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1,2-Migration of 2′-Oxoalkyl Group and Concomitant Synthesis of 2-*C*-Branched *O*-, *S*-Glycosides and Glycosyl Azides via 1,2-Cyclopropanated Sugars

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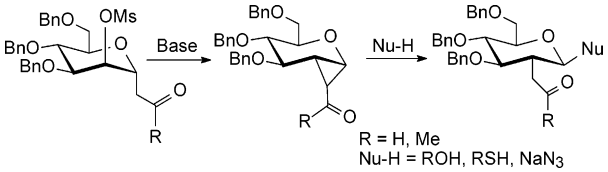

Treatment of 2′-oxoalkyl 2-*O*-Ms(Ts)-α-*C*-mannosides (**4**, **5**, and **6**) with base resulted in 1,2-cyclopropanation via an intramolecular S_N2 reaction due to their 1,2-*trans-diaxial* configurations. The 1,2-cyclopropanated sugars (**10** and **13**) were reacted with various alcohols, thiols, and sodium azide to produce 2-*C*-branched *O*- and *S*-glycosides and glycosyl azides (**11**, **14**−**28**) in good to excellent yields. In contrast, 1,2-*cis* 2′-oxoalkyl 2-*O*-Ms(Ts)-α-*C*-glucoside **9** formed an acyclic conjugated aldehyde (**31**) under basic conditions, which occurred by 1′-enolation followed by β-elimination. An intramolecular Michael addition from **31** produced 2-*O*-Ms-β-*C*-glucoside **30** as a major product. However, due to the electron-withdrawing effect exerted by 2-*O*-Ms compound **31** also undergoes a C2 epimerization to form **32**. Thereafter, the intramolecular Michael addition led to the formation of both 1,2-*trans* 2′-oxoalkyl 2-*O*-Ms-α-*C*-mannoside **4** and its β-anomer (**33**). Because β-elimination/Michael addition and C2 epimerization are reversible reactions, equilibriums among **9**, **31**, **30**, **32**, **33**, and **4** were established, which included the transformation of 1,2-*cis* *C*-glucoside **9** into 1,2-*trans* *C*-mannoside **4**. The subsequent 1,2-cyclopropanation of **4** was an irreversible reaction yielding 1,2-cyclopropanated **10** and further conversion to 1,2-migration products (**11** and **12**).

Introduction

Because of neighboring group participation the 2-position of sugars plays a critical role in the chemical reactivity and stereoselectivity at the anomeric center.[1] 2,1-Migration in glycosylation is rare because the anomeric carbon is generally more electrophilic due to the endo-oxonium stabilization, but 1,2-migrations do occur under certain conditions. For example, it is well-known that thioglycosides and selenoglycosides may undergo rearrangement to give alkylated 2-thioglycosides and 2-selenoglycosides through their respective 1,2-episulfonium[2] and 1,2-episelenonium[3] intermediates. These intermediates are formed by an intramolecular displacement of a leaving group at the 2-position by the nucleophilic sulfur or selenium atom at C1. 1,2-Migration via an aziridine intermediate has also been observed. Danishefsky et al.[4] first reported such 1,2-migration

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† Institute of Biological Chemistry, Academia Sinica.

(1) (a) *Carbohydrates in Chemistry and Biology*; Ernst, B., Hart, G. W., Sinaÿ, P., Eds.; Wiley-VCH: Weiheim, Germany, 2000;, Vol. 1. (b) *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker: New York, 1996. (c) Oscarsson, S. *Topics in Current Chemistry*: *Glycoscience*; Driguuez, H., Thiem, J., Eds.; Springer: Berlin, Germany, 1997; Vol. 186. (d) Lemieux, R. U. *Adv. Carbohydr. Chem.* **1954**, *9*, 1−57. (e) Lemieux, R. U.; Brice, C.; Huber, G. *Can. J. Chem.* **1955**, *33*, 134−147.

(2) (a) Auzanneau, F.-I.; Bundle, D. R. *Carbohydr. Res.* **1991**, *212*, 13−24. (b) Pozsgay, V. *Carbohydr. Res.* **1992**, *235*, 295−302. (c) Johnston, B. D.; Pinto, B. M. *J. Org. Chem.* **2000**, *65*, 4607−4617. (d) Yu, B.; Yang, Z. *Tetrahedron Lett.* **2000**, *41*, 2961−2964. (e) Yang, Z.; Yu, B. *Carbohydr. Res.* **2001**, *333*, 105−114. (f) Yu, B.; Yang, Z. *Org. Lett.* **2001**, *3*, 377−379.

(3) (a) Jaurand, G.; Beau, J.-M.; Sina, P. *J. Chem. Soc,. Chem. Commun.* **1981**, 572−573. (b) Kaye, A.; Neidle, S.; Reese, C. B. *Tetrahedron Lett.* **1988**, *29*, 2711−2714. (c) Perez, M.; Beau, J.-M. *Tetrahedron Lett.* **1989**, *30*, 75−78. (d) Roush, W. R.; Sebesta, D. P.; James, R. A. *Tetrahedron* **1997**, *53*, 8837−8852.

(4) (a) Griffith, D. A.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 5811−5819. (b) Griffith, D. A.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 5863−5864. (c) Danishefsky, S. J.; Koseki, K.; Griffith, D. A.; Gervay, J.; Peterson, J. M.; McDonald, F. E.; Oriyama, T. *J. Am. Chem. Soc.* **1992**, *114*, 8331−8333.

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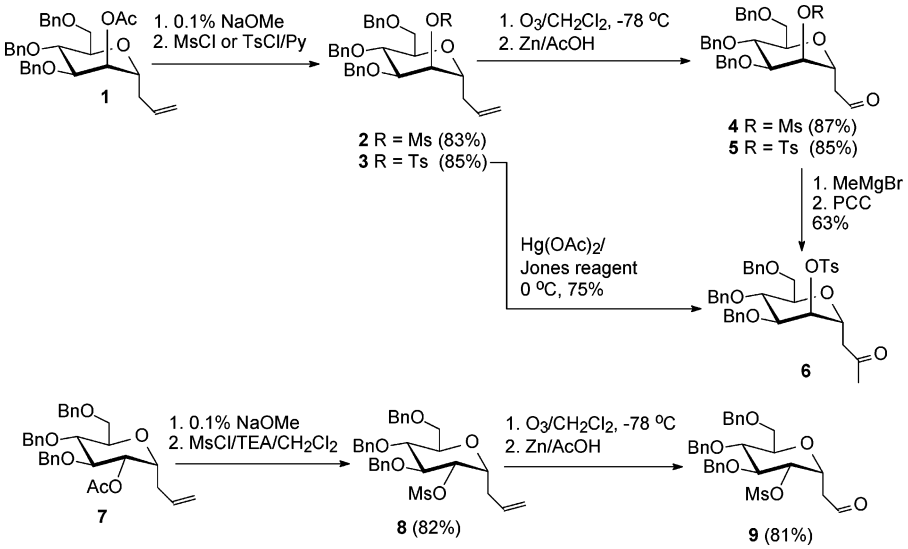
SCHEME 1. Synthesis of 2′-Carbonylalkyl 2-*O*-Ms(Ts)-*C*-glycosides



when a 2-iodo-1-*N*-sulfonamide sugar was treated with lithium ethanethiolate and yielded *trans*-2-*N*-sulfonamide-β-thioglycoside. Recently, Finney et al.[5] found that triazolines obtained from glycal and azides produced aziridine intermediates by photolysis, which following a subsequent S_N2 reaction at the anomeric carbon produced 2-aminoglycosides. In addition to 1,2-migrations via three-membered heterocyclic intermediates, we found that 1,2-cyclopropanated sugar intermediates were formed by base treatment of 2′-oxoalkyl 2-*O*-Ms(Ts)-α-*C*-mannopyranoside prior to their nucleophilic ring opening and the concomitant formation of the 2-*C*-branched glycosides.[6]

However, the above study on the 1,2-migration of the 2′-oxoalkyl group was limited to 2′-oxoalkyl 2-*O*-Ms(Ts)-α-mannosides, which have 1,2-trans configurations. Because 2′-oxoalkyl *C*-glycosides can also undergo a β-elimination under basic conditions to form an acyclic α,β-unsaturated aldehyde (ketone),[7] this β-elimination will compete with 1,2-cyclopropanation after the initial 1′-enolation. Furthermore, unlike the 1,2-cyclopropanated sugar from 2′-aldehydo 2-*O*-Ms-α-*C*-mannosides that reacted with various nucleophiles (alcohols, thiols, and sodium azide) the one derived from 2′-ketonyl 2-*O*-Ms-α-*C*-mannoside failed to give a 2-*C*-branched *O*-glycoside and a glycosyl azide and only reacted with thiols to produce 2-*C*-acetylmethyl-2-deoxy-β-thioglucosides. In this report, we describe the successful preparation of additional 2-*C*-branched glycosides including those 2-*C*-acetylmethyl-2-deoxy-β-*O*-glycosides and a glycosyl azide by a modified procedure. The mechanism controlling the competitive 1,2-cyclopropanation and β-elimination process is also discussed, using 1,2-*cis* 2′-oxoalkyl 2-*O*-Ms-α-*C*-glucoside as a substrate.

(5) Dahl, R. S.; Finney, N. S. *J. Am. Chem. Soc.* **2004**, *126*, 8356−8357.
(6) Shao, H.; Ekthawatchai, S.; Wu, S.-H.; Zou, W. *Org. Lett.* **2004**, *6*, 3497−3499.
(7) (a) Shao, H.; Wang, Z.; Laroix, E.; Wu, S.-H.; Jennings, H.; Zou, W. *J. Am. Chem. Soc.* **2002**, *124*, 2130−2131. (b) Wang, Z.; Shao, H.; Laroix, E.; Wu, S.-H.; Jennings, H.; Zou, W. *J. Org. Chem.* **2003**, *68*, 8097−8105.

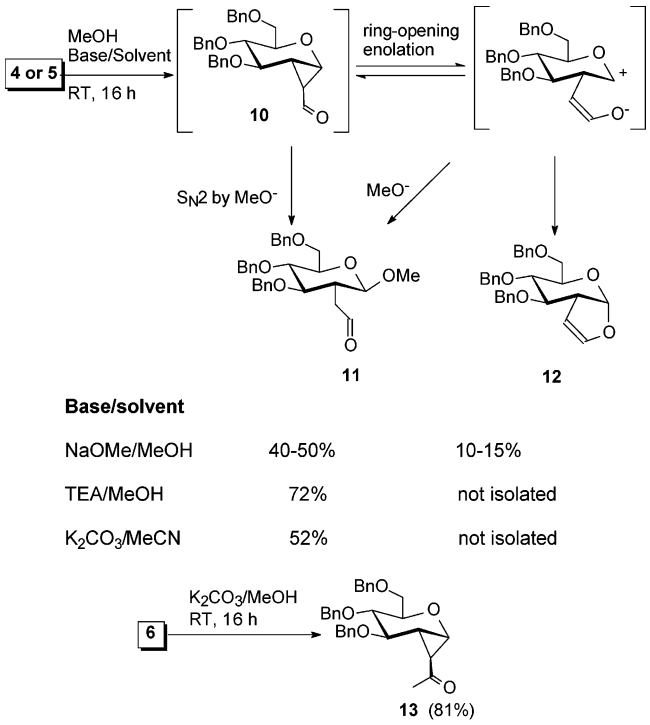
Results and Discussion

Synthesis of 2′-Oxoalkyl 2-*O*-Ms(Ts)-*C*-glycosides (4, 5, 6, and 9). Allyl *C*-mannoside **1** and *C*-glucoside **7** previously prepared were used as the starting materials.[8] Conventional removal of 2-*O*-Ac was followed by mesylation or tosylation as shown in Scheme 1 to afford **2**, **3**, and **8**, respectively, in good yields. These allyl *C*-glycosides were then subjected to ozonolysis to give respective 2′-aldehydo *C*-glycosides (**4**, **5**, and **9**). 2′-Ketonyl *C*-mannoside **6** was initially prepared from aldehyde **5** in two steps by a Grignard reaction (MeMgBr) followed by PCC oxidation of resultant 2′-alcohol. However, **6** can be more efficiently obtained from **3** by oxidizing the olefin double bond, using $Hg(OAc)_2$ and Jones reagent (see Scheme 1).[9]

1,2-Cyclopropanated Sugars and 2-*C*-Branched Glycosides. 1,2-Cyclopropaned sugars are often produced from glycals by treatment with diazo esters, Simmons−Smith reagents, or dihalocarbenes.[10] Four possible diastereomers are formed depending on the reaction conditions and the protecting groups. The addition to the alkene (cyclopropanation) is stereoselctive in most cases; however, the stereochemistry of the bridged carbon is less certain, resulting in a mixture of cis and trans diastereomers. Ring opening of the 1,2-cyclopropaned sugars by solvolysis in the presence of mercury,[11] strong acid,[12] halonium,[13] and platinum[14] gave

(8) Zou, W.; Wang, Z.; Lacroix, E.; Wu, S.-H.; Jennings, H. *Carbohydr. Res.* **2001**, *334*, 223−231.
(9) (a) Rogers, H. R.; McDermott, J. X.; Whitesides, G. M. *J. Org. Chem.* **1975**, *40*, 3577−3580. (b) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2555−2560.
(10) Cousins, G. S.; Hoberg, J. O. *Chem. Soc. Rev.* **2000**, *29*, 165−174.
(11) Scott, R. W.; Heathcock, C. H. *Carbohydr. Res.* **1996**, *291*, 205−208.
(12) (a) Kim, C.; Hoang, R.; Theodorakis, E. A. *Org. Lett.* **1999**, *1*, 1295−1297. (b) Hoberg, J. O.; Claffey, D. J. *Tetrahedron Lett.* **1996**, *37*, 2533−2536.
(13) (a) Ramana, C. V.; Murali, R.; Nagarajan, M. *J. Org. Chem.* **1997**, *62*, 7694−7703. (b) Ramana, C. V.; Nagarajan, M. *Synlett* **1997**, 763−764. (c) Bertinato, P.; Sorensen, E. J.; Meng, D.; Danishefsky, S. J. *J. Org. Chem.* **1996**, *61*, 8000−8001.
(14) (a) Beyer, J.; Skaanderup, P. R.; Madsen, R. *J. Am. Chem. Soc.* **2000**, *122*, 9575−9583. (b) Beyer, J.; Madsen, R. *J. Am. Chem. Soc.* **1998**, *120*, 12137−12138.

SCHEME 2. 1,2-Migration of the Formylmethyl Group



2-*C*-branched sugars with α-glycosides as major products, regardless of the configuration of the substrates, due to the involvement of an oxocarbonium-like intermediate and the anomeric effect. A two-step ring opening of cyclopropanecarboxylate sugars mediated by NIS favors 1,2-*trans* 2-*C*-branched glycosides, likely due to the neighboring group participation.[15]

Treatment of 2′-oxoalkyl 2-*O*-Ts(Ms)-α-*C*-*mannosides* (**4** and **5**) with sodium methoxide in methanol produced 2-*C*-branched methyl β-glycoside **11** and a bicyclic derivative **12** via 1,2-cyclopropanated sugar **10** (see Scheme 2).[16] The β-configuration of **11** was unambiguously determined by the observation of nOe between H1 and H3 and the large coupling constant of $J_{1,2}$ = 8.8 Hz. Compound **10**, an intermediate, was not stable and decomposed during the chromatographic purification but was detected as a major product by the TLC analysis when **4** and **5** were treated with base (K_2CO_3 and t-BuOK) in DMF. However, when 2′-ketone **6** was treated with K_2CO_3 in methanol, 1,2-cyclopropanated **13** was isolated as a major product (>80% yield) (see Scheme 2), which surprisingly did not transform to 2-*C*-branched methyl β-glucoside as expected. Compound **13** was a pure diasteroisomer with a trans configuration at bridged C1′ as indicated by the nOe between H1′ and H3 and supported by the coupling constants ($J_{H1',H1}$ = 1.6 Hz, $J_{H1',H2}$ = 5.6 Hz, and $J_{H1,H2}$ = 7.2 Hz). Those small coupling constants ($J_{H1',H1}$ and $J_{H1',H2}$) are consistent with the trans stereochemistry reported in the literature on the respective 1,2-cyclopropanated sugar esters,[12,17] while the cis configurations often have a large coupling constant, e.g., $J_{H1,H2}$ = 7.2 Hz as observed.

We proposed a mechanism in which the ring opening of cyclopropanated **10** to 2-*C*-formylmethyl-2-deoxy-β-glycoside **11** resulted from a S_N2 reaction at the anomeric center similar to those previously reported by Danishefsky et al.[4] and by Finney et al.[5] Although there was no α-anomer isolated, it was still possible that both **11** and the bicyclic **12** were formed through a zwitterionic intermediate[18] derived by ring-opening enolation. An intramolecular reaction between the enolate and oxycarbonium gave **12** while the intermolecular addition at the anomeric carbon afforded **11**. This mechanism was consistent with the fact that we were able to obtain **11** as the only major product without the bicyclic **12** when **4** and **5** were treated with TEA in methanol or potassium carbonate in acetonitrile (see Scheme 2), because the ring-opening enolation becomes less likely in the presence of weaker bases. On the basis of these observations we reasoned that the chemoselectivity of the reaction might depend on (1) the stability of the 1,2-cyclopropanated sugars and (2) the relative basicity and nucleophilicity of the reagent. A stable 1,2-cyclopropanated sugar such as **13** and a better nucleophile should favor the S_N2 substitution at the anomeric carbon over the ring-opening enolation, leading to 1,2-migration of the 2′-oxoalkyl group.

As predicted, when compounds **4** and **5** were treated with various nucleophiles (alcohol, thiols, and sodium azide) under TEA or K_2CO_3, 1,2-migration and concomitant glycosylation provided 2-*C*-branched glycosides (**14** to **22**) in good to excellent yields (see Table 1), and no rearrangement product **12** was isolated. The dependence of chemoselectivity on the nuleophilicity was evidenced further by the fact that we were able to obtain respective *O*- and *S*-glycosides (**15**, **19**−**21**) and glycosyl azide (**22**) in methanol (entries 3 and 7−10 in Table 1) when better nucleophiles such as allyl alcohol, thiols, and azide were used. Because **13** is a more stable 1,2-cyclopropanated sugar than **10** and methoxide is a poor nucleophile, treatment of **13** with K_2CO_3 in methanol at room temperature resulted in neither methoxide addition at the anomeric carbon nor rearrangement. In contrast, both 2′-ketone **6** and **13** reacted with thiols under K_2CO_3/MeOH at room temperature to form 2-*C*-acetylmethyl-2-deoxy-β-thioglycosides (**23** and **24**) in excellent yields (see entries 1 and 2 in Table 2). Indeed, we were also able to obtain **23** and **24** by treatment of **13** and the respective thiols in methanol without additional base. This result suggests that the 1,2-migration of acetylmethyl group might occur in alcohols at higher temperature to produce 2-*C*-branched *O*-glycosides as a result of the destabilization of 1,2-cyclopropanated **13** and increased nucleophilicity of alcohols. To our satisfaction, treatment of **13** with various alcohols and sodium azide produced 2-*C*-acetylmethyl-2-deoxy-β-*O*-glycosides (**25**−

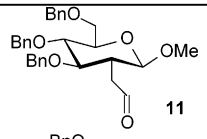
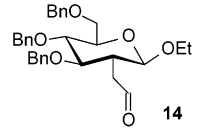
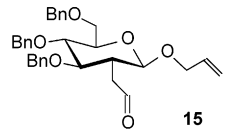
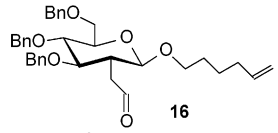
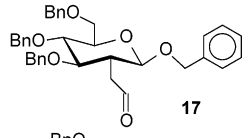
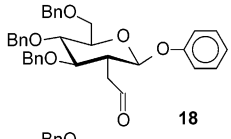
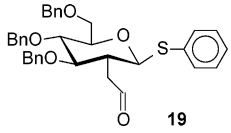
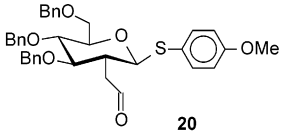
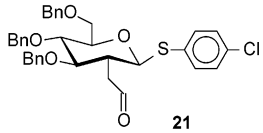
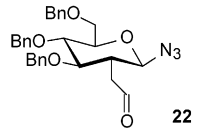
(15) Sridhar, P. R.; Ashalu, K. C.; Chandrasekaran, S. *Org. Lett.* **2004**, *6*, 1777−1779.

(16) For intramolecular S_N2 reactions to form other cyclopropanated sugars, see: (a) Fraser-Reid, B.; Holder, N. L.; Hicks, D. R.; Walker, D. L. *Can. J. Chem.* **1977**, *55*, 3978−3985. (b) Kawana, M.; Kuzuhara, H. *Synthesis* **1995**, 544−552.

(17) Proton−proton coupling constants in a cyclopropane system: J = 0−6 Hz for a trans stereochemistry and J = 8−10 Hz for a cis stereochemistry. See: (a) Kawabata, N.; Nakagawa, T.; Nakao, T.; Yamashita, S. *J. Org. Chem.* **1977**, *42*, 3031−3035. (b) Wiberg, K. B.; Barth, D. E.; Schertler, P. H. *J. Org. Chem.* **1973**, *38*, 378−381. (c) Williamson, K. L.; Lanford, C. A.; Nicholson, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 762−765.

(18) Biggs, T. N.; Swenton, J. S. *J. Org. Chem.* **1992**, *57*, 5568−5573.

TABLE 1. Synthesis of 2-*C*-Formylmethyl-2-deoxy-*β*-*O*- and *S*-glucosides and Glucosyl Azide

Entry	Substrate	Nucleophile /solvent	Base	Product	Yield
1	**4**	MeOH	TEA	 **11**	72%
2	**4**	EtOH	TEA	 **14**	71%
3	**5**	AllOH/MeOH	TEA	 **15**	76%
4	**5**	n-Hexanol	K_2CO_3	 **16**	78%
5	**5**	BnOH	K_2CO_3	 **17**	75%
6	**5**	PhOH /MeCN	K_2CO_3	 **18**	62%
7	**5**	PhSH /MeOH	K_2CO_3	 **19**	86%
8	**5**	4-MeOPhSH /MeOH	K_2CO_3	 **20**	85%
9	**5**	4-ClPhSH /MeOH	K_2CO_3	 **21**	83%
10	**5**	NaN_3 /MeOH	TEA	 **22**	52%

27) and glycosyl azide (**28**) in excellent yields (see entries 3−6 in Table 2). These experiments demonstrated that the ring opening of a 1,2-cyclopropanated sugar can be achieved by solvolysis without additional catalyst.[11−14] Unlike the catalytic solvolysis of 1,2-cyclopropanated sugars including 1,2-cyclopropanated esters which gave a mixture of anomers through an oxocarbonium intermediate, the formation of only the *β*-anomers suggests that the solvolysis of 1,2-cyclopropanated sugar ketones and aldehydes reported here likely followed an S_N2 mechanism.[19] In the absence of a good nucleophile the destabilized 1,2-cyclopropane **13** was forced to a thermal rearrangement to give bicyclic **29** (see entry 7 in Table 2).

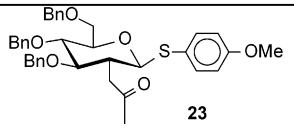
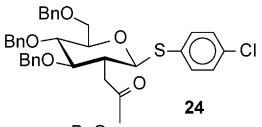
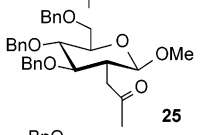
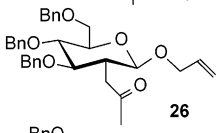
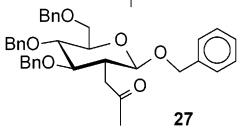
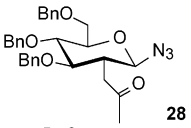
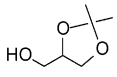
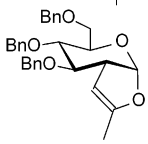
Because 2-*C*-branched sugars can mimic *N*-acylsugars[20] and are used as inhibitors of lipid A biosynthesis[21] by interacting with the *N*-acylase (LpxD),[22] these compounds could also have potential to be modified as inhibitors.

(19) 1,2-Cyclopropanated sugar esters were stable under these neutral solvolysis conditions, but decomposed under basic conditions.

(20) The glycoprocessing enzymes may promiscuously incorporate the 2-*C*-acetylmethyl-2-deoxy sugars into the biosynthetic pathway to replace 2-*N*-acetylsugars. See: Hang, H. C.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 1242−1243.

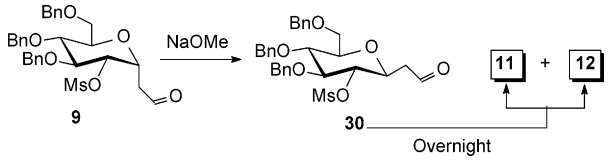
(21) Li, X.; Uchiyama, T.; Raetz, C. R. H.; Hindgaul, O. *Org. Lett.* **2003**, *5*, 539−541.

TABLE 2. Synthesis of 2-*C*-Acetylmethyl-2-deoxy-*β*-*O*- and *S*-glucosides and Glucosyl Azide

Entry	Substrate	Nucleophile /solvent	Base	Time /temperature	Product	Yield
1	**6**	4-MeOPhSH /MeOH	K_2CO_3	16 h/r. t.	 **23**	83%
2	**6**	4-ClPhSH /MeOH	K_2CO_3	16 h/r. t.	 **24**	85%
3	**13**	MeOH	none	16 h/ reflux	 **25**	95%
4	**13**	AllOH	none	16 h/70 °C	 **26**	96%
5	**13**	BnOH	none	16 h/100 °C	 **27**	82%
6	**13**	NaN_3 /MeOH	none	16 h/reflux	 **28**	92%
7	**13**	 /DMF	none	16 h/100 °C	 **29**	72%

1,2-Migration and Epimerization. Besides the S_N2 displacement at C2 to form 1,2-cyclopropanated sugars following C1′-enolation under basic conditions, *β*-elimination leading to an acyclic α,*β*-conjugated aldehyde (ketone) may also occur.[8] Due to the 1,2-trans configurations in α-*C*-mannosides (**4**, **5**, and **6**) 1,2-cyclopropanation was favored over *β*-elimination. We expected when α-*C*-glucoside **9**, which has the 1,2-cis configuration, was used, that *β*-elimination would be dominant leading to anomeric epimerization or an S_N2 displacement of 2-OMs by 5-OH to form a *C*-glycofuranoside.[23] Unexpectedly, we obtained **11** and **12** from **9** as major products in 50−70% yield when treated with NaOMe/MeOH at room temperature overnight (see Scheme 3). These were the same products obtained from the NaOMe/MeOH treatment of α-mannosides **4** and **5** (see Scheme 2). By monitoring the reaction on TLC we observed that a major intermediate was formed within 4 h at room temperature prior to its further transformation to **11** and **12**. Thus, this intermediate was isolated in 55−60% yield and characterized to be 2′-formylmethyl 2-*O*-Ms-*β*-*C*-glucoside **30**, an anomeric epimer of **9**. This result suggests that the *β*-elimination proceeded favorably in **9**, but not 1,2-cyclopropanation due to the lack of required 1,2-*trans-diaxial* configuration.

SCHEME 3. Epimerization and 1,2-Migration



The transformation of **30** to **11** and **12** was intriguing but could be explained through a mechanism illustrated in Figure 1. *β*-Elimination from **9** gave an acyclic conjugate **31**, which quickly underwent a hetero-Michael addition to form more stable *β*-anomer **30**. However, compound **30** can be converted to **31** by *β*-elimination, and be further converted to **32** by C2 epimerization through another equilibrium. Similar epimerizations at C2 have previously been observed in Horner−Emmons reaction on 2-acetamidosugar lactols and in 2-bromo sugars under basic conditions.[24] Meanwhile, an intra-

(22) Jackman, J. E.; Fierke, C. A.; Tumey, L. N.; Pirrung, M.; Uchiyama, T.; Tahir, S. H.; Hindsgaul, O.; Raetz, C. R. H. *J. Biol. Chem*. **2000**, *275*, 11002−11009.

(23) For examples of such intramolecular S_N2 reactions. See: (a) Sanjayan, G. J.; Stewart, A.; Hachisu, S.; Gonzalez, R.; Watterson, M. P.; Fleet, G. *Tetrahedron Lett.* **2003**, *44*, 5847−5851. (b) Watterson, M. P.; Edwards, A. A.; Leach, J. A.; Smith, M. D.; Ichihara, O.; Fleet, G. *Tetrahedron Lett.* **2003**, *44*, 5853−5857. (c) Harvey, J. E.; Raw, S. A.; Taylor, J. K. *Org. Lett.* **2004**, *6*, 2611−2614.

(24) (a) Allevi, P.; Ciuffreda, P.; Colombo, D.; Monti, D.; Speranza, G.; Manitto, P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1281−1283. (b) Werner, R. M.; Williams, L. M.; Davis, J. T. *Tetrahedron Lett.* **1998**, *39*, 9135−9138. (c) Marzabadi, C. H.; Spilling, C. D. *J. Org. Chem.* **1993**, *58*, 3761−3766. (d) Wen, X.; Hultin, P. *Tetrahedron Lett.* **2004**, *45*, 1773−1775.

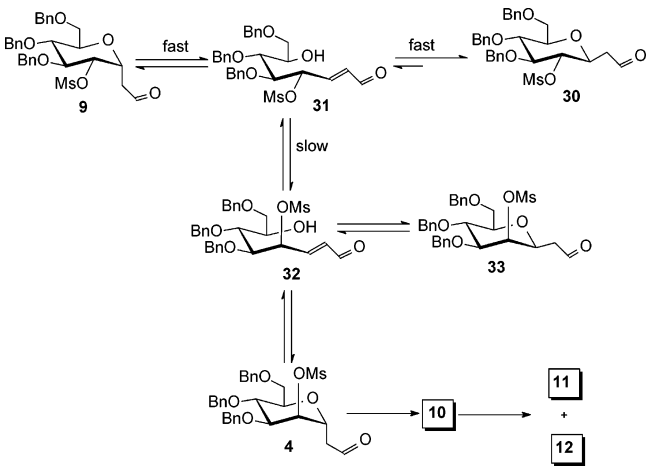
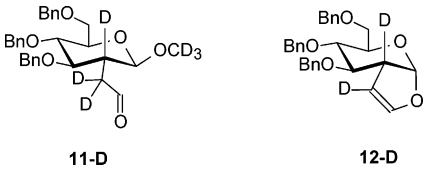


FIGURE 1. A mechanism of epimerization and 1,2-migration.

CHART 1



molecular hetero-Michael addition by 5-OH to C1, rather than an S_N2 substitution at C2, led to the formation of 2-*O*-Ms-α-*C*-mannoside **4** and its β-anomer **33**. Because the 1,2-cyclopropanation from **4** was not reversible (see Scheme 2) the equilibriums were eventually driven to the formation of **10**, which was then transformed to **11** (1,2-migration) and **12**. The direct evidence to support this mechanism was provided by the isolation of deuterated products, **11-D** and **12-D** (see Chart 1), when 2-*O*-Ms-α-*C*-glucoside **9** was treated with NaOMe in MeOH-d_4 overnight. Due to deuteration the proton resonances of H-2 at 2.29 ppm and 1′-CH_2 at 2.38 and 2.47 ppm in **11-D** disappeared, consequently, the double doublet aldehyde proton at 9.54 ppm and doublet H-1 at 4.15 ppm became two singlets, respectively. Similarly, two singlets, H-1 at 5.94 ppm and H-2′ at 6.47 ppm, were observed in **12-D**.

In summary, we have described a 1,2-migration of the 2′-oxoalkyl group via 1,2-cyclopropanated sugars from base treatment of 2′-oxoalkyl 2-*O*-Ms(Ts)-*C*-glycosides. The ring opening of 1,2-cyclopropanated sugars by various nucleophiles (alcohols, thiols, and azide) resulted in the concomitant formation of 2-*C*-branched *O*-, *S*-β-glycosides and glycosyl azides. The results also confirm that the 1,2-cyclopropanation requires the 1,2-*trans-diaxial* configuration, otherwise β-elimination dominates. Due to the epimerization at C2 under basic conditions this method can only be applied to prepare 1,2-*trans* 2-*C*-branched β-glycosides.

Experimental Section

3-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-α-D-mannopyranosyl)-propene (2). To a solution of **1** (0.76 g, 1.47 mmol) in MeOH (9 mL) was added 1% NaOMe−MeOH (1 mL). After being stirred for 30 min, the solution was neutralized by the addition of glacial acetic acid, and the solvent was evaporated. The residue was partitioned between EtOAc and water. The organic solution was washed with water and brine, dried, and concentrated to a residue. To a solution of the above residue and Et_3N (0.39 mL) in CH_2Cl_2 (10 mL) was added at 0 °C a solution of MsCl (0.239 g, 2.09 mmol) in CH_2Cl_2 (6 mL). The mixture was stirred overnight at room temperature, then methanol (1.5 mL) was added to destroy excess MsCl. Usual workup and chromatography (hexane/EtOAc 3:1) gave **2** (0.673 g, 83%) as a syrup: $[\alpha]_D$ +8.0 (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 2.32 (m, 1H, C*H*HCH=CH_2), 2.45 (m, 1H, CH*H*CH=CH_2), 3.02 (s, 3H, SO_2CH_3), 3.67−3.77 (m, 3H, H-5, H-6, H-6′), 3.80 (dd, 1H, H-4, *J* = 8.4, 8.4 Hz), 3.88 (dd, 1H, H-3, *J* = 8.0, 3.2 Hz), 4.23 (m, 1H, H-1), 4.52 (d, 1H, *J* = 10.8 Hz), 4.53 (d, 1H, *J* = 12.4 Hz), 4.62 (d, 1H, *J* = 11.2 Hz), 4.63 (d, 1H, *J* = 12.4 Hz), 4.76 (d, 1H, *J* = 11.2 Hz), 4.79 (d, 1H, *J* = 10.8 Hz), 4.98 (dd, 1H, H-2, *J* = 2.8, 2.8 Hz), 5.06−5.12 (m, 2H, −CH=CH_2), 5.77 (m, 1H, −C*H*=CH_2), 7.17−7.37 (m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 34.0, 39.2, 69.1, 72.9, 73.6, 73.7, 74.7, 75.0, 77.2, 78.4, 118.5, 127.8, 128.0, 128.2, 128.27, 128.5, 128.6, 128.7, 132.9, 137.3, 138.0, 138.3; HRFABMS Anal. calcd for $C_{31}H_{37}O_7S$ [M + H] 553.2260, found 553.2282.

3-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-tosyl-α-D-mannopyranosyl)propene (3). To a solution of 2-OH derivative (0.502 g) obtained by the same procedure described above in pyridine (6 mL) was added *p*-toluenesulfonyl chroride (0.406 g, 2.13 mmol) at 0 °C. After 24 h the mixture was poured into water/ethyl acetate. Usual workup and chromatography (hexane/EtOAc 6:1) gave **3** (0.566 g, 85%) as a colorless oil: $[\alpha]_D$ −0.61 (*c* 0.66, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 2.23 (dd, 2H, CH_2CH=CH_2, *J* = 6.8, 6.8 Hz), 2.40 (s, 3H, CH_3), 3.63−3.77 (m, 4H, H-4, H-5, H-6, H-6′), 3.83 (m, 1H, H-3), 4.06 (m, 1H, H-1), 4.42 (d, 1H, *J* = 12.0 Hz), 4.46 (d, 1H, *J* = 11.2 Hz), 4.50 (d, 1H, *J* = 14.0 Hz), 4.53 (d, 1H, *J* = 14.0 Hz), 4.56 (d, 1H, *J* = 11.2 Hz), 4.68 (d, 1H, *J* = 12.0 Hz), 4.79 (dd, 1H, H-2, *J* = 3.2, 3.2 Hz), 4.97−5.06 (m, 2H, −CH=CH_2), 5.68 (m, 1H, −C*H*=CH_2), 7.15−7.80 (m, 19H); ^{13}C NMR ($CDCl_3$) δ_C 21.8, 34.3, 69.0, 72.3, 72.9, 73.5, 73.9, 74.3, 74.7, 76.3, 78.0, 118.3, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 129.9, 133.3, 137.7, 138.0, 138.4; HRFABMS Anal. calcd for $C_{37}H_{41}O_7S$ [M + H] 629.2573, found 629.2524.

2-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-α-D-mannopyranosyl)acetaldehyde (4). A solution of **2** (122 mg, 0.221 mmol) in CH_2Cl_2 (26 mL) was cooled in a dry ice/acetone bath. A stream of ozone was passed into the solution through a sintered-glass sprayer. When the starting material disappeared, the solution was concentrated to a residue. To the above residue in glacial acetic acid (3 mL) was added zinc dust (65 mg, 1.0 mmol) and the mixture was stirred at room temperature overnight. Usual workup and chromatographic purification (hexane/ethyl acetate 6:1−2:1) afforded **4** (106 mg, 87%) as a syrup: $[\alpha]_D$ +0.3 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 2.66 (ddd, 1H, C*H*HCHO, *J* = 16.4, 4.8, 1.2 Hz), 2.77 (ddd, 1H, CH*H*CHO, *J* = 16.4, 8.8, 2.4 Hz), 2.97 (s, 3H, SO_2CH_3), 3.68 (dd, 1H, H-6, *J* = 10.8, 4.0 Hz), 3.76−3.82 (m, 2H, H-4, H-6′), 3.86 (dd, 1H, H-5, *J* = 5.8, 5.6 Hz), 3.91 (dd, 1H, H-3, *J* = 6.4, 2.8 Hz), 4.50 (d, 1H, *J* = 12.0 Hz), 4.53 (d, 1H, *J* = 11.2 Hz), 4.56 (d, 1H, *J* = 12.0 Hz), 4.57 (d, 1H, *J* = 12.0 Hz), 4.66 (d, 1H, *J* = 11.2 Hz), 4.67 (d, 1H, *J* = 12.0 Hz), 4.68 (m, 1H, H-1), 4.90 (dd, 1H, H-2, *J* = 5.6, 2.8 Hz), 7.20−7.33 (m, 15H), 9.74 (dd, 1H, C*H*O, *J* = 2.0, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ_C 38.9, 44.7, 68.0, 68.3, 73.3, 73.6, 73.9, 74.3, 74.5, 74.7, 76.3, 77.4, 127.9, 128.0, 128.1, 128.3, 128.4, 128.6, 128.7, 128.7, 137.3, 137.7, 138.1, 199.5; HRFABMS Anal. calcd for $C_{30}H_{35}O_8S$ [M + H] 555.2053, found 555.2276.

2-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-tosyl-α-D-mannopyranosyl)acetaldehyde (5). Compound **3** (588 mg, 0.936 mmol) was ozonized by the same procedure as described above. Purification by chromatography (hexane/ethyl acetate 6:1−2:1) gave **5** (501 mg, 85%) as a syrup: $[\alpha]_D$ +3.6 (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 2.43 (s, 3H, CH_3), 2.40−2.50 (m, 2H, CH_2-CHO), 3.62−3.68 (m, 2H, H-4, H-6), 3.78 (m, 1H, H-6′), 3.86−3.96 (m, 2H, H-3, H-5), 4.39−4.55 (m, 7H, H-1, 3 × CH_2Ph), 4.68 (d, 1H, H-2, *J* = 8.0 Hz), 7.19−7.78 (m, 19H), 9.63 (s, 1H, C*H*O); ^{13}C NMR ($CDCl_3$) δ_C 22.0, 44.6, 65.5, 68.0, 72.8, 73.4,

73.5, 74.5, 75.0, 75.3, 77.6, 127.9, 128.1, 128.2, 128.3, 128.6, 128.7, 130.2, 133.5, 137.6, 137.7, 138.3, 145.5, 199.6; HRFABMS Anal. calcd for $C_{36}H_{39}O_8S$ [M + H] 631.2366, found 631.2378.

1-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-tosyl-α-D-mannopyranosyl)acetone (6). To a solution of **3** (3.385 g, 5.39 mmol) and $Hg(OAc)_2$ (419 mg, 1.31 mmol) in acetone/water (4:1, 25 mL) was added dropwise at 0 °C a solution of Jones reagent (2 M, 6 mL). The dark greenish-brown mixture was stirred for 3 h at 0 °C and then poured into water (20 mL). The aqueous mixture was extracted with EtOAc (3 × 20 mL). Usual workup and chromatography (hexane/EtOAc 3:2) afforded **6** (2.611 g, 75%) as white powders: ^{1}H NMR ($CDCl_3$) δ_H 2.12 (s, 3H, COC*H*$_3$), 2.43 (s, 3H, C*H*$_3$), 2.51−2.53 (m, 2H, C*H*$_2$COCH$_3$), 3.64 (dd, 1H, H-4, J = 5.6, 4.0 Hz), 3.67−3.78 (m, 3H, H-3, H-6, H-6′), 3.87 (m, 1H, H-5), 4.36−4.53 (m, 7H, H-1, 3 × C*H*$_2$-Ph), 4.79 (dd, 1H, H-2, J = 7.2, 3.2 Hz), 7.16−7.79 (m, 19H); ^{13}C NMR ($CDCl_3$) δ_H 21.9, 30.9, 44.7, 67.1, 68.4, 73.0, 73.1, 73.5, 74.5, 74.9, 75.5, 77.5, 127.8, 127.9, 128.1, 128.3, 128.6, 130.1, 133.8, 137,7, 137.8, 138.4, 145.3, 205.7; HRFABMS Anal. calcd for $C_{37}H_{41}O_8S$ [M + H] 645.7816, found 645.7809.

3-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-α-D-glucopyranosyl)-propene (8). Compound **7** (7.33 g, 14.2 mmol) was converted to **8** by the same procedure as described above for the preparation of **2**. Purification by chromatography (hexane/EtOAc 3:1) gave **8** (6.43 g, 82%) as a syrup: $[\alpha]_D$ +23.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 2.51 (dd, 2H, C*H*$_2$CH=CH$_2$, J = 7.5, 7.0 Hz), 2.85 (s, 3H, SO$_2$C*H*$_3$), 3.63−3.67 (m, 2H, H-5, H-6), 3.74−3.77 (m, 2H, H-4, H-6′), 3.87 (dd, 1H, H-3, J = 9.0, 8.5 Hz), 4.33 (dd, 1H, H-1, J = 13.5, 7.0 Hz), 4.49 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 11.0 Hz), 4.63 (dd, 1H, H-2, J = 9.0, 2.0 Hz), 4.64 (d, 1H, J = 12.0 Hz), 4.74 (d, 1H, J = 11.0 Hz), 4.75 (d, 1H, J = 11.0 Hz), 4.90 (d, 1H, J = 11.0 Hz), 5.11−5.17 (m, 2H, CH=C*H*$_2$), 5.80 (m, 1H, C*H*=CH$_2$), 7.12−7.34 (m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 30.2, 38.0, 68.5, 71.7, 73.4, 73.8, 75.1, 75.6, 78.4, 79.5, 80.0, 118.0, 127.8, 128.0, 128.1, 128.6, 128.7, 128.8, 133.5, 137.8, 137.9, 138.1; HRFABMS Anal. calcd for $C_{31}H_{37}O_7S$ [M + H] 553.2260, found 553.2294.

2-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-α-D-glucopyranosyl)-acetaldehyde (9). Compound **8** (278 mg, 0.503 mmol) was converted to **9** by the same procedure as described above for the preparation of **4**. Purification by chromatography (hexane/ethyl acetate 6:1−2:1) gave **9** (237 mg, 85%) as a syrup: $[\alpha]_D$ +32.7 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 2.80−2.83 (m, 2H, C*H*$_2$CHO), 2.86 (s, 3H, SO$_2$C*H*$_3$), 3.61 (dd, 1H, H-6, J = 10.4, 2.4 Hz), 3.68 (m, 1H, H-5), 3.72−3.77 (m, 2H, H-4, H-6′), 3.81 (dd, 1H, H-3, J = 8.8, 8.0 Hz), 4.47 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 10.8 Hz), 4.60 (d, 1H, J = 12.0 Hz), 4.67 (m, 1H, H-2), 4.71(d, 1H, J = 11.2 Hz), 4.72 (d, 1H, J = 10.8 Hz), 4.86 (d, 1H, J = 11.2 Hz), 4.92 (m, 1H, H-1), 7.13−7.35 (m, 15H), 9.74 (dd, 1H, C*H*O, J = 2.8, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ_C 38.1, 41.3, 68.2, 68.8, 72.8, 73.8, 74.9, 75.5, 77.5, 78.1, 79.3, 127.9, 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 128.8, 137.7, 137.9, 199.0; HRFABMS Anal. calcd for $C_{30}H_{35}O_8S$ [M + H] 555.2053, found 555.2136.

1,2-Cyclopropanated Sugar 13. To a solution of **6** (202 mg, 0.31 mmol) in MeOH (3 mL) was added K_2CO_3 (128 mg, 0.93 mmol). The suspension was stirred at room temperature overnight, the mixture was filtrated, and the filtrate was concentrated. Purification by chromatography (hexane/EtOAc 4:1) afforded compound **13** (119 mg, 81%) as a syrup: $[\alpha]_D$ +42 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 1.98 (ddd, 1H, H-2, J = 7.2, 5.6, 1.6 Hz), 2.26 (s, 3H, COC*H*$_3$), 2.34 (dd, 1H, H-1′, J = 5.6, 1.6 Hz), 3.56 (dd, 1H, H-4, J = 6.0, 6.0 Hz), 3.59 (dd, 1H, H-6, J = 10.0, 3.6 Hz), 3.70 (dd, 1H, H-6′, J = 10.0, 5.6 Hz), 3.72−3.77 (m, 2H, H-3, H-5), 3.86 (dd, 1H, H-1, J = 7.2, 1.6 Hz), 4.53 (s, 2H), 4.55 (d, 2H, J = 11.6 Hz), 4.69 (d, 1H, J = 11.6 Hz), 4.71 (d, 1H, J = 11.6 Hz), 7.22−7.34 (m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 26.8, 31.4, 33.1, 61.1, 69.4, 71.6, 73.5, 73.7, 74.5, 75.5, 76.3, 128.0, 128.1, 128.2, 128.6, 128.7, 138.0, 138.2, 205.4; HRFABMS Anal. calcd for $C_{30}H_{33}O_5$ [M + H] 473.2328, found 473.2583.

General Procedures for 2-*C*-Branched Glycosyl Compounds (11−29). Procedure A (for 11, 15 and 22): To a solution of aldehyde (**4** or **5**) (50−100 mg, 0.1−0.2 mmol) and nucleophile (2−3 equiv) (MeOH, AllOH, and NaN_3) in MeOH (5−10 mL) was added triethylamine (5−10 equiv). The solution was stirred at room temperature overnight, and concentrated to a residue. Purification was then performed on a silica gel column.

Procedure B (for 12, 19, 20, 21, 23, and 24): To a solution of aldehyde (**5** or **6**) (60−120 mg, 0.1−0.2 mmol) and nucleophile (2−3 equiv) (MeOH, PhSH, 4-MeOPhSH, and 4-ClPhSH) in MeOH (5−10 mL) was added K_2CO_3 (10 equiv). The suspension was stirred at room temperature overnight. The reaction mixture was filtrated and the filtrate was concentrated. Purification was then performed on a silica gel column.

Procedure C (for 14): Similar to Procedure A except EtOH replaced MeOH.

Procedure D (for 18): Similar to Procedure B except MeCN replaced MeOH as a solvent.

Procedure E (for 16, and 17): Similar to Procedure B without solvent MeOH.

Procedure F (for 25, 26, 27, 28, and 29): A solution of **13** (50 mg, 0.11 mmol) and 3 equiv of MeOH, AllOH, BnOH, NaN_3/MeOH, or Solketal/DMF was stirred at difference temperatures (see Table 2) for 16 h. Purification was then performed on a silica gel column.

Methyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-β-D-glucopyranoside (11). Prepared by Procedure A and purified by chromatography (hexane/EtOAc 6:1) (72%): $[\alpha]_D$ +12.8 (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 2.29 (m, 1H, H-2), 2.38 (ddd, 1H, C*H*HCHO, J = 16.4, 6.8, 2.8 Hz), 2.47 (ddd, 1H, CH*H*CHO, J = 16.4, 6.4, 2.4 Hz), 3.37 (dd, 1H, H-3, J = 19.6, 10.8 Hz), 3.45 (m, 1H, H-5), 3.46 (s, 3H, OCH$_3$), 3.68 (dd, 1H, H-4, J = 9.6, 8.8 Hz), 3.76 (d, 2H, H-6, H-6′, J = 3.2 Hz), 4.15 (d, 1H, H-1, J = 8.8 Hz), 4.54 (d, 1H, J = 10.4 Hz), 4.57 (d, 1H, J = 12.0 Hz), 4.60 (d, 1H, J = 12.0 Hz), 4.66 (d, 1H, J = 12.0 Hz), 4.79 (d, 1H, J = 12.0 Hz), 4.88 (d, 1H, J = 10.4 Hz), 7.17−7.37 (m, 15H), 9.54 (dd, 1H, C*H*O, J = 2.8, 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ_C 42.5, 44.0, 57.1, 68.9, 73.7, 74.9, 75.1, 75.3, 79.9, 82.5, 103.9, 127.8, 127.9, 128.2, 128.5, 128.6, 137.8, 138.0, 138.2, 201.2; HRFABMS Anal. calcd for $C_{30}H_{35}O_6$ [M + H] 491.2435, found 491.2492.

11-D: ^{1}H NMR ($CDCl_3$) δ_H 3.37 (d, 1H, H-3, J = 8.4 Hz), 3.45 (m, 1H, H-5), 3.68 (dd, 1H, H-4, J = 9.6, 8.8 Hz), 3.76 (d, 2H, H-6, H-6′, J = 3.2 Hz), 4.15 (s, 1H, H-1), 4.54 (d, 1H, J = 10.8 Hz), 4.57 (d, 1H, J = 12.0 Hz), 4.60 (d, 1H, J = 12.0 Hz), 4.66 (d, 1H, J = 12.0 Hz), 4.79 (d, 1H, J = 12.0 Hz), 4.88 (d, 1H, J = 10.8 Hz), 7.17−7.37 (m, 15H), 9.54 (s, 1H, C*H*O); HRFABMS Anal. calcd for $C_{30}H_{29}D_6O_6$ [M + H] 497.2810, found 497.2785.

Bicyclic Compound 12. Obtained by Procedure B and purified by chromatography (hexane/EtOAc 6:1) (15%): $[\alpha]_D$ +26.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 3.17 (m, 1H, H-2), 3.63−3.70 (m, 4H, H-6, H-6′, H-3, H-4), 3.82 (m, 1H, H-5), 4.40 (d, 1H, J = 11.6 Hz), 4.52 (d, 1H, J = 12.4 Hz), 4.58 (d, 1H, J = 11.6 Hz), 4.59 (d, 1H, J = 12.4 Hz), 4.61 (s, 2H), 4.93 (dd, 1H, C*H*=CHO, J = 2.8, 2.4 Hz), 5.94 (d, 1H, H-1, J = 8.0 Hz), 6.47 (dd, 1H, CH=C*H*O, J = 2.8, 2.8 Hz), 7.17−7.35 (m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 44.1, 69.9, 71.3, 72.1, 72.9, 73.6, 75.8, 79.4, 102.4, 102.6, 127.7, 127.9, 128.0, 128.0, 128.5, 128.6, 128.7, 138.1, 138.3, 146.3; HRFABMS Anal. calcd for $C_{29}H_{31}O_5$ [M + H] 459.2171, found 459.2137.

12-D: ^{1}H NMR ($CDCl_3$) δ_H 3.63−3.70 (m, 4H, H-6, H-6′, H-3, H-4), 3.82 (m, 1H, H-5), 4.40 (d, 1H, J = 11.6 Hz), 4.52 (d, 1H, J = 12.4 Hz), 4.58 (d, 1H, J = 11.6 Hz), 4.59 (d, 1H, J = 12.4 Hz), 4.61 (s, 2H), 5.94 (s, 1H, H-1), 6.46 (s, 1H, CD=C*H*O), 7.17−7.35 (m, 15H); HRFABMS Anal. calcd for $C_{29}H_{29}D_2O_5$ [M + H] 461.2297, found 461.2313.

Ethyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-β-D-glucopyranoside (14). Prepared by Procedure C and purified by chromatography (hexane/EtOAc 6:1) (71%): $[\alpha]_D$ +0.8 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ_H 1.18 (t, 3H, CH_3, J =

7.2 Hz), 2.30 (m, 1H, H-2), 2.36 (ddd, 1H, C*H*HCHO, J = 22.8, 7.2, 3.2 Hz), 2.48 (ddd, 1H, CH*H*CHO, J = 22.8, 5.2, 1.6 Hz), 3.37 (dd, 1H, H-3, J = 10.0, 10.0 Hz), 3.43−3.49 (m, 2H, H-5, OC*H*HCH$_3$), 3.67 (dd, 1H, H-4, J = 9.2, 9.2 Hz), 3.75 (d, 2H, H-6, H-6′, J = 2.8 Hz), 3.92 (m, 1H, OCH*H*CH$_3$), 4.23 (d, 1H, H-1, J = 8.4 Hz), 4.53 (d, 1H, J = 10.8 Hz), 4.57 (d, 1H, J = 12.4 Hz), 4.60 (d, 1H, J = 12.0 Hz), 4.65 (d, 1H, J = 12.4 Hz), 4.79 (d, 1H, J = 12.0 Hz), 4.88 (d, 1H, J = 10.8 Hz), 7.18−7.36 (m, 15H), 9.56 (dd, 1H, C*H*O, J = 2.8, 2.8 Hz); ^{13}C NMR (CDCl$_3$) δ_C 15.2, 42.7, 44.0, 65.6, 69.0, 73.8, 75.0, 75.2, 75.3, 80.0, 82.6, 102.8, 127.8, 128.0, 128.1, 128.3, 128.5, 128.6, 128.7, 137.8, 138.0, 138.2, 201.4; HRFABMS Anal. calcd for $C_{31}H_{37}O_6$ [M + H] 505.2590, found 505.2515.

Allyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-glucopyranoside (15). Prepared by Procedure A and purified by chromatography (hexane/EtOAc 6:1) (76%): [α]$_D$ +1.0 (*c* 0.8, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 2.31−2.50 (m, 3H, H-2, CH_2CHO), 3.38 (dd, 1H, H-3, J = 10.8, 8.8 Hz), 3.45 (ddd, 1H, H-5, J = 9.6, 3.2, 3.2 Hz), 3.68 (dd, 1H, H-4, J = 9.2, 9.2 Hz), 3.75 (d, 2H, H-6, 6′, J = 3.2 Hz), 4.01 (m, 1H, CH_2CH=CH$_2$), 4.29 (d, 1H, H-1, J = 8.4 Hz), 4.34 (m, 1H, CH_2CH=CH$_2$), 4.54 (d, 1H, J = 10.8 Hz), 4.56 (d, 1H, J = 11.6 Hz), 4.60 (d, 1H, J = 11.2 Hz), 4.65 (d, 1H, J = 11.2 Hz), 4.79 (d, 1H, J = 11.6 Hz), 4.87 (d, 1H, J = 10.8 Hz), 5.21 (m, 2H, CH$_2$CH=CH_2), 5.86 (m, 1H, CH$_2$C*H*=CH$_2$), 7.18−7.36 (m, 15H), 9.57 (dd, 1H, C*H*O, J = 2.8, 2.4 Hz); ^{13}C NMR (CDCl$_3$) δ_C 42.3, 43.9, 69.0, 70.4, 73.7, 74.9, 75.1, 75.4, 80.0, 82.5, 101.8, 118.0, 127.8, 127.9, 128.0, 128.1, 128.3, 128.6, 128.7, 133.9, 137.9, 138.1, 138.3, 201.4; HRFABMS Anal. calcd for $C_{32}H_{37}O_6$ [M + H] 517.2590, found 517.2582.

5-Hexenyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-glucopyranoside (16). Prepared by Procedure E and purified by chromatography (hexane/EtOAc 5:1) (78%): [α]$_D$ +5.6 (*c* 0.5, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 1.41 (m, 2H, CH_2-CH$_2$CH=CH$_2$), 1.56 (m, 2H, CH_2CH$_2$O−), 2.05 (m, 2H, CH_2-CH=CH$_2$), 2.27−2.49 (m, 3H, H-2, CH_2CHO), 3.35−3.46 (m, 3H, H-3, OC*H*HCH$_2$, H-5), 3.66 (dd, 1H, H-4, J = 8.8, 8.8 Hz), 3.74 (s, 2H, H-6, 6′), 3.87 (m, 1H, OCH*H*CH$_2$), 4.22 (d, 1H, H-1, J = 8.4 Hz), 4.54 (d, 1H, J = 10.8 Hz), 4.56 (d, 1H, J = 12.4 Hz), 4.60 (d, 1H, J = 12.4 Hz), 4.64 (d, 1H, J = 12.4 Hz), 4.79 (d, 1H, J = 12.4 Hz), 4.87 (d, 1H, J = 10.8 Hz), 4.93−5.01 (m, 2H, CH$_2$CH=CH_2), 5.78 (m, 1H, CH$_2$C*H*=CH$_2$), 7.18−7.36 (m, 15H), 9.56 (s, 1H, C*H*O); ^{13}C NMR (CDCl$_3$) δ_C 25.5, 29.0, 33.6, 42.5, 44.0, 69.0, 70.0, 73.7, 75.0, 75.1, 75.4, 80.0, 82.5, 103.0, 114.8, 127.9, 128.0, 128.2, 128.3, 128.6, 128.7, 137.9, 138.1, 138.3, 138.8, 201.5; HRFABMS Anal. calcd for $C_{35}H_{43}O_6$ [M + H] 559.3060, found 559.3013.

Benzyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-glucopyranoside (17). Prepared by Procedure E and purified by chromatography (hexane/EtOAc 6:1) (75%): [α]$_D$ −28.0 (*c* 0.2, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 2.34−2.42 (m, 3H, H-2, CH_2CHO), 3.36 (dd, 1H, H-3, J = 10.4, 9.2 Hz), 3.45 (ddd, 1H, H-5, J = 10.0, 3.6, 3.6 Hz), 3.69 (dd, 1H, H-4, J = 9.2, 9.2 Hz), 3.77 (s, 2H, H-6, 6′), 4.31 (d, 1H, H-1, J = 8.4 Hz), 4.51 (d, 1H, J = 10.8 Hz), 4.55 (d, 1H, J = 11.6 Hz), 4.58 (d, 1H, J = 12.4 Hz), 4.61 (d, 1H, J = 10.8 Hz), 4.67 (d, 1H, J = 12.4 Hz), 4.79 (d, 1H, J = 10.8 Hz), 4.85 (d, 1H, J = 10.8 Hz), 4.87 (d, 1H, J = 11.6 Hz), 7.18−7.38 (m, 20H), 9.45 (dd, 1H, C*H*O, J = 2.4, 2.0 Hz); ^{13}C NMR (CDCl$_3$) δ_C 42.4, 43.9, 69.0, 71.0, 73.7, 74.9, 75.1, 75.4, 80.0, 82.6, 101.3, 127.9, 128.0, 128.2, 128.3, 128.5, 128.6, 128.7, 137.1, 137.9, 138.1, 138.3, 201.5; HRFABMS Anal. calcd for $C_{36}H_{39}O_6$ [M + H] 567.2747, found 567.2682.

Phenyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-glucopyranoside (18). Prepared by Procedure D and purified by chromatography (hexane/EtOAc 4:1) (62%): [α]$_D$ −12.5 (*c* 0.2, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 2.50−2.55 (m, 2H, H-2, CH_2CHO), 2.60 (m, 1H, CH_2CHO), 3.52 (m, 1H, H-3), 3.62 (m, 1H, H-5), 3.74−3.82 (m, 3H, H-4, H-6 and H-6′), 4.53−4.65 (m, 4H), 4.81−4.92 (m, 3H, H-1, CH_2Ph), 6.99−7.38 (m, 20H), 9.66 (s, 1H, C*H*O); ^{13}C NMR (CDCl$_3$) δ_C 41.9, 43.5, 68.4, 73.3, 74.6, 74.7, 75.1, 79.3, 81.7, 100.4, 116.3, 122.3, 127.2, 127.3, 127.6, 127.7, 127.9, 128.1, 129.0, 137.1, 137.3, 137.5, 156.5, 200.0; HRFABMS Anal. calcd for $C_{35}H_{37}O_6$ [M + H] 553.2590, found 553.2724.

Phenyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-thioglucopyranoside (19). Prepared by Procedure B and purified by chromatography (hexane/EtOAc 10:1−4:1) (86%): [α]$_D$ +26.0 (*c* 0.2, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 2.29 (m, 1H, H-2), 2.46 (ddd, 1H, CH_2CHO, J = 17.2, 7.2, 3.2 Hz), 2.83, (dd, 1H, CH_2CHO, J = 17.2, 3.6 Hz), 3.48−3.54 (m, 2H, H-3, H-5), 3.66 (m, 1H, H-4), 3.79 (m, 2H, H-6, H-6′), 4.50−4.87 (m, 7H, H-1, 3 × CH_2Ph), 7.22−7.53 (m, 20H), 9.50 (s, 1H, C*H*O); ^{13}C NMR (CDCl$_3$) δ_C 43.1, 44.5, 69.3, 73.8, 75.1, 79.6, 79.9, 84.0, 87.0, 127.8, 127.9, 128.1, 128.3, 128.5, 128.7, 129.1, 132.5, 137.7, 138.0, 199.9; HRFABMS Anal. calcd for $C_{35}H_{37}O_5S$ [M + H] 569.2362, found 569.2298.

4-Methoxyphenyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-thioglucopyranoside (20). Prepared by Procedure B and purified by chromatography (hexane/EtOAc 5:1) (85%): [α]$_D$ +7.9 (*c* 0.63, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 2.22 (m, 1H, H-2), 2.44 (ddd, 1H, C*H*HCHO, J = 17.2, 7.6, 3.2 Hz), 2.86 (dd, 1H, CH*H*CHO, J = 17.2, 3.6 Hz), 3.45−3.50 (m, 2H, H-3, H-5), 3.62 (dd, 1H, H-4, J = 9.6, 9.6 Hz), 3.76 (s, 3H, OCH_3), 3.79 (d, 2H, H-6, H-6′, J = 2.8 Hz), 4.51(d, 1H, CH_2Ph, J = 10.4 Hz), 4.52 (d, 1H, H-1, J = 10.4 Hz), 4.56 (d, 1H, J = 11.6 Hz), 4.63 (d, 1H, J = 10.8 Hz), 4.64 (d, 1H, J = 11.6 Hz), 4.77 (d, 1H, J = 10.8 Hz), 4.84 (d, 1H, J = 10.4 Hz), 6.73−7.48 (m, 19H), 9.50 (d, 1H, C*H*O, J = 3.2 Hz); ^{13}C NMR (CDCl$_3$) δ_C 42.7, 44.4, 55.5, 69.2, 73.6, 75.0, 79.5, 79.8, 84.0, 87.1, 114.7, 122.2, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.5, 128.6, 135.7, 137.7, 138.1, 138.5, 160.1, 200.2; HRFABMS Anal. calcd for $C_{36}H_{39}O_6S$ [M + H] 599.2467, found 599.2498.

4-Chlorophenyl 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-thioglucopyranoside (21). Prepared by Procedure B and purified by chromatography (hexane/EtOAc 4:1) (83%): [α]$_D$ +5.6 (*c* 0.5, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 2.27 (m, 1H, H-2), 2.46 (ddd, 1H, C*H*HCHO, J = 16.8, 6.8, 2.4 Hz), 2.79 (dd, 1H, CH*H*CHO, J = 16.8, 3.2 Hz), 3.48−3.54 (m, 2H, H-3, H-5), 3.64 (dd, 1H, H-4, J = 9.6, 9.6 Hz), 3.76−3.78 (m, 2H, H-6, H-6′), 4.52 (d, 1H, J = 11.2 Hz), 4.55 (d, 1H, J = 13.6 Hz), 4.58 (d, 1H, J = 13.6 Hz), 4.62 (d, 1H, J = 11.2 Hz), 4.65 (d, 1H, H-1, J = 10.4 Hz), 4.78 (d, 1H, J = 11.2 Hz), 4.86 (d, 1H, J = 11.2 Hz), 7.15−7.46 (m, 19H), 9.50 (d, 1H, C*H*O, J = 2.4 Hz); ^{13}C NMR (CDCl$_3$) δ_C 42.8, 44.0, 69.1, 73.6, 75.0, 79.4, 79.7, 83.6, 86.6, 127.9, 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 129.3, 129.5, 131.1, 134.0, 137.8, 138.0, 138.4, 200.0; HRFABMS Anal. calcd for $C_{35}H_{36}ClO_5S$ [M + H] 603.1972, found 603.2012.

Azido 3,4,6-Tri-*O*-benzyl-2-*C*-formylmethyl-2-deoxy-*β*-D-glucopyranoside (22). Prepared by Procedure A and purified by chromatography (hexane/EtOAc 5:1) (52%): [α]$_D$ +4.6 (*c* 0.13, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 2.18 (m, 1H, H-2), 2.39 (ddd, 1H, CH_2CHO, J = 2.6, 6.4, 17.0 Hz), 2.51 (ddd, 1H, CH_2CHO, J = 1.6, 5.2, 16.8 Hz), 3.45 (dd, 1H, H-3, J = 8.8, 10.4 Hz), 3.56 (m, 1H, H-5), 3.71 (dd, 1H, H-4, J = 9.4, 9.4 Hz), 3.77−3.78 (m, 2H, H-6, H-6′), 4.51−4.88 (m, 7H, H-1, 3 × CH_2Ph), 7.17−7.37 (m, 15H), 9.53 (s, 1H, C*H*O); ^{13}C NMR (CDCl$_3$) δ_C 41.7, 43.1, 68.0, 73.3, 74.6, 75.1, 77.1, 78.9, 81.2, 89.2, 127.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.1, 137.0, 137.2, 137.4, 199.2; HRFABMS Anal. calcd for $C_{29}H_{33}N_3O_5$ [M + 2H] 503.2420, found 503.2590.

4-Methoxyphenyl 3,4,6-Tri-*O*-benzyl-2-*C*-acetylmethyl-2-deoxy-*β*-D-thioglucopyranoside (23). Prepared by Procedure B and purified by chromatography (hexane/EtOAc 6:1) (83%): [α]$_D$ +5.0 (*c* 0.1, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ_H 1.99 (s, 3H, COCH_3), 2.13 (m, 1H, H-2), 2.57 (dd, 1H, CH_2 COCH$_3$, J = 17.6, 6.4 Hz), 2.80 (dd, 1H, CH_2 COCH$_3$, J = 17.6, 3.6 Hz), 3.49 (m, 1H, H-5), 3.59 (dd, 1H, H-4, J = 8.8, 8.8 Hz), 3.70 (dd, 1H, H-3, J = 8.8, 8.8 Hz), 3.75 (s, 3H, OCH$_3$), 3.76−3.82 (m, 2H, H-6, H-6′), 4.52 (d, 1H, J = 12.4 Hz), 4.55 (d, 1H, J = 13.2 Hz), 4.60−4.68 (m, 3H, H-1, CH_2Ph), 4.77 (d, 1H, J = 13.2 Hz), 4.87 (d, 1H, J = 12.4 Hz), 6.73−7.47 (m, 19H); ^{13}C NMR (CDCl$_3$) δ_C 30.4, 42.8, 43.5, 55.5, 69.4, 73.6, 74.9, 75.0,

79.4, 80.0, 83.4, 87.0, 114.6, 127.7, 127.9, 128.0, 128.1, 128.5, 128.7, 135.4, 138.4, 207.2; HRFABMS Anal. calcd for $C_{37}H_{41}O_6S$ [M + H] 613.2624, found 613.2685.

4-Chlorophenyl 3,4,6-Tri-*O*-benzyl-2-*C*-acetylmethyl-2-deoxy-*β*-D-thioglucopyranoside (24). Prepared by Procedure B and purified by chromatography (hexane/EtOAc 4:1) (85%): $[\alpha]_D$ +15.3 (*c* 0.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ_H 1.98 (s, 3H, COCH_3), 2.18 (m, 1H, H-2), 2.56 (dd, 1H, CH_2 $COCH_3$, *J* = 17.6, 5.6 Hz), 2.76 (dd, 1H, CH_2 $COCH_3$, *J* = 17.6, 5.6 Hz), 3.50 (m, 1H, H-5), 3.61 (dd, 1H, H-4, *J* = 8.4, 8.4 Hz), 3.70−3.77 (m, 3H, H-3, H-6, H-6′), 4.53 (d, 1H, *J* = 11.2 Hz), 4.54 (d, 1H, *J* = 11.6 Hz), 4.61 (d, 2H, *J* = 11.6 Hz), 4.77 (d, 1H, *J* = 11.6 Hz), 4.80 (d, 1H, H-1, *J* = 10.8 Hz), 4.88 (d, 1H, *J* = 11.2 Hz), 7.14−7.45 (m, 19H); ^{13}C NMR ($CDCl_3$) δ_C 30.2, 42.2, 43.4, 68.9, 73.6, 74.9, 75.0, 79.4, 80.0, 83.1, 87.0, 127.9, 128.0, 128.1, 128.6, 128.7, 129.5, 133.6, 138.2, 138.3, 138.4, 207.1; HRFABMS Anal. calcd for $C_{36}H_{38}ClO_5S$ [M + H] 617.2128, found 617.2198.

Methyl 3,4,6-Tri-*O*-benzyl-2-*C*-acetylmethyl-2-deoxy-*β*-D-glucopyranoside (25). Prepared by Procedure F and purified by chromatography (hexane/EtOAc 4:1) (95%): $[\alpha]_D$ +9.8 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ_H 1.97 (s, 3H, COCH_3), 2.10 (m, 1H, H-2), 2.38 (dd, 1H, C$H_2$$COCH_3$, *J* = 16.0, 6.0 Hz), 2.47 (dd, 1H, C$H_2$$COCH_3$, *J* = 16.0, 6.0 Hz), 3.37 (s, 3H, OCH_3), 3.39−3.46 (m, 2H, H-5, H-3), 3.58 (dd, 1H, H-4, *J* = 8.8, 8.8 Hz), 3.68−3.69 (m, 2H, H-6, 6′), 4.17 (d, 1H, H-1, *J* = 8.8 Hz), 4.47 (d, 1H, *J* = 11.2 Hz), 4.50 (d, 1H, *J* = 11.2 Hz), 4.52 (d, 1H, *J* = 11.2 Hz), 4.58 (d, 1H, *J* = 11.2 Hz), 4.71 (d, 1H, *J* = 11.2 Hz), 4.82 (d, 1H, *J* = 11.2 Hz), 7.10−7.29 (m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 29.8, 42.2, 45.1, 57.1, 69.1, 73.7, 74.9, 75.1, 75.3, 80.1, 82.5, 103.9, 127.8, 128.0, 128.1, 128.6, 128.7, 138.2, 138.3, 208.1; HRFABMS Anal. calcd for $C_{31}H_{37}O_6$ [M + H] 505.2590, found 505.2612.

Allyl 3,4,6-Tri-*O*-benzyl-2-*C*-acetylmethyl-2-deoxy-*β*-D-glucopyranoside (26). Prepared by Procedure F and purified by chromatography (hexane/EtOAc 6:1) (96%): $[\alpha]_D$ +9.2 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ_H 2.04 (s, 3H, COCH_3), 2.21 (m, 1H, H-2), 2.46 (dd, 1H, C$H_2$$COCH_3$, *J* = 16.0, 6.0 Hz), 2.54 (dd, 1H, C$H_2$$COCH_3$, *J* = 16.0, 6.0 Hz), 3.45−3.53 (m, 2H, H-5, H-3), 3.65 (dd, 1H, H-4, *J* = 9.6, 8.8 Hz), 3.74 (d, 2H, H-6, 6′, *J* = 3.2 Hz), 3.99 (dd, 1H, CH_2CH=CH_2, *J* = 12.4, 6.4 Hz), 4.32 (dd, 1H, CH_2CH=CH_2, *J* = 12.4, 5.2 Hz), 4.37 (d, 1H, H-1, *J* = 8.8 Hz), 4.53 (d, 1H, *J* = 11.2 Hz), 4.55 (d, 1H, *J* = 12.4 Hz), 4.56 (d, 1H, *J* = 10.8 Hz), 4.65 (d, 1H, *J* = 12.4 Hz), 4.78 (d, 1H, *J* = 10.8 Hz), 4.88 (d, 1H, *J* = 11.2 Hz), 5.19 (m, 2H, CH_2CH=CH_2), 5.86 (m, 1H, CH_2CH=CH_2), 7.17−7.36 (m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 29.8, 42.2, 45.1, 69.1, 70.3, 73.7, 74.9, 75.1, 75.3, 80.1, 82.5, 101.9, 117.8, 127.8, 128.0, 128.7, 134.0, 138.1, 138.3 (2), 208.1; HRFABMS Anal. calcd for $C_{33}H_{39}O_6$ [M + H] 531.2747, found 531.2702.

Benzyl 3,4,6-Tri-*O*-benzyl-2-*C*-acetylmethyl-2-deoxy-*β*-D-glucopyranoside (27). Prepared by Procedure F and purified by chromatography (hexane/EtOAc 6:1) (82%): $[\alpha]_D$ +112.2 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ_H 1.98 (s, 3H, COCH_3), 2.44 (m, 1H, H-2), 2.48 (m, 1H, C$H_2$$COCH_3$), 2.65 (m, 1H, C$H_2$-$COCH_3$), 3.65−3.74 (m, 3H, H-3, H-6, H-4), 3.77−3.85 (m, 2H, H-6′, H-5), 4.38 (d, 1H, *J* = 10.8 Hz), 4.53 (d, 1H, *J* = 10.8 Hz), 4.54 (d, 1H, *J* = 12.4 Hz), 4.58 (d, 1H, *J* = 12.4 Hz), 4.65 (d, 1H, *J* = 11.6 Hz), 4.68 (d, 1H, *J* = 11.6 Hz), 4.77 (d, 1H, *J* = 11.6 Hz), 4.91 (d, 1H, *J* = 11.6 Hz), 5.00 (d, 1H, H-1, *J* = 2.8 Hz), 7.13−7.38 (m, 20H); ^{13}C NMR ($CDCl_3$) δ_C 30.3, 41.8, 42.0, 68.9, 69.4, 71.4, 73.8, 75.0, 75.2, 80.0, 80.7, 98.2, 127.8, 127.9, 128.0, 128.1, 128.2, 128.6, 128.7, 137.9, 138.2, 138.3, 138.7, 207.7; HRFABMS Anal. calcd for $C_{37}H_{41}O_6$ [M + H] 581.2903, found 581.2886.

Azido 3,4,6-Tri-*O*-benzyl-2-*C*-acetylmethyl-2-deoxy-*β*-D-glucopyranoside (28). Prepared by Procedure F and purified by chromatography (hexane/EtOAc 4:1) (92%): $[\alpha]_D$ +16.5 (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ_H 2.00 (s, 3H, COCH_3), 2.07 (m, 1H, H-2), 2.46 (dd, 1H, C$H_2$$COCH_3$, *J* = 17.2, 5.2 Hz), 2.57 (dd, 1H, C$H_2$$COCH_3$, *J* = 17.2, 5.6 Hz), 3.56−3.70 (m, 3H, H-5, H-3, H-4), 3.77−3.78 (m, 2H, H-6, H-6′), 4.53 (d, 1H, *J* = 11.2 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.60 (d, 2H, *J* = 10.8 Hz), 4.66 (d, 1H, *J* = 10.8 Hz), 4.70 (d, 1H, H-1, *J* = 9.6 Hz), 4.77 (d, 1H, *J* = 11.2 Hz), 4.89 (d, 1H, *J* = 12.0 Hz), 7.17−7.37 (m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 30.2, 40.8, 44.1, 68.6, 73.8, 75.1 (2), 77.6, 79.7, 81.8, 89.7, 127.8, 128.0, 128.1, 128.3, 128.7, 128.8, 138.1, 138.2, 138.3, 207.1; HRFABMS Anal. calcd for $C_{30}H_{34}N_3O_5$ [M + H] 516.2498, found 516.2433.

Bicyclic Compound 29. Prepared by Procedure F and purified by chromatography (hexane/EtOAc 4:1) (72%) $[\alpha]_D$ −12.7 (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ_H 2.11 (s, 3H, CH_3), 3.53−3.55 (m, 3H, H-6, H-4, H-6′), 3.61 (m, 1H, H-2), 3.65 (m, 1H, H-5), 4.01 (d, 1H, *J* = 11.2 Hz), 4.27 (d, 1H, *J* = 11.2 Hz), 4.52 (d, 1H, *J* = 12.4 Hz), 4.53 (m, 1H, H-3), 4.57 (d, 1H, *J* = 12.4 Hz), 4.62 (d, 1H, *J* = 12.0 Hz), 4.70 (d, 1H, *J* = 12.0 Hz), 6.21 (d, 1H, H-1, *J* = 8.8 Hz), 7.05−7.43 (m, 16H, 3 × Ph, C*H*=CCH_3,); ^{13}C NMR ($CDCl_3$) δ_C 26.8, 40.6, 70.7, 70.8, 71.2, 71.6, 73.6, 75.5, 105.4, 127.8, 128.0, 128.4, 128.5, 128.6, 138.1, 138.2, 138.3, 158.4; HRFABMS Anal. calcd for $C_{30}H_{33}O_5$ [M + H] 473.2328, found 473.2392.

2-*C*-(3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-*β*-D-glucopyranosyl)-acetaldehyde (30). A solution of **9** (56 mg, 0.1 mmol) in 5 mL of 4% NaOMe was stirred at room temperature for 4 h, neutralized with acetic acid, and concentrated. The residue was purified by flash chromatography (hexane/ethyl acetate 6:1−4:1) to afford **30** (34 mg, 60%) as a syrup: ^1H NMR ($CDCl_3$) δ_H 2.80 (CH_3SO_2), 2.81 (m, 1H, CH_2CHO), 2.95 (m, 1H, CH_2CHO), 3.48 (m, 1H, H-5), 3.68−3.83 (m, 4H, H-3, H-4, H-6, 6′), 3.80 (m, 1H, H-1), 4.40 (m, 1H, H-2), 4.52−5.25 (m, 6H), 7.15−7.38 (m, 15H), 9.80 (s, 1H, C*H*O); ^{13}C NMR ($CDCl_3$) δ_C 38.4, 45.3, 68.0, 73.1, 73.5, 74.9, 75.3, 78.6, 79.1, 80.5, 83.6, 127.1, 127.6, 127.7, 127.8, 128.3, 128.4, 137.3, 137.4, 137.6, 198.8; HRFABMS Anal. calcd for $C_{30}H_{35}O_8S$ [M + H] 555.2053, found 555.2006.

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Supporting Information Available: ^1H, ^{13}C, COSY, NOESY, TOCSY, and HSQC NMR spectra for products **2**−**4**, **6**, **8**−**9**, **11-D**, **12-D**, **16**−**17**, and **25**−**30**; for compounds **5**, **11**−**15**, and **18**−**24** see ref 7. This material is available free of charge via the Internet at http://pubs.acs.org.

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