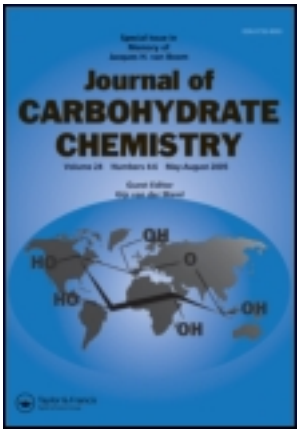

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Studies Towards the Synthesis of the β-D-Xyl-(1→3)-L-ara Disaccharide Moiety of OSW-1 from *Ornithogalum saundersiae*[1]

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CONTENTS

[1]This paper is dedicated to Professor Karsten Krohn on the occasion of his 60th birthday.
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ABSTRACT

The OSW-1 disaccharide having 2-*O*-*p*-methoxybenzoyl-β-D-xylopyranosyl-(1 → 3)-L-arabinopyranoside structure was obtained as the benzylated 4-*O*-acetyl derivative **19**. Also, the 4,2′-di-*O*-acetate **18** was synthesized by a short synthetic approach. The arabinose acceptor **15** was obtained in a three step-one pot sequence from easily available benzyl β-L-arabinopyranoside.

Key Words: Saponin glycosides; Arabinopyranose acceptor; Xylopyranose donor; β−D−Xyl−(1−3)−L−ara disaccharide.

INTRODUCTION

Natural products of plants show a broad spectrum of biological activities with a high potential for medicinal applications. A structurally diversified class of compounds are the saponins, complex glycosides with a steroid, a steroid alkaloid or triterpene aglycon.[1−4]

Several groups perform systematic research on the constitution and biological effects of this interesting class of compounds. Kubo et al. and Mimaki et al. described OSW-1 (**1**) and some of its derivatives with a variation in the benzoyl part and showed their high cytostatic potential concurrent with a low effect on non-transformed cells.[5,6] OSW-1 was tested in vitro ($IC_{50} = 0.25$ nM, leukemia HL-60 cell line) and in vivo (mice P388, enhanced life span by single application of 0.1 mg/kg: 59%). This activity is 10−100 times better than prominent cancer therapeutics presently in use, whereas the toxicity against non-transformed cells is low.

The synthesis of the aglycon part was performed by Guo and Fuchs in 1998[7,8] and the total synthesis of **1** was published by Deng et al.[9] Several other groups work on synthetic projects concerning this highly interesting compound.[10−13] As a part of our research on saponin chemistry,[14−17] our interest focused on alternative pathways and glycosylation studies towards the disaccharide moiety.

RESULTS AND DISCUSSION

Synthesis of D-Xylopyranose Donors

The xylopyranoside part of OSW-1 contains a 2-*O*-*p*-methoxybenzoyl group, whereas related compounds are substituted by other electron-rich benzoyl substituents such as cinnamoyl or 3,4-dimethoxybenzoyl (veratryl). These latter two OSW-1 derivatives are rare: they were isolated more recently and showed an even higher cytostatic activity than OSW-1 itself. Therefore, a variation of the 2-*O*-benzoyl substitution is of particular interest.

The introduction of the modified benzoate can occur on the level of the xylose donor, on the level of the disaccharide, or even on the level of the saponin. In order to obtain β-glycosidic bonds selectively, a neighboring participating group in the 2 position is required.

Scheme 1 shows the synthesis of two donors applying the orthoester methodology, which was introduced and investigated extensively by Kochetkov et al.[18–20] This group demonstrated the advantage of using orthoesters as efficient donors as well as intermediates, which are differentiated in the 2-position. Starting from acetobromoxylopyranose **2**,[21,22] ethanethiol or ethanol was reacted in the presence of *sym*-collidine as a hindered base in acetonitrile under catalysis of tetrabutylammonium bromide to give **3** and **6**,[23] respectively. The remaining acetates in 3- and 4-position were cleaved by the Zemplén method, and the resulting hydroxyl groups were benzylated. This short synthetic sequence with good to satisfactory yields for each step led to thioorthoester **5** as a β-selective donor.

To obtain a 2-*O*-*p*-methoxybenzoylated xylopyranose donor, the ethyl orthoester **8** was not isolated. The orthoester group was cleaved in 95% acetic acid, and the resulting hydroxyl groups were reacetylated by a standard procedure. The 1,2-diacetate **9** was obtained from **7** in 74% yield over three steps. The following thiomethylation at the anomeric position occurred with methylthiotrimethylsilane (TMSSMe) under TMSOTf catalysis and the remaining 2-*O*-acetate was transesterified under Zemplén conditions. The selectively dibenzylated thiomethyl xylopyranoside **10** was obtained as a mixture of anomers in 52% yield.

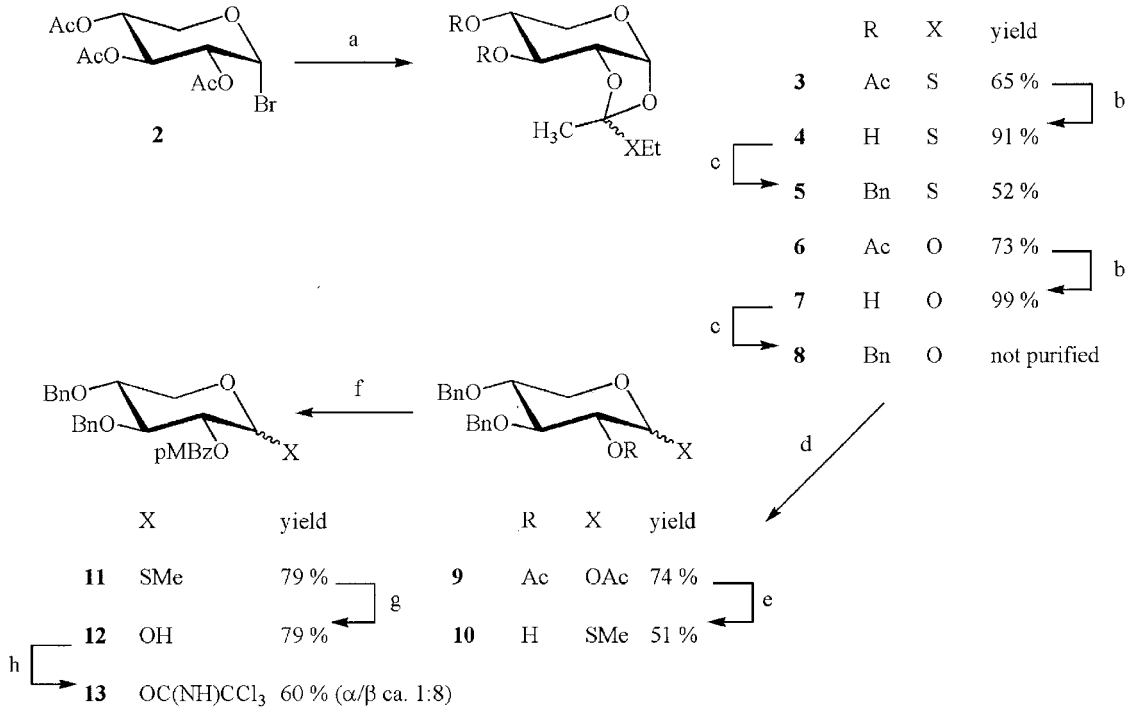
The acylation of the 2-*O*-position with *p*-methoxybenzoyl chloride was performed in pyridine to give donor **11**. TLC monitoring showed a different reactivity of the two anomers, of which the α-anomer appeared to be more reactive. In comparison, it may be noted that Deng et al.[9] obtained a selective 2-*O*-benzoylation of the benzyl α-D-xylopyranoside.

The synthetic flexibility of the thioglycosides allowed a facile preparation of the highly reactive trichloroacetimidate **13** in good yield, which was subjected to the glycosylation of the arabinose acceptor.

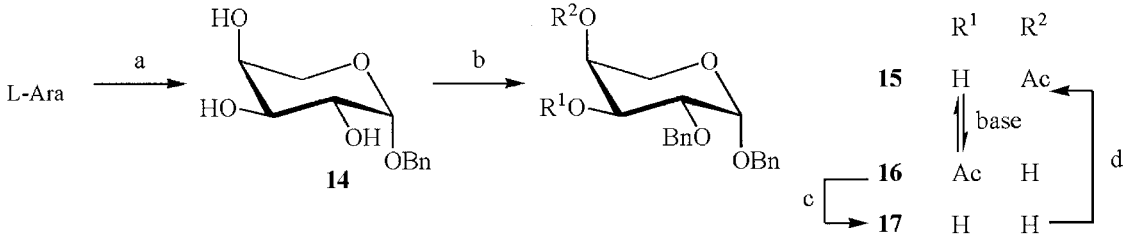
Preparation of Benzyl 4-*O*-Acetyl-2-*O*-benzyl-β-L-arabinopyranose as Acceptor

Fischer glycosylation of L-arabinose with benzyl alcohol led to benzyl β-L-arabinopyranoside **14**[24,25] in high yield. Whereas the β-L-arabinopyranosides are preferentially found as $^4C_1$ conformers (96%), the α-anomers undergo a rapid conformational change with a high amount of the less reactive $^1C_4$ form.[26] In order to obtain an acceptor with a free 3-hydroxyl group for differentiation of the 2-, 3-, and 4-position of the L-arabinopyranoside an easy three step-one pot procedure was chosen (Sch. 2). The 3,4-diol was protected as an orthoacetate, followed by benzylation of the 2 position. The orthoester group was selectively rearranged with 95% acetic acid to give the acceptor arabinopyranose derivative **15** with a free 3-hydroxyl group in high yield.

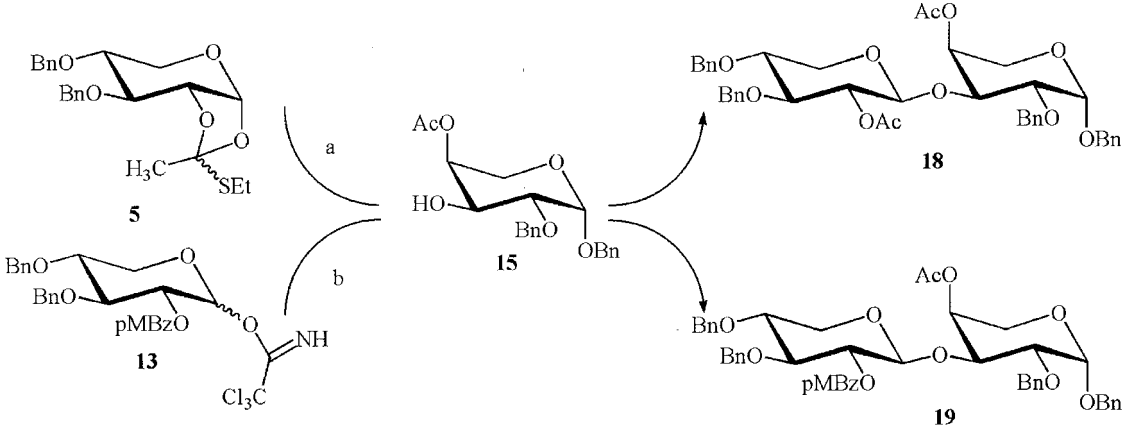
Under mild basic conditions an acetate migration to the 3 position occurred to give **16**, which might offer a pathway to other arabinose acceptors. In such a case, compound **15** could be obtained by deacetylation, to give **17**[27] followed by orthoacetate protection and orthoacetate rearrangement as described earlier (Sch. 2).



Scheme 1. (a) NBu_4Br, acetonitrile, *sym*-collidine, EtOH or EtSH; (b) NaOMe/MeOH; (c) DMF, BnBr, NaH; (d) (1) 95% AcOH, 1 hr, (2) Ac_2O, pyridine, over night; (e) (1) TMSSMe, TMSOTf, CH_2Cl_2, over night, (2) NaOMe/MeOH, 5 hr; (f) *p*-methoxybenzoyl chloride, pyridine, 0°C → RT, 24 hr; (g) NBS, water, acetonitrile, 0°C, 30 min; (h) Cl_3 CN, DBU, CH_2Cl_2.



Scheme 2. (a) BnOH, TosOH, 60°C; (b) (1) $CH_3C(OEt)_3$, TosOH, CH_2Cl_2, (2) BnBr, NaH, DMF, (3) AcOH 95%; c: NaOMe, MeOH; d: (1) $CH_3C(OEt)_3$. TosOH, CH_2Cl_2. (2) AcOH 95%.



Scheme 3. a: NIS, TfOH, CH_2Cl_2/Et_2O 1 : 1, MS 4 Å, argon, 61%; b: $BF_3{}^*OEt_2$ CH_2Cl_2 MS 4 Å, argon, 74%.

Formation of β-D-Xyl-(1 → 3)-L-ara Disaccharides

The xylose donors **13** and **5** were successfully reacted with benzyl 4-*O*-acetyl-2-*O*-benzyl-β-L-arabinopyranoside (**15**) to give the disaccharides **18** and **19** with β-D-xyl-(1→3)-β-L-ara structure. Thiol activation of **5** by NIS with a catalytic amount of TfOH to rearrange intermediate orthoesters[28] was performed in diethylether/dichloromethane, because glycosylations were slower and milder than in pure dichloromethane.[29] The disaccharide **18** with acetyl and benzyl protecting groups was obtained in 61% yield.

An even better yield was obtained with the trichloroacetimidate donor **13** in CH_2Cl_2 through activation with BF_3–etherate. By this reaction the 2′-*O*-*p*-methoxybenzoyl substituted disaccharide **19** resulted in 74% yield (Sch. 3).

CONCLUSIONS

In this work facile syntheses of both xylopyranose donors as well as the arabinopyranose acceptor could be favorably elaborated. Further, optimized glycosylations led to the title compound 2-*O*-*p*-methoxybenzoyl-β-D-xylopyranosyl-(1→3)-L-arabinopyranoside in form of a partially protected derivative.

EXPERIMENTAL

General Procedures

^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100.67 MHz) were recorded with the Bruker AMX-400 (400 MHz ^{1}H, 100.67 MHz ^{13}C) or DRX-500 (500 MHz ^{1}H, 125.77 MHz ^{13}C) spectrometers. Melting points were determined with an Olympus BH-2 polarizing microscope with a Mettler FP 82 heating desk. Optical rotations were determined with a Perkin–Elmer 241 polarimeter. Thin layer chromatography (TLC) was performed on precoated plates of silica gel 60 (GF_{254} by Merck or ALUGRAM SIL G/UV254 by Machery-Nagel), detection occurred by UV-absorption or spraying with 15% ethanolic sulfuric acid and subsequent heating. Column chromatography was performed by the flash technique on silica gel 230–400 mesh (Merck). Elemental analyses were performed in the Microanalytical Laboratory of the Institute of Organic Chemistry of the University of Hamburg.

3,4-Di-*O*-acetyl-1,2-*O*-(1-ethylthioethylidene)-α-D-xylopyranose (3). In a 500 mL round bottom flask acetobromoxylose (**2**, 55.50 g, 164 mmol)[21,22] was dissolved in anhydrous acetonitrile (170 mL) under argon. Then *sym*-collidine (28.0 mL, 25.0 g, 210 mmol) and tetrabutylammonium bromide (5.60 g, 17.0 mmol) were added. The round bottom flask was closed with a septum and an argon filled balloon was attached. Ethanethiol (16.0 mL, 13.0 g, 220 mmol) was added via a syringe and the reaction mixture was stirred for 21 hr at room temperature (RT) until TLC [petroleum ether (PE)/ethyl acetate (EA) 1 : 1, R_f (**2**) = 0.44] showed complete conversion of the starting material. The solvent was removed under reduced pressure and the remainder was coevaporated four times with toluene, dissolved in diethylether and washed seven times with water to remove collidinium

hydrobromide. After flash chromatography with PE/EA 3 : 1 + 1% pyridine **3** (34.30 g, 107 mmol, 65%) was obtained as a mixture of diastereomers (exo/endo ≈ 5 : 1 by ^{1}H NMR). Slightly yellow oily mass; TLC (PE/EA 1 : 1): $R_f = 0.80$ (PE/EA 3 : 1, +1% pyridine): $R_f = 0.34$; (H_2SO_4); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta_{exo} = 5.59$ (d, 1H, H-1, $^3J_{1,2} = 4.7$ Hz), 5.40 (d, 1H, H-1$_{endo}$, $^3J_{1,2} = 3.4$ Hz), 5.25 (dd ∼ t, 1H, H-3, $^3J_{2,3} = 2.8$, $^3J_{3,4} = 2.5$ Hz), 4.90 (m, 1H, H-4), 4.39 (m, 1H, H-2), 3.95 (dd, 1H, H-5a, $^3J_{4,5a} = 6.6$, $^2J_{5a,5b} = 12.0$ Hz), 3.63 (dd, 1H, H-5b, $^3J_{4,5a} = 8.5$, $^2J_{5a,5b} = 12.0$ Hz), 2.63 (q, 2H, SCH_2CH_3, $^3J = 7.5$ Hz), 2.09, 2.12 (2× s, ×3H, CH_3COO), 1.96 (s, 3H, *endo*-$CH_3C[OR]_2SEt_{exo}$), 1.26 (t, 3H, SCH_2CH_3, $^3J = 7.5$ Hz) ppm; ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta_{exo} = 169.92$, 169.21 (2× CH_3COO), 116.59 ($CH_3C[OR]_2SEt_{exo}$), 96.82 (C-1), 90.33 (C-1$_{endo}$), 73.58, 69.18, 67.90 (C-2, C-3, C-4), 58.97 (C-5), 27.66 (*endo*-$CH_3C[OR]_2SEt_{exo}$), 24.78 (SCH_2CH_3), 20.83, 20.75 (CH_3COO), 15.04 (SCH_2CH_3) ppm.

(*S*)-1,2-*O*-(1-Ethylthioethylidene)-α-D-xylopyranose (4). In a 500 mL round bottom flask acetobromoxylose (**2**, 30.91 g, 91.1 mmol),[21,22] was dissolved in anhydrous. acetonitrile (100 mL) under argon. Then *sym*-collidine (15.6 mL, 117.4 mmol) and tetrabutylammonium bromide (2.97 g, 9.1 mmol) were added. The round bottom flask was closed with a septum and an argon filled balloon was attached. Ethanethiol (11.2 mL, 151 mmol) was added via a syringe, and the reaction mixture was stirred overnight at RT until TLC (PE/EA 1 : 1, R_f (**2**) = 0.44) showed complete conversion of the starting material. The solvent was removed under reduced pressure, and the remainder was coevaporated four times with toluene, dissolved in diethylether and washed seven times with water to remove collidinium hydrobromide. The slightly yellow syrup was dissolved in anhydrous. methanol (120 mL), and a 1 M methanolic sodium methanolate solution (3.0 mL, 3 mmol) was added. The reaction mixture was stirred for 10 min at RT until TLC showed complete conversion of the starting material. The solvent was evaporated and the remainder was coevaporated with toluene. After crystallization from toluene (no heating!) at −30 °C compound **4** (19.64 g, 83.1 mmol, 91%) was obtained as pure exo-derivative. Colorless needles; mp: 67.5–68.5°C; $[\alpha]_D^{20} = +46.5$ ($c = 0.4$, MeOH); TLC (PE/EA 1 : 1 + 1% pyridine): $R_f = 0.36$ (H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta_{exo} = 5.55$ (d, 1H, H-1, $^3J_{1,2} = 3.6$ Hz), 4.26 (dd ∼ t, 1H, H-2, $^3J_{1,2} = 3.6$ Hz), 4.03 (m, 1H, H-3), 3.91 (dd, 1H, H-5a, $^3J_{4,5a} = 6.4$, $^2J_{5a,5b} = 14.0$ Hz), 3.72–3.64 (m, 2H, H-4, H-5b), 3.56 (bs, 2H, 3-OH, 4-OH), 2.65 (q, 2H, SCH_2CH_3, $^3J = 7.4$ Hz), 1.95 (s, 3H, $CH_3C(SEt)OR_2$), 1.26 (t, 3H, SCH_2CH_3, $^3J = 7.4$ Hz) ppm; ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta_{exo} = 116.79$ ($CH_3C[OR]_2SEt_{exo}$), 97.28 (C-1), 77.06, 79.85, 68.01 (C-2, C-3, C-4), 63.67 (C-5), 28.88 (*endo*-$CH_3C[OR]_2SEt_{exo}$), 24.78 (SCH_2CH_3), 15.00 (SCH_2CH_3) ppm.

3,4-Di-*O*-benzyl-1,2-*O*-(1-ethylthioethylidene)-α-D-xylopyranose (5). In a 1 L three neck round bottom flask with condenser and dropping funnel compound **4** (11.45 g, 48.45 mmol) was dissolved in anhydrous DMF (100 mL) and sodium hydride (3.48 g, 145 mmol) was cautiously added in small portions (gas development, solution became yellow). The suspension was stirred for 25 min until the gas development decreased. The reaction mixture was cooled in an ice bath and benzyl bromide (12.7 mL, 106.6 mmol) was added slowly via the dropping funnel. Stirring continued for 48 hr at RT until TLC showed complete conversion of the starting material. The mixture was again cooled in an ice bath and water (3 mL) was added slowly and stirring continued for 1/2 hr. The volume of the solvent was reduced under high vacuum, the remainder was dissolved in diethylether and was washed five times with water. After flash chromatography with PE/EA 5 : 1 compound **5** (10.48 g, 25.16 mmol, 52%) was obtained. Slightly yellow syrup; $[\alpha]_D^{20} = -16.2$

($c = 0.5, CHCl_3$); TLC (PE/EA 5 : 1): $R_f = 0.30$ (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta_{exo} = 7.47–7.25$ (m, 10H, 2× $C_6H_5CH_2O$), 5.67 (d, 1H, H-1, $^3J_{1,2} = 5.6$ Hz), 4.85–4.49 (m, 5H, $C_6H_5CH_2O$, H-2), 3.93 (dd ∼ t, 1H, H-3, $^3J_{3,4} = 3.1$ Hz), 3.81–3.59 (m, 3H, H-4, H-5a, H-5b), 2.61 (m, 2H, SCH_2CH_3), 1.98 (s, 1H, *endo*-$CH_3C[OR]_2SEt_{exo}$), 1.36 (t, 3H, SCH_2CH_3, $^3J = 7.4$ Hz); ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta_{exo} = 138.35$, 137.99, 137.6, 128.99–128.08 ($C_6H_5CH_2O$), 116.19 ($CH_3C[OR]_2SEt$), 98.24 (C-1), 78.20, 75.80, 75.07 (C-2, C-3, C-4), 72.47, 72.29 ($C_6H_5CH_2O$), 63.18 (C-5), 28.45 (*endo*-$CH_3C[OR]_2SEt_{exo}$), 25.22 (SCH_2CH_3), 15.63 (SCH_2CH_3).

1,2-Di-*O*-acetyl-3,4-di-*O*-benzyl-D-xylopyranose (9). In a 1 L three neck round bottom flask with condenser and dropping funnel compound **7**[23] (4.0 g, 18.2 mmol) was dissolved in anhydrous DMF (250 mL), and sodium hydride (1.7 g, 70.8 mmol) was cautiously added in small portions (gas development, solution became yellow). The suspension was stirred for 10 min until the gas development decreased. The reaction mixture was cooled in an ice bath and benzyl bromide (6.7 mL, 56.4 mmol) was added slowly via the dropping funnel. Stirring was continued for 1 hr at RT until TLC showed complete conversion of the starting material. The mixture was again cooled in an ice bath, and methanol (5 mL) was added slowly, and stirring was continued for 15 min. The volume of the solvent was reduced under high vacuum, and the remainder was dissolved in ethyl acetate and was washed five times with water. The crude **8** (PE/EA 3 : 1, $R_f = 0.46$) was dissolved in 95% acetic acid (10 mL) and the solution was left for 1 hr at RT. The solution was concentrated and coevaporated three times with toluene. Then the remainder was dissolved in pyridine (20 mL) and acetic acid anhydride (10 mL) was added. Stirring was continued overnight at RT. The reagents were removed under high vacuum and the crude product was purified by flash chromatography with PE/EA 3 : 1 to give **9** (5.57 g, 13.4 mmol, 74%) as a mixture of anomers. Colorless solid; TLC (PE/EA 3 : 1): $R_f = 0.34$, 0.29 (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta_\alpha = 7.37–7.25$ (m, 10H, 2× $C_6H_5CH_2O$), 6.18 (dd, 1H, H-1, $^3J_{1,2} = 1.0$, 3.6 Hz), 4.96 (ddd, 1H, H-2, $^3J_{1,2} = 1.0$, 3.6, $^3J_{2,3} = 9.7$ Hz), 4.88 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.7$ Hz), 4.77–4.73 (m, 2H, $C_6H_5CH_2O$), 4.63 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.2$ Hz), 3.90 (dd ∼ t, 1H, H-3, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 8.7$ Hz), 3.81 (dd, 1H, H-5eq, $^3J_{4,5eq} = 4.3$, $^3J_{5eq,5ax} = 9.4$ Hz), 3.74–3.61 (m, 2H, H-4, H-5a×), 2.13, 1.98 (2× s, 2× 3H, 2× CH_3COO) ppm.

Methyl 3,4-Di-*O*-benzyl-1-thio-β-D-xylopyranoside (10β) and methyl 3,4-di-*O*-benzyl-1-thio-α-D-xylopyranoside (10α). In a 250 mL round bottom flask diacetate **9** (5.57 g, 13.4 mmol) was dissolved in anhydrous dichloromethane (50 mL) under argon. The round bottom flask was closed with a septum and an argon filled balloon was attached. Then methylthiotrimethylsilane (TMSSMe, 2.48 mL, 17.5 mmol) was added, and the reaction mixture was cooled in an ice bath. TMSOTf (2.43 mL, 13.46 mmol) was added and stirring was continued over night with the temperature rising to RT until TLC (PE/EA 3 : 1) showed complete conversion. Then under cooling in an ice bath triethylamine (10 mL) was added, stirred for 10 min, and the solvent was removed under reduced pressure. The residue was coevaporated with toluene three times, dissolved in diethylether and washed twice with water, once with 10% aqueous $NaHCO_3$ solution and once again with water. The organic phase was dried over sodium sulfate, filtered, and evaporated. The crude product was dissolved in methanol (50 mL) and solid sodium methoxide was added until pH 9 was reached. The reaction mixture was stirred for 5 hr until TLC showed complete conversion, neutralized with Amberlite IR 120 (H^+), and the solvent was removed under reduced pressure. After crystallization from Et_2O/PE compound

10β (868 mg, 2.41 mmol, 18%) and a mixture of the anomers **10β** and **10α** (1.600 g, 4.43 mmol, 33%) were obtained. **10β:** Fine needles; mp: 107.8–108.5°C; $[\alpha]_D^{20} = -61.8$ ($c = 0.6$, $CHCl_3$); TLC (PE/EA 3 : 1): $R_f = 0.24$ (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.28–7.20$ (m, 10H, 2× $C_6H_5CH_2O$), 4.77, 4.72 (2× d, 2× 1H, $C_6H_5CH_2O$, $^2J = 11.4$ Hz), 4.62, 4.57 (2× d, 2× 1H, $C_6H_5CH_2O$, $^2J = 11.4$ Hz), 4.37 (d, 1H, H-1, $^3J_{1,2} = 7.1$ Hz), 4.08 (dd, 1H, H-5eq, $^3J_{4,5eq} = 3.7$, $^2J_{5eq,5ax} = 12.0$ Hz), 3.58–3.45 (m, 3H, H-2, H-3, H-4), 3.32 (dd, 1H, H-5ax, $^3J_{4,5ax} = 7.8$, $^2J_{5eq,5ax} = 12.0$ Hz), 2.35 (bs, 1H, 2-OH), 2.10 (s, 3H, SCH_3) ppm; ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 138.44$, 128.66–128.62, 128.11–127.97 (2× $C_6H_5CH_2O$), 87.04 (C-1), 81.61, 76.69, 71.34 (C-2, C-3, C-4), 74.45, 72.91 ($C_6H_5CH_2O$), 65.35 (C-5), 13.03 (SCH_3) ppm.

Anal. calcd for $C_{20}H_{24}O_4S$ (360.46): C 66.64, H 6.71. Found: C 66.30, H 6.51.

10α: TLC (PE/EA 3 : 1): $R_f = 0.19$ (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.28–7.20$ (m, 10H, 2× $C_6H_5CH_2O$), 4.95 (d, 1H, H-1, $^3J_{1,2} = 3.6$ Hz), 4.72–4.58 (m, 4H, 2× $C_6H_5CH_2O$), 4.04 (dd, 1H, H-5eq, $^3J_{4,5eq} = 3.6$, $^2J_{5eq,5ax} = 12.2$ Hz), 3.88–3.48 (m, 4H, H-2, H-3, H-4, H-5ax), 3.18 (m, 1H, 2-OH), 2.21 (s, 3H, SCH_3) ppm.

Methyl 3,4-Di-*O*-benzyl-2-*O*-*p*-methoxybenzoyl-1-thio-α-D-xylopyranoside (11α) and methyl 3,4-di-*O*-benzyl-2-*O*-*p*-methoxybenzoyl-1-thio-β-D-xylopyranoside (11β). Compound **10** (210 mg, 0.58 mmol) was dissolved in pyridine (2 mL). The solution was cooled in an ice bath and *p*-methoxybenzoyl chloride (0.16 mL, 200 mg, 1.17 mmol) was added in portions and stirred for 14 hr at RT. Then another portion of *p*-methoxybenzoyl chloride (0.08 mL, 100 mg, 0.59 mmol) was added, and stirring continued for another 24 hr at RT. The reaction was stopped by cooling in an ice bath, addition of methanol (1 mL) and stirring for 1 hr. The crude product was purified by flash chromatography with PE/EA 3 : 1 to give the α-anomer **11α** (45 mg, 0.09 mmol, 16%), the β-anomer **11β** (99 mg, 0.20 mmol, 36%) and a mixture of the anomers (83 mg, 0.17 mmol, 29%); total yield of **11**: 227 mg (0.46 mmol, 79%). **11α**: colorless solid; mp: 99.6–100.3°C; $[\alpha]_D^{20} = -18.9$ ($c = 0.4$, $CHCl_3$); TLC (PE/EA 3 : 1): $R_f = 0.36$ (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (ddd, 2H, β-$CH_3OC_6H_4COO$, $^3J = 9.2$, $^4J = 2.0$ Hz), 7.34–7.18 (m, 10H, 2× $C_6H_5CH_2O$), 6.91 (ddd, 2H, γ-$CH_3OC_6H_4COO$, $^3J = 9.2$, $^4J = 2.0$ Hz), 5.46 (d, 1H, H-1, $^3J_{1,2} = 5.6$ Hz), 5.21 (dd, 1H, H-2, $^3J_{1,2} = 5.1$, $^3J_{2,3} = 9.2$ Hz), 4.82 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.2$ Hz), 4.78 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.2$ Hz), 4.74 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.7$ Hz), 4.64 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.7$ Hz), 4.03–3.93 (m, 2H, H-3, H-5a), 3.86 (s, 3H, $CH_3OC_6H_4COO$), 3.77–3.64 (m, 2H, H-4, H-5b), 2.03 (s, 3H, SCH_3) ppm; ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta = 165.45$ ($CH_3OC_6H_4COO$), 163.79 (δ-$CH_3OC_6H_4COO$), 138.30 (*quart*-$C_6H_5CH_2O$), 132.12 (β-$CH_3OC_6H_4COO$), 128.59, 128.45, 128.06, 127.97, 127.93, 127.78 (2× $C_6H_5CH_2O$), 122.16 (α-$CH_3OC_6H_4COO$), 113.89 (γ-$CH_3OC_6H_4COO$), 83.99 (C-1), 79.19 (C-3), 77.79 (C-4), 75.34, 73.47 (2× $C_6H_5CH_2O$), 73.05 (C-2), 60.92 (C-5), 55.61 ($CH_3OC_6H_4COO$), 12.92 (SCH_3) ppm. **11β**: Colorless needles; mp: 177.2–178.0°C; $[\alpha]_D^{20} = +40.7$ (c = 0.8, $CHCl_3$); TLC (PE/EA 3:1): $R_f = 0.27$ (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (ddd, 2H, β-$CH_3OC_6H_4COO$, $^3J = 8.7$, $^4J = 3.1$, 2.0 Hz), 7.34–7.13 (m, 10H, 2× $C_6H_5CH_2O$), 6.91 (ddd, 2H, γ-$CH_3OC_6H_4$-COO, $^3J = 9.2$, $^4J = 2.5$, 2.0 Hz), 5.23 (dd ∼ t, 1H, H-2, $^3J_{1,2} = 8.7$, $^3J_{2,3} = 8.6$ Hz), 4.77 (d, 1H, $C_6H_5CH_2O$, ^{2}J = 11.2 Hz), 4.72 (d, 1H, $C_6H_5CH_2O$, $^2J = 8.6$ Hz), 4.69 (d, 1H, $C_6H_5CH_2O$, $^2J = 8.1$ Hz), 4.63 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.7$ Hz), 4.44 (d, 1H, H-1, $^3J_{1,2} = 8.7$ Hz), 4.14 (dd, 1H, H-5eq, $^3J_{4,5eq} = 4.6$, $^2J_{5eq,5ax} = 11.7$ Hz), 3.86 (s, 3H, $CH_3OC_6H_4COO$), 3.78–3.67 (m, 2H, H-3, H-4), 3.38 (dd, 1H, H-5ax,

$^3J_{4,5ax} = 9.2$, $^2J_{5eq,5ax} = 11.7$ Hz), 2.14 (s, 3H, SCH_3) ppm; ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta = 165.03$ ($CH_3OC_6H_4COO$), 163.71 (δ-$CH_3OC_6H_4COO$), 138.12 (*quart*-$C_6H_5CH_2O$), 132.11 (β-$CH_3OC_6H_4COO$), 128.63, 128.38, 128.14, 128.06, 128.00, 127.75 (2× $C_6H_5CH_2O$), 122.35 (α-$CH_3OC_6H_4COO$), 113.81 (γ-$CH_3OC_6H_4COO$), 84.05 (C-1), 81.96, 77.52 (C-3, C-4), 74.88, 73.38 (2× $C_6H_5CH_2O$) 70.96 (C-2), 67.34 (C-5), 55.61 ($CH_3OC_6H_4COO$), 11.90 (SCH_3) ppm.

3,4-Di-*O*-benzyl-2-*O*-*p*-methoxybenzoyl-D-xylopyranose (12). Thioglycoside **11** (689 mg, 1.39 mmol) was dissolved in acetonitrile (15 mL) and water (0.2 mL, 11.1 mmol) was added. The mixture was cooled in an ice bath, and NBS (545 mg, 3.06 mmol) was added in portions and the solution became yellow–brown. The reaction was monitored by TLC with PE/EA 1 : 1 and was complete after 30 min. A tenfold excess of diethylether was added and the solution was washed with saturated $NaHCO_3$ and H_2O, dried over sodium sulfate and evaporated to dryness. The crude product was crystallized from isopropanol to give **12** (510 mg, 1.10 mmol, 79%, $\alpha/\beta \approx 5:4$ by ^{1}H NMR). Colorless solid; TLC (PE/EA 1 : 1): $R_f = 0.50–0.36$; (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.03–7.94$ (m, 4H, 2× β-$CH_3OC_6H_4COO$), 7.34–7.18 (m, 20H, 4× $C_6H_5CH_2O$), 6.93–6.87 (m, 4H, 2× γ-$CH_3OC_6H_4COO$), 5.42 (d, 1H, H-1α, $^3J_{1,2} = 3.6$ Hz), 5.03 (dd, 1H, H-2α, $^3J_{1,2} = 3.6$, $^3J_{2,3} = 9.2$ Hz), 4.99 (dd ∼ t, 1H, H-2β, $^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.2$ Hz), 4.87–4.60 (m, 9H, H-1β, 4× $C_6H_5CH_2O$), 4.14, (dd ∼ t, 1H, H-3α, $^3J_{2,3} = 8.1$, $^3J_{3,4} = 9.2$ Hz), 4.07 (dd, 1H, H-5eqβ, $^3J_{4,5eq} = 5.1$, $^2J_{5eq,5ax} = 12.2$ Hz), 3.92–3.65 (2×m, 2H, 5H, 2× H-3, 2× H-4, 3× H-5), 3.86 (s, 3H, $CH_3OC_6H_4COO$), 3.41 (dd, 1H, H-5axβ, $^3J_{4,5ax} = 9.2$, $^2J_{5eq,5ax} = 12.2$ Hz), 2.45 (m, 2H, 2 × 1-OH) ppm; ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta = 166.63$, 165.67 (2× $CH_3OC_6H_4COO$), 163.80, 163.63 (2× δ-$CH_3OC_6H_4COO$), 138.25, 138.13 (2× *quart*-$C_6H_5CH_2O$), 132.07, 131.94 (2× β-$CH_3OC_6H_4COO$), 128.49–127.63 (4× $C_6H_5CH_2O$), 122.02, 121.69 (2× α-$CH_3OC_6H_4COO$), 113.72 (2× γ-$CH_3OC_6H_4COO$), 96.06, 90.90 (2× C-1), 79.74, 78.20, 77.58, 77.06, 74.60, 73.26 (je 2× C-2, C-3, C-4), 75.16, 74.83, 73.28, 73.14 (2× $C_6H_5CH_2O$), 63.16, 60.48 (C-5), 55.48, 55.47 (2× $CH_3OC_6H_4COO$) ppm.

***O*-(3,4-Di-*O*-benzyl-2-*O*-*p*-methoxybenzoyl-D-xylopyranosyl)-trichloroacetimidate (13).** In a 100 mL round bottom flask compound **12** (516 mg, 1.11 mmol) was co-evaporated three times with toluene and residual solvent was removed in vacuo. Then the remainder was dissolved under argon atmosphere in anhydrous CH_2Cl_2 (30 mL). The round bottom flask was closed with a septum and an argon filled balloon was attached. Trichloroacetonitrile (1.11 mL, 11.10 mmol) and DBU (16 μL, 0.11 mmol) were added via a syringe. The reaction was monitored by TLC with PE/EA 1 : 1. Because there was no reaction after stirring for 20 hr, another ten drops of DBU were added and stirring continued for 8.5 hr. The product was purified by flash chromatography with PE/EA 4 : 1 + 0.1% triethylamine to give **13** (411 mg, 0.67 mmol, $\alpha/\beta \approx 1:6$ by ^{1}H NMR, 60%). Syrup; TLC (PE/EA 1 : 1): $R_f = 0.71$ (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.60$ (s, 1H, NHβ), 8.50 (s, 1H, NHα), 7.97–7.90 (m, 2× 2H, 2× β-$CH_3OC_6H_4COO$), 7.34–7.18 (m, 2× 10H, 4× $C_6H_5CH_2O$), 6.88, 6.85 (2× m, 2× 2H, 2× γ-$CH_3OC_6H_4COO$), 6.48 (d, 1H, H-1α, $^3J_{1,2} = 3.6$ Hz), 6.03 (d, 1H, H-1β, $^3J_{1,2} = 5.1$ Hz), 5.43 (dd ∼ t, 1H, H-2β, $^3J_{1,2} = 5.6$, $^3J_{2,3} = 6.6$ Hz), 5.26 (dd, 1H, H-2α, $^3J_{1,2} = 3.6$, $^3J_{2,3} = 10.2$ Hz), 4.90–4.56 (m, 2× 4H, 4× $C_6H_5CH_2O$), 4.19 (dd, 1H, H-5aβ, $^3J_{4,5a} = 3.6$, $^2J_{5a,5b} = 11.7$ Hz), 3.92–3.72 (m, 5H, 6H, 2× H-3, 2×H-4, 2× $CH_3OC_6H_4COO$), 3.69 (dd, 1H, H-5bβ, $^3J_{4,5b} = 6.6$, $^2J_{5a,5b} = 11.7$ Hz) ppm; ^{13}C NMR (100.62 MHz, $CDCl_3$):

$\delta = 164.97$ ($CH_3OC_6H_4COO$), 163.73 (δ-$CH_3OC_6H_4COO$), 161.36 ($CCl_3C(OR)=NH$), 137.91 (2× *quart*-$C_6H_5CH_2O$), 132.10 (β-$CH_3OC_6H_4COO$), 128.60–127.79 (2× $C_6H_5CH_2O$), 122.06 (α-$CH_3OC_6H_4COO$), 113.77 (2× γ-$CH_3OC_6H_4COO$), 96.46 (C-1β), 90.90 (C-1α), 77.56, 75.72, 69.60 (C-2, C-3, C-4), 73.73, 72.17 (2× $C_6H_5CH_2O$), 63.16 (C-5), 55.56 ($CH_3OC_6H_4COO$) ppm.

Benzyl 4-*O*-acetyl-2-*O*-benzyl-β-L-arabinopyranoside (15), benzyl 3-*O*-acetyl-2-*O*-benzyl-β-L-arabinopyranoside (16), and benzyl 2-*O*-benzyl-β-L-arabinopyranoside (17). In a 500 mL round bottom flask benzyl β-L-arabinopyranoside (**14**)[24,25] (10.00 g, 41.62 mmol), triethyl orthoacetate (19.0 mL, 104 mmol), and *p*-toluene sulfonic acid (370 mg, 1.95 mmol) were suspended in anhydrous dichloromethane (250 mL) and stirred at RT for 1 hr, whereby the reaction mixture clarified. When TLC [PE/EA 1 : 1, R_f (**14**) = 0, R_f (3,4-orthoacetate) = 0.52] showed complete conversion of the starting material, sodium hydride (100 mg) was added, the volatile reagents and the solvent were evaporated. The remainder was coevaporated with toluene four times. The yellow syrup was dissolved in DMF (100 mL), and sodium hydride (1.50 g, 62.5 mmol) was added in small portions (gas development!). The suspension was stirred for 2.5 hr at RT. Then benzyl bromide (5.5 mL, 45.8 mmol) was added dropwise at RT, and stirring was continued overnight until TLC [R_f (2-*O*-benzyl-3,4-orthoacetate) = 0.75] showed complete conversion of the starting material. The mixture was cooled in an ice bath, water (3 mL) was added slowly, and stirring was continued for 1/2 hr. The volume of the solvent was reduced under high vacuum, the remainder was dissolved in diethylether and was washed five times with water. The solvent was removed, the crude product was dissolved in glacial acetic acid (15 mL) and water (1 mL). Stirring continued over night until TLC showed complete and selective conversion of the starting material to **15**. After evaporation of the volatile reagents under high vacuum slightly brown crystals of **15** were obtained. During the crystallization from diethylether, a partial migration of the acetate function occurred supposedly caused by acid impurities in the solvent. After flash chromatography with PE/EA 2 : 1 → 1 : 1 compound **15** (3.696 g, 9.92 mmol, 24%) and **16** with trace impurities of **17** (2.371 g, 6.37 mmol, 15%) and **17**[27] (2.185 g, 6.61 mmol, 16%) as well as a mixture of **15** and **16** (532 mg, 1.43 mmol, 3%) were obtained. All impure fractions were deacetylated by the Zemplén method to give **17**. Compound **15**: colorless solid; mp: 74.5–77.2°C; $[\alpha]_D^{20} = +180.3$ ($c = 0.8$, $CHCl_3$); TLC (PE/EA 1 : 1): $R_f = 0.31$ (UV, H_2SO_4); ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.41–7.23$ (m, 10H, 2× $C_6H_5CH_2O$), 5.20 (dd ∼ m, 1H, H-4), 4.95 (d, 1H, H-1, $^3J_{1,2} = 3.6$ Hz), 4.72 (d, 1H, $C_6H_5CH_2O$, $^2J = 12.2$ Hz), 4.59 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.7$ Hz), 4.53 (d, 1H, $C_6H_5CH_2O$, $^2J = 11.7$ Hz), 4.48 (d, 1H, $C_6H_5CH_2O$, $^2J = 12.2$ Hz), 4.21 (dd, 1H, H-3, $^3J_{2,3} = 9.9$, $^3J_{3,4} = 3.6$ Hz), 3.84 (dd, 1H, H-5a, $^3J_{4,5a} = 0$, $^2J_{5a,5b} = 13.0$ Hz), 3.75 (dd, 1H, H-2, $^3J_{1,2} = 3.3$, $^3J_{2,3} = 9.9$ Hz), 3.66 (dd, 1H, H-5b, $^3J_{4,5b} = 1.8$, $^2J_{5a,5b} = 13.0$ Hz), 2.24 (bs, 1H, 3-OH), 2.14 (s, 3H, CH_3COO); ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta = 170.88$ (CH_3COO), 137.86, 137.08, 128.49–127.93 (2× $C_6H_5CH_2O$), 95.56 (C-1), 76.88 (C-2), 72.47 ($C_6H_5CH_2O$), 71.34 (C-4), 69.33 ($C_6H_5CH_2O$), 67.16 (C-3), 60.78 (C-5), 21.16 (CH_3COO).

Anal. calcd for $C_{21}H_{24}O_6$ (372.41): C 67.73, H 6.50. Found: C 67.46, H 6.51.

Compound **16**: TLC (PE/EA 1 : 1): $R_f = 0.21$ (UV, H_2SO_4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.38–7.18$ (m, 10H, 2× $C_6H_5CH_2O$), 5.29 (dd, 1H, H-3, $^3J_{2,3} = 10.5$, $^3J_{3,4} = 3.2$ Hz), 4.87 (d, 1H, H-1, $^3J_{1,2} = 3.6$ Hz), 4.75–4.45 (m, 4H, 2× $C_6H_5CH_2O$), 4.08 (m, 1H, H-4), 3.92–3.83 (m, 2H, H-2, H-5a), 3.59 (dd, 1H, H-5b, $^3J_{4,5b} = 2.3$, $^2J_{5a,5b} = 11.8$ Hz), 2.27 (bs, 1H, 4-OH), 2.06 (s, 3H, CH_3COO); ^{13}C NMR

(100.67 MHz, $CDCl_3$): $\delta = 170.21$ (CH_3COO), 138.24, 137.98, 128.50–127.93 ($2\times C_6H_5CH_2O$), 96.42 (C-1), 73.75 (C-2), 72.80 ($C_6H_5CH_2O$), 71.99 (C-3), 69.27 ($C_6H_5CH_2O$), 68.25 (C-3), 62.42 (C-5), 21.33 (CH_3COO) ppm.

Benzyl 2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-benzyl-β-L-arabinopyranoside (18). Donor **5** (1.380 g, 3.31 mmol) and acceptor **15** (1.357 g, 3.64 mmol) were coevaporated twice in a 100 mL round bottom flask and dissolved in freshly anhydrous diethylether (20 mL) and freshly anhydrous dichloromethane (20 mL). Then freshly activated MS 4 Å was added and the mixture was stirred under argon for 1 hr at RT. Then *N*-iodosuccinimide (745 mg, 3.31 mmol) was added by which the colorless solution became violet, and stirring was continued for 5.5 hr. For orthoester rearrangement triflic acid (29 μL, 0.33 mmol) was added, and the reaction was stirred for another 16 hr at RT. The reaction was monitored by TLC with PE/EA 2 : 1 [R_f (**5**) = 0.67, R_f (**15**) = 0.13]. The molecular sieves were removed by filtration over celite, and the solid was washed with dichloromethane (200 mL). The red filtrate was decolorized with 10% aqueous sodium disulfite solution, washed once with saturated $NaHCO_3$, and dried over sodium sulfate. The solvent was removed, and the crude product was purified by flash chromatography to give **18** (1.463 g, 2.01 mmol, 61%). Colorless solid; mp: 67.2–68.6°C; $[\alpha]_D^{20} = +64.2$ ($c = 0.6$, $CHCl_3$); TLC (PE/EA 2 : 1): $R_f = 0.28$ (UV, H_2SO_4); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.39–7.23$ (m, 20H, $4\times C_6H_5CH_2O$), 5.22 (dd, 1H, H-4, $^3J_{3,4} = 3.2$, $^3J_{4,5} = 1.6$, 0 Hz), 4.95 (dd, 1H, H-2′, $^3J_{1',2'} = 7.1$, $^3J_{2',3'} = 8.7$ Hz), 4.80 (d, 1H, $C_6H_5CH_2O$-3′a, $^2J = 11.4$ Hz), 4.79 (d, 1H, H-1, $^3J_{1,2} = 4.1$ Hz), 4.69, 4.69 (2× d, 2× 1H, H-1′, $^3J_{1',2'} = 6.9$, $C_6H_5CH_2O$-1a, $^2J = 12.3$ Hz), 4.67–4.58 (m, 4H, $4\times C_6H_5CH_2O$), 4.50 (d, 1H, $C_6H_5CH_2O$-1b, $^2J = 12.3$ Hz), 4.41 (d, 1H, $C_6H_5CH_2O$-2b, $^2J = 12.0$ Hz), 4.12 (dd, 1H, H-3, $^3J_{2,3} = 10.1$, $^3J_{3,4} = 3.8$ Hz), 3.95 (dd, 1H, H-5′ eq, $^3J_{4',5'\ eq} = 5.0$, $^2J_{5'eq,5'ax} = 12.0$ Hz), 3.84 (dd, 1H, H-5eq, $^3J_{4,5eq} = 0$, $^2J_{5a,5b} = 12.6$ Hz), 3.75 (dd, 1H, H-2, $^3J_{1,2} = 3.5$, $^3J_{2,3} = 10.1$ Hz), 3.66 (ddd, 1H, H-4′, $^3J_{3',4'} = 8.2$, $^3J_{4',5'ax} = 8.5$, $^3J_{4',5'eq} = 5.1$ Hz), 3.61 (dd, 1H, H-5ax, $^3J_{4,5ax} = 1.7$, $^2J_{5ax,5eq} = 13.1$ Hz), 3.55 (dd ∼ t, 1H, H-3′, $^3J_{2',3'} = 8.8$, $^3J_{3',4'} = 8.2$ Hz), 3.26 (dd, 1H, H-5′ax, $^3J_{4',5'ax} = 8.8$, $^2J_{5'ax,5'eq} = 11.7$ Hz), 2.15 (s, 3H, 4-CH_3COO), 1.90 (s, 3H, 2′-CH_3COO); ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta = 171.03$ (4-CH_3COO), 169.85 (2′-CH_3COO), 138.82–137.40, 128.90–128.01 ($4\times C_6H_5CH_2O$), 102.03 (C-1′), 96.09 (C-1), 80.70 (C-3′), 77.56 (C-4′), 75.88 (C-2), 74.46 (C-3), 74.34 ($C_6H_5CH_2O$-3′), 73.19 ($C_6H_5CH_2O$-2), 72.98 ($C_6H_5CH_2O$-4′), 72.39 (C-2′), 71.61 (C-4), 69.17 ($C_6H_5CH_2O$-1), 63.13 (C-5′), 60.73 (C-5), 21.08, 20.91 ($2\times CH_3COO$).

Anal. calcd for $C_{42}H_{46}O_{11}$ (726.80): C 69.41, H 6.38. Found: C 68.94, H 6.40.

Benzyl 2-*O*-*p*-methoxybenzoyl-3,4-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-benzyl-β-L-arabinopyranoside (19). Donor **13** (347 mg, 0.57 mmol) and acceptor **15** (254 mg, 0.68 mmol) were dissolved under argon in freshly anhydrous dichloromethane (40 mL), and MS 4 Å (one spatula) was added. The round bottom flask was closed with a septum, an argon filled balloon was attached, and the mixture was stirred for 1 hr at RT. Boron trifluoride–etherate (7 μL) was added via a syringe and the reaction mixture was stirred for 2.5 hr at RT. To stop the reaction, one drop of triethylamine was added, and stirring was continued for 5 min. The molecular sieves were removed by filtration over celite, and the solvent was evaporated. The crude product was purified by flash chromatography with PE/EA 2 : 1 to give **19** (345 mg, 0.42 mmol, 74%). Colorless solid; mp: 116–117.5°C; $[\alpha]_D^{20} = +63.0$ ($c = 0.3$, $CHCl_3$); TLC (PE/EA 1 : 1): $R_f = 0.60$ (UV, H_2SO_4); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.91$ (d, 2H, β-$CH_3OC_6H_4COO$, $^3J = 8.8$ Hz), 7.35–7.27 (m, 10H, $C_6H_5CH_2O$), 7.19–7.12 (m, 8H,

$C_6H_5CH_2O$), 6.96 (d, 2H, $C_6H_5CH_2O$), 6.78 (d, 2H, γ-$CH_3OC_6H_4COO$, $^3J = 8.8$ Hz), 5.25 (ddd ∼ m, 1H, H-4), 5.22 (dd ∼ t, 1H, H-2′, $^3J_{1',2'} = 7.3$, $^3J_{2',3'} = 7.9$ Hz), 4.87 (d, 1H, H-1′, $^3J_{1',2'} = 6.9$ Hz), 4.74 (d, 1H, $C_6H_5CH_2O$-3′a, $^2J = 11.4$ Hz), 4.69–4.59 (m, 5H, H-1, $C_6H_5CH_2O$-1a, -3′b, -4′a,b), 4.44 (d, 1H, $C_6H_5CH_2O$-1b, $^2J = 12.3$ Hz), 4.41 (d, 1H, $C_6H_5CH_2O$-2a, $^2J = 12.3$ Hz), 4.19 (d, 1H, $C_6H_5CH_2O$-2b, $^2J = 12.6$ Hz), 4.14 (dd, 1H, H-3, $^3J_{2,3} = 9.8$, $^3J_{3,4} = 3.5$ Hz), 4.01 (dd, 1H, H-5′eq, $^3J_{4',5'eq} = 4.1$, $^2J_{5'eq,5'ax} = 12.0$ Hz),), 3.84 (dd ∼ d, 1H, H-5a, $^3J_{4,5a} = 0$, $^2J_{5a,5b} = 12.9$ Hz), 3.80 (s, 3H, $CH_3OC_6H_4COO$), 3.76–3.67 (m, 2H, H-3′, H-4′), 3.63 (dd, 1H, H-2, $^3J_{1,2} = 3.5$, $^3J_{2,3} = 10.1$ Hz), 3.59 (dd ∼ d, 1H, H-5b, $^3J_{4,5b} = 0$, $^2J_{5a,5b} = 12.9$ Hz), 3.35 (dd, 1H, H-5′ax, $^3J_{4',5'ax} = 8.4$, $^2J_{5'eq,5'ax} = 11.8$ Hz), 2.08 (s, 3H, CH_3COO); ^{13}C NMR (100.67 MHz, $CDCl_3$): $\delta = 170.76$ (CH_3COO), 164.87 ($CH_3OC_6H_4COO$), 163.42 (δ-$CH_3OC_6H_4COO$), 138.41, 138.06, 137.99, 136.94 (*quart*-$C_6H_5CH_2O$), 131.82 (β-$CH_3OC_6H_4COO$), 128.48–127.30 (4× $C_6H_5CH_2O$), 122.31 (α-$CH_3OC_6H_4COO$), 113.61 (γ-$CH_3OC_6H_4COO$), 102.21 (C-1′), 96.29 (C-1), 80.39 (C-3′), 77.53 (C-4′), 75.82 (C-2), 74.36 (C-3), 74.28 ($C_6H_5CH_2O$-3′), 73.28 ($C_6H_5CH_2O$-2), 72.97 ($C_6H_5CH_2O$-4′), 72.52 (C-2′), 71.72 (C-4), 69.14 ($C_6H_5CH_2O$-1), 63.07 (C-5′), 60.72 (C-5), 55.40 ($CH_3OC_6H_4COO$), 21.09 (CH_3COO).

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