

Preparation of C-Glycoside Pendant β^2 - and $\beta^{2,2}$ -Amino Acids

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Facile preparations of C-glycosyl β^2 - and $\beta^{2,2}$ -amino acids are described. Selective formation of a β -C-glycoside linkage was achieved by the reaction of a 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide (α -acetobromoglucose/galactose) with the carbanion of a cyanoacetate ester. Crystallization selectively afforded one of two diastereomers with respect to the chiral center at the α -carbon of the side chain (C-2), however, this compound was found to epimerize during the following nitrile reduction. Separation of the diastereomers was achieved via the Fmoc derivatives. Diastereomerically pure C-glycosyl $\beta^{2,2}$ -amino acids were prepared by diastereoselective alkylation of C-glycosylated enolate, followed by nitrile hydrogenation. The present procedure serves as an efficient route to C-glycosylated β -amino acids containing a non-biodegradable linkage.

Glycopeptides play key roles in numerous biological processes including metastasis, infection, and inflammation.¹ Generally, oligosaccharide residues of glycopeptides are connected to the peptide backbone via *N*- (via asparagine) or *O*-glycoside (via serine or threonine) linkage.² However, many researchers have recently turned their attention to C-glycosyl amino acids to probe biological processes, owing to their increased stability toward chemical and enzymatic hydrolysis.^{3–6} Hence, numerous C-glycosyl α -amino acids (Chart 1, **I**) have been reported.^{7–16}

In the past decade, β -amino acids have become an interesting synthetic target as well as precursors for β -lactams and other medicinally important molecules.^{17–20} β -Amino acids can be subdivided into three main categories, namely β^2 -, β^3 -, and $\beta^{2,3}$ -amino acids, depending on the substitution patterns of the 3-aminopropanoic acid skeleton. β -Amino acid oligomers, i.e. β -peptides, have been shown to fold into helical, sheet, and turn conformations in solution.^{21,22} Additionally, β -peptides are also known to be more resistant toward proteolytic degradation as compared to α -peptides.^{23,24} Considering the aforementioned characteristics, the synthesis of C-glycosyl β -amino acids would exhibit significant utility toward the development of stable glycosylase- and protease-resistant pharmaceuticals and functional materials.

Several preparations of C-glycosyl β^3 -amino acids (Chart 1, **III**) by Tripathi et al.,^{25,26} Sharma et al.,²⁷ Dondoni et al.,^{28–30} and Palomo et al.³¹ have been reported. Sharma and co-workers have reported the synthesis and conformational analysis of β -peptides with C-glycosyl β^3 -amino acids.^{32–36} However, there are very few examples describing the preparation of C-glycosyl β^2 -amino acid derivatives (Chart 1, **II**).^{37,38} Furthermore, the stereoselective synthesis of $\beta^{2,2}$ -amino acids with a quaternary stereogenic center (Chart 1, **IV**) remains an important challenge.^{39,40} In this paper, we report the versatile

synthesis of β^2 -, $\beta^{2,2}$ -amino acids with a glycosyl group directly connected to the C2 carbon.

Results and Discussion

Synthesis of C-Glycosyl β^2 -Amino Acids. The S_N2 reaction of 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide (α -acetobromoglucose) with the nucleophilic carbanion of *t*-butyl cyanoacetate affords compound **1a** exclusively as the β -anomer. X-ray crystallographic analysis of **1a** revealed an *S* absolute configuration of the stereoisomer at the side chain C2 (Figure 1).

Subsequent PtO_2 -catalyzed hydrogenation of the nitrile moiety of **1a** in $CHCl_3$ /EtOH affords a diastereomeric mixture **2a** and **3a** (74:26) via epimerization of compound **1a** likely due to the acidic nature of the C2-hydrogen. Diastereomerically pure **3a** was isolated by recrystallization of **2a/3a** from methanol–ether in 8% recovery. The absolute configuration of **3a** was determined to be *2S* by X-ray crystallography.³⁸ The difficulty in obtaining diastereomer **2a** and the poor recovery of **3a** from repeated recrystallization is far from ideal. Changing the ester moiety from *t*-butyl to ethyl increased the recovery of **3** (28% (**3b**)). Although the absolute configuration of **1b** was also determined to be *2S* by X-ray crystallography (Figure 2), compound **3b** does not afford single crystals. Hence, the absolute configuration of **3b** was determined by converting to the β -amino acid **5** and comparing the NMR spectra with that obtained from **3a**. More specifically, hydrolysis of amines **3a** and **3b** in 6 mol dm^{−3} HCl affords the corresponding β -amino acid as the hydrochloride salt in a diastereomerically pure form (Scheme 1).

A similar procedure was used for the galactose derivatives, affording **9(2R)/10(2S)** in 33–39% overall yield. The galactose derivatives formed the corresponding β -C-glycoside nitriles **6a** and **6b** whose structures were determined by X-ray crystallography (Figures 3 and 4). However, the amines **7a,7b(2R)/8a,8b(2S)** currently remain as a mixture of diastereomers.

To obtain both stereoisomers of the β -amino acids in dia-

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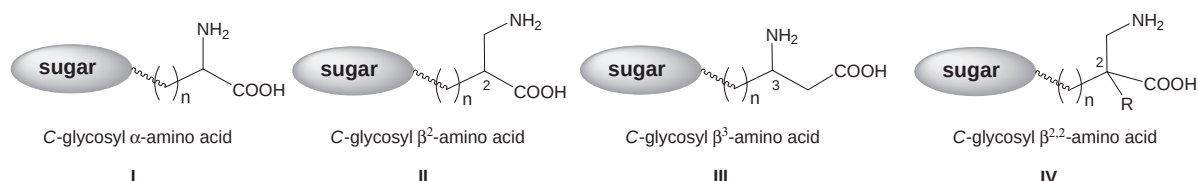
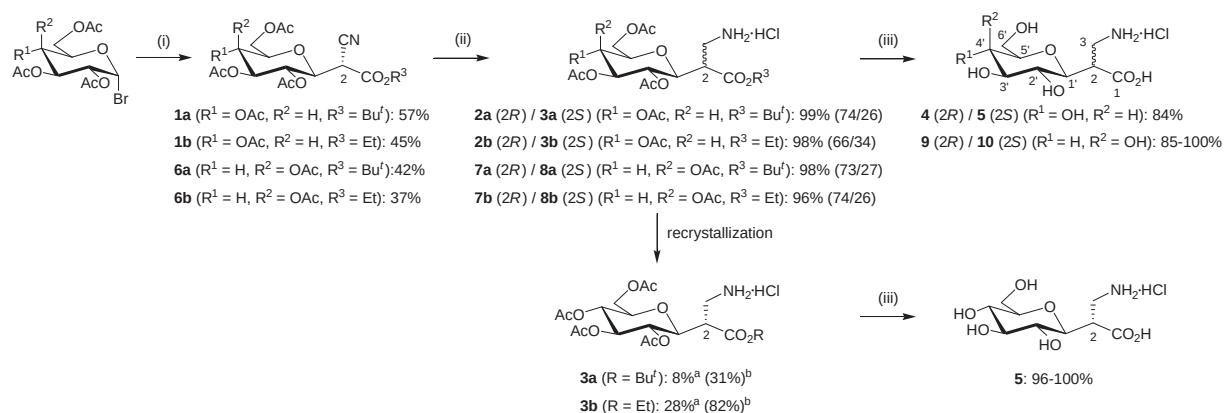


Chart 1.



Scheme 1. Synthesis of *C*-glycosyl β²-amino acids. Reagents and conditions: (i) *t*-butyl cyanoacetate or ethyl cyanoacetate, NaH, DMF, 0 °C, 2 h; (ii) H₂, PtO₂, CHCl₃, EtOH, overnight; (iii) 6 mol dm⁻³ HCl, reflux, 2 h–overnight. a) Recovery from total 2/3. b) Recovery of 3 from the mixture of 2/3.

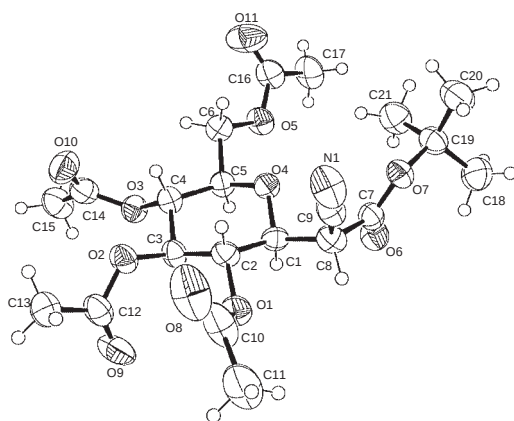


Figure 1. ORTEP plot for 1a.

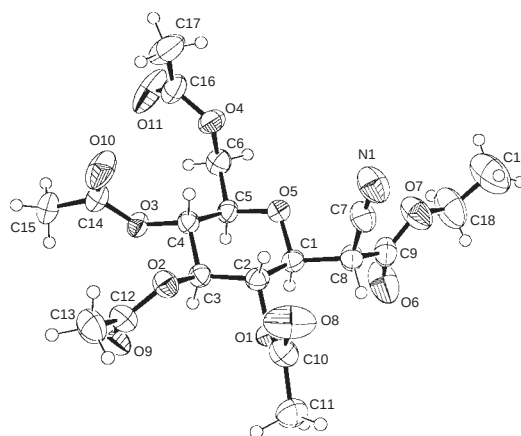


Figure 2. ORTEP plot for 1b.

stereomerically pure forms, the amines **2a/3a** (74/26) and **7a/8a** (73/27) were converted to the corresponding Fmoc-derivatives (Fmoc = 9-fluorenylmethoxycarbonyl) **11/12** and **15/16** by Fmoc-succinates and triethylamine in MeOH/CH₃CN. The diastereomers were then successfully separated by silica gel column chromatography. Deprotection of the *t*-butyl groups with formic acid led to both (2*R*)- and (2*S*)-Fmoc-protected *C*-glycosyl β²-amino acids **13/14** and **17/18**, useful synthons for solid-phase peptide synthesis (Scheme 2). Assignments of the absolute configurations of glucose derivatives **11** (Figure 5) and **14**³⁸ were established by crystallographic analysis. The configuration of the galactose derivatives were predicted by comparing the ¹H NMR chemical shifts of the C2-hydrogen NMR with the glucose derivatives (2.8 ppm for **11** and **15**, 2.7 ppm for **12** and **16**). A similar product ratio for the glucose **11/12** and galactose derivatives **15/16** also supports this prediction.

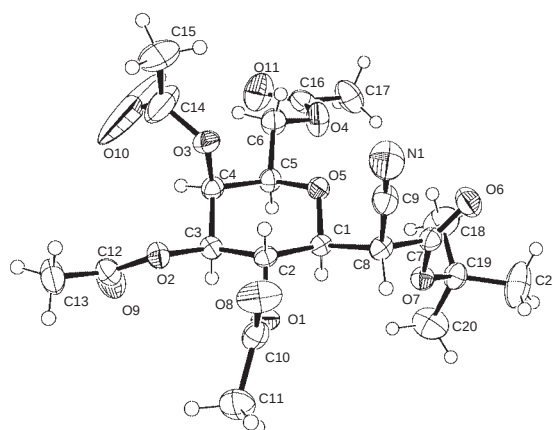
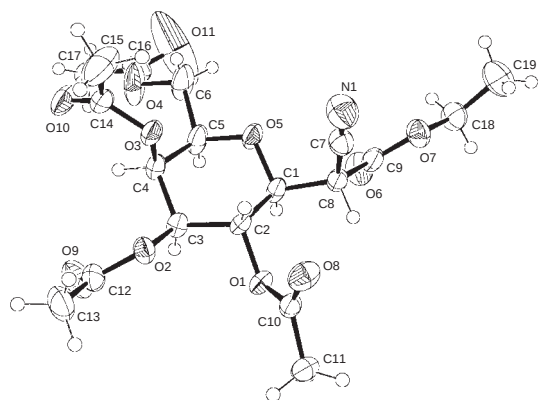
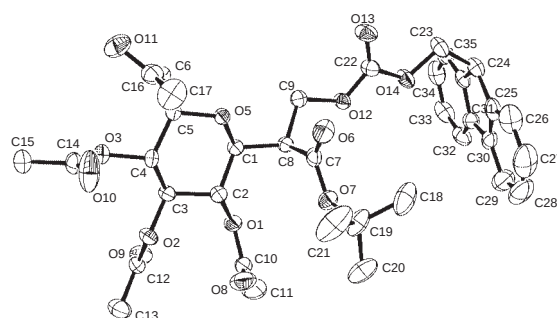
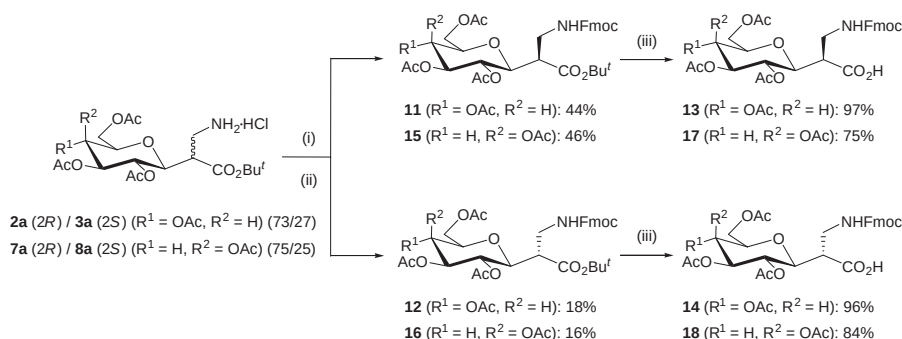
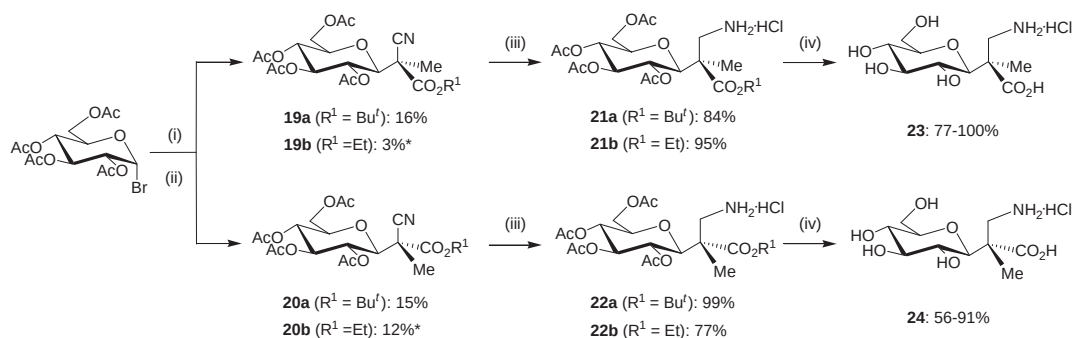


Figure 3. ORTEP plot for 6a.

Figure 4. ORTEP plot for **6b**.Figure 5. ORTEP plot for **11**.

Scheme 2. Synthesis of Fmoc-protected amino acids. Reagents and conditions: (i) FmocOSu, Et_3N , MeOH, CH_3CN , rt, 3 h; (ii) silica gel column chromatography; (iii) HCOOH , rt, 3 h.



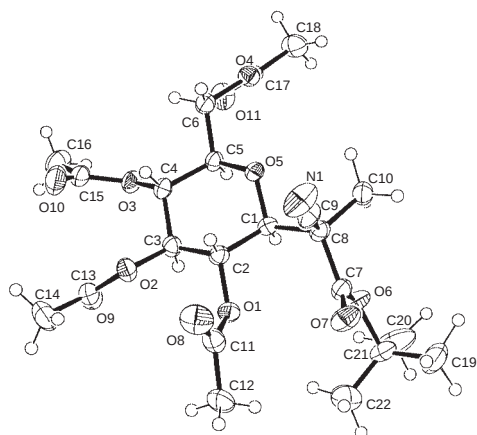
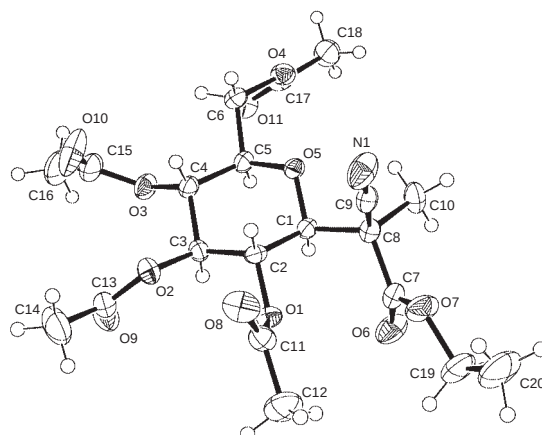
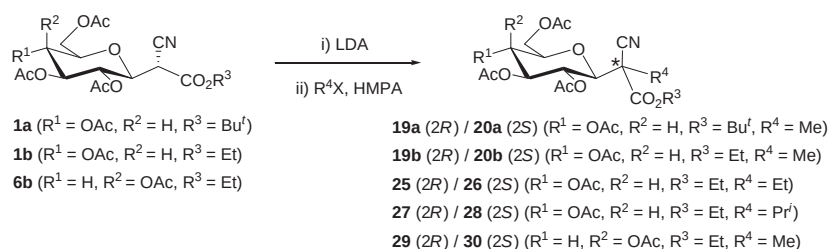
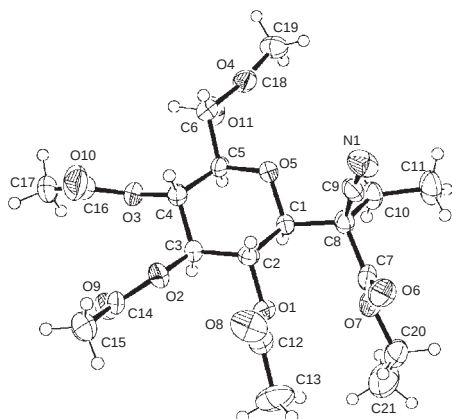
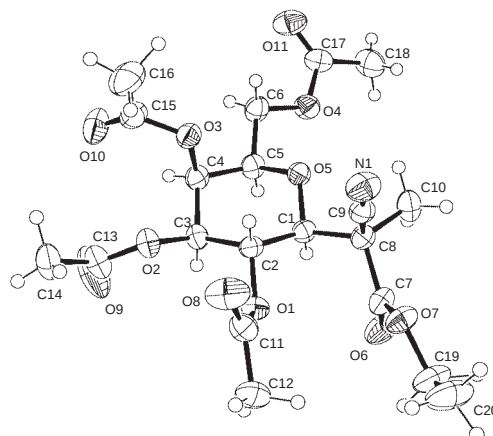
Scheme 3. Synthesis of C-glycosyl $\beta^{2,2}$ -amino acids. Reagents and conditions: (i) *t*-butyl or ethyl 2-cyanoacetate, NaH, DMF, 0°C , 2 h; (ii) silica gel column chromatography and recrystallization; (iii) H_2 , PtO_2 , CHCl_3 , EtOH, overnight; (iv) 6 mol dm^{-3} HCl, reflux, overnight. *) Unresolved mixture of **19b** and **20b**: 44%.

Synthesis of C-Glycosyl $\beta^{2,2}$ -Amino Acids. Our studies suggested that C-glycosylated cyanoacetate **1** was subject to epimerization owing to the high acidity of C2-H as previously described. We thus attempted to inhibit this isomerization by substituting the C2 hydrogen with an alkyl group to afford a $\beta^{2,2}$ -amino acid.

Compounds **19a**, **19b**/**20a**, **20b**, in which the C2-H of **1a** and **1b** is exchanged for a methyl group, were prepared by a similar procedure to that described above using *t*-butyl/ethyl 2-cyanoacetate in place of 2-cyanoacetate ester. Two diastereomers with respect to the quaternary carbon (C2) in the side chain were obtained in approximately 1:1 ratio and were separated by silica gel column chromatography and recrystallization.

No isomerization was observed in the subsequent nitrile hydrogenation. Thus, both stereoisomers of the $\beta^{2,2}$ -amino acids **23** and **24** were obtained in diastereomerically pure form (Scheme 3). Introduction of a methyl group at the C-2 carbon of **1a** and **1b** suppresses epimerization and allows efficient separation of the nitrile diastereomers. X-ray crystallography of **19a** and **19b** reveals the configuration of the C-2 carbon (Figures 6 and 7).

Cativiela and co-workers have reported that diastereoselective alkylation of the enolate form of alkylcyano[(1*S*,2*R*,4*R*)-1-(dicyclohexylsulfamoylmethyl)-7,7-dimethylbicyclo[2,2,1]-heptan-2-yl]acetates affords diastereomerically pure $\beta^{2,2}$ -di-alkylcyanoacetate.⁴¹ We employed this alternative method

Figure 6. ORTEP plot for **19a**.Figure 7. ORTEP plot for **19b**.Scheme 4. Alkylations of **1a**, **1b**, and **6b**.Figure 8. ORTEP plot for **25**.Figure 9. ORTEP plot for **29**.

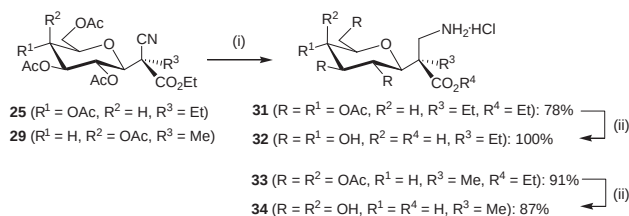
for the diastereoselective preparation of *C*-glycosyl $\beta^{2,2}$ -amino acids using the sugar moiety of **1a** and **1b** as a chiral auxiliary. The enolates of the *C*-glycosylated cyanoacetate esters **1a**, **1b**, and **6b** generated by lithium diisopropylamide in dry THF at -78°C were alkylated with MeI, EtI, and *i*-PrI in the presence of hexamethylphosphoric triamide (HMPA) (Scheme 4 and Table 1). The absolute configuration of the isolated products **25** and **29** were determined by X-ray crystallography (Figures 8 and 9).

We initially examined the alkylation of *t*-butyl/ethyl (2*S*)-(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)cyanoacetate **1a**/**1b** with methyl iodide (Table 1, Entries 1 and 2). As the ethyl ester **1b** was isolated in higher yield than the *t*-butyl ester **1a** without loss of diastereoselectivity, further experiments were

Table 1. Diastereoselective Alkylation of **1a**, **1b**, and **6b**

Entry	Starting material	Product	$R^4\text{X}$	Yield ^{a)} /%	dr(2 <i>R</i> /2 <i>S</i>) ^{b)}
1	1a	19a/20a	CH_3I	48 (38)	81/19
2	1b	19b/20b	CH_3I	80 (25)	81/19
3	1b	25/26	$\text{CH}_3\text{CH}_2\text{I}$	41 (35)	92/8
4	1b	27/28	$(\text{CH}_3)_2\text{CHI}$	6	87/13 ^{c)}
5	6b	29/30	CH_3I	86 (66)	82/18

a) Yield of a diastereomer mixture. Values in parentheses indicates isolated yield of the major isomer. b) Derived from ^1H NMR integral ratio of unresolved product. c) The absolute configuration was not determined.



Scheme 5. Synthesis of diastereomerically pure C-glycosyl $\beta^{2,2}$ -amino acids. Reagents and conditions: (i) H_2 , PtO_2 , CHCl_3 , EtOH , overnight; (ii) 6 mol dm^{-3} HCl , reflux, overnight.

conducted using ethyl esters **1b** and **6b**.

As seen in Entries 3 and 4 in Table 1, larger alkyl halides result in slightly better diastereoselectivity along with significant loss of product yield. In the case of the isopropyl derivatives, we were unable to isolate **27/28** from the reaction mixture, preventing further investigation.

The methylation of galactose derivative **6b** proceeds in similar yield and selectivity as compared to the glucose derivative. Thus, the close proximity of the attached C-glycoside moiety to the reaction center acts as an efficient chiral auxiliary for the diastereoselective preparation of C-glycosylated $\beta^{2,2}$ -amino acids. The nitriles **25** and **29** were converted to $\beta^{2,2}$ -amino acids **32** and **34** under the same conditions described above (Scheme 5).

Summary

We have developed a facile preparation of diastereomerically pure C-glycosyl β^2 - and $\beta^{2,2}$ -amino acids. Although epimerization with respect to C-glycosylated cyanoacetate **1** during nitrile reduction was unavoidable owing to the high acidity of C2-H, diastereomerically pure C-glycosyl β^2 -amino acids were obtained after recrystallization or Fmoc derivatization of amines. The yields of C-glycoside formation are moderate (31% to 57%), and the following two steps proceeded with nearly quantitative yield. Fmoc derivatives (*R*)-**13** and (*S*)-**14** were prepared from D-glucose in five steps without any special techniques, which is in contrast to Sharma's method to obtain amine-protected analogues.⁴⁰ The present procedure is applicable to other sugar moieties to display a library of C-glycosyl β^2 - and $\beta^{2,2}$ -amino acids. Readily available, well-resolved diastereomers of C-glycosyl β^2 - and $\beta^{2,2}$ -amino acids should be useful carbohydrate-containing β -amino acid building blocks for glycopeptide research and application to pharmaceuticals.^{42–44} The synthesis and investigation of C-glycosyl β^2 -peptides incorporating these sugar amino acids is currently underway.

Experimental

General. All reagents and solvents were from commercial sources and used as received. *N,N*-Dimethylformamide (dmf, Wako) was dried over CaSO_4 and distilled under reduced pressure. Tetrahydrofuran was distilled over sodium metal and benzophenone. TLC was performed on Merck silica gel 60 aluminium sheets. Melting points were determined on a Yanaco MP-J3 micro hotstage. Optical rotations were measured at room temperature (20 °C) with a Jasco DIP-140 digital polarimeter. ^1H NMR (300.07 MHz) and ^{13}C NMR (75.00 MHz) spectra were recorded on a Varian GEMINI 2000 spectrometer and referenced to internal

TMS or solvent signals. Mass spectra were obtained by electrospray ionization-mass spectrometry (ESI-MS) on a JEOL JMS-T 100LC.

t-Butyl (2*S*)-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-cyanoacetate (**1a**).

To a solution of *t*-butyl cyanoacetate (4.24 g, 30.0 mmol) in 12 mL of dmf was added sodium hydride (1.32 g, 33.0 mmol; previously washed with hexane) by portions with stirring at 0 °C. After the evolution of hydrogen gas ceased, a solution of α -acetobromoglucose (4.12 g, 10.0 mmol) in 8 mL of dmf was slowly added dropwise with stirring at 0 °C and the reaction mixture was stirred for 2 h. After aqueous acetic acid (10%) was added, the yellow precipitate was filtered and washed with water. The product was dissolved in dichloromethane (120 mL) and dried over sodium sulfate and concentrated in vacuo. The residue was recrystallized in ethanol to afford **1a** as colorless needles (2.72 g, 5.76 mmol) in 57% yield. Mp 138–139 °C (EtOH); ^1H NMR (CDCl_3 , Me_4Si): δ 5.28–5.09 (3H, m, H-3', H-2', H-4'), 4.20 (1H, dd, $J = 2.4, 12.2$ Hz, H-6'a), 4.15–4.07 (2H, m, H-6'b, H-1'), 3.72 (1H, ddd, $J = 2.4, 4.9, 9.8$ Hz, H-5'), 3.60 (1H, d, $J = 2.4$ Hz, H-2), 2.07 (3H, s, COCH_3), 2.06 (3H, s, COCH_3), 2.04 (3H, s, COCH_3), 2.02 (3H, s, COCH_3), 1.53 (9H, s, $(\text{CH}_3)_3\text{C}$). ^{13}C NMR (CDCl_3): δ 170.55, 170.31, 169.26, 169.11 (COCH_3), 162.25 (COO^tBu), 112.82 (CN), 85.24 ($(\text{CH}_3)_3\text{C}$), 76.24 (C-5'), 75.30 (C-1'), 73.76 (C-3'), 69.70 (C-2'), 68.02 (C-4'), 61.90 (C-6'), 41.42 (C-2), 27.78, 27.70 ($(\text{CH}_3)_3\text{C}$), 20.60 (COCH_3). ESI-MS Calcd for $\text{C}_{21}\text{H}_{29}\text{NO}_{11}\text{Na}$ ($[\text{M} + \text{Na}]^+$): 494.16. Found: 494.09. Anal. Found: C, 53.48; H, 6.25; N, 2.98%. Calcd for $\text{C}_{21}\text{H}_{29}\text{NO}_{11}$: C, 53.50; H, 6.20; N, 2.97%. Crystal data: monoclinic, space group *C*2, $a = 24.21(3)$ Å, $b = 5.838(6)$ Å, $c = 17.15(2)$ Å, $V = 2414.7(44)$ Å³, $Z = 4$, $R = 0.092$, $R_w = 0.271$, GOF = 1.055.

Ethyl (2*S*)-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)cyanoacetate (**1b**).

Compound **1b** was prepared by a method similar to the preparation of **1a** using ethyl cyanoacetate in place of *t*-butyl cyanoacetate. Yield: 45%. Mp 138–139 °C (EtOH); ^1H NMR (CDCl_3 , Me_4Si): δ 5.26 (1H, dd, $J = 8.7, 9.2$ Hz, H-3'), 5.18 (1H, dd, $J = 8.7, 9.5$ Hz, H-2'), 5.14 (1H, dd, $J = 9.2, 9.9$ Hz, H-4'), 4.32 (2H, q, $J = 7.0$ Hz, CH_2CH_3), 4.17 (2H, d, $J = 3.7$ Hz, H-6'a, H-6'b), 4.14 (1H, dd, $J = 2.7, 9.5$ Hz, H-1'), 3.73 (1H, m, H-5'), 3.68 (1H, d, $J = 2.7$ Hz, H-2), 2.08 (3H, s, COCH_3), 2.07 (3H, s, COCH_3), 2.04 (3H, s, COCH_3), 2.02 (3H, s, COCH_3), 1.35 (3H, t, $J = 7.0$ Hz, CH_2CH_3). ^{13}C NMR (CDCl_3): δ 170.55, 170.25, 169.23, 169.14 (COCH_3), 163.40 (COOEt), 112.50 (CN), 76.01 (C-5'), 75.04 (C-1'), 73.57 (C-3'), 69.67 (C-2'), 67.81 (C-4'), 63.52 (CH_2CH_3), 61.60 (C-6'), 40.45 (C-2), 20.55 (COCH_3), 13.90 (CH_2CH_3). ESI-MS Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_{11}\text{Na}$ ($[\text{M} + \text{Na}]^+$): 466.13. Found: 466.08. Anal. Found: C, 51.52; H, 5.77; N, 3.20%. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_{11}$: C, 51.47; H, 5.68; N, 3.16%. Crystal data: orthorhombic, space group *P*2₁2₁2₁, $a = 7.0872(15)$ Å, $b = 12.529(3)$ Å, $c = 25.424(6)$ Å, $V = 2257.5(8)$ Å³, $Z = 4$, $R = 0.052$, $R_w = 0.166$, GOF = 0.982.

t-Butyl (2*S*)-(2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl)-cyanoacetate (**6a**).

Compound **6a** was prepared by a method similar to the preparation of **1a** using 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide (α -acetobromogalactose) in place of α -acetobromoglucose. Yield: 42%. Mp 151–152 °C (EtOH); ^1H NMR (CDCl_3 , Me_4Si): δ 5.44 (1H, dd, $J = 0.92, 3.4$ Hz, H-4'), 5.38 (1H, dd, $J = 9.8, 10.1$ Hz, H-2'), 5.09 (1H, dd, $J = 3.4, 10.1$ Hz, H-3'), 4.18–4.04 (3H, m, H-1, H-6'a, H-6'b), 3.95 (1H, ddd, $J = 0.92, 5.5, 5.5$ Hz, H-5'), 3.60 (1H, d, $J = 2.7$ Hz, H-2), 2.18 (3H, s, COCH_3), 2.08 (3H, s, COCH_3),

2.02 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.53 (9H, s, (CH₃)₃C). ¹³C NMR (CDCl₃): δ 170.25, 170.03, 169.29 (COCH₃), 162.45 (COOBu^t), 112.97 (CN), 85.07 ((CH₃)₃C), 75.77, 74.62, 71.63, 67.13, 61.56, 41.68 (C-2), 27.78, 27.67 ((CH₃)₃C), 20.61 (COCH₃). HRMS (ESI) Calcd for C₁₇H₂₁NO₁₁Na ([M – Bu^t + H + Na]⁺): 438.10123. Found: 438.10091. Anal. Found: C, 53.52; H, 6.21; N, 3.02%. Calcd for C₂₁H₂₉NO₁₁: C, 53.50; H, 6.20; N, 2.97%. Crystal data: monoclinic, space group *P*2₁, *a* = 10.237(2) Å, *b* = 9.770(2) Å, *c* = 12.894(3) Å, β = 101.4403(10)°, *V* = 1263.9(5) Å³, *Z* = 2, *R* = 0.051, *R*_w² = 0.156, GOF = 1.084.

Ethyl (2S)-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-cyanoacetate (6b): Compound **6b** was prepared by a method similar to the preparation of **1b** using α-acetobromogalactose in place of α-acetobromoglucose and purified by silica gel column chromatography with hexane/ethyl acetate 1:1 (*R*_f = 0.25). Yield: 37%. Mp 121–123 °C (EtOH); ¹H NMR (CDCl₃, Me₄Si): δ 5.44 (1H, dd, *J* = 0.92, 3.2 Hz, H-4'), 5.38 (1H, dd, *J* = 9.8, 10.1 Hz, H-2'), 5.09 (1H, dd, *J* = 3.2, 9.8 Hz, H-3'), 4.32 (2H, q, *J* = 7.0 Hz, CH₂CH₃), 4.11 (2H, dd, *J* = 1.1, 7.0 Hz, H-6'a, H-6'b), 4.09 (1H, dd, *J* = 2.7, 10.1 Hz, H-1'), 3.96 (1H, ddd, *J* = 1.1, 7.0, 7.0 Hz, H-5'), 3.67 (1H, d, *J* = 2.7 Hz, H-2), 2.18 (3H, s, COCH₃), 2.08 (3H, s, COCH₃), 2.03 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.35 (3H, t, *J* = 7.0 Hz, CH₂CH₃). ¹³C NMR (CDCl₃): δ 170.21, 169.99, 169.36 (COCH₃), 163.61 (COOEt), 112.64 (CN), 75.54, 75.48, 74.44, 71.52, 66.94, 63.41, 61.18, 40.98 (C-2), 20.60, 20.42 (COCH₃), 13.85 (CH₂CH₃). ESI-MS Calcd for C₁₉H₂₅NO₁₁Na ([M + Na]⁺): 466.13. Found: 466.03. Anal. Found: C, 51.41; H, 5.69; N, 3.17%. Calcd for C₁₉H₂₅NO₁₁: C, 51.47; H, 5.68; N, 3.16%. Crystal data: monoclinic, space group *P*2₁, *a* = 9.2023(5) Å, *b* = 8.3030(4) Å, *c* = 14.3389(7) Å, β = 97.0267(10)°, *V* = 1087.36(10) Å³, *Z* = 2, *R* = 0.057, *R*_w² = 0.175, GOF = 1.117.

General Procedure for Alkylation. To a dry THF solution (10 mL) of lithium diisopropylamide (2.0 M solution, 0.275 mL, 0.55 mmol) was added a solution of **1a**, **1b**, and **6b** (0.5 mmol) in dry THF (9.0 mL) under argon at –78 °C. After 1 h, a solution of iodomethane (0.31 mL, 5.0 mmol)/iodoethane (0.40 mL, 5.0 mmol)/2-iodopropane (0.50 mL, 5.0 mmol) and HMPA (0.13 mL, 0.75 mmol) in dry THF (5.0 mL) was added by syringe. The reaction mixture was allowed to warm to room temperature and stirring was continued for 1 day. The reaction mixture was then quenched with saturated aqueous NH₄Cl solution (5 mL). An ether extraction, washing by water, drying over Na₂SO₄ and concentration in vacuo yielded a mixture of diastereomers of corresponding 2-alkylated 2-cyano ester as a crude oil, which was chromatographed on a silica gel column (eluent: hexane/ethyl acetate 1:1).

***t*-Butyl (2R)-2-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-2-cyanopropanoate (19a):** Mp 96–100 °C (EtOH); [α]_D²⁰ = 9.83 (*c* = 0.999, CHCl₃); ¹H NMR (CDCl₃, Me₄Si): δ 5.27 (1H, dd, *J* = 9.2, 9.3 Hz, H-3'), 5.21 (1H, dd, *J* = 7.9, 9.2 Hz, H-2'), 5.05 (1H, dd, *J* = 9.3, 9.8 Hz, H-4'), 4.15 (1H, dd, *J* = 4.8, 12.5 Hz, H-6'a), 4.13 (1H, d, *J* = 7.9 Hz, H-1'), 4.07 (1H, dd, *J* = 2.4, 12.5 Hz, H-6'b), 3.69 (1H, ddd, *J* = 2.4, 4.8, 9.8 Hz, H-5'), 2.09 (3H, s, COCH₃), 2.04 (3H, s, COCH₃), 2.03 (3H, s, COCH₃), 2.01 (3H, s, COCH₃), 1.56 (3H, s, 2-CH₃), 1.52 (9H, s, (CH₃)₃C). ¹³C NMR (CDCl₃): δ 170.39, 170.07, 169.55, 169.26 (COCH₃), 164.42 (COOBu^t), 117.39 (CN), 84.33 ((CH₃)₃C), 77.78 (C-1'), 76.21 (C-5'), 73.91 (C-3'), 68.34 (C-2'), 68.00 (C-4'), 61.97 (C-6'), 45.19 (C-2), 27.68, 27.65 ((CH₃)₃C), 20.79, 20.57, 20.53, 20.47 (COCH₃), 15.82 (2-CH₃).

ESI-MS Calcd for C₁₈H₂₃NO₁₁Na ([M – Bu^t + H + Na]⁺): 452.12. Found: 452.07. Anal. Found: C, 54.24; H, 6.44; N, 2.84%. Calcd for C₂₂H₃₁NO₁₁: C, 54.43; H, 6.44; N, 2.89%. Crystal data: monoclinic, space group *P*2₁, *a* = 6.394(2) Å, *b* = 21.419(5) Å, *c* = 9.530(3) Å, β = 108.259(3)°, *V* = 1239.3(6) Å³, *Z* = 2, *R* = 0.036, *R*_w² = 0.084, GOF = 1.118.

***t*-Butyl (2S)-2-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-2-cyanopropanoate (20a):** Mp 175–177 °C (EtOH); [α]_D²⁰ = 0.811 (*c* = 1.01, CHCl₃); ¹H NMR (CDCl₃, Me₄Si): δ 5.30 (1H, dd, *J* = 9.2, 9.6 Hz, H-2'), 5.20 (1H, dd, *J* = 9.2, 9.5 Hz, H-3'), 5.08 (1H, dd, *J* = 9.5, 9.8 Hz, H-4'), 4.20 (1H, dd, *J* = 5.2, 12.4 Hz, H-6'a), 4.14 (1H, dd, *J* = 2.4, 12.4 Hz, H-6'b), 3.95 (1H, d, *J* = 9.6 Hz, H-1'), 3.73 (1H, ddd, *J* = 2.4, 5.2, 9.8 Hz, H-5'), 2.07 (3H, s, COCH₃), 2.04 (6H, s, COCH₃), 2.01 (3H, s, COCH₃), 1.54 (12H, s, 2-CH₃, (CH₃)₃C). ¹³C NMR (CDCl₃): δ 170.49, 170.23, 169.23, 168.90 (COCH₃), 164.91 (COOBu^t), 117.63 (CN), 84.75 ((CH₃)₃C), 78.21 (C-1'), 76.09 (C-5'), 74.25 (C-3'), 68.91 (C-2'), 67.89 (C-4'), 61.73 (C-6'), 47.73 (C-2), 27.67 ((CH₃)₃C), 20.57, 20.47 (COCH₃), 18.45 (2-CH₃). ESI-MS Calcd for C₁₈H₂₃NO₁₁Na ([M – Bu^t + H + Na]⁺): 452.12. Found: 452.04. Anal. Found: C, 54.40; H, 6.18; N, 2.82%. Calcd for C₂₂H₃₁NO₁₁: C, 54.43; H, 6.44; N, 2.89%.

Ethyl (2R)-2-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-2-cyanopropanoate (19b): Mp 114–116 °C (EtOH); [α]_D²⁰ = 6.27 (*c* = 0.996, CHCl₃); ¹H NMR (CDCl₃, Me₄Si): δ 5.29–5.21 (2H, m, H-2', H-3'), 5.07 (1H, dd, *J* = 9.5, 10.1 Hz, H-4'), 4.29 (2H, tq, *J* = 3.3, 7.0 Hz, CH₂CH₃), 4.18–4.08 (3H, m, H-1, H-6'a, H-6'b), 3.70 (1H, ddd, *J* = 2.8, 4.9, 10.1 Hz, H-5'), 2.07 (3H, s, COCH₃), 2.06 (3H, s, COCH₃), 2.04 (3H, s, COCH₃), 2.01 (3H, s, COCH₃), 1.65 (3H, s, 2-CH₃), 1.34 (3H, t, *J* = 7.0 Hz, CH₂CH₃). ¹³C NMR (CDCl₃): δ 170.44, 170.18, 169.31 (COCH₃), 166.09 (COOEt), 116.82 (CN), 77.81 (C-1'), 76.26 (C-5'), 73.94 (C-3'), 68.83 (C-2'), 68.04 (C-4'), 63.20 (CH₂CH₃), 61.84 (C-6'), 45.30 (C-2), 20.53 (COCH₃), 17.26 (2-CH₃), 13.96 (CH₂CH₃). ESI-MS Calcd for C₂₀H₂₇NO₁₁Na ([M + Na]⁺): 480.15. Found: 480.12. Anal. Found: C, 52.42; H, 6.04; N, 3.15%. Calcd for C₂₀H₂₇NO₁₁: C, 52.51; H, 5.95; N, 3.06%. Crystal data: monoclinic, space group *C*2, *a* = 27.446(9) Å, *b* = 6.190(2) Å, *c* = 13.991(5) Å, β = 101.5687(10)°, *V* = 2328.5(13) Å³, *Z* = 4, *R* = 0.053, *R*_w² = 0.146, GOF = 1.062.

Ethyl (2S)-2-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-2-cyanopropanoate (20b): Mp 125–127 °C (EtOH); [α]_D²⁰ = –4.35 (*c* = 1.00, CHCl₃); ¹H NMR (CDCl₃, Me₄Si): δ 5.25–5.17 (2H, m, H-2', H-3'), 5.07 (1H, dd, *J* = 9.5, 10.1 Hz, H-4'), 4.39–4.19 (3H, m, CH₂CH₃, H-6'a), 4.13 (1H, dd, *J* = 2.4, 12.1 Hz, H-6'b), 4.04 (1H, m, H-1'), 3.76 (1H, ddd, *J* = 2.4, 5.5, 10.1 Hz, H-5'), 2.09 (3H, s, COCH₃), 2.04 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.99 (3H, s, COCH₃), 1.58 (3H, s, 2-CH₃), 1.37 (3H, t, *J* = 7.0 Hz, CH₂CH₃). ¹³C NMR (CDCl₃): δ 170.57, 170.26, 169.29, 168.84 (COCH₃), 166.01 (COOEt), 117.53 (CN), 78.05 (C-1'), 76.29 (C-5'), 74.17 (C-3'), 68.57 (C-2'), 67.99 (C-4'), 63.28 (CH₂CH₃), 61.73 (C-6'), 46.71 (C-2), 20.61, 20.53, 20.48 (COCH₃), 17.47 (2-CH₃), 13.90 (CH₂CH₃). HRMS (ESI) Calcd for C₂₀H₂₇NO₁₁Na ([M + Na]⁺): 480.14818. Found: 480.14721. Anal. Found: C, 52.48; H, 6.03; N, 3.08%. Calcd for C₂₀H₂₇NO₁₁: C, 52.51; H, 5.95; N, 3.06%.

Ethyl (2R)-2-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-2-cyanobutanoate (25): Mp 120–122 °C (EtOH); [α]_D²⁰ = –3.20 (*c* = 1.00, CHCl₃); ¹H NMR (CDCl₃, Me₄Si): δ 5.33 (1H, dd, *J* = 9.2, 9.8 Hz, H-2'), 5.21 (1H, dd, *J* = 9.2, 9.3 Hz, H-3'), 5.12 (1H, dd, *J* = 9.3, 9.8 Hz, H-4'), 4.31–4.21 (3H, m, OCH₂CH₃, H-6'a), 4.16 (1H, dd, *J* = 2.7, 4.6 Hz, H-6'b), 3.97

(1H, d, $J = 9.8$ Hz, H-1'), 3.71 (1H, ddd, $J = 2.7, 4.6, 9.8$ Hz, H-5'), 2.23 (1H, ddd, $J = 7.5, 7.5, 7.5$ Hz, 2-CH₂CH₃), 2.09 (3H, s, COCH₃), 2.05–1.92 (1H, m, 2-CH₂CH₃), 2.04 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.98 (3H, s, COCH₃), 1.35 (3H, t, $J = 7.0$ Hz, OCH₂CH₃), 1.06 (3H, t, $J = 7.5$ Hz, 2-CH₂CH₃). ¹³C NMR (CDCl₃): δ 170.52, 170.31, 169.21, 168.45 (COCH₃), 166.09 (COOEt), 115.59 (CN), 78.00 (C-1'), 76.32 (C-5'), 74.02 (C-3'), 69.99 (C-2'), 67.92 (C-4'), 62.86 (COOCH₂CH₃), 61.69 (C-6'), 53.39 (C-2), 27.43 (2-CH₂CH₃), 20.63, 20.48 (COCH₃), 13.98 (OCH₂CH₃), 9.17 (2-CH₂CH₃). HRMS (ESI) Calcd for C₂₁H₂₉NO₁₁Na ([M + Na]⁺): 494.16383. Found: 494.16341. Anal. Found: C, 53.29; H, 6.13; N, 3.01%. Calcd for C₂₁H₂₉NO₁₁: C, 53.50; H, 6.20; N, 2.97%. Crystal data: monoclinic, space group C2, $a = 35.450(3)$ Å, $b = 12.3686(8)$ Å, $c = 25.189(2)$ Å, $\beta = 121.121(3)^\circ$, $V = 9455.2(13)$ Å³, $Z = 16$, $R = 0.0872$, $R_w^2 = 0.3048$, GOF = 1.349.

Ethyl (2R)-2-(2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl)-2-cyanopropanoate (29): Mp 109–111 °C (EtOH); $[\alpha]_D^{20} = 19.7$ ($c = 0.995$, CHCl₃); ¹H NMR (CDCl₃, Me₄Si): δ 5.47–5.40 (2H, m, H-4', H-2'), 5.08 (1H, dd, $J = 3.6, 10.1$ Hz, H-3'), 4.28 (2H, tq, $J = 3.7, 7.3$ Hz, CH₂CH₃), 4.11 (1H, d, $J = 9.8$ Hz, H-1'), 4.06 (2H, d, $J = 5.8$ Hz, H-6'a, H-6'b), 3.93 (1H, dd, $J = 5.8, 7.0$ Hz, H-5'), 2.17 (3H, s, COCH₃), 2.08 (3H, s, COCH₃), 2.03 (3H, s, COCH₃), 1.99 (3H, s, COCH₃), 1.67 (3H, s, 2-CH₃), 1.35 (3H, t, $J = 7.3$ Hz, CH₂CH₃). ¹³C NMR (CDCl₃): δ 170.18, 170.03, 169.95, 169.44 (COCH₃), 166.07 (COOEt), 117.05 (CN), 78.26 (C-1'), 74.80 (C-5'), 71.95 (C-3'), 67.23 (C-4'), 65.92 (C-2'), 63.09 (CH₂CH₃), 61.37 (C-6'), 45.17 (C-2'), 20.79, 20.53, 20.50, 20.44 (COCH₃), 16.76 (2-CH₃), 13.88 (CH₂CH₃). HRMS (ESI) Calcd for C₂₀H₂₇NO₁₁Na ([M + Na]⁺): 480.14818. Found: 480.14722. Anal. Found: C, 52.42; H, 5.92; N, 3.17%. Calcd for C₂₀H₂₇NO₁₁: C, 52.51; H, 5.95; N, 3.06%. Crystal data: orthorhombic, space group P2₁2₁2₁, $a = 7.585(2)$ Å, $b = 14.418(4)$ Å, $c = 21.154(7)$ Å, $V = 2313.5(12)$ Å³, $Z = 4$, $R = 0.0488$, $R_w^2 = 0.1257$, GOF = 1.114.

***t*-Butyl (2S)-2-(2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosyl)-3-aminopropanoate Monohydrochloride (3a):** To a solution of **1a** (290 mg, 0.61 mmol) in chloroform (6 mL) and ethanol (30 mL) was added platinum(IV) oxide (100 mg). The suspension was hydrogenated under atmospheric pressure hydrogen at room temperature overnight. After removal of the catalyst by filtration, the solvent was removed by evaporation to give a mixture of amines (**2a/3a** = 74/26) as a white powder (311 mg, 0.608 mmol) in 99% yield. Recrystallization from methanol–ether gave a single diastereomer **3a** (23 mg, 0.049 mmol) as colorless needles in 8% yield. Mp 189–191 °C (MeOH, ether); $[\alpha]_D^{20} = 5.96$ ($c = 0.999$, MeOH); ¹H NMR (D₂O, DSS): δ 5.38 (1H, dd, $J = 9.3, 9.5$ Hz, H-3'), 5.17 (1H, dd, $J = 9.5, 10.3$ Hz, H-2'), 5.09 (1H, dd, $J = 9.3, 10.1$ Hz, H-4'), 4.40 (1H, dd, $J = 2.4, 10.3$ Hz, H-1'), 4.30 (1H, dd, $J = 5.2, 12.5$ Hz, H-6'a), 4.18 (1H, dd, $J = 2.7, 12.5$ Hz, H-6'b), 4.01 (1H, m, H-5'), 3.36 (2H, m, H-3a, H-3b), 3.01 (1H, br, H-2), 2.11 (3H, s, COCH₃), 2.09 (6H, s, COCH₃), 2.07 (3H, s, COCH₃), 1.50 (9H, s, (CH₃)₃C). ¹³C NMR (D₂O, dioxane): δ 173.68, 173.14, 172.74, 170.75 (COCH₃, COOBu^t), 84.75 ((CH₃)₃C), 76.73 (C-1'), 75.50 (C-5'), 74.28 (C-3'), 68.81 (C-2'), 68.26 (C-4'), 62.31 (C-6'), 43.06 (C-2), 35.58 (C-3), 27.05 ((CH₃)₃C), 20.02, 19.97 (COCH₃). HRMS (ESI) Calcd for C₂₁H₃₄NO₁₁ ([M – Cl]⁺): 476.2126. Found: 476.2124. Anal. Found: C, 47.66; H, 6.44; N, 2.74%. Calcd for C₂₁H₃₆NO₁₂Cl: C, 47.59; H, 6.85; N, 2.64%.

Ethyl (2S)-2-(2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosyl)-3-aminopropanoate Monohydrochloride (3b): Compound **3b**

was prepared by a method similar to the preparation of **3a** using **1b** in place of **1a**. Recrystallization from methanol–ether gave a single diastereomer **3b** as colorless needles in 27% yield. Mp 194–196 °C (MeOH, ether); $[\alpha]_D^{20} = 6.11$ ($c = 0.999$, MeOH); ¹H NMR (D₂O, DSS): δ 5.37 (1H, dd, $J = 9.5, 9.2$ Hz, H-3'), 5.17 (1H, dd, $J = 9.5, 9.9$ Hz, H-2'), 5.10 (1H, dd, $J = 9.2, 10.1$ Hz, H-4'), 4.42 (1H, dd, $J = 2.7, 9.9$ Hz, H-1'), 4.35–4.16 (4H, m, H-6', CH₂CH₃), 3.99 (1H, m, H-5'), 3.42 (2H, d, $J = 5.2$ Hz, H-3a, H-3b), 3.09 (1H, br, H-2), 2.10 (6H, s, COCH₃), 2.09 (3H, s, COCH₃), 2.06 (3H, s, COCH₃), 1.29 (3H, t, $J = 7.2$ Hz, CH₂CH₃). ¹³C NMR (D₂O, dioxane): δ 173.69, 173.14, 172.74, 171.62 (COCH₃, COOEt), 76.22 (C-1'), 75.35 (C-5'), 74.28 (C-3'), 69.20 (C-2'), 68.20 (C-4'), 63.07 (C-6'), 62.03 (CH₂CH₃), 42.83 (C-2), 35.84 (C-3), 20.05, 19.93 (COCH₃), 13.14 (CH₂CH₃). HRMS (ESI) Calcd for C₁₉H₃₀NO₁₁ ([M – Cl]⁺): 448.1813. Found: 448.1812. Anal. Found: C, 46.96; H, 6.23; N, 2.83%. Calcd for C₁₉H₃₀NO₁₁Cl: C, 47.16; H, 6.25; N, 2.89%.

***t*-Butyl (2R)/(2S)-2-(2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl)-3-aminopropanoate Monohydrochloride (7a/8a):** Compound **7a/8a** (diastereomer ratio: 70/30) was prepared by a method similar to the preparation of **3a** using **6a** in place of **1a**. Yield: 98%. ¹H NMR (D₂O, DSS): δ 5.71 (0.7H, dd, $J = 9.8, 10.1$ Hz, H-2' (**7a**)), 5.51 (1H, m, H-4' (**7a**), H-4' (**8a**)), 5.18 (1.3H, m, H-3' (**7a**), H-3' (**8a**), H-2' (**8a**)), 4.37 (0.3H, dd, $J = 2.4, 9.3$ Hz, H-1' (**8a**)), 4.17 (2.7H, m, H-6'a (**7a**), H-6'b (**7a**), H-6'a (**8a**), H-6'b (**8a**), H-5' (**7a**)), 4.00 (1H, m, H-1' (**7a**), H-5' (**8a**)), 3.37 (2H, m, H-3a (**7a**), H-3b (**7a**), H-3a (**8a**), H-3b (**8a**)), 3.11 (0.7H, m, H-2 (**7a**)), 3.04 (0.3H, m, H-2 (**8a**)), 2.23, 2.22, 2.16, 2.13, 2.11, 2.07, 2.06, and 2.02 (12H, s, COCH₃), 1.55 (7H, s, C(CH₃)₃), 1.51 (3H, s, C(CH₃)₃). ¹³C NMR (D₂O, dioxane): δ 173.53, 173.43, 173.11, 172.95, 172.72, 172.67, 172.58, 170.70, 169.97, 169.66 (COCH₃, COOBu^t), 84.75 (C(CH₃)₃), 77.02, 76.73, 76.60, 74.77, 73.75, 72.99, 72.71, 72.24, 68.52, 67.28, 67.05, 62.52 (C-6' (**8a**)), 62.03 (C-6' (**7a**)), 43.49 (C-2 (**8a**)), 42.15 (C-2 (**7a**)), 39.50 (C-3 (**7a**)), 35.66 (C-3 (**8a**)), 27.23 (C(CH₃)₃ (**7a**)), 27.13 (C(CH₃)₃ (**8a**)), 20.26, 20.13, 20.00 (COCH₃). HRMS (ESI) Calcd for C₂₁H₃₃NO₁₁Na ([M – HCl + Na]⁺): 498.19513. Found: 498.19546.

Ethyl (2R)/(2S)-2-(2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl)-3-aminopropanoate Monohydrochloride (7b/8b): Compound **7b/8b** (diastereomer ratio: 78/22) was prepared by a method similar to the preparation of **3a** using **6b** in place of **1a**. Yield: 96%. ¹H NMR (D₂O, DSS): δ 5.56 (1H, dd, $J = 9.8, 10.1$ Hz, H-2' (**7b**), H-2' (**8b**)), 5.49 (0.78H, d, $J = 3.4$ Hz, H-4' (**7b**)), 5.26 (0.22H, m, H-4' (**8b**)), 5.20 (1H, dd, $J = 3.4, 9.8$ Hz, H-3' (**7b**), H-3' (**8b**)), 4.40–4.12 (6H, m, H-1' (**7b**), H-1' (**8b**), H-5' (**7b**), H-5' (**8b**), H-6'a (**7b**), H-6'a (**8b**), CH₂CH₃ (**7b**), CH₂CH₃ (**8b**)), 3.43 (2H, m, H-3a (**7b**), H-3b (**7b**), H-3a (**8b**), H-3b (**8b**)), 3.25 (0.78H, m, H-2 (**7b**)), 3.12 (0.22H, m, H-2 (**8b**)), 2.21, 2.20, 2.12, 2.08, 2.02, and 2.01 (12H, s, COCH₃), 1.35 (3H, t, $J = 7.0$ Hz, CH₂CH₃ (**7b**), CH₂CH₃ (**8b**)). ¹³C NMR (D₂O, dioxane): δ 173.74, 173.45, 173.42, 173.09, 172.90, 172.64, 172.53, 171.59, 170.70, 170.57 (COCH₃ (**7b**), COCH₃ (**8b**), COOEt (**7b**), COOEt (**8b**)), 76.60 (C-1' (**8b**)), 76.47 (C-1' (**7b**)), 74.62 (C-5' (**8b**)), 73.98 (C-5' (**7b**)), 72.62 (C-3' (**7b**)), 72.21 (C-3' (**8b**)), 68.43 (C-2' (**7b**)), 67.33 (C-2' (**8b**)), 66.95 (C-4' (**7b**)), 66.86 (C-4' (**8b**)), 63.04 (C-6' (**8b**)), 62.75 (C-6' (**7b**)), 62.13 (CH₂CH₃ (**8b**)), 62.02 (CH₂CH₃ (**7b**)), 43.17 (C-2 (**8b**)), 42.04 (C-2 (**7b**)), 38.83 (C-3 (**7b**)), 35.95 (C-3 (**8b**)), 20.16, 20.00 (COCH₃ (**7b**), COCH₃ (**8b**)), 13.41 (CH₂CH₃ (**7b**)), 13.25 (CH₂CH₃ (**8b**)). HRMS (ESI) Calcd for C₁₉H₂₉NO₁₁Na

$([M - HCl + Na]^+)$: 470.16383. Found: 470.16344.

***t*-Butyl (2R)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-3-amino-2-methylpropanoate Monohydrochloride (21a):** Compound **21a** was prepared by a method similar to the preparation of **3a** using **19a** in place of **1a**. Yield: 84%. $[\alpha]_D^{20} = -4.86$ ($c = 0.830$, MeOH); 1H NMR (CD_3OD): δ 5.42 (1H, dd, $J = 9.2, 9.6$ Hz, H-2'), 5.26 (1H, dd, $J = 9.2, 9.5$ Hz, H-3'), 5.07 (1H, dd, $J = 9.5, 10.1$ Hz, H-4'), 4.29 (1H, dd, $J = 5.0, 12.5$ Hz, H-6'a), 4.21 (1H, dd, $J = 2.4, 12.5$ Hz, H-6'b), 3.95 (1H, ddd, $J = 2.4, 5.0, 10.1$ Hz, H-5'), 3.31 (1H, d, $J = 13.4$ Hz, H-3a), 3.16 (1H, d, $J = 13.4$ Hz, H-3b), 2.09 (3H, s, COCH₃), 2.06 (3H, s, COCH₃), 2.03 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.59 (9H, s, C(CH₃)₃), 1.36 (3H, s, 2-CH₃). ^{13}C NMR (CD_3OD): δ 172.91, 172.31, 171.63, 171.22, 171.16 (COCH₃, COOBu'), 84.63 (C(CH₃)₃), 80.57 (C-1'), 77.15 (C-5'), 76.21 (C-3'), 70.44 (C-2'), 69.26 (C-4'), 63.08 (C-6'), 48.77 (C-2), 44.24 (C-3), 28.40, 28.11 (C(CH₃)₃), 20.99, 20.73, 20.54 (COCH₃), 18.89 (2-CH₃). HRMS (ESI) Calcd for C₂₂H₃₅NO₁₁Na ($[M - HCl + Na]^+$): 512.21078. Found: 512.21091.

***t*-Butyl (2S)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-3-amino-2-methylpropanoate Monohydrochloride (22a):** Compound **22a** was prepared by a method similar to the preparation of **3a** using **20a** in place of **1a**. Yield: 99%. $[\alpha]_D^{20} = 24.3$ ($c = 0.983$, MeOH); 1H NMR (CD_3OD): δ 5.36 (1H, dd, $J = 9.2, 9.2$ Hz, H-3'), 5.25 (1H, dd, $J = 9.2, 10.1$ Hz, H-2'), 5.13 (1H, dd, $J = 9.2, 10.1$ Hz, H-4'), 4.29–4.23 (3H, m, H-6'a, H-6'b, H-1'), 3.95 (1H, ddd, $J = 3.4, 4.3, 10.1$ Hz, H-5'), 3.30 (1H, d, $J = 13.7$ Hz, H-3a), 3.23 (1H, d, $J = 13.7$ Hz, H-3b), 2.10 (3H, s, COCH₃), 2.07 (3H, s, COCH₃), 2.06 (3H, s, COCH₃), 2.01 (3H, s, COCH₃), 1.58 (9H, s, C(CH₃)₃), 1.22 (3H, s, 2-CH₃). ^{13}C NMR (CD_3OD): δ 172.82, 172.66, 171.58, 171.30, 171.26 (COCH₃, COOBu'), 84.43 (C(CH₃)₃), 81.41 (C-1'), 77.65 (C-5'), 75.73 (C-3'), 69.92 (C-2'), 69.47 (C-4'), 63.45 (C-6'), 49.10 (C-2), 44.02 (C-3), 28.27 (C(CH₃)₃), 20.88, 20.80, 20.54, 20.49 (COCH₃), 17.43 (2-CH₃). ESI-MS Calcd for C₂₂H₃₅NO₁₁Na ($[M - HCl + Na]^+$): 512.21. Found: 512.18. Anal. Found: C, 49.72; H, 6.80; N, 2.72%. Calcd for C₄₅H₇₆N₂O₂₃Cl₂: C, 49.86; H, 7.07; N, 2.58%.

Ethyl (2R)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-3-amino-2-methylpropanoate Monohydrochloride (21b): Compound **21b** was prepared by a method similar to the preparation of **3a** using **19b** in place of **1a**. Yield: 95%. $[\alpha]_D^{20} = -10.1$ ($c = 0.990$, MeOH); 1H NMR (D_2O , DSS): δ 5.35–5.27 (2H, m, H-2', H-3'), 5.08 (1H, dd, $J = 9.5, 10.1$ Hz, H-4'), 4.31–4.18 (5H, m, H-6', H-1', CH₂CH₃), 4.00 (1H, ddd, $J = 4.0, 9.8, 10.4$ Hz, H-5'), 3.35 (1H, d, $J = 13.4$ Hz, H-3a), 3.25 (1H, d, $J = 13.4$ Hz, H-3b), 2.11 (3H, s, COCH₃), 2.08 (3H, s, COCH₃), 2.06 (3H, s, COCH₃), 2.04 (3H, s, COCH₃), 1.40 (3H, s, 2-CH₃), 1.32 (3H, t, $J = 7.2$ Hz, CH₂CH₃). ^{13}C NMR (D_2O , dioxane): δ 173.66, 173.43, 173.04, 172.69 (COCH₃), 172.38 (COOEt), 78.98 (C-1'), 75.29 (C-5'), 74.96 (C-3'), 68.91 (C-2'), 68.01 (C-4'), 62.97 (CH₂CH₃), 61.92 (C-6'), 46.47 (C-2), 41.81 (C-3), 19.95 (COCH₃), 17.64 (2-CH₃), 13.06 (CH₂CH₃). HRMS (ESI) Calcd for C₂₀H₃₁NO₁₁Na ($[M - HCl + Na]^+$): 484.17948. Found: 484.17864.

Ethyl (2S)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-3-amino-2-methylpropanoate Monohydrochloride (22b): Compound **22b** was prepared by a method similar to the preparation of **3a** using **20b** in place of **1a**. Yield: 77%. $[\alpha]_D^{20} = 19.7$ ($c = 0.807$, MeOH); 1H NMR (D_2O , DSS): δ 5.33 (1H, dd, $J = 9.2, 9.3$ Hz, H-3'), 5.22 (1H, dd, $J = 9.2, 9.8$ Hz, H-2'), 5.12 (1H, dd, $J = 9.3, 9.9$ Hz, H-4'), 4.41–4.22 (5H, m, H-6'a, H-6'b, H-1',

CH₂CH₃), 4.03 (1H, ddd, $J = 2.1, 2.4, 9.9$ Hz, H-5'), 3.40 (1H, d, $J = 13.4$ Hz, H-3a), 3.32 (1H, d, $J = 13.4$ Hz, H-3b), 2.12 (3H, s, COCH₃), 2.09 (3H, s, COCH₃), 2.04 (6H, s, COCH₃), 1.40 (3H, s, 2-CH₃), 1.31 (3H, t, $J = 7.2$ Hz, CH₂CH₃). ^{13}C NMR (D_2O , dioxane): δ 173.76, 173.06, 172.64, 172.25 (COCH₃, COOEt), 78.65 (C-1'), 75.38 (C-5'), 74.82 (C-3'), 68.64 (C-2'), 68.07 (C-4'), 63.20 (CH₂CH₃), 61.92 (C-6'), 46.84 (C-2), 43.59 (C-3), 20.16, 20.05 (COCH₃), 13.82 (2-CH₃), 13.11 (CH₂CH₃). HRMS (ESI) Calcd for C₂₀H₃₁NO₁₁Na ($[M - HCl + Na]^+$): 484.17948. Found: 484.18249.

Ethyl (2R)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-2-aminomethylbutanoate Monohydrochloride (31): Compound **31** was prepared by a method similar to the preparation of **3a** using **25** in place of **1a**. Yield: 78%. 1H NMR (D_2O , DSS): δ 5.44–5.31 (2H, m, H-2', H-3'), 5.10 (1H, dd, $J = 9.5, 10.1$ Hz, H-4'), 4.35–4.24 (5H, m, OCH₂CH₃, H-6', H-1'), 4.02 (1H, m, H-5'), 3.40 (1H, d, $J = 14.0$ Hz, H-3a), 3.34 (1H, d, $J = 14.0$ Hz, H-3b), 2.12 (3H, s, COCH₃), 2.09 (3H, s, COCH₃), 2.05 (3H, s, COCH₃), 2.04 (3H, s, COCH₃), 1.95 (2H, q, $J = 7.5$ Hz, 2-CH₂CH₃), 1.32 (3H, t, $J = 7.3$ Hz, OCH₂CH₃), 0.90 (3H, t, $J = 7.5$ Hz, 2-CH₂CH₃). ^{13}C NMR (D_2O , dioxane): δ 173.69, 173.01, 172.70, 172.62, 172.35 (COCH₃, COOEt), 79.09, 75.66, 74.83, 68.77, 68.13, 62.89, 62.07, 49.84, 38.99, 24.43 (2-CH₂CH₃), 20.10, 20.05, 19.98, 19.92 (COCH₃), 13.11 (OCH₂CH₃), 7.15 (2-CH₂CH₃). HRMS (ESI) Calcd for C₂₁H₃₃NO₁₁Na ($[M + Na]^+$): 498.19513. Found: 498.20049.

Ethyl (2R)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl)-3-amino-2-methylpropanoate Monohydrochloride (33): Compound **33** was prepared by a method similar to the preparation of **3a** using **29** in place of **1a**. Yield: 91%. $[\alpha]_D^{20} = 15.3$ ($c = 1.16$, MeOH); 1H NMR (CD_3OD): δ 5.47 (1H, d, $J = 3.4$ Hz, H-4'), 5.35 (1H, dd, $J = 9.9, 10.1$ Hz, H-2'), 5.17 (1H, dd, $J = 3.4, 9.9$ Hz, H-3'), 4.42–4.32 (1H, m, CH₂CH₃-a), 4.28–4.11 (5H, m, H-6'a, H-6'b, H-5', H-1', CH₂CH₃-b), 3.45 (1H, d, $J = 12.8$ Hz, H-3a), 3.15 (1H, d, $J = 13.1$ Hz, H-3b), 2.18 (3H, s, COCH₃), 2.08 (3H, s, COCH₃), 2.02 (3H, s, COCH₃), 1.97 (3H, s, COCH₃), 1.45 (3H, s, 2-CH₃), 1.39 (3H, t, $J = 7.2$ Hz, CH₂CH₃). ^{13}C NMR (CD_3OD): δ 173.81, 172.15, 171.77, 171.34, 171.16 (COCH₃, COOEt), 80.91 (C-1'), 76.20 (C-5'), 73.74 (C-3'), 69.27 (C-4'), 67.38 (C-2'), 63.08 (CH₂CH₃), 62.82 (C-6'), 47.95 (C-2), 42.59 (C-3), 20.94, 20.72, 20.56, 20.46 (COCH₃), 18.68 (2-CH₃), 14.31 (CH₂CH₃). HRMS (ESI) Calcd for C₂₀H₃₁NO₁₁Na ($[M + Na]^+$): 484.17948. Found: 484.17885.

(2S)-3-Amino-2-(β -D-glucopyranosyl)propanoic Acid Monohydrochloride (5). **3a** (20 mg, 0.040 mmol) was added 6 mL dm⁻³ HCl (7 mL) and refluxed for 2 h. The solution was evaporated to 1 mL and decolorized with active carbon. To the filtrate was added EtOH and solvent was evaporated in vacuo to afford **5** as colorless crystalline material (12 mg, 0.040 mmol) in 100% yield. $[\alpha]_D^{20} = 6.97$ ($c = 2.97$, MeOH); 1H NMR (D_2O , DSS): δ 3.96 (1H, dd, $J = 2.1, 9.8$ Hz, H-5'), 3.85 (1H, d, $J = 12.5$ Hz, H-6'a), 3.68 (1H, dd, $J = 3.7, 12.5$ Hz, H-6'b), 3.51 (1H, m, H-3'), 3.44–3.38 (5H, m, H-2', H-4', H-3), 3.22 (1H, m, H-2). ^{13}C NMR (D_2O , dioxane): δ 175.08 (COO), 80.09 (C-1'), 78.65 (C-5'), 77.28 (C-3'), 70.40 (C-2'), 69.45 (C-4'), 60.72 (C-6'), 42.78 (C-2), 35.99 (C-3). HRMS (ESI) Calcd for C₉H₁₈NO₇ ($[M - Cl]^+$): 252.1078. Found: 252.1080. Anal. Found: C, 34.16; H, 6.96; N, 4.04%. Calcd for C₉H₁₈NO₇Cl·1.5H₂O: C, 34.35; H, 6.73; N, 4.45%.

(2R)/(2S)-3-Amino-2-(β -D-galactopyranosyl)propanoic Acid Monohydrochloride (9/10): Compound **9/10** was prepared by a method similar to the preparation of **5** using **7a/8a** in place

of **3a**. Yield: 100%. $^1\text{H NMR}$ (D_2O , DSS): δ 3.97 (1H, dd, $J = 2.7, 3.4$ Hz, H-4' (**9**), H-4' (**10**)), 3.87 (1H, dd, $J = 9.5, 9.8$ Hz, H-2' (**9**), H-2' (**10**)), 3.78–3.62 (5H, m, H-1' (**9**), H-1' (**10**), H-3' (**9**), H-3' (**10**), H-5' (**9**), H-5' (**10**), H-6'a (**9**), H-6'a (**10**), H-6'b (**9**), H-6'b (**10**)), 3.51–3.41 (2H, m, H-3a (**9**), H-3b (**9**), H-3a (**10**), H-3b (**10**)), 3.37–3.21 (1H, m, H-2 (**9**), H-2 (**10**)). $^{13}\text{C NMR}$ (D_2O , dioxane): δ 174.82, 173.27 (COO), 79.43 (C-1'), 79.20, 79.07 (C-5'), 73.98 (C-3'), 69.12, 68.98 (C-4'), 67.75, 67.62 (C-2'), 61.18 (C-6'), 42.68, 42.46 (C-2), 38.40, 35.97 (C-3). HRMS (ESI) Calcd for $\text{C}_9\text{H}_{17}\text{NO}_7\text{Na}$ ($[\text{M} - \text{HCl} + \text{Na}]^+$): 274.09027. Found: 274.09051.

(2R)-3-Amino-2-(β -D-glucopyranosyl)-2-methylpropanoic Acid Monohydrochloride (23): Compound **23** was prepared by a method similar to the preparation of **5** using **21a** in place of **3a**. Yield: 100%. $[\alpha]_{\text{D}}^{20} = 1.28$ ($c = 0.736$, MeOH); $^1\text{H NMR}$ (D_2O , DSS): δ 3.88 (1H, d, $J = 12.5$ Hz, H-6'a), 3.74–3.66 (2H, m, H-6'b, H-1'), 3.49–3.28 (6H, m, H-2', H-3', H-4', H-5', H-3a, H-3b), 1.43 (3H, s, 2-CH₃). $^{13}\text{C NMR}$ (D_2O , dioxane): δ 176.56 (COO), 81.26 (C-1'), 80.04 (C-5'), 77.58 (C-3'), 70.50 (C-2'), 69.54 (C-4'), 60.82 (C-6'), 46.19 (C-2), 41.94 (C-3), 17.70 (2-CH₃). HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_7\text{Na}$ ($[\text{M} - \text{HCl} + \text{Na}]^+$): 288.10592. Found: 288.10633.

(2S)-3-Amino-2-(β -D-glucopyranosyl)-2-methylpropanoic Acid Monohydrochloride (24): Compound **24** was prepared by a method similar to the preparation of **5** using **22a** in place of **3a**. Yield: 91% $[\alpha]_{\text{D}}^{20} = 13.2$ ($c = 1.00$, MeOH); $^1\text{H NMR}$ (D_2O , DSS): δ 3.94–3.85 (2H, m, H-6'a, H-1'), 3.68 (1H, dd, $J = 5.4, 12.4$ Hz, H-6'b), 3.50–3.46 (2H, m, H-2', H-3'), 3.42–3.37 (2H, m, H-4', H-5'), 3.32 (2H, s, H-3a, H-3b), 1.32 (3H, s, 2-CH₃). $^{13}\text{C NMR}$ (D_2O , dioxane): δ 176.38 (COO), 80.51 (C-1'), 79.82 (C-5'), 77.49 (C-3'), 70.36 (C-2'), 69.41 (C-4'), 60.76 (C-6'), 46.76 (C-2), 43.80 (C-3), 14.85 (2-CH₃). HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{20}\text{NO}_7$ ($[\text{M} - \text{Cl}]^+$): 266.1240. Found: 266.1244.

(2R)-2-Aminomethyl-2-(β -D-glucopyranosyl)butanoic Acid Monohydrochloride (32): Compound **32** was prepared by a method similar to the preparation of **5** using **31** in place of **3a**. Yield: 100%. $[\alpha]_{\text{D}}^{20} = 1.20$ ($c = 0.309$, MeOH); $^1\text{H NMR}$ (D_2O , DSS): δ 3.89 (1H, d, $J = 12.3$ Hz, H-6'a), 3.85 (1H, m, H-1'), 3.70 (1H, dd, $J = 12.3, 3.0$ Hz, H-6'b), 3.52 (2H, m, H-2', H-3'), 3.41 (4H, m, H-3a, H-3b, H-4', H-5'), 1.95 (2H, m, 2-CH₂CH₃), 0.92 (3H, t, $J = 7.3$ Hz, 2-CH₂CH₃). $^{13}\text{C NMR}$ (D_2O , dioxane): δ 175.52 (CO), 81.71 (C-1'), 80.63 (C-5'), 77.50 (C-3'), 70.58 (C-2'), 69.56 (C-4'), 60.76 (C-6'), 49.27 (C-2), 38.67 (C-3), 24.69 (2-CH₂CH₃), 7.15 (2-CH₂CH₃). HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{21}\text{NO}_7\text{Na}$ ($[\text{M} - \text{HCl} + \text{Na}]^+$): 302.12157. Found: 302.12244.

(2R)-3-Amino-2-(β -D-galactopyranosyl)-2-methylpropanoic Acid Monohydrochloride (34): Compound **34** was prepared by a method similar to the preparation of **5** using **33** in place of **3a**. Yield: 87%. $[\alpha]_{\text{D}}^{20} = 14.7$ ($c = 0.911$, MeOH); $^1\text{H NMR}$ (D_2O , DSS): δ 3.96 (1H, d, $J = 2.4$ Hz, H-4'), 3.75–3.62 (6H, m, H-1', H-2', H-3', H-5', H-6'a, H-6'b), 3.39 (2H, q, $J = 13.6$ Hz, H-3a, H-3b), 1.45 (3H, s, 2-CH₃). $^{13}\text{C NMR}$ (D_2O , dioxane): δ 176.67 (COO), 82.02, 79.48, 74.25, 69.02 (C-4'), 67.83, 61.23 (C-6'), 46.11 (C-2), 41.83 (C-3), 17.99 (2-CH₃). HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_7\text{Na}$ ($[\text{M} + \text{Na}]^+$): 288.10592. Found: 288.10631.

***t*-Butyl (2R)- and (2S)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-*N*-(9-fluorenylmethoxycarbonyl)- β -alaninate (11 and 12).** A mixture of compounds **2a/3a** (1.229 g, 2.40 mmol, **2a/3a** = 72/28) was dissolved in methanol (15 mL) and acetonitrile (15 mL) and stirred at room temperature. A solution of FmocOSu (1.214 g, 3.60 mmol) in acetonitrile (15 mL) was added,

followed by the dropwise addition of Et₃N (1.26 mL, 3.60 mmol) in order to maintain pH 8–9 (monitored by pH-test paper). After 1 h, TLC (chloroform/methanol 9:1) indicated no starting material ($R_f = 0.4$). Sufficient hydrochloric acid (1 mol dm⁻³) was added to reach pH 2. The aqueous layer was extracted with dichloromethane (2 $\times$ 50 mL) and combined extracts were washed with brine (50 mL), dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: chloroform/ethyl acetate 8:1 to 4:1) to afford **11** ($R_f = 0.35$ (chloroform/ethyl acetate, 4:1), 743 mg, 1.07 mmol) in 44% and **12** ($R_f = 0.4$ (chloroform/ethyl acetate, 4:1), 306 mg, 0.44 mmol) in 18% yield, respectively. For **11**: mp 175–176 °C (MeOH); $[\alpha]_{\text{D}}^{20} = -24.5$ ($c = 0.993$, CHCl₃); $^1\text{H NMR}$ (CDCl₃, Me₄Si): δ 7.76 (2H, d, $J = 7.3$ Hz, Fmoc-Ar-4), 7.58 (2H, d, $J = 7.3$ Hz, Fmoc-Ar-1), 7.40 (2H, dd, $J = 7.3, 7.5$ Hz, Fmoc-Ar-3), 7.31 (2H, dd, $J = 7.3, 7.5$ Hz, Fmoc-Ar-2), 5.38 (1H, dd, $J = 9.2, 9.5$ Hz, H-2'), 5.32 (1H, dd, $J = 5.5, 5.5$ Hz, NHCOO), 5.12 (1H, dd, $J = 9.2, 9.5$ Hz, H-3'), 5.05 (1H, dd, $J = 9.2, 9.5$ Hz, H-4'), 4.39 (2H, m, Fmoc-CH₂O), 4.23–4.02 (3H, m, Fmoc-CH, H-6'a, H-6'b), 3.67 (1H, dd, $J = 9.5$ Hz, H-1'), 3.58 (1H, m, H-5'), 3.49 (2H, m, H-3a, H-3b), 2.77 (1H, m, H-2), 2.03 (6H, s, COCH₃), 2.02 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.50 (9H, s, (CH₃)₃C). $^{13}\text{C NMR}$ (CDCl₃): δ 170.52, 170.39, 169.34, 169.23 (COCH₃, COOBu'), 156.40 (NHCOO), 143.79, 141.25 (Fmoc-Ar-C), 127.68 (Fmoc-Ar-3), 126.98 (Fmoc-Ar-2), 124.96 (Fmoc-Ar-1), 119.96 (Fmoc-Ar-4), 82.32 ((CH₃)₃C), 76.58 (C-1'), 75.95 (C-5'), 74.74 (C-3'), 69.70 (C-2'), 67.99 (C-4'), 66.65 (Fmoc-CH₂O), 61.84 (C-6'), 47.15 (Fmoc-CH), 45.85 (C-2), 40.21 (C-3), 28.12, 28.02 ((CH₃)₃C), 20.63, 20.50 (COCH₃). ESI-MS Calcd for $\text{C}_{36}\text{H}_{43}\text{NO}_{13}\text{Na}$ ($[\text{M} + \text{Na}]^+$): 720.26. Found: 720.15. Anal. Found: C, 61.86; H, 6.26; N, 2.04%. Calcd for $\text{C}_{36}\text{H}_{43}\text{NO}_{13}$: C, 61.97; H, 6.21; N, 2.01%. Crystal data: orthorhombic, space group with $P2_12_12_1$, $a = 10.8622(5)$ Å, $b = 12.9881(7)$ Å, $c = 25.340(1)$ Å, $V = 3575.0(3)$ Å³, $Z = 4$, $R = 0.083$, $R_w^2 = 0.120$, GOF = 0.912. For **12**: $[\alpha]_{\text{D}}^{20} = -21.4$ ($c = 0.999$, CHCl₃); $^1\text{H NMR}$ (CDCl₃, Me₄Si): δ 7.75 (2H, d, $J = 7.6$ Hz, Fmoc-Ar-4), 7.58 (2H, d, $J = 7.0$ Hz, Fmoc-Ar-1), 7.38 (2H, dd, $J = 7.3, 7.6$ Hz, Fmoc-Ar-3), 7.29 (2H, dd, $J = 7.0, 7.3$ Hz, Fmoc-Ar-2), 5.41 (1H, dd, $J = 5.5, 6.1$ Hz, NHCOO), 5.32 (1H, dd, $J = 9.0, 9.8$ Hz, H-3'), 5.13 (1H, dd, $J = 9.0, 9.3$ Hz, H-2'), 5.05 (1H, dd, $J = 9.3, 9.8$ Hz, H-4'), 4.34 (2H, d, $J = 7.0$ Hz, Fmoc-CH₂O), 4.22–4.06 (4H, m, Fmoc-CH, H-6'a, H-6'b, H-1'), 3.68–3.60 (1H, m, H-5'), 3.49–3.40 (2H, m, H-3a, H-3b), 2.70 (1H, m, H-2), 2.06 (3H, s, COCH₃), 2.03 (3H, s, COCH₃), 2.02 (3H, s, COCH₃), 2.01 (3H, s, COCH₃), 1.47 (9H, s, (CH₃)₃C). $^{13}\text{C NMR}$ (CDCl₃): δ 170.47, 170.25, 170.16, 169.37, 169.27 (COCH₃, COOBu'), 156.01 (NHCOO), 143.90, 143.76, 141.11 (Fmoc-Ar-C), 127.51 (Fmoc-Ar-3), 126.85 (Fmoc-Ar-2), 125.01 (Fmoc-Ar-1), 119.80 (Fmoc-Ar-4), 81.73 ((CH₃)₃C), 77.10 (C-1'), 76.30 (C-5'), 74.22 (C-3'), 69.12 (C-2'), 68.39 (C-4'), 66.58 (Fmoc-CH₂O), 62.16 (C-6'), 47.04 (Fmoc-CH), 45.90 (C-2), 37.20 (C-3), 27.94, 27.85 ((CH₃)₃C), 20.53, 20.45, 20.40 (COCH₃). HRMS (ESI) Calcd for $\text{C}_{36}\text{H}_{43}\text{NO}_{13}\text{Na}$ ($[\text{M} + \text{Na}]^+$): 720.26321. Found: 720.26201.

***t*-Butyl (2R)- and (2S)-2-(2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl)-*N*-(9-fluorenylmethoxycarbonyl)- β -alaninate (15 and 16):** Compound **15/16** was prepared by a method similar to the preparation of **11/12** using **7a/8a** in place of **2a/2a**. Yield: 46% (**15**) and 16% (**16**). For **15**: $[\alpha]_{\text{D}}^{20} = -13.3$ ($c = 0.999$, CHCl₃); $^1\text{H NMR}$ (CDCl₃, Me₄Si): δ 7.63 (2H, d, $J = 7.5$ Hz, Fmoc-Ar-4), 7.58 (2H, d, $J = 7.3$ Hz, Fmoc-Ar-1), 7.40 (2H, dd, $J = 7.0, 7.5$ Hz, Fmoc-Ar-3), 7.31 (2H, dd, $J = 7.0, 7.3$ Hz,

Fmoc-Ar-2), 5.61 (1H, dd, $J = 9.8, 10.0$ Hz, H-2'), 5.41 (1H, d, $J = 3.2$ Hz, H-4'), 5.33 (1H, t, $J = 6.3$ Hz, NHCOO), 4.97 (1H, dd, $J = 3.2, 10.0$ Hz, H-3'), 4.39 (2H, d, $J = 6.9$ Hz, Fmoc-CH₂O), 4.21 (1H, t, $J = 6.9$ Hz, Fmoc-CH), 4.04 (2H, d, $J = 6.6$ Hz, H-6'a, H-6'b), 3.83 (1H, dd, $J = 6.5, 6.5$ Hz, H-5'), 3.65 (1H, dd, $J = 7.8, 9.8$ Hz, H-1'), 3.51 (2H, dd, $J = 6.3, 6.3$ Hz, H-3a, H-3b), 2.78 (1H, m, H-2), 2.14 (3H, s, COCH₃), 2.03 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.98 (3H, s, COCH₃), 1.53 (9H, s, (CH₃)₃C). ¹³C NMR (CDCl₃): δ 170.28, 170.15, 169.95, 169.37, 169.19 (COCH₃, COOBu^t), 156.43 (NHCOO), 143.84, 143.76, 141.23 (Fmoc-Ar-C), 127.64 (Fmoc-Ar-3), 126.96 (Fmoc-Ar-2), 124.94 (Fmoc-Ar-1), 119.93 (Fmoc-Ar-4), 82.05 ((CH₃)₃C), 77.50 (C-1'), 74.28 (C-5'), 72.62 (C-3'), 67.55 (C-4'), 66.81 (C-2'), 66.63 (Fmoc-CH₂O), 61.14 (C-6'), 47.13 (Fmoc-CH), 45.72 (C-2), 40.30 (C-3), 27.96 ((CH₃)₃C), 20.73, 20.63, 20.53 (COCH₃). HRMS (ESI) Calcd for C₃₆H₄₃NO₁₃Na ([M + Na]⁺): 720.26321. Found: 720.26354. For **16**: $[\alpha]_D^{20} = -3.24$ ($c = 0.997$, CHCl₃); ¹H NMR (CDCl₃, Me₄Si): δ 7.76 (2H, d, $J = 7.5$ Hz, Fmoc-Ar-4), 7.59 (2H, d, $J = 7.0$ Hz, Fmoc-Ar-1), 7.39 (2H, dd, $J = 7.0, 7.5$ Hz, Fmoc-Ar-3), 7.30 (2H, dd, $J = 7.0, 7.0$ Hz, Fmoc-Ar-2), 5.42 (1H, d, $J = 3.4$ Hz, H-4'), 5.36 (1H, br, NHCOO), 5.32 (1H, dd, $J = 9.9, 9.9$ Hz, H-2'), 5.05 (1H, dd, $J = 3.4, 9.9$ Hz, H-3'), 4.35 (2H, d, $J = 7.4$ Hz, Fmoc-CH₂O), 4.22 (1H, t, $J = 7.4$ Hz, Fmoc-CH), 4.15–4.02 (3H, d, m, H-6', H-1'), 3.87 (1H, dd, $J = 5.8, 5.8$ Hz, H-5'), 3.70 (1H, m, H-3a), 3.50 (1H, m, H-3b), 2.72 (1H, m, H-2), 2.13 (3H, s, COCH₃), 2.07 (3H, s, COCH₃), 2.02 (3H, s, COCH₃), 1.99 (3H, s, COCH₃), 1.47 (9H, s, (CH₃)₃C). ¹³C NMR (CDCl₃): δ 170.36, 170.13, 169.52 (COCH₃, COOBu^t), 156.02 (NHCOO), 144.05, 143.84, 141.19 (Fmoc-Ar-C), 127.58 (Fmoc-Ar-3), 126.90 (Fmoc-Ar-2), 125.04 (Fmoc-Ar-1), 119.88 (Fmoc-Ar-4), 81.77 ((CH₃)₃C), 77.58 (C-1'), 75.01 (C-5'), 72.36 (C-3'), 67.78 (C-4'), 66.68 (Fmoc-CH₂O), 66.61 (C-2'), 61.76 (C-6'), 47.13 (Fmoc-CH), 46.11 (C-2), 37.38 (C-3), 27.98 ((CH₃)₃C), 20.65, 20.53 (COCH₃). HRMS (ESI) Calcd for C₃₆H₄₃NO₁₃Na ([M + Na]⁺): 720.26321. Found: 720.26441.

(2S)-2-(2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosyl)-N-(9-fluorenylmethoxycarbonyl)- β -alanine (13). Compound **11** (209 mg, 0.30 mmol) was dissolved in formic acid (10 mL) and stirred at room temperature for 3 h. TLC (ethyl acetate) indicated no starting material ($R_f = 0.7$). Water (30 mL) was added and the aqueous layer was extracted with chloroform (2 $\times$ 40 mL), dried (Na₂SO₄), and concentrated. The residue was purified by silica gel column chromatography (chloroform/ethyl acetate/methanol 7:1:0 to 40:2:3) to afford **13** as colorless needles ($R_f = 0.3$, 192 mg, 0.29 mmol) in 97% yield. $[\alpha]_D^{20} = -22.3$ ($c = 1.0$, CHCl₃); ¹H NMR (CD₃OD): δ 7.83 (2H, d, $J = 7.3$ Hz, Fmoc-Ar-4), 7.69 (2H, d, $J = 7.3$ Hz, Fmoc-Ar-1), 7.43 (2H, dd, $J = 6.7, 7.3$ Hz, Fmoc-Ar-3), 7.36 (2H, dd, $J = 7.3, 6.7$ Hz, Fmoc-Ar-2), 7.09 (1H, br, NHCOO), 5.34 (1H, dd, $J = 9.3, 9.8$ Hz, H-2'), 5.22 (1H, dd, $J = 9.3, 9.6$ Hz, H-3'), 5.05 (1H, dd, $J = 9.6, 9.8$ Hz, H-4'), 4.42 (2H, m, Fmoc-CH₂O), 4.26–4.10 (3H, m, H-6'a, H-6'b, Fmoc-CH), 3.86 (1H, dd, $J = 2.4, 9.8$ Hz, H-1'), 3.75 (1H, m, H-5'), 3.73 (2H, m, H-3a, H-3b), 2.92 (1H, m, H-2), 2.06 (3H, s, COCH₃), 2.05 (3H, s, COCH₃), 2.00 (3H, s, COCH₃), 1.99 (3H, s, COCH₃). ¹³C NMR (CD₃OD): δ 173.13, 172.37, 171.85, 171.22, 171.06 (COCH₃, COOH), 158.64 (NHCOO), 145.27, 145.17, 142.55 (Fmoc-Ar-C), 128.80 (Fmoc-Ar-3), 128.17 (Fmoc-Ar-2), 126.10 (Fmoc-Ar-1), 120.94 (Fmoc-Ar-4), 76.98 (C-5', C-1'), 76.20 (C-3'), 70.99 (C-2'), 69.53 (C-4'), 67.56 (Fmoc-CH₂O), 63.22 (C-6'), 48.43 (Fmoc-CH), 46.28 (C-2), 39.79 (C-3), 20.65, 20.62, 20.52 (COCH₃).

HRMS (ESI) Calcd for C₃₂H₃₄NO₁₃Na₂ ([M – H + 2Na]⁺): 686.18255. Found: 686.18287.

(2S)-2-(2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosyl)-N-(9-fluorenylmethoxycarbonyl)- β -alanine (14): Compound **14** was prepared by a method similar to the preparation of **13** using **12** in place of **11**. Yield: 96%. Mp 95–96 °C (MeOH); $[\alpha]_D^{20} = -15.8$ ($c = 1.01$, CHCl₃); ¹H NMR (CD₃OD): δ 7.83 (2H, d, $J = 7.5$ Hz, Fmoc-Ar-4), 7.69 (2H, d, $J = 7.3$ Hz, Fmoc-Ar-1), 7.43 (2H, dd, $J = 7.0, 7.5$ Hz, Fmoc-Ar-3), 7.35 (2H, dd, $J = 7.0, 7.3$ Hz, Fmoc-Ar-2), 5.25 (1H, dd, $J = 9.2, 9.5$ Hz, H-3'), 5.12 (1H, dd, $J = 9.5, 9.8$ Hz, H-2'), 5.07 (1H, dd, $J = 9.2, 9.2$ Hz, H-4'), 4.36–4.26 (4H, m, Fmoc-CH₂O, Fmoc-CH, H-6'a), 4.14–4.06 (2H, m, H-6'b, H-1'), 3.82 (1H, m, H-5'), 3.54 (2H, m, H-3a, H-3b), 2.83 (1H, m, H-2), 2.06 (6H, s, COCH₃), 2.03 (3H, s, COCH₃), 1.99 (3H, s, COCH₃). ¹³C NMR (CD₃OD): δ 174.54, 172.34, 171.76, 171.24, 171.21 (COCH₃, COOH), 158.51 (NHCOO), 145.34, 145.25, 142.50 (Fmoc-Ar-C), 128.75 (Fmoc-Ar-3), 128.14 (Fmoc-Ar-2), 126.24 (Fmoc-Ar-1), 120.90 (Fmoc-Ar-4), 77.87 (C-1'), 75.83 (C-5'), 75.83 (C-3'), 71.94 (C-2'), 69.76 (C-4'), 67.80 (Fmoc-CH₂O), 63.34 (C-6'), 48.37 (Fmoc-CH), 47.88 (C-2), 39.50 (C-3), 20.64 (COCH₃). ESI-MS Calcd for C₃₂H₃₅NO₁₃Na ([M + Na]⁺): 664.20. Found: 664.22. Anal. Found: C, 59.12; H, 5.58; N, 2.21%. Calcd for C₃₃H₃₉NO₁₄: C, 58.84; H, 5.84; N, 2.08%.

(2R)-2-(2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl)-N-(9-fluorenylmethoxycarbonyl)- β -alanine (17): Compound **17** was prepared by a method similar to the preparation of **13** using **15** in place of **11**. Yield: 75%. $[\alpha]_D^{20} = -12.0$ ($c = 1.00$, CHCl₃); ¹H NMR (CD₃OD): δ 7.84 (2H, d, $J = 7.0$ Hz, Fmoc-Ar-4), 7.69 (2H, d, $J = 7.3$ Hz, Fmoc-Ar-1), 7.45–7.33 (2H, m, Fmoc-Ar-2,3), 5.54 (1H, dd, $J = 10.1, 10.1$ Hz, H-2'), 5.43 (1H, d, $J = 3.1$ Hz, H-4'), 5.11 (1H, dd, $J = 3.1, 10.1$ Hz, H-3'), 4.41 (2H, dd, $J = 3.4, 6.1$ Hz, Fmoc-CH₂O), 4.25 (1H, t, $J = 6.1$ Hz, Fmoc-CH), 4.12 (2H, dd, $J = 6.2, 10.5$ Hz, H-6'a, H-6'b), 4.03 (1H, ddd, $J = 6.2, 10.5, 11.0$ Hz, H-5'), 3.90 (1H, dd, $J = 2.4, 10.1$ Hz, H-1'), 3.48 (2H, dd, $J = 2.4, 7.0$ Hz, H-3a, H-3b), 2.94 (1H, dd, $J = 2.4, 4.8$ Hz, H-2), 2.15 (3H, s, COCH₃), 2.05 (3H, s, COCH₃), 2.01 (3H, s, COCH₃), 1.98 (3H, s, COCH₃). ¹³C NMR (CD₃OD): δ 173.41, 172.16, 172.10, 171.68, 171.27 (COCH₃, COOH), 158.70 (NHCOO), 145.35, 145.24, 142.62 (Fmoc-Ar-C), 128.82 (Fmoc-Ar-3), 128.20 (Fmoc-Ar-2), 126.15 (Fmoc-Ar-1), 120.95 (Fmoc-Ar-4), 77.43 (C-1'), 75.62 (C-5'), 74.29 (C-3'), 69.27 (C-4'), 68.48 (C-2'), 67.66 (Fmoc-CH₂O), 62.64 (C-6'), 48.43 (Fmoc-CH), 46.67 (C-2), 39.83 (C-3), 20.77, 20.59, 20.52 (COCH₃). HRMS (ESI) Calcd for C₃₂H₃₄NO₁₃Na₂ ([M – H + 2Na]⁺): 686.18255. Found for: 686.18184.

(2S)-2-(2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl)-N-(9-fluorenylmethoxycarbonyl)- β -alanine (18): Compound **18** was prepared by a method similar to the preparation of **13** using **16** in place of **11**. Yield: 84%. $[\alpha]_D^{20} = -0.02$ ($c = 0.981$, CHCl₃); ¹H NMR (CD₃OD): δ 7.83 (2H, d, $J = 7.6$ Hz, Fmoc-Ar-4), 7.69 (2H, d, $J = 7.0$ Hz, Fmoc-Ar-1), 7.43 (2H, dd, $J = 7.2, 7.6$ Hz, Fmoc-Ar-3), 7.35 (2H, dd, $J = 7.0, 7.2$ Hz, Fmoc-Ar-2), 5.45 (1H, d, $J = 3.2$ Hz, H-4'), 5.31 (1H, dd, $J = 9.8, 10.1$ Hz, H-2'), 5.15 (1H, dd, $J = 3.2, 9.8$ Hz, H-3'), 4.34 (2H, dd, $J = 3.1, 7.9$ Hz, Fmoc-CH₂O), 4.26 (1H, t, $J = 6.7$ Hz, Fmoc-CH), 4.19–4.06 (4H, m, H-6'a, H-6'b, H-1', H-5'), 3.61 (1H, dd, $J = 5.0, 14.0$ Hz, H-3a), 3.51 (1H, dd, $J = 8.3, 14.0$ Hz, H-3b), 2.87 (1H, m, H-2), 2.15 (3H, s, COCH₃), 2.05 (3H, s, COCH₃), 2.04 (3H, s, COCH₃), 1.97 (3H, s, COCH₃). ¹³C NMR (CD₃OD): δ 174.70, 172.15, 172.02, 171.56, 171.47 (COCH₃, COOBu^t), 158.51 (NHCOO), 145.37, 145.27, 142.54 (Fmoc-Ar-C), 128.77

(Fmoc-Ar-3), 128.15 (Fmoc-Ar-2), 126.26 (Fmoc-Ar-1), 120.92 (Fmoc-Ar-4), 78.29 (C-1'), 75.81 (C-5'), 73.85 (C-2'), 69.37 (C-4'), 69.26 (C-3'), 67.88 (Fmoc-CH₂O), 62.69 (C-6'), 48.39 (Fmoc-CH), 47.95 (C-2), 39.55 (C-3), 20.73, 20.56 (COCH₃). HRMS (ESI) Calcd for C₃₂H₃₄NO₁₃Na₂ ([M - H + 2Na]⁺): 686.18255. Found for: 686.18273.

X-ray Crystallography. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-674992–675000 for compounds **1a**, **1b**, **6a**, **6b**, **19b**, **11**, **19a**, **29**, and **25**, respectively. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

This work was supported by the Sasakawa Scientific Research Grant from The Japan Science Society. The authors thank Dr. Tim Storr of Stanford University for critical reading of the manuscript.

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