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N-Benzyl-2,3-*trans*-Carbamate-Bearing Glycosyl Donors for 1,2-*cis*-Selective Glycosylation Reactions

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Glycosyl donors for the preparation of 1,2-*cis* glycosides of amino sugars have been developed. The 2,3-*trans*-cyclic-carbamate-carrying glycosyl donors were readily prepared from the corresponding known trichloroethyl carbamate protected amino sugars under standard hydroxy group benzylation conditions. The donors exhibit high 1,2-*cis* stereoselectivity towards secondary hydroxy group substrates. In the case of primary hydroxy acceptors, high stereoselectivities were achieved with the aid of the dioxane effect. After glycosylation, the carbamate was removed under alkaline conditions. Importantly, these glycosyl donors can be used in polymer-supported and solid-phase synthesis.

Introduction

The increased awareness of the biological importance of oligosaccharides has stimulated the development of efficient methods for the synthesis of glycoconjugates.[1] The 1,2-*cis*-linked 2-deoxy-2-amino sugar structure is found in various biologically interesting oligosaccharides such as amino glycoside antibiotics,[2] the GPI anchor,[3] and heparin/heparan sulfate.[4] In addition, multiple 1,2-*cis*-aminoglycoside-containing *N*-linked oligosaccharides have been found as protein modifications in *Campylobacter jejuni*.[5] Because oligosaccharides and glycoconjugates are usually found in low concentrations and/or in microheterogeneous forms, a major obstacle in the investigation of biologically important carbohydrates is the limited availability of pure and structurally well-defined sugar materials. Synthetic chemistry represents the main access route to oligosaccharides and glycoconjugates with rigorously defined chemical compositions.

Although there has been much progress in carbohydrate chemistry in the past two decades, 1,2-*cis*-selective glycosylation is still a challenge.[6] For the synthesis of 2-amino-2-deoxy sugars, 2-azidoglycosyl donors **1**, which were developed about 30 years ago, are still employed (Figure 1).[7] There are, however, some disadvantages of using these reagents. First, the glycosylation reaction is generally only moderately stereoselective. Typically, 1,2-*trans* aminoglycosides are obtained in significant amounts together with the desired 1,2-*cis* glycosides. Secondly, the preparation of azido sugars is not feasible. Attempts to generate these compounds from glycal by an azido nitration reaction resulted in the formation of many byproducts that required purification by column chromatography and ultimately provided unsatisfactory yields.[7a] An alternative method for the preparation of azido sugars from the corresponding 2-amino precursors requires the use of potentially explosive triflic azide.[8] The synthesis of 2-azido donors from mannose is possible by the transformation of the 2-hydroxy group with inversion of configuration, but this method requires a multistep reaction sequence.[9]

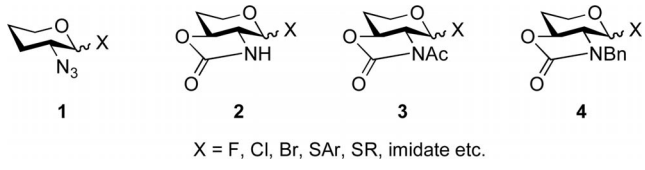

Figure 1. 1,2-*cis*-selective aminoglycosyl donors.

Progress in resolving these issues was made with the development of 2,3-*trans*-carbamate-carrying glycosyl donors **2**, which exhibit extremely high 1,2-*cis* selectivities in glycosylation reactions.[10,11] Although the 1,2-*cis* selectivity in the glycosylation reaction is high, several disadvantages of these glycosyl donors have also been reported, such as 1) significant side-reactions, including the sulfenylation and glycosylation of the nitrogen atom and 2) the requirement of at least 2 equiv. of the activator phenylsulfenyl triflate.[10b–10d] To address these disadvantages, Kerns and Oscarson and their co-workers independently reported the use of the acetylated carbamate **3**, a modified version of the carbamate glycosyl donor.[10,12] Ye and co-workers also reported the use of *N*-acetylated 2,3-*trans* carbamate donors with various acceptors for 1,2-*cis* aminoglycoside for-

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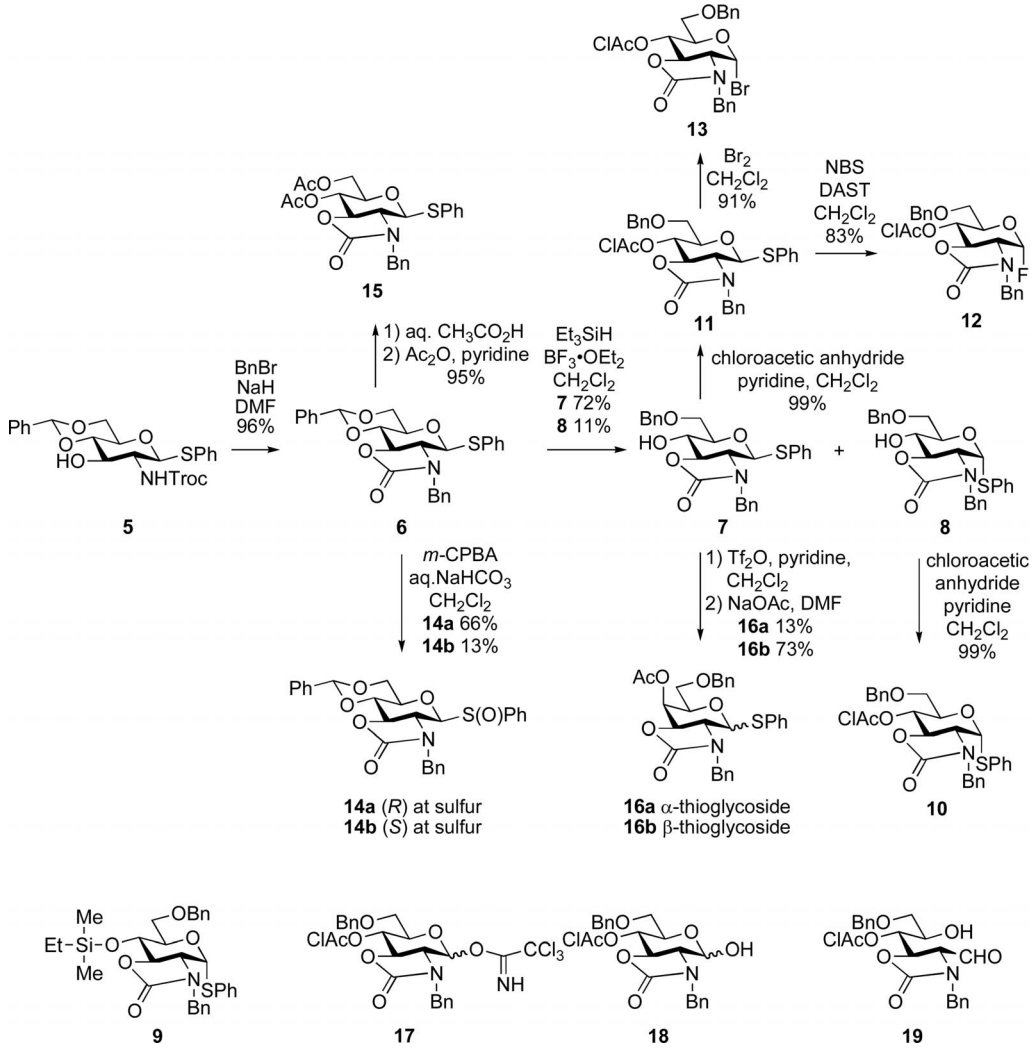
mation.[13] In reactions with acetylated oxazolidinone-carrying donor **3**, however, 1,2-*cis* selectivities were reduced significantly. In fact, β-selectivity was observed in some cases.[10c] In addition, selective removal of the cyclic carbamate of the imide was rather difficult.[10d]

We recently reported the novel *N*-benzyl-2,3-*trans*-oxazolidinone-carrying glycosyl donor **4** for 1,2-*cis*-selective glycosylation.[14] This type of donor shows extremely high 1,2-*cis* selectivity in glycosylation reactions and side-reactions at the carbamate nitrogen atom are negligible. We also recently reported the first highly efficient synthesis of an anti-*Helicobacter pylori* oligosaccharide using our novel glycosyl donor.[15] Herein we describe the scope of reactivity of our glycosyl donor with various substrates including polymer-supported and resin-bound acceptors.

Results and Discussion

Several donors were easily prepared from protected glucosamine **5** (Scheme 1).[14] Cyclic carbamate **6** was prepared in 96% yield under typical hydroxy group benzylation conditions. Compound **6** is crystalline and can be purified on a scale greater than 50 g by simple recrystallization from EtOAc/hexane. Reductive opening of the benzylidene group using $Et_3SiH/BF_3{\cdot}OEt_2$ afforded the C-4 hydroxy group **7** in 72% yield. Interestingly, the configuration of the anomeric carbon of **6** was labile under acidic conditions and the α-thioglycoside **8** was obtained in 11% yield, as described by Crich and Oscarson and their co-workers.[10e,12b] This anomerization was caused by an endocyclic cleavage/recyclization process.[16] By using similar conditions to those described above, dimethyl(ethyl)silane/$Cu(OTf)_2$ in CH_3CN[17] at room temperature gave a significant amount of anomerized product **8** in 38% yield together with dimethylethylsilylated compound **9** in 52% yield. After chloroacetylation of the hydroxy group, the thioglycosides **10** and **11** were used as glycosyl donors. The relatively stable bromide **13** was prepared from thioglycoside **11** by Br_2 treatment in 91% yield after purification by silica gel column chromatography. Fluoride donor **12** was also directly prepared from thioglycoside **11** in 83% yield using *N*-bromosuccinimide (NBS)/(diethylamino)sulfur trifluoride



Scheme 1. Preparation of various 2,3-*trans*-carbamate donors.

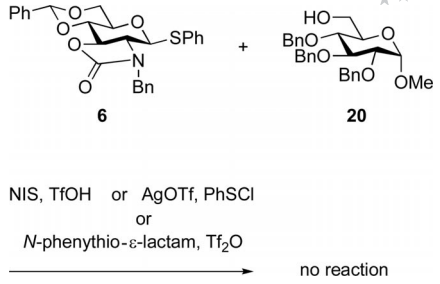
(DAST).[18] Interestingly, the bromide **13** was also obtained as a minor product in 14% in this reaction. From **6**, the corresponding sulfoxide **14** was prepared by *m*-chloroperbenzoic acid (*m*-CPBA) oxidation. The major compound **14a** possessed the *R* configuration at the sulfur atom and was obtained in 66% yield, whereas the minor isomer **14b** with the *S* configuration was obtained in 13% yield.[19] After separation of these two isomers by silica gel column chromatography, the stereochemistry at the sulfur was determined by X-ray crystallographic analysis of the ethyl acetate adduct of the minor isomer (see the Supporting Information).

The galactosamine-type donor **16** was prepared from 4-OH glucosamine derivative **7** by inversion of the configuration at the 4-position. The hydroxy group at the 4-position of **7** was changed to the corresponding triflate by using Tf_2O/pyridine and then the triflate was converted into the acetate by using NaOAc in DMF. The anomerized α-thioglycoside **16a** was also obtained in 13% yield together with β-thioglycoside **16b** (73%). Diacetylated donor **15** was prepared from **6** in two steps. Removal of the benzylidene acetal in aqueous AcOH at 100 °C was followed by acetylation to afford compound **15** in 95% yield. During removal of the benzylidene group under acidic conditions, no anomerization was observed. In summary, the glycosyl donors **10**–**16** were each readily prepared from thioglycoside **6** or **7**.

Unfortunately, it was not possible to prepare the corresponding trichloroacetimidate donor **17** because hemiacetal **18**, a precursor of the trichloroacetimidate compound **17**, could not be synthesized from thioglycoside **11**, presumably due to the strained pyranose ring. Instead, the ring-opened aldehyde **19** was obtained after treatment of thioglycoside **11** by NBS treatment in acetone/water.

With various donors in hand we turned our attention to the 1,2-*cis*-selective glycosylation reaction using reactive primary alcohol **20** as an acceptor. The benzylidene-protected glycosyl thioglycoside **6** was not activated by NIS/TfOH,[20] AgOTf/PhSCl,[21] nor *N*-(phenylthio)-ε-caprolactam/Tf_2O[22] even at room temperature (Scheme 2) and was recovered unchanged under these reaction conditions.

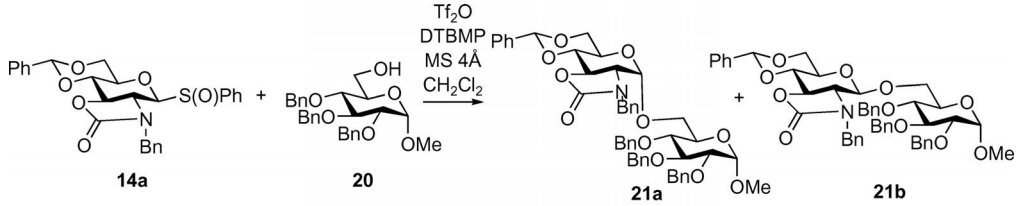
To enhance the reactivity of donor **6**, the sulfoxide group was used as a leaving group at the anomeric position.[23] Sulfoxide **14a** was activated by Tf_2O at –40 °C in the presence of acceptor **20**. Although the yield and stereoselectivity were low, the disaccharides **21a** and **21b** were obtained



Scheme 2. Glycosylation reaction with 4,6-benzylidene thioglycoside donor **6**.

(Scheme 3). Interestingly, the amount of Tf_2O affected the stereoselectivity. When 0.6 equiv. of Tf_2O were used as activator, the ratio of **21a** and **21b** was 87:13, whereas when 1.1 equiv. were used the 1,2-*cis* selectivity decreased to 57:43. The difference in stereoselectivity probably depends on the different intermediates involved in the glycosylation reaction.[24]

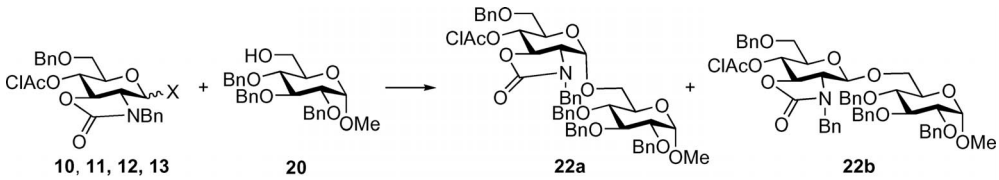
The glycosyl donor **11** lacking the cyclic benzylidene group was activated by using typical glycosylation conditions for thioglycoside activation (Table 1). Activating agents NIS/TMSOTf (entries 1 and 2), *N*-(phenylthio)-ε-caprolactam/Tf_2O (entry 3), dimethyl(methylthio)sulfonium triflate (DMTST; entry 4),[25] AgOTf/PhSCl (entries 5, 6, 8, and 9), and 1-(phenylsulfinyl)piperidine (BSP)/Tf_2O[26] (entry 10) were effective with thioglycoside **11**. The selectivity for the highly reactive primary alcohol in glycosyl acceptor **20** was low and essentially equimolar amounts of both α and β compounds were obtained in CH_2Cl_2 regardless of the activation method and reaction temperature (entries 1–6). The reactivities of the anomeric stereoisomer thioglycosides **10** and **11** were almost the same, although the α anomer **10** gave slightly higher β selectivity (entry 7). When the reaction was carried out in dioxane/toluene (3:1),[27] the desired α selectivity dramatically increased in a favorable manner (entries 8–10). When thioglycoside **11** was activated with AgOTf/PhSCl in toluene/dioxane at room temperature, α-disaccharide **22a** was obtained in 73% yield together with 10% of β-disaccharide **22b** (entry 8). Oscarson and coworkers reported the isomerization of the β-glycoside to the α-glycoside under glycosylation reaction conditions employing *N*-acetyloxazolidinone-carrying glycoside donors,[10e,12b] but we did not observe any isomerization under



Tf_2O amount	yield (%)	**21a/21b**
0.6	29	87/13
1.2	36	57/43

Scheme 3. Glycosylation reaction with 4,6-benzylidene sulfoxide donor **14a**.

Table 1. The selectivity of the glycosylation reaction with primary alcohol **20** under various conditions.[a]



Entry	Donor		Conditions	Temperature	Yield (%)	α/β
1	**11**	β-SPh	NIS, TMSOTf, CH_2Cl_2	–40 °C	51	39/61
2	**11**	β-SPh	NIS, TMSOTf, CH_2Cl_2	r.t.	49	31/69
3	**11**	β-SPh	*N*-phenylthio ε-caprolactam, Tf_2O, DTBMP, CH_2Cl_2	r.t.	82	43/57
4	**11**	β-SPh	DMTST, CH_2Cl_2	r.t.	78	38/62
5	**11**	β-SPh	AgOTf, PhSCl, DTBMP, CH_2Cl_2	–78 °C	26	54/46
6	**11**	β-SPh	AgOTf, PhSCl, DTBMP, CH_2Cl_2	r.t.	72	49/51
7	**10**	α-SPh	AgOTf, PhSCl, DTBMP, CH_2Cl_2	r.t.	68	35/65
8	**11**	β-SPh	AgOTf, PhSCl, DTBMP, dioxane/toluene	0 °C to r.t.	88	91/9
9	**11**	β-SPh	AgOTf, PhSCl, DTBMP, dioxane/toluene	–20 °C	70	91/9
10	**11**	β-SPh	BSP, TTBP, Tf_2O, dioxane/toluene	0 °C to r.t.	76	79/21
11	**12**	α-F	Cp_2HfCl_2, AgOTf, CH_2Cl_2	0 to 40 °C	0	–
12	**13**	α-Br	Ag_2O, CH_2Cl_2	r.t.	0	–
13	**13**	α-Br	Ag_2CO_2, CH_2Cl_2	r.t.	0	–
14	**13**	α-Br	AgOTf, TTBP, CH_2Cl_2	r.t.	88	44/56
15	**13**	α-Br	AgOTf, TTBP, dioxane/toluene	r.t.	90	90/10

[a] DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine; TTBP = 2,4,6-tri-*tert*-butylpyrimidine.

our glycosylation conditions. When the β-glycoside **22b** was submitted to the same reaction conditions used in entry 6, it was recovered unchanged in 89% yield.[16,28]

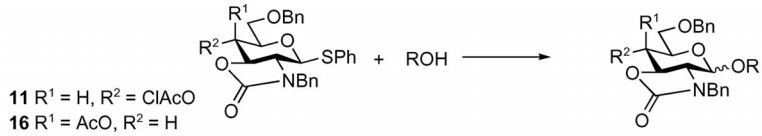
Unfortunately, fluoridated glycoside **12** was not activated under Suzuki conditions even at 40 °C in CH_2Cl_2 (entry 11).[29] Bromide donor **13** was not activated by the weak activators Ag_2O (entry 12) or Ag_2CO_3 (entry 13), but was activated by AgOTf. Selectivity was low in CH_2Cl_2 (entry 14) but high 1,2-*cis* selectivity was observed in dioxane/toluene (3:1; entry 15).

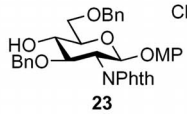
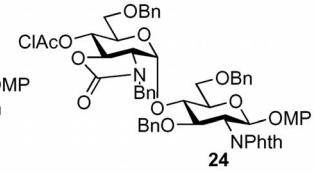
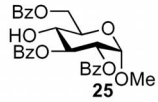
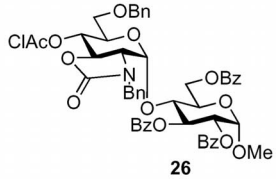
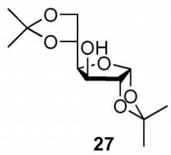
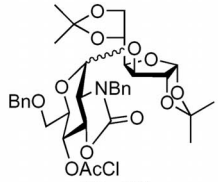
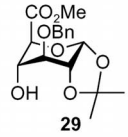
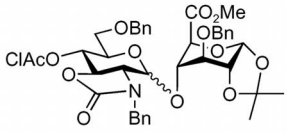
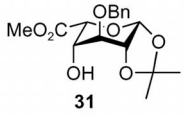
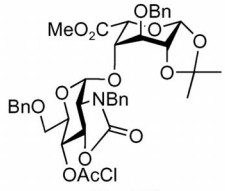
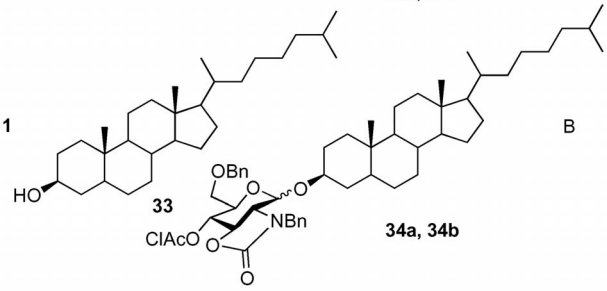
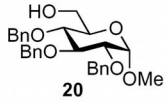
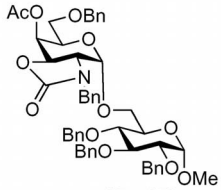
Next we explored the scope of the reaction with respect to the activity of different acceptors. High 1,2-*cis* selectivities were obtained with these donors when less reactive glycosyl donors were used as acceptors in CH_2Cl_2 (Table 2). For example, glycosylation of **11** with the hydroxy group at the 4-position of glucosamine **23** gave extremely high 1,2-*cis* selectivity (entry 1). Furthermore, although the hydroxy group at the 4-position of glucosamine is known to be unreactive as an acceptor,[30] disaccharide **24** was obtained in 54% yield. After the usual work-up and gel filtration of the crude mixture, the corresponding β-disaccharide was not observed within the detection limits of 400-MHz ^1H NMR analysis. In the case of the 4-position of glucose derivative **25** as an acceptor (entry 2), almost complete 1,2-*cis* selectivity was observed in 52% yield. Furanose-type derivative **27** was also found to be a good acceptor for 1,2-*cis* glycosylation (entry 3). Synthetic studies of glycosaminoglycan have recently increased as a result of its potential biological importance.[31] Thus, uronic acids such as iduronic and glucuronic acids are interesting structures as acceptors of the 1,2-*cis* glycosylation reaction of aminoglycosides. High 1,2-*cis* selectivities were observed for both glucuronic and idoronic acid derivatives **29**[32] and **31**[32] following activation using *N*-(phenylthio)-ε-caprolactam/Tf_2O (entries 4 and 5). In the case of glucuronic acid derivative **29**, almost complete α selectivity was achieved in dioxane/toluene with 75% yield (entry 5). In addition to these carbohydrate-derivative acceptors, chorestanol **33** also gave moderate selectivity (entry 6). Galactosamine-type thioglycoside **16** gave high *cis* stereoselectivity with the primary hydroxy group in **20** when the reaction was carried out in dioxane/toluene (entry 7). Comparing the above results, azido donor **36**,[14] which has a similar protecting group pattern to **11**, gave a lower yield and selectivity with acceptor **23** (Scheme 4). From this result, the superiority of the *N*-benzyl-2,3-*trans*-carbamate-carrying glycosyl donors for 1,2-*cis* glycoside formation is clear.

The different protecting group pattern of 6-acetate glycosyl donor **15** gave similar results to donors **11** and **16** (Table 3). When the primary alcohol **20** was used as an acceptor (entry 1), no selectivity was observed. When glycosyl acceptors **22** and **40** with secondary alcohols were used, however, complete *cis* stereoselectivity was once again achieved (entries 2 and 3).

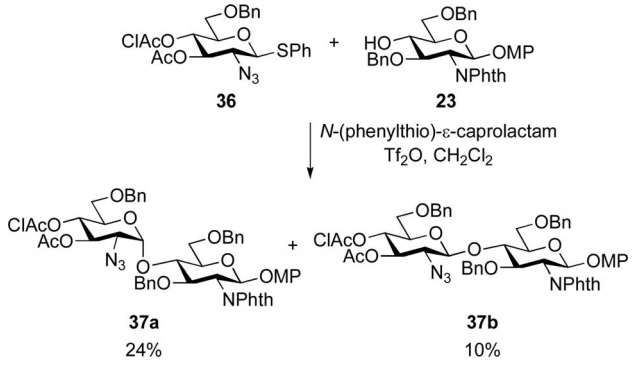
Our next concern was the application of our donor to polymer-supported or solid-phase oligosaccharide synthesis.[33] Because our reaction system does not require very low temperatures for 1,2-*cis* selectivity, these donors are expected to be suitable for automated oligosaccharide synthesis.[34] To demonstrate the utility of our donors under these conditions, their use in low-molecular-weight poly(ethylene glycol) methyl ether (MPEG, average molecular weight 750)

Table 2. Scope of acceptors in the glycosylation reaction.[a]



Entry		ROH	Product	Conditions	Yield (%)	α:β
1	**11**	 **23**	 **24**	A	56	>98/2
2	**11**	 **25**	 **26**	A	52	>98/2
3	**11**	 **27**	 **28a, 28b**	B	80	81/19
4	**11**	 **29**	 **30a, 30b**	B	75	95/5
5	**11**	 **31**	 **32a, 32b**	A B[b]	67 71	94/6 >98/2
6	**11**	 **33**	**34a, 34b**	B	64	69/31
7	**16**	 **20**	 **35a, 35b**	B	81	90/10

[a] Conditions A: *N*-(phenylthio)-ε-caprolactam, Tf_2O, CH_2Cl_2, room temp. Conditions B: AgOTf, PhSCl, DTBMP, 1,4-dioxane/toluene (3:1). [b] 1.6 equiv. of donor was used.



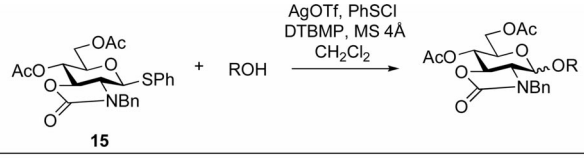
Scheme 4. Glycosylation reaction with 2-azide carrying donor **36**.

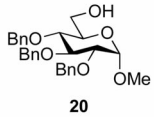
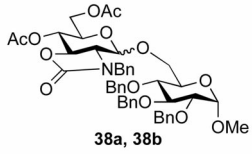
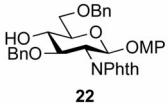
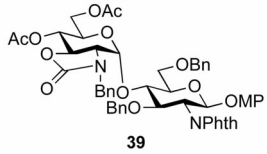
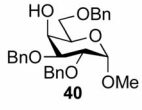
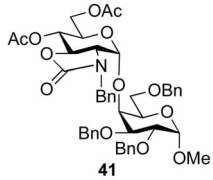
supported oligosaccharide synthesis was investigated.[35] First, a stable Lewis acid linker was attached to MPEG in two steps.[36] After Mitsunobu reaction of MPEG and commercially available phenol **42**, subsequent reduction of the aldehyde by $NaBH_4$ in MeOH gave alcohol **43** in quantitative yield (Scheme 5). Glucosaminyl imidate derivatives **44** and **45** were glycosylated to the MPEG linker in the presence of 0.5 equiv. of $BF_3{\cdot}OEt_2$. As we previously reported,[35] owing to the high polarity of MPEG, separation of the MPEG compound from any byproducts was easily achieved by chromatography by passage through a short silica gel column. The chloroacetyl group was removed under weakly basic conditions to afford acceptors **48** and **49** in 98% yields, respectively. The glycosylation reaction was carried out using glycosyl donor **11** and MPEG-supported acceptors **48** and **49**. The α/β ratios were determined by ^1H NMR integrations of the anomeric position and the 4-position without cleavage from MPEG after separation of the reagents and byproducts from MPEG-bound components. For the hydroxy group at the 4-position of glucosamine **48**, almost complete *cis* stereoselectivity was again observed in CH_2Cl_2. In the case of primary alcohol acceptor **49**, the α/β selectivity was 83:17 when using a mixture of dioxane/toluene as solvent.

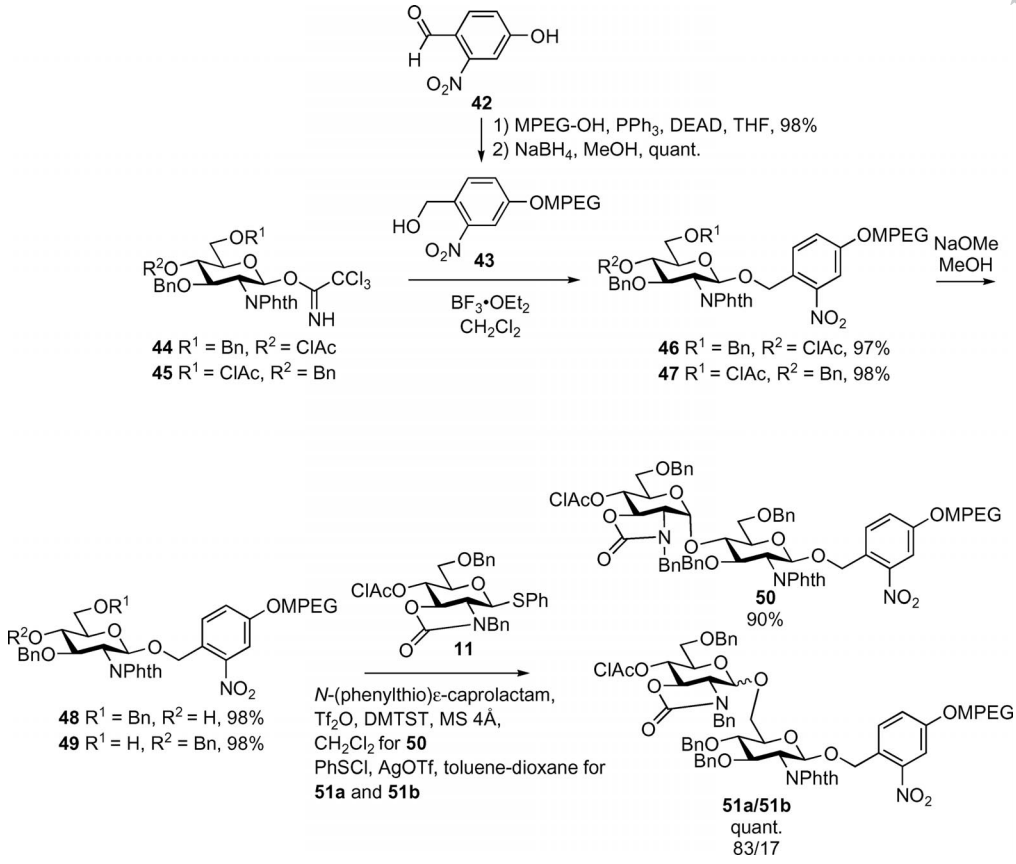
To apply our donor to solid-phase oligosaccharide synthesis, a resin-bound acceptor precursor **55** (Scheme 6) was prepared from the known pentenyl glycoside **52**[37] in seven steps. After removal of the acetyl group of **52**, the primary hydroxy group was protected as the TBDPS ether. After protecting other hydroxy groups as benzyl ethers under standard conditions, the TBDPS ether was removed and the resulting alcohol was protected as a chloroacetyl group.

The direct oxidation of the terminal alkene of **54** to a carboxylic acid was possible by using a combination of $RuO_2{\cdot}nH_2O/NaIO_4$, but the prolonged reaction time caused undesired oxidation of the benzyl ethers to benzoyl esters so that the reaction was difficult to reproduce.[38] The terminal alkene was instead transformed into the corresponding aldehyde, which was oxidized by Jones' reagent to afford carboxylic acid **55**. The *p*-nitrophenyl carbonate modified Tentagel resin **56** (0.23 mmol/g)[39] was used as the solid-phase (Scheme 7).[40] Resin **56** was treated with 2-aminoethanol to afford alcohol **57**. The progress of the reaction was monitored by following the production of yellow *p*-nitrophenolate released from the resin. The carboxylic acid

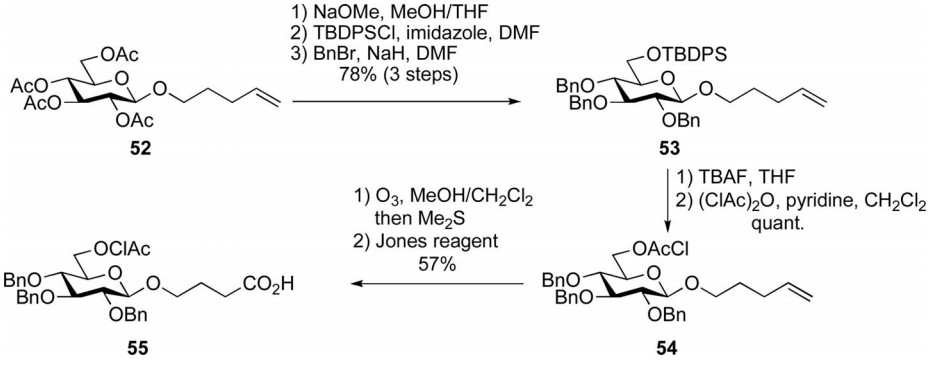
Table 3. Scope of glycosyl acceptors with 4,6-diacetate donor **15**.



Entry	ROH	Products	Yield (%)	α/β
1	 **20**	 **38a, 38b**	67	52/48
2	 **22**	 **39**	82	>98/2
3	 **40**	 **41**	73	>98/2

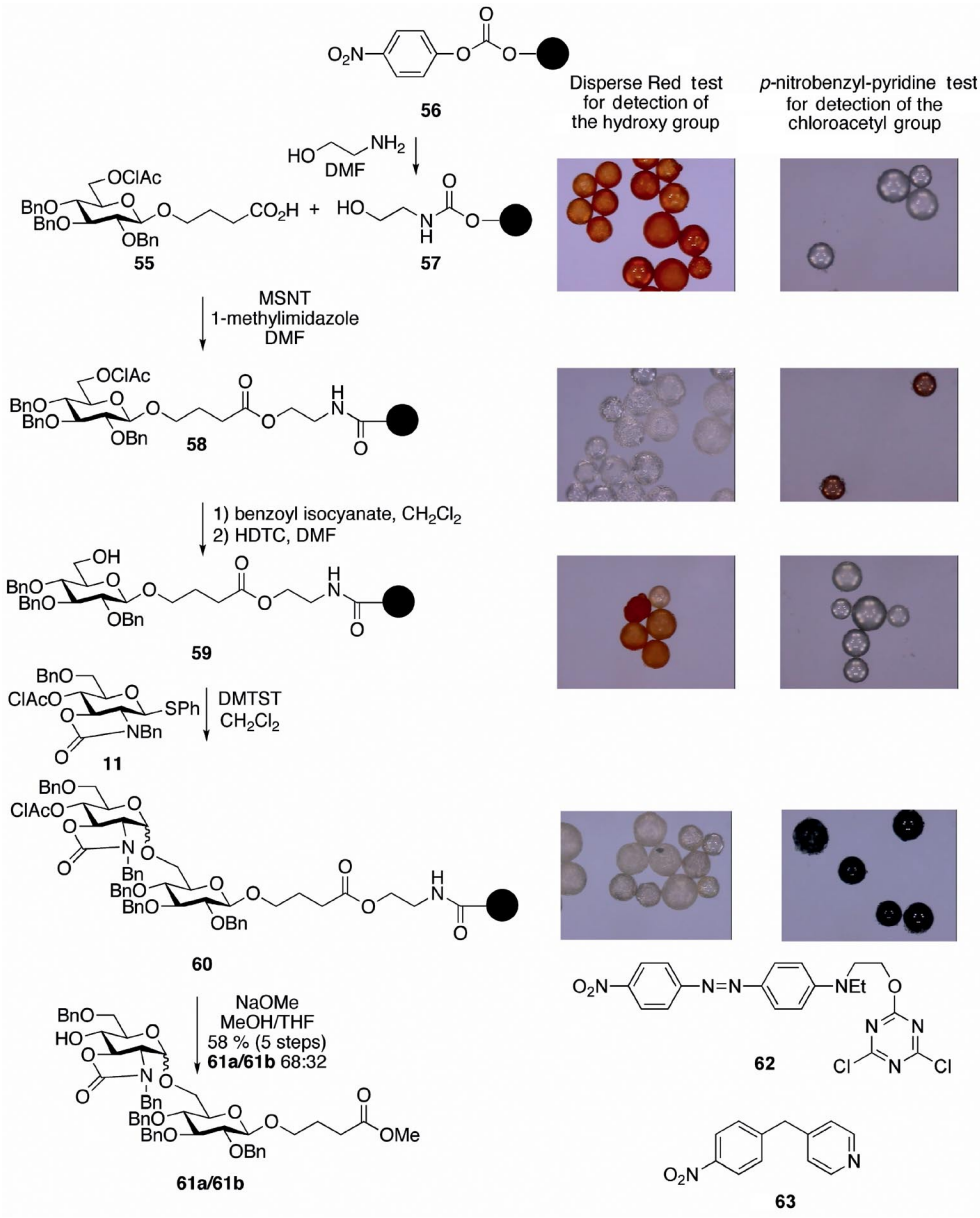


Scheme 5. Glycosylation of *N*-benzyl-2,3-*trans*-carbamate thioglycoside **11** with polymer-supported acceptors. MPEG = poly(ethylene glycol) methyl ether, average molecular weight 750.

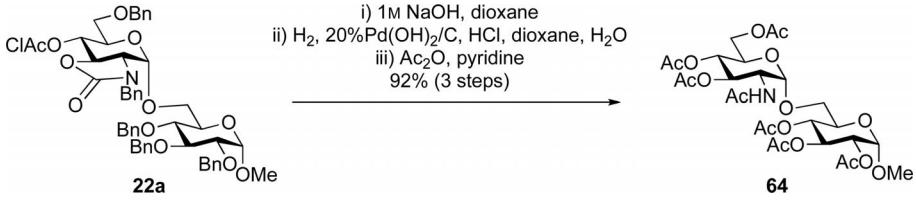


Scheme 6. Preparation of resin-bound acceptor precursor **55**.

55 was then immobilized on resin **57** using MSNT [1-(mesitylene-2-sulfonyl)-3-nitro-1*H*-1,2,4-triazole] and 1-methylimidazole.[41] Unlike solution-phase synthesis, a lack of methodology for monitoring the progress of solid-phase reactions hampers the setting-up of reaction conditions.[42] To overcome this difficulty, we have previously developed a color test for monitoring the glycosylation and deprotection reactions.[35c] The nucleophilic amino groups and hydroxy groups are detected with Disperse Red/cyanuric chloride conjugate **62**, whereas chloroacetyl groups are detected with *p*-nitrobenzylpyridine (**63**). After immobilization of acid **55** to the resin, the Disperse Red/cyanuric chloride test provided negative results, but the *p*-nitrobenzylpyridine test gave a red color. Although the Disperse Red color test showed the absence of a hydroxy group, the capping reaction with benzoyl isocyanate was carried out to cap the remaining hydroxy group.[43] After removal of the chloroacetyl group of the resin-bound compound **58** by HDTC (hydrazinedithiocarbonate),[44] the two color tests gave the opposite results. Then **59** was glycosylated using donor **11**. After glycosylation, the *p*-nitrobenzylpyridine test for the chloroacetyl group showed the existence of a chloroacetyl group, whereas the Disperse Red color test revealed the absence of the hydroxy group. Disaccharides **61a/61b** were obtained after cleavage from the resin in 58% yield in five steps in a 68:32 ratio in favor of the 1,2-*cis* product.



Scheme 7. Application of *N*-benzyl-2,3-*trans*-carbamate donor to solid-phase synthesis with the color test.



Scheme 8. Deprotection procedure for *N*-benzyl-2,3-*trans*-carbamates.

Deprotection of the glycosidation products prepared with our new donors proceeded under typical conditions. For example, the carbamate group of disaccharide **22a** was cleaved under basic conditions [$Ba(OH)_2$ in EtOH/THF/H_2O or aqueous NaOH in dioxane] followed by hydrogenolysis of both the *N*- and *O*-benzyl groups (Scheme 8). The fully deprotected disaccharide was then acetylated for easy handling. Disaccharide **64** was obtained in 94% overall yield for the three steps. The carbamate **6** was recovered without rupture of the carbamate group after stirring over-

night with a catalytic amount of NaOMe in MeOH, 10% ethylenediamine in BuOH at 90 °C, hydrazine monohydrate in DMF at 90 °C, or 10 equiv. of $NaBH_4$ in MeOH.

Conclusions

In this paper we have described the preparation of *N*-benzyl-2,3-*trans*-carbamate-carrying glycosyl donors and discussed the scope of the glycosylation reaction using these novel reagents.[45] We believe that our donors are excellent for 1,2-*cis* glycosidic bond formation with respect to their preparation, glycosylation selectivity, and deprotection procedures, as demonstrated by their reactivity with a variety of substrates including their use in polymer-supported and solid-phase oligosaccharide synthesis. Application of such donors to automated oligosaccharide synthesis is possible because no severe low temperature is required for 1,2-*cis* selectivity.[33,34]

The origin of the high 1,2-*cis* selectivity of the *trans*-carbamate-carrying donor in the glycosylation reaction is presently unclear. One example of a β-triflate of pyranoside has been reported[46] and thus the possibility of S_N2 displacement of an in situ generated β-triflate cannot be eliminated. Although only α-triflates derived from *N*-acetyl-2,3-*trans*-carbamate-carrying pyranosides have been observed,[10c] the higher-energy β-triflates may exist in minor amounts. The reaction, however, probably proceeds in an S_N1 manner via a very reactive oxacarbonium ion.[47] The *trans*-fused cyclic protecting group would severely decrease the flexibility of the attached oxacarbonium ion ring in the S_N1 reaction, which allows the alcohol to approach from only one side resulting in the high selectivity.[48] Recently, 1,2-*cis* selective glycosylation reactions using glycosyl donors bearing *trans*-cyclic protecting groups such as glucoside,[49] sialic acid,[50] and 2-keto-deoxy-D-glycero-D-galacto-nonulosonic acid (KDN) have been reported.[51] Investigations to further elucidate the mechanism behind the high 1,2-*cis* selectivity of these glycosylation reactions are underway.

Experimental Section

General Procedures: ^1H NMR spectra were with a JEOL EX-400 spectrometer as solutions in $CDCl_3$ unless otherwise stated. Chemical shifts are reported in ppm downfield from the signal for Me_4Si. ^{13}C NMR spectra were recorded in $CDCl_3$ unless otherwise stated and $CDCl_3$ (δ = 77.0 ppm) was used as the internal standard. Optical rotations were measured with a JASCO DIP3-10 instrument in $CHCl_3$ at ambient temperature. All chemicals were reagent grade and were used as supplied unless otherwise noted. Technical grade or reagent grade solvents for extraction and chromatography were used without further purification. Molecular sieves (4-Å) were activated by heating at 170 °C in vacuo just before use. Merrifield and Tentegel resins were purchased from NOVA Biochem. Bio-beads was purchased from BIO-RAD and used for gel filtration column chromatography. A cute mixer CM-1000 (EYELA) was used as a shaker for solid-phase reactions. Polypropylene tubes equipped with a filter (RT5-M100 and RT20-M50; EYELA) were used as a reaction vessel for solid-phase synthesis. A microscope (CCD Micro Scope Inf-550, from Moritex) and Image Pro Plus[52] were used to analyze the color of the resins on a computer.

Phenyl 2-Amino-*N*-benzyl-4,6-*O*-benzylidene-2-*N*,3-*O*-carbonyl-2-deoxy-1-thio-α-D-glucopyranoside (6): NaH (0.2 g, 8.22 mmol) was added to an ice-cold mixture of trichloroethyl carbamate **5** (2.20 g, 4.11 mmol) and benzyl bromide (0.98 mL, 8.22 mmol) in DMF (40 mL). After stirring the mixture for 30 min in an ice–water bath, the reaction mixture was warmed up to room temperature and stirred for 30 min. The excess benzyl bromide was quenched by the addition of Et_3N (1.5 mL) and the mixture was diluted with EtOAc, poured into saturated aqueous NH_4Cl, and extracted with EtOAc. The combined organic extracts were washed with water and brine, dried with Na_2SO_4, filtered, and concentrated. The crystalline residue was crystallized from EtOAc/hexane to give **6** (1.88 g, 96%) as a colorless crystal; m.p. 216–217 °C. $[\alpha]_D^{24}$ = 72 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.26 (m, 15 H, aromatic *H*), 5.59 (s, 1 H, acetal-PhC*H*), 4.85 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, 1-H), 4.83 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H, *N*-CH_2Ph), 4.78 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H, *N*-CH_2Ph), 4.32 (t, $^3J_{H,H}$ = 10.5 Hz, 1 H, 3-H), 4.32 (dd, $^3J_{H,H}$ = 10.5, 5.0 Hz, 1 H, 6a-H), 4.04 (dd, $^3J_{H,H}$ = 10.0, 8.5 Hz, 1 H, 4-H), 3.90 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 6b-H), 3.57 (m, 1 H, 5-H), 3.52 (dd, $^3J_{H,H}$ = 10.5, 10.0 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.8 (*C*=O), 136.4, 136.3, 132.6, 131.7, 129.3, 129.2, 128.7, 128.3, 128.0, 127.6, 126.1, 101.4 (acetal-*C*HPh), 87.7 (C-1), 78.9 (C-3), 78.4 (C-4), 72.8 (C-5), 68.2 (C-6), 61.5 (C-2), 47.7 (*N*-*C*H_2Ph) ppm. $C_{27}H_{25}NO_5S$ (475.56): calcd. C 68.19, H 5.30, N 2.95; found C 68.15, H 5.17, N 2.88.

Phenyl 6-*O*-Benzyl-2-benzylamino-2-*N*,3-*O*-carbonyl-2-deoxy-1-thio-α- (7) and -β-D-glucopyranoside (8): $BF_3{\cdot}OEt_2$ (3.9 mL, 30.8 mmol) was added slowly to an ice-cold mixture of **6** (7.3 g, 15.4 mmol) and triethylsilane (30 mL, 184.8 mmol) in CH_2Cl_2 (200 mL). After stirring the mixture for 80 min at the ice-cold temperature, the mixture was poured into saturated aqueous $NaHCO_3$ and extracted with $CHCl_3$. The combined organic extracts were washed with water, dried with Na_2SO_4, filtered, and concentrated. Purification of the residue by flash column chromatography on silica gel ($CHCl_3$/EtOAc, 3:1–2:1–1:9) and subsequent crystallization from EtOAc/hexane gave β-glycoside **7** (5.3 g, 72%) and α-glycoside **8** (0.78 g, 11%). Compounds **7** and **8** were crystallized from EtOAc and hexane, respectively.

β-Glycoside 7: M.p. 125–126 °C. $[\alpha]_D^{22}$ = –77 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.22 (m, 15 H, aromatic *H*), 4.77 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, 1-H), 4.74 (s, 2 H, *N*-CH_2Ph), 4.58 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph) 4.55 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.07 (t, $^3J_{H,H}$ = 10.5 Hz, 1 H, 3-H), 4.01 (m, 1 H, 4-H), 3.79 (dd, $^3J_{H,H}$ = 10.0, 5.0 Hz, 1 H, 6a-H), 3.76 (dd, $^3J_{H,H}$ = 8.0, 5.0 Hz, 1 H, 6b-H), 3.56 (m, 1 H, 5-H), 3.41 (dd, $^3J_{H,H}$ = 10.5, 9.0 Hz, 1 H, 2-H), 2.97 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, 4-O*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3 (*C*=O), 137.5, 136.22, 132.4, 132.3, 129.1, 128.6, 128.5, 128.4, 128.2, 127.9, 127.7, 127.6, 86.7 (C-1), 82.4 (C-3), 79.6 (C-5), 73.7 (*O*-*C*H_2Ph), 69.7 (C-6), 69.1 (C-4), 60.1 (C-2), 47.6 (*N*-*C*H_2Ph) ppm. $C_{27}H_{27}NO_5S$ (477.57): calcd. C 67.90, H 5.70, N 2.93; found C 67.89, H 5.56, N 2.84.

β-Glycoside 8: M.p. 118–119 °C. $[\alpha]_D^{22}$ = +210 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.50–7.24 (m, 15 H, aromatic *H*), 5.37 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H, 1-H), 4.79 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.60 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.50 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.36 (dd, $^3J_{H,H}$ = 12.0, 9.5 Hz, 1 H, 3-H), 4.17 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.14 (m, 1 H, 5-H), 4.02 (m, 1 H, 4-H), 3.78 (dd, $^3J_{H,H}$ = 10.5, 4.5 Hz, 1 H, 6a-H), 3.70 (dd, $^3J_{H,H}$ = 10.5, 4.0 Hz, 1 H, 6b-H), 3.50 (dd, $^3J_{H,H}$ = 12.0, 4.5 Hz, 1 H, 2-H), 2.71 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 4-O*H*) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 21 °C): δ = 158.6 (*C*=O), 137.5, 134.4, 132.9, 131.9, 129.1, 129.0, 128.9, 128.5, 128.4, 127.9, 127.7, 84.9 (C-1), 78.4 (C-3), 73.6 (*O*-*C*H$_2$Ph), 73.0 (C-5), 69.4 (C-4), 68.7 (C-6), 59.6 (C-2), 47.8 (*N*-*C*H$_2$Ph) ppm. $C_{27}H_{27}NO_5S$ (477.57): calcd. C 67.90, H 5.70, N 2.93; found C 67.96, H 5.64, N 2.85.

Phenyl 6-*O*-Benzyl-2-benzylamino-2-*N*,3-*O*-carbonyl-4-*O*-chloroacetyl-2-deoxy-1-thio-α-D-glucopyranoside (10): Chloroacetic anhydride (42 mg, 0.245 mmol) was added to a solution of alcohol **8** (78 mg, 0.163 mmol) in pyridine (26 μL, 0.326 mmol) and CH_2Cl_2 (3 mL) at 4 °C. After 1 h, the solution was diluted with $CHCl_3$ and washed with 1 M HCl. The aqueous layer was extracted with $CHCl_3$ and the whole extract was washed with brine. The organic layer was washed with brine and filtered. After concentration, the crude was purified by silica gel column chromatography (hexane/toluene/EtOAc, 2:1:1) to give the product **10** (90 mg, 99%). $[\alpha]_D^{24}$ = +220 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.24 (m, 15 H, aromatic *H*), 5.41 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, 1-H), 5.40 (t, $^3J_{H,H}$ = 10.5 Hz, 1 H, 4-H), 4.81 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-C*H*$_2$Ph), 4.57 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.44 (dd, $^3J_{H,H}$ = 12.0, 10.5 Hz, 1 H, 3-H), 4.30 (m, 1 H, 5-H), 4.19 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.17 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-C*H*$_2$Ph), 3.89 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.97 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.64 (dd, $^3J_{H,H}$ = 12.0, 5.0 Hz, 1 H, 2-H), 3.58 (dd, $^3J_{H,H}$ = 11.0, 2.5 Hz, 1 H, 6a-H), 3.56 (dd, $^3J_{H,H}$ = 11.0, 4.0 Hz, 1 H, 6b-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6 (oxazolidinone C=O), 157.8, 137.1, 134.1, 132.3, 131.9, 129.3, 129.1, 128.9, 128.6, 128.4, 128.2, 128.1, 128.0, 84.8 (C-1), 75.8 (C-3), 73.6 (*O*-*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) ppm. $C_{29}H_{28}ClNO_6S$ (554.05): calcd. C 62.87, H 5.09, N 2.53; found C 62.65, H 5.05, N 2.42.

Phenyl 6-*O*-Benzyl-2-benzylamino-2-*N*,3-*O*-carbonyl-4-*O*-chloroacetyl-2-deoxy-1-thio-β-D-glucopyranoside (11): Pyridine (0.59 mL, 5.44 mmol) was added to an ice-cold mixture of **7** (2.6 g, 3.64 mmol) and chloroacetic anhydride (0.94 g, 5.47 mmol) in CH_2Cl_2 was added. After stirring the mixture for 30 min, the mixture was poured into 0.1 M aqueous HCl and extracted with $CHCl_3$. The combined organic extracts were washed with water, dried with Na_2SO_4, filtered, and concentrated. Purification by column chromatography on silica gel (toluene/hexane/EtOAc, 2:1:1) gave 4-*O*-ClAc **11** (2.02 g, 99%) as a colorless syrup. $[\alpha]_D^{25}$ = –59 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.14 (m, 15 H, aromatic *H*), 5.37 (dd, $^3J_{H,H}$ = 10.5, 8.5 Hz, 1 H, 4-H), 4.80 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 1-H), 4.74 (s, 2 H, *N*-C*H*$_2$Ph), 4.55 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.47 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.18 (t, $^3J_{H,H}$ = 11.0 Hz, 1 H, 3-H), 3.99 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.91 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.74 (m, 1 H, 5-H), 3.57 (dd, $^3J_{H,H}$ = 11.0, 9.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8 (oxazolidinone C=O), 158.4, 137.4, 135.9, 132.5, 132.0, 129.1, 128.7, 128.5, 128.4, 128.2, 127.9, 127.9, 127.8, 86.8 (C-1), 79.5 (C-3), 78.3 (C-5), 73.6 (*O*-*C*H$_2$Ph), 69.6 (C-4), 68.6 (C-6), 60.1 (C-2), 47.6 (*N*-*C*H$_2$Ph), 40.4 (CO*C*H$_2$Cl) ppm. $C_{29}H_{28}ClNO_6S$ (554.05): calcd. C 62.87, H 5.09, N 2.53; found C 62.71, H 5.04, N 2.47.

6-*O*-Benzyl-2-benzylamino-2-*N*,3-*O*-carbonyl-4-*O*-chloroacetyl-2-deoxy-α-D-glucopyranosyl Fluoride (12): NBS (49 mg, 0.273 mmol) and DAST (48 μL, 0.364 mmol) were added to a solution of thioglycoside **11** (101 mg, 0.182 mmol) in CH_2Cl_2 (4 mL) at –10 °C. After stirring the mixture at 0 °C for 2 h, satd. $NaHCO_3$ was added. The aqueous layer was extracted with EtOAc. The combined layers were washed with satd. $NaHCO_3$ and brine. After drying the extract over Na_2SO_4, the solvent was removed. The residue was purified by silica gel column chromatography (hexane/toluene/EtOAc, 3:3:1) to give 70 mg (83%) of fluoride **12** as a colorless oil. $[\alpha]_D^{24}$ = –3.9 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.36–7.16 (m, 10 H, aromatic *H*), 5.49 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H, 4-H), 5.42 (dd, $^3J_{H,H}$ = 2.0, $^2J_{H,F}$ = 57.2 Hz, 1 H, 1-H), 4.60 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, *N*-C*H*$_2$Ph), 4.54 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.53 (t, $^3J_{H,H}$ = 10.8 Hz, 1 H), 4.39 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.32 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, *N*-C*H*$_2$Ph), 3.97 (m, 1 H, 5-H), 3.95 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, COC*H*$_2$Cl), 3.86 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, COC*H*$_2$Cl), 3.55 (dd, $^3J_{H,H}$ = 11.2, 2.4 Hz, 1 H), 3.47 (dd, $^3J_{H,H}$ = 10.8, 3.2 Hz, 1 H, 6a-H), 3.38 (dd, $^3J_{H,H}$ = 12.0, 1.6 Hz, 1 H, 6b-H), 3.32 (dd, $^3J_{H,H}$ = 12.0, 1.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 165.3, 157.5, 136.8, 134.0, 129.0, 128.6, 128.4, 128.1, 128.0, 127.9, 103.3, 101.0, 73.7, 73.6, 72.8, 69.3, 66.6, 60.5, 60.2, 48.6, 40.3 ppm. HRMS: calcd. for $C_{23}H_{23}ClFNO_6$ + Na [M + Na]$^+$ 486.1090; found 486.1093.

6-*O*-Benzyl-2-benzylamino-2-*N*,3-*O*-carbonyl-4-*O*-chloroacetyl-2-deoxy-α-D-glucopyranosyl Bromide (13): A solution of 1 M Br_2 in CH_2Cl_2 was added to a stirring ice-cold solution of **11** (360 mg, 0.65 mmol) in CH_2Cl_2. After stirring the mixture for 30 min, the mixture was poured into ice-cold 10% aqueous $Na_2S_2O_3$ and extracted with $CHCl_3$. The combined organic extracts were washed with brine, dried with Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography on silica gel (toluene/hexane/EtOAc, 3:3:1) gave **13** as a colorless foam (310 mg, 91%). $[\alpha]_D^{26}$ = +118 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.24 (m, 10 H, aromatic *H*), 6.25 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, 1-H), 5.52 (dd, $^3J_{H,H}$ = 10.5, 9.5 Hz, 1 H, 4-H), 4.82 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 4.66 (dd, $^3J_{H,H}$ = 11.5, 10.5 Hz, 1 H, 3-H), 4.45 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.39 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 3.96 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 4.05 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 3.95 (m, 1 H, 5-H), 3.87 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.56 (dd, $^3J_{H,H}$ = 11.0, 3.0 Hz, 1 H, 6a-H), 3.51 (dd, $^3J_{H,H}$ = 11.0, 3.5 Hz, 1 H, 6b-H), 3.37 (dd, $^3J_{H,H}$ = 11.5, 3.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.4 (*C*OCH$_2$Cl), 157.4 (oxazolidinone C=O), 136.8, 133.6, 129.3, 128.9, 128.8, 128.5, 128.2, 128.1, 83.4 (C-1), 75.3 (C-3), 74.7 (C-5), 73.6 (*O*-*C*H$_2$Ph), 68.5 (C-4), 66.2 (C-6), 60.7 (C-2), 47.6 (*N*-*C*H$_2$Ph), 40.2 (CO*C*H$_2$Cl) ppm. $C_{23}H_{23}BrClNO_6$ (524.79): calcd. C 52.64, H 4.42, N 2.67; found C 52.36, H 4.45, N 2.57.

Sulfoxides 14a and 14b: *m*-CPBA (0.20 g, 1.16 mmol) was added to a solution of thioglycoside **6** (0.5 g, 1.05 mmol) in CH_2Cl_2 and 10% aq. $NaHCO_3$ at 0 °C. After stirring the mixture at 0 °C for 1 h, the mixture was warmed to room temperature and stirred for 1 h. The mixture was diluted with $CHCl_3$ and washed with 10% $NaHCO_3$. After extracting the aqueous layer, the organic phase was washed with10% $Na_2S_2O_3$ and brine. The extract was dried with Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography ($CHCl_3$/EOAc, 3:1) to give **14a** (342 mg, 66%) and **14b** (68 mg, 13%) as products. Sulfoxide **14a**: m.p. 160 °C. $[\alpha]_D^{24}$ = –137.5 (*c* = 0.59, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.47–7.32 (m, 14 H, aromatic *H*), 7.14 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, aromatic *H*), 5.55 (s, 1 H, acetal PhC*H*), 5.14 (d, $^3J_{H,H}$ = 16.8 Hz, 1 H, *N*-C*H*$_2$Ph), 4.53 (d, $^3J_{H,H}$ = 16.8 Hz, 1 H, *N*-C*H*$_2$Ph), 4.39 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H), 4.12 (t, $^3J_{H,H}$ = 8.4 Hz, 1 H), 4.04–3.94 (m, 3 H), 3.90 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H), 3.42 (m, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 158.3 (oxazolidinone C=O), 137.8, 136.8, 136.0, 131.6, 129.2, 128.9, 128.7, 128.2, 127.7, 127.1, 125.9, 124.8, 101.4 (acetal Ph*C*H), 90.8 (C-1), 78.1, 77.8, 73.6, 67.6, 59.2, 48.9 ppm. HRMS for $C_{27}H_{25}NO_6S$ + Na [M + Na]$^+$ 514.1295; found 514.1289.

Sulfoxide 14b: M.p. 168 °C. $[\alpha]_D^{24}$ = –30.9 (*c* = 0.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.53–7.31 (m, 15 H, aromatic

H), 5.47 (s, 1 H, acetal PhC*H*), 5.11 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H, *N*-CH_2Ph), 4.87 (d, $^3J_{H,H}$ = 15.6 Hz, 1 H, *N*-CH_2Ph), 4.30 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H, 1-H), 4.26 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H), 3.99 (dd, $^3J_{H,H}$ = 10.0, 4.4 Hz, 1 H), 3.87 (t, $^3J_{H,H}$ = 8.8 Hz, 1 H), 3.62 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H), 3.56 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H), 3.40 (m, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 158.8 (oxazolidinone C=O), 139.2, 135.9, 134.9, 132.1, 129.2, 128.9, 128.8, 128.7, 128.2, 128.0, 125.9, 125.9, 101.4 (acetal Ph*C*H), 95.0 (C-1), 78.2, 77.8, 77.2, 73.5, 67.5, 60.8, 48.5 ppm. $C_{27}H_{25}NO_6S$ (491.56): calcd. C 65.97, H 5.13, N 2.85; found C 65.87, H 5.17, N 2.57.

Phenyl 4,6-Di-*O*-acetyl-2-benzylamino-2-*N*,3-*O*-carbonyl-2-deoxy-1-thio-α-D-glucopyranoside (15): A mixture of benzylidene acetal **6** (2.14 g, 4.51 mmol) in AcOH (40 mL) and water (10 mL) was stirred at 100 °C for 1 h. After concentration, the mixture was washed with diethyl ether/hexane to remove benzaldehyde. After drying the mixture in vacuo, the crude was dissolved in pyridine (20 mL) and Ac_2O (20 mL) was added. After stirring overnight, the mixture was evaporated. The residue was diluted with AcOEt and 1 M HCl. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was removed. The residue was purified by silica gel column chromatography (hexane/EtOAc, 7:3–1:1) to give the diacetate **15** (2.02 g, 95%). $[\alpha]_D^{24}$ = –74 (*c* = 0.85, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.38–7.26 (m, 10 H, aromatic *H*), 5.23 (t, $^3J_{H,H}$ = 9.2 Hz, 1 H, 4-H), 4.75 (d, $^3J_{H,H}$ = 9.6 Hz, 1 H, 1-H), 4.74 (s, 2 H, *N*-CH_2Ph), 4.21–4.11 (m, 3 H, 6-H, 3-H), 3.71 (m, 1 H, 5-H), 3.51 (t, $^3J_{H,H}$ = 9.6 Hz, 1 H, 2-H), 2.09 (s, 3 H, COCH_3), 2.04 (s, 3 H, COCH_3) ppm. ^{13}C NMR (500 MHz, $CDCl_3$, 22 °C): δ = 170.2 (*C*OCH$_3$), 167.0 (oxazolidinone C=O), 158.3, 135.7, 132.8, 129.0, 128.6, 128.1, 127.7, 86.7 (C-1), 79.8, 77.2, 67.4, 62.3, 60.3, 47.7, 20.9 (CO*C*H$_3$), 20.8 (CO*C*H$_3$) ppm. $C_{24}H_{25}NO_7S$ (471.52): calcd. C 61.13, H 5.34, N 2.97; found C 61.10, H 5.25, N 2.86.

Phenyl 4-*O*-Acetyl-2-benzylamino-6-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-1-thio-α- and β-D-galactopyranoside (16): Trifluoromethanesulfonic anhydride (Tf_2O, 1.8 mL, 10.5 mmol) was added to a mixture of **7** (2.5 g, 5.23 mmol) and pyridine (1.7 mL, 21.0 mmol) in CH_2Cl_2 (30 mL) at –40 °C and then the mixture was warmed to –20 °C. After stirring the mixture for 3 h, the mixture was poured into 0.1 M aqueous HCl and extracted with $CHCl_3$. The combined organic extracts were washed with satd. aqueous $NaHCO_3$ and water, dried (Na_2SO_4), filtered, and concentrated to dryness. The crude triflate was used in the next step without further purification. The triflate was treated with sodium acetate (4.3 g, 52.3 mmol) in DMF (30 mL) at 60 °C for 2 d. The mixture was diluted with EtOAc, poured into ice-cold water, and extracted with EtOAc. The combined organic extracts were washed with water and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash column chromatography ($CHCl_3$/EtOAc, 14:1). The first elution was α-galactoside **16a** (0.34 g, 13%) and eluted next was β-galactoside **16b** (2.0 g, 73%). Galactosides **16a** and **16b** were crystallized from EtOAc/hexane, respectively.

α-Galactoside 16a: M.p. 148–149 °C. $[\alpha]_D^{25}$ = +186 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.21 (m, 15 H, aromatic *H*), 5.66 (br. s, 1 H, 4-H), 5.40 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H, 1-H), 4.71 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.56 (m, 1 H, 5-H), 4.49 (dd, $^3J_{H,H}$ = 12.5, 2.5 Hz, 1 H, 3-H), 4.49 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.43 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.28 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 3.97 (dd, $^3J_{H,H}$ = 12.5, 4.5 Hz, 1 H, 2-H), 3.56 (dd, $^3J_{H,H}$ = 10.0, 5.5 Hz, 1 H, 6a-H), 3.51 (dd, $^3J_{H,H}$ = 10.0, 6.0 Hz, 1 H, 6b-H), 2.01 (s, 3 H, COCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3 (*C*OCH$_3$), 158.0 (oxazolidinone C=O), 137.5, 134.5, 132.3, 129.1, 129.0, 128.9, 128.4, 128.3, 128.1, 127.8, 127.7, 85.8 (C-1), 74.2 (C-3), 73.5 (*O*-CH_2Ph), 70.0 (C-5), 68.3 (C-6), 66.1 (C-4), 56.1 (C-2), 48.2 (*N*-CH_2Ph), 20.6 (CO*C*H$_3$) ppm. $C_{29}H_{29}NO_6S$ (519.61): calcd. C 67.03, H 5.63, N 2.70; found C 66.78, H 5.41, N 2.64.

β-Galactoside 16b: M.p. 119–120 °C. $[\alpha]_D^{25}$ = –95 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 15 H, aromatic *H*), 5.67 (br. s, 1 H, 4-H), 4.78 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H, *N*-CH_2Ph), 4.76 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 1-H), 4.70 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H, *N*-CH_2Ph), 4.52 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.42 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.21 (dd, $^3J_{H,H}$ = 11.5, 2.0 Hz, 1 H, 3-H), 3.93 (br. t, 1 H, 5-H), 3.84 (dd, $^3J_{H,H}$ = 11.5, 9.5 Hz, 1 H, 2-H), 3.57 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, 6a-H, 6b-H), 2.04 (s, 3 H, COCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.2 (C=O), 153.6 (oxazolidinone C=O), 137.5, 136.4, 132.4, 132.2, 129.1, 128.6, 128.4, 128.4, 128.0, 127.8, 127.5, 88.0 (C-1), 78.9 (C-3), 77.2 (C-5), 73.6 (*O*-CH_2Ph), 68.1 (C-6), 65.1 (C-4), 57.1 (C-2), 48.1 (*N*-CH_2Ph), 20.6 (CO*C*H$_3$) ppm. $C_{29}H_{29}NO_6S$ (519.61): C 67.03, H 5.63, N 2.70; found C 66.95, H 5.36, N 2.59.

Disaccharides 21a and 21b: Tf_2O (10 μL, 0.06 mmol) was added dropwise to a solution of acceptor (46 mg, 0.099 mmol), donor (58 mg, 0.119 mmol), DTBMP (41 mg, 0.198 mmol), and 4-Å molecular sieves (200 mg) in CH_2Cl_2 (4 mL) at –40 °C. After stirring the mixture at –40 °C for 12 h, Et_3N and satd. $NaHCO_3$ were added. The aqueous layer was extracted with EtOAc and the combined layers were washed with brine. After drying the mixture over Na_2SO_4, the solvent was evaporated. The residue was purified by preparative TLC (hexane/EtOAc, 7:3) to give **21a** (21 mg, 26%) and **21b** (3.2 mg, 3%).

Disaccharide 21a: $[\alpha]_D^{24}$ = 21.7 (*c* = 0.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.48–7.14 (m, 25 H, aromatic *H*), 5.50 (s, 1 H, acetal PhC*H*), 5.00 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-CH_2Ph), 4.90 (d, $^3J_{H,H}$ = 11.2 Hz, 1 H, *O*-CH_2Ph), 4.83 (d, $^3J_{H,H}$ = 11.2 Hz, 1 H, *O*-CH_2Ph), 4.83 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H, 1-H), 4.79 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H, *O*-CH_2Ph), 4.62 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.60–4.48 (m, 4 H), 4.13 (d, $^3J_{H,H}$ = 4.4 Hz, 1 H), 4.10–4.01 (m, 2 H), 3.88 (t, $^3J_{H,H}$ = 8.4 Hz, 1 H), 3.85–3.74 (m, 3 H), 3.73 (m, 1 H), 3.51–3.43 (m, 3 H), 3.42 (s, 3 H), 3.16 (dd, $^3J_{H,H}$ = 11.2, 2.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 158.2 (oxazolidinone C=O), 138.4, 137.8, 137.6, 136.4, 134.7, 129.1, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.5, 125.9, 101.3 (acetal Ph*C*H), 98.3 (C-1), 96.6 (C-1), 82.0, 80.1, 79.5, 77.2, 75.8, 74.9, 73.5, 73.0, 70.1, 68.5, 66.7, 65.5, 60.9, 55.5, 47.7 ppm. HRMS: calcd. for $C_{49}H_{51}NO_{11}$ + Na $[M + Na]^+$ 852.3354; found 852.3354.

Disaccharide 21b: $[\alpha]_D^{24}$ = 7.7 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.43–7.21 (m, 25 H, aromatic *H*), 5.47 (s, 1 H, acetal PhC*H*), 4.98 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, *O*-CH_2Ph), 4.87 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-CH_2Ph), 4.79 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-CH_2Ph), 4.78 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.60 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H, *O*-CH_2Ph), 4.55–4.39 (m, 3 H), 4.40 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H), 4.29 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, *N*-CH_2Ph), 4.24 (dd, $^3J_{H,H}$ = 10.4, 4.4 Hz, 1 H), 4.13 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H), 4.00 (t, $^3J_{H,H}$ = 9.2 Hz, 1 H), 3.94–3.79 (m, 4 H), 3.52 (dd, $^3J_{H,H}$ = 9.6, 3.2 Hz, 1 H), 3.47–3.22 (m, 4 H), 3.33 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 158.4 (oxazolidinone C=O), 138.3, 137.9, 137.8, 136.2, 135.1, 129.2, 129.1, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 125.9, 102.7, 101.2, 98.2, 81.9, 79.7, 78.7, 77.8, 77.3, 76.1, 75.9, 74.8, 73.5, 69.7, 69.5, 68.7, 68.3, 61.4, 55.6, 48.2 ppm. HRMS: calcd. for $C_{49}H_{51}NO_{11}$ + Na $[M + Na]^+$ 852.3354; found 852.3360.

General Glycosylation Procedure

Method A: Tf_2O (1 equiv., based on the donor) was added to a mixture of *N*-(phenylthio)-ε-caprolactam (1.1 equiv.), DTBMP (2.0 equiv., based on the donor), an acceptor, and a donor in CH_2Cl_2 containing activated molecular sieves (4 Å). After stirring the mixture for 0.5–1.5 h, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ and then filtered through Celite. The filter cake was washed with $CHCl_3$ and the filtrates were extracted with $CHCl_3$. The combined organic extracts were washed with water, dried with Na_2SO_4, filtered, and concentrated. The residue was purified by size-exclusion chromatography [Biobeads SX-3 (3.0 × 58 cm, toluene)] and subsequent silica gel column chromatography or preparative TLC.

Method B: PhSCl (1.2 equiv., based on the donor) was added to a mixture of DTBMP (2.0 equiv., based on the donor), AgOTf (1.5 equiv., based on the donor), an acceptor (1 equiv.), and a donor (1.2 equiv.) in 1,4-dioxane/toluene (3:1, v/v) containing activated 4-Å molecular sieves at 0 °C. The reaction mixture, whilst stirred, was warmed to room temperature and then stirred overnight. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ and then filtered through Celite. The filter cake was washed with EtOAc and the filtrates were extracted with EtOAc. The combined organic extracts were washed with brine, dried with Na_2SO_4, filtered, and concentrated. The residue was purified in the same manner as described for Method A.

Disaccharides 22a and 22b. Method A: Glycosylation of **11** (22 mg, 0.047 mmol) with **20** (31 mg, 0.056 mmol) in CH_2Cl_2 (3 mL) in the presence of *N*-(phenylthio)-ε-caprolactam (14 mg, 0.062 mmol), Tf_2O (13 μL, 0.074 mmol), and 4-Å molecular sieves (0.3 g) at room temperature for 1.5 h, subsequent work-up, and purification by preparative TLC (toluene/hexane/EtOAc, 4:1:1) gave **22a** (15 mg, 35%) and **22b** (20 mg, 47%).

Method B: Glycosylation of **10** (100 mg, 0.215 mmol) with **20** (143 mg, 0.258 mmol) in 1,4-dioxane/toluene (3:1, 8 mL) in the presence of DTBMP (106 mg, 0.516 mmol), AgOTf (99 mg, 0.387 mmol), PhSCl (36 μL, 0.310 mmol), and 4-Å molecular sieves (0.8 g) at 0 °C to room temperature overnight, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/toluene/EtOAc, 10:4:1–10:1:1) gave **22a** (156 mg, 80%) and **22b** (15 mg, 8%).

α-Linked Disaccharide 22a: $[\alpha]_D^{26}$ = +54 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.83–7.14 (m, 25 H, aromatic *H*), 5.38 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^{II}-H), 5.01 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.92 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.84 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1^{II}-H), 4.80 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.64 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.58 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.55 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-CH_2Ph), 4.51 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.38 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.35 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.50 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, 1^I-H), 4.41 (dd, $^3J_{H,H}$ = 12.0, 10.5 Hz, 1 H, 3^{II}-H), 4.01 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 3^I-H), 4.00 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-CH_2Ph), 3.92 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, COCH_2Cl), 3.85 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, COCH_2Cl), 3.75 (dd, $^3J_{H,H}$ = 11.5, 4.0 Hz, 1 H, 6^Ia-H), 3.68 (m, 1 H, 5^{II}-H), 3.67 (m, 1 H, 5^I-H), 3.50 (dd, $^3J_{H,H}$ = 11.5, 2.0 Hz, 1 H, 6^Ib-H), 3.46 (dd, $^3J_{H,H}$ = 9.5, 4.0 Hz, 1 H, 2^I-H), 3.44 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^I-H), 3.41 (dd, $^3J_{H,H}$ = 11.0, 3.0 Hz, 1 H, 6^{II}a-H), 3.39 (s, 3 H, OCH_3), 3.36 (dd, $^3J_{H,H}$ = 11.0, 3.5 Hz, 1 H, 6^{II}b-H), 3.24 (dd, $^3J_{H,H}$ = 10.5, 3.0 Hz, 1 H, 2^{II}-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.5 (*C*OCH$_2$Cl), 158.0 (oxazolidinone C=O), 138.5, 138.1, 137.8, 137.2, 134.6, 129.0–127.7, 98.3 (C-1^I), 95.6 (C-1^{II}), 82.0 (C-3^I), 79.6 (C-2^I), 77.0 (C-4^I), 75.8 (*O*-*C*H$_2$Ph), 74.8 (*O*-*C*H$_2$Ph), 73.6 (C-3^{II}), 73.5 (*O*-*C*H$_2$Ph), 70.8 (C-5^{II}), 70.2 (C-4^{II}), 70.0 (C-5^I), 67.1 (C-6^{II}), 66.6 (C-6^I), 59.9 (C-2^{II}), 55.4 (OCH_3), 47.8 (*N*-*C*H$_2$Ph), 40.3 (CO*C*H$_2$Cl) ppm. $C_{51}H_{54}ClNO_{12}$ (908.43): calcd. C 67.43, H 5.99, N 1.54; found C 67.41, H 5.88, N 1.57.

β-Linked Disaccharide 22b: $[\alpha]_D^{26}$ = +12 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.23 (m, 25 H, aromatic *H*), 5.22 (dd, $^3J_{H,H}$ = 10.5, 8.0 Hz, 1 H, 4^{II}-H), 4.99 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.87 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.80 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.80 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.62 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.56 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.56 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1^I-H), 4.52 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.49 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.41 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.40 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1^{II}-H), 4.27 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.02 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H), 4.01 (dd, $^3J_{H,H}$ = 12.5, 10.5 Hz, 1 H), 4.00 (dd, $^3J_{H,H}$ = 12.0, 10.5 Hz, 1 H, 3^{II}-H), 3.93 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.85 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.84 (m, 1 H, 5^{II}-H), 3.60 (m, 1 H, 5^{II}-H), 3.54 (m, 2 H, 6^{II}a-H, 6^{II}b-H), 3.52 (dd, $^3J_{H,H}$ = 12.5, 5.5 Hz, 1 H, 6^Ib-H), 3.47 (dd, $^3J_{H,H}$ = 9.5, 3.0 Hz, 1 H, 2^I-H), 3.34 (s, 3 H, OCH_3), 3.33 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^I-H), 3.30 (dd, $^3J_{H,H}$ = 12.0, 8.0 Hz, 1 H, 2^{II}-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7 (*C*OCH$_2$Cl), 158.1 (oxazolidinone C=O), 138.5, 138.1, 137.9, 137.3, 135.1, 129.3–127.7, 102.0 (C-1^I), 98.2 (C-1^{II}), 81.9 (C-3^I), 79.8 (C-2^I), 77.8 (C-4^I), 76.7 (C-3^{II}), 75.8 (*O*-*C*H$_2$Ph), 75.3 (C-5^{II}), 74.7 (*O*-*C*H$_2$Ph), 73.7 (*O*-*C*H$_2$Ph), 73.4 (*O*-*C*H$_2$Ph), 70.0 (C-4^{II}), 69.8 (C-5^I), 68.6 (C-6^{II}), 68.5 (C-6^I), 60.1 (C-2^{II}), 55.5 (OCH_3), 48.0 (*N*-*C*H$_2$Ph), 40.3 (CO*C*H$_2$Cl) ppm. $C_{51}H_{54}ClNO_{12}$ (908.43): calcd. C 67.43, H 5.99, N 1.54; found C 67.47, H 5.89, N, 1.49.

Disaccharide 24. Method A: Glycosylation of **23** (27 mg, 0.045 mmol) with **11** (30 mg, 0.054 mmol) in CH_2Cl_2 (3 mL) in the presence of *N*-(phenylthio)-ε-caprolactam (13 mg, 0.059 mmol), Tf_2O (11 μL, 0.065 mmol), and 4-Å molecular sieves (0.3 g) at room temperature for 40 min, subsequent work-up, and purification by preparative TLC (toluene/hexane/EtOAc, 4:1:1) gave **24** (26 mg, 56%). $[\alpha]_D^{26}$ = +69 (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.00 (m, 29 H, aromatic *H*), 5.60 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 1^I-H), 5.49 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1^{II}-H), 5.32 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^{II}-H), 4.73 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.64 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-CH_2Ph), 4.60 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.59 (dd, $^3J_{H,H}$ = 12.0, 10.5 Hz, 1 H, 3^{II}-H), 4.58 (t, $^3J_{H,H}$ = 9.0 Hz, 1 H, 2^I-H), 4.55 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.54 (t, $^3J_{H,H}$ = 9.0 Hz, 1 H, 3^I-H), 4.50 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.36 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.36 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.26 (t, $^3J_{H,H}$ = 9.0 Hz, 1 H, 4^I-H), 4.05 (dd, $^3J_{H,H}$ = 11.5, 3.0 Hz, 1 H, 6^Ia-H), 4.01 (m, 1 H, 5^I-H), 4.00 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-CH_2Ph), 3.96 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.88 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.79 (dd, $^3J_{H,H}$ = 11.5, 1.5 Hz, 1 H, 6^Ib-H), 3.71 (s, 3 H, PhOCH_3), 3.41 (dd, $^3J_{H,H}$ = 11.0, 2.5 Hz, 1 H, 6^{II}a-H), 3.36 (dd, $^3J_{H,H}$ = 11.0, 4.0 Hz, 1 H, 6^{II}b-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6 (*C*OCH$_2$Cl), 157.9 (oxazolidinone C=O), 155.5, 150.7, 138.0, 137.2, 134.2, 134.2, 131.4, 129.1–127.4, 123.5, 118.9, 114.4, 97.8 (C-1^I), 95.5 (C-1^{II}), 79.1 (C-3^I), 76.5 (C-4^I), 74.9 (C-5^I), 73.5 (*O*-*C*H$_2$Ph), 73.5 (C-3^{II}), 73.4 (*O*-*C*H$_2$Ph), 73.2 (*O*-*C*H$_2$Ph), 71.8 (C-5^{II}), 70.4 (C-4^{II}), 68.6 (C-6^I), 67.6 (C-6^{II}), 59.9 (C-2^{II}), 55.6 (PhO*C*H$_3$), 55.0 (C-2^I), 47.7 (*N*-*C*H$_2$Ph), 40.4 (CO*C*H$_2$Cl) ppm. $C_{58}H_{55}ClN_2O_{14}$ (1039.52): calcd. C 67.01, H 5.33, N 2.69; found C 66.83, H 5.29, N, 2.63.

Disaccharide 26. Method A: Glycosylation of **25** (26 mg, 0.051 mmol) with **11** (34 mg, 0.061 mmol) in CH_2Cl_2 (3 mL) in the presence of *N*-(phenylthio)-ε-caprolactam (15 mg, 0.067 mmol),

Tf_2O (12 μL, 0.073 mmol), and 4-Å molecular sieves (0.3 g) at room temperature for 30 min, subsequent work-up, and purification by preparative TLC ($CHCl_3$/EtOAc, 19:1) gave **26** (25 mg, 52%). $[\alpha]_D^{26}$ = +132 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11–7.01 (m, 25 H, aromatic *H*), 6.14 (dd, $^3J_{H,H}$ = 10.0, 9.0 Hz, 1 H, 3^I-H), 5.32 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, 1^{II}-H), 5.26 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^{II}-H), 5.26 (dd, $^3J_{H,H}$ = 10.0, 3.5 Hz, 1 H, 2^I-H), 5.15 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, 1^I-H), 4.76 (dd, $^3J_{H,H}$ = 12.5, 2.0 Hz, 1 H, 6^{I}a-H), 4.60 (dd, $^3J_{H,H}$ = 12.5, 3.5 Hz, 1 H, 6^{I}b-H), 4.52 (dd, $^3J_{H,H}$ = 12.0, 10.5 Hz, 1 H, 3^{II}-H), 4.50 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 4.41 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.20 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.37 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 4^I-H), 4.23 (m, 1 H, 5^I-H), 3.92 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, COC*H*$_2$Cl), 3.79 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, COC*H*$_2$Cl), 3.64 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 3.47 (s, 3 H, OC*H*$_3$), 3.30 (dd, $^3J_{H,H}$ = 11.0, 2.0 Hz, 1 H, 6^{II}a-H), 3.20 (dd, $^3J_{H,H}$ = 11.0, 3.5 Hz, 1 H, 6^{II}b-H), 3.13 (dd, $^3J_{H,H}$ = 12.0, 3.5 Hz, 1 H, 2^{II}-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.0 (*C*OPh), 165.9 (*C*OPh), 165.9 (*C*OPh), 165.5 (*C*OPh), 157.7, 136.9, 134.0, 133.8, 133.5, 129.9–127.9, 96.8 (C-1^I), 94.6 (C-1^{II}), 73.5 (*O*-*C*H$_2$Ph), 73.4 (C-4^I), 73.0 (C-3^{II}), 72.6 (C-3^I), 72.3 (C-5^{II}), 71.9 (C-2^I), 69.8 (C-4^{II}), 68.1 (C-5^I), 66.8 (C-6^{II}), 59.0 (C-2^I), 55.7 (OCH$_3$), 47.1 (*N*-*C*H$_2$Ph), 40.3 (CO*C*H$_2$Cl) ppm. $C_{51}H_{48}ClNO_{15}$ (950.38): calcd. C 64.45, H 5.09, N 1.47; found C 64.35, H 5.05, N 1.47.

Disaccharides 28a and 28b. Method B: Glycosylation of **27** (12 mg, 0.045 mmol) with **11** (30 mg, 0.054 mmol) in 1,4-dioxane/toluene (3:1, 8 mL) in the presence of DTBMP (106 mg, 0.516 mmol), AgOTf (99 mg, 0.387 mmol), PhSCl (36 μL, 0.310 mmol), and 4-Å molecular sieves (0.8 g) at 0 °C to room temperature overnight, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and preparative TLC (toluene/hexane/EtOAc, 4:1:1) gave **28a** (21 mg, 65%) and **28b** (4.8 mg, 15%).

α-Linked Disaccharide 28a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.24 (m, 10 H, aromatic *H*), 5.90 (d, $^3J_{H,H}$ = 3.7 Hz, 1 H, 1-H), 5.29 (t, $^3J_{H,H}$ = 9.7 Hz, 1 H, 4^{II}-H), 5.20 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, 1-H), 4.85 (d, $^3J_{H,H}$ = 14.7 Hz, 1 H, *N*-C*H*$_2$Ph), 4.65 (d, $^3J_{H,H}$ = 3.7 Hz, 1 H), 4.53 (t, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.43 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.28 (m, 1 H), 4.22–4.21 (m, 2 H), 4.14–4.08 (m, 3 H), 3.97 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, COC*H*$_2$Cl), 3.90 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, COC*H*$_2$Cl), 3.82 (m, 1 H), 3.55 (dd, $^3J_{H,H}$ = 10.6, 2.3 Hz, 1 H), 3.51 (dd, $^3J_{H,H}$ = 10.6, 5.1 Hz, 1 H), 3.28 (dd, $^3J_{H,H}$ = 12.4, 3.3 Hz, 1 H), 1.50 [s, 3 H, C(C*H*$_3$)$_2$], 1.49 [s, 3 H, C(C*H*$_3$)$_2$], 1.36 [s, 3 H, C(C*H*$_3$)$_2$], 1.22 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6 (*C*OCH$_2$Cl), 157.8 (oxazolidinone C=O), 137.0, 134.4, 129.2, 128.5, 128.0, 112.2, 109.6, 105.2, 96.6, 83.3, 82.7, 80.8, 73.7, 73.3, 72.1, 72.0, 70.2, 67.5, 59.3, 47.1, 40.3, 27.3, 26.7, 26.1, 25.3 ppm. $C_{35}H_{42}ClNO_{12}$ (704.16): calcd. C 59.70, H 6.01, N 1.99; found C 59.78, H 6.00, N 1.97.

α-Linked Disaccharide 28b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 10 H, aromatic *H*), 5.46 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, 1^I-H), 5.41 (dd, $^3J_{H,H}$ = 10.0, 8.3 Hz, 1 H, 4^{II}-H), 4.74 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 1^{II}-H), 4.60 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H, *N*-C*H*$_2$Ph), 4.54 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.46 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.35 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H, *N*-C*H*$_2$Ph), 4.28–4.19 (m, 4 H), 4.00 (d, $^3J_{H,H}$ = 19.7 Hz, 1 H, COC*H*$_2$Cl), 3.99 (s, 2 H), 3.93 (d, $^3J_{H,H}$ = 19.7 Hz, 1 H, COC*H*$_2$Cl), 3.73 (m, 1 H), 3.69 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H), 3.61 (m, 1 H), 3.41 (dd, $^3J_{H,H}$ = 12.0, 7.9 Hz, 1 H), 1.43 [s, 3 H, C(C*H*$_3$)$_2$], 1.38 [s, 3 H, C(C*H*$_3$)$_2$], 1.28 [s, 3 H, C(C*H*$_3$)$_2$], 1.18 [s, 3 H, C(C*H*$_3$)$_2$] ppm.

Disaccharides 30a and 30b. Method B: Glycosylation of **29** (81 mg, 0.239 mmol) with **11** (159 mg, 0.287 mmol) in 1,4-dioxane/toluene (3:1, 8 mL) at 0 °C to room temperature in the presence of DTBMP (118 mg, 0.574 mmol), AgOTf (111 mg, 0.431 mmol), PhSCl (40 μL, 0.344 mmol), and 4-Å molecular sieves (0.8 g), subsequent work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/EtOAc, 14:1–12:1) gave **30a** (135 mg, 71%) and **30b** (7 mg, 4%).

α-Linked Disaccharide 30a: $[\alpha]_D^{26}$ = +52 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.10 (m, 15 H, aromatic *H*), 5.79 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, 1^I-H), 5.39 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^{II}-H), 5.10 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1^{II}-H), 4.64 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.61 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 4.58 (dd, $^3J_{H,H}$ = 12.0, 10.0 Hz, 1 H, 3^{II}-H), 4.57 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.55 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.53 (d, $^3J_{H,H}$ = 5.5 Hz, 1 H, 5^I-H), 4.38 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.21 (t, $^3J_{H,H}$ = 4.0 Hz, 1 H, 2^I-H), 4.16 (dd, $^3J_{H,H}$ = 5.5, 4.0 Hz, 1 H, 4^I-H), 4.02 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 3.92 (m, 1 H, 5^{II}-H), 3.91 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.84 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.82 (t, 1 H, 3^I-H), 3.65 (s, 3 H, CO_2CH_3), 3.53 (dd, $^3J_{H,H}$ = 11.0, 2.5 Hz, 1 H, 6^{II}a-H), 3.46 (dd, $^3J_{H,H}$ = 11.0, 3.5 Hz, 1 H, 6^{II}b-H), 3.33 (dd, $^3J_{H,H}$ = 12.0, 3.0 Hz, 1 H, 2^{II}-H), 1.58 [s, 3 H, C(C*H*$_3$)$_2$], 1.38 [s, 3 H, C(C*H*$_3$)$_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.8 (C-6^I), 165.5 (*C*OCH$_2$Cl), 157.9 (oxazolidinone C=O), 137.1, 136.9, 134.6, 129.0, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.5, 111.1 [*C*(CH$_3$)$_2$], 95.5 (C-1^I), 94.2 (C-1^{II}), 75.1 (C-2^I), 74.5 (C-3^I), 73.6 (C-3^{II}), 73.5 (*O*-*C*H$_2$Ph), 72.5 (C-4^I), 71.9 (C-5^I), 71.8 (*O*-*C*H$_2$Ph), 71.6 (C-5^{II}), 67.0 (C-4^{II}), 66.9 (C-6^{II}), 59.7 (C-2^{II}), 52.4 (CO_2CH_3), 47.6 (*N*-*C*H$_2$Ph), 40.3 (CO*C*H$_2$Cl), 27.3 [C(*C*H$_3$)$_2$], 25.8 [C(*C*H$_3$)$_2$] ppm. $C_{40}H_{45}ClNO_{13}$ (783.24): calcd. C 61.34, H 5.79, N 1.79; found C 61.35, H 5.63, N 1.71.

β-Linked Disaccharide 30b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.20 (m, 5 H, aromatic *H*), 5.64 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H, 1^I-H), 5.28 (dd, $^3J_{H,H}$ = 10.0, 9.0 Hz, 1 H, 4^{II}-H), 5.37 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1^{II}-H), 4.72 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.64 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 4.55 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.42 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.39 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.36 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 5^I-H), 4.30 (br. d, 1 H, 4^I-H), 4.27 (m, $^3J_{H,H}$ = 4.0, 1.0 Hz, 1 H, 2^I-H), 4.24 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, 3^I-H), 4.24 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-C*H*$_2$Ph), 4.11 (dd, $^3J_{H,H}$ = 11.5, 10.0 Hz, 1 H, 3^{II}-H), 3.95 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.87 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.79 (s, 3 H, CO_2CH_3), 3.75 (m, 1 H, 5^{II}-H), 3.54 (dd, $^3J_{H,H}$ = 11.0, 5.0 Hz, 1 H, 6^{II}a-H), 3.49 (dd, $^3J_{H,H}$ = 11.0, 3.0 Hz, 1 H, 6^{II}b-H), 3.39 (dd, $^3J_{H,H}$ = 11.5, 8.0 Hz, 1 H, 2^{II}-H), 1.55 [s, 3 H, C(C*H*$_3$)$_2$], 1.35 [s, 3 H, C(C*H*$_3$)$_2$] ppm.

Disaccharides 32a and 32b. Method A: Glycosylation of **31** (24 mg, 0.071 mmol) with **11** (47 mg, 0.085 mmol) in CH_2Cl_2 (3 mL) in the presence of DTBMP (35 mg, 0.170 mmol), *N*-(phenylthio)-ε-caprolactam (21 mg, 0.093 mmol), Tf_2O (14 μL, 0.085 mmol), and 4-Å molecular sieves (0.3 g) at room temperature for 30 min, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/EtOAc, 10:1) gave **32a** (35 mg, 63%) and **32b** (2 mg, 4%).

Method B: Glycosylation of **31** (25 mg, 0.074 mmol) with **11** (65 mg, 0.118 mmol) in 1,4-dioxane/toluene (3:1, 3 mL) in the presence of DTBMP (48 mg, 0.236 mmol), AgOTf (45 mg, 0.177 mmol), PhSCl (16 μL, 0.142 mmol), and 4-Å molecular sieves (0.3 g) at 0 °C to room temperature overnight, then work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/EtOAc, 10:1) gave **32a** (44 mg, 71%).

α-Linked Disaccharide 32a: $[\alpha]_D^{26}$ = +8.0 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.10 (m, 15 H, aromatic *H*), 5.39 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^{II}-H), 5.37 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, 1^{I}-H), 4.91 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1^{II}-H), 4.75 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.70 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.67 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.58 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.48 (dd, $^3J_{H,H}$ = 12.0, 10.0 Hz, 1 H, 3^{II}-H), 4.48 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, 5^{I}-H), 4.37 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.10 (t, $^3J_{H,H}$ = 2.5 Hz, 1 H, 3^{I}-H), 3.99 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 3.88 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.82 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.74 (s, 3 H, CO_2CH_3), 3.73 (m, 1 H, 5^{II}-H), 3.54 (dd, $^3J_{H,H}$ = 11.0, 3.0 Hz, 1 H, 6^{II}a-H), 3.42 (dd, $^3J_{H,H}$ = 11.0, 3.5 Hz, 1 H, 6^{II}b-H), 3.26 (dd, $^3J_{H,H}$ = 12.0, 3.0 Hz, 1 H, 2^{II}-H), 1.57 [s, 3 H, C(CH_3)$_2$], 1.40 [s, 3 H, C(CH_3)$_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.2, 165.4, 157.8, 137.1, 136.5, 134.6, 129.1, 128.8, 128.6, 128.5, 128.5, 128.4, 128.2, 128.0, 127.8, 112.4, 96.7, 93.2, 74.7, 73.6, 73.5, 72.4, 71.4, 71.1, 71.0, 71.0, 69.8, 66.5, 58.9, 52.6, 47.1, 40.3, 28.0, 26.2 ppm. $C_{40}H_{45}ClNO_{13}$ (783.24): calcd. C 61.34, H 5.79, N 1.79; found C 61.51, H 5.63, N 1.79.

β-Linked Disaccharide 32b: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.21 (m, 15 H, aromatic *H*), 5.30 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, 1^{I}-H), 5.24 (dd, $^3J_{H,H}$ = 10.5, 9.0 Hz, 1 H, 4^{II}-H), 4.84 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1^{II}-H), 4.60 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.15 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.57 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.54 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.48 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.46 (m, 1 H, 5^{I}-H), 4.44 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.36 (t, $^3J_{H,H}$ = 2.0 Hz, 1 H, 1^{I}-H), 4.18 (br. s, 1 H, 2^{I}-H), 4.08 (dd, $^3J_{H,H}$ = 12.0, 10.5 Hz, 1 H, 3^{II}-H), 3.98 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.94 (br. s, 1 H, 2^{I}-H), 3.92 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COCH_2Cl), 3.74 (m, 1 H, 5^{II}-H), 3.70 (s, 3 H, CO_2CH_3), 3.58 (dd, $^3J_{H,H}$ = 10.5, 5.5 Hz, 1 H, 6^{II}a-H), 3.46 (dd, $^3J_{H,H}$ = 10.5, 2.5 Hz, 1 H, 6^{II}b-H), 1.44 [s, 3 H, C(CH_3)$_2$], 1.38 [s, 3 H, C(CH_3)$_2$] ppm.

Compounds 34a and 34b. Method B: Glycosylation of **33** (18 mg, 0.045 mmol) with **11** (30 mg, 0.054 mmol) in 1,4-dioxane/toluene (3:1, 8 mL) in the presence of DTBMP (106 mg, 0.516 mmol), AgOTf (99 mg, 0.387 mmol), PhSCl (36 μL, 0.310 mmol), and 4-Å molecular sieves (0.8 g) at 0 °C to room temperature overnight, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and preparative TLC (toluene/hexane/EtOAc, 4:1:1) gave **34a** (16.8 mg, 44%) and **34b** (7.5 mg, 20%).

α-Linked Compound 34a: $[\alpha]_D^{26}$ = –13.4 (*c* = 0.73, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.33–7.23 (m, 10 H, aromatic *H*), 5.36 (t, $^3J_{H,H}$ = 9.6 Hz, 1 H, 4-H), 4.95 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, 1-H), 4.60 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H, 3-H), 4.57 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-CH_2Ph), 4.51 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, *N*-CH_2Ph), 4.38 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-CH_2Ph), 4.23 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, *N*-CH_2Ph), 3.93 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, COCH_2Cl), 3.84 (m, 1 H), 3.84 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, COCH_2Cl), 3.35 (dd, $^3J_{H,H}$ = 16.0, 6.4 Hz, 1 H), 3.34 (m, 1 H), 3.25 (m, 1 H), 1.97 (m, 1 H), 1.85 (m, 1 H), 1.75–0.84 (m, 44 H), 0.63 (s, 3 H, CH_3), 0.57 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 165.4 (*C*OCH$_2$Cl), 158.1 (oxazolidinone C=O), 137.1, 134.9, 128.8, 128.4, 128.3, 128.2, 127.9, 127.8, 93.7 (C-1), 78.5, 77.3, 73.8, 73.6, 70.8, 70.5, 67.4, 60.8, 56.5, 56.4, 54.3, 48.4, 44.9, 42.7, 40.5, 40.5, 40.1, 39.6, 36.8, 36.3, 35.9, 35.8, 35.6, 35.6, 32.1, 28.8, 28.4, 28.1, 27.8, 24.3, 24.0, 23.0, 22.7, 21.4, 18.8, 12.5, 12.2 ppm. $C_{51}H_{73}ClNO_7$ (847.58): calcd. C 72.27, H 8.68, N 1.65; found C 72.38, H 8.49, N 1.48.

β-Linked Compound 34b: $[\alpha]_D^{26}$ = 170.8 (*c* = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.34–7.26 (m, 10 H, aromatic *H*), 5.25 (t, $^3J_{H,H}$ = 8.8 Hz, 1 H, 4-H), 4.75 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1-H), 4.52 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.50 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, *N*-CH_2Ph), 4.44 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, *N*-CH_2Ph), 4.43 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.10 (t, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-CH_2Ph), 3.94 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, COCH_2Cl), 3.86 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, COCH_2Cl), 3.68 (m, 1 H), 3.58–3.56 (m, 3 H), 3.34 (dd, $^3J_{H,H}$ = 12.0, 7.6 Hz, 1 H), 1.96 (m, 1 H), 1.9–0.76 (m, 45 H), 0.64 (s, 3 H, CH_3), 0.57 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 165.4 (*C*OCH$_2$Cl), 134.9, 128.8, 128.4, 128.3, 128.2, 127.9, 127.8, 93.7, 78.5, 73.9, 73.6, 70.8, 60.8, 56.5, 56.3, 54.3, 40.4, 44.9, 42.7, 40.5, 40.1, 39.6, 36.8, 36.3, 35.9, 35.8, 35.6, 35.5, 32.1, 28.8, 28.4, 28.1, 27.8, 24.3, 24.0, 23.0, 22.7, 21.4, 18.8, 12.5, 12.2 ppm. $C_{51}H_{73}ClNO_7$ (847.58): calcd. C 72.27, H 8.68, N 1.65; found C 72.31, H 8.49, N, 1.58.

Disaccharides 35a and 35b. Method B: Glycosylation of **16** (100 mg, 0.215 mmol) with **20** (134 mg, 0.258 mmol) in 1,4-dioxane/toluene (3:1, 8 mL) in the presence of DTBMP (106 mg, 0.516 mmol), AgOTf (99 mg, 0.387 mmol), PhSCl (36 μL, 0.310 mmol), and 4-Å molecular sieves (0.8 g) at 0 °C to room temperature overnight, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/toluene/EtOAc, 7:2:1–4:1:1) gave **35a** (143 mg, 76%) and **35b** (9 mg, 5%).

α-Linked Disaccharide 35a: $[\alpha]_D^{26}$ = +34 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.17 (m, 25 H, aromatic *H*), 5.54 (br. s, 1 H 4^{II}-H), 5.01 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.90 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.83 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.79 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.75 (d, $^3J_{H,H}$ = 3.0 Hz, 1 H, 1^{II}-H), 4.63 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.54 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.58 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.49 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, 1^{I}-H), 4.47 (dd, $^3J_{H,H}$ = 12.0, 3.0 Hz, 1 H, 3^{II}-H), 4.45 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.35 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.17 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.00 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 3^{I}-H), 3.93 (br. t, 1 H, 5^{II}-H), 3.67 (dd, $^3J_{H,H}$ = 10.5, 5.0 Hz, 1 H, 6^{I}a-H), 3.65 (m, 1 H, 5^{II}-H), 3.59 (dd, $^3J_{H,H}$ = 12.0, 3.0 Hz, 1 H, 2^{II}-H), 3.45 (dd, $^3J_{H,H}$ = 9.5, 3.5 Hz, 1 H, 2^{I}-H), 3.41 (dd, $^3J_{H,H}$ = 10.5, 1.5 Hz, 1 H, 6^{I}b-H), 3.38 (d, $^3J_{H,H}$ = 5.5 Hz, 2 H, 6^{II}-H), 3.38 (s, 3 H, OCH_3), 3.38 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 4^{I}-H), 1.97 (s, 3 H, COCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3 (*C*OCH$_3$), 158.2 (oxazolidinone C=O), 138.5, 138.1, 137.8, 137.4, 135.0, 128.8–127.6, 98.1, 96.4, 82.0, 79.6, 77.3, 75.8, 74.8, 73.5, 72.0, 69.8, 69.5, 67.9, 66.8, 66.3, 65.4, 55.3, 48.0, 20.6 ppm. $C_{51}H_{55}NO_{12}$ (873.98): calcd. C 70.09, H 6.34, N 1.60; found C 70.14, H 6.15, N 1.55.

β-Linked Disaccharide 35b: $[\alpha]_D^{26}$ = –12 (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.21 (m, 25 H, aromatic *H*), 5.56 (br. t, $^3J_{H,H}$ = 2.5 Hz, 1 H, 4^{II}-H), 4.99 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.83 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.79 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-CH_2Ph), 4.79 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H, *O*-CH_2Ph), 4.62 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H, *O*-CH_2Ph), 4.55 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, 1^{I}-H), 4.53 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.49 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.48 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-CH_2Ph), 4.40 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-CH_2Ph), 4.33 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, *N*-CH_2Ph), 4.33 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1^{II}-H), 4.00 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 3^{I}-H), 4.00 (dd, $^3J_{H,H}$ = 12.0, 2.5 Hz, 1 H, 3^{II}-H), 3.98 (dd, $^3J_{H,H}$ = 10.5, 2.0 Hz, 1 H, 6^{I}a-H), 3.83 (m, 1 H, 5^{I}-H), 3.81 (m, 1 H, 5^{II}-H), 3.58 (dd, $^3J_{H,H}$ = 12.0, 8.0 Hz, 1 H, 2^{II}-H), 3.48 (m, 1 H, 6^{I}b-H), 3.48 (m, 2 H, 6^{II}-H), 3.47 (m, 1 H, 2^{I}-H), 3.33 (s, 3 H, OCH_3), 3.32 (dd, *J* = 9.5, 10 Hz, 1 H, 4^{I}-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.1 (*C*OCH$_3$), 158.3 (oxazolidinone C=O), 138.5, 138.1, 138.0, 137.4, 135.7, 129.0, 127.9, 102.8 (C-1^{II}), 98.1 (C-1^{I}), 81.9 (C-3^{I}), 79.8 (C-2^{I}), 77.9 (C-

4^{I}), 76.4 (C-3^{II}), 75.8 (*O*-*C*H$_2$Ph), 74.7 (*O*-*C*H$_2$Ph), 74.3 (C-5^{II}), 73.7 (*O*-*C*H$_2$Ph), 73.4 (*O*-*C*H$_2$Ph), 69.7 (C-5^{I}), 68.4 (C-6^{I}), 67.5 (C-6^{II}), 64.7 (C-4^{II}), 57.5 (C-2^{II}), 57.5 (C-2^{I}), 55.5 (O*C*H$_3$), 48.3 (*N*-*C*H$_2$Ph), 20.5 (*C*OCH$_3$) ppm. $C_{51}H_{55}NO_{12}$ (873.98): calcd. C 70.09, H 6.34, N 1.60; found C 69.97, H 6.25, N, 1.55.

Disaccharides 37a and 37b. Method A at –40 °C: Glycosylation of **23** (42 mg, 0.085 mmol) with phenyl 2-acetyl-2-azido-6-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-1-thio-β-D-glucopyranoside (**36**; 43 mg, 0.071 mmol) in CH_2Cl_2 (3 mL) in the presence of *N*-(phenylthio)-ε-caprolactam (21 mg, 0.049 mmol), Tf_2O (14 μL, 0.085 mmol), and 4-Å molecular sieves (0.3 g) at –40 °C for 21 h, subsequent work-up, and purification by preparative TLC (toluene/hexane/EtOAc, 4:1:1) gave the α-linked disaccharide **37a** (17 mg, 24%) and the β-linked disaccharide **37b** (7 mg, 10%).

α-Linked Disaccharide 37a: $[\alpha]_D^{25}$ = +110 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78–6.68 (m, 23 H, aromatic *H*), 5.74 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, 1^{II}-H), 5.63 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 1^{I}-H), 5.43 (dd, $^3J_{H,H}$ = 10.5, 9.0 Hz, 1 H, 1^{I}-H), 5.20 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 4^{II}-H), 4.82 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.65 (dd, $^3J_{H,H}$ = 10.5, 8.5 Hz, 1 H, 3^{I}-H), 4.65 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.55 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.54 (dd, $^3J_{H,H}$ = 10.5, 8.5 Hz, 1 H, 2^{I}-H), 4.48 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.46 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.23 (dd, $^3J_{H,H}$ = 9.5, 8.5 Hz, 1 H, 4^{I}-H), 4.19 (d, $^3J_{H,H}$ = 11.5 Hz, 1 H, *O*-C*H*$_2$Ph), 4.01 (m, 1 H, 5^{II}-H), 3.93 (dd, $^3J_{H,H}$ = 11.5, 3.5 Hz, 1 H, 6^{I}a-H), 3.82 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-C*H*$_2$Ph), 3.81 (dd, $^3J_{H,H}$ = 11.5, 2.0 Hz, 1 H, 6^{I}b-H), 3.77 (m, 1 H, 5^{I}-H), 3.71 (s, 3 H, PhOC*H*$_3$), 3.71 (d, $^3J_{H,H}$ = 14.5 Hz, 1 H, *N*-C*H*$_2$Ph), 3.36 (dd, $^3J_{H,H}$ = 10.5, 4.0 Hz, 1 H, 2^{II}-H), 3.28 (dd, $^3J_{H,H}$ = 10.5, 2.5 Hz, 1 H, 6^{II}a-H), 3.25 (dd, $^3J_{H,H}$ = 10.5, 3.5 Hz, 1 H, 6^{II}b-H), 2.08 (s, 3 H, COC*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 166.1, 155.5, 150.7, 138.1, 137.4, 137.4, 134.1, 131.4, 128.3–127.2, 118.8, 114.4, 97.7, 97.1, 81.0, 74.7, 74.4, 73.8, 73.7, 73.4, 70.5, 68.7, 67.2, 61.0, 55.9, 55.5, 40.4, 20.7 ppm. $C_{52}H_{51}ClN_4O_{14}$ (991.43): calcd. C 63.00, H 5.18, N 5.65; found C 63.03, H 5.18, N, 5.57.

β-Linked Disaccharide 37b: $[\alpha]_D^{25}$ = +40 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–6.68 (m, 23 H, aromatic *H*), 5.62 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, aromatic *H*), 5.11 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 1^{I}-H), 4.87 (t, $^3J_{H,H}$ = 10.5 Hz, 1 H, 4^{II}-H), 4.83 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.77 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.50 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.44 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, 1^{II}-H), 4.42 (dd, $^3J_{H,H}$ = 10.5, 8.0 Hz, 1 H, 2^{I}-H), 4.42 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.38 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.35 (dd, $^3J_{H,H}$ = 10.5, 8.5 Hz, 1 H, 3^{I}-H), 4.32 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.23 (dd, $^3J_{H,H}$ = 10.0, 8.5 Hz, 1 H, 4^{I}-H), 3.95 (dd, $^3J_{H,H}$ = 11.5, 3.0 Hz, 1 H, 6^{I}a-H), 3.85 (dd, $^3J_{H,H}$ = 11.5, 1.5 Hz, 1 H, 6^{I}b-H), 3.84 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.75 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, COC*H*$_2$Cl), 3.73 (m, 1 H, 5^{I}-H), 3.71 (s, 3 H, PhOC*H*$_3$), 3.51 (dd, $^3J_{H,H}$ = 10.5, 4.0 Hz, 1 H, 6^{II}a-H), 3.47 (dd, $^3J_{H,H}$ = 10.5, 8.5 Hz, 1 H, 2^{II}-H), 3.40 (dd, $^3J_{H,H}$ = 10.5, 4.0 Hz, 1 H, 6^{II}b-H), 3.31 (m, 1 H, 5^{II}-H), 2.08 (s, 3H COC*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.1 (*C*OCH$_3$), 166.3 (*C*OCH$_2$Cl), 155.4 (Phth, CO), 150.8 (Phth CO), 138.4, 137.8, 137.5, 133.7, 128.6–127.1, 123.3, 118.7, 114.3, 100.9 (C-1^{II}), 97.6 (C-1^{I}), 78.2 (C-4^{I}), 77.0 (C-3^{I}), 74.8 (C-5^{I}, *O*-*C*H$_2$Ph), 73.5 (*O*-*C*H$_2$Ph), 72.7 (C-3^{II}), 72.3 (C-5^{II}), 71.0 (C-4^{II}), 68.2 (C-6^{II}), 67.7 (C-6^{I}), 64.4 (C-2^{II}), 55.6 (C-2^{I}, PhO*C*H$_3$), 40.4 (CO*C*H$_2$Cl), 20.7 (CO*C*H$_3$) ppm. $C_{52}H_{51}ClN_4O_{14}$ (991.43): calcd. C 63.00, H 5.18, N 5.65; found C 62.82, H 5.10, N, 5.60.

Disaccharides 38a and 38b: Glycosylation of **20** (82 mg, 0.177 mmol) with **15** (100 mg, 0.212 mmol) in CH_2Cl_2 (8 mL) in the presence of DTBMP (78 mg, 0.424 mmol), AgOTf (82 mg, 0.318 mmol), PhSCl (30 μL, 0.254 mmol), and 4-Å molecular sieves (0.8 g) at 0 °C to room temperature overnight, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/toluene/EtOAc, 7:2:1–4:1:1) gave **38a** (35 mg, 35%) and **38b** (32 mg, 32%).

38a: $[\alpha]_D^{24}$ = 6.1 (*c* = 1.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.34–7.15 (m, 20 H, aromatic *H*), 5.13 (t, $^3J_{H,H}$ = 10.4 Hz, 1 H, 4^{II}-H), 5.00 (d, $^3J_{H,H}$ = 11.2 Hz, 1 H, *O*-C*H*$_2$Ph), 4.92 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-C*H*$_2$Ph), 4.83–4.77 (m, 3 H), 4.63 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H, *O*-C*H*$_2$Ph), 4.58–4.50 (m, 3 H), 4.39 (t, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-C*H*$_2$Ph), 4.11–4.07 (m, 2 H), 4.03–3.96 (m, 3 H), 3.74–3.66 (m, 3 H), 3.50–3.35 (m, 3 H), 3.38 (s, 3 H, OC*H*$_3$), 3.19 (dd, $^3J_{H,H}$ = 12.0, 2.8 Hz, 1 H), 2.07 (s, 3 H, COC*H*$_3$), 2.03 (s, 3 H, COC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.2, 168.9, 157.9, 138.3, 137.9, 137.6, 134.4, 128.8, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.8, 127.8, 127.6, 127.5, 98.2, 95.6, 82.0, 79.5, 77.2, 75.8, 74.8, 73.6, 73.5, 70.2, 70.0, 68.2, 66.6, 61.5, 60.1, 55.4, 47.9, 20.8 ppm. $C_{46}H_{51}NO_{13}$ (825.90): calcd. C 66.90, H 6.22, N 1.70; found C 66.87, H 6.05, N 1.58.

38b: $[\alpha]_D^{24}$ = 15.2 (*c* = 0.73, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.22 (m, 20 H, aromatic *H*), 5.11 (t, $^3J_{H,H}$ = 8.8 Hz, 1 H, 4^{II}-H), 4.98 (d, *J* = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.86 (d, *J* = 11.6 Hz, 1 H, *O*-C*H*$_2$Ph), 4.79 (d, *J* = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.78 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H, *O*-C*H*$_2$Ph), 4.61 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.56 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-C*H*$_2$Ph), 4.54 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H), 4.51 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-C*H*$_2$Ph), 4.37 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1^{II}-H), 4.25 (d, $^3J_{H,H}$ = 14.4 Hz, 1 H, *N*-C*H*$_2$Ph), 4.15–4.10 (m, 3 H), 4.07–3.93 (m, 3 H), 3.82 (m, 1 H), 3.60 (m, 1 H), 3.52 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H), 3.45 (dd, $^3J_{H,H}$ = 9.6, 3.2 Hz, 1 H, 2^{I}-H), 3.33 (s, 3 H, OC*H*$_3$), 3.31–3.25 (m, 2 H), 2.06 (s, 3 H, Ac), 2.03 (s, 3 H, Ac) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C): δ = 170.3, 168.9, 158.0, 138.3, 137.9, 137.8, 134.9, 129.2, 128.8, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 102.0, 98.1, 81.8, 79.8, 77.8, 77.2, 75.8, 74.8, 74.4, 73.5, 69.7, 68.6, 67.7, 62.1, 60.2, 55.6, 48.1, 20.8, 20.8 ppm. $C_{46}H_{51}NO_{13}$ (825.90): calcd. C 66.90, H 6.22, N 1.70; found C 66.75, H 6.00, N, 1.48.

Disaccharide 39: Glycosylation of **22** (105 mg, 0.177 mmol) with **15** (100 mg, 0.212 mmol) in CH_2Cl_2 (8 mL) in the presence of DTBMP (78 mg, 0.424 mmol), AgOTf (82 mg, 0.382 mmol), PhSCl (30 μL, 0.254 mmol), and 4-Å molecular sieves (0.8 g) at 0 °C to room temperature overnight, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/toluene/EtOAc, 7:2:1–4:1:1) gave **39** (139 mg, 82%). $[\alpha]_D^{24}$ = 64.8 (*c* = 1.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.71–7.67 (m, 4 H, aromatic *H*), 7.31–6.89 (m, 15 H, aromatic *H*), 6.80 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, aromatic *H*), 6.69 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, aromatic *H*), 5.59 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 1^{I}-H), 5.43 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, 1^{II}-H), 5.14 (t, $^3J_{H,H}$ = 9.6 Hz, 1 H, 4^{II}-H), 4.73 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-C*H*$_2$Ph), 4.63 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H, *O*-C*H*$_2$Ph), 4.58–4.51 (m, 5 H), 4.35 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-C*H*$_2$Ph), 4.21 (t, $^3J_{H,H}$ = 9.2 Hz, 1 H), 4.13–3.98 (m, 5 H), 3.80 (d, $^3J_{H,H}$ = 11.2 Hz, 1 H, *O*-C*H*$_2$Ph), 3.69 (s, 3 H, OC*H*$_3$), 3.21 (dd, $^3J_{H,H}$ = 12.4, 2.8 Hz, 1 H, 2^{II}-H), 2.10 (s, 3 H, COC*H*$_3$), 2.11 (s, 3 H, COC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C): δ = 170.2, 168.9, 157.7, 155.4, 150.5, 137.7, 137.1, 134.1, 133.9, 131.3, 128.9, 128.6, 128.3, 128.2, 128.1, 127.6, 127.5, 127.3, 123.4, 118.8, 114.3, 97.8, 95.8, 78.9, 75.0, 73.5, 73.5, 71.2, 68.5, 68.4, 62.0, 60.4, 60.0, 55.6, 55.1, 47.8, 21.2, 20.9 ppm. $C_{45}H_{48}NO_{13}$ (810.86): calcd. C 66.66, H 5.97, N 1.73; found C 66.45, H 5.78, N 1.50.

Disaccharide 41: Glycosylation of **40** (82 mg, 0.177 mmol) with **15** (100 mg, 0.212 mmol) in CH_2Cl_2 (8 mL) in the presence of

DTBMP (78 mg, 0.424 mmol), AgOTf (82 mg, 0.382 mmol), PhSCl (30 μL, 0.254 mmol), and 4-Å molecular sieves (0.8 g) at 0 °C to room temperature overnight, subsequent work-up, and purification by size-exclusion chromatography (SX-3) and flash column chromatography on silica gel ($CHCl_3$/toluene/EtOAc, 7:2:1–4:1:1) gave **41** (107 mg, 73%). $[\alpha]_D^{24}$ = 39.3 (*c* = 1.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.40–7.10 (m, 20 H, aromatic *H*), 5.13–5.08 (m, 2 H), 4.85–4.80 (m, 3 H), 4.74–4.65 (m, 3 H), 4.56–4.51 (m, 3 H), 4.19 (s, 1 H), 3.93–3.88 (m, 4 H), 3.72 (dd, $^3J_{H,H}$ = 8.4, 2.6 Hz, 1 H, 2^{II}-H), 3.52 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H), 3.54–3.42 (m, 2 H), 3.37 (s, 3 H, COCH_3), 3.18 (dd, $^3J_{H,H}$ = 12.0, 2.4 Hz, 1 H), 2.04 (s, 3 H), 2.03 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 24 °C): δ = 170.2, 168.9, 158.3, 137.9, 137.1, 134.1, 129.8, 128.9, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.6, 127.2, 98.5, 95.5, 75.6, 75.4, 73.8, 73.7, 73.4, 73.3, 70.3, 68.2, 67.8, 67.5, 61.0, 60.0, 55.6, 47.5, 21.9, 20.8 ppm. $C_{46}H_{51}NO_{13}$: (825.90): calcd. C 66.90, H 6.22, N 1.70; found C 66.69, H 6.20, N 1.50.

MPEG-Bound Compound 46: BF_3·OEt_2 (20 μL, 0.157 mmol) was added to a solution of MPEG-bound linker **43** (288 mg, 0.314 mmol) and imidate **44** (335 mg, 0.471 mmol) in CH_2Cl_2 (2 mL) at 0 °C. After stirring the mixture overnight, satd. $NaHCO_3$ and EtOAc were added. The combined layers were washed with brine and dried with Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography (AcOEt/EtOAc/MeOH, 1:1) to give 451 mg (97%) of MPEG-bound compound **46** as a colorless oil.

MPEG-Bound Compound 47: BF_3·OEt_2 (18 μL, 0.144 mmol) was added to a solution of MPEG-bound linker **43** (264 mg, 0.288 mmol) and imidate **45** (307 mg, 0.432 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The mixture was stirred at 0 °C overnight. Then satd. $NaHCO_3$ and EtOAc were added. The aqueous layer was extracted with EtOAc and the combined layers were washed with brine. After drying the mixture over Na_2SO_4, the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (EtOAc to MeOH/EtOAc, 1:1) to give 420.6 mg (98%) of compound **47** as a colorless oil.

MPEG-Bound Compound 48: NaOMe (1 drop, 28% MeOH solution) was added in the presence of phenolphthalein to a solution of MPEG-bound chloroacetate **46** (220 mg, 0.148 mmol) in MeOH. After 1 h, Amberlist 15E was added. The resin was filtered and washed with MeOH and $CHCl_3$. The filtrate was concentrated and the residue was purified by silica gel column chromatography (AcOEt to AcOEt/MeOH, 1:1) to give 200 mg (98%) of the alcohol **48** as a colorless oil.

MPEG-Bound Compound 49: NaOMe (1 drop, 28% MeOH solution) was added in the presence of phenolphthalein to a solution of MPEG-bound chloroacetate **47** (220 mg, 0.148 mmol) in MeOH. After 1.5 h, Amberlist 15E was added. The resin was filtered and washed with MeOH and $CHCl_3$. The filtrate was concentrated and the residue was purified by silica gel column chromatography (AcOEt to AcOEt/MeOH, 1:1) to give 200 mg (98%) of the MPEG-bound alcohol **49** as a colorless oil.

MPEG-Bound Disaccharide 50: Tf_2O (67 mL, 0.397 mmol) was added to a mixture of thioglycoside **11** (214 mg, 0.394 mmol), MPEG-bound acceptor **48** (137 mg, 0.0986 mmol), *N*-phenylthio-ε-caprolactam (88 mg, 0.397 mmol), DTBMP (81 mg, 0.397 mmol), and 4-Å molecular sieves (300 mg) in CH_2Cl_2 (3 mL) at 4 °C. The mixture was stirred at room temperature overnight and then diluted with satd. $NaHCO_3$ and EtOAc. The mixture was filtered through Celite. After filtration, the Celite was washed with EtOAc. After separation, the aqueous layer was extracted with EtOAc. The combined layers were washed with satd. $NaHCO_3$ and brine. After drying the mixture over Na_2SO_4, the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (EtOAc to EtOAc/MeOH, 1:1) to give the 162.4 mg (90%) of the product as a colorless oil.

MPEG-Bound Disaccharides 51a and 51b: PhSCl (40 μL, 0.0868 mmol) was added to a mixture of MPEG-bound acceptor **49** (120.6 mg, 0.0868 mmol), thioglycoside **11** (188 mg, 0.347 mmol), AgOTf (89 mg, 0.347 mmol), DTBMP (107 mg, 0.521 mmol), and 4-Å molecular sieves (300 mg) in toluene (1 mL) and dioxane (3 mL) at 0 °C. The mixture was stirred at room temperature overnight and the mixture was diluted with EtOAc and satd. $NaHCO_3$. The mixture was filtered though Celite and the filtrate was separated. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried with Na_2SO_4. The residue was purified by silica gel column chromatography (EtOAc to EtOAc/MeOH, 1:1) to give 160.0 mg (quant.) of the product.

***n*-Pent-4-yl 2,3,4-*O*-Tribenzyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-glucopyranoside (53):** NaOMe solution (28% in MeOH, 0.2 mL) was added dropwise in the presence of phenolphthalein to a solution of tetraacetate **52** (15.00 g, 36.08 mmol) in MeOH (30 mL) and THF (30 mL). After stirring the mixture for 4 h, the mixture was neutralized with Amberlyst 15E. After filtration, the solvent was evaporated and dried under high vacuum. Then TBDPSCl (11.1 mL. 43.30 mmol) was added to a solution of the resulting tetraol and imidazole (5.70 g, 72.12 mmol) in DMF (30 mL) at 0 °C. The mixture was stirred at room temperature overnight. Satd. $NaHCO_3$ and EtOAc were added. After separation, the aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried with $NaSO_4$. After filtration and concentration, the residue was purified by silica gel column chromatography ($CHCl_3$/EtOAc, 1:1) to give 14.02 g of the TBDPS ether. NaH (4.61 g, 115.40 mmol) was added to a solution of the triol (14.02 g, 28.85 mmol) and benzyl bromide (13.71 mL, 115.40 mmol) in DMF (50 mL) at 0 °C. The mixture was stirred under N_2 at room temperature overnight. Triethylamine was added to the mixture to destroy the excess benzyl bromide. Then satd. NH_4Cl was added and the aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried with Na_2SO_4. After filtration and concentration, the residue was purified by silica gel column chromatography (hexane/EOAc, 20:1–10:1) to give 21.25 g (78%) of **53** as a colorless oil. $[\alpha]_D^{24}$ = 0.20 (*c* = 1.48, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.73 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, aromatic *H*), 7.70 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, aromatic *H*), 7.67–7.15 (m, 21 H, aromatic *H*), 5.81 (m, 1 H, allyl), 5.05–4.85 (m, 6 H, allyl), 4.80 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-CH_2Ph), 4.73 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-CH_2Ph), 4.65 (d, $^3J_{H,H}$ = 11.2 Hz, 1 H, *O*-CH_2Ph), 4.55 (s, 2 H), 4.39 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1-H), 4.00–3.74 (m, 3 H), 3.72 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H), 3.64 (t, $^3J_{H,H}$ = 9.2 Hz, 1 H), 3.60–3.51 (m, 1 H), 3.43 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, 2-H), 3.31 (m, 1 H, 5-H), 2.20 (m, 2 H, CH_2), 1.83 (m, 2 H, CH_2), 1.04 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 138.0, 137.9, 135.7, 135.4, 133.5, 133.0, 129.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.6, 127.6, 127.5, 127.5, 127.4, 114.9, 103.4, 84.7, 82.6, 77.7, 77.2, 75.9, 75.6, 75.1, 74.9, 72.1, 69.0, 62.8, 30.5, 29.2, 26.9, 19.4 ppm. HRMS: $C_{48}H_{56}O_6Si$ + Na [M + Na]$^+$ 779.3738; found 779.3742.

***n*-Pent-4-enyl 2,3,4-*O*-Tribenzyl-6-*O*-chloroacetyl-β-D-glucopyranoside (54):** TBAF (1.0 M THF solution, 10 mL, 10.0 mmol) was added to a solution of TBDPS ether **53** (5.44 g, 7.19 mmol) in THF (10 mL). The mixture was stirred at room temperature overnight. The mixture was diluted with EtOAc and washed with 1 M HCl.

The aqueous layer was extracted with EtOAc. The combined layers were washed with brine and dried with Na_2SO_4. After filtration and concentration, the residue was purified by silica gel column chromatography (hexane/EtOAc, 4:1–7:3) to give the product (3.71 g, 99%). $[\alpha]_D^{24}$ = 2.1 (*c* = 0.52, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.19 (m, 15 H, aromatic *H*), 5.74 (m, 1 H, allyl), 4.98–4.86 (m, 4 H, allyl), 4.80 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.75 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.67 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.57 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.37 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1-H), 3.87 (m, 1 H), 3.78 (m, 1 H), 3.66 (m, 1 H), 3.61 (t, $^3J_{H,H}$ = 8.8 Hz, 1 H), 3.50 (m, 2 H), 3.95 (t, $^3J_{H,H}$ = 8.8 Hz, 1 H, 2-H), 3.31 (m, 1 H, 5-H), 2.15 (m, 2 H), 1.82 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, C*H*$_2$), 1.70 (m, 2 H, C*H*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 138.3, 137.9, 137.8, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.6, 115.0, 103.6, 84.5, 82.3, 77.6, 75.7, 75.1, 75.0, 74.9, 69.6, 62.1, 30.2, 29.0 ppm. HRMS: calcd. for $[C_{32}H_{38}O_6 + Na]^+$ 541.2561; found 541.2558.

Chloroacetic anhydride (1.46 g, 8.54 mmol) was added to a solution of the resulting alcohol (3.71 g, 7.16 mmol) in pyridine (3 mL) and CH_2Cl_2 (20 mL) was added at 0 °C. After stirring overnight at room temperature, the mixture was diluted with EtOAc and washed with 1 M HCl. The aqueous layer was extracted with EtOAc and the extract was washed with brine and dried with Na_2SO_4. After filtration, the residue was purified by silica gel column chromatography (hexane/EtOAc, 4:1) to give 4.25 g (quant.) of chloroacetate **54**. $[\alpha]_D^{24}$ = 26.0 (*c* = 0.85, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.31–7.22 (m, 15 H, aromatic *H*), 5.80–5.78 (m, 1 H, allyl), 5.00–4.92 (m, 4 H, allyl), 4.85 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.78 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.70 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.56 (d, $^3J_{H,H}$ = 11.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.39 (m, 1 H), 4.37 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, COC*H*$_2$Cl), 4.26 (dd, $^3J_{H,H}$ = 11.7, 4.4 Hz, 1 H), 4.01 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, *N*-C*H*$_2$Ph), 3.94 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, COC*H*$_2$Cl), 3.88 (m, 1 H), 3.88–3.49 (m, 3 H), 3.42 (t, $^3J_{H,H}$ = 9.6 Hz, 1 H), 2.13 (m, 2 H, C*H*$_2$), 1.75 (m, 2 H, C*H*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 166.9, 137.8, 137.6, 128.5, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 115.0, 103.6, 84.7, 82.1, 75.7, 74.9, 74.9, 72.5, 69.6, 64.6, 40.8, 30.2, 29.0 ppm. HRMS: calcd. for $C_{34}H_{39}ClO_7$ + Na [M + Na]$^+$ 617.2277; found 617.2277.

3-Carboxypropyl 2,3,4-*O*-Tribenzyl-6-*O*-chloroacetyl-β-D-glucopyranoside (55): O_3 was passed through a solution of alkene **54** (350 mg, 0.589 mmol) in CH_2Cl_2 (5 mL) and MeOH (5 mL) at –78 °C until the reaction mixture turned pale blue. After removal of O_3 by O_2 gas, Me_2S (0.2 mL) was added. The reaction mixture was warmed to room temperature and stirred overnight. After evaporation, the crude mixture was purified by silica gel column chromatography (hexane/EtOAc, 4:1–3:2) to give 261.4 mg (75%) of aldehyde. $[\alpha]_D^{24}$ = 26.5 (*c* = 0.88, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): δ = 9.66 (s, 1 H, aldehyde), 7.26–7.17 (m, 15 H, aromatic *H*), 4.73 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.82 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, *O*-C*H*$_2$Ph), 4.80 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, C*H*$_2$Ph), 4.73 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.67 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.52 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.36 (d, $^3J_{H,H}$ = 12.0 Hz, 1 H, *O*-C*H*$_2$Ph), 4.31 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1-H), 4.19 (m, 1 H), 3.97 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, COC*H*$_2$Cl), 3.91 (d, $^3J_{H,H}$ = 15.2 Hz, 1 H, COC*H*$_2$Cl), 3.81 (m, 1 H), 3.60–3.43 (m, 4 H), 3.35 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, 2-H), 2.47 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H), 1.89 (m, 2 H), 1.19 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 201.61 (aldehyde), 168.89, 138.17, 137.50, 128.45, 128.35, 128.13, 128.03, 127.98, 127.84, 127.81, 127.69, 127.67, 103.42, 84.63, 82.14, 77.21, 76.88, 75.73, 74.90, 72.58, 68.92, 64.48, 40.74, 40.57, 22.41 ppm. HRMS: calcd. for $[C_{33}H_{37}ClO_8 + Na]^+$ 619.2069; found 619.2064.

Jones' reagent was added to a solution of the aldehyde (261.4 mg, 0.439 mmol) in acetone (2 mL) at 0 °C until the color of the mixture turned brown. Excess of the reagent was destroyed by adding *i*PrOH and the mixture was diluted with $CHCl_3$ and filtered through Celite. The Celite was washed with $CHCl_3$. After concentration, the mixture was purified by silica gel column chromatography (hexane/EtOAc, 7:3–1:1) to give (203 mg, 76%) of the acid **55**. $[\alpha]_D^{24}$ = 27.2 (*c* = 0.92, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 7.26–7.17 (m, 15 H, aromatic *H*), 4.89 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.84 (d, $^3J_{H,H}$ = 11.2 Hz, 1 H, *O*-C*H*$_2$Ph), 4.80 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.73 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.65 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.51 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-C*H*$_2$Ph), 4.37–4.31 (m, 2 H), 4.19 (dd, $^3J_{H,H}$ = 11.6, 3.6 Hz, 1 H), 3.96 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, COC*H*$_2$Cl), 3.90 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, COC*H*$_2$Cl), 3.86 (m, 1 H), 3.60–3.52 (m, 2 H), 3.45–3.44 (m, 2 H), 3.36 (t, $^3J_{H,H}$ = 8.8 Hz, 1 H, 2-H), 2.42 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, C*H*$_2$), 1.91 (m, 2 H, C*H*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 178.6 (carboxylic acid), 166.8, 138.1, 138.0, 137.4, 128.4, 128.3, 128.1, 128.9, 127.9, 127.9, 127.9, 127.7, 127.6, 127.6, 103.4, 84.6, 82.1, 76.8, 75.7, 74.9, 74.9, 72.5, 68.7, 64.5, 40.8, 31.6, 24.9 ppm. HRMS: calcd. for $[C_{33}H_{37}ClO_9 + Na]^+$ 635.2018; found 635.2017.

Immobilization: 1-Methylimidazole (32 μL, 0.4 mmol) and MSNT (59.2 mg, 0.2 mmol) were added to a suspension of resin **57** (500 mg, 0.115 mmol) and acid **55** (150 mg, 0.245 mmol) in DMF (1 mL). The mixture was shaken overnight. The resin was then filtered and washed with DMF, $CHCl_3$, and MeOH. The resins were dried in vacuo overnight. The weight of resin **58** obtained was 552 mg.

Detection of Chloroacetyl by the PNBP Method: Some resin was transferred to a plastic microtube. Then a PNBP toluene solution (80 mg/10 mL, ca. 0.3 mL) was added. After 5 min, the resin was spread over a TLC plate. After heating on a hot plate (1 min), a 10% piperidine solution (toluene) was sprayed over the sample. After heating the resin for 10 s, the color was observed with the naked eye or a computer analysis was performed by using a microscope equipped with a CCD camera [280×, CCD Micro Scope Inf-550 (Moritex)].

Capping: Benzoyl isocyanate (0.2 mL) was added to a suspension of the resin (550 mg) in CH_2Cl_2 (14 mL) and the mixture was shaken for 1 h. After the reaction, the resin was filtered and washed with CH_2Cl_2, MeOH, CH_2Cl_2, and diethyl ether, and dried at high vacuum. The weight of the resin obtained was 550 mg.

Deprotection of Chloroacetate by HDTC: Freshly prepared HDTC solution (0.37 M, 2 mL) was added to a suspension of the resin (540 mg) in DMF (10 mL). The mixture was shaken for 3 h at room temperature. The resin was filtered and washed with DMF, MeOH, CH_2Cl_2, and diethyl ether, and dried in vacuo. The weight of resin **59** obtained was 530 mg.

Glycosylation: DMTST (60 mg) was added to a suspension of the resin (528 mg) and donor **11** (382 mg, 0.690 mmol) in CH_2Cl_2 (3 mL). The mixture was shaken at room temperature overnight. The resin was filtered and washed with DMF, MeOH, CH_2Cl_2, and diethyl ether, and dried at high vacuum. This procedure was repeated twice. The weight of the resin **60** obtained was 585 mg.

Disaccharide Cleavage from the Resin: Sodium methoxide (0.15 mL, 28% MeOH solution) was added to a suspension of the resin (580 mg) in MeOH (2 mL) and THF (3 mL) at room temperature. The mixture was stirred at room temperature overnight and then Amberlyst 15E was added to neutralize the mixture. The resins were filtered and washed with CH_2Cl_2 and MeOH. After evapora-

tion, the crude material was purified by preparative TLC (hexane/EtOAc, 3:2) to give **61a** (42 mg, 39%) and **61b** (20 mg, 19%). Disaccharide **61a**: $[\alpha]_D^{24}$ = 27.8 (*c* = 1.1, $CHCl_3$). ^1H NMR: δ = 7.32–7.24 (m, 25 H, aromatic *H*), 4.93 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H), 4.89–4.78 (m, 5 H), 4.68 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, 1-H), 4.60 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, *N*-CH_2Ph), 4.60–4.55 (m, 3 H), 4.49–4.34 (m, 2 H), 4.23 (d, $^3J_{H,H}$ = 14.8 Hz, 1 H, *N*-CH_2Ph), 3.97–3.94 (m, 3 H), 3.67 (s, 3 H, CO_2CH_3), 3.94–3.62 (m, 10 H), 3.44 (t, $^3J_{H,H}$ = 9.6 Hz, 1 H), 3.36–3.34 (m, 2 H), 3.15 (dd, $^3J_{H,H}$ = 12.0, 2.8 Hz, 1 H, 2^{II}-H), 2.75 (m, 2 H, CH_2), 1.95 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 173.5, 158.7, 138.3, 138.2, 138.1, 137.9, 137.7, 137.7, 137.4, 134.9, 128.6, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 103.5, 95.5, 84.6, 82.3, 77.5, 76.2, 75.7, 75.1, 74.9, 74.4, 73.6, 73.0, 69.7, 69.1, 68.9, 68.6, 66.1, 62.0, 60.1, 51.8, 48.0, 30.6, 25.2 ppm. HRMS: calcd. for $[C_{53}H_{59}NO_{13} + Na]^+$ 940.3879; found 940.3880. Disaccharide **61b**: $[\alpha]_D^{24}$ = –5.1 (*c* = 0.96, $CHCl_3$). ^1H NMR: δ = 7.36–7.9 (m, 25 H, aromatic *H*), 4.86 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, *O*-CH_2Ph), 4.81 (d, $^3J_{H,H}$ = 10.8 Hz, 1 H, *O*-CH_2Ph), 4.78 (d, $^3J_{H,H}$ = 11.6 Hz, 1 H, *O*-CH_2Ph), 4.70 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, *O*-CH_2Ph), 4.62 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, *O*-CH_2Ph), 4.54–4.42 (m, 5 H), 4.28–4.23 (m, 2 H), 3.97 (d, $^3J_{H,H}$ = 9.6 Hz, 1 H, 1-H), 3.91–3.61 (m, 4 H), 3.57 (s, 3 H, CO_2CH_3), 3.56–3.41 (m, 5 H), 3.41 (t, $^3J_{H,H}$ = 8.8 Hz, 1 H), 3.29 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H), 3.07 (dd, $^3J_{H,H}$ = 11.2, 6.8 Hz, 1 H), 2.83 (br. s, 1 H), 2.29–2.26 (m, 2 H, CH_2), 1.82 (m, 1 H), 1.79 (m, 2 H, CH_2) ppm. ^{13}C NMR: δ = 173.2, 158.7, 138.1, 138.0, 137.6, 137.1, 135.4, 129.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 103.3, 102.0, 84.4, 82.1, 79.5, 78.0, 77.2, 76.3, 75.8, 74.9, 74.9, 74.7, 73.8, 69.7, 68.9, 68.5, 51.7, 48.0, 30.5, 25.2 ppm. HRMS: calcd. for $C_{53}H_{59}NO_{13}$ + Na $[M + Na]^+$ 940.3879; found 940.3878.

Chloroacetyl Detection by the PNBP Method: Some resin was transferred to a plastic microtube. Then a PNBP toluene solution (80 mg/10 mL, ca. 0.3 mL) was added. After 5 min, the resin was spread over a TLC plate. After heating on a hot plate (1 min), a 10% piperidine solution (toluene) was sprayed over the sample. After heating the resin for 10 s, the color was observed with the naked eye or a computer analysis was performed by using a microscope equipped with a CCD camera [280×, CCD Micro Scope Inf-550 (Moritex)].

Hydroxy Group Detection by the Disperse Red Method: The resin was transferred to a plastic tube and THF (ca. 0.1 mL) was added. Then a solution of Disperse Red (13 mg/13 mL in THF, 0.1 mL) and 1 drop of 0.5% *i*Pr_2NEt in THF solution were added. After 10 min, the solution was discarded. Then the resin was washed with THF and DMF several times. The color of the resin was observed with the naked eye or a computer analysis was performed by using a microscope with equipped with a CCD camera.

Disaccharide 64: Compound **22a** (64 mg, 0.07 mmol) was treated with 1 M aqueous NaOH/1,4-dioxane (1:1, 8 mL) at 40 °C for 2 d. 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. The residue was dissolved in 1,4-dioxane/water (2:1, 4.5 mL) containing 0.1 M aqueous HCl (90 μL, 2% of the volume of the solvent) and 20% $Pd(OH)_2$/C (30 mg) was added. The mixture was hydrogenated under an atmospheric pressure of hydrogen. After stirring for 12 h, water (1.5 mL) was added. The mixture was warmed to 50 °C, hydrogenated for a further 2 d, 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 in vacuo. The residue was acetylated with pyridine/Ac_2O (2:1, v/v, 3 mL) at room temperature overnight, concentrated with toluene, and purified by flash column chromatography on silica gel (EtOAc/$CHCl_3$, 4:1) to give **64** (42 mg, 92%) as a colorless foam. $[\alpha]_D^{24}$ = +147 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ = 6.26 (d, *J* = 9.5 Hz, 1 H, N*H*COCH$_3$), 5.48 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 3^I-H), 5.20 (t, $^3J_{H,H}$ = 9.5 Hz, 1 H, 3^{II}-H), 5.15 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^I-H), 5.12 (t, $^3J_{H,H}$ = 10.0 Hz, 1 H, 4^{II}-H), 5.06 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, 1^{II}-H), 4.92 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, 1^I-H), 4.79 (dd, $^3J_{H,H}$ = 10.0, 4.0 Hz, 1 H, 2^I-H), 4.40 (m, 1 H, 2^{II}-H), 4.22 (dd, $^3J_{H,H}$ = 12.5, 4.5 Hz, 1 H, 6^{II}a-H), 4.10 (dd, $^3J_{H,H}$ = 12.5, 2.5 Hz, 1 H, 6^{II}b-H), 3.98 (m, 1 H, 5^{II}-H), 3.97 (m, 1 H, 5^I-H), 3.76 (dd, $^3J_{H,H}$ = 12.5 H, 2.0 Hz, 1 H, 6^Ia-H), 3.72 (dd, $^3J_{H,H}$ = 12.5, 4.0 Hz, 1 H, 6^Ib-H), 3.41 (s, 3 H, OCH_3), 2.10 (s, 3 H, COCH_3), 2.09 (s, 3 H, COCH_3), 2.08 (s, 3 H, COCH_3), 2.04 (s, 3 H, COCH_3), 2.02 (s, 6 H, COCH_3), 2.00 (s, 3 H, COCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.1 (*C*OCH$_3$), 170.6 (*C*OCH$_3$), 170.2 (oxazolidinone C=O), 170.0 (*C*OCH$_3$), 169.9 (*C*OCH$_3$), 169.9 (*C*OCH$_3$), 169.3 (*C*OCH$_3$), 97.0 (C-1^{II}), 96.7 (C-1^I), 71.0 (C-3^{II}), 70.9 (C-2^I), 70.2 (C-3^I), 68.5 (C-4^I), 68.4 (C-5^I), 68.0 (C-4^{II}), 67.9 (C-5^{II}), 64.3 (C-6^I), 61.9 (C-6^{II}), 55.5 (O*C*H$_3$), 51.5 (C-2^{II}), 22.8 (CO*C*H$_3$), 20.7 (CO*C*H$_3$), 20.6 (CO*C*H$_3$) ppm. $C_{27}H_{39}NO_{17}$ (649.60): calcd. C 49.92, H, 6.05, N 2.16; found C 49.92, H 6.05, N, 2.16.

CCDC-790330 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via http:www.ccdc.cam.ac.uk/datarequest/cif.

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and spectroscopic data for the prepared compounds.

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