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Synthesis of erythro and threo furanoid glycals from 1- and 2-phenylselenenyl–carbohydrate derivatives☆

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Abstract

Differently protected erythro and threo furanoid glycals were synthesized by selenoxide elimination when phenyl 1-selenoglycosides were treated in oxidizing conditions (^{t}BuOOH, Ti(O^iPr)$_4$, Et^i_2PrN). The phenyl 1-selenoglycosides were obtained from methyl 2-deoxy-D-*erythro*-pentofuranoside by protection of the primary hydroxyl or both hydroxyls and further reaction with PhSeH in the presence of $BF_3{\cdot}Et_2O$. Erythro and threo furanoid glycals were also prepared by treating 2-deoxy-2-phenylselenenyl-1,4-anhydrocyclitols under similar conditions. The 2-deoxy-2-phenylselenenyl-1,4-anhydrocyclitols were obtained from 4-pentene-1,2,3-triols by a 5-endo selenium electrophilic induced cyclization. © 2001 Published by Elsevier Science Ltd.

Keywords: Glycal synthesis; Selenoglycosides; 1,4-Anhydro-2-phenylselenenyl-pentitols; Selenoxide elimination; Double bond formation

1. Introduction

The use of glycals (1,4- or 1,5-anhydro-2-deoxy-1-enitol) as glycosyl donors has been extensively discussed in the literature.[2] Indeed, a number of recent articles describe them as important precursors of oligosaccharides,[3] *C*-glycosyl compounds,[4] *C*-nucleosides,[5] nucleosides[6] and others.[†,‡,§] Glycals were first synthesized by Fischer and Zach, by reduction of halo sugars using zinc as the reducing agent.[10] Over the years a wide range of methodologies for glycal synthesis have been reported involving: (i) the use of good leaving groups at C-2 of glycosyl halides;[11] (ii) reaction of protected glycosyl halides with a reducing agent such as sodium, potassium and sodium–naphthalide,[12] zinc/silver-graphite,[13] potassium-graphite,[14] aluminium amalgam,[15] samarium(II) iodide,[16] lithium in liquid ammonia (Ireland's method),[17] titanocene dichloride in THF,[18] with vitamin B-12 and Zn as a source of Co(I),[19] with chromium(II) complexes in DMF,[20] with zinc dust in the presence of a N-base in various aprotic solvents;[21] (iii) reduction of sugar derivatives with a sulfur substituent at position 1, i.e., reaction of 1-thioglycosides and glycosyl phenyl sulfones with lithium-naphthalides in THF;[22] reaction of 1-thioglycosides with potassium-

☆ For preliminary communications see Ref. 1.

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† For use in cyclopropanation and ring expansion see Ref. 7.

‡ For use in a novel class of glycosidation based in a [4 + 2] cycloaddition see Ref. 8.

§ For the synthesis of thionucleosides from thioglycals see Ref. 9.

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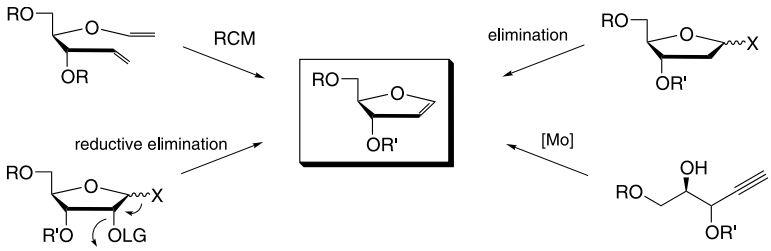
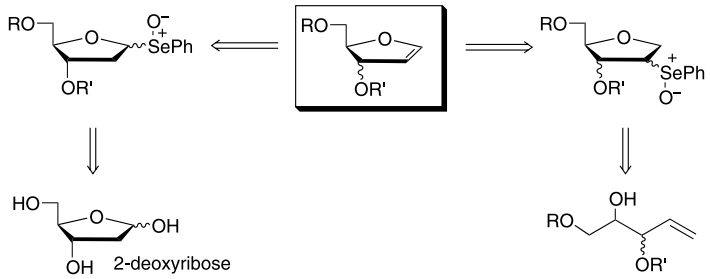


Scheme 1. Strategies for the synthesis of furanoid.



Scheme 2. Synthesis of furanoid glycals by elimination of selenoxides. Scheme of retrosynthesis.

graphite in THF;[23] reaction of glycosyl phenyl sulfones with samarium(II) iodide in THF;[24] reactions of glycosyl sulfoxides with butyllithium in THF;[25] (iv) electrolysis of acetobromo sugars in DMF or acetonitrile;[26] (v) radical-induced elimination from 1-thioglycoside-2-xanthates[22b,22c] and from 2-azido-2-deoxy-selenoglycosides;[27] (vi) elimination from 2-deoxy-pentofuranose derivatives, such as nucleosides,[28] 1-*O*-mesylates[29] and 1,2-diols;[30] (vii) tungsten and molybdenum-promoted alkynol endo-cycloisomerization;[3c,31] (viii) ring-closure metathesis[32] (Scheme 1 represents some of these methods applied to furanoid glycals). Despite the number of methods available, improvements are still desirable, since many of these approaches fail in the furanoid glycal series or meet with problems of protective group compatibility.

Here we report an efficient procedure for synthesizing furanoid glycals from 1-[1a] and 2-phenylselenenyl-1,4-anhydroalditols[1b] through oxidation and thermal elimination of the selenoxide generated at low temperature (Scheme 2). These seleno-derivatives, in turn, can be prepared from 2-deoxyribose and from pentenetriols,[33] respectively. Both procedures are compatible with the presence of a wide number of protecting groups.

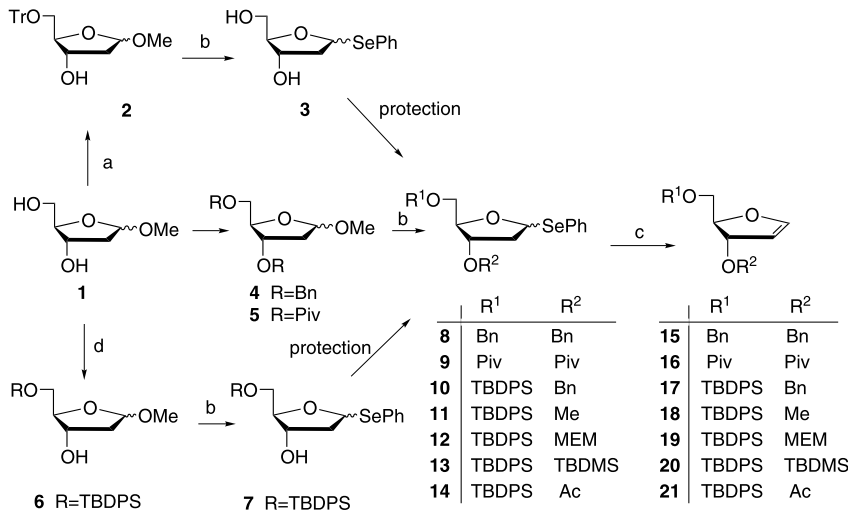
2. Results and discussion

Synthesis of furanoid glycals from 1-phenylselenenylfuranoside derivatives.—As described above, one of the problems associated with many glycal syntheses is the compatibility of the protective groups with the basic conditions. In this context, oxidation of 1-selenofuranosides and subsequent elimination could overcome this problem.[34,35] Moreover, both selenoxide anomers might be useful starting materials and, therefore, separation would be not necessary. These 1-seleno-derivatives, in turn, would be accessible from the corresponding methyl glycosides by glycosylation with PhSeH and $BF_3{\cdot}Et_2O$.[36]

2-Deoxy-D-*erythro*-pentose (2-deoxy-D-ribose) was the starting material of choice because not only did it provide the stereochemical pattern required for erythro glycals, but also it did not require deoxygenation at position 2.

Methyl 2-deoxy-D-*erythro*-pentofuranoside (**1**)[37] (readily available from 2-deoxy-D-*erythro*-pentose) reacted with PhSeH and a substoichiometric amount of $BF_3{\cdot}Et_2O$, to provide a mixture of phenyl 1-selenoglycosides **3** and the corresponding pyranosyl derivative.

In order to test the stability of common protecting groups in the step of formation of



	R1	R2
8	Bn	Bn
9	Piv	Piv
10	TBDPS	Bn
11	TBDPS	Me
12	TBDPS	MEM
13	TBDPS	TBDMS
14	TBDPS	Ac

	R1	R2
15	Bn	Bn
16	Piv	Piv
17	TBDPS	Bn
18	TBDPS	Me
19	TBDPS	MEM
20	TBDPS	TBDMS
21	TBDPS	Ac

Scheme 3. (a) TrCl, py. (b) 0.8 equiv $BF_3{\cdot}Et_2O$, 1.1 equiv PhSeH, -20 °C. (c) TBHP–Et^{i}Pr$_2$N–Ti(O^{i}Pr)$_4$. (d) TBDPSCl, imidazole, DMF.

the 1-selenofuranoside, we prepared compounds **2**, **4**, **5** and **6**. When trityl ether **2** was treated with PhSeH and $BF_3{\cdot}Et_2O$, selenoglycosylation took place with concomitant deprotection of the trityl group, even when a substoichiometric amount of the Lewis acid was used, to give compound **3** (Scheme 3) slightly contaminated by the 1-seleno-pyranosyl derivative.

Compound **1** was then protected at position 5 by reaction with TBDPSCl, imidazole in DMF to give the *tert*-butyldiphenylsilyl ether **6** in a 76% yield (Scheme 3).[38] Reaction of **6** with PhSeH $BF_3{\cdot}Et_2O$ (0.8 equiv) afforded **7** in an excellent yield (92%). Other Lewis acids such as $SnCl_4$ and Ti(O^{i}Pr)$_4$ resulted in a lower yield of the desired product or did not afford glycosylation.

Compound **7** was transformed into a set of differently protected selenoglycosides **10**–**14** (Scheme 3) by treatment with BnBr, MeI, MEMCl, TBDMSCl, and Ac_2O, respectively. Similarly, selenoglycosides **8** and **9**, with the same protecting groups at positions 3 and 5, were available from **4** and **5**, by reaction with PhSeH–$BF_3{\cdot}Et_2O$. Compounds **8** and **9** can be also obtained from **3**, by treating with acetic anhydride and pivaloyl chloride, respectively.

Oxidation was first attempted with 1-seleno-derivative **8** using MCPBA as an oxidant at -20 °C, but only a furan derivative was isolated. MCPBA promoted oxidation and elimination but the acidic conditions probably favored the subsequent aromatization of the glycal initially formed.

In an attempt to prevent furan formation, we studied other neutral or weakly acid oxidant systems. Oxidation of **7** with H_2O_2 in THF[34] afforded glycal **15** in a 30% yield in the best case.

We next investigated other peroxides such as *tert*-butyl hydroperoxide (TBHP) which have been successfully used for selenide oxidations,[34e] particularly, in the presence of Ti(O^{i}Pr)$_4$.[39] Table 1 shows a brief survey of the different conditions essayed in the reaction of **8** with the system TBHP–Ti(O^{i}Pr)$_4$.

From these experiments, we concluded the following: (i) the base is required to neutralize the phenylselenenic acid (PhSeOH) formed in the reaction, which may promote either electrophilic addition to the glycal also formed in the reaction or aromatization of the glycal to furan (Entries 1 and 2); (ii) titanium isopropoxide increases the rate of syn-elimination (Entries 5 and 6). In the absence of the Lewis acid, traces of glycal are obtained (Entry 4); (iii) when substoichiometric amounts of Ti(O^{i}Pr$_4$) were used, the reaction afforded the glycal in a low yield (Entry 5).

When **8** was treated with 1.1 equiv of TBHP, 1 equiv of Et^{i}Pr$_2$N and 1 equiv of Ti(O^{i}Pr)$_4$ at 0 °C, however, the glycal yield was good (Entry 6). The TBHP–Et^{i}Pr$_2$N–

Table 1
Trials of oxidation of 1-selenoglycoside **8** with 1.1 equiv of TBHP

Entry	Time (min)	Et^iPr_2N (equiv)	Temp (°C)	$Ti(O^iPr)_4$ (equiv)	**15** (%)
1	60	0	0	0	
2	120	0	20	0	
3	30	1	0	0	
4	60	1	20	0	5
5	20	1	0	0.5	54
6	30	1	0	1	84

$Ti(O^iPr)_4$ system was also applied to the oxidation of seleno-derivatives **9**–**14** (Scheme 3, Table 2).

Although, oxidation–elimination proved efficient with only 1.1 equiv of TBHP, the use of twofold excess of oxidant is desirable for the following reasons: (i) to accelerate the reaction of the least reactive seleno-anomer, as observed in several reactions; and (ii) to promote the oxidation of PhSeOH to $PhSeO_2H$, which does not undergo addition to alkenes under the reactions conditions.

In these conditions, compounds **8**, **10**, **11**, **12** and **13** were oxidized with TBHP to afford glycals **15**, **17**, **18**, **19** and **20** in yields of 84, 65, 72, 81 and 60%, respectively (Entries 1, 3, 4, 5 and 6, Table 2).

Oxidation of **14** using an excess of oxidant and base produced glycal **21**, but because of aromatization the yield was low. Formation of the furan derivative is favored both in acid or basic medium due to the presence of the labile acetate protective group. Oxidation of **14** was then carried out using 1.1 equiv of TBHP, 0.8 equiv of base and 1 equiv of $Ti(O^iPr)_4$ at lower temperatures (-10 °C) to produce glycal **21** in a 68% yield (Entry 8). Few reports on the synthesis of furanoid glycals with acyl protective groups have been published.

Table 2
Synthesis of erythro-configurated glycals **15**–**21** from the corresponding 1-phenylselenenylfuranosides **8**–**14**

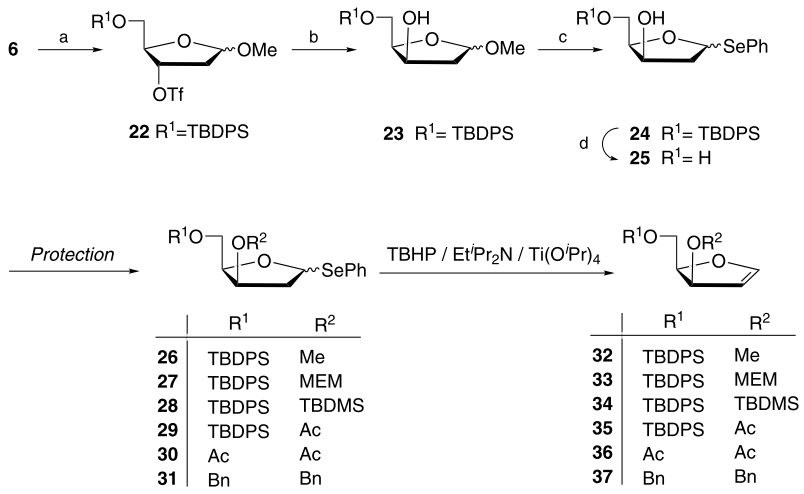
Entry	Seleno-derivative	Conditions [a]	Glycal	Yield (%)
1	**8**	B	**15**	84
2	**9**	A	**16**	71
3	**10**	B	**17**	65
4	**11**	B	**18**	72
5	**12**	B	**19**	81
6	**13**	B	**20**	60
7	**14**	A	**21**	68

[a] (A) 1.1 equiv of TBHP, 0.8 equiv of Et^iPr_2N and 1 equiv of $Ti(O^iPr)_4$ in CH_2Cl_2 at 0 °C. (B) 2.3 equiv of TBHP, 1.7 equiv of Et^iPr_2N and 1 equiv of $Ti(O^iPr)_4$ in CH_2Cl_2 at 0 °C.

Dipivaloyl derivative **9**, was oxidized under the same conditions as those used for **8** to produce the dipivaloyl glycal **16** in a 71% yield (Entry 3). This compound proved to be stable to purification and was fully characterized.

In order to have differently protected glycals with a pivaloyl group at position 5, compound **3** was treated with 1.1 equiv of PivCl in pyridine, but oxidation of this compound led to an untractable mixture. The same result was observed starting from **7**. Attempts at protecting the 3-OH in the 5-*O*-pivaloyl selenofuranoside with BnBr or MeI led to a mixture of starting material and the 3-*O*-pivaloyl derivative.

Glycals with the threo configuration were available by inversion of the configuration at position 3 on the corresponding methyl D-*erythro*-pentofuranosides. Various highly efficient methods for this purpose have been reported. Of these, the Mitsunobu reaction[40] is known to be very sensitive to steric hindrance,[41] as it is the case with the threo derivative. Moriarty et al.[42] described a method for inverting the configuration of hindered alcohols in high yields using sodium nitrite as a nucleophile. In particular, neopentyl alcohol was reactive towards Moriarty's conditions but it was not affected by the Mitsunobu reaction conditions. Thus, compound **6** was then transformed into **22** by treatment with Tf_2O and pyridine in CH_2Cl_2 at -20 °C. Reaction of **22** with KNO_2 and 18-crown-ether in DMF led to the methyl 2-deoxy-D-*threo*-pentofuran-



Scheme 4. Tf_2O, py, CH_2Cl_2, −20 °C, 91%. (b) KNO_2, 18-crown-ether, DMF, 62%. (c) PhSeH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 93%. (d) Bu_4NF, THF, 91%.

oside (**23**) in a 62% yield (Scheme 4). Compound **23** was then treated with PhSeH–$BF_3{\cdot}Et_2O$ using the standard conditions to produce **24**. Compound **24** was the precursor of a set of 3,5-differently protected seleno-derivatives **26**–**29**, which were obtained in a moderate to excellent yield (Scheme 4).

Desilylation with Bu_4NF in THF provided the unprotected seleno-derivative **25** which was subsequently transformed into the diacetate and dibenzyl derivatives **30** and **31** in excellent yields.

Surprisingly, it was not possible to synthesize phenyl 3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-2-deoxy-1-seleno-α,β-D-*threo*-pentofuranoside. When compound **23** was protected at position 3 as a benzyl ether, 1-selenoglycoside formation did not take place. On the other hand, as it was discussed previously, reaction of **23** to the corresponding seleno-derivative **24** proceeded efficiently but, in this case, subsequent benzylation at position 3 was unsuccessful. We assume that there must be a high steric hindrance in the final protected seleno-derivative that prevents the reaction from taking place.

Seleno-derivatives **26**–**31** were then transformed into the corresponding glycals **32**–**37**, respectively, using TBHP–Et^iPr_2N–$Ti(O^iPr)_4$ at 0 °C in the same conditions as those used for the erythro glycals (Scheme 4, Table 3).¶ The yields were in general lower than those of the erythro glycals.

Threo-configurated glycals may also be available from xylose. Dyatkina et al.[43] transformed xylose into the methyl 3,5-di-*O*-benzyl-2-deoxy-α,β-*threo*-pentofuranoside (**38**) through a series of sequences that involved deoxygenation of the hydroxyl function at C-2 with selective protection at the other positions, from which selenoglycoside **31** was obtained in 96% yield (Scheme 5). This new route makes threo glycals accessible from an inexpensive material such as xylose, and confirms the generalization of this method.

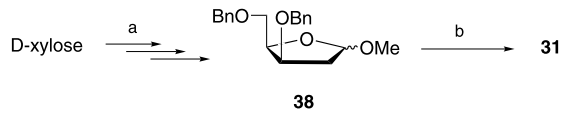
Synthesis of glycals from 2-deoxy-2-phenylseleneny-1,4-anhydroalditols.—The good results obtained in the synthesis of glycals from 1-seleno-derivatives encouraged us to try a

Table 3
Synthesis of threo-configurated glycals **32**–**37** from the corresponding 1-phenylselenenylfuranosides **26**–**31**

Entry	Seleno-derivative	Conditions [a]	Glycal	Yield (%)
1	**26**	B	**32**	68
2	**27**	B	**33**	53
3	**28**	B	**34**	74
4	**29**	A	**35**	68
5	**30**	A	**36**	70
6	**31**	B	**37**	87

[a] (A) 1.1 equiv of TBHP, 0.8 equiv of Et^iPr_2N and 1 equiv of $Ti(O^iPr)_4$ in CH_2Cl_2 at 0 °C. (B) 2.3 equiv of TBHP, 1.7 equiv of Et^iPr_2N and 1 equiv of $Ti(O^iPr)_4$ in CH_2Cl_2 at 0 °C.

¶ Glycal **37** was used as a starting material in a formal synthesis of AZT. Ref. 6b.



Scheme 5. (a) Ref. 43. (b) PhSeH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 96%.

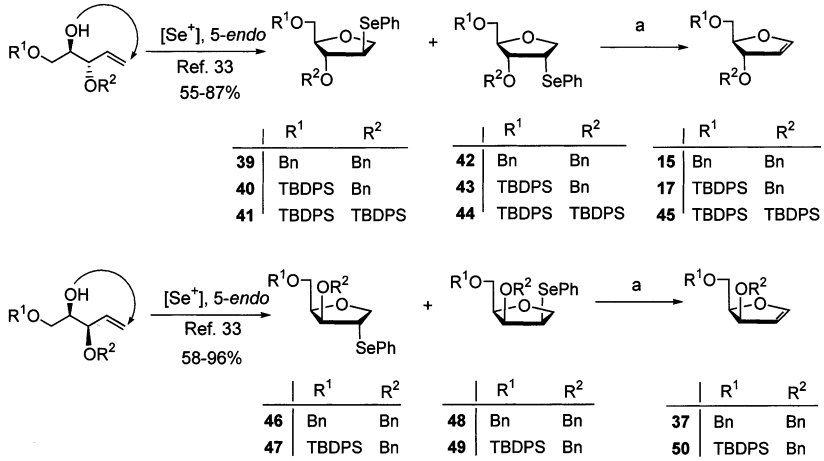
similar approach using 2-seleno-derivatives as precursors. Elimination of selenoxide from these derivatives may proceed on both β-carbon atoms, which, in turn, are bonded to oxygen atoms, to yield the desired glycal or the 2,5-dihydrofuran.

In order to make 2-deoxy-2-phenylselenenyl-1,4-anhydroalditols available we systematically explored the synthesis of tetrahydrofuran derivatives by electrophile-induced cyclization of 4-pentene-1,2,3-triols.[33]

We showed that the course of cyclization (5-exo vs. 5-endo) depends on the electrophilic species used (I^+, Se^+), the nucleophile counteranion and the protective groups. In particular, 5-endo products of interest may be synthesized by selenium-promoted cyclization from 4-pentene-1,2,3-triols appropriately protected at the primary hydroxyl group (Scheme 6). Both diastereomeric selenenyl-tetrahydrofurans were then separated by chromatographic techniques. The corresponding 4-pentene-1,2,3-triols, in turn, were accessible from 2,3-*O*-isopropylidene-glyceraldehyde by addition of vinylmagnesium chloride, benzylation of the free hydroxyl group, acetal hydrolysis and selective protection of the primary hydroxyl function.

We initially tried oxidation on single diastereomers. Our first attempts to prepare glycal **15** from diastereomer **39** by reaction with H_2O_2 and pyridine in dichloromethane for 6 h produced the corresponding selenoxide. No reaction even occurred when the selenoxide was heated in dichloromethane to force thermal elimination. Paquette reported that whenever elimination can only take place at a carbon bonded to an oxygen, the selenoxide was unusually stable and required more drastic conditions for elimination.[44] Reaction in refluxing dichloroethane for 24 h led to a mixture of decomposition products. The results were the same for compounds **42**, **46** and **48**.

Oxidation was then performed with the TBHP–Et^{i}Pr$_2$N–Ti(O^{i}Pr)$_4$ system, which had provided good results starting from 1-seleno-derivatives (Scheme 6, Table 4). Reaction of **39** using the standard conditions produced selenoxide very quickly (15 min), probably due to the homogeneity of the reaction medium, but it proved resistant to elimination. Reflux for 36 h, however, led to glycal **15** in a 62% yield. No traces of the 2,5-dihydrofuran were detected. Compounds **42**, **46** and **48** were also submitted to these reaction conditions (Entries 2, 3 and 4). Formation of the selenoxide was rapid in all cases, but subsequent elimination to yield the corresponding glycals (**15** from **39** or **42**, and **37** from **46** or **48**) required heating for 48 h. Both epimers at C-2 **39** and **42** underwent identical regioselective outcome, as we observed no syn elimination of selenoxide towards the more substituted position to produce the 2,5-dihydrofuran.



	R^1	R^2
39	Bn	Bn
40	TBDPS	Bn
41	TBDPS	TBDPS

	R^1	R^2
42	Bn	Bn
43	TBDPS	Bn
44	TBDPS	TBDPS

	R^1	R^2
15	Bn	Bn
17	TBDPS	Bn
45	TBDPS	TBDPS

	R^1	R^2
46	Bn	Bn
47	TBDPS	Bn

	R^1	R^2
48	Bn	Bn
49	TBDPS	Bn

	R^1	R^2
37	Bn	Bn
50	TBDPS	Bn

Scheme 6. (a) Et^{i}PrN–TBHP–Ti(O^{i}Pr)$_4$, CH_2Cl_2 or $C_2H_4Cl_2$, 0 °C → reflux.

Table 4
Synthesis of threo- and erythro-configurated glycals from the 2-deoxy-2-phenylselenenyl-1,4-anhydroalditols **39**–**44** and **46**–**49**

Entry	Seleno-derivative	Conditions [a]	Glycal	Yield (%)
1	**39**	A	**15**	62
2	**42**	A	**15**	61
3	**46**	A	**37**	73
4	**48**	A	**37**	74
5	**40**+**43**	A	**17**	82
6	**47**+**49**	A	**50**	65
7	**40**+**43**	B	**17**	94
8	**47**+**49**	B	**50**	82
9	**41**+**44**	B	**45**	89

[a] (A) TBHP, $Ti(O^iPr)_4$, Et^iPr_2N, CH_2Cl_2, 0 °C–reflux, 48 h. (B) TBHP, $Ti(O^iPr)_4$, $C_2H_4Cl_2$, 0 °C–reflux, 3 h.

This prompted us to try oxidation starting from the diastereomeric mixture of 2-deoxy-2-phenylselenenyl-1,4-anhydroalditols obtained from the 5-endo selenoetherification. Treatment of the mixture **40**/**43** and **47**/**49** with TBHP–Et^iPr_2N–$Ti(O^iPr)$ in refluxing dichloromethane afforded glycals **17** and **50** in 82 and 65% yields, respectively (Entries 5 and 6). Furthermore, reaction in refluxing dichloroethane instead of dichloromethane afforded glycals in considerably shorter reaction times (ca. 3 h) and better yields (Entries 7, 8 and 9).

In conclusion, both erythro- and threo-configurated glycals have been efficiently synthesized by oxidative elimination of 1-phenylselenenylfuranosides and 2-phenylselenenyl-1,4-anhydroalditols. 1-Phenylselenenylfuranosides were synthesized from 2-deoxy-D-*erythro*-pentose via the corresponding methyl furanosides. 4-Phenylselenenyltetrahydrofurans were obtained through an unusual 5-endo selenoetherification of 4-pentene-1,2,3-triols, which are obtained from inexpensive D-mannitol. Despite the instability of some protective groups such as esters, this method provides an efficient strategy for the synthesis of furanoid glycals, particularly for those with ether protective groups. The use of selenoxides ensures that elimination proceeds in mild conditions, which favors the easy obtention and stability of the desired glycals.

3. Experimental

General methods.—Melting points are uncorrected. Optical rotations were measured at 25 °C in 10 cm cells. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity-400 spectrometer operating at 399.93 (^1H) and 99.98 MHz (^{13}C), respectively, using $CDCl_3$ as a solvent at 30 °C with TMS as internal standard. Elemental analyses were determined at the 'Servei de Recursos Cientifics (Universitat Rovira i Virgili)'. Flash-column chromatography was performed using Silica Gel 60 A CC (40–63 microns). Preparative-layer chromatography was performed on Silica Gel 60. Radial chromatography was performed on 1, 2 or 4 mm plates of silica gel, depending on the amount of product. Medium-pressure chromatography (MPLC) was performed using Silica Gel 60 A CC (6–35 microns). Band separation was monitored by UV. TLC plates were prepared with Kieselgel 60 PF254. Solvents for chromatography were distilled at atmospheric pressure prior to use. Reaction solvents were purified and dried by using standard procedures.

Synthesis of furanoid glycals from phenyl 1-selenofuranosides: general procedure for conversion of methyl furanosides into the corresponding phenyl 1-selenofuranosides.—To a solution of differently protected 2-methyl deoxyribofuranoside (1 mmol) in dry CH_2Cl_2 (3 mL) under argon atmosphere at −20 °C, $BF_3{\cdot}Et_2O$ (0.8 mmol) was added dropwise. The resulting mixture was allowed to warm to −10 °C, and stirred for 10 min. The yellow solution was then cooled to −20 °C and phenylselenol (1.1 mmol) was added. The reaction mixture was maintained at this temperature until completion. Pyridine was then added, and the mixture was warmed to rt. The solvent was removed at reduced temperature, and the resulting crude product was purified by flash chromatography.

General procedure for glycal synthesis from phenyl 1-selenofuranosides (A)..—Ethyldiisopropylamine (0.8 mmol) was added to a cold solution (0 °C) of phenyl selenoglycoside (1 mmol) in dry CH_2Cl_2 (6 mL). *tert*-Butylhydroperoxide (1 mmol) was then added dropwise to this mixture over a period of 5 min.

Subsequent addition of titanium isopropoxide (1 mmol) gave a yellowish solution that was stirred at 0 °C until completion (ca. 45 min) and then warmed to rt. The solvent was removed under low pressure and the crude obtained was purified by column chromatography.

General procedure for glycal synthesis from phenyl 1-selenofuranosides (B)..—This procedure is similar to A using ethyldiisopropylamine (1.7 mmol), phenyl selenoglycoside (1 mmol) in dry CH_2Cl_2 (6 mL), *tert*-butylhydroperoxide (2.3 mmol) and titanium isopropoxide (1 mmol).

*Phenyl 5-O-(*tert-*butyldiphenylsilyl)-2-deoxy-1-seleno-α,β-*erythro-*pentofuranoside* (**7**).—Starting from **6** and following the general procedure, **7** as a mixture of anomers (α/β 1:2), was obtained as a thick yellow syrup in 82% yield. **7α**: ^{1}H NMR ($CDCl_3$): δ 7.69–7.18 (m, 15 H, Ph); 6.02 (dd, 1 H, $J_{1,2'}$ 2.5, $J_{1,2}$ 7.2 Hz, H-1); 4.45–4.38 (m, 1 H, H-3); 4.25–4.21 (m, 1 H, H-4); 3.84 (dd, 1 H, $J_{5,4}$ 3.8, $J_{5,5'}$ 10.9 Hz, H-5), 3.71 (dd, 1 H, $J_{5',4}$ 4.8 Hz, H-5); 2.76 (m, 1 H, $J_{2,3}$ 7.2, $J_{2,2'}$ 14.2 Hz, H-2); 2.37 (d, 1 H, $J_{OH,3}$ 7.4 Hz, OH); 2.21 (m, 1 H, $J_{2'1}$ 2.5, $J_{2',3}$ 2.5, $J_{2',2}$ 14.2 Hz, H-2); 1.04 (s, 9 H, Me_3CSi); ^{13}C NMR ($CDCl_3$): δ 135.6, 133.8, 129.8, 129.7, 129.0, 128.9, 127.7, 127.5 (Ph); 86.8 (C-1); 83.3 (C-4); 73.3 (C-3); 63.9 (C-5); 42.7 (C-2); 26.8 (Me_3CSi); 19.2 (Me_3CSi). **7β**: ^{1}H NMR ($CDCl_3$): δ 7.70–7.19 (m, 15 H, Ph); 5.82 (dd, 1 H, $J_{1,2}$ 6.3, $J_{1,2'}$ 7.1 Hz, H-1); 4.44–4.39 (m, 1 H, H-3); 3.99 (m, 1 H, $J_{4,3}$ 2.9, $J_{4,5}$ 4.7, $J_{4,5'}$ 7.2 Hz, H-4); 3.77 (dd, 1 H, $J_{5,5'}$ 10.5 Hz, H-5); 3.54 (dd, 1 H, $J_{5',5}$ 10.4 Hz, H-5′); 2.36 (ddd, 1 H, $J_{2,3}$ 4.0, $J_{2,1}$ 6.3, $J_{2,2'}$ 13.6 Hz, H-2); 2.26 (m, 1 H, $J_{2',3}$ 6.0 Hz, H-2′); 2.02 (bs, 1 H, OH); 1.04 (s, 9 H, Me_3CSi); ^{13}C NMR ($CDCl_3$): δ 135.6, 134.2, 133.0, 129.8, 129.0, 127.7, 127.5 (Ph); 87.7 (C-1); 81.5 (C-4); 73.5 (C-3); 64.3 (C-5); 41.7 (C-2); 26.9 (Me_3CSi); 19.2 (Me_3CSi).

*1,4-Anhydro-3,5-di-*O*-benzyl-2-deoxy-*D-erythro-*pent-1-enitol* (**15**).—Compound **4** (0.066 g, 0.2 mmol) was transformed into the phenyl 1-selenoglycoside **8** (0.071 g, 78%) with PhSeH and $BF_3{\cdot}Et_2O$ following the general procedure for synthesizing selenoglycosides. Oxidation of **8** with TBHP (0.12 mL, 0.359 mmol), Et^iPr_2N (0.046 mL, 0.265 mmol) and $Ti(O^iPr)_4$ (0.045 mL, 0.156 mmol) as described in the general procedure for glycal synthesis (B) and subsequent purification through a small neutral silica gel pad afforded 0.050 g (84%, overall yield) of compound **15** as a syrup; $[\alpha]_D^{25}$ + 145.0° (*c* 1.614, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35–7.24 (m, 10 H, Ph), 6.58 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1); 5,15 (dd, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 4.64–4.61 (m, 1 H, H-3), 4.57–4.48 (m, 1 H, H-4), 4.59 (d, 1 H, J_{gem} 12.2 Hz, CH_2Ph), 4.54 (d, 1 H, CH_2Ph), 4.50 (s, 2 H, CH_2Ph), 3.54 (dd, 1 H, $J_{5,4}$ 6.5, $J_{5,5'}$ 10.1 Hz, H-5), 3.41 (dd, 1 H, H-5′); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 150.4 (C-1), 138.9–127.6 (Ph), 100.5 (C-2), 84.8 (C-4), 82.6 (C-3), 73.4 (CH_2Ph), 69.8 (CH_2Ph), 69.6 (C-5). Anal Calcd for $C_{19}H_{20}O_3$: C, 77.02; H, 6.75. Found C, 77.37; H, 6.43.

*1,4-Anhydro-2-deoxy-3,5-di-*O*-pivaloyl-*D-erythro-*pent-1-enitol* (**16**).—Compound **5** (0.632g, 2 mmol) was transformed into the phenyl 1-selenoglycoside **9** (0.696 g, 79%) with PhSeH and $BF_3{\cdot}Et_2O$ following the general procedure for synthesizing selenoglycosides. This compound was then treated following the general procedure of glycal synthesis (A) to give compound **16** (0.324 g, 71%) as an oil; $[\alpha]_D^{25}$ + 188.00° (*c* 2.025, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.61 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1); 5.59 (t, 1 H, $J_{3,2} = J_{3,4}$ 2.7 Hz, H-3), 5.15 (dd, 1 H, H-2), 4.55 (td, 1 H, $J_{4,5'} = J_{4,5}$ 5.1 Hz, H-4), 4.25 (d, 2 H, H-5,H-5′), 1.15 (m, 18 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 178.4 (CO), 178.1 (CO), 151.6 (C-1), 99.5 (C-2), 83.6 (C-4), 78.5 (C-3), 63.3 (C-5), 27.2, 27.1, 27.0 (CH_3). Anal Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found C, 63.69; H, 8.80.

*1,4-Anhydro-3-*O*-benzyl-5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-*D-erythro-*pent-1-enitol* (**17**).—Compound **7** (0.5 g, 0.98 mmol) was dissolved in dry THF (3 mL) and added to a suspension of NaH (80%, 0.035 g, 1.17 mmol) in THF (3 mL). Benzyl bromide (0.196 mL, 1.17 mmol) was then added and the mixture was stirred for 2.5 h. Addition of MeOH and evaporation of the solvent afforded a residue that was purified by column chromatography in EtOAc–hexane to yield 0.40 g (68%) of **10** as a syrup. This material was then treated following the general procedure for glycal synthesis (B) to give glycal **17** (0.186 g, 71%)

as an oil, after purification by column chromatography over neutral silica gel (1:20 EtOAc–hexane); $[\alpha]_D^{25}$ +21.2° (*c* 1.110, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.70–7.18 (m, 15 H, Ph); 6.54 (dd, 1 H, $J_{1,3}$ 1.2, $J_{1,2}$ 2.6 Hz, H-1); 5.15 (td, 1 H, $J_{2,4}$ 1.3, $J_{2,3}$ 2.6 Hz, H-2); 4.76 (ddd, 1 H, $J_{3,4}$ 4.0 Hz, H-3); 4.55 (dddd, 1 H, $J_{4,5}$ 5.3, $J_{4,5'}$ 6.5 Hz, H-4); 4.54 (d, 1 H, J_{gem} 11.8 Hz, CH_2); 4.48 (d, 1 H, CH_2); 3.75 (dd, 1 H, $J_{5,5'}$ 10.7 Hz, H-5); 3.58 (dd, 1 H, H-5); 1.06 (s, 9 H, $(CH_3)_3CSi$); ^{13}C NMR ($CDCl_3$): δ 150.4 (C-1); 138.3, 135.6, 133.2, 129.7, 128.3, 127.7, 127.5 (Ph); 100.5 (C-2); 86.1 (C-4); 82.7 (C-3); 69.6 (OCH_2Ph); 63.5 (C-5); 26.8 ($CH_3)_3CSi$); 19.2 (($CH_3)_3CSi$). Anal Calcd for $C_{28}H_{32}O_3Si$: C, 75.64; H, 7.25. Found C, 75.99; H, 7.57.

*1,4-Anhydro-5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-3-*O*-methyl-*D*-*erythro*-pent-1-enitol* (**18**).—Compound **7** (0.115 g, 0.224 mmol) was dissolved in dry THF (2 mL) and added to a suspension of NaH (80%, 0.012 g, 1.17 mmol) in THF (1.5 mL). The reaction mixture was stirred for 20 min and after protection from light, methyl iodide (0.035 g, 1.17 mmol) was added and the mixture was stirred overnight. Addition of MeOH and evaporation of the solvent afforded a residue that was purified by column chromatography in EtOAc–hexane 1.20 to yield 0.090 g (76%) of **11** as a syrup. This material was then treated using the general procedure for glycal synthesis (B) to give 0.045 g (72%) of **18** as an oil, after purification by column chromatography in 1:12 EtOAc–hexane; $[\alpha]_D^{25}$ +115.0° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.71–7.24 (m, 10 H, Ph), 6.54 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1); 5.14 (t, 1 H, $J_{2,3}$ 2.7 Hz, H-2), 4.54 (t, 1 H, $J_{3,4}$ 2.7 Hz, H-3), 4.45 (ddd, 1 H, $J_{4,5}$ 5.4, $J_{4,5'}$ 6.0 Hz, H-4), 3.76 (dd, 1 H, $J_{5,5'}$ 10.5 Hz, H-5), 3.57 (dd, 1 H, H-5), 3.29 (s, 3 H, OCH_3), 1.06 (s, 9 H, $(CH_3)_3CSi$); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 150.4 (C-1), 135.6, 133.2, 129.8, 127.7 (Ph), 100.1 (C-2), 85.6 (C-4), 84.2 (C-3), 63.5 (C-5), 54.8 (OCH_3), 26.7 ($CH_3)_3CSi$), 19.2 (($CH_3)_3CSi$). Anal Calcd for $C_{22}H_{28}O_3Si$: C, 71.55; H, 7.64. Found C, 71.49; H, 7.78.

*1,4-Anhydro-5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-3-*O*-(methoxyethoxymethylene)-*D*-erythro-pent-1-enitol* (**19**).—A solution of **7** (0.500 g, 0.97 mmol) in CH_2Cl_2 was treated with Et^iPr_2N (0.185 mL, 1.067 mmol) and MEMCl (0.140 mL, 1.067 mmol) to give, after purification by column chromatography, 0.425 g (73%) of **12**. This compound was then treated following the general procedure for glycal synthesis (B) to give 0.340 g (81%) of **19** as an oil, after purification by column chromatography in 1:12 EtOAc–hexane; $[\alpha]_D^{25}$ +46.7° (*c* 1.215, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.77–7.34 (m, 10 H, Ph); 6.53 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1); 5.15 (t, 1 H, $J_{2,3}$ 2.7 Hz, H-2); 4.87 (m, 1 H, $J_{3,4}$ 2.8 Hz, H-3); 4.79 (s, 2 H, OCH_2O); 4.49 (td, 1 H, $J_{4,5} = J_{4,5'}$ 5.6 Hz, H-4); 3.77 (dd, 1 H, $J_{5,5'}$ 10.7 Hz, H-5); 3.73–3.67 (m, 2 H, OCH_2); 3.64 (dd, 1 H, H-5); 3.53 (t, 2 H, J_{CH_2,CH_2} 4.5 Hz, CH_2O); 3.36 (s, 3 H, OCH_3); 1.05 (s, 9 H, $(CH_3)_3CSi$); ^{13}C NMR ($CDCl_3$): δ 150.3 (C-1); 135.6, 133.2, 129.7, 127.6 (Ph); 101.0 (C-2); 94.1 (OCH_2O); 86.7 (C-3); 81.5 (C-4); 71.6 (OCH_2); 66.9 (CH_2O); 63.5 (C-5); 58.9 (OCH_3); 26.7 (Me_3CSi); 19.2 (Me_3CSi). Anal Calcd for $C_{25}H_{34}O_5Si$: C, 67.84; H, 7.74. Found C, 68.03; H, 7.78.

*1,4-Anhydro-3-*O*-(*tert*-butyldimethylsilyl)-5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-*D*-erythro-pent-1-enitol* (**20**).—1,8-Diazabicyclo-[5,4,0]undec-7-ene (DBU) (0.5 g, 3.25 mmol) was added to a cold solution (0 °C) of **7** (1.27 g, 2.5 mmol) in dry benzene (25 mL) and the mixture was stirred for 10 min. The cold bath was then removed and *tert*-butyldimethylsilyl chloride (0.45 g, 3 mmol) was added. The mixture was stirred for 20 h. The solvent was then removed under diminished pressure and the residue was purified by column chromatography with 1:15 EtOAc–hexane to afford 1.23 g (79%) of an anomeric mixture of **13** as a syrup. This compound (1 g, 1.60 mmol) was treated in the general procedure for glycal synthesis (B) to give a residue which was purified by column chromatography in 1:75 EtOAc–hexane to yield glycal 20 (0.45 g, 60%) as an oil; ^1H NMR ($CDCl_3$): δ 7.73–7.30 (m, 10 H, Ph); 6.48 (dd, 1 H, $J_{1,3}$ 0.9, $J_{1,2}$ 2.7 Hz, H-1); 5.02 (t, 1 H, $J_{2,3}$ 2.7 Hz, H-2); 4.95 (td, 1 H, $J_{3,4}$ 2.7 Hz, H-3); 4.34 (td, 1 H, $J_{4,5}$ 5.4, $J_{4,5'}$ 5.4 Hz, H-4); 3.70 (dd, 1 H, $J_{5,5'}$ 10.9 Hz, H-5); 3.62 (dd, 1 H, H-5′); 1.04 (s, 9 H, Me_3CSi); 0.87 (s, 9 H, Me_3CSi); 0.05 (s, 6 H, $(Me)_2Si$); ^{13}C NMR ($CDCl_3$): δ 149.1 (C-

1); 135.6, 133.2, 129.7, 127.7 (Ph); 103.4 (C-2); 89.0 (C-4); 76.0 (C-3); 63.6 (C-5); 26.7 ((CH_3)$_3$CSi); 25.8 ((CH_3)$_3$CSi); 19.2 ((CH_3)$_3$*C*Si); 19.0 (Me$_3$*C*Si); −4.2 ((CH_3)$_2$Si); −4.4 ((Me)$_2$Si). Anal Calcd for $C_{27}H_{40}O_3Si_2$: C, 69.18; H, 8.60. Found C, 69.02; H, 8.51.

*3-O-Acetyl-1,4-anhydro-5-O-(*tert*-butyldiphenylsilyl)-2-deoxy*-D-erythro-*pent-1-enitol* (**21**).—Compound **7** (0.127 g, 0.25 mmol) was acetylated by reaction with Ac_2O (1 mL) in dry pyridine (2 mL), overnight. The solvent was distilled off and the residue dissolved in CH_2Cl_2. The solution was washed with water, dried with $MgSO_4$ and evaporated to afford 0.119 g (86%) of crude **14**. This material (0.102 g, 0.186 mmol) was then treated in the general procedure for glycal synthesis (A). The resulting reaction mixture was then filtered through a small pad of neutral silica gel to yield 0.050 g (68%) of **21** as an oil; $[\alpha]_D^{25}$ +31.0° (*c* 1.952, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68–7.30 (m, 10 H, Ph), 6.63 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1); 5.81 (dd, $J_{3,2}$ 1.2, $J_{3,4}$ 2.1 Hz, H-3), 5.17 (dd, 1 H, H-2), 4.50 (m, 1 H, H-4), 3.84 (dd, 1 H, $J_{5,4}$ 5.1, $J_{5,5'}$ 10.8 Hz, H-5), 3.76 (dd, 1 H, $J_{5',4}$ 4.8 Hz, H-5), 2.04 (s, 3 H, $COCH_3$), 1.04 (s, 9 H, Me$_3$CSi); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 170.7 (CO), 151.8 (C-1), 135.5–129.7, 128.9–127.6 (Ph), 99.5 (C-2), 86.1 (C-4), 78.8 (C-3), 63.5 (C-5), 26.6 ((CH_3)$_3$CSi), 19.2 (Me$_3$*C*Si), 21.2 (Me). Anal. Calcd for $C_{23}H_{28}O_4Si$: C, 69.66; H, 7.12. Found C, 69.42; H, 7.23.

*Methyl 5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-3-*O*-(trifluoromethanesulfonyl)-α,β-*D*-erythro-pentofuranoside* (**22**).—In an oven-dried round-bottomed flask, provided with a magnetic stirring bar, a solution of 0.2 g (0.56 mmol) of **6** in dry CH_2Cl_2 (2 mL) was treated with dry pyridine (0.2 mL, 2.47 mmol) and the solution was stirred for 10 min under inert atmosphere. The solution was then cooled to −20 °C and triflic anhydride (0.104 mL, 0.6 mmol) was added. The resulting mixture was stirred for 15 min at low temperature and was then left for 45 min to warm to rt. Purification through a small pad of neutral silica gel produced 0.250 g (91%) of an anomeric mixture of triflate **22** as a syrup; **22α**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71, 7.29 (m 10 H, Ph), 5.55 (d, 1 H, $J_{3,2}$ 6.4 Hz, H-3), 5.15 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1); 4.37 (m, 1 H, H-4), 3.79 (d, 1 H, J_{gem} 10.8 Hz, H-5), 3.74 (dd, 1 H, $J_{5',4}$ 1.2 Hz, H-5), 3.36 (s, 3 H, OMe), 2.34 (m, 2 H, H-2, H-2′), 1.02 (s, 9 H, *t*Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 135.5, 129.9, 129.8, 127.8, 127.7 (Ph), 104.7 (C-1), 88.1 (C-3), 83.8 (C-4), 62.9 (C-5), 54.9 (OCH_3), 39.8 (C-2), 26.6, 19.1 (*t*Bu). **22β**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70, 7.31 (m, 10 H, Ph), 5.57 (ddd, 1 H, $J_{3,2}$ 6.0, $J_{3,2'}$ 3.1, $J_{3,4}$ 1.5 Hz, H-3), 5.17 (dd, 1 H, $J_{1,2}$ 5.4, $J_{1,2'}$ 3.6 Hz, H-1); 4.33 (ddd, 1 H, $J_{4,5}$ 4.8, $J_{4,5'}$ 7.8 Hz, H-4), 3.74 (dd, 1 H, J_{gem} 10.8 Hz, H-5), 3.61 (dd, 1 H, H-5′), 2.44 (ddd, 1 H, J_{gem} 15.0 Hz, H-2), 2.30 (ddd, 1 H, H-2′), 1.03 (s, 9 H, *t*Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 135.5, 129.9, 1278, 127.6 (Ph), 105.1 (C-1), 89.2 (C-3), 84.0 (C-4), 63.7 (C-5), 55.7 (OCH_3), 39.3 (C-2), 26.7, 19.1 (*t*Bu).

*Methyl 5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-α,β-*D*-threo-pentofuranoside* (**23**).—In a flask fitted with a magnetic stirring bar, 0.170 g (0.34 mmol) of **22** was dissolved in dry DMF (12 mL), and KNO_2 (0.173 g, 2.03 mmol) was then added. Once the mixture had turned into a homogeneous solution, 0.90 g (0.34 mmol) of 18-crown-6 ether and 0.030 g of water were added. The mixture was stirred overnight at rt. The solvent was then removed under diminished pressure and the resulting residue was purified by column chromatography in 1:4 EtOAc–hexane to afford 0.083 g (62%) of an anomeric mixture of **23** as syrup; **23α**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78, 7.29 (m, 10 H, Ph), 5.15 (t, 1 H, $J_{1,2}$ $J_{1,2'}$ 4.1 Hz, H-1); 4.60 (m, 1 H, H-3), 4.03 (m, 3 H, H-4, H-5, H-5′), 3.34 (s, 3 H, OCH_3), 2.99 (d, 1 H, $J_{OH,3}$ 4.0 Hz, OH), 2.17 (t, 2 H, H-2, H-2′), 1.04 (s, 9 H, *t*Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 135.6, 135.5, 129.9, 127.8, 127.6 (Ph), 104.5 (C-1), 79.1 (C-4), 72.6 (C-3), 62.9 (C-5), 55.2 (OCH_3), 42.6 (C-2), 26.7, 19.1 (*t*Bu). **23β**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79, 7.26 (m, 10 H, Ph), 5.04 (dd, 1 H, $J_{1,2}$ 3.2, $J_{1,2'}$ 1.2 Hz, H-1); 4.33 (ddd, 1 H, $J_{3,2}$ 6.0, $J_{3,2'}$ 3.6, $J_{3,OH}$ 9.0 Hz, H-3), 4.08 (m, 1 H, H-4), 4.05 (d, 1 H, J_{gem} 10.2 Hz, H-5), 3.87 (dd, 1 H, $J_{5',4}$ 5.7 Hz, H-5′), 3.30 (s, 3 H, OMe), 2.94 (d, 1 H, OH), 2.12 (m, 2 H, H-2, H-2′), 1.05 (s, 9 H, *t*Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 135.7, 135.6, 129.6, 127.7, 127.6

(Ph), 105.1 (C-1), 84.6 (C-4), 71.5 (C-3), 63.7 (C-5), 54.7 (OCH_3), 41.4 (C-2), 26.8, 18.9 (^{t}Bu).

*Phenyl 5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-1-seleno-α,β-*D*-threo-pentofuranoside* (**24**).—Following the general procedure, compound **23** (0.200 g 0.52 mmol) in CH_2Cl_2 (1.5 mL) was treated with $BF_3{\cdot}Et_2O$ (0.522 mL, 0.416 mmol) and PhSeH (0.06 mL, 0.572 mmol) for 50 min. The residue obtained after evaporation of the solvent was purified by column chromatography to yield 0.214 g (80%) of **24** (17:3 α/β mixture) as a thick yellow syrup. **24α**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80, 7.20 (m, 10 H, Ph), 6.11 (t, 1 H, $J_{1,2} = J_{1,2'}$ 6.5 Hz, H-1); 4.55 (m, 1 H, H-3), 4.17 (m, 1 H, H-4), 4.14 (d, 1 H, J_{gem} 12.6 Hz, H-5), 4.07 (dd, 1 H, $J_{5',4}$ 5.4 Hz, H-5′), 3.33 (d, 1 H, $J_{OH,3}$ 4.8 Hz, OH), 2.54 (ddd, 1 H, J_{gem} 14.3, $J_{2,3}$ 5.8 Hz, H-2), 2.33 (td, 1 H, $J_{2',3}$ 6.8 Hz, H-2′), 1.09 (s, 9 H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 135.6, 133.5, 129.9, 128.9, 127.8, 127.7, 127.3 (Ph), 82.3 (C-1), 80.2 (C-4), 72.7 (C-3), 62.5 (C-5), 43.5 (C-2), 26.7, 19.1 (^{t}Bu).

*Phenyl 3,5-di-*O*-benzyl-2-deoxy-1-seleno-α,β-*D*-threo-pentofuranoside* (**31**).—Compound **24** (0.226 g, 0.442 mmol) was dissolved in dry THF (1 mL) and treated with Bu_4NF (0.127 g, 0.487 mmol) at 0 °C for 1 h. The solvent was then removed under diminished pressure and the residue was purified by chromatography in 1:1 EtOAc–hexane to yield 0.110 g (91%) of **25** as an oil. Compound **25** (0.205 g, 0.750 mmol) was dissolved in dry THF (5 mL) and added to a suspension of NaH (80%, 0.055 g, 1.80 mmol) in 5 mL of THF. Benzyl bromide (0.300 mL, 1.80 mmol) was then added and the mixture was stirred for 2.5 h. Addition of MeOH and evaporation of the solvent afforded a residue that was purified by column chromatography in 1:15 EtOAc–hexane to yield 0.305 g (90%) of **31** as a syrup. **31α**: ^{1}H NMR ($CDCl_3$): δ 7.67–7.15 (m, 15 H, Ph); 6.04 (dd, 1 H, $J_{1,2\alpha}$ 5.8, $J_{1,2\beta}$ 7.1 Hz, H-1); 4.61 (d, 1 H, J_{gem} 11.8 Hz, CH_2); 4.56 (d, 1 H, J_{gem} 12.1 Hz, CH_2); 4.53 (d, 1 H, J_{gem} 11.8 Hz, CH_2); 4.42 (d, 1 H, CH_2); 4.35 (ddd, 1 H, $J_{4,3}$ 3.9, $J_{4,5'}$ 5.8, $J_{4,5}$ 6.2 Hz, H-4); 4.14 (ddd, 1 H, $J_{3,2\beta}$ 1.9, $J_{3,2\alpha}$ 5.8 Hz, H-3); 3.89 (dd, 1 H, $J_{5,5'}$ 10.2 Hz, H-5); 3.78 (dd, 1 H, $J_{5',4}$ 6.2, $J_{5',5}$ 10.2 Hz, H-5′); 2.62 (ddd, 1 H, $J_{2\beta,3}$ 1.9, $J_{2\beta,1}$ 7.1, $J_{2\beta,2\alpha}$ 14.5 Hz, H-2β); 2.19 (dt, 1 H, $J_{2\alpha,1}$ 5.8, $J_{2\alpha,3}$ 5.8, $J_{2\alpha,2\beta}$ 14.5 Hz, $H_{2\alpha}$); ^{13}C NMR ($CDCl_3$): δ 138.4, 137.8, 133.9, 128.9, 128.4, 128.3, 127.7, 127.4, 127.4, (Ph); 82.1 (C-1); 80.3 (C-4); 77.8, (C-3); 73.3, 71.3 (2 OCH_2Ph); 67.7 (C-5); 40.1 (C-2). **31β**: ^{1}H NMR ($CDCl_3$): δ 7.68–7.18 (m, 15 H, Ph); 5.85 (dd, 1 H, $J_{1,2\beta}$ 3.8, $J_{1,2\alpha}$ 6.2 Hz, H-1); 4.68 (d, 1 H, J_{gem} 12.1 Hz, CH_2); 4.63 (d, 1 H, CH_2); 4.55 (d, 1 H, CH_2); 4.46 (d, 1 H, CH_2); 4.28 (ddd, 1 H, $J_{4,3}$ 4.4, $J_{4,5}$ 5.4, $J_{4,5'}$ 6.7 Hz, H-4); 4.21 (td, 1 H, $J_{3,2\beta}$ 2.6, $J_{3,2\alpha}$ 4.4 Hz, H-3); 3.91 (dd, 1 H, $J_{5,5'}$ 10.2 Hz, H-5); 3.86 (dd, 1 H, $J_{5',4}$ 6.7, $J_{5',5}$ 10.2 Hz, H-5); 2.59–2.47 (m, 2 H, H-2α, H-2β); ^{13}C NMR ($CDCl_3$): δ 138.2, 137.8, 133.3, 128.9, 128.3, 127.7 (Ph); 83.7 (C-1), 83.1 (C-4); 77.4, (C-3), 73.4, 71.3 (2 OCH_2Ph); 69.3 (C-5); 39.9 (C-2).

Synthesis of **31** *from* **38**.—A cold (−20 °C) solution of 4 g (12.18 mmol) of methyl 2-deoxyfuranoside **31** in CH_2Cl_2 (36 mL) was treated with 1.22 mL (9.74 mmol) of $BF_3{\cdot}Et_2O$ and PhSeH (1.42 mL, 13.40 mmol) and stirred at low temperature for 1 h. The residue obtained after the standard work-up was purified by column chromatography (1:10 hexane–EtOAc then hexane) to afford 5.3 g (96%) of **31** as a syrup.

*1,4-Anhydro-5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-3-*O*-methyl-*D*-threo-pent-1-enitol* (**32**).—Compound **24** (0.100 g, 0.195 mmol) was dissolved in dry THF (2 mL) and added to a suspension of NaH (80%, 0.010 g, 1.02 mmol) in THF (1.5 mL). The reaction mixture was stirred for 20 min and it was then protected from light. Methyl iodide (0.035, 1.02 mmol) was then added and the mixture was stirred overnight. Addition of MeOH and evaporation of the solvent afforded a residue that was purified by column chromatography in 1:20 EtOAc–hexane to yield 0.080 g (0.152 mmol, 78%) of **26** as a syrup. This material was then treated following the general procedure for glycal synthesis (B) to obtain a residue that was purified by column chromatography in 1:12 EtOAc–hexane to give 0.039 g (68%) of **32** as an oil; $[\alpha]_D^{25}$ −54.60° (*c* 2.823, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74–7.24 (m, 10 H, Ph), 6.46 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1); 4.94 (dd, 1 H, $J_{3,2}$ 2.7, $J_{3,4}$ 6.9 Hz, H-3), 4.71

(t, 1 H, H-2), 4.29 (m, 1 H, H-4), 3.86 (s, 1 H, H-5), 3.83 (d, 1 H, $J_{5',4}$ 3.3 Hz, H-5), 3.47 (s, 3 H, OMe), 1.02 (s, 9 H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 149.40 (C-1), 135.89–129.58–127.47 (Ph), 104.09 (C-2), 83.60 (C-4), 74.44 (C-3), 70.80 (C-5), 59.23 (OCH_3), 26.80–19.27 (^{t}Bu).). Anal Calcd for $C_{22}H_{28}O_3Si$: C, 71.55; H, 7.64. Found C, 71.51; H, 7.71.

*1,4-Anhydro-5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-3-*O*-(methoxyethoxymethylene)-*D*-threo-pent-1-enitol* (**33**).—A solution of **24** (0.082 g, 0.159 mmol) in CH_2Cl_2 was treated with Et^{i}Pr$_2$N (0.030 mL, 0.175 mmol) and MEMCl (0.023 mL, 0.175 mmol) to give of **27** (0.046 g, 0.077 mmol, 48%). Treatment of this compound using the general procedure for glycal synthesis (B) and subsequent purification by column chromatography in 1:20 EtOAc–hexane gave 0.018 g (53%) of product **33** as an oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74–7.28 (m, 10 H, Ph), 6.61 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1); 5.24 (dd, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 4.82 (s, 2 H, OCH_2O), 4.75 (dd, 1 H, $J_{3,4}$ 6.4 Hz, H-3), 4.40 (q, 1 H, $J_{4,5}$ 6.4, $J_{4,5'}$ 6.1 Hz, H-4), 4.06 (dd, 1 H, $J_{5,5'}$ 10.8 Hz, H-5), 3.95 (dd, 1 H, H-5′), 3.51 (m, 4 H, OCH_2CH_2O), 3.39 (s, 3 H, OCH_3), 1.02 (s, 9 H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 150.2 (C-1), 135.6, 135.5, 129.6, 127.7, 127.5 (Ph), 102.2 (C-2), 94.5 (OCH_2O), 84.4 (C-4), 78.1 (C-$_3$), 71.6 (C-5), 66.7, 61.3 (OCH_2CH_2O), 59.0 (OCH_3), 26.8, 19.2 (^{t}Bu). Anal Calcd for $C_{25}H_{34}O_5Si$: C, 67.84; H, 7.74. Found C, 67.99; H, 7.81.

*1,4-Anhydro-5-*O*-(*tert*-butyldiphenylsilyl)-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-threo-pent-1-enitol* (**34**).—1,8-Diazabicyclo[5,4,0]-undec-7-ene (DBU) (0.032 g, 0.208 mmol) was added to a cold solution (0 °C) of **24** (0.080 g, 0.16 mmol) in dry benzene (2 mL) and the mixture was stirred for 10 min. The cold bath was then removed and *tert*-butyldimethylsilyl chloride (0.029 g, 0.192 mmol) was added. The mixture was stirred for 20 h. The solvent was then removed under reduced pressure and the residue was purified by column chromatography with 1:15 EtOAc–hexane to afford 0.063 g (63%) of **28** as a syrup. This material was then treated using the general procedure for glycal synthesis (B) resulting in a residue which was purified by column chromatography in 1:75 EtOAc–hexane to give 0.028 g (78%) of glycal **34** as an oil; $[\alpha]_D^{25}$ −18.2° (*c* 1.717, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76–7.30 (m, 10 H, Ph), 6.63 (d, 1 H, $J_{1,2}$ 2.1 Hz, H-1); 5.8 (dd, 1 H, $J_{2,3}$ 2.7 Hz, H-2), 4.87 (dd, 1 H, $J_{3,4}$ 4.2 Hz, H-3), 4.34 (ddd, 1 H, $J_{4,5}$ 3.9, $J_{4,5'}$ 7.8 Hz, H-4), 4.05 (dd, 1 H, $J_{5',5}$ 11.7 Hz, H-5), 3.92 (dd, 1 H, H-5′), 1.1 (s, 9 H, ^{t}Bu), 0.79 (s, 9 H, ^{t}Bu), 0.02 (s, 6 H, 2 Me); ^{13}C NMR ($CDCl_3$ 75.4 MHz): δ 149.5 (C-1), 135.6, 129.5, 127.6 (Ph), 103.9 (C-2), 85.7 (C-4), 73.3 (C-3), 62.6 (C-5), 26.8, 25.7, 19.3 (^{t}Bu). Anal Calcd for $C_{27}H_{40}O_3Si_2$: C, 69.18; H, 8.60. Found C, 69.28; H, 8.41.

*3-*O*-Acetyl-1,4-anhydro-5-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-D-threo-pent-1-enitol* (**35**).—Compound **24** (0.148 g, 0.290 mmol) was dissolved in dry pyridine (2 mL) and treated with Ac_2O (1 mL) overnight. The solvent was distilled off and the residue dissolved in CH_2Cl_2. The solution was washed with water, dried with $MgSO_4$ and evaporated to afford 0.130 g (81%) g of crude **29**. This material was pure enough to be treated using the general procedure for glycal synthesis (A). The resulting reaction mixture was then filtered through a small pad of neutral silica gel to yield 0.050 g (68%) of **35** as an oil; $[\alpha]_D^{25}$ −8.5° (*c* 3.505, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76–7.20 (m, 10 H, Ph), 6.66 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1); 5.82 (dd, 1 H, $J_{3,2}$ 2.7, $J_{3,4}$ 6.9 Hz, H-3), 5.20 (t, 1 H, H-2), 4.46 (m, 1 H, H-4), 3.99 (m, 2 H, H-5, H-5′), 1.9 (s, 3 H, Me), 1.05 (s, 9 H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 170.2 (CO), 151.8 (C-1), 135.5–129.7–127.6 (Ph), 100.8 (C-2), 83.2 (C-4), 74.9 (C-3), 60.9 (C-5), 26.6–19.1 (^{t}Bu), 21.0 (Me). Anal. Calcd for $C_{23}H_{28}O_4Si$: C, 69.66; H, 7.12. Found C, 69.31; H, 7.40.

*3,5-Di-*O*-acetyl-1,4-anhydro-2-deoxy-D-threo-pent-1-enitol* (**36**).—Compound **24** (0.226 g, 0.442 mmol) dissolved in dry THF (1 mL) was treated with Bu_4NF (0.127 g, 0.487 mmol) at 0 °C for 1 h. The solvent was then removed under diminished pressure and the residue purified by chromatography in 1:1 EtOAc–hexane to yield 0.110 g (91%) of **25** as an oil. Compound **25** (0.100 g, 0.366 mmol) was treated with dry pyridine (1.2 mL) and Ac_2O (0.5 mL) and the mixture was allowed to react overnight. Pyridine was removed by codistillation with toluene (3 × 2 mL)) under

diminished pressure. The resulting residue obtained was dissolved in CH_2Cl_2 (10 mL) and washed with water (4 mL), dried with $MgSO_4$ and evaporated to dryness to yield **30** in a quantitative yield. Crude **30** proved to be pure by TLC and 0.130 g (0.364 mmol) of this material was treated following the general procedure for glycal synthesis (A). The resulting reaction mixture was then filtered through a small pad of neutral silica gel–Et_3N with hexane and then 1:20 EtOAc–hexane to yield 0.046 g (63%) of **36** as an oil that decomposes slowly on standing; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.67 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1); 5.84 (dd, 1 H, $J_{3,2}$ 2.7, $J_{3,4}$ 7.2 Hz, H-3), 5.23 (dd, 1 H, H-2), 4.59 (ddd, 1 H, $J_{4,5'}$ 6.9, $J_{4,5}$ 6.1 Hz, H-4), 4.46 (dd, 1 H, $J_{5,5'}$ 12.0 Hz, H-5), 4.32 (dd, 1 H, H-5′), 2.19 (s, 3 H, Me), 2.06 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 170.5 (CO), 170.2 (CO), 151.7 (C-1), 100.8 (C-2), 80.2 (C-4), 75.2 (C-3), 61.4 (C-5), 20.9–20.7 ($2 \times CH_3$).

*1,4-Anhydro-3,5-di-*O*-benzyl-2-deoxy-*D*-threo-pent-1-enitol* (**37**).—Compound **31** (0.250 g, 0.55 mmol) was treated following the general procedure for glycal synthesis (B), and the resulting residue was purified by column chromatography in 1:20 EtOAc–hexane to give 0.142 g (87%) of glycal **37** as a colorless oil; $[\alpha]_D^{25}$ −12.9° (*c* 1.174, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27–7.10 (m, 10 H, Ph), 6.50 (d, 1 H, $J_{1,2}$ 2.6 Hz, H-1); 5.13 (dd, 1 H, $J_{2,3}$ 2.8 Hz, H-2), 4.53 (d, 1 H, J_{gem} 11.9 Hz, OCH_2Ph), 4.44 (d, 1 H, OCH_2Ph), 4.39 (d, 1 H, OCH_2Ph), 4.31 (d, 1 H, OCH_2Ph), 4.55–4.28 (m, 2 H, H-3, H-4); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 150.4 (C-1), 128.1–127.3 (Ph), 101.2 (C-2), 83.1 (C-4), 79.2 (C-3), 73.3–70.5 (OCH_2Ph), 67.6 (C-5). Anal Calcd for $C_{19}H_{20}O_3$: C, 77.02; H, 6.75. Found C, 77.33; H, 6.67.

General procedure for synthesis of furanoid glycals from 2-deoxy-2-phenylselenenyl-1,4-anhydroalditols (C).—In a round-bottomed, single necked flask, 0.17 mmol of seleno-derivative or the mixture of seleno-derivatives was dissolved in dry CH_2Cl_2 (10 mL) or $(CH_2)_2Cl_2$. The flask was immersed in a water–ice bath, and Et^{i}Pr$_2$N (50 μL, 0.29 mmol), TBHP 3 M (135 μL) in toluene (0.40 mmol) and Ti(O^{i}Pr)$_4$ (50 μL, 0.17 mmol) were sequentially added under argon atmosphere. After 20 min, TLC control showed that the starting material was fully consumed with the appearance of a new product that did not migrate in the elution system (3:1 hexane–EtOAc). The mixture was then refluxed up to the reaction was complete (ca. 48 h in CH_2Cl_2, 3 h in $(CH_2)_2Cl_2$). The solvent was evaporated under diminished pressure, and the glycal was purified by 'flash' chromatography with neutral silica gel.

Synthesis of **15** *from* **39**.—Starting from **39** (0.089 g, 0.20 mmol) and following the general procedure for glycal synthesis (C), 0.036 g (62%) of **15** were obtained, after purification by 'flash' chromatography eluting with 10:1 hexane–EtOAc.

Synthesis of **37** *from* **46**.—A total of 0.044 g of **46** (0.10 mmol) were treated under the general procedure conditions (C). The resulting residue was purified by column chromatography (10:1 hexane–EtOAc), to furnish 0.021 g (73%) of **37**.

Synthesis of **17** *from* **40** + **43**.—The mixture **40** + **43** (0.139 g, 0.24 mmol) was heated following the general procedure (C). The resulting residue was purified by 'flash' chromatography with neutral silica gel (20:1 hexane–EtOAc) to obtain glycal **17** (0.097 g, 94%).

*1,4-Anhydro-3,5-di-*O*-(*tert*-butyldiphenyl)-silyl-2-deoxy-*D*-erythro-pent-1-enitol* (**45**).—A 1:1 mixture of **41** and **44** (0.071 g, 0.09 mmol) was treated following the general procedure (C) to obtain 50 mg (89%) of glycal **45**, after purification by column chromatography (20:1 hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.8–7.2 (m, 20 H, Ph), 6.55 (dd, 1 H, $J_{1,2}$ 2.7, $J_{1,3}$ 0.7 Hz, H-1); 4.90 (td, 1 H, $J_{2,3}$ $J_{3,4}$ 2.7 Hz, H-2), 4.84 (t, 1 H, H-3), 4.47 (ddd, 1 H, $J_{4,5'}$ 5.7, $J_{4,5}$ 4.5 Hz, H-4), 3.41 (dd, 1 H, $J_{5,5'}$ 10.8 Hz, H-5), 3.58 (dd, 1 H, $J_{5,5'}$ 10.8 Hz, H-5′), 1.04 (s, 9 H, $3 \times CH_3$), 0.95 (s, 9 H, $3 \times$ Me); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 149.4 (C-1), 135.9, 135.8, 135.7, 134.1, 129.8, 129.7, 127.8, 127.7 (Ph), 103.4 (C-2), 89.1 (C-4), 76.8 (C-3), 63.7 (C-5), 26.8 (Me), 26.5 (Me), 19.1, 18.9. Anal. Calcd for $C_{37}H_{44}O_3Si_2$: C, 74.95; H, 7.48. Found C, 74.79; H, 7.40.

*1,4-Anhydro-3-*O*-benzyl-5-*O*-(*tert*-butyldiphenyl)silyl-2-deoxy-*D*-threo-pent-1-enitol*

(**50**).—Following the general procedure for glycal synthesis (C), 0.107 g (0.18 mmol) of the mixture of **47** and **49** afforded glycal **50** (0.065 g, 82%) as a colorless oil, after purification on neutral silica gel (15:1 hexane–EtOAc); $[\alpha]_D$ −6.78° (*c* 1.519, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.8–7.2 (m, 15 H, Ph), 6.61 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1); 5.24 (t, 1 H, $J_{2,3}$ 2.7 Hz, H-2), 4.61 (dd, 1 H, $J_{3,4}$ 6.9 Hz, H-3), 4.51 (d, 1 H, J_{AB} 12.0 Hz, CH_2Ph), 4.45 (d, 1 H, J_{AB} 12.0 Hz, CH_2Ph), 4.39 (q, 1 H, $J_{3,4} \approx J_{4,5} \approx J_{4,5'}$ 6.4 Hz, H-4), 4.18 (dd, 1 H, $J_{5,5'}$ 11.0 Hz, H-5), 4.03 (dd, 1 H, H-5′), 1.05 (s, 9 H, 3 × Me); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 150.6 (C-1), 138.6, 135.7, 135.7, 129.7, 128.4, 127.8, 127.5 (Ph), 101.6 (C-2), 84.9 (C-4), 79.2 (C-3), 70.8 (CH_2Ph), 61.4 (C-5), 26.7 (CH_3), 19.1 (CMe_3). Anal. Calcd for $C_{28}H_{32}O_3Si$: C, 75.64; H, 7.25. Found C, 75.41; H, 7.11.

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