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Note

A general route to pendant *C*-glycosyl 1,2- and 1,3-diamines

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Abstract—Practical and convenient preparations of *C*-glycosyl 1,2- and 1,3-alkanediamines are described. Two 1,2-ethylenediamine derivatives were synthesized from acetylated allyl α-*C*-glycosyl compounds via dibromination, azidation, carbohydrate deprotection, and azide reduction. Four 1,3-propanediamine derivatives were prepared from acetylated sugar halides via C-glycosylation with sodiomalononitrile, followed by the reduction of the nitrile moieties and the deacetylation of the carbohydrate moiety. These 1,3-propanediamine derivatives have the β-anomeric configurations. The methods reported here serve as general routes to access carbohydrate–diamine conjugates with *C*-glycosyl linkages.

Keywords: *C*-Glycosyl compounds; Diamines; Branched *C*-glycosyl diamines

O-Glycoside bonds are used extensively in nature to connect carbohydrates to proteins, other sugars, or other small molecules.[1,2] Synthetic methodologies for O-glycoside formation have been extensively developed, and thus most reported carbohydrate derivatives with an attached functional moiety contain an *O*-glycosyl linkage.[3–11] However, the O-glycosides are known to be susceptible to enzymatic degradation, and in addition, decompose under certain chemical conditions. In this context, S-glycosides or *C*-glycosyl bonds have also been studied as a more robust, nonbiodegradable linkage for carbohydrates.[12–17]

In this paper, facile routes for the coupling of 1,2- and 1,3-diamines to carbohydrate moieties via a *C*-glycosyl linkage are reported (Chart 1). Diamines are highly versatile functional group, which have been used in acid–base catalysis,[18,19] as molecular recognition devices,[20,21] as metal-chelating moieties,[22–24] and as functional groups in the synthesis of macrocycles[20,21,23] and other larger molecules.[25] The present paper provides details of the scope and limitations of synthetic routes to sugar-pendant diamines with a stable, glycosidase-resistant *C*-glycosyl linkage. Part of this work has been reported.[26]

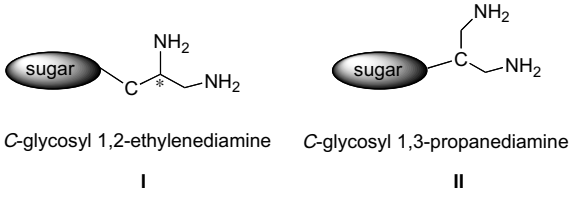

Chart 1.

Starting from the α-allyl *C*-D-gluco- (**1**) or D-galacto-pyranosyl derivatives (**6**),[27–29] diastereomeric mixtures of sugar-pendant 1,2-ethylenediamine derivatives (Chart 1, **I**) were prepared in 88 and 84% yields, respectively, over four steps via dibromination, azidation, carbohydrate deprotection, and azide reduction (Scheme 1). Initial dibromination generates an asymmetric carbon atom at C-2 in the side chain, and the following azide displacement was carried out using diastereomeric mixtures of dibromides. Repeated recrystallization of azide

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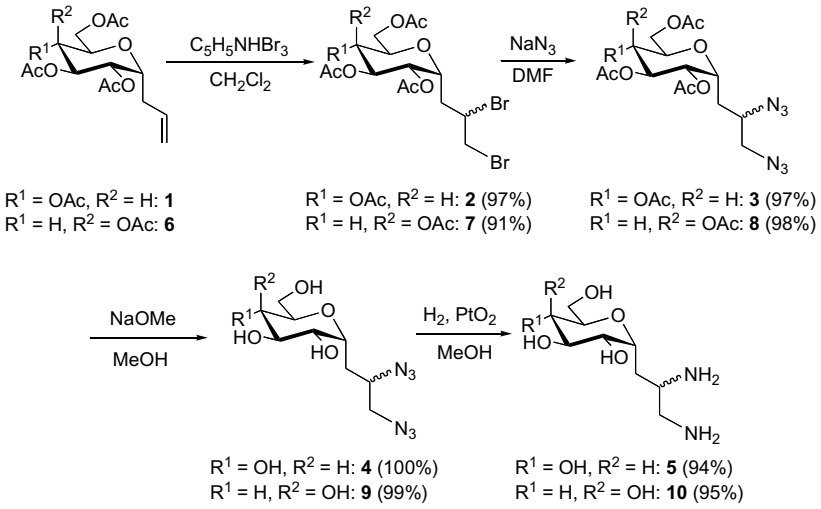


Scheme 1.

3 from ethanol increased the diastereomeric ratio to 24:1 as seen from ^{1}H NMR spectroscopy; however, the recovery was only 5%. X-ray crystallography of this material **3** exhibits very large thermal ellipsoids for the nitrogen atoms in the side chain (Fig. 1), and this disorder is likely caused by the presence of the minor diastereomer in the crystal lattice. We assigned the absolute configuration of the major isomer as (*R*)-**3** based on this crystal structure. All other trials for the separation of the diastereomers were unsuccessful.

As an alternative approach to prepare both the ethylenediamines with a *C*-glycosyl linkage in diastereomerically-pure form, a diastereomeric mixture of diazido compound **3** was converted to Boc-protected amine **11** and separated into diastereomers by silica gel column chromatography and HPLC to obtain a considerable amount of compound **12** (Scheme 2). Deprotection of the separated diastereomers (*R*)-**11** and (*S*)-**11** by refluxing in 6 N HCl afforded the hydrochloride salts of (*R*)-**5** and (*S*)-**5** without loss of diastereomeric purity (Scheme 2). The absolute configurations of these compounds were unambiguously assigned from the comparison of their ^{1}H NMR spectra with that of (*R*)-**5** as shown in Figure 2.

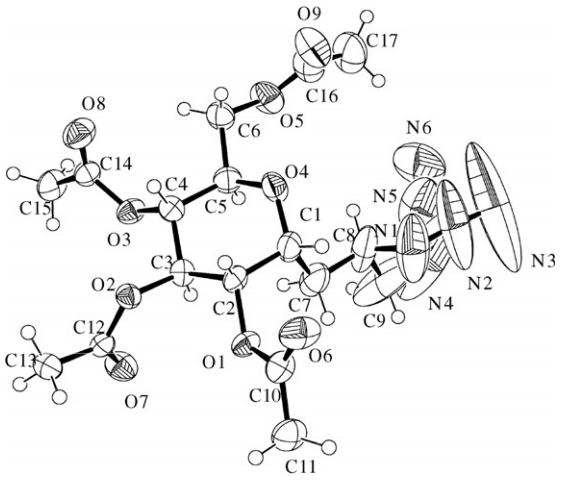
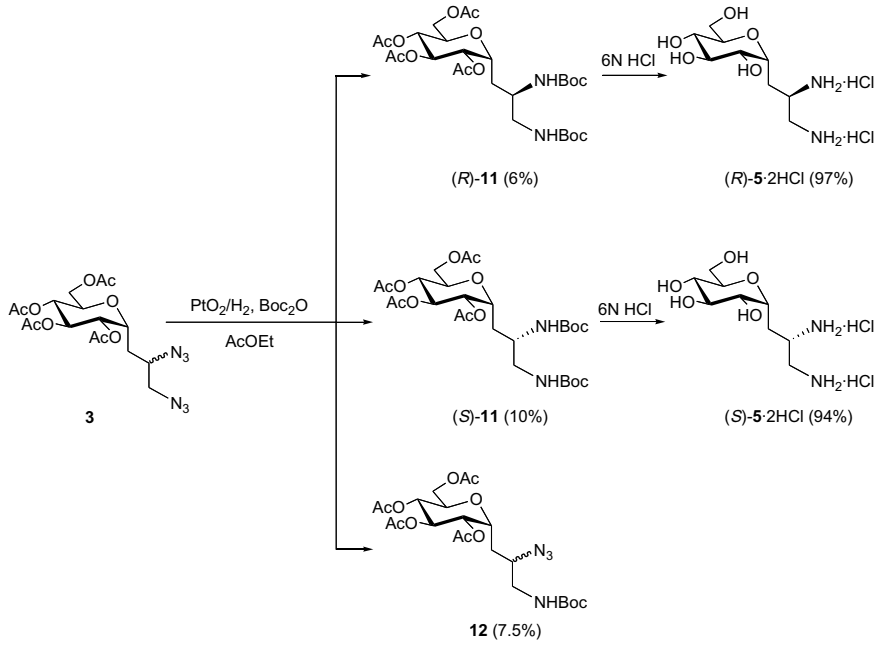


Figure 1. ORTEP plot for (*R*)-**3** at 50% probability level.

In similarity to our previous results with O-glycosides,[9] the diastereomeric separation of 1,2-diamines is not straightforward even in the presence of chirality at the sugar moiety. Practically, the present set of *C*-glycosyl 1,2-ethylenediamines is better used as a diastereomeric mixture for initial assays. If interesting properties come out, the preparation of diastereomerically-pure materials could be undertaken. After this point, the preparation of 'diastereomer-free' 1,3-propanediamine derivatives is described.

Changing the target skeleton from 2-substituted 1,2-ethylenediamines into 2-substituted 1,3-propanediamines eliminates the generation of an asymmetric center on the diamine backbone during the synthesis (Chart 1, **II**).[9] Such 1,3-propanediamine derivatives with *C*-glycosyl linkages were synthesized for D-glucose, D-galactose, D-xylose, and 2-amino-2-deoxy-D-glucose derivatives according to Scheme 3. The key step is the initial nucleophilic β-*C*-glycosyl bond formation with sodiomalononitrile from α-acetohalopyranoses derivatives **13**, **17**, **21**, and **25**. All products **14**,[26] **18**,[26] **22** (Fig. 3), and **26** (Fig. 4) afforded single crystals suitable for X-ray analysis. The resulting two nitrile moieties were hydrogenated to give 1,3-propanediamines and the carbohydrate moiety was deprotected with hydrochloric acid to give *C*-glycosyl 1,3-diaminopropane compounds **16**, **20**, **24**, and **28**. Compared to the corresponding O-glycosides[9] which decompose upon treatment with hydrochloric acid under the present deacetylation conditions, the *C*-glycosyl diamines prepared in this study exhibit considerable robustness. All steps proceeded in moderate to high yield and no sub-



Scheme 2.

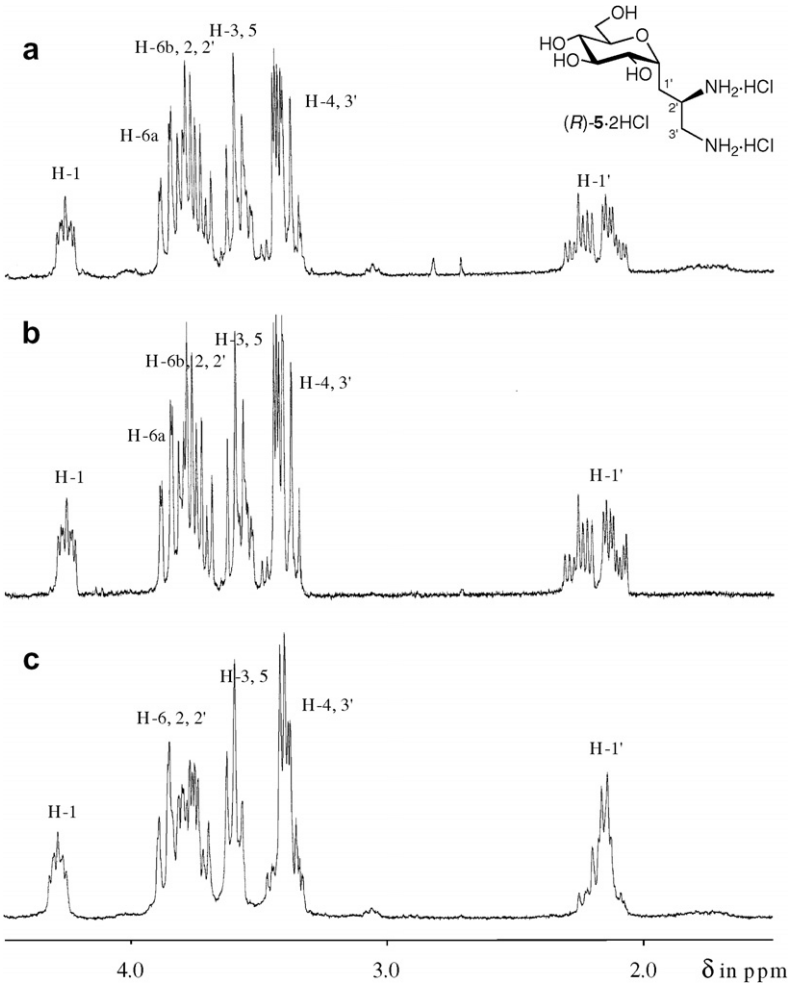
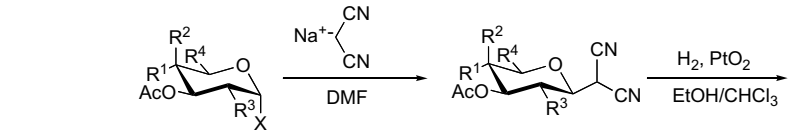


Figure 2. Comparison of ^{1}H NMR spectra for **5**·2HCl in D_2O. (a) (*R*)-**5**·2HCl prepared from (*R*)-**3**. (b) **5**·2HCl prepared from one of two diastereomers of **11**. (c) **5**·2HCl from the other diastereomer of **11**.



R^1 = OAc, R^2 = H, R^3 = OAc, R^4 = CH_2OAc, X = Br: **13**
R^1 = H, R^2 = OAc, R^3 = OAc, R^4 = CH_2OAc, X = Br: **17**
R^1 = OAc, R^2 = H, R^3 = OAc, R^4 = H, X = Br: **21**
R^1 = OAc, R^2 = H, R^3 = NHAc, R^4 = CH_2OAc, X = Cl: **25**

R^1 = OAc, R^2 = H, R^3 = OAc, R^4 = CH_2OAc: **14** (52%)
R^1 = H, R^2 = OAc, R^3 = OAc, R^4 = CH_2OAc: **18** (34%)
R^1 = OAc, R^2 = H, R^3 = OAc, R^4 = H: **22** (17%)
R^1 = OAc, R^2 = H, R^3 = NHAc, R^4 = CH_2OAc: **26** (21%)

R^1 = OAc, R^2 = H, R^3 = OAc, R^4 = CH_2OAc: **15**·2HCl (96%)
R^1 = H, R^2 = OAc, R^3 = OAc, R^4 = CH_2OAc: **19**·2HCl (100%)
R^1 = OAc, R^2 = H, R^3 = OAc, R^4 = H: **23**·2HCl (100%)
R^1 = OAc, R^2 = H, R^3 = NHAc, R^4 = CH_2OAc: **27**·2HCl (98%)

R^1 = OH, R^2 = H, R^3 = OH, R^4 = CH_2OH: **16**·2HCl (84%)
R^1 = H, R^2 = OH, R^3 = OH, R^4 = CH_2OH: **20**·2HCl (93%)
R^1 = OH, R^2 = H, R^3 = OH, R^4 = H: **24**·2HCl (100%)
R^1 = OH, R^2 = H, R^3 = NH_2·HCl, R^4 = CH_2OH: **28**·3HCl (100%)

Scheme 3.

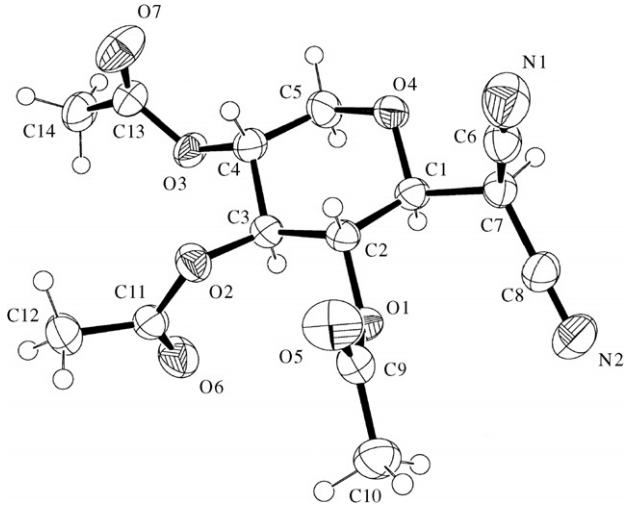


Figure 3. ORTEP plot for **22** at 50% probability level.

stantial amount of byproduct was formed except for the reaction of acetobromogalactose with an excess of sodiomalononitrile, where the 1:2 adduct **29** (Chart 2) was isolated in 14% yield. The present three-step synthesis offers a practical pathway for access to *C*-glycosyl-linked 1,3-propanediamines.

The glucose and glucosamine derivatives **16** and **28** were successfully characterized by X-ray crystallography (Figs. 5 and 6). The pyranose ring is puckered, adopting a $^4C_1$ chair conformation as evidenced by X-ray crystal-

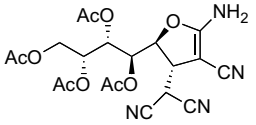


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Chart 2.

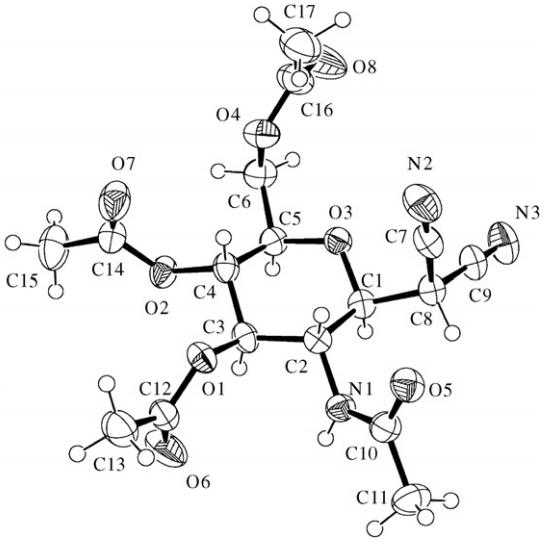

Figure 4. ORTEP plot for **26** at 50% probability level.

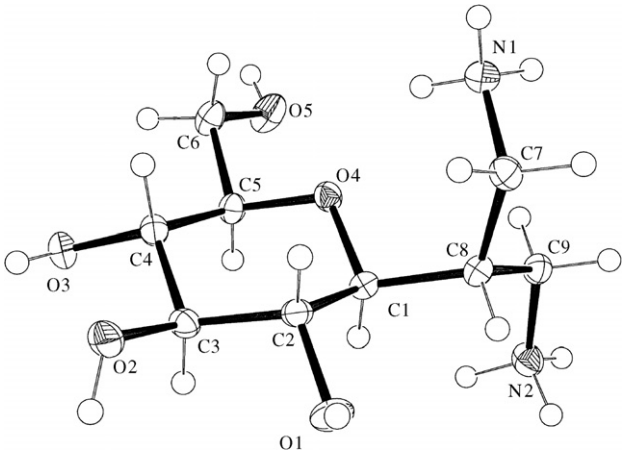

Figure 5. ORTEP plot for cationic portion of **16**·2HCl at 50% probability level.

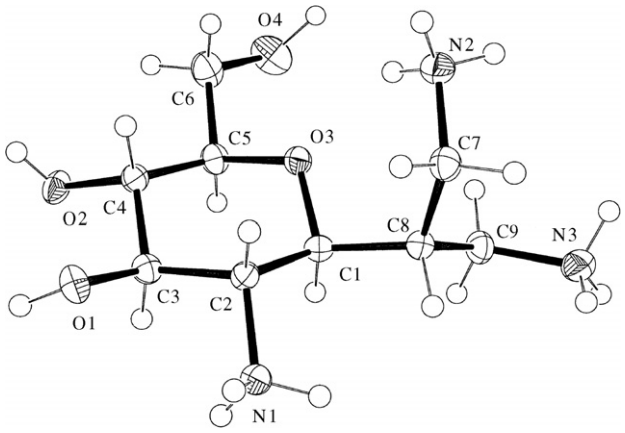

Figure 6. ORTEP plot for cationic portion of **28**·3HCl·H_2O at 50% probability level.

lography and ^1H–^1H coupling constants for **14** and **26**. Superior crystallizing ability of these simple sugar compounds provides significant advantages for the investigation of carbohydrate-functionalized materials. Also, the present synthetic strategy could be applied to a wide variety of sugar derivatives where an OH-protected anomeric halide is available.

In summary, two efficient, short-step syntheses to access *C*-glycosyl 1,2- and 1,3-diamines have been investigated. All transformations were achieved in moderate to high yield. The processes were simple and applicable to a diverse range of *C*-glycosyl diamines. For the 1,2-ethylenediamine derivatives, separation of the diastereomeric mixture proved difficult; however, it could be achieved by further transformations of the amine moiety as exemplified by the Boc-modified glucose derivatives. The preparation of 1,3-propanediamine derivatives does not require chromatography and exhibits sufficient yields for all steps. In addition, no stereogenic center is formed during preparation, eliminating the need for diastereomer separation. These efficient side-chain transformations provide a convenient preparative route to *C*-glycosyl diamines with pendant nature.

1. Experimental

1.1. General methods and materials

DMF (Wako Pure Chemicals, Inc.) was dried over $CaSO_4$ overnight and distilled under diminished pressure. All other reagents and solvents were from commercial sources and used as received. ^1H NMR (300 or 800 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded on a Varian GEMINI 2000 or Brucker AVANCE 800 spectrometer and referenced to internal TMS or solvent signals.

1.2. 1-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3-dibromopropane (2)

To a CH_2Cl_2 soln (50 mL) of 3-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)propene[27,28] (**1**) (1.12 g, 3.00 mmol) was added pyridinium bromide perbromide (1.45 g, 4.53 mmol) by portions. The reaction was monitored by ^1H NMR spectroscopy and after completion, 2% aq $Na_2S_2O_3$ (50 mL) was added and the soln was extracted twice with ether. The combined organic layers were washed with 1 N HCl, saturated sodium hydrogen carbonate, water, and brine, and then dried over sodium sulfate. Evaporation of the solvent gave **2** (1.55 g, 2.91 mmol, 97%), as a colorless solid. ^1H NMR ($CDCl_3$, 800 MHz): δ (ppm) diastereomer A, 5.25 (1H, dd, $J_{2,3}$ 9.2, $J_{3,4}$ 8.7 Hz, H-3), 5.16 (1H, dd, $J_{1,2}$ 5.7 Hz, H-2), 5.00 (1H, dd, $J_{4,5}$ 9.0 Hz, H-4), 4.50 (1H, ddd, $J_{1,1'a}$ 11.8, $J_{1,1'b}$ 2.4 Hz, H-1), 4.24 (1H, m, H-2′), 4.22 (1H, dd, $J_{5,6a}$ 5.6, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.14 (1H, m, H-6b), 3.95 (1H, dd, $J_{2',3'a}$ 3.9, $J_{3'a,3'b}$ 10.6 Hz, H-3′a), 3.86 (1H, m, H-5), 3.66 (1H, dd, $J_{2',3'b}$ 10.4 Hz, H-3′b), 2.76 (1H, ddd, $J_{1'a,1'b}$ 15.7, $J_{1'a,2'}$ 1.9 Hz, H-1′a), 2.00–2.10 (24H, acetyl), 1.80 (1H, ddd, $J_{1'b,2'}$ 11.2 Hz, H-1′b); diastereomer B, 5.24 (1H, dd, $J_{2,3}$ 9.3, $J_{3,4}$ 8.7 Hz, H-3), 5.10 (1H, dd, $J_{1,2}$ 5.7 Hz, H-2), 5.03 (1H, dd, $J_{4,5}$ 9.2 Hz, H-4), 4.56 (1H, ddd, $J_{1,1'a}$ 9.5, $J_{1,1'b}$ 3.1 Hz, H-1), 4.34 (1H, m, H-2′), 4.28 (1H, dd, $J_{5,6a}$ 4.8, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.14 (1H, m, H-6b), 4.02 (1H, ddd, $J_{5,6b}$ 2.6 Hz, H-5), 3.84–3.87 (1H, m, H-3′a), 3.82 (1H, dd, $J_{2'3'b}$ 9.7, $J_{3'a,3'b}$ 10.3 Hz, H-3′b), 2.51 (1H, ddd, $J_{1'a,1'b}$ 15.7, $J_{1'a,2'}$ 5.1 Hz, H-1′a), 2.32 (1H, dd, $J_{1'b,2'}$ 5.1 Hz, H-1′b), 2.00–2.10 (24H, acetyl). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) both diastereomers, 170.80, 170.75, 170.16, 169.65, 169.58, 70.72, 70.30, 70.12, 69.99, 69.54, 69.44, 69.33, 68.26, 68.15, 62.03, 61.87, 48.31, 46.89, 35.87, 35.43, 32.47, 30.35, 20.61, 20.53. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{25}O_9Br_2$, 530.9860; found, 530.9850. Anal. Calcd for $C_{17}H_{24}O_9Br_2$: H, 4.55; C, 38.37. Found: H, 4.35; C, 38.32.

1.3. 1-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3-diazidopropane (3)

Compound **2** (1.53 g, 2.87 mmol) was reacted with sodium azide (1.87 g, 28.7 mmol) in DMF (22.5 mL) at 70 °C for 3 h. The product was extracted with EtOAc and washed with water and brine. The organic layer was dried and evaporated to afford **3** (1.27 g, 2.79 mmol, 97%) as a colorless crystalline product. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.21–5.28 (m, H-3), 5.04–5.11 (m, H-2), 4.94–5.00 (m, H-4), 4.24–4.37 (m, H-1, H-6), 4.07–4.16 (m, H-6), 3.96 (m, H-5), 3.88 (m, H-5), 3.67 (br, H-2′), 3.41–3.53 (m, H-3′), 2.27 (s, acetyl), 2.11 (s, acetyl), 2.08 (s, acetyl), 2.06 (s, acetyl), 2.05 (s, acetyl), 1.76–1.81 (m, H-1′), 1.51–1.56 (m, H-1′). ^{13}C

NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.71, 170.00, 169.61, 169.58, 169.55, 69.72, 69.64, 69.59, 69.54, 69.33, 68.68, 68.17, 62.02, 61.90, 59.15, 58.04, 54.98, 53.88, 28.10, 27.43, 20.45. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{24}N_6O_9$, 457.1678; found, 457.1671. Anal. Calcd for $C_{17}H_{25}N_6O_9{\cdot}CH_3COOC_2H_5{\cdot}\ 0.5H_2O$: H, 5.74; C, 44.79; N, 16.50. Found: H, 5.21; C, 45.20; N, 16.11.

Crystal data for (*R*)-**3**: formula $C_{17}H_{24}N_6O_9$, monoclinic, space group $P2_1$, $a = 5.559(2)$, $b = 14.523(6)$, $c = 13.463(5)$ Å, $\beta = 98.1450(15)°$, $V = 1076.0(7)$ Å^3, $Z = 2$, $T = -100$ °C, 3283 data collected, 2480 data with $I > 2\sigma(I)$. $R = 0.0788$, R_w^2 (all data) = 0.2539, GOF = 1.057.

1.4. 1-(α-D-Glucopyranosyl)-2,3-diazidopropane (4)

Compound **3** (584 mg, 1.28 mmol) in MeOH was reacted with sodium methoxide at room temperature for 1 h, neutralized with Dowex, and concentrated to give 368 mg (1.28 mmol) of **4** in quantitative yield as a colorless syrup. ^{1}H NMR (D_2O, 300 MHz): δ (ppm): 4.9, 4.12–4.28, 3.20–3.88, 1.86–2.08, 1.76–1.80. ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 73.34, 73.09, 72.97, 72.42, 70.77, 70.58, 69.99, 60.82, 59.84, 58.12, 54.56, 53.57, 25.89. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_9H_{17}N_6O_5$, 289.1255; found, 289.1261.

1.5. 1-(α-D-Glucopyranosyl)-2,3-diaminopropane (5)

Compound **4** (368 mg, 1.28 mmol), dissolved in MeOH, was hydrogenated in the presence of PtO_2 (50 mg, 0.22 mmol) under an atmospheric pressure of hydrogen to give 282 mg (1.20 mmol) of **5** (94% yield) as a white powder. ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 4.12–4.28, 3.97–4.04, 3.80–3.88, 3.48–3.78, 3.35, 2.82–2.98, 2.72, 2.48–2.62, 2.0–2.3. ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 74.56, 73.18, 73.02, 72.84, 72.75, 72.58, 70.92, 70.87, 70.32, 70.27, 60.97, 61.02, 50.39, 48.30, 47.04, 45.60, 28.54, 27.96. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_9H_{21}N_2O_5$, 237.1455; found, 237.1452.

1.6. 1-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-2,3-dibromopropane (7)

A method similar to the preparation of **2** using 3-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)propene[27–29] (**6**, 1.14 g, 3.06 mmol) in place of **1** afforded **7** (1.45 g, 2.72 mmol, 91%) as a colorless syrup. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.44, 5.24–5.36, 5.02–5.20, 4.48–4.62, 4.03–4.40, 3.76–3.98, 3.65, 3.48, 2.60–2.72, 2.2–2.5, 2.0–2.1 (acetyl). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.58, 170.16, 170.07, 170.02, 169.94, 169.87, 169.74, 169.70, 69.91, 69.54, 69.30, 68.76, 67.97, 67.71, 67.60, 67.24, 67.15, 67.03, 66.94, 61.34, 60.84, 48.43, 47.43, 35.94, 35.61, 32.85, 31.24, 20.53. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{25}O_9Br_2$, 530.9860; found, 530.9853. Anal. Calcd for $C_{17}H_{24}O_9Br_2{\cdot}H_2O$: H, 4.76; C, 37.11. Found: H, 4.30; C, 37.11.

1.7. 1-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-2,3-diazidopropane (8)

A method similar to the preparation of **3** using **7** (1.44 g, 2.71 mmol) in place of **2** afforded compound **8** (1.21 g, 2.65 mmol, 98%) as a syrup. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.42, 5.14–5.26, 4.98–5.14, 4.30–4.44, 4.02–4.20, 3.84–3.95, 3.62–3.76, 3.36–3.54, 2.00–2.18. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.63, 169.92, 169.87, 169.74, 169.71, 169.63, 69.23, 69.15, 68.21, 68.09, 67.66, 67.49, 66.86, 66.76, 60.92, 60.74, 59.07, 58.43, 54.98, 53.83, 28.77, 28.19, 20.42, 20.39. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{25}N_6O_9$, 457.1678; found, 457.1669.

1.8. 1-(α-D-Galactopyranosyl)-2,3-diazidopropane (9)

A method similar to the preparation of **4** using **8** (581 mg, 1.27 mmol) in place of **3** afforded compound **9** (364 mg, 1.26 mmol, 99%) as a syrup. ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 4.15–4.32, 3.90–4.08, 3.55–3.90, 3.37–3.55, 1.85–2.10. ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 72.70, 72.08, 69.43, 68.90, 68.77, 67.80, 67.65, 61.00, 60.76, 59.61, 58.31, 54.64, 53.51, 25.87, 25.71. HRESIMS (*m*/*z*): $(M+Na)^+$ calcd for $C_9H_{16}N_6O_5Na$, 311.10799; found, 311.10862.

1.9. 1-(α-D-Galactopyranosyl)-2,3-diaminopropane (10)

A method similar to the preparation of **5** using **9** (360 mg, 1.25 mmol) in place of **4** afforded compound **10** (285 mg, 1.20 mmol, 95%) as a powder. ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 4.14–4.28, 3.94–4.03, 3.56–3.87, 3.36–3.41, 3.14–3.26, 2.98–3.14, 2.83–2.94, 2.72, 2.49–2.60, 1.87–1.95. ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 74.14, 72.08, 71.94, 69.61, 69.51, 69.06, 68.91, 67.96, 61.14, 61.00, 50.43, 48.40, 47.00, 45.68, 28.36, 27.98. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_9H_{21}N_2O_5$, 237.1455; found, 237.1447.

1.10. *N*,*N*′-Di-*tert*-butoxycarbonyl-1-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3-diaminopropane (11)

To a soln of compound **3** (456 mg, 1.0 mmol) in EtOAc (40 mL) were added Boc_2O (546 mg, 2.5 mmol) and PtO_2 (30 mg). The mixture was hydrogenated under atmospheric pressure of H_2 with vigorous stirring at room temperature. After 8 h, PtO_2 (10 mg) was added and further hydrogenated for 21 h. After the reaction completion, Celite powder was added to the reaction mixture and filtered, concentrated, and the residue was purified by silica gel column chromatography (1:1 hexane–EtOAc) to give (*R*)-*N*,*N*′-bis(*tert*-butoxycarbonyl)-

1-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3-diaminopropane ((*R*)-**11**) (65 mg, 0.11 mmol, 11%, 96% de), (*S*)-**11** (100 mg, 0.17 mmol, 17%, 92% de), and diastereomer mixture of *N*-*tert*-butoxycarbonyl-1-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-2-azido-3-aminopropane **12** (42 mg, 0.075 mmol, 7.5%). Compounds were further purified by HPLC (column: Kanto Chemical Co. Inc., Mightysil RP-18 250-20 (5 μm) Cica Reagent; eluent: 7:3 MeOH–water).

(*R*)-**11**: solid ($R_f = 0.25$, 1:1 hexane–EtOAc): mp 94–96 °C; $[\alpha]_D^{25}$ +50.4 (*c* 1.3, MeOH); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.18 (1H, dd, $J_{2,3}$ 8.1, $J_{3,4}$ 8.1 Hz, H-3), 4.91–5.01 (3H, m, H-2, H-4, NH), 4.27–4.33 (2H, m, H-1, H-6a), 4.11–4.16 (1H, m, H-6b), 3.93 (1H, br, H-5), 3.72 (1H, br, H-2′), 3.27 (2H, m, H-3′), 2.12 (3H, s, acetyl), 2.08 (3H, s, acetyl), 2.05 (6H, s, acetyl), 1.89–2.00 (1H, m, H-1a′), 1.65–1.72 (1H, m, H-1b′), 1.44 (9H, s, *t*-Bu), 1.43 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.65, 168.74, 169.57, 169.45, 156.45, 155.70, 79.52, 69.65 (C-2, C-3, C-5), 68.85 (C-1), 68.17 (C-4), 61.94 (C-6), 48.77 (C-2′), 44.03 (C-3′), 28.33, 28.25, 20.69, 20.61. HRESIMS (*m*/*z*): $(M+Na)^+$ calcd for $C_{27}H_{44}N_2O_{13}Na$, 627.2744; found, 627.2736. Anal. Calcd for $C_{27}H_{44}N_2O_{13}$: C, 53.63; H, 7.33; N, 4.63. Found: C, 54.23; H, 7.50; N, 4.07.

(*S*)-**11**: solid ($R_f = 0.30$, 1:1 hexane–EtOAc): mp 104–105 °C; $[\alpha]_D^{25}$ +45.4 (*c* 0.931, MeOH); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.27 (1H, dd, $J_{2,3}$ 9.2, $J_{3,4}$ 8.7 Hz, H-3), 5.07 (1H, dd, $J_{1,2}$ 5.7 Hz, H-2), 4.94 (1H, dd, $J_{4,5}$ 8.7 Hz, H-4), 4.82 (1H, br, NH), 4.35 (1H, m, H-1), 4.27 (1H, dd, $J_{5,6a}$ 5.2, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.14 (1H, dd, $J_{5,6a}$ 2.8 Hz, H-6b), 3.98 (1H, m, H-5), 3.77 (1H, br, H-2′), 3.22 (2H, br, H-3′), 2.10 (3H, s, acetyl), 2.06 (3H, s, acetyl), 2.04 (3H, s, acetyl), 2.03 (3H, s, acetyl), 1.89–1.99 (1H, m H-1a′), 1.73–1.74 (1H, m, H-1b′), 1.43 (18H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.65, 168.95, 169.53, 169.48, 156.73, 155.60, 79.59, 79.35, 70.08 (C-3), 69.82 (C-2), 69.40 (C-5, C-1), 68.30 (C-4), 61.99 (C-6), 48.65 (C-2′), 43.12 (C-3′), 28.72 (C-1′), 28.72, 28.33, 28.20, 20.63, 20.60. HRESIMS (*m*/*z*): $(M+Na)^+$ calcd for $C_{27}H_{44}N_2O_{13}Na$, 627.2744; found, 627.2753. Anal. Calcd for $C_{27}H_{44}N_2O_{13}$: C, 53.63; H, 7.33; N, 4.63. Found: C, 53.97; H, 7.42; N, 4.19.

Compound **12**: powder (2:1 diastereomeric mixture) ($R_f = 0.35$, 1:1 hexane–EtOAc) ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.23 (1H, H-3), 5.13–5.04 (1H, m, H-2), 4.98 (1H, H-2), 4.90 (1H, br, NH), 4.38 (1H, m, H-1), 4.27 (1H, H-6), 4.12 (1H, m, H-6), 3.98 (m, H-5 for diastereomer A), 3.85 (m, H-5 for diastereomer B), 3.73 (1H, br, H-2′), 3.81 (1H, m, H-3′), 3.23 (1H, m, H-3′), 2.10 (s, acetyl), 2.07 (s, acetyl), 2.05 (s, acetyl), 2.04 (s, acetyl), 1.96 (s, acetyl), 1.96 (1H, m, H-1′), 1.82 (1H, m, H-1′), 1.45 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.52, 169.81, 169.36, 155.70, 79.73, 69.85, 69.67, 69.4, 68.81, 68.23, 62.10, 58.26, 45.08, 43.69, 28.15, 27.46, 20.53. HRESIMS (*m*/*z*): $(M+Na)^+$ calcd for $C_{22}H_{34}N_4O_{11}Na$, 553.21218; found, 553.21187.

1.11. (*R*)-1-(α-D-Glucopyranosyl)-2,3-diaminopropane dihydrochloride ((*R*)-5·2HCl)

Compound (*R*)-**11** (217 mg, 0.36 mmol) was refluxed in 6 N HCl (30 mL) for 3 h. The reaction soln was evaporated to 1 mL and decolorized with active carbon. EtOH was added and the solvent was evaporated in vacuo to afford (*R*)-1-(α-D-glucopyranosyl)-2,3-diamino- propane dihydrochloride ((*R*)-**5**·2HCl) (109 mg, 0.35 mmol, 97%) as a colorless solid. $[\alpha]_D^{25}$ +69.3 (*c* 0.42, H_2O); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 4.26 (1H, m, H-1), 3.87 (1H, dd, $J_{5,6a}$ 2.4, $J_{6a,6b}$ 12.5 Hz, H-6a), 3.69–3.82 (3H, m, H-6b, H-2, H-2′), 3.54–3.63 (2H, m, H-3, H-5), 3.34–3.49 (3H, m, H-4, H-3′), 2.07–2.31 (2H, m, H-1′). ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 73.52 (C-5), 72.71 (C-3), 71.61 (C-1), 70.12 (C-2), 69.67, 70.12 (C-4), 60.79 (C-6), 47.31 (C-2′), 41.05 (C-3′), 26.08 (C-1′). HRESIMS (*m*/*z*): $(M+Na)^+$ calcd for $C_9H_{20}N_2O_5Na$, 259.1270; found, 259.1234.

1.12. (*S*)-1-(α-D-Glucopyranosyl)-2,3-diaminopropane dihydrochloride ((*S*)-5·2HCl)

A method similar to the preparation of (*R*)-**5**·2HCl using (*S*)-**11** (187 mg, 0.31 mmol) in place of (*R*)-**11** afforded compound (*S*)-**5**·2HCl (89 mg, 0.29 mmol, 94%) as a white powder. $[\alpha]_D^{25}$ +51.5 (*c* 0.33, H_2O); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 4.29 (1H, m, H-1), 3.70–3.89 (4H, m, H-6, H-2, H-2′), 3.60 (2H, m, H-5, H-3), 3.33–3.47 (3H, m, H-4, H-3′), 2.09–2.25 (2H, m, H-1′). ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 73.57 (C-5), 73.81 (C-1, C-3), 70.17 (C-2), 69.57 (C-4), 60.68 (C-6), 48.40 (C-2′), 40.48 (C-3′), 25.32 (C-1′). HRESIMS (*m*/*z*): $(M+Na)^+$ calcd for $C_9H_{20}N_2O_5Na$, 259.1270; found, 259.1255.

1.13. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-malononitrile (14)

To a DMF soln (20 mL) containing malononitrile (3.96 g, 60 mmol) was added NaH (2.8 g, 70 mmol) by portions. After gas evolution ceased, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**13**) (5.0 g, 12 mmol) in 10 mL of DMF was added dropwise at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then 10% aqueous AcOH (200 mL) was added and stirred overnight at room temperature. The precipitate was collected and dissolved in CH_2Cl_2, dried, evaporated, and recrystallized from hot MeOH to give **14** as white needles (2.47 g, 6.2 mmol, 52%). Mp 175–177 °C; $[\alpha]_D^{25}$ +2.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.29 (dd, $J_{2,3}$ 9.5, $J_{3,4}$ 9.2 Hz, H-3),

5.17 (dd, $J_{4,5}$ 9.5 Hz, H-4), 5.13 (dd, $J_{1,2}$ 9.2 Hz, H-2), 4.28 (dd, $J_{5,6a}$ 4.9, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.19 (dd, $J_{5,6b}$ 2.4 Hz, H-6b), 4.05 (d, $J_{1,\alpha}$ 4.3 Hz, H-α), 3.99 (dd, H-1), 3.84 (ddd, H-5), 2.113 (s, acetyl), 2.106 (s, acetyl), 2.06 (s, acetyl), 2.04 (s, acetyl). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.72, 170.24, 169.80, 169.36, 109.114, 76.43, 74.43, 72.86, 69.78, 67.46, 61.31, 26.59, 20.51, 20.36. HRESIMS (*m*/*z*): $(M-H)^-$ calcd for $C_{17}H_{19}N_2O_9$: 395.1096; found, 395.1095. Anal. Calcd for $C_{17}H_{20}N_2O_9$: H, 5.09; C, 51.52; N, 7.07. Found: H, 4.94; C, 51.37; N, 6.99. IR (KBr): 1732 (C=O) cm^{-1}.

1.14. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-1,3-diaminopropane dihydrochloride (15·2HCl)

Compound **14** (100 mg, 0.25 mmol) was hydrogenated with atmospheric pressure of H_2 in the presence of PtO_2 (30 mg) in ethanol (50 mL) and $CHCl_3$ (10 mL). After catalyst was filtered off, the solvent was removed to give compound **15**·2HCl as a white powder (115 mg, 0.24 mmol, 96%). $[\alpha]_D^{25}$ −5.36 (*c* 1.18, MeOH); ^{1}H NMR (CD_3OD, 300 MHz): δ (ppm) 5.31 (dd, $J_{2,3}$ 9.3, $J_{3,4}$ 9.3 Hz, H-3), 5.07–5.20 (m, H-2, H-4), 4.30 (dd, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.19 (dd, $J_{5,6b}$ 2.4 Hz, H-6b), 3.89–3.96 (m, H-1, H-5), 3.17–3.38 (m, H-β), 2.36 (br, H-α), 2.11 (s, acetyl), 2.07 (s, acetyl), 2.03 (s, acetyl), 2.00 (s, acetyl). ^{13}C NMR (CD_3OD, 75.5 MHz): δ (ppm) 173.27, 172.76, 172.28, 171.45, 77.52, 77.39, 75.11, 69.84, 69.47, 63.27, 39.57, 37.71, 36.35, 20.69, 20.46. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{29}N_2O_9$, 405.1867; found, 405.1864. IR (KBr): 1751 (C=O) cm^{-1}.

1.15. 2-(β-D-Glucopyranosyl)-1,3-diaminopropane dihydrochloride (16·2HCl)

Compound **15**·2HCl (234 mg, 0.59 mmol) was refluxed in 6 N HCl (60 mL) for 3 h. The reaction mixture was concentrated to 1 mL, and treated with activated carbon. Removal of the solvent by repeated co-evaporation with EtOH afforded **16**·2HCl (154 mg, 0.50 mmol, 84%) as a white powder. Recrystallization from water/EtOH afforded crystals. Mp 225–230 °C; $[\alpha]_D^{25}$ −0.121 (*c* −0.988, H_2O); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 3.82 (dd, $J_{5,6a}$ 1.8, $J_{6a,6b}$ 12.6 Hz, H-6a), 3.61–3.73 (m, H-6b, H-2), 3.24–3.52 (m, H-1, H-3, H-4, H-5, H-β), 2.62 (m, H-α). ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 81.08, 79.12, 78.36, 71.14, 70.40, 61.86, 39.64, 38.22, 36.26. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_9H_{21}N_2O_5$, 237.1455; found, 237.1452.

Crystal Data for **16**·2HCl: formula $C_9H_{22}Cl_2N_2O_5$, tetragonal, space group $P4_3$, $a = b = 8.4418(2)$, $c = 19.4455(7)$ Å, $V = 1385.76(7)$ Å^3, $Z = 4$, $T = -100$ °C, 3519 data collected, 3431 data with $I > 2\sigma(I)$. $R = 0.0307$, R_w^2 (all data) = 0.0741, GOF = 1.081.

1.16. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-malononitrile (18)

A method similar to the preparation of **14** using **17** (2.07 g, 5.03 mmol) in place of **13** afforded compound **18** (0.68 g, 1.70 mmol, 34%) as white needles. Compound **29** (0.325 g, 0.70 mmol, 14%) was also obtained.

Compound **18**: mp 158–161 °C; $[\alpha]_D^{25}$ +19.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 800 MHz): δ (ppm) 5.46 (dd, $J_{3,4}$ 3.3, $J_{4,5}$ 1.0 Hz, H-4), 5.35 (dd, $J_{1,2}$ 9.8, $J_{2,3}$ 10.8 Hz, H-2), 5.12 (dd, H-3), 4.21 (dd, $J_{5,6a}$ 6.9, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.13 (dd, $J_{5,6b}$ 6.1 Hz, H-6b), 4.07 (m, H-5), 4.05 (d, $J_{1,\alpha}$ 4.3 Hz, H-α), 3.96 (dd, H-1), 2.19 (s, acetyl), 2.13 (s, acetyl), 2.07 (s, acetyl), 2.01 (s, acetyl). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 70.53, 170.20, 170.11, 170.04, 110.05, 109.24, 74.96, 74.78, 70.97, 67.10, 66.68, 61.00, 26.86, 20.59, 20.47, 20.41, 20.34. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{21}N_2O_9$, 397.1242; found, 397.1238. Anal. Calcd for $C_{17}H_{20}N_2O_9$: H, 5.09; C, 51.52; N, 7.07. Found: H, 4.97; C, 51.42; N, 7.07.

Compound **29**: crystal, $[\alpha]_D^{25}$ −138 (*c* 0.505, MeOH); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.49 (dd, $J_{3,4}$ 9.3, $J_{4,5}$ 2.1 Hz, H-4), 5.43 (br, NH_2), 5.35 (m, H-5), 5.23 (dd, $J_{2,3}$ 1.4 Hz, H-3), 4.67 (dd, $J_{1,2}$ 3.8 Hz, H-2), 4.32 (dd, $J_{5,6a}$ 5.1, $J_{6a,6b}$ 11.7 Hz, H-6a), 3.97 (d, $J_{1,\alpha}$ 4.5 Hz, H-α), 3.87 (dd, $J_{5,6b}$ 7.4 Hz, H-6b), 3.62 (dd, H-1). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.69, 170.38, 169.99, 168.99, 115.84, 110.76, 110.42, 82.21, 81.89, 69.93, 69.56, 68.17, 67.97, 67.63, 67.31, 61.84, 50.95, 46.80, 46.50, 27.96, 27.77, 20.68, 20.38, 20.18. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{20}H_{23}N_4O_9$, 463.1460; found, 463.1452. Anal. Calcd for $C_{20}H_{22}N_4O_9$: H, 4.80; C, 51.95; N, 12.12. Found: H, 4.58; C, 51.71; N, 11.91.

1.17. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-1,3-diaminopropane dihydrochloride (19·2HCl)

A method similar to the preparation of **15**·2HCl using **18** (100 mg, 0.25 mmol) in place of **14** afforded compound **19**·2HCl (120 mg, 0.25 mmol, 100%) as a white powder. $[\alpha]_D^{25}$ +8.95 (*c* 1.03, MeOH); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 5.47 (s, H-4), 5.19–5.21 (m, H-2, H-3), 4.09–4.20 (m, H-5, H-6), 3.97 (1H, br, H-1), 3.16–3.39 (m, H-β), 2.41 (br, H-α), 2.15 (s, acetyl), 2.14 (s, acetyl), 2.05 (s, acetyl), 1.96 (s, acetyl). ^{13}C NMR (CD_3OD, 75.5 MHz): δ (ppm) 172.39, 171.68, 171.31, 77.18, 75.71, 72.81, 68.75, 66.91, 62.41, 39.16, 37.27, 36.11, 20.53, 20.35, 20.14. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{29}N_2O_9$, 405.1868; found, 405.1860.

1.18. 2-(β-D-Galactopyranosyl)-1,3-diaminopropane dihydrochloride (20·2HCl)

A method similar to the preparation of **16**·2HCl using **19**·2HCl (193 mg, 0.40 mmol) in place of **15**·2HCl affor-

ded compound **20**·2HCl (116 mg, 0.37 mmol, 93%) as a white powder. $[\alpha]_D^{25}$ + 22.9 (*c* 0.995, H_2O); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 3.99 (1H, dd), 3.64–3.75 (5H, m), 3.57 (1H, dd, *J* 9.0, 3.0 Hz), 3.27–3.45 (m, H-β), 2.64 (m, H-α). ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 80.37, 79.77, 75.03, 70.01, 68.56, 62.36, 39.77, 38.46, 36.26. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_9H_{21}N_2O_5$, 237.1455; found, 237.1470.

1.19. 2-(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)malononitrile (22)

A method similar to the preparation of **14** using **21** (3.4 g, 10 mmol) in place of **13** afforded compound **22** (560 mg, 1.7 mmol, 17%) as colorless crystals. Mp 139–143 °C; $[\alpha]_D^{25}$ −39.3 (*c* 0.999, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.28 (1H, dd, $J_{2,3}$ 9.5, $J_{3,4}$ 9.5 Hz, H-3), 5.10 (1H, dd, $J_{1,2}$ 9.8 Hz, H-2), 5.0–5.1 (1H, m, H-4), 4.29 (1H, dd, $J_{4,5a}$ 5.8, $J_{5a,5b}$ 11.3 Hz, H-5a), 4.02 (1H, d, $J_{1,\alpha}$ 4.0 Hz, H-α), 3.90 (1H, dd, H-1), 3.42 (1H, dd, $J_{4,5b}$ 10.7 Hz H-5b), 2.11 (3H, s, acetyl), 2.06 (6H, s, acetyl). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 170.07, 169.66, 169.53, 110.01, 109.17, 75.09, 72.45, 69.96, 68.04, 66.95, 26.65, 20.58, 20.53. Anal. Calcd for $C_{14}H_{16}N_2O_7$: H, 4.97; C, 51.85; N, 8.64. Found: H, 4.87; C, 51.86; N, 8.58.

Crystal data for **22**: formula $C_{14}H_{16}N_2O_7$, monoclinic, space group *C*2, $a = 21.316(9)$, $b = 6.842(3)$, $c = 10.788(4)$ Å, $\beta = 95.866(4)°$, $V = 1565.2(11)$ Å^3, $Z = 4$, $T = -100$ °C, 3343 data collected, 2850 data with $I > 2\sigma(I)$. $R = 0.0569$, R_w^2 (all data) = 0.0651, GOF = 1.087.

1.20. 2-(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-1,3-diaminopropane dihydrochloride (23·2HCl)

A method similar to the preparation of **15**·2HCl using **22** (81 mg, 0.25 mmol) in place of **14** afforded compound **23**·2HCl (101 mg, 0.25 mmol, 100%) as a white powder. $[\alpha]_D^{25}$ −37.4 (*c* 0.392, MeOH); ^{1}H NMR (CD_3OD, 300 MHz): δ (ppm) 5.28 (1H, dd, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0 Hz, H-3), 5.14 (1H, dd, $J_{1,2}$ 9.3 Hz, H-2), 5.0–5.1 (1H, m, H-4), 4.14 (1H, dd, $J_{4,5a}$ 5.4, $J_{5a,5b}$ 11.4 Hz, H-5a), 3.89 (1H, dd, *J* 10.2, 1.5 Hz, H-1), 3.51 (1H, dd, $J_{4,5b}$ 10.5 Hz, H-5b), 3.2–3.4 (1H, m, H-β), 2.3–2.5 (1H, m, H-α), 2.11 (3H, s, acetyl), 2.019 (3H, s, acetyl), 2.017 (3H, s, acetyl). ^{13}C NMR (CD_3OD, 75.5 MHz): δ (ppm) 172.06, 171.63, 171.47, 78.09, 74.86, 70.02, 69.99, 67.83, 39.63, 37.72, 36.19, 20.88, 20.60, 20.54. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{14}H_{25}N_2O_7$, 333.1661; found, 333.16174.

1.21. 2-(β-D-Xylopyranosyl)-1,3-diaminopropane dihydrochloride (24·2HCl)

A method similar to the preparation of **16**·2HCl using **23**·2HCl (88 mg, 0.22 mmol) in place of **15**·2HCl afforded compound **24**·2HCl (61 mg, 0.22 mmol, 100%) as a white powder. $[\alpha]_D^{25}$ −21.4 (*c* 1.61, MeOH); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 3.9–4.1 (2H, m), 3.2–3.8 (m), 2.5–2.7 (1H, m, H-α). ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 78.96, 77.39, 70.22, 69.27, 68.98, 38.74, 37.30, 35.16. HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_8H_{19}N_2O_4$, 207.1345; found, 207.13456.

1.22. 2-(2-Deoxy-2-acetamido-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)malononitrile (26)

A method similar to the preparation of **14** using **25** (1.83 g, 5.0 mmol) in place of **13** afforded compound **26** (417 mg, 1.05 mmol, 21%) as colorless needles. Mp 168–171 °C; $[\alpha]_D^{25}$ −10.8 (*c* 1.01, MeOH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.06 (1H, d, $J_{2,NH}$ 7.6 Hz, NH), 5.19 (1H, dd, $J_{2,3}$ 9.6, $J_{3,4}$ 9.5 Hz, H-3), 5.14 (1H, dd, $J_{3,4}$ 9.5, $J_{4,5}$ 9.5 Hz, H-4), 4.28 (1H, dd, $J_{5,6a}$ 4.8, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.21 (1H, dd, $J_{5,6b}$ 2.1 Hz, H-6b), 4.17 (1H, d, $J_{1,\alpha}$ 3.7 Hz, H-α), 4.08 (1H, ddd, $J_{1,2}$ 9.9 Hz, H-2), 3.97 (1H, dd, H-1), 3.81 (1H, ddd, H-5), 2.11 (3H, s, acetyl), 2.09 (3H, s, acetyl), 2.06 (3H, s, acetyl), 2.00 (3H, s, acetyl). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ (ppm) 171.80, 171.65, 170.65, 169.11 (*C*OCH$_3$), 110.91, 109.54 (*C*N), 76.27 (C-5), 76.02 (C-1), 72.39 (C-3), 67.54 (C-4), 61.53 (C-6), 53.15 (C-2), 27.38 (C-α), 23.09 (NHCO*C*H$_3$), 20.65, 20.60, 20.52 (CO*C*H$_3$). Anal. Calcd for $C_{17}H_{21}N_3O_8$: H, 5.35; C, 51.64; N, 10.63. Found: H, 5.38; C, 51.61; N, 10.56.

Crystal data for **26**: formula $C_{17}H_{21}N_3O_8$, orthorhombic, space group $P2_12_12_1$, $a = 8.959(2)$, $b = 11.584(3)$, $c = 19.234(5)$ Å, $V = 1996.2(8)$ Å^3, $Z = 4$, $T = -100$ °C, 4562 data collected, 3829 data with $I > 2\sigma(I)$. $R = 0.0307$, R_w^2 (all data) = 0.0741, GOF = 1.081.

1.23. 2-(2-Deoxy-2-acetamido-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-1,3-diaminopropane dihydrochloride (27·2HCl)

A method similar to the preparation of **15**·2HCl using **26** (79 mg, 0.20 mmol) in place of **14** afforded compound **27**·2HCl (93 mg, 0.19 mmol, 98%) as a white powder. $[\alpha]_D^{25}$ −12.5 (*c* 0.572, MeOH); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 5.26 (1H, dd, $J_{2,3}$ 8.7, $J_{3,4}$ 9.9 H-3), 5.10 (1H, dd, $J_{4,5}$ 9.5 Hz, H-4), 4.33 (2H, dd, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 12.8 Hz, H-6a), 4.23–4.29 (2H, m, H-6b, H-2), 3.96 (1H, m, H-5), 3.90 (1H, m, H-1), 3.33 (2H, m, H-β), 2.39 (1H, br, H-α), 2.12 (3H, s, acetyl), 2.09 (3H, s, acetyl), 2.07 (3H, s, acetyl), 2.00 (3H, s, acetyl). ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 174.78, 173.71, 173.16, 172.77 (*C*OCH$_3$), 77.50 (C-1), 75.12 (C-5), 73.81 (C-3), 68.43 (C-4), 62.20 (C-6), 49.96 (C-2), 38.78, 36.31 (C-β), 34.69 (C-α), 21.88, 20.15, 20.05, 19.93 (CO*C*H$_3$). HRESIMS (*m*/*z*): $(M+H)^+$ calcd for $C_{17}H_{30}N_3O_8$, 404.20329; found, 404.202094.

1.24. 2-(2-Deoxy-2-amino-β-D-glucopyranosyl)-1,3-diaminopropane trihydrochloride (28·3HCl)

A method similar to the preparation of **16**·2HCl using **27**·2HCl (56 mg, 0.12 mmol) in place of **15**·2HCl afforded compound **28**·3HCl (40 mg, 0.12 mmol, 100%) as colorless crystals. Mp 225–235 °C; $[\alpha]_D^{25}$ −14.4 (c 1.11, MeOH); ^{1}H NMR (D_2O, 300 MHz): δ (ppm) 4.03 (1H, H-1), 3.91 (1H, H-6a), 3.73 (1H, H-6b), 3.71 (1H, m, H-3), 3.50 (2H, m, H-5, H-2), 3.37–3.46 (6H, m, H-2, H-5, H-β), 2.58 (1H, m, H-α). ^{13}C NMR (D_2O, 75.5 MHz): δ (ppm) 80.11 (C-5), 75.24 (C-1), 73.20 (C-3), 69.23 (C-4), 60.40 (C-6), 51.91 (C-2), 38.36, 35.95 (C-β), 34.56 (C-α). HRESIMS (m/z): $(M+H)^+$ calcd for $C_9H_{22}N_3O_4$, 236.16103; found, 236.16346.

Crystal data for **28**·3HCl·H_2O: formula $C_9H_{26}Cl_3N_3O_5$, monoclinic, space group $P2_1$, $a = 8.271(2)$, $b = 8.057(2)$, $c = 12.393(3)$ Å, $\beta = 92.836(3)°$, $V = 824.8(4)$ Å^3, $Z = 2$, $T = -100$ °C, 3430 data collected, 3363 data with $I > 2\sigma(I)$. $R = 0.0407$, R_w^2 (all data) = 0.1181, GOF = 1.091.

1.25. X-ray crystallography

Single crystals of (*R*)-**3**, **16**·2HCl, **22**, **26**, and **28**·3HCl·H_2O were covered by paraffin oil and mounted on a glass fiber. All X-ray diffraction data were collected at 173 K on a Rigaku Mercury CCD detector, with monochromated MoKα radiation, operating at 50 kV/40 mA. Data were processed on a PC using CrystalClear Software (Rigaku). Structures were solved by direct methods (SIR-92) and refined by full-matrix least-squares methods on F^2 (SHELXS-97). The positions of hydrogen atoms were calculated and treated as a riding model. CCDC 651598 ((*R*)-**3**), 651599 (**16**·2HCl), 661308 (**22**), 661309 (**26**), and 661683 (**28**·3HCl·H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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