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A mild, efficient, and selective procedure for transprotection of acetonides to acetates catalyzed with $HClO_4$–SiO_2

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ABSTRACT

The transformation of acetonides into acetates is frequently required in synthetic chemistry. An efficient procedure for direct conversion of acetonides into acetates in the presence of $HClO_4$–SiO_2 under mild conditions was developed. The acetonides of primary hydroxy groups are directly converted to diacetates, and the anomeric acetonides of furanosides are stereoselectively transformed into the corresponding acetyl β-D-furanosides with a 2-acetoxyisopropyl group.

1. Introduction

Both acetonides and acetates are most frequently used as protecting groups in synthetic chemistry because they are readily introduced and removed,[1–3] particularly, in carbohydrate,[4–9] nucleoside,[10–13] and polyhydroxy compound chemistries.[14–16] In view the fact that the transformation of acetonides into corresponding diacetates is often required in organic synthesis due to the complementary stability of these two kinds of protecting groups,[17–24] studies in this transformation, here termed 'transprotection', are considerably worthy in spite of the limited methods that are currently available.[25]

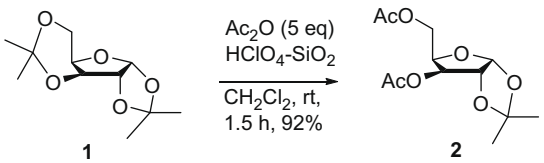
We herein wish to report an effective method for transprotection of isopropylidene acetals into acetates by making use of a cheaper, non-toxic, and reusable catalyst reported by Chakraborti and Gulhane,[26] namely, $HClO_4$–SiO_2 (Scheme 1), which has been used to catalyze a wide range of transformations such as the formation of acetals,[27–29] thioacetals,[30] and acylal,[31,32] acetylation of carbohydrates,[33–35] glycosylation,[36,37] synthesis of quinoxalines,[38] thio-Michael addition,[39] and *N*-Boc formation.[40]

2. Results and discussion

In order to transform 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (**1**) straightforwardly into 3,5-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**2**, Scheme 1) in large scale during the course of our studies in the synthesis of nucleoside mimetics, we found that $HClO_4$–SiO_2 (0.5 mmol/g) is an extremely efficient substitute for $Bi(OTf)_3{\cdot}xH_2O$[25] and is readily removed and recovered via filtration after the reaction is complete.[37]

Treatment of **1** (0.15 mol) with Ac_2O (5 equiv) in CH_2Cl_2 at rt in the presence of $HClO_4$–SiO_2 (7.5 g) afforded **2** in 92% isolated yield (Table 1, entry a). Therefore, we expected to investigate the generality of the application of $HClO_4$–SiO_2 in the transprotection of acetonides into acetates. It could be seen from the results listed in Table 1 that glucose derivatives **3**, **5**, **6,** and **8** were all smoothly and immediately transformed into corresponding acetates **4**, **7,** and **9**, respectively, at rt in quite good yields (Table 1, entries b–e). Additionally, these results also demonstrated that the isopropylidene acetals of primary hydroxyl groups could be selectively transformed into the corresponding acetates in the presence of anomeric acetonides under these one-pot conditions.

As anticipated, both isopropylidene and acyl groups in **10** were simultaneously transformed, respectively, into acetates and acylal



Scheme 1. Selective transprotection of terminal acetonides into diacetates.

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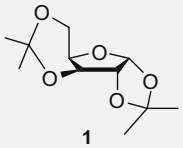
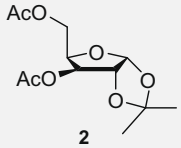
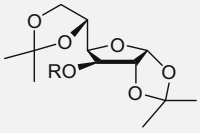
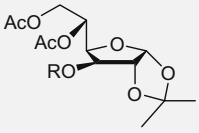
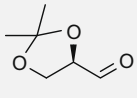
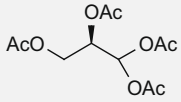
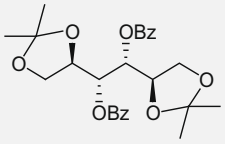
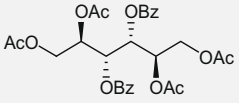
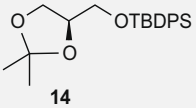
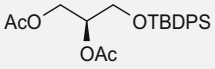
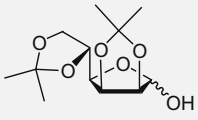
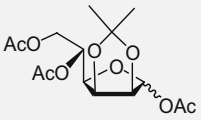
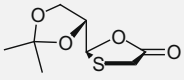
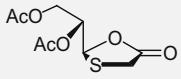
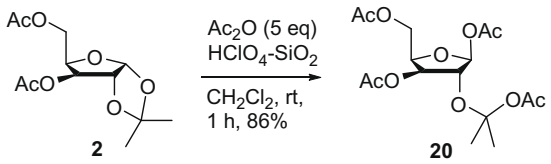
Table 1
Direct transprotection of terminal acetonides into diacetates in the presence of $HClO_4$–SiO_2

Entry	Substrate	Product[a]	Time (h)	Yield[b] (%)
a	 **1**	 **2**	1.5	92[25]
b	 3R H	 4R Ac	7	86[25,43]
c	5R Ac	4R Ac	7	88[25,43]
d	6R Bz	7R Bz	8	90[25]
e	8R Ts	9R Ts	6	90[25]
f	 **10**	 **11**	8	83[41]
g	 **12**	 **13**	4 (reflux)	81
h	 **14**	 **15**	2	78
i	 **16**	 **17**	8	89[25]
j	 **18**	 **19**	0.5	82[42]

[a] Characterized by ^1H NMR, ^{13}C NMR, and ESIMS: Calcd for.
[b] Isolated yields.

groups to give **11** in 83% yield (Table 1, entry f).[41] Surprisingly, transprotection of the two terminal isopropylidene acetals of D-mannitol derivative **12** failed at rt, and the tetra-acetyl product **13** was obtained under reflux in CH_2Cl_2 (Table 1, entry g). Moreover, it was also observed that the *tert*-butyldiphenylsilyl (TBDPS)-protecting group remained intact as the isopropylidene group was selectively transformed (Table 1, entry h). Furthermore, the formation of both products **17** and **19** provided further illustrations of the selectivity and efficiency of this one-pot transprotection procedure: (1) A terminal hydroxyl acetonide was selectively replaced by acetates in the presence of secondary hydroxyl isopropylidene acetal, and (2) the anomeric hydroxy function was concomitantly acetylated (Table 1, entry i).

In addition, we have also tested the application of this one-pot methodology to transprotection of anomeric acetonides (Scheme 2). Treatment of compound **2** with Ac_2O under the same conditions described as above afforded compound **20**, in which the anomeric acetonide was partially cleaved to generate a 2-acetoxyisopropyl group (Table 2, entry a). This isopropylidene chain-opened structure is similar to those that result from catalysis by $Bi(OTf)_3{\cdot}xH_2O$.[25] Following these one-pot conditions, all similar transprotections shown in Table 2 were performed smoothly as more candidates were employed as starting materials. It is noteworthy that hydroxyl group could not interrupt this type of transprotection, and these were acetylated simultaneously (Table 2, entries b and e). We also first observed that the primary *tert*-butyldimethylsilyl (TBDMS) ether group in **36** was selectively transprotected to the corresponding acetate along with the transprotection of the anomeric isopropylidene group to give **37** (Table 2, entry k). As to anomeric acetonide groups in a pyranose, a similar selective transformation was also observed



Scheme 2. Transprotection of anomeric acetonides of furanoses into corresponding acetylated 2-*O*-(2′-acetoxyisopropyl)-β-D-furanosides.

as L-arabinopyranose derivative **38** was converted into an anomeric mixture **39** in quite good yield (Table 2, entry l). The anomeric acetonide group in 6-*O*-acetyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**40**), however, was selectively transprotected to give a pure isomer **41** without an isopropylidene group at the 2-position (Table 2, entry m), which might arise from the participation of the 6-acetyloxy group.

The assignment of the isopropylidene acetal chain-opened structures listed in Table 2 are supported by ^{1}H NMR, ^{13}C NMR,

Table 2
Transprotection of anomeric acetonides of furanoses and pyranoses into corresponding 2-*O*-(2-acetoxyisopropyl)-1-*O*-acetyl-β-D-furanosides and 2-*O*-(2-acetoxyisopropyl)-1-*O*-acetyl-β-D-pyranosides with $HClO_4$–SiO_2

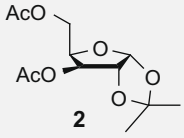
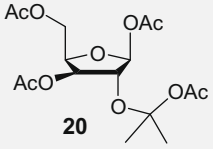
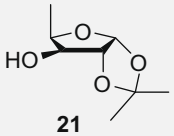
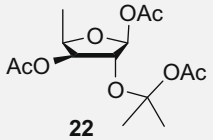
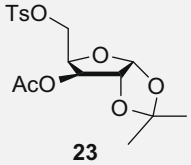
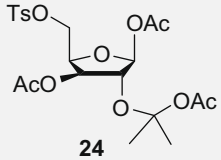
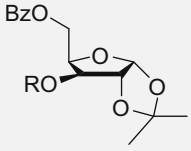
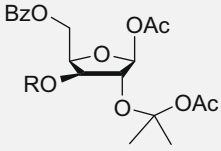
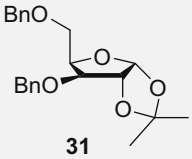
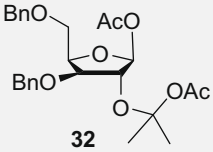
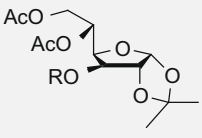
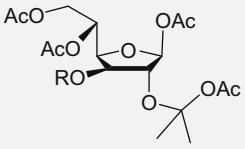
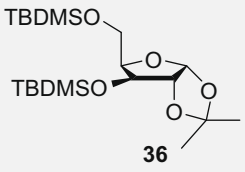
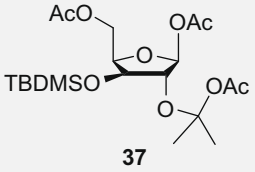
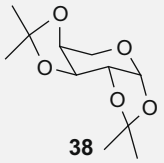
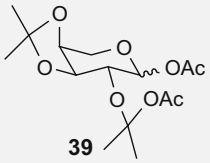
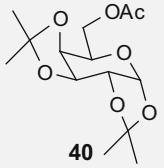
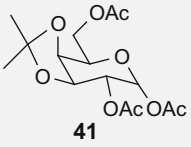
Entry	Substrate		Product[a]		Time (h)	Yield[b] (%)
a	 **2**		 **20**		1	86[25]
b	 **21**		 **22**		1	87
c	 **23**		 **24**		1	84
						
d	25R	Bz	26R	Bz	1	90[25]
e	27R	H	28R	Ac	4	90
f	29R	*p*-Ts	30R	*p*-Ts	1	85[25]
g	 **31**		 **32**		1.5	89[25]
						
h	7R	Bz	33R	Bz	2	89[25]
i	4R	Ac	34R	Ac	1.5	87[25]
j	9R	*p*-Ts	35R	*p*-Ts	2	83[25]

Table 2 (*continued*)

Entry	Substrate	Product[a]	Time (h)	Yield[b] (%)
k	 **36**	 **37**	0.5	84
l	 **38**	 **39**	7.5	82
m	 **40**	 **41**	8	88

[a] Characterized by ^{1}H NMR, ^{13}C NMR, and ESIMS: Calcd for.
[b] Isolated yields.

and ESIMS: Calcd for data, which also provide evidence that all these products are pure anomeric furanosides rather than a mixture. As to compound **20**, the molecular structure was further confirmed to be a β anomer by a NOESY spectrum. In the ^{1}H–^{1}H dimension of the NMR spectrum of compound **20**, two cross-peaks are observed between the resonance signals of the anomeric proton (at δ 6.16) and H-3, 4 (at δ 5.33), and the methyl protons in the isopropylidene group (at δ 1.45), respectively. Furthermore, it is also observed that the methyl protons of the isopropylidene group (at δ 1.45) interact with H-3, 4 (at δ 5.33) and not with H-5 (at δ 4.09–4.36). We believe that these NOESY spectroscopic data provide strong evidence for the β-anomeric configurational assignments.

In conclusion, we have developed a useful procedure for the direct transprotection of terminal hydroxy acetonides into their corresponding acetates in an efficient process and under mild conditions with $HClO_4$–SiO_2 as catalyst. This procedure also provides excellent selectivity in transprotection of primary hydroxy acetonides into acetates in the presence of anomeric acetonides of furanoses. Anomeric acetonides of furanoses are stereoselectively transformed into the corresponding acetyl 2-*O*-(2′-acetoxyisopropyl)-β-D-furanosides. In view of economy and environmental concerns, this one-pot mild procedure might be remarkably valuable in synthetic chemistry. The application of this methodology to the synthesis of nucleosides and their transformations is underway in our laboratory, and the results will be reported in due course.

3. Experimental

3.1. General

CH_2Cl_2 was dried over P_2O_5 and distilled. Ac_2O was distilled before use. All reactions were monitored by thin-layer chromatography (TLC) on silica gel F_{254} plates. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer or a Bruker AV300 spectrometer in $CDCl_3$ or DMSO-d_6 and using TMS as the internal standard. Exact mass measurements were performed on a LCMS2010 spectrometer equipped with a standard electrospray-ionization (ESI) interface.

3.2. Preparation of $HClO_4$–SiO_2

$HClO_4$ (1.8 g) was added to a stirred suspension of SiO_2 (23.7 g, 300–400 mesh) in EtOH (70 mL) and stirred for 10 min. The mixture was concentrated under reduced pressure to give a free-flowing powder ($HClO_4$, 0.5 mmol/g) for application.

3.3. Typical synthetic procedure

$HClO_4$–SiO_2 (0.5 mmol/g, 70 mg) was added to a stirred solution of substrate (1.0 mmol) and Ac_2O (0.45 mL, 5.0 mmol) in CH_2Cl_2 (5 mL) at rt or in CH_2Cl_2 (5 mL) heated under reflux. After complete conversion and filtration to remove catalyst, a satd aq solution of $NaHCO_3$ (10 mL) was added and separated. The aqueous solution was extracted with CH_2Cl_2 (2 × 10 mL). The organic layer was combined, washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified through short column chromatography on silica gel, which was eluted with EtOAc–petroleum ether (bp 60–90 °C) to give the products that are described in the following.

3.3.1. 3,5-Di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (2)

Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.32 (s, 3H), 1.53 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 4.19 (dd, *J* 7.2 Hz and 11.6 Hz, 1H), 4.29 (m, 1H), 4.50 (m, 2H), 5.25 (d, *J* 3.1 Hz, 1H), 5.94 (d, *J* 3.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ_C 20.9, 21.0, 26.4, 26.9, 61.6, 76.3, 77.3, 83.6, 105.1, 112.5, 169.8, 170.8; ESIMS: Calcd for $C_{12}H_{18}O_7$, *m/z* 274.11; found, 297.2 $(M+Na)^+$.

3.3.2. 3,5,6-Tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (4)

Colorless solid, mp 76–77 °C (lit[43] mp 78 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.32 (s, 3H), 1.53 (s, 3H), 2.02 (s, 3H), 2.06

(s, 6H), 4.13 (dd, *J* 5.6 Hz and 12.3 Hz, 1H), 4.42 (dd, *J* 3.0 Hz and 9.4 Hz, 1H), 4.49 (d, *J* 3.6 Hz, 1H), 4.57 (dd, *J* 2.4 and 12.3 Hz, 1H), 5.22 (m, 1H), 5.35 (d, *J* 2.8 Hz, 1H), 5.93 (d, *J* 4.0 Hz 1H); ^{13}C NMR ($CDCl_3$): δ_C 20.9, 21.0, 26.4, 27.0, 63.6, 67.7, 74.9, 77.0, 83.4, 105.4, 112.7, 169.8, 169.9, 170.8; ESIMS: Calcd for $C_{15}H_{22}O_9$, *m/z* 346.13; found, *m/z* 369.1 $(M+Na)^+$.

3.3.3. 5,6-Di-*O*-acetyl-3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (7)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.34 (s, 3H), 1.57 (s, 3H), 1.94 (s, 3H), 2.06 (s, 3H), 4.19 (dd, *J* 5.2 Hz and 12.4 Hz, 1H), 4.59 (m, 3H), 5.32 (m, 1H), 5.54 (d, *J* 2.4 Hz, 1H), 5.99 (d, *J* 3.2 Hz, 1H), 7.45 (m, 2H), 7.58 (m, 1H), 7.99 (d, *J* 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ_C 20.9, 21.0, 26.5, 27.0, 63.4, 68.1, 75.9, 77.3, 83.5, 105.4, 112.8, 128.8, 129.2, 130.0, 133.9, 165.5, 169.6, 170.8; ESIMS: Calcd for $C_{20}H_{24}O_9$, *m/z* 408.14; found, *m/z* 431.1 $(M+Na)^+$.

3.3.4. 5,6-Di-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-*p*-toluenesulfonyl-α-D-glucofuranose (9)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.28 (s, 3H), 1.48 (s, 3H), 1.95 (s, 3H), 2.03 (s, 3H), 2.44 (s, 3H), 4.06 (dd, *J* 4.0 Hz and 12.4 Hz, 1H), 4.45 (t, *J* 6.8 Hz, 1H), 4.57 (d, *J* 12.4 Hz, 1H), 4.69 (d, *J* 3.2 Hz, 1H), 5.03 (m, 2H), 5.89 (d, *J* 3.2 Hz, 1H), 7.34 (d, *J* 8.0 Hz, 2H), 7.77 (d, *J* 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ_C 21.0, 21.9, 26.5, 26.9, 29.9, 62.8, 67.8, 76.4, 80.2, 83.0, 105.1, 113.0, 128.3, 130.2, 132.8, 145.8, 169.8, 170.7; ESIMS: Calcd for $C_{20}H_{26}O_{10}S$, *m/z* 458.12; found, *m/z* 481.2 $(M+Na)^+$.

3.3.5. (*R*)-Propane-1,1,2,3-tetraol tetraacetate (1,1,2,3-tetra-*O*-acetyl-D-glyceraldehyde hydrate) (11)

Oil; ^{1}H NMR (DMSO-d_6): δ_H 2.01 (s, 3H), 2.04 (m, 6H), 2.09 (m, 3H), 4.16 (dd, *J* 7.2 Hz and 12.4 Hz, 1H), 4.29 (dd, *J* 3.2 Hz and 12 Hz, 1H), 5.20 (m, 1H), 6.84 (dd, *J* 1.6 Hz and 4.4 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ_C 20.9, 21.0, 21.1, 61.4, 69.9, 86.5, 169.0, 170.2, 170.7. The NMR spectra matched that reported[41] in the literature, allowing for the fact that the latter spectra were measured in $CDCl_3$ rather than in DMSO-d_6 solution.

3.3.6. 1,2,5,6-Tetra-*O*-acetyl-3,4-di-*O*-benzoyl-D-mannitol (13)

Oil; ^{1}H NMR (DMSO-d_6): δ_H 1.93 (s, 12H), 4.14 (dd, *J* 5.2 Hz and 12.0 Hz, 2H), 4.28 (dd, *J* 3.2 Hz and 12.4 Hz, 2H); 5.24 (m, 2H), 5.72 (d, *J* 7.2 Hz, 2H), 7.56 (m, 4H), 7.70 (m, 2H), 8.01 (m, 4H); ^{13}C NMR (DMSO-d_6): δ_C 20.5, 20.6, 61.6, 68.4, 68.5, 128.8, 129.1, 129.7, 134.1, 164.8, 169.4, 170.0; ESIMS: Calcd for $C_{28}H_{30}O_{12}$, *m/z* 558.17; found, *m/z* 581.3 $(M+Na)^+$.

3.3.7. 1,2-Di-*O*-acetyl-3-*O*-*tert*-butyldiphenylsilyl-D-glycerol (15)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.06 (s, 9H), 2.04 (s, 6H), 3.78 (m, 2H), 4.23 (dd, *J* 6.0 Hz and 12.0 Hz, 1H), 4.41 (m, 1H), 5.17 (m, 1H), 7.42 (m, 6H), 7.66 (m, 4H); ^{13}C NMR ($CDCl_3$): δ_C 19.5, 21.0, 21.2, 26.9, 62.4, 62.9, 71.9, 128.0, 130.1, 133.2, 133.3, 135.8, 170.5, 170.9; ESIMS: Calcd for $C_{23}H_{30}O_5Si$, *m/z* 414.19; found, *m/z* 437.2 $(M+Na)^+$.

3.3.8. 1,5,6-Tri-*O*-acetyl-2,3-*O*-isopropylidene-α,β-D-mannofuranoside (17)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.30 (s, 3H), 1.46 (s, 3H), 2.08 (s, 9H), 4.16 (dd, *J* 5.6 Hz and 12.4 Hz, 1H), 4.23 (dd, *J* 3.6 Hz and 7.6 Hz, 1H), 4.60 (dd, *J* 2.4 Hz and 12.4 Hz, 1H), 4.67 (d, *J* 6.0 Hz, 1H), 4.80 (dd, *J* 4.0 Hz and 6.0 Hz, 1H), 5.29 (m, 1H), 6.16 (s, 1H); ^{13}C NMR ($CDCl_3$): δ_C 21.0, 21.1, 21.2, 25.1, 26.2, 63.2, 69.2, 79.4, 80.2, 84.9, 100.8, 113.7, 169.4, 169.8 and 170.8; ESIMS: Calcd for $C_{15}H_{22}O_9$, *m/z* 346.33; found, 369.3 $(M+Na)^+$.

3.3.9. 2-(*R*)-[1′(*R*), 2′-Di-*O*-acetylethyl]-[1,3]oxathiolan-5-one (19)

Colorless solid, mp 75–77 °C; ^{1}H NMR (DMSO-d_6): δ_H 2.00 (s, 3H), 2.09 (s, 3H), 3.78 (d, *J* 16.8 Hz, 1H), 3.85 (d, *J* 16.8 Hz, 1H), 4.16 (dd, *J* 6.8 Hz and 12.0 Hz, 1H), 4.26 (dd, *J* 4.4 Hz and 12.0 Hz, 1H), 5.21 (m, 1H), 5.84 (d, *J* 4.0 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ_C 20.6, 20.7, 30.0, 61.9, 72.5, 78.8, 169.6, 170.2, 173.2; HRESIMS: Calcd for $C_9H_{12}O_6S$ *m/z* 248.0355; found, *m/z* 248.0357 $(M+Na)^+$.

3.3.10. 1,3,5-Tri-*O*-acetyl-2-*O*-(2-acetoxyisopropyl)-β-D-xylofuranoside (20)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.45 (s, 3H), 1.46 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 4.10 (dd, *J* 3.6 Hz and 8.0 Hz, 1H), 4.35 (m, 2H), 5.33 (m, 2H), 6.16 (d, *J* 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ_C 13.6, 13.7, 13.8, 14.1, 19.6, 20.0, 54.9, 62.4, 62.5, 73.3, 89.4, 106.8, 162.8, 162.9, 163.0, 163.5; ESIMS: Calcd for $C_{16}H_{24}O_{10}$, *m/z* 376.14; found, *m/z* 399.1 $(M+Na)^+$.

3.3.11. 1,3-Di-*O*-acetyl-2-*O*-(2-acetoxyisopropyl)-5-deoxy-β-D-xylofuranoside (22)

Oil; ^{1}H NMR (DMSO-d_6): δ_H 1.14 (d, *J* 6.4 Hz, 3H), 1.39 (s, 3H),1.41 (s, 3H), 1.99 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 4.35 (dd, *J* 2.4 Hz and 6.4 Hz, 1H), 5.05 (m, 1H), 5.12 (t, *J* 4.2 Hz, 1H), 6.13 (d, *J* 2.3 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ_C 16.2, 20.6, 20.8, 21.0, 26.7, 26.9, 68.2, 72.6, 80.2, 95.6, 112.7, 169.7, 170.0; ESIMS: Calcd for $C_{14}H_{22}O_8$, *m/z* 318.13; found, *m/z* 341.1 $(M+Na)^+$.

3.3.12. 2-*O*-(2-Acetoxyisopropyl)-1,3-di-*O*-acetyl-5-*O*-*p*-toluenesulfonyl-β-D-xylofuranoside (24)

Oil; ^{1}H NMR($CDCl_3$): δ_H 1.44 (s, 6H), 2.00 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 2.45 (s, 3H), 4.23 (dd, *J* 2.0 Hz and 4.0 Hz, 2H), 4.38 (dd, *J* 2.4 Hz and 4.0 Hz, 1H), 5.23 (d, *J* 5.2 Hz, 1H), 5.3 (dd, *J* 4.0 Hz and 5.6 Hz, 1H), 6.13 (d, *J* 1.0 Hz, 1H), 7.36 (d, *J* 4.0 Hz, 2H), 7.78 (d, *J* 4.0 Hz, 2H); ^{13}C NMR($CDCl_3$): δ_C 20.8, 20.9, 21.4, 21.9, 26.9, 27.2, 67.3, 69.3, 69.5, 80.3, 96.3, 114.1, 128.3, 130.2, 132.7, 145.4, 169.9, 170.2; ESIMS: Calcd for $C_{21}H_{28}O_{11}S$, *m/z* 488.14; found, *m/z* 511.2 $(M+Na)^+$.

3.3.13. 2-*O*-(2-Acetoxyisopropyl)-1-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-xylofuranoside (26)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.50 (s, 3H), 1.54 (s, 3H), 2.02 (s, 6H), 4.52 (m, 1H), 4.62 (m, 2H), 5.74 (m, 2H), 6.33 (d, *J* 2.4 Hz, 1H), 7.44 (m, 4H), 7.57 (m, 2H), 8.03 (m, 4H); ^{13}C NMR ($CDCl_3$): δ_C 20.8, 21.1, 26.7, 26.8, 62.9, 69.6, 70.1, 80.5, 96.5, 113.8, 128.4, 128.6, 128.9, 129.4, 129.7, 129.9, 133.3, 133.6, 165.5, 166.1, 170.0, 171.0; ESIMS: Calcd for $C_{26}H_{28}O_{10}$, *m/z* 500.49; found, *m/z* 523.1 $(M+Na)^+$.

3.3.14. 2-*O*-(2-Acetoxyisopropyl)-1,3-di-*O*-acetyl-5-*O*-benzoyl-β-D-xylofuranoside (28)

Oil; ^{1}H NMR (DMSO-d_6): δ_H 1.42 (s, 3H), 1.43 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 4.34 (dd, *J* 6.8 Hz and 12.0 Hz, 1H), 4.48 (m, 2H), 5.42 (m, 2H), 6.18 (d, *J* 2.0 Hz, 1H), 7.54 (m, 2H), 7.67 (m, 1H), 7.92 (m, 2H); ^{13}C NMR (DMSO-d_6): δ_C 20.6, 20.7, 21.0, 26.72, 27.0, 62.8, 69.1, 69.7, 80.2, 95.7, 113.0, 129.0, 129.4, 133.7, 165.4, 169.8, 169.9; ESIMS: Calcd for $C_{21}H_{26}O_{10}$, *m/z* 438.15; found, *m/z* 461.2 $(M+Na)^+$.

3.3.15. 2-*O*-(2-Acetoxyisopropyl)-1-*O*-acetyl-5-*O*-benzoyl-3-*O*-*p*-toluenesulfonyl-β-D-xylofuranoside (30)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.36 (s, 3H), 1.45 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.39 (s, 3H), 4.39 (m, 2H), 4.53 (m, 1H), 5.14 (dd, *J* 3.6 Hz and 5.2 Hz, 1H), 5.52 (dd, *J* 5.2 Hz and 10.4 Hz, 1H), 6.33 (d, *J* 2.2 Hz, 1H), 7.28 (t, *J* 8.0 Hz, 2H), 7.46 (m, 2H), 7.59 (m, 1H), 7.81 (d, *J* 8.3 Hz, 2H), 8.01 (d, *J* 0.7 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ_C

20.8, 21.1, 26.4, 26.8, 29.7, 62.2, 68.9, 77.0, 80.4, 96.5, 114.2, 127.8, 128.5, 129.3, 129.7, 129.9, 133.3, 145.4, 165.7, 169.9, 170.0; ESIMS: Calcd for $C_{26}H_{30}O_{11}S$, *m/z* 550; found, *m/z* 550 (M^+).

3.3.16. 2-*O*-(2-Acetoxyisopropyl)-1-*O*-acetyl-3,5-di-*O*-benzyl-β-D-xylofuranoside (32)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.45 (s, 3H), 1.48 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 3.68 (m, 2H), 3.94 (t, *J* 4.8 Hz, 1H), 4.34 (dd, *J* 2.4 Hz and 3.6 Hz, 1H), 4.51 (dd, *J* 12.0 Hz and 22.4 Hz, 2H), 4.72 (s, 2H), 5.30 (m, 1H), 6.26 (d, *J* 2.8 Hz, 1H), 7.32 (m, 10H); ^{13}C NMR ($CDCl_3$): δ_C 21.3, 21.4, 26.7, 27.0, 68.1, 72.0, 73.4, 74.6, 76.2, 81.6, 96.8, 113.2, 128.0, 128.1, 128.6, 138.0, 138.1, 170.4, 170.5; ESIMS: Calcd for $C_{26}H_{32}O_8$, *m/z* 472.53; found, *m/z* 495.3 ($M+Na)^+$.

3.3.17. 2-*O*-(2-Acetoxyisopropyl)-1,5,6-tri-*O*-acetyl-3-*O*-benzoyl-β-D-glucofuranoside (33)

Oil; ^{1}H NMR (DMSO-d_6): δ_H 1.39 (s, 6H), 1.92 (s, 3H), 1.99 (s, 3H), 2.02 (s, 3H), 2.05 (s, 3H), 4.12 (m 1H), 4.28 (dd, *J* 2.8 Hz and 12.3 Hz, 1H), 4.51 (dd, *J* 2.0 Hz and 4.6 Hz, 1H), 5.15 (m, 1H), 5.47 (dd, *J* 3.7 Hz and 6.8 Hz, 1H), 5.8 (t, *J* 4.2 Hz, 1H), 6.22 (d, *J* 2.0 Hz, 1H), 7.57 (m, 2H), 7.70 (m,1H), 7.96 (m, 2H); ^{13}C NMR (DMSO-d_6): δ_C 20.4, 20.5, 20.8, 26.6, 26.9, 61.4, 68.3, 68.8, 69.2, 80.7, 95.5, 112.9, 128.8, 128.9, 129.3, 133.9, 164.9, 169.2, 169.5, 169.6, 170.0; ESIMS: Calcd for $C_{24}H_{30}O_{12}$, *m/z* 510.17; found, *m/z* 533.2 ($M+Na)^+$.

3.3.18. 2-*O*-(2-Acetoxyisopropyl)-1,3,5,6-tetra-*O*-acetyl-β-D-glucofuranoside (34)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.44 (s, 3H), 1.45 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 4.12 (dd, *J* 3.2 Hz and 8.4 Hz, 1H), 4.22 (d, *J* 8.4 Hz, 1H), 4.32 (s, 1H), 5.13 (m, 1H), 5.34 (m, 1H), 5.44 (d, *J* 4.2 Hz, 1H), 6.20 (s, 1H); ^{13}C NMR ($CDCl_3$): δ_C 20.9, 21.0, 21.1, 21.4, 26.4, 27.1, 61.9, 68.2, 68.6, 68.9, 81.2, 96.4, 113.9, 170.0, 170.1, 170.3, 170.8; ESIMS: Calcd for $C_{19}H_{28}O_{12}$, *m/z* 448.16; found, *m/z* 487.2 ($M+K)^+$.

3.3.19. 2-*O*-(2-Acetoxyisopropyl)-1,5,6-tri-*O*-acetyl-3-*O*-*p*-toluenesulfonyl-β-D-glucofuranoside (35)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 1.32 (s, 3H), 1.42 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 2.45 (s, 3H), 4.14 (dd, *J* 4.8 Hz and 12.4 Hz, 1H), 4.37 (dd, *J* 2.0 Hz and 12.4 Hz, 1H), 4.46 (s, 1H), 5.18 (dd, *J* 3.6 Hz and 8.0 Hz, 2H), 5.51 (dd, *J* 4.4 Hz and 6.8 Hz, 1H), 6.30 (s, 1H), 7.35 (d, *J* 8.4 Hz, 2H), 7.81 (d, *J* 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ_C 20.9, 21.2, 21.3, 21.9, 26.5, 26.8, 29.9, 61.3, 68.7, 69.4, 76.0, 81.0, 96.5, 114.2, 128.2, 130.0, 133.5, 145.5, 169.8, 170.0, 170.3, 170.9; ESIMS: Calcd for $C_{24}H_{32}O_{13}S$, *m/z* 560.16; found, *m/z* 583.2 ($M+Na)^+$.

3.3.20. 2-*O*-(2-Acetoxyisopropyl)-1,5-di-*O*-acetyl-3-*O*-*tert*-butyldimethylsilyl-β-D-xylofuranoside (37)

Oil; ^{1}H NMR ($CDCl_3$): δ_H 0.13 (s, 6H), 0.9 (s, 9H), 1.48 (s, 6H), 2.05 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 4.05 (t, *J* 4.0 Hz, 1H), 4.22 (dd, *J* 3.6 Hz and 12.0 Hz, 1H), 4.28 (m, 1H), 4.35 (dd, *J* 3.6 Hz and 12.0 Hz, 1H), 5.19 (t, *J* 4.0 Hz, 1H), 6.30 (d, *J* 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ_C −4.5, 18.2, 21.0, 21.2, 21.4, 25.7, 25.8, 26.7, 62.76, 69.7, 72.0, 81.9, 96.8, 113.4, 170.5, 170.8; ESIMS: Calcd for $C_{20}H_{36}O_9Si$, *m/z* 448.21; found, *m/z* 471.2 ($M+Na)^+$.

3.3.21. 2-*O*-(2-Acetoxyisopropyl)-1-*O*-acetyl-3,4-*O*-isopropylidene-α,β-L-arabinopyranoside (39)

Oil; ^{1}H NMR (DMSO-d_6): δ_H 1.22–1.45 (m, 12H), 1.94–2.08 (m, 6H), 3.95–4.44 (m, 5H), 6.06–6.27 (m, 1H); ^{13}C NMR (DMSO-d_6): δ_C 25.2, 25.6, 26.0, 26.6, 26.7, 27.0, 27.7, 27.9, 28.1, 62.4, 63.4, 73.8, 74.4, 74.7, 75.6, 77.0, 77.3, 80.1, 83.9, 93.2, 96.7, 108.4, 108.6, 111.3, 112.5, 169.9, 170.0, 170.1, 170.3; ESIMS: Calcd for $C_{15}H_{24}O_8$, *m/z* 332.15; found, 355.2 ($M+Na)^+$.

3.3.22. 1,2,6-Tri-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (41)

Oil; ^{1}H NMR (DMSO-d_6): δ_H 1.29 (s, 3H), 1.42 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.10 (s, 3H), 4.18 (m, 2H), 4.32 (m, 1H), 4.38 (m, 2H), 4.88 (dd, *J* 3.6 Hz and 7.2 Hz, 1H), 6.04 (d, *J* 3.6 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ_C 20.5, 20.6, 25.9, 27.4, 62.8, 67.7, 69.2, 71.8, 72.3, 88.4, 109.3, 169.0, 169.8, 170.2; ESIMS: Calcd for $C_{15}H_{22}O_9$, *m/z* 346.13; found, 369.2 ($M+Na)^+$.

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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.2009.08.035.

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