

# Simple oxidation of 3-*O*-silylated glycols: application in deblocking 3-*O*-protected glycols

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A high yielding allylic oxidation of 3-*O*-silylated glycols **5–10** with the reagent system  $\text{PhI}(\text{OAc})_2\text{-TMSN}_3$  is presented. The iodine(III) species generated under these conditions is a lot more effective for generating carbohydrate-derived 3-trialkylsiloxy-2,3-dihydro-4*H*-pyran-4-ones **11–15** than is [hydroxy(tosyloxy)iodo]benzene, the Koser reagent. Even disaccharide **9** containing the oxidation-labile phenylseleno group is smoothly oxidized to the corresponding enone **15**. The hypervalent azido iodine reagent is complementary to the Koser reagent, because 3-*O*-benzylated or -acylated glycols cannot be oxidized. When the iodine(III)-mediated oxidation of 3-*O*-silylated or -benzylated glycols is followed by a reduction step, the formal 3-*O*-deblocking of glycols is achieved. In particular, the Luche reduction of enones obtained from the oxidation of *lyxo*-configured glycols **24** and **26** is highly selective and exclusively affords the corresponding *lyxo*-configured glycols **28** and **30**. In some cases, these products can be transformed under Mitsunobu conditions into glycols with inverted configuration at C-3 in moderate yield.

## Introduction

Glycols are carbohydrate-based enol ethers, and numerous examples have served as enantiopure synthetic intermediates; e.g., the use of glycols as chiral building blocks in various cycloaddition reactions<sup>1</sup> and for the synthesis of *C*-glycosides<sup>2</sup> are important applications. Furthermore, they have often been employed as useful intermediates for the construction of complex natural products, typical examples being the ionophores lasalocid A<sup>3a</sup> and calcimycin<sup>3b</sup> as well as the macrolactones rapamycin<sup>3c</sup> and avermectin A.<sup>3d</sup> Most frequently, however, they have proven to be useful for the preparation of oligosaccharides<sup>4</sup> including 2-deoxy glycosides.<sup>5</sup> Besides the development of efficient glycosidation methods the availability of partially protected glycols has turned out to be another key issue for the construction of oligosaccharide chains present in anthracyclines, angucyclines such as landomycin A **1**, the aureolic acids and other glycosylated antibiotics.<sup>5</sup>

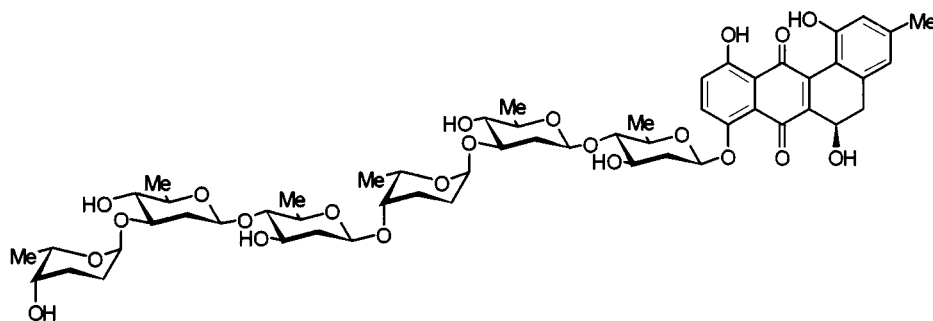
Although many studies have been conducted into the preparation of partially blocked glycols, and in particular 3-*O*-deprotected members of 2,6-dideoxy sugars, these approaches often lack a high degree of regioselectivity and afford mixtures of reaction products.<sup>6</sup> The methods employed typically rely on the selective protection of glycols by using alkylation methods under phase-transfer catalysis conditions,<sup>7,8</sup> the use of bulky silylating reagents,<sup>9</sup> and electrophilic attack on *cis*-*O,O'*-dibutylstannylene acetals.<sup>8</sup> During our efforts to synthesize the hexasaccharide chain of landomycin A **1**,<sup>10</sup> it became necessary

to develop a method for selectively deblocking the allylic position of glycols.<sup>11</sup>

## Results and discussion

### Improved iodine(III)-promoted oxidation of glycols

In this paper an oxidation/reduction strategy is presented which effectively deprotects fully protected glycols in the allylic position to afford glycols **3** (Scheme 1). With our discovery of the oxidative deblocking at O-3 of fully protected glycols **2** mediated by hypervalent iodine(III) reagents, we were able to achieve rapid synthetic access to carbohydrate-derived 2,3-dihydro-4*H*-pyran-4-ones **4**.<sup>12</sup> In the presence of [hydroxy(tosyloxy)iodo]benzene [ $\text{PhI}(\text{OH})\text{OTs}$ ], the Koser reagent, almost any O-3-protected glycol **2** can be used as a starting material.<sup>13</sup> In fact, the ketone functionality can be elaborated from diverse precursors including esters, acetals and ethers in a regioselective process. However, in most cases, namely esters, and benzyl or methoxymethyl ethers, yields for 2,3-dihydro-4*H*-pyran-4-ones **4** do not exceed 60% and additional by-products are formed. These by-products helped to elucidate the mechanism of this process.<sup>14</sup> Due to the synthetic versatility of the oxidation products as chiral building blocks,<sup>15</sup> we pursued an improvement of the allylic oxidation. In comparison with the Koser reagent, most common hypervalent iodine reagents such as  $\text{PhI}(\text{OAc})_2$ ,<sup>16</sup>  $\text{PhI}(\text{O}_2\text{CCF}_3)_2$ ,  $\text{PhI}(\text{OCH}_3)\text{OTs}$ <sup>17</sup> and  $\text{PhI}(\text{CN})_2$ <sup>18</sup> were ineffective oxidants, giving yields of 0–10%, as did  $\text{BF}_3$ .

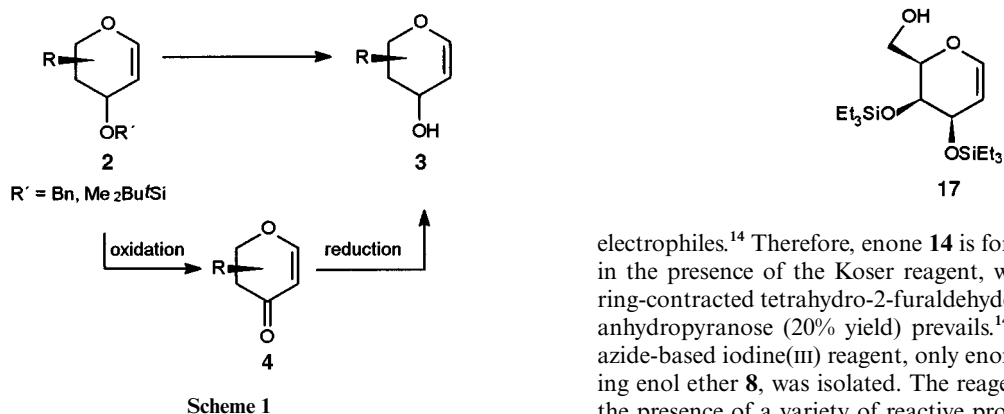


Landomycin A 1

**Table 1** PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub>-mediated oxidation of 3-*O*-silylated glycols

Glycol	Method <sup>a</sup>	Enone	Yield [%] <sup>b</sup>
	5 A (B)		11 95 (33)
	6 A (B)		12 92 (<10 <sup>c</sup> )
	7 A (B)		13 95 (67)
	8 A (B)		14 43 (18)
	9 A		15 79
	10 A		16 57 <sup>d</sup>

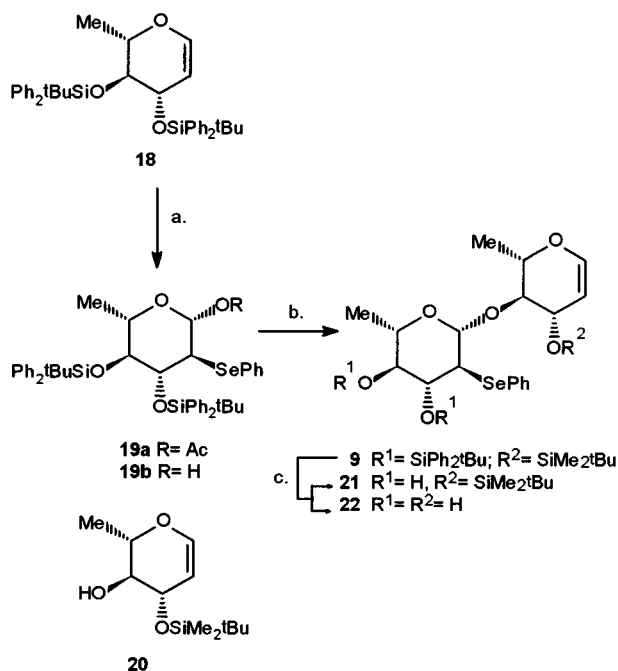
<sup>a</sup> Method A: PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub>; method B: PhI(OH)OTs. <sup>b</sup> The second value in the parentheses refers to the yield of method B. <sup>c</sup> Compound **17** is the major product. <sup>d</sup> Inseparable mixture of 3-epimers.



OEt<sub>2</sub> or trimethylxonium tetrafluoroborate-activated iodosylbenzene [PhIO]<sub>n</sub>.<sup>19</sup> However, we found that the reagent system PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub><sup>20</sup> was the best oxidant for the oxidative deblocking of 3-*O*-silylated glycols **5–9** to afford enones **11–15** (Table 1).<sup>13</sup> In all cases, the reaction proceeds in higher yields compared with those obtained with PhI(OH)OTs.<sup>12,14</sup> Due to the more acidic reaction conditions used when employing the Koser reagent, glycol **6** was selectively desilylated instead, yielding compound **17** in 52% yield, while the desired enone **12** was inefficiently formed. The 6-*O*-tosylated glycol **8** adopts a twist-boat or <sup>5</sup>H<sub>4</sub>(D) conformation with reduced reactivity for

electrophiles.<sup>14</sup> Therefore, enone **14** is formed in only 18% yield in the presence of the Koser reagent, whereas formation of a ring-contracted tetrahydro-2-furaldehyde (35% yield) and a 2,3-anhydropyranose (20% yield) prevails.<sup>14</sup> When employing the azide-based iodine(III) reagent, only enone **14**, along with starting enol ether **8**, was isolated. The reagent can be employed in the presence of a variety of reactive protective groups, such as acid-labile triethylsilyl ethers or tosyloxy groups. For studying the full scope of this oxidation we planned to treat disaccharide **9**, which contains an oxidation-labile phenylselenyl group and a glycosidic linkage with the reagent system PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub>.

For this purpose, we had to prepare glycol **9** which was achieved by utilizing a method developed by Perez and Beau<sup>21</sup> in the initial step. Glycol **18** was transformed into a single 1,2-addition product, the seleno acetate **19a** (Scheme 2). However, at this stage it was not possible to clearly prove the β-*gluco*-configuration of product **19a**, as the coupling constants *J* for the ring protons in the <sup>1</sup>H NMR-spectrum are not diagnostic (*J*<sub>1,2</sub> 4.0 Hz, *J*<sub>2,3</sub> 3.6 Hz, *J*<sub>3,4</sub> 3.6 Hz, *J*<sub>4,5</sub> not determined).



**Scheme 2** Reagents, conditions (and yields): (a) PhSeCl (1.3 equiv.), AgOAc (1.5 equiv.), toluene, rt, 3 h, (72%, crude); (b) Et<sub>2</sub>O, cat. TIPSOTf, -80 °C, 10 min; then addition of **20** (1.2 equiv.), -50 °C, 10 min (59%); (c) TBAF (3.0 equiv.), THF, 0 °C, 12 h, **21** (43%) and **22** (35%).

Unfortunately, the acetyl group in pyranosyl acetate **19a** turned out to be very sensitive and was hydrolysed upon attempted purification on silica gel to afford pyranose **19b**. Therefore, crude alcohol **19a** was glycosidated after activation with triisopropylsilyl triflate (TIPSOTf) in the presence of glycal **20** to provide disaccharide **9** in 59% yield. At this stage, the configuration of all stereogenic centers were assigned after fluoride-initiated removal of the silyl protection. Thus, treatment of compound **9** with TBAF furnished disaccharides **21** and **22**. With the large protective groups now missing, both compounds adopt a <sup>1</sup>C<sub>4</sub>(L)-conformation. From the ring-proton coupling constants *J* of the second pyran ring (between 9.2 and 11.2 Hz) the *gluco*-configuration in compounds **21** and **22** as well as **19a** was unequivocally established. Finally, iodine(III)-promoted oxidation afforded the 2,3-dihydro-4*H*-pyran-4-one **15** in satisfactory yield, thereby confirming the exceptional mildness of the azide-based hypervalent iodine reagent.

Clearly, both hypervalent iodine reagents [PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub> and PhI(OH)OTs] employed here differ in their reactivity, for which further support was obtained when other than silyl protection was introduced in the allylic position.<sup>13</sup> Glycals with a 3-*O*-acyl or 3-*O*-methoxymethyl group, which are good substrates for the Koser reagent,<sup>12</sup> do not react with the PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub> system or gave reduced yields, whereas 3-*O*-benzyl glycals showed substantial decomposition under the reaction conditions. The two hypervalent iodine reagents are obviously complementary. When a deoxygenation is introduced at C-3 as in glycal **10**, 3-azido glycals **16** were formed in a comparable yield to those obtained in the reagent system (PhIO)<sub>n</sub>-TMSN<sub>3</sub>.<sup>22</sup> These observations are in sharp contrast to earlier work by Ehrenfreund and Zbiral,<sup>23</sup> who observed oxidative ring-cleavage of 2,3-dihydropyran with the same reagent system, providing the corresponding formic acid 3-cyanopropyl ester in 61% yield. However it has to be pointed out that PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub> provides a large variety of reactions with alkenes which for most cases may either be explained by electrophilic attack of a hypervalent iodine species on the π-bond or alternatively may be rationalized on the basis that the reaction is initiated by a 1,3-dipolar cycloaddition of the azide group to the double bond. At present the precise structure of the intermediate reagent formed is still not clear. From IR

studies<sup>23</sup> it was concluded that PhI(N<sub>3</sub>)OAc is the active species while other authors<sup>24</sup> claim that in most cases (diazidoiodo)-benzene PhI(N<sub>3</sub>)<sub>2</sub> is involved. We believe that this oxidation proceeds *via* similar intermediates that were found for the analogous reaction using the Koser reagent<sup>13</sup> as well as for the iodine(III)-promoted oxidation of triisopropylsilyl enol ethers described by Magnus *et al.*<sup>24</sup>

### Chemical modifications of the keto group

In the next step, the crude products of the iodine(III)-mediated oxidations were directly reduced to the corresponding allylic alcohols, which terminates our allylic deprotection strategy. As is shown in Table 2, per-*O*-benzylated glycals **23–26** can efficiently be deblocked with this oxidation-reduction strategy, affording allyl alcohols **27–30**. However, for these glycals it became necessary to use PhI(OH)OTs in the primary oxidation step. We found that in most cases Luche reduction<sup>25</sup> proved to be a very effective protocol for the reduction of the keto functionality with yields in the range of 85–99%.<sup>26</sup> However, this method turned out to be ineffective in the presence of a siloxy substituent *α* to the carbonyl group as shown for enone **13**.<sup>27</sup> In this case, DIBAL-H was the reagent of choice which, starting from compound **7**, furnished glycals **31a,b**. Furthermore, the reduction is highly stereoselective for *threo*-configured pyranones with a pseudoaxial substituent next to the carbonyl group. Thus, *lyxo*-configured fully protected glycals **24** and **26** are selectively converted into the corresponding 3-*O*-unprotected glycals **28a** and **30a**; indeed, the corresponding *xylo*-configured epimers **28b** and **30b** were not detected in the crude product. *In fact, this route is the shortest one to 3-*O*-unprotected lyxo-configured glycals.* Also, for glycals **23**, **25**, **7** and **9** the starting *arabino*-configuration is preserved preferentially, leading to glycals **27a**, **29a**, **31a** and **32a**. Nevertheless, the corresponding *ribo*-configured isomers **27b**, **29b**, **31b** and **32b** are formed also. Apparently, a pseudoequatorial substituent at C-4 is responsible for the moderate stereoselectivity of this process.<sup>27</sup> However, for all examples the epimers could be separated by column chromatography, which is in contrast to several mixtures obtained by the regioselective blocking of unprotected glycals.<sup>6–9</sup>

The configuration of the newly formed stereogenic center at C-3 was confirmed by comparison of the relevant coupling constants in the <sup>1</sup>H NMR spectra (*arabino*: *J*<sub>2,3</sub> 2.0–2.4 Hz, *J*<sub>3,4</sub> 6.5–7.6 Hz; *ribo*: *J*<sub>2,3</sub> 4.8–5.8 Hz, *J*<sub>3,4</sub> 3.6–4.0 Hz; *lyxo*: *J*<sub>2,3</sub> 3.0–4.0 Hz, *J*<sub>3,4</sub> 4.4–4.6 Hz) which were in accordance with literature values<sup>6–9</sup> as well as NMR data collected from the starting glycals.

In order to unequivocally confirm its configuration, glycal **31a** was acetylated and the resulting product **35** was compared with authentic material obtained by an alternative and new chemo-enzymic route (Scheme 3). Thus, lipase-catalyzed irreversible transesterification<sup>28</sup> of L-rhamnal **33** afforded the 3-*O*-acylated glycal **34** as a single isomer, which was transformed into compound **35** under standard silylating conditions. Good yields are only achieved for this sequence if the alcohol **34** is not stored for too long, as acetyl migration to the 4-position can occur.<sup>9,29</sup> It should be noted that this chemo-enzymic route is restricted to a few glycals;<sup>28</sup> *e.g.*, we found that the 4-epimers of **33** (L-rhamnal) or di-*O*-acetyl-L-rhamnal cannot be used for this purpose.

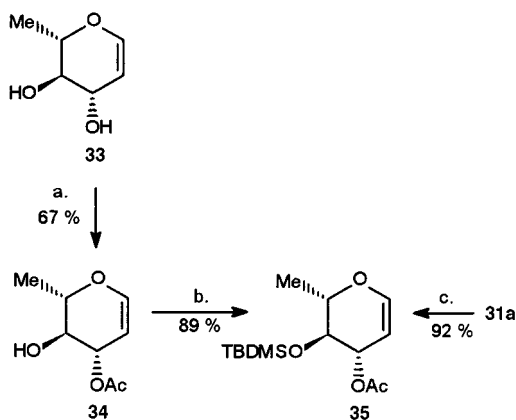
The oxidation/reduction sequence presented here can advantageously be exploited for the specific incorporation of deuterium at C-3, which became necessary for us during our ongoing studies on the biogenesis of deoxygenated sugars.<sup>30</sup> As depicted in Scheme 4, di-*O*-benzyl-L-arabinal **36** was oxidized to the corresponding enone **37**, which was in turn reduced to afford the allyl alcohol **38** or the deuterated analogue **39**. Formation of the *erythro*-configured 3-epimer was not observed.

Inversion of configuration at C-3 of glycals or substitution would increase the applicability of our oxidation/reduction

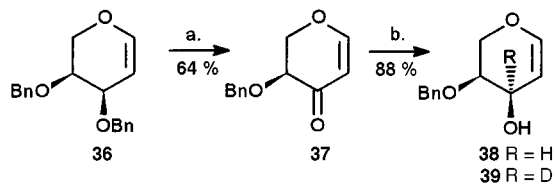
**Table 2** 3-*O*-Deblocking of protected glycols by the oxidation/reduction sequence

Glycol	R <sup>1</sup>	R <sup>2</sup>	Conditions	3- <i>O</i> -deblocked glycols	Ratio <sup>a</sup>	Yield [%] <sup>b</sup>		
	23	H	OBn	1. PhI(OH)OTs 2. NaBH <sub>4</sub> , CeCl <sub>3</sub>		27a,b	1.5:1	38
	24	OBn	H	1. PhI(OH)OTs 2. NaBH <sub>4</sub> , CeCl <sub>3</sub>		28a,b	>10:1	57
	25	OBn	H	1. PhI(OH)OTs 2. NaBH <sub>4</sub> , CeCl <sub>3</sub>		29a,b	1.1:1	47
	26	H	OBn	1. PhI(OH)OTs 2. NaBH <sub>4</sub> , CeCl <sub>3</sub>		30a,b	>10:1	59
	7			1. PhI(OAc) <sub>2</sub> , TMSN <sub>3</sub> 2. DIBAL-H		31a,b	2:1	65
	9			1. PhI(OAc) <sub>2</sub> , TMSN <sub>3</sub> 2. NaBH <sub>4</sub> , CeCl <sub>3</sub>		32a,b	1:1	67

<sup>a</sup> Determined from <sup>1</sup>H NMR spectra of crude products. <sup>b</sup> Refers to separated isomers.



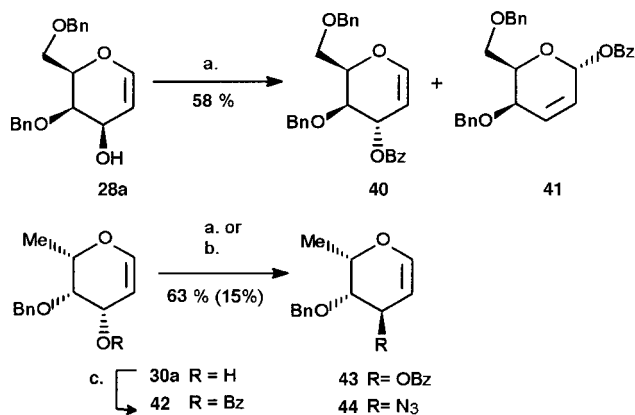
**Scheme 3** Reagents, conditions (and yields): (a) lipase PS, CH<sub>2</sub>=CHOAc, ethyl acetate, rt, 2 d, 67%; (b) <sup>t</sup>BuMe<sub>2</sub>SiCl, imidazole, DMF, rt, 12 h (89%); (c) Ac<sub>2</sub>O, pyr, rt, 10 h (92%).



**Scheme 4** Reagents, conditions (and yields): (a) PhI(OH)OTs, molecular sieves 3 Å, CH<sub>3</sub>CN, rt, 1 h (64%); (b) CeCl<sub>3</sub>·(H<sub>2</sub>O)<sub>7</sub>, NaBH<sub>4</sub> (NaBD<sub>4</sub>), EtOH, CH<sub>2</sub>Cl<sub>2</sub>, -50 °C→rt, 30 min 88%.

sequence as *O*-differentiated and stereochemically rare glycols would be accessible *via* a short route. We reckoned that Mitsunobu-type reactions<sup>31</sup> should be the transformation of choice for this purpose. However, Guthrie *et al.*<sup>32</sup> first reported that the Ph<sub>3</sub>P/ethyl diazoacetate mediated reaction of 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-hex-1-enitol with benzoic acid gave only the S<sub>N</sub>2'-product. Later, Sulikowski and Sobti employed the Mitsunobu reaction for the preparation of unsaturated aryl glycosides starting from various glycols.<sup>33</sup>

However, in only a few cases has the formation of the desired substitution product with inversion of configuration at C-3 been reported.<sup>34</sup> We found that Mitsunobu reaction of galactal **28a** with benzoic acid in toluene afforded a mixture of glycal **40** and enopyranoses **41** ( $\alpha$ : $\beta$  >8:1) (Scheme 5). Interestingly,



**Scheme 5** Reagents, conditions (and yields): (a) PPh<sub>3</sub>, BzOH, DEAD, toluene, 20 h, 0 °C→rt, 58% from **28a** and 63% from **30a**; (b) LiN<sub>3</sub>, PPh<sub>3</sub>, CBr<sub>4</sub>, DMF, rt, 12 h, 15% from **30a**; (c) BzCl, pyr, CH<sub>2</sub>Cl<sub>2</sub>, 12 h, rt, 30%.

fucal **30a** exclusively furnished S<sub>N</sub>2-product **43** under the same conditions.

A particularly useful application in this respect would be the stereoselective introduction of a masked amino functionality (the azide anion) at C-3. In fact, 3-azido glycols have served as important glycosyl precursors for the construction of glycosides containing 3-amino-2,3,6-trideoxyhexopyranoses.<sup>35</sup> These are constituents of various pharmaceutically important glycosylated antitumor agents. Treatment of glycal **30a** in the presence of lithium azide, carbon tetrabromide and triphenylphosphine in DMF afforded azido glycal **44** as a single isomer.<sup>36</sup> In principle, this reaction leads to stereochemically rare 3-azido glycols although the yield is far from satisfactory.

In summary we have shown a straightforward two-step

procedure for selectively deblocking fully protected glycals at C-3. The process is initiated by an iodine-promoted oxidation of 3-*O*-benzyl- or silyl-protected glycals to afford the corresponding enones, followed by chemoselective reduction of the ketone functionality. The 3-*O*-unprotected glycals obtained by this route may further be manipulated at C-3 by variants of the Mitsunobu reaction. This short sequence provides an efficient access to valuable, partially blocked glycals. These can serve as monosaccharide precursors in glycosylation reactions towards deoxygenated oligosaccharides which are constituents of numerous important glycoconjugates from microbial sources, including landomycin A 1.

## Experimental

### General procedures

All temperatures quoted are uncorrected. Optical rotations were recorded on a Perkin-Elmer 141 polarimeter and are given in  $10^{-1}$  deg  $\text{cm}^2 \text{g}^{-1}$ . IR spectra were obtained on a PYE Unicam SP3-200 as thin films on NaCl plates.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^1\text{H}$ ,  $^1\text{H}$ - and  $^1\text{H}$ ,  $^{13}\text{C}$ -COSY as well as NOESY spectra were recorded on a Bruker ARX 400-NMR spectrometer for solutions in  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$  using residual  $\text{CHCl}_3$  or  $\text{C}_6\text{H}_6$  as internal standards ( $\delta$  7.26 and 7.20, respectively) unless otherwise stated. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad. Coupling constants ( $J$ ) are quoted in Hz. Chemical-shift values of  $^{13}\text{C}$  NMR spectra are reported as values in ppm relative to residual  $\text{CHCl}_3$  ( $\delta_{\text{C}}$  77) or  $\text{C}_6\text{D}_6$  ( $\delta_{\text{C}}$  128) as internal standards. The multiplicities refer to the resonances in the off-resonance spectra and were elucidated using the distortionless enhancement by polarization transfer (DEPT) spectral editing technique, with secondary pulses at  $90^\circ$  and  $135^\circ$ . Multiplicities are reported using the following abbreviations: s = singlet (due to quaternary carbon), d = doublet (methine), t = triplet (methylene), q = quartet (methyl). Mass spectra were obtained using a Kratos MS-80RFA mass spectrometer (DS-55/DS-90 peak matching option) when electron impact (EI, 70 eV) was the ionization method of choice. Fast-atom bombardment (FAB) mass spectra were obtained on a BG Analytical ZAB-2F (Ion Tech FAB gun, 8 kV, Xe carrier gas). Ion mass ( $m/z$ ) signals are reported as values in atomic mass units followed, in parentheses, by the peak intensities relative to the base peak (100%). Combustion analyses were performed by the Institut für Pharmazeutische Chemie, Technische Universität Braunschweig and Institut für Chemie, Humboldt Universität zu Berlin. All solvents used were of reagent grade and were further dried. Petroleum spirit refers to the fraction with distillation range  $50\text{--}70^\circ\text{C}$ . Reactions were monitored by TLC on silica gel 60 F $^{254}$  (E. Merck, Darmstadt) and spots were detected either by UV-absorption or by charring with  $\text{H}_2\text{SO}_4$ -4-methoxybenzaldehyde in methanol. Preparative column chromatography was performed on silica gel 60 (E. Merck, Darmstadt). Lipase PS (*Pseudomonas fluorescens*) was obtained from Amano Pharmaceutical Co. [Hydroxy(tosyloxy)iodo]benzene [PhI(OH)OTs] was prepared according to Koser's procedure.<sup>37</sup> *O*-Silylated glycals **5**–**7** and **18** were synthesized according to the literature.<sup>12</sup> *O*-Benzylated glycals **23**–**26** and **36** were obtained as described in ref. 38. The 6-*O*-tosyl glucal **8**<sup>14</sup> and 3-deoxy glycal **10**<sup>22</sup> have been described before.

### Preparation of acetyl 3,4-bis-*O*-(*tert*-butyldiphenylsilyl)-6-deoxy-2-phenylseleno- $\beta$ -L-glucopyranose **19a**

To a solution of glycal **18** (1.05 g, 1.7 mmol) in absolute toluene (50 ml) under  $\text{N}_2$  at rt were added benzeneselenenyl chloride (422 mg, 2.2 mmol) and silver acetate (435 mg, 2.6 mmol). The suspension was stirred at rt for 3 h, before the reaction mixture was filtered, and concentrated *in vacuo*. The residue was puri-

fied by flash column chromatography ( $\text{SiO}_2$ ; petroleum spirit–ethyl acetate 12:1). The *title compound* **19a** (1.01 mg, 72%) was sufficiently pure for the next step. For analytical purposes, a small amount was further purified by column chromatography ( $\text{SiO}_2$ ; petroleum spirit–ethyl acetate 20:1).

1st fraction: acetyl 3,4-bis-*O*-(*tert*-butyldiphenylsilyl)-6-deoxy-2-phenylseleno- $\beta$ -L-glucopyranose **19a** (contaminated with ~10% of alcohol **19b**):  $\delta_{\text{H}}$ (400 MHz;  $\text{C}_6\text{D}_6$ ; TMS = 0.0 ppm) 7.7–7.1 (25H, m, Ph), 6.32 (1H, d,  $J$  4.0, 1-H), 4.39 (1H, dd,  $J$  3.6 and 3.6, 3-H), 3.81 (1H, dd,  $J$  3.6 and 4.0, 2-H), 3.64 (2H, m, 4- and 5-H), 2.12 (3H, s, OAc), 1.12 (3H, d,  $J$  7.2, 6-H<sub>3</sub>) and 0.97 and 0.79 (18H, 2 s,  $2 \times$  'Bu);  $\delta_{\text{C}}$ (100 MHz;  $\text{C}_6\text{D}_6$ ) 169.5 (s, OAc), 132.4, 132.3, 131.9, 131.8 and 129.9 (s, Ph), 135.6, 135.4, 134.6, 134.5, 132.0, 128.8, 128.7, 128.6, 128.5, 126.6, 126.5, 126.4, 126.3 and 126.2 (d, Ph), 91.0 (d, 1-C), 72.4, 71.5 and 70.8 (d, 3-, 4- and 5-C), 44.6 (d, 2-C), 26.2 and 25.6 (q,  $2 \times$  'Bu), 20.5 (q, OAc), 19.0 (q, 6-C) and 18.5 and 17.9 (s,  $2 \times$  'Bu).

2nd fraction: 3,4-bis-*O*-(*tert*-butyldiphenylsilyl)-6-deoxy-2-phenylseleno- $\beta$ -L-glucopyranose **19b**: mp  $58^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{25} + 32.5$  (c 0.925,  $\text{CHCl}_3$ );  $\delta_{\text{H}}$ (400 MHz;  $\text{C}_6\text{D}_6$ ; TMS = 0.0 ppm) 7.7–7.0 (25H, m, Ph), 5.30 (1H, dd,  $J$  13.2 and 2.0, 1-H), 4.78 (1H, dd,  $J$  2.0 and 2.0, 3-H), 3.96 (1H, q,  $J$  7.2, 5-H), 3.78 (1H, d,  $J$  13.2, OH), 3.54 (1H, d,  $J$  2.0, 4-H), 3.14 (1H, dd,  $J$  2.0 and 2.0, 2-H), 1.22 (3H, d,  $J$  7.2, 6-H<sub>3</sub>) and 1.06 and 0.95 (18H, 2 s,  $2 \times$  'Bu);  $\delta_{\text{C}}$ (50 MHz;  $\text{CDCl}_3$ ; TMS = 0.0 ppm) 135.9, 135.8, 135.6, 132.6, 130.0, 129.9, 129.7, 129.0, 128.2, 127.8, 127.7, 127.6, 127.5 and 126.8 (d, Ph), 133.4, 132.9 and 132.3 (q, Ph), 84.9 (d, 1-C), 76.9, 75.9 and 71.2 (d, 3-, 4- and 5-C), 54.3 (d, 2-C), 27.0 and 26.9 (q,  $2 \times$  'Bu), 19.1 and 18.9 (s,  $2 \times$  'Bu) and 16.6 (q, 6-C) (Found: C, 67.4; H, 7.1.  $\text{C}_{44}\text{H}_{52}\text{O}_4\text{Si}_2\text{Se}$  requires C, 67.75; H, 6.72%).

### Preparation of 1,5-anhydro-4-*O*-[3,4-bis-*O*-(*tert*-butyldiphenylsilyl)-6-deoxy-2-phenylseleno- $\beta$ -L-glucopyranosyl]-3-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-L-arabino-hex-1-enitol **9**

To a solution of monosaccharide **19a** (1.45 g, 1.76 mmol) in absolute diethyl ether (50 ml) under  $\text{N}_2$  at  $-80^\circ\text{C}$  was added TIPSOTf (0.048 ml, 55 mg, 0.18 mmol) and the solution was stirred for 10 min. Then, glycal **20** (0.52 g, 2.1 mmol) was added, the temperature was raised to  $-50^\circ\text{C}$  and stirring was continued for 10 min. For work-up, saturated aq.  $\text{NaHCO}_3$  was added, the phases were separated, and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times$ ). The combined organic layers were dried ( $\text{MgSO}_4$ ), and concentrated *in vacuo*. Flash chromatography (petroleum spirit–ethyl acetate 30:1) afforded the *title compound* **9** (1.06 g, 59%); mp  $95^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{19} + 63.3$  (c 1.01,  $\text{CHCl}_3$ );  $\delta_{\text{H}}$ (200 MHz;  $\text{C}_6\text{D}_6$ ) 7.8–7.6 and 7.3–7.0 (25H, m, ArH), 6.34 (1H, dd,  $J$  0.8 and 6.0, 1-H), 5.69 (1H, d,  $J$  6.4, 1'-H), 5.13 (1H, d,  $J$  3.2, 4'-H), 4.80 (1H, dd,  $J$  3.6 and 6.0, 2-H), 4.50 (1H, ddt,  $J$  0.8, 3.6 and 4.0, 3-H), 4.24 (1H, dq,  $J$  6.0 and 6.4, 5-H), 3.96 (1H, dd,  $J$  4.0 and 6.0, 4-H), 3.86 (2H, m, 2'- and 5'-H), 3.72 (1H, d,  $J$  3.6, 3'-H), 1.64 (3H, d,  $J$  6.4, 6-H<sub>3</sub>), 1.21, 1.14 and 1.08 (27H, 3 s,  $3 \times$  'Bu), 1.0 (3H, d,  $J$  6.4, 6'-H<sub>3</sub>) and 0.33 and 0.25 [6H, 2 s,  $\text{Si}(\text{CH}_3)_2$ ];  $\delta_{\text{C}}$ (50 MHz;  $\text{C}_6\text{D}_6$ ) 136.5, 136.4, 136.3, 136.2, 131.9, 130.2, 130.1, 130.0, 129.9, 129.0, 128.3, 128.1 and 126.5 (d, Ph), 133.7, 133.6, 133.5 and 133.4 (q, Ph), 143.1 (d, 1-C), 103.8 (d, 1'-C), 103.1 (d, 2-C), 79.7 (d, 4-C), 78.9 and 78.8 (d, 4'- and 5'-C), 73.7 (d, 3'-C), 73.3 (d, 5-C), 67.1 (d, 3-C), 49.5 (d, 2'-C), 27.4, 27.2 and 26.2 (q,  $3 \times$  'Bu), 20.2 (q, 6'-C), 19.3, 19.2 and 18.3 (s,  $3 \times$  'Bu), 17.6 (q, 6-C) and  $-4.0$  and  $-4.6$  [q,  $\text{Si}(\text{CH}_3)_2$ ] (Found: C, 66.9; H, 7.8.  $\text{C}_{56}\text{H}_{74}\text{O}_6\text{Si}_3\text{Se}$  requires C, 66.83; H, 7.41%).

### Desilylation of disaccharide **9**

TBAF trihydrate (800 mg) was dissolved in absolute THF (5 ml) under  $\text{N}_2$ . After rapid removal of the solvent *in vacuo* the compound was kept in high vacuum for 6 h. The compound was re-dissolved in absolute THF (25 ml) under  $\text{N}_2$  to afford a

0.1 molar solution. A portion (2.1 ml, 0.21 mmol) of this solution were added to a solution of disaccharide **9** (70 mg, 0.07 mmol) in absolute THF (3 ml) at 0 °C. Stirring was continued for 12 h before the reaction mixture was treated with aq. NaHCO<sub>3</sub> (5 ml), and the phases were separated. The aqueous layer was washed with methylene dichloride, and the combined organic extracts were dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. The crude product was chromatographed on silica gel (petroleum spirit–ethyl acetate 1.5:1) to afford two fractions:

1st fraction: 1,5-anhydro-3-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-4-*O*-(6-deoxy-2-phenylseleno-β-*L*-gluco-pyranosyl-*L*-arabino-hex-1-enitol) **21** (16 mg, 43%);  $[\alpha]_{\text{D}}^{22} -24.6$  (*c* 0.54, CHCl<sub>3</sub>);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 7.72–7.60 and 7.35–7.18 (5H, m, Ph), 6.32 (1H, dd, *J* 0.6 and 6.0, 1-H), 4.72 (1H, ddd, *J* 0.8, 4.8 and 6.0, 2-H), 4.58 (1H, d, *J* 9.2, 1'-H), 4.28 (1H, ddq, *J* 1.2, 4.0 and 6.8, 5-H), 4.16 (1H, ddd, *J* 1.2, 3.2 and 4.8, 3-H), 3.72 (1H, ddd, *J* 0.8, 3.2 and 4.0, 4-H), 3.36 (3H, m, 3'-, 4'- and 5'-H), 2.99 (1H, dd, *J* 9.2 and 10.8, 2'-H), 2.94 (1H, br, OH), 2.53 (1H, br, OH), 1.45 (3H, d, *J* 6.8, 6-H<sub>3</sub>), 1.32 (3H, *J* 5.6, 6'-H<sub>3</sub>), 0.88 (9H, s, 'Bu) and 0.06 and 0.05 [6H, 2 s, Si(CH<sub>3</sub>)<sub>2</sub>].

2nd fraction: 1,5-anhydro-4-*O*-(6-deoxy-2-phenylseleno-β-*L*-gluco-pyranosyl)-*L*-arabino-hex-1-enitol **22** (10 mg, 35%);  $[\alpha]_{\text{D}}^{22} -18.7$  (*c* 0.525, CHCl<sub>3</sub>);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 7.63–7.57 and 7.37–7.24 (5H, m, Ph), 6.32 (1H, dd, *J* 1.6 and 6.0, 1-H), 4.76 (1H, dd, *J* 2.0 and 6.0, 2-H), 4.58 (1H, d, *J* 9.2, 1'-H), 4.46 (1H, br, OH), 4.27 (1H, ddd, *J* 1.6, 2.0 and 7.2, 3-H), 3.86 (1H, dq, *J* 6.4 and 10.0, 5-H), 3.43 (1H, dq, *J* 6.4 and 9.2, 5'-H), 3.38 (1H, dd, *J* 7.2 and 10.0, 4-H), 3.32 (2H, m, 3'- and 4'-H), 3.08 (1H, dd, *J* 9.2 and 11.2, 2'-H), 1.59 (3H, d, *J* 6.4, 6-H<sub>3</sub>) and 1.37 (3H, d, *J* 6.4, 6'-H<sub>3</sub>).

#### General procedure for the allylic oxidation of glycols with PhI(OAc)<sub>2</sub>-TMSN<sub>3</sub>

A solution of (diacetoxyiodo)benzene (2 equiv.) and trimethylsilyl azide (4 equiv.) in absolute methylene dichloride (~20 ml mmol<sup>-1</sup>) was stirred for 5 min at -5 °C. A solution of the glycol (1 equiv.) in absolute methylene dichloride (~1 ml mmol<sup>-1</sup>) was added dropwise and the ice-bath was removed, whereupon the temperature rose to ambient. Note that due to the exothermic character of the oxidation, a reaction scale of 10 mmol and larger may lead to reflux of the solvent. After 1 h, aq. NaHCO<sub>3</sub> (10 ml mmol<sup>-1</sup>) was added, and the phases were separated. The aqueous layer was washed with methylene dichloride and the combined organic extracts were dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. Physical constants and spectroscopic data for 2,3-dihydro-4*H*-pyran-4-ones **13** (scale: 1.39 mmol, yield: 95%)<sup>12</sup> and **14** (scale: 0.56 mmol; yield: 43%)<sup>14</sup> as well as for 3-azido glycol **16** (scale: 0.7 mmol; yield: 57%)<sup>22</sup> have been presented before.

**1,5-Anhydro-6-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-4-*O*-triethylsilyl-*D*-threo-hex-1-en-3-ulose **11**.** Compound **5** (5.0 g, 10.2 mmol) was used to prepare the *title compound* **11** (3.61 g, 95%) *via* the general procedure described above. Compound **11** was subjected to filtration on silica gel (petroleum spirit–ethyl acetate 10:1) to afford an oil;  $[\alpha]_{\text{D}}^{21} +50.2$  (*c* 1.16, CHCl<sub>3</sub>);  $\delta_{\text{H}}$ (200 MHz; C<sub>6</sub>D<sub>6</sub>) 6.60 (1H, d, *J* 6.0, 1-H), 5.17 (1H, dd, *J* 1.0 and 6.0, 2-H), 4.09–3.82 (4H, m, 4-, 5-H and 6-H<sub>2</sub>), 4.04 (1H, dd, *J* 1.4 and 2.4, 4-H), 1.08–0.95 [9H, m, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] and 0.80–0.64 [6H, s, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>];  $\delta_{\text{C}}$ (50 MHz; C<sub>6</sub>D<sub>6</sub>) 191.1 (s, 3-C), 162.1 (d, 1-C), 104.8 (d, 2-C), 83.1 (d, 4-C), 69.5 (d, 5-C), 59.9 (t, 6-C), 6.7 and 6.6 [q, 2 × Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] and 4.6 and 4.3 [t, 2 Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>]; *m/z* 372 (M<sup>+</sup>, 5%), 343 (74) (Found: M<sup>+</sup>, 343.1789. C<sub>16</sub>H<sub>31</sub>O<sub>4</sub>Si<sub>2</sub> requires *M*, 343.1761).

**1,5-Anhydro-2-deoxy-4,6-bis-*O*-triethylsilyl-*D*-threo-hex-1-en-3-ulose **12**.** Compound **6** (9.1 g, 18.7 mmol) was used to prepare the *title compound* **12** (6.4 g, 92%) *via* the general procedure

described above. Compound **12** was subjected to filtration on silica gel (petroleum spirit–ethyl acetate 10:1) to afford an oil;  $[\alpha]_{\text{D}}^{24} +53.9$  (*c* 1.95, CHCl<sub>3</sub>);  $\delta_{\text{H}}$ (200 MHz; CDCl<sub>3</sub>) 7.31 (1H, d, *J* 6.0, 1-H), 5.36 (1H, dd, *J* 1.4 and 6.0, 2-H), 4.26 (1H, ddd, *J* 2.4, 6.4 and 6.4, 5-H), 4.04 (1H, dd, *J* 1.4 and 2.4, 4-H), 3.98–3.92 (2H, m, 6-H<sub>2</sub>), 1.02–0.87 [18H, m, 2 × Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] and 0.70–0.54 [12H, m, 2 × Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>];  $\delta_{\text{C}}$ (50 MHz; CDCl<sub>3</sub>) 191.1 (s, 3-C), 162.1 (d, 1-C), 104.8 (d, 2-C), 83.1 (d, 4-C), 69.5 (d, 5-C), 59.9 (t, 6-C), 6.7 and 6.6 [q, 2 × Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] and 4.6 and 4.3 [t, 2 × Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>]; *m/z* 372 (M<sup>+</sup>, 5%) (Found: M<sup>+</sup>, 372.2151. C<sub>18</sub>H<sub>36</sub>O<sub>4</sub>Si<sub>2</sub> requires *M*, 372.2152).

**1,5-Anhydro-4-*O*-[3,4-bis-*O*-(*tert*-butyldiphenylsilyl)-6-deoxy-2-phenylseleno-β-*L*-gluco-pyranosyl]-2,6-dideoxy-*L*-erythro-hex-1-en-3-ulose **15**.** Compound **9** (50 mg, 0.05 mmol) was used to prepare the *title compound* **15** (35 mg, 79%) *via* the general procedure described above. Compound **15** was chromatographed on silica gel (petroleum spirit–ethyl acetate 8:1), mp 43–47 °C;  $[\alpha]_{\text{D}}^{25.2} -0.6$  (*c* 1.05, CHCl<sub>3</sub>);  $\delta_{\text{H}}$ (400 MHz; C<sub>6</sub>D<sub>6</sub>; TMS = 0.0 ppm) 7.6–6.6 (25H, m, PhSe, PhSiO), 6.16 (1H, d, *J* 6.0, 1-H), 5.41 (1H, d, *J* 6.4, 1'-H), 4.88 (1H, dd, *J* 0.8 and 6.0, 2-H), 4.70 (1H, dd, *J* 3.6 and 3.6, 3'-H), 3.95 (1H, dq, *J* 6.4 and 6.8, 5-H), 3.66 (1H, q, *J* 6.8, 5'-H), 3.61 (1H, dd, *J* 3.6 and 6.4, 2'-H), 3.57 (1H, dd, *J* 0.8 and 6.4, 4-H), 3.53 (1H, d, *J* 3.6, 4'-H), 0.96 and 0.78 (18H, 2 s, 2 × 'Bu), 0.81 (3H, d, *J* 6.8, 6'-H<sub>3</sub>) and 0.72 (3H, d, *J* 6.8, 6-H<sub>3</sub>);  $\delta_{\text{C}}$ (100 MHz; C<sub>6</sub>D<sub>6</sub>) 188.3 (s, 3-C), 159.9 (d, 1-C), 136.6, 136.5, 136.3, 131.9, 130.3, 130.1, 130.0, 129.9, 129.0, 128.2, 127.9, 127.5, 127.4, 127.3 and 126.4 (d, Ph), 138.8, 133.7, 133.5, 133.4 and 133.3 (s, Ph), 105.3 (d, 2-C), 104.1 (d, 1'-C), 79.4 (d, 4-C), 78.6 (d, 5'-C), 78.3 (d, 5-C), 78.1 (d, 3'-C), 73.8 (d, 4'-C), 48.2 (d, 2'-C), 27.5 and 27.2 q (2 × 'Bu), 20.3 (q, 6'-C), 19.4 and 19.3 (s, 2 × 'Bu) and 14.2 (q, 6-C) (Found: C, 67.4; H, 6.9. C<sub>59</sub>H<sub>58</sub>O<sub>6</sub>Si<sub>2</sub>Se requires C, 67.47; H, 6.57%).

#### General procedure for the allylic oxidation of glycols with the Koser reagent [PhI(OH)OTs]

A suspension of the glycol (1 equiv.) and powdered molecular sieves (3 Å; 0.25 g mmol<sup>-1</sup> glycol) in absolute acetonitrile (20 ml mmol<sup>-1</sup>) under N<sub>2</sub> was stirred for 5 min at 0 °C. [Hydroxy-(tosyloxy)iodo]benzene (1.2 equiv.) was added in one portion and the temperature was raised to ambient. After 75 min the suspension was filtered through a pad of Celite and the residue was washed with methylene dichloride (2 ×). The combined filtrate and washings were dried (MgSO<sub>4</sub>) and were concentrated under reduced pressure to give a yellow oil. This crude product was rapidly purified by gel filtration. Following this procedure, glycols **23–26** were oxidized. Physical constants and spectroscopic data for the intermediate 2,3-dihydro-4*H*-pyran-4-ones have been presented before.<sup>12</sup>

**(-)-(3*S*)-3-Benzoyloxy-2,3-dihydro-4*H*-pyran-4-one **37**.** 3,4-Di-*O*-benzyl-*L*-arabinal **36** (3.65 g, 12.33 mmol) was used to prepare the *title compound* **37** (1.65 g, 66%) *via* the general procedure described above. Compound **37** was sufficiently pure for the next step. For collecting physical and spectroscopic data a small amount was purified by column chromatography (petroleum spirit–ethyl acetate 10:1) to give an oil;  $[\alpha]_{\text{D}}^{23} -94.8$  (*c* 1.2, CHCl<sub>3</sub>);  $\delta_{\text{H}}$ (400 MHz; C<sub>6</sub>D<sub>6</sub>; TMS = 0.0 ppm) 7.39–7.28 (5H, m, ArH), 7.31 (1H, d, *J* 6.0, 2-H) 5.40 (1H, dd, *J* 0.8 and 6.0, 3-H), 4.83 and 4.61 (2H, 2 d, *J* 12.0, CH<sub>2</sub>Ph), 4.45 (1H, dd, *J* 6.4 and 12.4, 6-H<sub>B</sub>), 4.36 (1H, dd, *J* 4.0 and 12.4, 6-H<sub>A</sub>) and 3.81 (1H, ddd, *J* 0.8, 4.0 and 6.4, 5-H);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 190.8 (s, 4-C), 163.5 (d, 6-C), 128.9–128.5 (d, Ph), 105.2 (d, 5-C), 73.5 (d, 3-C), 72.5 and 71.2 (t, CH<sub>2</sub>Ph, 2-C) (Found: C, 71.0; H, 6.2. C<sub>12</sub>H<sub>12</sub>O<sub>3</sub> requires C, 70.57; H, 5.92%).

#### Regioselective 3-*O*-deprotection of fully per-*O*-benzylated glycols

After CeCl<sub>3</sub>·7H<sub>2</sub>O (3.54 equiv.) was dissolved in ethanol (10 ml

mmol<sup>-1</sup>) at rt, methylene dichloride (10 ml mmol<sup>-1</sup>) was added and the solution was cooled to -50 °C. Crude or partially purified (gel filtration on silica gel) 2,3-dihydro-4*H*-pyran-4-ones (1 equiv.) obtained from the iodine(III)-promoted oxidations described above were added, followed by NaBH<sub>4</sub> or NaBD<sub>4</sub> (2.4 equiv.). The temperature was slowly raised to ambient and the reaction mixture was hydrolysed with methylene dichloride and water (1:1). The aqueous layer was washed with methylene dichloride (2 ×). The combined organic extracts were dried (MgSO<sub>4</sub>), then evaporated *in vacuo*, and the crude product was purified by column chromatography.

1. PhI(OH)OTs-promoted oxidation of compound **23** (1.45 g, 3.47 mmol) followed by reduction afforded 1,5-anhydro-4,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol **27a** and 1,5-anhydro-4,6-di-*O*-benzyl-2-deoxy-D-*ribo*-hex-1-enitol **27b** (0.43 g, 1.32 mmol; 38%; 1:1.5) after separation by column chromatography on silica gel (petroleum spirit–ethyl acetate 10:1).

1st fraction: compound **27a**: mp 47 °C (crystals); [α]<sub>D</sub><sup>19</sup> +44.8 (*c* 1.0, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.30 (10H, m, Ph), 6.43 (1H, dd, *J* 1.6 and 6.0, 1-H), 4.73 (1H, dd, *J* 2.4 and 6.0, 2-H), 4.79, 4.69, 4.64 and 4.58 (4H, 4 d, *J* 11.6, CH<sub>2</sub>Ph), 4.34 (1H, dt, *J* 2.4 and 6.5, 3-H), 3.99 (1H, ddd, *J* 3.0, 3.6 and 9.1, 5-H), 3.83 (1H, dd, *J* 3.6 and 10.2, 6-H<sub>A</sub>), 3.80 (1H, dd, *J* 3.0 and 10.2, 6-H<sub>B</sub>), 3.68 (1H, dd, *J* 6.5 and 9.1, 4-H) and 1.87 (1H, d, *J* 6.2, OH); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 144.6 (d, 2-C), 138.3 and 137.8 (s, Ph), 128.6–127.8 (d, Ph), 102.7 (d, 1-C), 77.3 and 76.3 (d, 3- and 4-C), 73.8 and 73.7 (t, 2 × CH<sub>2</sub>Ph), 69.1 (d, 5-C) and 68.9 (t, 6-C) (Found: C, 73.6; H, 6.55. C<sub>20</sub>H<sub>22</sub>O<sub>4</sub> requires C, 73.60; H, 6.79%).

2nd fraction: compound **27b**: oil; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.30 (10H, m, Ph), 6.47 (1H, d, *J* 6.0, 1-H), 4.92 (1H, dd, *J* 5.4 and 6.0, 2-H), 4.65, 4.64, 4.60 and 4.58 (4H, 4 d, *J* 11.8, CH<sub>2</sub>Ph), 4.18 (1H, dd, *J* 4.0 and 5.4, 3-H), 4.08 (1H, dt, *J* 3.0 and 10.2, 5-H), 3.81 (3H, m, 4-H and 6-H<sub>2</sub>) and 3.50 (1H, s, OH); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 146.6 (d, 1-C), 137.9 and 137.5 (s, Ph), 128.6–127.6 (d, Ph), 100.1 (d, 2-C), 74.1 and 70.7 (d, 3- and 4-C), 73.6 and 72.2 (t, 2 × CH<sub>2</sub>Ph), 68.6 (t, 6-C) and 59.9 (d, 5-C) (Found: C, 73.1; H, 6.9%).

2. PhI(OH)OTs-promoted oxidation of compound **24** (2.62 g, 6.3 mmol) followed by reduction afforded 1,5-anhydro-4,6-di-*O*-benzyl-2-deoxy-D-*lyxo*-hex-1-enitol **28a** (1.17 g, 57%) after purification by column chromatography on silica gel (petroleum spirit–ethyl acetate 10:1), mp 66 °C (crystals); [α]<sub>D</sub><sup>21</sup> -15 (*c* 1.0, CHCl<sub>3</sub>) {lit.<sup>39</sup> mp 65 °C; [α]<sub>D</sub> +12.06 (*c* 0.6, CHCl<sub>3</sub>)}; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.30 (10H, m, Ph), 6.35 (1H, dd, *J* 1.6 and 6.0, 1-H), 4.74 (1H, ddd, *J* 1.4, 3.0 and 6.0, 2-H), 4.72, 4.66, 4.75 and 4.47 (4H, 4 d, *J* 12.0, CH<sub>2</sub>Ph), 4.32 (1H, dddd, *J* 1.6, 3.0, 4.6 and 9.2, 3-H), 4.18 (1H, ddd, *J* 2.6, 5.6 and 6.6, 5-H), 3.90 (1H, ddd, *J* 1.0, 2.6 and 4.6, 4-H), 3.78 (1H, dd, *J* 6.6 and 9.8, 6-H<sub>A</sub>), 3.63 (1H, dd, *J* 5.6 and 9.8, 1H, 6-H<sub>B</sub>) and 2.35 (1H, d, *J* 9.2, OH); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 144.3 (d, 1-C), 137.7 (s, Ph), 128.6–127.8 (d, Ph), 102.9 (d, 2-C), 75.1, 73.1 (d, 3- and 4-C), 74.3 and 73.5 (t, 2 × CH<sub>2</sub>Ph), 68.1 (t, 6-C) and 62.8 (d, 5-C) (Found: C, 73.4; H, 6.7. C<sub>20</sub>H<sub>22</sub>O<sub>4</sub> requires C, 73.60; H, 6.79%).

3. PhI(OH)OTs-promoted oxidation of compound **25** (1.0 g, 3.2 mmol) followed by reduction afforded 1,5-anhydro-4-*O*-benzyl-2,6-dideoxy-L-*arabino*-hex-1-enitol **29a** and 1,5-anhydro-4-*O*-benzyl-2,6-dideoxy-L-*ribo*-hex-1-enitol **29b** (0.34 g, 47%) in a 1.1:1 ratio after separation by column chromatography on silica gel (petroleum spirit–ethyl acetate 10:1).

1st fraction: compound **29a**: mp 108 °C (crystals); [α]<sub>D</sub><sup>22</sup> -33.7 (*c* 1.29, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.36 (5H, m, Ph), 6.32 (1H, dd, *J* 1.6 and 6.0, 1-H), 4.85 and 4.79 (2H, 2 d, *J* 12.0, CH<sub>2</sub>Ph), 4.70 (1H, dd, *J* 2.4 and 6.0, 2-H), 4.36 (1H, m, 3-H), 3.91 (1H, dq, *J* 6.4 and 9.6, 5-H), 3.28 (1H, dd, *J* 7.0 and 9.6, 4-H), 1.68 (1H, d, *J* 5.6, OH) and 1.41 (3H, d, *J* 6.4, 6-H<sub>3</sub>); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 144.6 (d, 1-C), 138.3 (s, Ph), 128.6–128.0 (d, Ph), 103.1 (d, C-2), 82.4 and 74.1 (d, 3- and 4-C), 74.3

(t, CH<sub>2</sub>Ph), 70.0 (d, 5-C) and 17.6 (q, 6-C) (Found: C, 70.95; H, 7.4. C<sub>13</sub>H<sub>16</sub>O<sub>3</sub> requires C, 70.89; H, 7.32%).

2nd fraction: compound **29b**<sup>9</sup>: mp 92 °C (crystals); [α]<sub>D</sub><sup>22</sup> -206 (*c* 0.89, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.36 (5H, m, Ph), 6.40 (1H, d, *J* 6.0, 1-H), 4.92 (1H, dd, *J* 5.2 and 6.0, 2-H), 4.70 and 4.62 (2H, 2 d, *J* 12.0, CH<sub>2</sub>Ph), 4.20 (1H, m, 3-H), 4.05 (1H, dq, *J* 6.4 and 9.6, 5-H), 3.36 (1H, dd, *J* 3.6 and 9.6, 4-H), 2.46 (1H, br, OH) and 1.36 (3H, d, *J* 6.4, 6-H<sub>3</sub>); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 146.5 (d, 1-C), 137.4 (s, Ph), 128.6, 128.2 and 128.0 (d, Ph), 100.3 (d, 2-C), 79.1 (d, 3-C), 72.1 (t, CH<sub>2</sub>Ph), 69.1 (d, 4-C), 59.7 (d, 3-C) and 17.3 (q, 6-C) (Found: C, 70.80; H, 7.81%).

4. PhI(OH)OTs-promoted oxidation of compound **26** (2.0 g, 6.45 mmol) followed by reduction afforded 1,5-anhydro-4-*O*-benzyl-2,6-dideoxy-L-*lyxo*-hex-1-enitol **30a** (0.84 g, 59%) after purification by column chromatography on silica gel (petroleum spirit–ethyl acetate 10:1). Compound **30a**<sup>7</sup>: mp 73 °C (crystals from hexane); [α]<sub>D</sub><sup>20</sup> +36.2 (*c* 1.02, acetone); δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 7.4–7.2 (5H, m, Ph), 6.21 (1H, dd, *J* 1.2 and 6.4, 1-H), 4.64 (1H, dd, *J* 4.0 and 6.4, 2-H), 4.42 and 4.37 (2H, 2 d, *J* 11.6, CH<sub>2</sub>Ph), 4.17 (2H, m, 3- and 4-H), 3.65 (1H, q, *J* 6.8, 5-H), 3.10 (1H, s, OH) and 1.17 (3H, d, *J* 6.8, 6-H<sub>3</sub>); δ<sub>C</sub>(100 MHz; C<sub>6</sub>D<sub>6</sub>) 144.5 (d, 1-C), 137.8 (s, Ph), 128.2–127.5 (d, Ph), 102.7 (d, 2-C), 75.9 and 75.3 (d, 3- and 4-C), 72.8 (d, 5-C), 71.9 (t, CH<sub>2</sub>Ph) and 16.7 (q, 6-C) (Found: C, 70.9; H, 7.2. Calc. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.89; H, 7.32%).

##### 5. Preparation of 1,5-anhydro-4-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-L-*arabino*-hex-1-enitol **31a** and 1,5-anhydro-4-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-L-*ribo*-hex-1-enitol **31b**.

Glycal **7** (0.62 g, 1.74 mmol) was oxidized under the conditions described above and iodobenzene was removed by filtration on silica gel (petroleum spirit). (Due to the volatility of compound **13**, all solvents have to be evaporated with care.) Crude enone **13**<sup>12</sup> was dissolved in diethyl ether (35 ml) under nitrogen, the solution was cooled to -70 °C and was treated with DIBAL-H in *n*-hexane (1M; 1.36 ml, 1.36 mmol). After 1 h, water (0.3 ml) was added and stirring was continued for another 15 min at rt. After filtration through a pad of Celite, the filtrate was concentrated under reduced pressure and finally traces of water were removed by co-distillation with toluene. Purification by column chromatography (petroleum spirit–ethyl acetate 15:1) afforded the title compounds **31a** and **31b** (275 mg, 65%) in a 2:1 ratio.

1st fraction: compound **31b** (contaminated with ~10% of isomer **31a**): oil; δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 6.42 (1H, d, *J* 5.8, 1-H), 5.03 (1H, t, *J* 5.8, 2-H), 4.21 (1H, dq, *J* 6.2 and 9.6, 5-H), 4.02 (1H, dd, *J* 4.0 and 5.8, 3-H), 3.55 (1H, dd, *J* 4.0 and 9.6, 4-H), 2.63 (1H, br, OH), 1.35 (3H, d, *J* 6.2, 6-H<sub>3</sub>), 0.94 (9H, s, 'Bu) and 0.02 and 0.0 [6H, 2 s, Si(CH<sub>3</sub>)<sub>2</sub>]; δ<sub>C</sub>(100 MHz; C<sub>6</sub>D<sub>6</sub>) 146.3 (d, 1-C), 101.6 (d, 2-C), 74.1, 70.4 and 63.1 (d, 3-, 4- and 5-C), 25.8 (q, 'Bu), 18.1 (s, 'Bu), 17.7 (q, 6-C) and -4.6 and -4.9 (q, SiMe<sub>2</sub>).

2nd fraction: compound **31a**: oil; [α]<sub>D</sub><sup>22</sup> -17.9 (*c* 2.15, CHCl<sub>3</sub>) {lit.<sup>8</sup> [α]<sub>D</sub><sup>25</sup> -10.0 (*c* 1.0, CHCl<sub>3</sub>)}; δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 6.15 (1H, dd, *J* 1.2 and 6.0, 1-H), 4.42 (1H, dd, *J* 2.4 and 6.0, 2-H), 3.99 (1H, m, 3-H), 3.69 (1H, dq, *J* 6.4 and 9.6, 5-H), 3.31 (1H, dd, *J* 7.6 and 9.6, 4-H), 1.30 (3H, d, *J* 6.4, 6-H<sub>3</sub>), 0.96 (10H, s, 'Bu and OH) and 0.18 and 0.06 [6H, 2 s, Si(CH<sub>3</sub>)<sub>2</sub>]; δ<sub>C</sub>(100 MHz; C<sub>6</sub>D<sub>6</sub>) 144.7 (d, 1-C), 104.2 (d, 2-C), 77.2, 75.7 and 71.2 (d, 3-, 4-C and 5-C), 26.0 (q, 'Bu), 18.5 ('Bu), 17.2 (q, 6-C) and -3.1 and -3.5 (q, SiMe<sub>2</sub>) (Found: C, 58.7; H, 10.0. Calc. for C<sub>12</sub>H<sub>24</sub>O<sub>3</sub>Si: C, 58.97; H, 9.90%).

For further characterisation, the hydroxy group in compound **31a** (0.23 mmol) was acylated under standard conditions.<sup>40</sup> Column chromatography on silica gel (petroleum spirit–ethyl acetate 50:1) afforded 3-*O*-acetyl-1,5-anhydro-4-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-L-*arabino*-hex-1-enitol **35** (60 mg, 92%) as an oil; [α]<sub>D</sub><sup>22</sup> +68.9 (*c* 2.02, CHCl<sub>3</sub>) {lit.<sup>8</sup> [α]<sub>D</sub><sup>25</sup> +62 (*c* 1.0, CHCl<sub>3</sub>)}; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 6.36 (1H, dd, *J* 0.8 and 6.0, 1-H), 5.19 (1H, ddd, *J* 0.8, 2.2 and 7.0, 3-H), 4.73 (1H, dd, *J* 2.2 and 6.0, 2-H), 3.88 (1H, dq, *J* 6.4 and 9.6, 5-H), 3.69 (1H, dd,

*J* 7.0 and 9.6, 4-H), 2.09 (3H, s, OAc), 1.35 (3H, d, *J* 6.4, 6-H<sub>3</sub>), 0.90 (9H, s, 'Bu) and 0.13 and 0.10 [6H, 2 s, Si(CH<sub>3</sub>)<sub>2</sub>]; δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 170.8 (s, OAc), 145.9 (d, 1-C), 99.7 (d, 2-C), 75.5, 73.8 and 72.4 (3-, 4- and 5-C), 25.8 (q, 'Bu), 21.4 (s, 'Bu), 18.1 and 17.8 (q, 6-C and OAc) and -4.1 and -4.5 (q, SiMe<sub>2</sub>).

**6. Preparation of 1,5-anhydro-4-O-[3,4-bis-O-(*tert*-butyldiphenylsilyl)-6-deoxy-2-phenylseleno-β-L-gluco-pyranosyl]-L-arabino-hex-1-enitol 32a and 1,5-anhydro-4-O-[3,4-bis-O-(*tert*-butyldiphenylsilyl)-6-deoxy-2-phenylseleno-β-L-gluco-pyranosyl]-L-ribo-hex-1-enitol 32b.** To a solution of enone **15** (130 mg, 0.145 mmol) in THF-methanol (1:1; 9 ml) at rt were added CeCl<sub>3</sub>·7 H<sub>2</sub>O (59 mg, 0.16 mmol) and NaBH<sub>4</sub> (8 mg, 0.2 mmol). After 10 min the reaction mixture was hydrolysed with methylene dichloride and water (1:1). The aqueous layer was washed with methylene dichloride (2 ×). The combined organic extracts were dried (MgSO<sub>4</sub>), then evaporated *in vacuo*, and the crude product was purified by column chromatography (petroleum spirit-ethyl acetate 20:1).

1st fraction: compound **32a** (77 mg, 60%); mp 49 °C (crystals); [α]<sub>D</sub><sup>22.5</sup> +24.8 (*c* 1.005, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 7.79–7.57 and 7.40–6.90 (25H, m, ArH), 6.22 (1H, dd, *J* 1.6 and 6.0, 1-H), 5.50 (1H, d, *J* 6.8, 1'-H), 5.10 (1H, d, *J* 4.0, 4'-H), 5.07 (1H, dd, *J* 2.0 and 6.0, 2-H), 4.77 (1H, br, OH), 4.66 (1H, ddd, 1H, *J* 1.6, 2.0 and 7.2, 3-H), 3.89 (1H, dq, *J* 6.4 and 10.0, 5-H), 3.88–3.80 (3H, m, 2'-, 3'- and 5'-H), 3.64 (1H, dd, *J* 7.2 and 10.0, 4-H), 1.48 (3H, d, *J* 6.4, 6-H<sub>3</sub>), 1.20 and 1.07 (18H, 2 s, 2 × 'Bu) and 1.00 (3H, d, *J* 6.8, 6'-H<sub>3</sub>); δ<sub>C</sub>(100 MHz; C<sub>6</sub>D<sub>6</sub>) 143.3 (d, C-1), 136.4, 136.3, 136.2, 136.1, 130.9, 130.4, 130.2, 130.1, 129.1, 128.2, 127.9 and 126.4 (d, Ph), 133.6, 133.4, 133.3, 133.3 and 133.2 (s, Ph), 106.0 (d, 1'-C), 103.6 (d, 2-C), 85.8 (d, 4-C), 79.5 (d, 5-C), 79.0 (d, 4'-C), 73.7 and 73.4 (d, 3'- and 5'-C), 68.6 (d, 3-C), 48.6 (d, 2'-C), 27.0 and 26.9 (q, 2 × 'Bu), 19.8 (q, 6'-C), 19.3 and 19.1 (s, 2 × 'Bu) and 17.8 (q, 6-C).

2nd fraction: compound **32b** (32 mg, 25%) (oil); [α]<sub>D</sub><sup>22</sup> -11.7 (*c* 0.535, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 7.86–7.65 and 7.41–7.13 (25H, m, ArH), 6.40 (1H, d, *J* 6.0, 1-H), 5.62 (1H, d, *J* 6.8, 1'-H), 5.13 (1H, d, *J* 3.6, 4'-H), 5.04 (1H, dd, *J* 4.8 and 6.0, 2-H), 4.49 (1H, br dd, *J* 4.0 and 4.8, 3-H), 4.37 (1H, dq, *J* 6.4 and 10.0, 5-H), 3.98–3.88 (3H, m, 2'-, 3'- and 5'-H), 3.72 (1H, br, OH), 3.64 (1H, dd, *J* 4.0 and 10.0, 4-H), 1.28 and 1.13 (18H, 2 s, 2 × 'Bu), 1.24 (3H, d, *J* 6.4, 6-H<sub>3</sub>) and 1.03 (3H, d, *J* 6.8, 6'-H<sub>3</sub>); δ<sub>C</sub>(100 MHz; C<sub>6</sub>D<sub>6</sub>) 146.1 (d, 1-C), 136.5, 136.4, 136.3, 136.2, 131.5, 130.4, 130.2, 130.1, 129.2, 127.9 and 127.6 (d, Ph), 133.7, 133.5, 132.3, 133.2 and 132.7 (s, Ph), 106.3 (d, 1'-C), 101.3 (d, 2-C), 83.3 (d, 4-C), 79.2 and 73.9 (d, 3'- and 5'-C), 78.9 (d, 4'-C), 69.4 (d, 5-C), 62.3 (d, 3-C), 48.8 (d, 2'-C), 27.4 and 27.1 (q, 2 × 'Bu), 20.2 (q, 6'-C), 19.3 and 19.2 (s, 2 × 'Bu) and 17.4 (q, 6-C) (Found: C, 67.5; H, 7.0. C<sub>50</sub>H<sub>60</sub>O<sub>6</sub>Si<sub>2</sub>Se requires C, 67.31; H, 6.78%).

**7. PhI(OH)OTs-promoted oxidation of compound 36** (414 mg, 1.4 mmol) afforded enone **37** (183 mg, 64%), which gave 1,5-anhydro-4-O-benzyl-2-deoxy-L-erythro-pent-1-enitol **38** (162 mg, 88%) after reduction and purification by column chromatography on silica gel (petroleum spirit-ethyl acetate 6:1). Under identical conditions using NaBD<sub>4</sub> enone **37** was reduced to 1,5-anhydro-4-O-benzyl-2-deoxy-L-erythro-[3-<sup>2</sup>H]-pent-1-enitol **39**.

Compound **38**: mp 52 °C (crystals); [α]<sub>D</sub><sup>20</sup> -114.6 (*c* 1, CHCl<sub>3</sub>); for compound **39**: mp 53 °C; [α]<sub>D</sub><sup>23</sup> -115.9 (*c* 1, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.36 (5H, m, Ph), 6.41 (1H, d, *J* 6.0, 1-H), 4.88 (1H, dd, *J* 5.0 and 6.4, 2-H), 4.70 and 4.66 (2H, 2 d, *J* 12.0, CH<sub>2</sub>Ph), 4.24 (1H, m, 3-H), 3.93 (2H, br d, *J* 6.4, 5-H<sub>2</sub>), 3.73 (1H, ddd, *J* 4.0, 6.0 and 6.8, 4-H) and 2.47 (1H, br d, *J* 3.0, OH) (Found: C, 70.0; H, 6.6. C<sub>12</sub>H<sub>14</sub>O<sub>3</sub> requires C, 69.88; H, 6.84%).

#### 1,5-Anhydro-3-O-acetyl-2,6-dideoxy-L-arabino-hex-1-enitol<sup>3d</sup> **34**

A suspension of L-rhamnal **33** (139 mg, 1.07 mmol) and lipase PS (0.2 g) in vinyl acetate-ethyl acetate (10 ml; 1:1) at rt was

shaken for two days (280 rpm) and filtered through a pad of Celite. Concentration under reduced pressure afforded the title compound (123 mg, 67%) which was directly used for the next step. A small sample was purified by flash column chromatography (petroleum spirit-ethyl acetate 5:1); δ<sub>H</sub>(200 MHz; C<sub>6</sub>D<sub>6</sub>) 6.42 (1H, dd, *J* 1.4 and 6.0, 1-H), 5.22 (1H, ddd, *J* 1.4, 2.6 and 6.6, 3-H), 4.68 (1H, dd, *J* 2.6 and 6.0, 2-H), 3.91 (1H, dq, *J* 6.4 and 9.6, 5-H), 3.61 (1H, ddd, *J* 2.6, 6.6 and 9.6, 4-H), 3.28 (1H, br d, *J* 2.6, OH), 2.11 (3H, s, OAc) and 1.40 (3H, d, *J* 6.4, 6-H<sub>3</sub>); δ<sub>C</sub>(50 MHz; C<sub>6</sub>D<sub>6</sub>) 171.9 (s, OAc), 146.3 (d, 1-C), 99.0 (d, 2-C), 74.9, 74.0 and 72.6 (d, 3-, 4- and 5-C) and 20.3 and 16.9 (q, 6-C and OAc).

The crude product was silylated under standard conditions<sup>40</sup> to afford 3-O-acetyl-1,5-anhydro-4-O-(*tert*-butyldimethylsilyl)-2,6-dideoxy-L-arabino-hex-1-enitol **35** (183 mg, 89%). Physical and spectroscopic data are given above.

#### General procedure for Mitsunobu reactions of 3-O-unblocked glycols

To a solution of the glycol (1 equiv.) under N<sub>2</sub> in dry toluene (20 ml mmol<sup>-1</sup>) at 0 °C were added triphenylphosphine (2.67 equiv.) and benzoic acid (2.67 equiv.). Diethyl azodicarboxylate (DEAD; 2.71 equiv.) was dissolved in dry toluene (1.8 ml) and the solution was added dropwise to the reaction mixture. The resulting solution was allowed to warm to rt. After 20 h, a mixture of methylene dichloride and aq. NaHCO<sub>3</sub> (10 ml mmol<sup>-1</sup>; 1:1) was added and the phases were separated. The aqueous layer was washed with methylene dichloride (2 ×) and the combined organic extracts were dried (MgSO<sub>4</sub>), and concentrated under reduced pressure.

**1,5-Anhydro-3-O-benzoyl-4,6-di-O-benzyl-2-deoxy-D-xylo-hex-1-enitol 40 and 1-O-benzoyl-4,6-di-O-benzyl-2,3-dideoxy-α-D-threo-hex-2-enopyranose 41.** Compound **28a** (300 mg, 0.92 mmol) was used to prepare the title compounds **40** and **41** via the general procedure described above. The crude product was subjected to column chromatography on silica gel (petroleum spirit-ethyl acetate 10:1) to afford **40** (108 mg, 27.2%) and α-pyranose **41** (122 mg, 30.8%). The β-anomer **41** was detectable only in the <sup>1</sup>H NMR spectrum of the crude product.

1st fraction: compound **40**, oil; δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 8.1–6.9 (15H, m, Ph), 6.50 (1H, d, *J* 6.0, 1-H), 5.60 (1H, dd, *J* 1.8 and 5.2, 3-H), 4.93 (1H, ddd, *J* 1.6, 5.2 and 6.0, 2-H), 4.66, 4.43, 4.27 and 4.22 (4H, 4 d, *J* 11.6, CH<sub>2</sub>Ph), 4.34 (1H, br t, *J* 6.2, 5-H), 3.87 (1H, dd, *J* 1.8 and 1.2, 4-H), 3.82 and 3.68 (2H, 2 dd, *J* 6.2 and 9.6 and *J* 6.2 and 9.6, 6-H<sub>A</sub> and -H<sub>B</sub>); δ<sub>C</sub>(100 MHz; C<sub>6</sub>D<sub>6</sub>) 165.7 (s, OBz) 148.6 (d, C-1), 138.6, 133.1 (s, Ph), 130.8–127.8 (d, Ph), 97.1 (d, 2-C), 73.7 and 73.1 (d, 3- and 4-C), 73.5 and 72.2 (t, 2 × CH<sub>2</sub>Ph), 69.2 (t, 6-C) and 63.8 (d, 5-C) (Found: C, 75.6; H, 6.1. C<sub>27</sub>H<sub>26</sub>O<sub>5</sub> requires C, 75.33; H, 6.09%).

2nd fraction: α-pyranose **41**; mp 53 °C (crystals); [α]<sub>D</sub><sup>20</sup> -177.6 (*c* 1, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 8.1–6.9 (15H, m, Ph), 6.79 (1H, d, *J* 3.0, 1-H), 5.89 (1H, dd, *J* 10.0 and 6.2, 3-H), 5.75 (1H, dd, *J* 10.0 and 3.0, 2-H), 4.48 (1H, m, H-5), 4.46, 4.36, 4.34 and 4.27 (4H, 4 d, *J* 11.6, CH<sub>2</sub>Ph), 3.95 (1H, dd, *J* 9.6 and 7.2, 6-H), 3.74 (1H, dd, *J* 9.6 and 6.4, 6'-H<sub>3</sub>) and 3.65 (1H, dd, *J* 6.2 and 2.4, 4-H); δ<sub>C</sub>(100 MHz; C<sub>6</sub>D<sub>6</sub>) 165.3 (s, OBz), 139.2, 138.9 and 133.1 (s, Ph), 130.8 and 130.1–127.6 (d, 2- and 3-C, Ph), 89.5 (d, 1-C), 73.5 and 71.0 (t, 2 × CH<sub>2</sub>Ph), 72.4 and 69.2 (d, 4- and 5-C), 67.0 (t, 6-C) (Found: C, 75.59; H, 6.13. C<sub>27</sub>H<sub>26</sub>O<sub>5</sub> requires C, 75.10; H, 6.19%).

**1,5-Anhydro-3-O-benzoyl-4-O-benzyl-2,6-dideoxy-L-xylo-hex-1-enitol 43.** Compound **30a** (121 mg, 0.55 mmol) was used to prepare the title compound **43** (112 mg, 63%) via the general procedure described above. Column chromatography on silica gel (petroleum spirit-ethyl acetate 10:1) afforded an oil; δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.5–7.2 (10H, m, Ph), 6.69 (1H, d, *J* 6.0, 1-H), 5.46 (1H, dd, *J* 2.0 and 5.2, 3-H), 5.00 (1H, ddd, *J* 2.0, 5.2 and



6.0, 2-H), 4.88 and 4.67 (2H, 2 d, *J* 12.0, CH<sub>2</sub>Ph), 4.06 (1H, dq, *J* 0.8 and 6.6, 5-H), 3.50 (1H, br s, 4-H), 1.30 (3H, d, *J* 6.6, 6-H<sub>3</sub>); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 165.8 (s, OBz), 148.8 (d, 1-C), 137.6 (s, Ph), 133.2–127.9 (d, Ph), 96.5 (d, 2-C), 72.0 (t, CH<sub>2</sub>Ph), 74.6 and 70.3 (d, 3- and 4-C), 64.1 (d, 5-C) and 16.3 (q, 6-C) (Found: C, 73.9; H, 6.1. C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires C, 74.06; H, 6.21%).

For further elucidation of the configuration at C-3 in product **43**, the hydroxy group in compound **30a** (0.55 mmol) was benzoylated under standard conditions<sup>40</sup> to give, after column chromatography (petroleum spirit–ethyl acetate 8:1), 1,5-anhydro-3-*O*-benzoyl-4-*O*-benzyl-2,6-dideoxy-*L*-xylo-hex-1-enitol **42** (53 mg, 30%) as an oil; [α]<sub>D</sub><sup>20</sup> +109 (*c* 1.22, CHCl<sub>3</sub>); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 7.6–7.2 (10H, m, Ph), 6.47 (1H, dd, *J* 6.2 and 1.2, 1-H), 5.78 (1H, dddd, *J* 4.6, 3.2, 1.6 and 1.0, 3-H), 4.85 (1H, ddd, *J* 6.2, 3.2, 0.8, 2-H), 4.81 and 4.58 (2H, 2 d, *J* 12.4, CH<sub>2</sub>Ph), 4.25 (1H, ddd, *J* 6.6, 2.8 and 1.0, 5-H), 3.96 (1H, ddd, *J* 4.6, 2.8 and 0.8, 4-H) and 1.37 (3H, d, *J* 6.6, 6-H); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 166.5 (s, OBz), 146.0 (d, 1-C), 137.9 (Ph), 133.4–128.0 (d, Ph), 98.0 (d, 2-C), 73.5 (t, CH<sub>2</sub>Ph), 72.8 and 72.3 (d, 3- and 4-C), 66.4 (d, 5-C) and 15.6 (q, 6-C) (Found: C, 73.8; H, 6.3. C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires C, 74.06; H, 6.21%).

### 1,5-Anhydro-3-azido-4-*O*-benzyl-2,3,6-trideoxy-*L*-xylo-hex-1-enitol **44**

To a solution of alcohol **30a** (100 mg, 0.45 mmol) and LiN<sub>3</sub> (151 mg, 2.97 mmol) in dry DMF (3 ml) at 45 °C was added CBr<sub>4</sub> (280 mg, 0.86 mmol) in one portion. After a while, a yellow solution resulted and PPh<sub>3</sub> (225 mg, 0.86 mmol) was added in small portions with external cooling. After the addition was complete, the orange solution was stirred for 12 h at rt, and hydrolysed in an ice-cold mixture of NH<sub>4</sub>Cl<sub>aq</sub>–CH<sub>2</sub>Cl<sub>2</sub>. Extraction of the aqueous phase with CH<sub>2</sub>Cl<sub>2</sub> (3 ×) followed by washing of the combined organic extracts with brine, drying (MgSO<sub>4</sub>), and concentration *in vacuo* gave a brown oil (930 mg). Purification by flash chromatography on silica gel (petroleum spirit–ethyl acetate 20:1) afforded the *title compound* **44** (17 mg, 15%) as an oil, ν<sub>max</sub>/cm<sup>-1</sup> 2080; δ<sub>H</sub>(400 MHz; C<sub>6</sub>D<sub>6</sub>) 7.20–7.0 (5H, m, Ph), 6.36 (1H, d, *J* 6.4, 1-H), 4.44 (1H, ddd, *J* 6.4, 5.2 and 1.4, 2-H), 4.23 and 4.04 (2H, 2 d, *J* 12.0, CH<sub>2</sub>Ph), 3.78 (1H, dq, *J* 6.4 and 2.0, 5-H), 3.54 (1H, dd, *J* 5.2 and 2.0, 3-H), 3.09 (1H, ddd, *J* 2.0, 2.0 and 1.4, 4-H), 1.11 (3H, d, *J* 6.4, 6-H<sub>3</sub>); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 148.2 (d, 1-C), 133.2 (s, Ph), 128.0–127.8 (d, Ph), 94.3 (d, 2-C), 76.5 and 70.2 (d, 4- and 5-C), 72.3 (t, CH<sub>2</sub>Ph), 53.4 (d, 3-C) and 15.9 (q, 6-C) (Found: C, 63.8; H, 6.0. C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> requires C, 63.66; H, 6.16; N, 17.13%).

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