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Convenient Synthesis of Pyruvate Acetals of Carbohydrates by Coupling of Trialkylsilylated Diols and Pyruvates

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Abstract: Hexopyranoside diols, mainly 4,6-diols with α-*gluco*, β-*gluco*, α-*galacto*, β-*galacto*, and α-*manno* configurations could be converted effectively (40 – 74% yields), to the corresponding pyruvate acetals by the coupling of the *O*-trialkylsilylated, namely, *O*-TBDMS and/or *O*-TMS diols, and ethyl pyruvate in the presence of TMSOTf at temperatures between -30 °C and +3 °C. In the case of the β-*manno* isomer, the anomerization of the β-glycoside to the α-glycoside as well as the ring contraction of the pyranoside to the furanoside predominated.

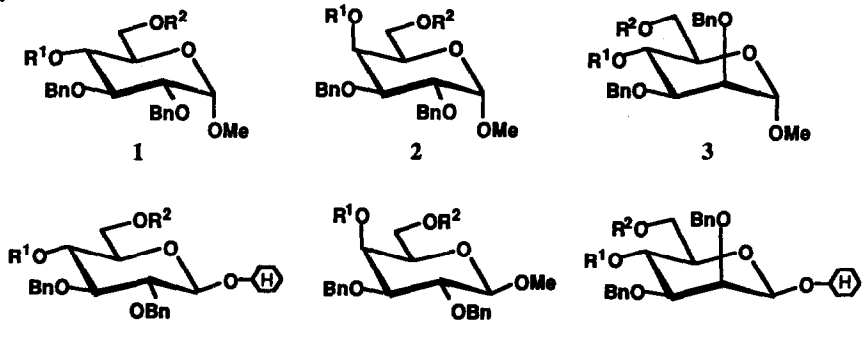
INTRODUCTION

Pyruvic acid acetal is a universal acidic component of bacterial polysaccharides and frequently found in extracellular polysaccharides[1] of Gram-negative bacteria, *i.e.*, capsular polysaccharides, and occasionally in cell wall lipopolysaccharides[1] and in lipooligosaccharides.[2] Pyruvic acid acetal of hexopyranosides has proven to be very useful tool for immunochemical studies of *Klebsiella* polysaccharides.[3] Acetalization of carbohydrate diol with pyruvate by direct condensation or acetal exchange in the presence of acid is supposed to have difficulty due to the adjacent electron-withdrawing carboxylate group and such unsuccessful attempts were indicated in the papers.[4,5] Therefore, several indirect methods for the acetalization were reported. The first pyruvate acetal was prepared by catalytic oxidation of 4,6-acetal of 1-hydroxy-2-propanone,[6] albeit in less than 10% yield. Recently ruthenium tetraoxide oxidation of furan-2-ylethylidene[7] and 1-(3,4-dimethoxyphenyl)ethylidene[8] intermediates which were obtained by transacetalization proved to give the desired pyruvate acetal in good yields. Further, transacetalization[9] of methyl pyruvate diphenyl dithioacetal, catalyzed by thiophilic reagents, was also reported. A new approach to this problem, namely, the pyruvate formation from the silylated carbohydrate diol and alkyl pyruvate in the presence of trimethylsilyl triflate (TMSOTf) has proven to be the method of choice by our[10] and other[4,11] groups, and has been employed in the synthesis of oligosaccharides containing the pyruvic acid acetal.[12] In this paper the detail and scope of this acetalization using trialkylsilylated diols reported preliminary for some years ago[10] are described.

RESULTS AND DISCUSSION

In order to study the scope of this acetalization reaction two different trialkylsilyl groups, namely, *tert*-butyldimethylsilyl and trimethylsilyl, were employed for the activation of hexopyranoside 4,6-diols. Six 2,3-di-*O*-benzylated hexopyranosides having α-*gluco* (**1a**), α-*galacto* (**2a**), α-*manno* (**3a**), β-*gluco* (**4a**), β-*galacto* (**5a**), and β-*manno* (**6a**) configurations were used as 4,6-diols. Among these, cyclohexyl β-D-glucopyranoside (**4a**) and cyclohexyl β-D-mannopyranoside (**6a**) were each synthesized from the corresponding α-glycosides, **1b** and **3a**, respectively, by a similar series of reactions: acetolysis, hydrobrominolysis and glycosylation with silver silicate as shown in the scheme (**1b**→**7**→**9**→**11**→**4a** and **3a**→**8**→**10**→**12**→**6a**).

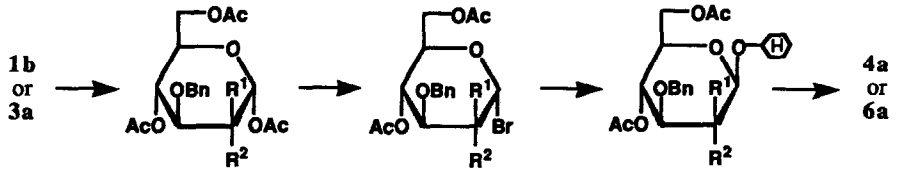
Treatment of the 4,6-diols of the *gluco* (**1a** and **4a**) and *manno* (**3a** and **6a**) configurations with *tert*-butylchlorodimethylsilane (TBDMSCl) and imidazole in *N*, *N*-dimethylformamide (DMF) at room temperature gave the corresponding 4,6-*O*-bis-TBDMS derivatives (**1c**, **3c**, **4c** and **6c**) each in over 80% yield. However, the same silylation of the 4,6-diols (**2a** and **5a**) of the *galacto* configuration afforded the 6-*O*-TBDMS derivatives (**2d** and **5d**), which were characterized as the 4-acetates (**2e** and **5e**) and further treated with chlorotrimethylsilane to provide the 6-*O*-TBDMS-4-*O*-TMS derivatives (**2f** and **5f**) in yields of 90% and 95%, respectively.



1 **2** **3**

4 **5** **6**

a $R^1 = R^2 = H$
b R^1, R^2 = PhCH <
c $R^1 = R^2$ = TBDMS
d R^1 = H, R^2 = TBDMS
e R^1 = Ac, R^2 = TBDMS
f R^1 = TMS, R^2 = TBDMS
g $R^1 = R^2$ = TMS

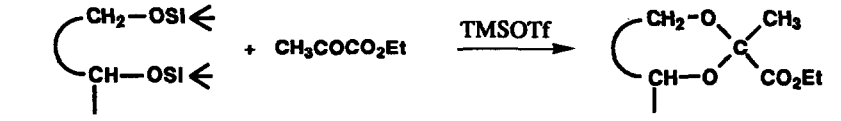


R^1 = H, R^2 = OBn **7** **9** **11**
R^1 = OBn, R^2 = H **8** **10** **12**

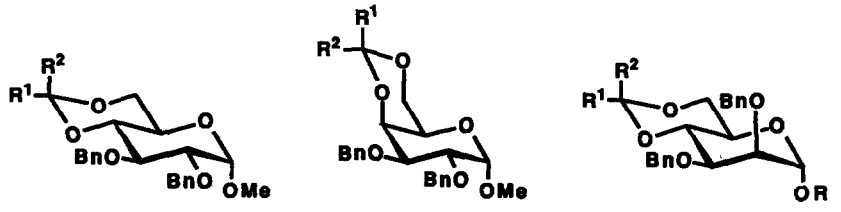
O-Trimethylsilylation with chlorotrimethylsilane in the same manner was not successful presumably due to hydrolysis of the 6-*O*-TMS ether during the extraction with water to remove imidazole. The 4,6-bis-*O*-trimethylsilylhexopyranosides (**1g**, **3g**, **4g**, and **6g**) could be obtained in yields of over 80% by treatment of the

diols (**1a**, **3a**, **4a**, and **6a**) with 1,1,1,3,3,3-hexamethyldisilazane in the presence of trifluoroacetic acid in dichloromethane. All these bis-*O*-trialkylsilyl derivatives were sufficiently stable to survive chromatographic purification on a short column of silica gel using ether.

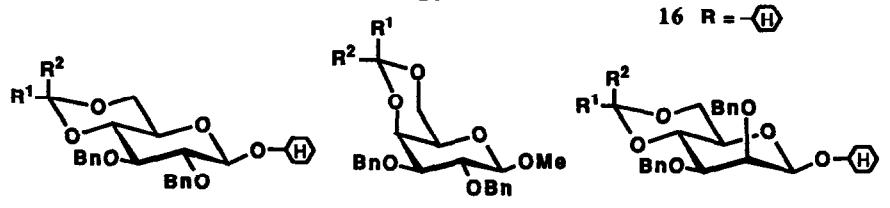
The acetalization reaction of pyruvate with trialkylsilylated diol in the presence of TMSOTf proved to be dependent on the type of silyl groups employed, the configuration of the hexopyranoside as well as the configuration of the anomeric position.



1c → **13S + 13R** **4c** → **17S + 17R**
2f → **14S + 14R** **5f** → **18S + 18R**
3c → **15S + 15R** **6c** → **16S + 16R + 20**

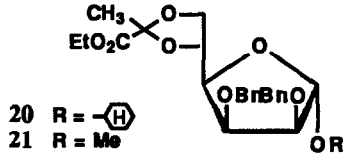


13 **14** **15** R = Me
16 R = -H



17 **18** **19**

S: $R^1 = CH_3$, $R^2 = CO_2Et$
R: $R^1 = CO_2Et$, $R^2 = CH_3$



20 R = -H
21 R = Me

Acetalization using the TBDMS ethers proved to be an efficient process. Namely, the reaction of a disilylated hexopyranoside (1 mmol) with ethyl pyruvate (2 mmol) in the presence of TMSOTf (0.4 mmol) in dichloromethane or ether at -5 – +3 °C for one – several days provided the 4,6-acetal in about 50 – 70% yield except the case of the β-*manno* isomer **6c** (Table 1). Although the reaction proceeded more slowly in ether than in dichloromethane, the total yield of the two stereoisomers remained relatively unchanged in the two solvents. The high stereoselectivities were observed in the cases of α-*manno* (in dichloromethane) and β-*galacto* isomers, where the corresponding (*S*)-acetals were formed in 100% and 35% diastereomer excess, respectively.

Table 1. Pyruvate[a] acetalation with TBDMS ethers[b] in the presence of TMSOTf.[c]

Entry	Disilyl ether		Solvent	Temp. (°C)	Time (d)	Product and Yield (%)			
						4,6-Acetal	*R*	*S*	Total
1	α-*gluco*	**1c**	CH_2Cl_2	-5	2	**13**	31	24	55
2	α-*gluco*	**1c**	Et_2O	-5	2	**13**	18	28	46
3	α-*galacto*	**2f**	CH_2Cl_2	-5	2	**14**	33	32	65
4	α-*galacto*	**2f**	Et_2O	-5	2	**14**	36	27	63
5	α-*manno*	**3c**	CH_2Cl_2	-5	3	**15**	0	60[d]	60
6	α-*manno*	**3c**	Et_2O	-5	5	**15**	28	34[d]	62
7	β-*gluco*	**4c**	CH_2Cl_2	-5	4	**17**	32	26	58
8	β-*gluco*	**4c**	Et_2O	+3	2	**17**	24	31	55
9	β-*galacto*	**5f**	CH_2Cl_2	-5	1	**18**	42	20	62
10	β-*galacto*	**5f**	Et_2O	-5	2	**18**	35	19	54
11	β-*manno*	**6c**	CH_2Cl_2	-5	3	**16**	<11[e]	11[d]	<22
12	β-*manno*	**6c**	Et_2O	-5	6	**16**	<10[e]	11[d]	<21

a: Ethyl pyruvate (2 equiv) was used. b: 4,6-Bis-*O*-TBDMS ethers were used in the cases of *gluco* and *manno* isomers, while 6-*O*-TBDMS-4-*O*-TMS ethers in the cases of *galacto* isomers. c: 40 Mol% (0.4 equiv) TMSOTf was used as catalyst. d: Estimated by ^{1}H-NMR signal and containing the 5,6-acetal **20** (3-6%). e: Contaminated with small amount of unidendified product.

These acetals having the axially oriented alkoxycarbonyl group were shown[11] to be the more thermodynamically stable based on the fact that the (*R*)-pyruvate acetal of the α-*gluco* isomer could be epimerized to the corresponding (*S*)-pyruvate acetal in the presence of TMSOTf at room temperature in dichloromethane. For all the reactions performed in ether the more thermodynamically stable isomers, *i.e.*, (*S*)-acetals for the *gluco* and *manno*[13] configurations, (*R*)-acetals for the *galacto* configurations, were found to slightly predominate. The reactions of *gluco* isomers in dichloromethane displayed a reversed selectivity resulting in acetals possessing the equatorially oriented ethoxycarbonyl group predominantly.[14]

The configuration of the acetal carbon atom of the 4,6-acetals **13**-**19** was determined by ^{1}H- and ^{13}C-NMR chemical shifts of the acetalic methyl groups (Table 2), by comparison with those previously reported.[15]

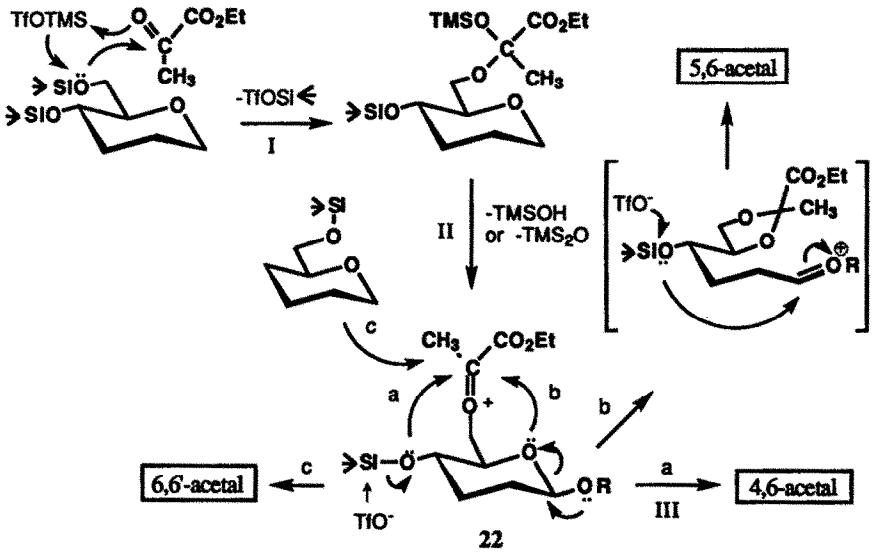
In the case of β-D-*manno* isomer **6c** the desired 4,6-acetal **19** could not be obtained. Instead, its α-anomer **16** and the 5,6-acetal **20** were formed both in low yields. The structure of **20** was suggested by the ^{13}C-NMR chemical shifts of the acetalic methyl (22.70 ppm) and quaternary carbon (105.59 ppm), which did not correspond to those of pyranosides. The furanoside structure was confirmed by the anomeric carbon chemical shift (104.23 ppm) and by the coupling constants of the ring protons measured at 500 MHz, indicating an equilibrium between the $^2T_3$ and $_2E$ conformers.

The formation of **20** can be explained by a competitive attack on the intermediary carbenium ion **22** by the ring oxygen (path b) as shown in the following scheme of the acetalization mechanism. The transition state resulting in the β-*manno*-4,6-acetal may be energetically elevated due to the axial substituent at C-2. In addition, the cleavage of C1-O ring bond may be accelerated due to the Δ2 effect.[16] Therefore, acetalization using the less sterically hindered TMS ether, which should also be a more reactive diol derivative, attracted our interest.

Table 2. ^{1}H- and ^{13}C-NMR chemical shifts of acetalic and adjacent methyl carbons in $CDCl_3$

Pyruvate acetal		$\delta^{1}H(C\text{-}CH_3)$		$\delta^{13}C(C\text{-}CH_3)$		$\delta^{13}C(C\text{-}CH_3)$	
		R	*S*	*R*	*S*	*R*	*S*
4,6-acetal							
α-Glc	**13**	1.67	1.55	17.88	25.46	97.68	98.98
α-Glc [a]		1.71	1.56	17.5	25.3		
α-Gal	**14**	1.64	1.56	26.00	20.37	98.76	97.19
α-Gal [a]		1.59	1.66	25.8	18.3		
α-Man	**15**	1.72	1.52	17.88	25.62	98.00	99.30
α-Man	**16**	1.72	1.57	17.82	25.57	97.89	99.25
β-Glc	**17**	1.68	1.55	17.82	25.46	97.51	98.92
β-Glc [a]		1.70	1.56	17.6	25.2		
β-Gal	**18**	1.65	1.58	25.90	23.35	98.76	96.97
β-Gal [a]		1.60	–	25.7	–		
β-Man	**19**	1.70	–	17.93	–	97.95	–
5,6-acetal							
α-Manf	**20**	1.57		22.70		105.59	

a: Reported data for methyl 4,6-*O*-(1-methoxycarbonylethylidene)-D-hexopyranosides.[15]



First of all, the difference of reactivity between the TBDMS and TMS ethers was examined using the α-*gluco* (**1 g**) and α-*manno* (**3 g**) isomers. The higher reactivity of these TMS ethers was displayed by the fact that the reaction proceeded effectively using less amount (0.2 equiv) of TMSOTf and at lower temperatures. While the 4,6-α-*manno*-acetal **1 5** was isolated in 46 – 64% yield together with the 5,6-acetal **2 1** (5 – 13%), the 4,6-α-*gluco*-acetal **1 3** was obtained in about 40% yield (Table 3).[17]

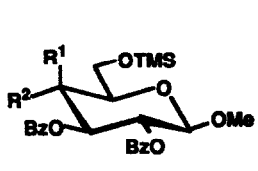
Table 3. Pyruvate[a] acetalation with TMS ethers in the presence of TMSOTf

Entry	Disilyl ether		Solvent	TMSOTf (mol %)	Temp. (°C)	Time (d)	Product and Yield (%)					
							4,6-Acetal				Other acetal	
								R	*S*	Total		
1	α-*gluco*	**1g**	Et_2O	20	-30→-20	3+6	**13**	18	22	40	**29a**	trace
2	α-*manno*	**3g**	CH_2Cl_2	40	-30	2	**15**	28	18[b]	46	**21**	9[b]
3	α-*manno*	**3g**	CH_2Cl_2	20	-20	2	**15**	25	21[b]	46	**21**	13[b]
4	α-*manno*	**3g**	Et_2O	40	-20→-5	4+1	**15**	29	24[b]	53	**21**	10[b]
5	α-*manno*	**3g**	Et_2O	20	-5	2	**15**	31	33[b]	64	**21**	5[b]
6	β-*gluco*	**4g**	CH_2Cl_2	40	-30→-20	1+1	**17**	12	12	24	20[c]	
7	β-*gluco*	**4g**	Et_2O	40	-20→-5	1+3	**17**	34	40	74	–	
8	β-*manno*	**6g**	CH_2Cl_2	40	-20	2	**16**	< 9[b,d]	10[b]	< 19	**20**	17[b]
9	β-*manno*	**6g**	Et_2O	40	-20	4	**19**	5	0	17[e]	**20**	21[b]

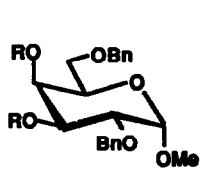
a: Ethyl pyruvate was (2 equiv) was used. b: Estimated by ^{1}H-NMR signal. c: A mixture of 6,6'-acetal (10%) and its unidentified regioisomer (10%). d: Comtaminated with small amount of unidentified product. e: The α-isomer **16** was also obtained (12%).

This acetalization procedure was successfully applied to the β-*gluco* isomer **4 g**, to give the 4,6-acetal **17** in 74% yield. In general, the desired 4,6-acetals were obtained in better yields in ether than in dichloromethane, indicating that the susceptibility of TMS ether to acid induces some side reactions described above and seems to be more easily controlled in ether. In contrast, the acetalization of **6 g** gave the desired 4,6-acetal **19** in low yield, while the 5,6-acetal **20** was obtained as the major product.[18]

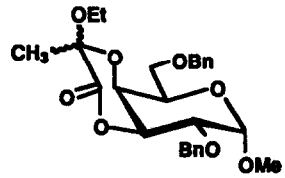
After our preliminary communication[10] extensive studies on synthesis of 4,6-pyruvate acetals using silylated hexopyranosides in the presence of TMSOTf were published.[4,11] In comparison with these reports the most characteristic feature of our acetalization conditions seems to be the lower reaction temperature. The first effect of low reaction temperature appears to suppress the undesired anomerization and ring contraction of β-glycopyranosides such as **23** and **24** to the furanosides, which were recently reported by Ziegler *et al.*[11] Under our conditions **4 g** and **5 f** did not give any rearranged products even in dichloromethane. On the contrary, the acetalization of **4 g** at room temperature gave, after 7 h, the expected 4,6-acetal **17** in 29% yield [27% (*S*)-isomer and 2% (*R*)-isomer] together with the α-anomer of **17S** (9%) and the 5,6-acetal, *i.e.*, D-*gluco* isomer of **20** (6%). In the case of **5 f**, after 9 h the anomerized 4,6-acetal **14R** was obtained predominantly in 10% yield together with very small amount of the desired 4,6-acetal **18** and the corresponding 5,6-acetal (10%). The second effect of the low reaction temperature is on the stereoselectivity of the 4,6-acetal formation. While at ambient temperature[4,11] the thermodynamically favored isomer is obtained predominantly, at the lower temperature (-30°C—5°C) it is possible to get the kinetically favored isomers as the major product depending on reaction conditions. The third effect is an induction time, which was suggested by the observation that the reaction started all at once after a day or a few days and is complete within another day or two. Among the three steps involved in this acetalization (I~III in the scheme of acetal formation) the late-determining step is thought to be the second one (II), the formation of the carbenium ion. As previously reported glycosylidenation, the trimethylsilyloxy group is considered at first to be eliminated as 1,1,1,3,3,3-hexamethyldisiloxane by the attack of TMSOTf. It was found very recently that addition of small amount of trifluoromethanesulfonic acid (TfOH) accelerated the acetalization.[19]



23 R^1 = H, R^2 = OTMS
24 R^1 = OTMS, R^2 = H



25 R = TMS



27

26 2R = CH_3 CO_2Et

In addition to the 4,6-acetal, the pyruvate acetals of vicinal diols have been found in nature. Although we reported the preparation of 3,4-pyruvate acetal (**26**) of α-D-galactopyranoside in the preliminary communication[10,20], the reported yield was incorrect and actually very low, giving also almost the same amount of an unexpected acetal[21] **27**. Namely, methyl 2,6-di-*O*-benzyl-3,4-bis-*O*-(trimethylsilyl)-α-D-galactopyranoside (**25**) was coupled with ethyl pyruvate in the presence of TMSOTf and TfOH in ether to give **26** and **27** in 13 % and 18 % yields, respectively. More efficient preparation of **26** could be carried out by a modified method using 1-acetoxy-2-propanone and will be reported elsewhere.

The characteristics of this pyruvate acetalization are summarized as follows. (1) Both TBDMS and TMS ethers of hexopyranoside 4,6-diols having α-*gluco*, β-*gluco*, α-*galacto*, β-*galacto*, and α-*manno* configurations can be acetalated to give the corresponding 4,6-acetals in about 50 – 70% yield. (2) In the cases of TMS ethers the acetalization is recommended to be carried out in ether in the presence of lower amount (20 mol%) of TMSOTf in order to prevent the side reactions. (3) The acetalization reaction in ether gives predominantly a pyruvate acetal having an equatorially oriented methyl group, that is, (*S*)-acetal for *gluco* and *manno* isomers and (*R*)-acetal for *galacto* one. However, pyruvate acetal having an axially oriented methyl group can be obtained as major product depending on the reaction conditions. (4) The acetalization of the β-*manno* isomer gave the 5,6-acetal predominantly. In conclusion, the pyruvate acetalization of trialkylsilylated carbohydrate diols in the presence of TMSOTf proved to be one of practical method, which is applicable widely to various types of naturally occurring pyruvic acid acetals.

EXPERIMENTAL

General methods. Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Solutions were evaporated under diminished pressure at a bath temperature not exceeding 50 °C. Optical rotations were measured in a 0.5-dm tube with a JASCO DIP-4 polarimeter for solutions in chloroform, unless stated otherwise. IR spectra were recorded with a Hitachi model EPI-G2 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded with JEOL JNM-PS100, JNM-FX90Q, EX-270, and GX-500 spectrometers for solutions in chloroform-d containing tetramethylsilane as a internal reference.

Cyclohexyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-glucopyranoside (11). To a stirred solution of 1,4,6-tri-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranose[22] (**7**, 743 mg, 1.52 mmol) in dry dichloromethane (0.5 ml) was added a solution 25 % hydrogen bromide in acetic acid (3.3 ml) at 0 °C. The mixture was diluted with

chloroform after the disappearance of **7**, washed twice with cold water, cold aqueous sodium hydrogencarbonate, and cold water again. The organic layer was dried over anhydrous sodium sulfate and concentrated to give 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranosyl bromide (**9**, 770 mg), whose structure was confirmed by ^{1}H-NMR data: δ 7.40-7.21 (m, 10H, 2Ph), 6.32 (d, $J_{1,2}$ 4.0 Hz, H-1), 5.08 (t, $J_{3,4} = J_{4,5}$ 9.6 Hz, H-4), 4.89, 4.64 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.70 (s, 2H, $PhCH_2$), 4.52-3.86 (m, 4H), 3.57 (dd, $J_{2,3}$ 9.8 Hz, H-2), 2.05, 1.93 (each s, each 3H, OAc).

To a solution of freshly distilled cyclohexanol (173 mg, 1.73 mmol) in dry toluene (2 ml) was added silver silicate (765 mg) with stirring at -15 °C. After 15 min, to the stirred mixture was added dropwise a solution of **9** prepared from **7** (743 mg, 1.52 mmol) in dry toluene (3.5 ml) at the same temperature for 12 min. After 30 min the mixture was brought to room temperature, diluted with chloroform and insoluble materials were filtered off. The organic layer was dried and evaporated, and the residue was purified by chromatography on silica gel with hexane-ethyl acetate (6:1) to give **11** (394 mg, 65 % from **7**) as a white crystal; mp 94.0-95.0 °C; $[\alpha]_D$ -21.8° (c 1.1, $CHCl_3$); IR ν_{max} (NaCl) 1735 cm^{-1} (ester); ^{1}H-NMR δ 7.46-7.26 (m, 10H, 2Ph), 5.07 (t, $J_{3,4} = J_{4,5}$ 8.0 Hz, H-4), 4.90, 4.67 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.90, 4.67 (ABq, *J* 10.0 Hz, $PhCH_2$), 4.64-4.56 (m, 1H, H-1), 4.33 (dd, $J_{5,6a}$ 5.0 Hz, J_{gem} 12.0 Hz, H-6a), 4.12 (dd, $J_{5,6b}$ 3.0 Hz, H-6b), 3.90-3.46 (m, 4H), 2.08, 1.92 (each s, each 3H, 2OAc), 2.18-1.14 (m, 10H, $5CH_2$); ^{13}C-NMR δ 170.76, 169.57 (C=O), 138.36, 128.34-127.64 (2Ph), 102.01 (d, $J_{C\text{-}H}$ 158.7 Hz, C-1), 81.97, 81.80, 78.17, 75.09, 74.98, 71.73, 70.16, 62.73, 33.64, 31.96, 25.62, 23.95, 20.75. Anal. Calcd. for $C_{30}H_{38}O_8$: C, 68.42; H, 7.27. Found: C, 68.77; H, 7.25.

Cyclohexyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-mannopyranoside (12). Compound **12** was prepared from 1,4,6-tri-*O*-acetyl-2,3-di-*O*-benzyl-α-D-mannopyranose[23] (**8**) in the same manner as described for **11**. Compound **8** prepared by acetolysis of methyl 2,3-di-*O*-benzyl-α-D-mannopyranoside[24] (**3a**) was converted to the corresponding α-bromide[25] **10**, whose glycosylation using silver silicate gave the β-glucoside **12**. The crude **12** was recrystallized from hexane-ethyl acetate to give white crystals (70 % from **8**); mp 87.0-89.0 °C; $[\alpha]_D$ -81.9° (c 1.1, $CHCl_3$); IR ν_{max} (NaCl) 1728 cm^{-1} (ester); ^{1}H-NMR δ 7.57-7.14 (m, 10 H, 2Ph), 5.33 (t, $J_{3,4} = J_{4,5}$ 8.0 Hz, H-4), 5.00, 4.84 (ABq, *J* 12.4 Hz, $PhCH_2$), 4.51 (s, 1H, H-1), 4.48, 4.29 (ABq, *J* 12.4 Hz, $PhCH_2$), 4.29-4.10 (m, 1H, H-6a), 3.90-3.34 (m, 5H), 2.05, 2.01 (each s, each 3H, 2OAc), 2.18-1.10 (m, 10H, $5CH_2$). Anal. Calcd. for $C_{30}H_{38}O_8$: C, 68.42; H, 7.27. Found: C, 68.07; H, 7.37.

Cyclohexyl 2,3-di-*O*-benzyl-β-D-glucopyranoside (4a). To a solution of **11** (382 mg, 0.72 mmol) in 70 % aqueous methanol (20 ml) was added triethylamine (2.0 ml) with stirring. The mixture was allowed to stand overnight and concentrated. The residue was purified by chromatography on silica gel with hexane-ethyl acetate (1:1) to give **4a** (296 mg, 93 %) as a white crystal; mp 112.0-113.0 °C; $[\alpha]_D$ -31.5° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 3550-2950 cm^{-1} (OH); ^{1}H-NMR δ 7.39-7.23 (m, 10H, 2Ph), 4.97, 4.77 (ABq, *J* 11.0 Hz, $PhCH_2$), 4.92, 4.77 (ABq, *J* 11.0 Hz, $PhCH_2$), 4.60-4.45 (br, 1H, H-1), 3.91-3.17 (m, 7H), 2.98-2.31 (br, 2H, OH-4,6), 2.09-1.11 (m, 10H, $5CH_2$); ^{13}C-NMR δ 138.63, 138.47, 128.50-127.69 (2Ph), 101.96 (d, $J_{C\text{-}H}$ 158.7 Hz, C-1), 84.13, 81.86, 77.90, 75.14, 74.92, 74.71, 70.54, 62.63 (C-6), 33.80, 31.96, 25.57, 24.05, 23.95. Anal. Calcd. for $C_{26}H_{34}O_6$: C, 70.56; H 7.74. Found: C, 70.16; H, 7.34.

Cyclohexyl 2,3-di-*O*-benzyl-β-D-mannopyranoside (6a). Compound **6a** was prepared from **12** in the same manner as described for **4a**. The crude **6a** was recrystallized from ethyl acetate-ether to give white crystals (87%); mp 103.5-104.5 °C; $[\alpha]_D$ -125.0° (c 1.1, $CHCl_3$); IR ν_{max} (NaCl) 3600-3100 cm^{-1} (OH); ^{1}H-NMR δ 7.53-7.25 (m, 10H, 2Ph), 5.04, 4.85 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.64 (d, $J_{1,2}$ 1.8 Hz, H-1), 4.54, 4.32 (ABq, *J* 11.0 Hz, $PhCH_2$), 4.13-3.32 (m, 7H), 2.82-2.31 (br, 2H, OH-4,6), 2.08-1.07 (m, 10H, $5CH_2$); ^{13}C-NMR δ 138.52, 137.77, 128.45-127.53 (2Ph), 99.52 (d, $J_{C\text{-}H}$ 156.3 Hz, C-1), 81.70, 77.25, 76.71, 75.90, 74.06, 71.13, 67.23, 62.73 (C-6), 33.43, 31.53, 25.62, 23.73, 23.62. Anal. Calcd. for $C_{26}H_{34}O_6$: C, 70.56; H, 7.74. Found: C, 70.69; H, 7.93.

Bis-*O*-*tert*-butyldimethylsilylation of 1a, 3a, 4a, and 6a. To a dried diols (**1a**,[22] **3a**, **4a**, or **6a**, 1.0 mmol) was added a solution of *tert*-butylchlorodimethylsilane (3.0 mmol) and imidazole (3.1 mmol) in dry N,N-dimethylformamide (DMF, 2.3 ml) and allowed to stand for one day. The mixture was diluted with ether, washed with water, and dried over anhydrous sodium sulfate. The organic layer was concentrated and the residue was purified on a short column of silica gel with ether to give silylated products **1c**, **3c**, **4c**, and **6c**, respectively.

Methyl 2,3-di-*O*-benzyl-4,6-bis-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (1c): Yield quantitative; $[\alpha]_D$ -50.1° (c 2.0, $CHCl_3$); IR ν_{max} (NaCl) 1255 cm^{-1} (SiMe); ^{1}H-NMR δ 7.32-7.12 (m, 10H, 2Ph), 5.02, 4.69 (ABq, *J* 11.0 Hz, $PhCH_2$), 4.67, 4.52 (ABq, *J* 11.5 Hz, $PhCH_2$), 4.64 (d, $J_{1,2}$ 3.0 Hz, H-1), 3.91-3.26 (m, 6H), 3.39 (s, 3H, OMe), 0.90 (s, 18H, $2CMe_3$), 0.06, 0.04 (each s, each 6H, $2SiMe_2$); ^{13}C-NMR δ 139.21, 138.08, 128.34-127.01 (2Ph), 97.45 (C-1), 81.67, 80.74, 75.02, 73.12, 72.74, 70.75, 62.59, 54.75 (OMe), 25.95, 25.86 ($2CMe_3$), 18.35, 18.06 ($2CMe_3$), -3.83, -4.78, -5.07, -5.37 ($2SiMe_2$). Anal. Calcd. for $C_{33}H_{54}O_6Si_2$: C, 65.74; H, 9.03. Found: C, 65.59; H, 9.09.

Methyl 2,3-di-*O*-benzyl-4,6-bis-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside (3c): Yield 80%; $[\alpha]_D$ -28.1° (c 1.4, $CHCl_3$); IR ν_{max} (NaCl) 1253 cm^{-1} (SiMe); ^{1}H-NMR δ 7.39-7.15 (m, 10H, 2Ph), 4.69 (d, $J_{1,2}$ 2.0 Hz, H-1), 4.58, 4.52 (each s, 4H, $2PhCH_2$), 4.07-3.37 (m, 6H), 3.31 (s, 3H, OMe), 0.88, 0.86 (each s, each 9H, $2CMe_3$), 0.07 (s, 12H, $2SiMe_2$); ^{13}C-NMR δ 138.62, 128.19-127.26 (2Ph), 98.87 (C-1), 80.50, 74.61, 72.63, 71.45, 67.94, 63.07, 54.43 (OMe), 25.98, 25.91 ($2CMe_3$), 18.38, 18.19 ($2CMe_3$),-3.90, -4.82, -5.07, -5.25 ($2SiMe_2$). Anal. Calcd. for $C_{33}H_{54}O_6Si_2$: C, 65.74; H, 9.03. Found: C, 65.37; H, 8.97.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-bis-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranoside (4c): Yield quantitative; $[\alpha]_D$ +23.5° (c 1.7, $CHCl_3$); IR ν_{max} (NaCl) 1254 cm^{-1} (SiMe); ^{1}H-NMR δ 7.34-7.14 (m, 10H, 2Ph), 4.99, 4.65 (ABq, *J* 11.8 Hz, $PhCH_2$), 4.97, 4.56 (ABq, *J* 10.4 Hz, $PhCH_2$), 4.74-4.56 (m, 1H, H-1), 3.99-3.11 (m, 7H), 2.12-1.12 (m, 10H, $5CH_2$), 0.92, 0.86 (each s, each 9H, $2CMe_3$), 0.10, 0.08, 0.04, 0.01 (each s, each 3H, $2SiMe_2$); ^{13}C-NMR δ 139.15, 138.66, 128.26-127.12 (2Ph), 101.88 (d, $J_{C\text{-}H}$ 153.8 Hz, C-1), 84.81, 82.92, 77.39, 74.85, 74.52, 70.78, 62.77, 33.84, 31.99, 24.09, 25.93, 25.71 ($2CMe_3$),

18.40, 18.13 (2*C*Me$_3$), -3.81,-4.79 (2SiMe$_2$). Anal. Calcd. for $C_{38}H_{62}O_6Si_2$: C, 68.01; H, 9.31. Found: C, 68.05; H, 9.20.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-bis-*O*-(*tert*-butyldimethylsilyl)-β-D-mannopyranoside (6c): Yield quantitative; $[\alpha]_D$ -50.6° (c 1.7, $CHCl_3$); IR ν_{max} (NaCl) 1254 cm^{-1} (SiMe); ^{1}H-NMR δ 7.48-7.14 (m, 10H, 2Ph), 4.95, 4.70 (ABq, *J* 11.6 Hz, PhCH$_2$), 4.50, 4.32 (ABq, *J* 11.2 Hz, PhCH$_2$), 4.50 (s, 1H, H-1), 4.02-3.08 (m, 7H), 2.00-1.18 (m, 10H, 5CH$_2$), 0.90, 0.86 (each s, each 9H, 2CMe$_3$), 0.06, 0.01 (each s, each 6H, 2SiMe$_2$); ^{13}C-NMR δ 139.37, 128.09-126.99 (2Ph), 99.39 (C-1), 82.41, 78.44, 76.19, 74.32, 73.64, 70.66, 68.12, 63.07, 33.52, 25.77, 23.83, 18.17, 25.97, 25.82 (2*C*Me$_3$), 18.17 (2*C*Me$_3$) -3.79, -4.92, -5.23, -5.32 (2SiMe$_2$). Anal. Calcd. for $C_{38}H_{62}O_6Si_2$: C, 68.01; H, 9.31. Found: C, 67.93; H,9.25.

Bis-*O*-trimethylsilylation of 1a, 3a, 4a, and 6a. To a stirred solution of **1a**, **3a**, **4a**, and **6a** (1.0 mmol) and 1,1,1,3,3,3-hexamethyldisilazane (2.0 mmol) in dry dichloromethane (3.2 ml) was added 2 drops of trifluoroacetic acid. After 4 – 23 h, the mixture was concentrated and the residue was purified on a column of silica gel with hexane-ethyl acetate (10 : 1 or 15 : 1) to give **1g**, **3g**, **4g**, and **6g**, respectively.

Methyl 2,3-di-*O*-benzyl-4,6-bis-*O*-trimethylsilyl-α-D-glucopyranoside (1g): Yield 84%; mp 42.5-45.0°C (petroleum ether); $[\alpha]_D$ +45.1° (c 1.7, $CHCl_3$); ^{1}H-NMR δ 7.28-7.23 (m, 10H, 2Ph), 5.00, 4.72 (ABq, *J* 11.2 Hz, PhCH$_2$), 4.70, 4.54 (ABq, *J* 12.0 Hz, PhCH$_2$), 4.58 (d, $J_{1,2}$ 4.0 Hz, H-1), 3.90-3.30 (m, 6H), 3.36 (s, 3H, OMe), 0.10 (s, 18H, 2SiMe$_3$). Anal. Calcd. for $C_{27}H_{42}O_6Si_2$: C, 62.51; H, 8.16. Found: C, 62.45; H, 8.43.

Methyl 2,3-di-*O*-benzyl-4,6-bis-*O*-trimethylsilyl-α-D-mannopyranoside (3g): Yield 92%; $[\alpha]_D$ +39.3° (c 1.4, $CHCl_3$); IR ν_{max} (NaCl) 1245 cm^{-1} (SiMe); ^{1}H-NMR δ 7.28-7.04 (m, 10H, 2Ph), 4.59 (d, $J_{1,2}$ 2.0 Hz, H-1), 4.58, 4.44 (ABq, *J* 12.0 Hz, PhCH$_2$), 4.45 (s, 2H, PhCH$_2$), 3.97-3.24 (m, 6H), 3.20 (s, 3H, OMe), 0.04, 0.01 (each s, each 9H, 2SiMe$_3$); ^{13}C-NMR δ 138.85, 128.34-127.47 (2Ph), 99.19 (C-1), 80.56, 75.03, 74.60, 72.81, 72.00, 68.37, 62.84, 54.61 (OMe), 0.76 (2SiMe$_3$). Anal. Calcd. for $C_{27}H_{42}O_6Si_2$: C, 62.43; H, 8.15. Found: C, 62.29; H, 8.24.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-bis-*O*-trimethylsilyl-β-D-glucopyranoside (4g): Yield 88%; mp 64.5-65.5°C; $[\alpha]_D$ +22.2° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1250 cm^{-1} (SiMe); ^{1}H-NMR δ 7.39-7.21 (m, 10H, 2Ph), 4.98, 4.73 (ABq, *J* 11.2 Hz, PhCH$_2$), 4.97, 4.62 (ABq, *J* 11.2 Hz, PhCH$_2$), 4.57-4.44 (m, 1H, H-1), 3.95-3.11 (m, 7H), 2.13-1.11 (m, 10H, 5CH$_2$), 0.12, 0.09 (each s, each 9H, 2SiMe$_3$); ^{13}C-NMR δ 139.34, 138.90, 128.50-127.36 (2Ph), 102.28 (C-1), 85.11, 82.89, 77.69, 76.87, 75.52, 74.98, 71.13, 62.35 (C-6), 34.08, 32.29, 25.95, 24.32, 0.76 (2SiMe$_3$). Anal. Calcd. for $C_{32}H_{50}O_6Si_2$: C, 65.49; H, 8.59. Found: C, 65.35; H, 8.56.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-bis-*O*-trimethylsilyl-β-D-mannopyranoside (6g): Yield 86%; mp 56.5-58.0°C; $[\alpha]_D$ -58.8° (c 1.1, $CHCl_3$); IR ν_{max} (NaCl) 1240 cm^{-1} (SiMe); ^{1}H-NMR δ 7.52-7.12 (m, 10H,

2Ph), 4.97, 4.73 (ABq, *J* 12.8 Hz, $PhCH_2$), 4.51, 4.37 (ABq, *J* 11.8 Hz, $PhCH_2$), 4.48 (s, 1H, H-1), 4.04-3.08 (m, 7H), 2.07-1.08 (m, 10H, $5CH_2$), 0.14, 0.11 (each s, each 9H, $2SiMe_3$); ^{13}C-NMR δ 139.66, 138.63, 128.34-127.20 (2Ph), 99.68 (C-1), 82.67, 78.44, 76.28, 75.14, 74.00, 71.35, 68.58, 63.06, 33.70, 31.80, 26.00, 24.05, 23.95, 0.81 ($2SiMe_3$). Anal. Calcd. for $C_{32}H_{50}O_6Si_2$: C, 65.49; H, 8.59. Found: C, 65.05; H, 8.29.

Methyl 2,3-di-*O*-benzyl-6-*O*-(tert-butyldimethylsilyl)-4-*O*-trimethylsilyl-α-D-galactopyranoside (2f): To a solution of *tert*-butylchlorodimethylsilane (287 mg, 1.91 mmol) and imidazole (134 mg, 1.97 mmol) in dry DMF (1.75 ml) was added methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside[26] (**2a**, 474 mg, 1.27 mmol). The starting material **2a** disappeared after 1 h to give a mono-TBDMS derivative **2d** exclusively and then to the mixture was added a solution of chlorotrimethylsilane (0.24 ml, 1.91 mmol) and imidazole (134 mg, 1.96 mmol) in dry DMF (1.75 ml). After 5 min, the mixture was concentrated and the residue was purified on a column of silica gel with hexane-ethyl acetate to give **2f** (639 mg, 90 %) as a syrup; $[\alpha]_D$ +29.7° (c 1.8, $CHCl_3$); IR ν_{max} (NaCl) 1252 cm^{-1} (SiMe); ^{1}H-NMR δ 7.44-7.24 (m, 10H, 2Ph), 4.85, 4.70 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.81, 4.64 (ABq, *J* 12.4 Hz, $PhCH_2$), 4.70 (d, $J_{1,2}$ 3.8 Hz, H-1), 4.16-3.60 (m, 6H), 3.38 (s, 3H, OMe), 0.91 (s, 9H, CMe_3), 0.09 (s, 15H, 5SiMe). Anal. Calcd. for $C_{30}H_{48}O_6Si_2$: C, 64.24; H, 8.63. Found: C, 64.17; H, 8.66.

The mono-TBDMS derivative **2d** was characterized as its 4-acetate **2e**: ^{1}H-NMR δ 7.42-7.08 (m, 10H, 2Ph), 5.59 (d, 1H, *J* 2.6 Hz, H-4), 4.84, 4.65 (ABq, *J* 11.2 Hz, $PhCH_2$), 4.78, 4.56 (ABq, *J* 11.1 Hz, $PhCH_2$), 4.68 (d, $J_{1,2}$ 4.0 Hz, H-1), 4.00-3.58 (m, 5H), 3.39 (s, 3H, OMe), 2.10 (s, 3H, OAc), 0.88 (s, 9H, CMe_3), 0.04 (s, 6H, $SiMe_2$).

Methyl 2,3-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-4-*O*-trimethylsilyl-β-D-galactopyranoside (5f): To a solution of *tert*-butylchlorodimethylsilane (0.73 g, 4.84 mmol) and imidazole (336 mg, 4.94 mmol) in dry DMF (5.0 ml) was added methyl 2,3-di-*O*-benzyl-β-D-galactopyranoside[27] (**5a**, 598 mg, 1.60 mmol). The starting material (**5a**) disappeared after 50 min to give a mono-TBDMS derivative **5d** and then to this mixture was added a solution of chlorotrimethylsilane (0.30 ml, 2.4 mmol) and imidazole (168 mg, 2.47 mmol) in dry DMF (2.5 ml). After 10 min, the mixture was concentrated and the residue was purified on a column of silica gel with hexane-ethyl acetate to give **5f** (885 mg, 95 %) as a syrup; $[\alpha]_D$ +8.1° (c 0.8, $CHCl_3$); IR ν_{max} (NaCl) 1252 cm^{-1} (SiMe); ^{1}H-NMR δ 7.41-7.21 (m, 10H, 2Ph), 4.75, 4.69 (ABq, *J* 11.5 Hz, $PhCH_2$), 4.71, 4.23 (s, 2H, $PhCH_2$), 4.23 (d, $J_{1,2}$ 7.6 Hz, H-1), 4.11-3.23 (m, 6H), 3.55 (s, 3H, OMe), 0.90 (s, 9H, CMe_3), 0.09 (s, 15H, $SiMe_2$, $SiMe_3$). Anal. Calcd. for $C_{30}H_{48}O_6Si_2$: C, 64.24; H, 8.63. Found: C, 63.90; H, 8.46.

The mono-TBDMS derivative **5d** was characterized as its 4-acetate **5e**: ^{1}H-NMR δ 7.40-7.10 (m, 10H, 2Ph), 5.54 (br d, 1H, H-4), 4.86, 4.70 (ABq, *J* 10.5 Hz, $PhCH_2$), 4.79, 4.51 (ABq, *J* 11.5 Hz, $PhCH_2$), 4.90-3.60 (m, 6H), 3.58 (s, 3H, OMe), 2.13 (s, 3H, OAc), 0.91 (s, 9H, CMe_3), 0.06 (s, 6H, $SiMe_2$).

General method of pyruvate acetalization. Thoroughly dried bis-silylated diol (1.0 mmol) and ethyl or benzyl pyruvate (2.0 mmol) were dissolved in dichloromethane or diethyl ether (1 ml). After the addition of TMSOTf (0.4 mmol) in the solvent (0.1 ml) at -20°C this solution was kept at the specified temperature for

several days as shown in Tables 1 and 3 to complete the reaction. Pyridine (1 ml) was added to this solution. The mixture was poured into cold aqueous sodium hydrogencarbonate (15 ml) and extracted with chloroform (15 ml x 3). The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was subjected to column chromatography on silica gel with hexane-ethyl acetate to give pyruvate acetal. Reaction conditions and yields are given in the tables.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-{(*R*)- and (*S*)-(1-ethoxycarbonyl)ethylidene}-α-D-glucopyranoside (13R and 13S). On chromatographic separation of two isomers hexane-ethyl acetate mixtures of the following ratios were used as eluant: **13S** (7:1); **13R** (5:1 to 4:1).

13R: mp 99.0-100.0 °C; $[\alpha]_D$ -9.6° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1720 cm^{-1} (ester); ^{1}H-NMR δ 7.49-7.25 (m, 10H, 2Ph), 4.90, 4.75 (ABq, *J* 11.0 Hz, $PhCH_2$), 4.84, 4.75 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.53 (d, $J_{1,2}$ 4.0 Hz, H-1), 4.23 (q, 2H, *J* 7.0 Hz, CH_2Me), 4.11-3.50 (m, 5H), 3.50 (dd, $J_{2,3}$ 9.0 Hz, H-2), 3.35 (s, 3H, OMe), 1.67 (s, 3H, CMe), 1.31 (t, 3H, *J* 7.0 Hz, CH_2Me); ^{13}C-NMR δ 168.43 (C=O), 138.25, 128.45-127.58 (2Ph), 99.41 (C-1), 97.68 (acetal), 78.93, 78.50, 74.81, 62.73 (C-2,3,4,5), 75.14, 73.84 (2PhCH_2), 63.28, 61.87 (C-6,CH_2Me), 55.37 (OMe), 17.88 (C*Me*), 14.09 (CH_2*Me*). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.02; H, 6.71.

13S: $[\alpha]_D$ +44.8° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1736 cm^{-1} (ester); ^{1}H-NMR δ 7.60-7.17 (m, 10H, 2Ph), 4.96, 4.77 (ABq, *J* 11.0 Hz, $PhCH_2$), 4.81, 4.61 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.50 (d, $J_{1,2}$ 3.5 Hz, H-1), 4.25 (q, 2H, *J* 7.5 Hz, CH_2Me), 4.05-3.28 (m, 6H), 3.34 (s, 3H, OMe), 1.55 (s, 3H, CMe), 1.30 (t, 3H, CH_2*Me*); ^{13}C-NMR δ 169.73 (C=O), 139.07, 138.31, 128.34-127.36 (2Ph), 99.25 (C-1), 98.98 (acetal), 78.82, 78.55, 78.28 (C-2,3,4,5), 74.60, 73.84 (2PhCH_2), 65.50, 61.70 (C-6, CH_2Me), 55.37 (OMe), 25.46 (C*Me*), 14.19 (CH_2*Me*). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.04; H, 6.90.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-{(*R*)- and (*S*)-(1-ethoxycarbonyl)ethylidene}-α-D-galactopyranoside (14R and 14S). On chromatographic separation of two isomers hexane-ethyl acetate mixtures of the following ratios were used as eluant: **14R** (3:1); **14S** (2:1).

14R: $[\alpha]_D$ +48.4° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1720 cm^{-1} (ester); ^{1}H-NMR δ 7.50-7.10 (m, 10H, 2Ph), 4.91, 4.69 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.87, 4.66 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.71 (d, $J_{1,2}$ 3.8 Hz, H-1), 4.30 (q, 2H, *J* 7.0 Hz, CH_2Me), 4.23 (m, 1H, H-6a), 4.12-3.79 (m, 4H), 3.48 (m, H-5), 3.35 (s, 3H, OMe), 1.64 (s, 3H, CMe), 1.36 (t, 3H, CH_2*Me*); ^{13}C-NMR δ 170.00 (C=0), 138.69, 138.42, 128.34-127.58 (2Ph), 99.52 (C-1), 98.76 (acetal), 75.19, 75.03, 69.61, 61.49 (C-2,3,4,5), 73.95, 71.13 (2PhCH_2), 65.44, 61.70 (C-6, CH_2Me), 55.53 (OMe), 26.00 (C*Me*), 14.30 (CH_2*Me*). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.40; H, 7.03.

14S: $[\alpha]_D$ +70.4° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1720 cm^{-1} (ester); ^{1}H-NMR δ 7.40-7.00 (m, 10H, 2Ph), 4.88, 4.65 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.82, 4.64 (ABq, *J* 12.5 Hz, $PhCH_2$), 4.60 (d, $J_{1,2}$ 3.0 Hz, H-1), 4.25-3.76 (m, 7H), 3.63 (m, H-5), 3.31 (s, 3H, OMe), 1.56 (s, 3H, CMe), 1.21 (t, 3H, *J* 7.0 Hz, CH_2*Me*); ^{13}C-NMR δ 168.97 (C=O), 138.69, 128.34-127.64 (2Ph), 99.25 (C-1), 97.19 (acetal), 75.74, 75.25, 67.66, 62.84 (C-2,3,4,5), 73.84, 72.38 (2PhCH_2), 63.98, 61.54 (C-6,CH_2Me), 55.53 (OMe), 20.37 (C*Me*), 14.03 (CH_2*Me*). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.02; H, 6.95.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-{(*R*)- and (*S*)-(1-ethoxycarbonyl)ethylidene}-α-D-mannopyranoside (15R and 15S). On chromatographic separation of two isomers hexane-ethyl acetate mixtures of the following ratios were used as eluant: **15S** (8:1 to 7:1); **15R** (6:1 to 5:1).

15R: $[\alpha]_D$ +44.7° (c 1.1, $CHCl_3$); IR ν_{max} (NaCl) 1730 cm^{-1} (ester); ^{1}H-NMR δ 7.48-7.17 (m, 10H, 2Ph), 4.88-4.58 (m, 5H, H-1, 2PhCH_2), 4.42-3.52 (m, 8H), 3.26 (s, 3H, OMe), 1.72 (s, 3H, CMe), 1.32 (t, 3H, *J* 7.2 Hz, CH_2*Me*); ^{13}C-NMR δ 168.59 (C=O), 138.96, 138.20, 128.39-127.42 (2Ph), 100.66 (C-1), 98.00 (acetal), 78.50, 76.28, 72.05, 64.36 (C-2,3,4,5), 73.68, 73.08 (2PhCH_2), 63.06, 61.81 (C-6, CH_2Me), 54.77 (OMe), 17.88 (C*Me*), 14.14 (CH$_2$*Me*). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.11; H, 6.92.

15S: $[\alpha]_D$ +70.6° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1735 cm^{-1} (ester); ^{1}H-NMR δ 7.44-7.20 (m, 10H, 2Ph), 4.96-4.66 (m, 5H, H-1, 2PhCH_2), 4.44-3.50 (m, 8H), 3.26 (s, 3H, OMe), 1.52 (s, 3H, CMe), 1.30 (t, 3H, *J* 7.0 Hz, CH_2*Me*); ^{13}C-NMR δ 169.95 (C=O), 139.23, 138.42, 128.18-127.31 (2Ph), 100.82 (C-1), 99.30 (acetal), 76.28, 75.90, 75.68, 63.60 (C-2,3,4,5), 73.73, 72.97 (2PhCH_2), 65.39, 61.70 (C-6, CH_2Me), 54.82 (OMe), 25.62 (C*Me*), 14.19 (CH$_2$*Me*). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 65.86; H, 6.98.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-*O*-{(*R*)- and (*S*)-(1-ethoxycarbonyl)ethylidene}-β-D-glucopyranoside (17R and 17S). On chromatographic separation of two isomers hexane-ethyl acetate mixtures of the following ratios were used as eluant: **17S** (10:1); **17R** (9:1 to 8:1).

17R: $[\alpha]_D$ -16.8° (c 1.1, $CHCl_3$); IR ν_{max} (NaCl) 1735 cm^{-1} (ester); ^{1}H-NMR δ 7.44-7.20 (m, 10H, 2Ph), 4.88, 4.71 (ABq, *J* 14.0 Hz, PhCH_2), 4.86, 4.71 (ABq, *J* 15.0 Hz, PhCH_2), 4.53 (d, $J_{1,2}$ 7.6 Hz, H-1), 4.25 (q, 2H, *J* 7.6 Hz, CH_2Me), 4.11 (dd, $J_{5,6a}$ 6.0 Hz, J_{gem} 11.2 Hz, H-6a), 3.98-3.24 (m, 6H), 2.08-1.08 (m, 10H, 5CH_2), 1.68 (s, 3H, CMe), 1.32 (t, 3H, CH$_2$*Me*); ^{13}C-NMR δ 168.43 (C=O), 138.69, 138.52, 128.18-127.58 (2Ph), 102.34 (d, $J_{C\text{-}H}$ 158.7 Hz, C-1), 97.51 (acetal), 82.02, 80.83, 78.06, 74.16, 66.36, 75.30, 74.81 (2PhCH_2), 63.00 (CH_2Me), 61.83 (C-6), 33.70, 31.90, 25.57, 24.05, 23.89, 17.82 (C*Me*), 14.08 (CH$_2$*Me*). Anal. Calcd. for $C_{31}H_{40}O_8$: C, 68.87; H, 7.46. Found: C, 68.47; H, 7.57.

17S: $[\alpha]_D$ +25.0° (c 1.1, $CHCl_3$); IR ν_{max} (NaCl) 1735 cm^{-1} (ester); ^{1}H-NMR δ 7.47-7.14 (m, 10H, 2Ph), 4.93, 4.72 (ABq, *J* 11.8 Hz, PhCH_2), 4.85, 4.66 (ABq, *J* 10 Hz, PhCH_2), 4.52 (d, $J_{1,2}$ 8.0 Hz, H-1), 4.24 (q, 2H, *J* 7.2 Hz, CH_2Me), 4.04 (dd, $J_{5,6a}$ 5.4 Hz, J_{gem} 10.6 Hz, H-6a), 3.88-3.16 (m, 7H), 2.04-1.08 (m, 10H, 5CH_2), 1.55 (s, 3H, CMe), 1.30 (t, 3H, CH$_2$*Me*); ^{13}C-NMR δ 169.67 (C=O), 138.96, 138.58, 128.23-127.36 (2Ph), 102.17 (d, $J_{C\text{-}H}$ 158.7, C-1), 98.92 (acetal), 81.91, 80.88, 77.90, 65.50, 75.41, 74.22 (2PhCH_2), 65.23 (CH_2Me), 61.76 (C-6), 33.70, 31.91, 25.57, 24.00, 23.89, 25.46 (C*Me*), 14.25 (CH$_2$*Me*). Anal. Calcd. for $C_{31}H_{40}O_8$: C, 68.87; H, 7.46. Found: C, 68.72; H, 7.56.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-{(*R*) and (*S*)-(1-ethoxycarbonyl)ethylidene}-β-D-galactopyranoside (18R and 18S). The two isomer were separated by elution with 3:1 mixture of hexane and ethyl acetate.

18R: $[\alpha]_D$ +12.8° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1735 cm^{-1} (ester); ^{1}H-NMR δ 7.48-7.20 (m, 10H, 2Ph), 4.88, 4.62 (ABq, *J* 12.2 Hz, PhCH_2), 4.84 (s, 2H, PhCH_2), 4.31 (q, 2H, *J* 7.2 Hz, CH_2Me), 4.29-3.18 (m,

6H), 3.79 (dd, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.0 Hz, H-2), 3.56 (s, 3H, OMe), 1.65 (s, 3H, CMe), 1.34 (t, 3H, CH_2Me); ^{13}C-NMR δ 170.11 (C=O), 138.90, 138.09, 128.29-127.47 (2Ph), 104.61 (C-1), 98.76 (acetal), 78.50, 78.17, 68.58, 65.61 (C-2,3,4,5), 75.30, 70.81 (2PhCH_2), 65.33, 61.65 (C-6, CH_2Me), 57.21 (OMe), 25.90 (C*Me*), 14.30 (CH_2Me). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 65.99; H, 6.94.

18S: $[\alpha]_D$ +12.2° (c 1.0, $CHCl_3$); IR ν_{max} 1715 cm^{-1} (ester); ^{1}H-NMR δ 7.48-7.20 (m, 10H, 2Ph), 4.89, 4.78 (ABq, *J* 10.2 Hz, $PhCH_2$), 4.76 (s, 2H, $PhCH_2$), 4.22 (q, 2H, *J* 7.2 Hz, CH_2Me), 4.24-3.31 (m, 6H,), 3.85 (dd, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.0 Hz, H-2), 3.50 (s, 3H, OMe), 1.58 (s, 3H, CMe), 1.33 (t, 3H, CH_2Me); ^{13}C-NMR δ 169.51(C=O), 138.90, 138.40 128.34-127.47 (2Ph), 104.18 (C-1), 96.97 (acetal), 79.09, 78.49, 67.23, 66.63 (C-2,3,4,5), 75.25, 72.00 (2PhCH_2), 64.85, 61.54 (C-6, CH_2Me), 56.77 (OMe), 23.35 (C*Me*), 13.98 (CH_2Me). Anal. Calcd. for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 65.26; H, 7.04.

Pyruvate acetalization of β-D-mannopyranoside 6g. The acetalization of **6g** in CH_2Cl_2 (Table 1, entry 11) gave a mixture of anomerized 4,6-acetals **16R** and **16S**, and 5,6-acetal **20**, which were separated by elution with hexane-ethyl acetate (8:1 to 5:1), and characterized only by ^{1}H-NMR and ^{13}C-NMR.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-*O*-{(*R*)-(1-ethoxycarbonyl)ethylidene}-α-D-mannopyranoside (**16R**): ^{1}H-NMR δ 7.44-7.20 (m, 10H, 2Ph), 4.92-4.51 (m, 5H, 2PhCH_2, H-1), 4.28 (q, 2H, *J* 7.0 Hz, CH_2Me), 4.36-3.36 (m, 7H), 2.0-1.0 (m, 10H, 5CH_2), 1.72 (s, 3H, CMe), 1.26 (t, 3H, CH_2Me); ^{13}C-NMR δ 168.59 (C=O), 138.07, 128.18-127.42 (2Ph), 97.89 (acetal), 97.46 (d, $J_{C\text{-}H}$ 168.46, C-1), 77.36, 76.55, 75.14, 73.68, 73.24, 72.32, 63.06, 61.76, 64.52, 33.26, 31.15, 25.57, 23.95, 23.73,17.82 (C*Me*), 14.08 (CH_2Me).

Its (*S*)-isomer **16S**: ^{1}H-NMR δ 7.47-7.17 (m, 10H, 2Ph), 4.97, 4.75 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.82, 4.59 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.59 (s, 1H, H-1), 4.45-3.68 (m, 9H), 2.03-1.05 (m, 10H, 5CH_2), 1.57 (s, 3H, CMe), 1.37 (t, 3H, CH_2Me); ^{13}C-NMR δ 169.95 (C=O), 139.34, 128.18-127.20 (2Ph), 99.25 (acetal), 97.62 (d, $J_{C\text{-}H}$ 168.5 Hz, C-1), 63.76 (QCH), 25.57 (C*Me*), 14.13 (CH_2Me).

Cyclohexyl 2,3-di-*O*-benzyl-5,6-*O*-{(1-ethoxycarbonyl)ethylidene}-D-mannopyranoside (**20**): ^{1}H-NMR δ 7.48-7.20 (m, 10H, 2Ph), 5.22 (d, $J_{1,2}$ 3.6 Hz, H-1), 4.75, 4.66 (ABq, *J* 11.8 Hz, $PhCH_2$), 4.63, 4.59 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.47 (dt, $J_{5,6a}$ 6.0 Hz, $J_{5,6b}$ 7.8 Hz, $J_{5,4}$ 7.5 Hz, H-5), 4.24 (dd, $J_{4,3}$ 4.5 Hz, H-4), 4.22 (dd, J_{gem} 8.8 Hz, H-6a), 4.20 (dd, H-6b), 3.90 (dd, H-2), 3.55-3.48 (m, 1H, OCH), 1.58 (s, 1H, CMe), 1.27 (t, 3H, CH_2Me), 1.92-1.12 (m, 10H, 5CH_2); ^{13}C-NMR δ 170.32 (C=O), 138.42, 128.34-127.58 (2Ph), 105.59 (acetal), 104.23 (C-1), 83.81, 79.15, 77.96, 76.28, 74.71, 73.68, 72.49, 68.91, 61.27, 33.64, 31.96, 25.68, 24.00, 22.70 (C*Me*), 14.09 (CH_2Me).

The acetalization of **6g** in Et_2O (Table 3, entry 9) gave the desired 4,6-acetals **19R** in low yields together with **20**, which were separated by elution with hexane-ethyl acetate (10:1 to 8:1) and characterized only by ^{1}H-NMR and ^{13}C-NMR.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-*O*-{(*R*)-(1-ethoxycarbonyl)ethylidene}-β-D-mannopyranoside (**19R**):^{1}H-NMR δ 7.52-7.18 (m, 10H, 2Ph), 4.97, 4.84 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.69, 4.54 (ABq, *J* 11.8 Hz, $PhCH_2$), 4.48 (s, 1H, H-1), 4.25 (q, 2H, *J* 7.0 Hz, CH_2Me), 4.41-3.18 (m, 7H), 2.00-1.04 (m, 10H, 5CH_2), 1.70 (s, 3H, CMe), 1.32 (t, 3H, CH_2Me); ^{13}C-NMR δ 168.50 (C=O), 138.63, 128.66-127.42 (2Ph), 100.06 (d, $J_{C\text{-}H}$ 152.6 Hz, C-1), 97.95 (acetal), 78.11, 76.71, 76.55, 74.59, 72.32, 71.62, 67.93, 62.84, 61.76, 33.37, 31.42, 25.68, 23.73, 23.57, 17.93 (C*Me*), 14.14 (CH_2Me).

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13. Coupling of the disilyl ether **3c** with benzyl pyruvate at 3 °C in dichloromethane or ether gave, albeit low yield (22–25%), the corresponding (*S*)-acetal exclusively. Methyl 2,3-di-*O*-benzyl-4,6-*O*-[(S)-(1-benzyloxycarbonyl) ethylidene]-α-D-mannopyranoside: $[\alpha]_D$ +70.3° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 1735 cm^{-1} (ester); ^{1}H-NMR δ 7.50-6.90 (m, 5H, 3Ph), 5.28, 5.11 (ABq, *J* 12.5 Hz, $PhCH_2$), 4.88, 4.64 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.68-4.46 (m, 3H, H-1, $PhCH_2$), 4.26-3.51 (m, 6H), 3.25 (s, 3H, OMe), 1.57 (s, 3H, CMe); ^{13}C-NMR δ 169.84 (C=O), 139.01, 138.31, 135.27, 128.83-126.82 (3Ph), 100.66 (C-1), 99.30 (acetal), 76.44, 76.33, 75.90, 63.44 (C-2,3,4,5), 73.57, 73.03, 67.28, 65.23 (3Ph*C*H_2, C-6), 54.72 (OMe), 25.57 (C*Me*). Anal. Calcd. for $C_{31}H_{34}O_8$: C, 69.64; H, 6.54. Found: C, 69.75; H, 6.42.
14. The stereoselectivities in the acetalization of both *gluco* isomers (**1c** and **4c**) in dichloromethane cannot be explained solely by thermodynamic factor. The acetalization of the α-manno isomer **3c** in the presence of TMSOTf (40 mol%) and TfOH (10 mol%) in dichloromethane at -5 °C for 1 day afforded the (*R*)-acetal **15R** and the (*S*)-acetal **15S** in yields of 18% and 45%, respectively, together with a small amount (6%) of the 5,6-acetal **20**. Thus, the acetalization reaction at the lower temperature may proceed under kinetic control.
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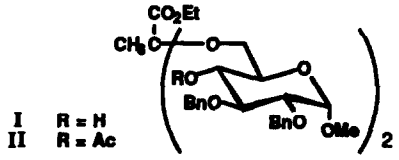
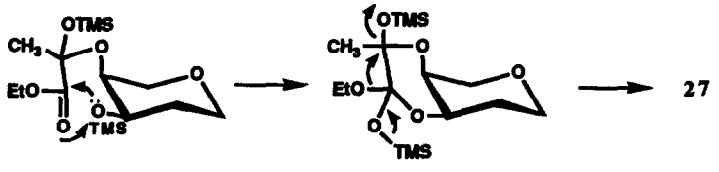
17. The acetalization of **1g** in CH_2Cl_2 or in ether containing 40 mol% TMSOTf gave, even at lower temperatures (-50 – -30 °C), mainly the intermolecular 6,6'-acetal **I** in 15 – 39% yield. The formation of **I** suggests that hydrolysis of 4-*O*-TMS ether competes with the 4,6-acetal ring formation. Ethyl pyruvate bis-(methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside-6-yl)acetal (**I**). $[\alpha]_D$ +14.9° (c 1.0, $CHCl_3$); IR ν_{max} (NaCl) 3600-3100 (OH), 1715 cm^{-1} (ester); ^{1}H-NMR δ 7.44-7.20 (m, 20H, 4Ph), 4.97, 4.80 (ABq, 4H, *J* 12.0 Hz, $2PhCH_2$), 4.76, 4.60 (ABq, 4H, *J* 12.0 Hz, $2PhCH_2$),4.62 (d, 2H, $J_{1,2}$ 3 Hz, H-1,1'), 4.20 (q, 2H, *J* 7.0 Hz, CH_2Me), 3.96-3.40 (m, 12H), 3.37 (s, 6H, 2OMe), 3.32-2.88 (br, 2H, 2OH), 1.55 (s,

3H, CMe), 1.28 (t, 3H, CH_2Me); ^{13}C-NMR δ 169.57 (C=O), 99.84 (acetal), 98.11 (C-1), 21.62 (*CMe*), 14.03 (CH_2Me). Anal. Calcd. for $C_{47}H_{58}O_{14}$: C, 66.65; H, 6.90. Found: C, 66.80; H, 6.93.The acetal I was further characterized as its 4, 4'-di-*O*-acetyl derivative II: ^{1}H-NMR δ 7.35-7.26 (m, 10H, 2Ph), 4.87, 4.64 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.78, 4.64 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.77, 4.64 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.77, 4.63 (ABq, *J* 12.0 Hz, $PhCH_2$), 4.85, 4.83 (each t, $J_{3,4} = J_{4,5}$ 10.0 Hz, H-4, H-4'), 4.59 (d, $J_{1,2}$ 3.4 Hz, H-1), 4.58 (d, $J_{1,2}$ 3.9 Hz, H-1'), 4.17 (q, *J* 7.0 Hz, CH_2Me), 3.87, 3.88 (each t, $J_{2,3} = J_{3,4}$ 9.4 Hz, H-3, H-3'), 3.56-3.39 (m, 8H), 3.38, 3.37 (each s, each 3H, 2OMe), 1.90, 1.86 (each s, each 3H, OAc), 1.45 (s, 3H, *CMe*), 1.24 (t, 3H, CH_2Me).



I R = H
II R = Ac

18. An attempt to prevent the ring contraction and anomerization employing the more bulky Lewis acid, TBDMSOTf instead of TMSOTf was unsuccessful. While the acetalization of **3g** in the presence of TBDMSOTf (40 mol%) in Et_2O gave only the 4,6-acetal **15**, the yield was rather low [14% (*R*)-isomer and 11% (*S*)-isomer]. Further, the acetalization of **6g** under the same conditions gave an anomeric mixture (15% yield) of the 4,6-acetal.
19. In the presence of additional TfOH (2 mol%) the reaction proceeded at -20 °C to afford **15R** and **15S** in yields of 31% and 28%, respectively. The induction time is deduced to be necessary for the formation of potential actual catalyst TfOH by decomposition of TMSOTf.
20. The data given for **25b** in the communication[10] including yields and 1H- and 13C-NMR chemical shifts were mistaken for those of **18S** and **18R**.
21. The structure of **27** was deduced by ^{13}C-NMR chemical shift of the acetal carbon (98.02 ppm) indicating 6-membered ring and by ^{1}H-NMR chemical shift of methylene in ethoxyl group, which resonates at the higher field (3.51 ppm) than that in ethyl ester (ca. 4.2 ppm). Further, the lactone structure was supported by the ^{1}H-detected heteronuclear multiple-bond correlation (HMBC) measurement, which confirmed the correlation between H-3 and carbonyl carbon. A possible mechanism for the formation of **27** may be shown as follows.



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