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FORMATION OF *O*-GLYCOSIDIC LINKAGES FROM 1-HYDROXY SUGARS BY BISMUTH(III) TRIFLATE-CATALYZED DEHYDRATIVE GLYCOSIDATION

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Abstract – This paper describes the direct formation of various *O*-glycosidic linkages from 1-hydroxy sugars by bismuth(III) triflate-catalyzed dehydrative glycosidation. The condensation reactions of 1-hydroxy sugars with some primary alcohols in the presence of only 5 mol% bismuth(III) triflate at reflux temperature for 15 min in dichloromethane afforded *O*-glycosides in good yields. An 1,6-anhydro-β-**D**-glucopyranosidic linkage was formed by the intramolecular condensation of the corresponding 1-hydroxy sugar performed with similar reaction conditions using 5 mol% bismuth(III) triflate. A reaction using 10 mol% bismuth(III) triflate at room temperature in dichloromethane promoted the self- or cross-condensations of 1-hydroxy sugars to produce several kinds of 1,1'-disaccharides. This paper reports some important properties of bismuth(III) triflate catalyzed dehydrative glycosidation using 1-hydroxy sugars to form various *O*-glycosidic linkages.

INTRODUCTION

The development of an efficient preparation of complex glycosides is a major focus in synthetic carbohydrate chemistry.[1] Dehydrative glycosidation of 1-hydroxy sugars, which are easy to prepare and handle, can be a simple and versatile method for glycosidic bond formations.[2] Due to the generally poor leaving ability of the anomeric hydroxyl group of 1-hydroxy sugars, most of the conventional dehydrative *O*-glycosidation methods using 1-hydroxy sugars require the formation of a highly reactive glycosyl

This paper is dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday.

donor in the reaction system by *in situ* introduction of a transient leaving group at its anomeric hydroxyl group.[3]

Dehydrative glycosidation by an acid catalyst, which can directly activate the hemiacetal hydroxyl group of 1-hydroxy sugars, is considered to be a more practical approach because it does not require a transient leaving group. However, there have been only a few reports on such dehydrative glycosidation approaches using an acid catalyst.[4] This type of dehydrative glycosidation, called "Fischer glycosidation", requires the use of large excesses of acid (activator) and alcohol (acceptor) in order to increase the reactivity.[5] It is problematic that the reaction system using the stoichiometric amounts of an alcohol produces 1,1'-disaccharide (a non-reducing disaccharide) as a byproduct through self-condensation of 1-hydroxy sugars.[6] Therefore, it is important to develop an efficient dehydrative *O*-glycosidation method that does not require excess amounts of acid and alcohol in order to prevent the formation of the 1,1′-disaccharides. On the other hand, there is currently a significant emphasis on the study of the biologically novel functions of 1,1'-disaccharide derivatives, which are structurally-classified as trehalose analogs.[7] Therefore, the establishment of an efficient method for preparing 1,1'-disaccharides directly from 1-hydroxy sugars also becomes one of the most noteworthy subjects in dehydrative glycosidation studies.[8]

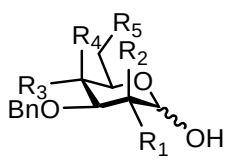
Our previous work showed that the *O*-ketopyranosidation[9] via the dehydrative condensation of artificial ketopyranoses, i.e., 1-*C*-alkylated sugar derivatives, proceeded easily when using catalytic bismuth(III) triflate ($Bi(OTf)_3$) as the activator.[10] This finding prompted us to test the applicability of $Bi(OTf)_3$ in dehydrative *O*-aldosylation using 1-hydroxy sugars.[11] We then investigated the direct formation of various *O*-glycosidic linkages from 1-hydroxy sugars by dehydrative glycosidation using $Bi(OTf)_3$. Part of the study, as reported in our preliminary letter, showed that the condensation of 1-hydroxy sugars with several primary alcohols in the presence of only 5 mol% $Bi(OTf)_3$ at reflux temperature for 15 min produced *O*-aldopyranosides and also controlled the production of undesirable 1,1'-disaccharides.[12] Our other studies of glycosidation using $Bi(OTf)_3$ revealed the following significant findings. The *O*-**D**-arabinofuranosidic and 1,6-anhydro-β-**D**-glucopyranosidic linkages were formed from the corresponding 1-hydroxy sugars under the similar glycosidation systems using 5 mol% $Bi(OTf)_3$. In addition, various 1,1'-disaccharides were produced in good yields by self- or cross-condensation with 1-hydroxy sugars in the presence of 10 mol% $Bi(OTf)_3$ at room temperature.

This paper describes the direct formation of various *O*-glycosidic linkages from 1-hydroxy sugars by $Bi(OTf)_3$-catalyzed dehydrative glycosidation.

RESULTS AND DISCUSSION

The 1-hydroxy sugars and alcohols used in this study are shown in Figures 1 and 2. The typical

O-glycosides and 1,1'-disaccharides produced are shown in Figures 3 and 4.



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2: R^1= H, R^2= OBn, R^3= OBn, R^4= H, R^5= OBn
3: R^1= OBn, R^2= H, R^3= H, R^4= OBn, R^5= OBn
4: R^1= N_3, R^2= H, R^3= OBn, R^4= H, R^5= OBn
5: R^1= OBn, R^2= H, R^3= OBn, R^4= H, R^5= OH

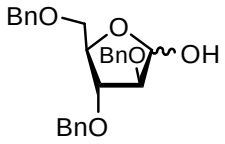

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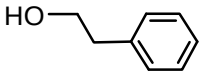
Figure 1. 1-Hydroxy sugars used



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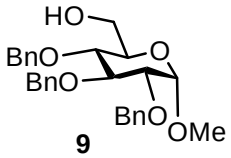

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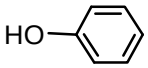

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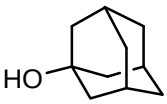

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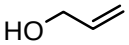

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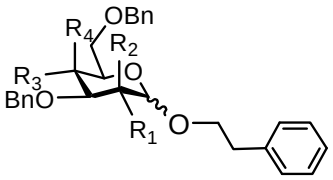
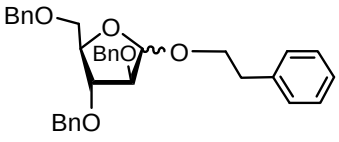
Figure 2. Alcohols used



13: R^1= OBn, R^2= H, R^3= OBn, R^4= H
14: R^1= H, R^2= OBn, R^3= OBn, R^4= H
15: R^1= OBn, R^2= H, R^3= H, R^4= OBn
16: R^1= N_3, R^2= H, R^3= OBn, R^4= H



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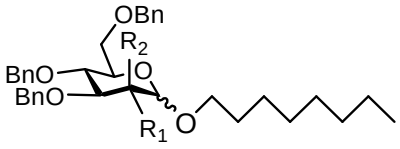
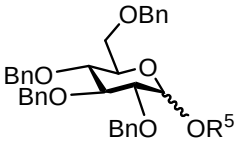


18: R^1= OBn, R^2= H
19: R^1= H, R^2= OBn



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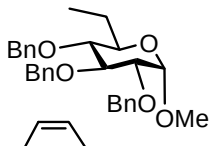
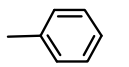


21: R^5=



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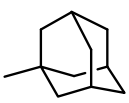
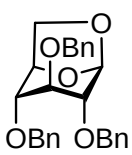


23: R^5= Bn



24

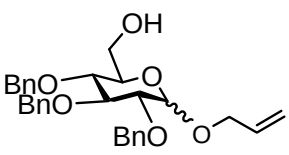


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Figure 3. Typical *O*-glycosides produced

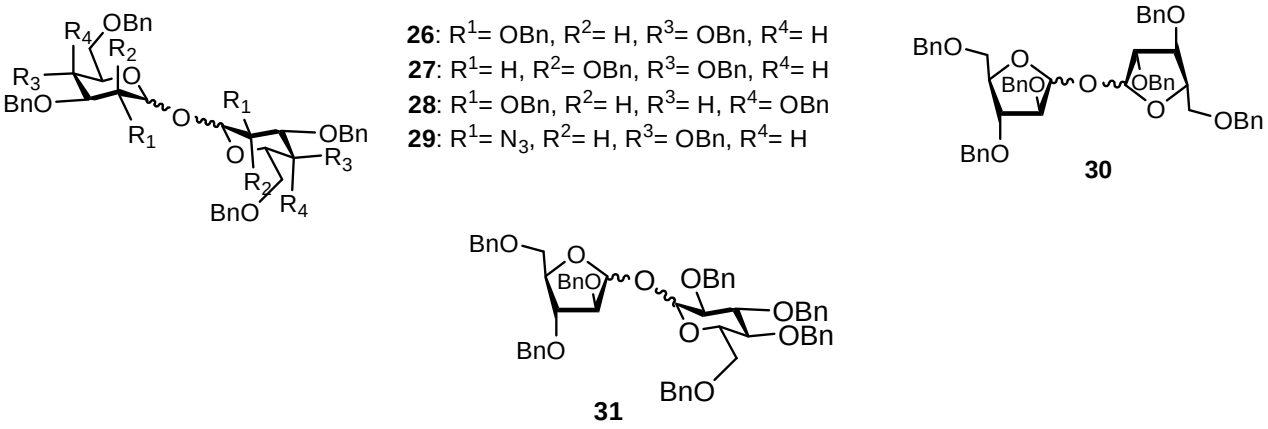
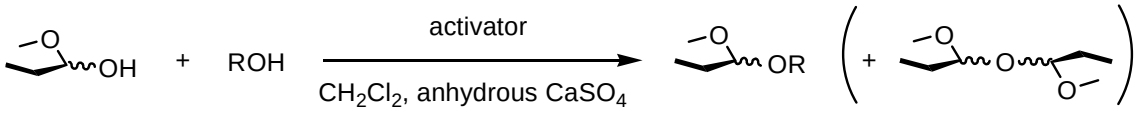


Figure 4. 1,1'-Disaccharides produced

1. Dehydrative glycosidation for producing typical *O*-glycosides (Scheme 1, Table 1)

We first investigated the glycosidation of 2,3,4,6-tetra-*O*-benzyl-**D**-glucopyranose (**1**) with an equimolar amount of 2-phenylethyl alcohol (**7**). The amount of $Bi(OTf)_3$ was varied in CH_2Cl_2 for 2 h at room temperature in the presence of a drying agent, anhydrous calcium sulfate ($CaSO_4$). These reaction conditions were similar to those previously reported.[13] The reaction using 5 mol% $Bi(OTf)_3$ afforded the corresponding glycoside **13** in only 35% yield. The use of 10 mol% $Bi(OTf)_3$ effectively promoted the glycosidation to produce **13** in a respectable yield of 85% with an α/β ratio of 71/29. It is noteworthy that under these reaction conditions the production of 1,1'-disaccharide **26** decreased only to a 7% yield. The use of 20 mol% $Bi(OTf)_3$ slightly reduced the yield of **13** to 68% with an increase in the yield of **26** to 13%. When the reaction temperature was raised to reflux temperature, the glycosidation using only 5 mol% $Bi(OTf)_3$ in CH_2Cl_2 for 15 min easily proceeded to produce **13** in a good yield of 87% (α/β = 69/31) with the formation of **26** in only 9% yield. A similar reaction using a mixed CH_2Cl_2/MeCN (v/v = 1/2) solvent at reflux temperature gave **13** in 72% yield (α/β = 34/66). The effect of other metal triflates was examined. Similar reaction conditions employing 5 mol% scandium(III) triflate ($Sc(OTf)_3$) and ytterbium(III) triflate ($Yb(OTf)_3$) afforded **13** in 82% yield (α/β = 65/35) and 14% yield (α/β = 44/56), respectively. $Sc(OTf)_3$ was fairly effective in dehydrative glycosidation. Thus, a reaction using only 5 mol% $Bi(OTf)_3$ at reflux temperature in CH_2Cl_2 for 15 min effectively promoted the glycosidation between **1** and **7** (1 equivalent) to produce the desired glycoside **13** with only a slight production of **26**.



1-6 **7-12** **13-25** **26-30**

Scheme 1

Table 1. The Formation of *O*-glycosides by the reactions of **1**-**6** with **7**-**12**.

Entry[a]	1-Hydroxy sugar	Alcohol	Activator (mol%)	Glycoside		1,1'-Disaccharide	
				Product	Yield/ % (α/β)[b]	Product	Yield/ %
1[c]	**1**	**7**	$Bi(OTf)_3$ (5)	**13**	35 (57/43)	**26**	4
2[c]	**1**	**7**	$Bi(OTf)_3$ (10)	**13**	85 (71/29)	**26**	7
3[d]	**1**	**7**	$Bi(OTf)_3$ (20)	**13**	68 (57/43)	**26**	13
4	**1**	**7**	$Bi(OTf)_3$ (5)	**13**	87 (69/31)	**26**	9
5[e]	**1**	**7**	$Bi(OTf)_3$ (5)	**13**	72 (34/66)	**26**	17
6	**1**	**7**	$Sc(OTf)_3$ (5)	**13**	82 (65/35)	**26**	11
7[f]	**1**	**7**	$Yb(OTf)_3$ (5)	**13**	14 (44/56)	**26**	4
8	**1**	**8**	$Bi(OTf)_3$ (5)	**18**	85 (62/38)	**26**	9
9	**1**	**8**	$Bi(N(SO_2\text{-}n\text{-}C_8F_{17})_2)_3$ (5)	**18**	71 (60/40)	**26**	10
10	**1**	**9**	$Bi(OTf)_3$ (5)	**20**	52 (75/25)	**26**	11
11[g]	**1**	**10**	$Bi(OTf)_3$ (5)	**21**	40 (80/20)	**26**	21
12	**1**	**11**	$Bi(OTf)_3$ (5)	**22**	58 (65/35)	**26**	17
13	**2**	**7**	$Bi(OTf)_3$ (5)	**14**	73 (α only)	**27**	16
14	**2**	**8**	$Bi(OTf)_3$ (5)	**19**	81 (91/9)	**27**	16
15	**3**	**7**	$Bi(OTf)_3$ (5)	**15**	70 (77/23)	**28**	10
16	**4**	**7**	$Bi(OTf)_3$ (5)	**16**	51 (52/48)	**29**	33
17	**6**	**7**	$Bi(OTf)_3$ (5)	**17**	81 (85/15)	**30**	5
18	**5**	**–**	$Bi(OTf)_3$ (5)	**24**	73	**–**	**–**
19[h]	**5**	**12**	$Bi(OTf)_3$ (20)	**25**	78 (65/35)	**–**	**–**

[a]Reaction conditions: molar ratio of donor : acceptor = 1 : 1; solvent = CH_2Cl_2; reflux temperature; reaction time = 15 min. [b]All the α/β ratios were determined by NMR. [c]Reaction conditions: room temperature; reaction time = 12 h. [d]Reaction conditions: room temperature; reaction time = 2 h. [e]The mixed solvent (CH_2Cl_2/MeCN = 1/2) was used. [f]Reaction time = 40 min. [g]Compound **23** was obtained in 31% yield as a byproduct. [h]Reaction conditions: molar ratio of donor : acceptor = 1 : 10; compound **24** was obtained in 16% yield.

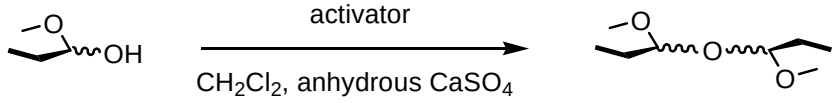
Next, we examined the glycosidation of **1** with various alcohols (1 equivalent) using 5 mol% $Bi(OTf)_3$ at reflux temperature in CH_2Cl_2 for 15 min. A reaction using *n*-octanol (**8**) produced the glycoside **18** in a good yield of 85% (α/β = 62/38) with the formation of **26** in only 9% yield. The glycosylation of **1** to methyl 2,3,4-tri-*O*-benzyl-α-**D**-glucopyranoside (**9**) afforded **20** in a moderate yield of 52% (α/β = 75/25) with the production of **26** in 11% yield. Even reactions using less reactive acceptors such as phenol (**10**) and 1-adamantanol (**11**) produced the corresponding glycosides **21** and **22** in 40% (α/β = 80/20) and 58%

(α/β = 65/35) yields with the formation of **26** in 21% and 17% yields, respectively. In addition, during the reaction using **10**, the benzyl glucoside **23** was obtained as a new byproduct in 31% yield. It seemed that the benzyl alcohol was formed along with the degradation of **1** under the given reaction conditions using **10**. The glycosidation of **1** with some primary alcohols afforded the desired glycosides in good yields. In contrast, for the reactions using less reactive alcohols, the yields of the desired glycosides decreased due to increase in the yield of **26** and the appearance of a new byproduct **23**.

Similarly, 2,3,4,6-tetra-*O*-benzyl-**D**-mannopyranose (**2**), 2,3,4,6-tetra-*O*-benzyl-**D**-galactopyranose (**3**), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-**D**-glucopyranose (**4**) and 2,3,5-tri-*O*-benzyl-**D**-arabinofuranose (**6**) were used as 1-hydroxy sugars. The reaction of **2** with **7** or **8** under the reaction conditions using 5 mol% $Bi(OTf)_3$ at reflux temperature for 15 min stereoselectively afforded the corresponding glycosides **14** or **19** in 73% yield (α only) or 81% yield (α/β = 91/9) and the production of the 1,1'-disaccharide **27** in 16% yield in both cases. Similar reaction conditions using **3**, **4**, or **6** with **7** gave the glycosides **15**, **16** or **17** in 70% yield (α/β = 77/23), 51% yield (α/β = 52/48) or 81% yield (α/β = 85/15) with the production of the 1,1'-disaccharide **28**, **29** or **30** in 10%, 15% or 5% yield, respectively. The reaction of **1** with **8** using 5 mol% $Bi(N(SO_2\text{-}n\text{-}C_8F_{17})_2)_3$[14] instead of $Bi(OTf)_3$ afforded **18** in 71% yield (α/β = 60/40) with the production of **26** in 16% yield.

The formation of an 1,6-anhydro-β-glucopyranosidic linkage from 2,3,4-tri-*O*-benzyl-**D**-glucopyranose (**5**) was examined. The reaction conditions using 5 mol% $Bi(OTf)_3$ at reflux temperature for 15 min in CH_2Cl_2 easily promoted intramolecular condensation of **5** to give 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-**D**-glucopyranose (**24**) in 73% yield. A reaction using **5** and allyl alcohol (10 equivalent) in the presence of 20 mol% $Bi(OTf)_3$ produced the allyl *O*-glycoside **25** in 78% yield (α/β = 65/35) as a main product and **24** was given in only 16% yield. This result indicated that under theses reaction conditions the intermolecular condensation of **5** with allyl alcohol preceded the intramolecular condensation of **5**.

2. Dehydrative glycosidation for producing 1,1'-disaccharides (Scheme 2, Table 2)



1-4, **6** **26-31**

Scheme 2

We next, investigated the formation of the symmetrical 1,1'-disaccharide **26** by the self-condensation of **1** in detail. The reactions using 5 mol% and 10 mol% $Bi(OTf)_3$ at reflux temperature for 15 min promoted

the self-condensation of **1** to produce **26** in 77% and 71% yields. At the same time, however, the benzyl glucoside **23** was obtained as a byproduct in 19% and 14% yields, respectively. The reaction using 5 mol% $Bi(OTf)_3$ at room temperature for 15 h afforded **26** in only 12% yield with no production of **23**. The use of 10 mol% $Bi(OTf)_3$ at room temperature increased the yield of **26** to 85% with an αα/αβ/ββ isomer ratio of 53/33/14. The use of 50 mol% $Bi(OTf)_3$ decreased the yield of **26** to 59% and increased the yield of **23** to 35%. The increase of $Bi(OTf)_3$ seemed to promote the degradation of **1**.

The effect of other metal triflates was also examined using $Sc(OTf)_3$ and $Yb(OTf)_3$. $Sc(OTf)_3$ was a fairly effective activator for the production of **26** in 67% yield, while $Yb(OTf)_3$ was completely ineffective. This result roughly corresponded to that of entries 6 and 7 in Table 1.

Table 2. The formation of 1,1'-disaccharides by the self- or cross-condensations of **1**-**6**.

Entry[a]	1-Hydroxy sugar	Activator (mol%)	1,1'-Disaccharide	
			Product	Yield/ % (αα/αβ/ββ)[b]
1[c]	**1**	$Bi(OTf)_3$ (5)	**26**	77
2[d]	**1**	$Bi(OTf)_3$ (10)	**26**	71
3	**1**	$Bi(OTf)_3$ (5)	**26**	12
4	**1**	$Bi(OTf)_3$ (10)	**26**	85 (53/33/14)
5	**1**	$Bi(OTf)_3$ (20)	**26**	84 (65/29/6)
6[e]	**1**	$Bi(OTf)_3$ (50)	**26**	59
7	**1**	$Sc(OTf)_3$ (20)	**26**	67 (55/32/13)
8	**1**	$Yb(OTf)_3$ (20)	**26**	–
9[f]	**2**	$Bi(OTf)_3$ (10)	**27**	85 (ααonly)
10[g]	**3**	$Bi(OTf)_3$ (10)	**28**	70 (71/29/0)
11	**4**	$Bi(OTf)_3$ (20)	**29**	–
12	**4**	$Bi(OTf)_3$ (50)	**29**	23
13	**4**	$Bi(OTf)_3$ (100)	**29**	53 (35/32/33)
14[h]	**6**	$Bi(OTf)_3$ (10)	**30**	93 (85/15/0)
15[h,i]	**6**, **1**	$Bi(OTf)_3$ (10)	**31**[j]	74 (31/31/31/7)[k]

[a]Reaction conditions: solvent = CH_2Cl_2; room temperature; reaction time = 1 d. [b]All the isomer ratios were determined by NMR. [c]Reaction conditions: reflux temperature; reaction time = 10 min; compound **23** was obtained in 19% yield as a byproduct. [d]Reaction conditions: reflux temperature; reaction time = 10 min; compound **23** was obtained in 14% yield as a byproduct. [e]Compound **23** was obtained in 35% yield. [f]Reaction conditions: room temperature; reaction time = 1 h. [g]Reaction conditions: 0 °C; reaction time = 1 d. [h]Reaction conditions: 0 °C; reaction time = 3.5 h. [i]Reaction conditions: molar ratio of **6** : **1** = 1 : 1.5. [j]Compound **30** was obtained in 11% yield. [k]Isomer ratios of Glcα-αAra/Glcα-βAra/Glcβ-αAra/Glcβ-βAra.

Subsequently, the synthesis of various symmetrical 1,1'-disaccharides **27**, **28**, **29** and **30** by the self-condensation of the 1-hydroxy sugars **2**-**4** and **6** was examined. Similar reaction conditions using 10 mol% $Bi(OTf)_3$ in CH_2Cl_2 at room temperature for 3 to 15 h successfully gave **27**, **28** and **30** in good yields of 85% (αα only), 70% (αα/αβ/ββ= 71/29/0) and 93% (αα/αβ/ββ= 85/15/0) from **2**, **3** and **6**. However, the same reaction conditions were not applicable to self-condensation using **4** at all. The reaction conditions using 100 mol% $Bi(OTf)_3$ increased the yield of **29** up to 53% (αα/αβ/ββ= 35/32/33). We observed that the reactivity of **6** was higher than that of **1**. Next, the synthesis of the unsymmetrical structural 1,1'-disaccharide **31** by the cross-condensation using **6** and **1** was examined. The reaction of **6** with **1** (1.5 equivalent) using 10 mol% $Bi(OTf)_3$ for 3.5 h afforded the desired **31** in a good yield of 74% with a mixture of αα/αβ/βα/ββ isomers = 31/31/31/7. Under these reaction conditions **30** was obtained in 11% yield and **26** was scarcely produced.

CONCLUSIONS

The direct formation of various *O*-glycosidic linkages from 1-hydroxy sugars by $Bi(OTf)_3$-catalyzed dehydrative glycosidation was demonstrated. The reactions of several benzylated 1-hydroxy sugars with certain primary alcohols using only 5 mol% $Bi(OTf)_3$ at reflux temperature in dichloromethane for 15 min successfully afforded the desired *O*-glycosides in good yields. These reaction conditions controlled the formation of unwanted 1,1'-disaccharides. The application of a similar reaction system effectively led to the formation of an 1,6-anhydro-β-**D**-glucopyranosidic linkage from the corresponding 1-hydroxy sugar. Self- or cross-condensation with 1-hydroxy sugars was promoted by 10 mol% $Bi(OTf)_3$ in CH_2Cl_2 at room temperature and produced various symmetrical or unsymmetrical 1,1'-disaccharides. Therefore, we believe that our dehydrative glycosidation procedure can contribute to the convenient production of certain chemically or biologically useful glycosides.

EXPERIMENTAL

^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a JEOL ECA-600 spectrometer in $CDCl_3$ using TMS as an internal standard. Optical rotations were recorded on a JASCO DIP-360 digital polarimeter. HRMS were obtained on a Mariner spectrometer (PerSeptive Biosystems Inc.). Preparative TLC was performed using Merck silica gel 60GF254. Column chromatography was conducted using silica gel 60 N (40~50 μm, Kanto Chemical Co., INC.). $Bi(OTf)_3$ was purchased from Sigma-Aldrich. All anhydrous solvents were purified according to standard methods.

2-Phenylethyl 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranoside (13) (Table 1, Entry 4): To a stirred suspension of $Bi(OTf)_3$ (5.4 mg, 0.0082 mmol) and **7** (20.3 mg, 0.17 mmol) in CH_2Cl_2 (3 mL) was added

1 (89.2 mg, 0.17 mmol) in the presence of anhydrous $CaSO_4$ (ca. 100 mg) under an Ar atmosphere. The resulting mixture was stirred at reflux temperature for 15 min. The reaction was then quenched by the addition of a saturated aqueous $NaHCO_3$ solution (5 mL). The reaction mixture was extracted with EtOAc, and the organic layer was washed with water and a saturated aqueous NaCl solution. After the organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure. The crude product was purified using a preparative silica gel TLC (PTLC; EtOAc/hexane = 1/3) to give the desired glycoside **13** (92.4 mg, 87%, a mixture of α and β anomers) as a colorless oil and 1,1'-disaccharide **26** (8.3 mg, 9%) as a colorless oil. ^{1}H NMR δ 2.92-2.99 (m, CH_2CH_2Phαβ), 3.99 (dd, *J* = 8.2 Hz, *J* = 8.9 Hz, H-3α), 4.19-4.23 (m, $CH_aH_bCH_2$Phβ), 4.41 (d, *J* = 7.6 Hz, H-1β), 4.77 (d, *J* = 3.4 Hz, H-1α); ^{13}C NMR δ 35.9, 36.2, 68.4, 68.7, 68.9, 70.1, 70.6, 73.1, 73.36, 73.41,74.6, 74.80, 74.82, 74.9, 75.59, 75.60, 77.6, 77.8, 80.0, 81.9, 82.2, 84.6, 96.8 (C-1α), 103.6 (C-1β); HRMS (ESI, α/β mixture) *m/z* calcd for 667.3030 ($C_{42}H_{44}O_6$+Na^+), found 667.2993.

Octyl 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranoside (18) (Table 1, Entry 8): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (5.1 mg, 0.0078 mmol), **8** (20.2 mg, 0.16 mmol), and **1** (84.1 mg, 0.16 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **18** (PTLC; EtOAc/hexane = 1/3, 85.6 mg, 85%, a mixture of α and β anomers) as a colorless oil and **26** (7.1 mg, 9%). **(Table 1, Entry 9):** The same procedure using $Bi(N(SO_2$-*n*-$C_8F_{17})_2)_3$ (32.2 mg, 0.01 mmol), **8** (27.0 mg, 0.2 mmol), and **1** (111.9 mg, 0.21 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **18** (92.1 mg, 71%, a mixture of α and β anomers) and **26** (11.5 mg, 10%). ^{1}H NMR δ 0.86-0.89 (m, CH_3), 1.27-1.70 (m, $(CH_2)_6$), 3.40-3.47 (m, H-2β, H-5β, $CH_aH_b(CH_2)_6CH_3$α), 3.51-3.69 (m, H-2α, H-4α, H_a-6α, $CH_aH_b(CH_2)_6CH_3$α, H-3β, H-4β, H_a-6β, $CH_aH_b(CH_2)_6CH_3$β), 3.72 (dd, *J* = 3.4 Hz, *J* = 10.3 Hz, H_b-6α), 3.73-3.75 (m, H_b-6β), 3.77-3.80 (m, H-5α), 3.95-3.99 (m, $CH_aH_b(CH_2)_6CH_3$β), 3.99 (dd, *J* = 8.9 Hz, *J* = 9.6 Hz, H-3α), 4.39 (d, *J* = 7.6 Hz, H-1β), 4.76 (d, *J* = 4.1 Hz, H-1α); ^{13}C NMR δ 14.1, 22.6, 26.11, 26.14, 29.18, 29.21, 29.3, 29.3, 29.4, 29.7, 31.8, 31.8, 68.2, 68.5, 69.0, 70.0, 70.1, 73.1, 73.4, 73.4, 74.7, 74.8, 74.9, 75.0, 75.6, 75.6, 77.7, 77.9, 80.1, 82.1, 82.2, 84.7, 96.8 (C-1α), 103.6 (C-1β); HRMS (ESI, α/β mixture) *m/z* calcd for 675.3656 ($C_{42}H_{52}O_6$+Na^+), found 675.3680. (Lit.,[15] α anomer: ^{1}H NMR δ 4.76 (*J* = 2.1 Hz, H-1); ^{13}C NMR δ 96.8 (C-1); β anomer: ^{1}H NMR δ 4.39 (*J* = 7.6 Hz, H-1); ^{13}C NMR δ 103.6 (C-1)).

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (20) (Table 1, Entry 10): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (5.0 mg, 0.0076 mmol), **9** (70.8 mg, 0.15 mmol), and **1** (82.4 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **20** (PTLC; EtOAc/hexane = 1/3, 77.7 mg, 52%, a mixture of α and β anomers) as a colorless oil and **26** (9.2 mg, 11%). ^{1}H NMR δ 3.25 (s, CH_3β), 3.35 (s, CH_3 α), 3.43 (dd, *J* = 3.4 Hz, *J* = 8.9 Hz,

H-2'α), 3.48-3.57 (m, H-2α, H-2'β), 3.94-4.01 (m, H-3'α, H-3α), 4.35 (d, *J* = 8.2 Hz, H-1'β), 4.50-4.62 (m, H-1α, H-1β), 4.98 (d, *J* = 4.1 Hz, H-1'α); ^{13}C NMR δ 97.2 (C-1'αα), 97.9 (C-1αα), 98.0 (C-1βα), 103.7 (C-1'βα); HRMS (ESI, α/β mixture) *m/z* calcd for 1009.4497 ($C_{62}H_{66}O_{11}$+Na^+), found 1009.4479. (Lit.,[16] α anomer: ^{1}H NMR δ 4.98 (*J* = 3.7 Hz, H-1'); ^{13}C NMR δ 97.9 (C-1'); β anomer: ^{1}H NMR δ 4.34 (*J* = 7.8 Hz, H-1'); ^{13}C NMR δ 103.7 (C-1')).

Phenyl 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranoside (21) (Table 1, Entry 11): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (5.4 mg, 0.0082 mmol), **10** (15.6 mg, 0.16 mmol), and **1** (89.0 mg, 0.16 mmol) in CH_2Cl_2 (3 mL) gave **21** (PTLC; toluene/EtOAc = 10/1, 40.3 mg, 40%, a mixture of α and β anomers) as a colorless oil, **26** (18.5 mg, 21%) as a colorless oil and **23**[17] (32.2 mg, 31%) as a colorless oil. ^{1}H NMR δ 3.56 (dd, *J* = 2.1 Hz, *J* = 10.3 Hz, H_a-6α), 3.60-3.80 (m, H-2α, H_b-6α, H-2β, H-3β, H-4β, H-5β, H_a-6β, H_b-6β), 3.79 (dd, *J* = 8.9 Hz, *J* = 10.3 Hz, H-4α), 3.87-3.89 (m, H-5α), 4.21 (dd, *J* = 8.9 Hz, *J* = 9.4 Hz, H-3α), 5.01 (d, *J* = 7.6 Hz, H-1β), 5.48 (d, *J* = 3.4 Hz, H-1α); ^{13}C NMR δ 68.2, 68.8, 70.8, 73.3, 73.4, 73.5, 75.02, 75.05, 75.11, 75.77, 75.78, 77.4, 77.7, 79.7, 82.0, 84.7, 95.4 (C-1α), 101.6 (C-1β); HRMS (ESI, α/β mixture) *m/z* calcd for 639.2717 ($C_{40}H_{40}O_6$+Na^+), found 639.2693. (Lit.,[16] α anomer: ^{1}H NMR δ 5.48 (*J* = 3.4 Hz, H-1); ^{13}C NMR δ 95.4 (C-1); β anomer: ^{1}H NMR δ 5.01 (*J* = 7.6 Hz, H-1); ^{13}C NMR δ 101.6 (C-1)).

1-Adamantyl 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranoside (22) (Table 1, Entry 12): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (5.6 mg, 0.0085 mmol), **11** (27.1 mg, 0.18 mmol), and **1** (89.9 mg, 0.17 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **22** (PTLC; EtOAc/hexane = 1/3, 65.2 mg, 58%, a mixture of α and β anomers) as a colorless oil and **26** (15.0 mg, 17%). ^{1}H NMR δ 1.56-2.17 (30H, m, 1-adamantyl), 3.42-3.50 (m, H-2β, H-4β, H-5β), 3.53 (dd, *J* = 4.1 Hz, *J* = 9.6 Hz, H-2α), 3.60-3.67 (m, H_a-6α, H-4α, H_a-6β, H-3β), 3.73 (dd, *J* = 2.1 Hz, *J* = 11.0 Hz, H_b-6β), 3.76 (dd, *J* = 3.4 Hz, *J* = 10.3 Hz, H_b-6α), 4.00-4.03 (m, H-5α), 4.01 (dd, *J* = 8.9 Hz, *J* = 9.6 Hz, H-3α), 4.70 (d, *J* = 7.6 Hz, H-1β), 5.28 (d, *J* = 3.4 Hz, H-1α); ^{13}C NMR δ 30.6, 30.7, 36.3, 36.3, 42.4, 42.8, 68.8, 69.5, 69.6, 72.8, 73.3, 73.4, 74.51, 74.54, 74.9, 75.1, 75.3, 75.5, 75.7, 78.1, 78.2, 80.1, 82.1, 82.3, 85.1, 89.8 (C-1α), 96.2 (C-1β); HRMS (ESI, α/β mixture) *m/z* calcd for 697.3500 ($C_{44}H_{50}O_6$+Na^+), found 697.3538. (Lit.,[18] β anomer: ^{1}H NMR δ 4.69 (*J* = 7.6 Hz, H-1); ^{13}C NMR δ 96.2 (C-1)).

2-Phenylethyl 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranoside (14) (Table 1, Entry 13): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (5.7 mg, 0.0087 mmol), **7** (21.3 mg, 0.17 mmol), and **2** (94.1 mg, 0.17 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **14** (PTLC; EtOAc/hexane = 1/3, 82.1 mg, 73%) as a colorless oil and **27** (14.7 mg, 16%) as a colorless oil. $[\alpha]_D^{22}$ +30.5° (*c* 4.1, $CHCl_3$);

^{1}H NMR δ 2.82 (2H, t, *J* = 6.9 Hz, CH_2CH_2Ph), 3.57-3.63 (2H, m, $CH_aH_bCH_2Ph$, H-5), 3.67 (1H, dd, *J* = 2.1 Hz, *J* = 11.0 Hz, H_a-6), 3.71-3.74 (2H, m, H-2, H_b-6), 3.84-3.88 (2H, m, $CH_aH_bCH_2Ph$, H-3), 3.95 (1H, t, *J* = 9.6 Hz, H-4), 4.84 (1H, d, *J* = 2.1 Hz, H-1); ^{13}C NMR δ 36.0, 68.1, 69.3, 71.8, 72.1, 72.5, 73.3, 74.7, 74.9, 74.9, 80.0, 97.7 (C-1, $J_{C1\text{-}H1}$ = 168.3 Hz); HRMS (ESI) *m/z* calcd for 667.3030 ($C_{42}H_{44}O_6$+Na^+), found 667.3073.

Octyl 2,3,4,6-Tetra-*O*-benzyl-D-mannopyranoside (19) (Table 1, Entry 14): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (5.3 mg, 0.0081 mmol), **8** (21.1 mg, 0.16 mmol), and **2** (87.3 mg, 0.16 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **19** (PTLC; EtOAc/hexane = 1/3, 84.9 mg, 81%, a mixture of α and β anomers) as a colorless oil and **27** (13.5 mg, 16%). ^{1}H NMR δ 0.88 (t, *J* = 6.9 Hz, $CH_3\alpha$), 1.26-1.52 (m, $CH_2(CH_2)_6CH_3$), 3.35 (ddd, *J* = 2.8 Hz, *J* = 6.9 Hz, *J* = 9.6 Hz, $CH_aH_b(CH_2)_6CH_3\alpha$), 3.65 (ddd, *J* = 2.8 Hz, *J* = 6.9 Hz, *J* = 9.6 Hz, $CH_aH_b(CH_2)_6CH_3\alpha$), 3.72-3.80 (m, H-2α, H-5α, H_a-6α, H_b-6α), 3.91 (dd, *J* = 3.4 Hz, *J* = 9.6 Hz, H-3α), 3.99 (t, *J* = 9.6 Hz, H-4α), 4.37 (d, *J* = 0.7 Hz, H-1β), 4.86 (d, *J* = 1.4 Hz, H-1α); ^{13}C NMR δ 14.1, 14.5, 22.61, 22.63, 26.08, 26.12, 29.16, 29.24, 29.3, 29.4, 29.7, 31.8, 67.6, 69.3, 69.7, 70.0, 71.3, 71.7, 72.1, 72.5, 73.3, 73.4, 73.5, 73.6, 74.8, 74.9, 75.0, 75.1, 75.9, 80.3, 82.3, 97.8 (C-1α, $J_{C1\text{-}H1}$ = 165.7 Hz), 101.7 (C-1β, $J_{C1\text{-}H1}$ = 152.6 Hz); HRMS (ESI, α/β mixture) *m/z* calcd for 675.3656 ($C_{42}H_{52}O_6$+Na^+), found 675.3663. (Lit.,[19] α anomer: ^{1}H NMR δ 4.86 (*J* = 2.1 Hz, H-1); ^{13}C NMR δ 97.8 (C-1)).

2-Phenylethyl 2,3,4,6-Tetra-*O*-benzyl-D-galacutopyranoside (15) (Table 1, Entry 15): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (4.6 mg, 0.007 mmol), **7** (17.1 mg, 0.14 mmol), and **3** (75.9 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **15** (PTLC; EtOAc/hexane = 1/3, 63.6 mg, 70%, a mixture of α and β anomers) as a colorless oil and **28** (7.6 mg, 10%) as a colorless oil. ^{1}H NMR δ 2.91-2.97 (m, CH_2CH_2Ph), 3.92 (dd, *J* = 2.8 Hz, *J* = 9.6 Hz, H-3α), 4.03 (dd, *J* = 3.4 Hz, *J* = 9.6 Hz, H-2α), 4.15-4.19 (m, $CH_aH_bCH_2Ph\beta$), 4.37 (d, *J* = 7.6 Hz, H-1β), 4.83 (d, *J* = 3.4 Hz, H-1α); ^{13}C NMR δ 36.0, 36.2, 68.6, 68.8, 68.9, 69.2, 70.5, 73.0, 73.1, 73.2, 73.30, 73.36, 73.39, 73.5, 74.4, 74.7, 75.0, 75.1, 76.5, 78.8, 79.5, 82.1, 97.4 (C-1α), 103.9 (C-1β); HRMS (ESI, α/β mixture) *m/z* calcd for 667.3030 ($C_{42}H_{44}O_6$+Na^+), found 667.3011.

2-Phenylethyl 2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (16) (Table 1, Entry 16): The same procedure used for the preparation of **13** using $Bi(OTf)_3$ (6.8 mg, 0.01 mmol), **7** (24 μL, 0.2 mmol), and **4** (95.2 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **16** (PTLC; EtOAc/hexane = 1/3, 59.5 mg, 51%, a mixture of α and β anomers) as a colorless oil and **29** (31.2 mg, 33%) as a colorless oil. ^{1}H NMR δ 2.92-2.99 (4H, m, CH_2CH_2Ph), 3.34 (dd, *J* = 3.4 Hz, *J* = 10.3 Hz, H-2α), 3.84-3.88 (m,

CH_aH$_b$CH$_2$Phα), 3.95 (t, *J* = 9.6 Hz, H-3α), 4.12-4.16 (m, CH_aH$_b$CH$_2$Phβ), 4.27 (d, *J* = 7.6 Hz, H-1β), 4.93 (d, *J* = 3.4 Hz, H-1α); ^{13}C NMR δ 36.0, 36.2, 63.3, 66.4, 68.2, 68.6, 68.9, 70.6, 70.9, 73.4, 73.5, 74.8, 75.0, 75.3, 75.5, 77.7, 78.2, 80.1, 83.1, 97.6 (C-1α), 102.1 (C-1β); HRMS (ESI, α/β mixture) *m/z* calcd for 602.2625 ($C_{35}H_{37}O_5N_3$+Na$^+$), found 602.2668.

2-Phenylethyl 2,3,5-Tri-*O*-benzyl-D-arabinofuranoside (17) (Table 1, Entry 17): The same procedure used for the preparation of **13** using Bi(OTf)$_3$ (7.9 mg, 0.012 mmol), **7** (29.3 mg, 0.24 mmol), and **6** (101.2 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) gave the desired glycoside **17** (PTLC; EtOAc/hexane = 1/3, 102.6 mg, 81%, a mixture of α and β anomers) as a colorless oil and **30** (4.5 mg, 5%) as a colorless oil. ^{1}H NMR δ 2.86 (t, *J* = 6.9 Hz, CH$_2$CH_2Phβ), 2.90 (t, *J* = 6.9 Hz, CH$_2$CH_2Phα), 3.42 (d, *J* = 6.2 Hz, H$_a$-5β, H$_b$-5β), 3.57 (dd, *J* = 5.5 Hz, *J* = 11.0 Hz, H$_a$-5α), 3.57 (ddd, *J* = 2.8 Hz, *J* = 6.9 Hz, *J* = 10.3 Hz, CH_aH$_b$CH$_2$Phβ), 3.61-3.66 (m, CH_aH$_b$CH$_2$Phα, H$_b$-5α), 3.87 (ddd, *J* = 2.8 Hz, *J* = 6.9 Hz, *J* = 9.6 Hz, CH$_a$$H_bCH_2$Phβ), 3.91 (dd, *J* = 2.8 Hz, *J* = 6.9 Hz, H-3α), 3.97 (ddd, *J* = 2.8 Hz, *J* = 6.9 Hz, *J* = 9.6 Hz, CH$_a$$H_bCH_2$Phα), 4.00 (d, *J* = 2.1 Hz, H-2α), 4.03 (dd, *J* = 4.1, 6.9 Hz, H-2β), 4.07-4.11 (m, H-3β, H-4β), 4.13-4.16 (m, H-4α), 4.86 (d, *J* = 4.1 Hz, H-1β), 5.02 (s, H-1α); ^{13}C NMR δ 36.0, 36.1, 68.3, 68.4, 69.6, 71.8, 72.0, 72.25, 72.28, 72.5, 73.2, 73.3, 80.2, 80.4, 83.3, 83.4, 84.2, 88.3, 100.4 (C-1β), 106.2 (C-1α); HRMS (ESI, α/β mixture) *m/z* calcd for 547.2455 ($C_{34}H_{36}O_5$+Na$^+$), found 547.2446. A part of α anomer was isolated. α Anomer: $[\alpha]_D^{25}$ +46.6° (*c* 4.1, $CHCl_3$).

1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (24) (Table 1, Entry 18): The same procedure used for the preparation of **13** using Bi(OTf)$_3$ (6.8 mg, 0.01 mmol) and **5** (93.4 mg, 0.21 mmol) in CH_2Cl_2 (3 mL) gave **24** (PTLC; EtOAc/hexane = 1/2, 65.5 mg, 73%) as white crystals. $[\alpha]_D^{22}$ -30.6° (*c* 1, $CHCl_3$); ^{1}H NMR δ 3.34 (1H, s, H-2 or H-3), 3.35 (1H, s, H-2 or H-3), 3.59 (1H, s, H-4), 3.67 (1H, dd, *J* = 6.2 Hz, *J* = 6.9 Hz, H$_a$-6), 3.90 (1H, d, *J* = 6.9 Hz, H$_b$-6), 4.54-4.60 (1H, m, H-5), 5.46 (1H, s, H-1); ^{13}C NMR δ 65.3, 71.1, 71.7, 71.9, 74.3, 76.0, 76.1, 76.8, 100.6 (C-1); HRMS (ESI) *m/z* calcd for 455.1829 ($C_{27}H_{28}O_5$+Na$^+$), found 455.1858. (Lit.,[20] $[\alpha]_D^{20}$ -29.5° (*c* 1, $CHCl_3$); Lit.,[21] ^{1}H NMR δ 5.45 (bs, H-1)).

Allyl 2,3,4-Tri-*O*-benzyl-D-glucopyranoside (25) (Table 1, Entry 19): The same procedure used for the preparation of **13** using Bi(OTf)$_3$ (22.5 mg, 0.034 mmol), **12** (117.1 μL, 1.7 mmol), and **5** (77.4 mg, 0.17 mmol) in CH_2Cl_2 (3 mL) gave **25**α (PTLC; EtOAc/hexane = 1/2, 43.1 mg, 51%) as a colorless oil, **25**β (22.9 mg, 27%) as a colorless oil, and **24** (12.2 mg, 16%) as a colorless oil. Compound **25**α: $[\alpha]_D^{25}$ +46.6° (*c* 4.1, $CHCl_3$); ^{1}H NMR δ 3.51 (1H, dd, *J* = 3.4 Hz, *J* = 9.6 Hz, H-2), 3.54 (1H, dd, *J* = 8.9 Hz, *J* = 9.6 Hz, H-4), 3.67-3.72 (2H, m, H-5, H$_a$-6), 3.74-3.77 (1H, m, H$_b$-6), 3.97-4.00 (1H, m, CH_aH$_b$CH=CH$_2$), 4.04 (1H, dd, *J* = 8.9 Hz, *J* = 9.6 Hz, H-3), 4.14 (1H, dd, *J* = 5.5 Hz, *J* = 13.6 Hz,

$CH_aH_bCH=CH_2$), 4.77 (1H, d, *J* = 3.4 Hz, H-1), 5.22 (1H, dd, *J* = 1.4 Hz, *J* = 10.3 Hz, $CH_2CH=CH_aH_b$), 5.31 (1H, dd, *J* = 1.4 Hz, *J* = 17.2 Hz, $CH_2CH=CH_aH_b$), 5.92 (1H, m, $CH_2CH=CH_2$); ^{13}C NMR δ 61.8, 68.2, 70.8, 73.2, 75.0, 75.7, 77.4, 80.0, 81.9, 95.6 (C-1), 118.2, 133.6; HRMS (ESI) *m/z* calcd for 513.2248 ($C_{30}H_{34}O_6$+Na^+), found 513.2293. Compound **25**β: $[\alpha]_D^{22}$ +4.5° (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 3.35-3.37 (1H, m, H-5), 3.45 (1H, dd, *J* = 8.3 Hz, *J* = 8.9 Hz, H-2), 3.57 (1H, t, *J* = 9.6 Hz, H-4), 3.67 (1H, dd, *J* = 8.9 Hz, *J* = 9.6 Hz, H-3), 3.70-3.73 (1H, m, H_a-6), 3.85-3.88 (1H, m, H_b-6), 4.16 (1H, dd, *J* = 6.2 Hz, *J* = 13.1 Hz, $CH_aH_bCH=CH_2$), 4.40 (1H, dd, *J* = 5.5 Hz, *J* = 13.1 Hz, $CH_aH_bCH=CH_2$), 4.50 (1H, d, *J* = 7.6 Hz, H-1), 5.22 (1H, dd, *J* = 1.4 Hz, *J* = 10.3 Hz, $CH_2CH=CH_aH_b$), 5.35 (1H, dd, *J* = 2.1 Hz, *J* = 17.1 Hz, $CH_2CH=CH_aH_b$), 5.96 (1H, m, $CH_2CH=CH_2$); ^{13}C NMR δ 62.0, 70.7, 74.97, 75.01, 75.1, 75.7, 77.5, 82.3, 84.5, 102.8 (C-1), 117.5, 133.87; HRMS (ESI) *m/z* calcd for 513.2248 ($C_{30}H_{34}O_6$+Na^+), found 513.2253.

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranoside (26) (Table 2, Entry 4): To a stirred solution of $Bi(OTf)_3$ (8.3 mg, 0.013 mmol) in CH_2Cl_2 (3 mL) was added **1** (68.4 mg, 0.13 mmol) in the presence of anhydrous $CaSO_4$ (ca. 100 mg) under an Ar atmosphere. The resulting mixture was stirred at rt for 1 d. The same procedure used for the preparation of **13** was followed. The crude product was purified using a preparative silica gel TLC (EtOAc/hexane = 1/3) to provide the desired 1,1'-disaccharide **26** (57.0 mg, 85%, a mixture of αα, αβ, and ββ isomers) as a colorless oil. ^{1}H NMR δ 3.36-3.38 (m, H_a-6αα), 3.48-3.54 (m, H_b-6αα, H-2αβ-β, H-5ββ), 3.53 (dd, *J* = 7.6 Hz, *J* = 8.2 Hz, H-2ββ), 3.57-3.65 (2H, m, H-2αα, H-2αβ-α), 3.68 (1H, t, *J* = 9.6 Hz, H-4αα), 3.76 (dd, *J* = 7.6 Hz, *J* = 10.3 Hz, H-4αβ-α), 4.02 (1H, dd, *J* = 8.9 Hz, *J* = 9.6 Hz, H-3αα-α), 4.09 (1H, t, *J* = 9.6 Hz, H-3αβ-α), 4.15-4.17 (1H, m, H-5αα-α), 4.58 (1H, d, *J* = 7.6 Hz, H-1αβ-β), 4.90 (d, *J* = 8.2 Hz, H-1ββ), 5.16 (1H, d, *J* = 3.4 Hz, H-1αβ-α), 5.23 (1H, d, *J* = 3.4 Hz, H-1αα-α); ^{13}C NMR δ 68.1, 68.9, 70.6, 73.5, 74.6, 74.97, 75.03, 75.6, 77.6, 77.7, 79.3, 81.7, 81.9, 82.2, 84.6, 94.4 (C-1αα), 99.3 (C-1ββ), 99.4 (C-1αβ-α), 104.1 (C-1αβ-β); HRMS (ESI, isomer mixture) *m/z* calcd for 1085.4810 ($C_{68}H_{70}O_{11}$+Na^+), found 1085.4798. A part of ββ isomer was isolated. ββ Isomer: $[\alpha]_D^{20}$ +15.9° (*c* 0.42, $CHCl_3$). (Lit.,[22] αα isomer: ^{13}C NMR δ 94.26 (C-1); αβ isomer: ^{13}C NMR δ 99.54 (C-1α), 104.27 (C-1β)).

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranoside (27) (Table 2, Entry 9): A similar procedure as employed for the preparation of **26** by stirring both $Bi(OTf)_3$ (12.5 mg, 0.019 mmol) and **2** (103.2 mg, 0.19 mmol) in CH_2Cl_2 (3 mL) at rt for 1 h gave the desired 1,1'-disaccharide **27** (PTLC; EtOAc/hexane = 1/3, 86.0 mg, 85%) as a colorless oil. $[\alpha]_D^{25}$ +30.2° (*c* 0.88, $CHCl_3$); ^{1}H NMR δ 3.53-3.56 (2H, m, H-5), 3.60 (2H, dd, *J* = 2.1 Hz, *J* = 3.4 Hz, H-2), 3.63 (2H, dd, *J* = 2.1 Hz, *J* = 11.0 Hz, H_a-6), 3.69-3.72 (4H, m, H_b-6, H-3), 3.97 (2H, dd, *J* = 9.6 Hz, *J* = 10.3 Hz, H-4),

5.20 (2H, d, J = 2.1 Hz, H-1); ^{13}C NMR δ 69.0, 72.1, 72.4, 72.6, 73.5, 74.0, 74.6, 75.3, 79.5, 93.3 (C-1, $J_{C1\text{-}H1}$ = 167.5 Hz); HRMS (ESI) *m/z* calcd for 1085.4810 ($C_{68}H_{70}O_{11}$+Na^+), found 1085.4823. (Lit.,[22] [α]$_D^{20}$ +40° (*c* 0.85, $CHCl_3$); ^{13}C NMR δ 93.25 (C-1)).

2,3,4,6-Tetra-*O*-benzyl-D-galactopyranosyl 2,3,4,6-Tetra-*O*-benzyl-D-galactopyranoside (28) (Table 2, Entry 10): A similar procedure as employed for the preparation of **26** by stirring both $Bi(OTf)_3$ (6.4 mg, 0.0098 mmol) and **3** (52.9 mg, 0.098 mmol) in CH_2Cl_2 (3 mL) at 0 °C for 1 d gave the desired 1,1'-disaccharide **28** (PTLC; EtOAc/hexane = 1/3, 36.3 mg, 70%, a mixture of αα and αβ isomers) as a colorless oil. ^{1}H NMR δ 4.54 (1H, d, J = 7.6 Hz, H-1αβ-β), 5.20 (1H, d, J = 3.4 Hz, H-1αβ-α), 5.28 (2H, d, J = 4.1 Hz, H-1αα); ^{13}C NMR δ 93.5 (C-1αα), 99.8 (C-1αβ-α), 103.7 (C-1αβ-β); HRMS (ESI, isomer mixture) *m/z* calcd for 1085.4810 ($C_{68}H_{70}O_{11}$+Na^+), found 1085.4816. A part of αα isomer was isolated. αα Isomer: [α]$_D^{21}$ +74.5° (*c* 0.81, $CHCl_3$). (Lit.,[22] αα isomer: [α]$_D^{20}$ +147.7° (*c* 0.65, $CHCl_3$); ^{13}C NMR δ 93.54 (C-1); αβ isomer: ^{13}C NMR δ 99.86 (C-1α), 103.82 (C-1β)).

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl
2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (29) (Table 2, Entry 13): A similar procedure as employed for the preparation of **26** by stirring both $Bi(OTf)_3$ (142.5 mg, 0.22 mmol) and **4** (103.8 mg, 0.22 mmol) in CH_2Cl_2 (3 mL) at rt for 1 d gave the desired 1,1'-disaccharide **29** (PTLC; EtOAc/hexane = 1/3, 53.8 mg, 53%, a mixture of αα, αβ, and ββ isomers) as a colorless oil. ^{1}H NMR δ 4.33 (1H, d, J = 7.56 Hz, H-1αβ-β), 4.72 (1H, d, J = 8.25 Hz, H-1ββ), 5.17 (1H, d, J = 3.44 Hz, H-1αβ-α), 5.21 (1H, d, J = 3.44 Hz, H-1αα); ^{13}C NMR δ 95.4 (C-1αα), 97.6 (C-1αβ-α), 101.3 (C-1αβ-β), 103.5 (C-1ββ); HRMS (ESI, isomer mixture) *m/z* calcd for 955.4001 ($C_{54}H_{56}O_9N_6$+Na^+), found 955.4026.

2,3,5-Tri-*O*-benzyl-D-arabinofuranosyl 2,3,5-Tri-*O*-benzyl-D-arabinofuranoside (30) (Table 2, Entry 14): A similar procedure as employed for the preparation of **26** by stirring both $Bi(OTf)_3$ (15.8 mg, 0.024 mmol) and **5** (101.2 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) at 0 °C for 3.5 h gave the desired 1,1'-disaccharide **30**αα (PTLC; EtOAc/hexane = 1/2, 78.2 mg, 79%) as a colorless oil and **30**αβ (13.7 mg, 14%) as a colorless oil. αα Isomer: [α]$_D^{22}$ +54.9° (*c* 3.9, $CHCl_3$); ^{1}H NMR δ 3.61-3.64 (2H, m, H_a-5), 3.65-3.68 (2H, m, H_b-5), 3.94-3.96 (2H, m, H-3), 4.10-4.11 (2H, m, H-2), 4.24-4.27 (2H, m, H-4), 5.50 (2H, s, H-1); ^{13}C NMR δ 69.7, 71.8, 72.1, 73.4, 81.2, 83.7, 87.9, 102.1 (C-1). HRMS (ESI) *m/z* calcd for 845.3660 ($C_{52}H_{54}O_9$+Na^+), found 845.3686. (Lit.,[23] αα isomer: ^{1}H NMR δ 5.51 (s)). αβ Isomer: [α]$_D^{25}$ +18.5° (*c* 0.69, $CHCl_3$); ^{1}H NMR δ 3.56-3.63 (3H, m, H_a-5α, H_b-5α, H_a-5β), 3.67 (1H, dd, J = 6.2 Hz, J = 10.3 Hz, H_b-5β), 3.99 (1H, dd, J = 2.8 Hz, J = 6.2 Hz, H-3α), 4.10-4.15 (4H, m, H-2α, H-2β, H-3β, H-4β), 4.30-4.32 (1H, m, H-4α), 5.18 (1H, d, J = 3.4 Hz, H-1β), 5.20 (1H, s, H-1α); ^{13}C NMR δ 69.5

(C-5α), 71.7 (*C*H_2Ph), 72.1 (*C*H_2Ph), 72.2 (*C*H_2Ph), 72.6 (*C*H_2Ph), 72.7 (C-5β), 73.1 (*C*H_2Ph), 73.3 (*C*H_2Ph), 80.8 (C-4β), 81.4 (C-4α), 83.58 (C-3α), 83.62 (C-2β or C-3β), 84.56 (C-2β or C-3β), 87.8 (C-2α), 99.5 (C-1β), 106.1 (C-1α); HRMS (ESI) *m/z* calcd for 845.3660 ($C_{52}H_{54}O_9$+Na^+), found 845.3659.

2,3,5-Tri-*O*-benzyl-D-arabinofuranosyl 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranoside (31) (Table 2, Entry 15): A similar procedure as employed for the preparation of **26** by stirring $Bi(OTf)_3$ (11.0 mg, 0.017 mmol), **1** (135.7 mg, 0.25 mmol), and **6** (70.5 mg, 0.17 mmol) in CH_2Cl_2 (3 mL) at 0 °C for 3.5 h gave the desired 1,1'-disaccharide **31** (PTLC; EtOAc/hexane = 1/4, 117.3 mg, 74%, a mixture of αα, αβ, βα, and ββ (Glc/Ara linkages: 31/31/31/7) isomers) as a colorless oil. ^{1}H NMR δ 4.62 (d, *J* = 8.2 Hz, H-1βα(Glc)), 4.78-4.80 (m, H-1ββ(Glc)), 5.20 (d, *J* = 3.4 Hz, H-1αβ(Glc)), 5.29 (d, *J* = 4.2 Hz, H-1'αβ(Ara)), 5.40 (1H, d, *J* = 3.4 Hz, H-1αα(Glc)), 5.42(1H, s, H-1'αα(Ara)), 5.43 (s, H-1'βα(Ara)), 5.60(d, *J* = 3.4 Hz, H-1'ββ(Ara));^{13}C NMR δ 92.7 (C-1αα(Glc)), 96.1 (C-1'ββ(Ara)), 96.2 (C-1αβ(Glc)), 97.5 (C-1ββ(Glc)), 100.6 (C-1'αβ(Ara)), 101.4 (C-1βα(Glc)), 102.0 (C-1'αα(Ara)), 106.6 (C-1'βα(Ara)); HRMS (ESI, isomer mixture) *m/z* calcd for 965.4235 ($C_{60}H_{62}O_{10}$+Na^+), found 965.4237.

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