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Reactions of some 2- and 4-*O*-triflylglycopyranosides with MeLi, *t*-BuOK, and pyridine

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Abstract

As an extension of our previous work on secondary triflates of carbohydrates [El Nemr, A.; Tsuchiya, T. *Tetrahedron Lett*. **1995**, *36*, 7665–7668. El Nemr, A.; Tsuchiya, T.; Kobayashi, Y. *Carbohydr. Res*. **1996**, *293*, 31–59. El Nemr, A.; Tsuchiya, T. *Carbohydr. Res*. **1997**, *301*, 77–87. El Nemr, A.; Tsuchiya, T. *Carbohydr. Res*. **1997**, *303*, 267–281], the reaction modes of several methyl 2- and 4-*O*-triflyl-D-glycopyranosides with MeLi (strong base), *t*-BuOK (moderately strong base), and pyridine (weak base) have been studied. This paper describes the reactions of 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-triflyl-D-gluco and -mannopyranosides with MeLi to give mainly the corresponding 2-*C*-methyl derivatives through α-elimination, with *t*-BuOK to give either the 2,3-unsaturated compounds through β-elimination or detriflyl 2-ols, and with hot pyridine to give the corresponding 2-pyridinium salts with inversion (except for the 2-*O*-triflyl-α-D-mannopyranoside (**8**)). 2,3,6-Tri-*O*-benzyl-4-*O*-triflyl-α-D-gluco and -mannopyranosides were also examined similarly.

Keywords: Triflate; MeLi; *t*-BuOK; Pyridine; Deuterated compound; α-Elimination; β-Elimination; Pyridinium salt; Nucleophilic substitution

We have recently reported[1–3] a new reaction with some carbohydrate triflates when they are treated with MeLi or BuLi in diethyl ether giving *C*-methyl (or butyl) or unsaturated compounds, both through α-elimination with removal of a hydrogen (or deuterium) atom at the carbon bearing a CF_3SO_3 group as a proton (deuteron). To clarify the reaction modes for these compounds when the strongly basic Me(Bu)Li is changed to a weaker base such as *t*-BuOK or pyridine, 3-*O*-triflyl-D-gluco- and -D-allo-furanoses and the corresponding pyranosides were examined. It was found that, when *t*-BuOK was used, the 3-*O*-triflyl-D-glucopyranosides afforded the corresponding 2,3- and/or 3,4-unsaturated compounds through α-elimination, and the 3-*O*-triflyl-D-allopyranosides gave the corresponding unsaturated compounds through β-elimination.[4] When pyridine was used, however, most of the compounds readily gave the corresponding 3-pyridinium derivatives with inversion;[4] it should be emphasized that methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-triflyl-α-D-glucopyranoside readily gave the corresponding 3-deoxy-3-pyridinium-D-allopyranoside, even though the steric and electrostatic 1,3-diaxial interactions[5] between MeO-1 and the pyridine molecule approaching C-3 would be expected, in the transition state, to hinder the reaction. The reaction should thus be facilitated by pyridine, a noncharged,[5,6] which may generate only weak electrostatic

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repulsion between its slightly negative-charged nitrogen and MeO-1. This paper is an extension of our previous work and describes the reactions of 2- and 4-*O*-triflyl-D-glycopyranosides with MeLi, *t*-BuOK, and pyridine to clarify the limitation of the foregoing reactions.

Synthesis of triflates

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-triflyl-β-D-(2-^{2}H)mannopyranoside (**10′**)† was prepared by the usual Swern oxidation–($NaBD_4$) reduction procedure for methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**),[7] followed by triflation (**5** → **2** → **9′** → **10′**; **2** was prepared in high yield through a different route already reported[8]). Likewise, the 2-deuterated 2-*O*-triflyl-α-D anomer (**8′**) of **10′** was prepared from methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**3**)[7] via a similar route involving oxidation–($NaBD_4$) reduction reactions (**3** → **1** → **3′**), with triflation of the resulting HO-2 group (to give **4′**), inversion of the C-2 function (with NaOBz–DMF), subsequent debenzoylation (to give **7′**), and triflation of the epi-HO-2 group.

Reactions of undeuterated and deuterated 2- and 4-triflates with MeLi, *t*-BuOK, and pyridine

At first, unlabeled methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-triflyl-α- (**4**)[9–11] and -β-D-glucopyranosides (**6**)[9] were treated with *t*-BuOK in diethyl ether, whereupon only the detriflyl 3-ols **3**[7] and **5**[7] were produced, in 76 and 68% yields, respectively (this suggests that the process can be used for detriflation in some cases). As previously reported, compounds **4** and **6** are known to give the *C*-2-alkyl derivatives when treated with the strongly basic Me(Bu)Li in diethyl ether[1,2] (Table 1). Compounds **4** and **6** were next treated with hot pyridine (~ 80 °C, 7 h). In this case, the 2-deoxy-2-pyridinium compounds having the D-manno structure (**13** and **17**, respectively) were produced as the sole products in high yields (Table 1). This means that the S_N2 reactions by pyridine proceed as smoothly as those by such anionic nucleophiles as N_3^- and F^- or by the strongly basic hydrazine.[6,9,12]

The D-mannopyranosides were examined next. When the 2-*O*-triflyl-α-D-mannopyranoside (**8**) was treated with MeLi, the *C*-2-methyl-D-gluco derivative (**12**)[2] was obtained in high yield unaccompanied by the D-manno isomer, along with the detriflyl 2-ol (**7**)[13] and a trace amount of unsaturated compounds **11**.[14] It is noteworthy that the abstraction of H-2 by Me(Bu)Li occurs readily, although, in **8**, the S_N2 reaction at C-2 is quite difficult.[5,6,15] In the reactions of **8** and the corresponding D-2-derivative (**8′**) with *t*-BuOK, the 2,3-unsaturated compounds, **11** and **11′**, respectively, were mainly produced as observed for **4**, **6**, and **10′**, through β-(H-3) [but not α-(H- or D-2)] elimination, as indicated by the retention of deuterium at C-2 in **11′**.

Compound **8** was next heated in pyridine. In this case, no pyridinium compound was produced and three 2,3-unsaturated products [**11**, **18**, and **19**[16] (major)] were formed. Compound **18** was assigned to be an α,β-unsaturated aldehyde based on the ^{1}H NMR (C*H*O, δ 9.98, $J_{1,2}$ 7 Hz), ^{13}C NMR (*C*HO, δ 190.5), and mass spectra. Compound **19** was assigned to be the 2-eno-1,5-lactone[16] having possibly an E_5 conformation based on the ^{1}H NMR (H-2, δ 5.46; H-3, δ 7.30) and mass spectra. As observed in many other 2-sulfonylated α-D-mannopyranosides, the S_N2 reactions at C-2 occur with difficulty,[5,6] possibly because of the steric repulsion between MeO-1 and the approaching nucleophiles to C-2 from the lower side in their transition states; in this case, however, electrostatic repulsion between MeO-1 and pyridine will be negligible, and the steric interaction should be the sole cause. Even so, the weakly basic, noncharged pyridine molecule can not attack at C-2 of **8** and instead attacks H-3 (to produce **11** by β-elimination) or H-1 (to produce **19** by β-elimination), as shown in Scheme 1. Compound **18** may be produced by hydrolysis of **11** with contaminant water in the pyridine, catalyzed by the CF_3SO_3H liberated during the reaction.

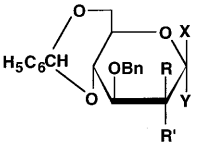
† Compounds with a primed number are for the deuterated derivatives of the corresponding nondeuterated compounds throughout this paper.

Next, the 2-labeled 2-*O*-triflyl-β-D-manno-pyranoside (**10′**) was examined. Treatment of **10′** with MeLi (this reaction is not reported in Refs. 1–4) gave a mixture of four compounds: **14**,[15] **14′**, **15**,[2] and **16**,[2] the ratio of the non-labeled (**14**) and 2-labeled 2,3-unsaturated compounds (**14′**) being 3:2 (20% in total). Compound **14** was considered to be produced by initial D-2 abstraction by MeLi (α-elimination) followed by 3 → 2 proton migration with subsequent removal of the 2-OTf group[1,2] (the whole reaction pattern closely resembles β-elimination and is liable to be so misjudged, in the absence of D-2 labeling). The 2-*C*-methyl-D-gluco (**15**) and -D-manno (**16**) derivatives (2:3, 76% in total) were considered to be produced by initial D-2 abstraction (α-elimination) followed by formation of the 2-oxo intermediate (by removal of the $F_3CSO_2^-$ group) and rapid reaction of the intermediate with excess MeLi.[1,2] The difference in the ratio of product-species between **8** and **10′** may be ascribed to the difference in anomeric configuration.

Compound **10′** was next treated with *t*-BuOK, whereupon a 2-labeled compound **14′** was exclusively produced by β-elimination; its ^{1}H NMR spectrum showed a very clear pattern, due to the absence of H-2, as compared with that obtained from the treatment of **10′** with MeLi (to give a mixture of **14** and **14′**; see Section 2). When **10′** was heated in pyridine, the 2-deoxy-2-pyridinium compound **20′** with the D-gluco structure was produced with inversion, in high yield and unaccompanied by any unsaturated or ring-contracted product[17] (Table 1).

The 4-deuterated-4-*O*-triflyl-α-D-gluco- (**21′**[3]) and -galactopyranosides (**25′**[2]) were next examined. As shown in Table 1, reactions of **21′**[3] and **25′**[2] with MeLi or *t*-BuOK gave the corresponding 3,4- (**26′**) and/or 4,5-unsaturated (**22**,[2] **22′**) compounds, or the detriflyl 4-ol (**23′**[2]), respectively; the reaction pattern (α- or β-elimination) and the product-species are fundamentally similar to that for the 3-*O*-triflyl-α-D-glycopyranosides already reported[1,2] (see Table 1). When **21** and **25** were treated with hot pyridine, the corresponding 4-deoxy-4-pyridinium compounds, **24** and **27**,[2] respectively were produced readily under inversion in high yields.

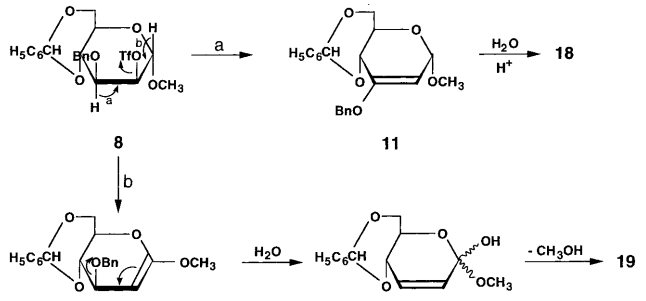
Summarizing all our data for the secondary triflates hitherto studied [Refs. 1–4 with this paper], it is concluded that, in treatment with Me(Bu)Li in diethyl ether, all 2-*O*-triflylglycopyranosides tested gave the 2-*C*-methyl (or butyl) derivatives, mainly through α-elimination, and the 3-[1,2] and 4-*O*-triflyl analogs gave mainly the corresponding unsaturated compounds through α-elimination or the detriflyl alcohols. In the reactions with *t*-BuOK, all compounds gave mainly the corresponding unsaturated compounds through β-elimination or the detriflyl alcohols. The foregoing results are therefore contradictory to the generally accepted concept that double bonds formed by removal of a sulfonyloxy group always arise through β-elimination, and, instead, indicate that double bonds are formed through either α- or β-elimination, depending upon the structures of the starting materials and the reaction conditions. In the case of pyridine, all compounds, except 2-*O*-triflyl-α-D-mannopyranoside (**8**), gave the corresponding pyridinium salts in high yields with inversion.



1 R, R' = =O, X = H, Y = OCH_3
2 R, R' = =O, X = OCH_3, Y = H
3 R = H, R' = OH, X = H, Y = OCH_3
3' R = D, R' = OH, X = H, Y = OCH_3
4 R = H, R' = OTf, X = H, Y = OCH_3
4' R = D, R' = OTf, X = H, Y = OCH_3
5 R = H, R' = OH, X = OCH_3, Y = H
5' R = D, R' = OH, X = OCH_3, Y = H
6 R = H, R' = OTf, X = OCH_3, Y = H
7 R = OH, R' = H, X = H, Y = OCH_3
7' R = OH, R' = D, X = H, Y = OCH_3
8 R = OTf, R' = H, X = H, Y = OCH_3
8' R = OTf, R' = D, X = H, Y = OCH_3
9 R = OH, R' = H, X = OCH_3, Y = H
9' R = OH, R' = D, X = OCH_3, Y = H
10' R = OTf, R' = D, X = OCH_3, Y = H

1. Experimental

General methods.—Optical rotations were determined with a Perkin–Elmer 241 polarimeter. Mass spectra were measured by the fast-atom bombardment method with a JEOL



Scheme 1.

SX-102 spectrometer. NMR spectra (^1H at 250 or 500 MHz, ^{13}C at 125.8 MHz, and ^{19}F at 235.35 MHz) were recorded with Bruker AC-250P or AMX-500 spectrometers, using Me_4Si and $CFCl_3$ (for ^{19}F) as the internal and external references, respectively. TLC was performed on Silica Gel 60 F_{254} (E. Merck 5715 and 5717), and detected by charring with aq 50% H_2SO_4. Column chromatography was performed on Wakogel C-200.

Preparation of starting materials

Methyl 3-O-benzyl-4,6-O-benzylidene-β-D-(2-^{2}H)glucopyranoside (**5′**) *and methyl 3-O-benzyl-4,6-O-benzylidene-β-D-(2-^{2}H)mannopyranoside* (**9′**). To a cold (−78 °C) solution of oxalyl chloride (0.94 mL, 10.7 mmol) in CH_2Cl_2 (20 mL) was added Me_2SO (1.52 mL, 21.5 mmol) and after 15 min, methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**)[7] (2.0 g, 5.37 mmol) in CH_2Cl_2 (15 mL) was added dropwise and the mixture was stirred for 30 min. After the addition of Et_3N (3 g), the mixture was warmed to rt and kept for 1 h. Water (20 mL) was added, and the organic layer separated was washed with water, dried (Na_2SO_4), and concentrated. The residue was recrystallized from MeOH to give **2** as needles (1.85 g), mp 179–180 °C (lit.[8] no data reported), $[\alpha]_D^{22}$ −76° (*c* 1, $CHCl_3$) (lit.[8] no data reported); *m/z* 371.22 ($M^+ + 1$); Anal. Calcd for $C_{21}H_{22}O_6$: *m/z* 370.14 for M^+; ^1H NMR ($CDCl_3$): δ 3.59 (s, 3 H, OCH_3), 3.75 (dt, 1 H, $J_{4,5} \approx J_{5,6}$ 10, $J_{5,6'}$ 4.3 Hz, H-5), 3.85 (t, 1 H, $J_{6,6'}$ 10 Hz, H-6), 3.94 (dd, 1 H, H-4), 4.23 (dd, 1 H, $J_{1,3} \sim 1$, $J_{3,4}$ 9.5 Hz, H-3), 4.45 (dd, 1 H, H-6′), 4.76 (d, 1 H, H-1), 4.86 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 5.58 (s, 1 H, C*H*Ph); ^{13}C NMR ($CDCl_3$): δ 58.01, 66.49, 68.58, 73.31, 81.92, 82.09, 101.11, 101.58, 196.45 (C-2). To a solution of **2** (1.50 g) in MeOH (40 mL) was added $NaBD_4$ (0.22 g, 5.27 mmol) and the solution was kept for 2 h at rt. Excess CO_2 (dry ice) was added, the solution was concentrated, and the residue was chromatographed (1:1 hexane–EtOAc) to give, from the faster-moving fractions, compound **5′** as needles (97 mg, 6% based on **5**), mp 182–183 °C (unlabeled compound, lit.[7] 184–185 °C); $[\alpha]_D^{22}$ −45° (*c* 0.5, $CHCl_3$), (unlabeled, lit.[7] $[\alpha]_D$ −48° ($CHCl_3$)); *m/z* 374.27 ($M^+ + 1$); Anal. Calcd for $C_{21}H_{23}DO_6$: *m/z* 373.16 for M^+; ^1H NMR ($CDCl_3$): δ 2.45 (s, 1 H, OH), 3.46 (dt, 1 H, $J_{4,5} \approx J_{5,6}$ 10.5, $J_{5,6'}$ 5.0 Hz, H-5), 3.57 (s, 3 H, OCH_3), 3.68 (dd, 1 H, H-4), 3.69 (d, 1 H, $J_{3,4}$ 8.0 Hz, H-3), 3.80 (t, 1 H, H-6), 4.33 (s, 1 H, H-1), 4.36 (dd, 1 H, H-6′), 4.88 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 5.58 (s, 1 H, C*H*Ph). From the slower-moving fractions compound **9′** was obtained as needles (1.38 g, 85% based on **5**), mp 116–118 °C (lit.[8] no data reported); $[\alpha]_D^{22}$ −30° (*c* 0.5, $CHCl_3$), (lit.[8] no data reported); *m/z* 374.24 ($M^+ + 1$); Anal. Calcd for $C_{21}H_{23}DO_6$: *m/z* 373.16 for M^+; ^1H NMR ($CDCl_3$): δ 2.55 (s, 1 H, OH), 3.35 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 10, $J_{5,6'}$ 4.5 Hz, H-5), 3.56 (s, 3 H, OCH_3), 3.65 (d, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.89 (t, 1 H, H-6), 4.14 (t, 1 H, H-4), 4.34 (dd, 1 H, H-6′), 4.41 (s, 1 H, H-1), 4.81 (ABq, 2 H, *J* 12 Hz, CH_2Ph) 5.61 (s, 1 H, C*H*Ph), no H-2 signal was observed.

Methyl 3-O-benzyl-4,6-O-benzylidene-α-D-(2-^{2}H)glucopyranoside (**3′**). A solution of **3**[7] (1.5 g, 4.03 mmol) in CH_2Cl_2 (10 mL) was oxidized as described for **2** to give **1** as needles (1.42 g), mp 146–147 °C, $[\alpha]_D^{22}$ +11° (*c* 1, $CHCl_3$); *m/z* 369.10 ($M^+ - 1$), 371.12 ($M^+ + 1$); Anal. Calcd for $C_{21}H_{22}O_6$: *m/z* 370.16 for M^+; ^1H NMR ($CDCl_3$): δ 3.47 (s, 3 H, OCH_3), 3.81 (t, 1 H, H-6), 3.87 (dd, 1 H, H-4), 4.19 (dt, 1 H, $J_{4,5} \approx J_{5,6}$ 10.5, $J_{5,6'}$ 5.0 Hz, H-5), 4.38 (dd, 1 H, H-6′), 4.53 (d, 1 H, $J_{3,4}$ 10.5 Hz, H-3), 4.75 (s, 1 H, H-1), 4.82 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 5.56 (s, 1 H, C*H*Ph). A solution of **1** (1.2 g) in MeOH (30 mL) was treated with $NaBD_4$ as described for **9′** to give **3′** as needles (1.16 g, 91% based on **3**), mp 186–188 °C (unlabeled compound, lit.[7] 187–188 °C), $[\alpha]_D^{22}$ +76° (*c* 1, $CHCl_3$) (unlabeled, lit.[7] $[\alpha]_D$ +78° ($CHCl_3$)); *m/z* 372.16 ($M^+ - 1$), 374.19 ($M^+ + 1$); Anal. Calcd for

$C_{21}H_{23}DO_6$: *m/z* 373.19 for M^+; ^1H NMR ($CDCl_3$): δ 2.33 (s, 1 H, OH), 3.45 (s, 3 H, OCH_3), 3.64 (t, 1 H, H-6), 3.75 (t, 1 H, H-4), 3.82 (d, 1 H, $J_{3,4}$ 10 Hz, H-3), 3.84 (dt, 1 H, $J_{4,5} \approx J_{5,6} \sim 10$, $J_{5,6'}$ 4 Hz, H-5), 4.30 (dd, 1 H, H-6′), 4.80 (s, 1 H, H-1), 4.87 (ABq, 2 H, *J* 11.5 Hz, CH_2Ph), 5.57 (s, 1 H, CHPh); no H-2 signal was observed.

Methyl 3-O-benzyl-4,6-O-benzylidene-2-O-triflyl-α-D-(2-^{2}H)glucopyranoside (**4′**). Prepared from **3′** (1.0 g, 2.68 mmol) as described in the general procedure for triflation to give **4′** as needles (1.21 g, 89%), mp 82–84 °C (unlabeled compound, lit.[9] 83–85 °C), $[\alpha]_D^{22}$ +34° (*c* 1, $CHCl_3$) (unlabeled, lit.[9] $[\alpha]_D$ +35.7° ($CHCl_3$)); *m/z* 504.14 (M^+

Table 1

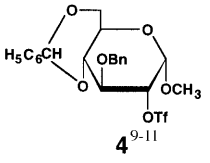
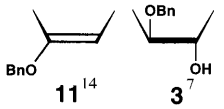
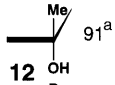
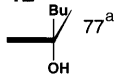
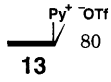
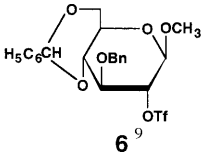
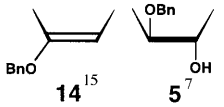
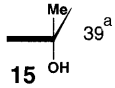
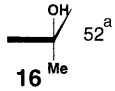
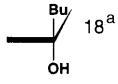
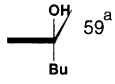
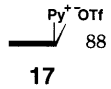
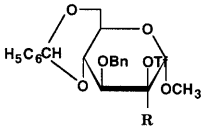
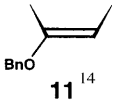
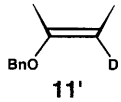
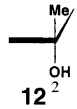
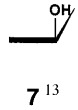
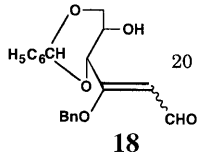
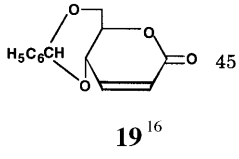
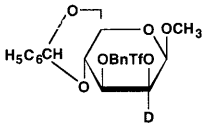
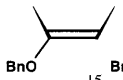
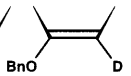
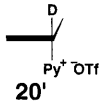
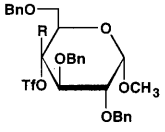
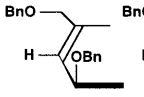
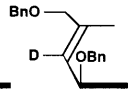
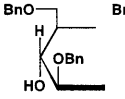
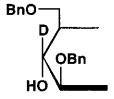
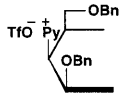
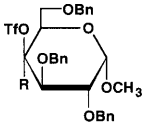
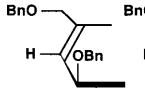
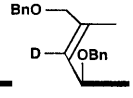
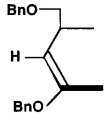
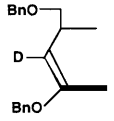
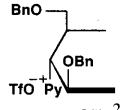
Reagant	Starting material	Product and yield (%)			Reference
	 **4**[9-11]	 **11**[14]	**3**[7]		
MeLi		0	0	 91[a] **12**	2
BuLi		0	0	 77[a]	2
^{t}BuOK		0	76		
Pyridine		0	0	 80 **13**	
	 **6**[9]	 **14**[15]	**5**[7]		
MeLi		0	0	 39[a] **15**  52[a] **16**	2 2
BuLi		0	0	 18[a]  59[a]	
^{t}BuOK		0	68		
Pyridine		0	0	 88 **17**	
		 **11**[14]	 **11′**	 **12**[2]	 **7**[13]
MeLi	**8** (R=H)	trace		77[a]	18
^{t}BuOK	**8**	93			0
^{t}BuOK	**8′** (R=D)	5[a]	89[b]		
Pyridine	**8**	8	 20 **18**	 45 **19**[16]	

Table 1 (*Continued*)

Reagant	Starting material	Product and yield (%)				Reference
	 **10'**	 **14** [15]	 **14'**	 **15** [2]	 **16** [2]	
MeLi		12[a]	8[b]	31[a]	45[a]	
^{t}BuOK		0	84[b]			
Pyridine		0	0	 **20'**	94	
		 **22** [2]	 **22'**	 **23**	 **23'** [2]	
MeLi	**21** (R=H) [18]	0		80		[2]
MeLi	**21'** (R=D) [3]	16[a]	0		79	[3]
^{t}BuOK	**21'**	2.5[a]	11.5[b]		81	
Pyridine	**21**			 **24**	82	
		 **22** [2]	 **22'**	 **26**	 **26'**	
MeLi	**25'** (R=D) [2]	36[a]	0	0	0	
MeLi[c]	**25** (R=H) [19]	45[a]		0		[3]
^{t}BuOK	**25'**	0	34[b]	0	54[b]	
Pyridine[c]	**25**			 **27** [2]	98	

[a] α-elimination
[b] β-elimination
[c] The reaction was performed as described in the general procedure.

– 1), 506.16 ($M^+ + 1$); Anal. Calcd for $C_{22}H_{22}DF_3O_8S$: *m/z* 505.11 for M^+; ^{1}H NMR ($CDCl_3$): δ 3.47 (s, 3 H, OCH_3), 3.69 (t, 1 H, H-4), 3.76 (t, 1 H, H-6), 3.88 (dt, 1 H, $J_{4,5}$ 9, $J_{5,6}$ 10, $J_{5,6'}$ 4.5 Hz, H-5), 4.12 (d, 1 H, $J_{3,4}$ 9 Hz, H-3), 4.31 (dd, 1 H, H-6′), 4.81 (ABq, 2 H, *J* 11.5 Hz, C*H*$_2$Ph), 4.96 (s, 1 H, H-1), 5.56 (s, 1 H, C*H*Ph); no H-2 signal was observed.

Methyl 3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (**7**). A mixture of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-triflyl-α-D-glucopyranoside (**4**)[9–11] (2.1 g, 4.17 mmol) and NaOBz (1.81 g, 12.6 mmol) in DMF (50 mL)

was heated at 80 °C for 8 h. Water (50 mL) was added and the mixture was extracted with $CHCl_3$ (70 mL × 3). The extracts combined were washed with water, dried (Na_2SO_4), and concentrated in vacuo to give the crude 2-*O*-Bz derivative of **7** as a syrup (1.98 g). A mixture of the syrup and NaOMe in MeOH was allowed to stand for 1 h. After excess CO_2 (dry ice) was added, the mixture was concentrated and the residue was chromatographed (1:1 hexane–EtOAc) to give **7** as a syrup (1.21 g, 78%), $[\alpha]_D^{22}$ + 50° (*c* 1, $CHCl_3$), (lit.[13] $[\alpha]_D^{25}$ + 51° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$): δ 2.74 (s, 1 H, OH), 3.36 (s, 3 H, OCH_3), 3.75–3.93 (m, 3 H, H-4,5,6), 4.02 (m, 1 H, H-2), 4.08 (m, 1 H, H-3), 4.27 (dd, 1 H, H-6′), 4.74 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.78 (ABq, 2 H, *J* 11.5 Hz, CH_2Ph), 5.61 (s, 1 H, C*H*Ph).

*Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-*D*-(2-^{2}H)mannopyranoside* (**7′**). A mixture of **4′** (1.05 g, 2.08 mmol) and NaOBz (0.91 g, 6.32 mmol) in DMF (30 mL) was heated as described for **7** to give the crude 2-*O*-Bz derivative of **7′** as a syrup (1.12 g). Debenzoylation (cat. NaOMe in MeOH) followed by chromatography (1:1 hexane–EtOAc) gave **7′** as a syrup (582 mg, 75%), $[\alpha]_D^{22}$ + 49° (*c* 1, $CHCl_3$), (unlabeled compound, lit.[13] $[\alpha]_D^{25}$ + 51° ($CHCl_3$)); *m*/*z* 372.17 ($M^+ - 1$), 374.19 ($M^+ + 1$); Anal. Calcd for $C_{21}H_{23}DO_6$: *m*/*z* 373.19 for M^+: ^{1}H NMR ($CDCl_3$): δ 2.74 (s, 1 H, OH), 3.36 (s, 3 H, OCH_3), 3.79 (dt, 1 H, $J_{4,5} \approx J_{5,6} \sim 10$, $J_{5,6'}$ 4 Hz, H-5), 3.86 (t, 1 H, H-6), 3.92 (t, 1 H, H-4), 4.08 (d, 1 H, $J_{3,4}$ 10 Hz, H-3), 4.27 (dd, 1 H, H-6′), 4.74 (s, 1 H, H-1), 4.78 (ABq, 2 H, *J* 11.5 Hz, CH_2Ph), 5.61 (s, 1 H, C*H*Ph).

General procedure for preparation of triflates.—To a cold (−10 °C) solution of an alcohol (1 mmol) in 2:1 CH_2Cl_2–pyridine (6 mL) was added $(CF_3SO_2)_2O$ (1.3 mmol) and the solution was kept for 2 h at 0 °C. After addition of water (0.5 mL), the mixture was concentrated, and the residue was purified by chromatography (3:1 hexane–EtOAc).

*Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-triflyl-α-*D*-mannopyranoside* (**8**). Prepared from **7**, needles (83%), mp 90–91 °C, $[\alpha]_D^{22}$ + 18° (*c* 1, $CHCl_3$); *m*/*z* 505.15 ($M^+ + 1$); Anal. Calcd for $C_{22}H_{23}F_3O_8S$: *m*/*z* 504.11 for M^+; ^{1}H NMR ($CDCl_3$): δ 3.40 (s, 3 H, OCH_3), 3.82 (m, 1 H, H-5), 3.87 (t, 1 H, H-6), 4.03 (m, 2 H, H-3,4), 4.26 (dd, 1 H, H-6′), 4.78 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 4.84 (d, 1 H, H-1), 5.08 (t, 1 H, $J_{1,2} \approx J_{2,3} \sim$ 1.5 Hz, H-2), 5.62 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{22}H_{23}F_3O_8S$: C, 52.38; H, 4.60. Found: C, 52.29; H, 4.59.

*Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-triflyl-α-*D*-(2-^{2}H)mannopyranoside* (**8′**). Prepared from **7′** as needles (81%), mp 91–93 °C (unlabeled compound, 90–91 °C), $[\alpha]_D^{22}$ + 18° (*c* 1, $CHCl_3$) (unlabeled, $[\alpha]_D^{22}$ + 18° ($CHCl_3$)); *m*/*z* 504.02 ($M^+ - 1$), 506.02 ($M^+ + 1$); Anal. Calcd for $C_{22}H_{22}DF_3O_8S$: *m*/*z* 505.11 for M^+; ^{1}H NMR ($CDCl_3$): δ 3.39 (s, 3 H, CH_3), 3.81 (dt, 1 H, $J_{4,5} \approx J_{5,6}$ 10, $J_{5,6'}$ 4 Hz, H-5), 3.85 (t, 1 H, H-6), 4.03 (m, 2 H, H-3,4), 4.26 (dd, 1 H, H-6′), 4.78 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 4.84 (s, 1 H, H-1), 5.08 (br s, 0.06 H, H-2), 5.62 (s, 1 H, C*H*Ph).

*Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-triflyl-β-*D*-(2-^{2}H)mannopyranoside* (**10′**). Prepared from **9′** as needles (93%), mp 98–99 °C (unlabeled compound, lit.[15] 99 °C), $[\alpha]_D^{22}$ − 35° (*c* 1, $CHCl_3$), (unlabeled, lit.[15] $[\alpha]_D$ − 36° ($CHCl_3$)); *m*/*z* 506.23 ($M^+ + 1$); Anal. Calcd for $C_{22}H_{22}DF_3O_8S$: *m*/*z* 505.11 for M^+; ^{1}H NMR ($CDCl_3$): δ 3.37 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 10.3, $J_{5,6'}$ 5 Hz, H-5), 3.55 (s, 3 H, OCH_3), 3.75 (d, 1 H, H-3), 3.90 (t, 1 H, H-6), 4.00 (t, 1 H, $J_{3,4} \approx J_{4,5}$ 9.5 Hz, H-4), 4.33 (dd, 1 H, H-6′), 4.51 (s, 1 H, H-1), 4.80 (ABq, 2 H, *J* 12 Hz, CH_2Ph), 5.62 (s, 1 H, C*H*Ph).

General procedure for the reactions of triflates with MeLi.—To a cold (−50 °C) solution of a triflate (0.2 mmol) in dry Et_2O (5 mL) was added MeLi (0.8 mmol, as a 1.4 M solution in Et_2O), and the solution was kept for 1 h at rt. Aq 2 M NH_4Cl (5 mL) and $CHCl_3$ (50 mL) were stirred in and the organic layer separated was washed with water, dried (Na_2SO_4), concentrated, and the reside was chromatographed.

Reaction of **8** *with MeLi.* After the general procedure followed by chromatography (1:1 hexane–EtOAc), **8** (100 mg) gave **12**[2] (59 mg) and **7**[13] (13 mg) as syrups, respectively.

Reaction of **10′** *with MeLi*. After the general procedure, **10′** (100 mg) gave, on chromatography (5:1 hexane–EtOAc), a 3:2 mixture of **14**[9] and **14′** as needles (14 mg, 20%), mp 82–84 °C (unlabeled compound, lit.[15] 83 °C), $[\alpha]_D^{22}$ −108° (*c* 0.5, $CHCl_3$) (unlabeled, lit.[15] $[\alpha]_D$ −110° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$): δ 3.42 (s, 3 H, OCH_3), 3.81 (dt, 1 H, $J_{4,5}$ 8.5, $J_{5,6}$ 10, $J_{5,6'}$ 4 Hz, H-5), 3.91 (t, 1 H, H-6), 4.32 (dd, 1 H, H-6′), 4.44 (d with narrow multiplets, 1 H, H-4), 4.70 (t, 0.6 H, $J_{1,2} \approx J_{2,4} \sim 1.5$ Hz, H-2), 4.88 (ABq, 2 H, *J* 12 Hz, C*H*$_2$Ph), 5.39 (dd, 0.6 H; d, 0.4 H, $J_{1,4} \sim 2.5$ Hz, H-1), 5.62 (s, 1 H, C*H*Ph). Further development with 1:1 hexane–EtOAc gave, from the faster-moving fractions, compound **15** as a syrup (24 mg, 31%), $[\alpha]_D^{22}$ −41° (*c* 1, $CHCl_3$), (unlabeled, lit.[2] $[\alpha]_D^{24}$ −43° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$): all signals are identical with those reported.[2] From the slower-moving fractions compound **16** was obtained as a solid (34 mg, 45%), $[\alpha]_D^{22}$ −37° (*c* 1, $CHCl_3$), (unlabeled, lit.[2] $[\alpha]_D^{24}$ −35° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$): all signals are identical with those reported.[2]

General procedure for the reactions of triflates with t-*BuOK*.—To a solution of a triflate (0.2 mmol) in dry ether (3 mL) was added *t*-BuOK (0.6 mmol), and the mixture was stirred for 3 h at rt. Water (7 mL) was added and the resulting mixture was extracted with $CHCl_3$ (20 mL × 3). The combined organic solution was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel with 1:1 hexane–EtOAc.

Reaction of **8** *with* t-*BuOK*. After the general procedure, **11** was obtained as needles (93%), mp 121–122 °C (lit.[14] 120–121 °C), $[\alpha]_D^{22}$ +56° (*c* 1, $CHCl_3$) (lit.[14] $[\alpha]_D^{22}$ +59° (*c* 0.6, $CHCl_3$)); *m*/*z* 353.17 ($M^+ - 1$), 355.17 ($M^+ + 1$); Anal. Calcd for $C_{21}H_{22}O_5$: *m*/*z* 354.15 for M^+; ^{1}H NMR ($CDCl_3$): δ 3.41 (s, 3 H, OCH_3), 3.83 (t, 1 H, H-6), 4.11 (dt, 1 H, $J_{4,5} \approx J_{5,6}$ 10, $J_{5,6'}$ 4.5 Hz, H-5), 4.26 (dd, 1 H, H-4), 4.30 (dd, 1 H, H-6′), 4.74 (dd, 1 H, $J_{1,2}$ 3.2, $J_{2,4} \sim 1.6$ Hz, H-2), 4.86 (ABq, 2 H, *J* 12 Hz, C*H*$_2$Ph), 5.01 (d, 1 H, H-1), 5.58 (s, 1 H, C*H*Ph).

Reaction of **8′** *with* t-*BuOK to give methyl 3*-O-*benzyl-4,6*-O-*benzylidene-2-deoxy-α*-D-*(2-*^{2}*H)*erythro-*hex-2-enopyranoside* (**11′**). Needles, mp 119–121 °C (unlabeled compound, lit.[14] 120–121 °C), $[\alpha]_D^{22}$ +57° (*c* 1, $CHCl_3$) (unlabeled, lit.[14] $[\alpha]_D$ +59° (*c* 0.6, $CHCl_3$)); *m*/*z* 354.13 ($M^+ - 1$), 356.13 ($M^+ + 1$); Anal. Calcd for $C_{21}H_{21}DO_5$: *m*/*z* 355.15 for M^+; ^{1}H NMR ($CDCl_3$): δ 3.41 (s, 3 H, OCH_3), 3.83 (t, 1 H, H-6), 4.11 (dt, 1 H, $J_{4,5}$ 9, $J_{5,6}$ 10, $J_{5,6'}$ 4.5 Hz, H-5), 4.26 (dd, 1 H, $J_{1,4} \sim 1$ $J_{4,5}$ 9 Hz, H-4), 4.30 (dd, 1 H, H-6′), 4.74 (dd, 0.06 H, H-2), 4.87 (ABq, 2 H, *J* 12 Hz, C*H*$_2$Ph), 5.02 (s, 1 H, H-1), 5.59 (s, 1 H, C*H*Ph).

Reaction of ***10′*** *with t-BuOK*. After the general procedure, **14′** was obtained as needles (84%), mp 83–84 °C (unlabeled compound, lit.[15] 83 °C), $[\alpha]_D^{22}$ −109° (*c* 1, $CHCl_3$), (unlabeled, lit.[15] $[\alpha]_D$ −110° ($CHCl_3$)); *m*/*z* 354.21 ($M^+ - 1$); Anal. Calcd for $C_{21}H_{21}DO_5$: *m*/*z* 355.15 for M^+; ^{1}H NMR ($CDCl_3$): δ 3.42 (s, 3 H, OCH_3), 3.81 (dt, 1 H, $J_{4,5}$ 8.5, $J_{5,6}$ 10, $J_{5,6'}$ 4 Hz, H-5), 3.90 (t, 1 H, H-6), 4.32 (dd, 1 H, H-6′), 4.44 (dd, 1 H, H-4), 4.70 (t, ~0.06 H, H-2), 4.88 (ABq, 2 H, *J* 12 Hz, C*H*$_2$Ph), 5.39 (d, 1 H, $J_{1,4}$ 2.5 Hz, H-1), 5.62 (s, 1 H, C*H*Ph).

Reaction of **21′**[3] *with* t-*BuOK to give methyl 2,3,6-tri*-O-*benzyl-4-deoxy-β*-L-threo-*hex-4-enopyranoside* (**22**[2]), *methyl 2,3,6-tri*-O-*benzyl-4-deoxy-β*-L-*(4-*^{2}*H)*threo-*hex-4-enopyranoside* (**22′**) *and methyl 2,3,6-tri*-O-*benzyl-α*-D-*(4-*^{2}*H)glucopyranoside* (**23′**[2]). Chromatography as described in the general procedure gave a 1:4.5 mixture of **22** and **22′** as a syrup (14%), $[\alpha]_D^{22}$ +79° (*c* 0.5, $CHCl_3$) (unlabeled compound, lit.[2] $[\alpha]_D^{22}$ +78° (*c* 1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$): δ 3.49 (s, 3 H, OCH_3), 3.78 (dd, 1 H, $J_{1,2}$ 2.5, $J_{2,3}$ 7 Hz, H-2), 3.92 (sl. br s, 2 H, H-6,6′), 4.23 (~dt, 1 H, $J_{2,3}$ 7, $J_{3,6} \approx J_{3,6'} \sim 1$ Hz, H-3); 4.54, 4.63, and 4.77 (each ABq, 2 H, *J* 12 Hz, C*H*$_2$Ph × 3), 4.85 (d, 1 H, H-1), 5.04 (d, 0.18 H, $J_{3,4}$ 3 Hz, H-4). Further development gave **23′** as a syrup (81%), $[\alpha]_D^{22}$ +11.5° (*c* 0.6, $CHCl_3$) (lit.[2] $[\alpha]_D^{22}$ +12° ($CHCl_3$)).

Reaction of **25′**[2] *with* t-*BuOK to give methyl 2,3,6-tri*-O-*benzyl-4-deoxy-β*-L-*(4-*^{2}*H)*threo-*hex-4-enopyranoside* (**22′**) *and 2,3,6-tri*-O-*benzyl-4-deoxy-α*-D-*(4-*^{2}*H)*erythro-*hex-3-enopyranoside* (**26′**). Chromatography as described in the general procedure gave **22′** as a syrup (34%), $[\alpha]_D^{22}$ +79° (*c* 1.2, $CHCl_3$) (unlabeled compound, lit.[2] $[\alpha]_D^{22}$ +78° (*c* 1, $CHCl_3$);

^{1}H NMR ($CDCl_3$): δ 3.49 (s, 3 H, OCH_3), 3.78 (dd, 1 H, $J_{1,2}$ 2.5, $J_{2,3}$ 7 Hz, H-2), 3.92 (sl. br s, 2 H, H-6,6′), 4.23 (dt, 1 H, $J_{2,3}$ 7, $J_{3,6} \approx J_{3,6'} \sim 1$ Hz, H-3); 4.54, 4.63, and 4.77 (each ABq, 2 H, J 12 Hz, CH_2Ph × 3), 4.85 (d, 1 H, H-1). Further development gave **26′** as a syrup (54%), $[\alpha]_D^{22}$ −40° (*c* 1.1, $CHCl_3$); *m/z* 446.30 ($M^+ - 1$); Anal. Calcd for $C_{28}H_{29}DO_5$: *m/z* 447.22 for M^+; ^{1}H NMR (acetone-d_6): δ 3.45 (s, 3 H, OCH_3), 3.50 (dd, 1 H, H-6), 3.58 (dd, 1 H, H-6′), 4.16 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,5}$ 2.5 Hz, H-2), 4.40 (dt, 1 H, $J_{2,5}$ 2.5, $J_{5,6}$ 5.0, $J_{5,6'}$ 6.0 Hz, H-5), 4.58, 4.75 and 4.82 (each ABq, 2 H, J 12 Hz, CH_2Ph × 3), 4.94 (d, 1 H, H-1).

General procedure for the reactions of triflates with pyridine.—A solution of a triflate (0.2 mmol) in pyridine (2 mL) was heated at 80 °C for 7 h, except for **8**. After excess pyridine has been evaporated in vacuo, the residue dissolved in $CHCl_3$ (20 mL) was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel (5:1 $CHCl_3$–MeOH) to give the pyridinium trifluoromethanesulfonate.

Reaction of **4**[9–11] *with pyridine to give methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(pyridinium-1-yl)-α-*D*-mannopyranoside triflate* (**13**). Syrup, $[\alpha]_D^{22}$ −41° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.45 (s, 3 H, OCH_3), 3.80 (t, 1 H, $J_{5,6} \approx J_{6,6'}$ 10 Hz, H-6), 4.06 (dt, 1 H, $J_{4,5} \approx J_{5,6}$ 10, $J_{5,6'}$ 5.5 Hz, H-5), 4.10 (t, 1 H, $J_{3,4}$ 10 Hz, H-4), 4.32 (dd, 1 H, H-3), 4.38 (dd, 1 H, H-6′), 4.78 (ABq, 2 H, J 12 Hz, CH_2Ph), 5.22 (d, 1 H, $J_{1,2} < 0.5$, $J_{2,3}$ 5.8 Hz, H-2), 5.39 (s, 1 H, H-1), 5.61 (s, 1 H, C*H*Ph), 8.00, 8.40 and 8.97 (each m of 2, 1, and 2 H, respectively, C_5H_5N); ^{19}F NMR ($CDCl_3$): δ −78.54 (s, CF_3SO_3).

Reaction of **6**[9] *with pyridine to give methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(pyridinium-1-yl)-β-*D*-mannopyranoside triflate* (**17**). Needles, mp 73–75 °C, $[\alpha]_D^{23}$ +38° (*c* 1, $CHCl_3$); *m/z* 434.16 (M^+); Anal. Calcd for $C_{26}H_{28}NO_5$: *m/z* 434.20 for M^+; ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 2 H, H_2O), 3.50 (s, 3 H, OCH_3), 3.63 (dt, 1 H, $J_{5,6'}$ 5 Hz, H-5), 3.83 (t, 1 H, H-6), 4.01 (t, 1 H, $J_{3,4} \approx J_{4,5}$ 10 Hz, H-4), 4.38 (dd, 1 H, H-6′), 4.41 (dd, 1 H, H-3), 4.82 (ABq, 2 H, J 12 Hz, CH_2Ph), 5.16 (d, 1 H, H-1), 5.60 (s, 1 H, C*H*Ph), 5.78 (dd, 1 H, $J_{1,2}$ 2.8, $J_{2,3}$ 5.5 Hz, H-2), 7.92, 8.31 and 9.06 (m of 2, 1, and 2 H, respectively, C_5H_5N). Anal. Calcd for $C_{27}H_{28}F_3NO_8S \cdot H_2O$: C, 53.90; H, 5.03; N, 2.33. Found: C, 54.03; H, 5.06; N, 2.38.

Reaction of **8** *with pyridine to give* **11**[14], *3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-erythro-hex-2-enal* (**18**), *and 4,6-*O*-benzylidene-2,3-dideoxy-*D*-erythro-hex-2-eno-1,5-lactone* (**19**)[16]. Heating **8** (120 mg, 0.24 mmol) in pyridine (4 mL) at 60 °C for 12 h followed by concentration of the solution in vacuo gave a residue, which was chromatographed (1:1 hexane–EtOAc) to give, from the faster-moving fractions, compound **11**[14] as needles (7 mg, 8%) and, from the second-moving fractions, compound **19** as a solid (25 mg, 45%), mp 135–136 °C (lit.[16] 136–137 °C), $[\alpha]_D^{22}$ +32° (*c* 1, $CHCl_3$) (lit.[16] $[\alpha]_D^{27}$ +33° (*c* 1, $CHCl_3$)); *m/z* 233.15 ($M^+ + 1$); Anal. Calcd for $C_{13}H_{12}O_4$: *m/z* 332.09 for M^+; ^{1}H NMR ($CDCl_3$): δ 4.04 (unresolved m, 1 H, H-6; signals are complex due to virtual couplings involving H-4), 4.38–4.53 (unresolved m, 3 H, H-4,5,6′), 5.46 (d, 1 H, H-2), 5.60 (s, 1 H, C*H*Ph), 7.30 (d, 1 H, H-3); $J_{2,3}$ 6 Hz; ^{13}C NMR ($CDCl_3$): δ 67.91 (C-6), 73.08 (C-4 or 5), 77.52 (C-5 or 4), 102.35 (*C*HPh); 106.32 (C-2), 126.45, 128.34, 129.47 and 136.23 (Ph), 161.36 (C-3), 188.07 (C-1), which were confirmed by the C–H correlation spectrum; the H-4,5, and 6′ could not be resolved even in the spectrum in pyridine-d_5. From the slowest-moving fractions compound **18** was obtained as a syrup (18 mg, 20%), $[\alpha]_D^{22}$ +0.2° (*c* 1, $CHCl_3$); *m/z* 339.16 ($M^+ - 1$), 341.16 ($M^+ + 1$); Anal. Calcd for $C_{20}H_{20}O_5$: *m/z* 340.13 for M^+; ^{1}H NMR ($CDCl_3$): δ 2.61 (d, 1 H, OH), 3.73 (dd, 1 H, $J_{5,6}$ 10, $J_{6,6'}$ 11 Hz, H-6), 4.20 (m, 1 H, H-5), 4.40 (dd, 1 H, $J_{5,6'}$ 5.5 Hz, H-6′), 4.90 (d, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.95 (ABq, 2 H, J 11.5 Hz, CH_2Ph), 5.59 (s, 1 H, C*H*Ph), 5.66 (d, 1 H, $J_{1,2}$ 7 Hz, H-2), 9.98 (d, 1 H, H-1); ^{13}C NMR ($CDCl_3$): δ 63.33 (C-5), 71.28 (C-6), 71.38 (C-4), 79.66 (*C*H$_2$Ph), 101.81 (*C*HPh), 108.33 (C-2), 190.50 (C-1).

Reaction of **10′** *with pyridine to give methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(pyridinium-1-yl)-β-*D*-(2-^{2}H)glucopyranoside triflate* (**20′**). Syrup, $[\alpha]_D^{23}$ +38° (*c* 1, $CHCl_3$); *m/z* 435.42 (M^+); Anal. Calcd for $C_{26}H_{27}$-

DNO_5: m/z 435.20 for M^+; ^1H NMR ($CDCl_3$): δ 3.37 (s, 3 H, OCH_3), 3.83 (t, 1 H, $J_{5,6} \approx J_{6,6'}$ 10.2 Hz, H-6), 3.87 (dd, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 9.5 Hz, H-4), 4.04 (dt, 1 H, H-5), 4.45 (dd, 1 H, $J_{5,6'}$ 4.5 Hz, H-6′), 4.57 (ABq, 2 H, J 12 Hz, CH_2Ph), 4.58 (d, 1 H, H-3), 5.36 (s, 1 H, H-1), 5.63 (s, 1 H, CHPh), 7.87, 8.34 and 8.83 (each m of 2, 1, and 2 H, respectively, C_5H_5N); ^{19}F NMR ($CDCl_3$): δ −78.62 (s, CF_3SO_3).

Reaction of **21**[18] *with pyridine to give methyl 4-deoxy-2,3,6-tri-*O*-benzyl-4-(pyridinium-1-yl)-α-*D*-galactopyranoside triflate* (**24**). Syrup, $[\alpha]_D^{22}$ +48° (*c* 2, $CHCl_3$), ^1H NMR ($CDCl_3$): δ 3.41 (s, 3 H, OCH_3), 3.58 (dd, 1 H, $J_{5,6}$ 5.5, $J_{6,6'}$ 10.5 Hz, H-6), 3.71 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.5 Hz, H-2), 3.86 (dd, 1 H, $J_{5,6'}$ 4.5 Hz, H-6′), 4.21 (s, 2 H, CH_2Ph), 4.38 (dd, 1 H, H-3), 4.51 (dt, 1 H, H-5), 4.64 and 4.80 (each ABq, 2 H, CH_2Ph × 2), 4.98 (d, 1 H, H-1), 5.55 (dd, 1 H, $J_{3,4}$ 5.5, $J_{4,5}$ 3.5 Hz, H-4); 7.70 (t, J 8.5 Hz, 2 H), 8.14 (m, 1 H) and 9.03 (d, 6 Hz, 2 H) (C_5H_5N).

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