Novel Glycosidation Methodology. The Use of Phenyl Selenoglycosides as Glycosyl Donors and Acceptors in Oligosaccharide Synthesis[1]

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The use of phenyl selenoglycosides as glycosyl donors and acceptors in glycosidation reactions is described. The versatility of these novel compounds is illustrated by the selective activation of both "disarmed" and "armed" phenyl selenoglycoside donors over "armed" ethyl thioglycoside acceptors with silver trifluoromethanesulfonate in the presence of potassium or silver carbonate to give disaccharides in excellent yield. Selective activation of glycosyl bromide donors over phenyl selenoglycoside acceptors is realized by silver trifluoromethanesulfonate promotion in the presence of collidine. Such selectivity is also demonstrated by the activation of a glycosyl trichloroacetimidate donor in the presence of selenoglycoside acceptors with triethylsilyl trifluoromethanesulfonate. The central role of selenoglycosides is illustrated by the synthesis of a trisaccharide that profits from the sequential, selective activation of a glycosyl bromide donor over a selenoglycoside acceptor and the resulting disaccharide selenoglycoside over a thioglycoside acceptor. The liberation of the anomeric hydroxyl group from a phenyl selenoglycoside is also described.

Introduction

Biological and biochemical processes that are mediated by carbohydrate–protein interactions are of widespread importance. Oligosaccharides located on cell surface glycoproteins and glycolipids serve as recognition markers for the immune system and also play critical roles in the binding of lectins, hormones, and enzymes, the targeting of viruses and bacteria to cells, and in cell–cell recognition and development.[2-5] Carbohydrate-binding proteins have also been implicated as receptors for bacterial active transport and chemotaxis.[6] More recently, a great deal of effort has been focused on the role of cell-surface carbohydrates as mediators of cell recruitment and cell–cell adhesion.[7]

The detailed investigation of the processes described above requires access to reasonable quantities of specific oligosaccharides. Chemical,[8-13] enzymatic,[14,15] and chemoenzymatic[16,17] glycosidation methodology has advanced rapidly in recent years and has provided many of the candidate structures on small scales. However, the practical synthesis of oligosaccharides on a large scale remains an enviable goal. The practicality of the enzymatic approach for large-scale synthesis is governed by the ready availability of the glycosyl transferases, the cost of the donor sugar nucleotides, and the problems of substrate or product inhibition.[17] Access to cloned and overexpressed enzymes and methodology for the in situ cofactor generation have reduced the severity of these problems.[17] The chemical approach still requires the development of general synthetic methods that require fewer manipulations and/or result in higher yields, increased stereoselectivity, and selective activation.

Particularly noteworthy recent contributions include the development of methods for the stereoselective synthesis of β-D-mannopyranosides[18,19] and α-sialosides.[20] With respect to reactivity, the use of "armed" and "disarmed" pentenyl glycosides,[21] glycals,[22] and thioglyc-

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(1) Presented at The 75th Canadian Chemical Conference, Edmonton, Alberta, Canada, June, 1992, Abstr. No. 636, and The XVIth International Chemical Carbohydrate Symposium, Paris, France, July, 1992, Abstr. No. A163.

(2) *Carbohydrate-Protein Interactions*; Clarke, A. E., Wilson, I. A., Eds.; Springer: Heidelberg, 1988.

(3) *Glycoconjugates*; Allen, H. J., Kisailus, E. C., Eds.; Marcel Dekker, Inc.: New York, 1992.

(4) Rademacher, T. W.; Parekh, R. B.; Dwek, R. A. *Annu. Rev. Biochem.* **1988**, *57*, 785.

(5) Lis, H.; Sharon, N. *Curr. Opin. Struct. Biol.* **1991**, *1*, 741. Wiley, D. C.; Skehel, J. J. *Annu. Rev. Biochem.* **1987**, *56*, 365. Bundle, D. R.; Young, N. M. *Curr. Opin. Struct. Biol.* **1992**, *2*, 666.

(6) Spurlino, J. C.; Lu, G.-Y.; Quiocho, F. A. *J. Biol. Chem.* **1991**, *266*, 5202, and refs therein.

(7) Hughes, K. C. *Curr. Opin. Struct. Biol.* **1992**, *2*, 687. Lasky, L. A. *Science* **1992**, *258*, 964, and refs cited therein.

(8) Lemieux, R. U.; Hendriks, K. B.; Stick, R. V.; James, K. *J. Am. Chem. Soc.* **1975**, *97*, 4056.

(9) Paulsen, H. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 155. *Ibid.* **1990**, *29*, 823.

(10) Schmidt, R. R. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 212.

(11) Fugedi, P.; Garegg, P. J.; Lonn, H.; Norberg, T. *Glycoconjugate J.* **1987**, *4*, 97.

(12) Sinay, P. *Pure Appl. Chem.* **1991**, *63*, 519.

(13) Garegg, P. J. *Acc. Chem. Res.* **1992**, *25*, 575.

(14) *Enzymes in Carbohydrate Synthesis*; Bednarski, M. D., Simon, E. S., Eds.; ACS Symposium Series 466; American Chemical Society: Washington, DC, 1991.

(15) See also: Thiem, J.; Treder, W. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1096. David, S.; Augé, C. *Pure Appl. Chem.* **1987**, *59*, 1501. Ichikawa, Y.; Liu, J. L.-C.; Shen, G.-J.; Wong, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6300. Wong, C.-H.; Ichikawa, Y.; Krach, T.; Gautheron-Le-Narvor, C.; Dumas, D. P.; Look, G. C. *J. Am. Chem. Soc.* **1991**, *113*, 8137. Wong, C.-H.; Krach, T.; Gautheron-Le-Narvor, C.; Ichikawa, Y.; Look, G. C.; Gaeta, F.; Thompson, D.; Nicolaou, K. C. *Tetrahedron Lett.* **1991**, *32*, 4867. Yuasa, H.; Hindsgual, O.; Palcic, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 5891.

(16) For example: Sabesan, S.; Paulson, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2068. Gokhale, U. B.; Hindsgaul, O.; Palcic, M. M. *Can. J. Chem.* **1990**, *68*, 1063. Kaur, K. J.; Hindsgaul, O. *Carbohydr. Res.* **1992**, *226*, 219. Ball, G. E.; O'Neill, R. A.; Schultz, J. E.; Lowe, J. B.; Weston, B. W.; Nagy, J. O.; Brown, E. G.; Hobbs, C. J.; Bednarski, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5449.

(17) Ichikawa, Y.; Lin, Y.-C.; Dumas, D. P.; Shen, C.-J.; Garcia-Junceda, E.; Williams, M. A.; Bayer, R.; Ketcham, C.; Walker, L. E.; Paulson, J. C.; Wong, C.-H. *J. Am. Chem. Soc.* **1992**, *114*, 9283.

(18) Barresi, F.; Hindsgaul, O. *J. Am. Chem. Soc.* **1991**, *113*, 9376. *Synlett* **1992**, 759.

(19) Stork, G.; Kim, G. *J. Am. Chem. Soc.* **1992**, *114*, 1087.

(20) Martin, T. J.; Schmidt, R. R. *Tetrahedron Lett.* **1992**, *33*, 6123.

(21) Mootoo, D. R.; Konradsson, P.; Udodong, U.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 5583. Mootoo, D. R.; Konradsson, P.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1989**, *111*, 8540.

(22) Friesen, R. W.; Danishefsky, S. J. *Tetrahedron* **1990**, *46*, 103.

0022-3263/93/1958-3269$04.00/0

cosides[23] for the selective activation of one of the partners in a glycosidation reaction has been described. Initially, the method was based on the differential reactivity conferred upon each of the partners by the nature of the protecting groups. However, as the method evolved, it became clear that the choice of the promoter was also an important consideration. Indeed, a "disarmed" pentenyl glycoside[24] or thioglycoside[25] could be activated in the presence of *N*-iodosuccinimide/trifluoromethanesulfonic acid (NIS/TfOH) whereas it remained unactivated in the presence of iodonium dicollidine perchlorate. In addition, an "armed" pentenyl glycoside can also be deactivated by its conversion to a vicinal dibromide.[26]

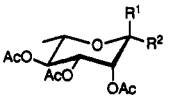
An alternative strategy derives from the availability of different glycosyl-X and glycosyl-Y units which can be selectively activated. The strategy was described initially by Silwanis et al.[27] wherein a methylthio or phenylthio glycoside was selectively activated over a (*p*-nitrophenyl)-thioglycoside. Very recently, Roy et al.[28] described a more complete study of the effects of activating and deactivating substituents on the reactivity of para-substituted (phenylthio)-α-sialosides in glycosidation reactions.

We have recently communicated[29] our strategy which relies on the latter approach and exploits the increased reactivity of phenyl selenoglycosides over ethyl thioglycosides. We now report on the scope of this novel glycosidation method and show that phenyl selenoglycosides are versatile donors and acceptors that provide the desired selectivity in glycosidation reactions. Thus, their selective activation over thioglycosides, together with their inertness under conditions in which glycosyl halides and glycosyl trichloroacetimidates may be activated, offer a significant and powerful addition to the repertoire of the synthetic oligosaccharide chemist.

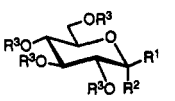
Results and Discussion

The selenoglycosides have been described previously by Witczak and Whistler.[30] Prior to our initial communication[29] this class of compounds had not, however, been exploited as glycosyl donors. The phenyl selenoglycosides 1–4 were prepared by the reaction of the peracetylated parent sugars with phenylselenol (obtained by the hypophosphorus acid reduction of diphenyldiselenide[31]) in the presence of boron trifluoride etherate. Compound **5** was obtained from 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose[32] in similar fashion. Zemplen deacetylation of compound **4** and subsequent benzylation afforded the selenoglycoside **6**. The phenyl selenoglycosides thus obtained are all crystalline, odorless, and stable compounds.

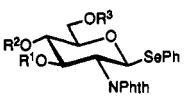
The strategy for the selective activation of selenoglycoside donors arose from three critical observations: (1) the donors could be activated by silver trifluoromethanesulfonate (triflate), (2) the activation was suppressed by the addition of conventional proton acceptors such as collidine and 1,1,3,3-tetramethylurea, and (3) an inorganic base such as anhydrous potassium carbonate or silver carbonate did not quench the reaction. These observations were used to advantage in the design of various selective activation strategies, as discussed below.



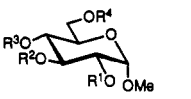
	R^1	R^2
1.	SePh	H
2.	H	SePh
14.	SEt	H



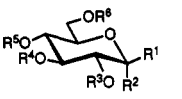
	R^1	R^2	R^3
3.	H	SePh	Ac
4.	SePh	H	Ac
6.	SePh	H	Bzl



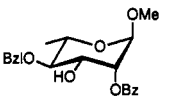
	R^1	R^2	R^3
5.	Ac	Ac	Ac
24.	H	CHPh	



	R^1	R^2	R^3	R^4
7.	Bzl	Bzl	Bzl	H
10.	Bzl	H	CHPh	



	R^1	R^2	R^3	R^4	R^5	R^6
15.	SEt	H	Bzl	Bzl	Bzl	H
16.	H	SEt	Bzl	Bzl	Bzl	H
17.	SEt	H	Bzl	Bzl	H	Bzl
23.	SePh	H	Bzl	Bzl	H	Bzl
31.	SePh	H	OH	OH	CHPh	
32.	SePh	H	Bzl	Bzl	CHPh	



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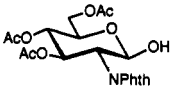

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Glycosidation of the methyl glycoside acceptor **7**[33] with selenoglycosides **1** and **5** in the presence of silver triflate and potassium carbonate afforded the 1,2-trans-linked disaccharides **8** and **9** in 85% and 84% yield, respectively, thereby establishing the viability of this mild glycosidation method. Similarly, the glycosyl acceptors **10**[34] and **11**[35] were glycosidated with **1** to give disaccharides **12** (70%) and **13** (60%), respectively (Table I).

Experiments were then performed in order to determine whether ethyl thioglycosides would remain inactive under the conditions established for selenoglycoside activation. A mixture of selenoglycoside **1** and the analogous thioglycoside **14**[36] were allowed to compete for glycosyl acceptor **7** under the conditions described above. The expected disaccharide **8** was obtained in a yield of 85% and the unreacted thioglycoside **14** was recovered in 91% yield. No reaction was observed between the thioglycoside donor **14** and the acceptor **7** under the aforementioned conditions.

Encouraged by the observed selectivity, and being cognizant of the potential of the intrinsic greater reactivity of phenyl selenoglycosides, we reasoned that activation of

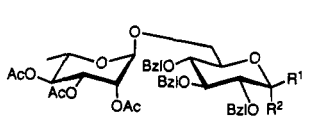
(23) Veeneman, G. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 275.
(24) Konradsson, P.; Mootoo, D. R.; McDevitt, R. E.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1990**, 270. Ratcliffe, A. J.; Konradsson, P.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1990**, *112*, 5665.
(25) Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 1331. Konradsson, P.; Udodong, U. E.; Fraser-Reid, B. *Tetrahedron Lett.* **1990**, *31*, 4313.
(26) Fraser-Reid, B.; Wu, Z.; Udodong, U. E.; Ottosson, H. *J. Org. Chem.* **1990**, *55*, 6068.
(27) Silwanis, B. A.; Dasgupta, F.; Garegg, P. J. Presented at *The Third Chemical Congress of North America*, Toronto, Canada, June, 1988, Abstr. CARB 92.
(28) Roy, R.; Andersson, F. O.; Letellier, M. *Tetrahedron Lett.* **1992**, *33*, 6053.
(29) Mehta, S.; Pinto, B. M. *Tetrahedron Lett.* **1991**, *32*, 4435.
(30) Witczak, Z. J.; Whistler, R. L. *Heterocycles* **1982**, *19*, 1719.
(31) Gunther, W. H. H. *J. Org. Chem.* **1966**, *31*, 1202.
(32) Lemieux, R. U.; Takeda, T.; Chung, B. Y. *Am. Chem. Soc. Symp. Ser. 1976*, *90*, 39.
(33) Liptak, A.; Jodal, I.; Nanasi, P. *Carbohydr. Res.* **1975**, *44*, 1.
(34) Garegg, P. J.; Iversen, T.; Oscarson, S. *Carbohydr. Res.* **1976**, *50*, c12.
(35) Prepared in analogous fashion to the corresponding allyl glycoside: Pinto, B. M.; Morissette, D. G.; Bundle, D. R. *J. Chem. Soc. Perkin Trans. 1* **1987**, 9.
(36) Auzanneau, F.-I.; Bundle, D. R. *Carbohydr. Res.* **1991**, *212*, 13.

Table I. Results of Glycosidation Reactions[a]

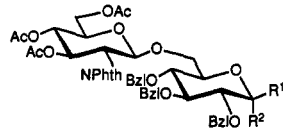
entry	donor	acceptor	molar ratio[b]	time (h)	product	yield (%)
1	1	7[33]	1:1.5:3.5	1	8	85
2	5	7	1:1.2:6	1	9	84
3	1	10[34]	1:1.2:3.5	1	12	70
4	1	11[35]	1:1.2:2	5	13	62
5	1 + 14[36]	7	1:1:2:4	24	8	86
6	14	7	1:1:2	24	no reaction	
7	15[37]	15	1:4.5	24	no reaction	
8	5	15	1:1:6	1	18	84
9	1	16[38]	1:1:3	1.5	19	80[c]
10	1	17[39]	2:1:6	2	20	78[d]
11	6	15	1:1:6	1.5	21/22	90
12	27	15	1.2:1:6	1.5	29	81

[a] Reactions in the presence of 5 equiv of K_2CO_3 with respect to AgTfl, unless otherwise stated. [b] Donor/Acceptor:AgTfl. [c] Reaction in the presence of Ag_2CO_3 instead of K_2CO_3, gave disaccharide **19** in 80% yield. [d] Reaction in the presence of 3 equiv of Ag_2CO_3 with respect to AgTfl, instead of K_2CO_3.

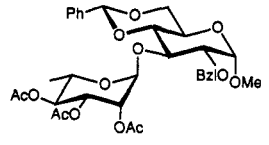
phenyl selenoglycoside donors in the presence of "armed" thioglycoside acceptors might be possible. Accordingly, the benzylated thioglycoside acceptors **15**,[37] **16**,[38] and **17**[39] were synthesized and their reactions were examined. No cross coupling of compound **16** was observed under silver triflate promotion in the presence of potassium carbonate. Furthermore, the "armed" thioglycoside acceptor **15** was glycosidated with the phenyl selenoglycoside donor **5** to yield disaccharide **18** in 84% yield. Similarly, reaction of



	R^1	R^2
8.	H	OMe
19.	H	SEt



	R^1	R^2
9.	H	OMe
18.	SEt	H



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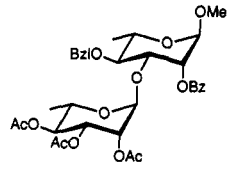

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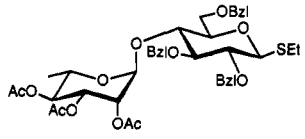

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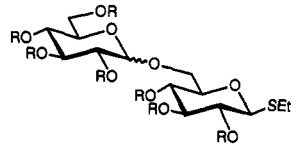
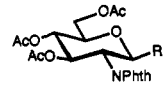


21. α, R = Bzl
22. β, R = Bzl

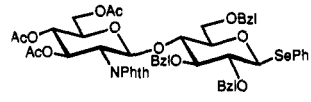
the thioglycosides **16** and **17** with selenoglycoside donor **1** afforded the corresponding disaccharides **19** and **20** in 80 and 78% yield, respectively (Table I). Thus, "disarmed" phenyl selenoglycosides are activated preferentially over "armed" thioglycosides, thereby providing added flexibility in oligosaccharide synthesis.

The selective activation of a benzylated ("armed") phenyl selenoglycoside **6** in the presence of an "armed" thioglycoside acceptor **15** was examined next. As expected, this reaction (Table I) proceeded in excellent yield (90%) and afforded an α/β mixture of disaccharides **21/22** in a ratio of 2.5:1. The preferential activation of a benzylated ("armed") phenyl selenoglycoside **6** over an "armed" thioglycoside **15** also augers well for the intrinsic higher reactivity of the former class of compounds. This observation is also corroborated by recent results reported by Zuurmond et al.[40] on the iodonium ion-mediated glycosidation reaction of **15** with the phenyl selenoglycoside of perbenzylated galactose.[41]

The fact that the phenyl selenoglycosides were rendered unreactive in the presence of an organic base such as collidine or 1,1,3,3-tetramethylurea suggested that preferential coordination of silver triflate to the base left it unavailable for coordination to and activation of the selenium atom. The former result suggested the possibility of selective activation of a glycosyl bromide over a selenoglycoside, and reaction of the selenoglycoside acceptors **23** and **24** with the glycosyl bromide donor **25**[32] gave the disaccharides **26** and **27**, respectively, in yields of about 60%.



25. R = Br
28. R = OC(NH)CCl$_3$



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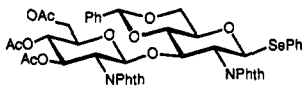

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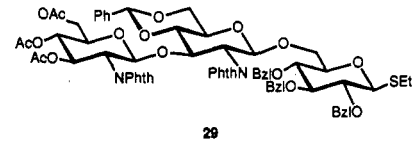

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The selective activation of glycosyl trichloroacetimidates over selenoglycosides was also demonstrated by glycosidation of selenoglycoside acceptors **23** and **24** with glycosyl trichloroacetimidate **28**[42] in the presence of a catalytic amount of triethylsilyl trifluoromethanesulfonate at −78 °C; the disaccharides **26** and **27**, respectively, were obtained in yields of 84 and 90%.

The versatility of selenoglycosides in oligosaccharide synthesis is illustrated by the synthesis of the trisaccharide **29**. The thioglycoside acceptor **15** was glycosidated with the disaccharide **27** to give the trisaccharide **29** in 81% yield. Compound **27** did not require any further manipulation prior to glycosidation and the trisaccharide **29**, present as its ethyl thioglycoside, is now available for direct glycosidation in the presence of thiophilic promoters.[11,24,25]

Finally, we investigated the possibility of liberation of the anomeric hydroxyl group from selenoglycosides. Treatment of the selenoglycoside **5** with silver triflate

(37) Ray, A. K.; Roy, N. *Carbohydr. Res.* **1990**, *196*, 95.
(38) Koto, S.; Uchida, T.; Zen, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2520.
(39) van Steijn, A. M. P.; Kamerling, J. P.; Vliegenthart, J. F. G. *Carbohydr. Res.* **1992**, *225*, 229.
(40) Zuurmond, H. M.; van der Klein, P. A. M.; van der Meer, P. H.; van der Marel, G. A.; van Boom, J. H. *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 365.
(41) These workers have also reported the preferential activation of benzoylated ("disarmed") phenyl selenoglycosides over their sulfur congeners with NIS/TfOH.
(42) Grundler, G.; Schmidt, R. R. *Carbohydr. Res.* **1985**, *135*, 203.

followed by a quench with water gave the hemiacetal **30**[43] in 80% yield.

Since our initial disclosure,[29] other groups have investigated the chemistry of selenoglycosides, and an alternative synthesis of selenoglycosides[44] and some preliminary attempts to activate phenyl selenoglycosides with other promoters[45] have been described. More significantly, Zuurmond et al.[40] have obtained promising results with the iodonium ion-mediated activation of phenyl selenoglycosides which complement our own and have also demonstrated that the "armed/disarmed" concept observed in benzylated versus benzoylated thioglycosides also applies to the corresponding phenyl selenoglycosides. Results to date suggest that phenyl selenoglycosides are versatile glycosyl donors and acceptors for glycosidation reactions.[46,52] In particular, the preferential activation or deactivation of these substrates relative to other glycosyl-X moieties indicates that they can play a pivotal role in the synthesis of an oligosaccharide, and suggest that they will certainly become part of the arsenal of the oligosaccharide chemist.

Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Optical rotations were measured with a Rudolph Research Autopol II automatic polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer at 400.13 and 100.6 MHz, for proton and carbon, respectively. All spectra were recorded in deuterochloroform and chemical shifts are given in ppm downfield from TMS. Chemical shifts and coupling constants were obtained from a first-order analysis of the spectra.

The ^{1}H-homonuclear chemical-shift correlated (COSY) spectra[56] were acquired with initial data sets of 512 × 1024 data points which were zero-filled once in the F_1 direction to give a final data set of 1024 × 1024 real data points. For the inverse detection experiments a four-pulse sequence was used for the ^{1}H{^{13}C}–^{13}C correlation.[57-59] The data sets of 512 × 2048 data points were zero-filled once in both the F_1- and the F_2-directions, to give a final data set of 1024 × 2048 real data points.

Analytical thin-layer chromatography (TLC) was performed on aluminum plates precoated with Merck silica gel 60F-254 as the adsorbent. The developed plates were air-dried, exposed to UV light and/or sprayed with 5% sulfuric acid in ethanol, and heated at 150 °C. All compounds were purified by medium-pressure column chromatography on Kieselgel 60 (230–400 mesh) according to a published procedure.[60]

Solvents were distilled before use and were dried, as necessary, by literature procedures. Solvents were evaporated under reduced pressure and below 40 °C.

Reactions performed under nitrogen were also carried out in deoxygenated solvents. Transfers under nitrogen were effected by means of standard Schlenk-tube techniques.

Phenyl 2,3,4-Tri-*O*-acetyl-1-seleno-α/β-L-rhamnopyranoside (1, 2). A mixture of diphenyl diselenide (1.2 g, 3.8 mmol) and 50% hypophosphorus acid (12 mL) was refluxed under nitrogen with vigorous stirring until the mixture was colorless (5 h). The reaction mixture was cooled and anhydrous dichloromethane (6 mL) was added. The solution of phenylselenol in CH_2Cl_2 was transferred under nitrogen into a round-bottom flask containing water (7 mL) by means of a syringe. The reaction mixture was rinsed with additional portions of CH_2Cl_2 (2 × 3 mL) which were transferred as above. After shaking the organic layer with water, it was syringed into a round-bottom flask containing magnesium sulfate, under N_2. The water layer was rinsed with CH_2Cl_2 (3 mL) and the CH_2Cl_2 layer transferred as above. The dried phenylselenol solution was then added to 1,2,3,4-tetra-*O*-acetyl-α-L-rhamnopyranoside (1.2 g, 3.6 mmol) with a syringe. The magnesium sulfate was washed with CH_2Cl_2 (3 × 5 mL) and the washings were transferred to the reaction mixture. The reaction mixture was cooled to 0 °C and BF_3OEt_2 (0.42 mL, 3.4 mmol) was added. After 22 h the reaction mixture was neutralized with Et_3N and washed with water (2 × 15 mL). The organic layer was dried over magnesium sulfate and concentrated to give a syrup which was chromatographed with hexane–ethyl acetate (3:1) as eluent. [R_f: α-isomer **1** = 0.35; β-isomer **2** = 0.27]. The products were obtained as powders and were crystallized from ethanol (α: 1.02 g, 66%; β: 0.28 g, 18%). **α-Isomer 1**: mp 117 °C; $[\alpha]^{25}_D$ −141° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 17.3 (C-6), 20.6, 20.8, 20.9 (3 $COCH_3$), 67.6 (C-5), 69.7 (C-3), 71.0 (C-4), 72.0 (C-2), 82.7 [$^1J(^{13}C,^1H)$ 171 Hz, (C-1)], 128.1–134.2 (Ar), 169.8 ($COCH_3$); ^{1}H NMR ($CDCl_3$) δ 1.25 (1 H, d, $J_{5,6}$ = 6.2 Hz, H-6), 2.00, 2.08, 2.12 (9 H, 3s, 3 $COCH_3$), 4.24 (1 H, m, H-5), 5.14 (1 H, t, $J_{3,4+4,5}$ = 19.8 Hz, H-4), 5.27 (1 H, dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 5.56 (1 H, dd, $J_{1,2}$ = 1.3 Hz, $J_{2,3}$ = 3.0 Hz, H-2), 5.65 (1 H, d, $J_{1,2}$ = 1.3 Hz, H-1), 7.1–7.7 (5 H, m, Ar). Anal. Calcd for $C_{18}H_{22}O_7Se$: C, 50.36; H, 5.17. Found: C, 50.50; H, 5.20. **β-Isomer 2**: mp 101 °C; $[\alpha]^{23}_D$ 31° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 17.7 (C-6), 20.5, 20.6 (3 $COCH_3$), 70.3 (C-4), 71.7 (C-2, C-3), 76.0 (C-5), 80.8 [$^1J(^{13}C,^1H)$ 156 Hz, (C-1)], 128.2–134.3 (Ar), 169.7, 170.1 (3 $COCH_3$); ^{1}H NMR ($CDCl_3$) δ 1.28 (1 H, d, $J_{5,6}$ = 6.2 Hz, H-6), 1.96, 2.03, 2.18 (3 s, 9 H, 3 $COCH_3$), 3.50 (1 H, m, H-5), 4.98 (1 H, dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 5.09 (1 H, d, $J_{1,2}$ = 1.0 Hz, H-1), 5.10 (1 H, t, $J_{3,4+4,5}$ = 19.6 Hz, H-4), 5.65 (1 H, dd, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 7.1–7.3 (5 H, m, Ar). Anal. Calcd for $C_{18}H_{22}O_7Se$: C, 50.36; H, 5.17. Found: C, 50.21; H, 5.22.

Phenyl 2,3,4,6-Tetra-*O*-acetyl-1-seleno-α/β-D-glucopyranoside (3, 4). A mixture of diphenyl diselenide (4.0 g, 12.8 mmol) and 50% hypophosphorus acid (40 mL) was refluxed under nitrogen with vigorous stirring until the mixture was colorless (6 h). The reaction mixture was cooled and anhydrous dichloromethane (20 mL) was added. The solution of phenylselenol in CH_2Cl_2 was transferred under N_2 into a round-bottom flask containing water by means of a syringe. The reaction mixture was rinsed with additional portions of CH_2Cl_2 (2 × 10 mL) which were transferred as above. After shaking the organic layer with water it was syringed into a round-bottom flask containing magnesium sulfate, under N_2. The water layer was rinsed with CH_2Cl_2 (10 mL) and the CH_2Cl_2 layer transferred as above. The dried phenylselenol solution was then added to 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranoside (5.01 g, 12.8 mmol) with a syringe. The magnesium sulfate was washed with CH_2Cl_2 (3 × 10 mL)

(43) Glasson, B.; Garegg, P. J.; Samuelsson, B. *Acta Chem. Scand. B* **1984**, *38*, 419.
(44) Sato, T.; Fujita, Y.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1992**, *33*, 239.
(45) Benhaddou, R.; Czernecki, S.; Randriamandimby, D. *XVIth International Carbohydrate Symposium*, Paris, France, July, 1992, Abstr. No. A057.
(46) We have also noted[47,48] that the phenyl selenoglycosides can be activated by other promoters such as methyl triflate,[49] phenylselenenyl triflate,[50] or $CuBr_2$–Bu_4NBr–silver triflate[51] to give disaccharides.
(47) Pinto, B. M. Presented at *The Sixth New Orleans Carbohydrate Symposium*, New Orleans, LA, April, 1990.
(48) Johnston, B. D.; Pinto, B. M., unpublished results.
(49) Lonn, H. *Carbohydr. Res.* **1985**, *139*, 105.
(50) Ho, Y.; Ogawa, T. *Tetrahedron Lett.* **1988**, *29*, 1061.
(51) Sato, S.; Mori, M.; Ito, Y.; Ogawa, T. *Carbohydr. Res.* **1986**, *155*, c6.
(52) The phenyl selenoglycosides are also amenable to electrochemical activation,[47] as described for the sulfur congeners.[53] More importantly, the radical cation-initiated glycosidation of phenyl selenoglycosides by oxidation with tris(4-bromophenyl)aminium hexachloroantimonate, as recently described for the case of thioglycosides,[12,54] gives disaccharides in moderate to good yields.[1,47,55]
(53) Amatore, C.; Jutland, A.; Mallet, J.-M.; Meyer, G.; Sinay, P. *J. Chem. Soc., Chem. Commun.* **1990**, 718. Balavoine, G.; Gref, A.; Fischer, J.-C.; Lubineau, A. *Tetrahedron* **1990**, *31*, 5761.
(54) Marra, A.; Mallet, J.-M.; Amatore, C.; Sinay, P. *Synlett* **1990**, 572. Zhang, Y.-M.; Mallet, J.-M.; Sinay, P. *Synlett* **1992**, *236*, 73.
(55) Mehta, S.; Pinto, B. M., manuscript in preparation.
(56) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542.
(57) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565.
(58) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.
(59) Marion, D.; Wutrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *117*, 967.
(60) Bundle, D. R.; Iversen, T.; Josephson, S. *Am. Lab.* (Fairfield, Conn.) **1980**, *12*, 93.

and the washings were transferred to the reaction mixture. The reaction mixture was cooled to 0 °C and BF_3OEt_2 (1.6 mL, 13.0 mmol) was added slowly. After 17 h the reaction mixture was neutralized with Et_3N and washed with water (2 × 25 mL). The organic layer was dried over magnesium sulfate and concentrated to give a syrup which was chromatographed with hexane–ethyl acetate (2:1) as eluant. [R_f α-isomer **3** = 0.38; β-isomer **4** = 0.31]. The products were obtained as powders and compound **4** was crystallized from ethanol (α: 0.21 g, 3%; β: 5.54 g, 89%). **3**: $[\alpha]^{22}_D$ = 240° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 20.5, 20.7 (4 $COCH_3$), 61.8 (C-6), 68.3 (C-4), 69.8 (C-5), 71.1 (C-3), 71.2 (C-2), 82.8 [$^1J(^{13}C,^1H)$ 173 Hz, (C-1)], 127.4–135.2 (Ar), 169.5, 169.6, 169.9, 170.4 (4 $COCH_3$); ^1H NMR ($CDCl_3$) δ 2.00, 2.02, 2.04, 2.08 (12 H, 4 s, 4 $COCH_3$), 3.96 (1 H, dd, $J_{5,6a}$ = 2.1 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.26 (1 H, dd, $J_{5,6b}$ = 5.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 4.50 (1 H, ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 2.1 Hz, $J_{5,6b}$ = 5.0 Hz, H-5), 5.04 (1 H, dd, $J_{1,2}$ = 5.6 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.08 (1 H, t, $J_{3,4+4,5}$ = 19.5 Hz, H-4), 5.38 (1 H, t, $J_{2,3+3,4}$ = 19.5 Hz, H-3), 6.15 (1 H, d, $J_{1,2}$ = 5.8 Hz, H-1), 7.1–7.6 (5 H, m, Ar). Anal. Calcd for $C_{20}H_{24}O_9Se$: C, 49.29; H, 4.96. Found: C, 49.07; H, 4.90. **4**: mp = 98.0 °C; $[\alpha]^{21}_D$ = −25.0° (*c* 0.1 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 20.5, 20.7 (4 $COCH_3$), 62.1 (C-6), 68.3 (C-4), 70.9 (C-2), 73.9 (C-3), 76.9 (C-5), 80.9 [$^1J(^{13}C,^1H)$ 159 Hz, (C-1)], 128.2–135.2 (Ar), 169.1, 169.2, 170.0, 170.4 (4 $COCH_3$); ^1H NMR ($CDCl_3$) δ 1.98, 2.01, 2.07 (12 H, 4 s, 4 $COCH_3$), 3.69 (1 H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 2.7 Hz, $J_{5,6b}$ = 4.5 Hz, H-5), 4.18 (2 H, m, H-6a, H-6b), 4.88 (1 H, d, $J_{1,2}$ = 10.2 Hz, $^2J_{H,Se}$ = 15.8 Hz, H-1), 5.0 (1 H, t, $J_{1,2+2,3}$ = 19.0 Hz, H-2), 5.03 (1 H, t, $J_{3,4+4,5}$ = 19.5 Hz, H-4), 5.19 (1 H, t, $J_{2,3+3,4}$ = 18.5 Hz, H-3), 7.2–7.5 (5 H, m, Ar). Anal. Calcd for $C_{20}H_{24}O_9Se$: C, 49.29; H, 4.96. Found: C, 49.44; H, 4.87.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-1-seleno-β-D-glucopyranoside (5). A mixture of diphenyl diselenide (1.3 g, 4.2 mmol) and 50% hypophosphorus acid (10 mL) was refluxed under N_2 with vigorous stirring until the mixture was colorless (3 h). The reaction mixture was cooled and anhydrous dichloromethane (8 mL) was added. The solution of phenylselenol was transferred under N_2 into a round-bottom flask containing water by means of a syringe. The reaction mixture was rinsed with additional portions of CH_2Cl_2 (2 × 4 mL) which were transferred as above. After washing the organic layer with water it was syringed into a round-bottom flask containing magnesium sulfate. The water layer was rinsed with CH_2Cl_2 (5 mL) and the washings were transferred as above. The dried phenylselenol solution was then added to 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (2.0 g, 4.2 mmol) with a syringe. The magnesium sulfate was washed with CH_2Cl_2 (2 × 5 mL) and the washings were transferred to the reaction mixture. The reaction mixture was cooled to 0 °C and BF_3OEt_2 (0.51 mL, 4.2 mmol) was added slowly. After 22 h the reaction mixture was neutralized with Et_3N and washed with water (2 × 15 mL). The organic layer was dried over magnesium sulfate and concentrated to give a syrup which was chromatographed with hexane–ethyl acetate (2.5:2) as eluant, R_f = 0.4. The product was obtained as a foam and was crystallized from hexane–ethyl acetate (5:1): 2.25 g, 93%; mp = 136.5 °C, $[\alpha]^{25}_D$ 35.0° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 20.3, 20.5, 20.7 (3 $COCH_3$), 54.7 (C-2), 62.1 (C-6), 68.7 (C-4), 71.4 (C-3), 76.9 (C-5), 78.4 (C-1), 123.6–135.4 (Ar), 169.4, 170.0, 170.5 (3 $COCH_3$); ^1H NMR ($CDCl_3$) δ 1.82, 2.02, 2.09 (3 s, 9 H, 3 $COCH_3$), 3.88 (1 H, ddd, H-5, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 4.8 Hz, H-5), 4.21 (1 H, dd, $J_{5,6a}$ = 2.3 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 4.27 (1 H, dd, $J_{5,6b}$ = 4.8 Hz, $J_{6b,6a}$ = 11.8 Hz, H-6b), 4.38 (1 H, t, $J_{1,2+2,3}$ = 20.8 Hz, H-2), 5.12 (1 H, dd, $J_{3,4}$ = 9.1 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 5.77 (1 H, t, $J_{2,3+3,4}$ = 19.3 Hz, H-3), 5.89 (1 H, d, $J_{1,2}$ = 10.5 Hz, $J_{H,Se}$ = 12.0 Hz, H-1), 7.2–7.9 (9 H, m, Ar). Anal. Calcd for $C_{26}H_{25}O_9NSe$: C, 54.36; H, 4.39; N, 2.44. Found: C, 54.49; H, 4.44; N, 2.37.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-1-seleno-β-D-glucopyranoside (6). Freshly prepared sodium methoxide solution in methanol (0.2 N, 35 mL) was added to phenyl 2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-glucopyranoside (**4**) (4.14 g, 8.5 mmol). The reaction mixture was stirred overnight, neutralized with amberlyst 15 ion-exchange resin, filtered, and concentrated to afford the deacetylated selenoglycoside. Phenyl 1-seleno-β-D-glucopyranoside (1.82 g, 7.1 mmol) was dissolved in dry, freshly distilled *N,N*-dimethylformamide (25 mL) and the solution was added slowly to a stirred suspension of sodium hydride (2.13 g, 53.2 mmol) in DMF (15 mL) at 0 °C. The flask was rinsed with additional portions of DMF (3 × 5 mL), and the contents were added to the reaction mixture. The reaction mixture was stirred for 30 min following which benzyl bromide (5.8 mL, 48.8 mmol) was added dropwise. The reaction mixture was stirred overnight under N_2. On completion of the reaction, as indicated by TLC, excess sodium hydride was decomposed by the addition of methanol. The reaction was poured into water (100 mL) and the desired compound was extracted into ethyl acetate (3 × 60 mL), and washed with water (30 mL) and sodium chloride (30 mL). The organic extracts were dried over magnesium sulfate and concentrated. The resulting syrup was purified by column chromatography using hexane–ethyl acetate (9:1) as eluant, R_f = 0.30. The desired product was obtained as a solid (4.1 g, 85%), which was crystallized from ethanol to yield fluffy white crystals: mp 79.0 °C, $[\alpha]^{26}_D$ 11° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 69.0 (C-6), 73.4, 75.0, 75.2, 75.7 (4 $CH_2C_6H_5$), 77.8 (C-3), 80.2 (C-5), 81.4 (C-2), 83.0 (C-1), 86.8 (C-4), 127.5–138.4 (Ar), ^1H NMR ($CDCl_3$) δ 3.49 (1 H, m, H-5), 3.53 (1 H, t, $J_{1,2+2,3}$ = 17.0 Hz, H-2), 3.68 (2 H, m, H-3, H-4), 3.75 (1 H, dd, $J_{5,6a}$ = 4.3 Hz, $J_{6a,6b}$ = 11.5 Hz, H-6a), 3.80 (1 H, dd, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 11.5 Hz, H-6b), 4.54 (1 H, d, *J* = 12.0 Hz, $CHHC_6H_5$), 4.60 (1 H, d, *J* = 10.8 Hz, $CHHC_6H_5$), 4.62 (1 H, d, *J* = 12.0 Hz, $CHHC_6H_5$), 4.73 (1 H, d, *J* = 10.2 Hz, $CHHC_6H_5$), 4.86 (1 H, d, $J_{1,2}$ = 9.5 Hz, H-1), 4.82–4.92 (4 H, m, 2 $CHHC_6H_5$), 7.1–7.8 (25 H, m, Ar). Anal. Calcd for $C_{40}H_{40}O_5Se$: C, 70.68; H, 5.93. Found: C, 70.94; H, 5.79.

Phenyl 4,6-*O*-Benzylidene-1-seleno-β-D-glucopyranoside (31). Phenyl 2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-glucopyranoside (**4**) (2.0 g, 4.1 mmol) was dissolved in methanol (25 mL) and ammonia gas was bubbled through the solution periodically, until deacetylation was complete. The solvent was evaporated, the dry deacetylated sugar was dissolved in freshly distilled *N,N*-dimethylformamide (8 mL), and α,α-dimethoxytoluene (1.2 mL, 8.0 mmol) and *p*-toluenesulfonic acid (0.15 g, 0.79 mmol) were added. The reaction mixture was heated under N_2 for 2 h. The reaction mixture was cooled, extracted into dichloromethane, and washed successively with sodium hydrogen carbonate (15 mL) and water (15 mL). The organic extracts were dried over sodium sulfate and concentrated. The dried residue was dissolved in ethyl acetate and excess hexane was added resulting in the precipitation of the desired compound. The precipitate was filtered and dried and the above procedure was repeated to yield the *title compound* as a white solid (1.67 g, 96%): $[\alpha]^{21}_D$ −43.3° (*c* 0.67 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 68.6 (C-6), 71.7 (C-4 or 5), 73.3 (C-2), 74.5 (C-3), 80.3 (C-5 or 4), 85.0 (C-1), 101.9 ($OCHC_6H_5$), 126.3–136.9 (Ar); ^1H NMR ($CDCl_3$) δ 3.40–3.54 (3 H, m, H-2, H-5, H-4), 3.76 (1 H, t, $J_{5,6a+6a,6b}$ = 20.0 Hz, H-6a), 3.82 (1 H, t, $J_{2,3+3,4}$ = 17.0 Hz, H-3), 4.38 (1 H, dd, $J_{5,6b}$ = 4.3 Hz, $J_{6a,6b}$ = 10.4 Hz, H-6b), 4.83 (1 H, d, $J_{1,2}$ = 9.9 Hz, $^2J_{H,Se}$ = 20.6 Hz, H-1), 5.50 (1 H, s, $OCHC_6H_5$), 7.2–7.7 (10 H, m, Ar). Anal. Calcd for $C_{19}H_{20}O_5Se$: C, 56.03; H, 4.95. Found: C, 56.00; H, 5.03.

Phenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-β-D-glucopyranoside (32). Phenyl 4,6-*O*-benzylidene-1-seleno-β-D-glucopyranoside (**31**) was dissolved in dry, freshly distilled *N,N*-dimethylformamide (15 mL) and the solution was added slowly to a stirred suspension of sodium hydride (0.43 g, 10.9 mmol) in DMF (5 mL) at 0 °C. Benzyl bromide (1.3 mL, 11.3 mmol) was then added dropwise. The reaction mixture was stirred overnight under nitrogen. On completion of the reaction, as indicated by TLC, excess sodium hydride was decomposed by the addition of methanol. The reaction was poured into water and the desired compound was extracted into ethyl acetate (3 × 15 mL), dried over magnesium sulfate, and concentrated. The resulting syrup was dried thoroughly under vacuum and the remaining solid was crystallized from hexane–ethyl acetate (10:1) to afford the *title compound* as fluffy white crystals (1.2 g). The mother liquor was purified by column chromatography using hexane–ethyl acetate (10:1) as eluant, R_f = 0.35. The desired product was obtained as a solid (0.24 g), overall yield (1.44 g, 91%): mp 135.5 °C; $[\alpha]^{26}_D$ −43.5° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 68.7 (C-6), 71.4 (C-5), 75.3, 75.7 (2 $CH_2C_6H_5$), 81.1 (C-2), 81.6 (C-4), 83.2 (C-3), 83.7 [$^1J(^{13}C,^1H)$ 157 Hz, (C-1)], 101.2 ($OCHC_6H_5$), 126.0–138.3 (Ar); ^1H NMR ($CDCl_3$) δ 3.46 (1 H, dt, $J_{4,5+5,6a}$ = 19.2 Hz, $J_{5,6b}$ = 4.8 Hz, H-5), 3.53 (1 H, dd, $J_{1,2+2,3}$ = 18.0 Hz, H-2), 3.68 (1 H, t, $J_{3,4+4,5}$ = 18.8 Hz, H-4), 3.79 (1 H, t, $J_{5,6a+6a,6b}$ = 20.0 Hz,

H-6a), 3.82 (1 H, t, $J_{2,3+3,4}$ = 18.0 Hz, H-3), 4.40 (1 H, dd, $J_{5,6b}$ = 4.9 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6b), 4.77 (1 H, d, J = 11.0 Hz, C*H*HC$_6$H$_5$), 4.82 (2 H, AB pattern, C*H*$_2$C$_6$H$_5$), 4.93 (1 H, d, $J_{1,2}$ = 9.2 Hz, H-1), 4.93 (1 H, d, J = 11.0 Hz, CH*H*C$_6$H$_5$), 5.50 (1 H, OC*H*C$_6$H$_5$), 7.20–7.70 (20 H, m, Ar). Anal. Calcd for $C_{33}H_{32}O_5Se$: C, 67.46; H, 5.49. Found: C, 67.52; H, 5.54.

Phenyl 2,3,6-Tri-*O*-benzyl-1-seleno-β-D-glucopyranoside (23). Hydrogen chloride in diethyl ether was added to phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-β-D-glucopyranoside (**32**) (1.2 g, 2.0 mmol) and $NaCNBH_3$ (0.88 g, 14.0 mmol) in THF (40 mL) containing 4-Å molecular sieves at 0 °C until the reaction mixture was acidic. The reaction was then stirred under N_2 at 0 °C. After 1.5 h the starting material had almost completely reacted, as determined by TLC. The reaction mixture was poured into ice-cold water and extracted into CH_2Cl_2. The combined organic extracts were washed with sodium hydrogen carbonate, dried over magnesium sulfate, and concentrated. Column chromatography of the resulting syrup with hexane–ethyl acetate (4:1) as eluant (R_f = 0.30) afforded the desired compound as a solid (1.1 g, 92%): $[\alpha]^{21}_D$ −43.0° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 70.4 (C-6), 71.7 (C-4), 73.7, 75.1, 75.4 (3 *C*H$_2$C$_6$H$_5$), 79.2 (C-5), 81.1 (C-2), 83.2 [$^1J(^{13}C,^1H)$ 157 Hz, (C-1)], 86.3 (C-3), 127.7–138.5 (Ar); ^{1}H NMR ($CDCl_3$) δ 3.47 (1 H, m, H-5), 3.50 (1 H, dd, $J_{1,2+2,3}$ = 18.2 Hz, H-2), 3.53 (1 H, t, $J_{2,3+3,4}$ = 17.0 Hz, H-3), 3.66 (1 H, t, $J_{3,4+4,5}$ = 19.0 Hz, H-4), 3.77 (2 H, d, H-6a, H-6b), 4.55 (1 H, d, J = 12.0 Hz, C*H*HC$_6$H$_5$), 4.60 (1 H, d, J = 12.0 Hz, CH*H*C$_6$H$_5$), 4.73 (1 H, d, J = 10.4 Hz, C*H*HC$_6$H$_5$), 4.79 (1 H, d, J = 11.4 Hz, C*H*HC$_6$H$_5$), 4.87 (1 H, d, J = 10.4 Hz, CH*H*C$_6$H$_5$), 4.88 (1 H, d, $J_{1,2}$ = 8.5 Hz, H-1), 4.92 (1 H, d, J = 11.4 Hz, CH*H*C$_6$H$_5$), 7.10–7.60 (20 H, m, Ar). Anal. Calcd for $C_{33}H_{34}O_5Se$: C, 67.23; H, 5.81. Found: C, 67.46; H, 6.07.

Phenyl 4,6-*O*-Benzylidene-2-deoxy-2-phthalimido-1-seleno-β-D-glucopyranoside (24). A freshly prepared solution of sodium methoxide in methanol (0.3 N, 3.5 mL) was added to a solution of phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-seleno-β-D-glucopyranoside (**5**) (6.0 g, 10.4 mmol) in dry methanol (50 mL). The reaction mixture was stirred for 2 h at pH 11. Upon completion, the reaction was adjusted to a pH of 5, with amberlyst 15 ion-exchange resin. The reaction mixture was filtered, concentrated, and dried under vacuum. The residue was dissolved in dry *N*,*N*-dimethylformamide (45 mL), and α,α-dimethoxytoluene (4.1 mL, 27.4 mmol) and *p*-toluenesulfonic acid were added. The reaction mixture was heated at approximately 60 °C for 4 h, cooled to room temperature, diluted with CH_2Cl_2, and washed twice with aqueous sodium hydrogen carbonate. The organic extracts were dried over magnesium sulfate and concentrated to give a syrup which was purified by column chromatography using hexane–ethyl acetate (1.6:1) as eluant; R_f = 0.4. The *title compound* was obtained as a foam (5.3 g, 95%): $[\alpha]^{23}_D$ 27.0° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 56.8 (C-2), 68.5 (C-6), 69.7 (C-3), 71.4 (C-5), 80.1 [$^1J(^{13}C,^1H)$ 163 Hz, (C-1)], 81.9 (C-4), 101.9 (O*C*HC$_6$H$_5$), 123.0–138.0 (Ar); ^{1}H NMR ($CDCl_3$) δ 3.57 (1 H, t, $J_{3,4+4,5}$ = 18.3 Hz, H-4), 3.67 (1 H, dt, $J_{4,5+5,6a}$ = 19.5 Hz, $J_{5,6b}$ = 4.7 Hz, H-5), 3.79 (1 H, t, $J_{5,6a+6a,6b}$ = 20.1 Hz, H-6a), 4.38 (1 H, t, $J_{1,2+2,3}$ = 20.5 Hz, H-2), 4.40 (1 H, dd, $J_{5,6b}$ = 4.7 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6b), 4.61 (1 H, dd, $J_{2,3+3,4}$ = 19.0 Hz, H-3), 5.55 (1 H, s, OC*H*C$_6$H$_5$), 5.85 (1 H, d, $J_{1,2}$ = 10.5 Hz, $^2J_{H-Se}$ = 13.3 Hz, H-1), 7.0–8.0 (14 H, m, Ar). Anal. Calcd for $C_{27}H_{23}O_6NSe$: C, 60.68; H, 4.32; N, 2.61. Found: C, 60.45; H, 4.21; N, 2.72.

Typical Glycosidation Procedure with Phenyl Selenoglycoside Donors. A mixture of the selenoglycoside donor (0.25 mmol), the glycosyl acceptor (0.21 mmol), and 4-Å molecular sieves was dried under vacuum overnight. Anhydrous dichloromethane (8 mL) was added and the reaction mixture was stirred under N_2 for 1 h. Dry potassium carbonate was added followed by silver triflate (see Table I). On completion of reaction, as indicated by TLC, the reaction mixture was filtered through Celite and washed with water (2 × 10 mL). The organic layer was dried over magnesium sulfate and concentrated, and the resulting residue was purified by column chromatography.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (8). The product was purified by column chromatography using hexane–ethyl acetate (2.5:1) as eluant: R_f = 0.37; $[\alpha]^{22}_D$ 13.0° (*c* 0.7 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 17.3 (C-6′), 20.7, 20.75, 20.8 (3 CO*C*H$_3$), 55.2 (O*C*H$_3$), 66.4 (C-5′), 66.9 (C-6), 69.1 (C-5), 69.9 (C-3′), 70.1 (C-2′), 71.2 (C-4′), 73.4, 75.0, 75.7 (3 *C*H$_2$C$_6$H$_5$), 77.9 (C-4), 80.2 (C-2), 82.1 (C-3), 97.8, 97.9 (C-1, C-1′), 127.6–138.8 (Ar), 169.85, 169.94 (3 *C*OCH$_3$); ^{1}H NMR ($CDCl_3$) δ 1.17 (3 H, d, $J_{5',6'}$ = 6.0 Hz, H-6′), 1.98, 2.05, 2.13 (9 H, 3 s, 3 COC*H*$_3$), 3.39 (3 H, s, OC*H*$_3$), 3.41 (1 H, dd, $J_{3,4+4,5}$ = 17.2 Hz, H-4), 3.50 (1 H, dd, $J_{5,6a}$ = 5.9 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6a), 3.54 (1 H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.78 (1 H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.9 Hz, $J_{5,6b}$ = 1.5 Hz, H-5), 3.84 (1 H, dd, $J_{5,6b}$ = 1.5 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6b), 3.85 (1 H, m, H-5′), 3.99 (1 H, t, $J_{2,3+3,4}$ = 18.5 Hz, H-3), 4.54 (1 H, d, J = 11.2 Hz, C*H*HC$_6$H$_5$), 4.58 (1 H, d, $J_{1,2}$ = 3.5 Hz, H-1), 4.66 (1 H, d, $J_{1',2'}$ = 1.7 Hz, H-1′), 4.67 (1 H, d, J = 11.9 Hz, C*H*HC$_6$H$_5$), 4.79 (1 H, d, J = 11.9 Hz, CH*H*C$_6$H$_5$), 4.81 (1 H, d, J = 10.8 Hz, C*H*HC$_6$H$_5$), 4.90 (1 H, d, J = 11.2 Hz, CH*H*C$_6$H$_5$), 4.96 (1 H, d, J = 10.8 Hz, CH*H*C$_6$H$_5$), 5.04 (1 H, t, $J_{3',4'+4',5'}$ = 19.8 Hz, H-4′), 5.21 (1 H, dd, $J_{1',2'}$ = 1.7 Hz, $J_{2',3'}$ = 3.6 Hz, H-2′), 5.27 (1 H, dd, $J_{2',3'}$ = 9.8 Hz, $J_{3',4'}$ = 9.8 Hz, H-3′), 7.20–7.40 (15 H, Ar). Anal. Calcd for $C_{40}H_{48}O_{13}$: C, 65.21; H, 6.57. Found: C, 65.11; H, 6.69.

Methyl 2,3,4-Tri-*O*-benzyl-(2,3,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-β-D-glucopyranoside (9). The product was purified by column chromatography using hexane–ethyl acetate (1.5:1) as eluant: R_f = 0.30; $[\alpha]^{21}_D$ 42.5° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 20.4, 20.6, 20.7 (3 CO*C*H$_3$), 54.5 (C-2′), 54.9 (O*C*H$_3$), 62.1 (C-6′), 68.7 (C-6), 69.0, 69.2 (C-4, C-5), 70.7 (C-3′), 71.9 (C-5′), 73.3, 74.7, 75.6 (3 *C*H$_2$C$_6$H$_5$), 77.6 (C-4), 79.7 (C-2), 81.8 (C-3), 97.9 [$^1J(^{13}C,^1H)$ 169 Hz, (C-1)], 98.3 [$^1J(^{13}C,^1H)$ 169 Hz, (C-1′)], 123.4–138.7 (Ar), 169.4, 170.1, 170.6 (3 *C*OCH$_3$); ^{1}H NMR ($CDCl_3$) δ 1.85, 2.02, 2.08 (9 H, 3 s, 3 COC*H*$_3$), 3.16 (3 H, s, OC*H*$_3$), 3.23 (1 H, t, $J_{3,4+4,5}$ = 18.4 Hz, H-4), 3.38 (1 H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 3.61–3.69 (2 H, m, H-5, H-6a), 3.84 (1 H, t, $J_{2,3+3,4}$ = 18.2 Hz, H-3), 3.86 (1 H, m, H-5′), 4.06–4.13 (2 H, m, H-6b, C*H*HC$_6$H$_5$), 4.16 (1 H, dd, $J_{5',6a'}$ = 2.3 Hz, $J_{6a',6b'}$ = 12.0 Hz, H-6a′), 4.32 (1 H, dd, $J_{5',6b'}$ = 4.5 Hz, $J_{6a',6b'}$ = 12.0 Hz, H-6b′), 4.36 (1 H, d, $J_{1,2}$ = 3.6 Hz, H-1), 4.39 (1 H, dd, $J_{1',2'+2',3'}$ = 18.6 Hz, H-2′), 4.41 (1 H, d, J = 10.5 Hz, C*H*HC$_6$H$_5$), 4.56 (1 H, d, J = 12.0 Hz, C*H*HC$_6$H$_5$), 4.64 (1 H, d, J = 10.8 Hz, C*H*HC$_6$H$_5$), 4.71 (1 H, d, J = 12.0 Hz, CH*H*C$_6$H$_5$), 4.85 (1 H, d, J = 10.8 Hz, CH*H*C$_6$H$_5$), 5.17 (1 H, t, $J_{3',4'+4',5'}$ = 19.0 Hz, H-4′), 5.43 (1 H, d, $J_{1',2'}$ = 8.5 Hz, H-1′), 5.79 (1 H, dd, $J_{2',3'+3',4'}$ = 19.6 Hz, H-3′), 7.0–7.9 (19 H, m, Ar). Anal. Calcd for $C_{48}H_{51}O_{15}N$: C, 65.37; H, 5.83; N, 1.59. Found: C, 65.41; H, 5.95; N, 1.62.

Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (12). The product was purified by column chromatography using hexane–ethyl acetate (2.25:1) as eluant, R_f = 0.30; $[\alpha]^{21}_D$ −19.0° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 16.6 (C-6′), 20.7, 20.75, 20.8 (3 CO*C*H$_3$), 55.3 (O*C*H$_3$), 62.5 (C-5), 65.9 (C-5′), 69.0 (C-6), 69.4 (C-3′), 69.7 (C-2′), 71.2 (C-4′), 73.4 (*C*H$_2$C$_6$H$_5$), 74.2 (C-3), 79.7 (C-4), 80.4 (C-2), 97.9 [$^1J(^{13}C,^1H)$ 174 Hz, (C-1′)], 98.6 [$^1J(^{13}C,^1H)$ 172 Hz, (C-1)], 101.7 (OCHC$_6$H$_5$), 126.3–137.6 (Ar), 169.8, 170.0, 170.2 (3 *C*OCH$_3$); ^{1}H NMR ($CDCl_3$) δ 0.77 (1 H, d, J = 6.2 Hz, H-6′), 1.95, 1.98, 2.10 (9 H, 3 s, 3 COC*H*$_3$), 3.36 (3 H, s, OC*H*$_3$), 3.52 (1 H, t, $J_{3,4+4,5}$ = 18.5 Hz, H-4), 3.54 (1 H, dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 3.70 (1 H, t, $J_{5,6a+6a,6b}$ = 20.0 Hz, H-6a), 3.81 (1 H, dt, $J_{5,6b}$ = 4.7 Hz, $J_{4,5+5,6a}$ = 18.5 Hz, H-5), 4.14 (1 H, t, $J_{2,3+3,4}$ = 19.0 Hz, H-3), 4.17 (1 H, m, H-5′), 4.25 (1 H, dd, $J_{5,6b}$ = 4.7 Hz, $J_{6a,6b}$ = 10.0 Hz, H-6b), 4.53 (1 H, d, $J_{1,2}$ = 3.5 Hz, H-1), 4.57 (1 H, d, J = 12.0 Hz, C*H*HC$_6$H$_5$), 4.74 (1 H, d, J = 12.0 Hz, CH*H*C$_6$H$_5$), 4.95 (1 H, t, $J_{3',4'+4',5'}$ = 20.0 Hz, H-4′), 5.13 (1 H, d, $J_{1',2'}$ = 1.5 Hz, H-1′), 5.29 (1 H, dd, $J_{2',3'}$ = 3.5 Hz, $J_{3',4'}$ = 9.3 Hz, H-3′), 5.35 (1 H, dd, $J_{1',2'}$ = 1.5 Hz, $J_{2',3'}$ = 3.5 Hz, H-2′), 5.52 (1 H, s, OC*H*C$_6$H$_5$), 7.20–7.50 (10 H, m, Ar). Anal. Calcd for $C_{33}H_{40}O_{13}$: C, 61.48; H, 6.25. Found: C, 61.31; H, 6.22.

Methyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (13). The product was purified by column chromatography using hexane–ethyl acetate (2.5:1) as eluant: R_f = 0.32; $[\alpha]^{21}_D$ −19.5° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 17.1, 18.1 (C-6, C-6′), 20.6, 20.7 (3 OCO*C*H$_3$), 54.9 (O*C*H$_3$), 67.2, 67.6 (C-5, C-5′), 69.0 (C-3′), 69.8 (C-2′), 70.7 (C-4′), 72.7 (C-2), 75.6 (*C*H$_2$C$_6$H$_5$), 78.3 (C-3), 80.2 (C-4), 98.0 [$^1J(^{13}C,^1H)$ 175 Hz, (C-1)], 99.5 [$^1J(^{13}C,^1H)$ 172 Hz, (C-1′)], 127.7–137.9 (Ar), 166.0, 169.7 (*C*OCH$_3$); ^{1}H NMR ($CDCl_3$) δ 1.06 (3 H, d, $J_{5',6'}$ = 6.0 Hz, H-6′), 1.36 (3 H, d, $J_{5,6}$ = 6.0 Hz, H-6), 1.91, 1.94, 2.08 (9 H, 3 s, 3 OCOC*H*$_3$), 3.37 (3 H, s, OC*H*$_3$), 3.61 (1 H, t, $J_{3,4+4,5}$ = 19.2 Hz, H-4), 3.78 (1 H, m, H-5′), 3.86 (1 H, m, H-5), 4.21 (1 H, dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 4.71

(1 H, d, J = 10.9 Hz, C*H*HC$_6$H$_5$), 4.77 (1 H, d, $J_{1,2}$ = 1.8 Hz, H-1), 4.89 (1 H, d, J = 10.9 Hz, CH*H*C$_6$H$_5$), 4.98 (1 H, t, $J_{3',4'+4',5'}$ = 19.8 Hz, H-4'), 5.03 (1 H, d, $J_{1',2'}$ = 1.7 Hz, H-1'), 5.20 (1 H, dd, $J_{2',3'}$ = 3.5 Hz, $J_{3',4'}$ = 10.0 Hz, H-3'), 5.30–5.34 (2 H, m, H-2, H-2'), 7.25–8.15 (10 H, m, Ar). Anal. Calcd for $C_{33}H_{40}O_{13}$: C, 61.48; H, 6.25. Found: C, 61.65; H, 6.22.

Selenoglycoside, Thioglycoside Competition Experiment (Table I, entry 5). A mixture of phenyl 2,3,4-tri-*O*-acetyl-1-seleno-α-L-rhamnopyranoside (**1**) (0.15 g, 0.35 mmol), ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (**14**) (0.12 g, 0.35 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**7**) (0.35 g, 0.75 mmol) and 4-Å molecular sieves was dried under vacuum overnight. Anhydrous dichloromethane (10 mL) was added and the reaction mixture was stirred under N_2 for 1 h. Dry potassium carbonate (0.8 g, 5.8 mmol) was added followed by silver triflate (0.35 g, 1.37 mmol). After 24 h, the reaction mixture was filtered through Celite and washed with water (2 × 10 mL). The organic layer was dried over magnesium sulfate and concentrated. The resulting syrup was purified by column chromatography using toluene–ethyl acetate (5:1) as eluant; R_f of recovered thioglycoside **14** = 0.4, disaccharide **8** = 0.28. The disaccharide **8** was obtained as a syrup (0.21 g, 86%), and the unreacted thioglycoside **14** was recovered as a powder (0.11 g, 91%).

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (18). The product was purified by column chromatography using hexane–ethyl acetate (1.5:1) as eluant: R_f = 0.31; $[\alpha]^{21}_D$ 14.0° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 15.9 (SCH_2CH_3), 20.5, 20.8 ($COCH_3$), 24.8 (SCH_2CH_3), 54.6 (C-2'), 62.1 (C-6'), 68.6 (C-6), 69.0 (C-4'), 70.9 (C-3'), 71.9 (C-5'), 74.8, 75.4, 75.6 (3 $CH_2C_6H_5$), 78.0 (C-2 or 4), 78.4 (C-5), 81.7 (C-2 or 4), 84.6 [$^1J(^{13}C,^1H)$ 154 Hz, (C-1)], 86.4 (C-3), 97.9 [$^1J(^{13}C,^1H)$ 166 Hz, (C-1')], 123.0–139.0 (Ar), 169.3, 170.2, 170.5 (3 $COCH_3$); ^{1}H NMR ($CDCl_3$) δ 1.17 (3 H, t, SCH_2CH_3), 1.85, 2.03, 2.06 (9 H, 3 s, 3 $COCH_3$), 2.54 (2 H, m, SCH_2CH_3), 3.30 (2 H, m, H-2, H-4), 3.40 (1 H, m, H-5), 3.58 (1 H, t, $J_{2,3+3,4}$ = 17.5 Hz, H-3), 3.62 (1 H, dd, $J_{5,6b}$ = 6.1 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6b), 3.84 (1 H, ddd, $J_{4',5'}$ = 10.1 Hz, $J_{5',6a'}$ = 2.3 Hz, $J_{5',6b'}$ = 4.5 Hz, H-5'), 4.06 (1 H, dd, $J_{5,6a}$ = 1.4 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6a), 4.16 (1 H, dd, $J_{5',6a'}$ = 2.3 Hz, $J_{6a',6b'}$ = 12.1 Hz, H-6a'), 4.31 (1 H, dd, $J_{5',6b'}$ = 4.5 Hz, $J_{6a',6b'}$ = 12.1 Hz, H-6b'), 4.35 (1 H, t, $J_{1',2'+2',3'}$ = 21.7 Hz, H-2'), 4.36 (1 H, d, J = 10.9 Hz, C*H*HC$_6$H$_5$), 4.37 (1 H, d, $J_{1,2}$ = 9.7 Hz, H-1), 4.62 (1 H, d, J = 10.9 Hz, CH*H*C$_6$H$_5$), 4.67 (1 H, d, J = 10.2 Hz, C*H*HC$_6$H$_5$), 4.74 (1 H, d, J = 11.0 Hz, C*H*HC$_6$H$_5$), 4.76 (2 H, d, 2 CH*H*C$_6$H$_5$), 5.18 (1 H, t, $J_{3',4'+4',5'}$ = 19.2 Hz, H-4'), 5.44 (1 H, d, $J_{1',2'}$ = 8.5 Hz, H-1'), 5.76 (1 H, dd, $J_{2',3'+3',4'}$ = 19.7 Hz, H-3'), 7.11–7.76 (19 H, m, Ar). Anal. Calcd for $C_{49}H_{53}O_{15}NS$: C, 64.53; H, 5.86; N, 1.54. Found: C, 64.40; H, 5.92; N, 1.47.

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-1-thio-α-D-glucopyranoside (19). The product was purified by column chromatography using toluene–ethyl acetate (8:1) as eluant: R_f = 0.34; $[\alpha]^{21}_D$ 44.0° (*c* 0.5 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 14.6 (SCH_2CH_3), 17.3 (C-6'), 20.6, 20.75, 20.8 (3 $COCH_3$), 23.5 (SCH_2CH_3), 66.3 (C-5'), 66.8 (C-6), 69.0 (C-3'), 69.7 (C-2'), 70.3 (C-5), 71.1 (C-4'), 72.3, 75.0, 75.7 (3 $CH_2C_6H_5$), 77.8 (C-4), 79.7 (C-2), 82.5 (C-1, C-3), 97.7 [$^1J(^{13}C,^1H)$ 172 Hz, (C-1')], 127.6–138.6 (Ar), 169.7, 169.91, 169.94 (3 $COCH_3$); ^{1}H NMR ($CDCl_3$) δ 1.18 (3 H, d, $J_{5',6'}$ = 6.2 Hz, H-6'), 1.31 (3 H, t, SCH_2CH_3), 1.98, 2.05, 2.14 (9 H, 3 s, 3 $COCH_3$), 2.58 (2 H, m, SCH_2CH_3), 3.40 (1 H, dd, $J_{3,4+4,5}$ = 18.8 Hz, H-4), 3.52 (1 H, dd, $J_{5,6a}$ = 6.4 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a), 3.83 (1 H, dd, $J_{1,2}$ = 5.4 Hz, $J_{2,3}$ = 9.2 Hz, H-2), 3.83–3.94 (3 H, m, H-3, H-6b, H-5'), 4.25 (1 H, ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 6.4 Hz, $J_{5,6b}$ = 1.5 Hz, H-5), 4.56 (1 H, d, J = 11.2 Hz, C*H*HC$_6$H$_5$), 4.65 (1 H, d, $J_{1',2'}$ = 1.7 Hz, H-1'), 4.66 (1 H, d, J = 11.5 Hz, C*H*HC$_6$H$_5$), 4.75 (1 H, d, J = 11.5 Hz, CH*H*C$_6$H$_5$), 4.77 (1 H, d, J = 10.8 Hz, C*H*HC$_6$H$_5$), 4.91 (1 H, d, J = 11.2 Hz, CH*H*C$_6$H$_5$), 4.97 (1 H, d, J = 10.8 Hz, CH*H*C$_6$H$_5$), 5.05 (1 H, t, $J_{3',4'+4',5'}$ = 19.8 Hz, H-4'), 5.22 (1 H, dd, $J_{1',2'}$ = 1.7 Hz, $J_{2',3'}$ = 3.5 Hz, H-2'), 5.26 (1 H, dd, $J_{2',3'}$ = 3.5 Hz, $J_{3',4'}$ = 10.0 Hz, H-3'), 5.39 (1 H, d, $J_{1,2}$ = 5.4 Hz, H-1), 7.10–7.50 (15 H, m, Ar). Anal. Calcd for $C_{41}H_{50}O_{12}S$: C, 64.21; H, 6.57. Found: C, 64.40; H, 6.80.

Ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-1-thio-β-D-glucopyranoside (20). The product was purified by column chromatography using hexane–ethyl acetate (2.5:1) as eluant: R_f = 0.39; $[\alpha]^{21}_D$ 1.0° (*c* 0.9 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 15.1 (SCH_2CH_3), 16.9 (C-6'), 20.6 ($COCH_3$), 24.7 (SCH_2CH_3), 66.7 (C-5'), 68.6 (C-6), 69.1 (C-3'), 70.1 (C-2'), 70.9 (C-4'), 73.0 ($CH_2C_6H_5$), 74.7 (C-4), 75.3 ($CH_2C_6H_5$), 75.6 ($CH_2C_6H_5$), 79.0 (C-5), 82.0 (C-2), 84.5 (C-3), 85.0 (C-1), 97.1 (C-1'); ^{1}H NMR ($CDCl_3$) δ 1.32 (3 H, t, SCH_2CH_3), 1.94, 1.99, 2.07 (9 H, 3 s, 3 $COCH_3$), 2.75 (2 H, m, SCH_2CH_3), 3.41 (1 H, m, H-5), 3.51 (1 H, t, $J_{1,2+2,3}$ = 18.3 Hz, H-2), 3.59 (1 H, t, $J_{2,3+3,4}$ = 17.8 Hz, H-3), 3.69–3.78 (2 H, m, H-6a, H-6b), 3.94 (1 H, t, $J_{3,4+4,5}$ = 18.6 Hz, H-4), 4.03 (1 H, m, H-5'), 4.46 (1 H, d, $J_{1,2}$ = 9.4 Hz, H-1), 4.55 (2 H, AB pattern, $CH_2C_6H_5$), 4.70 (1 H, d, J = 10.0 Hz, C*H*HC$_6$H$_5$), 4.77 (1 H, d, J = 11.3 Hz, C*H*HC$_6$H$_5$), 4.93 (1 H, d, J = 10.0 Hz, CH*H*C$_6$H$_5$), 4.96 (1 H, t, $J_{3',4'+4',5'}$ = 19.9 Hz, H-4'), 5.01 (1 H, d, $J_{1',2'}$ = 1.7 Hz, H-1'), 5.08 (1 H, d, J = 11.3 Hz, CH*H*C$_6$H$_5$), 5.16 (1 H, dd, $J_{1',2'}$ = 1.7 Hz, $J_{2',3'}$ = 3.5 Hz, H-2'), 5.23 (1 H, dd, $J_{2',3'}$ = 3.5 Hz, $J_{3',4'}$ = 10.0 Hz, H-3'), 7.20–7.40 (15 H, m, Ar). Anal. Calcd for $C_{41}H_{50}O_{12}S$: C, 64.21; H, 6.57. Found: C, 64.16; H, 6.54.

Ethyl 2,3,4-Tetra-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (21, 22). The product was purified by column chromatography using hexane–ethyl acetate (4:1) as eluant, R_f = 0.4, to give an α/β mixture. **α-Isomer 21**: ^{13}C NMR ($CDCl_3$) δ 15.1 (SCH_2CH_3), 25.0 (SCH_2CH_3), 65.8 (C-6), 72.3, 73.4, 74.9, 75.0, 75.4 (5 $CH_2C_6H_5$), 75.5 (2 $CH_2C_6H_5$), 79.0 (C-5), 81.7 (C-3'), 81.9 (C-2), 85.0 (C-1), 97.1 (C-1'), 68.9, 70.2, 77.7, 77.8, 80.2, 86.6 (C-3, C-4, C-2', C-4', C-5', C-6'), 127.5–138.7 (Ar); ^{1}H NMR ($CDCl_3$) δ 1.26 (3 H, t, SCH_2CH_3), 2.69 (2 H, m, SCH_2CH_3), 3.19 (1 H, dd, $J_{1,2+2,3}$ = 18.2 Hz, H-2), 3.48 (1 H, m, H-5), 3.59 (1 H, dd, $J_{1',2'}$ = 3.3 Hz, $J_{2',3'}$ = 9.7 Hz, H-2'), 3.60–3.74 (5 H, m, H-3, H-4', H-6a', H-4, H-6b'), 3.86 (1 H, m, H-5'), 3.98 (1 H, t, $J_{2',3'+3',4'}$ = 18.6 Hz, H-3'), 4.42–4.50 (3 H, m, H-1, 2 C*H*HC$_6$H$_5$), 4.57 (1 H, d, J = 10.2 Hz, C*H*HC$_6$H$_5$), 4.63 (1 H, d, J = 12.0 Hz, CH*H*C$_6$H$_5$), 4.67 (1 H, d, J = 11.0 Hz, C*H*HC$_6$H$_5$), 4.71–4.92 (8 H, m, 3 C*H*HC$_6$H$_5$, 5 CH*H*C$_6$H$_5$), 4.98 (1 H, d, J = 10.8 Hz, CH*H*C$_6$H$_5$), 5.07 (1 H, d, $J_{1',2'}$ = 2.3 Hz, H-1'), 7.1–7.5 (35 H, m, Ar). Anal. Calcd for $C_{63}H_{68}O_{10}S$: C, 74.38; H, 6.74. Found: (α/β mixture): C, 74.18; H, 6.98.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-seleno-β-D-glucopyranoside (26). A mixture of silver trifluoromethanesulfonate (0.25 g, 1.0 mmol), collidine (0.14 mL, 1.0 mmol), and dry 4-Å molecular sieves in anhydrous dichloromethane (2 mL) was stirred under N_2 for 1.5 h. The mixture was cooled to 0 °C and a solution of phenyl 2,3,6-tri-*O*-benzyl-1-seleno-β-D-glucopyranoside (**23**) (0.15 g, 0.25 mmol) in CH_2Cl_2 (1.5 mL) was added by means of a cannula, under N_2. The flask was rinsed with additional portions of CH_2Cl_2 (3 × 0.5 mL). The reaction mixture was stirred for 1 h and checked by TLC to confirm that no reaction had yet occurred. The reaction mixture was cooled to −78 °C and a solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (**25**)[32] (0.39 g, 0.8 mmol) in CH_2Cl_2 (1.5 mL), cooled to −78 °C, was added dropwise. The flask was rinsed with additional portions of CH_2Cl_2 (3 × 0.5 mL) and the dropping funnel was also rinsed with CH_2Cl_2 (2 × 1 mL). The reaction mixture was stirred for 36 h, filtered through Celite, and washed successively with hydrochloric acid (1 N, 2 × 7 mL) and aqueous sodium hydrogen carbonate. The organic extracts were dried over magnesium sulfate and concentrated to give a syrup which was chromatographed using toluene–ethyl acetate (5:1) as eluant, R_f = 0.32. The *title compound* **26** was obtained as a white foam (0.15 g, 60%): $[\alpha]^{22}_D$ −23° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 20.3, 20.6 ($COCH_3$), 55.4 (C-2'), 61.5 (C-6'), 68.2 (C-6), 68.8 (C-4'), 70.8 (C-3'), 71.8 (C-5'), 72.8, 74.8, 75.2 (3 $CH_2C_6H_5$), 75.2 (C-4), 79.5 (C-5), 81.1 (C-2), 82.9 (C-1), 84.9 (C-3), 97.3 (C-1'), 123.6–139.0 (Ar), 169.4, 170.0, 170.6 (3 $COCH_3$); ^{1}H NMR ($CDCl_3$) δ 1.82, 1.95, 1.98 (9 H, 3 s, 3 $COCH_3$), 3.23 (1 H, ddd, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 3.7 Hz, $J_{5,6b}$ = 1.0 Hz, H-5), 3.38–3.49 (3 H, m, H-6a, H-5', H-2), 3.54 (1 H, dd, $J_{5,6b}$ = 1.0 Hz, $J_{6a,6b}$ = 11.5 Hz, H-6b), 3.59 (1 H, t, $J_{3,4+4,5}$ = 17.5 Hz, H-3), 3.78 (1 H, dd, $J_{5',6a'}$ = 2.1 Hz, $J_{6a',6b'}$ = 12.4 Hz, H-6a'), 4.08 (2 H, m, H-4, H-6b'), 4.26 (1 H, dd, $J_{1',2'+2',3'}$ = 19.0 Hz, H-2'), 4.40 (2 H, AB pattern, $CH_2C_6H_5$), 4.61 (1 H, d, J = 10.0 Hz, C*H*HC$_6$H$_5$), 4.71 (1 H, d, $J_{1,2}$ = 9.7 Hz, H-1), 4.72 (1 H, d, J = 10.0 Hz, CH*H*C$_6$H$_5$), 4.80 (1 H, d, J = 11.5 Hz, C*H*HC$_6$H$_5$), 5.05 (1 H, d, J = 11.5 Hz, CH*H*C$_6$H$_5$), 5.11 (1 H, t, $J_{3',4'+4',5'}$ = 19.2 Hz, H-4'), 5.61 (1 H, d, $J_{1',2'}$ = 8.5 Hz, H-1'), 5.73 (1 H, dd, $J_{2',3'+3',4'}$ = 19.7 Hz, H-3'), 7.1–7.9 (24 H, m, Ar). Anal.

Calcd for $C_{53}H_{53}O_{14}NSe$: C, 63.17; H, 5.31; N, 1.39. Found: C, 63.28; H, 5.32; N, 1.19.

Phenyl 4,6-*O*-Benzylidene-2-deoxy-2-phthalimido-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-seleno-β-D-glucopyranoside (27). A mixture of silver trifluoromethanesulfonate (0.28 g, 1.1 mmol), collidine (0.15 mL, 1.0 mmol), and dry 4-Å molecular sieves in anhydrous dichloromethane (2 mL) was stirred under N_2 for 1.5 h. The mixture was cooled to 0 °C and a solution of phenyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-seleno-β-D-glucopyranoside (24) (0.15 g, 0.26 mmol) in CH_2Cl_2 (1.5 mL) was added by means of a cannula, under N_2. The flask was rinsed with additional portions of CH_2Cl_2 (3 × 0.5 mL). The reaction mixture was stirred for 1 h and checked by TLC to confirm that no reaction had yet occurred. The reaction mixture was cooled to −78 °C and a solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (25)[32] (0.41 g, 0.8 mmol) in CH_2Cl_2 (2 mL), cooled to −78 °C, was added dropwise. The flask was rinsed with additional portions of CH_2Cl_2 (3 × 0.5 mL) and the dropping funnel was also rinsed with CH_2Cl_2 (2 × 1.5 mL). After 24 h the reaction mixture was filtered through Celite, concentrated, and washed successively with hydrochloric acid (1 N) and aqueous sodium hydrogen carbonate. The organic extracts were dried over magnesium sulfate and concentrated to give a foam which was chromatographed using hexane–ethyl acetate (1:1.5) as eluant; R_f = 0.29. The *title compound* **27** was obtained as a white foam (0.15 g, 60%). It was crystallized from hexane–ethyl acetate: mp 272 °C; $[\alpha]^{22}_D$ 56.0° (*c* 1.0 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 20.2, 20.5, 20.7 (3 $COCH_3$), 55.0 (C-2′), 55.6 (C-2), 61.4 (C-6′), 68.5 (C-4′), 68.6 (C-6), 70.9 (C-3′), 71.6, 71.7 (C-5, C-5′), 76.2 (C-3), 80.3 (C-1), 80.7 (C-4), 97.4 (C-1′), 101.7 ($OCHC_6H_5$), 123.3–137.1 (Ar), 169.2, 170.0, 170.6 (3 $COCH_3$); ^1H NMR ($CDCl_3$) δ 1.68, 1.89, 2.01 (9 H, 3 s, 3 $COCH_3$), 3.35 (1 H, m, H-5′), 3.65 (1 H, dt, $J_{5,6}$ = 4.7 Hz, $J_{4,5+5,6}$ = 19.3 Hz, H-5), 3.74–3.84 (3 H, m, H-4, H-6a, H-6a′), 3.93 (1 H, dd, $J_{5',6b'}$ = 3.5 Hz, $J_{6a',6b'}$ = 12.2 Hz, H-6b′), 4.13 (1 H, dd, $J_{1',2'+2',3'}$ = 19.0 Hz, H-2′), 4.34 (1 H, dd, $J_{5,6b}$ = 4.7 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6b), 4.36 (1 H, $J_{1,2+2,3}$ = 20.3 Hz, H-2), 4.75 (1 H, dd, $J_{2,3+3,4}$ = 18.5 Hz, H-3), 5.04 (1 H, dd, $J_{3',4'+4',5'}$ = 19.3 Hz, H-4′), 5.45 (1 H, dd, $J_{2',3'+3',4'}$ = 19.7 Hz, H-3′), 5.50 (1 H, $J_{1',2'}$ = 8.5 Hz, H-1′), 5.57 (1 H, s, $OCHC_6H_5$), 5.59 (1 H, d, $J_{1,2}$ = 11.0 Hz, H-1), 7.0–7.9 (18 H, m, Ar). Anal. Calcd for $C_{47}H_{42}O_{15}N_2Se$: C, 59.19; H, 4.44; N, 2.94. Found: C, 59.18; H, 4.61; N, 2.81.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-seleno-β-D-glucopyranoside (26). A mixture of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (28)[42] (0.13 g, 0.2 mmol), phenyl 2,3,6-tri-*O*-benzyl-1-seleno-β-D-glucopyranoside (23), and 4-Å molecular sieves in anhydrous CH_2Cl_2 (3 mL) was stirred under nitrogen for 1 h. The reaction mixture was cooled to −78 °C and triethylsilyl triflate (0.003 mL, 0.013 mmol) was added. A TLC after 15 min indicated that the reaction was almost complete. After 1.5 h the reaction mixture was neutralized with triethylamine, filtered through Celite, and concentrated. The resulting syrup was chromatographed using hexane–ethyl acetate (2:1) as eluant; R_f = 0.32. The *title compound* **26** was isolated as a foam (0.14 g, 84%).

Phenyl 4,6-*O*-Benzylidene-2-deoxy-2-phthalimido-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-seleno-β-D-glucopyranoside (27). A mixture of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (28)[42] (0.20 g, 0.3 mmol), phenyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-seleno-β-D-glucopyranoside (24), and 4-Å molecular sieves in anhydrous dichloromethane (4 mL) was stirred under nitrogen for 1 h. The reaction mixture was cooled to −78 °C and triethylsilyl triflate (0.005 mL, 0.024 mmol) was added. A TLC after 20 min indicated that the reaction was almost complete. After 1.5 h the reaction mixture was neutralized with triethylamine, filtered through Celite, and concentrated. The resulting syrup was chromatographed using hexane–ethyl acetate (1:1.5) as eluant, R_f = 0.29. The *title compound* **27** was isolated as a foam (0.27 g, 90%).

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-[4,6-*O*-benzylidene-2-deoxy-2-phthalimido-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-β-D-glucopyranosyl]-1-thio-β-D-glucopyranoside (29). The product was purified by column chromatography using hexane–ethyl acetate (1:1.2) as eluant: R_f = 0.34; $[\alpha]^{22}_D$ 8.0° (*c* 0.6 in CH_2Cl_2); ^{13}C NMR ($CDCl_3$) δ 15.1 (SCH_2CH_3), 20.2, 20.5, 20.7 (3 $COCH_3$), 24.4 (SCH_2CH_3), 59.9 (C-2″), 55.3 (C-2′), 61.4 (C-6″), 66.3 (C-5′), 68.0 (C-6), 68.5 (C-4″), 68.8 (C-6′), 71.0 (C-3″), 71.6 (C-5″), 74.7, 75.2, 75.3, 75.5 (3 $CH_2C_6H_5$, C-3′), 77.8 (C-4), 78.3 (C-2), 80.8 (C-4′), 81.5 (C-5), 84.4 (C-1), 86.4 (C-3), 97.3 (C-1″), 98.4 (C-1′), 101.7 ($OCHC_6H_5$), 123.3–138.5 (Ar), 169.2, 170.0, 170.6 (3 $COCH_3$); ^1H NMR ($CDCl_3$) δ 1.18 (3 H, t, SCH_2CH_3), 1.17, 1.90, 2.03 (9 H, 3 s, 3 $COCH_3$), 2.49 (2 H, m, SCH_2CH_3), 3.15–3.28 (2 H, m, H-4, H-2, H-5), 3.29 (1 H, m, H-5″), 3.47 (1 H, dd, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6a), 3.50 (1 H, t, $J_{2,3+3,4}$ = 17.0 Hz, H-3), 3.57 (1 H, dt, $J_{4',5'+5',6a'}$ = 19.2 Hz, $J_{5',6b'}$ = 4.6 Hz, H-5′), 3.75–3.86 (3 H, m, H-4′, H-6a″, H-6a′), 3.90 (1 H, dd, $J_{5,6b}$ = 1.2 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6b), 3.96 (1 H, dd, $J_{5'',6b''}$ = 3.2 Hz, $J_{6a'',6b''}$ = 12.0 Hz, H-6b″), 4.15 (1 H, dd, $J_{1'',2''+2'',3''}$ = 19.0 Hz, H-2″), 4.21 (1 H, d, *J* = 11.0 Hz, $CHHC_6H_5$), 4.24 (1 H, dd, $J_{1',2'+2',3'}$ = 18.7 Hz, H-2′), 4.27 (1 H, d, $J_{1,2}$ = 9.7 Hz, H-1), 4.30 (1 H, dd, $J_{5',6b'}$ = 4.5 Hz, $J_{6a',6b'}$ = 10.0 Hz, H-6b′), 4.50 (1 H, d, *J* = 10.5 Hz, $CHHC_6H_5$), 4.64 (1 H, d, *J* = 10.0 Hz, $CHHC_6H_5$), 4.69 (1 H, d, *J* = 11.0 Hz, $CHHC_6H_5$), 4.77 (1 H, dd, $J_{2',3'+3',4'}$ = 19.5 Hz, H-3′), 4.81 (2 H, 2 d, 2 $CHHC_6H_5$), 5.05 (1 H, d, $J_{1',2'}$ = 8.5 Hz, H-1′), 5.06 (1 H, t, $J_{3'',4''+4'',5''}$ = 18.0 Hz, H-4″), 5.47 (1 H, t, $J_{2'',3''+3'',4''}$ = 19.6 Hz, H-3″), 5.51 (1 H, d, $J_{1'',2''}$ = 8.2 Hz, H-1″), 5.59 (1 H, s, $OCHC_6H_5$), 7.0–7.5 (28 H, m, Ar). Anal. Calcd for $C_{70}H_{70}O_{20}N_2S$: C, 65.12; H, 5.46; N, 2.17. Found: C, 65.16; H, 5.56; N, 2.04.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (30). Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-seleno-β-D-glucopyranoside (5) (0.07 g, 0.1 mmol) was dissolved in dichloromethane (5 mL) and the reaction mixture was stirred under nitrogen for 15 min. Silver triflate (0.19 g, 0.7 mmol) was then added followed by water (0.005 mL, 0.3 mmol). After 1.5 h the reaction mixture was quenched with excess K_2CO_3 and filtered through Celite. The filtrate was evaporated and the resulting residue was chromatographed using hexane–ethyl acetate (1:1.6) as eluant, R_f = 0.4. The *title compound* was isolated as a powder (0.46 g, 87%); the physical and ^1H NMR spectroscopic data matched those reported in the literature.[43] ^{13}C NMR ($CDCl_3$): δ 20.4, 20.6, 20.7 (3 $COCH_3$), 56.2 (C-2), 62.1 (C-6), 69.1 (C-4), 70.6 (C-3), 72.2 (C-5), 92.7 (C-1), 123.7–134.3 (Ar), 167.8, 169.5, 170.0, 170.7 (5 *C*O).

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