring of the reaction in this way clearly showed that complete transformation of the substrates occurred readily in the presence of two equivalents of allyltributyltin, to produce the 4-ulopyranosyl chlorides **4**−**6** chemo- and stereoselectively. Depending on the wavelength of the transmitted light, complete transformation of the substrates occurred either within ca. 30 min or, when the lamp was equipped with a Pyrex filter, 15−24 h. Such a filter, which confers no advantages, was used only in a few cases. Argon was always used as the inert gas. The yields of the isolated chlorides were found to depend on the sugar configuration, and to decrease along the sequence D-*gluco*, D-*galacto*, D-*manno*, (86, 51, 31% for **4**, **5**, **6**, respectively), probably due to the presence of axially oriented acetoxy substituents (at C-4 and C-2 in **5** and **6**, respectively), acting as participating groups, and favourably disposed to facilitate hydrolysis of chlorides **5** and **6**. Compound **6** would be expected to be more prone to hydrolysis, and this is in agreement with the low isolated yield. Losses during workup and column chromatography account for the isolation of **9** in a yield comparable to that of **7** and **8** (Scheme 1).

The ready accessibility of chlorides **4**, **5**, and **6** was a prerequisite for the development of a new radical-mediated route to 3-(β-D-glycopyranosyl)-1-propenes. As indicated previously, it is well established that glycopyranosyl radicals generally undergo a highly stereoselective quenching in radical-based reactions such as halogenation,[62] reduction,[40,63] and carbon−carbon bond forming processes.[31,63] Treatment of chlorides **4**−**6** with tri-*n*-butyltin hydride in excess led mainly to the expected 3-(β-D-glycopyranosyl)-1-propenes **10**−**12**, which were also prepared efficiently and conveniently from **1**−**3** by a "one-pot" procedure. No trace of the other diastereomers could be detected by NMR spectroscopy, so the diastereoselectivity of the reaction can be taken to be >95:5. Such a high diastereoselectivity, in full agreement with related data,[44] has been explained on the basis of the marked preference of aliphatic carbon substituents in *C*-substituted glycopyranosyl radicals for the equatorial orientation.[40] On this basis and taking into consideration the availability of the starting dihalides and the experimental protocol applied, this approach to acetylated 3-(β-D-glycopyranosyl)-1-propenes compares favourably with the few already reported.

On the basis of the dehydrochlorination observed for a related non-4-ulopyranosyl chloride,[61] it was assumed that chlorides **4**−**6** could undergo base-catalyzed 1,2-elimination to afford new glycopyranosylidene dienes. This was verified using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), with the conjugated dienes **13**−**15** isolated in 42/46% yield, while a "one-pot" procedure led to somewhat enhanced yields (50/63%). Deacetylation of **13** and **14** under Zemplén conditions led uneventfully to the corresponding deprotected di-



Scheme 1. i: C_6H_6, hv, nBu$_3$SnCH$_2$CH=CH$_2$; ii: C_6H_6, hv, nBu$_3$SnH; iii: DBU, CH_3CN; iv: MeONa, MeOH or NEt_3/MeOH/H_2O; *: yield for "one-pot" procedure

enes, in high yield. These glycopyranosylidenedienes might be of interest for Diels−Alder reactions, as shown by other investigations using *O*-dienyl glycosides[64,65] and *C*-(α-D-glucopyranosyl)alkanedienes.[26,66]

An (*R*) anomeric configuration was assigned to the non-4-ulopyranosyl chlorides **4−6**.[58] Further supporting evidence for this stereochemistry was provided by 2D NMR spectroscopy. Following a COSY correlation, a NOESY experiment showed, for **4**, connectivities between the 3-H and 3′-H protons of the allyl chain (see Scheme 1 for atom numbering), the neighbouring 2-H and more significantly the axially oriented 5-H, without any connectivity with the axially oriented 6-H and 8-H protons, thus supporting the equatorial orientation of the allyl chain. For the non-4-ulopyranoses **7−9**, the hydroxy group most probably adopts an axial orientation, as reported in the literature[7,8] and convincingly established, by nuclear Overhauser effect (nOe) difference spectra, for a related product.[67] ^{1}H NMR spectroscopy was the method of choice to confirm the structure assigned to 3-(β-D-glycopyranosyl)-1-propenes **10−12**, based on literature data reported for **10**,[13] and the α-configured epimers of **11**[16] and **12**,[17] and in agreement with the observed values of $^3J_{4,5}$ coupling constants in **10−12** (9.5, 9.5, and 0.85 Hz, respectively, corresponding to axial-axial (**10**, **11**) and axial-equatorial (**12**) orientations of the coupled protons). Compounds **4−9** are thermodynamic products stabilized by the anomeric effect. No convincing evidence could be obtained supporting the existence of kinetic products, which should be the β-anomers of **4−6**. However, their occurrence in the initial stages of the reaction was suggested by diffuse spots on TLC plates, which might correspond to anomeric mixtures. In view of the stabilizing stereoelectronic effects, anomerization of these transients would be expected to occur and, in the presence of trace amounts of water, to favour formation of **7−9**.

For the complete elucidation of structures **13−17**, it was necessary to establish the configuration of the exocyclic double bond. Convincing evidence pointing to a (*Z*) configuration of the exocyclic double bond in the peracetylated D-*manno*-diene **15** has been obtained by nOe difference spectra. Essentially, selective excitations of the 3-H and 5-H protons resulted in significant enhancements of the 5-H (9.8%) and 3-H (9.7%) signals, respectively. For compounds **13** and **14**, a (*Z*) configuration, minimizing unfavourable steric interactions, is also expected.

Conclusion

In summary, we found that peracetylated 1-bromo-β-D-glycopyranosyl chlorides react with allyltributyltin under photolytic conditions to afford the corresponding acetylated α-D-non-1-en-4-ulopyranosyl chlorides in variable yields, depending mainly on the parent sugar configuration (D-*gluco*: 86%; D-*galacto*: 51%; D-*manno*: 31%). The corresponding acetylated α-D-non-1-en-4-ulopyranoses produced by hydrolysis were obtained as by-products (8−23% yield). Diastereoselective quenching of glycopyranos-1-yl radicals could be used to produce acetylated 3-(β-D-glycopyranosyl)-1-propenes in good overall yield (50−57%) from

acetylated α-D-non-1-en-4-ulopyranosyl chlorides, by radical reduction mediated by nBu$_3$SnH. This approach, which combines tandem C−C, and C−H bond forming reactions involving glycopyranosyl radicals, constitutes a more efficient route to acetylated 3-(β-D-glycopyranosyl)-1-propenes. No traces of the 3-(α-D-glycopyranosyl)-1-propene epimers could be detected, so the diastereoselectivity of the radical-mediated reduction controlling the product structure was ascertained to be >95:5. On treatment with DBU, the 4-ulopyranosyl chlorides undergo stereoselective dehydrochlorination to afford new (3*Z*)-4,8-anhydro-nona-1,3-dienitols (42−63% yield). Since these syntheses can be carried out following one-pot procedures applied to readily accessible acetylated sugar dihalides, this work opens up easy access to acetylated 3-(β-D-glycopyranosyl)-1-propenes, difficult to prepare otherwise (β anomeric configuration), and to hitherto unknown (3*Z*)-4,8-anhydro-nona-1,3-dienitols.

Experimental Section

General Methods: Melting points were determined with a Büchi capillary apparatus and were not corrected. − Optical rotations were determined with a Perkin−Elmer 241 polarimeter. − ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 200/AM 300/DRX500 instruments for solutions in $CDCl_3$, with Me_4Si as the internal reference or in D_2O. − Mass spectra were obtained with a Nermag R10−10H spectrometer (70 eV). − Reactions were monitored by TLC on Silica Gel 60 F_{254} (Merck) plates exposed to H_2SO_4 (10% in 1:1 EtOH/H_2O) spray followed by charring (≈250 °C). Bromine-containing compounds were detected by successively spraying a fluorescein solution in absolute EtOH (0.1% w/v), then a mixture made up of H_2O_2 (30% in water) and AcOH (1:1, v/v), followed by charring. They appeared as pink spots. − Column chromatography was performed with Silica Gel Geduran Si 60 (E. Merck). − Solvents were distilled before use. Water was distilled twice.

5,6,7,9-Tetra-*O*-acetyl-1,2,3-trideoxy-α-D-*gluco*-non-1-en-4-ulopyranosyl Chloride and 5,6,7,9-Tetra-*O*-acetyl-1,2,3-trideoxy-α-D-*gluco*-non-1-en-4-ulopyranose (4 and 7): A mixture of the chlorobromo sugar **1**[59] (0.40 g, 0.90 mmol), allyltributyltin (0.596 g, 0.558 mL, 1.80 mmol) and a catalytic amount of AIBN in dry, deoxygenated benzene (9 mL) was introduced into a quartz tube (external diameter ≈13 mm), flushed with argon. The tube was placed beside a medium pressure mercury lamp (Hanovia, 450 W), inserted into a two-walled cooling jacket with tap water cooling. Irradiation was continued until TLC monitoring showed the disappearance of the starting material [≈35 min, or much more (≈15 h) when the lamp was equipped with a Pyrex filter], which was clearly detected when using the specific procedure for the detection of bromine-containing compounds. Two new compounds were formed as shown by the new spots visible on the plates (R_f ≈ 0.51 and 0.26, ethyl acetate/hexane 1:1). A solution of potassium fluoride (1.5 g) in a mixture of water (1 mL) and acetonitrile (10 mL) was added to the reaction mixture, which was stirred overnight at room temperature. The solids produced were removed by filtration and the liquid phase was concentrated under vacuum. The residue was applied to a column of silica gel eluted with ethyl acetate/hexane 1:1. Chloride **4** (312 mg, 0.77 mmol, 86% yield) was obtained first, followed by a small amount of the hydroxylated compound **7** (25.9 mg, 0.067 mmol, 7.5% yield).

Compound 4: White solid, m.p. 72−74 °C (diethyl ether/petroleum ether). − $[\alpha]_D^{23}$ = +95 (c = 0.5, $CHCl_3$). − IR (NaCl): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1645 cm^{-1} (C=C). − ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 5.85 (m, $J_{1(E),2}$ = 10.7 Hz, $J_{1(Z),2}$ = 17 Hz, $J_{2,3}$ = 7 Hz, $J_{2,3'}$ = 7 Hz, 1 H, 2-H), 5.50 (t, $J_{5,6}$ = 9.6 Hz, $J_{6,7}$ = 9.6 Hz, 1 H, 6-H), 5.20 [broad d, $J_{1(E),1(Z)}$ = ≈1.5 Hz, 1 H, 1-H(*E*)], 5.16 (t, $J_{7,8}$ = 9.7 Hz, 1 H, 7-H), 5.14 (d, 1 H, 5-H), 5.13 [dd, 1 H, 1-H(*Z*)], ≈4.3 (m, 2 H, 8-H, 9-H), 4.14 (d, $J_{9,9'}$ = 13.5 Hz, 1 H, 9′-H), ≈2.8 (broad dd, $J_{3,3'}$ = ≈15 Hz, 1 H, 3-H), ≈2.7 (broad dd, 3′-H), 2.10, 2.09, 2.04, 1.99 (4s, 12 H, acetyl). − ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 130.08 (C2), 120.43 (C1), 104.31 (C4), 72.16, 72.04, 71.78, 67.55 (C5, C6, C7, C8), 61.32 (C9), 45.76 (C3), 170.66, 170.07, 169.53, 169.45 (C=O), 20.80, 20.75, 20.66, 20.66 (acetyl). − MS (CI, NH_3): m/z = 424, 426 [M + 18]$^+$ 3:1 ratio, 406 [M]$^+$, 388 [M − Cl + 18]$^+$, 371 [M − Cl]$^+$. − $C_{17}H_{23}ClO_9$ (406.8): calcd. C 50.19, H 5.70, Cl 8.71, O 35.40; found C 50.62, H 5.82, Cl 8.46, O 35.30.

Compound 7: Colourless needles (diethyl ether/petroleum ether), m.p. 100 °C. − $[\alpha]_D^{20}$ = +31 (c = 0.4, $CHCl_3$) − IR (KBr): $\tilde{\nu}$ = 3400−3500 cm^{-1} (OH), 1750 cm^{-1} (C=O), 1640 cm^{-1} (C=C). − ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 5.83 (m, $J_{1(E),2}$ = 10.2 Hz, $J_{1(Z),2}$ = 17.4 Hz, $J_{2,3}$ = 5.5 Hz, $J_{2,3'}$ = 9.2 Hz, 1 H, 2-H), 5.48 (t, $J_{5,6}$ = 9.7 Hz, $J_{6,7}$ = 9.7 Hz, 1 H, 6-H), 5.31 [dd, $J_{1(E),1(Z)}$ = ≈1 Hz, 1 H, 1-H(*E*)], 5.21 [broad d, 1 H, 1-H(*Z*)], 5.11 (t, $J_{7,8}$ = 9.7 Hz, 1 H, 7-H), 5.04 (dd, $J_{5,OH}$ = ≈1 Hz, 1 H, 5-H), 4.26 (dd, $J_{8,9}$ = 4.1 Hz, $J_{9,9'}$ = 11.6 Hz, 1 H, 9-H), 4.17 (dq, $J_{8,9'}$ = 2 Hz, 1 H, 8-H), 4.07 (dd, 1 H, 9′-H), 2.89 (d, J = ≈1 Hz, 1 H, OH), 2.51 (broad dd, $J_{3,3'}$ = 13.6 Hz, 1 H, 3-H), 2.26 (dd, 3′-H), 2.10, 2.09, 2.03, 1.99 (4s, 12 H, acetyl). − ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 130.21 (C2), 121.90 (C1), 96.46 (C4), 72.07, 71.61, 68.67, 68.15 (C5, C6, C7, C8), 62.07 (C9), 42.17 (C3), 170.79, 170.22, 169.82, 169.61 (C=O), 20.78, 20.74, 20.65, 20.65 (acetyl). − MS (CI, NH_3): m/z = 406 [M + 18]$^+$, 371 [M − OH]$^+$. − $C_{17}H_{24}O_{10}$ (388.4): calcd. C 52.58, H 6.23, O 41.20; found C 52.63, H 6.27, O 39.89.

5,6,7,9-Tetra-*O*-acetyl-1,2,3-trideoxy-α-D-*galacto*-non-1-en-4-ulopyranosyl Chloride and 5,6,7,9-Tetra-*O*-acetyl-1,2,3-trideoxy-α-D-*galacto*-non-1-en-4-ulopyranose (5 and 8): These compounds were prepared as described for the D-*gluco* analogues, with minor modifications. Thus, irradiation of a deoxygenated benzene (10 mL) solution containing the D-*galacto* dihalide **2**[60] (445 mg, 1 mmol), allyltributyltin (660 mg, 2 mmol), and AIBN (20 mg) for 30 min (longer reaction times were occasionally observed, probably due to incomplete elimination of oxygen) resulted, as shown by TLC, in the formation of compound **5** (R_f = 0.40, ethyl acetate/petroleum ether 3:7), together with traces of the hydrolyzed compound **8** (R_f = 0.09, ethyl acetate/petroleum ether 3:7) and by-products visible on the plates as much less mobile spots. In order to limit the ready hydrolysis of chloride **5**, stirring was performed for only 1.5 h after the addition of potassium fluoride dissolved in acetonitrile/water (10:1, 11 mL). The resulting heterogeneous solution was filtered through a bed of celite and the residue obtained after concentration under reduced pressure was resolved by flash chromatography, using ethyl acetate/petroleum ether 3:7. Compound **5** was obtained first (207 mg, 51% yield), followed by the more polar hydrolyzed analogue **8** (88 mg, 23% yield).

Compound 5: IR (NaCl): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1640 cm^{-1} (C=C). − ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 5.87 (ddt, $J_{2,1(Z)}$ = 17.1 Hz, $J_{2,1(E)}$ = 10.3 Hz, $J_{2,3}$ = 6.9 Hz, $J_{2,3'}$ = 6.9 Hz, 1 H, 2-H), 5.48 (q, $J_{6,7}$ = <1 Hz, $J_{7,8}$ = 1.3 Hz, 1 H, 7-H), 5.34 (d, 2 H, 5-H, 6-H), 5.18 [dd, $J_{1(Z),1(E)}$ = 1.4 Hz, 1 H, 1-H(*E*)], 5.14 [dd, 1 H, 1-H(*Z*)], 4.47 (dt, $J_{8,9}$ = 6.7 Hz, $J_{8,9'}$ = 6.7 Hz, 1 H, 8-H), 4.13 (dd, 2 H, 9-H, 9′-H), 2.73 (dd, 2 H, 3-H, 3′-H), 2.14, 2.09, 2.03, 1.95

(4 s, 12 H, acetyl). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 130.05 (C2), 119.93 (C1), 105.43 (C4), 70.84, 69.41, 69.37, 67.11 (C5, C6, C7, C8), 60.75 (C9), 37.68 (C3), 170.30, 170.03, 169.85, 169.55 (C=O), 20.74, 20.61, 20.59, 20.51 (acetyl). − MS (CI, NH_3): *m*/*z* = 371 $[M - Cl]^+$.

Compound 8: Colourless syrup. − $[\alpha]_D^{25}$ = +29 (*c* = 0.4, $CHCl_3$). − IR (NaCl): $\tilde{\nu}$ = 3200−3600 cm^{-1} (OH), 1750 cm^{-1} (C=O), 1640 cm^{-1} (C=C). − ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 5.84 (dddd, $J_{2,1(Z)}$ = 17.1 Hz, $J_{2,1(E)}$ = 10.0 Hz, $J_{2,3}$ = 5.4 Hz, $J_{2,3'}$ = 9.4 Hz, 1 H, 2-H), 5.44 (dd, $J_{6,7}$ = 3.2 Hz, $J_{7,8}$ = 1.3 Hz, 1 H, 7-H), 5.34 (dd, $J_{5,6}$ = 10.5 Hz, 1 H, 6-H), 5.29 [dd, $J_{1(Z),1(E)}$ = 1.6 Hz, 1 H, 1-H(*E*)], 5.25 (d, 1 H, 5-H), 5.20 [dd, 1 H, 1-H(*Z*)], 4.36 (dt, $J_{8,9}$ = 7.3 Hz, $J_{8,9'}$ = 6.4 Hz, 1 H, 8-H), 4.09 (dd, $J_{9,9'}$ = 11.2 Hz, 1 H, 9′-H), 4.05 (dd, 1 H, 9-H), 2.97 (broad s, 1 H, OH), 2.54 (dd, $J_{3,3'}$ = 13.8 Hz, 1 H, 3-H), 2.25 (dd, 1 H, 3′-H), 2.14, 2.09, 2.02, 1.95 (4 s, 12 H, acetyl). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 130.27 (C2), 121.65 (C1), 97.03 (C4), 69.51, 69.08, 68.15, 67.03 (C5, C6, C7, C8), 61.47 (C9), 42.33 (C3), 170.53, 170.39, 170.14, 170.08 (C=O), 20.86, 20.71, 20.71, 20.63 (acetyl). − MS (CI, NH_3): *m*/*z* = 406 $[M + 18]^+$, 371 $[M - OH]^+$. − $C_{17}H_{24}O_{10}$ (388.4): calcd. C 52.58, H 6.23, O 41.20; found C 52.37, H 6.43.

5,6,7,9-Tetra-*O*-acetyl-1,2,3-trideoxy-α-D-*manno*-non-1-en-4-ulopyranosyl Chloride and 5,6,7,9-Tetra-*O*-acetyl-1,2,3-trideoxy-α-D-*manno*-non-1-en-4-ulopyranose (6 and 9): These compounds were prepared from **3**,[59] as described for preparing the D-*galacto* analogues **5** and **8**.

Compound 6: 31% yield; colourless syrup. − R_f = 0.53 (EtOAc/petroleum ether 1:1). − IR (NaCl): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1645 cm^{-1} (C=C). − ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 5.83 (dddd, $J_{2,1(Z)}$ = 16.9 Hz, $J_{2,1(E)}$ = 10.4 Hz, $J_{2,3}$ = 6 Hz, $J_{2,3'}$ = 8 Hz, 1 H, 2-H), 5.68 (dd, $J_{6,5}$ = 3.2 Hz, $J_{6,7}$ = 10.1 Hz, 1 H, 6-H), 5.44 (d, 1 H, 5-H), 5.31 (t, $J_{7,8}$ = 10 Hz, 1 H, 7-H), 5.21 [dt, $J_{1(E),1(Z)}$ = ≈1 Hz, $J_{1(E),3}$ = ≈1 Hz, 1 H, 1-H(*E*)], 5.14 [dt, $J_{1(Z),3}$ = ≈1 Hz, 1 H, 1-H(*Z*)], 4.34 (dd, $J_{8,9}$ = 5 Hz, $J_{9,9'}$ = 12.2 Hz, 1 H, 9-H), 4.27 (ddd, $J_{8,9'}$ = 2 Hz, 1 H, 8-H), 4.14 (dd, 1 H, 9′-H), 2.85 (ddt, $J_{3,3'}$ = 14.7 Hz, 1 H, 3-H), 2.74 (dd, 1 H, 3′-H), 2.18, 2.12, 2.07, 1.98 (4s, 12 H, acetyl). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 130.18 (C2), 120.37 (C1), 103.03 (C4), 72.73, 71.78, 69.22, 65.13 (C5, C6, C7, C8), 61.93 (C9), 44.24 (C3), 170.59, 169.75, 169.68, 169.31 (C=O), 20.73, 20.71, 20.71, 20.54 (acetyl). − MS (CI, NH_3): *m*/*z* = 388 $[M - Cl + 17]^+$, 371 $[M - Cl]^+$.

Compound 9: 8% yield; colourless syrup. − R_f = 0.34 (EtOAc/petroleum ether 1:1).− IR (NaCl): $\tilde{\nu}$ = 3400−3500 cm^{-1} (OH), 1745 cm^{-1} (C=O), 1645 cm^{-1} (C=C). − ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 5.73 (dddd, $J_{2,1(Z)}$ = 17.4 Hz, $J_{2,1(E)}$ = 10.3 Hz, $J_{2,3}$ = 5.1 Hz, $J_{2,3'}$ = 9.8 Hz, 1 H, 2-H), 5.39 (dd, $J_{6,5}$ = 3.3 Hz, $J_{6,7}$ = 9.9 Hz, 1 H, 6-H), 5.24 [dm, $J_{1(E),1(Z)}$ = ≈1 Hz, $J_{1(E),3}$ = 1 Hz, $J_{1(E),3'}$ = ≈1 Hz, 1 H, 1-H(*E*)], 5.20 (d, 1 H, 5-H), 5.18 (t, $J_{7,8}$ = 10 Hz, 1 H, 7-H), 5.15 [dm, $J_{1(Z),3}$ = ≈1 Hz, $J_{1(Z),3'}$ = ≈1 Hz, 1 H, 1-H(*Z*)], 4.20 (dd, $J_{8,9}$ = 5.1 Hz, $J_{9,9'}$ = 11.8 Hz, 1 H, 9-H), 4.07 (ddd, $J_{8,9'}$ = 2.5 Hz, 1 H, 8-H), 4.01 (dd, 1 H, 9′-H), 2.97 (s, 1 H, OH), 2.51 (ddt, $J_{3,3'}$ = 13.6 Hz, 1 H, 3-H), 2.17 (ddt, 1 H, 3′-H), 2.10, 2.02, 1.97, 1.90 (4s, 12 H, acetyl). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 130.51 (C2), 122.43 (C1), 96.72 (C4), 71.26, 70.13, 69.35, 66.35 (C5, C6, C7, C8), 62.98 (C9), 41.80 (C3), 170.91, 170.16, 170.15, 170.02 (C=O), 20.96, 20.91, 20.82, 19.45 (acetyl). − MS (CI, NH_3): *m*/*z* = 406 $[M + 18]^+$, 371 $[M - OH]^+$.

3-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1-propene (10): Pure chloroallyl D-*gluco* derivative **4** (24 mg, 0.065 mmol) was dissolved in deoxygenated benzene (0.7 mL) containing tri-*n*-butyltin hydride (43.7 mg, 41 μL, 0.15 mmol) and a catalytic amount of AIBN. Irradiation (UV light, no filter) was applied for 20 min, whereupon TLC showed the partial conversion of the starting material (R_f = 0.48, ethyl acetate/petroleum ether 1:2) into the 3-(β-D-glucopyranosyl)-1-propene **10** (R_f = 0.38, ethyl acetate/petroleum ether 1:2) and hydrolyzed compound **7** (R_f = 0.14). After addition of another portion of tri-*n*-butyltin hydride (10 μL, 0.036 mmol) and AIBN, irradiation was resumed for 100 min. The reaction mixture was stirred overnight with aqueous potassium fluoride. After separation of the solids by filtration, the residue was applied to a column of silica gel with mixtures of ethyl acetate/petroleum ether as the mobile phase (1:3, 1:2.5, 1:2 v/v, successively) to afford **10** (12.1 mg, 50% yield). ^{1}H NMR spectroscopy revealed no contamination by the α-anomer (β/α ratio > 95:5). The hydroxylated compound **7** was isolated in trace amounts (2 mg) corresponding to an 8% yield. More mobile minor compounds (1.4 mg, R_f = 0.52 and 2 mg, R_f = 0.47) formed in this experiment were not characterised (see below, the "one-pot" synthesis of **10**).[67,68]

One-Pot Synthesis of 10: Bromochloro D-glucopyranosylidene **1** (222.5 mg, 0.5 mmol), allyltri-*n*-butyltin (330 mg, 0.31 mL, 1 mmol, 2 equiv.) and AIBN (6 mg) were dissolved in deoxygenated benzene (5 mL) and the solution was poured into a quartz tube and stirred under an argon atmosphere for 2 h before exposure to UV light (no filter). After 40 min, TLC monitoring showed the disappearance of the dihalide and the presence of the chloroallyl intermediate **4** formed as the major compound (R_f = 0.48, ethyl acetate/petroleum ether 1:2). Tri-*n*-butyltin hydride (583 mg, 0.54 mL, 2 mmol, 4 equiv.) and AIBN (12 mg) were added prior to renewed exposure to UV light for 35 min. This resulted in the formation of the more polar compound **10** (R_f = 0.38, ethyl acetate/petroleum ether 1:2), together with minor by-products. The reaction mixture was stirred overnight at room temperature with KF (1.5 g) in a H_2O/CH_3CN solution (1.5:6 v/v, 7.5 mL). After removal of the white solid by filtration and concentration of the liquid phase under vacuum, the residue was applied to a column of silica gel eluted with ethyl acetate/petroleum ether (1:3, then 1:2.5 then 1:2 v/v) as the mobile phase. After first obtaining 1,3,4-tri-*O*-acetyl-2,6-anhydro-5,7,8,9-tetradeoxy-D-*lyxo*-nona-5,8-dienitol[68] (9 mg, 6% yield, R_f = 0.52, ethyl acetate/petroleum ether 1:2) and an unidentified product having only three acetyl groups[68] (12 mg, R_f = 0.47, ethyl acetate/petroleum ether 1:2), the desired β-D-glucopyranosyl compound **10** was collected (101 mg, 55% yield), followed by a minor amount of compound **7** (3 mg, 1.5% yield). On NMR examination, no α-anomer of **10** could be detected.

3-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-1-propene (11): The D-*galacto* chloroallyl derivative **5** was prepared from the chlorobromo sugar **2** (222.5 mg, 0.5 mmol) and allyltributyltin (0.31 mL, 1 mmol), with catalytic AIBN in benzene (5 mL) after a 35 min irradiation, as indicated above. Tri-*n*-butyltin hydride (291 mg, 1 mmol) and AIBN were added to the deoxygenated solution, which was further irradiated for 20 min. TLC monitoring showed that the intermediate chloride **5** (R_f = 0.48, ethyl acetate/petroleum ether 1:2) was converted into a major new product (R_f = 0.39, ethyl acetate/petroleum ether 1:2), in addition to several more or less polar by-products. After addition of potassium fluoride (1.5 g) in a 1:5 mixture of water and acetonitrile (6 mL) and stirring for 2 h, the solids formed were separated by filtration and the volatiles were removed under vacuum. The residue was applied to a column of silica gel eluted with ethyl acetate/petroleum ether 1:3, then 1:2.5, then 1:2. A minor compound, identified later as 1,3,4-tri-*O*-acetyl-2,6-anhydro-5,7,8,9-tetradeoxy-D-*arabino*-nona-5,8-dienitol[69] was eluted first (16 mg, 10%), followed by the β-D-galactopyranosyl

compound **11** (96 mg, 51% yield), which crystallized on standing at low temperature. Recrystallization from diethyl ether/petroleum ether afforded colourless needles, m.p. 49−52 °C. − IR (NaCl): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1640 cm^{-1} (C=C). − $[\alpha]_D^{23}$ = +6.6 (*c* = 0.4, $CHCl_3$). − ^1H NMR (300.13 MHz, $CDCl_3$): δ = 5.83 (ddt, $J_{2,1(Z)}$ = 17.1 Hz, $J_{2,1(E)}$ = 10.4 Hz, $J_{2,3}$ = 6.7 Hz, $J_{2,3'}$ = 6.7 Hz, 1 H, 2-H), 5.41 (dd, $J_{6,7}$ = 3.4 Hz, $J_{7,8}$ = 1.0 Hz, 1 H, 7-H), 5.12 (t, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 10.0 Hz, 1 H, 5-H), 5.09 [m, 2 H, 1-H(*E*), 1-H(*Z*)], 5.01 (dd, 1 H, 6-H), 4.15 (dd, $J_{8,9}$ = 6.7 Hz, $J_{9,9'}$ = 11.2 Hz, 1 H, 9-H), 4.06 (dd, $J_{8,9'}$ = 6.6 Hz, 1 H, 9′-H), 3.86 (dt, 1 H, 8-H), 3.47 (dt, $J_{3,4}$ = 6.7 Hz, $J_{3',4}$ = 6.7 Hz, 1 H, 4-H), 2.31 (t, 2 H, 3-H, 3′-H), 2.16, 2.04, 2.04, 1.98 (4 s, 12 H, acetyl). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 133.31 (C2), 117.41 (C1), 77.76, 74.09, 72.22, 69.24, 67.73 (C4, C5, C6, C7, C8), 61.60 (C9), 36.05 (C3), 170.43, 170.33, 170.24, 169.73 (C=O), 20.84, 20.72, 20.70, 20.63 (acetyl). − $C_{17}H_{24}O_9$ (372.37): calcd. C 54.83, H 6.50, O 38.67; found C 55.14, H 6.63, O 38.47.

3-(2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl)-1-propene (12): A solution of the D-*manno* bromochloro sugar **3** (222.5 mg, 0.5 mmol), allyltributyltin (0.31 mL, 1 mmol, 2 equiv.) and AIBN (catalytic amount) in dry benzene (5 mL) was placed in a quartz tube (volume ≈10 mL, 1 cm diameter) and stirred overnight under argon at room temperature. Prior to irradiation, the tube was immersed in ice-cooled water for 5 min. After 50 min irradiation with a medium pressure mercury lamp (no filter), the reaction was complete, as indicated by TLC. Tri-*n*-butyltin hydride (0.27 mL, 1 mmol, 2 equiv.) was added and the solution was cooled to ≈0 °C. Irradiation was performed for 20 min, after which the chloroallyl intermediate **6** was not visible on TLC plates. The reaction mixture was stirred with a solution of KF (1.5 g, 1 mmol, 2 equiv.) in H_2O/CH_3CN (1:5 v/v, 6 mL) for 1.5 h. The solids were filtered off and rinsed with Et_2O (2 × 10 mL). The organic phase, washed with water (2 × 8 mL), dried ($MgSO_4$), and concentrated under vacuum, afforded a solid (200 mg, 111%) corresponding to **12**, of high purity as determined by ^1H NMR spectroscopy (300.13 MHz). Column chromatography with ethyl acetate/petroleum ether 1:2 first afforded trace amounts of a bis-*C,C*-allyl compound[68] (10 mg, 5% yield), and then **12** (112.6 mg), which crystallized from diethyl ether/petroleum ether (107 mg, 57% yield), m.p. 100−101 °C. − R_f = 0.35 (ethyl acetate/petroleum ether 1:2, violet-coloured spot on charring). − $[\alpha]_D^{20}$ = −26 (*c* = 0.2, $CHCl_3$). − ^1H NMR (300.13 MHz, $CDCl_3$): δ = 5.74 (dddd, $J_{2,1(Z)}$ = 17.2 Hz, $J_{2,1(E)}$ = 11.2 Hz, $J_{2,3}$ = 6.4 Hz, $J_{2,3'}$ = 7.8 Hz, 1 H, 2-H), 5.35 (dd, $J_{4,5}$ = 0.85 Hz, $J_{5,6}$ = 3.5 Hz, 1 H, 5-H), 5.24 (t, $J_{6,7}$ = 10.0 Hz, $J_{7,8}$ = 10.0 Hz, 1 H, 7-H), 5.09 [dm, $J_{1(E),3}$ = 1.3 Hz, $J_{1(E),3'}$ = 1.3 Hz, 1 H, 1-H(*E*)], 5.08 [dm, $J_{1(Z),3}$ = 1.3 Hz, $J_{1(Z),3'}$ = 1.3 Hz, 1 H, 1-H(*Z*)], 5.05 (dd, 1 H, 6-H), 4.28 (dd, $J_{8,9}$ = 5.8 Hz, $J_{9,9'}$ = 12.2 Hz, 1 H, 9-H), 4.11 (dd, $J_{8,9'}$ = 2.4 Hz, 1 H, 9′-H), 3.64 (ddd, 1 H, 8-H), 3.64 (dt, $J_{3,4}$ = 6.7 Hz, $J_{3',4}$ = 6.7 Hz, 1 H, 4-H), 2.42 (dddt, $J_{3,3'}$ = ≈14 Hz, 1 H, 3-H), 2.23 (dddt, 1 H, 3′-H), 2.19, 2.11, 2.05, 1.99 (4s, 12 H, acetyl). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 132.64 (C2), 118.37 (C1), 76.73, 76.3, 72.47, 69.04, 66.21 (C4, C5, C6, C7, C8), 62.91 (C9), 34.94 (C3), 170.74, 170.38, 170.21, 169.72 (C=O), 20.81, 20.74, 20.74, 20.63 (acetyl). − MS (CI, NH_3): *m*/*z* = 390 $[M + 18]^+$, 373 $[M + 1]^+$, 313 $[M - 59]^+$. − $C_{17}H_{24}O_9$ (372.37): calcd. C 54.83, H 6.50, O 38.67; found C 54.66, H 6.49, O 38.35.

(3*Z*)-5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-D-*gluco*-nona-1,3-dienitol (13): A solution of the D-*gluco* chloroallyl sugar **4** (130 mg, 0.3 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (91.3 mg, 0.6 mmol) in dry acetonitrile (12 mL) was stirred for 1.5 h at room temperature, whereupon the TLC plates showed the formation of somewhat more polar compounds [R_f = 0.35 (**4**), 0.32 (by-product), 0.28 (**13**), ethyl acetate/petroleum ether 3:7] visible under UV light. After concentration under reduced pressure, the residue was applied to a column of silica gel eluted with ethyl acetate/petroleum ether 3:7. The diene **13** (46 mg, 42%) was crystallized from diethyl ether/petroleum ether to provide an analytical sample. When the reaction was conducted in diethyl ether, extended reaction times (at room temperature: 40 h, at reflux: 8 h) and comparable yields were observed.

Compound 13: M.p. 107−108 °C. − $[\alpha]_D^{25}$ = +74.3 (*c* = 0.5, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1660 cm^{-1} (C=C). − ^1H NMR (200.13 MHz, $CDCl_3$): δ = 6.66 (dt, $J_{2,1(Z)}$ = 17.3 Hz, $J_{2,1(E)}$ = 10.4 Hz, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 5.55 (broad d, 1 H, 3-H), 5.47 (d, $J_{5,6}$ = 6.8 Hz, 1 H, 5-H), 5.24 [dd, $J_{1(Z),1(E)}$ = 1.6 Hz, 1 H, 1-H(*Z*)], 5.21 (t, $J_{6,7}$ = ≈8 Hz, $J_{7,8}$ = ≈8 Hz, 1 H, 7-H), 5.13 (t, 1 H, 6-H), 5.10 [dd, 1 H, 1-H(*E*)], 4.32 (dd, $J_{8,9}$ = 4.4 Hz, $J_{9,9'}$ = 12.5 Hz, 1 H, 9-H), 4.24 (dd, $J_{8,9'}$ = 2.7 Hz, 1 H, 9′-H), 3.93 (dq, 1 H, 8-H), 2.14, 2.12, 2.05, 2.04 (4 s, 12 H, acetyl); ($[D_6]$acetone): δ = 6.70 (dt, $J_{2,1(Z)}$ = 17.3 Hz, $J_{2,1(E)}$ = 10.5 Hz, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 5.64 (broad d, 1 H, 3-H), 5.43 (broad d, $J_{5,6}$ = 7.5 Hz, 1 H, 5-H), 5.23 [dd, $J_{1(Z),1(E)}$ = 2.1 Hz, 1 H, 1-H(*Z*)], 5.17 (m, $J_{7,8}$ = ≈8.5 Hz, 2 H, 6-H, 7-H), 5.05 [dd, 1 H, 1-H(*E*)], 4.34 (dd, $J_{8,9}$ = 4.9 Hz, $J_{9,9'}$ = 12.5 Hz, 1 H, 9-H), 4.25 (dd, $J_{8,9'}$ = 2.7 Hz, 1 H, 9′-H), 4.04 (dq, 1 H, 8-H), 2.12, 2.06, 2.03, 2.00 (4 s, 12 H, acetyl). − ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 145.85 (C4), 128.75, 112.84 (C2, C3), 117.64 (C1), 75.64, 73.36, 69.40, 68.32 (C5, C6, C7, C8), 61.91 (C9), 170.61, 169.90, 169.37, 169.09 (C=O), 20.79, 20.72, 20.66, 20.60 (acetyl). − MS (CI, NH_3): *m*/*z* = 388 $[M + 18]^+$. − $C_{17}H_{22}O_9$ (370.36): calcd. C 55.13, H 5.99, O 38.88; found C 55.16, H 6.06, O 38.40.

One-Pot Synthesis of Diene 13: A mixture of the D-*gluco* bromochloro sugar **1** (225 mg, 0.5 mmol), allyltributyltin (331 mg, 1 mmol) and AIBN (6 mg) in dry benzene (5 mL) under argon was exposed to unfiltered UV light for 35 min. The solvent was removed under reduced pressure and the obtained residue was dissolved in acetonitrile (15 mL). After addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (137 mg, 0.9 mmol), the flask was immersed in a cleaning bath (BRANSON 3200, 90 W, 47 kHz) in order to promote the dehydrochlorination reaction (1.5 h at ≈35 °C). After addition of potassium fluoride (232 mg, 4 mmol) in an acetonitrile/water mixture (10:1, 5.5 mL) and stirring at room temperature for 2 h, the white solid formed was filtered off. The aforementioned treatments led to pure diene **13** (92.4 mg, 50% yield).

(3*Z*)-5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-D-*galacto*-nona-1,3-dienitol (14): Following the preparation of **13** from **4** described above, crude chloride **5**, prepared from dihalide **2** (112 mg, 0.25 mmol), was treated with DBU (2 equiv., reaction time ≈6 h), to afford **14** (43 mg, 46% yield), m.p. 112−114 °C (diethyl ether/petroleum ether). − IR (KBr): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1660 cm^{-1} (C=C). − $[\alpha]_D^{25}$ = +115.6 (*c* = 0.5, $CHCl_3$). − ^1H NMR (300.13 MHz, $CDCl_3$): δ = 6.63 (dt, $J_{2,1(Z)}$ = 17.3 Hz, $J_{2,1(E)}$ = 10.5 Hz, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 5.68 (broad d, $J_{5,6}$ = 9.9 Hz, 1 H, 5-H), 5.51 (dd, $J_{3,5}$ = ≈1.4 Hz, 1 H, 3-H), 5.50 (dd, $J_{6,7}$ = 3.3 Hz, $J_{7,8}$ = 1.8 Hz, 1 H, 7-H), 5.20 [broad d, $J_{1(Z),1(E)}$ = ≈1 Hz, 1 H, 1-H(*Z*)], ≈5.07 [broad d, 1 H, 1-H(*E*)], 5.04 (dd, 1 H, 6-H), 4.25 (dd, $J_{8,9}$ = 7.2 Hz, $J_{9,9'}$ = 11.5 Hz, 1 H, 9-H), 4.16 (dd, $J_{8,9'}$ = 5.7 Hz, 1 H, 9′-H'), 4.04 (ddd, 1 H, 8-H), 2.14, 2.13, 2.06, 1.99 (4 s, 12 H, acetyl). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 146.64 (C4), 128.70, 112.43 (C2, C3), 117.15 (C1), 75.37, 71.13, 67.33, 66.83 (C5, C6, C7, C8), 61.51 (C9), 170.21, 169.88, 169.71, 169.25 (C=O), 20.60, 20.49, 20.43, 20.43 (acetyl). − MS (CI, NH_3): *m*/

z = 388 $[M + 18]^+$, 371 $[M + 1]^+$. − $C_{17}H_{22}O_9$ (370.36): calcd. C 55.13, H 5.99, O 38.88; found C 55.07, H 5.93, O 38.72.

One-Pot Synthesis of Diene D-*galacto*-14: A mixture of the bromochloro sugar **2** (119 mg, 0.27 mmol), allyltributyltin (181 mg, 0.55 mmol) and AIBN (5 mg) in dry benzene (2.5 mL) under argon was exposed to unfiltered UV light for 35 min. The solvent was removed under reduced pressure and the obtained residue was dissolved in acetonitrile (8 mL). After addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (81 mg, 0.53 mmol), the flask was immersed in a cleaning bath (BRANSON 3200, 90 W, 47 kHz) in order to promote the dehydrochlorination reaction (3 h at ≈35 °C). After addition of potassium fluoride (250 mg, 4.3 mmol) dissolved in a 10:1 acetonitrile/water mixture (2.75 mL) and stirring at room temperature for 5 h, the white solid formed was filtered off. The aforementioned treatments led to pure diene (62 mg, 63% yield). Lower yields (≈55%) were achieved when the DBU-mediated dehydrochlorination was conducted in benzene.

(3*Z*)-5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-D-*manno*-nona-1,3-dienitol (15): Dehydrochlorination of chloride **6** was carried out as described above for **4** and **5** to afford **15** in 45% yield; colourless syrup. − R_f = 0.33, ethyl acetate/petroleum ether 1:1, brown spot on charring. − $[\alpha]_D^{20}$ = +18 (c = 0.5, $CHCl_3$). − ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 6.63 (dt, $J_{2,1(Z)}$ = 17.5 Hz, $J_{2,1(E)}$ = 10.4 Hz, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 5.73 (d, 1 H, 3-H), 5.67 (d, $J_{5,6}$ = 3.6 Hz, 1 H, 5-H), 5.46 (t, $J_{6,7}$ = 9.8 Hz, $J_{7,8}$ = 9.8 Hz, 1 H, 7-H), 5.30 [dd, $J_{1(Z),1(E)}$ = ≈1 Hz, 1 H, 1-H(*Z*)], 5.17 [dd, 1 H, 1-H(*E*)], 5.10 (dd, 1 H, 6-H), 4.35 (dd, $J_{8,9}$ = 5.3 Hz, $J_{9,9'}$ = 12.4 Hz, 1 H, 9-H), 4.24 (dd, $J_{8,9'}$ = 2.6 Hz, 1 H, 9′-H), 3.83 (ddd, 1 H, 8-H), 2.14, 2.14, 2.08, 2.03 (4s, 12 H, acetyl). By nOe difference spectroscopy, selective irradiations of *a*) 2-H, *b*) 6-H (300.13 MHz, $CDCl_3$), *c*) 3-H, and *d*) 5-H (500.13 MHz, $CDCl_3$) resulted in the following nOe effects (proton, %): *a*) 1-H(*E*) (4.4), 3-H (4.3); *b*) 5-H (6.0), 8-H (5.0); *c*) 1-H(*Z*) (4.8), 2-H (2.3), 5-H (9.8); *d*) 3-H (9.7), 6-H (11.2). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 145.28 (C4), 128.81 (C2), 119.34 (C1), 118.30 (C3), 78.0, 71.19, 69.55, 65.60 (C5, C6, C7, C8), 62.40 (C9), 170.62, 169.95, 169.95, 169.57 (C=O), 20.99, 20.73, 20.68, 20.63 (acetyl). − MS (CI, NH_3): m/z = 388 $[M + 18]^+$, 371 $[M + 1]^+$, 311 $[M - 59]^+$.

(3*Z*)-4,8-Anhydro-1,2,3-trideoxy-D-*gluco*-nona-1,3-dienitol (16): The D-*gluco*-diene **13** (132 mg, 0.35 mmol) was dissolved in a mixture of methanol (4 mL), water (0.5 mL, distilled twice) and triethyl amine (0.5 mL) and stirred overnight at room temperature. Completion of the reaction was checked by TLC, which showed a single spot on the plates (R_f = 0.65, ethyl acetate/ethanol 10:2). Removal of the volatiles under diminished pressure led to the pure deacetylated compound **16** (71 mg, quantitative), which could be lyophilized, as an amorphous solid. − $[\alpha]_D^{20}$ = +119 (c = 0.5, MeOH). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 1660 cm^{-1} (C=C). − ^{1}H NMR (200.13 MHz, D_2O): δ = 6.77 (dt, $J_{2,1(Z)}$ = 17.3 Hz, $J_{2,1(E)}$ = 10.4 Hz, $J_{2,3}$ = 10.9 Hz, 1 H, 2-H), 5.85 (d, 1 H, 3-H), 5.29 [dd, $J_{1(Z),1(E)}$ = ≈1 Hz, 1 H, 1-H(*Z*)], 5.10 [dd, 1 H, 1-H(*E*)], 3.99 (dm, $J_{5,6}$ = ≈9.5 Hz, 2 H, 5-H, 9-H), 3.82 (dd, $J_{9,9'}$ = 12.5 Hz, 1 H, 9′-H), 3.59 (dd, $J_{6,7}$ = 8.8 Hz, $J_{7,8}$ = 9.5 Hz, 1 H, 7-H), 3.48 (dq, $J_{8,9}$ = 2.1 Hz, $J_{8,9'}$ = 5.0 Hz 1 H, 8-H), 3.42 (t, 1 H, 6-H). − ^{13}C NMR (50.32 MHz, D_2O): δ = 152.68 (C4), 129.92, 111.05 (C2, C3), 117.05 (C1), 81.40, 77.38, 71.04, 69.70 (C5, C6, C7, C8), 61.23 (C9). − MS (EI): m/z (%) = 202 (14) $[M]^+$. − $C_9H_{14}O_5$ (202.21): calcd. H 6.98; found H 7.31.

(3*Z*)-4,8-Anhydro-1,2,3-trideoxy-D-*galacto*-nona-1,3-dienitol (17): A solution of D-*galacto*-diene **14** (90.6 mg, 0.245 mmol) in dry methanol (1 mL) was stirred for 26 h at room temperature after addition of a catalytic amount of sodium methoxide in methanol. Completion of the reaction was indicated by the appearance on the TLC plates of a single spot (R_f = 0.63, ethyl acetate/abs. ethanol 10:2), visible under UV light. The reaction mixture was filtered through a bed of silica gel and the solvent was removed under vacuum. The obtained solid was crystallized from an ethanol/ethyl acetate mixture (43.3 mg, 86% yield) to afford white crystals, m.p. 183−184 °C. − IR (KBr): $\tilde{\nu}$ = 3100−3600 cm^{-1} (OH), 1665 cm^{-1} (C=C). − $[\alpha]_D^{27}$ = +199.6 (c = 0.5, MeOH). − ^{1}H NMR (300.13 MHz, D_2O): δ = 6.75 (dt, $J_{2,1(Z)}$ = 17.3 Hz, $J_{2,1(E)}$ = 10.4 Hz, $J_{2,3}$ = 10.9 Hz, 1 H, 2-H), 5.83 (d, 1 H, 3-H), 5.25 [d, $J_{1(Z),1(E)}$ = ≈0 Hz, 1 H, 1-H(*Z*)], 5.05 [d, 1 H, 1-H(*E*)], 4.22 (d, $J_{5,6}$ = 10.0 Hz, 1 H, 5-H), 4.03 (broad d, $J_{6,7}$ = 1.8 Hz, $J_{7,8}$ = 3 Hz, 1 H, 7-H), 3.87 (m, 1 H, 6-H), 3.74 (m, 2 H, 9-H, 9′-H), 3.59 (ddd, $J_{8,9}$ = 1.5 Hz, $J_{8,9'}$ = 10.0 Hz, 1 H, 8-H). − ^{13}C NMR (75.47 MHz, D_2O): δ = 153.50 (C4), 130.19, 110.83 (C2, C3), 116.76 (C1), 80.92, 74.33, 69.68, 68.71 (C5, C6, C7, C8), 61.96 (C9). − MS (EI): m/z (%) = 202 (18) $[M]^+$; 184 (10) $[M - H_2O]^+$. − $C_9H_{14}O_5$ (202.21): calcd. C 53.46, H 6.98, O 39.56; found C 53.70, H 6.89, O 39.39.

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