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Organotransition metal modified sugars☆ Part 22. Direct metalation of glycals: short and efficient routes to diversely protected stannylated glycals

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Dedicated to Professor Jean Normant on the occasion of his 65th birthday

Abstract

A complete set of D-hexose-derived silyl and isopropylidene/silyl-protected glycals bearing complementary configurations at C-3 and C-4 has been synthesized in short and efficient 1–3 step sequences from standard precursors. The glycals have been applied to metalation reactions to give storable vinyl lithium equivalents by subsequent transmetalation to vinyl stannanes which represent valuable intermediates for transition metal-catalyzed cross-coupling reactions. A ^{1}H-NMR-assisted conformational analysis has been carried out with the protected glycals and the stannylated congeners. The isopropylidene/silyl-protected glycals adopt the $^4H_5$-conformation caused by the bicyclic system, whereas the conformations of the fully silyl-protected monocyclic glycals are mainly controlled by the vinylogous anomeric effect. The discussed galactal- and allal-derivatives show dynamic behaviour on the NMR-time-scale. At low temperatures the two possible conformers ($^4H_5$ and $^5H_4$) have been observed demonstrating competition of steric congestion and stereoelectronic interaction via the vinylogous anomeric effect (VAE).

Keywords: Carbohydrates; C-glycosidation; Glycals; Organostannanes

1. Introduction

Metalated glycals have been developed to versatile synthons in the synthesis of *C*-glycosides [1]. The structural diversity of target molecules synthesized or elaborated via metalated glycals covers *C*-aryl glycosidic structures [2] such as vineomycins [3], aquayamycin [4] or papulacandins [5] as well as fused pyran structures represented by herbicidins [6] or — more complex — by marine polyether antibiotics such as brevetoxins [7] (Scheme 1). Due to the easy access of a broad variety of glycals from naturally abundant carbohydrates they represent important enantiomerically pure building blocks [8]. However, the direct metalation at C-1 is hampered and impedes broader applications in this context. The limitations in the choice of different functional and even protective groups and the harsh deprotonation conditions required encouraged the development of alternative approaches to this type of compounds. A three-step procedure introduced by Ley [9] involves the activation of the anomeric position by addition of phenylsulfinic acid, subsequent deprotonation/stannylation followed by elimination of phenylsulfinic acid. The resulting stannane derivatives have been transmetalated to the lithio compounds and employed in Pd-catalyzed homocoupling reactions. The activated sulfone has been also obtained from lactones in a two-step procedure involving reduction to the lactol and substitution with phenylsulfinic acid. Lactones are the starting point of a second versatile method introduced by Kocienski [10] to avoid a direct metalation. Preparation of the enol triflate [11] and

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subsequent Stille-coupling with hexamethyldistannane [12] provides a two-step access to stannylated glycals. However, the 2-deoxy lactones required for their synthesis have to be prepared from the corresponding glycals in a two-step sequence [13], extending this approach to a very mild but rather lengthy four-step procedure. Recently, Nicolaou [14] introduced enol phosphonates for compounds with ring sizes larger than six which are usually difficult to obtain via the triflate route [15].

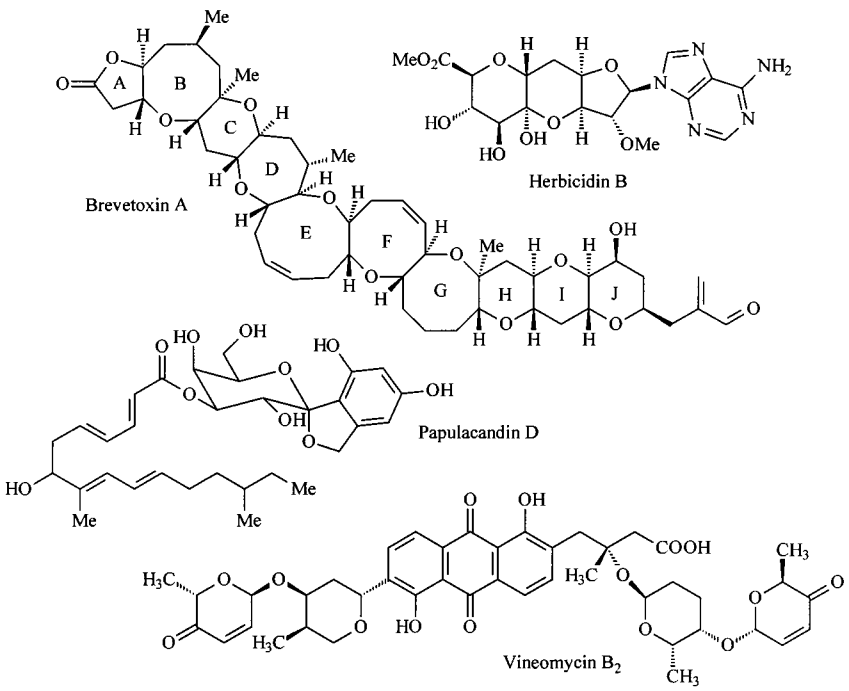
Thus, while efficient though lengthy and often low-yield alternative methods have been developed, we still considered the direct metalation approach to be beneficial if some major disadvantages could be overcome.

2. Preparation of fully protected glycals

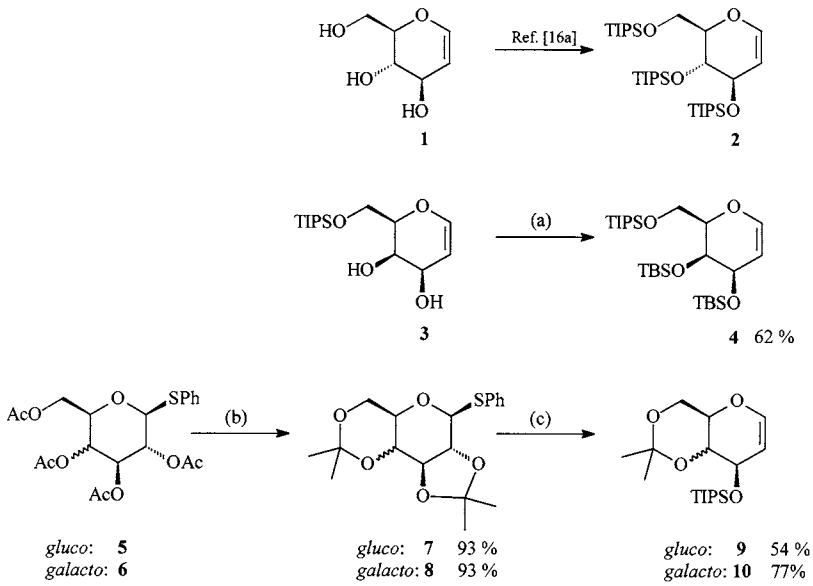
The multiple oxygen substitution pattern in glycals requires efficient protective groups. Only a few of them [16] are compatible with the metalation protocol [16a,17]. Thus, a tailored protection of the various hydroxy functionalities may be a challenge. Moreover, the metalation protocol demands a large excess of the metalating agent. Already Boeckmann noticed in an early work [17a] that two equivalents of *tert*-butyllithium are required for the effective metalation of cyclic enol ethers bearing an additional protected hydroxy group. A variety of 6-deoxy glycals have been metalated under identical conditions [2a,18]; however, an additional equivalent of *tert*-butyllithium is necessary in the presence of a primary hydroxy functionality. Friesen has shown for two glucal derivatives that high conversions to the lithioglucals require up to four equivalents of *tert*-butyllithium [16a]. This becomes an obvious problem when more complex and/or expensive electrophiles have to be used [2e,18c]. For this reason, it is advantageous to purify the resulting lithioglycal by transmetalation to the tri-*n*-butyl tin derivative, and, finally, to regenerate the lithioglycal by an additional transmetalation using *n*-butyllithium [6,19].

While the direct metalation of glucals and 6-deoxy glycals is well-known, the appropriate protection of galactal turns out to be problematic [18c], and to our knowledge there is no report of a direct metalation of an allal- or gulal-derivative at C-1. In this work we focus on the synthesis of fully silyl-protected and 4,6-isopropylidene-3-silylated glycals, their behaviour under the stannylation conditions and their conformation as a result of the protective group periphery.

While the preparation of the tris-triisopropylsilyl (TIPS)-protected glucal is known [16a], the per-TIPS protection of D-galactal has not been reported so far and is suggested to be highly unfavourable. Since the per-*tert*-butyldimethylsilyl (TBS)-protected galactal tends to competing α-silyl deprotonation at the 6-position [16b] the primary hydroxyl functionality has to be protected with a more bulky silyl protective group. Thus, we started from the known 6-TIPS derivative **3** [20] and installed the less bulky TBS groups at the 3- and 4-position under forcing conditions, providing the fully protected galactal derivative **4** in good yield (Scheme 2).



Scheme 1. Prominent natural products with *C*-glycosidic linkages.

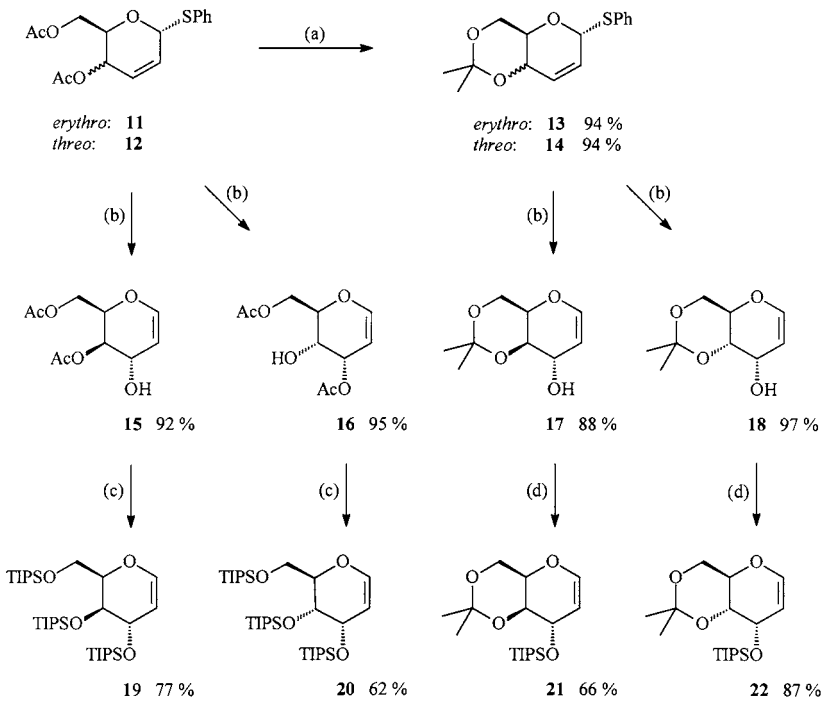


Scheme 2. Synthesis of protected glucals and galactals **2**, **4**, **9** and **10**. Reaction conditions: (a) TBSCl, imidazole, DMF, 60–80°C, 24 h. (b) 1) MeOH, LiOH, room temperature, 2 h, then NH_4Cl; 2) 2-methoxypropene, CSA, DMF, room temperature, 1 h. (c) 1) 3.2 eq. C_8K, THF, −40 to −20°C, 1.5 h; 2) 2.2 eq. TIPSCl, −20°C to room temperature, 1 h.

Recently, we introduced [16d] the isopropylidene group as a new cyclic protective group for the 4,6-position as an alternative to the expensive bis(*tert*-butyl)silylene group [16c]. Acid catalyzed introduction of an isopropylidene protective group is well-documented [21], but less suitable for acid-labile substrates. Furthermore, the kinetic protection of galactal results in incomplete regiochemistry [22]. Hoping to avoid the tedious purification problems and variable yields accompanied with the acid-catalyzed protection at the glycal stage [23], we decided to introduce the protective groups prior the formation of the glycal. Starting from the known phenylthio glycosides **5** and **6** [24], deacetylation and isopropylidenation proceeded in a 'one-pot' procedure in excellent yields. Unveiling the hidden carbanion present in the thioglycoside by reductive lithiation [25] should result in the formation of a metal alkoxide by a fragmentation of the labile anomeric carbanion. Intercepting of the alkoxide by a silylating agent offers the opportunity to protect the free hydroxide in the same step. Both, lithium–naphthalenide and graphite–potassium laminate have been reported to initiate this kind of transformation [26]. For our purposes, we found Fürstner's C_8K procedure superior because of reproducible yields and the enhanced reactivity of the potassium alkoxide in the silylation reaction. In the event, glucal **9** and galactal **10** have been obtained in satisfying yields (Scheme 2). This easy two-step sequence may be a valuable alternative for the facile access to differently protected glycals.

Allals and gulals are not readily available because of the relative rareness of allose and gulose [27]. Since allal is the C-3 epimer of glucal and gulal is the C-3 epimer of galactal, a straightforward strategy would employ an epimerization procedure at this stereocenter. Due to the allylic position to an enol ether double bond, an S_N2 process would be highly unfavourable, and substitution would preferentially occur at C-1 [28]. As a consequence, an allylic substitution occurs which is known in carbohydrate chemistry as the Ferrier-rearrangement [29]. To our knowledge, the most effective epimerization protocol [27e,30] makes use of the thio-Ferrier-reaction [31] obtaining the allylic α-sulfides as major products. Subsequent oxidation to the sulfoxides and shifting the sulfoxide–sulfenate equilibrium [32] by intercepting the sulfenates with diethylamine results in the isolation of the rearranged allylic alcohols [33].

Starting from the known pseudo-glycals [28,30a] **11** and **12** oxidation with dimethyl dioxirane (DMDO) [34] at low temperatures and subsequent [2,3]-sigmatropic rearrangement proceeded very cleanly in excellent yield. Oxidation may be even performed with MCPBA at low temperatures [35], however, the yields are lower and *m*-chloro-benzoate glycosides were identified as side products indicating the high reactivity of the anomeric sulfoxides as glycosyl donors. The *allo*-derivative was obtained as a 1:0.15:0.1 mixture of regioisomeric diacetates with the 3,6-diacetate as the major product. This result is in agreement with Danishefsky's observation [27e], under the slightly basic rearrangement conditions a transacetalization between *cis*-diols is favourable. Deacetylation and per-TIPS protection were performed as a 'one-pot' process; triisopropylsilyl triflate (TIPSOTf) was required to secure complete silylation. Due to the low solubility of the unprotected glycals in CH_2Cl_2, a small amount of DMF was added as solubi-



Scheme 3. Synthesis of protected allals and gulals **19**–**22**. Reaction conditions: (a) 1) MeOH, LiOH, room temperature, 1 h, then NH_4Cl; 2) 2-methoxypropene, CSA, DMF, room temperature, 2 h. (b) 1) DMDO, CH_2Cl_2, −78°C, 1 h; 2) Et_2NH, THF, room temperature, overnight. (c) 1) MeOH, LiOH, room temperature, 2 h, then NH_4Cl; 2) TIPSOTf, 2,6-lutidine, CH_2Cl_2, room temperature (to 40°C for the allo-isomer), 60 h. (d) TIPSOTf, 2,6-lutidine, CH_2Cl_2, 0°C to room temperature, 3 h.

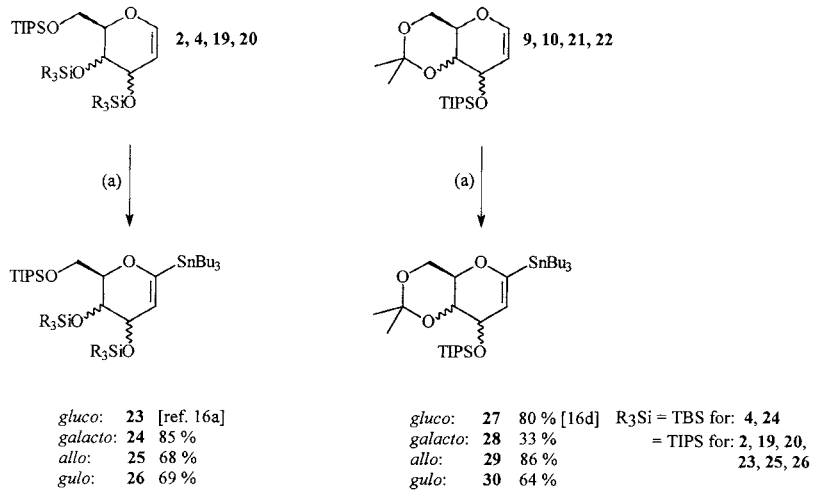
lizer. While the gulal reacted quite well, the final silylation of the allal derivative required more forcing conditions reflecting the relative steric bulk resulting from the *cis*-relationship of the 3- and 4-hydroxyl groups. Nevertheless, both gulal **19** and allal **20** were obtained in good yields according to this procedure (Scheme 3).

Similarly, the isopropylidene protected allal and gulal derivatives **21** and **22** are accessible in excellent yields from the pseudoglycals **11** and **12**. Deacetylation and isopropylidenation were performed as described for **5** and **6** to yield **13** and **14** [36]. DMDO-oxidation and subsequent rearrangement proceeded under the conditions described above in excellent yields. Noteworthy in this context is the relative stability of the sulfoxide derived from **14**, offering the opportunity to use this system directly for titration of the DMDO-solution; no DMDO is wasted by titration with triphenylphosphine [34]. The allylic alcohols **17** and **18** were silylated in CH_2Cl_2-solution with triisopropylsilyl triflate (TIPSOTf) in the presence of 2,6-lutidine under standard conditions [37] (Scheme 3).

3. Metalation

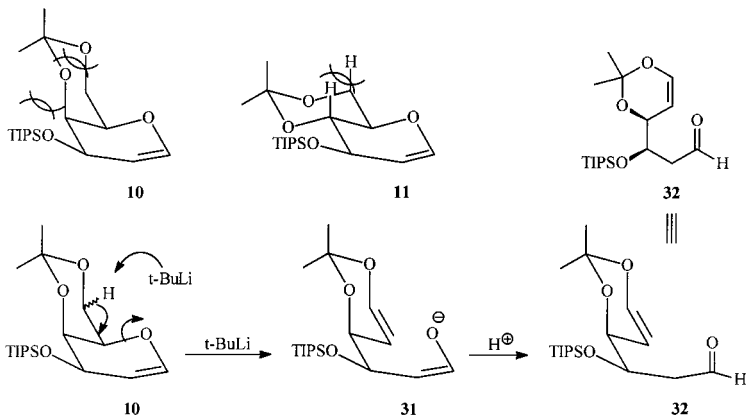
The appropriate protection of the glycals was exploited in their metalation. Considering literature precedence the per-silyl protected glycals were expected to give clean lithiation under the standard conditions [16a]. From earlier work in our laboratory [16d], we knew that side reactions in the isopropylidene series became serious when prolonged metalation times were applied. Restricting the reaction time to below 30 min, the glucal derivative **27** was obtained in good yield (vide infra). We now studied whether configurational changes affect the stability of the glycals under the metalation conditions (Scheme 4).

The per-silylated stannanes were obtained in good yields; varying amounts of starting material, however, indicated incomplete deprotonation. This may be due to the fact that these substances are viscous, glassy oils which resist sufficient drying even at 60–80°C in high vacuum for 30 min prior to use. The yields did not improve significantly upon prolonged deprotonation which supports the idea that deprotonation is fast at 0°C [17]. The isopropylidene-protected glycals may be divided in two classes: The derivatives with *gluco*- and *allo*-configuration represent a *trans*-decaline system while the *galacto*- and *gulo*- compounds contain a more strained *cis*-decaline system. The *galacto*-glycal **10** with the neighbouring siloxy group *cis* to the dioxane ring represents the most strained compound in this series which clearly affects the metalation as demonstrated by the contrasting low yield for the stannyl galactal **28**. Even under carefully adjusted conditions ring-opening



Reaction conditions: (a) 1) 3.5 eq. tert.-BuLi, THF, -78°C, then 0°C, 20 min; 2) 3.5 eq. Bu_3SnCl, THF, -78°C, 20 min; 3) H_2O (excess), -78°C.

Scheme 4. Lithiation/stannylation sequence to glycals **23**–**30**. Reaction conditions: (a) 1) 3.5 eq. tert.-BuLi, THF, − 78°C, then 0°C, 20 min; 2) 3.5 eq. Bu_3SnCl, THF, − 78°C, 20 min; 3) H_2O (excess), − 78°C.



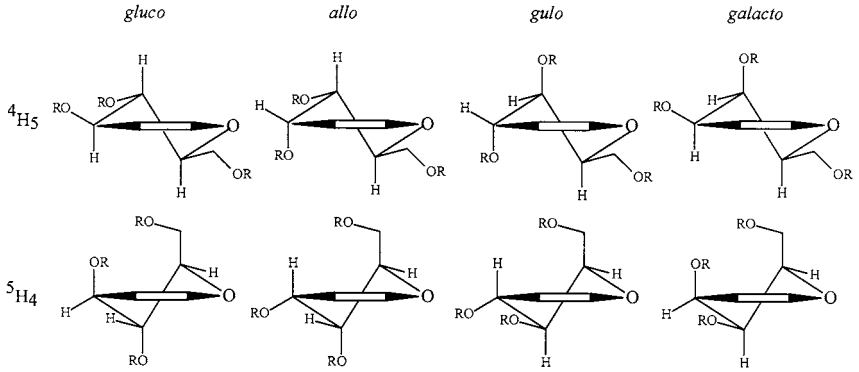
Scheme 5. Competing H-6 abstraction from the bicyclic galactal derivative **10**.

occurred resulting from a fragmentation initiated by deprotonation from C-6 to give the acyclic aldehyde **32** as the major product (Scheme 5). The stannyl glucal **27** and the stannyl allal **29** are obtained in good yields whereas strictly controlled conditions were required for gulal **30** to provide good yields.

Thus, the use of the isopropylidene protective group is an excellent alternative to the bulky silyl substituents when a 4,5-*trans*-relationship of the glycal results in the formation of a *trans*-decaline system. The efficiency of the protective group in the *cis*-decaline system is less straightforward. Especially the *galacto*-configuration results in considerable steric strain of the protected compound causing a facile fragmentation of the bicyclic system under the reaction conditions. Further progress in the use of ketals as base-stable protective groups may overcome these problems by either decreasing the strain or even protecting the methylene hydrogen atoms by an increase of the steric bulk of the protective group. The stannylated glycals described above are fairly stable compounds which can be stored in the refrigerator for months without decomposition which underlines their advantage as storable anion equivalents.

4. Conformational analysis

Stannyl glycals have been applied to the synthesis of C-2 functionalized carbene complexes [38,39]. This strategy relied on the intermediacy of carbene complex anions [40] which allowed a stereoselective addition of electrophiles at C-2 [16d,41]. In order to elucidate and predict the stereochemical outcome of these reactions we focused on a conformational study of the glycal precursors.



Scheme 6. $^4H_5$- and $^5H_4$-conformations of glycals.

In general two half-chair conformations, $^4H_5$ and $^5H_4$, are favoured for glycals [42]. The conformation with an axial substituent at C-3 may be unfavourable for steric reasons, but is strongly preferred due to the vinylogous anomeric effect (VAE) [43]. For this reason allals and gulals are expected to adopt predominantly a $^4H_5$-conformation. For galactals and glucals the $^5H_4$-conformer should be preferred if this stereoelectronic effect overrides the 1,3-diaxial-like interactions [42b]. If the glycal is fixed in a bicyclic system, the conformation is locked and should be mainly determined by the bicyclic system itself (Scheme 6).

NMR-spectroscopy is the method of choice to address the conformational aspects of glycals in solution, and it has been widely applied in analogous studies [44]. Two coupling constants, $J_{2,3}$ and $J_{2,4}$, are most diagnostic. The vinyl–allyl coupling $J_{2,3}$ depends on the torsion angle between the olefinic plane and the allylic hydrogen and is smallest when the angle is 90°. For this reason small $J_{2,3}$ coupling constants are indicative for a $^4H_5$-conformation in the glucal and galactal series as well as for a $^5H_4$-conformation in the allal and gulal series. A long range coupling constant $J_{2,4}$ is detectable when H-4 is equatorial. This is true for *gluco*- and *allo*-derivatives in the $^5H_4$-conformation whereas the *galacto*- and *gulo*-analogues require a $^4H_5$-conformation. In addition, glucals and galactals in a $^5H_4$-conformation should reveil small $J_{3,5}$ couplings due to the H-3, H-5 equatorial-equatorial relationship; glucals and allals in the $^4H_5$-conformation are expected to give large $J_{4,5}$ coupling constants resulting from the axial–axial setting of these hydrogen atoms [43a]. The important coupling constants for the bicyclic glycals **9**, **10**, **21**, **22** and **27**–**30** are summarized in Table 1. All isopropylidene protected glycals exhibit a $^4H_5$-conformation demonstrating the dominant influence of the cyclic protective group on the conformation.

A different situation was found for the monocyclic per-silylated glycals. The spectroscopic data of the tris-TIPS-protected glucals **2** and **23** clearly indicate a $^5H_4$-conformation preferring the 'all-axial'-orientation even stronger than for tri-*O*-acetyl-D-glucal [42b,43a]. For the gulal derivatives **19** and **26** the NMR data establish the $^4H_5$ conformation as the only detectable conformer at temperatures down to 223 K allowing the axial oxygen substituent at C-3 to interact with the enol ether π-bond (VAE). The galactals and allals show a dynamic behaviour at room temperature suggesting an equilibrium of the competing conformations. At low temperatures pairs of two conformers could be detected as separate compounds by NMR spectroscopy. In comparison, at 223 K both galactal **4** and the stannylated galactal **24** appear as a ~1:1 mixture of conformers displaying the competing effects of the VAE and the 1,3-diaxial-like interactions to a comparable extent. A similar situation was found for allal **20** and its stannylated congener **25**. As estimated from the analysis of the $J_{2,3}$-coupling constants the two conformers appear at 203 K as a ca. 10:1 (**20**) and ca. 5:1 (**25**) mixture in favour of the $^4H_5$-conformers. This small effect of substitution at C-1 may be correlated with a minor steric interaction of the bulky stannyl group with the axial-like TIPS-group at C-3. The preference of the $^4H_5$ conformation in the allal series in comparison with the galactal derivatives may be attributed to the inversion of stereochemistry at C-3 (Table 2).

In summary, the VAE seems to be the major dictating principle in the series of the monocyclic per-sily-

Table 1
Diagnostic coupling constants of bicylic glycals **9**, **10**, **21**, **22** and **27**–**30**

Compound	$J_{2,3}$	$J_{2,4}$	$J_{4,5}$	Conformation
9	1.9	[a]	10.4	$^4H_5$
22	5.8	[a]	10.4	$^4H_5$
21	5.1	1.6	1.6	$^4H_5$
10	1.8	1.5	1.2	$^4H_5$
27	2.0	[a]	10.4	$^4H_5$
29	5.5	[a]	10.5	$^4H_5$
30	5.1	1.6	1.5	$^4H_5$
28	1.5	1.5	1.5	$^4H_5$

[a] Not observed.

Table 2
Diagnostic coupling constants and estimated conformations of the per-silylated glycals **2**, **4**, **19**, **20** and **23**–**26**

Compound	$J_{2,3}$	$J_{2,4}$	$J_{3,5}$	$J_{4,5}$	Conformation	Ratio
2	5.2	1.8	2.0	1.8	$^5H_4$	
4	4.2 [b]	[a]	[a]	1.3 [b]	$^4H_5/^5H_4$	~1:1 [e]
20	4.9 [d]	[a]	[a]	8.2 [d]	$^4H_5/^5H_4$	~10:1 [f]
19	5.3	2.0	[a]	[a]	$^4H_5$	
23	5.1	1.6	2.0	2.0	$^5H_4$	
24	3.4 [c]	[a]	[a]	3.4 [c]	$^4H_5/^5H_4$	~1:1 [e]
25	4.2 [b]	[a]	[a]	7.3 [b]	$^4H_5/^5H_4$	~5:1 [f]
26	5.1	2.0	[a]	[a]	$^4H_5$	

[a] Not observed.
[b] Recorded at 363 K in toluene-d^8.
[c] Recorded at 343 K in toluene-d^8.
[d] Recorded at 333 K in toluene-d^8.
[e] Recorded at 223 K in toluene-d^8.
[f] Recorded at 203 K in CD_2Cl_2.

lated glycals irrespective of the steric bulk. C-1 substitution of glycals by the bulky tri(*n*-butyl)stannyl group has no significant influence [45] on the conformation of the glycals, in all cases they exhibit conformational properties comparable to their 'H-counterparts'.

5. Conclusion

In conclusion, we demonstrated that the direct metalation approach might be an effective transformation even in the case of highly functionalized enol ethers (i.e. glycals). The choice of the protective groups is crucial and for the protection of the sensitive primary alcohol functionality, we have introduced the isopropylidene functionality as a new inexpensive protective group, orthogonal to silyl ethers. Its 'stability' depends on the configuration of the glycal; while the *allo*- and *gluco*-configuration gives excellent results, the more strained bicyclic system resulting from the *galacto*- or *gulo*-configuration deserves further improvements. Protocols for the per-silylation of each configuration have been worked out which allow an efficient subsequent metalation as well. The monocyclic allals and galactals reveil an equilibrium consisting of two conformers. No significant influence of the stannyl substituent at C-1 on the distribution of the conformers was observed at low temperatures.

6. Experimental

6.1. General

All transformations were performed under argon using degassed solvents dried by standard procedures. All reagents were used as supplied commercially; chromatography was carried out on silica gel (Merck 60 (0.063–0.200)). All ^{1}H- and ^{13}C-NMR-spectra were recorded on a Bruker DRX-500 or AM-400 spectrometer. Spectra were recorded at 298 K unless otherwise stated. Chemical shifts refer to those of residual solvent signals based on $\delta_{Me_4Si} = 0.00$ ppm. Coupling constants are indicated in Hertz. Electron impact mass spectra were recorded on a Kratos MS 50 spectrometer; FAB mass spectra were recorded on a Kratos Concept 1H spectrometer. Elemental analyses were obtained from a Heraeus CHN–O-Rapid.

6.2. 1,5-Anhydro-3,4-di-O-(tert-butyl-dimethylsilyl)-6-O-triisopropylsilyl-2-deoxy-D-lyxo-hex-1-enitol (4)

Imidazol (2.45 g, 36 mmol) and TBSCl (3.62 g, 24 mmol) were added sequentially to a solution of 2.42 g (8.0 mmol) 1,5-anhydro-6-*O*-triisopropylsilyl-2-deoxy-D-*lyxo*-hex-1-enitol (**3**) in 25 ml DMF. The reaction mixture was stirred at 60°C for 24 h. After recooling to room temperature (r.t.) the solution was diluted with 100 ml water and 100 ml of Et_2O. The organic layer was separated, the aqueous phase was extracted three times with 30 ml portions of Et_2O. The combined organic fractions were washed five times with 20 ml portions of water, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, CH_2Cl_2/petroleum ether: 1:4) afforded 2.63 g (4.95 mmol, 62%) of a colourless oil. $R_f = 0.52$ (CH_2Cl_2/petroleum ether: 1:4). ^{1}H-NMR (500 MHz, 363 K, toluene-d^8): $\delta = 6.31$ (H-1, dd, $J = 6.2$, 1.0, 1H), 4.75 (H-2, dd, $J = 6.2$, 4.2, 1H), 4.39 (H-6, dd, $J = 10.5$, 7.1, 1H), 4.34 (H-4, dd, $J = 3.7$, 1.3, 1H), 4.32 (H-5, ddd, $J = 7.1$, 3.5, 1.3, 1H), 4.28 (H-6′, dd, $J = 10.5$, 3.5, 1H), 4.24 (H-3, dd, $J = 4.2$, 3.7, 1H); ^{1}H-NMR (500 MHz, 223 K, toluene-d^8): $\delta = 6.38$ (H-1, d, $J = 5.9$, 1H), 4.75 (H-2(1), dd, $J = 5.9$, 5.9, 0.6H), 4.69 (H-6(1), dd, $J =$ 11.5, 9.1, 0.7H), 4.64 (H-2(2), d, $J = 6.1$, ~0.6H), 4.59 (H-5(1), dd, $J =$ ~9.0, ~5.4, ~0.6H), 4.39 (H-6′(1), d, $J = 11.5$, ~0.7H), 4.19 (H-3(2), br, 0.7H), 4.13–4.09 (H-4(1), H-4(2), m, 1.4H), 3.83 (H-3(1), dd, $J =$ ~5, ~5, ~0.7H). ^{13}C-NMR (125 MHz, 343 K, C_6D_6): $\delta = 143.5$ (C-1), 102.8 (C-2), 80.4, 69.5, 66.2, 62.1 (C-3, C-4, C-5, C-6), 26.2 (-TBS), 18.3, 12.7 (–TIPS), −3.9, −4.3, −4.5, −4.7 (–TBS). MS (EI): $m/z = 515.2$ [$M^+ - CH_3$], 487.3 [$M^+ - C_3H_7$], 473.3 [$M^+ - CH_3 - C_3H_7$]. HR-MS Calc. for $C_{24}H_{51}O_4Si_3$ [$M^+ - C_3H_7$] 487.3095. Found 487.3085. Anal. Calc. for $C_{27}H_{58}O_4Si_3$: C, 61.07; H, 11.01. Found C, 60.64; H, 11.00%.

6.3. Phenyl 1-thio-2,3:4,6-di-O-isopropylidene-β-D-glucopyranoside (7)

LiOH (12.7 mg, 0.53 mmol) was added to a solution of 4.47 g (10.15 mmol) phenyl 1-thio-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside in 100 ml MeOH. After 1 h

stirring at r.t. the reaction mixture was neutralized by adding 28.8 mg (0.53 mmol) solid NH_4Cl, the solvent was removed in vacuo and the residue was distilled three times azeotropically with 20 ml portions of toluene under reduced pressure. DMF (40 ml) was added, and the resulting solution was treated with 0.2 g (0.81 mmol) camphorsulfonic acid (CSA). 2-Methoxypropene (4.5 ml, 45 mmol) was added at r.t. over a period of 30 min. After stirring for additional 30 min the mixture was diluted with 50 ml saturated aqueous sodium bicarbonate and extracted four times with 50 ml portions of Et_2O. The combined organic fractions were washed five times with 30 ml portions of water, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, ethyl acetate/cyclohexane: 3:7; 5‰ NEt_3) afforded 3.33 g (9.45 mmol, 93%) of a white solid. $R_f = 0.57$ (ethyl acetate/cyclohexane: 3:7). ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 7.69–7.65$ (Ar-H, m, 2H), 7.08–6.98 (Ar-H, m, 3H), 4.64 (H-1, d, $J = 9.6$, 1H), 3.87 (H-6_e, dd, $J = 10.6$, 5.1, 1H), 3.74 (H-4, dd, $J = 9.3$, 8.9, 1H), 3.68 (H-6_a, dd, $J = 10.6$, 10.4, 1H), 3.62 (H-3, dd, $J = 8.6$, 9.3, 1H), 3.42 (H-2, dd, $J = 9.6$, 8.6, 1H), 3.04 (H-5, ddd, $J = 10.4$, 8.9, 5.1, 1H), 1.42 (–CH_3, s, 3H), 1.39 (–CH_3, s, 3H), 1.36 (–CH_3, s, 3H), 1.10 (–CH_3, s, 3H). ^{13}C-NMR (125 MHz, C_6D_6): $\delta =$ 133.9, 132.3, 129.0, 128.3 (Ar-C's), 111.0 ($C(CH_3)_2$-oxolane), 99.4 ($C(CH_3)_2$–dioxane), 85.5 (C-1), 79.8, 76.8, 73.3, 73.2, 62.3 (C-2, C-3, C-4, C-5, C-6), 29.2, 26.8, 26.6, 18.9 (C(CH_3)$_2$). MS (EI): $m/z = 352.2$ [M^+], 337.2 [$M^+ - CH_3$]. HR-MS Calc. for $C_{18}H_{24}O_5S$ [M^+] 352.1344. Found 352.1338. Anal. Calc. for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86; S, 9.10. Found C, 61.27; H, 7.02; S, 9.22%.

6.4. Phenyl 1-thio-2,3:4,6-di-O-isopropylidene-β-D-galactopyranoside (8)

Starting from 16.4 g (37.2 mmol) phenyl 1-thio-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside, 50 mg (2.1 mmol) LiOH, 200 ml MeOH, 112.3 mg (2.1 mmol) NH_4Cl, 0.72 g (3.0 mmol) CSA, 16.3 ml (167 mmol) 2-methoxypropene and 140 ml DMF a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, ethyl acetate/petroleum ether: 1:1; 5‰ NEt_3) afforded 12.24 g (34.7 mmol, 93%) of a white solid. $R_f = 0.66$ (ethyl acetate/petroleum ether: 1:1). ^{1}H-NMR (500 MHz, C_6D_6): $\delta =$ 7.87–7.83 (Ar-H, m, 2H), 7.13–7.02 (Ar-H, m, 3H), 4.68 (H–1, d, $J = 9.4$, 1H), 4.19 (H-2, dd, $J = 9.4$, 9.4, 1H), 3.91 (H-4, dd, $J = 2.7$, 1.0, 1H), 3.86 (H-6, dd, $J = 12.7$, 1.6, 1H), 3.52 (H-6′, dd, $J = 12.7$, 2.3, 1H), 3.27 (H-3, dd, $J = 9.4$, 2.7, 1H), 2.54 (H-5, ddd, $J = 2.3$, 1.6, 1.0, 1H), 1.45 (–CH_3, s, 3H), 1.39 (–CH_3, s, 3H), 1.33 (–CH_3, s, 3H), 1.12 (–CH_3, s, 3H). ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 134.3$, 132.7, 128.8, 128.1 (Ar-C's), 110.2 ($C(CH_3)_2$–oxolane), 98.2 ($C(CH_3)_2$–dioxane), 85.6 (C-1), 80.1, 71.1, 70.0, 66.7, 63.0 (C-2, C-3, C-4, C-5, C-6), 29.3, 27.0, 26.6, 18.6 (C(CH_3)$_2$). MS (EI): $m/z = 352.2$ [M^+], 337.2 [$M^+ - CH_3$]. HR-MS Calc. for $C_{18}H_{24}O_5S$ [M^+] 352.1344. Found 352.1352. Anal. Calc. for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86; S, 9.10. Found C, 60.93; H, 7.07; S, 9.13%.

6.5. 1,5-Anhydro-4,6-O-isopropylidene-3-O-triisopropylsilyl-2-deoxy-D-arabino-hex-1-enitol (9)

Graphite (2.71 g, 225 mmol) was placed on the bottom of a long Schlenk-flask and was stirred in vacuo at 150°C for 30 min. After setting a positive pressure of argon on the flask 1.10 g (28.2 mmol) potassium was added in one portion at 150°C and stirring was continued until the material became homogeneous and bronze-coloured (ca. 45 min). The resulting C_8K was suspended in 60 ml THF at −40°C and 3.10 g (8.8 mmol) phenyl 1-thio-2,3:4,6-di-*O*-isopropylidene-β-D-glucopyranoside in 90 ml THF were added at this temperature over a period of 1 h. After additional 30 min the reaction mixture was warmed to −20°C and 4.2 ml (19.4 mmol) triisopropylsilyl chloride (TIPSCl) were slowly added. The suspension was allowed to reach r.t. within 1 h and filtered over a plug of silica gel. The resulting solution was concentrated in vacuo and the residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane: 1:25; 1‰ NEt_3) to afford 1.64g (4.79 mmol, 54%) of a colourless oil. $R_f = 0.36$ (ethyl acetate/cyclohexane: 1:25). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 6.21$ (H-1, dd, $J = 6.2$, 1.6, 1H), 4.63 (H-2, dd, $J = 6.2$, 1.6, 1H), 4.38 (H-3, ddd, $J = 7.2$, 1.9, 1.6, 1H), 3.88 (H-6_e, dd, $J = 10.7$, 5.6, 1H), 3.78 (H-4, dd, $J = 10.4$, 7.2, 1H), 3.76 (H-6_a, dd, $J = 10.7$, 10.2, 1H), 3.66 (H-5, ddd, $J = 10.4$, 10.2, 5.6, 1H), 1.46 (–CH_3, s, 3H), 1.35 (–CH_3, s, 3H), 1.07–0.99 (–TIPS, m, 21H). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 143.1$ (C-1), 105.7 (C-2), 99.5 ($C(CH_3)_2$), 73.2, 69.7, 67.7, 61.8 (C-3, C-4, C-5, C-6), 28.9, 18.9 (C(CH_3)$_2$), 17.9, 12.2 (TIPS). MS (EI): $m/z = 327.2$ [$M^+ - CH_3$], 299.2 [$M^+ - C_3H_7$], 241.1 [$M^+ - C_3H_7 - C_3H_6O$]. HR-MS Calc. for $C_{17}H_{31}O_4Si$ [$M^+ - CH_3$] 327.1992. Found 327.1984.

6.6. 1,5-Anhydro-4,6-O-isopropylidene-3-O-triisopropylsilyl-2-deoxy-D-lyxo-hex-1-enitol (10)

Starting from 7.22 g (20.49 mmol) phenyl 1-thio-2,3:4,6-di-*O*-isopropylidene-β-D-galactopyranoside, 6.10 g (508.2 mmol) graphite, 2.51 g (63.5 mmol) potassium and 9.3 ml (43.0 mmol) TIPSCl a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, ethyl acetate/CH_2Cl_2: 1:40; 2‰ NEt_3) afforded 5.43 g (15.85 mmol, 77%) of a colourless oil. $R_f = 0.42$ (ethyl acetate/CH_2Cl_2: 1:40). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 6.35$ (H-1, dd, $J = 6.4$, 2.1, 1H), 4.72 (H-2, ddd, $J = 6.4$, 1.8,

1.5, 1H), 4.68 (H-3, ddd, $J = 4.6$, 2.1, 1.8, 1H), 4.17 (H-4, ddd, $J = 4.6$, 1.5, 1.2, 1H), 4.07 (H-6, dd, $J = 12.8$, 1.6, 1H), 4.00 (H-6′, dd, $J = 12.8$, 2.0, 1H), 3.73 (H-5, ddd, $J = 2.0$, 1.6, 1.2, 1H), 1.48 (–CH_3, s, 3H), 1.47 (–CH_3, s, 3H), 1.09–1.01 (–TIPS, m, 21H). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 143.4$ (C-1), 102.1 (C-2), 99.0 ($C(CH_3)_2$), 68.1, 66.0, 64.2, 63.2 (C-3, C-4, C-5, C-6), 29.5, 18.4 ($C(CH_3)_2$), 17.9, 12.3 (TIPS). MS (EI): $m/z = 327.3$ [$M^+ - CH_3$], 299.3 [$M^+ - C_3H_7$], 241.2 [$M^+ - C_3H_7 - C_3H_6O$]. HR-MS Calc. for $C_{17}H_{31}O_4Si$ [$M^+ - CH_3$] 327.1991. Found 327.1991.

6.7. Phenyl 1-thio-4,6-O-isopropylidene-α-D-erythro-hex-2-enopyranoside (**13**)

LiOH (35.9 mg, 1.50 mmol) was added to a solution of 9.67 g (30.0 mmol) phenyl 1-thio-4,6-di-*O*-acetyl-α-D-*erythro*-hex-2-enopyranoside in 100 ml MeOH. After 1 h stirring at r.t. the reaction mixture was neutralized by adding 80.3 mg (1.50 mmol) solid NH_4Cl, the solvent was removed in vacuo and the residue was distilled three times azeotropically with 20 ml portions of toluene under reduced pressure. DMF (150 ml) was added and the resulting solution was treated with 0.56 g (2.4 mmol) CSA. 2-Methoxypropene (8.6 ml, 90 mmol) was added at r.t. over a period of 30 min. After stirring for additional 30 min the mixture was diluted with 50 ml saturated aqueous sodium bicarbonate and extracted four times with 50 ml portions of CH_2Cl_2. The combined organic fractions were washed five times with 30 ml portions of water, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, ethyl acetate/cyclohexane: 1:5; 5‰ NEt_3) afforded 7.85 g (28.2 mmol, 94%) of a white solid. $R_f = 0.56$ (ethyl acetate/cyclohexane: 1:5). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 7.55$–7.50 (Ar-H, m, 2H), 7.36–7.25 (Ar-H, m, 3H), 5.99 (H-2, dd, $J = 10.1$, 4.4, 1H), 5.92 (H-3, ddd, $J = 10.1$, 2.4, 2.4, 1H), 5.78 (H-1, dd, $J = 4.4$, 2.4, 1H), 4.34 (H-4, dd, $J = 8.9$, 2.4, 1H), 4.02 (H-5, ddd, $J = 10.5$, 8.9, 4.9, 1H), 3.96 (H-6_e, dd, $J = 10.5$, 4.9, 1H), 3.85 (H-6_a, dd, $J = 10.5$, 10.5, 1H), 1.56 (–CH_3, s, 3H), 1.49 (–CH_3, s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 135.3$, 131.4, 129.9, 128.9, 127.4, 126.9 (Ar-C's, C-2, C-3), 99.9 ($C(CH_3)_2$), 84.5 (C-1), 67.4, 65.5 (C-4, C-5), 62.9 (C-6), 29.2 (–CH_3), 19.0 (CH_3). MS (EI): $m/z = 278.1$ [M^+], 263.1 [$M^+ - CH_3$]. HR-MS Calc. for $C_{15}H_{18}O_3S$ [M^+] 278.0976. Found 278.0969. Anal. Calc. for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52; S, 11.52. Found C, 64.69; H, 6.71; S, 11.13%.

6.8. Phenyl 1-thio-4,6-O-isopropylidene-α-D-threo-hex-2-enopyranoside (**14**)

Starting from 2.77 g (8.6 mmol) phenyl 1-thio-4,6-di-*O*-acetyl-α-D-*threo*-hex-2-enopyranoside, 10.9 mg (0.45 mmol) LiOH, 100 ml MeOH, 24.4 mg (0.45 mmol) NH_4Cl, 0.16 g (0.7 mmol) CSA, 2.5 ml (25.8 mmol) 2-methoxypropene and 50 ml DMF a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, ethyl acetate/cyclohexane: 1:6; 1% NEt_3) afforded 2.26 g (8.12 mmol, 94%) of a colourless oil. $R_f = 0.33$ (ethyl acetate/cyclohexane: 1:6). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.55$–7.45 (Ar-H, m, 2H), 7.35–7.10 (Ar-H, m, 3H), 6.21 (H-2, ddd, $J = 9.8$, 3.6, 0.7, 1H), 5.99 (H-3, ddd, $J = 9.8$, 5.4, 1.7, 1H), 5.96 (H-1, dd, $J = 3.6$, 1.7, 1H), 4.26 (H-6, dd, $J = 13.0$, 3.4, 1H), 4.19 (H-4, dd, $J = 5.4$, 2.3, 1H), 4.15 (H-5, ddd, $J = 3.5$, 2.3, 2.1, 1H), 3.96 (H-6′, dd, $J = 13.0$, 2.1, 1H), 1.51 (–CH_3, s, 3H), 1.45 (–CH_3, s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 135.5$, 130.8, 130.7, 128.9, 127.1, 125.7 (Ar-C, C-2, C-3), 98.9 ($C(CH_3)_2$), 83.7 (C-1), 62.7 (C-6), 62.7, 60.9 (C-4, C-5), 28.8 (–CH_3), 19.2 (–CH_3). MS (EI): $m/z = 278.1$ [M^+], 263.1 [$M^+ - CH_3$]. HR-MS Calc. for $C_{15}H_{18}O_3S$ [M^+] 278.0976. Found 278.0971. Anal. Calc. for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52; S, 11.52. Found C, 64.78; H, 6.42; S 11.86%.

6.9. 1,5-Anhydro-3,6-di-O-acetyl-2-deoxy-D-ribo-hex-1-enitol (**16**)

To a solution of 0.32 g (1.00 mmol) phenyl 1-thio-4,6-di-*O*-acetyl-α-D-*erythro*-hex-2-enopyranoside in 10 ml CH_2Cl_2 at -78°C were added 10 ml of 0.1 M solution of dimethyldioxirane (DMDO) in acetone [34]. After one hour the solvent was removed in vacuo at 0°C and the residue was distilled two times azeotropically with 10 ml portions of toluene under reduced pressure. Et_2O (40 ml) and 0.54 ml (5.0 mmol) Et_2NH were added. The reaction mixture was stirred at r.t. overnight and was then concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/cyclohexane: 1:1, 1% NEt_3) to afford 0.22 g (0.95 mmol, 95%) of a colourless oil as an inseparable 1:0.15:0.1 mixture of regioisomeric diacetates (as judged by ^{1}H-NMR analysis). $R_f = 0.29$ (ethyl acetate/cyclohexane: 1:1). 1,5-Anhydro-3,6-di-*O*-acetyl-2-deoxy-D-*ribo*-hex-1-enitol: ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 6.19$ (H-1, d, $J = 5.9$, 1H), 5.25 (H-3, dd, $J = 5.9$, 4.1, 1H), 4.80 (H-2, dd, $J = 5.9$, 5.9, 1H), 4.50 (H-6, dd, $J = 12.2$, 2.2, 1H), 4.38 (H-6′, dd, $J = 12.2$, 4.9, 1H), 3.99 (H-5, ddd, $J = 10.7$, 4.9, 2.2, 1H), 3.71 (H-4, ddd, $J = 10.7$, 6.0, 4.1, 1H), 2.28 (–OH, d, $J = 6.0$, 1H), 1.70 (–CH_3, s, 3H), 1.67 (–CH_3, s, 3H). 1,5-Anhydro-4,6-di-*O*-acetyl-2-deoxy-D-*ribo*-hex-1-enitol: $\delta = 6.16$ (H-1, d, $J = 5.8$, 0.14H), 4.68 (H-2, dd, $J = 5.8$, 5.8, 0.15H), 4.42 (H-6, dd, $J = 12.2$, 4.27, 0.16H). 1,5-Anhydro-3,4-di-*O*-acetyl-2-deoxy-D-*ribo*-hex-1-enitol: $\delta = 6.12$ (H-1, dd, $J = 6.1$, 1.3, 0.10H), 4.65 (H-2, dd, $J = 6.1$, 3.0, 0.10H), 3.88 (H-4, ddd, $J = 8.6$, 5.8, 2.5, 0.11H), 2.28 (–OH, d, $J = 5.8$, 0.08H). ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 170.7$, 170.6 (acetyl-

CO), 147.8 (C-1), 98.0 (C-2), 73.4, 66.2, 65.7 (C-3, C-4, C-5), 63.3 (C-6), 20.6, 20.2 (acetyl-CH_3). MS (FAB, mNBA + NaOAc): $m/z = 253.0$ [$M^+ + Na$], 171.0 [$M^+ - C_2H_3O_2$]. Anal. Calc. for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found C, 51.81; H, 6.13%.

6.10. 1,5-Anhydro-4,6-di-O-acetyl-2-deoxy-D-xylo-hex-1-enitol (15)

Starting from 0.32 g (1.00 mmol) phenyl 1-thio-4,6-di-*O*-acetyl-α-D-*threo*-hex-2-enopyranoside, 10 ml CH_2Cl_2, 10 ml of a 0.1 M solution of DMDO in acetone, 40 ml Et_2O and 0.54 ml (5.00 mmol) a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, ethyl acetate/cyclohexane: 1:1; 1% NEt_3) afforded 0.21 g (0.92 mmol, 92%) of a colourless oil. $R_f = 0.25$ (ethyl acetate/cyclohexane: 1:1). ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 6.35$ (H-1, d, $J = 6.2$, 1H), 5.07 (H-4, ddd, $J = 2.4$, 1.6, 1.2, 1H), 4.72 (H-2, ddd, $J = 6.2$, 5.2, 1.6, 1H), 4.38 (H-6, dd, $J = 12.9$, 8.9, 1H), 4.32–4.27 (H-6′, H-5, m, 2H), 3.86 (H-3, ddd, $J = 5.0$, 5.0, 2.4, 1H), 2.00 (–OH, d, $J = 5.0$, 1H), 1.68 ($-CH_3$, s, 3H), 1.59 ($-CH_3$, s, 3H). ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 170.0$, 169.9 (acetyl-CO), 146.2 (C-1), 100.9 (C-2), 70.2, 69.6, 61.4 (C-3, C-4, C-5), 62.7 (C-6), 20.2, 20.2 (acetyl-CH_3). Anal. Calc. for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found C, 51.85; H, 6.14%.

6.11. 1,5-Anhydro-4,6-O-isopropylidene-2-deoxy-D-ribo-hex-1-enitol (18)

Starting from 2.78 g (10.00 mmol) phenyl 1-thio-4,6-*O*-isopropylidene-α-D-*erythro*-hex-2-enopyranoside, 100 ml CH_2Cl_2, 100 ml of a 0.1 M solution of DMDO in acetone, 200 ml Et_2O and 5.4 ml (50.0 mmol) Et_2NH a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, ethyl acetate/cyclohexane: 1:1; 5‰ NEt_3) afforded 1.81 g (9.72 mmol, 97%) of a colourless oil. $R_f = 0.53$ (ethyl acetate/cyclohexane: 1:1). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 6.22$ (H-1, dd, $J = 6.1$, 0.6, 1H), 4.91 (H-2, dd, $J = 6.1$, 5.8, 1H), 4.22 (H-5, ddd, $J = 10.7$, 10.4, 5.5, 1H), 3.99 (H-3, dd, $J = 5.8$, 3.9, 1H), 3.96 (H-6_e, dd, $J = 10.7$, 5.5, 1H), 3.71 (H-6_a, dd, $J = 10.7$, 10.7, 1H), 3.65 (H-4, dd, $J = 10.4$, 3.9, 1H), 2.56 (–OH, s, 1H), 1.42 ($-CH_3$, s, 3H), 1.20 ($-CH_3$, s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 146.1$ (C-1), 101.2 (C-2), 99.8 ($C(CH_3)_2$), 70.7, 64.7, 61.7, 60.3 (C-3, C-4, C-5, C-6), 28.9, 19.3 ($C(CH_3)_2$). MS (EI): $m/z = 186.1$ [M^+], 171.1 [$M^+ - CH_3$]. HR-MS Calc. for $C_9H_{14}O_4$ [M^+] 186.0892. Found 186.0884. Anal. Calc. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found C, 58.19; H, 7.52%.

6.12. 1,5-Anhydro-4,6-O-isopropylidene-2-deoxy-D-xylo-hex-1-enitol (17)

Starting from 3.38 g (12.14 mmol) phenyl 1-thio-4,6-*O*-isopropylidene-α-D-*threo*-hex-2-enopyranoside, 120 ml CH_2Cl_2, 120 ml of a 0.1 M solution of DMDO in acetone, 250 ml Et_2O and 6.6 ml (60.7 mmol) Et_2NH a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, ethyl acetate/cyclohexane: 3:1; 1% NEt_3) afforded 2.00 g (10.74 mmol, 88%) of a colourless oil. $R_f = 0.49$ (ethyl acetate/cyclohexane: 3:1). ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 6.45$ (H-1, dd, $J = 6.3$, 0.4, 1H), 4.72 (H-2, ddd, $J = 6.3$, 4.5, 2.0, 1H), 3.91 (H-6, dd, $J = 12.8$, 1.8, 1H), 3.86-3.82 (H-3, H-4, m, 2H), 3. (H-6′, dd, $J = 12.8$, 1.8, 1H), 3.37 (H-5, ddd, $J = 1.8$, 1.8, 1.8, 1H), 1.47 ($-CH_3$, s, 3H), 1.28 (–OH, d, $J = 4.7$, 1H), 1.20 ($-CH_3$, s, 3H). ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 146.5$ (C-1), 99.9 (C-2), 98.4 ($C(CH_3)_2$), 68.5, 64.9, 62.5 (C-3, C-4, C-5), 62.9 (C-6), 29.6, 18.5 ($C(CH_3)_2$). MS (EI): $m/z = 186.1$ [M^+], 171.1 [$M^+ - CH_3$]. HR-MS Calc. for $C_9H_{14}O_4$ [M^+] 186.0892. Found 186.0893. Anal. Calc. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found C, 57.96; H, 7.54%.

6.13. 1,5-Anhydro-3,4,6-tri-O-triisopropylsilyl-2-deoxy-D-ribo-hex-1-enitol (20)

LiOH (11.3 mg, 0.47 mmol) was added to a solution of 2.04 g (8.86 mmol) 1,5-anhydro-4,6-*O*-isopropylidene-2-deoxy-D-*ribo*-hex-1-enitol in 50 ml MeOH. After 2 h stirring at r.t. the reaction mixture was neutralized by adding 25.2 mg (0.47 mmol) solid NH_4Cl, the solvent was removed in vacuo and the residue was distilled two times azeotropically with 10 ml portions of toluene under reduced pressure. DMF (5 ml) and 6.8 ml (58.5 mmol) 2,6-lutidine were added. To this mixture was added a solution of 7.9 ml (29.2 mmol) TIPSOTf in 20 ml CH_2Cl_2 at 0°C over a period of 30 min. The reaction mixture was allowed to reach r.t. and stirred for 60 h. Finally the mixture was treated with additional 1.8 ml (6.7 mmol) TIPSOTf and heated under reflux for 4.5 h. After recooling to r.t. the mixture was diluted with 100 ml water, the organic layer was separated and the aqueous layer was extracted three times with 50 ml portions of CH_2Cl_2. The combined organic fractions were washed with brine, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, CH_2Cl_2/petroleum ether: 1:9; 5‰ NEt_3) afforded 3.40 g (5.53 mmol, 62%) of a colourless oil. $R_f = 0.46$ (CH_2Cl_2/petroleum ether: 1:9). ^{1}H-NMR (500 MHz, 333K, toluene-d^8): $\delta = 6.40$ (H-1, d, $J = 6.0$, 1H), 4.93 (H-2, dd, $J = 6.0$, 4.9, 1H), 4.63 (H-3, dd, $J = 4.9$, 3.1, 1H), 4.55 (H-5, ddd, $J = 8.2$, 5.3, 4.2, 1H), 4.38 (H-4, dd, $J = 8.2$, 3.1, 1H), 4.24 (H-6, dd, $J = 11.0$, 4.2, 1H), 4.20 (H-6′, dd, $J = 11.0$, 5.3, 1H), 1.40–1.10 (–TIPS, m, 63H); ^{1}H-NMR (500 MHz, 203 K, CD_2Cl_2): $\delta = 6.35$ (H-1(1), d, $J = 5.5$, 1H), 6.13 (H-1(2), d, $J = 6.1$, 0.11H), 4.84 (H-2(1), dd, $J = 5.5$, 5.5, 1H), 4.53 (H-2(2), d, $J = \sim 5.5$, 0.09H). ^{13}C-NMR (125 MHz, 333 K, toluene-d^8): $\delta = 137.7$ (C-1), 94.3 (C-2), 69.7, 62.4, 58.1 (C-3, C-4, C-5), 56.4 (C-6), 11.1–10.4, 6.5–5.2 (–TIPS).

MS (EI): $m/z = 571.5$ [$M^+ - C_3H_7$]. HR-MS Calc. for $C_{30}H_{63}O_4Si$ [$M^+ - C_3H_7$] 571.4034. Found 571.4039. Anal. Calc. for $C_{33}H_{70}O_4Si_3$: C, 64.45; H, 11.48. Found C, 64.47; H, 11.68%.

6.14. 1,5-Anhydro-3,4,6-tri-O-triisopropylsilyl-2-deoxy-D-xylo-hex-1-enitol (**19**)

LiOH (8.4 mg, 0.35 mmol) was added to a solution of 1.60 g (6.95 mmol) 1,5-anhydro-4,6-*O*-isopropylidene-2-deoxy-D-*xylo*-hex-1-enitol in 50 ml MeOH. After 2 h stirring at r.t. the reaction mixture was neutralized by adding 18.8 mg (0.35 mmol) solid NH_4Cl, the solvent was removed in vacuo and the residue was distilled two times azeotropically with 10 ml portions of toluene under reduced pressure. DMF (5 ml) and 5.3 ml (45.9 mmol) 2,6-lutidine were added. To this mixture was added a solution of 6.2 ml (22.9 mmol) TIPSOTf in 20 ml CH_2Cl_2 at 0°C over a period of 30 min. The reaction mixture was allowed to reach r.t. and stirred for 60 h. Over that period additional 1.0 ml (14 mmol) TIPSOTf were added in two portions. The mixture was diluted with 100 ml water, the organic layer was separated and the aqueous layer was extracted three times with 50 ml portions of CH_2Cl_2. The combined organic fractions were washed with brine, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, CH_2Cl_2/petroleum ether: 1:9; 5‰ NEt_3) afforded 3.40 g (5.36 mmol, 77%) of a colourless oil. $R_f = 0.55$ (CH_2Cl_2/petroleum ether: 1:9). ^{1}H-NMR (400 MHz, C_6D_6): $\delta = 6.50$ (H-1, d, $J = 6.2$, 1H), 4.89 (H-2, ddd, $J = 6.2$, 5.3, 2.0, 1H), 4.39 (H-4, dd, $J = 2.6$, 2.0, 1H), 4.34 (H-6, dd, $J = 9.2$, 3.5, 1H), 4.30 (H-6′, dd, $J = 9.2$, 8.3, 1H), 4.26 (H-3, dd, $J = 5.3$, 2.6, 1H), 4.14 (H-5, dd, $J = 8.3$, 3.5, 1H), 1.27–1.10 (–TIPS, m, 63H). ^{13}C-NMR (100 MHz, C_6D_6): $\delta = 146.2$ (C-1), 100.8 (C-2), 74.2, 68.6, 65.0 (C-3, C-4, C-5), 61.7 (C-6), 18.2-17.9, 13.4–12.1 (–TIPS). MS (EI): $m/z = 571.4$ [$M^+ - C_3H_7$]. HR-MS Calc. for $C_{30}H_{63}O_4Si$ [$M^+ - C_3H_7$] 571.4034. Found 571.4036. Anal. Calc. for $C_{33}H_{70}O_4Si_3$: C, 64.45; H, 11.48. Found C, 64.42; H, 11.67%.

6.15. 1,5-Anhydro-4,6-O-isopropylidene-3-O-triisopropylsilyl-2-deoxy-D-ribo-hex-1-enitol (**22**)

2,6-Lutidine (2.94 ml, 25.3 mmol) and 4.6 ml (17.2 mmol) TIPSOTf were added sequentially to a solution of 2.14 g (11.5 mmol) 1,5-anhydro-4,6-*O*-isopropylidene-2-deoxy-D-*ribo*-hex-1-enitol in 60 ml CH_2Cl_2 at 0°C. The reaction mixture was allowed to reach r.t. and stirred for 3 h. After dilution with 100 ml water the organic layer was separated and the aqueous layer was extracted three times with 50 ml portions of CH_2Cl_2. The combined organic fractions were washed with brine, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, ethyl acetate/cyclohexane: 1:15; 1% NEt_3) afforded 3.43 g (10.0 mmol, 87%) of a colourless oil. $R_f = 0.51$ (ethyl acetate/cyclohexane: 1:15). ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 6.19$ (H-1, d, $J = 6.1$, 1H), 4.81 (H-2, dd, $J = 6.1$, 5.8, 1H), 4.31 (H-5, dd, $J = 10.4$, 10.4, 5.8, 1H), 4.12 (H-3, dd, $J = 5.8$, 3.4, 1H), 3.98 (H-6_e, dd, $J = 10.9$, 5.8, 1H), 3.74 (H-6_a, dd, $J = 10.9$, 10.4, 1H), 3.72 (H-4, dd, $J = 10.4$, 3.4, 1H), 1.47 (–CH_3, s, 3H), 1.24 (–CH_3, s, 3H), 1.23–1.16 (–TIPS, m, 21H). ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 144.7$ (C-1), 103.3 (C-2), 99.4 ($C(CH_3)_2$), 71.6, 65.1, 62.0 (C-3, C-4, C-5,), 62.1 (C-6), 29.2, 19.1 ($C(CH_3)_2$), 18.3, 12.7 (–TIPS). MS (EI): $m/z = 327.2$ [$M^+ - CH_3$], 299.2 [$M^+ - C_3H_7$], 241.2 [$M^+ - C_3H_7 - C_3H_6O$]. HR-MS Calc. for $C_{15}H_{27}O_4Si$ [$M^+ - C_3H_7$] 299.1679. Found 299.1672. Anal. Calc. for $C_{18}H_{34}O_4Si$: C, 63.11; H, 10.00. Found C, 63.11; H, 10.22%.

6.16. 1,5-Anhydro-4,6-O-isopropylidene-3-O-triisopropylsilyl-2-deoxy-D-xylo-hex-1-enitol (**21**)

2,6-Lutidine (1.72 ml, 14.8 mmol) and 2.7 ml (10.1 mmol) TIPSOTf were added sequentially to a solution of 1.25 g (6.7 mmol) 1,5-anhydro-4,6-*O*-isopropylidene-2-deoxy-D-*xylo*-hex-1-enitol in 40 ml CH_2Cl_2 at 0°C. The reaction mixture was allowed to reach r.t. and stirred for 3 h. After dilution with 100 ml of water the organic layer was separated and the aqueous layer was extracted three times with 50 ml portions of CH_2Cl_2. The combined organic fractions were washed with brine, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, ethyl acetate/cyclohexane: 1:15; 1% NEt_3) afforded 1.52 g (4.44 mmol, 66%) of a colourless oil. $R_f = 0.32$ (ethyl acetate/cyclohexane: 1:15). ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 6.53$ (H-1, d, $J = 6.3$, 1H), 4.89 (H-2, ddd, $J = 6.3$, 5.1, 1.7, 1H), 4.10 (H-3, dd, $J = 5.1$, 2.0, 1H), 4.02 (H-4, ddd, $J = 2.0$, 1.6, 1.6, 1H), 3.95 (H-6, dd, $J = 12.7$, 1.6, 1H), 3.64 (H-5, ddd, $J = 1.6$, 1.6, 1.6, 1H), 3.60 (H-6′, dd, $J = 12.7$, 1.6, 1H), 1.50 (–CH_3, s, 3H), 1.29 (–CH_3, s, 3H), 1.19–1.07 (–TIPS, m, 21H). ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 145.8$ (C-1), 100.6 (C-2), 98.4 ($C(CH_3)_2$), 70.1, 65.1, 63.7 (C-3, C-4, C-5), 63.0 (C-6), 29.6, 18.5 ($C(CH_3)_2$), 18.2, 12.6 (–TIPS). MS (EI): $m/z = 327.3$ [$M^+ - CH_3$], 299.3 [$M^+ - C_3H_7$], 241.2 [$M^+ - C_3H_7 - C_3H_6O$]. HR-MS Calc. for $C_{17}H_{31}O_4Si$ [$M^+ - CH_3$] 327.1991. Found 327.1987. Anal. Calc. for $C_{18}H_{34}O_4Si$: C, 63.12; H, 10.01. Found C, 63.12; H, 10.11%.

6.17. 1,5-Anhydro-3,4-di-O-(tert-butyl-dimethylsilyl)-6-O-triisopropylsilyl-2-deoxy-1-(tri-n-butyl)stannyl-D-lyxo-hex-1-enitol (**24**)

tert-Butyllithium (10.9 ml, 17.5 mmol) (15% in hexanes) was added dropwise to a solution of 2.63 g (5.0 mmol) 1,5-anhydro-3,4-di-*O*-(*tert*-butyl-dimethylsilyl)-

6-*O*-triisopropylsilyl-2-deoxy-D-*lyxo*-hex-1-enitol in 20 ml THF at −78°C. The dry ice bath was removed and stirring was continued at 0°C for 20 min. After recooling to −78°C, 4.7 ml (17.5 mmol) tri-*n*-butylstannyl chloride were added dropwise and stirring was continued at this temperature for 20 minutes. The reaction mixture was diluted with 50 ml water, the organic layer was separated and the aqueous phase was extracted three times with 60 ml portions of Et_2O. The combined organic fractions were washed two times with 20 ml water, then with brine, dried over $MgSO_4$ and evaporated to dryness. Column chromatography of the residue (SiO_2, CH_2Cl_2/petroleum ether: 1:20; 5‰ NEt_3) afforded 3.50 g (4.3 mmol, 85%) of a colourless oil. $R_f = 0.57$ (CH_2Cl_2/petroleum ether: 1:20). ^{1}H-NMR (500 MHz, 343 K, C_6D_6): $\delta = 4.95$ (H-2, d, $J = 3.4$, 1H), 4.36 (H-3, dd, $J = 3.4$, 3.4, 1H), 4.28 (H-6, dd, $J = 9.5$, 6.4, 1H), 4.24 (H-4, dd, $J = 3.4$, 3.4, 1H), 4.22–4.18 (H-5, H-6′, m, 2H), 1.70–0.90 (–$SnBu_3$, –TIPS, –TBS, m, 66H), 0.25–0.15 (–TBS, m, 12H); ^{1}H-NMR (500 MHz, 223 K, toluene-d^8): $\delta = 5.21$ (H-2(1), d, $J = 5.5$, 1H), 4.99 (H-2(2), s, 1.2H). ^{13}C-NMR (125 MHz, 343 K, C_6D_6): $\delta = 162.8$ (C-1), 114.2 (C-2), 80.7, 69.3, 67.3 (C-3, C-4, C-5), 62.9 (H-6), 29.4, 27.6, 13.7, 10.3 (–$SnBu_3$), 26.4, −3.7, −4.2, −4.3, −4.5 (–TBS), 18.4, 12.7 (–TIPS). MS (FAB, mNBA): $m/z = 817.5$ [M^+], 761.4 [$M^+ - C_4H_9 + H$], 689.4 [$M^+ - C_9H_{21} + H$]. Anal. Calc. for $C_{39}H_{84}O_4Si_3Sn$: C, 57.12; H, 10.32. Found C, 57.29; H, 10.47%.

6.18. 1,5-Anhydro-4,6-O-isopropylidene-3-O-triisopropylsilyl-2-deoxy-1-(tri-n-butyl)stannyl-D-lyxo-hex-1-enitol (**28**)

Starting from 0.91 g (2.66 mmol) 1,5-anhydro-4,6-*O*-isopropylidene-3-*O*-triisopropylsilyl-2-deoxy-D-*lyxo*-hex-1-enitol, 6.6 ml (10.6 mmol) *tert*-butyllithium (15% in hexanes) and 2.9 ml (10.6 mmol) tri-*n*-butylstannyl chloride a crude oil was obtained following the procedure described above, except for the deprotonation time (10 min) and the deprotonation temperature (−10°C). Chromatographic purification (SiO_2, CH_2Cl_2/petroleum ether: 1:1; 1% NEt_3) afforded 0.56 g (0.88 mmol, 33%) of a colourless oil. $R_f = 0.71$ (CH_2Cl_2/petroleum ether: 1:1). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 4.67$ (H-2, dd, $J = 1.5$, 1.5, 1H), 4.59 (H-3, dd, $J = 3.5$, 1.5, 1H), 4.08 (H-4, ddd, $J = 3.5$, 1.5, 1.5, 1H), 3.95 (H-6, dd, $J = 12.5$, 1.8, 1H), 3.87 (H-6′, dd, $J = 12.5$, 1.8, 1H), 3.63 (H-5, br, 1H), 1.44 (–CH_3, s, 3H), 1.41 (–CH_3, s, 3H), 1.55–0.80 (–TIPS, –$SnBu_3$, m, 48H). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 162.7$ (C-1), 112.4 (C-2), 98.6 ($C(CH_3)_2$), 68.3, 66.3, 64.8, 63.7 (C-3, C-4, C-5), 29.4, 18.8 ($C(CH_3)_2$), 28.9, 27.2, 13.6, 9.6 (–$SnBu_3$), 18.0, 12.4 (–TIPS). MS (EI): $m/z = 589.3$ [$M^+ - C_3H_7$], 575.3 [$M^+ - C_4H_9$]. HR-MS Calc. for $C_{26}H_{51}O_4Si^{116}Sn$ [$M^+ - C_4H_9$] 571.2574. Found 571.2554. Anal. Calc. for $C_{30}H_{60}O_4SiSn$: C, 56.93; H, 9.58. Found C, 57.12; H, 9.40%.

The ring-opened aldehyde 2,5-dideoxy-4,6-*O*-isopropylidene-3-*O*-triisopropylsilyl-L-*threo*-hex-5-enose (**32**) was isolated as main product after a second chromatography (SiO_2, Et_2O/petroleum ether: 1:4) to afford 0.47 g (1.38 mmol, 52%). $R_f = 0.52$ (Et_2O/petroleum ether: 1:4). ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 9.83$ (H-1, dd, $J = 2.6$, 2.2, 1H), 6.38 (H-6, dd, $J = 6.5$, 1.6, 1H), 4.76 (H-5, dd, $J = 6.5$, 1.4, 1H), 4.29 (H-4, ddd, $J = 4.5$, 1.6, 1.4, 1H), 4.23 (H-3, ddd, $J = 6.0$, 4.5, 4.5, 1H), 2.66 (H-2, ddd, 16.2, 4.5, 2.6, 1H), 2.57 (H-2′, $J = 16.2$, 6.0, 2.2, 1H), 1.43 (–CH_3, s, 3H), 1.39 (–CH_3, s, 3H), 1.09–1.01 (–TIPS, m, 21H). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta =$ 201.7 (C-1), 142.3 (C-6), 100.1 (C-5), 99.5 ($C(CH_3)_2$), 71.6, 71.2 (C-3, C-4), 47.4 (C-2), 28.2, 21.6 ($C(CH_3)_2$), 18.5, 12.9 (–TIPS). MS (EI): $m/z = 299.2$ [$M^+ - C_3H_7$], 241.2 [$M^+ - 2C_3H_7 - CH_3$]. HR-MS Calc. for $C_{15}H_{27}O_4Si$ [$M^+ - C_3H_7$] 299.1679. Found 299.1670. Anal. Calc. for $C_{18}H_{34}O_4Si$: C, 63.11; H, 10.00. Found C, 63.17; H, 9.91%.

6.19. 1,5-Anhydro-3,4,6-tri-O-triisopropylsilyl-1-(tri-n-butyl)stannyl-2-deoxy-D-ribo-hex-1-enitol (**25**)

Starting from 10.07 g (16.37 mmol) 1,5-anhydro-3,4,6-tri-*O*-triisopropylsilyl-2-deoxy-D-*ribo*-hex-1-enitol, 35.8 ml (57.3 mmol) *tert*-butyllithium (15% in hexanes) and 15.4 ml (57.3 mmol) tri-*n*-butylstannyl chloride a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, petroleum ether; 5‰ NEt_3) afforded 10.05 g (11.12 mmol, 68%) of a colourless oil. $R_f = 0.79$ (petroleum ether). ^{1}H-NMR (500 MHz, 363 K, toluene-d^8): $\delta = 5.08$ (H-2, d, $J = 4.2$, 1H), 4.53 (H-3, dd, $J = 4.2$, 3.3, 1H), 4.41 (H-5, ddd, $J = 7.3$, 6.9, 4.8, 1H), 4.26 (H-4, dd, $J = 7.3$, 3.3, 1H), 4.18 (H-6, dd, $J = 10.3$, 4.8, 1H), 4.05 (H-6′, dd, $J = 10.3$, 6.9, 1H), 1.76–0.93 (–TIPS, –$SnBu_3$, m, 90H); ^{1}H-NMR (500 MHz, 233K, toluene-d^8): $\delta = 5.40$ (H-2(1), d, $J =$ 5.4, 1H), 5.18 (H-2(2), s, ∼0.1H). ^{1}H-NMR (500 MHz, 203K, CD_2Cl_2): $\delta = 4.85$ (H-2(1), d, $J = 6.0$, 1H), 4.56 (H-2(2), s, 0.2H). ^{13}C-NMR (125 Hz, 363 K, toluene-d^8): $\delta = 159.0$ (C-1), 108.1 (C-2), 73.2, 65.3, 60.8 (C-3, C-4, C-5), 59.4 (C-6), 23.9, 22.0, 7.2, 4.8 (–$SnBu_3$), 15.1–12.4, 8.6–7.9 (–TIPS). MS (FAB, mNBA): $m/z = 903.5$ [M^+], 861.6 [$M^+ - C_3H_7 + H$], 847.5 [$M^+ - C_4H_9 + H$]. Anal. Calc. for $C_{45}H_{96}O_4Si_3Sn$: C, 59.78; H, 10.70. Found C, 59.78; H, 10.73%.

6.20. 1,5-Anhydro-4,6-O-isopropylidene-3-O-triisopropylsilyl-2-deoxy-1-(tri-n-butyl)stannyl-D-ribo-hex-1-enitol (**29**)

Starting from 0.74 g (2.16 mmol) 1,5-anhydro-4,6-*O*-isopropylidene-3-*O*-triisopropylsilyl-2-deoxy-D-*ribo*-hex-1-enitol, 4.7 ml (7.6 mmol) *tert*-butyllithium (15% in hexanes) and 2.0 ml (7.6 mmol) tri-*n*-butylstannyl chloride a crude oil was obtained following the procedure described above. Chromatographic purification

(SiO_2, CH_2Cl_2/petroleum ether: 1:1; 5‰ NEt_3) afforded 1.17 g (1.85 mmol, 86%) of a colourless oil. $R_f = 0.67$ (CH_2Cl_2/petroleum ether: 1:1). ^{1}H-NMR (400 MHz, C_6D_6): $\delta = 5.26$ (H-2, d, $J = 5.5$, 1H), 4.42 (H-5, ddd, $J = 10.5$, 10.5, 5.9, 1H), 4.21 (H-3, dd, $J = 5.5$, 3.5, 1H), 4.09 (H-6_e, dd, $J = 11.0$, 5.9, 1H), 3.94 (H-4, dd, $J = 10.5$, 3.5, 1H), 3.87 (H-6_a, dd, $J = 11.0$, 10.5, 1H), 1.52 ($-CH_3$, s, 3H), 1.28 ($-CH_3$, s, 3H), 1.75–0.95 (–TIPS, $-SnBu_3$, m, 48H). ^{13}C-NMR (100 MHz, C_6D_6): $\delta =$ 164.5 (C-1), 114.9 (C-2), 99.4 ($C(CH_3)_2$), 72.0, 65.7, 62.5 (C-3, C-4, C-5), 62.5 (C-6), 29.1, 19.2 ($C(CH_3)_2$), 29.3, 27.5, 13.9, 10.2 ($-SnBu_3$), 18.4, 12.8 (–TIPS). MS (EI): $m/z = 631.4$ [M^+], 589.4 [$M^+ - C_3H_7$], 575.4 [$M^+ - C_4H_9$]. HR-MS Calc. for $C_{27}H_{53}O_4Si^{116}Sn$ [$M^+ - C_3H_7$] 585.2726. Found 585.2728. Anal. Calc. for $C_{30}H_{60}O_4SiSn$: C, 56.93; H, 9.58. Found C, 57.00; H, 9.54%.

6.21. 1,5-Anhydro-3,4,6-tri-O-triisopropylsilyl-1-(tri-n-butyl)stannyl-2-deoxy-D-xylo-hex-1-enitol (**26**)

Starting from 4.06 g (6.60 mmol) 1,5-anhydro-3,4,6-tri-*O*-triisopropylsilyl-2-deoxy-D-*xylo*-hex-1-enitol, 14.4 ml (23.1 mmol) *tert*-butyllithium (15% in hexanes) and 6.22 ml (23.1 mmol) tri-*n*-butylstannyl chloride a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, petroleum ether; 5‰ NEt_3) afforded 4.12 g (4.55 mmol, 69%) of a colourless oil. $R_f = 0.81$ (petroleum ether). ^{1}H-NMR (400 MHz, C_6D_6): $\delta = 5.29$ (H-2, dd, $J = 5.1$, 2.0, 1H), 4.41 (H-4, dd, $J = 2.5$, 2.0, 1H), 4.33 (H-6, dd, $J = 8.6$, 4.6, 1H), 4.30 (H-6′, dd, $J = 8.6$, 8.6, 1H), 4.24 (H-3, dd, $J = 5.1$, 2.5, 1H), 4.18 (H-5, dd, $J = 8.6$, 4.6, 1H), 1.85–0.91 (–TIPS, $-SnBu_3$, m, 100H). ^{13}C-NMR (90 MHz,C_6D_6): $\delta = 166.1$ (C-1), 112.2 (C-2), 74.6, 68.8, 65.1 (C-3, C-4, C-5), 62.2 (C-6), 29.2, 27.4, 13.1, 9.7 ($-SnBu_3$), 18.3–18.0, 13.1–12.1 (–TIPS). MS (FAB, mNBA): $m/z = 903.5$ [M^+], 861.6 [$M^+ - C_3H_7 + H$], 847.5 [$M^+ - C_4H_9 + H$]. Anal. Calc. for $C_{45}H_{96}O_4Si_3Sn$: C, 59.70; H, 10.70. Found C, 59.91; H, 10.77%.

6.22. 1,5-Anhydro-4,6-O-isopropylidene-3-O-triisopropylsilyl-2-deoxy-1-(tri-n-butyl)stannyl-D-xylo-hex-1-enitol (**30**)

Starting from 1.32 g (3.85 mmol) 1,5-anhydro-4,6-*O*-isopropylidene-3-*O*-triisopropylsilyl-2-deoxy-D-*xylo*-hex-1-enitol, 7.9 ml (13.5 mmol) *tert*-butyllithium (15% in hexanes) and 3,6 ml (13.5 mmol) tri-*n*-butylstannyl chloride a crude oil was obtained following the procedure described above. Chromatographic purification (SiO_2, CH_2Cl_2/petroleum ether: 2:3; 5‰ NEt_3) afforded 1.56 g (2.47 mmol, 64%) of a colourless oil. $R_f = 0.55$ (CH_2Cl_2/petroleum ether: 2:3). ^{1}H-NMR (400 MHz, C_6D_6): $\delta = 5.29$ (H-2, dd, $J = 5.1$, 1.6, 1H), 4.10 (H-3, dd, $J = 5.1$, 2.0, 1H), 4.07 (H-4, ddd, $J = 2.0$, 1.6, 1.5, 1H), 3.99 (H-6, dd, $J = 12.5$, 1.2, 1H), 3.72 (H-5, ddd, $J = 1.5$, 1.5, 1.2, 1H), 3.65 (H-6′, dd, $J = 12.5$, 1.5, 1H), 1.53 ($-CH_3$, s, 3H), 1.31 ($-CH_3$, s, 3H), 1.75–0.95 (–TIPS, $-SnBu_3$, m, 48H). ^{13}C-NMR (100 MHz, C_6D_6): $\delta = 165.6$ (C-1), 111.7 (C-2), 98.1 ($C(CH_3)_2$), 69.9, 65.3, 63.5 (C-3, C-4, C-5), 63.4 (C-6), 29.5, 18.4 ($C(CH_3)_2$), 29.2, 27.4, 13.7, 9.8 ($-SnBu_3$), 18.1, 12.5 (–TIPS). MS (EI): $m/z = 631.2$ [M^+], 589.2 [$M^+ - C_3H_7$], 575.3 [$M^+ - C_4H_9$]. HR-MS Calc. for $C_{26}H_{51}O_4Si^{116}Sn$ [$M^+ - C_4H_9$] 571.2574. Found 571.2568. Anal. Calc. for $C_{30}H_{60}O_4SiSn$: C, 56.93; H, 9.58. Found C, 57.28; H, 10.01%.

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