JOC*Note*

Efficient Synthesis of Methylene *exo*-Glycals: Another Use of Glycosylthiomethyl Chlorides

Xiangming Zhu,* Ying Jin, and John Wickham

Centre for Synthesis and Chemical Biology, UCD School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

xiangming.zhu@ucd.ie

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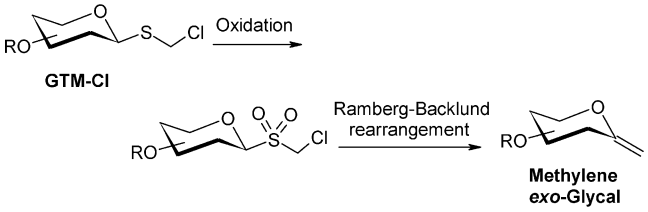
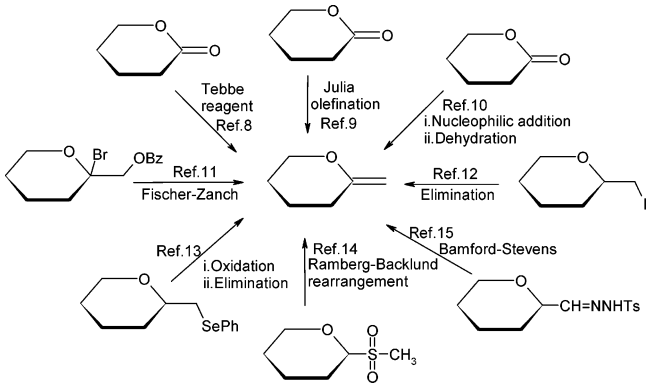


A new approach to the synthesis of methylene *exo*-glycals is described. Oxidation of glycosylthiolmethyl chloride (GTM-Cl) with *m*CPBA afforded the corresponding glycosylchloromethyl sulfone in almost quantitative yield, which underwent KO^{t}Bu-induced Ramberg−Bäcklund rearrangement to furnish the desired methylene *exo*-glycal in excellent yield.

The importance of carbohydrates and glycoconjugates in diverse biochemical processes has stimulated the development of glycomimetics as fundamental tools for biological research and as potential agents for therapeutic intervention. In this context, *C*-glycosides have received considerable attention because of their resistance to chemical and enzymatic hydrolysis and their similar or even better biological activities compared to those of the corresponding *O*-glycosides.[1] Therefore, numerous reliable methods[2] have been developed in the past two decades for the synthesis of *C*-glycosides, *C*-linked disaccharides, etc., among which *exo*-glycals are often important synthetic intermediates.[3]

exo-Glycals are unsaturated sugars that have an exocyclic C=C bond attached to the anomeric center. Methylene *exo*-glycals, often referred as *exo*-methylene sugars, are the simplest version of *exo*-glycals and have been employed widely to synthesize

SCHEME 1. Known Procedures for the Synthesis of Methylene *exo*-Glycals



C-glycosidic structures of biological interest.[4] For instance, they have been used to construct different types of glycosyltransferase inhibitors with *C*-glycosidic linkages.[4d] Recently, 1,3-dipolar cycloaddition of methylene *exo*-glycals with a nitrone has also been carried out to prepare a type of novel amino-ketosyl *C*-disaccharides.[4a] On the other hand, direct dimerization of methylene *exo*-glycals could also lead to *C*-linked disaccharides.[4k] Also, a Ramberg−Bäcklund approach has been developed by Taylor et al. for the construction of *C*-linked trehalose, in which a methylene *exo*-glucal was used as the key building block.[4e] In addition to their wide application in *C*-glycoside synthesis, methylene *exo*-glycals are also very useful in the synthesis of natural products and their analogues.[5] For example, methylene *exo*-mannals have been employed to synthesize a 1-*C*-methyl-substituted analogue of PI-88,[5a] a phosphomannopentaose sulfate with potent heparanase inhibitory activity and antiangiogenesis properties. Phlorizin, an aryl β-glucoside, can effectively lower the blood glucose level in diabetic animal models. Its analogues were also successfully prepared by using a methylene *exo*-glucal as the key building block.[5b] In short, methylene *exo*-glycals are important synthetic intermediates in both carbohydrate synthesis and natural product synthesis as a reseult of the potential for further elaboration of the enol ether functionality.[6] Moreover, very recent reports[7] that methylene *exo*-glycals could be readily

(1) For some recent examples of the synthesis of *C*-glycosides of biological relevance, see: (a) Yang, G.; Schmieg, J.; Tsuji, M.; Franck, R. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 3818−3822. (b) Kulkarni, S. S.; Gervay-Hague, J. *Org. Lett.* **2006**, *8*, 5765−5768. (c) Postema, M. H. D.; Piper, J. L.; Betts, R. L. *J. Org. Chem.* **2005**, *70*, 829−836. (d) Dondoni, A.; Catozzi, N.; Marra, A. *J. Org. Chem.* **2004**, *69*, 5023−5036. (e) Abdallah, Z.; Doisneau, G.; Beau, J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5209−5212.

(2) For some recent reviews on *C*-glycoside synthesis, see: (a) Taylor, R. J. K.; McAllister, G. D.; Franck, R. W. *Carbohydr. Res.* **2006**, *341*, 1298−1311. (b) Yuan, X.; Linhardt, R. J. *Curr. Top. Med. Chem.* **2005**, *5*, 1393−1430. (c) Smoliakova, I. P. *Curr. Org. Chem.* **2000**, *4*, 589−608.

(3) Reviewed in: (a) Lin, C. H.; Lin, H. C.; Yang, W. B. *Curr. Top. Med. Chem.* **2005**, *5*, 1431−1457. (b) Taillefumier, C.; Chapleur, Y. *Chem. Rev.* **2004**, *104*, 263−292.

(4) There are a large number of reports on *C*-glycoside synthesis using methylene *exo*-glycals. For some examples, see: (a) Li, X.; Takahashi, H.; Ohtake, H.; Ikegami, S. *Tetrahedron Lett.* **2004**, *45*, 4123−4126. (b) Paterson, D. E.; Griffin, F. K.; Alcaraz, M. L.; Taylor, R. J. K. *Eur. J. Org. Chem.* **2002**, 1323−1336. (c) Liu, H.; Smoliakova, I. P.; Koikov, L. N. *Org. Lett.* **2002**, *4*, 3895−3898. (d) Waldscheck, B.; Streiff, M.; Notz, W.; Kinzy, W.; Schmidt, R. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 4007−4011. (e) Griffin, F. K.; Paterson, D. E.; Taylor, R. J. K. *Angew. Chem., Int. Ed.* **1999**, *38*, 2939−2942. (f) Campbell, A. D.; Paterson, D. E.; Raynham, T. M.; Taylor, R. J. K. *Chem. Commun.* **1999**, 1599−1600. (g) Alcaraz, M. L.; Griffin, F. K.; Paterson, D. E.; Taylor, R. J. K. *Tetrahedron Lett.* **1998**, *39*, 8183−8186. (h) Witczak, Z. J.; Chhabra, R.; Chojnacki, J. *Tetrahedron Lett.* **1997**, *38*, 2215−2218. (i) Gervay, J.; Flaherty, T. M.; Holmes, D. *Tetrahedron* **1997**, *53*, 16355−16364. (j) Haudrechy, A.; Sinaÿ, P. *J. Org. Chem.* **1992**, *57*, 4142−4151. (k) Lay, L.; Nicotra, F.; Panza, L.; Russo, G.; Caneva, E. *J. Org. Chem.* **1992**, *57*, 1304−1306.

(5) (a) Namme, R.; Mitsugi, T.; Takahashi, H.; Ikegami, S. *Tetrahedron Lett.* **2005**, *46*, 3033−3036. (b) Link, J. T.; Sorensen, B. K. *Tetrahedron Lett.* **2000**, *41*, 9213−9217. (c) Sasaki, M.; Fuwa, H.; Inoue, M.; Tachibana, K. *Tetrahedron Lett.* **1998**, *39*, 9027−9030. (d) Sasaki, M.; Ishikawa, M.; Fuwa, H.; Tachibana, K. *Tetrahedron* **2002**, *58*, 1889−1911.

(6) Hsu, S. J.; Lin, H. C.; Lin, C. H. *Carbohydr. Res.* **2006**, *341*, 1428−1437.

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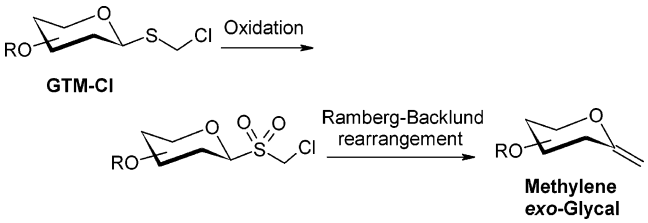
SCHEME 2. Proposed Procedure for the Synthesis of Methylene *exo*-Glycals

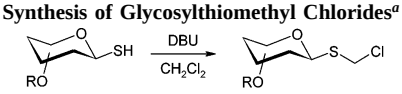


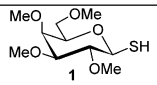
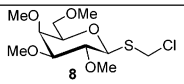
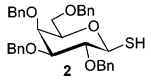
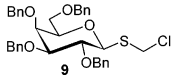
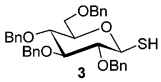
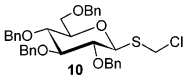
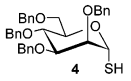
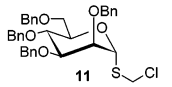
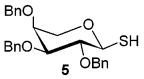
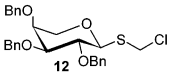
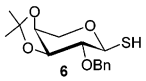
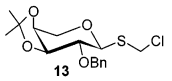
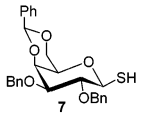
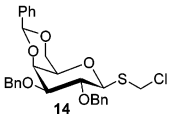
transformed into substituted *exo*-glycals undoubtedly further enhance their value in synthetic chemistry.

Accordingly, a number of methods have been reported so far to prepare methylene *exo*-glycals (Scheme 1): methylenation of sugar lactones with Tebbe or Petasis reagent,[8] Julia olefination of sugar lactones,[9] nucleophilic addition of sugar lactones with MeLi or MeMgX followed by dehydration,[10] reductive elimination of pyranoketosyl bromides in Fischer−Zanch conditions,[11] elimination of glycosylmethyl iodides,[5d,12] oxidation of glycosylmethyl phenyl selenide followed by elimination,[13] tandem halogenation-Ramberg−Bäcklund rearrangement of glycosylmethyl sulfones,[14] and rearrangement of glycosylmethylene carbenes generated by Bamford−Stevens reaction of anhydroaldose tosylhydrazones.[15]

However, most of these procedures suffer from either low yields of the glycosylidenes or extremely harsh conditions required for the transformations. Additionally, the low availability of some starting materials, such as anhydroaldose tosylhydrazones and glycosylmethyl iodides, has also restricted the further application of the corresponding procedures. In view of the great utility and potential of methylene *exo*-glycals in synthetic chemistry, we present here an efficient procedure based on Ramberg−Bäcklund rearrangement[16] for the synthesis of this type of compound using glycosylthiomethyl chloride (GTM-Cl), as shown in Scheme 2. Recently, a new sugar species, GTM-Cl,[17] has been developed and successfully applied to the synthesis of a series of *S*-linked neoglycoconjugates, such as novel sugar-triazole conjugates,[17] sugar-nucleotide conjugates,[18]

TABLE 1. Synthesis of Glycosylthiomethyl Chlorides[a]



Entry	Substrate	Product	Yield (%)[b]
1			78
2			73
3			86
4			70
5			71
6			86
7			73

[a] All reactions conducted at 0 °C to room temperature; see Experimental Section for details. [b] Yield of pure, isolated product with correct analytical and spectral data.

and neoglycopeptides.[19] The chemical stability and good mimicry of the *S*-neoglycoconjugates derived from GTM-Cl render the new species excellent building blocks to potentially allow access to a greater variety of *S*-glycosidic structures. Moreover, GTM-Cl itself could be readily prepared from the corresponding glycosyl thiol[20] by reaction with dichloromethane under the action of DBU. It should be noted here that Taylor and co-workers have developed a route for the synthesis of *exo*-glycals using the Ramberg−Bäcklund rearrangement, as depicted in Scheme 1, in which alkyl or aryl thioglycosides were used as starting materials.[14]

To generate methylene *exo*-glycals from GTM-Cl, galactosyl thiol **1**[21] was chosen as the model compound. It was first treated with dichloromethane in the presence of DBU as previously described,[17] and expectedly, GTM-Cl **8** was produced in very good yield, as shown in Table 1. Under the same conditions, glycosyl thiols **2**−**7**[22] were all efficiently converted into the corresponding GTM-Cl **9**−**14** in very good to high yields (70−86%). These glycosylthiomethyl chlorides are needed to test the feasibility of the proposed new route in Scheme 2 for the synthesis of methylene *exo*-glycals. In additioin, they could find

(7) (a) Gómez, A. M.; Barrio, A.; Amurrio, I.; Valverde, S.; Jarosz, S.; López, J. C. *Tetrahedron Lett.* **2006**, *47*, 6243−6246. (b) Gómez, A. M.; Pedregosa, A.; Valverde, S.; López, J. C. *Tetrahedron Lett.* **2003**, *44*, 6111−6116.

(8) (a) RajanBabu, T. V.; Reddy, G. S. *J. Org. Chem.* **1986**, *51*, 5458−5461. (b) Csuk, R.; Glänzer, B. I. *Tetrahedron* **1991**, *47*, 1655−1664.

(9) Gueyrard, D.; Haddoub, R.; Salem, A.; Bacar, N. S.; Goekjian, P. G. *Synlett* **2005**, 520−522.

(10) Yang, W. B.; Yang, Y. Y.; Gu, Y. F.; Wang, S. H.; Chang, C. C.; Lin, C. H. *J. Org. Chem.* **2002**, *67*, 3773−3782.

(11) Lichtenthaler, F. W.; Hahn, S.; Flath, F. J. *Liebigs Ann.* **1995**, 2081.

(12) Martin, O. R.; Xie, F. *Carbohydr. Res.* **1994**, *264*, 141−146.

(13) Lancelin, J. M.; Pougny, J. R.; Sinaÿ, P. *Carbohydr. Res.* **1985**, *136*, 369−374.

(14) (a) Griffin, F. K.; Murphy, P. V.; Paterson, D. E.; Taylor, R. J. K. *Tetrahedron Lett.* **1998**, *39*, 8179−8182. (b) Griffin, F. K.; Paterson, D. E.; Murphy, P. V.; Taylor, R. J. K. *Eur. J. Org. Chem.* **2002**, 1305−1322. (c) Murphy, P. V.; McDonnell, C.; Hämig, L.; Paterson, D. E.; Taylor, R. J. K. *Tetrahedron: Asymmetry* **2003**, *14*, 79−85.

(15) Tóth, M.; Somsák, L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 942−943.

(16) For reviews on the Ramberg−Bäcklund reaction, see: (a) Taylor, R. J. K.; Casy, G. *Org. React.* **2003**, *62*, 357−475. (b) Paquette, L. A. *Org. React.* **1977**, *25*, 1−71.

(17) Zhu, X.; Schmidt, R. R. *J. Org. Chem.* **2004**, *69*, 1081−1085.

(18) Zhu, X.; Stolz, F.; Schmidt, R. R. *J. Org. Chem.* **2004**, *69*, 7367−7370.

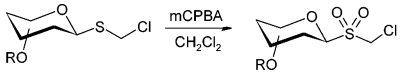
(19) Zhu, X.; Pachamuthu, K.; Schmidt, R. R. *Org. Lett.* **2004**, *6*, 1083−1085.

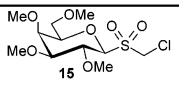
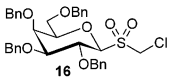
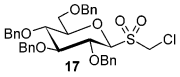
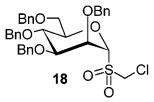
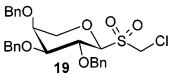
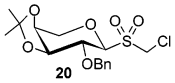
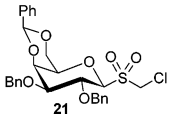
(20) It is important to note that glycosyl thiol could be readily prepared in a large scale by the following procedure: Černý, M.; Vrkoč, J.; Staněk, J. *Collect. Czech. Chem. Commun.* **1959**, *24*, 64−69.

(21) Zhu, X. *Tetrahedron Lett.* **2006**, *47*, 7935−7938.

(22) All glycosyl thiols were prepared by our previous procedure; see ref 21.

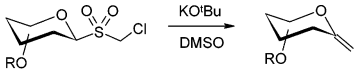
TABLE 2. Synthesis of Glycosylchloromethyl Sulfones[a]

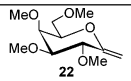
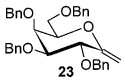
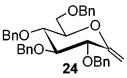
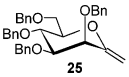
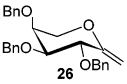
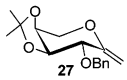
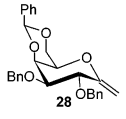


Entry	GTM-Cl	Sulfone	Yield (%)[b]
1	**8**	 **15**	99
2	**9**	 **16**	98
3	**10**	 **17**	quant.
4	**11**	 **18**	92
5	**12**	 **19**	95
6	**13**	 **20**	quant.
7	**14**	 **21**	quant.

[a] All compounds have been fully characterized by standard spectral methods. [b] Isolated yields based on starting chlorides after chromatographic separation.

TABLE 3. Synthesis of Methylene *exo*-Glycals[a]



Entry	Sulfone	*exo*-Glycal	Yield (%)[b]
1	**15**	 **22**	85
2	**16**	 **23**	87
3	**17**	 **24**	87
4	**18**	 **25**	81
5	**19**	 **26**	89
6	**20**	 **27**	94
7	**21**	 **28**	86

[a] All reactions conducted at room temperature; see Experimental Section for details. [b] Yield of pure, isolated product with correct analytical and spectral data.

valuable and versatile use in thioglycoside chemistry as mentioned above. Considering the fact that basic conditions may be required to effect the final Ramberg−Bäcklund rearrangement, non-base-labile protecting groups were used to protect these sugars. Synthesis of these methyl-, benzyl-, isopropylidene-, or benzylidene-protected glycosylthiomethyl chlorides also diversified the protecting group patterns of GTM-Cl, because GTM-Cl was only prepared previously with acyl-type protecting groups, such as acetyl and benzoyl.

Our attention turned then toward the formation of glycosylchloromethyl sulfones from these GTM-Cl. *m*-Chloroperoxybenzoic acid (*m*CPBA) was chosen as the oxidant to bring about the transformations. Fortunately, as outlined in Table 2, all reactions proceeded smoothly and led to the desired products **15**−**21** in excellent yields. Interestingly, although isopropylidene and benzylidene protecting groups are acid-labile, they are very stable under the present conditions as indicated by the quantitative yields of sulfones **20** and **21**. In addition, it should be noted here that a similar glycosyl α′-bromosulfone[14b] was reported as the reaction intermediate in Taylor's Ramberg−Bäcklund approach to *exo*-glycals and afterward could be converted smoothly into the expected *exo*-glycals. Nevertheless, neither glycosylbromomethyl sulfone nor glycosylchloromethyl sulfone has been reported in the literature, although they were assumed to be the intermediates in the tandem chlorination-Ramberg−Bäcklund reaction and tandem bromination-Ramberg−Bäcklund reaction of glycosylmethyl sulfones, respectively. Hence, the research presented here not only offered a new procedure for the synthesis of methylene *exo*-glycals but, to some extent, verified this assumption.

With these glycosylchloromethyl sulfones in hand, Ramberg−Bäcklund rearrangement induced by potassium *tert*-butoxide was investigated.[23] As expected, treatment of sulfone **15** with excessive KO^tBu in dimethyl sulfoxide gave rise to the desired *exo*-methylenic sugar **22** in very high yield (Table 3, entry 1). Gratifyingly, this reaction proceeded very cleanly as indicated by TLC, without any byproduct formation observed. Although β-elimination of the 2-alkoxy group to form *endo*-glycal could be a side reaction, the possible anomeric carbanion generated in the reaction must be intercepted completely by the γ-elimination process to form the episulfone intermediate because of the much better leaving property of the chloro group. The ready formation of compound **22** offered a preliminary suggestion that the present procedure may provide a general and convenient means to methylene *exo*-glycals. Indeed, the yields with other investigated sulfones (**16**−**21**) were invariably high, as show in Table 3, and the simplicity of the reaction conditions makes this approach an attractive way of preparing methylene *exo*-glycals, the versatile intermediates in the synthesis of carbohydrate and glycoconjugate mimetics. Also, it is noteworthy that recently Gueyrard et al. used the Julia olefination to prepare *exo*-glucal **24** in only modest yield (53%),[9] while Lin et al. synthesized the same compound in even lower yield (45%) via the nucleophilic addition-dehydration procedure.[10] Notably, by Taylor's Ramberg−Bäcklund approach,[14b] a satisfactory yield

(23) Schmittberger, T.; Uguen, D. *Tetrahedron Lett.* **1996**, *37*, 29−32.

(72%) of **24** could only be achieved under the harsh conditions (KOH, CCl_4, aqueous ^{t}BuOH, 60 °C); otherwise a significant amount of byproduct, *exo*-glucosylidenyl bromide, would be produced under other conditions (KOH/Al_2O_3, CBr_2F_2, ^{t}BuOH, CH_2Cl_2, 5 °C), resulting in a relatively low yield of the desired compound **24** (54%). Structural assignment of the new *exo*-glycals was made on the basis of NMR spectroscopy and exact mass spectral data.

In summary, from the new sugar species GTM-Cl, methylene *exo*-glycals were efficiently synthesized via a two-step oxidation-Ramberg−Bäcklund rearrangement procedure. The high yields and the mild conditions of this approach, together with the ready availability of GTM-Cl, are attractive features compared with previous methods. Extended studies on the scope and application of the procedure are currently underway.

Experimental Section

Chloromethyl 2,3,4,6-Tetra-*O*-methyl-1-thio-β-D-galactopyranoside (8). To a stirred solution of the thiol **1** (120 mg, 0.48 mmol) in CH_2Cl_2 (20 mL) was added DBU (0.14 mL, 0.93 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature, after which time TLC indicated the disappearance of the starting material. Dichloromethane was then removed in vacuo, and the residue was purified by flash column chromatography (cyclohexane/EtOAc, 2:1) to give the desired product **8** (112 mg, 78%) as a white amorphous solid: TLC R_f = 0.36 (cyclohexane/EtOAc, 2:1); $[\alpha]^{20}_D$ −46.7 (*c* 1.2 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.99, 4.75 (AB peak, J = 11.8 Hz, 2H, H-1′), 4.55 (d, J = 9.6 Hz, 1H, H-1), 3.72 (d, J = 2.8 Hz, 1H, H-4), 3.60−3.54 (overlapped m, 3H, H-5, H-6), 3.58 (s, 3H, Me), 3.57 (s, 3H, Me), 3.55 (s, 3H, Me), 3.45 (t, J = 9.6 Hz, 1H, H-2), 3.40 (s, 3H, Me), 3.24 (dd, J = 9.2, 3.2 Hz, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 86.0 (C-3), 82.3 (C-1), 79.6 (C-2), 77.3 (C-5), 75.2 (C-4), 70.7 (C-6), 61.6, 61.3, 59.4, 58.5 (4 Me), 46.1 (C-1′); ESI-MS *m*/*z* 323.1 $[M + Na]^+$; ESI-HRMS calcd for $C_{11}H_{21}ClNaO_5S$ $[M + Na]^+$ 323.0696, found 323.0685.

2,3,4,6-Tetra-*O*-methyl-β-D-galactopyranosyl Chloromethyl Sulfone (15). To a stirred solution of chloride **8** (105 mg, 0.35 mmol) in CH_2Cl_2 (13 mL) was added in one portion 70% *m*CPBA (345 mg, 1.40 mmol) at 0 °C. The resulting mixture was vigorously stirred for 20 h at ambient temperature; diluted with CH_2Cl_2; washed successively with H_2O, saturated aqueous $NaHCO_3$, and brine; dried over $MgSO_4$; and concentrated. The residue was purified by flash column chromatography (cyclohexane/EtOAc, 1:1) to afford title compound **15** (115 mg, 99%) as a white amorphous solid: TLC R_f = 0.19 (cyclohexane/EtOAc, 1:1); $[\alpha]^{20}_D$ −62.3 (*c* 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.76, 4.39 (AB peak, J = 12.2 Hz, 2H, H-1′), 4.53 (d, J = 9.2 Hz, 1H, H-1), 3.99 (t, J = 9.4 Hz, 1H, H-2), 3.71 (dd, J = 2.8, 0.8 Hz, 1H, H-4), 3.68−3.54 (overlapped m, 3H, H-5, H-6), 3.64, 3.57, 3.56, 3.39 (4s, 12H, Me), 3.35 (dd, J = 9.2, 2.8 Hz, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 87.9 (C-1), 85.7 (C-3), 78.5 (C-5), 75.2 (C-2), 74.7 (C-4), 70.4 (C-6), 61.6, 61.2, 59.4, 58.6 (4 Me), 54.2 (C-1′); ESI-MS *m*/*z* 355.2 $[M + Na]^+$, 371.2 $[M + K]^+$; ESI-HRMS calcd for $C_{11}H_{21}ClNaO_7S$ $[M + Na]^+$ 355.0594, found 355.0587.

2,3,4,6-Tetra-*O*-methyl-1-deoxy-1-methylidene-D-galactopyranose (22). KO^{t}Bu (1.0 M) in THF (1.32 mL, 1.32 mmol) was added dropwise to a solution of chloride **15** (110 mg, 0.33 mmol) in DMSO (5 mL) at room temperature, and the solution was stirred for 4 h and then diluted with Et_2O (30 mL) and water (5 mL). The aqueous phase was separated and extracted with Et_2O. The combined organic layer was washed brine, dried over $MgSO_4$, and evaporated to a residue, which was purified by flash column chromatography (cyclohexane/EtOAc, 2:1 + 1% Et_3N) to afford the desired product **22** (65 mg, 85%) as a colorless syrup: TLC R_f = 0.30 (cyclohexane/EtOAc, 2:1); $[\alpha]^{20}_D$ +54.2 (*c* 0.8 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.69 (dd, J = 1.6, 0.8 Hz, 1H, H-1′$_a$), 4.58 (dd, J = 1.6, 0.8 Hz, 1H, H-1′$_b$), 3.89 (dt, J = 8.8, 1.6 Hz, 1H, H-2), 3.76−3.72 (m, 2H, H-4, H-5), 3.62−3.54 (m, 2H, H-6), 3.53, 3.49, 3.48, 3.37 (4s, 12H, Me), 3.28 (dd, J = 8.8, 3.2 Hz, 1H, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.9 (C-1), 95.5 (C-1′), 83.5 (C-3), 78.6 (C-2), 78.2 (C-5), 75.8 (C-4), 70.9 (C-6), 60.9, 59.40, 59.37, 58.6 (4 Me); ESI-MS *m*/*z* 255.3 $[M + Na]^+$; ESI-HRMS calcd for $C_{11}H_{20}NaO_5$ $[M + Na]^+$ 255.1208, found 255.1212.

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Supporting Information Available: Experimental procedures and analytical and spectral characterization data for all other compounds; copies of NMR spectra of compounds **8**−**28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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