Total Synthesis of Woodrosin I—Part 1: Preparation of the Building Blocks and Evaluation of the Glycosylation Strategy

Alois Fürstner,* Fabien Jeanjean, Patrick Razon, Conny Wirtz, and Richard Mynott[a]

Abstract: The preparation of three building blocks required for the total synthesis of woodrosin I (**1**) is outlined, a complex resin glycoside bearing a macrolide ring which spans four of the five sugars of its oligosaccharide backbone. Key steps involve the enantioselective, titanium-catalyzed addition of dipentylzinc to 5-hexenal, the glycosylation of the resulting alcohol **18** with the glucose-derived trichloroacetimidate **7**, and further elaboration of the resulting product **19** into disaccharide **22** on treatment with the orthogonally protected glycosyl donor **15**. The trichloroacetimidate method is also used for the formation of the second synthon represented by disaccharide **38**. A model study shows that the assembly of the pentasaccharidic perimeter of **1** depends critically on the phasing of the glycosylation events between fragments **22**, **38** and the rhamnosyl donor **27** due to the severe steric hindrance in the product. A particularly noteworthy finding is the fact that diol **22** can be regioselectively glycosylated at the 3′-OH group in high yield without protection of the neighboring 2′-OH function.

Keywords: carbohydrates · glycolipids · glycosides · macrolides · natural products

Introduction

Plants belonging to the morning glory family (*Convolvulaceae*) are known as rich sources of alkaloids and resin glycosides. Although chemical investigations on the latter have been initiated as early as the middle of the 19th century,[1] it was not until the advent of modern spectroscopic techniques that the amazing structures of such glycolipids could be elucidated. Resin glycosides are conjugates between complex oligosaccharide entities and (11*S*)-hydroxyhexadecanoic acid (jalapinolic acid) as the common aglycon in virtually all members of this series. The latter is frequently tied back to form a characteristic macrolactone ring spanning two or more sugar units of the backbone.[2–14] Further carboxylic acids may complement the peripheral acylation pattern.[14] The sophisticated molecular arrays thus formed exhibit a well-balanced hydrophilicity/hydrophobicity profile.[15]

The biological properties of resin glycosides are by no means fully understood. A closer examination of this family of natural products, however, seems to be rewarding, especially since many of them are isolated from plants that are essential ingredients of traditional medicine recipes.[2–4, 8, 12, 13] In a few cases, purified resin glycosides have been studied and were found to elicit effects as diverse as cytotoxicity against human cancer cell lines,[2, 4b, 11, 12] hemolytic action,[13b] antibacterial activity,[2, 12] ionophoretic properties,[13] purgative function,[4, 14] or a significant capacity for regulating plant growth.[2, 17] A systematic survey, however, including a study of the immune response of mammals to resin glycosides is still missing.

To probe these diverse physiological properties in more detail, a synthesis-driven mapping of the structure/activity relationships is called for. Because of the difficulties posed by such intricate structures, however, hardly any systematic work has been devoted to this area and only few successful total syntheses have been reported.[16–22] Most prominent among them are three independent approaches to the cytotoxic agent tricolorin A (**2**)[20–22] together with a synthesis of its congener tricolorin G (**3**).[22] Outlined below and in the following paper of this issue is the first total synthesis of woodrosin I (**1**),[23] an ether-insoluble resin glycoside isolated from the stems of *Ipomoea tuberosa* L. (*Merremia tuberosa* (L.) Rendle), commonly called "woodrose" after the shape of its dried calyx.[24–26] Compound **1** is certainly the structurally most demanding resin glycoside to be conquered by total synthesis so far. Particular challenges arise from the 27-membered macrolide ring spanning four glucose (Glc) units, the complementary acylation pattern at its periphery which seriously restricts the choice of temporary protecting groups, as well as the branched pentasaccharide backbone entailing severe steric hindrance at vicinal positions.

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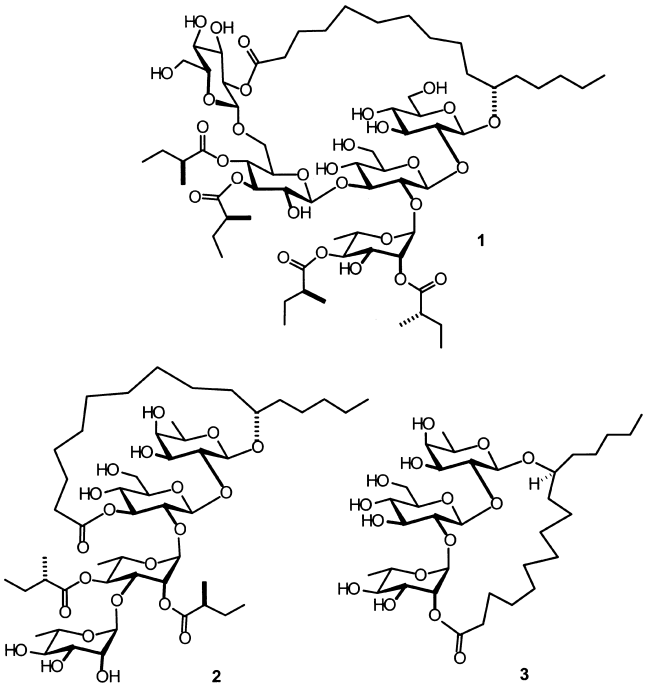


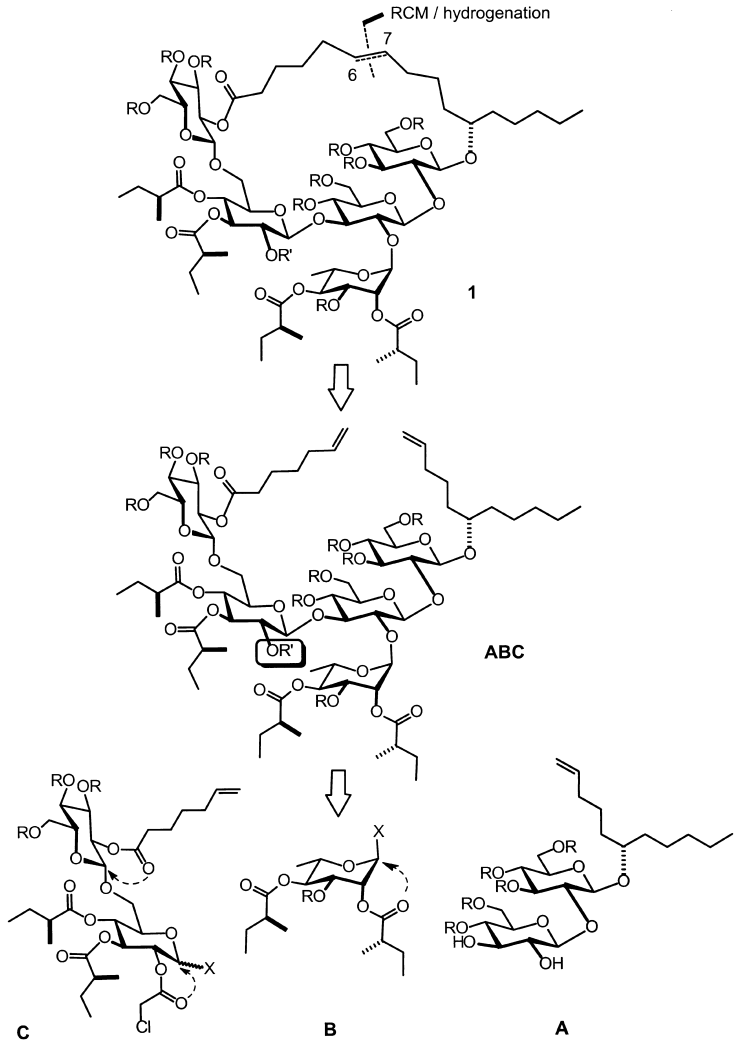
Results and Discussion

Retrosynthetic analysis: Encouraged by our previous successful implementation of ring closing metathesis (RCM)[27] in the total syntheses of **2** and **3**,[22] it was envisaged that the cyclization of the 27-membered core of **1** could be achieved by the same method. To ensure maximum efficiency, it is essential to avoid the formation of stable chelates between the intermediate Lewis-acidic metal carbene species with the polar substituents of the substrate as such arrays seriously attenuate the activity of the catalysts used.[28, 29] This should be possible by targeting the C-6/C-7 bond within the aliphatic tether (Scheme 1).

Since the cycloalkene formed by RCM has to be hydrogenated in any case, it is advantageous to choose the residual protecting groups R such that they are cleaved off simultaneously. For this purpose benzyl ethers or benzylidene acetals seemed to be most appropriate. Because these groups do not anchimerically assist in the formation of the required β-glycosidic linkages between the individual glucose units,[30] it seemed necessary to block the 2-OH function of Glc″ by a different substituent R′ that would direct the glycosylation as desired yet could be removed without damaging the macrolactone. A chloroacetyl group should fulfill these stringent criteria.[31] The stereoselective formation of the other glycosidic linkages is ensured by the 6-heptenoic acid residue in the terminal glucose which later serves the RCM event, as well as by the residual methylbutyrate ester in the rhamnosyl donor as indicated in Scheme 1.

To gain maximum efficiency, the cyclization precursor **ABC** must be assembled in a highly convergent manner from rhamnose **B** and the two disaccharidic building blocks **A** and **C**. Since steric as well as stereoelectronic factors were expected to render the formation of the branching point in the pentasaccharide backbone rather difficult, it was not clear at the outset which order of glycosylation events is optimal (**A**+**B** → **AB**+**C** → **ABC** versus **A**+**C** → **AC**+**B** → **ABC**). In any case, the trichloroacetimidate method[30b, 32] seemed to be most promising for these strategic maneuvers.

Preparation of the required building blocks—Synthon A: The synthesis of the first disaccharidic building block representing



Scheme 1. Retrosynthetic analysis.

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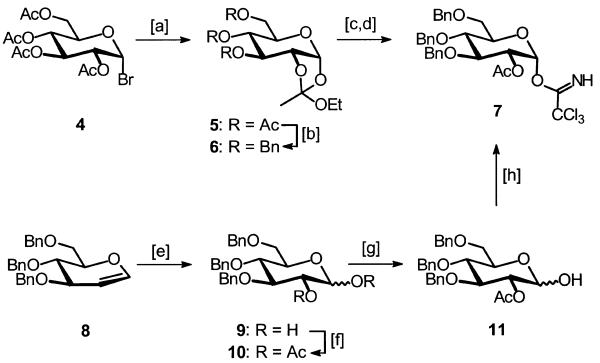
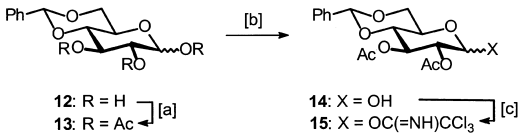
synthon **A** closely followed previous studies from our laboratory (Scheme 2).[33] Specifically, acetobromoglucose **4** was converted into orthoester **5** on a large scale following a literature procedure.[34] Substitution of the O-acetyl for O-benzyl groups (**5** → **6**),[33, 34b] acid catalyzed hydrolysis of the orthoester followed by treatment of the mixture of acetates thus formed with Cl_3CCN and Cs_2CO_3 delivers the differentially protected trichloroacetimidate **7** as the only product in good yield.[35]

Alternatively, the same compound was prepared from commercially available tri-*O*-benzyl-D-glucal (**8**), which was then dihydroxylated with OsO_4 cat. and *N*-methyl-morpholine-*N*-oxide (NMO) as the stoichiometric oxidant to afford 3,4,6-tri-*O*-benyzl-D-glucose (**9**) as the only product (Scheme 2).[36] Acetylation under standard conditions followed by regioselective cleavage of the anomeric OAc group in **10** with hydrazinium acetate[37] furnished hemiacetal **11** which reacts with Cl_3CCN and Cs_2CO_3 to give glycosyl donor **7** in excellent overall yield.



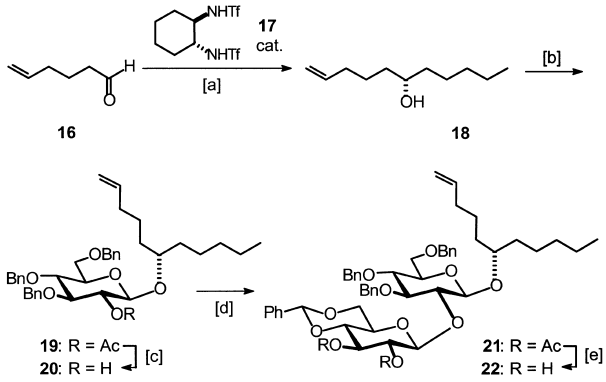
Scheme 2. [a] *sym*-Collidine, EtOH, ethyl orthoacetate, cf. ref. [34]. [b] BnBr, KOH, THF, 81%. [c] Aq. HOAc, 93%. [d] Cl_3CCN, Cs_2CO_3, CH_2Cl_2, 92%. [e] OsO_4 cat., NMO, acetone/H_2O. [f] Ac_2O, Et_3N, CH_2Cl_2, 94% (over both steps). [g] $H_2NNH_2 \cdot HOAc$, DMF, 90%. [h] Cl_3CCN, Cs_2CO_3, CH_2Cl_2, 83%.

The second glucosyl donor was derived from the well accessible 4,6-O-benzylidene acetal **12**[38] which was peracetylated, deprotected at the anomeric position and converted into trichloroacetimidate **15** (mixture of anomers) under standard conditions (Scheme 3).[22]



Scheme 3. [a] Ac_2O, pyridine, DMAP cat., 96%. [b] $BnNH_2$, THF, then HCl (1N), 78%. [c] Cl_3CCN, Cs_2CO_3, CH_2Cl_2, 76%.

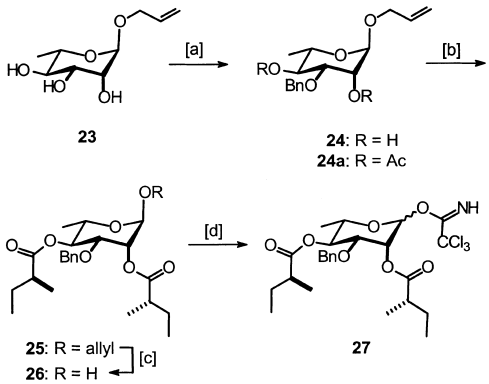
Compound **7** was then glycosylated with (6*S*)-undec-1-en-6-ol (**18**) which was obtained on a multigram scale in enantiomerically pure form (*ee* ≥ 99%) upon addition of dipentylzinc to 5-hexenal (**16**) in the presence of a catalyst formed in situ from Ti(O*i*Pr)$_4$ and bis-trifluoromethanesulfonamide (**17**)[39] as previously described (Scheme 4).[22] Cleavage of the 2-O-acetyl group (**19** → **20**) set the stage for the formation of



Scheme 4. [a] $Zn(C_5H_{11})_2$, **17** (2 mol%), Ti(O*i*Pr)$_4$, toluene, 86%, *ee* > 99%. [b] Compound **7**, $BF_3 \cdot Et_2O$, CH_2Cl_2/hexane, −20 °C, 68%. [c] NaOMe cat., MeOH, quant. [d] Compound **15**, $BF_3 \cdot Et_2O$, CH_2Cl_2/hexane, −20 °C, 82%. [e] NaOMe cat., MeOH, 88%.

disaccharide **21**. For this purpose, trichloroacetimidate **15** was treated with alcohol **20** in the presence of catalytic amounts of $BF_3 \cdot Et_2O$ in a mixture of CH_2Cl_2/hexane at −20 °C to give product **21** in 82% yield. Deacetylation completed the preparation of building block **22** required for the synthesis of woodrosin I.

Preparation of the rhamnosyl donor: Synthon **B** is obtained from allyl L-rhamnoside **23**[40] by regioselective benzylation at O-3 using established stannylation methodology (Scheme 5).[41] Esterification of the resulting product **24** with commercially available (2*S*)-methylbutyric acid in the presence of DCC and catalytic amounts of DMAP provided compound **25** which was deprotected at the anomeric position by means of palladium on charcoal in acidic MeOH as the reaction medium.[42] Hemiacetal **26** was then converted into trichloroacetimidate **27** on exposure to Cl_3CCN and Cs_2CO_3.

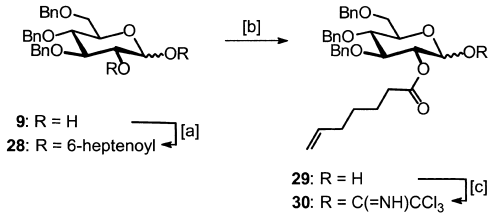


Scheme 5. [a] i) Bu_2SnO, toluene, reflux; ii) CsF, BnBr, DMF, 72%. [b] (2*S*)-Methylbutyric acid, DCC, DMAP, CH_2Cl_2, 89%. [c] Pd/C, pyridinum toluenesulfonate cat., MeOH, 80%. [d] Cl_3CCN, Cs_2CO_3, CH_2Cl_2, 92%.

Preparation of synthon C: Building block **C** was conceptually more challenging and various approaches can be envisaged. Originally, a synthesis based on the glycal assembly method was favored which promised to solve the selectivity issues quite elegantly.[43] Unfortunately, problems arose when the reactions were carried out on a larger scale. Therefore an

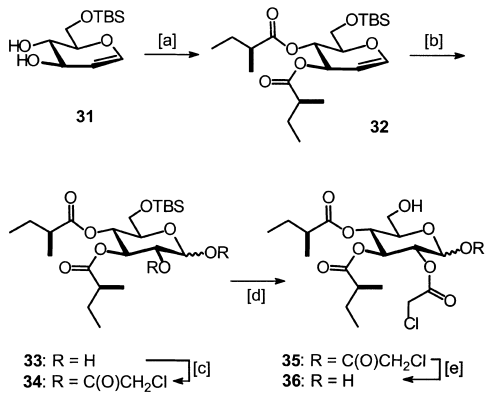
alternative solution was developed which featured a useful but as yet largely unexplored aspect of the powerful trichloroacetimidate method pioneered by Schmidt.[32]

Specifically, our synthesis (Scheme 6) started from 3,4,6-tri-*O*-benzyl-D-glucose (**9**) which derives from D-glucal as outlined above. Esterification with 6-heptenoic acid in the presence of DCC and DMAP followed by regioselective deprotection of the anomeric position in **28** provided product **29** which converted into the trichloroacetimidate **30** without any problems.



Scheme 6. [a] 6-Heptenoic acid, DCC, DMAP cat., CH_2Cl_2, 99%. [b] $H_2NNH_2 \cdot HOAc$, DMF, 83%. [c] Cl_3CCN, Cs_2CO_3, CH_2Cl_2, 87%.

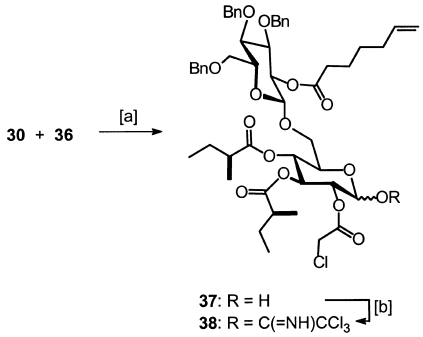
The glucosyl acceptor was also prepared from D-glucal (Scheme 7). Regioselective silylation of the primary OH group with TBSCl and imidazole followed by esterification of the resulting product **31**[44] with (2*S*)-methylbutyric acid afforded product **32** under standard conditions and set the stage for a dihydroxylation with OsO_4 cat. and NMO. This reaction was found to be virtually quantitative and delivered the *gluco*-configured diol **33** as the only product, which was chloroacetylated to provide compound **34** in excellent overall yield.



Scheme 7. [a] (2*S*)-methylbutyric acid, DCC, DMAP, CH_2Cl_2, 93%. [b] OsO_4 cat., NMO, acetone/H_2O (9:1), quant. [c] Chloroacetic acid anhydride, Et_3N, DMAP cat., CH_2Cl_2, $-20 \rightarrow -10\,^{\circ}C$, 83%. [d] $BF_3 \cdot Et_2O$, $CHCl_3$, 81%. [e] $H_2NNH_2 \cdot HOAc$, DMF, 79%.

To streamline the subsequent glycosylation events, it was desirable to cleave the OTBS group at C-6 and the chloroacetyl function at C-1. HF in pyridine was found to effect both deprotections simultaneously; unfortunately, however, only 48% of diol **36** could be obtained. Therefore a two-step protocol was favored comprising the selective removal of the OTBS function by means of $BF_3 \cdot Et_2O$ in $CHCl_3$ at ambient temperature (82%),[45] followed by treatment of the resulting product **35** with hydrazinium acetate[37] in DMF to unmask the anomeric center (79%).[46]

Gratifyingly, diol **36** thus obtained underwent a highly efficient, regio- as well as diastereoselective glycosylation with trichloroacetimidate **30** (Scheme 8). Because the anomeric position of the resulting disaccharide **37** was already



Scheme 8. [a] $BF_3 \cdot Et_2O$, CH_2Cl_2, $-20\,^{\circ}C$, 86%. [b] Cl_3CCN, Cs_2CO_3, CH_2Cl_2, 54%.

unmasked, this compound was directly amenable to the preparation of the next glycosyl donor, that is product **38**, which corresponds to building block **C** required for the assembly of woodrosin I. This *smooth reiterability* of the trichloroacetimidate method by using 1,ω-unprotected sugars such as **36** is an as yet largely unexplored feature deserving further in-depth investigation. It also comes into play during the further elaboration of the backbone as described below.

Study on the phasing of the glycosylation events during the assembly of the pentasaccharide backbone: With synthons **A** – **C** in hand, two options for a highly convergent assembly of the metathesis precursor required en route to woodrosin I (**1**) can be envisaged. In analogy to our previous total synthesis of tricolorin G (**3**),[22] we first pursued the coupling of synthons **A** and **B**, followed by the attachment of the disaccharidic building block **C** to the trisaccharide thus formed.

To put this plan into practice it is necessary to block the more reactive 3′-OH position of compound **22** prior to the introduction of the rhamnosyl moiety (Scheme 9). This was accomplished by reacting **22** with Bu_2SnO in toluene under reflux, followed by treatment of the resulting tin derivative with CsF and *p*-methoxybenzyl chloride in DMF at room temperature.[41] This transformation proceeded in excellent yield (82%) but provided a mixture of both possible regioisomers, slightly favoring the desired product (**39a**:**40a** 1:2) The site of *p*-methoxybenzylation was unambiguously determined by a full analysis of the NMR spectra of both isomers recorded at 600 MHz (cf. Table 1). Compounds **39** and **40** could be separated by recrystallization from MeOH.[47]

Attachment of the rhamnose unit to compound **40** was achieved by reaction with trichloroacetimidate **27**. This step, however, required considerable optimization since a very pronounced solvent effect was noticed. Specifically, attempted glycosylation in CH_2Cl_2 in the presence of TMSOTf afforded only 12% of the desired trisaccharide **41** and led to

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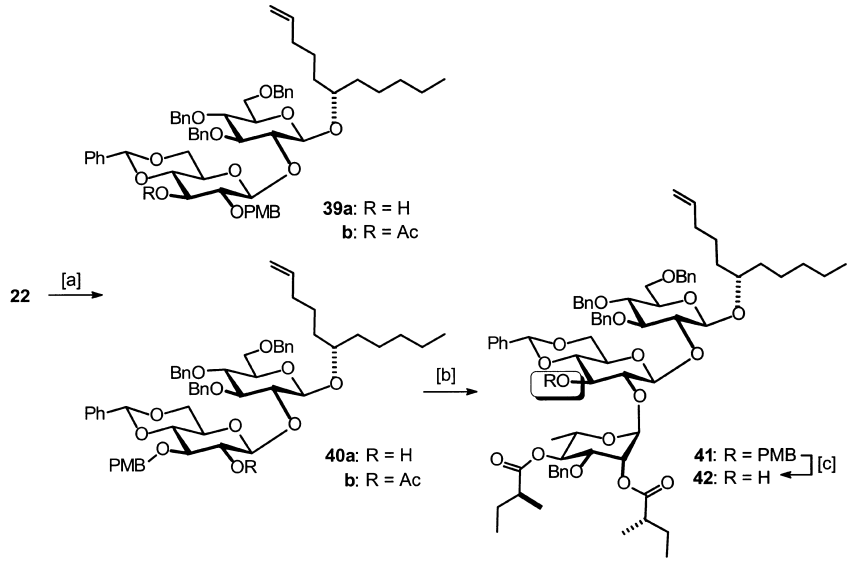
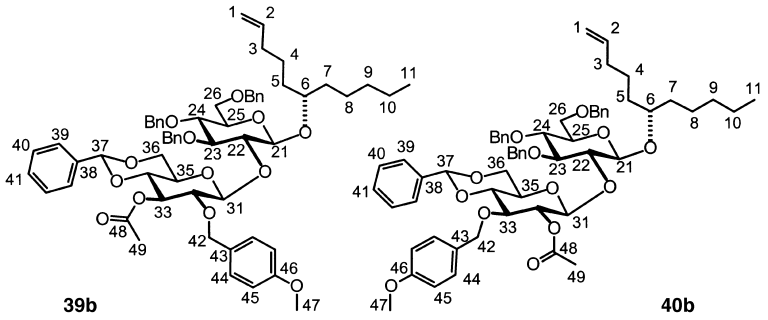


Scheme 9. [a] i) Bu_2SnO, toluene, reflux; ii) CsF, PMBCl, nBu_4NI, DMF, 82%, **39**:**40** 1:2. [b] Compound **27**, TMSOTf, Et_2O/THF (3:1), $-20^\circ C$, 62%. [c] DDQ, CH_2Cl_2/H_2O (19:1), 71%.

substantial amounts of by-products formed by cleavage of the OPMB group in **40**. We reasoned that the use of a more Lewis-basic medium might sufficiently attenuate the reactivity of TMSOTf and hence alleviate the problem with the instability of this particular protecting group. In fact, if THF is chosen as the solvent, no cleavage of the OPMB ether is observed; the desired product **41** was formed in 53% yield together with a homodimer derived from the rhamnosyl donor **27**. By using a mixture of Et_2O/THF (3:1)[48] we were able to raise the yield of **41** to 62%. However, the only means of removing admixed traces of the dimer derived from **27** was preparative HPLC. The subsequent selective cleavage of the OPMB group in **41** proceeded smoothly using DDQ[49] providing trisaccharide **42** ready for further use.

Despite the obvious shortcomings of this route (formation of regioisomers during PMB protection, need for an HPLC separation), the elaboration of this **AB**-synthon **42** into the pentasaccharide perimeter of woodrosin I was investigated. In spite of considerable experimentation with different promoters and solvents, however, we were *unable* to attach donor **38** to the 3′-OH position of this compound. Either no reaction occurred or complete degradation of **42** was observed when more forcing conditions were imposed. This lack of reactivity is likely due to the very crowded situation in **42** rendering the 3′-OH group virtually inaccessible. Even glycosyl donors less complex than **38** could not be attached to this site.

Table 1. Comparison of characteristic signals of the isomeric products **39b** and **40b**. Arbitrary numbering scheme as shown.

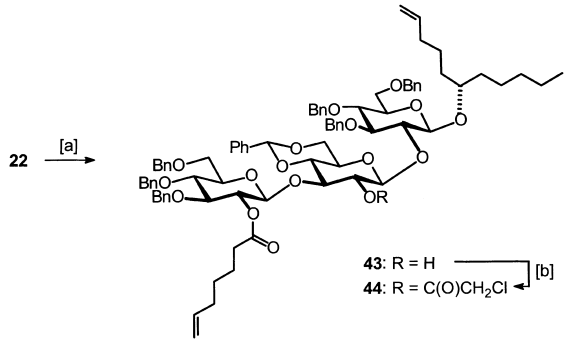


Position	δ ^{1}H		δ ^{13}C	
	39b	**40b**	**39b**	**40b**
1	5.08/5.00	5.08/5.00	114.76 (t)	114.70 (t)
2	5.90	5.90	139.60 (d)	139.64 (d)
6	3.68	3.59	86.31 (d)	85.77 (d)
11	0.90	0.89	14.30 (q)	14.30 (q)
21	4.41	4.35	101.81 (d)	101.43 (d)
22	3.75	3.63	77.98 (d)	78.94 (d)
23	3.64	3.62	80.91 (d)	80.55 (d)
24	3.60	3.62	78.85 (d)	78.82 (d)
25	3.47	3.40	75.30 (d)	75.10 (d)
26	3.74	3.71	69.42 (t)	69.54 (t)
31	5.11	5.02	102.73 (d)	100.90 (d)
32	3.39	4.92	80.61 (d)	73.84 (d)
33	5.18	3.62	73.27 (d)	78.71 (d)
34	3.60	3.76	79.32 (d)	81.97 (d)
35	3.34	3.34	66.29 (d)	66.57 (d)
36	4.31/3.72	4.33/3.79	69.13 (t)	69.11 (t)
37	5.45	5.58	101.65 (d)	101.50 (d)
38			137.79 (s)	137.99 (s)
39			126.51 (d)	126.43 (d)
43			130.72 (s)	130.85 (s)
45	6.84	6.84	113.97 (d)	113.97 (d)
46			159.72 (s)	159.70 (s)
47	3.77	3.77	55.55 (q)	55.55 (q)
48			170.22 (s)	169.44 (s)
49	2.00	1.95	21.14 (q)	21.23 (q)

Model studies for the AC/ABC strategy: As a consequence of this setback, it was vital for the ultimate success of this total synthesis project that the alternative phasing of the glycosylation events (i.e., **A**+**C** → **AC**+**B** → **ABC**) would give access to the intact sugar backbone of woodrosin I.

The inherently higher reactivity of the 3′-OH group in **22** became apparent during the installation of the PMB group described above. Therefore we envisaged using this diol directly in the next glycosylation step without recourse to protecting groups. However, since suspiciously few examples of selective glycosylation reactions of sugars with more than one hydroxy group have been reported in the literature,[50, 51] we decided to carry out some model studies to probe the viability of this concept prior to

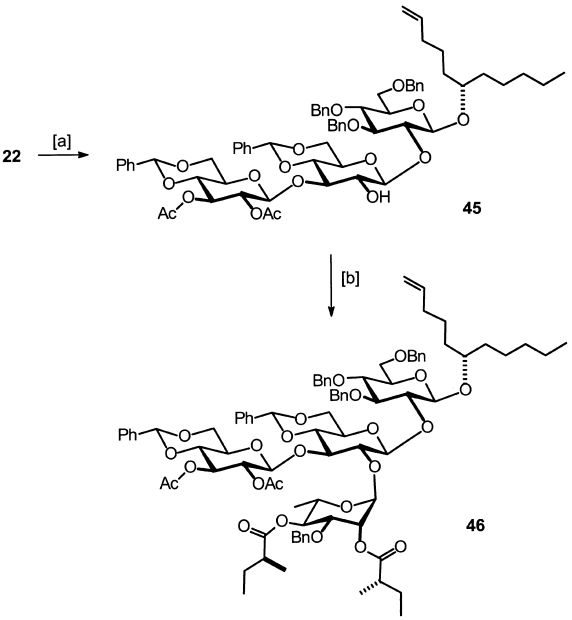
using the valuable synthon **C**. Gratifyingly though, the regioselective glycosylation of diol **22** worked exquisitely well as can be seen from the results depicted in Schemes 10 and 11. Thus, treatment of diol **22** with either compounds **30** or **15** as the chosen model donors in the presence of $BF_3 \cdot Et_2O$ in CH_2Cl_2 at $-20\,^{\circ}C$ led to exclusive glycosylation at the 3′-OH position. No traces of isomeric compounds were detected and the desired products **43** and **45**, respectively, were isolated in remarkably high yields.



Scheme 10. [a] Compound **30**, TMSOTf cat., CH_2Cl_2, $-20\,^{\circ}C$, 90%. [b] Chloroacetic acid anhydride, pyridine, CH_2Cl_2, 91%.

Next, we probed whether it would be possible to introduce a rhamnose unit at the adjacent site of such a compound (Scheme 11). Thus, product **45** was treated with trichloroacetimidate **27** in Et_2O/THF (3/1, see above) using catalytic amounts of TMSOTf as the promoter. Under these conditions, the desired product **46** was formed, albeit in rather low yield (35%).

Although this outcome was certainly far from optimal, it implied that the envisaged "**AC**+**B**" strategy might provide access to the woodrosin I backbone and pave the way to this demanding target molecule. As will be reported in the accompanying paper, this was indeed the case.[24, 25] It is noteworthy, however, that the end game of this project turned out to be even more challenging than this model study might suggest. The unforeseen interference of one of the protecting groups first seemed to dash our hopes but finally fostered the success of our synthetic endeavors.



Scheme 11. [a] Compound **15**, TMSOTf cat., CH_2Cl_2, $-20\,^{\circ}C$, 77%. [b] Compound **27**, TMSOTf cat., Et_2O/THF (3:1), 35%.

Experimental Section

General: All reactions were carried out under Ar in carefully dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF, DMA (Desmodur, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230–400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95. Melting points: Gallenkamp melting point apparatus (uncorrected). Optical rotation: Perkin Elmer 343 at $\lambda = 589$ nm (Na D-line). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Lancaster, Aldrich) were used as received. NMR: Spectra were recorded on Bruker DPX 300 or DMX 600 spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C = 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H = 7.24$ ppm; CD_2Cl_2: $\delta_C = 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H = 5.32$ ppm). Where indicated, the signal assignments are unambiguous; the numbering scheme is arbitrary and is shown in the inserts. The assignments were based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for $^1J(C,H) = 145$ Hz; HMBC (*inv4gslplrnd*) for correlations via $^nJ(C,H)$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl) trichloroacetimidate (7)**

Method A: A solution of orthoester **6** (1.908 g, 3.66 mmol)[34] in HOAc (24 mL) and H_2O (6 mL) was stirred for 1 h at ambient temperature. For work-up, the mixture was diluted with H_2O (30 mL), the aqueous layer was extracted with EtOAc, the combined organic phases were dried (Na_2SO_4) and evaporated, and the residue was purified by flash chromatography (hexane/EtOAc 2:1 → 1:1), affording a colorless solid (1.676 g, 93%) which consists of a mixture of three different acetates (characteristic signals in the ^{13}C NMR spectrum: $\delta = 95.5$, 91.9, 90.2 ppm).[35] This mixture was directly used for the next step: A solution of this product (1.673 g, 3.40 mmol) in CH_2Cl_2 (15 mL) was treated with Cl_3CCN (682 μL, 6.80 mmol) and Cs_2CO_3 (238 mg, 0.73 mmol) and the resulting mixture was stirred for 14 h before it was adsorbed on silica gel and purified by flash chromatography (hexane/EtOAc 4:1) to afford compound **7** as a colorless syrup (1.998 g, 92%).[52] $[\alpha]_D^{25} = +85.5$ ($c = 2.4$, $CHCl_3$); IR: $\tilde{\nu} = 3338$, 3031, 2924, 1748, 1673, 1231, 1053, 795, 738, 698; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.56$ (s, 1H, NH), 7.33–7.16 (m, 15H), 6.52 (d, $J = 3.6$ Hz, 1H), 5.07 (dd, $J = 10.0$ Hz, 3.6, 1H), 4.87–4.81 (m, 2H), 4.76 (A part of AB, $J = 11.5$ Hz, 1H), 4.50 and 4.63 (AB, $J = 12.0$ Hz, 2H), 4.58 (B part of AB, $J = 10.7$ Hz, 1H), 4.09 (m, 1H), 4.01 (ddd, $J = 10.0$, 3.3, 1.9 Hz, 1H), 3.87 (dd, $J = 10.0$, 9.2 Hz, 1H), 3.81 (dd, $J = 11.0$, 3.3 Hz, 1H), 3.69 (dd, $J = 11.0$, 1.9 Hz, 1H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.0$, 161.0, 138.3, 137.9, 128.4, 128.1, 127.9, 127.8, 127.7, 94.0, 91.1, 79.5, 77.1, 75.4, 75.3, 73.5, 73.4, 72.4, 67.9, 20.6; elemental analysis calcd (%) for $C_{31}H_{32}Cl_3NO_7$ (636.96): C 58.46, H 5.06, Cl 16.70, N 2.20; found: C 58.36, H 5.07, Cl 16.77, N 2.20.

Method B: Hydrazinium acetate (280 mg, 3.05 mmol) was added to a solution of compound **10** (1.37 g, 2.56 mmol)[53] in DMF (25 mL) and the mixture was stirred for 15 min at ambient temperature. A standard extractive work-up followed by flash chromatography (hexane/EtOAc 2:1) afforded 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (**11**) as a mixture of anomers (1.10 g, 90%).[54] This product was used in the next step without further characterization: A solution of product **11** (974 mg, 1.98 mmol) in CH_2Cl_2 (20 mL) was treated with Cl_3CCN (400 μL, 3.96 mmol) and Cs_2CO_3 (440 mg, 1.39 mmol) and the resulting mixture was stirred for 14 h before it

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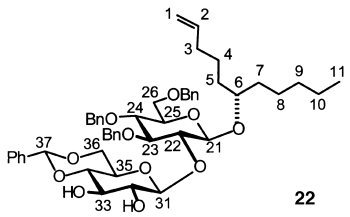
was adsorbed on silica gel and purified by flash chromatography (hexane/EtOAc 4:1) to afford compound **7** as a colorless syrup (1.04 g, 83%). The analytical data are identical to those compiled above.

[(6*S*)-1-Undecen-6-yl] 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (19): A solution of alcohol **18** (478 mg, 0.28 mmol)[22] and $BF_3 \cdot Et_2O$ (13.5 mL of a 0.25 M stock solution in CH_2Cl_2) in CH_2Cl_2/hexane (1:1, 34 mL) was added dropwise over a period of 3 h to a solution of imidate **7** (2.14 g, 3.37 mmol) in CH_2Cl_2/hexane (1:1, 15 mL) at −20 °C. After stirring for an additional 2 h, sat. aq. $NaHCO_3$ (60 mL) was added, the aqueous phase was extracted with EtOAc (3 × 90 mL), the combined organic layers were washed with brine (60 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (pentane/EtOAc 9:1) to give product **19** (1.23 g, 68%) as a colorless solid. M.p. 40–41 °C; $[\alpha]_D^{20} = +4.2$ ($c = 0.73$, CH_2Cl_2); IR (KAP): $\tilde{\nu} = 3064, 3031, 2929, 2859, 1750, 1640, 1497, 1454, 1362, 1232, 1150, 1987, 1058, 1028, 911, 735, 698$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.35–7.24$ (m, 13H), 7.22–7.19 (m, 2H), 5.85–5.71 (m, 1H), 5.03–4.92 (m, 3H), 4.81–4.53 (m, 6H), 4.37 (d, $J = 8.0$ Hz, 1H), 3.71 (d, $J = 3.4$ Hz, 2H), 3.67–4.64 (m, 2H), 3.55–3.44 (m, 2H), 2.04–1.99 (m, 2H), 1.61–1.19 (m, 12H), 0.92–0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.4, 138.6, 138.3, 138.0, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 114.6, 100.8, 83.2, 80.6, 79.3, 78.2, 75.2, 75.0, 73.6, 73.5, 69.0, 34.9, 33.9, 33.6, 31.9, 24.9, 24.2, 22.6, 21.0, 14.1$; MS (EI): *m*/*z* (%): 553 (1), 475 (1), 383 (12), 277 (8), 205 (7), 91 (100); elemental analysis calcd (%) for $C_{40}H_{52}O_7$ (644.84): C 74.50, H 8.13; found: C 74.41, H 8.04.

[(6*S*)-1-Undecen-6-yl] 3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (20): A solution of compound **19** (2.49 g, 3.86 mmol) and NaOMe (140 mg, 2.6 mmol) in MeOH (50 mL) was stirred overnight. The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL), the aqueous phase was extracted with EtOAc (3 × 40 mL), dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (pentane/EtOAc 4:1) to give product **20** (2.30 g, quant.) as a colorless syrup. IR (KBr): $\tilde{\nu} = 3487, 3064, 3030, 2931, 2859, 1640, 1606, 1586, 1497, 1454, 1359, 1113, 1063, 1028, 996, 911, 735, 697$; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.55–7.42$ (m, 15H), 6.02 (ddt, $J = 17.1$, 10.8, 6.4 Hz, 1H), 5.23–5.00 (m, 5H), 4.79–4.73 (m, 3H), 4.48 (d, $J =$ 7.6 Hz, 1H), 3.92–3.60 (m, 7H), 2.25 (br s, OH), 2.25 (m, 2H), 1.82–1.40 (m, 12H), 1.07 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 138.3, 138.0, 137.8, 127.5, 127.1, 127.0, 126.9, 126.8, 126.7, 113.6, 101.2, 83.8, 78.8, 76.9, 74.4, 74.3, 74.0, 73.9, 72.7, 68.5, 34.0, 33.1, 32.7, 31.2, 24.1, 23.7, 21.9, 13.12$; MS (EI): *m*/*z* (%): 511 (2), 341 (3), 253 (3), 235 (4), 181 (6), 163 (10), 91 (100); elemental analysis calcd (%) for $C_{38}H_{50}O_6$ (602.80): C 75.71, H 8.36; found: C 75.75, H 8.30.

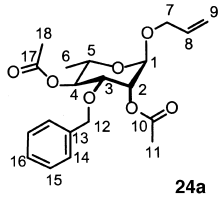
Disaccharide 21: $BF_3 \cdot Et_2O$ (3 mL of a 0.25 M stock solution in Et_2O) was added to a cooled (−20 °C) solution of substrates **15** (1.25 g, 2.52 mmol)[22] and **20** (1.96 g, 3.25 mmol) in CH_2Cl_2 (13.5 mL) and *n*-hexane (13.5 mL). The reaction mixture was stirred at −20 °C for 30 min and for 3 h at ambient temperature prior to the addition of sat. aq. $NaHCO_3$ (20 mL). A standard extractive work-up followed by flash chromatography (pentane/EtOAc 84:16) afforded disaccharide **21** as a pale yellow syrup (1.93 g, 82%). $[\alpha]_D^{20} = -38.6$ ($c = 0.7$, $CHCl_3$); IR (KBr): $\tilde{\nu} = 3067, 2926, 2858, 1756, 1640, 1455, 1239, 1100, 1064, 697$; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.54–7.41$ (m, 5H), 7.30–6.95 (m, 15H), 5.98 (ddt, $J = 17.1$, 10.2, 6.6 Hz, 1H), 5.45 (t, $J = 8.6$ Hz, 1H), 5.32–5.24 (m, 3H), 5.21 (dq, $J = 14.4$, 2.1 Hz, 1H), 5.12 (dq, $J = 10.2$, 1.0 Hz, 1H), 4.88 (AB, $J = 10.5$ Hz, 2H), 4.77 and 4.59 (AB, $J = 11.3$ Hz, 2H), 4.47 (AB, $J = 12.0$ Hz, 2H), 4.30 (d, $J = 7.6$ Hz, 1H), 4.11 (dd, $J = 10.3$, 5.0 Hz, 1H), 3.85 (t, $J = 8.4$ Hz, 1H), 3.70–3.51 (m, 6H), 3.23 (m, 1H), 3.14 (hex., $J = 5.0$ Hz, 1H), 2.19 (m, 1H), 1.77 (s, 3H), 1.71 (s, 3H), 1.68–1.26 (m, 14H), 0.92 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 170.4, 169.7, 139.6, 138.9, 138.7, 137.6, 129.4, 129.2, 128.7, 128.6, 128.2, 127.9, 126.5, 114.7, 101.8, 101.3, 100.7, 85.5, 80.2, 79.3, 78.8, 75.7, 75.1, 73.9, 73.6, 72.5, 69.4, 69.0, 66.7, 35.1, 34.4, 33.7, 32.4, 25.3, 24.5, 23.1, 21.0, 20.9, 14.3$; MS (EI): *m*/*z* (%): 767 (0.44) [$M^+ - 169$], 336 (15), 335 (77), 275 (29), 181 (9), 169 (13), 149 (34), 107 (7), 91 (100), 55 (7), 43 (23); elemental analysis calcd (%) for $C_{55}H_{68}O_{13}$ (937.12): C 70.49, H 7.31; found: C 70.34, H 7.26.

Disaccharide 22: A solution of disaccharide **21** (422 mg, 0.65 mmol) and NaOMe (35 mg, 0.65 mmol) in MeOH (5 mL) was stirred overnight. The solution was diluted with aq. sat. $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 60:40) affording product **22** as a colorless solid (136 mg, 88%). M.p. 82–83 °C; $[\alpha]_D^{20} = -25.8$ ($c = 1.0$, $CHCl_3$); IR (KBr): $\tilde{\nu} = 3451, 3032, 2928, 2864, 1640, 1454, 1362, 1088, 748, 697$; ^{1}H NMR (600 MHz, [$D_8$]toluene): $\delta = 7.53–7.07$ (m, 20H), 5.87 (ddt, $J = 16.9$, 10.2, 6.7 Hz, H-2), 5.25 (s, 1H, H-37), 5.13 (dq, $J = 16.9$, 1.7 Hz, 1H, H-1(*Z*)), 5.06 (ddt, $J =$ 10.3, 1.7, 1.0 Hz, 1H, H-1(*E*)), 4.82 and 4.85 (AB, $J = 11.0$ Hz, 2H, 23-O-CH_2Ph), 4.67 (d, $J = 7.7$ Hz, 1H, H-31), 4.54 and 4.69 (AB, $J = 11.1$ Hz, 2H, 24-O-CH_2Ph), 4.44 and 4.52 (AB, $J = 12.2$ Hz, 2H, 26-O-CH_2Ph), 4.35 (d, $J = 7.6$ Hz, 1H, H-21), 4.20 (dd, $J = 10.2$, 5.0 Hz, 1H, H-36a), 4.0 (m, 1H, H-24), 3.78 (dd, $J = 9.0$, 7.7 Hz, 1H, H-22), 3.70 (m, 1H, H-6), 3.65 (dd, $J =$ 11.0, 4.4 Hz, 1H, H-26a), 3.62 (m, 1H, H-33), 3.61 (m, 1H, H-26b), 3.56 (m, 1H, H-23), 3.55 (br s, 1H, 32-OH), 3.55 (m, 1H, H-36b), 3.47 (ddd, $J = 8.9$, 7.9, 2.5 Hz, 1H, H-32), 3.40 (t, $J = 9.1$ Hz, 1H, H-34), 3.21 (m, 1H, H-35), 3.23 (m, 1H, H-25), 2.23 (br d, $J = 1.6$ Hz, 1H, 33-OH), 2.09 (m, 2H, H-3), 1.66–1.51 (m, 8H, H-4,5,7,8), 1.36 (m, 2H, H-10), 1.31 and 1.36 (m, 2H, H-9), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, [D_8]toluene): $\delta = 139.05$ (d, C-2), 115.03 (t, C-1), 104.54 (d, C-31), 101.93 (d, C-21), 101.79 (d, C-37), 84.81 (d, C-23), 81.16 (d, C-34), 80.45 (d, C-22), 79.63 (d, C-6), 79.07 (d, C-24), 76.67 (d, C-32), 76.00 (t, O-23-*C*H_2Ph), 75.39 (d, C-25), 74.76 (t, O-24-*C*H_2Ph), 73.80 (t, O-26-*C*H_2Ph), 73.45 (d, C-33), 69.33 (t, C-26), 69.01 (t, C-36), 67.42 (d, C-35), 35.42 (t, C-7), 34.57 (t, C-3), 34.19 (t, C-5), 32.53 (t, C-9), 25.45 (t, C-8), 24.72 (t, C-4), 23.21 (t, C-10), 14.43 (q, C-11), phenyl signals: 139.00, 138.96, 138.49, 138.40, 128.56, 128.53, 128.35, 126.86; MS (EI): *m*/*z* (%): 683 (0.3) [$M^+ - 169$], 413 (7), 251 (21), 181 (10), 163 (8), 107 (14), 97 (6), 92 (9), 91 (100), 69 (6), 55 (7); elemental analysis calcd (%) for $C_{51}H_{64}O_{11}$ (853.05): C 71.81, H 7.56; found: C 71.94, H 7.56.



22

Allyl 3-*O*-benzyl-*α*-L-rhamnopyranoside (24): A mixture of allyl *α*-L-rhamnopyranoside (593 mg, 2.9 mmol)[40] and dibutyltin oxide (512 mg, 2.9 mmol) in toluene (10 mL) was refluxed for 3.5 h in a Dean–Stark apparatus. Powdered CsF (624 mg, 5.8 mmol) was added before the mixture was concentrated. The residue was suspended in DMF (10 mL), benzyl bromide (0.49 mL, 5.8 mmol) was added and the resulting mixture was stirred at room temperature overnight. After concentration, the residue was triturated with CH_2Cl_2, the mixture was filtered, and the solids were repeatedly washed with CH_2Cl_2. The combined filtrates were washed with brine, the organic phase was concentrated, and the residue was purified by chromatography (pentane/EtOAc 3:2) to give pure **24** (490 mg, 72%) as a colorless syrup. To unambiguously determine the site of benzylation, a small sample of product **24** was acetylated (Ac_2O, pyridine) to afford allyl 2,4-di-*O*-acetyl-3-benzyl-*α*-L-rhamnopyranoside (**24a**) which exhibits the following analytical and spectroscopic data: $[\alpha]_D^{20} = -39.5$ ($c = 0.85$, $CHCl_3$); IR (KBr): $\tilde{\nu} = 3440, 3031, 2975, 2915, 1647, 1454, 1380, 1050, 739, 700$; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.30$ (dd, 1H, H-15), 7.25 (m, 2H, H-14,16), 5.87 (dddd, $J = 17.0$, 11.0, 6.0, 5.1 Hz, 1H, H-8), 5.35 (dd, $J = 3.5$, 1.8 Hz, 1H, H-2), 5.26 (dt, $J = 17.0$, 1.5 Hz, 1H, H-9(*Z*)), 2.12 (s, 3H, H-11), 5.20 (dt, $J = 10.0$, 1.5 Hz, 1H, H-9(*E*)), 5.01 (t, $J = 10.0$ Hz, 1H, H-4), 4.78 (d, $J = 1.8$ Hz, 1H, H-1), 4.63 (d, $J = 12.2$ Hz, 1H, H-12a), 4.40 (d, $J =$ 12.2 Hz, 1H, H-12b), 4.13 (ddd, $J = 13.0$, 5.1, 1.5 Hz, 1H, H-7a), 3.97 (ddd, $J = 13.0$, 6.0, 1.5 Hz, 1H, H-7b), 3.82 (dd, $J = 10.0$, 3.5 Hz, 1H, H-3), 3.76 (dt, $J = 10.0$, 6.2 Hz, 1H, H-5), 2.00 (s, 3H, H-18), 1.18 (d, $J = 6.2$ Hz, 3H, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 170.40$ (s, C-10), 169.95 (s, C-17), 137.98 (s, C-13), 133.39 (d, $J = 156$ Hz, C-8), 128.29 (d, $J = 160$ Hz, C-15), 127.64 (d, $J = 161$ Hz, C-14), 127.64 (d, $J = 161$ Hz, C-16), 117.70 (t, $J =$ 156 Hz, C-9), 96.85 (d, $J = 171$ Hz, C-1), 74.61 (d, $J = 143$ Hz, C-3), 72.46 (d, $J = 153$ Hz, C-4), 71.25 (t, $J = 143$ Hz, C-12), 68.54 (d, $J = 153$ Hz, C-2), 68.20 (t, $J = 143$ Hz, C-7), 66.57 (d, $J = 145$ Hz, C-5), 21.03 (q, $J = 130$ Hz, C-11), 20.91 (q, $J = 130$ Hz, C-18), 17.44 (q, $J = 128$ Hz, C-6); MS (EI): *m*/*z* (%): 294 (0.3) [M^+], 150 (7), 128 (8), 121 (4), 100 (4), 92 (9), 91 (100), 73 (5),



24a

71 (4), 65 (4), 41 (13); elemental analysis calcd (%) for $C_{16}H_{22}O_5$ (294.34): C 65.29, H 7.53; found: C 65.32, H 7.54.

Allyl 2,4-di-*O*-[(2*S*)-2-methylbutyryl]-3-*O*-benzyl-α-L-rhamnopyranoside (25): A solution of diol **24** (1.11 g, 3.78 mmol), (2*S*)-2-methylbutyric acid (1.65 mL, 8.3 mmol), DCC (3.2 g, 8.3 mmol) and DMAP (198 mg, 0.4 mmol) in CH_2Cl_2 (22 mL) was stirred overnight. MeOH (2 mL) was added to the solution followed by hexane (100 mL) after the mixture had been stirred for another 10 min. Filtration through a pad of Celite, concentration of the filtrate and flash chromatography of the residue (pentane/EtOAc 94:6) gave product **25** as a colorless syrup (1.55 g, 89%). $[\alpha]_D^{20} = -2.9$ ($c = 1.0$, $CHCl_3$); IR (KBr): $\tilde{\nu} = 2972, 2936, 1742, 1457, 1382, 1137, 1075, 699$; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.31-7.21$ (m, 5H), 5.97–5.84 (m, 1H), 5.41 (dd, $J = 3.3$, 1.9 Hz, 1H), 5.37 (dq, $J = 17.2$, 1.6 Hz, 1H), 5.23 (dq, $J = 10.4$, 1.4 Hz, 1H), 5.09 (t, $J = 9.8$ Hz, 1H), 4.80 (d, $J = 1.8$ Hz, 1H), 4.64 and 4.40 (AB, $J = 11.6$ Hz, 2H), 4.18 (ddt, $J = 12.9$, 5.2, 1.5 Hz, 1H), 4.00 (ddt, $J = 12.9$, 6.1, 1.3 Hz, 1H), 3.89 (dd, $J = 9.8$, 3.3 Hz, 1H), 3.87–3.77 (m, 1H), 2.54–2.42 (m, 1H), 2.39–2.27 (m, 1H), 1.76–1.60 (m, 2H), 1.54–1.34 (m, 2H), 1.20 (d, $J = 6.3$ Hz, 3H), 1.15 (d, $J = 7.1$ Hz, 3H), 1.12 (d, $J = 7.1$ Hz, 3H), 0.87 (t, $J = 7.4$ Hz, 3H), 0.86 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 176.1$, 175.6, 137.8, 133.5, 128.1, 127.5, 127.4, 117.7, 97.0, 75.0, 72.0, 71.1, 68.3, 67.9, 66.8, 41.3, 40.9, 26.7, 26.5, 17.5, 16.7, 16.4, 11.7, 11.4; MS (EI): *m*/*z* (%): 462 (0.9) [M^+], 210 (14), 196 (28), 168 (11), 126 (23), 112 (12), 91 (93), 85 (81), 57 (100), 41 (22), 29 (10); elemental analysis calcd (%) for $C_{26}H_{38}O_7$ (462.58): C 67.51, H 8.28; found: C 67.36, H 8.34.

2,4-Di-*O*-[(2*S*)-2-methylbutyryl]-3-*O*-benzyl-α-L-rhamnopyranose (26): A suspension of compound **25** (935 mg, 2 mmol), pyridinium *p*-toluenesulfonate (187 mg, 0.4 mmol) and Pd/C (10% w/w, 40 mg) in MeOH (40 mL) was heated under reflux for 24 h. After cooling to room temperature, the mixture was filtered through a pad of Celite, the filtrate was concentrated and the residue was purified by flash chromatography (pentane/EtOAc 80:20) to afford product **26** as a colorless syrup (680 mg, 80%). Mixture of anomers: $\alpha:\beta = 92:8$ as determined by ^{1}H NMR. $[\alpha]_D^{20} = 15.5$ ($c = 1.1$, $CHCl_3$); IR (KAP): $\tilde{\nu} = 3448, 2971, 2937, 1741, 1457, 1180, 1148, 1092, 699$; ^{1}H NMR (300 MHz, CD_2Cl_2, α-anomer): $\delta = 7.32-7.21$ (m, 5H), 5.41 (dd, $J = 3.3$, 1.9 Hz, 1H), 5.18 (dd, $J = 3.8$, 1.9 Hz, 1H), 5.10 (t, $J = 9.8$ Hz, 1H), 4.65 and 4.42 (AB, $J = 11.6$ Hz, 2H), 4.09–4.00 (m, 1H), 3.93 (dd, $J = 9.8$, 3.3 Hz, 1H), 2.67 (d, $J = 3.8$ Hz, 1H), 2.55–2.43 (m, 1H), 2.40–2.29 (m, 1H), 1.77–1.60 (m, 2H), 1.55–1.32 (m, 2H), 1.19 (d, $J = 6.3$ Hz, 3H), 1.15 (d, $J = 7.0$ Hz, 3H), 1.12 (d, $J = 7.0$ Hz, 3H), 0.88 (t, $J = 7.5$ Hz, 3H), 0.87 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2, α-anomer): $\delta = 176.3$, 175.7, 137.7, 128.1, 127.5, 127.4, 92.5, 74.4, 72.0, 71.1, 68.3, 67.0, 41.2, 40.9, 26.7, 26.5, 17.6, 16.6, 16.4, 11.6, 11.3; MS (EI): *m*/*z* (%): 422 (0.6) [M^+], 196 (24), 170 (12), 112 (24), 95 (12), 91 (70), 85 (100), 57 (95), 41 (11), 29 (11); elemental analysis calcd (%) for $C_{23}H_{34}O_7$ (422.51): C 65.38, H 8.11; found: C 65.44, H 8.06.

***O*-(2,4-Di-*O*-[(2*S*)-2-methylbutyryl]-3-*O*-benzyl-L-rhamnopyranosyl) trichloroacetimidate (27)**: A slurry of compound **26** (333 mg, 0.79 mmol), Cl_3CCN (222 μL, 2.21 mmol) and Cs_2CO_3 (145 mg, 0.44 mmol) in CH_2Cl_2 (10 mL) was stirred overnight at room temperature. The reaction mixture was concentrated and the residue was purified by flash chromatography (pentane/EtOAc 80:20) to give product **27** as a pale yellow syrup (408 mg, 92%). Ratio of anomers $\alpha:\beta = 92:8$ as determined by ^{1}H NMR. $[\alpha]_D^{20} = -12.5$ ($c = 0.75$, $CHCl_3$); IR (KBr): $\tilde{\nu} = 3340, 2971, 2937, 1745, 1676, 1457, 1144, 973, 797$; spectroscopic data of the α-anomer: ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.66$ (br s, 1H), 7.22–7.15 (m, 5H), 6.10 (d, $J = 2.1$ Hz, 1H), 5.40 (dd, $J = 3.3$, 2.1 Hz, 1H), 5.09 (dd, $J = 3.8$, 1.9 Hz, 1H), 5.10 (t, $J = 9.8$ Hz, 1H), 4.65 and 4.42 (AB, $J = 11.6$ Hz, 2H), 4.09–4.00 (m, 1H), 3.93 (dd, $J = 9.8$, 3.3 Hz, 1H), 2.55–2.43 (m, 1H), 2.40–2.29 (m, 1H), 1.77–1.60 (m, 2H), 1.55–1.32 (m, 2H), 1.19 (d, $J = 6.3$ Hz, 3H), 1.15 (d, $J = 7.0$ Hz, 3H), 1.12 (d, $J = 7.0$ Hz, 3H), 0.88 (t, $J = 7.5$ Hz, 3H), 0.87 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 176.3$, 175.8, 160.3, 137.9, 128.6, 128.4, 128.1, 95.5, 74.8, 71.9, 71.6, 70.0, 67.0, 41.6, 41.3, 27.1, 26.9, 17.8, 16.8, 16.6, 11.9, 11.6; MS (EI): *m*/*z* (%): 405 (1.6), 197 (14), 196 (60), 181 (15), 112 (59), 111 (14), 95 (37), 91 (89), 85 (98), 57 (100); elemental analysis calcd (%) for $C_{25}H_{34}Cl_3NO_7$ (566.90): C 52.97, H 6.05; found: C 52.90, H 6.09.

1,2-Di-*O*-(6-heptenoyl)-4,5,6-tri-*O*-benzyl-D-glycopyranose (28): A solution of diol **9** (1.34 g, 3 mmol), 6-heptenoic acid (1.61 mL, 11.9 mmol), DCC (2.45 g, 11.9 mmol), and DMAP (76 mg, 0.6 mmol) in CH_2Cl_2 (17 mL) was stirred overnight. MeOH (1.5 mL) was added followed by hexane (80 mL) after the mixture had been stirred for another 20 min. Filtration of the mixture through a pad of Celite, evaporation of the filtrate, and flash chromatography of the residue (pentane/EtOAc 92:8) afforded compound **28** as a colorless syrup (1.97 g, 99%). Ratio of anomers $\alpha:\beta = 1.7:1$ as determined by NMR. $[\alpha]_D^{20} = +51.8$ ($c = 1.1$, $CHCl_3$); IR (KBr): $\tilde{\nu} = 3064, 2928, 2861, 1751, 1640, 1497, 1454, 1155, 1079, 913, 698$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.36-7.24$ (m, H arom.), 7.18–7.13 (m, H arom.), 6.33 (d, $J = 3.6$ Hz, H-1, α-anomer), 5.85–5.67 (m, 6H), 5.63 (d, $J = 8.3$ Hz, H-1, β-anomer), 5.16 (dd, $J = 9.1$, 8.3 Hz), 5.08 (dd, $J = 10.0$, 3.6 Hz), 5.04–4.91 (m), 4.83–4.72 (m), 4.69–4.47 (m), 3.98 (v.t, $J = 9.4$ Hz), 3.92–3.57 (m), 2.36 (t, $J = 7.3$ Hz), 2.35–2.30 (m), 2.25–2.13 (m), 2.11–1.97 (m), 1.70–1.52 (m), 1.49–1.30 (m); ^{13}C NMR (75 MHz, $CDCl_3$, α-anomer): $\delta = 172.4$, 171.6, 138.2, 138, 137.7, 128.4, 128.1, 127.9, 127.7, 127.5, 114.9, 114.7, 89.7, 79.9, 77.1, 75.3, 73.5, 73.1, 71.8, 67.9, 33.9, 33.3, 28.2, 28.1, 24.3, 24.2, 24.0; characteristic shift of the β-anomer: $\delta = 92.1$; MS (EI): *m*/*z* (%): 579 (3), 451 (7), 345 (7), 217 (4), 181 (5), 111 (11), 92 (8), 91 (100), 83 (9), 55 (17); elemental analysis calcd (%) for $C_{41}H_{50}O_8$ (670.83): C 73.41, H 7.51; found: C 73.34, H 7.59.

2-*O*-(6-Heptenoyl)-4,5,6-tri-*O*-benzyl-D-glucopyranose (29): Hydrazinium acetate (326 mg, 3.57 mmol) was added at 45 °C to a solution of compound **28** (1.87 g, 2.79 mmol) in DMF (27 mL). Heating was discontinued after the hydrazine acetate had dissolved and the resulting mixture was stirred overnight. The reaction was quenched with water (50 mL) and extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with water (40 mL) and brine (40 mL), dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 77:23) to afford product **29** (1.30 g, 83%) as a colorless solid. Mixture of anomers, $\alpha:\beta = 1.7:1$ according to NMR. M.p. 100–101 °C; $[\alpha]_D^{20} = +50.1$ ($c = 1$, $CHCl_3$); IR (KBr): $\tilde{\nu} = 3364, 3065, 2928, 2870, 1725, 1641, 1496, 1453, 1188, 1154, 911, 696$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.36-7.24$ (m), 7.17–7.12 (m), 5.82–5.68 (m, 3H), 5.42 (t, $J = 3.5$ Hz, H-1, α-anomer), 5.01–4.85 (m), 4.84–4.73 (m), 4.64–4.48 (m), 4.10–4.02 (m), 3.74–3.60 (m), 2.90 (dd, $J = 3.4$, 1.4 Hz), 2.38–2.19 (m), 2.05–1.98 (m), 1.66–1.56 (m), 1.43–1.33 (m); ^{13}C NMR (75 MHz, $CDCl_3$, α-anomer): $\delta = 172.9$, 138.4, 138.3, 137.9, 137.6, 128.3, 127.9, 127.4, 114.7, 90.3, 79.7, 78.0, 75.3, 74.9, 73.5, 73.3, 70.0, 68.6, 33.9, 33.2, 28.1, 24.1; characteristic shift of the β-anomer: $\delta = 95.7$; MS (EI): *m*/*z* (%): 341 (2), 182 (2), 181 (6), 108 (2), 107 (3), 92 (8), 91 (100), 79 (3), 77 (3), 65 (4); elemental analysis calcd (%) for $C_{34}H_{40}O_7$ (560.68): C 72.83, H 7.19; found: C 72.66, H 7.14.

***O*-[2-*O*-(6-Heptenoyl)-4,5,6-tri-*O*-benzyl-D-glucopyranosyl] trichloroacetimidate (30)**: A slurry of glucopyranose **29** (3.29 g, 5.87 mmol), Cl_3CCN (1.2 mL, 11.9 mmol) and Cs_2CO_3 (1.12 g, 3.53 mmol) in CH_2Cl_2 (50 mL) was stirred overnight at room temperature. The reaction mixture was quenched with water (50 mL), the aqueous layer was extracted with CH_2Cl_2 (3 × 80 mL), the combined organic phases were dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 90:10) to give product **30** as a pale yellow syrup (3.60 g, 87%). IR (KBr): $\tilde{\nu} = 3342, 3063, 2920, 2863, 1744, 1673, 1640, 1497, 1454, 1287, 1068, 913, 795$; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.56$ (s, 1H), 7.35–7.23 (m, 13H), 7.20–7.12 (m, 2H), 6.54 (d, $J = 3.6$ Hz, 1H), 5.80–5.66 (m, 1H), 5.09 (dd, $J = 10.0$, 3.6 Hz, 1H), 5.00–4.90 (m, 2H), 4.85 and 4.76 (AB, $J = 11.4$ Hz, 2H), 4.82 and 4.57 (AB, $J = 10.6$ Hz, 2H), 4.63 and 4.50 (AB, $J = 12.0$ Hz, 2H), 4.10 (t, $J = 9.5$ Hz, 1H), 4.04–3.99 (m, 1H), 3.91–3.84 (m, 1H), 3.81 (dd, $J = 11.1$, 3.3 Hz, 1H), 3.69 (dd, $J = 11.1$, 1.9 Hz, 1H), 2.21–2.16 (m, 2H), 2.04–1.95 (m, 2H), 1.61–1.51 (m, 2H), 1.41–1.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 172.6$, 160.9, 138.2, 137.8, 128.4, 128.1, 127.9, 127.7, 114.7, 94.0, 91.1, 79.5, 77.0, 75.4, 75.3, 73.5, 73.4, 72.2, 67.9, 33.9, 33.3, 28.2, 24.1; MS (EI): *m*/*z* (%): 345 (2), 252 (4), 250 (4), 181 (4), 111 (5), 92 (8), 91 (100), 83 (3), 55 (8), 41 (3); elemental analysis calcd (%) for $C_{36}H_{40}Cl_3NO_7$ (705.06): C 61.33, H 5.72; found: C 61.19, H 5.80.

3,4-Di-*O*-[(2*S*)-2-methylbutyroyl]-6-*O*-*tert*-butyldimethylsilyl-D-glucal (32): A solution of diol **31** (5.31 g, 20.4 mmol),[44] (2*S*)-2-methylbutyric acid (6.66 mL, 61.2 mmol), DCC (12.6 g, 61.2 mmol), and DMAP (0.5 g, 4.1 mmol) in CH_2Cl_2 (110 mL) was stirred overnight. MeOH (11 mL) was added followed by addition of hexane (400 mL) after the mixture had been stirred for another 20 min. Filtration through a pad of Celite, concentration of the filtrate and flash chromatography of the residue (pentane/EtOAc 98:2) afforded product **32** as a colorless syrup (8.15 g, 93%). $[\alpha]_D^{20} = -16.4$ ($c = 1.7$, $CHCl_3$); IR (KAP): $\tilde{\nu} = 2964, 2935, 2880, 1738, 1650, 1463, 1252, 1141, 838, 778$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.45$ (dd, $J = 6.1$, 1.2 Hz, 1H), 5.33–5.24 (m, 2H), 4.78 (dd, $J = 6.1$, 3.1 Hz, 1H), 4.12–4.06 (m, 1H), 3.83 and 3.78 (ddAB, $J = 11.5$, 5.7, 3.6 Hz, 2H), 2.43–2.29 (m, 2H), 1.75–

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1.60 (m, 2H), 1.52–1.38 (m, 2H), 1.12 (d, J = 7.1 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 0.92–0.86 (m, 15H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.2, 175.1, 146.1, 99.0, 77.5, 67.8, 67.3, 61.7, 41.3, 27.0, 25.9, 18.6, 16.6, 16.5, 11.7, −5.3; MS (EI): m/z (%): 371 (12), 269 (22), 167 (31), 160 (12), 159 (93), 97 (15), 85 (56), 75 (13), 73 (12), 57 (100); elemental analysis calcd (%) for $C_{22}H_{40}O_6Si$ (428.63): C 61.65, H 9.41; found: C 61.56, H 9.35.

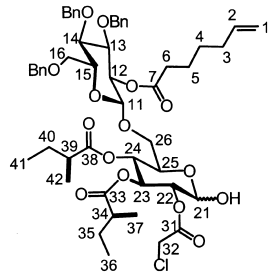
3,4-Di-*O*-[(2*S*)-2-methylbutyroyl]-6-*O*-*tert*-butyldimethylsilyl-D-glucopyranose (33): A solution of OsO_4 (0.05 M in THF, 19 mL) was added to a solution of glucal **32** (8.15 g, 19.0 mmol) and 4-methylmorpholine *N*-oxide (2.66 g, 22.5 mmol) in acetone/H_2O (9:1, 110 mL) and the mixture was stirred for 12 h. The solution was concentrated under reduced pressure and the residue was diluted with sat. aq. $Na_2S_2O_3$ (50 mL). After stirring for 20 min the aqueous phase was extracted with EtOAc (4 × 100 mL), the combined organic layers were washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 70:30) to yield diol **33** as a pale yellow syrup (8.80 g, quant.). $[\alpha]_D^{20}$ = +88.8 (c = 1.05, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3463, 2966, 2931, 2881, 1748, 1463, 1257, 1145, 838, 778; ^{1}H NMR (300 MHz, [D$_8$]toluene, α-anomer): δ = 5.49 (t, J = 9.7 Hz, 1H), 5.30 (t, J = 9.8 Hz, 1H), 4.79 (t, J = 3.9 Hz, 1H), 4.04–3.98 (m, 1H), 3.73–3.65 (m, 2H), 3.53–3.45 (m, 1H), 2.57 (d, J = 3.2 Hz, 1H), 1.78–1.58 (m, 2H), 1.44–1.23 (m, 2H), 1.10 (d, J = 6.9 Hz, 3H), 1.06 (d, J = 7.1 Hz, 3H), 0.98 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 176.3, 175.3, 92.8, 73.6, 71.7, 70.7, 68.2, 62.7, 41.3, 27.1, 26.8, 26.1, 18.7, 16.7, 16.5, 11.8, 11.6, −5.2; MS (EI): m/z (%): 303 (10), 201 (12), 159 (16), 117 (12), 85 (48), 81 (10), 75 (23), 73 (16), 57 (100), 41 (13), 29 (13); elemental analysis calcd (%) for $C_{22}H_{42}O_8Si$ (462.65): C 57.11, H 9.15; found: C 57.19, H 9.11.

1,2-Di-*O*-chloroacetyl-3,4-di-*O*-[(2*S*)-2-methylbutyroyl]-6-*O*-*tert*-butyldimethylsilyl-D-glucopyranose (34): Triethylamine (12 mL, 85.80 mmol), 4-dimethylaminopyridine (301 mg, 2.20 mmol) and chloroacetic acid anhydride (9.65 g, 56.40 mmol) were added at −20 °C to a solution of diol **33** (8.70 g, 14.80 mmol) in CH_2Cl_2 (140 mL) and the resulting mixture was stirred for 3 h while keeping the temperature between −10 and −20 °C. The excess of the anhydride was then hydrolyzed upon addition of sat. aq. $NaHCO_3$ (100 mL), the mixture was extracted with EtOAc (3 × 150 mL), the combined organic layers were washed with sat. aq. $NaHCO_3$ (100 mL) and water (100 mL), dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 92:8) to afford product **34** as a pale yellow syrup (9.66 g, 83%, mixture of anomers). $[\alpha]_D^{20}$ = +71.6 (c = 0.6, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 2965, 2936, 2881, 1776, 1751, 1463, 1256, 1137, 838, 780; ^{1}H NMR (300 MHz, CD_2Cl_2, α-anomer): δ = 6.42 (d, J = 3.7 Hz, 1H), 5.52 (t, J = 9.9 Hz, 1H), 5.25 (t, J = 9.9 Hz, 1H), 5.17 (dd, J = 10.2, 3.7 Hz, 1H), 4.16 (s, 2H), 4.03–3.91 (m, 3H), 3.74–3.64 (m, 2H), 2.40–2.28 (m, 2H), 1.74–1.54 (m, 2H), 1.50–1.34 (m, 2H), 1.08 (t, J = 7.3 Hz, 6H), 0.92–0.82 (m, 15H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2, α-anomer): δ = 175.7, 174.6, 166.2, 165.7, 90.7, 73.3, 71.0, 69.2, 66.9, 61.2, 40.7, 40.6, 40.5, 40.1, 26.3, 25.7, 18.2, 16.2, 16.1, 11.4, 11.3, −5.5; MS (EI): m/z (%): 559 (15), 557 (20), 277 (15), 247 (17), 159 (61), 151 (13), 109 (27), 85 (75), 75 (12), 73 (11), 57 (100); elemental analysis calcd (%) for $C_{26}H_{44}Cl_2O_{10}Si$ (615.61): C 50.73, H 7.20; found: C 50.83, H 7.31.

1,2-Di-*O*-chloroacetyl-3,4-di-*O*-[(2*S*)-2-methylbutyroyl]-D-glucopyranose (35): $BF_3 \cdot Et_2O$ (0.49 mL, 3.4 mmol) was added to a solution of compound **34** (363 mg, 0.59 mmol) in $CHCl_3$ (18 mL). The mixture was stirred for 2 h before being neutralized with sat. aq. $NaHCO_3$. After extraction with CH_2Cl_2 (320 mL) the combined organic layers were dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 70:30) to give product **35** as a colorless solid (239 mg, 81%, mixture of anomers). M.p. 79–80 °C; $[\alpha]_D^{20}$ = +84 (c = 1.0, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3463, 2970, 2936, 2876, 1771, 1736, 1463, 1264, 1181, 1133, 1024; ^{1}H NMR (300 MHz, $CDCl_3$, α-anomer): δ = 6.43 (d, J = 3.7 Hz, 1H), 5.60 (t, J = 9.9 Hz, 1H), 5.19 (dd, J = 10.2, 3.7 Hz, 1H), 5.16 (t, J = 10.0 Hz, 1H), 4.17 (s, 2H), 4.03–3.91 (m, 3H), 3.75–3.52 (m, 2H), 2.45–2.28 (m, 3H), 1.73–1.54 (m, 2H), 1.51–1.33 (m, 2H), 2.20 (d, J = 7.1 Hz, 3H), 2.14 (d, J = 6.9 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 175.5, 166.2, 165.69, 90.6, 72.8, 71.0, 68.4, 67.4, 60.6, 40.8, 40.7, 40.5, 40.1, 26.4, 16.2, 11.5, 11.3; MS (EI): m/z (%): 181 (11), 127 (6), 97 (6), 86 (6), 85 (100), 77 (8), 57 (93), 56 (4), 41 (9), 29 (9); elemental analysis calcd (%) for $C_{20}H_{30}Cl_2O_{10}$ (501.35): C 47.91, H 6.03; found: C 48.49, H 6.38.

2-*O*-Chloroacetyl-3,4-di-*O*-[(2*S*)-2-methylbutyroyl]-D-glucopyranose (36): Hydrazinium acetate (65 mg, 0.72 mmol) was added to a solution of compound **35** (302 mg, 0.6 mmol) in DMF (5.5 mL). After stirring for 10 min, the reaction was quenched with water (10 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 3:2) to give product **36** as a colorless syrup (202 mg, 79%, mixture of anomers). $[\alpha]_D^{20}$ = +60.3 (c = 1.9, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3456, 2971, 2939, 2880, 1748, 1464, 1262, 1183, 1151, 1087, 1052; ^{1}H NMR (300 MHz, $CDCl_3$, α-anomer): δ = 6.43 (d, J = 3.7 Hz, 1H), 5.67 (t, J = 9.9 Hz, 1H), 5.19 (dd, J = 10.2, 3.7 Hz, 1H), 5.16 (t, J = 10.0 Hz, 1H), 4.17 (s, 2H), 3.99–3.91 (m, 3H), 3.75–3.52 (m, 2H), 2.45–2.28 (m, 3H), 1.74–1.54 (m, 2H), 1.51–1.34 (m, 2H), 1.10 (d, J = 7.1 Hz, 3H), 1.07 (d, J = 6.9 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.4, 175.6, 166.8, 89.7, 74.8, 73.0, 69.4, 68.6, 61.1, 40.8, 40.5, 26.4, 16.2, 11.5, 11.4; MS (EI): m/z (%): 233 (4), 175 (5), 98 (11), 97 (5), 86 (6), 85 (100), 81 (5), 57 (76), 41 (8), 29 (7); elemental analysis calcd (%) for $C_{18}H_{29}ClO_9$ (424.87): C 50.88, H 6.88; found: C 50.74, H 6.86.

Disaccharide 37: $BF_3 \cdot Et_2O$ (8.8 mL of a stock solution, c = 0.25 M in CH_2Cl_2) was added to a solution of imidate **30** (3.10 g, 4.4 mmol) and diol **36** (1.50 g, 3.67 mmol) in CH_2Cl_2 (40 mL) at −20 °C. After stirring 1.5 h, the reaction was quenched with sat. aq. $NaHCO_3$ (60 mL), the aqueous phase was extracted with CH_2Cl_2 (3 × 80 mL), the combined organic layers were dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 77:23) to give product **37** as a colorless syrup (3.70 g, 86%). Mixture of anomers: α:β = 7:3 as determined by HPLC (125 mm Nucleosil-5-100-C18/A, ∅2.0 mm, MeCN/H_2O 85:15, 0.2 mL min^{-1}, 6.0 MPa, 313 K; α-anomer: 12.24 min retention time; β-anomer: 10.90 min retention time). $[\alpha]_D^{20}$ = +27.1 (c = 0.85, $CHCl_3$); IR (KAP): $\tilde{\nu}$ = 3470, 3064, 2966, 2934, 1747, 1640, 1497, 1455, 1362, 1150, 1071, 913, 737; ^{1}H NMR (600 MHz, CD_2Cl_2, characteristic and resolved signals of



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the α-anomer): δ = 5.55 (t, J = 9.5 Hz, 1H, H-23), 5.43 (d, J = 3.6 Hz, 1H, H-21), 4.91 (d, J = 3.6 Hz, 1H, H-22), 4.36 (t, J = 8.0 Hz, 1H, H-11), 4.10 and 4.03 (d, 2H, H-32); ^{13}C NMR (150 MHz, CD_2Cl_2, major isomer): δ = 175.81 (s, C-33), 175.40 (s, C-38), 172.78 (s, C-7), 166.84 (s, C-31), 139.00 (d, C-2), 114.72 (t, C-1), 101.59 (d, C-11), 90.03 (d, C-21), 83.18 (d, C-13), 78.16 (d, C-14), 75.25 (d, C-15), 73.30 (d, C-22), 73.15 (d, C-12), 69.53 (d, C-23), 69.26 (t, C-16), 68.97 (d, C-24), 68.64 (t, C-26), 68.44 (d, C-25), 41.15 (d, C-34), 41.11 (t, C-32), 41.11 (d, C-39), 34.30 (t, C-6), 33.76 (t, C-3), 28.74 (t, C-4), 26.76 (t, C-35), 26.76 (t, C-40), 24.57 (t, C-5), 16.45 (q, C-42), 16.41 (q, C-37), 11.76 (q, C-41), 11.56 (q, C-36), phenyl signals: 138.71, 138.49, 138.27, 128.0–128.8; MS (ESI) m/z: 989 [M^++Na]; elemental analysis calcd (%) for $C_{52}H_{67}ClO_{15}$ (967.53): C 64.55, H 6.98; found: C 64.48, H 6.90.

Disaccharide 38: A solution of compound **37** (325 mg, 0.34 mmol), Cl_3CCN (71 μL, 0.71 mmol) and Cs_2CO_3 (64 mg, 0.2 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 4 h. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 84:16) to give imidate **38** as a colorless syrup (202 mg, 54%). $[\alpha]_D^{20}$ = +21.5 (c = 2.3, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2, characteristic signals): δ = 8.65 (s, 1H, NH), 6.49 (d, J = 3.6 Hz, 1H), 5.68 (ddt, J = 17.1, 10.8, 6.4 Hz, 1H), 5.53 (t, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 176.1, 175.6, 172.9, 167.1, 161.5, 139.5, 139.1, 139.0, 129.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2,

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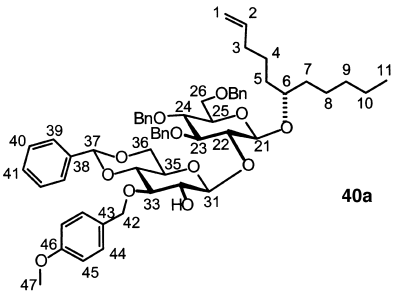
115.0, 101.6, 93.5, 83.6, 78.6, 75.9, 75.7, 75.6, 74.1, 73.2, 72.3, 72.2, 69.8, 69.5, 68.0, 67.3, 41.5, 41.4, 41.2, 34.6, 34.2, 29.2, 27.2, 24.9, 16.9, 16.8, 12.1, 12.0; elemental analysis calcd (%) for $C_{52}H_{67}ClO_{15}$ (967.53): C 64.55, H 6.98; found: C 64.46, H 6.96.

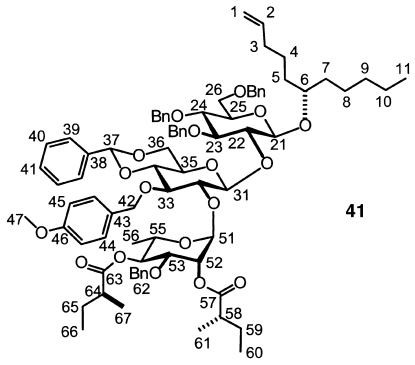
Disaccharides 39 and 40: A mixture of substrate **22** (1.43 g, 1.7 mmol) and dibutyltin oxide (0.41 g, 1.7 mmol) in toluene (8 mL) was heated under reflux for 4.5 h in a Dean–Stark apparatus. Powdered CsF (0.51 g, 3.4 mmol) was added before the mixture was concentrated. The residue was suspended in DMF (8 mL), *p*-methoxybenzyl chloride (0.45 mL, 3.4 mmol) and tetra-*n*-butylammonium iodide (0.06 g, 0.17 mmol) were introduced, and the resulting mixture was stirred at room temperature for 16 h. After concentration, the residue was triturated with CH_2Cl_2, the mixture was filtered, the solid residues were carefully rinsed with CH_2Cl_2, the combined filtrates were washed with brine, dried (Na_2SO_4) and concentrated. The crude material thus obtained was purified by flash chromatography (pentane/EtOAc 82:18) to afford a mixture of the regioisomers **39a** and **40a** (1.32 g, 82%) in a 1:2 ratio (NMR and HPLC).



These products can be separated by crystallization: For this purpose, the mixture was suspended in MeOH (20 mL), the suspension was filtered, the solid residue was dissolved in the minimum amount of MeCN. Product **40a** was crystallized by keeping this solution in a refrigerator overnight. The resulting material was recrystallized again from MeCN, thus affording compound **40a** in > 99% purity. M.p. 138–139 °C; $[\alpha]_D^{20} = -24.8$ ($c = 1.2$, CH_2Cl_2); IR (KBr): $\tilde{\nu} = 3472, 2914, 2871, 1616, 1516, 1452, 1516, 1096, 1064, 698$; ^{1}H NMR (600 MHz, [D$_8$]toluene): $\delta = 7.57$ (m, 1H, H-39), 7.32 (m, 1H, H-44), 7.20–7.08 (m, 19H), 6.76 (m, 1H, H-45), 5.88 (ddt, $J = 16.9$, 10.1, 6.7 Hz, 1H, H-2), 5.13 (dq, $J = 16.9$, 1.7 Hz, 1H, H-1(*Z*)), 5.06 (ddt, $J = 10.2$, 1.7, 1.2 Hz, 1H, H-1(*E*)), 4.90 (d, $J = 11.7$ Hz, 1H, H-42a), 4.86 (d, $J = 11.7$ Hz, 1H, H-42b), 4.85 (s, 2H, 23-OCH_2Ph), 4.70 (d, $J = 7.5$ Hz, 1H, H-31), 4.55 and 4.72 (AB, $J = 11.4$ Hz, 2H, 24-OCH_2Ph), 4.44 and 4.52 (AB, $J = 12.2$ Hz, 2H, 26-OCH_2Ph), 4.36 (d, $J = 7.7$ Hz, 1H, H-21), 4.23 (dd, $J = 10.3$, 5.0 Hz, 1H, H-36a), 3.80 (dd, $J = 7.8$, 8.9 Hz, 1H, H-22), 3.70 (m, 1H, H-6), 3.70 (m, H-32), 3.65 (dd, $J = 11.0$, 4.4 Hz, 1H, H-26a), 3.61 (m, H-26b), 3.59 (m, H-23), 3.59 (m, H-24), 3.56 (m, H-33), 3.55 (m, H-34), 3.44 (d, $J = 2.5$ Hz, 1H, OH), 3.34 (s, 3H, H-47), 3.24 (m, 1H, H-25), 3.20 (m, 1H, H-35), 2.10 (m, 1H, H-3), 1.69–1.30 (m, 12H, H-4,5,7,8,9,10), 0.94 (t, $J = 7.1$ Hz, 3H, H-11); ^{13}C NMR (150 MHz, [D$_8$]toluene): $\delta = 159.64$ (s, C-46), 139.09 (d, C-2), 139.05 (s, C-38), 131.83 (s, C-43), 129.67 (d, C-44), 126.72 (d, C-39), 115.01 (t, C-1), 113.87 (d, C-45), 104.97 (d, C-31), 101.94 (d, C-21), 101.56 (d, C-37), 84.81 (d, C-23), 81.81 (d, C-34), 80.75 (d, C-22), 79.96 (d, C-33), 79.60 (d, C-6), 79.10 (d, C-24), 76.89 (d, C-32), 76.05 (t, 23-OCH_2Ph), 75.39 (d, C-25), 74.75 (t, 24-OCH_2Ph), 74.15 (t, C-42), 73.80 (t, 26-OCH_2Ph), 69.36 (t, C-26), 69.12 (t, C-36), 67.25 (d, C-35), 54.60 (q, C-47), 35.44 (t, C-7), 34.59 (t, C-3), 34.20 (t, C-5), 32.55 (t, C-9), 25.46 (t, C-8), 24.73 (t, C-4), 23.22 (t, C-10), 14.43 (q, C-11), phenyl signals obscured by signals of [D$_8$]toluene; MS (EI): *m*/*z* (%): 803 (0.4) [$M^+ - 169$], 211 (4), 181 (7), 163 (4), 137 (4), 122 (9), 121 (100), 107 (5), 91 (64), 83 (4) 55 (5); elemental analysis calcd (%) for $C_{59}H_{72}O_{12}$ (973.20): C 72.81, H 7.46; found: C 72.75, H 7.37.

For analytical purposes, small samples of **39a** and **40a** were acetylated (Ac_2O, pyridine, CH_2Cl_2). The NMR spectra of the acetates **39b** and **40b** allow the site of *p*-methoxybenzylation in these products to be determined beyond doubt. A comparison of relevant signals of these isomers is given in Table 1.

Trisaccharide 41: TMSOTf (360 μL of a stock solution, $c = 0.014$ M in Et_2O) was added to a cooled (−20 °C) solution of trichloroacetimidate **27** (326 mg, 0.58 mmol) and disaccharide **40** (306 mg, 0.31 mmol) in Et_2O/THF (3:1, 3.2 mL) and the resulting mixture was stirred for 3 h. Quenching of the reaction with sat. aq. $NaHCO_3$ (5 mL) followed by a standard extractive work-up and flash chromatography (pentane/EtOAc, 92:8 → 86:14) afforded a mixture containing trisaccharide **41** and the homodimer derived from the rhamnosyl donor **27** (346 mg, 9:1 ratio as determined by HPLC). This mixture was separated by preparative HPLC (column: 125 mm N-5-C18/A, ∅2.0 mm, MeCN/H_2O 99:1, 0.2 mL min^{-1}, 4.0 MPa, 313 K; dimers derived from **27**: 3.62 and 4.03 min retention time, compound **41**: 23.21 min retention time) to give pure **41** as pale yellow syrup (269 mg, 62%). $[\alpha]_D^{20} = -5.6$ ($c = 1.8$, CH_2Cl_2); IR (KBr): $\tilde{\nu} = 3091, 2971, 2937, 1741, 1461, 1378,$



1180, 1092, 749; ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 7.51$ (m, 1H, H-39), 7.40 (m, 1H, H-40), 7.39 (m, 1H, H-41), 7.29 (m, 1H, H-44), 6.86 (m, 1H, H-45), 5.90 (ddt, $J = 17.0$, 10.3, 6.6 Hz, 1H, H-2), 5.59 (s, 1H, H-37), 5.51 (dd, $J = 3.3$, 1.8 Hz, 1H, H-52), 5.34 (d, $J = 1.8$ Hz, 1H, H-51), 5.09 (dq, $J = 17.0$, 1.8 Hz, 1H, H-1(*Z*)), 5.06 (d, $J = 7.7$ Hz, 1H, H-31), 5.02 (t, $J = 9.7$ Hz, 1H, H-54), 5.00 (m, 1H, H-1(*E*)), 4.89 (s, 2H, 23-OCH_2Ph), 4.75 and 4.85 (d each, $J = 10.7$ Hz, 1H each), 4.67 and 4.80 (d each, $J = 11.1$ Hz, 1H each, 24-OCH_2Ph), 4.56 and 4.63 (d each, $J = 12.0$ Hz, 26-OCH_2Ph), 4.50 (dq, $J = 9.9$, 6.2 Hz, 1H, H-55), 4.35 (dd, $J = 10.5$, 5.0 Hz, 1H, H-36a), 4.27 (d, $J = 7.7$ Hz, 1H, H-21), 3.91 and 4.42 (d each, $J = 11.3$ Hz, 1H each, H-62), 3.85 (dd, $J = 9.7$, 3.3 Hz, 1H, H-53), 3.80 (dd, $J = 7.7$, 8.8 Hz, 1H, H-22), 3.77 (m, 1H, H-33), 3.77 (s, 3H, H-47), 3.76 (m, 1H, H-36b), 3.75 (m, 2H, H-26), 3.70 (t, $J = 9.4$ Hz, 1H, H-34), 3.65 (m, 1H, H-23), 3.65 (m, 1H, H-32), 3.62 (t, $J = 9.2$ Hz, 1H, H-24), 3.57 (m, 1H, H-6), 3.38 (dt, $J = 9.4$, 2.9 Hz, 1H, H-25), 3.31 (ddd, $J = 9.4$, 9.7, 5.5 Hz, 1H, H-35), 2.46 (m, 1H, H-58), 2.29 (m, 1H, H-64), 2.11 (m, 2H, H-3), 1.66 and 1.53 (m, 2H, H-4), 1.53 (m, 2H, H-5), 1.52 and 1.65 (m, 2H, H-7), 1.47 and 1.69 (m, 1H each, H-59), 1.37 (m, 2H, H-8), 1.33 and 1.59 (m, 1H each, H-65), 1.31 (m, 2H, H-10), 1.29 (m, 2H, H-9), 1.21 (d, $J = 6.2$ Hz, 3H, H-56), 1.14 (d, $J = 7.0$ Hz, 3H, H-61), 1.04 (d, $J = 7.1$ Hz, 3H, H-67), 0.90 (t, $J = 7.1$ Hz, 3H, H-11), 0.87 (t, $J = 7.3$ Hz, 3H, H-60), 0.78 (t, $J = 7.4$ Hz, 3H, H-66); ^{13}C NMR (150 MHz, CD_2Cl_2): $\delta = 175.85$ (s, C-57), 175.54 (s, C-63), 156.81 (s, C-46), 139.63 (d, C-2), 138.04 (s, C-38), 130.63 (d, C-44), 130.60 (s, C-43), 129.25 (d, C-41), 128.56 (d, C-40), 126.41 (d, C-39), 114.85 (t, C-1), 114.05 (d, C-45), 102.19 (d, $J = 156$ Hz, C-21), 101.48 (d, $J = 162$ Hz, C-37), 100.98 (d, $J = 165$ Hz, C-31), 98.96 (dd, $J = 175$, 5 Hz, C-51), 86.79 (d, C-23), 82.68 (d, C-34), 81.80 (d, C-6), 81.17 (d, C-33), 78.99 (d, C-24), 77.62 (d, C-32), 76.96 (d, C-22), 76.04 (d, C-53), 75.84 (t, C-29), 75.43 (d, C-25), 74.91 (t, C-28), 74.56 (t, C-42), 73.88 (t, C-27), 72.66 (d, C-54), 71.42 (t, C-62), 69.43 (t, C-26), 69.14 (t, C-36), 67.82 (d, C-52), 66.86 (d, C-55), 66.28 (d, C-35), 55.50 (q, C-47), 41.78 (d, C-64), 41.29 (d, C-58), 35.18 (t, C-7), 34.49 (t, C-3), 33.94 (t, C-5), 32.45 (t, C-9), 27.10 (t, C-59), 26.99 (t, C-65), 25.27 (t, C-8), 24.23 (t, C-4), 23.09 (t, C-10), 17.01 (q, C-67), 16.65 (q, C-61), 17.93 (q, C-56), 14.29 (q, C-11), 11.89 (q, C-66), 11.62 (q, C-60); MS (EI): *m*/*z* (%): 775 (12), 406 (13), 405 (51), 297 (12), 195 (16), 181 (11), 121 (100), 91 (80), 85 (46), 57 (20); elemental analysis calcd (%) for $C_{82}H_{104}O_{18}$ (1377.69): C 71.49, H 7.61; found: C 71.32, H 7.54.

Trisaccharide 42: DDQ (22 mg, 0.1 mmol) was added to a solution of compound **41** (109 mg, 0.08 mmol) in CH_2Cl_2/H_2O (17:1, 990 μL). After stirring for 3 h, the reaction was quenched with sat. aq. $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water (5 mL) and brine (5 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (pen-

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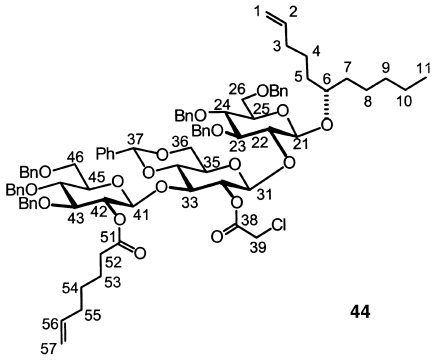
tane/EtOAc 94:6 → 86:14) to give product **42** (71 mg, 71 %) as a pale yellow syrup. $[\alpha]_D^{20} = -11.9$ ($c = 2.3$, CH_2Cl_2); IR (KBr): $\tilde{\nu} = 3458, 3065, 2969, 2934, 1742, 1498, 1455, 1365, 1142, 1076, 698$; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta =$ 7.49–7.00 (m, 25H), 5.91 (ddt, $J = 17.1, 10.3, 6.6$ Hz, 1H), 5.51 (s, 1H), 5.48 (m, 1H), 5.33 (dd, $J = 7.1, 1.5$ Hz, 1H), 5.12–4.96 (m, 4H), 4.89 (AB, $J =$ 7.2 Hz, 2H), 4.78 and 4.63 (AB, $J = 11.1$ Hz, 2H), 4.55 (AB, $J = 12.7$ Hz, 2H), 4.44–4.24 (m, 5H), 3.97 (d, $J = 11.4$ Hz, 1H), 3.84–3.92 (m, 2H), 3.82–3.54 (m, 7H), 3.47 (t, $J = 9.3$ Hz, 1H), 3.39 (m, 1H), 3.28 (dt, $J = 9.7$, 5.0 Hz, 1H), 2.72 (brs, OH), 2.45 (hex., $J = 6.9$ Hz, 1H), 2.28 (hex., $J =$ 6.9 Hz, 1H), 2.12–2.01 (m, 2H), 1.71–1.24 (m, 3H), 1.19 (d, $J = 6.2$ Hz, 3H), 1.12 (d, $J = 6.9$ Hz, 3H), 1.03 (d, $J = 7.0$ Hz, 3H), 0.92–0.83 (m, 6H), 0.77 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 176.1, 175.6, 139.7, 138.9, 138.8, 138.6, 138.3, 137.8, 129.5, 129.0, 128.7, 128.6, 128.4, 128.0, 127.9, 127.7, 127.6, 126.6, 114.8, 114.1, 102.2, 102.0, 100.9, 98.8, 86.7, 81.7, 81.3, 78.9, 78.6, 77.1, 76.0, 75.9, 75.8, 75.4, 75.3, 75.0, 73.9, 72.6, 71.5, 69.4, 69.1, 67.9, 67.1, 66.2, 41.7, 41.3, 35.2, 34.5, 33.9, 32.4, 27.1, 27.0, 25.3, 24.2, 23.1, 17.9, 17.0, 16.6, 14.3, 11.9, 11.6$; MS (EI): m/z (%): 655 (6), 406 (5), 405 (20), 196 (6), 181 (8), 107 (6), 91 (100), 85 (42), 83 (5), 57 (32), 55 (5); elemental analysis calcd (%) for $C_{74}H_{96}O_{17}$ (1257.54): C 70.68, H 7.69; found: C 70.56, H 7.78.

Trisaccharides 43 and 44: TMSOTf (200 μL of a stock solution, $c = 0.014$ M in CH_2Cl_2) was added to a solution of imidate **30** (102 mg, 0.14 mmol) and diol **22** (100 mg, 0.12 mmol) in CH_2Cl_2 (1.2 mL) at −20 °C. After stirring for 3 h, the reaction was quenched with sat. aq. $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc, 78/22) to give product **43** as a colorless syrup (149 mg, 90 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.33-7.07$ (m, 35H), 5.90 (brs, OH), 5.75 (ddt, $J = 17.0, 10.3, 6.6$ Hz, 1H), 5.64 (ddt, $J =$ 17.0, 10.2, 6.7 Hz, 1H), 5.38 (s, 1H), 5.22–5.19 (m, 2H), 4.97–4.30 (m, 18H), 4.15 (dd, $J = 10.4, 4.8$ Hz, 1H), 3.73 (t, $J = 9$ Hz, 1H), 3.64–3.18 (m, 16H), 2.05–1.83 (m, 6H), 1.48–1.16 (m, 16H), 0.80 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 172.8, 139.3, 138.9, 138.8, 138.7, 138.6, 138.5, 138.3, 137.9, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 126.6, 114.8, 114.7, 104.4, 102.0, 101.3, 100.8, 84.2, 83.3, 81.1, 80.0, 79.8, 79.6, 79.0, 78.2, 76.2, 75.8, 75.3, 75.2, 75.1 (2x), 75.0, 73.8, 73.7, 73.6, 69.3, 69.1, 69.0, 67.3, 35.0, 34.4, 34.3, 33.8, 33.6, 28.7, 25.11, 24.6, 24.5, 23.1, 14.4, 14.3$; elemental analysis calcd (%) for $C_{85}H_{102}O_{17}$ (1395.71): C 73.15, H 7.37; found: C 73.09, H 7.33.

To determine the site of glycosylation unambiguously, this product was further analyzed after conversion of a small sample into chloroacetate **44** on treatment with chloroacetic acid anhydride and pyridine. Compound **44**



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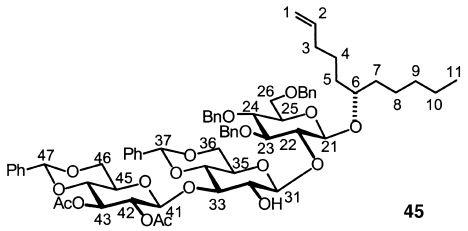
gave the following spectroscopic properties: ^{1}H NMR (600 MHz, [D$_8$]toluene, fully resolved signals only): $\delta = 7.59-7.05$ (m, 35H, Ph), 6.02 (ddt, $J =$ 17.0, 10.2, 6.6 Hz, 1H, H-2), 5.70 (ddt, $J = 17.0, 10.2, 6.7$ Hz, 1H, H-56), 5.24 (dq, $J = 17.0$, 1.8 Hz, 1H, H-1(Z)), 5.17 (ddt, $J = 10.2$, 1.8, 1.2 Hz, 1H, H-1(E)), 5.16 (d, $J = 7.9$ Hz, 1H, H-31), 4.98 (dq, $J = 17.0$, 2.0 Hz, 1H, H-57(Z)), 4.94 (ddt, $J = 10.2$, 2.0, 1.2 Hz, 1H, H-57(E)), 4.75 (d, $J = 7.9$ Hz, 1H, H-41), 4.31 (d, $J = 7.2$ Hz, 1H, H-21), 4.16 (dd, $J = 10.4$, 5.0 Hz, 1H, H-36a), 3.98 (t, $J = 9.1$ Hz, 1H, H-33), 3.94 (d, $J = 4.0$ Hz, 2H, H-39), 3.87 (dd, $J = 7.6$ Hz, 1H, H-22), 3.75 (dd, $J = 12.8, 11.1$ Hz, 1H, H-46a), 3.54 (t, $J = 9.1$ Hz, 1H, H-43), 3.50 (m, 1H, H-45), 3.40 (dd, $J = 9.5, 9.1$ Hz, 1H, H-44), 2.47 (dt, $J = 16.2, 7.4$ Hz, 1H, H-52a), 2.17 (dt, $J = 16.2, 7.6$ Hz, 1H, H-52b); ^{13}C NMR (150 MHz, [D$_8$]toluene): $\delta = 171.97$ (s, C-51), 165.58 (s, C-38), 139.39 (d, C-2), 138.74 (d, C-56), 115.19 (t, C-1), 114.77 (t, C-57), 101.63 (d, C-37), 101.39 (d, C-21), 100.81 (d, C-41), 100.25 (d, C-31), 86.05 (d, C-23), 83.61 (d, C-43), 79.85 (d, C-6), 79.54 (d, C-34), 79.01 (d, C-24), 78.50 (d, C-22), 78.47 (d, C-44), 77.47 (d, C-33), 76.26 (d, C-45), 76.07 (d, C-32), 75.44 (t, 23-OCH_2Ph), 75.26 (d, C-25), 74.88 (t, 44-OCH_2Ph), 74.75 (t, 24-OCH_2Ph), 74.60 (t, 43-OCH_2Ph), 74.01 (t, 46-OCH_2Ph), 73.78 (26-OCH_2Ph), 73.41 (d, C-42), 69.87 (t, C-46), 69.27 (t, C-26), 68.82 (t, C-36), 67.24 (d, C-35), 41.04 (t, C-39), 35.38 (t, C-7), 34.59 (t, C-3), 34.20 (t, C-5), 34.13 (t, C-52), 33.86 (t, C-55), 32.52 (t, C-10), 28.78 (t, C-54), 25.56 (t, C-8), 24.67 (t, C-53), 24.64 (t, C-4), 23.20 (t, C-9), 14.43 (q, C-11), phenyl signals: 139.18, 139.12, 139.01, 139.00, 138.98, 138.89, 138.20, 128.65, 128.54, 128.52, 128.51, 128.48, 128.45, 128.02, 127.85, 127.69, 126.94.

Trisaccharide 45: TMSOTf (200 μL of a stock solution, $c = 0.014$ M in CH_2Cl_2) was added to a solution of imidate **15** (71 mg, 0.14 mmol) and diol **22** (100 mg, 0.12 mmol) in CH_2Cl_2 (1.2 mL) at −20 C. After stirring for 3 h, the reaction was quenched with sat. aq. $NaHCO_3$ (5 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated, and the residue was purified by flash chromatography (pentane/EtOAc 7:3) to give product **45** (106 mg, 77 %) as a colorless solid. $[\alpha]_D^{20} = -48.0$ ($c = 0.51$, CH_2Cl_2); IR (KAP): $\tilde{\nu} =$ 3431, 3065, 3033, 2929, 2868, 1755, 1640, 1497, 1454, 1370, 1243, 1219, 1097,



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1030, 915, 750, 699; ^{1}H NMR (600 MHz, [D$_8$]toluene): $\delta = 7.75-7.06$ (m, 25H, Ph), 5.86 (ddt, $J = 17.0$, 10.1, 6.7 Hz, 1H, H-2), 5.44 (dd, $J = 9.5$, 8.0 Hz, 1H, H-43), 5.29 (dd, $J = 8.0$, 7.1 Hz, 1H, H-42), 5.20 (s, 1H, H-37), 5.13 (ddt, $J = 17.0$, 2.0, 1.8 Hz, 1H, H-1(Z)), 5.07 (ddt, $J = 10.1$, 2.0, 1.2 Hz, 1H, H-1(E)), 5.03 (s, 1H, H-47), 4.93 (d, $J = 7.0$ Hz, 1H, H-41), 4.84 (s, 2H, 23-OCH_2Ph), 4.64 (d, $J = 7.7$ Hz, 1H, H-31), 4.53 and 4.66 (AB, $J = 11.5$ Hz, 2H, 24-OCH_2Ph), 4.43 and 4.51 (AB, $J = 12.0$ Hz, 2H, 26-OCH_2Ph), 4.36 (d, $J = 7.6$ Hz, 1H, H-21), 4.23 (dd, $J = 10.3$, 5.0 Hz, 1H, H-36a), 4.10 (dd, $J = 10.3$, 5.0 Hz, 1H, H-46a), 3.78 (t, $J = 9.1$ Hz, 1H, H-33), 3.75 (dd, $J = 8.9$, 7.8 Hz, 1H, H-22), 3.70 (d, $J = 2.4$ Hz, 1H, 32-OH), 3.65 (m, 1H, H-6), 3.65 (dd, $J = 11.1$, 4.4 Hz, 1H, H-26a), 3.61 (m (overlapped), 1H, H-24), 3.60 (m (overlapped), 1H, H-26b), 3.60 (m (overlapped), 1H, H-32), 3.59 (m (overlapped), 1H, H-44), 3.58 (m (overlapped), 1H, H-23), 3.53 (t, $J =$ 10.2 Hz, 1H, H-36b), 3.50 (t, $J = 10.2$ Hz, 1H, H-46b), 3.44 (t, $J = 9.4$ Hz, 1H, H-34), 3.30 (dt, $J = 10.0$, 5.0 Hz, 1H, H-45), 3.23 (m (overlapped), 1H, H-25), 3.22 (m (overlapped), 1H, H-35), 2.09 (m, 2H, H-3), 1.81 (s, 3H, -OC(O)CH_3), 1.73 (s, 3H, -OC(O)CH_3), 1.70–1.50 (m, 8H, H-4,5,7,8), 1.40–1.30 (m, 4H, H-9,10), 0.95 (t, $J = 7.1$ Hz, 3H, H-11); ^{13}C NMR (150 MHz, [D$_8$]toluene): $\delta = 138.98$ (d, C-2), 115.09 (t, C-1), 105.09 (d, C-31), 101.55 (d, C-47), 101.78 (d, C-21), 101.78 (d, C-37), 101.60 (d, C-41), 84.42 (d, C-23), 81.34 (d, C-22), 80.26 (d, C-33), 80.16 (d, C-34), 79.47 (d, C-6), 79.13 (d, C-24), 78.29 (d, C-44), 76.36 (d, C-32), 75.95 (t, 23-OCH_2Ph), 75.35 (d, C-25), 74.74 (t, 24-OCH_2Ph), 73.81 (t, 26-OCH_2Ph), 73.70 (d, C-42), 72.79 (d, C-43), 69.26 (t, C-26), 68.99 (t, C-36), 68.90 (t, C-46), 67.37 (d, C-35), 66.53 (d, C-45), 35.38 (t, C-7), 34.54 (t, C-3), 34.19 (t, C-5), 32.51 (t, C-10), 25.43 (t, C-8), 24.80 (t, C-4), 23.21 (t, C-9), 14.44 (q, C-11), acetyl signals: 169.50 (s), 169.399 (s), 20.53 (q), 20.31 (q), phenyl signals: 138.94, 138.86, 138.34, 138.29, 138.08, 138.29, 138.08, 128.93, 128.57, 128.53, 128.25, 128.19, 126.76, 126.75; MS (EI): m/z (%): 335 (44), 275 (12), 181 (12), 149 (33), 127 (13), 107 (14), 105 (11), 91 (100), 69 (11), 43 (24); elemental analysis calcd (%) for $C_{68}H_{82}O_{18}$ (1187.37): C 68.78, H 6.96; found: C 68.72, H 6.95.

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