Glycosyl cations in glycosylation reactions

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Chapter 6

Summary and Perspectives

Summary

The central reaction in synthetic carbohydrate chemistry is the glycosylation reaction, in which two building blocks are united to form more complex carbohydrates. Insufficient knowledge of this reaction thwarts the routine assembly of synthetic oligosaccharides. In essence, the glycosylation reaction is a substitution reaction between a nucleophile and an electrophile. Figure 1 depicts the general mechanism for the glycosylation reaction, in which the first step consists of the activation of a donor molecule by a promotor system. This activation leads to an array of reactive intermediates, including covalent species which can partake in S_N2-like pathways, while cationic intermediates can undergo S_N1-type substitutions. Glycosyl cations, also known as glycosyl oxocarbenium ions, are key reactive intermediates in the S_N1-like pathways of the glycosylation reaction. Although significant progress has been made in the field, studying these highly reactive intermediate remains to date a daunting challenge and lies at the forefront of current efforts to advance glycosylation chemistry.

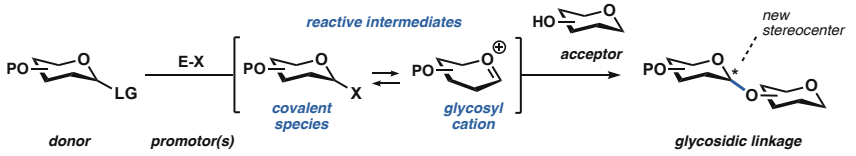


Figure 1. General overview of the glycosylation reaction. Glycosylation reactions are best considered as taking place at a continuum between two formal extremes of the mechanisms, the S_N1- and S_N2-mechanism; LG = leaving group; P = protection group; E-X = promoter system.

The research described in this thesis aimed to gain more insight into the mechanisms of chemical glycosylation reactions and their reactive intermediates. Chapter 1 provides an overview of research directed at understanding the behavior of glycosyl cations in terms of stability, selectivity and conformational preference.

The study described in Chapter 2 is focused on the development of a novel computational approach to investigate the stability and reactivity of glycosyl cations in a quantitative manner. The developed computational method probes the complete conformational space of these flexible six-membered ring cations (Figure 2A). This was accomplished by systematically scanning three dihedral angles (*i.e.*, C1–C2–C3–C4, C3–C4–C5–O5, and C5–O5–C1–C2) and computing their geometries and energies by DFT (Figure 2B). Based on the conformational preference of the intermediate ions, a prediction of the product stereoselectivity, formed in model S_N1 glycosylation reactions, could be made.

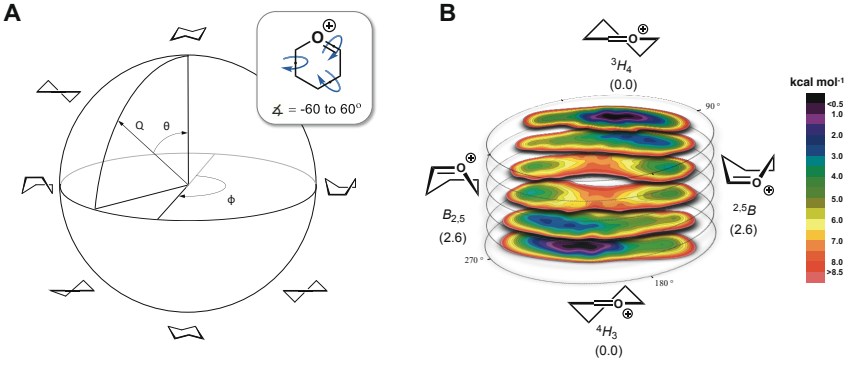


Figure 2. The developed method probes the complete conformational space of these highly flexible six-membered ring cations. (A) The complete conformational space of a six membered ring was scanned by computing 729 pre-fixed structures; A few canonical conformations (chair, half-chair, envelope and boat) are depicted; (B) The associated energies were graphed on slices dividing the Cremer-Pople sphere. All energies are computed at PCM(CH_2Cl_2)-B3LYP/6-311G(d,p) at T=213.15 K and expressed as solution-phase Gibbs free energy.

More than 30 different glycosyl oxocarbenium ions with varying substitution patterns were evaluated. The stability, reactivity and conformational mobility of these glycosyl oxocarbenium ions could be fully understood by computing the complete conformational

energy landscape (CEL), and the conformational preference of the cations could be directly related to the experimental stereochemical outcome of addition reactions with a typical S_N1-nucleophile, triethylsilane-*d*. The CEL maps showed in detail how the stereoelectronic effects of various ring substituents (halogens, chalcogens, azides, and carbon-based substituents) determine the overall shape of the cations and thereby the stereochemical course of the reactions. To obtain direct experimental evidence for the computed conformations using the CEL mapping method two 2-deoxy diacetylated oxocarbenium were generated and studied in 'non'-nucleophilic superacid media (*i.e.*, HF/SbF_5). The simulated NMR spectra of the selected cations, reconstituted by using the Boltzmann weighted averaged coupling constants determined by the CEL mapping method, perfectly matched the experimental ones obtained in superacid.

Where glycosyl oxocarbenium ions were previously thought to be at the basis of non-selective coupling reactions because of their high reactivity, the findings described in Chapter 2 show that these species – including the glycosyl cations derived from L-fucose, L-rhamnose, D-glucose, D-mannose and D-galactose – have an intrinsic preference to generate the challenging 1,2-*cis*-linkages. Chapter 2 firmly establishes the CEL mapping method as valuable tool for future research towards flexible six-membered ring oxocarbenium ion intermediates.

Chapter 3 expands on Chapter 2 with the focus on the reaction between the glycosyl cations and different S_N1-type nucleophiles. By performing model glycosylation reactions with two typical S_N1-nucleophiles, allyltrimethylsilane (allyl-TMS) and triethylsilane-*d* (TES-*d*), it was experimentally found that most of the substituted glycosyl cations react with similar stereoselectivities with both nucleophiles.

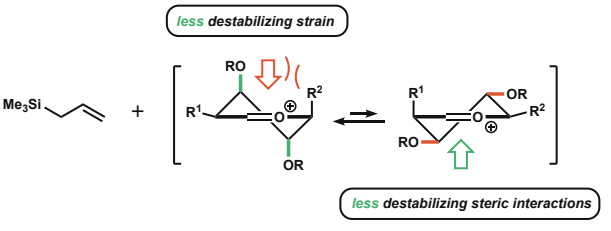


Figure 3. Schematic representation of the controlling factors (green = stabilizing; red = destabilizing factors) of the stereoselectivity of *C*-glycosylation reactions, in which the strain is always less destabilizing for the more stable conformer (*i.e.*,$^3H_4$), while the Pauli repulsion is also always more destabilizing for this conformation; R^1 = H or OBn and R^2 = H, Me or CH_2OBn.

In parallel, computational studies showed that most of these cations react via barrierless reaction pathways, and therefore the conformational preference of these glycosyl cations dictates the stereochemical outcome of addition reactions to these cations. However, a selected number of glycosyl cations reacted in a different stereoselective manner. For these latter cases, addition barriers were computationally found and Curtin-Hammett analyses of these reactions showed that these activation barriers are strongly influenced by the nature

of the nucleophile. By performing activation strain and Kohn-Sham molecular orbital analyses, it was found that the disparate stereoselectivity originated from (i) the stability of the different glycosyl cation conformers; (ii) the steric repulsion between the nucleophile and the glycosyl cation; and (iii) the position of the transition state along the reaction coordinate. (Figure 3).

The subject of Chapter 4 covered the possible formation of dioxolenium ions from their parent oxocarbenium ion through participation of remote acyl groups present on donor molecules (Figure 4). This long-range participation can steer the stereochemical outcome of glycosylation reactions. In this Chapter a three-pronged approach consisting of infrared ion spectroscopy (IRIS), CEL computations, and model glycosylation reactions, was used to assess the effect of long-range participation (LRP) in a set of glycosyl donors. First, the DFT protocol, developed as described in Chapter 2, was used to compute the relative stability of the dioxolenium ions, to analyze which systems were susceptible for LRP.

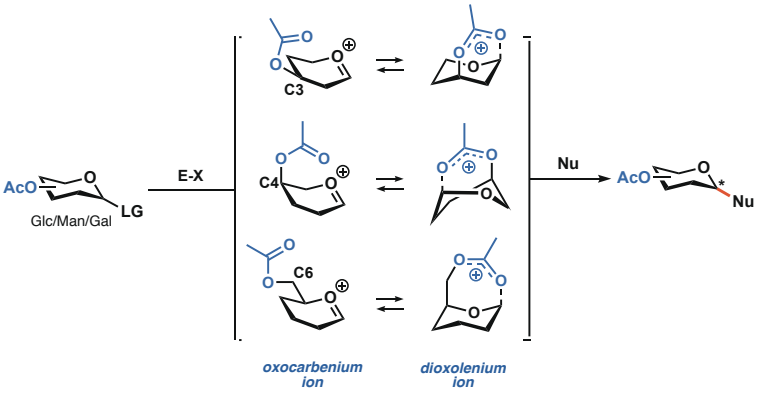


Figure 4. LRP in glycosylation reactions offers an opportunity to control the stereoselectivity of glycosylations. P = protection group; E-X = promoter system; and Nu = nucleophile.

To get direct experimental support for the computed reactive intermediates, IRIS was performed. In this method, glycosyl donors are introduced into the mass spectrometer via electrospray ionization (ESI) and, in a tandem-mass spectrometric (MS^2) scheme, glycosyl cations could be formed from the isolated donors by collision induced dissociation (CID). This allowed the generation of "naked" glycosyl cations, and characterization using multi photon infrared ion spectroscopy. In order to verify if the postulated LRP based on the DFT computations and IRIS measurements could also be found in a relevant experimental setup for glycosylation chemistry, an array of glycosylation experiments was performed.

Together these studies confirm that LRP can play a decisive role in shaping the stereochemical outcome of a glycosylation reaction. LRP plays a major role in glycosylations of C-3 acyl mannosides and to a somewhat lesser extent with C-4 acyl galactosides. C-3 acyl groups in glucose and galactosyl donors can engage in LRP but this anchimeric assistance has relatively little influence on the stereochemical course of

glycosylations of these donors. No important role for C-6 acyl LRP has been found. The strength of LRP thus follows the order: 3-Ac-Man >> 4-Ac-Gal > 3-Ac-Glc ~ 3-Ac-Gal > 4-Ac-Glc > 4-Ac-Man ~ 6-Ac-Glc/Gal/Man.

The research described in Chapter 5 implements the fundamental insights gained in the previous chapters in the assembly of a biologically relevant complex mycobacterial glycolipid, built up from (amongst others) rare and complex monosaccharides, featuring tetrasubstituted tertiary carbon stereocenters (Figure 5A). An integrated approach, consisting of a systematic series of glycosylation reactions in combination with the detection and characterization of different reactive intermediates using variable-T NMR and CEL computations, were used to assess reactivity-stereoselectivity relationships.

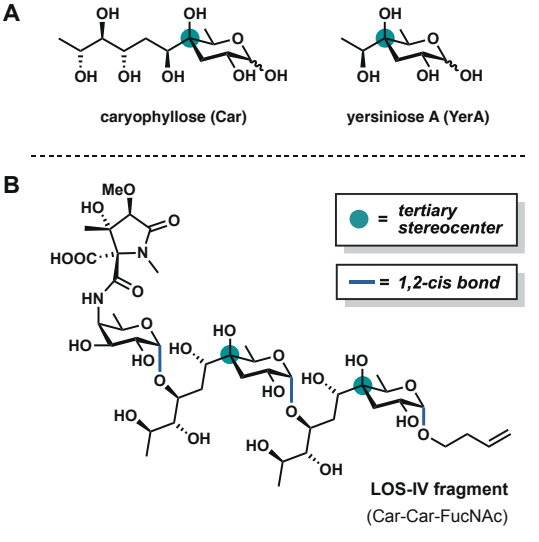


Figure 5. Tetrasubstituted tertiary-*C* sugars present in lipooligosaccharides from *M. marinum*. (A) Tertiary *C*-sugar caryophyllose (Car) found in mycobacterial lipooligosaccharides and the related smaller Yersiniose A (YerA); (B) Synthesized fragment of a lipooligosaccharide from *M. marinum*.

Pre-activation of these donors revealed that the protected oxygen of the ether functionalities in the appended side chain of caryophyllose (Car) and yersioniose (YerA) readily attack the activated anomeric center of the donors, providing bridged structures leading to unproductive glycosylation reactions. This behavior has been explained using the structural preference of the oxocarbenium ion intermediates that can form. Prevention of this nucleophilic attack is a prerequisite to generate effective donor glycosides, and this could be achieved by tethering of the C4 side-chain. It was found that Car and YerA donors, equipped with a tethering carbonate protecting group, can efficiently form the desired 1,2-*cis* linkages, as long as weak nucleophiles are employed in the glycosylation. In order to achieve 1,2-*cis* selectivity, the reactivity of the Car-acceptors was tuned using electron-withdrawing protecting groups. The rationally designed building blocks enabled the

effective and stereoselective assembly of a Car-Car-FucNAc LOS-IV fragment, and related shorter fragments (Figure 5B).

/ In conclusion, this thesis describes the use of a combined approach of computational and experimental techniques to gain novel insights to understand the glycosylation reaction and its reactive intermediates. The research in this thesis shows that glycosyl cations can act as reactive intermediates in glycosylation reactions for the introduction of glycosidic linkages. Furthermore, computational and experimental evidence has been provided showing that dioxolenium ions, formed by participation of remote acyl groups, are relevant reactive intermediates and can effectively steer the stereochemical course of glycosylation reactions. Ultimately, the techniques developed and insights gained in these studies were used in the synthesis of a complex mycobacterial glycolipid. The fundamental knowledge presented in this thesis can be further exploited in future synthetic endeavors, delivering more and more complex glycans to fuel glycobiological and glycomedical research. /

Future perspectives

The main goal of this thesis was to shed light on the glycosylation reaction mechanisms and especially its reactive intermediates that can form during these reactions. The insights gained during these studies will have to be applied in target-oriented syntheses, delivering new oligosaccharides and glycoconjugates for further study. This section describes several studies to extend the presented work and translate the fundamental insights to synthetic applications.

Further applications of the CEL mapping method

The developed CEL mapping method can be applied to a wide range of systems to understand the conformational behavior of these six membered rings. The method can be applied to popular donors used in synthetic chemistry, such as cyclic protected donors (Figure 6A). It can also be applied to probe cations of differently substituted glycosyl donors, derived from bacterial monosaccharides[1] or sialic acid derivatives (Figure 6C-D). Also, the effect of a counter ion on the structure of intermediates can be studied (Figure 6B). The role of the counter ion is largely debated, and it is to date exceedingly difficult to experimentally or computationally study these elusive species.[2–8]

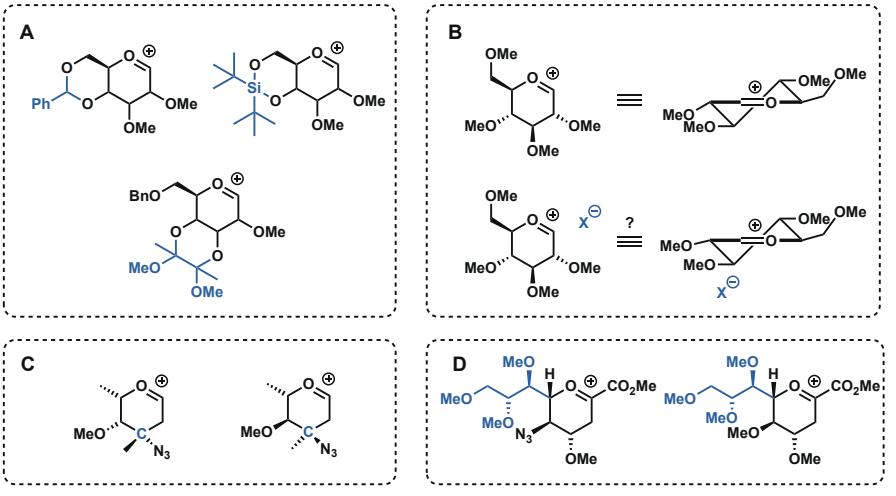


Figure 6. Further applications of the CEL mapping method for studying oxocarbenium ions. (A) Studying the influence of cyclic protection groups; (B) Presence of a counter-ion; (C) Tertiary-*C* motives; (D) Appended side-chains.

A selection of the endeavors towards these applications is shown in Figure 7, in which the CEL maps of two popular donors used in synthetic chemistry, benzylidene protected glucose **1** and mannose **2** are presented. The CEL maps of the cations formed from these donors, support the currently accepted model, in which the glucosyl cation **1** preferably adopts a $^{4}H_{3}/^{4}E$-like structure, while mannosyl ion **2** takes up a $B_{2,5}$ conformation. This conformational preference translates to the 1,2-*cis* selectivity observed in glycosylations of these donors, in which glucosyl cation **1** is attacked at the bottom-face of the $^{4}H_{3}/^{4}E$-like conformer and mannosyl cation **2** by a top-face addition at the $B_{2,5}$ intermediate.[9,10]

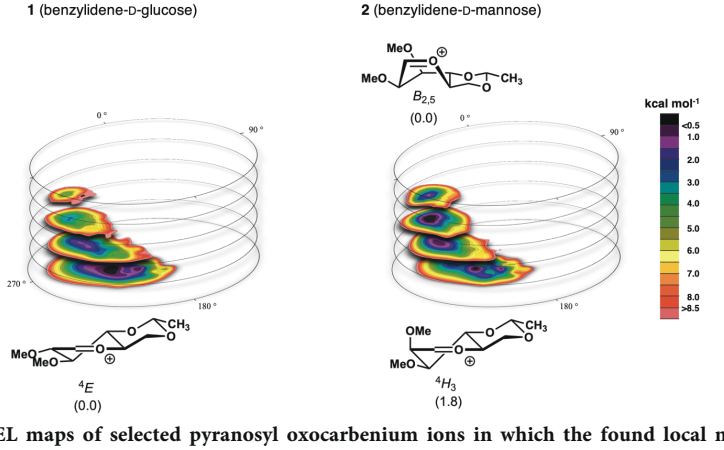
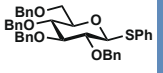
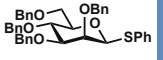
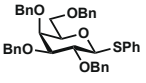
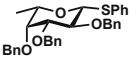
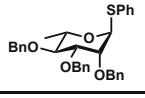
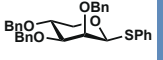
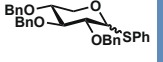
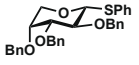
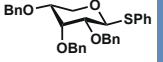
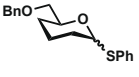


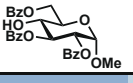
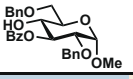
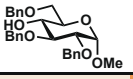
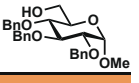
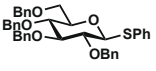
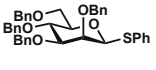
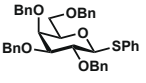
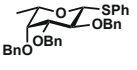
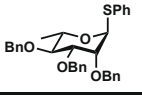
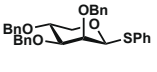
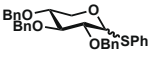
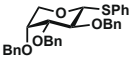
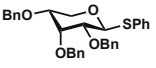
Figure 7. CEL maps of selected pyranosyl oxocarbenium ions in which the found local minima are indicated with their respective energy. CEL maps of benzylidene protected pyranosyl oxocarbenium ions **1** and **2**. All energies are as computed at PCM(CH_2Cl_2)-B3LYP/6-311G(d,p) and expressed as solution-phase Gibbs free energy.

Table 1. Experimentally found stereoselectivity for glycosylation reactions on a series of mono- and multi-substituted donors with a variety of model *d*-, *C*- and *O*-nucleophiles. For the mono-substituted pyranosides the *cis*:*trans* ratio is expressed as the relationship between the substituent and the coupled nucleophile; for the other glycopyranosides the *cis*:*trans* ratio is expressed as the relationship between the substituent on C-2 and the coupled nucleophile. The experimental results for the *gluco*-, *manno*-, and *galacto*-entries are from Chapter 4.

	TES-*d*	TMS	CF_3 HO CF_3	HO CF_3	HO F F	HO F	HO
	>98:2 (70%)	>98:2 (71%)	>98:2 (41%)	75:25 (80%)	48:52 (58%)	36:64 (75%)	15:85 (70%)
	>98:2 (93%)	34:66 (80%)	<2:98 (39%)	<2:98 (84%)	20:80 (58%)	40:60 (75%)	67:33 (70%)
	>98:2 (86%)	>98:2 (80%)	>98:2 (33%)	87:13 (79%)	66:34 (69%)	33:67 (84%)	17:83 (73%)
	>98:2 (74%)	>98:2 (76%)	>98:2 (33%)	100:0 (89%)	67:33 (82%)	40:60 (100%)	29:71 (100%)
	>98:2 (79%)	23:77 (70%)	<2:98 (46%)	8:92 (95%)	30:70 (70%)	77:23 (92%)	54:46 (86%)
	>98:2 (81%)	>98:2 (76%)	>98:2 (46%)	59:41 (62%)	64:36 (93%)	73:27 (100%)	53:47 (87%)
	>98:2 (86%)	>98:2 (72%)	34:66 (55%)	34:66 (78 %)	33:67 (89%)	29:71 (100%)	15:85 (89%)
	>98:2 (79%)	>98:2 (68%)	>98:2 (26%)	88:12 (90%)	62:38 (54%)	56:44 (96%)	18:82 (100%)
	>98:2 (69%)	>98:2 (70%)	>98:2 (36%)	52:48 (68%)	50:50 (72%)	39:61 (100%)	28:72 (100%)
	<2:98 (80%)	<2:98 (79%)	<2:98 (100%)	<2:98 (20%)	22:88 (73%)	50:50 (63%)	52:48 (40%)

>90:10 >80:20 >60:40 >50:50 <50:50 <40:60 <20:80 <10:90 (1,2-*cis*:1,2-*trans*)

Table 2. Experimentally found stereoselectivity for glycosylation reactions on a series of mono- and multi-substituted donors with a variety of model carbohydrate acceptors. The *cis*:*trans* ratio is expressed as the relationship between the substituent on C-2 and the coupled nucleophile.

				
	88:12 (58%)	61:39 (62%)	42:58 (91%)	15:85 (76%)
	<2:98 (59%)	<2:98 (77%)	<2:98 (70%)	77:23 (79%)
	>98:2 (66%)	92:8 (70%)	70:30 (70%)	30:70 (75%)
	>98:2 (76%)	93:7 (85%)	90:10 (75%)	45:55 (90%)
	<2:98 (51%)	10:90 (78%)	12:88 (84%)	66:34 (91%)
	61:39 (67%)	55:45 (74%)	90:10 (84%)	60:40 (95%)
	60:40 (54%)	60:40 (91%)	60:40 (70%)	38:62 (90%)
	78:22 (59%)	75:25 (79%)	53:47 (84%)	30:70 (93%)
	50:50 (67%)	40:60 (61%)	40:60 (75%)	35:65 (63%)

>90:10 | >80:20 | >60:40 | >50:50 | <50:50 | <40:60 | <20:80 | <10:90 (1,2-*cis*:1,2-*trans*)

Glycosylation reaction with *O*-nucleophiles

Chapter 2 and 3 focused on the use of typical S_N1-nucleophiles (*d*- and *C*-nucleophiles; TES-*d* and allyl-TMS). An important extension of these studies is the investigation in reactions involving *O*-nucleophiles, since these types of acceptors are mainly used in synthetically relevant glycosylation reactions. To this end, an array of glycosylation reactions was performed with a set of pyranosyl donors in combination with a set of model alcohol nucleophiles (for their use see also Chapter 4), of gradually decreasing nucleophilicity. The glycosylation reactions were performed under pre-activation

conditions using diphenyl sulfoxide (Ph_2SO)/triflic anhydride (Tf_2O) as an activator.[11] A panel of 10 benzyl protected donors was selected, ranging from mono-substituted pyranoses to fully decorated donors. The results are summarized in Table 1. Based on earlier work, the changes in stereochemistry of the reactions can be related to changes in mechanism.[10] Strong nucleophiles (*i.e.*, EtOH and MFE) generally show direct displacement, in a S_N2-type substitution fashion, of the covalent intermediate (*e.g.*, α-triflate) to form the β-product. Weaker *O*-nucleophiles (*i.e.*, HFIP and TFE) are expected to follow a reaction pathway with significant oxocarbenium ion character, reacting in S_N1-like fashion. In most cases the results support this and the obtained stereoselectivities for HFIP are in agreement with allyl-TMS and TES-*d*, the typical S_N1-nucleophiles. However, in some cases the stereochemical results deviate. This suggests that the mechanism of these reactions involving the weak *O*-nucleophiles could be differing from the established S_N1-like mechanisms. Perhaps these nucleophiles follow more of a S_Ni-like pathway (*i.e.*, S_N2-f), which has been established for enzyme-catalyzed glycosylations.[12–14] In this type of nucleophilic substitution, the incoming acceptor is assisted by the departing leaving group by forming a hydrogen bond. Whitfield and co-workers supported this concept by stretching the importance of hydrogen bonding in the glycosylation reaction by the use of DFT computations.[15] In the future, DFT calculations (similar to the ones described in Chapter 3) can be used to shed light on the exact mechanism(s) at play investigating different transition states through which the reactions may proceed. The study with *O*-nucleophiles was further extended by the use of a set of carbohydrate acceptors and these results are summarized in Table 2. These carbohydrate acceptors also represent a set of nucleophiles of gradually decreasing nucleophilicity. The trends found for the model ethanol acceptors translates well to the carbohydrate acceptors. This further supports the use of these model acceptors as surrogates for carbohydrate acceptors.[10,16,17]

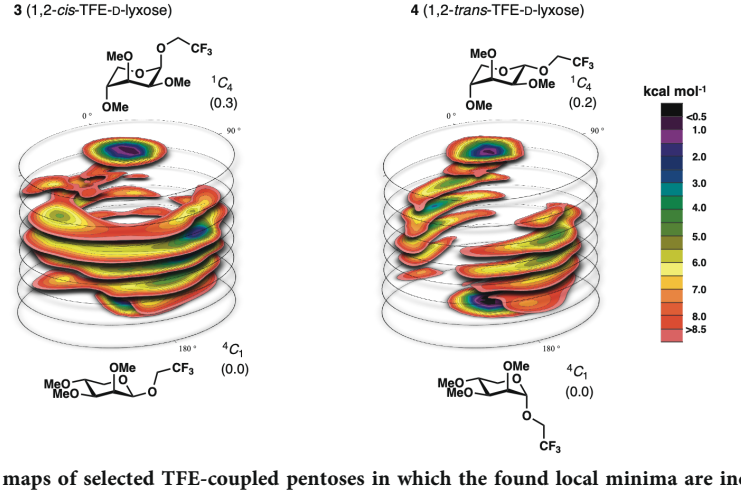


Figure 8. CEL maps of selected TFE-coupled pentoses in which the found local minima are indicated with their respective energy. CEL maps of trifluoroethanol coupled lyxose **3** and **4**. All energies are as computed at PCM($CHCl_3$)-B3LYP/6-311G(d,p) and expressed as solution-phase Gibbs free energy.

Several glycosylation products were exceptionally difficult to characterize by NMR spectroscopy because the pentose systems proved to be highly flexible, leading to coupling constants for the ring protons, deviating from values, commonly obtained for the canonical $^{1}C_{4}$ or $^{4}C_{1}$ chair conformer. In order to probe the conformational space that was available for these molecules, the CEL mapping method was applied. From the generated maps (Figure 8), it becomes apparent that for lyxose products **3** and **4**, a mixture of conformers can be expected, in accounting for the *J*-values found in the NMR analysis.

Novel remote-participating groups

Chapter 4 establishes dioxolenium ion intermediates as relevant reactive intermediates in glycosylation reactions. With the gained fundamental knowledge described in this chapter these species can be exploited by searching for groups that could potentially strengthen the LRP effect and allow for full control over the stereochemical preference of the glycosylation reaction. This is supported by the work of the group of Boons (Figure 9).[18] They showed that by placing a variety of ester groups, which differ in electron-withdrawing character, a clear trend in stereoselectivity was found.

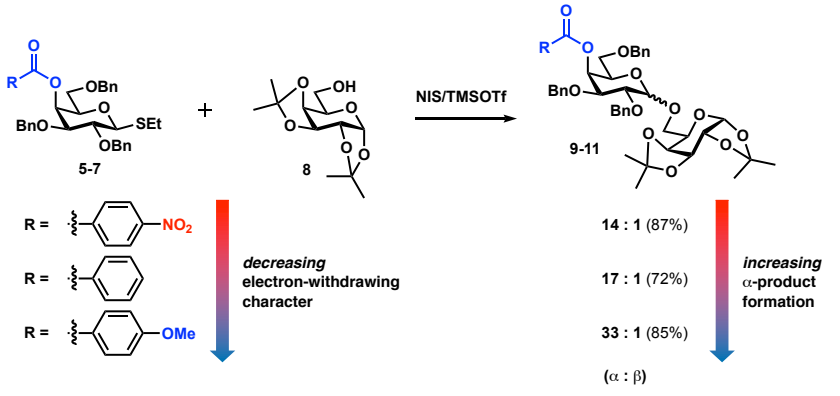


Figure 9. Using ester groups with varying electron-withdrawing character provides a way to steer the stereoselectivity of the reaction.[18]

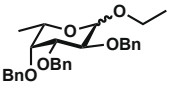
The stereoselectivity of these three couplings can be traced back to the stability of the corresponding dioxolenium ions, which can form upon activation. This suggests that it is possible to manipulate the stability of the dioxolenium ion by tuning the properties of the appended acyl esters, to steer glycosylation reactions. Early attempts in this direction show promising results. The 2,2-dimethyl-2-(*ortho*-nitrophenyl)acetyl (DMNPA) group was used as protection group, which showed more efficient LRP control compared to a classical benzoyl group.[19,20]

Supporting information

Organic synthesis

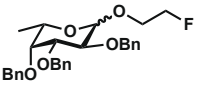
General experimental procedures. All chemicals (Merck, Sigma-Aldrich, Alfa Aesar, Honeywell, Boom and Merck KGaA) were of commercial grade and were used as received unless stated otherwise. Dichloromethane, tetrahydrofuran and toluene were stored over activated 4 Å molecular sieves (beads, 8-12 mesh, Sigma-Aldrich). Deuterated chloroform was stored over activated 3 Å molecular rods (rods, size 1/16 in., Sigma Aldrich) and potassium carbonate. Flash column chromatography was performed on silica gel 60 Å (0.04 – 0.063 mm, Screening Devices B.V.). Size exclusion chromatography was performed on SephadexTM (LH-20, GE Healthcare Life Sciences) by isocratic elution with DCM:MeOH (1:1, v:v). TLC-analysis was performed on TLC Silica gel 60 (Kieselgel 60 F254, Merck) with UV detection (254 nm) and by spraying with 20% H_2SO_4 in ethanol followed by charring at ± 260 °C or by spraying with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$ (10 g/L) in 10% sulfuric acid in water followed by charring at ± 260 °C. TLC-MS analysis was performed on a Camag TLC-MS Interface coupled with an API165 (SCIEX) mass spectrometer (eluted with *tert*-butylmethylether/EtOAc/MeOH, 5/4/1, v/v/v +0.1% formic acid, flow rate 0.12 mL/min). High-resolution mass spectra (HRMS) were recorded on a Waters Synapt G2-Si (TOF) equipped with an electrospray ion source in positive mode (source voltage 3.5 kV) and an internal lock mass LeuEnk ($M+H^+$ = 556.2771). Amberlite resin (Sigma Aldrich Amberlite IR120 H^+ form, Amberlite IRA-67 free base) was pre-washed with MeOH. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 NMR instrument (400 and 101 MHz respectively), a Bruker AV-500 NMR instrument (500 and 126 MHz respectively), a Bruker AV-600 NMR instrument (600 and 151 MHz respectively) or a Bruker AV-850 NMR instrument (850 and 214 MHz respectively. All samples were measured in $CDCl_3$, unless stated otherwise. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard or the residual signal of the deuterated solvent. Coupling constants (J) are given in Hz. All given ^{13}C APT spectra are proton decoupled. NMR peak assignment was accomplished using COSY, HSQC. If necessary, an additional NOESY, HMBC, and HMBC-gated experiment were used to further elucidate the structure. Stereochemical product ratios were based on integration of ^1H NMR (crude and purified). IR spectra were recorded on a Shimadzu FTIR-8300 IR spectrometer and are reported in cm^{-1}. Specific rotations were measured on an Anton Paar Polarimeter MCP 100 in $CHCl_3$ (10 mg/mL) at 589 nm, unless stated otherwise.

General procedure I: pre-activation Tf_2O/Ph_2SO based glycosylation
To a solution of the donor (100 µmol, 1 eq.) in DCM (2 mL, 0.05 M), Ph_2SO (26 mg, 130 µmol, 1.3 eq.) and TTBP (62 mg, 250 µmol, 2.5 eq.) were added. The solution was stirred over activated 3 Å molecular sieves (rods, size 1/16 in., Sigma Aldrich) for 30 minutes. The solution was cooled to −80 °C upon which Tf_2O (22 µL, 130 µmol, 1.3 eq.) was added slowly (5 seconds). Subsequently, the solution was allowed to attain to −60 °C to secure full activation of the donor followed by cooling back to −80 °C after which the acceptor was added (0.2 mL, 0.5 M solution, 2.0 eq.). The reaction was stirred for 16 hours at −60 °C (for ethanol, 2-fluoroethanol, 2,2-difluoroethanol and 2,2,2-trifluoroethanol) or for 40 hours at −60 °C (for 1,1,1,3,3,3-hexafluoro-2-propanol). The reaction was quenched with sat. aq. $NaHCO_3$ followed by the dilution with EtOAc. The aqueous layer was extracted three times with EtOAc. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, filtered off and concentrated under reduced pressure. Purification was performed by flash column chromatography to afford the corresponding coupled glycoside.

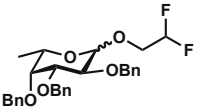


Ethyl 2,3,4-tri-*O*-benzyl-L-fucopyranoside (S1). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (46 mg, 100 µmol, *quant.*, colorless oil, 1,2-*cis*:1,2-*trans*; 29:71). TLC: R_f 0.49 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 731, 1027, 1064, 1092, 1360, 1453, 2892; Data for the major stereoisomer (1,2-*trans*): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.44 – 7.22 (m, 15H, CH_{arom}), 5.01 – 4.92 (m, 2H, C*H*H Bn, C*H*H Bn), 4.82 – 4.65 (m, 6H, CH*H* Bn, CH*H* Bn, CH_2 Bn, CH_2 Bn), 4.32 (d, J = 7.7 Hz, 1H, H-1), 4.05 – 3.92 (m, 2H, C*H*H Et), 3.80 (dd, J = 9.7, 7.7 Hz, 1H, H-2), 3.60 – 3.53 (m, 2H, H-4, CH*H* Et), 3.50 (dd, J = 9.7, 3.0 Hz, 1H, H-3), 3.44 (qd, J = 6.4, 1.0 Hz, 1H, H-5), 1.26 (t, J = 7.0 Hz, 3H, CH_3 Et), 1.17 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz,

$CDCl_3$ HSQC, HMBC-Gated): δ 139.1, 138.8, 138.7 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.6 (CH_{arom}), 103.7 (C-1), 82.6 (C-3), 79.6 (C-2), 76.4 (C-4), 75.2, 74.6, 73.3 (CH_2 Bn), 70.3 (C-5), 65.4 (CH_2 Et), 17.0 (CH_3 Et), 15.4 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 103.7 ($J_{H1\text{-}C1}$ = 157 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.44 – 7.22 (m, 15H), 4.89 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 3.88 (qd, *J* = 6.4, 0.9 Hz, 1H, H-5), 3.71 – 3.61 (m, 2H, C*H*H Et, H-3/H-4), 1.25 – 1.20 (m, 3H, CH_3 Et), 1.10 (d, *J* = 6.5 Hz, 2H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.2, 138.8, 138.8 ($C_{q\text{-}arom}$), 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 127.5 (CH_{arom}), 97.2 (C-1), 79.6, 78.0 (C-3/C-4), 76.6 (C-2), 74.9, 73.5, 73.4 (CH_2 Bn), 66.2 (C-5), 63.3 (CH_2 Et), 16.8 (CH_3 Et), 15.2 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 97.2 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{34}O_5$ 485.2304, found 485.2307.

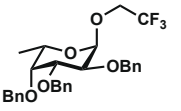


2-Fluoroethyl 2,3,4-tri-*O*-benzyl-L-fucopyranoside (S2). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (48 mg, 100 µmol, *quant.*, colorless oil, 1,2-*cis*:1,2-*trans*; 40:60). TLC: R_f 0.32, 0.40 (pentane:EtOAc, 85:15, v:v); IR (thin film, cm^{-1}): 694, 732, 913, 1027, 1042, 1089, 1360, 1497, 2919; Data for the major stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.44 – 7.21 (m, 15H, CH_{arom}), 5.03 – 4.45 (m, 8H, CH_2 Bn, CH_2 Bn, CH_2 Bn, $CH_2C\mathit{H}_2F$), 4.38 (d, *J* = 7.7 Hz, 1H, H-1), 4.16 – 4.01 (m, 1H, $C\mathit{H}_2CH_2F$), 3.90 – 3.72 (m, 1H, H-2), 3.55 (dd, *J* = 3.0, 1.0 Hz, 1H, H-4), 3.51 (dd, *J* = 9.7, 2.9 Hz, 1H, H-3), 3.45 (qd, *J* = 6.4, 0.8 Hz, 1H, H-5), 1.16 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.8, 138.7, 138.6 ($C_{q\text{-}arom}$), 128.7, 128.5, 128.4, 128.3, 127.7, 127.7, 127.6 (CH_{arom}), 104.1 (C-1), 82.9 (d, *J* = 169.5 Hz, $CH_2\mathit{CH}_2F$), 82.5 (C-3), 79.4 (C-2), 76.2 (C-4), 75.3, 74.6, 73.4 (CH_3 Bn), 70.5 (C-5), 68.6 (d, *J* = 20.1 Hz, CH_2CH_2F), 16.9 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 104.1 ($J_{H1\text{-}C1}$ = 158 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.44 – 7.21 (m, 15H, CH_{arom}), 4.05 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 4.01 – 3.88 (m, 2H, H-4, H-5), 1.10 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.1, 138.7, 138.7 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.6 (CH_{arom}), 98.0 (C-1), 82.8 (d, *J* = 169.4 Hz, $CH_2\mathit{CH}_2F$), 79.4 (C-4), 77.8 (C-3), 76.4 (C-2), 75.0, 73.5, 73.5 (CH_2 Bn), 67.0 (d, *J* = 20.1 Hz, CH_2CH_2F), 66.4 (C-5), 16.7 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 98.0 ($J_{H1\text{-}C1}$ = 168 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{33}FO_5$ 503.2210, found 503.2217.

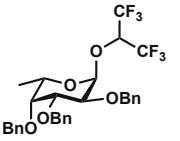


2,2-Difluoroethyl 2,3,4-tri-*O*-benzyl-L-fucopyranoside (S3). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (41 mg, 82 µmol, 82%, colorless oil, 1,2-*cis*:1,2-*trans*; 67:33). TLC: R_f 0.29, 0.42 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 732, 1027, 1047, 1097, 1168, 1361, 1453, 1497, 2934; Data for the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.42 – 7.24 (m, 15H, CH_{arom}), 6.07 – 5.79 (m, 1H, CHF_2), 4.98 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.89 – 4.80 (m, 2H, CH_2 Bn), 4.79 – 4.70 (m, 1H, C*H*H Bn), 4.73 (d, *J* = 3.7 Hz, 1H, H-1), 4.70 – 4.62 (m, 2H, CH*H* Bn, CH*H* Bn), 4.05 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2), 3.92 (dd, *J* = 10.2, 2.9 Hz, 1H, H-3), 3.88 (q, *J* = 6.5 Hz, 1H, H-5), 3.71 (ddd, *J* = 14.3, 12.9, 4.4 Hz, 2H, CH_2CHF_2) 3.66 (m, 1H, H-4), 1.11 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9, 138.6, 138.6 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 128.3, 128.1, 127.7, 127.6 (CH_{arom}), 114.3 (t, *J* = 241.2 Hz, $CH_2\mathit{CH}F_2$) , 98.7 (C-1), 79.2 (C-3), 77.7 (C-4), 76.3 (C-2), 75.0, 73.7, 73.5 (CH_2 Bn), 67.3 (t, *J* = 28.8 Hz), 66.9 (C-5) 16.6 (CH_3); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 98.7 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.42 – 7.24 (m, 15H, CH_{arom}), 6.07 – 5.79 (m, 1H, CHF_2), 4.37 (d, *J* = 7.7 Hz, 1H, H-1), 3.83 (dd, *J* = 9.7, 7.6 Hz, 1H, H-2), 3.55 (dd, *J* = 3.0, 1.0 Hz, 1H, H-4), 3.51 (dd, *J* = 9.7, 2.9 Hz, 1H, H-3), 3.45 (t, *J* = 6.4, 1.0 Hz, 1H, H-5), 1.17 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.6, 138.5, 128.7, 128.4, 128.4, 128.4, 128.3, 127.9, 127.7, 127.7, 127.6 ($C_{q\text{-}arom}$), 114.5 (dd, *J* = 242.3, 239.4 Hz, $CH_2\mathit{CH}F_2$) (CHF_2), 104.2 (C-1), 82.4

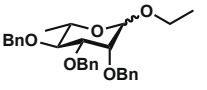
(C-3), 79.2 (C-2), 76.1 (C-4), 75.3, 74.7, 73.4 (CH_3 Bn), 70.7 (C-5), 68.5 (dd, J = 30.9, 26.4 Hz), 16.9 (CH_3); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 104.2 ($J_{H1\text{-}C1}$ = 157 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{32}F_2O_5$ 521.2116, found 521.2122.



2,2,2-Trifluoroethyl 2,3,4-tri-*O*-benzyl-1,2-*cis*-L-fucopyranoside (S4). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (46 mg, 89 µmol, 89%, colorless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.55 (pentane:EtOAc, 90:10, v:v); $[\alpha]_D^{20}$ –44.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 696, 736, 969, 1045, 1079, 1160, 1276, 1454, 1717, 2916; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.47 – 7.18 (m, 15H, CH_{arom}), 4.98 (d, J = 11.5 Hz, 1H, C*H*H Bn), 4.88 (d, J = 11.8 Hz, 1H, C*H*H Bn), 4.85 – 4.79 (m, 2H, H-1, CH*H* Bn), 4.74 (d, J = 11.7 Hz, 1H, CH*H* Bn), 4.65 (dd, J = 11.7, 4.5 Hz, 2H, C*H*H Bn, CH*H* Bn), 4.07 (dd, J = 10.1, 3.7 Hz, 1H, H-2), 3.98 – 3.81 (m, 4H, H-3, H-5, C*H*HCF$_3$, CH*H*CF$_3$), 3.67 (dd, J = 2.9, 1.2 Hz, 1H, H-4), 1.11 (d, J = 6.5 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9, 138.6, 138.5 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6 (CH_{arom}), 98.6 (C-1), 79.0 (C-3), 77.6 (C-4), 76.2 (C-2), 75.0, 73.6, 73.5 (CH_2 Bn), 67.2 (C-5), 64.9 (q, J = 34.7 Hz, *C*H$_2$CF$_3$), 16.6 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$) δ 98.6 ($J_{H1\text{-}C1}$= 170 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{31}F_3O_5$ 539.2021, found 539.2026.

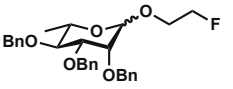


1,1,1,3,3,3-Hexafluoro-2-propyl 2,3,4-tri-*O*-benzyl-1,2-*cis*-L-fucopyranoside (S5). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (19 mg, 33 µmol, 33%, colorless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.48 (pentane:EtOAc, 95:5, v:v); $[\alpha]_D^{20}$ –22.6° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 960, 1071, 1105, 1143, 12201, 1290, 1375, 1440, 2915; ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated, NOESY): δ 7.72 – 7.13 (m, 15H, CH_{arom}), 5.13 (d, J = 3.9 Hz, 1H, H-1), 4.98 (d, J = 11.5 Hz, 1H, C*H*H Bn), 4.87 (d, J = 11.6 Hz, 1H, C*H*H Bn), 4.79 – 4.67 (m, 3H, CH*H* Bn, CH*H* Bn, C*H*H Bn), 4.65 (d, J = 11.5 Hz, 1H, CH*H* Bn), 4.45 (hept, J = 6.0 Hz, 1H, CH(CF$_3$)$_2$), 4.13 (dd, J = 10.3, 3.9 Hz, 1H, H-2), 4.01 – 3.89 (m, 2H, H-3, H-5), 3.71 (dd, J = 2.8, 1.2 Hz, 1H, H-4); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.8, 138.4, 138.2 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.4, 128.1, 127.9, 127.9, 127.7, 127.6 (CH_{arom}), 100.1 (C-1), 78.8 (C-3), 77.3 (C-4), 75.4 (C-2), 75.0 (CH_2 Bn), 73.5 (CH_2 Bn, CH_2 Bn), 72.6 (dt, J = 65.0, 32.4 Hz, *C*H(CF$_3$)$_2$), 68.3 (C-5), 16.5 (CH_3); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 100.1 ($J_{H1\text{-}C1}$= 174 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{31}F_3O_5$ 539.2021, found 539.2026.

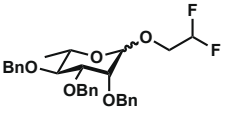


Ethyl 2,3,4-tri-*O*-benzyl-L-rhamnopyranoside (S6). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (40 mg, 86 µmol, 86%, colorless oil, 1,2-*cis*:1,2-*trans*; 54:46). TLC: R_f 0.53, 0.69 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 733, 1027, 1061, 1103, 1309, 1363, 1497, 2922; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (54:46) anomers; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.51 – 7.23 (m, 34.5H), 5.01 – 4.92 (m, 3H, C*H*H Bn, C*H*H Bn, C*H*H Bn), 4.89 (d, J = 12.6 Hz, 1H, CH*H* Bn), 4.78 – 4.73 (m, 3H, CH_2 Bn, H-1$_{1,2\text{-}trans}$), 4.64 (d, J = 11.0 Hz, 5H, CH*H* Bn, CH*H* Bn, CH_2 Bn), 4.50 (d, J = 11.9 Hz, 1H, C*H*H Bn), 4.43 (d, J = 11.9 Hz, 1H, CH*H* Bn), 4.34 (d, J = 0.7 Hz, 1H, H-1$_{1,2\text{-}cis}$), 3.98 (dq, J = 9.3, 7.1 Hz, 1H, C*H*H Et$_{1,2\text{-}cis}$), 3.91 – 3.86 (m, 2.26H, H-2$_{1,2\text{-}cis}$, H-3$_{1,2\text{-}trans}$), 3.79 (dd, J = 3.2, 1.8 Hz, 1.3H, H-2$_{1,2\text{-}trans}$), 3.75 – 3.56 (m, 4.8H, H-4$_{1,2\text{-}cis}$, H-4$_{1,2\text{-}trans}$, H-5$_{1,2\text{-}trans}$, C*H*H Et$_{1,2\text{-}trans}$), 3.52 – 3.43 (m, 2H, H-3$_{1,2\text{-}cis}$, CH*H* Et$_{1,2\text{-}cis}$), 3.39 (dq, J = 9.7, 7.1 Hz, 1.26H, CH*H* Et$_{1,2\text{-}trans}$), 3.31 (dq, J = 9.2, 6.1 Hz, 1H, H-5$_{1,2\text{-}cis}$), 1.38 (d, J = 6.2 Hz, 3H, $CH_{3\text{-}1,2\text{-}cis}$), 1.33 (d, J = 6.1 Hz, 3.8H,

$CH_{3\text{-}1,2\text{-}trans}$), 1.26 (t, J = 7.0 Hz, 3H, CH_3 $Et_{1,2\text{-}cis}$), 1.14 (t, J = 7.1 Hz, 3.8H, CH_3 $Et_{1,2\text{-}trans}$); ^{13}C NMR (101 MHz, $CDCl_3$ HSQC, HMBC-Gated): δ 138.9, 138.8, 138.7, 138.6, 138.5, 138.4 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.2, 128.2, 128.2, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5 (CH_{arom}), 101.4 (C-$1_{1,2\text{-}cis}$), 97.8 (C-$1_{1,2\text{-}trans}$), 82.3 (C-$3_{1,2\text{-}cis}$), 80.7, 80.4, 80.3 (C-$2_{1,2\text{-}cis}$/C-$4_{1,2\text{-}cis}$/C-$4_{1,2\text{-}trans}$), 75.6 (CH_2 Bn, CH_2 Bn), 75.0 (C-$2_{1,2\text{-}trans}$), 73.9 (CH_2 Bn), 73.9 (C-$3_{1,2\text{-}trans}$), 72.9, 72.2 (CH_2 Bn), 72.0 (C-$5_{1,2\text{-}cis}$), 71.4 (CH_2 Bn), 68.0 (C-$5_{1,2\text{-}trans}$), 65.3 (CH_2 $Et_{1,2\text{-}cis}$), 62.9 (CH_2 $Et_{1,2\text{-}trans}$), 18.1 ($CH_{3\text{-}1,2\text{-}cis}$, $CH_{3\text{-}1,2\text{-}trans}$), 15.4 ($CH_3$ $Et_{1,2\text{-}cis}$), 15.1 (CH_3 $Et_{1,2\text{-}trans}$); GATED NMR (101 MHz, $CDCl_3$): δ 101.4 ($J_{H1\text{-}C1}$ = 152 Hz, 1,2-*cis*); 97.8 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{34}O_5$ 485.2304, found 485.2314.

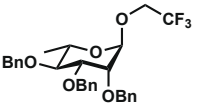


2-Fluoroethyl 2,3,4-tri-*O*-benzyl-L-rhamnopyranoside (S7). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (44 mg, 92 µmol, 92%, colorless oil, 1,2-*cis*:1,2-*trans*; 77:23). TLC: R_f 0.42, 0.56 (pentane:EtOAc, 85:15, v:v); IR (thin film, cm^{-1}): 696, 731, 1028, 1072, 1154, 1308, 1449, 1719, 2908; Data for the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.68 – 7.21 (m, 15H, CH_{arom}), 5.00 – 4.85 (m, 4H, C*H*H Bn, CH_2 Bn), 4.79 – 4.39 (m, 6H, CH*H* Bn, CH_2 Bn, H-1, CH2CH_2F), 4.09 (dddd, J = 35.8, 12.1, 3.9, 2.4 Hz, 1H, C*H*HCH$_2$F), 3.95 (dd, J = 3.0, 0.6 Hz, 1H, H-2), 3.67 – 3.55 (m, 1H, H-4), 3.45 (dd, J = 9.4, 3.1 Hz, 1H, H-3), 3.31 (dp, J = 9.2, 6.0 Hz, 1H, H-5), 1.38 (d, J = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.5, 138.2 ($C_{q\text{-}arom}$), 131.2, 129.4, 128.6, 128.5, 128.5, 128.2, 128.2, 127.7, 124.9 (CH_{arom}), 101.6 (C-1), 83.0 (d, J = 169.3 Hz, CH_2CH_2F), 82.1 (C-3), 80.1 (C-4), 75.6, 74.1 (CH_2 Bn), 73.8 (C-2), 72.1 (C-5), 71.5 (CH_2 Bn), 68.6 (d, J = 19.6 Hz, CH_2CH$_2$F), 18.1 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 101.6 ($J_{H1\text{-}C1}$ = 154 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.68 – 7.21 (m, 15H, CH_{arom}), 4.81 (d, J = 1.8 Hz, 1H, H-1), 3.89 (dd, J = 9.1, 3.2 Hz, 1H, H-3), 1.33 (d, J = 6.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.6, 138.4 ($C_{q\text{-}arom}$), 128.6, 128.6, 128.2, 128.1, 128.0, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6 (CH_{arom}), 98.3 (C-1), 82.6 (d, J = 169.7 Hz, CH_2CH_2F), 80.5 (C-4), 80.2 (C-3), 75.5 (CH_2 Bn), 74.9 (C-2), 73.0, 72.3 (CH_2 Bn), 68.3 (C-5), 66.4 (d, J = 19.9 Hz, CH_2CH$_2$F), 18.1 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 98.3 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{33}FO_5$ 503.2210, found 503.2216.

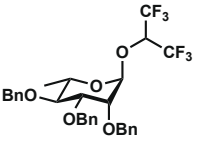


2,2-Difluoroethyl 2,3,4-tri-*O*-benzyl-L-rhamnopyranoside (S8). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (35 mg, 70 µmol, 70%, colorless oil, 1,2-*cis*:1,2-*trans*; 30:70). TLC: R_f 0.35, 0.52 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 697, 736, 1028, 1068, 1146, 1363, 1454, 1729, 2891; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (30:70) anomers; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.39 – 7.26 (m, 49.6H, CH_{arom}), 5.92 (dddd, J = 56.4, 54.7, 5.6, 2.8 Hz, 1H, $CH_2CHF_{2\text{-}1,2\text{-}cis}$), 5.81 (tdd, J = 55.4, 4.6, 3.7 Hz, 2.3H, $CH_2CHF_{2\text{-}1,2\text{-}trans}$), 4.99 – 4.90 (m, 4.3H, C*H*H $Bn_{1,2\text{-}cis}$, C*H*H $Bn_{1,2\text{-}cis}$, C*H*H $Bn_{1,2\text{-}trans}$), 4.85 (d, J = 12.5 Hz, 1H, CH*H* $Bn_{1,2\text{-}cis}$), 4.80 – 4.74 (m, 4.6H, C*H*H $Bn_{1,2\text{-}trans}$, H-$1_{1,2\text{-}trans}$), 4.70 (d, J = 12.4 Hz, 2.3H, CH*H* $Bn_{1,2\text{-}trans}$), 4.67 – 4.53 (m, 7.8H, CH*H* $Bn_{1,2\text{-}cis}$, CH*H* $Bn_{1,2\text{-}trans}$, CH_2 $Bn_{1,2\text{-}trans}$), 4.52 (d, J = 11.9 Hz, 1H, C*H*H $Bn_{1,2\text{-}cis}$), 4.46 (d, J = 11.8 Hz, 1H, CH*H* $Bn_{1,2\text{-}cis}$), 4.41 (d, J = 0.8 Hz, 1H, H-$1_{1,2\text{-}cis}$), 4.04 (dddd, J = 21.7, 11.6, 10.2, 2.8 Hz, 1H, C*H*HCHF$_{2\text{-}1,2\text{-}cis}$), 3.93 (dd, J = 3.0, 0.8 Hz, 1H, H-$2_{1,2\text{-}cis}$), 3.87 – 3.55 (m, 18H, H-$4_{1,2\text{-}cis}$, H-$2_{1,2\text{-}trans}$, H-$3_{1,2\text{-}trans}$, H-$4_{1,2\text{-}trans}$, H-$5_{1,2\text{-}trans}$, C*H*HCHF$_{2\text{-}1,2\text{-}trans}$, CH*H*CHF$_{2\text{-}1,2\text{-}trans}$), 3.45 (dd, J = 9.4, 3.0 Hz, 1H, H-$3_{1,2\text{-}cis}$), 3.45 – 3.35 (m, 1H, CH*H*CHF$_{2\text{-}1,2\text{-}cis}$), 3.32 (dq, J = 9.2, 6.1 Hz, 1H, H-$5_{1,2\text{-}cis}$), 1.38 (d, J = 6.1 Hz, 3H, $CH_{3\text{-}1,2\text{-}cis}$), 1.33 (d, J = 5.9 Hz, 6.8H, $CH_{3\text{-}1,2\text{-}trans}$); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.6, 138.5 ($C_{q\text{-}arom\text{-}1,2\text{-}trans}$), 138.5, 138.4 ($C_{q\text{-}arom\text{-}1,2\text{-}cis}$), 138.2 ($C_{q\text{-}arom\text{-}1,2\text{-}trans}$), 138.2 ($C_{q\text{-}arom\text{-}1,2\text{-}cis}$), 128.9, 128.6, 128.6, 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7 (CH_{arom}), 114.4 (dd, J = 242.0, 239.8 Hz, $CH_2CHF_{2\text{-}1,2\text{-}cis}$), 114.1 (t, J = 241.2 Hz, $CH_2CHF_{2\text{-}1,2\text{-}trans}$), 101.7 (C-$1_{1,2\text{-}cis}$), 98.9 (C-$1_{1,2\text{-}trans}$), 82.0 (C-$3_{1,2\text{-}cis}$), 80.3 (C-$4_{1,2\text{-}trans}$), 80.0 (C-$4_{1,2\text{-}cis}$), 79.9 (C-$3_{1,2\text{-}trans}$), 75.6 ($CH_2$ $Bn_{1,2\text{-}cis}$), 75.6 (CH_2 $Bn_{1,2\text{-}trans}$), 74.7 (C-$2_{1,2\text{-}trans}$), 74.2 (CH_2 $Bn_{1,2\text{-}cis}$), 73.7 (C-$2_{1,2\text{-}cis}$), 73.1, 72.4 (CH_2 $Bn_{1,2\text{-}trans}$), 72.3 (C-

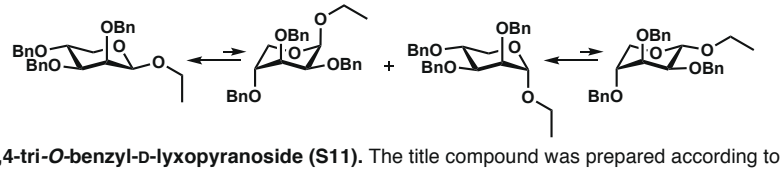
$5_{1,2\text{-}cis}$), 71.7 (CH_2 $Bn_{1,2\text{-}cis}$), 68.7 (C-$5_{1,2\text{-}trans}$),68.4 (dd, *J* = 30.6, 26.0 Hz, $CH_2CHF_{2\text{-}1,2\text{-}cis}$), 66.5 (t, *J* = 28.2 Hz, $CH_2CHF_{2\text{-}1,2\text{-}trans}$), 18.1 ($CH_{3\text{-}1,2\text{-}cis}$), 18.0 ($CH_{3\text{-}1,2\text{-}trans}$); GATED NMR (101 MHz, $CDCl_3$): δ 101.7 ($J_{H1\text{-}C1}$ = 155 Hz, 1,2-*cis*); 98.9 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{32}F_2O_5$ 521.2116, found 521.2126.



2,2,2-Trifluoroethyl 2,3,4-tri-*O*-benzyl-L-rhamnopyranoside (S9). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (49 mg, 95 µmol, 95%, colorless oil, 1,2-*cis*:1,2-*trans*; 8:92). TLC: R_f 0.66 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 696, 735, 982, 1028, 1084, 1162, 1277, 1454, 2893; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, HMBC-Gated): δ 7.48 – 7.10 (m, 15H, CH_{arom}), 4.93 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.82 (d, *J* = 1.4 Hz, 1H, H-1), 4.78 (d, *J* = 12.3 Hz, 1H, C*H*H Bn), 4.69 (d, *J* = 12.5 Hz, 1H, CH*H* Bn), 4.66 – 4.60 (m, 3H, CH*H* Bn, C*H*H Bn, CH*H* Bn), 3.99 – 3.74 (m, 4H, H-2, H-3, C*H*HCF$_3$, CH*H*CF$_3$), 3.75 – 3.58 (m, 2H, H-4, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.5, 138.5, 138.1 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8 (CH_{arom}), 98.8 (C-1), 80.2 (C-4), 79.8 (C-3), 75.6 (CH_2 Bn), 74.7 (C-2), 73.3, 72.5 (CH_2 Bn), 69.0 (C-5), 64.1 (q, *J* = 34.9 Hz, CH_2CF_3), 18.1 (CH_3); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 98.8 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{31}F_3O_5$ 539.2021, found 539.2021.

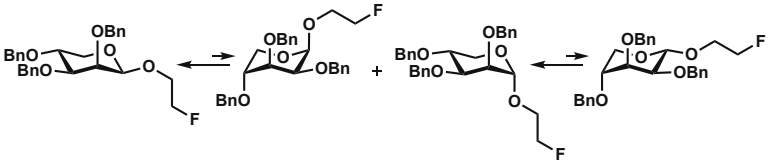


1,1,1,3,3,3-Hexafluoro-2-propyl 2,3,4-tri-*O*-benzyl-1,2-*trans*-L-rhamnopyranoside (S10). The title compound was prepared according to general procedure I. The reaction was quenched after 112 h. Flash column chromatography (100:0 → 80:20, pentane:Et_2O) afforded the title compound (27 mg, 46 µmol, 46%, white solid, 1,2-*cis*:1,2-*trans*; <2:98). TLC: R_f 0.45 (pentane:EtOAc, 95:5, v:v); $[\alpha]_D^{20}$ –20.0° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 685, 696, 966, 1073, 1100, 1146, 1196, 1220, 1287, 1366, 1449, 2917; ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated, ^1H-^{19}F Decoupled): δ 7.38 – 7.26 (m, 15H, CH_{arom}), 4.94 (d, *J* = 2.1 Hz, 1H, H-1), 4.87 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.76 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.65 (dd, *J* = 11.7, 2.7 Hz, 3H, CH_2 Bn, CH*H* Bn), 4.59 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.38 (hept, *J* = 6.0 Hz, 1H, C*H*$(CF_3)_2$), 3.86 – 3.72 (m, 3H, H-2, H-3, H-5), 3.62 (t, *J* = 9.0 Hz, 1H, H-4), 1.30 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.3, 138.3, 137.8 ($C_{q\text{-}arom}$), 129.6, 128.9, 128.6, 128.6, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.7 (CH_{arom}), 100.9 (C-1), 80.0 (C-4), 79.1 (C-3), 75.3 (CH_2 Bn), 74.8 (C-2), 73.5, 72.8 (CH_2 Bn), 72.2 (p, *J* = 33.0 Hz), 70.0 (C-5), 18.0 (CH_3); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 100.9 ($J_{H1\text{-}C1}$ = 174 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{30}H_{30}F_6O_5$ 607.1895, found 607.1911.

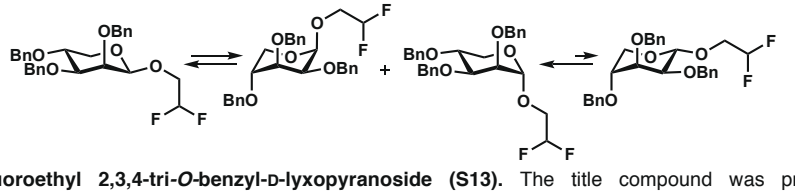


Ethyl 2,3,4-tri-*O*-benzyl-D-lyxopyranoside (S11). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (39 mg, 87 µmol, 87%, colorless oil, 1,2-*cis*:1,2-*trans*; 53:47). TLC: R_f 0.31, 0.55 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 694, 732, 907, 1089, 1308, 1362, 2903; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (53:47) anomers: ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, HMBC-Gated): δ 7.48 – 7.25 (m, 30H, $CH_{arom\text{-}1,2\text{-}cis}$, $CH_{arom\text{-}1,2\text{-}trans}$), 4.84 (d, *J* = 12.4 Hz, 1H, C*H*H Bn), 4.79 (d, *J* = 12.4 Hz, 1H, CH*H* Bn), 4.76 – 4.67 (m, 7H, CH_2 Bn, CH_2 Bn, CH_2 Bn, H-$1_{1,2\text{-}trans}$), 4.67 – 4.52 (m, 4H, CH_2 Bn, CH_2 Bn), 4.47 (d, *J* = 1.8 Hz, 1H, H-$1_{1,2\text{-}cis}$), 4.05 (dd, *J* = 11.7, 4.4 Hz, 1H, H-

5$_{eq\text{-}1,2\text{-}cis}$), 3.98 – 3.81 (m, 5H, H-2$_{1,2\text{-}cis}$, H-3$_{1,2\text{-}cis}$, H-4$_{1,2\text{-}cis}$, H-4$_{1,2\text{-}trans}$, C*H*HCH$_3$ Et$_{1,2\text{-}trans}$), 3.80 – 3.68 (m, 3H, H-2$_{1,2\text{-}trans}$, H-5$_{1,2\text{-}trans}$, C*H*HCH$_3$ Et$_{1,2\text{-}cis}$), 3.59 – 3.46 (m, 3H, H-3$_{1,2\text{-}trans}$, H-5$_{1,2\text{-}trans}$, CH*H*CH$_3$ Et$_{1,2\text{-}trans}$), 3.42 (dq, *J* = 9.6, 7.1 Hz, 1H, CH*H*CH$_3$ Et$_{1,2\text{-}cis}$), 3.23 (dd, *J* = 11.8, 7.7 Hz, 1H, H-5$_{ax\text{-}1,2\text{-}cis}$), 1.26 (t, *J* = 7.1 Hz, 3H, CH$_3$ Et$_{1,2\text{-}cis}$), 1.17 (t, *J* = 7.1 Hz, 3H, CH$_3$ Et$_{1,2\text{-}trans}$); ^{13}C NMR (101 MHz, CDCl$_3$, HSQC, HMBC, HMBC-Gated): δ 138.9, 138.7, 138.6, 138.6, 138.5 (C$_{q\text{-}arom}$), 128.5, 128.4, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6 (CH$_{arom}$), 100.5 (C-1$_{1,2\text{-}trans}$), 98.7 (C-1$_{1,2\text{-}cis}$), 79.2 (C-2$_{1,2\text{-}cis}$/C-3$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}trans}$), 79.1 (C-3$_{1,2\text{-}trans}$), 75.7 (C-2$_{1,2\text{-}trans}$), 75.0 (C-2$_{1,2\text{-}cis}$/C-3$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}trans}$), 74.9 (C-2$_{1,2\text{-}cis}$/C-3$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}trans}$), 74.3 (C-2$_{1,2\text{-}cis}$/C-3$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}cis}$/C-4$_{1,2\text{-}trans}$), 73.4, 73.3, 73.3, 73.0, 72.8, 72.2 (CH$_2$ Bn), 64.8 (*CH*$_2$CH$_3$ Et$_{1,2\text{-}trans}$), 63.4 (*CH*$_2$CH$_3$ Et$_{1,2\text{-}cis}$), 62.7 (C-5$_{1,2\text{-}cis}$), 61.6 (C-5$_{1,2\text{-}trans}$), 15.4 (CH$_3$ Et$_{1,2\text{-}trans}$), 15.2 (CH$_3$ Et$_{1,2\text{-}cis}$); ^{13}C-GATED NMR (101 MHz, CDCl$_3$): δ 100.5 (*J*$_{H1\text{-}C1}$ = 157 Hz, 1,2-*cis*), δ 98.7 (*J*$_{H1\text{-}C1}$ = 169 Hz, 1,2-*trans*); HRMS: [M+Na]$^+$ calcd for $C_{28}H_{32}O_5$ 471.2147, found 471.2153.

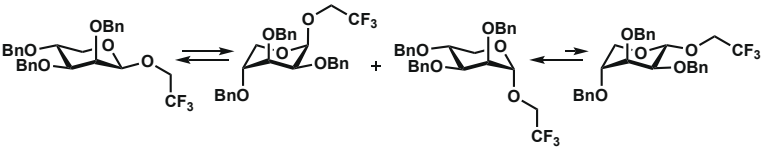


2-Fluoroethyl 2,3,4-tri-*O*-benzyl-D-lyxopyranoside (S12). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (47 mg, 100 µmol, *quant.*, colorless oil, 1,2-*cis*:1,2-*trans*; 73:27). TLC: R$_f$ 0.26, 0.46 (pentane:EtOAc, 85:15, v:v); IR (thin film, cm^{-1}): 694, 732, 1042, 1088, 1453, 1722, 2916; ^{1}H NMR (400 MHz, CDCl$_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.71 – 7.19 (m, 15H, CH$_{arom}$), 4.85 – 4.44 (m, 8H, CH$_2$ Bn, CH$_2$ Bn, CH$_2$ Bn, H-1, CH$_2$C*H*HF, CH$_2$CH*H*F), 4.12 – 4.00 (m, 1H, H-5$_{eq}$), 4.00 – 3.69 (m, 4H, H-2, H-4, C*H*HCH$_2$F, CH*H*CH$_2$F), 3.57 (dd, *J* = 7.3, 3.1 Hz, 1H, H-3), 3.27 (dd, *J* = 11.9, 7.2 Hz, 1H, H-5$_{ax}$); ^{13}C NMR (101 MHz, CDCl$_3$, HSQC, HMBC-Gated): δ 138.6, 138.5, 138.4 (C$_{q\text{-}arom}$), 131.1, 129.4, 128.5, 128.4, 128.4, 128.3, 127.8, 127.7, 127.7, 124.9 (CH$_{arom}$), 100.6 (C-1), 83.0 (d, *J* = 169.4 Hz, CH$_2$*CH*$_2$F), 78.4 (C-3), 74.7 (C-4), 74.1 (C-2), 73.4, 72.9, 72.2 (CH$_2$ Bn), 68.1 (d, *J* = 20.0 Hz, *CH*$_2$CH$_2$F), 62.3 (C-5); ^{13}C-GATED NMR (101 MHz, CDCl$_3$): δ 100.6 (*J*$_{H1\text{-}C1}$ = 158 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, CDCl$_3$, HH-COSY, HSQC, HMBC-Gated): all signals overlap with 1,2-*trans* anomer peaks; ^{13}C NMR (101 MHz, CDCl$_3$, HSQC, HMBC-Gated): δ 138.7, 138.5, 138.4 (C$_{q\text{-}arom}$), 128.5, 128.4, 128.4, 128.0, 127.8, 127.7, 127.6 (CH$_{arom}$), 99.2 (C-1), 82.6 (d, *J* = 169.7 Hz, CH$_2$*CH*$_2$F), 78.9, 75.5, 74.8 (C-2/C-3/C-4), 66.8 (d, *J* = 19.9 Hz, *CH*$_2$CH$_2$F), 61.7 (C-5); ^{13}C-GATED NMR (101 MHz, CDCl$_3$): δ 99.2 (*J*$_{H1\text{-}C1}$ = 169 Hz, 1,2-*trans*); HRMS: [M+Na]$^+$ calcd for $C_{28}H_{31}FO_5$ 489.2053, found 489.2057.

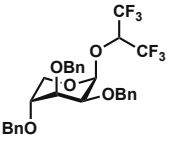


2,2-Difluoroethyl 2,3,4-tri-*O*-benzyl-D-lyxopyranoside (S13). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (45 mg, 93 µmol, 93%, colorless oil, 1,2-*cis*:1,2-*trans*; 64:36). TLC: R$_f$ 0.40, 0.44 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 732, 887, 1062, 1308, 1362, 1453, 1496, 2874; Data for the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, CDCl$_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.42 – 7.25 (m, 15H, CH$_{arom}$), 5.94 (tdd, *J* = 55.6, 5.1, 3.4 Hz, 1H, CHF$_2$), 4.78 – 4.66 (m, 3H, C*H*H Bn, C*H*H Bn, CH*H* Bn), 4.63 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.60 – 4.53 (m, 3H, CH*H* Bn, CH*H* Bn, H-1), 4.05 (dd, *J* = 12.0, 3.7 Hz, 1H, H-5$_{eq}$), 3.99 – 3.86 (m, 2H, H-2, C*H*HCF$_3$), 3.85 – 3.70 (m, 2H, H-4, CH*H*CF$_3$), 3.61 (dd, *J* = 6.8, 3.2 Hz, 1H, H-3), 3.31 (dd, *J* = 12.0, 6.3 Hz, 1H, H-5$_{ax}$); ^{13}C NMR (101 MHz, CDCl$_3$, HSQC, HMBC-Gated): δ 138.6, 138.3, 138.2 (C$_{q\text{-}arom}$), 128.5, 128.4, 128.4, 128.3, 127.9, 127.7 (CH$_{arom}$), 114.5 (t, *J* = 241.0 Hz), 100.4 (C-1), 77.5 (C-3), 74.7 (C-4), 73.9 (C-2), 73.3, 72.7, 72.5 (CH$_2$ Bn), 68.1 (t, *J* = 28.6 Hz, *CH*$_2$CHF$_2$), 61.7 (C-5); ^{13}C-GATED NMR (101 MHz, CDCl$_3$): δ 100.4 (*J*$_{H1\text{-}C1}$ = 162 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, CDCl$_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.42 – 7.25 (m, 15H), 5.85 (tdd, *J* = 55.4, 4.8, 3.6 Hz, 1H, CHF$_2$), 3.55 (dd, *J* = 11.3, 8.3 Hz, 1H, H-5$_{ax}$); ^{13}C NMR (101 MHz, CDCl$_3$, HSQC, HMBC-Gated): δ 138.6, 138.4 (C$_{q\text{-}arom}$), 128.5, 128.5, 128.5,

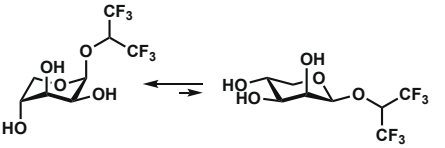
128.1, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7 (CH_{arom}), 114.2 (t, J = 241.1 Hz, CHF_2), 99.8 (C-1), 78.5, 75.4, 74.6 (C-2/C-3/C-4), 73.5, 73.2, 73.0 (CH_2 Bn), 67.0 (t, J = 28.2 Hz, CH_2CHF_2), 62.1 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 99.8 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{30}F_2O_5$ 507.1959, found 507.1967.



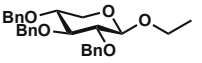
2,2,2-Trifluoroethyl 2,3,4-tri-*O*-benzyl-D-lyxopyranoside (S14). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (97:3 → 90:10, pentane:EtOAc) afforded the title compound (31 mg, 62 µmol, 62%, colorless oil, 1,2-*cis*:1,2-*trans*; 59:41). TLC: R_f 0.40, 0.57 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 697, 736, 986, 1084, 1161, 1278, 1362, 1454, 1497, 2893; Data for the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.43 – 7.22 (m, 15H, CH_{arom}), 4.81 – 4.58 (m, 6H, CH_2 Bn, CH_2 Bn, C*H*H Bn, H-1) , 4.55 (d, J = 12.2 Hz, 1H, CH*H* Bn), 4.18 – 4.03 (m, 2H, H-5_{eq}, C*H*HCF$_3$), 4.02 – 3.75 (m, 6H, H-2, H-4, CH*H*CF$_3$), 3.62 (dd, J = 6.9, 3.1 Hz, 1H, H-3), 3.32 (dd, J = 12.0, 6.4 Hz, 1H, H-5_{ax}); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.6, 138.3, 138.3 ($C_{q\text{-}arom}$), 128.5, 128.4, 128.3, 128.1, 127.9, 127.7 (CH_{arom}), 124.0 (q, J = 278.5 Hz, CF_3), 100.2 (C-1), 77.7 (C-3), 74.9 (C-4), 73.9 (C-2), 73.3, 72.7, 72.5 (CH_2 Bn), 65.6 (q, J = 34.6 Hz), 62.0 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 100.2 ($J_{H1\text{-}C1}$ = 163 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.43 – 7.22 (m, 15H, CH_{arom}), 3.54 (dd, J = 11.3, 8.5 Hz, 1H, H-5_{ax}); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.6, 138.4, 138.2 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6 (CH_{arom}), 121.1 (d, J = 278.3 Hz, CF_3), 99.7 (C-1), 78.5, 75.3, 74.5 (C-2/C-3/C-4), 73.7, 73.2, 73.1 (CH_2 Bn), 64.5 (q, J = 34.7 Hz, CH_2CF_3), 62.3 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 99.7 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}F_3O_5$ 525.1865, found 525.1872.



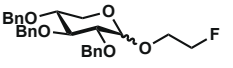
1,1,1,3,3,3-Hexafluoro-2-propyl 2,3,4-tri-*O*-benzyl-1,2-*cis*-D-lyxopyranoside (S15). The title compound was prepared according to general procedure I. The reaction was quenched after 112 h. Flash column chromatography (100:0 → 90:10, pentane:EtOAc) afforded the title compound (26 mg, 46 µmol, 46%, colorless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.32 (pentane:EtOAc, 95:5, v:v); $[\alpha]_D^{20}$ 11.3° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 688, 749, 1103, 1146, 1194, 1219, 1287, 1371, 1454, 2921; ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated, NOESY, ^{1}H-^{19}F Decoupled): δ 7.38 – 7.24 (m, 15H, CH_{arom}), 4.99 (d, J = 2.9 Hz, 1H, H-1), 4.82 (d, J = 11.9 Hz, 1H, C*H*H Bn), 4.75 (d, J = 11.9 Hz, 1H, C*H*H Bn), 4.62 (d, J = 11.9 Hz, 1H, CH*H* Bn), 4.59 – 4.51 (m, 4H, $CH(CF_3)_2$, CH_2 Bn, CH*H* Bn), 4.15 (dd, J = 12.2, 2.3 Hz, 1H, H-5), 3.96 (t, J = 2.7 Hz, 1H, H-2), 3.78 – 3.72 (m, 2H, H-3, H-4), 3.46 (dd, J = 12.3, 4.3 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.1 ($C_{q\text{-}arom}$), 129.6, 128.9, 128.6, 128.5, 128.4, 128.0, 127.9, 127.6 (CH_{arom}), 99.9 (C-1), 75.9 (C-3), 75.3 (C-4), 73.7 (C-2), 72.8 , 72.8 (CH_2 Bn), 72.5 (C*H*$(CF_3)_2$), 72.3 (CH_2 Bn), 61.3 (C-5); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 99.9 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{28}F_6O_5$ 593.1739, found 593.1755.



1,1,1,3,3,3-Hexafluoro-2-propyl 1,2-*cis*-D-lyxopyranoside (S16). 1A (100 mg, 0.175 mmol) was dissolved in dissolved in 5 mL 9:1 MeOH/H_2O under N_2 atmosphere. Then $Pd(OH)_2$ (50 mg, 0.071 mmol) and acetic acid (10 eq, 100 µl) were added and the mixture was purged with H_2. The mixture was stirred under H_2 atmosphere for 16 h after which filtration over a Celite© Hyflo Supercel (Merck) pad and subsequent concentration afforded (30 mg, 0.175 mmol, *quant.*, colorless oil). TLC: R_f 0.20 (DCM:MeOH, 90:10, v:v); $[\alpha]_D^{20}$ –32.6° (*c* 1, MeOH); IR (thin film, cm^{-1}): 687, 1105, 1198, 1370, 1639, 3328; ^1H NMR (500 MHz, DMSO-d_6, HH-COSY, HSQC, HMBC-Gated, NOESY, ^1H-^{19}F Decoupled): δ 5.53 (hept, *J* = 6.6 Hz, 1H, $CH(CF_3)_2$), 4.79 (d, *J* = 2.7 Hz, 1H, H-1), 3.85 (dd, *J* = 11.6, 3.4 Hz, 1H, H-5_{eq}), 3.74 (t, *J* = 3.1 Hz, 1H, H-2), 3.59 (td, *J* = 6.0, 3.3 Hz, 1H, H-4), 3.46 (dd, *J* = 6.3, 3.2 Hz, 1H, H-3), 3.17 (dd, *J* = 11.6, 5.7 Hz, 1H, H-5_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 121.8 (qd, *J* = 282.1, 281.4, 63.1 Hz, $CH(CF_3)_2$), 102.0 (C-1), 72.3 (p, *J* = 31.4 Hz, $CH(CF_3)_2$), 71.3 (C-3), 67.5 (C-4), 67.0 (C-2), 62.8 (C-5). ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 102.0 ($J_{H1\text{-}C1}$ = 165 Hz, 1,2-*cis*).

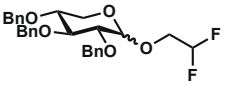


Ethyl 2,3,4-tri-*O*-benzyl-1,2-*trans*-D-xylopyranoside (S17). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (40 mg, 89 µmol, 89%, colorless oil, 1,2-*cis*:1,2-*trans*; 15:85). TLC: R_f 0.57 (pentane:EtOAc, 90:10, v:v); $[\alpha]_D^{20}$ –19.3° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 694, 732, 997, 1070, 1358, 1444, 2894; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.39 – 7.25 (m, 15H), 4.92 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.86 (d, *J* = 3.6 Hz, 2H, CH_2 Bn), 4.73 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.72 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.62 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.34 (d, *J* = 7.6 Hz, 1H, H-1), 4.00 – 3.87 (m, 2H, H-5_{eq}, C*H*HCH$_3$ Et), 3.66 – 3.51 (m, 3H, H-3, H-4, CH*H*CH$_3$ Et), 3.36 (dd, *J* = 8.8, 7.6 Hz, 1H, H-2), 3.19 (dd, *J* = 11.6, 9.8 Hz, 1H, H-5_{ax}), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3 Et); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.8, 138.7, 138.3 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7 (CH_{arom}), 104.2 (C-1), 83.9 (C-4), 82.1 (C-2), 78.0 (C-3), 75.8, 75.1, 73.6 (CH_2 Bn), 65.7 (CH_2 Et), 64.0 (C-5), 15.5 (CH_3 Et); ^{13}C-GATED NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 104.2 ($J_{H1\text{-}C1}$ = 158 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 4.65 (d, *J* = 3.5 Hz, 1H, H-1); ^{13}C-GATED NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.1, 138.5, 138.4 ($C_{q\text{-}arom}$), 96.7 (C-1), 81.6 (C-4), 79.8 (C-2), 78.3 (C-3), 75.9, 73.7, 73.5 (CH_2 Bn), 63.3 (CH_2 Et), 60.0 (C-5), 15.1 (CH_3 Et); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 104.2 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{32}O_5$ 471.2147, found 471.2151.

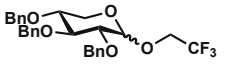


2-Fluoroethyl 2,3,4-tri-*O*-benzyl-D-xylopyranoside (S18). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (95:5 → 80:20 pentane:EtOAc) afforded the title compound (47 mg, 100 µmol, *quant.*, colorless oil, 1,2-*cis*:1,2-*trans*; 29:71). TLC: R_f 0.46 (pentane:EtOAc, 85:15, v:v); IR (thin film, cm^{-1}): 694, 732, 738, 881, 1072, 1444, 1718, 2886; ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.69 – 7.25 (m, 15H, CH_{arom}), 4.97 – 4.80 (m, 4H, CH_2 Bn, C*H*H Bn), 4.79 – 4.69 (m, 2H, CH*H* Bn, C*H*H Bn), 4.68 – 4.58 (m, 2H, CH*H* Bn, CH_2C*H*HF), 4.58 – 4.47 (m, 1H, CH_2CH*H*F), 4.39 (d, *J* = 7.6 Hz, 1H, H-1), 4.04 (dddd, *J* = 32.3, 12.1, 4.7, 2.6 Hz, 1H, C*H*HCH$_2$F), 3.93 (dd, *J* = 11.5, 5.0 Hz, 1H, H-5_{eq}), 3.89 – 3.76 (m, 1H, CH*H*CH$_2$F), 3.64 – 3.52 (m, 2H, H-3, H-4), 3.40 (dd, *J* = 8.9, 7.5 Hz, 1H, H-2), 3.21 (dd, *J* = 11.7, 9.6 Hz, 1H, H-5_{ax}); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.5, 138.2 ($C_{q\text{-}arom}$), 131.2, 129.4, 128.6, 128.4, 128.1, 127.9, 124.9 (CH_{arom}), 104.4 (C-1), 83.7 (C-3), 82.7 (d, *J* = 170.3 Hz, CH_2CH_2F), 81.8 (C-2), 77.8 (C-4), 75.7, 75.1, 73.5 (CH_2 Bn), 68.89 (d, *J* = 19.9 Hz, CH_2CH_2F), 64.0 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 104.4 ($J_{H1\text{-}C1}$ = 159 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.69 – 7.25 (m, 15H, CH_{arom}), 3.47 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.0, 138.4, 138.3 ($C_{q\text{-}arom}$), 128.5, 128.4, 128.2, 128.1, 128.0, 127.9,

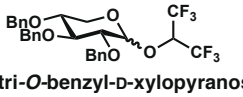
127.8, 127.7, 127.7 (CH_{arom}), 97.4 (C-1), 82.7 (d, J = 169.7 Hz, $CH_2\mathit{CH_2}F$), 81.3 (C-3), 79.7 (C-2), 78.1 (C-4), 75.9, 73.6, 73.4 (CH_2 Bn), 66.9 (d, J = 20.2 Hz, $\mathit{CH_2}CH_2F$), 60.1 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 97.4 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{31}FO_5$ 489.2053, found 489.2058.



2,2-Difluoroethyl 2,3,4-tri-*O*-benzyl-D-xylopyranoside (S19). The title compound was prepared according to general procedure I. The reaction was quenched after 2 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (43 mg, 89 µmol, 89%, colorless oil, 1,2-*cis*:1,2-*trans*; 37:63). TLC: R_f 0.42 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 737, 1070, 1363, 1454, 1497, 1727, 2867; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.68 – 7.25 (m, 15H, CH_{arom}), 5.90 (tdd, J = 55.3, 5.0, 3.3 Hz, 1H, $CH_2C\mathit{H}F_2$), 4.98 – 4.55 (m, 12H), 4.39 (d, J = 7.5 Hz, 1H, H-1), 4.04 – 3.85 (m, 2H, H-5_{eq}, $C\mathit{H}HCHF_2$), 3.85 – 3.68 (m, 1H, $CH\mathit{H}CHF_2$), 3.68 – 3.49 (m, 2H, H-3, H-4), 3.39 (dd, J = 8.8, 7.5 Hz, 1H, H-2), 3.21 (dd, J = 11.7, 9.4 Hz, 1H, H-5_{ax}); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.6, 138.3, 138.1 ($C_{q\text{-}arom}$), 131.2, 129.5, 128.6, 128.5, 128.0, 124.9 (CH_{arom}), 114.2 (t, J = 241.2 Hz, $CH_2\mathit{CH}F_2$), 104.6 (C-1), 83.6 (C-3), 81.7 (C-2), 77.7 (C-4), 75.8, 75.2, 73.5 (CH_2 Bn), 68.65 (dd, J = 29.3, 27.4 Hz), 64.1 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 104.6 ($J_{H1\text{-}C1}$ = 161 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.68 – 7.25 (m, 15H, CH_{arom}), 5.95 (tt, J = 55.5, 4.3 Hz, 1H, $CH_2C\mathit{H}F_2$), 4.80 (d, J = 11.9 Hz, 1H, $C\mathit{H}$H Bn), 3.46 (dd, J = 9.6, 3.6 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9, 138.3, 138.2 ($C_{q\text{-}arom}$), 128.6, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8 (CH_{arom}), 114.3 (t, J = 241.4 Hz, $CH_2C\mathit{H}F_2$), 98.0 (C-1), 81.2 (C-3), 79.6 (C-2), 77.9 (C-4), 76.0, 73.7, 73.7 (CH_2 Bn), 67.00 (t, J = 28.9 Hz, $\mathit{CH_2}CHF_2$), 60.4 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 98.0 ($J_{H1\text{-}C1}$ = 169 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{30}F_2O_5$ 507.1959, found 507.1960.

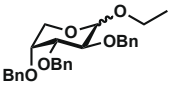


2,2,2-Trifluoroethyl 2,3,4-tri-*O*-benzyl-D-xylopyranoside (S20). The title compound was prepared according to general procedure I. The reaction was quenched after 40 h. Flash column chromatography (97:3 → 90:10, pentane:EtOAc) afforded the title compound (39 mg, 78 µmol, 78%, colorless oil, 1,2-*cis*:1,2-*trans*; 36:64). TLC: R_f 0.60 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 734, 1028, 1072, 1161, 1276, 1358, 1454, 1497, 2872; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (36:64) anomers: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.39 – 7.25 (m, 23.6H), 4.95 – 4.58 (m, 10.4H, CH_2 $Bn_{1,2\text{-}cis}$, CH_2 $Bn_{1,2\text{-}cis}$, CH_2 $Bn_{1,2\text{-}cis}$, H-$1_{1,2\text{-}cis}$, CH_2 $Bn_{1,2\text{-}trans}$, CH_2 $Bn_{1,2\text{-}trans}$, CH_2 $Bn_{1,2\text{-}trans}$), 4.46 (d, J = 7.4 Hz, 1H, H-$1_{1,2\text{-}trans}$), 4.14 (dq, J = 12.3, 8.7 Hz, 1H, $C\mathit{H}HCF_3$), 4.00 – 3.79 (m, 3.7H, H-$3_{1,2\text{-}cis}$, $C\mathit{H}HCF_{3\text{-}1,2\text{-}cis}$, $CH\mathit{H}CF_{3\text{-}1,2\text{-}cis}$, H-$5_{eq\text{-}1,2\text{-}trans}$, $CH\mathit{H}CF3_{\text{-}1,2\text{-}trans}$), 3.66 – 3.45 (m, 3.7H, H-$2_{1,2\text{-}cis}$, H-$4_{1,2\text{-}cis}$, H-$5_{1,2\text{-}cis}$, H-$5_{1,2\text{-}cis}$, H-$3_{1,2\text{-}trans}$, H-$4_{1,2\text{-}trans}$), 3.42 (t, J = 8.0 Hz, 1H, H-$2_{1,2\text{-}trans}$), 3.23 (dd, J = 11.7, 9.1 Hz, 1H, H-$5_{ax\text{-}1,2\text{-}trans}$); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9 ($C_{q\text{-}arom\text{-}1,2\text{-}cis}$), 138.6 ($C_{q\text{-}arom\text{-}1,2\text{-}trans}$), 138.3, 138.2 ($C_{q\text{-}arom\text{-}1,2\text{-}cis}$), 138.1, 138.1 ($C_{q\text{-}arom\text{-}1,2\text{-}trans}$), 128.6, 128.6, 128.5, 128.5, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 125.3, 125.2, 122.5, 122.4 (CH_{arom}), 104.3 (C-$1_{1,2\text{-}trans}$), 97.9 (C-$1_{1,2\text{-}cis}$), 83.4 (C-$3_{1,2\text{-}trans}$), 81.4 (C-$2_{1,2\text{-}trans}$), 81.0 (C-$3_{1,2\text{-}cis}$), 79.5 (C-$2_{1,2\text{-}cis}$), 77.7 (C-$4_{1,2\text{-}cis}$), 77.7 (C-$4_{1,2\text{-}trans}$), 76.0 (CH_2 $Bn_{1,2\text{-}cis}$), 75.8, 75.1 (CH_2 $Bn_{1,2\text{-}trans}$), 73.7 (CH_2 $Bn_{1,2\text{-}cis}$), 73.5 (CH_2 $Bn_{1,2\text{-}cis}$, CH_2 $Bn_{1,2\text{-}trans}$), 66.0 (q, J = 34.8 Hz, $\mathit{CH_2}CF_{3\text{-}1,2\text{-}trans}$), 64.6 (q, J = 34.8 Hz, $\mathit{CH_2}CF_{3\text{-}1,2\text{-}cis}$), 64.1 (C-$5_{1,2\text{-}trans}$), 60.6 (C-$5_{1,2\text{-}cis}$); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 104.3 ($J_{H1\text{-}C1}$ = 162 Hz, 1,2-*trans*), 97.9 ($J_{H1\text{-}C1}$ = 169 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}F_3O_5$ 525.1865, found 525.1870.

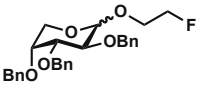


1,1,1,3,3,3-Hexafluoro-2-propyl 2,3,4-tri-*O*-benzyl-D-xylopyranoside (S21). The title compound was prepared according to general procedure I. The reaction was quenched after 112 h. Flash column chromatography (100:0 → 80:20, pentane:Et_2O) afforded the title compound (28 mg, 0.049 mmol, 49%, colorless oil, 1,2-*cis*:1,2-*trans*; 32:68). TLC: R_f 0.23, 0.38 (pentane:EtOAc, 95:5, v:v); IR (thin film, cm^{-1}): 688, 743, 898, 1028, 2073, 1194, 1220, 1286, 1369, 1454, 2916; Data for the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated, ^{1}H-^{19}F Decoupled): δ 7.41 – 7.28 (m,

15H, CH_{arom}), 4.91 – 4.85 (m, 2H, C*H*H Bn, C*H*H Bn), 4.83 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.76 – 4.66 (m, 3H, C*H*H Bn, CH*H* Bn, H-1), 4.63 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.58 (p, *J* = 6.0 Hz, 1H, $CH(CF_3)_2$), 4.00 (dd, *J* = 11.9, 4.6 Hz, 1H, H-5_{eq}), 3.71 – 3.62 (m, 2H, H-3, H-4), 3.56 – 3.49 (m, 1H, H-2), 3.36 (dd, *J* = 11.9, 7.7 Hz, 1H, H-5_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.5, 138.0, 137.8 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.4, 128.0, 127.9, 127.9 (CH_{arom}), 104.1 (C-1), 82.8 (C-3), 80.7 (C-2), 77.6 (C-4), 75.5, 75.0, 73.1 (CH_2 Bn), 72.07 (p, *J* = 32.8 Hz, *C*H($CF_3)_2$), 64.1 (C-5); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 104.1 ($J_{H1\text{-}C1}$ = 168 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated, ^{1}H-^{19}F Decoupled): δ 7.41 – 7.28 (m, 15H), 5.06 (d, *J* = 3.7 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.78 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.44 (hept, *J* = 5.7 Hz, 1H, $CH(CF_3)_2$),), 3.92 (dd, *J* = 9.8, 8.6 Hz, 1H, H-3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.1, 137.8 ($C_{q\text{-}arom}$), 128.9, 128.5, 128.5, 128.1, 128.1, 128.0, 127.7, 127.7 (CH_{arom}), 99.3 (C-1), 80.7 (C-3), 78.8 (C-2), 77.4 (C-4), 75.9, 73.8, 73.6 (CH_2 Bn), 61.4 (C-5); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 99.3 ($J_{H1\text{-}C1}$ = 171 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{28}F_6O_5$ 593.1739, found 593.1749.

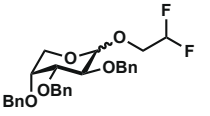


Ethyl 2,3,4-tri-*O*-benzyl-D-arabinopyranoside (S22). The title compound was prepared according to general procedure I. The reaction was quenched after 1.5 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (45 mg, 100 µmol, *quant.*, colorless oil, 1,2-*cis*:1,2-*trans*; 18:82). TLC: R_f 0.24, 0.31 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 694, 732, 1045, 1087, 1444, 2920; Data for the major stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.51 – 7.21 (m, 15H, CH_{arom}), 4.90 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.80 – 4.73 (m, 2H, C*H*H Bn, CH*H* Bn), 4.70 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.66 – 4.63 (m, 2H, CH*H* Bn , CH*H* Bn), 4.31 (d, *J* = 7.1 Hz, 1H, H-1), 4.03 (dd, *J* = 12.7, 2.9 Hz, 1H, H-5), 3.97 (dq, *J* = 9.5, 7.0 Hz, 1H, C*H*HCH$_3$ Et), 3.80 (dd, *J* = 9.2, 7.1 Hz, 1H, H-2), 3.68 (td, *J* = 3.1, 1.3 Hz, 1H, H-4), 3.58 (dq, *J* = 9.5, 7.0 Hz, 1H, CH*H*CH$_3$ Et), 3.49 (dd, *J* = 9.2, 3.4 Hz, 1H, H-3), 3.25 (dd, *J* = 12.8, 1.3 Hz, 1H, H-5), 1.27 (t, *J* = 7.0 Hz, 3H, CH_3 Et); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9, 138.6, 138.3 ($C_{q\text{-}arom}$), 128.4, 128.4, 128.2, 128.1, 127.8, 127.7, 127.7, 127.6 (CH_{arom}), 103.8 (C-1), 80.0 (C-3), 79.3 (C-2), 75.2, 72.5 (CH_2 Bn), 72.3 (C-4), 71.2 (CH_2 Bn), 65.4 (CH_2 Et), 62.9 (C-5), 15.4 (CH_3 Et); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 103.8 ($J_{H1\text{-}C1}$ = 158 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): All peaks overlap with 1,2-*trans* anomer peaks; ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 128.0, 128.0, 127.6 (CH_{arom}), 97.8 (C-1), 77.4, 76.6, 74.1 (C-2/C-3/C-4), 73.6, 72.9, 71.8 (CH_2 Bn), 63.5 (CH_2 Et), 60.4 (C-5), 15.1 (CH_3 Et); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 97.8 ($J_{H1\text{-}C1}$ = 169 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{32}O_5$ 471.2147, found 471.2160.

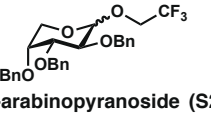


2-Fluoroethyl 2,3,4-tri-*O*-benzyl-D-arabinopyranoside (S23). The title compound was prepared according to general procedure I. The reaction was quenched after 1.5 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) afforded the title compound (45 mg, 96 µmol, 96%, colorless oil, 1,2-*cis*:1,2-*trans*; 56:44). TLC: R_f 0.16, 0.24 (pentane:EtOAc, 85:15, v:v); IR (thin film, cm^{-1}): 694, 736, 997, 1044, 1088, 1334, 1723, 2908; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (1.29:1) anomers: ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.69 – 7.21 (m, 34.4H, CH_{arom}), 4.91 (d, *J* = 10.8 Hz, 1H, C*H*H Bn$_{1,2\text{-}trans}$), 4.88 – 4.81 (m, 2.6H, C*H*H Bn$_{1,2\text{-}cis}$, H-1$_{1,2\text{-}cis}$), 4.80 – 4.47 (m, 16.1H, CH*H* Bn$_{1,2\text{-}cis}$, CH*H* Bn$_{1,2\text{-}trans}$, CH_2 Bn$_{1,2\text{-}cis}$, CH_2 Bn$_{1,2\text{-}cis}$, CH_2C*H*$_2$F$_{1,2\text{-}cis}$, CH_2 Bn$_{1,2\text{-}trans}$, CH_2 Bn$_{1,2\text{-}trans}$, CH_2C*H*$_2$F$_{1,2\text{-}trans}$), 4.37 (d, *J* = 6.9 Hz, 1H, H-1$_{1,2\text{-}trans}$), 4.15 – 3.99 (m, 3.29H, H-2$_{1,2\text{-}cis}$, H-5$_{1,2\text{-}trans}$, C*H*HCH$_2$F$_{1,2\text{-}trans}$), 3.95 – 3.63 (m, 10.7H, H-3$_{1,2\text{-}cis}$, H-4$_{1,2\text{-}cis}$, H-5$_{1,2\text{-}cis}$, H-5$_{1,2\text{-}cis}$, C*H*HCH$_2$F$_{1,2\text{-}cis}$, CH*H*CH$_2$F$_{1,2\text{-}cis}$, H-2$_{1,2\text{-}trans}$, H-4$_{1,2\text{-}trans}$, CH*H*CH$_2$F$_{1,2\text{-}trans}$), 3.51 (dd, *J* = 9.0, 3.3 Hz, 1H, H-3$_{1,2\text{-}trans}$), 3.27 (dd, *J* = 12.6, 1.4 Hz, 1H, H-5$_{1,2\text{-}trans}$); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.8, 138.8, 138.7, 138.5, 138.4, 138.3 ($C_{q\text{-}arom}$), 131.2, 129.4, 128.5, 128.5, 128.4, 128.4, 128.4, 128.1, 128.1, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 124.9 (CH_{arom}), 104.0 (C-1$_{1,2\text{-}trans}$), 98.5 (C-1$_{1,2\text{-}cis}$), 83.7 (CH_2*CH*$_2$F$_{1,2\text{-}cis}$), 82.0 (CH_2*CH*$_2$F$_{1,2\text{-}trans}$), 79.7 (C-3$_{1,2\text{-}trans}$), 79.0 (C-2$_{1,2\text{-}trans}$), 77.2 (C-3$_{1,2\text{-}cis}$), 76.4 (C-2$_{1,2\text{-}cis}$), 75.2 (CH_2 Bn$_{1,2\text{-}trans}$), 74.0 (C-4$_{1,2\text{-}cis}$), 73.7, 72.9 (CH_2 Bn$_{1,2\text{-}cis}$), 72.6 (CH_2 Bn$_{1,2\text{-}trans}$), 72.2 (C-4$_{1,2\text{-}trans}$), 71.9 (CH_2 Bn$_{1,2\text{-}cis}$), 71.4(CH_2 Bn$_{1,2\text{-}trans}$), 68.6 (d, *J* = 20.1 Hz, *CH*$_2$CH$_2$F$_{1,2\text{-}trans}$), 67.1 (d, *J* = 20.0 Hz, *CH*$_2$CH$_2$F$_{1,2\text{-}cis}$), 63.0 (C-5$_{1,2\text{-}trans}$), 60.5 (C-5$_{1,2\text{-}cis}$); ^{13}C-

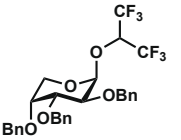
GATED NMR (101 MHz, $CDCl_3$): δ 104.0 ($J_{H1\text{-}C1}$ = 160 Hz, 1,2-*trans*), 98.5 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{31}FO_5$ 489.2053, found 489.2064.



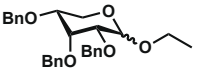
2,2-Difluoroethyl 2,3,4-tri-*O*-benzyl-D-arabinopyranoside (S24). The title compound was prepared according to general procedure I. The reaction was quenched after 1.5 h. Flash column chromatography (95:5 → 85:15, pentane:EtOAc) afforded the title compound (26 mg, 54 µmol, 54%, colorless oil, 1,2-*cis*:1,2-*trans*; 62:38). TLC: R_f 0.13, 0.25 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 694, 734, 903, 1046, 1349, 1453, 1723, 2920; Data for the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.70 – 7.24 (m, 15H, CH_{arom}), 6.10 – 5.77 (m, 1H, CH_2CHF_2), 4.87 – 4.81 (m, 2H, C*H*H Bn, H-1), 4.79 – 4.59 (m, 5H, CH*H* Bn, CH_2 Bn, CH_2 Bn), 4.09 – 3.92 (m, 1H, H-2), 3.87 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3), 3.85 – 3.61 (m, 5H, H-4, H-5, H-5, C*H*HCHF$_2$, C*H*HCHF$_2$); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.6, 138.3 ($C_{q\text{-}arom}$), 131.2, 129.5, 128.5, 128.5, 128.1, 128.0, 127.8, 127.7, 124.9 (CH_{arom}), 114.3 (t, *J* = 240.3 Hz, CH_2CHF_2), 99.1 (C-1), 77.0 (C-3), 76.2 (C-2), 73.9 (CH_2 Bn), 73.8 (C-4), 72.9, 72.0 (CH_2 Bn), 67.35 (t, *J* = 28.7 Hz, CH_2CHF_2), 60.9 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 99.1 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC-Gated): δ 7.70 – 7.24 (m, 15H, CH_{arom}), 4.37 (d, *J* = 6.8 Hz, 1H, H-1), 3.51 (dd, *J* = 8.9, 3.3 Hz, 1H, H-3), 3.28 (dd, *J* = 12.6, 1.6 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$ HSQC, HMBC-Gated): δ 138.5, 138.4, 138.2 ($C_{q\text{-}arom}$), 128.3, 128.1, 127.9, 127.9, 127.8, 127.7, 127.7 (CH_{arom}), 114.4 (dd, *J* = 241.9, 240.0 Hz, CH_2CHF_2), 104.0 (C-1), 79.5 (C-3), 78.7 (C-2), 75.2, 72.6 (CH_2 Bn), 72.1 (C-4), 71.5 (CH_2 Bn), 68.4 (dd, *J* = 30.3, 26.9 Hz, CH_2CHF_2), 63.1 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 104.0 ($J_{H1\text{-}C1}$ = 160 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{30}F_2O_5$ 507.1959, found 507.1958.



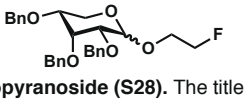
2,2,2-Trifluoroethyl 2,3,4-tri-*O*-benzyl-D-arabinopyranoside (S25). The title compound was prepared according to general procedure I. The reaction was quenched after 40 h. Flash column chromatography (97:3 → 90:10, pentane:EtOAc) afforded the title compound (45 mg, 90 µmol, 90%, colorless oil, 1,2-*cis*:1,2-*trans*; 88:12). TLC: R_f 0.19, 0.40 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 735, 1088, 1147, 1277, 1453, 2923; Data for the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.32 (tdd, *J* = 11.8, 9.0, 6.2 Hz, 15H, CH_{arom}), 4.87 (d, *J* = 3.4 Hz, 1H, H-1), 4.83 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.70 (s, 2H, CH_2 Bn), 4.67 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.63 (d, *J* = 11.8 Hz, 1H, CH*H* bn), 4.03 (dd, *J* = 9.5, 3.4 Hz, 1H, H-2), 3.96 – 3.83 (m, 3H, H-3, CH_2CF_3), 3.79 (dt, *J* = 4.7, 2.2 Hz, 1H, H-4), 3.67 (m, 2H, H-5, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.7, 138.6, 138.2 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.4, 128.0, 128.0, 127.8, 127.7, 127.7 (CH_{arom}), 125.3, 122.5, 119.8 (CF_3), 99.0 (C-1), 76.8 (C-4), 76.0 (C-2), 73.7 (C-3), 73.7, 72.9, 72.0 (CH_2 Bn), 64.9 (q, *J* = 34.7 Hz, CH_2CF_3), 61.1 (C-5); ^{13}C-GATED NMR NMR (101 MHz, $CDCl_3$): δ 99.0 ($J_{H1\text{-}C1}$ = 170 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.47 – 7.24 (m, 15H, CH_{arom}), 4.44 (d, *J* = 6.6 Hz, 1H, H-1), 4.24 – 4.11 (m, 2H, CH_2CF_3), 3.52 (dd, *J* = 8.7, 3.3 Hz, 1H, H-3), 3.29 (dd, *J* = 12.5, 1.6 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.4, 138.3, 138.1 ($C_{q\text{-}arom}$), 128.4, 128.1, 127.9, 127.8, 127.7 (CH_{arom}), 103.5 (C-1), 79.2 (C-3), 78.4 (C-2), 72.09 (C-4), 65.7 (q, *J* = 34.7 Hz), 63.0 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 103.5 ($J_{H1\text{-}C1}$ = 160 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}F_3O_5$ 525.1865, found 525.1874.



1,1,1,3,3,3-Hexafluoro-2-propyl 2,3,4-tri-*O*-benzyl-1,2-*cis*-D-arabinopyranoside (S26). The title compound was prepared according to general procedure I. The reaction was quenched after 112 h. Flash column chromatography (100:0 → 80:20, pentane:Et_2O) afforded the title compound (8 mg, 14 µmol, 14%, colorless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.17 (pentane:EtOAc, 95:5, v:v); $[\alpha]_D^{20}$ -11.7° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 696, 735, 1102, 1195, 1219, 1286, 1369, 1454, 2924; ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated, ^1H-^{19}F Decoupled): δ 7.41 – 7.26 (m, 15H, CH_{arom}), 5.17 (d, *J* = 3.6 Hz, 1H, H-1), 4.93 – 4.86 (m, 1H, C*H*H Bn), 4.81 – 4.67 (m, CH*H* Bn, ,CH*H* BnCH_2 Bn), 4.66 – 4.58 (m, 1H, CH*H* Bn), 4.46 (hept, *J* = 6.2 Hz, 1H, ($CH(CF_3)_2$), 4.10 (dd, *J* = 9.7, 3.6 Hz, 1H, H-2), 3.89 (dd, *J* = 9.7, 3.1 Hz, 1H, H-3), 3.86 – 3.81 (m, 1H, H-4), 3.74 (m, 2H, H-5, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.6, 138.3, 138.2 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.0, 128.0, 127.8, 127.7 (CH_{arom}), 100.4 (C-1), 76.7 (C-3), 75.4 (C-2), 73.8 (CH_2 Bn), 73.7 (C-4), 73.0 (CH_2 Bn), 72.7, 72.5, 72.2 (*CH*$(CF_3)_2$), 72.2 (CH_2 Bn), 62.1 (C-5); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 100.4 ($J_{H1\text{-}C1}$ = 171 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{28}F_6O_5$ 593.1739, found 593.1746.

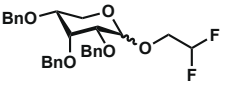


Ethyl 2,3,4-tri-*O*-benzyl-D-ribopyranoside (S27). The title compound was prepared according to general procedure I. The reaction was quenched after 1.5 h. Flash column chromatography (97:3 → 85:15, pentane:EtOAc) afforded the title compound (45 mg, 100 µmol, *quant.*, colorless oil, 1,2-*cis*:1,2-*trans*; 28:72). TLC: R_f 0.43 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 695, 732, 1064, 1318, 1453, 1497, 1723, 2879; Data for the major stereoisomer (1,2-*trans*): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.49 – 7.20 (m, 15H, CH_{arom}), 4.90 – 4.77 (m, 3H, H-1, C*H*H Bn, C*H*H Bn), 4.65 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.61 (s, 1H, CH*H* Bn), 4.53 (m, 2H, CH_2 Bn), 4.10 – 4.04 (m, 1H, H-3), 3.89 (dq, *J* = 9.6, 7.0 Hz, 1H, C*H*HCH_3 Et), 3.87 – 3.72 (m, 2H, H-5, H-5), 3.59 (dq, *J* = 9.6, 7.1 Hz, 1H, CH*H*CH_3 Et), 3.50 – 3.40 (m, 1H, H-4), 3.25 (dd, *J* = 7.3, 2.8 Hz, 1H, H-2), 1.24 (t, *J* = 7.1 Hz, 3H, CH_3 Et); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.1, 138.9, 138.2 ($C_{q\text{-}arom}$), 131.2, 129.4, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6 (CH_{arom}), 100.9 (C-1), 78.4 (C-2), 75.6 (C-3), 75.3 (C-4), 74.0, 73.1, 71.5 (CH_2 Bn), 65.3 (CH_2 Et), 62.2 (C-5), 15.5 (CH_3 Et); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 100.9 ($J_{H1\text{-}C1}$ = 162 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 4.94 (d, *J* = 12.3 Hz, 1H, C*H*H Bn), 4.75 (d, *J* = 3.8 Hz, 1H, H-1), 3.38 (t, *J* = 3.3 Hz, 1H, H-2), 1.29 (t, *J* = 7.1 Hz, 3H, CH_3 Et); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.6, 138.4, 138.3 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.1, 127.8, 127.6, 127.1 (CH_{arom}), 96.8 (C-1), 76.3 (C-2), 73.2, 71.3, 71.0 (CH_2 Bn), 64.0 (CH_2 Et), 57.4 (C-5), 15.3 (CH_3 Et); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 96.8 ($J_{H1\text{-}C1}$ = 166 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{32}O_5$ 471.2147, found 471.2155.

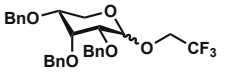


2-Fluoroethyl 2,3,4-tri-*O*-benzyl-D-ribopyranoside (S28). The title compound was prepared according to general procedure I. The reaction was quenched after 1.5 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) afforded the title compound (47 mg, 100 µmol, *quant.*, colorless oil, 1,2-*cis*:1,2-*trans*; 39:61). TLC: R_f 0.22, 0.44 (pentane:EtOAc, 85:15, v:v); IR (thin film, cm^{-1}): 694, 734, 1066, 1444, 2883; Data for the minor stereoisomer (1,2-*trans*): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.49 – 7.20 (m, 15H, CH_{arom}), 3.54 (ddd, *J* = 9.4, 4.7, 2.5 Hz, 1H, H-4), 3.30 (dd, *J* = 7.0, 2.8 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$ HSQC, HMBC-Gated): δ 139.0, 138.8, 138.2 ($C_{q\text{-}arom}$), 128.4, 128.3, 128.0, 127.6, 127.5 (CH_{arom}), 101.3 (C-1), 82.77 (d, *J* = 169.6 Hz, CH_2CH_2F), 78.1 (C-2), 75.5 (C-3), 75.1 (C-4), 73.9, 73.1, 71.4 (CH_2 Bn), 68.6 (d, *J* = 20.0 Hz, CH_2CH_2F), 62.2 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 101.3 ($J_{H1\text{-}C1}$ = 164 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*cis*): ^1H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.49 – 7.20 (m, 15H, CH_{arom}), 4.94 (d, *J* = 12.3 Hz, 1H, C*H*H Bn), 4.88 – 4.76 (m, 2H, C*H*H Bn, H-1), 4.74 – 4.45 (m, 6H, CH_2 Bn, CH_2 Bn, CH_2CH_2F), 4.16 – 4.02 (m, 2H, H-3, H-

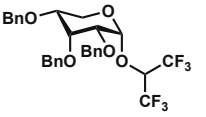
5), 4.01 – 3.69 (m, 2H, C*H*$_2$CH$_2$F), 3.50 – 3.43 (m, 2H, H-4, H-5), 3.40 (t, *J* = 3.4 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.5, 138.3, 138.2 ($C_{q\text{-arom}}$), 128.5, 128.5, 128.1, 127.8, 127.8, 127.6, 127.1 (CH_{arom}), 97.3 (C-1), 83.1 (d, *J* = 169.2 Hz, CH$_2$*CH$_2$*F), 76.3 (C-2), 74.7 (C-4), 73.5 (C-3), 73.3, 71.5, 71.0 (CH_2 Bn), 67.4 (d, *J* = 20.5 Hz, C*H$_2$*CH$_2$F), 57.5 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 97.3 ($J_{H1\text{-}C1}$ = 165 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{31}FO_5$ 489.2053, found 489.2054.



2,2-Difluoroethyl 2,3,4-tri-*O*-benzyl-D-ribopyranoside (S29). The title compound was prepared according to general procedure I. The reaction was quenched after 1.5 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) afforded the title compound (35 mg, 72 µmol, 72%, colorless oil, 1,2-*cis*:1,2-*trans*; 50:50). TLC: R_f 0.23, 0.42 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 697, 735, 1064, 1389, 1454, 2877; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (50:50) anomers: ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.49 – 7.21 (m, 30H, CH_{arom}), 5.96 (tdd, *J* = 55.7, 5.0, 3.7 Hz, 1H, CH$_2$C*H*F$_2$), 5.90 (tdd, *J* = 55.6, 4.8, 3.6 Hz, 1H, CH$_2$C*H*F$_2$), 4.92 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.87 – 4.74 (m, 6H, C*H*H Bn, CH*H* Bn, CH$_2$ Bn, H-1$_{1,2\text{-}cis}$, H-1$_{1,2\text{-}trans}$), 4.66 – 4.48 (m, 7H, CH*H* Bn, CH$_2$ Bn, CH$_2$ Bn, CH$_2$ Bn), 4.14 (s, 1H, H-3$_{1,2\text{-}cis}$), 4.12 – 4.02 (m, 2H, H-3$_{1,2\text{-}trans}$, H-5$_{1,2\text{-}trans}$), 3.98 – 3.67 (m, 7H, H-5$_{1,2\text{-}cis}$, H-5$_{1,2\text{-}cis}$, *CH$_2$*CHF$_2$, *CH$_2$*CHF$_2$), 3.55 – 3.44 (m, 3H, H-4$_{1,2\text{-}cis}$, H-4$_{1,2\text{-}trans}$, H-5$_{1,2\text{-}trans}$), 3.39 (t, *J* = 3.4 Hz, 1H, H-2$_{1,2\text{-}cis}$), 3.27 (dd, *J* = 7.1, 2.8 Hz, 1H, H-2$_{1,2\text{-}trans}$); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.5, 139.0, 138.6, 138.2, 138.1, 138.1 ($C_{q\text{-arom}}$), 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.2 (CH_{arom}), 114.8 (t, *J* = 241.1 Hz, CH$_2$*CH*F$_2$), 114.3 (t, *J* = 240.9 Hz, CH$_2$*CH*F$_2$), 101.8 (C-1$_{1,2\text{-}trans}$), 97.7 (C-1$_{1,2\text{-}cis}$), 78.1 (C-2$_{1,2\text{-}trans}$), 76.3 (C-2$_{1,2\text{-}cis}$), 75.4 (C-3$_{1,2\text{-}trans}$), 75.0 (C-4$_{1,2\text{-}cis}$), 74.7 (C-4$_{1,2\text{-}trans}$), 74.1, 73.5 (CH_2 Bn), 73.4 (C-3$_{1,2\text{-}cis}$), 73.1 (CH_2 Bn), 71.6 (CH_2 Bn, CH_2 Bn), 71.1 (CH_2 Bn), 68.7 (t, *J* = 28.5 Hz, *CH$_2$*CHF$_2$), 67.8 (t, *J* = 29.0 Hz, *CH$_2$*CHF$_2$), 62.4 (C-5$_{1,2\text{-}cis}$), 57.6 (C-5$_{1,2\text{-}trans}$); GATED NMR (126 MHz, $CDCl_3$): δ 101.8 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*trans*); 97.7 ($J_{H1\text{-}C1}$ = 168 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{30}F_2O_5$ 507.1959, found 507.1964.

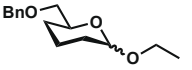


2,2,2-Trifluoroethyl 2,3,4-tri-*O*-benzyl-D-ribopyranoside (S30). The title compound was prepared according to general procedure I. The reaction was quenched after 40 h. Flash column chromatography (97:3 → 90:10, pentane:EtOAc) afforded the title compound (35 mg, 68 µmol, 68%, colorless oil, 1,2-*cis*:1,2-*trans*; 52:48). TLC: R_f 0.30, 0.57 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 696, 735, 1068, 1153, 1278, 1454, 2889; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (52:48): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.47 – 7.20 (m, 29.1H, CH_{arom}), 4.95 – 4.87 (m, 2H, C*H*H Bn, H-1$_{1,2\text{-}trans}$), 4.87 – 4.76 (m, 5H, CH$_2$ Bn, CH$_2$ Bn, H-1$_{1,2\text{-}cis}$), 4.66 – 4.48 (m, 5H, CH*H* Bn, CH$_2$ Bn, CH$_2$ Bn), 4.18 – 3.97 (m, 5H, H-3$_{1,2\text{-}cis}$, H-4$_{1,2\text{-}cis}$, H-5$_{1,2\text{-}trans}$, , C*H*HCF$_3$, CH*H*CF$_3$), 3.96 – 3.74 (m, 4H, H-5$_{1,2\text{-}cis}$, H-5$_{1,2\text{-}cis}$, C*H*HCF$_3$, CH*H*CF$_3$), 3.57 – 3.44 (m, 3H, H-3$_{1,2\text{-}trans}$, H-4$_{1,2\text{-}trans}$, H-5$_{1,2\text{-}trans}$), 3.42 (t, *J* = 3.3 Hz, 1H, H-2$_{1,2\text{-}cis}$), 3.31 (dd, *J* = 7.0, 2.8 Hz, 1H, H-2$_{1,2\text{-}trans}$); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.4, 138.9, 138.5, 138.2, 138.1, 138.0 ($C_{q\text{-arom}}$), 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.1 (CH_{arom}), 125.5, 125.1, 122.7, 122.4 (CF_3), 101.4 (C-1$_{1,2\text{-}trans}$), 97.5 (C-1$_{1,2\text{-}cis}$), 77.7 (C-2$_{1,2\text{-}trans}$), 76.4 (C-2$_{1,2\text{-}cis}$), 75.3 (C-3$_{1,2\text{-}trans}$), 74.8 (C-4$_{1,2\text{-}trans}$), 74.3 (C-3$_{1,2\text{-}cis}$), 74.0, 73.4 (CH_2 Bn), 73.4 (C-4$_{1,2\text{-}cis}$), 73.1 (CH_2 Bn) 71.6 (CH_2 Bn, CH_2 Bn), 70.9 (CH_2 Bn), 66.1 (q, *J* = 34.8 Hz, *CH$_2$*CF$_3$), 65.2 (q, *J* = 34.6 Hz, *CH$_2$*CF$_3$), 62.5 (C-5$_{1,2\text{-}cis}$), 57.9 (C-5$_{1,2\text{-}trans}$); GATED NMR (101 MHz, $CDCl_3$): δ 101.4 ($J_{H1\text{-}C1}$ = 165 Hz, 1,2-*trans*); 97.5 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}F_3O_5$ 525.1865, found 525.1876.

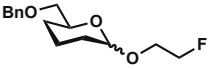


1,1,1,3,3,3-Hexafluoro-2-propyl 2,3,4-tri-*O*-benzyl-1,2-*cis*-D-ribopyranoside (S31). The title compound was prepared according to general procedure I. The reaction was quenched after 112 h. Flash column chromatography (100:0 → 80:20, pentane:Et$_2$O) afforded the title compound (14 mg, 25 µmol, 25%,

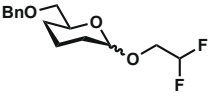
colorless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.19 (pentane:EtOAc, 95:5, v:v); $[\alpha]_D^{20}$ 67.0° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 689, 696, 733, 1071, 1103, 1193, 1218, 1287, 1370, 1454, 2917; ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated, ^1H-^{19}F Decoupled): δ 7.37 – 7.20 (m, 15H, CH_{arom}), 5.08 (d, *J* = 3.9 Hz, 1H, H-1), 4.94 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.65 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.59 – 4.52 (m, 2H, C*H*H Bn, CH*H* Bn), 4.52 – 4.41 (m, 2H, $CH(CF_3)_2$, CH*H* Bn), 4.21 – 4.12 (bs, 1H, H-3), 4.16 (t, *J* = 10.7 Hz, 1H, H-5_{ax}), 3.54 (dd, *J* = 10.5, 4.7, 1H, H-5_{eq}), 3.48 (ddd, *J* = 10.6, 4.9, 2.5 Hz, 1H, H-4), 3.42 (dd, *J* = 4.0, 2.6 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.3, 138.0, 137.7 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.0, 127.9, 127.9, 127.6, 127.6, 127.5, 127.0 (CH_{arom}), 98.2 (C-1), 76.4 (C-2), 74.0 (C-4), 73.4 (CH_2 Bn), 72.7 (p, *J* = 32.8 Hz, C*H*$(CF_3)_2$), 72.7 (C-3), 71.3, 70.8 (CH_2 Bn), 58.2 (C-5); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 98.2 ($J_{H1\text{-}C1}$ = 171 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{28}F_6O_5$ 593.1739, found 593.1748.



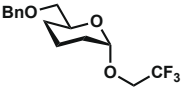
6-Benzyloxymethyl-2-ethyloxy-tetrahydropyran (S32). The title compound was prepared according to a modified general procedure I: after Tf_2O addition, the reaction mixture was stirred for 5 min after which the acceptor was added at –80 °C. The reaction was quenched after 1 h. Flash column chromatography (100:0 → 90:10, pentane:Et_2O) afforded the title compound (8 mg, 12 µmol, 12%, colorless oil, 2,6-*cis*:2,6-*trans*; 50:50). TLC: R_f 0.75 (pentane:Et_2O, 95:5, v:v); TLC: R_f 0.70 (pentane:Et_2O, 95:5, v:v); IR (thin film, cm^{-1}): 697, 736, 967, 1043, 1089, 1136, 1279, 1455, 2856, 2925; NMR data reported as a mixture of 2,6-*cis*:2,6-*trans* (52:48) anomers: ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.54 – 7.17 (m, 10H, CH_{arom}), 4.89 (s, 1H, H-$1_{2,6\text{-}trans}$), 4.64 – 4.48 (m, 4H, C*H*H $Bn_{2,6\text{-}cis}$, CH*H* $Bn_{2,6\text{-}cis}$, C*H*H $Bn_{2,6\text{-}trans}$, CH*H* $Bn_{2,6\text{-}trans}$), 4.44 (dd, *J* = 9.4, 2.2 Hz, 1H, H-$1_{2,6\text{-}cis}$), 4.02 – 3.92 (m, 2H, H-5, H-6), 3.76 (dq, *J* = 9.8, 7.1 Hz, 1H, H-6), 3.69 – 3.41 (m, 7H, H-5, H-$6_{2,6\text{-}cis}$, H-$6_{2,6\text{-}trans}$, C*H*HCH$_3$ $Et_{2,6\text{-}cis}$, CH*H*CH$_3$ $Et_{2,6\text{-}cis}$, C*H*HCH$_3$ $Et_{2,6\text{-}trans}$, CH*H*CH$_3$ $Et_{2,6\text{-}trans}$), 1.92 – 1.16 (m, 18H, H-$2_{2,6\text{-}cis}$, H-$2_{2,6\text{-}trans}$, H-$3_{2,6\text{-}cis}$, H-$3_{2,6\text{-}trans}$, H-$4_{2,6\text{-}cis}$, H-$4_{2,6\text{-}trans}$, CH$_3$ $Et_{2,6\text{-}cis}$, CH$_3$ $Et_{2,6\text{-}trans}$); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 128.5, 128.5, 127.8, 127.7, 127.6 (CH_{arom}), 102.0 (C-$1_{2,6\text{-}cis}$), 97.1 (C-$1_{2,6\text{-}trans}$), 75.6 (C-5), 73.7 (CH_2 Bn), 73.6 (CH_2 Bn), 73.6 (*C*H$_2$ Et), 73.4(*C*H$_2$ Et), 68.0 (C-5), 64.2 (C-6), 62.3 (C-6), 31.0, 29.8, 27.8, 22.0, 18.8, 17.9 (C-$2_{2,6\text{-}cis}$, C-$2_{2,6\text{-}trans}$, C-$3_{2,6\text{-}cis}$, C-$3_{2,6\text{-}trans}$, C-$4_{2,6\text{-}cis}$, C-$4_{2,6\text{-}trans}$), 15.4 (*C*H$_3$ Et), 15.3 (*C*H$_3$ Et).



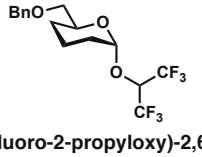
6-Benzyloxymethyl-2-(2-fluoroethyloxy)-tetrahydropyran (S33). The title compound was prepared according to a modified general procedure I: after Tf_2O addition, the reaction mixture was stirred for 5 min after which the acceptor was added at –80 °C. The reaction was quenched after 1 h. Flash column chromatography (100:0 → 90:10, pentane:Et_2O) afforded the title compound (8 mg, 12 µmol, 12%, colorless oil, 2,6-*cis*:2,6-*trans*; 48:52). TLC: R_f 0.75 (pentane:Et_2O, 95:5, v:v); TLC: R_f 0.60, 0.55 (pentane:Et_2O, 95:5, v:v); IR (thin film, cm^{-1}): 696,736, 1028, 1454, 2853, 2923; NMR data reported as a mixture of 2,6-*cis*:2,6-*trans* (48:50) anomers: ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC): δ 7.98 – 7.15 (m, 10H, $CH_{arom\text{-}2,6\text{-}cis}$, $CH_{arom\text{-}2,6\text{-}trans}$), 4.92 (d, *J* = 3.3 Hz, 1H, H-$1_{2,6\text{-}trans}$), 4.70 – 4.50 (m, 8H, C*H*H $Bn_{2,6\text{-}cis}$, C*H*H $Bn_{2,6\text{-}cis}$, C*H*H $Bn_{2,6\text{-}trans}$, C*H*H $Bn_{2,6\text{-}trans}$, C*H*HCHF$_{2\text{-}2,6\text{-}cis}$, CH*H*CHF$_{2\text{-}2,6\text{-}ciss}$, C*H*HCHF$_{2\text{-}2,6\text{-}trans}$, CH*H*CHF$_{2\text{-}2,6\text{-}trans}$), 4.49 (dd, *J* = 9.3, 2.2 Hz, 1H, H-$1_{2,6\text{-}cis}$), 4.07 (dddd, *J* = 33.8, 12.2, 4.5, 2.6 Hz, 1H, C*H*HF$_{2,6\text{-}trans}$), 4.00 – 3.85 (m, 2H, H-$5_{2,6\text{-}trans}$, C*H*HF$_{2,6\text{-}cis}$), 3.85 – 3.63 (m, 3H, H-5, CH*H*F$_{2,6\text{-}cis}$, CH*H*F$_{2,6\text{-}trans}$), 3.57 (dd, *J* = 10.1, 6.2 Hz, 1H, H-$6_{2,6\text{-}trans}$), 3.52 – 3.40 (m, 3H, H-$6_{2,6\text{-}cis}$, H-$6_{2,6\text{-}cis}$, H-$6_{2,6\text{-}trans}$), 1.95 – 1.37 (m, 12H, H-$2_{2,6\text{-}cis}$, H-$2_{2,6\text{-}cis}$, H-$2_{,6\text{-}trans}$, H-$2_{,6\text{-}trans}$, H-$3_{2,6\text{-}cis}$, H-$3_{2,6\text{-}cis}$, H-$3_{,6\text{-}trans}$, H-$3_{2,6\text{-}trans}$, H-$4_{2,6\text{-}cis}$, H-$4_{2,6\text{-}cis}$, H-$4_{,6\text{-}trans}$ H-$4_{,6\text{-}trans}$); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 138.5 ($C_{q\text{-}arom}$), 138.5 ($C_{q\text{-}arom}$), 128.5, 128.4, 127.8, 127.7, 127.7, 127.6 (CH_{arom}), 102.4 (C-$1_{2,6\text{-}trans}$), 97.6 (C-$1_{2,6\text{-}cis}$), 83.8 (d, *J* = 2.0 Hz, *C*H$_2$CH$_2$F$_{2,6\text{-}trans}$), 82.4 (d, *J* = 2.0 Hz, *C*H$_2$CH$_2$F$_{2,6\text{-}cis}$), 75.6 (C-$5_{2,6\text{-}cis}$), 73.6, 73.6, 73.4 (C-$6_{2,6\text{-}cis}$, C-$6_{2,6\text{-}trans}$, CH_2 $Bn_{2,6\text{-}cis}$, CH_2 $Bn_{2,6\text{-}trans}$), 68.2 (C-$5_{2,6\text{-}trans}$), 67.7 (d, *J* = 20.0 Hz, *C*H$_2$F$_{2,6\text{-}trans}$), 66.1 (d, *J* = 19.7 Hz, *C*H$_2$F$_{2,6\text{-}cis}$), 31.1 (C-$2_{2,6\text{-}cis}$), 29.8, 29.5, 27.5, 21.7 (C-$3_{2,6\text{-}cis}$, C-$3_{2,6\text{-}trans}$, C-$4_{2,6\text{-}cis}$, C-$4_{2,6\text{-}trans}$), 17.7 (C-$2_{2,6\text{-}trans}$); HRMS: $[M+Na]^+$ calcd for $C_{15}H_{21}F_1O_3$ 291.13641, found 291.13669.



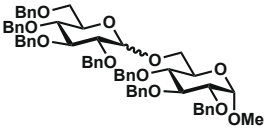
6-Benzyloxymethyl-2-(2,2-difluoroethyloxy)-tetrahydropyran (S34). The title compound was prepared according to a modified general procedure I: after Tf_2O addition, the reaction mixture was stirred for 5 min after which the acceptor was added at –80 °C. The reaction was quenched after 1 h. Flash column chromatography (100:0 → 90:10, pentane:Et_2O) afforded the title compound (8 mg, 12 µmol, 12%, colorless oil, 2,6-*cis*:2,6-*trans*; 12:88). TLC: R_f 0.70, 0.65 (pentane:Et_2O, 95:5, v:v; IR (thin film, cm^{-1}): 698, 737, 1040, 1073, 1116, 1454, 2856, 2925; Data for the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC): δ 7.37 – 7.26 (m, 5H, CH_{arom}), 5.97 (tdd, *J* = 55.7, 4.9, 3.6 Hz, 1H, CH_2F), 4.91 (d, *J* = 3.2 Hz, 1H, H-1), 4.57 (s, 2H, CH_2 Bn), 3.95 (dddd, *J* = 11.8, 6.0, 4.3, 2.3 Hz, 1H, H-5), 3.84 (dddd, *J* = 15.5, 14.8, 11.9, 3.6 Hz, 1H, C*H*HCHF$_2$), 3.70 (tdd, *J* = 13.3, 11.9, 4.9 Hz, 1H, CH*H*CH$_2$F), 3.44 (h, *J* = 4.3 Hz, 2H, H-6, H-6), 1.91 – 1.38 (m, 6H, H-2, H-2, H-3, H-3, H-4, H-4); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 138.4 ($C_{q\text{-}arom}$), 128.5, 127.7, 127.7 (CH_{arom}), 114.7 (t, *J* = 240.6 Hz, *C*HF$_2$), 98.3 (C-1), 73.4 (C-6), 68.6 (C-5), 66.6 (t, *J* = 28.0 Hz, *C*H$_2$CH$_2$F), 29.3 (C-2), 27.3 (C-4), 17.6 (C-3); 2,6-*cis* anomer reference peaks: ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC): δ 6.09 – 5.81 (m, 1H, CH_2F), 4.47 (dd, *J* = 9.3, 2.2 Hz, 1H, H-1); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 102.8 (C-1), 75.7 (C-5), 73.6 (CH_2 Bn), 73.2 (C-6), 67.9 (dd, *J* = 29.7, 27.2 Hz, *C*H$_2$CH$_2$F), 30.8 (C-2), 27.3 (C-4), 21.6 (C-3); HRMS: [M+Na]$^+$ calcd for $C_{15}H_{20}F_2O_3$ 309.12727, found 309.12719.



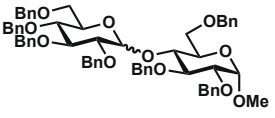
6-Benzyloxymethyl-2-(2,2,2-trifluoroethyloxy)-2,6-*trans*-tetrahydropyran (S35). The title compound was prepared according to a modified general procedure I: after Tf_2O addition, the reaction mixture was stirred for 5 min after which the acceptor was added at –80 °C. The reaction was quenched after 1 h. Flash column chromatography (100:0 → 90:10, pentane:Et_2O) afforded the title compound (8 mg, 12 µmol, 12%, colorless oil, 2,6-*cis*:2,6-*trans*; <2:98). TLC: R_f 0.85 (pentane:Et_2O, 95:5, v:v); $[\alpha]_D^{25}$ –0.4° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}); IR (thin film, cm^{-1}): 697, 736, 969, 1043, 1089, 1136, 1279, 1454, 2855, 2927; ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, ^{1}H-^{19}F Decoupled): δ 7.37 – 7.26 (m, 5H, CH_{arom}), 4.96 (d, *J* = 3.2 Hz, 1H, H-1), 4.57 (s, 2H, C*H*H Bn, CH*H* Bn), 4.00 (dq, *J* = 12.3, 9.1 Hz, 1H, C*H*HCF$_3$), 3.96-3.81 (m, 2H, H-5, CH*H*CF$_3$), 3.45 (dd, *J* = 4.9, 3.8 Hz, 2H, H-6), 1.93 – 1.75 (m, 2H, H-2, H-3), 1.72 – 1.55 (m, 3H, H-2, H-3, H-4), 1.45 (tdd, *J* = 13.0, 11.1, 4.1 Hz, 1H, H-4); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 138.4 (Cq_{arom}), 128.5, 127.7, 127.7 (CH_{arom}), 125.4, 123.2 (CH_2CF_3), 97.9 (C-1), 73.5 (CH_2 Bn), 73.3 (C-6), 68.9 (C-5), 63.8 (q, *J* = 34.4 Hz, C-3), 29.1 (C-3), 27.3 (C-4), 17.4 (C-2); HRMS: [M+Na]$^+$ calcd for $C_{15}H_{19}F_3O_3$ 327.11785, found 309.11732.



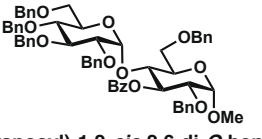
6-Benzyloxymethyl-2-(1,1,1,3,3,3-Hexafluoro-2-propyloxy)-2,6-*trans*-tetrahydropyran (S36). The title compound was prepared according to a modified general procedure I: after Tf_2O addition, the reaction mixture was stirred for 5 min after which the acceptor was added at –80 °C. The reaction was quenched after 1 h. Flash column chromatography (100:0 → 90:10, pentane:Et_2O) afforded the title compound (8 mg, 12 µmol, 12%, colorless oil, 2,6-*cis*:2,6-*trans*; <2:98). TLC: R_f 0.75 (pentane:Et_2O, 95:5, v:v); $[\alpha]_D^{25}$ –0.9° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 688, 1028, 1146, 1028, 1216, 1288, 2925; ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, ^{1}H-^{19}F Decoupled): δ 7.37 – 7.26 (m, 5H, CH_{arom}), 5.16 (d, *J* = 3.4 Hz, 1H, H-1), 4.60 – 4.51 (m, 3H, CH(CF$_3$)$_2$, C*H*H Bn, C*H*H Bn), 4.01 (dtd, *J* = 11.6, 4.6, 2.3 Hz, 1H, H-5), 3.46 (m, 2H, H-6, H-6), 1.90 – 1.78 (m, 2H, H-2, H-3), 1.77 – 1.46 (m, 4H, H-2, H-3, H-4, H-4); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 138.3 ($C_{q\text{-}arom}$), 128.5, 127.7, 127.6 (CH_{arom}), 125.8 – 119.0 (m, CH(*C*F$_3$)$_2$), 99.4 (d, *J* = 1.6 Hz, C-1), 73.4 (CH_2 Bn), 72.9 (C-6), 71.5 (dt, *J* = 64.7, 32.4 Hz, *CH*(CF$_3$)$_2$), 69.6 (d, *J* = 1.5 Hz, C-5), 28.9 (C-3), 27.0 (C-4), 17.1(C-2); HRMS: [M+Na]$^+$ calcd for $C_{16}H_{18}F_6O_3$ 395.10523, found 395.10532.



Methyl 6-*O*-(2,3,4-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S37). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (75 mg, 76 µmol, 79%, colorless oil, 1,2-*cis*:1,2-*trans*; 15:85). TLC: R_f 0.63 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 1029, 1041, 1366, 1455, 1489, 2921; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.7 – 7.1 (m, 35H, CH_{arom}), 5.0 – 4.5 (m, 15H, H-1', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.3 (d, *J* = 7.8 Hz, 1H, H-1), 4.2 (dd, *J* = 10.8, 2.0 Hz, 1H, H-6), 4.0 (t, *J* = 9.3 Hz, 1H, H-3'), 3.8 (ddd, *J* = 10.3, 4.9, 2.1 Hz, 1H, H-5'), 3.7 – 3.5 (m, 9H, H-2, H-3, H-4, H-2', H-4', H-6', H-6, H-6), 3.4 (dtd, *J* = 6.8, 4.8, 2.8 Hz, 1H, H-5), 3.32 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.0, 138.7, 138.5, 138.5, 138.4, 138.3 ($C_{q\text{-}arom}$), 138.2, 131.2, 129.4, 128.6, 128.5, 128.5, 128.5, 128.3, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7, 124.9 (CH_{arom}), 103.9 (C-1), 98.2 (C-1'), 84.9 (C-4'), 82.2 (C-2), 82.1 (C-3'), 79.9 (C-2'), 78.1 (C-4), 78.0 (C-3), 75.8, 75.8 (CH_2 Bn), 75.2 (C-5), 75.1, 75.0, 75.0, 73.6, 73.5 (CH_2 Bn), 70.0 (C-5'), 69.1 (C-6), 68.7 (C-6'), 55.3 (CH_3'); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.98 (signal overlaps with major stereoisomer, 1H, H-1), 4.55 (signal overlaps with major stereoisomer, 1H, H-1'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 98.1 (C-1'), 97.4 (C-1), 55.3 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.45028, found 1009.44947.

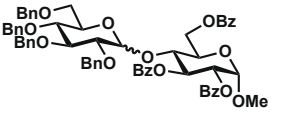


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S38). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (90 mg, 91 µmol, 91%, colorless oil, 1,2-*cis*:1,2-*trans*; 42:58). TLC: R_f 0.51 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 1031, 1042, 1367, 1465, 1491, 2920; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.6 – 7.1 (m, 35H, CH_{arom}), 5.1 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 5.0 – 4.4 (m, 14H, H-1, H-1', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.3 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.2 – 3.5 (m, 10H, H-3, H-4, H-6, H-6, H-2', H-3', H-4', H-5', H-6', H-6'), 3.4 (m, 4H, H-2, CH_3') 3.35 (ddd, *J* = 9.8, 4.7, 1.8 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 139.7, 138.9, 138.7, 138.7, 138.5, 138.4, 138.1 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9,, 127.8, 127.7, 127.6, 127.5, 127.4 (CH_{arom}), 102.6 (C-1), 98.5 (C-1'), 85.0, 82.9 (C-2), 82.2, 82.1, 80.5, 79.0, 78.2, 76.7, 75.7 (CH_2 Bn), 75.5 (CH_2 Bn), 75.3 (C-5), 75.0 (CH_2 Bn), 74.9 (CH_2 Bn), 73.8 (CH_2 Bn), 73.5 (CH_2 Bn), 70.1 (C-5'), 69.1 (C-6/C-6'), 68.0 (C-6'/C-6), 55.4 (CH_3'); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 5.75 (d, *J* = 3.6 Hz, 1H, H-1), 5.08 (d, *J* = 11.6 Hz, 1H, C*H*H Bn); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 139.1, 138.7, 138.6, 138.3, 138.1, 138.0 ($C_{q\text{-}arom}$), 97.9 (C-1'), 96.8 (C-1), 79.6 (C-2), 75.7, 75.1, 74.5, 73.6, 73.5, 73.4, 73.3 (CH_2 Bn), 69.2 (C-6/C-6'), 68.3 (C-6'/C-6), 55.3 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.45028, found 1009.44951.

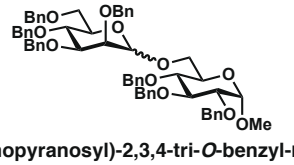


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-lyxopyranosyl)-1,2-*cis*-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S39). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (62 mg, 62 µmol, 62%, colorless oil,

1,2-*cis*:1,2-*trans*; 61:39). TLC: R_f 0.33 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 814, 1034, 1253, 1451, 1725, 2929; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.10 – 7.03 (m, 35H, CH_{arom}), 5.92 (t, J = 9.6 Hz, 1H, H-3'), 5.01 (d, J = 3.3 Hz, 1H, H-1), 4.85 – 4.21 (m, 7H, H-1', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.18 – 4.00 (m, 1H, H-4'), 3.99 – 3.76 (m, 3H, H-3, H-6', H-5'), 3.75 – 3.60 (m, 4H, H-6', H-2', H-5), 3.56 – 3.12 (m, 7H, H-2, H-6, H-6, H-4, CH_3'); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 165.5 (C=O Bz), 139.0 ($C_{q\text{-}arom}$), 138.6 (CH_{arom}), 138.3 ($C_{q\text{-}arom}$), 138.2, 137.9, 132.8, 130.9, 130.0, 128.6, 128.4, 128.4, 128.4, 128.2, 128.2, 128.2, 128.1, 128.0, 127.8, 127.7 (CH_{arom}), 98.0 (C-1), 97.8 (C-1'), 81.6, 79.4 (C-2), 77.5, 77.2, 75.6 (CH_2 Bn), 74.9 (CH_2 Bn), 74.7, 73.9 (C-3'), 73.5 (CH_2 Bn), 73.4 (CH_2 Bn), 72.9 (CH_2 Bn, CH_2 Bn), 72.5 (CH_2 Bn), 71.3, 69.9, 68.6 (C-6'), 68.6 (C-6), 55.4 (CH_3'); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 5.69 (t, J = 9.7 Hz, 1H, H-3'), 4.24 (d, J = 7.8 Hz, 1H, H-1); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 165.6 (C=O Bz), 138.8, 138.7, 138.6, 138.3, 137.9, 137.8 ($C_{q\text{-}arom}$), 132.6 (CH_{arom}), 131.1 ($C_{q\text{-}arom}$), 102.5 (C-1), 98.1 (C-1'), 75.6 (CH_2 Bn), 75.1 (CH_2 Bn), 73.6 (CH_2 Bn), 69.3 (C-6/C-6'), 67.7 (C-6/C-6'), 55.5 (CH_3);HRMS: $[M+Na]^+$ calcd for $C_{62}H_{64}O_{12}Na$ 1023.42955, found 1023.42900.

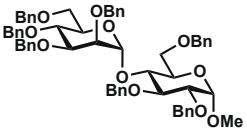


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-glucopyranosyl)-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S40). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound afforded the title compound (60 mg, 58 µmol, 58%, colorless oil, 1,2-*cis*:1,2-*trans*; 88:12). TLC: R_f 0.50 (1,2-*cis*) and 0.40 (1,2-*trans*) (pentane:EtOAc, 80:20, v:v); $[\alpha]_D^{25}$ 22.5° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 751, 809, 1029, 1277, 1412, 1730, 2913; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.15 – 7.05 (m, 35H, CH_{arom}), 6.21 (dd, J = 10.2, 8.1 Hz, 1H, H-3'), 5.27 (dd, J = 10.3, 3.6 Hz, 1H, H-2'), 5.15 (d, J = 3.6 Hz, 1H, H-1), 5.04 (d, J = 3.5 Hz, 1H, H-1), 4.90 – 4.07 (m, 11H, H-4', H-6', H-6', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.00 – 3.91 (m, 2H, H-3, H-5'), 3.86 (dt, J = 9.9, 2.9 Hz, 1H, H-5), 3.81 – 3.49 (m, 3H, H-4, H-6, H-6), 3.45 (s, 3H, CH_3'), 3.31 (dd, J = 9.9, 3.4 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 166.3, 166.3, 165.7 (C=O Bz), 138.9, 138.6, 138.3, 138.0 ($C_{q\text{-}arom}$), 133.5, 133.4, 133.2 (CH_{arom}), 130.3, 130.2 ($C_{q\text{-}arom}$), 130.2, 130.0, 129.3, 128.7, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7 (CH_{arom}), 99.3 (C-1), 97.0 (C-1'), 81.7 (C-3), 79.2 (C-2), 77.6 (C-4), 76.2 (C-5'), 75.8, 75.1, 73.7, 73.0 (CH_2 Bn), 72.3 (C-2'), 72.1 (C-3'), 72.0 (C-5), 69.0 (C-4'), 68.4 (C-6), 63.6 (C-6'), 55.6 (CH_3'); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 6.01 (dd, J = 10.2, 9.3 Hz, 1H, H-3), 5.23 (dd, J = 10.2, 3.7 Hz, 1H, H-2), 5.18 (d, J = 3.5 Hz, 1H, H-1), 5.13 (d, J = 10.0 Hz, 1H, H-1'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 99.7 (C-1'), 99.5 (C-1), 55.7 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{60}O_{14}Na$ 1051.38808, found 1051.38750.

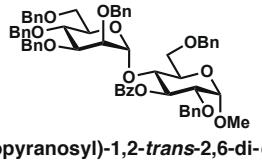


Methyl 6-*O*-(2,3,4-*O*-benzyl-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S41). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (78 mg, 79 µmol, 79%, colorless oil, 1,2-*cis*:1,2-*trans*; 77:23). TLC: R_f 0.37 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 710, 739, 1031, 1051, 1354, 1420, 1486, 2913; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.48 – 7.08 (m, 35H, CH_{arom}), 5.01 (d, J = 10.9 Hz, 1H, C*H*H Bn), 4.93 (d, J = 12.5 Hz, 1H, C*H*H Bn), 4.88 (d, J = 10.8 Hz, 1H, C*H*H Bn), 4.85 – 4.41 (m, 12H, H-1', CH*H* Bn, CH*H* Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn C*H*H Bn, CH*H* Bn C*H*H Bn, CH*H* Bn C*H*H Bn, CH*H* Bn), 4.16 (dd, J = 10.5, 2.0 Hz, 1H, H-6'), 4.12 (s, 1H, H-1), 4.01 (t, J = 9.2 Hz, 1H, H-3'), 3.89 – 3.63 (m, 5H, H-3, H-4, H-6, H-6, H-5'), 3.50 (dd, J = 9.7, 3.5 Hz, 1H, H-2'), 3.48 – 3.35 (m, 4H, H-2, H-5, H-4', H-6'), 3.32 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.0,

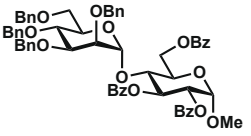
138.9, 138.6, 138.4, 138.3, 138.2 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5 (CH_{arom}), 101.6 (C-1), 97.9 (C-1'), 82.4 (C-2), 82.3 (C-3'), 80.0 (C-2'), 77.8 (C-4'), 76.1 (C-5), 75.8, 75.2 (CH_2 Bn), 75.1 (C-4), 74.9, 73.8 (CH_2 Bn), 73.7 (C-3), 73.6, 73.5, 71.7 (CH_2 Bn), 69.9 (C-5'), 69.9 (C-6), 68.4 (C-6'), 55.2 (CH_3'); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.96 (d, *J* = 2.2 Hz, 1H, H-1), 4.58 (signal overlaps with major isomer, 1H, H-1'), 3.60 (td, *J* = 10.7, 1.8 Hz, 1H, H-6'), 3.30 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.8, 138.8, 138.5, 138.5, 138.3, 138.3 ($C_{q\text{-}arom}$), 98.4 (C-1'), 97.9 (C-1), 75.9, 75.1, 75.1, 73.4, 72.6, 72.1 (CH_2 Bn), 69.2 (C-6), 65.9 (C-6'), 55.2 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.45503, found 1009.44973.



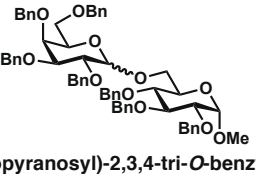
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-mannopyranosyl)-1,2-*trans*-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S42). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (69 mg, 70 µmol, 70%, colorless oil, 1,2-*cis*:1,2-*trans*; <2:98). TLC: R_f 0.29 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 699, 731, 1042, 1089, 1467, 1499, 2910; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.38 – 7.09 (m, 35H, CH_{arom}), 5.29 (d, *J* = 2.2 Hz, 1H, H-1'), 5.08 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.83 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.72 – 4.39 (m, 11H, H-1, CH*H* Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.31 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.21 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 3.97 (t, *J* = 9.4 Hz, 1H, H-4'), 3.89 – 3.75 (m, 3H, H-3, H-3', H-5'), 3.75 – 3.59 (m, 6H, H-2, H-4, H-5, H-6, H-6', H-6'), 3.60 – 3.50 (m, 2H, H-2', H-6') 3.39 (s, 3H, CH_3'); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 139.0, 138.8, 138.7, 138.6, 138.5, 138.0 ($C_{q\text{-}arom}$), 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.5, 127.5, 127.2, 127.2, 126.8 (CH_{arom}), 100.6 (C-1), 97.8 (C-1'), 81.7 (C-3'), 80.1 (C-2'), 79.9 (C-3), 77.9 (C-4), 76.4 (C-2) ,75.1, 75.1 (CH_2 Bn), 75.0 (C-4'), 73.5, 73.4, 73.3 (CH_2 Bn), 73.1 (C-5), 72.4, 72.2 (CH_2 Bn), 70.0 (C-5'), 69.5 (C-6), 69.5 (C-6'), 55.4 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.45503, found 1009.45509.



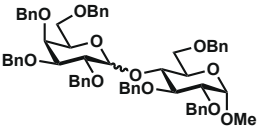
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-mannopyranosyl)-1,2-*trans*-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S43). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (77 mg, 77 µmol, 77%, colorless oil, 1,2-*cis*:1,2-*trans*; <2:98). TLC: R_f 0.37 (pentane:EtOAc, 80:20, v:v); $[\alpha]_D^{25}$ 20.2° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 813, 1021, 1254, 1446, 1726, 2912; ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.09 – 6.90 (m, 35H, CH_{arom}), 5.77 (dd, *J* = 10.0, 9.0 Hz, 1H, H-3'), 5.09 (d, *J* = 2.0 Hz, 1H, H-1), 4.81 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 3.5 Hz, 1H, H-1'), 4.62 – 4.35 (m, 9H, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.16 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 3.99 – 3.51 (m, 12H, H-2, H-3, H-4, H-5, H-6, H-6, H-2', H-4', H-5', H-6', H-6', CH*H* Bn), 3.42 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 165.4 (C=O Bz), 138.7, 138.6, 138.4, 138.4, 138.3, 137.7 ($C_{q\text{-}arom}$), 133.5 (CH_{arom}), 130.1 ($C_{q\text{-}arom}$), 128.5, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5 (CH_{arom}), 100.6 (C-1), 97.6 (C-1'), 79.7 (C-3), 77.1 (C-4'), 76.9 (C-2'), 75.9 (C-2), 75.0 (CH_2 Bn), 74.5 (C-3', C-4), 73.5, 73.4 (CH_2 Bn), 73.1 (C-5), 72.8, 72.6, 71.6 (CH_2 Bn), 69.7 (C-5'), 69.5 (C-6/C-6'), 69.0 (C-6'/C-6), 55.5 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{64}O_{12}Na$ 1023.42955, found 1023.42900.



Methyl 4-*O*-(2,3,4-*O*-benzyl-D-mannopyranosyl)-1,2-*trans*-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S44). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (61 mg, 59 µmol, 59%, colorless oil, 1,2-*cis*:1,2-*trans*; <2:98). TLC: R_f 0.49 (pentane:EtOAc, 80:20, v:v); $[\alpha]_D^{25}$ –80.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 745, 817, 1021, 1275, 1454, 1743, 2809, 2921; ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.2 – 6.9 (m, 35H, CH_{arom}), 6.1 (dd, *J* = 10.0, 8.5 Hz, 1H, H-3'), 5.2 – 5.1 (m, 3H, H-1, H-1', H-2'), 4.8 – 4.7 (m, 2H, H-6', C*H*H Bn), 4.6 – 4.4 (m, 4H, H-6', CH*H* Bn, C*H*H Bn, C*H*H Bn), 4.4 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.3 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.2 – 4.1 (m, 3H, H-4', H-5', C*H*H Bn), 4.0 (t, *J* = 9.4 Hz, 1H, H-4), 3.9 – 3.8 (m, 3H, H-3, H-5, CH*H* Bn), 3.7 (dd, *J* = 10.9, 4.0 Hz, 1H, H-6), 3.6 – 3.5 (m, 2H, H-2, H-6), 3.4 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 166.3, 166.0, 165.6 (C=O Bz), 138.7, 138.5, 138.5, 138.4 ($C_{q\text{-}arom}$), 133.7, 133.5, 133.2 (CH_{arom}), 130.1 ($C_{q\text{-}arom}$), 130.0, 129.9 (CH_{arom}), 129.4, 129.2 ($C_{q\text{-}arom}$), 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 128.1, 127.8, 127.6, 127.6, 127.5, 127.4, 127.2, 127.2 (CH_{arom}), 100.8 (C-1), 96.9 (C-1'), 79.6 (C-3), 76.5 (C-4'), 76.3 (C-2), 75.0 (CH_2 Bn), 74.5 (C-4), 73.5 (C-5), 73.5 (CH_2 Bn), 73.1 (C-3'), 72.8 (CH_2 Bn), 72.0 (C-2'), 71.9 (CH_2 Bn), 68.9 (C-6), 68.6 (C-5'), 63.6 (C-6'), 55.6 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{60}O_{14}Na$ 1051.38808, found 1051.38753.

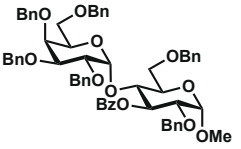


Methyl 6-*O*-(2,3,4-*O*-benzyl-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S45). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (74 mg, 75 µmol, 75%, colorless oil, 1,2-*cis*:1,2-*trans*; 30:70). TLC: R_f 0.67 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 721, 1047, 1367, 1464, 1481, 2921; Data of the major stereoisomer (1,2-*trans*): ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 7.68 – 7.13 (m, 35H, CH_{arom}), 4.97 – 4.33 (m, 16H, H-1', H-4'or H-4, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.30 (d, *J* = 7.7 Hz, 1H, H-1), 4.14 (dd, *J* = 10.8, 2.0 Hz, 1H, H-6/H-6'), 3.94 – 3.87 (m, 3H, H-3', H-4/H-4', H-5/H-5'), 3.88 – 3.66 (m, 2H, H-2, H-5'/H-5), 3.66 – 3.42 (m, 9H, H-3, H-2', H-6/H-6', H-6/H-6', H-6/H-6'), 3.29 (s, 3H, CH_3'); δ 139.0, 138.8, 138.8, 138.6, 138.5, 138.3, 138.0 ($C_{q\text{-}arom}$), 131.2, 129.4, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 124.9 (CH_{arom}), 104.3 (C-1), 98.0 (C-1'), 82.4 (C-3), 82.1 (C-3'), 80.0 (C-2'), 79.4 (C-2), 78.2 (C-4/C-4'), 75.8, 75.3, 74.9, 74.6, 73.6 (CH_2 Bn), 73.6 (C-4'/C-4), 73.5 (C-5/C-5'), 73.4 (CH_2 Bn, CH_2Bn), 73.0 (C-6/C-6'), 70.0 (C-5/C-5'), 68.7 (C-6'/C-6), 55.3 (CH_3'); Data for the minor stereoisomer (1,2-*cis*): ^1H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.99 (d, *J* = 3.6 Hz, 1H, H-1), 4.53 (d, *J* = 3.6 Hz, 1H, H-1'), 4.03 (dd, *J* = 9.3, 3.6 Hz, 1H, H-2), 3.41 (dd, *J* = 9.6, 3.5 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.0, 138.8, 138.5, 138.3, 138.1 ($C_{q\text{-}arom}$), 98.0 (C-1), 98.0 (C-1'), 80.3, 76.6, 75.8, 75.1, 74.9, 73.5, 72.9, 72.6 (CH_2 Bn), 69.0 (C-6/C-6'), 66.5 (C-6'/C-6), 55.1 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.45503, found 1009.44973.

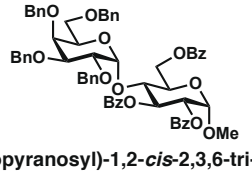


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S46). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h.

Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (69 mg, 70 µmol, 70%, colorless oil, 1,2-*cis*:1,2-*trans*; 70:30). TLC: R_f 0.51 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 687, 745, 1031, 1076, 1471, 2912; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.40 – 7.09 (m, 35H, CH_{arom}), 5.76 (d, *J* = 3.9 Hz, 1H, H-1), 4.97 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.89 – 4.49 (m, 11H, H-1', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.42 (d, *J* = 12.3 Hz, 1H, CH*H* Bn), 4.38 – 4.19 (m, 2H, C*H*H Bn, CH*H* Bn), 4.06 (t, *J* = 9.0 Hz, 1H, H-3'), 4.03 – 3.78 (m, 5H, H-2, H-3, H-4, H-5, H-4'), 3.78 – 3.57 (m, 2H, H-6, H-6), 3.57 – 3.40 (m, 4H, H-2', H-5', H-6', H-6'); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 139.1, 138.7, 138.7, 138.5, 138.4, 138.1 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.6, 127.5, 127.5, 126.8 (CH_{arom}), 97.9 (C-1'), 97.6 (C-1), 82.2 (C-3'), 80.3 (C-2'), 79.3 (C-3), 75.7 (C-2), 74.9 (CH_2 Bn), 74.7 (C-4'), 74.5, 73.9, 73.5, 73.5, 73.2, 72.9 (CH_2 Bn), 72.8 (C-4), 70.0 (C-5'), 69. (C-5)6, 69.5 (C-6), 68.8 (C-6'), 55.2 (CH_3'); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): 4.57 (signal overlaps with major stereoisomer, 1H, H-1'), 4.30 (signal overlaps with major stereoisomer, 1H, H-1); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 139.6, 139.2, 139.1, 138.7, 138.6, 138.3, 138.2 ($C_{q\text{-}arom}$), 102.9 (C-1), 98.6 (C-1'), 75.6, 75.4, 74.8, 73.8, 73.3, 72.7 (CH_2 Bn), 68.3 (C-6/C-6'), 68.1 (C-6'or C-6), 55.4 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.45503, found 1009.45511.

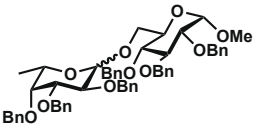


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-galactopyranosyl)-1,2-*cis*-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S47). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (70 mg, 70 µmol, 70%, colorless oil, 1,2-*cis*:1,2-*trans*; 92:8). TLC: R_f 0.55 (pentane:EtOAc, 80:20, v:v); $[\alpha]_D^{25}$ 10.2° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 814, 1042, 1271, 1451, 1728, 2921; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.13 – 7.02 (m, 35H, CH_{arom}), 5.88 (t, *J* = 9.6 Hz, 1H, H-3'), 5.05 (d, *J* = 3.2 Hz, 1H, H-1), 4.83 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 3.6 Hz, 1H, H-1'), 4.60 – 4.53 (m, 5H, C*H*H Bn, C*H*H Bn, C*H*H Bn, C*H*H Bn, C*H*H Bn), 4.47 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.43 – 4.28 (m, 3H, CH*H* Bn CH*H* Bn CH*H* Bn), 4.11 (t, *J* = 9.5 Hz, 1H, H-4'), 4.02 – 3.88 (m, 3H, H-5, H-6, CH*H* Bn), 3.86 (ddd, *J* = 9.9, 3.4, 1.9 Hz, 1H, H-5'), 3.83 – 3.71 (m, 3H, H-2, H-3, H-4), 3.66 (dd, *J* = 9.8, 3.4 Hz, 1H, H-2'), 3.60 (dd, *J* = 10.8, 2.0 Hz, 1H, H-6), 3.48 – 3.35 (m, 5H, H-6', H-6', CH_3'); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 165.6 (C=O Bz), 139.1, 138.7, 138.7, 138.2, 138.2, 137.9 ($C_{q\text{-}arom}$), 132.8 (CH_{arom}), 130.9 ($C_{q\text{-}arom}$), 130.0, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.4 (CH_{arom}), 98.8 (C-1), 97.8 (C-1'), 78.7 (C-3), 77.1 (C-2'), 76.1 (C-4), 75.4 (C-2), 75.2 (C-4'), 74.8 (CH_2 Bn), 73.8 (C-3'), 73.5, 73.4, 73.3, 72.9, 72.8 (CH_2 Bn), 70.4 (C-5), 70.0 (C-5'), 69.3 (C-6'), 68.7 (C-6), 55.4 (CH_3'); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): 5.66 (t, *J* = 9.6 Hz, 1H, H-3'), 4.72 (d, *J* = 3.7 Hz, 1H, H-1'), ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 103.1 (C-1), 74.3, 73.2, 72.4, 70.7 (CH_2 Bn), 69.5 (C-6/C-6'), 67.6 (C-6'/C-6), 55.5 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{64}O_{12}Na$ 1023.42955, found 1023.42906.

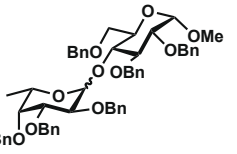


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-galactopyranosyl)-1,2-*cis*-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S48). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (68 mg, 66 µmol, 66%, colorless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.52 (pentane:EtOAc, 80:20, v:v); $[\alpha]_D^{25}$ 34.3° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 765, 1060, 1232, 1451, 1725, 2939; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.14 – 7.01

(m, 35H, CH_{arom}), 6.20 (dd, *J* = 10.3, 8.8 Hz, 1H, H-3'), 5.22 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2'), 5.16 (d, *J* = 3.6 Hz, 1H, H-1), 5.13 (d, *J* = 3.5 Hz, 1H, H-1'), 4.85 – 4.75 (m, 2H, H-6', C*H*H Bn), 4.68 – 4.57 (m, 3H, H-6', CH_2 Bn), 4.43 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.36 – 4.20 (m, 4H, H-6, H-4', C*H*H Bn, C*H*H Bn), 4.15 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.05 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.00 (t, *J* = 6.5 Hz, 1H, H-4), 3.94 – 3.87 (m, 2H, H-3, H-5'), 3.82 (dd, *J* = 9.8, 3.6 Hz, 1H, H-2), 3.47 – 3.32 (m, 5H, H-5, H-6, CH_3'); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 166.2, 166.2, 165.6 (C=O Bz), 138.9, 138.6, 138.4, 138.1 ($C_{q\text{-}arom}$), 133.4, 133.2, 133.1, 130.1 (CH_{arom}), 130.0 ($C_{q\text{-}arom}$), 129.9, 129.8 (CH_{arom}), 129.2 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7, 127.5 (CH_{arom}), 99.1 (C-1), 96.9 (C-1'), 78.8 (C-3), 75.4 (C-2), 75.1 (C-5'), 74.9 (CH_2 Bn), 74.7 (C-4'), 73.4, 73.3, 73.1 (CH_2 Bn), 72.4 (C-2'), 72.3 (C-3'), 70.7 (C-4), 68.7 (C-5), 68.6 (C-6), 63.6 (C-6'), 55.5 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{62}H_{60}O_{14}Na$ 1051.38808, found 1051.38753.

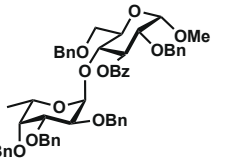


Methyl 6-*O*-(2,3,4-*O*-benzyl-D-fucopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S49). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (89 mg, 90 µmol, 90%, colorless oil, 1,2-*cis*:1,2-*trans*; 45:55). TLC: R_f 0.29 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 732, 1028, 1375, 1451, 1499, 2922; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.50 – 7.06 (m, 30H, CH_{arom}), 5.01 – 4.93 (m, 2H, C*H*H Bn, C*H*H Bn), 4.88 – 4.52 (m, 11H, H-1', CH*H* Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.40 (d, *J* = 7.7 Hz, 1H, H-1), 4.17 (dd, *J* = 11.4, 3.9 Hz, 1H, H-6'), 4.01 – 3.93 (m, 1H, H-3'), 3.85 – 3.71 (m, 3H, H-2, H-5', H-6'), 3.71 – 3.39 (m, 5H, H-3, H-4, H-5, H-2', H-4'), 3.32 (s, 3H, CH_3'), 1.16 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 144.8, 139.1, 139.0, 138.8, 138.5, 138.4 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.4, 128.3, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6 (CH_{arom}), 103.9 (C-1), 98.1 (C-1'), 82.5 (C-3), 82.1 (C-3'), 80.4 (C-2'), 79.6 (C-2), 77.9 (C-4, C-4'), 75.8, 75.2, 75.2, 74.7, 73.5, 73.3 (CH_2 Bn), 70.4 (C-5), 70.2 (C-5'), 67.6 (C-6'), 55.2 (CH_3'), 17.0 (CH_3); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.90 (d, *J* = 3.5 Hz, 1H, H-1), 4.04 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2), 3.90 (q, *J* = 6.5 Hz, 1H, H-5), 3.31 (s, 3H, CH_3'), 1.10 (d, *J* = 6.5 Hz, 3H. CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 98.1 (C-1), 98.1 (C-1'), 80.2 (C-3), 76.4 (C-2), 75.9, 75.0, 74.9, 73.4, 73.2, 73.0 (C-6), 70.2 (C-5'), 66.5 (C-6'), 66.4 (C-5), 55.2 (CH_3'), 16.7 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{60}O_{10}Na$ 903.40842, found 903.40787.

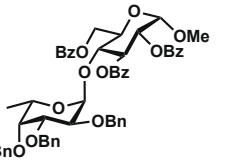


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-fucopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S50). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (74 mg, 75 µmol, 75%, colorless oil, 1,2-*cis*:1,2-*trans*; 90:10). TLC: R_f 0.31 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 694, 735, 1031, 1095, 1443, 1470, 2913; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.49 – 7.12 (m, 30H, CH_{arom}), 5.05 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.99 (d, *J* = 3.7 Hz, 1H, H-1), 4.89 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.79 – 4.67 (m, 5H, C*H*H Bn, C*H*H Bn, CH*H* Bn, CH*H* Bn), 4.64 – 4.53 (m, 5H, C*H*H Bn, C*H*H Bn, CH*H* Bn, CH*H* Bn), 4.40 – 4.30 (m, 2H, C*H*H Bn, CH*H* Bn), 4.02 – 3.95 (m, 2H, H-2, H-5), 3.90 (ddd, *J* = 9.3, 7.2, 1.6 Hz, 1H, H-3'), 3.85 (dd, *J* = 10.3, 2.8 Hz, 1H, H-3), 3.79 (m, *J* = 7.5 Hz, 2H, H-4', H-5'), 3.70 (dd, *J* = 10.8, 3.0 Hz, 1H, H-6'), 3.64 (dd, *J* = 10.9, 1.5 Hz, 1H, H-6'), 3.57 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2'), 3.36 – 3.32 (m, 4H, H-4, CH_3'), 0.66 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.0, 138.9, 138.8, 138.5, 138.1, 138.1 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5 (CH_{arom}), 97.9 (C-1'), 97.7 (C-1), 80.6 (C-2'), 80.3 (C-3'), 79.6 (C-3), 77.6 (C-4), 76.4 (C-2), 75.7, 74.8, 74.5 (CH_2 Bn), 73.8 (C-4'), 73.4, 73.3, 72.8 (CH_2

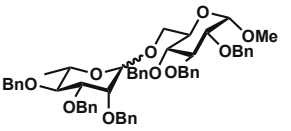
Bn), 70.4 (C-5'), 68.7 (C-6'), 66.8 (C-5), 55.1 (CH_3'), 16.4 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{60}O_{10}Na$ 903.40842, found 903.40788.



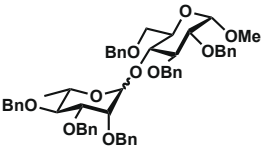
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-fucopyranosyl)-1,2-*cis*-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S51). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound afforded the title compound (85 mg, 85 µmol, 85%, colorless oil, 1,2-*cis*:1,2-*trans*; 93:7). TLC: R_f 0.25 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 822, 1041, 1272, 1453, 1728, 2917; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.11 – 6.98 (m, 30H, CH_{arom}), 5.75 (dd, *J* = 9.9, 9.0 Hz, 1H, H-3'), 4.94 (d, *J* = 3.4 Hz, 1H, H-1), 4.82 (m, 2H, C*H*H Bn, C*H*H Bn), 4.75 – 4.63 (m, 3H, H-1', C*H*H Bn, C*HH* Bn), 4.57 – 4.45 (m, 4H, C*H*H Bn, CH*H* Bn, CH*H* Bn, CH*H* Bn), 4.40 – 4.29 (m, 2H, C*H*H Bn, CH*H* Bn), 4.01 – 3.81 (m, 5H, H-2, H-3, H-4', H-5', H-6'), 3.73 (qd, *J* = 6.4, 1.1 Hz, 2H, H-5), 3.64 (dd, *J* = 11.0, 1.9 Hz, 1H, H-6'), 3.56 (dd, *J* = 9.9, 3.5 Hz, 1H, H-2'), 3.47 (dd, *J* = 2.5, 1.4 Hz, 1H, H-4), 3.38 (s, 3H, CH_3'), 0.57 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 165.9 (C=O Bz), 138.7, 138.7, 138.5, 138.2, 137.6 ($C_{q\text{-}arom}$), 133.0 (CH_{arom}), 130.5 ($C_{q\text{-}arom}$), 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5 (CH_{arom}), 99.5 (C-1), 97.4 (C-1'), 79.8 (C-3), 77.7 (C-4), 77.6 (C-2'), 76.1 (C-2), 75.3 (C-4'), 75.0, 74.5 (CH_2 Bn), 73.4 (C-3'), 73.3, 72.7, 72.7 (CH_2 Bn), 70.3 (C-5'), 68.3 (C-6'), 67.2 (C-5), 55.3 (CH_3'), 16.2 (C-6); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 5.86 (t, *J* = 9.6 Hz, 1H, H-3'), 4.42 (d, *J* = 7.7 Hz, 1H, H-1), 3.25 (q, *J* = 6.2 Hz, 1H, H-5), 3.04 (dd, *J* = 9.7, 3.0 Hz, 1H, H-3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 103.7 (C-1), 97.6 (C-1'), 82.3 (C-2), 70.6 (C-5); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{58}O_{11}Na$ 917.38768, found 917.38713.



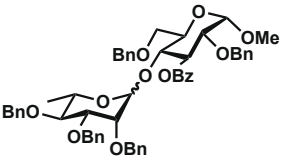
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-fucopyranosyl)-1,2-*cis*-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S52). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound afforded the title compound (78 mg, 76 µmol, 76%, colorless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.19 (pentane:EtOAc, 80:20, v:v); $[\alpha]_D^{25}$ 22.6° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 817, 1024, 1281, 1451, 1721, 2890; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 8.13 – 7.14 (m, 30H), 5.99 (ddd, *J* = 11.3, 9.0, 1.6 Hz, 1H, H-3'), 5.13 – 5.07 (m, 2H, H-1', H-2'), 4.97 – 4.66 (m, 10H, H-1, H-6', H-6', C*H*H Bn, C*HH* Bn, C*H*H Bn, C*HH* Bn, C*H*H Bn), 4.51 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.17 (ddd, *J* = 10.0, 4.5, 2.1 Hz, 1H, H-5'), 4.06 – 3.90 (m, 3H, H-2, H-3, H-4'), 3.80 (dd, *J* = 6.4, 1.4 Hz, 1H, H-5), 3.51 (dd, *J* = 2.4, 1.4 Hz, 1H, H-4), 3.39 (s, 3H, CH_3'), 0.64 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 166.2, 166.1, 166.0 (C=O Bz), 138.8, 138.6, 138.2 ($C_{q\text{-}arom}$), 133.4, 133.2, 133.1 (CH_{arom}), 130.2 ($C_{q\text{-}arom}$), 130.0 (CH_{arom}), 129.9 ($C_{q\text{-}arom}$), 129.8, 129.1 (CH_{arom}), 128.6 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 127.8, 127.6, 127.6, 127.5 (CH_{arom}), 100.7 (C-1), 96.8 (C-1'), 79.5 (C-3), 77.8 (C-4), 76.9 (C-4'), 75.8 (C-2), 75.0, 74.5, 72.8 (CH_2 Bn), 72.6 (C-2'), 71.9 (C-3'), 69.1 (C-5'), 67.8 (C-5), 63.1 (C-6'), 55.4 (CH_3), 16.1 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{54}O_{13}$ 945.34621, found 945.34566.



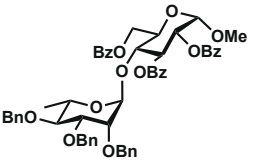
Methyl 6-*O*-(2,3,4-*O*-benzyl-D-rhamnopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S53). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (90 mg, 91 µmol, 91%, colorless oil, 1,2-*cis*:1,2-*trans*; 66:34). TLC: R_f 0.20 (1,2-*cis*) and 0.50 (1,2-*trans*) (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 731, 1031, 1033, 1366, 1451, 1489, 2850, 2912; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.49 – 7.12 (m, 30H, CH_{arom}), 5.01 – 4.91 (m, 2H, C*H*H Bn, C*H*H Bn), 4.87 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.85 – 4.74 (m, 2H, C*H*H Bn, C*H*H Bn), 4.75 – 4.57 (m, 6H, H-1', CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.55 – 4.40 (m, 3H, H-1, C*H*H Bn, CH*H* Bn), 4.28 (dd, *J* = 11.1, 3.1 Hz, 1H, H-6'), 4.03 – 3.90 (m, 2H, H-2, H-4'), 3.77 – 3.53 (m, 4H, H-4, H-2', H-5', H-6'), 3.52 – 3.40 (m, 2H, H-3, H-3'), 3.38 – 3.29 (m, 4H, H-5, CH_3'), 1.35 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.0, 138.9, 138.6, 138.5, 138.3, 138.3 ($C_{q\text{-}arom}$), 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.5 (CH_{arom}), 101.5 (C-1), 98.4 (C-1'), 82.1 (C-4), 82.0 (C-3), 80.3 (C-3'), 79.9 (C-2'), 77.9 (C-2), 75.9, 75.5, 75.3 (CH_2 Bn), 74.3 (C-4'), 74.1, 73.6 (CH_2 Bn), 72.1 (C-5), 71.4 (CH_2 Bn), 70.1 (C-5'), 67.3 (C-6'), 55.3 (CH_3'), 18.1 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$) δ 101.5 ($J_{H1\text{-}C1}$ = 154 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.71 (d, *J* = 1.8 Hz, 1H, H-1), 4.52 (d, *J* = 3.5 Hz, 1H, H-1'), 4.36 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 3.26 (s, 3H, CH_3'), 1.30 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.8, 138.7, 138.6, 138.4, 138.2, 138.2 ($C_{q\text{-}arom}$), 98.3 (C-1), 97.9 (C-1'), 75.9, 75.6, 75.1, 73.4, 72.8, 72.4 (CH_2 Bn), 70.0 (C-5), 68.1 (C-5'), 66.1 (C-6'), 55.1 (CH_3'), 18.1 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$) δ 98.3 ($J_{H1\text{-}C1}$ = 168 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{60}O_{10}Na$ 903.40842, found 903.40787.



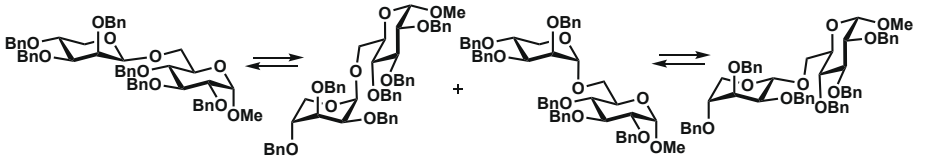
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-rhamnopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S54). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (83 mg, 84 µmol, 84%, colorless oil, 1,2-*cis*:1,2-*trans*; 12:88). TLC: R_f 0.55 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 731, 1022, 1089, 1458, 1456, 2916; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.63 – 7.04 (m, 30H, CH_{arom}), 5.04 (d, *J* = 1.9 Hz, 1H, H-1), 4.96 (d, *J* = 10.2 Hz, 1H, C*H*H Bn), 4.91 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.77 – 4.69 (m, 2H, C*H*H Bn, C*H*H Bn), 4.63 – 4.53 (m, 9H, H-1', CH*H* Bn, CH*H* Bn, CH*H* Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.48 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 3.91 (td, *J* = 9.4, 4.6 Hz, 1H, H-5), 3.86 – 3.73 (m, 2H, H-3', H-4'), 3.68 (t, *J* = 2.5 Hz, 2H, H-2), 3.63 (ddd, *J* = 9.0, 3.7, 1.7 Hz, 1H, H-5'), 3.60 – 3.48 (m, 4H, H-3, H-4, H-2', H-6'), 3.47 – 3.39 (m, 1H, H-6'), 3.35 (s, 3H, CH_3'), 1.06 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9, 138.7, 138.7, 138.5, 138.1, 138.0 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.4 (CH_{arom}), 98.2 (C-1), 98.0 (C-1'), 80.8 (C-4), 80.6 (C-2'), 80.1 (C-3'), 79.8 (C-3), 75.6, 75.3 (CH_2 Bn), 75.2 (C-2), 75.2 (C-4'), 73.6, 73.5, 72.5, 72.2 (CH_2 Bn), 70.1 (C-5'), 69.0 (C-6'), 68.8 (C-5), 55.4 (CH_3'), 18.0 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$) δ 98.2 ($J_{H1\text{-}C1}$ = 168 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.61 (signal overlaps with major stereoisomer, 1H, H-1), 4.21 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.16 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.44 (s, 3H, CH_3'); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 102.5 (C-1), 55.5 (CH_3'), 18.1 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{60}O_{10}Na$ 903.40842, found 903.40789.



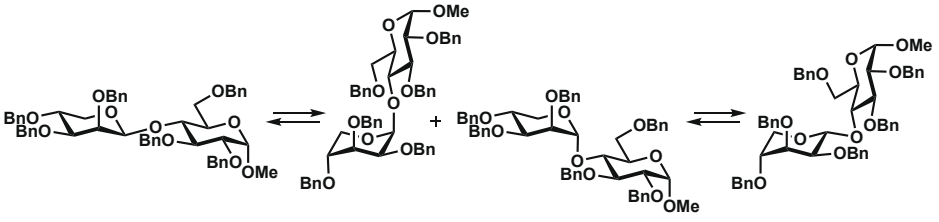
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-rhamnopyranosyl)-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S55). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (78 mg, 78 µmol, 78%, colorless oil, 1,2-*cis*:1,2-*trans*; 10:90). TLC: R_f 0.27 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 843, 1054, 1261, 1451, 1743, 2925; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 8.09 – 7.11 (m, 30H, CH_{arom}), 5.70 (t, *J* = 9.6 Hz, 1H, H-3'), 4.88 (d, *J* = 2.0 Hz, 1H, H-1), 4.77 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 3.5 Hz, 1H, H-1'), 4.67 – 4.40 (m, 11H, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 3.96 (t, *J* = 9.7 Hz, 1H, H-4'), 3.77 (ddd, *J* = 9.9, 3.4, 1.9 Hz, 1H, H-5'), 3.70 (dd, *J* = 9.2, 2.9 Hz, 1H, H-3), 3.61 (t, *J* = 2.4 Hz, 1H, H-2), 3.60 – 3.49 (m, 2H, H-5, H-2'), 3.49 – 3.35 (m, 6H, H-4, H-6', H-6', CH_3'); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 165.7 (C=O Bz), 139.0, 138.8, 138.6, 137.9, 137.8 ($C_{q\text{-}arom}$), 132.9 (CH_{arom}), 130.5 ($C_{q\text{-}arom}$), 130.1, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4 (CH_{arom}), 99.0 (C-1), 97.8 (C-1'), 80.5 (C-4), 79.6 (C-3), 77.4 (C-2'), 75.8 (C-2), 75.3 (C-4'), 74.6, 73.8, 72.8, 72.7 (CH_2 Bn), 72.6 (C-3'), 72.5 (CH_2 Bn), 69.9 (C-5'), 69.0 (C-5), 68.7 (C-6'), 55.5 (CH_3'), 17.7 (CH_3); ^{13}C-GATED NMR (101 MHz, $CDCl_3$) δ 99.0 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 5.81 (dd, *J* = 10.2, 8.9 Hz, 1H, H-3'), 4.41 (signa loverlaps with major stereoisomer, 1H, H-1); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 102.9 (C-1), 18.0 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{58}O_{11}Na$ 917.38768, found 917.38713.



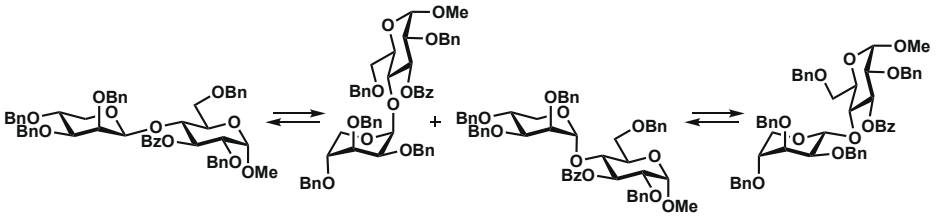
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-rhamnopyranosyl)-1,2-*trans*-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S56). The title The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (52 mg, 51 µmol, 51%, colorless oil, 1,2-*cis*:1,2-*trans*; <2:98). TLC: R_f 0.30 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 809, 1013, 1251, 1442, 1713, 2933; ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 8.15 – 7.16 (m, 30H, CH_{arom}), 5.94 (tt, *J* = 9.0, 1.9 Hz, 1H, H-3'), 5.12 – 5.06 (m, 2H, H-1', H-2'), 4.86 – 4.78 (m, 2H, H-1, C*H*H Bn), 4.72 – 4.46 (m, 5H, H-6', CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.20 (dd, *J* = 12.2, 4.0 Hz, 1H, H-6'), 4.07 – 3.93 (m, 2H, H-4', H-5'), 3.80 – 3.70 (m, 2H, H-2, H-3), 3.58 (dq, *J* = 9.4, 6.2 Hz, 1H, H-5), 3.48 – 3.37 (m, 4H, H-4, CH_3'), 0.81 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 166.2, 166.1, 165.9 (C=O Bz), 138.9, 138.6, 138.3 ($C_{q\text{-}arom}$), 133.5, 133.4, 133.1, 130.0, 129.9, 129.9(CH_{arom}), 129.9, 129.8, 129.1 ($C_{q\text{-}arom}$), 128.8, 128.5, 128.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.7, 127.7, 127.5 (CH_{arom}), 99.9 (C-1), 96.9 (C-1'), 80.3 (C-4), 79.3 (C-3), 76.0 (C-4'), 75.4 (C-2), 74.9, 73.1, 72.5 (CH_2 Bn), 72.4 (C-2'), 71.1 (C-3'), 69.3 (C-5), 68.8 (C-5'), 62.7 (C-6'), 55.6 (CH_3'), 17.6 (CH_3); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 99.9 ($J_{H1\text{-}C1}$ = 165 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{54}O_{13}$ 945.34621, found 945.34566.



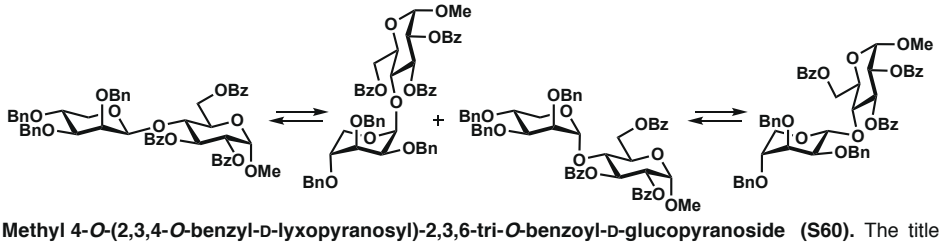
Methyl 6-*O*-(2,3,4-*O*-benzyl-D-lyxopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S57). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (94 mg, 95 µmol, 95%, colorless oil, 1,2-*cis*:1,2-*trans*; 60:40). TLC: R_f 0.25 and 0.33 and (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 730, 1031, 1045, 1367, 1451, 1491, 2922; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.42 – 7.15 (m, 60H, CH_{arom}), 4.98 (d, *J* = 10.8 Hz, 2H, C*H*H Bn), 4.92 – 4.50 (m, 12H, H-1', CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.29 (bs, 1H, H-1), 4.10 – 3.38 (m, 10H, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', H-6', H-6'), 3.30 (s, 3H, CH_3'), 3.18 (dd, *J* = 11.6, 7.8 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9, 138.7, 138.6, 138.5, 138.3, 138.2 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7 (CH_{arom}), 100.8 (C-1), 97.9 (C-1'), 82.2 (C-3'), 82.2 (C-4'), 80.0 (C-2'), 77.7 (C-3), 75.9, 75.8, 75.1 (CH_2 Bn), 74.9 (C-2, C-4), 74.9, 73.4, 73.2 (CH_2 Bn), 69.9 (C-5'), 66.2 (C-6'), 62.9 (C-5), 55.2 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 100.8 ($J_{H1\text{-}C1}$= 159 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 4.80 (signal overlaps with major stereoisomer, 1H, H-1) 3.31 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 99.1 (C-1), 98.3 (C-1'), 67.9 (C-6'), 70.0 (C-5'), 62.0 (C-5), 55.1 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 99.1 ($J_{H1\text{-}C1}$= 165 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{58}O_{10}Na$ 889.39277, found 889.39222.



Methyl 4-*O*-(2,3,4-*O*-benzyl-D-lyxopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S58). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound afforded the title compound (73 mg, 0.084 mmol, 84%, colorless oil, 1,2-*cis*:1,2-*trans*; 90:10). TLC: R_f 0.30 and 0.25 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 695, 734, 1027, 1086, 1452, 1496, 2925; ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.39 – 7.17 (m, 30H, CH_{arom}), 4.99 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.92 – 4.48 (m, 7H, H-1, CH*H* Bn, CH_2 Bn, CH_2 Bn, H-3), 4.30 (s, 1H, H-1), 4.07 – 3.97 (m, 3H, H-5_{eq}, H-3', H-6'), 3.87 (td, *J* = 7.5, 4.3 Hz, 1H, H-4), 3.78 (ddd, *J* = 10.4, 5.0, 1.8 Hz, 1H, H-5'), 3.74 (dd, *J* = 3.1, 1.8 Hz, 1H, H-2), 3.56 – 3.42 (m, 4H, H-3, H-2', H-4', H-6'), 3.31 (s, 3H, OMe'), 3.19 (dd, *J* = 11.9, 7.7 Hz, 1H, H-5_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.9, 138.4, 138.2 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6 (CH_{arom}), 100.7 (C-1), 97.9 (C-1'), 82.2 (C-3'), 80.0 (C-2'), 77.7 (C-4'), 75.0 (CH_2 Bn), 74.9 (C-4, CH_2 Bn), 75.0, 74.9, 74.9 (CH_2 Bn), 74.4 (C-2), 73.4, 73.3, 73.0, 72.3 (CH_2 Bn), 69.9 (C-5'), 67.8 (C-6'), 62.7 (C-5), 55.1 (Me'); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 100.7 ($J_{H1\text{-}C1}$ = 159 Hz, 1,2-*cis*); HRMS: $[M+NH_4]^+$ calcd for $C_{54}H_{58}O_{10}$ 884.43682, found 884.43612.

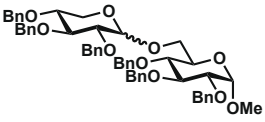


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-lyxopyranosyl)-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S59). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (74 mg, 74 µmol, 74%, colorless oil, 1,2-*cis*:1,2-*trans*; 55:45). TLC: R_f 0.26 and 0.35 and (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 814, 1053, 1251, 1431, 1723, 2919; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (55:45) anomers: ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated) δ 8.16 – 6.86 (m, 60H, $CH_{arom\text{-}1,2\text{-}trans}$, $CH_{arom\text{-}1,2\text{-}cis}$), 5.88 – 5.72 (m, 2H, H-$3_{1,2\text{-}trans}$', H-$3_{1,2\text{-}cis}$'), 4.98 (d, *J* = 3.0 Hz, 1H, H-$1_{1,2\text{-}trans}$), 4.75 (d, *J* = 3.4 Hz, 1H, H-1'$_{1,2\text{-}trans}$), 4.74 (d, *J* = 3.5 Hz, 1H, H-1'$_{1,2\text{-}cis}$), 4.70 – 4.62 (m, 2H, H-$1_{1,2\text{-}cis}$, C*H*H Bn), 4.62 – 4.30 (m, 17H, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.23 (d, *J* = 11.7 Hz, 1H, C*H*H $Bn_{1,2\text{-}trans}$), 4.09 – 3.49 (m, 18H, CH*H* $Bn_{1,2\text{-}trans}$, H-$2_{1,2\text{-}trans}$, H-$2_{1,2\text{-}cis}$, H-$3_{1,2\text{-}trans}$, H-$3_{1,2\text{-}cis}$, H-$4_{1,2\text{-}trans}$, H-$5_{1,2\text{-}trans}$, H-$5_{1,2\text{-}cis}$, H-2'$_{1,2\text{-}trans}$, H-2'$_{1,2\text{-}cis}$, H-4'$_{1,2\text{-}trans}$, H-4'$_{1,2\text{-}cis}$, H-5'$_{1,2\text{-}trans}$, H-5'$_{1,2\text{-}cis}$, H-$6_{1,2\text{-}trans}$, H-$6_{1,2\text{-}trans}$, H-6'$_{1,2\text{-}cis}$, H-6'$_{1,2\text{-}cis}$), 3.49 – 3.33 (m, 8H, H-$4_{1,2\text{-}cis}$, H-$5_{1,2\text{-}trans}$, CH_3'$_{1,2\text{-}trans}$, CH_3'$_{1,2\text{-}cis}$), 2.89 (dd, *J* = 12.3, 4.4 Hz, 1H, H-$5_{1,2\text{-}cis}$); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 165.6 (C=O $Bz_{1,2\text{-}cis}$), 165.4 (C=O $Bz_{\text{-}1,2\text{-}trans}$), 138.9, 138.8, 138.6, 138.4, 138.3, 138.2, 138.1, 137.9, 137.7 ($C_{q\text{-}arom}$), 133.3, 132.6, 131.1, 130.2, 129.9, 129.9, 128.7, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3 (CH_{arom}), 100.9 (C-$1_{1,2\text{-}trans}$), 100.3 (C-$1_{1,2\text{-}cis}$), 97.8 (C-1'$_{1,2\text{-}cis}$), 97.7 (C-1'$_{1,2\text{-}trans}$), 77.5 (C-$3_{1,2\text{-}cis}$), 77.0 (C-$3_{1,2\text{-}trans}$, C-4'$_{1,2\text{-}trans}$), 76.5 (C-$2_{1,2\text{-}cis}$), 76.0 (C-4'$_{1,2\text{-}cis}$), 75.0 (C-$4_{1,2\text{-}cis}$), 74.6 (C-$2_{1,2\text{-}trans}$), 74.5 (C-3'$_{1,2\text{-}trans}$), 74.5 (C-$4_{1,2\text{-}trans}$), 73.7 (CH_2 $Bn_{1,2\text{-}cis}$), 73.4 (CH_2 $Bn_{1,2\text{-}cis}$), 73.3 (CH_2 $Bn_{1,2\text{-}trans}$), 72.9 (C-3'$_{1,2\text{-}cis}$), 72.7 (CH_2 $Bn_{1,2\text{-}trans}$, CH_2 $Bn_{1,2\text{-}cis}$, CH_2 $Bn_{1,2\text{-}cis}$), 72.4 (CH_2 $Bn_{1,2\text{-}trans}$), 72.2 (CH_2 $Bn_{1,2\text{-}cis}$), 72.1 (CH_2 $Bn_{1,2\text{-}trans}$), 71.9 (CH_2 $Bn_{1,2\text{-}trans}$), 69.9 (C-5'$_{1,2\text{-}cis}$), 69.6 (C-5'$_{1,2\text{-}trans}$), 68.7 (C-6'$_{1,2\text{-}trans}$), 68.3 (C-6'$_{1,2\text{-}cis}$), 62.5 (C-$5_{1,2\text{-}trans}$), 60.3 (C-$5_{1,2\text{-}cis}$), 55.5 (CH_3'$_{1,2\text{-}trans}$), 55.4 (CH_3'$_{1,2\text{-}cis}$); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 100.9 ($J_{H1\text{-}C1}$= 167 Hz, 1,2-*cis*), 100.3 ($J_{H1\text{-}C1}$= 164 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{56}O_{11}Na$ 903.37029, found 903.37148.

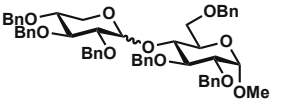


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-lyxopyranosyl)-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S60). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (61 mg, 0.067 mmol, 67%, colorless oil, 1,2-*cis*:1,2-*trans*; 61:39). TLC: R_f 0.30, 0.25 (pentane:EtOAc, 90:10, v:v); IR (thin film, cm^{-1}): 735, 1008, 1068, 1452, 1720, 2923; Data for the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 8.17 – 6.96 (m, 30H, CH_{arom}), 6.14 – 6.05 (m, 1H, H-3'), 5.19 – 5.11 (m, 4H, H-1', H-2'), 5.01 (d, *J* = 4.4 Hz, 1H, H-1), 4.79 – 4.23 (m, 9H, H-4, H-6', H-6', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.20 – 4.12 (m, 2H, H-4', H-5'), 3.72 – 3.61 (m, 3H, H-3, H-5), 3.60 – 3.53 (m, 2H, H-2, H-5), 3.44 (s, 3H, Me); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 166.3, 166.0, 165.6 (C=O Bz), 138.9, 138.7, 138.4, 138.3, 138.0, 138.0 ($C_{q\text{-}arom}$), 133.4, 133.3, 133.3, 133.2, 133.1, 132.8, 130.4, 130.2, 130.1, 130.0, 129.8, 129.8, 129.7, 129.6, 129.2, 129.1, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.1, 127.8, 127.8, 127.7, 127.7, 127.7, 127.4, 127.4, 127.3 (CH_{arom}), 101.1 (C-1), 97.0 (C-1'), 78.1 (C-3), 76.7 (C-2), 75.8 (C-4'), 73.5 (CH_2 Bn), 72.7 (C-3'), 72.5

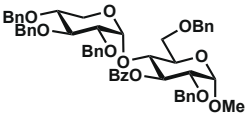
(CH_2 Bn), 72.3 (CH_2 Bn), 72.2 (C-2'), 68.6 (C-5'), 63.4 (C-6'), 62.8 (C-5), 55.6 (Me'); HRMS: $[M+NH_4]^+$ calcd for $C_{54}H_{52}O_{13}$ 926.37462, found 926.37443.



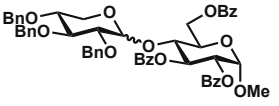
Methyl 6-*O*-(2,3,4-*O*-benzyl-D-xylopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S61). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (89 mg, 90 µmol, 90%, colorless oil, 1,2-*cis*:1,2-*trans*; 38:62). TLC: R_f 0.22 and 0.31 and (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 723, 1053, 1376, 1461, 1497, 2933; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.41 – 7.11 (m, 30H, CH_{arom}), 5.00 – 4.55 (m, 12H, H-1', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.50 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.28 (d, *J* = 7.6 Hz, 1H, H-1), 4.07 (dd, *J* = 10.8, 2.0 Hz, 1H, H-6'), 3.98 (m, 1H, H-3'), 3.90 (dd, *J* = 11.6, 5.1 Hz, 1H, H-5), 3.89 – 3.73 (m, 1H, H-5'), 3.73 – 3.47 (m, 5H, H-3, H-4, H-2', H-4', H-6'), 3.47 – 3.38 (m, 1H, H-2), 3.32 (s, 3H, CH_3'), 3.15 (dd, *J* = 11.6, 9.9 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.9, 138.7, 138.5, 138.4, 138.2 ($C_{q\text{-}arom}$), 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6 (CH_{arom}), 104.2 (C-1), 98.2 (C-1'), 84.1 (C-3), 82.1 (C-3'), 81.8 (C-2), 79.8 (C-2'), 77.9 (C-4), 77.9 (C-4'), 75.8, 75.8, 75.1, 73.5 (CH_2 Bn), 73.5 (CH_2 Bn, CH_2 Bn), 69.8 (C-5'), 68.3 (C-6'), 64.0 (C-5), 55.3 (CH_3'); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.86 (d, *J* = 3.5 Hz, 1H, H-1), 4.56 (d, *J* = 3.6 Hz, 1H, H-1'), 3.35 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.0, 138.6, 138.6, 138.5, 138.3 ($C_{q\text{-}arom}$), 98.1 (C-1'), 97.4 (C-1), 75.9, 75.7, 75.1, 73.5, 72.7 (CH_2 Bn), 70.5 (C-5'), 66.2 (C-6'), 60.2 (C-5), 55.3 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{58}O_{10}Na$ 889.39277, found 889.39223.



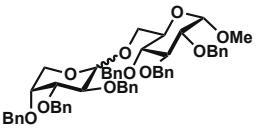
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-xylopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S62). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (69 mg, 70 µmol, 70%, colorless oil, 1,2-*cis*:1,2-*trans*; 60:40). TLC: R_f 0.27 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 685, 744, 1031, 1094, 1422, 1487, 2921; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.50 – 7.04 (m, 30H, CH_{arom}), 5.57 (d, *J* = 3.6 Hz, 1H, H-1), 5.03 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.92 – 4.48 (m, 12H, H-1', CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.08 (t, *J* = 9.1 Hz, 1H, H-3'), 4.04 (t, *J* = 8.7 Hz, 1H, H-4'), 3.93 – 3.76 (m, 3H, H-4, H-5', H-6'), 3.72 (dd, *J* = 10.3, 1.8 Hz, 1H, H-6'), 3.59 (dd, *J* = 9.0, 3.4 Hz, 1H, H-2'), 3.57 – 3.44 (m, 2H, H-5, H-5), 3.42 – 3.35 (m, 5H, H-2, H-3, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.0, 138.9, 138.4, 138.3, 138.1, 138.0 ($C_{q\text{-}arom}$), 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.5, 126.9 (CH_{arom}), 97.9 (C-1'), 96.4 (C-1), 82.1 (C-3'), 81.2 (C-3), 80.3 (C-2'), 79.2 (C-2), 78.0 (C-4), 75.7, 74.4, 73.6, 73.5, 73.4, 73.3 (CH_2 Bn), 71.9 (C-4'), 69.4 (C-5'), 69.1 (C-6'), 61.0 (C-5), 55.3 (CH_3'); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 4.55 (signal overlaps with major stereoisomer, 1H, H-1'), 4.34 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.25 (d, *J* = 7.7 Hz, 1H, H-1), 3.37 (s, 3H, CH_3'), 3.27 (dd, *J* = 9.2, 7.7 Hz, 1H, H-2), 2.95 (dd, *J* = 11.7, 10.4 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.0, 138.8, 138.7, 138.5, 138.0 ($C_{q\text{-}arom}$), 103.2 (C-1), 98.7 (C-1'), 82.6 (C-2), 76.0, 75.7, 75.2, 73.9, 73.4, 73.3 (CH_2 Bn), 70.2 (C-5'), 67.8 (C-6'), 63.8 (C-5), 55.5 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{58}O_{10}Na$ 889.39277, found 889.39220.



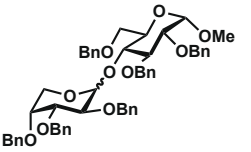
Methyl 4-*O*-(2,3,4-*O*-benzyl-D-xylopyranosyl)-1,2-*cis*-2,6-di-*O*-benzyl-3-*O*-benzoyl-1,2-*cis*-D-glucopyranoside (S63). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (91 mg, 91 µmol, 91%, colorless oil, 1,2-*cis*:1,2-*trans*; 60:40). TLC: R_f 0.38 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 691, 732, 1031, 1089, 1453, 1490, 1730, 2924; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 8.09 – 7.06 (m, 30H, CH_{arom}), 5.92 (dd, *J* = 10.0, 9.1 Hz, 1H, H-3'), 4.93 (d, *J* = 3.3 Hz, 1H, H-1), 4.77 (d, *J* = 3.5 Hz, 1H, H-1'), 4.76 – 4.49 (m, 12H, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn), 4.47 (d, *J* = 12.4 Hz, 1H, CH*H* Bn), 4.36 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.14 (t, *J* = 9.3 Hz, 1H, H-4'), 4.06 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 3.97 – 3.85 (m, 2H, H-5', H-6'), 3.77 (dd, *J* = 9.6, 8.7 Hz, 1H, H-3), 3.75 – 3.69 (m, 1H, H-6'), 3.69 – 3.59 (m, 2H, H-2', H-4), 3.55 (t, *J* = 10.9 Hz, 1H, H-5), 3.51 – 3.43 (m, 1H, H-5), 3.41 (s, 3H, CH_3'), 3.21 – 3.11 (m, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 165.4 (C=O Bz), 139.0, 138.8, 138.2, 138.1, 137.8 ($C_{q\text{-}arom}$), 132.9 (CH_{arom}), 130.8 ($C_{q\text{-}arom}$), 129.9, 129.8, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.1, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5 (CH_{arom}), 97.8 (C-1'), 97.4 (C-1), 80.7 (C-3), 79.0 (C-2), 77.6 (C-2'), 77.2 (C-4), 75.5 (CH_2 Bn), 73.9 (C-3'), 73.8 (C-4'), 73.4, 73.4, 72.8, 72.7 (CH_2 Bn), 69.7 (C-5'), 68.6 (C-6'), 61.3 (C-5), 55.4 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 97.4 ($J_{H1\text{-}C1}$ = 168 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 5.66 (dd, *J* = 10.0, 9.2 Hz, 1H, H-3'), 4.11 (d, *J* = 7.5 Hz, 1H, H-1), 2.77 (td, *J* = 9.4, 1.2 Hz, 1H, H-5), 3.40 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 165.8 (C=O Bz), 138.6, 138.3, 138.0, 137.9, 131.4 ($C_{q\text{-}arom}$), 103.4 (C-1), 98.2 (C-1'), 75.3, 75.2, 73.5, 73.0, 72.9 (CH_2 Bn), 72.9 (C-3'), 69.8 (C-5'), 67.7 (C-6'), 63.1 (C-5), 55.5 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 103.4 ($J_{H1\text{-}C1}$ = 164 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{56}O_{11}Na$ 903.37029, found 903.37147.



Methyl 4-*O*-(2,3,4-*O*-benzyl-D-xylopyranosyl)-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S64). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (56 mg, 54 µmol, 54%, colorless oil, 1,2-*cis*:1,2-*trans*; 60:40). TLC: R_f 0.25 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 811, 1037, 1265, 1454, 1725, 2912; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 8.13 – 7.03 (m, 30H, CH_{arom}), 5.95 (dd, *J* = 10.3, 8.7 Hz, 1H, H-3'), 5.18 – 5.08 (m, 2H, H-1', H-2'), 4.90 – 4.56 (m, 15H, H-6', H-6', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.54 – 4.43 (m, 1H, C*H*H Bn), 4.35 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.33 (d, *J* = 7.5 Hz, 1H, H-1), 4.09 – 3.90 (m, 2H, H-4', H-5'), 3.69 – 3.35 (m, 4H, H-3, CH_3'), 3.30 – 3.15 (m, 3H, H-2, H-4, H-5), 2.85 (m, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 166.1, 166.0, 165.9 (C=O Bz), 138.7, 138.4, 138.1 ($C_{q\text{-}arom}$), 133.4, 133.3, 132.7 (CH_{arom}), 130.7 ($C_{q\text{-}arom}$), 130.1 (CH_{arom}), 130.0 ($C_{q\text{-}arom}$), 129.8, 129.9 (CH_{arom}), 129.3 ($C_{q\text{-}arom}$), 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 127.9, 127.9, 127.9, 127.8, 127.6 (CH_{arom}), 103.8 (C-1), 96.9 (C-1'), 83.9 (C-3), 82.1 (C-2), 77.9 (C-4), 76.5 (C-4'), 75.5, 75.5, 73.1 (CH_2 Bn), 72.0 (C-2'), 70.9 (C-3'), 68.9 (C-5'), 63.9 (C-5), 63.4 (C-6'), 55.6 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 103.8 ($J_{H1\text{-}C1}$ = 161 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 6.20 (ddd, *J* = 10.2, 7.8, 2.1 Hz, 1H, H-3'), 5.23 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2'), 4.89 (d, *J* = 3.4 Hz, 1H, H-1), 4.28 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 3.82 (t, *J* = 9.1 Hz, 1H, H-3), 3.18 (dd, *J* = 9.5, 3.5 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 166.2, 166.2, 165.6 (C=O Bz), 138.9, 138.4, 138.1, 130.1, 129.2 ($C_{q\text{-}arom}$), 98.7 (C-1), 96.9 (C-1'), 80.7 (C-3), 78.6 (C-2), 75.6, 73.4, 73.1 (CH_2 Bn), 68.7 (C-5'), 62.8 (C-6'), 61.5 (C-5), 55.6 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 96.9 ($J_{H1\text{-}C1}$ = 169 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{52}O_{13}Na$ 931.33056, found 931.33001.

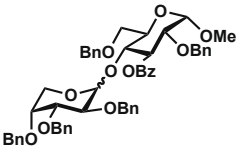


Methyl 6-*O*-(2,3,4-*O*-benzyl-D-arabinopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S65). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (92 mg, 93 µmol, 93%, colorless oil, 1,2-*cis*:1,2-*trans*; 30:70). TLC: R_f 0.41 and 0.49 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 745, 1031, 1053, 1320, 1464, 1489, 2921; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.47 – 7.06 (m, 30H, CH_{arom}), 5.00 – 4.55 (m, 13H, H-1', C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.41 (d, *J* = 6.6 Hz, 1H, H-1), 4.14 (dd, *J* = 11.4, 4.2 Hz, 1H, H-6'), 4.04 – 3.89 (m, 2H, H-5, H-3'), 3.81 (dd, *J* = 8.7, 6.5 Hz, 1H, H-2), 3.79 – 3.59 (m, 4H, H-4, H-4', H-5', H-6'), 3.52 (dd, *J* = 8.7, 3.4 Hz, 1H, H-3), 3.44 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2'), 3.32 (s, 3H, CH_3'), 3.25 (dd, *J* = 12.6, 1.6 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.0, 138.9 ($C_{q\text{-}arom}$), 138.6 ($C_{q\text{-}arom}$), 138.4, 138.4 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6 (CH_{arom}), 103.7 (C-1), 98.2 (C-1'), 82.2 (C-3'), 80.3 (C-2'), 79.5 (C-3), 79.0 (C-2), 77.9 (C-4'), 75.8, 75.1, 74.9, 73.5 (CH_2 Bn), 72.6 (C-4), 72.5, 71.2 (CH_2 Bn), 70.2 (C-5'), 67.7 (C-6'), 62.5 (C-5), 55.2 (CH_3') ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 103.7 ($J_{H1\text{-}C1}$= 161 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 4.91 (d, *J* = 3.2 Hz, 1H, H-1), 4.58 (signa loverlaps with major isomer, 1H, H-1'), 3.86 (dd, *J* = 10.8, 1.6 Hz, 1H, H-6'), 3.48 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2'), 3.30 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 138.9, 138.8, 138.8, 138.6, 138.5, 138.4 ($C_{q\text{-}arom}$), 98.5 (C-1), 98.1 (C-1'), 75.9, 75.1, 73.6, 73.4, 72.5, 71.8 (CH_2 Bn), 70.1 (C-5'), 66.6 (C-6'), 60.6 (C-5), 55.2 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 98.5 ($J_{H1\text{-}C1}$= 167 Hz, 1,2-*cis*); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{58}O_{10}Na$ 889.39277, found 889.39230.

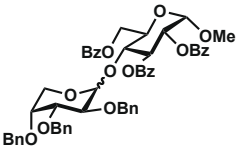


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-arabinopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S66). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 80:20, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (83 mg, 84 µmol, 84%, colorless oil, 1,2-*cis*:1,2-*trans*; 53:47). TLC: R_f 0.30 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 690, 741, 1020, 1043, 1330, 1476, 1491, 2909; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (53:47) anomers: ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated) δ 7.40 – 7.13 (m, 60H, CHarom), 5.03 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 5.01 (d, *J* = 3.2 Hz, 1H, H-$1_{1,2\text{-}cis}$), 4.90 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.83 – 4.48 (m, 23H, H-$1_{1,2\text{-}trans}$, H-$1'_{1,2\text{-}cis}$, H-$1'_{1,2\text{-}trans}$, CH*H* Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.41 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.29 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 3.99 – 3.69 (m, 14H, H-$2_{1,2\text{-}cis}$, H-$2_{1,2\text{-}trans}$, H-$3_{1,2\text{-}cis}$, H-$5_{1,2\text{-}cis}$, H-$5_{1,2\text{-}trans}$, H-$3'_{1,2\text{-}cis}$, H-$3'_{1,2\text{-}trans}$, H-$4'_{1,2\text{-}cis}$, H-$4'_{1,2\text{-}trans}$, H-$5'_{1,2\text{-}cis}$, H-$5'_{1,2\text{-}trans}$, H-$6'_{1,2\text{-}cis}$, H-$6'_{1,2\text{-}trans}$, H-$6'_{1,2\text{-}trans}$), 3.62 – 3.58 (m, 2H, H-$4_{1,2\text{-}trans}$, H-$6'_{1,2\text{-}cis}$), 3.56 (dd, *J* = 9.5, 3.5 Hz, 1H, H-$2'_{1,2\text{-}cis}$), 3.52 (dd, *J* = 9.6, 3.5 Hz, 1H, H-$2'_{1,2\text{-}trans}$), 3.48 – 3.32 (m, 8H, H-$3_{1,2\text{-}trans}$, H-$4_{1,2\text{-}cis}$, $CH_3'_{1,2\text{-}cis}$, $CH_3'_{1,2\text{-}trans}$), 3.29 (dd, *J* = 12.9, 2.5 Hz, 1H, H-$5_{1,2\text{-}cis}$), 3.07 (dd, *J* = 12.8, 1.4 Hz, 1H, H-$5_{1,2\text{-}trans}$); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.9, 138.8, 138.7, 138.6, 138.6, 138.5, 138.4, 138.2, 138.1, 138.1 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.4 (CH_{arom}), 103.2 (C-$1_{1,2\text{-}trans}$), 98.4 (C-$1_{1,2\text{-}cis}$), 98.0 (C-$1'_{1,2\text{-}cis}$), 98.0 (C-$1'_{1,2\text{-}trans}$), 82.3 (C-$3'_{1,2\text{-}trans}$), 80.5 (C-$2'_{1,2\text{-}cis}$), 80.1 (C-$3'_{1,2\text{-}cis}$), 80.1 (C-$2'_{1,2\text{-}trans}$), 79.8 (C-$2_{1,2\text{-}cis}$), 79.6 (C-$2_{1,2\text{-}trans}$), 77.5 (C-$3_{1,2\text{-}trans}$), 76.6 (C-$3_{1,2\text{-}cis}$), 75.5, 75.4, 75.3, 74.7 (CH_2 Bn), 74.3 (C-$4'_{1,2\text{-}trans}$), 74.0 (C-$4'_{1,2\text{-}cis}$), 73.5, 73.5, 73.4 (CH_2 Bn), 73.4 (C-$4_{1,2\text{-}cis}$), 73.3 (CH_2 Bn), 72.9 (C-$4_{1,2\text{-}trans}$), 72.4, 72.1, 71.3, 71.2 (CH_2 Bn), 70.4 (C-$5'_{1,2\text{-}cis}$), 69.9 (C-$5'_{1,2\text{-}trans}$), 69.2 (C-$6'_{1,2\text{-}trans}$), 68.4 (C-$6'_{1,2\text{-}cis}$), 62.7 (C-$5_{1,2\text{-}trans}$), 60.3 (C-$5_{1,2\text{-}cis}$), 55.4

(CH3'$_{1,2\text{-}cis}$), 55.2 (CH3'$_{1,2\text{-}trans}$); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 103.2 ($J_{H1\text{-}C1}$= 164 Hz, 1,2-*trans*), 98.3 ($J_{H1\text{-}C1}$= 171 Hz, 1,2-*cis*); HRMS: [M+Na]$^+$ calcd for $C_{54}H_{58}O_{10}Na$ 889.39277, found 889.39241.

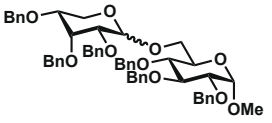


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-arabinopyranosyl)-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S67). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (79 mg, 79 µmol, 79%, colorless oil, 1,2-*cis*:1,2-*trans*; 75:25). TLC: R_f 0.21 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 812, 1031, 1262, 1449, 1731, 2920; Data of the major stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 8.11 – 7.00 (m, 30H, CH_{arom}), 5.70 (t, *J* = 9.4 Hz, 1H, H-3'), 4.97 (d, *J* = 3.7 Hz, 1H, H-1), 4.85 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.72 (d, *J* = 3.4 Hz, 1H, H-1'), 4.72 – 4.44 (m, 8H, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.29 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.00 (dd, *J* = 11.0, 3.5 Hz, 1H, H-6'), 3.98 – 3.90 (m, 2H, H-2, H-4'), 3.89 – 3.84 (m, 1H, H-5'), 3.80 (dd, *J* = 10.2, 3.1 Hz, 1H, H-3), 3.65 – 3.56 (m, 2H, H-4, H-6'), 3.54 (dd, *J* = 9.9, 3.4 Hz, 1H, H-2'), 3.47 (dd, *J* = 12.8, 1.3 Hz, 1H, H-5), 3.39 (s, 3H, CH_3'), 3.13 (dd, *J* = 12.7, 2.2 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 166.1 (C=O Bz), 138.7, 138.6, 138.4, 138.3, 137.7 ($C_{q\text{-}arom}$), 132.9 (CH_{arom}), 130.7 ($C_{q\text{-}arom}$), 129.9, 128.4, 128.4, 128.4, 128.4, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6 (CH_{arom}), 100.6 (C-1), 97.5 (C-1'), 78.1 (C-3), 77.7 (C-2'), 76.7 (C-4'), 76.3 (C-2), 74.7 (CH_2 Bn), 73.3 (C-4), 73.2 (C-3'), 72.7, 72.0, 71.6 (CH_2 Bn), 70.2 (C-5'), 68.2 (C-6'), 60.6 (C-5), 55.4 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 100.6 ($J_{H1\text{-}C1}$= 168 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 5.86 (dd, *J* = 10.1, 9.1 Hz, 1H, H-3'), 4.77 (d, *J* = 3.5 Hz, 1H, H-1'), 4.65 (d, *J* = 6.1 Hz, 1H, H-1), 4.07 (t, *J* = 9.5 Hz, 1H, H-4'), 3.43 (s, 3H, CH_3'), 3.35 (dd, *J* = 6.5, 3.3 Hz, 1H, H-3), 3.20 (dd, *J* = 11.7, 2.8 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 165.3 (C=O Bz), 138.6, 138.5, 138.5, 138.4, 137.8, 130.5 ($C_{q\text{-}arom}$), 101.7 (C-1), 97.7 (C-1'), 74.9 (C-3'), 73.9 (CH_2 Bn), 73.7 (C-4'), 73.6, 72.7, 72.0, 71.1 (CH_2 Bn), 69.6 (C-5'), 68.7 (C-6'), 60.9 (C-5), 55.5 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 101.7 ($J_{H1\text{-}C1}$= 164 Hz, 1,2-*trans*); HRMS: [M+Na]$^+$ calcd for $C_{54}H_{56}O_{11}Na$ 903.37029, found 903.37137.

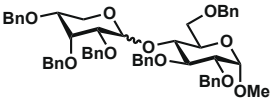


Methyl 4-*O*-(2,3,4-*O*-benzyl-D-arabinopyranosyl)-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S68). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (53 mg, 59 µmol, 59%, colorless oil, 1,2-*cis*:1,2-*trans*; 78:22). TLC: R_f 0.30 and 0.25 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 736, 1026, 1271, 1452, 1720, 2923; Data for the major stereoisomer (1,2-*cis*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, HMBC-Gated): δ 8.18 – 7.08 (m, 30H, CH_{arom}), 5.97 (dd, *J* = 10.0, 9.0 Hz, 1H, H-3'), 5.12 – 5.09 (m, 1H, H-1'), 5.06 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2'), 4.96 (d, *J* = 3.6 Hz, 1H, H-1), 4.92 (dd, *J* = 12.0, 2.1 Hz, 1H, H-6'), 4.85 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.78 (dd, *J* = 11.9, 4.1 Hz, 1H, H-6'), 4.70 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.65 – 4.60 (m, 2H, CH_2 Bn), 4.54 – 4.51 (m, 2H, CH_2 Bn), 4.17 (ddd, *J* = 9.9, 4.2, 2.1 Hz, 1H, H-5'), 4.06 – 3.95 (m, 2H, H-2, H-4'), 3.85 (dd, *J* = 10.1, 3.1 Hz, 1H, H-3), 3.67 – 3.58 (m, 1H, H-4), 3.49 (dd, *J* = 12.7, 1.3 Hz, 1H, H-5), 3.39 (s, 3H, CH_3'), 3.15 (dd, *J* = 12.6, 2.3 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 166.2, 166.2, 166.0 (C=O Bz), 138.6, 138.2, 138.1 ($C_{q\text{-}arom}$), 133.4, 133.2, 133.1 (CH_{arom}), 130.2 ($C_{q\text{-}arom}$), 130.0, 129.8, 129.7 (CH_{arom}), 129.2 ($C_{q\text{-}arom}$), 128.6, 128.6, 128.5, 128.4, 128.4, 127.9, 127.8, 127.7, 127.6 (CH_{arom}), 101.6 (C-1), 96.8 (C-1'), 78.0 (C-3), 77.9 (C-4'), 75.7 (C-2), 74.7 (CH_2 Bn), 73.5 (C-4), 72.7 (C-2'), 72.1, 71.8 (CH_2 Bn), 71.6 (C-3'), 69.0 (C-5'), 62.8 (C-6'), 61.0 (C-5), 55.4 (CH_3'); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 101.6 ($J_{H1\text{-}C1}$ = 167 Hz, 1,2-*cis*); Data for the minor stereoisomer (1,2-*trans*): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, HMBC-Gated δ 8.18 – 7.08 (m, 30H, CH_{arom}), 6.14 (ddt, *J* = 10.9, 9.0, 2.1 Hz, 1H, H-3'), 4.57 (d, *J* = 6.2 Hz,

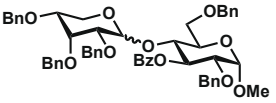
1H, H-1), 4.49 – 4.46 (m, 1H, C*H*H Bn), 4.40 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.33 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 3.67 – 3.58 (m, 2H, H-2, H-5), 3.44 (s, 3H, CH_3'), 3.25 (dd, *J* = 7.8, 3.2 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 166.3, 166.1, 165.5 (C=O Bz), 138.7, 138.5, 138.3 ($C_{q\text{-arom}}$), 133.4, 133.1, 133.0, 129.8, 128.5, 128.5, 128.3, 128.0, 128.0, 127.9 (CH_{arom}), 103.0 (C-1), 97.0 (C-1'), 78.3 (C-2), 74.4, 72.1, 70.9 (CH_2 Bn), 63.5 (C-6'), 61.6 (C-5), 55.5 (CH_3'); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 103.0 ($J_{H1\text{-}C1}$ = 163 Hz, 1,2-*trans*); HRMS: $[M+NH_4]^+$ calcd for $C_{54}H_{52}O_{13}$ 926.37462, found 926.37408.



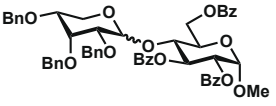
Methyl 6-*O*-(2,3,4-*O*-benzyl-D-ribopyranosyl)-2,3,4-tri-*O*-benzyl-D-glucopyranoside (S69). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (100:0 → 90:10, pentane:EtOAc) afforded the title compound (55 mg, 63 µmol, 63%, colorless oil, 1,2-*cis*:1,2-*trans*; 35:65). TLC: R_f 0.40, 0.30 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 733, 1027, 1043, 1364, 1452, 1496, 2923; NMR data reported as a mixture of 1,2-*cis*:1,2-*trans* (44:56) anomers: ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.47 – 7.11 (m, 55.8H, CH_{arom}), 5.01 (d, *J* = 11.5 Hz, 0.85H, C*H*H $Bn_{1,2\text{-}cis}$), 4.97 – 4.93 (m, 2H, H-$1_{1,2\text{-}trans}$, C*H*H $Bn_{1,2\text{-}trans}$), 4.83 – 4.75 (m, 1.86H, CH*H* $Bn_{1,2\text{-}cis}$, CH*H* $Bn_{1,2\text{-}trans}$), 4.72 – 4.68 (m, 1.85H, C*H*H $Bn_{1,2\text{-}cis}$, C*H*H $Bn_{1,2\text{-}trans}$), 4.64 – 4.53 (m, 4.58H, H-$1_{1,2\text{-}cis}$, H-1'$_{1,2\text{-}cis}$, , H-1'$_{1,2\text{-}trans}$, CH*H* $Bn_{1,2\text{-}cis}$, CH*H* $Bn_{1,2\text{-}trans}$), 4.53 – 4.37 (m, 2.72H, CH_2 $Bn_{1,2\text{-}cis}$, C*H*H $Bn_{1,2\text{-}trans}$,), 4.28 (d, *J* = 11.5 Hz, 1H, CH*H* $Bn_{1,2\text{-}trans}$), 4.14 (t, *J* = 2.6 Hz, 1H, H-$3_{1,2\text{-}trans}$), 4.04 (t, *J* = 9.1 Hz, 0.86H, H-4'$_{1,2\text{-}cis}$), 3.97 – 3.89 (m, 1H, H-$5_{ax\text{-}1,2\text{-}cis}$), 3.88 – 3.77 (m, 1.86H, H-6'$_{1,2\text{-}cis}$, H-6'$_{1,2\text{-}trans}$), 3.77 – 3.73 (m, 2H, H-$5_{1,2\text{-}trans}$, H-$5_{1,2\text{-}trans}$), 3.68 (dd, *J* = 10.4, 2.1 Hz, 0.86H, H-6'$_{1,2\text{-}cis}$), 3.61 (dd, *J* = 10.6, 1.9 Hz, 1H, H-6'$_{1,2\text{-}trans}$), 3.56 (dd, *J* = 9.6, 3.5 Hz, 1H, H-$3_{1,2\text{-}cis}$ or H-5'$_{1,2\text{-}cis}$), 3.53 – 3.46 (m, 1H, H-$4_{1,2\text{-}trans}$, H-2'$_{1,2\text{-}trans}$), 3.39 (s, 2,58H, CH_3'$_{1,2\text{-}cis}$), 3.36 (s, 3H, CH_3'$_{1,2\text{-}trans}$), 3.30 (dd, *J* = 11.3, 3.8 Hz, 0.86H, H-$5_{eq\text{-}1,2\text{-}cis}$), 3.22 (dd, *J* = 7.7, 2.7 Hz, 1H, H-$2_{1,2\text{-}trans}$); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{58}O_{10}Na$ 889.39277, found 889.39212.



Methyl 4-*O*-(2,3,4-*O*-benzyl-D-ribopyranosyl)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (S70). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (74 mg, 75 µmol, 75%, colorless oil, 1,2-*cis*:1,2-*trans*; 40:60). TLC: R_f 0.35 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 698, 745, 1031, 1097, 1453, 1491, 2921; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 7.43 – 7.10 (m, 30H, CH_{arom}), 4.98 – 4.91 (m, 2H, H-1, C*H*H Bn), 4.83 – 4.37 (m, 21H, H-1', CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.28 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.14 (t, *J* = 2.6 Hz, 1H, H-3), 3.98 – 3.88 (m, 1H, H-4'), 3.87 – 3.77 (m, 2H, H-3', H-6'), 3.77 – 3.72 (m, 2H, H-5, H-5), 3.71 – 3.58 (m, 2H, H-5', H-6'), 3.54 – 3.46 (m, 2H, H-4, H-2'), 3.36 (s, 3H, CH_3'), 3.22 (dd, *J* = 7.7, 2.7 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 139.2 ($C_{q\text{-arom}}$), 138.7, 138.5 ($C_{q\text{-arom}}$), 138.1 ($C_{q\text{-arom}}$, $C_{q\text{-arom}}$), 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.4, 127.0 (CH_{arom}), 101.0 (C-1'), 98.6 (C-1), 80.5 (C-3'), 79.4 (C-2), 79.1 (C-2'), 77.2 (C-4'), 75.8 (CH_2 Bn), 75.7 (C-4), 75.5 (C-3), 73.8, 73.1, 73.1, 72.8, 71.4 (CH_2 Bn), 70.3 (C-5'), 68.1 (C-6'), 62.4 (C-5), 55.4 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 101.0 ($J_{H1\text{-}C1}$= 167 Hz, 1,2-tran*s*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 5.27 (bs, 1H, H-1), 5.01 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.62 (d, *J* = 3.5 Hz, 1H, H-1'), 4.04 (t, *J* = 9.2 Hz, 1H, H-3'), 3.56 (dd, *J* = 9.6, 3.5 Hz, 1H, H-2'), 3.40 (s, 3H, CH_3'), 3.30 (dd, *J* = 11.3, 3.8 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.1, 138.8, 138.2 ($C_{q\text{-arom}}$), 97.9 (C-1'), 82.5 (C-3'), 80.2 (C-2'), 69.6 (C-5'), 69.1 (C-6'), 55.3 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{58}O_{10}Na$ 889.39277, found 889.39250.



Methyl 4-*O*-(2,3,4-*O*-benzyl-D-ribopyranosyl)-2,6-di-*O*-benzyl-3-*O*-benzoyl-D-glucopyranoside (S71). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Flash column chromatography (95:5 → 70:30, pentane:EtOAc) and size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (55 mg, 61 µmol, 61%, colorless oil, 1,2-*cis*:1,2-*trans*; 40:60). TLC: R_f 0.25 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 731, 803, 1235, 1261, 1451, 1730, 2923; Data of the major stereoisomer (1,2-*trans*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC-Gated): δ 8.18 – 6.91 (m, 30H, CH_{arom}), 5.68 (dd, *J* = 10.0, 9.1 Hz, 1H, H-3'), 4.79 – 4.72 (m, 3H, H-1, C*H*H Bn, CH*H* Bn), 4.70 (d, *J* = 3.5 Hz, 1H, H-1'), 4.65 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.61 – 4.23 (m, 7H, CH*H* Bn, CH*H* Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn, C*H*H Bn, CH*H* Bn), 3.99 (td, *J* = 2.4, 0.9 Hz, 1H, H-3), 3.97 – 3.85 (m, 1H, H-4'), 3.86 – 3.73 (m, 2H, H-5', H-6'), 3.66 – 3.55 (m, 2H, H-2', H-6'), 3.47 (t, *J* = 10.4 Hz, 1H, H-5), 3.39 (s, 3H, CH_3'), 3.22 – 3.15 (m, 1H, H-4), 3.12 (dd, *J* = 7.5, 2.7 Hz, 1H, H-2), 2.97 (ddd, *J* = 10.9, 4.9, 1.2 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC-Gated): δ 166.0 (C=O Bz), 139.1, 138.6, 138.0, 138.0 ($C_{q\text{-}arom}$), 132.4 (CH_{arom}), 131.4 ($C_{q\text{-}arom}$), 129.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3 (CH_{arom}), 101.6 (C-1), 98.1 (C-1'), 79.1 (C-2), 77.1 (C-4'), 76.8 (C-2'), 75.4 (C-3), 75.3 (C-4), 74.3, 73.5 (CH_2 Bn), 73.1 (C-3'), 72.9, 72.8, 71.3 (CH_2 Bn), 69.9 (C-5'), 68.0 (C-6'), 61.7 (C-5), 55.5 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$) δ 101.6 ($J_{H1\text{-}C1}$ = 165 Hz, 1,2-*trans*); Data for the minor stereoisomer (1,2-*cis*): ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC): δ 5.95 (dd, *J* = 10.0, 9.1 Hz, 1H, H-3'), 4.97 (bs, 1H, H-1), 4.16 (t, *J* = 9.3 Hz, 1H, H-4'), 3.41 (s, 3H, CH_3'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 165.3 (C=O Bz), 139.3, 138.4, 130.6 ($C_{q\text{-}arom}$), 97.6 (C-1'), 97.3 (C-1), 73.3, 72.7, 71.1 (CH_2 Bn), 69.5 (C-5'), 68.7 (C-6'), 55.4 (CH_3'); HRMS: $[M+Na]^+$ calcd for $C_{54}H_{56}O_{11}Na$ 903.37029, found 903.37121.



Methyl 4-*O*-(2,3,4-*O*-benzyl-D-ribopyranosyl)-2,3,6-tri-*O*-benzoyl-D-glucopyranoside (S72). The title compound was prepared according to general procedure I. The reaction was quenched after 16 h. Size-exclusion column chromatography (DCM:MeOH 1:1) afforded the title compound (61 mg, 67 µmol, 67%, colorless oil, 1,2-*cis*:1,2-*trans*; 50:50). TLC: R_f 0.35, 0.30 (pentane:EtOAc, 80:20, v:v); IR (thin film, cm^{-1}): 736, 806, 1025, 1267, 1452, 1720, 2923; Data for the 1,2-*trans* stereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, HMBC-Gated): δ 8.12 – 7.02 (m, 30H, CH_{arom}), 5.98 (dd, *J* = 9.7, 9.0 Hz, 1H, H-3'), 5.17 – 5.10 (m, 2H, H-1', H-2'), 4.83 (d, *J* = 7.3 Hz, 1H, H-1), 4.81 – 4.25 (m, 8H, H-6', H-6', CH_2 Bn, CH_2 Bn, CH_2 Bn), 4.15 (dddd, *J* = 18.0, 10.1, 4.8, 2.0 Hz, 1H, H-5'), 4.06 – 3.93 (m, 1H, H-4'), 3.92 (t, *J* = 2.3 Hz, 1H, H-3), 3.44 – 3.35 (m, 4H, H-5, CH_3'), 3.22 – 3.13 (m, 2H, H-2, H-4), 3.01 (dd, *J* = 11.3, 4.4 Hz, 1H, H-5);); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 166.0, 166.0, 165.4 (C=O Bz), 139.0, 138.2, 138.0 ($C_{q\text{-}arom}$), 133.4, 133.3, 133.1, 133.0, 132.7 (CH_{arom}), 130.5 ($C_{q\text{-}arom}$), 130.1, 130.0, 129.8, 129.7 ($C_{q\text{-}arom}$), 129.3, 129.2 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.4, 127.3 ($C_{q\text{-}arom}$), 102.1 (C-1), 96.7 (C-1'), 78.8 (C-2), 78.2 (C-4'), 74.8 (C-4), 74.6 (C-3), 73.9 (CH_2 Bn), 72.6 (CH_2 Bn), 72.1 (C-2'), 71.2 (CH_2 Bn), 68.9 (C-5'), 63.0 (C-6'), 62.0 (C-5), 55.5 (CH_3); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 102.1 ($J_{H1\text{-}C1}$ = 164 Hz, 1,2-*trans*); Data for the 1,2-*cis* stereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$, HH-COSY, HSQC, HMBC, HMBC-Gated): δ 8.12 – 7.02 (m, 30H, CH_{arom}), 6.23 (t, *J* = 9.3 Hz, 1H, H-3'), 5.17 – 5.10 (m, 2H, H-1', H-2'), 5.08 (br s, 1H, H-1), 4.81 – 4.25 (m, 8H, H-6', H-6', CH_2 Bn, CH_2 Bn, CH_2 Bn), 3.44 – 3.35 (m, 3H, CH_3'), 3.22 – 3.13 (m, 1H , H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 166.2, 166.1, 166.0 ($C_{q\text{-}arom}$), 96.8 (C-1' and C-1), 75.3 (C-2), 73.9 (CH_2 Bn), 71.1 (CH_2 Bn), 63.2 (C-6'), 55.3 (CH_3'); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 96.8 ($J_{H1\text{-}C1}$ = 174 Hz, 1,2-*cis*); HRMS: $[M+NH_4]^+$ calcd for $C_{54}H_{52}O_{13}$ 926.37462, found 926.37411.

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