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Note

An efficient and practical synthesis of β-(1→3)-linked xylooligosaccharides

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Dedicated to Professor Derek Horton on the occasion of his 70th birthday

Abstract

A facile and practical method was developed for the synthesis of β-(1→3)-linked xylooligosaccharides. Dibezoylation of allyl α-D-xylopyranoside (**1**) afforded 2,4-dibenzoate **6** as the major product. Chloroacetylation of **6**, followed by deallylation and trichloroacetimidation, gave a 1:3 α/β imidate (**10** and **11**) mixture. Coupling of the imidate mixture with **6** gave a disaccharide **13**, whose dechloroacetylation afforded the disaccharide acceptor **16**. Condensation of perbenzoylated xylosyl α/β imidate (**7** and **8**) mixture with **6** gave the disaccharide **12**. Deallylation of **12**, followed by trichloroacetimidation, furnished the disaccharide donor as a 1:1 α/β mixture. Coupling of the disaccharide donor mixture with the disaccharide acceptor **16** yielded the tetrasaccharide **17**. Reiteration of deallylation and trichloroacetimidation transformed **17** to the tetrasaccharide donor mixture. Condensation of the tetrasaccharide donor mixture with the acceptor **16** gave the hexasaccharide **21**. Debenzoylation with saturated ammonia–methanol afforded β-(1→3)-linked allyl xylotetraoside and xylohexaoside. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Oligosaccharide; Xylose; Regioselective synthesis

β-(1→3)-Linked xylan occurs in algae cell-wall polysaccharides. Treatment of β-(1→3)-linked xylan from *Caulerpa racemesa laete-virens* with β-(1→3)-xylanase of *Vibrio* sp. AX-4 gave β-(1→3)-linked xylooligosaccahrides with average DP ≤ 5. These xyloolgosaccharides show in vitro 70% inhibition of DNA synthesis of human leukemia HL 60 cells, and thus have potential use as cancer cell apoptosis inducers.[1] For investigation of structure–bioactivity relationships among xylooligosaccharides, we report herein a concise and efficient synthesis of β-(1→3)-linked xylooligosaccahrides.

β-(1→4)-Linked xylans as the main components of arabinoxylans widely occur in the cell walls of grass and legume forage plants, and the synthesis of β-(1→4)-linked xylooligosaccharides have been reported.[2] However, to the best of our knowledge, there have rarely been reports regarding the syntheses of β-(1→3)-linked xylooligosaccharides.[3] Perhaps, the difficulty for regioselective protection[4] of xylose limits the use of xylose in the glycosylation. An α-linked trisaccharide, α-D-Xyl*p*-(1→3)-α-D-Xyl*p*-(1→3)-D-Glcp, and its serine conjugate have been synthesized with benzylated xylose derivatives.[5] We present herein the syntheses of β-(1→3)-linked xylopyranose di-, tetra-, and hexamers using peracylated trichloroacetimidates[6] as the donors and corresponding acylated xylose derivatives as the acceptors.

As outlined in Scheme 1, allyl α-D-xylopyranoside (**1**) was dibenzoylated to afford a mixture of 2,3,4-tribenzoate **4** (25%), 2,3-dibenzoate **5** (20%), and 2,4-dibenzoate **6** (45%), and unidentified byproducts (10%). Compounds **4**, **5**, and **6** were identified by their ^{1}H NMR spectra, which gave a multiplet for H-4, and a triplet with $J_{2,3} = J_{3,4}$ 9.8 Hz for H-3, and a doublet of doublets with $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 9.8 Hz for H-2, respectively. The 2,3-dibenzoate **5** showed H-2 and H-3

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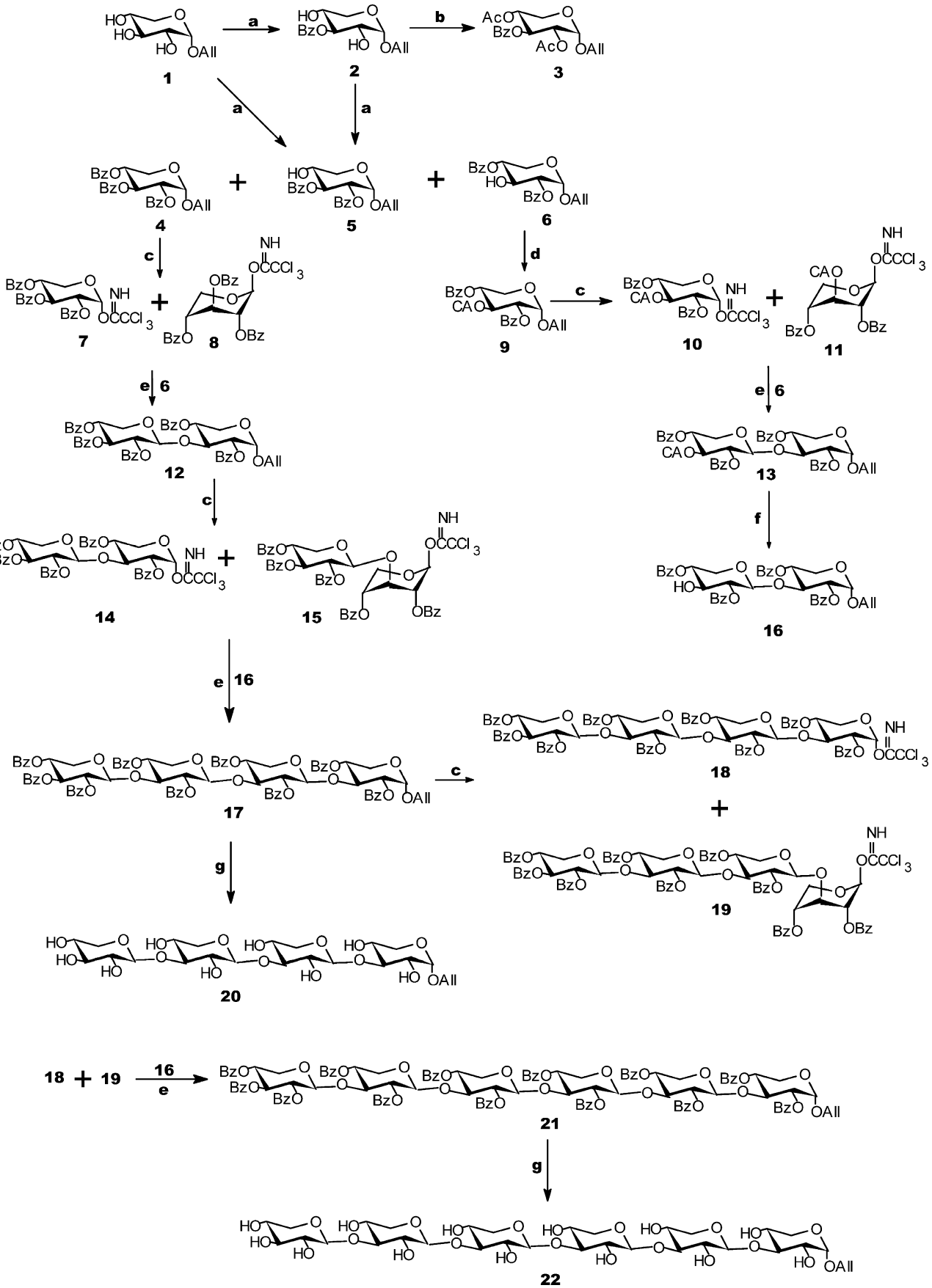

Scheme 1. Reagents and conditions: (a) PhCOCl, Pyr, rt. (b) Ac_2O, Pyr, rt. (c) (i) $PdCl_2$, CH_3OH, 40 °C; (ii) CCl_3CN, CH_2Cl_2, K_2CO_3, rt. (d) $ClCH_2COCl$, Pyr, rt. (e) TMSOTf, CH_2Cl_2, −25 °C to rt. (f) Thiourea, EtOH, CH_2Cl_2, reflux. (g) NH_3–CH_3OH, rt.

moved downfield, while the 2,4-dibenzoate **6** showed H-2 and H-4 moved downfield. An alternative preparation of **4**, **5**, and **6** was also successful. Thus, monobenzoylation of **1** with benzoyl chloride in pyridine afforded allyl 3-*O*-benzoyl-α-D-xylopyranoside (**2**) in high yield (75%). Subsequent monobenzoylation of **2** gave **4**, **5**, and **6** in 24, 19, and 45%, respectively, together with 12% unidentified byproducts. It was noted that during bezoylation of **2**, benzoyl group migration occurred as the 2,4-dibenzoate **6** was the major product. With the tribenzoate **4** and the 2,4-dibenzoate **6** in hand, the β-(1→3)-linked xylooligosaccharides were readily constructed, since the former was easily transformed to a donor by activation of C-1, and the latter was an acceptor for the disaccharide synthesis and used to prepare the disaccharide acceptor. Therefore, deallylation of **4** with $PdCl_2$ in methanol,[7] followed by trichloroacetimidation with Cl_3CCN, gave an inseparable mixture of 2,3,4-tri-*O*-benzoyl-α- (**7**) and -β-D-xylopyranosyl trichloroacetimidate (**8**) in 3:17 ratio. It was noted that the ^1H NMR spectrum of **7** indicated a $^4C_1$ conformation as judged from $J_{1,2}$ 3.6 Hz, $J_{2,3} = J_{3,4}$ 10 Hz, while the ^1H NMR spectrum of **8** indicated a $^1C_4$ conformation, i.e., 'tetra axial' substitution form, as judged from $J_{1,2}$ 2.6 Hz, $J_{2,3} = J_{3,4}$ 4.2 Hz. The mixture of **7** and **8** was coupled with the acceptor **6** in the presence of TMSOTf to afford a unique disaccharide **12** in high yield (85%). Deallylation of **12**, followed by trichloroacetimidation, again gave an inseparable mixture of 2,3,4-tri-*O*-benzoyl-(1→3)-2,4-di-*O*-benzoyl-α- (**14**) and -β-D-xylopyranosyl trichloroacetimidate (**15**) in a ratio of ~1:1. The disaccharide acceptor was obtained from allyl 2,4-di-*O*-benzoyl-α-D-xylopyranoside (**6**). Thus, chloroacetylation of **6** with chloroacetyl chloride in pyridine furnished allyl 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-D-xylopyranoside (**9**) in high yield (96%), and subsequent deallylation and trichloroacetimidation gave an inseparable mixture (80% for two steps) of 2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α- (**10**) and -β-D-xylopyranosyl trichloroacetimidate (**11**) in 1:3 ratio. Condensation of the mixture of **10** and **11** with the acceptor **6** furnished a unique β-(1→3)-linked disaccharide **13** in 85% yield. Dechloroacetylation of **13** with thiourea gave the disaccharide acceptor **16** in satisfactory yield (80%). Then coupling of the disaccharide donor mixture of **14** and **15** with the disaccharide acceptor **16** gave β-(1→3)-linked tetrasaccharide **17** as the sole product in 80% yield. Reiteration of deallylation and trichloroacetimidation transformed **17** in 80% yield to a 1:1 mixture of anomers, 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-D- (**18**) and -β-D-xylopyranosyl trichloroacetimidate (**19**). Condensation of **18** and **19** with the acceptor **16** gave sole β-(1→3)-linked hexasaccharide **21** in 75% yield as the sole product. Finally, debenzoylation of **17** and **21** in saturated ammonia–methanol solution gave the target tetrasaccharide **20** and the hexasaccharide **22** as their allyl glycosides. The use of ammonia–methanol solution instead of sodium methoxide–methanol ensured the mildness and completion of the debenzoylation. The bioassay of the synthetic xylotetraose and hexaose is in progress.

In summary, we present herewith a very facile and convergent synthesis of β-(1→3)-linked xylooligosaccharides. It should be possible to carry out large-scale preparation of the xylotetraose, xylohexaose and higher xylooligosaccharides employing this method.

1. Experimental

General methods.—Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined with a Perkin–Elmer model 241-MC automatic polarimeter for solutions in a 1-dm, jacketed cell. ^1H NMR spectra were recorded with Varian XL-400 and Varian XL-200 spectrometers, for solutions in $CDCl_3$ with tetramethylsilane (Me_4Si) as the internal standard or for solutions in D_2O with acetone as the internal standard. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the electrospray-ionization mode. The progress of all reactions was followed by thin-layer chromatography (TLC) that was performed on silica gel HF with detection by charring with 30% (v/v) sulfuric acid in methanol or by UV detection. Column chromatography was conducted by elution of a column (8 × 100 mm, 16 × 240 mm, 18 × 300 mm, 35 × 400 mm) of silica gel (100–200 mesh) and EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), stainless steel column packed with silica gel (Spherisorb SiO_2, 10 × 300 mm or 4.6 × 250 mm), differential refractometer (132-RI detector) and UV/vis detector (model 118). EtOAc–petroleum ether (bp 60–90 °C) was used as the eluent at a flow rate of 1–4 mL/min. Solutions were concentrated at a temperature < 60 °C under diminished pressure.

*Allyl 2,4-di-*O*-acetyl-3-*O*-benzoyl-α-D-xylopyranoside* (**3**).—To a solution of **1** (3.80 g, 20.0 mmol) in pyridine (10 mL) was added benzoyl chloride (2.32 mL, 20.0 mmol). The reaction mixture was stirred overnight at rt. TLC (EtOAc) indicated that the reaction was complete. Water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The extract was washed with M HCl and satd aq $NaHCO_3$, dried (Na_2SO_4) and concentrated. Purification by flash chromatography (EtOAc) gave **2** (4.41 g, 75%). To a solution of **2** (0.30 g, 1.0 mmol) in pyridine (5 mL) was added Ac_2O (0.5 mL, 5.3 mmol). The reaction mixture

was stirred overnight at rt. TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Water (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The extract was washed with M HCl and satd aq $NaHCO_3$, dried (Na_2SO_4) and concentrated. Purification by flash chromatography (3:1 petroleum ether–EtOAc) gave **3** (0.36 g, 95%) as a foamy solid: ^{1}H NMR ($CDCl_3$): δ 8.04–7.43 (m, 5 H, PhH), 5.83 (m, 1 H, CH_2=C*H*-CH_2-), 5.74 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.9 Hz, H-3), 5.30–5.11 (m, 2 H, C*H*$_2$=CH-CH_2-), 5.21 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.07 (m, 1 H, H-4), 5.04 (dd, 1 H, H-2), 4.23–3.97 (m, 2 H, CH_2=CH-C*H*$_2$-), 3.87 (dd, 1 H, $J_{4,5}$ 6.0 Hz, H-5), 3.71 (dd, 1 H, $J_{4,5'} = J_{5,5'}$ 10.8 Hz, H-5′), 2.06 (s, 3 H, Ac), 1.97 (s, 3 H, Ac). Anal. Calcd for $C_{15}H_{18}O_6$: C, 47.62; H, 4.76. Found: C, 47.48; H, 4.87.

Allyl 2,3,4-tri-O-*benzoyl*-α-D-*xylopyranoside* (**4**), *allyl 2,3-di*-O-*benzoyl*-α-D-*xylopyranoside* (**5**) *and allyl 2,4-di*-O-*benzoyl*-α-D-*xylopyranoside* (**6**).—To a solution of **1** (3.80 g, 20.0 mmol) in pyridine (12 mL) was added benzoyl chloride (5.0 mL, 43.1 mmol). The reaction mixture was stirred overnight at rt. TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The extract was washed with M HCl and satd aq $NaHCO_3$, dried (Na_2SO_4) and concentrated. Purification by flash chromatography (3:1 petroleum ether–EtOAc) gave **4** (2.51 g, 25%), and **5** (1.59 g, 20%), **6** (3.58 g, 45%) as a foamy solid, respectively.

Or, to a solution of **2** (2.94 g, 10.0 mmol) in pyridine (8 mL) was added benzoyl chloride (1.3 mL, 11.2 mmol). The reaction mixture was stirred overnight at rt. TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The extract was washed with M HCl and satd aq $NaHCO_3$, dried (Na_2SO_4) and concentrated. Purification by flash chromatography (3:1 petroleum ether–EtOAc) gave **4** (1.20 g, 24%), and **5** (0.76 g, 19%), **6** (1.79 g, 45%) as a foamy solid, respectively; **4**: $[\alpha]_D$ + 65.1° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.00–7.31 (m, 15 H, PhH), 6.18 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.6 Hz, H-3), 5.86 (m, 1 H, CH_2=CH-CH_2-), 5.41 (m, 1 H, H-4), 5.34–5.14 (m, 2 H, CH_2=CH-CH_2-), 5.30–5.26 (m, 2 H, H-1, H-2), 4.29–4.03 (m, 2 H, CH_2=CH-CH_2-), 4.11–4.07 (dd, 1 H, $J_{4,5}$ 5.9 Hz, H-5), 3.89 (dd, 1 H, $J_{4,5'} = J_{5,5'}$ 10.8 Hz, H-5′). Anal. Calcd for $C_{29}H_{26}O_8$: C, 69.32; H, 5.18. Found: C, 69.51; H, 5.15. **5**: $[\alpha]_D$ + 141.1° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.00–7.35 (m, 10 H, PhH), 5.84 (m, 1 H, CH_2=CH-CH_2-), 5.66 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.8 Hz, H-3), 5.34–5.14 (m, 2 H, CH_2=CH-CH_2-), 5.26 (dd, 1 H, H-2), 5.19 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.28–4.00 (m, 2 H, CH_2=CH-CH_2-), 4.04 (m, 1 H, H-4), 3.87 (dd, 1 H, $J_{4,5}$ 5.8 Hz, H-5), 3.78 (dd, 1 H, $J_{4,5'} = J_{5,5'}$ 11.0 Hz, H-5′), 2.73 (br, 1 H, OH). Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.33; H, 5.53. Found: C, 66.19; H, 5.55. **6**: $[\alpha]_D$ + 75.3° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.09–7.40 (m, 10 H, PhH), 5.85 (m, 1 H, CH_2=CH-CH_2-), 5.33–5.13 (m, 2 H, CH_2=CH-CH_2-), 5.22–5.15 (m, 1 H, H-4), 5.17 (d, 1 H, H-1) 5.06 (dd, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.46 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.6 Hz, H-3), 4.25–3.98 (m, 2 H, CH_2=CH-CH_2-), 3.95 (dd, 1 H, $J_{4,5}$ 5.8 Hz, H-5), 3.77 (dd, 1 H, $J_{4,5'} = J_{5,5'}$ 10.8 Hz, H-5′), 2.60 (br, 1 H, OH). Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.33; H, 5.53. Found: C, 66.10; H, 5.60.

2,3,4-Tri-O-*benzoyl*-α-D-*xylopyranosyl trichloroacetimidate* (**7**) *and 2,3,4-tri*-O-*benzoyl*-β-D-*xylopyranosyl trichloroacetimidate* (**8**).—To a solution of **4** (5.02 g, 10.0 mmol) in anhyd CH_3OH (100 mL) was added $PdCl_2$ (0.5 g), and the mixture was stirred at 40 °C for 4 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated to dryness. To the residue were added CCl_3CN (4.2 mL, 20 mmol), anhyd K_2CO_3 (5.00 g), and dry CH_2Cl_2 (70 mL). The mixture was stirred overnight and was then filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give a mixture (**7**:**8** = 3:17) as a foamy solid (4.85 g, 80%): $[\alpha]_D$ − 18.6° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.80 (s, 0.85 H, NH (**8**)), 8.62 (s, 0.15 H, NH (**7**)), 8.16–7.32 (m, 15 H, PhH), 6.73 (d, 0.15 H, $J_{1,2}$ 3.6 Hz, H-1 (**7**)), 6.44 (d, 0.85 H, $J_{1,2}$ 2.6 Hz, H-1 (**8**)), 6.25 (dd, 0.15 H, $J_{2,3} = J_{3,4}$ 10.0 Hz, H-3 (**7**)), 5.72 (dd, 0.85 H, $J_{2,3} = J_{3,4}$ 4.2 Hz, H-3 (**8**)), 5.56 (dd, 0.15 H, H-2 (**7**)), 5.51 (dd, 0.85 H, H-2 (**8**)), 5.51 (m, 0.15 H, H-4 (**7**)), 5.30 (m, 0.85 H, H-4 (**8**)), 4.61 (dd, 0.85 H, $J_{4,5}$ 2.6 Hz, H-5 (**8**)), 4.30 (dd, 0.15 H, $J_{4,5}$ 5.8 Hz, $J_{5,5'}$ 11.2 Hz, H-5 (**7**)), 4.08 (dd, 0.85, 1 H, $J_{4,5'}$ 3.5 Hz, $J_{5,5'}$ 13.0 Hz, H-5′ (**8**)), 4.08 (m, 0.15 H, H-5′ (**7**)). Anal. Calcd for $C_{28}H_{22}Cl_3NO_8$: C, 55.40; H, 3.63. Found: C, 55.22; H, 3.64.

Allyl 2,4-di-O-*benzoyl-3*-O-*chloroacetyl*-α-D-*xylopyranoside* (**9**).—To a solution of **6** (6.04 g, 15.2 mmol) in 1:3 pyridine–CH_2Cl_2 (40 mL) was added chloroacetyl chloride (2.6 mL, 32.7 mmol). The reaction mixture was stirred overnight at rt. TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The extract was washed with M HCl and satd aq $NaHCO_3$, dried (Na_2SO_4) and concentrated. Purification by flash chromatography (3:1 petroleum ether–EtOAc) gave **9** as a foamy solid (6.92 g, 96%): $[\alpha]_D$ − 0.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.05–7.44 (m, 10 H, PhH), 5.99 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.9 Hz, H-3), 5.83 (m, 1 H, CH_2=C*H*-CH_2-), 5.32–5.13 (m, 2 H, C*H*$_2$=CH-CH_2-), 5.32–5.27 (m, 2 H, H-4, H-1), 5.17–5.13 (dd, 1 H, H-2), 4.27–4.01 (m, 2 H, CH_2=CH-C*H*$_2$-), 4.09–4.04 (dd, 1 H, $J_{4,5}$ 4.5 Hz, H-5), 3.91 (s, 2 H, ClC*H*$_2$CO), 3.82 (t, 1 H, $J_{4,5'} = J_{5,5'}$ 10.8

Hz, H-5′). Anal. Calcd for $C_{24}H_{23}ClO_8$: C, 60.70; H, 4.85. Found: C, 60.95; H, 4.83.

2,4-Di-O-benzoyl-3-O-chloroacetyl-α-D-xylopyranosyl trichloroacetimidate (**10**) *and 2,4-di-O-benzoyl-3-O-chloroacetyl-β-D-xylopyranosyl trichloroacetimidate* (**11**).—To a solution of **9** (5.51 g, 11.6 mmol) in anhyd CH_3OH (100 mL) was added $PdCl_2$ (0.5 g), and the mixture was stirred at 40 °C for 4 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated to dryness. To the residual solid were added CCl_3CN (4.2 mL, 20 mmol), anhyd K_2CO_3 (5.10 g), and dry CH_2Cl_2 (80 mL). The mixture was stirred overnight and was then filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give a mixture (**10**:**11** = 1:3) as a foamy solid (5.33 g, 80%): $[\alpha]_D$ −12.9° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.76 (s, 0.75 H, NH (**11**)), 8.61 (s, 0.25 H, NH (**10**)), 8.05–7.32 (m, 10 H, PhH), 6.69 (d, 0.25 H, $J_{1,2}$ 3.6 Hz, H-1 (**10**)), 6.28 (d, 0.75 H, $J_{1,2}$ 3.9 Hz, H-1 (**11**)), 6.03 (dd, 0.25 H, $J_{2,3} = J_{3,4}$ 10.0 Hz, H-3 (**10**)), 5.58 (dd, 0.75 H, $J_{2,3} = J_{3,4}$ 5.5 Hz, H-3 (**11**)), 5.46–5.37 (m, 1 H, H-2), 5.30–5.22 (m, 1 H, H-4), 4.51 (dd, 0.75 H, $J_{4,5}$ 3.4 Hz, $J_{5,5'}$ 12.7 Hz, H-5 (**11**)), 4.27 (dd, 0.25 H, $J_{4,5}$ 5.9 Hz, $J_{5,5'}$ 11.2 Hz, H-5 (**10**)), 4.10 (s, 1.5 H, $ClCH_2CO$ (**11**)), 3.99 (m, 1 H, H-5), 3.93 (s, 0.5 H, $ClCH_2CO$ (**10**)). Anal. Calcd for $C_{23}H_{14}Cl_4NO_8$: C, 48.08; H, 2.44. Found: C, 48.28; H, 2.43.

Allyl 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-O-benzoyl-α-D-xylopyranoside (**12**).—The mixture of **7** and **8** (2.18 g, 3.6 mmol) and acceptor **6** (1.44 g, 3.6 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (60 mL). TMSOTf (90 μL, 0.13 equiv) was added dropwise at −25 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the mixture was gradually warmed to ambient temperature. The mixture was then neutralized with Et_3N, concentrated and purified by flash chromatography (3:1 petroleum ether–EtOAc) to afford **12** as a foamy solid (2.58 g, 85%): $[\alpha]_D$ −1.7° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.13–7.13 (m, 25 H, PhH), 5.77 (m, 1 H, CH_2=C*H*-CH_2-), 5.55 (dd, 1 H, $J_{2,3} = J_{3,4}$ 6.0 Hz, H-3^{II}), 5.32 (m, 1 H, H-4), 5.27–5.09 (m, 2 H, C*H*$_2$=CH-CH_2-), 5.25 (d, 1 H, H-1^{II}), 5.17 (dd, $J_{1,2}$ 4.1 Hz, $J_{2,3}$ 6.0 Hz, H-2^{II}), 5.14 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 5.12–5.09 (m, 1 H, H-2), 5.03 (m, 1 H, H-4^{II}), 4.66 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3^{I}), 4.28 (dd, 1 H, *J* 3.5 Hz, *J* 12.6 Hz, H-5^{II}), 4.21–3.92 (m, 2 H, CH_2=CH-C*H*$_2$-), 4.02 (dd, 1 H, $J_{4,5}$ 5.9 Hz, $J_{5,5'}$ 10.8 Hz, H-5^{I}), 3.79 (dd, 1 H, $J_{4,5'} = J_{5,5'}$ 10.7 Hz, H-5$^{I\prime}$), 3.58 (dd, 1 H, $J_{4,5'}$ 5.2 Hz, $J_{5,5'}$ 12.6 Hz, H-5$^{II\prime}$); ^{13}C NMR ($CDCl_3$): δ 165.54, 165.31, 165.31, 164.94, 164.50 (Ph*C*O), 133.40, 133.34, 133.25, 133.11, 132.89, 129.76, 129.71, 129.56, 129.41, 129.16, 129.09, 128.82, 128.70, 128.40, 128.32, 128.26, 127.96, 117.66 (*C*H$_2$=CH-CH_2-), 99.82, 95.11 (C-1), 75.22, 73.70, 70.15, 69.37, 68.63, 68.59, 68.36, 60.25, 58.92, $J_{C\text{-}1-H\text{-}1}$ 166.8 Hz (C-1^{II}, β), $J_{C\text{-}1-H\text{-}1}$ 173.2 Hz (C-1^{I}, α). Anal. Calcd for $C_{48}H_{42}O_{14}$: C, 68.41; H, 4.99. Found: C, 68.17; H, 5.04.

Allyl 2,4-di-O-benzoyl-3-O-chloroacetyl-β-D-xylopyranosyl-(1→3)-2,4-di-O-benzoyl-α-D-xylopyranoside (**13**).—The mixture of **10** and **11** (2.35 g, 4.1 mmol) and acceptor **6** (1.64 g, 4.1 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (60 mL). TMSOTf (90 μL, 0.11 equiv) was added dropwise at −25 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the mixture was gradually warmed to ambient temperature. Then the mixture was neutralized with Et_3N, concentrated and purified by flash chromatography (3:1 petroleum ether–EtOAc) to afford **13** as a foamy solid (2.84 g, 85%): $[\alpha]_D$ −1.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.12–7.15 (m, 20 H, PhH), 5.76 (m, 1 H, CH_2=C*H*-CH_2-), 5.39 (dd, 1 H, $J_{2,3} = J_{3,4}$ 6.9 Hz, H-3^{II}), 5.30 (m, 1 H, H-4^{I}), 5.27–5.07 (m, 2 H, C*H*$_2$=CH-CH_2-), 5.12–5.07 (m, 4 H, H-1^{I}, H-1^{II}, H-2^{II}, H-2^{I}), 4.96 (m, 1 H, H-4^{II}), 4.59 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.9 Hz, H-3^{I}), 4.20–3.91 (m, 2 H, CH_2=CH-C*H*$_2$-), 4.15 (dd, 1 H, H-5^{II}), 3.98 (dd, 1 H, $J_{4,5}$ 5.8 Hz, $J_{5,5'}$ 10.8 Hz, H-5), 3.91 (d, 2 H, $ClCH_2CO$), 3.78 (dd, 1 H, $J_{4,5'} = J_{5,5'}$ 10.8 Hz, H-5′), 3.48 (dd, 1 H, $J_{4,5}$ 6.3 Hz, $J_{5,5}$ 10.8 Hz, H-5$^{II\prime}$); ^{13}C NMR ($CDCl_3$): δ 166.35 ($ClCH_2CO$), 165.47, 165.27, 165.24, 164.56 (PhCO), 133.46, 133.37, 133.23, 133.06, 129.74, 129.70, 129.58, 129.51, 129.47, 129.39, 129.01, 128.86, 128.40, 128.26, 128.10, 127.96, 117.71 (*C*H$_2$=CH-CH_2-), 100.06, 95.08 (C-1), 75.44, 75.21, 73.40, 71.08, 69.86, 69.66, 68.63, 68.57, 60.75, 60.32, 40.27 (Cl*C*H$_2$CO), $J_{C\text{-}1-H\text{-}1}$ 172.7 Hz (C-1^{I}, α), $J_{C\text{-}1-H\text{-}1}$ 168.5 Hz (C-1^{II}, β). Anal. Calcd for $C_{43}H_{39}ClO_{14}$: C, 63.35; H, 4.79. Found: C, 63.11; H, 4.81.

2,3,4-Tri-O-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-O-benzoyl-α-D-xylopyranosyl trichloroacetimidate (**14**) *and 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-O-benzoyl-β-D-xylopyranosyl trichloroacetimidate* (**15**).—To a solution of **12** (3.14 g, 3.7 mmol) in anhyd 2:1 CH_3OH–CH_2Cl_2 (75 mL) was added $PdCl_2$ (0.3 g), and the mixture was stirred at 40 °C for 4 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated to dryness. To the residual solid were added CCl_3CN (1.4 mL, 6.7 mmol), anhyd K_2CO_3 (3.00 g), and dry CH_2Cl_2 (40 mL). The mixture was stirred overnight and was then filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give a mixture (**14**:**15** = 47:53) as a foamy solid (2.80 g, 80%): $[\alpha]_D$ −31.2° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.63 (s,

0.53 H, NH (**15**)), 8.54 (s, 0.47 H, NH (**14**)), 6.56 (d, 0.47 H, $J_{1,2}$ 3.6 Hz, H-1 (**14**)), 6.32 (s, 0.53 H, H-1 (**15**)), 5.45 (m, 0.47 H, H-4 (**14**)), 4.71 (dd, 0.47 H, $J_{2,3} = J_{3,4}$ 9.4 Hz, H-3 (**14**)), 4.22 (dd, 0.47 H, H-5 (**14**)). Anal. Calcd for $C_{47}H_{38}Cl_3NO_{14}$: C, 59.59; H, 4.01. Found: C, 59.79; H, 4.07.

Allyl 2,4-di-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-α*-D-*xylopyranoside* (**16**).—To a solution of **13** (3.04 g, 3.7 mmol) in 1:4 EtOH–CH_2Cl_2 (125 mL) was added thiourea (0.36 g), and the mixture was refluxed for 16 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated. The residue was passed through a silica-gel column with 3:1 petroleum ether–EtOAc as the eluent to give **16** as a foamy solid (2.18 g, 80%): $[\alpha]_D$ −2.3° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.12–7.19 (m, 20 H, PhH), 5.78 (m, 1 H, CH_2=C*H*-CH_2-), 5.32 (m, 1 H, H-4^{I}), 5.29–5.11 (m, 5 H, CH_2=CH-CH_2-, H-1^{II}, H-1^{I}, H-2^{II}), 4.91 (dd, 1 H, $J_{1,2}$ 3.8 Hz, $J_{2,3}$ 5.3 Hz, H-2^{II}), 4.86 (m, 1 H, H-4^{II}), 4.63 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3^{I}), 4.23–3.95 (m, 5 H, CH_2=CH-CH_2-, H-5^{II}, H-5^{I}, H-3^{II}), 3.80 (dd, 1 H, $J_{4,5} = J_{5,5}$ 10.7 Hz, H-5), 3.50 (dd, 1 H, $J_{4,5}$ 4.2 Hz, $J_{5,5'}$12.8 Hz, H-5^{II}), 2.90 (br, 1 H, OH). Anal. Calcd for $C_{41}H_{38}O_{13}$: C, 66.67; H, 5.15. Found: C, 66.45; H, 5.17.

Allyl 2,3,4-tri-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-α*-D-*xylopyranoside* (**17**).—The mixture of **14** and **15** (1.51 g, 1.6 mmol) and acceptor **16** (1.18 g, 1.6 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (45 μL, 0.15 equiv) was added dropwise at −25 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the mixture was gradually warmed to ambient temperature. Then the mixture was neutralized with Et_3N, concentrated and purified by flash chromatography (2:1 petroleum ether–EtOAc) to afford **17** as a foamy solid (1.95 g, 80%): $[\alpha]_D$ −7.3° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–6.98 (m, 45 H, PhH), 5.73 (m, 1 H, CH_2=CH-CH_2-), 5.65 (dd, 1 H, $J_{2,3} = J_{3,4}$ 6.8 Hz, H-3^{IV}), 5.26 (dd, 1 H, H-2^{IV}), 5.21–5.04 (m, 2 H, CH_2=CH-CH_2-), 5.14 (m, 1 H, H-4^{IV}), 5.11 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1^{III}), 5.01 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1^{IV}), 5.00 (m, 2 H, H-2^{III}, H-4^{III}), 4.99 (d, 1 H, H-1^{I}), 4.90 (m, 1 H, H-4^{I}), 4.84 (d, 1 H, $J_{1,2}$ 4.3 Hz, H-1^{II}), 4.79 (dd, 1 H, $J_{1,2}$ 4.3 Hz, $J_{2,3}$ 6.3 Hz, H-2^{II}), 4.73 (dd, 1 H, $J_{1,2}$ 3.6 Hz, H-2^{I}), 4.66 (m, 1 H, H-4^{II}), 4.39 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.3 Hz, H-3^{I}), 4.27 (dd, 1 H, $J_{4,5}$ 3.9 Hz, $J_{5,5}$ 12.3 Hz, H-5), 4.23 (dd, 1 H, $J_{2,3} = J_{3,4}$ 5.7 Hz, H-3^{III}), 4.13–3.87 (m, 2 H, CH_2=CH-CH_2-), 4.13–4.05 (m, 2 H), 3.93–3.87 (m, 2 H), 3.64–3.57 (m, 2 H, H-5, H-5), 3.34–3.28 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 165.34, 165.27, 165.22, 165.11, 165.03, 164.99, 164.48, 164.22, 164.15 (PhCO), 133.30, 133.27, 133.16, 133.07, 133.02, 132.95, 132.70, 129.86, 129.78, 129.75, 129.71, 129.66, 129.53, 129.48, 129.38, 129.15, 129.12, 128.99, 128.85, 128.60, 128.60, 128.36, 128.30, 128.24, 128.21, 128.17, 128.14, 128.05, 127.92, 117.92, 117.41 (CH_2=CH-CH_2-), 100.29, 98.74, 98.60, 94.93 (C-1), 75.66, 73.33, 72.67, 70.10, 69.94, 69.69, 69.56, 69.47, 69.36, 69.04, 68.87, 68.80, 68.45, 60.81, 60.42, 60.42, 60.02, 58.83. Anal. Calcd for $C_{86}H_{74}O_{26}$: C, 67.81; H, 4.86. Found: C, 67.55; H, 4.88.

2,3,4-Tri-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-α*-D-*xylopyranosyl trichloroacetimidate* (**18**) *and 2,3,4-tri*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl trichloroacetimidate* (**19**).—To a solution of **17** (1.38 g, 0.91 mmol) in anhyd 1:1 CH_3OH–CH_2Cl_2 (50 mL) was added $PdCl_2$ (0.1 g), and the mixture was stirred at 40 °C for 4 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated to dryness. To the residual solid were added CCl_3CN (0.7 mL, 3.3 mmol), anhyd K_2CO_3 (1.30 g), and dry CH_2Cl_2 (30 mL). The mixture was stirred overnight and was then filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give a mixture (**18**:**19** = 1:1) as a foamy solid (1.18 g, 80%): $[\alpha]_D$ −23.9° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.56 (s, 1 H, NH (**19**)), 8.50 (s, 1 H, NH (**18**)), 6.36 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1 (**18**)), 6.14 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1 (**19**)). Anal. Calcd for $C_{85}H_{70}Cl_3NO_{26}$: C, 62.71; H, 4.30. Found: C, 62.94; H, 4.28.

Allyl β-D-*xylopyranosyl-(1→3)-β*-D-*xylopyranosyl-(1→3)-β*-D-*xylopyranosyl-(1→3)-α*-D-*xylopyranoside* (**20**).—Compound **17** (0.15 g, 0.10 mmol) was dissolved in a satd solution of NH_3 in anhyd CH_3OH (20 mL). After one week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **20** as a syrup (53 mg, 90%): $[\alpha]_D$ +2.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR (D_2O): δ 5.88 (m, 1 H, CH_2=C*H*-CH_2-), 5.29–5.16 (m, 2 H, CH_2=CH-CH_2-), 4.83 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 4.60 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^{IV}), 4.57 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^{III}), 4.55 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1^{II}), 4.16–3.94 (m, 2 H, CH_2=CH-CH_2-), 3.92–3.85 (m, 3 H), 3.75–3.70 (m, 1 H), 3.64–3.34 (m, 11 H), 3.25–3.18 (m, 4 H); ^{13}C NMR (D_2O): δ 135.82 (CH_2=*C*H-CH_2-), 120.66 (*C*H_2=CH-CH_2-), 105.81, 105.64, 105.55, 99.70 (C-1), 86.01, 85.96, 84.18 (C-3$^{III,\ II,\ I}$), 77.98, 75.74, 75.48, 75.43, 73.20, 71.57, 70.91, 70.12, 70.05, 70.05, 67.53, 67.18, 67.18, 63.49. MALDI TOFMS Calcd for $C_{23}H_{38}O_{17}$: [M] 586.2, Found: [M + Na] 609.0.

Allyl 2,3,4-tri-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylopyranosyl-(1→3)-2,4-di*-O-*benzoyl-β*-D-*xylo-*

*pyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-*D*-xylopyranoside* (**21**).—The mixture of **18** and **19** (0.55 g, 0.34 mmol) and acceptor **16** (0.25 g, 0.34 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (15 μL, 0.23 equiv) was added dropwise at −25 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the mixture was gradually warmed to ambient temperature. Then the mixture was neutralized with Et_3N, concentrated and purified by flash chromatography (1.5:1 petroleum ether–EtOAc) to afford **21** as a foamy solid (0.56 g, 75%): $[\alpha]_D$ −1.1° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.10–6.92 (m, 65 H, PhH), 5.70 (m, 1 H, CH_2=CH-CH_2-), 5.65 (dd, 1 H, $J_{2,3} = J_{3,4}$ 7.0 Hz, H-3^{VI}), 5.26 (dd, 1 H, $J_{1,2}$ 5.3 Hz, $J_{2,3}$ 7.0 Hz, H-2^{VI}), 5.19–5.03 (m, 2 H, CH_2=CH-CH_2-), 5.15–5.03 (m, 4 H), 5.00 (m, 1 H, H-4^{V}), 4.95 (m, 3 H), 4.88 (m, 1 H, H-4^{IV}), 4.78 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1^{IV}), 4.72–4.62 (m, 5 H), 4.52 (m, 2 H), 4.38–4.23 (m, 3 H), 4.15–4.06 (m, 3 H), 4.09–3.82 (m, 2 H, CH_2=CH-CH_2-), 3.98–3.77 (m, 5 H), 3.63–3.57 (m, 2 H), 3.42 (dd, 1 H, $J_{4,5}$ 5.3 Hz, $J_{5,5'}$ 12.7 Hz, H-5), 3.27 (dd, 1 H, $J_{4,5}$ 4.5 Hz, $J_{5,5'}$ 12.6 Hz, H-5), 3.21–3.10 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 165.34, 165.28, 165.28, 165.03. 165.03, 165.03, 164.99, 164.99, 164.50, 164.24, 164.19, 164.05, 164.05 (PhCO), 133.34, 133.25, 133.17, 133.12, 133.09, 133.06, 132.96, 132.86, 132.71, 129.91, 129.79, 129.75, 129.72, 129.68, 129.58, 129.49, 129.43, 129.28, 129.17, 129.03, 129.00, 128.84. 128.73, 128.52, 128.42, 128.28, 128.22, 128.19, 128.16, 128.11, 127.96, 117.46 (CH_2=CH-CH_2-), 100.52, 98.95, 98.90, 99.69, 99.69, 94.88 (C-1), 77.17, 75.68, 73.29, 70.17, 70.00, 69.83, 69.70, 69.66, 69.54, 68.98, 68.46, 60.90, 60.64, 60.48, 60.29, 60.21, 58.76, $J_{C\text{-}1-H\text{-}1}$ 174.8 Hz (C-1^{I}, α), 167.6 Hz, 167.6 Hz, 165.8 Hz, 165.8 Hz, 161.6 Hz (C-1$^{VI, V, IV, III, II}$, β). Anal. Calcd for $C_{125}H_{106}O_{38}$: C, 67.75; H, 4.79. Found: C, 68.01; H, 4.77.

*Allyl β-*D*-xylopyranosyl-(1→3)-β-*D*-xylopyranosyl-(1→3)-β-*D*-xylopyranosyl-(1→3)-β-*D*-xylopyranosyl-(1→3)-β-*D*-xylopyranosyl-(1→3)-α-*D*-xylopyranoside* (**22**).—Compound **21** (0.26 g, 0.12 mmol) was dissolved in a satd solution of NH_3 in anhyd CH_3OH (20 mL). After one week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **22** as a syrup (87 mg, 85%): $[\alpha]_D$ +1.6° (*c* 1.1, $CHCl_3$); ^{1}H NMR (D_2O): δ 5.88 (m, 1 H, CH_2=CH-CH_2-), 5.29–5.16 (m, 2 H, CH_2=CH-CH_2-), 4.83 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 4.62–4.54 (m, 5 H, H-1$^{VI, V, IV, III, II}$), 4.15–3.94 (m, 2 H, CH_2=CH-CH_2-), 3.92–3.85 (m, 5 H), 3.75–3.33 (m, 19 H), 3.25–3.19 (m, 6 H); ^{13}C NMR (D_2O): δ 135.82 (CH_2=CH-CH_2-), 120.67 (CH_2=CH-CH_2-), 105.82, 105.65, 105.57, 105.57, 105.57, 99.70 (C-1), 86.03, 85.99, 85.91, 85.91, 84.20 (C-3$^{V, IV, III, II, I}$), 77.99, 75.74, 75.48, 75.43, 73.20, 71.57, 70.91, 70.15, 70.05, 67.53, 67.18, 63.49 MALDI TOFMS Calcd for $C_{33}H_{54}O_{25}$: [M] 850.3, Found: [M + Na] 873.0.

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