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Stereoselective Synthesis of 2-Deoxy-2-phenylselenenyl Glycosides from Furanoses: Implication of the Phenylselenenyl Group in the Stereocontrolled Preparation of 2-Deoxy-*ribo*- and 2-Deoxy-*xylo*-oligosaccharides

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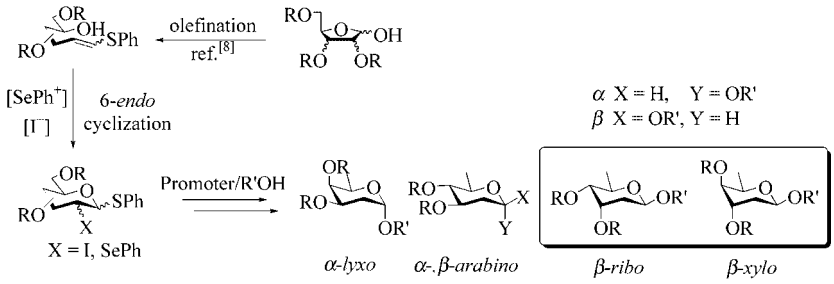
A series of 2-deoxy-2-phenylselenenyl-1-thioglycosides were evaluated as a class of glycosyl donors that provide access to 2-deoxyglycosides from furanoses. This short synthetic route involves olefination, selenonium ion mediated *6-endo* cyclization and glycosylation reactions. The cyclization reaction proceeds with complete regio- and stereoselectivity, which are enhanced by employing 3,4-*O*-isopropylidene as a cyclic bifunctional protecting group. The implication of the phenylselenenyl group at C-2 in the stereocontrolled preparation of 2-deoxyoligosaccharides is discussed. Its presence gives some insights into the likely pathway of glycosylation reactions by using 2-deoxy-2-phenylselenenyl-1-thioglycosyl donors in comparison with the previously described 2-deoxy-2-iodo derivatives. We also demonstrated that the glycosylation of 2-deoxy-2-phenylselenenyl-1-thioglycosides is highly substrate dependent, as well as particularly effective in providing 2-deoxy-2-phenylselenenyl-β-D-*gulo*- and -β-D-*allo*-glycosides.

Introduction

2-Deoxy- and 2,6-dideoxy carbohydrates are structurally important motifs present in many biologically active natural products.[1] The stereocontrolled formation of 2-deoxyglycosidic linkages represents one of the most challenging synthetic problems in carbohydrate chemistry.[2] Although in recent years a wide variety of methods[3,4] for the stereoselective synthesis of 2-deoxy- and 2,6-dideoxyglycosides have been developed, those involving special glycosyl donors[5] and 2-deoxy-2-X-glycosyl donors (X = Br, I, SPh and SePh) are still valuable and attractive[6,7]

As recently reported in our group, 2-deoxy-2-iodo-1-thioglycosides[8] were synthesized from pentoses and used as glycosyl donors for the stereocontrolled synthesis of 2-deoxy-2-iododisaccharides. This short synthetic route involves olefination, iodonium ion mediated *6-endo* cyclization and glycosylation reactions, and provides access to 2-deoxy-β-*hexo*-glycosides of D-*ribo* and D-*xylo* configuration (Scheme 1). Motivation to develop this new procedure prompted us to investigate 2-deoxy-2-phenylselenenyl-1-thioglycosides as a new class of glycosyl donors and evaluate



Scheme 1. Stereoselective synthesis of 2-deoxy- and 2,6-dideoxyglycosides of D-*lyxo*, D-*arabino*, D-*ribo* and D-*xylo* configurations through an olefination–cyclization–glycosylation sequence.

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the effect of the phenylselenenyl[9] group in the stereochemical outcome of the glycosylation reaction since there are no examples reported with 2-deoxy-2-phenylselenenyl-D-*gulo* and -D-*allo* glycosides.

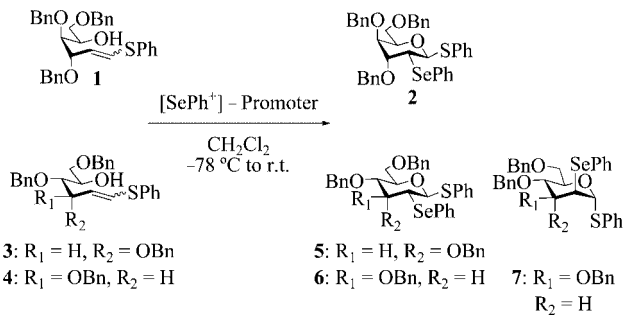
Results and Discussion

The first step in the proposed synthesis of 2-deoxy-2-phenylselenenyl-1-thioglycosides was the electrophile-induced cyclization (Scheme 1). For this purpose, vinyl sulfides **1**, **3**, **4**, **8** and **9** were easily prepared in one step from the corresponding protected furanoses and used as the starting materials.[8c]

In this context, functionalization of double bonds promoted by electrophilic selenium species was employed successfully for the synthesis of different versatile building blocks in organic synthesis.[10] When the alkene moiety is tethered to a nucleophilic substituent, intramolecular attack of the latter upon the intermediate selenonium ion takes place, leading to the corresponding cyclized product. Although different alkene derivatives, reagents and reaction conditions were employed for this general transformation,[11–13] no publication dealing with the electrophilic selenenylation reaction of carbohydrate-based vinyl sulfides has been reported to date.

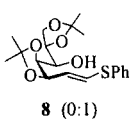
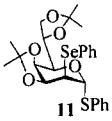
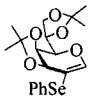
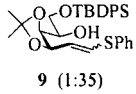
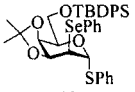
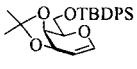
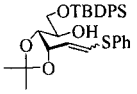
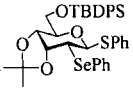
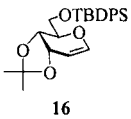
The reaction conditions for cyclization were optimized by starting from derivative **1** (Scheme 1). Initial attempts under basic conditions with the use of phenylselenenyl triflate (PhSeOTf)[14] proved ineffective as this selenenylating agent gave an inseparable mixture of products. However, when *N*-(phenylselenenyl)phthalimide (NPSP)[15] was employed without a promoter, expected product **2** was obtained in yields lower than 11% but with total regio- and stereoselectivity.[16]

Cyclization with NPSP and ZnI_2[17] as the promoter led to desired product **2** in a similar yield (<15%) maintaining the same regio- and stereoselectivity. The presence of the promoter allows the reaction to proceed under milder conditions. Other promoters such as (±)-camphor-10-sulfonic acid (CSA),[14] $Mg(ClO_4)_2$,[18] $SnCl_4$[19] and I_2[20] resulted in unsuccessful cyclization reactions. Other alkenyl sulfides such as D-*arabino* **3** and D-*ribo* **4** derivatives also reacted with similar selectivity, but the reactions were sluggish with yields lower than 15% (Scheme 2).The synthetic scope of the current cyclization method was examined by changing the structural patterns of the alkenyl sulfides (Table 1). The cyclization of 3,4-*O*-isopropylidene-protected derivative **8** proceeded smoothly and afforded desired thioglycoside **11** with complete α-selectivity in good yield (Table 1, Entry 1). Forcing the reaction conditions in the absence of ZnI_2 led to the formation of 2-phenylselenenyl glycal **12** in 34% yield together with small amounts of **11** (Table 1, Entry 2). Cyclization of 3,4-*O*-isopropylidene-protected D-*lyxo* **9** and D-*ribo* **10** derivatives also afforded thioglycosides **13** and **15**, respectively, in moderate yields (15–33%) and complete selectivity together with glycals **14** (60%) and **16** (74%) as major products (Table 1, Entries 3 and 4). These cyclization assays revealed that the cyclization conditions are very sensitive to the configuration, as well as the nature, of the hexenyl sulfide protecting groups. These experiments established that hydroxy hexenyl sulfides **8**–**10** undergo a completed 6-*endo* regioselective electrophilic selenium-induced cyclization enhanced by employing 3,4-*O*-isopropylidene as the cyclic bifunctional protecting group.[21] However, it is less obvious why phenylselenenyl-promoted cyclization led to such a different product distribution (thioglycosides, gly-



Scheme 2. Cyclization of tri-*O*-benzyl-protected alkenyl sulfides **1**, **3** and **4** to obtain 2-deoxy-2-phenylselenenylthioglycosides **2** and **5**–**7**.

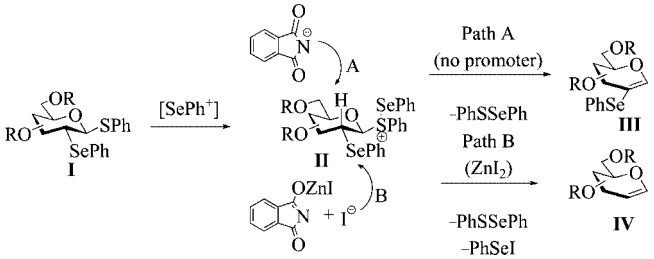
Table 1. Cyclization of 3,4-*O*-isopropylidene-protected alkenyl sulfides **8**–**10** induced by electrophilic selenium containing reagents.

Entry	Starting material (*Z*/*E* ratio)[a]	Cyclization conditions[b] equiv.	Cyclization product	Yield [%] (*α*/*β*)[c]
1	 **8** (0:1)	NPSP (2) ZnI_2 (2) –65 to –10°C, 3 h	 **11**	60[d] (1:0)
2	**8** (0:1)	NPSP (2) r.t., 15 h	**11**	11 (1:0)
			 **12**	34
3	 **9** (1:35)	NPSP (1.5) ZnI_2 (1.5) –78 to –50°C, 9 h	 **13**	33 (1:0)
			 **14**	60
4	 **10** (1:33)	NPSP (2) ZnI_2 (2) –78 to –30°C, 6.5 h	 **15**	15 (0:1)
			 **16**	74

[a] Determined by integration of the anomeric proton signals in the ^1H NMR spectrum after chromatographic purification. [b] Solvent = CH_2Cl_2. [c] Determined by integration of the anomeric proton signals in the ^1H NMR spectrum of the crude reaction mixture. [d] 10% of the corresponding glycal was also obtained.

cals and 2-phenylselenenyl glycals) related to the alkene substrate, although being performed under similar conditions.

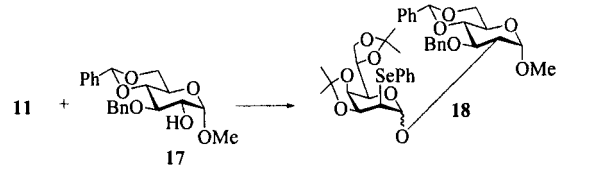
A plausible explanation for the observed product distribution is outlined in Scheme 3. The conversion of compound **I** into **III** represents an overall base-promoted PhSSePh elimination process, and might be occurring through initial *S*-phenylselenenylation followed by the elimination of a "phenylselenol equivalent" PhSSePh in **II** to give a 2-phenylselenenyl glycal. Similarly, the production of **IV** might be explained in terms of reductive elimination of PhSSePh–PhSeI in **II** to afford the corresponding glycal.[22]



Scheme 3. Plausible mechanism for the observed product distribution during the cyclization of 3,4-*O*-isopropylidene-protected alkenyl sulfides induced by electrophilic selenium species.

Having our target donor thioglycosides in hand, we turned our attention to the investigation of their glycosylation properties. On the basis of our experience with 2-deoxy-2-iodo-1-thioglycosides[8c] we anticipated that 2-deoxy-2-phenylselenenyl-1-thioglycosides **2**, **5**–**7**, **11** and **15** would have the reactivity characteristics that we desired. Thus, we found that the glycosylation of **11** with several promoters, such as NIS/TfOH, NIS/TMSOTf and dimethyl(methythio)-sulfonium fluoroborate (DMTSF) proceed smoothly at low temperature to give corresponding 2-deoxy-2-phenylselenenyl-glycoside **18** with high stereocontrol (α/β ratio range from 7:1 to 40:1) in moderate-to-good yields (21–68%). The results are summarized in Table 2. In NIS-promoted glycosylations the use of toluene/dioxane (1:3) enhanced α-selectivity[23] (Table 2, Entries 1 and 2). However, the most dramatic effect in terms of anomeric ratio is the nature of the promoter, as well as the counterion of the Lewis acid that activates the NIS. The best selectivities were obtained when DMTSF (Table 2, Entry 4) was used, followed by NIS/TMSOTf and TfOH, respectively (Table 2, Entries 2 and 3). Unfortunately, DMTSF and NIS/TMSOTf led to low yields of **18**.

Table 2. Optimization of the stereoselective glycosylation conditions of 2-deoxy-2-phenylselenenyl-1-thioglycoside **11** to obtain **18** containing reagents.

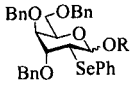
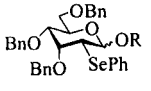
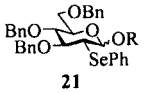
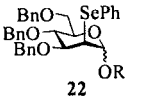
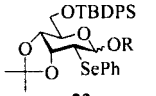


Entry[a]	Solvent (v/v)	Promoter (equiv.)	T [°C]	Yield [%] (α/β)[b]
1	CH_2Cl_2	NIS/TfOH (2/0.2)	–78	60 (7:1)
2	Toluene–Dioxane (1:3)	NIS/TfOH (2/0.2)	0	68 (15:1)
3	Toluene–Dioxane (1:3)	NIS/TMSOTf (1.2/0.6)	0	21 (25:1)
4[c]	CH_2Cl_2	DMTSF (2)	–78 to – 50	30 (40:1)

[a] Glycosyl donor **11** (1 equiv.) and glycosyl acceptor **17** (2 equiv.) were stirred with 4 Å MS at –78 or 0 °C for 1 h unless otherwise indicated. [b] Determined by integration of the anomeric proton signals in the ^{1}H NMR spectrum of the crude reaction mixture. [c] The reaction mixture was stirred from –78 to –50 °C for 2 h.

Accordingly, glycosylation reactions of **2**, **5**–**7** and **15** were performed by treating a mixture of the 2-deoxy-2-phenylselenenyl-1-thioglycosyl donor (1 equiv.) and glycosyl acceptor **17** (2 equiv.) with NIS (2.2 equiv.) and TfOH (0.2 equiv.) in toluene/dioxane (1:3) in the presence of 4 Å molecular sieves (Table 3). This procedure typically provides the desired products in good yields (50–70%). When

Table 3. Stereoselective glycosylation of **17** from 2-deoxy-2-phenylselenenyl-1-thioglycosides **2**, **5**–**7** and **15**.

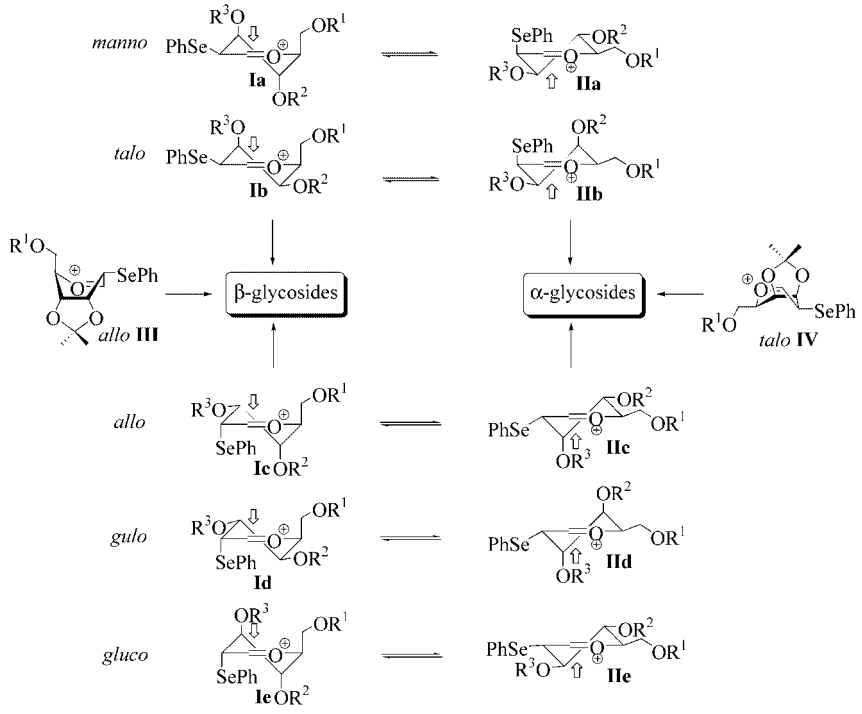
Entry[a]	Starting material	T [°C]	t [h]	Glycosylation product	Yield [%][b] (α/β)[c]
1	**2**	0	4	 **19**	50 (1:14)
2	**5**	0	1	 **20**	66 (1:4)
3	**6**	0	1	 **21**	55 (1:1)
4	**7**	0	1	 **22**	64 (15:1)
5	**15**	0 to r.t.	2	 **23**	70[d] (2:3)

[a] Glycosyl donor (1 equiv.), glycosyl acceptor (ROH) **17** (2 equiv.), NIS (2.2 equiv.), TfOH (20 mol-%), 4 Å MS, toluene/dioxane (1:3). [b] Determined by ^{1}H NMR spectroscopy in the presence of an internal standard unless otherwise indicated. [c] Determined by integration of the anomeric proton signals in the ^{1}H NMR spectrum of the crude reaction mixture. [d] Isolated yield.

compared with **5**, **6** and **15** (Table 3, Entries 2, 3 and 5), glycosyl donors **11** (Table 2) and **7** (Table 3, Entry 4) provided improved stereoselectivities. These results are in agreement with those reported by Roush and coworkers for the glycosylation of 2-deoxy-2-iodo-*manno*- and 2-deoxy-2-*talo*-pyranosyl acetates.[7i] However, an interesting result was obtained with gulose derivative **2** (Table 3, Entry 1). In this case, even using toluene/dioxane (1:3) as solvent system, the high β-selectivity observed is comparable to **11** (Table 2, Entry 2) and **7** (Table 3, Entry 4), as well as to that previously observed for analogous glycosylation reactions of 2-deoxy-2-iodo-1-thio-*gulo*-glycosyl donors in CH_2Cl_2 (α/β, 1:16).[8c] Interestingly, a similar behaviour was issued in previous studies with 2-deoxy-2-iodo-glucosyl trichloroacetimidates in which no improvement in the α/β ratio was found by changing solvent properties.[7d] Glycosyl donor **6** displayed no β-selectivity in agreement with prior studies with 2-phenylsulfanyl- and 2-phenylselenenyl-*gluco*-pyranosyl donors which indicated that selectivity was highly substrate dependent, and the 2-iodo substituent was found to be the more general stereodirecting group[9b,9c,24] (Table 3, Entry 3). Other glycosyl donors bearing an equatorial phenylselenenyl group such as **5** and **15** provided modest β-selectivities (Table 3, Entries 2 and 5).

In light of these results, we envisioned that oxocarbenium intermediates play an important role in the stereoselectivity of the glycosylation reactions of 2-deoxy-2-phenylselenenyl-1-thioglycosides rather than the corresponding selenonium ion intermediates.[7a,25] The selectivity is determined by both the ground-state conformational preferences of oxocarbenium intermediates **Ia**–**e** and **IIa**–**e** and the relative reactivity of each conformer, as mandated by Curtin–Hammet/Winstein–Holness kinetics[26] (Scheme 4). Thus, according to the results reported by Billings and coworkers,[27] PhSe-axial intermediates **IIa**,**b** (D-*manno* and D-*talo*) and **Ic**–**e** (D-*gluco*, D-*allo* and D-*gulo*) are likely to be more stable than the corresponding PhSe-equatorial conformers due to stabilizing hyperconjugative interactions between σ_{C-Se} and π^*_{C-O} of the oxocarbenium. Besides, it is known that nucleophilic attack on the oxocarbenium cations along a pseudoaxial trajectory to maximize overlap of the nucleophile HOMO with the LUMO of the oxocarbenium ion occurs with a facial preference to give a chair-like transition state. According to this stereoelectronic effect, the reaction of each conformer is expected to provide a different diastereomer of the product. However, the selectivity obtained in the glycosylation experiments cannot only be addressed in terms of relative conformer population but developing destabilizing interactions in the transition state (transition-state effects) should also be accounted for. Thus, the reactivity of the oxocarbenium conformers towards nucleophilic attack may be affected by steric interactions between the C-3 alkoxy substituent and the incoming nucleophile.

Consistent with this, glycosylation of D-*manno* **7** and D-*gulo* **2** derivatives provided excellent α- and β-selectivities, respectively; by far the more stable axial PhSe conformers **IIa** (D-*manno*) and **Id** (D-*gulo*) are also the more reactive ones towards nucleophilic attack. The D-*allo* derivative **5** showed moderate β-selectivity. When compared with the D-*gulo* derivative **2**, the lower selectivity magnitude obtained could be explained by ground-state conformational preference variations.



Scheme 4. Stereochemical courses of glycosylation reactions of 2-deoxy-2-phenylselenenyl-1-thioglycosyl donors.

In the D-*allo* derivative **5**, the more reactive conformer **Ic** is also the more stable one (axial PhSe) although in this case 1,3-diaxial interactions between PhSe and the C-4 alkoxy group may increase its energy with respect to the case of D-*gulo* derivative **2**, where such destabilizing interactions do not exist. The D-*gluco* donor **6** provided no selectivity, probably because the reactivity of the more stable PhSe-axial conformer **Ie** is seriously attenuated by steric interactions of the incoming nucleophile with the pseudoaxial C-3 substituent. Finally, to rationalize the observed β- and α-face approach of donors **15** and **11**, respectively, we speculated that the reaction might operate by way of a constrained conformation[21,7a] such as **III** and **IV** (Scheme 4). However, β-selectivity in 3,4-*O*-isopropylidene protected derivative **15** is lower than that observed in **5** suggesting that the relative enhancement of α-selectivity is, in this case, predominantly a temperature effect (Table 3, Entry 5).

Conclusions

We developed 2-deoxy-2-phenylselenenyl-1-thioglycosides as a new class of glycosyl donors that provide access to 2-deoxyglycosides. This short synthetic route involves olefination, iodonium ion mediated *6-endo* cyclization and glycosylation reactions. The olefination reaction affords the alkenyl sulfanyl derivatives in good-to-excellent yields. The cyclization reaction proceeds with complete regio- and stereoselectivity enhanced by employing 3,4-*O*-isopropylidene as cyclic bifunctional protecting group. We have also demonstrated that the glycosylation of 2-deoxy-2-phenylselenenyl-1-thioglycosides is highly substrate dependent. Although glycosylation products of all configurations can be accessed by employing the present methodology, it is particularly effective providing 2-deoxy-2-phenylselenenyl-β-D-*gulo* and -β-D-*allo*-glycosides. In particular, regardless of the nature of the solvent employed, the high β-selectivity observed in D-*gulo* **19** (α/β, 1:14) and D-*allo* **20** (α/β, 1:4) series is comparable to that previously observed for analogous glycosylation reactions of 2-deoxy-2-iodo-1-thio-D-*gulo* (α/β, 1:16) and -D-*allo*-glycosyl donors (α/β, 1:6). Furthermore, the use of the phenylselenenyl group at C-2 gave us insight into the likely pathway of glycosylation reactions by using 2-deoxy-2-phenylselenenyl-1-thioglycosyl donors. Since the stereoselectivity observed is similar to that obtained by using 2-deoxy-2-iodo-1-thioglycosides it can be concluded that this explanation is general for the different glycosylations assisted by chalcogens and halogens at C-2.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded with Varian Gemini 300 MHz and Varian Mercury 400 MHz spectrometers. TMS was used as an internal reference in all ^{1}H NMR spectra, and in the ^{13}C NMR spectra the residual solvent signal was used as an internal reference ($CDCl_3$, triplet at δ = 77.23 ppm) unless otherwise stated. Elemental analyses (C, H, N, S) were performed with a Carlo Erba EA 1108 Analyser in the Servei de Recursos Científics (URV). Optical rotations were recorded with a Perkin–Elmer 241 MC polarimeter in a 1-dm cell at 20 °C. Flash column chromatography was performed with silica gel 60 (E. Merck, 40–63 μm). Radial chromatography was performed on 1, 2 or 4 mm plates of Kieselgel 60 PF_{254} silica gel (E. Merck), depending on the amount of product. Solvents were purified by using standard procedures. Thin-layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F_{254} (E. Merck). Compounds were visualized by UV (254 nm), and also by spraying the TLC plates with 6% H_2SO_4 in EtOH, or 2% $PdCl_2$ and 15% H_2SO_4 in water, followed by charring at 150 °C for a few minutes. Starting materials **1**, **3**, **4**, **8** and **9** were prepared as described in the literature.[8c] All other reagents were used as received from commercial suppliers.

General Procedure for Electrophile-Induced Cyclization: A mixture of *N*-(phenylselenenyl)phthalimide (2 mmol) with or without a promoter (2 mmol) was added in one portion to a stirred solution of alkene (1 mmol) in dry CH_2Cl_2 (5 mL) at –78 °C. The reaction temperature was left to increase depending on the reactivity of the substrate (–78 °C to r.t.). After several hours of continuous stirring, the reaction mixture was poured into a 10% aqueous NaOH solution and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$ and concentrated. The residue was purified by chromatographic techniques.

Phenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylselenenyl-1-thio-β-D-gulopyranoside (2): Prepared following the general procedure above starting from **1** (*Z*/*E*, 1:2; 388 mg, 0.737 mmol), *N*-(phenylselenenyl)phthalimide (343.1 mg, 1.14 mmol) and ZnI_2 (362 mg, 1.14 mmol) in dry CH_2Cl_2 (13 mL). The reaction mixture was warmed from –40 °C to r.t. over 3 d. After the standard workup, the crude product was purified by radial chromatography (EtOAc/hexane, 1:3) to afford **2** (70.4 mg, 14%) as a yellowish syrup. R_f = 0.33 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.15 (m, 25 H, Ar), 5.24 (d, $J_{1,2}$ = 10.8 Hz, 1 H, 1-H), 4.50–4.37 (m, 6 H, 3 CH_2Ph), 4.16 (m, 1 H, 5-H), 3.80 (dd, $J_{3,2}$ = 3.2 Hz, $J_{3,4}$ = 6.8 Hz, 1 H, 3-H), 3.82 (dd, $J_{1,2}$ = 10.8 Hz, $J_{2,3}$ = 2.8 Hz, 1 H, 2-H), 3.64 (dd, $J_{6a,5}$ = 6.0 Hz, J = 9.6 Hz, 1 H, 6a-H), 3.59 (dd, $J_{6b,5}$ = 6.8 Hz, $J_{6a,b}$ = 9.6 Hz, 1 H, 6b-H), 3.46 (d, $J_{4,5}$ = 3.6 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.7, 138.5, 138.4, 138.1 (C, Ar), 134.8, 131.6, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.5 (CH, Ar), 86.0 (C-1), 76.9 (C-3), 74.9 (C-4), 73.7, 73.5, 73.1 (3 CH_2Ph), 72.5 (C-5), 63.4 (C-6), 47.2 (C-2) ppm.

Phenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylselenenyl-1-thio-β-D-allopyranoside (5): Prepared following the general procedure above starting from **3** (*Z*/*E*, 1:2; 100 mg, 0.190 mmol), *N*-(phenylselenenyl)phthalimide (114.8 mg, 0.380 mmol) and ZnI_2 (121.3 mg, 0.380 mmol) in dry CH_2Cl_2 (950 μL). The reaction mixture was warmed from –78 °C to 10 °C over 24 h. After standard workup, the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:3) to afford **5** (20 mg, 15%) as a yellowish syrup. R_f = 0.41 (EtOAc/hexane, 1:3). $[\alpha]_D^{20}$ = –15.7 (c = 0.90, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61–7.12 (m, 25 H, Ar), 5.23 (d, $J_{1,2}$ = 11.2 Hz, 1 H, 1-H), 4.99–4.44 (m, 6 H, 3 CH_2Ph), 4.30 (m, 1 H, 3-H), 4.14 (m, 1 H, 5-H), 3.77–3.67 (m, 3 H, 4,6a,b-H), 3.37 (dd, $J_{1,2}$ = 11.2 Hz, $J_{2,3}$ = 2.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.7, 138.6, 138.4, 138.0 (C, Ar), 134.6, 132.1, 129.3, 128.8, 128.7, 128.5, 128.4, 128.1, 128.3, 127.9, 127.7 (CH, Ar), 85.6 (1-C), 77.8 (C-3), 77.4 (C-4), 75.7 (C-5), 75.6, 73.6, 72.4 (3 CH_2Ph), 69.6 (C-6), 50.6 (C-2) ppm. $C_{39}H_{38}O_4SSe$ (681.74): calcd. C 68.71, H 5.62, S 4.70; found C 68.73, H 5.65, S 4.73.

Phenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylselenenyl-1-thio-β-D-*gluco*-pyranoside (6) and Phenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylselenenyl-1-thio-α-D-mannopyranoside (7): The title compounds were prepared following the general procedure above starting from **4** (*Z*/*E* ratio 2:5) (100 mg, 0.190 mmol), and *N*-(Phenylselenenyl)-phthalimide (114.8 mg, 0.380 mmol) in dry CH_2Cl_2 (950 μL). The reaction mixture was stirred at r.t. for 8 d. After standard workup, the crude was purified by radial chromatography (from hexane to 1:3 EtOAc/hexane) to afford **7** (5 mg, 4%) and **6** (6 mg, 5%) as a yellowish syrups, Data for **7**: R_f = 0.47 (1:3 EtOAc/hexane). $[\alpha]_D^{20}$ = –18.4 (*c* = 0.25, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.62–7.18 (m, 25 H, Ar), 5.71 (s, 1 H, 1-H), 4.92 (d, J_{AB} = 10.8 Hz, 1 H, CH_2Ph), 4.68 (d, J_{AB} = 12.4 Hz, 1 H, CH_2Ph), 4.65 (d, J_{AB} = 11.6 Hz, 1 H, CH_2Ph), 4.55 (d, J_{AB} = 11.6 Hz, 1 H, CH_2Ph), 4.54 (d, J_{AB} = 10.8 Hz, 1 H, CH_2Ph), 4.48 (d, J_{AB} = 12.4 Hz, 1 H, CH_2Ph), 4.35 (m, 1 H, 5-H), 4.17 (dd, $J_{3,4}$ = 8.8 Hz, $J_{2,3}$ = 4.4 Hz, 1 H, 3-H), 4.08 (d, $J_{2,3}$ = 4.4 Hz, 1 H, 2-H), 3.93 (dd, $J_{3,4}$ = 8.8 Hz, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.84 (dd, *J* = 11.2 Hz, $J_{6a,5}$ = 4.8 Hz, 1 H, 6a-H), 3.72 (dd, *J* = 11.2 Hz, $J_{6b,5}$ = 2 Hz, 1 H, 6b-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.7, 138.5, 138.4, 138.0 (C, Ar), 135.2,132.0, 129.4, 129.2, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6 (CH, Ar), 88.3 (C-1), 79.5 (C-3), 76.0 (C-4), 75.4, 73.5 (2 CH_2Ph), 73.2 (C-5), 71.7 (CH_2Ph), 69.2 (C-6), 50.8 (C-2) ppm. $C_{39}H_{38}O_4SSe$ (681.74): calcd. C 68.71, H 5.62, S 4.70; found C 68.68, H 5.64, S 4.69. Data for **6**: R_f = 0.40 (EtOAc/hexane, 1:3). $[\alpha]_D^{20}$ = –9.1 (*c* = 0.30, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.69–7.13 (m, 25 H, Ar), 5.11 (d, J_{AB} = 10 Hz, 1 H, CH_2Ph), 4.89 (d, J_{AB} = 10 Hz, 1 H, CH_2Ph), 4.81 (d, J_{AB} = 10.8 Hz, 1 H, CH_2Ph), 4.61–4.48 (m, 4 H, 1-H, CH_2Ph), 3.75–3.58 (m, 4 H, 3,5-H), 3.38 (m, 1 H, 4-H), 3.10 (dd, $J_{1,2}$ = $J_{2,3}$ = 10.8 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.7, 138.5, 138.3, 138.0 (C, Ar), 136.2, 132.8, 129.3, 128.9, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7 (CH, Ar), 87.4 (C-1), 84.4 (C-5), 79.8 (C-3), 79.2 (C-4), 76.2, 75.2, 73.6 (3 CH_2Ph), 69.1 (C-6), 49.8 (C-2) ppm. $C_{39}H_{38}O_4SSe$ (681.74): calcd. 68.71 C, 5.62 H, 4.70 S, found 68.70 C, 5.60 H, 4.72 S.

(*Z*/*E*)-6-*O*-(*tert*-Butyldiphenylsilyl)-3,4-*O*-isopropylidene-1,2-dideoxy-1-phenylsulfanyl-D-*ribo*-hex-1-enitol (10): As described in the literature,[8c] a solution of 5-*O*-(*tert*-butyldiphenylsilyl)-2,3-*O*-isopropylidene-α/β-D-ribofuranose (905 mg, 2.11 mmol) in dry THF (1.7 mL) was olefinated by treatment with diphenyl phenylsulfanylmethyl phosphane oxide (2.74 g, 5.28 mmol) in dry THF (57 mL), and *n*-BuLi (1.6 M in hexane, 5.8 mL, 9.28 mmol). After stirring at r.t. for 15 h, the reaction mixture was quenched, and the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:3) to afford **6** (443 mg, 40%) as an inseparable (*Z*/*E*) isomeric mixture (1:33) as a colourless syrup. Data obtained from the mixture: R_f = 0.60 (EtOAc/hexane, 1:3). $C_{31}H_{38}O_4SSi$ (534.78): calcd. C 69.62, H 7.16, S 6.00; found C 69.60, H 7.21, S 5.97. Data for (*E*)-**10**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.70–7.18 (m, 15 H, Ar), 6.53 (d, $J_{1,2}$ = 15.0 Hz, 1 H, 1-H), 5.98 (dd, $J_{1,2}$ = 14.8 Hz, $J_{2,3}$ = 6.8 Hz, 1 H, 2-H), 4.77 (dd, $J_{2,3}$ = 6.8 Hz, $J_{3,4}$ = 6.6 Hz, 1 H, 3-H), 4.15 (dd, $J_{3,4}$ = 6.0 Hz, $J_{4,5}$ = 8.8 Hz, 1 H, 4-H), 3.87 (dd, *J* = 10.1 Hz, $J_{6a,5}$ = 3.0 Hz, 1 H, 6a-H), 3.80 (dd, *J* = 10.1 Hz, $J_{6b,5}$ = 5.6 Hz, 1 H, 6b-H), 3.71–3.66 (m, 1 H, 5-H), 2.59 (d, *J* = 6.0 Hz, 1 H, OH), 1.37, 1.33 (s, 6 H, 2 CH_3), 1.08 (s, 9 H, 3 CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 135.7–126.8 (C, CH, Ar, C-1, C-2), 109.0 (C_{ketal}), 78.4 (C-3), 77.6 (C-4), 70.0 (C-5), 65.5 (C-6), 27.9, 25.6 (2 CH_3), 27.0 (CH_3, *t*Bu), 19.4 (C, *t*Bu) ppm.

Phenyl 2-Deoxy-3,4:6,7-di-*O*-isopropylidene-2-phenylselenenyl-1-thio-D-*glycero*-α-D-*talo*-heptopyranoside (11): Prepared following the general procedure above starting from **8** (*Z*/*E*, 0:1; 75 mg, 0.210 mmol), *N*-(phenylselenenyl)phthalimide (130 mg, 0.420 mmol) and ZnI_2 (134 mg, 0.420 mmol) in dry CH_2Cl_2 (3.6 mL). The reaction mixture was warmed from –65 °C to –10 °C over 3 h. After the standard workup, the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:3) to afford **11** (64 mg, 60%) as a yellowish syrup. R_f = 0.54 (EtOAc/hexane, 1:3). $[\alpha]_D^{20}$ = +45.7 (*c* = 0.005, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.78–7.24 (m, 10 H, Ar), 5.57 (d, $J_{1,2}$ = 10.0 Hz, 1 H, 1-H), 4.73 (dd, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 7.8 Hz 1 H, 3-H), 4.36 (dd, $J_{3,4}$ = 7.8 Hz, $J_{4,5}$ = 1.8 Hz, 1 H, 4-H), 4.20–4.16 (m, 1 H, 6-H), 3.94 (dd, $J_{7a,6}$ = 6.0 Hz, $J_{7a,b}$ = 8.5 Hz, 1 H, 7a-H), 3.85 (dd, $J_{7b,6}$ = 4.2 Hz, $J_{7a,b}$ = 8.5 Hz, 1 H, 7b-H), 3.60 (dd, $J_{4,5}$ = 1.8 Hz, $J_{5,6}$ = 8.2 Hz, 1 H, 5-H), 3.05 (dd, $J_{2,1}$ = 10.0 Hz, $J_{2,3}$ = 2.4 Hz, 1 H, 2-H), 1.48–1.33 (s, 12 H, 4 CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 136.0, 134.6, 131.8, 131.7, 129.4, 129.1, 128.9, 128.8, 127.5 (C, CH, Ar), 110.0, 109.7 (C_{ketal}), 88.3 (C-1), 75.7 (C-5), 74.0 (C-6), 73.3 (C-4), 70.5 (C-3), 67.2 (C-7), 43.8 (C-2), 27.2, 26.3, 25.4, 25.3 (4 CH_3) ppm. $C_{25}H_{30}O_5SSe$ (521.53): calcd. C 57.57, H 5.80, S 6.15; found C 57.59, H 5.78, S 6.15.

3,4:6,7-Di-*O*-Isopropylidene-2-phenylselenenyl-D-*glycero*-D-talal (12): Prepared following the general procedure above starting from **8** (*Z*/*E*, 0:1; 170 mg, 0.463 mmol), and *N*-(phenylselenenyl)phthalimide (280 mg, 0.925 mmol) in dry CH_2Cl_2 (2.3 mL). The reaction mixture was stirred at r.t. for 15 h. After the standard workup, the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:4) to afford **12** (60 mg, 34%) as a yellowish solid. M.p. 80–82 °C. R_f = 0.37 (EtOAc/hexane, 1:3). $[\alpha]_D^{25}$ = +133.4 (*c* = 1.3, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.19 (m, 5 H, Ar), 6.90 (s, 1 H, 1-H), 4.58 (d, $J_{3,4}$ = 6.0 Hz, 1 H, 3-H), 4.51 (dd, $J_{4,3}$ = 6.0 Hz, $J_{4,5}$ = 0.8 Hz, 1 H, 4-H), 4.40 (dt, $J_{6,7a}$ = $J_{6,7b}$ = 5.6 Hz, $J_{6,5}$ = 7.6 Hz, 1 H, 6-H), 4.13 (d, $J_{7a,6}$ = $J_{7b,6}$ = 5.6 Hz, 2 H, 7ab-H), 3.91 (dd, $J_{5,6}$ = 7.6 Hz, $J_{5,4}$ = 0.8 Hz, 1 H, 5-H), 1.45, 1.38 (s, 12 H, 4 CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 151.1 (C-1), 131.1, 129.3, 127.0 (C, CH, Ar), 111.1, 109.8 (C_{ketal}), 106.4 (C-2), 75.7 (C-5), 74.1 (C-6), 72.8 (C-4), 71.6 (C-3), 66.7 (C-7), 28.0, 27.1, 27.0, 25.4 (4 CH_3) ppm. $C_{19}H_{24}O_5Se$ (411.35): calcd. C 55.48, H 5.88; found C 55.43, H 5.86.

Phenyl 6-*O*-(*tert*-Butyldiphenylsilyl)-2-deoxy-3,4-*O*-isopropylidene-2-phenylselenenyl-1-thio-α-D-talopyranoside (13) and Phenyl 6-*O*-(*tert*-Butyldiphenylsilyl)-3,4-*O*-isopropylidene-D-galactal (14): Prepared following the general procedure above starting from **9** (*Z*/*E*, 1:35; 160 mg, 0.299 mmol), *N*-(phenylselenenyl)phthalimide (135.6 mg, 0.449 mmol) and ZnI_2 (143.2 mg, 0.449 mmol) in dry CH_2Cl_2 (1.5 mL). The reaction mixture was warmed from –78 °C to –50 °C over 9 h. After the standard workup, the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:3) to afford **13** (41.3 mg, 33%) and **14** (76.1 mg, 60%) as yellowish syrups. Data for **13**: R_f = 0.5 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.79–7.18 (m, 20 H, Ar), 5.48 (d, $J_{1,2}$ = 9.6 Hz, 1 H, 1-H), 4.67 (m, 1 H, 3-H), 4.28 (dd, $J_{3,4}$ = 7.6 Hz, $J_{4,5}$ = 1.6 Hz, 1 H, 4-H), 3.99–3.90 (m, 1 H, 5-H), 3.82–3.72 (m, 2 H, 6a,b-H), 3.08 (dd, $J_{1,2}$ = 9.6 Hz, $J_{2,3}$ = 2.8 Hz, 1 H, 2-H), 1.40, 1.33 (s, 6 H, 2 CH_3), 1.02 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.1–136.4 (C, CH, Ar), 136.0–127.6 (CH, Ar), 109.8 (C_{ketal}), 88.1 (C-1), 75.8 (C-3), 74.3 (C-4), 70.4 (C-5), 62.7 (C-6), 44.3 (C-2), 27.0, (CH_3, *t*Bu), 26.4, 25.5 (2 CH_3), 19.5 (C, *t*Bu) ppm. Spectroscopic data for **14** consistent with those reported.[8b]

Phenyl 6-(*O*-*tert*-Butyldiphenylsilyl)-2-deoxy-3,4-*O*-isopropylidene-2-phenylselenenyl-1-thio-β-D-allopyranoside (15) and Phenyl 6-*O*-(*tert*-Butyldiphenylsilyl)-3,4-*O*-isopropylidene-D-allal (16): Prepared

following the general procedure above starting from **10** (*Z*/*E*, 1:33; 443 mg, 0.854 mmol), *N*-(phenylselenenyl)phthalimide (516.1 mg, 1.71 mmol) and ZnI_2 (545 mg, 1.71 mmol) in dry CH_2Cl_2 (15 mL). The reaction mixture was warmed from –78 °C to –30 °C over 6.5 h. After the standard workup, the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:3) to afford **15** (90 mg, 15%) and **16** (270 mg, 74%) as yellowish syrups. Data for **15**: R_f = 0.86 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.72–7.18 (m, 20 H, Ar), 5.12 (d, $J_{1,2}$ = 11.2 Hz, 1 H, 1-H), 4.31 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 4.0 Hz, 4.01 H, 3-H), 3.84 (m, 1 H, 4-H), 3.76 (dd, $J_{6a,5}$ = 6.2 Hz, $J_{6a,b}$ = 11.4 Hz, 1 H, 6a-H), 3.65–3.61 (m, 1 H, 5-H), 3.55 (dd, $J_{2,1}$ = 11.2 Hz, $J_{2,3}$ = 4.0 Hz, 1 H, 2-H), 1.39, 1.36 (s, 6 H, 2 CH_3), 1.05 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (°100.6 MHz, $CDCl_3$, 25 °C): δ = 135.0–127.4 (C, CH, Ar), 109.4 (C_{ketal}), 86.0 (C-1), 79.6 (C-5), 75.4 (C-3), 71.5 (C-4), 64.0 (C-6), 43.4 (C-2), 28.5, 26.2 (2 CH_3), 27.0 (CH_3, *t*Bu), 19.4 (C, *t*Bu) ppm. Data for **16**: R_f = 0.78 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.72–7.19 (m, 25 H, Ar), 6.64 (d, $J_{1,2}$ = 5.6 Hz, 1 H, 1-H), 5.08 (dd, $J_{1,2}$ = 5.6 Hz, $J_{2,3}$ = 5.4 Hz, 1 H 2-H), 4.44 (dd, $J_{2,3}$ = 5.4 Hz, $J_{3,4}$ = 5.2 Hz 1 H, 3-H), 4.10 (m, 1 H, 4-H), 4.03 (dd, $J_{6a,5}$ = 1.2 Hz, J = 11.5 Hz, 1 H, 6a-H), 3.93 (dd, $J_{6b,5}$ = 5.2 Hz, $J_{6ba,b}$ = 11.5 Hz, 1 H, 6b-H), 3.50–3.47 (m, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 148.5 (C-1), 135.0–127.4 (C, CH Ar), 108.4 (C_{ketal}), 98.7 (C-2), 76.4 (C-5), 70.2 (C-4), 67.8, (C-3), 63.0 (C-6), 28.7, 26.0 (2 CH_3), 27.0 (CH_3, *t*Bu), 19.5 (C, *t*Bu) ppm.

General Procedure for Glycosylation: A solution of the glycosyl donor (1 mmol) and the glycosyl acceptor (2 mmol) in toluene/dioxane (1:3, 23 mL) was stirred with 4 Å molecular sieves for 2 h at 0 °C. NIS (2.2 mmol) and TfOH (0.2 mmol) were added at the same temperature. The reaction mixture was then diluted with CH_2Cl_2 and washed with a solution of $Na_2S_2O_3$. The combined organic layers were dried with $MgSO_4$ and concentrated.

Methyl (2′-Deoxy-3′,4′:6′,7′-di-*O*-isopropylidene-2′-phenylselenenyl-D-*glycero*-α/β-D-*talo*-heptopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (18): Prepared following the general procedure above starting from **8** (51 mg, 0.098 mmol), glycosyl acceptor **17** (72 mg, 0.196 mmol), NIS (53 mg, 0.216 mmol), TfOH (2 μL, 0.020 mmol) and 4 Å MS (100 mg) in toluene/dioxane (1:3, 400 μL). The reaction mixture was stirred at 0 °C for 1 h. After the standard workup, the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:3) to afford **18** (52 mg, 68%) as an inseparable 15:1 α/β mixture as a yellowish syrup. Data obtained from the mixture: R_f = 0.39 (EtOAc/hexane, 1:3). $C_{40}H_{48}O_{11}Se$ (783.76): calcd. C 61.30, H 6.17; found C 61.25, H 6.20. Data for **18**α: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.80–7.19 (m, 15 H, Ar), 5.57 (s, 1 H, 7-H), 5.21 (d, $J_{1′,2′}$ = 7.6 Hz, 1 H, 1′-H), 4.88 (d, $J_{1,2}$ = 2.0 Hz, 1 H, 1-H), 4.84 (d, J_{AB} = 12.4 Hz, 1 H, CH_2Ph), 4.78 (d, J_{AB} = 12.4 Hz, 1 H, CH_2Ph), 4.77 (dd, $J_{3′,2′}$ = 2.4 Hz, $J_{3′,4′}$ = 7.6 Hz, 1 H, 3′-H), 4.37 (dd, $J_{3′,4′}$ = 7.6 Hz, $J_{4′,5′}$ = 1.6 Hz, 1 H, 4′-H), 4.32 (dd, $J_{7a′,6′}$ = 3.4 Hz, $J_{7a′,7b′}$ = 8.5 Hz, 1 H, 7a′-H), 4.27 (dd, $J_{6a,5}$ = 4.8 Hz, J = 10.0 Hz, 1 H, 6a-H), 4.24–4.20 (m, 1 H, 6′-H), 4.03 (dd, $J_{7b′,6′}$ = 6.0 Hz, $J_{7b′,7a′}$ = 8.5 Hz, 1 H, 7′b-H), 4.00–3.93 (m, 2 H, 2-H, 4-H), 3.84 (ddd, $J_{5,4}$ = 9.9 Hz, $J_{5,6a}$ = 4.4 Hz, $J_{5,6b}$ = 10.0 Hz, 1 H, 5-H), 3.74 (dd, $J_{6b,5}$ = 10.0 Hz, J = 10.0 Hz, 1 H, 6b-H), 3.62 (dd, $J_{3,2}$ = 8.0 Hz, $J_{3,4}$ = 8.0 Hz, 1 H, 3-H), 3.52 (dd, $J_{5′,4′}$ = 1.6 Hz, $J_{5′,6′}$ = 8.5 Hz), 3.30 (s, 3 H, OCH_3), 3.00 (dd, $J_{2′,1′}$ = 7.0 Hz, $J_{2′,3′}$ = 2.4 Hz), 1.49–1.33 (s, 12 H, 4 CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.9–130.5 (C, CH Ar), 134.6–126.3 (CH, Ar), 109.9, 109.5 (C_{ketal}), 101.6 (C-7), 99.3 (C-1′), 98.0 (C-1), 82.3 (C-3),76.1 (C-3′), 75.7 (C-2, C-4), 74.5 (CH_2Ph), 74.3 (C-4′), 73.6 (C-6′), 70.5 (C-5′), 69.4 (C-6), 67.2 (C-7′), 62.6 (C-5), 55.5 (OCH_3), 45.0 (C-2′), 27.4–25.1 (4 CH_3) ppm.

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-2′-phenylselenenyl-α/β-D-gulopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (19): Data obtained from the crude reaction mixture of **19**β: R_f = 0.30 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.83–7.16 (m, 30 H, Ar), 5.54 (s, 1 H, 7-H), 5.00 (d, 1 H, $J_{1′–2′}$ = 9.0 Hz, 1′-H), 4.97–4.64 (m, 10 H, 4 CH_2Ph, 1-H, 2′-H), 4.23–3.80 (m, 3 H, 6a-H, 5′-H, 3-H), 3.80–3.45 (m, 7 H, 5-H, 3′-H, 2-H, 6b-H, 4-H, 6′a,b-H), 3.38–3.30 (m, 4 H, OCH_3, 4′-H) ppm.

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-2′-phenylselenenyl-α/β-D-*allo*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*gluco*-pyranoside (20): Data obtained from the crude reaction mixture of **20**β: R_f = 0.30 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61–7.12 (m, 30 H, Ar), 5.53 (s 1 H, 7-H), 5.33 (d, $J_{1′,2′}$ = 8.8 Hz, 1 H, 1′-H), 4.92 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1-H), 4.98–4.49 (m, 8 H, 4 CH_2Ph), 4.29 (dd, J = 9.5 Hz, $J_{5,6a}$ = 4.4 Hz, 1 H, 6a-H), 4.28–3.59 (m, 11 H, 2,3,4,5,6b-H, 2′,3′,4′,5′,6′a,b-H), 3.39 (s, 3 H, OCH_3) ppm.

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-2′-phenylselenenyl-α/β-D-*gluco*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (21): Data obtained from the crude reaction mixture of **21**α: R_f = 0.30 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.69–7.13 (m, 30 H, Ar), 5.57 (s 1 H, 7-H), 4.98–4.28 (m, 12 H, 4 CH_2Ph, 1,2-H, 1′,2′-H), 4.29 (dd, J = 9.6 Hz, $J_{5,6a}$ = 4 Hz, 1 H, 6a-H), 4.09 (m, 1 H, 3-H), 3.93–3.36 (m, 8 H, 4,5,6b-H, 3′,4′,5′,6′a,b-H), 3.36 (s, 3 H, OCH_3) ppm. Data for **21**β: R_f = 0.30 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.69–7.13 (m, 30 H, Ar), 5.52 (s 1 H, 7-H), 5.02 (d, $J_{1′,2′}$ = 8.9 Hz, 1 H, 1′-H), 4.98–4.28 (m, 11 H, 4 CH_2Ph, 1,2-H,2′-H), 4.29 (dd, J = 9.6 Hz, $J_{5,6a}$ = 4 Hz, 1 H, 6a-H), 4.09 (m, 1 H, 3-H), 3.93–3.36 (m, 8 H, 4,5,6b-H, 3′,4′,5′,6′a,b-H), 3.44 (s, 3 H, OCH_3) ppm.

Methyl (3′,4′,6′-Tri-*O*-benzyl-2′-deoxy-2′-phenylselenenyl-α/β-D-*manno*-pyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*gluco*-pyranoside (22): Data obtained from the crude reaction mixture of **22**α: R_f = 0.30 (EtOAc/hexane, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.18 (m, 30 H, Ar), 5.51 (s, 1 H, 7-H), 5.09 (s, 1 H, 1′-H), 4.98–4.34 (m, 10 H, 4 CH_2Ph, 1-H, 2′-H), 4.24 (dd, J = 9.6 Hz, $J_{5,6a}$ = 4 Hz, 1 H, 6a-H), 4.14 (m, 1 H, 5′-H), 3.92–3.63 (m, 7 H, 2,4,5,6b-H, 4′,6′a,b-H), 3.59 (m, 1 H, 3-H), 3.45 (s, 3 H, OCH_3), 3.41 (m, 1 H, 3′-H) ppm.

Methyl [(6′-*O*-*tert*-Butyldiphenylsilyl)-3′,4′-*O*-isopropylidene-2′-deoxy-2′-phenylselenenyl-α/β-D-allopyranosyl]-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (23): Prepared following the general procedure above starting from **15** (90 mg, 0.130 mmol), glycosyl acceptor **17** (97 mg, 0.260 mmol), NIS (71 mg, 0.286 mmol), TfOH (2.5 μL, 0.026 mmol) and 4 Å MS (180 mg) in toluene/dioxane (1:3, 520 μL). The reaction mixture was warmed from 0 °C to r.t. for 2 h. After the standard workup, the crude product was purified by radial chromatography (hexane, then EtOAc/hexane, 1:3) to afford **23** (88 mg, 70%) as an inseparable 2:3 α/β mixture as a yellowish syrup. R_f = 0.33 (EtOAc/hexane, 1:3). $C_{52}H_{60}O_{10}SeSi$ (952.07): calcd. C 65.60, H 6.35; found C 65.57, H 6.38. Data for **23**α: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.85–7.23 (m, 25 H, Ar), 5.56 (s, 1 H, 7-H), 5.35 (d, $J_{1,2}$ = 8.8 Hz, 1 H, 1′-H), 5.04 (d, J_{AB} = 10.2 Hz, 1 H, CH_2Ph), 4.91 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-Ha), 4.81 (d, J_{AB} = 10.2 Hz, 1 H, CH_2Ph), 4.55 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 4.0 Hz, 1 H, 3′-Ha), 4.34–4.30 (m, 1 H, 6a-H), 4.13–4.07 (m, 1 H, 3-H), 4.01–3.55 (m, 5 H, 2,5,6b-H, 4′,5′-H), 3.50–3.39 (m, 5 H, OCH_3, 4-H, 2′-H), 1.41–1.24 (6 H, 2 CH_3), 1.06 (9 H, 3 CH_3, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.7–126.2 (CH, Ar), 109.7 (C_{ketal}), 102.7 (C-1′), 101.5 (C-7), 100.7 (C-1), 82.8 (C-

4), 79.1 (C-5′), 78.5–77.1 (C-2, C-3, CH_2Ph), 78.5–77.1 (C-2, C-3, CH_2Ph), 75.3 (C-3′), 72.0 (C-4′), 69.5, 69.4 (C-6, C-6′), 63.8 (C-5), 55.6 (OCH_3), 44.7 (C-2′), 29.8–23.9 (2 CH_3, 3 CH_3, *t*Bu), 19.5 (C, *t*Bu), 19.5 (C, *t*Bu) ppm. Data for **23**β: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.85–7.23 (m, 25 H, Ar), 5.57 (s, 1 H, 7-H), 5.15 (d, $J_{1,2}$ = 9.0 Hz, 1 H, 1′-H), 5.11 (d, J_{AB} = 10.6 Hz, 1 H, CH_2Ph), 4.98 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.86 (d, J_{AB} = 10.6 Hz, 1 H, CH_2Ph), 4.47 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 4.0 Hz, 1 H, 3′-H), 4.34–4.30 (m, 1 H, 6a-H), 4.18 (dd, $J_{2,3}$ = 4.0 Hz, $J_{2,1}$ = 9.0 Hz, 1 H, 2′-H), 4.13–4.07 (m, 1 H, 3-H), 4.01–3.55 (m, 5 H, 2,5,6b-H, 4′,5′-H), 3.50–3.39 (m, 4 H, OCH_3, 4-H), 1.41–1.24 (6 H, 2 CH_3), 1.06 (9 H, 3 CH_3, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.7–126.2 (CH, Ar), 109.2 (C_{ketal}), 102.2 (C-1′), 101.5 (C-7), 100.4 (C-1), 82.9 (C-4), 79.1 (C-5′), 78.5–77.1 (C-2, C-3, CH_2Ph), 75.4 (C-3′), 71.6 (C-4′), 69.4, 69.3 (C-6, C-6′), 63.6 (C-5), 55.4 (OCH_3),44.7 (C-2′), 29.8–23.9 (2 CH_3, 3 CH_3, *t*Bu), 19.5 (C, *t*Bu) ppm.

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