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Note

Synthesis of a library of allyl α-L-arabinofuranosyl-α- or β-D-xylopyranosides; route to higher oligomers

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Dedicated to Professor A. S. Perlin on the occasion of his 85th year

Abstract—Six isomeric disaccharides allyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-α-D-xylopyranosides and β-D-xylopyranosides were synthetized by the stereoselective glycosylation of pure allyl α- or β-D-xylopyranosides with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-L-arabinofuranose as donor, catalyzed with $BF_3{\cdot}Et_2O$ in DCM. Regio- and stereoselective glycosylation with excess of donor furnished almost exclusively the trisaccharides allyl 2,3-di-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-α- or β-D-xylopyranosides. Extension of the reaction to the triol β-D-xylopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-α-D-xylopyranose, obtained from the 4-hydroxyl penta-*O*-acetyl-α-xylobiose, gave in the same manner the tetrasaccharide [2,3-di-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-β-D-xylopyranosyl]-(1→4)-1,2,3-tri-*O*-acetyl-α-D-xylopyranose. The protocol described herein should offer the possibility to produce branched oligosaccharides with a 2,3-di-*O*-(α-L–Ara_f)-β-D-Xyl_p block unit at the terminal non-reducing end.

Keywords: α-L-Arabinofuranosyl-D-xylopyranosides; Library; Oligosaccharides

General methods for the synthesis of di- and oligosaccharides have developed considerably throughout the last 20 years, but oligosaccharide preparation through chemical syntheses is still a tedious task. In order to shorten the route towards the preparation of L-arabinofuranosyl-D-xylopyranosyl oligosaccharides, we reasoned that regio- and stereoglycosylation of unprotected allyl α or β-D-xylopyranoside acceptors by a 2,3,5-tri-*O*-benzoyl-L-arabinofuranosyl donor should offer a direct way to the six possible allyl α-L-arabinofuranosyl-α- or β-D-xylopyranoside disaccharides. Furthermore, our hypothesis was that the use of an excess of the donor should lead to a preferential trimer (α-L-Ara_f)$_2$–β-D-Xyl_p as the consequence of the different reactivities of the acceptor hydroxyl-groups. The α-L-Ara_f–β-D-Xyl_p oligosaccharides belong to the arabinoxylan family, which represent a considerable part of the building blocks of the cell wall in cereals.[1–7] The polymer backbone consists of β-(1→4)-linked-D-xylopyranosyl units, which are unsubstituted or to a variable extent, mono or di-substituted with α-L-Ara_f moities. Occasionally α-L-Ara_f are substituted at the C-5 position by ferulic or coumaric esters.[8] Few reports[9–12a] show the difficulties of preparing the L-Ara_f-D-Xyl_p block unit by chemical synthesis. The procedure adopted in our report is amenable to a library of dimers and would design a way to the series of linear D-xylo-oligosaccharides, substituted regiospecifically both at the C-2 and C-3 positions of the non-reducing end residue by α-L-Ara_f moities. We illustrate our strategy by the synthesis of the six isomeric disaccharides, the trimers, allyl 2,3-di-*O*-(α-L-arabinofuranosyl)-α- and β-D-xylopyranosides and tetramer [2,3-di-*O*-(α-L-arabinofuranosyl)-β-D-xylopyranosyl]-(1→4)-D-xylopyranose.

The donor, namely, 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-L-arabinofuranose α/β (9:1) **2**[13] was prepared by

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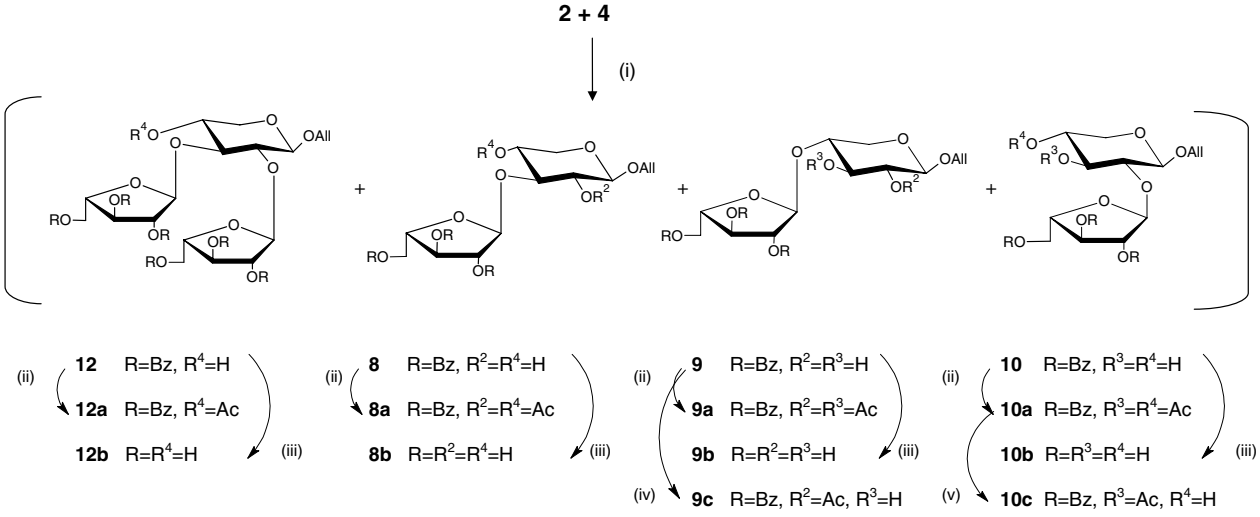
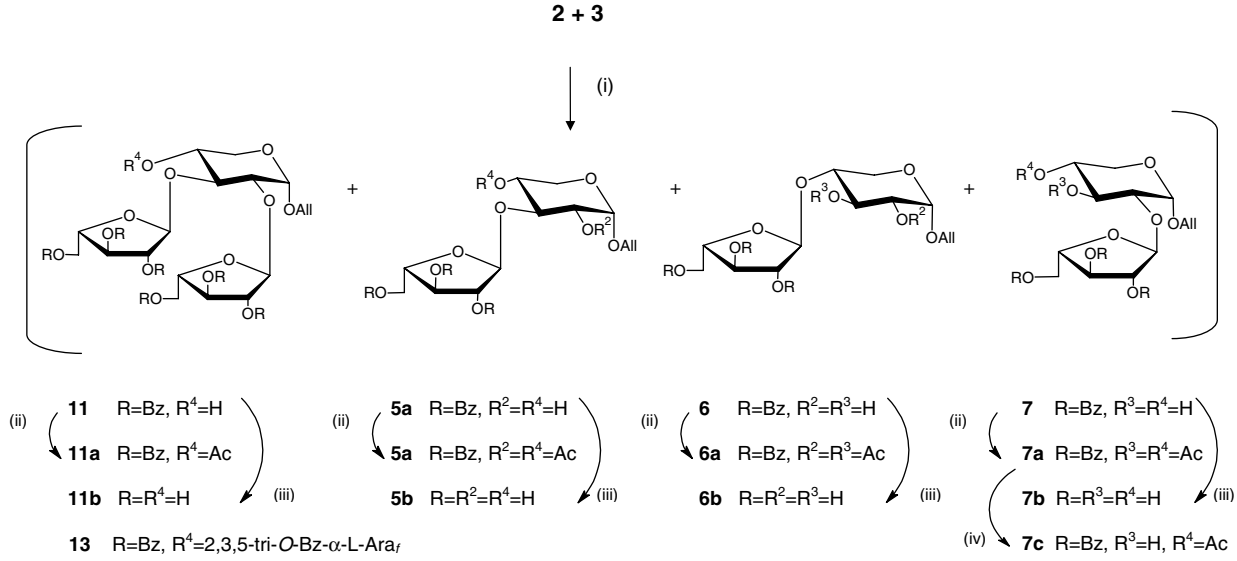
conventional means from methyl L-arabinofuranoside.[14] For glycosylation reactions, donor **2** in dry DCM solution was allowed to react, in presence of $BF_3{\cdot}Et_2O$, with the triols α[12b,c] or β[12a]-D-xylopyranoside **3**, **4**. In the case of allyl β-D-xylopyranoside acceptor **4**, the products formed during the reaction show well-dispersed TLC indicating that easy separation of the products should be possible (Scheme 1).

In a typical chromatography run, the elution of the reaction mixture on a silica gel column with solvent (toluene/EtOAc from 9:1 to 3:2) successively led to, first unreacted donor **2**, traces of hydrolyzed donor, then the fast running trisaccharide **12**, resulting from the L-Ara$_f$ coupling both at C-2 and C-3 of the β-D-Xyl$_p$ entity **4**, then the α-L-(1→3)- linked L-Ara$_f$-D-xyloside dimer **8**, followed by the α-L-(1→4)-linked disaccharide **9**, and the α-L-(1→2)-linked dimer **10**. The amounts of **12**, **8**, **9** and **10** obtained for 1.5 equiv of donor **4**, were in the ratio (~1:6:2:1). Meanwhile, the same experiment with an excess of donor (2.3 equiv) led to **12** as the major product (**12**, **8**, **9**, **10** ~12:6:1:1); the high stereospecificity of the reaction was noted and no traces of β-L-linked products were detected by NMR.[15] The structures of the isolated compounds were characterized by ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectroscopy by 1D and 2D experiments and the linkage sites were con-



Scheme 1. Reagents and conditions: (i) CH_2Cl_2, $BF_3{\cdot}Et_2O$, rt, 2 h; silica gel chromatography: toluene–EtOAc; (ii) Ac_2O, py, rt, 16 h, ~quant; (iii) NaOMe, MeOH, rt, 16 h,[25] ~quant; (iv) Ac_2O, py, 1.3 equiv, rt, 16 h, 65%; (v) lipase: *Candida antartica*, isopropanol, 18 h, 50 °C, 98%.

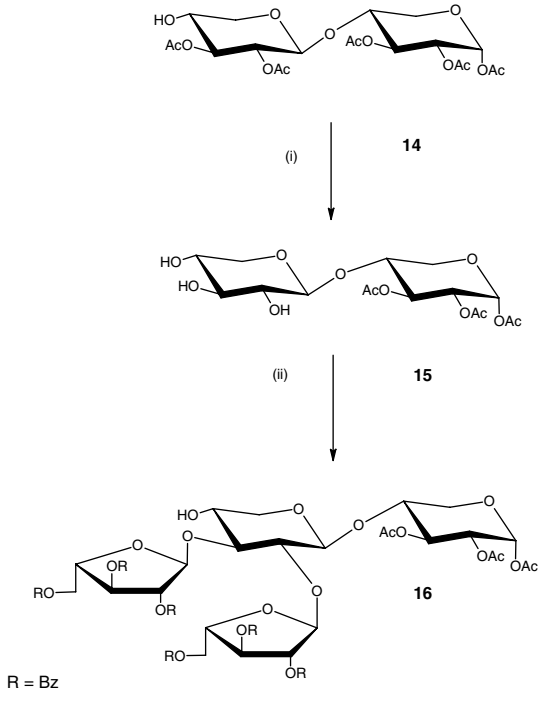


Scheme 2. Reagents and conditions: (i) DCM, $BF_3{\cdot}Et_2O$, rt, 2 h; silica gel chromatography: toluene–EtOAc; (ii) Ac_2O, py, rt, 16 h, ~quant; (iii) NaOMe, MeOH, rt, 16 h,[25] ~quant; (iv) lipase: *Candida antartica*, EtOAc, 48 h, 50 °C, 98%.

firmed by studying the effects of the chemical shifts between the acetylated and non-acetylated derivatives **12**, **8**, **9** and **10** (discussed thereafter). Coupling of donor **2** with allyl α-D-xylopyranoside **3** under the same conditions (1.5 equiv) gave in TLC a quite similar resolved pattern: the order of elution being, respectively, trisaccharide **11** then the α-L-(1→3)-linked dimer **5**, followed by the couple of **6** and **7** (Scheme 2).

Further experiments of selective acetylation on **6** and **7** by lipase *Candida antartica*[16] in dry EtOAc as acylating reagent produced the 4-*O*-acetyl- derivative α-L-(1→2)-linked **7c**, while the α-L-(1→4)-linked **6** was not affected, and separation was much easier via this method. It is worth noting that **11**, conserved the stereo- and regiospecificity observed for **12** with 2,3-di-*O*-L-Ara$_f$ substitution of the α-D-xylopyranoside unit **3**. Furthermore, coupling with 2.3 equiv of donor **2**, gave after chromatography, a pure tetrasaccharide **13** with a trisubstitution at C-2, C-3 and C-4 of the acceptor **3** showing less steric hindrance of the 4-hydroxyl group on **11**, in comparison with the same site on the β-D-xylopyranoside unit of **12**. This observation should lead to an easier chain elongation of the D-Xyl$_p$ backbone from the non-reducing end. In another experiment, we studied the coupling of donor **2** with the triol 1,2,3-tri-*O*-acetyl-α-xylobiose derivative **15** (Scheme 3).

This compound was prepared by the selective removal of the 2′- and 3′-*O*-acetyl groups by treating the penta-*O*-acetyl derivative **14** with DCM/MeOH/K_2CO_3; **14** being the result of selective removal[17,18] of the 4′-*O*-acetyl group of hexa-*O*-acetyl-α-xylobiose by immobilized lipase *Candida antartica*[17] in isopropanol. **15** was obtained in a fairly good yield (50%) and tetrasaccharide **16** was prepared in the same manner with 2.3 equiv of donor **2** with a 60% yield; NMR spectroscopy confirmed the regio- and stereospecificity of the substitution at C-2′ and C-3′ of **15**, and the resulting product **16** was easily separated on a silica gel column.



Scheme 3. Coupling reaction of donor **2** with the tri-*O*-acetyl xylobiose derivative **15**.

NMR spectroscopy: All new compounds (**1**–**16**) were fully characterized by ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectroscopy, several reports[19–24] having dealt with numerous data concerning Ara$_f$–Xyl$_p$ ^{1}H and/or ^{13}C NMR studies. The α-L-Ara$_f$ configuration in **5**–**13** and **16** was proved by ^{1}H NMR spectroscopy from the $J_{1,2}$ values (<1.8 Hz), which were in agreement with those given by Mitsutani et al.[15] The structures of **5**–**12** were determined both through their acetylated derivatives **5a**–**12a** by ^{1}H NMR with the downfield shift observed for the proton signals on the esterified sites (Table 1) and by ^{13}C NMR, by examining the signal shifts for the carbons belonging to the glycosidic bonds (Table 2).

For example, the presence of unprotected OH groups at C-2 and C-4 of **5** was confirmed by acetylation: in the ^{1}H NMR spectrum of diacetate **5a**, the signals for H-2 and H-4 had shifted downfield, respectively, to δ 4.87 and 4.99 compared with the positions at 3.74 and 3.70 in the spectrum of **5** ($\Delta\delta$ 1.13 and 1.29). In the same manner, the spectra of **6**–**12** and **6a**–**12a** offered comparable chemical shifts (Table 1). In the ^{13}C NMR spectra, the formation of glycosidic bonds shows downfield shifts of the glycosidic carbon signal between 5.42 and 11.65 ppm. For example, with compound **8** (1→3)-linked, the C-3 signal shifted from 76.41 for triol **4** to

Table 1. ^{1}H NMR: chemical shifts ($\Delta\delta_{H\text{-}Xyl}$) resulting from the acetylation of **5**–**12**

	H-1	H-2	H-3	H-4	H-5a	H-5b
5 (1→3)	4.91	3.74	3.76	3.70	3.77	3.58
$\Delta\delta_{5a-5}$	(0.12)	(1.13)	(0.52)	(1.29)		
6 (1→4)	4.85	3.57	3.84	3.74	3.77	3.63
$\Delta\delta_{6a-6}$		(1.20)	(1.68)	(0.23)		
7 (1→2)	5.01	3.52	3.98	3.72	3.68	3.57
$\Delta\delta_{7a-7}$		(0.19)	(1.56)	(1.21)		
8 (1→3)	4.32	3.59	3.50	3.74	4.05	3.23
$\Delta\delta_{8a-8}$		(1.49)	(0.42)	(1.25)		
9 (1→4)	4.52	3.52	3.79	3.82	4.09	3.50
$\Delta\delta_{9a-9}$		(1.38)	(1.41)	(0.20)		
10 (1→2)	4.61	3.70	3.78	3.70	4.04	3.38
$\Delta\delta_{10a-10}$		(0.12)	(1.51)	(1.20)		
11 (1→2; 1→3)	4.99	3.80	4.03	3.74	3.72	3.58
$\Delta\delta_{11a-11}$			(0.35)	(1.19)		
12 (1→2; 1→3)	4.39	3.91	3.76	3.74	4.07	3.27
$\Delta\delta_{12a-12}$			(0.35)	(1.25)		

$\Delta\delta \leqslant 0.10$ are neglected **5a**–**10a** (di-*O*-acetyl); **11a** and **12a** (mono-*O*-acetyl).

Table 2. ^{13}C NMR: chemical shifts ($\Delta\delta_{C\text{-}Xyl}$) resulting from the glycosylation of **3** and **4**

	C-1	C-2	C-3	C-4	C-5
3 All α-D-Xyl$_p$	98.13	71.90	73.86	70.05	61.84
5 (1→3)	97.06	71.23	84.53	69.39	59.44
$\Delta\delta_{5-3}$	(−1.07)	(−0.67)	(10.67)	(−0.66)	(−2.40)
6 (1→4)	97.10	72.24	73.33	76.84	59.44
$\Delta\delta_{6-3}$	(−1.03)	(0.34)	(−0.53)	(6.79)	(−2.40)
7 (1→2)	97.46	80.31	73.20	70.11	61.08
$\Delta\delta_{7-3}$	(−0.67)	(8.41)	(−0.66)	(0.06)	(−0.76)
11 (1→2; 1→3)	97.62	77.32	82.17	69.50	61.33
$\Delta\delta_{11-3}$	(−0.51)	(5.42)	(8.31)	(−0.55)	(−0.51)
4 All β-D-Xyl$_p$	102.71	73.66	76.41	69.85	65.76
8 (1→3)	102.17	72.66	86.68	68.52	65.28
$\Delta\delta_{8-4}$	(−0.54)	(−1.00)	(10.27)	(−1.33)	(−0.48)
9 (1→4)	101.31	71.64	72.54	76.06	61.21
$\Delta\delta_{9-4}$	(−1.40)	(−2.02)	(−3.87)	(6.21)	(−4.55)
10 (1→2)	100.07	76.74	75.68	69.71	63.80
$\Delta\delta_{10-4}$	(−2.64)	(3.08)	(−0.73)	(−0.14)	(−1.96)
12 (1→2; 1→3)	101.19	74.62	88.06	69.30	65.28
$\Delta\delta_{12-4}$	(−1.52)	(0.96)	(11.65)	(−0.55)	(−0.48)

86.68 for **8** ($\Delta\delta$ 10.27 ppm); similars effects were observed for all the other products (Table 2).

In conclusion, we have shown a convenient method for accessing to 2,3-di-*O*-L-Ara$_f$-substitued-D-Xyl$_p$ entities, giving by this pathway a strategy for the synthesis of α-L-Ara$_f$-D-Xyl$_p$ oligosaccharides. The reaction had both good regio- and stereoselectivities. The large scale production of α-L-Ara$_f$-D-Xyl$_p$ disaccharides was shown to be easier by glycosylation of allyl β-D-xylopyranoside **4**, which led to convenient chromatographic separation of the α-(1→2)-, -(1→3)-, -(1→4)-linked isomers. The use of allyl α-D-xylopyranoside **3** as acceptor was less practical since the α-(1→2)- and -(1→4)-linked disaccharides had similar chromatographic behaviour. Furthermore, we showed that 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-α-L-arabinofuranose was a stable and effective glycosyl donor. We expected that the present synthetic scheme would be useful for chain elongation by adding β-D-Xyl$_p$ unit(s) onto the terminal unprotected 4-hydroxyl group of structures like **11** and **12**.

1. Experimental

1.1. General methods

^1H and ^{13}C NMR spectra were recorded with an AVANCE 400 spectrometer (Bruker Biospin); all spectra were run in $CDCl_3$ for derivatives, in D_2O for unprotected compounds. Assignments of ^1H NMR spectra were achieved using 2D methods (COSY), ^{13}C NMR spectra using HMQC and HMBC sequences. Residual signal of the solvent was used as internal standard: C*H*Cl$_3$ 7.24 ppm, and *H*OD 4.80 ppm; for ^{13}C NMR, the central peak $CDCl_3$: 77.0 ppm was taken as reference. Analytical thin layer chromatography (TLC) was performed on pre-coated plates (Silica Gel, 60F$_{254}$, E. Merck Co.) and the products were visualized with H_2SO_4/EtOH/H_2O (15:15:1) by charring. Silica Gel 60 (E. Merck Co.) was employed for flash chromatography. Optical rotations were measured at 20 °C in a 1-dm cell on a Perkin–Elmer 341 polarimeter. All solvents and reagents were purified according to standard procedures. Melting points were determined on a Büchi 535 apparatus and are uncorrected. ESI mass spectra were obtained on a Waters micromass ZQ mass spectrometer. Enzymic acetylation (dry EtOAc) or deacetylation (isopropanol) were performed with lipase from *Candida antartica* (Novozym 435, Sigma). Derivatizations: for some compounds mono-or di-O-acetylation or de-acylation were worked up as indicated; all the products were characterized (see Supplementary data).

1.2. 1-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-α-L-arabinofuranose 2[13]

1.3. Allyl α,β-D-xylopyranoside 3, 4[12]

1.4. Coupling reactions: with allyl α-D-xylopyranoside 3

1.4.1. 1.5 equiv of donor 2. Compound **3** (190 mg, 1 mmol) was dissolved in dry DCM (3 mL), then **2** (756 mg, 1.5 mmol) was added. The solution was cooled in an ice-water bath and after 15 min stirring, addition of $BF_3{\cdot}Et_2O$ (50 μL) was performed. After 2 h more stirring, TLC indicated that the reaction was quite complete: traces of **3** (EtOAc, R_f 0.25) and presence of 4 spots, respectively, with R_f: 0.75, 0.72, 0.53, 0.19 (3:2 toluene/EtOAc) corresponding, respectively, to donor **2**, trisaccharide **11**, the major product α-(1→3)-linked disaccharide **5**, then a mixture of α-(1→4)-, α-(1→2)-linked dimers **6**, **7**. The reactional mixture was diluted with DCM, neutralized with Et_3N, washed with satd NaCl aqueous solution; then the organic layer was dried on anhydrous sodium sulfate and concentrated; the crude residue was purified by silica gel chromatography with toluene/EtOAc with gradually increasing polarity. Pure products **11**, **5** were isolated, **6** and **7** separated as a mixture, which on treatment by the immobilized lipase[16] *Candida antartica* in dry EtOAc as acetylating reagent, furnished 4-*O*-acetyl derivative **7c** and quite pure **6**. Total yield for the coupling between **2** and **3**: 78%, **11**: 377 mg, 0.35 mmol, **5**: 158 mg, 0.25 mmol, **6**, **7**: 114 mg, 0.18 mmol.

1.4.2. 2.3 equiv of donor 2. Same protocol as before, except the amount of donor **2**. TLC (9:1 toluene/EtOAc) indicated the presence of two spots with a major one (R_f 0.14) corresponding to trisaccharide **11** and a fast running product at R_f 0.36 further identified to tetrasaccharide **13**; TLC (3:2 toluene/EtOAc) shows the pres-

ence of **5** and small amounts of **6**, **7**. Total yield for the coupling: 82%, **13**: 0.10 mmol, **11**: 0.50 mmol, **5**: 0.14 mmol, **6**, **7**: 0.08 mmol.

1.5. Allyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-α-D-xylopyranoside (5)

Product **5** was isolated as a syrup (158 mg, 0.25 mmol); $[\alpha]_D$ +51.6 (*c* 1.0, $CHCl_3$), R_f 0.53 (3:2, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.15 (m, 15H, arom H), 5.92 (m, 1H, CH_2=C*H*–), 5.67 (dd, 1H, H-3′, $J_{2',3'}$ 2.93 Hz, $J_{3',4'}$ 5.86 Hz), 5.58 (dd, 1H, H-2′, $J_{1',2'}$ 0.98 Hz), 5.52 (br s, H1′, 1H), 5.30, 5.20 (m, 2H, CH_2=CH–), 4.91 (d, 1H, H-1, $J_{1,2}$ 2.98 Hz), 4.79–4.73 (m, 2H, H-4′, H-5′a, $J_{4',5'a}$ 3.42 Hz, $J_{4',5'b}$ 6.83 Hz, $J_{5'a,5'b}$ 12.0 Hz), 4.62 (dd, 1H, H-5′b), 4.22, 4.03 (m, 2H, CH_2=CH–CH_2O–), 3.77 (dd, 1H, H-5a, $J_{4,5a}$ 5.59 Hz), 3.76 (t, 1H, H-3, $J_{2,3} = J_{3,4}$ 7.91 Hz), 3.74 (dd, 1H, H-2), 3.70 (m, 1H, H-4), 3.58 (t, 1H, H-5b, $J_{4,5b} = J_{5a,5b}$ 11.90 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7–165.5 (3C, 3Ph*C*O), 133.8–128.2 (18C, arom C; 1C, CH_2=*C*H–), 118.1 (1C, *C*H_2=CH–), 107.7 (C-1′), 97.1 (C-1), 84.5 (C-3), 82.8 (C-2′), 80.4 (C-4′), 77.0 (C-3′), 71.2 (C-2), 68.7 (CH_2=CH–*C*H_2–O–), 68.4 (C-4), 63.8 (C-5′), 61.8 (C-5); ESIMS: *m*/*z* 657.3 $[M+Na]^+$.

1.6. Allyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→4)-α-D-xylopyranoside (6)

Pure compound **6** was isolated during the preparation of **7c** from a mixture of **6** and **7** (see **7c**). Amorphous solid; $[\alpha]_D$ +38.5 (*c* 1.0, $CHCl_3$), R_f 0.19 (3:2, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.15 (m, 15H, arom H), 5.91 (m, 1H, CH_2=C*H*–), 5.57 (dd, 1H, H-3′, $J_{2',3'}$ 1.44 Hz, $J_{3',4'}$ 4.51 Hz), 5.48 (br d, 1H, H-2′, $J_{1',2'}$ <0.5 Hz), 5.39 (br s, 1H, H-1′), 5.33, 5.29 (m, 2H, CH_2=CH–), 4.85 (d, 1H, H-1, $J_{1,2}$ 3.79 Hz), 4.80 (dd, 1H, H-5′a, $J_{4',5'a}$ 3.71 Hz, $J_{5'a,5'b}$ 10.93 Hz), 4.77 (m, 1H, H-4′), 4.65 (dd, 1H, H-5′b, $J_{4',5'b}$ 4.26 Hz), 4.22, 4.02 (m, 2H, CH_2=CH–CH_2O–), 3.84 (t, 1H, H-3, $J_{2,3} = J_{3,4}$ 9.20 Hz), 3.77 (dd, 1H, H-5a, $J_{4,5a,}$ 5.23 Hz, $J_{5a,5b}$ 10.95 Hz), 3.74 (m, 1H, H-4), 3.63 (t, 1H, H-5b, $J_{4,5b}$ 10.95 Hz), 3.57 (dd, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 165.7, 165.5 (3C, 3Ph*C*O), 133.7–128.2 (18C, arom C; 1C, CH_2=*C*H–), 117.9 (*C*H_2=CH–), 105.3 (C-1′), 97.1 (C-1), 82.0 (C-2′), 81.4 (C-4′), 77.4 (C-3′), 76.8 (C-4) 73.3 (C-3), 72.2 (C-2), 68.6 (1C, CH_2=CH–*C*H_2O–), 63.6 (C-5′), 59.4 (C-5); ESIMS: *m*/*z* 657.3 $[M+Na]^+$.

1.7. Allyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→2)-α-D-xylopyranoside (7)

Amorphous solid; $[\alpha]_D$ +50.2 (*c* 1.0, $CHCl_3$); R_f 0.19 (3:2, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.15 (m, 15H, arom H), 5.83 (m, 1H, CH_2=C*H*–), 5.64 (dd, 1H, H-3′, $J_{2',3'}$ 2.47 Hz, $J_{3',4'}$ 5.78 Hz), 5.53 (br d, 1H, H-2′, $J_{1',2'}$ <0.5 Hz), 5.43 (d, 1H, H-1′), 5.26, 5.06 (m, 2H, CH_2=CH–), 5.01 (d, 1H, H-1, $J_{1,2}$ 3.61 Hz), 4.76 (dd, 1H, H-5′a, $J_{4',5'a}$ 3.40 Hz, $J_{5'a,5'b}$ 10.90 Hz), 4.64 (m, 1H, H-4′), 4.61 (dd, 1H, H-5′b, $J_{4',5'b}$ 5.35 Hz), 4.18 (m, 1H, CH_2=CH–CH_2O–), 3.98 (t, 1H, H-3, $J_{2,3} = J_{3,4}$ 9.10 Hz), 3.94 (m, 1H, CH_2=CH–CH_2O–), 3.72 (m, 1H, H-4), 3.68 (dd, 1H, H-5a, $J_{4,5a}$ 5.46 Hz, $J_{5a,5b}$ 10.44 Hz), 3.57 (t, 1H, H-5b, $J_{4,5b}$ 10.44 Hz), 3.52 (dd, 1H, H-2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2–165.6 (3C, Ph*C*O), 133.8–128.4 (18C, arom C; 1C, CH_2=*C*H–), 117.5 (1C, *C*H_2=CH–), 107.9 (C-1′), 97.5 (C-1), 83.3 (C-2′), 80.3 (C-2), 80.1 (C-4′), 77.1 (C-3′), 73.2 (C-3), 70.1 (C-4), 68.4 (1C, CH_2=CH–*C*H_2O–), 63.6 (C-5′), 61.1 (C-5); ESIMS: *m*/*z* 657.3 $[M+Na]^+$.

1.8. Allyl 2,3-di-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-α-D-xylopyranoside (11)

Amorphous solid; $[\alpha]_D$ +33.8 (*c* 1.0, $CHCl_3$); TLC R_f 0.72 (3:2, toluene/EtOAc), R_f 0.14 in (9:1, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15–8.15 (m, 30H, arom H), 5.77 (m, 1H, CH_2=C*H*–), 5.65 (1s, 2 br d, 3H, H-1′, H-2′, H-2″), 5.61 (1s, 1H, H-1″, $J_{1'',2''}$ <0.5 Hz), 5.59 (br d, 1H, H-3″, $J_{3''4''}$ 3.81 Hz), 5.54 (br d, 1H, H-3′, $J_{3',4'}$ 4.84 Hz), 5.24 (m, 1H, CH_2=CH–), 5.04 (m, 1H, CH_2=CH–), 4.99 (d, 1H, H-1), 4.80 (dd 1H, H-5′a, $J_{4',5'a}$ 3.23 Hz), 4.78 (dd, 1H, H-5″a, $J_{4'',5''a}$ 4.80 Hz), 4.76 (m, 1H, H-4″), 4.66 (dd, 1H, H-5′b, $J_{4',5'b}$ 5.98 Hz), 4.62 (m, 1H, H-5″b, $J_{4'',5''b}$ 6.40 Hz), 4.56 (m, 1H, H-4′), 4.15 (m, 1H, CH_2=CH–CH_2O-), 4.03 (dd, 1H, H-3, $J_{2,3}$ 9.58 Hz, $J_{3,4}$ 8.11 Hz), 3.91 (m, 1H, CH_2=CH–CH_2O-), 3.80 (dd, 1H, H-2), 3.74 (m, 1H, H-4), 3.72 (dd, 1H, H-5a, $J_{4,5a}$ 3.25 Hz, $J_{5a,5b}$ 12.10 Hz), 3.58 (t, 1H, H-5b, $J_{4,5b}$ 12.10 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9–165.1 (6C, 6Ph*C*O), 133.4–128.1 (36C, arom C; 1C, CH_2=*C*H–), 117.3 (1C, *C*H_2=CH–), 107.7 (C-1′), 107.6 (C-1″), 97.6 (C-1), 82.3, 82.2 (C-2″, C-3), 81.8–81.6 (C-2′, C-4′, C-4″), 77.8 (C-3′), 77.5 (C-3″), 77.3 (C-2), 69.5 (C-4), 68.3 (CH_2=CH–*C*H_2O–), 63.9 (C-5′, C-5″), 61.3 (C-5); ESIMS: *m*/*z* 1101.6 $[M+Na]^+$.

1.9. Allyl 2,3,4-tri-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-α-D-xylopyranoside (13)

Amorphous solid; $[\alpha]_D$ +26.63 (*c* 1.0, $CHCl_3$); TLC R_f 0.36 (9:1, toluene/EtOAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1–165.1 (9C, 9Ph*C*O), 133.5–128.1 (54C, arom C; 1C, CH_2=*C*H–), 117.1 (1C, *C*H_2=CH–), 107.6, 106.1, 105.8 (C-1′, C-1″, C-1‴, Ara), 97.7 (C-1, Xyl), 82.3, 82.2, 81.9, 81.7, 81.5, 81.4, 80.8, 78.2, 77.4, 77.0 (10 C, C-2′, C-2″, C-2‴, C-3, C-3′, C-3″, C-3‴, C-4′, C-4″, C-4‴), 74.2, 73.8 (C-2, C-4), 68.4 (1C,

CH_2=CH–CH_2–O–), 64.0, 63.7, 63.5 (C-5′, C-5″, C-5‴), 59.7 (C-5, Xyl); ESIMS: *m*/*z* 1546.0 $[M+Na]^+$.

1.10. Coupling reactions: with allyl β-D-xylopyranoside 4 as acceptor

1.10.1. 1.5 equiv of donor 2. Same conditions as described for **3**; 1 mmol of acceptor **4**, total yield 72%, **12**: 0.07 mmol, **8**: 0.43 mmol, **9**: 0.14 mmol, **10**: 0.08 mmol.

1.10.2. 2.3 equiv of donor 2. 1 mmol of acceptor **4**, total yield 82%; **12**: 0.49 mmol, **8**: 0.10 mmol, **9**: 0.12 mmol, **10**: 0.11 mmol.

1.11. Allyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-β-D-xylopyranoside (8)

Amorphous solid; $[\alpha]_D$ −1.9 (*c* 1.0, $CHCl_3$); TLC R_f 0.48 (3:2, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.15 (m, 15H, arom H), 5.93 (m, 1H, CH_2=C*H*–), 5.66 (dd, 1H, H-3′, $J_{2',3'}$ 2.65 Hz, $J_{3',4'}$ 5.50 Hz), 5.57 (dd, 1H, H-2′, $J_{1',2'}$ 1.15 Hz), 5.50 (br s, 1H, H1′), 5.49 (dd, 1H, H-5′a, $J_{4',5'a}$ 3.60 Hz, $J_{5'a,5'b}$ 12.80 Hz), 5.48 (m, 1H, H-4′, $J_{4',5'b}$ 6.67 Hz), 5.35–5.18 (m, 2H, CH_2=CH–), 4.61 (dd, 1H, H-5′b), 4.34 (m, 1H, CH_2=CH–CH_2–O–), 4.32 (d, 1H, H-1, $J_{1,2}$ 7.43 Hz), 4.13 (m, 1H, CH_2=CH–CH_2–O–), 4.05 (dd, 1H, H-5a, $J_{4,5a}$ 5.52 Hz, $J_{5a,5b}$ 11.70 Hz), 3.74 (m, 1H, H-4, $J_{4,5b}$ 10.16 Hz), 3.59 (dd, 1H, H-2, $J_{2,3}$ 8.72 Hz), 3.50 (t, 1H, H-3, $J_{3,4}$ 8.72 Hz), 3.23 (dd, 1H, H-5b); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1–165.6 (3C, 3Ph*C*O), 133.8–128.4 (18C, arom C; 1C, CH_2=*C*H–), 117.9 (1C, *C*H_2=CH–), 107.9 (C-1′), 102.2 (C-1), 86.7 (C-3), 82.9 (C-2′), 80.6 (C-4′), 77.0 (C-3′), 72.7 (C-2), 70.0 (CH_2=CH–*C*H_2O–), 68.5 (C-4), 65.3 (C-5), 63.6 (C-5′); ESIMS: *m*/*z* 657.3 $[M+Na]^+$.

1.12. Allyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→4)-β-D-xylopyranoside (9)

Amorphous solid; $[\alpha]_D$ −22.5 (*c* 1.0, $CHCl_3$); TLC R_f 0.31 (3:2, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.15 (m, 15H, arom H), 5.85 (m, CH_2=C*H*–), 5.57 (br d,1H, H-3′, $J_{2',3'}$ 1.20 Hz, $J_{3',4'}$ 4.30 Hz), 5.51 (br d, 1H, H-2′, $J_{1',2'}$ <1 Hz), 5.41 (s, 1H, H-1′), 5.17–5.13 (m, 2H, CH_2=CH–), 4.80 (dd, 1H, H-5′a, $J_{4',5'a}$ 3.20 Hz, $J_{5'a,5'b}$ 11.36 Hz), 4.74 (m, 1H, H-4′, $J_{4',5'b}$ 4.73 Hz), 4.65 (dd, 1H, H-5′b), 4.52 (d, 1H, H-1, $J_{1,2}$ 5.33 Hz), 4.30 (m, 1H, CH_2=CH–CH_2O–), 4.09 (dd, 1H, H-5a, $J_{4,5a}$ 3.73 Hz, $J_{5a,5b}$ 11.33 Hz), 4.07 (m, 1H, CH_2=CH–CH_2O–), 3.82 (m, 1H, H-4, $J_{4,5b}$ 7.20 Hz), 3.79 (br t, 1H, H-3, $J_{2,3} = J_{3,4}$ 7.11 Hz), 3.52 (br dd, 1H, H-2), 3.50 (dd, 1H, H-5b); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7–165.4 (3C, Ph*C*O), 133.6–128.3 (18C, arom C; 1C, CH_2=*C*H–), 118.1 (1C, *C*H_2=CH–), 105.2 (C-1′), 101.3 (C-1), 82.0 (C-2′), 81.7 (C-4′), 77.5 (C-3′), 76.1 (C-4), 72.5 (C-3), 71.6 (C-2), 69.7 (CH_2=CH–*C*H_2O–), 63.6 (C-5′), 61.21 (C-5); ESIMS: *m*/*z* 657.3 $[M+Na]^+$.

1.13. Allyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→2)-β-D-xylopyranoside (10)

Amorphous solid; $[\alpha]_D$ −7.5 (*c* 1.0, $CHCl_3$); TLC R_f 0.18 (3:2, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.15 (m, 15H, arom H), 5.83 (m, 1H, CH_2=C*H*–), 5.62 (br d, 1H, H-3′, $J_{2',3'}$ 1.60 Hz, $J_{3',4'}$ 5.27 Hz), 5.57 (s, 1H, H-1′, $J_{1',2'}$ <1 Hz), 5.49 (br d, 1H, H-2′), 5.24, 5.08 (m, 2H, CH_2=CH–), 4.78 (dd, 1H, H-5′a, $J_{4',5'a}$ 3.27 Hz, $J_{5'a,5'b}$ 11.46 Hz), 4.72 (m, 1H, H-4′, $J_{4',5'b}$ 4.53 Hz), 4.66 (dd, 1H, H-5′b), 4.61 (d, 1H, H-1, $J_{1,2}$ 5.63 Hz), 4.25 (m, 1H, CH_2=CH–CH_2O–), 4.04 (dd, 1H, H-5a, $J_{4,5a}$ 4.14 Hz, $J_{5a,5b}$ 11.80 Hz), 3.95 (m, 1H, CH_2=CH–CH_2O–), 3.78 (t, 1H, H-3, $J_{2,3} = J_{3,4}$ 7.11 Hz), 3.70 (dd, 2H, H-2, H-4, $J_{4,5a}$ 4.14 Hz, $J_{4,5b}$ 7.38 Hz), 3.38 (dd, 1H, H-5b); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1–165.7 (3C, Ph*C*O), 133.7–128.3 (18C, arom C; 1C, CH_2=*C*H–), 117.7 (1C, *C*H_2=CH–), 106.3 (C-1′), 100.1 (C-1), 83.0 (C-2′), 80.8 (C-4′), 77.7 (C-3′), 76.7 (C-2), 75.7 (C-3), 69.8 (1C, CH_2=CH–*C*H_2O–), 69.7 (C-4), 63.8 (C-5), 63.6 (C-5′); ESIMS: *m*/*z* 657.3 $[M+Na]^+$.

1.14. Allyl 2,3-di-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-β-D-xylopyranoside (12)

Amorphous solid; $[\alpha]_D$ +3.9 (*c* 1, $CHCl_3$); TLC R_f 0.52 (7:3, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.15 (m, 30H, arom H), 5.88 (s, 1H, H-1′, $J_{1',2'}$ <1 Hz), 5.73 (m, 1H, CH_2=C*H*–), 5.63 (br d, 1H, H-2′, $J_{2',3'}$ 0.85 Hz), 5.61 (br s, 1H, H-1″, $J_{1'',2''}$ <1 Hz), 5.58 (br d 1H, H-3″, $J_{2'',3''}$ 0.75 Hz, $J_{3'',4''}$ 4.08 Hz), 5.57 (br d, 1H, H-2″), 5.52 (br d, 1H, H-3′, $J_{3',4'}$ 4.56 Hz), 5.10–4.94 (m, 2H, CH_2=CH–), 4.88 (m, 1H, H-4′), 4.82 (dd, 1H, H-5′a, $J_{4',5'a}$ 3.02 Hz, $J_{5'a,5'b}$ 11.98 Hz), 4.78 (dd, 1H, H-5″a, $J_{4'',5''a}$ 3.73 Hz, $J_{5''a,5''b}$ 13.02 Hz), 4.76 (m, 1H, H-4″), 4.68 (dd, 1H, H-5′b, $J_{4',5'b}$ 4.61 Hz, $J_{5'a,5'b}$ 11.96 Hz), 4.63 (dd, 1H, H-5″b, $J_{4'',5''b}$ 7.44 Hz), 4.39 (d, 1H, H-1, $J_{1,2}$ 7.55 Hz), 4.27 (m, 1H, CH_2=CH–CH_2O–), 4.07 (dd, 1H, H-5a, $J_{4,5a}$ 4.87 Hz, $J_{5a,5b}$ 11.75 Hz), 3.91 (dd, 1H, H-2, $J_{2,3}$ 8.90 Hz), 3.87 (m, 1H, CH_2=CH–CH_2O), 3.76 (m, 1H, H-4), 3.74 (t, 1H, H-3), 3.27 (dd, 1H, H-5b, $J_{4,5b}$ 9.40 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3–165.2 (6C, Ph*C*O), 133.7–128.2 (36 C, arom C; 1C, CH_2=*C*H–), 117.9 (1C, *C*H_2=CH–), 107.9 (C-1″), 105.8 (C-1′), 101.2 (C-1), 88.1 (C-3), 82.2 (C-4″), 82.0 (C-2′), 81.7 (C-4′), 81.6 (C-2″), 78.1 (C-3′), 77.1 (C-3″), 74.6 (C-2), 70.1 (1C, CH_2=CH–*C*H_2O–), 69.3 (C-4), 65.3 (C-5), 63.9 (C-5′), 63.8 (C-5″); ESIMS: *m*/*z* 1101.5 $[M+Na]^+$.

1.15. β-D-Xylopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-α-D-xylopyranose (15)

To a solution of 1,2,3,2′,3′-penta-*O*-acetyl-α-xylobiose[18] **14** (443 mg, 0.9 mmol) in DCM/MeOH (9:1; 10 mL) was added dry K_2CO_3 (187 mg, excess 1.5/1), the mixture was stirred at rt for 2 h; additional K_2CO_3 (125 mg, 0.9 mmol) was added and stirring continued for 2 h. The solution was filtered and concentrated in vacuo; the residue was chromatographed on silica gel and product **15** isolated: 50% yield, amorphous solid; $[\alpha]_D$ +17.3 (*c* 1, $CHCl_3$); TLC R_f 0.27 (3:2, EtOAc/acetone); selected data, ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.11(d, H-1, $J_{1,2}$ 3.62 Hz), 5.25 (t, H-3, $J_{2,3} = J_{3,4}$ 9.5 Hz), 4.89 (dd, H-2), 4.21 (d, H-1′, 6.1 Hz), 3.85–3.12 (m, 8H, H-4, H-5a,b, H-2′, H-3′, H-4′, H-5′a,b); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.8, 169.1 (CH_3CO), 102.4 (C-1′), 89.1 (C-1), 75.8, 74.6, 72.7, 70.1, 69.4, 69.2 (C-2, C-2′, C-3, C-3′, C-4, C-4′), 65.3 (C-5′), 61.3 (C-5), 20.8–20.3 (3s, CH_3CO).

1.16. 2,3-Di-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-β-D-xylopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-α-D-xylopyranose (16)

Amorphous solid; 60% yield; $[\alpha]_D$ + 9.2 (*c* 1, $CHCl_3$); TLC R_f 0.25 (7:3, toluene/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-8.15 (m, 30 H, arom H), 6.09 (d, 1H, H-1, $J_{1,2}$ 3.62 Hz), 5.74 [s, 1H, H-1″, Ara-(1→2)-linked, $J_{1'',2''}$ <0.5 Hz], 5.66 (d, 1H, H-2″, $J_{2'',3''}$ 0.99 Hz), 5.61 (br. d, 1H, H-2‴, $J_{1''',2'''}$ <0.5 Hz, $J_{2'''3'''}$ 1.07 Hz), 5.58 (br d, 1H, H-3″, $J_{3'',4''}$ 4.83 Hz), 5.55 [s, 1H, H-1‴, Ara-(1→3)-linked, $J_{1''',2'''}$ <0.5 Hz], 5.54 (br d, 1H, H-3‴, $J_{3''',4'''}$ 5.60 Hz), 5.33 (t, 1H, H-3, $J_{2,3}$ 9.81 Hz, $J_{3,4}$ 9.13 Hz), 4.91 (dd, 1H, H-5″a, $J_{4'',5''a}$ 3.70 Hz, $J_{5''a,5''b}$ 12.20 Hz), 4.90 (dd, 1H, H-2), 4.78 (dd, 1H, H-5‴a, $J_{4''',5'''a}$ 3.50 Hz, $J_{5'''a,5'''b}$ 11.54 Hz), 4.77 (m, 1H, H-4″), 4.74 (dd, 1H, H-5″b, $J_{4'',5''b}$ 3.30 Hz), 4.72 (m, 1H, H-4‴), 4.62 (dd, 1H, H 5‴b, $J_{4''',5'''b}$ 5.94 Hz), 4.39 (d, 1H, H-1′, $J_{1',2'}$ 7.04 Hz), 4.01 (dd, 1H, H-5′a, $J_{4',5'a}$ 4.90 Hz, $J_{5'a,5'b}$ 11.95 Hz), 3.88 (m, 1H, H-4), 3.78 (dd, 1H, H-5a, $J_{4,5a}$ 5.42 Hz, $J_{5a,5b}$ 11.07 Hz), 3.76 (dd, 1H, H-2′, $J_{2',3'}$ 8.10 Hz), 3.72 (m, 1H, H-4′), 3.70 (t, 1H, H-3′, $J_{3',4'}$ 8.10 Hz), 3.62 (t, 1H, H-5b, $J_{4,5b}$ 10.07 Hz), 3.26 (dd, 1H, H-5′b, $J_{4',5'b}$ 8.85 Hz), 2.03, 1.99, 1.96 (3s, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 169.8, 169.1 (3C, CH_3CO), 166.3, 166.1, 165.8, 165.6, 165.6, 165.1 (6C, 6Ph*C*O), 133.6–128.3 (36C, arom C), 107.8 [C-1‴; Ara-(1→3)-linked], 106.7 [C-1″; Ara-(1→2)-linked], 101.3 (C-1′, Xyl), 89.1 (C-1, Xyl), 87.3 (C-3′), 82.3 (C-2″), 82.1 (C-4‴), 81.7 (C-2‴), 81.7 (C-4″), 78.0 (C-3″), 77.2 (C-3‴), 76.1 (C-2′), 74.1 (C-4), 69.9 (C-3), 69.3 (C-2, C-4′), 65.2 (C-5′), 63.9, 63.8 (C-5″, C-5‴), 61.4 (C-5), 20.9, 20.6, 20.5 (CH_3CO); ESIMS *m*/*z* 1319.6 $[M+Na]^+$.

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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.2007.08.007.

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