ELSEVIER

Carbohydrate Research 337 (2002) 2089–2110

CARBOHYDRATE RESEARCH

www.elsevier.com/locate/carres

D-Glucose as a multivalent chiral scaffold for combinatorial chemistry

Till Opatz,[a] Christopher Kallus,[a] Tobias Wunberg,[a] Wolfgang Schmidt,[b] Stefan Henke,[b] Horst Kunz[a,*]

[a]*Institut für Organische Chemie, Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany*
[b]*Aventis Pharma Deutschland GmbH, Industriepark Höchst, Frankfurt, Germany*

Received 9 April 2002; accepted 21 May 2002

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

Abstract

Due to their high density of functional groups and their availability in a variety of diastereomeric forms, monosaccharides are considered attractive scaffolds for combinatorial chemistry that allow the attachment and defined spatial alignment of up to five different pharmacophoric groups. For their application in combinatorial syntheses on solid phase, a set of selectively removable hydroxy protecting groups in combination with a cleavable anchor is required. Herein, we report on the construction and use of a versatile multivalent glucose building block for parallel synthesis on the solid phase. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Scaffold; Combinatorial chemistry; Solid phase; Thioglycoside anchor

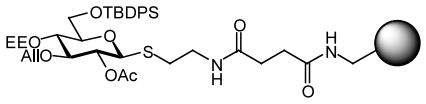
1. Introduction

Some years ago, Hirschmann et al.[1,2] and others[3] have shown that mimetics of biologically active peptides can be constructed using a carbohydrate as a polyfunctional core.

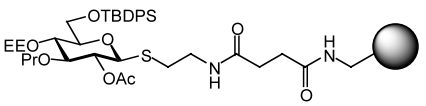
However, no truly combinatorial approach involving a set of selectively removable protecting groups on a solid-phase bound template has been developed so far.[4–6] The requirements for a suitable combination of protecting groups and a cleavable anchor capable of blocking all hydroxy functions of D-glucopyranose and linking the template to a polymeric support are considerable. Besides the general limitations that apply for manipulations on solid support such as homogeneity of the reaction media and sufficient swelling of the polymer beads, none of the conditions for the deprotections (including cleavage of the linker) must affect the functionalities introduced during the course of the combinatorial synthesis. The linker itself has to be inert during all deprotection and derivatization reactions that precede its selective cleavage. Moreover, since Williamson etherifications of deprotected hydroxy functions should be one option of derivatization, all except for one of the protecting groups need to be stable against strong bases.

2. Results and discussion

In initial experiments, a combination of a *tert*-butyldiphenylsilyl (TBDPS) ether, an 1-ethoxyethyl (EE) group, an allyl ether and an acetyl group with a



1

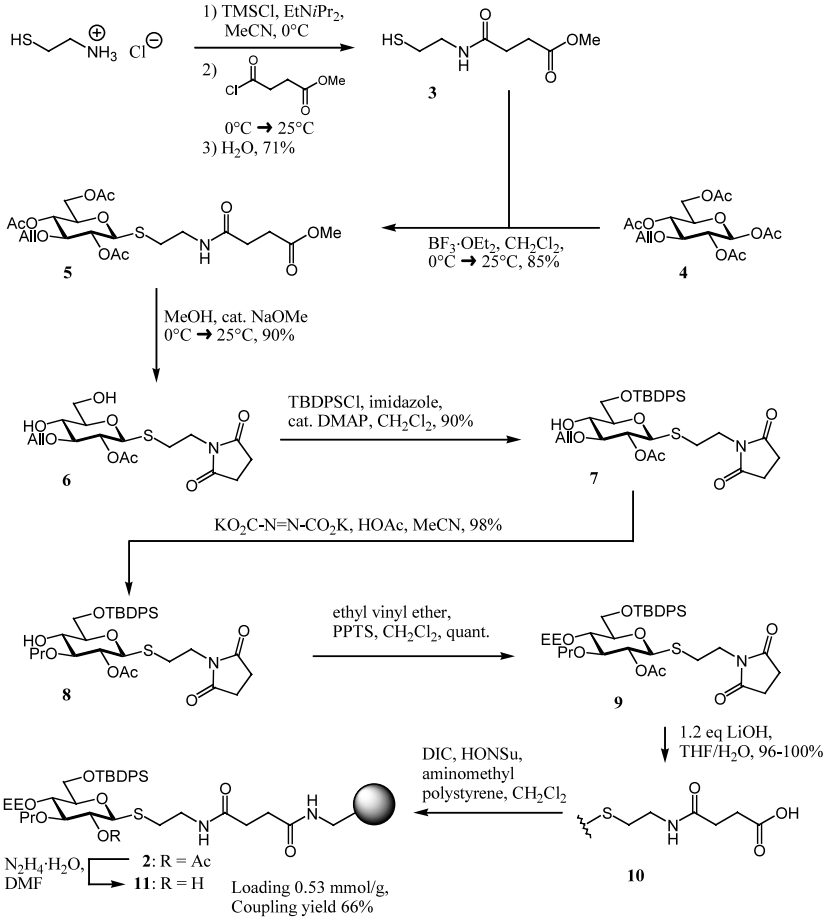


2

Fig. 1. Selectively deprotectable monosaccharide templates.

* Corresponding author. Tel.: +49-6131-3922272; fax: +49-6131-39-24786
E-mail address: hokunz@mail.uni-mainz.de (H. Kunz).

PII: S0008-6215(02)00301-4



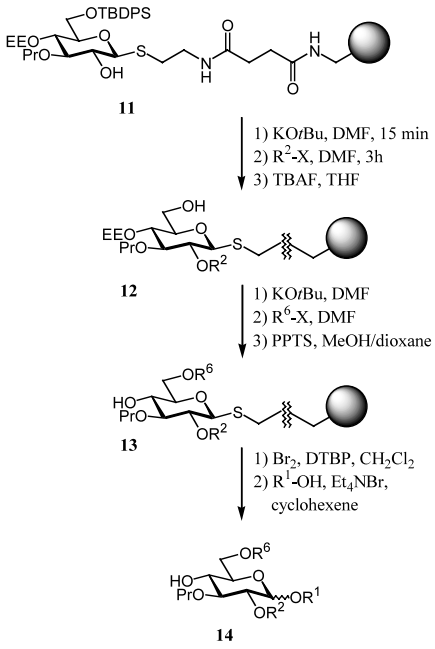
Scheme 1. Preparation of templates **2** and **11**.

thioglycoside anchor, as represented in compound **1** (Fig. 1), was chosen. The thioglycoside anchor serves as a masked protecting group for the anomeric center that can be exchanged for a heteroatom nucleophile such as an alcohol upon activation of the sulfur by an electrophile and subsequent cleavage of the C-1–S bond.[7]

In a first approach, evaluation and optimization of selective derivatizations were performed on the propyl-substituted template **2**. This hydrogenated analog of scaffold **1** was used, since the allyl protecting group turned out to be susceptible to side reactions during activation of the thioglycoside anchor.[8]

In the meantime, the feasibility of the inclusion of all five hydroxy functions of a monosaccharide has been demonstrated for a galactose scaffold.[9] The tetravalent template **2**, bound to solid phase, was obtained from thioglucoside **9**, the synthesis of which starts from 1,2,4,6-tetra-*O*-acetyl-3-*O*-allyl-β-D-glucopyranose **4** (Scheme 1).[10] Compound **9** is accessible in five steps from **4** as follows (Scheme 2): Lewis acid-promoted glycosylation with thiol **3**, obtained by reaction of cysteamine hydrochloride with succinic acid monomethylester chloride,[11] furnished thioglycoside **5** in 85% yield. Zemplén deacetylation under controlled conditions left the acetyl group in the 2-position intact but surprisingly led to formation of the succinimide.[12] Diol **6** was obtained in a yield of 90%. Introduction of the TBDPS-group yielded **7**, which, after chromatographic purification, was subjected to reduction of the double bond with diimine.[13] The product **8** thus obtained was reacted with ethyl vinyl ether in the presence of a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) to form the fully protected template **9**. Basic hydrolysis of the succinimide and coupling of the resulting carboxylic acid **10** to aminomethylated polystyrene using *N*,*N*′-diisopropylcarbodiimide and *N*-hydroxysuccinimide[14] or 1-hydroxybenzotriazole[15] furnished the solid-phase bound scaffold **2**.† Finally, deacetylation with hydrazine hydrate furnished scaffold **11**, the deblocked hydroxy function of which is ready for derivatization.

† Experiments revealed that substitution of the polystyrene resin by more polar support such as Tentagel™ is not beneficial and leads to lower yields and increased amounts of side products. We reasoned that traces of water, which cannot be completely removed from the hygroscopic polar resins by drying in vacuo, might cause these problems.



Scheme 2. Combinatorial alkylation of O-2 and O-6. Preparation of library **14**.

In order to probe the synthetic potential of scaffold **11**, the parallel synthesis of a small library of bisalkylated products by stepwise Williamson etherification of the 2- and the 6-position was carried out as follows (Scheme 2): the 2-hydroxy function of template **11** was deprotonated by potassium *tert*-butoxide in DMF. Subsequent reaction with *n*-iodoheptane, benzyl bromide, 4-bromobenzyl bromide or 2-cyanobenzyl bromide introduced the first side chain at O-2. After removal of the TBDPS group by tetrabutylammonium fluoride, the OH group in the 6-position was alkylated likewise using iodomethane, *n*-iodopropane, benzyl bromide, 4-bromobenzyl bromide and 2-(bromomethyl)naphthalene. The 1-ethoxyethyl (EE) group was removed from all resin samples by transacetalization using a solution of pyridinium *p*-toluenesulfonate (PPTS) in a mixture of methanol and dioxane. Upon addition of bromine in dichloromethane, the thioglycoside anchor was cleaved, and final substitution at the anomeric center was achieved in a Lemieux glycosylation, i.e., by addition of an alcohol, 2,6-di-*tert*-butylpyridine (DTBP), cyclohexene (to trap excess bromine) and tetraethylammonium bromide in dichloromethane.[16]

After concentration of the crude cleavage solutions in vacuo, a simple solid-phase extraction step using small polyethylene cartridges filled with silica gel was carried out in order to separate the desired products from the nonpolar (dibromocyclohexane, DTBP) and the polar (tetraalkylammonium salt, DTBP-hydrobromide) components.

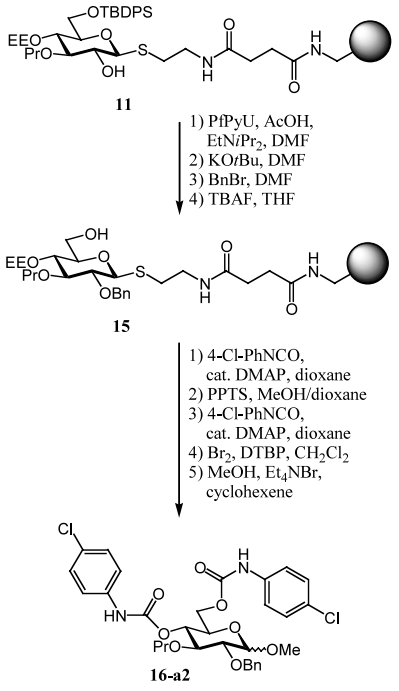
Analysis of the products by HPLC, TLC and mass spectrometry revealed that only 18 of the 30 expected products were formed; yields and purities of the corresponding samples are given in Table 1.

To our surprise, the attempted alkylation of the 6-position with the two primary alkyl halides failed, whereas the etherification of the 2-position with iodoheptane proceeded smoothly. A more detailed investigation of this unexpected outcome of substitution

Table 1
2,6-Di-*O*-alkylglucosides (library **14**)

	R^1	R^2	R^6	Crude yield (%)	HPLC-purity[a]
14-a1	Et	Bn	Bn	74	53.3% (α), 9.3% (β)
14-a2	Et	Bn	4-Br-Bn	67	51.9% (α), 6.9% (β)
14-a3	Et	Bn	2-Naph-CH_2	62	50.4% (α), 11.4% (β)
14-b1	Me	2-CN-Bn	Bn	73	33.0% (α), 12.4% (β)
14-b2	Me	2-CN-Bn	4-Br-Bn	70	32.0% (α), 9.0% (β)
14-b3	Me	2-CN-Bn	2-Naph-CH_2	69	29.7% (α), 8.0% (β)
14-c1	Me	*n*-Hep	Bn	95	39.3% (α), 13.8% (β)
14-c2	Me	*n*-Hep	4-Br-Bn	90	43.7% (α), 13.0% (β)
14-c3	Me	*n*-Hep	2-Naph-CH_2	91	37.1% (α), 14.4% (β)
14-d1	Me	Bn	Bn	89	48.1% (α), 13.4% (β)
14-d2	Me	Bn	4-Br-Bn	69	50.0% (α), 12.6% (β)
14-d3	Me	Bn	2-Naph-CH_2	76	43.2% (α), 15.1% (β)
14-e1	Me	4-Br-Bn	Bn	70	32.3% (α), 9.7% (β)
14-e2	Me	4-Br-Bn	4-Br-Bn	67	39.1% (α), 9.6% (β)
14-e3	Me	4-Br-Bn	2-Naph-CH_2	69	32.2% (α), 10.2% (β)
14-f1	Et	*n*-Hep	Bn	76	38.7% (α)
14-f2	Et	*n*-Hep	4-Br-Bn	68	50.6% (α)
14-f3	Et	*n*-Hep	2-Naph-CH_2	69	44.7% (α), 9.3% (β)

[a] UV-detection at 220 nm.



Scheme 3. Preparation of compound **16-a2**.

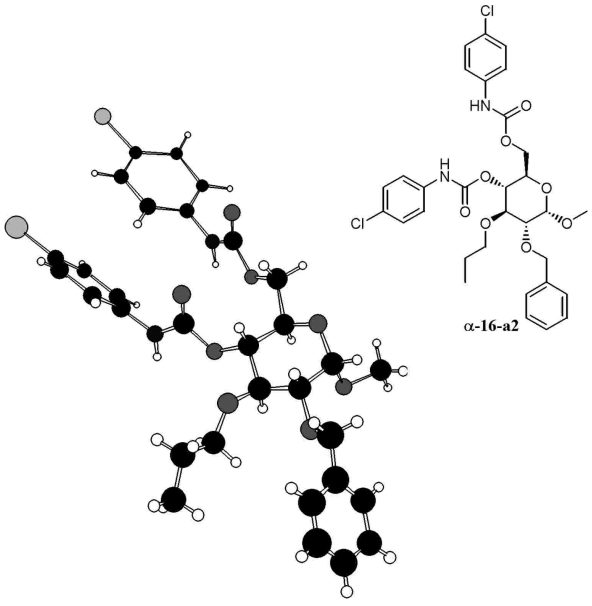


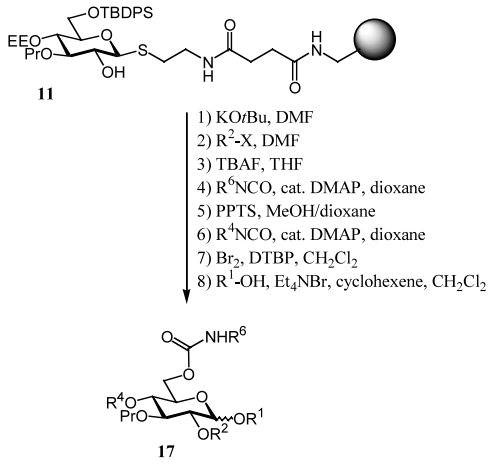
Fig. 2. Crystal structure of **α-16-a2**.

reactions at the glucose scaffold showed that not only the 6- but also the 4-position exhibits an unexpectedly low reactivity. We concluded that free amino groups remaining after loading of the polymer may cause the observed ambiguities. Their alkylation up to quaternization during the first alkylation step introduces positive charges to the backbone of the polymer that could interfere with the subsequent etherification reactions. As a consequence, a capping step was performed, by which all remaining amino groups were acetylated. Parallel synthesis on scaffold **11** linked to this modified polymer led to significantly improved yields in alkylations at the remaining positions. Nevertheless, the Williamson procedure appeared to be efficient only for unbranched primary alkyl iodides or benzylic bromides. In order to improve both purity and diversity of the products, other derivatization reactions such as carbamoylations and esterifications were studied on model compounds linked to the solid phase. Especially reactions with aryl or alkyl isocyanates turned out to be useful (Scheme 3).

In preparations of smaller libraries of products carrying two carbamoyl substituents in the 4- and the 6-position, several crystalline derivatives were obtained. The bis-*O*-(4-chlorophenylcarbamoyl)-glucoside **16-a2** gave crystals suitable for X-ray analysis. See Fig. 2 for the corresponding crystal structure that proves the α configuration of the major anomer and confirms the NMR data.

In order to explore the scope and limitations of the sequential introduction of two arylcarbamoyl substituents, a 60-member library of glucosides was synthesized using the alkylation of the 2-position (*n*-iodobutane, 2-methylbenzyl bromide or 4-fluorobenzyl bromide), followed by carbamoylation of both the 6- and the 4-position with different isocyanates (2,4-difluorophenyl isocyanate, *n*-propyl isocyanate, 3-cyanophenyl isocyanate, (*S*)-phenylethyl isocyanate or 4-methyl-3-nitrophenyl isocyanate for addition to O-6, 4-fluorophenyl isocyanate, 4-(trifluoromethyl)phenyl isocyanate, 4-chlorophenyl isocyanate or no reagent for dervatization of O-4; see also Scheme 4).

The solid-phase bound products that were obtained were converted to *O*-glycosides by reaction of the thioglycoside anchor with bromine, and subsequent reaction of the intermediate glucosyl bromide with *n*-butanol or isobutanol. The results are summarized in Table 2.



Scheme 4. Combinatorial synthesis of carbamoylglucosides (library **17**).

Table 2
Carbamoylglucosides (library **17**)

	R^1	R^2	R^4	R^6	Crude yield (%)	HPLC-purity[a]
17-1a1	*n*-Bu	*n*-Bu	H	2,4-F_2-Ph	61	76.4% (α), 9.2% (β)
17-2a1	*n*-Bu	*n*-Bu	H	*n*-Pr	47	–[b]
17-3a1	*n*-Bu	*n*-Bu	H	3-CN-Ph	46	66.2% (α), 17.2% (β)
17-4a1	*n*-Bu	*n*-Bu	H	(*S*)-1-Ph-Et	43[c]	25.5% (α)
17-5a1	*n*-Bu	*n*-Bu	H	4-Me-3-NO_2-Ph	45	66.4% (α), 13.4% (β)
17-1a2	*n*-Bu	4-F-Bn	H	2,4-F_2-Ph	59	70.5% (α), 5.4% (β)
17-2a2	*n*-Bu	4-F-Bn	H	*n*-Pr	43	66.9% (α), 13.3% (β)
17-3a2	*n*-Bu	4-F-Bn	H	3-CN-Ph	71	66.5% (α), 15.0% (β)
17-4a2	*n*-Bu	4-F-Bn	H	(*S*)-1-Ph-Et	53[c]	26.7% (α), 3.7% (β)
17-5a2	*n*-Bu	4-F-Bn	H	4-Me-3-NO_2-Ph	66	70.3% (α)
17-1a3	*n*-Bu	2-Me-Bn	H	2,4-F_2-Ph	87	57.7% (α), 4.0% (β)
17-2a3	*n*-Bu	2-Me-Bn	H	*n*-Pr	82	68.0% (α), 9.7% (β)
17-3a3	*n*-Bu	2-Me-Bn	H	3-CN-Ph	67	69.2% (α), 14.7% (β)
17-4a3	*n*-Bu	2-Me-Bn	H	(*S*)-1-Ph-Et	73[c]	50.1% (α), 7.8% (β)
17-5a3	*n*-Bu	2-Me-Bn	H	4-Me-3-NO_2-Ph	56	66.4% (α), 14.0% (β)
17-1b1	*n*-Bu	*n*-Bu	4-F-PhNHCO	2,4-F_2-Ph	61	73.7% (α), 5.0% (β)
17-2b1	*n*-Bu	*n*-Bu	4-F-PhNHCO	*n*-Pr	38	77.0% (α), 9.2% (β)
17-3b1	*n*-Bu	*n*-Bu	4-F-PhNHCO	3-CN-Ph	33	70.3% (α), 12.3% (β)
17-4b1	*n*-Bu	*n*-Bu	4-F-PhNHCO	(*S*)-1-Ph-Et	32[c]	34.5% (α), 9.5% (β)
17-5b1	*n*-Bu	*n*-Bu	4-F-PhNHCO	4-Me-3-NO_2-Ph	55	73.7% (α), 11.1% (β)
17-1b2	*n*-Bu	4-F-Bn	4-F-PhNHCO	2,4-F_2-Ph	56	78.2% (α), 5.4% (β)
17-2b2	*n*-Bu	4-F-Bn	4-F-PhNHCO	*n*-Pr	49	61.9% (α), 7.2% (β)
17-3b2	*n*-Bu	4-F-Bn	4-F-PhNHCO	3-CN-Ph	55	78.0% (α), 13.8% (β)
17-4b2	*n*-Bu	4-F-Bn	4-F-PhNHCO	(*S*)-1-Ph-Et	66[c]	34.5% (α), 3.7% (β)
17-5b2	*n*-Bu	4-F-Bn	4-F-PhNHCO	4-Me-3-NO_2-Ph	52	76.5% (α), 6.3% (β)
17-1b3	*n*-Bu	2-Me-Bn	4-F-PhNHCO	2,4-F_2-Ph	80	68.7% (α), 4.1% (β)
17-2b3	*n*-Bu	2-Me-Bn	4-F-PhNHCO	*n*-Pr	62	64.2% (α), 9.3% (β)
17-3b3	*n*-Bu	2-Me-Bn	4-F-PhNHCO	3-CN-Ph	58	80.6% (α), 13.6% (β)
17-4b3	*n*-Bu	2-Me-Bn	4-F-PhNHCO	(*S*)-1-Ph-Et	68[c]	53.1% (α), 6.6% (β)
17-5b3	*n*-Bu	2-Me-Bn	4-F-PhNHCO	4-Me-3-NO_2-Ph	71	70.2% (α), 10.1% (β)
17-1c1	*i*-Bu	*n*-Bu	4-CF_3-PhNHCO	2,4-F_2-Ph	66	71.3% (α), 3.7% (β)
17-2c1	*i*-Bu	*n*-Bu	4-CF_3-PhNHCO	*n*-Pr	31	73.2% (α), 7.3% (β)
17-3c1	*i*-Bu	*n*-Bu	4-CF_3-PhNHCO	3-CN-Ph	63	75.9% (α), 10.0% (β)
17-4c1	*i*-Bu	*n*-Bu	4-CF_3-PhNHCO	(*S*)-1-Ph-Et	37[c]	38.7% (α), 6.7% (β)
17-5c1	*i*-Bu	*n*-Bu	4-CF_3-PhNHCO	4-Me-3-NO_2-Ph	57	69.9% (α), 9.0% (β)
17-1c2	*i*-Bu	4-F-Bn	4-CF_3-PhNHCO	2,4-F_2-Ph	56	77.4% (α), 4.5% (β)
17-2c2	*i*-Bu	4-F-Bn	4-CF_3-PhNHCO	*n*-Pr	56	51.5% (α), 7.0% (β)
17-3c2	*i*-Bu	4-F-Bn	4-CF_3-PhNHCO	3-CN-Ph	62	77.3% (α), 10.2% (β)
17-4c2	*i*-Bu	4-F-Bn	4-CF_3-PhNHCO	(*S*)-1-Ph-Et	63[c]	34.8% (α), 4.4% (β)
17-5c2	*i*-Bu	4-F-Bn	4-CF_3-PhNHCO	4-Me-3-NO_2-Ph	52	77.3% (α), 9.1% (β)
17-1c3	*i*-Bu	2-Me-Bn	4-CF_3-PhNHCO	2,4-F_2-Ph	85	73.2% (α), 5.4% (β)
17-2c3	*i*-Bu	2-Me-Bn	4-CF_3-PhNHCO	*n*-Pr	69	76.4% (α), 7.1% (β)
17-3c3	*i*-Bu	2-Me-Bn	4-CF_3-PhNHCO	3-CN-Ph	66	74.6% (α), 10.3% (β)
17-4c3	*i*-Bu	2-Me-Bn	4-CF_3-PhNHCO	(*S*)-1-Ph-Et	71[c]	59.9% (α), 7.5% (β)
17-5c3	*i*-Bu	2-Me-Bn	4-CF_3-PhNHCO	4-Me-3-NO_2-Ph	61	76.0% (α), 7.9% (β)
17-1d1	*i*-Bu	*n*-Bu	4-Cl-PhNHCO	2,4-F_2-Ph	61	75.5% (α), 4.7% (β)
17-2d1	*i*-Bu	*n*-Bu	4-Cl-PhNHCO	*n*-Pr	41	70.6% (α), 9.7% (β)
17-3d1	*i*-Bu	*n*-Bu	4-Cl-PhNHCO	3-CN-Ph	58	70.2% (α), 10.8% (β)
17-4d1	*i*-Bu	*n*-Bu	4-Cl-PhNHCO	(*S*)-1-Ph-Et	37[c]	37.4% (α), 10.8% (β)
17-5d1	*i*-Bu	*n*-Bu	4-Cl-PhNHCO	4-Me-3-NO_2-Ph	56	71.0% (α), 13.4% (β)
17-1d2	*i*-Bu	4-F-Bn	4-Cl-PhNHCO	2,4-F_2-Ph	63	75.5% (α), 4.3% (β)
17-2d2	*i*-Bu	4-F-Bn	4-Cl-PhNHCO	*n*-Pr	64	61.4% (α), 6.8% (β)
17-3d2	*i*-Bu	4-F-Bn	4-Cl-PhNHCO	3-CN-Ph	57	73.5% (α), 11.7% (β)
17-4d2	*i*-Bu	4-F-Bn	4-Cl-PhNHCO	(*S*)-1-Ph-Et	61[c]	37.8% (α), 5.0% (β)
17-5d2	*i*-Bu	4-F-Bn	4-Cl-PhNHCO	4-Me-3-NO_2-Ph	56	73.8% (α), 11.2% (β)
17-1d3	*i*-Bu	2-Me-Bn	4-Cl-PhNHCO	2,4-F_2-Ph	82	66.3% (α), 3.8% (β)

Table 2 (*Continued*)

	R^1	R^2	R^4	R^6	Crude yield (%)	HPLC-purity[a]
17-2d3	*i*-Bu	2-Me-Bn	4-Cl-PhNHCO	*n*-Pr	59	69.8% (α), 9.0% (β)
17-3d3	*i*-Bu	2-Me-Bn	4-Cl-PhNHCO	3-CN-Ph	70	80.9% (α), 12.1% (β)
17-4d3	*i*-Bu	2-Me-Bn	4-Cl-PhNHCO	(*S*)-1-Ph-Et	67[c]	58.7% (α), 8.7% (β)
17-5d3	*i*-Bu	2-Me-Bn	4-Cl-PhNHCO	4-Me-3-NO_2-Ph	62	69.7% (α), 14.0% (β)

[a] UV-detection at 205–208 nm.
[b] UV-absorption too low.
[c] Contains larger amounts of the 6-allophanate.

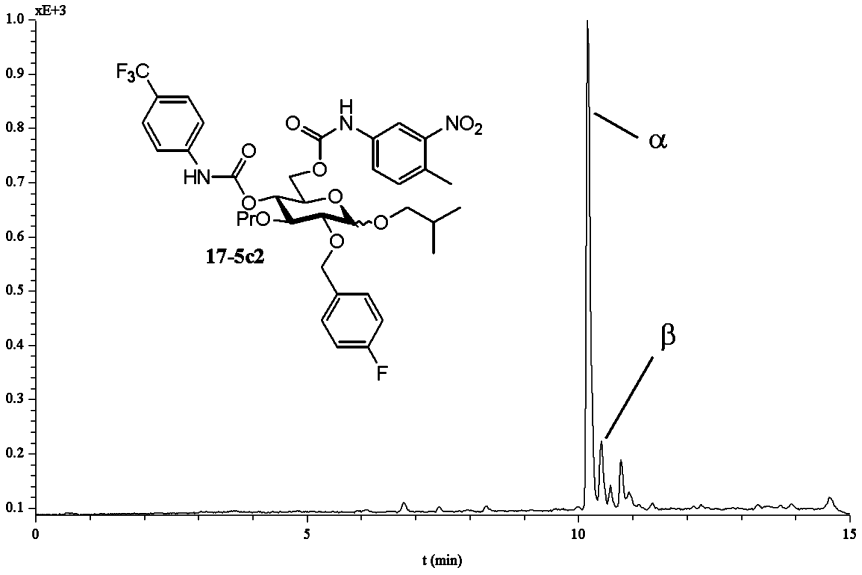


Fig. 3. RP-HPLC chromatogram of compound **17-5c2** (UV, 205–208 nm).

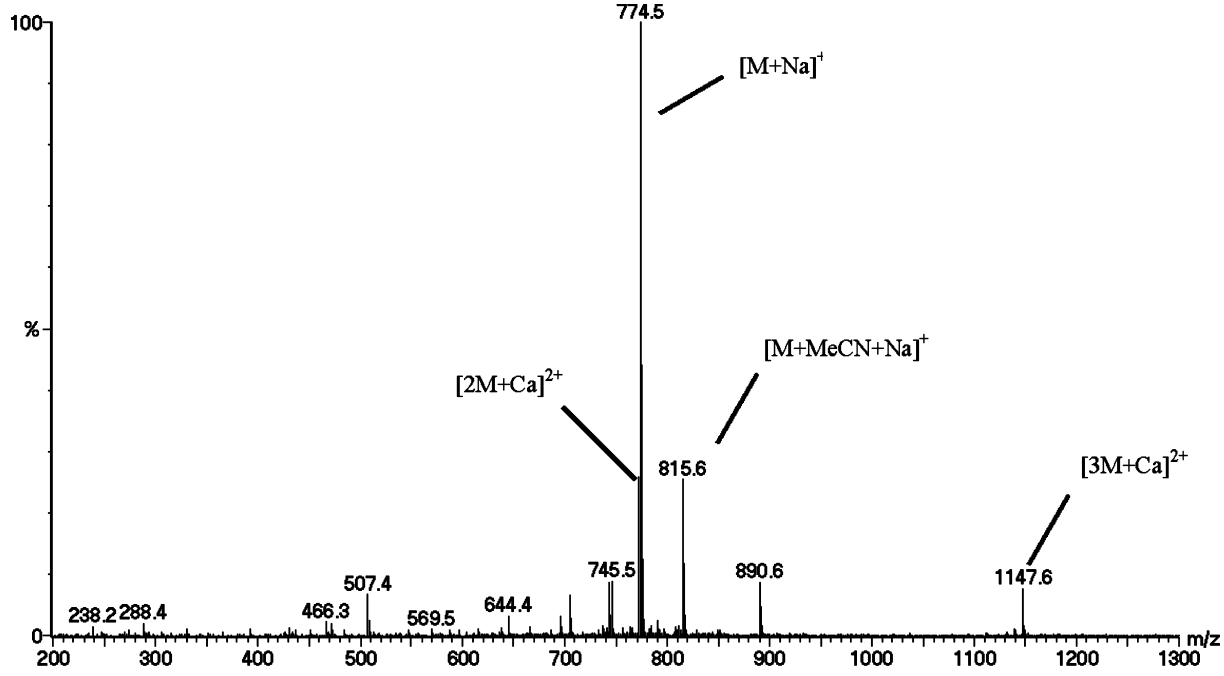


Fig. 4. ESIMS of compound **17-5c2** (crude product).

The majority of the products obtained were of high purity. Only in the case of the reactions of O-6 with (*S*)-phenylethyl isocyanate, considerable amounts of an undesired side product were formed: HPLC–MS analysis revealed that, unexpectedly, allophanates had been formed in this case, possibly by reaction of the dimeric isocyanate.[17]

Despite the presence of the corresponding β anomers as minor components (anomeric ratios ranging between 4:1 for the 6-*O*-(3-cyanophenylcarbamoyl)- and up to 18:1 for the 6-*O*-(2,4-difluorophenylcarbamoyl) derivatives), a number of the substances crystallized after the solid-phase extraction procedure. The ^{1}H NMR spectrum of compound **17-5c2** (crude product) depicted in Fig. 5, as well as the HPLC trace shown in Fig. 3 and the ESIMS spectrum shown in Fig. 4, are exemplary examples that illustrate the purity of these products formed in six synthetic steps on solid support and the in situ-glycosylation reaction.

When the ESIMS spectra of all 60 library members were examined, a signal with an m/z-value of about three units lower than the one of the ubiquitous $[M + Na]^+$ complex of the corresponding sample was observed in most cases. Since it showed no regular isotope pattern, this signal was attributed to contaminants in the samples. However, a closer look not only revealed the ubiquity of the 'M + 20' peak but also showed the strong dependence of its intensity on the structure of the compound. A continuum spectrum (recorded without data reduction) revealed that the isotope pattern of all of these signals was not absent but compressed by a factor of 2 with respect to the pattern of signals from singly charged ions. Based upon these findings, the unknown signals could be attributed to the complexes of two molecules of the corresponding glucoside with one calcium ion ($[2M + Ca]^{2+}$). Fig. 6 shows the intensity of the $[2M + Ca]^{2+}$ signal relative to the $[M + Na]^+$ peak for all 60 compounds measured under nearly identical conditions.

As shown in Fig. 6, the compounds containing an *n*-butyl substituent in the 2-position in combination with a *p*-(trifluoromethyl)phenylcarbamoyl group in the 4-position show the highest affinity to calcium. At present, however, no explanation of this effect can be given. It should be noted that changes in the substitution at positions 2, 4 as well as 6 can have a strong influence on the magnitude of the effect.

The anomers of the *O*-glycosides produced in the Lemieux glycosylation exhibit a different retention behaviour in RP-HPLC. The β anomers are less mobile in all cases. When HPLC–MS spectra of some of the crude products that were obtained were recorded, marked differences could be found in the tendency of sodium complexes of the anomers to additionally coordinate (i.e., the major constituent of the eluent). In the case of compound **17-5a3**, the spectra obtained from the α anomer showed only the $[M + Na]^+$ complex, whereas the β anomer also forms the ternary complex $[M + MeCN + Na]^+$ (see Fig. 7).

The complexation of calcium ions under the conditions of mass spectrometry may not correlate with any biological effect exerted by the compounds in vitro or in vivo. However, the remarkable differences found within a combinatorial library of alkylated glucosyl carbamates clearly show that subtle structural changes in the periphery of such molecules can determine its affinity to other components. Thus, the combinatorial synthesis of series of multiply substituted scaffold molecules is well suited for selection of candidates exhibiting binding to desired target structures.

In conclusion, the combinatorial derivatization of a selectively deprotectable glucose scaffold on solid support provides access to structurally diverse *O*-alkylated and *O*-carbamoylated glucosides of high purity in good yield. All procedures require only readily available chemicals. Moreover, since all deprotection and derivatization reactions can be run at ambient temperature, the elaborated protocols are amenable for automation. In addition, other thiophilic activation reagents for the thioglycoside anchor (such as DMTST) can also be applied, provided a suitable parallel workup procedure has been developed. The allyl moiety, which is stable under the conditions of all manipulations at O-2, O-4 and O-6, can also be included in this concept, allowing the synthesis of glucose derivatives with five dimensions of diversity, if a novel selective Pd(0)-catalyzed cleavage of allyl ethers on solid phase is utilized.[18] Results of this extended strategy will be reported in due course.

3. Experimental

Materials and methods.—Analytical TLC was performed on aluminium-backed TLC plates coated with Silica Gel 60 F_{254} (E. Merck). Column chromatography was performed on silica gel (63–200 μm, Baker or 40–63 μm, E. Merck). Aminomethylated polystyrene was purchased from Rapp Polymere. Solid-phase extraction cartridges and 13-mm polyethylene frits for standard 5-mL polyethylene syringes were purchased from Isolute. Melting points were measured on a Dr. Tottoli apparatus and are uncorrected. Optical rotations were measured at 22 °C on a Perkin–Elmer 241 polarimeter. NMR spectra were recorded on a Bruker AC-200 or a Bruker ARX-400 spectrometer; chemical shifts are expressed in ppm downfield from tetramethylsilane. FABMS spectra were measured between m/z 200 and 1300 on a ZAB-2Seq-VG (Vacuum Generators) in 3-nitrobenzyl alcohol (NBA) after addition of LiCl. ESIMS spectra were measured on a Navigator (ThermoQuest) between m/z 200 and 1300 at a cone voltage of 70V using 7:3 CH_3CN–water at a flow rate

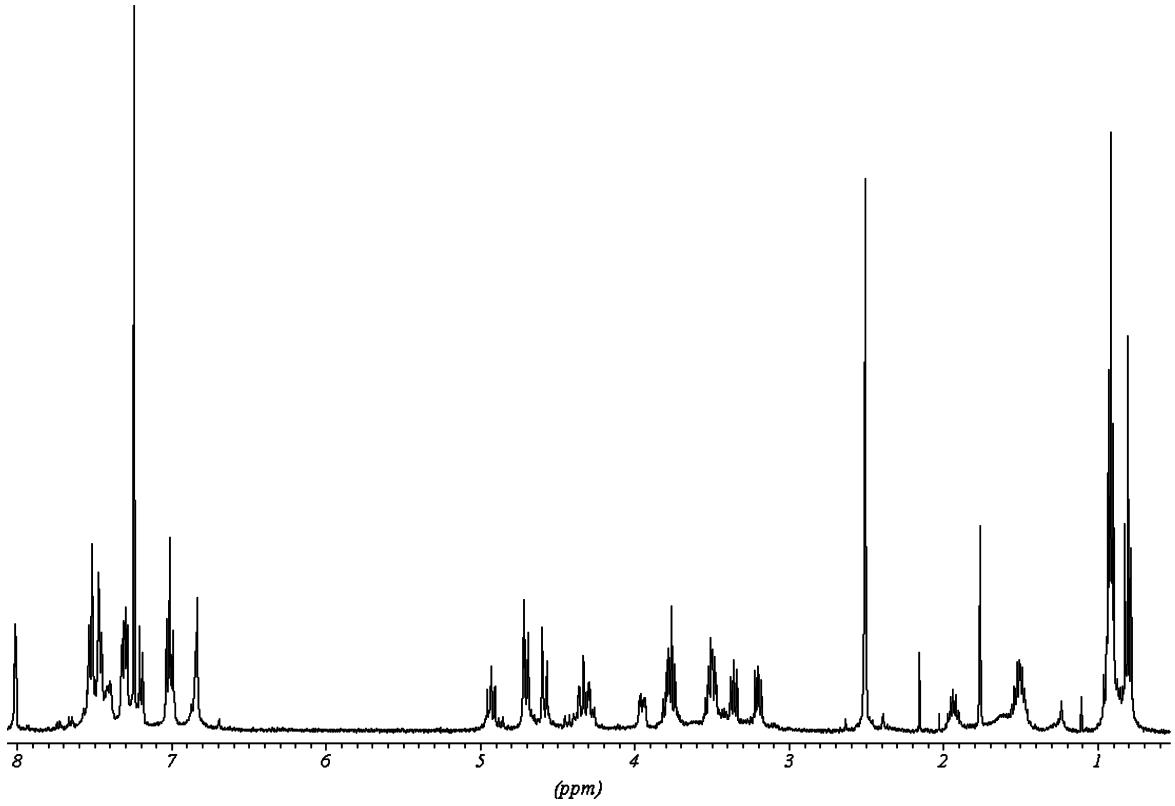


Fig. 5. ^{1}H NMR spectrum of compound **17-5c2** (crude product).

of 0.75 mL/min and a nitrogen flow of 300 L/h unless stated otherwise. A Basic–Marathon autosampler was employed for sample injection (20 μL at 0.1 g/L). HPLC analyses were performed on a Beckmann apparatus (System Gold) equipped with a Nucleosil 300-5 C_{18} column (250 × 4 mm) using the following gradient (t, %MeCN): 0 min, 50%; 2 min, 50%; 20 min, 99%; 24 min, 99%; 26 min, 50%; 30 min, 50% (column A, gradient A; both eluents contained 0.1% trifluoroacetic acid). Alternatively, a Knauer system with a Luna C_{18}-2 column (Phenomenex, 75 × 4.6 mm, 3 μm particle size) and the following gradient was used (t, %MeCN): 0 min, 50%; 0.75 min, 50%; 10 min, 99%; 12.5 min, 99%; 13.5 min, 50%; 15 min, 50% (column B, gradient B). Both HPLC systems were equipped with an autosampler, an online degasser, a column oven (25 °C) and a diode array UV-detector. The Beckmann detector was operated at 220 nm, whereas the Knauer system was operated at 205–208 nm. For analytical HPLC, the flow rate was 1 mL/min, the sample concentration amounted to 1 g/L, and the injection volumes were 30 μL for the Beckmann and 20 μL for the Kanuer system. HPLC–MS analyses were performed on the Navigator instrument using the Knauer HPLC in combination with a flow splitter (ratio 10:1) and a sample concentration of 0.1 g/L. The notation of the ions detected in mass spectra uses the numbering of the glucose skeleton. All substituents denoted are attached to the oxygen atoms at the indicated positions with the sole exception of substituents at the anomeric center. All signals showed isotope patterns consistent with the composition of the indicated ion species and the corresponding charge state.

Succinic acid methyl ester monocysteamide (**3**).—To a stirred suspension of cysteamine hydrochloride (11.0 g, 96.8 mmol) in dry CH_3CN (75 mL), *N*-ethyldiisopropylamine (60 mL, 345 mmol) was slowly added at 0 °C under Ar. After stirring for 5 min, Me_3SiCl (16.4 mL, 130 mmol) was added in one portion. Stirring was continued for 10 min at 0 °C, and a solution of succinic acid monomethylester chloride (11.93 mL, 96.8 mmol) in dry CH_3CN (20 mL) was added slowly. After complete addition, the mixture was stirred for 30 min at 0 °C and 2 h at room temperature. The solution was poured into a mixture of ice and water (200 mL) and extracted with EtOAc (2 × 200 mL). The combined organic layers were washed with 1N HCl, satd aq $NaHCO_3$ and brine. After drying over $MgSO_4$, concentration in vacuo gave 13.1 g (71%) of **3** as a yellowish oil: R_f 0.54 (EtOAc); ^{1}H NMR (90 MHz, $CDCl_3$): δ 3.62 (s, 3H, OMe), 3.37 (Ψq, 2H, J_{gem} 6.3 Hz, NCH_2), 2.80–2.17 (m, 6H, SCH_2, 2 × CH_2CO). Anal. Calcd for $C_7H_{13}NO_3S$: C, 43.96; H, 6.85; N, 7.32; S, 16.76. Found: C, 43.97; H, 6.78; N, 7.65; S, 16.16.

Methyl N-*[2-(2,4,6-tri*-O-*acetyl-3*-O-*allyl-β*-D-*gluco-pyranosylsulfanyl)ethyl]succinamate* (**5**).—To a stirred

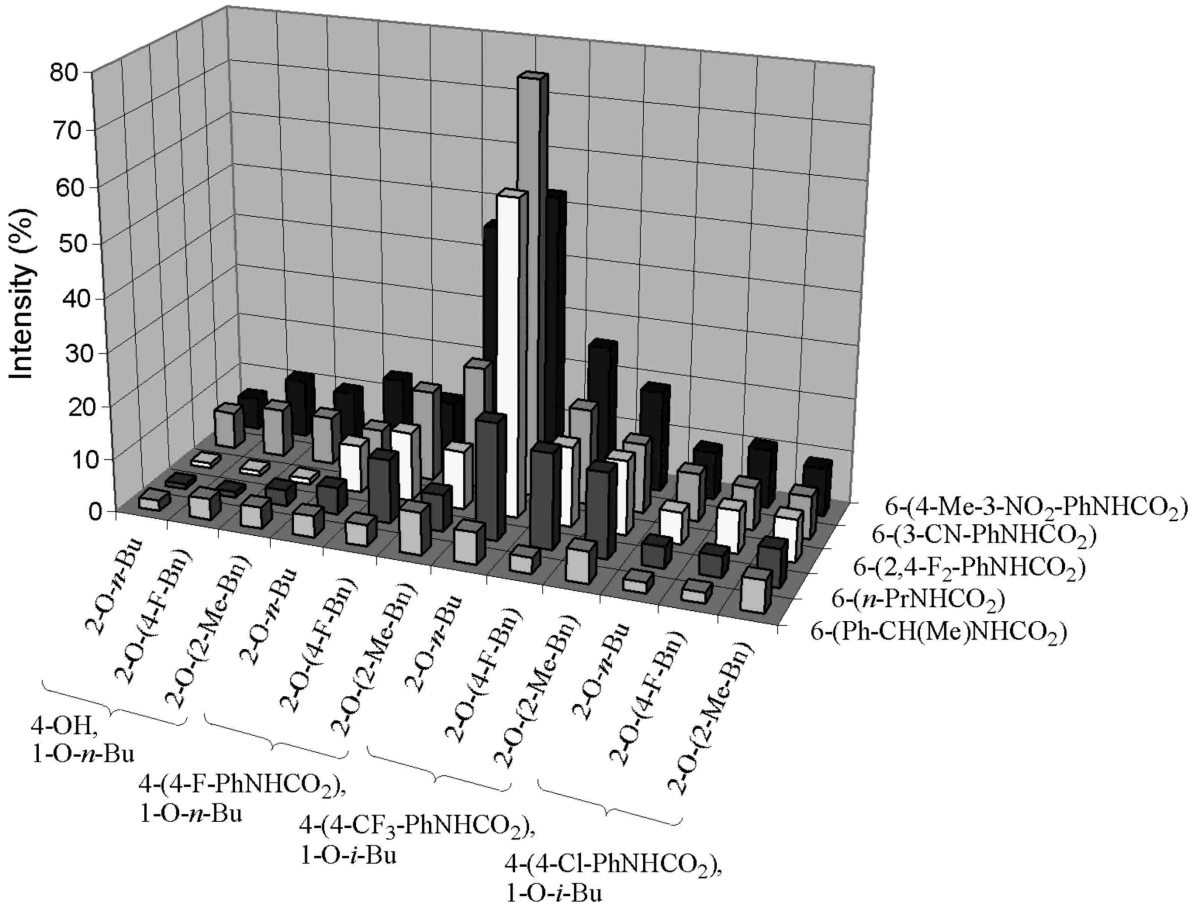


Fig. 6. Intensities of the $[2M + Ca]^{2+}$ signals relative to the $[M + Na]^{+}$ signals in the ESIMS spectra of the members of library **17**.

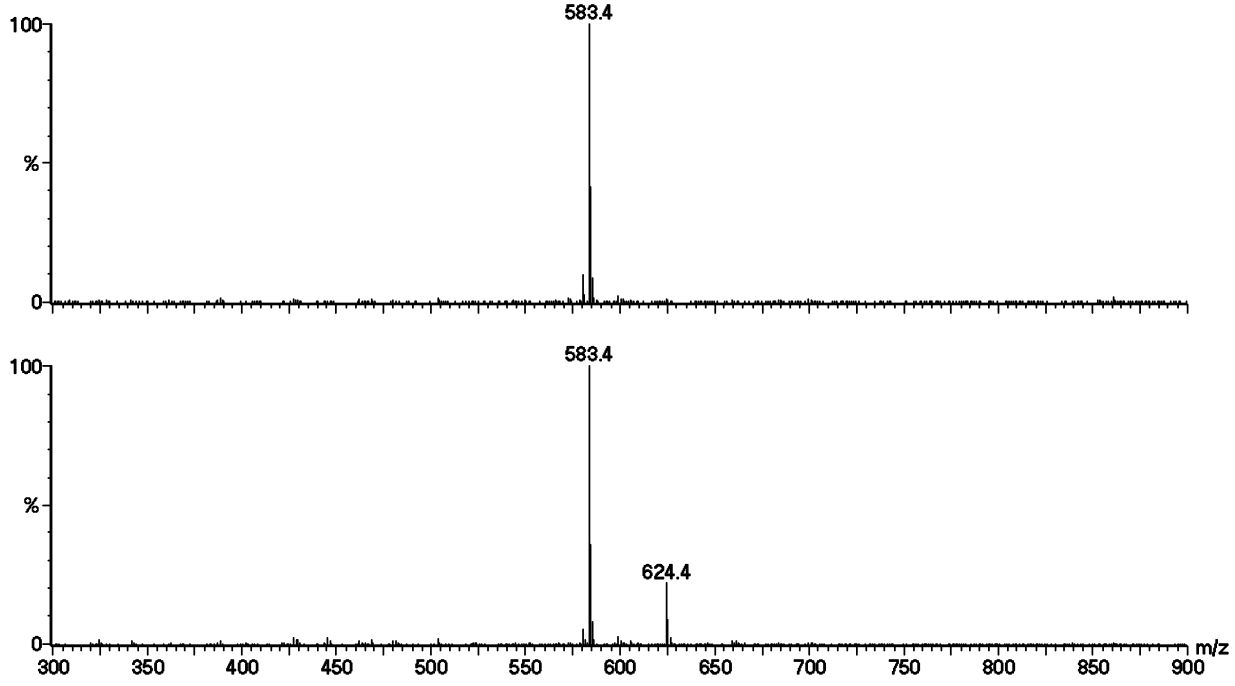


Fig. 7. ESIMS spectra of the α anomer (upper trace) and the β anomer (lower trace) of compound **17-5a3**.

solution of 1,2,4,6-tetra-*O*-acetyl-3-*O*-allyl-β-D-glucopyranoside (6.0 g, 15.5 mmol) and **5** (3.32 g, 18.5 mmol) in dry CH_2Cl_2 (120 mL), a solution of $BF_3{\cdot}OEt_2$ (17.5 mL, 139 mmol) in 20 mL dry CH_2Cl_2 was added dropwise at 0 °C under an Ar atmosphere. After complete addition, the ice bath was removed, and stirring was continued for 6 h while the solution was allowed to warm up to room temperature. The mixture was washed with satd aq $NaHCO_3$ (2 ×), and the organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: 60:30:1 hexanes–EtOAc–HOAc) to yield 6.80 g (85%) **5** as a colorless amorphous solid: R_f 0.44 (EtOAc); mp 75–77 °C. $[\alpha]_D$ −5.3° (*c* 1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.33 (t, br, 1H, *J* 5.1 Hz, NH), 5.80–5.61 (m, 1H, CH_2CH-), 5.18–4.87 (m, 4H, CH_2CH-, H-2′, H-4′), 4.38 (d, 1H, *J* 9.8 Hz, H-1′), 4.11–4.00 (m, 4H, H-6′a + b, allyl-OCH_2), 3.62 (s, 3H, OMe), 3.59–3.41 (m, 3H, H-3′, H-4′, H-5′), 3.38–3.24 (m, 2H, CH_2N), 2.89–2.51 (m, 4H, SCH_2, CH_2CO_2Me), 2.43 (t, 2H, *J* 6.4 Hz, CH_2CONH), 2.05, 2.02, 2.01 (3s, 9H, OAc). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 173.3, 171.6 ($COCH_2$), 170.7, 169.4, 169.3 ($COCH_3$), 134.1 (CH_2CH-), 117.0 (CH_2CH-), 83.9, 81.0, 76.2, 73.3, 71.1, 69.4 (C-1′–C-5′, allyl-OCH_2), 62.3 (C-6′), 51.8 (OMe), 39.3 (NCH_2), 30.7, 30.4 (CH_2CO), 29.2 (SCH_2), 21.0, 20.8, 20.7 (Ac). Anal. Calcd for $C_{22}H_{33}NO_{11}S$: C, 50.82; H, 6.40; N, 2.70; S, 6.17. Found: C, 50.74; H, 6.44; N, 2.76; S, 6.23.

N-*[2-(2-*O*-Acetyl-3-*O*-allyl-β-*D*-glucopyranosylsulfanyl)ethyl]succinimide* (**6**).—To a solution of **5** (2.6 g, 5 mmol) in MeOH (50 mL), NaOMe (54 mg, 1 mmol) was added, and the resulting solution was stirred under Ar at 0 °C until TLC monitoring showed complete conversion of the starting material (ca. 6 h). The reaction mixture was neutralized by addition of the acidic cation-exchange resin, Amberlyst™ 15. After filtration, the solution was concentrated in vacuo, and the resulting crude product was subjected to column chromatography on silica gel (toluene–EtOH) to yield **6** (1.8 g, 90%) as a colorless amorphous solid: R_f 0.44 (4:1 toluene–EtOH); mp 90–91 °C. $[\alpha]_D$ −18.7° (*c* 1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.92–5.73 (m, 1H, CH_2CH-), 5.24–5.08 (m, 2H, CH_2CH-), 4.86 (Ψt, 1H, $J \approx 9.5$ Hz, H-2′), 4.37 (d, 1H, *J* 9.8 Hz, H-1′), 4.25–4.08 (m, 2H, allyl-OCH_2), 3.91–3.55 (m, 4H, H-3′, H-4′, H-6′a + b), 3.49–3.34 (m, 4H, H-5′, NCH_2, OH), 2.99–2.71 (m, 2H, SCH_2), 2.68 (s, 4H, 2 × CH_2CO), 2.04 (s, 3H, OAc). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 177.2 ($COCH_2$), 169.5 ($COCH_3$), 134.7 (CH_2CH-), 116.9 (CH_2CH-), 83.5, 83.2, 80.4, 73.5, 71.2, 69.6 (C-1′–C-5′, allyl-OCH_2), 62.0 (C-6′), 39.2 (NCH_2), 28.1 (CH_2CO), 26.6 (SCH_2), 20.9 (Ac). Anal. Calcd for $C_{17}H_{25}NO_8S$: C, 50.61; H, 6.25; N, 3.47; S, 7.95. Found: C, 49.85; H, 6.59; N, 3.87; S, 7.95.

N-*[2-(2-*O*-Acetyl-3-*O*-allyl-6-*O*-tert-butyldiphenylsilyl-β-*D*-glucopyranosylsulfanyl)ethyl]succinimide* (**7**).—To a solution of **6** (1.0 g, 2.48 mmol) in dry CH_2Cl_2 (20 mL) were added imidazole (583 mg, 10.7 mmol) and *tert*-butylchlorodiphenylsilane (0.74 mL, 3.57 mmol). After addition of catalytic amounts of DMAP, the solution was stirred for 2 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with 1N HCl and brine. The organic layer was dried over $MgSO_4$, concentrated in vacuo, and the crude product was purified by column chromatography on silica gel (3:1 hexanes–EtOAc) to yield **7** (1.43 g, 90%) as a colorless solid: R_f 0.47 (1:1 hexanes–EtOAc); mp 39–40 °C. $[\alpha]_D$ −2.0° (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.65 (m, 4H, PhSi), 7.42–7.33 (m, 6H, PhSi), 5.89–5.82 (m, 1H, CH_2CH-), 5.24 (dd, 1H J_{trans} 17.2 Hz, J_{gem} 1.6 Hz, CH_2CH-), 5.14 (dd, 1H, J_{cis} 10.4 Hz, J_{gem} 1.6 Hz, CH_2CH-), 4.91 (Ψt, 1H, $J \approx 9.6$ Hz, H-2′), 4.42 (d, 1H, *J* 10.0 Hz, H-1′), 4.25–4.14 (m, 2H, allyl-OCH_2), 3.90 (d, 2H, *J* 4.5 Hz, H-6′a + b), 3.76 (Ψt, 1H, $J \approx 9.2$ Hz, H-4′), 3.70–3.63 (m, 2H, H-3′, H-5′), 3.47–3.41 (m, 2H, NCH_2), 2.89 (s, 1H, OH), 2.87–2.81 (m, 1H, SCH_2), 2.75–2.62 (m, 1H, SCH_2), 2.61 (s, 4H, 2 × CH_2CO), 2.07 (s, 3H, OAc), 1.01 (s, 9H, *t*Bu). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.6 ($COCH_2$), 169.5 ($COCH_3$), 135.6, 135.5 (PhSi), 134.8 (CH_2CH-), 133.1, 133.0 (PhSi), 129.8, 127.7 (PhSi), 117.0 (CH_2CH-), 83.7, 83.1, 79.3, 73.4, 71.4 (C-1′–C-5′, allyl-OCH_2), 64.4 (C-6′), 38.2 (NCH_2), 28.1 (CH_2CO), 27.1 (SCH_2), 26.8 (*t*Bu), 21.0 (Ac), 19.2 (C_q, *t*Bu). Anal. Calcd for $C_{33}H_{43}NO_9SSi$: C, 61.75; H, 6.75; N, 2.18; S, 5.00. Found: C, 61.58; H, 7.12; N, 2.17; S, 4.81.

N-*[2-(2′-*O*-Acetyl-6′-O-tert-butyldiphenylsilyl-3-O-propyl-β-D-glucopyranosylsulfanyl)ethyl]succinimide* (**8**).—In an ice cold solution of **7** (10.0 g, 15.5 mmol) in dry CH_3CN (200 mL), potassium azodicarboxylate (3.7 g, 21.8 mmol) was suspended. HOAc (2.8 mL, 44.0 mmol) was added, and the mixture stirred at 0 °C for 2 h. The solution was poured into a mixture of 2:1 Et_2O–water (600 mL). The organic layer was washed twice with 1 N HCl and with satd aq $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed in vacuo. Since the ^{1}H NMR spectrum still showed small amounts of the nonhydrogenated compound, the hydrogenation procedure was repeated three times. Finally, the crude product was purified by column chromatography on silica gel (3:1 hexanes–EtOAc) to yield **8** (10.0 g, 98%) as a colorless oil: R_f 0.47 (hexanes–EtOAc 1:1). $[\alpha]_D$ −30.8° (*c* 1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.69–7.64 (m, 4H, PhSi), 7.39–7.30 (m, 6H, PhSi), 4.89 (Ψt, 1H, $J \approx 9.8$ Hz, H-2′), 4.42 (d, 1H, *J* 10.0 Hz, H-1′), 3.91–3.89 (m, 2H, H-6′a + b), 3.77–3.33 (m, 7H, H-3′, H-4′, H-5′, NCH_2, propyl-OCH_2), 3.00 (s, br, 1H, OH), 2.89–2.67 (m, 2H, SCH_2, 2.60 (s, 4H, 2 × CH_2CO), 2.06 (s, 3H, OAc),

1.58–1.48 (m, 2H, CH_2CH_3), 1.01 (s, 9H, *t*Bu), 0.86 (t, 3H, *J* 7.3 Hz, CH_2CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 176.8 (**C**OCH_2), 169.6 (**C**OCH_3), 135.7, 135.6 (PhSi), 134.8 (CH_2**CH**-), 133.1, 132.9 (PhSi), 129.8, 127.8 (PhSi), 84.0, 83.0, 79.4, 74.5, 71.2 (C-1′–C-5′, propyl-OCH_2), 60.4 (C-6′), 38.1 (NCH_2), 28.1 (CH_2CO), 27.0 (SCH_2), 26.8 (*t*Bu), 23.5 (CH_2CH_3), 21.0 (Ac), 19.2 (C_q, *t*Bu), 10.5 (CH_2CH_3).

Preparation of building block **11**.—To a solution of **8** (9.0 g, 14 mmol) in dry CH_2Cl_2, (90 mL) were added $EtOCH{=}CH_2$ (6.7 mL, 140 mmol) and pyridinium *p*-toluenesulfonate (176 mg, 1.4 mmol), and the solution was stirred for 3 h at room temperature. After addition of satd aq $NaHCO_3$ (250 mL), the mixture was extracted with CH_2Cl_2 (2 × 100 mL). Drying over $MgSO_4$ and removal of the solvent in vacuo gave the crude product **9** as a slightly orange oil (10.0 g, quant) which proved to be sufficiently pure for the next synthetic step: under an Ar atmosphere, the crude EE-protected succinimide derivative **9** (5.48 g, 7.65 mmol) was dissolved in 3:1 THF–water (100 mL), and lithium hydroxide (215 mg, 9.37 mmol) was added. The course of the reaction was monitored by TLC, and when complete conversion of the starting material was reached (ca. 1.5 h), the reaction was quenched by addition of phosphate buffer (pH 7). Extraction with EtOAc (2 × 150 mL), drying of the organic layer over $MgSO_4$ and removal of the solvent in vacuo gave the crude carboxylic acid **10** as a viscous colorless oil (5.36 g, 7.30 mmol, 95.5%), which decomposed during storage and therefore was coupled directly to the resin.

The crude material was dissolved in dry CH_2Cl_2 (180 mL), and aminomethyl polystyrene (200–400 mesh, crosslinked with 1% DVB, loading 1.36 mmol/g, 4.75 g, 6.5 mmol) was added. To this mixture, *N*-hydroxysuccinimide (1.32 g, 11.5 mmol) and *N*,*N*-diisopropylcarbodiimide (1.19 mL, 7.7 mmol) were added. The mixture was shaken for 16 h at room temperature. After filtration, the resin was washed with CH_2Cl_2 (3 × 50 mL) and DMF (2 × 50 mL).

To remove the 2′-*O*-acetyl group, hydrazine hydrate (31.4 mL, 646 mmol) and DMF (30 mL) were added, and the mixture was shaken for 16 h at room temperature. The resin was washed with DMF (5 × 50 mL) and CH_2Cl_2 (3 × 50 mL) and dried in vacuo to yield the polymer-bound building block **11** (8.05 g, loading 0.53 mmol/g). The coupling yield was 65.7%.

Combinatorial alkylation of the 2- and the 6-position: preparation of library **14**.—A solid-phase reaction vessel was filled with 1.25 g (loading 0.53 mmol/g, 0.66 mmol) of the polymer **11**, and after flushing with Ar, a solution of *t*-BuOK (0.75 g, 6.6 mmol) in dry DMF (6.6 mL) was added. The mixture was shaken under argon for 15 min at room temperature, and the supernatant solution was removed by suction. A solution of 4-bromobenzyl bromide (5 g, 20 mmol) in dry DMF (6.6 mL) was added. The mixture was shaken for 1 h at room temperature. Again, the supernatant solution was removed and the resin washed with DMF, MeOH, DMF, toluene and Et_2O (30 mL, each).

Likewise, resin from the same batch (1.25 g, 0.66 mmol) was alkylated with 2-cyanobenzyl bromide, and two portions of resin **11** (loading 0.57 mmol/g, 1.75 g, 1 mmol) were alkylated with *n*-iodoheptane and benzyl bromide according to the same protocol (10 equiv *t*-BuOK as a 1 M solution, 30 equiv alkyl halide as a 3 M solution). The TBDPS protecting group was removed by shaking the resin with a solution of *n*-$Bu_4NF{\cdot}3H_2O$ in THF (1 M, 10 equiv with respect to the resin loading) for 16 h. The resins were washed with THF, DMF, dioxane, toluene, twice with Et_2O and dried in vacuo. The 30 reaction vessels of a semiautomatic synthesis block (MultiSynTech) were filled with the polymer-bound 2-*O*-alkylated building blocks **12** (150 mg each, ca. 79 μmol according to combustion analysis; 10 samples of 2-*O*-Hep- and 2-*O*-Bn-resin, five samples of 2-*O*-(2-CN-Bn)- and 2-*O*-(4-Br-Bn)-resin). The block was flushed with dry nitrogen, and a 1 M solution of *t*-BuOK (1 mL each, 1 mmol) in dry DMF was added to each vessel. The samples were stirred (discontinuous stirring to prevent destruction of the resin beads) under nitrogen for 15 min at room temperature. Solutions of iodomethane, *n*-iodopropane, benzyl bromide, 4-bromobenzyl bromide and 2-bromomethylnaphthalene in dry DMF (3 M, 1 mL, 3 mmol) were added to the vessels. Stirring under nitrogen was continued for 3 h at room temperature. All solutions were simultaneously filtered off. The resin samples were washed with DMF, MeOH, toluene and Et_2O, dried in vacuo and transferred into 5-mL polyethylene syringes equipped with 2-μm polyethylene frits. For cleavage of the ethoxyethyl protecting group, a solution of pyridinium *p*-toluenesulfonate (PPTS, 22 mg, 89 μmol) in a mixture of MeOH (0.2 mL) and dioxane (1.8 mL) was added to each resin sample. The syringes were shaken for 10 min, the solutions were discarded (by pushing the plungers in), and the same amount of fresh solution was again transferred to the syringes, followed by shaking for 16 h. The resins (**13**) were washed with DMF, dioxane, Et_2O, dioxane and twice more with Et_2O (2–3 mL each). The resin samples were washed with dry CH_2Cl_2 and a solution of bromine (13.8 μL, 270 μmol) and 2,6-di-*tert*-butylpyridine (100 μL, 445 μmol) in dry CH_2Cl_2 (1.3 mL) was added. The syringes were shaken for 1 h. A solution of Et_4NBr (25.2 mg, 120 μmol), cyclohexene (60 μL, 592 μmol) and the acceptor alcohol (MeOH or EtOH, 250 μL) in dry CH_2Cl_2 (750 μL) was added. Shaking was continued for 2 h, and the solutions containing the desired *O*-glycosides were removed from the syringes through the frits by pushing the plungers in. Each resin portion was washed with dry CH_2Cl_2 (2

mL), the solutions were combined with the reaction mixtures from the corresponding syringe, and the volatile components of the reaction mixtures were removed in vacuo. Solid-phase extraction cartridges (30, 3 mL, with 20 μm polyethylene frit) were filled with silica gel (2 mL each), and the adsorbent was wetted with hexanes (2–3 mL). The remaining compound mixtures were dissolved in CH_2Cl_2 (400 μL each) and applied on top of the silica layers. All nonpolar components were washed out with hexanes (10 mL), and the desired products were eluted with 1:2 hexanes–EtOAc (7.5 mL each). After removal of the solvents in vacuo, the products (**14**) that were obtained were weighed and analyzed by TLC, RP-HPLC and FABMS. Physicochemical data and characterization of the products follow.

Ethyl 2,6-di-O-*benzyl-3*-O-*propyl-α,β*-D-*glycopyranoside* (**14-a1**). 24.5 mg (74%), colorless oil; R_f (α/β) 0.26 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (13.1%, DTBP; signal is present in all chromatograms of the series); 4.28 min (6.0%); 6.85 min (12.9%); 8.42 min (5.5%); 11.28 min (53.3%, α); 12.07 min (9.3%, β). FABMS (NBA + LiCl): m/z 821.6 (11%, [disaccharide + Li]$^+$); 437.4 (100%, [M + Li]$^+$); calcd for $C_{25}H_{34}O_6$ + Li: 437.2; 409.4 (15%, [1−OH + Li]$^+$).

Ethyl 2-O-*benzyl-6*-O-*(4-bromobenzyl)-3*-O-*propyl-α,β*-D-*glycopyranoside* (**14-a2**). 26.1 mg (67%), colorless oil; R_f (α/β) 0.26 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (12.4%); 4.28 min (5.7%); 8.42 min (6.6%); 11.29 min (9.8%, 2,6-Bn_2); 13.33 min (51.9%, α); 14.05 min (6.9%, β); 15.21 min (6.7%). FABMS (NBA + LiCl): m/z 515.3 (100%, [M + Li]$^+$); calcd for $C_{25}H_{33}BrO_6$ + Li: 515.1; 437.4 (64%, [2,6-Bn_2 + Li]$^+$).

Ethyl 2-O-*benzyl-6*-O-*(2-naphthylmethyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-a3**). 22.8 mg (62%), colorless oil; R_f (α/β) 0.26 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (17.3%); 9.17 min (5.8%); 9.34 min (8.46%); 11.29 min (5.0%, 2,6-Bn_2); 13.68 min (50.4%, α); 14.39 min (11.4%, β). FABMS (NBA + LiCl): m/z 487.4 (100%, [M + Li]$^+$); calcd for $C_{29}H_{36}O_6$ + Li: 487.3; 459.4 (12%, [1 − OH + Li]$^+$); 437.4 (21%, [2,6-Bn_2 + Li]$^+$).

Methyl 6-O-*benzyl-2*-O-*(2-cyanobenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-b1**). 24.8 mg (73%), colorless oil; R_f (α/β) 0.16 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (17.3%); 6.24 min (13.8%); 8.51 min (11.4%); 9.13 min (33.0%, α); 9.95 min (12.4%, β); 11.38 min (7.1%); 13.36 min (5.0%). FABMS (NBA + LiCl): m/z 538.4 (28%); 448.2 (100%, [M + Li]$^+$); calcd for $C_{25}H_{31}NO_6$ + Li: 448.2; 434.3 (35%, [1−OH + Li]$^+$); 410.4 (39%).

Methyl 6-O-*(4-bromobenzyl)-2*-O-*(2-cyanobenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-b2**). 28.0 mg (70%), colorless oil; R_f (α/β) 0.14 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): 3.69 min (16.6%); 8.07 min (21.8%); 8.36 min (12.2%); 11.02 min (32.0%, α); 11.78 min (9.0%, β); 13.98 min (8.4%). FABMS (NBA + LiCl): (m/z) 588.4 (54%); 526.3 (100%, [M + Li] +); calcd for $C_{25}H_{30}BrNO_6$ + Li: 526.1; 488.3 (71%, contains Br).

Methyl 2-O-*(2-cyanobenzyl)-6*-O-*(2-naphthylmethyl)-3*-O-*propyl-α,β*-D-*glycopyranoside* (**14-b3**). 25.9 mg (69%), colorless oil; R_f (α/β) 0.15 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 371 min (6.8%); 8.60 min (35.6%); 11.47 min (29.7%, α); 12.21 min (8.0%, β); 14.79 min (4.5%); 16.76 min (3.5%); 19.48 min (3.7%). FABMS (NBA + LiCl): m/z 498.4 (100%, [M + Li]$^+$); calcd for $C_{29}H_{33}NO_6$ + Li: 498.2; 484.4 (96%, [1 − OH + Li]$^+$).

Methyl 6-O-*benzyl-2*-O-*heptyl-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-c1**). 30.8 mg (95%), colorless oil; R_f (α/β) 0.33 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (33.0%); 8.41 min (13.9%); 14.85 min (39.3%, α); 15.78 min (13.8%, β). FABMS (NBA + LiCl): m/z 431.3 (100%, [M + Li]$^+$); calcd for $C_{24}H_{40}O_6$ + Li: 431.3; 439.4 (42%, [2,6-Hep_2 + Li]$^+$).

Methyl 6-O-*(4-bromobenzyl)-2*-O-*heptyl-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-c2**). 34.7 mg (90%), colorless oil; R_f (α/β) 0.31 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.70 min (20.8%); 8.41 min (8.7%); 14.11 min (13.8%); 16.72 min (43.7%, α); 17.56 min (13.0%, β). FABMS (NBA + LiCl): m/z 509.3 (90%, [M + Li]$^+$); calcd for $C_{25}H_{39}BrO_6$ + Li: 509.2; 439.4 (100%, [2,6-Hep_2 + Li]$^+$).

Methyl 2-O-*heptyl-6*-O-*(2-naphthylmethyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-c3**). 33.1 mg (91%), colorless oil; R_f (α/β) 0.30 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (5.6%); 11.62 min (3.6%); 13.08 min (5.7%); 13.58 min (7.3%); 14.78 min (14.7%); 15.50 min (4.4%); 16.99 min (37.1%, α); 17.81 min (14.4%, β); 19.66 min (4.9%). FABMS (NBA + LiCl): m/z 481.4 (100%, [M + Li]$^+$); calcd. for $C_{28}H_{42}O_6$ + Li: 481.3; 467.4 (38%, [1 − OH + Li]$^+$); 439.4 (55%, [2,6-Hep_2 + Li]$^+$).

Methyl 2,6-di-O-*benzyl-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-d1**). 28.2 mg (89%), colorless oil; R_f (α/β) 0.24 (3:1 hexanes–EtOAc). HPLC (column A, gradient A) t_R 3.71 min (15.9%); 4.27 min (9.2%); 6.83 min (13.5%); 10.01 min (48.1%, α); 10.84 min (13.4%, β). FABMS (NBA + LiCl): m/z 807.5 (21%, [disaccharide + Li]$^+$); 793.5 (15%, [disaccharide-1 − OH + Li]$^+$); 423.3 (100%, [M + Li]$^+$); calcd for $C_{24}H_{32}O_6$ + Li: 423.2; 409.3 (24%, [1 − OH + Li]$^+$).

Methyl 2-O-*benzyl-6*-O-*(4-bromobenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-d2**). 26.3 mg (69%), colorless oil; R_f (α/β) 0.24 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.70 min (14.6%); 4.26 min (7.5%); 10.01 min (8.6%, 2,6-Bn_2); 12.13 min (50.0%, α); 12.89 min (12.6%, β); 15.18 min (6.7%). FABMS (NBA + LiCl): m/z 501.2 (100%, [M + Li]$^+$); calcd for $C_{24}H_{31}BrO_6$ + Li: 501.1; 423.1 (62%, [2,6-Bn_2 + Li]$^+$).

Methyl 2-O-*benzyl-6*-O-*(2-naphthylmethyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-d3**). 27.1 mg (76%), colorless oil; R_f (α/β) 0.23 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (5.1%); 9.15 min (3.2%); 9.32 min (4.2%); 10.01 min (3.1%, 2,6-Bn_2); 12.51 min (43.2%, α); 13.26 min (15.1%, β); 14.78 min (3.8%); 15.15 min (4.9%); 15.43 min (10.57%). FABMS (NBA + LiCl): m/z 473.3 (100%, $[M + Li]^+$); calcd for $C_{28}H_{34}O_6 + Li$: 473.2; 423.1 (28%, $[2,6\text{-}Bn_2 + Li]^+$).

Methyl 6-O-*benzyl-2*-O-*(4-bromobenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-e1**). 26.7 mg (70%), colorless oil; R_f (α/β) 0.22/0.25 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.70 min (11.4%); 4.27 min (4.3%); 8.41 min (4.7%); 8.93 min (8.8%); 12.17 min (32.3%, α); 13.15 min (9.7%, β); 14.1 min (7.6%). FABMS (NBA + LiCl): m/z 671.1 (21%, contains 2Br); 501.2 (40%, $[M + Li]^+$); calcd for $C_{24}H_{31}BrO_6 + Li$: 501.1; 169.1 (100%, contains Br).

Methyl 2,6-bis-O-*(4-bromobenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-e2**). 29.7 mg (67%), colorless oil; R_f (α/β) 0.30 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (10.3%); 4.26 min (6.1%); 10.78 min (9.0%); 14.11 min (39.1%, α); 14.99 min (9.6%, β); 16.83 min (4.4%); 21.42 min (17.6%); 21.83 min (3.9%). FABMS (NBA + LiCl): m/z 749.1 (9%, contains 3Br); 581.1 (18%, $[M + Li]^+$); calcd for $C_{24}H_{30}Br_2O_6 + Li$: 581.0; 169.1 (100%, contains Br).

Methyl 2-O-*(4-bromobenzyl)-6*-O-*(2-naphthylmethyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-e3**). 28.8 mg (69%), colorless oil; R_f (α/β) 0.32 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 11.25 min (14.1%); 14.52 min (32.2%, α); 15.20 min (10.2%, β). FABMS (NBA + LiCl): low signal intensity, m/z 721.1 (67%, contains 2Br); 551.3 (18%, $[M + Li]^+$); calcd for $C_{28}H_{33}BrO_6 + Li$: 551.2.

Ethyl 6-O-*benzyl-2*-O-*heptyl-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-f1**). 25.4 mg (76%), colorless oil; R_f (α/β) 0.36 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (22.3%); 4.27 min (13.3%); 8.40 min (9.4%); 11.27 min (16.3%); 16.06 min (38.7%, α); 17.00 min (β, not integrated). FABMS (NBA + LiCl): m/z 845.6 (15%, heterodisaccharide, [6-Hep-disaccharide + Li]$^+$ + [6′-Hep-disaccharide + Li]$^+$); 837.6 (28%, [disaccharide + Li]$^+$). 453.4 (45%, $[2,6\text{-}Hep_2 + Li]^+$); 445.4 (100%, $[M + Li]^+$); calcd for $C_{25}H_{42}O_6 + Li$: 445.3.

Ethyl 6-O-*(4-bromobenzyl)-2*-O-*heptyl-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-f2**). 27.1 mg (68%), colorless oil; R_f (α/β) 0.35 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (18.9%); 4.27 min (7.5%); 8.41 min (8.0%); 15.22 min (14.9%); 17.84 min (50.6%, α); 18.74 min (β, not integrated). FABMS (NBA + LiCl): m/z 995.4 (28%, [disaccharide + Li]$^+$); 523.3 (80%, $[M + Li]^+$); calcd for $C_{25}H_{41}BrO_6 + Li$: 523.2; 453.4 (100%, $[2,6\text{-}Hep_2 + Li]^+$).

Ethyl 2-O-*heptyl-6*-O-*(2-naphthylmethyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**14-f3**). 25.8 mg (69%), colorless oil; R_f (α/β) 0.35 (3:1 hexanes–EtOAc). HPLC (column A, gradient A): t_R 3.71 min (4.9%); 13.08 min (4.7%); 13.58 min (5.3%); 15.80 min (15.2%); 18.06 min (44.7%, α); 18.93 min (9.3 min, β); 19.69 min (6.0%). FABMS (NBA + LiCl): m/z 937.6 (16%, [disaccharide + Li]$^+$); 495.4 (100%, $[M + Li]^+$); calcd for $C_{29}H_{44}O_6 + Li$: 495.3; 453.4 (16%, $[2,6\text{-}Hep_2 + Li]^+$).

Methyl 2-O-*benzyl-4,6-bis*-O-*(4-chlorophenylcarbamoyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**16-a2**).—A sample of the polymer-bound thioglycoside **11** (2-OH, 6-OTBDPS, 4 g, loading 0.6 mmol/g, 2.4 mmol, max. 0.5 mmol/g free amino groups) was shaken with a solution of the coupling reagent *N*,*N*,*N*′,*N*′-bis-(tetramethylene)-*O*-pentafluorophenyluronium hexafluorophosphate[19] (PfPyU, 2.88 g, 6 mmol), HOAc (340 μL, 6 mmol) and *N*-ethyldiisopropylamine (2.05 mL, 12 mmol) in dry DMF (30 mL) for 3 h. The resin was washed (2 × DMF, 2 × dioxane, toluene, 3 × Et_2O) and dried in vacuo. The resulting polymer **11-Ac** (with capped amino functions) was benzylated in 2-position and subsequently desilylated according to the protocols given for the preparation of library **14**. A sample of the product (2-OBn, 6-OH, 50 mg, loading 0.45 mmol/g, 22.5 μmol) was shaken for 16 h with a 10% solution of 4-chlorophenyl isocyanate in dioxane (1 mL) containing catalytic amounts of DMAP. The resin was washed with dioxane, EtOH, DMF and EtOH again (2–3 mL each). Then, the ethoxyethyl protecting group was removed by addition of a solution of pyridinium *p*-toluenesulfonate (PPTS, 22 mg, 89 μmol) in a mixture of MeOH (0.2 mL) and dioxane (1.8 mL). After shaking for 10 min, the solution was discarded and the same amount of fresh PPTS-solution (same composition) was filled in the syringes, followed by shaking for 16 h. After washing (dioxane, DMF, dioxane, Et_2O, dioxane, 2 × Et_2O; 2–3 mL each), the resin was shaken for 16 h with a 10% solution of 4-chlorophenyl isocyanate in dioxane (1 mL) containing catalytic amounts of DMAP. The final washing procedure (DMF, MeOH, dioxane, 2 × Et_2O and finally with toluene, 2–3 mL each) was followed by cleavage of the thioglycoside anchor as follows: the resin was washed with dry CH_2Cl_2, and a solution of bromine (15.4 μL, 300 μmol) and 2,6-di-*tert*-butylpyridine (100 μL, 445 μmol) in dry CH_2Cl_2 (1.3 mL) was added. The syringes were shaken for 15 min, and the solution containing the glycosyl bromide was filtered directly into an Ar-flushed glass vial containing a solution of Et_4NBr (36 mg, 171 μmol), cyclohexene (100 μL, 987 μmol) and MeOH (300 μL, 7.4 mmol) in dry CH_2Cl_2 (1 mL). The polymer was washed one time, and the resulting mixture was kept in the closed vial for 3 h at room temperature (Ar atmosphere). The volatile components of the reaction mixtures were removed by evaporation overnight. For

purification of the methyl glycoside, a solid-phase extraction cartridge (3 mL, with 20-μm polyethylene frit) filled with silica gel (2 mL each) was wetted with hexanes (2–3 mL each). The remaining solid was dissolved in dichloromethane (400 μL) and was applied on top of the silica layer. The desired product was washed with hexanes (10 mL), then eluted with 1:2 hexanes–EtOAc (7.5 mL each). Removal of the solvents in vacuo gave **16-a2** as a colorless, crystalline solid (12.3 mg, 96%): R_f (α) 0.63 (1:1 hexanes–EtOAc); mp 219–221 °C (from $CDCl_3$). ESIMS: (crude material, VG BIO-Q, 400–1150 amu, addition of formic acid): m/z 633.3 (71%, $[M+H]^+$); calcd for $C_{31}H_{34}Cl_2N_2O_8+H$: 633.2; 601.2 (29%, glycosyl cation); 570.3 (48%, [2,6-Bn_2 + H]$^+$); 538.3 (100%, 2,6-Bn_2-glycosyl cation). After washing of the crystals with ether–hexanes and drying, an NMR spectrum was recorded: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.36 (m, Ph, 2 × 4-Cl-Ph), 6.70 (s, br, 1H, NH), 6.66 (s, br, 1H, NH), 4.93 (t, br, 1H, J 9.7 Hz, H-4), 4.82 (d, 1H, J_{gem} 12.2 Hz, C**H**$_2$Ph), 4.64 (d, 1H, J_{gem} 12.2 Hz, C**H**$_2$Ph), 4.58 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.34 (dd, 1H, J_{gem} 12.0 Hz, $J_{5,6a}$ 2.6 Hz, H-6a), 4.28 (dd, 1H, J_{gem} 12.0 Hz, $J_{5,6b}$ 4.7 Hz, H-6b), 3.92 (ddd, 1H, $J_{4,5}$ 10.3 Hz, $J_{5,6b}$ 4.7 Hz, $J_{5,6a}$ 2.6 Hz, H-5), 3.81 (dt, 1H, J_d 9.1 Hz, J_t 6.3 Hz, propyl-OC**H**$_2$), 3.76 (t, 1H, J 9.5 Hz, H-3), 3.48–3.59 (m, 2H, H-2, propyl-OC**H**$_2$), contained in this multiplet: 3.51 (dd, 1H, $J_{2,3}$ 9.5 Hz, $J_{1,2}$ 3.5 Hz, H-2), 3.39 (s, 3H, OMe), 1.54 (mc, 2H, propyl-C**H**$_2$CH$_3$), 0.84 (t, 3H, J 7.5 Hz, propyl-CH_3).

Combinatorial synthesis of a library of biscarbamoyl glucosides (library **17***).*—Under an Ar atmosphere, the fully protected building block **9** (8.78 g, 12.3 mmol, crude material, preparation from **8** according to the protocol described above) was dissolved in a mixture of THF (90 mL) and water (30 mL). After addition of LiOH (379 mg, 15.8 mmol), the solution was stirred until TLC indicated complete hydrolysis of the starting material (ca. 1 h). The solution was neutralized by addition of phosphate buffer (pH 7) and extracted with EtOAc (2 × 150 mL).

The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to yield carboxylic acid **10** (8.97 g, quant) as a colorless oil. In a solid-phase reaction vessel, the building block was dissolved in dry CH_2Cl_2 (90 mL) and aminomethyl polystyrene (100–200 mesh, crosslinked with 1% divinylbenzene, loading 1.1 mmol/g, 15 g, 16.5 mmol), 1-hydroxybenzotriazole (containing 17% water, 1.99 g, 12.3 mmol) and *N*,*N*-diisopropylcarbodiimide were (1.89 mL, 12.3 mmol) were added. While shaking under Ar, small portions of dry CH_2Cl_2 were added to keep the reaction mixture liquid. After shaking for 16 h, the supernatant solution was removed by suction, and the polymer was washed with CH_2Cl_2 (5 ×), DMF (2 ×), CH_2Cl_2, DMF, MeOH (2 ×), toluene and Et_2O (2 ×) and dried in vacuo. To the polymer, a mixture of Ac_2O (10 mL), pyridine (30 mL) and CH_2Cl_2 (100 mL) was added, and the mixture was shaken for 30 min before excess liquid was removed by suction. The resin (**2**) was washed (CH_2Cl_2, DMF, Et_2O, toluene, 3 × Et_2O) and dried in vacuo. A mixture of hydrazine hydrate (58 mL, 1.2 mol) and dry DMF (50 mL) were added, and the reaction vessel was shaken for 16 h. The reagents were removed and the resin was washed (DMF, Et_2O, 2 × DMF, 3 × toluene, 3 × Et_2O) and dried in vacuo, yielding polymer **11** (23.3 g, loading 0.43 mmol/g, coupling yield 81.7%). Three solid-phase reaction vessels were filled with polymer-bound thioglycoside **11** (3.5 g each, loading 0.43 mmol/g, 1.5 mmol). After addition of a solution of *t*-BuOK (1.69 g, 15 mmol) in dry DMF (15 mL) to each vessel, the mixtures were shaken for 30 min under an Ar atmosphere. After removal of the *t*-BuOK solution, alkylation was performed by addition of *n*-iodobutane, 4-fluorobenzyl bromide or 2-methylbenzyl bromide (15 mL of 3 M solution in dry DMF, 45 mmol) and shaking for 1 h. The resin was washed (DMF, MeOH, DMF, toluene, 2 × Et_2O) and desilylation (10 equiv 1 M TBAF in THF, 16 h) was performed as described above. The washed and dried resins had the following loadings: R^2 = *n*-Bu, 0.41 mmol/g; R^2 = 4-F-Bn, 0.39 mmol/g; R^2 = 2-Me-Bn, 0.37 mmol/g.

Portions of the 2-alkylated resins were weighed in 5-mL syringes equipped with polyethylene frits (20 syringes for each resin, 50 mg each, ca. 20 μmol) and reacted with 2,4-difluorophenyl isocyanate, *n*-propyl isocyanate, 3-cyanophenyl isocyanate, (*S*)-α-methylbenzyl isocyanate and 4-methyl-3-nitrophenyl isocyanate according to the protocol for preparation of **16-a2** (0.1 g isocyanate, 1 mL dioxane, catalytic amounts of DMAP, 16 h). In the case of the two alkyl isocyanates, the reaction time was extended to 30 h to ensure a complete conversion. Cleavage of the ethoxyethyl protecting group as described before was followed by carbamoylation of the 4-position with 4-fluorophenyl isocyanate, 4-trifluormethylphenyl isocyanate and 4-chlorophenyl isocyanate (standard procedure, 16 h). A fourth portion of 15 resin samples was left underivatized (free 4-OH group). Cleavage from the resin was performed as described for the preparation of **16-a2** using isobutanol or *n*-butanol as the acceptor alcohols. Solid-phase extraction also was performed as described.

*Butyl 2-*O*-butyl-6-*O*-(2,4-difluorophenylcarbamoyl)-3-*O*-propyl-α,β-*D*-glucopyranoside* (**17-1a1**). 5.5 mg (61%), colorless oil; R_f (α) 0.42 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 6.25 min (8.1%); 6.68 min (3.3%); 7.90 min (76.4%, α); 8.58 min (9.2%, β). ESIMS: m/z 611.4 (12%, [2,6-(2,4-F_2-PhNHCO)$_2$ + Na]$^+$); 553.6 (21%, $[M+MeCN+Na]^+$); 512.5 (100%, $[M+Na]^+$); calcd for $C_{28}H_{37}F_2NO_7+Na$: 512.2; 413.6 (10%, [2,6-Bu_2 + Na]$^+$).

Butyl 2-O-butyl-3-O-propyl-6-O-propylcarbamoyl-α,β-D-glucopyranoside (**17-2a1**). 3.6 mg (47%), colorless oil; R_f (α) 0.40 (4:1 hexanes–EtOAc); HPLC: UV-absorption too weak. ESIMS: *m/z* 527.6 (15%, [6-allophanate + Na]$^+$); 483.5 (24%, [M + MeCN + Na]$^+$); 442.5 (100%, [M + Na]$^+$); calcd for $C_{21}H_{41}NO_7$ + Na: 442.3.

Butyl 2-O-butyl-6-O-(3-cyanophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-3a1**). 4.1 mg (46%), colorless oil; R_f (α) 0.40 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 6.80 min (6.9%); 7.32 min (66.2%, α); 7.95 min (17.2%, β); 11.63 min (6.5%). ESIMS: *m/z* 542.6 (13%, [M + MeCN + Na]$^+$); 501.5 (100%, [M + Na]$^+$); calcd for $C_{25}H_{38}N_2O_7$ + Na: 501.3; 498.8 (7%, [2M + Ca]$^{2+}$); 442.5 (10%, cross contamination); 413.6 (13%, [2,6-Bu_2 + Na]$^+$).

Butyl 2-O-butyl-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-4a1**). 3.8 mg (43%), colorless oil; R_f (α) 0.43/0.64 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 7.88 min (25.5%, α); 9.47 min (8.3%); 10.67 min (3.2%); 11.12 min (42.1%, 6-allophanate); 11.42 min (12.0%, 6-allophanate (β)); 11.78 min (3.8%). ESIMS: *m/z* 651.6 (43%, [6-allophanate + Na]$^+$); 504.5 (100%, [M + Na]$^+$); calcd for $C_{26}H_{43}NO_7$ + Na: 504.3.

Butyl 2-O-butyl-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-5a1**). 4.5 mg (45%), yellow oil; R_f (α) 0.47 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 7.87 min (9.0%); 8.33 min (66.4%, α); 8.92 min (13.4%, β); 9.85 min (6.0%); 12.57 min (5.1%). ESIMS: *m/z* 576.6 (8%, [M + MeCN + Na]$^+$); 535.6 (100%, [M + Na]$^+$); calcd for $C_{25}H_{40}N_2O_7$ + Na: 535.3; 504.5 (10%, cross contamination); 413.6 (8%, [2,6-Bu_2 + Na]$^+$).

Butyl 6-O-(2,4-difluorophenylcarbamoyl)-2-O-(4-fluorbenzyl)-3-O-propyl-α,β-D-glucopyranoside (**17-1a2**). 5.6 mg (59%), colorless oil; R_f (α) 0.47 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 4.42 min (3.5%); 7.05 min (4.3%); 7.43 min (3.1%); 7.57 min (70.5%, α); 8.15 min (5.4%, β); 8.50 min (4.6%, 2,6-(4-F-Bn)$_2$). ESIMS: *m/z* 605.4 (7%, [M + MeCN + Na]$^+$); 564.5 (100%, [M + Na]$^+$); calcd for $C_{27}H_{34}F_3NO_7$ + Na: 564.2; 517.5 (7%, [2,6-(4-F-Bn)$_2$ + Na]$^+$).

Butyl 2-O-(4-fluorobenzyl)-3-O-propyl-6-O-propylcarbamoyl-α,β-D-glucopyranoside (**17-2a2**). 3.6 mg (43%), colorless oil; R_f (α) 0.42 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 6.30 min (66.9%, α); 7.02 min (13.3%, β); 8.47 min (9.5%, 2,6-Bu_2); 8.95 min (3.5%); 10.50 min (6.9%). ESIMS: *m/z* 535.6 (6%, [M + MeCN + Na]$^+$); 494.5 (100%, [M + Na]$^+$); calcd for $C_{24}H_{38}FNO_7$ + Na: 494.3.

Butyl 6-O-(3-cyanophenylcarbamoyl)-2-O-(4-fluorobenzyl)-3-O-propyl-α,β-D-glucopyranoside (**17-3a2**). 6.6 mg (71%), colorless oil; R_f (α) 0.38 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 2.60 min (4.7%); 6.53 min (4.7%); 7.03 min (66.5%, α); 7.55 min (15.0%, β); 10.38 min (6.1%). ESIMS: *m/z* 594.5 (8%, [M + MeCN + Na]$^+$); 553.6 (100%, [M + Na]$^+$); calcd for $C_{28}H_{35}FN_2O_7$ + Na: 553.2; 550.8 (9%, [2M + Ca]$^{2+}$); 517.5 (12%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 494.4 (28%, cross contamination).

Butyl 2-O-(4-fluorobenzyl)-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-4a2**). 5.0 mg (53%), colorless oil; R_f (α) 0.38/0.64 (4:1 hexanes–EtOAc); HPLC–MS (column B, gradient B): t_R (*m/z*) 3.08 min (6.3%, 448.3, [2-OH(α) + Na]$^+$); 6.83 min (7.1%; 595.3, [2,6-(PhCH(Me)NHCO)$_2$(α) + Na]$^+$); 6.95 min (10.9%; 595.3, [2,6-(PhCH(Me)NHCO)$_2$(β) + Na]$^+$); 7.53 min (26.7%; 556.3, [M(α) + Na]$^+$); 8.27 min (3.7%; 556.3, [M(β) + Na]$^+$); 10.05 min (3.2%; 554.3); 10.37 min (18.6%; 703.4, [6-allophanate(α) + Na]$^+$). ESIMS: *m/z* 703.7 (50%, [6-allophanate + Na]$^+$); 595.5 (29%, [2,6-(PhCH(Me)NHCO)$_2$ + Na]$^+$); 556.6 (100%, [M + Na]$^+$); calcd for $C_{29}H_{40}FNO_7$ + Na: 556.3; 448.5 (31%, [2-OH + Na]$^+$).

Butyl 2-O-(4-fluorobenzyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-5a2**). 6.5 mg (66%), colorless oil; R_f (α) 0.39 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 7.50 min (4.8%); 7.92 min (70.3%, α); 8.45 min (20.2%, β + 2,6-(4-F-Bn)$_2$). ESIMS: *m/z* 703.7 (8%, cross contamination); 628.5 (5%, [M + MeCN + Na]$^+$); 587.5 (100%, [M + Na]$^+$); calcd for $C_{28}H_{37}N_2O_9$ + Na: 587.2; 584.8 (11%, [2M + Ca]$^{2+}$); 556.6 (15%, cross contamination); 517.5 (9%, [2,6-(4-F-Bn)$_2$ + Na]$^+$).

Butyl 6-O-(2,4-difluorophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-α,β-D-glucopyranoside (**17-1a3**). 7.8 mg (87%), colorless oil; R_f (α) 0.41 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 4.43 min (7.3%); 5.60 min (3.8%); 8.25 min (57.7%, α); 8.82 min (4.0%, β); 9.92 min (3.5%, 2,6-(2-Me-Bn)$_2$); 10.08 min (3.1%); 10.25 min (4.1%). ESIMS: *m/z* 664.6 (6%, [2,4-(2-Me-Bn)$_2$ + Na]$^+$); 560.6 (100%, [M + Na]$^+$); calcd for $C_{28}H_{37}F_2NO_7$ + Na: 560.2; 509.5 (35%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$).

Butyl 2-O-(2-methylbenzyl)-3-O-propyl-6-O-propylcarbamoyl-α,β-D-glucopyranoside (**17-2a3**). 6.4 mg (82%), colorless oil; R_f (α) 0.41 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 6.30 min (4.0%); 7.08 min (68.0%, α); 7.83 min (9.7%, β); 9.72 min (5.2%); 9.95 min (6.7%, 2,6-(2-Me-Bn)$_2$); 11.67 min (3.2%). ESIMS: (*m/z*) 490.5 (100%, [M + Na]$^+$); calcd for $C_{25}H_{41}NO_7$ + Na: 490.3.

Butyl 6-O-(3-cyanophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-α,β-D-glucopyranoside (**17-3a3**). 5.9 mg (67%), colorless oil; R_f (α) 0.36 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 7.17 min (6.1%); 7.72 min (69.2%, α); 8.23 min (14.7%, β); 11.47 min (3.6%). ESIMS: *m/z* 653.6 (6%, [2,4-(2-Me-Bn)$_2$ + Na]$^+$); 549.6 (100%, [M + Na]$^+$); calcd for $C_{29}H_{38}N_2O_7$ + Na: 549.3; 547.0 (9%, [2M + Ca]$^{2+}$); 509.5 (40%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 490.5 (16%, cross contamination).

Butyl 2-O-(2-methylbenzyl)-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-4a3**). 6.4 mg (73%), colorless oil; R_f (α) 0.41/0.51 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 6.95 min (3.1%); 8.23 min (50.1%, α); 8.95 min (7.8%, β); 9.92 min (4.1%, 2,6-(2-Me-Bn)$_2$); 11.02 min (28.1%, 6-allophanate). ESIMS: m/z 699.7 (25%, [6-allophanate + Na]$^+$); 595.5 (6%, [2,6-(PhCH(Me)-NHCO)$_2$ + Na]$^+$); 552.6 (100%, [M + Na]$^+$); calcd for $C_{30}H_{43}NO_7$ + Na: 552.3; 509.5 (5%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$).

Butyl 2-O-(2-methylbenzyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-5a3**). 5.2 mg (56%), colorless oil; R_f (α) 0.41 (4:1 hexanes–EtOAc); HPLC–MS (column B, gradient B): t_R (m/z) 8.12 min (5.7%; 509.4, 550.4); 8.60 min (66.4%; 583.4, [M(α) + Na]$^+$); 9.10 min (14.0%; 583.4, [M(β) + Na]$^+$; 624.4, [M(β) + MeCN + Na]$^+$); 9.93 min (3.9%; 509.4, [2,6-(2-Me-Bn)$_2$(α) + Na]$^+$; 550.4, [2,6-(2-Me-Bn)$_2$(α) + MeCN + Na]$^+$). ESIMS: m/z 699.7 (8%, cross contamination); 583.5 (100%, [M + Na]$^+$); calcd for $C_{29}H_{40}N_2O_9$ + Na: 583.3; 581.0 (10%, [2M + Ca]$^{2+}$); 552.6 (28%, cross contamination); 509.5 (28%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$).

Butyl 2-O-butyl-6-O-(2,4-difluorophenylcarbamoyl)-4-O-(4-fluorophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-1b1**). 7.0 mg (61%), colorless crystals; R_f (α) 0.66 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.07 min (6.2%); 8.47 min (6.2%); 9.82 min (73.7%, α); 10.22 min (5.0%, β); 11.17 min (5.8%, 2,6-Bu$_2$). ESIMS: m/z 1276.0 (17%, [2M + Na]$^+$); 748.5 (18%, [2,6-(2,4-F$_2$-PhNHCO)$_2$ + Na]$^+$); 690.7 (50%, [M + MeCN + Na]$^+$); 665.6 (7%); 649.6 (100%, [M + Na]$^+$); calcd for $C_{31}H_{41}F_3N_2O_8$ + Na: 649.3; 647.0 (9%, [2M + Ca]$^{2+}$); 550.7 (26%, [2,6-Bu$_2$ + Na]$^+$); 494.4 (7%, [M − (4-F-PhNHCO$_2$) + Na]$^+$).

Butyl 2-O-butyl-4-O-(4-fluorophenylcarbamoyl)-3-O-propyl-6-O-propylcarbamoyl-α,β-D-glucopyranoside (**17-2b1**). 3.9 mg (38%), colorless crystals; R_f (α) 0.40 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.08 min (77.0%, α); 9.62 min (9.2%, β); 11.10 min (13.9%, 2,6-Bu$_2$). ESIMS: m/z 1136.0 (14%, [2M + Na]$^+$); 693.7 (10%, [2-PrNHCO-6-allophanate + Na]$^+$); 664.7 (38%, [6-allophanate + Na]$^+$); 620.5 (35%, [M + MeCN + Na]$^+$); 608.6 (19%, 2,6-(PrNHCO)$_2$ + Na]$^+$); 579.6 (100%, [M + Na]$^+$); calcd for $C_{28}H_{45}FN_2O_8$ + Na: 579.3; 550.7 (11%, [2,6-Bu$_2$ + Na]$^+$); 498.6 (7%, [2,4-Bu$_2$ + Na]$^+$); 424.5 (20%, [M − (4-F-PhNHCO$_2$) + Na]$^+$).

Butyl 2-O-butyl-6-O-(3-cyanophenylcarbamoyl)-4-O-(4-fluorophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-3b1**). 3.7 mg (33%), pale reddish crystals; R_f (α) 0.40 (4:1 hexanes–EtOAc); HPLC–MS (column B, gradient B): t_R (m/z) 7.48 min (6.5%; 726.4, [2,6-(3-CN-PhNHCO)$_2$(β) + Na]$^+$); 9.33 min (70.3%; 638.4, [M(α) + Na]$^+$); 9.68 min (12.3%; 638.4, [M(β) + Na]$^+$). ESIMS: m/z 1254.1 (21%, [2M + Na]$^+$); 726.5 (6%); 638.6 (100%, [M + Na]$^+$); calcd for $C_{32}H_{42}FN_3O_8$ + Na: 638.3; 635.9 (7%, [2M + Ca]$^{2+}$); 591.6 (26%, [2,6-Bu$_2$ + MeCN + Na]$^+$); 579.6 (11%, cross contamination); 550.7 (28%, [2,6-Bu$_2$ + Na]$^+$).

Butyl 2-O-butyl-4-O-(4-fluorophenylcarbamoyl)-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-4b1**). 3.7 mg (32%), colorless crystals; R_f (α) 0.47/0.68 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 5.53 min (11.4%); 9.88 min (34.5%, α); 10.40 min (9.5%, β); 11.90 min (44.6%, 6-allophanate). ESIMS: m/z 1260.1 (5%, [2M + Na]$^+$); 1026.7 (5%); 879.7 (10%); 788.7 (92%, [6-allophanate + Na]$^+$); 641.6 (100%, [M + Na]$^+$); calcd for $C_{33}H_{47}FN_2O_8$ + Na: 641.3; 550.7 (7%, [2,6-Bu$_2$ + Na]$^+$); 504.5 (5%, [4-OH + Na]$^+$); 486.5 (8%, [M − (4-F-PhNHCO$_2$) + Na]$^+$).

Butyl 2-O-butyl-4-O-(4-fluorophenylcarbamoyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-5b1**). 6.6 mg (55%), colorless crystals; R_f (α) 0.47 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.92 min (4.2%); 9.98 min (73.7%, α); 10.32 min (11.1%, β); 11.22 min (3.5%, 2,6-Bu$_2$). ESIMS: m/z 994.8 (6%, [3M + Ca]$^{2+}$); 788.7 (5%, cross contamination); 713.6 (10%, [M + MeCN + Na]$^+$); 672.7 (100%, [M + Na]$^+$); calcd for $C_{32}H_{34}FN_3O_{10}$ + Na: 672.3; 670.0 (14%, [2M + Ca]$^{2+}$); 641.6 (7%, cross contamination); 591.6 (11%, [2,6-Bu$_2$ + MeCN + Na]$^+$); 550.7 (33%, [2,6-Bu$_2$ + Na]$^+$).

Butyl 6-O-(2,4-difluorophenylcarbamoyl)-2-O-(4-fluorbenzyl)-4-O-(4-fluorophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-1b2**). 6.7 mg (56%), colorless crystals; R_f (α) 0.37 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.28 min (78.2%, α); 9.62 min (5.4%, β); 10.07 min (6.0%, 2,6-(4-F-Bn)$_2$); 10.62 min (3.6%). ESIMS: m/z 742.6 (32%, [M + MeCN + Na]$^+$); 701.6 (100%, [M + Na]$^+$); calcd for $C_{34}H_{38}F_4N_2O_7$ + Na: 701.2; 699.0 (13%, [2M + Ca]$^{2+}$); 695.6 (8%, [2,6-(2-F-Bn)$_2$ + MeCN + Na]$^+$); 654.6 (29%, [2,6-(4-F-Bn)$_2$ + Na]$^+$).

Butyl 2-O-(4-fluorobenzyl)-4-O-(4-fluorophenylcarbamoyl)-3-O-propyl-6-O-propylcarbamoyl-α,β-D-glucopyranoside (**17-2b2**). 5.2 mg (49%), colorless crystals; R_f (α) 0.34 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.58 min (61.9%, α); 9.00 min (7.2%, β); 10.07 min (9.6%, 2,6-(4-F-Bn)$_2$); 10.37 min (5.3%); 12.45 min (3.5%); 12.72 min (6.1%). ESIMS: m/z 1270.0 (11%); 1240.1 (13%, [2M + Na]$^+$); 716.7 (15%, [6-allophanate + Na]$^+$); 672.7 (28%, [M + MeCN + Na]$^+$); 654.6 (11%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 631.6 (100%, [M + Na]$^+$); calcd for $C_{31}H_{42}F_2N_2O_7$ + Na: 631.3; 628.8 (12%, [2M + Ca]$^{2+}$); 602.5 (7%, [2,4-(4-F-Bn)$_2$ + Na]$^+$); 476.4 (19%, [M − (4-F-PhNHCO$_2$) + Na]$^+$).

Butyl 6-O-(3-cyanophenylcarbamoyl)-2-O-(4-fluorobenzyl)-4-O-propyl-(4-fluorophenylcarbamoyl)-3-O-α,β-D-glucopyranoside (**17-3b2**). 6.4 mg (55%), colorless crystals; R_f (α) 0.33 (4:1 hexanes–EtOAc); HPLC

(column B, gradient B): t_R 8.88 min (78.0%, α); 9.17 min (13.8%, β); 10.08 min (3.2%, 2,6-(4-F-Bn)$_2$); 12.07 min (3.0%). ESIMS: m/z 695.6 (10%, [2,6-(4-F-Bn)$_2$ + MeCN + Na]$^+$); 690.7 (100%, [M + Na]$^+$); calcd for $C_{33}H_{39}F_2N_3O_7$ + Na: 690.3; 654.6 (32%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 631.5 (17%, cross contamination).

Butyl 2-O-(4-fluorobenzyl)-4-O-(4-fluorophenylcarbamoyl)-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-4b2**). 7.8 mg (66%), colorless wax; R_f (α) 0.36/0.50 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.38 min (34.5%, α); 9.77 min (3.7%, β); 10.08 min (4.6%, 2,6-(4-F-Bn)$_2$); 11.22 min (46.1%, 6-allophanate). ESIMS: m/z 856.8 (6%, [6-allophanate + K]$^+$); 840.8 (98%, [6-allophanate + Na]$^+$); 837.8 (10%, [2 × 6-allophanate + Ca]$^{2+}$); 811.8 (5%); 764.5 (7%, [6-allophanate + M + Ca]$^{2+}$); 693.7 (100%, [M + Na]$^+$); calcd for $C_{36}H_{44}F_2N_2O_7$ + Na: 693.3; 654.6 (10%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 274.3 (6%).

Butyl 2-O-(4-fluorobenzyl)-4-O-(4-fluorophenylcarbamoyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-5b2**). 6.4 mg (52%), colorless crystals; R_f (α) 0.36 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.48 min (76.5%, α); 9.77 min (6.3%, β); 10.08 min (4.7%, 2,6-(4-F-Bn)$_2$). ESIMS: m/z 840.7 (11%, cross contamination); 765.6 (8%, [M + MeCN + Na]$^+$); 724.6 (100%, [M + Na]$^+$); calcd for $C_{35}H_{41}F_2N_3O_9$ + Na: 724.3; 721.8 (11%, [2M + Ca]$^{2+}$); 695.7 (14%, [2,6-(4-F-Bn)$_2$ + MeCN + Na]$^+$); 693.7 (11%, cross contamination); 654.6 (28%, [2,6-(4-F-Bn)$_2$ + Na]$^+$).

Butyl 6-O-(2,4-difluorophenylcarbamoyl)-4-O-(4-fluorophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-α,β-D-glucopyranoside (**17-1b3**). 9.0 mg (80%), colorless crystals; R_f (α) 0.46 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 4.63 min (3.4%); 9.88 min (68.7%, α); 10.20 min (4.1%, β); 11.10 min (14.3%, 2,6-(2-Me-Bn)$_2$). ESIMS: m/z 1031.9 (5%, [3M + Ca]$^{2+}$); 738.5 (8%, [M + MeCN + Na]$^+$); 697.6 (100%, [M + Na]$^+$); calcd for $C_{35}H_{41}F_3N_2O_8$ + Na: 697.3; 694.9 (11%, [2M + Ca]$^{2+}$); 687.6 (8%, [2,6-(2-Me-Bn)$_2$ + MeCN + Na]$^+$); 646.6 (28%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 419.1 (7%).

Butyl 4-O-(4-fluorophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-6-O-propylcarbamoyl-α,β-D-glucopyranoside (**17-2b3**). 6.2 mg (62%), colorless crystals; R_f (α) 0.35 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.30 min (64.2%, α); 9.72 min (9.3%, β); 11.02 min (3.9%); 11.18 min (6.9%, 2,6-(2-Me-Bn)$_2$); 11.53 min (3.4%); 12.65 min (4.6%). ESIMS: m/z 1232.0 (14%, [2M + Na]$^+$); 927.2 (6%, [3M + Ca]$^{2+}$); 712.6 (5%, [6-allophanate + Na]$^+$); 668.6 (10%, [M + MeCN + Na]$^+$); 646.5 (10%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 627.5 (100%, [M + Na]$^+$); calcd for $C_{32}H_{45}FN_2O_8$ + Na: 627.3; 624.8 (7%, [2M + Ca]$^{2+}$); 594.5 (7%, [2,4-(2-Me-Bn)$_2$ + Na]$^+$).

Butyl 6-O-(3-cyanophenylcarbamoyl)-4-O-(4-fluorophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-α,β-D-glucopyranoside (**17-3b3**). 6.4 mg (58%), colorless oil; R_f (α) 0.35 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.47 min (80.6%, α); 9.73 min (13.6%, β). ESIMS: m/z 686.6 (100%, [M + Na]$^+$); calcd for $C_{36}H_{32}FN_3O_8$ + Na: 686.3; 683.9 (23%, [2M + Ca]$^{2+}$); 646.5 (23%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 606.4 (6%); 454.5 (8%); 393.1 (34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, br, 1H, H-2 (CN-Ph)), 7.45 (dt, 1H, J_d 7.9 Hz, $J_t \approx$ 1.8 Hz, H-6 (CN-Ph)), 7.27–7.36 (m, o-H$_2$ (F-Ph), H-4 + H-5 (CN-Ph)), 7.12–7.22 (m, 4H, Me-Bn), 6.97 (mc, 2H, m-H2 (F-Ph)), 6.92 (s, br, 1H, CN-Ph-N**H**), 6.62 (s, br, 1H, F-Ph-N**H**), 4.92 (ψt, br, 1H, $J \approx$ 9.8 Hz, H-4), 4.76 (d, 1H, J_{gem} 12.1 Hz, OCH_2 (Me-Bn)), 4.67 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.61 (d, 1H, J_{gem} 12.1 Hz, OCH_2 (Me-Bn)), 4.34 (dd, 1H, J_{gem} 12.1 Hz, $J_{5,6a}$ 2.1 Hz, H-6a), 4.26 (dd, 1H, J_{gem} 12.1 Hz, $J_{5,6b}$ 4.7 Hz, H-6b), 3.92 (ddd, 1H, $J_{4,5}$ 10.1 Hz, $J_{5,6b}$ 4.7 Hz, $J_{5,6a}$ 2.1 Hz, H-5), 3.71–3.82 (m, 2H, H-3, OCH_2 (Pr)), 3.60 (dt, 1H, J_d 9.7 Hz, J_t 7.1 Hz, OCH_2 (Bu)), 3.37–3.55 (m, 3H, H-2, OCH_2 (Pr), OCH_2 (Bu), in this multiplet: 3.48 (dd, 1H, $J_{2,3}$ 9.5 Hz, $J_{1,2}$ 3.5 Hz, H-2), 2.35 (s, 3H, Ar-CH_3), 1.46–1.65 (m, 2-CH_2 (Pr), 2-CH_2 (Bu)), 1.24–1.43 (m, 2H, 3-CH_2 (Bu)), 0.89 (t, 3H, J 7.4 Hz, CH_3 (Bu)), 0.82 (t, 3H, J 7.5 Hz, CH_3 (Pr)).

Butyl 4-O-(4-fluorophenylcarbamoyl)-2-O-(2-methylbenzyl)-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-4b3**). 7.6 mg (68%), colorless crystals; R_f (α) 0.39/0.59 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.95 min (53.1%, α); 10.33 min (6.6%, β); 11.15 min (4.4%, 2,6-(2-Me-Bn)$_2$); 11.75 min (28.5%, 6-allophanate). ESIMS: m/z 836.7 (38%, [6-allophanate + Na]$^+$); 760.2 (6%, [6-allophanate + M + Ca]$^{2+}$); 689.7 (100%, [M + Na]$^+$); calcd for $C_{37}H_{47}FN_2O_8$ + Na: 689.3; 687.0 (8%, [2M + Ca]$^{2+}$); 646.5 (14%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$).

Butyl 4-O-(4-fluorophenylcarbamoyl)-2-O-(2-methylbenzyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-5b3**). 8.2 mg (71%), colorless crystals; R_f (α) 0.37 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.05 min (70.2%, α); 10.32 min (10.1%, β); 11.17 min (3.5%, 2,6-(2-Me-Bn)$_2$); 14.05 min (4.0%). ESIMS: m/z 1067.3 (12%, [3M + Ca]$^{2+}$); 720.5 (100%, [M + Na]$^+$); calcd for $C_{36}H_{44}FN_3O_{10}$ + Na: 720.3; 717.9 (46%, [2M + Ca]$^{2+}$); 646.5 (14%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 503.4 (6%); 410.1 (12%).

Isobutyl 2-O-butyl-6-O-(2,4-difluorophenylcarbamoyl)-3-O-propyl-4-O-(4-trifluoromethylphenylcarbamoyl)-α,β-D-glucopyranoside (**17-1c1**). 8.2 mg (66%), colorless crystals; R_f (α) 0.56 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.82 min (4.7%); 9.20 min (6.4%); 10.58 min (71.3%, α); 10.92 min (3.7%, β); 11.90 min (6.1%, 2,6-Bu$_2$); 12.57 min (4.2%). ESIMS: m/z 1084.5 (12%); 1035.3 (49%, [3M + Ca]$^{2+}$); 798.6

(14%, [2,6-[2,4-F_2PhNHCO)$_2$ + Na]$^+$); 766.6 (9%); 746.6 (8%); 740.5 (100%, [M + MeCN + Na]$^+$); 737.9 (14%, 2M + 2MeCN + Ca]$^{2+}$); 717.3 (32%, [2M + MeCN + Ca]$^{2+}$); 699.6 (63%, [M + Na]$^+$); calcd for $C_{32}H_{41}F_5N_2O_8$ + Na: 699.3; 696.9 (37%, [2M + Ca]$^{2+}$); 688.6 (13%); 641.5 (22%, [2,6-Bu_2 + MeCN + Na]$^+$); 600.5 (18%, [2,6-Bu_2 + Na]$^+$); 455.4 (27%); 441.1 (10%).

*Isobutyl 2-*O*-butyl-3-*O*-propyl-6-*O*-propylcarbamoyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-2c1**). 3.5 mg (31%), colorless wax; R_f (α) 0.40 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.27 min (8.0%); 10.08 min (73.2%, α); 10.52 min (7.3%, β); 11.78 min (11.4%, 2,6-Bu_2). ESIMS: *m*/*z* 1236.0 (29%, [2M + Na]$^+$); 930.3 (23%, [3M + Ca]$^{2+}$); 714.6 (15%, [6-allophanate + Na]$^+$); 670.6 (65%, [M + MeCN + Na]$^+$); 647.3 (32%, [2M + MeCN + Ca]$^{2+}$); 629.5 (100%, [M + Na]$^+$); calcd for $C_{29}H_{45}F_3N_2O_8$ + Na: 629.3; 626.9 (22%, [2M + Ca]$^{2+}$); 641.6 (15%, [2,6-Bu_2 + MeCN + Na]$^+$); 600.5 (12%, [2,6-Bu_2 + Na]$^+$); 558.5 (29%).

*Isobutyl 2-*O*-butyl-6-*O*-(3-cyanophenylcarbamoyl)-3-*O*-propyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-3c1**). 7.7 mg (63%), colorless crystals; R_f (α) 0.38 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.32 min (5.8%); 10.15 min (75.9%, α); 10.43 min (10.0%, β). ESIMS: *m*/*z* 1018.6 (35%, [3M + Ca]$^{2+}$); 729.6 (22%, [M + MeCN + Na]$^+$); 707.7 (7%); 688.6 (100%, [M + Na]$^+$); calcd for $C_{33}H_{42}F_3N_3O_8$ + Na: 688.3; 686.0 (77%, [2M + Ca]$^{2+}$); 405.7 (7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, br, 1H, H-2 (CN-Ph)), 7.43–7.56 (m, CF_3-Ph, H-6 (CN-Ph)), 7.30–7.37 (m, 2H, H-4 + H-5 (CN-Ph)), 6.94 (s, br, 1H, CN–Ph–N**H**), 6.84 (s, br, 1H, CF_3-Ph-N**H**), 4.90–4.97 (m, 2H, H-4, H-1), 4.39 (dd, 1H, J_{gem} 12.2 Hz, $J_{5,6a}$ 2.2 Hz, H-6a), 4.27 (dd, 1H, J_{gem} 12.2 Hz, $J_{5,6b}$ 4.4 Hz, H-6b), 3.96 (ddd, 1H, $J_{4,5}$ 10.3 Hz, $J_{5,6b}$ 4.4 Hz, $J_{5,6a}$ 2.2 Hz, H-5), 3.78 (dt, 1H, J_d 9.4 Hz, J_t 6.2 Hz, OCH_2 (Pr)), 3.68 (ψt, 1H, $J \approx 9.4$ Hz, H-3), 3.58 (mc, 2H, OCH_2 (Bu)), 3.47 (dt, br, 1H, $J_d \approx 9$ Hz, $J_t \approx 6.7$ Hz, OCH_2 (Pr)), 3.36–3.43 (m, 2H, H-2, OCH_2 (*i*-Bu)), 1.95 (mc, 1H, CH (*i*-Bu)), 1.42–1.58 (m, 2-CH_2 (Pr), 2-CH_2 (Bu)), 1.32–1.41 (m, 3-CH_2 (Bu)), 0.86–0.94 (m, 2 × CH_3 (*i*-Bu), CH_3 (Bu)), 0.79 (t, 3H, *J* 7.5 Hz, CH_3 (Pr)).

*Isobutyl 2-*O*-butyl-6-*O*-((*S*)-α-methylbenzylcarbamoyl)-3-*O*-propyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-4c1**). 4.5 mg (37%), colorless crystals; R_f (α/β) 0.47/0.66 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.28 min (3.9%); 10.70 min (38.7%, α); 10.97 min (6.7%, β); 11.07 min (6.3%); 11.87 min (3.7%, 2,6-Bu_2); 12.33 min (4.3%); 12.47 min (35.2%, 6-allophanate). ESIMS: *m*/*z* 838.7 (70%, [6-allophanate + Na]$^+$); 836.0 (7%, [2 × 6-allophanate + Ca]$^{2+}$); 762.4 (6%, [6-allophanate + M + Ca]$^{2+}$); 707.6 (7%); 691.6 (100%, [M + Na]$^+$); calcd for $C_{34}H_{47}F_3N_2O_8$ + Na: 691.3; 689.1 (6%, [2M + Ca]$^{2+}$).

*Isobutyl 2-*O*-butyl-6-*O*-(4-methyl-3-nitrophenylcarbamoyl)-3-*O*-propyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-5c1**). 7.4 mg (57%), colorless crystals; R_f (α) 0.47 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.55 min (4.8%); 10.68 min (69.9%, α); 10.98 min (9.0%, β); 11.08 min (5.6%); 11.92 min (4.1%, 2,6-Bu_2). ESIMS: *m*/*z* 1069.6 (18%, [3M + Ca]$^{2+}$); 763.5 (35%, [M + MeCN + Na]$^+$); 722.5 (100%, [M + Na]$^+$); calcd for $C_{33}H_{44}F_3N_3O_{10}$ + Na: 722.3; 720.0 (53%, [2M + Ca]$^{2+}$); 641.6 (16%, [2,6-Bu_2 + MeCN + Na]$^+$); 600.5 (14%, [2,6-Bu_2 + Na]$^+$); 592.5 (7%); 455.4 (8%).

*Isobutyl 6-*O*-(2,4-difluorophenylcarbamoyl)-2-*O*-(4-fluorobenzyl)-3-*O*-propyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-1c2**). 7.2 mg (56%), colorless crystals; R_f (α) 0.52 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.05 min (77.4%, α); 10.35 min (4.5%, β); 10.80 min (10.2%, 2,6-(4-F-Bn)$_2$). ESIMS: *m*/*z* 1113.7 (12%, [3M + Ca]$^{2+}$); 792.6 (95%, [M + MeCN + Na]$^+$); 751.4 (100%, [M + Na]$^+$); calcd for $C_{35}H_{38}F_6N_2O_8$ + Na: 751.2; 748.9 (15%, [2M + Ca]$^{2+}$); 745.6 (21%, [2,6-(4-F-Bn)$_2$ + MeCN + Na]$^+$); 704.6 (16%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 507.4 (10%).

*Isobutyl 2-*O*-(4-fluorobenzyl)-3-*O*-propyl-6-*O*-propylcarbamoyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-2c2**). 6.5 mg (56%), colorless crystals; R_f (α) 0.45 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.30 min (3.5%); 9.53 min (51.5%, α); 9.90 min (7.0%, β); 10.82 min (10.4%, 2,6-(4-F-Bn)$_2$); 11.07 min (5.6%); 13.67 min (3.5%). ESIMS: (*m*/*z*) 1008.4 (8%, [3M + Ca]$^{2+}$); 766.6 (12%, [6-allophanate + Na]$^+$); 722.6 (71%, [M + MeCN + Na]$^+$); 681.6 (100%, [M + Na]$^+$); calcd for $C_{32}H_{42}F_4N_2O_8$ + Na: 681.3; 679.0 (18%, [2M + Ca]$^{2+}$); 602.5 (9%, [2,4-(4-F-Bn)$_2$ + Na]$^+$); 476.4 (6%).

*Isobutyl 6-*O*-(3-cyanophenylcarbamoyl)-2-*O*-(4-fluorobenzyl)-3-*O*-propyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-3c2**). 7.8 mg (62%), colorless crystals; R_f (α) 0.41 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.60 min (77.3%, α); 9.87 min (10.2%, β); 10.78 min (4.1%, 2,6-(4-F-Bn)$_2$). ESIMS: *m*/*z* 1097.3 (8%, [3M + Ca]$^{2+}$); 781.6 (15%, [M + MeCN + Na]$^+$); 745.6 (10%, [2,6-(4-F-Bn)$_2$ + MeCN + Na]$^+$); 740.5 (100%, [M + Na]$^+$); calcd for $C_{36}H_{39}F_4N_2O_8$ + Na: 740.3; 738.2 (18%, [2M + Ca]$^{2+}$); 704.6 (8%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 610.4 (13%).

*Isobutyl 2-*O*-(4-fluorobenzyl)-6-*O*-((*S*)-α-methylbenzylcarbamoyl)-3-*O*-propyl-4-*O*-(4-trifluoromethylphenylcarbamoyl)-α,β-*D*-glucopyranoside* (**17-4c2**). 8.0 mg (63%), colorless crystals; R_f (α/β) 0.45/0.59 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.65 min (3.6%); 10.13 min (34.8%, α); 10.45 min (4.4%,

β); 10.78 min (4.1%, 2,6-(4-F-Bn_2)); 10.95 min (3.1%); 11.73 min (41.5%, 6-allophanate). ESIMS: *m/z* 890.6 (100%, [6-allophanate + Na]$^+$); 782.6 (13%, contains Cl); 743.5 (98%, [M + Na]$^+$); calcd for $C_{37}H_{44}F_4N_2O_8$ + Na: 743.3; 635.5 (8%).

Isobutyl 2-O-(4-fluorobenzyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-4-O-(4-trifluoromethylphenylcarbamoyl)-α,β-D-glucopyranoside (**17-5c2**). 6.8 mg (52%), colorless crystals; R_f (α) 0.45 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.17 min (77.3%, α); 10.42 min (9.1%, β); 10.78 min (6.5%, 2,6-(4-F-$Bn)_2$). ESIMS: *m/z* 1147.6 (8%, [3M + Ca]$^{2+}$); 890.6 (8%); 815.6 (25%, [M + MeCN + Na]$^+$); 774.5 (100%, [M + Na]$^+$); calcd for $C_{36}H_{41}F_4N_3O_{10}$ + Na: 774.3; 771.9 (26%, [2M + Ca]$^{2+}$); 745.5 (8%, [2,6-(4-F-$Bn)_2$ + MeCN + Na]$^+$); 743.5 (8%, cross contamination); 704.6 (8%, [2,6-(4-F-$Bn)_2$ + Na]$^+$); 507.4 (7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, 1H, $J_{2,6}$ 2.4 Hz, H-2 (3-NO_2-4-Me-Ph)), 7.38–7.55 (m, CF_3-Ph, H-6 (3-NO_2-4-Me-Ph)), 7.30 (mc, 2H, *o*-H_2 (F-Bn)), 7.20 (d, 1H, $J_{5,6}$ 8.2 Hz, H-5 (3-NO_2-4-Me-Ph)), 7.01 (mc, 2H, *m*-H_2 (F-Bn)), 6.82–6.85 (m, br, 2H, 2 × NH), 4.93 (ψt, 1H, $J \approx 10.0$ Hz, H-4), 4.68–4.73 (m, 2H, H-1, OCH_2 (F-Bn)), 4.58 (d, 1H, J_{gem} 12.0 Hz, OCH_2 (F-Bn)), 4.34 (dd, 1H, J_{gem} 12.3 Hz, $J_{5,6a}$ 2.5 Hz, H-6a), 4.28 (dd, 1H, J_{gem} 12.3 Hz, $J_{5,6b}$ 4.4 Hz, H-6b), 3.95 (ddd, 1H, $J_{4,5}$ 10.2 Hz, $J_{5,6b}$ 4.4 Hz, $J_{5,6a}$ 2.5 Hz, H-5), 3.73–3.81 (m, 2H, H-3, OCH_2 (Pr)), 3.46–3.55 (m, 2H, H-2, OCH_2 (Pr)), 3.36 (dd, 1H, J_{gem} 9.5 Hz, J_{vic} 7.5 Hz, OCH_2 (*i*-Bu)), 3.20 (dd, 1H, J_{gem} 9.5 Hz, J_{vic} 6.4 Hz, OCH_2 (*i*-Bu)), 2.51 (s, 3H, Ar-CH_3), 1.93 (mc, 1H, CH (*i*-Bu)), 1.50 (mc, 2-CH_2 (Pr)), 0.91 (t, 6H, *J* 6.5 Hz, 2 × CH_3 (*i*-Bu)), 0.80 (t, 3H, *J* 7.5 Hz, CH_3 (Pr)).

Isobutyl 6-O-(2,4-difluorophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-4-O-(4-trifluoromethylphenylcarbamoyl)-α,β-D-glucopyranoside (**17-1c3**). 10.3 mg (85%), colorless crystals; R_f (α) 0.56 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.57 min (73.2%, α); 10.87 min (5.4%, β); 11.55 min (6.7%); 11.80 min (7.1%, 2,6-(2-Me-$Bn)_2$). ESIMS: *m/z* 1107.6 (8%, [3M + Ca]$^{2+}$); 788.6 (16%, [M + MeCN + Na]$^+$); 747.5 (100%, [M + Na]$^+$); calcd for $C_{36}H_{41}F_5N_2O_8$ + Na: 747.3; 744.9 (14%, [2M + Ca]$^{2+}$); 737.6 (12%, [2,6-(2-Me-$Bn)_2$ + MeCN + Na]$^+$); 696.6 (30%, [2,6-(2-Me-$Bn)_2$ + Na]$^+$); 664.6 (10%, [2,4-(2-Me-$Bn)_2$ + Na]$^+$).

Isobutyl 2-O-(2-methylbenzyl)-3-O-propyl-6-O-propylcarbamoyl-4-O-(4-trifluoromethylphenylcarbamoyl)-α,β-D-glucopyranoside (**17-2c3**). 7.5 mg (69%), colorless crystals; R_f (α) 0.44 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.13 min (76.4%, α); 10.50 min (7.1%, β); 11.05 min (3.5%); 11.62 min (3.9%). ESIMS: *m/z* 1002.5 (10%, [3M + Ca]$^{2+}$); 762.6 (10%, [6-allophanate + Na]$^+$); 718.6 (10%, [M + MeCN + Na]$^+$); 696.6 (13%, [2,6-(2-Me-$Bn)_2$ + Na]$^+$); 677.7 (100%, [M + Na]$^+$); calcd for $C_{33}H_{45}F_3N_2O_8$ + Na: 677.3; 675.0 (16%, [2M + Ca]$^{2+}$); 594.5 (13%, [2,4-(2-Me-$Bn)_2$ + Na]$^+$); 472.4 (6%).

Isobutyl 6-O-(3-cyanophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-4-O-(4-trifluoromethylphenylcarbamoyl)-α,β-D-glucopyranoside (**17-3c3**). 7.9 mg (66%), colorless crystals; R_f (α) 0.42 (4:1 hexanes–EtOAc); (713.7). HPLC–MS (column B, gradient B): t_R (*m/z*) 10.15 min (74.6%; 736.5, [M(α) + Na]$^+$); 10.40 min (10.3%; 736.5, [M(β) + Na]$^+$); 11.02 min (4.7%; 736.5, [4,6-(4-CF_3-PhNHCO)$_2$(α) + Na]$^+$); 11.75 min (3.2%; 696.7, [2,6-(2-Me-$Bn)_2$(α) + Na]$^+$). ESIMS: *m/z* 1090.6 (7%, [3M + Ca]$^{2+}$); 736.5 (100%, [M + Na]$^+$); calcd for $C_{37}H_{42}F_3N_3O_8$ + Na: 736.3; 734.0 (13%, [2M + Ca]$^{2+}$); 696.6 (34%, [2,6-(2-Me-$Bn)_2$ + Na]$^+$); 677.6 (12%, cross contamination); 653.6 (5%, [2,4-(2-Me-$Bn)_2$ + Na]$^+$).

Isobutyl 2-O-(2-methylbenzyl)-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-4-O-(4-trifluoromethylphenylcarbamoyl)-α,β-D-glucopyranoside (**17-4c3**). 8.5 mg (71%), colorless crystals; R_f (α/β) 0.47/0.60 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 7.13 min (4.4%); 10.67 min (59.9%, α); 11.00 min (7.5%, β); 11.78 min (4.7%, 2,6-(2-Me-$Bn)_2$); 12.25 min (14.7%, 6-allophanate). ESIMS: *m/z* 886.6 (28%, [6-allophanate + Na]$^+$); 782.6 (7%); 739.5 (100%, [M + Na]$^+$); calcd for $C_{38}H_{47}F_3N_2O_8$ + Na: 739.3; 696.6 (7%, [2,6-(2-Me-$Bn)_2$ + Na]$^+$); 656.6 (7%, [2,4-(2-Me-$Bn)_2$ + Na]$^+$); 635.5 (12%, [2-OH + Na]$^+$).

Isobutyl 2-O-(2-methylbenzyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-4-O-(4-trifluoromethylphenylcarbamoyl-α,β-D-glucopyranoside (**17-5c3**). 7.6 mg (61%), colorless crystals; R_f (α) 0.42 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.68 min (76.0%, α); 10.95 min (7.9%, β); 11.08 min (3.7%); 11.82 min (6.4%, 2,6-(2-Me-$Bn)_2$). ESIMS: *m/z* 1141.6 (7%, [3M + Ca]$^{2+}$); 770.5 (100%, [M + Na]$^+$); calcd for $C_{37}H_{44}F_3N_3O_{10}$ + Na: 770.3; 767.8 (19%, [2M + Ca]$^{2+}$); 739.5 (8%, cross contamination); 737.5 (8%, [2,6-(2-Me-$Bn)_2$ + MeCN + Na]$^+$); 696.6 (27%, [2,6-(2-Me-$Bn)_2$ + Na]$^+$).

Isobutyl 2-O-butyl-4-O-(4-chlorophenylcarbamoyl)-6-O-(2,4-difluorophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-1d1**). 7.2 mg (61%), colorless crystals; R_f (α) 0.53 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.63 min (5.8%); 9.07 min (7.3%); 10.50 min (75.7%, α); 10.85 min (4.7%, β); 11.90 min (3.8%, 2,6-Bu_2). ESIMS: *m/z* 984.8 (6%, [3M + Ca]$^{2+}$); 764.4 (13%, [2,6-(2,4-F_2-PhNHCO)$_2$ + Na]$^+$); 706.6 (84%, [M + MeCN + Na]$^+$); 665.5 (100%, [M + Na]$^+$); calcd for $C_{31}H_{41}ClF_2N_2O_8$ + Na: 665.3; 607.5 (16%, [2,6-Bu_2 + MeCN + Na]$^+$); 566.5 (28%, [2,6-Bu_2 + Na]$^+$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, br, 1H, H-2 (2,4-F_2-PhN**H**)), 7.21–7.33 (m, Cl–Ph, H-6 (2,4-F_2-Ph)), 6.77–6.85 (m, H-3 + H-5 (2,4-F_2-Ph)), 6.63 (s, br, 1H, Cl-Ph-N**H**), 4.84–4.91 (m, 2H, H-1, H-4), 4.36 (dd, 1H, J_{gem} 12.2 Hz, $J_{5,6a}$ 2.4 Hz, H-6a), 4.26 (dd, 1H,

J_{gem} 12.2 Hz, $J_{5,6b}$ 5.3 Hz, H-6b), 3.95 (ddd, 1H, $J_{4,5}$ 10.2 Hz, $J_{5,6b}$ 5.3 Hz, $J_{5,6a}$ 2.4 Hz, H-5), 3.76 (dt, 1H, J_d 9.0 Hz, J_t 6.3 Hz, OCH_2 (Pr)), 3.66 (ψt, 1H, $J \approx 9.5$ Hz, H-3), 3.58 (mc, 2H, OCH_2 (Bu)), 3.47 (dt, br, 1H, $J_d \approx 9.0$ Hz, $J_t \approx 6.7$ Hz, OCH_2 (Pr, 1H)), 3.36–3.42 (m, 2H, H-2, OCH_2 (*i*-Bu)), 3.27 (dd, 1H, J_{gem} 9.6 Hz, J_{vic} 6.3 Hz, OCH_2 (*i*-Bu)), 1.95 (mc, 1H, CH (*i*-Bu)), 1.43–1.58 (m, 4H, 2-CH_2 (Pr), 2-CH_2 (Bu)), 1.36 (mc, 2H, 3-CH_2 (Bu)), 0.87–0.92 (m, 9H, 2 × CH_3 (*i*-Bu), CH_3 (Bu)), 0.80 (t, 3H, *J* 7.4 Hz, CH_3 (Pr)).

Isobutyl 2-O-*butyl-4*-O-*(4-chlorophenylcarbamoyl)-3*-O-*propyl-6*-O-*propylcarbamoyl-α,β*-D-*glucopyranoside* (**17-2d1**). 4.3 mg (41%), colorless crystals; R_f (α) 0.39 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.90 min (70.6%, α); 10.35 min (9.7%, β); 11.77 min (6.7%); 11.87 min (5.3%, 2,6-Bu_2). ESIMS: *m*/*z* 1167.8 (15%, $[2M + Na]^+$); 680.7 (12%, [6-allophanate + Na]$^+$); 636.5 (36%, $[M + MeCN + Na]^+$); 595.5 (100%, $[M + Na]^+$); calcd for $C_{28}H_{45}ClN_2O_8 + Na$: 595.3; 566.5 (6%, [2,6-Bu_2 + Na]$^+$); 424.5 (8%).

Isobutyl 2-O-*butyl-4*-O-*(4-chlorophenylcarbamoyl)-6*-O-*(3-cyanophenylcarbamoyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-3d1**). 6.8 mg (58%), colorless crystals; R_f (α) 0.38 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 8.15 min (5.9%); 10.03 min (70.2%, α); 10.33 min (10.8%, β); 11.00 min (3.3%). ESIMS: *m*/*z* 1285.8 (23%, $[2M + Na]^+$); 1197.9 (6%, [2,6-Bu_2 + M + Na]$^+$); 695.6 (8%, $[M + MeCN + Na]^+$); 654.5 (100%, $[M + Na]^+$); calcd for $C_{32}H_{42}ClN_3O_8 + Na$: 654.3; 652.3 (9%, $[2M + Ca]^{2+}$); 607.5 (14%, [2,6-Bu_2 + MeCN + Na]$^+$); 566.5 (25%, [2,6-Bu_2 + Na]$^+$).

Isobutyl 2-O-*butyl-4*-O-*(4-chlorophenylcarbamoyl)-6*-O-*((S)-α-methylbenzylcarbamoyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-4d1**). 4.3 mg (37%), colorless oil; R_f (α/β) 0.47/0.65 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.63 min (37.4%, α); 10.97 min (10.8%, β); 11.97 min (4.7%, 2,6-Bu_2); 12.58 min (38.6%, 6-allophanate). ESIMS: *m*/*z* 1291.9 (5%, $[2M + Na]^+$); 895.6 (5%); 804.7 (75%, [6-allophanate + Na]$^+$); 657.6 (100%, $[M + Na]^+$); calcd for $C_{33}H_{47}ClN_2O_8 + Na$: 657.3; 566.6 (6%, [2,6-Bu_2 + Na]$^+$); 330.3 (6%).

Isobutyl 2-O-*butyl-4*-O-*(4-chlorophenylcarbamoyl)-6*-O-*(4-methyl-3-nitrophenylcarbamoyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-5d1**). 6.9 mg (56%), colorless crystals; R_f (α) 0.49 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.48 min (4.9%); 10.62 min (71.0%, α); 10.90 min (13.4%, β); 12.03 min (3.6%). ESIMS: *m*/*z* 729.5 (14%, $[M + MeCN + Na]^+$); 688.6 (100%, $[M + Na]^+$); calcd for $C_{32}H_{44}ClN_3O_{10} + Na$: 688.3; 686.6 (9%, $[2M + Ca]^{2+}$); 607.5 (12%, [2,6-Bu_2 + MeCN + Na]$^+$); 566.6 (22%, [2,6-Bu_2 + Na]$^+$).

Isobutyl 4-O-*(4-chlorophenylcarbamoyl)-6*-O-*(2,4-difluorophenylcarbamoyl)-2*-O-*(4-fluorobenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-1d2**). 7.7 mg (63%), colorless crystals; R_f (α) 0.43 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.93 min (75.5%, α); 10.22 min (4.3%, β); 10.75 min (7.8%, 2,6-(4-F-Bn)$_2$); 11.12 min (5.3%). ESIMS: *m*/*z* 1062.7 (6%, $[3M + Ca]^{2+}$); 758.4 (45%, $[M + MeCN + Na]^+$); 717.5 (100%, $[M + Na]^+$); calcd for $C_{34}H_{38}ClF_3N_2O_8 + Na$: 717.2; 715.7 (8%, $[2M + Ca]^{2+}$); 711.5 (13%, [2,6-(4-F-Bn)$_2$ + MeCN + Na]$^+$); 670.5 (19%, [2,6-(4-F-Bn)$_2$ + Na]$^+$).

Isobutyl 4-O-*(4-chlorophenylcarbamoyl)-2*-O-*(4-fluorobenzyl)-3*-O-*propyl-6*-O-*propylcarbamoyl-α,β*-D-*glucopyranoside* (**17-2d2**). 7.0 mg (64%), colorless wax; R_f (α) 0.37 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.40 min (61.4%, α); 9.75 min (6.8%, β); 10.78 min (10.2%, 2,6-(4-F-Bn)$_2$); 11.07 min (9.7%); 14.05 min (4.6%). ESIMS: *m*/*z* 1271.8 (11%, [2M + Na]$^+$); 732.5 (18%, [6-allophanate + Na]$^+$); 688.6 (37%, $[M + MeCN + Na]^+$); 670.5 (7%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 647.5 (100%, $[M + Na]^+$); calcd for $C_{31}H_{42}ClFN_2O_8 + Na$: 647.3; 602.5 (7%, [2,4-(4-F-Bn)$_2$ + Na]$^+$); 476.4 (8%).

Isobutyl 4-O-*(4-chlorophenylcarbamoyl)-6*-O-*(3-cyanophenylcarbamoyl)-2*-O-*(4-fluorobenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-3d2**). 6.9 mg (57%), colorless crystals; R_f (α) 0.37 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.52 min (73.5%, α); 9.72 min (11.7%, β); 10.72 min (5.1%, 2,6-(4-F-Bn)$_2$). ESIMS: *m*/*z* 747.4 (6%, $[M + MeCN + Na]^+$); 706.5 (100%, $[M + Na]^+$); calcd for $C_{35}H_{39}ClFN_3O_8 + Na$: 706.2; 704.7 (8%, $[2M + Ca]^{2+}$); 670.5 (21%, [2,6-(4-F-Bn)$_2$ + Na]$^+$).

Isobutyl 4-O-*(4-chlorophenylcarbamoyl)-2*-O-*(4-fluorobenzyl)-6*-O-*((S)-α-methylbenzylcarbamoyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-4d2**). 7.4 mg (61%), colorless crystals; R_f (α/β) 0.39/0.53 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.07 min (37.8%, α); 10.37 min (5.0%, β); 10.75 min (5.6%, 2,6-(4-F-Bn)$_2$); 11.77 min (42.6%, 6-allophanate). ESIMS: *m*/*z* 856.6 (93%, [6-allophanate + Na]$^+$); 709.5 (100%, $[M + Na]^+$); calcd for $C_{36}H_{44}ClFN_2O_8 + Na$: 709.3; 670.5 (7%, [2,6-(4-F-Bn)$_2$ + Na]$^+$); 247.3 (6%).

Isobutyl 4-O-*(4-chlorophenylcarbamoyl)-2*-O-*(4-fluorobenzyl)-6*-O-*(4-methyl-3-nitrophenylcarbamoyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-5d2**). 7.0 mg (56%), yellowish crystals; R_f (α) 0.38 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.12 min (73.8%, α); 10.33 min (11.2%, β); 10.47 min (3.3%); 10.75 min (6.9%, 2,6-(4-F-Bn)$_2$). ESIMS: *m*/*z* 781.5 (11%, $[M + MeCN + Na]^+$); 740.4 (100%, $[M + Na]^+$); calcd for $C_{35}H_{41}ClFN_3O_{10}$ + Na: 740.2; 738.6 (11%, $[2M + Ca]^{2+}$); 670.6 (19%, [2,6-(4-F-Bn)$_2$ + Na]$^+$).

Isobutyl 4-O-*(4-chlorophenylcarbamoyl)-6*-O-*(2,4-difluorophenylcarbamoyl)-2*-O-*(2-methylbenzyl)-3*-O-*propyl-α,β*-D-*glucopyranoside* (**17-1d3**). 9.4 mg (82%), colorless crystals; R_f (α) 0.50 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.50 min (66.3%, α); 10.78 min (3.8%, β); 11.58 min (9.2%); 11.81 min (8.2%, 2,6-(2-Me-Bn)$_2$). ESIMS: *m*/*z* 754.4 (8%, [M +

MeCN + Na]$^+$); 713.5 (100%, [M + Na]$^+$); calcd for $C_{35}H_{41}ClF_2N_2O_8$ + Na: 713.2; 711.5 (8%, [2M + Ca]$^{2+}$); 703.6 (6%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 662.6 (29%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$).

Isobutyl 4-O-(4-chlorophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-6-O-propylcarbamoyl-α,β-D-glucopyranoside (**17-2d3**). 6.1 mg (59%), colorless crystals; R_f (α) 0.39 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 9.98 min (69.8%, α); 10.35 min (9.0%, β); 11.63 min (4.4%); 11.82 min (7.8%, 2,6-(2-Me-Bn)$_2$). ESIMS: *m/z* 1263.9 (15%, [2M + Na]$^+$); 728.6 (10%, [6-allophanate + Na]$^+$); 784.6 (12%, [M + MeCN + Na]$^+$); 662.6 (14%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 643.5 (100%, [M + Na]$^+$); calcd for $C_{32}H_{45}ClN_2O_8$ + Na: 643.3; 641.6 (7%, [2M + Ca]$^{2+}$); 594.5 (13%, [2,4-(2-Me-Bn)$_2$ + Na]$^+$); 472.4 (10%).

Isobutyl 4-O-(4-chlorophenylcarbamoyl)-6-O-(3-cyanophenylcarbamoyl)-2-O-(2-methylbenzyl)-3-O-propyl-α,β-D-glucopyranoside (**17-3d3**). 7.9 mg (70%), colorless crystals; R_f (α) 0.39 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.12 min (80.9%, α); 10.33 min (12.1%, β); 11.03 min (3.4%); 11.83 min (3.6%, 2,6-(2-Me-Bn)$_2$). ESIMS: *m/z* 702.5 (100%, [M + Na]$^+$); calcd for $C_{36}H_{42}ClN_3O_8$ + Na: 702.2; 700.6 (8%, [2M + Ca]$^{2+}$); 662.6 (35%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 653.5 (6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, br, 1H, H-2 (CN-Ph)), 7.44 (dt, 1H, J_d 7.7 Hz, $J_t \approx 1.9$ Hz, H-6 (CN–Ph)), 7.08–7.37 (m, Cl-Ph, Me-Bn, H-4 + H-5 (CN-Ph)), 6.86 (s, br, 1H, CN-Ph-N**H**), 6.66 (s, br, 1H, Cl-Ph-N**H**), 4.92 (ψt, br, 1H, $J \approx 9.7$ Hz, H-4), 4.74 (d, 1H, J_{gem} 12.1 Hz, OCH_2 (Me-Bn)), 4.69 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.61 (d, 1H, J_{gem} 12.1 Hz, OCH_2 (Me-Bn)), 4.34 (dd, 1H, J_{gem} 12.0 Hz, $J_{5,6a}$ 2.3 Hz, H-6a), 4.26 (dd, 1H, J_{gem} 12.0 Hz, $J_{5,6b}$ 4.4 Hz, H-6b), 3.93 (ddd, 1H, $J_{4,5}$ 10.2 Hz, $J_{5,6b}$ 4.4 Hz, $J_{5,6a}$ 2.3 Hz, H-5), 3.71–3.82 (m, 2H, H-3, OCH_2 (Pr)), 3.46–3.53 (m, 2H, H-2, OCH_2 (Pr)), 3.34 (dd, 1H, J_{gem} 9.4 Hz, J_{vic} 7.5 Hz, OCH_2 (*i*-Bu)), 3.17 (dd, 1H, J_{gem} 9.4 Hz, J_{vic} 6.2 Hz, OCH_2 (*i*-Bu)), 2.34 (s, 3H, Ar-CH_3), 1.92 (mc, 1H, CH (*i*-Bu)), 1.51 (mc, 2H, 2-CH_2 (Pr)), 0.88–0.93 (m, 6H, 2 × CH_3 (*i*-Bu)), 0.80 (t, 3H, *J* 7.4 Hz, CH_3 (Pr)).

Isobutyl 4-O-(4-chlorophenylcarbamoyl)-2-O-(2-methylbenzyl)-6-O-((S)-α-methylbenzylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-4d3**). 7.6 mg (67%), colorless crystals; R_f (α/β) 0.44/0.58 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.60 min (58.7%, α); 10.93 min (8.7%, β); 11.80 min (5.0%, 2,6-(2-Me-Bn)$_2$); 12.33 min (20.0%, 6-allophanate). ESIMS: *m/z* 852.6 (33%, [6-allophanate + Na]$^+$); 705.6 (100%, [M + Na]$^+$); calcd for $C_{37}H_{47}ClN_2O_8$ + Na: 705.3; 662.6 (10%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$); 656.6 (10%, [2,4-(2-Me-Bn)$_2$ + Na]$^+$).

Isobutyl 4-O-(4-chlorophenylcarbamoyl)-2-O-(2-methylbenzyl)-6-O-(4-methyl-3-nitrophenylcarbamoyl)-3-O-propyl-α,β-D-glucopyranoside (**17-5d3**). 7.4 mg (62%), yellowish crystals; R_f (α) 0.42 (4:1 hexanes–EtOAc); HPLC (column B, gradient B): t_R 10.67 min (69.7%, α); 10.87 min (14.0%, β); 11.80 min (5.6%, 2,6-(2-Me-Bn)$_2$); 13.82 min (4.4%). ESIMS: (*m/z*) 736.5 (100%, [M + Na]$^+$); calcd for $C_{36}H_{44}ClN_3O_{10}$ + Na: 736.3; 734.6 (9%, [2M + Ca]$^{2+}$); 705.6 (7%, cross contamination); 703.6 (5%, [2,6-(2-Me-Bn)$_2$ + MeCN + Na]$^+$); 687.6 (7%, [2,4-(2-Me-Bn)$_2$ + Na]$^+$); 662.6 (33%, [2,6-(2-Me-Bn)$_2$ + Na]$^+$).

Acknowledgements

T.O. is grateful to the *Fonds der Chemischen Industrie* for a Kekulé-fellowship. We thank Dr. D. Schollmeyer for the X-ray crystallographic analysis of compound **16-a2**.

References

1. Hirschmann, R.; Nicolaou, K. C.; Pietranico, S.; Salvino, J.; Leahy, E. M.; Shakespeare, W. C.; Sprenler, P. S.; Hamley, P.; Smith, A. B., III; Reisine, T.; Raynor, K.; Donaldson, C.; Vale, W.; Maechler, L.; Freidinger, R. M.; Cascieri, M. R.; Strader, C. D. *J. Am. Chem. Soc.* **1993**, *115*, 12550–12568.
2. Hirschmann, R.; Hynes, J.; Cichy-Knight, M. A.; van Rijn, R. D.; Sprengeler, P. A.; Spoors, P. G.; Shakespeare, W. C.; Pietranico-Cole, S.; Barbosa, J.; Liu, J.; Yao, W.; Rohrer, S.; Smith, A. B., III *J. Med. Chem.* **1998**, *41*, 1382–1391.
3. See also: (a) Dinh, T. Q.; Smith, C. D.; Du, X.; Armstrong, R. W. *J. Med. Chem.* **1998**, *41*, 981–987;
(b) Papageorgiou, C.; Haltiner, R.; Bruns, C.; Petcher, T. J. *Bioorg. Med. Chem. Lett.* **1992**, *2*, 135–140;
(c) Nicolaou, K. C.; Trujillo, J. I.; Chibale, K. *Tetrahedron* **1997**, *53*, 8751–8778;
(d) Von Roedern, E.; Lohof, E.; Hessler, G.; Hoffmann, M.; Kessler, H. *J. Am. Chem. Soc.* **1996**, *118*, 10156–10167;
(e) Chakraborty, T. K.; Jayaprakash, S.; Diwan, P. V.; Nagaraj, R.; Jampani, S. R. B.; Kunwar, A. C. *J. Am. Chem. Soc.* **1998**, *120*, 12962–12963;
(f) Sofia, M. J.; Hunter, R.; Chan, T. Y.; Vaughan, A.; Dulina, R.; Wang, H. M.; Gange, D. *J. Org. Chem.* **1998**, *63*, 2802–2803.
4. For a recent overview of multivalent templates, see: Oliver, S. F.; Abell, C. *Curr. Opin. Chem. Biol.* **1999**, *3*, 299–306.
5. Combinatorial synthesis of carbohydrates: Schweizer, F.; Hindsgaul, O. *Curr. Opin. Chem. Biol.* **1999**, *3*, 291–298.
6. For a combinatorial synthesis of oligosaccharides in solution, see: Wong, C.-H.; Ye, X.-S.; Zhang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 7137–7138.
7. For a different thioglycoside anchor, see: Rademann, J.; Schmidt, R. R. *Tetrahedron Lett.* **1996**, *37*, 3989–3990.
8. Wunberg, T.; Kallus, C.; Opatz, T.; Schmidt, W.; Henke, S.; Kunz, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2503–2505.
9. Kallus, C.; Opatz, T.; Wunberg, T.; Schmidt, W.; Henke, S.; Kunz, H. *Tetrahedron Lett.* **1999**, *40*, 7783–7786.
10. (a) Takeo, K.; Nakaji, T.; Shinmitsu, K. *Carbohydr. Res.* **1984**, *133*, 275–288;

(b) Itoh, Y.; Tejima, S. *Chem. Pharm. Bull.* **1983**, *31*, 1632–1640.
11. Shinkai, I.; Liu, T.; Reamer, R.; Sletzinger, M. *Synthesis* **1980**, 924–926.
12. Szurmai, Z.; Lipták, A.; Snatzke, G. *Carbohydr. Res.* **1990**, *200*, 201–208.
13. (a) Hünig, S.; Müller, H. R.; Thier, W. *Angew. Chem.* **1965**, *77*, 368–377;
(b) Thiele, J. *Liebigs Ann. Chem.* **1892**, *271*, 127–136.
14. (a) Weygand, F.; Hoffmann, D.; Wünsch, E. *Z. Naturforschung* **1966**, *21b*, 426–428;
(b) Anderson, G. W.; Zimmermannn, J. E.; Callahan, F. M. *J. Am. Chem. Soc.* **1964**, *86*, 1839–1842.
15. König, W.; Geiger, R. *Chem. Ber.* **1970**, *103*, 788–789.
16. Lemieux, R. U.; Hendriks, K. B.; Stick, R. V.; James, K. J. *J. Am. Chem. Soc.* **1975**, *97*, 4056–4062.
17. Kogon, I. C. *J. Am. Chem. Soc.* **1956**, *78*, 4911–4914.
18. Opatz, T.; Kunz, H. *Tetrahedron Lett.* **2000**, *41*, 10185–10188.
19. Habermann, J.; Kunz, H. *J. Prakt. Chem.* **1998**, *340*, 233–239.