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A SYNTHETIC APPROACH TO DERIVE *EXO*-GLUCAL DERIVATIVES THROUGH THE REACTION OF A 1-*C*-VINYLATED GLUCOPYRANOSE DERIVATIVE WITH PHENOLS†

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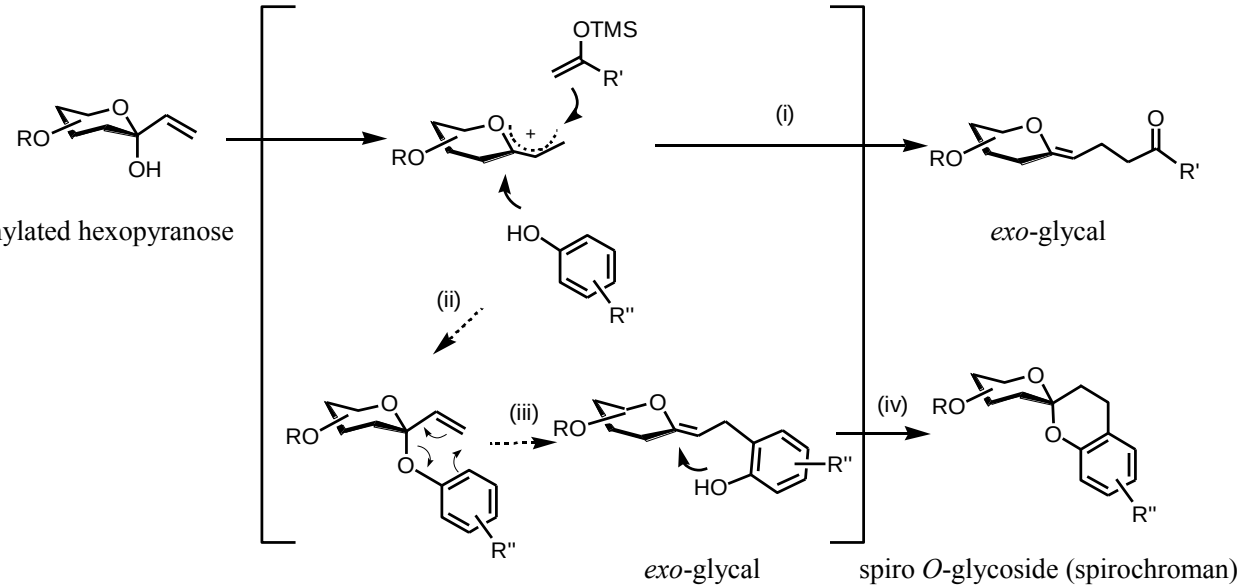
†Dedicated to Professor Dr. Kiyoshi Tomioka on his 70th Birthday

Abstract – In this study, a synthetic approach to prepare *exo*-glucal derivatives through the reaction of a 1-*C*-vinylated glucopyranose derivative with phenols in the presence of an appropriate promoter has been investigated. The reaction between 2,3,4,6-tetra-*O*-benzyl-1-*C*-vinyl-α-D-glucopyranose and different phenols using 5 mol% $Bi(OTf)_3$ produced the corresponding *exo*-glucal derivatives as major products along with spiro *O*-glucoside derivatives as minor products.

exo-Glycals are cyclic unsaturated sugars that contain a double bond attached to the anomeric center outside the sugar ring. Due to their utility as precursors for the synthesis of various carbohydrate-related compounds,[1] the development of methods for the synthesis of *exo*-glycals has been an important topic in carbohydrate chemistry. Although a number of methods, such as the Wittig olefination of sugar lactones, the Ramberg–Backlund rearrangement of *S*-glycosides, and the Keck reaction of glycosyl dihalides, have proved to be useful for the synthesis of *exo*-glycals,[2] the development of various methods for obtaining functionalized *exo*-glycals has recently attracted a great deal of attention. In this situation, we have successfully reported a synthetic approach to *exo*-glycals based on an S_N1' reaction mechanism using

1-*C*-vinylated hexopyranose derivatives and trimethylsilyl enol ethers, as illustrated in Scheme 1 (i).[3] The 1-*C*-vinylated hexopyranose derivatives are thus demonstrated to be useful precursors for the synthesis of valuable compounds. Van Hooft et al. reported the reaction of a 1-*C*-vinylated glucopyranose derivative with phenols using K-10 clay as a promoter to produce spiro *O*-glucoside derivatives that depict a similar spirochroman structure, as depicted in Scheme 1 (ii–iv).[4] This reaction was proposed to proceed through a consecutive three-step mechanism as follows: first, the *O*-glycosylation between a 1-*C*-vinylated glucopyranose derivative and phenols produces aryl *O*-glucosides; the second step involves the conversion of aryl *O*-glucosides into *exo*-glucal derivatives through a Claisen rearrangement; in the third step, the intramolecular *O*-glycosylation of the *exo*-glucal derivatives was conducted to form the corresponding spiro *O*-glucoside derivatives, which were successfully isolated. However, the intermediates, such as aryl *O*-glucoside and *exo*-glucal derivatives were not isolated, which indicates that the second and third steps proceeded smoothly after initiating *O*-glycosylation. We further envisaged a virtually novel method for synthesizing the *exo*-glucal derivatives that would require a precise control of the reaction between 1-*C*-vinylated glucopyranose derivatives and phenols in order to terminate the reaction at the Claisen rearrangement stage. This study describes a synthetic approach to produce *exo*-glucal derivatives through the reaction of 1-*C*-vinylated glucopyranose with phenols in the presence of an appropriate promoter. The elucidation of the reaction mechanism to form spiro *O*-glucoside derivatives from *exo*-glucal during this consecutive reaction process has also been included in this study.

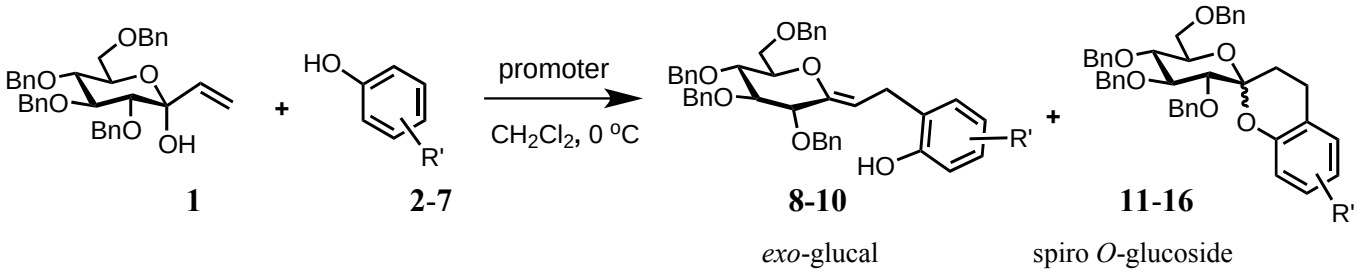


(i) S_N1' reaction, (ii) *O*-glycosylation, (iii) Claisen rearrangement reaction, (iv) intramolecular *O*-glycosylation

Scheme 1. Synthetic mechanisms to produce *exo*-glycals and spiro *O*-glycosides from 1-*C*-vinylated hexoses

First, we investigated the reaction between 2,3,4,6-tetra-*O*-benzyl-1-*C*-vinyl-α-D-glucopyranose (**1**) and phenol (**2**) as a model reaction using a promoter, as depicted in Scheme 2. The reaction of **1** with **2** was performed under conditions that were similar to those of our formerly reported ketosylation reactions.[5] We tested some rare metal triflates or Brφnsted acids, such as scandium triflate ($Sc(OTf)_3$), ytterbium(III) triflate ($Yb(OTf)_3$), bismuth(III) triflate ($Bi(OTf)_3$), triflic acid (TfOH), or triflimide (Tf_2NH) as the promoters, which had proved to be useful in the ketosylation reactions. When the reactions of **1** with **2** were conducted using 5 mol% promoter in dichloromethane at 0 °C for 0.5 to 2 h in the presence of anhydrous calcium sulfate, those using $Bi(OTf)_3$ and TfOH produced spiro *O*-glucoside **11** in yields of only 55% and 47%, respectively (Table 1, Entries 3 and 4). However, $Yb(OTf)_3$ and $Sc(OTf)_3$ did not effectively promote the reactions (Table 1, Entries 1 and 2). The reaction using 1 mol% $Bi(OTf)_3$ did not proceed at all (Table 1, Entry 5), whereas 20 mol% $Bi(OTf)_3$ produced **11** in a moderate yield of 45% (Table 1, Entry 6). Since the formation of the phenyl *O*-glucoside and *exo*-glucal derivatives was not observed during the aforementioned reactions, both the Claisen rearrangement and the following intramolecular *O*-glycosylation during this consecutive reaction process would proceed smoothly immediately after the occurrence of the initial *O*-glycosylation reaction, as was predicted.

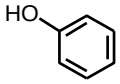
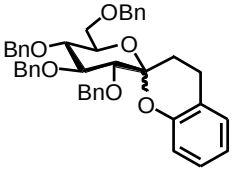
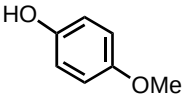
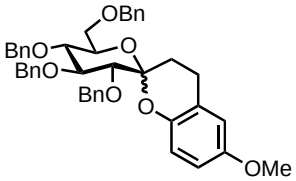
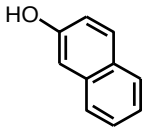
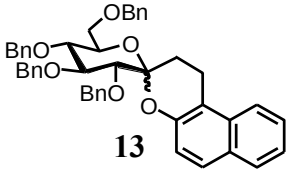
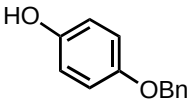
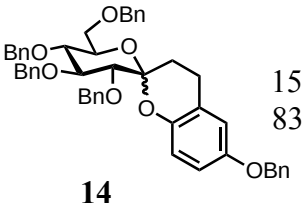
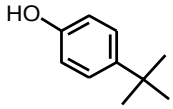
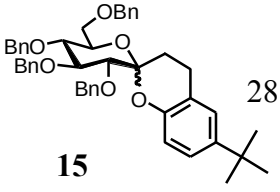
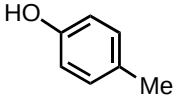
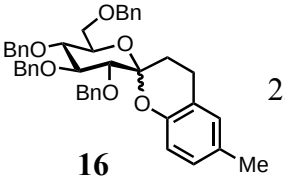
Further, we investigated whether the structure of phenols could have an influence on the progress of this consecutive process. Several reactions were investigated using other types of phenols (**3**–**7**). When the reaction of **1** and *p*-methoxyphenol (**3**) was performed under similar conditions using 5 mol% $Bi(OTf)_3$, TfOH, or Tf_2NH, spiro *O*-glucoside **12** was obtained in 78%–84% yields (Table 1, Entries 7–9). Modifying the reaction temperature did not seem to cause any effect and generated **12** in yields of 73% and 82% at room temperature and −10 °C, respectively (Table 1, Entries 10 and 11). When 5 mol% $Bi(OTf)_3$ or TfOH were used, the reaction of **1** with β-naphtol (**4**) produced the spiro *O*-glucoside **13** in high yields of 94% or 98%, respectively (Table 1, Entries 12 and 13).



Scheme 2. Reaction of 1-*C*-vinylated glucopyranose with phenols in the presence of a promoter

Different results were obtained from the reactions using *p*-benzyloxyphenol (**5**), *p*-*tert*-butylphenol (**6**), and *p*-methylphenol (**7**). The desired *exo*-glucal derivative **8** was successfully isolated in a yield of 74% as a major product from the reaction of **1** with **5** in the presence of 5 mol% $Bi(OTf)_3$, along with the

Table 1. Products formed by the reaction of **1** with phenols in the presence of a promoter

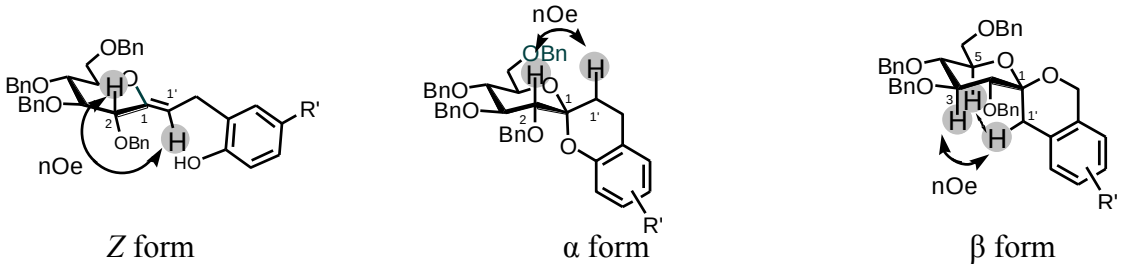
Entry[a)]	Phenols	Promoter (mol%)	Product		
			exo-Glucal Yield/%	Spiro *O*-glucoside Yield/%	(α/β ratio)
1	 **2**	$Yb(OTf)_3$ (5)	-[b)]	 **11**	trace
2		$Sc(OTf)_3$ (5)	-		trace
3		$Bi(OTf)_3$ (5)	-		55 (49/51)
4		TfOH (5)	-		47 (53/47)
5		$Bi(OTf)_3$ (1)	-		-
6		$Bi(OTf)_3$ (20)	-		45 (54/46)
7	 **3**	$Bi(OTf)_3$ (5)	-	 **12**	80 (63/37)
8		TfOH (5)	-		84 (88/12)
9		Tf_2NH (5)	-		78 (88/12)
10		$Bi(OTf)_3$ (5)[c)]	-		73 (90/10)
11		$Bi(OTf)_3$ (5)[d)]	-		82 (48/52)
12	 **4**	$Bi(OTf)_3$ (5)	-	 **13**	94 (51/49)
13		TfOH (5)	-		98 (53/47)
14	 **5**	$Bi(OTf)_3$ (5)	74	 **14**	15 (56/44)
15		TfOH (5)	-		83 (53/47)
16	 **6**	$Bi(OTf)_3$ (5)	68	 **15**	28 (56/44)
17	 **7**	$Bi(OTf)_3$ (5)	67	 **16**	23 (55/45)

a) Reaction conditions: molar ratio; **1**: phenols= 1: 2; Reaction time= 0.5-2 h. b) Not detected. c) Temperature= rt. d) Temperature= -10 °C.

concomitant formation of spiro *O*-glucoside **14** in 15% yield as a minor product (Table 1, Entry 14).[6] The reactions using **6** and **7** depicted a similar behavior. Thus, the reaction of **1** with **6** or **7** using 5 mol%

$Bi(OTf)_3$ produced the corresponding *exo*-glucal derivatives **9** or **10** as major products in 68% and 67% yield, respectively, and spiro *O*-glucoside **15** or **16** as minor products in 28% and 23% yield, respectively (Table 1, Entries 16 and 17). Therefore, the reactions of **1** and phenols proved to be successful in producing several *exo*-glucal derivatives as isolable compounds. Additionally, the involvement of the *exo*-glucal derivatives as intermediates in the formation of the spiro *O*-glucosides during this reaction is supported in these results. It is worth noting that the difference between the promoting abilities of $Bi(OTf)_3$ and TfOH was evident during this process because 5 mol% TfOH in the reaction between **1** and **5** produced only spiro *O*-glucoside **14** in a yield of 83%. Although the promoters that were used in this study work both at the initial *O*-glycosylation and at the final intramolecular *O*-glycosylation, $Bi(OTf)_3$ does not seem to promote the intramolecular *O*-glycosylation step to form the spiro O-glucoside derivatives from the *exo*-glucal derivatives in the reactions using **5**–**7**. Although the reason for $Bi(OTf)_3$ hindering this intramolecular *O*-glycosylation is not clear, steric or electronic factors of the *exo*-glucal derivatives that were produced *in situ* can be considered to be accountable for this behavior.

As nOe interactions between H-1′ and H-2 were observed as depicted in Figure 1 (i), the geometric isomers of the produced *exo*-glucal derivatives **8**–**10** were determined to be the *Z* forms. All the spiro *O*-glucosides **14**–**16** were obtained as mixtures of α- and β-isomers, whose stereochemistry were also determined by the nOe interactions between H-1′ and H-2 or between H-1′ and H-3 or H-5, as depicted in Figure 1 (ii).



Z form α form β form

(i) *exo*-glucal (ii) spiro *O*-glucoside

Figure 1. Determination of the geometric isomers of **8**–**10** and the anomeric isomers of **11**–**16**

Thus, a successful synthetic approach to derive *exo*-glucal derivatives through the reaction of a 1-*C*-vinylated hexopyranose with a variety of phenols was demonstrated. We observed that the reactions between 2,3,4,6-tetra-*O*-benzyl-1-*C*-vinyl-α-D-glucopyranose and different phenols using 5 mol% $Bi(OTf)_3$ produced the corresponding *exo*-glucal derivatives as major products along with spiro *O*-glucoside derivatives as minor products. The *exo*-glucal derivatives were thereby demonstrated to be intermediates in the formation of the spiro *O*-glucoside derivatives during this consecutive reaction.

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6. Typical reaction procedure: $Bi(OTf)_3$ and $CaSO_4$ were dried under vacuum at 200 °C for 2 h. A solution of **5** (76 mg, 0.38 mmol) in CH_2Cl_2 (1.5 mL) was added to a solution containing **1** (106.6 mg, 0.188 mmol) and $Bi(OTf)_3$ (6.4 mg, 0.0098 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C. The resulting mixture was stirred for 1 h at 0 °C. The reaction was further quenched by adding a saturated aqueous $NaHCO_3$ solution (5 mL). The reaction mixture was extracted using EtOAc, and the organic layer was washed with water and a saturated aqueous NaCl solution. After the organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure. The crude products were purified using preparative silica-gel TLC (EtOAc/hexane = 1/3) to produce **8** (104.9 mg, 74% yield) and **14** (21.3 mg, 15% yield) as oils. Compound **8**: ^{1}H NMR ($CDCl_3$): δ 3.29 (dd, *J* = 8.2 Hz, *J* = 14.4 Hz, Ha-2'), 3.44 (dd, *J* = 7.6 Hz, *J* = 14.4 Hz, Hb-2'), 3.92 (d, *J* = 4.8 Hz, H-2), 5.09 (t, *J* = 8.2 Hz, H-1'), 6.25 (s, OH); ^{13}C NMR ($CDCl_3$): δ 26.2 (C-2'), 68.8 (C-6), 77.6 (C-4, C-5), 78.1 (C-2), 84.3 (C-3), 108.6 (C-1'), 142.7(C-1): ESI-MS *m/z* calcd for $C_{49}H_{48}O_7 \cdot Na^+$: 771.3292; found: 771.3283. Compound **14** (α and β mixture): α Form: ^{1}H NMR ($CDCl_3$): δ 1.64 (dd, *J* = 5.5 Hz, *J* = 13.8 Hz, H-1'ax), 2.09-2.18 (m, H-1'eq), 2.54 (dd, *J* = 5.5 Hz, *J* = 15.8 Hz, Ha-2'), 2.98 (dt, *J* = 6.2 Hz, *J* = 15.8 Hz, Hb-2'), 4.33 (t, *J* = 9.6 Hz, H-3): ^{13}C NMR ($CDCl_3$): δ 20.0 (C-2'), 26.9 (C-1'), 68.4 (C-6), 71.7 (C-5), 78.4 (C-4), 82.6 (C-2), 83.1 (C-3), 98.3 (C-1): β Form: ^{1}H NMR ($CDCl_3$): δ 2.09-2.18 (m, H-1'eq), 2.25 (dd, *J* = 3.4 Hz, *J* = 14.4 Hz, H-1'ax), 2.56 (dd, *J* = 4.1 Hz, *J* = 15.8 Hz, Ha-2'), 2.85 (dt, *J* = 5.5 Hz, *J* = 15.2 Hz, Hb-2'): ^{13}C NMR ($CDCl_3$): δ 16.5 (C-2'), 21.2 (C-1'), 69.2 (C-6), 73.2 (C-5), 78.3 (C-4), 83.5 (C-3), 83.9 (C-2), 100.4 (C-1): ESI-MS *m/z* calcd for $C_{49}H_{48}O_7 \cdot Na^+$: 771.3292; found: 771.3267. Compound **9**: ^{1}H NMR ($CDCl_3$): δ 1.30 (s, CH_3), 3.33 (dd, *J* = 7.6 Hz, *J* = 14.4 Hz, Ha-2'), 3.47 (dd, *J* = 8.2 Hz, *J* = 14.4 Hz, Hb-2'), 3.92 (d, *J* = 5.5 Hz, H-2), 5.09 (t, *J* = 8.2 Hz, H-1'), 6.33 (s, OH): ^{13}C NMR ($CDCl_3$): δ 26.4 (C-2'), 31.6 (CH_3), 34.0 ($C(CH_3)_3$), 68.8

(C-6), 77.5 (C-5), 77.7 (C-3 or C-4), 78.1 (C-2), 84.4 (C-3 or C-4), 109.0 (C-1'), 147.3 (C-1): ESI-MS *m/z* calcd for $C_{46}H_{50}O_6 \cdot Na^+$: 721.3500; found: 721.3508. Compound **15** (α and β mixture): α Form: ^{1}H NMR ($CDCl_3$): δ 1.23 (s, CH_3), 1.71 (dd, *J* = 5.5 Hz, *J* = 13.1 Hz, H-1'ax), 2.14 (dt, *J* = 5.5 Hz, *J* = 13.0 Hz, H-1'eq), 2.56 (dd, *J* = 5.5 Hz, *J* = 15.8 Hz, Ha-2'), 3.00 (dt, *J* = 5.5 Hz, *J* = 15.1 Hz, Hb-2'), 3.50 (d, *J* = 9.6 Hz, H-2), 4.35 (t, *J* = 9.0 Hz, H-3): ^{13}C NMR ($CDCl_3$): δ 21.0 (C-2'), 27.2 (C-1'), 31.5 (CH_3), 34.0 ($C(CH_3)_3$), 68.5 (C-6), 71.7 (C-5), 78.5 (C-4), 82.8 (C-2), 83.1 (C-3), 98.4 (C-1): β Form: ^{1}H NMR ($CDCl_3$): δ 1.31 (s, $C(CH_3)_3$), 2.11-2.21 (m, H-1'eq), 2.27-2.30 (m, H-1'ax), 2.62 (dd, *J* = 4.2 Hz, *J* = 15.8 Hz, Ha-2'), 2.87 (dt, *J* = 4.8 Hz, *J* = 15.1 Hz, Hb-2'), 3.59 (dd, *J* = 4.8 Hz, *J* = 10.3 Hz, H-6a), 3.80 (d, *J* = 7.6 Hz, H-2): ^{13}C NMR ($CDCl_3$): δ 21.3 (C-2'), 30.9 (C-1'), 31.6 (CH_3), 34.1 ($C(CH_3)_3$), 69.1 (C-6), 73.1 (C-5), 78.2 (C-4), 83.4 (C-3), 84.0 (C-2), 100.7 (C-1): ESI-MS *m/z* calcd for $C_{46}H_{50}O_6 \cdot Na^+$: 721.3500; found: 721.3467. Compound **10**: ^{1}H NMR ($CDCl_3$): δ 2.25 (s, CH_3), 3.29 (dd, *J* = 7.6 Hz, *J* = 14.4 Hz, Ha-2'), 3.43 (dd, *J* = 8.9 Hz, *J* = 14.4 Hz, Hb-2'), 3.92 (d, *J* = 5.5 Hz, H-2), 5.09 (t, *J* = 8.3 Hz, H-1'), 6.28 (s, OH): ^{13}C NMR ($CDCl_3$): δ 20.4 (CH_3), 26.1 (C-2'), 68.8 (C-6), 77.6 (C-5), 77.7 (C-3 or C-4), 78.2 (C-2), 84.4 (C-3 or C-4), 108.9 (C-1'), 147.5 (C-1); ESI-MS *m/z* calcd for $C_{43}H_{44}O_6 \cdot Na^+$: 679.3030; found: 679.3031. Compound **16** (α and β mixture): α Form: ^{1}H NMR ($CDCl_3$): δ 1.67 (dd, *J* = 5.5 Hz, *J* = 13.1 Hz, H-1'ax), 2.12 (dt, *J* = 5.5 Hz, *J* = 13.0 Hz, H-1'eq), 2.24 (s, C*H*$_3$), 2.53 (dd, *J* = 5.5 Hz, *J* = 15.8 Hz, Ha-2'), 2.96 (dt, *J* = 5.5 Hz, *J* = 15.2 Hz, Hb-2'), 4.34 (t, *J* = 9.0 Hz, H-3): ^{13}C NMR ($CDCl_3$): δ 20.5 (CH_3), 20.7 (C-2'), 27.1 (C-1'), 68.5 (C-6), 71.8 (C-5), 78.5 (C-4), 82.8 (C-2), 83.2 (C-3), 98.4 (C-1): β Form: ^{1}H NMR ($CDCl_3$): δ 2.15 (dt, *J* = 5.5 Hz, *J* = 14.5 Hz, H-1'eq), 2.29 (s, CH_3), 2.26-2.28 (m, H-1'ax), 2.59 (dd, *J* = 4.1 Hz, *J* = 15.8 Hz, Ha-2'), 2.84 (dt, *J* = 5.5 Hz, *J* = 15.1 Hz, Hb-2'), 3.77 (d, *J* = 8.2 Hz, H-2), 3.78 (d, *J* = 7.6 Hz, H-3): ^{13}C NMR ($CDCl_3$): δ 19.6 (CH_3), 21.2 (C-2'), 23.3 (C-1'), 69.2 (C-6), 73.0 (C-5), 78.2 (C-4), 83.4 (C-3), 84.0 (C-2), 100.7 (C-1): ESI-MS *m/z* calcd for $C_{43}H_{44}O_6 \cdot Na^+$: 679.3030; found: 679.3073. Compound **11** (α and β mixture): α Form: ^{1}H NMR ($CDCl_3$): δ 1.69 (dd, *J* = 6.2 Hz, *J* = 13.1 Hz, H-1'ax), 2.03-2.20 (m, H-1'eq), 2.64 (dd, *J* = 4.8 Hz, *J* = 15.8 Hz, Ha-2'), 2.88 (dt, *J* = 4.8 Hz, *J* = 15.1 Hz, Hb-2'), 3.50 (d, *J* = 9.6 Hz, H-2), 4.36 (t, *J* = 9.6 Hz, H-3): ^{13}C NMR ($CDCl_3$): δ 19.6 (C-2'), 27.0 (C-1'), 69.1 (C-6), 71.8 (C-5), 82.6 (C-2), 83.2 (C-3), 98.4 (C-1): β Form: ^{1}H NMR ($CDCl_3$): δ 2.03-2.20 (m, H-1'eq), 2.29 (dd, *J* = 4.8 Hz, *J* = 14.4 Hz, H-1'ax), 2.58 (dd, *J* = 6.2 Hz, *J* = 15.8 Hz, Ha-2'), 3.01 (dt, *J* = 6.2 Hz, *J* = 14.5 Hz, Hb-2'), 3.78-3.86 (m, H-2, H-3, H-4): ^{13}C NMR ($CDCl_3$): δ 20.7 (C-2'), 21.1 (C-1'), 68.4 (C-6), 73.0 (C-5), 78.4 (C-2 or C-4), 83.4 (C-3), 83.9 (C-2 or C-4), 100.7 (C-1): ESI-MS *m/z* calcd for $C_{42}H_{42}O_6 \cdot Na^+$: 665.2874; found: 665.2815. Compound **12** (α and β mixture): α Form: ^{1}H NMR ($CDCl_3$): δ 1.65 (dd, *J* = 6.2 Hz, *J* = 13.7 Hz, H-1'ax), 2.11-2.18 (m, H-1'eq), 2.55 (dd, *J* = 5.5 Hz, *J* = 15.9 Hz, Ha-2'), 2.98 (dt, *J* = 5.5 Hz, *J* = 15.1 Hz, Hb-2'), 3.50 (d, *J* = 9.6 Hz, H-2), 3.70 (s, CH_3), 4.33-4.34 (m,

H-3): ^{13}C NMR ($CDCl_3$): δ 20.1 (C-2'), 27.0 (C-1'), 55.5 (CH_3), 68.4 (C-6), 71.7 (C-5), 78.5 (C-4), 82.7 (C-2), 83.2 (C-3), 98.3 (C-1): β Form: ^{1}H NMR ($CDCl_3$): δ 2.11-2.18 (m, H-1'eq), 2.26 (dd, *J* = 5.5 Hz, *J* = 14.4 Hz, H-1'ax), 2.59 (dd, *J* = 4.8 Hz, *J* = 12.8 Hz, Ha-2'), 2.85 (dt, *J* = 5.5 Hz, *J* = 14.5 Hz, Hb-2'), 3.74 (s, CH_3), 3.80-3.85 (m, H-2, H-3): ^{13}C NMR ($CDCl_3$): δ 21.0 (C-2'), 21.1 (C-1'), 55.6 (CH_3), 60.3 (C-6), 69.2 (C-5), 78.2 (C-4), 83.4 (C-2), 84.0 (C-3), 100.6 (C-1): ESI-MS *m/z* calcd for $C_{46}H_{50}O_6 \cdot Na^+$: 695.2979; found: 695.2956. Compound **13** (α and β mixture): α Form: ^{1}H NMR ($CDCl_3$): δ 1.86 (dd, *J* = 5.5 Hz, *J* = 13.1 Hz, H-1'ax), 2.24-2.34 (m, H-1'eq), 3.03-3.15 (m, H-2'), 3.44 (d, *J* = 11.7 Hz, Ha-6), 3.58 (d, *J* = 9.6 Hz, H-2), 3.67-3.74 (m, H-4): ^{13}C NMR ($CDCl_3$): δ 17.6 (C-2'), 26.8 (C-1'), 68.4 (C-6), 71.9 (C-5), 78.5 (C-4), 82.6 (C-2), 83.3 (C-3), 98.3 (C-1): β Form: ^{1}H NMR ($CDCl_3$): δ 2.24-2.34 (m, H-1'eq), 2.47 (dd, *J* = 5.5 Hz, *J* = 14.5 Hz, H-1'ax), 2.95 (dt, *J* = 5.5 Hz, *J* = 13.8 Hz, Hb-2'), 3.03-3.09 (m, Ha-2'), 3.80-3.87 (m, H-3, H-4), 3.91 (d, *J* = 9.6 Hz, H-2): ^{13}C NMR ($CDCl_3$): δ 16.5 (C-2'), 21.1 (C-1'), 69.2 (C-6), 73.2 (C-5), 78.3 (C-4), 83.5 (C-3), 83.9 (C-2), 100.4 (C-1): ESI-MS *m/z* calcd for $C_{46}H_{50}O_6 \cdot Na^+$: 695.2979; found: 695.2956.