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Differentiating the 2,3-diols of glucopyranosides by 4,6-*O*-benzylidene-protected-1,2-D-glucopyranosylorthoesters strategy

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ABSTRACT

A facile and efficient method to differentiate the 2,3-diols of glucopyranosides based on 1,2-orthoesters strategy was developed. Stable thioglucosides were employed as the starting materials to prepare the corresponding 1,2-orthoesters. When treated with HCl aqueous solution and followed with Et_3N, differentiation of the 2,3-diols was efficiently achieved along with the generation of a convertible anomeric hydroxyl group. In addition, an easy and practical method based on NOE was proposed to determine whether the 1,2-orthoesters were *endo*-type or *exo*-type.

1. Introduction

Synthetic oligosaccharides and glycoconjugates are increasingly used as probes for biological research and as leading compounds for drug and vaccine discovery.[1] Challenges in carbohydrate synthesis are not only the stereoselective glycosylation, but also the preparation of selectively protected monosaccharide units for regioselective glycosylation.[2] While effective differentiation of the hydroxyls for some monosaccharides can hardly be achieved. For example, differentiating 2,3-diols of D-glucopyranoside is a big challenge because all the secondary hydroxyls are *trans*-equatorial. Although some approaches are available,[2–8] in most cases 2-protected and 3-protected derivatives are obtained simultaneously.

Sugar 1,2-orthoesters were one type of important intermediates in carbohydrate synthesis. Since first reported by Kochetkov and co-workers,[9–11] they have been explored constantly over the past decades. Usually 1,2-orthoesters were formed as intermediates in glycosylation, and they could be converted to the corresponding 1,2-*trans*-glycosides by the action of protonic or Lewis acids.[12,13] The 1,2-orthoesters were also used to differentiate the 2-OH from other hydroxyls of a pyranose ring.[14–17] For example, we have accomplished the differentiating of 2,3-diols of glucopyranosides in our previous work.[18,19] The highlight of this strategy was that 1,2-orthoesters served as a temporary protecting groups to differentiate the 2,3-diols of glucopyranosides.

The routine method for the preparation of 1,2-orthoesters was achieved by treating per-acetylated α-glycosyl bromide with an alcohol in the presence of tetrabutylammonium bromide and *sym*-collidine or silver triflate and 2,6-lutidine.[20–24] However, the instability of glycosyl bromide made it difficult to manipulate the protecting groups on their non-anomeric regions. In addition, 1,2-orthoesters were not always efficient during the glycosylation, and in many cases they were needed to be converted to other glycosyl donors.

In this paper, we developed a facile and efficient method to differentiate the 2,3-diols of glucopyranosides based on 1,2-orthoesters strategy. Stable thioglycosides, with 4,6-diols protected by benzylidene, were employed as the starting materials to prepare the corresponding 1,2-orthoesters.

2. Results and discussion

Thioglycosides **1**, which could be easily synthesized from the known compounds,[25,26] were explored as the starting materials. As depicted in Table 1, treated with CH_3OH in the presence of NBS/TMSOTf at 0 °C, three thio-β-D-glucosides **1a–c** were all transformed to 1,2-orthoesters **2a–c** in 30 min monitored by TLC. Subsequently, 3-acyl groups were removed by CH_3ONa/CH_3OH to afford compounds **3a–c** with excellent yield in one-pot. With compounds **3a–c** in hands, it was easy to put an orthogonal protecting group

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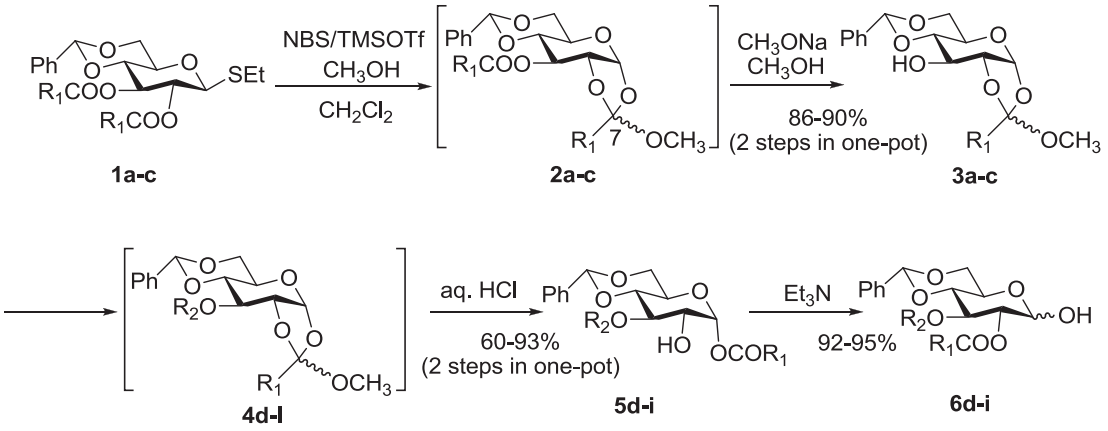
Table 1
Differentiate the 2,3-diols of glucopyranosides based on 1,2-orthoesters strategy



Compounds	3[a]			4			5[b]		6 (yield %)
	R_1	Isomer 1:isomer 2	Yield (%)		R_2	Yield (%)	Isomer 1 yield (%)/time (h)	Isomer 2 yield (%)/time (h)	
a	CH_3	2.2:1	89	**d**	Bz	—	85/1.0	75/12.0	93
				e	Bn	—	90/0.5	82/4.0	94
				f	TBS	—	93/0.5	85/4.0	95
b	Ph	2.0:1	86	**g**	Ac	—	76/2.0	60/12.0	93
				h	Bn	—	88/1.0	79/6.0	92
				i	TBS	—	92/1.0	84/6.0	94
c	$ClCH_2$	3.0:1	90	**j**	Ac	93	—	—	—
				k	Bn	92	—	—	—
				l	TBS	85	—	—	—

[a] Isomer 1 was more polar than isomer 2 which was observed by TLC.
[b] The yields of compounds **5** were calculated from compounds **3**.

(R_2) on the free 3-OH to differentiate the 2,3-diols of glucopyranosides. When TLC indicated the full generation of compounds **4d–i**, the reaction mixture was washed with 2 M aqueous HCl solution to provide **5d–i** smoothly. Treating **5d–i** with Et_3N induced the migration of the acyl group from 1-OH to 2-OH to provide **6d–i**.[27] Thus differentiation of 2-OH from 3-OH was accomplished completely. Compounds **6d–i** with a convertible 1-OH at the reducing end were very useful building blocks in oligosaccharide synthesis, which could be converted to the corresponding glycosyl donors, such as trichloroacetimidate,[28,29] trifluoroacetimidate,[30,31] *ortho*-alkynylbenzoates[32–34] and so on, for the next coupling with glycosyl acceptors. They could also be irreversible activated in situ with a sulfonic acid anhydride and a sulfoxide in the presence of a base, and then be coupled with glycosyl acceptors in one-pot.[35,36]

Although the procedure was easy to handle, there were some interesting details to be discussed, especially the configurations of these orthoesters' chiral center (C7) and their effects on the following hydrolysis. During the formation of 1,2-orthoesters, a new chiral center (C7) was generated. The two isomers were easily separated from each other by silica gel chromatography (Table 1, 2.2:1 for **3a**, 2.0:1 for **3b**, 3.0:1 for **3c**). We noticed that for the isomers with *endo*-type, the methoxy group should be *cis* to the glucopyranose ring. Thus H-8 was supposed to be close to H-3 and H-5. As for those with *exo*-type, the methoxy group should be *trans* to the glucopyranose ring, and H-8 was supposed to be close to H-1 and H-2. In this respect, a method based on NOE was proposed to determine the configurations of C-7 of these 1,2-orthoesters. The NOE observed in the experiments for all the 1,2-orthoesters **(3a–c, 4j)** were fully consistent with the proposed method. By irradiating the protons on methoxy group, clear signal enhancements were detected on H-3/H-5 for 1,2-orthoesters with *endo*-type, and on H-1/H-2 for *exo*-type ones (Fig. 1). At the same time, cultivation of the single crystals of 1,2-orthoesters were attempted and the single

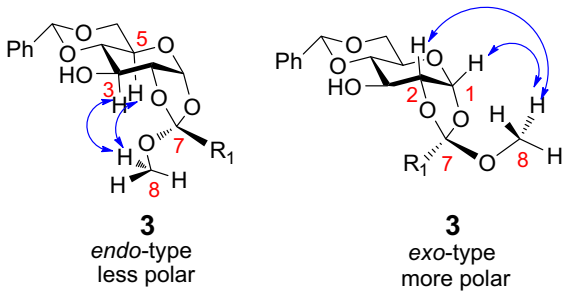


Figure 1. Determination of the configuration of 1,2-orthoesters by NOE.

crystals of the two isomers of **4j** were obtained. As expected, the X-ray analysis results of the single crystals of **4j** consistent with the NOEs experimental results (Fig. 2). By using NOEs, the absolute configurations of all the 1,2-orthoesters **(3a–c)** were easily and rapidly determined.

From the above results, we could find that the configuration of 1,2-orthoesters was an important factor in the hydrolysis. As shown in Table 1, all the more reactive 1,2-orthoesters (isomers 1 of compounds **4d–i**) upon hydrolysis had an *exo*-configuration, while those less reactive 1,2-orthoesters (isomers 2 of compounds **4d–i**) upon hydrolysis had an *endo*-configuration. In addition, the *exo*-type ones hydrolyzed much faster (about 5–10 times) and were obtained in higher yield than the *endo*-type ones. These results might have been caused by steric effects, because the oxygen atoms in methoxy groups (O-7, Fig. 2) of *exo*-type were easier to be protonated, which was the key to active 1,2-orthoesters for the subsequent hydrolysis. However, the chloromethyl 1,2-orthoesters **4j–l**, with of both the *endo*-type and the *exo*-type, were very stable upon hydrolysis under the same acidic condition. This might be due to the presence of an electronegative chloro atom in R_1, which

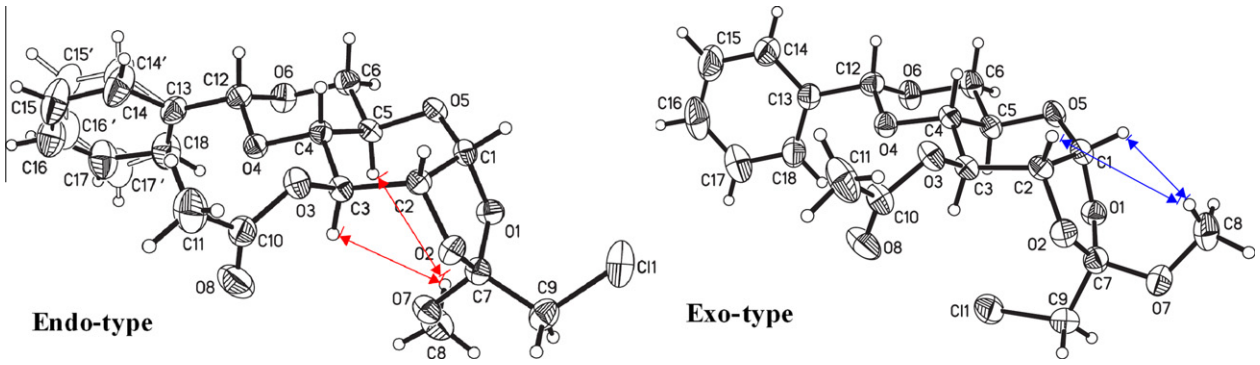


Figure 2. X-ray crystal structure of compound **4j**.

lowered the electrodensity of the nearby oxygen atom in methoxy group, and made it more difficult to be protonated.

Besides, the protecting group on position 3 was also an impact factor. While the 1,2-orthoesters had the same R_1 part and configuration, 1,2-orthoesters with C-3 esters were more stable than those with C-3 benzyl or C-3 TBS (Table 1).

3. Conclusion

In conclusion, an efficient and facile method for the differentiation of the 2,3-diols of glucopyranoside along with some interesting details were described. The key intermediates 4,6-*O*-benzylidene-protected 1,2-D-glucopyranosylorthoesters were prepared conveniently from the corresponding stable thioglucosides. When treated with HCl aqueous solution and followed with Et_3N, differentiation of the 2,3-diols of glucopyranoside was achieved efficiently along with the generation of a convertible anomeric hydroxyl group, which could be easily converted to various leaving groups. In addition, an easy and practical method based on NOE was proposed to determine the 1,2-orthoesters were *endo*-type or *exo*-type.

4. Experimental section

4.1. General experimental methods

All chemical reagents were used as supplied unless indicated. Solvents used in organic reactions were distilled under an inert atmosphere. Unless otherwise noted, all reactions were carried out at room temperature and were performed under a positive pressure of argon. Crushed 4 Å molecular sieves were activated by thorough flame-drying and cooled in vacuo prior to use. Silica gel (50 g) was added in Et_3N/CH_2Cl_2 = 1:50 (500 mL), then the mixture was stirred for 1 h at rt, concentrated and dried in vacuo to afford Et_3N activated silica gel. ^1H NMR spectra were recorded at 600 or 400 MHz, and the ^{13}C NMR spectra were recorded at 150 or 100 MHz at rt. Chemical shifts of the ^1H NMR spectra are expressed in ppm relative to the solvent residual signal 7.26 in $CDCl_3$ or to tetramethylsilane (δ = 0.00). Chemical shifts of the ^{13}C NMR spectra are expressed in ppm relative to the solvent signal 77.00 in $CDCl_3$ or to tetramethylsilane (δ = 0.00) unless otherwise noted. The corresponding peaks are reported as s (singlet), d (doublet), t (triplet), and m (multiplet) as well as br (broad).

4.2. Ethyl 4,6-*O*-benzylidene-2,3-di-*O*-acetyl-1-thio-β-D-glucopyranoside (1a)

By following the same procedure as for compound **1b**/**1c**.[18] Yield 95%, as a white solid was obtained. $[\alpha]_D^{20}$ = −94.2 (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.44–7.34 (m, 5H), 5.50 (s, 1H), 5.34 (t like, 1H, *J* = 9.66, 9.12 Hz), 5.04 (t like, 1H, *J* = 9.60, 9.18 Hz), 4.58 (d, 1H, *J* = 10.08 Hz), 4.37 (dd, 1H, *J* = 10.50, 5.04 Hz), 3.77 (t like, 1H, *J* = 10.56, 10.08 Hz), 3.69 (t, 1H, *J* = 9.60 Hz), 3.59–3.56 (m, 1H), 2.74–2.69 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 1.27 (t, 3H, *J* = 7.80 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.0, 169.6, 136.7, 129.1, 127.3, 126.1, 101.4, 84.1, 78.3, 72.7, 70.7, 70.6, 68.4, 24.2, 20.7, 14.8. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{24}O_7SNa$ $[M+Na]^+$ 419.1140, found 419.1146.

4.3. General procedure for compound 3[19]

After a mixture of **1a**–**c** (1.0 mmol), CH_3OH (1 mL) and 4 Å molecular sieves in freshly distilled CH_2Cl_2 (50 mL) were stirred for 0.5 h at rt and then cooled to 0 °C, NBS (178 mg, 1.0 mmol) was added and the reaction mixture was stirred for 2 min. TMSOTf (18 μL, 0.1 mmol) was added dropwise and the reaction mixture was stirred for 15 min at 0 °C. Then NBS (178 mg, 1.0 mmol) and TMSOTf (18 μL, 0.1 mmol) were added for the second time. The reaction mixture was stirred for another 15 min at 0 °C, TLC (*n*-Hexane/EtOAc = 2:1) indicated that compound **1** completely converted to 1,2-orthoesters **2**. Then a solution of CH_3ONa in MeOH (0.1 M, 40 mL) was added dropwise to the reaction mixture. The solution was allowed to warm to rt and stirred for 30 min, then filtered through celite. Silica gel (activated by Et_3N, 4 g) was added to the filtrate, and then concentrated in vacuo. The crude mixture was purified by column chromatography on silica gel (silica gel had been activated by Et_3N) to afford **3** (Et_3N/EtOAc/petroleum ether = 1:50:100 for the mixture of *endo*-type and *exo*-type, and Et_3N/EtOAc/petroleum ether = 1:20:100 for separating *endo*-type and *exo*-type from each other).

4.4. 4,6-*O*-Benzylidene-α-D-glucopyranose 1,2-(methyl methoxyl orthoacetate) (3a)

endo-Type: $[\alpha]_D^{20}$ = +66.0 (*c* 0.23, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.49–7.35 (m, 5H, Ar*H*), 5.62 (d, 1H, *J* = 5.94 Hz, H-1), 5.53 (s, 1H, PhC*H*), 4.36 (dd, 1H, *J* = 10.50, 5.46 Hz, H-6a), 4.32 (dd, 1H, *J* = 9.60, 5.46 Hz, H-3), 4.16 (t like, 1H, *J* = 5.94, 5.46 Hz, H-2), 3.94–3.90 (m, 1H, H-5), 3.68 (t like, 1H, *J* = 10.50, 10.08 Hz, H-6b), 3.49 (t like, 1H, *J* = 10.08, 9.60 Hz, H-4), 3.38 (s, 3H, CH_3O), 1.57 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 129.2, 128.3, 126.1, 121.3, 101.6, 99.1, 79.3, 78.5, 73.1, 68.6, 62.7, 45.8, 21.8. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{20}O_7Na$ $[M+Na]^+$ 347.1107, found 347.1101.

exo-Type: $[\alpha]_D^{20}$ = +61.4 (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.49–7.35 (m, 5H, Ar*H*), 5.74 (d, 1H, *J* = 5.46 Hz, H-1), 5.54 (s, 1H, PhC*H*), 4.37 (dd, 1H, *J* = 10.56, 5.52 Hz, H-6a), 4.26 (t like, 1H, *J* = 5.46, 5.04 Hz, H-2), 3.97 (dd, 1H, *J* = 9.60, 5.04 Hz, H-3), 3.82–3.78 (m, 1H, H-5), 3.69 (t like, 1H, *J* = 10.56, 10.08 Hz, H-6b), 3.53 (t like, 1H, *J* = 9.66, 9.18 Hz, H-4), 3.28 (s, 3H, CH_3O), 1.67 (s, 3H, CH_3). ^{13}C NMR: (150 MHz, $CDCl_3$): δ 129.3, 128.3,

126.2, 120.4, 101.7, 98.3, 79.3, 78.9, 73.3, 68.5, 62.8, 50.1, 45.7, 22.8. HRMS (ESI) m/z calcd for $C_{16}H_{20}O_7Na$ $[M+Na]^+$ 347.1107, found 347.1122.

4.5. 4,6-*O*-Benzylidene-α-D-glucopyranose 1,2-(phenyl methoxyl orthoacetate) (3b)

endo-Type: $[\alpha]_D^{20}$ = +72.0 (*c* 0.38, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.59–7.38 (m, 10H), 5.69 (d, 1H, *J* = 6.0 Hz, H-1), 5.59 (s, 1H, PhC*H*), 4.53 (dd, 1H, *J* = 10.08, 5.94 Hz, H-3), 4.44 (dd, 1H, *J* = 10.5, 5.46 Hz, H-6a), 4.29 (t like, 1H, *J* = 6.0, 5.46 Hz, H-2), 4.11–4.07 (m, 1H, H-5), 3.75 (t like, 1H, *J* = 10.56, 10.02 Hz, H-6b), 3.57 (t, 1H, *J* = 9.6 Hz, H-4), 3.25 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 136.9, 129.3, 128.4, 128.3, 126.2, 126.0, 120.5, 101.8, 99.3, 79.2, 78.6, 73.3, 68.6, 63.0, 53.4, 51.6, 45.9. HRMS (ESI) m/z calcd for $C_{21}H_{22}O_7Na$ $[M+Na]^+$ 409.1263, found 409.1273.

exo-Type: $[\alpha]_D^{20}$ = +67.4 (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.63–7.33 (m, 10H), 5.94 (d, 1H, *J* = 5.52 Hz, H-1), 5.51 (s, 1H, PhC*H*), 4.39 (t like, 1H, *J* = 5.52, 5.46 Hz, H-2), 4.36 (dd, 1H, *J* = 10.08, 5.04 Hz, H-6a), 3.82 (dd, 1H, *J* = 9.60, 5.52 Hz, H-3), 3.79–3.75 (m, 1H, H-5), 3.70 (t like, 1H, *J* = 10.50, 10.08 Hz, H-6b), 3.51 (t, 1H, *J* = 9.6 Hz, H-4), 3.24 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.1, 136.7, 129.3, 129.3, 128.4, 128.3, 126.1, 125.9, 119.6, 101.7, 98.7, 79.1, 78.7, 72.5, 68.5, 63.2, 50.8, 45.9. HRMS (ESI) m/z calcd for $C_{21}H_{22}O_7Na$ $[M+Na]^+$ 409.1263, found 409.1282.

4.6. 4,6-*O*-Benzylidene-α-D-glucopyranose 1,2-(chloromethyl methoxyl orthoacetate) (3c)

endo-Type: $[\alpha]_D^{20}$ = +69.9 (*c* 0.31, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.51–7.37 (m, 5H), 5.80 (d, 1H, *J* = 5.52 Hz), 5.56 (s, 1H), 4.39 (dd, 1H, *J* = 10.5, 5.46 Hz), 4.31–4.28 (m, 2H), 3.95–3.92 (m, 1H), 3.74–3.67 (m, 3H), 3.54 (t like, 1H, *J* = 9.66, 9.60 Hz), 3.47 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 129.4, 128.4, 126.2, 119.4, 101.8, 99.9, 78.9, 78.6, 73.2, 68.5, 63.1, 51.3, 44.6. HRMS (ESI) m/z calcd for $C_{16}H_{19}O_7ClNa$ $[M+Na]^+$ 381.0717, found 381.0727.

exo-Type: $[\alpha]_D^{20}$ = +60.1 (*c* 0.28, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.50–7.37 (m, 5H), 5.85 (d, 1H, *J* = 5.52 Hz), 5.55 (s, 1H), 4.40 (t like, 1H, *J* = 5.46, 5.04 Hz), 4.37 (t like, 1H, *J* = 5.52, 5.46 Hz), 4.21 (dd, 1H, *J* = 8.7, 5.46 Hz), 3.99–3.95 (m, 1H), 3.78 (d, 1H, *J* = 12.36 Hz), 3.74 (d, 1H, *J* = 11.94 Hz), 3.69 (t like, 1H, *J* = 10.56, 10.50 Hz), 3.54 (t, 1H, *J* = 9.6 Hz), 3.34 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$): δ 129.4, 128.4, 126.2, 118.6, 101.8, 98.9, 79.4, 78.8, 73.5, 68.4, 63.1, 50.6, 44.3. HRMS (ESI) m/z calcd for $C_{16}H_{19}O_7ClNa$ $[M+Na]^+$ 381.0717, found 381.0712.

4.7. 3-*O*-Acetyl-4,6-*O*-benzylidene-α-D-glucopyranose 1,2-(chloromethyl methoxyl orthoacetate) (4j)

Compound **3c** (1.0 mmol), DMAP (12 mg, 0.1 mmol) and pyridine (322 μL, 4.0 mmol) were dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C, Ac_2O (151 μL, 1.5 mmol) was added dropwise. The reaction was stirred for 1 h at rt, CH_3OH (1.5 mmol) was added and was stirred for 30 min, the solution was diluted with CH_2Cl_2 (50 mL) and was washed with aqueous 2 N HCl, saturated aqueous $NaHCO_3$ and brine, and dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:3) to afford **4j**. Recrystallized by EtOAc/hexane = 1:10 to afford **5j** as a colorless solid.

endo-Type: Yield: 93%. A colorless solid. Mp 138.5–139.4 °C. $[\alpha]_D^{20}$ = +58.2 (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.46–7.35 (m, 5H, Ar*H*), 5.84 (d, 1H, *J* = 5.94 Hz, H-1), 5.58 (dd, 1H, *J* = 9.60, 5.04 Hz, H-3), 5.52 (s, 1H, PhC*H*), 4.40 (dd, 1H, *J* = 10.56, 5.04 Hz, H-6a), 4.35 (t like, 1H, *J* = 5.52, 5.46 Hz, H-2), 4.11–4.07 (m, 1H, H-5), 3.74–3.66 (m, 4H, H-4, H-6b, ClCH_2), 3.54 (s, 3H, CH_3O), 2.13 (s, 3H, CH_3CO). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.7, 136.7, 129.1, 128.2, 126.1, 119.6, 101.3, 99.6, 77.3, 76.6, 73.3, 68.5, 63.0, 51.6, 44.7, 20.9. HRMS (ESI) m/z calcd for $C_{18}H_{21}O_8ClNa$ $[M+Na]^+$ 423.0823, found 423.0815.

exo-Type: Yield: 93%. A colorless solid. Mp 131.5–132.2 °C. $[\alpha]_D^{20}$ = +50.6 (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.47–7.35 (m, 5H, ArH), 5.86 (d, 1H, *J* = 5.48 Hz, H-1), 5.52 (s, 1H, PhC*H*), 5.38 (dd, 1H, *J* = 8.7, 3.66 Hz, H-3), 4.43–4.40 (m, 2H, *J* = 2H, H-2, H-6a), 4.09–4.05 (m, 1H, H-5), 3.83 (d, 1H, *J* = 12.84 Hz, ClCH_2), 3.80 (d, 1H, *J* = 12.42 Hz, ClCH_2), 3.74 (t like, 1H, *J* = 9.18, 8.82 Hz, H-4), 3.71 (t like, 1H, *J* = 10.56, 10.08 Hz, H-6), 3.34 (s, 3H, CH_3O), 2.13 (s, 3H, CH_3CO). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.7, 136.7, 129.1, 128.2, 126.1, 118.7, 101.5, 98.5, 77.7, 76.9, 73.1, 68.5, 62.7, 50.7, 43.8, 20.9. HRMS (ESI) m/z calcd for $C_{18}H_{21}O_8ClNa$ $[M+Na]^+$ 423.0823, found 423.0821.

4.8. 3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-glucopyranose 1,2-(chloromethyl methoxyl orthoacetate) (4k)

Following the same procedure as for compound **5e**.

endo-Type: Yield: 92%. A white solid. $[\alpha]_D^{20}$ = +58.2 (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.52–7.28 (m, 10H), 5.82 (d, 1H, *J* = 6.0 Hz), 5.60 (s, 1H), 4.86 (d, 1H, *J* = 11.88 Hz), 4.84 (d, 1H, *J* = 11.88 Hz), 4.42 (dd, 1H, *J* = 5.94, 5.04 Hz), 4.40 (dd, 1H, *J* = 10.56, 5.52 Hz), 4.10 (dd, 1H, *J* = 9.18, 4.56 Hz), 3.99–3.95 (m, 1H), 3.75–3.66 (m, 4H), 3.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.8, 137.1, 129.0, 128.3, 128.2, 127.9, 127.8, 126.0, 119.5, 101.1, 99.7, 79.4, 79.1, 79.0, 73.0, 68.6, 62.9, 51.0, 44.8. HRMS (ESI) m/z calcd for $C_{23}H_{25}O_7ClNa$ $[M+Na]^+$ 471.1187, found 471.1198.

exo-Type: Yield: 91%. A white solid. $[\alpha]_D^{20}$ = +43.8 (*c* 0.32, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.51–7.29 (m, 10H), 5.86 (d, 1H, *J* = 5.46 Hz), 5.59 (s, 1H), 4.83 (s, 2H), 4.50 (dd, 1H, *J* = 5.52, 4.14 Hz), 4.40 (dd, 1H, *J* = 10.50, 5.04 Hz), 4.05 (dd, 1H, *J* = 8.7, 4.14 Hz), 4.00–3.95 (m, 1H), 3.74–3.69 (m, 4H), 3.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.6, 137.0, 129.0, 128.5, 128.4, 128.2, 128.0, 127.8, 126.9, 126.0, 118.7, 101.2, 99.0, 79.4, 79.2, 79.0, 73.0, 68.6, 62.8, 50.5, 44.2. HRMS (ESI) m/z calcd for $C_{23}H_{25}O_7ClNa$ $[M+Na]^+$ 471.1187, found 471.1164.

4.9. 3-*O*-*tert*-Butyldimethylsiloxy-4,6-*O*-benzylidene-α-D-glucopyranose 1,2-(chloromethyl methoxyl orthoacetate) (4l)

Following the same procedure as for compound **5f**.

endo-Type: Yield: 85%. A white solid. $[\alpha]_D^{20}$ = +43.1 (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.50–7.35 (m, 5H), 5.79 (d, 1H, *J* = 6.0 Hz), 5.55 (s, 1H), 4.37 (dd, 1H, *J* = 10.56, 5.52 Hz), 4.26–4.21 (m, 2H), 3.94–3.90 (m, 1H), 3.72–3.66 (m, 3H), 3.51 (t like, 1H, *J* = 9.66, 9.12 Hz), 3.46 (s, 3H), 0.90 (s, 9H), 0.13, 0.05 (s, 3H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.1, 128.9, 128.1, 126.0, 119.3, 101.3, 99.8, 81.0, 79.7, 74.1, 68.6, 63.1, 51.1, 44.8, 25.7, 18.1, −4.5, −4.9. MS (ESI) m/z calcd for $C_{22}H_{34}O_7ClSi$ $[M+H]^+$ 473.1762, found 473.1248.

exo-Type: Yield: 86%. A white solid. $[\alpha]_D^{20}$ = +30.4 (*c* 0.39, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.50–7.35 (m, 5H), 5.85 (d, 1H, *J* = 5.46 Hz), 5.55 (s, 1H), 4.38 (dd, 1H, *J* = 10.56, 5.04 Hz), 4.33 (t like, 1H, *J* = 5.46, 4.62 Hz), 4.18 (dd, 1H, *J* = 9.12, 4.14 Hz), 3.97–3.93 (m, 1H), 3.78 (d, 1H, *J* = 12.36 Hz), 3.75 (d, 1H, *J* = 12.36 Hz), 3.68 (t like, 1H, *J* = 10.56, 10.08 Hz), 3.53 (t, 1H, *J* = 9.18 Hz), 3.35 (s, 3H), 0.90 (s, 9H), 0.14, 0.08 (s, 3H each); ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.1, 128.9, 128.1, 126.0, 118.5, 101.3, 99.1, 81.4, 79.6, 74.2, 68.5, 63.2, 50.5, 44.2, 25.7, 18.1, −4.5, −4.9. HRMS (ESI) m/z calcd for $C_{22}H_{34}O_7SiCl$ $[M+H]^+$ 473.1762, found 473.1776.

4.10. 1-*O*-Acetyl-3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranose (5d)

Compound **3a** (324 mg, 1.0 mmol), DMAP (12 mg, 0.1 mmol) and pyridine (2.0 mmol) were dissolved in CH_2Cl_2 (10 mL) and

cooled to 0 °C, Ac_2O (142 μL, 1.5 mmol) was added dropwise. The reaction was stirred for 1 h at rt, CH_3OH (1.0 mL) was added and stirred for 30 min, the solution was diluted with CH_2Cl_2 (50 mL). Subsequently, aqueous 2 M HCl (30 mL) and 1 g silica gel (100–200 mesh) was added. The reaction mixture was stirred until TLC (*n*-Hexane/EtOAc = 4:1) indicated that 1,2-orthoesters completely hydrolyzed. The organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:3) to afford **5d** as a white solid. Yield: 75% (from *endo*-type of **3a**); 85% (from *exo*-type of **3a**). $[\alpha]_D^{20} = -16.5$ (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.08–7.32 (m, 10H), 6.27 (d, 1H, *J* = 3.84 Hz), 5.65 (t, 1H, *J* = 9.60 Hz), 5.57 (s, 1H), 4.36 (dd, 1H, *J* = 10.44, 4.68 Hz), 4.04–4.01 (m, 2H), 3.87 (t, 1H, *J* = 9.60 Hz), 3.80 (t, 1H, *J* = 10.44 Hz), 2.18 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 167.7, 136.6, 133.5, 130.1, 129.9, 129.1, 128.4, 128.2, 126.1, 101.5, 92.0, 78.2, 73.0, 71.0, 68.7, 64.8, 20.9. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{22}O_8Na$ $[M+Na]^+$ 437.1212, found 437.1230.

4.11. 1-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranose (5e)

Compound **3a** (324 mg, 1.0 mmol) were dissolved in DMF (5 mL) and cooled to 0 °C, NaH (60 mg (60%), 1.5 mmol) was added, the solution was allowed to warm to rt and stirred for 30 min. Then the solution was cooled to 0 °C, TBAI (37 mg, 0.1 mmol) was added and then BnBr (179 μL, 1.5 mmol) was added dropwise, the solution was allowed to warm to rt gradually and stirred for 30 min at rt. The following procedure was the same as that for compound **5d**. Yield: 82% (from *endo*-type of **3a**); 90% (from *exo*-type of **3a**). $[\alpha]_D^{20} = +79.3$ (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.51–7.30 (m, 10H), 6.22 (d, 1H, *J* = 3.66 Hz), 5.60 (s, 1H), 5.03 (d, 1H, *J* = 11.04 Hz), 4.76 (d, 1H, *J* = 11.88 Hz), 4.32 (dd, 1H, *J* = 10.08, 4.62 Hz), 3.95–3.90 (m, 2H), 3.86 (dd, 1H, *J* = 9.18, 4.62 Hz), 3.76–3.71 (m, 2H), 2.17 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 138.1, 137.0, 129.0, 128.5, 128.2, 128.0, 127.9, 125.9, 101.3, 91.6, 81.6, 78.4, 74.9, 70.8, 68.7, 64.8, 21.0. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{24}O_7Na$ $[M+Na]^+$ 423.1420, found 423.1423.

4.12. 1-*O*-Acetyl-3-*O*-*tert*-butyldimethylsiloxy-4,6-*O*-benzylidene-α-D-glucopyranose (5f)

To a solution of **3a** (324 mg, 1.0 mmol) in DMF (5 mL) was added imidazole (136 mg, 2.0 mmol), TBAI (37 mg, 0.1 mmol), and TBSCl (301 mg, 2.0 mmol). The solution was stirred for 24 h at rt. The following procedure was the same as that for compound **5d**. Yield: 85% (from *endo*-type of **3a**); 93% (from *exo*-type of **3a**). $[\alpha]_D^{20} = +61.3$ (*c* 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.50–7.35 (m, 5H), 6.23 (d, 1H, *J* = 3.66 Hz), 5.51 (s, 1H), 4.28 (dd, 1H, *J* = 10.08, 4.56 Hz), 3.96 (t like, 1H, *J* = 9.18, 9.12 Hz), 3.89–3.85 (m, 1H), 3.77 (dd, 1H, *J* = 9.12, 4.56 Hz), 3.71 (t, 1H, *J* = 10.08 Hz), 3.50 (t like, 1H, *J* = 10.08, 9.12 Hz), 2.19 (s, 3H), 0.88 (s, 9H), 0.12, 0.05 (s, 3H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.7, 138.0, 129.0, 128.1, 126.2, 101.8, 91.8, 81.2, 72.5, 72.5, 68.7, 64.9, 25.8, 21.1, 18.2, −4.2, −4.8. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{32}O_7SiNa$ $[M+Na]^+$ 447.1815, found 447.1803.

4.13. 3-*O*-Acetyl-1-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranose (5g)

Following the same procedure as for compound **5d**. Yield: 60% (from *endo*-type of **3a**); 76% (from *exo*-type of **3a**). $[\alpha]_D^{20} = +125.7$ (*c* 0.31, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.12–7.37 (m, 10H), 6.48 (d, 1H, *J* = 3.84 Hz), 5.55 (s, 1H), 5.51 (t like, 1H, *J* = 9.90, 9.60 Hz), 4.32 (dd, 1H, *J* = 10.44, 4.98 Hz), 4.08–4.03 (m, 1H), 3.98 (dd, 1H, *J* = 9.66, 3.84 Hz), 3.79–3.74 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.8, 164.9, 136.7, 133.9, 130.0, 129.2, 128.8, 128.7, 128.2, 126.1, 101.6, 92.5, 78.1, 72.4, 71.1, 68.6, 65.1, 21.0. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{22}O_8Na$ $[M+Na]^+$ 437.1212, found 437.1211.

4.14. 1-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranose (5h)

By following the same procedure as for compound **5e**. Yield: 79% (from *endo*-type of **3b**); 88% (from *exo*-type of **3b**). $[\alpha]_D^{20} = +107.1$ (*c* 0.32, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.07–7.19 (m, 15H), 6.49 (d, 1H, *J* = 3.66 Hz), 5.63 (s, 1H), 5.08 (d, 1H, *J* = 11.46 Hz), 5.08 (d, 1H, *J* = 11.46 Hz), 4.83 (d, 1H, *J* = 11.46 Hz), 4.33 (dd, 1H, *J* = 10.50, 5.04 Hz), 4.08–4.03 (m, 2H), 3.99 (dd, 1H, *J* = 9.18, 3.66 Hz), 3.83–3.77 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.0, 138.0, 137.0, 133.7, 129.9, 129.0, 128.6, 128.5, 128.3, 128.2, 128.2, 128.0, 125.9, 101.3, 92.2, 81.7, 78.4, 75.0, 71.1, 68.7, 65.2. HRMS (ESI) *m*/*z* calcd for $C_{27}H_{26}O_7Na$ $[M+Na]^+$ 485.1576, found 485.1560.

4.15. 1-*O*-Benzoyl-3-*O*-*tert*-butyldimethylsiloxy-4,6-*O*-benzylidene-α-D-glucopyranose (5i)

Following the same procedure as for compound **5f**. Yield: 84% (from *endo*-type of **3b**); 92% (from *exo*-type of **3b**). $[\alpha]_D^{20} = +64.9$ (*c* 0.32, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, 2H, *J* = 7.38 Hz), 7.62 (t, 1H, *J* = 7.32 Hz), 7.52–7.49 (m, 4H), 7.39–7.36 (m, 3H), 6.51 (d, 1H, *J* = 3.66 Hz), 5.55 (s, 1H), 4.30 (dd, 1H, *J* = 10.08, 4.62 Hz), 4.12 (t, 1H, *J* = 9.18 Hz), 4.02–3.98 (m, 1H), 3.90 (dd, 1H, *J* = 8.28, 3.66 Hz), 3.75 (t like, 1H, *J* = 10.98, 10.08 Hz, 3.59 (t, 1H, *J* = 10.08, 9.12 Hz), 0.90 (s, 9H), 0.10, 0.09 (s, 3H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 137.0, 133.7, 129.9, 129.4, 129.0, 128.6, 128.1, 126.2, 101.8, 92.4, 81.2, 72.8, 72.8, 68.7, 65.3, 25.8, 25.6, 18.3, −3.7, −4.2, −4.8. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{35}O_7Si$ $[M+H]^+$ 487.2152, found 487.2131.

4.16. 2-*O*-Acetyl-3-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranose (6d)

Yield: 93%. α/β = 1:0.5, a white amorphous solid. ^1H NMR (600 MHz, $CDCl_3$): δ 8.04–7.29 (m, 15H, ArH), 5.91 (t like, 1H, *J* = 10.08, 9.60 Hz), 5.65 (t like, 1H, *J* = 9.66, 9.60 Hz), 5.53 (s, 1H), 5.52 (s, 0.5H), 5.49 (d, 1H, *J* = 3.66 Hz), 5.15 (dd, 1H, *J* = 10.08, 3.66 Hz), 5.09 (dd, 0.5H, *J* = 9.6, 8.22 Hz), 4.91 (d, 0.5H, *J* = 8.28 Hz), 4.41 (dd, 0.5H, *J* = 10.98, 5.04 Hz), 4.33 (dd, 1H, *J* = 10.08, 5.04 Hz), 4.30–4.26 (m, 1H), 3.87–3.78 (m, 3H), 3.68–3.64 (m, 0.5H), 2.02 (s, 1.5H), 2.01 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.0, 170.5, 165.6, 136.8, 136.6, 133.4, 133.2, 129.8, 129.5, 129.2, 129.0, 129.0, 128.4, 128.4, 128.1, 126.1, 126.1, 101.5, 101.4, 96.0, 91.1, 79.4, 78.7, 74.0, 71.7, 71.7, 69.4, 68.8, 68.5, 66.7, 62.5, 20.7. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{22}O_8Na$ $[M+Na]^+$ 437.1212, found 437.1224.

4.17. 2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (6e)

Yield: 94%. α/β = 1:0.8, a white amorphous solid. ^1H NMR (600 MHz, $CDCl_3$): δ 7.51–7.26 (m, 20H), 5.60 (s, 1H), 5.58 (s, 0.8H), 4.92–4.85 (m, 4H), 4.72 (d, 1H, *J* = 11.82 Hz), 4.70 (d, 1H, *J* = 12.90 Hz), 4.67 (d, 0.8H, *J* = 7.98 Hz), 4.37 (dd, 1H, *J* = 10.44,

4.98 Hz), 4.29 (dd, 1H, *J* = 10.44, 4.92 Hz), 4.14–4.07 (m, 2H), 3.82–3.71 (m, 5H), 3.50–3.46 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 170.4, 138.3, 138.0, 137.2, 137.0, 129.0, 128.3, 128.3, 128.2, 128.8, 127.7, 126.0, 126.0, 101.3, 101.2, 96.3, 91.1, 82.0, 81.5, 77.9, 75.7, 75.5, 74.8, 74.4, 73.1, 68.9, 68.5, 66.5, 62.4, 20.9. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{24}O_7Na$ $[M+Na]^+$ 423.1420, found 423.1429.

4.18. 2-*O*-Acetyl-3-*O*-*tert*-butyldimethylsiloxy-4,6-*O*-benzylidene-D-glucopyranose (6f)

Yield: 95%. α/β = 1:0.9, a white amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50–7.33 (m, 10H), 5.53 (s, 1H), 5.52 (s, 0.8H), 5.42 (d, 1H, *J* = 3.84 Hz), 4.80–4.76 (m, 2H), 4.66 (d, 1H, *J* = 8.28 Hz), 4.36 (dd, 1H, *J* = 10.44, 4.98 Hz), 4.26 (dd, 1H, *J* = 10.20, 4.98 Hz), 4.19 (t like, 1H, *J* = 9.30, 9.06 Hz), 4.10–4.05 (m, 1H), 3.91 (t like, 1H, *J* = 9.06, 8.76 Hz), 3.78 (t like, 1H, *J* = 10.44, 10.14 Hz), 3.73 (t like, 1H, *J* = 10.44, 10.14 Hz), 3.55–3.50 (m, 2H), 3.48–3.44 (m, 1H), 2.15 (s, 3H), 2.14 (s, 3H), 0.83 (s, 9H), 0.82 (s, 9H), 0.07, 0.05, 0.01, 0.00 (s, 3H each); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.7, 170.4, 137.1, 136.9, 129.0, 128.9, 128.1, 128.1, 126.2, 126.2, 101.8, 101.8, 96.3, 91.1, 82.0, 81.5, 74.5, 72.1, 69.1, 68.9, 68.5, 66.5, 62.4, 25.6, 25.6, 21.1, 21.0, 18.1, 18.0, −4.3, −4.9, −5.0. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{32}O_7SiNa$ $[M+Na]^+$ 447.1815, found 447.1821.

4.19. 3-*O*-Acetyl-2-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranose (6g)

Yield: 93%. α/β = 1:0.4, a white amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05–7.34 (m, 15H), 5.85 (t like, 1H, *J* = 10.08, 9.6 Hz), 5.62 (d, 1H, *J* = 3.66 Hz), 5.58 (t like, 0.5H, *J* = 9.66, 9.60 Hz), 5.54 (s, 1H), 5.53 (s, 0.5H), 5.12 (dd, 0.5H, *J* = 9.60, 7.74 Hz), 5.08 (dd, 1H, *J* = 10.08, 3.66 Hz), 4.92 (d, 0.5H, *J* = 7.8 Hz), 4.40 (dd, 0.5H, *J* = 10.56, 5.04 Hz), 4.32 (dd, 1H, *J* = 10.08, 5.04 Hz), 4.27–4.23 (m, 1H), 3.85–3.71 (m, 3H), 3.64–3.60 (m, 0.5H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.1, 170.0, 166.9, 165.9, 136.9, 136.7, 133.8, 133.6, 130.0, 129.9, 129.1, 128.9, 128.6, 128.2, 126.2, 126.1, 101.6, 101.5, 96.3, 91.0, 79.0, 78.5, 74.9, 72.7, 70.9, 68.8, 68.6, 68.5, 66.7, 62.5, 20.8, 20.7. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{22}O_8Na$ $[M+Na]^+$ 437.1212, found 437.1228.

4.20. 2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (6h)

Yield: 92%. α/β = 1:0.8, a white amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04–7.16 (m, 30H), 5.63 (s, 1H), 5.61 (s, 0.8H), 5.56 (d, 1H, *J* = 3.66 Hz), 5.15–5.12 (m, 1.8H), 4.90 (d, 1H, *J* = 11.94 Hz), 4.87 (d, 0.8H, *J* = 11.88 Hz), 4.82–4.78 (m, 1.8H), 4.76 (d, 0.8H, *J* = 11.88 Hz), 4.40 (dd, 0.8H, *J* = 10.56, 5.04 Hz), 4.32 (dd, 1H, *J* = 10.08, 5.04 Hz), 4.26 (t like, 1H, *J* = 9.60, 9.18 Hz), 4.20–4.16 (m, 1H), 3.95 (t like, 0.8H), 3.85–3.79 (m, 4H), 3.56–3.53 (m, 0.8H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 165.9, 138.1, 137.6, 137.3, 137.1, 133.6, 133.3, 130.0, 129.9, 129.7, 129.4, 129.1, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 126.0, 126.0, 101.3, 101.3, 96.4, 91.2, 82.2, 81.7, 77.4, 76.1, 75.3, 74.7, 74.3, 73.6, 68.9, 68.6, 66.5, 62.4. HRMS (ESI) *m*/*z* calcd for $C_{27}H_{26}O_7Na$ $[M+Na]^+$ 485.1576, found 485.1579.

4.21. 2-*O*-Benzoyl-3-*O*-*tert*-butyldimethylsiloxy-4,6-*O*-benzylidene-D-glucopyranose (6i)

Yield: 94%. α/β = 1:0.85, a white amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11–7.36 (m, 20H), 5.56 (s, 1H), 5.55 (s, 0.85H), 5.12 (dd, 1H, *J* = 9.12, 3.66 Hz), 5.09 (t, 0.85H, *J* = 8.7 Hz), 4.82 (d, 0.85H, *J* = 8.22 Hz), 4.40–4.35 (m, 2H), 4.30 (dd, 1H, *J* = 10.08, 4.62 Hz), 4.17–4.07 (m, 2H), 3.82 (t, 1H, *J* = 10.08 Hz), 3.77 (t, 1H, *J* = 10.08 Hz), 3.64–3.59 (m, 2H), 3.56–3.52 (m, 0.9H), 0.71 (s, 9H), 0.69 (s, 9H), 0.00 (s, 3H), −0.02 (s, 2.7H), −0.04 (s, 3H), −0.08 (s, 2.7H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.9, 165.9, 137.2, 133.5, 133.3, 139.9, 129.6, 129.0, 129.0, 128.4, 128.2, 128.1, 126.3, 126.2, 101.9, 101.8, 96.4, 91.4, 82.2, 81.6, 74.5, 74.6, 72.4, 69.3, 68.9, 68.6, 66.6, 62.5, −4.2, −4.84, −5.0. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{34}O_7SiNa$ $[M+Na]^+$ 509.1972, found 509.1976.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2011.08.008.

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