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S-Thiazolinyl (STaz) Glycosides as Versatile Building Blocks for Convergent Selective, Chemoselective, and Orthogonal Oligosaccharide Synthesis

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Abstract: In the aim of developing new procedures for efficient oligosaccharide assembly, a range of *S*-thiazolinyl (STaz) glycosides have been synthesized. These novel derivatives were evaluated against a variety of reaction conditions and were shown to be capable of being chemoselectively activated in the armed–disarmed fashion. Moreover, the *S*-thiazolinyl moiety exhibited a remarkable propensity for selective activation over other common leaving groups. Conversely, a variety of leaving groups could be selectively activated over the *S*Taz moiety, which, in turn, allowed STaz/*S*-ethyl and STaz/*S*-phenyl orthogonal approaches. To demonstrate versatility of novel STaz derivatives, a number of oligosaccharide targets have been synthesized in a convergent selective, orthogonal, and chemoselective fashion.

Keywords: carbohydrates · glycosyl donors · glycosylation · synthetic methods · thioimidates

Introduction

Carbohydrates are the most abundant biomolecules on earth. Although information about these fascinating natural compounds is not yet complete, the explosive growth of the field of glycobiology in recent years has significantly improved our understanding of carbohydrate involvement in a broad range of damaging processes in our cells including bacterial and viral infections, development and growth of tumors, metastasis, tissue rejection, septic shock, and so forth.[1,2] Many of these processes are directly associated with various deadly diseases of the 21st century: AIDS, cancer, meningitis, hepatitis, septicemia, to name but a few. Elucidation of the exact mechanisms of carbohydrate involvement in disease progression would be further improved if we could rely on the comprehensive knowledge of the structure, conformation, and properties of the carbohydrate molecules. Therefore, the development of stereoselective methods and efficient strategies for the synthesis of complex carbohydrates is critical for the field of glycosciences.

As a result of extensive investigations in carbohydrate chemistry, a number of glycosyl donors have been developed.[3,4] However, in spite of their ubiquity and synthetic usefulness, even the most commonly used halides,[5,6] *O*-trichloroacetimidates,[7] and alkyl/aryl thioglycosides[8,9] have significant drawbacks. For example, thioglycosides are inert under other glycosyl donor activation conditions and are therefore useful for orthogonal and (chemo)selective strategies for complex oligosaccharide assembly.[10–12] Unfortunately, in many cases, only average 1,2-*cis* stereoselectivity was achieved with these stable compounds. Conversely, rather unstable glycosyl donors such as *O*-trichloroacetimidates or halides (especially iodides)[13,14] often allow 1,2-*cis* glycosides stereoselectively (or even stereospecifically); however, these leaving groups have to be introduced directly prior to glycosylation as they do not tolerate other leaving-group activation conditions. This significantly limits their applicability to oligosaccharide synthesis by means of a convergent selective fashion with no additional protecting/leaving-group manipulations between the glycosylation steps. Hence, the development of highly reactive, yet stable and stereoselective glycosyl donors will significantly facilitate the oligosaccharide synthesis and help to fill the gap between methods currently used for simple glycosylation and convergent multistep saccharide assembly.

Our research program for development novel, highly reactive, but stable and stereoselective glycosyl donors, has already resulted in the discovery of novel classes of substituted glycosyl thioimidates ($SCR^1{=}NR^2$). A fairly low stability of the previously studied thioimidates was the major reason that the use of benzothiazolyl,[15] pyridin-2-yl,[16–18] pyrimidin-2-yl,[16,19] imidazolin-2-yl,[16] and 1′-phenyl-1H-tetrazolyl[20] glycosides in oligosaccharide synthesis was limited. Our

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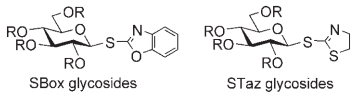
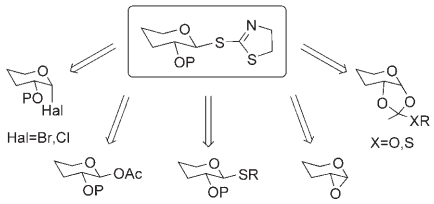
preliminary evaluation of *S*-benzoxazolyl (SBox),[21] *S*-thiazolinyl (STaz) glycosides,[22] and a variety of other derivatives of this class[23] has demonstrated their remarkable potential as versatile building blocks. Thus, high stability and excellent stereoselectivity make the glycosyl thioimidates suitable for both single-step glycosylations and for use as building blocks in sophisticated oligosaccharide syntheses. Herein, we describe our thorough evaluation of the STaz glycosides as versatile building blocks for oligosaccharide synthesis.



Results and Discussion

Synthesis of the STaz glycosyl donors: Since mercaptans share the same chemistry with alcohols, we reasoned that various synthetic precursors; such as anomeric halides, acetates, 1,2-anhydrosugars, 1,2-orthoesters, or *S*-ethyl glycosides, commonly used in *O*-glycosylations, could be also applied to the synthesis of STaz glycosides. 2-Mercaptothiazoline (HSTaz), the aglycone source, is an odorless solid, readily available from a variety of commercial sources. As a matter of fact, HSTaz is even cheaper than thiophenol, the aglycone source used in the syntheses of *S*-phenyl glycosides, which are amongst the most common glycosyl donors developed to date.



While the STaz glycosides can be directly obtained from halides in the presence of a base, we found that this conversion worked more efficiently if HSTaz was initially converted into a sodium or potassium salt (NaSTaz or KSTaz, respectively). Overall, synthesis of the STaz glycosides from alkyl halides of the D-gluco series was limited by side reactions that occurred, presumably, as a result of relatively high basicity of HSTaz ($pK_a = 13.01$) or its conjugate base ($^-$STaz) and its ambient reactivity (nitrogen vs. sulfur atom). Thus, along with the desired S-linked derivatives, significant amounts of byproducts, such as N-linked "NTaz" glycosides and/or 1,2-dehydro derivatives, were also detected in some experiments, as summarized in Table 1. For example, bromides **1** or **3**[24] afforded the corresponding STaz glycosides **2** or **4** in average yields of 41–60% (entries 1–2, Table 1). Conversely, the reactions of bromides of the D-galacto (**5**) or D-manno series (**7**)[24] were significantly more efficient. The corresponding STaz glycosides **6** and **8** were obtained in 90 and 70% yield, respectively, with no significant byproduct formation interference (entries 4 and 5, Table 1).

The exact nature of this phenomenon is not yet certain; yet, it can be directly attributed to the structural difference of the sugars involved. For example, the top face of the pyranose ring of D-galacto derivatives is significantly more sterically hindered by the axially oriented substituent at C-4. This should minimize the opportunity of the base to approach C-2 from the top face of the ring and abstract H-2 to give the elimination product. Glycosyl chlorides **11**,[25] **13**,[26] and **15**[27] were also found suitable precursors for the synthesis of the STaz glycosides (see entries 7–9, Table 1); although highly reactive **13** also afforded significant amounts of the N-linked side product **33** (entry 8).

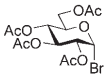
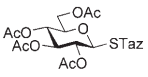
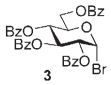
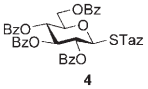
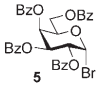
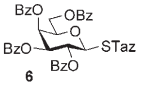
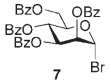
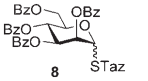
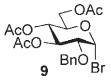
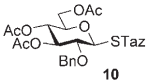
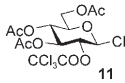
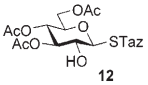
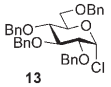
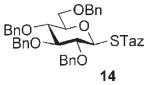
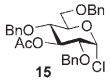
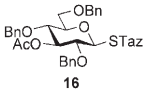
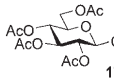
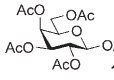
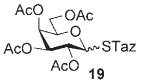
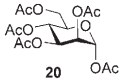
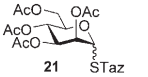
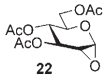
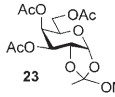
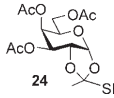
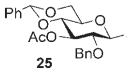
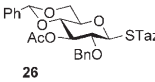
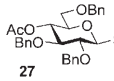
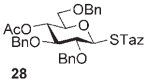
Direct synthesis of the STaz glycosides from pentaactetates **17**, **18**, or **20** with HSTaz in the presence of $BF_3{\cdot}Et_2O$ was much cleaner overall in comparison to the synthesis from alkyl halides affording the corresponding STaz glycosides **2**, **19**, or **21** in 91, 85, or 70%, respectively (entries 10–12, Table 1). Interestingly, the opposite was observed with the SBox glycosides. These compounds are best synthesized from halides using 2-mercaptobenzoxazole salts, while the direct synthesis from acetates typically was less efficient.[21,28]

The bicyclic derivatives, 1,2-anhydro derivative **22**,[29] or 1,2-orthoesters **23**[30] and **24**[31] were also rather efficient precursors. Their Lewis acid catalyzed transformations gave the corresponding STaz glycosides in good yields in the range of 80% (see entries 13–15, Table 1). We also determined that the STaz derivatives could be efficiently obtained from ethyl thioglycosides by means of a two-step conversion procedure involving the treatment with bromine followed by coupling with NaSTaz. See, for example, the synthesis of **26** and **28** from thioglycosides **25** and **27**,[32] respectively (entries 16 and 17, Table 1).

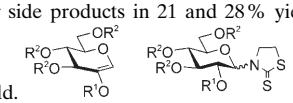
It should be noted that very high or, in most cases, complete 1,2-*trans* stereoselectivity was achieved in the synthesis of the STaz glycosides under all reaction conditions described.

Stability of the STaz glycoside toward various reaction conditions associated with major protecting-group manipulations—synthesis of the STaz glycosyl acceptors: A very attractive feature of the STaz glycosides is their high stability toward many protecting group manipulations. As shown in Scheme 1, the STaz moiety was stable under standard conditions for acylation, deacylation, alkylation, acetal formation, and cleavage through reductive or acid-catalyzed hydrolysis pathways. To summarize our findings, we demonstrated that the STaz moiety is stable toward strong bases (MeONa, NaH, NaOH) and moderately stable in the presence of dilute strong organic acids (triflic acid (TfOH), trifluoroace-

Table 1. Synthesis of *S*-thiazolinyl derivatives.

Entry	Starting material	Conditions	Product	Yield [%]	α/β ratio
1	 **1**	NaSTaz, MeCN, RT	 **2**	53[a]	β only
2	 **3**	KSTaz, 18C6, MeCN, RT	 **4**	41[b]	β only
3		NaSTaz, 15C5, acetone, RT		60[b]	β only
4	 **5**	KSTaz, 18C6, MeCN, RT	 **6**	90	β only
5	 **7**	KSTaz, 18C6, MeCN, RT	 **8**	70	13:1
6	 **9**	NaSTaz, 15C5, MeCN, RT	 **10**	46[c]	β only
7	 **11**	KSTaz, acetone, RT	 **12**	71	β only
8	 **13**	NaSTaz, 15C5, acetone, RT	 **14**	55[d]	β only
9	 **15**	KSTaz, 18C6, MeCN, RT	 **16**	89	β only
10	 **17**	HSTaz, $BF_3{\cdot}Et_2O$, MS 3 A, CH_2Cl_2, 45 °C	**2**	91	β only
11	 **18**	HSTaz, $BF_3{\cdot}Et_2O$, MS 3 A, CH_2Cl_2, 45 °C	 **19**	85	1:11
12	 **20**	HSTaz, $BF_3{\cdot}Et_2O$, MS 3 A, CH_2Cl_2, 45 °C	 **21**	70	22:1
13	 **22**	HSTaz, $ZnCl_2$, CH_2Cl_2, RT	**12**	78	β only
14	 **23**	HSTaz, TMSOTf, MS 4 A, CH_2Cl_2, RT	**19**	77	β only
15	 **24**	HSTaz, TMSOTf, MS 4 A, CH_2Cl_2, RT	**19**	82	β only
16	 **25**	a) Br_2, CH_2Cl_2, RT; b) NaSTaz, MeCN, RT	 **26**	53	β only
17	 **27**	a) Br_2, CH_2Cl_2, RT; b) NaSTaz, MeCN, RT	 **28**	40	β only

[a] Tetraacetyl glycal **29** and NTaz **32** were isolated as major side products in 13 and 11 % yield, respectively. [b] Tetrabenzoyl glycal **30** was isolated as major side product in 39 % (entry 2) or 20 % yield (entry 3). [c] 2,3-Dehydro derivative **31** and NTaz **34** were isolated as major side products in 21 and 28 % yield, respectively; [d] NTaz **33** was isolated as a major side product in 38 % yield.



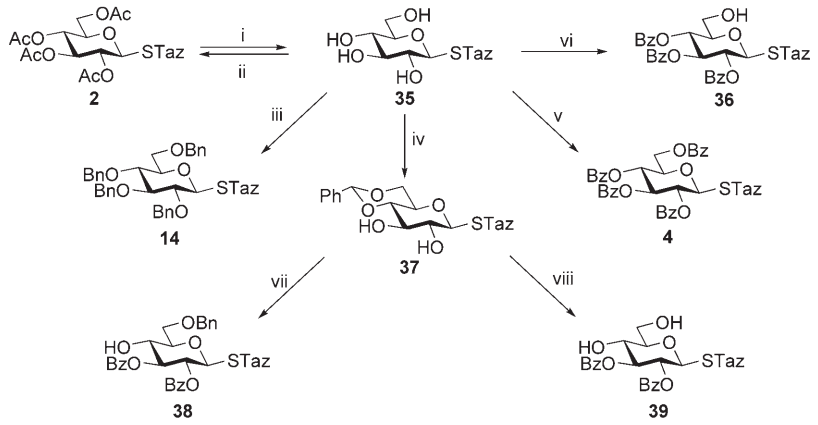
29: $R^1=R^2=Ac$
30: $R^1=R^2=Bz$
31: $R^1=Bn$, $R^2=Ac$

32: $R^1=R^2=Ac$
33: $R^1=R^2=Bz$
34: $R^1=Bn$, $R^2=Ac$

tic acid (TFA)). Due to the marginal stability under acidic conditions, benzylidene acetal formation was found to be more efficient when performed with benzaldehyde in the presence of $ZnCl_2$ (synthesis of **37**, Scheme 1), as opposed to the more conventional protic acid-catalyzed *trans*-acetalation reaction with α,α-dimethoxytoluene (DMT).[33] Overall, these studies allowed us to perform efficient synthesis of a variety of partially substituted STaz glycosides (**36**, **38**, and **39**), and evaluate their suitability as glycosyl acceptors in (chemo)selective couplings for oligosaccharide syntheses.

In this context, as evident from entry 8 (Table 1), the synthesis of the per-benzylated STaz glycoside **14** was achieved in a disappointing yield of 55 %. To address this concern, we developed a more efficient synthesis of **14** from its per-acetylated counterpart **2**, readily available from glucose pentaacetate (see entry 10, Table 1). This transformation was achieved by means of a conventional deacetylation–benzylation sequence in a high yield exceeding 80 % overall (Scheme 1).

Hydrolytic stability of the STaz glycosides in comparison to their *S*-ethyl and *S*-phenyl counterparts: Herein, the hydrolytic stability of perbenzylated STaz glycoside **14** toward hydrolysis was compared to ethyl per-*O*-benzyl-1-thio-β-D-glycopyranoside (**40**, Table 2)[34] and its 1-*S*-phenyl counterpart (**41**).[35] The competitive hydrolytic stability studies have been carried out under a range of reaction conditions involving soft thiophilic reagents (*N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS)/TfOH),[36,37] relatively hard acidic reagents (TFA or



Scheme 1. Conditions: i) NaOMe, MeOH, RT, 98%; ii) Ac_2O, pyridine, RT, 95%; iii) BnBr, NaOH, DMF, 83%; iv) PhCHO, $ZnCl_2$, 0°C, 88%; v) BzCl, pyridine, 0°C → RT, 89%; vi) a) TrCl, pyridine, RT, b) BzCl, pyridine, 0°C → RT, c) 3% TFA in wet CH_2Cl_2, RT, 58%; vii) a) BzCl, pyridine, 0°C → RT; b) $NaCNBH_3$, HCl, MS 3 A, THF, 0°C, 65%; viii) a) BzCl, pyridine, 0°C → RT, b) 15% TFA in wet CH_2Cl_2, RT, 95%.

TfOH), or oxidative acidic hydrolysis (70% aq. TfOH and Bu_4NIO_4).[38] The formation of the hemiacetal **42**[39] was monitored and quantitatively estimated by TLC.

In our opinion, a very important correlation was obtained as a result of these experiments (summarized in Table 2). On the one hand, we established reaction conditions (NIS/TfOH) under which the STaz moiety is significantly more stable than either *S*-ethyl or *S*-phenyl glycosides (entries 1–3, Table 2). Similarly, STaz can be reliably differentiated from SPh in the presence of 70% aq. TfOH and $BuNIO_4$ (entries 4 and 6, Table 2). Conversely, we found reaction conditions (TFA of TfOH) under which the STaz moiety hydrolyses completely, whereas the SEt or SPh derivatives remain entirely stable (entries 10–15, Table 2). These findings offer the possibility of selective activation of STaz versus *S*-alkyl/aryl glycosides, possibly in the orthogonal fashion.

STaz glycosides as glycosyl donors for the synthesis of 1,2-*trans*-glycosides: Having established the relative stability of the STaz glycosides, we turned our attention to the investigation of their properties as glycosyl donors. Hence, peracylated STaz glycosides were investigated as precursors for the formation of 1,2-*trans* glycosidic linkages. We discovered that the STaz glycosides could be activated by a range of promoters, including AgOTf, $Cu(OTf)_2$, or MeOTf, the latter being a common activator for the glycosylation of thioglycosides. It should be highlighted that virtually no reaction took place in the presence of NIS/catalytic TfOH, whereas the reaction was smoothly driven to completion by NIS in the presence of a stoichiometric amount of TfOH. Although other thioglycoside promoters dimethyl(methylthio)sulfonium triflate (DMTST), NBS, NIS/trimethylsilyl triflate (TMSOTf), and NIS/$TrClO_4$ (Tr = trityl) were also able to activate the STaz moiety for glycosidation, somewhat lower yields have been obtained in comparison to those presented in Table 3.

It should be noted that while the glycosidation of peracetylated STaz glycoside **2** was found to be fast and efficient, the results obtained were not very reliable. As a matter of fact, in some cases the yields of the coupling products were significantly compromised by undesired *O*-acetyl migration. This major side reaction, resulting in the acetylation of a free hydroxyl of the glycosyl acceptor, was detected across a spectrum of reaction conditions. Most frequently, the competing acetyl migration process reduced the yields of disaccharides to a dismal 40–60%.

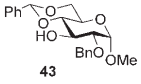
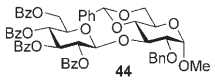
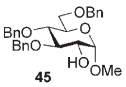
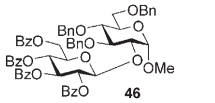
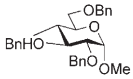
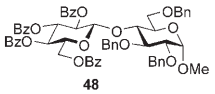
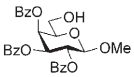
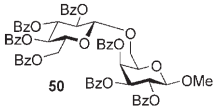
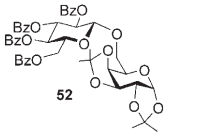
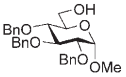
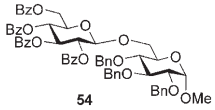
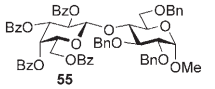
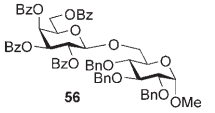
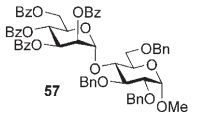
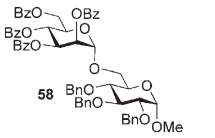
Table 2. Relative stability of STaz **14** versus SEt and SPh glycosides **40** and **41** under a variety of acidic hydrolytic conditions.

Entry	Conditions[a]	Starting Material	[%] of hemiacetal **42**[b] formed after 1 h	after 16 h
1	A	**14**	0	60
2	A	**40**	quant.	–
3	A	**41**	quant.	–
4	B	**14**	0	quant.
5	B	**40**	5	90
6	B	**41**	quant.	–
7	C	**14**	60	quant.
8	C	**40**	60	90
9	C	**41**	90	quant.
10	D	**14**	25	quant.
11	D	**40**	0	0
12	D	**41**	0	0
13	E	**14**	20	quant.
14	E	**40**	0	0
15	E	**41**	0	0

[a] Conditions: A) NIS/TfOH, CH_2Cl_2/water, 95:5, v/v; B) 70% aq. TfOH, Bu_4NIO_4, −10°C; C) NBS, acetone/water, 9:1, v/v; D) TFA (1 equiv); E) TfOH (2 equiv). [b] The conversions have been estimated based on TLC.

In contrast, perbenzoylated glycosyl donors of the D-gluco, D-galacto-, and D-manno series (**4**, **6**, and **8**, respectively) have proven to be very efficient glycosyl donors for the synthesis of 1,2-*trans*-linked disaccharides. Reactions with differently protected glycosyl acceptors **43**,[40] **45**,[41] **47**,[42] **49**,[43] **51**, and **53**[44] of the D-gluco and D-galacto series gave the corresponding disaccharides in high yield and complete stereoselectivity in all cases (Table 3). The complete 1,2-*trans* stereoselectivity obtained herein is attributed to the assistance of a participating substituent at the C-2 position. While AgOTf, NIS/TfOH, or MeOTf performed nearly

Table 3. Synthesis of 1,2-*trans*-linked disaccharides.

Entry	Donor	Acceptor	Promoter	Time	Product	Yield [%]
1	**4**	 **43**	AgOTf	16 h	 **44**	91
2	**4**	 **45**	MeOTf	20 h	 **46**	99
3	**4**	 **47**	NIS/TfOH	16 h	 **48**	93
4	**4**	 **49**	AgOTf	2 h	 **50**	90
5	**4**	 **51**	MeOTf	1 h	 **52**	82
6	**4**	 **53**	$Cu(OTf)_2$	4 days	 **54**	99
7	**6**	**47**	AgOTf	40 min	 **55**	92
8	**6**	**53**	AgOTf	30 min	 **56**	84
9	**8**	**47**	AgOTf	6 days	 **57**	85
10	**8**	**53**	AgOTf	6 days	 **58**	87

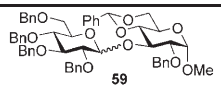
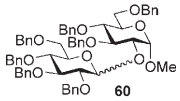
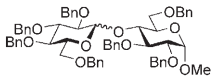
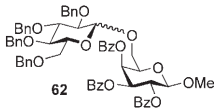
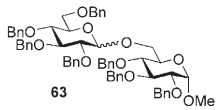
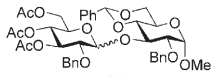
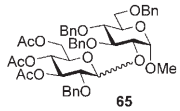
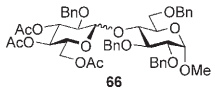
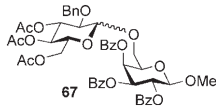
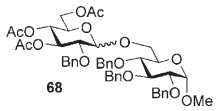
equally well as promoters, only the best results were presented in Table 3. In this context, although $Cu(OTf)_2$-promoted reactions were very high yielding, they were significantly slower than those performed in the presence of more potent promoters. For a relevant example, see entry 6 (Table 3), in which the glycosylation of a highly reactive primary hydroxyl of the acceptor **53** required enduring four days to complete.

STaz glycosides as glycosyl donors for the synthesis of 1,2-*cis*-glycosides: Stereoselective synthesis of 1,2-*cis*-glycosides from STaz glycosyl donors was also investigated. In this case, glycosyl donors bearing a nonparticipating substituent at C-2, that is, 2-*O*-benzylated or perbenzylated STaz glycosides **10** or **14**, respectively, were investigated. Glycosylation of different acceptors in the presence of AgOTf provided high yields, but the stereoselectivity was average, commonly in the range of α/β 3–5:1 in 1,2-dichloroethane (DCE, Table 4). As a result of varying solvent, promoter, or protecting groups,[45] the stereoselectivity could be significantly improved (up to α/β 19:1). Application of partially acetylated glycosyl donors[46] or a toluene/dioxane participating solvent mixture (1:3, v/v)[47] were found to be especially beneficial for 1,2-*cis* glycosylation. It should be noted that in spite a number of significant improvements that have emerged during past decade,[21,47–53] stereocontrolled synthesis of 1,2-*cis*-glycosides remains a significant challenge.[45,54] Arguably, the stereoselectivity achieved could not match the best procedures for 1,2-*cis* glycosylation developed to date,[45] yet it was notable higher compared to that achieved with *S*-alkyl/aryl glycosides (α/β 1–1.5.1).

STaz glycosides in oligosaccharide synthesis—selective activation of the STaz moiety over other potential leaving groups (STaz glycosides as glycosyl donors): An important feature of any glycosyl donor under development would be to provide coupling products in stereoselective and high-yielding fashion. Further importance of new building blocks is commonly related to their applicability to multistep oligosaccharide synthesis.[12] It should be noted that although significant improvements of the oligosaccharide synthesis have already emerged with the introduction of programmable[55–58] and automated syntheses,[59] these approaches are still applicable to a fairly narrow range of synthetic targets.

Having completed preliminary stereoselectivity studies (see Tables 3 and 4), we decided to investigate whether the STaz derivatives could be coupled with glycosyl acceptors containing relatively latent anomeric leaving groups. The key feature of such activation would be availability of a promoter that would be capable of activating the STaz moiety selectively over the anomeric moieties at the glycosyl acceptor unit such as *S*-ethyl, *S*-phenyl, or *O*-pentenyl. Our initial assumption was that the selective activation of the STaz moiety over these other potential leaving groups could be accomplished by using AgOTf as a promoter. In addition,

Table 4. AgOTf-promoted synthesis of 1,2-*cis*-linked disaccharides.

Entry	Donor	Acceptor	Solvent	Product	Yield [%]	α/β ratio
1	**14**	**43**	T/D[a]	 **59**	85	7.7:1
2	**14**	**45**	T/D	 **60**	97	4.5:1
3	**14**	**47**	T/D	 **61**	95	3.5:1
4	**14**	**49**	T/D	 **62**	82	4.1:1
5	**14**	**53**	T/D	 **63**	85	2.7:1
6	**10**	**43**	DCE[b]	 **64**	78	15:1
7	**10**	**45**	DCE	 **65**	88	9.3:1
8	**10**	**47**	DCE	 **66**	89	>19:1
9	**10**	**49**	DCE	 **67**	74	4.8:1
10	**10**	**53**	DCE	 **68**	70	2.7:1

[a] Toluene/dioxane (1:3, v/v). [b] 1,2-Dichloroethane.

we assumed that the activation of the STaz moiety over the *O*-pentenyl moiety would be possible in the presence of MeOTf.[60] To perform these studies we chose a number of suitable glycosyl acceptors, *S*-ethyl glycosides **69**,[44] **72**,[61] **75**,[62] and **77**;[63] *S*-phenyl glycosides **79**[64] and **81**;[65] and *O*-pentenyl glycosides **83**[66] and **85**[67] (Table 5).

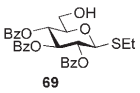
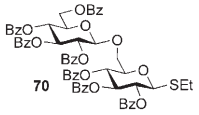
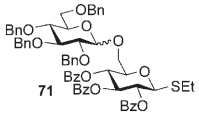
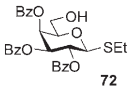
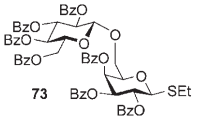
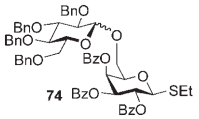
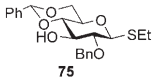
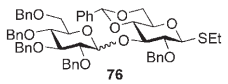
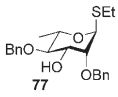
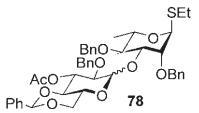
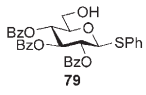
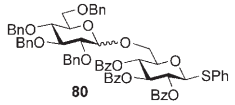
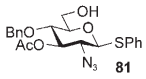
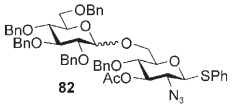
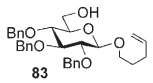
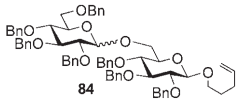
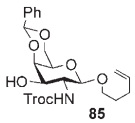
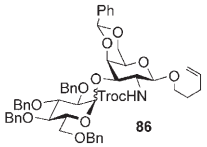
All glycosylations summarized in Table 5 afforded the intended disaccharide products in good yields. Very importantly, no side products of the acceptor self-condensation were detected. The advantage of the oligosaccharide synthesis through selective activation is that all formed disaccharides **70**, **71**, **73**, **74**, **76**, **78**, **80**, **82**, **84**, and **86** could be subsequently activated for the second-step glycosidation. Apparently, the second-step activation should be feasible in the presence of NIS/TfOH or other activators suitable for the activation of *S*-alkyl/aryl or *O*-pentenyl moieties.[8,9,68] To explore this opportunity we performed the coupling of the *S*-ethyl or *S*-phenyl disaccharide donors **76** or **80** with glycosyl acceptor **53** in the presence of NIS/TfOH to afford the corresponding trisaccharide derivatives **87** or **88** in 89 or 75% yield, respectively (Scheme 2). These examples clearly illustrated our emergent ability to obtain trisaccharide units by means of sequential STaz-SEt or STaz-SPh activation in a convergent selective fashion with no additional protecting/leaving group manipulations between the glycosylation steps.

STaz glycosides in oligosaccharide synthesis—selective activation of other leaving groups over the STaz moiety (STaz glycosides as glycosyl acceptors): The next step of the method development was to see whether the STaz moiety would be able to act as a temporary anomeric protection for the glycosyl acceptor. A principal motivation for these investigations derives from the fact that prior to our studies, thioimidates had been considered too labile to be selectively glycosylated with other classes of glycosyl donors.[69] To perform these studies we synthesized a number of partially protected glycosyl acceptors bearing the STaz moiety at the anomeric position. STaz glycoside **36** bearing the primary hydroxyl group was obtained from **35** as shown in Scheme 1. Secondary glycosyl acceptors **89** and **91** were obtained by simple deacetylation (MeONa/MeOH) of the STaz glycosides **26** and **16**, respectively. Representative examples of common classes of glycosyl donors[3,4] have been employed, for instance, *S*-ethyl glycoside **40**, *S*-phenyl glycoside **41**, bromides **3** and **97**,[70] and trichloroacetimidate **99**.[71] We also experimented with the *S*-benzoxazolyl derivatives **94** and **96**, developed in our laboratory.[21,46]

Although the yields and stereoselectivities of the glycosylations summarized in Table 6 were largely dependent on the nature of the glycosyl donors and activation conditions used, no self-condensation of the STaz glycosyl acceptors **36**, **89**, or **91** was detected. As a result of these studies, we established that the STaz glycosides withstand reaction conditions associated with the activation of the SEt or SPh (NIS/cat. TfOH), bromo ($HgO/HgBr_2$), trichloroacetamido (BF_3-OEt_2), and SBox moieties [$Cu(OTf)_2$].

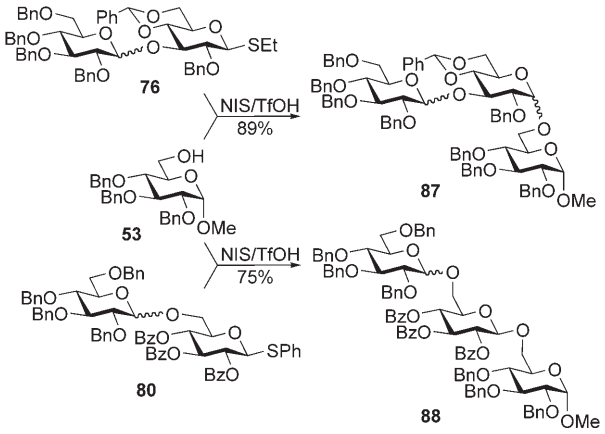
Apparently, all of the formed disaccharides **90**, **92**, **93**, **95**, and **98** can be directly activated for subsequent glycosidations as they all bear the STaz anomeric moiety. This can be achieved in the presence of AgOTf or other suitable activators (see Table 3). To confirm this opportunity we performed the coupling of the STaz disaccharide donors **90** or **93** with glycosyl acceptor **53** in the presence of AgOTf to afford the corresponding trisaccharide derivatives **87** or **88** in 81 and 80% yield, respectively (Scheme 3). Since disaccharides **90** and **93** could be obtained by selective activation of either SEt or SPh over the STaz moiety, these syntheses clearly illustrate our ability to obtain trisaccharide units through sequential SEt-STaz or SPh-STaz activation in a convergent selective fashion with no additional protecting/leaving group manipulations between the glycosylation steps.

Table 5. Selective activation of the STaz moiety in **4** or **14** over other leaving groups in AgOTf-promoted glycosylations.

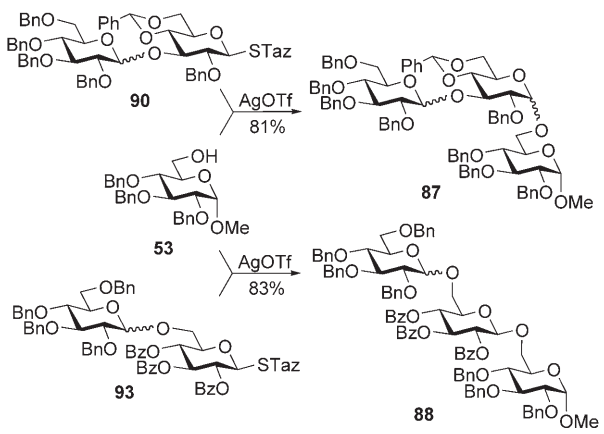
Entry	Donor	Acceptor	Product	Yield [%]	α/β ratio
1	**4**	 **69**	 **70**	81	β only
2	**14**	**69**	 **71**	90	2:1
3	**4**	 **72**	 **73**	85	β only
4	**14**	**72**	 **74**	86	1.8:1
5	**14**	 **75**	 **76**	93	5:1
6	**26**	 **77**	 **78**	71	α only
7	**14**	 **79**	 **80**	99	2:1
8	**14**	 **81**	 **82**	83	1.5:1
9	**14**	 **83**	 **84**	91	2:1
10	**14**	 **85**	 **86**	85	2:1

STaz glycosides in oligosaccharide synthesis—orthogonality of STaz versus *S*-ethyl/phenyl glycosides: Based on the reaction sequences presented in Schemes 2 and 3, describing the syntheses of **87** and **88** by means of two conceptually different approaches, we conclude that STaz glycosides and *S*-ethyl/phenyl glycosides fit into the concept of orthogonality. Convergent oligosaccharide synthesis in orthogonal fashion is based on a combination of two chemically distinct glycosylation reactions, in which one of the leaving groups is selectively activated, while the other stays intact and vice versa.[72,73] Overall, the orthogonal approach offers one of the most convenient and shortest routes to complex oligosaccharide sequences.

In our case, the STaz moiety can be orthogonally activated with SEt and SPh glycosides in the presence of AgOTf, whereas the SEt or SPh glycosides can be activated with NIS/cat. TfOH over the STaz moiety: compare syntheses of **87** and **88** presented in Schemes 2 and 3. These observations were further extended to the synthesis of a pentasaccharide derivative **102**. As mentioned above, the disaccharide **93** was obtained by selective activation of SEt

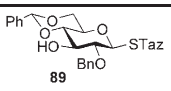
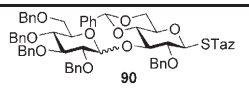
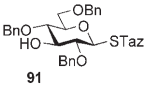
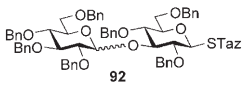
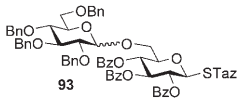
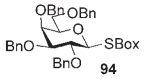
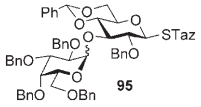
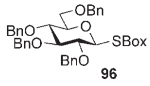
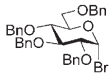
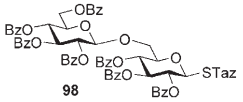
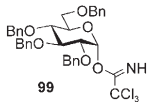


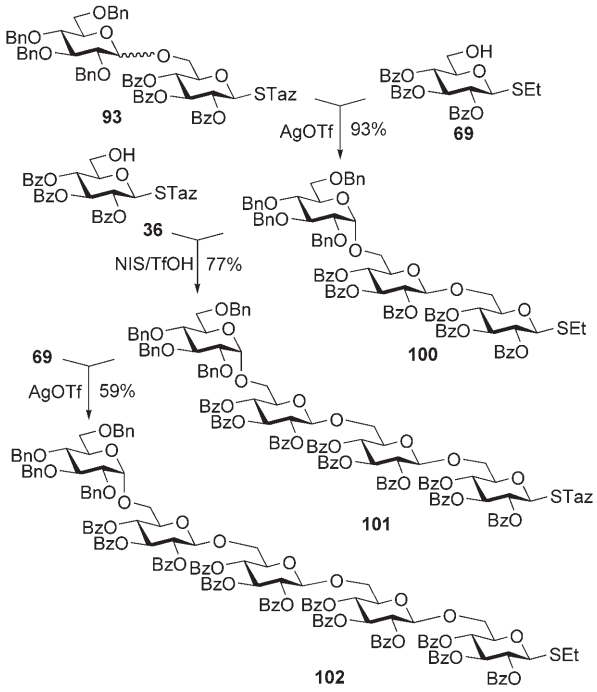
Scheme 2. Synthesis of trisaccharides **87** and **88** by sequential STaz-SEt or STaz-SPh activation.



Scheme 3. Synthesis of trisaccharides **87** and **88** by sequential SEt-STaz or SPh-STaz activation.

Table 6. Selective activation of other leaving groups over the STaz moiety.

Entry	Donor	Acceptor	Promoter	Product	Yield [%]	α/β ratio
1	**40**	 **89**	NIS/TfOH	 **90**	85	1.2:1
2	**40**	 **91**	NIS/TfOH	 **92**	80	2.1:1
3	**40**	**36**	NIS/TfOH	 **93**	98	1.1:1
4	**41**	**89**	NIS/TfOH	**90**	77	2:1
5	**41**	**36**	NIS/TfOH	**93**	75	1.4:1
6	 **94**	**89**	$Cu(OTf)_2$	 **95**	99	7:1
7	 **96**	**36**	$Cu(OTf)_2$	**93**	66	1.4:1
8	 **97**	**36**	$HgO/HgBr_2$	**93**	45	1.2:1
9	**3**	**36**	$HgO/HgBr_2$	 **98**	66	β only
10	 **99**	**36**	$BF_3{\cdot}Et_2O$	**93**	50	1.1:1
11	**99**	**89**	$BF_3{\cdot}Et_2O$	**90**	87	2:1



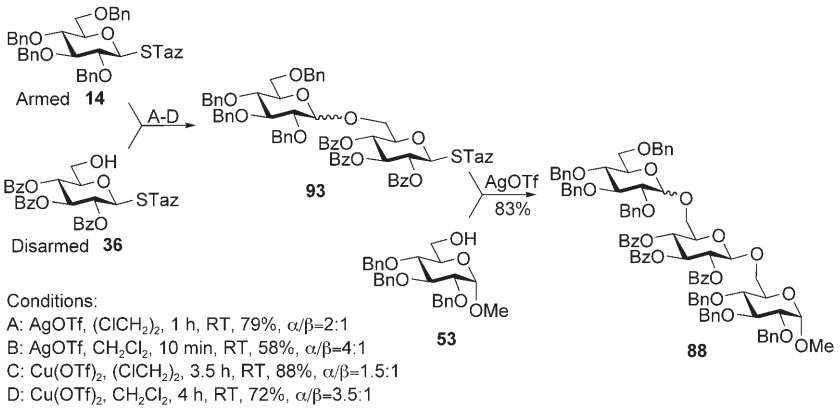
Scheme 4. Synthesis of pentasaccharide **102** by convergent orthogonal pathway.

glycosyl donor **40** over the STaz moiety of the glycosyl acceptor **36** (see entry 3, Table 6) in 98% yield. The STaz disaccharide **93** was then activated in the presence of AgOTf over the SEt moiety of the glycosyl acceptor **69** to afford trisaccharide **100** in 93% yield (Scheme 4).

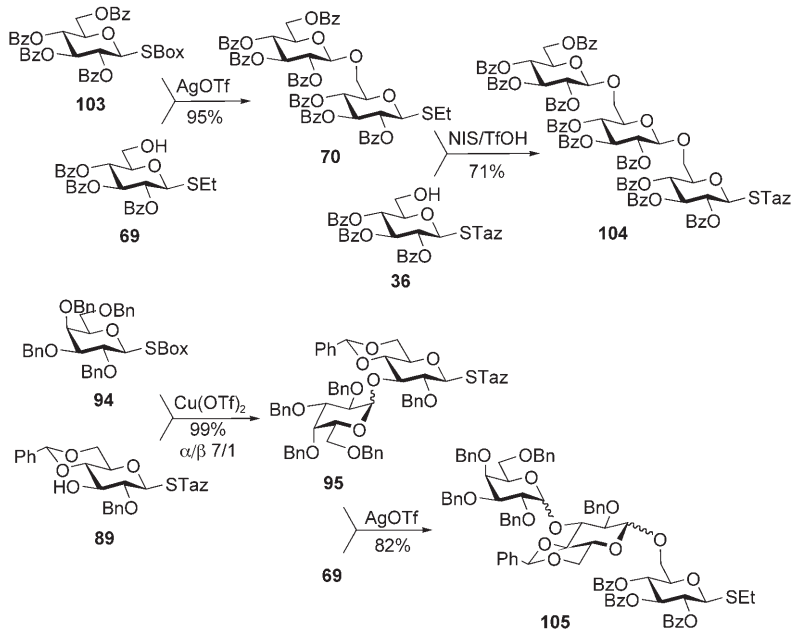
The synthesis of **100** alone serves as direct illustration of orthogonality of these types of anomeric moieties. Nevertheless, we performed an additional activation cycle that included activation of the SEt trisaccharide **100** with the STaz moiety of the glycosyl acceptor **36**, followed by the activation of the STaz tetrasaccharide **101** with the SEt moiety of the glycosyl acceptor **69**. Therefore, the obtained pentasaccharide **102** still bears an anomeric leaving group (SEt), and, in principle, can be used for subsequent chain elongation, if necessary. Although the yields decrease with the increase of the size of the glycosyl acceptor, which is a typical trend in oligosaccharide synthesis, the overall yield of the pentasaccharide **102** was relatively high (41%, Scheme 4).

STaz glycosides in oligosaccharide synthesis—chemoselective activation (armed–disarmed strategy): Another direction in our studies was to determine whether the STaz glycosides can be activated in the chemoselective fashion in accordance with the armed–disarmed approach, developed by Fraser-Reid.[74,75] According to this strategy, a benzylated (armed) glycosyl donor can be chemoselectively activated in the presence of the acylated (disarmed) derivative to afford a disaccharide. The latter can be activated directly in the presence of a more potent promoter. Initially developed for *O*-pentenyl glycosides, this concept was further explored for the chemoselective glycosidations of many other common glycosyl donors.[12]

Herein we report that the STaz glycosides also follow general chemoselectivity principle, according to which armed STaz glycoside donor **14** could be activated over electronically disarmed STaz glycosyl acceptor **36** in the presence of AgOTf or $Cu(OTf)_2$ (Scheme 5). Interestingly, a notably higher stereoselectivity was achieved by using dichloromethane as the reaction solvent, although the yield of the coupling product was higher in 1,2-dichloroethane. The ob-



Scheme 5. Synthesis of the trisaccharide **88** by chemoselective activation of the STaz glycosides.



Scheme 6. STaz glycosides in sequential oligosaccharide syntheses.

tained disaccharide **93** was then coupled with acceptor **53** to afford the trisaccharide **88** in 83% yield.

STaz glycosides in oligosaccharide synthesis—efficient sequential saccharide assembly with the use of three different anomeric moieties: Investigation of various building blocks in selective activations has allowed us to elaborate a number of sequential glycosylation protocols. For example, the synthesis of a trisaccharide **104** was accomplished from building blocks **36**, **69**, and **103**[28] by sequential activation as follows: SBox → SEt → STaz (Scheme 6). Similarly, a trisaccharide **105** was obtained from building blocks **69**, **89**, and **94**; however, in this case, the activation was accomplished by means of a different sequence as follows: SBox→STaz→SEt (Scheme 6). While these syntheses serve as clear examples of the STaz glycoside versatility and flexibility in the context of oligosaccharide synthesis, both trisaccharides **104** and **105** can be employed in subsequent chain elongations directly.

Conclusion

Based on the results presented, we conclude that the STaz glycosides can be successfully prepared and applied as building blocks in glycosylations. These derivatives fulfil major requirements for the versatile glycosyl donor: accessibility, high stability toward protecting group manipulations, and activation under mild conditions. These compounds provided high stereoselectivities in single step glycosylations. It has been determined that the STaz moiety can be selectively activated over conventional thioglycosides and *O*-pentenyl glycosides, while bromides, trichloroacetimidates, and thioglycosides could be activated over the STaz moiety. Based on extensive experimenting, we discovered fully orthogonal character of STaz and *S*-ethyl/phenyl anomeric moieties. The STaz glycosides were found to be suitable building blocks for chemoselective armed–disarmed activations, and in selective sequential activations with the use of three, and possibly more, different leaving groups. Many other synthetic strategies could be developed with these unique glycosyl donors, amongst which are temporary deactivation[76] and inverse armed–disarmed concepts,[77] further evaluation of which is underway in our laboratory. It should be noted that glycosyl thioimidates have recently found application in anomeric phosphorylation.[78,79] The roles and applications of this class of compounds have been recently reviewed.[69,80]

Experimental Section

General: Column chromatography was performed on silica gel 60 (EM Science, 70–230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254} (EM Science). The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at $<40\,^{\circ}C$. CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, and toluene were distilled from CaH_2 directly prior to application. Methanol was dried by refluxing with magnesium methoxide, distilled and stored under argon. Pyridine was dried by refluxing with CaH_2 and then distilled and stored over molecular sieves

(3 Å). 1,4-Dioxane and acetone were dried and stored over molecular sieves (3 Å) and K_2CO_3, respectively. Anhydrous DMF (EM Science) was used as received. Molecular sieves (3 or 4 Å) used for reactions were crushed and activated in vacuo at 390 °C during 8 h in the first instance and then for 2–3 h at 390 °C directly prior to application. AgOTf (Acros) was co-evaporated with toluene (3×10 mL) and dried in vacuo for 2–3 h directly prior to application. $Cu(OTf)_2$ (Sigma-Aldrich) was dried in vacuo during 2–3 h prior to application. Optical rotations were measured with a Jasco P-1020 polarimeter. Unless noted otherwise, ^{1}H NMR spectra were recorded in $CDCl_3$ at 300 MHz (Bruker Avance), ^{13}C NMR spectra and two-dimensional experiments were recorded in $CDCl_3$ at 75 MHz (Bruker Avance) or at 125 MHz (Bruker ARX-500). HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

Synthesis of NaSTaz: A solution NaOMe (10 mmol) in distilled methanol (20 mL) was added dropwise to a stirred solution of 2-mercaptothiazoline (10 mmol) in methanol (30 mL) at RT under argon. The reaction mixture was stirred for 1 h at RT, methanol was then evaporated off and the residue was dried in vacuo.

Synthesis of KSTaz: KOH (pellets, 4.2 mmol) was added to a stirred solution of 2-mercaptothiazoline (4.2 mmol) in dry acetone (7 mL). The reaction mixture was refluxed for 3 h at 60 °C, acetone was then evaporated off and the residue was dried in vacuo.

Preparation of the STaz glycosides

Method A—typical procedure for the preparation from glycosyl halides: Crown ether ([15]crown-5 or [18]crown-6, 0.6 mmol) and salt (NaSTaz or KSTaz, 6.0 mmol) were added to a stirred solution of a glycosyl halide (**1**, **3**, **5**, **7**, **9**, **11**, **13** or **15**, 3.0 mmol) in a dry solvent (acetone or acetonitrile, 24 mL, Table 1) under argon. The reaction mixture was stirred for 1 h at RT. Upon completion, the mixture was diluted with toluene (30 mL) and washed with 1% aq. NaOH (15 mL) and water (3×10 mL), the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford the STaz glycoside (**2**, **4**, **6**, **8**, **10**, **12**, **14** or **16**).

Method B—typical procedure for the preparation from glycosyl acetates: The solution of a glycosyl acetate (**17**, **18** or **20**, 0.128 mmol), 2-mercaptothiazoline (0.256 mmol) and activated molecular sieves 3 Å (100 mg) in CH_2Cl_2 (1.0 mL) was stirred under argon for 30 min at RT. $BF_3{\cdot}Et_2O$ (0.256 mmol) was then added dropwise and the reaction mixture was kept for 45 min at RT. After that, another portion of 2-mercaptothiazoline (0.256 mmol) and $BF_3{\cdot}Et_2O$ (0.256 mmol) were added and the reaction mixture was kept for 1 h at reflux (45 °C). Upon completion, the mixture was diluted with toluene, the solid was filtered-off, and the residue was washed with toluene. The combined filtrate (30 mL) was washed with 1% aq. NaOH (15 mL) and water (3×10 mL), the organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the STaz glycoside (**2**, **19**, or **21**).

*Method C—preparation from Brigl's anhydride **22** and orthoesters **23** or **24***: 2-Mercaptothiazoline (0.347 mmol) and Lewis acid ($ZnCl_2$ or TMSOTf, 0.0087 mmol) were added to a stirred solution of a bicyclic derivative (0.174 mmol) in anhydrous CH_2Cl_2 containing molecular sieves 4 Å (in the case of orthoesters) under argon. The reaction mixture was stirred for 10 min at RT. Upon completion, Et_3N was added dropwise until neutral pH. The mixture was diluted with CH_2Cl_2 (30 mL) and washed with saturated aq. $NaHCO_3$ (2×15 mL) and water (3×10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexanes gradient elution) to afford STaz glycoside **12** or **19**. In some experiments, neutralization with Et_3N followed by washing with saturated aq. $NaHCO_3$, was substituted by washing with 1 M aq. NaOH.

Method D—preparation from thioglycosides: The solution of a thioglycoside (**25** or **27**, 0.128 mmol) and activated molecular sieves 3 Å (70 mg) in CH_2Cl_2 (2 mL) was stirred under argon for 1 h. A freshly prepared solution of Br_2 in CH_2Cl_2 (1.2 mL, 1:165, v/v) was then added and the reaction mixture was kept for 5 min at RT. After that, CH_2Cl_2 was evaporated off under reduced pressure at RT. The crude residue was then treated with NaSTaz (0.51 mmol) in dry acetonitrile (1 mL) under argon for 2 h at RT. Upon completion, the mixture was diluted with toluene, the solid was filtered-off, and the residue was washed with toluene. The combined filtrate (30 mL) was washed with 1% aq. NaOH (15 mL) and water (3x10 mL), the organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford STaz glycosides **26** or **28**.

2-Thiazolinyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (2): This compound was obtained from 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**)[24] by method A (NaSTaz, [15]crown-5, acetone) in 53% yield as white crystals. Compound **2** was also obtained from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**17**) by method B in 91% yield. R_f= 0.28 (ethyl acetate/toluene, 1:1, v/v); m.p. 128 °C (ether/hexanes); $[\alpha]_D^{28}$= +1.8° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=2.02, 2.03, 2.06, 2.09 (4s, 12H; 4 $COCH_3$), 3.33 (t, J=8.1 Hz, 2H; CH_2N), 3.75 (m, $J_{5,6a}$=2.3 Hz, $J_{5,6b}$= 4.5 Hz, 1H; H-5), 4.05–4.25 (m, J_{CH_2S,CH_2N}=8.1 Hz, 4H; H-6a, 6b, CH_2S), 5.08 (dd, $J_{4,5}$=9.5 Hz, 1H; H-4), 5.09 (dd, $J_{2,3}$=8.3 Hz, 1H; H-2), 5.17 (dd, $J_{3,4}$=8.3 Hz, 1H; H-3), 5.38 ppm (d, $J_{1,2}$=10.4 Hz, 1H; H-1); ^{13}C NMR (500 MHz): δ=20.79 (×2), 20.84, 20.97, 35.55, 61.98, 64.41, 68.18, 69.63, 74.08, 76.34, 83.18, 162.78, 169.58 (×2), 170.30, 170.87 ppm; HR-FAB MS: calcd for $C_{17}H_{24}NO_9S_2$ $[M+H]^+$: 450.0892; found: 450.0891.

2-Thiazolinyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (4): This compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**3**)[24] by Method A (NaSTaz, [15]crown-5, acetone) in 60% yield as white crystals. R_f=0.24 (ethyl acetate/hexanes, 3:7, v/v); m.p. +108 °C (ether/hexanes); $[\alpha]_D^{26}$= +64.3° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=3.20–3.35 (m, 2H; CH_2N), 4.12 (t, J_{CH_2S,CH_2N}=8.2 Hz, 2H; CH_2S), 4.30 (m, $J_{5,6a}$=2.6 Hz, $J_{5,6b}$=5.5 Hz, 1H; H-5), 4.50 (dd, $J_{5,6b}$=5.5 Hz, 1H; H-6b), 4.64 (dd, $J_{5,6a}$=2.9 Hz, $J_{6a,6b}$= 12.3 Hz, 1H; H-6a), 5.60–5.75 (m, 2H; H-2, 4) ,5.82 (d, $J_{1,2}$=10.3 Hz, 1H; H-1), 5.99 (dd, $J_{3,4}$=9.4 Hz, 1H; H-3), 7.20–8.10 ppm (m, 20H; aromatic); ^{13}C NMR: δ=29.90, 35.42, 63.30, 64.25, 69.54, 70.45, 74.24, 83.47, 128.49 (×2), 128.52 (×2), 128.58, 128.64 (×2), 128.91 (×2), 128.98 (×2), 129.23, 129.93 (×3), 130.05 (×4), 130.19 (×2), 133.27, 133.50, 133.67, 162.84, 165.34, 165.40, 165.90, 166.28 ppm; HR-FAB MS: calcd for $C_{37}H_{32}NO_9S_2$ $[M+H]^+$: 698.1518; found: 698.1515.

2-Thiazolinyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (6): This compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (**5**)[24] by method A (KSTaz, [18]crown-6, acetonitrile) in 90% yield as white foam. R_f=0.27 (ethyl acetate/hexanes, 3:7, v/v); $[\alpha]_D^{28}$=+121.7° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=3.25–3.40 (m, 2H; CH_2N), 4.15 (t, J_{CH_2S,CH_2N}=8.1 Hz, 2H; CH_2S), 4.47 (m, 2H; H-5, 6b), 4.66 (dd, $J_{5,6a}$=5.5 Hz, $J_{6a,6b}$=9.7 Hz, 1H; H-6a), 5.73 (dd, $J_{3,4}$=3.4 Hz, $J_{2,3}$=9.7 Hz, 1H; H-3), 5.81 (d, $J_{1,2}$=10.3 Hz, 1H; H-1), 5.94 (dd, $J_{2,3}$= 9.9 Hz, 1H; H-2), 6.06 (d, $J_{3,4}$=3.3 Hz, 1H; H-4), 7.10–8.10 ppm (m, 20H; aromatic); ^{13}C NMR: δ=35.06, 62.06, 64.01, 67.76, 68.22, 72.49, 75.42, 83.45, 128.17, 128.24, 128.34, 128.53, 128.68, 128.81, 129.38, 129.60, 129.67, 129.70, 129.75, 129.88, 133.09, 133.21, 133.35, 133.54, 162.31, 165.20, 165.26, 165.36, 165.81 ppm; HR-FAB MS: calcd for $C_{37}H_{32}NO_9S_2$ $[M+H]^+$: 698.1518; found: 698.1515.

2-Thiazolinyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-D-mannopyranoside (8): This compound was obtained from 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide (**7**)[24] by method A (KSTaz, [18]crown-6, acetonitrile) as an anomeric mixture (α/β 13:1), white foam, 70% combined yield. R_f=0.40 (ethyl acetate/toluene, 2:3, v/v); ^{1}H NMR: δ=3.39 (t, J=8.0 Hz, 2H; CH_2N), 4.21 (t, J_{CH_2S,CH_2N}=8.0 Hz, 2H; CH_2S), 4.30 (m, $J_{5,6a}$=2.6 Hz, $J_{5,6b}$=4.7 Hz, 1H; H-5), 4.52 (dd, 1H; H-6b), 4.72 (dd, $J_{6a,6b}$=12.2 Hz, H1H; -6a), 5.72 (dd, $J_{3,4}$=3.3 Hz, 1H; H-3), 6.02 (dd, $J_{4,5}$=10.0 Hz, 1H; H-4), 6.12 (dd, $J_{2,3}$=3.3 Hz, 1H; H-2), 6.13 (d, $J_{1,2}$=1.0 Hz, 1H; H-1), 7.24–8.12 ppm (m, 20H; aromatic); ^{13}C NMR: δ=29.69 (×2), 35.65 (×2), 62.98, 64.03, 66.36, 71.23, 72.59, 76.81, 77.20, 82.02, 128.29 (×2), 128.36 (×3), 128.44 (×2), 128.60 (×2), 128.78, 129.01, 129.76 (×3), 129.81, 130.04 (×2), 133.03, 133.27, 133.49, 133.56, 162.50, 165.19, 165.54, 166.09 ppm; HR-FAB MS: calcd for $C_{37}H_{32}NO_9S_2$ $[M+H]^+$: 698.1518; found: 698.1515.

2-Thiazolinyl 2-*O*-benzyl-3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (10): This compound was obtained from 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl bromide (**9**)[81] by method A (NaSTaz, [15]crown-5, acetonitrile), cream crystals, 46% yield. R_f=0.42 (ethyl acetate/toluene, 1:1, v/v); m.p. +121°C (ether/hexanes); $[\alpha]_D^{27}$=+22.4° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=1.89, 1.99, 2.05 (3s, 9H; 3$COCH_3$), 3.36 (dd, J=8.2 Hz, 2H; CH_2N), 3.66 (dd, $J_{2,3}$=9.2 Hz, 1H; H-2), 3.77 (m, $J_{5,6a}$=2.2 Hz, $J_{5,6b}$=4.6 Hz, 1H; H-5), 4.18–4.62 (m, J_{CH_2S,CH_2N}=8.2 Hz, 4H; H-6a, 6b, CH_2S), 4.67 (dd, J=11.2 Hz, 2H; CH_2Ph), 5.03 (dd, $J_{4,5}$=9.9 Hz, 1H; H-4), 5.24 (dd, $J_{3,4}$=9.2 Hz, 1H; H-3), 5.33 (d, $J_{1,2}$=10.1 Hz, 1H; H-1), 7.24–7.38 ppm (m, 5H; aromatic); ^{13}C NMR: δ=20.56, 20.62, 20.72, 35.13, 61.88, 64.26, 68.20, 75.18, 75.56, 75.81, 78.05, 84.06, 127.99, 128.08, 128.40 (×2), 137.14, 162.65, 169.62, 169.84, 170.56 ppm; HR-FAB MS: calcd for $C_{22}H_{28}NO_8S_2$ $[M+H]^+$: 498.1256; found: 498.1254.

2-Thiazolinyl 3,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (12): This compound was obtained from 3,4,6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucopyranosyl chloride (**11**)[25] by method A (KSTaz, acetone), cream foam, 71% yield. Compound **12** was also obtained from 3,4,6-tri-*O*-acetyl-1,2-anhydro-α-D-glucopyranose (**22**)[29] by method C in 78% yield. R_f=0.24 (ethyl acetate/CH_2Cl_2, 3:7, v/v); $[\alpha]_D^{28}$=+25.7° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=2.01, 2.07, 2.06 (3s, 9H; 3$COCH_3$), 3.41 (m, J_{CH_2S,CH_2N}=8.5 Hz, 2H; CH_2N), 3.70–3.83 (m, 2H; H-2, 5), 4.04–4.28 (m, 4H; H-5, 6a, CH_2S), 4.51 (brs, 1H; OH), 5.03 (dd, 1H; H-4), 5.13 (dd, $J_{2,3}$=9.4 Hz, $J_{3,4}$=9.1 Hz, 1H; H-3), 5.27 ppm (d, $J_{1,2}$=9.9 Hz, 1H; H-1); ^{13}C NMR: δ=20.55, 20.69, 20.75, 35.45, 61.92, 63.65, 67.84, 72.15, 76.25, 76.34, 85.15, 165.30, 169.55, 170.59, 170.62 ppm; HR-FAB MS: calcd for $C_{15}H_{22}NO_8S_2$ $[M+H]^+$: 408.0787; found: 408.0779.

2-Thiazolinyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (14): This compound was obtained from 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride (**13**)[26] by method A (NaSTaz, [15]crown-5, acetone), colorless syrup, 55% yield. R_f=0.41 (ethyl acetate/hexanes, 3:7, v/v); $[\alpha]_D^{26}$=+18.6° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=3.34 (t, J_{CH_2S,CH_2N}=8.0 Hz, 2H; CH_2N), 3.52–3.65 (m, 2H; H-2, 4), 3.70–3.82 (m, 4H; H-3, 5, 6a, 6b), 4.08–4.32 (m, 2H; CH_2S), 4.50–4.95 (m, 8H; CH_2Ph), 5.28 (d, $J_{1,2}$=9.9 Hz, 1H; H-1), 7.10–7.40 ppm (m, 20H; aromatic); ^{13}C NMR (500 MHz): δ=14.34, 29.91, 31.13, 35.19, 64.52, 68.75, 73.61, 75.21, 75.77, 75.95, 79.64, 81.05, 84.89, 86.85, 127.77, 127.94 (×3), 128.07 (×4), 128.53 (×4), 128.58 (×4), 128.64 (×2), 137.84, 138.26, 138.37, 138.59, 163.92 ppm; HR-FAB MS: calcd for $C_{37}H_{40}NO_5S_2$ $[M+H]^+$: 642.2348; found: 642.2343.

2-Thiazolinyl 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (16): This compound was obtained from 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-α-D-glucopyranosyl chloride (**15**)[27] by method A (KSTaz, [18]crown-6, acetonitrile) in 89% as colorless syrup. R_f=0.38 (ethyl acetate/hexanes, 2:3, v/v); $[\alpha]_D^{28}$=+8.0° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=1.80 (s, 3H; $COCH_3$), 3.32 (t, 2H; J_{CH_2S,CH_2N}=8.1 Hz, CH_2N), 3.52–3.62 (m, 2H; H-4, 6a), 3.65–3.80 (m, 3H; H-2, 5, 6b), 4.06–4.30 (m, 2H; CH_2S), 4.46–4.78 (m, 6H; CH_2Ph), 5.26 (dd, $J_{2,3}$=12.6 Hz, 1H; H-3), 5.31 (d, $J_{1,2}$=10.3 Hz, 1H; H-1), 7.10–7.35 ppm (m, 15H; aromatic); ^{13}C NMR: δ=21.13, 35.24, 64.50, 68.43, 73.68, 74.50, 74.90, 75.86, 78.86, 79.36, 84.80, 127.88, 127.99, 128.07 (×3), 128.17 (×2), 128.36 (×2), 128.55 (×2), 128.59 (×3), 137.63, 137.98, 138.71, 170.00 ppm; HR-FAB MS: calcd for $C_{32}H_{36}NO_6S_2$ $[M+H]^+$: 594.1984; found: 594.1984.

2-Thiazolinyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (19): This compound was obtained from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (**18**) by method B as an anomeric mixture (α/β 1:11), white foam, 85% combined yield. Compound **19** was obtained as pure β-anomer from 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-*O*-methyl)ethylidene-α-D-galactopyranose (**23**)[30] and 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-thioethyl)ethylidene-α-D-galactopyranose (**24**)[31] by method C in 77 and 82% yield, respectively. R_f=0.30 (ethyl acetate/toluene, 1:1, v/v); ^{1}H NMR: δ=1.98, 2.04, 2.05, 2.15 (4s, 12H; 4$COCH_3$), 3.40 (t, J=8.0 Hz, 2H; CH_2N), 3.95–4.10 (m, 1H; H-5), 4.10–4.35 (m, 4H; H-6a, 6b, CH_2S), 5.10 (dd, $J_{3,4}$=3.4 Hz, 1H; H-3), 5.31 (dd, $J_{2,3}$=10.2 Hz, 1H; H-2), 5.45 (s, 1H; H-4), 5.46 ppm (d, $J_{1,2}$=9.9 Hz, 1H; H-1); ^{13}C NMR: δ=20.50, 20.60, 20.64, 20.68, 35.24, 61.11, 64.14, 66.73, 67.06, 71.76, 74.70, 83.41, 162.76, 169.51, 169.87, 170.14, 170.27 ppm; HR-FAB MS: calcd for $C_{17}H_{24}NO_9S_2$ $[M+H]^+$: 450.0892; found: 450.0891.

2-Thiazolinyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-mannopyranoside (21): This compound was obtained from 1,2,3,4,6-penta-*O*-acetyl-α-D-mannopyranose (**20**) by method B as an anomeric mixture (α/β 22:1), white foam, 70% combined yield. R_f=0.26 (ethyl acetate/toluene, 2:3, v/v); ^{1}H NMR: δ=1.96, 2.01, 2.05, 2.13 (4s, 12H; 4$COCH_3$), 3.38 (t, J=8.1 Hz, 2H; CH_2N), 4.04–4.13 (m, 2H; H-5, 6b), 4.16–4.38 (m, J_{CH_2S,CH_2N}=8.1 Hz, 3H; H-6a, CH_2S), 5.12 (dd, $J_{3,4}$=10.0 Hz, 1H; H-3), 5.32 (dd, 1H; H-4), 5.42 (dd, $J_{2,3}$=3.2 Hz, 1H; H-2), 6.20 ppm (d, $J_{1,2}$=1.5 Hz, 1H; H-1); ^{13}C NMR: δ=20.42, 20.50, 20.56, 20.68, 35.38, 61.96, 63.94, 65.63, 69.24, 70.50, 71.39, 82.52, 161.29, 169.39, 169.51, 169.56, 170.38 ppm; HR-FAB MS: calcd for $C_{17}H_{24}NO_9S_2$ $[M+H]^+$: 450.0892; found: 450.0891.

Ethyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (25): Acetic anhydride (7.5 mL) was added dropwise to a stirred solution of ethyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[62] (500 mg, 1.29 mmol) in dry pyridine (15 mL) under argon at RT. The resulting mixture was stirred for 16 h, then quenched with methanol (10 mL) and the volatiles were evaporated in vacuo. The residue was diluted with CH_2Cl_2 (60 mL) and the organic layer was washed with water (15 mL), saturated aq. $NaHCO_3$ (15 mL), 1 M HCl (2×15 mL), and water (3×15 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to give **25** as white solid (530 mg, 96% yield). R_f=0.53 (ethyl acetate/hexanes, 3:7, v/v); $[\alpha]_D^{24}$=+29.1° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=1.29 (t, J=7.5 Hz, 3H; CH_2CH_3), 1.92 (s, 3H; $COCH_3$), 2.65–2.77 (m, 2H; CH_2CH_3), 3.43–3.59 (m, 3H; H-2, 4, 6b), 3.70 (dd, $J_{6a,6b}$=10.1 Hz, 1H; H-6a), 4.27–4.33 (m, $J_{5,6a}$=4.6 Hz, $J_{5,6b}$=4.6 Hz, 1H; H-5), 4.59 (d, $J_{1,2}$=9.7 Hz, 1H; H-1), 4.61 (d, J=11.1 Hz, 1H; CH_2Ph), 4.89 (d, J=11.1 Hz, 1H; CH_2Ph), 5.38 (dd, $J_{3,4}$=9.1 Hz, 1H; H-3), 5.43 (s, 1H; CHPh), 7.26–7.50 ppm (m, 10H; aromatic); ^{13}C NMR: δ=14.89, 20.55, 25.01, 29.14, 68.18, 69.89, 73.85, 74.87, 78.31, 79.61, 85.47, 100.82, 125.89 (×2), 127.57, 127.81 (×2), 127.88 (×2), 128.25 (×2), 128.66, 136.83, 137.48, 169.32 ppm; HR-FAB MS: calcd for $C_{24}H_{29}O_6S$ $[M+H]^+$: 445.1685; found: 445.1686.

2-Thiazolinyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (26): This compound was obtained from **25** by method D in 53% yield as white foam. R_f=0.40 (ethyl acetate/hexanes, 2:3, v/v); $[\alpha]_D^{28}$=+1.21° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=1.97 (s, 3H; $COCH_3$), 3.40 (t, J_{CH_2S,CH_2N}=8.0 Hz, 2H; CH_2N), 3.60–3.80 (m, 4H; H-2, 4, 6a, 6b), 4.10–4.35 (m, 1H; CH_2S), 4.42 (dd, $J_{5,6a}$=3.3 Hz, $J_{5,6b}$=4.0 Hz, 1H; H-5), 4.62 (d, J=11.0 Hz, 1H; CH_2Ph), 4.83 (d, J=11.0 Hz, 1H; CH_2Ph), 5.42 (dd, $J_{2,3}$=8.9 Hz, 1H; H-3), 5.47 (d, $J_{1,2}$=10.0 Hz, 1H; H-1), 5.48 (s, 1H; CHPh), 7.30–7.43 ppm (m, 10H; aromatic); ^{13}C NMR: δ=21.07, 35.39, 64.44, 68.74, 70.71, 70.92, 74.37, 75.34, 78.64, 79.04, 85.13, 101.58, 126.32 (×2), 128.19, 128.36, 128.40 (×2), 128.62 (×2), 129.24, 137.03, 137.44 ppm; HR-FAB MS: calcd for $C_{25}H_{28}NO_6S_2$ $[M+H]^+$: 502.1358; found: 502.1355.

2-Thiazolinyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (28): This compound was obtained from ethyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**27**)[32] by method D, as a colorless syrup in 40% yield. R_f=0.43 (ethyl acetate/hexanes, 2:3, v/v); $[\alpha]_D^{28}$=−4.4° (c=1.0 in $CHCl_3$); ^{1}H NMR: δ=1.77 (s, 3H; $COCH_3$), 3.28 (t, J_{CH_2S,CH_2N}=8.1 Hz, 2H; CH_2N), 3.50–3.53 (m, 2H; H-2, 6a), 3.59–3.70 (m, 3H; H-3, 5, 6b), 4.09–4.20 (m, 2H; CH_2S), 4.48 (s, 2H; CH_2Ph), 4.58–4.81 (m, 4H; CH_2Ph), 5.04 (dd, $J_{3,4}$=9.2 Hz, 1H; H-4), 5.28 (d, $J_{1,2}$=9.6 Hz, 1H; H-1), 7.20–7.30 ppm (m, 15H; aromatic); ^{13}C NMR: δ=20.92, 35.22, 64.41, 69.38, 70.69, 73.56, 75.48, 75.76, 77.97, 80.69, 83.98, 84.59, 127.72, 127.90, 127.95 (×2), 128.02 (×2), 128.12, 128.40 (×2), 128.52 (×2), 128.56 (×2), 137.57, 138.05, 138.19, 169.76 ppm; HR-FAB MS: calcd for $C_{32}H_{36}NO_6S_2$ $[M+H]^+$: 594.1984; found: 594.1984.

2-Thiazolinyl 1-thio-β-D-glucopyranoside (35): A solution of NaOMe in MeOH (1.0 M, 1 mL, 1.0 mmol of MeONa) was added to a stirred suspension of **2** (320 mg, 0.71 mmol) in dry methanol (4 mL) and the reaction mixture was stirred for 1 h at RT. The reaction was then neutralized with Dowex (H^+), filtered, and concentrated in vacuo to yield crude **35** as white foam (196 mg, 98%). R_f=0.30 (methanol/dichloromethane, 1:4, v/v); $[\alpha]_D^{25}$=−34.0° (c=1.0 in methanol); ^{1}H NMR (CD_3OD): δ=3.27–3.50 (m, 6H; H-2, 3, 4, 5, CH_2S), 3.71 (dd, $J_{5,6a}$=2.3 Hz, 1H; H-6a), 3.87 (dd, J=11.9 Hz, 1H; H-6b), 4.10–4.32 (m, 2H; CH_2N), 5.14 ppm (d, $J_{1,2}$=

9.8 Hz, 1H; H-1); ^{13}C NMR: δ = 35.56, 62.60, 65.10, 70.94, 73.82, 79.65, 82.26, 87.24, 168.27 ppm; HR-FAB MS: calcd for $C_9H_{16}NO_5S_2$ $[M+H]^+$: 282.0470; found: 282.0466.

2-Thiazolinyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (36): Compound **35** was dissolved in dry pyridine (35 mL) and triphenylmethyl chloride (4.18 g, 15 mmol) was added. The reaction mixture was left for 24 h at RT, cooled to 0 °C and then benzoyl chloride (7.65 mL, 44.6 mmol) was added dropwise. The reaction mixture was stirred under argon at RT for 16 h, and then was quenched with methanol (35 mL). Volatile solvents were evaporated in vacuo, the residue was diluted with CH_2Cl_2 (125 mL) and the organic layer was washed with water (40 mL), saturated aq. $NaHCO_3$ (40 mL), water (40 mL), 1 M HCl (2×30 mL), and water (3×40 mL). The organic phase was separated, dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution). After that, the product was dissolved in CH_2Cl_2 (100 mL) containing trifluoroacetic acid (3 mL) and water (0.5 mL). The reaction mixture was kept for 1 h at RT, then diluted with CH_2Cl_2 (50 mL.), transferred into a separatory funnel and washed with water (40 mL), saturated aq. $NaHCO_3$ (2×50 mL), and water (3×50 mL). The organic phase was separated, dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to give **36** as a white foam (4.20 g, 58 %). R_f = 0.44 (acetone/toluene, 1:5, v/v), $[\alpha]_D^{23}$ = +45.2° (c = 1 in $CHCl_3$); ^{1}H NMR: δ = 3.25 (m, 2H; CH_2N), 3.70–3.80 (m, 2H; H-6a, 6b), 3.99 (m, 1H; H-5), 4.05–4.30 (m, 2H; CH_2S), 5.49 (dd, $J_{4,5}$ = 9.8 Hz, 1H; H-4), 5.57 (dd, $J_{2,3}$ = 9.7 Hz, 1H; H-2), 5.75 (d, $J_{1,2}$ = 10.3 Hz, 1H; H-1), 5.97 (dd, $J_{3,4}$ = 9.4 Hz, 1H; H-3), 7.10–7.90 ppm (m, 15H; aromatic); ^{13}C NMR: δ = 35.27, 61.55, 64.10, 69.23, 70.33, 73.85, 77.42, 79.28, 83.11, 128.31 (×2), 128.36 (×2), 128.50 (×2), 128.72, 128.76, 129.70 (×2), 129.91 (×2), 129.96 (×2), 133.29, 133.45, 133.67, 162.99, 165.15, 165.69, 165.82 ppm; HR-FAB MS: calcd for $C_{30}H_{28}NO_8S_2$ $[M+H]^+$: 594.1256; found: 594.1255.

2-Thiazolinyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (37): Compound **35** (50 mg, 0.183 mmol) was dissolved in dry benzaldehyde (1.2 mL), and the mixture was cooled to 0 °C and stirred under argon. Anhydrous $ZnCl_2$ (25 mg, 0.183 mmol) was then added and the reaction mixture was stirred at 0 °C for 5 h. The volatiles were evaporated under vacuum and the crude residue was purified by column chromatography on silica gel (methanol/dichloromethane gradient elution) to give **37** as white solid (58 mg, 88 %). R_f = 0.50 (methanol/dichloromethane, 1:9, v/v); $[\alpha]_D^{30}$ = −8.94° (c = 1 in $CHCl_3$); ^{1}H NMR: δ = 3.38 (t, J_{CH_2S,CH_2N} = 8.5 Hz, 2H; CH_2N), 3.45–3.70 (m, 3H; H-2, 3, 5), 3.74 (dd, $J_{6a,6b}$ = 9.9 Hz, 1H; H-6a), 3.84 (dd, $J_{4,5}$ = 8.6 Hz, 1H; H-4), 4.15–4.25 (ddd, J = 8.1 Hz, 2H; CH_2S), 4.37 (dd, $J_{5,6a}$ = 3.7 Hz, 1H; H-6b), 5.30 (d, $J_{1,2}$ = 9.9 Hz, 1H; H-1), 5.53 (s, 1H; CHPh), 7.30–7.52 ppm (m, 5H; aromatic); ^{13}C NMR: δ = 35.65, 64.02, 68.68, 71.11, 74.28, 75.21, 80.17, 85.69, 102.10, 126.55, 128.55, 129.51, 137.09, 165.12 ppm; HR-FAB MS: calcd for $C_{16}H_{20}NO_5S_2$ $[M+H]^+$: 370.7083; found: 370.0782.

2-Thiazolinyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (37a): Compound **37** (1.17 g, 3.17 mmol) was dissolved in pyridine (15 mL). The reaction was cooled down to 0 °C and BzCl (1.1 mL, 9.51 mmol) was then added dropwise. The reaction mixture was stirred under argon at RT for 16 h, and then it was quenched with methanol (5 mL). Volatile solvents were evaporated in vacuo, the residue was diluted with CH_2Cl_2 (100 mL), and the organic layer was washed with water (20 mL), saturated aq. $NaHCO_3$ (20 mL), water (20 mL), 1 M HCl (2× 20 mL), and water (3×20 mL). The organic phase was separated, dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to afford **37a** as white solid (1.7 g, 94 %). R_f = 0.42 (ethyl acetate/hexanes, 1:1, v/v); $[\alpha]_D^{30}$ = +67.7° (c = 0.39 in $CHCl_3$); ^{1}H NMR: δ = 3.20–3.41 (m, 2H; CH_2N), 3.80–3.98 (dd, $J_{6a,6b}$ = 7.4 Hz, 2H; H-6a, 6b), 4.00 (dd, $J_{4,5}$ = 9.3 Hz, 1H; H-4), 4.10–4.32 (m, 2H; CH_2S), 4.50 (dd, $J_{5,6a}$ = 5.6 Hz, 1H; H-5), 5.58 (s, 1H; CHPh), 5.67 (dd, $J_{2,3}$ = 9.2 Hz, 1H; H-2), 5.86 (d, $J_{1,2}$ = 10.3 Hz, 1H; H-1), 5.92 (dd, $J_{3,4}$ = 9.4 Hz, 1H; H-3), 7.30–7.99 ppm (m, 15H; aromatic); ^{13}C NMR: δ = 35.44, 64.19, 68.58, 70.77, 71.25, 73.19, 78.62, 83.72, 101.64, 126.26, 128.31, 128.43, 128.48, 128.89, 129.12, 129.32, 129.86, 130.07, 133.30, 133.57, 136.80, 162.54, 165.39, 165.59 ppm; HR-FAB MS: calcd for $C_{30}H_{28}NO_7S_2$ $[M+H]^+$: 578.1307; found: 578.1302.

2-Thiazolinyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-1-thio-β-D-glucopyranoside (38): Freshly activated molecular sieves (3 Å, 175 mg) ware added to a solution of compound **37a** (50 mg, 0.08 mmol) in THF (2 mL), and the mixture was stirred under argon for 1 h. Sodium cyanoborohydride (73.6 mg, 1.16 mmol) was then added, followed by 2 M HCl in dry ether (0.58 mL, 1.16 mmol) until no H_2 gas was released from the reaction. The reaction mixture was stirred at RT for 20 h and then diluted with CH_2Cl_2, the solid was filtered-off, and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20 % aq. $NaHCO_3$ (15 mL) and water (3×10 mL), the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to obtain **38** as a colorless syrup (32.9 mg, 65 %). R_f = 0.57 (acetone/toluene, 2:3, v/v); $[\alpha]_D^{29}$ = +28.4° (c = 1.0 in $CHCl_3$); ^{1}H NMR: δ = 3.27 (brs, 1H; OH), 3.30–3.60 (m, 2H; CH_2N), 3.80–3.95 (m, 3H; H-5, 6a, 6b), 4.07 (dd, $J_{4,5}$ = 8.8 Hz, 1H; H-4), 4.15–4.47 (m, 2H; CH_2S), 4.64 (dd, J = 11.8 Hz, 2H; CH_2Ph), 5.20 (d, $J_{1,2}$ = 9.4 Hz, 1H; H-1), 5.50–5.70 (m, 2H; H-2, 3), 7.20–7.96 ppm (m, 15H; aromatic); ^{13}C NMR: δ = 31.04, 62.98, 69.53, 69.80, 70.12, 74.06, 79.82, 84.23, 126.56, 128.01, 128.08, 128.22, 128.42, 128.78, 130.18, 130.22, 133.99, 134.08, 137.78, 141.49, 147.54, 165.40, 167.15, 183.56 ppm; HR-FAB MS: calcd for $C_{30}H_{30}NO_7S_2$ $[M+H]^+$: 580.1464; found: 580.1464.

2-Thiazolinyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-1-thio-β-D-glucopyranoside (39): Compound **37a** (50 mg, 0.087 mmol) was dissolved in CH_2Cl_2 (1 mL) containing trifluoroacetic acid (0.15 mL) and water (0.1 mL). The reaction mixture was kept for 30 min at 0 °C, then diluted with CH_2Cl_2 (30 mL), transferred into a separating funnel and washed with water (10 mL), saturated aq. $NaHCO_3$ (2×10 mL), and water (3×10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to give **39** as white foam in 95 % yield. R_f = 0.62 (acetone/toluene, 1:9, v/v); $[\alpha]_D^{24}$ = +128.4° (c = 1 in $CHCl_3$); ^{1}H NMR: δ = 3.10–3.30 (m, 2H; CH_2N), 3.75–3.85 (m, 2H; H-5, OH), 3.86–4.10 (m, 4H; H-4, 6a, 6b, CH_2S), 4.14–4.25 (m, 1H; CH_2S), 4.40 (brs, 1H; OH), 5.44 (dd, $J_{2,3}$ = 9.7 Hz, 1H; H-2), 5.55–5.65 (m, 2H; H-1, 3), 7.20–7.90 ppm (m, 10H; aromatic); ^{13}C NMR: δ = 31.04, 35.17, 62.16, 64.17, 69.27, 70.20, 80.66, 82.98, 128.51, 128.80, 128.97, 129.22, 129.95, 130.04, 133.5, 133,53, 163.94, 165.55, 166.82 ppm; HR-FAB MS: calcd for $C_{23}H_{24}NO_7S_2$ $[M+H]^+$: 490.0994; found: 490.0995.

2-Thiazolinyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (89): This compound was obtained from **26** by using a procedure similar to that described for the synthesis of **35**. The crude residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to yield **89** as white foam in 90 % yield. R_f = 0.32 (ethyl acetate/hexanes, 3:7, v/v); $[\alpha]_D^{28}$ = −7.3° (c = 1.0, $CHCl_3$); ^{1}H NMR: δ = 2.90 (brs, 1H; OH), 3.25 (t, J_{CH_2S,CH_2N} = 8.2 Hz, 2H; CH_2N), 3.39–3.47 (m, $J_{2,3}$ = 3.8 Hz, 3H; H-2, 5, 6b), 3.58–3.70 (m, 1H; H-6a), 3.79 (dd, $J_{4,5}$ = 7.6 Hz, 1H; H-4), 4.00–4.20 (m, 2H; CH_2S), 4.29 (dd, $J_{3,4}$ = 10.3 Hz, 1H; H-3), 4.75 (dd, J_2 = 10.9 Hz, 2H; CH_2Ph), 5.27 (d, $J_{1,2}$ = 10.1 Hz, 1H; H-1), 5.42 (s, 1H; CHPh), 7.20–7.42 ppm (m, 10H; aromatic); ^{13}C NMR: δ = 35.03, 64.18, 68.49, 70.21, 75.30, 75.44, 80.16, 80.39, 84.62, 101.74, 126.25 (×2), 127.98, 128.27 (×4), 128.41 (×2), 129.21, 136.90, 137.62, 163.21 ppm; HR-FAB MS: calcd for $C_{23}H_{26}NO_5S_2$ $[M+H]^+$: 460.1252; found: 460.1249.

2-Thiazolinyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (91): This compound was obtained from **16** by using a procedure similar to that described for the synthesis of **35**. The crude residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to yield **91** as a colorless syrup in 85 % yield. R_f = 0.31 (acetone/toluene, 1:9, v/v); $[\alpha]_D^{26}$ = −2.0° (c = 1, $CHCl_3$); ^{1}H NMR: δ = 3.34 (t, J_{CH_2S,CH_2N} = 8.1 Hz, 2H; CH_2N), 3.46 (dd, $J_{2,3}$ = 9.8 Hz, 1H; H-2), 3.53–3.67 (m, 2H; H-6a, 6b), 3.70–3.90 (m, 3H; H-3, 4, 5), 4.10–4.32 (m, 2H; CH_2S), 4.52–4.88 (m, 6H; CH_2Ph), 5.26 (d, $J_{1,2}$ = 10.0 Hz, 1H; H-1), 7.15–7.40 ppm (m, 15H; aromatic); ^{13}C NMR (500 MHz): δ = 138.24, 138.12, 137.75, 128.55(×2), 128.47 (×2), 128.31 (×2), 128.30(×2), 128.07, 127.90(×2), 127.84, 127.59, 84.35, 80.52, 79.18, 78.60, 77.17, 75.20, 74.58, 73.42, 68.58, 64.31, 60.37,

34.98, 21.03, 14.19 ppm; HR-FAB MS: calcd for $C_{30}H_{34}NO_5S_2$ $[M+H]^+$: 552.1878; found: 552.1879.

Comparative hydrolytic stability studies—synthesis of 42

Method A—general NIS/TfOH-promoted leaving group hydrolysis: A mixture of **14**, **40**, or **41** (0.10 mmol), *N*-iodosuccinimide (0.20 mmol), and TfOH (0.01–0.02 mmol) in CH_2Cl_2/water (95:5 v/v, 2.5 mL) was stirred for 1–16 h at RT. Quantitative estimates were made based on the accumulation of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**42**) observed by TLC.

Method B—general TfOH/Bu_4NIO_4-mediated leaving group hydrolysis: A mixture of **14**, **40**, or **41** (0.10 mmol), tetrabutyl ammonium periodate (0.05 mmol) and 70% aq. TfOH (5 μL) was stirred for 1–16 h at −10 °C. Quantitative TLC estimates were made based on the accumulation of **42**.

Method C—general NBS-promoted leaving group hydrolysis: A mixture of **14**, **40**, or **41** (0.10 mmol), *N*-bromosuccinimide (0.20 mmol) in acetone/water (9:1 v/v, 1.5 mL) was stirred for 1–16 h at RT. Quantitative TLC estimates were made based on the accumulation of **42**.

Methods D and E—general acid-catalyzed leaving group hydrolysis: A mixture of **14**, **40**, or **41** (0.10 mmol) and acid (TFA, 0.10 mmol or TfOH, 0.02 mmol) in acetone/water (9:1 v/v, 1.5 mL) was stirred for 1–16 h at RT. Quantitative TLC estimates were made based on the accumulation of **42**.

Preparation of di- and oligosaccharides

Method A—typical AgOTf-promoted glycosylation procedure (activation of the STaz glycosides): A mixture the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $ClCH_2CH_2Cl$ (2 mL) was stirred under argon for 1.5 h. Freshly conditioned AgOTf (0.22 mmol) was added and the reaction mixture was stirred for 1–2 h at RT and then diluted with CH_2Cl_2, the solid was filtered-off, and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (15 mL) and water (3× 10 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford a di- or an oligosaccharide derivative.

Method B—typical NIS/TfOH-promoted glycosylation procedure (activation of the S-*ethyl,* S-*phenyl and STaz glycosides)*: A mixture the glycosyl donor (0.125 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4 Å, 200 mg) in $ClCH_2CH_2Cl$ (2 mL) was stirred for 1 h under argon. NIS (0.25 mmol) and TfOH (0.025 mmol for SEt/SPh or 0.130 mmol for STaz) were added and the reaction mixture was stirred for 2–24 h at RT. Upon completion, the solid was filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $Na_2S_2O_3$ (15 mL) and water (3×10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford a di- or an oligosaccharide derivative.

Method C—typical $Cu(OTf)_2$-promoted glycosylation procedure (activation of STaz and SBox glycosides): A mixture the glycosyl donor (0.13 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4 Å, 200 mg) in $ClCH_2CH_2Cl$ (1.6 mL) was stirred under argon for 1 h followed by addition of freshly conditioned $Cu(OTf)_2$ (141 mg, 0.39 mmol). The reaction mixture was stirred for 16–48 h at RT and then diluted with CH_2Cl_2, the solid was filtered-off, and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with water (3×15 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to yield the corresponding di- or oligosaccharide.

Method D—typical MeOTf-promoted glycosylation procedure (activation of STaz glycosides): A mixture the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $ClCH_2CH_2Cl$ (2 mL) was stirred for 2 h under argon. MeOTf (0.33 mmol) was added and the reaction mixture was stirred for 2–24 h at room temperature; then Et_3N (0.5 mL) was added, the mixture was diluted with CH_2Cl_2 (30 mL), the solid was filtered-off, and the residue was washed with CH_2Cl_2. The combined filtrate was washed with water (4× 10 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to yield the corresponding di- or oligosaccharide.

Method E—typical HgO/$HgBr_2$-promoted glycosylation procedure (activation of glycosyl bromides): A mixture the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $ClCH_2CH_2Cl$ (2 mL) was stirred under argon for 1.5 h. HgO (0.11 mmol) and $HgBr_2$ (0.006 mmol) were added and the reaction mixture was stirred for 16 h at RT and then diluted with CH_2Cl_2. The solid was then filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (15 mL) and water (3×10 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford a disaccharide derivative.

Method F—typical $BF_3{\cdot}Et_2O$-promoted glycosylation procedure (activation of glycosyl trichloroacetimidates): A mixture the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4 Å, 200 mg) in $ClCH_2CH_2Cl$ (2 mL) was stirred under argon for 1.5 h. $BF_3{\cdot}Et_2O$ (0.011 mmol) was added and the reaction mixture was stirred for 20 h at RT and then diluted with CH_2Cl_2. The solid was then filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (15 mL) and water (3× 10 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford a disaccharide derivative.

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (44): This compound was obtained by method A from **4** and **43**[40] in 91% yield. Analytical data for **44** were essentially the same as reported previously.[82]

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (46): This compound was obtained by method D from **4** and **45**[41] in 99% yield. R_f=0.27 (ethyl acetate/hexane, 3:7, v/v); $[\alpha]_D^{24}$=+29.1° (c=1, $CHCl_3$); ^{1}H NMR: δ=3.27 (s, 3H; OCH_3), 3.46–3.68 (m, 4H; H-4, 5, 6a, 6b), 3.70–3.75 (dd, $J_{2,3}$=3.4 Hz, 1H; H-2), 3.85 (dd, $J_{3,4}$=9.4 Hz, 1H; H-3), 4.04–4.10 (m, $J_{5',6a'}$=1.5 Hz, $J_{5',6b'}$= 4.8 Hz, 1H; H-5′), 4.27–4.43 (m, 4H; H-6b′, CH_2Ph), 4.48–4.62 (m, 3H; CH_2Ph), 4.62–4.67 (dd, $J_{6a',6b'}$=3.0 Hz, 1H; H-6a′), 4.98 (d, $J_{1,2}$=3.4 Hz, 1H; H-1), 5.09 (d, $J_{1',2'}$=7.7 Hz, 1H; H-1′), 5.64 (dd, J=9.6 Hz, 2H; H-2′,4′), 5.83 (dd, $J_{3',4'}$=9.6 Hz, 1H; H-3′), 6.85–8.00 ppm (m, 35H; aromatic); ^{13}C NMR: δ=55.48, 63.06, 68.75, 69.66, 70.03, 72.18, 72.52, 73.46, 73.71, 75.10, 75.44, 77.44, 77.96, 81.07, 82.09, 127.31, 127.41, 127.73, 127.87, 127.95, 128.09, 128.27, 128.41, 128.46, 128.57, 128.63, 128.66, 128.92, 128.95, 129.06, 129.63, 129.88, 129.92, 130.00, 130.06, 133.21, 133.40, 133.68, 138.21, 138.39, 138.67, 165.21, 165.37, 166.02, 166.25 ppm; HR-FAB MS: calcd for $C_{62}H_{59}O_{15}$ $[M+H]^+$: 1043.3854; found: 1043.3855.

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (48): This compound was obtained by method B from **4** and **47**[42] in 93% yield. R_f=0.58 (ethyl acetate/hexane, 1:1, v/v); $[\alpha]_D^{27}$=+4.27° (c=1 in $CHCl_3$); ^{1}H NMR: δ=3.28 (s, 3H; OCH_3), 3.39–3.54 (m, 3H; H-2, 5 ,6a), 3.68–3.77 (m, 2H; H-5′, 6b), 3.89 (dd, $J_{3,4}$= 8.9 Hz, 1H; H-3), 3.98 (dd, $J_{4,5}$=9.4 Hz, 1H; H-4), 4.23–4.29 (dd, $J_{6a',6b'}$= 5.0 Hz, 1H; H-6a′), 4.35 (d, J=12.2 Hz, 1H; CH_2Ph), 4.38–4.43 (dd, J= 3.4 Hz, 1H; H-6b′), 4.54–4.69 (m, 3H; CH_2Ph), 4.73–4.82 (m, $J_{1,2}$= 2.7 Hz, 3H; H-1, CH_2Ph), 5.08 (d, $J_{1',2'}$=11.2 Hz, 1H; H-1′), 5.47 (dd, $J_{3',4'}$=8.2 Hz, 1H; H-3′), 5.55 (dd, $J_{4',5'}$=9.3 Hz, 1H; H-4′), 7.20–8.00 ppm (m, 35H; aromatic); ^{13}C NMR: δ=55.53, 63.33, 67.75, 69.65, 70.04, 72.01, 72.43, 73.34, 73.75, 73.79, 75.54, 77.46, 78.96, 80.14, 98.67, 100.59, 127.32, 127.58 (×2), 127.80, 127.92, 128.18, 128.22 (×2), 128.31, 128.45 (×3), 128.51 (×3), 128.52 (×3), 128.57 (×3), 128.63 (×2), 129.04 (×2), 129.10, 129.30, 129.81, 129.86 (×2), 129.92 (×4), 133.13, 133.34, 133.51, 133.53, 138.07, 138.52, 139.47, 164.99, 165.27, 165.90, 166.21 ppm; HR-FAB MS: calcd for $C_{62}H_{59}O_{15}$ $[M+H]^+$: 1043.3854; found: 1043.3855.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-galactopyranoside (50): This compound was obtained by meth-

od A from **4** and **49**[43] in 90% yield. Analytical data for **50** were essentially the same as reported previously.[83]

6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (52): This compound was obtained by method D from **4** and **51** in 82% yield. $R_f = 0.55$ (ethyl acetate/hexane, 1:1, v/v); $[\alpha]_D^{27} = +2.82°$ ($c = 1$ in $CHCl_3$); ^{1}H NMR: $\delta = 1.12$, 1.16, 1.29 (3s, 12H; CH_3), 3.75–3.84 (m, 2H; H-5, 6b), 3.92–3.96 (dd, $J_{6a,6b} = 2.5$ Hz, 1H; H-6a), 4.00–4.03 (dd, $J = 1.2$ Hz, 1H; H-6a′), 4.07–4.11 (m, 1H; H-5′), 4.12–4.15 (dd, $J_{2,3} = 2.4$ Hz, 1H; H-2), 4.34–4.37 (dd, $J_{6a',6b'} = 2.4$ Hz, 1H; H-6b′), 4.42 (dd, $J_{3,4} = 5.2$ Hz, 1H; H-3), 4.54–4.58 (dd, $J_{4,5} = 3.4$ Hz, 1H; H-4), 4.97 (d, $J_{1',2'} = 7.9$ Hz, 1H; H-1′), 5.34 (d, $J_{1,2} = 5.0$ Hz, 1H; H-1), 5.43–5.50 (dd, $J_{2',3'} = 7.9$ Hz, 1H; H-2′), 5.60 (dd, 1H; H-4′), 5.83 (dd, $J_{3'4'} = 9.6$ Hz, 1H; H-3′), 7.18–8.00 ppm (m, 20H; aromatic); ^{13}C NMR: $\delta = 24.41$, 25.02, 25.84, 26.05, 63.07, 63.42, 67.72, 68.48, 69.98, 70.51, 70.70, 71.15, 71.99, 72.33, 73.20, 96.33, 101.41, 108.66, 109.44, 128.38, 128.45 (×2), 128.53 (×2), 128.57 (×3), 128.63, 129.98, 129.01, 129.52, 129.79, 129.86, 129.94 (×3), 130.00 (×2), 130.09, 130.18, 133.24, 133.37, 133.58, 165.34, 165.38, 165.99, 166.36 ppm; HR-FAB MS: calcd for $C_{46}H_{47}O_{15}$ $[M+H]^+$: 839.2915; found: 839.2915.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (54): This compound was obtained by method C from **4** and **53**[44] in 99% yield. Analytical data for **54** were essentially the same as reported previously.[84]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (55): This compound was obtained by method A from **6** and **47**[42] in 92% yield. $R_f = 0.20$ (ethyl acetate/hexane, 3:7, v/v); $[\alpha]_D^{27} = +6.24°$ ($c = 1$ in $CHCl_3$); ^{1}H NMR: $\delta = 3.31$ (s, 3H; OCH_3), 3.40–3.42 (dd, 1H; H-6a), 3.49–3.56 (m, 2H; H-2, 5), 3.68–3.73 (dd, $J_{6a,6b} = 2.5$ Hz, 1H; H-6b), 3.89–3.96 (m, 2H; H-4, 5′), 4.02 (dd, $J_{3,4} = 5.9$ Hz, 1H; H-3), 4.19 (dd, $J_{6a',6b'} = 7.6$ Hz, 1H; H-6b′), 4.33 (d, $J = 9.7$ Hz, 1H; CH_2Ph), 4.38–4.44 (m, 1H; H-6a′), 4.59 (d, $J_{1,2} = 3.6$ Hz, 1H; H-1), 4.65 (d, $J = 12.3$ Hz, 1H; CH_2Ph), 4.72–4.83 (m, 3H; H-4′, CH_2Ph), 4.92 (d, $J = 11.2$ Hz, 1H; CH_2Ph), 5.19 (d, $J = 11.1$ Hz, 1H; CH_2Ph), 5.28–5.36 (dd, $J_{2',3'} = 4.5$ Hz, 1H; H-2′), 5.67–5.74 (dd, $J_{3',4'} = 8.1$ Hz, 1H; H-3′), 5.86 (d, $J_{1',2'} = 3.4$ Hz, 1H; H-1′), 7.19–8.05 ppm (m, 35H; aromatic); ^{13}C NMR: $\delta = 55.59$, 61.62, 67.76, 68.03, 69.71, 70.51, 71.16, 72.07, 73.81, 73.86, 75.45, 76.93, 77.43, 78.84, 80.05, 98.77, 100.60, 127.38, 127.43 (×3), 127.98, 128.29 (×4), 128.46 (×2), 128.52 (×3), 128.57 (×3), 128.66 (×4), 128.78 (×2), 129.00, 129.27, 129.38, 129.73, 129.87 (×2), 129.92 (×2), 130.02 (×2), 130.05 (×2), 133.39, 133.52, 133.64, 138.01, 138.55, 139.59, 165.10, 165.65, 166.05 ppm; HR-FAB MS: calcd for $C_{62}H_{59}O_{15}$ $[M+H]^+$: 1043.3854 found 1043.3855.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (56): This compound was obtained by method A from **6** and **53**[44] in 84% yield. Analytical data for **56** were essentially the same as reported previously.[85]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (57): This compound was obtained by method A from **8** and **47**[42] in 85% yield. Analytical data for **57** were essentially the same as reported previously.[86]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (58): This compound was obtained by method A from **8** and **53**[44] in 87% yield. $R_f = 0.37$ (ethyl acetate/hexane, 3:7, v/v); $[\alpha]_D^{26} = +12.0°$ ($c = 1$ in $CHCl_3$); ^{1}H NMR: $\delta = 3.41$ (s, 3H; OCH_3), 3.50 (dd, $J_{4,5} = 9.3$ Hz, H; H-4), 3.51–3.57 (dd, $J_{2,3} = 3.6$ Hz, 1H; H-2), 3.75–3.85 (m, 2H; H-5, 6b), 3.88–3.94 (dd, $J_{6a,6b} = 4.9$ Hz, 1H; H-6a), 4.00 (dd, $J_{3,4} = 9.2$ Hz, 1H; H-3), 4.27–4.33 (dd, $J_{6a',6b'} = 4.3$ Hz, 1H; H-6b′), 4.34–4.40 (m ,1H; H-5, 4.57–4.67 (m, $J_{1,2} = 3.6$ Hz, 4H; H-1, 6a′, CH_2Ph), 4.74–4.82 (m, 2H; CH_2Ph), 4.96–5.00 (dd, $J = 11.1$ Hz, 2H; CH_2Ph), 5.12 (d, $J_{1',2'} = 1.5$ Hz, 1H; H-1′), 5.69 (dd, $J_{2',3'} = 1.7$ Hz, 1H; H-2′), 5.82–5.87 (dd, $J_{3',4'} = 3.3$ Hz, 1H; H-3′), 6.04 (dd, $J_{4',5'} = 10.0$ Hz, 1H; H-4′), 7.20–8.10 ppm (m, 35H; aromatic); ^{13}C NMR: $\delta = 55.41$, 60.56, 62.89, 66.83, 67.08, 68.82, 69.08, 70.06, 70.15, 70.45, 73.64, 75.21, 75.90, 76.28, 77.43, 77.91, 79.10, 80.41, 82.30, 97.93, 98.09, 127.77, 127.82 (×2), 127.95, 128.06, 128.14 (×2), 128.29 (×2), 128.48 (×2), 128.58 (×3), 128.63 (×4), 128.65 (×5), 128.75 (×2), 129.18, 129.29, 129.54, 129.89 (×4), 130.03 (×2), 130.12, 133.23, 133.33, 133.60, 133.85, 134.26, 138.36, 138.39, 138.92 ppm; HR-FAB MS: calcd for $C_{62}H_{59}O_{15}$ $[M+H]^+$: 1043.3854, found: 1043.3855.

Methyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-4,6-*O*-benzylidene-α-D-glucopyranoside (59): This compound was obtained by method A from **14** and **43**[40] in 85% yield (α/β 7.7:1). Analytical data for **59** were essentially the same as reported previously.[87]

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (60): This compound was obtained by method A from **14** and **45**[41] in 99% yield (α/β 4.5:1). Selected analytical data for α-**60**: $R_f = 0.40$ (ethyl acetate/hexane, 3:7, v/v); ^{1}H NMR: $\delta = 4.95$ (d, $J_{1,2} = 3.1$ Hz, 1H; H-1), 4.97 ppm (d, $J_{1',2'} = 4.5$ Hz, 1H; H-1′); ^{13}C NMR: $\delta = 29.91$, 55.06, 68.26, 68.73, 70.27, 70.40, 73.05, 73.53, 73.71, 74.88, 75.06, 75.16, 75.88, 76.44, 77.43, 77.77, 78.18, 79.18, 80.96, 82.37, 94.34, 96.54, 127.58, 127.71, 127.77, 127.81, 127.86 (×2), 127.89 (×3), 128.04, 128.10 (×2), 128.19 (×2), 128.24 (×3), 128.37 (×2), 128.50 (×2), 128.51 (×2), 128.57 (×4), 128.59 (×4), 128.69 (×2), 138.10, 138.15, 138.34, 138.51, 138.66, 138.90, 138.96 ppm; HR-FAB MS: calcd for $C_{62}H_{67}O_{11}$ $[M+H]^+$: 987.4683; found: 987.4685

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (61): This compound was obtained by method A from **14** and **47**[42] in 95% yield (α/β 3.5:1). Analytical data for **61** were essentially the same as reported previously.[88]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-β-D-galactopyranoside (62): This compound was obtained by method A from **14** and **49**[43] in 82% yield (α/β 4.1:1). Selected analytical data for α-**62**: $R_f = 0.32$ (ethyl acetate/hexane, 3:7, v/v); ^{1}H NMR: $\delta = 4.46$ (d, $J_{1'\beta\beta,\ 2'\beta\beta} = 5.3$ Hz, 1H; H-1′(ββ)), 4.63 (d, $J_{1\beta\beta,2\beta\beta} = 5.5$ Hz, 1H; H-1 (ββ)), 4.66 (d, $J_{1\alpha\beta,2\alpha\beta} = 6.8$ Hz, 1H; H-1 (αβ)), 4.77 ppm (d, $J_{1'\alpha\beta,2'\alpha\beta} = 8.1$ Hz, 1H; H-1′ (αβ)); ^{13}C NMR: $\delta = 97.23$ (α′), 102.49 (β), 102.52 (β), 103.93 ppm (β′); HR-FAB MS: calcd for $C_{62}H_{61}O_{14}$ $[M+H]^+$: 1029.4261; found: 1029.4260.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (63): This compound was obtained by method A from **14** and **53**[44] in 85% yield (α/β 2.7:1). Analytical data for **63** were essentially the same as reported previously.[89]

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (64): This compound was obtained by method A from **10** and **43**[40] in 78% yield (α/β 15:1). Selected analytical data for α-**64**: $R_f = 0.50$ (ethyl acetate/hexane, 1:1, v/v); ^{1}H NMR: $\delta = 4.54$ (d, $J_{1,2} = 3.3$ Hz, 1H; H-1 (βα)), 4.66 (d, $J_{1',2'} = 4.5$ Hz, 1H; H-1′ (βα)), 5.35 (d, $J_{1,2} = 6.4$ Hz, 1H; H-1 (αα)), 5.47 ppm (d, $J_{1',2'} = 3.6$ Hz, 1H; H-1′ (αα)); ^{13}C NMR: $\delta = 95.86$, 97.91, 98.53, 98.83, 102.20, 102.51 ppm; HR-FAB MS: calcd for $C_{40}H_{47}O_{14}$ $[M+H]^+$: 751.2966 found 751.2963.

Methyl 2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (65): This compound was obtained by method A from **10** and **45**[41] in 88% yield (α/β 9.3:1). Selected analytical data for α-**65**: $R_f = 0.62$ (ethyl acetate/hexane, 1:1, v/v); ^{1}H NMR: $\delta = 1.88$, 2.01, 2.02 (3s, 9H; $3COCH_3$), 3.44 (s, 3H; OCH_3), 3.57–3.62 (dd, $J_{2',3'} = 3.6$ Hz, 1H; H-2′), 3.66–3.84 (m, 6H; H-2, 4, 5, 6a, 6b, 6b′), 3.91–3.97 (dd, $J_{5',6a'} = 3.3$ Hz, $J_{6a',6b'} = 12.5$ Hz, 1H; H-6a′), 4.05 (dd, $J_{3,4} = 8.9$ Hz, 1H; H-3), 4.13–4.18 (m, 1H; H-5), 4.48–4.70 (m, 7H; CH_2Ph), 4.82 (d, $J = 10.6$ Hz, 1H; CH_2Ph), 4.87–4.96 (m, $J_{1,2} = 9.0$ Hz, $J_{1',2'} = 5.6$ Hz, 3H; H-1, 1′, 4′), 5.52 (dd, $J_{3',4'} = 9.7$ Hz, 1H; H-3′), 7.21–7.36 ppm (m, 20H; aromatic); ^{13}C NMR: $\delta = 20.82$, 20.91, 21.07, 55.21, 55.43, 67.39, 68.42, 68.62, 68.70, 70.48, 70.66, 72.30, 72.83, 73.15, 73.75, 75.13, 75.26, 75.44, 75.58, 75.91, 76.22, 77.44, 78.24, 80.62, 83.50, 94.33, 96.58, 99.60, 127.73, 127.92, 127.96, 128.02, 128.07 (×2), 128.13 (×2), 128.52, 128.61 (×3), 128.73, 137.99, 138.11, 138.29, 138.62, 170.05, 170.79 ppm; HR-FAB MS: calcd for $C_{47}H_{55}O_{14}$ $[M+H]^+$: 843.3592 found 843.3594.

Methyl 4-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (66): This compound was obtained by method A from **10** and **47**[42] in 89% yield (α/β >19:1). Analytical data for α-**66**: $R_f = 0.50$ (ethyl acetate/hexane, 1:1, v/v); ^{1}H NMR: $\delta = 1.91$, 1.99, 2.00 (3s, 9H; $3COCH_3$), 3.38 (s, 3H; OCH_3), 3.43–3.48 (dd, $J_{2',3'} = 10.1$ Hz, 1H; H-2′), 3.55–3.60 (dd, $J_{5,6a} = 3.6$ Hz, $J_{5,6b} = 9.0$ Hz, 1H; H-5), 3.66 (dd, $J = 9.2$ Hz, 1H; H-6b′), 3.75–3.80 (dd, $J_{6a',6b'} = 12.3$ Hz, 1H; H-6a′), 3.80.3.90 (m, 2H; H-6b, CH_2Ph), 3.95–4.10 (m, 4H; H-5′, 6a, CH_2Ph), 4.30–4.45 (dd, $J = 12.3$ Hz, 2H; CH_2Ph), 4.45–4.60 (m, 4H; H-4, CH_2Ph), 4.66 (s, 1H; H-3), 4.70–4.76 (dd, $J_{2,3} = 4.2$ Hz, 1H; H-2), 4.92 (dd, $J_{4',5'} =$

9.9 Hz, 1H; H-4′), 5.02 (d, $J_{1,2}$ = 11.8 Hz, 1H; H-1), 5.40 (dd, $J_{3',4'}$ = 9.7 Hz, 1H; H-3′), 5.69 (d, $J_{1',2'}$ = 3.6 Hz, 1H; H-1′), 7.05–7.35 ppm (m, 20H; aromatic); ^{13}C NMR: δ = 20.92, 20.96, 21.02, 55.47, 62.05, 67.95, 68.71, 69.16, 69.70, 71.96, 73.16, 73.51, 73.70, 74.51, 77.45, 80.36, 81.83, 96.63, 97.95, 126.82 (×2), 127.29, 127.63 (×2), 127.76 (×2), 127.87, 128.00, 128.17, 128.39 (×2), 128.44 (×2), 128.57 (×3), 128.61 (×2), 128.67 (×2), 137.74, 138.13, 139.30, 169.92, 170.28, 170.78 ppm; HR-FAB MS: calcd for $C_{47}H_{55}O_{14}$ $[M+H]^+$: 843.3592 found 843.3594.

Methyl 6-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (67): This compound was obtained by method A from **10** and **49**[43] in 74% yield (α/β 4.8:1). Analytical data for α-**67**: R_f = 0.40 (ethyl acetate/hexane, 1:1, v/v); ^{1}H NMR: δ = 1.99, 2.00, 2.01 (3s, 9H; 3 $COCH_3$), 3.56 (dd, $J_{2,3}$ = 3.5 Hz, 1H; H-2), 3.61 (s, 3H; OCH_3), 3.61–3.66 (m, 1H; H-5′), 3.88 (dd, $J_{6a',6b'}$ = 10.3 Hz, 1H; H-6b′), 4.01–4.06 (dd, $J_{6a,6b}$ = 12.2 Hz, 1H; H-6b), 4.13–4.19 (m, 1H; H-5), 4.23–4.29 (m, 2H; H-6a, 6a′), 4.55–4.67 (m, 2H; CH_2Ph), 4.72 (d, $J_{4',5'}$ = 8.0 Hz, 1H; H-4′), 4.79 (d, $J_{1,2}$ = 3.5 Hz, 1H; H-1), 4.97 (dd, $J_{4,5}$ = 10.0 Hz, 1H; H-4), 5.47 (dd, $J_{3,4}$ = 9.6 Hz, 1H; H-3), 5.57 (dd, $J_{2',3'}$ = 3.4 Hz, 1H; H-2′), 5.74–5.82 (dd, $J_{3',4'}$ = 7.9 Hz, 1H; H-3′), 5.87 (d, $J_{1',2'}$ = 3.4 Hz, 1H; H-1′), 7.20–8.10 ppm (m, 20H; aromatic); ^{13}C NMR: δ = 21.03, 21.24, 57.72, 62.27, 66.84, 67.83, 68.94, 69.23, 70.20, 72.17, 72.98, 73.53, 77.64, 96.85, 102.76, 128.25 (×2), 128.35, 128.48 (×2), 128.58 (×2), 128.75 (×2), 128.88 (×2), 128.96, 129.12, 129.56, 129.95 (×2), 130.02 (×2), 130.17 (×2), 133.45, 133.91, 137.76, 165.62, 165.65, 165.86, 169.96, 170.33, 170.79 ppm; HR-FAB MS: calcd for $C_{47}H_{49}O_{17}$ $[M+H]^+$: 885.2970; found: 885.2970.

Methyl 6-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (68): This compound was obtained by method A from **10** and **53**[44] in 70% yield (α/β 2.7:1). Selected analytical data for α-**68**: R_f = 0.57 (ethyl acetate/hexane, 1:1, v/v); ^{1}H NMR: ^{1}H NMR: δ = 2.00, 2.01, 2.03 (3s, 9H; 3 $COCH_3$), 3.39 (s, 3H; OCH_3), 4.55 (d, $J_{1,2}$ = 7.3 Hz, 1H; H-1), 4.93 (d, $J_{1',2'}$ = 8.1 Hz, 1H; H-1′), 7.21–7.36 ppm (m, 20H; aromatic); ^{13}C NMR: δ = 97.09 (α′), 98.24 ppm (α); HR-FAB MS: calcd for $C_{47}H_{55}O_{14}$ $[M+H]^+$: 843.3592 found 843.3594.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (70): This compound was obtained by method A from **4** and **69**[44] in 81% yield. Analytical data for **70** were essentially the same as reported previously.[90]

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glycopyranosyl)-1-thio-β-D-glucopyranoside (71): This compound was obtained by method A from **14** and **69**[44] in 90% yield (α/β 2:1). Analytical data for **71** were essentially the same as reported previously.[90]

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-galactopyranoside (73): This compound was obtained by method A from **4** and **72**[61] in 85% yield. Analytical data for **73** were essentially the same as reported previously.[90]

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glycopyranosyl)-1-thio-β-D-galactopyranoside (74): This compound was obtained by method A from **14** and **72**[61] in 86% yield (α/β 1.8:1). Analytical data for **74** were essentially the same as reported previously.[90]

Ethyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (76): This compound was obtained by method A from **14** and **75**[62] in 93% yield (α/β 5:1). Analytical data for **76** were essentially the same as reported previously.[22]

Ethyl 3-*O*-(3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-D-glycopyranosyl)-2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (78): This compound was obtained by method A from **26** and **77**[63] in 71% yield (α only). Analytical data for α-**78**: R_f = 0.48 (ethyl acetate/hexane, 3:7, v/v); $[\alpha]_D^{28} = -3.8°$ (c = 1 in $CHCl_3$); ^{1}H NMR: δ = 1.28 (t, J = 7.4 Hz, 3H; CH_2CH_3), 1.42 (d, J = 6.2 Hz, 3H; CH_3), 2.11 (s, 3H; $COCH_3$), 2.50–2.70 (m, 2H; CH_2CH_3), 3.61–3.77 (m, 4H; H-2, 4, 6a, 6b), 4.05–4.15 (m, 3H; H-2′, 4′, 5′), 4.15–4.27 (m, 2H; H-3′, 5), 4.60–4.76 (m, 5H; CH_2Ph), 5.06 (d, J = 10.5 Hz, 1H; CH_2Ph), 5.24 (d, $J_{1,2}$ = 3.4 Hz, 1H; H-1), 5.30 (s, 1H; H-1′), 5.50 (s, 1H; CHPh), 5.80 (dd, $J_{2,3}$ = 9.7 Hz, 1H; H-3), 7.20–7.50 ppm (m, 20H; aromatic); ^{13}C NMR: δ = 15.22, 18.03, 21.23, 25.54, 29.90, 63.39, 68.93, 69.03, 70.87, 72.99, 73.11, 75.89, 77.53, 77.84, 77.92, 79.75, 80.42, 82.33, 126.51 (×2), 127.77, 127.84, 127.95, 128.03 (×2), 128.07 (×2), 128.28 (×2), 128.52 (×2), 128.54 (×2), 128.59 (×2), 128.63 (×2), 129.09, 137.40, 137.82, 138.16, 138.46 ppm; HR-FAB MS: calcd for $C_{44}H_{50}O_{10}S$ $[M+H]^+$: 771.3125; found: 771.3202.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (80): This compound was obtained by method A from **14** and **79**[64] in 99% yield (α/β 2:1). Selected analytical data for α- and β-**80**: R_f = 0.40 (ethyl acetate/hexane, 3:7, v/v); ^{1}H NMR: δ = 4.58 (d, $J_{1',2'}$ = 5.8 Hz, 1H; H-1′), 4.97 (d, $J_{1,2}$ = 10.0 Hz, 1H; H-1), 5.28–5.43 (m, 4H; H-2(α), 4(β), 2(α), 4(β)), 5.74–5.84 ppm (m, 2H; H-3(α), 3(β)); ^{13}C NMR: δ = 67.49, 68.56, 68.84, 69.80, 70.03, 70.36, 70.69, 70.80, 73.55, 73.67, 74.49, 74.54, 75.01, 75.10, 75.17, 77.44, 77.54, 77.86, 78.45, 80.36, 82.15, 82.52, 84.74, 86.00, 87.09, 97.53, 104.11, 127.63, 127.80, 127.90, 127.94, 127.98, 128.08, 128.11, 128.12, 128.14, 128.33, 128.39, 128.46, 128.53, 128.55, 128.58, 128.64, 129.04, 129.17, 129.33, 129.45, 129.93, 130.09,132.31, 132.54, 132.65, 133.05, 133.38, 133.49, 133.68, 138.18, 138.26, 138.32, 138.43, 138.70, 138.80, 139.17, 165.25, 165.29, 165.35, 165.58, 165.96 ppm; HR-FAB MS: calcd for $C_{67}H_{63}O_{13}S$ $[M+H]^+$: 1107.3989; found: 1107.3987.

Phenyl 3-*O*-acetyl-2-azido-4-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-2-deoxy-1-thio-β-D-glucopyranoside (82): This compound was obtained by method A from **14** and **81**[65] in 83% yield (α/β 1.5:1). Selected analytical data for α- and β-**82**: R_f = 0.50 (ethyl acetate/hexane, 3:7, v/v); ^{1}H NMR: δ = 5.17 ppm (d, $J_{1,2}$ = 3.5 Hz, 1H; H-1); ^{13}C NMR: δ = 21.01, 21.05, 63.42, 63.57, 65.22, 68.42, 68.69, 70.63, 72.38, 73.68, 74.55, 74.69, 74.88, 74.96, 75.23, 75.34, 75.86, 75.94, 76.16, 77.43, 78.05, 78.93, 79.84, 80.57, 82.03, 82.45, 84.86, 85.88, 87.15, 97.51, 104.16, 127.23, 127.73, 127.85, 127.91, 127.99, 128.07, 128.12, 128.16, 128.20, 128.49, 128.55, 128.59, 128.63, 128.67, 128.72, 129.39, 131.18, 131.99, 133.60, 133.95, 137.77, 137.97, 138.14, 138.27, 138.48, 138.63, 138.68, 138.92, 169.89, 169.96 ppm; HR-FAB MS: calcd for $C_{55}H_{58}N_3O_{10}S$ $[M+H]^+$: 952.3843; found: 952.3845.

4-Pentenyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (84): This compound was obtained by method A from **14** and **83**[66] in 91% yield (α/β 2:1). Selected analytical data: R_f = 0.30 (ethyl acetate/hexane, 1:4, v/v); ^{1}H NMR: δ = 4.36 (d, J = 7.8 Hz, 1H; H-1 (β′)), 4.40 (d, J = 7.8 Hz, 1H; H-1 (β)), 4.49 (d, J = 7.6 Hz, 1H; H-1 (β)), 5.05 ppm (d, J = 3.4 Hz, 1H; H-1 (α′)); ^{13}C NMR: δ = 97.23 (β′), 103.60 (β), 103.69 (β), 104.17 ppm (α′); HR-FAB MS: calcd for $C_{66}H_{72}NaO_{11}$: 1063.4972; found: 1063.4976.

4-Pentenyl 3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranoside (86): This compound was obtained by method A from **14** and **85**[67] in 85% yield (α/β 2:1). Selected analytical data for α-**86**: R_f = 0.32 (ethyl acetate/hexane, 2:3, v/v); ^{1}H NMR: δ = 1.68 (m, 2H; $CH_2CH_2CH_2$), 2.10 (m, 2H; CH_2CH=), 3.41–3.49 (m, 2H; H-5′, OCH_2), 3.52–3.71 (m, 4H; H-2, 2′ ,4, 5), 3.72–3.88 (m, 2H; H-3, 3′), 3.88–4.00 (m, 2H; H-4′, OCH_2), 4.06 (dd, 1H; H-6a′), 4.27–4.39 (m, 3H; H-6a, 6b, 6b′), 4.43–4.59 (m, 4H; CH_2Ph), 4.54–4.63 (m, 3H; CH_2Ph, CH_2CCl_3), 4.70–4.84 (m, 3H; H-1, CH_2Ph), 4.92 (d, J = 10.9 Hz, 1H; CH_2Ph), 4.94–5.10 (m, 2H; CH_2=), 5.20 (d, $J_{1',2'}$ = 3.5 Hz, 1H; H-1′), 5.49 (m, 1H; NH), 5.53 (s, 1H; CHPh), 5.80 (m, 1H; CH=), 7.00–7.56 ppm (m, 25H; aromatic); ^{13}C NMR: δ = 28.86, 29.91, 30.26, 31.15, 53.72, 66.52, 68.82, 69.14, 69.73, 70.77, 71.53, 72.25, 73.73, 74.42, 75.12, 75.89, 77.43 (×2), 79.50, 82.14, 95.54, 101.42, 126.67 (×2), 127.81 (×2), 128.00 (×4), 128.12 (×2), 128.24 (×5), 128.41 (×4), 128.49 (×2), 128.56 (×2), 128.61 (×2), 129.30, 137.81, 137.99, 138.08, 138.40, 138.49, 138.93, 154.11 ppm; HR-FAB MS: calcd for $C_{55}H_{60}NaCl_3NO_{12}$ $[M+H]^+$: 1054.3079; found: 1054.3079.

Methyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (87): This compound was obtained by method A from **53** and **90** in 81% yield and also by method B from **53** and **76** in 89% yield. Analytical data for **87** were essentially the same as reported previously.[22]

Methyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (88): This compound was obtained by method A from **53** and **93** in 80% yield and also by method B from **53** and **80** in 75% yield. Analytical data for **88** were essentially the same as reported previously.[91]

2-Thiazolinyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (90): This compound was

obtained by method B from **40** and **89** in 85% yield (α/β 1.2:1). Compound **90** was also obtained from **41** and **49** (method B) in 77% yield (α/β 2:1), as well as from **99** and **89** (method F) in 87% yield (α/β 2:1). Analytical data for **90** were essentially the same as reported previously.[22]

2-Thiazolinyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (92): This compound was obtained by method B from **40** and **91** in 80% yield (α/β 2.1:1). Analytical data for **92** were essentially the same as reported previously.[76]

2-Thiazolyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (93): This compound was obtained by method B from **40** and **36** in 98% yield (α/β 1.1:1). Compound **93** was also obtained from **41** and **36** (method B) in 75% yield (α/β 2:1); from **96** and **36** (method C) in 93% yield (α/β 1.4:1); from **97** and **36** (method E) in 45% yield (α/β 1.2:1); as well as from **99** and **36** (method F) in 50% yield (α/β 1.1:1). Analytical data for **93** were essentially the same as reported previously.[76]

2-Thiazolinyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (95): This compound was obtained by method C from **89** and **94** in 99% yield (α/β 7:1). Selected analytical data for α-**95**: $R_f = 0.42$ (acetone/toluene, 1:9, v/v); ^{1}H NMR: $\delta = 3.29$ (dd, $J = 7.3$ Hz, 1H; H-4), 3.37–3.45 (m, 3H; H-5, CH_2N), 3.70–3.76 (m, 2H; H-2, 4′), 3.85 (dd, $J = 9.3$ Hz, 1H; H-6a′), 3.90 (dd, $J_{3',4'} = 2.6$ Hz, 1H; H-3′), 4.00 (dd, $J_{2',3'} = 3.5$ Hz, 1H; H-2′), 4.10–4.28 (m, 6H; H- 3, 5′, 6a, 6b′, CH_2S), 4.29–4.40 (m, 2H; H-6b, CH_2Ph), 4.47–4.90 (m, 9H; CH_2Ph), 5.38 (d, $J_{1,2} = 9.9$ Hz, 1H; H-1), 5.45 (s, 1H; CHPh), 5.70 (d, $J_{1',2'} = 3.4$ Hz, 1H; H-1′), 7.10–7.40 ppm (m, 30H; aromatic); ^{13}C NMR: $\delta = 29.93$, 35.02, 68.81, 68.94, 69.15, 70.29, 72.16, 73.05, 73.29, 75.09, 75.55, 76.01, 76.47, 77.45 (×4), 78.13, 79.71, 82.33, 85.45, 126.44 (×2), 127.55, 127.58, 127.62 (×2), 127.69, 127.75 (×3), 127.77 (×3), 128.08, 128.18, 128.35 (×4), 128.40 (×3), 128.45 (×2), 128.50 (×2), 128.62 (×4), 129.52, 137.05, 137.42, 138.52, 138.65, 138.84, 139.10 ppm; HR-FAB MS: calcd for $C_{57}H_{60}O_{10}S_2$ $[M+H]^+$: 982.3659; found: 982.3649.

2-Thiazolinyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (98): This compound was obtained by method E from **3** and **36** in 98% yield. Analytical data for **98** were essentially the same as reported previously.[76]

Ethyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (100): This compound was obtained by method A from **69** and **93** in 93% yield. Selected analytical data: $R_f = 0.35$ (ethyl acetate/hexane, 2:3, v/v); $[\alpha]_D^{25} = +19.6°$ ($c = 1$ in $CHCl_3$); ^{1}H NMR: $\delta = 1.15$ (t, 3H; CH_2CH_3), 2.58 (m, 2H; CH_2CH_3), 4.47 (d, $J_{1,2} = 7.8$ Hz, 1H; H-1), 4.71 (d, $J_{1'',2''} = 3.4$ Hz, 1H; H-1″), 4.90 ppm (d, $J_{1',2'} = 7.9$ Hz, 1H; H-1′); ^{13}C NMR: $\delta = 14.93$, 23.68, 67.03, 67.85, 68.75, 69.60, 69.98, 70.39, 70.48, 70.93, 72.23, 73.05, 73.34, 73.51, 73.61, 74.32, 74.95, 75.06, 75.75, 77.43, 80.15, 82.02, 83.27, 97.34, 101.11, 127.67, 127.84, 127.98, 128.05, 128.14, 128.18, 128.24, 128.46, 128.53, 128.55, 128.58, 128.62, 129.04, 129.12, 129.18, 129.22, 129.50, 129.66, 129.89, 129.97, 130.03, 130.13, 133.34, 133.50, 133.62, 138.25, 138.53, 138.85, 139.18, 165.21, 165.29, 165.34, 165.89, 165.99 ppm; HR-FAB MS: calcd for $C_{90}H_{84}O_{21}S$ $[M+H]^+$: 1532.5226; found: 1533.5304.

2-Thiazolinyl *O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (101): This compound was obtained by method B from **36** and **100** in 77% yield. Selected analytical data: $R_f = 0.52$ (ethyl acetate/hexane, 1:1, v/v); ^{1}H NMR: $\delta = 4.40$ (d, $J = 3.4$ Hz, 1H), 4.50 (d, $J = 7.8$ Hz, 1H), 4.90 (d, $J = 7.9$ Hz, 1H), 5.82 ppm (d, $J = 10.3$ Hz, 1H); ^{13}C NMR: $\delta = 97.87$, 100.17, 101.30, 101.81 ppm; HR-FAB MS: calcd for $C_{119}H_{109}O_{29}NS_2$ $[M+H]^+$: 2080.6526; found: 2080.6604.

Ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (102): This compound was obtained by method A from **69** and **101** in 59% yield. Selected analytical data: $R_f = 0.38$ (ethyl acetate/hexane, 2:3, v/v); $[\alpha]_D^{27} = 0.2°$ ($c = 1$ in $CHCl_3$); ^{1}H NMR: $\delta = 4.57$ (d, $J = 4.8$ Hz, 1H), 4.67 (d, $J = 7.2$ Hz, 1H), 4.76 (d, $J = 3.5$ Hz, 1H), 4.85 (d, $J = 11.5$ Hz, 1H), 5.01 ppm (d, $J = 7.8$ Hz, 1H); ^{13}C NMR: $\delta = 81.80$, 97.35 (α), 100.05 (β), 101.00 (β), 104.20 ppm (β); HR-FAB MS: calcd for $C_{144}H_{128}O_{37}NaS$ $[M+Na]^+$: 2503.7753; found: 2503.7754.

2-Thiazolinyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (104): This compound was obtained by method B from **36** and **70** in 71% yield. Selected analytical data: $R_f = 0.47$ (acetone/toluene, 1:9, v/v); ^{1}H NMR: $\delta = 4.97$ (d, $J = 7.7$ Hz, 1H), 5.19 (d, $J = 7.8$ Hz, 1H), 5.82 ppm (d, $J = 10.3$ Hz, 1H); ^{13}C NMR: $\delta = 100.13$, 101.51, 102.35 ppm; HR-FAB MS: calcd for $C_{91}H_{75}NO_{25}S_2$ $[M+H]^+$: 1646.4148; found: 1646.4148.

Ethyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl-(1→3)-2-*O*-benzyl-4,6-benzylidene-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (105): This compound was obtained by method A from **69** and **95** in 82% yield. Selected analytical data for **105**: $R_f = 0.35$ (ethyl acetate/hexane, 3:7, v/v); ^{1}H NMR: $\delta = 5.48$ (d, $J = 9.6$ Hz, 1H), 5.60 ppm (d, $J = 3.6$ Hz, 1H); ^{13}C NMR: $\delta = 96.61$, 101.82, 104.75 ppm; HR-FAB MS: calcd for $C_{83}H_{82}NaO_{18}S$ $[M+Na]^+$: 1421.5120; found: 1421.5116.

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[1] Z. J. Witczak, in *Carbohydrates in Drug Design* (Eds.: Z. J. Witczak, K. A. Nieforth), Dekker, New York, **1997**, p. 1.
[2] J. C. McAuliffe, O. Hindsgaul, in *Molecular and Cellular Glycobiology* (Eds.: M. Fukuda, O. Hindsgaul), University Press, Oxford, **2000**, p. 250.
[3] K. Toshima, K. Tatsuta, *Chem. Rev.* **1993**, *93*, 1503.
[4] B. G. Davis, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2137.
[5] M. Nitz, D. R. Bundle, in *Glycoscience: Chemistry and Chemical Biology, Vol. 2* (Eds.: B. Fraser-Reid, K. Tatsuta, J. Thiem), Springer, Berlin, Heidelberg, New York, **2001**, p. 1497.
[6] K. Igarashi, *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 243.
[7] R. R. Schmidt, K. H. Jung, in *Carbohydrates in Chemistry and Biology, Vol. 1* (Eds.: B. Ernst, G. W. Hart, P. Sinay), Wiley-VCH, Weinheim, New York, **2000**, p. 5.
[8] P. J. Garegg, *Adv. Carbohydr. Chem. Biochem.* **1997**, *52*, 179.
[9] S. Oscarson, in *Carbohydrates in Chemistry and Biology, Vol. 1* (Eds.: B. Ernst, G. W. Hart, P. Sinay), Wiley-VCH, Weinheim, New York, **2000**, p. 93.
[10] G. J. Boons, *Tetrahedron* **1996**, *52*, 1095.
[11] J. D. C. Codee, R. E. J. N. Litjens, L. J. van den Bos, H. S. Overkleeft, G. A. van der Marel, *Chem. Soc. Rev.* **2005**, *34*, 769.
[12] A. V. Demchenko, *Lett. Org. Chem.* **2005**, *2*, 580.
[13] J. Gervay, T. N. Nguyen, M. J. Hadd, *Carbohydr. Res.* **1997**, *300*, 119.
[14] J. Gervay, M. J. Hadd, *J. Org. Chem.* **1997**, *62*, 6961.
[15] T. Mukaiyama, T. Nakatsuka, S. I. Shoda, *Chem. Lett.* **1979**, 487.
[16] S. Hanessian, C. Bacquet, N. Lehong, *Carbohydr. Res.* **1980**, *80*, c17.
[17] R. B. Woodward, E. Logusch, K. P. Nambiar, K. Sakan, D. E. Ward, B. W. Au-Yeung, P. Balaram, L. J. Browne, P. J. Card, C. H. Chen, *J. Am. Chem. Soc.* **1981**, *103*, 3215.
[18] G. V. Reddy, V. R. Kulkarni, H. B. Mereyala, *Tetrahedron Lett.* **1989**, *30*, 4283.
[19] Q. Chen, F. Kong, *Carbohydr. Res.* **1995**, *272*, 149.
[20] K. Tsuboyama, K. Takeda, K. Torii, M. Ebihara, J. Shimizu, A. Suzuki, N. Sato, K. Furuhata, H. Ogura, *Chem. Pharm. Bull.* **1990**, *38*, 636.
[21] A. V. Demchenko, N. N. Malysheva, C. De Meo, *Org. Lett.* **2003**, *5*, 455.

[22] A. V. Demchenko, P. Pornsuriyasak, C. De Meo, N. N. Malysheva, *Angew. Chem.* **2004**, *116*, 3131; *Angew. Chem. Int. Ed.* **2004**, *43*, 3069.
[23] A. Ramakrishnan, P. Pornsuriyasak, A. V. Demchenko, *J. Carbohydr. Chem.* **2005**, *24*, 649.
[24] R. U. Lemieux, in *Methods in Carbohydrate Chemistry, Vol. 2* (Eds.: R. L. Whistler, M. L. Wolform), Academic Press, New York, London, **1963**, p. 226.
[25] P. Brigl, H. Keppler, *Ber. Dtsch. Chem. Ges. B* **1926**, *59*, 1588.
[26] T. Iversen, D. R. Bundle, *Carbohydr. Res.* **1982**, *103*, 29.
[27] T. Ogawa, T. Nukada, T. Kitajima, *Carbohydr. Res.* **1983**, *123*, c12.
[28] A. V. Demchenko, M. N. Kamat, C. De Meo, *Synlett* **2003**, 1287.
[29] R. U. Lemieux, J. Howard, in *Methods in Carbohydrate Chemistry, Vol. 2* (Eds.: R. L. Whistler, M. L. Wolfrom), Academic Press, New York, London, **1963**, p. 400.
[30] N. Asai, N. Fusetani, S. Matsunaga, *J. Nat. Prod.* **2001**, *64*, 1210.
[31] N. K. Kochetkov, L. V. Backinowsky, Y. E. Tsvetkov, *Tetrahedron Lett.* **1977**, *18*, 3681.
[32] A. M. P. Van Steijn, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1992**, *225*, 229.
[33] A. V. Demchenko, P. Pornsuriyasak, C. De Meo, *J. Chem. Educ.* **2006**, *83*, 782.
[34] F. Dasgupta, P. J. Garegg, *Acta Chem. Scand.* **1989**, *43*, 471.
[35] R. J. Ferrier, R. W. Hay, N. Vethaviyasar, *Carbohydr. Res.* **1973**, *27*, 55.
[36] M. S. Motawia, J. Marcussen, B. L. Moeller, *J. Carbohydr. Chem.* **1995**, *14*, 1279.
[37] H. I. Duynstee, M. C. de Koning, H. Ovaa, G. A. van der Marel, J. H. van Boom, *Eur. J. Org. Chem.* **1999**, 2623.
[38] H. Uchiro, Y. Wakiyama, T. Mukaiyama, *Chem. Lett.* **1998**, 567.
[39] M. Mikamo, *Carbohydr. Res.* **1989**, *191*, 150.
[40] Y. Kondo, *Agric. Biol. Chem.* **1975**, *39*, 1879.
[41] M. Sollogoub, S. K. Das, J.-M. Mallet, P. Sinay, *C. R. Seances Acad. Sci. Ser. 2* **1999**, *2*, 441.
[42] P. J. Garegg, H. Hultberg, *Carbohydr. Res.* **1981**, *93*, C10.
[43] I. E. Valashek, M. K. Shakhova, V. A. Minaev, G. I. Samokhvalov, *Zh. Obshch. Khim.* **1974**, *44*, 1161.
[44] G. H. Veeneman, J. H. van Boom, *Tetrahedron Lett.* **1990**, *31*, 275.
[45] A. V. Demchenko, *Curr. Org. Chem.* **2003**, *7*, 35.
[46] M. N. Kamat, A. V. Demchenko, *Org. Lett.* **2005**, *7*, 3215.
[47] A. Demchenko, T. Stauch, G. J. Boons, *Synlett* **1997**, 818.
[48] J. H. Kim, H. Yang, J. Park, G. J. Boons, *J. Am. Chem. Soc.* **2005**, *127*, 12090.
[49] J. H. Kim, H. Yang, G. J. Boons, *Angew. Chem.* **2005**, *117*, 969; *Angew. Chem. Int. Ed.* **2005**, *44*, 947.
[50] A. J. Fairbanks, *Synlett* **2003**, 1945.
[51] H. Jona, K. Takeuchi, T. Mukaiyama, *Chem. Lett.* **2000**, 1278.
[52] M. Gelin, V. Ferrieres, D. Plusquellec, *Eur. J. Org. Chem.* **2000**, 1423.
[53] A. V. Demchenko, E. Rousson, G. J. Boons, *Tetrahedron Lett.* **1999**, *40*, 6523.
[54] A. V. Demchenko, *Synlett* **2003**, 1225.
[55] N. L. Douglas, S. V. Ley, U. Lucking, S. L. Warriner, *J. Chem. Soc. Perkin Trans. 1* **1998**, 51.
[56] Z. Zhang, I. R. Ollmann, X. S. Ye, R. Wischnat, T. Baasov, C. H. Wong, *J. Am. Chem. Soc.* **1999**, *121*, 734.
[57] X. S. Ye, C. H. Wong, *J. Org. Chem.* **2000**, *65*, 2410.
[58] L. G. Green, S. V. Ley, in *Carbohydrates in Chemistry and Biology, Vol. 1* (Eds.: B. Ernst, G. W. Hart, P. Sinay), Wiley-VCH, Weinheim, New York, **2000**, p. 427.
[59] O. J. Plante, E. R. Palmacci, P. H. Seeberger, *Science* **2001**, *291*, 1523.
[60] A. V. Demchenko, C. De Meo, *Tetrahedron Lett.* **2002**, *43*, 8819.
[61] W. Birberg, H. Lonn, *Tetrahedron Lett.* **1991**, *32*, 7453.
[62] P. J. Garegg, I. Kvarnstrom, A. Niklasson, G. Niklasson, S. C. T. Svensson, *J. Carbohydr. Chem.* **1993**, *12*, 933.
[63] A. Liptak, I. Jodal, J. Harangi, P. Nanasi, *Acta Chim. Hung.* **1983**, *113*, 415.
[64] L. A. J. M. Sliedregt, G. A. van der Marel, J. H. van Boom, *Tetrahedron Lett.* **1994**, *35*, 4015.
[65] K. Fukase, Y. Aoki, I. Kinoshita, Y. Suda, M. Kurosawa, U. Zahringer, E. T. Rietschel, S. Kusumoto, *Tetrahedron Lett.* **1995**, *36*, 8645.
[66] S. Houdier, P. J. A. Vottero, *Angew. Chem.* **1994**, *106*, 365; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 354.
[67] P. Pornsuriyasak, A. V. Demchenko, *Carbohydr. Res.* **2006**, in press.
[68] B. Fraser-Reid, G. Anilkumar, M. B. Gilbert, S. Joshi, R. Kraehmer, in *Carbohydrates in Chemistry and Biology, Vol. 1* (Eds.: B. Ernst, G. W. Hart, P. Sinay), Wiley-VCH, Weinheim, New York, **2000**, p. 135.
[69] P. Pornsuriyasak, M. N. Kamat, A. V. Demchenko, *ACS Symp. Ser.* **2006**, in press.
[70] F. Weygand, H. Ziemann, *Justus Liebigs Ann. Chem.* **1962**, *657*, 179.
[71] R. R. Schmidt, J. Michel, *Angew. Chem.* **1980**, *92*, 763; *Angew. Chem. Int. Ed.* **1980**, *19*, 731.
[72] O. Kanie, Y. Ito, T. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 12073.
[73] O. Kanie, in *Carbohydrates in Chemistry and Biology, Vol. 1* (Eds.: B. Ernst, G. W. Hart, P. Sinay), Wiley-VCH, Weinheim, New York, **2000**, p. 407.
[74] D. R. Mootoo, P. Konradsson, U. Udodong, B. Fraser-Reid, *J. Am. Chem. Soc.* **1988**, *110*, 5583.
[75] B. Fraser-Reid, U. E. Udodong, Z. F. Wu, H. Ottosson, J. R. Merritt, C. S. Rao, C. Roberts, R. Madsen, *Synlett* **1992**, 927.
[76] P. Pornsuriyasak, U. B. Gangadharmath, N. P. Rath, A. V. Demchenko, *Org. Lett.* **2004**, *6*, 4515.
[77] J. T. Smoot, P. Pornsuriyasak, A. V. Demchenko, *Angew. Chem.* **2005**, *117*, 7285; *Angew. Chem. Int. Ed.* **2005**, *44*, 7123.
[78] V. Ferrieres, S. Blanchard, D. Fischer, D. Plusquellec, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 3515.
[79] R. Euzen, V. Ferrieres, D. Plusquellec, *J. Org. Chem.* **2005**, *70*, 847.
[80] E. S. H. El Ashry, L. F. Awad, A. I. Atta, *Tetrahedron* **2006**, *62*, 2943.
[81] S. Brennan, P. A. Finan, *J. Chem. Soc. C* **1970**, 1742.
[82] F. Dasgupta, P. J. Garegg, *Carbohydr. Res.* **1988**, *177*, C13.
[83] T. Ziegler, H. Sutoris, C. P. J. Glaudemans, *Carbohydr. Res.* **1992**, *229*, 271.
[84] S. Hashimoto, T. Honda, S. Ikegami, *J. Chem. Soc. Chem. Commun.* **1989**, 685.
[85] J. D. C. Codee, L. J. Van den Bos, R. E. J. N. Litjens, H. S. Overkleeft, C. A. A. Van Boeckel, J. H. Van Boom, G. A. van der Marel, *Tetrahedron* **2004**, *60*, 1057.
[86] B. A. Garcia, D. Y. Gin, *J. Am. Chem. Soc.* **2000**, *122*, 4269.
[87] F. Dasgupta, P. J. Garegg, *Carbohydr. Res.* **1990**, *202*, 225.
[88] J. R. Pougny, M. A. M. Nassr, N. Naulet, P. Sinay, *Nouveau J. Chem.* **1978**, *2*, 389.
[89] R. Eby, C. Schuerch, *Carbohydr. Res.* **1975**, *39*, 33.
[90] P. Pornsuriyasak, A. V. Demchenko, *Tetrahedron: Asymmetry* **2005**, *16*, 433.
[91] H. Chiba, S. Funasaka, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1629.

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