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A SYNTHETIC APPROACH TO ANHYDROKETOPYRANOSES HAVING A 6,8-DIOXABICYCLO[3.2.1]OCTANE STRUCTURE FROM KETOPYRANOSES†

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†Dedicated to Professor Dr. Albert Eschenmoser on his 85th birthday.

Abstract – We investigated a synthetic approach to the anhydroketopyranoses having a 6,8-dioxabicyclo[3.2.1]octane structure from **D**-glucopyranose derivatives. The paper describes the nucleophilic addition of the organometallic reagents RLi or RMgX to the glucono-1,5-lactone derivatives to produce the ketopyranose derivatives having a glucose backbone and their intramolecular cyclization into the desired structural anhydroketopyranoses.

INTRODUCTION

The anhydroketopyranoses having a 6,8-dioxabicyclo[3.2.1]octane structure are found in biologically important natural products such as *Sedum spectabile*,[1] *Smallanthus sonchifolius*,[2] and *Coriaria japonica*.[3] Some of them have been prepared by the acid-catalyzed conversions of aldoses[4] and by the intramolecular cyclization of *C*-glycopyranosides via the intramolecular hydrogen abstraction reaction using radical species.[5] However, there is a limit to the structure of the anhydroketopyranoses that these methods can synthesize. It is important to develop convenient and useful methods for producing the various types of anhydroketopyranoses.

The anhydroketopyranoses having a 6,8-dioxabicyclo[3.2.1]octane can be structurally regarded as intramolecular *O*-ketopyranosides. Therefore, we investigated the anydroketopyranosylation based on the intramolecular *O*-ketosidation to synthesize the anhydroketopyranoses from ketopyranoses. The ketopyranoses used in the reaction were the **D**-glucopyranose derivatives whose anomeric carbons were bound to functional groups via a carbon–carbon linkage, i.e., '1-*C*-functionalized glucopyranoses'. Our study showed that these ketopyranoses could be converted into anhydroketopyranoses using 5 mol%

trifluoromethanesulfonic acid (TfOH).[6] We also applied this anydroketopyranosylation to the synthesis of a naturally occurring anhydroketopyranose found in *Coriaria japonica*.[7,8]

The anhydroketopyranosylation method requires the appropriately protected ketopyranose derivatives having a C-6 hydroxy group. The addition reaction of the organometallic reagents RLi or RMgX to a protected sugarlactone derivative is a generally convenient technique for synthesizing various ketopyranoses.[9] Prior to the anhydroketopyranosylation research, we had investigated the preparation of several appropriate ketopyranose derivatives having a **D**-glucose backbone from a 6-*O*-acetyl-**D**-glucono-1,5-lactone derivative according to the protocol. This investigation led us to the finding that the nucleophilic susceptibility of the two carbonyl carbon atoms, at C-1 and within the C-6 acetyl group of the lactones, remarkably varied based on the RLi or RMgX species.

This full paper comprehensively describes a synthetic approach to the anhydroketopyranoses having a 6,8-dioxabicyclo[3.2.1]octane structure from the ketopyranose derivatives. It consists of (1) the nucleophilic addition of the organometallic reagents, RLi or RMgX, to the 6-*O*-acetyl-**D**-glucono-1,5-lactone to produce the ketopyranose derivatives with a **D**-glucose backbone, and (2) the anhydroketopyranosylation to convert the ketopyranose derivatives into the desired structural anhydroketopyranoses based on the intramolecular *O*-ketosidation. The former part describes in detail our interesting findings about the nucleophilic reaction behaviors of the organometallic reagents to the lactone derivative, which is useful information for preparing the ketopyranose derivatives.

RESULTS AND DISCUSSION

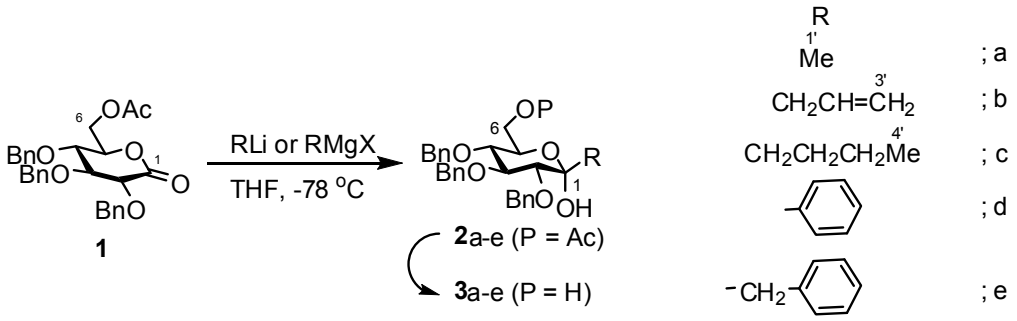
1. Nucleophilic addition of RLi or RMgX to 6-*O*-acetyl-D-glycono-1,5-lactone

We investigated the nucleophilic addition to the 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-**D**-glucono-1,5-lactone (**1**)[10] obtained by the oxidation of 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-**D**-glucopyranose using DMSO-Ac_2O, as shown in Scheme 1. The main purpose of this study was to chemoselectively introduce the functional groups into the carbonyl carbon atom at the C-1 of **1** to produce the corresponding ketopyranose derivatives having a **D**-glucose backbone. As the nucleophiles of the organometallic reagents, methyllithium (MeLi), allylmagnesium bromide (AllMgBr), *n*-butyllithium (*n*-BuLi), phenylmagnesium bromide (PhMgBr), and benzylmagnesium chloride ($PhCH_2MgCl$) were used. The addition reaction of the nucleophile (2.4 equiv.) to **1** was carried out in dry THF at -78 ºC. These results are shown in Table 1.

The reaction of **1** with MeLi produced the two products, 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-*C*-methyl-**D**-glucopyranose (**2**a) and 2,3,4-tri-*O*-benzyl-1-*C*-methyl-**D**-glucopyranose (**3**a) in 14% and 64% yields, respectively.

The reaction of **1** with AllMgBr and *n*-BuLi similarly produced the products 6-*O*-acetyl-1-*C*-allyl-2,3,4-tri-*O*-benzyl-**D**-glucopyranose (**2**b) and 1-*C*-allyl-2,3,4-tri-*O*-benzyl-**D**-glucopyranose (**3**b) in

11% and 68% yields, and 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-*C*-*n*-butyl-**D**-glucopyranose (**2**c) and 2,3,4-tri-*O*-benzyl-1-*C*-*n*-butyl-**D**-glucopyranose (**3**c) in 64% and 12% yields, respectively. In addition, the addition reaction of MeLi (1.2 equiv.) to **1** gave **2**a and **3**a in 63% and 10% yields, respectively.



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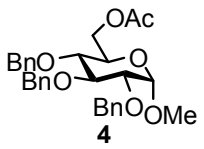
Scheme 1

Table 1. Nucleophilic addition to **1** using RLi or RMgX

Entry[a]	Nucleophile	Product (Yield/%)	
1	MeLi	**2**a (14)	**3**a (64)
2	AllMgBr	**2**b (11)	**3**b (68)
3	*n*-BuLi	**2**c (64)	**3**c (12)
4[b]	MeLi	**2**a (63)	**3**a (10)
5	PhMgBr	**2**d (89)	**3**d (Trace)
6	$PhCH_2MgCl$	**2**e (82)	**3**e (Trace)

[a]Reaction conditions: molar ratio; **1**: nucleophile = 1: 2.4; solvent = THF; temperature = -78 °C. [b]Molar ratio; **1**: nucleophile = 1: 1.2.



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These results showed that the nucleophiles attacked both carbonyl carbon atoms, C-1 and within the C-6 acetyl group, and that the bulky nucleophile tended not to attack the carbonyl carbon atom within the C-6 acetyl group. It is also noteworthy that there was no case when only the C-6 acetyl group was selectively deprotected. Based on these observations, the carbonyl carbon atom C-1 was more reactive to these nucleophiles than the carbonyl carbon atom within the C-6 acetyl group.

The differences in susceptibility to nucleophilic attack between the two carbonyl carbon atoms, C-1 and within the C-6 acetyl group, can be explained by the stereoelectronic effect shown in Figure 1.[11] The C-6 acetyl group assumes the Z-conformation and is stabilized by the n-$\sigma^*_{C\text{-}O}$ interaction between the lone pair on the OR' oxygen and the σ* antibonding orbital of the C=O group. This interaction never takes place in lactones having the E-conformation. Thus, the carbonyl carbon atom C-1 will indicate the higher reactivity than the carbonyl carbon atom within the C-6 acetyl group.

Ester (Z-conformation) Lactone (E-conformation)

Figure 1

Furthermore, the nucleophilic reagents, PhMgBr and $PhCH_2MgCl$, were utilized. The addition of PhMgBr or $PhCH_2MgCl$ to **1** gave 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-*C*-phenyl-**D**-glucopyranose (**2**d) and 6-*O*-acetyl-1-*C*-benzyl-2,3,4-tri-*O*-benzyl-**D**-glucopyranose (**2**e) in 89% and 82% yields, respectively, with almost no production of the deacetylated **D**-glucopyranoses (**3**d and **3**e). When we attempted the deacetylation reaction using methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-**D**-glucopyranoside (**4**) by PhMgBr or $PhCH_2MgCl$, its C-6 acetyl group was not removed under the given reaction conditions using the nucleophile (1.2 equiv.) in dry THF at -78 ºC. This indicates that the PhMgBr and $PhCH_2MgCl$ nucleophiles lack the potential nucleophilicity to attack the carbonyl carbon atom within the C-6 acetyl group of **4**. It became evident that the PhMgBr and $PhCH_2MgCl$ nucleophiles chemoselectively attacked the C-1 carbonyl carbon atom of **1** to produce the ketopyranose derivatives (**2**d and **2**e). As already mentioned, we clarified the nucleophilic susceptibility of the two carbonyl carbon atoms, C-1 and within the C-6 acetyl group, of **1** to the RLi or RMgX species.

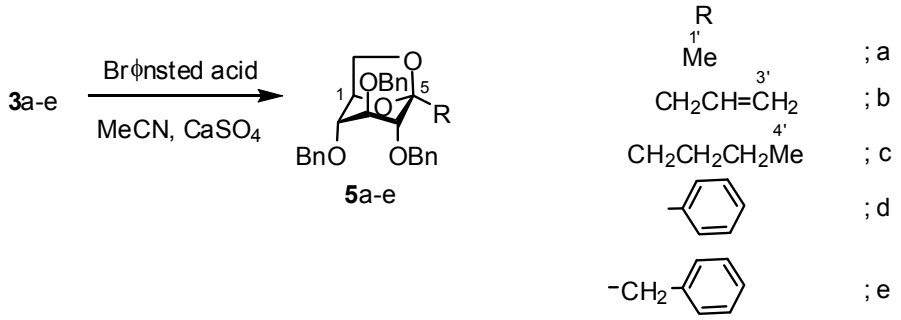
The C-6 acetyl group of **2**a-e was quantitatively removed using NaOMe in MeOH to produce the desired ketopyranose derivatives **3**a-e.

2. Conversion of ketopyranose derivatives into anhydroketopyranoses

We first investigated the conversion of **3**a into the corresponding anhydroketopyranose (**5**a) having a 6,8-dioxabicyclo[3.2.1]octane structure by the anhydroketopyranosylation based on the intramolecular *O*-ketosidation, as shown in Scheme 2. Brϕnsted acids were considered to be the useful activating reagents for this dehydration condensation type reaction as we previously reported for the intermolecular *O*-ketosidations using the ketopyranose derivatives.[12,13] Each reaction using 20 mol% of camphorsulfonic acid, Tf_2NH, and TfOH as the Brϕnsted acids in MeCN at 0 ºC gave the desired **5**a in 59%, 82%, and 84% yields, respectively. Tf_2NH and TfOH were very efficient for this reaction. The amount of TfOH was then varied. The reactions using only 1 or 0.5 mol% of TfOH proceeded to give **5**a in 86% and 68% yields, respectively. The maximum yield of 93% was attained for the reaction using 5 mol% of TfOH.

In order to investigate the effect of the methyl group at C-1 of **3**a on this anhydroketopyranosylation, we attempted the conversion of 2,3,4-tri-*O*-benzyl-**D**-glucopyranose (**6**), which had no methyl group at C-1, into 1,6-anhydro-2,3,4-tri-*O*-benzyl-**D**-glucopyranose (**7**). The production of **7** was scarcely observed by

TLC under similar reaction conditions using 20 mol% TfOH for 2 h, and the unreacted **6** was quantitatively recovered from the reaction mixture. This observation indicated that the presence of the methyl group at the anomeric position of **3**a drastically increased the reactivity of the anhydroketopyranosylation using **3**a. We inferred that the presence of the anomeric methyl group of **3**a would promote not only the generation of the oxocarbenium cation intermediate from **3**a, but also the conformation flip of the pyranosyl ring from $^4C_1$ into $^1C_4$ because of its equatorial orientation in the anhydroketopyranose form.

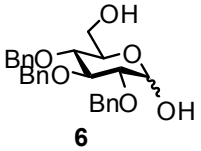


Scheme 2

Table 2. Conversion of ketopyranoses into anhydroketopyranoses having the 6,8-dioxabicyclo[3.2.1]octane structure

Entry[a]	ketopyanose	Brϕnsted acid (mol%)	Product (Yield/%)
1[b]	**3**a	Camphorsulfonic acid (20)	**5**a (59)
2	**3**a	Tf_2NH (20)	**5**a (82)
3	**3**a	TfOH (20)	**5**a (84)
4	**3**a	TfOH (5)	**5**a (93)
5	**3**a	TfOH (1)	**5**a (86)
6	**3**a	TfOH (0.5)	**5**a (68)
7	**6**	TfOH (20)	**7** (trace)
8	**3**b	TfOH (5)	**5**b (90)
9	**3**c	TfOH (5)	**5**c (95)
10	**3**d	TfOH (5)	**5**d (78), **5**d-t[c] (14)
11	**3**e	TfOH (5)	**5**e (70), **5**e-t[d] (26)
12	**8**	TfOH (5)	**5**a (80)

[a]Reaction conditions: solvent = MeCN; reaction time = 2 h; reaction temperature = 0 °C. [b]Reaction time = 30 h. [c]The twist-boat isomer of **5**d was produced. [d]The twist-boat isomer of **5**e was produced.



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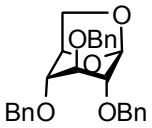

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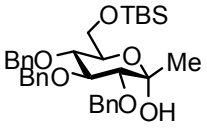

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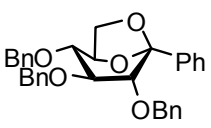
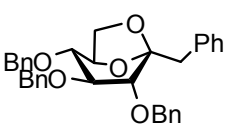


5d-t



5e-t

We next attempted the anhydroketopyranosylation of **3**b-e in order to demonstrate the synthesis of various kinds of anhydroketopyranoses (**5**b-e). The reactions using **3**b and **3**c in MeCN at 0 ºC for 2h in the presence of 5 mol% TfOH afforded the desired anhydroketopyranoses (**5**b and **5**c) in the excellent yields of 90% and 95%, respectively. The $^1C_4$ conformational **5**d and **5**e were similarly obtained from **3**d and **3**e in 78% and 70% yields, respectively. Interestingly, in these two reactions, the twist-boat conformational isomers **5**d-t and **5**e-t were also formed in 14% and 26 % yields, respectively.[14] Therefore, the total yields of these reactions reached 92% and 96%, respectively. These results showed that the difference in the 1-*C*-functional groups of **3**a-e had almost no influence on the anhydroketopyranosylation yields, although the benzyl and phenyl groups of **3**d and **3**e influenced the ring conformations of the anhydroketopyranoses.

Furthermore, the reaction using 2,3,4-tri-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-**D**-glucopyranose (**8**) also afforded **5**a in 80% yield. In this reaction, TfOH not only promoted the anhydroketopyranosylation, but also removed the TBS group of **8**, which is a great advantage of this anhydroketopyranosylation. In none of the above reactions did we observe the production of oligosaccharides by intermolecular *O*-ketosidation. These results are summarized in Table 2.

CONCLUSIONS

This paper described the synthetic approach to several anhydroketopyranoses having a 6,8-dioxabicyclo[3.2.1]octane structure from the ketopyranose derivatives. We clarified the nucleophilic reaction behaviors of RLi or RMgX to the **D**-glucono-1,5-lactone to produce the ketopyranose derivatives and the anhydroketopyranosylation characteristics to convert them into the desired structural anhydroketopyranoses.

EXPERIMENTAL

^{1}H 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.). All anhydrous solvents were purified according to standard methods.

6-*O*-Acetyl-2,3,4,-tri-*O*-benzyl-D-glucono-1,5-lactone (1)[10]: To a solution of 6-*O*-acetyl-2,3,4,-tri-*O*-benzyl-**D**-glucopyranose (3.5 g, 7.2 mmol) in DMSO (20 mL) was added Ac_2O (13 mL). After stirring overnight, the cool water was added to the reaction mixture. The reaction mixture

was extracted with AcOEt (200 mL), and the organic layer was washed with water and brine. After the organic layer was dried over anhydrous Na_2SO_4, the solvent was filtered and evaporated under reduced pressure. The crude product was purified by preparative flash silica-gel column chromatography (1:15 AcOEt-hexane) to give **1** (3.2 g, 92%) as an amorphous solid. *Rf* 0.48 (1:2 AcOEt-hexane); $[\alpha]_D^{25}$ +102° (c 3.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.00 (3H, s, CH_3), 3.75 (1H, dd, *J* = 5.5 Hz, *J* = 9.6 Hz, H-4), 3.95 (1H, t, *J* = 5.5 Hz, H-3), 4.13 (1H, d, *J* = 5.5 Hz, H-2), 4.24 (1H, dd, *J* = 4.1 Hz, *J* = 12.4 Hz, H-6a), 4.33 (1H, dd, *J* = 2.7 Hz, *J* = 12.4 Hz, H-6b), 4.43 (1H, d, *J* = 11.7 Hz, CH_2Ph), 4.44 (1H, d, *J* = 11.7 Hz, CH_2Ph), 4.63-4.66 (4H, m, H-5, CH_2Ph), 4.85 (1H, d, *J* = 11.7 Hz, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 20.7 (CH_3), 62.3 (C-6), 73.0 (CH_2Ph), 73.28 (CH_2Ph), 73.29 (CH_2Ph), 75.5 (C-4 or C-5), 75.6 (C-4 or C-5), 76.7 (C-2), 80.8 (C-3), 168.3 (C-1), 170.4 ($COCH_3$); HRMS(ESI): *m/z* calcd for 513.1884 ($C_{29}H_{30}O_7 \cdot Na^+$); Found: 513.1902.

6-*O*-Acetyl-2,3,4,-tri-*O*-benzyl-1-*C*-methyl-D-glucopyranose (2a) and 2,3,4,-tri-*O*-benzyl-1-*C*-methyl-D-glucopyranose (3a): To a solution of **1** (1 g, 2 mmol) in THF (5 mL) was added dropwise a 1.14 M Et_2O solution of MeLi (4.3 mL, 4.9 mmol) at -78 °C under an Ar atmosphere. After the resulting mixture was stirred at -78 °C for 1 h, the reaction was then quenched by the addition of water (5 mL). The reaction mixture was extracted with AcOEt (30 mL), and the organic layer was washed with water and brine. After the organic layer was dried over anhydrous Na_2SO_4, the solvent was filtered and evaporated under reduced pressure. The crude product was purified by preparative flash silica-gel column chromatography (1:10 → 1:4 → 1:2 AcOEt-hexane) to give **2**a (0.14 g, 14%) as an amorphous solid and **3**a (0.61 g, 64%) as an amorphous solid. **2**a: *Rf* 0.23 (1:2 AcOEt-hexane); ^{1}H NMR ($CDCl_3$): δ 1.39 (3H, s, H-1'), 2.03 (3H, s, $COCH_3$), 3.35 (1H, d, *J* = 9.6 Hz, H-2), 3.54 (1H, t, *J* = 9.6 Hz, H-4), 4.00 (1H, t, *J* = 9.6 Hz, H-3), 4.05-4.07 (1H, m, H-5), 4.23-4.28 (2H, m, H-6), 4.58 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.71 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.87 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.91 (2H, s, CH_2Ph), 4.94 (1H, d, *J* = 11.0 Hz, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 20.9 ($COCH_3$), 26.4 (C-1'), 63.3 (C-6), 69.7 (C-5), 74.9 (CH_2Ph), 75.6 (CH_2Ph), 75.8 (CH_2Ph), 78.0 (C-4), 83.2 (C-2), 83.5 (C-3), 97.3 (C-1), 170.9 (C=O); HRMS(ESI): *m/z* calcd for 529.2197 ($C_{30}H_{34}O_7 \cdot Na^+$); Found: 529.2242. **3**a: *Rf* 0.09 (1:2 AcOEt-hexane); ^{1}H NMR ($CDCl_3$): δ 1.30 (3H, s, H-1'), 3.26 (1H, d, *J* = 9.3 Hz, H-2), 3.52 (1H, t, *J* = 9.5 Hz, H-4), 3.64 (1H, dd, *J* = 4.2 Hz, *J* = 12.0 Hz, H-6a), 3.74 (1H, dd, *J* = 2.7 Hz, *J* =12.0 Hz, H-6b), 3.81-3.85 (1H, m, H-5), 3.91 (1H, t, *J* = 9.3 Hz, H-3), 4.61 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.64 (1H, d, *J* = 11.2 Hz, CH_2Ph), 4.80-4.88 (4H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 26.7 (C-1'), 61.9 (C-6), 72.0 (C-5), 74.9 (CH_2Ph), 75.6 (CH_2Ph), 75.7 (CH_2Ph), 78.0 (C-4), 83.2 (C-2), 83.4 (C-3), 97.3 (C-1); HRMS (ESI): *m/z* calcd for 487.2091 ($C_{28}H_{32}O_6 \cdot Na^+$); Found: 487.2138. The ordinary treatment of **2**a using NaOMe in MeOH quantitatively afforded **3**a.

6-*O*-Acetyl-1-*C*-allyl-2,3,4,-tri-*O*-benzyl-D-glucopyranose (2b) and 1-*C*-allyl-2,3,4,-tri-*O*-benzyl-D-glucopyranose (3b): The above same procedure using a 1.0 M diethyl ether solution of AllMgBr (0.75 mL, 0.750 mmol) and **1** (153 mg, 0.31 mmol) in THF (3 mL) gave **2**b (PTLC; 1:2 AcOEt-hexane, 19 mg, 11%) as an amorphous solid and **3**b (115 mg, 68%) as an amorphous solid. **2**b: *Rf* 0.41 (1:2 AcOEt-hexane); ^{1}H NMR ($CDCl_3$): δ 1.97 (3H, s, CH_3), 2.30 (1H, dd, *J* = 6.8 Hz, *J* = 13.7 Hz, H-1'a), 2.38 (1H, dd, *J* = 8.0 Hz, *J* = 13.7 Hz, H-1'b), 3.35 (1H, d, *J* = 9.5 Hz, H-2), 3.46 (1H, t, *J* = 9.5 Hz, H-4), 3.91-3.97 (1H, m, H-5), 3.98 (1H, t, *J* = 9.3 Hz, H-3), 4.16 (1H, dd, *J* = 4.4 Hz, *J* = 12.0 Hz, H-6a), 4.21 (1H, dd, *J* = 1.9 Hz, *J* = 11.7 Hz, H-6b), 4.52 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.63 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.88-4.92 (4H, m, CH_2Ph), 5.04-5.15 (2H, m, H-3'), 5.66-5.80 (1H, m, H-2'); ^{13}C NMR ($CDCl_3$): δ 20.9 (CH_3), 42.6 (C-1'), 63.1 (C-6), 69.6 (C-5), 74.9 (CH_2Ph), 75.4 (CH_2Ph), 75.6 (CH_2Ph), 78.1 (C-4), 81.4 (C-2), 83.6 (C-3), 97.5 (C-1), 120.3 (C-3'), 131.9 (C-2'), 170.8 (C=O); HRMS (ESI): *m/z* calcd for 555.2353 ($C_{32}H_{36}O_7 \cdot Na^+$); Found: 555.2371. **3**b: *Rf* 0.16 (1:2 AcOEt-hexane); ^{1}H NMR ($CDCl_3$): δ 2.38 (1H, dd, *J* = 6.9 Hz, *J* = 13.7 Hz, H-1'a), 2.46 (1H, dd, *J* = 7.6 Hz, *J* = 13.7 Hz, H-1'b), 3.41 (1H, d, *J* = 8.9 Hz, H-2), 3.58 (1H, t, *J* = 9.6 Hz, H-4), 3.71-3.75 (1H, m, H-6a), 3.80 (1H, dd, *J* = 2.1 Hz, *J* = 11.7 Hz, H-6b), 3.86-3.89 (1H, m, H-5), 4.04 (1H, t, *J* = 8.9 Hz, H-3), 4.68-4.70 (2H, m, CH_2Ph), 4.87-4.90 (2H, m, CH_2Ph), 4.92-4.95 (2H, m, CH_2Ph), 5.11-5.21 (2H, m, H-3'), 5.81 (1H, m, H-2'); ^{13}C NMR ($CDCl_3$): δ 42.7 (C-1'), 61.8 (C-6), 71.8 (C-5), 75.0 (CH_2Ph), 75.4 (CH_2Ph), 75.6 (CH_2Ph), 78.0 (C-4), 81.4 (C-2), 83.5 (C-3), 97.6 (C-1), 120.4 (C-3'), 131.8 (C-2'); HRMS (ESI): *m/z* calcd for 513.2248 ($C_{30}H_{34}O_6 \cdot Na^+$); Found: 513.2295. The ordinary treatment of **2**b using NaOMe in MeOH quantitatively afforded **3**b.

6-*O*-Acetyl-2,3,4,-tri-*O*-benzyl-1-*C*-butyl-D-glucopyranose (2c) and 2,3,4,-tri-*O*-benzyl-1-*C*-butyl-D-glucopyranose (3c): The above same procedure using a 1.59 M *n*-hexane solution of *n*-BuLi (0.39 mL, 0.61 mmol) and **1** (126 mg, 0.26 mmol) in THF (3 mL) gave **2**c (PTLC; 1:19 AcOEt-toluene, 90 mg, 64%) as a colorless oil and **3**c (16 mg, 12%) as an amorphous solid. **2**c: *Rf* 0.36 (1:2 AcOEt-hexane); ^{1}H NMR ($CDCl_3$): δ 0.85 (3H, t, *J* = 6.9 Hz, H-4'), 1.19-1.35 (4H, m, H-2', H-3'), 1.61-1.64 (2H, m, H-1'), 2.03 (3H, s, $COCH_3$), 3.42 (1H, d, *J* = 9.6 Hz, H-2), 3.51 (1H, t, *J* = 9.6 Hz, H-4), 4.02 (1H, t, *J* = 9.6 Hz, H-3), 4.02-4.05 (1H, m, H-5), 4.22 (1H, dd, *J* = 4.8 Hz, *J* = 11.7 Hz, H-6a), 4.30 (1H, dd, *J* = 2.1 Hz, *J* = 11.7 Hz, H-6b), 4.59 (1H, d, *J* = 10.3 Hz, CH_2Ph), 4.69 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.86-4.94 (4H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 14.0 (C-4'), 20.9 ($COCH_3$), 22.7 (C-3'), 24.6 (C-2'), 38.2 (C-1'), 63.2 (C-6), 69.6 (C-5), 75.0 (CH_2Ph), 75.5 (CH_2Ph), 75.6 (CH_2Ph), 78.2 (C-4), 81.3 (C-2), 83.8 (C-3), 98.4 (C-1), 170.8 (C=O); HRMS (ESI): *m/z* calcd for 571.2666 ($C_{33}H_{40}O_7 \cdot Na^+$); Found: 571.2687. **3**c: *Rf* 0.17 (1:2 AcOEt-hexane); ^{1}H NMR ($CDCl_3$): δ 0.85 (3H, t, *J* = 6.9 Hz, H-4'), 1.16-1.36 (4H, m, H-2', H-3'), 1.60-1.65 (2H, m, H-1'), 3.40 (1H, d, *J* = 8.9 Hz, H-2), 3.56 (1H, t, *J* = 9.6 Hz, H-4), 3.71-3.74 (1H, m,

H-6a), 3.81 (1H, bd, *J* = 11.7 Hz, H-6b), 3.87-3.91 (1H, m, H-5), 4.02 (1H, t, *J* = 9.6 Hz, H-3), 4.67-4.94 (6H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 14.0 (C-4'), 22.8 (C-3'), 24.6 (C-2'), 38.3 (C-1'), 61.9 (C-6), 71.7 (C-5), 74.9 (CH_2Ph), 75.4 (CH_2Ph), 75.6 (CH_2Ph), 78.1 (C-4), 81.2 (C-3), 83.6 (C-2), 98.4 (C-1); HRMS (ESI): *m/z* calcd for 529.2561 ($C_{31}H_{38}O_6 \cdot Na^+$); Found: 529.2610. The ordinary treatment of **2**c using NaOMe in MeOH quantitatively afforded **3**c.

6-*O*-Acetyl-2,3,4,-tri-*O*-benzyl-1-*C*-phenyl-D-glucopyranose (2d) and 2,3,4,-tri-*O*-benzyl-1-*C*-phenyl-D-glucopyranose (3d): The above same procedure using a 1.08 M THF solution of PhMgBr (0.95 mL, 1 mmol) and **1** (209 mg, 0.43 mmol) in THF (3 mL) gave **2**d (PTLC; 1:2 AcOEt-hexane, 215 mg, 89%) as a colorless oil. **2**d: *Rf* 0.43 (1:2 AcOEt-hexane); ^1H NMR ($CDCl_3$): δ 2.03 (3H, s, CH_3), 3.54 (1H, d, *J* = 8.9 Hz, H-2), 3.71 (1H, t, *J* = 8.9 Hz, H-4), 3.80 (1H, d, *J* = 10.3 Hz, CH_2Ph), 4.11 (1H, t, *J* = 8.9 Hz, H-3), 4.22-4.25 (1H, m, H-5), 4.31 (1H, dd, *J* = 4.2 Hz, *J* = 11.7 Hz, H-6a), 4.35 (1H, dd, *J* = 2.1 Hz, *J* = 11.7 Hz, H-6b), 4.39 (1H, d, *J* = 10.3 Hz, CH_2Ph), 4.64 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.88-4.92 (2H, m, CH_2Ph), 4.96 (1H, d, *J* = 11.0 Hz, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 20.9 (CH_3), 63.3 (C-6), 70.1 (C-5), 75.0 (CH_2Ph), 75.5 (CH_2Ph), 75.7 (CH_2Ph), 77.8 (C-4), 83.4 (C-3), 85.0 (C-2), 97.8 (C-1), 170.8 (C=O); HRMS (ESI): *m/z* calcd for 591.2353 ($C_{35}H_{36}O_7 \cdot Na^+$); Found 591.2398. The ordinary treatment of **2**d using NaOMe in MeOH quantitatively afforded **3**d as an amorphous solid. **3**d: *Rf* 0.18 (1:2 AcOEt-hexane); ^1H NMR ($CDCl_3$): δ 3.56 (1H, d, *J* = 9.0 Hz, H-2), 3.71 (1H, t, *J* = 9.6 Hz, H-4), 3.75 (1H, dd, *J* = 4.1 Hz, *J* = 11.7 Hz, H-6a), 3.80 (1H, d, *J* = 10.3 Hz, CH_2Ph), 3.85 (1H, m, H-6b), 3.89 (1H, m, H-5), 4.08 (1H, t, *J* = 8.9 Hz, H-3), 4.38 (1H, d, *J* = 10.3 Hz, CH_2Ph), 4.71 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.89-4.94 (3H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 62.0 (C-6), 72.3 (C-5), 75.0 (CH_2Ph), 75.4 (CH_2Ph), 75.7 (CH_2Ph), 78.1 (C-4), 83.3 (C-3), 85.1 (C-2), 97.9 (C-1); HRMS (ESI): *m/z* calcd for 549.2248 ($C_{33}H_{34}O_6 \cdot Na^+$); Found: 549.2250.

6-*O*-Acetyl-1-*C*-benzyl-2,3,4,-tri-*O*-benzyl-D-glucopyranose (2e) and 1-*C*-benzyl-2,3,4,-tri-*O*-benzyl-D-glucopyranose (3e): The above same procedure using a 1.0 M Et_2O solution of $PhCH_2MgCl$ (1.05 mL, 1 mmol) and **1** (214 mg, 0.44 mmol) in THF (3 mL) gave **2**e (PTLC; 1:2 AcOEt-hexane, 172 mg, 82%) as a colorless oil. **2**e: *Rf* 0.41 (1:2 AcOEt-hexane); ^1H NMR ($CDCl_3$): δ 2.02 (3H, s, CH_3) , 2.82 (1H, d, *J* = 13.7 Hz, H-1'a), 3.00 (1H, d, *J* = 13.7 Hz, H-1'b), 3.40 (1H, d, *J* = 8.9 Hz, H-2), 3.50 (1H, t, *J* = 9.6 Hz, H-4), 3.93-3.95 (1H, m, H-5), 4.09 (1H, t, *J* = 8.9 Hz, H-3), 4.24 (1H, dd, *J* = 4.9 Hz, *J* = 11.7 Hz, H-6a), 4.28 (1H, dd, *J* = 1.4 Hz, *J* = 11.7 Hz, H-6b), 4.59 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.72 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.87 (1H, d, *J* = 11.0 Hz, CH_2Ph), 4.90-4.94 (2H, m, CH_2Ph), 5.00 (1H, d, *J* = 11.0 Hz, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 20.9 (CH_3), 43.5 (C-1'), 63.0 (C-6), 69.5 (C-5), 75.0 (CH_2Ph), 75.4 (CH_2Ph), 75.7 (CH_2Ph), 78.3 (C-4), 81.3 (C-3), 83.8 (C-2), 97.7 (C-1), 170.7 (C=O); HRMS (ESI): *m/z* calcd for

605.2510 ($C_{36}H_{38}O_7 \cdot Na^+$); Found: 605.2532. The ordinary treatment of **2**e using NaOMe in MeOH quantitatively afforded **3**e as an amorphous solid. **3**e: *Rf* 0.25 (1:2 AcOEt-hexane); ^{1}H NMR ($CDCl_3$): δ 2.80 (1H, d, *J* = 13.0 Hz, H-1'a), 3.02 (1H, d, *J* = 13.8 Hz, H-1'b), 3.41 (1H, d, *J* = 9.0 Hz, H-2), 3.54 (1H, t, *J* = 9.6 Hz, H-4), 3.68-3.84 (3H, m, H-5, H-6), 4.08 (1H, t, *J* = 9.0 Hz, H-3), 4.65-5.03 (6H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 43.7 (C-1'), 62.0 (C-6), 71.6 (C-5), 75.0 (CH_2Ph), 75.4 (CH_2Ph), 75.7 (CH_2Ph), 78.2 (C-4), 81.4 (C-2), 83.7 (C-3), 97.5 (C-1); HRMS (ESI): *m/z* calcd for 563.2404 ($C_{34}H_{36}O_6 \cdot Na^+$); Found: 563.2443.

(1*R*,2*R*,3*S*,4*R*,5*R*)-2,3,4-Tris(benzyloxy)-5-methyl-6,8-dioxabicyclo[3.2.1]octane (5a): To a stirred solution of TfOH (0.48 μL, 0.0054 mmol) was added **3**a (50 mg, 0.11 mmol) in MeCN (2 mL) at 0 °C in the presence of dry $CaSO_4$ (ca. 100 mg) in an Ar atmosphere. The resulting mixture was stirred for 2 h. The reaction was then quenched by the addition of a sat. aq. $NaHCO_3$ solution (5 mL). The reaction mixture was extracted with AcOEt, and the organic layer was washed with water and a sat. aq. NaCl solution. After the organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure. The crude product was purified by preparative silica gel TLC (1:2 AcOEt-hexane) to give **5**a (45 mg, 93%) as a colorless oil. **5**a: *Rf* 0.54 (1:2 AcOEt-hexane); $[\alpha]_D^{23}$ -47.7° (c 1.54, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.49 (3H, s, H-1'), 3.23 (1H, s, H-4), 3.31 (1H, s, H-2), 3.59 (1H, s, H-3), 3.75 (1H, t, *J* = 6.9 Hz, H-7a), 3.96 (1H, d, *J* = 6.9 Hz, H-7b), 4.34-4.39 (3H, m, CH_2Ph), 4.53 (1H, m, CH_2Ph), 4.53 (1H, d, *J* = 6.2 Hz, H-1), 4.58-4.61 (2H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 21.0 (C-1'), 65.5 (C-7), 71.0 (CH_2Ph), 71.2 (CH_2Ph), 72.3 (CH_2Ph), 74.5 (C-2), 75.2 (C-3), 75.7 (C-1), 77.3 (C-4), 107.0 (C-5); HRMS (ESI): *m/z* calcd for 469.1991 ($C_{28}H_{30}O_5 \cdot Na^+$); Found: 469.2032.

(1*R*,2*R*,3*S*,4*R*,5*R*)-5-Allyl-2,3,4-tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (5b): The above same procedure using TfOH (0.95 μL, 0.011 mmol) and **3**b (104.9 mg, 0.21 mmol) in MeCN (2 mL) gave **5**b (PTLC; 1:2 AcOEt-hexane, 91.4 mg, 90%) as a colorless oil. **5**b: *Rf* 0.64 (1:2 AcOEt-hexane); $[\alpha]_D^{23}$ +7.6° (c 4.57, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.56 (1H, dd, *J* = 7.6 Hz, *J* = 14.4 Hz, H-1'a), 2.64 (1H, dd, *J* = 7.6 Hz, *J* = 14.4 Hz, H-1'b), 3.24 (1H, s, H-4), 3.26 (1H, s, H-2), 3.54 (1H, s, H-3), 3.66 (1H, dd, *J* = 6.2 Hz, *J* = 6.9 Hz, H-7a), 3.94 (1H, d, *J* = 6.9 Hz, H-7b), 4.29-4.34 (3H, m, CH_2Ph), 4.41-4.52 (3H, m, CH_2Ph), 4.56 (1H, d, *J* = 5.5 Hz, H-1), 5.03-5.05 (2H, m, H-3'), 5.74-5.79 (1H, m, H-2'); ^{13}C NMR ($CDCl_3$) δ 38.1 (C-1'), 65.7 (C-7), 70.9 (CH_2Ph), 71.5 (CH_2Ph), 72.2 (CH_2Ph), 74.6 (C-2), 74.9 (C-3), 75.5 (C-1), 76.2 (C-4), 107.2 (C-5), 118.4 (C-3'), 132.0 (C-2'); HRMS (ESI): *m/z* calcd for 495.2147 ($C_{30}H_{32}O_5 \cdot Na^+$); Found: 495.2195.

(1*R*,2*R*,3*S*,4*R*,5*R*)-2,3,4-Tris(benzyloxy)-5-butyl-6,8-dioxabicyclo[3.2.1]octane (5c): The above same

procedure using TfOH (0.53 μL, 0.006 mmol) and **3**c (53.6 mg, 0.11 mmol) in MeCN (2 mL) gave **5**c (PTLC; 1:2 AcOEt-hexane, 49.1 mg, 95%) as a colorless oil. **5**c: *Rf* 0.7 (1:2 AcOEt-hexane); $[\alpha]_D^{23}$ -36.7° (c 1.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.84 (3H, t, *J* = 6.9 Hz, H-4'), 1.13-1.19 (1H, m, H-2'a), 1.20-1.31 (2H, m, H-3'), 1.33-1.40 (1H, m, H-2'b), 1.75 (1H, dt, *J* = 4.1 Hz, *J* = 13.7 Hz, H-1'a), 1.90 (1H, dt, *J* = 3.4 Hz, *J* = 13.7 Hz, H-1'b), 3.25 (1H, s, H-4), 3.31 (1H, s, H-2), 3.60 (1H, s, H-3), 3.70 (1H, t, *J* = 6.9 Hz, H-7a), 3.98 (1H, d, *J* = 6.9 Hz, H-7b), 4.32-4.40 (3H, m, CH_2Ph), 4.49-4.57 (3H, m, CH_2Ph), 4.59 (1H, d, *J* = 6.2 Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 14.0 (C-4'), 22.9 (C-3'), 24.1 (C-2'), 32.9 (C-1'), 65.6 (C-7), 70.9 (CH_2Ph), 71.4 (CH_2Ph), 72.0 (CH_2Ph), 74.7 (C-2), 75.0 (C-3), 75.4 (C-1), 76.2 (C-4), 107.9 (C-5). HRMS (ESI): *m/z* calcd for 511.2460 ($C_{31}H_{36}O_5 \cdot Na^+$); Found: 511.2510.

(1*R*,2*R*,3*S*,4*R*,5*R*)-2,3,4-Tris(benzyloxy)-5-phenyl-6,8-dioxabicyclo[3.2.1]octane (5d): The above same procedure using TfOH (0.58 μL, 0.0065 mmol) and **3**d (67.9 mg, 0.13 mmol) in MeCN (2 mL) gave **5**d (PTLC; 1:2 AcOEt-hexane, 51.2 mg, 78%) as a colorless oil and **5**d-t (9 mg, 14%) as a colorless oil. **5**d: *Rf* 0.66 (1:2 AcOEt-hexane); $[\alpha]_D^{23}$ -3.5° (c 2.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.39 (1H, s, H-4), 3.50 (1H, s, H-2), 3.68 (1H, s, H-3), 3.81 (1H, t, *J* = 6.2 Hz, H-7a), 4.01-4.06 (2H, m, CH_2Ph), 4.07 (1H, d, *J* = 6.9 Hz, H-7b), 4.31-4.36 (2H, m, CH_2Ph), 4.56 (1H, d, *J* = 13.1 Hz, CH_2Ph), 4.67 (1H, d, *J* = 13.1 Hz, CH_2Ph), 4.79 (1H, d, *J* = 6.2 Hz, H-1); ^{13}C NMR ($CDCl_3$): δ 65.6 (C-7), 71.0 (CH_2Ph), 71.6 (CH_2Ph), 72.2 (CH_2Ph), 74.6 (C-2), 76.2 (C-3), 76.3 (C-1), 77.6 (C-4), 106.9 (C-5); HRMS (ESI): *m/z* calcd for 531.2147 ($C_{33}H_{32}O_5 \cdot Na^+$); Found: 531.2196. Its twist boat isomer (**5**d-t): *Rf* 0.59 (1:2 AcOEt-hexane); $[\alpha]_D^{23}$ -74.5° (c 0.47, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.55 (1H, s, H-2), 3.77 (1H, d, *J* = 5.5 Hz, H-4), 3.86 (1H, d, *J* = 5.5 Hz, H-3), 3.94 (1H, dd, *J* = 8.2 Hz, *J* = 5.5 Hz, H-7a), 3.95 (1H, d, *J* = 11.7 Hz, CH_2Ph), 4.40 (1H, d, *J* = 11.7 Hz, CH_2Ph), 4.42 (1H, d, *J* = 8.2 Hz, H-7b), 4.44 (1H, d, *J* = 12.4 Hz, CH_2Ph), 4.45 (1H, d, *J* = 12.4 Hz, CH_2Ph), 4.53 (1H, d, *J* = 12.4 Hz, CH_2Ph), 4.63 (1H, d, *J* = 6.2 Hz, H-1), 4.66 (1H, d, *J* = 12.4 Hz, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 66.1 (C-7), 71.2 (CH_2Ph), 72.4 (CH_2Ph), 73.3 (CH_2Ph), 75.0 (C-3), 75.4 (C-1), 76.9 (C-2), 77.7 (C-4), 107.6 (C-5); HRMS (ESI): *m/z* calcd for 531.2147 ($C_{33}H_{32}O_5 \cdot Na^+$); Found: 531.2178.

(1*R*,2*R*,3*S*,4*R*,5*R*)-5-Benzyl-2,3,4-tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (5e): The above same procedure using TfOH (0.53 μL, 0.006 mmol) and **3**e (64.4 mg, 0.12 mmol) in MeCN (2 mL) gave **5**e (PTLC; 1:2 AcOEt-hexane, 45.3 mg, 70%) as a colorless oil and **5**e-t (16.3 mg, 26%) as a colorless oil. **5**e: *Rf* 0.66 (1:2 AcOEt-hexane); $[\alpha]_D^{23}$ -35.1° (c 2.32, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.97 (1H, d, *J* = 13.4 Hz, H-1'a), 3.23 (1H, s, H-4), 3.29 (1H, s, H-2), 3.34 (1H, d, *J* = 13.7 Hz, H-1'b), 3.45 (1H, t, *J* = 6.9 Hz, H-7a), 3.60 (1H, s, H-3), 3.91 (1H, d, *J* = 6.9 Hz, H-7b), 4.33 (3H, m, CH_2Ph), 4.43 (1H, d, *J* = 12.4 Hz,

CH_2Ph), 4.50 (1H, d, *J* = 12.4 Hz, CH_2Ph), 4.53 (1H, d, *J* = 5.5 Hz, H-1), 4.56 (1H, d, *J* = 13.0 Hz, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 39.5 (C-1'), 65.7 (C-7), 70.9 (CH_2Ph), 71.5 (CH_2Ph), 72.0 (CH_2Ph), 74.5 (C-2), 74.9 (C-3), 75.3 (C-1), 76.8 (C-4), 107.2 (C-5); HRMS (ESI): *m/z* calcd for 545.2304 ($C_{34}H_{34}O_5 \cdot Na^+$); Found: 545.2354. Its twist boat isomer (**5**e-t): *Rf* 0.52 (1:2 AcOEt-hexane); $[\alpha]_D^{23}$ -19.3° (c 1.97, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 2.95 (1H, d, *J* = 14.4 Hz, H-1'a), 3.43 (1H, d, *J* = 14.4 Hz, H-1'b), 3.48 (1H, d, *J* = 1.4 Hz, H-2), 3.52 (1H, t, *J* = 5.5 Hz, H-7a), 3.56 (1H, d, *J* = 4.8 Hz, H-4), 3.81 (1H, d, *J* = 5.5 Hz, H-3), 4.11 (1H, d, *J* = 6.9 Hz, H-7b), 4.25 (1H, d, *J* = 11.6 Hz, CH_2Ph), 4.40 (1H, d, *J* = 5.5 Hz, H-1), 4.43-4.51 (5H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$): δ 39.1 (C-1'), 65.9 (C-7), 71.2 (CH_2Ph), 71.3 (CH_2Ph), 73.0 (CH_2Ph), 74.2 (C-3), 75.1 (C-1), 76.2 (C-2), 76.5 (C-4), 107.8 (C-5); HRMS (ESI): *m/z* calcd for 545.2304 ($C_{34}H_{34}O_5 \cdot Na^+$); Found: 545.2352.

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