# Synthesis of Novel Guanidinoglycoside: 2-Glycosylamino 4,5-dihydro-6-pyrimidinone

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Guanidine moiety is an important feature commonly found in many biologically active compounds.[1] For example, Streptothricin **1**, one of the first actinomycete antibiotics reported in the early 40's,[2] possesses a cyclic guanidine moiety attached to the reducing end of a sugar (Figure 1). Several new members of the family have been discovered thus far.[3] However, despite their broad spectrum of potent antimicrobial and antiviral activities, none of them has been brought into medical use because of cytotoxicity.[4] Recently, guanidine-containing sugars have attracted the attention of the pharmaceutical industry. For example, Zanamivir,[5] a neuraminidase inhibitor, is now marketed as a drug for anti-influenza. Goodman has identified some guanidinoglycosides with improved anti-HIV activities,[6] while both Wong[7] and Merrer[8] have developed six- and seven-membered ring cyclic guanidine-sugars, respectively, as new classes of transition-state mimics of enzymatic glycosidic cleavage. Preliminary research on glucoguanidinium derivative **2**, and its galactoguanidinium analogue has shown that they were inhibitors of the corresponding $\beta$- and α-glycosidases.[9] Similarly, 5,6-dihydroisocytidine **3** was reported in the early 70's to be involved in the cytosine mutagenic process.[10] However, this class of compounds was very poorly studied during the last two decades. On the basis of the above results, it will be of great interest to develop novel compounds containing similar structural feature as well as possessing the desired biological activity. A novel class of guanidinoglycosides **4** was thus designed and synthesized.

Since the base's structure of 5,6-dihydroisocytidine **3** closely resembled that of guanidinoglycosides **4**, their related literature synthetic routes were carefully studied.[11] In general, the reported methods for the synthesis of compound **3** and its base counterpart fell into four classes: (i) hydrogenation of isocytidine counterpart over 5% rhodium−carbon;[10b] (ii) condensation of guanidines with acrylates;[11a] (iii) reaction of guanidines with diphenylcyclopropenone;[11b] and (iv) intramolecular cyclization of guanidine intermediate in refluxing concentrated hydrochloric acid.[11c] These methods employed fairly harsh conditions and were restricted to a limited choice of substituents on the pyrimidinone.

While searching for a milder condition for the synthesis of guanidinoglycosides **4**, we came across a report by Pintér and co-workers.[12] They had employed an iminophosphorane-based approach to generate unsymmetrical glycosyl carbodiimides from glycosyl isothiocyanates. In their work, one of the carbodiimides was reacted with morpholine to yield the guanidine derivative. In view of its mild conditions, this approach was adapted to the synthesis of glycosyl carbodiimides in our work. The commercially available $\beta$-glucosyl isothiocyanate was first employed in our model study (Scheme 1). The formation of glucosyl carbodiimide **5a** proceeded smoothly and completely in 2 h. The crude product was purified via flash chromatography as prolonged purification time usually led to the formation of the corresponding urea. The addition of methyl (*S*)-3-amino-3-phenylpropanoate to the purified carbodiimide **5a** gave the guanidine intermediate, which underwent spontaneous cyclization in the presence of $Et_3N$ to yield the dihydropyrimidinone.

In theory, there are two possible cyclization pathways for the guanidine intermediate, that is, either via the benzylamine to give the guanidinoglycoside **4a**, or via the glycosylamine to form the guanidinoglycoside **6**. In our hands, two products corresponding to the α and $\beta$ anomers of **4a** were obtained. Their structures were carefully studied using $^1$H, $^{13}$C, and 2D NMR spectroscopy. For the α-guanidinoglycoside **4a** (Figure 2), $^{13}$C NMR signal associated with C-1′ of the glucosyl residue at 80.64 ppm was consistent with an N,O-acetal structure.[13] Furthermore, its HMBC spectrum revealed correlated signals between $CH_2$N-1 proton and C-2 (150.50 ppm), C-6 (167.48 ppm). No correlation was observed between H-1′ and C-6. The same correlation was observed for the $\beta$-guanidinoglycoside **4a**, which confirmed that the reaction proceeded solely to compound **4a**. The result is not surprising as the alkylamine is more reactive and sterically less hindered than the glycosylamine.

$^1$H−$^{15}$N 2D NMR experiments were also carried out to determine the location of imino-group in compound **4a**

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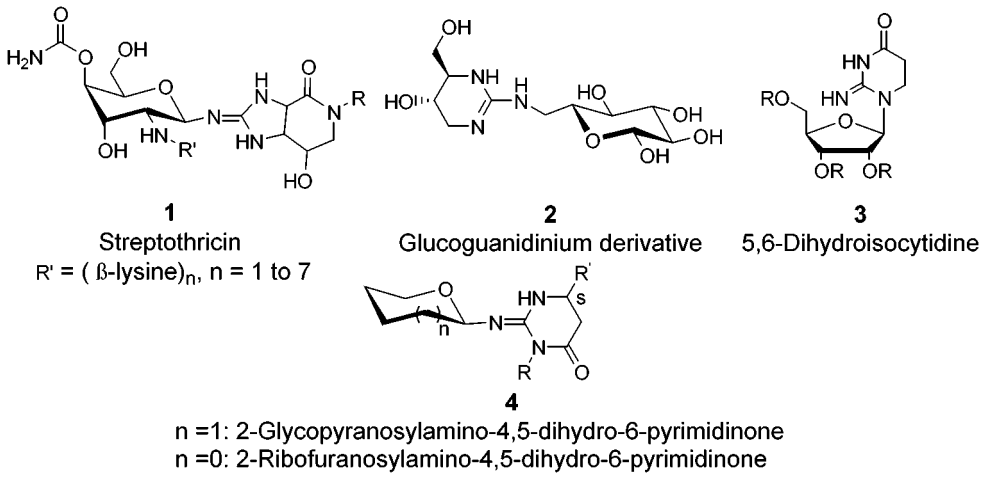
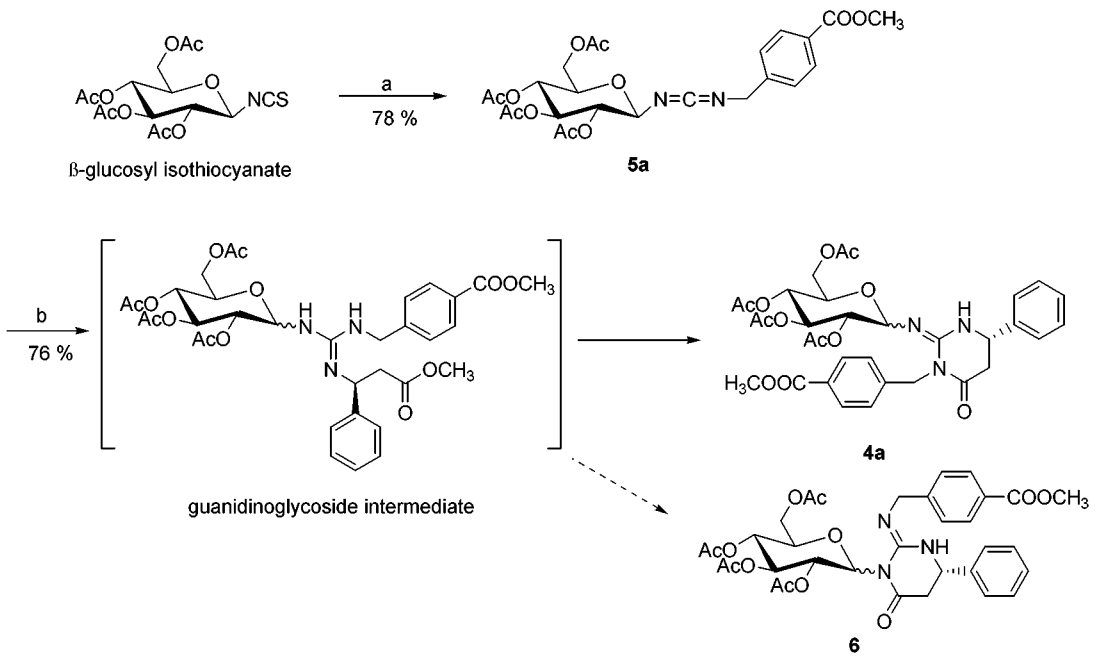



**Figure 1.** Structures of guanidinoglycosides.

**Scheme 1**[a]




[a] Reagents and conditions: (a) 4-$MeOOCC_6H_4CH_2N_3$, $PPh_3$, toluene, rt, 2 h; (b) $MeOOCCH_2CH(Ph)NH_2$·HCl, $Et_3N$, $CH_2Cl_2$, rt, 12 h.

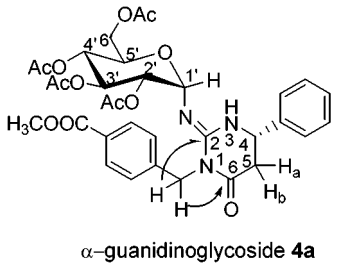



**Figure 2.** $^1H-^{13}C$ HMBC correlation of compound **4a**.

(α-anomer). The signal of a secondary amine at 83.79 ppm from the spectrum of $^1H-^{15}N$ HSQC was confirmed as N-3. In addition, the signals observed from the spectrum of $^1H-^{15}N$ HMBC (Figure 3) indicated that there were three pairs of correlations between N-3 (83.79 ppm) and H-5a/H-5b, N-1 (152.84 ppm) and $CH_2N$-1, as well as N-2 (176.28 ppm) and H-1′, H-2′. This study showed that there was no amino−imino tautomerism at the guanidine moiety and therefore confirmed the structure of α-guanidinoglycoside **4a**.

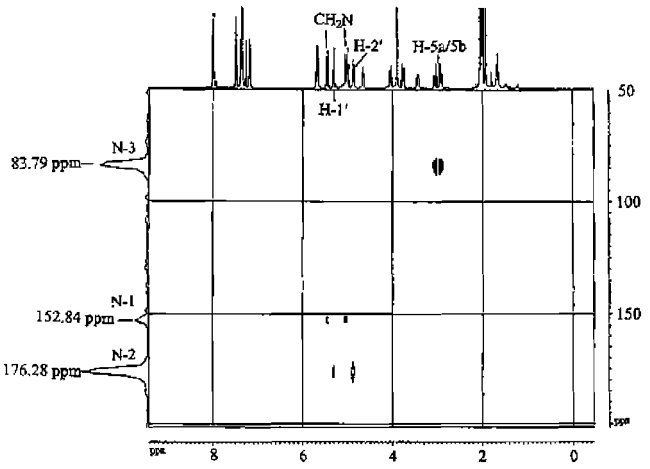
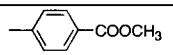
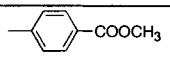
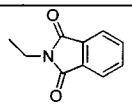
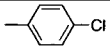
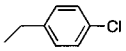
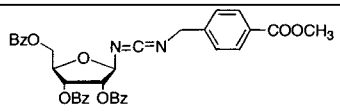
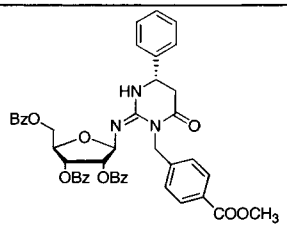



**Figure 3.** 400 MHz $^1H-^{15}N$ HMBC 2D NMR spectrum of compound **4a**. A solution of 80% $MeNO_2$ in $CDCl_3$ was used as reference at 380 ppm.

Several different glycosyl isothiocyanates, azides, and *β*-amino acid methyl esters were employed in the syn-

**Table 1. Guanidinylation and Cyclization Products and Corresponding Carbodiimides**

| Entry | Carbodiimide | Guanidinoglycoside product | Ratio (α:β) |
|---|---|---|---|
| 1 | **5a**: X = OAc; Y =  | **4a**: Z =  | 2:1 |
| 2 | **5b**: X = NHAc; Y =  | **4b**: Z =  | α only |
| 3 | **5c**: X = OAc; Y =  | **4c**: Z =  <br>**4d**: Z =  | 1:1<br>1:1 |
| 4 | **5d**: X = OAc; Y =  | **4e**: Z =  <br>**4f**: Z =  | 8:1<br>3:1 |
| 5 | **5e**:  | **4g**:  | β only |

thesis of guanidinoglycosides **4**, which allowed the stepwise introduction of substituents into the 4,5-dihydro-6-pyrimidinone. Following the same synthetic route as shown in Scheme 1, compounds **4b**−**g** (Table 1) were synthesized. The respective glycosyl isothiocyanates were prepared according to the reported method[14] by heating glycosyl bromide[15] with potassium thiocyanate in the presence of tetrabutylammonium hydrogen sulfate. Five carbodiimides **5a**−**e** (Table 1) were synthesized starting from their respective isothiocyanates by reacting with different azides. The yield of **5b** was relatively low as compared to the other carbodiimides; this was mainly due to the low solubility of the corresponding isothiocyanate in the tandem aza-Wittig reaction. Carbodiimides **5a** and **5c** reacted readily and cyclized spontaneously upon addition of (*S*)-methyl 3-amino-3-phenylpropanoate to afford compounds **4a** and **4c**. Heating was required for complete cyclization in compounds **4d**−**f**. When (*S*)-methyl 3-amino-5-phenylpentanoate was employed to react with carbodiimide **5a**, only partial cyclization occurred to afford the dihydropyrimidinone as a minor product. No further cyclization occurred upon heating at 80 °C in neat $Et_3N$ (data not shown). Urea formation was observed during the guanylation of carbodiimides **5b** and **5e**, which might contribute to their relatively low yields.

The structure elucidations of **4b**−**g** were also carried out and were in accordance with the structure of **4a**. It was worth mentioning that while all the carbodiimides **5a**−**e** retained the $\beta$ configuration ($J_{1-2}$ = 8.7−9.1 Hz), compounds **4a**−**f** underwent anomerization at C-1′ during the guanylation step. Compounds **4a**, **4c**−**f** were isolated as α and $\beta$ mixtures, whereas compounds **4b** was isolated as α anomer, and compound **4g** was isolated as $\beta$ anomer only. This observation was in consistent with the Lemieux[16] anomeric effect.

The seven guanidinoglycosides **4a**−**g** were deprotected (2 M $NH_3$ in MeOH for **4a**−**f** and 0.5 M NaOMe in MeOH for **4g**) and screened as α and $\beta$ anomeric mixtures against MRSA and *E. coli*. Although they were found to be inactive, they were not cytotoxic up to 100 $\mu$g/mL toward human embryonal lung MRC5 cells and human hepatoma HuH7 cells (Streptothricin D was cytotoxic toward 3T3 cells at 20 $\mu$g/mL).[3d] Little precedent exists for the synthesis as well as the biological application of monosaccharides with a C-1′ guanidino-moiety. The synthetic route described herein therefore provides a convenient and efficient way to synthesize the novel 2-glycosylamino-4, 5-dihydro-6-pyrimidinone for future biological evaluation.

## Experimental Section

All chemicals were obtained from commercial suppliers and used without further purification. Analytical TLC was carried out on precoated glass plates (Merck silica gel 60, $F_{254}$). Column

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chromatography was performed with silica gel (70−230 mesh) from Merck. All NMR spectra were recorded with a Bruker Avance DMX 400 MHz instrument in $CDCl_3$ solutions. Assignments of α and β anomers were based on the sugar H1−H2 coupling constant. High-resolution mass spectra were determined using a Marina Biospectrometry workstation via $ESI^+$. The purification solvent system employed for compounds **5a**−**d**, **4a**−**f** was 50% hexane in EtOAc, and for compounds **5e** and **4g** was 75% hexane in EtOAc. HPLC analysis was performed with a Hewlett-Packard 1040 equipped with a Hypersil ODS C18 reverse-phase column (2.1 × 200 mm). Runs used two gradients (A: 40% to 100% $CH_3CN$ in $H_2O$ with 0.1% of TFA; B: 30% to 100% $CH_3CN$ in $H_2O$ with 0.1% of TFA; flow rate: 0.3 mL/min over 20 min). The HPLC purities for compounds **4a**, **4b** and **4d** were determined at 220 nm.

**General Procedure for Compounds 4.** A mixture of glycosyl isothiocyanate (0.1−0.5 mmol) and triphenylphosphine (1.1 equiv) in anhydrous toluene was stirred for 10 min. Azides (1.1 equiv) was then added, and the reaction mixture was stirred for another 2 h. The carbodiimide intermediate **5** purified on column chromatography was redissolved in $CH_2Cl_2$, followed by the addition of β-amino acid methyl ester hydrochloride salt (1.1 equiv with respect to compound **5**) and $Et_3N$ (1.8 equiv). The reaction mixture was stirred for 12 h, and the crude guanidinoglycosides **4** were purified on preparative TLC plate to yield the α and β anomers separately.

***N*-[4-(Methoxycarbonyl)benzyl]-*N*′-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)carbodiimide 5a** (202 mg, yield 78%, white solid): $^1$H NMR δ 1.90, 1.92, 1.97 (3s, 12H, $COCH_3$), 3.68 (ddd, 1H, $J$ = 9.9, 4.7, 2.2 Hz, H-5), 3.81 (s, 3H, $OCH_3$), 4.04 (dd, 1H, $J$ = 12.4, 2.0 Hz, H-6a), 4.14 (dd, 1H, $J$ = 12.4, 4.8 Hz, H-6b), 4.41, 4.47 (ABd, 2H, $J$ = 15.2 Hz, $CH_2Ph$), 4.59 (d, 1H, $J$ = 8.8 Hz, H-1), 4.82 (t, 1H, $J$ = 9.1 Hz, H-2), 4.99 (t, 1H, $J$ = 9.7 Hz, H-4), 5.09 (t, 1H, $J$ = 9.5 Hz, H-3), 7.29 (d, 2H, $J$ = 8.1 Hz, 4-$MeOCOC_6H_4$), 7.91 (d, 2H, $J$ = 8.2 Hz, 4-$MeOCOC_6H_4$); $^{13}$C NMR δ 20.4, 20.5, 20.6, 49.4, 52.0, 61.8, 68.1, 72.8(1), 72.8(3), 73.8, 84.4, 127.1, 129.5, 129.9, 137.4, 142.3, 166.5, 169.2, 170.0, 170.4; HRMS calcd for $C_{24}H_{28}N_2O_{11}Na$ $(M + Na)^+$ 543.1593, found 543.1596.

**(*S*)-1-[4-(Methoxycarbonyl)benzyl]-2-(2′,3′,4′,6′-tetra-*O*-acetyl-D-glucopyranosyl) amino-4-phenyl-4, 5-dihydro-6-pyrimidinone 4a** (197 mg, yield 76%, α:β = 2:1), α anomer (white solid, 100% HPLC purity): $^1$H NMR δ 1.93, 1.99, 2.02, 2.05 (4s, 12H, $COCH_3$), 2.93 (dd, 1H, $J$ = 16.24, 8.40 Hz, H-5a), 3.06 (dd, 1H, $J$ = 16.24, 4.96 Hz, H-5b), 3.44 (br d, 1H, $J$ = 9.72 Hz, H-5′), 3.76 (dd, 1H, $J$ = 12.43, 2.02 Hz, H-6a′), 3.90 (s, 3H, $OCH_3$), 4.04 (dd, 1H, $J$ = 12.39, 3.66 Hz, H-6b′), 4.65 (dd, 1H, $J$ = 8.10, 5.14 Hz, H-4), 4.87 (dd, 1H, $J$ = 10.06, 4.06 Hz, H-2′), 5.01 (t, 1H, $J$ = 9.70 Hz, H-4′), 5.04 (d, 1H, $J$ = 13.98 Hz, $NCH_2$), 5.31 (d, 1H $J$ = 4.07 Hz, H-1′), 5.45 (d, 1H, $J$ = 14.06 Hz, $NCH_2$), 5.65 (br s, 1H, NH), 5.68 (t, 1H, $J$ = 9.72 Hz, H-3′), 7.18−7.20 (m, 2H, $C_6H_5$), 7.36−7.38 (m, 3H, $C_6H_5$), 7.48 (d, 2H, $J$ = 8.16 Hz, 4-$MeOCOC_6H_4$), 7.99 (d, 2H, $J$ = 8.12 Hz, 4-$MeOCOC_6H_4$); $^{13}$C NMR δ 20.5, 20.6, 20.8, 20.9, 39.9, 43.8, 51.4, 52.0, 62.0, 67.7, 68.6, 70.5, 71.7, 80.6, 125.8, 128.9, 129.1, 129.4, 129.7, 139.1, 143.3, 150.5, 167.0, 167.5, 169.7, 170.2, 170.5, 170.6; HRMS calcd for $C_{33}H_{38}N_3O_{12}$ $(M + H)^+$ 668.2456, found 668.2453.

β anomer (colorless syrup): $^1$H NMR δ 1.40, 1.73, 1.92, 1.95 (4s, 12H, $COCH_3$), 2.68 (dd, 1H, $J$ = 16.22, 10.78 Hz, H-5a), 2.86 (dd, 1H, $J$ = 16.38, 4.38 Hz, H-5b), 3.68−3.72 (m, 1H, H-5′), 3.83 (s, 3H, $OCH_3$), 3.85 (dd, 1H, $J$ = 12.60, 7.25 Hz, H-6a′), 4.05 (d, 1H, $J$ = 10.80 Hz, H-6b′), 4.62 (br d, 1H, $J$ = 7.34 Hz, H-4), 4.75 (d, 1H, $J$ = 8.65 Hz, H-1′), 4.90 (t, 1H, $J$ = 9.72 Hz, H-4′), 4.99 (d, 1H, $J$ = 14.53 Hz, $NCH_2$), 5.06 (t, 1H, $J$ = 9.21 Hz, H-2′), 5.09 (d, 1H, $J$ = 15.13 Hz, $NCH_2$), 5.19 (t, 1H, $J$ = 9.52 Hz, H-3′), 5.98 (s, 1H, NH), 7.24−7.33 (m, 7H, aromatic), 7.86 (d, 2H, $J$ = 8.18 Hz, 4-$MeOCOC_6H_4$); $^{13}$C NMR δ 19.8, 20.6, 40.6, 44.0, 51.8, 52.0, 62.7, 68.7, 72.5, 73.0, 73.9, 86.3, 125.8, 128.1, 128.8, 129.3, 129.5, 140.0, 143.1, 151.3, 167.3, 169.4, 169.5, 170.3, 170.5.

***N*-[4-(Methoxycarbonyl)benzyl]-*N*′-(2-acetamido-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)carbodiimide 5b** (47 mg, 53%, light yellow solid): $^1$H NMR δ 1.92, 2.03, 2.08 (3s, 12H, $COCH_3$), 3.72 (ddd, 1H, $J$ = 9.72, 4.54, 2.33 Hz, H-5), 3.91 (s, 3H, $OCH_3$), 3.96 (t, 1H, $J$ = 9.70 Hz, H-2), 4.14 (dd, 1H, $J$ = 12.15, 1.58 Hz, H-6a), 4.23 (dd, 1H, $J$ = 12.30, 4.81 Hz, H-6b), 4.52, 4.59 (ABd, 2H, $J$ = 15.10 Hz, $NCH_2$), 4.71 (d, 1H, $J$ = 9.09 Hz, H-1), 5.06 (t, 1H, $J$ = 9.63 Hz, H-4), 5.17 (t, 1H, $J$ = 9.86 Hz, H-3), 5.50 (d, 1H, $J$ = 9.14 Hz, NH), 7.39 (d, 2H, $J$ = 8.06 Hz, $C_6H_4$), 8.00 (d, 2H, $J$ = 8.15 Hz, $C_6H_4$); $^{13}$C NMR δ 20.6, 20.7, 23.3, 49.5, 52.2, 56.3, 62.0, 68.2, 72.6, 73.9, 85.2, 127.1, 129.4, 129.9, 137.3, 142.5, 166.7, 169.3, 170.4, 170.7, 171.1; HRMS calcd for $C_{24}H_{29}N_3O_{10}Na$ $(M + Na)^+$ 542.1753, found 542.1750.

**(*S*)-1-[4-(Methoxycarbonyl)benzyl]-2-(2′-acetamido-3′,4′,6′-tri-*O*-acetyl-α-D-glucopyranosyl)amino-4-phenyl-4, 5-dihydro-6-pyrimidinone 4b** (7 mg, yield 33%, α only, light brown syrup, 100% HPLC purity): $^1$H NMR δ 1.62, 1.86, 1.96, 1.98 (4s, 12H, $COCH_3$), 2.91 (dd, 1H, $J$ = 16.28, 7.87 Hz, H-5a), 3.06 (dd, 1H, $J$ = 16.29, 5.18 Hz, H-5b), 3.42 (br d, 1H, $J$ = 9.14 Hz, H-5′), 3.72 (dd, 1H, $J$ = 12.42, 2.07 Hz, H-6a′), 3.83 (s, 3H, $OCH_3$), 4.00 (dd, 1H, $J$ = 12.46, 3.62 Hz, H-6b′), 4.22 (td, 1H, $J$ = 10.05, 3.92 Hz, H-2′), 4.65 (br t, 1H, $J$ = 5.92 Hz, H-4), 4.89 (d, 1H, $J$ = 3.88 Hz, H-1′), 5.01 (t, 1H, $J$ = 9.77 Hz, H-4′), 5.21 (br s, 2H, $NCH_2$), 5.29 (t, 1H, $J$ = 9.91 Hz, H-3′), 5.32 (br d, 1H, $J$ = 7.13 Hz, NH), 5.72 (br s, 1H, NH), 7.13−7.15 (m, 2H, aromatic), 7.27−7.34 (m, 5H, aromatic), 7.94 (d, 2H, $J$ = 8.11 Hz, 4-$CH_3OCOC_6H_4$); $^{13}$C NMR δ 20.5, 20.8, 23.1, 39.6, 44.1, 51.4, 52.1, 52.2, 62.0, 68.1, 68.3, 71.7, 82.1, 125.7, 127.6, 129.1, 129.4, 130.0, 139.0, 143.6, 151.0, 166.7, 167.5, 169.3, 169.8, 170.6, 171.5; HRMS calcd for $C_{33}H_{39}N_4O_{11}$ $(M + H)^+$ 667.2616, found 667.2614.

***N*-[2-(*N*-Phthalimido)ethyl]-*N*′-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)carbodiimide 5c** (150 mg, yield 72%, colorless syrup): $^1$H NMR δ 1.92, 1.95, 1.96, 2.01 (4s, 12H, $COCH_3$), 3.54−3.64 (m, 2H, $NCH_2$), 3.64−3.67 (m, 1H, H-5), 3.80−3.84 (m, 2H, $NCH_2$), 4.01 (dd, 1H, $J$ = 12.49, 2.09 Hz, H-6a), 4.11 (dd, 1H, $J$ = 12.35, 4.81 Hz, H-6b), 4.58 (d, 1H, $J$ = 8.74 Hz, H-1), 4.82 (t, 1H, $J$ = 9.12 Hz, H-2), 5.00 (t, 1H, $J$ = 9.65 Hz, H-4), 5.08 (t, 1H, $J$ = 9.44 Hz, H-3), 7.68−7.71 (m, 2H, $C_6H_4$), 7.79−7.82 (m, 2H, $C_6H_4$); $^{13}$C NMR δ 20.5, 20.7, 38.4, 43.9, 61.8, 68.1, 72.6, 72.9, 73.7, 84.5, 123.4, 131.9, 134.2, 136.6, 168.0, 169.3, 170.1, 170.6; HRMS cacld for $C_{25}H_{27}N_3O_{11}Na$ $(M + Na)^+$ 568.1546, found 568.1545.

**(*S*)-1-[2-(*N*-Phthalimido)ethyl]-2-(2′,3′,4′,6′-tetra-*O*-acetyl-D-glucopyranosyl)amino-4-phenyl-4, 5-dihydro-6-pyrimidinone 4c** (41 mg, yield 65%, α:β = 1:1), α anomer (light yellow syrup): $^1$H NMR δ 2.03, 2.04, 2.05, 2.08 (4s, 12H, $COCH_3$), 2.64−2.68 (m, 2H, H-5), 4.02 (dd, 1H, $J$ = 12.48, 1.96 Hz, H-6a′), 4.13−4.17 (m, 3H, H-5′, $NCH_2$), 4.28 (dd, 2H, $J$ = 12.15, 3.46 Hz, H-6b′), 4.22−4.29 (m, 1H, $NCH_2$), 4.42 (ddd, 1H, $J$ = 13.32, 6.78, 2.89 Hz, $NCH_2$), 4.54 (dd, 1H, $J$ = 10.19, 5.69 Hz, H-4), 4.94 (dd, 1H, $J$ = 10.03, 4.19 Hz, H-2′), 5.11 (t, 1H, $J$ = 9.76 Hz, H-4′), 5.32 (d, 1H, $J$ = 4.10 Hz, H-1′), 5.61 (br s, 1H, NH), 5.67 (t, 1H, $J$ = 9.65 Hz, H-3′), 7.30 (d, 2H, $J$ = 6.62 Hz, $C_6H_5$), 7.37−7.43 (m, 3H, $C_6H_5$), 7.69−7.72 (m, 2H, phthalimide), 7.82−7.85 (m, 2H, phthalimide); $^{13}$C NMR δ 20.7(0), 20.7(1), 20.7(7), 20.8, 36.3, 40.0, 40.1, 51.6, 62.2, 67.8, 68.7, 70.8, 71.7, 81.0, 123.2, 126.2, 129.1, 129.4, 132.1, 133.9, 138.8, 150.8, 168.2, 168.6, 169.8, 170.2, 170.5, 170.7; HRMS calcd for $C_{34}H_{37}N_4O_{12}$ $(M + H)^+$ 693.2409, found 693.2409. Anal. Calcd for $C_{34}H_{36}N_4O_{12}$ (692.2): C, 58.96; H, 5.24; N, 8.09. Found: C, 57.24; H, 5.56; N, 7.78.

β anomer: $^1$H NMR δ 1.26, 1.92, 1.93, 1.98 (4s, 12 H, $COCH_3$), 2.48 (dd, 1H, $J$ = 16.01, 12.47 Hz, H-5a), 2.68 (dd, 1H, $J$ = 15.98, 2.20 Hz, H-5b), 3.51 (t, 1H, $J$ = 8.56 Hz, H-5′), 3.58 (dd, 1H, $J$ = 11.69, 7.90 Hz, H-6a′), 3.82−3.86 (m, 1H, $NCH_2$), 3.89 (d, 1H, $J$ = 11.39 Hz, H-6b′), 3.93−3.97 (m, 1H, $NCH_2$), 3.98−4.03 (m, 1H, $NCH_2$), 4.26−4.31 (m, 1H, $NCH_2$), 4.49 (t, 1H, $J$ = 9.68 Hz, H-4′), 4.55 (t, 1H, $J$ = 8.72 Hz, H-1′), 4.57−4.61 (m, 1H, H-4), 4.63 (t, 1H, $J$ = 9.06 Hz, H-2′), 5.07 (t, 1H, $J$ = 9.46 Hz, H-3′), 5.76 (br s, 1H, NH), 7.26−7.34 (m, 5H, $C_6H_5$), 7.65−7.67 (m, 2H phthalimide), 7.77−7.80 (m, 2H, phthalimide); $^{13}$C NMR δ 19.6, 20.6, 20.7, 20.8, 36.9, 40.0, 40.8, 52.0, 62.9, 68.7, 72.7, 72.8, 73.5, 85.9, 123.2, 125.9, 128.7, 129.3, 132.5, 133.8, 140.4, 151.8, 167.8, 168.6, 169.2, 169.6, 170.3, 170.5.

**(*S*)-1-[2-(*N*-Phthalimido)ethyl]-2-(2′,3′,4′,6′-tetra-*O*-acetyl-D-glucopyranosyl)amino-4-(2-thienyl)-4,5-dihydro-6-pyrimidinone 4d** (47 mg, yield 73%, α:β = 1:1), α anomer (light yellow syrup, 91% and 100% HPLC purity in A and B solvent systems, respectively): $^1$H NMR δ 1.99, 2.02, 2.07, 2.11 (4s, 12H, $COCH_3$), 2.32 (dd, 1H, $J$ = 16.01, 10.04 Hz, H-5a), 2.57 (dd, 1H, $J$ = 16.01, 4.16 Hz, H-5b), 2.67 (dd, 1H, $J$ = 13.90, 9.26 Hz, $CH_2$ of thienyl), 2.82 (dd, 1H, $J$ = 13.95, 4.44 Hz, $CH_2$ of thienyl), 3.55−3.61 (m, 1H, H-4), 3.63 (dd, 1H, $J$ = 12.47, 1.28 Hz, H-6a′), 4.02−4.13 (m, 4H, H-5′, H-6b′, $NCH_2$), 4.27−4.29 (m, 2H, $NCH_2$), 4.91 (dd, 1H, $J$ = 10.02, 4.24 Hz, H-2′), 5.07 (t, 1H, $J$ = 9.77 Hz,

H-4′), 5.31 (d, 1H, $J$ = 4.20 Hz, H-1′), 5.59 (t, 1H, $J$ = 9.67 Hz, H-3′), 5.63 (s, 1H, NH), 6.92 (d, 1H, $J$ = 4.78 Hz, thiophene), 7.09 (br s, 1H, thiophene), 7.35 (dd, 1H, $J$ = 4.72, 2.99 Hz, thiophene), 7.68−7.72 (m, 2H, phthalimide), 7.80−7.82 (m, 2H, phthalimide); $^{13}$C NMR $\delta$ 20.7, 20.8(0), 20.8(1), 20.9, 35.9, 36.2, 37.4, 39.6, 48.2, 62.1, 67.6, 68.6, 70.7, 71.8, 80.8, 123.1, 123.2, 127.2, 127.6, 132.0, 133.9, 136.1, 150.7, 168.1, 168.5, 169.7, 170.1, 170.5, 170.8; HRMS calcd for $C_{33}H_{37}N_4O_{12}S$ $(M + H)^+$ 713.2130, found 713.2131.

$\beta$ anomer (colorless syrup): $^1$H NMR $\delta$ 1.97, 2.00, 2.06 (3s, 12H, $COCH_3$), 2.40 (dd, 1H, $J$ = 15.95, 10.01 Hz, H-5a), 2.58 (dd, 1H, $J$ = 15.93, 3.61 Hz, H-5b), 2.79 (dd, 1H, $J$ = 14.36, 8.62 Hz, $CH_2$ of thienyl), 2.87 (dd, 1H, $J$ = 14.24, 5.38 Hz, $CH_2$ of thienyl), 3.38−3.41 (m, 1H, H-5′), 3.63−3.70 (m, 1H, H-4), 3.80−3.84 (m, 1H, $NCH_2$), 3.91−4.03 (m, 4H, $NCH_2$, H-6a′, H-6b′), 4.04−4.17 (m, 1H, $NCH_2$), 4.27 (d, 1H, $J$ = 8.66 Hz, H-1′), 4.71 (t, 1H, $J$ = 9.19 Hz, H-2′), 4.79 (t, 1H, $J$ = 9.76 Hz, H-4′), 5.01 (t, 1H, $J$ = 9.57 Hz, H-3′), 5.42 (br s, 1H, NH), 6.92 (d, 1H, $J$ = 4.69 Hz, thiophene), 7.07 (br s, 1H, thiophene), 7.30 (dd, 1H, $J$ = 4.48, 3.13 Hz, thiophene), 7.63−7.66 (m, 2H, phthalimide), 7.75−7.77 (m, 2H, phthalimide); $^{13}$C NMR $\delta$ 20.6(5), 20.6(9), 20.7, 20.9, 35.6, 36.5, 37.8, 39.9, 47.5, 62.4, 68.5, 72.4, 73.1, 73.3, 86.5, 122.8, 123.3, 127.0, 127.9, 132.3, 133.8, 136.4, 150.8, 168.4, 168.6, 169.3, 169.5, 170.4, 170.5.

***N*-(4-Chlorobenzyl)-*N*′-(2,3,4,6-tetra-*O*-acetyl-$\beta$-D-glucopyranosyl)carbodiimide 5d** (128 mg, yield 63%, colorless syrup): $^1$H NMR $\delta$ 1.97, 1.99, 2.05 (3s, 12H, $COCH_3$), 3.72 (ddd, 1H, $J$ = 9.88, 4.73, 2.23 Hz, H-5), 4.10 (dd, 1H, $J$ = 12.37, 2.09 Hz, H-6b), 4.21 (dd, 1H, $J$ = 12.36, 4.82 Hz, H-6a), 4.38, 4.44 (ABd, 2H, $J$ = 14.81 Hz, $CH_2Ph$), 4.61 (d, 1H, $J$ = 8.83 Hz, H-1), 4.87 (t, 1H, $J$ = 9.11 Hz, H-2), 5.05 (t, 1H, $J$ = 9.68 Hz, H-4), 5.15 (t, 1H, $J$ = 9.46 Hz, H-3), 7.21 (d, 2H, $J$ = 8.39 Hz, $C_6H_4$), 7.29 (d, 2H, $J$ = 8.35 Hz, $C_6H_4$); $^{13}$C NMR $\delta$ 20.6(0), 20.6(3), 20.7, 49.2, 61.9, 68.1, 72.8, 72.9, 73.8, 84.5, 128.7, 128.8, 133.5, 135.8, 137.6, 169.4, 170.2, 170.6; HRMS calcd for $C_{22}H_{25}ClN_2O_9Na$ $(M + Na)^+$ 519.1149, found: 519.1145.

**(*S*)-1-(4-Chlorobenzyl)-2-(2′, 3′, 4′, 6′-tetra-*O*-acetyl-D-glucopyranosyl)amino-4-(2-thienyl)-4,5-dihydro-6-pyrimidinone 4e** (39 mg, yield 49%, $\alpha$:$\beta$ = 8:1) $\alpha$ anomer (colorless syrup): $^1$H NMR $\delta$ 1.95, 1.96(2), 1.96(5), 1.97 (4s, 12H, $COCH_3$), 2.46 (dd, 1H, $J$ = 16.14, 10.50 Hz, H-5a), 2.60 (dd, 1H, $J$ = 13.95, 9.21 Hz, $CH_2$ of thienyl), 2.77 (dd, 1H, $J$ = 16.14, 3.10 Hz, H-5b), 2.83 (dd, 1H, $J$ = 13.92, 4.52 Hz, $CH_2$ of thienyl), 3.01 (br d, 1H, $J$ = 9.82 Hz, H-5′), 3.31 (dd, 1H, $J$ = 12.30, 2.88 Hz, H-6a′), 3.55−3.59 (m, 1H, H-4), 3.75 (dd, 1H, $J$ = 12.29, 3.51 Hz, H-6b′), 4.75 (dd, 1H, $J$ = 10.18, 4.19 Hz, H-2′), 4.80 (d, 1H, $J$ = 13.98 Hz, $NCH_2$), 4.87 (t, 1H, $J$ = 9.75 Hz, H-4′), 5.15 (d, 1H, $J$ = 4.12 Hz, H-1′), 5.20 (d, 1H, $J$ = 13.94 Hz, $NCH_2$), 5.47 (br s, 1H, NH), 5.47 (t, 1H, $J$ = 9.70 Hz, H-3′), 6.80 (dd, 1H, $J$ = 5.62, 0.91 Hz, thiophene), 6.97 (d, 1H, $J$ = 1.92 Hz, thiophene), 7.20 (d, 2H, $J$ = 8.65 Hz, 4-$ClC_6H_4$), 7.26 (dd, 1H, $J$ = 4.87, 2.98 Hz, thiophene), 7.30 (d, 2H, $J$ = 8.33 Hz, 4-$ClC_6H_4$); $^{13}$C NMR $\delta$ 20.6, 20.7, 20.8, 20.9, 36.0, 37.9, 43.4, 48.3, 62.3, 67.1, 68.8, 70.4, 71.7, 80.6, 123.1, 127.4, 127.6, 128.5, 130.2, 132.6, 135.8, 136.7, 150.5, 167.8, 169.7, 170.2, 170.4, 170.5; HRMS calcd for $C_{30}H_{35}ClN_3O_{10}S$ $(M + H)^+$ 664.1732, found 664.1730. Anal. Calcd for $C_{30}H_{34}ClN_3O_{10}S$ (663.2): C, 54.26; H, 5.16; N, 6.33. Found: C, 53.59; H, 5.29; N, 6.16.

$\beta$ anomer (colorless syrup): $^1$H NMR $\delta$ 1.75, 1.95, 1.98, 2.00 (4s, 12H, $COCH_3$), 2.48 (dd, 1H, $J$ = 16.18, 9.71 Hz, H-5a), 2.70 (dd, 1H, $J$ = 16.05, 4.59 Hz, H-5b), 2.74 (dd, 1H, $J$ = 13.79, 8.03 Hz, $CH_2$ of thienyl), 2.86 (dd, 1H, $J$ = 14.07, 5.10 Hz, $CH_2$ of thienyl), 3.52−3.55 (m, 1H, H-5′), 3.60−3.64 (m, 1H, H-4), 4.00 (dd, 1H, $J$ = 12.35, 2.10 Hz, H-6a′), 4.05 (dd, 1H, $J$ = 12.25, 4.96 Hz, H-6b′), 4.46 (d, 1H, $J$ = 8.30 Hz, H-1′), 4.81 (d, 1H, $J$ = 14.26 Hz, $NCH_2$), 4.99 (d, 1H, $J$ = 14.45 Hz, $NCH_2$), 5.00 (t, 1H, $J$ = 9.39 Hz, H-4′), 5.06 (t, 1H, $J$ = 9.04 Hz, H-2′), 5.12 (t, 1H, $J$ = 9.38 Hz, H-3′), 5.50 (br s, 1H, NH), 6.89 (d, 1H, $J$ = 4.74 Hz, thiophene), 7.03 (br s, 1H, thiophene), 7.15 (d, 4H, $J$ = 8.42 Hz, $C_6H_4$), 7.19 (d, $J$ = 8.26 Hz, $C_6H_4$), 7.31 (dd, 1H, $J$ = 4.65, 2.96 Hz, thiophene); $^{13}$C NMR $\delta$ 20.4, 20.5, 20.6, 35.5, 37.8, 43.0, 47.4, 62.1, 68.3, 72.2, 73.0, 73.4, 86.4, 122.8, 127.0, 127.6, 128.1, 128.7, 129.7, 135.9, 136.3, 150.8, 167.6, 169.1, 169.2, 170.2, 170.3.

**(*S*)-1-(4-Chlorobenzyl)-2-(2′,3′,4′,6′-tetra-*O*-acetyl-$\alpha$-D-glucopyranosyl)amino-4-(4-chlorobenzyl)-4,5-dihydro-6-pyrimidinone 4f** (45 mg, yield 59%, $\alpha$:$\beta$ = 3:1) $\alpha$ anomer (colorless syrup): $^1$H NMR $\delta$ 1.94, 1.96, 1.97 (3s, 12H, $COCH_3$), 2.47 (dd, 1H, $J$ = 16.24, 9.64 Hz, H-5a), 2.51 (dd, 1H, $J$ = 13.67, 9.33 Hz, $CH_2C_6H_4$), 2.76 (dd, 1H, $J$ = 13.25, 4.68 Hz, $CH_2C_6H_4$), 2.77 (dd, 1H, $J$ = 16.55, 3.30 Hz, H-5b), 3.02 (br d, 1H, $J$ = 10.08 Hz, H-5′), 3.24 (dd, 1H, $J$ = 12.39, 2.84 Hz, H-6a′), 3.52−3.58 (m, 1H, H-4), 3.80 (dd, 1H, $J$ = 12.37, 3.41 Hz, H-6b′), 4.74 (dd, 1H, $J$ = 10.22, 4.22 Hz, H-2′), 4.79 (d, 1H, $J$ = 13.95 Hz, $NCH_2$), 4.86 (t, 1H, $J$ = 9.75 Hz, H-4′), 5.14 (d, 1H, $J$ = 4.15 Hz, H-1′), 5.20 (d, 1H, $J$ = 13.92 Hz, $NCH_2$), 5.42 (br s, 1H, NH), 5.48 (t, 1H, $J$ = 9.74 Hz, H-3′), 6.96 (d, 2H, $J$ = 8.31 Hz, 4-$ClC_6H_4$), 7.20 (d, 2H, $J$ = 7.51 Hz, 4-$ClC_6H_4$), 7.24 (d, 2H, $J$ = 8.27 Hz, 4-$ClC_6H_4$), 7.30 (d, 2H, $J$ = 8.36 Hz, 4-$ClC_6H_4$); $^{13}$C NMR $\delta$ 20.6, 20.7, 20.8, 20.9, 37.8, 41.0, 43.4, 48.8, 62.0, 67.2, 68.6, 70.4, 71.8, 80.6, 128.5, 129.3, 130.2, 130.3, 132.8, 133.5, 134.1, 136.7, 150.5, 167.6, 169.7, 170.2, 170.4; HRMS calcd for $C_{32}H_{36}Cl_2N_3O_{10}$ $(M + H)^+$ 692.1779, found 692.1775. Anal. Calcd for $C_{23}H_{35}Cl_2N_3O_{10}$ (691.2): C, 55.50; H, 5.09; N, 6.07. Found: C, 55.18; H, 5.41; N, 5.97.

$\beta$ anomer (colorless syrup): $^1$H NMR $\delta$ 1.83, 2.02, 2.05, 2.06 (4s, 12H, $COCH_3$), 2.54 (dd, 1H, $J$ = 16.09, 8.60 Hz, H-5a), 2.73 (dd, 1H, $J$ = 16.06, 4.32 Hz, H-5b), 2.76 (dd, 1H, $J$ = 13.66, 8.18 Hz, $CH_2C_6H_4$), 2.82 (dd, 1H, $J$ = 13.72, 6.31 Hz, $CH_2C_6H_4$), 3.61 (ddd, 1H, $J$ = 10.08, 4.90, 2.68 Hz, H-5′), 3.65−3.68 (m, 1H, H-4), 4.05 (dd, 1H, $J$ = 12.37, 4.92 Hz, H-6′a), 4.10(dd, 1H, $J$ = 12.37, 2.64 Hz, H-6′b), 4.60 (d, 1H, $J$ = 8.55 Hz, H-1′), 4.88 (d, 1H, $J$ = 14.24 Hz, $NCH_2$), 5.04 (d, 1H, $J$ = 14.32 Hz, $NCH_2$), 5.04 (t, 1H, $J$ = 9.61 Hz, H-4′), 5.11 (t, 1H, $J$ = 9.12 Hz, H-2′), 5.20 (t, 1H, $J$ = 9.40 Hz, H-3′), 5.68 (br s, 1H, NH), 7.11 (d, 2H, $J$ = 8.35 Hz, 4-$ClC_6H_4$), 7.22 (d, 2H, $J$ = 8.61 Hz, 4-$ClC_6H_4$), 7.26 (d, 2H, $J$ = 8.55 Hz, 4-$ClC_6H_4$), 7.33 (d, 2H, $J$ = 8.32 Hz, 4-$ClC_6H_4$); $^{13}$C NMR $\delta$ 20.6, 20.8, 37.6, 40.7, 43.3, 48.4, 62.4, 68.6, 72.4, 73.1, 73.8, 86.7, 128.3, 129.2, 129.9, 130.4, 132.8, 133.5, 134.4, 136.5, 150.4, 167.6, 169.3, 169.4, 170.3, 170.4.

***N*-[4-(Methoxycarbonyl)benzyl]-*N*′-(2,3,5-tribenzoyl-$\beta$-D-ribofuranosyl)carbodiimide 5e** (66 mg, yield 80%, white solid): $^1$H NMR $\delta$ 3.82 (s, 3H, $OCH_3$), 4.41 (d, 2H, $J$ = 3.84 Hz, $NCH_2$), 4.45−4.48 (m, 1H, H-5a), 4.59−4.65 (m, 2H, H-4, H-5b), 5.47 (d, 1H, $J$ = 4.32 Hz, H-2), 5.48 (s, 1H, H-1), 5.71 (dd, 1H, $J$ = 6.16, 4.45 Hz, H-3), 7.24−7.34 (m, 11H, aromatic), 7.82 (d, 2H, $J$ = 7.55 Hz, aromatic), 7.89−7.92 (m, 4H, aromatic), 8.00 (d, 2H, $J$ = 7.52 Hz, aromatic); $^{13}$C NMR $\delta$ 49.3, 51.9, 64.2, 71.6, 76.6, 79.0, 89.5, 127.0, 128.4, 128.5, 128.7, 128.9, 129.4, 129.5, 129.7, 129.8, 129.9, 133.2, 133.5, 133.6, 138.4, 142.3, 165.0, 165.1, 166.0, 166.6; HRMS calcd for $C_{36}H_{30}N_2O_9Na$ $(M + Na)^+$ 657.1851, found 657.1856.

**(*S*)-1-[4-(Methoxycarbonyl)benzyl]-2-(2′,3′,5′-tribenzoyl-$\beta$-D-ribofuranosyl)amino-4-phenyl-4, 5-dihydro-6-pyrimidinone 4g** (20 mg, yield 35%, light yellow solid, mp 165−168 °C, $\beta$ only): $^1$H NMR $\delta$ 2.71 (dd, 1H, $J$ = 16.16, 9.44 Hz, H-5a), 2.78 (dd, 1H, $J$ = 16.26, 4.75 Hz, H-5b), 3.76 (s, 3H, $OCH_3$), 4.29 (dd, 1H, $J$ = 11.40, 5.09 Hz, H-5a′), 4.46−4.54 (m, 2H, H-4′, H-5b′), 4.56−4.59 (m, 1H, H-4), 4.91, 5.00 (ABd, 2H, $J$ = 14.37 Hz, $NCH_2$), 5.46 (s, 1H, H-1′), 5.56 (d, 1H, $J$ = 4.50 Hz, H-2′), 5.68 (dd, 1H, $J$ = 7.00, 4.60 Hz, H-3′), 6.10 (s, 1H, NH), 7.04−7.54 (m, 16H, aromatic), 7.86 (d, 4H, $J$ = 8.04 Hz, aromatic), 7.91 (d, 4H, $J$ = 7.62 Hz, aromatic); $^{13}$C NMR $\delta$ 39.8, 43.7, 51.4, 51.9, 64.5, 72.6, 77.5, 78.3, 91.0, 126.1, 128.3, 128.4(0), 128.4-(3), 128.5, 128.8, 129.0, 129.3, 129.6(0), 129.6(1), 129.7, 129.8, 133.2, 133.4, 133.5, 139.5, 143.2, 149.7, 165.4, 165.8, 166.1, 167.0, 167.6; HRMS calcd for $C_{45}H_{40}N_3O_{10}$ $(M + H)^+$ 782.2715, found 782.2716. Anal. Calcd for $C_{45}H_{39}N_3O_{10}$ (781.3): C, 69.13; H, 5.03; N, 5.37. Found: C, 68.63; H, 5.14; N, 5.00.

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**Supporting Information Available:** $^1$H NMR, $^{13}$C NMR for compounds **4** (all $\alpha$ anomers and $\beta$ anomers of compounds **4c** and **4e**) and **5**. This material is available free of charge via the Internet at http://pubs.acs.org..

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