Synthesis of *C*-Glycosyl Lactones and Protected *C*-Glycosyl Amino Acids: Use of Radical Cyclization

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Received July 22, 1998

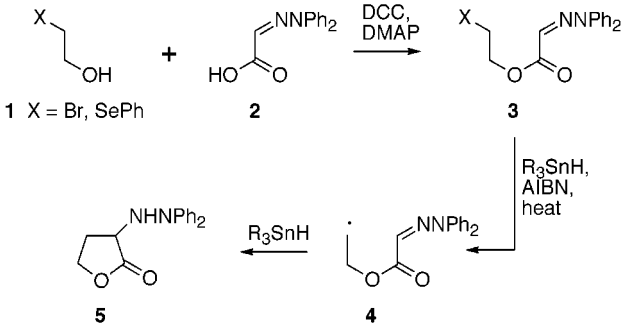
Protected carbohydrates **6a**−**13a**, having one free hydroxyl and a phenylseleno group or halogen on the adjacent carbon, were condensed with (2,2-diphenylhydrazono)acetic acid (**2**); the resulting esters undergo radical cyclization to afford carbohydrates fused to a 2,2-diphenylhydrazino lactone unit (**6c**,**d**−**13c**,**d**). In suitable cases (**9c**,**d**) such carbohydrate lactones can be elaborated into *C*-glycosyl amino acids.

Introduction

Hydrazono esters of type **3** (X = halogen or PhSe; Scheme 1), which are easily available by esterification of the crystalline reagent (2,2-diphenylhydrazono)acetic acid (**2**),[1] are converted into hydrazino lactones **5**, on treatment with a stannane and initiator (**3** → **4** → **5**).[2] We describe here the use of this sequence to make carbohydrates fused to hydrazino lactones and show that, in favorable cases, such lactones can be elaborated into protected *C*-glycosyl amino acids.[3] A number of antibiotics belong to the class of *C*-glycosyl amino acids,[4] and the compounds are of value as components of carbon-linked analogues of glycopeptides[5] and as building blocks for combinatorial synthesis.[6]

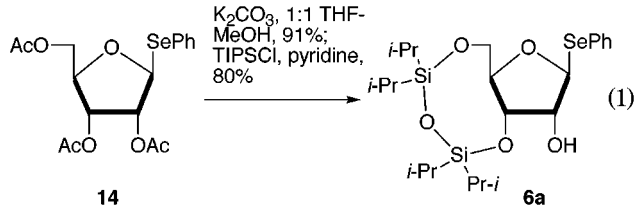
Preparation of Starting Materials. The starting materials for this work were modified carbohydrates, some of which (**6a**,**b**−**13a**,**b**) are shown in Table 1. Each of the hydrazono esters **6b**−**13b** was made by DCC-mediated coupling of the appropriate alcohol with reagent **2**, using DMAP as a catalyst, and in every case the reaction was efficient, the yields always being at least

Scheme 1



90%. The alcohols required for the esterification were prepared by conventional methods, as follows:

Treatment of commercial tetra-*O*-acetyl-*β*-D-ribofuranose with PhSeH in the presence of $BF_3{\cdot}Et_2O$[7] gave (92%) the *β*-phenyl selenide **14**[8] (eq 1), from which **6a** was



formed by base hydrolysis (K_2CO_3, THF−MeOH; 91%) and silylation [*i*-$Pr_2Si(Cl)OSi(Cl)Pr_2$-*i*, pyridine; 80%].

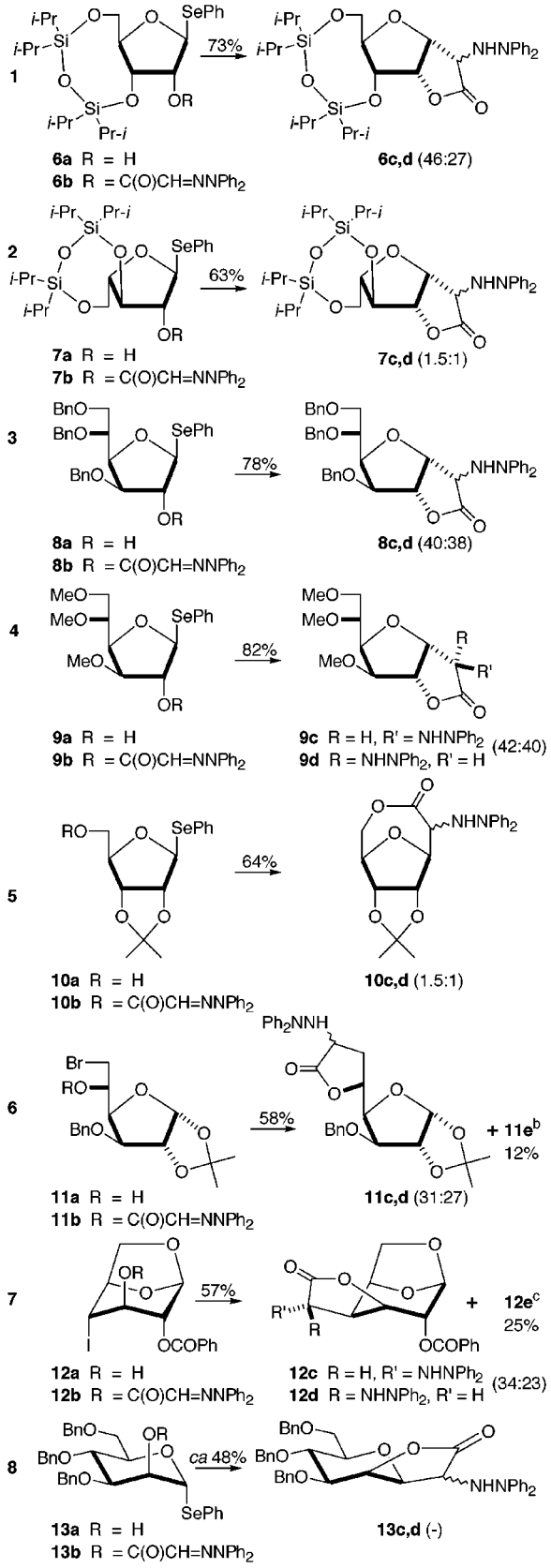
L-Arabinose was converted (Scheme 2) by a known procedure[9] into its tetraacetate **15** (as a mixture of anomers) which, on treatment with $PhSeH/BF_3{\cdot}Et_2O$, gave α-selenide **16** (64%). Mild base hydrolysis (**16** → **17**, K_2CO_3, THF−MeOH; 93%) and silylation [*i*-$Pr_2Si(Cl)OSi(Cl)Pr_2$-*i*, pyridine; 77%] afforded **7a**.

A mixture of the anomeric diacetates **18** (Scheme 3), made from diacetone glucose,[10] afforded the *β*-selenide **19** on treatment with $PhSeH/BF_3{\cdot}Et_2O$ (73%), and alcohol

(1) Barber, H. J.; Lunt, E. *J. Chem. Soc.* **1965**, 1468−1473.
(2) Clive, D. L. J.; Zhang, J. *Chem. Commun.* **1997**, 549.
(3) For leading references to other preparations of *C*-glycosyl amino acids, see, for example: (a) Dondoni, A.; Junquera, F.; Merchán, F. L.; Merino, P.; Scherrmann, M.-C.; Tejero, T. *J. Org. Chem.* **1997**, *62*, 5484−5496. Recent examples of the synthesis of *C*-glycosyl amino acids or peptides: (b) Czernecki, S.; Horns, S.; Valery, J.-M. *J. Org. Chem.* **1995**, *60*, 650−655. (c) Urban, D.; Skrydstrup, T.; Beau, J.-M. *Chem. Commun.* **1998**, 955−956. (d) Coutrot, P.; Grison, C.; Coutrot, F. *Synlett* **1998**, 393−395. (e) Tedebark, U.; Meldal, M.; Panza, L.; Bock, K. *Tetrahedron Lett.* **1998**, *39*, 1815−1818. (f) Hoffmann, M.; Burkhart, F.; Hessler, G.; Kessler, H. *Helv. Chim. Acta* **1996**, *79*, 1519−1532. (g) Rassu, G.; Zanardi, F.; Battistini, L.; Casiraghi, G. *Tetrahedron: Asymmetry* **1995**, *6*, 371−374. (h) Petruš, L.; BeMillar, J. N. *Carbohydr. Res.* **1992**, *230*, 197−200. (i) Bertozzi, C. R.; Hoeprich, P. D., Jr.; Bednarski, M. D. *J. Org. Chem.* **1992**, *57*, 6092−6094. (j) Kessler, H.; Wittmann, V.; Köck, M.; Kottenhahn, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 902−904. (k) Colombo, L.; Casiraghi, G.; Pittalis, A. *J. Org. Chem.* **1991**, *56*, 3897−3900. (l) Pochet, S.; Allard, P.; Huynh-Dinh, T.; Igolen, J. *J. Carbohydr. Chem.* **1982-3**, *1*, 277−288. (m) Bischofberger, K.; Brink, A. J.; de Villiers, O. G.; Hall, R. H. *J. Chem. Soc., Perkin Trans I* **1977**, 1472−1476. (n) Cf. Debenham, S. D.; Debenham, J. S.; Burk, M. J.; Toone, E. J. *J. Am. Chem. Soc.* **1997**, *119*, 9897−9898.
(4) For examples of recent synthetic work related to such antibiotics, see: (a) Zhang, D.; Miller, M. J. *J. Org. Chem.* **1998**, *63*, 755−759. (b) Barrett, A. G. M.; Lebold, S. A. *J. Org. Chem.* **1990**, *55*, 3853−3857. (c) Garner, P.; Park, J. M. *J. Org. Chem.* **1990**, *55*, 3772−3787.
(5) Review on glycobiology: Dwek, R. A. *Chem. Rev.* **1996**, *96*, 683−720.
(6) Cf. McDevitt, J. P.; Lansbury, P. T., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 3818−3828.
(7) Giese, B.; Gilges, S.; Gröninger, K. S.; Lamberth, C.; Witzel, T. *Justus Liebigs Ann. Chem.* **1988**, 615−617.
(8) A mixture of both anomers is formed by using PhSeSePh/Zn−AcOH (Fourrey, J.-L.; Henry, G.; Jouin, P. *Tetrahedron Lett.* **1980**, 455−458).
(9) Backinowsky, L. V.; Nepogod'ev, S. A.; Shashkov, A. S.; Kochetkov, N. K. *Carbohydr. Res.* **1985**, *138*, 41−54.
(10) Du, Y.; Kong, F. *J. Carbohydr. Chem.* **1996**, *15*, 797−817.

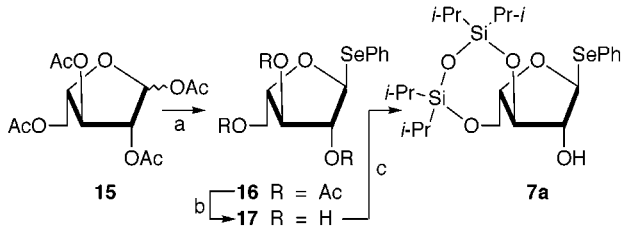
10.1021/jo981435w CCC: $18.00
Published on Web 01/13/1999

Table 1



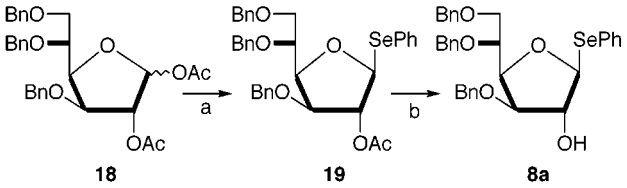
[a] Isomer ratios are given in brackets, but we did not establish which is the **c** or **d** isomer, except for **9c**,**d** (**9c**:**9d** = 42:40) and **12c**,**d** (**12c**:**12d** = 34:23). [b] Structure of **11e** is same as structure of **11b**, but with H instead of Br. [c] Structure of **12e** is the same as the structure of **12b**, but with H instead of I.

Scheme 2[a]



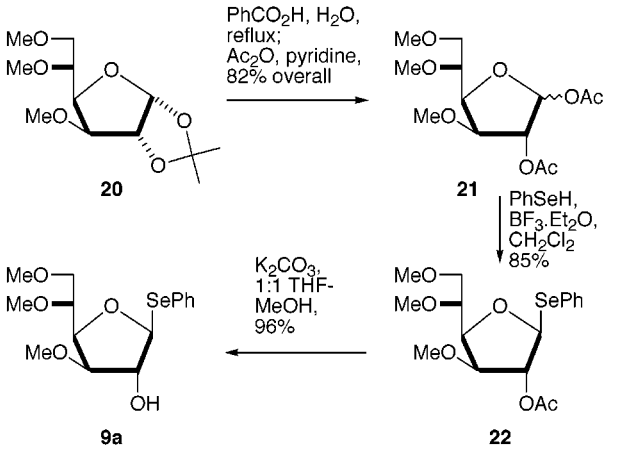
[a] (a) PhSeH, $BF_3{\cdot}Et_2O$, CH_2Cl_2; 64%. (b) K_2CO_3, 1:1 THF−MeOH; 93%. (c) TIPSCl, pyridine, 77%.

Scheme 3[a]



[a] (a) PhSeH, $BF_3{\cdot}Et_2O$, CH_2Cl_2; 73%. (b) K_2CO_3, 1:1 THF−MeOH; 96%.

Scheme 4



8a was then obtained by base hydrolysis (**19** → **8a**, K_2CO_3, THF−MeOH; 96%).

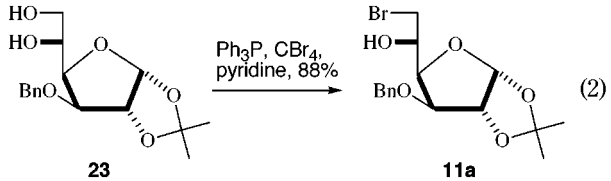
Diacetone glucose was also used (Scheme 4) to synthesize **9a**. Selective deprotection of diacetone glucose at C(5)−C(6) by acid hydrolysis,[11] and tris-methylation[12] (Me_2SO_4, DMSO, NaOH; 82% overall), gave **20** (Scheme 4).[13] Mild hydrolysis ($PhCO_2H$ in water at reflux), followed by acetylation took the route as far as **21** (82%). This was treated with PhSeH/$BF_3{\cdot}Et_2O$ (**21** → **22**, 85%), and the required alcohol was again obtained by base hydrolysis (**22** → **9a**, K_2CO_3, THF−MeOH; 96%).

Alcohol **10a** was made by hydrolysis (K_2CO_3, THF−MeOH; 92%) and ketalization (acetone, TsOH; 92%) of selenide **14**.

Diol **23** (eq 2) was prepared by the literature procedure[14] in two steps from diacetone glucose, and treatment

(11) Schmidt, O. Th. In *Methods in Carbohydrate Chemistry*; Whistler, R. L., Wolfrom, M. L., Eds.; Academic Press: London, 1963; Vol. 2, p 322.
(12) Cf. Kuszmann, J.; Sohár, P.; Kiss, L. *Carbohydr. Res.* **1978**, *63*, 115−125.
(13) de Jong, E. G.; Heerma, W.; Dujardin, B.; Haverkamp, J.; Vliegenthart, J. F. G. *Carbohydr. Res.* **1978**, *60*, 229−239.
(14) Nayak, U. G.; Whistler, R. L. *J. Org. Chem.* **1969**, *34*, 97−100.

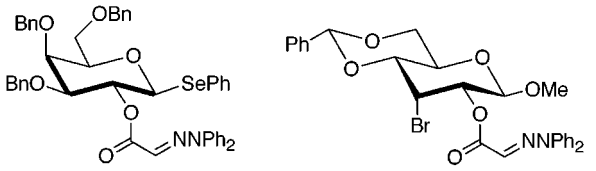
with Ph_3P/CBr_4 served to convert it into **11a** (88%).



23 **11a**

β-D-Galactose pentaacetate and D-mannose were converted by literature procedures into **12a**[15] and the acetate[16] corresponding to **13a**, respectively. Simple hydrolysis of the acetate gave **13a** (90%).

A number of other modified carbohydrates (**24**−**27**) were also prepared,[17] but without full characterization, as the critical radical closure proceeded poorly or not at all (see below).



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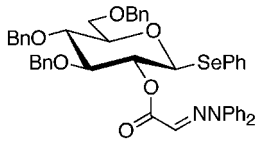

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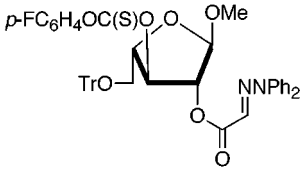

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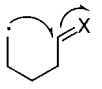
Radical Cyclizations. Our general procedure (see Experimental Section) for radical cyclization involves slow addition (ca. 10 h) of individual solutions of Bu_3SnH (0.06−0.2 M, 1.5−3.0 equiv) and AIBN (0.003−0.020 M, 0.2−0.4 equiv) in PhMe to a stirred solution of the hydrazono ester (0.015 M) in the same solvent at reflux. With the exception of **13b**, cyclization generally occurred smoothly to give the product lactones **6c**,**d**−**12c**,**d** in yields of 57−82% (Table 1), and even a seven-membered ring can be formed (**10c**,**d**; 64%). A mixture of isomers was always obtained, and in all but two cases (**7c**,**d** and **10c**,**d**) the isomers could be separated by flash chromatography. In a few cases the simple reduction product was also isolated [**11e**, 12% (as judged by ^{1}H NMR measurements); **12e**, 25%], and trace amounts of Ph_2NH were sometimes detected. Use of an excess of stannane (1.2−3.0 equiv, depending on the case) generally gives better results. The structures of the lactones were clear from their NMR spectra, and NOE measurements allowed us to assign the stereochemistry at the position α to the lactone carbonyl for compounds **9c**,**d** and **12c**,**d**. In the former case, X-ray analysis of one of the isomers (**9d**) confirmed our assignment.

A notable feature of the radical closure step is the absence −at least to any major extent − of acyl migration.[7,18,19] 5-*Exo*-cyclization of a radical onto a C=$NNPh_2$ group is extremely fast and, for an all-carbon chain, as in **28** (X = $NNPh_2$), the rate constant at 80 °C is of the



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order of 10^7−10^8 s^{-1}, while the corresponding value for closure onto a carbon−carbon double bond (**28**, X = CH_2) is only about 10^5 s^{-1}.[20] 1,2-Acyl migrations have rate constants that span the range[18] (at 75 °C) of about 10^2−10^6 s^{-1} and can be significantly faster than closure onto a hydrazono unit.[21] The fact that acyl migration does not compete with the closures reported here shows that the rotational barrier about the ester C(O)−O single bond is sufficiently low[22] to permit easy access to a conformation in which the radical center is close to the C=N double bond and that closure onto an α-acyl (as opposed to α-alkyl) hydrazono unit is fast.

In exploratory experiments with hydrazono esters of the six-membered sugars **24**−**26**, and the furanose example **27**, the radical cyclization step gave complex mixtures.[23] With **13b** (Table 1) the desired lactones are formed inefficiently (ca. 48%) and, except for anhydrosugar **12b** (Table 1), the six-membered series was not examined further.

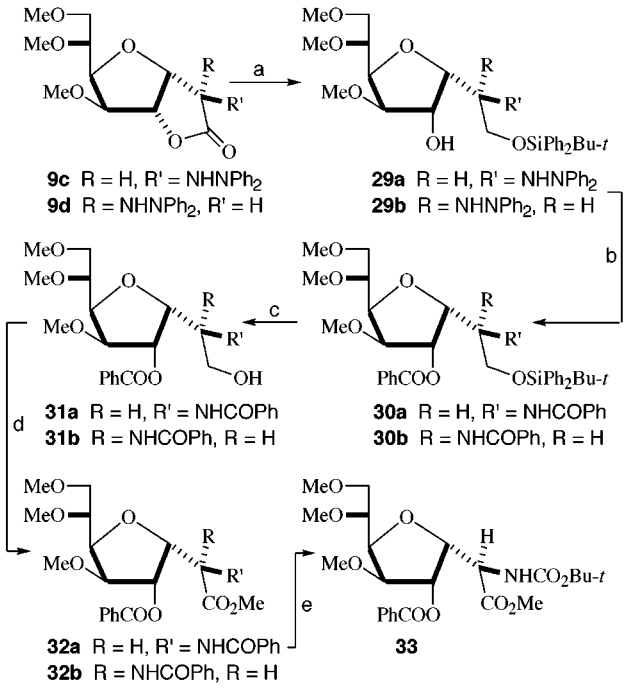
It is not clear whether the axial nature of the hydrazono pendant in the anhydrosugar **12b** and the mannose derivative **13b** contributes to the relative efficiency of closure, as compared with the galactose- (**24**) or glucose-derived examples (**25**, **26**), as efficient closures involving both axial and equatorial pendants have been observed experimentally.[24]

Modification of the Hydrazino Lactones and Formation of *C*-Glycosyl Amino Acids. In principle, opening of the lactone unit of the radical cyclization products and hydrogenolysis of the N−N single bond should afford a *C*-glycosyl amino acid, but in practice this overall transformation had to be effected indirectly. Our general experience[25] is that hydrogenolysis of 2,2-diphenylhydrazino lactones is unsuccessful, and lactone opening with a base results in expulsion of diphenylamine. Formation of *C*-glycosyl amino acids was therefore achieved in the following way.

Hydride reduction ($LiAlH_4$) of **9c** (Scheme 5), selective silylation of the resulting primary hydroxyl (*t*-$BuPh_2SiCl$, imidazole; 79% overall), hydrogenolysis (H_2, Pd−C, camphorsulfonic acid, MeOH), and benzoylation (PhCOCl, Et_3N, DMAP; 76% overall) gave **30a** (**9c** → **29a** → **30a**). Desilylation, using Bu_4NF, is complicated by benzoyl migration, but this process could be suppressed by using Bu_4NF in the presence of 1.5 equiv of pyridinium hydrochloride,[26] and under these conditions the yield was

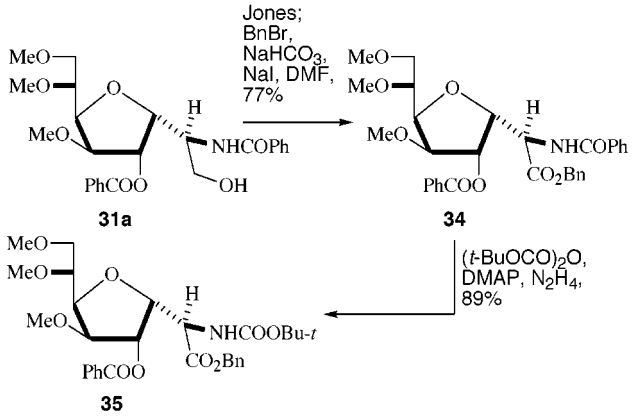
(15) Knapp, S.; Naughton, A. B. J.; Jaramillo, C.; Pipik, B. *J. Org. Chem.* **1992**, *57*, 7328−7334.
(16) Vauzeilles, B.; Cravo, D.; Mallet, J.-M.; Sinaÿ, P. *Synlett* **1993**, 522−524.
(17) The procedures are outlined in the Supporting Information.
(18) Beckwith, A. L. J.; Crich, D.; Duggan, P. J.; Yao, Q. *Chem. Rev.* **1997**, *97*, 3273−3313.
(19) Giese, B.; Gröninger, K. S. *Org. Synth.* **1990**, *69*, 66−71.
(20) Sturino, C. F.; Fallis, A. G. *J. Org. Chem.* **1994**, *59*, 6514−6516.
(21) For an example of rearrangement before closure, see ref 2.
(22) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 618.
(23) The ^{13}C NMR spectrum of the crude reaction product from an attempted radical cyclization of **26** showed signals at δ 172.9, 163.7, and 101.0, suggesting the presence of a γ-lactone (δ 163.7) resulting from acyl migration and cyclization [C(1) O**C**HO], as well as simple reduction product or starting material (δ 172.9).
(24) (a) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* **1981**, *22*, 2811−2814. (b) Clive, D. L. J.; Joussef, A. C. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2797−2799 and references therein.
(25) J. Zhang, unpublished observations.
(26) Cf.: Verdegaal, C. H. M.; Jansse, P. L.; de Rooij, J. F. M.; van Boom, J. H. *Tetrahedron Lett.* **1980**, 1571−1574.

Scheme 5[a]



[a] (a) $LiAlH_4$, THF, 0 °C; *t*-$BuPh_2SiCl$, imidazole; 79% overall for **29a**, 81% for **29b**. (b) Camphorsulfonic acid, 10% Pd−C, H_2 (50 psi); PhCOCl, Et_3N; 76% overall for **30a**, 75% for **30b**. (c) Bu_4NF, pyridinium hydrochloride; 83% for **31a**, 81% for **31b**. (d) Jones reagent; CH_2N_2; 76% overall for **32a**, 77% for **32b**. (e) $(t\text{-}BuOCO)_2O$, DMAP; MeOH, N_2H_4; 86%.

Scheme 6



83%. The resulting primary alcohol was oxidized and esterified (**31a** → **32a**; 76%), and the *N*-benzoyl group was replaced directly by a *tert*-butyloxycarbonyl group [$(t\text{-}BuOCO)_2O$, DMAP, NH_2NH_2; 86%],[27] so as to afford the protected *C*-glycosyl amino acid **33**. The other isomeric hydrazone closure product (**9d**) was subjected to the same operations, except for the last step (Scheme 5), and provided the protected *C*-glycosyl amino acid **32b**.

In a slightly different set of reactions, alcohol **31a** was oxidized to the corresponding acid, and this was converted into its benzyl ester (**31a** → **34**; BnBr, $NaHCO_3$, NaI; 77%). Finally, the *N*-benzoyl group was replaced directly by a *tert*-butyloxycarbonyl group [$(t\text{-}BuOCO)_2O$, DMAP, NH_2NH_2; 89%; **34** → **35**].

The formation of compounds **32a**, **33**, and **35** shows that *C*-glycosyl amino acid derivatives are accessible by the radical cyclization approach described here. The stereochemistry α to the carboxyl is not controlled, but the epimers are often separable, and the α or *β* stereochemistry with respect to the carbohydrate subunit is determined by the stereochemistry of the hydroxyl that is initially acylated with reagent **2**.

(27) Burke, M. J.; Allen, J. G. *J. Org. Chem.* **1997**, *62*, 7054−7057.

Experimental Section

General Procedures. Unless stated to the contrary, the general procedures used previously[28] were followed. Optical rotations were measured at room temperature.

The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate zero, one, two, or three attached hydrogens, respectively.

(2,2-Diphenylhydrazono)acetic Acid (2). This procedure differs from that reported[1] in the literature. Glyoxylic acid monohydrate (5.520 g, 60 mmol) was added to a stirred solution of commercial Ph_2NNH_2·HCl (13.248 g, 60 mmol) in H_2O (720 mL). Stirring was continued for 2 h, and the precipitate was filtered off, washed with H_2O (5 × 30 mL), and dried under oil-pump vacuum to afford **2** (13.901 g, 96%) as a gray power: mp 201−203 °C (lit.[1] 200−202 °C).

General Procedure for Coupling of Alcohols with Reagent 2. Glyoxylic acid diphenylhydrazone (1.2 equiv) was added to a stirred mixture of the alcohol (1.0 equiv), DCC (1.32 equiv), and DMAP (0.12 equiv) in dry CH_2Cl_2. Stirring was continued for 12 h, and the mixture was then filtered. The insoluble material was washed with dry CH_2Cl_2 and the combined filtrates were evaporated to give a residue, which was processed as described for the individual experiments.

General Procedure for Radical Cyclization. The substrate was placed in a round-bottomed flask equipped with a Teflon-coated stirring bar and a reflux condenser sealed with a rubber septum. The system was flushed with argon for 5−10 min, and dry PhMe was injected into the flask. The flask was placed in an oil bath preheated to 110 °C, and solutions of Bu_3-SnH and AIBN in PhMe were injected simultaneously by syringe pump over 10 h. Refluxing was continued for an arbitrary period of 1−4 h after the addition, except in the preparation of **12c**,**d**, where a longer period (7 h) was used. The reaction mixture was cooled, and the solvent was evaporated to give a residue which was processed as described for the individual experiments.

Phenyl 1-Seleno-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-*β*-D-ribofuranoside (6a). (a) Phenyl 1-Seleno-*β*-D-ribofuranoside. K_2CO_3 (123.1 mg, 0.891 mmol) was added to a stirred solution of **14**[8] (370.0 mg, 0.891 mmol) in 1:1 THF−MeOH (5 mL). Stirring was continued for 6 h, and the mixture was filtered through a pad (1 cm × 2 mm) of silica gel and evaporated. Flash chromatography of the residue over silica gel (1.2 × 21 cm), using 2% MeOH-EtOAc, gave phenyl 1-seleno-*β*-D-ribofuranoside (235.8 mg, 91%) as a pale yellow oil: FTIR (MeOH cast) 3374 cm^{-1}; ^1H NMR (CD_3OD, 360 MHz) *δ* 3.54−3.66 (m, 2 H), 3.92−3.97 (m, 1 H), 4.03 (dd, *J* = 6.1, 5.0 Hz, 1 H), 4.13−4.15 (m, 1 H), 4.75−4.97 (br, 3 H), 5.48 (d, *J* = 3.3 Hz, 1 H), 7.25−7.36 (m, 3 H), 7.58−7.70 (m, 2 H); ^{13}C NMR (CD_3OD, 100.6 MHz) *δ* 63.72 (t′), 72.44 (d′), 77.64 (d′), 86.32 (d′), 88.17 (d′), 128.83 (d′), 130.12 (d′), 130.20 (s′), 135.63 (d′); exact mass *m*/*z* calcd for $C_{11}H_{14}O_4Se$ 290.0057, found 290.0062.

(b) Phenyl 1-Seleno-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-*β*-D-ribofuranoside (6a). 1.3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (470 *μ*L, 1.4678 mmol) was added dropwise to a stirred and cooled (0 °C) solution of the above triol (424.2 mg, 1.468 mmol) in dry pyridine (14 mL). Stirring was continued for 30 min at 0 °C and then for 6 h after removal of the ice bath. Pyridine was evaporated under vacuum, and flash chromatography of the residue over silica gel (2.6 × 25 cm), using 5% EtOAc−hexane, gave **6a** (624.0 mg, 80%) as a colorless oil: $[\alpha]_D = -112.3$ (*c* 1.14, $CHCl_3$); ^1H NMR (CD_2Cl_2,

(28) Clive, D. L. J.; Wickens, P. L.; Sgarbi, P. W. M. *J. Org. Chem.* **1996**, *61*, 7426−7437.

360 MHz) δ 0.93−1.17 (m, 28 H), 3.03 (d, J = 1.6 Hz, 1 H), 3.88−4.02 (m, 3 H), 4.27 (dt, J = 5.1, 1.4 Hz, 1 H), 4.37 (dd, J = 6.2, 5.2 Hz, 1 H), 5.59 (d, J = 1.2 Hz, 1 H), 7.26−7.35 (m, 3 H), 7.57−7.62 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 13.03 (d′), 13.22 (d′), 13.57 (d′), 13.64 (d′), 17.16 (q′), 17.19 (q′), 17.22 (q′), 17.40 (q′), 17.49 (q′), 17.60 (q′), 17.65 (q′), 64.44 (t′), 74.55 (d′), 77.96 (d′), 83.37 (d′), 86.10 (d′), 128.39 (d′), 128.81 (s′), 129.52 (d′), 135.25 (d′); exact mass (electrospray) m/z calcd for $C_{23}H_{40}NaO_5SeSi_2$ (M + Na) 555.1477, found 555.1485.

Phenyl 2-*O*-(Diphenylhydrazono)acetyl-1-seleno-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranoside (6b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (341.4 mg, 1.423 mmol), **6a** (630.0 mg, 1.186 mmol), DCC (322.9 mg, 1.565 mmol), and DMAP (20.0 mg, 0.164 mmol) in CH_2Cl_2 (10 mL). Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 5% EtOAc−hexane, gave **6b** (839.4 mg, 94%) as a pale yellow oil: $[\alpha]_D$ = −57.7 (c 1.05, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1740, 1711 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 360 MHz) δ 0.84−1.19 (m, 28 H), 3.90−4.06 (m, 3 H), 4.42−4.49 (m, 1 H), 5.62−5.68 (m, 2 H), 6.51 (d, J = 2.2 Hz, 1 H), 7.14−7.69 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 13.19 (d′), 13.48 (d′), 13.63 (d′), 17.19 (q′), 17.25 (q′), 17.34 (q′), 17.49 (q′), 17.64 (q′), 63.36 (t′), 72.71 (d′), 79.16 (d′), 82.95 (d′), 83.68 (d′), 122.71 (d′), 123.97 (d′), 126.52 (d′), 128.52 (s′), 128.63 (d′), 129.59 (d′), 130.38 (d′), 135.58 (d′), 142.60 (s′), 163.49 (s′); exact mass (electrospray) m/z calcd for $C_{37}H_{50}N_2NaO_6SeSi_2$ (M + Na) 777.2270, found 777.2276.

3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-5,7-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-*glycero*-D-*manno*-heptono-1,4-lactone (6c) and 3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-5,7-*O*-(tetraisopropyldisiloxane-1,3-diyl)-D-*glycero*-D-*gluco*-heptono-1,4-lactone (6d). The general procedure for radical cyclization was followed, using **6b** (316.8 mg, 0.421 mmol) in PhMe (30 mL), Bu_3SnH (340 μL, 1.261 mmol) in PhMe (10 mL), and AIBN (30 mg, 0.183 mmol) in PhMe (10 mL). Flash chromatography of the residue over silica gel (1.6 × 29 cm), using 3% EtOAc−hexane, gave the chromatographically less polar product **6c** (or **6d**) (117.2 mg, 46%), and the more polar product **6d** (or **6c**) (69.7 mg, 27%) as colorless oils. The chromatographically less polar diastereomer: $[\alpha]_D$ = +27.6 (c 1.09, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1779 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.01−1.17 (m, 28 H), 3.64 (dt, J = 9.2, 2.3 Hz, 1 H), 3.77−3.79 (m, 1 H), 3.89−4.01 (m, 2 H), 4.28−4.35 (m, 2 H), 4.80 (dd, J = 4.8, 0.6 Hz, 1 H), 5.13 (t, J = 4.6 Hz, 1 H), 7.06−7.38 (m, 10 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 12.95 (d′), 13.19 (d′), 13.37 (d′), 13.85 (d′), 17.02 (q′), 17.13 (q′), 17.29 (q′), 17.42 (q′), 17.48 (q′), 17.56 (q′), 60.08 (t′), 63.83 (d′), 71.75 (d′), 79.63 (d′), 79.76 (d′), 82.81 (d′), 121.22 (d′), 123.77 (d′), 129.81 (d′), 147.45 (s′), 174.87 (s′); exact mass (electrospray) m/z calcd for $C_{31}H_{46}N_2NaO_6Si_2$ (M + Na) 621.2792, found 621.2792.

The chromatographically more polar diastereomer: $[\alpha]_D$ = +69.6 (c 1.09, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1786 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.01−1.13 (m, 28 H), 3.76 (dt, J = 9.2, 2.4 Hz, 1 H), 3.79 (dd, J = 5.8, 3.5 Hz, 1 H), 3.94−4.10 (m, 2 H), 4.37 (dd, J = 9.2, 4.1 Hz, 1 H), 4.56 (dd, J = 5.8, 3.8 Hz, 1 H), 4.83 (t, J = 3.9 Hz, 1 H), 4.86 (d, J = 3.5 Hz, 1 H), 7.01−7.35 (m, 10 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 13.08 (d′), 13.24 (d′), 13.44 (d′), 13.87 (d′), 17.07 (q′), 17.17 (q′), 17.31 (q′), 17.42 (q′), 17.46 (q′), 17.49 (q′), 17.60 (q′), 60.40 (d′), 60.53 (t′), 72.52 (d′), 75.67 (d′), 80.20 (d′), 81.21 (d′), 121.05 (d′), 123.22 (d′), 129.54 (d′), 147.56 (s′), 174.79 (s′); exact mass (electrospray) m/z calcd for $C_{31}H_{46}N_2NaO_6Si_2$ (M + Na) 621.2792, found 621.2791.

Phenyl 2,3,5-Tri-*O*-acetyl-1-seleno-α-L-arabinofuranoside (16). $BF_3{\cdot}Et_2O$ (232 μL, 1.88 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **15**[9] (636.6 mg, 2.00 mmol) and PhSeH (314 μL, 2.96 mmol) in CH_2Cl_2 (20 mL). Stirring was continued for 28 h at 0 °C, and then saturated aqueous $NaHCO_3$ (5 mL) was added. The organic phase was washed with water (3 × 5 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.6 × 26 cm), using 20% EtOAc−hexane, gave **16** (533.4 mg, 64%) as a colorless oil: $[\alpha]_D$ = −161.4 (c 1.98, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1747 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 360 MHz) δ 2.06 (s, 3 H) 2.07 (s, 3 H), 2.12 (s, 3 H), 4.25 (dd, J = 12.0, 5.6 Hz, 1 H), 4.40 (dd, J = 12.0, 3.7 Hz, 1 H), 4.46−4.50 (m, 1 H), 5.03−5.05 (m, 1 H), 5.34−5.38 (m, 1 H), 5.80−5.82 (m, 1 H), 7.29−7.34 (m, 3 H), 7.60−7.66 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 20.84 (q′), 62.90 (t′), 77.56 (d′), 81.54 (d′), 82.45 (d′), 87.31 (d′), 128.29 (d′), 129.49 (d′), 129.60 (s′), 134.60 (d′), 169.81 (s′), 170.17 (s′), 170.63 (s′); exact mass m/z calcd for $C_{17}H_{20}O_7Se$ 416.0374, found 416.03774.

Phenyl 1-Seleno-α-L-arabinofuranoside (17). K_2CO_3 (173.7 mg, 1.257 mmol) was added to a stirred solution of **16** (521.9 mg, 1.257 mmol) in 1:1 THF−MeOH (8 mL), and the mixture was stirred for 1 h, filtered through a pad (1 cm × 2 mm) of silica gel, and evaporated. Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 2% MeOH-EtOAc, gave **17** (337.8 mg, 93%) as a pale yellow oil: $[\alpha]_D$ = −267.9 (c 1.04, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3373 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 3.71 (d, J = 11.5 Hz, 1 H), 3.79 (d, J = 11.5 Hz, 1 H), 4.11 (br s, 2 H), 4.20−4.59 (br m, 4 H), 5.69 (d, J = 2.6 Hz, 1 H), 7.22−7.30 (m, 3 H), 7.57−7.62 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 61.34 (t′), 77.27 (d′), 83.11 (d′), 84.61 (d′), 89.21 (d′), 128.13 (d′), 129.57 (d′), 130.08 (s′), 134.32 (d′); exact mass m/z calcd for $C_{11}H_{14}O_4Se$ 290.0057, found 290.0056.

Phenyl 1-Seleno-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-L-arabinofuranoside (7a). 1.3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (304 μL, 0.9516 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **17** (275.0 mg, 0.952 mmol) in dry pyridine (10 mL). Stirring was continued for 30 min at 0 °C and then for 6 h after removal of the ice bath. Pyridine was evaporated under vacuum, and flash chromatography of the residue over silica gel (1.6 × 28 cm), using 5% EtOAc−hexane, gave **7a** (390.5 mg, 77%) as a colorless oil: $[\alpha]_D$ = −141.2 (c 1.32, $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 0.96−1.15 (m, 28 H), 2.54 (d, J = 5.1 Hz, 1 H), 3.91−4.04 (m, 3 H), 4.16−4.26 (m, 1 H), 3.33 (dd, J = 10.4, 5.0 Hz, 1 H), 5.62 (d, J = 4.6 Hz, 1 H) 7.27−7.33 (m, 3 H), 7.60−7.67 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 13.00 (d′), 13.32 (d′), 13.56 (d′), 13.93 (d′), 17.21 (q′), 17.27 (q′), 17.34 (q′), 17.55 (q′), 17.70 (q′), 61.88 (t′), 77.45 (d′), 82.05 (d′), 83.20 (d′), 88.55 (d′), 127.93 (d′), 129.45 (d′), 130.49 (s′), 134.03 (d′); exact mass (electrospray) m/z calcd for $C_{23}H_{40}NaO_5SeSi_2$ (M + Na) 555.1477, found 555.1477.

Phenyl 2-*O*-(Diphenylhydrazono)acetyl-1-seleno-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-L-arabinofuranoside (7b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (162.6 mg, 0.677 mmol), **7a** (240.0 mg, 0.452 mmol), DCC (153.7 mg, 0.745 mmol), and DMAP (10.0 mg, 0.082 mmol) in CH_2Cl_2 (4 mL). Flash chromatography of the residue over silica gel (1.6 × 300 cm), using 5% EtOAc−hexane, gave **7b** (308.2 mg, 90%) as a pale yellow oil: $[\alpha]_D$ = −56.9 (c 1.27, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1711 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 0.98−1.17 (m, 28 H) 3.95 (dd, J = 12.4, 5.4 Hz, 1 H), 4.07 (dd, J = 12.4, 3.3 Hz, 1 H), 4.19−4.24 (m, 1 H), 4.46−4.50 (m, 1 H), 5.46−5.49 (m, 1 H), 5.72−5.76 (m, 1 H), 7.16−7.66 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 12.89 (d′), 13.34 (d′), 13.63 (d′), 13.88 (d′), 17.17 (q′), 17.20 (q′), 17.59 (q′), 17.71 (q′), 62.04 (t′), 76.35 (d′), 82.52 (d′), 84.05 (d′), (86.08 (d′), 123.39 (d′), 127.96 (d′), 129.39 (d′), 130.40 (d′), 130.56 (s′), 134.22 (d′), 163.92 (s′), exact mass (electrospray) m/z calcd for $C_{37}H_{50}N_2NaO_6SeSi_2$ (M + Na) 777.2270, found 777.2279.

3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-5,7-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-*glycero*-L-*gulo*-heptono-1,4-lactone and 3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-5,7-*O*-(tetraisopropyldisiloxane-1,3-diyl)-L-*glycero*-L-*ido*-heptono-1,4-lactone (7c,d). The general procedure for radical cyclization was followed, using **7b** (194.0 mg, 0.258 mmol) in PhMe (15 mL), Bu_3SnH (208 μL, 0.773 mmol) in PhMe (5 mL), and AIBN (20 mg, 0.122 mmol) in PhMe (5 mL). Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 2% EtOAc−hexane, gave **7c**,**d** (97.4 mg, 63%) as a colorless oil, which was a chromatographically inseparable mixture of two isomers in a 1.5:1 ratio (^{1}H NMR, 400 MHz): $[\alpha]_D$ = +70.5 (c 0.88, $CHCl_3$); FTIR (CH_2Cl_2

cast) 1791 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.02−1.17 (m, 28 H), 3.75−3.79 (m, 0.44 H), 3.84−4.03 (m, 2.54 H), 4.17 (dd, J = 10.8, 3.2 Hz, 0.61 H), 4.32 (d, J = 2.0 Hz, 0.40 H), 4.37 (dd, J = 7.5, 3.1 Hz, 0.37 H), 4.45−4.47 (m, 0.57 H), 4.53−4.55 (m, 0.58 H), 4.73 (dd, J = 3.6, 0.6 Hz, 0.58 H), 4.77 (dd, J = 5.9, 1.4 Hz, 0.39 H), 4.81 (d, J = 3.7 Hz, 0.56 H), 5.14 (dd, J = 5.9, 3.1 Hz, 0.36 H), 7.02−7.38 (m, 10 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 12.98 (d′), 13.20 (d′), 13.32 (d′), 13.57 (d′), 13.67 (d′), 13.73 (d′), 13.76 (d′), 17.08 (q′), 17.12 (q′), 17.17 (q′), 17.24 (q′), 17.33 (q′), 17.37 (q′), 17.51 (q′), 17.58 (q′), 17.66 (q′), 17.74 (q′), 61.34 (d′), 62.87 (t′), 63.27 (d′), 64.86 (t′), 77.46 (d′), 78.76 (d′), 80.47 (d′), 80.62 (d′), 84.86 (d′), 87.71 (d′), 88.65 (d′), 89.77 (d′), 120.97 (d′), 121.28 (d′), 123.21 (d′), 123.84 (d′), 129.56 (d′), 129.85 (d′), 147.46 (s′), 147.61 (s′), 173.41 (s′), 174.07 (s′); exact mass (electrospray) m/z calcd for $C_{31}H_{46}N_2NaO_6Si_2$ (M + Na) 621.2792, found, 621.2805.

Phenyl 2-*O*-Acetyl-3,5,6-tri-*O*-benzyl-1-seleno-*β*-D-glucofuranoside (19). $BF_3{\cdot}Et_2O$ (476 μL, 3.8726 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **18**[10] (2.2001 g, 4.120 mmol) and PhSeH (648 μL, 6.0974 mmol) in CH_2Cl_2 (40 mL). Stirring was continued for 2 h at 0 °C, and then saturated aqueous $NaHCO_3$ (5 mL) was added. The organic phase was washed with water (2 × 10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2.6 × 28 cm), using 10% EtOAc−hexane, gave **19** (1.9090 g, 73%) as a colorless oil: $[\alpha]_D = -117.8$ (c 1.27, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1747 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 2.12 (s, 3 H), 3.80 (dd, J = 10.8, 4.6 Hz, 1 H), 3.99 (dd, J = 10.8, 2.0 Hz, 1 H), 4.21 (ddd, J = 9.4, 4.5, 1.9 Hz, 1 H), 4.26 (d, J = 4.0 Hz, 1 H), 4.44 (dd, J = 9.4, 4.0 Hz, 1 H), 4.52 (d, J = 11.3 Hz, 1 H), 4.61−4.65 (m, 3 H), 4.79 (d, J = 11.3 Hz, 1 H), 4.95 (d, J = 11.4 Hz, 1 H), 5.74 (s, 1 H), 7.29−7.51 (m, 18 H), 7.66−7.73 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 21.08 (q′), 70.48 (t′), 72.55 (t′), 72.64 (t′), 73.73 (t′), 76.37 (d′), 80.90 (d′), 81.12 (d′), 81.96 (d′), 87.51 (d′), 127.78 (d′), 127.86 (d′), 127.95 (d′), 128.16 (d′), 128.32 (d′), 128.56 (d′), 128.64 (d′), 128.73 (d′), 129.47 (d′), 131.92 (s′), 133.87 (d′), 137.90 (s′), 139.11 (s′), 139.30 (s′), 170.07 (s′); exact mass (electrospray) m/z calcd for $C_{35}H_{36}NaO_6Se$ (M + Na) 655.1575, found 655.1577.

Phenyl 3,5,6-Tri-*O*-benzyl-1-seleno-*β*-D-glucofuranoside (8a). K_2CO_3 (177.8 mg, 1.287 mmol) was added to a stirred solution of **19** (811.9 mg, 1.287 mmol) in 1:1 THF−MeOH (10 mL), and the mixture was stirred vigorously for 15 min, filtered through a pad (2 cm × 1 mm) of silica gel, and evaporated. Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 20% EtOAc−hexane, gave **8a** (727.5 mg, 96%) as a colorless oil: $[\alpha]_D = -143.7$ (c 1.47, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3415 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 2.38 (br, 1 H), 3.74 (dd, J = 10.8, 4.8 Hz, 1 H), 3.93 (dd, J = 10.8, 2.0 Hz, 1 H), 4.07 (d, J = 4.2 Hz, 1 H), 4.14 (ddd, J = 9.2, 4.8, 2.0 Hz, 1 H), 4.43 (dd, J = 9.2, 4.2 Hz, 1 H), 4.49 (dd, J = 11.4, 2.2 Hz, 1 H), 4.59 (s, 2 H), 4.67−4.77 (m, 3 H), 5.56 (br s, 1 H), 7.22−7.41 (m, 18 H), 7.58−7.65 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 70.79 (t′), 72.61 (t′), 72.69 (t′), 73.70 (t′), 76.66 (d′), 80.09 (d′), 81.63 (d′), 83.20 (d′), 90.43 (d′), 127.56 (d′), 127.72 (d′), 127.76 (d′), 127.88 (d′), 127.96 (d′), 128.08 (d′), 128.12 (d′), 128.56 (d′), 128.61 (d′), 128.71 (d′), 129.44 (d′), 132.17 (s′), 133.59 (d′), 138.14 (s′), 139.08 (s′), 139.35 (s′); exact mass (electrospray) m/z calcd for $C_{33}H_{34}NaO_5Se$ (M + Na) 613.1469, found 613.1480.

Phenyl 3,5,6-Tri-*O*-benzyl-2-*O*-(diphenylhydrazono)-acetyl-1-seleno-*β*-D-glucofuranoside (8b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (293.4 mg, 1.223 mmol), **8a** (600.1 mg, 1.019 mmol), DCC (277.4 mg, 1.345 mmol), and DMAP (15.0 mg, 0.123 mmol) in CH_2Cl_2 (10 mL). Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 10% EtOAc−hexane, gave **8b** (804.7 mg, 97%) as a pale yellow oil: $[\alpha]_D = -81.7$ (c 1.26, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1731, 1704 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 3.78 (dd, J = 10.8, 4.6 Hz, 1 H), 3.98 (dd, J = 10.8, 1.9 Hz, 1 H), 4.21 (ddd, J = 9.4, 4.6, 1.9 Hz, 1 H), 4.31 (d, J = 4.0 Hz, 1 H), 4.43 (dd, J = 9.3, 4.0 Hz, 1 H), 4.51 (d, J = 11.3 Hz, 1 H), 4.61−4.68 (m, 3 H), 4.77 (d, J = 11.3 Hz, 1 H), 4.99 (d, J = 11.4 Hz, 1 H), 5.78 (s, 1 H), 5.87 (s, 1 H), 6.51 (s, 1 H), 7.19−7.72 (m, 30 H); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 70.53 (t′), 72.58 (t′), 72.66 (t′), 73.69 (t′), 76.36 (d′), 80.98 (d′), 81.20 (d′), 82.00 (d′), 87.51 (d′), 123.3 (d′), 126.69 (d′), 127.75 (d′), 127.81 (d′), 127.92 (d′), 128.15 (d′), 128.34 (d′), 128.53 (d′), 128.63 (d′), 128.71 (d′), 129.45 (d′), 130.39 (d′), 131.86 (s′), 133.93 (d′), 137.93 (s′), 139.11 (s′), 139.29 (s′), 142.38 (s′), 163.51 (s′); exact mass (electrospray) m/z calcd for $C_{47}H_{44}N_2NaO_6Se$ (M + Na) 835.2262, found 835.2264.

3,6-Anhydro-5,7,8-tri-*O*-benzyl-2-deoxy-2-(2,2-diphenylhydrazino)-D-*erythro*-L-*gulo*-octono-1,4-lactone (8c) and 3,6-Anhydro-5,7,8-tri-*O*-benzyl-2-deoxy-2-(2,2-diphenylhydrazino)-D-*erythro*-L-*ido*-octono-1,4-lactone (8d). The general procedure for radical cyclization was followed, using **8b** (335.0 mg, 0.413 mmol) in PhMe (30 mL), Bu_3SnH (334 μL, 1.239 mmol) in PhMe (10 mL), and AIBN (30 mg, 0.183 mmol) in PhMe (10 mL). Flash chromatography of the residue over silica gel (1.6 × 27 cm), using 10% EtOAc−hexane, gave the chromatographically less polar product **8c** (or **8d**) (108.8 mg, 40%), and the more polar product **8d** (or **8c**) (105.5 mg, 38%) as a colorless oil. The chromatographically less polar diastereomer: $[\alpha]_D = +1.9$ (c 1.13, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3277, 1784 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 3.62 (dd, J = 10.7, 5.0 Hz, 1 H), 3.78−3.82 (m, 1 H), 3.88 (dd, J = 10.7, 2.0 Hz, 1 H), 3.99 (ddd, J = 8.6, 5.0, 2.0 Hz, 1 H), 4.09 (dd, J = 8.6, 3.3 Hz, 1 H), 4.32−4.38 (m, 2 H), 4.47−4.82 (m, 6 H), 4.93 (d, J = 4.9 Hz, 1 H), 5.18 (d, J = 4.9 Hz, 1 H), 7.07−7.40 (m, 25 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 62.96 (d′), 70.69 (t′), 72.51 (t′), 72.99 (t′), 73.68 (t′), 76.18 (d′), 80.10 (d′), 81.27 (d′), 81.38 (d′), 84.68 (d′), 121.19 (d′), 123.73 (d′), 127.77 (d′), 127.81 (d′), 127.93 (d′), 128.11 (d′), 128.33 (d′), 128.62 (d′), 128.83 (d′), 129.76 (d′), 137.79 (s′), 138.97 (s′), 139.17 (s′), 147.51 (s′), 174.24 (s′); exact mass (electrospray) m/z calcd for $C_{41}H_{40}N_2NaO_6$ (M + Na) 679.2784, found 679.2783.

The chromatographically more polar diastereomer: $[\alpha]_D = +47$ (c 1.19, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3289, 1791 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 3.72 (dd, J = 10.6, 5.2 Hz, 1 H), 3.78−3.83 (m, 1 H), 3.93 (dd, J = 10.6, 1.8 Hz, 1 H), 3.98−4.03 (m, 1 H), 4.16 (dd, J = 9.0, 3.3 Hz, 1 H), 4.36 (d, J = 3.1 Hz, 1 H), 4.41−4.66 (m, 6 H), 4.78−4.86 (m, 3 H), 7.00−7.41 (m, 25 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 60.76 (d′), 70.95 (t′), 72.48 (t′), 73.23 (t′), 73.86 (t′), 76.07 (d′), 77.49 (d′), 80.57 (d′), 81.53 (d′), 82.19 (d′), 120.90 (d′), 123.08 (d′), 127.74 (d′), 127.92 (d′), 128.03 (d′), 128.10 (d′), 128.38 (d′), 128.59 (d′), 128.74 (d′), 128.84 (d′), 129.46 (d′), 137.71 (s′), 139.00 (s′), 139.22 (s′), 147.53 (s′), 173.99 (s′); exact mass (electrospray) m/z calcd for $C_{41}H_{40}N_2NaO_6$ (M + Na) 679.2784, found 679.2781.

1,2-Di-*O*-acetyl-3,5,6-tri-*O*-methyl-α,*β*-D-glucofuranoses (21). $PhCO_2H$ (170.5 mg, 1.398 mmol) was added to a stirred solution of **20**[13] (1.0970 g, 4.187 mmol) in water (8.5 mL) and the mixture was refluxed for 6 h, cooled in an ice bath, and filtered. The insoluble material was washed with cold H_2O (2 × 1 mL), and the combined filtrates were evaporated. Water (6 mL) was added, and the solution was evaporated. The procedure was repeated with a further portion of water (6 mL), and water (25 mL) was added to the residue. The resulting solution was extracted with Et_2O (2 × 4 mL). Evaporation of the aqueous solution afforded a colorless syrup, which was dried under vacuum. Pyridine (9 mL) and Ac_2O (6 mL) were added to the dried residue, and the mixture was stirred for 14 h. Excess of pyridine and Ac_2O were evaporated under vacuum, and flash chromatography of the residue over silica gel (1.6 × 28 cm), using 30% EtOAc−hexane, gave **21** (1.0500 g, 82%) as a 67:33 mixture of α and β anomers [^1H NMR (300 MHz)]: $[\alpha]_D = +8.7$ (c 1.47, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1751 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 2.03 (s, 2 H), 2.05 (s, 1 H), 2.07 (br s, 3 H), 3.34−3.47 (m, 10 H), 3.52−3.69 (m, 2 H), 3.76 (d, J = 4.5 Hz, 0.33 H), 3.91−3.93 (m, 0.67 H), 4.13−4.22 (m, 1 H), 5.14 (br s, 0.33 H), 5.19 (dd, J = 4.5, 2.6 Hz, 0.67 H), 6.02 (s, 0.33 H), 6.29 (d, J = 4.4 Hz, 0.67 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 20.68 (q′), 20.93 (q′), 21.03 (q′), 21.28 (q′), 58.07 (q′), 58.27 (q′), 59.39 (q′), 72.26 (t′), 75.69 (d′), 77.48 (d′), 77.53 (d′), 78.81 (d′), 78.97 (d′), 81.91 (d′), 82.34 (d′), 83.21 (d′), 95.03 (d′), 99.87 (d′), 169.68 (s′), 169.81 (s′), 169.93 (s′); exact mass (electrospray) m/z calcd for $C_{13}H_{22}NaO_8$ (M + Na) 329.1212, found 329.1211.

Phenyl 2-*O*-Acetyl-3,5,6-tri-*O*-methyl-1-seleno-*β*-D-glucofuranoside (22). $BF_3{\cdot}Et_2O$ (404 μL, 3.2869 mmol) was added dropwise to a stirred and cooled (0 °C) solution of **21** (1.0701 g, 3.497 mmol) and PhSeH (557 μL, 5.2451 mmol) in CH_2Cl_2 (35 mL). Stirring was continued for 1.5 h at 0 °C, and then saturated aqueous $NaHCO_3$ (5 mL) was added. The organic phase was washed with water (2 × 10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 20% EtOAc−hexane, gave **22** (1.2015 g, 85%) as a colorless oil: $[\alpha]_D = -147.7$ (*c* 1.33, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1748 cm^{-1}; ^1H NMR (CD_2Cl_2, 360 MHz) δ 2.04 (s, 3 H), 3.36 (s, 3 H), 3.42 (s, 3 H), 3.47−3.51 [m, including s (3 H) at δ 3.50, 4 H in all], 3.67−3.73 (m, 2 H), 3.83 (d, J = 4.0 Hz, 1 H), 4.12 (dd, J = 9.5, 4.0 Hz, 1 H), 5.50 (s, 1 H), 5.57 (s, 1 H), 7.27−7.32 (m, 3 H), 7.57−7.63 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 21.04 (q′), 58.07 (q′), 58.20 (q′), 59.45 (q′), 72.14 (t′), 77.41 (d′), 80.88 (d′), 81.69 (d′), 82.72 (d′), 87.38 (d′), 127.75 (d′), 129.41 (d′), 131.78 (s′), 133.90 (d′), 170.02 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{17}H_{24}NaO_6Se$ (M + Na) 427.0636, found 427.0634.

Phenyl 3,5,6-Tri-*O*-methyl-1-seleno-*β*-D-glucofuranoside (9a). K_2CO_3 (385.3 mg, 2.788 mmol) was added to a stirred solution of **22** (1.1235 g, 2.788 mmol) in 1:1 THF−MeOH (20 mL) and the mixture was stirred vigorously for 15 min, filtered through a pad (1 cm × 2 mm) of silica gel, and evaporated. Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 40% EtOAc−hexane, gave **9a** (0.9641 g, 96%) as a colorless oil: $[\alpha]_D = -196.0$ (*c* 1.30, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3410 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 2.88 (d, J = 4.2 Hz, 1 H), 3.35 (s, 3 H), 3.42 (s, 3 H), 3.44 (s, 3 H), 3.47−3.53 (m, 1 H), 3.68−3.77 (m, 3 H), 4.19 (dd, J = 9.2, 4.2 Hz, 1 H), 4.58−4.63 (m, 1 H), 5.50 (br s, 1 H), 7.25−7.32 (m, 3 H), 7.56−7.63 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 58.05 (q′), 58.09 (q′), 59.40 (q′), 72.31 (t′), 77.66 (d′), 79.74 (d′), 81.26 (d′), 84.91 (d′), 90.31 (d′), 127.53 (d′), 129.40 (d′), 132.09 (s′), 133.57 (d′); exact mass (electrospray) *m*/*z* calcd for $C_{15}H_{22}NaO_5Se$ (M + Na) 385.0530, found 385.0532.

Phenyl 2-*O*-(Diphenylhydrazono)acetyl-3,5,6-tri-*O*-methyl-1-seleno-*β*-D-glucofuranoside (9b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (714.0 mg, 2.975 mmol), **9a** (895.0 mg, 2.479 mmol), DCC (675.2 mg, 3.273 mmol), and DMAP (36.3 mg, 0.298 mmol) in CH_2Cl_2 (25 mL). Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 30% EtOAc−hexane, gave **9b** (1.5001 g, ca. 103%) as a partially crystalline light brown mass which contained a small amount [<10 mol % by ^1H NMR (400 MHz)] of chromatographically inseparable impurities. An analytical sample was prepared by swirling the material in 40% EtOAc−hexane (15 mL) and evaporating the clear supernatant. The resulting **9b**: $[\alpha]_D = -116.4$ (*c* 1.12, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1734, 1708 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 3.36 (s, 3 H), 3.42 (s, 3 H), 3.48−3.55 [m, including s (3 H) at δ 3.54, 4 H in all], 3.68−3.75 (m, 2 H), 3.90 (d, J = 4.0 Hz, 1 H) 4.14 (dd, J = 9.1, 4.0 Hz, 1 H), 5.62 (s, 1 H), 5.65 (s, 1 H), 6.43 (s, 1 H), 7.15−7.65 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 58.12 (q′), 58.27 (q′), 59.46 (q′), 72.23 (t′), 77.44 (d′), 81.02 (d′), 81.76 (d′), 82.83 (d′), 87.43 (d′), 123.38 (d′), 127.77 (d′), 129.43 (d′), 130.40 (d′), 131.79 (s′), 133.98 (d′), 163.48 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{29}H_{32}N_2NaO_6Se$ (M + Na) 607.1323, found 607.1323.

3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octono-1,4-lactone (9c) and 3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-5,7,8-tri-*O*-methyl-D-*erythro*-L-*gulo*-octono-1,4-lactone (9d). The general procedure for radical cyclization was followed, using **9b** [containing 3% impurities (^1H NMR, 400 MHz)] (392.6 mg, 0.651 mmol) in PhMe (45 mL), Bu_3SnH (544 μL, 2.020 mmol) in PhMe (10 mL), and AIBN (30 mg, 0.182 mmol) in PhMe (10 mL). Flash chromatography of the residue over silica gel (1.6 × 30 cm), using 15% EtOAc−hexane, gave **9c** (117.2 mg, 42%) as a colorless oil, and further elution, using 30% EtOAc−hexane, gave **9d** (113.3 mg, 40%) as a crystalline solid. Compound **9c**: $[\alpha]_D = +14.7$ (*c* 1.13, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3265, 1783 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 3.31 (s, 3 H), 3.37−3.41 [m, including s (3 H) at δ 3.40, 4 H in all), 3.47 (s, 3 H), 3.49−3.55 (m, 1 H), 3.65 (dd, J = 10.7, 2.1 Hz, 1 H), 3.74−3.78 (m, 1 H), 3.85 (dd, J = 8.8, 3.4 Hz, 1 H), 3.98 (d, J = 3.4 Hz, 1 H), 4.29 (d, J = 2.0 Hz, 1 H), 4.84 (d, J = 4.9 Hz, 1 H), 5.12 (d, J = 4.9 Hz, 1 H), 7.05−7.37 (m, 10 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 58.13 (q′), 58.47 (q′), 59.4 (q′), 62.90 (d′), 72.36 (t′), 77.31 (d′), 79.74 (d′), 81.37 (d′), 83.04 (d′), 84.40 (d′), 121.23 (d′), 123.73 (d′), 129.74 (d′), 147.55 (s′), 174.36 (s′); exact mass *m*/*z* calcd for $C_{23}H_{28}N_2O_6$ 428.1947, found 428.1951. Compound **9d**: mp 141−142 °C; $[\alpha]_D = +59.7$ (*c* 1.16, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1790 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 3.39 (s, 3 H), 3.41 (s, 3 H), 3.44−3.49 [m, including s (3 H) at δ 3.45, 4 H in all], 3.51−3.55 (m, 1 H), 3.70 (dd, J = 10.5, 1.8 Hz, 1 H), 3.80 (t, J = 4.9 Hz, 1 H), 3.92 (dd, J = 9.0, 3.4 Hz, 1 H), 4.01 (d, J = 3.4 Hz, 1 H), 4.52 (dd, J = 5.2, 3.8 Hz, 1 H), 4.80−4.83 (m, 1 H), 7.00−7.34 (m, 10 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 58.15 (q′), 58.70 (q′), 59.54 (q′), 60.78 (d′), 72.71 (t′), 77.23 (d′), 77.44 (d′), 80.37 (d′), 81.99 (d′), 83.26 (d′), 120.97 (d′), 123.14 (d′), 129.48 (d′). 147.61 (s′), 174.05 (s′); exact mass *m*/*z* calcd for $C_{23}H_{28}N_2O$ 428.1947, found 428.1947. Irradiation of the **H**CNHNPh$_2$ ^1H NMR signal (for **9d**) caused an NOE of 13.3% in the signal for the C(1)**H** of the furanose ring, and 4.4% for the C(2)**H**; in the case of **9c**, the corresponding values were 4.9% and 1.2%, respectively. On this basis, we assigned the stereochemistries as shown, and our assignment was confirmed by an X-ray structure of **9d**. Crystal data: monoclinic space group $P2_1$ with a = 9.2836(5) Å, b = 8.5947(4) Å, c = 13.8264(6) Å, β = 91.089(5)°, V = 1103.01(9) Å^3, Z = 2, d_{calcd} = 1.290 g cm^{-3}, μ (Cu Kα [λ = 1.541 78 Å]) = 0.772 mm^{-1}; 3347 reflections measured (2913 unique; 2749 with $F_o^2 \geq 2\sigma(F_o^2)$); $R_1(F)$ = 0.0327 ($F_o^2 \geq 2\sigma(F_o^2)$), $wR_2(F^2)$ = 0.0868 (all data), GOF = 1.055 (all data).

Phenyl 2,3-*O*-Isopropylidene-1-seleno-*β*-D-ribofuranoside (10a). *p*-$MeC_6H_4SO_3H{\cdot}H_2O$ (9.2 mg, 0.048 mmol) was added to a stirred solution of phenyl 1-seleno-*β*-D-ribofuranoside (see above) (140.0 mg, 0.484 mmol) in acetone (5 mL). Stirring was continued for 5 h, $NaHCO_3$ (12.2 mg, 0.145 mmol) was then added. Stirring was continued for another 0.5 h, and the mixture was then evaporated. Flash chromatography of the residue over silica gel (1.0 × 20 cm), using 30% EtOAc−hexane, gave **10a** (148.3 mg, 92%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3462 cm^{-1}; ^1H NMR (CD_2Cl_2, 360 MHz) δ 1.32 (s, 3 H), 1.48 (s, 3 H), 2.10 (dd, J = 7.0, 6.3 Hz, 1 H), 3.69−3.81 (m, 2 H), 4.30−4.33 (m, 1 H), 4.76 (dd, J = 6.1, 1.8 Hz, 1 H), 4.88 (dd, J = 6.1, 2.1 Hz, 1 H), 5.82 (d, J = 2.1 Hz, 1 H), 7.28−7.40 (m, 3 H), 7.59−7.68 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 25.43 (q′), 27.08 (q′), 63.10 (t′), 82.17 (d′), 87.13 (d′), 88.82 (d′), 88.94 (d′), 113.70 (s′), 128.34 (d′), 129.37 (s′), 129.65 (d′), 134.45 (d′); exact mass *m*/*z* calcd for $C_{14}H_{18}O_4Se$ 330.0370, found 330.0364.

Phenyl 5-*O*-(Diphenylhydrazono)acetyl-2,3-*O*-isopropylidene-1-seleno-*β*-D-ribofuranoside (10b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (121.0 mg, 0.504 mmol), alcohol **10a** (148.3 mg, 0.449 mmol), DCC (114.0 mg, 0.550 mmol), and DMAP (6.1 mg, 0.050 mmol) in CH_2Cl_2 (2 mL). Flash chromatography of the residue over silica gel (1.0 × 20 cm), using 20% EtOAc−hexane, gave **10b** (230.0 mg, 92%) as a pale yellow oil: FTIR (CH_2Cl_2 cast) 1731, 1706 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.37 (s, 3 H), 1.45 (s, 3 H), 4.39 (dd, J = 10.0, 4.7 Hz, 1 H), 4.46−4.54 (m, 2 H), 4.81 (dd, J = 6.0, 1.6 Hz, 1 H), 4.96 (dd, J = 6.0, 1.8 Hz, 1 H), 5.82 (d, J = 1.8 Hz, 1 H), 6.56 (s, 1 H), 7.20−7.64 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 25.50 (q′), 27.04 (q′), 63.99 (t′), 82.67 (d′), 85.40 (d′), 87.16 (d′), 88.38 (d′), 113.86 (s′), 123.95 (d′), 126.59 (d′), 128.18 (d′), 129.45 (d′), 129.50 (d′), 130.37 (d′), 134.62 (d′), 164.17 (s′); exact mass *m*/*z* calcd for $C_{28}H_{28}N_2O_5Se$ 552.1163, found 552.1157.

3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-4,5-*O*-isopropylidene-D-*glycero*-D-*allo*-heptono-1,7-lactone and 3,6-Anhydro-2-deoxy-2-(2,2-diphenylhydrazino)-4,5-*O*-isopropylidene-D-*glycero*-D-*altro*-heptono-1,7-lactone (10c,d). The general procedure for radical cyclization was followed, using **10b** (160.0 mg, 0.290 mmol) in PhMe (20 mL), Bu_3SnH (120 μL, 0.4456 mmol) in PhMe (5 mL), and AIBN (10 mg, 0.061 mmol) in PhMe (5 mL). Flash chromatography of the residue over silica gel (1.0 × 20 cm), using 20% EtOAc−

hexane, gave **10c**,**d** (73.9 mg, 64%) as a crystalline solid which was a chromatographically inseparable mixture of two isomers in a 1.5:1 ratio (^{1}H NMR, 400 MHz): FTIR (CH_2Cl_2 cast) 3292, 1736 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.29 (s, 1.2 H), 1.37 (s, 1.8 H), 1.46 (s, 1.2 H), 1.48 (s, 1.8 H), 3.86 (d, J = 2.4 Hz, 0.6 H), 3.98 (dd, J = 4.9, 2.2 Hz, 0.4 H), 4.15−4.46 (m, 3.6 H), 4.60 (d, J = 5.7 Hz, 0.4 H), 4.75−4.97 (m, 3 H), 7.03−7.37 (m, 10 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 24.45 (q′), 24.52 (q′), 26.09 (q′), 26.16 (q′), 64.22 (d′), 66.18 (d′), 70.64 (t′), 72.59 (t′), 80.75 (d′), 81.25 (d′), 81.55 (d′), 81.98 (d′), 82.61 (d′), 82.83 (d′), 83.49 (d′), 83.58 (d′), 112.79 (s′), 113.03 (s′), 121.05 (d′), 123.57 (d′), 129.73 (d′), 147.65 (s′), 170.83 (s′), 172.31 (s′); exact mass m/z calcd for $C_{22}H_{24}N_2O_5$ 396.1685, found 396.1686.

3-*O*-Benzyl-6-bromo-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (11a). Ph_3P (642.0 mg, 2.448 mmol) was added to a stirred and cooled (0 °C) solution of **23**[14] (379.4 mg, 1.224 mmol), in pyridine (20 mL), and then CBr_4 (405.9 mg, 1.224 mmol) was added in several portions at 0 °C. After the addition, the mixture was heated to 60 °C for 10 min. MeOH (5 mL) was added to destroy any excess of reagents, and the mixture was evaporated. Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 20% EtOAc−hexane, gave **11a** (402.8 mg, 88%) as a colorless oil: $[\alpha]_D$ = −41.8 (c 1.25, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3482 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 1.31 (br s, 3 H), 1.46 (br s, 3 H), 2.38 (d, J = 5.9, 1 H), 3.58 (dd, J = 10.5, 5.7 Hz, 1 H), 3.71 (dd, J = 10.5, 2.7 Hz, 1 H), 4.03−4.14 (m, 3 H), 4.58 (d, J = 11.7 Hz, 1 H), 4.64 (d, J = 3.7 Hz, 1 H), 4.72 (d, J = 10.7 Hz, 1 H), 5.89 (d, J = 3.7 Hz, 1 H), 7.32−7.40 (m, 5 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 26.46 (q′), 27.00 (q′), 38.83 (t′), 68.47 (d′), 72.56 (t′), 81.13 (d′), 81.98 (d′), 82.58 (d′), 105.62 (d′), 112.29 (s′), 128.24 (d′), 128.45 (d′), 128.92 (d′), 137.85 (s′); exact mass (electrospray) m/z calcd for $C_{16}H_{21}BrNaO_5$ (M + Na) 395.0470, found 395.0475.

3-*O*-Benzyl-6-bromo-6-deoxy-5-*O*-(diphenylhydrazono)-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (11b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (303.3 mg, 1.264 mmol), **11a** (392.8 mg, 1.053 mmol), DCC (286.8 mg, 1.390 mmol), and DMAP (20.0 mg, 0.164 mmol) in CH_2Cl_2 (10 mL). Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 10% EtOAc−hexane, gave **11b** (601.4 mg, 96%) as a pale yellow oil: $[\alpha]_D$ = −38.1 (c 2.0, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1732, 1708 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 360 MHz) δ 1.33 (s, 3 H), 1.50 (s, 3 H), 3.75 (dd, J = 11.5, 4.2 Hz, 1 H), 3.94 (dd, J = 11.5, 2.7 Hz, 1 H), 4.01 (d, J = 3.1 Hz, 1 H), 4.45−4.48 (m, 2 H), 4.60−4.66 (m, 2 H), 5.35−5.39 (m, 1 H), 5.90 (d, J = 3.6 Hz, 1 H), 6.43 (s, 1 H), 7.16−7.52 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 26.54 (q′), 27.09 (q′), 34.33 (t′), 69.27 (d′), 72.53 (t′), 79.35 (d′), 81.21 (d′), 82.38 (d′), 105.68 (d′), 112.55 (s′), 123.60 (d′), 128.32 (d′), 128.49 (d′), 128.82 (d′), 130.40 (d′), 137.60 (s′), 163.30 (s′); exact mass m/z calcd for $C_{30}H_{31}N_2O_6Br$ 596.1345, found 596.1345.

3-*O*-Benzyl-6-deoxy-5-*O*-(diphenylhydrazono)acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (11e), 3-*O*-Benzyl-6,7-dideoxy-7-(2,2-diphenylhydrazino)-1,2-*O*-isopropylidene-L-*glycero*-α-D-glucofuranurono-8,5-lactone (11c), and 3-*O*-Benzyl-6,7-dideoxy-7-(2,2-diphenylhydrazino)-1,2-*O*-isopropylidene-D-*glycero*-α-D-glucofuranurono-8,5-lactone (11d). The general procedure for radical cyclization was followed, using **11b** (303.0 mg, 0.509 mmol) in PhMe (30 mL), Bu_3SnH (274 μL, 1.0185 mmol) in PhMe (10 mL), and AIBN (10 mg, 0.061 mmol) in PhMe (10 mL). Flash chromatography of the residue over silica gel (1.6 × 29 cm), using 10% EtOAc−hexane, gave fractions 1, 2, and 3, which all contained a small amount of tributyltin residues (^{1}H NMR, 400 MHz). Each fraction was further purified by flash chromatography over silica gel (1.0 × 20 cm), using 10% EtOAc−hexane. Fraction 1 gave a 1:1.7 mixture (51.4 mg) of the starting material and the simple reduction product **11e** (12% as judged by ^{1}H NMR measurements); fraction 2 gave the chromatographically less polar lactone **11c** (or **11d**) (71.0 mg, 27%) as a colorless oil; fraction 3 gave the chromatographically more polar lactone **11d** (or **11c**) (81.3 mg, 31%) as a colorless oil.

The fraction containing **11e**: FTIR (CH_2Cl_2 cast) 1730, 1704 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.29−1.34 (m, 3 H), 1.40 (d, J = 6.3 Hz, 2 H), 1.49 (s, 3 H), 3.72−3.76 (m, 0.40 H), 3.92−4.01 (m, 1.43 H), 4.18 (dd, J = 8.4, 3.2 Hz, 0.65 H), 4.43−4.47 (m, 1.42 H), 4.59−4.65 (m, 2.12 H), 5.24−5.38 (m, 1 H), 5.90−5.91 (m, 1 H), 6.42 (s, 0.65 H), 6.46 (s, 0.35 H), 7.15−7.52 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 17.90 (q′), 26.34 (q′), 26.51 (q′), 26.90 (q′), 27.08 (q′), 34.33 (t′), 68.21 (d′), 69.23 (d′), 72.37 (t′), 72.51 (t′), 79.32 (d′), 81.18 (d′), 81.38 (d′), 82.34 (d′), 82.44 (d′), 105.56 (d′), 105.66 (d′), 111.99 (s′), 112.53 (s′), 122.81 (d′), 123.58 (d′), 124.77 (d′), 126.44 (d′), 128.18 (d′), 128.31 (d′), 128.40 (d′), 128.48 (d′), 128.75 (d′), 130.36 (d′), 137.58 (s′), 137.82 (s′), 142.61 (s′), 163.29 (s′), 163.47 (s′); exact mass (electrospray) m/z calcd for $C_{30}H_{32}N_2NaO_6$ (M + Na) 539.2158, found 539.2153.

The chromatographically less polar lactone: $[\alpha]_D$ = −27.3 (c 1.19, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3278, 1782 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.34 (s, 3 H), 1.51 (s, 3 H), 2.32−2.40 (m, 1 H), 2.65−2.71 (m, 1 H), 3.92−3.97 (m, 1 H), 4.11 (d, J = 3.2 Hz, 1 H), 4.32 (dd, J = 7.4, 3.2 Hz, 1 H), 4.56−4.73 (m, 5 H), 5.92 (d, J = 3.7 Hz, 1 H), 7.02−7.39 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 26.38 (q′), 27.03 (q′), 33.71 (t′), 56.54 (d′), 72.66 (t′), 74.50 (d′), 81.77 (d′), 82.03 (d′), 82.69 (d′), 105.68 (d′), 112.44 (s′), 120.83 (d′), 123.19 (d′), 128.10 (d′), 128.31 (d′), 128.81 (d′), 129.63 (d′), 137.86 (s′), 147.38 (s′), 175.09 (s′); exact mass (electrospray) m/z calcd for $C_{30}H_{32}N_2NaO_6$ (M + Na) 539.2158, found 539.2160.

The chromatographically more polar lactone: $[\alpha]_D$ = −16.2 (c 1.25, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3282, 1779 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.31 (s, 3 H), 1.45 (s, 3 H), 2.42−2.49 (m, 1 H), 2.59−2.65 (m, 1 H), 3.94−3.99 (m, 1 H), 4.05 (d, J = 3.5 Hz, 1 H), 4.27 (dd, J = 5.5, 3.4 Hz, 1 H), 4.53−4.56 (m, 2 H), 4.64−4.70 (m, 2 H), 4.93−4.99 (m, 1 H), 5.89 (d, J = 3.7 Hz, 1 H), 7.02−7.39 (m, 15 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 26.36 (q′), 26.97 (q′), 31.12 (t′), 55.96 (d′), 72.62 (t′), 76.54 (d′), 81.20 (d′), 82.28 (d′), 82.67 (d′), 105.72 (d′), 112.39 (s′), 120.89 (d′), 123.27 (d′), 128.13 (d′), 128.36 (d′), 128.86 (d′), 129.63 (d′), 137.76 (s′), 147.72 (s′), 175.42 (s′); exact mass (electrospray) m/z calcd for $C_{30}H_{32}N_2NaO_6$ (M + Na) 539.2158, found, 539.2153.

1,6-Anhydro-2-*O*-benzoyl-4-deoxy-3-*O*-(diphenylhydrazono)acetyl-4-iodo-β-D-glucopyranose (12b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (674.3 mg, 2.810 mmol), **12a**[15] (880.3 mg, 2.341 mmol), DCC (637.7 mg, 3.091 mmol), and DMAP (34.3 mg, 0.281 mmol) in CH_2Cl_2 (20 mL). Flash chromatography of the residue over silica gel (2.6 × 28 cm), using first 10% EtOAc−hexane (300 mL) and then 20% EtOAc−hexane, gave **12b** (1.2769 g, 91%) as a pale yellow oil: $[\alpha]_D$ = −25.2 (c 1.0, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1722 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 3.74 (dd, J = 7.7, 5.6 Hz, 1 H), 4.29 (br s, 1 H), 4.33−4.36 (m, 1 H), 4.83 (d, J = 5.1 Hz, 1 H), 4.92−4.96 (m, 1 H), 5.40−5.44 (m, 1 H), 5.64 (br s, 1 H), 6.49 (s, 1 H), 7.19−7.67 (m, 13 H), 8.18−8.26 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 21.34 (d′), 67.63 (t′), 69.44 (d′), 73.69 (d′), 78.11 (d′), 99.53 (d′), 122.63 (d′), 128.83 (d′), 129.58 (s′), 130.44 (d′), 133.83 (d′), 162.99 (s′), 165.44 (s′); exact mass m/z calcd for $C_{27}H_{23}N_2O_6I$ 598.0601, found 598.0610.

1,6-Anhydro-2-*O*-benzyl-4-deoxy-3-*O*-(diphenylhydrazono)acetyl-β-D-*xylo*-hexopyranose (12e), 1,6-Anhydro-2-*O*-benzoyl-4-deoxy-4-*C*-[(*R*)-(2,2-diphenylhydrazino)carboxymethyl)]-β-D-galactopyranose 2′,3-Lactone (12d), and 1,6-Anhydro-2-*O*-benzoyl-4-deoxy-4-*C*-[(*S*)-α-(2,2-diphenylhydrazino)carboxymethyl)]-β-D-galactopyranose 2′,3-Lactone (12c). The general procedure for radical cyclization was followed, using **12b** (268.0 mg, 0.448 mmol) in PhMe (30 mL), Bu_3SnH (181 μL, 0.6723 mmol) in PhMe (10 mL), and AIBN (5 mg, 0.031 mmol) in PhMe (10 mL). Refluxing was continued for 7 h after the addition. Flash chromatography of the residue over silica gel (1.6 × 30 cm), using 10% EtOAc−hexane, gave fractions 1, 2, and 3, which all contained a small amount of tributyltin residues (^{1}H NMR). Fraction 1 was further purified by flash chromatography over silica gel (1.0 × 20 cm), using 10% EtOAc−hexane, and gave **12c** (73.6 mg, 34%) as a colorless oil. Fraction 2 was purified similarly, using 20% EtOAc−hexane, and gave **12e** (53.2 mg, 25%) as a

crystalline solid. Fraction 3 was purified similarly, using 20% EtOAc−hexane, and gave **12d** (48.6 mg, 23%) as a colorless oil.

Compound **12c**: $[\alpha]_D = +87.8$ (*c* 1.0, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1782, 1725 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 3.32−3.37 (m, 1 H), 3.84 (dd, $J = 8.9$, 5.4 Hz, 1 H), 4.01 (d, $J = 8.9$ Hz, 1 H), 4.11 (dd, $J = 8.1$, 1.4 Hz, 1 H), 4.42 (br s, 1 H), 4.47−4.49 (m, 1 H), 4.58 (t, $J = 5.2$ Hz, 1 H), 5.11−5.13 (m, 1 H), 5.56−5.58 (m, 1 H), 7.08−7.17 (m, 6 H), 7.32−7.66 (m, 7 H), 8.03−8.11 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 38.53 (d′), 57.89 (d′), 65.39 (t′), 67.59 (d′), 71.57 (d′), 75.04 (d′), 99.40 (d′), 121.22 (d′), 124.19 (d′), 128.92 (d′), 129.50 (s′), 129.95 (d′), 130.13 (d′), 134.02 (d′), 147.61 (s′), 165.35 (s′), 173.84 (s′); exact mass *m*/*z* calcd for $C_{27}H_{24}N_2O_6$ 472.1634, found 472.1629. Irradiation of the C**H**NHNPh$_2$ ^1H NMR signal caused an NOE of 7% in the pyranose C(3)**H** signal; the corresponding value for **12d** was 0%.

Compound **12e**: mp 169−171 °C; $[\alpha]_D = +126$ (*c* 1.0, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1722 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.85−1.89 (m, 1 H), 2.50−2.56 (m, 1 H), 3.79−3.82 (m, 1 H), 4.33 (d, $J = 6.9$ Hz, 1 H), 4.62−4.64 (m, 1 H), 4.88 (d, $J = 1.2$ Hz, 1 H), 5.15−5.17 (m, 1 H), 5.55 (br s, 1 H), 6.50 (s, 1 H), 7.18−7.64 (m, 13 H), 8.05−8.11 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ 31.57 (t′), 67.63 (t′), 67.84 (d′), 69.86 (d′), 71.66 (d′), 99.36 (d′), 123.82 (d′), 126.57 (d′), 128.82 (d′), 130.10 (d′), 130.39 (d′), 133.73 (d′), 163.70 (s′), 165.36 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{27}H_{24}N_2NaO_6$ (M + Na) 495.1532, found 495.1537.

Compound **12d**: $[\alpha] = +42.1$ (*c* 0.73, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3280, 1783, 1725 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 3.23−3.26 (m, 1 H), 3.58 (d, $J = 2.2$ Hz, 1 H), 3.60−3.66 (m, 2 H), 4.38 (d, $J = 2.2$ Hz, 1 H), 4.47−4.49 (m, 1 H), 4.88−4.94 (m, 1 H), 5.17 (br s, 1 H), 5.58−5.59 (m, 1 H), 7.05−7.68 (m, 13 H), 8.02−8.08 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 38.94 (d′), 59.35 (d′), 64.88 (t′), 68.32 (d′), 71.96 (d′), 77.28 (d′), 99.56 (d′), 120.98 (d′), 123.86 (d′), 128.92 (d′), 129.00 (s′), 129.90 (d′), 130.17 (d′), 134.0 (d′), 147.30 (s′), 165.40 (s′), 172.79 (s′); exact mass *m*/*z* calcd for $C_{27}H_{24}N_2O_6$ 472.1634, found 472.1635.

Phenyl 3,4,6-Tri-*O*-benzyl-1-seleno-α-D-mannopyranoside (13a). K_2CO_3 (153.0 mg, 1.107 mmol) was added to a stirred solution of phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-seleno-α-d-mannopyranoside[16] (350.0 mg, 0.555 mmol) in 1:1 THF−MeOH (10 mL), and the mixture was stirred vigorously for 30 min, filtered through a pad (1 cm × 2 mm) of silica gel, and evaporated. Flash chromatography of the residue over silica gel (1.6 × 27 cm), using 20% EtOAc−hexane, gave **13a** (326.9 mg, 90%) as a colorless oil: $[\alpha]_d = +158.6$ (*c* 1.2, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3428 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 2.87 (br, 1 H), 3.70 (dd, $J = 10.8$, 1.9 Hz, 1 H); 3.82 (dd, $J = 10.8$, 4.5 Hz, 1 H), 3.89 (dd, $J = 9.1$, 3.2 Hz, 1 H), 3.94−3.99 (m, 1 H), 4.19−4.23 (m, 1 H), 4.37 (dd, $J = 3.0$, 1.5 Hz, 1 H), 4.50 (d, $J = 11.8$, 1 H), 4.59−4.63 (m, 2 H), 4.73 (dd, $J = 17.1$, 11.5 Hz, 1 H), 4.89 (d, $J = 10.9$ Hz, 1 H), 5.90 (d, $J = 1.3$ Hz, 1 H), 7.25−7.45 (m, 18 H), 7.62−7.66 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 69.24 (t′), 70.68 (d′), 72.28 (t′), 73.63 (t′), 74.39 (d′), 74.71 (d′), 75.41 (t′), 80.94 (d′), 85.88 (d′), 127.93 (d′), 127.96 (d′), 128.11 (d′), 128.26 (d′), 128.33 (d′), 128.36 (d′), 128.63 (d′), 128.67 (d′), 128.87 (d′), 129.51 (d′), 129.66 (s′), 134.41 (d′), 138.25 (s′), 138.69 (s′), 138.94 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{33}H_{34}NaO_5Se$ (M + Na) 613.1469, found 613.1477.

Phenyl 3,4,6-Tri-*O*-benzyl-2-*O*-(diphenylhydrazono)-acetyl-1-seleno-α-D-mannopyranoside (13b). The general procedure for coupling alcohols with reagent **2** was followed, using **2** (156.5 mg, 0.652 mmol), alcohol **13a** (310.0 mg, 0.526 mmol), DCC (148.0 mg, 0.717 mmol), and DMAP (15.0 mg, 0.123 mmol) in CH_2Cl_2 (10 mL). Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 10% EtOAc−hexane, gave **13b** (396.1 mg, 92%) as a pale yellow oil: $[\alpha]_D = +61.5$ (*c* 0.96, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1728, 1705 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 3.71 (dd, $J = 10.9$, 1.9 Hz, 1 H), 3.81 (dd, $J = 10.9$, 4.9 Hz, 1 H), 3.94−4.00 (m, 2 H), 4.18−4.26 (m, 1 H), 4.49 (d, $J = 12.1$ Hz, 1 H), 4.55−4.61 (m, 3 H), 4.77 (d, $J = 11.3$ Hz, 1 H), 4.89 (d, $J = 10.9$ Hz, 1 H), 5.8 (t, $J = 2.0$ Hz, 1 H), 5.84 (d, $J = 1.3$ Hz, 1 H), 6.56 (s, 1 H), 7.20−7.48 (m, 28 H), 7.61−7.65 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 69.34 (t′), 71.51 (d′), 72.14 (t′), 73.59 (t′), 74.83 (d′), 75.01 (d′), 75.51 (t′), 79.28 (d′), 84.19 (d′), 123.48 (d′), 127.86 (d′), 127.96 (d′), 128.10 (d′), 128.18 (d′), 128.26 (d′), 128.62 (d′), 128.66 (d′), 128.75 (d′), 129.56 (d′), 129.64 (s′), 130.36 (d′), 134.43 (d′), 138.20 (s′), 138.75 (s′), 138.92 (s′), 163.85 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{47}H_{44}N_2NaO_6Se$ (M + Na) 835.2262, found 835.2256.

3,6-Anhydro-1-*O*-[(1,1-dimethylethyl)diphenylsilyl]-2-deoxy-2-(2,2-diphenylhydrazino)-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octitol (29a). A solution of **9c** (124.2 mg, 0.291 mmol) in THF (0.5 mL, plus 2 × 0.5 mL as a rinse) was added to a stirred and cooled (0 °C) suspension of $LiAlH_4$ (24.3 mg, 0.639 mmol) in THF (1.5 mL). Stirring was continued for 30 min at 0 °C, and then for 1 h after removal of the ice bath. MeOH (0.2 mL) was added carefully to quench the reaction, followed by saturated $NaHCO_3$ (0.1 mL). The mixture was stirred for 15 min, filtered through a pad (1 cm × 2 mm) of Celite, using EtOAc, and evaporated, to give the expected diol.

t-BuPh_2SiCl (77 μL, 0.2960 mmol) was added dropwise to a stirred solution of the above diol and imidazole (37.0 mg, 0.543 mmol) in CH_2Cl_2 (3 mL). Stirring was continued for 3.5 h, and the solvent was evaporated. Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 20% EtOAc−hexane, gave **29a** (154.0 mg, 79%) as a colorless oil: $[\alpha]_D = +3.5$ (*c* 1.18, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3444 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.08 (s, 9 H), 3.43 (s, 3 H), 3.45 (s, 3 H), 3.48 (s, 3 H), 3.52−3.67 (m, 5 H), 3.75−3.85 (m, 2 H), 3.94−3.98 (m, 2 H), 4.12 (dd, $J = 9.1$, 3.3 Hz, 1 H), 4.44 (br s, 1 H), 4.79 (s, 1 H), 6.95−7.05 (m, 6 H), 7.21−7.66 (m, 14 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 19.20 (s′), 26.97 (q′), 58.13 (q′), 58.20 (q′), 59.53 (q′), 59.71 (d′), 64.20 (t′), 73.17 (t′), 74.16 (d′), 77.57 (d′), 79.21 (d′), 83.70 (d′), 86.02 (d′), 120.49 (d′), 122.53 (d′), 128.27 (d′), 129.27 (d′), 130.41 (d′), 130.47 (d′), 132.45 (s′), 132.64 (s′), 135.87 (d′), 135.98 (d′), 148.20 (s′); exact mass *m*/*z* calcd for $C_{39}H_{50}N_2O_6Si$ 670.3438, found 670.3434.

3,6-Anhydro-2-benzamido-4-*O*-benzoyl-1-*O*-[(1,1-dimethylethyl)diphenylsilyl]-2-deoxy-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octitol (30a). Camphorsulfonic acid (72.4 mg, 0.312 mmol) and then 10% Pd−C (30.0 mg) were added to a solution of **29a** (95.0 mg, 0.142 mmol) in a mixture of EtOAc (2.4 mL) and MeOH (0.6 mL). The mixture was shaken under H_2 (50 psi) for 2 h (Parr shaker) and then filtered through a pad of Celite. The pad was washed with EtOAc (3 × 5 mL), and the combined filtrates were evaporated, and stored under oil-pump vacuum for 4 h. CH_2Cl_2 (5 mL), Et_3N (197 μL, 1.4170 mmol), PhCOCl (131 μL, 1.1336 mmol), and DMAP (15.0 mg, 0.123 mmol) were added in that order to a stirred solution of the resulting yellow foam. Stirring was continued for 24 h, and the solvent was evaporated. Flash chromatography of the residue over silica gel (1.6 × 28 cm), using 30% EtOAc−hexane, gave **30a** (77.0 mg, 76%) as a pale yellow oil: $[\alpha]_D = -7.5$ (*c* 1.06, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3438, 1723, 1667 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.07 (s, 9 H), 3.39 (s, 3 H), 3.43 (s, 3 H), 3.56 (dd, $J = 10.5$, 4.4 Hz, 1 H), 3.59 (s, 3 H), 3.63 (ddd, $J = 9.3$, 4.4, 1.8 Hz, 1 H), 3.74−3.79 (m, 3 H), 3.93 (d, $J = 3.4$ Hz, 1 H), 4.19 (dd, $J = 9.3$, 3.4 Hz, 1 H), 4.52−4.60 (m, 1 H), 4.79−4.82 (m, 1 H), 5.64 (dd, $J = 4.0$, 0.6 Hz, 1 H), 6.81 (d, $J = 8.3$ Hz, 1 H), 7.15−7.54 (m, 12 H), 7.62−7.84 (m, 8 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 19.52 (s′), 26.99 (q′), 50.21 (d′), 58.12 (q′), 58.32 (q′), 59.53 (q′), 64.63 (t′), 72.48 (t′), 77.08 (d′), 77.42 (d′), 77.46 (d′), 79.89 (d′), 84.36 (d′), 127.23 (d′), 128.07 (d′), 128.11 (d′), 128.58 (d′), 128.82 (d′), 129.72 (s′), 129.99 (d′), 130.08 (d′), 130.13 (d′), 131.67 (d′), 133.54 (d′), 133.66 (s′), 134.89 (s′), 135.91 (d′), 165.95 (s′), 166.08 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{41}H_{49}NNaO_8Si$ (M + Na) 734.3125, found 734.3130.

3,6-Anhydro-2-benzamido-4-*O*-benzoyl-2-deoxy-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octitol (31a). Bu_4NF (1.0 M solution in THF, 388 μL, 0.3880 mmol) was added dropwise to a stirred solution of **30a** (92.0 mg, 0.129 mmol) and anhydrous pyridinium hydrochloride (22.4 mg, 0.194 mmol) in THF (1 mL). Stirring was continued for 12 h, and the mixture was then evaporated. Flash chromatography of the residue over silica gel (1.6 × 27 cm), using 80% EtOAc−

hexane, gave **31a** (51.0 mg, 83%) as a pale yellow oil: $[\alpha]_D = -12.3$ (*c* 1.4, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3427, 1722, 1651 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 3.25−3.35 (br, 1 H), 3.41 (br s, 6 H), 3.55−3.79 [m, including s (3 H) at δ 3.56, 8 H in all], 3.93 (dd, $J = 3.4$, 0.8 Hz, 1 H), 4.22 (dd, $J = 9.2$, 3.4 Hz, 1 H), 4.38−4.47 (m, 1 H), 4.59 (t, $J = 3.9$ Hz, 1 H), 5.64 (dd, $J = 3.9$, 0.8 Hz, 1 H), 6.97 (d, $J = 7.5$ Hz, 1 H), 7.15−7.55 (m, 6 H), 7.68−7.87 (m, 4 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 51.65 (d′), 58.01 (q′), 58.37 (q′), 59.56 (q′), 64.56 (t′), 72.25 (t′), 76.81 (d′), 77.24 (d′), 77.69 (d′), 79.95 (d′), 84.30 (d′), 127.29 (d′), 128.61 (d′), 128.84 (d′), 129.63 (s′), 129.95 (d′), 131.88 (d′), 133.60 (d′), 134.46 (s′), 165.90 (s′), 167.40 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{25}H_{31}NNaO_8$ (M + Na) 496.1947, found 496.1933.

Methyl 3,6-Anhydro-2-benzamido-4-*O*-benzoyl-2-deoxy-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octonate (32a). Jones reagent (125 μL, 8 N) was added dropwise to a stirred and cooled (0 °C) solution of **31a** (53.0 mg, 0.112 mmol) in acetone (0.8 mL). Stirring was continued for 1.5 h before the excess of Jones reagent was quenched with *i*-PrOH (70 μL). Stirring was continued for 2 h, the mixture was filtered, and the green precipitate was washed with Et_2O (3 × 4 mL). The combined filtrates were evaporated, dissolved in a little Et_2O, and treated with an ethereal solution of CH_2N_2 until a slight yellow color persisted. The excess of CH_2N_2 was destroyed with a few drops of AcOH, and the solvent was evaporated. Flash chromatography of the residue over silica gel (1.6 × 27 cm), using 40% EtOAc−hexane, gave **32a** (43.0 mg, 76%) as a white foam: $[\alpha]_D = -11.2$ (*c* 0.86, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3344, 1725, 1667 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 3.41 (br s, 6 H), 3.52−3.62 (m, 5 H), 3.70 (s, 3 H), 3.71−3.77 (m, 1 H), 3.92 (d, $J = 3.4$ Hz, 1 H), 4.24 (dd, $J = 9.0$, 3.4 Hz, 1 H), 4.79 (t, $J = 3.9$ Hz, 1 H), 5.02 (dd, $J = 8.1$, 3.6 Hz, 1 H), 5.71 (d, $J = 4.2$ Hz, 1 H), 6.96 (d, $J = 8.1$ Hz, 1 H), 7.19−7.57 (m, 6 H), 7.70−7.88 (m, 4 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 52.20 (d′) or (q′), 52.96 (d′) or (q′), 58.08 (q′), 58.42 (q′), 59.56 (q′), 72.23 (t′), 76.53 (d′), 77.23 (d′), 78.55 (d′), 80.37 (d′), 84.22 (d′), 127.40 (d′), 128.65 (d′), 128.88 (d′), 129.56 (s′), 130.00 (d′), 132.05 (d′), 133.68 (d′), 134.12 (s′), 165.85 (s′), 166.73 (s′), 171.11 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{26}H_{31}NNaO_9$ (M + Na) 524.1896, found 524.1900.

Methyl 3,6-Anhydro-4-*O*-benzoyl-2-[[(1,1-dimethylethoxy)carbonyl]amino]-2-deoxy-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octonate (33). $(t\text{-BuOCO})_2O$ (56.0 mg, 0.257 mmol) was added to a stirred solution of **32a** (35.0 mg, 0.070 mmol) and DMAP (2.1 mg, 0.017 mmol) in THF (1 mL), and the mixture was refluxed for 4 h. The solution was cooled to room temperature, MeOH (1 mL) and N_2H_4 (13 μL, 0.4194 mmol) were added, and the mixture was stirred for 4 h (TLC indicated complete reaction) and evaporated. Flash chromatography of the residue over silica gel (1.6 × 24 cm), using first 30% EtOAc−hexane (200 mL) and then 40% EtOAc−hexane, gave **33** (30.0 mg, 86%) as a colorless oil: $[\alpha]_D = -5.6$ (*c* 1.02, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3365, 1723, 1601, 1585 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.30 (s, 9 H), 3.38 (s, 3 H), 3.40 (s, 3 H), 3.45−3.49 (m, 1 H), 3.52−3.58 [m, including s (3 H) at δ 3.54, 4 H in all], 3.66 (s, 3 H), 3.71 (dd, $J = 10.5$, 1.9 Hz, 1 H), 3.91 (dd, $J = 3.6$, 0.8 Hz, 1 H), 4.13 (dd, $J = 9.2$, 3.6 Hz, 1 H), 4.48−4.58 (m, 2 H), 5.26 (d, $J = 8.3$ Hz, 1 H), 5.60 (d, $J = 3.4$ Hz, 1 H), 7.42−7.62 (m, 3 H), 8.00−8.05 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 28.25 (q′), 52.73 (d′) or (q′), 53.63 (d′) or (q′), 58.30 (q′), 58.44 (q′), 59.44 (q′), 72.96 (t′), 76.39 (d′), 77.41 (d′), 78.57 (d′), 79.92 (s′), 80.14 (d′), 84.32 (d′), 128.84 (d′), 129.83 (s′), 130.14 (d′), 133.75 (d′), 155.57 (s′), 165.80 (s′), 171.43 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{24}H_{35}NNaO_{10}$ (M + Na) 520.2159, found 520.2167.

Benzyl 3,6-Anhydro-2-benzamido-4-*O*-benzoyl-2-deoxy-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octonate (34). Jones reagent (121 μL, 8 N) was added dropwise to a stirred and cooled (0 °C) solution of **31a** (51.0 mg, 0.108 mmol) in acetone (0.9 mL). Stirring was continued for 1.5 h before the excess of Jones reagent was quenched with *i*-PrOH (70 μL). Stirring was continued for 2 h, the mixture was filtered, and the green precipitate was washed with Et_2O (3 × 5 mL). The combined filtrates were washed with brine (2 × 2 mL), dried ($MgSO_4$), and evaporated. DMF (1 mL), $NaHCO_3$ (27.2 mg, 0.323 mmol), BnBr (64 μL, 0.539 mmol), and NaI (1.0 mg, 0.007 mmol) were added to the resulting residue, and the mixture was stirred for 22 h (TLC indicated complete reaction). The DMF was evaporated under oil-pump vacuum. Flash chromatography of the residue over silica gel (1.6 × 27 cm), using 40% EtOAc−hexane, gave **34** (48.0 mg, 77%) as a colorless oil: $[\alpha]_D = -19.7$ (*c* 0.98, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3350, 1725, 1668 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 3.39 (s, 3 H), 3.41 (s, 3 H), 3.52 (dd, $J = 10.6$, 4.3 Hz, 1 H), 3.55 (s, 3 H), 3.59 (ddd, $J = 9.2$, 4.3, 1.8 Hz, 1 H), 3.73 (dd, $J = 10.6$, 1.8 Hz, 1 H), 3.94 (dd, $J = 3.4$, 0.6 Hz, 1 H), 4.24 (dd, $J = 9.2$, 3.4 Hz, 1 H), 4.82 (t, $J = 3.9$ Hz, 1 H), 5.09 (dd, $J = 8.2$, 3.7 Hz, 1 H), 5.14 (d, $J = 12.4$ Hz, 1 H), 5.20 (d, $J = 12.4$ Hz, 1 H), 5.69 (dd, $J = 4.1$, 0.7 Hz, 1 H), 7.00 (d, $J = 8.2$ Hz, 1 H), 7.19−7.56 (m, 11 H), 7.70−7.87 (m, 4 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 52.50 (d′), 58.10 (q′), 58.42 (q′), 59.53 (q′), 67.68 (t′), 72.31 (t′), 76.56 (d′), 77.23 (d′), 78.51 (d′), 80.34 (d′), 84.22 (d′), 127.40 (d′), 128.35 (d′), 128.63 (d′), 128.86 (d′), 129.54 (s′), 130.00 (d′), 132.02 (d′), 133.65 (d′), 134.15 (s′), 135.88 (s′), 165.81 (s′), 166.87 (s′), 170.51 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{32}H_{35}NNaO_9$ (M + Na) 600.2209, found 600.2218.

Benzyl 3,6-Anhydro-4-*O*-benzoyl-2-[[(1,1-dimethylethoxy)carbonyl]amino]-2-deoxy-5,7,8-tri-*O*-methyl-D-*erythro*-L-*ido*-octonate (35). $(t\text{-BuOCO})_2O$ (56.0 mg, 0.257 mmol) was added to a stirred solution of **34** (41.0 mg, 0.071 mmol) and DMAP (2.2 mg, 0.018 mmol) in THF (1 mL), and the mixture was refluxed for 4 h. The solution was cooled to room temperature, MeOH (1 mL) and N_2H_4 (16 μL, 0.5097 mmol) were added, and the mixture was stirred for 6 h (TLC indicated complete reaction) and evaporated. Flash chromatography of the residue over silica gel (1.6 × 25 cm), using 40% EtOAc−hexane, gave **35** (36.5 mg, 89%) as a colorless oil: $[\alpha]_D = -2.7$ (*c* 1.12, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3367, 1723, 1601, 1585 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 1.29 (s, 9 H), 3.37 (s, 3 H), 3.40 (s, 3 H), 3.41−3.48 (m, 1 H), 3.51−3.58 [m, including s (3 H) at δ 3.52, 4 H in all], 3.68 (dd, $J = 10.6$, 1.9 Hz, 1 H), 3.92 (d, $J = 3.5$ Hz, 1 H), 4.13 (dd, $J = 9.2$, 3.7 Hz, 1 H), 4.55−4.63 (m, 2 H), 5.12 (s, 2 H), 5.30 (d, $J = 8.1$ Hz, 1 H), 5.58 (d, $J = 3.3$ Hz, 1 H), 7.25−7.62 (m, 8 H), 7.97−8.02 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 28.23 (q′), 53.86 (d′), 58.30 (q′), 58.43 (q′), 59.43 (q′), 67.49 (t′), 72.94 (t′), 76.46 (d′), 77.39 (d′), 78.47 (d′), 79.91 (s′), 80.09 (d′), 84.26 (d′), 128.33 (d′), 128.56 (d′), 128.80 (d′), 129.79 (s′), 130.15 (d′), 133.70 (d′), 135.89 (s′), 155.57 (s′), 165.75 (s′), 170.87 (s′); exact mass (electrospray) *m*/*z* calcd for $C_{30}H_{39}NNaO_{10}$ (M + Na) 596.2472, found 596.2473.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. J. Z. held an Alberta Province Graduate Fellowship.

Supporting Information Available: An outline of the procedure for making **24**−**27** and procedures for preparation of **13c**,**d** and **29b**−**32b**, and copies of NMR spectra for compounds not analyzed (59 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. X-ray data on **9d** has been submitted to the Cambridge Crystallographic Data Centre.

JO981435W