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FORMATION OF 2-ACETAMIDO-2-DEOXY-D-GLUCOPYRANOSIDIC LINKAGES *VIA* GLYCOSIDATION USING A COMBINATION OF TWO LEWIS ACIDS[†]

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[†] Dedicated to Professor Dr. Isao Kuwajima on his 77th birthday

Abstract – A mixed activation system composed of ytterbium(III) triflate and a catalytic boron trifluoride diethyl etherate complex efficiently promotes the glycosylation of various alcohol acceptors using 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl acetate in dichloromethane at room temperature to afford 2-acetamido-2-deoxy-D-glucopyranosides in good yields with significant formation of the α-isomers. Notably, stereoselective glycosylations of phenol derivatives as the acceptors afforded aryl 1,2-*cis*-α-glycosides without the formation of any β-isomers. This highly stereocontrolled 1,2-*cis*-α-glycosidation was applied to the synthesis of a novel hydroquinone α-glycoside.

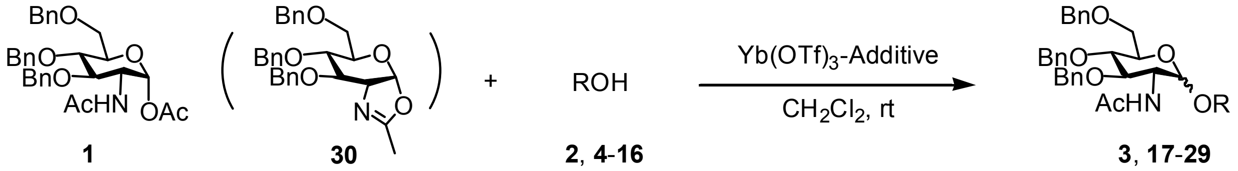
INTRODUCTION

Glycosidation is an indispensable tool for glycoside synthesis; however, identifying appropriate glycosyl donors and activating agents is a major challenge for the development of glycosidation methods. Lewis acids are probably the most widely used activators for glycosidation. Among them, ytterbium(III) triflate ($Yb(OTf)_3$) is known to be a powerful activator for a few glycosidation reactions.[1] We previously showed that $Yb(OTf)_3$ is effective with several glycosyl acetates.[2] Several glycosidation methods using a combination of two Lewis acids such as bismuth(III) triflate-boron trifluroride diethyletherate ($BF_3 \cdot OEt_2$),[3] silver perchlorate-lithium perchlorate,[4] and $Yb(OTf)_3$-zinc chloride[5] have been reported. In addition, we recently showed that a mixed activating system based on $Yb(OTf)_3$ and a catalytic amount of $BF_3 \cdot OEt_2$ was useful for glycosidation using certain less reactive glycosyl acetates.[6] When our attention was directed toward glycosidation using 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl acetate (**1**),[7] which is a less reactive glycosyl donor, the use of the mixed $Yb(OTf)_3$-$BF_3{\cdot}OEt_2$ activating system exhibited interesting glycosyl acceptor specificities,[8] i.e., the glycosidation using certain aliphatic alcohols afforded the corresponding 2-acetamido-2-deoxy-D-glucopyranosides with a considerable amount of formation of the α-isomers, while glycosidations of phenol derivatives proceeded stereoselectively, affording aryl α-glycosides without the formation of any β-isomers.

The 2-acetamido-2-deoxy-α-D-glucopyranosidic linkage is involved in some glycosidic natural products such as *O*-glycans of gastric mucins,[9] lipopolysaccharides of bacteria,[10] and tunicamycin[11,12] Therefore, the development of a convenient method for the formation of the 1,2-*cis*-α-glycosidic linkage directly from 2-acetamido-2-deoxy-D-glucopyranose derivatives is an important goal in synthetic carbohydrate chemistry.[13] Herein, we describe in detail the formation of the 2-acetamido-2-deoxy-α-D-glucopyranosidic linkage based on the glycosyl acceptor properties for glycosidations using **1** with a mixed activation system composed of $Yb(OTf)_3$-$BF_3{\cdot}OEt_2$. To demonstrate the applicability of the method, the synthesis of a novel hydroquinone α-glycoside was achieved using the highly stereocontrolled 1,2-*cis*-aryl-α-glycosidation.

RESULTS AND DISCUSSION

Glycosidation using **1** with the mixed activating system composed of $Yb(OTf)_3$ (1 equiv.)-$BF_3{\cdot}OEt_2$ (0.03 equiv.) was first investigated with phenethyl alcohol (**2**) as the substrate (Scheme 1). This reaction, which proceeded in CH_2Cl_2 overnight at room temperature, gave the desired phenethyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (**3**) in a high yield of 95% with an α/β ratio of 40/60 (Entry 1, Table 1). Interestingly, this reaction resulted in the formation of a considerable amount of α-glycoside. This finding that the 1,2-*cis*-α-glycosidic linkage was directly formed from a 2-acetamido-2-deoxy-D-glucopyranosyl donor was very rare. It is known that glycosidations using 2-acetamido-2-deoxy-D-glucopyranosyl donors bearing a natural *N*-acetyl protecting group typically form the corresponding β-glycosides *via* S_N2-like nucleophilic substitution of alcohols with in situ generated oxazoline derivatives (or oxazolinium cation intermediates).[14] Therefore, this unusual stereoselectivity of the glycosidation between **1** and **2** using our mixed activating system suggests that the reaction may proceed *via* a different pathway that does not involve the generation of an oxazoline intermediate.



Scheme 1

Table 1. Reaction of **1**(and **30**) with aliphatic alcohols (**2**, **4-11**) and phenol derivatives (**12-16**)[a]

Entry	Donor	Acceptor	Additive	Glycoside	Yield (%)	α/β Ratio
1	**1**	**2**	$BF_3 \cdot OEt_2$	**3**	95	40/60
2	**1**	**2**	none	**3**	Trace	-
3	**1**	**2**	TfOH	**3**	68	47/53
4	**1**	**2**	AcOH	**3**	72	51/49
5	**1**	**4**	$BF_3 \cdot OEt_2$	**17**	83	19/81
6	**1**	**5**	$BF_3 \cdot OEt_2$	**18**	86	49/51
7	**1**	**6**	$BF_3 \cdot OEt_2$	**19**	94	37/63
8	**1**	**7**	$BF_3 \cdot OEt_2$	**20**	71	38/62
9	**1**	**8**	$BF_3 \cdot OEt_2$	**21**	70	23/77
10	**1**	**9**	$BF_3 \cdot OEt_2$	**22**	68	53/47
11	**1**	**10**	$BF_3 \cdot OEt_2$	**23**	71	31/69
12	**1**	**11**	$BF_3 \cdot OEt_2$	**24**	37	35/65
13	**1**	**12**	$BF_3 \cdot OEt_2$	**25**	67	α
14	**1**	**13**	$BF_3 \cdot OEt_2$	**26**	84	α
15	**1**	**14**	$BF_3 \cdot OEt_2$	**27**	57	α
16	**1**	**15**	$BF_3 \cdot OEt_2$	**28**	46	α
17	**1**	**16**	$BF_3 \cdot OEt_2$	**29**	60	α
18	**30**	**2**	$BF_3 \cdot OEt_2$	**3**	53	β
19	**30**	**12**	$BF_3 \cdot OEt_2$	**25**	No reaction	-

[a] Reaction conditions; molar ratio; Donor: Acceptor: $Yb(OTf)_3$: Additive= 1.2: 1: 1: 0.03; overnight; room temperature.

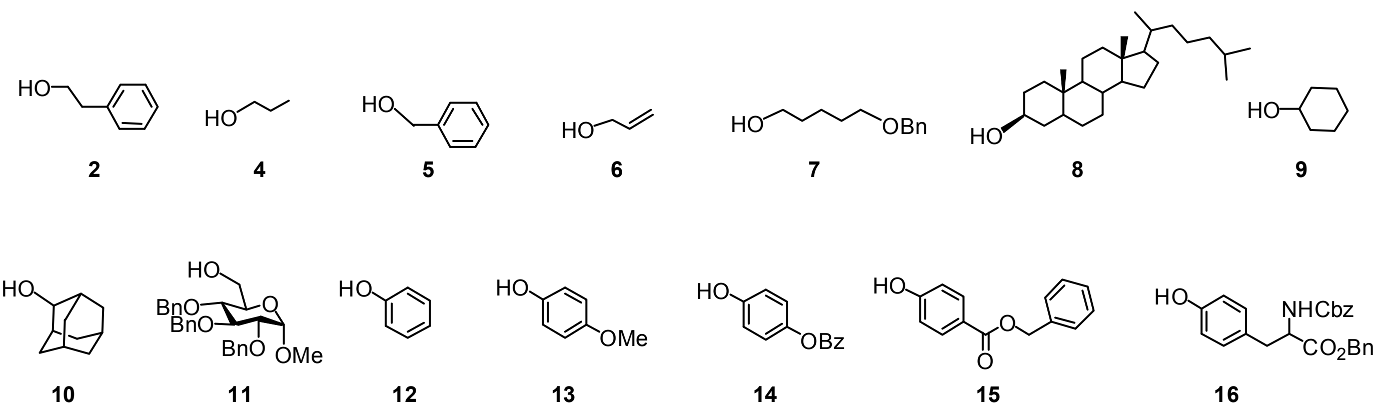


Figure 1

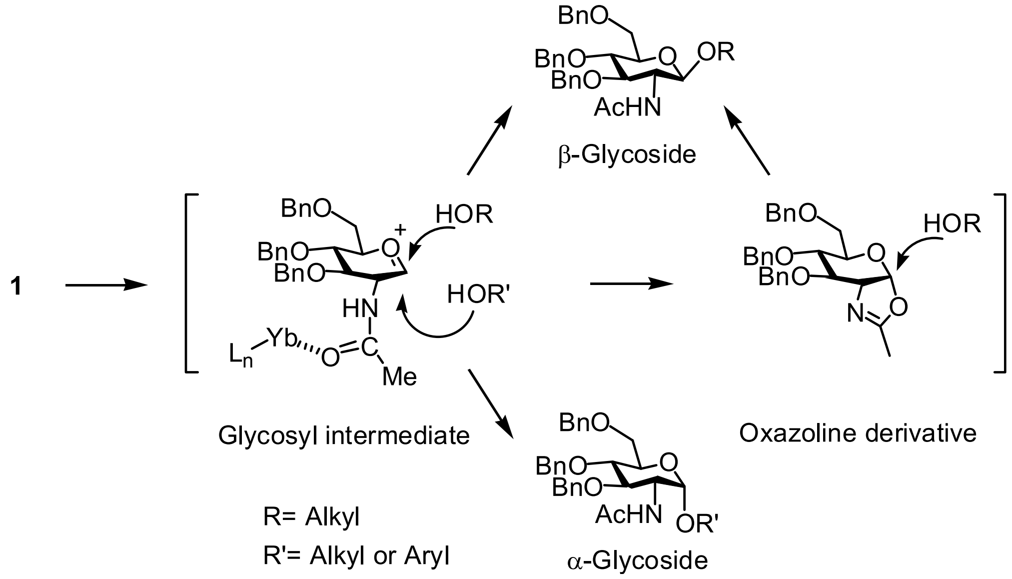
A catalytic amount of $BF_3 \cdot OEt_2$ is essential for promoting the glycosidation because the reaction barely proceeds without added $BF_3 \cdot OEt_2$ (Entry 2). We speculate that the ROH-BF_3 complex formed *in situ* between $BF_3 \cdot OEt_2$ and the alcohol acceptor acts as a Brønsted acid and influences the glycosidation reactivity.[15] The effect of the Brønsted acids, acetic acid (AcOH) and triflic acid (TfOH), as additives was thus examined (Entries 3 and 4). The addition of 3 mol% of AcOH and TfOH to the glycosidation reaction using **1** (1.2 equiv.), phenethyl alcohol (1 equiv.), and $Yb(OTf)_3$ (1 equiv.) in CH_2Cl_2 at room temperature produced **3** in 72% and 68% yield with α/β ratios of 49/51 and 47/53, respectively. The addition of AcOH and TfOH was also effective for the promotion of glycosidations using **1** and $BF_3 \cdot OEt_2$, and these reactions also afforded a considerable amount of the α-glycoside.

Next, we investigated the glycosidation of several types of alcohols under similar reaction conditions using **1** in order to examine the effect of the acceptor on the stereoselectivity of the reaction. Primary and secondary alkyl alcohols **2**, **4**–**11** gave the corresponding glycosides **3**, **17**–**24**, respectively, in good yields with α/β ratios of ca. 1/1–1/5 (Entries 1 and 5–12, Table 1). Thus, each of these reactions gave a mixture of α- and β-glycosides. However, surprisingly, the reactions using phenol derivatives **12**–**16** gave aryl α-glycosides **25**–**29**, respectively, in good yields with no formation of the β-glycosides (Entries 13–17). The steric and electronic effects of the phenol derivatives may strongly influence the α-stereoselectivity of the reaction. The configuration of the glycosidic bond of these glycosides was determined based on the coupling constant values in their ^{1}H-NMR spectra (α form: J = 3.3–4.1 Hz; β form: J = 7.2–8.4 Hz).

In addition, we confirmed that the β-anomer of **25** was not isomerized to the α-anomer under acidic conditions in the presence of $Yb(OTf)_3$ (1 equiv.) and $BF_3 \cdot OEt_2$ (0.03 equiv.) in CH_2Cl_2 at room temperature. Therefore, the α-glycosides formed in the glycosidation using **1** are not conversion products of *in situ* acid-catalyzed anomerization of the β-glycosides.

Furthermore, to clarify the difference in the reaction mechanism, we performed glycosidations using 3,4,6-tri-*O*-benzyl-1,2-oxazoline-glucopyranose (**30**),[16] which appeared to at least partially proceed via an *in situ* generated intermediate under the same conditions (see Table 2). The reaction of **30** (1.2 equiv.) with **2** and **12** was examined in the presence of $Yb(OTf)_3$ (1 equiv.) and $BF_3 \cdot OEt_2$ (0.03 equiv.) in CH_2Cl_2 at room temperature. Acceptor **2** afforded the corresponding β-glycoside in 53% yield with no formation of the α-glycoside (Entry 18), while phenol (**12**) did not react at all (Entry 19). Thus, the reactivity and stereoselectivity of the glycosidation using **30** were found to be quite different from those of the glycosidation using **1**.

We speculate that the complexation of ytterbium metal to the carbonyl group of **1** may generate a glycosyl cation intermediate, as shown in Scheme 2. Formation of this complex would prevent the generation of the oxazoline derivative because of the decrease in the Lewis basicity of the oxygen atom of the carbonyl group, thus allowing the alcohol to attack the glycosyl cation intermediate from the α-face to form the 1,2-*cis*-α-glycosidic linkage.[17] The formation of 1,2-*trans*-β-glycosides during the glycosidation using alkyl alcohols can be explained by the β-attack of the alcohol on the glycosyl cation intermediate or the *in situ* generated oxazoline derivative. However, we have not yet found a sufficient explanation for the high α-stereoselectivities of the glycosidations using phenol derivatives.

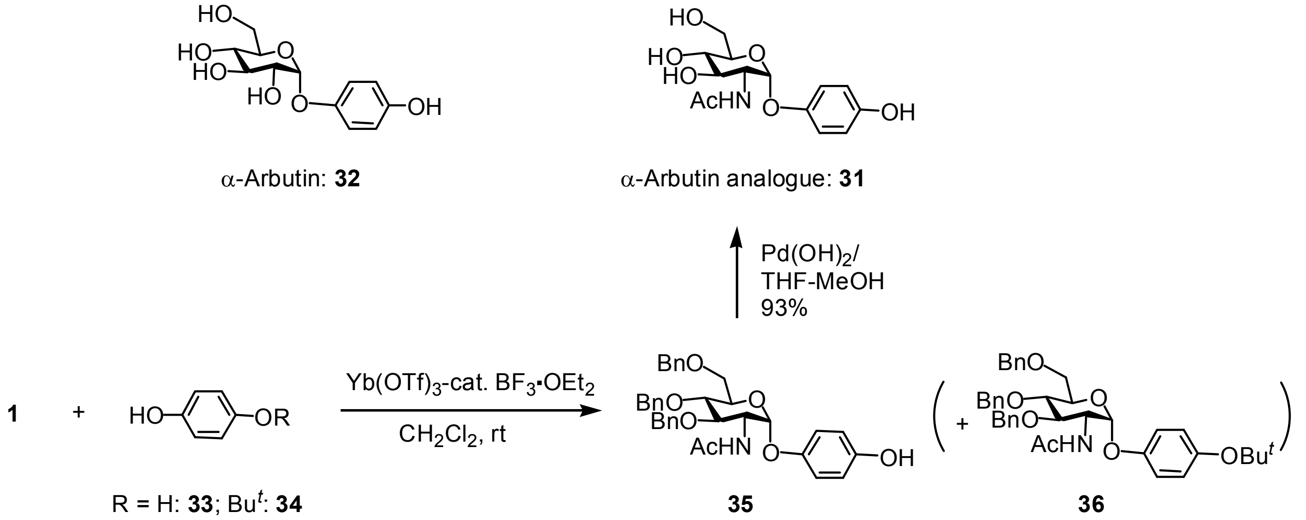


Scheme 2

Finally, the 1,2-*cis*-α-aryl-D-glycosidation method was applied to the synthesis of the novel hydroquinone α-glycoside 4-hydroxyphenyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**31**)[18]; **31** is an analogue of arbutin (4-hydroxyphenyl D-glucopyranoside) (**32**), which exhibits inhibitory activity against tyrosinase, a key enzyme for the synthesis of melanin, the overproduction of which results in hyperpigmentation in the epidermis. Notably, the α-anomeric isomer of **32** has stronger inhibitory activity against mammalian tyrosinases than the β-anomeric isomer.[19] As a result, the synthesis of α-arbutin analogues and the investigation of their performance as skin-lightening agents has recently attracted attention.[20]

Hydroquinone (**33**) has been utilized as a glycosyl acceptor for the preparation of several hydroquinone glycosides using both enzymatic and chemical glycosylation methods.[21] We conducted a detailed investigation of the glycosidation of **33** using **1**, including evaluation of the by-products formed in the reaction (Scheme 3). When the $Yb(OTf)_3$ (1 equiv.)-$BF_3{\cdot}OEt_2$ (0.03 equiv.) mixed activating system was used in CH_2Cl_2 for 1 h at room temperature, the desired hydroquinone α-glycoside **35** was obtained in only 18% yield. However, the production of its β-anomer isomer was not observed at all. Further, **1** was recovered in 45% yield, and **30** was produced in 15% yield (Entry 1, Table 2). These results suggested that the low yield was due to the poor solubility of **33** in CH_2Cl_2. However, when the reaction was run in a mixed CH_2Cl_2/Et_2O (v/v= 1/1) solvent in which **33** was soluble, only a trace amount of the desired **35** was formed (Entry 2). Thus, the use of Et_2O inhibited the glycosylation.

Next, 4-*tert*-butoxyphenol (**34**) was utilized as the glycosyl acceptor; **34** was observed to be moderately soluble in CH_2Cl_2, and the Lewis acid glycosylation promoter was expected to cleave the *tert*-butyl group during the reaction. Rewardingly, the desired **35** was obtained in 66% yield using $Yb(OTf)_3$ (1 equiv.)-$BF_3{\cdot}OEt_2$ (0.03 equiv.) in CH_2Cl_2 for 1 h at room temperature (Entry 3). Interestingly, the glycoside **36** with the *tert*-butyl group retained was also obtained in 8% yield. Thus, the total yield of the glycoside products in this reaction reached 74%. In addition, **30** was formed in 21% yield. When the reaction was allowed to proceed for 6 h, no **36** remained; however, **30** and **37** were produced as byproducts in 22% and 10% yields, respectively (Entry 4). The deprotection of the benzyl groups of **35** using $Pd(OH)_2$ in THF-MeOH yielded an excellent quantity of desired **31**.

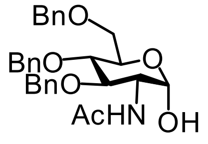


Scheme 3

Table 2. Preparation of hydroquinone α-glycoside **31** *via* glycosylation of **33** and **34** using **1**

Entry[a]	Acceptor	Time (h)	Product (%)			
			35	**36**	**30**	**37**
1[b]	**33**	1	18	-	15	trace
2[c]	**33**	1	trace	-	-	-
3	**34**	1	66	8	21	-
4	**34**	6	52	-	22	10

a Molar ratio; **1**: Acceptor: $Yb(OTf)_3$: $BF_3{\cdot}OEt_2$= 1.2: 1: 1: 0.03. Solvent; CH_2Cl_2. Temperature; room temperature.
b 45% of **1** was recovered.
c Solvent; CH_2Cl_2: Et_2O= 1:1.



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In summary, several 2-acetamido-2-deoxy-D-glucopyranosides were directly synthesized from glycosyl acetate **1** in good yields with the formation of a considerable amount of α-isomers using a $Yb(OTf)_3$-catalytic $BF_3{\cdot}OEt_2$ mixed activating system. Notably, reactions of phenol derivatives as acceptors only afforded aryl α-glycosides, with no formation of β-glycosides. The synthesis of the novel hydroquinone 2-acetamido-2-deoxy-α-D-glucopyranoside as an α-arbutin analogue was also successfully achieved using the highly stereocontrolled 1,2-*cis*-α-aryl-D-glycosidation method.

EXPERIMENTAL

^{1}H-NMR (600 MHz) and ^{13}C-NMR (150 MHz) spectra were recorded using a JEOL ECA-600 spectrometer. Melting points were determined using B-545 (BÜCHI Labortechnik AG) and are uncorrected. Optical rotations were recorded using a JASCO DIP-360 digital polarimeter. Preparative TLC was performed on Merck silica gel 60GF254. Column chromatography was conducted using silica gel 60N (40–50 μm, Kanto Chemical Co. Inc.). All anhydrous solvents were purified according to standard methods.

Typical glycosidation procedure

$Yb(OTf)_3$ (98.2 mg, 0.2 mmol) was added to a solution of **1** (101.4 mg, 0.2 mmol), **2** (19.34 mg, 0.2 mmol), and $BF_3{\cdot}OEt_2$ (47 μL, 0.005 mmol) in CH_2Cl_2 (3 mL) at 0 °C, and the resulting mixture was stirred for 16 h at room temperature. The reaction was then quenched by the addition of sat. aq. $NaHCO_3$ solution (5 mL), and the reaction mixture was extracted with CH_2Cl_2. The organic layer was then washed with water and sat. aq. NaCl solution and dried over Na_2SO_4, the solvent. The crude product obtained after evaporation of the solvent under reduced pressure was purified *via* preparative silica gel TLC (EtOAc/hexane = 2/1) to give **3** (95% yield, α form; 35.7 mg, β form; 53.7 mg, α/β ratio = 40/60) as white crystals.

Phenethyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (3)

α Form; *Rf* 0.48 (EtOAc/hexane = 2/1); mp 152.5–154.5 °C; $[\alpha]^{25}_{D}$ +72.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.62 (3H, s, CH_3), 2.84 (2H, m, CH_2CH_2Ph), 3.35 (1H, dt, *J* = 6.7 Hz, *J* = 8.9 Hz, $CH_aH_bCH_2Ph$), 3.63–3.65 (2H, m, H-3, H_a-6), 3.69–3.72 (3H, m, H-4, H-5, H_b-6), 3.94 (1H, dt, *J* = 5.7 Hz, *J* = 9.6 Hz, $CH_aH_bCH_2Ph$), 4.18 (1H, dt, *J* = 3.6 Hz, *J* = 10.0 Hz, H-2), 4.35–4.84 (6H, m, CH_2Ph), 4.68 (1H, d, *J* = 3.6 Hz, H-1), 4.93 (1H, d, *J* = 9.5 Hz, NH), 7.10–7.31 (20H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.3 (CH_3), 35.8 (CH_2CH_2Ph), 52.3 (C-2), 68.2 (CH_2CH_2Ph), 68.5 (C-6), 71.0 (C-5), 73.4–74.9 (CH_2Ph), 78.3 (C-4), 80.1 (C-3), 97.7 (C-1), 126.3 (Ph), 127.6-128.8 (Ph), 128.8 (Ph), 138.9 (Ph), 169.6 (C=O), 138.0–138.4 (Ph); HRMS (ESI): *m/z* calcd for $C_{37}H_{41}NO_6Na^+$: 618.2826; found: 618.2828. β

Form; *Rf* 0.65 (EtOAc/hexane = 2/1); mp 154.7–157.5 °C; $[\alpha]^{25}_{D}$ +10.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.73 (3H, s, CH_3), 2.87 (2H, m, $CH_2C\mathit{H_2}Ph$), 3.44 (1H, m, H-2), 3.56 (1H, m, H-5), 3.62 (1H, t, *J* = 8.9 Hz, H-4), 3.65–3.75 (3H, m, H-6, $C\mathit{H_a}H_bCH_2Ph$), 4.05 (1H, t, *J* = 8.9 Hz, H-3), 4.10 (1H, dt, *J* = 6.5 Hz, *J* = 8.9 Hz, $CH_a\mathit{H_b}CH_2Ph$), 4.51–4.80 (6H, m, CH_2Ph), 4.76 (1H, d, *J* = 7.6 Hz, H-1), 5.45 (1H, d, *J* = 7.6 Hz, NH), 7.18–7.33 (20H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.5 (CH_3), 36.0 ($CH_2\mathit{C}H_2Ph$), 56.7 (C-2), 69.0 (C-6), 70.0 ($\mathit{C}H_2CH_2Ph$), 73.4–74.5 (CH_2Ph), 74.7 (C-5), 78.5 (C-4), 80.4 (C-3), 99.8 (C-1), 126.1 (Ph), 127.6-128.7 (Ph), 129.0 (Ph), 138.8 (Ph), 170.2 (C=O), 138.0-138.4 (Ph); HRMS (ESI): *m/z* calcd for $C_{37}H_{41}NO_6Na^+$: 618.2826; found: 648.2823.

Propyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (17)

Using the same procedure as described above for **3**, $Yb(OTf)_3$ (123.3 mg, 0.2 mmol) was added to a solution of **1** (127.3 mg, 0.2 mmol), **4** (12.0 mg, 0.2 mmol), and $BF_3{\cdot}OEt_2$ (60 μL, 0.006 mmol) in CH_2Cl_2 (3 mL) to give **17** (PTLC; EtOAc/hexane = 2/1, 95% yield, α form; 16.9 mg, β form; 71.5 mg, α/β ratio = 19/81) as white crystals. α Form; *Rf* 0.50 (EtOAc/hexane = 2/1); mp 142.0–142.1 °C; $[\alpha]^{26}_{D}$ +102.7 (*c* 0.34, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.90 (3H, t, *J* = 7.4 Hz, $CH_2C\mathit{H_3}$), 1.57 (2H, m, $C\mathit{H_2}CH_3$), 1.84 (3H, s, CH_3), 3.34 (1H, dt, *J* = 6.6 Hz, *J* = 9.8 Hz, $C\mathit{H_a}H_bCH_2CH_3$), 3.61 (1H, dt, *J* = 6.8 Hz, *J* = 9.6 Hz, $CH_a\mathit{H_b}CH_2CH_3$), 3.68 (1H, dd, *J* = 1.5 Hz, *J* = 10.4 Hz, H_a-6), 3.69 (1H, t, *J* = 9.5 Hz, H-3), 3.70 (1H, t, *J* = 9.2 Hz, H-4), 3.78 (1H, dd, *J* = 1.8 Hz, *J* = 11.3 Hz, H_b-6), 3.79 (1H, m, H-5), 4.26 (1H, dt, *J* = 3.7 Hz, *J* = 9.9 Hz, H-2), 4.51–4.86 (6H, m, CH_2Ph), 4.78 (1H, d, *J* = 3.6 Hz, H-1), 5.28 (1H, d, *J* = 9.5 Hz, NH), 7.17-7.35 (15H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 10.6 ($CH_2\mathit{C}H_3$), 22.7 ($\mathit{C}H_2CH_3$), 23.5 (CH_3), 52.6 (C-2), 68.6 (C-6), 69.4 ($\mathit{C}H_2CH_2CH_3$), 71.0 (C-5), 73.5–75.1 (CH_2Ph), 78.5 (C-4), 80.5 (C-3), 97.5 (C-1), 127.6–128.5 (Ph), 138.1-138.5 (Ph), 169.6 (C=O); HRMS (ESI): *m/z* calcd for $C_{32}H_{39}NO_6Na^+$: 556.2670; found: 556.2668. β Form; *Rf* 0.57 (EtOAc/hexane = 2/1); mp 138.2–138.4 °C; $[\alpha]^{26}_{D}$ +25.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 7.5 Hz, $CH_2C\mathit{H_3}$), 1.58 (2H, m, $C\mathit{H_2}CH_3$), 1.85 (3H, s, CH_3), 3.38 (1H, q, *J* = 8.2 Hz, H-2), 3.42 (1H, dt, *J* = 6.8 Hz, *J* = 9.1 Hz, $C\mathit{H_a}H_bCH_2CH_3$), 3.59 (1H, m, H-5), 3.62 (1H, t, *J* = 8.6 Hz, H-4), 3.71 (1H, dd, *J* = 4.7 Hz, *J* = 10.4 Hz, H_a-6), 3.76 (1H, bd, *J* = 12.4 Hz, H_b-6), 3.81 (1H, td, *J* = 6.8 Hz, *J*= 9.5 Hz, $CH_a\mathit{H_b}CH_2CH_3$), 4.13 (1H, t, *J* = 8.9 Hz, H-3), 4.54–4.84 (6H, m, CH_2Ph), 4.81 (1H, d, *J* = 8.4 Hz, H-1), 5.58 (1H, d, *J* = 7.4 Hz, NH), 7.19–7.34 (15H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 10.4 ($CH_2\mathit{C}H_3$), 22.8 ($\mathit{C}H_2CH_3$), 23.5 (CH_3), 57.1 (C-2), 69.0 (C-6), 71.1 ($C\mathit{H_2}CH_2CH_3$), 73.4–74.5 (CH_2Ph), 74.8 (C-5), 78.7 (C-4), 80.3 (C-3), 99.8 (C-1), 127.5–128.4 (Ph), 138.1-138.5 (Ph), 170.2 (C=O); HRMS (ESI): *m/z* calcd for $C_{32}H_{39}NO_6Na^+$: 556.2670; found: 556.2708.

Benzyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (18)[22-24]

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (125.1 mg, 0.2 mmol) was added to a solution of **1** (129.0 mg, 0.2 mmol), **5** (22.0 mg, 0.2 mmol), and BF$_3$·OEt$_2$ (60 μL, 0.006 mmol) in CH$_2$Cl$_2$ (3 mL) to give **18** (PTLC; EtOAc/hexane = 2/1, 86% yield, α form[22]; 52.1 mg, β form[23, 24]; 49.6 mg, α/β ratio = 51/49) as white crystals.

Allyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (19)[25,26]

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (126.4 mg, 0.2 mmol) was added to a solution of **1** (130.5 mg, 0.2 mmol), **6** (11.8 mg, 0.2 mmol), and BF$_3$·OEt$_2$ (61 μL, 0.006 mmol) in CH$_2$Cl$_2$ (3 mL) to give **19** (PTLC; EtOAc/hexane = 2/1, 102.1 mg, 94% yield, α/β ratio = 37/63) as white crystals. α[25,26] And β form mixture; *Rf* 0.58 (EtOAc/hexane = 2/1); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.84 (3H, s, α-CH$_3$), 1.85 (3H, s, β-CH$_3$), 3.46 (1H, q, *J* = 8.4 Hz, β-H-2), 3.59 (1H, dt, *J* = 2.2 Hz, *J* = 6.9 Hz, β-H-5), 3.63–3.78 (7H, m, α-CH$_2$=CHCH_2, β-CH$_2$=CHCH_2, α-H-3, α-H-4, β-H-4), 3.80 (1H, dd, *J* = 2.2 Hz, *J* = 9.7 Hz , α-H-5), 3.94 (1H, dd, *J* = 6.1 Hz, *J* = 13.0 Hz, α-H$_a$-6), 4.06 (1H, dd, *J* = 6.7 Hz, *J* = 13.4 Hz, β-H$_a$-6), 4.10 (1H, t, *J* = 9.0 Hz, β-H-3), 4.14 (1H, dd, *J* = 5.2 Hz, *J* = 12.9 Hz, α-H$_b$-6), 4.28 (1H, td, *J* = 3.7 Hz, *J* = 9.8 Hz, α-H-2), 4.32 (1H, dd, *J* = 5.2 Hz, *J* = 12.9 Hz, β-H$_b$-6), 4.80 (1H, d, *J* =3.6 Hz, α-H-1), 4.50–4.86 (12H, m, CH$_2$Ph), 4.85 (1H, d, *J* =7.6 Hz, β-H-1), 5.17 (2H, bdd, *J* = 10.5 Hz, *J* = 14.4 Hz, α-CH_aH$_b$=CHCH$_2$, β-CH_aH$_b$=CHCH$_2$), 5.24 (2H, td, *J* = 0.8 Hz, *J* = 10.4 Hz, *J* = 17.2 Hz, α-CH$_a$$H_b$=CHCH$_2$, β-CH$_a$$H_b$=CHCH$_2$), 5.31 (1H, d, *J* = 9.5 Hz, α-NH), 5.60 (1H, d, *J* = 7.7 Hz, β-NH), 5.86 (2H, m, α-CH$_2$=CHCH$_2$, β-CH$_2$=CHCH$_2$), 7.17–7.35 (30H, m, Ph); ^{13}C NMR (150 MHz, CDCl$_3$): δ 23.4 (α-CH$_3$), 23.6 (β-CH$_3$), 52.5 (α-C-2), 56.8 (β-C-2), 68.1 (α-C-6), 68.5 (α-CH$_2$=CHCH$_2$), 69.0 (β-C-6), 69.8 (β-CH$_2$=CHCH$_2$), 71.1 (α-C-5), 73.5–75.1 (CH$_2$Ph), 74.8 (β-C-5), 78.4 (α-C-4), 78.5 (β-C-4), 80.2 (β-C-3), 80.4 (α-C-3), 96.9 (α-C-1), 99.0 (β-C-1), 117.3 (α-CH$_2$=CHCH$_2$), 117.6 (β-CH$_2$=CHCH$_2$), 127.6-128.5 (Ph), 133.7 (α-CH$_2$=CHCH$_2$), 134.1 (β-CH$_2$=CHCH$_2$), 138.0-138.5 (Ph), 169.7 (α-C=O), 170.3 (β-C=O); HRMS (ESI): *m/z* calcd for $\mathrm{C_{32}H_{37}NO_6Na^+}$: 554.2513; found: 554.2509.

5-Benzyloxypenthyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (20)

Using the above same procedure as described above for **3**, Yb(OTf)$_3$ (142.5 mg, 0.2 mmol) was added to a solution of **1** (147.2 mg, 0.3 mmol), **7** (44.6 mg, 0.2 mmol), and BF$_3$·OEt$_2$ (69 μL, 0.007 mmol) in CH$_2$Cl$_2$ (3 mL) to give **20** (PTLC; EtOAc/hexane = 2/1, 71% yield, α form; 41.8 mg, β form; 69.5 mg, α/β ratio = 38/62) as white crystals. α From; *Rf* 0.48 (EtOAc/hexane = 2/1); mp 84.0–84.8 °C; $[\alpha]^{26}_{\mathrm{D}}$ +70.0 (*c* 0.64, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.41 (2H, m, BnOCH$_2$CH$_2$CH_2), 1.57 (2H, q, *J* = 7.4 Hz, BnOCH$_2$CH_2), 1.62 (2H, q, *J* = 7.1 Hz, BnOCH$_2$CH$_2$CH$_2$CH_2), 1.81 (3H, s, CH$_3$), 3.36 (1H, td, *J* = 6.5 Hz, *J* = 9.8 Hz, BnOCH$_2$CH$_2$CH$_2$CH$_2$CH_aH$_b$), 3.46 (2H, t, *J* = 6.5 Hz, BnOCH_2), 3.66 (1H, dt, *J* = 6.4 Hz, *J* = 9.8 Hz, BnOCH$_2$CH$_2$CH$_2$CH$_2$CH$_a$$H_b$), 3.67 (1H, bd, *J* = 10.3 Hz, H$_a$-6), 3.69 (1H, t, *J* = 10.0 Hz, H-3), 3.74 (1H, t, *J* = 9.0 Hz, H-4), 3.76 (1H, bd, *J* = 9.6 Hz, H$_b$-6), 3.77 (1H, m, H-5), 4.26 (1H, dt, *J* = 3.7 Hz, *J* = 9.9 Hz, H-2), 4.49–4.84 (8H, m, CH$_2$Ph), 4.76 (1H, d, *J* = 3.8 Hz, H-1), 5.31 (1H, d, *J* = 9.5 Hz, NH), 7.16–7.33 (20H, m, Ph); ^{13}C NMR (150 MHz, CDCl$_3$): δ 22.9 (BnOCH$_2$CH$_2$*C*H$_2$), 23.4 (CH$_3$), 29.1 (BnOCH$_2$*C*H$_2$), 29.4 (BnOCH$_2$CH$_2$CH$_2$*C*H$_2$), 52.5 (C-2), 67.7 (BnO*C*H$_2$), 68.6 (C-6), 70.1 (BnOCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 70.9 (C-5), 72.9–75.0 (CH$_2$Ph), 78.4 (C-4), 80.5 (C-3), 97.6 (C-1), 127.5–128.5 (Ph), 138.0-138.5 (Ph), 169.6 (C=O); HRMS (ESI): *m/z* calcd for $C_{41}H_{49}NO_7Na^+$: 690.3401; found: 690.3380. β Form; *Rf* 0.65 (EtOAc/hexane = 2/1); mp 83.2–85.5 °C; $[\alpha]^{26}_D$ +10.1 (*c* 1.0, CHCl3); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.41 (2H, q, *J* = 7.7 Hz, BnOCH$_2$CH$_2$C*H$_2$*), 1.57 (2H, q, *J* = 7.3 Hz, BnOCH$_2$CH$_2$CH$_2$C*H$_2$*), 1.61 (2H, q, *J* = 7.1 Hz, BnOCH$_2$C*H$_2$*), 1.81 (3H, s, CH$_3$), 3.37 (1H, dt, *J* = 7.9 Hz, *J* = 9.6 Hz, H-2), 3.44 (2H, t, *J* = 6.6 Hz, BnOC*H$_2$*), 3.43-3.47 (1H, m, BnOCH$_2$CH$_2$CH$_2$CH$_2$C*H$_a$*H$_b$), 3.57 (1H, ddd, *J* = 2.3 Hz, *J* = 4.6 Hz, *J* = 9.3 Hz, H-5), 3.60 (1H, t, *J* = 8.8 Hz, H-4), 3.70 (1H, dd, *J* = 4.5 Hz, *J* = 10.7 Hz, H$_a$-6), 3.75 (1H, dd, *J* = 2.4 Hz, *J* = 10.7 Hz, H$_b$-6), 3.86 (1H, dt, *J* = 6.4 Hz, *J* = 9.6 Hz, BnOCH$_2$CH$_2$CH$_2$CH$_2$CH$_a$*H$_b$*), 4.10 (1H, dd, *J* = 8.3 Hz, *J* = 9.6 Hz, H-3), 4.79 (1H, d, *J* = 7.7 Hz, H-1), 5.53 (1H, d, *J* = 7.9 Hz, NH), 4.47–4.82 (8H, m, CH$_2$Ph), 7.19–7.34 (20H, m, Ph); ^{13}C NMR (150 MHz, CDCl$_3$): δ 22.7 (BnOCH$_2$CH$_2$*C*H$_2$), 23.5 (CH$_3$), 29.3 (BnOCH$_2$*C*H$_2$), 29.5 (BnOCH$_2$CH$_2$CH$_2$*C*H$_2$), 57.1 (C-2), 69.1 (C-6), 69.4 (BnOCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 70.3 (BnO*C*H$_2$), 72.9–74.6 (CH$_2$Ph), 74.8 (C-5), 78.7 (C-4), 80.4 (C-3), 99.8 (C-1), 127.5–128.5 (Ph), 138.1–138.6 (Ph), 170.3 (C=O); HRMS (ESI): *m/z* calcd for $C_{41}H_{49}NO_7Na^+$: 690.3401; found: 690.3389.

3-β-Cholestanyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (21)

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (129.0 mg, 0.2 mmol) was added to a solution of **1** (133.2 mg, 0.2 mmol), **8** (80.8 mg, 0.1 mmol), and BF$_3$·OEt$_2$ (62 μL, 0.006 mmol) in CH$_2$Cl$_2$ (3 mL) to give **21** (PTLC; EtOAc/hexane = 2/1, 70% yield, α form; 28.8 mg, β form; 96.4 mg, α/β ratio = 23/77) as white crystals. α Form; *Rf* 0.28 (EtOAc/hexane = 2/1); mp 164.4–166.0 °C; $[\alpha]^{27}_D$ +82.6 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.86 (3H, s, CH$_3$), 0.57-1.97 (47H, m, 3-β-cholestanyl), 3.50 (1H, dt, *J* = 5.4 Hz, *J*= 10.9 Hz, CH), 3.68 (1H, t, *J* = 9.5 Hz, H-3), 3.67 (1H, dd, *J* = 1.9 Hz, *J* = 10.9 Hz, H$_a$-6), 3.72 (1H, t, *J* = 9.3 Hz, H-4), 3.76 (1H, dd, *J* = 4.3 Hz, *J* = 8.8 Hz, H$_b$-6), 3.89 (1H, ddd, *J* = 1.9 Hz, *J* = 4.1 Hz, *J* = 9.4 Hz, H-5), 4.24 (1H, dt, *J* = 3.8 Hz, *J* = 9.8 Hz, H-2), 4.50–4.85 (6H, m, CH$_2$Ph), 4.91 (1H, d, *J* = 3.8 Hz, H-1), 5.32 (1H, d, *J* = 9.3 Hz, NH), 7.16–7.35 (15H, m, Ph); ^{13}C NMR (150 MHz, CDCl$_3$): δ 23.5 (CH$_3$), 12.1–56.4 (3-β-cholestanyl), 52.5 (C-2), 68.7 (C-6), 70.9 (C-5), 73.4–75.0 (CH$_2$Ph), 77.0 (CH), 78.5 (C-4), 80.8 (C-3), 96.2 (C-1), 169.6 (C=O), 127.6–128.5 (Ph), 138.1-138.6 (Ph); HRMS (ESI): *m/z* calcd for $C_{56}H_{79}NO_6Na^+$: 884.5800; found: 884.5843. β Form; *Rf* 0.41 (EtOAc/hexane = 2/1); mp 164.0–165.3 °C; $[\alpha]^{26}_D$ +28.8 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.84 (3H, s, CH$_3$), 0.63-1.97 (47H, m, 3-β-cholestanyl), 3.19 (1H, td, *J* = 7.9 Hz, *J* = 9.6 Hz, H-2), 3.54–3.59 (3H, m, H-4, H-5, CH), 3.68 (1H, dd, *J* = 4.1 Hz, *J* = 10.7 Hz, H_a-6), 3.75 (1H, dd, *J* = 1.0 Hz, *J* = 10.7 Hz, H_b-6), 4.25 (1H, dd, *J* = 9.6 Hz, *J* = 8.3 Hz, H-3), 4.54–4.83 (6H, m, CH_2Ph), 5.00 (1H, d, *J* = 7.9 Hz, H-1), 5.57 (1H, d, *J* = 7.2 Hz, NH), 7.20-7.34 (15H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.6 (CH_3), 12.1–56.5 (3-β-cholestanyl), 58.2 (C-2), 69.2 (C-6), 73.4–74.7 (CH_2Ph), 74.7 (C-5), 78.8 (C-4), 79.1 (CH), 80.4 (C-3), 98.1 (C-1), 127.5-128.4 (Ph), 138.1-138.6 (Ph), 170.3 (C=O); HRMS (ESI): *m/z* calcd for $C_{56}H_{79}NO_6Na^+$: 884.5800; found: 884.5833.

Cyclohexyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (22)[27]

Using the above same procedure as described above for **3**, Yb(OTf)$_3$ (130.0 mg, 0.2 mmol) was added to a solution of **1** (134.2 mg, 0.2 mmol), **9** (21 mg, 0.3 mmol), and $BF_3 \cdot OEt_2$ (63 µL, 0.006 mmol) in CH_2Cl_2 (3 mL) to give **21** (PTLC; EtOAc/hexane = 2/1, 81.7 mg, 68% yield, α/β ratio = 53/47) as white crystals. α And β[27] from mixture; *Rf* 0.72 (EtOAc/hexane = 2/1); ^1H NMR (600 MHz, $CDCl_3$): δ 1.83 (3H, s, α-CH_3), 1.84 (3H, s, β-CH_3), 1.17–1.93 (20H, m, cyclohexyl), 3.21 (1H, dt, *J* = 7.9 Hz, *J* = 9.8 Hz, β-H-2), 3.55–3.57 (3H, m, α-CH, β-H-5, β-H-4), 3.59–3.63 (2H, m, β-CH, α-H-3), 3.66–3.78 (5H, m, α-H-6, β-H-6, α-H-4), 3.89 (1H, ddd, *J* = 1.7 Hz, *J* = 4.0 Hz, *J* = 9.6 Hz, α-H-5), 4.23–4.27 (2H, m, α-H-2, β-H-3), 4.50–4.86 (12H, m, CH_2Ph), 4.92 (1H, d, *J* = 3.8 Hz, α-H-1), 5.00 (1H, d, *J* = 8.1 Hz, β-H-1), 5.26 (1H, d, *J* = 9.3 Hz, α-NH), 5.69 (1H, d, *J* = 7.6 Hz, β-NH), 7.17–7.35 (30H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.4 (α-CH_3), 23.6 (β-CH_3), 23.4-25.6 (cyclohexyl), 52.6 (α-C-2), 58.2 (β-C-2), 68.7 (α-C-6), 69.2 (β-C-6), 71.0 (α-C-5), 73.4-74.8 (CH_2Ph), 74.7 (β-C-5), 75.1 (α-CH), 77.3 (β-CH), 78.5 (α-C-4), 79.0 (β-C-4), 80.4 (β-C-3), 80.5 (α-C-3), 95.9 (α-C-1), 98.0 (β-C-1), 127.5-128.5 (Ph), 138.1-138.6 (Ph), 169.6 (α-C=O), 170.3 (β-C=O); HRMS (ESI): *m/z* calcd for $C_{35}H_{43}NO_6Na^+$: 596.2983; found: 596.2981.

2-Adamantyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (23)

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (144.2 mg, 0.2 mmol) was added to a solution of **1** (148.9 mg, 0.3 mmol), **10** (35.4 mg, 0.2 mmol), and $BF_3 \cdot OEt_2$ (70 µL, 0.007 mmol) in CH_2Cl_2 (3 mL) to give **23** (PTLC; EtOAc/hexane = 2/1, 71% yield, α form; 31.5 mg, β form; 71.4 mg, α/β ratio = 31/69) as white crystals. α Form; *Rf* 0.63 (EtOAc/hexane = 2/1); mp 121.0–122.8 °C; $[\alpha]^{26}_D$ +82.6 (*c* 0.55, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.79 (3H, s, CH_3), 1.50–2.17 (14H, m, 2-adamantyl), 3.67 (1H, dd, *J* = 1.6 Hz, *J* = 10.7 Hz, H_a-6), 3.72-3.80 (4H, m, H-3, H-4, H_b-6, CH), 3.88 (1H, bd, *J* = 9.8 Hz, H-5), 4.20 (1H, dt, *J* = 3.5 Hz, *J* = 9.7 Hz, H-2), 4.50–4.87 (6H, m, CH_2Ph), 4.94 (1H, d, *J* = 3.6 Hz, H-1), 5.12 (1H, d, *J* = 9.1 Hz, NH), 7.20–7.36 (15H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.4 (CH_3), 27.1–37.4 (2-adamantyl), 52.7 (C-2), 68.7 (C-6), 71.3 (C-5), 73.4–75.2 (CH_2Ph), 78.5 (C-4), 79.5 (CH), 79.8 (C-3), 95.8 (C-1), 127.6-128.5 (Ph), 138.0-138.7 (Ph), 169.5 (C=O); HRMS (ESI): *m/z* calcd for $C_{39}H_{47}NO_6Na^+$: 648.3296; found: 648.3252. β Form; *Rf* 0.78 (EtOAc/hexane = 2/1); mp 119.8–121.8 °C; $[\alpha]^{26}_D$ +19.4 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.83 (3H, s, CH_3), 1.44–2.17 (14H, m, 2-adamantyl), 3.36 (1H, dt, *J* = 8.4 Hz, *J*= 9.7 Hz, H-2), 3.60 (1H, t, *J* = 8.8 Hz, H-4), 3.68 (1H, dd, *J* = 4.6 Hz, *J* = 10.7 Hz, H_a-6), 3.76 (1H, dd, *J* = 1.9 Hz, *J* = 10.7 Hz, H_b-6), 3.87 (1H, s, CH), 3.88 (1H, m, H-5), 4.19 (1H, t, *J* = 9.0 Hz, H-3), 4.55–4.84 (6H, m, CH_2Ph), 4.92 (1H, d, *J* = 7.9 Hz, H-1), 5.56 (1H, d, *J* = 7.6 Hz, NH), 7.21–7.35 (15H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.6 (CH_3), 27.1–37.6 (2-adamantyl), 57.8 (C-2), 69.1 (C-6), 73.4–74.6 (CH_2Ph), 74.8 (C-5), 79.0 (C-4), 80.4 (C-3), 80.7 (CH), 97.7 (C-1), 127.5-128.5 (Ph), 138.2-138.7 (Ph), 170.2 (C=O); HRMS (ESI): *m/z* calcd for $C_{39}H_{47}NO_6Na^+$: 648.3296; found: 648.3255.

Methyl 6-*O*-(2'-Acetamido-3',4',6'-tri-*O*-benzyl-2'-deoxy-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (24)[24]

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (128.2 mg, 0.2 mmol) was added to a solution of **1** (132.4 mg, 0.2 mmol), **11** (96.0 mg, 0.2 mmol), and $BF_3{\cdot}OEt_2$ (62 µL, 0.006 mmol) in CH_2Cl_2 (3 mL) to give **24** (PTLC; EtOAc/hexane = 2/1, 37% yield, α form; 24.9 mg, β form[24]; 45.7 mg, α/β ratio = 35/65) as white crystals. α Form; *Rf* 0.23 (EtOAc/hexane = 2/1); mp 164.0–165.6 °C; $[\alpha]^{26}_D$ +86.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.70 (3H, s, CH_3), 3.33 (3H, s, OCH_3), 3.37 (1H, t, *J* = 9.5 Hz, H-4'), 3.42 (1H, dd, *J* = 3.6 Hz, *J* = 9.6 Hz, H-3), 3.56-3.59 (2H, m, H_a-6' H_a-6), 3.61 (1H, dd, *J* = 8.3 Hz, *J* = 10.4 Hz, H-3'), 3.67 (1H, dd, *J* = 3.4 Hz, *J* = 10.7 Hz, H_b-6'), 3.69–3.74 (3H, m, H-5, H-5', H-4'), 3.85 (1H, dd, *J* = 4.6 Hz, *J* = 11.3 Hz, H_b-6), 3.98 (1H, t, *J* = 9.2 Hz, H-2), 4.19 (1H, dt, *J* = 3.6 Hz, *J* = 9.9 Hz, H-2'), 4.45–5.02 (12H, m, CH_2Ph), 4.52 (1H, d, *J* = 2.9 Hz, H-1), 4.80 (1H, d, *J* = 4.1 Hz, H-1'), 5.20 (1H, d, *J* = 9.3 Hz, NH), 7.17–7.37 (30H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.4 (CH_3), 52.6 (C-2'), 55.2 (OCH_3), 66.7 (C-6), 68.4 (C-6'), 69.7 (C-5'), 71.3 (C-5), 72.9–74.6 (CH_2Ph), 77.7 (C-4), 78.3 (C-4'), 79.7 (C-3'), 80.0 (C-3), 82.0 (C-2), 97.9 (C-1), 98.5 (C-1'), 127.5–128.5 (Ph), 138.1–138.6 (Ph), 169.5 (C=O); HRMS (ESI): *m/z* calcd for $C_{57}H_{63}NO_{11}Na^+$: 960.4293; found: 960.4283. β Form; *Rf* 0.65 (EtOAc/hexane = 2/1); mp 194.5–195.8 °C; $[\alpha]^{26}_D$ +25.9 (*c* 2.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.70 (3H, s, CH_3), 3.34 (3H, s, OCH_3), 3.49–3.51 (1H, m, H-3'), 3.52 (1H, t, *J* = 8.9 Hz, H-4), 3.59 (2H, m, H-4', H-5'), 3.68 (1H, dd, *J* = 3.6 Hz, *J* = 11.2 Hz, H_a-6), 3.70-3.74 (3H, m, H-5', H-6'), 3.97 (1H, t, *J* = 9.3 Hz, H-2), 4.09 (1H, t, *J* = 9.2 Hz, H-3), 4.09–4.11 (1H, m, H_b-6), 4.49–4.98 (12H, m, CH_2Ph), 4.58 (1H, d, *J* = 3.3 Hz, H-1), 4.83 (1H, d, *J* = 7.2 Hz, H-1'), 5.44 (1H, d, *J* = 7.7 Hz, NH), 7.19–7.34 (30H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.5 (CH_3), 52.1 (OCH_3), 56.7 (C-2'), 67.4 (C-6), 69.1 (C-6'), 69.6 (C-5'), 73.3-75.7 (CH_2Ph), 74.9 (C-5), 77.6 (C-4), 78.6 (C-4'), 79.7 (C-3'), 80.1 (C-3), 82.0 (C-2), 98.0 (C-1), 99.8 (C-1'), 127.5–128.4 (Ph), 138.0–138.8 (Ph), 170.1 (C=O); HRMS (ESI): *m/z* calcd for $C_{57}H_{63}NO_{11}Na^+$: 960.4293; found: 961.4316.

Phenyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (25)

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (124 mg, 0.2 mmol) was added to a solution of **1** (141 mg, 0.3 mmol), **12** (20.6 mg, 0.2 mmol), and BF$_3$·OEt$_2$ (66 μL, 0.007 mmol) in CH$_2$Cl$_2$ (3 mL) to give **25** (PTLC; EtOAc/hexane = 2/1, 83.4 mg, 67% yield) as white crystals. *Rf* 0.47 (EtOAc/hexane = 2/1); mp 161.1–161.8 °C; $[\alpha]^{28}_{D}$ +148.8 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.75 (3H, s, CH$_3$), 3.44 (1H, dt, *J* = 3.4 Hz, *J* = 9.6 Hz, H-2), 3.54 (1H, d, *J* = 11.0 Hz, H$_a$-6), 3.68 (1H, dd, *J* = 2.1 Hz, *J* = 11.0 Hz, H$_b$-6), 3.78-3.90 (3H, m, H-3, H-4, H-5), 4.37-4.85 (6H, m, CH$_2$Ph), 5.28 (1H, d, *J* = 8.9 Hz, NH), 5.47 (1H, d, *J* = 4.1 Hz, H-1), 6.80–7.40 (20H, m, Ph); ^{13}C NMR (150 MHz, CDCl$_3$): δ 23.3 (CH$_3$), 52.5 (C-2), 68.3 (C-6), 71.6 (C-5), 73.4–75.1 (CH$_2$Ph), 78.2 (C-4), 79.8 (C-3), 96.3 (C-1), 116.6 (Ph), 122.6 (Ph), 129.6 (Ph), 156.1 (Ph), 169.9 (C=O), 127.6–128.5 (Ph), 137.9–138.4 (Ph); HRMS (ESI): *m/z* calcd for C$_{35}$H$_{37}$NO$_6$Na$^+$: 590.2513; found: 590.2514.

4-*O*-Methylphenyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (26)

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (124.2 mg, 0.2 mmol) was added to a solution of **1** (128.0 mg, 0.2 mmol), **13** (25 mg, 0.2 mmol), and BF$_3$·OEt$_2$ (60 μL, 0.006 mmol) in CH$_2$Cl$_2$ (3 mL) to give **26** (PTLC; EtOAc/hexane = 2/1, 100.6 mg, 84% yield) as white crystals. *Rf* 0.58 (EtOAc/hexane = 2/1); mp 189.2–189.8 °C; $[\alpha]^{25}_{D}$ +172.1 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.77 (3H, s, CH$_3$), 3.56 (1H, dd, *J* = 2.1 Hz, *J* = 11.0 Hz, H$_a$-6), 3.68 (1H, s, PhCH$_3$), 3.69 (1H, bd, *J* = 11.0 Hz, H$_b$-6), 3.78 (1H, t, *J* = 8.9 Hz, H-4), 3.82 (1H, t, *J* = 9.3 Hz, H-3), 3.87 (1H, ddd, *J* = 9.6 Hz, *J* = 3.4 Hz, *J* = 1.4 Hz, H-5), 4.32 (1H, dt, *J* = 3.4 Hz, *J* = 9.6 Hz, H-2), 4.38–4.84 (6H, m, CH$_2$Ph), 5.28 (1H, d, *J* = 8.9 Hz, NH), 5.35 (1H, d, *J* = 3.4 Hz, H-1), 6.72 (2H, d, *J* = 8.9 Hz, Ph), 6.87 (2H, d, *J* = 8.9 Hz, Ph), 7.17–7.31 (15H, m, Ph); ^{13}C NMR (150 MHz, CDCl$_3$): δ 23.4 (CH$_3$), 52.6 (C-2), 55.6 (PhCH$_3$), 68.4 (C-6), 71.5 (C-5), 73.4–75.1 (CH$_2$Ph), 78.3 (C-4), 79.9 (C-3), 97.2 (C-1), 114.6 (Ph), 118.0 (Ph), 128.5–127.6 (Ph), 150.1 (Ph), 155.2 (Ph), 169.8 (C=O), 138.0-138.4 (Ph); HRMS (ESI): *m/z* calcd for C$_{36}$H$_{39}$NO$_7$Na$^+$: 620.2619; found: 620.2616.

4-Benzoyloxyphenyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (27)

Using the same procedure as described above for **3**, Yb(OTf)$_3$ (113.8 mg, 0.2 mmol) was added to a solution of **1** (117.5 mg, 0.2 mmol), **14** (39.3 mg, 0.2 mmol), and BF$_3$·OEt$_2$ (55 μL, 0.006 mmol) in CH$_2$Cl$_2$ (3 mL) to give **27** (PTLC; EtOAc/hexane = 2/1, 70.2 mg, 57% yield) as white crystals. *Rf* 0.81 (EtOAc/hexane = 2/1); mp 190.5–191.7 °C; $[\alpha]^{27}_{D}$ +160.8 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.84 (3H, s, CH$_3$), 3.64 (1H, d, *J* = 10.8 Hz, H$_a$-6), 3.78 (1H, dd, *J* = 1.5 Hz, *J* = 11.0 Hz, H$_b$-6), 3.90–3.92 (3H, m, H-3, H-4, H-5), 4.42 (1H, ddd, *J* = 3.3 Hz, *J* = 6.7 Hz, *J* = 12.5 Hz, H-2), 4.46–4.93 (6H, m, CH$_2$Ph), 5.30 (1H, d, *J* = 9.1 Hz, NH), 5.54 (1H, d, *J* = 3.4 Hz, H-1), 7.07 (2H, d, *J* = 9.1 Hz, Ph), 7.12 (2H, d, *J* = 9.1 Hz, Ph), 7.20–7.40 (15H, m, Ph), 7.51 (2H, t, *J* = 7.8 Hz, Ph), 7.63 (1H, dt, *J* = 1.3 Hz, *J* = 7.5 Hz, Ph), 8.19 (2H, dd, *J* = 1.3 Hz, *J* = 8.3 Hz, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.4 (CH_3), 52.5 (C-2), 68.2 (C-6), 71.8 (C-5), 73.5-75.1 (CH_2Ph), 78.2 (C-4), 79.8 (C-3), 96.8 (C-1), 117.4 (Ph), 122.7 (Ph), 127.7-128.6 (Ph), 129.5 (Ph), 130.1-130.2 (Ph), 133.6 (Ph), 137.9–138.4 (Ph), 145.9 (Ph), 153.9 (Ph), 165.4 (C=O), 169.9 (C=O(CH_3)); HRMS (ESI): *m/z* calcd for $C_{42}H_{39}NO_8Na^+$: 710.2724; found: 710.2734.

4-*O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-benzoic acid benzyl ester (28)

Using the same procedure as described above for **3**, $Yb(OTf)_3$ (80.0 mg, 0.13 mmol) was added to a solution of **1** (82.6 mg, 0.15 mmol), **15** (29.4 mg, 0.13 mmol), and $BF_3\cdot OEt_2$ (39 μL, 0.004 mmol) in CH_2Cl_2 (3 mL) to give **28** (PTLC; EtOAc/hexane = 2/1, 19.2 mg, 46% yield) as white crystals. *Rf* 0.57 (EtOAc/hexane = 2/1); mp 147.2–148.1 °C; $[\alpha]^{25}_{D}$ +163.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.74 (3H, s, CH_3), 3.49 (1H, d, *J* = 9.8 Hz, H_a-6), 3.66 (1H, dd, *J* = 3.5 Hz, *J* = 10.9 Hz, H_b-6), 3.71 (1H, d, *J* = 8.1 Hz, H-5), 3.82 (2H, m, H-3, H-4), 4.33 (1H, dd, *J* = 6.7 Hz, *J* = 8.9 Hz, H-2), 4.35–4.85 (6H, m, CH_2Ph), 5.15 (1H, d, *J* = 8.8 Hz, NH), 5.25 (2H, d, *J* = 2.6 Hz, CH_2Ph), 5.56 (1H, d, *J* = 3.3 Hz, H-1), 6.97 (2H, d, *J* = 8.8 Hz, Ph), 7.10–7.35 (20H, m, Ph), 7.93 (2H, d, *J* = 8.6 Hz, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.2 (CH_3), 52.4 (C-2), 66.5 (CH_2Ph), 68.1 (C-6), 71.8 (C-5), 73.4–75.1 (CH_2Ph), 78.0 (C-4), 79.4 (C-3), 95.9 (C-1), 116.0 (Ph), 124.3 (Ph), 131.7 (Ph), 136.1 (Ph), 159.7 (Ph), 165.8 (C=O), 170.0 (*C*=O(CH_3)), 127.7-128.6 (Ph), 137.7-138.2 (Ph); HRMS (ESI): *m/z* calcd for $C_{43}H_{43}NO_8Na^+$: 724.2881; found: 724.2883.

4-*O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-*N*-benzyloxycarbonyl-L-tyrosine benzyl ester (29)

Using the same procedure as described above for **3**, $Yb(OTf)_3$ (76.0 mg, 0.1 mmol) was added to a solution of **1** (78.4 mg, 0.1 mmol), **16** (49.7 mg, 0.1 mmol), and $BF_3\cdot OEt_2$ (37 μL, 0.004 mmol) in CH_2Cl_2 (3 mL) to give **29** (PTLC; EtOAc/hexane = 2/1, 64.8 mg, 60% yield) as white crystals. *Rf* 0.70 (EtOAc/hexane = 2/1); mp 169.9–170.1 °C; $[\alpha]^{25}_{D}$ +105.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.74 (3H, s, CH_3), 2.96 (2H, m, $PhC\mathit{H}_2CH$), 3.50 (1H, d, *J* = 9.8 Hz, H_a-6), 3.67 (1H, dd, *J* = 3.2 Hz, *J* = 10.9 Hz, H_b-6), 3.76 (1H, bd, *J* = 6.9 Hz, H-5), 3.81–3.82 (2H, m, H-3, H-4), 4.33 (1H, td, *J* = 4.0 Hz, *J* = 9.3 Hz, H-2), 4.35–4.84 (6H, m, CH_2Ph), 4.57 (1H, dd, *J* = 5.5 Hz, *J* = 13.2 Hz, CH), 5.00 (2H, s, $NHC(O)OC\mathit{H}_2Ph$), 5.02 (1H, d, *J* = 12.5 Hz, $C(O)OC\mathit{H_a}H_bPh$), 5.07 (1H, d, *J* = 12.0 Hz, $C(O)OCH_a\mathit{H_b}Ph$), 5.16 (1H, d, *J* = 8.1 Hz, NH), 5.22 (1H, d, *J* = 9.1 Hz, NH), 5.41 (1H, d, *J* = 3.4 Hz, H-1), 6.76 (1H, d, *J* = 8.3 Hz, Ph), 6.80 (1H, d, *J* = 8.4 Hz, Ph), 7.10–7.31 (25H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.3 (CH_3), 37.2 ($Ph\mathit{C}H_2CH$), 52.3 (C-2), 54.8 (CH), 66.9 ($NHC(O)O\mathit{C}H_2Ph$), 67.2

(C(O)O*C*H_2Ph), 68.1 (C-6), 71.6 (C-5), 73.3–75.0 (CH_2Ph), 78.0 (C-4), 79.7 (C-3), 96.2 (C-1), 116.5 (Ph), 127.6-128.6 (Ph), 129.6 (Ph), 130.4 (Ph), 135.0-136.1 (Ph), 137.8–138.3 (Ph), 155.1 (Ph), 155.5 (Ph), 169.8 (C=O(CH_3)), 172.2 (C=O); HRMS (ESI): *m/z* calcd for $C_{53}H_{54}NO_{10}Na^+$: 901.3671; found: 901.3675.

4-Hydroxyphenyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (35) and 4-*tert*-butoxyphenyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (36)

Yb(OTf)$_3$ (126.9 mg, 0.20 mmol) was added to a solution of **1** (133.8 mg, 0.25 mmol), **34** (35.0 mg, 0.21 mmol), and $BF_3 \cdot OEt_2$ (0.8 μL, 0.006 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The resulting mixture was stirred for 1 h at room temperature and then quenched by the addition of sat. aq. $NaHCO_3$ solution (5 mL). The reaction mixture was then extracted with CH_2Cl_2, and the organic layer was rinsed with water and sat. aq. NaCl solution. After the organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure. The crude products were purified *via* preparative silica gel TLC (EtOAc/hexane = 1/1) to give **35** (80.3 mg, 66%) and **36** (10.7 mg, 8%) as white crystals. Compound **35**; *Rf* 0.12 (EtOAc/hexane = 1/1); mp 207.2–209.2 °C; $[\alpha]^{23}_{D}$ +38 (*c* 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ: 1.81 (3H, s, CH_3), 3.63 (1H, d, *J* = 10.7 Hz, H_a-6), 3.76 (1H, dd, *J* = 3.9 Hz, *J* = 9.5 Hz, H_b-6), 3.84–3.94 (3H, m, H-3, H-4, H-5), 4.33 (1H, dt, *J* = 3.9 Hz, *J* = 9.5 Hz, H-2), 4.44 (1H, d, *J* = 12.2 Hz, C*H*$_2$Ph), 4.57 (1H, d, *J* = 10.7 Hz, C*H*$_2$Ph), 4.60 (1H, d, *J* = 12.2 Hz, C*H*$_2$Ph), 4.68 (1H, d, *J* = 11.7 Hz, C*H*$_2$Ph), 4.83 (1H, d, *J* = 10.7 Hz, C*H*$_2$Ph), 4.90 (1H, d, *J* = 11.7 Hz, C*H*$_2$Ph), 5.30 (1H, d, *J* = 8.5 Hz, NH), 5.40 (1H, d, *J* = 3.7 Hz, H-1), 6.68 (2H, d, *J* = 9.1 Hz, Ph), 6.82 (2H, d, *J* = 8.8 Hz, Ph), 7.20–7.37 (15H, m, Ph); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 23.4 (CH_3), 52.8 (C-2), 68.3 (C-6), 71.5 (C-5), 73.4 (*C*H_2Ph), 74.9 (*C*H_2Ph), 75.1 (*C*H_2Ph), 78.3 (C-4), 79.6 (C-3), 97.1 (C-1), 116.1 (Ph), 118.1 (Ph), 127.6-151.5 (Ph), 170.2 (C=O); Anal. Calcd for $C_{35}H_{37}NO_7$: C, 72.02; H, 6.39; N, 2.40. Found: C, 71.80; H, 6.40; N, 2.36. Compound **36**; *Rf* 0.36 (EtOAc/hexane = 1/1); mp 135.2–137.2 °C; $[\alpha]^{23}_{D}$ +134 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.29 (9H, s, CH_3), 1.83 (3H, s, CH_3), 3.63 (1H, dd, *J* = 1.7 Hz, *J* = 11.0 Hz, H_a-6), 3.76 (1H, dd, *J* = 3.4 Hz, *J* = 11.0 Hz, H_b-6), 3.86-3–89 (2H, m, H-3, H-4), 3.91-3.93 (1H, m, H-5), 4.38 (1H, dt, *J* = 3.7 Hz, *J* = 9.5 Hz, H-2), 4.46 (1H, d, *J* = 12.2 Hz, CH_2Ph), 4.56 (1H, d, *J* = 10.8 Hz, CH_2Ph), 4.62 (1H, d, *J* = 11.9 Hz, CH_2Ph), 4.70 (1H, d, *J* = 11.7 Hz, CH_2Ph), 4.83 (1H, d, *J* = 10.8 Hz, CH_2Ph), 4.90 (1H, d, *J* = 11.7 Hz, CH_2Ph), 5.28 (1H, d, *J* = 9.0 Hz, NH), 5.44 (1H, d, *J* = 3.5 Hz, H-1), 6.89 (4H, m, Ph), 7.18–7.39 (15H, m, Ph); ^{13}C NMR (150 MHz, $CDCl_3$): δ 23.4 (Ac), 28.7 (Me x 3), 52.4 (C-2), 68.3 (C-6), 71.6 (C-5), 73.4 (CH_2Ph), 74.8 (CH_2Ph), 75.1 (CH_2Ph), 78.2 (C-4), 78.4 (C), 79.8 (C-3), 97.0 (C-1), 117.1 (Ph), 125.4 (Ph), 127.7–128.6 (Ph), 137.8 (Ph), 137.9 (Ph), 138.3 (Ph), 150.4 (Ph), 152.2 (Ph), 169.8 (C=O); Anal. Calcd for $C_{39}H_{45}NO_7 \cdot 2.5H_2O$: C, 68.40; H, 7.36; N, 2.05. Found: C, 68.69; H, 7.09; N, 1.99.

4-Hydroxyphenyl 2-acetamido-2-deoxy-α-D-glucopyranoside (31)

Palladium hydroxide (26.4 mg, 0.1 mmol) was added to a solution of **35** (54.6 mg, 0.1 mmol) in THF/MeOH (5 mL/5 mL). Hydrogen was then bubbled through the solution for 1 h. After the solvent was filtered and evaporated under reduced pressure, the crude product was purified *via* flash column chromatography on silica gel ($CHCl_3$/MeOH = 8/1) to afford **31** (27.3 mg, 93%) as white crystals. *Rf* 0.10 ($CHCl_3$/MeOH = 8/1); mp 78.8–80.8 °C; $[\alpha]^{23}_{D}$ +150 (*c* 1.1, MeOH); ^{1}H NMR (600 MHz, D_2O) δ: 1.91 (3H, s, CH_3), 3.44 (1H, t, *J* = 9.6 Hz, H-4), 3.65–3.67 (2H, m, H-6), 3.69–3.71 (1H, m, H-5), 3.80 (1H, t, *J* = 10.3 Hz, H-3), 3.91 (1H, dd, *J* = 3.4 Hz, *J* = 11.0 Hz, H-2), 5.27 (1H, d, *J* = 2.7 Hz, H-1), 6.70 (2H, d, *J* = 9.0 Hz, Ph), 6.87 (2H, d, *J* = 9.0 Hz, Ph); ^{13}C NMR (150 MHz, D_2O) δ: 22.6 (CH_3), 54.3 (C-2), 61.0 (C-6), 70.5 (C-4), 71.6 (C-3), 73.2 (C-5), 97.7 (C-1), 116.8 (Ph), 119.5 (Ph), 150.3 (Ph), 151.9 (Ph), 175.0 (C=O); Anal. Calcd for $C_{14}H_{19}NO_7$: C, 53.67; H, 6.11; N, 4.47. Found: C, 53.45; H, 6.44; N, 4.23.

REFERENCES AND NOTE

1. S. Kobayashi, M. Sugiura, H. Kitagawa, and W. W.-L. Lam, *Chem. Rev.*, 2002, **102**, 2227.
2. (a) T. Yamanoi, Y. Iwai, and T. Inazu, *Heterocycles,* 2000, **53**, 1263; (b) T. Yamanoi and I. Yamazaki, *Tetrahedron Lett.*, 2001, **42**, 4009.
3. K. Ikeda, Y. Torisawa, T. Nishi, J. Minamikawa, K. Tanaka, and M. Sato, *Bioorg. Med. Chem.*, 2003, **11**, 3073.
4. T. Mukaiyama and N. Shimomura, *Chem. Lett.*, 1993, 781.
5. S. Hosono, W.-S. Kim, H. Sasai, and M. Shibasaki, *J. Org. Chem.*, 1995, **60**, 4. Other references cited therein.
6. (a) T. Yamanoi, Y. Iwai, and T. Inazu, *J. Carbohydr. Chem.*, 1998, **17**, 819; (b) It was found that $Yb(OTf)_3$ was basically ineffective for the less reactive glycosyl acetates such as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl acetate. J. Inanaga, Y. Yokoyama, and T. Hashimoto, *Tetrahedron Lett.*, 1993, **34**, 2791.
7. R. Harrison and H. G. Fletcher, *J. Org. Chem.*, 1965, **30**, 2317.
8. T. Yamanoi, M. Midorikawa, and Y. Oda, *Heterocycles*, 2014, **88**, 201.
9. For example, M. Kawakubo, Y. Ito, Y. Okimura, M. Kobayashi, K. Sakura, S. Kasama, M. N. Fukuda, M. Fukuda, T. Katsuyama, and J. Nakayama, *Science*, 2004, **305**, 1003. Other references cited therein.
10. For example, (a) L. Feng, A. V. Perepelov, G. Zhao, S. D. Shevelev, Q. Wang, S. N. Senchenkova, A. S. Shashkov, Y. Geng, P. R. Reeves, Y. A. Knirel, and L. Wang, *Microbiology*, 2007, **153**, 139; (b) A. N. Kondakova, R. Fudala, S. N. Senchenkova, A. S. Shashkov, Y. A. Knirel, and W. Kaca, *Carbohydr. Res.*, 2003, **338**, 1191; (c) A. D. Cox, J.-R. Brisson, P. Thibault, and M. B. Perry,

Carbohydr. Res., 1997, **304**, 191; (d) H. Parolis, S. M. R. Stanley, A. Dell, and A. J. Reason, *Carbohydr. Res.*, 1995, **266**, 95.

11. For example, (a) A. Takatsuki, K. Arima, and G. Tamura, *J. Antibiot.*, 1971, **24**, 215; (b) T. Suami, H. Sasai, K. Matsuno, N. Suzuki, Y. Fukuda, and O. Sakanaka, *Tetrahedron Lett.*, 1984, **25**, 4533; (c) A. Tordai, L. F. Brass, and E. W. Gelfand, *Biochem. Biophys. Res. Commun.*, 1975, **65**, 248.
12. K.-F. Mo, X. Li, H. Li, L. Y. Low, C. P. Quinn, and G.-J. Boons, *J. Am. Chem. Soc.*, 2012, **134**, 15556.
13. Manabe et al. reported the synthetic approach of the 2-acetamido-2-deoxy-α-D-glucopyranosides through the glycosidation using a *N*-benzyl-2,3-oxazolidinone-protected glucosamine derivative. (a) S. Manabe, K. Ishii, and Y. Ito, *J. Am. Chem. Soc.*, 2006, **128**, 10666; (b) S. Manabe, K. Ishii, and Y. Ito, *J. Org. Chem.*, 2007, **72**, 6107. The typical approaches for the preparation of the 2-amido-2-deoxy-α-D-glucopyranosides utilized the glycosyl donors having an azido group or a benzylideneamino group at C-2. For example, (c) J. Park, S. Kawatkar, J.-H. Kim, and G.-J. Boons, *Org. Lett.*, 2007, **9**, 1959; (d) E. A. Mensah, F. Yu, and H. M. Nguyen, *J. Am. Chem. Soc.*, 2010, **132**, 14288.
14. For example, (a) M. Kiso and L. Anderson, *Carbohydr. Res.*, 1985, **136**, 309; (b) G. Arsequell, L. Krippner, R. A. Dwek, and S. Y. C. Wong, *J. Chem. Soc., Chem. Commun.*, 1994, 2383; (c) I. Carvalho, S. L. Scheuerl, K. P. R. Kartha, and R. A. Field, *Carbohydr. Res.*, 2003, **338**, 1039; (d) A β-glycosidation method has been reported directly from 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl diethyl phosphate in the presence of bis(trifluoromethanesulfonyl)imide *via* the α-glycosyl triflate intermediate, not the oxazoline derivative. R. Arihara, S. Nakamura, and S. Hashimoto, *Angew. Chem. Int. Ed.*, 2005, **44**, 2245.
15. The addition of a Brønsted acid, such as hydrochloric or carboxylic acid, dramatically accelerated the aldol and allylation reactions catalyzed by a Lewis acid in water. K. Manabe, Y. Mori, S. Nagayama, K. Odashima, and S. Kobayashi, *Inorg. Chim. Acta*, 1999, **296**, 158.
16. P. Rollin and P. Sinay, *J. Chem. Soc., Perkin Trans. 1*, 1977, **22**, 2513.
17. We have also found that the glycosidation of **1** with triallylborate in the presence of $Yb(OTf)_3$ gave allyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside with a considerable amount of α-isomer. See ref. 2a.
18. We also have applied the 1,2-*cis*-α-aryl-D-glycosidation method to the synthesis of a β-cyclodextrin derivative conjugated with a 2-acetamido-2-deoxy-α-D-glucopyranoside residue. Y. Oda, M. Miura, K. Hattori, and T. Yamanoi, *Chem. Pharm. Bull.*, 2009, **57**, 74.
19. (a) M. Funayama, H. Arakawa, R. Yamamoto, T. Nishino, T. Shin, and S. Murao, *Biosci. Biotech. Biochem.*, 1995, **59**, 143; (b) K. Sugimoto, T. Nishimura, K. Nomura, K. Sugimoto, and T. Kuriki,

Chem. Pharm. Bull., 2003, **51**, 798.

20. For example, (a) S. Mathew and P. Adlercreutz, *Biochem. Eng. J.*, 2003, **79**, 187; (b) R. Prodanović, N. Milosavić, D. Sladić, M. Zlatović, B. Božić, T. C. Veličković, and Z. Vujčić, *J. Mol. Catal. B: Enzym.*, 2005, **35**, 142; (c) K. Sugimoto, K. Nomura, T. Nishimura, T. Kiso, K. Sugimoto, and T. Kuriki, *J. Biosci. Bioeng.*, 2005, **99**, 272; (d) J.-P. Praly, L. He, B. B. Qin, M. Tanoh, and G.-R. Chen, *Tetrahedron Lett.*, 2005, **46**, 7081; (e) P. Wang, B. D. Martin, S. Parida, D. G. Rethwisch, and J. S. Dordick, *J. Am. Chem. Soc.*, 1995, **117**, 12885; (f) H. Nakano, M. Shizuma, H. Murakami, T. Kiryu, and T. Kiso, *J. Mol. Catal. B: Enzym.*, 2005, **33**, 1.
21. (a) Z.-X. Wang, X.-X. Shi, G.-R. Chen, Z.-H. Ren, L. Luo, and J. Yan, *Carbohydr. Res.*, 2006, **341**, 1945; (b) H. G. Thomas and J.-L. Mieusset, *Tetrahedron*, 2008, **64**, 5124.
22. J.-C. Jacquinet and P. Sinay, *Carbohydr. Res.*, 1976, **46**, 138.
23. A. Mbongo, C. Fréchou, D. Beaupère, R. Uzan, and G. Demailly, *Carbohydr. Res.*, 1993, **246**, 361.
24. J. Liu and D. Y. Gin, *J. Am. Chem. Soc.*, 2002, **124**, 9789.
25. C. D. Warren, M. A. E. Shaban, and R. W. Jeanloz, *Carbohydr. Res.*, 1977, **59**, 427.
26. M. A. Nashed, C. W. Slife, M. Kiso, and L. Anderson, *Carbohydr. Res.*, 1980, **82**, 237.
27. W.-S. Kim, S. Hosono, H. Sasai, and M. Shibasaki, *Heterocycles*, 1996, **42**, 795.