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S-Benzoxazolyl as a Stable Protecting Moiety and a Potent Anomeric Leaving Group in Oligosaccharide Synthesis

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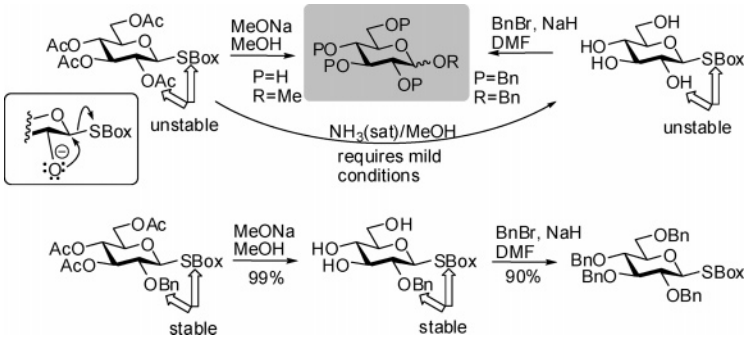

As a part of a program for developing new versatile building blocks for stereoselective glycosylation and convergent oligosaccharide synthesis, we demonstrated that *S*-benzoxazolyl (SBox) glycosides are stable toward major protecting group manipulations employed in carbohydrate chemistry. On the other hand, they can be glycosidated under relatively mild reaction conditions to afford either 1,2-*trans* or 1,2-*cis*-linked disaccharides. Selective and chemoselective activations of the SBox moiety were also proved to be feasible, which was demonstrated by synthesizing a number of oligosaccharide sequences.

Introduction

Glycosyl thioimidates, compounds bearing SCR[1]═NR[2] aglycon, have been known for decades, yet their synthetic value as versatile intermediates in carbohydrate chemistry has only recently come to the fore.[1] Relatively low stability of the previously studied thioimidates was the major reason the use of benzothiazolyl,[2] pyridin-2-yl,[3−5] pyrimidin-2-yl,[3,6] imidazolin-2-yl,[3] and 1′-phenyl-1*H*-tetrazolyl[7] glycosides in oligosaccharide synthesis was limited. Our laboratory has been primarily investigating a family of substituted oxazol(in)es and thiazol(in)es as complimentary glycosyl donors for chemical glycosylation.[8] We already demonstrated that this class of compounds can serve as excellent intermediates in stereoselective glycosylations[9−11] and convergent oligosaccharide syntheses via conceptually novel strategies.[12−15] Another important recent development in this area is the anomeric phosphorylation of glycosyl thioimidates.[16,17]

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(11) Demchenko, A. V.; Malysheva, N. N.; De Meo, C. *Org. Lett.* **2003**, *5*, 455−458.
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(15) Pornsuriyasak, P.; Gangadharmath, U. B.; Rath, N. P.; Demchenko, A. V. *Org. Lett.* **2004**, *6*, 4515−4518.
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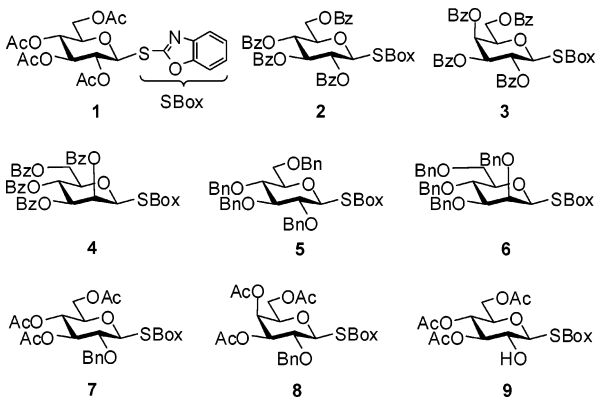

FIGURE 1. Differently protected SBox glycosides of the D-gluco, D-galacto, and D-manno series.

Side-by-side comparison of an array of structurally related cyclic thioimidates[18] revealed that 1-*S*-benzoxazolyl (SBox) derivatives bear major positive traits of a modern glycosyl donor: accessibility, odorless preparation, stability toward many reaction conditions employed in carbohydrate chemistry, mild and selective activation for glycosylation, and excellent stereoselectivity. In the preceding paper,[19] we demonstrated that the SBox glycosides **1**−**9** (Figure 1) can be successfully prepared from a variety of synthetic precursors and can be applied as glycosyl donors for stereoselective glycosylation. Herein we present our thorough evaluation of the SBox derivatives in glycoside synthesis and their application to the synthesis of a variety of compounds ranging from relatively simple partially protected glycosyl acceptors to elaborate oligosaccharide sequences.

Results and Discussion

In the preceding paper, we established the activation pathways and experimental conditions for the glycosidation of SBox glycosides;[19] herein, we turn our attention to investigating their properties as glycosyl donors in the formation of various glycosidic linkages. A unique feature of the SBox glycosyl donors is that a broad range of conceptually different approaches can be applied to their glycosidation. The reaction conditions range from traditional thioglycoside activators: MeOTf and NIS/TfOH to mildly electrophilic metal salts, such as AgOTf and $Cu(OTf)_2$. In addition, protic and Lewis acids were also shown as promoters for this class of compounds, although at this stage the effectiveness of this type of activation is modest.

Glycosidation of the SBox Derivatives: Synthesis of 1,2-*trans*-Glycosides. As previously reported,[19] per-acetylated SBox glycosides (such as **1**) provide somewhat compromised results due to competing acetyl migration from the O-2 of glycosyl donor to the free hydroxyl of the glycosyl acceptor.[19] Hence, our main effort for the synthesis of 1,2-trans-linked glycosides has been focused on the investigation of the perbenzoylated SBox glycosides (**2**−**4**). Also, having already ascertained that the perbenzoylated SBox glycosides could be efficiently activated with AgOTf or MeOTf, our main effort has been directed on the application of these two promoters. Herein, we report that perbenzoylated SBox glycosyl donors of the D-gluco, D-galacto-, and D-manno series (**2**, **3**, and **4**, respectively) are very efficient glycosyl donors for the synthesis of 1,2-trans-linked disaccharides. As highlighted in Table 1, reactions with differently protected glycosyl acceptors **10**, **12**, **14**, **16**, **18**, and **20** of the D-gluco and D-galacto series gave the corresponding disaccharides **11, 13**, **15**, **17**, **19**, and **21**−**23** in high yields of 86−95% and complete stereoselectivity. The complete 1,2-trans stereoselectivity is attributed to the assistance of a participating substituent at the C-2 position.

Glycosidation of the SBox Derivatives: Synthesis of 1,2-*cis*-Glycosides. Stereoselective synthesis of 1,2-*cis*-glycosides from SBox glycosyl donors was also investigated. In this case, we investigated glycosyl donors bearing a nonparticipating substituent at C-2, perbenzylated SBox glycoside **5** or its 2-*O*-benzyl-3,4,6-tri-*O*-acetyl counterpart **7**. Similarly, glycosidations of the SBox derivatives of the D-manno (**3**) and D-galacto series (**4** or **8**), respectively, were probed. For the highly reactive perbenzylated glycosyl donors **5** or **6**, $Cu(OTf)_2$ was found to be the promoter of choice. Although reactions performed in 1,2-DCE were found to be high yielding, the stereoselectivity was below average (typically α/β 2/1) in the majority of cases. While no improvement in stereoselectivity was achieved by changing promoters, significantly higher stereoselectivity was accomplished when the glycosylation was performed in toluene-dioxane (1/3, v/v), a participating solvent mixture.[20] As a result of varying the reaction solvent, significantly improved stereoselectivity could be achieved (up to α/β 7/1, entries 1−5, Table 2).

Application of partially acetylated glycosyl donors **7** or **8** was found to be especially beneficial for 1,2-cis glycosylation. In a number of cases, very high or even complete 1,2-cis stereoselectivity was achieved in dichloromethane, a solvent that does not usually favor 1,2-cis glycosylation (see entries 6−14, Table 2). Arguably, the stereoselectivity achieved herein favorably compares with the best procedures for direct 1,2-cis glycosylation developed to date.[21,22] It should be noted that, in spite of significant improvements that have emerged in the past decade, stereocontrolled synthesis of 1,2-*cis*-glycosides still remains a significant challenge.

Stability of the 1-SBox Glycosides: Synthesis of Glycosyl Acceptors. A significant drawback of many classes of glycosyl donors is their poor stability toward protecting group manipulations. For instance, labile glycosyl donors such as bromides,[23,24] trichloroacetimidates,[25] phosphites,[26] phosphates,[27] etc. should be obtained directly prior to the glycosylation. In this respect, stable glycosyl donors, such as fluorides,[28,29] alkyl or aryl

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(19) Kamat, M. N.; Rath, N. P.; Demchenko, A. V. *J. Org. Chem.* **2007**, *72*, 6938−6946.
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(25) Schmidt, R. R.; Jung, K. H. In *Carbohydrates in Chemistry and Biology*; Ernst, B., Hart, G. W., Sinay, P., Eds.; Wiley-VCH: Weinheim, New York, 2000; Vol. 1, p 5−59.
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(27) Plante, O. J.; Palmacci, E. R.; Andrade, R. B.; Seeberger, P. H. *J. Am. Chem. Soc.* **2001**, *123*, 9545−9554.
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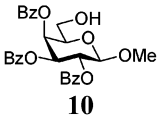
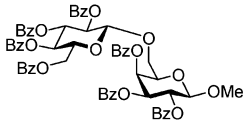
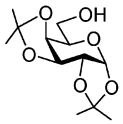
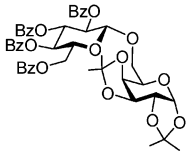
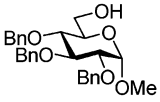
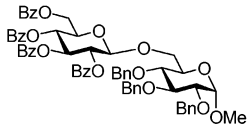
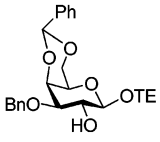
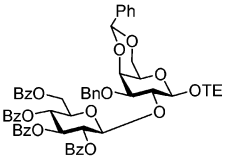
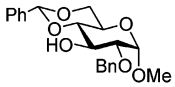
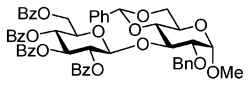
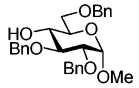
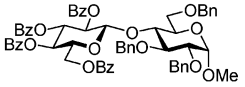
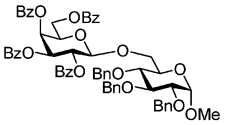
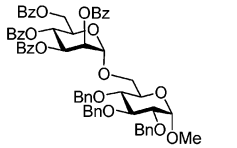
(29) Mukaiyama, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5590−5614.

TABLE 1. Synthesis of 1,2-*trans*-Glycosides

Entry	*Donor*	*Acceptor*[a]	*Promoter*[b]	*Time*	*Product*	*Yield, %*
1	**2**	 **10**	MeOTf	1 h	 **11**	92
2	**2**	 **12**	AgOTf	10 min	 **13**	91
3	**2**	 **14**	MeOTf	1 h	 **15**	95
4	**2**	 **16**	MeOTf	1 h	 **17**	94
5	**2**	 **18**	MeOTf	15 min	 **19**	86
6	**2**	 **20**	MeOTf	15 min	 **21**	86
8	**3**	**14**	AgOTf	5 min	 **22**	92
9	**4**	**14**	MeOTf	1 h	 **23**	92

[a] Abbreviation: TE, (2-trimethylsilyl)ethyl. [b] AgOTf and MeOTf performed nearly equally well; only the best selected results are presented herein.

thioglycosides,[30,31] *O*-alkenyl glycosides,[32,33] or selenoglycosides,[34] offer a significant advantage in that a stable leaving group can also serve as a temporary anomeric protecting group. This would allow the installation of a required protecting group pattern and preclude additional manipulations at the anomeric center prior to glycosylation. The evaluation of the compatibility of SBox glycosides with reaction conditions required for installing or removing common classes of protecting groups seemed to be a logical step in the systematic study of these novel derivatives.

It should be noted that the majority of SBox derivatives investigated in our laboratory were found to be stable crystalline compounds that could be stored at ambient temperature and humidity.[19] As to the chemical stability of the SBox glycosides, we performed a number of experiments that demonstrated the relatively high stability of the SBox moiety. Thus, preliminary experiments with SBox derivative **7** demonstrated that this

(30) Garegg, P. J. *Adv. Carbohydr. Chem. Biochem.* **1997**, *52*, 179−205.

(31) Oscarson, S. In *Carbohydrates in Chemistry and Biology*; Ernst, B.; Hart, G. W.; Sinay, P.; Eds.; Wiley-VCH: Weinheim, New York, 2000; Vol. 1, p 93−116.

(32) Fraser-Reid, B.; Anilkumar, G.; Gilbert, M. B.; Joshi, S.; Kraehmer, R. In *Carbohydrates in Chemistry and Biology*; Ernst, B., Hart, G. W., Sinay, P., Eds.; Wiley-VCH: Weinheim, New York, 2000; Vol. 1, p 135−154.

(33) Boons, G. J. In *Glycoscience: Chemistry and Chemical Biology*; Fraser-Reid, B.; Tatsuta, K.; Thiem, J.; Eds.; Springer: Berlin - Heidelberg - New York, 2001; Vol. 1, p 551−581.

(34) Mehta, S.; Pinto, B. M. *J. Org. Chem.* **1993**, *58*, 3269−3276.

TABLE 2. **Synthesis of 1,2-*cis*-Glycosides**[a]

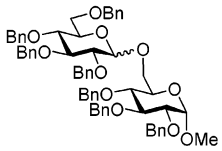
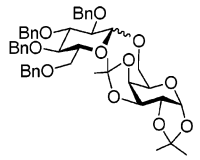
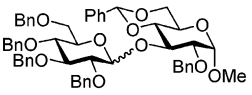
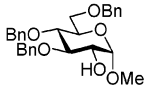
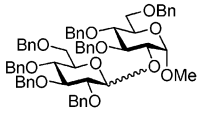
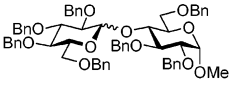
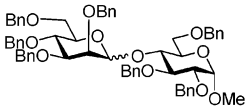
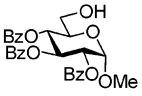
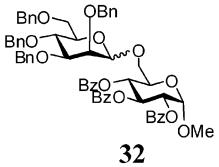
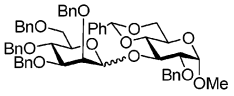
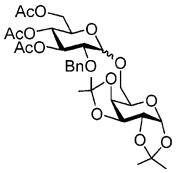
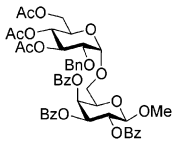
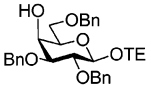
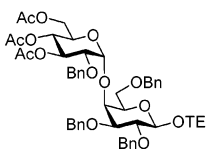
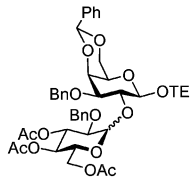
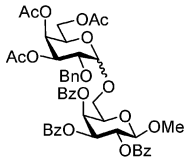
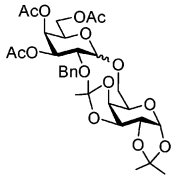
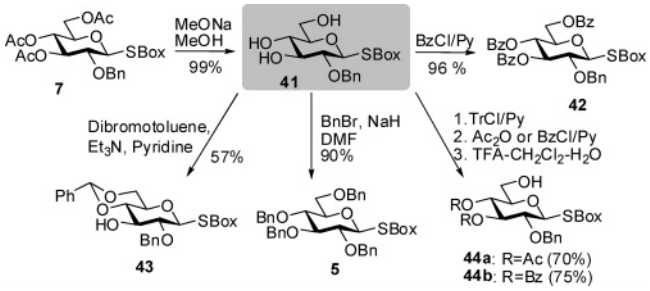
Entry	*Donor*	*Acceptor*	*Solvent*	*Promoter*	*Product*	*Yield, %*	*α/β ratio*
1	**5**	**14**	T/D[b]	$Cu(OTf)_2$	 **24**	95	6/1
2	**5**	**12**	T/D	$Cu(OTf)_2$	 **25**	89	5.4/1
3	**5**	**18**	T/D	$Cu(OTf)_2$	 **26**	65	4/1
4	**5**	 **27**	T/D	$Cu(OTf)_2$	 **28**	68	7/1
5	**5**	**20**	T/D	$Cu(OTf)_2$	 **29**	67	3/1
6	**6**	**20**	DCM	MeOTf	 **30**	83	1/5.9
7	**6**	 **31**	DCM	MeOTf	 **32**	72	1/2.2
8	**6**	**18**	DCM	MeOTf	 **33**	83	1/2.5
9	**7**	**12**	DCM	AgOTf	 **34**	99	11/1
10	**7**	**10**	DCM	AgOTf	 **35**	97	α only[c]
11	**7**	 **36**	DCM	MeOTf		88	α only[c]

Table 2. (Continued)

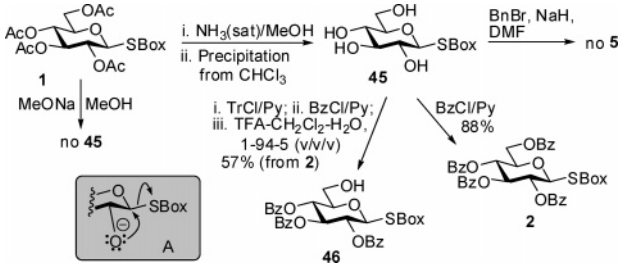
Entry	*Donor*	*Acceptor*	*Solvent*	*Promoter*	*Product*	*Yield, %*	*α/β ratio*
12	**7**	**16**	DCM	MeOTf	**37** 	78	3/1
13	**8**	**10**	DCM	AgOTf	**38** 	97	4/1
14	**8**	**12**	DCM	AgOTf	**39**  **40**	99	5/1

[a] Extended table can be found in the Supporting Information. [b] Toluene−dioxane (1/3, v/v). [c] No formation of the β-anomer has been detected by ^{1}H NMR (α/β > 95/5).

SCHEME 1



SCHEME 2



compound could be efficiently deacetylated under conventional Zemplen conditions.[35] The intermediate **41** was found to be stable under standard reaction conditions for the introduction of alkyl, acyl, and acetal substituents (Scheme 1).[36] As a result, we accomplished the syntheses of a range of differently protected building blocks **5** and **42**−**44** containing the SBox anomeric moiety.

However, when Zemplen conditions (catalytic MeONa in MeOH) were applied to the deprotection of the tetraacetyl derivative **1** or its triacetylated counterpart **9**, only traces of the expected intermediate **45** were detected in the reaction mixture. Disappointingly, methyl D-glucopyranoside (α/β = 1.3/1) was found to be the major product of this reaction — an indication of the anomeric leaving group displacement. Taking into consideration that deacetylation of the 2-benzyl derivative **7** proceeded in a nearly quantitative yield (see the synthesis of **41**, Scheme 1), the results with compounds **1** or **9** were rather surprising. To overcome this problem, the deacetylation of **1** was performed using a saturated solution of ammonia in MeOH (pH ≤ 8). Simple precipitation from the reaction mixture afforded the desired reaction intermediate **45**, which was found to be compatible with conventional tritylation, benzoylation, and detritylation conditions. As a result, derivatives **2** and **46** were obtained in good overall yields (Scheme 2).

However, when the intermediate **45** was subjected to strongly basic reaction conditions (BnBr and NaH in DMF, see the attempted synthesis of **5**, Scheme 2), departure of the SBox moiety resulted in the formation of D-glucose, which was subsequently benzylated. It should be reminded that per-benzylated SBox derivative **5** could be readily obtained from the 2-benzyl SBox intermediate **41** under the same reaction conditions in 90% yield. The disparity of results obtained from 2-benzyl (**7** → **41** → **5**) and 2-acyl/hydroxyl derivatives (**1** → **45** → **5**) made us believe that while the SBox moiety itself is stable toward strong bases (MeONa, NaH, NaOH, see for example the syntheses of **5** and **41**, Scheme 1), it readily departs upon the nucleophilic attack of the deprotonated C-2 hydroxyl

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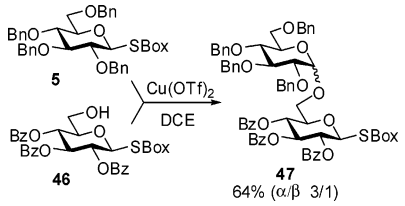
SCHEME 3



on the anomeric center (see the proposed reaction intermediate A, Scheme 2).

SBox Glycosides as Building Blocks in Expeditious Oligosaccharide Synthesis. An important feature of a glycosyl donor would be its applicability to multistep oligosaccharide synthesis via expeditious building block based pathways.[37] Having completed the stereoselectivity studies (see Tables 1 and 2), we wanted to investigate whether the SBox glycosides could be chemoselectively activated in accordance with the armed-disarmed approach developed by Fraser-Reid.[38,39] According to this strategy, a significantly more reactive (armed) benzylated glycosyl donor can be chemoselectively activated in the presence of the acylated (disarmed) derivative to afford a disaccharide. We found that the SBox glycosides also follow general chemoselectivity principle. Thus, armed SBox glycoside donor **5** could be activated over electronically disarmed SBox glycosyl acceptor **46** in the presence of $Cu(OTf)_2$ (Scheme 3). Therefore, obtained disaccharide **47** bearing the SBox leaving group can then be coupled with a suitable acceptor under typical reaction conditions for the SBox activation.

Our other aim was to determine whether the SBox derivatives could be coupled with glycosyl acceptors containing other types of anomeric leaving groups. The key requirement for such activation would be the availability of a promoter that could selectively activate the SBox moiety over a stable anomeric moiety of the glycosyl acceptor, such as *S*-ethyl. Our initial assumption was that such selective activation could be accomplished using AgOTf as a promoter. Thus, in studies with glycosyl donors **2** and **7**, we chose *S*-ethyl glycoside **49** as glycosyl acceptor (Scheme 4). Remarkably, the glycosylations involving selective activation of the SBox leaving group afforded the corresponding disaccharide products **50** and **52** with excellent stereoselectivity and yields of 98−99%. Very importantly, no side products involving self-condensation of the glycosyl acceptor were detected. Similarly, the SBox moiety could be activated in the presence of the *O*-pentenyl moiety.[11] Furthermore, in an independent study of the STaz glycosidation protocol, it was also established that the SBox moiety can be selectively activated over the STaz anomeric moiety using $Cu(OTf)_2$ as a promoter.[9]

The key feature of the oligosaccharide synthesis via selective activation is that the disaccharides obtained can be immediately used in subsequent glycosidation. In the case of the disaccharides **50** and **52**, the second step activation should be feasible in the presence of NIS/TfOH or other suitable activators for *S*-alkyl/aryl moieties.[30−32] Additionally, selective activation of *S*-ethyl over the *O*-pentenyl moiety can be achieved in the presence of MeOTf in accordance with the semi-orthogonal strategy developed in our laboratory.[40] To explore this possibility, we performed the coupling of the *S*-ethyl disaccharide donors **50** or **52** with glycosyl acceptors **48** or **53** in the presence of MeOTf to afford the corresponding trisaccharide derivatives **51** or **54** in 92 or 90% yield, respectively (Scheme 4). The *O*-pentenyl moiety of the trisaccharide donor **54** was then activated for the reaction with glycosyl acceptor **14** in the presence of NIS/TfOH. As a result, a tetrasaccharide derivative **55** was isolated in 73% yield. These examples serve as a clear illustration of the enhanced ability to obtain oligosaccharides via sequential activation in a convergent fashion with no additional protecting/leaving group manipulations between the glycosylation steps.

Conclusions

Based on the results presented, we conclude that the SBox glycosides are stable toward majority of protecting group manipulations employed in carbohydrate chemistry. It has been demonstrated that the SBox moiety is even stable toward strong bases if the O-2 position of the pyranose ring is protected with a stable moiety, such as benzyl. When the protection is removed, stability of the SBox moiety significantly decreases. The SBox glycosides were also found to be suitable building blocks for chemoselective armed-disarmed activations and for selective sequential activations over other classes of leaving groups.

Experimental Part

For general procedures for the preparation of di- and oligosaccharides, refer to the preceding article: method A, MeOTf; method B, AgOTf; method C, $Cu(OTf)_2$.[19]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-galactopyranoside (**11**) was obtained using method A from **2** and **10**[41] in 92% yield. Analytical data for **11** were essentially the same as reported previously.[42]

6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (13) was obtained from **2** and **12** using method B in 91% or by method C in 70% yield. Analytical data for **13** were essentially the same as reported previously.[9]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**15**) was obtained using method A from **2** and **14**[43] in 95% yield. Analytical data for **15** were essentially the same as reported previously.[44]

2-Trimethylsilylethyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (17) was obtained using method A from **2** and **16**[45] in 94% yield. Analytical data for **17**: R_f = 0.37 (ethyl acetate−hexane, 3/7, v/v); $[\alpha]^{22}_D$ 39.9 (c = 1.0, $CHCl_3$); ^{1}H NMR δ 0.00 (s, 9H, $SiCH_3$), 1.01 (t, 2H, J = 8.7 Hz, CH_2TMS), 3.40 (dd, 1H, $J_{3,4}$ = 3.6 Hz, H−3), 3.63 (m, 1H, CH_2^a), 3.80 (dd, 1H, H-4), 3.87 (dd, 1H, $J_{5,6a}$ = 2.7, $J_{6a,6b}$ = 12.4, H-6a), 3.97−4.27 (m, 5H, CH_2^b, H-2′, 5, 5′, 6b), 4.35 (dd, 2H, J^2 = 12.8 Hz, CH_2Ph), 4.42 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.50 (dd, 1H, H-6b′), 4.65 (dd, 1H, $J_{5',6a'}$ = 3.8 Hz, $J_{6a',6b'}$ = 12.6, H-6a′), 5.25 (s, 1H, C*H*Ph), 5.39 (d, 1H, $J_{1',2'}$ = 7.9

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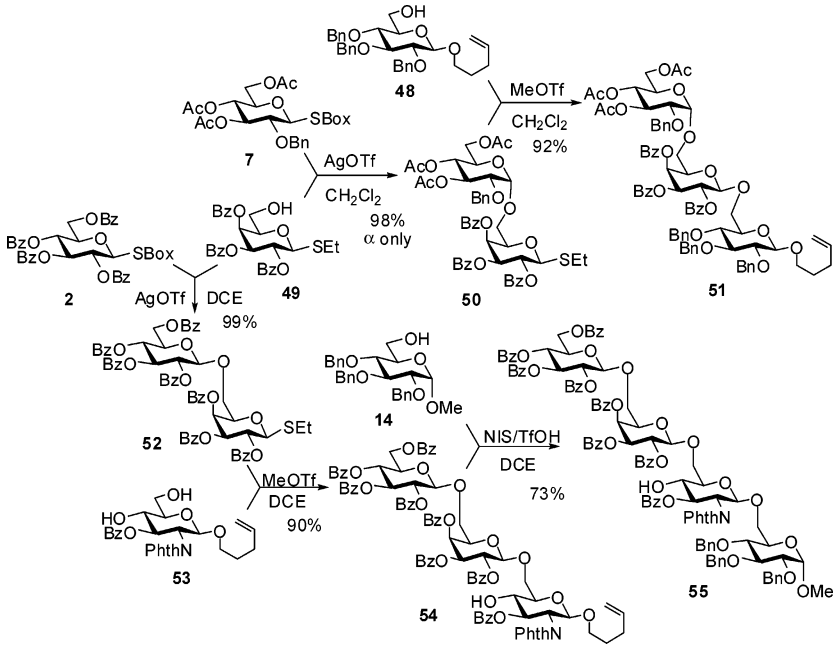
SCHEME 4



Hz, H-1′), 5.65 (dd, 1H, $J_{2',3'}$ = 8.7 Hz, H-2′), 5.79 (dd, 1H, $J_{4',5'}$ = 9.4 Hz, H-4′), 5.86 (dd, 1H, $J_{3',4'}$ = 9.5 Hz, H-3′); ^{13}C NMR δ 55.4, 60.6, 62.9, 66.8, 67.1, 68.8, 69.1, 70.1, 70.2, 70.5, 73.6, 75.2, 75.9, 76.3, 77.4, 77.9, 79.1, 80.4, 82.3, 97.9, 98.1, 127.8 (×3), 128.0, 128.1 (×3), 128.3 (×2), 128.5 (×2), 128.6 (×7), 128.7 (×5), 128.8 (×2), 129.2, 129.3, 129.5, 129.9 (×4), 130.0 (×2), 130.1, 133.2, 133.3, 133.6, 133.9, 134.3, 138.4 (x 2), 138.9 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{59}H_{60}NaO_{15}Si$ 1059.3579, found 1059.3589.

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**19**) was obtained using method A from **2** and **18**[46] in 86% yield. Analytical data for **19** were essentially the same as reported previously.[47]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**21**) was obtained using method A from **2** and **20**[48] in 86% yield. Analytical data for **21** were essentially the same as reported previously.[9]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**22**) was obtained using method B from **3** and **14** in 92% yield. Analytical data for **22** were essentially the same as reported previously.[49]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**23**) was obtained using method A from **4** and **14** in 92% yield Analytical data for **23** were essentially same as reported previously.[9]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (**24**) was obtained using method C from **5** and **14** in toluene - dioxane (1/3, v/v, 1 mL) in 95% yield (α/β = 6/1). Analytical data for **24** were essentially the same as reported previously.[50]

6-*O*-(2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**25**) was obtained using method C from **5** and **12** in toluene−dioxane (1 mL, 3/1, v/v) in 89% yield (α/β = 5.4/1). Analytical data for **25** were essentially the same as reported previously.[51]

Methyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-4,6-*O*-benzylidene-α-D-glucopyranoside (**26**) was obtained using method C from **5** and **18** in toluene−dioxane (1:3, v/v, 1 mL) in 65% (α/β = 4/1) or in 1,2-DCE in 89% (α/β = 3/1) yield. Analytical data for **26** were essentially the same as reported previously.[52]

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**28**) was obtained using method C from **5** and **27**[53] in toluene−dioxane (1/3, v/v, 1 mL) in 68% (α/β = 7/1) or in 1,2-DCE in 61% (α/β = 2/1) yield. Analytical data for α-**28** were essentially the same as reported previously.[9]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (**29**) was obtained using method C from **5** and **20** in toluene−dioxane (1/3, v/v, 1 mL) in 67% (α/β = 3/1) or in 1,2-DCE in 41% (α/β = 1.5/1) yield. Analytical data for **29** were essentially the same as reported previously.[54]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-α-D-glucopyranoside (**30**) was obtained using method A from **6** and **20** in 83% yield (α/β = 1/5.9). Analytical data for **30** were essentially the same as reported previously.[55]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-α-D-glucopyranoside (**32**) was obtained using method A from **6** and **31** in 72% yield (α/β = 1/2.2). Analytical data for **32** were essentially the same as reported previously.[55]

Methyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-4,6-*O*-benzylidene-α-D-glucopyranoside (**33**) was obtained using method A from **6** and **18** in 83% yield (α/β = 1/2.5). Analytical data for **33** were essentially the same as reported previously.[52]

6-*O*-(3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (34) was obtained using method B from **7** and **12** in 99% yield (α/β = 11/1). Selected analytical data for α-**34**: R_f = 0.35 (ethyl acetate−hexane, 1/1,

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v/v); ^{1}H NMR δ 1.26, 1.27, 1.30, 1.34 (4 s, 12H, 4 × CCH_3), 2.01, 2.02, 2.08 (3 s, 9H, 3 × $COCH_3$), 3.48 (dd, 1H, $J_{2',3'}$ = 9.3 Hz, H-2′), 3.6 (m, 2H, H-6a,6b), 3.96 (dd, 1H, $J_{6a',6b'}$ = 12.4 Hz, H-6b′), 3.98 (m, 1H, H-5), 4.02 (m, 1H, H-5′), 4.23 (dd, 1H, $J_{5',6a'}$ = 4.1 Hz, H-6a′), 4.24 (dd, 1H, $J_{2',3'}$ = 9.4 Hz, H-2′), 4.27 (dd, 1H, $J_{4,5}$ = 1.9 Hz, H-4), 4.51 (dd, 1H, $J_{3,4}$ = 2.5 Hz, H-3), 4.56 (dd, 2H, J^2 = 12.2 Hz, CH_2Ph), 4.88 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1′), 4.90 (dd, 1H, $J_{4',5'}$ = 9.9 Hz, H-4′), 5.36 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3′), 5.43 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1); ^{13}C NMR δ 20.9, 21.0 (× 2), 24.8, 25.2, 26.3, 26.4, 62.2, 66.5, 67.4, 67.7, 68.8, 70.8 (×2), 71.0, 72.2, 72.5, 96.5, 97.44, 109.0, 109.4, 127.9 (×2), 128.2, 128.7 (×2), 138.0, 170.1, 170.4, 171.0 ppm; HR-FAB MS [M + Na]$^+$ calcd for $C_{31}H_{42}NaO_{14}$ 661.2472, found 661.2468.

Methyl 6-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-*β*-D-galactopyranoside (**35**) was obtained using method B from **7** and **10** in 97% yield (α only). Analytical data for α-**35** were essentially the same as reported previously.[9]

2-Trimethylsilylethyl 4-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-*β*-D-galactopyranose (37) was obtained using method A from **7** and **36**[56] in 88% yield (α only). Selected analytical data for α-**37**: R_f = 0.39 (ethyl acetate−hexane, 3/7, v/v); ^{1}H NMR δ 0.03 (s, 9H, Si$(CH_3)_3$), 0.96 (m, 2H, CH_2-TMS), 1.96, 2.01, 2.02 (3 s, 9H, 3 × $COCH_3$), 3.41 (dd, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 3.50−3.55 (m, 3H, H-5, −OCH_2[a], H-6b′), 3.60 (dd, 1H, $J_{2',3'}$ = 9.9 Hz, H-2′), 3.70 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H−2), 3.87 (dd, 1H, $J_{6a,6b}$ = 12.8 Hz, H-6a), 3.99 (m, 1H, −OCH_2[b]), 4.00 (m, 1H, H-6a′), 4.02 (dd, 1H, H-4), 4.32 (s, 2H, CH_2Ph), 4.34 (d, 1H, $J_{1,2}$ = 11.3 Hz, H-1), 4.40 (m, 1H, H-5′), 4.61 (s, 2H, CH_2-Ph), 4.71 (s, 2H, CH_2Ph), 4.91 (dd, 2H, J^2 = 11.1 Hz, CH_2Ph), 4.97 (dd, 1H, $J_{4',5'}$ = 10.2 Hz, H-4′), 5.11 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1′), 5.51 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3′), 7.19−7.42 (m, 20H, aromatic) ppm; ^{13}C NMR δ −1.0 (×3), 19.0, 21.1 (×2), 21.3, 61.8, 67.9 (×2), 68.9, 69.0, 72.7, 73.6 (×3), 75.3, 76.5, 79.5, 80.7, 99.5, 104.1, 128.03 (×6), 128.1, 128.2 (×3), 128.6 (×2), 128.7 (×2), 128.8 (×6), 138.3, 138.5, 138.6, 139.1, 170.4 (×2), 171.0 ppm; HR-FAB MS [M + Na]$^+$ calcd for $C_{51}H_{64}NaO_{14}Si$ calcd 951.3963, found 951.3961.

2-Trimethylsilylethyl 2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (**38**) was obtained using method A from **7** and **16** colorless syrup in 78% yield (α/*β* = 3/1). Selected analytical data for α-**38**: R_f = 0.51 (ethyl acetate−hexane, 1/1, v/v); ^{1}H NMR δ −0.40 (s, 9H, Si$(CH_3)_3$), 0.99 (m, 2H, CH_2TMS), 1.86, 1.93, 1.99 (3 s, 9H, 3 × $COCH_3$), 3.38 (m, 1H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.5 Hz, H-5), 3.50 (m, 1H, −OCH_2[a]), 3.59 (dd, 1H, $J_{2',3'}$ = 9.6 Hz, H-2′), 3.70 (dd, 1H, $J_{3,4}$ = 3.8 Hz, H− 3), 3.77 (dd, 1H, $J_{6a,6b}$ = 12.8 Hz, H-6b), 3.87 (dd, 1H, H-6a), 4.00 (m, 1H, −OCH_2[b]), 4.05 (m, 2H, H-6a′,6b′), 4.10 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 4.28 (dd, 1H, H-4), 4.38 (d, 1H, $J_{1,2}$ = 11.3 Hz, H-1), 4.58 (m, 1H, H-5′), 4.89 (dd, 1H, $J_{4',5'}$ = 10.4 Hz, H-4′), 5.49 (dd, 1H, $J_{3',4'}$ = 9.8, H-3′), 5.78 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1′), 7.26−7.56 (m, 15H, aromatic); ^{13}C NMR δ −1.3, 18.8, 20.8, 21.1, 29.9, 62.0, 66.5, 66.8, 67.1, 68.8, 69.5, 70.8, 71.8, 71.9, 72.6, 72.7, 95.1, 101.4, 102.9, 126.6 (×2), 127.7 (×2), 128.1, 128.2, 128.3 (×2), 128.5 (×2), 128.7 (×4), 129.2, 137.9 (×2), 138.1, 170.0, 170.1, 171.1; HR-FAB MS [M + Na]$^+$ calcd for $C_{44}H_{56}NaO_{14}Si$ calcd 859.3337, found 859.3351.

Methyl 6-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-galactopyranosyl)-2,3,4-tri-*O*-benzoyl-*β*-D-galactopyranoside (39) was obtained using method B from **8** and **10** in 97% yield (α/*β* = 4/1). Analytical data for α-**39**: R_f= 0.54 (ethyl acetate−hexanes, 1/1, v/v); ^{1}H NMR δ 1.96, 1.99, 2.10 (3 s, 9H, 3 × $COCH_3$), 3.59 (s, 3H, OCH_3), 3.54 (dd, 1H, H-6b), 3.75 (dd, 1H, $J_{2',3'}$ = 7.6 Hz, H-2′), 3.86 (dd, 1H, $J_{6a,6b}$ = 10.4 Hz, H-6a), 4.33 (dd, 1H, H-6b′), 4.67 (dd, 1H, $J_{6a',6b'}$ = 10.7 Hz, H-6a′), 4.21 (m, 1H, $J_{5,6a}$ = 4.3 Hz, $J_{5,6b}$ = 2.8 Hz, H-5), 4.31 (dd, 1H, $J_{5',6a'}$ = 4.2 Hz, $J_{5',6b'}$ = 3.1 Hz, H-5′), 4.65 (s, 2H, CH_2Ph), 4.69 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 4.76 (d, 1H, $J_{1',2'}$ = 3.4, H-1′), 5.25 (dd, 1H, $J_{3',4'}$ = 3.8 Hz, H-3′), 5.36 (dd, 1H, $J_{4',5'}$ = 0.8 Hz, H-4′), 5.49 (dd, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 5.69 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 5.80 (dd, 1H, $J_{4,5}$ = 1.1 Hz, H-4), 7.21−8.09 (m, 20H, aromatic); ^{13}C NMR δ 20.8, 20.9, 21.0, 29.9, 57.5, 66.9, 67.0, 68.7, 69.1, 69.7, 70.1, 72.0, 72.9, 73.4, 73.6, 97.6, 102.6, 128.2 (×2), 128.5 (×2), 128.6 (×2), 128.7 (×2), 128.9 (×2), 129.1, 129.3, 129.6, 130.0 (×4), 130.2 (×2), 133.4 (×2), 133.9, 138.2, 142.1, 142.4, 142.6, 165.7 (×2), 165.9, 170.2, 170.3, 170.6; HR-FAB MS [M + Na]$^+$ calcd for $C_{47}H_{48}NaO_{17}$ 907.2789, found 907.2798.

6-*O*-(3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (40) was obtained using method B from **8** and **12** in 99% yield (α/*β* 5/1). Selected analytical data for α-**40**: R_f = 0.35 (ethyl acetate−hexane, 1/1, v/v); ^{1}H NMR δ 1.29, 1.33, 1.45, 1.56 (4 s, 12H, 4 × CCH_3), 1.99, 2.05, 2.11 (3 s, 9H, 3 × $COCH_3$), 3.48 (dd, 1H, $J_{2',3'}$ = 9.3 Hz, H-2′), 3.6 (m, 2H, H-6a, 6b), 3.96 (dd, 1H, $J_{6a',6b'}$ = 12.4 Hz, H-6b′), 3.98 (m, 1H, H-5), 4.02 (m, 1H, H-5′), 4.23 (dd, 1H, $J_{5',6a'}$ = 4.1 Hz, H-6a′), 4.24 (dd, 1H, $J_{2',3'}$ = 9.4 Hz, H-2′), 4.27 (dd, 1H, $J_{4,5}$ = 1.9 Hz, H-4), 4.51 (dd, 1H, $J_{3,4}$ = 2.5 Hz, H-3), 4.56 (dd, 2H, J = 12.2 Hz, CH_2Ph), 4.88 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1′), 4.90 (dd, 1H, $J_{4',5'}$ = 9.9 Hz, H-4′), 5.36 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3′), 5.43 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1) ppm; ^{13}C NMR δ 20.9, 21.0, 21.1, 24.8, 25.2, 26.3, 26.4, 62.2, 66.5, 67.4, 67.7, 68.8, 70.8 (×2), 71.0, 72.2, 72.5, 96.5, 97.4, 109.0, 109.4, 127.9 (×2), 128.2, 128.7 (×2), 138.0, 170.1, 170.4, 171.0; HR-FAB MS [M + Na]$^+$ calcd for $C_{31}H_{42}NaO_{14}$ 661.2472, found 661.2468.

Benzoxazolyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (47) was obtained using method C from **5** and **46** as a colorless syrup in 64% yield (α/*β* = 3/1). Selected analytical data for α-**47**: R_f = 0.40 (ethyl acetate−toluene, 1/9, v/v); ^{1}H NMR δ 3.42−3.52 (m, 4H), 3.66 (dd, 1H, H-6b′), 3.74−3.83 (m, 2H), 3.89 (dd, 1H, $J_{6a',6b'}$ = 9.2 Hz, H-6a′), 4.23−4.34 (m, 2H), 4.39 (m, 1H, $J_{5',6a'}$ = 6.8 Hz, $J_{5',6b'}$ = 2.3 Hz, H-5′), 4.43−4.47 (m, 2H), 4.57 (dd, 2H, J^2 = 12.1 Hz, CH_2Ph), 4.70 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 4.73−4.77 (m, 2H), 5.64 (dd, 1H, $J_{4',5'}$ = 10.0 Hz, H-4′), 5.70 (dd, 1H, $J_{3',4'}$ = 10.0 Hz, H-3′), 6.03 (dd, 1H, $J_{2',3'}$ = 9.4 Hz, H-2′), 6.07 (d, 1H, $J_{1',2'}$ = 10.6 Hz, H-1′), 7.01−7.98 (m, 39H, aromatic); ^{13}C NMR δ 66.5, 68.5, 69.6, 70.2, 70.7, 73.4, 73.4, 74.3, 74.7, 75.7, 78.0, 80.1, 82.1, 84.0, 97.1, 110.4, 119.0, 124.4, 124.6, 127.5, 127.6, 127.7, 127.9 (×4), 128.0 (×2), 128.1 (×3), 128.3 (×2), 128.3 (×3), 128.5 (×4), 128.5 (×2), 128.6 (×2), 128.6 (×2), 128.7 (×2), 128.8, 128.9, 129.1, 130.1 (×5), 133.5, 133.7, 138.2, 138.5, 138.9, 139.2, 141.8, 152.2, 161.4, 165.2, 165.5, 165.9; HR-FAB MS [M + Na]$^+$ calcd for $C_{68}H_{61}NNaO_{14}S$ 1170.3710, found 1170.3724.

Ethyl 6-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (**50**) was obtained from **7** and **49**[57] using method B in 98% (α only) as a colorless syrup. Analytical data for **50**: R_f = 0.51 (ethyl acetate−hexane, 1/1, v/v); $[\alpha]^{22}_D$ 140.0 (c = 1.0, $CHCl_3$); ^{1}H NMR δ 1.35 (dd, 3H), 2.01, 2.01, 2.18 (3 s, 9H, 3 × $COCH_3$), 2.84 (m, 2H), 3.54−3.65 (m, 2H), 3.74 (s, 2H), 3.86 (dd, 1H, J = 7.2, J = 10.4 Hz), 4.04 (dd, 1H, J = 2.0, J = 12.4 Hz), 4.17 (m, 1H), 4.24−4.30 (m, 2H), 4.62 (dd, 2H, J = 12.5 Hz), 4.77 (d, 1H, J = 3.5 Hz), 4.85 (d, 1H, J = 10.0 Hz), 4.97 (dd, 1H, J = 10.4 Hz), 5.44 (dd, 1H, J = 9.6 Hz), 5.60 (dd, 1H, J = 3.3, J = 10.0 Hz), 5.81 (dd, 1H, J = 5.0 Hz), 5.90 (d, 1H, J = 3.3 Hz), 7.20−8.10 (m, 20H); ^{13}C NMR δ 20.8 (×2), 21.0, 24.9, 29.5, 29.6, 29.9, 31.9, 32.1, 54.0, 62.0, 67.3, 67.6, 68.5, 68.7, 69.3, 69.7, 72.0, 73.0, 73.3, 76.6, 76.7, 84.4, 96.9, 128.2, 128.3, 128.5, 128.6, 128.7, 128.9, 129.0, 129.4, 129.9, 130.1, 133.4, 133.5, 133.9, 137.8, 165.6 (×2), 165.8, 169.9, 170.2, 170.8; HR-FAB MS [M + Na]$^+$ calcd for $C_{48}H_{50}NaO_{16}S$ 937.2717, found 937.2717.

Pent-4-enyl *O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-*β*-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*β*-D-glucopyranoside (**51**) was prepared from

(56) Nilsson, U.; Ray, A. K.; Magnusson, G. *Carbohydr. Res.* **1994**, *252*, 117−136.

(57) Birberg, W.; Lonn, H. *Tetrahedron Lett.* **1991**, *32*, 7453−7456.

48 and **50** using method A in 92% yield as a colorless syrup. Analytical data for **51**: $R_f = 0.57$ (ethyl acetate−hexane, 1/1, v/v); $[\alpha]^{22}_D$ 98.9 ($c = 1.0$, $CHCl_3$); ^{1}H NMR δ 1.61−1.74 (m, 2H), 1.94, 1.97, 1.98 (3 s, 9H, 3 × $COCH_3$), 2.05−2.18 (m, 2H), 3.31−3.46 (m, 4H), 3.51−3.56 (m, 2H), 3.63 (dd, 1H, $J = 6.0$, $J = 10.5$ Hz), 3.80−3.86 (m, 3H), 3.97−4.12 (m, 3H), 4.22−4.29 (m, 3H), 4.44−4.67 (m, 6H), 4.78−5.03 (m, 7H), 5.42 (dd, 1H, $J = 9.6$ Hz), 5.53 (dd, 1H, $J = 3.5$, $J = 10.4$ Hz), 5.76−5.84 (m, 2H), 5.87 (dd, 1H, $J = 3.2$ Hz), 7.10−8.15 (m, 35H); ^{13}C NMR δ 20.8, 21.0, 29.1, 29.9, 30.4, 32.1, 62.0, 66.6, 67.8, 68.4, 68.7, 68.8, 69.4, 70.2, 72.0, 72.6, 73.1, 74.9, 75.1, 75.7, 76.6, 77.8, 82.3, 84.7, 97.2, 101.8, 103.7, 115.2, 127.7, 127.9, 128.0, 128.3, 128.5, 128.6, 128.7, 128.9, 129.2, 129.9, 129.9, 130.3, 133.4, 133.8, 137.9, 138.2, 138.6, 138.8, 165.4, 165.6, 165.9, 169.9, 170.7 (×2); HR-FAB MS $[M + Na]^+$ calcd for $C_{78}H_{82}NaO_{22}$ 1393.5196, found 1393.5216.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-galactopyranoside (52) was obtained using method A from **2** and **49**[57] in 99% yield. Analytical data for **52** were essentially the same as reported previously.[13]

Pent-4-enyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-3-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (54) was prepared from **50** and **51** using method A in 90% yield as a colorless syrup. Analytical data for **54**: $R_f = 0.47$ (ethyl acetate−hexane, 1/1, v/v); $[\alpha]^{22}_D$ 90.1 ($c = 0.6$, $CHCl_3$); ^{1}H NMR δ 1.27 (m,2H, $-OCH_2CH_2CH_2CH_2$), 1.67 (m, 2H, $-OCH_2CH_2CH_2CH_2$), 3.18 (m, 1H, OCH_2^b), 3.50 (m, 1H, OCH_2^a), 3.60 (m, 1H, H-6b), 3.68 (m, 1H, H-4), 3.71 (m, 1H, H-6a), 3.90 (m, 1H, H-5′), 3.94 (m, 1H, H-6b′), 4.06 (m, 1H, H-6a′), 4.09 (m, 1H, $J_{5',6a'} = 3.2$ Hz, $J_{5',6b'} = 3.2$ Hz, H-5′), 4.33 (dd, 1H, H-6b′), 4.52 (dd, 1H, $J_{6a',6b'} = 11.9$ Hz, H-6a′), 4.57 (m, 1H, $=CH_2^a$), 4.63 (d, 1H, $J_{1',2'} = 7.9$ Hz, H-1′), 4.66 (m, 1H, $=CH_2^b$), 5.08 (d, 1H, $J_{1',2'} = 8.1$ Hz, H-1′), 5.23 (d, 1H, $J_{1,2} = 7.7$ Hz, H-1), 5.41 (dd, 1H, $J_{3',4'} = 9.8$ Hz, H-3′), 5.44 (m, 1H, $-CH=$), 5.46 (dd, 1H, $J_{2',3'} = 9.8$ Hz, H-2′), 5.61 (dd, 1H, $J_{4',5'} = 9.4$ Hz, H-4′), 5.70 (dd, 1H, $J_{2',3'} = 8.1$ Hz, H-2′), 5.75 (m, 1H, H-4′), 5.77 (dd, 1H, $J_{3,4} = 9.8$ Hz, H-3), 5.81 (dd, 1H, $J_{3',4'} = 9.6$ Hz, H-3′), 7.10−8.00 (m, 59H, aromatic); ^{13}C NMR δ 28.6, 29.9, 30.0, 31.1, 68.2, 69.0, 69.1, 69.6 (×2), 69.9, 70.8, 71.8, 71.9, 72.5, 73.3, 74.6, 75.0 (×2), 98.1, 101.4, 101.9, 114.8, 123.7 (×2), 128.5 (×14), 128.8, 129.0 (×6), 129.2, 129.4, 129.5, 129.8 (×3), 130.0 (×10), 130.1 (×3), 130.2 (×3), 133.4 (×2), 133.5 (×2), 133.7, 133.8, 134.3 (×2), 138.0 (×2), 165.3, 165.3, 165.4, 165.6, 165.8, 166.3, 166.5, 166.9, 207.2 (×2); HR-FAB MS $[M + Na]^+$ calcd for $C_{87}H_{75}NaNO_{25}$ 1556.4526, found 1556.4497.

Methyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-*O*-(3-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (55) was obtained from **54** and **14** using conventional NIS/TMSOTf activation (see the Supporting Information) in 73% yield as a colorless syrup. Selected analytical data for **55**: $R_f = 0.5$ (ethyl acetate−hexane, 1/1, v/v); $[\alpha]^{22}_D$ 26.1 ($c = 1.0$, $CHCl_3$); ^{1}H NMR δ 3.06 (s, 3H), 3.13 (m, 1H), 3.28 (dd, 1H, $J = 3.4$, 9.6 Hz), 3.34 (dd, 1H, $J = 3.1$ Hz), 3.42−3.48 (m, 2H), 3.62−3.77 (m, 4H), 3.87−4.24 (m, 7H), 4.26−4.36 (m, 3H), 4.52 (dd, 1H, $J = 3.2$ Hz), 4.56 (dd, 2H, $J = 12.2$ Hz), 4.66 (d, 1H, $J = 7.9$ Hz), 4.67 (dd, 2H, $J = 10.9$ Hz), 5.01 (d, 1H, $J = 7.8$ Hz), 5.30 (d, 1H, $J = 8.4$ Hz), 5.40 (dd, 1H, $J = 3.5$, $J = 10.4$ Hz), 5.46 (dd, 1H, $J = 7.9$, $J = 9.7$ Hz), 5.6 (dd, 1H, $J = 8.4$ Hz), 5.66 (dd, 1H, $J = 7.8$, $J = 10.4$ Hz), 5.72−5.76 (m, 2H), 5.80 (dd, 1H, $J = 9.5$ Hz), 6.87−8.01 (m, 59H); ^{13}C NMR δ 29.9, 54.6, 55.3, 62.9, 68.1, 68.3, 69.0, 69.3, 69.4, 69.6, 69.6, 70.1, 70.6, 71.8, 71.9, 72.5, 73.2, 73.6, 74.3, 74.9, 75.3, 75.8, 80.0, 82.0, 98.1, 98.2, 101.4, 102.0, 127.7−139.0 (72 signals), 165.3, 165.3, 165.4, 165.6, 165.8, 166.3, 166.3, 166.9; HR-FAB MS $[M + Na]^+$ calcd for $C_{110}H_{97}NaNO_{30}$ 1934.5993, found 1934.5965.

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Supporting Information Available: Spectra for all new compounds and experimental procedures and characterization data for compounds **42**−**44**, **46**, **48**, and **53**. This material is available free of charge via the Internet at http://pubs.acs.org.

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