Tetrahedron 71 (2015) 4757–4769

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Study on the synthesis of regio- and stereoisomers of the disaccharide unit of the OSW-1 saponin

Zbigniew Pakulski *, Piotr Cmoch

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

ARTICLE INFO

Article history:
Received 17 March 2015
Received in revised form 5 May 2015
Accepted 18 May 2015
Available online 22 May 2015

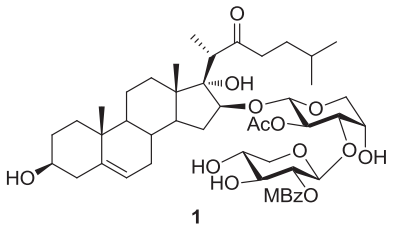
Keywords:
OSW-1
OSW-1 analogues
Disaccharide unit
Hydrogen bond network
Flow chemistry
Regioselectivity of glycosylation

ABSTRACT

A convenient method for the preparation of the OSW-1 disaccharide unit was developed and used for the synthesis of its regio- and stereoisomers. The corresponding allyl and 1-propenyl xylopyranosides and arabinopyranosides were used as starting materials. In all cases studied the groups protecting the anomeric position were easily removed under very mild conditions. The influence of the configuration at the anomeric centre on the regioselectivity of glycosylation was studied and discussed. New disaccharides were synthesized with a view to use them in the preparation of OSW-1 analogues.

1. Introduction

Saponin OSW-1 [**1**,3β,16β,17α-trihydroxycholest-5-en-22-one 16-*O*-(2-*O*-4-methoxybenzoyl)-β-D-xylopyranosyl)-(1→3)-2-*O*-acetyl-α-L-arabinopyranoside] was isolated in 1992 by Sashida et al. from the bulbs of *Ornithogalum saudersiae* classified in the family Hyacinthaceae together with a number of other cholestane glycosides (Fig. 1).[1] Five years later it was found that OSW-1 exhibited extremely potent cytotoxicity against a wide range of malignant tumor cells in nanomolar concentration (IC_{50} 0.1–0.7 nM), about 10–100 times more potent than that of the clinically applied anticancer agents.[2] The structure, biological activity, chemical synthesis and modifications of saponin OSW-1 and its congeners have been recently reviewed exhaustively.[3]



1

Fig. 1. OSW-1 saponin (MBz=4-methoxybenzoyl).

Saponin OSW-1 can be disconnected into two parts: cholestane aglycon and the disaccharide moiety. In all known approaches to this natural product and its congeners, coupling of the aglycon with a sugar donor is considered as one of the key steps. Therefore, a simple and efficient method for the synthesis of the disaccharide unit is necessary. Few synthetic methods for its preparation have been published up to date;[4–6] among them, the first synthesis by Yu et al. seems to be the simplest and the most convenient.[6] However, benzyl xyloside and benzyl arabinoside derivatives used by Yu's group were extremely resistant to hydrogenation. High pressure of hydrogen (40–50 bar), elevated temperature (40–50 °C), and prolonged reaction time (up to 3 days) were necessary during deprotection steps; only partial chromatographic separations of regioisomers were possible, and several percent of unreacted starting materials were also recovered. Thus, although the yield of the reaction was relatively high, due to inconveniences during hydrogenolysis, preparation of the desired disaccharide unit on a large scale might be problematic. On the other hand, reaction in the presence of butane-2,3-diacetyl (BDA) derivatives proposed by Russian scientists suffers from low regioselectivity.[5]

In this paper we report the synthesis of regio- and stereoisomers of the OSW-1 disaccharide unit from easily available allyl glycosides, which allow us to avoid the high pressure of hydrogen during the deprotection step. The influence of the anomeric configuration on the regioselectivity of glycosylation was also studied.

* Corresponding author. E-mail address: zbigniew.pakulski@icho.edu.pl (Z. Pakulski).

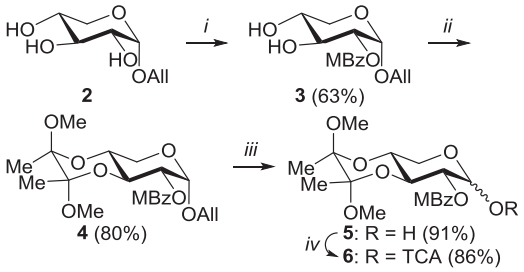
http://dx.doi.org/10.1016/j.tet.2015.05.058
0040-4020/

2. Results and discussion

2.1. Synthesis of *xylo*- and arabinopyranose derivatives

Allyl xylopyranosides and allyl arabinopyranosides, starting materials in our studies, were obtained by the Fisher method as α,β-mixtures from D- (or L-) xylose and L-arabinose. Pure anomers might be easily isolated by crystallization or chromatographic separation of the corresponding peracetates. In the case of xylose derivatives, separation was not necessary and crude α,β-mixture of allyl xylosides was used for large scale synthesis. This significantly improved the yield and made the process highly economical. However, for an analytical reason, preliminary experiments were performed using pure α-xylosides.

Our first synthesis began with allyl α-D-xylopyranoside **2**,[7] which was selectively acylated with *p*-methoxybenzoyl chloride (MBzCl) to ester **3**. Acid catalyzed reaction of **3** with diacetyl and trimethyl orthoformate in methanol afforded butane-2,3-diacetal (BDA-acetal) derivative **4**. Hydrolysis of allyl glycoside **4** in the presence of $PdCl_2$ provided hemiacetal **5**, which was subsequently transformed into required donor **6**[5] by reaction with trichloroacetonitrile in the presence of K_2CO_3 (Scheme 1).



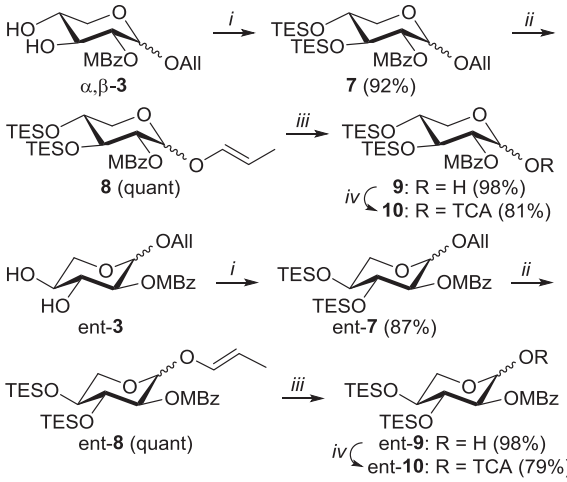
Scheme 1. Reagents and conditions: (*i*) MBzCl, pyridine; (*ii*) diacetyl, $HC(OMe)_3$, CSA, methanol; (*iii*) $PdCl_2$, methanol; (*iv*) Cl_3CCN, K_2CO_3, DCM.

Similarly, starting from allyl D-xylopyranoside **3**, silylated glycosyl donor **10** was obtained. Reaction of **3** with triethylsilyl chloride gave fully protected xylopyranoside **7** in high yield (92%). Due to the high sensitivity of TES group to acidic hydrolysis, deallylation was performed under neutral conditions by a two-step procedure. Isomerization of the double bond in the presence of an iridium complex afforded 1-propenyl α-D-xylopyranoside **8** quantitatively. Further treatment with mercury chloride/mercury oxide gave known xylopyranose **9**, which was transformed into Schmidt donor **10** according to the literature procedure.[6] As noted above, preliminary experiments were performed starting from allyl α-D-xylopyranoside **3**, whereas for the synthesis in preparative scale a mixture of allyl α,β-D-xylopyranosides (α,β-**3**) was used (Scheme 2). By the same way L-xylopyranoside derivatives **ent-3**, and **ent-7**–**ent-10** were obtained. Required Schmidt donor **ent-10** was prepared in 67% total yield, after four steps (Scheme 2).

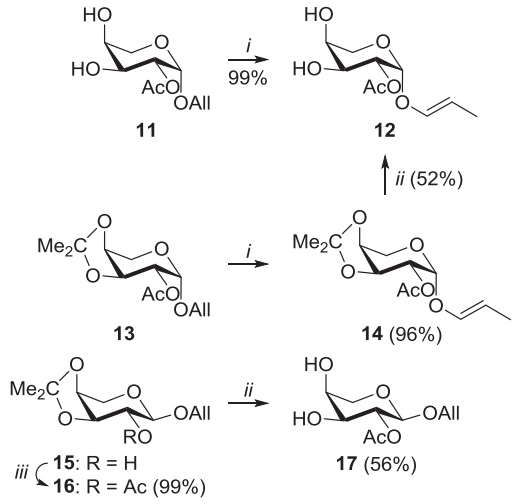
Independently, glycosyl acceptors **11**, **12**, and **17** were prepared from L-arabinose. Known allyl β-L-arabinopyranoside **11**[8] was isomerized into 1-propenyl β-L-arabinopyranoside **12** in the presence of iridium complex. The same compound was also obtained by isomerisation and deprotection of **13**,[8] however, due to sensitivity of 1-propenyl glycoside to acidic conditions, final hydrolysis of isopropylidene group in **14** proceeded in moderate yield, only. By the similar way, allyl α-L-arabinopyranoside **17** was prepared starting from **15**[9] (Scheme 3).

2.2. Regioselectivity in glycosylation of allyl and 1-propenyl 2-*O*-acetyl-L-arabinopyranosides

First we tested the regioselectivity of reaction between conformationally rigid glycosyl donor **6** and acceptors **11** and **12**.



Scheme 2. Reagents and conditions: (*i*) TESCl, imidazole, DMAP, DMF; (*ii*) $[Ir(COD)(PMePh_2)_2]PF_6$, H_2, THF; (*iii*) HgO, $HgCl_2$, acetone, water; (*iv*) Cl_3CCN, DBU, DCM.

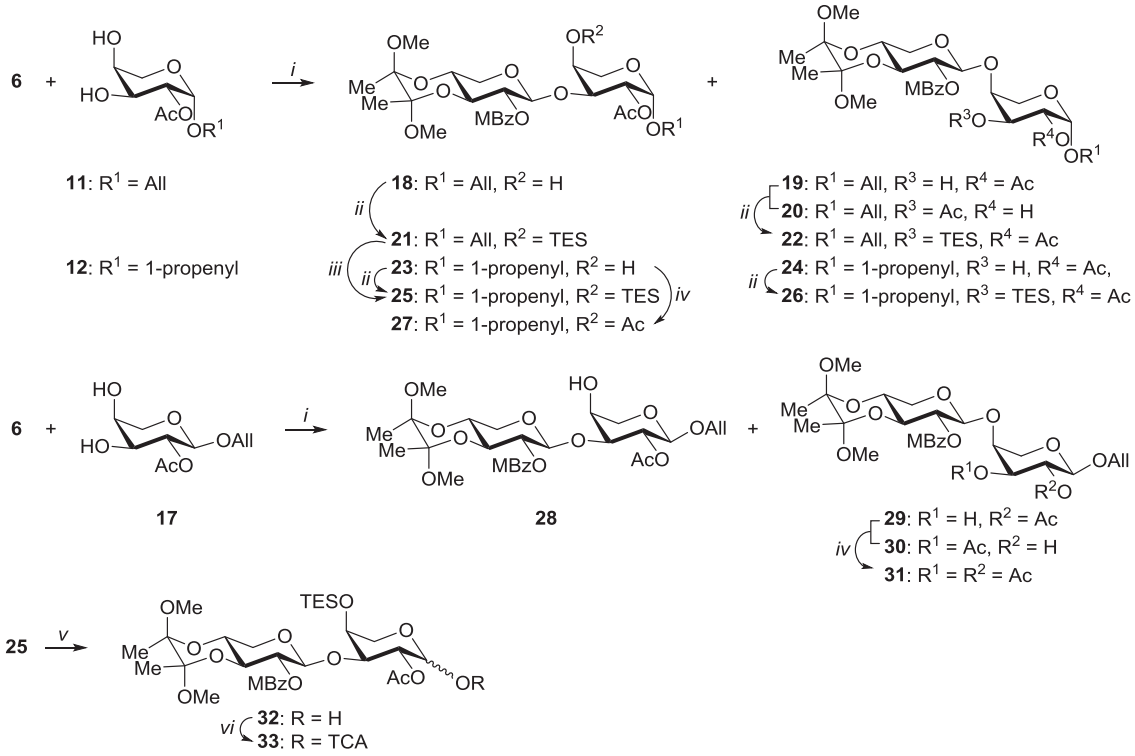


Scheme 3. Reagents and conditions: (*i*) $[Ir(COD)(PMePh_2)_2]PF_6$, H_2, THF; (*ii*) *p*-TsOH, ethyl acetate, methanol; (*iii*) Ac_2O, pyridine.

Glycosylation of **11** with **6** in the presence of $BF_3 \cdot OEt_2$ afforded an inseparable mixture of 1→3 linked disaccharide **18** and 1→4 linked disaccharides **19** and **20** (86% total yield). The presence of **20** was deduced from 2D NMR spectra. Obviously, it was formed by a migration of the acetyl group. Such migration of acetyl group from the *O*-2 to *O*-3 positions in 1→4 linked disaccharides was common and observed in many cases during our studies. Further treatment with triethylsilyl chloride and chromatographic separation gave required disaccharides **21** (58%) and **22** (20%). Product of silylation of **20** was not identified in the reaction mixture. Isomerisation of the double bond of **21** in the presence of iridium complex gave 1-propenyl derivative **25** quantitatively (Scheme 4).

Similar glycosylation of 1-propenyl acceptor **12** with **6** gave an inseparable mixture of disaccharides **23** and **24**. Silylation of the above mixture with triethylsilyl chloride and chromatographic separation afforded the TES protected disaccharides **25** (69%) and **26** (21%). High regioselectivity towards 1→3 linked disaccharide was observed in this case. Acetylation of an analytical sample of **23**/**24** mixture gave diacetate **27** as the main product in 65% yield (Scheme 4).

By comparison, glycosylation of allyl α-L-arabinopyranoside **17** with **6** gave the 1→3 linked disacharide **28** but in low yield (21%); the 1→4 linked derivatives **29** and **30** obtained as an inseparable mixture in 46% yield were isolated as main products. Composition



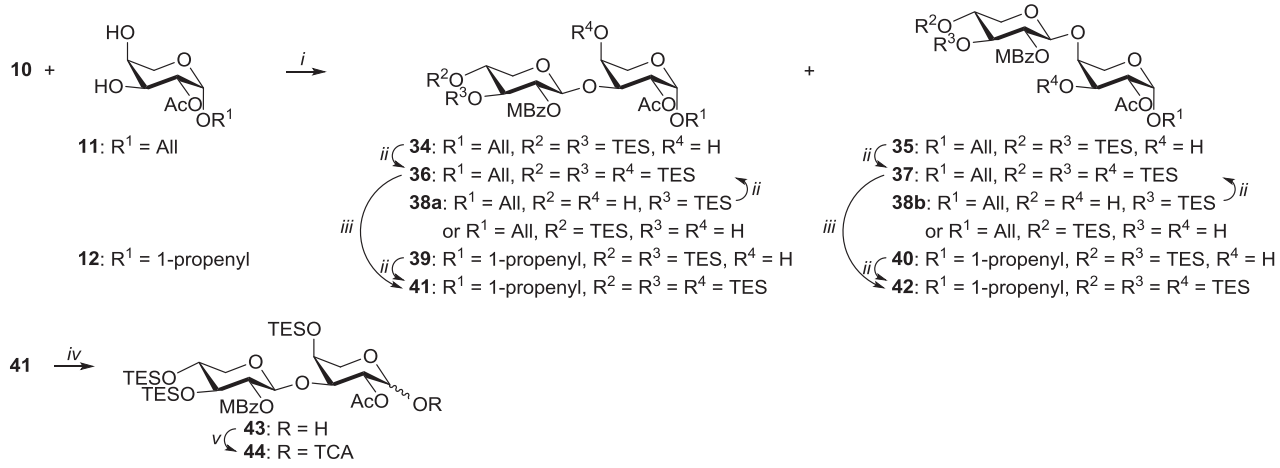
Scheme 4. Reagents and conditions: (*i*) $BF_3 \cdot OEt_2$, DCM, −40 °C (86% for **18**–**20**; 82% for **23** and **24**; 67% for **28**–**30**); (*ii*) TESCl, imidazole, DMAP, DMF (**18**–**20**→**21** (58%)+**22** (20%); **23**–**24**→**25** (69%)+**26** (21%); **21**→**25** (quant)); (*iii*) $[Ir(COD)(PMePh_2)_2]PF_6$, H_2, THF (quant); (*iv*) Ac_2O, Py (**23**→**27** (65%); **29**/**30**→**31** (81%)); (*v*) HgO, $HgCl_2$, acetone, water (73%); (*vi*) Cl_3CCN, K_2CO_3 (78%).

of this mixture was confirmed by acetylation, which afforded diacetate **31** as the only product in 81% yield (Scheme 4).

Finally, hydrolysis of 1-propenyl glycoside **25** in the presence of mercury salts yielded hemiacetal **32** (73%), which was further transformed in 78% yield into stable glycosyl donor **33** by treatment with trichloroacetonitrile under the standard conditions (Scheme 4). The donor **33** was prepared in 28% total yield from **11** in five steps and from **12** in 32% total yield in four steps.

Deprotection of BDA acetals requires rather harsh conditions,[10] so the donor **33** might not be suitable for some applications, especially when sensitive compounds are prepared. Therefore, we propose an alternative approach in which silylated donor **44** was prepared from allyl (or 1-propenyl) glycosides used as convenient starting materials. As we showed above, both the allyl and 1-propenyl group, can be efficiently and selectively removed under very mild conditions without the need of high pressure and high temperature processes required in the case of benzyl glycosides. As a promoter, boron trifluoride etherate was chosen, because trimethylsilyl triflate caused fast decomposition of the donor.

Glycosylation of **11** with **10** under the standard conditions afforded a mixture of disaccharides **34** and **35** in high yield (89%). Its treatment with triethylsilyl chloride and simple chromatographic separation gave 1→3 linked disaccharide **36** (47%) as the main product, and its regioisomer **37** (23%) as the second product (Scheme 5).



Scheme 5. Reagents and conditions: (*i*) $BF_3 \cdot OEt_2$, DCM, −40 °C (89% for **34**/**35**; 67% for **39**/**40**); (*ii*) TESCl, imidazole, DMAP, DMF (**34**/**35**→**36** (47%)+**37** (23%); **39**/**40**→**41** (49%)+**42** (36%)); (*iii*) $[Ir(COD)(PMePh_2)_2]PF_6$, H_2, THF (**36**→**41** (98%); **37**→**42** (92%)); (*iv*) HgO, $HgCl_2$, acetone, water (89%); (*v*) Cl_3CCN, DBU (76%).

Glycosylation of **11** with **10** was also tested under the flow conditions (coil reactor, reagents added via syringe pumps, reaction time 5 min, Fig. 2). Due to solubility problems, reaction was performed at 0 °C. In this case, a mixture of **34** and **35** was isolated in 53% yield together with partially desilylated disaccharides **38** (29%); exact position of desilylation was not determined. Reaction of both fractions with TESCl gave **36** (26%) and **37** (32%). Slight preference for 1→4 linked regioisomers was observed under flow conditions (Scheme 5).

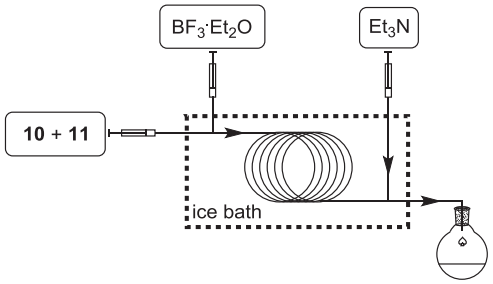


Fig. 2. Coil reactor.

Glycosylation of 1-propenyl β-L-arabinopyranoside **12** with donor **10** afforded a mixture of **39** and **40** in 67% yield, which, after treatment with TESCl and chromatographic separation, gave fully protected disaccharide **41** (49%) and **42** (36%). The same disaccharides were obtained by an isomerization of the allyl group in **36** and **37** in the presence of an iridium complex. The expected 1-propenyl glycosides were isolated in 98% (**41**) and 92% (**42**), respectively. Final hydrolysis of 1-propenyl substituent in **41** in the presence of mercury salts gave known hemiacetal **43**[6] in 89% yield. It may be easily transformed into donor **44**[6] in 76% yield (Scheme 5).

Glycosylation of **17** with **10** afforded a mixture of disaccharides **45** and **46** in excellent yield (92%). Unfortunately, its silylation with TESCl gave inseparable mixture of **47** and **48** in 66% yield. Separation of 1→3 and 1→4 linked regioisomers was possible by desilylation of **45**/**46** mixture in the presence of camphorsulfonic acid (CSA). After chromatographic separation two fractions were collected. The first one comprised a mixture of 1→4 linked disaccharides acetylated at *O*-2 (**49**) or *O*-3 (**50**) positions of the arabinose fragment in a ~5:2 ratio and in 40% yield. The latter was formed by an acetyl migration as described above. Composition of the mixture was confirmed by 2D NMR spectra analysis. Additionally, this fraction was acetylated to tetraacetate **52** isolated as the only product in 94% yield. The second fraction contained the 1→3 linked disaccharide **51** (19%). Due to the low yield of the 1→3 linked regioisomer, high ratio of acetyl migration in 1→4 linked disacharide, and separation problems this reaction path was not explored further (Scheme 6).

2.3. Synthesis of stereoisomers of OSW-1 disaccharide unit

Having a well performing procedure in hand, we started to prepare unknown stereoisomers of the OSW-1 disaccharide unit. Synthesis of such modified congeners opens the route to new, potentially active analogues of OSW-1 saponin. Depending on the configuration of the sugar, four possible stereoisomers of OSW-1 disaccharide unit are possible. The natural isomer is formed from D-xylose and L-arabinose fragments (D-L, **53**). The remaining, unnatural isomers, are built from L-D (**54**), D-D (**55**), and L-L (**56**) sugars, respectively (Fig. 3). Preparation of natural D-L disaccharide was presented above; the synthesis of L-L congener will be discussed in the following part of this paper. Keeping in mind that D-L/L-D and D-D/L-L pairs are in enantiomeric relations, the remaining L-D and D-D partners may be obtained by exactly the same methods.

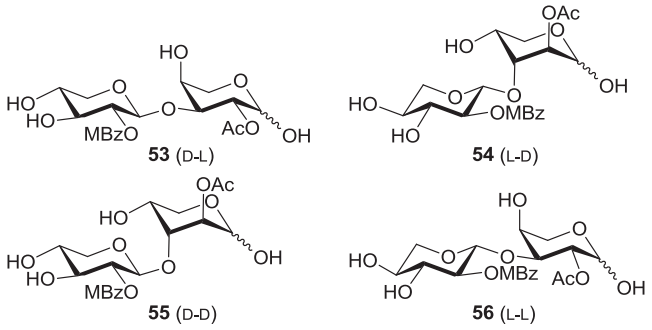
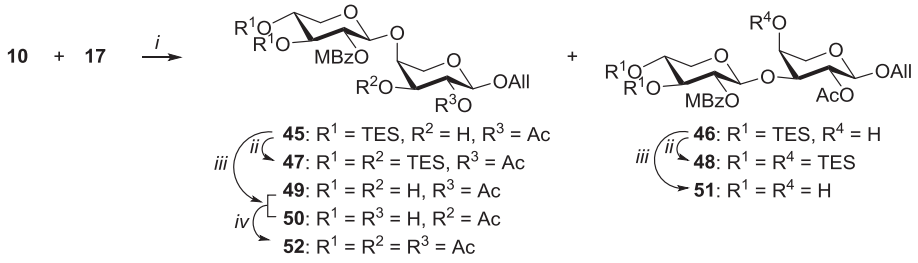


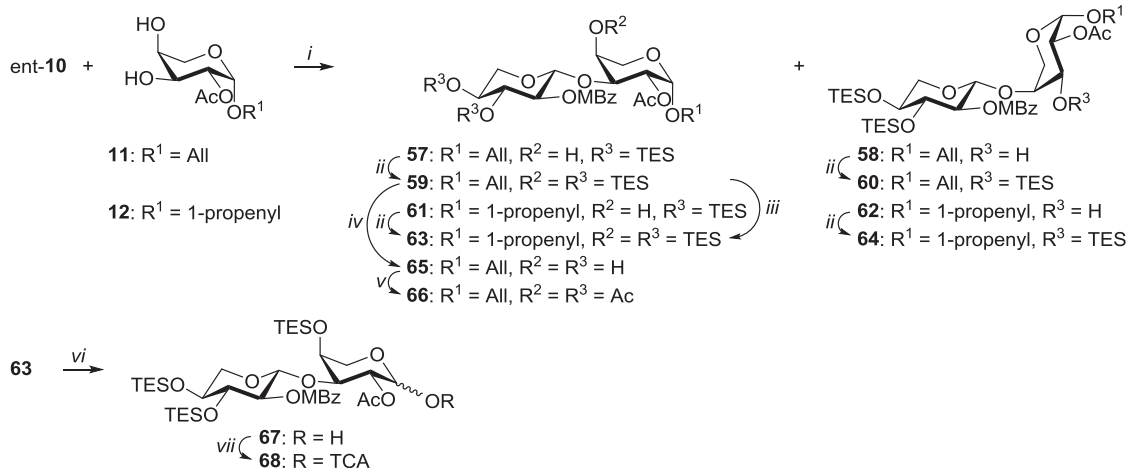
Fig. 3. Stereoisomers of OSW-1 disaccharide unit.

Glycosylation of **11** with **ent-10** under the standard conditions afforded an inseparable mixture of disaccharides **57** and **58** in high yield (85%). Treatment with triethylsilyl chloride gave the 1→3 linked isomer as main product, however, only partial chromatographic separation was possible. Pure disaccharide **59** was isolated in 51% yield, as the second fraction 1→4 linked regioisomer **60** slightly contaminated with **59** was obtained in 24% yield. By comparison, glycosylation of 1-propenyl β-L-arabinopyranoside **12** with donor **ent-10** afforded inseparable mixture of **61** and **62** in 91% yield. Treatment with TESCl gave, after chromatographic separation, fully protected disaccharide **63** (48%) and **64** (27%). As above, only partial separation of regioisomers was possible; 1→4 linked regioisomer contained minute amount of the 1→3 linked isomer. Disaccharide **63** was also obtained by isomerization of the allyl group in **59** in the presence of iridium complex (93%). Position of the glycosidic linkage was additionally confirmed by desilylation of **59** (to afford **65**) followed by acetylation to give **66** (Scheme 7).

Final hydrolysis of the 1-propenyl substituent in the presence of mercury salts gave hemiacetal **67** in 84% yield. Further reaction with trichloroacetonitrile in the presence of DBU afforded donor **68** (67%), which was found to be very unstable and should be used directly in the glycosylation step (Scheme 7). Both paths led to the



Scheme 6. Reagents and conditions: (*i*) $BF_3 \cdot OEt_2$, DCM, −40 °C (92%); (*ii*) TESCl, imidazole, DMAP, DMF (66%); (*iii*) CSA, MeOH, EtOAc (40% for **49**/**50**+19% for **51**); (*iv*) Ac_2O, Py (94%).



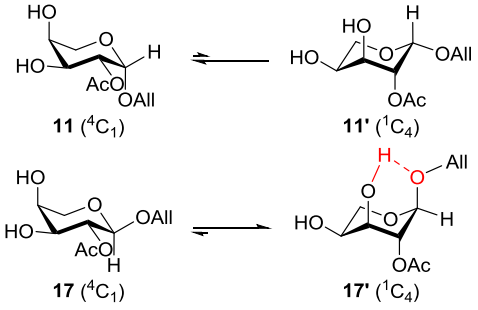
Scheme 7. Reagents and conditions: (*i*) $BF_3 \cdot OEt_2$, DCM, −40 °C (85% for **57**/**58**; 91% for **61**/**62**); (*ii*) TESCl, imidazole, DMAP, DMF (**57**/**58**→**59** (51%)+**59**/**60** (24%); **61**/**62**→**63** (48%)+**63**/**64** (27%)); (*iii*) $[Ir(COD)(PMePh_2)_2]PF_6$, H_2, THF (93%); (*iv*) CSA, MeOH, EtOAc (86%); (*v*) Ac_2O, Py (91%); (*vi*) HgO, $HgCl_2$, acetone, water (84%); (*vii*) Cl_3CCN, DBU (67%).

donor **68** in almost identical total yield (23% and 25% starting from **11** and **12**, respectively).

2.4. Influence of the hydrogen bond on the regioselectivity of glycosylation

It is commonly believed that hydroxyl groups in equatorial positions are more reactive than axially oriented ones in six-membered rings. Therefore, equatorially oriented 3-OH group of arabinopyranoside ring was expected to be more reactive than axially oriented 4-OH hydroxyl group. Our results clearly showed that the configuration at the anomeric centre of acceptor significantly influenced the regioselectivity of the glycosylation of 3,4-diols. Acceptors, bearing the axially oriented substituent at the anomeric position (**11**, **12**) provided the expected 1→3 linked regioisomers preferrentially. In the case of acceptor **17**, in which the aglycon part occupies the equatorial position, the 1→4 linked regioisomers were obtained as slightly preferred products. Such reversed reactivity was already reported in the literature for arabinopyranoside derivatives, and was explained by an influence of bulky substituent at the *O*-2 position[11–13] or inversion of the pyranoside ring.[14–16] As a result of conformational mobility, arabinopyranoside ring adopted unusual $^1C_4$ chair conformation and the 4-OH group occupied more reactive equatorial position. Flipping of the pyranoside ring and consequences of this behavior were discussed in the literature.[14,15] However, the origin of preference for the $^1C_4$ conformation was not defined yet. It is interesting that the ring-mobility was observed only for the corresponding diols. The pyranoside ring returns to the normal $^4C_1$ chair conformation after glycosylation reaction or protection of the hydroxyl groups.

Based on the results reported above we propose a simple explanation for this phenomenon. In the case of β-L-arabinoside **11** ring-flipping to conformer **11′** is unfavored, because two substituents are placed in axial positions and the anomeric effect is missing. Both coupling constants measured in $CDCl_3$ solution $-J_{1,2}$=3.7 Hz and $^1J_{C1,H1}$=171.5 Hz—confirm the equatorial position of the anomeric hydrogen atom.[17] For α-L-arabinoside **17** ring-flipping to unusual conformer **17′** is strongly supported by the formation of the hydrogen bond between the 3-OH and the anomeric oxygen atom and additionally strengthened by the anomeric effect. Corresponding coupling constants—$J_{1,2}$=3.6 Hz and $^1J_{C1,H1}$=166.7 Hz—prove the equatorial position of the anomeric hydrogen atom and preference for conformer **17′**. Addition of methanol should change the above values if intramolecular hydrogen bonds are present. In fact, the NMR spectra recorded in CD_3OD solution revealed that in the case of **11** coupling constant $^1J_{C1,H1}$=171.5 Hz remained identical as observed in $CDCl_3$ solution ($J_{1,2}$ was not found due to signal overlapping). However, for **17** coupling constants were changed significantly: $J_{1,2}$=7.2 Hz and $^1J_{C1,H1}$=160.8 Hz; such values are characteristic for the axially oriented anomeric hydrogen atom in conformer **17**. These data clearly confirm the participation of the hydrogen bond in stabilization of preffered conformer **17′** in aprotic solvents and return to conformer **17** by breaking the hydrogen bond in the presence of methanol (Scheme 8).



Scheme 8. Proposed formation of the hydrogen bond under an aprotic conditions.

3. Configurational assignments

The structures of all new compounds were confirmed by extended 1D and 2D NMR experiments, as well as elemental analysis and HRMS. Structures of **43** and **44** were confirmed by comparison with literature data. As expected, the presence of the *p*-methoxybenzoyl protecting group in the donor molecules directed the anomeric selectivity of the glycosidation reaction, and in all cases studied in this report, 1,2-*trans*-glycosides were formed exclusively.[18] These observations were strongly supported by the $^1J_{C1\text{-}H1}$ coupling constants measuring 162.1—165.0 Hz (for xylopyranoside part of **36**, **37**, **41**, **42** and **51**) indicating the presence of an axial proton at the anomeric position, and 172.1—174.8 (for arabinopyranoside part of **36**, **37**, **41**, and **42**) clearly indicating the presence of equatorial proton. For arabinopyranoside part of **51** $^1J_{C1\text{-}H1}$ coupling constant was equal 161.3 Hz, which proved the presence of axial proton.[17]

Isomerization of the double bond in the allyl group to a 1-propenyl substituent led to inseparable mixtures of (*E*) and (*Z*) olefins. Coupling constants (if available) for olefinic protons of the

main 1-propenyl derivatives were equal 12.2–13.7 Hz, which confirms the (*E*) configuration across the double bond. (*Z*) Isomers were detected only in small amount, usually below 10%.

The classification of the glycosylation position was readily confirmed by HMBC analyses, which showed the correlation between the ^{1}H signals of H-3 (or H-4) and ^{13}C signals of C-1′. Additionally, the ^{13}C NMR spectra of disaccharides indicated characteristic deshielding effects of the C-3 (or C-4) signals. In some cases, free hydroxyl groups were acetylated and the ^{1}H NMR spectra of acetates **27**, **31**, **52** and **66** showed characteristic 'acylation shift'; the H-3 or H-4 resonances (depending on the glycosylation position) of the arabinose residues were deshielded with comparison to the free hydroxyl derivatives. These observations clearly proved the position of the glycosidic linkages.

4. Conclusion

In summary, we have developed new modifications for the synthesis of the OSW-1 disaccharide unit from D-xylose and L-arabinose. New OSW-1 disaccharide unit donor **33** was obtained in 28% total yield after five steps. Donor **44** was obtained by modified method in 28% total yield after five steps from allyl β-L-arabinopyranoside **11**, and 23% total yield after four steps from 1-propenyl β-L-arabinopyranoside **12**. Although regioselectivity was a little lower than for benzyl glycosides, neither high pressure of hydrogen nor high temperature or prolonged reaction time were needed and all steps were performed under very mild conditions. The same compound was prepared by Yu et al.[6] in similar yield (23%), but the literature method suffer from some technical difficulties during debenzylation steps. A mixture of α,β-anomers was used as starting materials improving yield and atom efficiency in the preparation of the monosaccharide building blocks. This new synthetic strategy was employed to prepare stereoisomers of OSW-1 disaccharide unit in which L-xylo- and L-arabinopyranoses were applied. It opens the way to the new, potentially biologically active analogues of OSW-1 saponin. Influence of configuration at the anomeric centre on regioselectivity of glycosylation was studied, and plausible explanation of the observed differences was also presented.

5. Experimental section

5.1. General

Silica gel HF_{254} and Silica gel 230–400 mesh (E. Merck) were used for TLC and column chromatography, respectively. ^{1}H and ^{13}C NMR spectra were recorded at 298 K with a Varian NMR-vnmrs600 or vnmrs500 spectrometer, using standard experimental conditions and Varian software (ChemPack 4.1). Configurational assignments were based on the NMR measurements, generated using two-dimensional techniques like COSY and ^{1}H–^{13}C gradient selected HSQC (*g*-HSQC), as well as ^{1}H–^{13}C gradient selected HMBC (*g*-HMBC) in several cases. Internal TMS was used as the ^{1}H and ^{13}C NMR chemical shift standard. *J* values are given in hertz (Hz). High-resolution mass spectra (HRMS ESI) were acquired with MARINER and MaldiSYNAPT G2-S HDMS (Waters) mass spectrometers. Optical rotations were measured with a JASCO P-2000 automatic polarimeter. IR spectra were recorded on Jasco 6200 FTIR spectrophotometer.

5.2. Synthesis

*5.2.1. Allyl 2-O-(4-methoxybenzoyl)-α-D-xylopyranoside (**3**).* To a cooled (−40 °C) solution of allyl α-D-xylopyranoside (**2**, 3.81 g, 20.0 mmol) in pyridine (30 mL) 4-methoxybenzoyl chloride (4.09 g, 24.0 mmol) was slowly added. Then, the reaction temperature was elevated to room temperature, and the mixture was stirred overnight. An excess of acid chloride was decomposed with methanol (10 mL), the reaction mixture was concentrated in vacuo and co-evaporated with toluene (3×20 mL). Column chromatography of the residue (hexane–ethyl acetate, 20:1→1:1, then ethyl acetate for product removal) afforded 4.11 g (63%) of the title compound as a thick sirup. $[\alpha]_D^{20}$ 102.8 (*c* 0.7, chloroform); ν_{max} (film): 3426, 2937, 2841, 1713, 1606, 1512, 1333, 1259, 1170, 1103, 1035, 940, 848, 771 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.02–8.04 (m, 2H, Ar), 6.92–6.94 (m, 2H, Ar), 5.80–5.88 (m, 1H,=C*H*), 5.26–5.31 and 5.13–5.16 (2m, 2H,=CH_2), 5.09 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.89 (dd, 1H, $J_{2,1}$ 3.6, $J_{2,3}$ 9.9 Hz, H-2), 4.18–4.22 (m, 1H, OC*H*), 4.09 (dd, 1H, $J_{3,2}$ 9.9, $J_{3,4}$ 8.8 Hz, H-3), 3.97–4.01 (m, 1H, OC*H*), 3.87 (s, 3H, OCH_3), 3.80 (ddd, 1H, $J_{4,3}$ 8.8, $J_{4,5}$ 5.6, $J_{4,5}$ 10.5 Hz, H-4), 3.75 (dd, 1H, $J_{5,4}$ 5.6, $J_{5,5'}$ 10.8 Hz, H-5), 3.64 (dd, 1H, $J_{5,4}$ 10.5, $J_{5,5'}$ 10.8 Hz, H-5). ^{13}C NMR ($CDCl_3$) δ: 166.3, 163.8, 133.6, 132.0, 121.8, 117.3, 113.7, 95.6, 73.6, 72.5, 70.7, 68.3, 61.3, 55.5. Anal. Calcd for $C_{16}H_{20}O_7$ (324.34): C, 59.25; H, 6.22. Found: C, 59.27; H, 6.01.

*5.2.2. Allyl 2-O-(4-methoxybenzoyl)-α,β-L-xylopyranoside (**ent-3**).* The title compound was prepared from L-xylose using the procedure described for **3**. Preliminary experiment was performed with pure α-anomer to give allyl 2-*O*-(4-methoxybenzoyl)-α-L-xylopyranoside: $[\alpha]_D^{20}$ −92.7 (*c* 0.7, chloroform); NMR data of **ent-3** were identical to those measured for **3**. Anal. Calcd for $C_{16}H_{20}O_7 \times {}^1/_3\ H_2O$ (330.34): C, 58.17; H, 6.31. Found: C, 58.08; H, 6.47.

*5.2.3. Allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-α-D-xylopyranoside (**4**).* A solution of xylopyranoside **3** (1.622 g, 5.0 mmol), diacetyl (0.7 mL, 8.0 mmol), trimethyl orthoformate (2.8 mL, 25.0 mmol) and CSA (100 mg) in methanol (25 mL) was heated under reflux for 16 h (complete consumption of the starting material was detected by TLC). Then triethylamine (1 mL) was added, the reaction mixture was cooled to room temp. The solvents were evaporated and the residue was purified by column chromatography (hexane–ethyl acetate, 20:1→5:1) to give 1.756 g (80%) of the title compound. Mp: 117–119 °C. $[\alpha]_D^{20}$ 241.1 (*c* 1.0, chloroform). ^{1}H NMR ($CDCl_3$) δ: 7.99–8.01 (m, 2H, Ar), 6.91–6.93 (m, 2H, Ar), 5.74–5.82 (m, 1H,=C*H*), 5.20–5.25 and 5.07–5.10 (2m, 2H,=CH_2), 5.19 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.98 (dd, 1H, $J_{2,1}$ 3.7, $J_{2,3}$ 10.6 Hz, H-2), 4.27 (dd, 1H, $J_{3,2}$ 10.6, $J_{3,4}$ 10.1 Hz, H-3), 4.14–4.18 (m, 1H, OC*H*), 3.92–3.97 (m, 1H, OC*H*), 3.87–3.91 (m, 1H, H-4), 3.86 (s, 3H, OCH_3), 3.76 (dd, 1H, $J_{5,4}$ 10.7, $J_{5,5'}$ 10.4 Hz, H-5), 3.61 (dd, 1H, $J_{5,4}$ 5.3, $J_{5,5'}$ 10.4 Hz, H-5), 3.35 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3), 1.31 (s, 3H, CH_3), 1.28 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 165.6, 163.5, 133.7, 131.8. 122.4, 117.1, 113.6, 99.9, 99.6, 95.7, 71.1, 68.4, 67.5, 66.5, 59.6, 55.4, 48.0, 47.8, 17.8, 17.6. Anal. Calcd for $C_{22}H_{30}O_9$ (438.48): C, 60.26; H, 6.90. Found: C, 60.28; H, 6.70.

*5.2.4. 3,4-O-(2′,3′-Dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-α,β-D-xylopyranose (**5**).* A solution of xylopyranoside **4** (3.000 g, 6.8 mmol) and $PdCl_2$ (200 mg) in methanol (40 mL) was stirred at room temp for 3 h, then triethylamine (1 mL) was added and solvents were evaporated to dryness. The residue was purified by column chromatography (hexane–ethyl acetate, 9:1→7:3) to give 2.477 g (91%) of the title compound as white foam. ν_{max} (film): 3442, 2994, 2951, 2906, 2837, 1717, 1606, 1512, 1258, 1170, 1146, 1133, 1112, 1035, 937, 848, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: major isomer—7.99–8.01 (m, 2H, Ar), 6.91–6.93 (m, 2H, Ar), 5.58 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.99 (dd, 1H, $J_{2,1}$ 3.6, $J_{2,3}$ 10.6 Hz, H-2), 4.30 (dd, 1H, $J_{3,2}$ 10.6, $J_{3,4}$ 9.6 Hz, H-3), 3.88–3.98 (m, 2H, H-4, H-5), 3.86 (s, 3H, OCH_3), 3.64 (dd, 1H, $J_{5,4}$ 4.7, $J_{5,5'}$ 10.0 Hz, H-5), 3.35 (s, 3H, OCH_3), 3.29 (s, 3H, OCH_3), 1.31 (s, 3H, CH_3), 1.29 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: major isomer—165.6, 163.6, 131.8. 122.1, 113.7, 99.9, 99.6,

90.9, 71.4, 67.1, 66.4, 59.6, 55.4, 48.0, 47.8, 17.8, 17.6. Anal. Calcd for $C_{19}H_{26}O_9$ (398.42): C, 57.28; H, 6.58. Found: C, 57.26; H, 6.78.

*5.2.5. 3,4-O-(2′,3′-Dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-α,β-D-xylopyranosyl trichloroacetimidate (**6**).* To a solution of xylopyranose **5** (1.295 g, 3.25 mmol) and trichloroacetonitrile (2.0 mL, 20.0 mmol) in dichloromethane (25 mL) K_2CO_3 (500 mg) was added, and stirred at room temp overnight. Then solvents were evaporated to dryness. The residue was purified by column chromatography (hexane–ethyl acetate, 9:1) to give the title compound as a mixture of anomers (1.520 g, 86%, light yellow foam). ^{1}H NMR ($CDCl_3$) δ: major isomer, selected signals—8.63 (s, 1H, NH), 7.96–7.97 (m, 2H, Ar), 6.89–6.91 (m, 2H, Ar), 5.88 (d, 1H, $J_{1,2}$ 7.2 Hz, H-1), 5.47 (dd, 1H, $J_{2,1}$ 7.2, $J_{2,3}$ 9.7 Hz, H-2), 3.85 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3), 3.22 (s, 3H, OCH_3), 1.30 (s, 3H, CH_3), 1.26 (s, 3H, CH_3); minor isomer, selected signals—8.49 (s, 1H, NH), 7.94–7.96 (m, 2H, Ar), 6.88–6.90 (m, 2H, Ar), 6.62 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 5.27 (dd, 1H, $J_{2,1}$ 3.8, $J_{2,3}$ 10.6 Hz, H-2), 4.34 (dd, 1H, $J_{3,2}$ 10.6, $J_{3,4}$ 9.6 Hz, H-3), 3.85 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 1.33 (s, 3H, CH_3), 1.29 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: major isomer, selected signals—164.4, 163.5, 161.4, 131.7. 122.0, 113.7, 99.8, 99.6, 97.7, 70.3, 70.2, 65.2, 64.9, 55.4, 48.0, 47.7, 17.6, 17.5; minor isomer, selected signals—165.1, 163.6, 160.8, 131.8. 121.8, 113.6, 100.0, 99.7, 94.1, 69.8, 67.5, 65.8, 62.3, 55.4, 48.1, 47.7, 17.7, 17.6. Anal. Calcd for $C_{21}H_{26}Cl_3NO_9$ (542.81): C, 46.47; H, 4.83; N, 2.58. Found: C, 46.25; H, 4.88; N, 2.74.

*5.2.6. Allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-α,β-D-xylopyranoside (**7**).* To a solution of allyl 2-*O*-(4-methoxybenzoyl)-α,β-D-xylopyranoside (**3**, 4.29 g, 13.2 mmol), imidazole (3.41 g, 50.0 mmol) and DMAP (50 mg) in DMF (50 mL), triethylsilyl chloride (5.9 mL, 35.2 mmol) was slowly added and stirred at room temp for 1 h. Then solvents were evaporated to dryness, and coevaporated twice with toluene (20 mL). The residue was purified by column chromatography (hexane–ethyl acetate, 40:1 →20:1) to afford 6.73 g (92%) of the title compound as thick oil. Preliminary experiment was performed with pure α-anomer to give allyl 2-*O*-(4-methoxybenzoyl)-3,4-di-*O*-triethylsilyl-α-D-xylopyranoside. $[\alpha]_D^{20}$ 81.1 (*c* 0.4, chloroform); ^{1}H NMR ($CDCl_3$) δ: 8.01–8.03 (m, 2H, Ar), 6.91–6.92 (m, 2H, Ar), 5.75–5.81 (m, 1H,=C*H*), 5.22–5.25 and 5.06–5.08 (2m, 2H,=CH_2), 4.96 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.88 (dd, 1H, $J_{2,1}$ 3.7, $J_{2,3}$ 9.4 Hz, H-2), 4.13–4.17 (m, 1H, OC*H*), 4.06 (dd, 1H, $J_{3,2}$ 9.3, $J_{3,4}$ 8.1 Hz, H-3), 3.89–3.93 (m, 1H, OC*H*), 3.86 (s, 3H, OCH_3), 3.67–3.71 (m, 1H, H-4), 3.53–3.59 (m, 2H, H-5, H-5′), 0.96 (t, 9H, *J* 8.0 Hz, 3×CH_3), 0.84 (t, 9H, *J* 8.0 Hz, 3×CH_3), 0.61–0.65 (m, 6H, 3×CH_2), 0.51–0.56 (m, 6H, 3×CH_2). ^{13}C NMR ($CDCl_3$) δ: 165.8, 163.4, 133.9, 131.8, 122.5, 116.8, 113.5, 95.7 (C-1), 73.9, 72.9, 72.2, 68.2 (OCH_2), 62.4 (C-5), 55.4, 6.8 (CH_3), 6.8 (CH_3), 5.1 (CH_2), 5.1 (CH_2). Anal. Calcd for $C_{28}H_{48}O_7Si_2$ (552.86): C, 60.83; H, 8.75. Found: C, 60.77; H, 8.69.

*5.2.7. Allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-α,β-L-xylopyranoside (**ent-7**).* The title compound was prepared from **ent-3** using the procedure described for **7**. Preliminary experiment was performed with pure α-anomer to give allyl 2-*O*-(4-methoxybenzoyl)-3,4-di-*O*-triethylsilyl-α-L-xylopyranoside. $[\alpha]_D^{20}$ −85.7 (*c* 0.8, chloroform). NMR data of **ent-7** were identical to those measured for **7**. Anal. Calcd for $C_{28}H_{48}O_7Si_2$ (552.86): C, 60.83; H, 8.75. Found: C, 60.90; H, 8.83.

*5.2.8. (E,Z)-1-Propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-α,β-D-xylopyranoside (**8**).* A solution of iridium complex was prepared from $[Ir(COD)(MePPh_2)_2]PF_6$ (20 mg) according to literature procedure[19] and transfered into a solution of **7** (6.58 g, 11.9 mmol) in THF (80 mL), stirred at room temp for 1 h, and then concentrated. The residue was purified by column chromatography (hexane–ethyl acetate, 20:1) to give the title compound (6.58 g, quant.) as an oil in approx. (*E*):(*Z*) ratio=9:1. Preliminary experiment was performed with pure α-anomer to give (*E,Z*)-1-propenyl 2-*O*-(4-methoxybenzoyl)-3,4-di-*O*-triethylsilyl-α-D-xylopyranoside, which had the following physicochemical properties: $[\alpha]_D^{20}$ 93.3 (*c* 0.4, chloroform); ^{1}H NMR ($CDCl_3$) δ: 8.00–8.02 (m, 2H, Ar), 6.90–6.92 (m, 2H, Ar), 6.08 (dq, 1H, *J* 1.6, 12.2 Hz,=C*H*O), 5.08–5.14 (m, 2H), 4.90 (dd, 1H, *J* 3.6, 9.4 Hz), 4.06 (dd, 1H, *J* 8.2, 9.3 Hz), 3.86 (s, 3H, OCH_3), 3.68–3.72 (m, 1H, H-4), 3.60 (dd, 1H, $J_{5,4}$ 5.4, $J_{5,5'}$ 11.0 Hz, H-5), 3.53 (t, 1H, $J_{5,4}$=$J_{5,5'}$=11.0 Hz, H-5), 1.49 (dd, 3H, *J* 1.6, 6.9 Hz, CH_3), 0.96 (t, 9H, *J* 8.0 Hz, 3×CH_3), 0.85 (t, 9H, *J* 8.0 Hz, 3×CH_3), 0.60–0.65 (m, 6H, 3×CH_2), 0.52–0.56 (m, 6H, 3×CH_2). ^{13}C NMR ($CDCl_3$) δ: 165.8, 163.5, 143.1, 131.9, 122.3, 113.5, 104.6, 96.0 (C-1), 73.4, 72.8, 72.0, 62.7 (C-5), 55.4, 12.3, 6.8 (2×CH_3), 5.1 (CH_2), 5.1 (CH_2). Anal. Calcd for $C_{28}H_{48}O_7Si_2$ (552.86): C, 60.83; H, 8.75. Found: C, 61.00; H, 8.77.

*5.2.9. (E,Z)-1-Propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-α,β-L-xylopyranoside (**ent-8**).* The title compound (cont. approx. 20% of (*Z*)-isomer) was prepared from **ent-7** using the procedure described for **8**. Preliminary experiment was performed with pure α-anomer to give (*E,Z*)-1-propenyl 2-*O*-(4-methoxybenzoyl)-3,4-di-*O*-triethylsilyl-α-L-xylopyranoside. NMR data of **ent-8** were identical to those measured for **8**. Anal. Calcd for $C_{28}H_{48}O_7Si_2$ (552.86): C, 60.83; H, 8.75. Found: C, 60.98; H, 8.75.

*5.2.10. 2-O-(4-Methoxybenzoyl)-3,4-di-O-triethylsilyl-α,β-D-xylopyranose (**9**).* To a solution of **8** (7.05 g, 12.75 mmol) in a mixture of acetone–water (10:1, 80 mL), yellow mercury oxide (3.69 g, 17.0 mmol) followed by a solution of mercury(II) chloride (3.94 g, 14.5 mmol) in a mixture of acetone–water (10:1, 30 mL) were added and the suspension was stirred at room temperature for 2 h. The mixture was concentrated, and the residue was purified by column chromatography (hexane–ethyl acetate, 40:1 →5:1) to give the title compound (6.41.g, 98%) as an oil. NMR data of **9** matches the literature.[6]

*5.2.11. 2-O-(4-Methoxybenzoyl)-3,4-di-O-triethylsilyl-α,β-L-xylopyranose (**ent-9**).* The title compound was prepared from **ent-8** using the procedure described for **9**. NMR data of **ent-9** were identical to those published for **9**.[6] Anal. Calcd for $C_{25}H_{44}O_7Si_2$ (512.80): C, 58.56; H, 8.65. Found: C, 58.57; H, 8.50.

*5.2.12. 2-O-(4-Methoxybenzoyl)-3,4-di-O-triethylsilyl-α,β-L-xylopyranosyl trichloroacetimidate (**ent-10**).* The title compound was prepared from **ent-9** using the literature procedure published for **10**.[6] NMR data of **ent-10** were identical to those published for **10**.[6] Anal. Calcd for $C_{27}H_{44}Cl_3NO_7Si_2$ (657.19): C, 49.35; H, 6.75; N, 2.13. Found: C, 49.67; H, 6.65; N, 2.00.

*5.2.13. (E,Z)-1-Propenyl 2-O-acetyl-β-L-arabinopyranoside (**12**).* *Method A*. L-Arabinopyranoside **11** (1.000 g, 4.31 mmol) was converted into 1-propenyl derivative **12** using the procedure described for **8**. Column chromatography of the crude product (hexane–ethyl acetate, 5:1, hexane–ethyl acetate–methanol, 5:3:1) afforded 990 mg (99%) of the title compound in approx. (*E*):(*Z*) ratio=95:5.

Method B. To a solution of arabinoside **14** (112 mg, 0.41 mmol) in EtOAc (1 mL) and MeOH (1 mL), a solution of *p*-TsOH (10 mg) in EtOAc (0.2 mL) and MeOH (0.2 mL) was added and stirred at room temp for 2 h. Then triethylamine (0.5 mL) was added, and the solvents were evaporated to dryness. Column chromatography of the residue (hexane–ethyl acetate, 5:1, hexane–ethyl acetate–methanol, 5:3:1) afforded 50 mg (52%) of the title compound. $[\alpha]_D^{20}$ 195.9 (*c* 0.3, chloroform); ν_{max} (film): 3318, 2973, 2934, 2890, 1733, 1681, 1660, 1374, 1243, 1167, 1092, 1063, 1011, 923, 838, 784 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.15 (dq, 1H, *J* 1.6, 12.3 Hz, OC*H*=), 5.21

(d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 5.15 (dq, 1H, J 6.9, 13.7 Hz,=C*H*), 5.03 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2), 4.07–4.11 (m, 1H), 4.04 (br s, 1H), 3.87 (d, 1H, $J_{5,5'}$ 12.7 Hz, H-5), 3.76 (dd, 1H, $J_{5,4}$ 1.8, $J_{5,5'}$ 12.7 Hz, H-5), 2.15 (s, 3H, CH_3), 1.56 (dd, 3H, J 1.6, 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 171.6, 142.8, 105.0, 96.0, 71.3, 69.3, 67.7, 62.6, 21.0, 12.3. Anal. Calcd for $C_{10}H_{16}O_6$ (232.24): C, 51.72; H, 6.94. Found: C, 51.60; H, 6.87.

*5.2.14. (E,Z)-1-Propenyl 2-O-acetyl-3,4-O-isopropylidene-β-L-arabinopyranoside (**14**).* Arabinoside **13** (139 mg, 0.50 mmol) was converted into 1-propenyl derivative **14** using the procedure described for **8**. Column chromatography of the crude product (hexane–ethyl acetate, 20:1→5:1) afforded 134 mg (96%) of the title compound in approx. (*E*):(*Z*) ratio=9:1. $[\alpha]_D^{20}$ 221.2 (*c* 0.2, chloroform); ^{1}H NMR ($CDCl_3$) δ: 6.14 (dq, 1H, J 1.5, 12.3 Hz, OC*H*=), 5.12–5.19 (m, 2H, H-1,=C*H*), 4.92 (dd, 1H, $J_{2,1}$ 3.3, $J_{2,3}$ 8.1 Hz, H-2), 4.37 (dd, 1H, $J_{3,2}$ 8.1, $J_{3,4}$ 5.6 Hz, H-3), 4.28 (dd, 1H, $J_{4,3}$ 5.6, $J_{4,5}$ 2.6 Hz, H-4), 4.02 (d, 1H, $J_{5,5'}$ 13.5 Hz, H-5), 3.96 (dd, 1H, $J_{5,4}$ 2.6, $J_{5,5'}$ 13.5 Hz, H-5), 2.13 (s, 3H, CH_3), 1.55–1.58 (m, 6H, 2×CH_3), 1.37 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.6, 142.8, 109.5, 105.0, 95.4, 73.4, 72.8, 71.8, 59.0, 27.9, 26.3, 21.0, 12.4. Anal. Calcd for $C_{13}H_{20}O_6$ (272.30): C, 57.34; H, 7.40. Found: C, 57.29; H, 7.41.

*5.2.15. Allyl 2-O-acetyl-3,4-O-isopropylidene-α-L-arabinopyranoside (**16**).* A mixture of α-L-arabinoside **15** (1.240 g, 5.39 mmol), pyridine (6 mL) and acetyl anhydride (3 mL) was stirred at room temp overnight, coevaporated with toluene (3×20 mL) and purified by column chromatography (hexane–ethyl acetate, 20:1→7:3) to give the title compound (1.45 g, 99%) as an oil. $[\alpha]_D^{20}$ 13.9 (*c* 0.3, chloroform); ^{1}H NMR ($CDCl_3$) δ: 5.82–5.90 (m, 1H,=C*H*), 5.25–5.30 and 5.17–5.20 (m, 2H,=CH_2), 5.07 (t, 1H, $J_{2,1}$=$J_{2,3}$=6.6 Hz, H-2), 4.44 (d, 1H, $J_{1,2}$ 6.4 Hz, H-1), 4.24–4.29 (m, 2H, OC*H*, H-4), 4.15 (dd, 1H, $J_{3,2}$ 6.4, $J_{3,4}$ 6.1 Hz, H-3), 4.09 (dd, 1H, $J_{5,4}$ 4.5, $J_{5,5'}$ 12.9 Hz, H-5), 4.02–4.06 (m, 1H, OC*H*), 3.76 (dd, 1H, $J_{5,4}$ 4.3, $J_{5,5'}$ 12.9 Hz, H-5), 2.11 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.36 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 169.5 (C=O), 133.7 (=*C*H), 117.1 (=*C*H_2), 110.4 (*C*Me_2), 98.4 (C-1, $^1J_{C1,H1}$ 162.4 Hz), 75.8 (C-3), 72.2 (C-2), 72.2 (C-4), 68.9 (O*C*H_2), 61.9 (C-5), 27.7 (CH_3), 26.1 (CH_3), 21.0 (CH_3). Anal. Calcd for $C_{13}H_{20}O_6$ (272.30): C, 57.34; H, 7.40. Found: C, 57.41; H, 7.48.

*5.2.16. Allyl 2-O-acetyl-α-L-arabinopyranoside (**17**).* To a solution of arabinoside **16** (1.690 g, 6.21 mmol) in EtOAc (15 mL) and MeOH (15 mL) a solution of *p*-TsOH (100 mg) in EtOAc (1 mL) and MeOH (1 mL) was added and stirred at room temp for 5 h. Then triethylamine (1 mL) was added, and the solvents were evaporated to dryness. Column chromatography of the residue (hexane–ethyl acetate, 7:3, hexane–ethyl acetate–methanol, 5:3:1) afforded 800 mg (56%) of the title compound as oil, and 240 mg (20%) of allyl α-L-arabinopyranoside. Data for **17**: $[\alpha]_D^{20}$ −33.5 (*c* 0.3, chloroform); ν_{max} (film): 3392, 3016, 2974, 2858, 1743, 1371, 1240, 1132, 1087, 1058, 1022, 933, 774, 752 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.76–5.84 (m, 1H,=C*H*), 5.19–5.24 and 5.14–5.17 (m, 2H,=CH_2), 4.90 (dd, 1H, $J_{2,1}$ 3.6, $J_{2,3}$ 5.6 Hz, H-2), 4.56 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.16–4.20 (m, 1H, OC*H*), 3.95–3.99 (m, 1H, OC*H*), 3.82–3.85 (m, 1H, H-4), 3.75 (dd, 1H, $J_{3,2}$ 5.6, $J_{3,4}$ 3.6 Hz, H-3), 3.68 (dd, 1H, $J_{5,4}$ 7.9, $J_{5,5'}$ 11.9 Hz, H-5), 3.54 (dd, 1H, $J_{5,4}$ 4.2, $J_{5,5'}$ 11.9 Hz, H-5), 2.12 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.2, 133.0, 118.3, 97.1, 71.0, 69.7, 69.0, 65.3, 61.1, 20.9. Anal. Calcd for $C_{10}H_{16}O_6$ (232.24): C, 51.72; H, 6.94. Found: C, 51.67; H, 7.06.

5.2.17. General method for glycosylation. Method A. A solution of glycosyl donor (0.53 mmol) and corresponding acceptor (0.50 mmol) in CH_2Cl_2 (15 mL) was stirred for 20 min. at rt over molecular sieves (4 Å, 400 mg, finely ground), then cooled to −40 °C and $BF_3 \cdot OEt_2$ (40 μL, 0.3 mmol) in CH_2Cl_2 (4 ml) was added via syringe pump (10 min). After 30 min the reaction was quenched with Et_3N (1 mL), and the solvents were evaporated under diminished pressure. Column chromatography of the residue gave the protected disaccharides as white foams.

Method B. A solution of glycosyl donor (0.75 mmol) and corresponding acceptor (0.60 mmol) in CH_2Cl_2 (15 mL) was stirred for 20 min at rt over molecular sieves (4 Å, 400 mg, finely ground), then cooled to −40 °C and $BF_3 \cdot OEt_2$ (40 μL, 0.3 mmol) in CH_2Cl_2 (4 ml) was added via syringe pump (10 min). After 30 min the reaction was quenched with Et_3N (1 mL), and the solvents were evaporated under diminished pressure. Column chromatography of the residue gave the protected disaccharides as white foams.

Method C. A flow microreactor was made of PTFE microtube (OD×ID×L, $^1/_{16}''\times0.040''\times2$m) and equipped with two Y-connectors. The whole system was filled with dry dichloromethane. Glycosyl donor (0.75 mmol) and corresponding acceptor (0.60 mmol) were dissolved in dry CH_2Cl_2 (16 mL) and the solution was placed in a 20 mL syringe. Similarly, the solution of $BF_3 \cdot OEt_2$ (80 μL, 0.6 mmol) in CH_2Cl_2 (20 ml) was placed in a 20 mL syringe. Both syringes were then attached to a syringe pump and connected to the Y-connector at the microreactor inlet. Syringe (20 mL) filled with a solution of triethylamine (1 mL) in dichloromethane (19 mL) was then connected to the Y-connector at the microreactor outlet. Microreactor, including both Y-connectors, was immersed in ice-bath. The resulting reaction mixtures were then fed into the microreactor and the residence time was adjusted to be 5 min by controlling the pumping speed of syringe pump. The product solution was collected, concentrated and purified by column chromatography.

*5.2.17.1. Allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-β-L-arabinopyranoside (**18**), allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2-O-acetyl-β-L-arabinopyranoside (**19**), and allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-3-O-acetyl-β-L-arabinopyranoside (**20**).* According to *Method A*. Column chromatography (hexane–ethyl acetate, 7:3) of the crude reaction product gave inseparable mixture of **18**–**20** (262 mg, 86%). Anal. Calcd for $C_{29}H_{40}O_{14}\times\frac{1}{2}\ H_2O$ (621.65): C, 56.03; H, 6.65. Found: C, 56.27; H, 6.82. HRMS (ESI) calcd for $C_{29}H_{40}O_{14}Na$: 635.2316. Found: 653.2311.

*5.2.17.2. (E,Z)-1-Propenyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-β-L-arabinopyranoside (**23**) and (E)-1-propenyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2-O-acetyl-β-L-arabinopyranoside (**24**).* According to *Method A*. Column chromatography (hexane–ethyl acetate, 7:3) of the crude reaction product gave inseparable mixture of **23** and **24** (252 mg, 82%). Anal. Calcd for $C_{29}H_{40}O_{14}$ (612.64): C, 56.86; H, 6.58. Found: C, 56.98; H, 6.51.

*5.2.17.3. Allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-α-L-arabinopyranoside (**28**), allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2-O-acetyl-α-L-arabinopyranoside (**29**), and allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-3-O-acetyl-α-L-arabinopyranoside (**30**).* According to *Method A*. Column chromatography (hexane–ethyl acetate, 5:1→7:3) of the crude reaction product gave inseparable mixture of **29** and **30** (141 mg, 46%), and **28** (66 mg, 21%). Data for **28**: $[\alpha]_D^{20}$ 111.4 (*c* 0.3, chloroform); ν_{max} (film): 2948, 2839, 1746, 1719, 1606, 1372, 1258, 1234, 1169, 1140, 1114, 1046, 931, 884, 848, 768, 765 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.00–8.01 (m, 2H, Ar), 6.92–6.93 (m, 2H, Ar), 5.48–5.55 (m, 1H,=CH), 5.19 (dd, 1H, $J_{2,1}$ 7.6, $J_{2,3}$ 9.7 Hz, H-2′), 5.06–5.09 (m, 1H,=C*H*H), 5.01–5.03 (m, 1H,=CH*H*), 4.95 (dd, 1H, $J_{2,1}$ 4.5, $J_{2,3}$ 6.2 Hz, H-2), 4.66 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1′), 4.35 (d, 1H, $J_{1,2}$ 4.5 Hz, H-1), 3.80–3.97 (m, 11H, H-3,3′,4,4′,5,5′, OCH_3, OCH_2), 3.44–3.50 (m, 2H,

H-5,5′), 3.26 (s, 3H, CH_3), 3.18 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.22 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 169.3 (C=O), 164.3 (C), 163.4 (C), 133.7, 131.7, 122.4, 117.1, 113.6, 102.6 (C-1′), 99.8 (C), 99.5 (C), 97.4 (C-1), 78.2 (C-3), 70.6, 70.5 (C-2′), 69.9 (C-2), 68.0 (OCH_2), 65.7, 65.6, 64.2 (C-5′), 62.0 (C-5), 55.4 (CH_3), 47.9 (CH_3), 47.6 (CH_3), 20.5 (CH_3), 17.6 (CH_3), 17.5 (CH_3). Anal. Calcd for $C_{29}H_{40}O_{14}$ (612.64): C, 56.86; H, 6.58. Found: C, 56.88; H, 6.61.

*5.2.17.4. Allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→3)-2-O-acetyl-β-L-arabinopyranoside (**34**) and allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→4)-2-O-acetyl-β-L-arabinopyranoside (**35**).* According to *Method B*. Column chromatography (hexane–ethyl acetate, 40:1→7:3; all eluents contained 0.5% Et_3N) of the crude reaction product gave inseparable mixture of **34** and **35** (392 mg, 89%).

According to *Method C*. Column chromatography (hexane–ethyl acetate, 40:1→7:3; all eluents contained 0.5% Et_3N) of the crude reaction product gave inseparable mixture of **34** and **35** (231 mg, 53%), and mixture of **38** (107 mg, 29%).

*5.2.17.5. (E,Z)-1-Propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→3)-2-O-acetyl-β-L-arabinopyranoside (**39**) and (E,Z)-1-propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→4)-2-O-acetyl-β-L-arabinopyranoside (**40**).* According to *Method B*. Column chromatography (hexane–ethyl acetate, 40:1→7:3; all eluents contained 0.5% Et_3N) of the crude reaction product gave inseparable mixture of **39** and **40** (292 mg, 67%).

*5.2.17.6. Allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→4)-2-O-acetyl-α-L-arabinopyranoside (**45**) and allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→3)-2-O-acetyl-α-L-arabinopyranoside (**46**).* According to *Method B*. Column chromatography (hexane–ethyl acetate, 20:1→7:3; all eluents contained 0.5% Et_3N) of the crude reaction product gave inseparable mixture of **45** and **46** (405 mg, 92%).

*5.2.17.7. Allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→3)-2-O-acetyl-β-L-arabinopyranoside (**57**) and allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→4)-2-O-acetyl-β-L-arabinopyranoside (**58**).* According to *Method B*. Column chromatography (hexane–ethyl acetate, 20:1→7:3; all eluents contained 0.5% Et_3N) of the crude reaction product gave inseparable mixture of **57** and **58** (372 mg, 85%).

*5.2.17.8. (E,Z)-1-Propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→3)-2-O-acetyl-β-L-arabinopyranoside (**61**) and (E,Z)-1-propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→4)-2-O-acetyl-β-L-arabinopyranoside (**62**).* According to *Method B*. Column chromatography (hexane–ethyl acetate, 20:1→7:3; all eluents contained 0.5% Et_3N) of the crude reaction product gave inseparable mixture of **61** and **62** (395 mg, 91%).

*5.2.18. Allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-β-L-arabinopyranoside (**21**) and allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2-O-acetyl-3-O-triethylsilyl-β-L-arabinopyranoside (**22**).* A mixture of **18**–**20** (112 mg, 0.18 mmol) was silylated using the procedure described for **7**. Column chromatography of the crude product (hexane–ethyl acetate, 5:1 contained 0.5% Et_3N) afforded **21** (77 mg, 58%) and **22** (26 mg, 20%).

Data for **21**: $[\alpha]_D^{20}$ 132.4 (*c* 0.3, chloroform); ^1H NMR ($CDCl_3$) δ: 7.92–7.93 (m, 2H, Ar), 6.89–6.90 (m, 2H, Ar), 5.78–5.84 (m, 1H, C*H*=), 5.21–5.24 (m, 1H,=C*H*H), 5.12–5.16 (m, 2H, H-2′,=CH*H*), 5.03 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2), 4.99 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.76 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1′), 4.09–4.12 (m, 2H, H-4, OC*H*H), 3.96 (dd, 1H, $J_{3,2}$ 10.0, $J_{3,4}$ 2.9 Hz, H-3), 3.86–3.92 (m, 4H, H-3′, H-4′, H-5′, OCH*H*), 3.85 (s, 3H, OCH_3), 3.78 (bd, 1H, $J_{5,5'}$ 11.6 Hz, H-5), 3.43–3.49 (m, 2H, H-5, H-5′), 3.28 (s, 3H, CH_3), 3.18 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 0.96 (t, 9H, *J* 8.0 Hz, 3×CH_3), 0.58–0.69 (m, 6H, 3×CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.9, 164.1, 163.3, 133.8, 131.5, 122.6, 117.6, 113.6, 103.4 (H-1′), 99.8, 99.5, 95.6 (H-1), 74.9 (H-3), 71.1 (H-2′), 70.9 (H-3′ or H-4′), 70.6 (H-4), 70.5 (H-2), 68.3 (CH_2O), 66.0 (H-3′ or H-4′), 64.2 (H-5), 63.8 (H-5′), 55.4, 47.9, 47.6, 20.4, 17.6, 17.5, 6.8, 4.8. HRMS (ESI) calcd for $C_{35}H_{54}NaO_{14}Si$: 749.3181. Found: 749.3169.

Data for **22**: $[\alpha]_D^{20}$ 133.1 (*c* 0.3, chloroform); ^1H NMR ($CDCl_3$) δ: 8.00–8.01 (m, 2H, Ar), 6.86–6.88 (m, 2H, Ar), 5.77–5.83 (m, 1H, C*H*=), 5.17–5.23 (m, 2H, H-2′,=C*H*H), 5.11–5.13 (m, 1H,=CH*H*), 5.02 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), 4.90 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1′), 4.62 (dd, 1H, $J_{2,1}$ 3.2, $J_{2,3}$ 9.5 Hz, H-2), 4.09–4.12 (m, 1H, OC*H*H), 3.89–3.95 (m, 3H, H-4′, H-5′, OC*H*H), 3.87–3.88 (m, 1H, H-4), 3.83–3.85 (m, 4H, H-3′, OCH_3), 3.78 (bd, 1H, $J_{5,5'}$ 11.3 Hz, H-5), 3.69 (dd, 1H, $J_{5,4}$ 3.1, $J_{5,5'}$ 12.0 Hz, H-5), 3.40–3.44 (m, 2H, H-5′, H-5′), 3.26 (s, 3H, CH_3), 3.19 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 0.91 (t, 9H, *J* 8.0 Hz, 3×CH_3), 0.52–0.56 (m, 6H, 3×CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.6, 164.6, 163.1, 134.0, 131.9, 122.7, 116.7, 113.3, 103.3 (H-1′), 99.7, 99.5, 95.5 (H-1), 76.6 (H-4), 71.9 (H-2), 71.1 (H-2′), 70.9 (H-3′), 68.4 (H-3), 68.3 (CH_2O), 65.9 (H-4′), 63.9 (H-5′), 62.6 (H-5), 55.3, 47.9, 47.6, 20.7, 17.6, 17.5, 6.8, 4.8. HRMS (ESI) calcd for $C_{35}H_{54}NaO_{14}Si$: 749.3181. Found: 749.3171.

*5.2.19. (E,Z)-1-Propenyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-β-L-arabinopyranoside (**25**) and (E,Z)-1-propenyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2-O-acetyl-3-O-triethylsilyl-β-L-arabinopyranoside (**26**). Method A.* A mixture of **23** and **24** (487 mg, 0.79 mmol) was silylated using the procedure described for **7**. Column chromatography of the crude product (hexane–ethyl acetate, 5:1→7:3; all eluents contained 0.5% Et_3N) afforded **25** (397 mg, 69%) and **26** (119 mg, 21%).

Method B. Disaccharide **21** (171 mg, 0.20 mmol) was converted into 1-propenyl derivative **25** using the procedure described for **8**. Column chromatography of the crude product (hexane–ethyl acetate, 5:1→7:3; all eluents contained 0.5% Et_3N) afforded 170 mg (quant.) of the title compound.

Data for **25**: $[\alpha]_D^{20}$ 167.5 (*c* 0.3, chloroform); ^1H NMR ($CDCl_3$) δ: 7.92–7.93 (m, 2H, Ar), 6.89–6.90 (m, 2H, Ar), 6.05–6.07 (m, 1H, OC*H*=), 5.16 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1), 5.08–5.15 (m, 2H, H-2′, OCH=C*H*), 5.06 (dd, 1H, $J_{2,1}$ 3.4, $J_{2,3}$ 10.1 Hz, H-2), 4.77 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1′), 4.12 (br s, 1H, H-4), 3.98 (dd, 1H, $J_{3,2}$ 10.1, $J_{3,4}$ 2.9 Hz, H-3), 3.86–3.93 (m, 3H, H-3′, H-4′, H-5′), 3.85 (s, 3H, CH_3), 3.76 (bd, 1H, $J_{5,5'}$ 12.1 Hz, H-5), 3.49 (dd, 1H, $J_{5,5'}$ 12.1, $J_{5,4}$ 2.4 Hz, H-5), 3.45–3.47 (m, 1H, H-5′), 3.29 (s, 3H, CH_3), 3.19 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.52 (dd, 3H, *J* 1.5 and 6.9 Hz, OCH=CH–C*H*$_3$), 1.29 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 0.96 (t, 9H, *J* 7.9 Hz, 3×CH_3), 0.59–0.69 (m, 6H, 3×CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.9, 164.0, 163.3, 143.0, 131.5, 122.6, 113.6, 104.6 (OCH=*C*H), 103.4 (H-1′), 99.8, 99.5, 96.2 (H-1), 74.8 (H-3), 71.1 (H-2′), 70.9 (H-3′), 70.5 (H-4), 70.0 (H-2), 66.0 (H-4′), 64.6 (H-5), 63.9 (H-5′), 55.4, 48.0, 47.7, 20.4, 17.7, 17.5, 12.4, 6.8, 4.8. Anal. Calcd for $C_{35}H_{54}O_{14}Si$ (726.90): C, 57.83; H, 7.49. Found: C, 57.91; H, 7.53.

Data for **26**: $[\alpha]_D^{20}$ 151.5 (*c* 0.3, chloroform); ^1H NMR ($CDCl_3$) δ: 7.99–8.01 (m, 2H, Ar), 6.86–6.88 (m, 2H, Ar), 6.05–6.08 (m, 1H, OC*H*=), 5.18–5.21 (m, 2H, H-1, H-2′), 5.02–5.07 (m, 1H, OCH=C*H*), 4.90 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1′), 4.64 (dd, 1H, $J_{2,1}$ 3.3, $J_{2,3}$ 9.7 Hz, H-2), 4.07 (dd, 1H, $J_{3,2}$ 9.7, $J_{3,4}$ 2.9 Hz, H-3), 3.91–3.94 (m, 2H, H-4′, H-5′), 3.89 (br s, 1H, H-4), 3.82–3.86 (m, 4H, H-3′, OCH_3), 3.76 (bd, 1H, $J_{5,5'}$ 12.1 Hz, H-5), 3.71 (dd, 1H, $J_{5,5'}$ 12.1, $J_{5,4}$ 2.7 Hz, H-5), 3.40–3.44 (m, 1H, H-5′), 3.26 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.50 (dd, 3H, *J* 1.4 and 6.8 Hz, OCH=CH–C*H*$_3$), 1.28 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 0.91 (t, 9H, *J* 8.0 Hz, 3×CH_3), 0.53–0.57 (m, 6H, 3×CH_2). ^{13}C

NMR ($CDCl_3$) δ: 169.6, 164.6, 163.1, 143.3, 131.9, 122.7, 113.3, 104.2 (OCH=*C*H), 103.4 (H-1′), 99.7, 99.5, 95.9 (H-1), 76.5 (H-4), 71.3 (H-2), 71.1 (H-2′), 70.9 (H-3′), 68.3 (H-3), 65.9 (H-4), 64.0 (H-5′), 63.0 (H-5), 55.3, 47.9, 47.6, 20.7, 17.6, 17.5, 12.3, 6.8, 4.8. Anal. Calcd for $C_{35}H_{54}O_{14}Si$ (726.90): C, 57.83; H, 7.49. Found: C, 57.84; H, 7.43.

*5.2.20. (E,Z)-1-Propenyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2,4-di-O-acetyl-β-L-arabinopyranoside (**27**).* A sample of **23** and **24** mixture (60 mg, 0.10 mmol) was acetylated under standard conditions (Ac_2O, pyridine). Column chromatography (hexane–ethyl acetate, 2:1) of the crude reaction product gave diacetate **27** (44 mg, 65%) as main product. $[\alpha]_D^{20}$ 198.6 (*c* 0.3, chloroform); ν_{max} (film): 2945, 2837, 1739, 1605, 1373, 1256, 1230, 1168, 1151, 1139, 1099, 1068, 1035, 930, 884, 849, 764 cm^{-1}. ^1H NMR ($CDCl_3$) δ: (600 MHz) 7.95–7.96 (m, 2H, Ar), 6.90–6.92 (m, 2H, Ar), 6.04–6.06 (m, 1H, OC*H*=), 5.29–5.31 (m, 1H, H-4), 5.16 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 5.07–5.13 (m, 2H, H-2′, OCH=C*H*), 5.01 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 10.2 Hz, H-2), 4.68 (d, 1H, $J_{1,2}$ 7.0 Hz, H-1′), 4.12 (dd, 1H, $J_{3,2}$ 10.2, $J_{3,4}$ 3.7 Hz, H-3), 3.84–3.94 (m, 6H, H-3′, H-4′, H-5′, CH_3), 3.82 (bd, 1H, $J_{5,5'}$ 13.1 Hz, H-5), 3.68 (dd, 1H, $J_{5,5'}$ 13.1, $J_{5,4}$ 2.3 Hz, H-5), 3.43–3.47 (m, 1H, H-5), 3.26 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.51–1.53 (m, 3H, OCH=CH–*CH*$_3$), 1.28 (s, 3H, CH_3), 1.22 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.6, 170.0, 164.3, 163.4, 142.8, 131.6, 122.3, 113.6, 105.0, 103.5, 99.7, 99.5, 95.8, 72.8, 71.3, 70.9, 70.5, 69.6, 65.4, 63.9, 60.9, 60.3, 55.4, 48.0, 47.6, 21.1, 20.2, 17.6, 17.5, 12.3. Anal. Calcd for $C_{31}H_{42}O_{15}$ (654.68): C, 56.87; H, 6.47. Found: C, 56.86; H, 6.40.

*5.2.21. Allyl 3,4-O-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2,3-di-O-acetyl-α-L-arabinopyranoside (**31**).* Mixture of **29** and **30** (60 mg, 0.10 mmol) was acetylated under standard conditions (Ac_2O, pyridine). Column chromatography (hexane–ethyl acetate, 2:1) of the crude reaction product gave slightly contaminated diacetate **31** (52 mg, 81%). $[\alpha]_D^{20}$ 67.8 (*c* 0.34, chloroform); ν_{max} (film): 2949, 2838, 1744, 1605, 1372, 1256, 1224, 1169, 1138, 1109, 1048, 931, 884, 848, 765 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.99–8.01 (m, 2H, Ar), 6.91–6.92 (m, 2H, Ar), 5.80–5.86 (m, 1H,=CH), 5.24–5.28 (m, 1H,=C*H*H), 5.13–5.16 (m, 2H, H-2′,=CH*H*), 4.98 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 5.9 Hz, H-2), 4.96 (dd, 1H, $J_{3,2}$ 5.9, $J_{3,4}$ 2.7 Hz, H-3), 4.60 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1′), 4.52 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.19–4.22 (m, 1H, OC*H*H), 4.03–4.07 (m, 2H, H-4,5), 3.87–3.97 (m, 3H, H-3′,4′,5′), 3.85 (s, 3H, OCH_3), 3.54–3.57 (m, 1H, H-5), 3.45–3.48 (m, 1H, H-5′), 3.26 (s, 3H, CH_3), 3.19 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.22 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.2 (C=O), 169.0 (C=O), 164.4 (C), 163.4 (C), 133.7, 131.7, 122.4, 116.7, 113.6, 102.0 (C-1′), 99.7 (C), 99.5 (C), 97.2 (C-1), 71.2 (C-4), 71.0 (C-2′), 70.5 (C-3′), 69.1 (C-2), 68.4 (C-3), 68.3 (OCH_2), 65.7 (C-4′), 64.0 (C-5′), 60.6 (C-5), 55.4 (CH_3), 47.9 (CH_3), 47.6 (CH_3), 20.8 (CH_3), 20.2 (s, 3H, CH_3), 17.6 (CH_3), 17.5 (CH_3). HRMS (ESI) calcd for $C_{31}H_{42}NaO_{15}$ $(M+Na)^+$: 677.2421. Found: 677.2419.

*5.2.22. 3,4-O-(2′,3′-Dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-α,β-L-arabinopyranose (**32**).* Hydrolysis of 1-propenyl glycoside **25** (290 mg, 0.40 mmol) was performed using the procedure described for **9**. Column chromatography of the crude product (hexane–ethyl acetate, 10:1→1:1; all eluents contained 0.5% Et_3N) afforded **32** (200 mg, 73%). Major anomer–selected signals: ^{13}C NMR ($CDCl_3$) δ: 169.9, 164.2, 163.3, 131.5, 122.5, 113.6, 103.3 (H-1′), 99.8, 99.5, 90.9 (H-1), 74.6, 71.2, 70.9, 70.8, 70.5, 66.0, 64.1, 63.8, 55.4, 47.9, 47.6, 20.5, 17.6, 17.5, 10.8, 6.8, 4.8. Anal. Calcd for $C_{32}H_{50}O_{14}Si$ (686.84): C, 55.96; H, 7.34. Found: C, 56.23; H, 7.42.

*5.2.23. 3,4-O-(2′,3′-Dimethoxybutane-2′,3′-diyl)-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-α,β-L-arabinopyranosyl trichloroacetimidate (**33**).* To a solution of hemiacetal **32** (152 mg, 0.22 mmol) and trichloroacetonitrile (0.25 mL, 2.5 mmol) in dichloromethane (5 mL) DBU (15 μL) was added, and stirred at room temp overnight. Then solvents were evaporated to dryness. The residue was purified by column chromatography (hexane–ethyl acetate, 20:1→3:1; all eluents contained 0.5% Et_3N) to give **33** (144 mg, 78%) as a mixture of anomers in approx. ratio=10:1 as white foam. Major anomer: ^1H NMR ($CDCl_3$) δ: 8.50 (s, 1H, C=NH), 7.92–7.94 (m, 2H, Ar), 6.88–6.90 (m, 2H, Ar), 6.43 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 5.24 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 10.3 Hz, H-2), 5.15 (dd, 1H, $J_{2,1}$ 7.5, $J_{2,3}$ 9.7 Hz, H-2′), 4.75 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1′), 4.21 (br s, 1H, H-4), 4.01 (dd, 1H, $J_{3,2}$ 10.3, $J_{3,4}$ 2.8 Hz, H-3), 3.97 (d, 1H, $J_{5,5'}$ 12.2 Hz, H-5), 3.86–3.94 (m, 3H, H-3′, H-4′, H-5′), 3.85 (s, 3H, CH_3), 3.67 (dd, 1H, $J_{5,5'}$ 12.2, $J_{5,4}$ 2.3 Hz, H-5), 3.45–3.49 (m, 1H, H-5′), 3.29 (s, 3H, CH_3), 3.19 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 0.97 (t, 9H, *J* 7.9 Hz, 3×CH_3), 0.60–0.70 (m, 6H, 3×CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.7, 164.0, 163.3, 161.0, 131.5, 122.5, 113.6, 103.7 (H-1′), 99.8, 99.5, 95.0 (H-1), 91.2 (CCl_3) 75.1 (H-3), 71.0 (H-2′), 70.8 (H-3′), 70.3 (H-4), 69.2 (H-2), 66.7 (H-5), 66.0 (H-4′), 63.9 (H-5′), 55.4, 48.0, 47.7, 20.0, 17.6, 17.5, 6.8, 4.8. Anal. Calcd for $C_{34}H_{50}Cl_3NO_{14}Si$ (831.23): C, 49.13; H, 6.06; N, 1.69; Cl, 12.80. Found: C, 49.17; H, 6.08; N, 1.77; Cl, 12.76.

*5.2.24. Allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-β-L-arabinopyranoside (**36**) and allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→4)-2-O-acetyl-3-O-triethylsilyl-β-L-arabinopyranoside (**37**).* A mixture of **34** and **35** (362 mg, 0.50 mmol) was silylated using the procedure described for **7**. Column chromatography of the crude product (hexane–ethyl acetate, 40:1→5:1; all eluents contained 0.5% Et_3N) afforded **36** (196 mg, 47%) and **37** (98 mg, 23%). The same disaccharides were obtained by treatment of partially desilylated mixture **38** with TESCl as described above.

Data for **36**: $[\alpha]_D^{20}$ 53.5 (*c* 0.25, chloroform); ^1H NMR ($CDCl_3$) δ: 7.94–7.95 (m, 2H, Ar), 6.88–6.90 (m, 2H, Ar), 5.75–5.82 (m, 1H, C*H*=), 5.19–5.22 (m, 1H,=C*H*H), 5.12–5.14 (m, 1H,=CH*H*), 4.95–5.01 (m, 3H, H-1,2,2′), 4.69 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1′), 4.07–4.10 (m, 2H, H-4, OC*H*H), 3.90–3.95 (m, 2H, H-3,5′), 3.83–3.86 (m, 4H, OCH*H*, OCH_3), 3.67–3.76 (m, 3H, H-3′, H-4′, H-5), 3.48 (dd, 1H, $J_{5,4}$ 3.3, $J_{5,5'}$ 11.9 Hz, H-5), 3.22 (dd, 1H, $J_{5,4}$ 9.2, $J_{5,5'}$ 11.6 Hz, H-5′), 1.80 (s, 3H, CH_3), 0.98 (t, 9H, *J* 8.0 Hz, CH_3), 0.94 (t, 9H, *J* 7.9 Hz, CH_3), 0.84 (t, 9H, *J* 8.0 Hz, CH_3), 0.59–0.66 (m, 12H, CH_2), 0.48–0.52 (m, 6H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.9, 164.4, 163.2, 133.8, 131.6, 122.8, 117.4, 113.4, 102.4 (C-1′, $^1J_{C1'-H1'}$: 164.0 Hz), 95.6 (C-1, $^1J_{C1-H1}$: 172.1 Hz), 76.0 (C-3′), 74.7 (C-3), 73.9 (C-2′), 71.8 (C-4′), 70.7 (C-2), 70.2 (C-4), 68.4 (CH_2O), 65.8 (C-5′), 64.2 (C-5), 55.4, 20.6, 6.8, 6.8, 5.1, 5.1, 4.8. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 58.60; H, 8.77.

Data for **37**: $[\alpha]_D^{20}$ 48.5 (*c* 0.25, chloroform); ^1H NMR ($CDCl_3$) δ: 8.02–8.04 (m, 2H, Ar), 6.86–6.88 (m, 2H, Ar), 5.77–5.83 (m, 1H, C*H*=), 5.20–5.23 (m, 1H,=C*H*H), 5.11–5.13 (m, 1H,=CH*H*), 4.99–5.02 (m, 2H, H-1,2′), 4.88 (d, 1H, $J_{1,2}$ 6.0 Hz, H-1′), 4.61 (dd, 1H, $J_{2,1}$ 3.3, $J_{2,3}$ 9.5 Hz, H-2), 4.09–4.12 (m, 1H, OC*H*H), 4.07 (dd, 1H, $J_{3,2}$ 9.5, $J_{3,4}$ 3.0 Hz, H-3), 4.03 (dd, 1H, $J_{5,4}$ 4.2, $J_{5,5'}$ 11.7 Hz, H-5′), 3.88–3.91 (m, 4H, OCH*H*, OCH_3), 3.86 (s, 3H, CH_3), 3.83–3.85 (m, 1H, H-4), 3.74–3.78 (m, 2H, H-3′,5), 3.67–3.70 (m, 2H, H-4′,5), 3.23 (dd, 1H, $J_{5,4}$ 7.9, $J_{5,5'}$ 11.7 Hz, H-5′), 1.93 (s, 3H, CH_3), 0.92–0.96 (m, 18H, CH_3), 0.88 (t, 9H, *J* 8.0 Hz, CH_3), 0.53–0.63 (m, 18H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.6, 164.9, 163.1, 134.0, 132.0, 122.9, 116.7, 113.2, 101.9 (C-1′, $^1J_{C1'-H1'}$: 164.6 Hz), 95.5 (C-1, $^1J_{C1-H1}$: 173.5 Hz), 76.6 (C-4), 73.9 (C-3′), 73.1 (C-2′), 72.0 (C-2), 71.1 (C-4′), 68.3 (C-3), 68.2 (CH_2O), 64.6 (C-5′), 62.6 (C-5), 55.3, 20.7, 6.8, 6.8, 6.8, 4.9, 4.8. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 58.60; H, 8.79.

5.2.25. (E,Z)-1-Propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-β-L-

*arabinopyranoside (**41**) and (E,Z)-1-propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-D-xylopyranosyl-(1→4)-2-O-acetyl-3-O-triethylsilyl-β-L-arabinopyranoside (**42**). Method A*. A mixture of disaccharides **39** and **40** (292 mg, 0.40 mmol) was converted into 1-propenyl derivatives **41** and **42** using the procedure described for **7**. Column chromatography of the crude product (hexane–ethyl acetate, 40:1→5:1, all eluents contained 0.5% Et_3N) afforded **41** (164 mg, 49%) and **42** (120 mg, 36%).

Method B. Disaccharides **36** (171 mg, 0.20 mmol) or **37** (72 mg, 0.09 mmol) were converted into 1-propenyl derivatives **41** or **42** using the procedure described for **8**. Column chromatography of the crude product (hexane–ethyl acetate, 5:1, contained 0.5% Et_3N) afforded **41** (168 mg, 98%) or **42** (66 mg, 92%), respectively.

Data for **41**: $[\alpha]_D^{20}$ 57.9 (*c* 0.25, chloroform); ^1H NMR ($CDCl_3$) δ: 7.93–7.95 (m, 2H, Ar), 6.88–6.90 (m, 2H, Ar), 6.01 (bd, 1H, *J* 12.1 Hz, OC*H*=), 5.14 (d, 1H, $J_{1,2}$ 2.8 Hz, H-1), 5.06 (dq, 1H, *J* 6.8, 13.7 Hz,=C*H*), 4.98–5.01 (m, 2H, H-2,2′), 4.70 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1′), 4.10 (bd, 1H, H-4), 3.96 (dd, 1H, $J_{3,2}$ 9.8, $J_{3,4}$ 2.9 Hz, H-3), 3.93 (dd, 1H, $J_{5,4}$ 4.6, $J_{5,5'}$ 11.6 Hz, H-5′), 3.86 (s, 3H, OCH_3), 3.68–3.74 (m, 3H, H-3′, H-4′, H-5), 3.49 (dd, 1H, $J_{5,4}$ 3.0, $J_{5,5'}$ 12.0 Hz, H-5), 3.24 (dd, 1H, $J_{5,4}$ 9.3, $J_{5,5'}$ 11.6 Hz, H-5′), 1.78 (s, 3H, CH_3), 1.50 (dd, 1H, *J* 1.5, 6.8 Hz, CH_3), 0.98 (t, 9H, *J* 8.0 Hz, CH_3), 0.94 (t, 9H, *J* 7.9 Hz, CH_3), 0.84 (t, 9H, *J* 8.0 Hz, CH_3), 0.59–0.67 (m, 12H, CH_2), 0.48–0.52 (m, 6H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 170.0, 164.4, 163.3, 143.1, 131.6, 122.8, 113.5, 104.5, 102.5 (C-1′, $^1J_{C1'\text{-}H1'}$: 162.1 Hz), 95.1 (C-1, $^1J_{C1\text{-}H1}$: 174.4 Hz), 76.0 (C-3′), 74.5 (C-3), 74.0 (C-2′), 71.9 (C-4′), 70.3 (C-4), 70.2 (C-2), 65.9 (C-5′), 64.6 (C-5), 55.4, 20.6, 12.4, 6.9, 6.9, 6.8, 5.2, 5.1, 4.8. HRMS (ESI) calcd for $C_{41}H_{72}NaO_{12}Si_3$ $[M+Na]^+$: 863.4229. Found: 863.4212. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 59.00; H, 8.81.

Data for **42**: $[\alpha]_D^{20}$ 54.6 (*c* 0.20, chloroform); ^1H NMR (C_6D_6) δ: 8.36–8.38 (m, 2H, Ar), 6.75–6.77 (m, 2H, Ar), 6.02 (dq, 1H, *J* 1.5, 12.2 Hz, OC*H*=), 5.55 (dd, 1H, $J_{2,1}$ 5.6, $J_{2,3}$ 6.8 Hz, H-2′), 5.53 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1), 5.21–5.23 (m, 2H, H-1′,2), 5.10 (dq, 1H, *J* 6.8, 13.7 Hz,=C*H*), 4.29 (dd, 1H, $J_{3,2}$ 9.8, $J_{3,4}$ 3.0 Hz, H-3), 4.21 (dd, 1H, $J_{5,4}$ 4.0, $J_{5,5'}$ 11.6 Hz, H-5′), 4.13 (t, 1H, $J_{3,2}$ 6.8, $J_{3,4}$ 6.8 Hz, H-3′), 3.95–3.97 (m, 2H, H-4,5), 3.79–3.84 (m, 2H, H-4′,5), 3.41 (dd, 1H, $J_{5,4}$ 7.3, $J_{5,5'}$ 11.6 Hz, H-5′), 3.17 (s, 3H, OCH_3), 1.68 (s, 3H, CH_3), 1.30 (dd, 1H, *J* 1.6, 6.8 Hz, CH_3), 1.11 (t, 9H, *J* 8.0 Hz, CH_3), 0.96–1.00 (m, 12H, CH_3), 0.80–0.84 (m, 6H, CH_2), 0.56–0.63 (m, 12H, CH_2). ^{13}C NMR (C_6D_6) δ: 169.3, 165.2, 163.7, 144.2, 132.6, 123.7, 113.8, 103.8, 102.4 (C-1′, $^1J_{C1'\text{-}H1'}$: 165.0 Hz), 96.8 (C-1, $^1J_{C1\text{-}H1}$: 174.8 Hz), 77.0 (C-4), 74.2 (C-3′), 73.6 (C-2′), 72.0 (C-2), 71.7 (C-4′), 69.1 (C-3), 64.7 (C-5′), 63.4 (C-5), 54.8, 20.5, 12.4, 7.3, 7.1, 7.1, 5.5, 5.4, 5.2. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 58.27; H, 8.68.

*5.2.26. 3,4-Di-O-triethylsilyl-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-α,β-L-arabinopyranose (**43**)*. Hydrolysis of 1-propenyl glycoside **41** (141 mg, 0.17 mmol) was performed using the procedure described for **9**. Column chromatography of the crude product (hexane–ethyl acetate, 3:1→1:1; all eluents contained 0.5% Et_3N) afforded **43** (119 mg, 89%). NMR data of **43** matches the literature.[6]

*5.2.27. 3,4-Di-O-triethylsilyl-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-α,β-L-arabinopyranosyl trichloroacetimidate (**44**)*. The title compound was prepared using the procedure described for **33**. Reaction of **43** (160 mg, 0.20 mmol) with trichloroacetonitrile in the presence of DBU gave, after column chromatography (hexane–ethyl acetate, 5:1; contained 0.5% Et_3N), 144 mg (76%) of the title compound as a mixture of anomers in approx. ratio=10:1 as white foam. NMR data of **44** matches the literature.[6]

*5.2.28. Allyl 2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2-O-acetyl-α-L-arabinopyranoside (**49**), allyl 2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-3-O-acetyl-α-L-arabinopyranoside (**50**), and allyl 2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→3)-2-O-acetyl-α-L-arabinopyranoside (**51**)*. To a solution of **45** and **46** mixture (353 mg, 0.48 mmol) in methanol (3 mL) and dichloromethane (3 mL) 10-camphorsulfonic acid (12 mg) was added and stirred at room temp for 30 min. Reaction was quenched by the addition of triethylamine (0.5 mL) and solvents were evaporated to dryness. Column chromatography (hexane–ethyl acetate–methanol, 5:3:1) of the reasidue gave inseparable mixture of **49** and **50** (96 mg, 40%), and **51** (47 mg, 19%).

Data for **49** and **50** mixture: ^1H NMR ($CDCl_3$) δ: major component; selected signals—5.00 (dd, 1H, $J_{2,1}$ 6.2, $J_{2,3}$ 7.9 Hz, H-2′), 4.91 (dd, 1H, $J_{2,1}$ 4.9, $J_{2,3}$ 7.0 Hz, H-2), 4.78 (d, 1H, $J_{1,2}$ 6.2 Hz, H-1′), 4.47 (d, 1H, $J_{1,2}$ 4.9 Hz, H-1), 3.92–3.94 (m, 1H, H-4), 3.79–3.82 (m, 1H, H-4′), 3.74–3.77 (m, 2H, H-3,3′). Minor component; selected signals—5.00–5.02 (m, 1H, H-2′), 4.75–4.78 (dd, 1H, *J* 3.3, 9.7 Hz, H-3), 4.61 (d, 1H, $J_{1,2}$ 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$) δ: major component; selected signals—101.3 (C-1′), 98.1 (C-1), 75.2 (C-4), 74.0 (C-3′), 73.7 (C-2′), 71.8 (C-2), 69.6 (C-4′), 69.5 (C-3), 64.5 (C-5′), 61.6 (C-5). Minor component; selected signals—102.2 (C-1′), 102.1 (C-1), 74.8 (C-4), 74.4 (C-3′), 73.8 (C-2′), 73.6 (C-3), 69.8 (C-4′), 68.9 (C-2), 65.4 (C-5), 64.6 (C-5′). Anal. Calcd for $C_{23}H_{30}O_{12}\times H_2O$ (516.51): C, 53.48; H, 6.25. Found: C, 53.60; H, 5.91.

Data for **51**: $[\alpha]_D^{20}$ −32.1 (*c* 0.40, chloroform); ν_{max} (film): 3442, 3014, 2979, 2932, 1742, 1720, 1605, 1512, 1258, 1171, 1099, 1069, 1046, 986, 849, 768 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.93–7.94 (m, 2H, Ar), 6.85–6.86 (m, 2H, Ar), 5.60–5.66 (m, 1H, C*H*=), 5.10–5.14 (m, 1H,=C*H*H), 5.04–5.07 (m, 1H,=CH*H*), 5.03 (dd, 1H, $J_{2,1}$ 6.1, $J_{2,3}$ 7.9 Hz, H-2), 5.00 (dd, 1H, $J_{2,1}$ 7.1, $J_{2,3}$ 8.7 Hz, H-2′), 4.64 (d, 1H, $J_{1,2}$ 7.1 Hz, H-1′), 4.31 (d, 1H, $J_{1,2}$ 6.1 Hz, H-1), 4.03–4.08 (m, 2H, OCH*H*, H-5′), 4.01–4.03 (m, 1H, H-4), 3.94 (dd, 1H, $J_{5,4}$ 4.5, $J_{5,5'}$ 12.3 Hz, H-5), 3.87–3.91 (m, 1H, OCH*H*), 3.78–3.82 (m, 4H, H-4′, OCH_3), 3.70–3.74 (m, 2H, H-3,3′), 3.45 (dd, 1H, $J_{5,4}$ 2.2, $J_{5,5'}$ 12.3 Hz, H-5), 3.33 (dd, 1H, $J_{5,4}$ 9.6, $J_{5,5'}$ 11.6 Hz, H-5′), 1.65 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 169.6, 165.7, 163.6, 133.7, 132.1, 121.9, 117.0, 113.6, 101.7 (C-1′, $^1J_{C1'\text{-}H1'}$: 164.1 Hz), 98.7 (C-1, $^1J_{C1\text{-}H1}$: 161.3 Hz), 79.3 (C-3), 74.5 (C-3′), 73.5 (C-2′), 70.0 (C-2), 69.6 (C-4′), 68.6 (*C*H_2O), 66.8 (C-4), 65.1 (C-5′), 63.7 (C-5), 55.4, 20.3. Anal. Calcd for $C_{23}H_{30}O_{12}\times ½H_2O$ (507.50): C, 54.43; H, 6.16. Found: C, 54.48; H, 5.97.

*5.2.29. Allyl 3,4-di-O-acetyl-2-O-(4-methoxybenzoyl)-β-D-xylopyranosyl-(1→4)-2,3-di-O-acetyl-α-L-arabinopyranoside (**52**)*. A mixture of **49** and **50** (42 mg, 0.084 mmol) was acetylated under standard conditions (Ac_2O, pyridine). Column chromatography of the crude reaction mixture (hexane–ethyl acetate, 7:3) gave 50 mg (94%) of the title compound as a foam. $[\alpha]_D^{20}$ −3.8 (*c* 0.30, chloroform); ν_{max} (film): 2940, 2867, 1748, 1606, 1371, 1239, 1170, 1099, 1054, 767 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.95–7.96 (m, 2H, Ar), 6.88–6.89 (m, 2H, Ar), 5.79–5.85 (m, 1H, C*H*=), 5.23–5.28 (m, 2H, H-3′,=C*H*H), 5.13–5.16 (m, 1H,=CH*H*), 5.10 (dd, 1H, $J_{2,1}$ 5.3, $J_{2,3}$ 7.2 Hz, H-2′), 5.06 (dd, 1H, $J_{2,1}$ 5.0, $J_{2,3}$ 7.3 Hz, H-2), 4.91–4.95 (m, 2H, H-3,4′), 4.74 (d, 1H, $J_{1,2}$ 5.3 Hz, H-1′), 4.46 (d, 1H, $J_{1,2}$ 5.0 Hz, H-1), 4.27 (dd, 1H, $J_{5,4}$ 4.3, $J_{5,5'}$ 12.4 Hz, H-5′), 4.22–4.25 (m, 1H, OCH*H*), 4.07 (dd, 1H, $J_{5,4}$ 5.9, $J_{5,5'}$ 11.8 Hz, H-5), 4.02–4.04 (m, 1H, H-4), 3.97–4.00 (m, 1H, OCH*H*), 3.83 (s, 3H, OCH_3), 3.49–3.54 (m, 2H, H-5,5′), 2.06 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.77 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.3, 169.9, 169.8, 169.1, 164.5, 163.7, 133.7, 131.9, 121.7, 116.9, 113.6, 100.2 (C-1′), 98.3 (C-1), 72.9 (C-4), 69.7 (C-3), 69.6 (C-3′), 69.5 (C-2′), 69.2 (C-2), 68.7 (*C*H_2O), 68.4 (C-4′), 62.1 (C-5), 61.2 (C-5′), 55.4, 20.8, 20.8, 20.6, 20.4. Anal. Calcd for $C_{29}H_{36}O_{15}$ (624.61): C, 55.77; H, 5.81. Found: C, 55.74; H, 5.71.

*5.2.30. Allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-β-L-arabinopyranoside (**59**) and allyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→4)-2-O-acetyl-3-O-triethylsilyl-β-L-arabinopyranoside (**60**)*. A mixture of **57** and **58** (372 mg, 0.51 mmol) was silylated

using the procedure described for **7**. Column chromatography of the crude product (hexane–ethyl acetate, 40:1→5:1; all eluents contained 0.5% Et_3N) afforded **59** (220 mg, 51%) and a mixture of **59** and **60** (102 mg, 24%).

Data for **59**: $[\alpha]_D^{20}$ 52.7 (*c* 0.3, chloroform); ^1H NMR ($CDCl_3$) δ: 8.01–8.02 (m, 2H, Ar), 6.89–6.91 (m, 2H, Ar), 5.83–5.89 (m, 1H, C*H*=), 5.23–5.26 (m, 1H,=C*H*H), 5.16–5.17 (m, 1H,=CH*H*), 5.10 (dd, 1H, $J_{2,1}$ 2.2, $J_{2,3}$ 6.5 Hz, H-2), 4.97 (dd, 1H, $J_{2,1}$ 5.9, $J_{2,3}$ 7.2 Hz, H-2′), 4.84 (br s, 1H, H-1), 4.80 (d, 1H, $J_{1,2}$ 5.9 Hz, H-1′), 4.18–4.21 (m, 1H, OC*H*H), 4.05 (dd, 1H, $J_{5,4}$ 4.1, $J_{5,5'}$ 11.7 Hz, H-5′), 3.98–4.01 (m, 2H, H-3, OCH*H*), 3.92–3.94 (m, 1H, H-4), 3.87 (s, 3H, OCH_3), 3.73 (t, 1H, $J_{3,2}$=$J_{3,4}$=7.2 Hz, H-3′), 3.66–3.69 (m, 1H, H-4′), 3.47 (dd, 1H, $J_{5,4}$ 3.2, $J_{5,5'}$ 11.3 Hz, H-5), 3.38 (dd, 1H, $J_{5,4}$ 7.4, $J_{5,5'}$ 11.3 Hz, H-5), 3.24 (dd, 1H, $J_{5,4}$ 7.8, $J_{5,5'}$ 11.7 Hz, H-5′), 2.10 (s, 3H, CH_3), 0.86–0.96 (m, 27H, 9×CH_3), 0.50–0.63 (m, 18H, 9×CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.9, 164.9, 163.3, 133.8, 131.8, 122.8, 117.2, 113.4, 100.5 (C-1′), 96.0 (C-1), 74.0 (C-3′), 73.6 (C-3), 73.4 (C-2′), 71.1 (C-4′), 70.7 (C-2), 69.3 (CH_2O), 66.9 (C-4), 64.7 (C-5′), 63.9 (C-5), 55.4, 21.0, 6.8, 6.7, 5.0, 4.9, 4.7. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 58.44; H, 8.68.

Data for **60**: ^1H NMR ($CDCl_3$) δ: 8.00–8.02 (m, 2H, Ar), 6.89–6.92 (m, 2H, Ar), 5.78–5.86 (m, 1H, C*H*=), 5.20–5.24 (m, 1H,=C*H*H), 5.12–5.14 (m, 1H,=CH*H*), 4.96 (dd, 1H, $J_{2,1}$ 6.0, $J_{2,3}$ 7.0 Hz, H-2), 4.85–4.87 (m, 2H, H-1, H-2′), 4.62 (d, 1H, $J_{1,2}$ 5.7 Hz, H-1′), 4.14–4.18 (m, 1H, OC*H*H), 4.11 (dd, 1H, $J_{5,4}$ 2.9, $J_{5,5'}$ 11.7 Hz, H-5), 4.07 (dd, 1H, $J_{3,2}$ 6.4, $J_{3,4}$ 2.9 Hz, H-3′), 3.92–3.96 (m, 1H, OCH*H*), 3.88–3.90 (m, 1H, H-4′), 3.87 (s, 3H, OCH_3), 3.75 (t, 1H, $J_{3,2}$=$J_{3,4}$=7.0 Hz, H-3), 3.64–3.68 (m, 1H, H-4), 3.62 (dd, 1H, $J_{5,4}$ 3.1, $J_{5,5'}$ 11.7 Hz, H-5′), 5.57 (dd, 1H, $J_{5,4}$ 6.3, $J_{6,6'}$ 11.7 Hz, H-5′), 3.23 (dd, 1H, $J_{5,4}$ 7.7, $J_{5,5'}$ 11.7 Hz, H-5), 2.10 (s, 3H, CH_3), 0.96 (t, 9H, *J* 7.9 Hz, CH_3), 0.92 (t, 9H, *J* 7.9 Hz, CH_3), 0.88 (t, 9H, *J* 7.9 Hz, CH_3), 0.52–0.64 (m, 18H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 170.1, 164.7, 163.3, 134.0, 131.8, 122.8, 116.9, 113.4, 99.5, 95.7, 74.0, 73.0, 72.0, 71.1, 68.9, 68.3, 64.8, 60.4, 55.4, 21.0, 6.8, 6.7, 5.0, 5.0, 4.7. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 58.31; H, 8.60.

*5.2.31. (E,Z)-1-Propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-β-L-arabinopyranoside (**63**) and (E,Z)-1-propenyl 2-O-(4-methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→4)-2-O-acetyl-3-O-triethylsilyl-β-L-arabinopyranoside (**64**). Method A*. A mixture of **61** and **62** (395 mg, 0.54 mmol) was silylated using the procedure described for **7**. Column chromatography of the crude product (hexane–ethyl acetate, 40:1→5:1; all eluents contained 0.5% Et_3N) afforded **63** (219 mg, 48%) and a mixture of **63** and **64** (125 mg, 27%).

Method B. Disaccharide **59** (98 mg, 0.12 mmol) was converted into 1-propenyl derivative **63** using the procedure described for **8**. Column chromatography of the crude product (hexane–ethyl acetate, 40:1→5:1; all eluents contained 0.5% Et_3N) afforded **63** (91 mg, 93%).

Data for **63**: $[\alpha]_D^{20}$ 56.2 (*c* 0.30, chloroform); ^1H NMR ($CDCl_3$) δ: 8.02–8.03 (m, 2H, Ar), 6.90–6.91 (m, 2H, Ar), 6.12 (dq, 1H, *J* 1.5, 12.2 Hz, OC*H*=), 5.14 (dd, 1H, $J_{2,1}$ 2.4, $J_{2,3}$ 7.1 Hz, H-2′), 5.05–5.11 (m, 2H, H-1′,=C*H*), 4.96 (dd, 1H, $J_{2,1}$ 5.6, $J_{2,3}$ 6.8 Hz, H-2), 4.80 (d, 1H, $J_{1,2}$ 5.6 Hz, H-1), 4.08 (dd, 1H, $J_{5,4}$ 3.9, $J_{5,5'}$ 11.8 Hz, H-5), 4.03 (dd, 1H, $J_{3,2}$ 7.1, $J_{3,4}$ 2.6 Hz, H-3′), 3.93–3.95 (m, 1H, H-4′), 3.87 (s, 3H, OCH_3), 3.74 (t, 1H, $J_{3,2}$ 6.8, $J_{3,4}$ 6.8 Hz, H-3), 3.65–3.68 (m, 1H, H-4), 3.50 (dd, 1H, $J_{5,4}$ 3.0, $J_{5,5'}$ 11.5 Hz, H-5′), 3.42 (dd, 1H, $J_{5,4}$ 6.6, $J_{5,5'}$ 11.5 Hz, H-5′), 3.26 (dd, 1H, $J_{5,4}$ 7.5, $J_{5,5'}$ 11.8 Hz, H-5), 2.10 (s, 3H, CH_3), 1.53 (dd, 1H, *J* 1.5, 6.9 Hz, CH_3), 0.94 (t, 9H, *J* 7.9 Hz, CH_3), 0.87–0.90 (m, 18H, CH_3), 0.49–0.63 (m, 18H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 169.9, 164.9, 163.3, 143.4, 131.8, 122.7, 113.4, 104.6, 100.0 (C-1), 96.2 (C-1′), 73.6 (C-3), 73.3 (C-2,3′), 70.9 (C-4), 70.0 (C-2′), 66.7 (C-4′), 64.4 (C-5), 64.2 (C-5′), 55.4, 20.9, 12.3, 6.8, 6.7, 4.9, 4.9, 4.7. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 58.46; H, 8.41.

Data for **64**: ^1H NMR ($CDCl_3$) δ: selected signals—6.08 (dq, 1H, *J* 1.4, 12.3 Hz, OC*H*=), 5.00–5.05 (m, 2H, H-1′,=C*H*), 4.96 (dd, 1H, $J_{2,1}$ 5.9, $J_{2,3}$ 6.7 Hz, H-2), 4.89 (dd, 1H, $J_{2,1}$ 2,7, $J_{2,3}$ 7.8 Hz, H-2′), 4.63 (d, 1H, $J_{1,2}$ 5.9 Hz, H-1), 4.11–4.15 (m, 1H, H-5), 4.08 (dd, 1H, $J_{3,2}$ 7.8, $J_{3,4}$ 3.0 Hz, H-3′), 3.88–3.90 (m, 1H, H-4′), 3.87 (s, 3H, OCH_3), 3.74–3.77 (m, 1H, H-3), 3.65–3.68 (m, 1H, H-4), 3.60–3.61 (m, 1H, H-5′, H-5′), 3.24 (dd, 1H, $J_{5,4}$ 7.5, $J_{5,5'}$ 11.7 Hz, H-5), 2.09 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: selected signals—104.3 (=CH), 99.2 (C-1), 96.1 (C-1′), 74.0 (C-4′), 73.8 (C-3), 73.0 (C-2), 71.4 (C-2′), 71.0 (C-4), 68.1 (C-3′), 64.7 (C-5), 60.6 (C-5′), 55.4, 21.0. Anal. Calcd for $C_{41}H_{72}O_{12}Si_3$ (841.28): C, 58.54; H, 8.63. Found: C, 58.74; H, 8.63.

*5.2.32. Allyl 2-O-(4-methoxybenzoyl)-β-L-xylopyranosyl-(1→3)-2-O-acetyl-β-L-arabinopyranoside (**65**)*. Desilylation of **59** (84 mg, 0.10 mmol) was performed using the procedure described for **51**. Column chromatography of the crude product (hexane–ethyl acetate, 10:1→1:1) afforded **65** (43 mg, 86%). $[\alpha]_D^{20}$ 101.2 (*c* 0.3, chloroform); ν_{max} (film): 3444 (br), 2928, 2872, 1716, 1604, 1256, 1171, 1141, 1098, 1065, 1030, 848, 768 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.93–7.95 (m, 2H, Ar), 6.88–6.89 (m, 2H, Ar), 5.82–5.90 (m, 1H, C*H*=), 5.26–5.30 (m, 1H,=C*H*H), 5.18–5.20 (m, 2H, H-2,=CH*H*), 4.98 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.94 (dd, 1H, $J_{2,1}$ 5.7, $J_{2,3}$ 7.3 Hz, H-2), 4.08–4.17 (m, 3H), 3.97–4.00 (m, 1H, OC*H*H), 3.90–3.92 (m, 1H, H-4), 3.84 (s, 3H, OCH_3), 3.73–3.78 (m, 3H), 3.66 (dd, 1H, $J_{5,4}$ 2.3, $J_{5,5'}$ 12.5 Hz, H-5), 3.40 (dd, 1H, $J_{5,4}$ 7.5, $J_{5,5'}$ 11.8 Hz, H-5), 2.08 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.6, 166.1, 164.0, 133.6, 131.9, 121.2, 117.7, 113.9, 99.3, 95.8, 75.1, 73.7, 73.4, 69.4, 69.1, 68.4, 66.9, 64.1, 61.9, 55.5, 21.0. HRMS (ESI) calcd for $C_{23}H_{30}NaO_{12}$ $[M+Na]^+$: 521.1635. Found: 521.1644. Anal. Calcd for $C_{23}H_{30}O_{12}$×½H_2O (507.50): C, 54.43; H, 6.16. Found: C, 54.77; H, 6.35.

*5.2.33. Allyl 3,4-di-O-acetyl-2-O-(4-methoxybenzoyl)-β-L-xylopyranosyl-(1→3)-2,4-di-O-acetyl-β-L-arabinopyranoside (**66**)*. Triol **65** (43 mg, 0.086 mmol) was acetylated under standard conditions (Ac_2O, pyridine). Column chromatography of the crude reaction mixture (hexane–ethyl acetate, 5:1) gave 49 mg (91%) of the title compound as a foam. $[\alpha]_D^{20}$ 97.3 (*c* 0.3, chloroform); ν_{max} (film): 3020, 2936, 1745, 1606, 1512, 1372, 1235, 1101, 1065, 1027, 849, 759 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.97–7.99 (m, 2H, Ar), 6.91–6.93 (m, 2H, Ar), 5.84–5.90 (m, 1H, C*H*=), 5.28–5.31 (m, 1H,=C*H*H), 5.26 (t, 1H, $J_{3,2}$=$J_{3,4}$=7.4 Hz, H-3′), 5.20–5.23 (m, 2H, H-4,=CH*H*), 5.13 (dd, 1H, $J_{2,1}$ 3.6, $J_{2,3}$ 10.1 Hz, H-2), 5.05–5.07 (m, 2H, H-1, H-2′), 4.95 (m, 1H, H-4′), 4.82 (d, 1H, $J_{1,2}$ 5.1 Hz, H-1′), 4.29 (dd, 1H, $J_{3,2}$ 10.2, $J_{3,4}$ 3.5 Hz, H-3), 4.24 (dd, 1H, $J_{5,4}$ 4.5, $J_{5,5'}$ 12.3 Hz, H-5′), 4.15–4.20 (m, 1H, OC*H*H), 3.98–4.02 (m, 1H, OC*H*H), 3.86 (s, 3H, OCH_3), 3.83 (dd, 1H, $J_{5,4}$ 1.2, $J_{5,5'}$ 12.9 Hz, H-5), 3.65 (dd, 1H, $J_{5,4}$ 2.4, $J_{5,5'}$ 12.9 Hz, H-5), 3.53 (dd, 1H, $J_{5,4}$ 6.4, $J_{5,5'}$ 12.3 Hz, H-5′), 2.13 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.82 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.3, 170.2, 169.9, 169.7, 164.3, 163.7, 133.5, 132.0, 121.6, 117.9, 113.7, 97.3 (C-1′), 95.5 (C-1), 70.3 (C-3), 70.0 (C-3′), 69.9 (C-2′), 69.2 (C-2), 68.7 (C-4′), 68.6 (OCH_2), 67.4 (C-4), 61.3 (C-5′), 60.4 (C-5), 55.4, 20.9, 20.8, 20.6, 20.5. HRMS (ESI) calcd for $C_{29}H_{36}NaO_{15}$ $[M+Na]^+$: 647.1952. Found: 647.1946.

*5.2.34. 2-O-(4-Methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-α,β-L-arabinopyranose (**67**)*. Hydrolysis of 1-propenyl glycoside **63** (264 mg, 0.31 mmol) was performed using the procedure described for **9**. Column chromatography of the crude product (hexane–ethyl acetate, 7:3; contained 0.5% Et_3N) afforded **67** (210 mg, 84%, α,β mixture in 1:1 ratio) as foam. ^{13}C NMR ($CDCl_3$) δ: selected signals—170.2, 169.4, 165.8, 165.1, 163.5, 163.3, 132.0, 131.9, 122.8, 122.4, 113.5, 113.4, 101.3, 101.3, 91.6, 91.2, 75.5, 74.2, 73.5, 73.5, 72.8, 72.7, 72.0, 71.3, 70.7, 70.6, 70.6, 66.3, 65.2, 65.1, 64.2, 64.1, 58.6, 55.4, 55.4, 20.9, 20.9.

Anal. Calcd for $C_{38}H_{68}O_{12}Si_3$ (801.22): C, 56.97; H, 8.55. Found: C, 56.91; H, 8.75.

*5.2.35. 2-O-(4-Methoxybenzoyl)-3,4-di-O-triethylsilyl-β-L-xylopyranosyl-(1→3)-2-O-acetyl-4-O-triethylsilyl-α,β-L-arabinopyranosyl trichloroacetimidate (**68**).* The title compound was prepared using the procedure described for **33**. Reaction of **65** (185 mg, 0.23 mmol) with trichloroacetonitrile in the presence of DBU gave, after column chromatography (hexane–ethyl acetate, 5:1; contained 0.5% Et_3N), 146 mg (67%) of the title compound as a mixture of anomers in approx. ratio 10: 1 as white foam. ^{1}H NMR ($CDCl_3$) δ: major isomer, selected signals—8.58 (s, 1H, NH), 8.02–8.04 (m, 2H, Ar), 6.90–6.92 (m, 2H, Ar), 6.33 (br s, 1H, H-1), 5.36 (dd, 1H, $J_{2,1}$ 2.9, $J_{2,3}$ 8.5 Hz, H-2), 4.97 (dd, 1H, $J_{2,1}$ 5.0, $J_{2,3}$ 6.0 Hz, H-2′), 4.82 (d, 1H, $J_{1,2}$ 5.0 Hz, H-1′), 4.10–4.16 (m, 2H, H-3, H-5′), 4.03–4.05 (m, 1H, H-4), 3.87 (s, 3H, OCH_3), 3.77 (t, 1H, $J_{3,2}$=$J_{3,4}$=6.0 Hz, H-3′), 3.72 (dd, 1H, $J_{5,4}$<1, $J_{5,5'}$ 11.9 Hz, H-5), 3.64–3.67 (m, 1H, H-4′), 3.62 (dd, 1H, $J_{5,4}$ 4.8, $J_{5,5'}$ 11.9 Hz, H-5), 3.29 (dd, 1H, $J_{5,4}$ 6.5, $J_{5,5'}$ 11.8 Hz, H-5′), 2.05 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: major isomer, selected signals—169.7, 164.8, 163.4, 101.3, 94.6, 91.5, 91.1, 74.2, 72.8, 72.7, 72.6, 70.6, 70.5, 69.0, 66.6, 55.4, 20.7, 11.4, 6.8, 6.8, 6.7, 4.9, 4.8, 4.7. MS (ESI): 968.30 $[M+Na]^+$; 823.39 $[M\text{-}TCA+Na]^+$; 1624.80 $[2(M\text{-}TCA)+Na]^+$.

Acknowledgements

This work was financed by grant from the National Science Centre, Poland (No. 2012/07/B/ST5/00823).

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.05.058.

References and notes

1. Kubo, S.; Mimaki, Y.; Terao, M.; Sashida, Y.; Nikaido, T.; Ohmoto, T. *Phytochemistry* **1992**, *31*, 3969–3973.
2. Mimaki, Y.; Kuroda, M.; Kameyama, A.; Sashida, Y.; Hirano, T.; Oka, K.; Maekawa, R.; Wada, T.; Sugita, K.; Beutler, J. A. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 633–636.
3. (a) Morzycki, J. W.; Wojtkielewicz, A. *Phytochem. Rev.* **2005**, *4*, 259–277; (b) Tang, Y.; Li, N.; Duan, J.; Tao, W. *Chem. Rev.* **2013**, *113*, 5480–5514.
4. (a) Ma, X.; Yu, B.; Hui, Y.; Xiao, D.; Ding, J. *Carbohydr. Res.* **2000**, *329*, 495–505; (b) Yu, W.; Jin, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6576–6583; (c) Xue, J.; Liu, P.; Pan, Y. B.; Guo, Z. W. *J. Org. Chem.* **2008**, *73*, 157–161; (d) Zheng, D.; Zhou, L.; Guan, Y.; Chen, X.; Zhou, W.; Chen, X.; Lei, P. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 5439–5442; (e) Kongkathip, B.; Kongkathip, N.; Rujirawanich, J. *Synth. Commun.* **2014**, *44*, 2248–2255.
5. Khasanova, L. S.; Gimalova, F. A.; Torosyan, S. A.; Fatykhov, A. A.; Miftakhov, M. S. *Russ. J. Org. Chem.* **2011**, *47*, 1125–1129.
6. Deng, S. J.; Yu, B.; Lou, Y.; Hui, Y. Z. *J. Org. Chem.* **1999**, *64*, 202–208.
7. Jenkins, D. J.; Potter, B. V. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 41–49.
8. Gu, G.; Du, Y. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2075–2079.
9. Bang, S.-C.; Seo, H.-H.; Yun, H.-Y.; Jung, S.-H. *Chem. Pharm. Bull.* **2007**, *55*, 1734–1739.
10. Cmoch, P.; Pakulski, Z. *Tetrahedron: Asymmetry* **2008**, *19*, 1493–1502.
11. Wang, P.; Li, C.; Zang, J.; Song, N.; Zhang, X.; Li, Y. *Carbohydr. Res.* **2005**, *340*, 2086–2096.
12. Kim, M.; Lim, E.; Jung, M. *Tetrahedron* **2013**, *69*, 5481–5486.
13. Wang, B.; Chun, J.; Liu, Y.; Han, L.; Wang, Y.; Joo, E.-J.; Kim, Y.-S.; Cheng, M. *Org. Biomol. Chem.* **2012**, *10*, 8822–8834.
14. Yan, M.-C.; Liu, Y.; Lu, W.-X.; Wang, H.; Sha, Y.; Cheng, M.-S. *Carbohydr. Res.* **2008**, *343*, 780–784.
15. Gauthier, C.; Legault, J.; Lavoie, S.; Rondeau, S.; Tremblay, S.; Pichette, A. *Tetrahedron* **2008**, *64*, 7386–7399.
16. Liu, Q.; Wang, P.; Zhang, L.; Guo, T.; Lv, G.; Li, Y. *Carbohydr. Res.* **2009**, *344*, 1276–1281.
17. (a) Bock, K.; Lundt, I.; Pedersen, C. *Tetrahedron Lett.* **1973**, *14*, 1037–1040; (b) Bock, K.; Pedersen, C. *J. Chem. Soc. Perkin Trans. II* **1974**, 293–297; (c) Bock, K.; Pedersen, C. *Acta Chem. Scand.* **1975**, *B29*, 258–264.
18. Fügedi, P. In *The Organic Chemistry of Sugars*; Levy, D. E., Fügedi, P., Eds.; CRC: Boca Raton, FL, 2006, Chapter 4.
19. Cmoch, P.; Korda, A.; Rárová, L.; Oklešťková, J.; Strnad, M.; Gwardiak, K.; Karczewski, R.; Pakulski, Z. *Eur. J. Org. Chem.* **2014**, 4089–4098.