 

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

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Facile preparations of *C*-glycosyl $\beta^2$- and $\beta^{2,2}$-amino acids are described. Selective formation of a $\beta$-*C*-glycoside linkage was achieved by the reaction of a 2,3,4,6-tetra-*O*-acetyl-$\alpha$-D-gluco/galactopyranosyl bromide ($\alpha$-acetobromoglucose/galactose) with the carbanion of a cyanoacetate ester. Crystallization selectively afforded one of two diastereomers with respect to the chiral center at the $\alpha$-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 $\beta$-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 $\alpha$-amino acids (Chart 1, **I**) have been reported.[7–16]

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

Several preparations of *C*-glycosyl $\beta^3$-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 $\beta$-peptides with *C*-glycosyl $\beta^3$-amino acids.[32–36] However, there are very few examples describing the preparation of *C*-glycosyl $\beta^2$-amino acid derivatives (Chart 1, **II**).[37,38] Furthermore, the stereoselective synthesis of $\beta^{2,2}$-amino acids with a quanternary stereogenic center (Chart 1, **IV**) remains an important challenge.[39,40] In this paper, we report the versatile synthesis of $\beta^2$-, $\beta^{2,2}$-amino acids with a glycosyl group directly connected to the C2 carbon.

## Results and Discussion

**Synthesis of *C*-Glycosyl $\beta^2$-Amino Acids.** The $S_N2$ reaction of 2,3,4,6-tetra-*O*-acetyl-$\alpha$-D-glucopyranosyl bromide ($\alpha$-acetobromoglucose) with the nucleophilic carbanion of *t*-butyl cyanoacetate affords compound **1a** exclusively as the $\beta$-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 2*S* 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 2*S* 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 $\beta$-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 $\beta$-amino acid as the hydrochloride salt in a diastereomerically pure form (Scheme 1).

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

To obtain both stereoisomers of the $\beta$-amino acids in dia-

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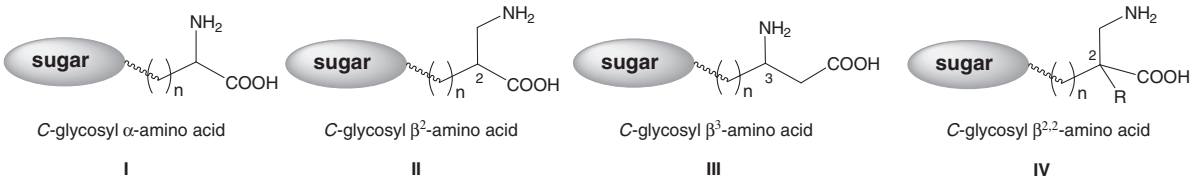
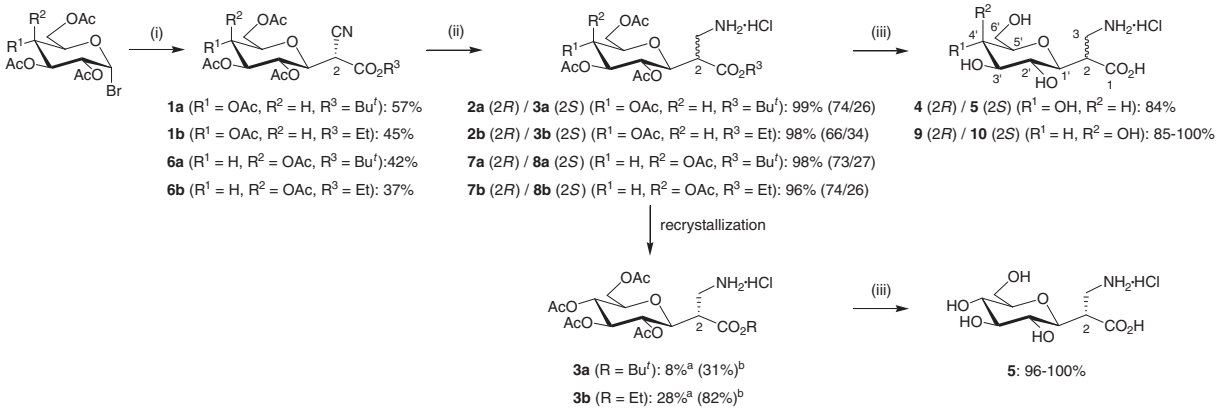



**Chart 1.**




**Scheme 1.** Synthesis of *C*-glycosyl $\beta^2$-amino acids. Reagents and conditions: (i) *t*-butyl cyanoacetate or ethyl cyanoacetate, NaH, DMF, 0 °C, 2 h; (ii) $H_2$, $PtO_2$, $CHCl_3$, 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**.

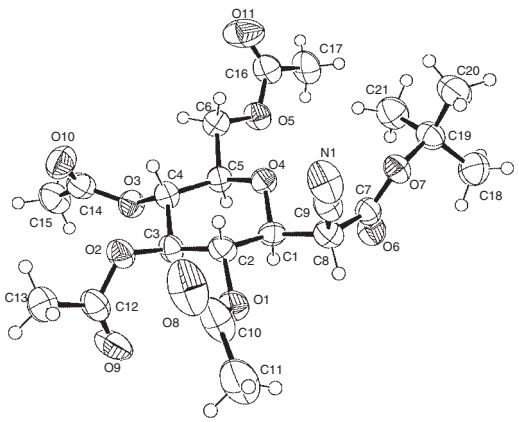


**Figure 1.** ORTEP plot for **1a**.

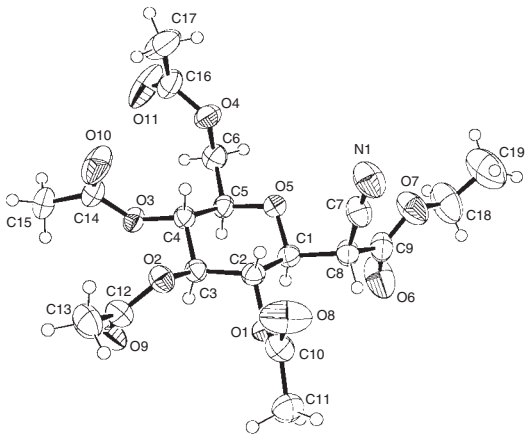


**Figure 2.** ORTEP plot for **1b**.

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-succinate and triethylamine in MeOH/$CH_3CN$. 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 $\beta^2$-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 $^1$H 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.

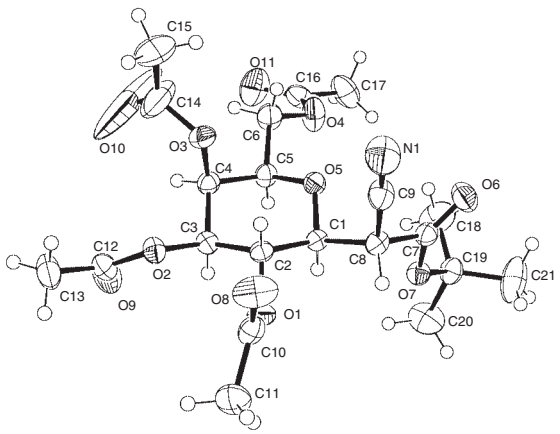


**Figure 3.** ORTEP plot for **6a**.

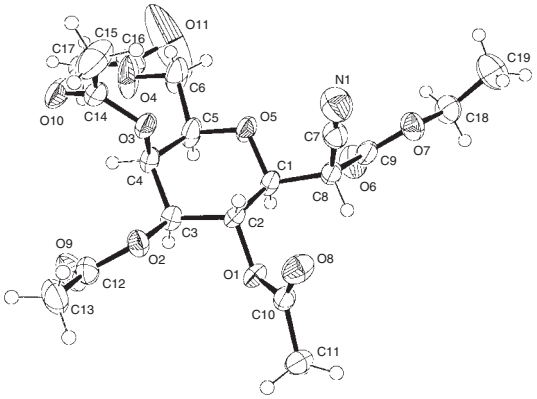



**Figure 4.** ORTEP plot for **6b**.

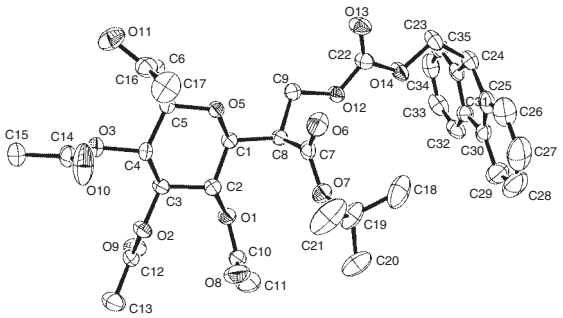
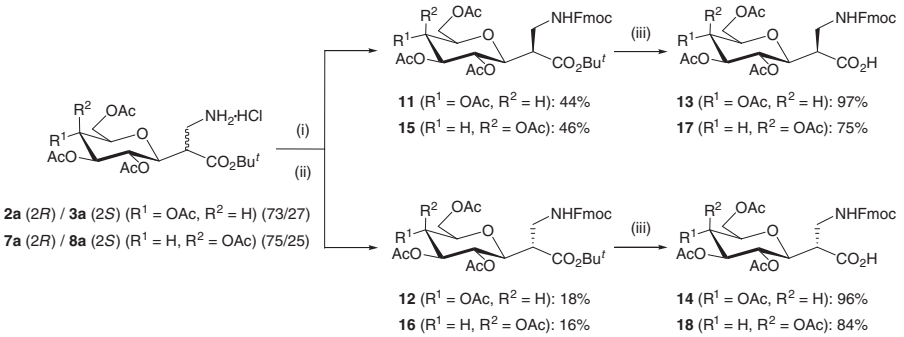
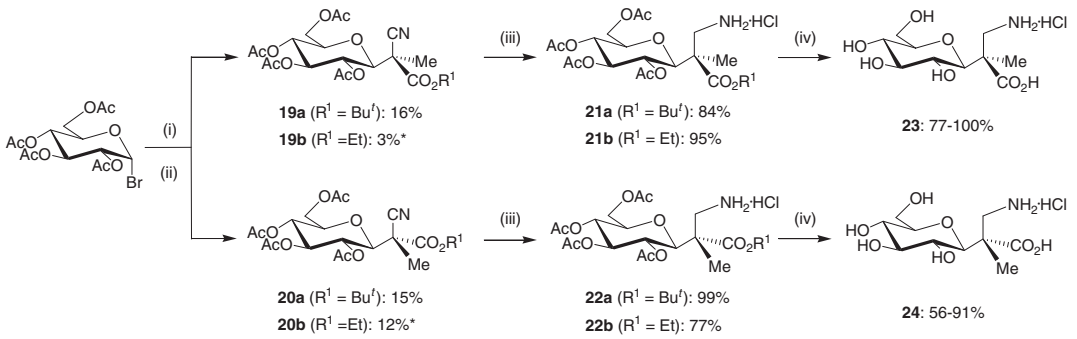



**Figure 5.** ORTEP plot for **11**.




**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-cyanopropionate, 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-cyanopropionate 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 $\beta^{2,2}$-dialkylcyanoacetate.[41] We employed this alternative method

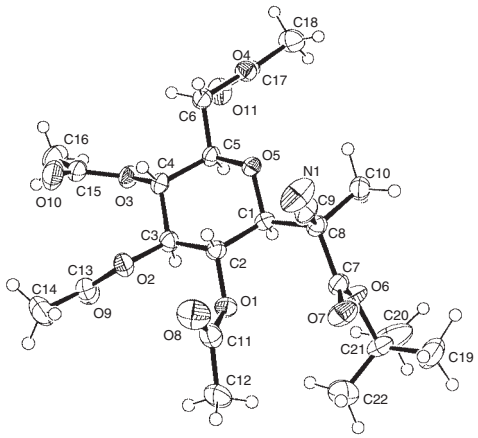



**Figure 6.** ORTEP plot for **19a**.

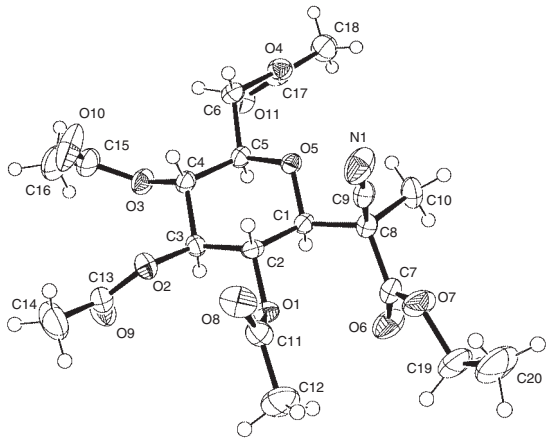
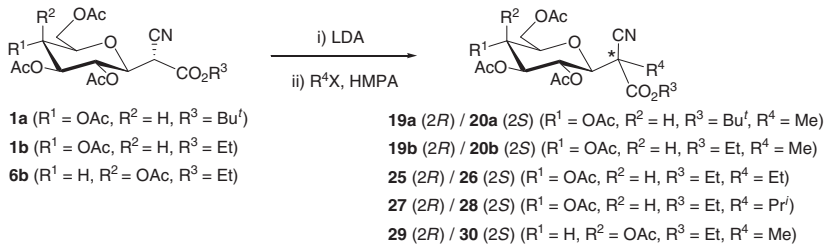



**Figure 7.** ORTEP plot for **19b**.




**1a** ($R^1$ = OAc, $R^2$ = H, $R^3$ = Bu$^t$)
**1b** ($R^1$ = OAc, $R^2$ = H, $R^3$ = Et)
**6b** ($R^1$ = H, $R^2$ = OAc, $R^3$ = Et)

**19a** (2*R*) / **20a** (2*S*) ($R^1$ = OAc, $R^2$ = H, $R^3$ = Bu$^t$, $R^4$ = Me)
**19b** (2*R*) / **20b** (2*S*) ($R^1$ = OAc, $R^2$ = H, $R^3$ = Et, $R^4$ = Me)
**25** (2*R*) / **26** (2*S*) ($R^1$ = OAc, $R^2$ = H, $R^3$ = Et, $R^4$ = Et)
**27** (2*R*) / **28** (2*S*) ($R^1$ = OAc, $R^2$ = H, $R^3$ = Et, $R^4$ = Pr$^i$)
**29** (2*R*) / **30** (2*S*) ($R^1$ = H, $R^2$ = OAc, $R^3$ = Et, $R^4$ = Me)

**Scheme 4.** Alkylations of **1a**, **1b**, and **6b**.

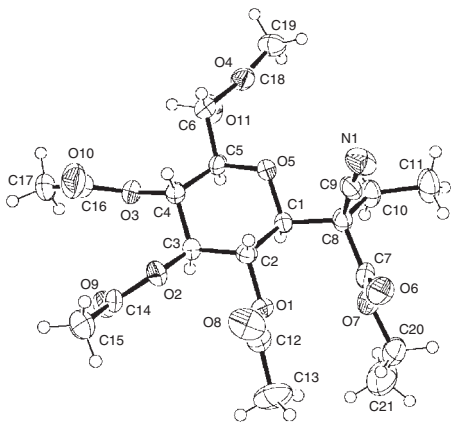



**Figure 8.** ORTEP plot for **25**.

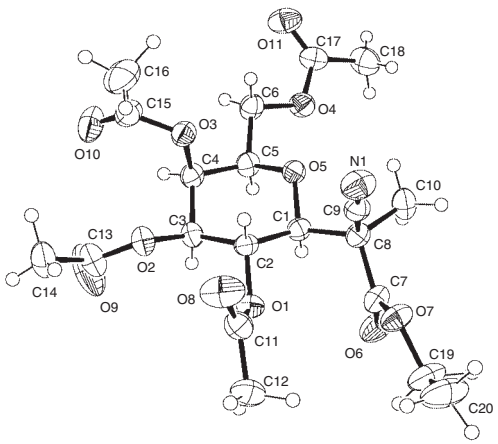



**Figure 9.** ORTEP plot for **29**.

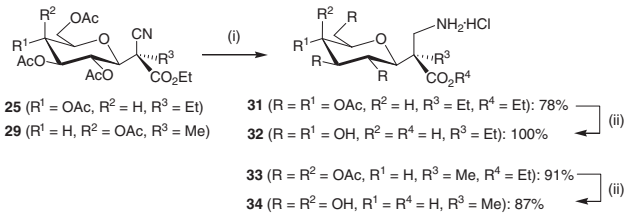
for the diastereoselective preparation of *C*-glycosyl $\beta^{2,2}$-amino acids using the sugar moiety of **1a** and **1b** as a chiral auxiliary. The enolates of the *C*-glycosylated cyanoacetate esters **1a**, **1b**, and **6b** generated by lithium diisopropylamide in dry THF at −78 °C were alkylated 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-$\beta$-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 | $R^4X$ | Yield[a)]/% | dr(2*R*/2*S*)[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** | $CH_3CH_2I$ | 41 (35) | 92/8 |
| 4 | **1b** | **27**/**28** | $(CH_3)_2CHI$ | 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 $^1$H 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 $\beta^2$- 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 $\beta^2$-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 $\beta^2$- and $\beta^{2,2}$-amino acids. Readily available, well-resolved diastereomers of *C*-glycosyl $\beta^2$- and $\beta^{2,2}$-amino acids should be useful carbohydrate-containing $\beta$-amino acid building blocks for glycopeptide research and application to pharmaceuticals.[42–44] The synthesis and investigation of *C*-glycosyl $\beta^2$-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. $^1$H 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); $^1$H 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, $(CH_3)_3C$). $^{13}$C NMR ($CDCl_3$): δ 170.55, 170.31, 169.26, 169.11 (*C*OCH$_3$), 162.25 (*C*OOBu$^t$), 112.82 (CN), 85.24 ((CH$_3$)$_3$*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 ((*C*H$_3$)$_3$C), 20.60 (CO*C*H$_3$). ESI-MS Calcd for $C_{21}H_{29}NO_{11}Na$ ($[M + Na]^+$): 494.16. Found: 494.09. Anal. Found: C, 53.48; H, 6.25; N, 2.98%. Calcd for $C_{21}H_{29}NO_{11}$: C, 53.50; H, 6.20; N, 2.97%. Crystal data: monoclinic, space group $C2$, $a$ = 24.21(3) Å, $b$ = 5.838(6) Å, $c$ = 17.15(2) Å, $V$ = 2414.7(44) Å$^3$, $Z$ = 4, $R$ = 0.092, $R_w{}^2$ = 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); $^1$H 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, C*H*$_2$CH$_3$), 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$_2$C*H*$_3$). $^{13}$C NMR ($CDCl_3$): δ 170.55, 170.25, 169.23, 169.14 (*C*OCH$_3$), 163.40 (*C*OOEt), 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 (*C*H$_2$CH$_3$), 61.60 (C-6′), 40.45 (C-2), 20.55 (CO*C*H$_3$), 13.90 (CH$_2$*C*H$_3$). ESI-MS Calcd for $C_{19}H_{25}NO_{11}Na$ ($[M + Na]^+$): 466.13. Found: 466.08. Anal. Found: C, 51.52; H, 5.77; N, 3.20%. Calcd for $C_{19}H_{25}NO_{11}$: C, 51.47; H, 5.68; N, 3.16%. Crystal data: orthorhombic, space group $P2_12_12_1$, $a$ = 7.0872(15) Å, $b$ = 12.529(3) Å, $c$ = 25.424(6) Å, $V$ = 2257.5(8) Å$^3$, $Z$ = 4, $R$ = 0.052, $R_w{}^2$ = 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); $^1$H 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, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.53 (9H, s, $(CH_3)_3C$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 170.25, 170.03, 169.29 ($COCH_3$), 162.45 ($COOBu^t$), 112.97 (CN), 85.07 ($(CH_3)_3C$), 75.77, 74.62, 71.63, 67.13, 61.56, 41.68 (C-2), 27.78, 27.67 ($(CH_3)_3C$), 20.61 ($COCH_3$). HRMS (ESI) Calcd for $C_{17}H_{21}NO_{11}Na$ ($[M - Bu^t + H + Na]^+$): 438.10123. Found: 438.10091. Anal. Found: C, 53.52; H, 6.21; N, 3.02%. Calcd for $C_{21}H_{29}NO_{11}$: C, 53.50; H, 6.20; N, 2.97%. Crystal data: monoclinic, space group $P2_1$, $a = 10.237(2)$ Å, $b = 9.770(2)$ Å, $c = 12.894(3)$ Å, $\beta = 101.4403(10)^\circ$, $V = 1263.9(5)$ Å$^3$, $Z = 2$, $R = 0.051$, $R_w{}^2 = 0.156$, GOF = 1.084.

**Ethyl (2*S*)-(2,3,4,6-Tetra-*O*-acetyl-$\beta$-D-galactopyranosyl)-cyanoacetate (6b):** Compound **6b** was prepared by a method similar to the preparation of **1b** using $\alpha$-acetobromogalactose in place of $\alpha$-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 ($CDCl_3$, $Me_4Si$): $\delta$ 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, $CH_2CH_3$), 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, $COCH_3$), 2.08 (3H, s, $COCH_3$), 2.03 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.35 (3H, t, $J = 7.0$ Hz, $CH_2CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 170.21, 169.99, 169.36 ($COCH_3$), 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 ($COCH_3$), 13.85 ($CH_2CH_3$). ESI-MS Calcd for $C_{19}H_{25}NO_{11}Na$ ($[M + Na]^+$): 466.13. Found: 466.03. Anal. Found: C, 51.41; H, 5.69; N, 3.17%. Calcd for $C_{19}H_{25}NO_{11}$: C, 51.47; H, 5.68; N, 3.16%. Crystal data: monoclinic, space group $P2_1$, $a = 9.2023(5)$ Å, $b = 8.3030(4)$ Å, $c = 14.3389(7)$ Å, $\beta = 97.0267(10)^\circ$, $V = 1087.36(10)$ Å$^3$, $Z = 2$, $R = 0.057$, $R_w{}^2 = 0.175$, 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 $NH_4Cl$ solution (5 mL). An ether extraction, washing by water, drying over $Na_2SO_4$ 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 (2*R*)-2-(2,3,4,6-Tetra-*O*-acetyl-$\beta$-D-glucopyranosyl)-2-cyanopropanoate (19a):** Mp 96–100 °C (EtOH); $[\alpha]_D^{20} = 9.83$ ($c = 0.999$, $CHCl_3$); $^1H$ NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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, $COCH_3$), 2.04 (3H, s, $COCH_3$), 2.03 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.56 (3H, s, 2-$CH_3$), 1.52 (9H, s, $(CH_3)_3C$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 170.39, 170.07, 169.55, 169.26 ($COCH_3$), 164.42 ($COOBu^t$), 117.39 (CN), 84.33 ($(CH_3)_3C$), 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 ($(CH_3)_3C$), 20.79, 20.57, 20.53, 20.47 ($COCH_3$), 15.82 (2-$CH_3$). ESI-MS Calcd for $C_{18}H_{23}NO_{11}Na$ ($[M - Bu^t + H + Na]^+$): 452.12. Found: 452.07. Anal. Found: C, 54.24; H, 6.44; N, 2.84%. Calcd for $C_{22}H_{31}NO_{11}$: C, 54.43; H, 6.44; N, 2.89%. Crystal data: monoclinic, space group $P2_1$, $a = 6.394(2)$ Å, $b = 21.419(5)$ Å, $c = 9.530(3)$ Å, $\beta = 108.259(3)^\circ$, $V = 1239.3(6)$ Å$^3$, $Z = 2$, $R = 0.036$, $R_w{}^2 = 0.084$, GOF = 1.118.

***t*-Butyl (2*S*)-2-(2,3,4,6-Tetra-*O*-acetyl-$\beta$-D-glucopyranosyl)-2-cyanopropanoate (20a):** Mp 175–177 °C (EtOH); $[\alpha]_D^{20} = 0.811$ ($c = 1.01$, $CHCl_3$); $^1H$ NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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, $COCH_3$), 2.04 (6H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.54 (12H, s, 2-$CH_3$, $(CH_3)_3C$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 170.49, 170.23, 169.23, 168.90 ($COCH_3$), 164.91 ($COOBu^t$), 117.63 (CN), 84.75 ($(CH_3)_3C$), 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 ($(CH_3)_3C$), 20.57, 20.47 ($COCH_3$), 18.45 (2-$CH_3$). ESI-MS Calcd for $C_{18}H_{23}NO_{11}Na$ ($[M - Bu^t + H + Na]^+$): 452.12. Found: 452.04. Anal. Found: C, 54.40; H, 6.18; N, 2.82%. Calcd for $C_{22}H_{31}NO_{11}$: C, 54.43; H, 6.44; N, 2.89%.

**Ethyl (2*R*)-2-(2,3,4,6-Tetra-*O*-acetyl-$\beta$-D-glucopyranosyl)-2-cyanopropanoate (19b):** Mp 114–116 °C (EtOH); $[\alpha]_D^{20} = 6.27$ ($c = 0.996$, $CHCl_3$); $^1H$ NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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, $CH_2CH_3$), 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, $COCH_3$), 2.06 (3H, s, $COCH_3$), 2.04 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.65 (3H, s, 2-$CH_3$), 1.34 (3H, t, $J = 7.0$ Hz, $CH_2CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 170.44, 170.18, 169.31 ($COCH_3$), 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 ($CH_2CH_3$), 61.84 (C-6′), 45.30 (C-2), 20.53 ($COCH_3$), 17.26 (2-$CH_3$), 13.96 ($CH_2CH_3$). ESI-MS Calcd for $C_{20}H_{27}NO_{11}Na$ ($[M + Na]^+$): 480.15. Found: 480.12. Anal. Found: C, 52.42; H, 6.04; N, 3.15%. Calcd for $C_{20}H_{27}NO_{11}$: C, 52.51; H, 5.95; N, 3.06%. Crystal data: monoclinic, space group $C2$, $a = 27.446(9)$ Å, $b = 6.190(2)$ Å, $c = 13.991(5)$ Å, $\beta = 101.5687(10)^\circ$, $V = 2328.5(13)$ Å$^3$, $Z = 4$, $R = 0.053$, $R_w{}^2 = 0.146$, GOF = 1.062.

**Ethyl (2*S*)-2-(2,3,4,6-Tetra-*O*-acetyl-$\beta$-D-glucopyranosyl)-2-cyanopropanoate (20b):** Mp 125–127 °C (EtOH); $[\alpha]_D^{20} = -4.35$ ($c = 1.00$, $CHCl_3$); $^1H$ NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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, $CH_2CH_3$, 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, $COCH_3$), 2.04 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$), 1.58 (3H, s, 2-$CH_3$), 1.37 (3H, t, $J = 7.0$ Hz, $CH_2CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 170.57, 170.26, 169.29, 168.84 ($COCH_3$), 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 ($CH_2CH_3$), 61.73 (C-6′), 46.71 (C-2), 20.61, 20.53, 20.48 ($COCH_3$), 17.47 (2-$CH_3$), 13.90 ($CH_2CH_3$). HRMS (ESI) Calcd for $C_{20}H_{27}NO_{11}Na$ ($[M + Na]^+$): 480.14818. Found: 480.14721. Anal. Found: C, 52.48; H, 6.03; N, 3.08%. Calcd for $C_{20}H_{27}NO_{11}$: C, 52.51; H, 5.95; N, 3.06%.

**Ethyl (2*R*)-2-(2,3,4,6-Tetra-*O*-acetyl-$\beta$-D-glucopyranosyl)-2-cyanobutanoate (25):** Mp 120–122 °C (EtOH); $[\alpha]_D^{20} = -3.20$ ($c = 1.00$, $CHCl_3$); $^1H$ NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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, $OCH_2CH_3$, 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-C$H_2$CH$_3$), 2.09 (3H, s, COCH$_3$), 2.05–1.92 (1H, m, 2-C$H_2$CH$_3$), 2.04 (3H, s, COCH$_3$), 2.00 (3H, s, COCH$_3$), 1.98 (3H, s, COCH$_3$), 1.35 (3H, t, $J = 7.0$ Hz, OCH$_2$C$H_3$), 1.06 (3H, t, $J = 7.5$ Hz, 2-CH$_2$C$H_3$). $^{13}$C NMR (CDCl$_3$): δ 170.52, 170.31, 169.21, 168.45 (*C*OCH$_3$), 166.09 (*C*OOEt), 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 (COO*C*H$_2$CH$_3$), 61.69 (C-6′), 53.39 (C-2), 27.43 (2-*C*H$_2$CH$_3$), 20.63, 20.48 (CO*C*H$_3$), 13.98 (OCH$_2$*C*H$_3$), 9.17 (2-CH$_2$*C*H$_3$). HRMS (ESI) Calcd for $C_{21}H_{29}NO_{11}Na$ ([M + Na]$^+$): 494.16383. Found: 494.16341. Anal. Found: C, 53.29; H, 6.13; N, 3.01%. Calcd for $C_{21}H_{29}NO_{11}$: C, 53.50; H, 6.20; N, 2.97%. Crystal data: monoclinic, space group *C*2, $a = 35.450(3)$ Å, $b = 12.3686(8)$ Å, $c = 25.189(2)$ Å, $\beta = 121.121(3)°$, $V = 9455.2(13)$ Å$^3$, $Z = 16$, $R = 0.0872$, $R_w{}^2 = 0.3048$, GOF = 1.349.

**Ethyl (2*R*)-2-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2-cyanopropanoate (29):** Mp 109–111 °C (EtOH); $[\alpha]_D^{20} = 19.7$ ($c = 0.995$, CHCl$_3$); $^1$H NMR (CDCl$_3$, Me$_4$Si): 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, C$H_2$CH$_3$), 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, COCH$_3$), 2.08 (3H, s, COCH$_3$), 2.03 (3H, s, COCH$_3$), 1.99 (3H, s, COCH$_3$), 1.67 (3H, s, 2-CH$_3$), 1.35 (3H, t, $J = 7.3$ Hz, CH$_2$C$H_3$). $^{13}$C NMR (CDCl$_3$): δ 170.18, 170.03, 169.95, 169.44 (*C*OCH$_3$), 166.07 (*C*OOEt), 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 (*C*H$_2$CH$_3$), 61.37 (C-6′), 45.17 (C-2′), 20.79, 20.53, 20.50, 20.44 (CO*C*H$_3$), 16.76 (2-CH$_3$), 13.88 (CH$_2$*C*H$_3$). HRMS (ESI) Calcd for $C_{20}H_{27}NO_{11}Na$ ([M + Na]$^+$): 480.14818. Found: 480.14722. Anal. Found: C, 52.42; H, 5.92; N, 3.17%. Calcd for $C_{20}H_{27}NO_{11}$: C, 52.51; H, 5.95; N, 3.06%. Crystal data: orthorhombic, space group $P2_12_12_1$, $a = 7.585(2)$ Å, $b = 14.418(4)$ Å, $c = 21.154(7)$ Å, $V = 2313.5(12)$ Å$^3$, $Z = 4$, $R = 0.0488$, $R_w{}^2 = 0.1257$, GOF = 1.114.

***t*-Butyl (2*S*)-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); $^1$H NMR (D$_2$O, 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, COCH$_3$), 2.09 (6H, s, COCH$_3$), 2.07 (3H, s, COCH$_3$), 1.50 (9H, s, (CH$_3$)$_3$C). $^{13}$C NMR (D$_2$O, dioxane): δ 173.68, 173.14, 172.74, 170.75 (*C*OCH$_3$, *C*OOBu$^t$), 84.75 ((CH$_3$)*C*), 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 ((*C*H$_3$)C), 20.02, 19.97 (CO*C*H$_3$). HRMS (ESI) Calcd for $C_{21}H_{34}NO_{11}$ ([M − Cl]$^+$): 476.2126. Found: 476.2124. Anal. Found: C, 47.66; H, 6.44; N, 2.74%. Calcd for $C_{21}H_{36}NO_{12}Cl$: C, 47.59; H, 6.85; N, 2.64%.

**Ethyl (2*S*)-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); $^1$H NMR (D$_2$O, 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′, C$H_2$CH$_3$), 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, COCH$_3$), 2.09 (3H, s, COCH$_3$), 2.06 (3H, s, COCH$_3$), 1.29 (3H, t, $J = 7.2$ Hz, CH$_2$C$H_3$). $^{13}$C NMR (D$_2$O, dioxane): δ 173.69, 173.14, 172.74, 171.62 (*C*OCH$_3$, *C*OOEt), 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 (*C*H$_2$CH$_3$), 42.83 (C-2), 35.84 (C-3), 20.05, 19.93 (CO*C*H$_3$), 13.14 (CH$_2$*C*H$_3$). HRMS (ESI) Calcd for $C_{19}H_{30}NO_{11}$ ([M − Cl]$^+$): 448.1813. Found: 448.1812. Anal. Found: C, 46.96; H, 6.23; N, 2.83%. Calcd for $C_{19}H_{30}NO_{11}Cl$: C, 47.16; H, 6.25; N, 2.89%.

***t*-Butyl (2*R*)/(2*S*)-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%. $^1$H NMR (D$_2$O, 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, COCH$_3$), 1.55 (7H, s, C(CH$_3$)$_3$), 1.51 (3H, s, C(CH$_3$)$_3$). $^{13}$C NMR (D$_2$O, dioxane): δ 173.53, 173.43, 173.11, 172.95, 172.72, 172.67, 172.58, 170.70, 169.97, 169.66 (*C*OCH$_3$, *C*OOBu$^t$), 84.75 (*C*(CH$_3$)$_3$), 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(*C*H$_3$)$_3$ (**7a**)), 27.13 (C(*C*H$_3$)$_3$ (**8a**)), 20.26, 20.13, 20.00 (CO*C*H$_3$). HRMS (ESI) Calcd for $C_{21}H_{33}NO_{11}Na$ ([M − HCl + Na]$^+$): 498.19513. Found: 498.19546.

**Ethyl (2*R*)/(2*S*)-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%. $^1$H NMR (D$_2$O, 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**), C$H_2$CH$_3$ (**7b**), C$H_2$CH$_3$ (**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, COCH$_3$), 1.35 (3H, t, $J = 7.0$ Hz, CH$_2$C$H_3$ (**7b**), CH$_2$C$H_3$ (**8b**)). $^{13}$C NMR (D$_2$O, dioxane): δ 173.74, 173.45, 173.42, 173.09, 172.90, 172.64, 172.53, 171.59, 170.70, 170.57 (*C*OCH$_3$ (**7b**), *C*OCH$_3$ (**8b**), *C*OOEt (**7b**), *C*OOEt (**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 (*C*H$_2$CH$_3$ (**8b**)), 62.02 (*C*H$_2$CH$_3$ (**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 (CO*C*H$_3$ (**7b**), CO*C*H$_3$ (**8b**)), 13.41 (CH$_2$*C*H$_3$ (**7b**)), 13.25 (CH$_2$*C*H$_3$ (**8b**)). HRMS (ESI) Calcd for $C_{19}H_{29}NO_{11}Na$

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

***t*-Butyl (2*R*)-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); $^1$H NMR ($CD_3OD$): $\delta$ 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, $COCH_3$), 2.06 (3H, s, $COCH_3$), 2.03 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.59 (9H, s, $C(CH_3)_3$), 1.36 (3H, s, 2-$CH_3$). $^{13}$C NMR ($CD_3OD$): $\delta$ 172.91, 172.31, 171.63, 171.22, 171.16 (*C*OCH$_3$, *C*OOBu$^t$), 84.63 (*C*(CH$_3$)$_3$), 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(*C*H$_3$)$_3$), 20.99, 20.73, 20.54 (CO*C*H$_3$), 18.89 (2-$CH_3$). HRMS (ESI) Calcd for $C_{22}H_{35}NO_{11}Na$ ([M − HCl + Na]$^+$): 512.21078. Found: 512.21091.

***t*-Butyl (2*S*)-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); $^1$H NMR ($CD_3OD$): $\delta$ 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, $COCH_3$), 2.07 (3H, s, $COCH_3$), 2.06 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.58 (9H, s, $C(CH_3)_3$), 1.22 (3H, s, 2-$CH_3$). $^{13}$C NMR ($CD_3OD$): $\delta$ 172.82, 172.66, 171.58, 171.30, 171.26 (*C*OCH$_3$, *C*OOBu$^t$), 84.43 (*C*(CH$_3$)$_3$), 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*(CH$_3$)$_3$), 20.88, 20.80, 20.54, 20.49 (CO*C*H$_3$), 17.43 (2-$CH_3$). ESI-MS Calcd for $C_{22}H_{35}NO_{11}Na$ ([M − HCl + Na]$^+$): 512.21. Found: 512.18. Anal. Found: C, 49.72; H, 6.80; N, 2.72%. Calcd for $C_{45}H_{76}N_2O_{23}Cl_2$: C, 49.86; H, 7.07; N, 2.58%.

**Ethyl (2*R*)-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); $^1$H NMR ($D_2O$, DSS): $\delta$ 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′, C*H*$_2$CH$_3$), 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, $COCH_3$), 2.08 (3H, s, $COCH_3$), 2.06 (3H, s, $COCH_3$), 2.04 (3H, s, $COCH_3$), 1.40 (3H, s, 2-$CH_3$), 1.32 (3H, t, $J = 7.2$ Hz, CH$_2$C*H*$_3$). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 173.66, 173.43, 173.04, 172.69 (*C*OCH$_3$), 172.38 (*C*OOEt), 78.98 (C-1′), 75.29 (C-5′), 74.96 (C-3′), 68.91 (C-2′), 68.01 (C-4′), 62.97 (*C*H$_2$CH$_3$), 61.92 (C-6′), 46.47 (C-2), 41.81 (C-3), 19.95 (CO*C*H$_3$), 17.64 (2-$CH_3$), 13.06 (CH$_2$*C*H$_3$). HRMS (ESI) Calcd for $C_{20}H_{31}NO_{11}Na$ ([M − HCl + Na]$^+$): 484.17948. Found: 484.17864.

**Ethyl (2*S*)-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); $^1$H NMR ($D_2O$, DSS): $\delta$ 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′, C*H*$_2$CH$_3$), 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, $COCH_3$), 2.09 (3H, s, $COCH_3$), 2.04 (6H, s, $COCH_3$), 1.40 (3H, s, 2-$CH_3$), 1.31 (3H, t, $J = 7.2$ Hz, CH$_2$C*H*$_3$). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 173.76, 173.06, 172.64, 172.25 (*C*OCH$_3$, *C*OOEt), 78.65 (C-1′), 75.38 (C-5′), 74.82 (C-3′), 68.64 (C-2′), 68.07 (C-4′), 63.20 (*C*H$_2$CH$_3$), 61.92 (C-6′), 46.84 (C-2), 43.59 (C-3), 20.16, 20.05 (CO*C*H$_3$), 13.82 (2-$CH_3$), 13.11 (CH$_2$*C*H$_3$). HRMS (ESI) Calcd for $C_{20}H_{31}NO_{11}Na$ ([M − HCl + Na]$^+$): 484.17948. Found: 484.18249.

**Ethyl (2*R*)-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%. $^1$H NMR ($D_2O$, DSS): $\delta$ 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, OC*H*$_2$CH$_3$, 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, $COCH_3$), 2.09 (3H, s, $COCH_3$), 2.05 (3H, s, $COCH_3$), 2.04 (3H, s, $COCH_3$), 1.95 (2H, q, $J = 7.5$ Hz, 2-C*H*$_2$CH$_3$), 1.32 (3H, t, $J = 7.3$ Hz, OCH$_2$C*H*$_3$), 0.90 (3H, t, $J = 7.5$ Hz, 2-CH$_2$C*H*$_3$). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 173.69, 173.01, 172.70, 172.62, 172.35 (*C*OCH$_3$, *C*OOEt), 79.09, 75.66, 74.83, 68.77, 68.13, 62.89, 62.07, 49.84, 38.99, 24.43 (2-*C*H$_2$CH$_3$), 20.10, 20.05, 19.98, 19.92 (CO*C*H$_3$), 13.11 (OCH$_2$*C*H$_3$), 7.15 (2-CH$_2$*C*H$_3$). HRMS (ESI) Calcd for $C_{21}H_{33}NO_{11}Na$ ([M + Na]$^+$): 498.19513. Found: 498.20049.

**Ethyl (2*R*)-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); $^1$H NMR ($CD_3OD$): $\delta$ 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, C*H*$_2$CH$_3$-a), 4.28–4.11 (5H, m, H-6′a, H-6′b, H-5′, H-1′, C*H*$_2$CH$_3$-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, $COCH_3$), 2.08 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 1.97 (3H, s, $COCH_3$), 1.45 (3H, s, 2-$CH_3$), 1.39 (3H, t, $J = 7.2$ Hz, CH$_2$C*H*$_3$). $^{13}$C NMR ($CD_3OD$): $\delta$ 173.81, 172.15, 171.77, 171.34, 171.16 (*C*OCH$_3$, *C*OOEt), 80.91 (C-1′), 76.20 (C-5′), 73.74 (C-3′), 69.27 (C-4′), 67.38 (C-2′), 63.08 (*C*H$_2$CH$_3$), 62.82 (C-6′), 47.95 (C-2), 42.59 (C-3), 20.94, 20.72, 20.56, 20.46 (CO*C*H$_3$), 18.68 (2-$CH_3$), 14.31 (CH$_2$*C*H$_3$). HRMS (ESI) Calcd for $C_{20}H_{31}NO_{11}Na$ ([M + Na]$^+$): 484.17948. Found: 484.17885.

**(2*S*)-3-Amino-2-(β-D-glucopyranosyl)propanoic Acid Monohydrochloride (5).** **3a** (20 mg, 0.040 mmol) was added 6 mol 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); $^1$H NMR ($D_2O$, DSS): $\delta$ 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): $\delta$ 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 $C_9H_{18}NO_7$ ([M − Cl]$^+$): 252.1078. Found: 252.1080. Anal. Found: C, 34.16; H, 6.96; N, 4.04%. Calcd for $C_9H_{18}NO_7Cl \cdot 1.5H_2O$: C, 34.35; H, 6.73; N, 4.45%.

**(2*R*)/(2*S*)-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%. $^1$H NMR ($D_2O$, DSS): $\delta$ 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**)). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 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 $C_9H_{17}NO_7Na$ ([M − HCl + Na]$^+$): 274.09027. Found: 274.09051.

**(2*R*)-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%. $[\alpha]_D^{20} = 1.28$ ($c = 0.736$, MeOH); $^1$H NMR ($D_2O$, DSS): $\delta$ 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-$CH_3$). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 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-$CH_3$). HRMS (ESI) Calcd for $C_{10}H_{19}NO_7Na$ ([M − HCl + Na]$^+$): 288.10592. Found: 288.10633.

**(2*S*)-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% $[\alpha]_D^{20} = 13.2$ ($c = 1.00$, MeOH); $^1$H NMR ($D_2O$, DSS): $\delta$ 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-$CH_3$). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 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-$CH_3$). HRMS (ESI) Calcd for $C_{10}H_{20}NO_7$ ([M − Cl]$^+$): 266.1240. Found: 266.1244.

**(2*R*)-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%. $[\alpha]_D^{20} = 1.20$ ($c = 0.309$, MeOH); $^1$H NMR ($D_2O$, DSS): $\delta$ 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-$CH_2CH_3$), 0.92 (3H, t, $J = 7.3$ Hz, 2-$CH_2CH_3$). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 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-$CH_2CH_3$), 7.15 (2-$CH_2CH_3$). HRMS (ESI) Calcd for $C_{11}H_{21}NO_7Na$ ([M − HCl + Na]$^+$): 302.12157. Found: 302.12244.

**(2*R*)-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%. $[\alpha]_D^{20} = 14.7$ ($c = 0.911$, MeOH); $^1$H NMR ($D_2O$, DSS): $\delta$ 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-$CH_3$). $^{13}$C NMR ($D_2O$, dioxane): $\delta$ 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-$CH_3$). HRMS (ESI) Calcd for $C_{10}H_{19}NO_7Na$ ([M + Na]$^+$): 288.10592. Found: 288.10631.

***t*-Butyl (2*R*)- and (2*S*)-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 $Et_3N$ (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 × 50 mL) and combined extracts were washed with brine (50 mL), dried ($Na_2SO_4$), 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); $[\alpha]_D^{20} = -24.5$ ($c = 0.993$, $CHCl_3$); $^1$H NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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-C$H_2$O), 4.23–4.02 (3H, m, Fmoc-C*H*, 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, $COCH_3$), 2.02 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.50 (9H, s, $(CH_3)_3C$). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.52, 170.39, 169.34, 169.23 (*C*O*C*H$_3$, *C*OOBu$^t$), 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 ((CH$_3$)$_3$*C*), 76.58 (C-1′), 75.95 (C-5′), 74.74 (C-3′), 69.70 (C-2′), 67.99 (C-4′), 66.65 (Fmoc-*C*H$_2$O), 61.84 (C-6′), 47.15 (Fmoc-*C*H), 45.85 (C-2), 40.21 (C-3), 28.12, 28.02 ((*C*H$_3$)$_3$C)), 20.63, 20.50 (CO*C*H$_3$). ESI-MS Calcd for $C_{36}H_{43}NO_{13}Na$ ([M + Na]$^+$): 720.26. Found: 720.15. Anal. Found: C, 61.86; H, 6.26; N, 2.04%. Calcd for $C_{36}H_{43}NO_{13}$: 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, $V = 3575.0(3)$ Å$^3$, $Z = 4$, $R = 0.083$, $R_w{}^2 = 0.120$, GOF = 0.912. For **12**: $[\alpha]_D^{20} = -21.4$ ($c = 0.999$, $CHCl_3$); $^1$H NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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-C$H_2$O), 4.22–4.06 (4H, m, Fmoc-C*H*, 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, $COCH_3$), 2.03 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.47 (9H, s, $(CH_3)_3C$). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.47, 170.25, 170.16, 169.37, 169.27 (*C*O*C*H$_3$, *C*OOBu$^t$), 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 ((CH$_3$)$_3$*C*), 77.10 (C-1′), 76.30 (C-5′), 74.22 (C-3′), 69.12 (C-2′), 68.39 (C-4′), 66.58 (Fmoc-*C*H$_2$O), 62.16 (C-6′), 47.04 (Fmoc-*C*H), 45.90 (C-2), 37.20 (C-3), 27.94, 27.85 ((*C*H$_3$)$_3$C), 20.53, 20.45, 20.40 (CO*C*H$_3$). HRMS (ESI) Calcd for $C_{36}H_{43}NO_{13}Na$ ([M + Na]$^+$): 720.26321. Found: 720.26201.

***t*-Butyl (2*R*)- and (2*S*)-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**: $[\alpha]_D^{20} = -13.3$ ($c = 0.999$, $CHCl_3$); $^1$H NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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-C$H_2$O), 4.21 (1H, t, $J = 6.9$ Hz, Fmoc-C*H*), 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, $COCH_3$), 2.03 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.53 (9H, s, $(CH_3)_3C$). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.28, 170.15, 169.95, 169.37, 169.19 (*C*O$CH_3$, *C*OOBu$^t$), 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 ((CH$_3$)$_3$*C*), 77.50 (C-1′), 74.28 (C-5′), 72.62 (C-3′), 67.55 (C-4′), 66.81 (C-2′), 66.63 (Fmoc-*C*H$_2$O), 61.14 (C-6′), 47.13 (Fmoc-*C*H), 45.72 (C-2), 40.30 (C-3), 27.96 ((*C*H$_3$)$_3$C), 20.73, 20.63, 20.53 (CO*C*H$_3$). HRMS (ESI) Calcd for $C_{36}H_{43}NO_{13}Na$ ($[M + Na]^+$): 720.26321. Found: 720.26354. For **16**: $[\alpha]_D^{20} = -3.24$ ($c = 0.997$, $CHCl_3$); $^1$H NMR ($CDCl_3$, $Me_4Si$): $\delta$ 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-C$H_2$O), 4.22 (1H, t, $J = 7.4$ Hz, Fmoc-C*H*), 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, $COCH_3$), 2.07 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$), 1.47 (9H, s, $(CH_3)_3C$). $^{13}$C NMR ($CDCl_3$): $\delta$ 170.36, 170.13, 169.52 (*C*O$CH_3$, *C*OOBu$^t$), 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 ((CH$_3$)$_3$*C*), 77.58 (C-1′), 75.01 (C-5′), 72.36 (C-3′), 67.78 (C-4′), 66.68 (Fmoc-*C*H$_2$O), 66.61 (C-2′), 61.76 (C-6′), 47.13 (Fmoc-*C*H), 46.11 (C-2), 37.38 (C-3), 27.98 ((*C*H$_3$)$_3$C), 20.65, 20.53 (CO*C*H$_3$). HRMS (ESI) Calcd for $C_{36}H_{43}NO_{13}Na$ ($[M + Na]^+$): 720.26321. Found: 720.26441.

**(2*R*)-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 × 40 mL), dried ($Na_2SO_4$), 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. $[\alpha]_D^{20} = -22.3$ ($c = 1.0$, $CHCl_3$); $^1$H NMR ($CD_3OD$): $\delta$ 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-C$H_2$O), 4.26–4.10 (3H, m, H-6′a, H-6′b, Fmoc-C*H*), 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, $COCH_3$), 2.05 (3H, s, $COCH_3$), 2.00 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$). $^{13}$C NMR ($CD_3OD$): $\delta$ 173.13, 172.37, 171.85, 171.22, 171.06 (*C*O$CH_3$, 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-*C*H$_2$O), 63.22 (C-6′), 48.43 (Fmoc-*C*H), 46.28 (C-2), 39.79 (C-3), 20.65, 20.62, 20.52 (CO*C*H$_3$). HRMS (ESI) Calcd for $C_{32}H_{34}NO_{13}Na_2$ ($[M - H + 2Na]^+$): 686.18255. Found: 686.18287.

**(2*S*)-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); $[\alpha]_D^{20} = -15.8$ ($c = 1.01$, $CHCl_3$); $^1$H NMR ($CD_3OD$): $\delta$ 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-C$H_2$O, Fmoc-C*H*, 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, $COCH_3$), 2.03 (3H, s, $COCH_3$), 1.99 (3H, s, $COCH_3$). $^{13}$C NMR ($CD_3OD$): $\delta$ 174.54, 172.34, 171.76, 171.24, 171.21 (*C*O$CH_3$, 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-*C*H$_2$O), 63.34 (C-6′), 48.37 (Fmoc-*C*H), 47.88 (C-2), 39.50 (C-3), 20.64 (CO*C*H$_3$). ESI-MS Calcd for $C_{32}H_{35}NO_{13}Na$ ($[M + Na]^+$): 664.20. Found: 664.22. Anal. Found: C, 59.12; H, 5.58; N, 2.21%. Calcd for $C_{33}H_{39}NO_{14}$: C, 58.84; H, 5.84; N, 2.08%.

**(2*R*)-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%. $[\alpha]_D^{20} = -12.0$ ($c = 1.00$, $CHCl_3$); $^1$H NMR ($CD_3OD$): $\delta$ 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-C$H_2$O), 4.25 (1H, t, $J = 6.1$ Hz, Fmoc-C*H*), 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, $COCH_3$), 2.05 (3H, s, $COCH_3$), 2.01 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$). $^{13}$C NMR ($CD_3OD$): $\delta$ 173.41, 172.16, 172.10, 171.68, 171.27 (*C*O$CH_3$, COOH), 158.70 (NHCO), 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-*C*H$_2$O), 62.64 (C-6′), 48.43 (Fmoc-*C*H), 46.67 (C-2), 39.83 (C-3), 20.77, 20.59, 20.52 (*C*O$CH_3$). HRMS (ESI) Calcd for $C_{32}H_{34}NO_{13}Na_2$ ($[M - H + 2Na]^+$): 686.18255. Found for: 686.18184.

**(2*S*)-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%. $[\alpha]_D^{20} = -0.02$ ($c = 0.981$, $CHCl_3$); $^1$H NMR ($CD_3OD$): $\delta$ 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-C$H_2$O), 4.26 (1H, t, $J = 6.7$ Hz, Fmoc-C*H*), 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, $COCH_3$), 2.05 (3H, s, $COCH_3$), 2.04 (3H, s, $COCH_3$), 1.97 (3H, s, $COCH_3$). $^{13}$C NMR ($CD_3OD$): $\delta$ 174.70, 172.15, 172.02, 171.56, 171.47 (*C*O$CH_3$, *C*OOBu$^t$), 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-$CH_2O$), 62.69 (C-6′), 48.39 (Fmoc-*C*H), 47.95 (C-2), 39.55 (C-3), 20.73, 20.56 ($COCH_3$). HRMS (ESI) Calcd for $C_{32}H_{34}NO_{13}Na_2$ ($[M - H + 2Na]^+$): 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).

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