Stereocontrolled Synthesis of α-*C*-Galactosamine Derivatives via Chelation-Controlled *C*-Glycosylation

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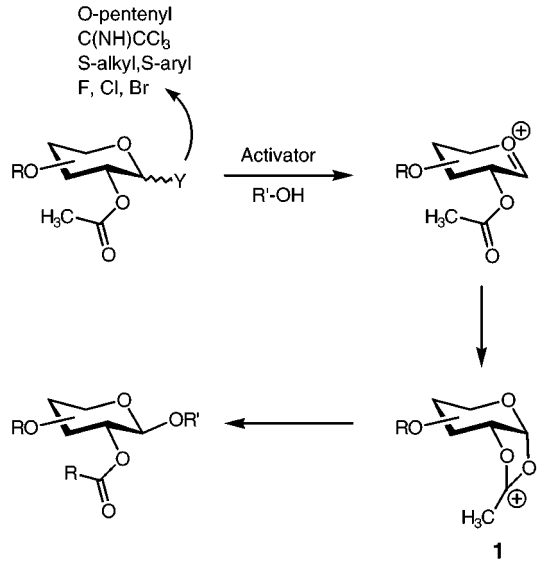
The samarium diiodide-promoted reduction of 2-deoxy-2-acetamidogalactosyl pyridyl sulfone α-**5** with ketones or aldehydes under Barbier conditions led unexpectedly to the stereoselective synthesis of α-*C*-galactosamine derivatives in good yields. With carbonyl substrates, α:*β* selectivities ranged from 20:1 to 5:1, and with aldehydes a stereoselectivity of approximately 5:1 was observed at C7 in favor of the *S*-isomer. The stereochemical preference of these *C*-glycosylation reactions is explained by the intermediacy of an α-oriented anomeric glycosyl samarium(III) compound that is stabilized via chelation of the metal ion to the C2-acetamido group.

Introduction

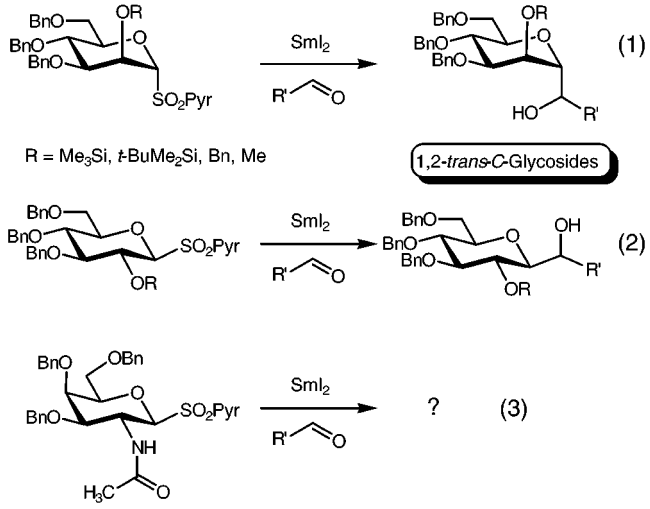
A well-known doctrine in classical glycoside synthesis is the employment of an assisting group at C2 for the stereocontrolled synthesis of 1,2-*trans*-*O*-glycosides.[1] As shown in Scheme 1 and as exemplified with a C2-acetate substituent, their directing abilities are made possible by evoking a stabilized carbocation intermediate **1**, which leads to direct S_N2 substitution at the anomeric center affording a *β*-*O*-glycoside. The groups typically used are composed either of an ester (carbonate) linkage at the C2 position or that of an amide (carbamate) linkage when working with the corresponding amino sugars.

We have recently developed a mild and rapid entry to 1,2-*trans*-*C*-glycosides via the room-temperature reductive samariation of glycosyl 2-pyridyl sulfones of neutral hexopyranoses in the presence of a carbonyl substrate, which, contrary to *O*-glycoside synthesis, does not require an assisting group at C2 (Scheme 2, eqs 1 and 2).[2,3] The success of this umpolung strategy to *C*-glycosides originates from the inherent stability of the intermediate anomeric organosamarium toward *β*-elimination, when a 1,2-trans spacial arrangement is assumed. In connection with our work in preparing analogous *C*-glycosides of biologically important sugars,[2b] we were recently confronted with the problem of having to prepare a carbon mimic of *N*-acetyl-D-galactosamine linked to serine in either anomeric configuration.[4,5] We therefore proceeded to examine whether our SmI_2-promoted *C*-glycoside methodology[2] could likewise be extended to galactosyl pyridyl sulfones bearing a C2-acetamide

Scheme 1



Scheme 2



(Scheme 2, eq 3). Although, a 1,2-*trans*-selectivity was originally anticipated, we were skeptical as to the efficiency of these coupling reactions owing to the availibil-

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(1) (a) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. (b) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212. (c) Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503.

(2) (a) Mazéas, D.; Skrydstrup, T.; Beau, J.-M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 909. (b) Jarreton, O.; Skrydstrup, T.; Beau, J.-M. *J. Chem. Soc., Chem. Commun.* **1996**, 1661. (c) Jarreton, O.; Skrydstrup, T.; Beau, J.-M. *Tetrahedron Lett.* **1997**, *36*, 303. (d) Skrydstrup, T.; Jarreton, O.; Mazéas, D.; Urban, D.; Beau, J.-M. *Chem. Eur. J.*, in press.

(3) For other reductive samariation approaches to *C*-glycosides, see: (a) de Pouilly, P.; Chénedé, A.; Mallet, J.-M.; Sinaÿ, P. *Bull. Soc. Chim. Fr.* **1993**, *130*, 256. (b) Hung, S.-C.; Wong, C.-H. *Tetrahedron Lett.* **1996**, *37*, 4903. (c) Hung, S.-C.; Wong, C.-H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2671. (d) Vlahov, I. R.; Vlahova, P. I., Linhardt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 1480.

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ity of an acidic proton on the acetamido group. In a series of elegant papers from the Kessler group,[5a,g,h] it was found that for the low-temperature preparation of the corresponding anomeric lithium reagent of *N*-acetyl-D-glucosamine prepared via the reductive lithiation or transmetalation of an anomeric chloride or stannane, respectively, prior deprotonation of the amide proton is necessary to avoid competitive protonation at the anomeric center.

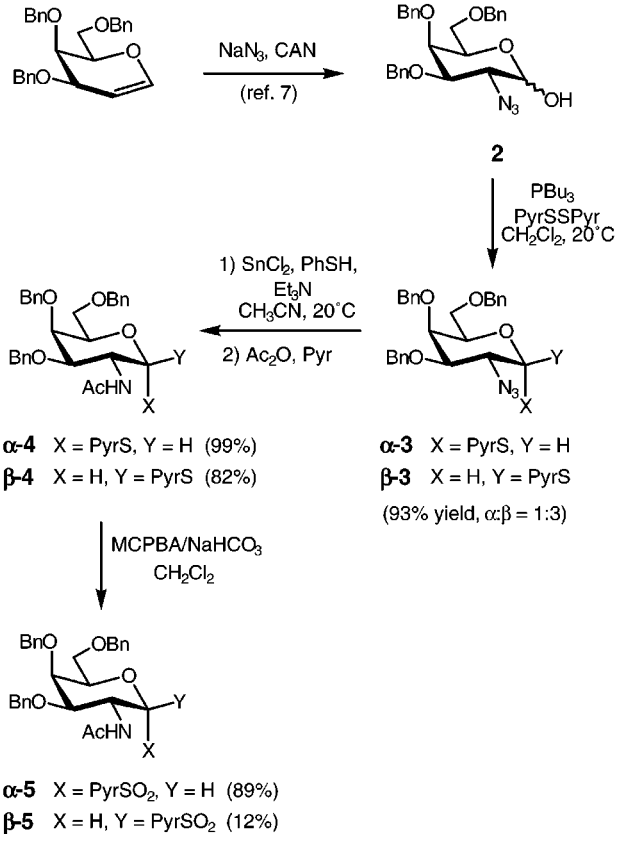
In this paper, we show that such coupling reactions are possible, but contrary to the previously observed *trans*-selectivity, 1,2-*cis*-*C*-galactosamines are the predominant products. In addition, under the conditions described the reaction of the intermediate organosamarium with a carbonyl substrate is preferred to protonation from the acetamido group. These results point out the opposing influence such an anchimeric assisting group may have in the stereoselective synthesis of both *O*- and *C*-glycosides.[6]

Results and Discussion

Preparation of the Pyridyl Sulfone of *N*-Acetylgalactosamine. For the synthesis of the required galactosyl pyridyl sulfone illustrated in Scheme 3, we started from the known hemiacetal **2**, easily obtained from the azidonitration of tribenzyl-D-galactal and subsequent hydrolysis of the anomeric nitrate formed.[7] To introduce the pyridyl sulfone moiety at the anomeric position, we originally subjected hemiacetal **2** to the conditions described by Williams with tri-*n*-butylphosphine and 2,2′-dipyridyl disulfide in CH_2Cl_2.[8] This led to the expected and chromatographically separable pyridyl sulfides α-**3** and *β*-**3** as a 1:3 anomeric mixture in high yield. It was somewhat surprising that even with an excess of Bu_3P the azido group was not reduced under the conditions employed.

Different protocols for the transformation of the azide functionality to an acetamido group were then attempted. Treatment of α-**3** with triphenylphosphine in THF[9] did not lead to any azide reduction at room temperature as

Scheme 3



was expected considering the above results. However, upon heating the solution to reflux for 8 h followed by the addition of 4 equiv of water and then acetylation (pyridine/Ac_2O), the sulfide α-**4** could be obtained after careful chromatographic separation from the closely migrating triphenylphosphine oxide side product. Unfortunately, this separation was impossible with the *β*-anomer after treatment of sulfide *β*-**3** under identical conditions, thus giving *β*-**4** contaminated with considerable amounts of Ph_3PO.[10] Other azide reduction conditions, such as the $NiCl_2/NaBH_4$ combination[11] and SmI_2,[12,13] followed by acetylation were less efficient, affording yields of only approximately 50% of the desired sulfide α-**4** or *β*-**4**. Finally, the protocol described by Bartra et al. ($SnCl_2$/PhSH/NEt_3)[14] proved the most effective, leading to the rapid reduction of the azide group

(4) For several reviews on the synthesis of *C*-glycosides: (a) Postema, M. H. D. *C-Glycoside Synthesis*; CRC Press: Boca Raton, FL, 1995. (b) Levy, D. E.; Tang, C. *The Chemistry of C-Glycosides*; Pergamon Press: Exeter, U.K., 1995. (c) Casiraghi, G.; Zanardi, F.; Rassu, G.; Spanu, P. *Chem. Rev.* **1995**, *95*, 1677. (d) Postema, M. H. D. *Tetrahedron* **1992**, *48*, 8545. (e) Herscovici, J.; Antonakis, K. In *Studies in Natural Product Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1992; Vol. 10.

(5) For other syntheses of *C*-glycosyl analogues of 2-aminoglycosides not discussed in the above reviews, see: (a) Hoffmann, M.; Kessler, H. *Tetrahedron Lett.* **1994**, *35*, 6067. (b) Wei, A.; Haudrechy, A.; Audin, C.; Jun, H.-S.; Haudrechy-Bretel, N.; Kishi, Y. *J. Org. Chem.* **1995**, *60*, 2160. (c) Ayadi, E.; Czernecki, S.; Xie, J. *Chem. Commun.* **1996**, 347. (d) Jobron, L.; Leteux, C.; Veyrières, A.; Beau, J.-M. *J. Carbohydr. Chem.* **1994**, *13*, 507. (e) Kim, K. H.; Hollingsworth, R. I. *Tetrahedron Lett.* **1994**, *35*, 1031. (f) Mbongo, A.; Frèchou, C.; Beaupère, D.; Uzan, R.; Demailly, G. *Carbohydr. Res.* **1993**, *246*, 361. (g) Hoffmann, M.; Burkhart, F.; Hessler, G.; Kessler, H. *Helv. Chem. Acta* **1996**, *79*, 1519. (h) Burkhart, F.; Hoffmann, M.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2671. (i) Burkhart, F.; Hoffmann, M.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1191. (j) Rubinstenn, G.; Esnault, J.; Mallet, J.-M.; Sinaÿ, P. *Tetrahedron: Asymmetry* **1997**, *8*, 1327.

(6) Part of this work was previously published as a preliminary communication. Urban, D.; Skrydstrup, T.; Riche, C.; Chiaroni, A.; Beau, J.-M. *J. Chem. Soc., Chem. Commun.* **1996**, 1883.

(7) (a) Lemieux, R. U.; Ratcliffe, R. M. *Can. J. Chem.* **1979**, *57*, 1244. (b) Gauffeny, F.; Marra, A.; Shun, L. K. S.; Sinaÿ, P.; Tabeur, C. *Carbohydr. Res.* **1991**, *219*, 237.

(8) Stewart, A. O.; Williams, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 4289. See also: Mereyala, H. B.; Reddy, G. V. *Tetrahedron* **1991**, *47*, 6435.

(9) Vaultier, M.; Knouzi, N.; Carrie, R. *Tetrahedron Lett.* **1983**, *24*, 763.

(10) Likewise, the corresponding sulfones exhibited similar R_f values as that of the sulfides making it impossible to separate the triphenylphosphine oxide impurity at this stage. It is necessary that Ph_3PO be removed from the sulfone as trace amounts were detrimental for the coupling reactions discussed below.

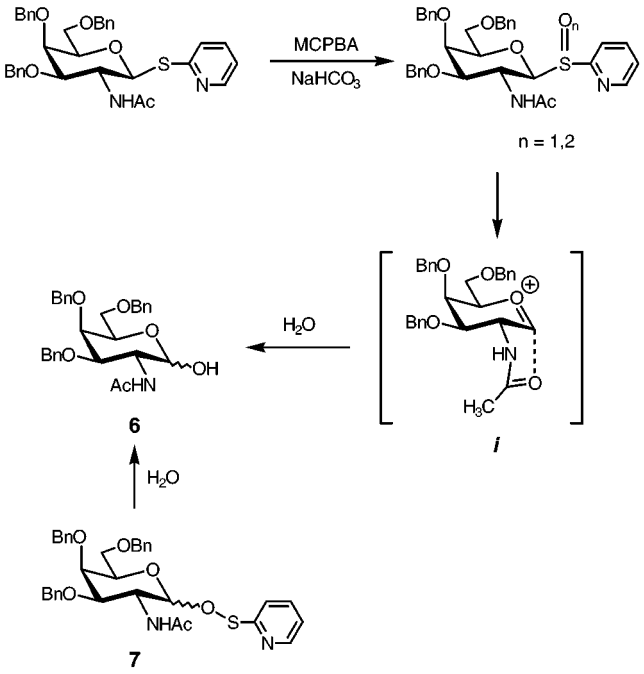
(11) Paulsen, H.; Schnell, D. *Chem. Ber.* **1981**, *114*, 333.

(12) (a) Benati, L.; Montevecchi, P. C.; Nanni, D.; Spagnolo, P.; Volta, M. *Tetrahedron Lett.* **1995**, *36*, 7313. (b) Goulaouic-Dubois, C.; Guggisberg, A.; Hesse, M. *Tetrahedron* **1995**, *51*, 12035.

(13) For reviews on the use of SmI_2 in organic synthesis, see: (a) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307. (b) Molander, G. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 1, p 251. (c) Molander, G. A. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley: New York, 1994; Vol. 46, p 211. (d) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (e) Curran, D. P.; Fevig, T. L.; Jaspersen, C. P., Totleben, M. L. *Synlett* **1992**, 943. (f) Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573.

(14) (a) Bartra, M.; Urpf, F.; Vilarrasa, J. *Tetrahedron Lett.* **1987**, *47*, 5941. (b) Bartra, M.; Romea, P.; Urpf, F.; Vilarrasa, J. *Tetrahedron* **1990**, *46*, 587.

Scheme 4



and affording α-**4** or *β*-**4** in the respective yields of 99% and 82% after acetylation.

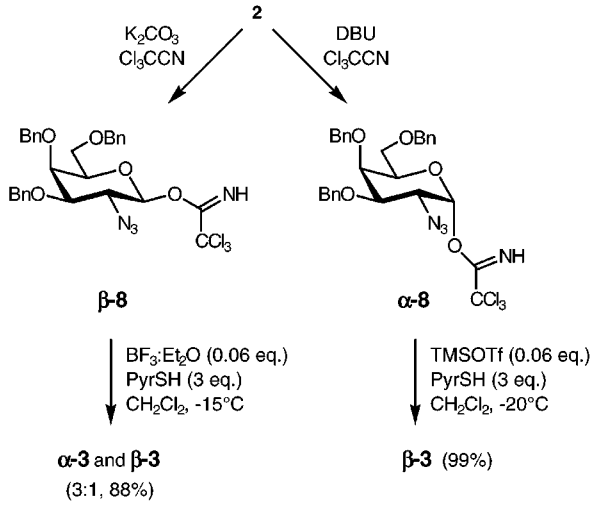
Whereas α-**4** could be cleanly converted to the corresponding sulfone α-**5** in 89% with *m*-CPBA in CH_2Cl_2, we quickly discovered that this was not the case for *β*-**4**. Under the same oxidizing conditions, this sulfide led to a mixture of two compounds in which one was the required sulfone *β*-**5** (12%). The other component was identified as the hemiacetal **6** (Scheme 4), whose formation during oxidation was surprising and unprecedented from our previous work on the preparation of other glycosyl pyridyl sulfones. The production of **6** could be the result of the easier formation of an oxonium ion intermediate ***i*** from *β*-**4** than that for the α-anomer, assisted by the proper positioning of the acetamide group for displacement of the *β*-pyridyl sulfoxide or sulfone. Subsequent hydrolysis then leads to the hemiacetal. Another possibility would be for the *β*-sulfoxides, formed after the first oxidation step, to undergo a Meisenheimer rearrangement to the corresponding and unstable sulfenate esters, which are then hydrolyzed to **6** upon aqueous workup.[15]

With these results in hand, it became evident that a more efficient synthesis of the sulfide α-**3** was required as the previous method to glycosylpyridylsulfides only led to predominant *β*-sulfide formation. We initially examined the influence of temperature and solvent on the introduction of the pyridyl sulfide from 2,2′-dipyridyl disulfide. Neither the temperature nor the solvent (CH_2Cl_2, THF, CH_3CN) greatly influenced the stereochemical outcome at the anomeric center of α-**3** with α:*β* selectivities of approximately 1:1.5, although the yields of the sulfides were greater than 90%. The high reactivity of both the cyclic oxonium ion intermediate and the pyridyl thiolate generated under the reaction conditions is most likely responsible for the nonselectivity observed at the anomeric center.

We next turned to the trichloroimidates as a potential remedy to this problem owing to their ease in preparation

(15) Marichich, T. J.; Harrington. *J. Am. Chem. Soc.* **1972**, *94*, 5115.

Scheme 5

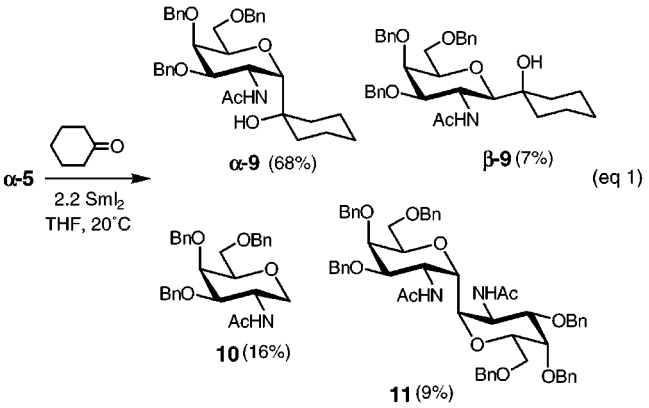


and as well as their characteristically high anomeric selectivities upon glycosylation. Hence, hemiacetal **2** could be converted stereoselectively to either the imidate α-**8** or *β*-**8** under standard conditions described by Schmidt (Scheme 5).[1b] Treatment of imidate α-**8** with 2-mercaptopyridine and a catalytic amount of TMSOTf or $BF_3{\cdot}Et_2O$ in CH_2Cl_2 led to the sole production of the *β*-pyridyl sulfide in high yield. In contrast, no selectivity was obtained when subjecting the imidate *β*-**8** to identical conditions with TMSOTf. With the weaker Lewis acid, $BF_3{\cdot}Et_2O$, a more favorable selectivity was observed (approximately 3:1) in preference for the α-isomer.[16] Examination of solvents other than CH_2Cl_2 led to lower α:*β* selectivities. Although some improvement of the α,*β*-selectivity would be desirable, the synthetic sequence to pyridyl sulfone α-**5** is still performant, providing an overall yield of 58% from hemiacetal **2**.

Samarium Diiodide-Promoted Coupling Reactions. With a viable route to the pyridyl sulfone α-**5**, the stage was now set for its samarium diiodide-promoted coupling with carbonyl compounds. Upon combination of a THF solution of α-**5** and cyclohexanone (2 equiv) with samarium diodide (2.2 equiv), an instantaneous reaction ensued, resulting in the isolation of a chromatographically inseparable 10:1 anomeric mixture of *C*-glycosides α-**9** and *β*-**9** in 75% yield (eq 1). That the *C*-glycosides were themselves generated was itself noteworthy considering the need for protective metalation of the amide proton in coupling reactions with the corresponding anomeric lithium reagents.[5a,g,h] The 1-deoxy derivative **10** was only isolated in 18% yield.

Even more remarkable was the identification of the major isomer as the α-anomer instead of the anticipated *β*-isomer, which contradicts our previous results in 1,2-*trans*-*C*-glycoside synthesis.[2] This assignment was based on the small coupling constants observed between H1,H2 (1.3 Hz) for the major isomer in the ^1H NMR spectrum, clearly indicative of the α-orientation of the C1-substituent. In addition, small coupling constants were noted between all the other vicinal ring protons, suggesting that the conformation of the α-*C*-glycoside deviated considerably from that of the normal $^4C_1$ chair conformation. These spectral observations are in agree-

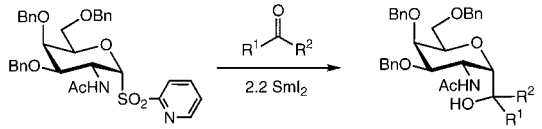
(16) It is somewhat surprising that, unlike in *O*-glycoside synthesis, no general method exists for the synthesis of α-thioglycosides with high stereoselectivity.

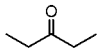
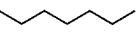


ment with that of other α-*C*-glycosides obtained from anionic condensations.[2,5a,17] On the other hand, the minor isomer was found to possess a large coupling constant ($J_{H1,H2}$ = 9.7 Hz) characteristic of a *β*-*C*-glycoside (see discussion below). A third minor component was also isolated from the reaction mixture, whose structure elucidation was based on the following spectral evidence. Its ^{1}H NMR spectrum revealed signals for a single acetamido sugar moiety displaying similar proton coupling constants as that observed for the major *C*-glycoside, though none for that of the aglycon moiety. On the other hand, mass spectral data conformed with a structure whose mass was composed of two *N*-acetylgalactosamine units. These data combined suggested that this component was the symmetrical α,α-dimer **11**, a class of compounds that we have previously not observed in these SmI_2-promoted *C*-glycosylation reactions.[2] Finally, it is interesting to note the absence of the elimination product, tribenzylgalactal, implying that *β*-elimination is not a competing reaction. Coupling reactions with the corresponding *β*-pyridyl sulfone *β*-**5** led to similar results with cyclohexanone, but because of the problems encountered in its synthesis further work with this isomer was not pursued.

The generality of this *C*-glycosylation method for the selective construction of various α-*C*-galactosamine derivatives is illustrated in Table 1. Comparable coupling yields with other simple ketones and aldehydes (60−72%) were obtained with α:*β* selectivities ranging from 5:1 to 20:1. With aldehydes, a stereoselectivity of approximately 5:1 was noted at the newly created acyclic stereocenter C7.[18] As with the previous condensation employing cyclohexanone, the α- and *β*-*C*-glycosides obtained from the ketones studied (Table 1, entries 1 and 2) were chromatographically inseparable. Like α-**9**, the ^{1}H NMR coupling constants of the ring hydrogens in the major coupling products deviated from those normally found in a $^4C_1$ conformation, which is clearly indicative of the formation of α-*C*-glycosides. In contrast to the ketones, it was possible to isolate the α-anomers by careful column chromatography of the coupling products furnished from the aldehyde substrates (Table 1, entries 3−5). However, the minor *β*-isomers comigrated with dimer **11**. In one case (Table 1, entry 3) this mixture

Table 1. Anionic Coupling of Pyridyl Sulfone 5a with Carbonyl Compounds



Entry	Carbonyl compound	*C*-Glycoside (isolated yields)	α:β	Stereosel.
1		α-**12** 67%	10:1	-
2		α-**13** 60%	5:1	-
3		α-**14** 67%	20:1	6:1
4		α-**15** 72%	12:1	5:1
5		α-**16** 69%	9:1	6:1

was acetylated thus allowing for a chromatographic separation of **11** and acetylated *β*-**14**. The *β*-configuration of this minor component was deduced from the coupling constants in the ^{1}H NMR spectrum (e.g., $J_{1,2} = J_{2,3} \approx 10$ Hz), indicating an equatorial orientation of the newly formed carbon−carbon bond in an expected $^4C_1$ conformation of the ring. Literature precedence has shown that α-*C*-glycosides, formed from the coupling of C1-anions with carbonyl substrates, deviate from this conformation as indicated from their ^{1}H NMR coupling constants.[2,5a,17] In all cases, the *β*-anomers also displayed characteristic chemical shifts. For example, the NH chemical shifts for *β*-**9** and **12**−**16** were typically found between 5.07 and 5.36 ppm, where for α-**9**, **12**, **13** this peak could be located between 6.92 and 7.03 ppm, and for α-**14**−**16**, between 6.27 and 6.54. This large chemical shift difference of the NHAc group has also been reported for similar α- and *β*-*C*-glycosides prepared in the *N*-acetylglucosamine series.[5g]

Confirmation of the above results was provided by a single-crystal X-ray structure of the major diastereoisomer α-**14** (mp 137−138 °C) obtained in entry 3 (Table 1, Figure 1). Although it was found that all the α-*C*-galactosamine derivatives possessed solution conformations that deviate considerably from the $^4C_1$ conformation, it was interesting to observe a chair conformation for α-**14** in the solid state. The X-ray structure also assigns unambiguously the configuration at the acyclic stereocenter to be *S*. Hence, we assume that the major diastereomer furnished from the other coupling reactions also possesses this configuration (Table 1, entries 4 and 5). The predominant formation of the *S*-isomer parallels earlier results obtained in the *manno*-series.[2c]

To determine the dominating factors leading to preferential and unanticipated formation of the α-anomer from pyridyl sulfone α-**5**, the above observations were compared to results obtained with other galactosyl pyridyl sulfones with varying C2-substitutents (see Table 2). The condensation of the galactosyl pyridyl sulfone **17** with ketone substrates afforded *C*-galactosides possessing only the *β*-configuration at the anomeric center (Table 2, entries 1 and 2).[2d] In contrast, the 2-deoxygalactosyl derivative **18** led to a 1:1 anomeric mixture of *C*-glycosides (Table 2, entry 3).[2d] With a galactosyl

(17) (a) Wittman, V.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1091. (b) Lesimple, P.; Beau, J.-M. *Bioorg. Med. Chem.* **1994**, *2*, 1319.

(18) We were only able to detect one *β*-*C*-glycoside in the condensation of pyridyl sulfone α-**5** with aldehyde substrates, although our limit of detection was low owing to the high α,*β*-selectivities obtained in these reactions. It does suggest, however, that some stereoselectivity is achieved at C7 in the formation of the *β*-isomers.

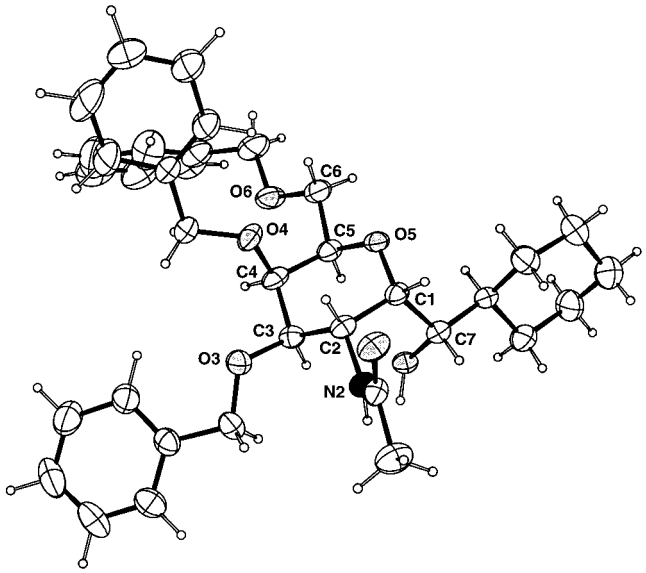
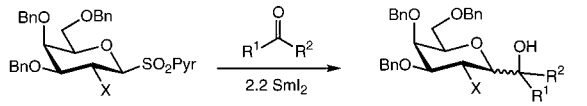


Figure 1. Single-crystal X-ray structure of *C*-glycoside α-**14**.

Table 2. Anionic Coupling of Pyridyl Sulfones 17−19 with Carbonyl Compounds



17-20

Entry	Sulfone	Carbonyl compound	*C*-Glycoside (isolated yields)	α:β
1	**17** (X = OTMS)		25%[2d]	0:1
2	**17** (X = OTMS)		**21** 31%	0:1
3	**18** (X = H)		86%[2d]	1:1
4	**19** (X = N_3)		0%	-
5	**20** (X = $NHCO_2Bn$)		0%	-

pyridyl sulfone possessing a C2-azido group as in **19**, attempted coupling with cyclohexanone gave only the elimination product, tribenzylgalactal (Table 2, entry 4). Apparently, the pyridyl sulfone group in **19** is reduced faster in the presence of divalent samarium than the azido functionality at C2. Finally, it was found that even the exchange of the acetamido group with that of a benzylcarbamoyl as in **20** did not afford a significant amount of *C*-glycosides upon treatment with SmI_2 in the presence of cyclohexanone (Table 2, entry 5). These results thus unveil an important directing effect displayed by C2-acetamido group in the intermediate glycosyl organosamarium.

The α-selectivity displayed by pyridyl sulfone α-**5** is tentatively explained in Scheme 6. One-electron transfer from SmI_2 to the aryl sulfone moiety and subsequent C1−S bond fragmentation generates the α-oriented anomeric radical **22**.[19,20] That this anomeric radical is formed is seen from the isolation of the dimer **11** produced from the dimerization of the glycosyl radical intermediate. It is interesting to note the α,α-selectivity, whereas in the few other examples reported on this type of dimerization a statistical mixture of anomeric dimers was obtained.[21] Further one-electron transfer from the reducing species then leads to the corresponding kinetic α-oriented Sm(III) species **23a**. Rather than preferring a configurational change to the thermodynamically more stable β-anomer **24** as seen with other C2-equatorially-substituted glycosyl pyridyl sulfones (path a),[2a,d,22] a strong six-membered ring complex between the C1−metal ion and the acetamido group disfavors this anomerization process. It is possible that either the intermediate **23a** couples directly to the carbonyl substrate or instead experiences a conformational change to a skew boat as in **23b** placing the C1−Sm bond in a thermodynamically more stable equatorial position before the condensation step. In both six-membered ring complexes, the NH bond is likely pointing away from the C1−Sm bond, which diminishs the rate of intramolecular deprotonation. Apparently, the condensation rate of **23a** or **23b** to a carbonyl substrate is sufficiently fast compared to the rate of deprotonation whether it be inter- or intramolecular, which is explained by the lower basicity and higher oxophilicity of organolanthanide(III) reagents in general. It is somewhat surprising though that the C2-carbamate derivative is not synthetically useful (Table 2, entry 5), considering the important role this group has been given in the SmI_2-promoted intermolecular reductive couplings of α-(alkoxycarbonyl)amino ketones with α,β-unsaturated esters.[23] It may be that the expected weaker O−Sm bond in this chelate complex compared to **23a** is not strong enough to prevent a C1-configurational change, hence leading to a β-oriented organosamarium that subsequently undergoes protonation. There is undoubtedly a fine balance between the energies of complexation, anomerization, and sugar ring conformational changes.[24]

Finally, preliminary studies were conducted to employ these results for the synthesis of a *C*-glycopeptide analogue of the tumor-associated Tn-antigen,[25] composed of *N*-acetylgalactosamine unit linked to L-serine or L-threonine (Figure 2). The elegant asymmetric amino acid synthesis developed by Evans and co-workers[26] served

(19) (a) Mazéas, D.; Skrydstrup, T.; Doumeix, O.; Beau, J.-M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1383. (b) Skrydstrup, T.; Mazéas, D.; Elmouchir, M.; Doisneau, G.; Riche, C.; Chiaroni, A.; Beau, J.-M. *Chem. Eur. J.* **1997**, *8*, 1342.

(20) (a) Dupuis, J.; Giese, B.; Rüegge, D.; Fischer, H.; Korth, H.-G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 896. (b) Korth, H.-G.; Sustmann, R.; Dupuis, J.; Giese, B. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1453. (c) Chandra, H.; Symons, M. C. R. *Tetrahedron Lett.* **1987**, *28*, 1455. (d) Korth, H.-G.; Sustmann, R. *J. Chem. Soc., Faraday Trans. 1* **1987**, 95. (e) Korth, H.-G.; Sustmann, R.; Giese, B.; Rückert, B.; Gröninger, K. S. *Chem. Ber.* **1990**, *123*, 1891. (f) Giese, B.; Dupuis, J.; Kröniger, K.; Hasskerl, T.; Nix, M.; Witzel, T. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenyi, R., Eds.; Reidel: Dordrecht, 1986; p 285. (g) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.

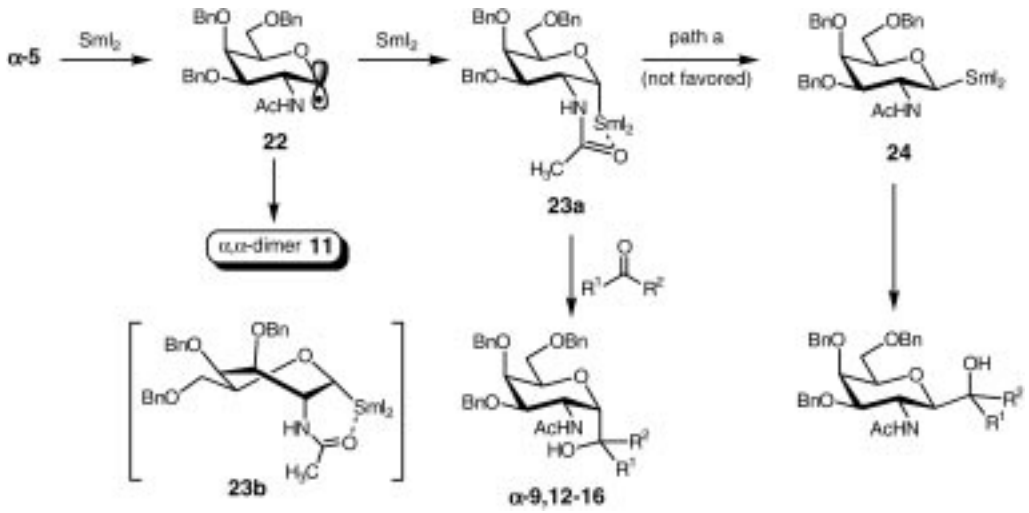
(21) (a) Giese, B.; Rückert, B.; Gröninger, K. S.; Muhn, R.; Lindner, H. J. *Liebigs Ann. Chem.* **1988**, 997. (b) Collins, P. M.; Whitton, B. R. *J. Chem. Soc., Perkin Trans 1* **1974**, 1069.

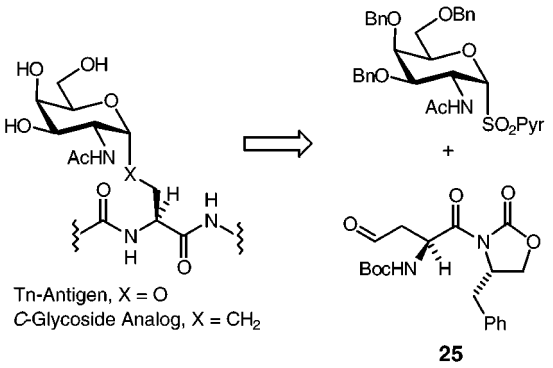
(22) Little is known about the nature of this anomerization process, although we have previously suggested the possibility that it may be a unimolecular three-step process involving metal ion dissociation, anion inversion, and association.[2d]

(23) Kawatsura, M.; Dekura, F.; Shirahama, H.; Matsuda, F. *Synlett* **1996**, 373.

(24) Preliminary investigations with the corresponding pyridyl sulfone of *N*-acetylglucosamine show that this compound does not couple to carbonyl substrates. It is therefore apparent that the stereochemistry at the C4 carbon is important for the *C*-glycosylation event. Prehaps the energy barrier to the conformational change in the organosamarium intermediate **23a** is of lower energy than in the case for the glucosamine derivative since the C4-substituent in **23a** shifts from an axial to equatorial orientation in **23b**.

Scheme 6





Scheme 7

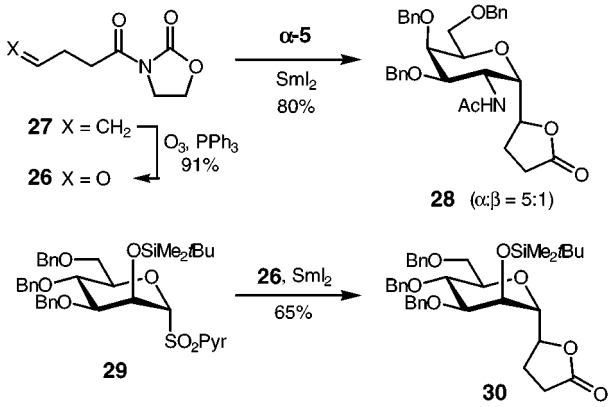


Figure 2.

as a suitable route for the construction of the aldehyde partner **25**, which was to be coupled with the pyridyl sulfone α-**5**. With this approach in mind, we synthesized the simple model oxazolidinone **26** and investigated its ability to couple with α-**5**. Hence, ozonolysis of the easily available alkene **27** furnished cleanly the crystalline aldehyde **26** (mp 43 °C). Treatment of pyridyl sulfone α-**5** with 2 equiv of **26** and SmI_2 then led to the formation of a diastereomeric mixture of α-*C*-galactosamines (Scheme 7). However, instead of the expected *C*-galactosamine, the lactones α-**28** were obtained in 80% yield with an α:*β* selectivity of 5:1, in which the condensation product had undergone internal cyclization with expulsion of the oxazolidine moiety. The preferential formation of the lactone upon *C*-glycosylation was confirmed by subjecting the mannosyl pyridyl sulfone **29**, known for its high yielding SmI_2-promoted coupling reactions, to the same conditions. This case, too, led to the production of a pair of isomeric lactones **30** at C7 (ratio 3:1) as their α-anomers in 65% yield.

In conclusion, we have presented a mild and rapid method for the stereoselective synthesis of α-*C*-galactosamine derivatives via chelation-controlled *C*-glycosylation. The stereoselectivity observed at the anomeric center contrasts earlier results seen with glucosyl, galactosyl, and mannosyl pyridyl sulfones where 1,2-*trans*-*C*-glycosides were exclusively formed. These results suggest the interesting dual role an anchimeric assisting group may have at the C2 position of glycosyl donors for the stereoselective synthesis of 1,2-*trans*-*O*- and 1,2-*cis*-*C*-glycosides. Further work directed to the application of this chemistry to prepare a *C*-glycoside analogue of the Tn-antigen will be reported in due course.

Experimental Section

General Considerations. Unless otherwise stated, all reactions were carried out under argon. THF was dried and freshly distilled over sodium/benzophenone. Dichloromethane was freshly distilled over P_2O_5. Reactions were monitored by thin-layer chromatography (TLC) analysis. The following compounds were prepared according to literature procedures: 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose (**2**),[7] 3,4,6-tri-*O*-benzyl-2-*O*-(trimethylsilyl)-α-D-galactopyranosyl 2-pyridyl sulfone (**17**),[2d] and mannosyl pyridyl sulfone **29**.[2d]

2-Pyridyl 2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-1-thio-α-D-galactopyranoside (α-3). To a stirred solution of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose (**2**) (2.52 g, 5.3 mmol) and trichloroacetonitrile (3.2 mL, 32 mmol) in CH_2Cl_2 (25 mL) was added K_2CO_3 (1.1 g, 8.0 mmol). The mixture was stirred for 6 h at 30 °C, after which it was filtered and evaporated to dryness in vacuo. Purification of the residue by flash chromatography (cyclohexane/EtOAc 5:1 containing 1% NEt_3) provided the *β*-imidate as a colorless oil (2.76 g, 84%). This compound was then redissolved in CH_2Cl_2 (140 mL), and 2-mercaptopyridine (1.17 g, 10.5 mmol) was added. The stirred solution was cooled to −15 °C and $BF_3{\cdot}Et_2O$ (131 μL, 1.1 mmol) was added. After being stirred at this temperature for 1 h, the solution was washed with aqueous $NaHCO_3$ (sat.)

(25) See: Toyokuni, T.; Dean, B.; Cai, S.; Boisin, D.; Hakamori, S.; Singhal, A. K. *J. Am. Chem. Soc.* **1994**, *116*, 395 and references therein.

(26) Evans, D. A.; Britton, T. C.; Ellman, J. A.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 4011.

and then dried (Na_2SO_4) and evaporated to dryness in vacuo. Purification by flash chromatography (cyclohexane/EtOAc 5:1) provided first the α-anomer α-**3** (1.61 g) and then the β-anomer β-**3** (0.62 g) in a combined yield of 88%: $[\alpha]_D = 142°$ ($c = 0.94$, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 8.46 (dd, $J = 4.8$, 1.9 Hz, 1 H), 7.48 (dd, $J = 7.3$, 1.9 Hz, 1 H), 7.42−7.17 (m, 16 H), 7.02 (dd, $J = 7.3$, 4.8 Hz, 1 H), 6.54 (d, $J = 5.6$ Hz, 1 H), 4.94 (d, $J = 11.5$ Hz, 1 H), 4.77 (d, $J = 11.5$ Hz, 1 H), 4.72 (d, $J = 11.5$ Hz, 1 H), 4.55 (d, $J = 11.5$ Hz, 1 H), 4.52 (dd, $J = 10.8$, 5.6 Hz, 1 H), 4.39 (d, $J = 11.5$ Hz, 1 H), 4.33 (d, $J = 11.5$ Hz, 1 H), 4.28 (dd, $J = 7.4$, 5.8 Hz, 1 H), 4.06 (d, $J = 3.0$ Hz, 1 H), 3.72 (dd, $J = 10.8$, 3.0 Hz, 1 H), 3.64 (dd, $J = 9.2$, 7.4 Hz, 1 H), 3.50 (dd, $J = 9.2$, 5.8 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.9, 149.4, 138.0, 137.5, 137.1, 136.2, 128.2, 128.0, 128.0, 127.6, 127.5, 123.5, 120.3, 83.6, 79.3, 74.6, 73.0, 72.9, 71.9, 71.5, 68.0, 59.7; IR (neat) (cm^{-1}) 3031, 2875, 2112, 1456. Anal. Calcd for $C_{32}H_{32}N_4O_4S$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.77; H, 5.72; N, 9.69.

2-Pyridyl 2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-1-thio-β-D-galacto-pyranoside (β-3). To a stirred solution of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose (**2**) (530 mg, 1.1 mmol) and trichloroacetonitrile (1.1 mL, 10.1 mmol) in CH_2Cl_2 (6 mL) was added DBU (82 μL, 0.55 mmol). The solution was stirred for 1 h at 30 °C, after which time it was evaporated to dryness in vacuo. Purification of the residue by flash chromatography (cyclohexane/EtOAc 5:1 containing 1% NEt_3) provided the α-imidate as a colorless oil (516 g, 75%). The α-imidate (500 mg, 0.81 mmol) was then redissolved in CH_2Cl_2 (26 mL), and 2-mercaptopyridine (270 mg, 2.43 mmol) and 4 Å molecular sieves (400 mg) were added. The stirred solution was cooled to −20 °C and TMSOTf (10 μL, 0.052 mmol) was added dropwise. After being stirred at this temperature for 1 h, the solution was filtered through Celite and then washed with aqueous $NaHCO_3$ (sat.), dried (Na_2SO_4), and evaporated to dryness in vacuo. Purification by flash chromatography (cyclohexane/EtOAc 5:1) provided the β-anomer β-**3** (526 mg) in 99% yield as a colorless solid. Recrystallization from EtOAc/pentane provided colorless needles: mp 86 °C; $[\alpha]_D = 15.7°$ ($c = 0.85$, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 8.47 (dd, $J = 4.8$, 1.9 Hz, 1 H), 7.50−7.25 (m, 17 H), 7.05 (dd, $J = 7.8$, 4.8 Hz, 1 H), 5.40 (d, $J = 10.4$ Hz, 1 H), 4.95 (d, $J = 11.2$ Hz, 1 H), 4.81 (d, $J = 11.2$ Hz, 1 H), 4.74 (d, $J = 11.2$ Hz, 1 H), 4.63 (d, $J = 11.2$ Hz, 1 H), 4.49 (d, $J = 11.2$ Hz, 1 H), 4.42 (d, $J = 11.2$ Hz, 1 H), 4.09 (dd, $J = 10.4$, 9.8 Hz, 1 H), 4.05 (d, $J = 3.0$ Hz, 1 H), 3.75 (dd, $J = 7.2$, 6.6 Hz, 1 H), 3.69−3.63 (m, 2 H), 3.59 (dd, $J = 9.8$, 3.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.7, 149.1, 137.9, 137.4, 137.1, 136.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.3, 123.1, 120.2, 82.6, 82.3, 77.1, 74.2, 73.0, 71.9, 71.8, 67.9, 61.5; IR (neat) (cm^{-1}) 3031, 2875, 2106, 1450, 1418. Anal. Calcd for $C_{32}H_{32}N_4O_4S$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.51; H, 5.71; N, 9.64.

Pyridyl Sulfides α-3 and β-3 from 2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-β-D-galactopyranose (2). Tributylphosphine (1.36 mL, 5.46 mmol) was added to a stirred solution of hemiacetal **2** (2.0 g, 4.2 mmol) and 2,2′-dipyridyl disulfide (1.11 g, 5.0 mmol) in CH_2Cl_2 (65 mL). After being stirred for 1 h, the solution was evaporated to dryness in vacuo. Purification of the residue by flash chromatography (cyclohexane/EtOAc 5:1) provided first the α-anomer α-**3** (614 mg) and then the β-anomer β-**3** (1.61 g) in a combined yield of 93%.

2-Pyridyl 2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-1-thio-α-D-galactopyranoside (α-4). To a stirred solution of $SnCl_2$ (341 mg, 1.79 mmol) in acetonitrile (10 mL) was added consecutively thiophenol (740 μL, 7.22 mmol), triethylamine (750 μL, 5.41 mmol), and azide α-**3** (684 mg, 1.20 mmol). The solution was stirred for 20 min, after which time it was diluted with CH_2Cl_2 and washed with 2 N NaOH. The aqueous phase was reextracted with CH_2Cl_2, and the combined organic phase was then dried (Na_2SO_4) and evaporated to dryness in vacuo. The residue was redissolved in pyridine (18 mL) and Ac_2O (7 mL) and left standing overnight. The solution was evaporated to dryness in vacuo and then coevaporated with toluene (3×). Purification of the residue by flash chromatography (cyclohexane/EtOAc 1:3) provided the acetamide α-**4** (703 mg) in a yield of 99%: $[\alpha]_D = 115.6°$ ($c = 0.30$, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 8.40 (dd, $J = 5.2$, 2.0 Hz, 1 H, pyr), 7.50 (dd, $J = 7.4$, 2.0 Hz, 1 H), 7.45−7.20 (m, 16 H), 7.04 (dd, $J = 7.4$, 5.2 Hz), 6.41 (d, $J = 5.2$ Hz, 1 H), 5.22 (d, $J = 7.5$ Hz, 1 H), 4.97 (d, $J = 11.7$ Hz, 1 H), 4.92 (ddd, $J = 11.2$, 7.5, 5.2 Hz, 1 H), 4.78 (d, $J = 11.7$ Hz, 1 H), 4.63 (d, $J = 11.7$ Hz, 1 H), 4.43 (d, $J = 11.7$ Hz, 1 H), 4.40 (s, 2 H), 4.32 (dd, $J = 7.0$, 5.2 Hz, 1 H), 4.12 (m, 1 H), 3.72 (dd, $J = 9.2$, 7.0 Hz, 1 H), 3.60 (dd, $J = 11.2$, 2.9 Hz, 1 H), 3.56 (dd, $J = 9.2$, 5.2 Hz, 1 H), 1.88 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.3, 157.4, 149.2, 138.2, 137.7, 137.5, 136.7, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 127.7, 127.6, 127.5, 123.0, 120.5, 84.9, 77.0, 74.5, 73.2, 72.2, 71.6, 71.1, 68.3, 49.4, 23.1; IR (neat) (cm^{-1}) 3054, 2985, 1684, 1438, 1265; MS (CI, NH_3) *m/z* 585 (M + 1), 474 (M + 1 − HSPyr). Unsatisfactory elemental analyses were given for this compound.

2-Pyridyl 2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (β-4). The procedure described for the obtention of α-**4** was adopted, providing pyridyl sulfide β-**4** (89 mg, 82%) as a colorless syrup after purification by flash chromatography (cyclohexane/EtOAc 1:3): $[\alpha]_D = 41.4°$ ($c = 1.26$, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 8.37 (broad d, $J = 4.9$ Hz, 1 H), 7.50 (dd, $J = 7.4$, 2.0 Hz, 1 H), 7.41−7.24 (m, 17 H), 7.01 (ddd, $J = 6.0$, 4.9, 2.7 Hz), 5.75 (d, $J = 8.2$ Hz, 1 H), 5.69 (d, $J = 10.8$ Hz, 1 H), 4.96 (d, $J = 11.7$ Hz, 1 H), 4.74 (d, $J = 11.7$ Hz, 1 H), 4.63 (d, $J = 11.7$ Hz, 1 H), 4.53 (d, $J = 11.7$ Hz, 1 H), 4.48 (d, $J = 11.7$ Hz, 1 H), 4.41 (d, $J = 11.7$ Hz, 1 H), 4.26 (ddd, $J = 10.8$, 10.2, 8.2 Hz, 1 H), 4.07 (d, $J = 2.9$ Hz, 1 H), 4.01 (dd, $J = 10.2$, 2.9 Hz, 1 H), 3.81 (dd, $J = 7.6$, 5.3 Hz, 1 H), 3.63 (m, 2 H), 1.88 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.5, 157.3, 149,1, 138.5, 138.0, 137.8, 136.6, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.5, 123.9, 120.4, 82.8, 79.8, 77.6, 74.4, 73.3, 72.4, 71.8, 68.6, 51.7, 23.5; IR (neat) (cm^{-1}) 3054, 2985, 1684, 1438, 1265; MS (CI, NH_3) *m/z* 585 (M + 1), 474 (M + 1 − HSPyr). Unsatisfactory elemental analyses were given for this compound.

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl 2-Pyridyl Sulfone (α-5). *m*-CPBA of approximately 85% purity (735 mg, 2.13 mmol) was added to a stirred mixture of sulfide α-**4** (580 mg, 0.99 mmol) and $NaHCO_3$ (584 mg, 6.95 mmol) in CH_2Cl_2 (10 mL) at 0 °C. Stirring was continued for 2.5 h at 0 °C, after which time the reaction mixture was diluted with CH_2Cl_2 and then washed consecutively with a 50% saturated solution of $Na_2S_2O_3$, saturated $NaCO_3$, and brine. The organic phase was dried with Na_2SO_4 and concentrated to dryness in vacuo. Flash chromatography (cyclohexane/EtOAc 1:5) gave α-**5** (545 mg, 89%) as a colorless solid. Recrystallization from EtOAc/pentane provided colorless needles: mp 151 °C; $[\alpha]_D = 95.0°$ ($c = 0.97$, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 8.64 (broad d, $J = 4.8$ Hz, 1 H), 7.97 (broad d, $J = 7.9$ Hz, 1 H), 7.74 (dd, $J = 7.9$, 1.7 Hz, 1 H), 7.42−7.18 (m, 16 H, 3Ph), 5.83 (d, $J = 8.0$ Hz, 1 H), 5.60 (d, $J = 5.8$ Hz, 1 H), 5.07 (ddd, $J = 10.8$, 8.0, 5.8 Hz, 1 H), 4.86 (d, $J = 11.8$ Hz, 1 H), 4.78 (d, $J = 11.8$ Hz, 1 H), 4.68 (d, $J = 11.8$ Hz, 1 H), 4.53 (d, $J = 11.8$ Hz, 1 H), 4.52 (m, 1 H), 4.33 (d, $J = 11.8$ Hz, 1 H), 4.27 (d, $J = 11.8$ Hz, 1 H), 4.43 (dd, $J = 10.8$, 2.8 Hz, 1 H), 4.08 (dd, $J = 3.0$, 2.8 Hz, 1 H), 3.45 (dd, $J = 9.8$, 6.2 Hz, 1 H), 3.35 (dd, $J = 9.8$, 6.2 Hz, 1 H), 1.80 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.7, 156.0, 137.9, 137.7, 137.7, 137.5, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.3, 123.3, 87.7, 75.1, 74.9, 74.1, 73.0, 72.1, 71.9, 67.9, 47.3, 23.0; IR (neat) (cm^{-1}) 3055, 2987, 1684, 1422, 1265. Anal. Calcd for $C_{34}H_{36}N_2O_7S$: C, 66.22; H, 5.89; N, 4.54. Found: C, 66.25; H, 6.05; N, 4.48.

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl 2-Pyridyl Sulfone (β-5). The procedure described for the obtention of α-**5** was adopted. Flash chromatography (cyclohexane/EtOAc 1:5) gave β-**5** (74 mg, 12%) as a colorless syrup that was difficult to obtain in pure form: ^1H NMR (250 MHz, $CDCl_3$) δ 8.60 (dd, $J = 5.0$, 2.0 Hz, 1 H), 8.04 (d, $J = 8.1$ Hz, 1 H), 7.80 (ddd, $J = 8.1$, 8.1, 2.0 Hz, 1 H), 7.41−7.11 (m, 16 H), 6.21 (d, $J = 7.1$ Hz, 1 H), 5.60 (d, $J = 10.1$ Hz, 1 H), 4.82 (d, $J = 11.5$ Hz, 1 H), 4.68 (dd, $J = 10.8$, 2.9 Hz, 1 H), 4.67 (d, $J = 11.5$ Hz, 1 H), 4.57 (d, $J = 11.5$ Hz, 1 H), 4.46 (d, $J = 11.5$ Hz, 1 H), 4.38 (s, 2 H), 4.08 (ddd, $J = 10.8$, 10.1, 7.1

Hz, 1 H), 3.88 (d, J = 3.0 Hz, 1 H), 3.77 (dd, J = 7.2, 5.5 Hz, 1 H), 3.40 (m, 2 H), 1.88 (s, 3 H); IR (neat) (cm^{-1}) 3056, 1666, 1438, 1185; MS (CI, NH_3) m/z 617 (M + 1), 474 (M + 1 − HSO_2-Pyr).

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl-1-cyclohexanol (α-9). A 0.1 M solution of SmI_2 in THF (1.6 mL, 0.16 mmol) was added to a stirred solution of sulfone α-**5** (50 mg, 0.081 mmol) and cyclohexanone (17 μL, 0.17 mmol) in THF (0.5 mL) at 20 °C. After the mixture was stirred for 10 min, saturated aqueous NH_4Cl was added, and the resulting mixture was then extracted twice with CH_2Cl_2. The combined organic phases were washed twice with water, dried, with Na_2SO_4, and evaporated to dryness. Flash chromatography (cyclohexane/EtOAc 1:3) afforded two fractions. The first fraction (39 mg) contained a mixture of the α- and β-*C*-glycosides, as well as dimer **11** (see below) in the ratio of 10.0:1.0:1.6, respectively, according to the ^{1}H NMR spectrum. This corresponded to a 75% yield for the *C*-glycosylation step and a 9% yield for the dimer production. α-**9**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40−7.27 (m, 15 H), 6.92 (d, J = 4.8 Hz, 1 H), 4.77 (d, J = 12.3 Hz, 1 H), 4.67 (d, J = 12.3 Hz, 1 H), 4.56 (d, J = 12.1 Hz, 1 H), 4.47 (d, J = 12.1 Hz, 1 H), 4.47 (d, J = 11.8 Hz, 1 H), 4.40 (d, J = 11.8 Hz, 1 H), 4.39 (ddd, J = 9.4, 6.7, 2.0 Hz, 1 H), 4.30 (dd, J = 3.4, 3.4 Hz, 1 H), 4.21 (dd, J = 11.7, 9.4 Hz, 1 H), 4.06 (broad dd, J = 4.8, 3.4 Hz, 1 H), 3.83 (dd, J = 6.7, 3.4 Hz, 1 H), 3.80 (dd, J = 11.7, 2.0 Hz, 1 H), 3.74 (bs, 1 H), 2.08 (s, 1 H), 1.94 (s, 3 H), 1.67−1.16 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.6, 138.8, 138.3, 137.9, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 75.2, 73.3, 73.1, 73.1, 72.6, 70.6, 67.7, 65.7, 49.8, 36.9, 31.9, 25.4, 23.5, 21.6, 21.5; MS (CI, NH_3) m/z 574 (M + 1), 556 (M + 1 − H_2O), 482 (M + 1 − $PhCH_3$); IR (neat) (cm^{-1}) 3054, 2987, 2936, 2850, 1496, 1422, 1267. Characteristic signals for the β-isomer β-**9** were seen at δ 5.24 (d, J = 8.5 Hz, 1 H), 4.92 (d, J = 11.9 Hz, 1 H), 3.42 (d, J = 9.7 Hz, 1 H), 1.89 (s, 3 H). The second fraction was identified as the 1-deoxy derivative **10** (6 mg, 16%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.75−7.26 (m, 15 H), 5.18 (d, J = 6.3 Hz, 1 H), 4.90 (d, J = 11.7 Hz, 1 H), 4.75 (d, J = 12.3 Hz, 1 H), 4.61 (d, J = 11.7 Hz, 1 H), 4.52 (d, J = 11.9 Hz, 1 H), 4.45 (d, J = 11.9 Hz, 1 H), 4.41 (d, J = 12.3 Hz, 1 H), 4.26−4.15 (m, 2 H), 4.01 (d, J = 3.0 Hz, 1 H), 3.66−3.46 (m, 4 H), 3.16 (dd, J = 12.0, 12.0 Hz, 1 H), 1.87 (s, 3 H); MS (CI, NH_3) m/z 494 (M + 18), 476 (M + 1), 384 (M + 1 − $PhCH_3$).

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl-3-pentanol (α-12). The *C*-glycosides were prepared according to the general procedure outlined for α-**9**. Flash chromatography (cyclohexane/EtOAc 1:3) afforded two fractions. The first fraction (40 mg) contained a mixture of the α- and β-*C*-glycosides, as well as dimer **11** (see below) in a ratio of 10.0:1.0:1.1, respectively, according to the ^{1}H NMR spectrum. This corresponded to a 67% yield for the *C*-glycosylation step and a 7% yield for the dimer production. The second fraction was identified as the 1-deoxy derivative **10** (8 mg, 18%). α-**12**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40−7.24 (m, 15 H), 6.98 (d, J = 4.8 Hz, 1 H), 4.82 (d, J = 12.3 Hz, 1 H), 4.73 (d, J = 12.3 Hz, 1 H), 4.58 (d, J = 11.8 Hz, 1 H), 4.54 (d, J = 12.1 Hz, 1 H), 4.52 (d, J = 11.8 Hz, 1 H), 4.43 (d, J = 12.1 Hz, 1 H), 4.38 (ddd, J = 9.4, 7.0, 2.1 Hz, 1 H), 4.30 (dd, J = 3.4, 3.4 Hz, 1 H), 4.21 (dd, J = 11.6, 9.4 Hz, 1 H), 4.05 (ddd, J = 4.8, 3.4, 3.0 Hz, 1 H), 3.81 (dd, J = 7.0, 3.4 Hz, 1 H), 3.79 (d, J = 3.0 Hz, 1 H), 3.78 (dd, J = 11.7, 2.1 Hz, 1 H), 1.97 (s, 3 H), 1.77−1.21 (m, 4 H), 0.79 (t, J = 11.9 Hz, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.8, 139.0, 138.4, 138.0, 128.5, 128.2, 127.9, 127.6, 75.3, 73.4, 73.3, 72.7, 70.8, 66.0, 65.9, 50.3, 28.6, 24.9, 23.7, 7.7; IR (neat) (cm^{-1}) 3054, 2987, 1669, 1422, 1266; MS (electrospray) m/z 584 (M + Na); HRMS m/e calcd for $C_{34}H_{43}NNaO_6$ (M + Na), 584.2988, found 584.3015. Characteristic signals for the β-isomer were seen at δ 5.24 (d, J = 8.8 Hz, 1 H), 4.96 (d, J = 11.7 Hz, 1 H), 3.57 (d, J = 9.7 Hz, 1 H), 1.90 (s, 3 H), 0.88 (t, J = 11.9 Hz, 6 H).

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl-1-cyclopentanol (α-13). The *C*-glycosides were prepared according to the general procedure outlined for α-**9**. Flash chromatography (cyclohexane/EtOAc 2:3) afforded two fractions. The first fraction (30 mg) contained a mixture of the α- and β-*C*-glycosides, as well as dimer **11** (see below) in a ratio of 5.0:1.0:0.8, respectively, according to the ^{1}H NMR spectrum. This corresponded to a 60% yield for the *C*-glycosylation step and an 8% yield for the dimer production. The second fraction was identified as the 1-deoxy derivative **10** (4 mg, 10%). α-**13**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40−7.24 (m, 15 H), 7.03 (d, J = 4.8 Hz, 1 H), 4.81 (d, J = 12.0 Hz, 1 H), 4.70 (d, J = 12.0 Hz, 1 H), 4.62 (d, J = 12.0 Hz, 1 H), 4.55 (d, J = 12.1 Hz, 1 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.45 (d, J = 12.1 Hz, 1 H), 4.38 (ddd, J = 9.5, 6.7, 2.1 Hz, 1 H), 4.27 (dd, J = 3.3, 3.3 Hz, 1 H), 4.20 (dd, J = 11.8, 9.5 Hz, 1 H), 4.05 (ddd, J = 4.8, 3.3, 2.2 Hz, 1 H), 3.81 (dd, J = 6.7, 3.3 Hz, 1 H), 3.78 (dd, J = 11.8, 2.1 Hz, 1 H), 3.67 (d, J = 2.1 Hz, 1 H), 1.97 (s, 3 H), 1.85−1.18 (m, 8 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.7, 138.8, 137.8, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 83.7, 75.3, 73.4, 73.3, 73.1, 72.6, 70.7, 69.1, 65.6, 51.2, 41.4, 34.4, 23.8, 23.6; IR (neat) (cm^{-1}) 3054, 2987, 1422, 1265; MS (electrospray) m/z 582 (M + Na); HRMS m/e calcd for $C_{34}H_{41}NNaO_6$ (M + Na) 582.2832, found 582.2843. Characteristic signals for the β-isomer were seen at δ 5.36 (d, J = 7.4 Hz, 1 H), 4.85 (d, J = 11.6 Hz, 1 H), 1.90 (s, 3 H).

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl-1-cyclohexylmethanol (α-14). The *C*-glycosides were prepared according to the general procedure outlined for α-**9**. Flash chromatography (cyclohexane/EtOAc 1:3) afforded two fractions (A and B), in which the first contained four compounds (51 mg) according to its ^{1}H NMR spectrum and the latter (B) was the 1-deoxy derivative **10** (3 mg, 6%). Subjection of the first fraction to flash chromatography (toluene/EtOAc 7:2) led to two new fractions (C and D), the first of which contained the isomeric α-*C*-glycosides in a ratio of 6:1 (41 mg, 64%), whereas the other contained a mixture of dimer **11** and the β-*C*-glycoside. Fraction C was then rechromatographed in cyclohexane/EtOAc (1:3), affording first a mixture of the α-*C*-glycosides in favor of the minor isomer and then the pure major isomer, which was recrystallized from EtOAc/Et_2O/pentane. α-**14** (major C7-isomer): mp 137−138 °C; $[\alpha]_D$ = 15.1° (c = 1.23, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.37−7.24 (m, 15 H), 6.54 (d, J = 5.9 Hz, 1 H), 4.77 (d, J = 11.8 Hz, 1 H), 4.70 (d, J = 11.8 Hz, 1 H), 4.69 (d, J = 12.0 Hz, 1 H), 4.54 (d, J = 11.8 Hz, 1 H), 4.53 (d, J = 12.0 Hz, 1 H), 4.44 (d, J = 11.8 Hz, 1 H), 4.37 (ddd, J = 9.4, 6.2, 2.4 Hz, 1 H), 4.23 (dd, J = 11.3, 9.4 Hz, 1 H), 4.13 (dd, J = 3.0, 2.9 Hz, 1 H), 4.07 (dd, J = 3.4, 2.9 Hz, 1 H), 4.05 (ddd, J = 5.9, 3.0, 2.9 Hz, 1 H), 3.78 (dd, J = 6.2, 2.9 Hz, 1 H), 3.73 (dd, J = 11.3, 2.4 Hz, 1 H), 3.31 (ddd, J = 7.2, 5.0, 3.4 Hz, 1 H), 2.41 (d, J = 7.2 Hz, 1 H), 1.97 (s, 3 H), 1.80−1.07 (m, 11 H, CH, $5CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.5, 138.7, 138.3, 137.9, 128.5, 128.4, 128.0, 127.7, 75.8, 75.2, 73.8, 73.6, 73.1, 72.6, 71.0, 65.8, 64.9, 51.8, 41.1, 29.8, 27.3, 26.4, 26.4, 26.1, 23.6; IR (neat) (cm^{-1}) 3429, 3054, 2987, 2929, 2856, 1675, 1497, 1454, 1422, 1372; MS (electrospray) m/z 610 (M + Na); HRMS m/e calcd for $C_{36}H_{45}NNaO_6$ (M + Na) 610.3145, found 610.3158. Characteristic signals for the minor α-*C*-glycoside were seen at δ 7.37−7.24 (m, 15 H), 6.43 (d, J = 6.8 Hz, 1 H), 4.72 (s, 2 H), 4.57 (s, 2 H), 4.54 (d, J = 12.3 Hz, 1 H), 4.46 (d, J = 12.3 Hz, 1 H), 4.37 (ddd, J = 9.2, 6.8, 2.7 Hz, 1 H), 4.24 (ddd, J = 6.8, 3.6, 2.5 Hz, 1 H), 4.18 (dd, J = 11.8, 9.2 Hz, 1 H), 4.08 (dd, J = 3.6, 3.6 Hz, 1 H), 3.94 (dd, J = 5.5, 2.5 Hz, 1 H), 3.76 (dd, J = 11.8, 2.7 Hz, 1 H), 3.75 (dd, J = 6.8, 3.6 Hz, 1 H), 3.43 (ddd, J = 5.5, 5.5, 3.8 Hz, 1 H), 2.65 (d, J = 3.8 Hz, 1 H), 2.00 (s, 3 H), 1.90−1.05 (m, 11 H). Fraction D was subjected to standard acetylation conditions (Ac_2O, pyridine) and then rechromatographed in toluene/EtOAc (7:2), affording first a fraction containing the acetylated β-*C*-glycosides (2 mg, 3%) contaminated with **11** and then dimer **11** (3 mg, 6%). β-Isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40−7.22 (m, 15 H), 5.22 (d, J = 8.8 Hz, 1 H), 4.99 (d, J = 11.6 Hz, 1 H), 4.73 (d, J = 12.3 Hz, 1 H), 4.56 (d, J = 11.6 Hz, 1 H), 4.53 (m, 1 H), 4.47 (s, 2 H), 4.46 (d, J = 12.3 Hz, 1 H), 4.23 (ddd, J = 10.0, 10.0, 8.8 Hz, 1 H), 4.01 (d, J = 2.9 Hz, 1 H), 3.63−3.47 (m, 5 H), 2.03 (s, 3 H), 1.95 (s, 3 H), 1.86−1.05 (m, 11 H). Dimer **11**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38−7.15 (m, 30 H), 6.88 (d, J = 4.7 Hz, 2 H), 4.68 (d, J = 11.9 Hz, 2 H), 4.62 (d, J = 11.9 Hz, 2 H), 4.51 (d, J = 12.2 Hz, 2 H), 4.50 (d, J = 12.0 Hz, 2 H), 4.44 (d, J = 12.2

Hz, 2 H), 4.37 (ddd, J = 9.5, 6.2, 2.0 Hz, 2 H), 4.34 (d, J = 12.0 Hz, 2 H), 4.34 (d, J = 4.6 Hz, 2 H), 4.18 (dd, J = 3.2, 3.2 Hz, 2 H), 4.15 (dd, J = 12.1, 9.5 Hz, 2 H), 4.06 (dd, J = 4.7, 4.6 Hz, 2 H), 3.76 (dd, J = 6.2, 3.2 Hz, 2 H), 3.57 (dd, J = 12.1, 2.0 Hz, 2 H), 1.79 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.4, 138.5, 138.0, 137.9, 75.8, 73.7, 73.6, 73.5, 72.2, 71.4, 67.6, 66.2, 53.7, 23.3; IR (neat) (cm^{-1}) 3054, 2987, 1419, 1266; MS (CI, NH_3) m/z 949 (M + 1).

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl-2-methylpropanol (α-15). The *C*-glycosides were prepared according to the general procedure outlined for α-**9**. Flash chromatography (cyclohexane/EtOAc 1:2) afforded two fractions. The first fraction (40 mg) contained a mixture of two α-*C*-glycosides and one detectable β-*C*-glycoside, as well as dimer **11** (see above) in the ratio of 10.0:2.0:1.0:0.8, respectively, according to the ^{1}H NMR spectrum. This corresponded to a 72% yield for the *C*-glycosylation step and a 4% yield for the dimer production. The second fraction was identified as the 1-deoxy derivative **10** (2 mg, 4%). Further careful purification of the first fraction afforded pure α-**15** (major isomer) as a colorless syrup: $[\alpha]_D$ = 18.3° (c = 0.93, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40−7.21 (m, 15 H), 6.37 (d, J = 6.4 Hz, 1 H), 4.75 (d, J = 11.9 Hz, 1 H), 4.69 (d, J = 11.9 Hz, 1 H), 4.59 (d, J = 11.8 Hz, 1 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.50 (d, J = 11.8 Hz, 1 H), 4.43 (d, J = 12.0 Hz, 1 H), 4.36 (ddd, J = 9.2, 6.5, 2.6 Hz, 1 H), 4.21 (dd, J = 11.6, 9.2 Hz, 1 H), 4.12−4.05 (m, 2 H, H2), 4.00 (dd, J = 4.7, 1.7 Hz, 1 H), 3.76 (dd, J = 6.4, 2.6 Hz, 1 H), 3.71 (dd, J = 11.3, 2.6 Hz, 1 H), 3.31 (broad dd, J = 4.7, 4.7 Hz, 1 H), 2.54 (broad d, J = 4.7 Hz, 1 H), 1.99 (s, 3 H), 1.73 (m, 1 H), 0.97 (d, J = 7.0 Hz, 3 H), 0.93 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.4, 138.6, 138.2, 137.8, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 75.9, 75.1, 73.9, 73.5, 73.0, 72.6, 71.0, 65.8, 65.6, 51.1, 30.9, 29.8, 23.5, 19.8, 16.6; IR (neat) (cm^{-1}) 3054, 2987, 1675, 1496, 1422, 1267; MS (electrospray) m/z 570 (M + Na); HRMS m/e calcd for $C_{33}H_{41}NNaO_6$ (M + Na) 570.2832, found 570.2832. Characteristic signals for the minor α-*C*-glycoside were seen at δ 6.46 (d, J = 7.2 Hz, 1 H), 3.94 (dd, J = 6.7, 2.2 Hz, 1 H), 3.42 (ddd, J = 6.2, 6.2, 3.7 Hz, 1 H), 2.02 (s, 3 H), 1.90−1.05 (m, 11 H, CH, $5CH_2$), 0.89 (d, J = 7.0 Hz, 3 H, Me), 0.83 (d, J = 7.0 Hz, 3 H, Me). Characteristic signals for the β-isomer were seen at δ 5.24 (d, J = 7.7 Hz, 1 H), 4.92 (d, J = 11.7 Hz, 1 H), 1.95 (s, 3 H), 0.88 (t, J = 11.9 Hz, 6 H), 1.04 (d, J = 7.0 Hz, 3 H), 0.97 (d, J = 7.0 Hz, 3 H).

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl-1-octanol (α-16). The *C*-glycosides were prepared according to the general procedure outlined for α-**9**. Flash chromatography (cyclohexane/EtOAc 2:3) afforded two fractions. The first fraction (46 mg) contained a mixture of two α-*C*-glycosides and one detectable β-*C*-glycoside as well as dimer **11** (see above) in a ratio of 7.7:1.3:1.0:1.2, respectively, according to the ^{1}H NMR spectrum. This corresponded to a 69% yield for the *C*-glycosylation step and a 10% yield for the dimer production. The second fraction was identified as the 1-deoxy derivative **10** (5 mg, 11%). α-**15** (major C7-isomer): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.38−7.20 (m, 15 H), 6.27 (d, J = 7.0 Hz, 1 H), 4.77 (d, J = 12.2 Hz, 1 H), 4.68 (d, J = 12.2 Hz, 1 H), 4.59 (d, J = 12.0 Hz, 1 H), 4.54 (d, J = 12.0 Hz, 1 H), 4.53 (d, J = 12.0 Hz, 1 H), 4.45 (d, J = 12.0 Hz, 1 H), 4.36 (ddd, J = 9.3, 6.5, 2.3 Hz, 1 H), 4.22 (dd, J = 11.1, 9.3 Hz, 1 H), 4.15 (ddd, J = 7.0, 3.3, 2.5 Hz, 1 H), 4.06 (dd, J = 3.8, 3.3 Hz, 1 H), 3.82 (dd, J = 5.5, 2.5 Hz, 1 H), 3.77 (dd, J = 6.5, 3.8 Hz, 1 H), 3.73 (dd, J = 11.1, 2.3 Hz, 1 H), 3.57 (m, 1 H), 2.47 (broad d, J = 5.2 Hz, 1 H), 1.97 (s, 3 H), 1.47−1.20 (m, 12 H), 0.97 (t, J = 6.5 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.2, 138.5, 138.3, 137.8, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 75.2, 74.0, 73.4, 73.1, 72.7, 71.2, 71.0, 68.4, 65.6, 50.3, 33.3, 31.9, 29.8, 29.5, 29.3, 25.3, 23.5, 22.8, 14.2; IR (neat) (cm^{-1}) 3054, 2987, 1507, 1419, 1266; MS (electrospray) m/z 626 (M + Na); HRMS m/e calcd for $C_{37}H_{49}NNaO_6$ (M + Na) 626.3458, found 626.3460. Characteristic signals for the minor α-*C*-glycoside were seen at δ 6.40 (d, J = 7.0 Hz, 1 H), 1.99 (s, 3 H), 1.90−1.05 (m, 11 H). Characteristic signals for the β-isomer were seen at δ 5.07 (d, J = 7.7 Hz, 1 H), 4.92 (d, J = 11.7 Hz, 1 H), 1.90 (s, 3 H).

3,4,6-Tri-*O*-benzyl-β-D-galactopyranosyl-3-pentanol (21). A 0.1 M solution of SmI_2 in THF (2.2 mL, 0.22 mmol) was added to a stirred solution of sulfone **17**[2d] (68 mg, 0.11 mmol) and 3-pentanone (16 μL, 0.15 mmol) in THF (0.5 mL) at 20 °C. After the mixture was stirred for 10 min, saturated aqueous NH_4Cl was added, and the resulting mixture was then extracted twice with CH_2Cl_2. The combined organic phases were washed twice with water, dried (Na_2SO_4), and evaporated to dryness. The residue was redissolved in THF (5 mL) and cooled to 0 °C, and 1.0 M Bu_4NF in THF (210 μL, 0.210 mmol) was added. After the mixture was stirred for 5 min, water and CH_2Cl_2 were added, and the organic phase was washed twice with water, dried with Na_2SO_4, and evaporated to dryness. Flash chromatography (cyclohexane/EtOAc 7:1−3:1) gave first tribenzyl-D-galactal (12 mg, 29%) and then **21** (16 mg, 31%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40−7.24 (m, 15 H), 4.85 (d, J = 11.6 Hz, 1 H), 4.73 (d, J = 12.0 Hz, 1 H), 4.56 (d, J = 11.6 Hz, 1 H), 4.48 (d, J = 12.0 Hz, 1 H), 4.48 (d, J = 11.8 Hz, 1 H), 4.42 (d, J = 11.8 Hz, 1 H), 4.21 (dd, J = 9.4, 9.0 Hz, 1 H), 3.98 (d, J = 2.8 Hz, 1 H), 3.73 (dd, J = 6.5, 6.5 Hz, 1 H), 3.64−3.52 (m, 2 H), 3.44 (dd, J = 9.0, 2.8 Hz, 1 H), 3.24 (d, J = 9.4 Hz, 1 H), 2.99 (broad s, 1 H), 2.87 (broad s, 1 H), 1.83−1.39 (m, 4 H), 1.89−1.74 (m, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.8, 137.8, 137.7, 128.6, 128.4, 128.2, 128.0, 127.8, 127.5, 84.4, 80.8, 75.7, 74.3, 73.5, 72.8, 71.8, 68.9, 68.2, 29.1, 28.0, 7.6, 7.1; IR (neat) (cm^{-1}) 3054, 2986, 1419, 1263; MS (electrospray) m/z 543 (M + Na); HRMS m/e calcd for $C_{32}H_{40}NaO_6$ (M + Na) 543.2723, found 543.2729.

2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl 2-Pyridyl Sulfone (19). The procedure described for the obtention of α-**5** was adopted, providing pyridyl sulfone **19** (111 mg, 80%) as a colorless syrup after purification by flash chromatography (cyclohexane/EtOAc 5:2): $[\alpha]_D$ = −46.3° (c = 0.90, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.9, 1.7 Hz, 1 H), 8.09 (d, J = 7.8 Hz, 1 H), 7.88 (ddd, J = 7.8, 7.8, 1.7 Hz, 1 H), 7.47−7.14 (m, 17 H), 4.85 (d, J = 11.2 Hz, 1 H), 4.73 (s, 2 H), 4.64 (d, J = 10.0 Hz, 1 H), 4.49 (d, J = 11.2 Hz, 1 H), 4.47 (dd, J = 10.0, 10.0 Hz, 1 H), 4.28 (s, 2 H), 3.89 (d, J = 2.9 Hz, 1 H), 3.59 (dd, J = 7.1, 5.2 Hz, 1 H), 3.49 (dd, J = 10.0, 2.9 Hz, 1 H), 3.41 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.4, 150.1, 138.0, 137.6, 137.1, 128.6, 128.4, 128.2, 128.1, 127.9, 127.4, 124.2, 88.6, 81.9, 78.2, 74.4, 73.4, 72.7, 71.6, 68.0, 57.9. Anal. Calcd for $C_{32}H_{32}N_4O_6S$: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.11; H, 5.42; N, 9.21.

3-(4′-Pentenoyl)-2-oxazolidinone (27). To a stirred solution of 4-pentenoic acid (1.28 mL, 12.1 mmol) and triethylamine (1.92 mL, 13.8 mmol) in THF (50 mL) at −78 °C was added dropwise trimethylacetyl chloride (1.5 mL, 12.1 mmol). After being stirred for 10 min at −78 °C and 30 min at 0 °C, the suspension was recooled to −78 °C, and to this was added a solution of metalated oxazolidinone (prepared by the addition of 2.5 M BuLi in hexanes (4.6 mL, 1.84 mmol) to a −78 °C stirred suspension of 2-oxazolidinone (1.00 g, 11.5 mmol) in THF (50 mL), followed by warming to 20 °C). The mixture was warmed to 0 °C and left stirring at this temperature for 1.5 h. The reaction mixture was quenched with aqueous NH_4Cl and then extracted with CH_2Cl_2 (3×). The combined organic phases were washed with 1 N NaOH and water and then dried (Na_2SO_4) and evaporated to dryness in vacuo. Purification of the residue by flash chromatography (cyclohexane/EtOAc 3:1) afforded **27** as a colorless syrup (1.24 g, 73%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.88 (ddt, J = 17.0, 10.2, 6.5 Hz, 1 H), 5.10 (ddd, J = 17.0, 3.4, 1.5 Hz, 1 H), 5.03 (dd, J = 10.2, 1.5 Hz, 1 H), 4.39 (t, J = 8.0 Hz, 2 H), 3.39 (t, J = 8.0 Hz, 2 H), 3.02 (t, J = 7.0 Hz, 2 H), 2.40 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.1, 153.3, 136.5, 115.1, 61.9, 42.1, 34.0, 27.7; IR (neat) (cm^{-1}) 3057, 2987, 2925, 1782, 1700, 1612, 1481, 1387, 1268. Anal. Calcd for $C_8H_{11}NO_3$: C, 56.80; H, 6.55. Found: C, 56.65; H, 6.53.

3-(4′-Oxobutanoyl)-2-oxazolidinone (26). Ozone was bubbled through a solution of alkene **27** (155 mg, 0.92 mmol) in CH_2Cl_2 (15 mL) at −78 °C until the solution turned blue. Argon was then allowed to bubble though the solution for 20 min at the same temperature, after which time triphenylphosphine (362 mg, 1.38 mmol) was added, and the mixture was

stirred for an additional 10 min. After evaporation to dryness in vacuo, the residue was purified by flash chromatography (cyclohexane/EtOAc 3:1), giving **26** as a colorless solid (143 mg, 91%). Recrystallization from EtOAc/Et_2O/pentane afforded colorless needles: mp 43 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.72 (s, 1 H), 4.37 (t, J = 8.0 Hz, 2 H), 3.94 (t, J = 8.0 Hz, 2 H), 3.17−3.09 (t, 2 H), 2.80−2.72 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.3, 171.8, 153.7, 62.4, 42.5, 37.6, 28.1; IR (neat) (cm^{-1}) 3054, 2987, 1783, 1700, 1422, 1388, 1267. Anal. Calcd for $C_7H_9NO_4$: C, 49.12; H, 5.30. Found: C, 48.99; H, 5.21.

α-*C*-Galactosamine (α-28). The *C*-glycosides were prepared from pyridyl sulfone α-**5** according to the general procedure outlined for α-**9**. Flash chromatography (cyclohexane/EtOAc 1:3) afforded a fraction containing a mixture of two α-*C*-glycosides and one detectable *β*-*C*-glycoside, as well as the 1-deoxy derivative **10** (see above) in the ratio of 3.5:1.5:1.0:0.8, respectively, according to the ^{1}H NMR spectrum. This corresponded to an 80% yield for the *C*-glycosylation step and a 10% yield for the 1-deoxy sugar formation. An approximately 2% yield of the dimer was also obtained. α-**28** (major C7-isomer): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40−7.24 (m, 15 H), 5.71 (d, J = 8.5 Hz, 1 H), 4.74 (d, J = 11.7 Hz, 1 H), 4.68 (d, J = 11.7 Hz, 1 H), 4.61 (d, J = 11.7 Hz, 1 H), 4.60 (m, 1 H), 4.48 (d, J = 11.7 Hz, 1 H), 4.48 (d, J = 12.3 Hz, 1 H), 4.43 (d, J = 12.3 Hz, 1 H), 4.40 (m, 1 H), 4.26 (m, 1 H), 4.22 (m, 1 H), 3.96 (dd, J = 4.2, 3.5 Hz, 1 H), 3.90 (dd, J = 6.8, 2.4 Hz, 1 H), 3.76 (dd, J = 6.2, 3.5 Hz, 1 H), 3.75 (dd, J = 11.6, 2.5 Hz, 1 H), 2.70−2.07 (m, 4 H), 2.00 (s, 3 H); charateristic peaks for ^{13}C NMR (50 MHz, $CDCl_3$) δ 176.5, 169.7, 75.5, 73.9, 72.3, 71.1, 67.7, 65.1, 48.2, 27.7, 24.4, 23.4; IR (neat) (cm^{-1}) 3054, 2987, 1457, 1265; MS (electrospray) *m*/*z* 582 (M + Na); HRMS *m*/*e* calcd for $C_{33}H_{37}NNaO_7$ (M + Na) 582.2468, found 582.2473. α-**28** (minor C7-isomer): ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.06 (d, J = 7.2 Hz, 1 H), 4.78 (d, J = 11.8 Hz, 1 H), 4.65 (d, J = 11.8 Hz, 1 H), 4.60 (m, 1 H), 4.59 (d, J = 12.0 Hz, 1 H), 4.54 (d, J = 12.0 Hz, 1 H), 4.54 (d, J = 12.0 Hz, 1 H), 4.48 (d, J = 12.0 Hz, 1 H), 4.40 (m, 1 H1), 4.33 (ddd, J = 9.4, 6.1, 3.1 Hz, 1 H), 4.14 (dd, J = 11.4, 9.4 Hz, 1 H), 4.02 (dd, J = 3.1, 3.1 Hz, 1 H), 4.01 (dd, J = 2.5 Hz, 1 H), 3.81 (dd, J = 6.1, 3.1 Hz, 1 H), 3.72 (dd, J = 11.4, 3.1 Hz, 1 H), 2.70−2.07 (m, 4 H), 1.97 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.3, 170.6, 80.0, 74.9, 74.7, 73.2, 73.1, 72.5, 71.6, 68.1, 65.8, 51.2, 27.8, 25.4, 23.6. Characteristic signals for the *β*-isomer were seen at δ 4.93 (d, J = 11.6 Hz, 1 H), 1.92 (s, 3 H).

α-*C*-Mannoside (30). The *C*-mannosides was prepared from pyridyl sulfone **29** according to the general procedure outlined for α-**9**, affording the title compound as a colorless syrup and as a 3:1 mixture of diastereomers (24 mg, 65%) after flash chromatography (cyclohexane/EtOAc 7:1−1:1). Major isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40−7.24 (m, 15 H), 4.82 (ddd, J = 7.3, 5.5, 1.5 Hz, 1 H), 4.66 (d, J = 11.7 Hz, 1 H), 4.51 (d, J = 12.2 Hz, 1 H), 4.51 (d, J = 11.7 Hz, 1 H), 4.51 (d, J = 11.3 Hz, 1 H), 4.43 (d, J = 12.2 Hz, 1 H), 4.43 (d, J = 11.3 Hz, 1 H), 4.27 (dd, J = 9.4, 3.1 Hz, 1 H), 4.10 (ddd, J = 7.3, 5.4, 3.1 Hz, 1 H), 3.77 (dd, J = 10.2, 7.3 Hz, 1 H), 3.76 (dd, J = 9.4, 1.5 Hz, 1 H), 3.74 (dd, J = 3.1, 3.1 Hz, 1 H), 3.62 (dd, J = 3.1, 3.1 Hz, 1 H), 3.56 (dd, J = 10.2, 5.4 Hz, 1 H), 2.82−2.67 (m, 4 H), 0.94 (s, 9 H), 0.18 (s, 3 H), 0.12 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.1, 138.3, 138.1, 128.5, 127.8, 127.7, 78.2, 77.8, 75.2, 74.5, 73.5, 73.0, 71.7, 68.5, 67.1, 28.5, 26.0, 23.8, 18.1, −4.0, −4.9; IR (neat) (cm^{-1}) 2928, 2857, 1779, 1497, 1253; IR (neat) (cm^{-1}) 3032, 2927, 2857, 1778, 1454, 1362; MS (electrospray) *m*/*z* 655 (M + Na); HRMS *m*/*e* calcd for $C_{37}H_{48}NaO_6Si$ (M + Na) 655.3067, found 655.3074. Minor isomer: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38−7.23 (m, 15 H), 4.79 (ddd, J = 8.3, 4.5, 3.7 Hz, 1 H), 4.67 (d, J = 11.5 Hz, 1 H), 4.61 (d, J = 11.9 Hz, 1 H), 4.55 (d, J = 11.9 Hz, 1 H), 4.52 (d, J = 11.3 Hz, 1 H), 4.51 (d, J = 11.5 Hz, 1 H), 4.47 (d, J = 11.3 Hz, 1 H), 4.08 (dd, J = 7.6, 2.5 Hz, 1 H), 4.04 (dd, J = 7.6, 3.7 Hz, 1 H), 3.94 (ddd, J = 6.5, 5.5, 3.9 Hz, 1 H), 3.82 (dd, J = 5.6, 3.9 Hz, 1 H), 3.76 (dd, J = 10.2, 6.5 Hz, 1 H), 3.73 (dd, J = 5.6, 2.5 Hz, 1 H), 3.70 (dd, J = 10.2, 5.5 Hz, 1 H), 2.75−2.17 (m, 4 H), 0.93 (s, 9 H), 0.18 (s, 3 H), 0.07 (s, 6 H).

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Supporting Information Available: NMR peak assignments (**9**-**16**, **21**, **28** and **30**) and X-ray crystallographic data of α-**14** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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