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Synthesis of a Natural Oligosaccharide Antibiotic Active against *Helicobacter pylori*

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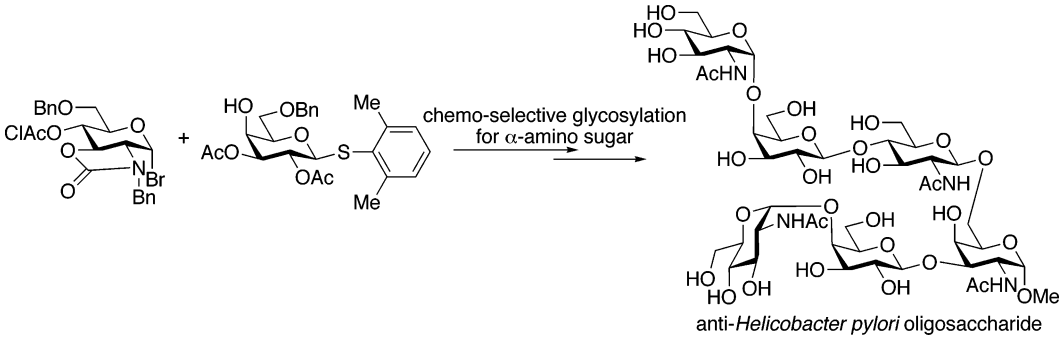

An oligosaccharide active against *Helicobacter pylori* was synthesized in a highly efficient manner for the first time. The anti-*H. pylori* oligosaccharide structure is a core-2 branched-type oligosaccharide with a characteristic α-*N*-acetylglucosamine at the nonreducing end. The oligosaccharide was synthesized from the nonreducing end to the reducing end, with an *N*-benzyl-2,3-oxazolidinone-carrying glycosyl donor used to introduce an α-*N*-acetylglucosamine at the nonreducing end. Complete chemoselective activation of a bromo sugar in the presence of a thioglycoside acceptor was achieved, and the use of 2,6-dimethylphenyl thioglycoside prevented the aglycon transfer observed when the corresponding phenyl thioglycoside is used as an acceptor.

Introduction

Helicobacter pylori, a Gram-negative bacterium, infects the stomachs of nearly half the human population.[1] Phylogeographic studies indicate that *H. pylori* originated in Africa and that *H. pylori* accompanied anatomically modern humans during their migrations from Africa.[2] Thus, *H. pylori* has infected humans for the past 50 000 years. Since the potential pathogenic character of *H. pylori* was first demonstrated,[3] accumulated evidence strongly suggests that *H. pylori* causes gastric ulcers, carcinoma, and cancer.[4] In 1994, the International Agency for Research on Cancer (IARC) classified *Helicobacter pylori* as a class I carcinogenic agent.

Gastric mucins are classified into two types based on their histochemical properties.[5] The first is a surface mucous cell-type mucin, secreted from surface mucous cells, while the second is found in deeper portions of the mucosa and is secreted by gland mucous cells including mucous neck cells, cardiac gland cells, and pyloric gland cells. *H. pylori* bacteria colonize surface mucous cell-type mucin[6] where two carbohydrate structures, Lewis b and sialyl dimeric Lewis X, act as specific ligands for *H. pylori* infection. *H. pylori* bacteria are rarely found deep in the mucous. In 2004, Nakayama's group found an O-linked glycoprotein, secreted from deeper mucins, that inhibits *H. pylori* growth.[7] This anti-*H. pylori* glycoprotein (**1a**) has a core-2 branched-type oligosaccharide with a characteristic α-*N*-acetylglucosamine at the nonreducing end.[8] Growth inhibition

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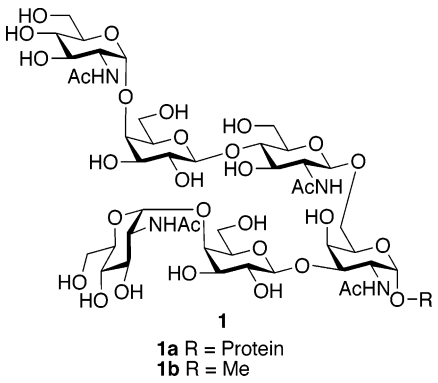

FIGURE 1. Structures of the anti-*Helicobacter pylori* oligosaccharides.

is not unique to this O-linked glycoprotein: *p*-nitrophenyl α-*N*-acetylglucosamine also suppresses the growth of bacteria in a dose dependent manner, although the inhibition is weak. It is believed that the nonreducing terminal α-1,4-GlcNAc is essential for growth inhibition of *H. pylori* and that the antibiotic activity is due to biosynthesis inhibition of cholesteryl-α-D-glucoside, an important component of the *H. pylori* cell membrane. At present, an anti-*H. pylori* oligosaccharide is available only as a recombinant glycoprotein (CD43) form, synthesized using α-1,4-*N*-acetylglucosaminyl transferase in Chinese hamster ovary cells.[9,10] Since synthesis by enzymatic synthesis is limited in the amount that can be produced and does not allow for structural variations of the hexasaccharide, the validation of these biological hypotheses is difficult. A facile and efficient strategy for chemically synthesizing this hexasaccharide and its derivatives would therefore provide a powerful tool for elucidating the biosynthesis of cholesteryl-α-D-glucoside inhibition mechanism central to its antibacterical activity and facilitate structure−activity relationship studies.

The stereoselective 1,2-cis glycosylation reaction of the 2-amino-2-deoxy sugar was a crucial problem in the synthesis of anti-*Helicobacter pylori* oligosaccharide **1b**. To date, the stereoselective glycosylation of 1,2-cis glycosides remains the principal challenge in complex oligosaccharide syntheses.[11,12] In particular, there has been little progress in devising strategies for the 1,2-cis stereoselective glycosylation of 2-amino-2-deoxy sugars since Lemieux and Paulsen introduced an azido moiety at the 2-position as a nonparticipating group about 30 years ago.[13,14] Recently, we reported several 1,2-cis-selective glycosyl donors for 2-amino-2-deoxy sugars.[15,16] The *N*-benzyl-2,3-oxazolidinone group carrying glycosyl donors shows high α-selectivity in glycosylation reactions near room temperature. We believed that the preparation, glycosylation, and deprotection procedures of this novel donor make it an ideal glycosyl donor for 1,2-cis glycosidic bond formation for 2-amino-2-deoxy sugars, and thus we expected that this novel glycosyl donor would prove useful in the synthesis of anti-*Helicobacter pylori* oligosaccharides.

The hexasaccharide was synthesized from the nonreducing end to the reducing end. This strategy should be useful later for structure−activity relationship studies because the putative essential structure, α-GlcNAc, is included in all the intermediates, allowing these intermediates to be screened for biological activity following deprotection.

Results and Discussion

The α-selective glycosylation reaction was carried out using cyclic carbamate donor **2**[15] and galactosyl phenyl thioglycoside **3a**[17] by AgOTf activation (Scheme 1) in dioxane−toluene near room temperature.[18] The moderate yield of **4a** (56%) was due to a side reaction in which the aglycon thiophenyl group was transferred from **3a** to activated donor **2** (Scheme 2). The aglycon-transferred α-phenyl thioglycoside **5** was isolated as a byproduct. This aglycon transfer is considered to proceed via sulfonium ion intermediate.

To prevent this problem, we used 2,6-dimethylphenyl thioglycoside **3b**, recently reported by Gindersleeve.[19] Acceptor **3b** was prepared from the reported benzylidene compound **6**[19] (Scheme 3); following acetylation, subsequent reductive benzylidene cleavage gave 2,6-dimethylphenyl thioglycoside **3b** in 84% yield. Using **3b**, complete chemoselective glycosylation was performed again under the same reaction conditions to provide disaccharide **4b** in 92% yield (Scheme 1). In both glycosylation reactions, the corresponding *β*-products were not observed by 400 MHz ^{1}H NMR after gel filtration column chromatography of the crude material.

Subsequently, thioglycoside **4b** was directly activated by *N*-(phenylthio)-ϵ-caprolactam−Tf_2O[20] in the presence of the less reactive glycosyl acceptor, 4-OH of the glucosamine derivative **8**,[21] to afford trisaccharide **9** in 77% yield (Scheme 4). Thioglycoside **4a** was activated similarly and gave trisaccharide **9** in 75% yield under the same conditions applied to donor **4b** and **8**. Oxidative removal of the *p*-methoxyphenyl group of **9**

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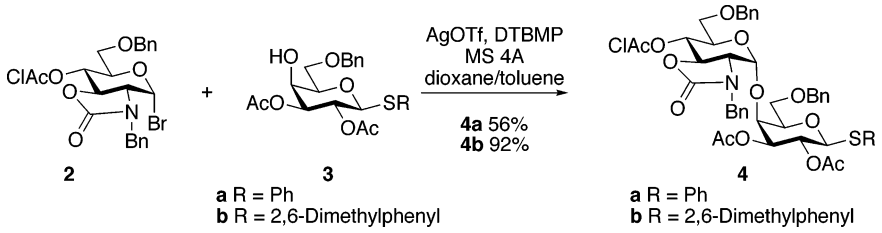
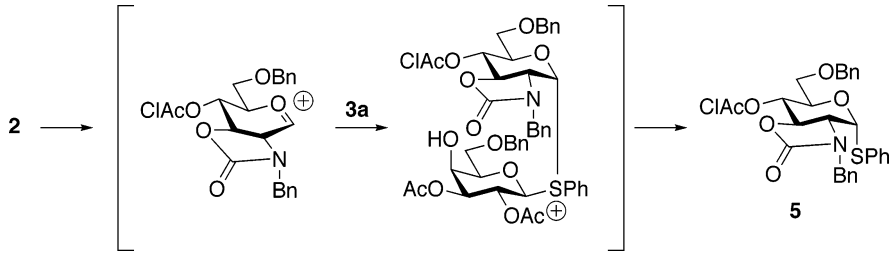
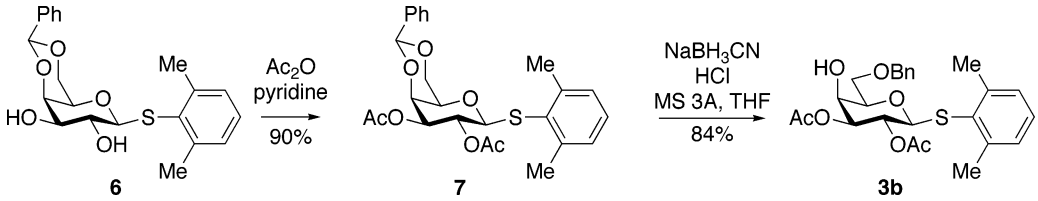
SCHEME 1. 1,2-*Cis* Stereoselective Glycosylation Using an *N*-Benzyloxazolidinone-Carrying Glycosyl Donor



SCHEME 2. Migration of the Thiophenyl Group



SCHEME 3. Preparation of 2,6-Dimethylphenyl Thioglycoside 3b



was achieved using ceric ammonium nitrate in water to afford exclusively β-hemiacetal **10**, which was subsequently converted into trichloroacetimidate donor **11** in 82% overall yield for the two steps. Similarly, the bottom part of trisaccharide **13** was prepared in 65% yield from disaccharide **4b** and *O*-methyl galactosamine derivative **12**.[22] The completely regioselective reductive opening of the benzylidene group of **13** by $Cu(OTf)_2$−BH_3[23] afforded trisaccharide acceptor **14** in 76% yield. When 0.05 equiv of $Cu(OTf)_2$ was used as described, the yield of **14** was only 22%, and unidentified byproducts were generated. Increasing the amount of $Cu(OTf)_2$ up to 0.5 equiv gave better yields.

The final glycosylation reaction was performed using imidate **11** and acceptor **14** in the presence of $BF_3{\cdot}OEt_2$ (Scheme 5) at −20 °C to give the hexasaccharide **15** in 83% yield.

Deprotected hexasaccharide **1b** was obtained after stepwise deprotection of **15** (Scheme 6). The phthalimide group was removed by *N*,*N*′-ethylenediamine in BuOH at 90 °C to give **16**. The cyclic carbamate group was not opened by this treatment and was subsequently removed under alkaline conditions. After both the *N*- and *O*-benzyl groups were removed by hydrogenolysis, selective N-acetylation using Ac_2O in MeOH gave hexasaccharide **1b** in 57% overall yield in the four steps.

Conclusion

We have achieved the first total synthesis of an anti-*Helicobacter pylori* oligosaccharide, compound **1b**, which is completed with high overall efficancy by employing a previously described cyclic carbamate-equipped glycosyl donor, **2**. All glycosylation reactions were achieved in complete stereoselectivities including the 1,2-cis glycosylation of amino sugar. The establishment of a facile methodology for the synthesis of **1b**, together with the recent cloning of cholesteryl α-glucosyl transferase,[24,25] means that the structure−activity relationship of **1** against *H. pylori* can now be rigorously investigated.[25] This is important because strains of *H. pylori* resistant to antibiotics that inhibit bacterial protein biosynthesis have been reported.[26] It has also been reported that intrinsic α-glucosylation of cholesterol abrogates phagocytosis of *H. pylori* and subsequent T cell activation.[27] It might be possible to develop a novel drug candidate that produces minimal side effects and is specific against *H. pylori*: first, because the putative target, cholesteryl α-glucosides, have only been detected in *H. pylori* and *Acholeplasma axanthum*[28] and second, because few proteins encoded in other bacterial species such as *Clostridium thermocellum* and *Lactobacillus johnsonii* are homologous to *H. pylori* cholsteryl glucosyl transferase.[25,29]

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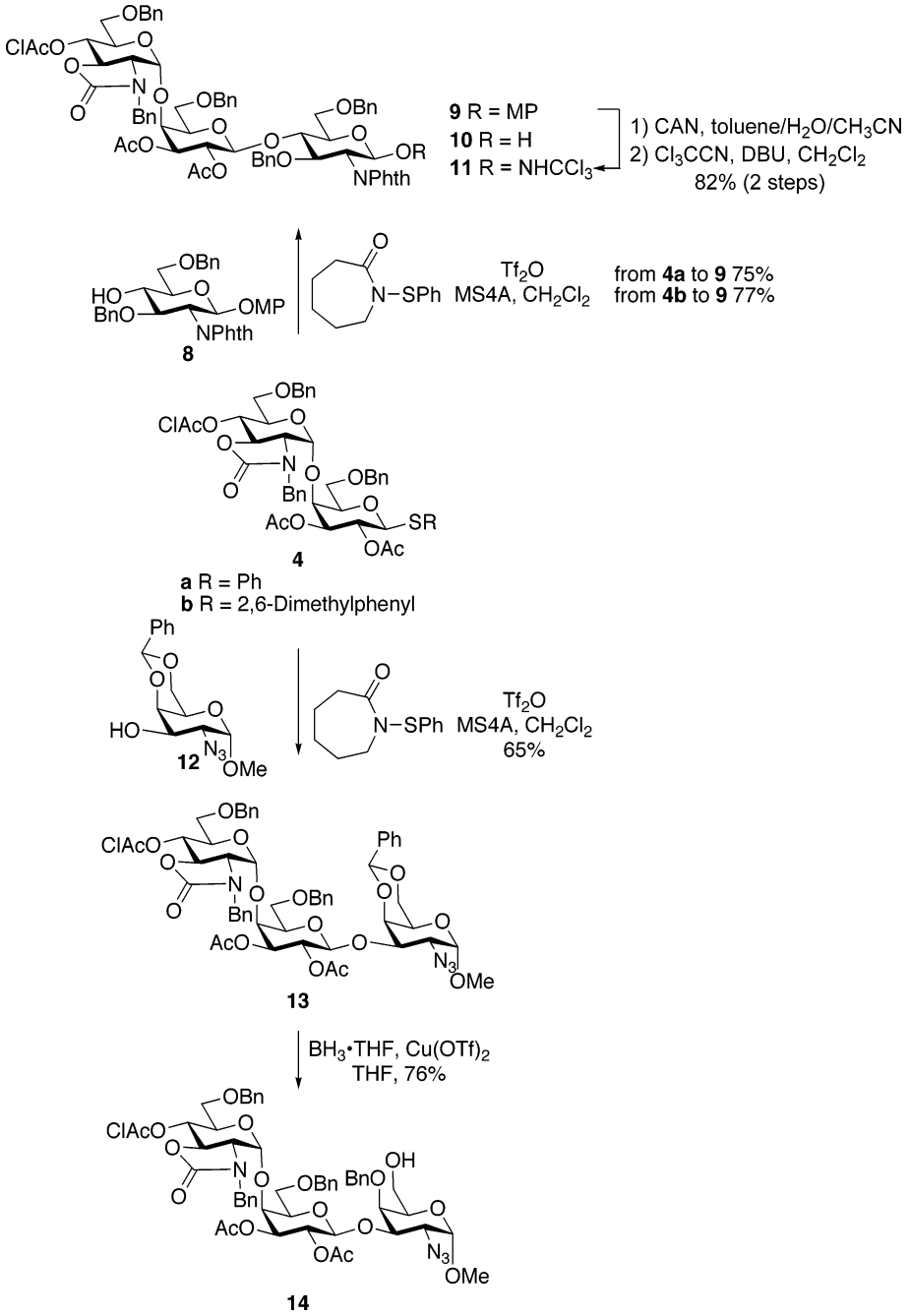
SCHEME 4. The Synthesis of Trisaccharides



Structure−activity relationship study will be reported in due course.

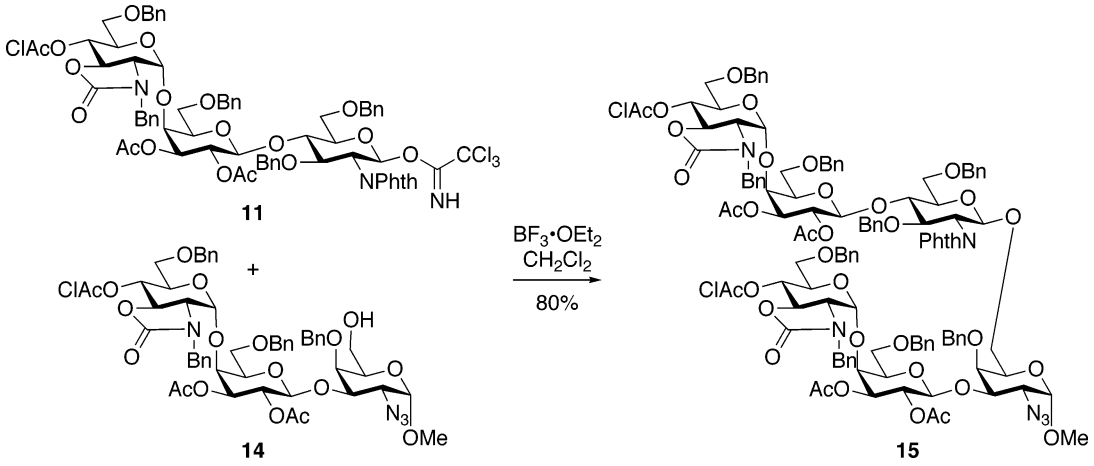
Experimental Section

NMR peak assignments including the identification of the residue connection were carried out by DQF (double-quantum-filtered)−COSY, HMBC, and HMQC experiments.

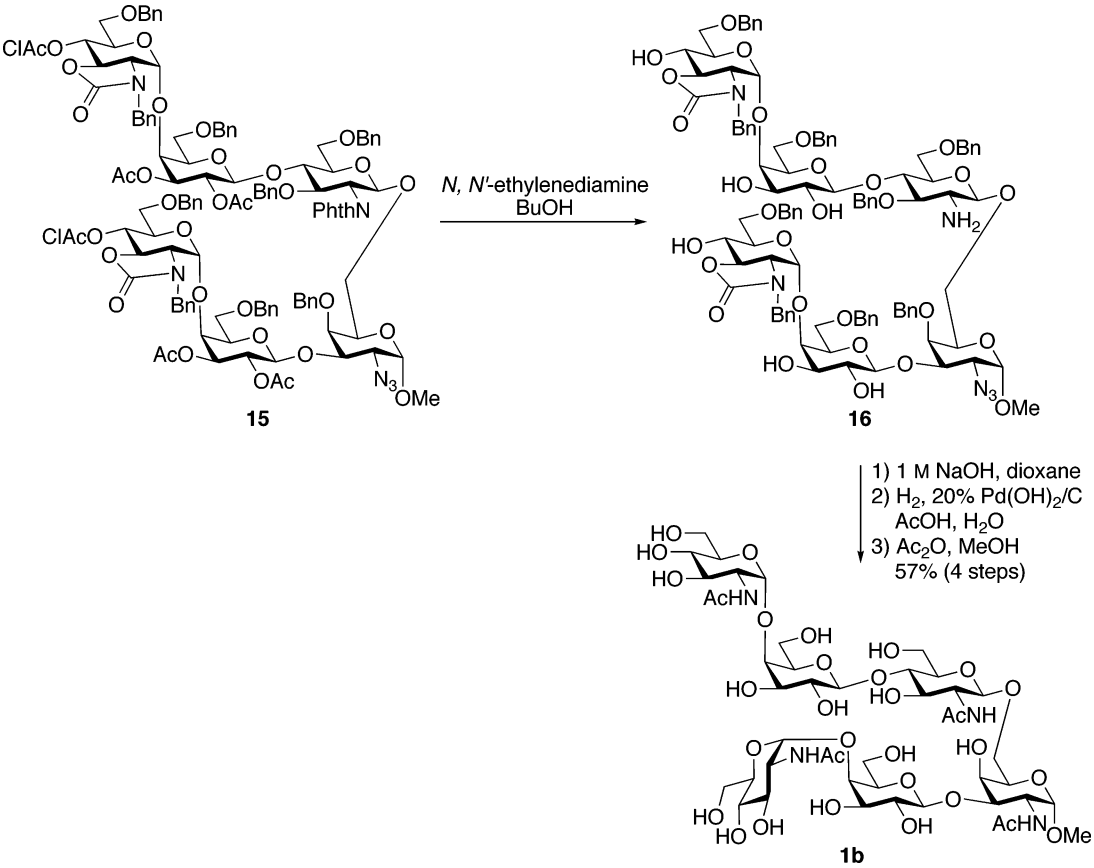
Compound (7). A diol 2,6-dimethylphenyl 4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside **6** (3.0 g, 7.72 mmol) was acetylated with Ac_2O−pyridine (1:2, 30 mL) at room temperature overnight. The mixture was concentrated with toluene several times to give a crystalline residue. Crystallization of the residue from EtOAc/hexane gave **7** (3.3 g, 90%). Mp 184−185 °C. $[\alpha]_D^{24}$ +18 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.55−7.36 (m, 5 H, aromatic *H*), 7.26−7.11 (m, 3 H, aromatic *H*), 5.47 (t, $J_{1,2}$ = 10.0 Hz, 1 H, H-2), 5.47 (s, 1 H, acetal-C*H*Ph), 4.95 (dd, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3.5 Hz, 1 H, H-3), 4.48 (d, 1 H, H-1), 4.35 (dd, $J_{4,5}$ = 1.0 Hz, 1 H, H-4), 4.18 (dd, $J_{5,6a}$ = 1.5 Hz, $J_{6a,6b}$ = 12.5 Hz, 1 H, H-6a), 3.95 (dd, $J_{5,6b}$ = 1.5 Hz, 1 H, H-6b), 3.34 (d, 1 H, H-5), 2.57 (s, 6 H, 2 CH_3), 2.14 and 2.08 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 170.7 (*C*OCH_3), 169.4 (*C*OCH_3), 144.3, 137.5, 131.4, 129.1, 128.2 and 126.4 (aromatic *C*), 101.0 (acetal-*C*HPh), 88.5 (C-1), 73.4 (C-4), 73.0 (C-3), 69.3 (C-5), 69.1 (C-6), 67.8 (C-2), 22.4 (2 C, 2 *C*H_3), 20.9 (CO*C*H_3), 20.8 (CO*C*H_3). Anal. Calcd for $C_{25}H_{28}O_7S$: C, 63.54; H, 5.97. Found: C, 63.61; H, 5.91.

Compound 3b. A solution of hydrogen chloride in 1,4-dioxane (4 M; 28 mL) was added to an ice-cold mixture of the 4,6-*O*-benzylidene acetal **7** (4.4 g, 9.31 mmol), sodium cyanoborohydride (7.2 g, 111.7 mmol), and molecular sieves 3 Å (3.0 g) in THF (70 mL) containing methyl orange as a pH indicator. The deep red

SCHEME 5. The Hexasaccharide Synthesis



SCHEME 6. The Deprotection Sequence To Provide 1b



mixture was stirred for 30 min and then filtered through Celite. The filtrate was diluted with EtOAc and washed with 1 M HCl. The separated aqueous layer was extracted with EtOAc. The combined organic extracts were washed with water and brine, dried (Na_2SO_4), filtered, and concentrated. Purification by flash column chromatography on silica gel (4:1, $CHCl_3$−EtOAc) gave **3b** (3.7 g, 84%) which was crystallized from Et_2O/hexane. Mp 117−118 °C. $[\alpha]_D^{24}$ +14 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35−7.10 (m, 8 H, aromatic *H*), 5.41 (t, $J_{1,2}$ = 10.5 Hz, 1 H, H-2), 4.93 (dd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.0 Hz, 1 H, H-3), 4.53 and 4.50 (d, J = 12.0 Hz, 1 H each, CH_2Ph), 4.41 (d, 1 H, H-1), 4.15 (br t, $J_{H-4,4-OH}$ = 4.0 Hz, 1 H, H-4), 3.73 (dd, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 11.0 Hz, 1 H, H-6a), 3.66 (dd, $J_{5,6b}$ = 5.0 Hz, 1 H, H-6b), 3.52 (br t, 1 H, H-5), 2.75 (d, 1 H, 4-O*H*), 2.54 (s, 6 H, 2 CH_3), 2.12 and 2.11 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.2 (*C*OCH_3), 169.6 (*C*OCH_3), 144.0, 137.5, 131.3, 129.2, 128.4, 128.2, 127.8 and 127.6 (aromatic *C*), 88.9 (C-1), 76.6 (C-5), 74.5 (C-3), 73.7 (*C*H_2Ph), 69.5 (C-6), 68.3 (C-2), 68.2 (C-4), 22.4 (2 C, 2 *C*H_3), 20.9 and 20.8 (CO*C*H_3). Anal. Calcd for $C_{25}H_{30}O_7S$: C, 63.27; H, 6.37. Found: C, 62.97; H, 6.29.

Compound 4a. To an ice-cold suspension of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP; 0.49 g, 2.38 mmol), silver trifluoromethanesulfonate (AgOTf; 0.76 g, 2.97 mmol), and molecular sieves 4 Å (2.0 g) in 1,4-dioxane−toluene (3:1, 20 mL) was added a mixture of *N*-benzyl-6-*O*-benzyl-2,3,-*N*,*O*-carbonyl-4-*O*-chloroacetyl-2-deoxy-α-D-glucopyranosyl bromide **2** (1.04 g, 1.98 mmol) and phenyl 2,3-di-*O*-acetyl-6-*O*-benzyl-1-thio-β-D-galactopyranoside **3a** (0.59 g, 1.32 mmol) in 1,4-dioxane−toluene (3:1, 20 mL) via a cannula. The stirring mixture was allowed to warm to room temperature and stirred for 1 day. The mixture was diluted with

EtOAc and filtered through Celite. The filtrate was washed with saturated aqueous $NaHCO_3$. The separated aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated. Purification by flash column chromatography (3:2, hexane−EtOAc) gave an α-linked disaccharide **4a** (645 mg, 56%) as a colorless foam. $[\alpha]_D^{24}$ −30 (*c* 0.83, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.50−7.05 (m, 20 H, aromatic *H*), 5.33 (t, $J_4^{II},_5^{II} = 9.5$ Hz, 1 H, H-4^{II}), 5.08 (t, $J_2^{I},_3^{I} = 10.5$ Hz, 1 H, H-2^{I}), 4.92 (dd, $J_3^{I},_4^{I} = 2.5$ Hz, 1 H, H-3^{I}), 4.90 (d, $J_1^{II},_2^{II} = 3.0$ Hz, 1 H, H-1^{II}), 4.87 and 3.92 (d, $J = 14.5$ Hz, 1 H each, N-CH_2Ph), 4.64 (d, $J_1^{I},_2^{I} = 9.5$ Hz, 1 H, H-1^{I}), 4.59 and 4.51 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.49 and 4.33 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.23 (d, 1 H, H-4^{I}), 4.19 (dd, $J_2^{II},_3^{II} = 12.0$ Hz, $J_3^{II},_4^{II} = 10.5$ Hz, 1 H, H-3^{II}), 3.99 and 3.89 (d, $J = 14.5$ Hz, 1 H each, COCH_2Cl), 3.87 (m, 1 H, H-5^{I}), 3.79 (dddd, $J_5^{II},_6^{II}{}_a = J_5^{II},_6^{II}{}_b = 3.0$ Hz, 1 H, H-5^{II}), 3.74 (dd, $J_5^{I},_6^{I}$a = 8.5 Hz, $J_6^{I}{}_a,_6^{I}{}_b = 10.0$ Hz, 1 H, H-6^{I}a), 3.66 (dd, $J_5^{I},_6^{I}{}_b = 6.0$ Hz, 1 H, H-6^{I}b), 3.45 (dd, $J_6^{II}{}_a,_6^{II}{}_b = 11.0$ Hz, 1 H, H-6^{II}a), 3.38 (dd, 1 H, H-6^{II}b), 3.20 (dd, 1 H, H-2^{II}), 2.09 and 1.92 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.3 (*C*OCH$_3$), 169.1 (*C*OCH$_3$), 165.6 (oxazolidinone, *C*═O), 158.4 (*C*OCH$_2$Cl), 137.1, 134.6, 134.1, 129.7 and 129.1−127.9 (aromatic *C*), 96.7 (C-1^{II}), 84.6 (C-1^{I}), 76.0 (C-5^{I}), 75.8 (C-4^{I}), 74.1 (C-3^{I}), 73.7 (*C*H$_2$Ph), 73.5 (*C*H$_2$-Ph), 72.9 (C-3^{II}), 71.4 (C-5^{II}), 70.2 (C-4^{II}), 66.9 (C-2^{I}), 66.7 (C-6^{II}), 55.5 (C-6^{I}), 59.7 (C-2^{II}), 47.2 (N-*C*H$_2$Ph), 40.4 (CO*C*H$_2$Cl), 20.9 (CO*C*H$_3$), 20.8 (CO*C*H$_3$). Anal. Calcd for $C_{46}H_{48}ClNO_{13}S$: C, 62.05; H, 5.43; N, 1.57. Found: C, 61.90; H, 5.33; N, 1.64.

Compound 4b. To an ice-cold suspension of DTBMP (0.39 g, 1.90 mmol), AgOTf (0.61 g, 2.37 mmol), and molecular sieves 4 Å (2.0 g) in 1,4-dioxane−toluene (3:1, 20 mL) was added a mixture of donor **2** (0.83 g, 1.58 mmol) and acceptor **3b** (0.5 g, 1.05 mmol) in 1,4-dioxane−toluene (3:1, 20 mL) via a cannula. After addition, the ice-bath was removed. The mixture was stirred at room temperature overnight. The work-up was achieved in the same manner as described for **4a**. Purification by flash column chromatography (3:2, hexane−EtOAc) gave an α-linked disaccharide **4b** (896 mg, 93%) as a colorless foam. $[\alpha]_D^{27}$ +33 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.34−7.07 (m, 18 H, aromatic *H*), 5.43 (t, $J_4^{II},_5^{II} = 9.5$ Hz, 1 H, H-4^{II}), 5.23 (t, $J_1^{I},_2^{I} = J_2^{I},_3^{I} = 10.5$ Hz, 1 H, H-2^{I}), 4.97 (d, $J_1^{II},_2^{II} = 2.5$ Hz, 1 H, H-1^{II}), 4.91 (dd, $J_3^{I},_4^{I} = 2.5$ Hz, 1 H, H-3^{I}), 4.89 and 3.98 (d, $J = 15.0$ Hz, 1 H each, N-CH_2Ph), 4.71 (dd, $J_2^{II},_3^{II} = 12.0$ Hz, $J_3^{II},_4^{II} = 10.5$ Hz, 1 H, H-3^{II}), 4.52 and 4.37 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.48 (s, 2 H, CH_2Ph), 4.47 (d, 1 H, H-1^{I}), 4.23 (d, 1 H, H-4^{I}), 4.08 (dd, $J_5^{II},_6^{II}{}_a = J_5^{II},_6^{II}{}_b = 2.5$ Hz, 1 H, H-5^{II}), 4.02 and 3.90 (d, $J = 15.0$ Hz, 1 H each, COCH_2Cl), 3.73 (dd, $J_5^{I},_6^{I}{}_a = 8.5$ Hz, $J_6^{I}{}_a,_6^{I}{}_b = 10.0$ Hz, 1 H, H-6^{I}a), 3.66 (dd, $J_5^{I},_6^{I}{}_b = 5.5$ Hz, 1 H, H-5^{I}), 3.54 (dd, $J_6^{II}{}_a,_6^{II}{}_b = 11.0$ Hz, 1 H, H-6^{II}a), 3.52 (dd, 1 H, H-6^{I}b), 3.48 (dd, 1 H, H-6^{II}b), 3.32 (dd, 1 H, H-2^{II}), 2.53 (s, 6 H, 2 CH_3), 2.11 and 1.96 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.2 (*C*OCH$_3$), 169.3 (*C*OCH$_3$), 165.7 (*C*OCH$_2$Cl), 158.4 (oxazolidinone, *C*═O), 144.0, 137.1, 137.1, 134.1, 130.8 and 129.3−127.6 (aromatic *C*), 96.6 (C-1^{II}), 88.6 (C-1^{I}), 75.8 (C-5^{I}), 75.6 (C-4^{I}), 73.9 (C-3^{I}), 73.6 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 73.2 (C-3^{II}), 71.5 (C-5^{II}), 70.3 (C-4^{II}), 68.1 (C-2^{I}), 66.9 (C-6^{I}), 66.9 (C-6^{II}), 59.8 (C-2^{II}), 47.2 (N-*C*H$_2$Ph), 40.4 (CO*C*H$_2$Cl), 22.4 (2 C, 2 *C*H$_3$), 20.8 and 20.7 (CO*C*H$_3$). Anal. Calcd for $C_{48}H_{52}ClNO_{13}S$: C, 62.77; H, 5.71; N, 1.53. Found: C, 62.76; H, 5.75; N, 1.48.

Compound 5. $[\alpha]_D^{24}$ +220 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.44−7.24 (m, 15 H, aromatic *H*), 5.41 (d, $J_{1,2} = 5.0$ Hz, 1 H, H-1), 5.40 (t, $J_{3,4} = 10.5$ Hz, 1 H, H-4), 4.81 and 4.17 (d, $J = 14.5$ Hz, 1 H each, N-CH_2Ph), 4.57 and 4.19 (d, $J = 11.5$ Hz, 1 H each, CH_2Ph), 4.44 (dd, $J_{2,3} = 12.0$ Hz, 1 H, H-3), 4.30 (dddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 2.5$ Hz, $J_{5,6b} = 4.0$ Hz, 1 H, H-5), 3.97 and 3.89 (d, $J = 15.0$ Hz, 1 H each, COCH_2Cl), 3.64 (dd, 1 H, H-2), 3.58 (dd, $J_{6a,6b} = 11.0$ Hz, 1 H, H-6a), 3.56 (dd, 1 H, H-6b). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6 (COCH$_2$Cl), 157.8 (oxazolidinone, *C*═O), 137.1, 134.1, 132.3, 131.9, 129.3, 129.1, 128.9, 128.6, 128.4, 128.2, 128.1 and 128.0 (aromatic *C*), 84.8 (C-1), 75.8 (C-3), 73.6 (*C*H$_2$Ph), 71.2 (C-5), 69.9 (C-4), 67.2 (C-6), 59.6 (C-2), 47.9 (N-*C*H$_2$Ph), 40.3 (CO*C*H$_2$Cl). Anal. Calcd for $C_{29}H_{28}ClNO_6S$: C, 62.87; H, 5.09; N, 2.53. Found: C, 62.65; H, 5.05; N, 2.42.

Compound 9. Using Compound 4a as a Glycosyl Donor. To a mixture of donor **4a** (410 mg, 0.46 mmol), acceptor **8** (411 mg, 0.69 mmol), *N*-(phenylthio)-ϵ-caprolactam (102 mg, 0.46 mmol), and molecular sieves 4 Å (3.0 g) in CH_2Cl_2 was added Tf_2O (78 μL, 0.46 mmol) slowly at −20 °C. After the mixture was stirred at −20 °C for 45 min, the mixture was quenched with saturated aqueous $NaHCO_3$ and filtered through Celite. The filtrate was extracted with $CHCl_3$. The combined organic extracts were washed with water, dried (Na_2SO_4), filtered, and concentrated. Purification by flash column chromatography (4:3 → 5:4, hexane−EtOAc) gave compound **9** (477 mg, 75%) as a colorless foam.

Using Compound 4b as a Glycosyl Donor. To a mixture of donor **4b** (1.45 g, 1.58 mmol), acceptor **8** (1.41 g, 2.37 mmol), *N*-(phenylthio)-ϵ-caprolactam (0.35 g, 1.58 mmol), and activated molecular sieves 4 Å (4.0 g) in CH_2Cl_2 (40 mL) was added Tf_2O (0.27 mL, 0.46 mmol) slowly at 4 °C. After the ice-cold mixture was stirred for 1 h, the mixture was worked-up in a manner similar to that described above for preparation of **9** using **4a**. Purification by flash column chromatography (4:3, hexane−EtOAc) gave **9** (1.68 mg, 77%) as a colorless foam. $[\alpha]_D^{27}$ +51 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.68−7.01 (m, 33 H, aromatic *H*), 5.59 (d, $J_1^{I},_2^{I} = 8.5$ Hz, 1 H, H-1^{I}), 5.36 (t, $J_4^{III},_5^{III} = 10.0$ Hz, 1 H, H-4^{III}), 5.14 (dd, $J_1^{II},_2^{II} = 8.0$ Hz, $J_2^{II},_3^{II} = 11.0$ Hz, 1 H, H-2^{II}), 4.89 (d, $J_1^{III},_2^{III} = 3.0$ Hz, 1 H, H-1^{III}), 4.78 and 4.50 (d, $J = 12.5$ Hz, 1 H each, CH_2Ph), 4.76 (dd, $J_3^{II},_4^{II} = 2.5$ Hz, 1 H, H-3^{II}), 4.76 and 4.51 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.73 and 3.83 (d, $J = 15.0$ Hz, 1 H each, N-CH_2Ph), 4.67 (d, 1 H, H-1^{II}), 4.51 and 4.35 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.49 (dd, $J_2^{III},_3^{III} = 12.0$ Hz, $J_3^{III},_4^{III} = 10.5$ Hz, 1 H, H-3^{III}), 4.45 (s, 2 H, CH_2Ph), 4.40 (dd, $J_2^{I},_3^{I} = 11.0$ Hz, 1 H, H-2^{I}), 4.30 (dd, $J_3^{I},_4^{I} = 8.5$ Hz, 1 H, H-3^{I}), 4.14 (t, $J_4^{I},_5^{I} = 9.5$ Hz, 1 H, H-4^{I}), 4.14 (d, 1 H, H-4^{II}), 4.02 (dddd, $J_5^{III},_6^{III}{}_a = {}_5^{III},_6^{III}{}_b = 3.0$ Hz, 1 H, H-5^{III}), 3.80 (br s, 2 H, H-6^{I}a and H-6^{I}b), 3.70 (s, 3 H, PhOCH_3), 3.62 and 3.51 (d, $J = 15.0$ Hz, 1 H each, COCH_2Cl), 3.61 (m, 1 H, H-5^{I}), 3.59 (m, 1 H, H-6^{II}a), 3.56 (m, 1 H, H-5^{II}), 3.55 (m, 1 H, H-6^{III}a), 3.45 (m, 2 H, H-6^{II}b and H-6^{III}b), 2.02 and 1.96 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.2 (*C*OCH$_3$), 169.1 (*C*OCH$_3$), 165.6 (*C*OCH$_2$Cl), 158.1 (oxazolidinone, *C*═O), 155.3 (phthalimide, *C*═O), 150.8 (phthalimide, *C*═O), 138.0, 137.9, 137.2, 137.1, 134.0, 133.8, 131.5, 129.1−127.2, 123.4, 118.7 and 114.3 (aromatic *C*), 100.3 (C-1^{I}), 97.6 (C-1^{II}), 96.4 (C-1^{III}), 77.8 (C-4^{I}), 76.1 (C-3^{I}), 75.5 (C-4^{II}), 75.0 (C-5^{I}), 74.1 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 73.5 (2 C, 2 *C*H$_2$Ph), 73.4 (C-3^{III}), 72.7 (C-3^{II}), 72.2 (C-5^{II}), 71.5 (C-5^{III}), 70.0 (C-4^{III}), 69.7 (C-2^{II}), 67.6 (C-6^{I}), 66.7 (C-6^{III}), 66.5 (C-6^{II}), 59.7 (C-2^{III}), 55.5 (PhO*C*H$_3$), 55.5 (C-2^{I}), 47.1 (N-*C*H$_2$Ph), 40.1 (CO*C*H$_2$Cl), 20.8 (CO*C*H$_3$), 20.7 (CO*C*H$_3$). Anal. Calcd for $C_{75}H_{75}ClN_2O_{21}$: C, 65.47; H, 5.49; N, 2.04. Found: C, 65.46; H, 5.48; N, 2.00.

Compound 10. Compound **9** (733 mg, 0.53 mmol) was treated with cerium (IV) ammonium nitrate (CAN; 1.75 g, 3.20 mmol) in CH_3CN-H_2O−toluene (8:3:2, 26 mL) on an ice−water bath for 20 min. The mixture was diluted with EtOAc and washed with water. The separated aqueous layer was extracted with EtOAc. The combined organic extracts were washed with water and brine, dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography (3:2, EtOAc /hexane) gave hemiacetal **10** (603 mg, 89%) as a yellow foam. $[\alpha]_D^{25}$ +54 (*c* 0.82, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.73−7.00 (m, 29 H, aromatic *H*), 5.36 (t, $J_4^{III},_5^{III} = 9.5$ Hz, 1 H, H-4^{III}), 5.31 (t, $J_1^{I},_2^{I} = J_{H-1}^{I},_{1-OH}^{I} = 8.5$ Hz, 1 H, H-1^{I}), 5.11 (dd, $J_1^{II},_2^{II} = 7.5$ Hz, $J_2^{II},_3^{II} = 10.5$ Hz, 1 H, H-2^{II}), 4.87 (d, $J_1^{III},_2^{III} = 2.5$ Hz, 1 H, H-1^{III}), 4.79 and 4.48 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.77 and 4.47 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.72 and 3.82 (d, $J = 14.5$ Hz, 1 H each, N-CH_2Ph), 4.71 (dd, $J_3^{II},_4^{II} = 2.5$ Hz, 1 H, H-3^{II}), 4.59 (d, 1 H, H-1^{II}), 4.50 and 4.35 (d, $J = 12.0$ Hz, 1 H each, CH_2Ph), 4.47 (m, 1 H, H-3^{III}), 4.44 (s, 2 H, CH_2Ph), 4.31 (dd, $J_2^{I},_3^{I} = 10.5$ Hz, $J_3^{I},_4^{I} = 8.5$ Hz, 1

H, H-3^{I}), 4.12 (d, 1 H, H-4^{II}), 4.10 (dd, $J_{4^{I},5^{I}}$ = 9.5 Hz, 1 H, H-4^{I}), 4.00 (dddd, $J_{5^{III},6^{III}a}$ = $J_{5^{III},6^{III}b}$ = 3.0 Hz, 1 H, H-5^{III}), 3.80 (dd, $J_{5^{I},6^{I}a}$ = 3.0 Hz, $J_{6^{I}a,6^{I}b}$ = 10.5 Hz, 1 H, H-6^{I}a), 3.76 (dd, $J_{5^{I},6^{I}b}$ = 2.0 Hz, 1 H, H-6^{I}b), 3.62 and 3.51 (d, J = 15.0 Hz, 1 H each, COCH_2Cl), 3.58 (m, 1 H, H-6^{II}a), 3.56 (m, 1 H, H-5^{I}), 3.54 (m, 1 H, H-6^{III}a), 3.51 (m, 1 H, H-5^{II}), 3.45 (dd, $J_{6^{III}a,6^{III}b}$ = 11.0 Hz, 1 H, H-6^{III}b), 3.42 (dd, $J_{5^{II},6^{II}b}$ = 5.0 Hz, $J_{6^{II}a,6^{II}b}$ = 9.5 Hz, 1 H, H-6^{II}b), 3.22 (dd, 1 H, H-2^{III}), 3.09 (d, 1 H, O*H*-1^{I}), 2.00 and 1.95 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.2 (*C*OCH$_3$), 169.1 (*C*OCH$_3$), 168.0 (2 C, phthalimide, *C*═O), 165.6 (*C*OCH$_2$Cl), 158.1 (oxazolidinone, *C*═O), 138.1, 137.7, 137.2, 137.1, 134.0, 133.8, 131.5, 129.0−127.2 and 123.3 (aromatic *C*), 100.2 (C-1^{II}), 96.4 (C-1^{III}), 92.8 (C-1^{I}), 77.7 (C-4^{I}), 75.7 (C-3^{I}), 75.5 (C-4^{II}), 74.7 (C-5^{I}), 73.9 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 73.5 (3 C, 2 *C*H$_2$Ph and C-3^{III}), 72.7 (C-3^{II}), 72.1 (C-5^{II}), 71.5 (C-5^{III}), 69.9 (C-4^{III}), 69.6 (C-2^{II}), 67.6 (C-6^{I}), 66.6 (C-6^{III}), 66.5 (C-6^{II}), 59.7 (C-2^{III}), 57.4 (C-2^{I}), 47.1 (N-*C*H$_2$Ph), 40.1 (CO*C*H$_2$Cl), 20.8 (CO*C*H$_3$), 20.7 (CO*C*H$_3$). Anal. Calcd for $C_{68}H_{69}ClN_2O_{20}$: C, 64.32; H, 5.48; N, 2.21. Found: C, 64.10; H, 5.50; N, 2.13.

Compound 11. To an ice-cold mixture of hemiacetal **10** (358 mg, 0.28 mmol) and trichloroacetonitrile (0.28 mL, 2.80 mmol) in CH_2Cl_2 (6 mL) was added 0.32 M solution of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in CH_2Cl_2 (88 μL, 0.028 mmol). After the mixture was stirred for 10 min, the mixture was purified directly by flash column chromatography (1:1, hexane−EtOAc) to give compound **11** (366 mg, 92%) as a pale yellow foam. $[\alpha]_D^{25}$ +70 (*c* 0.66, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.53 [s, 1 H, C(N*H*)CCl$_3$], 7.67−7.01 (m, 29 H, aromatic *H*), 6.36 (d, $J_{1^{I},2^{I}}$ = 9.0 Hz, 1 H, H-1^{I}), 5.36 (t, $J_{4^{III},5^{III}}$ = 9.5 Hz, 1 H, H-4^{III}), 5.12 (dd, $J_{1^{II},2^{II}}$ = 8.0 Hz, $J_{2^{II},3^{II}}$ = 11.0 Hz, 1 H, H-2^{II}), 4.88 (d, $J_{1^{III},2^{III}}$ = 2.5 Hz, 1 H, H-1^{III}), 4.80 and 4.51 (d, J = 12.5 Hz, 1 H each, C*H*$_2$Ph), 4.77 and 4.51 (d, J = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.73 and 3.84 (d, J = 15.0 Hz, 1 H each, *N*-C*H*$_2$Ph), 4.37 (dd, $J_{3^{II},4^{II}}$ = 3.0 Hz, 1 H, H-3^{II}), 4.64 (d, 1 H, H-1^{II}), 4.51 and 4.35 (d, J = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.48 (dd, $J_{2^{III},3^{III}}$ = 12.0 Hz, $J_{3^{III},4^{III}}$ = 10.0 Hz, 1 H, H-3^{III}), 4.47 and 4.45 (d, J = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.44 (dd, $J_{2^{I},3^{I}}$ = 10.5 Hz, 1 H, H-2^{I}), 4.34 (t, $J_{3^{I},4^{I}}$ = 10.0 Hz, 1 H, H-3^{I}), 4.20 (t, $J_{4^{I},5^{I}}$ = 10.0 Hz, 1 H, H-4^{I}), 4.13 (d, 1 H, H-4^{II}), 4.01 (dddd, $J_{5^{III},6^{III}a}$ = $J_{5^{III},6^{III}b}$ = 3.5 Hz, 1 H, H-5^{III}), 3.83 (d, $J_{5^{I},6^{I}a}$ = $J_{5^{I},6^{I}b}$ = 2.5 Hz, 2 H, H-6^{I}a and H-6^{I}b), 3.71 (dddd, 1 H, H-5^{I}), 3.60 and 3.49 (d, J = 15.0 Hz, 1 H each, COC*H*$_2$Cl), 3.59 (m, 1 H, H-6^{II}a), 3.55 (dd, $J_{6^{III}a,6^{III}b}$ = 11.0 Hz, 1 H, H-6^{III}a), 3.53 (m, 1 H, H-5^{II}), 3.45 (dd, 1 H, H-6^{III}b), 3.45 (m, 1 H, H-6^{II}b), 3.22 (dd, 1 H, H-2^{III}), 2.02 and 1.96 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.2 (*C*OCH$_3$), 169.1 (*C*OCH$_3$), 168.0 and 167.4 (broadened each, phtalimide, *C*═O), 165.6 (*C*OCH$_2$Cl), 160.9 [*C*(NH)CCl$_3$], 158.1 (oxazolidinone, *C*═O), 138.0, 137.8, 137.2, 137.1, 134.0, 133.9, 131.3, 129.1−127.3 and 123.3 (aromatic *C*), 100.1 (C-1^{II}), 96.4 (C-1^{III}), 94.0 (C-1^{I}), 90.3 [C(NH)*C*Cl$_3$], 77.3 (C-4^{I}), 75.8 (2 C, C-3^{I} and C-5^{I}), 75.5 (C-4^{II}), 74.0 (*C*H$_2$Ph), 73.5 (4 C, 3 *C*H$_2$Ph and C-3^{III}), 72.7 (C-3^{II}), 72.1 (C-5^{II}), 71.5 (C-5^{III}), 69.9 (C-4^{III}), 69.6 (C-2^{III}), 67.1 (C-6^{I}), 66.7 (C-6^{III}), 66.5 (C-6^{II}), 59.7 (C-2^{III}), 54.4 (C-2^{I}), 47.1 (N-*C*H$_2$Ph), 40.1 (CO*C*H$_2$Cl), 20.8 (CO*C*H$_3$), 20.7 (CO*C*H$_3$). Anal. Calcd for $C_{70}H_{69}Cl_4N_3O_{20}$: C, 59.45; H, 4.92; N, 2.97. Found: C, 59.20; H, 4.96; N, 2.93.

Compound 13. To a mixture of donor **4b** (877 mg, 0.96 mmol), acceptor **12** (352 mg, 1.15 mmol), *N*-(phenylthio)-ϵ-caprolactam (211 mg, 0.96 mmol), and molecular sieves 4 Å (3.0 g) in CH_2Cl_2 (20 mL) was added Tf_2O (162 μL, 0.96 mmol) slowly at 4 °C. After the chilled mixture was stirred for 30 min, the mixture was warmed to room temperature and stirred for 30 min. Then the mixture was worked-up in a manner similar to that described for **9**. The crude mixture was purified by flash column chromatography (1:1, hexane−EtOAc) to give **13** (674 mg, 65%) as a colorless foam. $[\alpha]_D^{27}$ +89 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50−7.07 (m, 20 H, aromatic *H*), 5.52 (s, 1 H, acetal-C*H*Ph), 5.42 (t, $J_{4^{III},5^{III}}$ = 10.0 Hz, 1 H, H-4^{III}), 5.23 (dd, $J_{1^{II},2^{II}}$ = 7.5 Hz, $J_{2^{II},3^{II}}$ = 10.5 Hz, 1 H, H-2^{II}), 4.93 (d, $J_{1^{III},2^{III}}$ = 2.5 Hz, 1 H, H-1^{III}), 4.92 (d, $J_{1^{I},2^{I}}$ = 3.5 Hz, 1 H, H-1^{I}), 4.85 (dd, $J_{3^{II},4^{II}}$ = 3.0 Hz, 1 H, H-3^{II}), 4.85 and 3.92 (d, J = 14.5 Hz, 1 H each, N-C*H*$_2$Ph), 4.80 (d, 1 H, H-1^{II}), 4.66 (dd, $J_{2^{III},3^{III}}$ = 12.0 Hz, $J_{3^{III},4^{III}}$ = 10.5 Hz, 1 H, H-3^{III}), 4.56 (s, 2 H, C*H*$_2$Ph), 4.52 and 4.35 (d, J = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.38 (d, $J_{3^{I},4^{I}}$ = 3.5 Hz, 1 H, H-3^{I}), 4.23 (dd, $J_{5^{I},6^{I}a}$ = 1.5 Hz, $J_{6^{I}a,6^{I}b}$ = 12.0 Hz, 1 H, H-6^{I}b), 4.21 (d, 1 H, H-4^{II}), 4.11 (dd, $J_{2^{I},3^{I}}$ = 10.5 Hz, 1 H, H-3^{I}), 4.07 (dddd, $J_{5^{III},6^{III}a}$ = $J_{5^{III},6^{III}b}$ =3.0 Hz, 1 H, H-5^{III}), 3.97 (dd, $J_{5^{I},6^{I}b}$ = 1.5 Hz, 1H, H-6^{I}b), 3.90 (dd, 1 H, H-2^{I}), 3.87 and 3.74 (d, J = 14.5 Hz, 1 H each, COC*H*$_2$-Cl), 3.86 (br t, $J_{5^{II},6^{II}a}$ = $J_{5^{II},6^{II}b}$ = 7.5 Hz, 1 H, H-5^{II}), 3.77 (dd, $J_{6^{II}a,6^{II}b}$ = 9.5 Hz, 1 H, H-6^{II}a), 3.64 (dd, 1 H, H-6^{II}b), 3.64 (br s, 1 H, H-5^{I}), 3.54 (dd, $J_{6^{III}a,6^{III}b}$ =11.0 Hz, 1 H, H-6^{III}a), 3.46 (dd, 1 H, H-6^{III}b), 3.45 (s, 3 H, OC*H*$_3$), 3.30 (dd, 1 H, H-2^{III}), 2.03 and 1.95 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.4 (*C*OCH$_3$), 169.4 (*C*OCH$_3$), 165.7 (*C*OCH$_2$Cl), 158.4 (oxazolidinone, *C*═O), 137.5, 137.1, 134.0, 129.2−127.7 and 126.1 (aromatic *C*), 102.2 (C-1^{II}), 100.8 (acetal-*C*HPh), 99.5 (C-1^{I}), 96.8 (C-1^{III}), 75.9 (C-4^{II}), 75.8 (C-3^{I}), 75.7 (C-4^{I}), 73.6 (*C*H$_2$Ph). 73.5 (2 C, C-3^{III} and *C*H$_2$Ph), 73.1 (C-3^{II}), 72.5 (C-5^{II}), 71.6 (C-5^{I}), 70.1 (C-4^{III}), 69.0 (C-6^{I}), 68.7 (C-2^{II}), 67.2 (C-6^{II}), 66.5 (C-6^{III}), 62.9 (C-5^{I}), 59.8 (C-2^{III}), 59.0 (C-2^{I}), 55.6 (OCH$_3$), 47.3 (N-*C*H$_2$Ph), 40.4 (CO*C*H$_2$-Cl), 20.9 (CO*C*H$_3$), 20.7 (CO*C*H$_3$). Anal. Calcd for $C_{54}H_{59}ClN_4O_{18}$: C, 59.64; H, 5.47; N, 5.15. Found: C, 59.73; H, 5.49; N, 4.98.

Compound 14. To a solution of compound **13** (674 mg, 0.62 mmol) in CH_2Cl_2 (15 mL) were added BH_3·THF in THF (1 M; 3.1 mL, 3.10 mmol) and copper(II) trifluoromethanesulfonate (112 mg, 0.31 mmol). After being stirred for 30 min at room temperature, the mixture was cooled on an ice−water bath, quenched by sequential addition of triethylamine (68 μL, 0.62 mmol) and methanol. The mixture was filtered through Celite. The filtrate was washed with water and the separated aqueous layer was extracted with $CHCl_3$. The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography on silica gel (3:2, $CHCl_3$−EtOAc) gave **14** (512 mg, 76%) as a colorless foam. $[\alpha]_D^{24}$ +53 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39−7.05 (m, 20 H, aromatic *H*), 5.37 (t, $J_{4^{III},5^{III}}$ = 9.5 Hz, 1 H, H-4^{III}), 5.28 (dd, $J_{1^{II},2^{II}}$ = 7.5 Hz, $J_{2^{II},3^{II}}$ = 10.5 Hz, 1 H, H-2^{II}), 4.95 (d, $J_{1^{III},2^{III}}$ = 2.5 Hz, 1 H, H-1^{III}), 4.91 and 4.57 (d, J = 11.0 Hz, 1 H each, C*H*$_2$Ph), 4.90 (dd, $J_{3^{II},4^{II}}$ = 2.5 Hz, 1 H, H-3^{II}), 4.84 and 3.98 (d, J = 15.0 Hz, 1 H, N-C*H*$_2$Ph), 4.83 (d, $J_{1^{I},2^{I}}$ = 3.0 Hz, 1 H, H-1^{I}), 4.82 (d, 1 H, H-1^{II}), 4.67 and 4.58 (d, J = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.52 (dd, $J_{2^{III},3^{III}}$ = 11.5 Hz, $J_{3^{III},4^{III}}$ = 11.5 Hz, 1 H, H-3^{III}), 4.51 and 4.34 (d, J = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.25 (d, 1 H, H-4^{II}), 4.07 (dd, $J_{2^{I},3^{I}}$ = 10.5 Hz, $J_{3^{I},4^{I}}$ = 3.0 Hz, 1 H, H-3^{I}), 4.01 (dddd, $J_{5^{III},6^{III}a}$ = $J_{5^{III},6^{III}b}$ = 2.5 Hz, 1 H, H-5^{III}), 3.96 (br s, 1 H, H-4^{I}), 3.86 (m, 2 H, H-6^{II}a and H-5^{II}), 3.81 (dd, 1 H, H-2^{I}), 3.74 (m, 1 H, H-5^{I}), 3.70 (m, 1 H, H-6^{I}a), 3.64 (dd, $J_{5^{II},6^{II}b}$ = 9.5 Hz, $J_{6^{II}a,6^{II}b}$ = 13.0 Hz, 1 H, H-6^{II}), 3.55 (dd, $J_{6^{III}a,6^{III}b}$ = 11.0 Hz, 1 H, H-6^{III}a), 3.49 (m, 1 H, H-6^{I}b), 3.47 and 3.39 (d, J = 15.0 Hz, 1 H each, COC*H*$_2$Cl), 3.43 (dd, 1 H, H-6^{III}b), 3.40 (s, 3 H, OC*H*$_3$), 3.28 (dd, 1 H, H-2^{III}), 2.09 and 1.97 (s, 3 H each, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.4 (*C*OCH$_3$), 169.6 (*C*OCH$_3$), 165.5 (*C*OCH$_2$Cl), 158.3 (oxazolidinone, *C*═O), 137.7, 137.1, 137.0, 134.0, and 129.2−127.7 (aromatic *C*), 102.1 (C-1^{II}), 98.9 (C-1^{I}), 96.8 (C-1^{III}), 77.8 (C-3^{I}), 76.1 (C-4^{I}), 76.0 (C-4^{II}), 74.6 (*C*H$_2$Ph), 73.7 (*C*H$_2$Ph), 73.6 (C-3^{III}), 73.4 (*C*H$_2$Ph), 72.7 (C-3^{II}), 72.4 (C-5^{II}), 71.7 (C-5^{III}), 70.4 (C-5^{I}), 69.7 (C-4^{III}), 69.1 (C-2^{II}), 66.7 (C-6^{II}), 66.4 (C-6^{III}), 62.0 (C-6^{I}), 60.3 (C-2^{I}), 59.8 (C-2^{III}), 55.3 (OCH$_3$), 47.4 (N-*C*H$_2$Ph), 40.0 (CO*C*H$_2$Cl), 20.8 and 20.7 (CO*C*H$_3$). Anal. Calcd for $C_{54}H_{61}ClN_4O_{18}$: C, 59.53; H, 5.64; N, 5.14. Found: C, 59.33; H, 5.69; N, 4.97.

Compound 15. A solution of BF_3·Et_2O in CH_2Cl_2 (0.1 M; 50 μL, 0.050 mmol) was added to a mixture of donor **11** (359 mg, 0.254 mmol), acceptor **14** (254 mg, 0.233 mmol), and molecular sieves 4 Å (0.5 g) in CH_2Cl_2 (10 mL) at −20 °C. After being stirred for 30 min at −20 °C, the mixture was quenched by addition of saturated aqueous $NaHCO_3$ and filtered through Celite. The filtrate was extracted with $CHCl_3$. The combined organic extracts were

washed with water, dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography on silica gel (1:1 → 4:3, EtOAc-hexane) gave a hexasaccharide **15** (434 mg, 80%) as a colorless foam. $[\alpha]_D^{24}$ +48 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.66−7.05 (m, 49 H, aromatic *H*), 5.35 (t, $J_3{}^{IV},_4{}^{IV} = J_4{}^{IV},_5{}^{IV} = 10.0$ Hz, 1 H, H-4^{IV}), 5.34 (t, $J_3{}^{VI},_4{}^{VI} = J_4{}^{VI},_5{}^{VI} = 10.0$ Hz, 1 H, H-4^{VI}), 5.22 (dd, $J_1{}^{V},_2{}^{V} = 7.5$ Hz, $J_2{}^{V},_3{}^{V} = 11.0$ Hz, 1 H, H-2^{V}), 5.09 (dd, $J_1{}^{III},_2{}^{III} = 8.0$ Hz, $J_2{}^{III},_3{}^{III} = 11.0$ Hz, 1 H, H-2^{III}), 5.02 (d, $J_1{}^{II},_2{}^{II} = 8.0$ Hz, 1 H, H-1^{II}), 4.94 (d, $J_1{}^{VI},_2{}^{VI} = 2.5$ Hz, 1 H, H-1^{VI}), 4.86 (d, $J_1{}^{IV},_2{}^{IV} = 3.0$ Hz, 1 H, H-1^{IV}), 4.86 (dd, $J_3{}^{V},_4{}^{V} = 3.5$ Hz, 1 H, H-3^{V}), 4.86 and 3.96 (d, *J* = 15.0 Hz, 1 H each, N-C*H*$_2$Ph), 4.84 and 4.45 (d, *J* = 11.0 Hz, 1 H each, C*H*$_2$Ph), 4.77 and 4.41 (d, *J* = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.74 and 4.45 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.72 and 3.82 (d, *J* = 15.0 Hz, 1 H each, N-C*H*$_2$Ph), 4.72 (d, 1 H, H-1^{V}), 4.68 (dd, $J_3{}^{III},_4{}^{III} = 3.0$ Hz, 1 H, H-3^{III}), 4.62 and 4.60 (d, *J* = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.57 (d, 1 H, H-1^{III}), 4.51 and 4.35 (d, *J* = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.50 and 4.32 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.47 (dd, $J_2{}^{VI},_3{}^{VI} = 12.0$ Hz, 1 H, H-3^{VI}), 4.46 (dd, $J_2{}^{IV},_3{}^{IV} = 12.0$ Hz, 1 H, H-3^{IV}), 4.44 and 4.41 (d, *J* = 11.0 Hz, 1 H each, C*H*$_2$Ph), 4.34 (d, $J_1{}^{I},_2{}^{I} = 3.0$ Hz, 1 H, H-1^{I}), 4.25 (d, 1 H, H-4^{V}), 4.23 (dd, $J_2{}^{II},_3{}^{II} = 10.5$ Hz, $J_3{}^{II},_4{}^{II} = 8.5$ Hz, 1 H, H-3^{II}), 4.12 (d, 1 H, H-4^{III}), 4.11 (t, $J_4{}^{II},_5{}^{II} = 8.5$ Hz, 1 H, H-4^{II}), 4.11 (d, 1 H, H-2^{II}), 4.00 (m, 1 H, H-5^{IV}), 3.98 (m, 1 H, H-5^{VI}), 3.87 (dd, $J_2{}^{I},_3{}^{I} = 10.5$ Hz, $J_3{}^{I},_4{}^{I} = 2.5$ Hz, 1 H, H-3^{I}), 3.84 (t, $J_5{}^{V},_6{}^{V}{}_a = J_6{}^{V}{}_a,_6{}^{V}{}_b = 9.5$ Hz, 1 H, H-6^{V}a), 3.81 (m, 1 H, H-6^{II}a), 3.80 (m, 1 H, H-5^{V}), 3.79 (br s, 1 H, H-4^{I}), 3.75 (dd, $J_5{}^{II},_6{}^{II}{}_b = 1.0$ Hz, $J_6{}^{II}{}_a,_6{}^{II}{}_b = 11.0$ Hz, 1 H, H-6^{II}b), 3.71 (dd, $J_5{}^{I},_6{}^{I}{}_a = 3.0$ Hz, $J_6{}^{I}{}_a,_6{}^{I}{}_b = 11.5$ Hz, 1 H, H-6^{I}a), 3.64 (m, 1 H, H-5^{I}), 3.64 (m, 1 H, H-6^{V}b), 3.61 and 3.50 (d, *J* = 15.0 Hz, 1 H each, COC*H*$_2$Cl), 3.60 (dd, 1 H, H-2^{I}), 3.55 (m, 1 H, H-6^{III}a), 3.54 (dd, $J_5{}^{IV},_6{}^{IV}{}_a = 2.5$ Hz, $J_6{}^{IV}{}_a,_6{}^{IV}{}_b = 11.0$ Hz, 1 H, H-6^{IV}a), 3.51 (dd, $J_5{}^{VI},_6{}^{VI}{}_a = 2.5$ Hz, $J_6{}^{VI}{}_a,_6{}^{VI}{}_b = 11.0$ Hz, 1 H, H-6^{VI}a), 3.50 and 3.43 (d, *J* = 15.0 Hz, 1 H each, COC*H*$_2$Cl), 3.49 (m, 1 H, H-5^{II}), 3.46 (m, 1 H, H-5^{III}), 3.44 (dd, $J_5{}^{IV},_6{}^{IV}{}_b = 2.5$ Hz, 1 H, H-6^{IV}b), 3.41 (m, 1 H, H-6^{I}b), 3.40 (m, 1 H, H-6^{III}b), 3.39 (dd, $J_5{}^{VI},_6{}^{VI}{}_b = 2.5$ Hz, 1 H, H-6^{VI}b), 3.27 (dd, 1 H, H-2^{VI}), 3.21 (dd, 1 H, H-2^{IV}), 2.86 (s, 3 H, OC*H*$_3$), 2.03, 2.01, 1.95 and 1.95 (s, 3 H each, COC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.3 (*C*OCH$_3$), 170.2 (*C*OCH$_3$), 169.6 (*C*OCH$_3$), 169.1 (*C*OCH$_3$), 167.8 (broadened each, phthalimide, *C*═O), 167.4 (broadened each, phthalimide, *C*═O), 165.5 (2 C, 2 *C*OCH$_2$Cl), 158.2 and 158.0 (oxazolidinone, *C*═O), 138.1, 138.0, 137.8, 137.2, 137.1, 137.0, 137.0, 134.0, 134.0, 133.7, 131.5, 129.1−127.1, 123.2 and 122.9 (aromatic *C*), 102.1 (C-1^{V}), 100.1 (C-1^{III}), 98.8 (C-1^{II}), 98.3 (C-1^{I}), 96.8 (C-1^{VI}), 96.5 (C-1^{IV}), 77.9 (C-3^{I}), 77.5 (C-4^{II}), 76.6 (C-4^{I}), 75.8 (C4^{V}), 75.7 (C-3^{II}), 75.5 (C-4^{III}), 74.7 (*C*H$_2$Ph), 74.6 (C-5^{II}), 73.9 (*C*H$_2$Ph), 73.7 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 73.5 (2 C, C-3^{IV} and C-3^{VI}), 73.4 (2 C, 2 *C*H$_2$Ph), 73.4 (*C*H$_2$Ph), 72.7 (C-3^{III}), 72.6 (C-3^{V}), 72.2 (C-5^{V}), 71.9 (C-5^{III}), 71.5 (C-5^{VI}), 71.4 (C-5^{IV}), 69.9 (C-4^{VI}), 69.8 (C-4^{IV}), 69.6 (2 C, C-6^{I} and C-2^{V}), 69.4 (C-5^{I}), 69.0 (C-2^{III}), 67.6 (C-6^{II}), 66.6 (2 C, C-6^{III} and C-6^{V}), 66.4 (2 C, C-6^{IV} and C-6^{VI}), 59.9 (C-2^{I}), 59.7 (2 C, C-2^{IV} and C-2^{VI}), 55.6 (C-2^{II}), 54.4 (OC*H*$_3$), 47.2 and 47.0 (N-*C*H$_2$Ph), 40.1 (2 C, 2 CO*C*H$_2$Cl), 20.8−20.6 (CO*C*H$_3$). Anal. Calcd for $C_{122}H_{128}Cl_2N_6O_{37}$: C, 62.59; H, 5.51; N, 3.59. Found: C, 62.31; H, 5.48; N, 3.59.

Compound 16. A solution of compound **15** (102 mg, 0.043 mmol) and *N*,*N*′-ethylenediamine (0.5 mL) in BuOH (5 mL) was stirred at 90 °C overnight. The mixture was concentrated *in vacuo*, and the residue was chromatographed on silica gel with $CHCl_3$−MeOH (9:1) to give a N-dephthaloylated compound **16** (77 mg, 95%). $[\alpha]_D^{25}$ +26 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37−7.00 (aromatic *H*), 5.08 and 4.58 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 5.08 (d, $J_1{}^{GlcN'},_2{}^{GlcN'} = 2.5$ Hz, 1 H, H-1$^{GlcN'}$), 4.97 (d, $J_1{}^{GlcN},_2{}^{GlcN} = 3.0$ Hz, 1 H, H-1^{GlcN}), 4.92 and 4.65 (d, *J* = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.83 and 3.91 (d, *J* = 15.0 Hz, 1 H each, N-C*H*$_2$-Ph), 4.80 and 3.78 (d, *J* = 15.0 Hz, 1 H each, N-C*H*$_2$Ph), 4.78 (d, $J_1{}^{I},_2{}^{I} = 3.5$ Hz, 1 H, H-1^{I}), 4.65 and 4.45 (d, *J* = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.58 and 4.54 (d, *J* = 11.0 Hz, 1 H each, C*H*$_2$Ph), 4.56 (d, $J_1{}^{Gal},_2{}^{Gal} = 7.5$ Hz, 1 H, H-1^{Gal}), 4.52 and 4.42 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.50 and 4.42 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.41 (d, $J_1{}^{Gal'},_2{}^{Gal'} = 7.5$ Hz, 1 H, H-1$^{Gal'}$), 4.37 and 4.34 (d, *J* = 11.5 Hz, 1 H each, CH$_2$Ph), 4.37 (dd, $J_2{}^{GlcN'},_3{}^{GlcN'} = 12.0$ Hz, $J_3{}^{GlcN'},_4{}^{GlcN'} = 9.5$ Hz, 1 H, H-3$^{GlcN'}$), 4.28 (dd, $J_2{}^{GlcN},_3{}^{GlcN} = 12.0$ Hz, $J_3{}^{GlcN},_4{}^{GlcN} = 9.5$ Hz, 1 H, H-3^{GlcN}), 4.20 (d, $J_1{}^{II},_2{}^{II} = 7.5$ Hz, 1 H, H-1^{II}), 4.08 (dd, $J_2{}^{I},_3{}^{I} = 10.5$ Hz, $J_3{}^{I},_4{}^{I} = 3.0$ Hz, 1 H, H-3^{I}), 4.06 (br s, 1 H, H-4^{Gal}), 4.03 (t, $J_3{}^{II},_4{}^{II} = J_4{}^{II},_5{}^{II} = 9.5$ Hz, 1 H, H-4^{II}), 4.00 (dd, $J_5{}^{II},_6{}^{II}{}_a = 3.0$ Hz, $J_6{}^{II}{}_a,_6{}^{II}{}_b = 11.5$ Hz, 1 H, H-6^{II}a), 3.95 (br s, 1 H, H-4$^{Gal'}$), 3.91 (br s, 1 H, H-4^{Gal}), 3.95−3.90 (m, 3 H, H-5^{GlcN}, H-5$^{GlcN'}$ and H-5^{I}), 3.84 (dd, 1 H, H-2^{I}), 3.70 (m, 1 H, H-6^{II}b), 3.68 (m, 1 H, H-4^{GlcN}), 3.67 (m, 1 H, H-4$^{GlcN'}$), 3.62 (m, 1 H, H-2^{Gal}), 3.59 (m, 2 H, H-3^{Gal} and H-6^{Gal}b), 3.56 (m, 1 H, H-6$^{Gal'}$a), 3.49 (m, 1 H, H-2$^{Gal'}$), 3.46 (m, 1 H, H-5^{II}), 3.71−3.52 (m, 6 H, H-6^{I}a, H-6^{I}b, H-6^{GlcN}a, H-6^{GlcN}b, H-6$^{GlcN'}$a and H-6$^{GlcN'}$b), 3.39 (t, $J_2{}^{II},_3{}^{II} = 9.5$ Hz, 1 H, H-2^{II}), 3.40 (m, 1 H, H-5$^{Gal'}$), 3.36 (s, 3 H, OC*H*$_3$), 3.30 (dd, $J_5{}^{Gal'},_6{}^{Gal'}{}_b = 5.0$ Hz, $J_6{}^{Gal'}{}_a,_6{}^{Gal'}{}_b = 9.5$ Hz, 1 H, H-6$^{Gal'}$b), 3.29 (m, 1 H, H-3$^{Gal'}$), 3.11 (dd, 1 H, H-2$^{GlcN'}$), 3.04 (dd, 1 H, H-2^{GlcN}), 2.80 (dd, 1 H, H-2^{II}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.8 and 158.6 (oxazolidinone, *C*═O), 138.8, 138.3, 138.1, 137.5, 137.4 (2 C), 137.3, 134.2 (2 C), 129.1−127.0 (aromatic *C*), 104.8 (C-1^{Gal}), 103.5 (C-1^{II}), 103.1 (C-1$^{Gal'}$), 98.7 (C-1^{I}), 96.6 (C-1^{GlcN}), 96.2 (C-1$^{GlcN'}$), 81.7 (C-3^{II}), 78.6 (C-4^{Gal}), 77.9 (2 C, C-3^{I} and C-4$^{Gal'}$), 76.9 (C-4^{II}), 76.5 (C-3$^{GlcN'}$), 76.2 (2 C, C-4^{I} and C-3^{GlcN}), 74.6 (C-5^{GlcN}), 74.5 (C-5^{II}), 74.3 (*C*H$_2$Ph), 74.2 (C-5$^{GlcN'}$), 74.0 (*C*H$_2$Ph), 73.5 (3 C, 2 *C*H$_2$Ph and C-3$^{Gal'}$), 73.3 (2 C, C-3^{Gal} and *C*H$_2$Ph), 73.0 (2 C, 2 *C*H$_2$Ph), 72.4 (C-5^{Gal}), 72.4 (C-2$^{Gal'}$), 72.0 (2 C, C-2^{Gal} and C-5$^{Gal'}$), 69.7 (C-5^{I}), 69.5 (C-6^{I}), 68.9 (C-4$^{GlcN'}$), 68.7 (2 C, C-4^{GlcN} and C-6^{GlcN} either C-6$^{GlcN'}$), 68.6 (C-6^{GlcN} either C-6$^{GlcN'}$), 67.4 (C-6^{Gal}), 66.8 (C-6$^{Gal'}$), 59.9 (C-2^{I}), 59.2 (C-2$^{GlcN'}$), 58.9 (C-2^{GlcN}), 55.1 (OC*H*$_3$), 47.2 (N-*C*H$_2$Ph), 46.7 (N-*C*H$_2$Ph).

Compound 1b. A solution of compound **16** (77 mg, 0.041 mmol) in 1 M NaOH (4 mL) and 1,4-dioxane (4 mL) was stirred at 80 °C overnight. The mixture was cooled to room temperature, diluted with EtOAc, and washed with water. The separated aqueous layer was extracted with EtOAc. The combined organic extracts were washed with water and brine, dried (Na_2SO_4), filtered, and concentrated. Purification by flash column chromatography on silica gel (8:1, $CHCl_3$−MeOH) gave a N,O-deacylated intermediate (68 mg, 90%). $[\alpha]_D^{24}$ +54 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34−7.15 (m, 45 H, aromatic *H*), 5.15 and 4.60 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 5.00 (d, $J_1{}^{GlcN'},_2{}^{GlcN'} = 3.5$ Hz, 1 H, H-1$^{GlcN'}$), 4.89 (d, $J_1{}^{GlcN},_2{}^{GlcN} = 3.5$ Hz, 1 H, H-1^{GlcN}), 4.88 and 4.55 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.82 (d, $J_1{}^{I},_2{}^{I} = 4.0$ Hz, 1 H, H-1^{I}), 4.61 and 4.43 (d, *J* = 11.0 Hz, 1 H each, C*H*$_2$Ph), 4.55 and 4.49 (d, *J* = 11.5 Hz, 1 H each, C*H*$_2$Ph), 4.53 and 4.48 (d, *J* = 11.0 Hz, 1 H each, C*H*$_2$Ph), 4.50 (d, $J_1{}^{Gal},_2{}^{Gal} = 8.0$ Hz, 1 H, H-1^{Gal}), 4.40 and 4.36 (d, *J* = 12.0 Hz, 1 H each, C*H*$_2$Ph), 4.38 (d, $J_1{}^{Gal'},_2{}^{Gal'} = 8.0$ Hz, 1 H, H-1$^{Gal'}$), 4.22 (s, 2 H, C*H*$_2$Ph), 4.19 (d, $J_1{}^{II},_2{}^{II} = 8.0$ Hz, 1 H, H-1^{II}), 4.05 (dd, $J_2{}^{I},_3{}^{I} = 10.5$ Hz, $J_3{}^{I},_4{}^{I} = 3.0$ Hz, 1 H, H-3^{I}), 4.04 (m, 1 H, H-5$^{GlcN'}$), 4.00 (t, $J_3{}^{II},_4{}^{II} = J_4{}^{II},_5{}^{II} = 9.5$ Hz, 1 H, H-4^{II}), 3.98 (br s, 1 H, H-4^{Gal}), 3.97 (m, 1 H, H-5^{GlcN}), 3.95 (dd, $J_5{}^{II},_6{}^{II}{}_a = 3.0$ Hz, $J_6{}^{II}{}_a,_6{}^{II}{}_b = 11.0$ Hz, H-6^{II}a), 3.92 (m, 1 H, H-5^{I}), 3.90 (br s, 1 H, H-4^{I}), 3.84 (dd, 1 H, H-2^{I}), 3.82 (br s, 1 H, H-4$^{Gal'}$), 3.76 (m, 1 H, H-6^{GlcN}a), 3.76 (m, 1 H, H-6^{I}a), 3.75 (m, 1 H, H-5^{Gal}), 3.74 (m, 1 H, H-6$^{Gal'}$a), 3.74 and 3.64 (d, *J* = 15.0 Hz, 1 H each, N-C*H*$_2$Ph), 3.69 and 3.56 (d, *J* = 15.0 Hz, 1 H each, N-C*H*$_2$Ph), 3.67 (m, 1 H, H-6^{I}b), 3.65 (m, 1 H, H-2^{Gal}), 3.56 (m, 1 H, H-6^{Gal}b), 3.56 (m, 1 H, H-6$^{GlcN'}$b), 3.53 (dd, $J_5{}^{GlcN},_6{}^{GlcN}{}_b = 7.5$ Hz, $J_6{}^{GlcN}{}_a,_6{}^{GlcN}{}_b = 10.0$ Hz, H-6^{GlcN}b), 3.49 (dd, $J_2{}^{Gal'},_3{}^{Gal'} = 10.0$ Hz, 1 H, H-2$^{Gal'}$), 3.45 (dd, $J_2{}^{GlcN'},_3{}^{GlcN'} = 10.0$ Hz, $J_3{}^{GlcN'},_4{}^{GlcN'} = 8.5$ Hz, 1 H, H-3$^{GlcN'}$), 3.44 (m, 1 H, H-5^{II}), 3.40 (m, 1 H, H-4$^{GlcN'}$), 3.38 (t, $J_2{}^{II},_3{}^{II} = J_3{}^{II},_4{}^{II} = 9.5$ Hz, 1 H, H-3^{II}), 3.38 (m, 1 H, H-5$^{Gal'}$), 3.38 (s, 3 H, OC*H*$_3$), 3.35 (m, 1 H, H-4^{GlcN}), 3.34 (m, 1 H, H-3^{GlcN}), 3.31 (dd, $J_5{}^{Gal'},_6{}^{Gal'}{}_b = 4.5$ Hz, $J_6{}^{Gal'}{}_a,_6{}^{Gal'}{}_b = 8.5$ Hz, 1 H, H-6$^{Gal'}$b), 3.19 (br m, 1 H, H-3$^{Gal'}$), 2.79 (dd, 1 H, H-2^{II}), 2.54 (dd, 1 H, H-2$^{GlcN'}$), 2.47 (dd, 1 H, H-2^{GlcN}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.7, 139.6, 139.2, 138.4, 138.0, 137.7 (2 C), 137.6, 137.3 and 128.5−127.1 (aromatic *C*), 104.9 (C-1^{II}), 104.1 (C-1^{Gal}), 103.1 (C-

1$^{Gal'}$), 98.8 (C-1^{I}), 98.5 (C-1^{GlcN}), 98.2 (C-1$^{GlcN'}$), 82.9 (C-3^{II}), 78.8 (C-4$^{Gal'}$), 78.0 (C-3^{I}), 77.7 (C-4^{Gal}), 76.9 (C-4^{II}), 76.4 (C-4^{I}), 74.8 (C-5^{II}), 74.5 (*C*H$_2$Ph), 74.3 (*C*H$_2$Ph), 74.1 (C-3$^{Gal'}$), 73.6 (3 C, 2 *C*H$_2$Ph and C-3^{Gal}), 73.4 (*C*H$_2$Ph), 73.2 (*C*H$_2$Ph), 73.0 (*C*H$_2$Ph), 72.8 (C-5^{Gal}), 72.6 (C-5$^{Gal'}$), 72.5 (C-3^{GlcN}), 72.4 (C-2$^{Gal'}$), 72.2 (C-3$^{GlcN'}$), 71.9 (C-2^{Gal}), 71.7 (C-5^{GlcN}), 71.5 (C-5$^{GlcN'}$), 71.3 (C-4^{GlcN}), 71.2 (C-4$^{GlcN'}$), 69.7 (C-5^{I}), 69.6 (C-6^{GlcN}), 69.5 (C-6$^{GlcN'}$), 69.0 (C-6^{I}), 68.3 (C-6^{II}), 67.7 (C-6^{Gal}), 67.4 (C-6$^{Gal'}$), 61.2 (C-2$^{GlcN'}$), 61.00 (C-2^{GlcN}), 59.7 (C-2^{I}), 56.7 (C-2^{II}), 55.3 (O*C*H$_3$), 51.6 (*N*-*C*H$_2$Ph), 51.4 (*N*-*C*H$_2$Ph).

The mixture of the N,O-deacylated compound (68 mg, 0.037 mmol) and 20% Pd(OH)$_2$/C (50 mg) in 80% acetic acid (6 mL) was stirred at 60 °C under H$_2$ atmosphere overnight. The mixture was filtered through a syringe filter (Millipore Millex LG, hydrophilic PTFE 0.2 μm cartridge), and the cartridge was washed with MeOH and water. The filtrates were concentrated with toluene and dried *in vacuo*. The residue was dissolved in MeOH−water (1:1, 4 mL), neutralized by ion-exchange resin (PS-Trisamine; Argonaut Tecnologies), and filtered. The filtrate was concentrated *in vacuo*, and the residue was N-acetylated with Ac$_2$O−MeOH (3:7, 5 mL) at room temperature for 2 h. The residue was concentrated, neutralized, and re-N-acetylated as described above to give fully N-acetylated products containing partial *O*-acetates. The product was dissolved in MeOH (3 mL), and the solution was adjusted to pH 9 by addition of a 0.1 M solution of NaOMe in methanol for 3 h, neutralized by Amberlyst (15 DRY), filtered, and concentrated. The residue was fractionated by size-exclusion chromatography (Sephadex LH-20; 1:1, MeOH−water) and lyophilized to give **1b** (29 mg, 67%) as a white powder. [α]$_D^{26}$ +110 (*c* 1.0, H$_2$O). ^{1}H NMR (500 MHz, D$_2$O at 30 °C) δ: 4.88 (d, $J_1^{VI},_2^{VI}$ = 4.0 Hz, 1 H, H-1^{VI}), 4.87 (d, $J_1^{IV},_2^{IV}$ = 3.5 Hz, 1 H, H-1^{IV}), 4.76 (d, $J_1^{I},_2^{I}$ = 3.5 Hz, 1 H, H-1^{I}), 4.57 (d, $J_1^{II},_2^{II}$ = 8.0 Hz, 1 H, H-1^{II}), 4.53 (d, $J_1^{III},_2^{III}$ = 7.5 Hz, 1 H, H-1^{III}), 4.52 (d, $J_1^{V},_2^{V}$ = 8.0 Hz, 1 H, H-1^{V}), 4.36 (dd, $J_2^{I},_3^{I}$ = 11.0 Hz, 1 H, H-2^{I}), 4.18 (d, 1 H, $J_3^{I},_4^{I}$ = 3.5 Hz, 1 H, H-4^{I}), 4.18 (m, 1 H, H-5^{IV}), 4.17 (m, 1 H, H-5^{VI}), 4.08 (dd, $J_5^{I},_6^{I}{}_a$ = 3.0 Hz, $J_6^{I}{}_a,_6^{I}{}_b$ = 12.5 Hz, 1 H, H-6^{I}a), 4.05 (m, 1 H, H-5^{I}), 4.04 (dd, 1 H, H-3^{I}), 4.02 (dd, $J_5^{II},_6^{II}{}_a$ = 2.0 Hz, $J_6^{II}{}_a,_6^{II}{}_b$ = 11.0 Hz, 1 H, H-6^{II}a), 3.99 (d, $J_3^{III},_4^{III}$ = 3.5 Hz, 1 H, H-4^{III}), 3.97 (d, $J_3^{V},_4^{V}$ = 3.0 Hz, 1 H, H-4^{V}), 3.92 (dd, $J_2^{IV},_3^{IV}$ = 10.5 Hz, 1 H, H-2^{IV}), 3.91 (dd, $J_2^{VI},_3^{VI}$ = 10.5 Hz, 1 H, H-2^{VI}), 3.85 (dd, $J_5^{II},_6^{II}{}_b$ = 5.5 Hz, 1 H, H-6^{II}b), 3.83 (dd, $J_5^{IV},_6^{IV}{}_a$ = 3.5 Hz, $J_6^{IV}{}_a,_6^{IV}{}_b$ = 12.5 Hz, 1 H, H-6^{IV}a), 3.79 (dd, $J_3^{IV},_4^{IV}$ = 9.0 Hz, 1 H, H-3^{IV}), 3.79 (dd, $J_3^{VI},_4^{VI}$ = 9.0 Hz, 1 H, H-3^{VI}), 3.77 (dd, $J_2^{II},_3^{II}$ = 10.0 Hz, 1 H, H-2^{II}), 3.77 (m, 1 H, H-6^{IV}b), 3.76 (m, 1 H, H-6^{VI}b), 3.74 (dd, $J_2^{III},_3^{III}$ = 10.5 Hz, 1 H, H-3^{III}), 3.73 (m, 1 H, H-4^{II}), 3.73 (m, 1 H, H-6^{I}b), 3.69 (dd, $J_2^{V},_3^{V}$ = 10.5 Hz, 1 H, H-3^{V}), 3.61 (m, 1 H, H-5^{II}), 3.59 (dd, 1 H, H-2^{III}), 3.55 (dd, 1 H, H-2^{V}), 3.54 (dd, $J_4^{IV},_5^{IV}$ = 9.5 Hz, 1 H, H-4^{IV}), 3.54 (dd, $J_4^{VI},_5^{VI}$ = 10.0 Hz, 1 H, H-4^{VI}), 3.79−3.67 (m, 6 H, H-5^{III}, H-6^{III}a, H-6^{III}b, H-5^{V}, H-6^{V}a and H-6^{V}b), 3.36 (s, 3 H, OC*H*$_3$), 2.08, 2.06, 2.02 and 2.01 (s, 3 H each, NAc); ^{13}C NMR (125 MHz, D$_2$O at 30 °C) δ: 175.3, 175.0 and 174.9 (2 C) (N*C*OCH$_3$), 105.5 (C-1^{V}), 103.9 (C-1^{III}), 102.1 (C-1^{II}), 99.1 (C-1^{VI}), 98.9 (C-1^{I}), 98.8 (C-1^{IV}), 79.4 (C-4^{II}), 77.7 (2 C, C-3^{I} and C-4^{III}), 77.3 (C-4^{V}), 76.3 (C-5^{III} either C-5^{V}), 76.0 (C-5^{III} either C-5^{V}), 75.5 (C-5^{II}), 73.1 (C-3^{II}), 72.6 (4 C, C-3^{III}, C-3^{V}, C-5^{IV} and C-5^{VI}), 71.4 (C-3^{III}), 71.1 (2 C, C-3^{IV} and C-3^{VI}), 71.1 (C-2^{V}), 70.6 (C-6^{I}), 70.3 (2 C, C-4^{IV} and C-4^{VI}), 70.1 (C-5^{I}), 69.7 (C-4^{I}), 60.9 (C-6^{V} either C-6^{III}), 60.8 (C-6^{V} either C-6^{III}), 60.7 (3 C, C-6^{II}, C-6^{IV} and C-6^{VI}), 55.9 (C-2^{II}), 55.6 (O*C*H$_3$), 54.6 (2 C, C-2^{IV} and C-2^{VI}), 49.2 (C-2^{I}), 22.8, 22.7, 22.5 and 22.5 (NCO*C*H$_3$). HRMS (ESI-Q-TOF) calcd for C$_{45}$H$_{76}$N$_4$O$_{31}$+Na 1191.4391; found 1191.4387.

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Supporting Information Available: Copies of NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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