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Regioselective ring opening of *exo*- and *endo*-3,4-benzylidene acetals of arabinopyranoside derivatives with Lewis acids and reducing agents

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ABSTRACT

Dioxolane type 3,4-benzylidene acetals of benzyl β-L-arabinose either as a mixture or pure *exo*- and *endo*-isomers cleavaged with $BF_3{\cdot}OEt_2/Et_3SiH$ in dichloromethane or acetonitrile regioselectively, provided the 4-*O*-benzyl-3-hydroxy derivative. The reaction with $TiCl_4/Et_3SiH$ or $Cu(OTf)_2/Et_3SiH$ provided a mixture of 3- and 4-*O*-benzyl derivatives whereas with $Cu(OTf)_2/BH_3{\cdot}THF$ gave only hydrolyzed product. The regioselectivity of the reaction was proved to be directed by the acetyl substitution at C-2. Benzyl substitution provided a mixture of 3- and 4-*O*-benzyl derivatives in 1:1 ratio whereas non-substitution yielded the same mixture in 2:1 ratio.

1. Introduction

Selective protection of different hydroxyl groups in a carbohydrate molecule is a key step in the chemical synthesis of complex carbohydrates and glycosides. The reductive opening of cyclic benzylidene acetals to the corresponding *O*-benzyl ethers in a regioselective manner is among the methods of choice and has great utility in synthetic works.[1] In the synthetic field of carbohydrate chemistry such reactions have been applied to 4,6-*O*-benzylidene acetal derivatives and high regioselectivity has been often documented. A number of effective reagents have been utilized such as $NaBH_3CN–HCl$,[2] Et_3SiH–trifluoroacetic acid,[3] $Me_3N{\cdot}BH_3–AlCl_3$ in THF,[4] $Me_3N{\cdot}BH_3–BF_3{\cdot}OEt_2$,[5] $LiAlH_4–AlCl_3$,[6], $BH_3{\cdot}THF–Bu_2BOTf$[7] and $Et_3SiH–Cu(OTf)_2$ in acetonitrile.[8] To the best of our knowledge only a few studies have been published on the reductive ring opening of 3,4-*O*-benzylidene acetal hexapyranosides and the only reagent used in the reaction was $LiAlH_4–AlCl_3$ in THF.[6a,6b] However this reagent is too strong, it reduced not only benzylidene acetal but also other functionalities such as esters and amides. Our interest focused on the synthesis of a coupling partner of the disaccharide moiety of an anticancer OSW-1[9] which contains 2-*O*-*p*-methoxybenzoyl-β-D-xylopyranosyl-(1→3)-2-*O*-acetyl-L-arabinopyranoside. The acceptor arabinopyranose derivative with a free 3-hydroxyl group and 2-*O*-acetyl group was required for the synthesis of the OSW-1 disaccharide. In this paper we report a result of our finding on the reductive opening of 2-*O*-acetyl-3,4-*O*-benzylidene-β-L-arabinopyranoside and also 2-*O*-hydroxyl/benzyl-3,4-*O*-benzylidene-β-L-arabinopyranoside derivatives with various Lewis acids and reducing agents.

2. Results and discussion

In the investigation of the reductive opening of 3,4-benzylidene acetal, a model system was designed using the 3,4-*O*-benzylidene derivative of β-L-arabinopyranoside, varying protecting groups at C-2. The 2-acetyl derivative was prepared from the corresponding unprotected syn-1,2-diol **4**[10,11] by the modified method described by Josephson.[10] Thus treatment of **4** with benzaldehyde dimethyl acetal in the presence of *p*-toluenesulfonic acid provided an 1:4 mixture (NMR) of benzyl 2-*O*-acetyl-*exo*/*endo*-3,4-*O*-benzylidene-β-L-arabinopyranosides (**5***exo* and **5***endo*)[12] in 80% yield. The benzyl-2-*O*-acetyl-β-L-arabinose **4** was prepared from β-L-arabinose in four steps involving, that is, benzylation of 1-OH (**1**),[9,11,13] isopropylidenation of 3,4-diOH (**2**),[9,11] acetylation of 2-OH (**3**),[9,11] and final removal of isopropylidene as shown in Scheme 1. Compound **5***exo* and **5***endo* were separated by column chromatography. The *endo*-configuration of the benzylidene ring of **5***endo* was confirmed on the basis of ^1H and ^{13}C NMR spectroscopic data; the benzylidene proton resonated at δ 5.82 ppm, the signal of the acetalic carbon atom appeared at 104.39 ppm, whereas the benzylidene proton of the *exo*-isomer **5***exo* was found at δ 6.12 ppm and the signal of the acetalic carbon atom appeared at 102.78 ppm. These values are in good agreement with the corresponding data reported in the literature.[6f]

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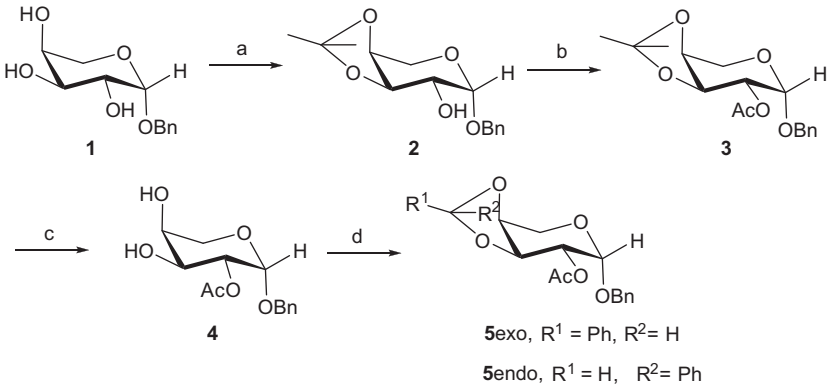


Scheme 1.

In our initial studies the mixture of **5***exo* and **5***endo* (1:4) obtained directly from the synthesis was employed. $TiCl_4$ in conjugation with Et_3SiH was found to be effective in the reductive ring opening of our benzylidene acetal compound at −78 °C to give **A5** and **B5** but regioselectivity was low and some starting material was recovered (Table 1, entry 1). When $BF_3{\cdot}OEt_2$, a weaker Lewis acid was used and the amount of Et_3SiH was increased, the reaction was completed in 10 min at −78 °C to give 53.3% of 4-*O*-benzyl-3-hydroxy derivative (**A5**) and only trace amount of other isomer **B5** was detected (entry 2). This reagent at 0 °C gave a similar yield of **A5** but the hydrolyzed product (**4**) was increased (entry 3). The best result was obtained when the isomeric mixture **5***exo*/**5***endo* was treated with $BF_3{\cdot}OEt_2/Et_3SiH$ in acetonitrile at 0 °C the benzyl 4-*O*-benzyl derivative **A5** in 69.4% yield, with only trace amount of the **B5** isomer and hydrolysis product **4** (entry 4), while the pure **5***exo* or **5***endo* isomer gave similar selectivity but a significant amount of hydrolysis product was isolated.

$Cu(OTf)_2$, a catalyst which was used to alter the ring opening of the 4,6-benzylidene compound[8] was also examined in our 3,4-benzylidene compounds. The reaction of the isomeric mixture **5***exo* and **5***endo* with $Cu(OTf)_2/Et_3SiH$ in CH_3CN at 0 °C gave only hydrolyzed product, no ring opening product was obtained (entry 7). Pure **5***endo* in CH_2Cl_2 also yielded similar result to that of entry 7, only hydrolyzed product was obtained and trace amount of staring compound (**5***exo*/**5***endo* = 1:1) was detected (entry 8). Increasing the reducing agent (entry 9) provided slight increase of hydrolyzed product. Since only hydrolyzed products were obtained when using this reagent system, it may be assumed that the reducing agent Et_3SiH is not strong enough. Indeed when $Cu(OTf)_2$ was used with $BH_3{\cdot}THF$ in CH_3CN, benzyl 4-*O*-benzyl derivative **A5** was the only isomer obtained as a minor product (18.1%) together with the hydrolyzed product **4** (23.4%) and the major product resulted from the isomerization of the starting compound (entry 10). However when the reaction was carried out in CH_2Cl_2 or without solvent, a mixture of **A5** and **B5** was obtained in 5:3 ratio (entry 11, 12).

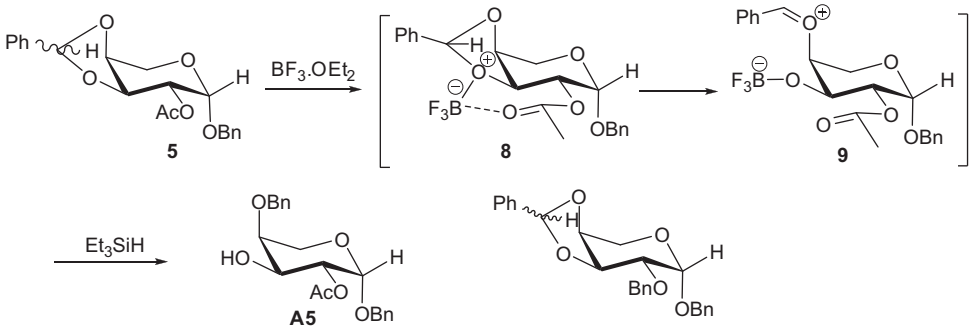
From the above result, the regioselective ring opening of **5***exo* and **5***endo* may be altered by the presence of 2-OAc functional group which is capable of coordinating with the BF_3 to form the bidentate complex **8** (see Scheme 2), which allows cleavage of the C4–O bond to give benzyl 4-*O*-benzyl isomer **A5** as a major product whereas $TiCl_4$ and $Cu(OTf)_2$ can form complex at both O-3 and O-4 of the benzylidene ring to permit O-C cleavage to give a mixture of both benzyl 3-*O*- and 4-*O*-benzyl isomers.

To prove our assumption, the free hydroxyl 3,4-benzylidene acetal compound **6**[6f,14] and the benzyl substituted compound **7** were prepared by the method described by Liptak.[6c] Treatment of benzyl β-L-arabinose(**1**) with α,α-dimethoxytoluene resulted in a 4:5 mixture of the **6***exo* and **6***endo* isomers in good yield. Since these isomers could not be completely separated by column chromatography, the mixture was then benzylated and the separation of the resulting mixture of **7***exo* and **7***endo* was successful (Scheme 3).

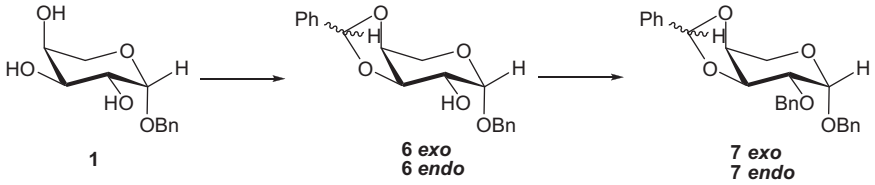
We examined the cleavage of **6** and **7** by using $BF_3{\cdot}OEt_2/Et_3SiH$ at 0 °C; the results are shown in Table 1. Treatment of **6***exo* and **6***endo* with $BF_3{\cdot}OEt_2/Et_3SiH$ in CH_3CN at 0 °C gave 4-*O*-benzyl ether

Table 1
Reductive cleavage of 3,4-*O*-benzylidene acetals of benzyl β-L-arabinose derivatives

Entry	Substrate (ratio)	Lewis acid	Reducing agent	Quantity (equiv)	Solv.	Temp (°C)/time	Yield (%)			
							A 4-*O*-Bzy type	B 3-*O*-Bzy type	C Hydrolysis type	Starting compd (%) (*exo*:*endo*)
1	**5***exo*/*endo* (1:4)	$TiCl_4$	Et_3SiH	1.35	CH_2Cl_2	−78/5 h	41.0	20.2	—	17.0
2	**5***exo*/*endo* (1:4)	$BF_3{\cdot}Et_2O$	Et_3SiH	12.0	CH_2Cl_2	78/10 min	53.3	Trace	5.43	—
3	**5***exo*/*endo* (1:4)	$BF_3{\cdot}Et_2O$	Et_3SiH	12.0	CH_2Cl_2	0/1 h	52.5	Trace	21.6	—
4	**5***exo*/*endo* (1:4)	$BF_3{\cdot}Et_2O$	Et_3SiH	12.0	CH_3CN	0/30 min	69.4	Trace	Trace	—
5	**5***endo*	$BF_3{\cdot}Et_2O$	Et_3SiH	12.0	CH_3CN	0/30 min	57.9	Trace	31.0	—
6	**5***exo*	$BF_3{\cdot}Et_2O$	Et_3SiH	—	CH_3CN	0/30 min	64.3	Trace	20.5	—
7	**5***exo*/*endo* (1:4)	$Cu(OTf)_2$	Et_3SiH	2.0	CH_3CN	0/30 min	—	—	64.2	—
8	**5***endo*	$Cu(OTf)_2$	Et_3SiH	2.0	CH_2Cl_2	rt/24 h	—	—	48.5	Trace (1:1)
9	**5***endo*	$Cu(OTf)_2$	Et_3SiH	12.0	CH_2Cl_2	rt/24 h	—	—	58.4	—
10	**5***exo*/*endo* (1:4)	$Cu(OTf)_2$	$BH_3{\cdot}THF$	5.0	CH_3CN	rt/24 h	18.1	—	23.4	54.7 (2:1)
11	**5***exo*/*endo* (1:4)	$Cu(OTf)_2$	$BH_3{\cdot}THF$	5.0	CH_2Cl_2	rt/1.25 min	47.6	28.7	—	—
12	**5***exo*/*endo* (1:4)	$Cu(OTf)_2$	$BH_3{\cdot}THF$	5.0	—	rt/24 h	45.6	28.7	—	—
13	**6***exo*/*endo* (4:5)	$BF_3{\cdot}Et_2O$	Et_3SiH	2.0	CH_3CN	0/10 min	20.7	9.1	—	—
14	**7***endo*	$BF_3{\cdot}Et_2O$	Et_3SiH	2.0	CH_2Cl_2	0/30 min	36.3	12.8	29.5	—
15	**7***exo*	$BF_3{\cdot}Et_2O$	Et_3SiH	2.0	CH_2Cl_2	0/30 min	25.9	23.4	35.5	—



Scheme 2.



Scheme 3.

(**A6**) and 3-*O*-benzyl ether derivative (**B6**) in 2:1 ratio (entry 13) whereas the benzyl substitution of both **7***endo* and **7***exo* isomers yielded a mixture of **A7** and **B7**[15] in 3:1 and 1:1 ratios, respectively, as well as a considerable amount of hydrolyzed product **C7** (entry 14 and 15). These results clearly indicated that the direction of ring cleavage by $BF_3{\cdot}OEt_2/Et_3SiH$ is strongly influenced by the acetate substitution at C-2.

In conclusion, among the Lewis acids tested by us, $BF_3{\cdot}OEt_2/Et_3SiH$ in acetonitrile gave the best result for highly regioselective ring opening of 3,4-*O*-benzylidene acetals of arabinoside derivatives bearing 2-acetoxyl, to furnish the corresponding 4-*O*-benzyl ethers with the 3-hydroxy unsubstituted. The reaction condition is mild, and benzyl or ester protecting groups in the substrates are tolerated. Our investigation also revealed that the regioselective ring opening was not directed by the stereochemistry of the acetalic center but was altered by an adjacent-acetyl group which could coordinate with the BF_3 to form a bidentate metal complex intermediate.

3. Experimental section

3.1. General methods

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian Gemini 300 spectrophotometer. Chemical shifts were recorded as δ values in ppm. Spectra were acquired in $CDCl_3$ unless otherwise stated. The peak due to residual $CHCl_3$ (7.26 ppm for ^{1}H and 77.23 ppm for ^{13}C) was used as the internal reference. Coupling constants (*J*) are given in Hz, and multiplicity is defined as follows: br = broad, s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplet, t = triplet, q = quartet, m = multiplet. Infrared (IR) spectra were recorded in cm^{-1} on a Perkin–Elmer 2000 Fourier transform infrared spectrophotometer at the Chemistry Department, Faculty of Science, Kasetsart University. Samples were analyzed as KBr disks. Mass spectra were obtained on an Agilent Technology 1100 series LL/MSD Trap. Melting points (mp) were determined on a Fisher John apparatus and MEL-TEMP capillary melting point apparatus at the Chemistry Department, Kasetsart University and are reported uncorrected in °C. All chemicals and solvents were purchased from the Fluka Co. Ltd as analytical grade and solvents were purified by general methods before being used.

3.2. Benzyl 3,4-acetonide-β-L-arabinose (2)

To a solution of **1** (40.0 mg, 0.17 mmol) in DMF (0.8 mL) was added 2,2-dimethoxypropane (0.024 mL, 0.2 mmol) and *p*-TsOH·H_2O (3.1 mg, 0.02 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 h and was quenched with saturated aqueous sodium bicarbonate. The organic layer was separated and the water layer was extracted with methylene chloride three times. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/hexane, 3:2) to give **2** as a colorless syrup. (38.0 mg, 82.0%): $[\alpha]_D^{20}$ +272 (*c* 0.20, CH_2Cl_2); IR (NaCl) ν_{max} 3437 (O–H), 1219 (C–O), 1079 (C–O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (ArH, m, 2H), 7.19 (ArH, m, 3H), 4.49 (CH-1, d, *J* = 9.0 Hz, 1H), 4.16 (CH-4, m, 1H), 4.14 (CH_2-5, m, 1H), 4.01 (CH-3, t, *J* = 6.1 Hz, 1H), 3.68 (CH_2-5, m, 1H), 3.58 (CH-2, ddd, *J* = 3.5, 6.6, 9.0 Hz, 1H), 1.37 (CH_3, s, 3H), 1.26 (CH_3, s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.5, 132.2, 132.2, 128.8, 128.8, 127.7, 109.9, 87.8, 78.1, 72.6, 71.2, 65.2, 27.7, 25.9.

3.3. Benzyl 2-*O*-acetyl-3,4-acetonide-β-L-arabinose (3)

Compound **2** (20.0 mg, 0.07 mmol) was dissolved in methylene chloride (1 mL). Triethylamine (0.02 mL, 0.11 mmol), acetyl anhydride (0.008 mL, 0.09 mmol), and DMAP (0.2 mg) were added. The reaction mixture was stirred at room temperature for 2 h then was quenched with saturated aqueous sodium bicarbonate. The organic layer was separated and the water layer was extracted with methylenechloride three times. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate. The solvent was removed and the product was purified by flash column chromatography (EtOAc/hexane, 1:4) to give **3** as pale yellow syrup (20.8 mg, 91.0%): $[\alpha]_D^{20}$ +216 (*c* 0.28, CH_2Cl_2); IR (NaCl) ν_{max} 1753 (C=O), 1222 (C–O–C), 1052 (C–O–C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20–7.33 (ArH, m, 5H), 4.94 (CH-1, d,

J = 3.6 Hz, 1H), 4.85 (CH-2, dd, J = 8.9 Hz, 1H), 4.66 (–OCH_2Ar, d, J = 11.8 Hz, 1H), 4.65 (–OCH_2Ar, d, J = 12.4 Hz, 1H), 4.46 (–OCH_2Ar, d, J = 11.8 Hz, 1H), 4.44 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 3.96–4.02 (CH-3, m, 1H), 3.71 (CH-4, dd, J = 3.5, 2.1 Hz, 1H), 3.75 (CH_2-5, dd, J = 12.6, 1.9 Hz, 1H), 3.68 (CH_2-5, dd, J = 12.6, 1.1 Hz, 1H), 2.36 (OH, br d, J = 10.3 Hz, 1H), 2.01 (–OCOCH_3, s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 133.9, 131.6, 131.6, 128.8, 128.8, 127.4, 110.3, 85.6, 75.4, 71.9, 71.1, 64.0, 27.5, 26.2, 20.8.

3.4. Benzyl 2-*O*-acetyl-β-L-arabinose (4)

A solution of **3** (312 mg, 0.96 mmol) in 70% aqueous acetic acid (4.7 mL) was stirred at 70 °C for 1 h and then concentrated in vacuo, and the traces of acetic acid and water were removed by co-evaporation with toluene several times. The residue was purified by flash column chromatography (EtOAc/hexane, 7:3) to afford **4** as a white solid (264 mg, 96%): mp 98–100 °C (hexane/Et_2O) (lit.[10] 101 °C); $[\alpha]_D^{20}$ +230 (c 0.20, CH_2Cl_2); IR (NaCl) ν_{max} 3428 (O–H), 1732 (C=O), 1372 (C–H), 1244 (C–O–C), 1059 (C–O–C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.31 (ArH, m, 5H), 4.99 (CH-1, d, J = 3.7 Hz, 1H), 4.94 (CH-2, dd, J = 3.7, 10.0 Hz, 1H), 4.66 and 4.44 (–OCH_2Ar, J = 12.3 Hz, 2H), 4.01 (CH-3, dd, J = 3.5, 10.0 Hz, 1H), 3.93–3.94 (CH-4, m, 1H), 3.85 (CH_2-5, dd, J = 1.4, 12.6 Hz, 1H), 3.68 (CH_2-5, dd, J = 2.0, 12.6 Hz, 1H), 2.03 (–OCOCH_3, s, 3H), 2.95 (–OH, br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 137.1, 128.4, 127.9, 127.6, 95.2, 73.5, 72.8, 72.2, 69.4, 58.8, 20.9; ESIMS: m/z calcd for $C_{14}H_{18}O_6Na$ $[M+Na]^+$ 305.1001; found: 305.1005.

3.5. Benzyl 2-*O*-acetyl-*exo*/*endo*-3,4-*O*-benzylidene-β-L-arabinopyranosides (5*exo*/5*endo*)

To a solution of **4** (200 mg, 0.71 mmol) in dry acetonitrile (2.5 mL) were added α,α-dimethoxytoluene (0.16 mL, 1.13 mmol) and *para*-toluenesulfonic acid (1.4 mg, 0.007 mmol). The reaction mixture was stirred at room temperature for 6 h. Triethylamine was added before concentration and the syrup which was dissolved in EtOAc was extracted with saturated aqueous $NaHCO_3$, water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/hexane, 3:17 to afford **5***exo* as a yellow syrup (42.0 mg, 16%) and **5***endo* as a yellow syrup (168 mg, 64%) and starting material (10.0 mg, 5%).

Compound **5***exo*: $[\alpha]_D^{20}$ +177 (c 0.30, CH_2Cl_2); IR (NaCl) ν_{max} 1749 (C=O), 1272 (C–O–C), 1089, 1026 (C–O–C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.44 (ArH, m, 2H), 7.21–7.38 (ArH, m, 8H), 6.12 (CH-6, s, 1H), 5.01 (CH-1, d, J = 4.0 Hz, 1H), 5.00 (CH-2, dd, J = 11.8, 3.96 Hz, 1H), 4.60 (CH-3, dd, J = 7.7, 5.3 Hz, 1H), 4.67 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.44 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.18 (CH-4, dd, J = 5.6, 2.5 Hz, 1H), 3.92 (CH_2-5, dd, J = 13.4, 2.6 Hz, 1H), 4.00 (CH_2-5, d, J = 13.5 Hz, 1H), 2.03 (–OCOCH_3, s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 137.0, 138.7, 129.6, 128.6, 128.5, 128.5, 127.6, 126.8, 126.8, 126.8, 126.1, 126.1, 102.8, 95.1, 73.4, 74.1, 69.5, 69.6, 58.8, 20.9; ESIMS: m/z calcd for $C_{21}H_{22}O_6Na$ $[M+Na]^+$ 393.1314; found: 393.1310.

Compound **5***endo*: $[\alpha]_D^{20}$ +206 (c 0.30, CH_2Cl_2); IR (NaCl) ν_{max} 1736 (C=O), 1233 (C–O–C), 1067 (C–O–C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.44 (ArH, m, 2H), 7.21–7.38 (ArH, m, 8H), 5.82 (CH-6, s, 1H), 4.98 (CH-1, d, J = 3.5 Hz, 1H), 4.90 (CH-2, dd, J = 7.8, 3.5 Hz, 1H), 4.46 (CH-3, dd, J = 7.6, 6.4 Hz, 1H), 4.67 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.44 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.25 (CH-4, dd, J = 6.1, 2.2 Hz, 1H), 4.00 (CH_2-5, dd, J = 13.5, 3.0 Hz, 1H), 4.08 (CH_2-5, d, J = 13.2 Hz, 1H), 1.99 (–OCOCH_3, s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 136.6, 137.0, 129.1, 128.5, 128.5, 127.6, 127.6, 126.8, 126.8, 126.8, 126.1, 126.1, 104.4, 95.0, 75.8, 72.6, 72.7, 69.6, 58.7, 20.9; ESIMS: m/z calcd for $C_{21}H_{22}O_6Na$ $[M+Na]^+$ 393.1314; found 393.1310.

3.6. Benzyl *exo*/*endo*-3,4-*O*-benzylidene-β-L-arabinopyranosides (6*exo* and 6*endo*)

To a solution of **1** (100 mg, 0.42 mmol) in dry *N*,*N*-dimethylformamide (1.5 mL) were added α,α-dimethoxytoluene (0.09 mL, 0.67 mmol) and *para*-toluenesulfonic acid (0.8 mg, 0.004 mmol). The reaction mixture was stirred at room temperature for 24 h. Triethylamine was added before concentration and the syrup which was dissolved in EtOAc was extracted with saturated aqueous $NaHCO_3$, water, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/hexane, 1:4) to afford **6***exo* and **6***endo* as a white solid in 4:5 ratio (106 mg, 77.2%); $[\alpha]_D^{20}$ +139 (c 0.21, CH_2Cl_2); IR (NaCl) ν_{max} 3436 (OH), 1091, 1067, 1022 (C–O–C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.53 (ArH, m, 16H), 7.43–7.44 (ArH, m, 2H), 7.27–7.40 (ArH, m, 2H), 6.16 (CH-6-exo, s, 1H), 5.85 (CH-6-endo, s, 1H), 4.96 (CH-1-exo, d, J = 3.7 Hz, 1H), 4.91 (CH-1-endo, d, J = 3.6 Hz, 1H), 4.53 (–OCH_2Ar-exo, d, J = 11.80 Hz, 2H), 4.75 (–OCH_2Ar-exo, d, J = 11.8 Hz, 2H), 4.54 (–OCH_2Ar-*endo*, d, J = 11.8 Hz, 2H), 4.78 (–OCH_2Ar-endo, d, J = 11.7 Hz, 2H), 4.41 (CH-2-exo, dd, J = 7.1, 5.6 Hz, 1H), 4.33 (CH-2-endo, dd, J = 6.4, 6.4 Hz, 1H), 4.14–4.16 (CH-3-exo, m, 1H), 4.23–4.25 (CH-3-endo, m, 1H), 3.89 (CH-4-exo, dd, J = 7.2, 3.7 Hz, 1H), 3.86 (CH-4-endo, dd, J = 6.2, 3.6 Hz, 1H), 3.93 (CH_2-5-exo, dd, J = 13.3, 2.5 Hz, 1H), 4.04 (CH_2-5-exo, dd, J = 13.3, 2.4 Hz, 1H), 3.98 (CH_2-5-endo, dd, J = 13.2, 1.0 Hz, 1H), 4.00 (CH_2-5-endo, d, J = 13.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.9, 137.0, 138.9, 129.6, 129.4, 129.3, 128.9, 128.8, 128.5, 128.5, 128.5, 128.4, 127.9, 126.6, 125.9, 103.8, 102.8, 97.0, 96.5, 76.9, 75.7, 73.0, 74.7, 69.6, 69.6, 67.9, 69.7, 59.4, 59.8; ESIMS: m/z calcd for $C_{19}H_{20}O_5Na$ $[M+Na]^+$ 351.1208; found 351.1209.

3.7. Benzyl 2-*O*-benzyl-(7*exo*) and *endo*-3,4-*O*-benzylidene-β-L-arabinopyranosides (7*endo*)

A mixture of **6***exo* and **6***endo* (100 mg, 0.30 mmol) were treated with benzyl bromide (1.1 mL, 9.14 mmol) in the presence of KOH (205 mg, 3.65 mmol) for 5 h at 50 °C. The reaction mixture was diluted with dichloromethane and filtered, and benzyl bromide was removed by stream distillation. The oily residue was purified by flash column chromatography (EtOAc/hexane, 1:9) to afford **7***exo* as a yellow syrup (44.4 mg, 35%) and **7***endo* as a yellow syrup (54.3 mg, 41%).

Compound **7***exo*: $[\alpha]_D^{20}$ +134 (c 0.45, CH_2Cl_2); IR (NaCl) ν_{max} 1274 (C–O), 1099, 1045, 1019 (C–O–C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.38 (ArH, m, 15H), 5.95 (CH-6, s, 1H), 4.88 (CH-1, d, J = 3.4 Hz, 1H), 4.71 (–OCH_2Ar, d, J = 12.5 Hz, 1H), 4.64 (–OCH_2Ar, d, J = 11.56 Hz, 1H), 4.63 (–OCH_2Ar, d, J = 12.2 Hz, 1H), 4.62 (CH-3, dd, J = 8.0, 5.4 Hz, 1H), 4.48 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.13 (CH-4, m, 1H), 3.92 (CH_2-5, dd, J = 13.4, 1.0 Hz, 1H), 3.88 (CH_2-5, dd, J = 13.3, 2.4 Hz, 1H), 3.62 (CH-2, dd, J = 8.0, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.1, 137.1, 129.0, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 127.9, 127.8, 127.8, 127.8, 127.7, 126.1, 102.6, 95.8, 76.6, 73.8, 73.4, 72.2, 69.3, 58.9; ESIMS: m/z calcd for $C_{26}H_{26}O_5Na$ $[M+Na]^+$ 441.1678; found 441.1680.

Compound **7***endo*: $[\alpha]_D^{20}$ +170 (c 0.24, CH_2Cl_2); IR (NaCl) ν_{max} 1272 (C–O), 1090, 1068, 1022 (C–O–C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.37 (ArH, m, 15H), 5.84 (CH-6, s, 1H), 4.77 (CH-1, d, J = 3.4 Hz, 1H), 4.68 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.59 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.47 (–OCH_2Ar, d, J = 12.6 Hz, 1H), 4.46 (–OCH_2Ar, d, J = 12.3 Hz, 1H), 4.44 (CH-3, dd, J = 6.0, 1.9 Hz, 1H), 4.23 (CH-4, ddd, J = 6.2, 2.8, 1.3 Hz, 1H), 4.01 (CH_2-5, dd, J = 13.4, 1.2 Hz, 1H), 3.96 (CH_2-5, dd, J = 13.3, 3.0 Hz, 1H), 3.52 (CH-2, dd, J = 7.5, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.5, 137.2, 129.2, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9,

127.9, 127.8, 127.8, 127.6, 127.6, 126.6, 103.8, 95.8, 76.7, 75.9, 75.3, 72.0, 69.3, 58.9; ESIMS: *m/z* calcd for $C_{26}H_{26}O_5Na$ $[M+Na]^+$ 441.1678; found 441.1670.

3.8. Regioselective reductive ring opening of various benzylidene acetals

3.8.1. General procedure

Method A: To a solution mixture of **5***exo* and **5***endo* (110 mg, 0.3 mmol) in dichloromethane (3.0 mL) was added Et_3SiH (0.07 mL, 0.40 mmol). The reaction mixture was cooled to −78 °C and a solution of $TiCl_4$ (0.04 ml, 0.33 mmol) in dichloromethane (0.3 mL) was slowly added. The reaction was stirred at −78 °C for 5 h. The reaction mixture was poured into ice and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/hexane, 3:7).

Method B: To a solution mixture of **5***exo* and **5***endo* (60.4 mg, 0.16 mmol) in dichloromethane (3.0 mL) at 0 °C was added Et_3SiH (0.32 mL, 1.96 mmol) and $BF_3{\cdot}Et_2O$ (0.04 mL, 0.33 mmol). The reaction was stirred at 0 °C for 1 h. The mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/hexane, 3:7).

Method C: To a solution mixture of **5***exo* and **5***endo* (56.0 mg, 0.15 mmol) in acetonitrile (3.0 mL) and Et_3SiH (0.05 ml, 0.30 mmol) at 0 °C was added $Cu(OTf)_2$ (5.5 mg, 0.02 mmol). The reaction was warmed to room temperature and stirred for 30 min. The mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/hexane, 1:4).

Method D: A 1 M solution of $BH_3{\cdot}THF$ complex in tetrahydrofuran (0.23 mL, 0.23 mmol) was added to a solution mixture of **5***exo* and **5***endo* (17.0 mg, 0.05 mmol) at room temperature under nitrogen. The mixture was stirred for 10 min, and $Cu(OTf)_2$ (1.7 mg, 0.005 mmol) was added. After stirring for 30 min, the mixture was cooled down to 0 °C, and the reaction was quenched by sequential addition of triethylamine and methanol (*caution*: hydrogen gas was evolved). The resulting mixture was concentrated at reduced pressure followed by coevaporation with methanol. The residue was purified by flash column chromatography (EtOAc/hexane, 3:7).

3.8.2. Benzyl 2-*O*-acetyl-4-*O*-benzyl-β-L-arabinopyranoside (A5)

Pale yellow syrup; $[\alpha]_D^{20}$ +218 (*c* 0.30, CH_2Cl_2); IR (NaCl) ν_{max} 3462 (OH), 1735 (C=O), 1371 (C–H), 1239 (C–O), 1140, 1057, 1026 (C–O–C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19–7.28 (ArH, m, 10H), 4.99 (CH-2, dd, *J* = 11.4, 3.6 Hz, 1H), 4.98 (CH-1, d, *J* = 8.7 Hz, 1H), 4.66 (–O*CH*$_2$Ar, d, *J* = 11.8 Hz, 1H), 4.65 (–O*CH*$_2$Ar, d, *J* = 12.4 Hz, 1H), 4.46 (–O*CH*$_2$Ar, d, *J* = 11.8 Hz, 1H), 4.44 (–O*CH*$_2$Ar, d, *J* = 12.3 Hz, 1H), 3.96–4.02 (CH-3, m, 1H), 3.71 (CH-4, dd, *J* = 3.5, 2.1 Hz, 1H), 3.75 (CH_2-5, dd, *J* = 12.6, 1.9 Hz, 1H), 3.68 (CH_2-5, dd, *J* = 12.6, 1.1 Hz, 1H), 2.36 (–OH, br d, *J* = 10.1 Hz, 1H), 2.01 (–OCO*CH*$_3$, s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 137.3, 137.5, 128.5 × 2, 128.4 × 2, 127.9, 127.8, 127.8 × 2, 127.6 × 2, 95.9, 76.7, 76.6, 71.5, 69.4, 67.3, 59.0, 20.9; ESIMS: *m/z* calcd for $C_{21}H_{24}O_6Na$ $[M+Na]^+$ 395.1471; found 395.1460.

3.8.3. Benzyl 2-*O*-acetyl-3-*O*-benzyl-β-L-arabinopyranoside (B5)

Pale yellow syrup; $[\alpha]_D^{20}$ +161 (*c* 0.40, CH_2Cl_2); IR (NaCl) ν_{max} 3470 (OH), 1737 (C=O), 1370 (C–H), 1238 (C–O), 1143, 1061, 1023 (C–O–C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.30 (ArH, m, 10H), 5.10 (CH-2, dd, *J* = 9.9, 3.6 Hz, 1H), 5.00 (CH-1, d, *J* = 3.6 Hz, 1H), 4.65 (–O*CH*$_2$Ar, d, *J* = 12.3 Hz, 1H), 4.60 (–O*CH*$_2$Ar, s, 2H), 4.44 (–O*CH*$_2$Ar, d, *J* = 12.3 Hz, 1H), 3.95–3.96 (CH-4, m, 1H), 3.88 (CH-3, dd, *J* = 9.8, 3.5 Hz, 1H), 3.77 (CH_2-5, dd, *J* = 12.6, 1.6 Hz, 1H), 3.70 (CH_2-5, dd, *J* = 12.6, 2.2 Hz, 1H), 2.54 (–OH, s, 1H), 1.98 (–OCO*CH*$_3$, s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 137.3, 137.8, 128.5 × 2, 128.4 × 2, 128.0, 127.9, 127.7 × 2, 127.5 × 2, 95.9, 75.0, 72.4, 69.4, 70.2, 67.3, 61.8, 20.9; ESIMS: *m/z* calcd for $C_{21}H_{24}O_6Na$ $[M+Na]^+$ 395.1471; found 395.1471.

3.8.4. Benzyl 4-*O*-benzyl-β-L-arabinopyranoside (A6)

A white solid; mp 114–116 °C; $[\alpha]_D^{20}$ +165 (*c* 0.23, CH_2Cl_2); IR (NaCl) ν_{max} 3430 (O–H), 1266 (C–O–C), 1140, 1077, 1048, 1025 (C–O–C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22–7.32 (ArH, m, 10H), 4.94 (CH-1, d, *J* = 3.3 Hz, 1H), 4.69 (–O*CH*$_2$Ar, d, *J* = 12.0 Hz, 1H), 4.66 (–O*CH*$_2$Ar, d, *J* = 12.3 Hz, 1H), 4.62 (–O*CH*$_2$Ar, d, *J* = 11.7 Hz, 1H), 4.51 (–O*CH*$_2$Ar, d, *J* = 11.5 Hz, 1H), 3.92–3.94 (CH-3, m, 1H), 3.79–3.80 (CH-4, m, 1H), 3.74 (CH_2-5, dd, *J* = 12.2, 2.4 Hz, 1H), 3.71–3.72 (CH_2-5, m, 1H), 3.62 (CH-2, dd, *J* = 3.5, 9.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.1, 128.6, 128.6, 128.6, 128.6, 128.5, 128.0, 128.0, 127.9, 127.8, 127.8, 98.0, 78.1, 71.7, 70.4, 70.4, 69.8, 59.8; ESIMS: *m/z* calcd for $C_{19}H_{22}O_5Na$ $[M+Na]^+$ 353.1365; found 353.1367.

3.8.5. Benzyl 3-*O*-benzyl-β-L-arabinopyranoside (B6)

A white crystal; mp 128–129 °C (hexane–CH_2Cl_2); $[\alpha]_D^{20}$ +147 (*c* 0.08, CH_2Cl_2); IR (NaCl) ν_{max} 3437 (O–H), 1257 (C–O–C), 1137, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.33 (ArH, m, 10H), 4.89 (CH-1, d, *J* = 3.4 Hz, 1H), 4.66 (–O*CH*$_2$Ar, d, *J* = 12.2 Hz, 1H), 4.49 (–O*CH*$_2$Ar, d, *J* = 11.7 Hz, 1H), 4.43 (–O*CH*$_2$Ar, d, *J* = 11.8 Hz, 1H), 4.42 (–O*CH*$_2$Ar, d, *J* = 12.2 Hz, 1H), 4.02 (CH-4, ddd, *J* = 0.3, 3.2, 9.4 Hz, 1H), 3.94–3.95 (CH-3, m, 1H), 3.80 (CH_2-5, dd, *J* = 12.7, 1.3 Hz, 1H), 3.67 (CH-2, dd, *J* = 9.7, 3.5 Hz, 1H), 3.66 (CH_2-5, dd, *J* = 12.6, 1.8 Hz, 1H), 2.46 (–OH, s, 1H), 2.43 (–OH, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.3, 130.0, 128.6, 128.6, 128.4, 128.4, 128.1, 128.1, 128.0, 127.9, 95.4, 76.5, 72.3, 69.2, 69.0, 68.5, 62.0; ESIMS: *m/z* calcd for $C_{19}H_{22}O_5Na$ $[M+Na]^+$ 353.1365; found 353.1363.

3.8.6. Benzyl 2-*O*-benzyl-4-*O*-benzyl-β-L-arabinopyranoside (A7)

A colorless needle; mp 78–79 °C (hexane–Et_2O); $[\alpha]_D^{20}$ +128 (*c* 0.23, CH_2Cl_2); IR (NaCl) ν_{max} 3453 (O–H), 1344 (C–H), 1260 (C–O–C), 1093, 1048, 1025 (C–O–C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.32 (ArH, m, 15H), 4.86 (CH-1, d, *J* = 3.4 Hz, 1H), 4.65 (–O*CH*$_2$Ar, d, *J* = 11.9 Hz, 1H), 4.64 (–O*CH*$_2$Ar, d, *J* = 12.2 Hz, 1H), 4.59 (–O*CH*$_2$Ar, d, *J* = 11.9 Hz, 1H), 4.55 (–O*CH*$_2$Ar, d, *J* = 12.1 Hz, 1H), 4.50 (–O*CH*$_2$Ar, d, *J* = 11.9 Hz, 1H), 4.42 (–O*CH*$_2$Ar, d, *J* = 12.2 Hz, 1H), 4.00–4.06 (CH-3, m, 1H), 3.7 (CH-4, ddd, *J* = 3.6, 1.8, 1.8 Hz, 1H), 3.70 (CH-2, dd, *J* = 9.6, 3.4 Hz, 1H), 3.67–3.68 (CH_2-5, m, 2H), 2.36 (–OH, br d, *J* = 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.0, 137.4, 128.0 × 3, 128.4 × 4, 128.5 × 3, 127.8 × 6, 127.7, 96.2, 76.6, 76.2, 72.8, 71.9, 69.2, 69.0, 59.8; ESIMS: *m/z* calcd for $C_{26}H_{28}O_5Na$ $[M+Na]^+$ 443.1834.; found 443.1834.

3.8.7. Benzyl 2-*O*-benzyl-3-*O*-benzyl-β-L-arabinopyranoside (B7)

Pale yellow syrup; $[\alpha]_D^{20}$ +132 (*c* 0.11, CH_2Cl_2); IR (NaCl) ν_{max} 3467 (O–H), 1342 (C–H), 1261 (C–O–C), 1140, 1098, 1067, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21–7.34 (ArH, m, 15H), 4.82 (CH-1, d, *J* = 3.6 Hz, 1H), 4.75 (–O*CH*$_2$Ar, d, *J* = 11.5 Hz, 1H), 4.66 (–O*CH*$_2$Ar, d, *J* = 12.3 Hz, 1H), 4.63 (–O*CH*$_2$Ar, d, *J* = 12.0 Hz, 1H), 4.62 (–O*CH*$_2$Ar, d, *J* = 11.5 Hz, 1H), 4.50 (–O*CH*$_2$Ar, d, *J* = 12.0 Hz, 1H), 4.48 (–O*CH*$_2$Ar, d, *J* = 12.3 Hz, 1H), 3.93–4.94 (CH-4, m, 1H), 3.88 (CH-3, dd, *J* = 9.5, 3.5 Hz, 1H), 3.76 (CH-2, dd, *J* = 9.5, 3.5 Hz, 1H), 3.73–3.77 (CH_2-5, m, 1H), 3.64 (CH_2-5, dd, *J* = 12.5, 2.0 Hz, 1H), 2.50 (–OH, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 138.4, 138.2, 137.3, 128.5 × 2, 128.4, 128.3 × 2, 128.2 × 2, 127.9, 127.8 × 4, 127.6 × 2, 96.3, 77.2, 76.7, 73.1, 72.9, 69.0, 67.7, 61.8; ESIMS: *m/z* calcd for $C_{26}H_{28}O_5Na$ $[M+Na]^+$ 443.1834; found 443.1839.

3.8.8. Benzyl 2-*O*-benzyl-β-L-arabinopyranoside (C7)

A white foam; mp 128–130 °C (hexane–CH_2Cl_2); $[\alpha]_D^{20}$ +176 (*c* 0.21, CH_2Cl_2); IR (NaCl) ν_{max} 3357, 3272 (O–H), 1261 (C–O–C), 1129, 1099, 1066, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.33 (ArH), m, 10H), 4.89 (CH-1, d, *J* = 3.44 Hz, 1H), 4.66 (–OCH_2Ar, d, *J* = 12.2 Hz, 1H), 4.49 (–OCH_2Ar, d, *J* = 11.8 Hz, 1H), 4.43 (–OCH_2Ar, d, *J* = 11.8 Hz, 1H), 4.41 (–OCH_2Ar, d, *J* = 12.2 Hz, 1H), 3.99–4.03 (CH-3, m, 1H), 3.93–3.94 (CH-4, m, 1H), 3.79 (CH_2-5, d, *J* = 12.4 Hz, 1H), 3.67 (CH-2, dd, *J* = 9.7, 3.5 Hz, 1H), 3.65 (CH_2-5, dd, *J* = 12.6, 1.8 Hz, 1H), 2.49 (–OH, d, *J* = 12.4 Hz, 1H), 2.48 (–OH, d, *J* = 10.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.3, 128.6 × 2, 128.4 × 2, 128.1, 128.0 × 4, 127.9, 95.4, 76.6, 72.2, 69.2, 68.9, 68.5, 62.1; ESIMS: *m/z* calcd for $C_{19}H_{22}O_5Na$ $[M+Na]^+$ 353.1365; found 353.1359.

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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.2011.01.031.

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