Studies on the Synthesis of Aureolic Acid Antibiotics: Highly Stereoselective Synthesis of Aryl 2-Deoxy-β-glycosides via the Mitsunobu Reaction and Synthesis of the Olivomycin A−B Disaccharide

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Abstract: The Mitsunobu reaction of phenols and 1,2-*cis*-2-thiophenyl-α-D-glycopyranoses or 1,2-*cis*-2-selenophenyl-α-D-glycopyranoses is a very effective method for the highly stereoselective synthesis of aryl 2-deoxy-β-D-glycosides. The equatorial 2-thiophenyl or 2-selenophenyl- substituents are easily removed by Bu_3SnH reduction following the glycosidation reaction to provide the aryl 2-deoxy-β-D-glycosides in good to excellent yield. The aryl β-D-glycosides are obtained with 6.5:1 selectivity in the least selective case (Table 1) and up to >20:1 selectivity in others. The reaction appears to be S_N2-like in character (see **30**), in that the β:α reaction stereoselectivity correlates well with the α:β anomeric composition of the pyranose starting material. The equatorial 2-thiophenyl or 2-selenophenyl substituents play an important role by increasing the α: β anomer ratio of the pyranose starting materials. The reactions do not appear to proceed by way of free oxonium ions such as **17**, since several reactions in which **17** was deliberately generated (e.g., TMS-OTf promoted reactions of glycosyl acetate **14**, $BF_3{\cdot}Et_2O$ catalyzed reactions of imidate **15**) gave at best 1:1 mixtures of α- and β-glycosides, and in several cases gave α-glycosides with >10:1 selectivity. These data also rule out the involvement of episulfonium ion **18** as a kinetically significant intermediate in reactions that proceed by way of oxonium ion **17**. A short and highly effective synthesis of reducing disaccharide **53** from D-fucal was developed. This functionalized disaccharide readily undergoes Mitsunobu glycosidation with 2-naphthol, providing the model naphthyl A−B disaccharide **5** with 11:1 β,α:α,α selectivity. Finally, olivin precursor **63** has also been glycosylated with **53**, providing the advanced synthetic intermediate **6** with excellent diastereoselectivity.

Olivomycin A (**1**), chromomycin A_3 (**2**), and mithramycin (**3**) are the most well-known members of the aureolic acid antitumor antibiotic family.[2] The aureolic acids are inhibitors of DNA-dependent RNA polymerase and are known to bind as 2:1 antibiotic:Mg^{2+} complexes in the DNA minor groove with selectivity for GC rich sequences.[3−5] Mithramycin has been shown to bind to the GC rich promoter region of the c-myc protooncogene, thereby preventing its translation, leading to the suggestion that this may be the molecular basis of the antitumor activity of the drug.[6] Available structure activity data indicate that the two intact oligosaccharide chains are essential for DNA binding and biological activity.[2,7] Moreover, Kahne has shown that the complete C−D−E trisaccharide is required for formation of the 2:1 complex with Mg^{2+}.[5] Kahne has also recently demonstrated that the simplified TEG−chromophore conjugate **4** forms 2:1 complexes with Mg^{2+}, and has indicated that the $[\mathbf{4}]_2Mg^{2+}$ complex interacts with DNA.[8]

Although the aureolic acids have been used as chemotherapeutic agents, they are highly toxic and have found limited application except in severe cases.[2] With the ultimate goal of developing less toxic analogs and understanding the role of the oligosaccharides in the DNA binding and recognition events,[9] we are pursuing a total synthesis of olivomycin A.[10] Thus far, our two syntheses of olivin are the only approaches that provide

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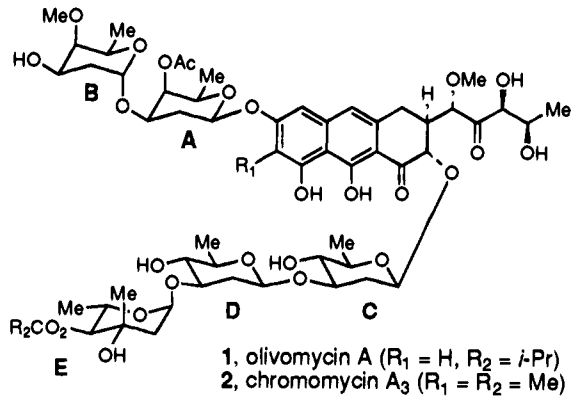
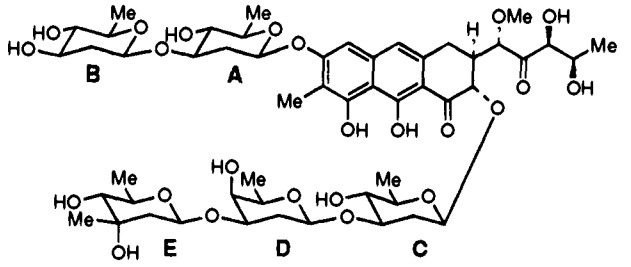
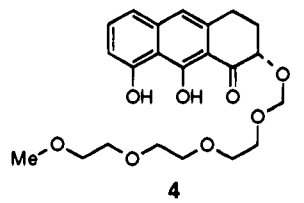


1, olivomycin A (R_1 = H, R_2 = *i*-Pr)
2, chromomycin A_3 (R_1 = R_2 = Me)



mithramycin (**3**)



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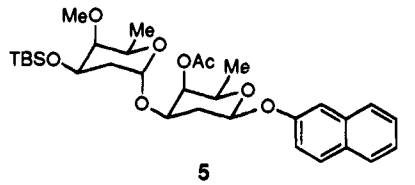
an aglycon in fully deprotected form.[11,12] Concerning the oligosaccharides, Thiem has reported stereostructure assignments and pioneering syntheses of the A−B disaccharides and C−D−E trisaccharides of **1**−**3**.[13−15] Binkley,[16] Franck,[17] Crich,[18] and Toshima[19] have also made important contributions toward the synthesis of the A−B and C−D−E oligosaccharides.

We have synthesized the olivomycin A−B disaccharide,[20] the olivomycin C−D−E trisaccharide,[21] and an A−B disaccharide corresponding to the originally assigned (but incorrect)[13,14b,d,15] mithramycin structure.[20b] We have also developed a highly diastereoselective procedure for the synthesis of aryl 2-deoxy-β-glycosides, as occurs between the A−B disaccharides and the aglycons in all of the aureolic acids, via the Mitsunobu reaction.[22]

We describe herein our developmental studies of the Mitsunobu glycosidation procedure for the synthesis of aryl 2-deoxy-β-glycosides. Applications of this methodology to the synthesis of model olivomycin A−B aryl disaccharides **5** and **6** are also described. Preliminary accounts of portions of this work have appeared.[20b,22]



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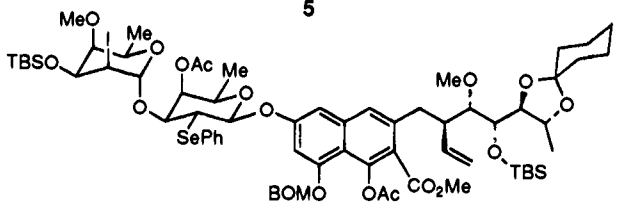

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Background: Methods for the Synthesis of 2-Deoxy-β-Glycosides. The synthesis of the aureolic acid antibiotics is a formidable challenge, particularly in view of the stereochemical features of the oligosaccharide substructures:[23] three out of the five glycosidic linkages are β for olivomycin A and chromomycin A_3, whereas all five of the glycosidic bonds are β in mithramycin. While 2-deoxy-α-glycosides are generally easily prepared either from glycals[24,25] or activated 2-deoxysugar precursors[23a] (e.g., glycosyl halides,[14a,26] acyl glycosides,[27] thioglycosides,[28] or sulfoxides[29]), no completely general or broadly applicable methods for the formation of the troublesome 2-deoxy-β-glycosidic linkage from 2-deoxyhexose precursors

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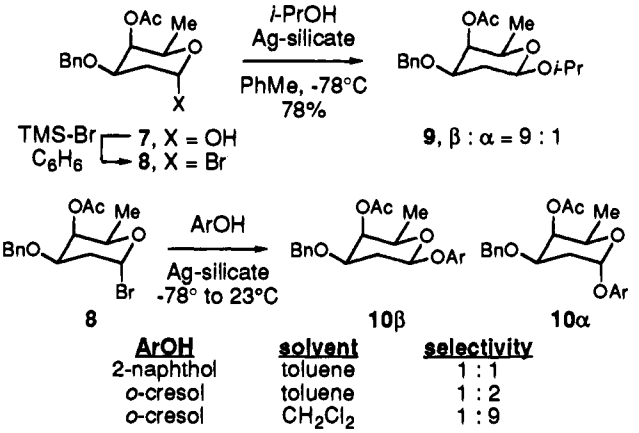
yet exist. The main problem associated with the stereoselective synthesis of 2-deoxy-β-glycosides derives from the fact that the activated donors are very reactive, owing to the absence of inductively stabilizing C(2) heteroatom substituents.[30] Consequently, most of the glycosylation reactions proceed by way of oxonium ion (or ion pair) intermediates. In the absence of a neighboring group at C(2), the substitution reactions proceed via axial addition of the alcohol acceptor to C(1) of the donor cation since this transition state is stabilized by a developing anomeric effect.[31]

The most successful procedure for the direct synthesis of 2-deoxy-β-glycosides from 2-deoxyhexose precursors is the silver silicate mediated reaction of alcohols and 2-deoxypyranosyl bromides.[16,32] This reaction with 2-alkoxy-sugars is believed to proceed by an S_N2 substitution of surface-bound α-D-glycopyranosyl bromide,[32] although it is also possible that the reaction proceeds by way of a complex between the pyranosyl cation and the insoluble, anionic catalyst, which effectively blocks the α face from attack by the alcohol. The selectivity of this method, however, is highly dependent on the combination of protecting groups at the C(3) and C(4) hydroxyl groups of the pyranose donor and on the reactivity of the acceptor.[32a,33] Moreover, application of this method to the glycosylation of *o*-cresol with a 2-deoxypyranosyl bromide gave only a 3:1 mixture of the β/α aryl glycosides.[16b] Other more generally applicable (but indirect) procedures rely on neighboring group assistance involving equatorial C(2) heteroatom substituents (−Br,[14c,34] −SAr,[17,35] −SePh,[36] −OAc,[37] and −NHCHO[37b,38]) that are removed reductively after the glycosylation event. Still another strategy involves the Bu_3SnH reduction of radical intermediates generated at the anomeric position.[18,39] However, application of these methods to the synthesis of aryl glycosides have met with modest success. For example, substituted phenyl 2-deoxy-β-D-glucopyranosides have been prepared with up to 5.7:1 selectivity via the phenylbis(phenylthio)sulfonium salt mediated electrophilic functionalization of tribenzyl D-glucal and aryl tributylstannyl ethers.[17b,c] On the other hand, 4-cresyl 2-deoxy-β-D-galactopyranoside has been prepared with 16:1 selectivity via the radical reduction of the corresponding ulosonate ester.[39b] However, the overall yield of the 2-deoxy-β-glycoside was only 18% for the two key steps.

After our work was completed, two additional procedures for the synthesis of aryl 2-deoxy-β-glycosides were published. The first involves the reaction of 1,2-anhydro sugars, prepared by dimethyldioxirane oxidation of glycals, with phenolate anions.[40] This method provides the aryl β-glycosides with excellent selectivity and in good yield, which are readily deoxygenated via radical chemistry to the targeted aryl 2-deoxy-β-glycosides. The second method involves the TMS-OTf promoted 1,2-trans-glycosidation reactions of 1,2-*cis*-2-(*p*-methoxyphenylthio)-α-D-glycopyranosyl phosphoroamidate donors.[41] Whereas this procedure gave excellent β/α selectivity in glycosylations of alcohols, the reaction of the *galacto*-pyranose donor [the configuration required for the synthesis of olivomycin or chromomycin] with 2-naphthol provided a 72:28 mixture favoring the α-aryl glycoside.

Results and Discussion

Initial Experiments. Although Binkley had shown that the silver silicate mediated glycosylation of cresol and a 2-deoxypyranosyl bromide provided the aryl 2-deoxy-β-glycoside with only 3:1 selectivity,[16b] the experimental simplicity of this approach prompted us to consider adopting this methodology for the synthesis of aryl 2-deoxy-β-glycosides related to the aureolic acids. Thus, the readily available monosaccharide **7**[20a] was converted into α-bromide **8**.[42] Although the reaction of **8** with *i*-PrOH gave excellent selectivity (9:1) for the β-glycoside, the reaction of **8** with representative phenols under comparable conditions (−78 °C to 23 °C) gave at best 1:1 mixtures of the β and α glycosides. Interestingly, when the reaction with *o*-cresol was performed in CH_2Cl_2 rather than toluene, α-glycoside **10α** was obtained with 9:1 selectivity.



ArOH	solvent	selectivity
2-naphthol	toluene	1 : 1
o-cresol	toluene	1 : 2
o-cresol	CH_2Cl_2	1 : 9

These results prompted us to initiate studies of glycosylation reactions with donors containing C(2)-neighboring group sub-

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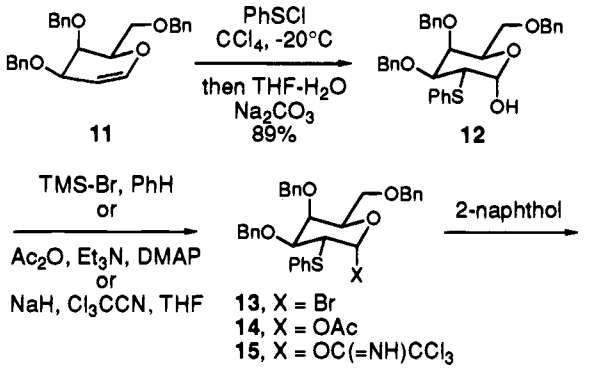
(41) Hashimoto, S.; Yanagiya, Y.; Honda, T.; Ikegami, S. *Chem. Lett.* **1992**, 1511.

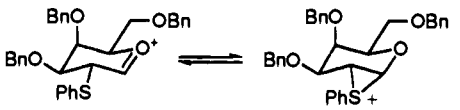
(42) Thiem, J.; Meyer, B. *Chem. Ber.* **1980**, *113*, 3075.

stituents. Thus, treatment of tri-*O*-benzyl galactal **11**[43] with PhSCl[44] in CCl_4 at −20 °C and hydrolysis of the intermediate glycosyl chloride gave lactol **12** in 89% yield. Lactol **12** was transformed into the corresponding bromide **13**, acetate **14**, and trichloroacetimidate **15** under standard conditions.[35c,42] Surprisingly, the silver silicate mediated reaction of **13** and 2-naphthol at 23 °C gave greater than 10:1 selectivity for the α-glycoside **16α**, whereas a 1:1 mixture of the two anomers was obtained at −78 °C. Similarly, poor selectivity was obtained in the TMS-OTf promoted glycosidation of 2-naphthol and acetate **14** and in the reactions of the Schmidt trichloroacetimidate derivative **15**. Interestingly, the $BF_3{\cdot}Et_2O$ catalyzed reaction of 2-naphthol and **15** at −78 °C favored the α-glycoside **16α** with ≥10:1 selectivity. Control experiments established that **16β** is stable toward TMS−OTf and $BF_3{\cdot}OEt_2$ (within ^1H NMR detection limits), and thus **16α** is a kinetic product of these experiments.



Substrate	Conditions	Selectivity (β : α)
13	silver silicate, toluene, -78°C	ca. 1 : 1
13	silver silicate, toluene, 23°C	<1 : >10
14	TMS-OTf, CH_2Cl_2, 23°C	ca. 1 : 1
15	no catalyst, 23°C	ca. 1 : 1
15	$BF_3{\cdot}Et_2O$, CH_2Cl_2, -78°C	<1 : >10

The selective formation of **16α** from both **13** and **15** requires that the C−O bond formation occurs via axial addition of 2-naphthol to oxonium ion **17**. This is a most surprising result, since we had anticipated that the C(2)-thiophenyl substituent would stabilize **17** by formation of episulfonium ion **18**, which in turn would react with nucleophiles in an S_N2 fashion leading to β-glycosides. Episulfonium ions have been invoked many times to rationalize the stereochemical course of the reactions of 1- and 2-thiophenyl pyranoside derivatives.[17,35,45,46] However, our data are inconsistent with **18** serving as the kinetically dominant reactive intermediate in phenol glycosidation reactions. Evidently, phenols are not sufficiently nucleophilic to react with the episulfonium ion intermediate **18**, as is postulated for the reactions of alcohols and 2-arylthio substituted glycosyl donors.[17,35,45] Other factors that may contribute to the tendency of phenol glycosidations to proceed by way of **17** are that the transition state for the axial substitution of **17** is stabilized by a developing anomeric effect[31] and that the β-face (e.g., equatorial) substitution of **18** is stereoelectronically disfavored since the transition state must be boatlike.[31a] Further experimentation is required to probe the factors that control the nucleophile dependent stereoselectivity of glycosidation reactions of 2-arylthio substituted pyranose derivatives.



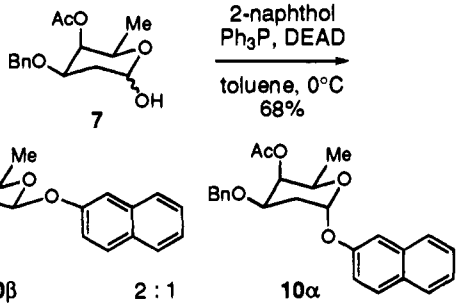
17 **18**

The Mitsunobu Glycosidation Protocol. It was clear from the preceding studies that the development of an efficient synthesis of aryl 2-deoxy-β-glycosides would be difficult to accomplish by using existing literature strategies. One of the problems with achieving high stereoselectivity in the glycosidation of phenols is their relatively low nucleophilicity (compared to alcohols). We reasoned that better success might be possible if phenoxides were used as the nucleophile, thereby permitting the substitution reaction to proceed via the S_N2 (or tight ion pair) mechanistic manifold, rather than the S_N1 pathways that dominated the reactions of **13**−**15** summarized above.[47,48] This logic led us to consider the Mitsunobu reaction as a method of glycoside synthesis.[49] The Mitsunobu reaction had been used on a number of occasions previously for the synthesis of aryl glycosides,[50] glycosyl esters,[51] *O*-glycosyl hydroxylamines,[52] and glycosides of simple alcohols.[53] A recent report has also described the use of oxyphosphonium salts in glycosidation reactions of alcohols.[54]

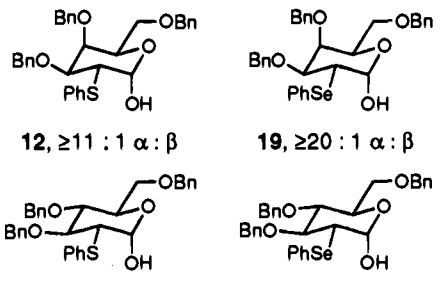
In an initial experiment, pyranose **7** was treated with 1.2 equiv of 2-naphthol and 1.6 equiv each of Ph_3P and diethyl azodicarboxylate (DEAD) in toluene at 0 °C, providing an ca. 2:1 mixture of aryl glycoside **10β** and its α anomer, **10α**. This result was encouraging since **7** exists as a 2.3:1 mixture of α:β anomers in C_6D_6, suggesting that each anomer of **7** had reacted

(43) Kaye, A.; Neidle, S.; Reese, C. B. *Tetrahedron Lett.* **1988**, *29*, 2711.
(44) Mueller, W. H.; Butler, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2075.
(45) (a) Baldwin, M. J.; Brown, R. K. *Can. J. Chem.* **1967**, *45*, 1195. (b) Baldwin, M. J.; Brown, R. K. *Can. J. Chem.* **1968**, *46*, 1093. (c) White, J. D.; Theramongkol, P.; Kuroda, C.; Engebrecht, J. R. *J. Org. Chem.* **1988**, *53*, 5909. (d) Ito, Y.; Ogawa, T. *Tetrahedron Lett.* **1988**, *29*, 3987. (e) Ito, Y.; Ogawa, T. *Tetrahedron* **1990**, *46*, 89. (f) Nicolaou, K. C.; Hummel, C. W.; Bockovich, N. J.; Wong, C.-H. *J. Chem. Soc., Chem. Commun.* **1991**, 870.
(46) A recent computational study (MOPAC 5.0) by Liotta that suggests that the oxonium ion intermediates (e.g., **17**) are more stable than the episulfonium ions (e.g., **18**): Jones, D. K.; Liotta, D. C. *Tetrahedron Lett.* **1993**, *34*, 7209. However, it is the relative energy of the competing transition states that determines product selectivity and not the relative energy of **17** and **18**.
(47) The displacement of 1α-bromide leaving groups by phenoxides is a well established method for the synthesis of β-aryl glycosides: (a) Dea, I. C. M. *Carbohydr. Res.* **1969**, *11*, 363; **1970**, *12*, 297. (b) Shah, R. H.; Bahl, O. P. *Carbohydr. Res.* **1979**, *74*, 105, and literature cited therein. (c) Dess, D.; Kleine, H. P.; Weinberg, D. V.; Kaufman, R. J.; Sidhu, R. S. *Synthesis* **1981**, 883. (d) Kleine, H. P.; Sidhu, R. S. *Carbohydr. Res.* **1988**, *182*, 307.
(48) Aryl 2-deoxy-β-glycosides have also been prepared via the S_N2 displacement of *O,O*-dimethylphosphorodithioate: Bielawska, H.; Michalska, M. *J. Carbohydr. Chem.* **1986**, *5*, 445.
(49) Reviews: (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Hughes, D. L. *Organic Reactions* **1992**, *42*, 335.
(50) (a) Grynkiewicz, G. *Carbohydr. Res.* **1977**, *53*, C11. (b) Garegg, P. J.; Iversen, T.; Norberg, T. *Carbohydr. Res.* **1979**, *73*, 313. (c) Åkerfeldt, K.; Garegg, P. J.; Iversen, T. *Acta Chem. Scand.* **1979**, *B 33*, 467. (d) Kometani, T.; Kondo, H.; Fujimori, Y. *Synthesis* **1988**, 1005. (e) Chida, N.; Ohtsuka, M.; Nakazawa, K.; Ogawa, S. *J. Org. Chem.* **1991**, *56*, 2976. (f) Chida, N.; Ohtsuka, M.; Ogawa, S. *Chem. Lett.* **1988**, 969. (g) Sobti, A.; Sulikowski, G. A. *Tetrahedron Lett.* **1994**, *35*, 3661.
(51) (a) Smith, A. B., III; Hale, K. J.; Rivero, R. A. *Tetrahedron Lett.* **1986**, *27*, 5813. (b) Smith, A. B., III; Rivero, R. A.; Hale, K. J.; Vaccaro, H. A. *J. Am. Chem. Soc.* **1991**, *113*, 2092.
(52) Nicolaou, K. C.; Groneberg, R. D. *J. Am. Chem. Soc.* **1990**, *112*, 4085.
(53) Szarek, W. A.; Jarrell, H. C.; Jones, J. K. N. *Carbohydr. Res.* **1977**, *57*, C13.
(54) Mukaiyama, T.; Suda, S. *Chem. Lett.* **1990**, 1143.

with inversion of configuration in an S_N2-like process. Recalling that Smith had reported that inversion of configuration is usually observed in the synthesis of pyranosyl esters under Mitsunobu conditions,[51] we sought substrates with a greater α-anomeric preference in anticipation that they might give better β-selectivity in the Mitsunobu reaction with phenols. This, of course, assumes that the rates of oxyphosphonium salt formation and nucleophilic displacement by the phenol are faster than anomerization of the substrate.



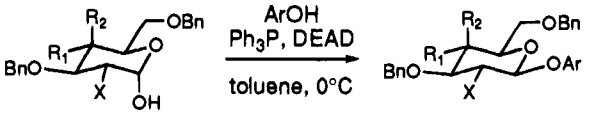
Pyranoses **12**, **19**,[43] **20**,[35c] and **21**[43] containing equatorial 2-thiophenyl and 2-selenophenyl substituents nicely satisfied this criterion. We noticed during our unsuccessful attempts to synthesize aryl 2-deoxy-β-glycosides from **13**–**15** that 2-thiophenyl-D-galactopyranose **12** preferentially existed as the α-anomer in $CDCl_3$ (11:1 α:β anomeric preference). The known lactols **19**–**21** similarly exist primarily as the α-anomers in $CDCl_3$ (data provided below). While the reasons for the increased α-preference for **12** and **19**–**21** compared to 2-deoxypyranose **7** are not entirely clear at present, we speculate that this may be a consequence of the gauche effect.[31c,55] Whatever the origin of this thermodynamic preference, the anomeric composition of the pyranose substrate clearly plays an important role in the success of the Mitsunobu glycosidation reactions subsequently described.



Results of the Mitsunobu reactions of **12** and **19**–**21** with 2-naphthol, phenol, and 2-cresol are summarized in Table 1. These reactions were performed in toluene (0.2 M) at 0 °C in the presence of molecular sieves typically using 1.2 equiv of phenol, 1.4 equiv of Ph_3P, and 1.6 equiv of DEAD. The reactions were quite rapid and were worked up after 30 min by addition of 1 N aqueous NaOH to remove excess phenol. The least selective of these experiments using **19** as the substrate provided an 87:13 mixture of β and α glycosides, while only the β-glycoside was observed (>95:5 selectivity) in the glycosylations of **21**. The aryl β-D-glycosides were isolated chromatographically in 70–85% yield. Isolated yields of the α-anomers were ≤8% (not shown).

(55) (a) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102. (b) Juaristi, E. *J. Chem. Ed.* **1979**, *56*, 438.

Table 1. Mitsunobu Glycosidations of **12** and **19**–**21**[a]



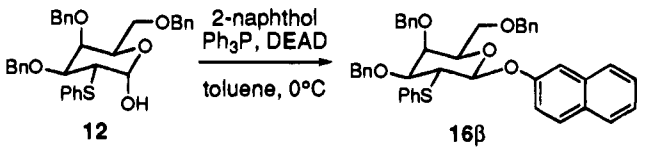
12, R_1 = H, R_2 = OBn, X = SPh — **16β, 22β, 23β**
19, R_1 = H, R_2 = OBn, X = SePh — **24β, 25β, 26β**
20, R_1 = OBn, R_2 = H, X = SPh — **27β**
21, R_1 = OBn, R_2 = H, X = SePh — **28β, 29β**

ArOH
a, 2-naphthol
b, phenol
c, *o*-cresol

Substrate	ArOH	Product	Selectivity[b]	Yield[c]
12	a	16β	88 : 12	74%
12	b	22β	88 : 12	70%
12	c	23β	90 : 10	73%
19	a	24β	93 : 7	71%
19	b	25β	87 : 13	71%
19	c	26β	90 : 10	73%
20	a	27β	93 : 7	82%
21	a	28β	>95 : 5	80%
21	c	29β	>95 : 5	85%

[a] All glycosidation experiments were performed in toluene at 0 °C as described in text. [b] Ratio of β:α glycosides determined by 500 MHz ^{1}H NMR analysis of the crude reaction mixtures. Ratios determined by product isolation were similar. [c] Yield of β-glycoside isolated by chromatography.

The Mitsunobu reaction of **12** and 2-naphthol was examined in a variety of solvents to probe the dependence of the stereoselectivity on the α:β anomer composition. Our results show that the anomeric composition of **12** is solvent dependent (determined by 500 MHz ^{1}H NMR analysis). Interestingly, the

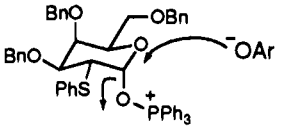


NMR Solvent	Anomer ratio (12α : 12β)[a]	Reaction Solvent	Product ratio (16β : 16α)[a]
$CDCl_3$	92 : 8	--	--
CD_2Cl_2	89 : 11	CH_2Cl_2	88 : 12
C_6D_6	90 : 10	toluene	88 : 12
--	--	Et_2O	86 : 14
THF-d_8	90 : 10	THF	82 : 18
CD_3CN	83 : 17	CH_3CN	82 : 18

[a]Determined by 500 MHz ^{1}H NMR analysis

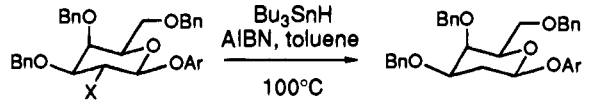
stereoselectivity of the Mitsunobu reactions nicely parallels the anomeric composition of **12** in the range of solvents examined. Consequently, it appears that very little anomerization of **12** occurs before the displacement of the oxyphosphonium salt intermediate, and that the reaction probably occurs by S_N2 displacement of an oxyphosphonium salt intermediate (**30**). Although it also could be argued that the excellent β-selectivity is the consequence of neighboring-group assistance by the thiophenyl or selenophenyl substituents in oxonium ion intermediates (e.g., **17**–**18**), we consider this mechanistic possibility to be less reasonable in these cases since we have already

presented evidence that reactions in which neighboring group-participation should have occurred (e.g., silver silicate mediated reactions of bromide **13**, TMS-OTf promoted reactions of glycosyl acetate **14**, $BF_3{\cdot}Et_2O$ catalyzed reactions of imidate **15**) provide at best 1:1 mixtures of the β- and α-aryl glycosides.



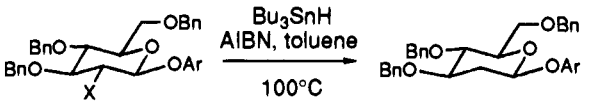
30

The thiophenyl and selenophenyl substituents of the β-glycosides were removed in high yield by treatment with Bu_3SnH and AIBN in toluene at 100 °C.[56] While this is a standard procedure for reduction of phenyl selenides, there are considerably fewer successful examples of tin hydride reductions of phenyl sulfides.[45d-f,56,57] The reductions of the thiophenyl-substituted glycosides were noticeably slower than those of the selenophenyl-substituted glycosides, and it was necessary to add AIBN several times over the course of an 8−12 h reaction period in order to achieve complete reduction of **16β**, **22β**, **23β**, and **27β**. In spite of this experimental deficiency, the Bu_3SnH reduction was judged to be superior to the more commonly employed Ra−nickel protocol,[17,21,35,41] since attempted reduction of either **16β** or **24β** with W-2 Raney−nickel in EtOH resulted in the formation of multiple products, including tribenzyl galactal (**11**) resulting from reductive elimination of 2-naphthol.[41]



16β, X = SPh, Ar = 2-naphthyl
22β, X = SPh, Ar = phenyl
23β, X = SPh, Ar = 2-cresyl
24β, X = SePh, Ar = 2-naphthyl
25β, X = SePh, Ar = phenyl
26β, X = SePh, Ar = 2-cresyl

31, Ar = 2-naphthyl
32, Ar = phenyl
33, Ar = 2-cresyl

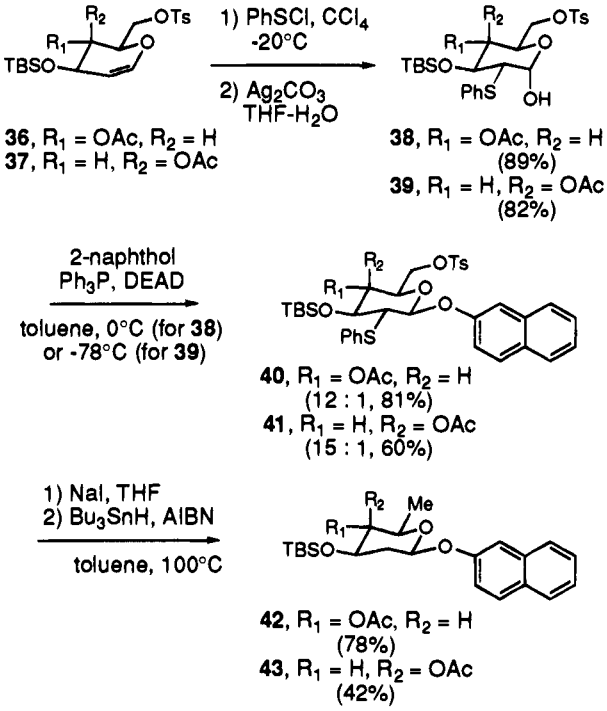


27β, X = SPh, Ar = 2-naphthyl
28β, X = SePh, Ar = 2-naphthyl
29β, X = SePh, Ar = 2-cresyl

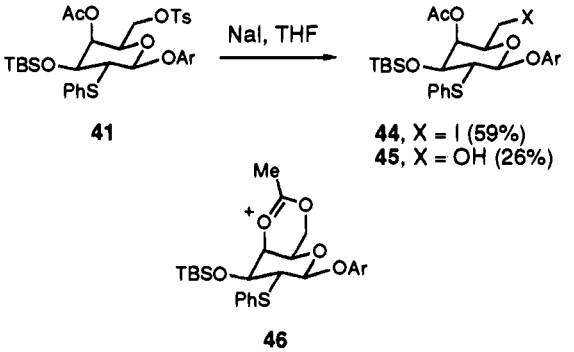
34, Ar = 2-naphthyl
35, Ar = 2-cresyl

Substrate	Product	Yield
16β	31	94%
22β	32	76%
23β	33	89%
24β	31	94%
25β	32	85%
26β	33	86%
27β	34	92%
28β	34	95%
29β	35	92%

The Mitsunobu glycosidation protocol has also been applied to differentially functionalized glycals **36** and **37**. Thus, treatment of D-glucal derivative **36**[21,58] with PhSCl in CCl_4 at −20 °C followed by hydrolysis of the intermediate glycosyl chloride using Ag_2CO_3 in aqueous THF gave pyranoses **38** in 89% yield.[59] Mitsunobu couplings with 2-naphthol then provided β-D-glucoside **40** with 12:1 selectivity. Treatment of **40** with NaI in THF followed by Bu_3SnH reduction completed the synthesis of the differentially protected naphthyl 2,6-dideoxy-β-D-glucoside **42** (78% yield). The Mitsunobu reaction of the analogous D-galactose derivative **39** proceeded with



excellent selectivity for the β-glycoside (15:1 selectivity, 60% yield). However, treatment of **41** with NaI in THF followed by Bu_3SnH provided the naphthyl 2,6-dideoxy-β-galactoside **43** in only 42% yield. The low yielding step in this sequence is the NaI substitution of **41** that provides iodide **44** in 59% yield along with 26% of alcohol **45**, which presumably arises from displacement of iodide by the axial C(4)-acetate group to give **46** which hydrolyzes upon workup.



41

44, X = I (59%)
45, X = OH (26%)

46

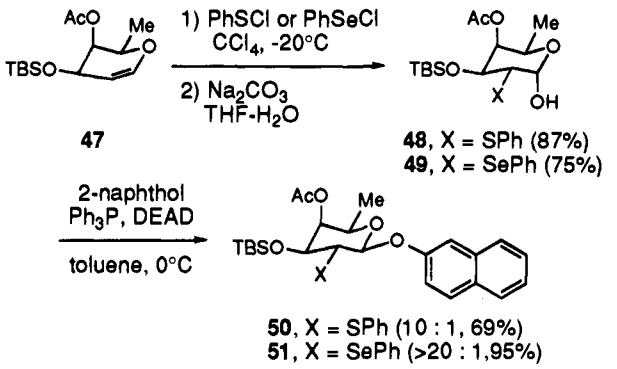
(56) (a) Neumann, W. P. *Synthesis* **1987**, 665. (b) Curran, D. P. *Synthesis* **1988**, 417 and 489. (c) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541.

(57) Gutierrez, C. G.; Stringham, R. A.; Nitasaka, T.; Glasscock, K. G. *J. Org. Chem.* **1980**, *45*, 3393. (b) Hart, D. J.; Tsai, Y. M. *J. Am. Chem. Soc.* **1982**, *104*, 1430. (c) Schmidt, K.; O'Neal, S.; Chan, T. C.; Alexis, C. P.; Uribe, J. M.; Lossener, K.; Gutierrez, C. G. *Tetrahedron Lett.* **1989**, *30*, 7301.

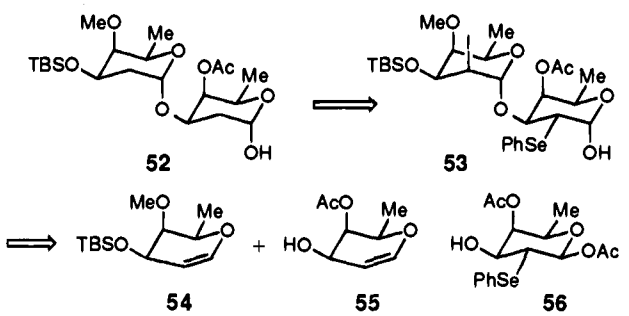
(58) Crich, D.; Ritchie, T. J. *Carbohydr. Res.* **1990**, *197*, 324.

(59) Ag_2CO_3 was used in the hydrolysis of the intermediate glycosyl chloride prepared from **36** since substantial (up to 30%) epimerization at C(2) was observed when Na_2CO_3 was used instead. Either Na_2CO_3 or Ag_2CO_3 can be used in the hydrolysis of the glycosyl chloride prepared from D-galactal derivative **37**, since **39** is much less sensitive to epimerization than **38**.

The latter problem can be avoided by beginning with a D-fucal derivative, **47**. As shown below, the Mitsunobu reactions of **48** (X = SPh) and **49** (X = SePh) proceeded with excellent selectivity (10:1 β:α for **48**, >20:1 for **49**) and in good yield. Although we did not attempt to remove the C(2) thiophenyl or selenophenyl substituents of **50/51**, it is noted that **50** is an intermediate in the reduction of **44** to **43**, which proceeded in 72% yield.



Synthesis of Functionalized Olivomycin A−B Disaccharide 53 and Model Naphthyl A−B Disaccharide 5. Our strategy for the total synthesis of olivomycin A calls for the intact A−B and C−D−E oligosaccharides to be coupled to an advanced aglycon synthetic precursor. Unfortunately, two significant tactical considerations make the parent disaccharide **52** unsuited for these purposes. First, as discussed earlier in this paper, we have not discovered a suitable method for synthesis of aryl 2-deoxy-β-glycosides from 2-deoxy sugar precursors; an equatorial 2-thiophenyl or selenophenyl substituent is required to achieve high selectivity in the Mitsunobu glycosidation protocol. Second, 2-deoxyglycosides are very sensitive to acidic conditions,[30] which renders them incompatible with acid catalyzed protecting group manipulations late in the synthesis (e.g., hydrolysis of the ketal protecting group for the aglycon side chain diol[11]).[60] However, evidence exists that this problem can be solved by incorporating a −Br or −I substituent at C(2).[61,62]



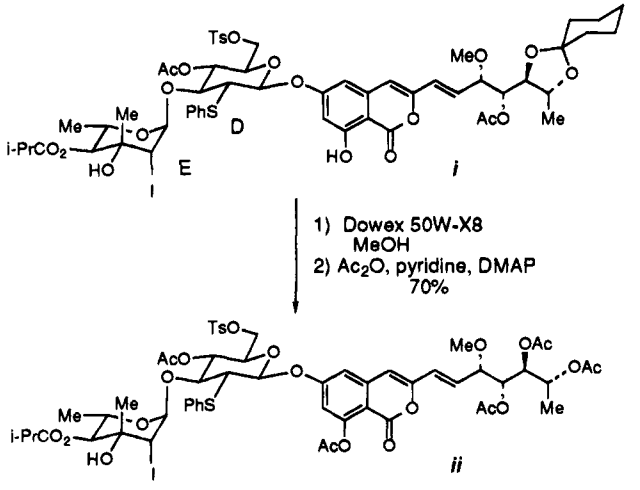
These considerations prompted us to target reducing disaccharide **53** as a functionalized equivalent of the A−B disaccharide required for glycosylation reactions with the aglycon. The most direct strategy for the synthesis of **53** would involve the direct coupling of glycals **54** and **55**. Unfortunately, the electronic properties of glycals **54** and **55** are too evenly matched for application of the "armed−disarmed" protocol to this problem.[24f,63] After considerable experimentation we identified **56** as a suitable synthetic equivalent of **55** for use in this synthesis.

The B-residue glycal **54** was synthesized in 94% overall yield by selective monosilylation of D-fucal **57**[57] followed by methylation of the axial hydroxyl group. D-Fucal **57** was also elaborated into glycal **58**, a precursor to the A monosaccharide residue of **5**, in 92% overall yield by protection as a mono triethylsilyl (TES) ether and acylation of the axial hydroxyl group. It should be noted that the same silyl protecting groups could not be used for **54** and **58** since a TES group in the B residue (**54**) is incompatible with chemistry planned for completion of the synthesis, while a TBDMS group could not be removed at the stage of **59** without competitive migration of the acetyl group from C(4) to C(3). Treatment of **58** with PhSeCl in CH_2Cl_2 at 0 °C followed by AgOAc in THF provided the *galacto* 2-phenylseleno acetate **59** in 73% overall yield.[36] Removal of the TES protecting group was accomplished by treatment of **59** with excess HF−pyridine in THF, thereby providing alcohol **56** in 88% yield. The A−B α-glycosidic bond was introduced by treating a mixture of **56** and **54** (1.5 equiv) with 1.5 equiv of $I(coll)_2ClO_4$ in CH_2Cl_2 at 0 °C to 23 °C.[24a,f,63a] This provided the β,α-disaccharide **60** in 72% yield (63% from **59**) along with 6% of an isomer with an equatorial iodide in the B residue. Selective cleavage of the anomeric acetate was accomplished by treating **60** with 1.6 equiv of hydrazine in MeOH at 23 °C overnight, thereby providing **53** in 92% yield.[64] Reducing disaccharide **53** exists predominantly (≥8:1) as the α,α anomer by ^{1}H NMR analysis ($CDCl_3$). The Mitsunobu coupling of **53** and 2-naphthol then provided the aryl β-glycoside **61** in 65% yield along with 4% of the α,α-anomer which was separated chromatographically (11:1 selectivity by ^{1}H NMR analysis). Finally, reductive removal (Bu_3SnH, AIBN, toluene, 80 °C) of the iodo and phenylseleno substituents completed the synthesis of the model naphthyl A−B disaccharide **5**.

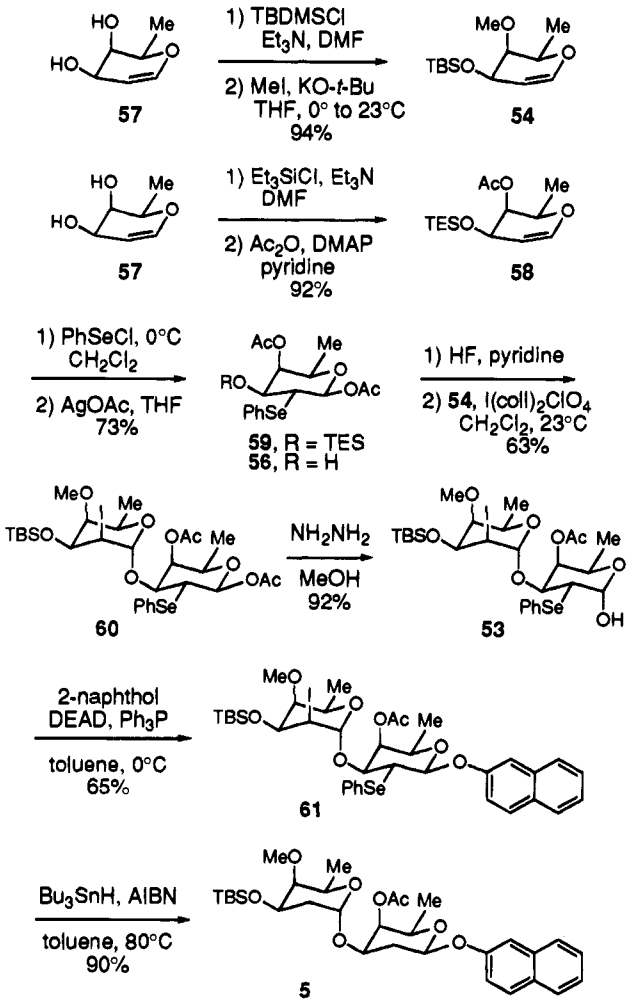
(60) (a) Honda, S.; Kakehi, K.; Takai, H.; Takiura, K. *Carbohydr. Res.* **1973**, *29*, 477. (b) Miyamoto, M.; Kawamatsu, Y.; Shinohara, M.; Nakadaira, Y.; Nakanishi, K. *Tetrahedron*, **1966**, *22*, 2785.

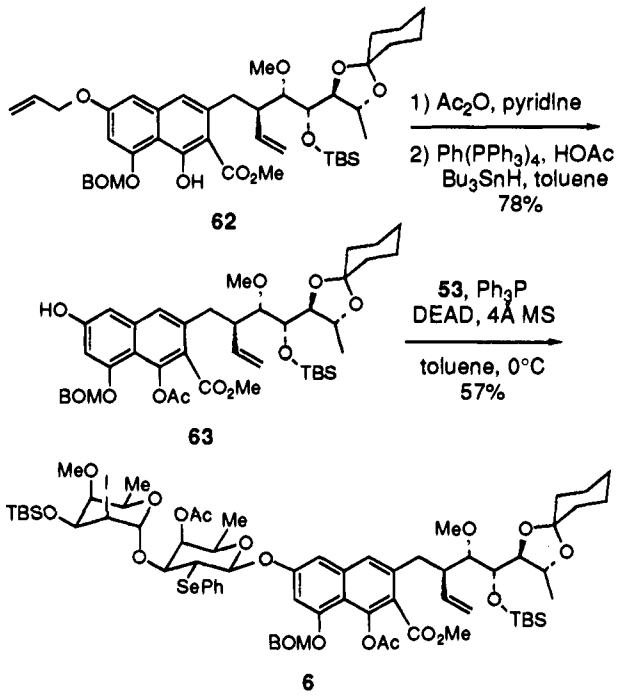
(61) (a) Tatsuta, K.; Tanaka, A.; Fujimoto, K.; Kinoshita, M.; Umezawa, S. *J. Am. Chem. Soc.* **1977**, *99*, 5826. (b) Tatsuta, K.; Amemiya, Y.; Kanemura, Y.; Takahashi, H.; Kinoshita, M. *Tetrahedron Lett.* **1982**, *23*, 3375. (c) Danishefsky, S. J.; Armistead, D. M.; Wincott, F. E.; Selnick, H. G.; Hungate, R. *J. Am. Chem. Soc.* **1989**, *111*, 2967.

(62) We have synthesized the model D-E aryl glycoside *i* shown below and have established that no detectable glycoside hydrolysis occurs during the deprotection of the side chain ketal (Murphy, M., 1993 Ph.D. Thesis, Indiana University, Bloomington, IN). The D-E glycosidic linkage is the most acid labile in chromomycin.



(63) (a) Mootoo, D. R.; Konradsson, P.; Udodong, U.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 5583. (b) Veeneman, G. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 275.





Synthesis of Functionalized Aryl Disaccharide 6. As a final demonstration of the Mitsunobu glycosidation procedure we have synthesized disaccharide **6** starting from olivin precursor **62**.[11c,65] Acylation of **62** followed by cleavage[66] of the allyl phenyl ether provided phenol **63** in 78% yield. Treatment of **63** (1.1 equiv) with 1.0 equiv of reducing disaccharide **53**, 1.4 equiv of Ph_3P, and 1.6 equiv of DEAD in toluene at 0 °C in the presence of 4Å molecular sieves provided the aryl β-disaccharide **6** in 57% yield; 35% of naphthol **63** and approximately 20% of disaccharide **53** were recovered. Thus, the Mitsunobu glycosidation protocol is effective for the glycosidation of advanced olivin synthetic intermediates.

Summary. We have demonstrated that the Mitsunobu reaction of phenols and 1,2-*cis*-2-thiophenyl-α-D-glycopyranoses or 1,2-*cis*-2-selenophenyl-α-D-glycopyranoses is a very effective method for the highly stereoselective synthesis of aryl 2-deoxy-β-D-glycosides. The equatorial 2-thiophenyl or 2-selenophenyl substituents are easily removed by Bu_3SnH reduction following the glycosidation reaction to provide the aryl 2-deoxy-β-D-glycosides in good to excellent yield. The aryl β-D-glycosides are obtained with 6.5:1 selectivity in the least selective case (Table 1), and up to >20:1 selectivity in others. The reaction appears to be S_N2-like in character (see **30**),[67] in that the β:α reaction stereoselectivity correlates well with the α:β anomeric composition of the pyranose starting material. The equatorial 2-thiophenyl or 2-selenophenyl substituents play an important role by increasing the α: β anomer ratio of the pyranose starting materials. The reactions do not appear to proceed by way of free oxonium ions such as **17**, since several reactions in which **17** was generated (e.g., TMS-OTf promoted reactions of glycosyl acetate **14**, $BF_3{\cdot}Et_2O$ catalyzed reactions of imidate **15**) gave at best 1:1 mixtures of α- and β-glycosides, and in several cases gave α-glycosides with >10:1 selectivity. These data also rule out the involvement of episulfonium ion **18** as a kinetically significant intermediate in reactions that proceed by way of oxonium ion **17**. A short and highly effective synthesis of reducing disaccharide **53** from D-fucal was developed. This functionalized disaccharide readily undergoes Mitsunobu glycosidation with 2-naphthol, providing the model naphthyl A−B disaccharide **5** with 11:1 β,α:α,α selectivity. Finally, olivin precursor **63** has also been glycosylated with **53**, providing the advanced synthetic intermediate **6** with excellent diastereoselectivity.

Experimental Section

General Methods. All reactions were conducted in flame-dried glassware under dry nitrogen. All solvents were purified before use: diethyl ether, THF, and toluene were distilled from sodium benzophenone ketyl; dichloromethane and triethylamine were distilled from CaH_2, and methanol was distilled from magnesium turnings. Commercial samples of DMF and pyridine were dried over 4Å molecular sieves before use.

^1H and ^{13}C NMR spectra were recorded on a Brucker AM 500 MHz instrument (500 MHz for ^1H and 125 MHz for ^{13}C), in most cases using $CDCl_3$ as solvent. Chemical shifts are reported in δ units with

(64) Excoffier, G.; Gagnaire, D.; Utille, J.-P. *Carbohydr. Res.* **1975**, *39*, 368.
(65) The synthesis of **6** was performed by Karin Briner.
(66) Four, P.; Guibe, F. *Tetrahedron Lett.* **1982**, *23*, 1825.
(67) We cannot rule out the possibility that the reactions involve nucleophilic addition to a solvent caged oxonium ion that is solvated on the α-face by the triphenylphosphine oxide leaving group. However, the results cannot be explained by invoking an unsolvated oxonium ion such as **17**.
(68) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(69) (a) The yields reported in Table 1 refer to the β-anomer only. (b) Isolated yields of the α-anomers were ≤8%.
(70) Whistler, R. L.; Wolfrom, M. L.; BeMiller, J. N. *Methods Carbohydr. Chem. Vol. II Reactions of Carbohydrates;* Academic Press: New York, 1963; p 409.
(71) Iselin, B.; Reichstein, T. *Helv. Chim. Acta* **1944**, *27*, 1200.
(72) Alcohol **56** was obtained in 69% yield when the deprotection was performed by using 1.2 N HF in CH_3CN. Also obtained under these conditions was a 1,3-diol (22%) resulting from hydrolysis of the anomeric acetate.

coupling constants reported in Hz. Residual chloroform (δ 7.26 for ^{1}H, δ 77.0 for ^{13}C) was used as internal reference for calibration purposes. IR spectra were recorded on a Perkin Elmer Model 1420 infrared spectrophotometer and calibrated with the 1601 cm^{-1} absorption of polystyrene. High resolution mass spectra were measured at 70 eV on a Kratos GC/MS 80 RFA mass spectrometer at the Indiana University Mass Spectrometry Laboratory. Optical rotations were measured on a Rudolph Autopol III polarimeter using a quartz cell with 1 mL capacity and a 10 cm path length. Melting points were measured on a Fisher-Johns hot stage melting point apparatus and are uncorrected. Elemental analyses were performed by Robertson Laboratories, Florham Park, NJ.

Analytical HPLC was performed with a system composed of a Waters 6000A solvent delivery system, a Waters R401 differential refractometer, and a Shimadzu CR601 recorder using either a Rheodyne Dynamax 60A or Whatman Partisil M9 silica column. Analytical TLC was performed with the use of plates coated with a 0.25 mm thickness of silica gel containing PF254 indicator (Analtech); compounds were visualized with UV light, iodine, *p*-anisaldehyde, or ceric ammonium molybdate stain. Preparative TLC was performed by using 20 cm × 20 cm plates coated with a 0.50 mm thickness of silica gel containing PF254 indicator (Analtech). Flash chromatography was performed as described by Still[68] with Kieselgel 60 (230–400 mesh). Unless otherwise noted, all compounds isolated by chromatography were sufficiently pure (>95% by NMR analysis) for use in subsequent preparative reactions.

2-Naphthyl 4-*O*-Acetyl-3-*O*-benzyl-2,6-dideoxy-β-D-*galacto*-pyranoside (10β) and 2-Naphthyl 4-*O*-Acetyl-3-*O*-benzyl-2,6-dideoxy-α-D-*galacto*-pyranoside (10α). To a mixture of pyranose **7**[20a] (38 mg, 0.134 mmol), Ph_3P (50 mg, 0.19 mmol), 2-naphthol (23 mg, 0.16 mmol), and activated 4Å sieves (25 mg) in toluene (1 mL) at 0 °C was added DEAD (36 μL, 0.23 mmol). The mixture was stirred at 0 °C for 50 min and then was concentrated in vacuo. Purification of the crude product (a 2:1 mixture of **10β**:**10α** by 500 MHz ^{1}H NMR analysis) by silica gel chromatography (15% EtOAc–hexanes) gave α-glycoside **10α** (14.2 mg, 26%) and β-glycoside **10β** (22.9 mg, 42%).

Data for 10β: R_f 0.34 (20% EtOAc–hexanes); $[\alpha]^{26}_D$ +41.7° (*c* 2.23, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.65–7.10 (m, 12 H), 5.19 (br d, J = 3.2 Hz, 1 H), 4.76 (dd, J = 9.9, 2.2 Hz, 1 H), 4.65 (d, A of AB, J = 12.1 Hz, 1 H), 4.39 (d, B of AB, J = 12.1 Hz, 1 H), 3.24 (ddd, J = 12.3, 4.7, 3.2 Hz, 1 H), 2.96 (qd, J = 6.4, 0.9 Hz, 1 H), 2.43 (ddd, J = 12.3, 12.2, 9.9 Hz, 1 H), 2.10 (dddd, J = 12.2, 4.7, 2.2, 0.8 Hz, 1 H), 1.75 (s, 3 H), 1.11 (d, J = 6.4 Hz, 3 H); IR ($CHCl_3$) 3070, 3040, 3010, 1740, 1635, 1605, 1515, 1470, 1395, 1380, 1370, 1250, 1175, 1120, 1200, 1065, 1035 cm^{-1}; high resolution mass spectrum (CI) for $C_{25}H_{26}O_5$ (M^+) calcd 406.1780, found 406.1791.

Data for 10α: R_f 0.44 (20% EtOAc–hexanes); $[\alpha]^{26}_D$ +249° (*c* 0.95, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.63–7.10 (m, 12 H), 5.52 (d, J = 3.5 Hz, 1 H), 5.33 (d, J = 3.1 Hz, 1 H), 4.73 (d, A of AB, J = 11.3 Hz, 1 H), 4.33 (d, B of AB, J = 11.3 Hz, 1 H), 4.04 (ddd, J = 12.0, 5.0, 3.1 Hz, 1 H), 3.81 (q, J = 6.5 Hz, 1 H), 2.20 (ddd, J = 13.1, 12.0, 3.5 Hz, 1 H), 2.06 (dd, J = 13.1, 5.0 Hz, 1 H), 1.78 (s, 3 H), 1.04 (d, J = 6.5 Hz, 3 H); IR ($CHCl_3$) 3060, 3030, 3005, 1735, 1630, 1600, 1510, 1465, 1385, 1365, 1250, 1175, 1110, 1060, 1020, 970, 880, 845, 810 cm^{-1}; high resolution mass spectrum (CI) for $C_{25}H_{27}O_5$ (M^+ + 1) calcd 407.1858, found 407.1836.

2-Deoxy-3,4,5-tri-*O*-benzyl-2-thiophenyl-α-D-*galacto*-pyranose (12). To a stirred solution of 3,4,5-tri-*O*-benzyl-D-galactal **11** (2.10 g, 5.05 mmol) in CCl_4 (23 mL) at −20 °C was slowly added neat benzenesulfenyl chloride (0.78 mL, 8.60 mmol). The resulting yellow solution was stirred at −20 °C for 1 h, and then CCl_4 was removed in vacuo. The orange oily residue was dissolved in THF–H_2O (30 mL, 1:1), and Na_2CO_3 (1.3 g, 4.5 mmol) was added. The mixture was stirred at room temperature for 15 min and at 50 °C for 4 h. The mixture was cooled to 23 °C, treated with H_2O (50 mL), and extracted with ether (3 × 100 mL). The extracts were washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo and the residue purified by flash column chromatography (25% EtOAc–hexanes) to give 2.44 g (89%) of the pyranose **12** as a 11:1 mixture (^{1}H NMR analysis, $CDCl_3$) in favor of the α-OH anomer.

Data for 12α: R_f 0.42 (30% EtOAc–hexanes); $[\alpha]^{23}_D$ −6.6° (*c* 1.40, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$; the chemical shifts of the ring protons are concentration dependent) δ 7.56–7.52 (m, 2 H), 7.37–7.16 (m, 18 H), 5.40 (dd, J = 3.4, 2.8 Hz, 1 H), 4.90 (d, A of AB, J = 11.5 Hz, 1 H), 4.79 (d, A′ of A′, J = 11.5 Hz, 1 H), 4.75 (d, B′ of A′, J = 11.5 Hz, 1 H), 4.56 (d, B of AB, J = 11.5 Hz, 1 H), 4.54 (d, A′ of A′, J = 12.0 Hz, 1 H), 4.44 (d, B′ of A′, J = 12.0 Hz, 1 H), 4.24 (br t, decouplings revealed as ddd, J = 7.0, 5.5, 0.9 Hz, 1 H), 4.10 (dd, J = 3.4, 1.2 Hz, 1 H for OH), 3.99 (dd, J = 11.3, 2.3 Hz, 1 H), 3.94 (ddd, J = 11.3, 2.8, 1.2 Hz, 1 H), 3.90 (br s, decouplings revealed as br d, J = 2.3 Hz, 1 H), 3.57 (dd, J = 9.5, 7.0 Hz, 1 H), 3.42 (dd, J = 9.5, 5.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$; the 24 aromatic carbons between δ 138.3–126.1 are not included) δ 93.8, 78.6, 74.5, 74.1, 73.4, 73.0, 69.8, 69.5, 50.8; IR (neat) 3400, 3055, 3020, 1200, 1140, 1090, 1050, 1020, 735, 690 cm^{-1}; high resolution mass spectrum for $C_{33}H_{35}O_5S$ (M^+ + 1) calcd 543.2205, found 543.2186. Anal. Calcd for $C_{33}H_{34}O_5S$: C, 73.04; H, 6.31. Found: C, 72.78; H, 6.39.

Partial data for the β-OH anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (dd, J = 8.6, 7.0 Hz, 1 H, H_1), 4.23 (d, J = 7.0 Hz, 1 H for OH), 3.55–3.50 (m, 2 H), 3.33 (dd, J = 11.2, 2.7 Hz, 1H, H_3). The resonances at δ 3.42 for the α-anomer and δ 3.33 for the β-anomer were used to determine the composition of the mixture.

Representative Procedure for the Mitsunobu Glycosidation Reaction: 2-Naphthyl 2-Deoxy-2-(thiophenyl)-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (16β). To a stirred solution of **12** (369 mg, 0.670 mmol), Ph_3P (252 mg, 0.961 mmol), 2-naphthol (118 mg, 0.821 mmol), and 100 mg of 4Å molecular sieves in 3.5 mL of toluene at 0 °C was slowly added diethyl azodicarboxylate (170 μL, 1.08 mmol). The mixture was stirred at 0 °C for 40 min, and then 1 N NaOH solution (40 mL) was added. The mixture was filtered and extracted with ether (3 × 40 mL). The combined ether extracts were washed with 1 N NaOH (30 mL), brine (2 × 30 mL), and dried ($MgSO_4$). The crude product was purified by flash chromatography (silica gel; 5% EtOAc–hexanes to elute the α-anomer, then 10% EtOAc–hexanes to elute the β-anomer) providing β-glycoside **16β** (339 mg, 74%) and α-anomer **16α** (55 mg, 8%).

Data for 16β: R_f 0.67 (30% EtOAc–hexanes); $[\alpha]^{25}_D$ −0.79° (*c* 3.42, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.24 (m, 26 H), 6.94 (m, 1 H), 5.09 (d, J = 8.8 Hz, 1 H), 4.96 (d, A of AB, J = 11.7 Hz, 1 H), 4.80 (d, A′ of A′, J = 11.4 Hz, 1 H), 4.75 (d, B′ of A′, J = 11.4 Hz, 1 H), 4.64 (d, B of AB, J = 11.7 Hz, 1 H), 4.47 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.41 (d, B′ of A′, J = 11.6 Hz, 1 H), 3.99 (d, J = 2.7 Hz, 1 H), 3.95 (dd, J = 11.4, 8.8 Hz, 1 H), 3.73 (dd, J = 6.5, 6.0 Hz, 1 H), 3.68 (dd, J = 9.4, 6.0 Hz, 1 H), 3.62 (dd, J = 9.4, 6.5 Hz, 1 H), 3.49 (dd, J = 11.4, 2.7 Hz, 1 H); IR ($CHCl_3$) 3060, 3030, 1625,-1595,1505, 1460, 1450, 1350, 1250, 1175, 1150, 1095, 1055, 1020 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4S$ (M^+ − $C_{10}H_7O$) calcd 525.2099, found 525.2173.

Partial data for 16α: R_f 0.79 (30% EtOAc–hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82–7.20 (m, 27 H), 5.81 (d, J = 2.2 Hz, 1 H), 4.98 (d, A of AB, J = 11.2 Hz, 1 H), 4.91 (d, A′ of A′, J = 11.5 Hz, 1 H), 4.87 (d, B′ of A′, J = 11.5 Hz, 1 H), 4.63 (d, B of AB, J = 11.2 Hz, 1 H), 4.45 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.40 (d, B′ of A′, J = 11.6 Hz, 1 H), 4.25 (dd, J = 7.4, 5.8 Hz, 1 H), 4.23 (dd, J = 11.1, 2.2 Hz, 1 H), 4.14 (dd, J = 11.1, 3.3 Hz, 1 H), 4.13 (br s, 1 H), 3.69 (dd, J = 9.3, 7.4 Hz, 1 H), 3.59 (dd, J = 9.3, 5.8 Hz, 1 H); high resolution mass spectrum (CI) for $C_{33}H_{33}O_4S$ (M^+ − $C_{10}H_7O$) calcd 525.2099, found 525.2074.

Phenyl 2-Deoxy-2-(thiophenyl)-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (22β). Obtained in 70% yield from the reaction of **12** and phenol:[69] mp 84–86 °C; R_f 0.70 (30% EtOAc–hexanes); $[\alpha]^{25}_D$ −13.1° (*c* 4.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.45 (m, 2 H), 7.38–7.18 (m, 18 H), 6.97 (m, 1 H), 6.86 (m, 2 H), 4.94 (d, A of AB, J = 11.7 Hz, 1 H), 4.93 (d, J = 8.8 Hz, 1 H), 4.78 (d, A′ of A′, J = 11.4 Hz, 1 H), 4.73 (d, B′ of A′, J = 11.4 Hz, 1 H), 4.62 (d, B of AB, J = 11.7 Hz, 1 H), 4.45 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.40 (d, B′ of A′, J = 11.6 Hz, 1 H), 3.96 (d, J = 2.7 Hz, 1 H), 3.88 (dd, J = 11.4, 8.8 Hz, 1 H), 3.67–3.58 (m, 3 H), 3.45 (dd, J = 11.4, 2.7 Hz, 1 H), 1.57 (s, 1 H for 0.5 H_2O); IR ($CHCl_3$) 3060, 3030, 3010, 1595, 1585, 1490, 1450, 1350, 1100, 1060, 1020 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4S$ (M^+ − C_6H_5O) calcd 525.2099, found 525.2110. Anal. Calcd for $C_{39}H_{38}O_5S$−0.5H_2O: C, 74.61; H, 6.26. Found: C, 74.54; H, 6.13.

Data for the α-anomer:[69b] R_f 0.81 (30% EtOAc–hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.05 (m, 25 H), 5.63 (d, J = 3.3 Hz, 1 H), 4.93 (d, A of AB, J = 11.2 Hz, 1 H), 4.86 (d, A′ of A′, J = 11.4 Hz, 1 H), 4.82 (d, B′ of A′, J = 11.4 Hz, 1 H), 4.59 (d, B of AB, J = 11.2 Hz, 1 H), 4.44 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.38 (d, B′ of A′, J = 11.6 Hz, 1 H), 4.18 (dd, J = 7.5, 5.7 Hz, 1 H), 4.15 (dd, J = 11.3, 2.4 Hz, 1 H), 4.09 (br s, 1 H), 4.05 (dd, J = 11.3, 3.3 Hz, 1 H), 3.64 (dd, J = 9.3, 7.5 Hz, 1 H), 3.53 (dd, J = 9.3, 5.7 Hz, 1 H); high resolution mass spectrum (CI) for $C_{33}H_{33}O_4S$ ($M^+ - C_6H_5O$) calcd 525.2099, found 525.2080.

***o*-Cresyl 2-Deoxy-2-(thiophenyl)-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (23β).** Obtained in 73% yield from the reaction of **12** and *o*-cresol:[69a] R_f 0.76 (30% EtOAc–hexanes); $[\alpha]^{25}_D$ −21.7° (*c* 3.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–6.88 (m, 24 H), 4.94 (d, J = 8.9 Hz, 1 H), 4.92 (d, A of AB, J = 11.7 Hz, 1 H), 4.78 (d, A′ of A′, J = 11.4 Hz, 1 H), 4.71 (d, B′ of A′, J = 11.4 Hz, 1 H), 4.62 (d, B of AB, J = 11.7 Hz, 1 H), 4.45 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.40 (d, B′ of A′, J = 11.6 Hz, 1 H), 3.97 (d, J = 2.7 Hz, 1 H), 3.90 (dd, J = 11.3, 8.9 Hz, 1 H), 3.66–3.58 (m, 3 H), 3.47 (dd, J = 11.3, 2.7 Hz, 1 H), 2.05 (s, 3 H); IR (neat) 3060, 3015, 1600, 1580, 1490, 1450, 1435, 1350, 1300, 1230, 1190, 1150, 1080, 1020, 910, 835, 740, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4S$ ($M^+ - C_7H_7O$) calcd 525.2099, found 525.2086. Anal. Calcd for $C_{40}H_{40}O_5S$: C, 75.92; H, 6.37. Found: C, 76.06; H, 6.43.

Data for the α-anomer:[69b] R_f 0.83 (30% EtOAc–hexanes); $[\alpha]^{25}_D$ +84.4° (*c* 1.62, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–6.92 (m, 24 H), 5.69 (d, J = 3.2 Hz, 1 H), 4.95 (d, A of AB, J = 11.2 Hz, 1 H), 4.87 (d, A′ of A′, J = 11.5 Hz, 1 H), 4.85 (d, B′ of A′, J = 11.5 Hz, 1 H), 4.62 (d, B of AB, J = 11.2 Hz, 1 H), 4.44 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.40 (d, B′ of A′, J = 11.6 Hz, 1 H), 4.16 (dd, J = 11.3, 2.4 Hz, 1 H), 4.13 (dd, J = 7.8, 5.6 Hz, 1 H), 4.10 (br s, 1 H), 4.07 (dd, J = 11.3, 3.2 Hz, 1 H), 3.67 (dd, J = 9.2, 7.8 Hz, 1 H), 3.54 (dd, J = 9.2, 5.6 Hz, 1 H), 2.33 (s, 3 H); high resolution mass spectrum (CI) for $C_{33}H_{33}O_4S$ ($M^+ - C_7H_7O$) calcd 525.2099, found 525.2072.

2-Naphthyl 2-Deoxy-2-selenophenyl-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (24β). Obtained in 71% yield (93:7 selectivity) from the reaction of **19** and 2-naphthol:[69a] R_f 0.58 (30% EtOAc–hexanes); $[\alpha]^{25}_D$ −0.29° (*c* 6.2, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.68–6.84 (m, 27 H), 5.18 (d, J = 9.0 Hz, 1 H), 4.92 (d, A of AB, J = 11.4 Hz, 1 H), 4.54 (d, B of AB, J = 11.4 Hz, 1 H), 4.46 (d, A′ of A′, J = 11.4 Hz, 1 H), 4.39 (d, B′ of A′, J = 11.4 Hz, 1 H), 4.33 (dd, J = 11.6, 9.0 Hz, 1 H), 4.27 (d, A′ of A′, J = 11.7 Hz, 1 H), 4.18 (d, B′ of A′, J = 11.7 Hz, 1 H), 3.80 (d, J = 2.7 Hz, 1 H), 3.69 (dd, J = 9.3, 6.8 Hz, 1 H), 3.63 (dd, J = 9.3, 6.1 Hz, 1 H), 3.42 (dd, J = 6.8, 6.1 Hz, 1 H), 3.24 (dd, J = 11.6, 2.7 Hz, 1 H); IR (neat) 3060, 3030, 1630, 1600, 1510, 1495, 1470, 14550, 1360, 1250, 1210, 1150, 1100, 1050, 1020, 900, 840, 810, 730, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{37}H_{35}O_5$ (M^+ − SePh) calcd 559.2484, found 559.2495. Anal. Calcd for $C_{43}H_{40}O_5Se$: C, 72.16; H, 5.63. Found: C, 72.31; H, 5.69.

Data for the α-anomer:[69b] R_f 0.67 (30% EtOAc–hexanes); $[\alpha]^{24}_D$ +116° (*c* 2.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.10 (m, 27 H), 5.85 (d, J = 3.3 Hz, 1 H), 4.92 (d, A of AB, J = 11.2 Hz, 1 H), 4.85 (s, 2 H), 4.58 (d, B of AB, J = 11.2 Hz, 1 H), 4.42 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.36 (d, B′ of A′, J = 11.6 Hz, 1 H), 4.23 (dd, J = 11.5, 2.4 Hz, 1 H), 4.22 (dd, J = 7.4, 5.8 Hz, 1 H), 4.10 (d, J = 2.4 Hz, 1 H), 4.06 (dd, J = 11.5, 3.3 Hz, 1 H), 3.65 (dd, J = 9.3, 7.4 Hz, 1 H) 3.55 (dd, J = 9.3, 5.8 Hz, 1 H); IR (neat) 3060, 3030, 1630, 1600, 1510, 1495, 1470, 1455, 1350, 1250, 1170, 1100, 1050, 1020, 905, 840, 810, 730, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4Se$ ($M^+ - C_{10}H_7O$) calcd 573.1544, found 573.1559.

Phenyl 2-Deoxy-2-selenophenyl-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (25β). Obtained in 71% yield (87:13 selectivity) from the reaction of **19** and phenol:[69a] R_f 0.62 (30% EtOAc–hexane); $[\alpha]^{23}_D$ −2.20° (*c* 4.40, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59–6.84 (m, 25 H), 4.98 (d, J = 9.1 Hz, 1 H), 4.92 (d, A of AB, J = 11.7 Hz, 1 H), 4.76 (d, A′ of A′, J = 11.3 Hz, 1 H), 4.62 (d, B of AB, J = 11.7 Hz, 1 H), 4.61 (d, B′ of A′, J = 11.3 Hz, 1 H), 4.45 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.40 (d, B′ of A′, J = 11.6 Hz, 1 H), 3.97 (d, J = 2.7 Hz, 1 H), 3.93 (dd, J = 11.6, 9.1 Hz, 1 H), 3.65–3.58 (m, 3 H), 3.44 (dd, J = 11.6, 2.7 Hz, 1 H); IR (neat) 3060, 3030, 1600, 1590, 1490, 1475, 1450, 1355, 1225, 1150, 1100, 1050, 1020, 910, 810, 740, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4Se$ (M^+ − C_6H_5O), calcd 573.1544, found 573.1574. Anal. Calcd for $C_{39}H_{38}O_5Se$: C, 70.37; H, 5.75. Found: C, 70.55; H, 5.71.

Data for the α-anomer:[69b] R_f 0.71 (30% EtOAc–hexanes); $[\alpha]^{24}_D$ +88.3° (*c* 3.45, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64–7.04 (m, 25 H), 5.72 (d, J = 3.2 Hz, 1 H), 4.90 (d, A of AB, J = 11.2 Hz, 1 H), 4.84 (s, 2 H), 4.57 (d, B of AB, J = 11.2 Hz, 1 H), 4.44 (d, A′ of A′, J = 11.7 Hz, 1 H), 4.38 (d, B′ of A′, J = 11.7 Hz, 1 H), 4.19 (dd, J = 11.5, 2.4 Hz, 1 H), 4.18 (dd, J = 7.7, 5.7 Hz, 1 H), 4.09 (br s, 1 H), 4.01 (dd, J = 11.5, 3.2 Hz, 1 H), 3.64 (dd, J = 9.2, 7.7 Hz, 1 H), 3.53 (dd, J = 9.2, 5.7 Hz, 1 H); IR (neat) 3060, 3030, 1600, 1590, 1495, 1480, 1455, 1350, 1240, 1225, 1140, 1100, 1070, 1050, 1020, 950, 900, 750, 730, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4Se$ ($M^+ - C_6H_5O$) calcd 573.1544, found 573.1520.

***o*-Cresyl 2-Deoxy-2-selenophenyl-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (26β).** Obtained in 73% yield (90:10 selectivity) from the reaction of **19** and *o*-cresol:[69a] R_f 0.65 (30% EtOAc–hexanes); $[\alpha]^{23}_D$ −10.1° (*c* 2.84, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.68–6.85 (m, 24 H), 5.07 (d, J = 9.1 Hz, 1 H), 4.93 (d, A of AB, J = 11.5 Hz, 1 H), 4.57 (d, B of AB, J = 11.5 Hz, 1 H), 4.47 (d, A′ of A′, J = 11.4 Hz, 1 H), 4.41 (d, B′ of A′, J = 11.4 Hz, 1 H), 4.30 (d, A′ of A′, J = 11.7 Hz, 1 H), 4.25 (dd, J = 11.5, 9.1 Hz, 1 H), 4.21 (d, B′ of A′, J = 11.7 Hz, 1 H), 3.84 (d, J = 2.7 Hz, 1 H), 3.73 (dd, J = 9.1, 7.2 Hz, 1 H), 3.60 (dd, J = 9.1, 5.9 Hz, 1 H), 3.40 (dd, J = 7.2, 5.9 Hz, 1 H), 3.24 (dd, J = 11.5, 2.7 Hz, 1 H), 2.29 (s, 3 H); IR (neat) 3060, 3030, 1590, 1490, 1450, 1355, 1235, 1100, 1055, 1020, 740, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4Se$ ($M^+ - C_7H_7O$) calcd 573.1544, found 573.1590. Anal. Calcd for $C_{40}H_{40}O_5Se$: C, 70.68; H, 5.93. Found: C, 70.70; H, 5.84.

Data for the α-anomer:[69b] R_f 0.72 (30% EtOAc–hexanes); $[\alpha]^{26}_D$ +77.5° (*c* 2.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (m, 2 H), 7.30–6.90 (m, 22 H), 5.77 (d, J = 3.3 Hz, 1 H), 4.90 (d, A of AB, J = 11.2 Hz, 1 H), 4.84 (d, A′ of A′, J = 11.5 Hz, 1H), 4.83 (d, B′ of A′, J = 11.5 Hz, 1 H), 4.57 (d, B of AB, J = 11.2 Hz, 1 H), 4.42 (d, A′ of A′, J = 11.6 Hz, 1 H), 4.37 (d, B′ of A′, J = 11.6 Hz, 1 H), 4.19 (dd, J = 11.5, 2.4 Hz, 1 H), 4.10 (dd, J = 7.7, 5.4 Hz, 1 H), 4.09 (br s, 1 H), 4.02 (dd, J = 11.5, 3.3 Hz, 1 H), 3.65 (dd, J = 9.1, 7.7 Hz, 1 H), 3.51 (dd, J = 9.1, 5.4 Hz, 1 H), 2.29 (s, 3 H); IR ($CHCl_3$) 3060, 3030, 1590, 1450, 1345, 1100, 1050, 1020, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4Se$ ($M^+ - C_7H_7O$) calcd 573.1544, found 573.1561.

2-Naphthyl 2-Deoxy-2-thiophenyl-3,4,6-tri-*O*-benzyl-β-D-*gluco*-pyranoside (27β). Obtained in 82% yield (93:7 selectivity) from the reaction of **20** and 2-naphthol:[69a] mp 95–97 °C; R_f 0.49 (20% EtOAc–hexanes); $[\alpha]^{26}_D$ +7.8° (*c* 1.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–6.98 (m, 27 H), 5.16 (d, J = 8.7 Hz, 1 H), 5.14 (d, A of AB, J = 10.3 Hz, 1 H), 4.94 (d, B of AB, J = 10.3 Hz, 1 H), 4.92 (d, A′ of A′, J = 10.9 Hz, 1 H), 4.66 (d, B′ of A′, J = 10.9 Hz, 1 H), 4.61 (d, A′ of A′, J = 11.9 Hz, 1 H), 4.56 (d, B′ of A′, J = 11.9 Hz, 1 H), 3.88–3.72 (m, 4 H), 3.69 (dd, J = 10.7, 8.4 Hz, 1 H), 3.60 (dd, J = 10.7, 8.7 Hz, 1 H); IR ($CHCl_3$) 3060, 3030, 3010, 1630, 1600, 1510, 1495, 1465, 1455, 1355, 1250, 1100, 1050, 1020, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4S$ ($M^+ - C_{10}H_7O$) calcd 525.2099, found 525.2123. Anal. Calcd for $C_{43}H_{40}O_5S$: C, 77.22; H, 6.03. Found: C, 77.01; H, 6.28.

2-Naphthyl 2-Deoxy-2-selenophenyl-3,4,6-tri-*O*-benzyl-β-D-*gluco*-pyranoside (28β). Obtained in 80% yield (>95:5 selectivity) from the reaction of **21** and 2-naphthol:[69a] mp 106–108 °C; R_f 0.44 (20% EtOAc–hexanes); $[\alpha]^{23}_D$ +5.5° (*c* 2.55, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.81–6.95 (m, 27 H), 5.16 (d, J = 9.0 Hz, 1 H), 5.12 (d, A of AB, J = 10.6 Hz, 1 H), 4.96 (d, B of AB, J = 10.6 Hz, 1 H), 4.84 (d, A′ of A′, J = 11.4 Hz, 1 H), 4.57 (d, B′ of A′, J = 11.4 Hz, 1 H), 4.43 (d, A′ of A′, J = 12.0 Hz, 1 H), 4.37 (d, B′ of A′, J = 12.0 Hz, 1 H), 3.76 (dd, J = 11.0, 9.0 Hz, 1 H), 3.74 (m, decoupling at δ 3.43 revealed as dd, J = 9.5, 8.5 Hz, 1 H), 3.73 (m, decoupling at δ 3.43 revealed as dd, J = 10.9, 1.8 Hz, 1 H), 3.64 (dd, J = 10.9, 5.4 Hz, 1 H), 3.60 (dd, J = 11.0, 8.5 Hz, 1 H), 3.43 (ddd, J = 9.5, 5.4, 1.8 Hz, 1 H); IR ($CHCl_3$) 3060, 3035, 3010, 1630, 1600, 1510, 1495, 1465, 1455, 1390,1355, 1250, 1100, 1040, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4Se$ ($M^+ - C_{10}H_7O$) calcd 573.1544, found 573.1567. Anal. Calcd for $C_{43}H_{40}O_5Se$: C, 72.16; H, 5.63. Found: C, 72.36; H, 5.64.

o-Cresyl 2-Deoxy-2-selenophenyl-3,4,6-tri-*O*-benzyl-β-D-*gluco*-pyranoside (29β). Obtained in 85% yield (>95:5 selectivity) from the reaction of **21** and *o*-cresol:[69a] mp 71−73 °C; R_f 0.51 (20% EtOAc−hexanes); $[\alpha]^{26}_D$ −15.2° (*c* 3.40, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.60−6.93 (m, 24 H), 5.08 (d, A of AB, *J* = 10.3 Hz, 1 H), 4.96 (d, *J* = 9.0 Hz, 1 H), 4.91 (d, B of AB, *J* = 10.3 Hz, 1 H), 4.84 (d, A′ of A′, *J* = 10.8 Hz, 1 H), 4.60 (d, B′ of A′, *J* = 10.8 Hz, 1 H), 4.57 (d, A′ of A′, *J* = 12.0 Hz, 1 H), 4.52 (d, B′ of A′, *J* = 12.0 Hz, 1 H), 3.78 (dd, *J* = 10.8, 1.9 Hz, 1 H), 3.73 (dd, *J* = 9.5, 8.5 Hz, 1 H), 3.70 (dd, *J* = 10.8, 5.3 Hz, 1 H), 3.68 (dd, *J* = 10.7, 8.5 Hz, 1 H), 3.55 (ddd, *J* = 9.5, 5.3, 1.9, Hz, 1 H), 3.51 (dd, *J* = 10.7, 9.0 Hz, 1 H), 2.19 (s, 3 H); IR ($CHCl_3$) 3060, 3010, 1590, 1490, 1450, 1360, 1235, 1105, 1050, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{33}O_4Se$ (M^+ − C_7H_7O) calcd 573.1544, found 573.1517. Anal. Calcd for $C_{40}H_{40}O_5Se$: C, 70.68; H, 5.93. Found: C, 71.17; H, 5.98.

General Procedure for the Tributyltin Hydride Reductions. The thiophenyl (**16β**, **22β**, **23β**, and **27β**) or selenophenyl (**24β**, **25β**, **26β**, **28β**, and **29β**) containing glycosides and a catalytic amount of recrystallized AIBN in freshly distilled toluene (0.05−0.1 M) was degassed with argon and sealed with a septum. Five equivalents of Bu_3SnH were added via syringe. The mixture was then stirred at 100 °C overnight. For the reduction of the 2-thiophenyl glycosides, catalytic amounts of AIBN had to be added 3−4 times to drive the reaction to completion. Purification of the crude product mixture on silica gel (hexanes to elute tin-containing materials, then 10% EtOAc−hexanes) provided the 2-deoxyglycosides **31**−**35** in 76−95% yield.

2-Naphthyl 2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (31). Obtained in 94% yield from both **16β** and **24β**: R_f 0.43 (20% EtOAc−hexanes); $[\alpha]^{26}_D$ −55.3° (*c* 7.38, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78−7.24 (m, 22 H), 5.18 (dd, *J* = 9.8, 2.2 Hz, 1 H), 4.97 (d, A of AB, *J* = 11.7 Hz, 1 H), 4.66 (d, B of AB, *J* = 11.7 Hz, 1 H), 4.62 (d, A′ of A′, *J* = 12.2 Hz, 1 H), 4.61 (d, B′ of A′, *J* = 12.2 Hz, 1 H), 4.47 (d, A′ of A′, *J* = 11.6 Hz, 1 H), 4.40 (d, B′ of A′, *J* = 11.6 Hz, 1 H), 3.88 (br d, *J* = 2.0 Hz, 1 H), 3.71−3.62 (m, 4 H), 2.44 (ddd, *J* = 12.1, 12.0, 9.8 Hz, 1 H), 2.27 (br d, *J* = 12.0 Hz, 1 H); IR ($CHCl_3$) 3080, 3060, 3010, 1630, 1600, 1510, 1495, 1465, 1455, 1390, 1360, 1255, 1180, 1155, 1100, 1060, 1025, 700 cm^{-1}; high resolution mass spectrum (CI) for $C_{37}H_{36}O_5$ (M^+) calcd 560.2562, found 560.2572.

Phenyl 2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (32). Obtained in 76% yield from **22β** and 85% yield from **25β**: R_f 0.41 (20% EtOAc−hexanes); $[\alpha]^{26}_D$ −40.6° (*c* 5.40, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.40−6.85 (m, 20 H), 5.03 (d, A of AB, *J* = 11.5 Hz, 1 H), 4.77 (dd, *J* = 9.7, 2.1 Hz, 1 H), 4.60 (d, B of AB, *J* = 11.5 Hz, 1 H), 4.32 (d, A′ of A′, *J* = 12.1 Hz, 1 H), 4.30 (d, A′ of A′, *J* = 11.8 Hz, 1 H), 4.29 (d, B′ of A′, *J* = 12.1 Hz, 1 H), 4.21 (d, B′ of A′, *J* = 11.8 Hz, 1 H), 3.74 (dd, *J* = 9.2, 6.9 Hz, 1 H), 3.73 (br s, 1 H), 3.63 (dd, *J* = 9.2, 5.9 Hz, 1 H), 3.39 (ddd, *J* = 6.9, 5.9, 0.6 Hz, 1 H), 3.24 (ddd, *J* = 12.2, 4.2, 2.7 Hz, 1 H), 2.63 (ddd, *J* = 12.2, 11.9, 9.7 Hz, 1 H), 2.08 (br d, *J* = 11.9 Hz, 1 H); IR ($CHCl_3$) 3080, 3060, 3030, 3005, 1595, 1590, 1495, 1450, 1385, 1360, 1155, 1095, 1065, 1025, 695 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{34}O_5$ (M^+) calcd 510.2406, found 510.2415. Anal. Calcd for $C_{33}H_{34}O_5$: C, 77.62; H, 6.71. Found: C, 77.92; H, 6.85.

***o*-Cresyl 2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-*galacto*-pyranoside (33).** Obtained in 89% from **23β** and 86% from **26β**: mp 47−49 °C; R_f 0.52 (20% EtOAc−hexanes); $[\alpha]^{26}_D$ −37.6° (*c* 2.16, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.40−6.85 (m, 19 H), 5.04 (d, A of AB, *J* = 11.5 Hz, 1 H), 4.74 (dd, *J* = 9.7, 2.1 Hz, 1 H), 4.61 (d, B of AB, *J* = 11.5 Hz, 1 H), 4.32 (d, A′ of A′, *J* = 12.2 Hz, 1 H), 4.31 (d, A′ of A′, *J* = 11.8 Hz, 1 H), 4.28 (d, B′ of A′, *J* = 12.2 Hz, 1 H), 4.21 (d, B′ of A′, *J* = 11.8 Hz, 1 H), 3.77 (dd, *J* = 9.2, 7.0 Hz, 1 H), 3.75 (br s, 1 H), 3.63 (dd, *J* = 9.2, 5.9 Hz, 1 H), 3.39 (dd, *J* = 7.0, 5.9 Hz, 1 H), 3.25 (ddd, *J* = 12.2, 4.2, 2.7 Hz, 1 H), 2.65 (ddd, *J* = 12.2, 11.9, 9.7 Hz, 1 H), 2.26 (s, 3 H), 2.08 (br d, *J* = 11.9 Hz, 1 H); IR ($CHCl_3$) 3080, 3060, 3030, 3005, 1590, 1490, 1450, 1380, 1360, 1235, 1090, 1060, 695 cm^{-1}; high resolution mass spectrum (EI) for $C_{27}H_{29}O_4$ (M^+ − C_7H_7O) calcd 417.2066, found 417.2060. Anal. Calcd for $C_{34}H_{36}O_5$: C, 77.84; H, 6.92. Found: C, 77.70; H, 6.88.

2-Naphthyl 2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-*gluco*-pyranoside (34). Obtained in 92% yield from **27β** and 95% yield from **28β**: mp 88−90 °C; R_f 0.44 (20% EtOAc−hexanes); $[\alpha]^{23}_D$ −45.6° (*c* 1.89, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.80−7.20 (m, 22 H), 5.24 (dd, *J* = 9.7, 2.0 Hz, 1 H), 4.96 (d, A of AB, *J* = 10.9 Hz, 1 H), 4.76 (d, A′ of A′, *J* = 11.7 Hz, 1 H), 4.67 (d, B′ of A′, *J* = 11.7 Hz, 1 H), 4.63 (d, B of AB, *J* = 10.9 Hz, 1 H), 4.61 (d, A′ of A′, *J* = 12.0 Hz, 1 H), 4.56 (d, B′ of A′, *J* = 12.0 Hz, 1 H), 3.87 (dd, *J* = 10.6, 1.8 Hz, 1 H), 3.81 (ddd, *J* = 11.6, 8.5, 5.1 Hz, 1 H), 3.76 (dd, *J* = 10.6, 5.6 Hz, 1 H), 3.69 (ddd, *J* = 9.5, 5.6, 1.8 Hz, 1 H), 3.63 (dd, *J* = 9.5, 8.5 Hz, 1 H), 2.59 (ddd, *J* = 12.5, 5.1, 2.0 Hz, 1 H), 2.03 (ddd, *J* = 12.5, 11.6, 9.7 Hz, 1 H); IR ($CHCl_3$) 3070, 3020, 1630, 1600, 1510, 1495, 1390, 1360, 1250, 1080, 1050, 1020, 695 cm^{-1}; high resolution mass spectrum (CI) for $C_{37}H_{36}O_5$ (M^+) calcd 560.2562, found 560.2595. Anal. Calcd for $C_{37}H_{36}O_5$: C, 79.26; H, 6.47. Found: C, 79.31; H, 6.73.

***o*-Cresyl 2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-*gluco*-pyranoside (35).** Obtained in 92% yield from **29β**: mp 71−73 °C; R_f 0.28 (10% EtOAc−hexanes); $[\alpha]^{26}_D$ −31.4° (*c* 2.70, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.35−6.90 (m, 19 H), 4.96 (d, A of AB, *J* = 11.4 Hz, 1 H), 4.75 (dd, *J* = 9.6, 2.0 Hz, 1 H), 4.60 (d, B of AB, *J* = 11.4 Hz, 1 H), 4.52 (d, A′ of A′, *J* = 12.0 Hz, 1 H), 4.44 (d, A′ of A′, *J* = 12.2 Hz, 1 H), 4.41 (d, B′ of A′, *J* = 12.0 Hz, 1 H), 4.39 (d, B′ of A′, *J* = 12.2 Hz, 1 H), 3.75 (dd, *J* = 10.8, 1.9 Hz, 1 H), 3.67 (dd, *J* = 10.8, 5.2 Hz, 1 H), 3.64 (dd, *J* = 9.5, 8.6 Hz, 1 H), 3.53 (ddd, *J* = 11.5, 8.6, 5.0 Hz, 1 H), 3.41 (ddd, *J* = 9.5, 5.2, 1.9 Hz, 1 H), 2.31 (s, 3 H), 2.29 (ddd, *J* = 12.2, 5.0, 2.0 Hz, 1 H), 2.03 (ddd, *J* = 12.2, 11.5, 9.6 Hz, 1 H); IR ($CHCl_3$) 3060, 3030, 3005, 1590, 1490, 1450, 1385, 1360, 1235, 1080, 695 cm^{-1}; high resolution mass spectrum (CI) for $C_{34}H_{36}O_5$ (M^+) calcd 524.2563, found 524.2613. Anal. Calcd for $C_{34}H_{36}O_5$: C, 77.84; H, 6.92. Found: C, 77.80; H, 6.66.

4-*O*-Acetyl-3-*O*-((*tert*-butyldimethyl)silyl)-2-deoxy-2-thiophenyl-6-*O*-tosyl-α-D-*gluco*-pyranose (38). A solution of glucal **36**[21,58] (2.68 g, 2.36 mmol) in CH_2Cl_2 (35 mL) was treated with PhSCl (1.07 g, 7.40 mmol). The reaction mixture was stirred from −20 °C to 10 °C for 1.5 h and then was concentrated in vacuo. The residue was dissolved in THF:H_2O (50 mL, 9:1) and stirred with Ag_2CO_3 (5.0 g, 18.1 mmol) in the dark for 3 days. The mixture was then filtered through Celite and washed with EtOAc. The solution was concentrated in vacuo and the crude product purified on silica gel (25% EtOAc−hexanes) to give pyranose **38**[21] (2.93 g, 89%) as a ca. 10:1 mixture favoring α-anomer: R_f 0.33 (30% EtOAc−hexanes); $[\alpha]^{24}_D$ +7.5° (*c* 2.75, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.76−7.17 (m, 9 H), 5.14 (dd, *J* = 3.5, 3.1 Hz, 1 H), 4.83 (dd, *J* = 9.8, 8.5 Hz, 1 H), 4.20 (ddd, *J* = 9.8, 6.1, 3.2 Hz, 1 H), 4.11 (dd, *J* = 10.4, 8.5 Hz, 1 H), 4.03 (dd, *J* = 10.9, 3.2 Hz, 1 H), 3.98 (dd, *J* = 10.9, 6.1 Hz, 1 H), 3.20 (ddd, *J* = 10.4, 3.1, 1.4 Hz, 1 H), 3.02 (dd, *J* = 3.5, 1.4 Hz, 1 H, -OH), 2.43 (s, 3 H), 2.07 (s, 3 H), 0.83 (s, 9 H), 0.12 (s, 3 H), 0.075 (s, 3 H); IR ($CHCl_3$) 3580, 3300, 3020, 1740, 1370, 1250, 1235, 1180, 1120, 1040, 980, 860, 840 cm^{-1}; high resolution mass spectrum (CI) for $C_{27}H_{36}O_7SiS_2$ (M^+ − H_2O) calcd 564.1672, found 564.1657. Anal. Calcd for $C_{27}H_{38}O_8SiS_2$: C, 55.64; H, 6.57. Found: C, 55.67; H, 6.65.

Partial data for the β-OH anomer: ^1H NMR (500 MHz, $CDCl_3$) δ 4.81(dd, *J* = 9.4, 8.1 Hz, 1 H, H_4), 4.70 (d, *J* = 8.2 Hz, 1 H, H_1), 3.76 (dd, *J* =9.5, 8.1 Hz, 1 H, H_3), 3.67 (ddd, *J* = 9.4, 5.6, 3.7 Hz, 1 H, H_5), 3.00 (dd, *J* = 9.5, 8.2 Hz, 1 H, H_2).

2-Naphthyl 4-*O*-Acetyl-3-*O*-((*tert*-butyldimethylsilyl)-2-deoxy-2-(thiophenyl)-6-*O*-tosyl-β-D-*gluco*-pyranoside (40). A 0 °C solution of **38** (197 mg, 0.34 mmol), Ph_3P (143 mg, 0.54 mmol), 2-naphthol (73 mg, 0.51 mmol), and ca. 100 mg of 4Å molecular sieves in toluene (2 mL) was treated with diethyl azodicarboxylate (91 μL, 0.58 mmol). The reaction mixture was stirred for 1.5 h and then was diluted with ether and filtered. The filtrate was concentrated, and the crude product was purified on silica gel (20% EtOAc−hexanes) to give a 12:1 mixture of glycosides, which was further separated by preparative TLC (four 0.5 mm, 20 mm × 20 mm silica gel plates, 10% EtOAc−hexanes, five elutions). In this way, 179 mg (75%) of the β-glycoside **40** and 15 mg (6%) of the α-glycoside were obtained.

Data for 40β: R_f 0.52 (30% EtOAc−hexanes); $[\alpha]^{26}_D$ −26.7° (*c* 2.11, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78−6.75 (m, 16 H), 5.14 (d, *J* = 8.3 Hz, 1 H), 4.90 (dd, *J* = 9.4, 8.2 Hz, 1 H), 4.16 (dd, *J* = 10.9, 3.2 Hz, 1 H), 4.06 (dd, *J* = 10.9, 7.5 Hz, 1 H), 3.89 (ddd, *J* = 9.4, 7.5, 3.2 Hz, 1 H), 3.88 (dd, *J* = 9.7, 8.2 Hz, 1 H), 3.44 (dd, *J* = 9.7, 8.3 Hz, 1 H), 2.27 (s, 3 H), 2.17 (s, 3 H), 0.92 (s, 9 H), 0.26 (s, 3 H), 0.13 (s, 3 H); IR ($CHCl_3$) 3030, 1745, 1630, 1600, 1465, 1370, 1250, 1175, 1120, 1100, 970, 840 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{35}O_8SiS_2$ (M^+ − C_4H_9) calcd 651.1542, found 651.1503.

Data for the α-anomer: $[\alpha]^{26}_D$ +103° (*c* 1.47, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.85−7.10 (m, 16 H), 5.54 (d, *J* = 3.1 Hz, 1 H), 5.03 (dd, *J* = 10.1, 8.8 Hz, 1 H), 4.31 (dd, *J* = 10.7, 8.8 Hz, 1 H), 4.17 (ddd, *J* = 10.1, 5.9, 3.1 Hz, 1 H), 4.11 (dd, *J* = 11.0, 3.1 Hz, 1 H), 4.06 (dd, *J* = 11.0, 5.9 Hz, 1 H), 3.40 (dd, *J* = 10.7, 3.1 Hz, 1 H), 2.34 (s, 3 H), 2.11 (s, 3 H), 0.88 (s, 9 H), 0.20 (s, 3 H), 0.15 (s, 3 H); IR ($CHCl_3$) 3050, 3030, 1740, 1630, 1600, 1510,1465, 1365, 1175, 1120, 840 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{35}O_8SiS_2$ ($M^+ - C_4H_9$) calcd 651.1542, found 651.1514.

2-Naphthyl 4-*O*-Acetyl-3-*O*-((*tert*-butyldimethyl)silyl)-2,6-dideoxy-β-D-*gluco*-pyranoside (42). A mixture of tosylate **40** (69 mg, 0.097 mmol) and NaI (35 mg, 0.23 mmol) in THF (1 mL) was heated at reflux overnight. The mixture was allowed to cool to 23 °C and then concentrated in vacuo. The residue was purified on silica gel (10% EtOAc−hexanes) to provide the intermediate iodide (62 mg, 96%): R_f 0.34 (10% EtOAc−hexanes); $[\alpha]^{26}_D$ +1.01° (*c* 0.69, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78−7.30 (m, 11 H), 6.84 (m, 1 H), 5.17 (d, *J* = 8.4 Hz, 1 H), 4.94 (dd, *J* = 9.1, 8.2 Hz, 1 H), 3.86 (dd, *J* = 9.8, 8.2 Hz, 1 H), 3.74 (ddd, *J* = 10.1, 9.1, 2.8 Hz, 1 H), 3.53 (dd, *J* = 9.8, 8.4 Hz, 1 H), 3.33 (dd, *J* = 10.8, 2.8 Hz, 1 H), 3.18 (dd, *J* = 10.8, 10.1 Hz, 1 H), 2.19 (s, 3 H), 0.93 (s, 9 H), 0.26 (s, 3 H), 0.14 (s, 3 H); IR ($CHCl_3$) 3050, 1740, 1630, 1600, 1465, 1370, 1250, 1120, 1100, 1060, 840 cm^{-1}; high resolution mass spectrum (CI) for $C_{26}H_{28}O_5SiSI$ ($M^+ - C_4H_9$) calcd 607.0473, found 607.0477.

A solution of the intermediate 6-iodo glycoside (62 mg, 0.093 mmol) and a catalytic amount of AIBN in toluene (2 mL) was degassed with argon. Tributyltin hydride (0.15 mL, 0.56 mmol) was added, and the mixture was stirred at 110 °C. Additional catalytic amounts of AIBN were added three times at 2 h intervals, and the mixture was left at 110 °C overnight. The reaction was then cooled, diluted with CH_2Cl_2 (10 mL), and shaken vigorously with 3% NH_3 solution (10 mL). The organic phase was dried ($MgSO_4$), and the crude product was purified on silica gel (10% EtOAc−hexanes) to afford 2,6-dideoxy glycoside **42** (33 mg, 81%): R_f 0.31 (10% EtOAc−hexanes); $[\alpha]^{28}_D$ −49.7° (*c* 3.09, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.72−7.25 (m, 7 H), 5.01 (dd, *J* = 9.5, 8.9 Hz, 1 H), 4.94 (dd, *J* = 9.7, 2.2 Hz, 1 H), 3.73 (ddd, *J* = 11.5, 8.9, 5.3 Hz, 1 H), 3.23 (dq, *J* = 9.5, 6.2 Hz, 1 H), 2.29 (ddd, *J* = 12.5, 5.3, 2.2 Hz, 1 H), 2.19 (ddd, *J* = 12.5, 11.5, 9.7 Hz, 1 H), 1.83 (s, 3 H), 1.25 (d, *J* = 6.2 Hz, 3 H), 0.99 (s, 9 H), 0.097 (s, 3 H), 0.081 (s, 3 H); IR ($CHCl_3$) 3050, 3030, 1745, 1630, 1600, 1510, 1465, 1390, 1370, 1250, 1110, 1055, 840 cm^{-1}; high resolution mass spectrum (CI) for $C_{20}H_{25}O_5Si$ ($M^+ - C_4H_9$) calcd 373.1471, found 373.1450. Anal. Calcd for $C_{24}H_{34}O_5Si$: C, 66.94; H, 7.96. Found: C, 66.98; H, 8.06.

4-*O*-Acetyl-3-*O*-((*tert*-butyldimethyl)silyl)-6-*O*-tosyl-D-galactal (37). A solution of D-galactal[70] (2.01 g, 13.7 mmol) in dry pyridine (18 mL) was treated with a CH_2Cl_2 solution (20 mL) of TsCl (3.93 g, 20.6 mmol) at 23 °C for 3 h. Water (10 mL) was added at 0 °C, and the mixture stirred at 0 °C for 0.5 h. The organic phase was washed with aqueous $NaHSO_4$ (2 × 40 mL) and $NaHCO_3$ solution (2 × 40 mL) and then dried (Na_2SO_4). After being filtered and concentrated, the residue was dissolved in CH_2Cl_2−DMF (20 mL, 3:1), and then pyridine (18 mL) and TBDMS-Cl (2.07 g, 13.73 mmol) were added. The mixture was stirred at 23 °C overnight and then treated with acetic anhydride (2.6 mL, 21.8 mmol) and a catalytic amount of DMAP at 23 °C for 5 h. Ether (50 mL) and water (50 mL) were added. The organic phase was separated and washed with water (2 × 40 mL), $CuSO_4$ solution (3 × 40 mL) and brine (40 mL), and dried ($MgSO_4$). Filtration, concentration of the filtrate, and purification of the residue on silica gel (15% EtOAc−hexanes) gave the protected D-galactal derivative **37** (2.32 g, 37%): R_f 0.37 (20% EtOAc−hexanes); $[\alpha]^{27}_D$ −11.0° (*c* 6.70, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.79 (m, 2 H), 6.66 (m, 2 H), 5.92 (br d, *J* = 6.1 Hz, 1 H), 5.04 (dd, *J* = 3.1, 2.3 Hz, 1 H), 4.46 (dd, *J* = 11.1, 8.3 Hz, 1 H), 4.39 (dd, *J* = 6.1, 3.8 Hz, 1 H), 4.29 (dd, *J* = 11.1, 3.3 Hz, 1 H), 4.13 (distorted m, decouplings revealed as ddd, *J* = 8.3, 3.3, 2.3 Hz, 1 H), 4.09 (br t, decouplings revealed as ddd, *J* = 3.8, 3.1, 1.0 Hz, 1 H), 1.78 (s, 3 H), 1.59 (s, 3 H), 0.88 (s, 9 H), −0.048 (s, 3 H), −0.065 (s, 3 H); IR (neat) 3060, 1745, 1640, 1595, 1370, 1250, 1230, 1190, 1180, 1100, 1070, 1050, 985, 960, 950, 890, 840, 810, 780, 660 cm^{-1}; high resolution mass spectrum (CI) for $C_{21}H_{32}O_7SiS$ (M^+) calcd 456.1638, found 456.1630. Anal. Calcd for $C_{21}H_{32}O_7SiS$: C, 55.24; H, 7.06. Found C, 54.95; H, 7.25.

4-*O*-Acetyl-3-*O*-((*tert*-butyldimethyl)silyl)-2-deoxy-2-thiophenyl-6-*O*-tosyl-α-D-*galacto*-pyranose (39). A solution of D-galactal derivative **37** (1.02 g, 2.23 mmol) in CCl_4 (20 mL) was treated with neat PhSCl (0.60 g, 4.15 mmol) at 23 °C for 1 h and then concentrated in vacuo. The residue was dissolved in THF−H_2O (22 mL, 10:1) and the resulting mixture stirred with Ag_2CO_3 (3.0 g, 10.7 mmol) in the dark for 2 days. The mixture was then filtered through Celite and washed with EtOAc. The solution was then concentrated and the crude product was purified by silica gel chromatography (20% EtOAc−hexanes) to give lactol **39** (1.04 g, 80%) as ca. 10:1 mixture of anomers favoring the α-OH isomer: mp 51−53 °C; R_f 0.23 (25% EtOAc−hexanes); $[\alpha]^{26}_D$ +8.7° (*c* 2.70, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78−7.18 (m, 9 H), 5.32 (d, *J* = 3.1 Hz, 1 H), 5.23 (dd, *J* = 3.2, 1.3 Hz, 1 H), 4.43 (ddd, *J* = 7.1, 4.7, 1.3 Hz, 1 H), 4.12 (dd, *J* = 10.7, 3.2 Hz, 1 H), 4.03 (dd, *J* = 10.7, 4.7 Hz, 1 H), 4.01 (dd, *J* = 10.7, 7.1 Hz, 1 H), 3.54 (dd, *J* = 10.7, 3.1 Hz, 1 H), 2.44 (s, 3 H), 2.07 (s, 3 H), 0.79 (s, 9 H), 0.10 (s, 3 H), 0.095 (s, 3 H); IR ($CHCl_3$) 3580, 3320, 3010, 1745, 1370, 1250, 1185, 1100, 1050, 985, 860, 840, 690 cm^{-1}; high resolution mass spectrum (CI) for $C_{37}H_{36}O_7SiS_2$ ($M^+ - H_2O$) calcd 564.1672, found 564.1675. Anal. Calcd for $C_{27}H_{38}O_8SiS_2$: C, 55.64; H, 6.57. Found: C, 55.43; H, 6.31.

Partial ^1H NMR data for the β-OH anomer: (500 MHz, $CDCl_3$) δ 5.23 (dd, *J* = 3.4, 1.2 Hz, 1 H, H_4), 4.74 (d, *J* = 8.5 Hz, 1 H, H_1), 3.70 (dd, *J* = 10.5, 3.4 Hz, 1 H, H_3), 3.21 (dd, *J* = 10.5, 8.5 Hz, 1 H, H_2).

2-Naphthyl 4-*O*-Acetyl-3-*O*-((*tert*-butyldimethyl)silyl)-2-deoxy-2-(thiophenyl)-6-*O*-tosyl-β-D-*galacto*-pyranoside (41). A mixture of pyranose **39** (110 mg, 0.19 mmol), Ph_3P (75 mg, 0.29 mmol), 2-naphthol (34 mg, 0.24 mmol), and 4Å molecular sieves (ca. 100 mg) in toluene (2 mL) at −78 °C was treated with diethyl azodicarboxylate (48 μL, 0.31 mmol). The mixture was stirred at −78 °C for 1 h and 23 °C overnight. The reaction mixture was then filtered, the filtrate was concentrated, and the residue was purified by chromatography on silica gel (15% EtOAc−hexanes) to give glycoside **41** (80 mg, 60%) as a ca. 15:1 mixture (^1H NMR analysis) favoring the β-anomer: R_f 0.34 (20% EtOAc−hexanes); $[\alpha]^{27}_D$ +2.3° (*c* 1.75, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.94 (m, 1 H), 7.68−6.95 (m, 14 H), 6.40 (m, 1 H), 5.26 (d, *J* = 3.5 Hz, 1 H), 4.95 (d, *J* = 8.8 Hz, 1 H), 4.31 (dd, *J* = 10.5, 3.6 Hz, 1 H), 4.16 (dd, *J* = 10.5, 8.2 Hz, 1 H), 3.85 (dd, *J* = 10.8, 8.8 Hz, 1 H), 3.57 (dd, *J* = 10.8, 3.5 Hz, 1 H), 3.43 (dd, *J* = 8.2, 3.6 Hz, 1 H), 1.60 (s, 3 H), 1.57 (s, 3 H), 1.00 (s, 9 H), 0.31 (s, 3 H), 0.23 (s, 3 H); IR ($CHCl_3$) 1745, 1630, 1600, 1510, 1465, 1365, 1250, 1235, 1175, 1120, 1100, 1065, 840, 810 cm^{-1}; high resolution mass spectrum (CI) for $C_{33}H_{35}O_8SiS_2$ ($M^+ - C_4H_9$) calcd 651.1542, found 651.1551. Anal. Calcd for $C_{37}H_{44}O_8SiS_2$: C, 62.68; H, 6.26. Found: C, 63.19; H, 6.35.

Partial ^1H NMR data for the α-anomer: (500 MHz, $CDCl_3$) δ 5.62 (d, *J* = 3.2 Hz, 1 H, H_1), 5.33 (br d, *J* = 3.2 Hz, 1 H, H_4), 4.41 (br dd, *J* = 7.5, 4.5 Hz, 1 H, H_5), 4.31 (dd, *J* = 11.0, 3.2 Hz, 1 H, H_3), 4.11 (dd, *J* = 10.7, 4.5 Hz, 1 H, H_6), 4.05 (dd, *J* = 10.7, 7.5 Hz, 1 H, H_6), 3.71 (dd, *J* = 11.0, 3.2 Hz, 1 H, H_2).

2-Naphthyl 4-*O*-Acetyl-3-*O*-((*tert*-butyldimethyl)silyl)-2,6-dideoxy-6-iodo-2-(thiophenyl)-β-D-*galacto*-pyranoside (44). A solution of tosylate **41** (72 mg, 0.10 mmol) in dry acetone (1 mL) was treated with NaI (46 mg, 0.31 mmol) in a sealed tube at 130 °C for 20 h. The mixture was allowed to cool to 23 °C, then filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (10% EtOAc−hexanes) to provide iodide **44** (40 mg, 59%) and alcohol **45** (14 mg, 26%).

Data for Iodide 44: R_f 0.33 (10% EtOAc−hexanes); $[\alpha]^{25}_D$ + 50.2° (*c* 2.76, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78−7.28 (m, 11 H), 6.87 (m, 1 H), 5.38 (br d, *J* = 3.4 Hz, 1 H), 5.14 (d, *J* = 8.8 Hz, 1 H), 3.98 (ddd, *J* = 9.7, 3.5, 0.7 Hz, 1 H), 3.79 (dd, *J* = 10.9, 3.4 Hz, 1 H), 3.66 (dd, *J* = 10.9, 8.8 Hz, 1 H), 3.31 (dd, *J* = 10.8, 3.5 Hz, 1 H), 3.21 (dd, *J* = 10.8, 9.7 Hz, 1 H), 2.19 (s, 3 H), 0.90 (s, 9 H), 0.23 (s, 3 H), 0.16 (s, 3 H); IR ($CHCl_3$) 3060, 1740, 1630, 1600, 1465, 1370, 1250, 1240, 1180, 1120, 1100, 1060, 910, 840 cm^{-1}; high resolution mass spectrum (EI) for $C_{26}H_{28}O_5SiSI$ ($M^+ - C_4H_9$) calcd 607.0431, found 607.0427.

Partial data for alcohol 45: R_f 0.06 (10% EtOAc−hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.82−7.58 (m, 5 H), 7.52−7.27 (m, 5 H), 7.23 (m, 1 H), 6.90 (m, 1 H), 5.20 (d, *J* = 3.4 Hz, 1 H), 5.17 (d, *J* =

8.9 Hz, 1 H), 3.82 (dd, J = 7.2, 6.6 Hz, 1 H), 3.79 (dd, J = 11.0, 3.4 Hz, 1 H), 3.70 (dd, J = 12.0, 6.6 Hz, 1 H), 3.58 (dd, J = 11.0, 8.9 Hz, 1 H), 3.51 (dd, J = 12.0, 7.2 Hz, 1 H), 2.68 (br s, 1 H, OH), 2.25 (s, 3 H), 0.95 (s, 9 H), 0.26 (s, 3 H), 0.19 (s, 3 H); IR ($CHCl_3$) 3500 (br), 1730, 1630, 1600, 1510, 1465, 1370, 1250, 1210, 1175, 1115, 1100, 1060, 840 cm^{-1}.

2-Naphthyl 4-*O*-Acetyl-3-*O*-((*tert*-butyldimethyl)silyl)-2,6-dideoxy-*β*-D-*galacto*-pyranoside (43). Tributyltin hydride (0.10 mL, 0.37 mmol) was added to a degassed solution of the 6-iodo glycoside **44** (41.3 mg, 0.062 mmol) and a catalytic amount of AIBN in toluene (1.5 mL), and the resulting mixture was stirred at 110 °C. Additional catalytic quantities of AIBN were added three times at 2 h intervals, and the mixture was left at 110 °C overnight. The reaction was then cooled, diluted with CH_2Cl_2 (10 mL), and shaken vigorously with 3% NH_3 solution (10 mL). The organic phase was dried ($MgSO_4$), and the crude product was purified by silica gel chromatography (8% EtOAc–hexanes) to afford the 2,6-dideoxy glycoside **43** (19 mg, 72%): R_f 0.33 (10% EtOAc–hexanes); $[\alpha]^{26}_D$ −21.0° (c 1.32, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.80–7.21 (m, 7 H), 5.26 (dd, J = 9.9, 2.3 Hz, 1 H), 5.07 (br d, J = 3.4 Hz, decouplings revealed as ddd, J = 3.4, 1.1, 0.8 Hz, 1 H), 3.98 (ddd, J = 11.8, 5.0, 3.4 Hz, 1 H), 3.84 (qd, J = 6.4, 1.1 Hz, 1 H), 2.20 (ddd, J = 12.4, 11.8, 9.9 Hz, 1 H), 2.17 (s, 3 H), 2.10 (dddd, J = 12.4, 5.0, 2.3, 0.8 Hz, 1 H), 1.30 (d, J = 6.4 Hz, 3 H), 0.88 (s, 9 H), 0.11 (s, 3 H), 0.087 (s, 3 H); IR ($CHCl_3$) 3060, 3030, 3010, 1740, 1630, 1600, 1510, 1465, 1390, 1360, 1250, 1120, 1025, 900, 840 cm^{-1}; high resolution mass spectrum (EI) for $C_{24}H_{34}O_5Si$ (M^+) calcd 430.2175, found 430.2157.

3-*O*-((*tert*-Butyldimethyl)silyl)-4-*O*-methyl-D-fucal (54). To a stirred solution of D-fucal **57**[57,71] (2.80 g, 21.5 mmol) and Et_3N (7.0 mL, 50 mmol) in DMF (30 mL) at 0 °C was added *tert*-butyldimethylsilyl chloride (3.90 g, 25.87 mmol). The mixture was allowed to warm to 23 °C and stir for 4.5 h, then it was diluted with ether (100 mL). The mixture was washed with half-saturated brine (75 mL) and brine (75 mL). The aqueous layers were extracted with ether (2 × 100 mL). The combined organic layers were washed with brine (2 × 150 mL) and dried over $MgSO_4$. The mixture was filtered and solvent was removed in vacuo. The crude product was purified by flash column chromatography (10% EtOAc–hexanes) to give 3-*O*-(*tert*-butyldimethylsilyl-D-fucal (5.07 g, 96%): R_f 0.38 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (dd, J = 6.3, 1.5 Hz, 1 H, H_1), 4.50 (ddd, J = 6.3, 2.0, 1.9 Hz, 1 H, H_2), 4.46 (m, 1 H, H_3), 3.97 (q, J = 6.7 Hz, 1 H, H_5), 3.64 (m, 1 H, H_4), 2.78 (s, 1 H, for the OH), 1.40 (d, J = 6.7 Hz, 3 H, H_6), 0.91 (s, 9 H), 0.12 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 101.7, 72.6, 68.1, 65.4, 25.7, 18.1, 16.8, −4.6, −4.9; IR (neat) 3545, 3060, 1640, 1250, 1235, 1170, 1090, 1075, 1050, 865, 835, 775 cm^{-1}; high resolution mass spectrum for $C_{12}H_{25}O_3Si$ (M^+ + 1) calcd 245.1573, found 245.1568.

To a 0 °C solution of 3-*O*-(*tert*-butyldimethyl)silyl-D-fucal (5.07 g, 20.7 mmol) and MeI (6.50 mL, 104 mmol) in THF (40 mL) was added KO^{t}Bu (4.89 g, 43.6 mmol). The mixture was stirred for 1 h, then was diluted with ether (200 mL), and washed with half-saturated brine (100 mL) and brine (100 mL). The aqueous layers were extracted with ether (3 × 100 mL), and the extracts were washed with brine (100 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated, and the residue was purified by chromatography on silica gel (5% EtOAc–hexanes) to provide **54** (5.28 g, 99%) as a colorless liquid. The product is volatile under high vacuum: R_f 0.45 (10% EtOAc–hexanes); $[\alpha]^{24}_D$ −60.5° (c 1.43, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 6.29 (dd, J = 6.2, 1.7 Hz, 1 H, H_1), 4.58 (ddd, J = 6.2, 2.1, 1.9 Hz, 1 H, H_2), 4.54 (m, 1 H, H_3), 4.03 (q, J = 6.6 Hz, 1 H, H_5), 3.63 (s, 3 H), 3.22 (dd, J = 2.1, 1.9 Hz, 1 H, H_4), 1.34 (d, J = 6.6 Hz, 3 H, H_6), 0.92 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 102.9, 78.2, 72.8, 66.6, 61.4, 25.9, 18.2, 16.6, −4.6, −4.8; IR (neat) 3060, 1640, 1250, 1235, 1130, 1100, 1075, 1050, 1000, 945, 875, 835, 770 cm^{-1}; high resolution mass spectrum for $C_{12}H_{23}O_3Si$ (M^+ − CH_3) calcd 243.1416, found 243.1471. Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.66; H, 10.09.

4-*O*-Acetyl-3-*O*-((triethyl)silyl)-D-fucal (58). To a 0 °C solution of D-fucal **57**[71] (7.13 g, 54.8 mmol) and Et_3N (19.0 mL, 136 mmol) in DMF (100 mL) was slowly added neat triethylsilyl chloride (10.0 mL, 59.6 mmol). Upon the addition of TES-Cl, a white precipitate appeared immediately. The mixture was stirred at 0 °C for 1 h and diluted with ether (200 mL). The mixture was then washed with half-saturated brine (100 mL) and brine (2 × 100 mL). The aqueous layers were extracted with ether (2 × 100 mL). The combined organic extracts were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (5% EtOAc/hexanes) to give 3-*O*-triethylsilyl-D-glucal (13.4 g, 100%): R_f 0.43 (10% EtOAc–hexanes); $[\alpha]^{26}_D$ −40.0° (c 1.74, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (dd, J = 6.3, 1.4 Hz, 1 H, H_1), 4.50 (ddd, J = 6.3, 2.0, 1.9 Hz, 1 H, H_2), 4.47 (m, 1 H, H_3), 3.96 (q, J = 6.7 Hz, 1 H, H_5), 3.63 (m, 1 H, H_4), 2.81 (dd, J = 1.6, 1.3 Hz, 1 H, for the OH), 1.40 (d, J = 6.7 Hz, 3 H, H_6), 0.98 (t, J = 8.0 Hz, 9 H), 0.64 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 101.8, 72.6, 68.2, 65.1, 16.9, 6.7, 4.8; IR (neat) 3550, 3070, 1650, 1240, 1180, 1095, 1080, 1055, 860, 740, 730 cm^{-1}; high resolution mass spectrum for $C_{12}H_{25}O_3Si$ (M^+ + 1) calcd 245.1573, found 245.1582.

3-*O*-Triethylsilyl-D-glucal (13.4 g, 54.8 mmol) was dissolved in pyridine (26.6 mL, 329 mmol) and cooled to 0 °C. Ac_2O (15.5 mL, 164 mmol) was added followed by a catalytic amount of DMAP. The mixture was then stirred from 0 °C to 23 °C overnight. The mixture was diluted with ether (200 mL) and washed with water (2 × 100 mL) and 20% HOAc solution (2 × 100 mL). The aqueous layers were extracted with ether (2 × 150 mL). The combined organic layers were washed with aqueous $CuSO_4$ solution (2 × 200 mL), water (200 mL) and brine (2 × 200 mL), and dried over $MgSO_4$. After filtration, the mixture was concentrated in vacuo to give the crude product that was purified by chromatography on silica gel (5% EtOAc–hexanes). This provided **58** (14.5 g, 92%) as a liquid: R_f 0.35 (10% EtOAc–hexanes); $[\alpha]^{25}_D$ −34.8° (c 1.04, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (dd, J = 6.3, 1.8 Hz, 1 H, H_1), 5.14 (br d, J = 4.9 Hz, 1 H, H_4), 4.61 (ddd, J = 6.3, 1.9, 1.8 Hz, 1 H, H_2), 4.57 (m, 1 H, H_3), 4.14 (q, J = 6.6 Hz, 1 H, H_5), 2.16 (s, 3 H), 1.25 (d, J = 6.6 Hz, 3 H, H_6), 0.95 (t, J = 8.0 Hz, 9 H), 0.61 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 144.2, 103.2, 71.8, 69.0, 63.6, 20.9, 16.8, 6.7, 4.7; IR (neat) 3060, 1745, 1650, 1460, 1370, 1240, 1165, 1110, 1075, 1065, 1015, 865, 830, 740, 730 cm^{-1}; high resolution mass spectrum for $C_{12}H_{21}O_4Si$ (M^+ − C_2H_5) calcd 257.1209, found 257.1212. Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.99; H, 8.97.

Acetyl 4-*O*-Acetyl-2-deoxy-2-selenophenyl-3-*O*-(triethyl)silyl-*β*-D-*fuco*-pyranoside (59). A 0 °C solution of glycal **58** (14.4 g, 50.4 mmol) in CH_2Cl_2 (3 mL) was treated with PhSeCl (12.6 g, 65.7 mmol) for 45 min and then concentrated in vacuo to give the intermediate α-glycosyl chloride [(500 MHz, $CDCl_3$) δ 7.42 (m, 2 H), 7.25 (m, 3 H), 6.30 (d, J = 3.2 Hz, 1 H, H_1), 5.22 (dd, J = 3.1, 1.3 Hz, 1 H, H_4), 4.49 (br q, J = 6.7 Hz, 1 H, H_5), 4.36 (dd, J = 10.9, 3.1 Hz, 1 H, H_3), 3.81 (dd, J = 10.9, 3.2 Hz, 1 H, H_2), 2.14 (s, 3 H), 1.16 (d, J = 6.7 Hz, 3 H, H_6), 0.95 (dd, J = 7.9, 7.5 Hz, 9 H), 0.68 (q, J = 7.5 Hz, 3 H), 0.67 (q, J = 7.9 Hz, 3 H)]. This intermediate was dissolved in THF (100 mL). AgOAc (17.0 g, 102 mmol) was then added slowly; the reaction is exothermic. The mixture was stirred in the dark for 5 h, then diluted with CH_2Cl_2, and filtered through Celite. The filtrate was concentrated and the residue purified by chromatography on silica gel with 10% EtOAc/hexanes to give *β*-acetate **59** as an oil (18.5 g, 73%) and 3.33 g of the α-acetate anomer (13%).

Data for the *β*-glycosyl acetate 59: R_f 0.38 (20% EtOAc–hexanes); $[\alpha]^{24}_D$ +26.9° (c 3.01, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 2 H), 7.25 (m, 3 H), 5.75 (d, J = 9.6 Hz, 1 H, H_1), 5.08 (dd, J = 3.4, 0.9 Hz, 1 H, H_4), 3.82 (dd, J = 11.2, 3.4 Hz, 1 H, H_3), 3.78 (qd, J = 6.4, 0.9 Hz, 1 H, H_5), 3.54 (dd, J = 11.2, 9.6 Hz, 1 H, H_2), 2.18 (s, 3 H), 1.73 (s, 3 H), 1.17 (d, J = 6.4 Hz, 3 H, H_6), 0.97 (t, J = 8.0 Hz, 9 H), 0.68 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 169.0, 133.8, 129.6, 128.9, 127.3, 95.0, 72.5, 71.5, 70.1, 48.2, 20.9, 20.5, 16.5, 6.9, 4.9; IR (neat) 3050, 1765, 1740, 1575, 1475, 1455, 1435, 1410, 1370, 1230, 1250, 1225, 1090, 1060, 1040, 1015, 865, 805, 735, 685 cm^{-1}; high resolution mass spectrum for $C_{22}H_{34}O_6SiSe$ (M^+) calcd 502.1289, found 502.1279. Anal. Calcd for $C_{22}H_{34}O_6SiSe$: C, 52.68; H, 6.83. Found: C, 52.65; H, 6.69.

Partial data for the α-glycosyl acetate 59α: R_f 0.44 (20% EtOAc–hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 2 H), 7.33 (m, 3 H), 6.31 (d, J = 3.4 Hz, 1 H, H_1), 5.17 (d, J = 3.1 Hz, 1 H, H_4), 4.19 (dd, J = 11.2, 3.1 Hz, 1 H, H_3), 4.10 (q, J = 6.5 Hz, 1 H, H_5), 3.59 (dd, J = 11.2, 3.4 Hz, 1 H, H_2), 2.15 (s, 3 H), 2.14 (s, 3 H), 1.11 (d, J = 6.5

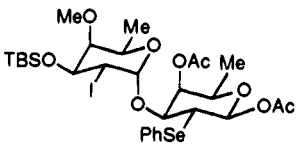
Hz, 3 H, H_6), 0.97 (dd, J = 8.2, 7.7 Hz, 9 H), 0.679 (q, J = 7.7 Hz, 3 H), 0.676 (q, J = 8.2 Hz, 3 H).

Acetyl 4-*O*-Acetyl-2-deoxy-2-(selenophenyl)-β-D-*fuco*-pyranoside (56). A solution of **59** (3.74 g, 7.45 mmol) in THF (20 mL) at 0 °C was treated with an excess of hydrogen fluoride-pyridine. The reaction was carefully monitored by TLC analysis. After 0.5 h, the reaction was quenched by the slow addition of $NaHCO_3$ solution at 0 °C and extracted with EtOAc (2 × 100 mL). The extracts were washed with $NaHCO_3$ solution (3 × 100 mL) and brine (200 mL) and dried over $MgSO_4$. The crude product was purified by chromatography on silica gel (30% EtOAc–hexanes) to give alcohol **56** as a colorless oil (2.53 g, 88%). Also obtained was a small amount of the corresponding α-glycosyl fluoride (112 mg, 4.3%).[72]

Data for 56: R_f 0.27 (30% EtOAc–hexanes); $[\alpha]^{26}_D$ +47.5° (*c* 1.18, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (m, 2 H), 7.37 (m, 1 H), 7.33 (m, 2 H), 5.66 (d, J = 9.5 Hz, 1 H, H_1), 5.17 (dd, J = 3.4, 1.0 Hz, 1 H, H_4), 3.70 (qd, J = 6.4, 1.0 Hz, 1 H, H_5), 3.54 (ddd, J = 11.4, 3.4, 2.6 Hz, 1 H, H_3), 3.28 (dd, J = 11.4, 9.5 Hz, 1 H, H_2), 2.68 (d, J = 2.6 Hz, 1 H for the OH), 2.19 (s, 3 H), 2.08 (s, 3 H), 1.17 (d, J = 6.4 Hz, 3 H, H_6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 169.1, 136.4, 129.3, 128.9, 124.5, 93.3, 70.9, 70.1, 69.2, 47.4, 20.79, 20.77, 16.2; IR ($CHCl_3$) 3500 (br), 3020, 1740, 1370, 1230, 1055 cm^{-1}; high resolution mass spectrum for $C_{16}H_{20}O_6Se$ (M^+) calcd 388.0425, found 388.0489.

Partial data for the glycosyl fluoride: R_f 0.40 (30% EtOAc–hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (m, 2 H), 7.35–7.30 (m, 3 H), 5.84 (dd, J = 51.1 ($J_{F\text{-}H1}$), 2.4 Hz, 1 H, H_1), 5.30 (d, J = 3.3 Hz, 1 H, H_4), 4.27 (q, J = 6.5 Hz, 1 H, H_5), 4.11 (ddd, J = 11.5, 3.3, 3.3 Hz, 1 H, H_3), 3.36 (ddd, J = 32.4 ($J_{F\text{-}H2}$), 11.5, 2.4 Hz, 1 H, H_2), 2.47 (d, J = 3.3 Hz, 1 H for the C-3 OH), 2.16 (s, 3 H), 1.18 (d, J = 6.5 Hz, 3 H, H_6).

Acetyl 4-*O*-Acetyl-3-*O*-[3-*O*-((*tert*-butyldimethyl)silyl)-2,6-dideoxy-2-iodo-4-*O*-methyl-α-D-*talo*-pyranosyl]-2,6-dideoxy-2-(selenophenyl)-β-D-*galacto*-pyranoside (60). A solution of glycal **54** (88 mg, 0.34 mmol) and alcohol **56** (88 mg, 0.23 mmol) in CH_2Cl_2 (2 mL) was stirred at 23 °C in the presence of 4 Å molecular sieves (~20 mg) for 0.5 h and then cooled to 0 °C. $I(coll)_2ClO_4$ (160 mg, 0.34 mmol) was added in one portion. The mixture was stirred in the dark from 0 °C to 23 °C for 8.5 h. The mixture was diluted with EtOAc (20 mL), washed with $Na_2S_2O_3$ (2 × 20 mL), and water (20 mL) and dried over $MgSO_4$. Purification of the crude product by flash column chromatography (20% EtOAc–hexanes) furnished the α,β-disaccharide **60** (127 mg, 72%) along with an isomeric disaccharide **64** (12 mg, 6%) with an equatorial iodide in the B residue. No disaccharides with β-linkages between the two monosaccharides were detected.



64

A larger scale experiment performed with glycal **54** (1.92 g, 7.42 mmol), alcohol **56** (2.39 g, 6.18 mmol), and $I(coll)_2ClO_4$ (4.30 g, 9.16 mmol) in CH_2Cl_2 (20 mL) for a shorter reaction period (1 h, 0 °C) provided disaccharide **60** (2.50 g, 52% yield; 81% based on recovered **56**), recovered alcohol **56** (0.84 g, 35% yield), and the isomeric disaccharide **64** (0.28 g, 6%).

Data for disaccharide 60: R_f 0.48 (30% EtOAc–hexanes); $[\alpha]^{26}_D$ +49.3° (*c* 1.11, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 2 H), 7.30–7.25 (m, 3 H), 5.68 (d, J = 9.6 Hz, 1 H, H_1), 5.55 (br s, 1 H, $H_{1'}$), 5.22 (br d, J = 3.1 Hz, 1 H, H_4), 4.55 (qd, J = 6.5, 1.3 Hz, 1 H, $H_{5'}$), 3.93 (dd, J = 4.7, 0.9 Hz, 1 H, $H_{2'}$), 3.85 (dd, J = 11.8, 3.1 Hz, 1 H, H_3), 3.75 (qd, J = 6.4, 0.8 Hz, 1 H, H_5), 3.58 (s, 3 H), 3.49 (dd, J = 4.7, 3.0 Hz, 1 H, $H_{3'}$), 3.43 (dd, J = 11.8, 9.6 Hz, 1 H, H_2), 3.24 [dd, J = 3.0, 1.3 Hz, 1 H, $H_{4'}$, becomes a doublet with J = 3.0 Hz upon irradiation at δ 4.55 ($H_{5'}$)], 2.17 (s, 3 H), 1.86 (s, 3 H), 1.29 (d, J = 6.5 Hz, 3 H, $H_{6'}$, becomes a singlet upon irradiation at δ 4.55 ($H_{5'}$)), 1.20 (d, J = 6.4 Hz, 3 H, H_6), 0.95 (s, 9 H), 0.10 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 168.7, 133.9, 129.1, 128.7, 127.7, 100.6, 94.2, 80.6, 74.2, 69.6, 68.3, 68.2, 67.6, 60.8, 45.6, 27.1, 25.7, 20.6, 20.5, 18.0, 16.4, 16.3, −4.8, −4.9; IR ($CHCl_3$) 3020, 1740, 1365, 1235, 1115, 1085, 1060, 1040, 950, 860, 840 cm^{-1}; high resolution mass spectrum for $C_{25}H_{36}O_9SiSeI$ ($M^+ - C_4H_9$) calcd 715.0338, found 715.0373. Anal. Calcd for $C_{29}H_{45}O_9SiSeI$: C, 45.14; H, 5.88. Found: C, 44.82; H, 5.59.

NMR data for the minor disaccharide 64: ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (m, 2 H), 7.30–7.28 (m, 3 H), 5.80 (d, J = 9.7 Hz, 1 H, H_1), 5.34 (d, J = 3.0 Hz, 1 H, H_4), 5.22 (d, J = 3.2 Hz, 1 H, $H_{1'}$, becomes singlet upon irradiation at δ 4.40 ($H_{2'}$)), 4.40 (dd, J = 11.0, 3.2 Hz, 1 H, $H_{2'}$), 4.29 (q, J = 6.5 Hz, 1 H, $H_{5'}$), 4.17 (dd, J = 11.0, 2.5 Hz, 1 H, $H_{3'}$, becomes a doublet with J = 2.5 Hz upon irradiation at δ 4.40 ($H_{2'}$)), 3.80 (q, J = 6.4 Hz, 1 H, H_5), 3.75 (dd, J = 11.9, 3.0 Hz, 1 H, H_3), 3.59 (s, 3 H), 3.588 (dd, J = 11.9, 9.7 Hz, 1 H, H_2), 3.20 (d, J = 2.5 Hz, 1 H, $H_{4'}$, becomes a singlet upon irradiation at δ 4.17 ($H_{3'}$)), 2.22 (s, 3 H), 1.87 (s, 3 H), 1.24 (d, J = 6.5 Hz, 3 H, $H_{6'}$, becomes a singlet upon irradiation at δ 4.29 ($H_{5'}$)), 1.18 (d, J = 6.4 Hz, 3 H, H_6), 0.93 (s, 9 H), 0.12 (s, 3 H), 0.050 (s, 3 H).

4-*O*-Acetyl-3-*O*-[3-*O*-((*tert*-butyldimethyl)silyl)-2,6-dideoxy-2-iodo-4-*O*-methyl-α-D-*talo*-pyranosyl]-2,6-dideoxy-2-(selenophenyl)-α-D-*galacto*-pyranose (53). A mixture of disaccharide **60** (208 mg, 0.27 mmol) and anhydrous hydrazine (13.5 μL, 0.43 mmol) in MeOH (7 mL) was stirred from 0 °C to 23 °C overnight and then concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (20% EtOAc–hexanes) to give the reducing disaccharide **53** (180 mg, 92%) as a white foamy solid. 500 MHz ^1H NMR analysis indicated that **53** was a 14:1 mixture of α:β anomers at one concentration (dilute) but a 7.5:1 (α:β) mixture in a more concentrated NMR experiment: R_f 0.33 (30% EtOAc–hexanes); IR ($CHCl_3$) 3450–3100 (br), 1740, 1370, 1240, 1120, 1090, 1040, 1015, 970, 950, 860, 840 cm^{-1}; high resolution mass spectrum for $C_{27}H_{42}O_7SiSeI$ (M^+ − OH) calcd 713.0909, found 713.0915. Anal. Calcd for $C_{27}H_{43}O_8SiSeI$: C, 44.45; H, 5.94. Found: C, 44.71; H, 5.95.

NMR Data for the α-anomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.25–7.20 (m, 3 H), 5.54 (s, 1 H, $H_{1'}$), 5.49 (dd, J = 3.7, 2.7 Hz, 1 H, H_1), 5.29 (br d, J = 2.8 Hz, 1 H, H_4), 4.39 (qd, J = 6.5, 1.2 Hz, 1 H, $H_{5'}$), 4.34 (br q, J = 6.6 Hz, 1 H, H_5, becomes a sharp quartet upon irradiation at δ 5.29 (H_4)), 4.31 (dd, J = 11.8, 2.8 Hz, 1 H, H_3), 3.88 (d, J = 4.8 Hz, 1 H, $H_{2'}$), 3.55 (dd, J = 11.8, 3.7 Hz, 1 H, H_2), 3.54 (s, 3 H), 3.25 (dd, J = 4.8, 3.0 Hz, 1 H, $H_{3'}$), 3.08 (br s, 1 H, $H_{4'}$), 2.90 (br s, 1 H for the OH), 2.16 (s, 3 H), 1.26 (d, J = 6.5 Hz, 3 H, $H_{6'}$, becomes a singlet upon irradiation at δ 4.39 ($H_{5'}$)), 1.16 (d, J = 6.6 Hz, 3 H, H_6), 0.92 (s, 9 H), 0.03 (s, 3 H), −0.04 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 131.5, 131.2, 129.2, 126.8, 100.2, 94.7, 80.8, 72.2, 70.0, 67.8, 67.6, 65.1, 60.8, 45.8, 27.7, 25.8, 20.6, 18.0, 16.5, 16.4, −4.8, −4.9.

Partial NMR data for the β-anomer (measured on the mixture): ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (m, 2 H), 7.30–7.20 (m, 3 H), 5.53 (s, 1 H, $H_{1'}$)), 5.18 (d, J = 3.1 Hz, 1 H, H_4), 4.63 (qd, J = 6.5, 1.1 Hz, 1 H, $H_{5'}$), 4.59 (br d, J = 8.9 Hz, 1 H, H_1), 3.93 (d, J = 4.8 Hz, 1 H, $H_{2'}$), 3.81 (dd, J = 11.6, 3.1 Hz, 1 H, H_3), 3.62 (q, J = 6.5 Hz, 1 H, H_5), 3.58 (s, 3 H), 3.46 (dd, J = 4.8, 3.0 Hz, 1 H, $H_{3'}$), 3.35 (br s, 1 H, -OH), 3.16 (dd, J = 11.6, 8.9 Hz, 1 H, H_2), 3.11 (br s, 1 H, $H_{4'}$), 2.14 (s, 3 H), 1.29 (d, J = 6.5 Hz, 3 H), 1.19 (d, J = 6.5 Hz, 3 H), 0.94 (s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H).

2-Naphthyl 4-*O*-Acetyl-3-*O*-[3-*O*-((*tert*-butyldimethyl)silyl)-2,6-dideoxy-2-iodo-4-*O*-methyl-α-D-*talo*-pyranosyl]-2,6-dideoxy-2-(selenophenyl)-β-D-*galacto*-pyranoside (61). A solution of reducing disaccharide **53** (146 mg, 0.200 mmol), 2-naphthol (40 mg, 0.28 mmol), and Ph_3P (81 mg, 0.309 mmol) in toluene (3 mL) was stirred with 4Å molecular sieves (~100 mg) for 0.5 h and cooled to 0 °C. DEAD (63 μL, 0.400 mmol) was added, and the reaction mixture was stirred overnight. The mixture was then diluted with EtOAc and filtered. ^1H NMR analysis (500 MHz) of the crude product showed that it consisted of an 11:1 mixture of α,β- and α,α-disaccharides. Separation of this mixture by flash chromatography (20% EtOAc–hexanes) afforded the α,α-disaccharide (6.2 mg, 3.6%) and the α,β-disaccharide **61** (170 mg, contaminated by 2-naphthol). The impure β-anomer was further purified by preparative TLC (15% EtOAc–hexanes, five elutions) to give pure **61** (111 mg, 65%): R_f 0.33 (20% EtOAc–hexanes); $[\alpha]^{26}_D$ +54.7° (*c* 1.56, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79–7.59 (m, 5 H), 7.47–7.18 (m, 6 H), 6.99 (m, 1 H), 5.60 (s, 1 H, $H_{1'}$), 5.28 (d, J = 3.1 Hz, 1 H, H_4), 5.10 (d, J = 9.1 Hz, 1 H, H_1), 4.69 (qd, J = 6.5, 1.2 Hz, 1 H, $H_{5'}$), 3.97 (d, J = 4.7 Hz, 1 H, $H_{2'}$), 3.92 (dd, J = 11.8, 3.1 Hz, 1 H, H_3), 3.82 (q, J = 6.4 Hz, 1 H, H_5), 3.60 (s, 3 H),

3.59 (dd, J = 11.8, 9.1 Hz, 1 H, H_2), 3.55 (dd, J = 4.7, 3.0 Hz, 1 H, $H_{3'}$), 3.28 (dd, J = 3.0, 1.2 Hz, 1 H, H_4), 2.19 (s, 3 H), 1.31 (d, J = 6.5 Hz, 3 H, $H_{6'}$, becomes a singlet upon irradiation at δ 4.69 ($H_{5'}$)), 1.28 (d, J = 6.4 Hz, 3 H, H_6), 0.97 (s, 9 H), 0.13 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 154.8, 134.7, 134.2, 129.8, 129.3, 129.0, 128.5, 127.8, 127.6, 127.1, 126.3, 124.3, 118.8, 110.6, 101.2, 100.9, 80.8, 74.4, 69.0, 68.5, 68.3, 67.7, 60.9, 46.8, 27.4, 25.8, 20.7, 18.1, 16.6, 16.5, −4.7, −4.8; IR ($CHCl_3$) 3050, 1740, 1630, 1600, 1465, 1370, 1240, 1175, 1120, 1090, 1060, 970, 950, 860, 840 cm^{-1}; high resolution mass spectrum for $C_{27}H_{42}O_7SiSeI$ ($M^+ - C_{10}H_7O$) calcd 713.0909, found 713.0892. Anal. Calcd for $C_{37}H_{49}O_8SiSeI$: C, 51.93; H, 5.77. Found: C, 51.78; H, 5.80.

Partial data for the minor α,α-disaccharide: R_f 0.45 (20% EtOAc−hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81−7.74 (m, 3 H), 7.48−7.36 (m, 5 H), 7.26−7.18 (m, 4 H), 5.89 (d, J = 3.3 Hz, 1 H, H_1, becomes a singlet upon irradiation at δ 3.71 (H_2)), 5.62 (s, 1 H, $H_{1'}$), 5.38 (d, J = 2.8 Hz, 1 H, H_4), 4.53 (dd, J = 11.7, 2.8 Hz, 1 H, H_3), 4.50 (q, J = 6.6 Hz, 1 H, $H_{5'}$), 4.28 (br q, J = 6.5 Hz, 1 H, H_5, becomes a sharp quartet upon irradiation at δ 5.38 (H_4)), 3.93 (d, J = 4.8 Hz, 1 H, $H_{2'}$), 3.71 (dd, J = 11.7, 3.3 Hz, 1 H, H_2), 3.57 (s, 3 H), 3.30 (dd, J = 4.8, 3.2 Hz, 1 H, $H_{3'}$), 3.12 (br s, 1 H, $H_{4'}$, becomes a doublet with J = 3.2 Hz upon irradiation at δ 4.50 ($H_{5'}$)), 2.20 (s, 3 H), 1.33 (d, J = 6.6 Hz, 3 H, $H_{6'}$, becomes a singlet upon irradiation at δ 4.50 ($H_{5'}$)), 1.17 (d, J = 6.5 Hz, 3 H, H_6), 0.93 (s, 9 H), 0.055 (s, 3 H), −0.017 (s, 3 H).

2-Naphthyl 4-*O*-Acetyl-3-*O*-[3-*O*-((*tert*-butyldimethyl)silyl)-2,6-dideoxy-4-*O*-methyl-α-D-*galacto*-pyranosyl]-2,6-dideoxy-β-D-*galacto*-pyranoside (5). A mixture of disaccharide **61** (40 mg, 0.047 mmol), Bu_3SnH (150 μL, 0.56 mmol), and a catalytic amount of AIBN in toluene (1.5 mL) was degassed under vacuum and placed under a N_2 atmosphere. This process was repeated three times. The flask was then sealed with a septum and heated at 80 °C for 9 h. The mixture was then directly applied to a silica gel column and eluted with hexanes and then 10% followed by 20% EtOAc−hexanes to give disaccharide **5** as an oil (24 mg, 90%): R_f 0.21 (20% EtOAc−hexanes); $[\alpha]^{26}_D$ +65.5° (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80−7.73 (m, 3 H), 7.47 (m, 1 H), 7.38−7.33 (m, 2 H), 7.22 (m, 1 H), 5.29 (dd, J = 9.7, 2.4 Hz, 1 H, H_1), 5.17 (br d, J = 3.3 Hz, 1 H, H_4), 5.08 (d, J = 3.7 Hz, 1 H, $H_{1'}$), becomes a singlet upon irradiation at δ 2.03 ($H_{2'ax}$), 4.07 (ddd, J = 11.8, 4.6, 2.6 Hz, 1 H, $H_{3'}$, becomes a broad singlet upon irradiation at δ 2.03 ($H_{2'ax}$)), 3.97 (ddd, J = 12.2, 5.1, 3.3 Hz, 1 H, H_3, becomes a dd, J = 12.2, 5.1 Hz upon irradiation at δ 5.17 (H_4)), 3.86 (q, J = 6.5 Hz, 1 H, $H_{5'}$, becomes a singlet upon irradiation at δ 1.22 ($H_{6'}$)), 3.83 (br q, J = 6.5 Hz, 1 H, H_5, becomes a sharp quartet upon irradiation at δ 5.17 (H_4)), 3.60 (s, 3 H), 3.09 (br s, 1 H, $H_{4'}$), 2.18 (ddd, J = 12.2, 12.1, 9.7 Hz, 1 H, H_{2ax}), 2.16 (s, 3 H), 2.11 (ddd, J = 12.1, 5.1, 2.4 Hz, 1 H, H_{2eq}), 2.03 (ddd, J = 12.6, 11.8, 3.7 Hz, 1 H, $H_{2'ax}$, becomes a dd, J = 12.6, 3.7 Hz upon irradiation at δ 4.07 ($H_{3'}$)), 1.57 (m, 1 H, $H_{2'eq}$, obscured by the residual H_2O from the solvent), 1.31 (d, J = 6.5 Hz, 3 H, H_6), 1.22 (d, J = 6.5 Hz, 3 H, $H_{6'}$), 0.91 (s, 9 H), 0.085 (s, 3 H), 0.080 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 154.8, 134.3, 129.8, 129.4, 127.6, 127.1, 126.3, 124.2, 118.9, 110.6, 97.9, 96.4, 81.6, 70.9, 69.6, 68.4, 67.9, 67.3, 61.7, 33.36, 33.33, 25.8, 20.7, 18.1, 17.0, 16.8, −4.7, −4.8; IR ($CHCl_3$) 3030, 1735, 1630, 1600, 1510, 1465, 1380, 1250, 1170, 1100, 1055, 1045, 1025, 1015, 940, 855, 835 cm^{-1}; high resolution mass spectrum for $C_{31}H_{46}O_8Si$ (M^+) calcd 574.2962, found 574.2972. Anal. Calcd for $C_{31}H_{46}O_8Si$: C, 64.78; H, 8.07. Found: C, 64.49; H, 8.12.

Methyl 1-Acetoxy-8-((benzyloxy)methoxy)-3-{2′*R*, 3′*S*, 4′*R*, 5′*S*, 6′*R*)-4′-[(*tert*-butyldimethylsilyl)oxy]-5′,6′-[cyclohexylidenebis(oxy)]-2′-ethenyl-3′-methoxyheptyl}-6-hydroxy-2-naphthoate (63). A solution of naphthoate **62** (45 mg, 0.057 mmol) in pyridine (0.5 mL) and acetic anhydride (0.5 mL) was left at 22 °C for 4 h. The mixture was diluted with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layers were washed with H_2O, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude product by flash chromatography (6:1 hexane/EtOAc) gave the acetate (42 mg, 88%).

Tributyltin hydride (13 μL, 0.048 mmol) was added to a stirred mixture of the above acetate (40 mg, 0.048 mmol), $Pd(PPh_3)_4$ (1.5 mg, 0.001 mmol), and glacial acetic acid (3 μL, 0.052 mmol) in toluene (0.5 mL) at 22 °C. The mixture was stirred for 5 min, then it was diluted with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the crude product by flash chromatography (4:1 hexane/EtOAc) provided the 6-hydroxynaphthoate **63** (34 mg, 89%): R_f 0.23 (3:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.09 (m, 6 Ar H), 6.71 (d, J = 2.0, 1 Ar H), 6.57 (d, J = 2.0, 1 Ar H), 5.57 (ddd, J = 8.0, 10.0, 17.2, 1 olefin H), 5.55 (br s, OH), 5.25 (s, OCH_2OBn), 4.78 (dd, J = 1.2, 10.4, 1 olefin H), 4.65 (s, CH_2Ph), 4.65 (dd, J = 1.2, 17.2, 1 olefin H), 4.07 (dq app. as quint, J = 6.4, H6′), 3.87−3.84 (m, H4′), 3.85 (s, CO_2CH_3), 3.67 (dd, J = 6.0, 6.4, H5′), 3.43 (s, OCH_3), 3.16 (br d, J = 10.4, H_A1'), 3.09 (dd, J = 4.8, 5.6, H3′), 2.65−2.59 (m, H_B1', H2′), 2.19 (s, CH_3CO), 1.60−1.47 (m, 8 H), 1.26 (d, J = 6.4, H_3C7'), 1.31−1.18 (m, 2 H), 0.85 (s, $(CH_3)_3C$), 0.05 (s, $SiCH_3$), 0.03 (s, $SiCH_3$).

Methyl 1-Acetoxy-8-((benzyloxy)methoxy)-6-{[4″-*O*-acetyl-3″-*O*-(3‴-*O*-(*tert*-butyldimethylsilyl)-2‴,6‴-dideoxy-2‴-iodo-4‴-*O*-methyl-α-D-talopyranosyl)-2″,6″-dideoxy-2″-(phenylselenyl)-β-D-galactopyranosyl]oxy}-3-{2′*R*, 3′*S*, 4′*R*, 5′*S*, 6′*R*)-4′-[(*tert*-butyldimethylsilyl)oxy]-5′,6′-[cyclohexylidenebis(oxy)]-2′-ethenyl-3′-methoxyheptyl}-2-naphthoate (6). A mixture of lactol **53** (22 mg, 0.030 mmol), naphthol **63** (26 mg, 0.033 mmol), and triphenylphosphine (11 mg, 0.042 mmol) in toluene (0.5 mL) was stirred over powdered 4Å molecular sieves (20 mg) under Ar at 22 °C for 30 min. Then the mixture was cooled to 0 °C, and diethyl azodicarboxylate (7.5 μL, 0.048 mmol) was added dropwise over 5 min. The mixture was stirred at 22 °C for 12 h and then filtered, and the filtrate was concentrated *in vacuo*. Purification of the crude product by flash chromatography (10:1 toluene/EtOAc, then 8:1) gave a mixture of glycoside **6** and naphthol **63**, which was separated by preparative HPLC (10 mm × 25 cm Dynamax-60A column (83-111-C); 3:1 hexane/EtOAc, 5 mL/min) to give **6** (26 mg, 57%) and recovered **63** (9 mg, 35%).

Data for 6: R_f 0.29 (3:1 hexane/EtOAc); $[\alpha]_D^{25}$ + 27.3° (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.53 (m, 2 Ar H), 7.41−7.12 (m, 9 Ar H), 6.73 (d, J = 2.0, 1 Ar H), 6.69 (d, J = 2.0, 1 Ar H), 5.66 (m, 1 olefin. H), 5.58 (br s, H1‴), 5.27 (s, OCH_2OBn), 5.24 (br d, J = 3.2, H4″), 5.02 (d, J = 9.2, H1″), 4.88 (dd, J = 10.0, 1.6, 1 olefin. H), 4.77−4.65 (m, 1 olefin. H, CH_2Ph, H5‴), 4.15 (dq app. as quint., J = 6.4, H6′), 3.96 (br d, J = 4.4, H2‴) 3.93 (s, CO_2CH_3), 3.94−3.90 (m, 1 H), 3.87 (dd, J = 3.0, 12.0, H3″), 3.73 (dd, J = 6.4, 6.0, H5′), 3.69 (br q, J = 6.4, H5″), 3.60 (s, OCH_3), 3.58−3.49 (m, H3‴, H2″), 3.50 (s, OCH_3), 3.27 (br s, H4‴), 3.24 (br d, J =11.2, H_A1'), 3.17 (dd, J = 4.8, 5.6, H3′), 2.72−2.67 (m, H_B1', H2′), 2.27 (s, CH_3CO), 2.17 (s, CH_3CO), 1.7−1.4 (m, 10 H), 1.33 (d, J = 6.0, H_3-C7′), 1.31 (d, J = 6.8, H_3C6'''), 1.21 (d, J = 6.4, H_3C6''), 0.96 (s, $(CH_3)_3C$), 0.93 (s, $(CH_3)_3C$), 0.130 (s, $SiCH_3$), 0.126 (s, $SiCH_3$), 0.11 (s, $SiCH_3$), 0.10 (s, $SiCH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.6, 169.2, 167.6, 159.3, 157.7, 156.1, 154.2, 138.8, 137.0, 136.8, 136.6, 134.9, 129.0, 128.5, 128.3, 128.1, 128.0, 127.9, 124.2, 119.0, 116.9, 114.6, 114.0, 108.7, 103.3, 101.3, 101.1, 100.9, 92.9, 85.1, 82.2, 80.8, 74.3, 73.6, 73.4, 70.0, 69.0, 68.4, 68.2, 67.7, 61.1, 60.9, 52.3, 47.2, 46.9, 37.0, 36.9, 33.1, 27.3, 26.2, 25.8, 25.2, 23.9, 20.7, 20.6, 18.3, 18.1, 16.5, −3.6, −3.9, −4.7, −4.8; IR ($CHCl_3$) 3005 *m*, 2935 *s*, 2860 *m*, 1740 *s*, 1630 *m*, 1580 *w*, 1450 *m*, 1370 *m*, 1240 *s*, 1170 *s*, 1110 *s*, 1090 *s*, 1065 *s*, 950 *m*; FAB-MS (3-nitrobenzyl alcohol matrix + NaOAc) 1528 ($M^{\cdot+}$ + Na).

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Supplementary Material Available: Experimental procedures and ^{1}H NMR spectra for the synthesis of **47-51** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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