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Novel Approaches for the Synthesis and Activation of Thio- and Selenoglycoside Donors

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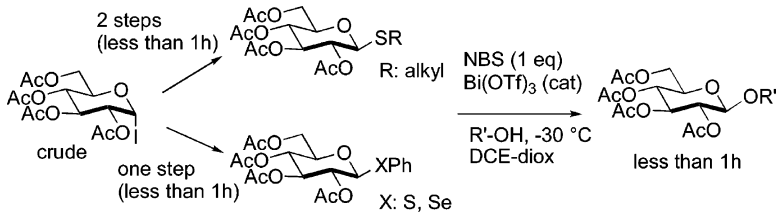

Alkyl thio-, phenyl seleno-, and phenyl thioglycosides can be prepared through short synthetic sequences based on the generation of glycosyl iodides as versatile intermediates. In addition, a novel cheap combined system (stoichiometric NBS and catalytic $Bi(OTf)_3$) has been developed for rapid and efficient activation of a wide variety of thio- and selenoglycoside donors.

Introduction

Thioglycosides are broadly used as glycosyl donors in oligosaccharide synthesis. Their usefulness is evidenced by the numerous activation protocols reported over the years,[1,2] and their prevalent employment in recently developed procedures for the one-pot assemblage of oligosaccharide fragments.[2,3] Important advantages of such donors are the specific activation conditions under the agency of "soft" promoters and the stability to the wide range of conditions typically adopted in manipulating the saccharidic functionalities. Anomeric thio groups can thereby act themselves as temporary protecting groups. Alkyl- and aryl thioglycosides are more routinely prepared by treating the corresponding peracetylated precursors with the proper thiol or thiotrimethylsilane in the presence of a Lewis acid.[4−16] These procedures suffer from the use of malodorous agents and substoichiometric or excess amounts of harsh and sensitive acidic reagents. In addition, reactions can be lengthy, and undesired anomeric mixtures are occasionally observed. Recently, a mild thioglycosidation promoter (MoO_2Cl_2) was found to be efficient in catalytic amounts, although use of thiols and lengthy reactions were still necessary.[17] These problems can be circumvented for alkyl thioglycosides by exploiting an alternative synthetic scheme which contemplates the generation of an *S*-glycosyl isothiouronium intermediate from a peracetylated glycosyl bromide and thiourea[18] and the subsequent *S*-alkylation in the presence of a mild base and an appropriate alkyl halide. In another related approach, the generation of the anomeric isothiouronium intermediate is achieved by coupling a peracetylated sugar and thiourea in presence of an excess

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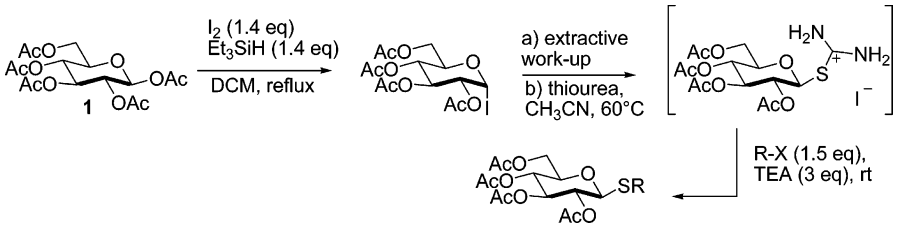
SCHEME 1. Synthesis of Alkyl Thioglycosides via Thiouronium Intermediates Generated from Glycosyl Iodides



amount of a strong Lewis acid such as $BF_3{\cdot}OEt_2$.[19] Very recently, peracetylated glycosyl bromides were again adopted in another access to thioglycosides based on the preliminary generation of the nucleophilic thiolate by reduction of a suitable disulfide with activated zinc.[20]

Phenyl selenoglycosides are representing another class of useful glycosyl donors activable by "soft" promoters.[21−22] Analogous to thioglycosides, they are mostly prepared by acid activation of peracetylated sugars in the presence of phenylselenol generated "in situ" by a laborious procedure.[21] Another protocol relies on the generation of the phenylselenolate anion by "in situ" reduction of phenyldiselenide with activated zinc and its subsequent nucleophilic attack on glycosyl bromides.[20] Alternatively, InI can be used to mediate the same transformation, although a different anomeric profile for the products is observed as a consequence of a different reaction mechanism.[23]

Results and Discussion

1. Synthesis of Thio- and Selenoglycoside Donors via Glycosyl Iodides. In the first part of this paper, we describe the kinetic advantages associated with the use of glycosyl iodides as precursors of thioalkyl-, thiophenyl-, and selenophenylglycosides. In a very recent paper by Field and co-workers glycosyl iodides were shown to be useful intermediates for the synthesis of peracetylated ethyl or methyl thioglycosides, and an efficient "one-pot" procedure from unprotected sugars was developed.[24] This sequence was based on initial fast peracetylation of the sugar with catalytic iodine and acetic anhydride,[25] subsequent anomeric iodination by addition of stoichiometric iodine and hexamethyldisilane,[26] and final installation of an anomeric thioalkyl group by addition of the proper disulfide or thiol. The overall procedure requires just one extractive workup and a single chromatographical purification. While the acetylation step is extremely fast, both the iodination and the thioglycosidation step can take several hours. Recently, we have shown that glycosyl iodides can be readily prepared from peracetylated sugars by treatment with a moderate stoichiometric excess of I_2 and triethylsilane (1.4 equiv each) in refluxing dichloromethane.[27] These reactions are extremely fast, with TLC analysis generally displaying their completion within 5 min. After a simple extractive workup, anomeric iodides can be recovered contaminated only by a triethylsilane-derived byproduct (NMR), which was found not to be detrimental for several subsequent synthetic elaborations.[27] The availability of this fast protocol spurred us to examine the feasible use of the glycosyl iodides thus obtained as intermediates toward the generation of thio- and selenoglycoside donors.

In a first approach, the generation of thioalkyl glycosides via thiouronium salts was examined (Scheme 1). Crude iodides obtained from I_2/Et_3SiH system were treated with a slight excess of thiourea in acetonitrile at 60 °C. After 10−25 min, TLC analysis displayed the consumption of the starting material and the generation of a polar product. It should be noted that refluxing conditions are needed for the analogous process to be accomplished at a comparable rate starting from glycosyl bromides.[18] Direct addition of a suitable alkylating agent (EtI, MeI, or $BrCH_2(CH_2)_8CH{=}CH_2$) and triethylamine at room temperature led to the quick generation of the corresponding thioglycosides (10−15 min were generally sufficient with EtI and MeI). Concentration of the mixture and chromatographical purification afforded a variety of thioalkyl glycosides in a good overall yield as shown in Table 1. The whole sequence required one extractive workup and a single chromatographical purification and took less than 25 min for each step. In all cases, 1,2-trans thioglycosides largely predominated, and they were easily separated from the minor anomer. The process proved efficient with a variety of saccharidic precursors and alkylating agents. Notably, the procedure was also applicable to the perbenzoylated precursor **3** (entry 3), which is reacting sluggishly in standard Lewis acid promoted procedures,[4] and the partially benzylated derivative **7** (entry 7), which could be converted into the corresponding iodide at a very low temperature (−20 °C) with a reduced amount of I_2 and triethylsilane (0.6 and 0.9 equiv, respectively). Higher temperatures led to decomposition of the saccharidic precursor, whereas use of TMSI as anomeric iodinating agent was reported for the analogous substrate to work at 0 °C in 2 h.[28] Only in the synthesis of the 2-*O*-benzylated thioglycoside **15** was the product obtained with predominance of the 1,2-cis anomer (Table 1, entry 7). Expectedly, the procedure was also compatible with 6-deoxy sugars (entries 5 and 6) and disaccharides (entry 8). Long thioalkyl chains (entry

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(25) Kartha, K. P. R.; Field, R. A. *Tetrahedron* **1997**, *53*, 11753−11766.
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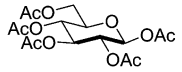
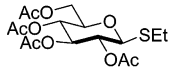
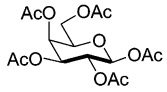
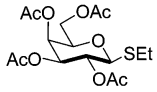
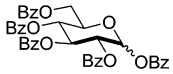
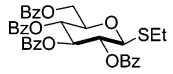
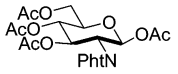
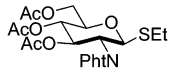
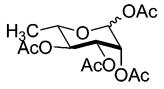
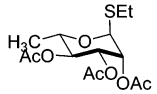
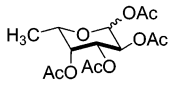
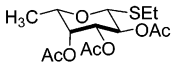
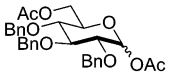
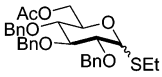
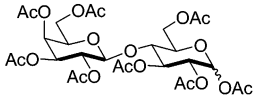
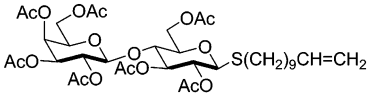
(27) (a) Adinolfi, M.; Iadonisi, A.; Schiattarella, M.; Ravidà, A. *Tetrahedron Lett.* **2003**, *44*, 7863−7866. (b) For an application of these intermediates, see: Adinolfi, M.; Iadonisi, A.; Pezzella, A.; Ravidà, A. *Synlett* **2005**, 1848−1852.
(28) (a) Lam, S. N.; Gervay-Hague, J. *Org. Lett.* **2002**, *4*, 2039−2042. (b) Lam, S. N.; Gervay-Hague, J. *Carbohydr. Res.* **2002**, *337*, 1953−1965.

TABLE 1. Synthesis of Alkyl Thioglycosides from 1-*O*-Acetylated Precursors (See Scheme 1)

Entry	Starting compound	Product	Yield (β:α)
1[a]	 **1**	 **9**	84 (>20)
2[a]	 **2**	 **10**	91 (>30)
3[a]	 **3**	 **11**	75 (>17)
4[a]	 **4**	 **12**	69 (β only)
5[a]	 **5**	 **13**	67 (<0.1)
6[a]	 **6**	 **14**	80 (>15)
7[a,c]	 **7**	 **15**	75 (0.38)
8[b]	 **8**	 **16**	67 (>10)

[a] EtI as the alkylating agent. [b] $BrCH_2(CH_2)_8CH{=}CH_2$ as the alkylating agent. [c] Iodination step at −20 °C (see text and the Experimental Section).

8) could be attached onto the anomeric position even though several hours were needed in this case for the final *S*-alkylation step.

The analogous synthetic scheme was then also pursued starting from unprotected saccharidic precursors by adding the aforementioned acetylation step under Field's conditions (catalytic iodine and a slight stoichiometric excess of acetic anhydride)[25] at its beginning (Table 2). After completion, anomeric iodination was conducted by simply adding dichloromethane, a further amount of iodine (up to overall 1.4 equiv), and triethylsilane (1.4 equiv) to the reaction vessel and heating the mixture to reflux. In all cases, the reactions proceeded in high yields and the acetic acid generated in the first step did not slow appreciably the conversions. After an extractive workup, crude iodides were then submitted to the analogous conditions previously shown in Scheme 1.

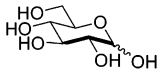
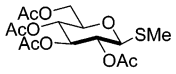
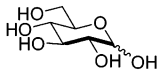
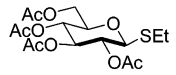
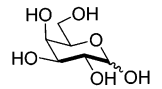
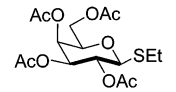
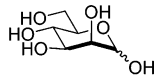
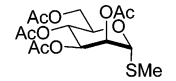
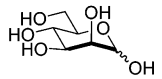
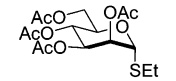
Reactivity of glycosyl iodides was also examined in the generation of phenyl seleno- and phenyl thioglycosides, which are broadly used in oligosaccharide synthesis but not accessible via thiouronium intermediates. In preliminary tests, we observed that phenylselenolate and phenylthiolate anions can be quickly generated (10−15 min) by treating the corresponding diselenide or disulfide precursors with a stoichiometric amount of sodium borohydride in ethanol[29] or acetonitrile (Scheme 2) without working under inert atmosphere.

Subsequent addition of these mixtures to the crude iodides resulted in the formation of the corresponding seleno- and thiophenylglycosides in moderate to high yields and excellent stereocontrol (Table 3). Less than 1 h was generally sufficient to perform the whole procedure without resorting to high temperatures in the final substitution step as a recently reported approach based on glycosyl bromides.[20] Interestingly, the *N*-phtalimido precursor **4** gave only α-glycosides in both cases, albeit in moderate yield (Table 3, entries 5 and 6), and in these cases only acetonitrile served well as the solvent. These latter results are quite unexpected, as the bulky phtalimido group is known to induce *β*-orientation in thio- and selenoglycosidations even in approaches affording high α-selectivity with other saccharidic precursors.[23] Complete *β*-selectivity was instead observed in other cases even when a precursor devoid of a participating 2-*O*-acyl group was used (Table 3, entries 7 and 8).

On the other hand, this protocol of phenyl selenoglycosidation was not very efficient when starting from the peracetylated

(29) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697−2699.

TABLE 2. Synthesis of Alkyl Thioglycosides from Unprotected Precursors (See Text and Scheme 1)

Entry	Starting compound	Product	Yield (β:α)
1[a]		 **17**	73 (>20)
2[b]		 **9**	78 (>20)
3[b]		 **10**	80 (>30)
4[a]		 **18**	77 (<0.05)
5[b]		 **19**	72 (<0.05)

[a] MeI as the alkylating agent. [b] EtI as the alkylating agent.

SCHEME 2. Synthesis of Phenyl Seleno- and Phenyl Thioglycosides

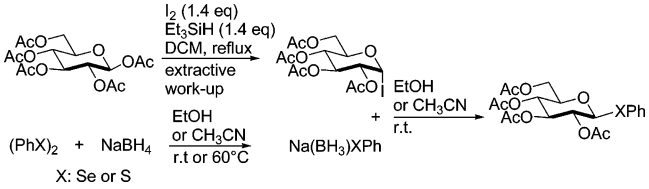
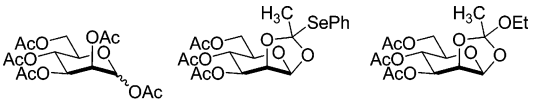


CHART 1

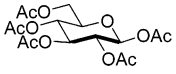
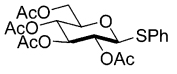
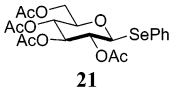
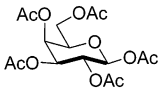
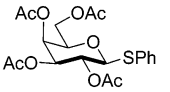
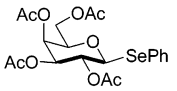
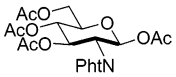
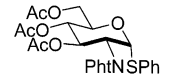
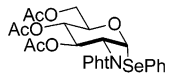
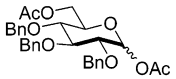
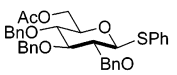
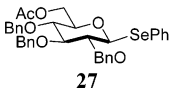


28 **29** **30**

manno precursor **28** (Chart 1), as in acetonitrile the mixture of anomeric selenoglycosides was obtained in average yield together with the inseparable orthoester-like product **29** (Chart 1), whereas ethyl orthoester **30** was the predominant product in EtOH. Attempted use of alternative solvents did not lead to improved results.

2. Activation of Thio- and Selenoglycosides by NBS/Bi(OTf)$_3$. Having in our hands efficient procedures to access a variety of thio- and selenoglycosides, the donor ability of these compounds was surveyed in test glycosidations. Thio- and selenoglycosides can be activated by a wide range of promoters of variable reactivity, and in all cases, at least a stoichiometric reagent is needed.[1,2,21,22] One of the most reliable procedures is represented by Van Boom's protocol based on the combined use of stoichiometric (often in excess amounts) *N*-iodosuccinimide and catalytic triflic acid (or other harsh Lewis acids such as trialkylsilyl triflates).[22,30] The efficacy of this approach is well witnessed by the numerous successful applications reported over the years by several laboratories. Softer Lewis acids have been reported as copromoters with *N*-iodosuccinimide in occasional examples.[31,32]

TABLE 3. Synthesis of Phenyl Seleno- and Phenyl Thioglycosides from 1-*O*-Acetylated Precursors (See Scheme 2)

Entry	Starting compound	Solvent	Product	Yield (β:α)
1	 **1**	CH_3CN	 **20**	71
2	**1**	EtOH	 **21**	87
3	 **2**	EtOH	 **22**	96
4	**2**	EtOH	 **23**	77
5	 **4**	CH_3CN	 **24**	35
6	**4**	CH_3CN	 **25**	50
7	 **7**	CH_3CN	 **26**	75
8	**7**	CH_3CN	 **27**	76

Due to the cost of *N*-iodosuccinimide, some attempt has been made for using *N*-bromosuccinimide as a much cheaper stoichiometric component of the activation system. Actually, the sole NBS can activate reactive thioglicosides from deoxysugars,[33] while a suitable copromoter is necessary to achieve a time-effective activation of ordinary sugars. For example, Kusumoto reported the quick activation of armed and disarmed thioglycosides by adopting several strong acid salts in substoichiometric amounts (0.5 equiv) together

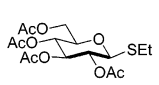
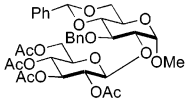
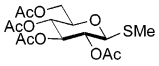
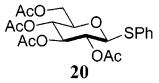
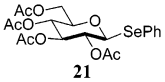
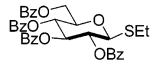
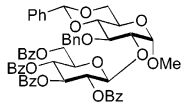
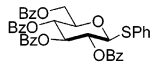
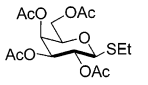
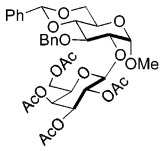
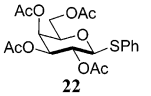
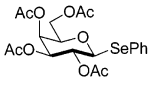
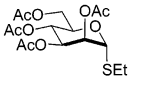
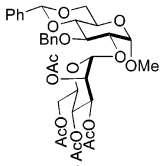
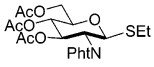
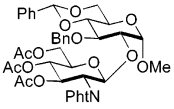
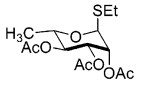
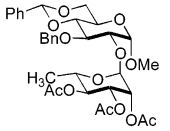
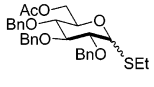
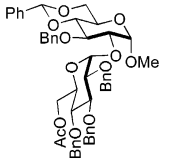
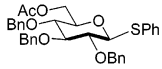
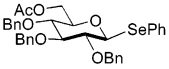
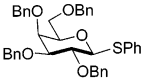
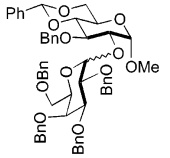
(30) Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 1331−1334.

(31) (a) Gelin, M.; Ferrières, V.; Plusquellec, D. *Eur. J. Org. Chem.* **2000**, 1423−1431. (b) Périon, R.; Lemée, L.; Ferrières, V.; Duval, R.; Plusquellec, D. *Carbohydr. Res.* **2003**, *338*, 2779−2792. (c) Jayaprakash, K. N.; Faser-Reid, B. *Org. Lett.* **2004**, *6*, 4211−4214.

(32) Some examples of thio- and selenoglycoside activation based on a single-electron-transfer (SET) mechanism have also been reported: (a) Marra, A.; Mallett, J.-M.; Amatore, C.; Sinaÿ, P. *Synlett* **1990**, 572−574. (b) Mehta, S.; Pinto, B. M. *Carbohydr. Res.* **1998**, *310*, 43−51. (c) van Well, R. M.; Kärkkäinen, T. S.; Kartha, K. P. R.; Field, R. A. *Carbohydr. Res.* **2006**, *341*, 1391−1397.

(33) Nicolaou, K. C.; Seitz, S. P.; Papahatjis, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 2430−2434.

TABLE 4. Glycosidations of the Model Acceptor 31 with Thio- and Selenoglycosides[a]

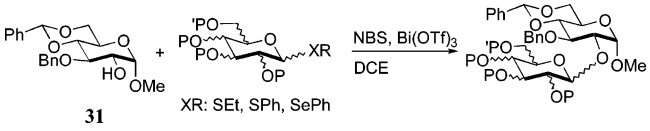
Entry	Donor	Product	Yield
1	 **9**	 **34**	69
2	 **17**	**34**	76
3	 **20**	**34**	74
4	 **21**	**34**	86
5	 **11**	 **35**	74
6	 **32**	**35**	81
7	 **10**	 **36**	65
8	 **22**	**36**	96
9	 **23**	**36**	78
10	 **19**	 **37**	83
11	 **12**	 **38**	94
12	 **13**	 **39**	85
13[b]	 **15**	 **40**	91
14[b]	 **26**	**40**	92
15[b]	 **27**	**40**	60
16[c]	 **33**	 **41**	89 (α/β 4:1)

[a] General conditions: acceptor (1 equiv), donor (1.3 equiv), NBS (1.3 equiv), $Bi(OTf)_3$ (0.1 equiv), DCE-dioxane, −30 to −25 °C for 30 min then spontaneous warming if necessary. [b] 0.05 equiv of $Bi(OTf)_3$ used. [c] 0.01 equiv of $Bi(OTf)_3$ used.

with NBS (1.5 equiv) at −20 °C.[34] In another protocol, harsh and moisture-sensitive TMSOTf was used in catalytic amounts (0.2 equiv) as copromoter with stoichiometric NBS in reactions conducted at even lower temperatures (− 50 °C).[35] In this latter paper, the electrophilic bromination of electron-rich aromatic systems was observed as a feasible side process.

In recent years, we have been interested in the development of glycosidation protocols based on moisture-stable and easy to handle Lewis acid promoters. Along this line, we have very recently disclosed the high reactivity of bismuth(III) triflate which can activate glycosyl trihaloacetimidates at rates comparable to those of strong standard promoters.[36] This behavior spurred us to investigate the reactivity of this salt in other glycosidation approaches. The interest was thus focused on the combined NBS/$Bi(OTf)_3$ system which appeared of practical value due to the use of cheap and easily storable reagents. A preliminary screening of conditions evidenced that disarmed thioglycosides can be activated in dichloroethane at temperatures as low as −30 °C by a catalytic amount of $Bi(OTf)_3$ (added as a solution in dioxane). Having established suitable conditions of activation, a wide variety of thio- and selenoglycosides were coupled with the model acceptor **31** (Scheme 3).

SCHEME 3. Glycosidation of Model Acceptor 31 with Alkyl Thio-, Phenyl Thio-, and Phenyl Selenoglycosides



31

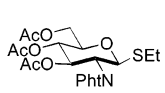
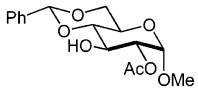
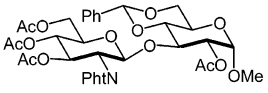
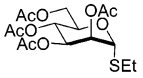
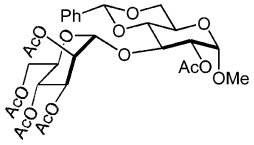
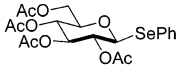
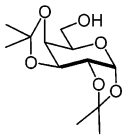
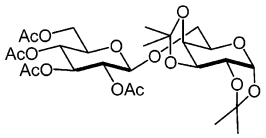
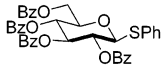
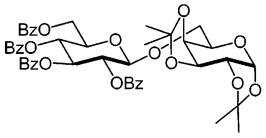
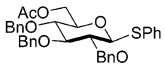
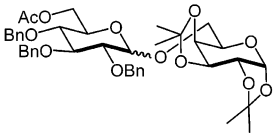
A number of 2-*O*-linked disaccharides could be prepared in high yields adopting glycosyl donors from glucose, galactose, *N*-phtalimidoglucosamine, mannose, and rhamnose (Table 4).

(34) (a) Fukase, K.; Hasuoka, A.; Kusumoto, S. *Tetrahedron Lett.* **1993**, *34*, 2187−2190. (b) Fukase, K.; Hasuoka, A.; Kinoshita, I.; Aoki, Y.; Kusumoto, S. *Tetrahedron* **1995**, *51*, 4923−4932.

(35) Qin, Z. H.; Li, H.; Cai, M. S.; Li, Z. J. *Carbohydr. Res.* **2002**, *337*, 31−36.

(36) Adinolfi, M.; Iadonisi, A.; Ravidà, A.; Valerio, S. *Tetrahedron Lett.* **2006**, *47*, 2595−2599.

TABLE 5. Glycosidations of the Model Acceptors 42 and 43 with Thio- and Selenoglycosides[a]

Entry	Donor	Acceptor	Product	Yield
1	 **12**	 **42**	 **44**	55
2	 **19**	**42**	 **45**	78
3	 **21**	 **43**	 **46**	36
4	 **32**	**43**	 **47**	85
5[b]	 **26**	**43**	 **48**	90 (α/β 1.6)

[a] General conditions: acceptor (1 equiv), donor (1.3 equiv), NBS (1.3 equiv), $Bi(OTf)_3$ (0.1 equiv), DCE-dioxane, −30 to −25 °C for 30 min then spontaneous warming if necessary. [b] 0.05 equiv of $Bi(OTf)_3$ used.

Reaction times generally did not exceed 1 h, and in some cases a few minutes were sufficient. The amounts of bismuth(III) triflate could be reduced (from 0.1 to 0.01 equiv) when benzylated armed donors were used in place of the peracylated counterparts (Table 4, entries 13−16). Predominance of α-linked anomers was expectedly obtained in absence of participating groups in the donors, reasonably due to the α-directing ability of the dioxane cosolvent (Table 4, entries 13−16).[37] Further experiments were then conducted with other model acceptors (**42** and **43**, Table 5) of differentiated reactivity, and rewarding results were obtained in almost all cases. Interestingly, glycosidation of the primary acceptor **43** with the acetylated glucosyl donor **21** proceeded in low yield (Table 5, entry 3), the 6-*O*-acetylated acceptor being obtained as the predominant product (55% yield) arising from an acetyl transfer from the donor.[38]

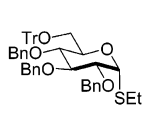
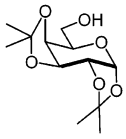
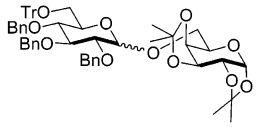
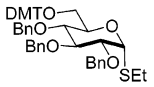
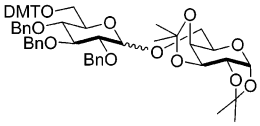
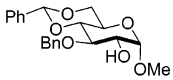
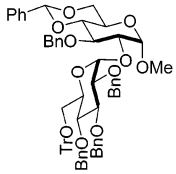
This undesired process was absent in the case of a benzoylated glucosyl donor (Table 5, entry 4) which afforded a markedly higher yield. The coupling of primary acceptor **43** with donor **26**, devoid of a participating group at O-2, proceeded in excellent yield but with modest α-selectivity (entry 5), whereas an excellent α-selectivity had been observed in coupling the same donor with the secondary acceptor **31** (Table 4, entry 14). In an attempt to improve this selectivity, and concomitantly to test the compatibility of the approach with acid-labile functionalities, 6-*O*-tritylated donors **49** and **50** (Table 6) were prepared from the corresponding 6-*O*-acetylated precursor **15** via Zemplen deacetylation and standard tritylation in pyridine. Indeed, installation of sterically bulky groups at the 6-OH of glycosyl donors represents a known option to improve the α-selectivity of glycosidations with a variety of glycosyl donors.[39] As a matter of fact, both **49** and **50** coupled with **43** to afford disaccharides **51** and **52** in high yields and with a sensible improvement of selectivity (Table 6, entries 1 and 2). Interestingly, no electrophilic aromatic bromination[35] of the electron-rich dimethoxytrityl group was detected by MS analysis of the disaccharide anomers **52** deriving from donor **50**. The compatibility of the acid-labile trityl group was also confirmed in the coupling of **49** with the less reactive secondary acceptor **31** (Table 6, entry 3) to afford the α-linked disaccharide **53** in satisfying yield and high stereocontrol.

(37) Demchenko, A.; Stauch, T.; Boons. G. J. *Synlett* **1997**, 818−820.

(38) Nakada, T.; Berces, A.; Whitfield, D. M. *J. Org. Chem.* **1999**, *64*, 9030−9045.

(39) For some examples, see: (a) Tanaka, H.; Sakamoto, H.; Sano, A.; Nakamura, S.; Nakajima, M.; Hashimoto, S. *Chem. Commun.* **1999**, 1259−1260. (b) Houdier, S.; Vottero, P. J. A. *Carbohydr. Res.* **1992**, *232*, 349−352. (c) Boons, G.-J.; Bowers, S.; Coe, D. M. *Tetrahedron Lett.* **1997**, *38*, 3773−3776. (d) Fukase, K.; Nakai, Y.; Kanoh, T.; Kusumoto, S. *Synlett* **1998**, 84−87. (e) Adinolfi, M.; Iadonisi, A.; Schiattarella, M. *Tetrahedron Lett.* **2003**, *44*, 6479−6482.

TABLE 6. Glycosidations with 6-*O*-Tritylated Donors 49 and 50[a]

Entry	Donor	Acceptor	Product	Yield
1	 **49**	 **43**	 **51**	75 (α/β 3.7:1)
2	 **50**	**43**	 **52**	81 (α/β 4.5:1)
3	**49**	 **31**	 **53**	64

[a] General conditions: acceptor (1 equiv), donor (1.3−1.4 equiv), NBS (1.3 equiv), $Bi(OTf)_3$ (0.1 equiv), DCE−dioxane, −15 °C for 30 min then spontaneous warming if necessary.

In conclusion, in this paper we have shown that glycosyl iodides, readily prepared by the I_2/Et_3SiH procedure, can be converted into alkyl thio-, phenyl thio-, and phenyl selenoglycosides taking advantage of rapid, experimentally simple, and efficient procedures. In addition, we have demonstrated that the combined system NBS (stoichiometric)/$Bi(OTf)_3$ (cat.) may represent a cheap and efficient alternative procedure for the activation of seleno- and thioglycoside donors under mild conditions.

Experimental Section

General Procedure for Preparation of Thioalkyl Glycosides (from Peracylated Precursors). To a solution of 1-*O*-acylated sugar (5 mmol) in anhydrous DCM (10 mL) were added I_2 (1.780 g, 7 mmol) and Et_3SiH (1.12 mL, 7 mmol) (caution: exothermic reaction). The system was refluxed until TLC analysis displayed complete consumption of the starting material (5 min are generally sufficient for peracetylated compounds, ca. 60 min are needed for the perbenzoylated precursor **3**). The mixture was then diluted with DCM and the organic phase washed with aq sodium carbonate containing sodium thiosulfate (this latter was added portionwise until consumption of residual iodine in the organic phase). The organic phase was then washed with water, dried, and concentrated. Thiourea (570 mg, 7.5 mmol) was added to the crude residue, and the mixture was suspended in acetonitrile (10 mL) and then heated to 60 °C. After 10−25 min (ca. 60 min from the benzoylated precursor **3**), TLC analysis evidenced the consumption of the iodide and the generation of a polar product. The vessel was cooled to rt, and then alkyl iodide (10 mmol) and TEA (2.78 mL, 20 mmol) were sequentially added. After 10−15 min, the reaction was complete (TLC), and the mixture was concentrated under vacuum. The residue was purified by flash silica gel chromatography (petroleoum ether/ethyl acetate mixtures) to afford the alkyl thioglycosides (see Tables 1 and 2 for yields).

Compound 16: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.80−5.70 (1H, m, $-CH{=}CH_2$), 5.34 (1H, bd, $J_{4,5} = 2.7$ Hz, H-4′), 5.20 (1H, t, $J = 9.0$ Hz, H-3), 5.08 (1H, dd, $J_{1,2} = 8.1$ Hz, H-2′), 5.02−4.90 (4H, m, $-CH{=}CH_2$, H-3′, H-2), 4.48 (1H, d, H-1′), 4.46 (1H, d, $J_{1,2} = 10.2$ Hz, H-1), 4.20−4.00 (4H, m, H_2-6 and H_2-6′), 3.88 (1H, bt, $J_{5,6} = 6.6$ Hz, H-5′), 3.78 (1H, t, $J = 9.3$ Hz, H-4), 3.66−3.48 (1H, m, H-5), 2.70−2.56 (2H, m, $-SCH_2-$), 2.15, 2.11, 2.07, 2.05, 2.04 (×2), 1.97 (21H, 7s, $-COCH_3$), 2.10−1.20 (16H, m, alkyl chain methylenes); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.2 (×2), 170.1, 170.0, 169.6, 169.5, 169.0, 139.1, 114.1, 101.0, 83.4, 76.2, 73.7, 70.9, 70.6, 70.3, 69.0, 66.5, 62.2, 60.7, 33.7, 30.2, 29.6, 29.3, 29.0, 28.8, 20.7, 20.5; $[\alpha]^{25}_D$ −24.2 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{37}H_{56}O_{17}SNa^+$) 827. 31, found 827.2. Anal. Calcd for $C_{37}H_{56}O_{17}S$: C, 55.21; H, 7.01. Found: C, 55.33; H, 7.21.

Preparation of Thioalkyl Glycoside 15 from Partially Benzylated Precursor 7. I_2 (56 mg, 0.22 mmol) and Et_3SiH (53 μL, 0.33 mmol) were sequentially added at −20 °C to a solution of **7** (198 mg, 0.37 mmol) in DCM (1 mL). After the consumption of the starting material (ca. 30 min, TLC analysis), the mixture was worked up as described in the previous paragraph. The crude glycosyl iodide was then elaborated essentially following the analogous protocol described above (the generation of thiouronium intermediate took less than 10 min, whereas the final alkylation step took ca. 20 min).

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-1-thio-α/β-D-glucopyranoside (15): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.00−7.00 (Ar), 5.38 (1H, d, $J_{1,2} = 5.4$ Hz, H-1 α), 5.00−4.50 (benzyl protons), 4.48 (1H, d, $J_{1,2} = 9.9$ Hz, H-1 β), 4.40−4.15 (3H, m, H-5, H_2-6), 3.90 (1H, t, $J = 9.6$ Hz, H-3 α), 3.80 (1H, dd, H-2 α), 3.60−3.40 (m, H-4, H-5 β and H-3 β), 2.80−2.45 (2H, m, SCH_2CH_3 β), 2.64−2.45 (2H, m, SCH_2CH_3 α), 2.04 (3H, $-COCH_3$ β), 2.02 (3H, $-COCH_3$ α), 1.33 (3H, t, $J = 7.5$ Hz, SCH_2CH_3 β), 1.29 (3H, t, $J = 7.5$ Hz, SCH_2CH_3 α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.4, 138.4, 137.7, 137.6, 128.3−127.5, 82.8, 82.3, 79.3, 76.9, 75.6, 74.8, 72.1, 68.8, 62.9, 23.5, 20.6, 14.6; MS (MALDI-TOF) calcd for ($C_{31}H_{36}O_6SNa^+$) 559. 21, found 559.3. Anal. Calcd for $C_{31}H_{36}O_6S$: C, 69.38; H, 6.76. Found: C 69.21; H 6.84.

General Procedure for Preparation of Alkyl Thioglycosides (from Unprotected Sugars). Iodine (98 mg, 0.38 mmol) was added to a suspension of the unprotected sugar (1.00 g, 5.5 mmol) in acetic anhydride (3.1 mL, 28.3 mmol) (caution: exhotermic reaction). After completion of the acetylation (10−30 min), the mixture was diluted with DCM (4 mL), and a further amount of I_2 (1.82 g, 7.2 mmol) and triethylsilane (1.23 mL, 7.7 mmol) were sequentially added. The mixture was refluxed until consumption of the peracetylated compound (less than 20 min, TLC) and then diluted with DCM. The organic phase was sequentially washed with aq

thiosulfate and aq carbonate. The organic phase was then dried and concentrated under vacuum to yield the crude glycosyl iodide, which was submitted to the synthesis of isothiuronium intermediate and the final alkylation as illustrated above.

General Procedure for Preparation of Phenyl Seleno- and Phenyl Thioglycosides. To a mixture of phenyl diselenide (or phenyl disulfide) (0.7 mmol) and $NaBH_4$ (53 mg, 1.4 mmol) was added ethanol (12 mL) or acetonitrile (5 mL). The mixture was stirred until evolution of hydrogen ceased and then was shortly heated at 50 °C to ensure completion of the reduction. The mixture was then added to the crude glycosyl iodide (obtained from 1.0 mmol of precursor as described above). After the mixture was stirred at rt for 5−60 min, acetic acid was added until neutrality, and the mixture was diluted with DCM and washed with water. The aqueous phase was re-extracted with DCM, and collected organic phases were dried and evaporated under vacuum. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate mixtures).

Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-α-D-glucopyranoside (24): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90−7.20 (Ar), 6.53 (1H, dd, $J_{3,4}$ = 9.3 Hz, $J_{2,3}$ = 12.0 Hz, H-3), 5.76 (1H, d, $J_{1,2}$ = 5.7 Hz, H-1), 5.10 (1H, dd, $J_{4,5}$ = 10.2 Hz, H-4), 4.89 (1H, dd, H-2), 4.70−4.60 (1H, m, H-5), 4.41 (1H, dd, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6a), 4.11 (1H, dd, $J_{5,6b}$ = 1.2 Hz, H-6b), 2.08, 2.07, 1.88 (9H, 3s, 3 $COCH_3$); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 170.6, 170.1, 169.3, 167.7, 167.1, 134.4, 133.3, 131.2, 129.0, 127.6, 123.8, 86.6, 70.4, 68.6, 67.6, 62.0, 53.7, 20.7; $[\alpha]^{25}_D$ +74.8 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{26}H_{25}NO_9SNa^+$) 550.11, found 550.1. Anal. Calcd for $C_{26}H_{25}NO_9S$: C, 59.19; H, 4.78. Found: C, 59.10; H, 4.67.

Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-seleno-α-D-glucopyranoside (25): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90−7.20 (Ar), 6.42 (1H, dd, $J_{3,4}$ = 8.7 Hz, $J_{3,2}$ = 11.7 Hz, H-3), 5.99 (1H, d, $J_{1,2}$ = 5.4 Hz, H-1), 5.09 (1H, dd, $J_{4,5}$ = 10.0 Hz, H-4), 4.86 (1H, dd, H-2), 4.74−4.64 (1H, m, H-5), 4.40 (1H, dd, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.07 (1H, dd, $J_{5,6b}$ = 2.1 Hz, H-6b), 2.06, 2.05, 1.86 (9H, 3s, 3 - $COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.4, 169.8, 169.1, 134.4, 133.5, 129.0, 128.6, 127.7, 84.4 (C-1), 69.9, 69.8, 67.9, 61.7, 54.0, 20.5; $[\alpha]^{25}_D$ +69.6 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{26}H_{25}NO_9SeNa^+$) 598.06, found 598.1. Anal. Calcd for $C_{26}H_{25}NO_9Se$: C, 54.36; H, 4.39. Found: C, 54.62; H, 4.18.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-1-thio-β-D-glucopyranoside (26): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−7.20 (Ar), 5.00−4.55 (6H, CH_2Ph), 4.68 (1H, d, $J_{1,2}$ = 9.9 Hz, H-1), 4.38 (1H, bd, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.20 (1H, dd, $J_{5,6b}$ = 3.0 Hz, H-6b), 3.80−3.70 (1H, m, H-5), 3.60−3.45 (3H, m, H-2, H-3, H-4), 2.06 (3H, s, $COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.3, 138.0, 137.7, 137.4, 133.4, 131.8, 128.7, 127.4, 87.2, 86.5, 80.7, 77.3, 76.7, 75.6, 75.3, 74.8, 63.0, 20.6. $[\alpha]^{25}_D$ +14.1 (*c* 1, $CHCl_3$); mp (MeOH) 69−70 °C; MS (MALDI-TOF) calcd for ($C_{35}H_{36}O_6SNa^+$) 607.22, found 607.1. Anal. Calcd for $C_{35}H_{36}O_6S$: C, 71.89; H, 6.21. Found: C, 72.06; H, 6.19.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-1-seleno-β-D-glucopyranoside (27): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75−7.15 (Ar), 4.90−4.50 (7H, CH_2Ph and anomeric proton), 4.26 (1H, bd, J = 12.0 Hz, H-6a), 4.28 (1H, dd, $J_{5,6b}$ = 3.6 Hz, H-6b), 3.80−3.75 (1H, m, H-5), 3.64−3.55 (3H, m, H-2, H-3, H-4), 1.98 (3H, s, $COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1, 138.0, 137.7, 137.4, 137.2, 134.2, 128.5−127.4, 86.4, 82.4, 80.9, 76.3, 75.4, 74.8, 74.6, 62.7, 20.4; $[\alpha]^{25}_D$ +11.1 (*c* 1.0, $CHCl_3$); mp (MeOH) 68−69 °C; MS (MALDI-TOF) calcd for ($C_{35}H_{36}O_6SeNa^+$) 655.15, found 655.0. Anal. Calcd for $C_{35}H_{36}O_6Se$: C, 66.56; H, 5.74. Found: C, 66.29; H, 5.67.

General Procedure for Glycosidation with the NBS/Bi(OTf)$_3$ System. Donor **22** (46 mg, 0.10 mmol) and acceptor **31** (30 mg, 0.08 mmol) were coevaporated three times in anhydrous toluene (3 × 1 mL). The mixture was kept under vacuum for 30−60 min, and then activated 4 Å acid washed molecular sieves (AW 300 MS) and NBS (19 mg, 0.10 mmol) were added under argon. In another vessel, a weighted amount of $Bi(OTf)_3$ was coevaporated with toluene and dried under vacuum for 30−60 min, and then activated 4 Å molecular sieves were added under argon. The mixture of donor, acceptor, and NBS was dissolved in anhydrous 1,2-dichloroethane (0.9 mL) at low temperature (ice bath), while $Bi(OTf)_3$ was dissolved at rt with dioxane (final concentration 20 mg/mL). After being stirred for 15 min, the mixture of saccharidic compounds was cooled to −30 °C, and then the solution of $Bi(OTf)_3$ in dioxane was added (0.26 mL, 0.008 mmol). After 10 min, the reaction was complete (TLC analysis), and a few drops of pyridine were added. The mixture was filtered on a short silica gel plug and the residue from the organic phase chromatographed on a silica gel column (eluant toluene/acetone 4:1) to yield disaccharide **36** (56 mg, 96% yield). In the case of slower reactions, the mixture was kept at −30 to −25 °C for 30 min, and then, if necessary (TLC analysis), allowed to spontaneously raise until the end of conversion.

Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-gluco-pyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (34): amorphous solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−7.20 (Ar), 5.55 (1H, s, benzylidene benzyl proton), 5.20 (1H, t, J = 9.3 Hz, H-3′), 5.12 (1H, t, J = 9.3 Hz, H-2′), 5.09 (1H, t, J = 9.3 Hz, H-4′), 4.86 (1H, d, $J_{1,2}$ = 8.1 Hz, H-1′), 4.85−4.68 (2H, AB, -CH_2Ph), 4.29 (1H, dd, $J_{6eq,6ax}$ = 9.9 Hz, $J_{6eq,5}$ = 4.2 Hz, H-6eq), 4.28−4.10 (2H, m, H_2-6′), 4.00 (1H, t, J= 9.6 Hz, H-3), 3.82 (1H, td, $J_{4,5}$ = 9.6 Hz, H-5), 3.76−3.64 (3H, m, H-2, H-6ax, H-5′), 3.61 (1H, t, J = 9.3 Hz, H-4), 3.42 (3H, s, $-OCH_3$), 2.09, 2.03, 2.00, 1.84 (12H, 4s, $-COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.5, 170.3, 169.4, 169.3, 138.3, 137.2, 128.9−126.0, 101.8, 101.3, 100.0, 82.2, 80.2, 75.0, 73.0, 71.8, 71.5, 69.0, 68.3, 62.0 (×2), 55.4, 20.6; $[\alpha]^{25}_D$ +9.5 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{35}H_{42}O_{15}Na^+$) 725.24, found 725.3. Anal. Calcd for $C_{35}H_{42}O_{15}$: C, 59.82; H, 6.02. Found: C, 59.70; H, 6.11.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (35): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10−7.20 (Ar), 5.92 (1H, t, J= 9.9 Hz, H-3′), 5.75−5.67 (2H, m, H-4′, H-2′), 5.50 (1H, s, benzylidene benzyl proton), 5.19 (1H, d, $J_{1,2}$ = 7.8 Hz, H-1′), 4.97 (1H, d, $J_{1,2}$ = 3.3 Hz, H-1), 4.74 (1H, dd, $J_{5,6a}$ = 3.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6′a), 4.56−4.38 (2H, AB, -CH_2Ph), 4.45 (1H, dd, $J_{5,6b}$ = 5.7 Hz, H-6′b), 4.27 (1H, dd, $J_{5,6eq}$ = 4.8 Hz, $J_{6ax,6eq}$ = 10.2 Hz, H-6eq), 4.20−4.15 (1H, m, H-5′), 3.93 (1H, t, J= 9.6 Hz, H-3), 3.81−3.76 (2H, m, H-5, H-2), 3.72 (1H, t, H-6ax), 3.54 (1H, t, H-4), 3.38 (3H, s, $-OCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.0, 165.8, 165.2, 165.0, 138.4, 137.3, 133.5, 133.2−127.4, 127.2, 126.0, 102.3, 101.4, 100.3, 82.1, 80.7, 74.7, 73.1, 72.3, 72.0, 69.6, 69.1, 62.7, 62.0, 55.5; $[\alpha]^{25}_D$ +33.6 (*c* 0.90, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{55}H_{50}O_{15}Na^+$) 973.31, found 973.2. Anal. Calcd for $C_{55}H_{50}O_{15}$: C, 69.46; H, 5.30. Found: C, 69.51; H, 5.39.

Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (36): oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−7.20 (Ar), 5.55 (1H, s, benzylidene benzyl proton), 5.34 (1H, dd, $J_{2,1}$ = 8.1 Hz, $J_{2,3}$ = 10.5 Hz, H-2′), 5.37 (1H, bd, $J_{3,4}$ = 3.6 Hz, H-4′), 5.00 (1H, dd, H-3′), 4.85 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 4.83−4.68 (2H, AB, $-CH_2Ph$), 4.79 (1H, d, J= 7.8 Hz, H-1′), 4.28 (1H, dd, $J_{5,6eq}$ = 4.5 Hz, $J_{6eq,6ax}$ = 9.9 Hz, H-6eq), 4.14 (2H, d, J = 6.3 Hz, H_2-6′), 4.01 (1H, t, J= 9.3 Hz, H-3), 3.86−3.68 (4H, m, H-5, H-5′, H-2, H-6ax), 3.64 (1H, t, H-4), 3.41 (3H, s, $-OCH_3$), 2.15, 2.04, 1.97, 1.83 (12H, 4s, 4 × $-COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1 (×2), 169.9, 169.0, 138.1, 137.0, 128.6−125.7, 102.1, 101.1, 99.7, 82.0, 80.3, 76.4, 74.8, 70.9, 70.6, 68.8, 68.7, 66.8, 62.0, 61.4, 55.1, 20.4; $[\alpha]^{25}_D$ +10.3 (*c* 0.90, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{35}H_{42}O_{15}Na^+$) 725.24, found 725.2. Anal. Calcd for $C_{35}H_{42}O_{15}$: C, 59.82; H, 6.02. Found: C, 59.59; H, 6.23.

Methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (37): oil; ^{1}H

NMR ($CDCl_3$, 300 MHz) δ 7.50−7.20 (Ar), 5.61 (1H, s, benzylidene benzyl proton), 5.41 (1H, dd, $J_{3,2}$ = 3.3 Hz, $J_{3,4}$ = 9.9 Hz, H-3′), 5.31 (1H, dd, $J_{1,2}$ = 1.5 Hz, H-2′), 5.29 (1H, t, J = 9.9 Hz, H-4′), 4.97−4.75 (2H, AB, $-CH_2Ph$), 4.95 (1H, bs, H-1′), 4.86 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 4.32 (1H, dd, $J_{5,6eq}$ = 4.5 Hz, $J_{6ax,6eq}$ = 9.6 Hz, H-6eq), 4.28−4.20 (1H, m, H-5′),4.04 (1H, t, J= 9.6 Hz, H-3), 4.00 (1H, dd, $J_{6a,6b}$ = 9.7, $J_{6a,5}$ = 4.8 Hz, H-6a′), 3.94−3.80 (3H, m, H-6b′, H-5), 3.77 (1H, t, H-6ax), 3.70 (1H, t, H-4), 3.46 (3H, s, $-OCH_3$), 2.18, 2.08, 2.02, 2.00 (12H, 4xs, $-COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.6, 170.1, 169.7, 169.6, 138.1, 137.2, 129.0−126.0, 101.3, 97.1, 94.7, 82.5, 75.4, 74.5, 69.8, 69.0, 68.9, 68.5, 65.6, 62.2, 61.7, 55.5, 20.9, 20.6; $[\alpha]^{25}_D$ +51.5 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{35}H_{42}O_{15}Na^+$) 725.24, found 725.1. Anal. Calcd for $C_{35}H_{42}O_{15}$: C, 59.82; H, 6.02. Found: C, 59.96; H, 5.89.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (38): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80−6.80 (Ar), 5.77 (1H, t, 9.6 Hz, H-3′), 5.65 (1H, d, $J_{1,2}$ = 8.7 Hz, H-1′), 5.43 (1H, s, benzylidene benzyl proton), 5.17 (1H, t, J= 9.6 Hz, H-4′), 4.93 (1H, d, $J_{1,2}$ = 3.3 Hz, H-1), 4.51 (1H, dd, H-2′), 4.36−4.15 (5H, m, $-CH_2Ph$, H-6eq, and H_2-6′), 3.95−3.60 (5H, m, H-3, H-5, H-6ax, H-5′, and H-2), 3.49 (1H, t, J = 9.3 Hz, H-4), 3.41 (3H, s, $-OCH_3$), 2.12, 2.04, 1.86 (9H, 3s, 3 $-COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.4, 170.1, 169.4, 138.2, 137.1, 134.1, 131.1, 128.9−125.9, 123.4, 101.2, 99.9, 99.7, 82.1, 81.8, 76.0, 73.9, 71.9, 70.7, 68.9, 68.8, 62.2, 62.1, 55.3, 54.5, 20.7, 20.5, 20.3. $[\alpha]^{25}_D$ +25.5 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{41}H_{43}NO_{15}Na^+$) 812.25, found 812.1. Anal. Calcd for $C_{41}H_{43}NO_{15}$: C, 62.35; H, 5.49. Found: C, 62.46; H, 5.56.

Methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (39): oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−7.20 (Ar), 5.81 (1H, s, benzylidene benzyl proton), 5.40−5.35 (2H, H-3′, H-2′), 5.08 (1H, t, J = 9.6 Hz, H-4′), 4.98 (1H, bs, H-1′), 4.89−4.78 (3H, $-CH_2Ph$ and H-1), 4.29 (1H, dd, $J_{5,6eq}$ = 3.6 Hz, $J_{6ax,6eq}$ = 9.3 Hz, H-6eq), 4.10−3.97 (2H, m, H-5′ and H-3), 3.88−3.81 (1H, td, J = 9.6 Hz, H-5), 3.75 (1H, t, J = 10.2 Hz, H-6ax), 3.68 (1H, dd, $J_{1,2}$ = 3.6 Hz, H-2), 3.62 (1H, t, H-4), 3.42 (3H, s, $-OCH_3$), 2.13, 2.07, 2.01 (9H, 3s, $-COCH_3$), 1.23 (1H, d, J = 6.3 Hz, H_3-6′); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.0, 169.8, 169.7, 138.2, 137.2, 128.9, 128.3, 128.2, 127.6, 126.0, 101.3, 100.1, 99.6, 82.0, 80.7, 77.2, 75.3, 71.0, 69.6, 69.0, 66.9, 62.2, 55.1, 20.8, 20.7, 17.5; $[\alpha]^{25}_D$ −8.6 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{33}H_{40}O_{13}Na^+$) 667.24, found 667.2. Anal. Calcd for $C_{33}H_{40}O_{13}$: C, 61.48; H, 6.25. Found: C 61.32; H 6.20.

Methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (40): amorphous solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−7.00 (Ar), 5.59 (1H, s, benzylidene benzyl proton), 5.06−4.51 (6H, 3 × AB, $-CH_2Ph$), 4.90 (1H, d, J = 3.6 Hz, H-1), 4.87 (1H, d, J = 3.9 Hz, H-1′), 4.32 (1H, dd, $J_{6eq,5}$ = 4.5, $J_{6eq,6ax}$ = 9.9 Hz, H-6eq), 4.24−4.18 (1H, m, H-5′), 4.16−4.08 (2H, m, H-3′ and H-3), 4.15−3.98 (2H, m, H_2-6′), 3.92−3.80 (2H, m, H-2′ and H-5), 3.76 (1H, t, J = 9.9 Hz, H-6ax), 3.66 (1H, t, J = 9.3 Hz, H-4′), 3.56 (1H, dd, $J_{2,3}$ = 9.6 Hz, H-2), 3.52 (1H, t, J = 9.9 Hz, H-4), 3.46 (3H, s, $-OCH_3$), 1.97 (3H, s, $-COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.5 138.6, 138.2 (×2), 137.9,137.3, 128.6−125.9, 101.2, 97.1, 94.2, 82.5, 81.9, 79.2, 77.1, 76.7, 75.6(×2), 74.9, 74.4, 72.9, 68.9, 68.6, 62.4, 62.2, 54.9, 20.7; $[\alpha]^{25}_D$ +39.5 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{50}H_{54}O_{12}Na^+$) 869.35, found 869.2. Anal. Calcd for $C_{50}H_{54}O_{12}$: C, 70.91; H, 6.43. Found: C, 71.11; H, 6.54.

Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranoside (41): amorphous solid; ^{1}H NMR ($CDCl_3$, 300 MHz) signals of α-anomer δ 7.60−7.00 (Ar), 5.53 (1H, s, benzylidene benzyl proton), 4.97 (1H, d, J= 3.3 Hz, H-1′), 4.93 (1H, d, J= 3.3 Hz, H-1), 5.00−4.20 ($-CH_2Ph$ and H-6eq), 4.11 (1H, t, J= 9.6 Hz, H-3), 4.04 (1H, dd, $J_{2,3}$ = 10.2 Hz, H-2′), 3.96 (1H, dd, $J_{3,4}$ = 2.4 Hz, H-3′), 3.95−3.80 (2H, m, H-5 and H-5′), 3.78 (1H, bd, H-4′), 3.71 (1H, t, J = 10.6 Hz, H-6ax), 3.58−3.30 (4H, m, H-4, H-2, H_2-6′), 3.43 (3H, s, $-OCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.8 (×2), 138.7 (×2), 138.4, 137.8, 128.8−125.9, 101.2, 97.3, 94.9, 82.3, 78.8, 77.3, 75.9, 75.3, 74.9, 74.7, 73.9, 73.0, 72.8, 72.7, 68.9, 62.3, 55.0; MS (MALDI-TOF) calcd for ($C_{55}H_{58}O_{11}Na^+$) 917.39, found 917.4. Anal. Calcd for $C_{55}H_{58}O_{11}$: C, 73.81; H, 6.53. Found: C, 73.58; H, 6.38.

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (44): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80−7.20 (Ar), 5.74 (1H, dd, J = 10.8 Hz, J = 9.09 Hz, H-3′), 5.56 (1H, d, $J_{1,2}$ = 8.4 Hz, H-1′), 5.52 (1H, s, benzylidene benzyl proton), 5.14 (1H, dd, H-4′), 4.80 (1H, d, $J_{1,2}$ = 3.9 Hz, H-1), 4.65 (1H, dd, $J_{2,3}$ = 9.6 Hz, H-2), 4.33−4.18 (2H, m, H-3 and H-2′), 4.12 (1H, dd, $J_{5,6a}$ = 4.2 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6′a), 3.91 (1H, dd, $J_{5,6b}$ = 2.4 Hz, H-6′b), 3.79−3.70 (2H, m, H-5 and H-6ax), 3.65−3.55 (2H, m, H-4 and H-5′), 3.30 (3H, s, $-OCH_3$), 2.01, 1.98, 1.92, 1.81 (12H, 4s, 4 $-COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.7, 170.2 (×2), 169.4, 137.1, 134.3, 131.2, 129.0, 128.2, 126.0, 125.3, 123.5, 101.3, 97.2, 97.0, 79.3, 74.8, 72.7, 71.6, 70.6, 68.9, 68.7, 62.0, 61.7, 55.2, 54.7, 20.7, 20.6, 20.4; $[\alpha]^{25}_D$ +43.0 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{36}H_{39}NO_{16}Na^+$) 764.22, found 764.4. Anal. Calcd for $C_{36}H_{39}NO_{16}$: C, 58.30; H, 5.30. Found: C, 58.53; H, 5.56.

Methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (45): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.20 (Ar), 5.55 (1H, s, benzylidene benzyl proton), 5.33 (1H, t, J = 1.8 Hz, H-2′), 5.29 (1H, d, H-1′), 5.26−5.18 (2H, m, H-4′ and H-3′), 4.97 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 4.81 (1H, dd, $J_{2,3}$ = 9.9 Hz, H-2), 4.34−4.24 (2H, m, H-6eq, H-3), 4.22−4.10 (3H, m, H-5′ and H_2-6′), 3.86−3.68 (3H, m, H-4, H-5 and H-6ax), 3.37 (3H, s, $-OCH_3$), 2.12, 2.10, 2.07, 2.02, 1.96 (15H, 5s, 5 × $-COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.7, 170.0, 169.8, 169.7, 169.6, 136.7, 128.9, 128.1 (×2), 126.0 (×2), 101.2, 97.5 (×2), 81.9, 72.0, 71.6, 69.1, 68.9, 68.7, 66.0, 62.2, 61.9, 55.3, 20.6; $[\alpha]^{25}_D$ +81.2 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{30}H_{38}O_{16}Na^+$) 677.22, found 677.2. Anal. Calcd for $C_{30}H_{38}O_{16}$: C, 55.04; H, 5.85. Found: C, 54.93; H, 5.99.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)-1,2:3,4-*O*-diisopropylidene-α-D-galactopyranose (46): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.49 (1H, d, $J_{1,2}$ = 4.8 Hz, H-1), 5.22 (1H, t, J= 9.3 Hz, H-3′), 5.09 (1H, t, H-4′), 5.01 (1H, dd, H-2′), 4.62 (1H, d, $J_{1,2}$ = 8.1 Hz, H-1′), 4.59 (1H, dd, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 8.1 Hz, H-3), 4.30−4.23 (2H, m, H-2, H-6′a), 4.18−4.09 (2H, m, H-6′b, H-4), 4.01 (1H, dd, $J_{5,6a}$ = 3.6 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6a), 3.96−3.88 (1H, m, H-5), 3.74−3.60 (2H, m, H-5′, H-6b), 2.07, 2.06, 2.01, 1.99 (4H, 4s, 4 $-COCH_3$), 1.49, 1.43, 1.31 (×2) (12H, 3s, isopropylidene methyls); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.7, 170.3, 169.6, 169.4, 109.4, 108.7, 101.4, 96.2, 72.7, 71.7, 71.2, 71.0, 70.6, 70.4, 69.5, 68.5, 67.8, 61.9, 26.0, 25.9, 25.0, 24.3, 20.6; $[\alpha]^{25}_D$ −52.8 (*c* 1.0, $CHCl_3$); mp (EtOH) 139−140 °C; MS (MALDI-TOF) calcd for ($C_{26}H_{38}O_{15}Na^+$) 613.21, found 613.3. Anal. Calcd for $C_{26}H_{38}O_{15}$: C, 52.88; H, 6.49. Found: C, 52.80; H, 6.58.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (47): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10−7.20 (Ar), 5.91 (1H, t, J = 9.6 Hz, H-3′), 5.69 (1H, t, J = 9.6 Hz, H-4′), 5.55 (1H, dd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2′), 5.42 (1H, d, $J_{1,2}$ = 4.8 Hz, H-1), 5.05 (1H, d, $J_{1,2}$ = 7.8 Hz, H-1′), 4.65 (1H, dd, $J_{5,6a}$ = 3.3 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6′a), 4.49 (1H, dd, $J_{5,6b}$ = 5.1 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6′b), 4.43 (1H, dd, $J_{3,2}$ = 2.1, $J_{3,4}$ = 8.1, H-3), 4.25−4.15 (3H, m, H-2, H-4 and H-5′), 4.15−4.00 (2H, m, H_2-6), 3.95−3.85 (1H, m, H-5), 1.37, 1.24, 1.21, 1.20 (12H, 4s, isopropylidene methyls); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.1, 165.7, 165.2, 165.1, 133.3, 133.1, 133.0, 130.0−128.1, 109.2, 108.4, 101.2, 96.1, 73.0, 72.1, 71.7, 70.9, 70.5, 70.3, 69.7, 68.2, 67.5, 63.2, 25.8, 25.6, 24.8, 24.2; $[\alpha]^{25}_D$ −15.7 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{46}H_{46}O_{15}Na^+$) 861.27,

found 861.3. Anal. Calcd for $C_{46}H_{46}O_{15}$: C, 65.86; H, 5.53. Found: C, 65.98; H, 5.63.

6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-D-glucopyranosyl-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (48): oil; ^{1}H NMR ($CDCl_3$, 300 MHz) signals of α anomer at δ 7.50−7.10 (Ar), 5.53 (1H, d, $J_{1,2}$ = 5.1 Hz, H-1), 5.10−4.50 (7H, -CH_2Ph and H-3), 4.96 (1H, d, $J_{1,2}$ = 3.9 Hz, H-1′), 4.37−4.00 (5H, m, H-2, H-4, H-5, H_2-6′, H-3′), 3.98−3.90 (1H, m, H-5′), 3.82−3.44 (4H, m, 6-*CH_2*, H-2′, H-4′), 2.03 (3H, s, -$COCH_3$), 1.54, 1.46, 1.33, and 1.32 (12H, 4s, isopropylidene methyls); significant signals of the β-linked disaccharide at δ 5.57 (1H, d, $J_{1,2}$ = 4.8 Hz, H-1), 4.47 (1H, d, $J_{1,2}$ = 8.1 Hz, H-1′), 2.04 (3H, s, −CO*CH_3*). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.8, 138.7, 138.5, 137.9, 137.7, 128.6−127.6, 109.4, 109.2, 108.6, 104.5 (C-1′ β), 97.3 (×2) (C-1 α and β), 97.0 (C-1′ α), 84.5, 81.8, 81.5, 79.8, 75.7, 75.0, 74.8, 74.3, 72.8, 72.4, 71.4, 70.8, 70.7, 70.6, 70.4, 70.0, 68.6, 67.3, 66.6, 65.8, 63.0, 24.9, 24.6, 24.4, 20.9; MS (MALDI-TOF) calcd for ($C_{41}H_{50}O_{12}Na^+$) 757.21, found 757.1. Anal. Calcd for $C_{41}H_{50}O_{12}$: C, 67.01; H, 6.86. Found: C, 67.29; H, 7.02.

2,3,4-Tri-*O*-benzyl-6-*O*-trityl-D-glucopyranosyl-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (51): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) signals of the α anomer δ 7.60−6.80 (Ar), 5.56 (1H, d, $J_{1,2}$ = 4.8 Hz, H-1), 5.17 (1H, d, $J_{1,2}$ = 3.9 Hz, H-1′), 5.00−4.30 (6H, 3 × AB, −CH_2Ph), 4.64 (1H, dd, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 8.1 Hz, H-3), 4.41 (1H, dd, $J_{4,5}$ = 2.4 Hz, H-4), 4.35 (1H, dd, H-2), 4.10 (1H, dt, $J_{5,6}$ = 6.3 Hz, H-5), 4.00 (1H, t, J = 9.3 Hz, H-3′), 3.92−3.66 (4H, m, H-4′, H-5′, H_2-6), 3.57 (1H, dd, $J_{5,6a}$ = 2.1 Hz, $J_{6a,6b}$ = 9.9 Hz, H-6a′), 3.23 (1H, dd, $J_{5,6b}$ = 4.2, H-6b′), 1.54, 1.50, 1.35, 1.34 (12H, 4s, isopropylidene methyls); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.9, 138.8, 138.5, 137.9, 128.7−126.9, 109.2, 108.5, 96.3, 86.3, 82.1, 80.1, 77.9, 75.9, 72.9, 72.2, 70.7, 70.6, 70.4, 65.4, 62.4, 26.1 (×2), 24.9, 24.6; MS (MALDI-TOF) calcd for ($C_{58}H_{62}O_{11}Na^+$) 957.41, found 957.5. Anal. Calcd for $C_{58}H_{62}O_{11}$: C, 74.50; H, 6.68. Found: C, 74.63; H, 6.73.

2,3,4-Tri-*O*-benzyl-6-*O*-dimethoxytrityl-D-glucopyranosyl-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (52): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) signals of the α anomer δ 7.60−6.70 (Ar), 5.53 (1H, d, $J_{1,2}$ = 4.8 Hz, H-1), 5.13 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1′), 4.98−4.29 (6H, 3 × AB, -CH_2Ph), 4.61 (1H, dd, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 8.1 Hz, H-3), 4.38 (1H, dd, $J_{4,5}$ = 1.8 Hz, H-4), 4.32 (1H, dd, H-2), 4.06 (1H, bt, $J_{5,6}$ = 7.5 Hz, H-5), 3.97 (1H, t, J = 9.3 Hz, H-3′), 3.88−3.72 (4H, m, H-4′, H-5′, H_2-6), 3.77 and 3.76 (6H, 2s, 2 × −OCH_3), 3.67 (1H, dd, H-2′), 3.52 (1H, bd, $J_{6a,6b}$ = 9.6 Hz, H-6′a), 3.22 (1H, bd, $J_{5,6b}$ = 3.9 Hz, H-6′b),1.52, 1.48, 1.33 (×2) (12H, 3s, isopropylidene methyls); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.3, 145.0, 138.8, 138.5, 136.3, 135.9, 130.01−126.6, 113.0, 109.1, 108.5, 96.3 (×2), 85.6, 82.0, 80.0, 77.9, 77.8, 76.0, 74.9, 72.1, 70.8, 70.7, 70.5, 65.3, 62.0, 55.1, 26.1 (×2), 24.9, 24.6; MS (MALDI-TOF) calcd for ($C_{60}H_{66}O_{13}Na^+$) 1017.44, found 1017.5. Anal. Calcd for $C_{60}H_{66}O_{13}$: C, 72.41; H, 6.68. Found: C, 72.49; H, 6.79.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-trityl-α-D-glucopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (53): foam; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−6.80 (Ar), 5.55 (1H, s, benzylidene benzyl proton), 5.06 (1H, d, $J_{1,2}$ = 3.6 Hz, H-1), 5.00 (1H, d, $J_{1,2}$ = 3.3 Hz, H-1′), 5.00−4.30 (8H, 4 × AB, −CH_2Ph), 4.31 (1H, dd, $J_{6eq,6ax}$ = 9.6 Hz, $J_{6eq,5}$ = 3.0 Hz, H-6eq), 4.28−4.20 (1H, m, H-5′), 4.16−4.07 (2H, m, H-3 and H-3′), 3.97 (1H, dd, $J_{2,3}$ = 9.6 Hz, H-2′), 3.94−3.85 (1H, m, H-5), 3.77 (2H, overlapped t, J= 9.9 Hz, H-6ax and H-4′), 3.67 (1H, dd, $J_{2,3}$ = 9.9 Hz, H-2), 3.64 (1H, t, J = 9.3 Hz, H-4), 3.49 (3H, s, −OCH_3), 3.40 (1H, bd, J = 10.2 Hz, H-6′a), 2.96 (1H, dd, $J_{5,6b}$ = 4.2 Hz, H-6′b); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.9, 138.7, 138.6, 138.3, 137.9, 137.3, 128.8−125.9, 101.2, 97.2, 93.9, 86.1, 82.2, 79.5, 79.2, 78.1, 76.0, 75.6, 74.8, 73.9, 72.9, 70.4, 69.0, 62.3, 62.1, 55.0; $[\alpha]^{25}_D$ +19.6 (*c* 1.0, $CHCl_3$); MS (MALDI-TOF) calcd for ($C_{67}H_{66}O_{11}Na^+$) 1069.46, found 1069.5. Anal. Calcd for $C_{67}H_{66}O_{11}$: C, 76.84; H, 6.35. Found: C, 76.61; H, 6.27.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of compounds **9**−**27** and disaccharides **34**−**41**, **44**−**48**, and **51**−**53**. This material is available free of charge via the Internet at http://pubs.acs.org.

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