Peracetylated β-Allyl C-Glycosides of D-Ribofuranose and 2-Deoxy-D-ribofuranose in the Chemical Literature: Until Now, Mirages in the Literature

Heike Otero Martinez,[a,1] Helmut Reinke,[a] Dirk Michalik,[b] Christian Vogel*[a]

[a] Institute of Chemistry, University of Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany
Fax +49(381)4986412; E-mail: christian.vogel@uni-rostock.de

[b] Leibniz Institute for Catalysis, University of Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Received 27 January 2009; revised 25 March 2009

Dedicated to Professor Dr. Klaus Peseke on the occasion of his 70th birthday

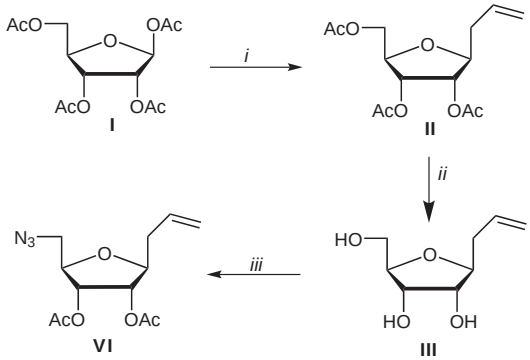
Abstract: The peracetylated β-allyl C-glycosides of D-ribofuranose (**8**) and 2-deoxy-D-ribofuranose (**13**) were stereoselectively prepared via the isopropylidene derivatives **3** and **4**. These reactions represent what are, to the best of our knowledge, the first preparation of these apparently simple derivatives whose structures were carefully proved by NMR and X-ray investigations. Publications which allegedly described the synthesis of **8** and **13** were critically examined.

Key words: allylation, glycosylation, C-glycosides, nucleosides, stereoselectivity

The preparation of novel nucleoside analogues as antiviral and antitumor agents is critical for drug development. In addition to the modification of the sugar residue of nucleosides, there is an increasing interest in compounds with a tetrahydrofuran ring and C-linked substituents at the anomeric center, the C-nucleosides. Due to the replacement of the N-glycosidic bond, these compounds possess greater stability towards enzyme catalyzed metabolism. Homonucleosides are a variation of C-nucleosides in which a methylene or alkylidene group is inserted between C-1 of the tetrahydrofuran ring and the heterocycle.[2,3] β-*C*-Allyl glycosides of D-ribofuranose and 2-deoxy-D-ribofuranose are convenient precursors for the synthesis of homonucleosides, and so there is interest to prepare these compounds stereoselectively and on gram-scale.

A supposedly simple procedure for synthesis of the peracetylated β-*C*-allyl glycosides of D-ribofuranose has been described by McDevitt and Lansbury, Jr. as shown in Scheme 1.[4] To confirm the structures **I** and **II** we carried out the complementary experiments as shown in Scheme 2.

In order to fix the furanose form, D-ribose was condensed with acetone to provide 2,3-*O*-isopropylidene-D-ribose (**2**),[5–7] which was transformed into the diacetyl derivative **3**[6] in 94% yield. Selective protection of the primary hydroxyl group of **2** with a *tert*-butyldiphenylsilyl group (TBDPS) followed by acetylation provided compound **4**[8] in 75% overall yield from **2**. 1-*O*-Acetates **3** and **4** were both converted into the *C*-allyl glycosides **5** and **6** by treatment with allyltrimethylsilane (AllTMS) and zinc bromide in $MeNO_2$ as solvent.[9] While Fürstner et al. who used instead trimethylsilyl triflate ((TMSOTf) as promoter and MeCN as solvent obtained the α/β-epimers in 63% overall yield (α/β ratio of 1:10)[10] we were able to isolate the pure β-*C*-allyl glycoside **5** in 78% yield from the reaction mixture (α/β ratio 1:7).



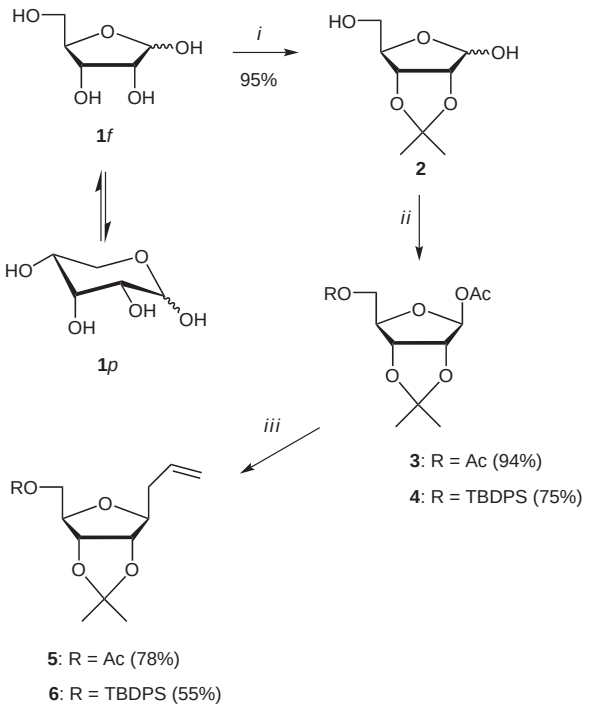
Scheme 1 Alleged synthesis of compound **II** and consecutive reactions. *Reagents and conditions*: (*i*) AllTMS, TMSOTf, MeCN; (*ii*) LiOMe, MeOH; (*iii*) TsCl, py, then NaN_3, DMF, finally Ac_2O, Et_3N, DMAP, CH_2Cl_2.

The employment of a bulkier protecting group at the O-5 position, in our example a TBDPS group, resulted in a decrease in both in yield and stereoselectivity. Although Wilcox and Otoski obtained the corresponding *C*-allyl glycosides bearing a *tert*-butyldimethylsilyl group (TBDMS) in 84% overall yield and in an α/β ratio of 1:16,[9] we obtained a reaction mixture with an α/β ratio of 1:3 from which nearly pure β-*C*-allyl glycoside **6** was isolated in 55% yield. X-ray diffraction studies of compound **6** (Figure 1) established its structure and confirmed the tetrahydrofuran ring as well as the β-linkage to the allyl residue with C-1′ possessing *S*-configuration.

At present, the best pathway to synthesize a β-allyl C-glycoside of D-ribofuranose proceeds via the 2,3-*O*-isopropylidene diacetate **3**.

Next, complete deprotection of C-glycoside **5** was achieved by treatment with hydrogen chloride in ethanol–water for 2 days at room temperature in 80% yield (Scheme 3). In a similar fashion, compound **6** was deprotected using a two-step procedure in which the TBDPS group was cleaved off by tetrabutylammonium fluoride (TBAF) followed by removal of the isopropylidene group

SYNTHESIS 2009, No. 11, pp 1834–1840
Advanced online publication: 12.05.2009
DOI: 10.1055/s-0029-1216794; Art ID: T01909SS



Scheme 2 Efficient synthesis of a β-allyl C-glycoside of D-ribofuranose **5**. *Reagents and conditions*: (*i*) H_2SO_4 (cat.), acetone; (*ii*) Ac_2O, py (**3**) or TBDPSCl, DMF, imidazole, followed by Ac_2O, py (**4**); (*iii*) AllTMS, $ZnBr_2$, $MeNO_2$.

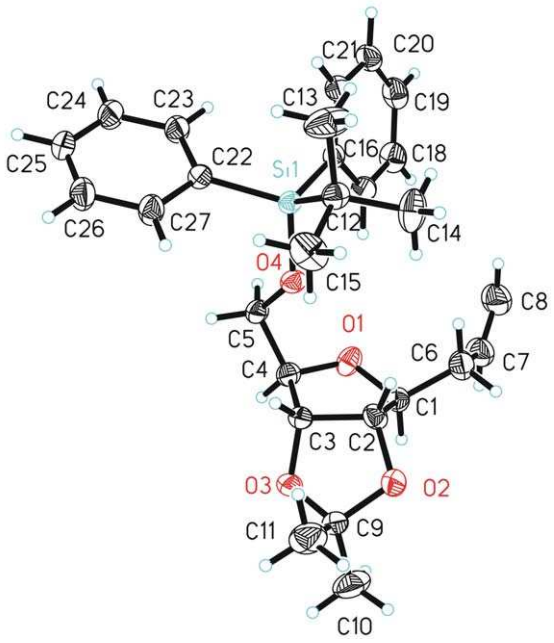
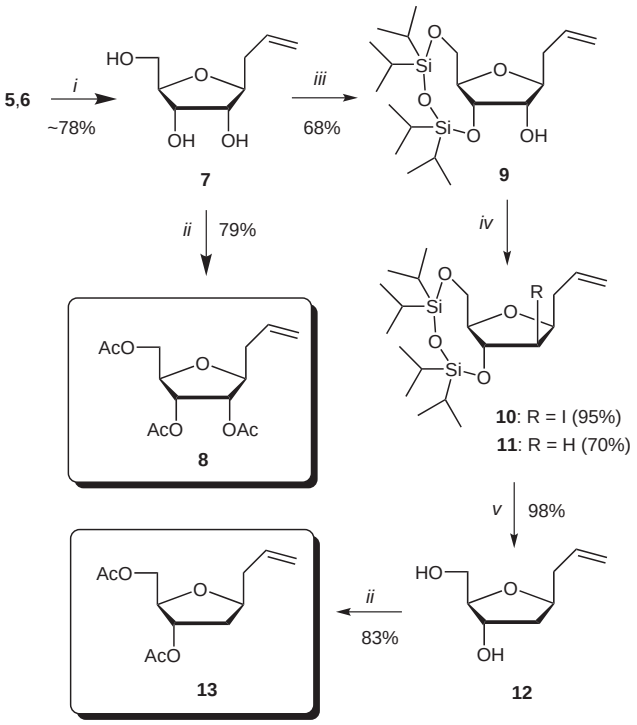


Figure 1 ORTEP plot of compound **6** with *S*-configured C1A; puckering parameters are Q = 0.2993(10) Å, F = 56.39(19)°

with dilute acid. Simple acetylation of **7** with acetic anhydride in pyridine furnished pure triacetate **8** in 80% yield.

The furanose structure of compound **8** was confirmed by NMR measurements. Thus, in a two-dimensional NOESY NMR spectrum a correlation was found between the protons H-1′ and H-4′. On the other hand, no NOE was observed between the protons H-1′ and H-5′ (Figure 2).



Scheme 3 Synthesis of the title compounds **8** and **13**. *Reagents and conditions*: (*i*) aq HCl, EtOH (for **5**); TBAF, 1,4-dioxane, then aq HCl, EtOH (for **6**); (*ii*) Ac_2O, py; (*iii*) TIPDSCl, py; (*iv*) I_2, Ph_3P, imidazole, toluene (**10**), then Bu_3SnH, AIBN, toluene (**11**); (*v*) TBAF, 1,4-dioxane.

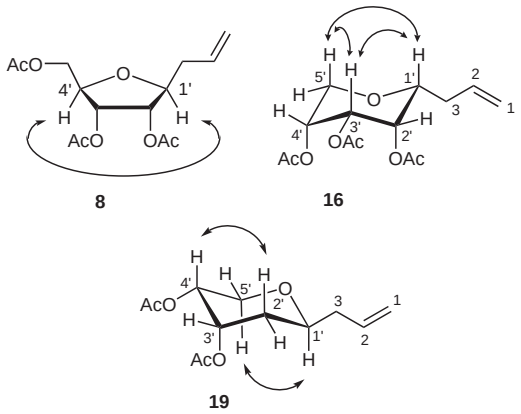


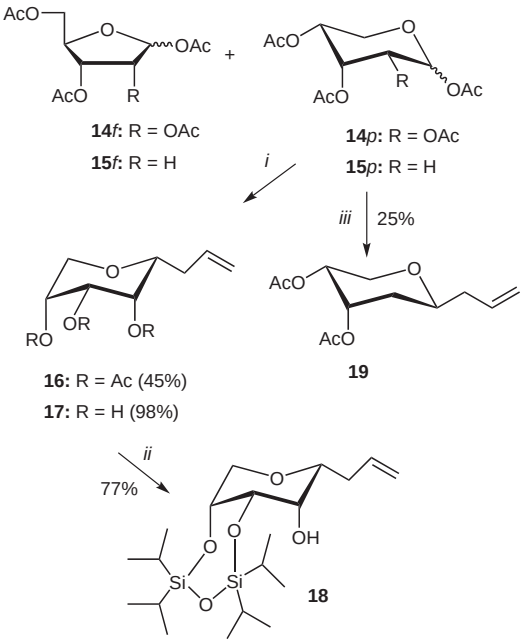
Figure 2 Relevant NOE correlations of compounds **8**, **16**, and **19**

In order to synthesize the corresponding 2-deoxy derivative, the unprotected compound **7** was treated with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (TIPDSCl) in pyridine (Scheme 3). The TIPDS-protected derivative **9** was thus obtained in 68% yield. The first strategy employed for the free radical deoxygenation of compound **9** was based on a method originally developed by Barton and McCombie.[11] The coupling reaction between compound **9** and phenyl chlorothionocarbonate[12] or 1,1′-thiocarbonyldiimidazole[13] yielded the corresponding thiocarbonyl derivatives in 80% and 90%, respectively.

Unfortunately, the subsequent reduction with Bu_3SnH or hypophosphorous acid did not provide compound **11**. On the contrary, the starting material was quantitatively recovered. Alternatively, iodination procedure developed by Garegg and Samuelsson[14] gave the 2-iodo-2-deoxy-*arabino* derivative **10** in 95% yield. Now, radical-based reduction of **10** with Bu_3SnH[15] furnished the desired derivative **11** in 70% yield. However, only a cautious removal of Ph_3P and its oxide led to the successful formation of **11**. Finally, treatment of **11** with TBAF followed by classical acetylation of the unprotected derivative **12** led to the diacetate **13** in 83% overall yield.

Both acetylated β-*C*-allyl D-ribofuranosyl derivatives **8** and **13** in hands, we compared our analytical data with those of McDevitt and Lansbury, Jr.[4] as well as Diederichsen and Biro.[16] The first group described the reaction of 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose (Scheme 1, compound **I**) with AllTMS in the presence of TMSOTf as promoter in MeCN as the solvent. Apparently, they obtained an α/β mixture of the corresponding *C*-allyl ribofuranose derivatives in a ratio of 1:3 in cumulative 87% yield. The supposed β-derivative was purified and characterized by ^{1}H NMR spectroscopy. Unfortunately, there is no reference to the origin of the peracetylated ribofuranose **I** not even in the supplementary material. Obviously, the authors ignored the fact that acetylation of free D-ribose to get the peracetylated furanose derivatives **I** is not a simple task. In 1953 two procedures have been published by Zinner to synthesize either the pyranose or the furanose of peracetylated ribose.[17] The acetylation procedure at low temperature (0 °C) provided compound **14*p*** in 80% yield predominantly as β-isomer, at higher temperature (136 °C) the furanose derivative **14*f*** was isolated in 43% yield; both by crystallization (Scheme 4). Presumably, McDevitt and Lansbury, Jr. used a furanose-pyranose mixture of peracetylated D-ribose, which led to the observed 1:3 mixture of products, that is, *C*-allyl ribofuranose and *C*-allyl ribopyranose. The real problem is that the authors continued their work with the major product, which was the ribopyranose. That explains why they got only moderate or poor yields during the following steps including tosylation and exchange of the tosyl group by azide at a not existing primary hydroxyl group (Scheme 1). Additionally, they did not obtain the β-isomer, but they got the α-isomer **16** (Scheme 4). It is known from the literature that steric hindrance of the isopropylidene group favors the *trans*-1′,2′ isomer since peracetylated sugar derivatives show a general increase in the ratio of *cis*-1′,2′ isomers.[10,18]

We repeated the C-allylation with a furanose/pyranose mixture of peracetylated D-ribose obtained by acetylation at room temperature and got exactly the same ratio of compounds as described by McDevitt and Lansbury, Jr.[4] Isolation of the major product gave the α-isomer **16** in 45% yield (Scheme 4). The ^{1}H NMR data of **16** are in excellent accordance with data published for the supposed β-*C*-allyl ribofuranose. Comparing the values of optical rotation, there are significant differences between compound **8** and **16** with $[\alpha]_D^{23}$ –0.7 and $[\alpha]_D^{23}$ +18.6, respectively. But, the determination of optical rotation in the case of chiral compounds seems to become an old-fashioned method since there are no data in the literature.[4] Furthermore, in the ^{1}H NMR spectra of **8** the signal of H-1′ appeared δ = 4.01 while for **16** the signal of H-1′ was downfield shifted to δ = 3.53. On the contrary, in ^{13}C NMR spectra of **8** the signals of C-2′–C-4′ (δ = 71.5–79.0) appeared at lower field than the same signals of compound **16** (δ = 66.7–68.3).



Scheme 4 Synthesis of allyl C-glycosides of D-ribopyranose and 2-deoxy-D-ribopyranose with the object of comparison. *Reagents and conditions*: (*i*) AllTMS, TMSOTf, MeCN (**16**), then NaOMe, MeOH (**17**); (*ii*) TIPDSCl, py; (*iii*) AllTMS, TMSOTf, MeCN.

By detailed NMR investigation, based on coupling constants and NOE's, the conformation of compound **16** could be established as an α-configured $^1C_4$-tetrahydropyran ring. Thus, in a NOESY spectrum of **16**, NOE correlations were observed for the proton H-1′ with H-2′, H-3′ and H-5′-axial as well as for H-5′-axial with H-1′, H-3′, and H-4′ (Figure 2). Furthermore, due to the small coupling constants found for the ring protons (^3J < 3.8 Hz) any other structure with bis-axial positions of the ring protons can be excluded.

Fortunately, deacetylation of **16** to compound **17** followed by introduction of the TIPDS group at O-3 and O-4 position gave the crystalline derivative **18**. In the NOESY spectra recorded for **18** the same correlations as for compound **16** were found and the coupling constants of **18** correspond to those of **16** and **17** proving also the α-configured $^1C_4$-tetrahydropyran structure. Besides NMR studies, the structure of the compound **18** could be additionally proven by X-ray structure analysis (Figure 3). The solid crystallizes in the orthorhombic space group $P2_12_12_1$ with two conformers per asymmetric unit. The main difference between both structures lies in the confor-

mation of the *C*-allyl group (see also the puckering parameters below). But even for conformer 1 there are hints from the refinement calculations for a disorder in the allyl group. All the other analytical data were also in good agreement with the proposed structure of **18**.

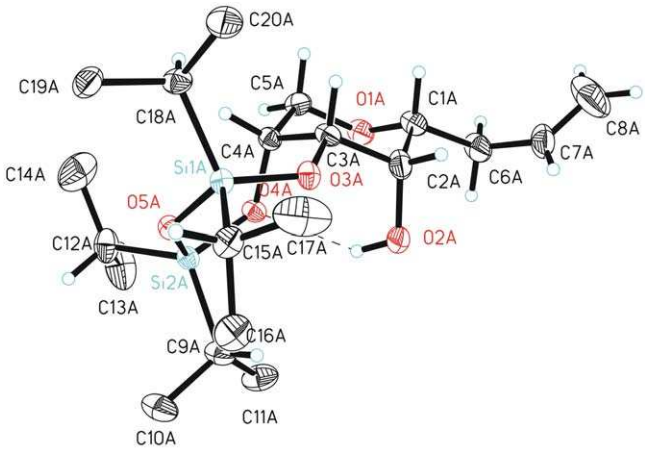


Figure 3 ORTEP plot of compound **18** (conformer 2: 30% probability for the displacement ellipsoids, hydrogens of methyl groups omitted for clarity); puckering parameters of conformer 1 are Q = 0.587(5) Å, Θ = 175.8(6)°, Φ = 268(6)°, and of conformer 2 are Q = 0.577(6) Å, Θ = 177.8(7)°, Φ = 246(12)°

The work of McDevitt and Lansbury, Jr.[4] has to be revised because other research groups used their procedure. Thus, Roy and co-workers investigated the stereoselective isomerization of *C*-allyl glycosides into *C*-vinyl glycosides or *exo*-glycals using, among other things, the alleged β-*C*-allyl ribofuranose prepared according to the published procedure.[19] Moreover, Diederichsen and Biro transferred the false synthetic course to peracetylated 2-deoxy-D-ribose.[16] They ignored the fact that acetylation of free 2-deoxy-D-ribose always led to a complex mixture from which the isolation of the desired furanose derivative is time-consuming and cumbersome.[20]

We repeated the C-allylation under the same conditions as described by Diederichsen and Biro[16] and isolated compound **19** in 25% yield as the main product. As expected, the ^{1}H NMR data of **19** were in excellent accordance with those of their supposed diacetate of β-*C*-allyl 2-deoxy-ribofuranose. Again, the publication did not provide data for optical rotation or a further evidence for the ring size and the stereochemistry at C-1′. Indeed, the analytical data of compound **13** and **19** differ from each other significantly. For instance, the optical rotation of **13** was $[\alpha]_D^{22}$ +27.9, whereas **19** gave a value of $[\alpha]_D^{22}$ +48.4. Furthermore, in the ^{1}H NMR spectra the signal of H-1′ of **13** at δ = 4.01–4.25 occurs at lower field compared to the signal of H-1′ at δ = 3.67–3.74 of compound **19**. Conspicuously, in the ^{13}C NMR spectra the signals of the carbon atoms C-3′ and C-4′ of **13** appeared at δ = 76.3 and 78.3, respectively, while the signals of the same carbon atoms of **19** were assigned at δ = 67.1 and 67.8, respectively. Additionally, coupling constants and results of NOESY measurements led to the conclusion that compound **19** adopts a β-configured $^4C_1$-tetrahydropyran ring structure. The vicinal coupling constants $^3J_{1',2'ax}$ = 11.4 Hz and $^3J_{4',5'ax}$ = 10.7 Hz prove a bis-axial arrangement of these protons. Further, a long-range coupling between the protons H-3′ and H-5′$_{eq}$ (^4J = 1.2 Hz) has been found indicating a bis-equatorial position of these protons (W-coupling). Furthermore, a NOESY spectrum of **19** showed correlations between the protons H-1′ and H-5′-axial, as well as H-2′-axial and H-4′, which prove the β-$^4C_1$ conformation (Figure 2).

In summary, this paper describes the first safe route for the synthesis of peracetylated β-allyl C-glycosides of D-ribofuranose (**8**) and 2-deoxy-D-ribofuranose (**13**). In addition, our reinvestigation of the synthetic pathways for compound **8** and **13** published by McDevitt and Lansbury, Jr.[4] and by Diederichsen and Biro,[16] respectively, has shown that both pathways given therein lead mainly to derivatives with six-membered rings instead of five-membered rings (compounds **16**, **17**, and **19**). Presumably, the reason for this mistake was the use of a mixture of peracetylated ribo- and deoxy-ribofuranose and -pyranose, respectively, as starting material and the selection of the wrong compounds from the reaction mixture for further investigation.

Melting points were determined with a Boetius micro-heating plate BHMK 05 (Rapido, Dresden) and are not corrected. Optical rotations were measured for solutions in a 2-cm cell with an automatic polarimeter GYROMAT (Dr. Kernchen Co.). ^{1}H NMR spectra (250.13 MHz, 300.13 MHz, and 500.13 MHz) and ^{13}C NMR spectra (62.9 MHz, 75.5 MHz and 125.8 MHz) were recorded on Bruker instruments AV 250, AV 300, and AV 500, respectively, with $CDCl_3$ or DMSO-d_6 as solvents. The calibration of spectra was carried out on solvent signals ($CDCl_3$: δ_H = 7.25, δ_C = 77.0; DMSO-d_6: δ_H = 2.50, δ_C = 39.7). ^{1}H and ^{13}C NMR signals were assigned by DEPT, two-dimensional ^{1}H–^{1}H COSY and NOESY and ^{1}H–^{13}C correlation spectra (HMBC and HSQC). For NMR numbering of atoms, see Figure 2. Mass spectra were recorded on an AMD 402/3 spectrometer (AMD Intectra GmbH). Elemental analysis was performed on a CHNS-Flash-EA-1112 instrument (Thermoquest). For the X-ray structure determination of compounds **6** and **18** an X8Apex system with CCD area detector was used (λ = 0.71073 Å, graphite monochromator). The structures were solved by direct methods (Bruker-SHELXTL). The refinement calculations were done by the full-matrix least-squares method of Bruker SHELXTL, Vers.5.10 (Copyright 1997, Bruker Analytical X-ray Systems). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into theoretical positions and refined using the riding model.[21]

All solutions used for washings were cooled to ~5 °C; aq sat. $NaHCO_3$ was used for washings. Reactions were monitored by TLC (Silica Gel 60, F_{254}, Merck KGaA). The following solvent systems (v/v) were used: (A_1) 2:1, (A_2) 5:1, (A_3) 6:1, (A_4) 10:1, (A_5) 30:1, (A_6) 50:1, (A_7) 80:1, (A_8) 100:1 *n*-hexane–EtOAc; (B) 10:1 EtOAc–MeOH. The spots were made visible by dipping the TLC plates into a methanolic 10% H_2SO_4 solution and charring with a heat gun for 3–5 min. Preparative flash chromatography was performed by elution from columns of slurry-packed Silica Gel 60 (Merck, 63–200 μm). All solvents and reagents were purified and dried according to standard procedures.[22] After classical workup of the reactions mixtures, the organic layers were dried over $MgSO_4$, and then concentrated under reduced pressure (rotary evaporator).

C-Allyl Glycosides 5 and 6

Allyltrimethylsilane (10.28 g, 90.0 mmol) was added to a stirred solution of 1,5-di-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranose (**3**; 5.49 g, 20.0 mmol) or of 1-*O*-acetyl-5-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranose (**4**; 9.41 g, 20.0 mmol) and $ZnBr_2$ (11.26 g, 50.0 mmol) in anhyd $MeNO_2$ (100 mL). After stirring for 1 h at r.t., aq sat. $NaHCO_3$ (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic phases were dried and concentrated. The residue was then purified by flash chromatography (solvent A_3 for **5** and solvent A_5 for **6**) to provide **5** as a colorless syrup (4.00 g, 78%) and **6** (4.98 g, 55%) as colorless crystals, respectively.

3-(5-*O*-Acetyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)prop-1-ene (5)

The analytical data agree perfectly with those published by Fürstner et al.[10]

3-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)prop-1-ene (6)

Mp 73–75 °C (EtOH); $[\alpha]_D^{21}$ +9.7 (*c* 1.0, $CHCl_3$); R_f = 0.45 (solvent A_4).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 [s, 9 H, $C(CH_3)_3$], 1.36, 1.55 [2 s, 6 H, $C(CH_3)_2$], 2.38–2.44 (m, 2 H, H-3), 3.80 (m, AB part of ABX, ^2J = 11.0 Hz, 2 H, H-5′), 3.98 (dt, $^3J_{1',2'}$ = 5.0 Hz, $^3J_{1',3}$ = 6.6 Hz, 1 H, H-1′), 4.05 ('q', $^3J_{3',4'} \approx {}^3J_{4',5'a} \approx {}^3J_{4',5'b}$ ≈ 3.8 Hz, 1 H, H-4′), 4.38 (dd, $^3J_{2',3'}$ = 6.7 Hz, 1 H, H-2′), 4.74 (dd, $^3J_{3',4'}$ = 3.8 Hz, $^3J_{2',3'}$ = 6.7 Hz, 1 H, H-3′), 5.10–5.17 (m, 2 H, H-1), 5.88 (m, 1 H, H-2), 7.37–7.45 (m, 6 H, 2 × C_6H_5), 7.69–7.73 (m, 4 H, 2 × C_6H_5).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 19.2 [*C*$(CH_3)_3$], 25.6, 27.5 [2 × C(*C*$H_3)_2$], 26.8 [C(*C*$H_3)_3$], 38.1 (C-3), 64.1 (C-5′), 81.8 (C-3′), 83.7 (C-1′), 84.2 (C-2′), 84.2 (C-4′), 114.0 [*C*$(CH_3)_2$], 117.4 (C-1), 127.6, 127.7 (2 × *m*-CH of Ph), 129.6, 129.7 (2 × *p*-CH of Ph), 133.2, 133.3 (2 × *i*-C of Ph), 134.0 (C-2), 135.6, 135.6 (2 × *o*-CH of Ph).

Anal. Calcd for $C_{27}H_{36}O_4Si$ (452.66): C, 71.64; H, 8.02. Found: C, 71.56; H, 8.31.

3-(β-D-Ribofuranosyl)prop-1-ene (7)

From **5**: Aq HCl (0.1 M, 30 mL) was added to a soln of compound **5** (14.61 g, 57.0 mmol) in EtOH (25 mL), and the mixture was stirred for 2 d at r.t. (monitored by TLC). The mixture was then neutralized by the addition of solid $NaHCO_3$, and concentrated after addition of a small amount of silica gel (suitable for flash chromatography). The residue was purified by flash chromatography (solvent A_4) to afford compound **7** (7.94 g, 80%) as a colorless syrup.

From **6**: A soln of TBAF in 1,4-dioxane (0.1 M, 7.3 mL) was added dropwise to a soln of compound **6** (2.26 g, 5.0 mmol) in 1,4-dioxane (73 mL) at r.t. The mixture was stirred at r.t. for 24 h, and concentrated. After dissolving the residue in EtOH (30 mL), aq 0.1 M HCl (10 mL) was added and the mixture was stirred for 24 h at r.t. The workup was done in the same way as described above to provide **7** (653 mg, 75%); $[\alpha]_D^{23}$ –4.6 (*c* 1.0, MeOH); R_f = 0.35 (solvent B).

^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.09–2.34 (m, 2 H, H-3), 3.30–3.45 (m, 2 H, H-5′), 3.52 (m, 1 H, H-1′), 3.64–3.48 (m, 2 H, H-2′, H-4′), 3.72 (m, 1 H, H-3′), 4.58 (t, $^3J_{5',OH}$ = 5.7 Hz, 1 H, OH-5′), 4.67 (br, 1 H), 4.69 (br, 1 H, OH-2′, OH-3′), 4.97–5.11 (m, 2 H, H-1), 5.83 (m, 1 H, H-2).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 37.7 (C-3), 62.2 (C-5′), 71.2 (C-3′), 74.0 (C-1′), 81.6, 84.5 (C-2′, C-4′), 116.8 (C-1), 135.5 (C-2).

ESI-MS (+): *m*/*z* = 197 $[M + Na]^+$.

Anal. Calcd for $C_8H_{14}O_4$ (174.19): C, 55.16; H, 8.10. Found: C, 55.07; H, 7.84.

3-(2,3,5-Tri-*O*-acetyl-β-D-ribofuranosyl)prop-1-ene (8)

Freshly distilled Ac_2O (0.5 mL) was added to a stirred soln of compound **7** (174 mg 1.0 mmol) in anhyd pyridine (1.0 mL) at 5 °C. The mixture was allowed to attain r.t. and stirring was continued overnight. For workup, the reaction mixture was poured into ice-water (40 mL), the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phases were washed successively with cold aq $NaHCO_3$ (2 × 20 mL), H_2O (20 mL), aq 1 M HCl (2 × 20 mL), H_2O (2 × 20 mL), dried, and concentrated. Purification by flash chromatography (solvent A_1) afforded compound **8** (237 mg, 79%) as a colorless syrup; $[\alpha]_D^{23}$ +18.6 (*c* 1.0, CH_2Cl_2); R_f = 0.33 (solvent A_1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 2.03 (s, 3 H), 2.05 (s, 3 H, 3 × $COCH_3$), 2.28–2.42 (m, 2 H, H-3), 4.01 ('q', 1 H, $^3J_{1',2'} = {}^3J_{1',3}$ = 5.9 Hz, H-1′), 4.07 (dd, $^3J_{4',5'a}$ = 4.7 Hz, $^2J_{5'a,5'b}$ = 11.4 Hz, 1 H, H-5′a), 4.08–4.11 (m, 1 H, H-4′), 4.28 (dd, $^3J_{4',5'b}$ = 2.8 Hz, $^2J_{5'a,5'b}$ = 11.4 Hz, 1 H, H-5′b), 4.95 ('t', 1 H, $^3J_{2',3'}$ = 5.9 Hz, H-2′), 5.07–5.13 (m, 3 H, H-1, H-3′), 5.77 (m, 1 H, H-2).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.8 (3 × CO*C*H_3), 37.1 (C-3), 63.5 (C-5′), 71.5 (C-3′), 73.4 (C-2′), 79.0 (C-4′), 80.4 (C-1′), 118.3 (C-1), 132.7 (C-2), 169.7, 169.8, 170.6 (3 × C=O).

CI-MS: *m*/*z* (%) = 301 (100, $[M + H]^+$).

Anal. Calcd for $C_{14}H_{20}O_7$ (300.30): C, 55.99; H, 6.71. Found: C, 55.91; H, 6.78.

3-[3,5-*O*-(Tetraisopropyldisiloxan-1,3-diyl)-β-D-ribofuranosyl]prop-1-ene (9)

1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (8.4 mL, 27.0 mmol) was added to a soln of compound **7** (4.36 g, 25.0 mmol) in anhyd pyridine (60 mL). After stirring at r.t. for 24 h, the reaction mixture was diluted with EtOAc (200 mL), and the organic phase was washed successively with ice-water (100 mL), aq 1 M HCl (2 × 100 mL), H_2O (2 × 100 mL), dried, and concentrated. Purification by flash chromatography (solvent A_4) afforded compound **9** (7.08 g, 68%) as a colorless syrup; $[\alpha]_D^{24}$ –20.7 (*c* 1.0, CH_2Cl_2); R_f = 0.48 (solvent A_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90–1.11 [m, 28 H, 4 × $CH(CH_3)_2$], 2.25–2.44 (m, 2 H, H-3), 2.82 (d, $^3J_{2',OH}$ = 3.7 Hz, 1 H, OH-2′), 3.75–3.90 (m, 3 H, H-1′, H-2′, H-4′), 3.87 (dd, $^3J_{4',5'a}$ = 6.0 Hz, $^2J_{5'a,5'b}$ = 11.9 Hz, 1 H, H-5′a), 4.00 (dd, $^3J_{4',5'b}$ = 3.2 Hz, 1 H, H-5′b), 4.18 ('t', $^3J_{2',3'} = {}^3J_{3',4'}$ = 6.4 Hz, 1 H, H-3′), 5.05–5.16 (m, 2 H, H-1), 5.86 (m, 1 H, H-2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.6, 12.8, 13.2, 13.4 [4 × *C*$H(CH_3)_2$], 16.9, 17.0, 17.0, 17.1, 17.2, 17.3, 17.3, 17.4 [8 × CH(*C*$H_3)_2$], 37.7 (C-3), 62.7 (C-5′), 72.2 (C-3′), 73.8 (C-2′), 82.2, 83.4 (C-1′, C-4′), 117.5 (C-1), 133.9 (C-2).

CI-MS: *m*/*z* (%) = 417 (100, $[M + H]^+$).

Anal. Calcd for $C_{20}H_{40}O_5Si_2$ (416.70): C, 57.65; H, 9.68. Found: C, 57.41; H, 9.75.

3-[2-Deoxy-2-iodo-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-β-D-arabinofuranosyl]prop-1-ene (10)

A mixture of compound **9** (1.04 g, 2.5 mmol), Ph_3P (1.65 g, 6.3 mmol), imidazole (436 mg, 6.4 mmol), and I_2 (947 mg, 7.5 mmol) in toluene (30 mL) was heated under reflux for 5–6 h (monitored by TLC). The reaction mixture was cooled to r.t., aq sat. $NaHCO_3$ (50 mL) was added, and the mixture was stirred for 5 h. The toluene phase was then separated and concentrated. Flash chromatography (solvent A_8) of the residue provided compound **10** (1.32 g, 95%) as a colorless syrup; $[\alpha]_D^{24}$ –72.3 (*c* 1.0, CH_2Cl_2); R_f = 0.32 (solvent A_6).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00–1.10 [m, 28 H, 4 × $CH(CH_3)_2$], 2.40 (m, 2 H, H-3), 3.19 (dt, $^3J_{1',2'}$ = 3.8 Hz, $^3J_{1',3}$ = 6.7 Hz, 1 H, H-1′), 3.78 (d't', $^3J_{3',4'}$ = 3.5 Hz, $^3J_{4',5'b}$ = 4.0 Hz,

$^3J_{4',5'a}$ = 9.8 Hz, 1 H, H-4′), 3.93 (dd, $^2J_{5'a,5'b}$ = 11.0 Hz, 1 H, H-5′a), 4.17 (dd, $^3J_{4',5'b}$ = 4.0 Hz, 1 H, H-5′b), 4.24 (dd, $^3J_{2',3'}$ = 1.6 Hz, 1 H, H-2′), 4.92 (dd, $^3J_{3',4'}$ = 3.5 Hz, 1 H, H-3′), 5.10–5.27 (m, 2 H, H-1), 5.80 (m, 1 H, H-2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.4, 13.1, 13.4, 13.6 [4 × *C*H(CH$_3$)$_2$], 16.9, 17.0, 17.0, 17.2, 17.4 (two signals are isochronic), 17.5, 17.5 [8 × CH(*C*H$_3$)$_2$], 38.6 (C-2′), 41.2 (C-3), 65.6 (C-5′), 78.9 (C-1′), 87.3 (C-4′), 84.4 (C-3′), 118.0 (C-1), 133.3 (C-2).

ESI-MS (+): *m*/*z* = 527 [M + H]$^+$.

Anal. Calcd for $C_{20}H_{39}IO_4Si_2$ (526.60): C, 45.62; H, 7.46. Found: C, 45.53; H, 7.51.

3-[2-Deoxy-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-β-D-*erythro*-pentofuranosyl]prop-1-ene (11)

A mixture of compound **10** (790 mg, 1.5 mmol), Bu_3SnH (873 mg, 3,0 mmol), and azobisisobutyronitrile (AIBN, 49 mg, 0.3 mmol) in toluene (20 mL) was stirred under reflux for 5 h, after which additional Bu_3SnH (437 mg, 1,5 mmol) and AIBN (49 mg, 0.3 mmol) were added. Stirring under reflux was continued for further 5 h, and the reaction mixture was then concentrated. Purification by flash chromatography (solvent A_7) afforded compound **11** (421 mg, 70%) as a colorless syrup; $[\alpha]_D^{23}$ –13.2 (*c* 1.0, CH_2Cl_2); R_f = 0.27 (solvent A_6).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99–1.09 [m, 28 H, 4 × CH(CH$_3$)$_2$], 1.81 (d′t′, $^3J_{1',2'a}$ = $^3J_{2'a,3'}$ = 7.8 Hz, $^2J_{2'a,2'b}$ = 12.5 Hz, 1 H, H-2′a), 2.00 (ddd, $^3J_{2'b,3'}$ = 4.5 Hz, $^3J_{1',2'b}$ = 6.6 Hz, 1 H, H-2′b), 2.18–2.37 (m, 2 H, H-3), 3.68–3.77 (m, 2 H, H-4′, H-5′a), 3.98–4.06 (m, 1 H, H-5′b), 4.12 (m, 1 H, H-1′), 4.36 (d′t′, $^3J_{2'b,3'}$ = 4.5 Hz, $^3J_{2'a,3'}$ = $^3J_{3',4'}$ = 7.8 Hz, 1 H, H-3′), 5.02–5.12 (m, 2 H, H-1), 5.80 (m, 1 H, H-2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.6, 12.9, 13.4, 13.5 [4 × *C*H(CH$_3$)$_2$], 17.0, 17.0, 17.1, 17.3, 17.4, 17.4 (two signals are isochronic), 17.5 [8 × CH(*C*H$_3$)$_2$], 39.7 (C-2′), 39.8 (C-3), 63.8 (C-5′), 73.5 (C-3′), 76.9 (C-1′), 85.9 (C-4′), 117.2 (C-1), 134.3 (C-2).

ESI-MS (+): *m*/*z* = 401 [M + H]$^+$.

Anal. Calcd for $C_{20}H_{40}O_4Si_2$ (400.70): C, 59.95; H, 10.06. Found: C, 60.03; H, 9.81.

3-(2-Deoxy-3,5-di-*O*-acetyl-β-D-*erythro*-pentofuranosyl)prop-1-ene (13)

A soln of TBAF in 1,4-dioxane (1.0 M, 0.4 mL) was added dropwise to a soln of compound **11** (100 mg, 0.25 mmol) in 1,4-dioxane (3.0 mL) at r.t. The reaction mixture was stirred at r.t. for 5 h, and then concentrated. The residue (compound **12**) was dissolved in anhyd pyridine (0.5 mL) and freshly distilled Ac_2O (0.25 mL) was added, and the obtained soln was stirred overnight at r.t.. The mixture was then poured into ice-water (20 mL), the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL), and the combined organic phases were washed successively with cold aq $NaHCO_3$ (2 × 15 mL), H_2O (15 mL), aq 1 M HCl (2 × 15 mL), H_2O (2 × 15 mL), dried, and concentrated. Purification by flash chromatography (solvent A_2) afforded compound **13** (50 mg, 83%) as a colorless syrup; $[\alpha]_D^{22}$ +27.9 (*c* 0.9, CH_2Cl_2); R_f = 0.22 (solvent A_2).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.79 (ddd, $^3J_{2'a,3'}$ = 6.4 Hz, $^3J_{1',2'a}$ = 10.4 Hz, $^2J_{2'a,2'b}$ = 13.7 Hz, 1 H, H-2′a), 1.99 (ddd, $^3J_{2'b,3'}$ = 1.5 Hz, $^3J_{1',2'b}$ = 5.2 Hz, 1 H, H-2′b), 2.04, 2.06 (2 s, 6 H, 2 × COCH$_3$), 2.22–2.47 (m, 2 H, H-3), 4.01–4.25 (m, 4 H, H-1′, H-4′, H-5′), 5.04–5.14 (m, 3 H, H-1, H-3′), 5.78 (m, 1 H, H-2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.8, 21.0 (2 × CO*C*H$_3$), 37.5, 39.1 (C-2′, C-3), 64.4 (C-5′), 76.3 (C-3′), 78.3 (C-4′), 82.1 (C-1′), 117.5 (C-1), 133.8 (C-2), 170.5, 170.7 (2 × C=O).

EI-MS: *m*/*z* (%) = 242 (1, [M]$^+$).

Anal. Calcd for $C_{12}H_{18}O_5$ (242.27): C, 59.49; H, 7.49. Found: C, 59.44; H, 7.71.

O-Acetates 14 and 15

Freshly distilled Ac_2O (25 mL) was added at 0 °C to a stirred soln of D-ribose (4.5 g, 30.0 mmol) or D-deoxyribose in anhyd pyridine (50 mL). After stirring for 12 h at r.t., the reaction mixture was poured into ice-water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 120 mL) and the combined organic layers were washed successively with aq 3% HCl (100 mL), ice-water (100 mL), aq sat. $NaHCO_3$ (100 mL) and ice-water (100 mL), dried, and concentrated.

3-(2,3,4-Tri-*O*-acetyl-α-D-ribopyranosyl)prop-1-ene (16)

TMSOTf (1.89 g, 8.5 mmol) was added dropwise to a soln of 1,2,3,4-tetra-*O*-acetyl-D-ribose (mixture of **14*f*** and **14*p***, 2.23 g, 7.0 mmol) and allyltrimethylsilane (3.2 mL, 20 mmol) in anhyd MeCN (20 mL) at 0 °C. The ice bath was removed, and the mixture was stirred for 6 h at r.t. Cold aq sat. $NaHCO_3$ (50 ml) was then added and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with brine (2 × 100 mL), dried, and concentrated. Purification by flash chromatography (solvent A_2) afforded compound **16** (946 mg, 45%) as colorless crystals. The synthesis corresponds to the procedure described in the literature[4] for the alleged preparation of compound **8**; mp 80 °C (EtOAc); $[\alpha]_D^{23}$ –0.7 (*c* 1.0, CH_2Cl_2); R_f = 0.21 (solvent A_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98, 2.13, 2.15 (3 s, 9 H, 2 × COCH$_3$), 2.18–2.27, 2.40–2.46 (2 m, 2 H, H-3), 3.53 (ddd, $^3J_{1',2'}$ = 1.2 Hz, $^3J_{1',3b}$ = 6.0 Hz, $^3J_{1',3a}$ = 7.8 Hz, 1 H, H-1′), 3.68 (dd, 1 H, $^3J_{4',5'ax}$ = 1.5 Hz, $^2J_{5'ax,5'eq}$ = 13.7 Hz, H-5′ax), 4.11 (dd, $^3J_{4',5'eq}$ = 1.8 Hz, 1 H, H-5′eq), 5.05 (′t′, $^3J_{2',3'}$ = $^3J_{3',4'}$ = 3.8 Hz, 1 H, H-3′), 5.05–5.10 (m, 2 H, H-1), 5.15 (m, 1 H, H-4′), 5.21 (m, 1 H, H-2′), 5.75 (m, 1 H, H-2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6, 20.7, 21.0 (3 × CO*C*H$_3$), 35.4 (C-3), 66.7 (C-4′), 67.8 (C-2′), 68.3 (C-3′), 69.0 (C-5′), 77.5 (C-1′), 118.3 (C-1), 132.9 (C-2), 169.8, 170.3, 170.4 (3 × C=O).

CI-MS: *m*/*z* (%) = 301 (100, [M + H]$^+$).

Anal. Calcd for $C_{14}H_{20}O_7$ (300.30): C, 55.99; H, 6.71. Found: C, 56.26; H 6.78.

3-(α-D-Ribopyranosyl)prop-1-ene (17)

Methanolic NaOMe (0.5 M, 0.15 mL) was added to a soln of compound **16** (905 mg, 3.0 mmol) in anhyd MeOH (7 mL). After stirring at r.t. for 2 h, the reaction mixture was neutralized with IR 120 (H$^+$) Amberlite resign, filtered, dried, and concentrated. Flash chromatography (solvent B) of the residue provided compound **17** (525 mg, 98%) as colorless crystals; mp 155 °C; $[\alpha]_D^{24}$ –11.8 (*c* 1.0, CH_3OH); R_f = 0.29 (solvent B).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.27 (m, 2 H, H-3), 3.22 (ddd, $^3J_{1',2'}$ = 1.1 Hz, $^3J_{1',3b}$ = 6.2 Hz, $^3J_{1',3a}$ = 7.5 Hz, 1 H, H-1′), 3.37 (dd, $^3J_{4',5'ax}$ = 1.0 Hz, $^2J_{5'ax,5'eq}$ = 12.0 Hz, 1 H, H-5′ax), 3.41 (br, 1 H, H-3′), 3.47 (m, 1 H, H-2′), 3.60 (br, 1 H, H-4′), 3.75 (dd, $^3J_{4',5'eq}$ = 2.2 Hz, 1 H, H-5′eq), 4.59 (d, $^3J_{2',OH}$ = 7.5 Hz, 1 H, OH-2′), 4.88 (br s, 1 H, OH-3′), 4.97–5.09 (m, 2 H, H-1), 5.06 (br d, $^3J_{4',OH}$ = 6.2 Hz, 1 H, OH-4′), 5.78 (m, 1 H, H-2).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 35.5 (C-3), 68.7 (C-3′), 69.3 (C-4′), 70.6 (C-5′), 70.9 (C-2′), 78.2 (C-1′), 116.7 (C-1), 135.4 (C-2).

CI-MS: *m*/*z* (%) = 197 (100, [M + Na]$^+$).

Anal Calcd for $C_8H_{14}O_4$ (174.19): C, 55.16; H, 8.10. Found: C, 55.39; H 8.37.

3-[3,4-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-α-D-ribopyranosyl]prop-1-ene (18)

Starting from compound **17** (525 mg, 3.0 mmol), compound **18** (963 mg, 77%) was obtained as colorless crystals according to the procedure described for compound **9**; mp 56–58 °C; $[\alpha]_D^{23}$ –27.3 (*c* 1.0, CH_2Cl_2); R_f = 0.41 (solvent A_4).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02–1.08 [m, 28 H, 4 × CH(CH_3)$_2$], 2.48 (m, 2 H, H-3), 3.20 (d, $^3J_{2',OH}$ = 10.5 Hz, 1 H, OH-2′), 3.26 (ddd, $^3J_{1',2'}$ = 1.1 Hz, $^3J_{1',3b}$ = 6.5 Hz, $^3J_{1',3a}$ = 7.5 Hz, 1 H, H-1′), 3.55 (dd, $^3J_{4',5'ax}$ = 1.3 Hz, $^2J_{5'ax,5'eq}$ = 12.4 Hz, 1 H,H-5′ax), 3.67 (m, 1 H, H-2′), 3.89 ('t', $^3J_{2',3''} \approx {}^3J_{3',4'}$ = 3.2 Hz, 1 H, H-3′), 4.04 (dd, $^3J_{4',5'eq}$ = 2.2 Hz, 1 H, H-5′eq), 4.18 (m, 1 H, H-4′), 5.05–5.17 (m, 2 H, H-1), 5.83 (m, 1 H, H-2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.5, 12.6, 13.6, 14.2 [4 × *C*H(CH_3)$_2$], 17.0, 17.1, 17.2, 17.3, 17.3, 17.6, 17.6, 17.6 [8 × CH(*C*H$_3$)$_2$], 35.8 (C-3), 71.0 (C-5′), 71.6, 71.7, 73.5 (C-2′, C-3′, C-4′), 80.0 (C-1′), 117.4 (C-1), 134.5 (C-2).

CI-MS: *m*/*z* (%) = 417 (100, $[M + H]^+$).

Anal. Calcd for $C_{20}H_{40}O_5Si_2$ (416.70): C, 57.65; H, 9.68. Found: C, 57.53; H, 9.95.

3-(2-Deoxy-3,4-di-*O*-acetyl-α-D-ribopyranosyl)prop-1-ene (19)

For transformation of 1,3,4-tri-*O*-acetyl-2-desoxy-D-ribose (mixture of **15*f*** and **15*p***, 520 mg, 2.0 mmol) into compound **18** conditions of McDevitt and Lansbury, Jr.[4] were used again (see preparation of **16**). Purification by flash chromatography (solvent A_2) afforded the main product **19** (121 mg, 25%) of the reaction as a colorless syrup; $[\alpha]_D^{22}$ +48.4 (*c* 0.5, CH_2Cl_2); R_f = 0.26 (solvent A_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.65 (ddd, $^3J_{2'ax,3'}$ = 2.5 Hz, $^3J_{1',2'ax}$ = 11.4 Hz, $^2J_{2'ax,2'eq}$ = 14.5 Hz, 1 H, H-2′ax), 1.87 (ddd, $^3J_{1',2'eq}$ = 2.0 Hz, $^3J_{2'eq,3'}$ = 3.8 Hz, 1 H, H-2′eq), 1.99, 2.10 (2 s, 6 H, 2 × $COCH_3$), 2.16–2.30 (m, 2 H, H-3), 3.67 ('t', $^3J_{4',5'ax} = {}^2J_{5'ax,5'eq}$ = 10.7 Hz, 1 H, H-5′ax), 3.67–3.74 (m, 1 H, H-1′), 3.80 (ddd, $^3J_{4',5'eq}$ = 5.4 Hz, $^4J_{3',5'eq}$ = 1.2 Hz, 1 H, H-5′eq), 4.88 (ddd, $^3J_{3',4'}$ = 3.0 Hz, 1 H, H-4′), 5.05–5.10 (m, 2 H, H-1), 5.40 (m, 1 H, H-3′), 5.79 (m, 1 H, H-2).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.8, 21.0 (2 × CO*C*H$_3$), 34.9 (C-2′), 39.5 (C-3), 63.9 (C-5′), 67.1 (C-3′), 67.8 (C-4′), 71.5 (C-1′), 117.4 (C-1), 134.1 (C-2), 169.9, 170.1 (2 × C=O).

EI-MS: *m*/*z* (%) = 242 (1, $[M]^+$).

HRMS: *m*/*z* calcd for $C_{12}H_{18}O_5$: 242.1142, found: 242.1149.

Acknowledgment

This work has been supported by Research Training Group 1213 'New Methods for Sustainability in Catalysis and Technique' (DFG). Further we would like to thank Prof. Dr. Udo Kragl for support and fruitful discussions.

References

(1) Present address: University Karlsruhe, Institute of Organic Chemistry, Fritz-Haber-Weg 6, 76131, Karlsruhe, Germany.
(2) Boal, J. H.; Wilk, A.; Scremin, C. L.; Gray, G. N.; Philips, L. R.; Beaucage, S. L. *J. Org. Chem.* **1996**, *61*, 1687.
(3) Hossain, N.; Blaton, N.; Peeters, O.; Rozenski, J.; Herdewijn, P. A. *Tetrahedron* **1996**, *52*, 5563.
(4) McDevitt, J. P.; Lansbury, P. T. Jr. *J. Am. Chem. Soc.* **1996**, *118*, 3818.
(5) Levene, P. A.; Stiller, E. T. *J. Biol. Chem.* **1933**, *102*, 187.
(6) Kiso, M.; Hasegawa, A. *Carbohydr. Res.* **1976**, *52*, 95.
(7) Kaskar, B.; Heise, G. L.; Michalak, R. S.; Vishnuvajjala, B. R. *Synthesis* **1990**, 1031.
(8) Lloyd, A. E.; Coe, P. L.; Walker, R. T.; Howarth, O. W. *J. Fluorine Chem.* **1993**, *60*, 239.
(9) Wilcox, C. S.; Otoski, R. M. *Tetrahedron Lett.* **1986**, *27*, 1011.
(10) Fürstner, A.; Radkowski, K.; Wirtz, C.; Goddard, R.; Lehmann, C. W.; Mynott, R. *J. Am. Chem. Soc.* **2002**, *124*, 7061.
(11) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.
(12) Genu-Dellac, C.; Gosselin, G.; Imbach, J.-L. *Carbohydr. Res.* **1991**, *216*, 249.
(13) Jun, S. J.; Moon, M. S.; Lee, S. H.; Cheong, C. S.; Kim, K. S. *Tetrahedron Lett.* **2005**, *46*, 5063.
(14) Garegg, P. J.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2866.
(15) Gimisis, T.; Ialongo, G.; Chatgilialoglu, C. *Tetrahedron* **1998**, *54*, 573.
(16) Diederichsen, U.; Biro, C. M. *Biorg. Med. Chem. Lett.* **2000**, *10*, 1417.
(17) Zinner, H. *Chem. Ber.* **1953**, *86*, 817.
(18) Kam, B. L.; Barascut, J.-L.; Imbach, J.-L. *Carbohydr. Res.* **1980**, *78*, 285.
(19) Patnam, R.; Juarez-Ruiz, J. M.; Roy, R. *Org. Lett.* **2006**, *8*, 2691.
(20) Venner, H.; Zinner, H. *Chem. Ber.* **1960**, *93*, 137.
(21) Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre under CCDC No. 717935 and 717936 for compounds **6** and **18**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax: +44(1223)336033 or via e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.
(22) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, **1988**.