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Note

The use of tri-*O*-acetyl-D-glucal and -D-galactal in the synthesis of ω-aminoalkyl 2-deoxy- and 2,3-dideoxy-D-hexopyranosides

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ABSTRACT

We report a simple, efficient, and mild method for the synthesis of ω-aminoalkyl 2-deoxy-D-*arabino/lyxo*-hexopyranoside and 2,3-dideoxy-α-D-*erythro*-hexopyranoside. The total synthesis is accomplished in two sequential reactions. The first step consists of an addition reaction of *N*-(ω-hydroxyalkyl)phthalimide and *N*-(ω-hydroxyalkyl)succinimide to peracetylated D-glycals, which is promoted by triphenylphosphine hydrobromide or borontrifluoride/diethyl etherate. The second step involves reacting the appropriate glycoside with methylamine.

The cyclic imides of dicarboxylic acids are versatile tools for introducing an amino group into a target molecule; in particular, phthalimide is a useful reagent for preparing several amino-deoxysaccharides, and it can also be used to synthesize nucleosides bearing amino groups.[1–3] Cyclic imides themselves exhibit interesting pharmacological properties. Thus, succinimide derivatives are used as anticonvulsants to control seizures in the treatment of epilepsy. These medicines act on the central nervous system (CNS) to reduce the number and severity of seizures.[4–6] Phthalimide derivatives possess a broad spectrum of biological activity. The N-substituted phthalimides exhibit cytostatic,[7] anti-inflammatory,[8] and hypolipidemic[9] activities. *N*-Arylphthalimdes can lower serum cholesterol and triglyceride levels,[10] and they have been reported to have antimicrobial activity.[11] The phthalimide moiety is present in thalidomide which inhibits tumor necrosis factor-α (TNF-α).[12,13]

As part of our research, we are interested in the synthesis of 1-(2-deoxy-D-hexopyranosyl)- and 1-(2,3-dideoxy-D-hexopyranosyl)-ω-aminoalkoxyalkanes. Previously, Petrig et al. reported the four-step synthesis of 2′-aminoethyl-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranoside toluene-4-sulfonic acid salt.[14] The first step of the synthesis is the glycosylation of tri-*O*-acetyl-D-glucal with ethylene glycol to give the corresponding alcohol of 2-deoxyglucose. Next, the 2-hydroxyethyl 3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucoside is tosylated to give the appropriate tosylated product, which is converted to an azide using NaN_3. Finally, the reduction of 2-azidoethyl 3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucoside yields the corresponding amine as a toluene-4-sulfonic acid salt.

D-Glycals react with simple alcohols in the presence of triphenylphosphine hydrobromide to produce glycosides,[15–18] and this reaction occurs without Ferrier rearrangement. We decided to apply this reaction strategy to the preparation of *N*-phthalimidoalkyl and *N*-succinimidoalkyl D-hexopyranosides, which are useful reagents for building heterocyclic rings on unmasked amino groups. Prior to the addition reaction, the amino alcohols **1a** and **1b** were transformed into the appropriate imide derivatives by refluxing with phthalic anhydride **2a** and succinic anhydride **2b**, respectively, in solvent-free medium, as described elsewhere.[19–21] After recrystallization from ethanol, the imide derivatives **3a–d** were obtained in satisfactory yield (Scheme 1).

The *N*-(ω-hydroxyalkyl)imides **3a–d** were coupled with the commercially available glycals 3,4,6-tri-*O*-acetyl-D-glucal **4a** and 3,4,6-tri-*O*-acetyl-D-galactal **4b**. Preliminary trials carried out using D-glucal **4a** and *N*-(2-hydroxyethyl)phthalimide **3a** as reagents indicated that the addition reaction proceeded efficiently when 1 equiv of unsaturated sugar **4a** was treated with 1.1 equiv of **3a** in the presence of 0.15 equiv of catalyst in anhydrous dichloromethane at room temperature (Scheme 2).

The product of addition, **5a**, was obtained in 89% yield (Table 1, entry 1). Inspection of ^1H NMR and ^{13}C NMR spectra revealed the predominant diastereomer to be the α-anomer. In all reactions involving imide substrates **3a–d** and glucal **4a**, the main products possess a trans configuration with respect to the acyl group present on carbon C-3 of the pyranosyl ring. The amounts of cis isomer vary between 10% and 18% (entries 2–4). In the case of D-galactal

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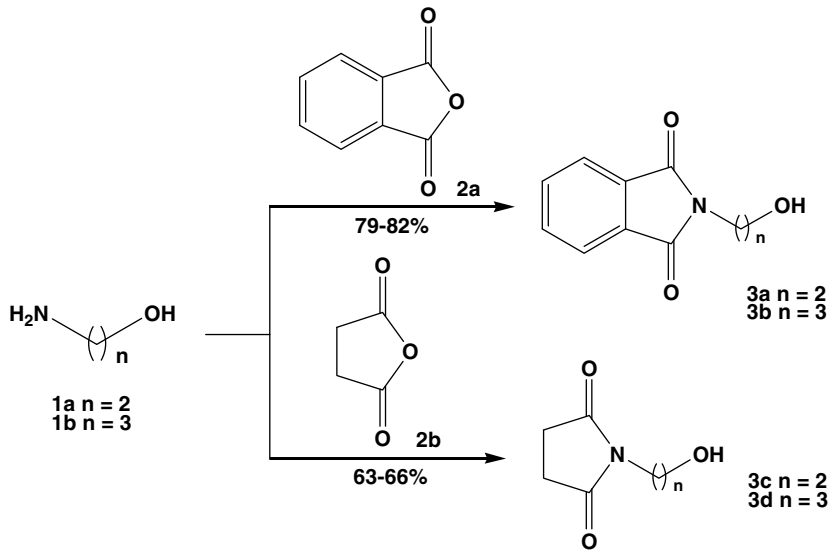
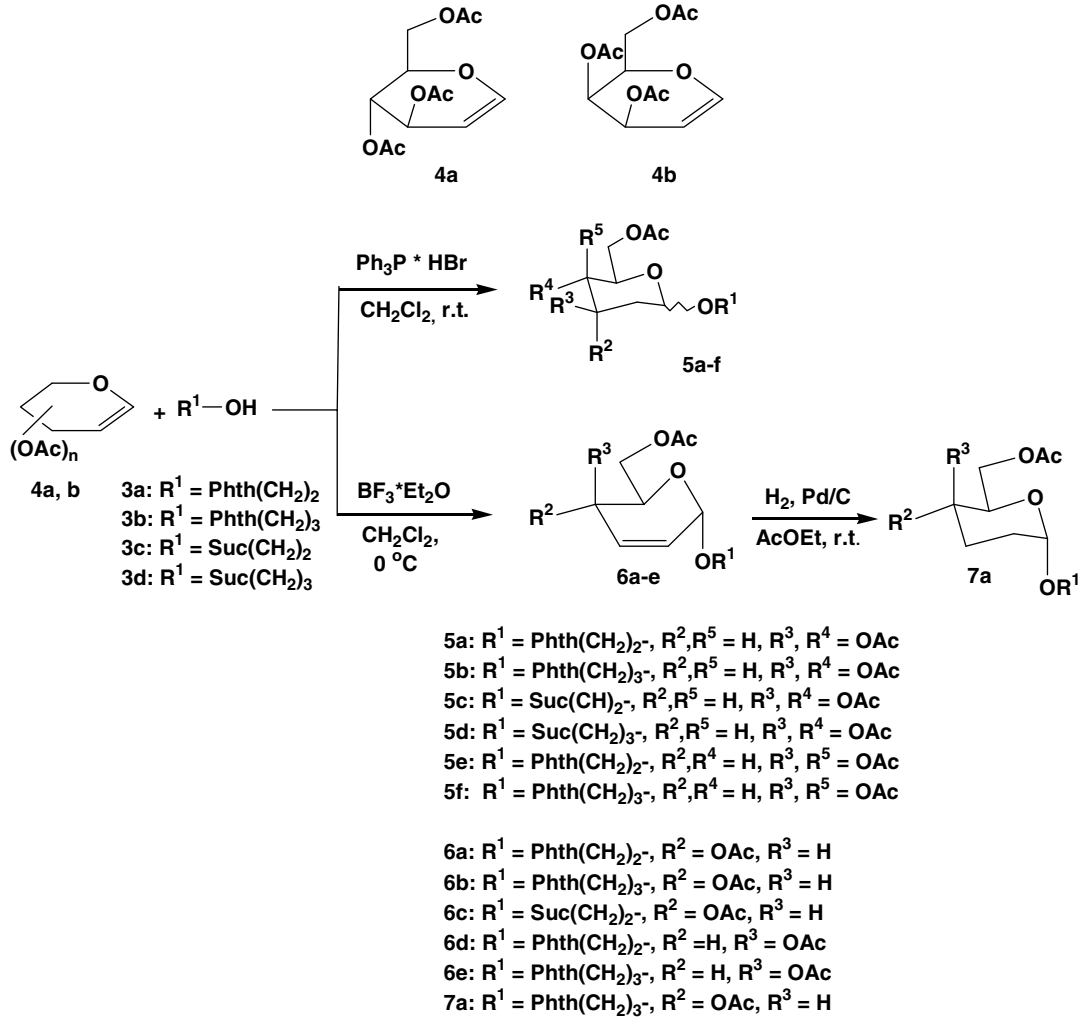


Scheme 1.



Scheme 2.

derivatives **5e**–**f**, only α-anomers were detected in the post-reaction mixture (entries 5 and 6). Attempts to separate the anomers were unsuccessful.

For comparison, we decided to repeat the reaction of the *N*-phthalimidoalkyl compounds **3a** and **3b** and *N*-succinimidoalkyl derivative **3c** with D-glycals **4a** and **4b** in the presence of borontri-

Table 1
The *N*-phthalimidoalkyl and *N*-succinimidoalkyl D-hexopyranosides synthesized in this report

Entry	Glycal	Imide	Glycoside	Reaction on time (h)	Catalyst	Relative proportions of anomers[a] α/β	Yield (%)
1	**4a**	**3a**	**5a**	48	$HBr{\cdot}PPh_3$	87/13	89[b]
2	**4a**	**3b**	**5b**	48	$HBr{\cdot}PPh_3$	82/18	88[b]
3	**4a**	**3c**	**5c**	24	$HBr{\cdot}PPh_3$	90/10	83[b]
4	**4a**	**3d**	**5d**	24	$HBr{\cdot}PPh_3$	86/14	54[b]
5	**4b**	**3a**	**5e**	3	$HBr{\cdot}PPh_3$	α	68
6	**4b**	**3b**	**5f**	4	$HBr{\cdot}PPh_3$	α	69
7	**4a**	**3a**	**6a**	1	$BF_3{\cdot}Et_2O$	α	78
8	**4a**	**3b**	**6b**	1	$BF_3{\cdot}Et_2O$	α	68
9	**4a**	**3c**	**6c**	1	$BF_3{\cdot}Et_2O$	α	59
10	**4b**	**3a**	**6d**	1	$BF_3{\cdot}Et_2O$	α	45
11	**4b**	**3b**	**6e**	1	$BF_3{\cdot}Et_2O$	α	39

[a] α/β anomer ratio based on ^1H NMR.
[b] Total yield (for both anomers).

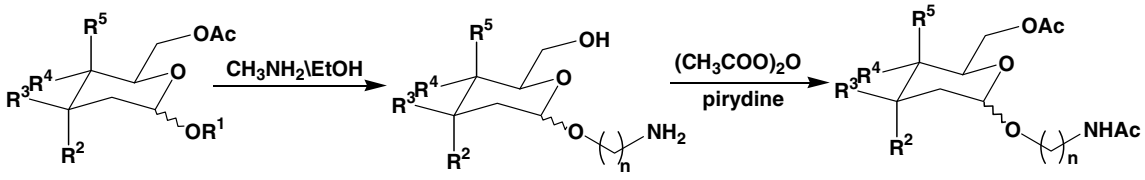
fluoride/diethyl etherate. This is a Ferrier reaction, which occurs through rearrangement.[22–28] The appropriate products of Ferrier's rearrangement, 4,6-di-*O*-acetyl-2,3-dideoxyhexenopyranosides **6a–e**, were achieved in satisfactory yield (Scheme 2). The NMR data indicated the formation of α-anomers exclusively (Table 1, entries 7–11). In order to confirm the α-configuration of the adducts obtained, a representative molecule **6b** was hydrogenated at atmospheric pressure in the presence of Pd/C catalyst. The hydrogenation reaction yielded product **7a** in satisfactory yield (Scheme 2). In ^1H NMR spectra of compound **7a**, the anomeric protons appear as a broad singlet at δ 4.78 ppm, suggesting an axial configuration for the phthalimidoalkoxy group.

As part of our continuing efforts to prepare ω-aminoalkyl D-hexopyranosides, we report here a procedure to cleave an *N*-phthalimido protective group of compounds **5a, 5b, 5e**, and **7a** (Scheme 3). The reaction proceeds smoothly at room temperature. In a typical experiment, a solution of *N*-phthalimidoalkyl D-hexopyranosides in ethanol was stirred with methylamine for 24 h. Appropriate ω-aminoalkyl D-hexopyranosides **8a–d** were obtained in satisfactory yield (Table 2, entries 1–4). In experiments in which the starting material was a mixture of two anomers (α and β) of compounds **5a** and **5b**, the anomeric ratios of the product amine were found to favor the α-anomer as a major product. When 2-aminoethyl 2-deoxy-α-D-*lyxo*-hexopyranoside or 2-aminopropyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside was used exclusively, the α-anomer was formed.

At the end of the reaction, we examined the acylation of ω-aminoalkyl D-hexopyranosides **8a–d** with acetic anhydride in pyridine at room temperature (Scheme 3). The corresponding amides **9a–d** were obtained in good yield. The results of this study are summarized in Table 2.

All compounds were purified by column chromatography and characterized on the basis of ^1H NMR and ^{13}C NMR spectroscopy, mass spectrometry, or elemental analysis. Compounds **3a–d** and **6a** were identified based on comparison with literature data. All new compounds gave satisfactory ^1H NMR and ^{13}C NMR spectra, as well as ESI-MS or elemental analysis.

In summary, we describe here a simple, efficient, and mild method to synthesize ω-aminoalkyl 2-deoxy-D-*arabin/lyxo*-hexopyranoside and 2,3-dideoxy-α-D-*erythro*-hexopyranoside using glycals as starting materials. The method is accomplished in only two steps and offers advantages such as mild reaction conditions and good yields. We have also developed a method to synthesize *N*-imidoalkyl-2-deoxy-D-hexopyranosides by adding appropriate



5a, 5b, 5e, 7a

5a: R^1 = Phth$(CH_2)_2$-, R^2,R^5 = H, R^3, R^4 = OAc
5b: R^1 = Phth$(CH_2)_3$-, R^2,R^5 = H, R^3, R^4 = OAc
5e: R^1 = Phth$(CH_2)_2$-, R^2,R^4 = H, R^3, R^5 = OAc
7a: R^1 = Phth$(CH_2)_3$-, R^4 = OAc, R^2, R^3,R^5 = H

8a-d

8a: R^2,R^5=H, R^3,R^4=OH, n=2
8b: R^2,R^5=H R^3,R^4=OH, n=3
8c: R^2,R^4=H, R^3,R^5=OH, n=2
8d: R^4=OH, R^2,R^3,R^5=H, n=3

9a-b

9a: R^2,R^5=H, R^3,R^4=OAc, n=2
9b: R^2,R^5=H R^3,R^4=OAc, n=3
9c: R^2,R^4=H, R^3,R^5=OAc, n=2
9d: R^4=OAc, R^2,R^3,R^5=H, n=3

Scheme 3.

Table 2
Synthesis and acylation of ω-aminoalkyl D-hexopyranosides **8a–d**

Entry	Phthalimidoalkyl glycoside	Reaction on time (h)	Anomer ratio[a] α/β	Yield (%)	Amine	Reaction time (h)	Anomer ratio[a] α/β	Yield (%)	Amide
1	**5a**	24	86/14	75[b]	**8a**	24	96/4	83[b]	**9a**
2	**5b**	24	85/15	85[b]	**8b**	24	93/7	63[b]	**9b**
3	**5e**	24	α	74	**8c**	24	α	93	**9c**
4	**7a**	24	α	72	**8d**	24	α	81	**9d**

[a] α/β anomer ratio based on ^1H NMR.
[a] Total yield (for both anomers).

N-(ω-hydroxyalkyl)imides to D-glycals in the presence of triphenylphosphine hydrobromide as a catalyst. In an alternative procedure, the corresponding 2,3-dideoxy-D-glycosides were obtained by the addition of *N*-(ω-hydroxyalkyl)imides to D-glycals under Ferrier conditions, followed by hydrogenolysis.

1. Experimental

1.1. General methods

NMR spectra were recorded at 300 MHz for ^{1}H NMR and 75.5 MHz for ^{13}C NMR on a Varian Inova 300 MHz spectrometer; δ-values are in parts per million relative to tetramethylsilane as an internal standard. Mass spectra were recorded in positive-ion mode on a Mariner detector (Perceptive Biosystems) using electrospray ionization (ESI). Elemental analyses were obtained using a Perkin–Elmer 240C apparatus. Optical rotation measurements were performed at 25 °C on a Perkin–Elmer 141 Polarimeter at the D sodium line. Melting points were determined in an open capillary setup and are uncorrected. Thin-layer chromatography plates ($60F_{254}$) and Silica Gel 60 (0.040–0.063 mm) for column chromatography were purchased from Merck. Solvents were purified and dried by standard procedures. All reagents used were purchased from Lancaster. The solvent systems to develop the TLC plates and carry out column chromatography were as follows: system A, toluene/EtOAc (1:1, v/v); system B, toluene/EtOAc (2:1); system C, toluene/EtOAc (1:2); system D, EtOAc/CH_2Cl_2 (1:9); system E, 10% MeOH/$CHCl_3$; system E, 50% MeOH/$CHCl_3$; and system F, 25% MeOH + 2% NH_3/H_2O.

1.2. General procedure for synthesis of compounds 3a and 3b

ω-Hydroxyalkylphthalimides were prepared by mixing phthalic anhydride (0.05 mol) and ethanol- or propanolamine (0.05 mol) and by heating at 160–180 °C for 4 h. The product solidified on cooling and was recrystallized from methanol to yield the compounds **3a** and **3b**.[19]

1.2.1. *N*-(2-Hydroxyethyl)phthalimide (3a)

Yield: 82% mp 126–127 °C (126–130 °C[17]); ^{1}H NMR ($CDCl_3$): δ 2.80 (s, 1H, OH), 3.87 (s, 4H, NCH_2, CH_2O), 7.71 (dd, 2H, *J* 3.0, 5.4 Hz, H-6, H-7), 7.83 (dd, 2H, *J* 3.0, 5.4 Hz, H-5, H-8). ^{13}C NMR ($CDCl_3$): δ 40.84 (NCH_2), 60.84 (OCH_2), 123.41, 132.03, 134.14 (C-4, C-5, C-6, C-7, C-8, C-9), 168.87 (2C=O).

1.2.2. *N*-(3-Hydroxypropyl)phthalimide (3b)

Yield: 79% mp 74–75 °C (mp 75–76 °C[18]); ^{1}H NMR ($CDCl_3$): δ 1.89 (dt, 2H, *J* 5.9, 6.4 CH_2), 2.92 (s, 1H, OH), 3.64 (t, 2H, *J* 5.9 Hz, OCH_2), 3.85 (t, 2H, *J* 6.4 Hz, NCH_2), 7.74 (dd, 2H, *J* 3.0, 5.6 Hz, H-6, H-7), 7.85 (dd, 2H, *J* 3.0, 5.6 Hz, H-5, H-8). ^{13}C NMR ($CDCl_3$): δ 31.39 (CH_2), 34.39 (NCH_2), 59,15 (OCH_2), 123.39, 132.04, 134.14 (C-4, C-5, C-6, C-7, C-8, C-9), 168.91 (2C=O).

1.3. General procedure for synthesizing compounds 3c and 3d

Succinic anhydride **2b** (0.05 mol) was suspended in 2-aminoethanol **1a** or 3-aminopropanol **1b** (0.05 mol). The reaction mixture was carefully warmed to 60–80 °C for 30 min and then heated at 150 °C for 3.5 h. The crude syrup was crystallized from methanol to yield **3c** or distilled under reduced pressure to give **3d**.[21]

1.3.1. *N*-(2-Hydroxyethyl)succinimide (3c)

Yield 66%; mp 57–59 °C (lit. mp 55 °C[19]); ^{1}H NMR ($CDCl_3$): δ 2.75 (s, 4H, H-3, H-4), 2.94 (s, 1H, OH), 3.70 (dd, 2H, *J* 3.3 7.8 Hz, NCH_2), 3.77 (dd, 2H, *J* 3.3, 7.8 Hz, CH_2O). ^{13}C NMR ($CDCl_3$): δ 28.24 (C-3, C-4), 41.53 (NCH_2), 60.04 (CH_2O), 178.08 (2C=O).

1.3.2. *N*-(3-Hydroxypropyl)succinimide (3d)

Yield 63%; bp 196–198 °C/14 mmHg (lit. bp 176–178 °C/3 mmHg[20]); ^{1}H NMR ($CDCl_3$): δ 1.78 (dt, 2H, *J* 6.5, 5.8 Hz, CH_2), 2.75 (s, H-3, H-4), 2.98 (s, 1H, OH), 3.56 (t, 2H, *J* 5.8 Hz, OCH_2), 3.66 (t, 2H, *J* 6.5 Hz, NCH_2). ^{13}C NMR ($CDCl_3$): 28.16 (C-3, C-4), 30.43 (CH_2), 35.37 (NCH_2), 59.08 (OCH_2), 177.95 (2C=O).

1.4. General procedure for synthesizing compounds 5a–f using $HBr{\cdot}PPh_3$ as catalyst

A solution was prepared containing glycal **4a**,**b** (1 mmol) and an imide derivative **3a–d** (1.1 mmol), and anhydrous CH_2Cl_2 (5 mL) containing $HBr{\cdot}PPh_3$ (0.15 mmol) was added at room temperature while stirring. When the TLC indicated the total consumption of substrate (3–48 h, Table 1), the mixture was concentrated under reduced pressure. The oily residue was purified by column chromatography (solvent system A, B, or C) to give the desired products **5a–f**. Attempts to separate anomeric mixtures were unsuccessful.

1.4.1. Phthalimidoethyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside (5a)

The mixture of anomers was eluted; R_f 0.52 (solvent A); ^{1}H NMR ($CDCl_3$): α anomer: δ 1.80 (ddd, 1H, $J_{2a,2b}$ 12.9, $J_{2a,3}$ 11.7, $J_{2a,1}$ 3.3 Hz, H-2^a), 1.99 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.21 (ddd, 1H, $J_{2b,2a}$ 12.9, $J_{2b,3}$ 5.4, *J* 0.6 Hz, H-2^b), 3.89 (m, 5H, H-5, NC_2H_4O), 4.01 (dd, 1H, $J_{6b,6a}$ 12.2, *J* 4.8 Hz, H-6^b), 4.24 (dd, 1H, $J_{6a,6b}$ 12.2, *J* 2.1 Hz, H-6^a), 4.95 (dd, 1H, $J_{4,3}$ 9.6, *J* 9.8 Hz, H-4), 5.06 (d, 1H, $J_{1,2a}$ 3.3 Hz, H-1), 5.23 (ddd, 1H, $J_{3,2a}$ 11.7, $J_{3,4}$ 9.6, $J_{3,2b}$ 5.4 Hz, H-3), 7.74 (dd, 2H, *J* 5.6, *J* 3.1, H-5′, H-6′), 7.87 (dd, 2H, *J* 5.6, *J* 3.1, H-4′, H-7′). β anomer: δ 1.68 (ddd, 1H, $J_{2a,2b}$ 12.3, $J_{2a,3}$ 12.1, $J_{2a,1}$ 9.6 Hz, H-2^a), 2.01 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.26 (ddd, 1H, $J_{2b,2a}$ 12.5, $J_{2b,3}$ 5.1, $J_{2b,1}$ 2.0 Hz, H-2^b), 3.56 (ddd, 1H, *J* 2.4, *J* 5.0, *J* 9.5 Hz, CH_2^aO), 4.09 (dd, 1H, *J* 12.1, *J* 5.0 Hz, H-6^a), 4.59 (dd, 1H, $J_{1,2a}$ 9.6, $J_{1,2b}$ 2.0 Hz, H-1). ^{13}C NMR ($CDCl_3$): α anomer: δ 20.81, 20.94, 21.02 ($3CH_3$), 34.79, 36.96 (C-2, CH_2N), 62.33, 63.73 (C-6, OCH_2), 68.21, 68.92, 69.30 (C-3, C-4, C-5), 96.24 (C-1), 123.34, 134.03, 134.12 (C′-4, C′-5, C′-6, C′-7, C′-8, C′-9), 168.17 (2C′=O), 169.84, 170.01, 170.69 (C=O). Anal. Calcd for $C_{22}H_{25}NO_{10}$: C, 57.02; H, 5.44; N, 3.02. Found: C, 56.84; H, 5.28; N, 2.87.

1.4.2. Phthalimidopropyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside (5b)

The mixture of anomers was eluted; R_f 0.41 (solvent A); α anomer: ^{1}H NMR ($CDCl_3$): δ 1.81 (ddd, 1H, $J_{2a,2b}$ 13.0, $J_{2a,3}$ 11.7, $J_{2a,1}$ 3.2 Hz, H-2^a), 2.00 (s, 3H, CH_3), 2.03 (m, 5H, CH_2, CH_3), 2.07 (s, 3H, CH_3), 2.21 (ddd, 1H, $J_{2b,2a}$ 13.0, $J_{2b,3}$ 5.4, *J* 0.8 Hz, H-2^b), 3.40 (dt, 1H, $J_{OCH_2^a,OCH_2^b}$ 10.2, $J_{OCH_2^a,CH_2}$ 6.1 Hz, $J_{OCH_2^a}$), 3.73 (dt, 1H, $J_{OCH_2^b,OCH_2^a}$ 10.2, $J_{OCH_2^b,CH_2}$ 5.8, $J_{OCH_2^b}$), 3.92 (m, 2H, NCH_2), 4.03 (m, 2H, H-5, H-6^b), 4.33 (dd, 1H, *J* 12.2, *J* 4.4 Hz, H-6^a), 4.93 (d, 1H, $J_{1,2a}$ 3.2 Hz, H-1), 4.98 (dd, 1H, $J_{4,3}$ 9.6, *J* 9.8 Hz, H-4), 5.25 (ddd, 1H, $J_{3,2a}$ 11.7, $J_{3,4}$ 9.6, $J_{3,2b}$ 5.4 Hz, H-3), 7.72 (dd, 2H, *J* 5.5, *J* 3.1, H-5′, H-6′), 7.85 (dd, 2H, *J* 5.5, *J* 3.1, H-4′, H-7′). β anomer: δ 1.64 (ddd, 1H, $J_{2a,2b}$ 12.1, $J_{2a,3}$ 11.9, $J_{2a,1}$ 9.9 Hz, H-2^a), 2.02 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.26 (ddd, 1H, $J_{2b,2a}$ 12.6, $J_{2b,3}$ 4.9, $J_{2b,1}$ 2.0 Hz, H-2^b), 4.59 (dd, 1H, $J_{1,2a}$ 9.6 $J_{1,2b}$ 1.9 Hz, H-1). ^{13}C NMR ($CDCl_3$): α anomer: δ 20.67, 20.71, 20.92 ($3CH_3$), 28.59 (CH_2), 35.05, 35.39 (C-2, CH_2N), 62.51, 65.52 (C-6, OCH_2), 67.96, 69.16, 69.26 (C-3, C-4, C-5), 97.47 (C-1), 123.33, 132.20, 134.08 (C′-4, C′-5, C′-6, C′-7, C′-8, C′-9), 168.50 (2C′=O), 170.07, 170.15, 170.87 (3C=O). Anal. Calcd for $C_{23}H_{27}NO_{10}$: C, 57.86; H, 5.70; N, 2.93. Found: C, 57.64; H, 5.38; N, 2.87.

1.4.3. Succinimidoethyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside (5c)

The mixture of anomers was eluted; R_f 0.26 (solvent C); ^{1}H NMR ($CDCl_3$): α anomer: δ 1.79 (ddd, 1H, $J_{2a,2b}$ 13.0, $J_{2a,3}$ 11.6, $J_{2a,1}$ 3.2 Hz, H-2^a), 2.00 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.18 (ddd, 1H, $J_{2b,2a}$ 13.0, $J_{2b,3}$ 5.3, J 1.0 Hz, H-2^b), 2.76 (s, 4H, CH_2-3′, CH_2-4′), 3.73 (m, 4H, NC_2H_4O), 3.93 (ddd, 1H, $J_{5,4}$ 9.9, $J_{5,6b}$ 4.8, $J_{5,6a}$ 2.2 Hz, H-5), 4.07 (dd, 1H, $J_{6a,6b}$ 12.3, $J_{6a,5}$ 2.2 Hz, H-6^a), 4.27 (dd, 1H, $J_{6b,6a}$ 12.3, $J_{6b,5}$ 4.8 Hz, H-6^b), 4.97 (dd, 1H, $J_{4,3}$ 9.7, $J_{4,5}$ 9.9 Hz, H-4), 5.02 (d, 1H, $J_{1,2a}$ 3.2 Hz, H-1), 5.22 (ddd, 1H, $J_{3,2a}$ 11.6, $J_{3,4}$ 9.7, $J_{3,2b}$ 5.3 Hz, H-3). β anomer: δ 1.68 (ddd, 1H, $J_{2a,2b}$ 12.6, $J_{2a,3}$ 11.2, $J_{2a,1}$ 9.6 Hz, H-2^a), 2.02 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.26 (ddd, 1H, $J_{2b,2a}$ 12.6, $J_{2b,3}$ 5.1, $J_{2b,1}$ 1.37 Hz, H-2^b), 4.57 (dd, 1H, J 2.0, 9.6 Hz, H-6^a). ^{13}C NMR ($CDCl_3$): α anomer: δ 20.85, 20.98, 21.06 ($3CH_3$), 28.23 (C′-4, C′-5), 34.80, 37.56 (C-2, CH_2N), 62.42, 62.67 (C-6, OCH_2), 68.94, 69.03, 69.28 (C-3, C-4, C-5), 96.07 (C-1), 169.84, 170.24, 170.83 (3C=O), 177.21 (2C′=O). Anal. Calcd for $C_{18}H_{25}NO_{10}$: C, 52.05; H, 6.07; N, 3.37. Found: C, 52.39; H, 5.98; N, 3.30.

1.4.4. Succinimidopropyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside (5d)

The mixture of anomers was eluted; R_f 0.31 (solvent C); ^{1}H NMR ($CDCl_3$): α anomer: δ 1.79 (ddd, 1H, $J_{2a,2b}$ 13.0, $J_{2a,3}$ 11.6, $J_{2a,1}$ 3.3 Hz, H-2^a), 1.90 (m, 2H, CH_2), 2.02 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.22 (ddd, 1H, $J_{2b,2a}$ 13.0, $J_{2b,3}$ 5.3, J 1.1 Hz, H-2^b), 2.74 (s, 4H, CH_2-3′, CH_2-4′), 3.40 (td, 1H, J 5.8, J 5.8, J 10.1, CH^b_2O), 3.66 (m, 3H, NCH_2, CH^a_2O), 3.96 (ddd, 1H, $J_{5,4}$ 10.0, $J_{5,6b}$ 4.4, $J_{5,6a}$ 2.4 Hz, H-5), 4.04 (dd, 1H, $J_{6a,6b}$ 12.3, $J_{6a,5}$ 2.4 Hz, H-6^a), 4.31 (dd, 1H, $J_{6b,6a}$ 12.3, $J_{6b,5}$ 4.4 Hz, H-6^b), 4.89 (d, 1H, $J_{1,2a}$ 3.3 Hz, H-1), 5.01 (dd, 1H, $J_{4,3}$ 9.6, $J_{4,5}$ 10.0 Hz, H-4), 5.20 (ddd, 1H, $J_{3,2a}$ 11.6, $J_{3,4}$ 9.6, $J_{3,2b}$ 5.3 Hz, H-3). β anomer: δ 2.02 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.26 (ddd, 1H, J 12.4, J 5.3 $J_{2b,1}$ 1.9 Hz, H-2^b), 4.53 (dd, 1H, J 9.6 $J_{1,2b}$ 1.9 Hz, H-1). ^{13}C NMR ($CDCl_3$): α anomer: δ 20.96, 20.97, 21.18 ($3CH_3$), 28.37 (C′-4, C′-5), 28.41 (CH_2), 34.97, 36.83 (C-2, CH_2N), 62.38, 66.18, 67.90, 69.15, 69.25 (C-6, OCH_2, C-3, C-4, C-5), 96.14 (C-1), 169.87, 170.31, 170.74 (3C=O), 177.45 (C′=O). Anal. Calcd for $C_{19}H_{27}NO_{10}$: C, 53.14; H, 6.34; N, 3.26. Found: C, 52.89; H, 5.98; N, 3.12.

1.4.5. Phthalimidoethyl 3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*lyxo*-hexopyranoside (5e)

$[\alpha]_D^{25}$ +65.5 (*c* 0.74, MeOH); R_f 0.48 (solvent A); ^{1}H NMR ($CDCl_3$): δ 1.82 (dd, 1H, J 12.8, $J_{2a,3}$ 5.1 Hz, H-2^a), 1.96 (s, 3H, CH_3), 2.05 (m, 4H, H-2^b, CH_3), 2.12 (s, 3H, CH_3), 3.75 (dd, 1H, J 13.0, J 5.5 Hz, CH^a_2O), 3.88 (m, 2H, $NCH^a_2CH^b_2O$), 3.97 (dd, 1H, J 9.3, J 5.1 Hz, H-6^b), 4.07 (m, 3H, H-5, H-6^a, N-CH^b_2), 5.10 (d, 1H, $J_{4,3}$ 3.0 Hz, H-4), 5.19 (ddd, 1H, J 12.4 $J_{3,2a}$ 5.1, $J_{3,4}$ 3.0 Hz, H-3), 5.27 (d, 1H, J 2.9 Hz, H-1), 7.74 (dd, 2H, J 5.5, J 3.0, H-5′, H-6′), 7.87 (dd, 2H, J 5.5, J 3.0, H-4′, H-7′). ^{13}C NMR ($CDCl_3$): δ 20.82, 20.95 ($3CH_3$), 30.03 (C-2), 37.27 (CH_2N), 62.62, 64.09 (C-3, C-6), 66.15, 66.78, 67.16 (OCH_2, C-4, C-5), 96.98 (C-1), 123.51, 132.16, 134.20 (C′-4, C′-5, C′-6, C′-7, C′-8, C′-9), 168.27 (2C′=O), 169.99, 170.38, 170.63 (3C=O). Anal. Calcd for $C_{22}H_{25}NO_{10}$: C, 57.02; H, 5.44; N, 3.02. Found: C, 57.36; H, 5.62; N, 2.69.

1.4.6. Phthalimidopropyl 3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*lyxo*-hexopyranoside (5f)

$[\alpha]_D^{25}$ +69.8 (*c* 0.88, MeOH); R_f 0.50 (solvent A); ^{1}H NMR ($CDCl_3$): δ 1.80 (dd, 1H, J 12.68, $J_{2a,3}$ 5.10 Hz, H-2^a), 1.97 (s, 3H, CH_3), 2.04 (m, 6H, H-2^b, CH_2, CH_3), 2.12 (s, 3H, CH_3), 3.41 (td, 1H, $J_{OCH^a_2,OCH^b_2}$ 10.2, J 6.14, J 6.14 Hz, CH^a_2O), 3.72 (td, 1H, $J_{OCH^b_2,OCH^a_2}$ 10.2, J 5.61, J 5.61 Hz, CH^b_2O), 3.82 (m, 2H, NCH_2), 4.06 (m, 2H, H-6^b, H-6^a), 4.15 (dd, 1H, J 6.81, J 7.11 Hz, H-5), 4.98 (d, 1H, $J_{4,3}$ 3.0 Hz, H-4), 5.18 (ddd, 1H, J 12.38, J 4.93, $J_{3,4}$ 3.0 Hz, H-3), 5.32 (d, 1H, J 2.71 Hz, H-1), 7.74 (dd, 2H, J 5.54, J 2.98, H-5′, H-6′), 7.77 (dd, 2H, J 5.53, J 2.98, H-4′, H-7′). ^{13}C NMR ($CDCl_3$): δ 20.82, 20.95 ($3CH_3$), 28.51 (CH_2), 30.19 (C-2), 35.51 (CH_2N), 62.62, 65,53, 66.31, 66.81, 66.81 (OCH_2, C-4, C-5, C-3, C-6), 97.88 (C-1), 123.37, 132.26, 134.05 (C′-4, C′-5, C′-6, C′-7, C′-8, C′-9), 168.45 (2C′=O), 169.97, 170.42, 170.61 (C=O). Anal. Calcd for $C_{23}H_{27}NO_{10}$: C, 57.86; H, 5.70; N, 2.93. Found: C, 57.88; H, 5.61; N, 2.79.

1.5. General procedure for synthesizing compounds 6a–e using $BF_3{\cdot}Et_2O$ as catalyst

A solution of the glycal **4a** or **4b** (1 mmol) and imide derivative **3a**, **3b**, or **3c** (1.1 mmol) was prepared in anhydrous CH_2Cl_2 (5 mL), and $BF_3{\cdot}Et_2O$ (0.10 mmol) was added at 0 °C with stirring. When TLC indicated the complete consumption of substrate **4** (Table 1, entries 9–13), the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$. The organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to yield a colorless oil. This residue was purified by column chromatography on silica gel (solvent A or B) to give the products **6a–e**.

1.5.1. Phthalimidoethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (6a)

$[\alpha]_D^{25}$ +47.7 (*c* 1.09, MeOH); R_f 0.54 (solvent A); ^{1}H NMR ($CDCl_3$): δ 2.08 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.93 (m, 4H, NCH_2, CH_2O), 4.07 (ddd, 1H, $J_{5,6a}$ 2.3, $J_{5,6b}$ 5.3, $J_{5,4}$ 9.51 Hz, H-5), 4.15 (dd, 1H, $J_{6a,5}$ 2.3, $J_{6a,6b}$ 12.2 Hz, H-6^a), 4.23 (dd, 1H, $J_{6b,5}$ 5.3, $J_{6^b,6^a}$ 12.2 Hz, H-6^b), 5.12 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1), 5.30 (ddd, 1H, $J_{4,3}$ 1.3, $J_{4,2}$ 2.7, $J_{4,5}$ 9.70 Hz, H-4), 5.78 (ddd, 1H, $J_{2,1}$ 1.8, $J_{2,4}$ 2.7, $J_{2,3}$ 10.2, H-2), 5.87 (dd, 1H, $J_{3,4}$ 1.3, $J_{3,2}$ 10.2 Hz, H-3), 7.74 (dd, 2H, J 3.0, 5.5 Hz, H-5′, H-6′), 7.69 (dd, 2H, J 2.0, 5.5 Hz, H-4′, H-7′). ^{13}C NMR ($CDCl_3$): δ 20.82, 21.00 ($2CH_3$), 37.56 (CH_2N), 62.92 65.19, 65.21, 67.14, (C-4, C-5, C-6, OCH_2), 94.07 (C-1), 123.36 (C′-4, C′-9), 127.56, 129.37 (C-2, C-3), 132.12, 134.08 (C′-5, C′-6, C′-7, C′-8), 168.22 (C′=O), 170.27, 170.83 (2C=O). Anal. Calcd for $C_{20}H_{21}NO_8$: C, 59.55; H, 5.25; N, 3.47. Found: C, 59.17; H, 5.17; N, 3.27.

1.5.2. Phthalimidopropyl 3,4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (6b)

$[\alpha]_D^{25}$ +47.5 (*c* 0.87, MeOH); R_f 0.52 (solvent A); ^{1}H NMR ($CDCl_3$): δ 2.01 (m, 2H, CH_2), 2.08 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 3.52 (td, 1H, J 5.91, J 5.91, J 10.00 Hz, CH^a_2O) 3.85 (m, 3H, NCH_2, CH^b_2O), 4.15 (m, 2H, Hz, H-5, H-6^a), 4.28 (dd, 1H, J 5.05, J 12.03 Hz, H-6^b), 4.99 (s, 1H, H-1), 5.30 (ddd, 1H, $J_{4,3}$ 1.1, $J_{4,2}$ 2.7, J 9.71 Hz, H-4), 5.76 (ddd, 1H, J 1.86, $J_{2,4}$ 2.7, $J_{2,3}$ 10.3, H-2), 5.82 (dd, 1H, $J_{3,4}$ 1.1, $J_{3,2}$ 10.3 Hz, H-3), 7.69 (dd, 2H, J 3.0, 5.5 Hz, H-5′, H-6′), 7.82 (dd, 2H, J 3.0, 5.5 Hz, H-4′, H-7′). ^{13}C NMR ($CDCl_3$): δ 20.41, 20.73 ($2CH_3$), 28.10 (CH_2), 35.14 (CH_2N), 62.57, 64.74, 65.90, 66.37, (C-4, C-5, C-6, OCH_2), 93.70 (C-1), 122.95 (C′-4, C′-9), 128.09, 128.47 (C-2, C-3), 131.68, 134.29 (C′-5, C′-6, C′-7, C′-8), 167.94 (C′=O), 169.87, 170.04 (2C=O). Anal. Calcd for $C_{21}H_{23}NO_8$: C, 60.43; H, 5.55; N, 3.36. Found: C, 60.17; H, 5.19; N, 3.22.

1.5.3. Succinimidoethyl 3,4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (6c)

$[\alpha]_D^{25}$ +56.8 (*c* 1.15, MeOH); R_f 0.28 (solvent A); ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.73 (s, 4H, CH_2-3′, CH_2-4′), 3.78 (m, 4H, NCH_2, CH_2O), 4.08 (ddd, 1H, J 2.67, J 5.10, $J_{5,4}$ 9.6 Hz, H-5), 4.20 (m, 2H, H-6^a, H-6^b), 5.09 (br s, 1H, H-1), 5.29 (ddd, 1H, J 1.63, $J_{4,2}$ 2.8, $J_{4,5}$ 9.6 Hz, H-4), 5.77 (ddd, 1H, J 1.9, $J_{2,4}$ 2.8, $J_{2,3}$ 10.2, H-2), 5.88 (dd, 1H, $J_{3,2}$ 10.2 Hz, H-3). ^{13}C NMR ($CDCl_3$): δ 20.88 ($2CH_3$), 28.24 (CH_2), 38.23 (CH_2N), 62.99, 64.31, 65.28, 67.14, (C-4, C-5, C-6, OCH_2), 93.87 (C-1), 127.52, 129.48 (C-2, C-3), 170.34, 170.91 (2C=O), 177.14 (C′=O). Anal. Calcd for $C_{16}H_{21}NO_8$: C, 54.08; H, 5.96; N, 3.94. Found: C, 53.82; H, 5.73; N, 3.69.

1.5.4. Phthalimidoethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*treo*-hex-2-enopyranoside (6d)

$[\alpha]_D^{25}$ −121.5 (*c* 0.91, MeOH); R_f 0.50 (solvent A); ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 3.91 (m, 4H, NCH_2, CH_2O), 4.16 (dd, 1H, $J_{6a,5}$ 7.5, $J_{6a,6b}$ 11.3 Hz, H-6^a), 4.21 (dd, 1H, $J_{6b,5}$ 4.9, $J_{6b,6a}$ 11.3 Hz, H-6^b), 4.32 (ddd, 1H, $J_{5,4}$ 2.5, $J_{5,6b}$ 4.9, $J_{5,6a}$ 7.5 Hz, H-5), 4.98 (dd, 1H, $J_{4,3}$ 5.4, $J_{4,5}$ 2.5 Hz, H-4), 5.14 (d, 1H, $J_{1,2}$ 2.9 Hz, H-1), 5.98 (dd, 1H, $J_{2,1}$ 2.9, $J_{2,3}$ 10.0, H-2), 6.09 (ddd, 1H, *J* 0.8, $J_{3,4}$ 5.4, $J_{3,2}$ 10.0 Hz, H-3), 7.73 (dd, 2H, *J* 3.0, 5.6 Hz, H-5′, H-6′), 7.85 (dd, 2H, *J* 3.0, 5.6 Hz, H-4′, H-7′). ^{13}C NMR ($CDCl_3$): δ 20.86, 20.92 ($2CH_3$), 37.58 (CH_2N), 62.85, 62.92, 64.87, 67.07, (C-4, C-5, C-6, OCH_2), 93.58 (C-1), 123.45 (C′-4, C′-9), 125.41, 130.25 (C-2, C-3), 132.19, 134.14 (C′-5, C′-6, C′-7, C′-8), 168.28 (C′=O), 170.41, 170.75 (2C=O). Anal. Calcd for $C_{20}H_{21}NO_8$: C, 59.55; H, 5.25; N, 3.47. Found: C, 59.61; H, 5.13; N, 3.23.

1.5.5. Phthalimidopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*treo*-hex-2-enopyranoside (6e)

$[\alpha]_D^{25}$ −125.2 (*c* 1.01, MeOH); R_f 0.46 (solvent A); ^{1}H NMR ($CDCl_3$): δ 2.02 (m, 2H, CH_2), 2.04 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 3.52 (td, 1H, *J* 5.96, *J* 5.96, *J* 10.05 Hz, CH_2^aO), 3.84 (m, 3H, NCH_2, CH_2^bO), 4.20 (d, 2H, $J_{5,6}$ 6.3, CH_2-6), 4.32 (td, 1H, $J_{5,6}$ 6.3, $J_{5,6}$ 6.3 $J_{5,4}$ 2.5 Hz, H-5), 4.99 (dd, 1H, $J_{4,3}$ 5.3, $J_{4,5}$ 2.5 Hz, H-4), 5.02 (d, 1H, $J_{1,2}$ 2.8 Hz, H-1), 5.94 (dd, 1H, $J_{2,1}$ 2.8, $J_{2,3}$ 10.0, H-2), 6.09 (ddd, 1H, *J* 0.6, $J_{3,4}$ 5.3, $J_{3,2}$ 10.0 Hz, H-3), 7.73 (dd, 2H, *J* 3.0, *J* 5.5 Hz, H-5′, H-6′), 7.83 (dd, 2H, *J* 3.0, *J* 5.5 Hz, H-4′, H-7′). ^{13}C NMR ($CDCl_3$): δ 20.80, 20.88 ($2CH_3$), 28.62 (CH_2), 35.56 (CH_2N), 62.88, 62.91, 66.07, 66.83, (C-4, C-5, C-6, OCH_2), 94.23 (C-1), 123.53 (C′-4, C′-9), 125.05, 130.58 (C-2, C-3), 132.27, 134.00 (C′-5, C′-6, C′-7, C′-8), 168.44 (C′=O), 170.39, 170.66 (2C=O). Anal. Calcd for $C_{21}H_{23}NO_8$: C, 60.43; H, 5.55; N, 3.36. Found: C, 60.25; H, 5.21; N, 3.17.

1.6. Procedure for synthesizing phthalimidopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hexopyranoside (7a)

Compound **6b** (1 mmol) was dissolved in EtOAc (15 mL) and hydrogenated at room temperature in the presence of 10% palladium on carbon (100 mg). The reaction progress was monitored by TLC; when the unsaturated sugar derivative had disappeared completely after approximately 18 h, the catalyst was filtered off, and the filtrate was evaporated under reduced pressure. The residual oil was purified on a column of silica gel using solvent system A or B as eluent. The product **7a** was obtained as a semi-solid mass; $[\alpha]_D^{25}$ +31.2 (*c* 0.85, MeOH); ^{1}H NMR ($CDCl_3$): δ 1.70 (m, 3H, CH_2^a-2, CH_2-3), 1.88 (m, 1H, CH_2^b-2), 2.00 (m, 2H, CH_2), 2.04 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 3.44 (td, 1H, *J* 5.95, *J* 5.95, *J* 10.1 Hz CH_2^aO), 3.76 (td, 1H, *J* 5.72, *J* 5.72, *J* 10.1 Hz CH_2^bO), 3.83 (m, 2H, NCH_2), 3.90 (ddd, 1H, $J_{5,6a}$ 2.1, $J_{5,6b}$ 5.1, $J_{5,4}$ 10.1 Hz, H-5), 4.06 (dd, 1H, $J_{6a,5}$ 2.1, $J_{6a,6b}$ 12.0 Hz, H-6^a), 4.25 (dd, 1H, $J_{6b,5}$ 5.1, $J_{6a,6b}$ 12.0 Hz, H-6^a), 4.72 (ddd, 1H, *J* 4.56, *J* 10.2, $J_{4,5}$ 10.1 Hz, H-4), 4.78 (br s, 1H, H-1), 7.72 (dd, 2H, *J* 3.0, *J* 5.5 Hz, H-5′, H-6′), 7.85 (dd, 2H, *J* 3.0, *J* 5.5 Hz, H-4′, H-7′). ^{13}C NMR ($CDCl_3$): δ 20.93, 21.23 ($2CH_3$), 23.97, 28.56, 28.79 (C-2, C-3, CH_2), 35.79 (CH_2N), 63.28, 65.17, 67.88, 68.80 (C-4, C-5, C-6, OCH_2), 96.79 (C-1), 123.31, 132.30, 134.06 (C′-4, C′-5, C′-6, C′-7, C′-8, C′-9), 168.50 (C′=O), 170.3, 171.01 (2C=O). Anal. Calcd for $C_{21}H_{25}NO_8$: C, 60.14; H, 6.01; N, 3.34. Found: C, 60.25; H, 5.71; N, 3.16.

1.7. General procedure for synthesizing compounds 8a–d (cleavage *N*-phthalimido protective group)

To a solution of compound **5a, 5b, 5e**, or **7a** (2.59 mmol) in ethanol (2 mL), 33% ethanolic methylamine (5 mL) was added. The reaction mixture was stirred for 24 h at room temperature, after which it was concentrated under reduced pressure. This residue was purified by column chromatography on silica gel using solvent system F, followed by system G as eluent. The products **8a–d** were obtained as a foam.

1.7.1. 2-Aminoethyl 2-deoxy-D-*arabino*-hexopyranoside (8a)

The mixture of anomers was eluted; ^{1}H NMR ($CDCl_3$): α anomer: 1.61 (ddd, 1H, $J_{2a,2b}$ 13.0, *J* 11.9, $J_{2a,1}$ 3.6 Hz, H-2^a), 2.02 (ddd, 1H, $J_{2b,2a}$ 13.0, *J* 5.2, *J* 0.9 Hz, H-2^b), 2.89 (m, 2H, NCH_2), 3.22 (m, 1H, CH_2^aO), 3.49 (m, 2H, H-5, CH_2^bO), 3.68 (dd, 1H, *J* 5.8, *J* 11.8 Hz, H-6^a), 3.83 (m, 3H, H-3, H-4, H-6^a), 4.93 (br s, 1H, $J_{2b,1}$ 3.3 Hz, H-1). β anomer: δ 1.50 (ddd, 1H, $J_{2a,2b}$ 12.3, $J_{2a,3}$ 12.1, $J_{2a,1}$ 9.8 Hz, H-2^a), 2.17 (ddd, 1H, $J_{2b,2a}$ 12.3, $J_{2b,3}$ 5.1, $J_{2b,1}$ 1.9 Hz, H-2^b), 4.58 (dd, 1H, $J_{1,2a}$ 9.8, $J_{1,2b}$ 1.9 Hz, H-1). δ ^{13}C NMR (CD_3CD): α anomer: 38.72 (C-2), 41.76 (CH_2N), 62.84 (C-6), 68.47, 69.77, 73.29, 74.15 (OCH_2, C-3, C-4,C-5), 98.86 (C-1); ESI-MS *m*/*z* calcd for $C_8H_{17}NO_5$: 208.1 $[M+H]^+$. Found: 208.3.

1.7.2. 2-Aminopropyl 2-deoxy-D-*arabino*-hexopyranoside (8b)

The mixture of anomers was eluted; ^{1}H NMR (CD_3OD): α anomer: 1.60 (ddd, 1H, $J_{2a,2b}$ 12.5, *J* 12.3, $J_{2a,1}$ 3.3 Hz, H-2^a), 1.87 (m, 2H, CH_2), 2.60 (ddd, 1H, $J_{2b,2a}$ 12.5, *J* 5.1, *J* 0.4 Hz, H-2^b), 2.94 (m, 2H, NCH_2), 3.20 (dt, 1H, *J* 9.4, *J* 3.4 Hz, CH_2^aO), 3.48 (m, 2H, H-5, CH_2^bO), 3.67 (dd, 1H, *J* 6.0, *J* 11.8 Hz, H-6^a), 3.81 (m, 3H, H-3, H-4, H-6^a), 4.89 (d, 1H, $J_{2b,1}$ 3.3 Hz, H-1). β anomer: δ 1.48 (ddd, 1H, $J_{2a,2b}$ 12.2, $J_{2a,3}$ 12.1, $J_{2a,1}$ 9.8 Hz, H-2^a), 2.13 (ddd, 1H, $J_{2b,2a}$ 12.3, $J_{2b,3}$ 5.1, $J_{2b,1}$ 1.8 Hz, H-2^b), 4.57 (dd, 1H, $J_{1,2a}$ 9.8 $J_{1,2b}$ 1.8 Hz, H-1); ^{13}C NMR (CD_3CD): α anomer: 30.50 (CH_2), 38.80, 39.30 (C-2, CH_2N), 62.91 (C-6), 65.71, 69.84, 73.37, 74.22 (OCH_2, C-3, C-4, C-5), 98.69 (C-1); ESI-MS *m*/*z* calcd for $C_9H_{19}NO_5$: 222.1 $[M+H]^+$. Found: 222.4.

1.7.3. 2-Aminoethyl 2-deoxy-α-D-*lyxo*-hexopyranoside (8c)

$[\alpha]_D^{25}$ +100.5 (*c* 076, MeOH); ^{1}H NMR (CD_3OD): 1.81 (dd, 1H, $J_{2a,2b}$ 12,5 $J_{2a,3}$ 5.3 Hz, H-2^a), 1.95 (ddd, 1H, $J_{2b,2a}$ 12.5, $J_{2b,3}$ 12.0, $J_{2b,1}$ 3.5 Hz, H-2^b), 2.88 (m, 2H, NCH_2), 3.46 (ddd, 1H, *J* 10.5, *J* 5.9, *J* 4.9 Hz, H-5), 3.73 (m, 4H, H-4 H-6, CH_2O), 3.96 (ddd, 1H, $J_{2b,3}$ 12.0, $J_{2a,3}$ 5.3, *J* 3.1 Hz, H-3), 4.94 (d, 1H, $J_{2b,1}$ 3.5 H-1). ^{13}C NMR (CD_3OD): δ 33.54 (C-2), 41.82 (CH_2N), 63.35 (C-6), 66.56, 68.72, 69.59 (OCH_2, C-3, C-4), 72.62 (C-5), 99.22 (C-1); ESI-MS *m*/*z* calcd for $C_8H_{17}NO_5$: 208.1 $[M+H]^+$. Found: 208.3.

1.7.4. 2-Aminopropyl 2,3-dideoxy-α-D-*erythro*-hexopyranoside (8d)

$[\alpha]_D^{25}$ +89.8 (*c* 2.57, MeOH); ^{1}H NMR (CD_3OD): δ 1.79 (m, 6H, H-2, H-3, CH_2), 3.84 (m, 2H, NCH_2), 3.45 (m, 3H, H-6^a, CH_2O), 3.62 (dd, 1H, *J* 5.8, *J* 11.6 Hz, H-6^b), 3.81 (m, 2H, H-4, H-5), 4.76 (d, 1H, *J* 1.6 Hz, H-1), ^{13}C NMR (CD_3OD): δ 28.23, 30.31, 31.86 (CH_2, C-2, C-3), 39.68 (CH_2N), 63.21, 65.69, 67.13, 75.52 (OCH_2, C-4, C-5, C-6), 97.41 (C-1); ESI-MS *m*/*z* calcd for $C_9H_{19}NO_4$: 206.1 $[M+H]^+$. Found: 206.4.

1.8. General procedure for synthesizing compounds 9a–d

To a solution of compound **8a–d** (0.63 mmol) in dry pyridine (4 mL), acetic anhydride (5.29 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. After removal of pyridine by evaporation with toluene under reduced pressure, the residue was purified by column chromatography on silica gel (solvent E). The products **9a–d** were obtained as a syrup.

1.8.1. *N*-[2′-(3,4,6-Tri-*O*-acetylo-2-deoxy-D-*arabino*-hexopyranosyl)ethoxy]acetamide (9a)

The mixture of anomers was eluted; R_f 0.45 (solvent E); ^{1}H NMR ($CDCl_3$): α anomer: δ 1.84 (ddd, 1H, $J_{2a,2b}$ 12.6, $J_{2a,3}$ 11.0, $J_{2a,1}$ 3.6 Hz, H-2^a), 2.02 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.26 (ddd, 1H, $J_{2b,2a}$ 12.6, $J_{2b,3}$ 5.3, *J* 0.8 Hz, H-2^b), 3.47 (m, 3H, $OCH_2^aCH_2N$), 3.71 (m, 1H, OCH_2^b), 3.95 (ddd, 1H, $J_{5,4}$ 10.0, $J_{5,6b}$

5.0, $J_{5,6a}$ 2.3 Hz, H-5), 4.07 (dd, 1H, $J_{6a,6b}$ 12.2, $J_{6a,5}$ 2.3 Hz, H-6^a), 4.28 (dd, 1H, $J_{6b,6a}$ 12.2, $J_{5,6b}$ 5.3 Hz, H-6^b), 4.96 (d, 1H, $J_{1,2a}$ 3.6 Hz, H-1), 4.98 (dd, 1H, $J_{4,3}$ 9.6, $J_{4,5}$ 10.0 Hz, H-4), 5.23 (ddd, 1H, $J_{3,2a}$ 11.0, $J_{3,4}$ 9.6, $J_{3,2b}$ 5.3 Hz, H-3), 6.04 (s, 1H, NH); β anomer: δ 1.75 (m, 1H, H-2^a), 2.00 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.17 (ddd, 1H, *J* 12.8, *J* 4.8, $J_{2b,1}$ 2.0 Hz, H-2^b), 4.13 (dd, 1H, *J* 12.3, *J* 2.3 Hz, H-6^a), 4.58 (dd, 1H, *J* 9.6, $J_{1,2b}$ 2.0 Hz, H-1); ^{13}C NMR ($CDCl_3$): α anomer: δ 20.58, 20.83 ($3CH_3$), 23.10 (CH_3), 30.73 (C-2), 39.01 (CH_2NH), 62.24 (C-6), 66.67, 67.91, 68.77, 68.99 (C-3, OCH_2, C-4, C-5), 97.01 (C-1), 169.66, 170.03, 170.19, 170.54 (4C=O); ESI-MS *m*/*z* calcd for $C_{16}H_{25}NO_9$: 398.4 [M+Na]$^+$. Found: 398.0.

1.8.2. *N*-[3′-(3,4,6-Tri-*O*-acetylo-2-deoxy-D-*arabino*-hexopyranosyl)propoxy]acetamide (9b)

The mixture of anomers was eluted; R_f 0.62 (solvent E); ^{1}H NMR ($CDCl_3$): α anomer: δ 1.85 (m, 4H, CH_2, H-2^a), 2.01 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.26 (ddd, 1H, *J* 13.0, $J_{2b,3}$ 5.4, *J* 1.0 Hz, H-2^b), 3.47 (m, 3H, $OCH_2^aCH_2N$), 3.71 (td, 1H, *J* 9.0, *J* 5.7, *J* 5.7, OCH_2^b), 3.95 (ddd, 1H, $J_{5,4}$ 9.9, $J_{5,6b}$ 4.6, $J_{5,6a}$ 2.6 Hz, H-5), 4.06 (dd, 1H, $J_{6a,6b}$ 12.2, $J_{6a,5}$ 2.6 Hz, H-6^a), 4.28 (dd, 1H, $J_{6b,6a}$ 12.2, $J_{5,6b}$ 4.6 Hz, H-6^b), 4.96 (d, 1H, *J* 2.8 Hz, H-1), 4.98 (dd, 1H, $J_{4,3}$ 9.6, $J_{4,5}$ 9.9 Hz, H-4), 5.23 (ddd, 1H, $J_{3,2a}$ 11.7, $J_{3,4}$ 9.6, $J_{3,2b}$ 5.4 Hz, H-3), 5.92 (s, 1H, NH); β anomer: δ 1.97 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.26 (ddd, 1H, $J_{2b,2a}$ 12.5, $J_{2b,3}$ 4.6, $J_{2b,1}$ 1.8 Hz, H-2^b), 4.15 (dd, 1H, *J* 12.2, *J* 2.5 Hz, H-6^a), 4.57 (dd, 1H, $J_{1,2a}$ 9.7, $J_{1,2b}$ 2.0 Hz, H-1); ^{13}C NMR ($CDCl_3$): α anomer: δ 20.86, 20.91, 21.09 ($3CH_3$), 23.43 (CH_3), 29.25 (CH_2) 35.11 (C-2), 37.97 (CH_2NH), 62.65 (C-6), 66.59, 68.11, 69.14, 69.46 (C-3, OCH_2, C-4, C-5), 97.21 (C-1), 169.96, 170.36, 170.49, 170.87 (4C=O); ESI-MS *m*/*z* calcd for $C_{17}H_{27}NO_9$: 412.2 [M+Na]$^+$. Found: 412.1.

1.8.3. *N*-[2′-(3,4,6-Tri-*O*-acetylo-2-deoxy-α-D-*lyxo*-hexopyranosyl)ethoxy]acetamide (9c)

$[\alpha]_D^{25}$ +103.7 (*c* 2.57, MeOH); R_f 0.45 (solvent E); ^{1}H NMR ($CDCl_3$): δ 1.89 (dd, 1H, $J_{2a,3}$ 5.0Hz, *J* 12.4 Hz, H-2^b), 2.00 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.08 (m, 4H, CH_3, H-2^a), 2.15 (s, 3H, CH_3), 3.47 (m, 3H, $OCH_2^aCH_2N$), 3.71 (ddd, 1H, *J* 3.0Hz, *J* 6.2Hz, *J* 10.1 Hz, OCH_2^b), 4.11 (m, 3H, H-5, H-6^a, H-6^b), 5.02 (d, 1H, $J_{4,3}$ 3.0 Hz, H-4), 5.26 (ddd, 1H, $J_{3,4}$ 3.0, $J_{3,2a}$ 5.0, *J* 12.4, H-3), 5.32 (d, 1H, *J* 3.0 Hz, H-1), 5.97 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 20.92, 23.40 ($4CH_3$), 30.23 (C-2), 39.41 (CH_2NH), 62.62 (C-6), 66.16, 66.62, 67.00, 67.22 (C-3, OCH_2, C-4, C-5), 97.80 (C-1), 170.0, 170.19, 170.33, 170.45 (4C=O); ESI-MS *m*/*z* calcd for $C_{16}H_{25}NO_9$: 398.4 [M+Na]$^+$. Found: 398.2.

1.8.4. *N*-[3′-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hexopyranosyl)propoxy]acetamide (9d)

$[\alpha]_D^{25}$ +93.7 (*c* 0.97, MeOH); R_f 0.46 (solvent E); ^{1}H NMR ($CDCl_3$): δ 1.82 (m, 5H, CH_2, H-2^a, H-3), 2.00 (s, 4H, CH_3, H-2^b), 2.05 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 3.37 (m, 2H, CH_2N), 3.48 (td, 1H, *J* 10.0, *J* 5.6, *J* 5.6, OCH_2^a), 3.59 (1H, *J* 10.0, *J* 5.9, *J* 5.9, OCH_2^b), 3.89 (ddd, 1H, $J_{5,4}$ 10.1, $J_{5,6b}$ 5.2, $J_{5,6a}$ 2.5 Hz, H-5), 4.09 (dd, 1H, $J_{6a,6b}$ 12.0, $J_{6a,5}$ 2.5 Hz, H-6^a), 4.25 (dd, 1H, $J_{6b,6a}$ 12.0, $J_{6b,5}$ 5.2 Hz, H-6^b), 4.73 (td, 1H, $J_{4,5}$ 10.1, *J* 4.8, *J* 4.8 Hz, H-4), 4.81 (br s, 1H, H-1), 5.99 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 20.82, 21.05 ($2CH_3$), 23.29, 24.03, 28.73, 29.25 (CH_3, C-2, C-3, CH_2), 37.72 (CH_2NH), 63.32, 65.76, 67.89, 68.69, (OCH_2, C-4, C-5, C-6), 96.48 (C-1), 169.92, 196.96, 170.86, (3C=O); ESI-MS *m*/*z* calcd for $C_{15}H_{25}NO_7$: 354.2 [M+Na]$^+$. Found: 354.5.

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