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Maltose and Maltotriose Derivatives as Potential Inhibitors of the Maltose-Binding Protein

Heinz Malik,[a] Winfried Boos,[b] and Richard R. Schmidt*[a]

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Inhibition of substrate binding to maltose-binding protein (MBP) was investigated with structurally modified maltose and maltotriose derivatives that were designed based on the X-ray analysis of maltose and maltotriose bound to MBP. In maltose, positions 1a, 2a, 2b, 4b and 6b were modified (compounds **1**–**3**, **18a**, **b**, **28a**–**c**, **39** and **44**) of which only the trivalent maltose derivatives **39** and **44** exhibited high affinity to MBP. Maltotriose modifications were carried out at position 6a and 6c (compounds **45**–**51**). Compound **50**, possessing a 6a-*O*-propyl group, and compound **51**, where the 6c-hydroxy group is replaced by bromide, showed higher affinity to MBP than the parent maltotriose. Hence, the structurally quite different compounds **39**, **50** and **51** are important lead compounds for further studies.
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Introduction

The active transport of substances through biological membranes is of great importance for the uptake, for instance, of nutrients and signalling molecules. The ATP-binding-cassette (ABC) transport proteins serve this role.[1] The ABC transporter for maltose in *Escherichia coli* is supported by a maltose-binding protein (MBP) that is located in-between the (outer) cell wall and the (inner) plasma membrane. MBPs bind maltose (and also maltotriose and higher oligomers) that have passed the cell wall via maltoporin and provide it to the ABC maltose transport system in the plasma membrane.[1–3] Hence, blocking of this transport system by inhibiting maltose and maltodextrin binding to MBP could perhaps lead to a new type of antibacterials. Therefore, we investigated variously modified maltose and maltotriose derivatives for their inhibition of maltose and maltotriose binding to MBP. The modifications are based on X-ray analyses of substrate binding to MBP.[4,5] Oxidation and reduction products of the reducing end of maltose and higher analogs were already investigated as inhibitors of maltose binding to MBP, however they did not reach the affinity of maltose.[6] Also maltotriose analogs with a spacer group for the middle glycosyl residue were prepared and investigated for this purpose[7] and the α-glucosidase inhibitor acarbose, formally a maltotetraose analog, was shown to possess affinity to MBP as well.[8]

[a] Fachbereich Chemie, Universität Konstanz,
Fach M 725, 78457 Konstanz, Germany
Fax: + 49-7531-883135
E-mail: Richard.Schmidt@uni-konstanz.de
[b] Fachbereich Biologie, Universität Konstanz,
78457 Konstanz, Germany

Results and Discussion

Modifications of Maltose

Maltose bound to MBP shows in the X-ray analysis[4] Glu^{111} close to the 2a-hydroxy group, Asp^{65} close to the 2b-hydroxy group and Glu^{153} close to the 4b-hydroxy group. Therefore, it was decided to introduce at these positions amino groups. Hence, compounds **1**–**3** (Scheme 1) were target molecules. It was also speculated that, because of structural similarity, aminoglycoside antibiotics like neamycine, streptomycine, kanamycine, gentamycine and amikacine may act as MBP inhibitors. Therefore, they were included in this study.

For the synthesis of compounds **1**–**3**, known glycosyl donor **4**[9] and glycosyl donor **5** were required. **5** was readily obtained from 6-*O*-unportected 2-azido-2-deoxy-glucopyranoside **9**.[10,11] The 6-hydroxy group was replaced by the azido group under Mitsunobu conditions[12] affording 2,6-diazido derivative **10**. *O*-Desilylation with HF–pyridine complex furnished 1-*O*-unprotected **11** that gave with trichloroacetonitrile in the presence of DBU as base[13] the desired *O*-glucosyl trichloroacetimidate **5**. As glycosyl acceptors 4-*O*-unprotected glucopyranosides **6**–**8** were selected, which have been previously prepared.[14–16]

Glycosylation of acceptor **6** with donor **4** in ether and triflic acid (0.05 equiv.) as catalyst at room temperature[17] afforded the desired α-linked disaccharide **12** in 69% yield. Hence, with the selected electron-withdrawing protecting group pattern in donor **4** and the selected reaction conditions α-linkage in the disaccharide could be readily obtained.[13] Cleavage of the *O*-acetyl groups of **12** under Zemplén conditions[18] led to compound **13** that gave on hydrogenolysis with Pearlman's catalyst[19] target molecule

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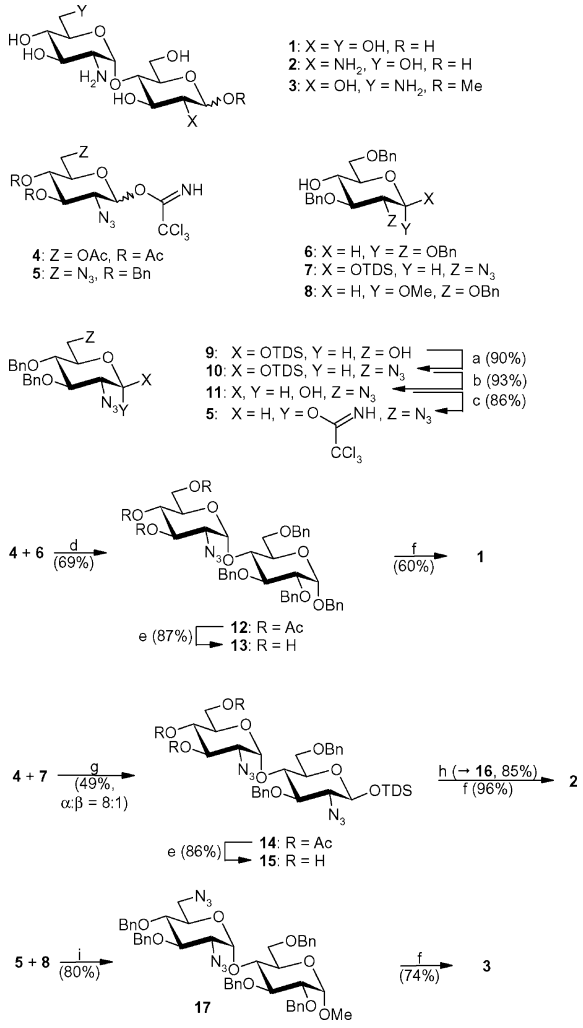

Scheme 1. Structure and synthesis of target molecules **1**–**3**. *Reagents and conditions:* a) PPh_3, DEAD, HN_3, C_6H_6, THF; b) HF, Pyr; c) CCl_3CN, DBU, CH_2Cl_2; d) TfOH (0.05 equiv.), Et_2O, room temp.; e) NaOMe, MeOH; f) $Pd(OH)_2/C$, H_2, MeOH, HCl/Et_2O; g) TBDMSOTf (0.01 equiv.), Et_2O, room temp.; h) TBAF, HOAc, THF; i) TMSOTf (0.01 equiv.), Et_2O, room temp.

1; the structural assignment was confirmed by comparison with previously reported physical data.[20] Glycosylation of acceptor **7** with **4** in ether with *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) as catalyst at room temperature afforded an 8:1 α/β-mixture of which the desired α-anomer **14** could be readily separated. In order to obtain this result, variation of the catalyst and solvent had to be investigated, thus exhibiting the different influence of acceptors **6** and **7** on the glycosylation result. *O*-Deacetylation of **14** (→ **15**), then cleavage of the 1-*O*-thexyl-dimethylsilyl (TDS) group with tetrabutylammonium fluoride (TBAF) in the presence of acetic acid in THF (→**16**) afforded after hydrogenolysis target molecule **2** as a 3:2-mixture of anomers in high overall yield. Glycosylation of acceptor **8** with glycosyl donor **5** in ether with TMSOTf as catalyst at room temperature[13] furnished the desired α-linked disaccharide **17** in 80% yield; no β-anomer was found. Hydrogenolysis under the above-described conditions led to target molecule **3**. The ^1H NMR spectrum confirmed the α-linkages ($J_{1a,2a} = J_{1b,2b} = 3.7$ Hz).

Binding studies to MBP with compounds **1**–**3** showed very low affinity compared with maltose that binds in the low μmolar range (see below, Table 1). Similar results were obtained for the above-mentioned aminoglycoside antibiotics (not shown). Hence, strengthening ionic interactions to increase binding to MBP was not successful. Therefore, it was decided to replace the 4b-hydroxy group of maltose by aryl–O–CH_2CH_2–O residues. This way, glucosyl residues could be mimicked with binding affinities in the range of maltotriose that has a sub-μmolar K_d value (Table 1). This group could also strongly inhibit transportation by the ABC maltose transport system.

Table 1. Binding affinities of the target molecules to MBP compared to maltose and maltotriose.

Compound	IC50 [μM]	K_d [μM]
Maltose	–	1–4
1	1000	850
2	> 1000	850
3	> 500	> 450
18a	> 750	> 450
18b	> 750	> 450
19	60	44
20	500	366
28a	260	160
28b	450	275
28c	125	76
29	96	58
39	1.5	0.91
44	2.4	1.4
Maltotriose	0.19	0.11
45	1.5	0.91
46	1.5	0.91
47	31	18
48	1.4	0.85
49	0.70	0.42
50	0.11	0.07
51	0.07	0.04

The synthesis of target molecules **18a**,**b** (Scheme 2) was performed via methyl maltoside **19**,[21] its benzylidene derivative **20**,[22] and the benzylation product **21**,[23] which was transformed into the 4b-*O*-unprotected maltoside **22**[24] following literature procedures. Alkylation of **22** with 8-(triisopropylsilyloxy)-3,6-dioxa-octyl bromide (**23**) with sodium hydride as base in the presence of tetrabutylammonium iodide (TBAI) as promoter in DMF afforded compound **24**. Cleavage of the silyl group with TBAF in THF (→**25**) and then replacement of the ω-hydroxy group by bromide with Appel's reagent[25] led to intermediate **26**. Reaction of **26** with 3,5-dimethoxyphenol with NaH/TBAI in DMF gave aryl ether derivative **27a** in good yield. Similarly, from **26** and 3,5-diisopropyloxyphenol analog **27b** was generated. Hydrogenolytic *O*-debenzylation of **27a** and **27b** as described above led to target molecules **18a** and **18b**, respectively.

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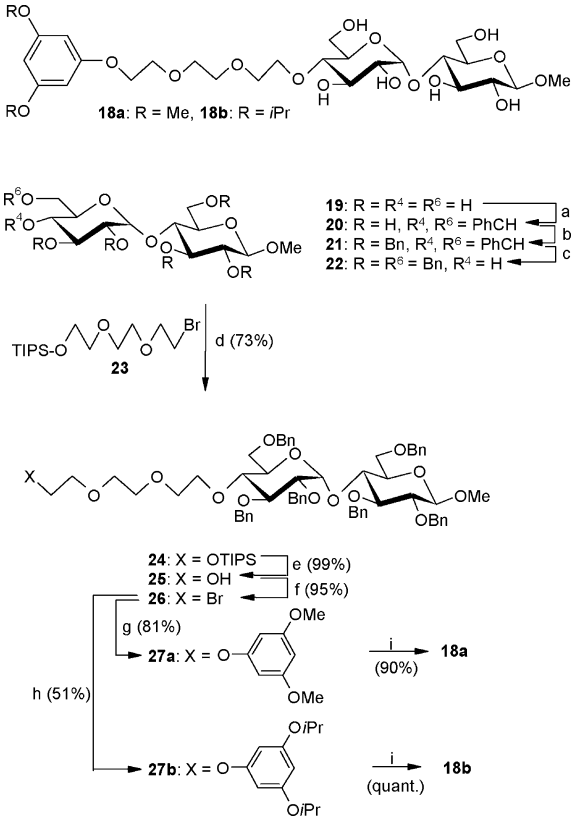
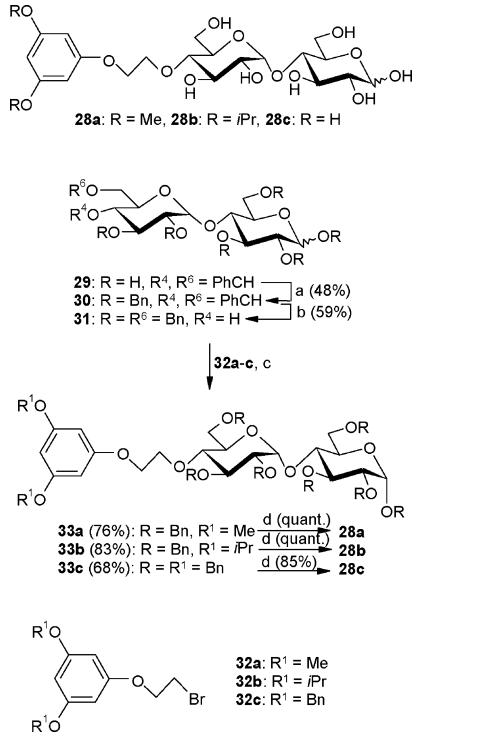


Scheme 2. Structure and synthesis of target molecules **18a**,**b**. *Reagents and conditions:* a) $PhCH(OMe)_2$, TsOH (ref.[22]); b) BnBr, NaH, DMF (ref.[23]); c) $NaCNBH_3$, Et_2O/HCl (ref.[24]); d) NaH, TBAI, DMF, e) TBAF, THF; f) CBr_4, PPh_3, CH_2Cl_2; g) 3,5-dimethoxyphenol, NaH, TBAI, DMF; h) 3,5-diisopropoxyphenol, NaH, TBAI, DMF; i) $Pd(OH)_2$/C, H_2, dioxane.

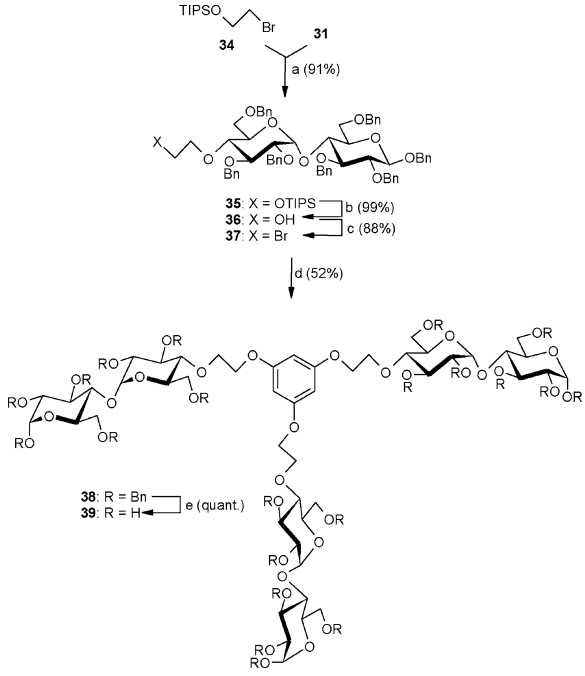
The synthesis of 4b-*O*-modified target molecules **28a**–**c** (Scheme 3), having an unprotected glucose residue at the reducing end and only one ethylene glycol residue, started from known 4b,6b-*O*-benzylidene-maltose (**29**).[22,26] Following benzylation under standard conditions afforded fully protected maltoside **30**; reductive cleavage of the benzylidene ring with sodium cyanoborohydride in hydrogen chloride containing ether[24] afforded known 4b-*O*-unprotected compound **31**.[14,27] 4b-*O*-Alkylation with 3,5-dialkoxyphenyloxyethyl bromides **32a**–**c** furnished **33a**–**c** that on hydrogenolytic *O*-debenzylation provided target molecules **28a**–**c**. Compounds **28a**–**c** showed for the first time affinities to MBP in the μmolar range whereas **18a**, **b** had still very low affinities (Table 1). Surprisingly, all these affinities to MBP were easily reached or even surpassed by simple maltose derivatives **19**, **20** and **29** (Table 1).

Based on these results the multivalency effect was investigated by ligating three maltose residues either via their 4b-hydroxy groups or via their anomeric hydroxy groups formally to 1,3,5-tris-*O*-hydroxyethylphloroglucine, thus leading to target molecules **39** and **44**, respectively (Scheme 4 and Scheme 5). To this end, 4b-*O*-unprotected maltoside was alkylated with tris(isopropylsilyloxy)ethyl bromide **34** with NaH/TBAI in DMF providing compound **35**. Cleavage of the TIPS group with TBAF in THF (→**36**), then



Scheme 3. Structure and synthesis of target molecules **28a**–**c**. *Reagents and conditions:* a) BnBr, NaH, DMF; b) $NaCNBH_3$, Et_2O/HCl; c) NaH, TBAI, DMF; d) $Pd(OH)_2$/C, H_2, dioxane.

transformation of **36** with Appel's reagent[25] into 4b-*O*-bromoethylated derivative **37**, and then *O*-alkylation of phloroglucine with **37** and NaH/TBAI in DMF furnished trivalent



Scheme 4. Synthesis of maltose cluster **39**. *Reagents and conditions:* a) $BrCH_2CH_2OTIPS$, NaH, TBAI, DMF; b) TBAF, THF; c) CBr_4, PPh_3, CH_2Cl_2; d) phloroglucine, NaH, TBAI, DMF; e) $Pd(OH)_2$/C, H_2, THF.

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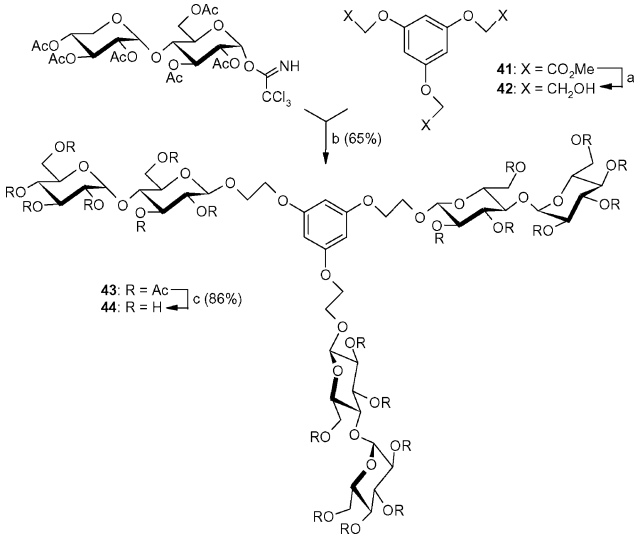
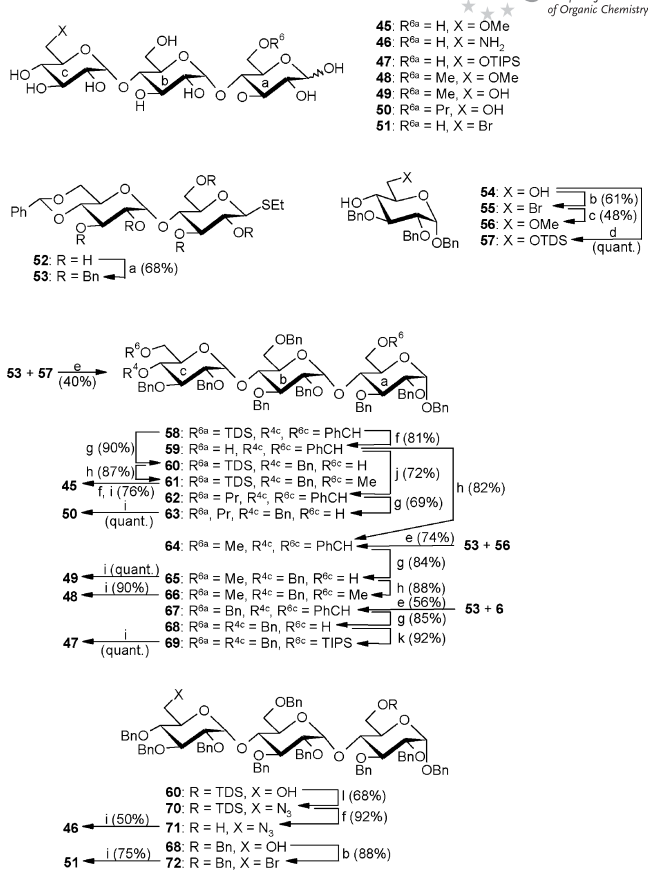
intermediate **38** in 52% yield. Hydrogenolytic *O*-debenzylation afforded target molecule **39**. Glycosylation of 1,3,5-tris-(hydroxyethyloxy)benzene **42**,[28] that is readily obtained from **41**,[29] with *O*-acetyl-protected *O*-maltosyl trichloroacetimidate **40**[13,30] as glycosyl donor and TMSOTf as catalyst in acetonitrile at room temperature[13] led to the desired β-linked tris-*O*-maltosyloxyethyl phloroglucine ether **43**. *O*-Deacetylation under Zemplén conditions[18] furnished target molecule **44**. To our delight, trivalent compounds **39** and **44** showed affinities to MBP in the range of maltose and maltotriose (Table 1).



Scheme 5. Synthesis of maltose cluster **44**. *Reagents and conditions:* a) $LiAlH_4$, THF; b) TMSOTf (0.025 equiv.), MeCN, room temp.; c) NaOMe, MeOH.



Scheme 6. Structure and synthesis of target molecules **45**–**51**. *Reagents and conditions:* a) BnBr, NaH, DMF; b) CBr_4, PPh_3, CH_2Cl_2; c) NaOMe, TBAI, 15-crown-5, DMF; d) TDS-Cl, imidazole, CH_2Cl_2; e) NIS TfOH, Et_2O, room temp.; f) TBAF, THF; g) $H_3B{\cdot}THF$, Bn_2BOTf, CH_2Cl_2; h) MeI, NaH, DMF; i) $Pd(OH)_2/C$, H_2, THF, H_2O, HOAc; j) PrI, NaH, DMF; k) TIPS-Cl, imidazole, CH_2Cl_2; l) PPh_3, DEAD, HN_3, C_6H_6, CH_2Cl_2.

Modification of Maltotriose

The higher affinity of maltotriose to MBP compared with maltose was reason to prepare modifications that are essentially designed based on the X-ray analysis of maltotriose binding to MBP.[5] It was speculated that substitution of water molecules in the active site by hydrophobic residues might lead to increased hydrophobic interactions and thus to increased overall binding.[31] Therefore, following the X-ray analysis, modifications of the 6a- and/or 6c-hydroxy group were investigated. The target molecules **45**–**51** are compiled in Scheme 6.

For the construction of **45**–**51** an appropriately protected maltosyl donor and a 4-*O*-unprotected glucose acceptor were chosen. This time, for the generation of the α-glycosidic linkage, maltothioglycoside **53** was investigated that was readily obtained from 4b,6b-*O*-benzylidene derivative **52**.[32] As acceptors glucopyranosides **56** and **57** were employed, which were obtained from known glucoside **54**.[33] Chemoselective introduction of bromide at C-6 with Appel's reagent[25] afforded **55**, which gave with sodium methoxide in the presence of TBAI and crown ether 15-crown-5 in DMF 6-*O*-methyl-glucoside **56**. Regioselective silylation of the 6-hydroxy group in **54** with TDS-Cl and imidazole in dichloromethane afforded 4-*O*-unportected glucoside **57**. Glycosylation of **57** as acceptor with donor **53** and *N*-iodosuccinimide (NIS, 2 equiv.) and catalytic amounts of triflic acid (TfOH) as promoter[34] afforded the desired α-linked maltotrioside **58** though in only 40% yield. 6a-*O*-Deacetylation with TBAF in THF furnished **59** that was used to introduce a 6a-*O*-propyl or a 6a-*O*-methyl group under standard conditions affording compounds **62** and **64**, respectively. Reductive cleavage of the 4c,6c-*O*-benzylidene groups with the borohydride-THF complex in the presence of dibutylboron-trifluoromethanesulfonate[10] afforded 6c-*O*-unprotected compounds **63** and **65**. Hydrogenolytic cleavage of the *O*-benzyl groups gave target molecules **50** and **49**, respectively. The same reductive cleavage applied to the 4c,6c-*O*-benzylidene group in **58** furnished 6c-*O*-unportected maltotriose **60** that gave on 6c-*O*-methylation maltotrioside **61**; then desilylation and hydrogenolytic *O*-debenzylation afforded target molecule **45**.

The intermediate **64**, required for the synthesis of target molecules **48** and **49**, could also be obtained by glycosylation of acceptor **56** with donor **53** under the above-de-

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scribed conditions. Reductive cleavage of the 4c,6c-*O*-benzylidene group with the boronhydride–THF complex,[10] as mentioned earlier, led to compound **65** that was then transformed with methyl iodide and NaH as base into 6c-*O*-methyl derivative **66**. Hydrogenolytic *O*-debenzylation of **65** and **66** led to target molecules **49** and **48**, respectively. Glycosylation of acceptor **6** with donor **53** under the standard conditions furnished the desired maltotrioside **67**, though in only 56% yield. Reductive cleavage of the 4c,6c-*O*-benzylidene group afforded 6c-*O*-unprotected compound **68** that was silylated with TIPS-Cl in the presence of imidazole furnishing fully protected maltotrioside **69** which gave on hydrogenolytic *O*-debenzylation target molecule **47**. Target molecule **46** was readily obtained from 6c-*O*-unprotected compound **60**. Application of the Mitsunobu procedure for azide introduction[12] gave 6c-azido-6c-deoxymaltotrioside **70**. Desilylation with TBAF in THF (→ **71**) and then hydrogenolytic *O*-debenzylation led to **46**. Target molecule **51** was obtained from 6c-*O*-unprotected compound **68** by transformation into bromide **72** with Appel's reagent and then hydrogenolytic *O*-debenzylation.

With the exception of 6c-*O*-triisopropylsilyl-protected maltotriose **47** all other target molecules exhibited excellent affinities to MBP (Table 1). It is particularly worth mentioning that compounds **50** and **51** having lipophilic groups in 6a- or 6c-position, respectively, show the highest binding affinities to MBP.

Biological Studies

The binding affinities to MBP were measured following known procedures.[35] From these results, the IC_{50} and the K_d values were obtained[36] which are compiled in Table 1. As mentioned above, the replacement of maltose hydroxy groups by amino groups as in **1**–**3** led to a big decrease in binding to MBP. Also the introduction of aryl–O–$(CH_2CH_2–O)_3$ residues at the 4b-hydroxy group of maltose (compounds **18a**, **b**) did not improve this result. Surprisingly, the corresponding compounds with a 4b-*O*-arylethylene glycol residue (compounds **28a**–**c**) showed improved affinity to MBP, yet they did not reach the affinities of simple maltose derivatives as **19** and **29** or maltose. However, the trivalent maltose derivatives **39** and **44**, which were derived from **28a**–**c**, reached (compound **44**) or even surpassed (compound **39**) the affinity of maltose to MBP. As expected, compound **39** with a nonmodified reducing end showed the highest affinity in this series.

The approximately tenfold higher affinity of maltotriose to MBP than maltose indicates that the α-D-glucopyranosyl residue at the nonreducing end contributes to some extent to MBP binding. Yet, introduction of a 6c-*O*-methyl group or replacement of the 6c-hydroxy group by an amino group in maltotriose (compounds **45** and **46**) led to a slight decrease and introduction of a 6c-*O*-TIPS group (compound **47**) to a dramatic loss in binding. With compound **48** having a 6a- and 6c-*O*-methyl group the previous affinity was restored which could be improved by having only a 6a-*O*-methyl group (compound **49**) and even further by a 6a-*O*-propyl group (compound **50**), thus indicating that replacement of water molecules in the binding site leads to higher affinity to MBP than found for maltotriose. Even higher affinity was obtained by replacement of the 6c-hydroxy group by bromide (compound **51**; K_d = 40 nmol) which compared to the 6c-*O*-methyl compound **45**, led to a roughly 20-fold increase in binding affinity and compared to maltotriose to a threefold higher affinity.

A few preliminary studies on maltose transport inhibition of the ABC-transporter were carried out by measuring the ^{14}C-maltose uptake by *E. coli*.[35] It was observed that transport inhibition by compounds **18a**,**b**, **28a**–**c** and **29** followed the inhibitions found for maltose binding to MBP; hence, only compounds **28c** and **29** show significant transport inhibition.

Conclusions

Based on X-ray analyses of maltose and maltotriose binding to MBP structural modifications were carried out. This led to compounds **39** and **50**, **51** showing higher affinity to MBP than maltose or maltotriose, respectively. These structurally quite different lead compounds provide a good basis for further inhibition studies including detailed studies on maltose transport inhibition.

Experimental Section

General: Solvents were purified by standard procedures. NMR spectra were recorded at 22 °C on a Bruker AC 250 Cryospec or a Bruker DRX 600 spectrometer. Tetramethylsilane (TMS) or the resonance of the undeuterated solvent was used as internal standard; solvent $CDCl_3$, δ = 7.24; D_2O, δ = 4.63; [D_6]DMSO, δ = 2.49 ppm. MALDI mass spectra were recorded on a Kratos Kompact Maldi 2 spectrometer and 2,5-dihydroxybenzoic acid (DHB) was used as matrix. FAB MS spectra were obtained with a Finnigan MAT 312/AMD 5000 instrument; +6 kV for positive ions, –4 kV for negative ions. Thin-layer chromatography was performed on Merck 60 F_{254} silica gel plastic plates or Merck RP-18 glass plates; compounds were visualized by treatment with a solution of $[(NH_4)_6Mo_7O_{24}·4H_2O]$ (20 g) and $Ce(SO_4)_2$ (0.4 g) in 10% sulfuric acid (400 mL) and then heating to 120 °C. Flash chromatography was performed on J. T. Baker silica gel 60 (40–63 μm) at a pressure of 0.3 bar. Preparative RP-18 HPLC was carried out on a Eurospher 100 C18 column (Fa. Knauer) with a Shimadzu LC-8A pump and a Rainin Dynamax UV-1 detector at a flow rate of 10 mL/min. Optical rotations were measured at 20 °C with a Büchi Polar-Monitor using the light of the sodium D line.

Thexyldimethylsilyl 2,6-Diazido-3,4-*O*-benzyl-2,6-dideoxy-β-D-glucopyranoside (10): To a solution of **9**[10,11] (200 mg, 0.379 mmol, 1 equiv.) in dry THF (5.0 mL) was added diethyl azodicarboxylate (DEAD, 88.4 μL, 0.569 mmol, 1.5 equiv.) and triphenylphosphane (148 mg, 0.569 mmol, 1.5 μmol, 1.5 equiv.). At room temp. a solution of HN_3 (0.569 mmol, 1.5 equiv.) in benzene (225 μL) was added. After 30 min (TLC monitoring) the reaction mixture was diluted with $NaHCO_3$ solution (20 mL) and ethyl acetate (20 mL). The aqueous phase was extracted with ethyl acetate (3 × 20 mL) and the solvent of the combined organic phases was then removed

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in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 20:1) furnishing **10** (189 mg, 0.341 mmol, 90%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 5:1): R_f = 0.68. $[\alpha]_D$ = +10.3 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.21 [2s, 6 H, $Si(CH_3)_2$], 0.90 [4s, 12 H, $C(CH_3)$], 1.66 [hept, ^3J = 6.0 Hz, 1 H, $CH(CH_3)_2$], 3.25 (dd, $^3J_{5,6}$ = 5.8, $^2J_{6,6'}$ = 13.0 Hz, 1 H, 6-H), 3.33 (dd, $^3J_{1,2}$ = 7.6, $^3J_{3,2}$ = 10.0 Hz, 1 H, 2-H), 3.38–3.42 (m, 2 H, 3-H, 5-H), 3.46–3.50 (m, 2 H, 4-H, 6′-H), 4.51 (d, $^3J_{2,1}$ = 7.6 Hz, 1 H, 1-H), 4.57 (d, ^2J = 11.1 Hz, 1 H, PhC*H*H), 4.77–4.91 (m, 3 H, PhC*H*H), 7.23–7.36 (m, 10 H, Ph) ppm. MALDI MS: m/z = 554 [MH^+], 575 [MNa^+]. $C_{28}H_{40}N_6O_4Si$ (552.75): calcd. C 60.84, H 7.29, N 15.20; found C 60.81, H 7.11, N 14.92.

2,6-Diazido-3,4-*O*-benzyl-2,6-dideoxy-α/β-D-glucopyranose (11): To a solution of **10** (726 mg, 1.31 mmol) and pyridine (5.0 mL) was added a solution of hydrogen fluoride in pyridine (1.10 mL, 65% HF) at room temp. The reaction mixture was stirred for 3 d at room temp. (TLC monitoring) and diluted with $NaHCO_3$ solution (20 mL) and ethyl acetate (20 mL). The aqueous phase was extracted with ethyl acetate (3 × 20 mL). The solvent of the combined organic phases was then removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 6:1) furnishing **11** (503 mg, 1.23 mmol, 93%) as colourless amorphous solid. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.20. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.84 (br. s, 0.6 H, OH_α), 3.21–3.59 (m, 5.2 H, OH_β, 2-H, 3-H_β, 4-H, 5-H_β, 6-H, 6′-H), 3.94–4.11 (m, 1.2 H, 3-H_α, 5-H_α), 4.53–4.66 (m, 1.4 H, 1-H_β, PhC*H*H), 4.75–4.94 (m, 3 H, PhC*H*H), 5.31 (d, $^3J_{2,1}$ = 3.8 Hz, 0.6 H, 1-H_α), 7.20–7.41 (m, 10 H, Ph) ppm. MALDI MS: m/z = 433 [MNa^+], 449 [MK^+]. $C_{20}H_{22}N_6O_4$ (410.43): calcd. C 58.53, H 5.40, N 20.48; found C 58.52, H 5.37, N 20.21.

***O*-(2,6-Diazido-3,4-*O*-benzyl-2,6-dideoxy-α-D-glucopyranosyl) Trichloroacetimidate (5):** To a solution of **11** (150 mg, 0.365 mmol) in dry CH_2Cl_2 (10.0 mL) were added trichloroacetonitrile (500 µL, 3.46 mmol) and 2 drops DBU. After 3 h at room temp. the reaction mixture was concentrated in vacuo and purified by flash chromatography (ethyl acetate/Et_2O/triethylamine, 10:1:0.1) furnishing **5** (174 mg, 0.314 mmol, 86%) as α-anomer (with traces of the β-anomer) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.59. $[\alpha]_D$ = +79.4 (c = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.36 (dd, $^3J_{5,6}$ = 5.4, $^2J_{6,6'}$ = 13.4 Hz, 1 H, 6-H), 3.52 (dd, $^3J_{1,2}$ = 3.5, $^3J_{3,2}$ = 12.5 Hz, 1 H, 2-H), 3.62–3.72 (m, 2 H, 4-H, 6′-H), 3.96–4.08 (m, 2 H, 3-H, 5-H), 4.62 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.85–4.93 (m, 3 H, PhC*H*H), 6.41 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1-H), 7.21–7.41 (m, 10 H, Ph), 8.73 (s, 1 H, NH) ppm. $C_{22}H_{22}Cl_3N_7O_4$ (554.82): calcd. C 47.63, H 4.00, N 17.67; found C 47.70, H 4.08, N 17.37.

Benzyl *O*-(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (12): To a solution of **6**[14] (260 mg, 0.481 mmol, 1.0 equiv.) and **4**[9] (300 mg, 0.631 mmol, 1.3 equiv.) in dry diethyl ether (6.0 mL) was added trifluoromethanesulfonic acid (2.1 µL, 0.024 mmol, 0.05 equiv.) at room temp. After 20 min, the reaction mixture was neutralised with triethylamine and the solvent removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnished **12** (241 mg, 0.33 mmol, 69%) as colourless syrup. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.25. $[\alpha]_D$ = +100.5 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 2.00, 2.01, 2.08 (3s, 9 H, $COCH_3$), 3.23 (dd, $^3J_{1,2}$ = 3.9, $^3J_{3,2}$ = 10.6 Hz, 1 H, 2b-H), 3.55–3.59 (m, 2 H, 2a-H, 6a-H), 3.72–3.77 (m, 2 H, 6a′-H), 3.90–3.97 (m, 3 H, 4a-H, 5a-H, 5b-H), 4.10 (dd, $^3J_{5,6}$ = 3.6, $^2J_{6,6'}$ = 12.5 Hz, 1 H, 6′b-H), 4.17 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.0 Hz, 1 H, 3a-H), 4.48–4.61 (m, 5 H, PhC*H*H), 4.71 (d, ^2J = 12.3 Hz, 1 H, PhC*H*H), 4.79 (d, ^2J = 10.9 Hz, 1 H, PhC*H*H), 4.86 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1a-H), 4.97 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.8 Hz, 1 H, 4b-H), 5.14 (d, ^2J = 10.9 Hz, 1 H, PhC*H*H), 5.39 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.0 Hz, 1 H, 3b-H), 5.81 (d, $^3J_{2,1}$ = 3.9 Hz, 1 H, 1b-H), 7.20–7.45 (m, 20 H, Ph) ppm. $C_{46}H_{51}N_3O_{13}$ (853.34): calcd. C 64.70, H 6.02, N 4.92; found C 64.38, H 5.96, N 4.78.

Benzyl *O*-(2-Azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (13): To a solution of **12** (270 mg, 0.316 mmol) in dry methanol (6.0 mL) at room temp. was added a solution of NaOMe in methanol (20 µL, 1.0 M). The reaction mixture was stirred overnight at room temp. and then neutralised with Amberlite IR 120 H^+. After filtration and removal of the solvent in vacuo the crude product was purified by flash chromatography with silica gel (petroleum ether/ethyl acetate, 1:1) furnishing **13** (200 mg, 0.275 mmol, 87%) as colourless foam. TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.16. $[\alpha]_D$ = +103.5 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.85 (br. s, 1 H, OH), 2.75–2.90 (2br.s, 2 H, OH), 3.01 (dd, $^3J_{1,2}$ = 3.8, $^3J_{3,2}$ = 9.8 Hz, 1 H, 2b-H), 3.47 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.8 Hz, 1 H, 4b-H), 3.54–3.58 (m, 5 H, 2a-H, 6a-H, 6′a-H, 5b-H, 6b-H, 6′b-H), 3.70 (dd, $^3J_{5,6}$ = 3.7, $^2J_{6,6'}$ = 11.4 Hz, 1 H, 6a-H), 3.83 (ddd, $^3J_{4,5}$ = 9.5, $^3J_{6,5}$ = 3.7, $^2J_{5,6'}$ = 1.8 Hz, 1 H, 5a-H), 3.88 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.8 Hz, 1 H, 3b-H), 3.94 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.5 Hz, 1 H, 4a-H), 4.16 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.5 Hz, 1 H, 3a-H), 4.50–4.60 (m, 5 H, PhC*H*H), 4.71 (d, ^2J = 11.0 Hz, 1 H, PhC*H*H), 4.81–4.86 (m, 2 H, 1a-H, PhC*H*H), 5.12 (d, ^2J = 11.0 Hz, 1 H, PhC*H*H), 5.71 (d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H), 7.24–7.41 (m, 20 H, Ph) ppm. $C_{40}H_{45}N_3O_{10}$ (727.81): calcd. C 66.01, H 6.23, N 5.77; found C 65.83, H 6.22, N 5.16.

***O*-(2-Amino-2-deoxy-α-D-glucopyranosyl)-(1→4)-α/β-D-glucopyranose Hydrochloride (1):** To a solution of **13** (50.0 mg, 68.7 µmol) in methanol (5.0 mL) was added Pearlman catalyst[19] (10.0 mg). Then the argon atmosphere was replaced completely by hydrogen. To ensure a complete hydrogenation the pH value had to be kept slightly acidic with HCl/Et_2O (ca. 1 equiv.). Hydrogenation was continued overnight at room temp. After TLC monitoring the catalyst was removed with celite, which was then washed with methanol (3 × 10 mL). The filtrate and the wash solution were combined and the solvent removed under reduced pressure. A concentrated solution in distilled water (2–3 drops) was produced of the crude product precipitated with ethanol. Desiccation furnished **1** (16 mg, 41.2 µmol, 60%) as pale yellow crystals. M.p. 173–181 °C (dec.). TLC (EtOH/H_2O/AcOH, 5:5:0.5): R_f = 0.66. ^1H NMR (600 MHz, CD_3OD): δ = 3.14–3.18 (m, 1.5 H, 2a-H_β, 2b-H), 3.37–3.43 (m, 2 H, 2a-H_α, 5a-H_β, 4b-H), 3.60–3.95 (m, 8.5 H, 3a-H, 4a-H, 5a-H_α, 6a-H, 6′a-H, 3b-H, 5b-H, 6b-H, 6′b-H), 4.47 (d, $^3J_{2,1}$ = 7.5 Hz, 0.5 H, 1a-H_β), 5.10 (d, $^3J_{2,1}$ = 3.8 Hz, 0.5 H, 1a-H_α), 5.50 (2d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H) ppm. FAB MS: m/z = 342 [MH^+], 364 [MNa^+]. $C_{12}H_{23}NO_{10}$·HCl (377.77). Other physical data have already been reported.[20]

Thexyldimethylsilyl *O*-(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (14): To a solution of **7**[15] (200 mg, 0.38 mmol, 1.0 equiv.) in dry diethyl ether (2.0 mL) was added TBDMSOTf (1.0 µL, 3.8 µmol, 0.01 equiv.). Then a solution of **4**[9] (235 mg, 0.49 mmol, 1.3 equiv.) in dry diethyl ether (5.0 mL) was added within 5 min at room temp. After 30 min the reaction mixture was neutralised with triethylamine and then the solvent removed in vacuo. Purification by flash chromatography with silica gel (petroleum ether/ethyl acetate, 5:1) furnished an α/β-diastereomer mixture that was separated after further chromatography (toluene/acetone, 10:1) furnishing the α-diastereomer **14** (131 mg, 0.16 mmol, 41%) as colourless syrup.

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TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.50. $[\alpha]_D$ = +53.0 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.22 [2s, 6 H, $Si(CH_3)_2$], 0.91 [4s, 12 H, $C(CH_3)$], 1.68 [hept, ^3J = 6.9 Hz, 1 H, $CH(CH_3)_2$], 2.00, 2.02, 2.08 (3s, 9 H, $COCH_3$), 3.24 (dd, $^3J_{1,2}$ = 3.8, $^3J_{3,2}$ = 10.6 Hz, 1 H, 2b-H), 3.39 (dd, $^3J_{1,2}$ = 7.6, $^3J_{3,2}$ = 9.4 Hz, 1 H, 2a-H), 3.43 (ddd, $^3J_{4,5}$ = 9.7, $^3J_{6,5}$ = 4.1, $^3J_{6',5}$ = 2.0 Hz, 1 H, 5a-H), 3.51 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.4 Hz, 1 H, 3a-H), 3.65 (dd, $^3J_{5,6}$ = 2.0, $^2J_{6,6'}$ = 11.9 Hz, 1 H, 6a-H), 3.73 (dd, $^3J_{5,6}$ = 2.4, $^2J_{6,6'}$ = 12.6 Hz, 1 H, 6b-H), 3.80 (dd, $^3J_{5,6}$ = 3.8, $^2J_{6,6'}$ = 11.9 Hz, 1 H, 6′a-H), 3.98 (m, 2 H, 4a-H, 5b-H), 4.16 (dd, $^3J_{5,6}$ = 3.5, $^2J_{6,6'}$ = 12.6 Hz, 1 H, 6′b-H), 4.57 (m, 3 H, 1a-H, PhC*H*H), 4.74 (d, ^2J = 12.4 Hz, 1 H, PhC*H*H), 4.97 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.7 Hz, 1 H, 4b-H), 5.06 (d, ^2J = 10.7 Hz, 1 H, PhC*H*H), 5.38 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 10.6 Hz, 1 H, 3b-H), 5.78 (d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H), 7.26–7.36 (m, 10 H, Ph) ppm. $C_{40}H_{56}N_6O_{12}Si$ (840.99): calcd. C 57.12, H 6.72, N 9.99; found C 57.22, H 6.69, N 9.74.

Thexyldimethylsilyl *O*-(2-Azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-2-azido-3,6-di-*O*-benzyl-2-desoxy-β-D-glucopyranoside (15): To a solution of **14** (200 mg, 0.238 mmol) and dry methanol (5.0 mL) was added a solution of NaOMe in methanol (19 μL, 1.0 M) at room temp. The reaction mixture was stirred overnight at room temp. and then neutralised with Amberlite IR 120 H^+. After filtration and removal of the solvent in vacuo the crude product was purified by flash chromatography with silica gel (toluene/ethyl acetate, 3:2) furnishing **15** (146 mg, 0.205 mmol, 86%) as colourless, amorphous solid. TLC (toluene/ethyl acetate, 1:1): R_f = 0.21. $[\alpha]_D$ = +51.4 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.21 [2s, 6 H, $Si(CH_3)_2$], 0.90 [4s, 12 H, $C(CH_3)$], 1.68 [hept, ^3J = 6.0 Hz, 1 H, $CH(CH_3)_2$],1.83 (br. s, 1 H, OH), 2.61, 2.63 (2br.s, 2 H, OH), 3.04 (dd, $^3J_{1,2}$ = 3.8, $^3J_{3,2}$ = 9.9 Hz, 1 H, 2b-H), 3.37 (dd, $^3J_{1,2}$ = 7.6, $^3J_{3,2}$ = 9.4 Hz, 1 H, 2a-H), 3.43 (m, 1 H, 5a-H), 3.50–3.53 (m, 2 H, 3a-H, 4b-H), 3.62–3.67 (m, 3 H, 5b-H, 6b-H, 6a-H), 3.78 (dd, $^3J_{5,6}$ = 3.8, $^2J_{6,6'}$ = 11.7 Hz, 1 H, 6a-H), 3.89 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.9 Hz, 1 H, 3b-H), 3.97 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.1 Hz, 1 H, 4a-H),4.54–4.63 (m, 3 H, 1a-H, PhC*H*H), 4.78 (d, ^2J = 11.0 Hz, 1 H, PhC*H*H), 5.04 (d, ^2J = 11.0 Hz, 1 H, PhC*H*H), 5.66 (d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H), 7.26–7.38 (m, 10 H, Ph) ppm. $C_{34}H_{50}N_6O_9Si$ (714.34): calcd. C 57.12, H 7.05, N 11.76; found C 56.48, H 6.96, N 11.47.

***O*-(2-Azido-2-deoxy-α-D-glucopyranosyl)-(1→4)-2-azido-3,6-di-*O*-benzyl-2-desoxy-α/β-D-glucopyranose (16):** To a solution of **15** (30 mg, 0.042 mmol) in THF (0.5 mL) was added catalytic amount of acetic acid (2.5 μL). Then TBAF solution (50 μL, 1.0 M in THF) was added portionwise to the reaction mixture and the silyl deprotection was tracked under TLC monitoring (0.5–5.0 h). For the purification the reaction mixture was diluted with ethyl acetate (10.0 mL) and the organic phase washed with concentrated NaCl solution (3 × 10 mL). The aqueous phase was concentrated in vacuo and reextracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried with $MgSO_4$ and then the solvent removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 1:3) furnished **16** (21 mg, 0.036 mmol 85%) as colourless foam. In $CDCl_3$ an anomeric mixture appears (α/β, 3:2). TLC (ethyl acetate 100%): R_f = 0.64. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.79 (br. s, 1 H, 6b-OH), 2.67 (m, 2.4 H, 2 OH, 1a-OH_β), 3.07 (m, 1.6 H, 2b-H, 1a-OH_α), 3.37–4.14 (m, 11 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H), 4.53–4.69 (m, 2.4 H, 1a-H_β, 2 PhC*H*H), 4.82 (d, ^2J = 11.0 Hz, 0.4 H, PhC*H*H_β), 4.88 (d, ^2J = 11.0 Hz, 0.6 H, PhC*H*H_α), 4.99 (d, ^2J = 11.0 Hz, 0.6 H, PhC*H*H_α), 5.04 (d, ^2J = 11.0 Hz, 0.4 H, PhC*H*H_β), 5.37 (m, 0.6 H, 1a-H_α), 5.62 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1b-H), 7.25–7.40 (m, 10 H, Ph) ppm. MALDI MS: m/z = 595.0 [MNa^+]. $C_{26}H_{32}N_6O_9 \cdot 0.5H_2O$ (581.23): calcd. C 53.70, H 5.72, N 14.45; found C 53.71, H 5.87, N 13.94.

***O*-(2-Amino-2-deoxy-α-D-glucopyranosyl)-(1→4)-2-amino-2-deoxy-α/β-D-glucopyranose Dihydrochloride (2):** To a solution of **16** (50.0 mg, 0.087 mmol) in methanol (4.0 mL) was added Pearlman catalyst[19] (10.0 mg). Then the argon atmosphere was replaced completely by hydrogen. To ensure a complete hydrogenation the pH value had to be kept slightly acidic with HCl/Et_2O (ca. 2 equiv.). Hydrogenation was continued overnight at room temp. After TLC monitoring the catalyst was removed with celite, which was then washed with methanol (3 × 10 mL). The filtrate and the wash solution were combined and the solvent removed under reduced pressure. A concentrated solution in distilled water (2–3 drops) was produced of the crude product which was precipitated with ethanol. Desiccation furnished **2** (36 mg, 0.086 mmol, 96%) as pale yellow crystals. RP 18-TLC (EtOH/H_2O/AcOH, 5:5:0.5): R_f = 0.62. M.p. 162 °C (dec.). ^1H NMR (600 MHz, CD_3OD): δ = 2.86 (dd, $^3J_{2,1}$ = 8.2, $^3J_{3,2}$ = 10.6 Hz, 0.4 H, 2a-H_β), 3.15–3.23 (m, 1.6 H, 2a-H_α, 2b-H), 3.36 (m, 1 H, 4b-H), 3.51 (m, 0.4 H, 5a-H_β), 3.64–3.96 (m, 8 H, 3a-H_β, 4a-H, 5a-H_α, 6a-H, 6′a-H, 3b-H, 5b-H, 6b-H, 6′b-H), 4.13 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.5 Hz, 0.6 H, 2a-H_α), 4.75–4.90 (m, 0.4 H, 1a-H_β), 5.33 (d, $^3J_{2,1}$ = 3.8 Hz, 0.6 H, 1a-H_α), 5.72 (d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H) ppm. FAB MS: m/z = 341 [MH^+], 363 [MNa^+]. $C_{12}H_{24}N_2O_9 \cdot 2HCl$ (413.25).

Methyl *O*-(2,6-Diazido-3,4-*O*-benzyl-2,6-dideoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (17): To a solution of **8**[16] (115 mg, 0.248 mmol, 1.0 equiv.) and **5** (165 mg, 0.297 mmol, 1.2 equiv.) in dry diethyl ether (5.0 mL) was added TMSOTf (0.46 μL, 2.48 μmol, 0.01 equiv.) at room temp. After 20 min the reaction mixture was neutralised with triethylamine and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate, 100:1 → 50:1) furnished **17** (170 mg, 0.198 mmol, 80%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.43. $[\alpha]_D$ = +40.3 (c = 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.02–3.29 (m, 3 H, 2b-H, 6b-H, 6′b-H), 3.38 (s, 3 H, OCH_3), 3.42–3.93 (m, 8 H, 2a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 3b-H, 4b-H, 5b-H), 4.06 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 10.4 Hz, 1 H, 3a-H), 4.48–4.90 (m, 10 H, 1a-H, PhC*H*H), 5.08 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.67 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1b-H), 7.16–7.39 (m, 25 H, Ph) ppm. $C_{48}H_{52}N_6O_9 \cdot 1.5H_2O$ (883.40): calcd. C 65.22, H 6.27, N 9.51; found C 65.31, H 6.23, N 9.11.

Methyl *O*-(2,6-Diamino-2,6-dideoxy-α-D-glucopyranosyl)-(1→4)-α-D-glucopyranoside Dihydrochloride (3): To a solution of **17** (52.0 mg, 60.7 μmol) in methanol (5.0 mL) was added Pearlman catalyst[19] (15.0 mg). Then the argon atmosphere was replaced completely by hydrogen. To ensure a complete hydrogenation the pH value had to be kept slightly acidic with HCl/Et_2O (ca. 2 equiv.). Hydrogenation was continued overnight at room temp. After TLC monitoring the catalyst was removed with celite, which was then washed with methanol (3 × 10 mL). The filtrate and the wash solution were then combined and the solvent removed under reduced pressure. A concentrated solution in distilled water (2–3 drops) was produced of the crude product which was precipitated with ethanol. Desiccation furnished **3** (19 mg, 44.9 μmol, 74%) as pale yellow, hygroscopic solid. Therefore, it was difficult to obtain a correct elemental analysis and m.p. TLC (EtOH/H_2O/TFA, 5:5:0.5): R_f = 0.78. $[\alpha]_D$ = +27.5 (c = 0.33, H_2O). ^1H NMR (250 MHz, CD_3OD): δ = 2.99–3.54 (m, 8 H, 2a-H, 2b-H, 4b-H, 6b-H, 6b′-H, OCH_3), 3.55–4.01 (m, 7 H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 3b-H, 5b-H), 4.71 (d, $^3J_{1,2}$ = 3.7 Hz,1 H, 1a-H), 5.78 (d, $^3J_{1,2}$ = 3.7 Hz, 1 H, 1b-H) ppm. FAB MS: m/z = 355 [MH^+]. $C_{13}H_{26}N_2O_9 \cdot 2HCl$ (427.28).

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8-Bromo-1-(triisopropylsilyoxy)-3,6-dioxaoctane (23): Triethylene glycol (15.0 g, 99.89 mmol, 4.0 equiv.) was combined with tetrabromoethane (8.28 g, 24.97 mmol, 1 equiv.) and triphenylphosphane (6.56 g, 24.97 mmol, 1 equiv.) under ice cooling in dry dichloromethane (70.0 mL). After 20 min the ice bath was removed and the reaction mixture stirred for 2 h. Then the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 1:1). TLC (ethyl acetate 100%) R_f = 0.48. A solution of triphenylphosphane oxide and the monobromo compound (7.0 g) was isolated and without further purification added TIPSCl (3.48 mL, 3.17 g, 16.43 mmol) and imidazole (1.68 g, 24.65 mmol) in dry dichloromethane (50.0 mL) at room temp. After stirring for 3 h the reaction mixture was concentrated and purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) which furnished **23** (4.38 g, 11.86 mmol, 48%) as colourless oil. TLC (petroleum ether/ethyl acetate, 10:1): R_f = 0.49. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.94–1.15 [m, 21 H, SiC*H*(CH)$_3$, SiCH(C*H*)$_3$], 3.42 (t, ^3J = 5.3 Hz, 2 H, CH_2Br), 3.52–3.70 (m, 6 H, OCH_2), 3.72–3.88 (m, 4 H, OCH_2) ppm. $C_{15}H_{33}BrO_3Si$ (369.42): calcd. C 48.77, H 9.00; found C 48.82, H 8.92.

Methyl *O*-[2,3,6-Tri-*O*-benzyl-4-*O*-(8-triisopropylsilyloxy-3,6-dioxaoctyl)-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (24): To a solution of **22**[24] (200 mg, 0.223 mmol, 1 equiv.), **23** (165 mg, 0.446 mmol, 2 equiv.) and TBAI (8.2 mg, 0.022 mmol, 0.1 equiv.) in DMF (10.0 mL) at room temp. was added portionswise NaH (9.0 mg, 0.375 mmol, 1.7 equiv.). After 4 h methanol (10.0 mL) was added and the reaction mixture concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 7:1) furnishing **24** (193 mg, 0.163 mmol, 73%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 5:1): R_f = 0.20. $[\alpha]_D$ = +30.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.98–1.30 [m, 21 H, SiC*H*(CH)$_3$, SiCH(C*H*)$_3$], 3.41–3.91 (m, 26 H, 2a-H, 3a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, OCH_2, OCH_3), 4.01 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 8.7 Hz, 1 H, 4a-H), 4.32 (d, $^3J_{2,1}$ = 7.7 Hz, 1 H, 1a-H), 4.38 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.44–4.61 (m, 6 H, PhC*H*H), 4.73–4.93 (m, 5 H, PhC*H*H), 5.58 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1b-H), 7.10–7.29 (m, 30 H, Ph) ppm. $C_{70}H_{92}O_{14}Si$ (1184.63): calcd. C 70.92, H 7.82; found C 70.49, H 7.91.

Methyl *O*-[2,3,6-Tri-*O*-benzyl-4-*O*-(8-hydroxy-3,6-dioxaoctyl)-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (25): To a solution of **24** (50.0 mg, 42.2 μmol, 1.0 equiv.) in THF (3.0 mL) at room temp. was added portionwise a solution of TBAF in THF (42.2 μL, 1.0 M, 1.0 equiv.). After 30 min the reaction mixture was neutralised with acetic acid and concentrated in vacuo. The residue was purified with flash chromatography (petroleum ether/ethyl acetate, 1:1) furnishing **25** (43.0 mg, 41.8 μmol, 99%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.13. $[\alpha]_D$ = +17.0 (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.29 (br. s, 1 H, OH), 3.42–3.95 (m, 26 H, 2a-H, 3a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, OCH_2, OCH_3), 4.03 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.0 Hz, 1 H, 4a-H), 4.33 (d, $^3J_{2,1}$ = 7.7 Hz, 1 H, 1a-H), 4.38 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.45–4.63 (m, 6 H, PhC*H*H), 4.75–4.95 (m, 5 H, PhC*H*H), 5.62 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1b-H), 711–7.40 (m, 30 H, Ph) ppm. $C_{61}H_{72}O_{14}$ (1028.49): calcd. C 71.14, H 7.05; found C 70.78, H 7.27.

Methyl *O*-[2,3,6-Tri-*O*-benzyl-4-*O*-(8-bromo-3,6-dioxaoctyl)-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (26): To a solution of **24** (120.0 mg, 0.117 mmol, 1.0 equiv.) and tetrabromomethane (77.3 mg, 0.233 mmol, 2.0 equiv.) in dry dichloromethane (5.0 mL) was added triphenylphosphane (61.1 mg, 0.233 mmol, 2.0 equiv.) at room temp. After 1 h the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnishing **26** (121 mg, 0.111 mmol, 95%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.88. $[\alpha]_D$ = +26.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.33–3.85 (m, 26 H, 2a-H, 3a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, OCH_2, OCH_3), 4.02 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.1 Hz, 1 H, 4a-H), 4.34 (d, $^3J_{2,1}$ = 7.6 Hz, 1 H, 1a-H), 4.39 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.47–4.63 (m, 6 H, PhC*H*H), 4.76–4.92 (m, 5 H, PhC*H*H), 5.62 (d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H), 7.06–7.37 (m, 30 H, Ph) ppm. $C_{61}H_{71}BrO_{13}\cdot H_2O$ (1110.15): calcd. C 66.00, H 6.63; found C 65.82, H 6.56.

Methyl *O*-{2,3,6-Tri-*O*-benzyl-4-*O*-[8-(3,5-dimethoxyphenoxy)-3,6-dioxaoctyl]-α-D-glucopyranosyl}-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (27a): To a solution of **26** (200 mg, 0.183 mmol), 3,5-dimethoxyphenol (28.2 mg, 0.183 mmol) and TBAI (6.8 mg, 18.3 μmol) in dry DMF (7.0 mL)was added NaH (6.6 mg, 0.275 mmol) at room temp. After 5 h the reaction was quenched with methanol (2.0 mL) and neutralised with acetic acid. The volatile components were removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate, 9:1) furnished **27a** (173 mg, 0.148 mmol, 81%) as colourless oil. TLC (toluene/ethyl acetate, 3:2): R_f = 0.62. $[\alpha]_D$ = +25.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.38–4.08 (m, 33 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, β-OCH_3, $PhOCH_3$, OCH_2^{Spacer}), 4.31–4.40 (m, 2 H, 1a-H, PhC*H*H), 4.48–4.63 (m, 6 H, PhC*H*H), 4.75–4.97 (m, 5 H, PhC*H*H), 5.62 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1b-H), 6.05–6.08 (m, 3 H, $C_6H_3^{Phloro}$), 7.08–7.41 (m, 30 H, Ph) ppm. MALDI MS: m/z = 1188 [MNa^+], 1204 [MK^+]. $C_{69}H_{80}O_{16}\cdot 0.75H_2O$ (1178.89): calcd. C 70.30, H 6.97; found C 70.26, H 7.18.

Methyl *O*-{2,3,6-Tri-*O*-benzyl-4-*O*-[8-(3,5-diisopropyloxyphenoxy)-3,6-dioxaoctyl]-α-D-glucopyranosyl}-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (27b): To a solution of **26** (294 mg, 0.269 mmol), 3,5-diisopropyloxyphenol (56.6 mg, 0.269 mmol) and TBAI (9.9 mg, 0.027 mmol) in dry DMF (10.0 mL) at room temp. was added NaH (9.7 mg, 0.404 mmol). After 5 h the reaction was quenched with methanol (3.0 mL) and neutralised with acetic acid. The volatile components were removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate, 9:1) furnished **27b** (166 mg, 0.136 mmol, 51%) as colourless oil. TLC (toluene/ethyl acetate, 5:1): R_f = 0.38. $[\alpha]_D$ = +16.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 (d, ^3J = 6.0 Hz, 12 H, OCH(C*H*$_3$)$_2$), 3.40–4.08 (m, 27 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, β-OCH_3, OCH_2^{Spacer}), 4.29–4.62 (m, 10 H, 1a-H, OC*H*(CH$_3$)$_2$, PhC*H*H), 4.72–4.98 (m, 5 H, PhC*H*H), 5.62 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1b-H), 6.02–6.05 (m, 3 H, $C_6H_3^{Phloro}$), 7.09–7.38 (m, 30 H, Ph) ppm. $C_{73}H_{88}O_{16}\cdot 0.75H_2O$ (1221.49): calcd. C 71.78, H 7.26; found C 71.63, H 7.20.

Methyl *O*-{4-*O*-[8-(3,5-Dimethoxyphenoxy)-3,6-dioxaoctyl]-α-D-glucopyranosyl}-(1→4)-β-D-glucopyranoside (18a): To a solution of **27a** (125 mg, 107 μmol) in dioxane (10.0 mL) was added Pearlman catalyst[19] (10.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After stirring for 2 h at room temp. the catalyst was separated with celite and the celite washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. Purification by flash chromatography (ethyl acetate/EtOH, 4:1) and lyophilisation from dioxane furnished **18a** (60 mg, 96.1 μmol, 90%) as colourless lyophilisate. TLC (ethyl acetate/EtOH, 4:1): R_f = 0.10. $[\alpha]_D$ = +27.1 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, CD_3OD): δ = 3.11–3.23 (m, 2 H, 2a-H, 4b-H), 3.24–3.38 (m, 1 H, 5a-H), 3.36–4.10 (m, 30 H, 3a-H, 4a-H, 6a-H, 6′a-

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H, 2b-H, 3b-H, 5b-H, 6b-H, 6′b-H, OCH_2^{Spacer}, β-OCH_3, $PhOCH_3$), 4.13 (d, $^3J_{2,1}$ = 8.0 Hz, 1 H, 1a-H), 5.10 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1b-H), 6.03–6.11 (m, 3 H, $C_6H_3^{Phloro}$) ppm. $C_{27}H_{44}O_{16}$·1.25H_2O (647.15): calcd. C 50.11, H 7.19; found C 50.07, H 7.06.

Methyl *O*-{4-*O*-[8-(3,5-Diisopropyloxyphenoxy)-3,6-dioxaoctyl]-α-D-glucopyranosyl}-(1→4)-β-D-glucopyranoside (18b): To a solution of **27b** (100 mg, 83.79 μmol) in dioxane (8.0 mL) was added Pearlman catalyst[19] (10.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After stirring for 4 h at room temp. the catalyst was separated with celite and the celite washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. Purification by flash chromatography (ethyl acetate/EtOH, 4:1) and lyophilisation from dioxane furnished **18b** (57 mg, 84 μmol, quant. yield, colourless lyophilisate. TLC (ethyl acetate/EtOH, 4:1): R_f = 0.15. $[a]_D$ = +20.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, CD_3OD): δ = 1.27 (d, ^3J = 6.0 Hz, 12 H, $OCH(CH_3)_2$), 3.15–3.23 (m, 2 H, 2a-H, 4b-H), 3.27–3.36 (m, 1 H, 5a-H), 3.40–3.88 (m, 21 H, 3a-H, 4a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 5b-H, 6b-H, 6′b-H, OCH_2^{Spacer}, β-OCH_3), 3.95 (m, 1 H, $OCHH^{Spacer}$), 4.05 (m, 2 H, OCH_2^{Spacer}), 4.16 (d, $^3J_{2,1}$ = 7.8 Hz, 1 H, 1a-H), 4.50 (hept, ^3J = 6.0 Hz, 2 H, $OCH(CH_3)_2$), 5.13 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1b-H), 6.03 (t, $^4J_{meta}$ = 1.8 Hz, 1 H, $C_6H_2H^{Phloro}$), 6.06 (d, $^4J_{meta}$ = 1.8 Hz, 2 H, $C_6H_2H^{Phloro}$) ppm. $C_{31}H_{52}O_{16}$·0.75H_2O (694.25): calcd. C 53.63, H 7.77; found C 53.61, H 7.84.

1-Bromo-2-(3,5-dimethoxyphenoxy)-1-ethane (32a): To a solution of 3,5-dimethoxyphenol (4.0 g, 25.95 mmol) in DMF (40.0 mL) and 1,2-dibromoethane (40.0 mL) was slowly (1 h) added NaH (5.00 g, 208.4 mmol) at 10 °C. After 2 h at room temp. the reaction was quenched with the slow addition of methanol (20.0 mL), and, if necessary, neutralised with acetic acid. The solvent was then removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 9:1) furnished **32a** (4.23 g, 16.20 mmol, 62%) as colourless oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.61. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.61 (t, ^3J = 5.9 Hz, 2 H, CH_2Br), 3.75 (s, 6 H, OCH_3), 4.23 (t, ^3J = 5.9 Hz, 2 H, OCH_2CH_2Br), 6.05–6.12 (m, 3 H, $C_6H_3^{Phloro}$) ppm. $C_{10}H_{13}BrO_3$ (261.12): calcd. C 46.00, H 5.02; found C 45.93, H 4.94.

1-Bromo-2-(3,5-diisopropyloxyphenoxy)-1-ethane (32b): To a solution of 3,5-diisopropyloxyphenol (1.0 g, 4.76 mmol) in DMF (20.0 mL) and 1,2-dibromoethane (15.0 mL) was slowly (1 h) added NaH (1.0 g, 41.67 mol) at room temp. After 2 h at room temp. the reaction was quenched with the slow addition of methanol (20.0 mL) and, if necessary, neutralised with acetic acid. The solvent was then removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 11:1) furnished **32b** (927 mg, 2.90 mmol, 61%) as colourless oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.76. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (d, ^3J = 6.5 Hz, 12 H, $CH(CH_3)_2$), 3.58 (t, ^3J = 6.2 Hz, 2 H, CH_2Br), 4.19 (t, ^3J = 6.2 Hz, 2 H, OCH_2CH_2Br), 4.46 (hept, ^3J = 6.5 Hz, 2 H, $CH(CH_3)_2$), 5.98–6.08 (m, 3 H, $C_6H_3^{Phloro}$) ppm. $C_{14}H_{21}BrO_3$ (317.22): calcd. C 53.01, H 6.67; found C 53.23, H 6.69.

2-(3,5-Dibenzyloxyphenoxy)-1-bromoethane (32c): To a solution of 3,5-dibenzyloxyphenol (370 mg, 1.21 mmol) in DMF (5.0 mL) and 1,2-dibromoethane (5.0 mL) was slowly (1 h) added NaH (200 mg, 8.70 mmol) at room temp. After 2 h the reaction was quenched with the slow addition of methanol (5.0 mL) and, if necessary, neutralised with acetic acid. The solvent was then removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 10:1) furnished **32c** (295 mg, 0.713 mmol, 59%) as colourless oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.71. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.95 (t, ^3J = 6.4 Hz, 2 H, CH_2Br), 4.21 (t, ^3J = 6.4 Hz, 2 H, OCH_2CH_2Br), 4.99 (s, 4 H, $PhCH_2$), 6.18 (d, $^4J_{meta}$ = 1.8 Hz, 2 H, $C_6H_2H^{Phloro}$), 6.27 (t, $^4J_{meta}$ = 1.8 Hz, 1 H, $C_6H_2H^{Phloro}$), 7.26–7.43 (m, 10 H, Ph) ppm. $C_{22}H_{21}BrO_3$ (413.31): calcd. C 63.93, H 5.12; found C 63.93, H 4.87.

Benzyl *O*-{2,3,6-Tri-*O*-benzyl-4-*O*-[2-(3,5-dimethoxyphenoxy)ethyl]-α-D-glucopyranosyl}-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33a): To a solution of **31** (200 mg, 0.206 mmol, 1.0 equiv.), **32a** (215 mg, 0.824 mmol, 4.0 equiv.) and TBAI (7.6 mg, 20.6 μmol, 0.1 equiv.) in dry DMF (10.0 mL) at 0 °C was slowly added NaH (16.3 mg, 0.824 mmol, 4.0 equiv.). After 8 h the reaction was quenched with methanol (5.0 mL) and, if necessary, neutralised with acetic acid. The volatile components were removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate, 20:1) furnished **33a** (181 mg, 0.157 mmol, 76%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.28. $[a]_D$ = +12.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.33–3.56 (m, 6 H, 2a-H, 5a-H, 2b-H, 4b-H, 6b-H, 6′b-H), 3.57–3.85 (m, 14 H, 3a-H, 6a-H, 6′a-H, 3b-H, 5b-H, CH_2O^{Spacer}, $CHHO^{Spacer}$, OCH_3), 3.92–4.02 (m, 2 H, 4a-H, $CHHO^{Spacer}$), 4.26 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.41–4.56 (m, 7 H, 1a-H, PhC*H*H), 4.61 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.69 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.70–4.90 (m, 5 H, PhC*H*H), 5.57 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1b-H), 5.93 (d, $^4J_{meta}$ = 1.9 Hz, 2 H, $C_6H_2H^{Phloro}$), 5.99 (t, $^4J_{meta}$ = 1.9 Hz, 1 H, $C_6H_2H^{Phloro}$), 7.01–7.39 (m, 35 H, Ph) ppm. $C_{71}H_{76}O_{14}$ (1153.38). Calcd. C 73.94, H 6.64; found C 73.89, H 6.70.

Benzyl *O*-{2,3,6-Tri-*O*-benzyl-4-*O*-[2-(3,5-diisopropyloxyphenoxy)-ethyl]-α-D-glucopyranosyl}-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33b): To a solution of **31** (150 mg, 0.154 mmol, 1.0 equiv.), **32b** (244 mg, 0.77 mmol, 5.0 equiv.) and TBAI (5.7 mg, 15.4 μmol, 0.1 equiv.) in dry DMF (10.0 mL) at room temp. was slowly added NaH (18.5 mg, 0.77 mmol, 5.0 equiv.). After 4 h the reaction was quenched with methanol (5.0 mL) and, if necessary, neutralised with acetic acid. The volatile components were removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 5:1) furnished **33b** (155 mg, 0.128 mmol, 83%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.43. $[a]_D$ = +12.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.27 (d, ^3J = 6.0 Hz, 12 H, $CH(CH_3)_2$), 3.43–3.64 (m, 6 H, 2a-H, 5a-H, 2b-H, 4b-H, 6b-H, 6′b-H), 3.70–3.88 (m, 8 H, 3a-H, 6a-H, 6′a-H, 3b-H, 5b-H, CH_2O^{Spacer}, $CHHO^{Spacer}$), 3.99–4.08 (m, 2 H, 4a-H, $CHHO^{Spacer}$), 4.35 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.34 (hept, ^3J = 6.0 Hz, 2 H, $CH(CH_3)_2$), 4.44–4.61 (m, 7 H, 1a-H, PhC*H*H), 4.62 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.76 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.80–4.84 (m, 2 H, PhC*H*H), 4.85–4.99 (m, 3 H, PhC*H*H), 5.64 (d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H), 5.97 (d, $^4J_{meta}$ = 2.0 Hz, 2 H, $C_6H_2H^{Phloro}$), 6.04 (t, $^4J_{meta}$ = 2.0 Hz, 1 H, $C_6H_2H^{Phloro}$), 7.09–7.39 (m, 35 H, Ph) ppm. $C_{75}H_{84}O_{14}$ (1209.48): calcd. C 74.48, H 7.00; found C 74.55, H 7.14.

Benzyl *O*-{2,3,6-Tri-*O*-benzyl-4-*O*-[2-(3,5-dibenzyloxyphenoxy)-ethyl]-α-D-glucopyranosyl}-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33c): To a solution of **31** (150 mg, 0.154 mmol, 1.0 equiv.), **32c** (446 mg, 1.079 mmol, 7.0 equiv.) and TBAI (5.7 mg, 15.4 μmol, 0.1 equiv.) in dry DMF (7.0 mL) at room temp. was added NaH (25 mg, 1.079 mmol, 7.0 equiv.). After 5 h the reaction was quenched with methanol (3.0 mL) and neutralised with acetic acid. The volatile components were removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 6:1) furnished **33c** (137 mg, 0.105 mmol, 68%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.47. $[a]_D$ = +11.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.32–

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3.56 (m, 6 H, 2a-H, 5a-H, 2b-H, 4b-H, 6b-H, 6′b-H), 3.60–3.83 (m, 8 H, 3a-H, 6a-H, 6′a-H, 3b-H, 5b-H, C*H*$_2$O, CH*H*O), 3.92–4.05 (m, 2 H, 4a-H, CH*H*O), 4.25 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.42–4.94 (m, 18 H, 1a-H, PhC*H*H), 5.57 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1b-H), 6.02 (d, $^4J_{meta}$ = 1.8 Hz, 2 H, C$_6$*H*$_2$H^{Phloro}), 6.16 (t, $^4J_{meta}$ = 1.8 Hz, 1 H, C$_6$H$_2$*H*^{Phloro}), 7.02–7.30 (m, 45 H, Ph) ppm. $C_{83}H_{84}O_{14}$·1.5H_2O (1332.59): calcd. C 74.81, H 6.58; found C 74.53, H 6.74.

***O*-{4-*O*-[2-(3,5-Dimethoxyphenoxy)ethyl]-α-D-glucopyranosyl}-(1→4)-α/β-D-glucopyranose (28a):** To a solution of **33a** (130 mg, 0.113 mmol) and dioxane (10.0 mL) was added Pearlman catalyst[19] (20.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After stirring for 3 h at room temp. the catalyst was separated with celite and the celite washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. Purification by flash chromatography with silica gel (ethyl acetate/EtOH, 3:1) and lyophilisation from dioxane furnished **28a** (59 mg, 0.113 mmol, quant.) als colourless lyophilisate. TLC (ethyl acetate/EtOH, 2:1): R_f = 0.11. ^{1}H NMR (250 MHz, CD_3OD): δ = 3.11–4.19 (m, 22 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, OCH$_2^{Spacer}$, OCH$_3$), 4.47 (d, $^3J_{2,1}$ = 7.9 Hz, 0.5 H, 1a-H$_β$), 5.09 (d, $^3J_{2,1}$ = 3.6 Hz, 0.5 H, 1b-H$_α$), 5.14 (2 d, $^3J_{2,1(α)}$ = $^3J_{2,1(β)}$ = 3.6 Hz, 1 H, 1b-H), 6.06–6.12 (m, 3 H, C$_6$H$_3^{Phloro}$) ppm. $C_{22}H_{34}O_{14}$·1H_2O (540.52): calcd. C 48.89, H 6.71; found C 48.85, H 6.79.

***O*-{4-*O*-[2-(3,5-Diisopropyloxyphenoxy)ethyl]-α-D-glucopyranosyl}-(1→4)-α/β-D-glucopyranose (28b):** To a solution of **33b** (140 mg, 0.116 mmol) and dioxane (8.0 mL) was added Pearlman catalyst[19] (14.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After stirring for 5 h at room temp. the catalyst was separated with celite and the celite washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. Purification by flash chromatography with silica gel (ethyl acetate/EtOH, 3:1) and lyophilisation from dioxane furnished **28b** (67 mg, 0.116 mmol, quant. as colourless lyophilisate. TLC (ethyl acetate/EtOH, 4:1): R_f = 0.09. ^{1}H NMR (600 MHz, CD_3OD): δ = 1.27 (d, ^3J = 6.0 Hz, 12 H, CH(C*H*$_3$)$_2$), 3.16 (dd, $^3J_{1,2} \approx {}^3J_{3,2}$ = 8.5 Hz, 0.5 H, 2a-H$_β$), 3.21–3.52 (m, 4 H, 2a-H$_α$, 4a-H, 5a-H$_β$, 2b-H, 4b-H), 3.59 (dd, $^3J_{2,3} \approx {}^3J_{4,3}$ = 8.5 Hz, 0.5 H, 3a-H$_β$), 3.66–4.08 (m, 10 H, 3a-H$_α$, 5a-H$_α$, 6a-H, 6′a-H, 3b-H, 5b-H, 6b-H, 6′b-H, OCH$_2^{Spacer}$, C*H*HO^{Spacer}), 4.11–4.17 (m, 1 H, C*H*HO^{Spacer}), 4.45–4.56 (m, 2.5 H, 1a-H$_β$, C*H*(CH$_3$)$_2$), 5.08 (d, $^3J_{2,1}$ = 3.6 Hz, 0.5 H, 1a-H$_α$), 5.14, 5.15 (2d, $^3J_{2,1(α)}$ = $^3J_{2,1(β)}$ = 3.6 Hz, 1 H, 1b-H), 6.02–6.08 (m, 3 H, C$_6$H$_3^{Phloro}$). $C_{26}H_{42}O_{14}$ (578.26): calcd. C 53.95, H 7.32; found C 53.55, H 7.58.

***O*-{4-*O*-[2-(3,5-Dihydroxyphenoxy)ethyl]-α-D-glucopyranosyl}-(1→4)-α/β-D-glucopyranose (28c):** To a solution of **33c** (230 mg, 0.176 mmol) in dioxane (10.0 mL) was added Pearlman catalyst[19] (20.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After stirring for 4 h at room temp. the catalyst was separated with celite and the celite washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. Purification by flash chromatography with silica gel (ethyl acetate/EtOH, 2:1) then with *RP18*-Kieselgel (CH_3CN/H_2O, 1:10) and lyophilisation from dioxane furnished **28c** (74 mg, 0.150 mmol, 85%) as wine red lyophilisate. TLC (ethyl acetate/EtOH, 2:1): R_f = 0.10. ^{1}H NMR (250 MHz, CD_3OD): δ = 3.12–4.19 (m, 16 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, OCH$_2^{Spacer}$), 4.49 (d, $^3J_{2,1}$ = 7.7 Hz, 0.5 H, 1a-H$_β$), 5.09 (d, $^3J_{2,1}$ = 3.6 Hz, 0.5 H, 1b-H$_α$), 5.14 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1b-H), 5.86–5.93 (m, 3 H, C$_6$H$_3^{Phloro}$). $C_{20}H_{30}O_{14}$·1.25H_2O (516.96): calcd. C 46.47, H 6.34; found C 46.51, H 6.35.

2-Bromo-1-(triisopropylsilyloxy)ethane (34): To a solution of 2-bromoethanol (1.69 mL, 3.00 g, 24.01 mmol, 1.0 equiv.) and TIPSCl (5.09 g, 26.41 mmol, 1.1 equiv.) in dry CH_2Cl_2 (40.0 mL) at room temp. was added imidazole (2.45, 36.02 mmol, 1.5 equiv.). After 4 h the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) furnishing **34** (4.26 g, 15.13 mmol, 63%) as colourless oil. TLC (petroleum ether/ethyl acetate, 9:1): R_f = 0.85. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.98–1.15 (m, 21 H, SiCH(CH_3)$_2$), 3.40 (t, ^3J = 6.4 Hz, 2 H, CH_2Br), 3.93 (t, ^3J = 6.4 Hz, 2 H, CH_2O). $C_{11}H_{25}BrOSi$ (281.31): calcd. C 46.97, H 8.96; found C 46.79, H 8.94.

Benzyl *O*-{2,3,6-Tri-*O*-benzyl-4-*O*-[2-(triisopropylsilyloxy)ethyl]-α-D-glucopyranosyl}-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (35): To a solution of **31**[14,27] (200 mg, 0.206 mmol, 1.0 equiv.), **34** (289 mg, 1.028 mmol, 5.0 equiv.) and TBAI (7.6 mg, 20.6 μmol, 0.1 equiv.) in dry DMF (15.0 mL) at room temp. was slowly added NaH (24.7 mg, 1.028 mmol, 5.0 equiv.). After 4 h the reaction was quenched with methanol (5.0 mL) and, if necessary, neutralised with acetic acid. The solvent was removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 20:1→10:1) furnished **35** (200 mg, 0.187 mmol, 91%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.57. $[α]_D$ = +23.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.95–1.15 (m, 21 H, SiCH(CH_3)$_2$), 3.41–3.89 (m, 15 H, 2a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, CH_2O^{Spacer}), 4.07 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.1 Hz, 1 H, 3a-H), 4.39 (d, ^2J = 12.3 Hz, 1 H, PhC*H*H), 4.48–4.89 (m, 11 H, 1a-H, 10 PhC*H*H), 4.90–4.98 (m, 3 H, PhC*H*H), 5.65 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1b-H), 7.11–7.38 (m, 35 H, Ph). $C_{72}H_{88}O_{12}Si$ (1173.57): calcd. C 73.69, H 7.56; found C 73.38, H 7.57.

Benzyl *O*-[2,3,6-Tri-*O*-benzyl-4-*O*-(2-hydroxyethyl)-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (36): To a solution of **35** (320 mg, 0.273 mmol) in THF (4.0 mL) at room temp. was added portionwise a solution of TBAF in THF (273 μL, 1.0 M). After 30 min the reaction mixture was neutralised with acetic acid and then concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) furnishing **36** (275 mg, 0.270 mmol, 99%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.33. $[α]_D$ = +29.8 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.59 (br. s, 1 H, OH), 3.41–3.72 (m, 11 H, 2a-H, 5a-H, 2b-H, 4b-H, 5b-H, 6b-H, 6′b-H, CH_2O^{Spacer}, CH_2OH^{Spacer}), 3.77–3.83 (m, 4 H, 4a-H, 6a-H, 6′a-H, 3b-H), 4.08 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.2 Hz, 1 H, 3a-H), 4.35 (d, ^2J = 12.1 Hz, 1 H, PhC*H*H), 4.45–4.63 (m, 7 H, 1a-H, 10 PhC*H*H), 4.64–4.75 (m, 3 H, PhC*H*H), 4.85–4.99 (m, 4 H, PhC*H*H), 5.66 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1b-H), 7.05–7.48 (m, 35 H, Ph). $C_{63}H_{68}O_{12}$ (1017.23): calcd. C 74.39, H 6.74; found C 74.35, H 6.74.

Benzyl *O*-[2,3,6-Tri-*O*-benzyl-4-*O*-(2-bromoethyl)-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (37): To a solution of **36** (200 mg, 0.197 mmol, 1.0 equiv.) and tetrabromomethane (326 mg, 0.983 mmol, 5.0 equiv.) in dry CH_2Cl_2 (30.0 mL) at room temp. was added triphenylphosphane (258 mg, 0.983 mmol, 5 equiv.). After 45 min the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 5:1) furnishing **37** (187 mg, 0.173 mmol, 88%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.49. $[α]_D$ = +23.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.17–3.29 (m, 2 H, CH_2Br), 3.38–3.50 (m, 3 H, 2b-H, 4b-H, 6b-H), 3.51–3.87 (m, 9 H, 2a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 3b-H, 5b-H, 6′b-H, C*H*HO^{Spacer}), 3.99 (m, 1 H, C*H*HO^{Spacer}), 4.08 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.2 Hz, 1 H, 3a-H), 4.36 (d, ^2J = 12.0 Hz, 1 H,

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PhC*H*H), 4.48–5.01 (m, 14 H, 1a-H, PhC*H*H), 5.05 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1b-H), 7.08–7.45 (m, 35 H, Ph). $C_{63}H_{67}BrO_{11}$ (1080.12): calcd. C 70.06, H 6.25; found C 70.03, H 6.25.

1,3,5-Tris{2-[benzyl *O*-(2,3,6-Tri-*O*-benzyl-4-yl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside]ethyloxy}benzene (38): To a solution of **37** (176 mg, 163 μmol), water-free phloroglucine (7.0 mg, 55.5 μmol) and TBAI (6.0 mg, 16.3 μmol) in dry DMF (6.0 mL) at room temp. was added NaH (20.0 mg, 833 μmol) over 3 d. Then the reaction was quenched with methanol (5.0 mL) and, if necessary, neutralised with acetic acid. The solvent was removed in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnished **38** (90 mg, 28.8 μmol, 52%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.67. $[\alpha]_D$ = +11.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.43–3.51 (m, 9 H, 2b-H, 2b′-H, 2b′′-H, 4b-H, 4b′-H, 4b′′-H, 6b-H, 6b′-H, 6b′′-H), 3.52–3.67 (m, 9 H, 2a-H, 2a′-H, 2a′′-H, 5a-H, 5a′-H, 5a′′-H, 6′b-H, 6′b′-H, 6′b′′-H), 3.68–3.95 (m, 24 H, 3a-H, 3a′-H, 3a′′-H, 6a-H, 6a′-H, 6a′′-H, 6′a-H, 6′a′-H, 6′a′′-H, 3b-H, 3b′-H, 3b′′-H, 5b-H, 5b′-H, 5b′′-H, 3CH_2O^{Spacer}, 3C*H*HO^{Spacer}), 3.97–4.11 (m, 6 H, 4a-H, 4a′-H, 4a′′-H, 3C*H*HO), 4.31 (d, ^2J = 12.1 Hz, 3 H, PhC*H*H), 4.48–4.60 (m, 18 H, 1a-H, 1a′-H, 1a′′-H, PhC*H*H), 4.61 (d, ^2J = 12.0 Hz, 3 H, PhC*H*H), 4.67 (d, ^2J = 12.1 Hz, 3 H, PhC*H*H), 4.70–4.85 (m, 9 H, PhC*H*H), 4.86–4.99 (m, 9 H, PhC*H*H), 5.64 (d, $^3J_{2,1}$ = 3.4 Hz, 3 H, 1b-H, 1b′-H, 1b′′-H), 5.90 (s, 3 H, $C_6H_3^{Phloro}$), 7.09–7.39 (m, 105 H, Ph). MALDI MS: *m*/*z* = 3140 [MNa^+]. FAB MS: *m*/*z* = 3146 [MNa^+], 3297 [(MNaI)Na^+]; (abs. mass 3121.41). $C_{195}H_{204}O_{36}$ (3123.74): calcd. C 74.98, H 6.58; found C 74.58, H 6.78.

1,3,5-Tris-{2-[*O*-(4-yl-α-D-glucopyranosyl)-(1→4)-α/β-D-glucopyranoside]ethyloxy}benzene (39): To a solution of **38** (55.0 mg, 17.61 μmol) in THF (7.0 mL) was added Pearlman catalyst[19] (10.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After 2 d at hydrogen overpressure of 0.1 bar the catalyst was separated with celite in order to quench the reaction. The celite was washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified with *RP-18*-silica gel (CH_3CN/H_2O, 1:4) by flash chromatography and lyophilised from D_2O furnishing **39** (22 mg, 17.61 μmol, quant. as colourless lyophilisate in D_2O (anomeric ratio α/β, 2:3). *RP-18* DC (CH_3CN/H_2O, 1:4): R_f = 0.63. ^{1}H NMR (600 MHz, D_2O): δ = 3.17 (dd, $^3J_{1,2}$ = 7.9 Hz, $^3J_{3,2}$ = 9.0 Hz, 1.8 H, 2a-H$_\beta$, 2a′-H$_\beta$, 2a′′-H$_\beta$), 3.30 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.5 Hz, 3 H, 4b-H, 4b′-H, 4b′′-H), 3.43–3.57 (m, 9 H, 2a-H$_\alpha$, 2a′-H$_\alpha$, 2a′′-H$_\alpha$, 4a-H, 4a′-H, 4a′′-H, 5a-H$_\beta$, 5a′-H$_\beta$, 5a′′-H$_\beta$, 2b-H, 2b′-H, 2b′′-H), 3.61–3.90 (m, 22.2 H, 3a-H$_\alpha$, 3a′-H$_\alpha$, 3a′′-H$_\alpha$, 3a-H$_\beta$, 3a′-H$_\beta$, 3a′′-H$_\beta$, 5a-H$_\alpha$, 5a′-H$_\alpha$, 5a′′-H$_\alpha$, 6a-H, 6a′-H, 6a′′-H, 6′a-H, 6′a′-H, 6′a′′-H, 3b-H, 3b′-H, 3b′′-H, 5b-H, 5b′-H, 5b′′-H, 6b-H, 6b′-H, 6b′′-H, 6′b-H, 6′b′-H, 6′b′′-H), 3.91–3.96 (m, 3 H, C*H*HO^{Spacer}), 4.04–4.14 (m, 9 H, C*H*HO^{Spacer}), 4.54 (d, $^3J_{2,1}$ = 7.9 Hz, 1.8 H, 1a-H$_\beta$, 1a′-H$_\beta$, 1a′′-H$_\beta$), 5.12 (d, $^3J_{2,1}$ = 3.6 Hz, 1.2 H, 1a-H$_\alpha$, 1a′-H$_\alpha$, 1a′′-H$_\alpha$), 5.30 (d, $^3J_{2,1}$ = 3.4 Hz, 3 H, 1b-H, 1b′-H, 1b′′-H), 6.22 (s, 3 H, $C_6H_3^{Phloro}$). FAB MS: *m*/*z* = 1231 [MH^+], 1253 [MNa^+]; (abs. mass 1230.43). $C_{48}H_{78}O_{36}$·$5H_2O$ (1321.20): calcd. C 43.64, H 6.71; found C 43.79, H 6.86.

1,3,5-Tris-{2-[*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyloxy]-ethyloxy}benzene (43): To a solution of **42**[28] (20.0 mg, 77.44 μmol, 1.0 equiv.) in dry acetonitrile (4.0 mL) was added TMSOTf (0.35 μL, 1.94 μmol, 0.025 equiv.) and then slowly at room temp. a solution of **40**[13,30] (200 mg, 255.6 μmol, 3.3 equiv.) in dry acetonitrile (3.0 mL). After 1 h the reaction mixture was neutralised with triethylamine and then concentrated in vacuo. Purification by flash chromatography (petroleum ether/ethyl acetate, 1:3) furnished **43** (106 mg, 50.34 μmol, 65%) as colourless foam. TLC (petroleum ether/ethyl acetate, 1:3): R_f = 0.23. $[\alpha]_D$ = +35.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.85–2.23 (m, 63 H, CH_3CO), 3.68 (m, 3 H, 5a-H, 5a′-H, 5a′′-H), 3.84–4.11 (m, 21 H, 4a-H, 4a′-H, 4a′′-H, 5b-H, 5b′-H, 5b′′-H, 6b-H, 6b′-H, 6b′′-H, 6 CH_2O^{Spacer}), 4.12–4.26 (m, 6 H, 6′b-H, 6′b′-H, 6′b′′-H, 6a-H, 6a′-H, 6a′′-H), 4.46 (dd, $^3J_{5,6}$ = 1.9, $^2J_{6,6'}$ = 10.0 Hz, 3 H, 6′a-H, 6′a′-H, 6′a′′-H), 4.64 (d, $^3J_{2,1}$ = 7.8 Hz, 3 H, 1a-H, 1a′-H, 1a′′-H), 4.78–4.86 (m, 6 H, 2a-H, 2a′-H, 2a′′-H, 2b-H, 2b′-H, 2b′′-H), 5.03 (dd, $^3J_{3,4}$ = 1.9, $^2J_{5,4}$ = 9.8 Hz, 3 H, 4b-H, 4b′-H, 4b′′-H), 5.24 (dd, $^3J_{2,3}$ = $^2J_{4,3}$ = 9.1 Hz, 3 H, 3a-H, 3a′-H, 3a′′-H), 5.33 (dd, $^3J_{2,3}$ = $^2J_{4,3}$ = 10.0 Hz, 3 H, 3b-H, 3b′-H, 3b′′-H), 5.38 (d, $^3J_{2,1}$ = 3.7 Hz, 3 H, 1b-H, 1b′-H, 1b′′-H), 6.02 (s, 3 H, $C_6H_3^{Phloro}$). MALDI MS: *m*/*z* = 2154 [MK^+]. FAB MS: *m*/*z* = 2137 [MNa^+], 2287 [(MNaI)Na^+]; (abs. mass 2112.65). $C_{90}H_{120}O_{57}$·H_2O (2131.91): calcd. C 50.70, H 5.77; found C 50.73, H 5.87.

1,3,5-Tris-{2-[*O*-(α-D-glucopyranosyl)-(1→4)-β-D-glucopyranosyloxy]ethyloxy}benzene (44): To a solution of **43** (50.0 mg, 23.65 μmol) in dry methanol (15.0 mL) was added sodium methylate in methanol (10.0 μL, 1.0 M). After stirring for 2 d at room temp. the reaction mixture was neutralised with Amberlite IR 120 H^+ and then the solvent removed in vacuo. Purification by flash chromatography (CH_3CN/H_2O, 1:8, *RP-18*) furnished **44** (25 mg, 20.34 μmol, 86%) as colourless lyophilisate (D_2O). *RP-18* TLC (CH_3CN/H_2O, 1:8): R_f = 0.29. $[\alpha]_D$ = +36.6 (*c* = 1.0, H_2O). ^{1}H NMR (600 MHz, D_2O): δ = 3.21 (dd, $^3J_{1,2}$ = 8.0, $^3J_{3,2}$ = 9.0 Hz, 3 H, 2a-H, 2a′-H, 2a′′-H), 3.29 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 8.7 Hz, 3 H, 4b-H, 4b′-H, 4b′′-H), 3.42–3.48 (m, 6 H, 5a-H, 5a′-H, 5a′′-H, 2b-H, 2b′-H, 2b′′-H), 3.49–3.69 (m, 18 H, 3a-H, 3a′-H, 3a′′-H, 4a-H, 4a′-H, 4a′′-H, 6a-H, 6a′-H, 6a′′-H, 3b-H, 3b′-H, 3b′′-H, 5b-H, 5b′-H, 5b′′-H, 6b-H, 6b′-H, 6b′′-H), 3.70–3.78 (m, 6 H, 6′a-H, 6′a′-H, 6′a′′-H, 6′b-H, 6′b′-H, 6′b′′-H), 3.88–3.95 (m, 3 H, C*H*HO^{Spacer}), 4.06–4.15 (m, 9 H, C*H*HO^{Spacer}), 4.43 (d, $^3J_{2,1}$ = 8.0 Hz, 3 H, 1a-H, 1a′-H, 1a′′-H), 5.27 (d, $^3J_{2,1}$ = 3.7 Hz, 3 H, 1b-H, 1b′-H, 1b′′-H), 6.20 (s, 3 H, $C_6H_3^{Phloro}$). FAB MS: *m*/*z* = 1231 [MH^+], 1253 [MNa^+], 1269 [MK^+]; (abs. mass 1230.43). $C_{48}H_{78}O_{36}$·$4H_2O$ (1303.18): calcd. C 44.24, H 6.65; found C 44.23, H 6.57.

Ethyl *O*-(2,3-Di-*O*-Benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (53): To a solution of **52**[32] (7.9 g, 16.65 mmol, 1.0 equiv.) in dry DMF (150.0 mL) was added benzyl bromide (10.88 mL, 15.66 g, 91.58 mmol, 5.5 equiv.). Then NaH (2.20 g, 91.58 mmol, 5.5 equiv.) was added portionwise over 2 h at room temp. After 20 h slow addition of methanol (20 mL) destroyed excess NaH and the reaction mixture was neutralised with acetic acid. The solvent was then removed in vacuo and the residue dissolved in distilled water (50 mL) and ethyl acetate (250 mL). The aqueous phase was washed with ethyl acetate (3 × 100 mL) and the combined organic phases dried with $MgSO_4$. Purification by flash chromatography (petroleum ether/ethyl acetate, 5:1) furnished **53** (10.5 g, 11.32 mmol, 68%) as highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.56. $[\alpha]_D$ = +2.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, 3 H, ^3J = 7.4 Hz, SCH_2CH_3), 2.65–2.86 (m, 2 H, SCH_2CH_3), 3.44–4.20 (m, 12 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H), 4.42–4.96 (m, 1a-H, 10 PhC*H*H), 5.52 (s, 1 H, PhC*H*), 5.67 (d, 1 H, $^3J_{1,2}$ = 3.9 Hz, 1b-H), 7.08–7.51 (m, 30 H, Ph). $C_{56}H_{60}O_{10}S$ (925.15): calcd. C 72.70, H 6.54; found C 73.06, H 6.54.

Benzyl *O*-2,3-Di-*O*-benzyl-6-bromo-6-deoxy-α-D-glucopyranoside (55): To a solution of **54** (200 mg, 0.444 mmol, 1.0 equiv.) and tetra-

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bromomethane (177 mg, 0.533 mmol, 1.2 equiv.) in dry CH_2Cl_2 (20.0 mL) was added triphenylphosphane (140 mg, 0.533 mmol, 1.2 equiv.) at room temp. After 4 h the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 8:1) furnishing **55** (140 mg, 0.273 mmol, 61%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.78. $[\alpha]_D$ = +61.1 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.25 (s, 1 H, OH), 3.44–3.56 (m, 3 H, 2-H, 4-H, 6-H), 3.63 (dd, $^3J_{5,6'}$ = 1.9, $^3J_{6,6'}$ = 11.0 Hz, 1 H, 6′-H), 3.77–3.89 (m, 2 H, 3-H, 5-H), 4.54 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 4.57–4.65 (m, 2 H, PhC*H*H), 4.69 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 4.76 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 4.88 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1-H), 5.05 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 7.25–7.46 (m, 15 H, Ph). MALDI MS: m/z = 536, 538 [MNa^+], 552, 554 [MK^+]. $C_{27}H_{29}BrO_5$ (513.43): calcd. C 63.16, H 5.69; found C 63.07, H 5.65.

Benzyl 2,3-Di-*O*-Benzyl-6-*O*-methyl-α-D-glucopyranoside (56): To a solution of **55** (120 mg, 0.234 mmol, 1.0 equiv.), TBAI (8.64 mg, 0.023 mmol, 0.1 equiv.) and crown ether 15-crown-5 (103 mg, 0.468 mmol, 2.0 equiv.) in dry DMF (10.0 mL) was added portionwise sodium methoxide (126 mg, 2.34 mmol, 10.0 equiv.) at room temp. After 3 d at room temp. the reaction mixture was neutralised with acetic acid and after aqueous workup purified by flash chromatography (toluene/ethyl acetate, 5:1) furnishing **56** (52 mg, 0.112 mmol, 48%) as colourless, highly viscous oil. TLC (toluene/ethyl acetate, 5:1): R_f = 0.26. $[\alpha]_D$ = +56.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.33 (br. s, 1 H, OH), 3.38 (s, 3 H, OCH_3), 3.50–3.62 (m, 4 H, 2-H, 4-H, 6-H, 6′-H), 3.74 (m, 1 H, 5-H), 3.85 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.2 Hz, 1 H, 3-H), 4.51–4.58 (m, 2 H, PhC*H*H), 4.63 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.70–4.76 (m, 2 H, PhC*H*H), 4.85 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1-H), 5.03 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 7.25–7.44 (m, 15 H, Ph). $C_{28}H_{32}O_6$ (464.22): calcd. C 71.39, H 6.94; found C 71.48, H 6.93.

Benzyl *O*-2,3-Di-*O*-benzyl-6-*O*-thexyldimethylsilyl-α-D-glucopyranoside (57): To a solution of **54** (3.30 g, 7.325 mmol, 1.0 equiv.) in dry CH_2Cl_2 (40.0 mL) was added thexyldimethylsilyl chloride (1.58 mL, 1.44 g, 8.06 mmol, 1.1 equiv.) and imidazole (0.748 g, 10.99 mmol, 1.5 equiv.) at room temp. After 5 h (TLC monitoring) the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) furnishing **57** (4.34 g, 7.325 mmol, quant. as colourless oil. TLC (petroleum ether/ethyl acetate, 8:1): R_f = 0.42. $[\alpha]_D$ = +48.2 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08, 0.09 [2s, 6 H, $Si(CH_3)_2$], 0.78–0.89 [m, 12 H, 2 $C(CH_3)_2$], 1.59 [hept, ^3J = 6.6 Hz, 1 H, $CH(CH_3)_2$], 2.58 (br. s, 1 H, OH), 3.41–3.55 (m, 2 H, 2-H, 4-H), 3.59–3.76 (m, 3 H, 5-H, 6-H, 6′-H), 3.84 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 8.5 Hz, 1 H, 3-H), 4.48–4.83 (m, 6 H, 1-H, 5 PhC*H*H), 4.97 (d, ^2J = 11.2 Hz, 1 H, PhC*H*H), 7.19–7.44 (m, 15 H, Ph). $C_{35}H_{48}O_6Si$ (592.85): calcd. C 70.91, H 8.16; found C 71.04, H 8.14.

Benzyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-thexyldimethylsilyl-α-D-glucopyranoside (58): To a solution of **57** (2.14 g, 3.61 mmol, 1.0 equiv.) and **53** (5.00 g, 5.40 mmol, 1.5 equiv.) in dry diethyl ether (200 mL) was added *N*-iodosuccinimide (1.21 g, 5.40 mmol, 1.5 equiv.) at room temp. The reaction was then initiated with catalytic amounts of trifluoromethane sulfonic acid (1.6 μL, 0.005 equiv.). After 30 min the reaction mixture was washed with $NaHCO_3$ solution (50.0 mL) and Na_2SO_3 solution (3 × 50 mL) and dried with $MgSO_4$. The reaction mixture was then concentrated in vacuo and the residue purified by flash chromatography (toluene/ethyl acetate, 75:1) furnishing **58** (2.10 g, 0.319 mmol, 40%) as colourless, highly viscous oil. TLC (toluene/ethyl acetate, 50:1): R_f = 0.37. $[\alpha]_D$ = +47.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.08, 0.10 [2s, 6 H, $Si(CH_3)_2$], 0.83–0.88 [m, 12 H, 2 $C(CH_3)_2$], 1.53–1.64 [m, 1 H, $CH(CH_3)_2$], 3.46–3.57 (m, 3 H, 2a-H, 2b-H, 2c-H), 3.58–3.69 (m, 3 H, 4c-H, 6b-H, 6c-H), 3.77–3.92 (m, 6 H, 4a-H, 5a-H, 6a-H, 6′a-H, 6′b-H, 5c-H), 3.94–3.97 (m, 1 H, 5b-H), 3.98–4.09 (m, 2 H, 3b-H, 3c-H), 4.10–4.19 (m, 3 H, 3a-H, 4b-H, 6′c-H), 4.43–4.62 (m, 7 H, PhC*H*H), 4.63–4.71 (m, 2 H, PhC*H*H), 4.72–4.78 (m, 3 H, PhC*H*H), 4.80 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1a-H), 4.84–4.96 (m, 3 H, PhC*H*H), 5.03 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.53 (s, 1 H, PhC*H*), 5.62 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1b-H), 5.70 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1c-H), 7.02–7.56 (m, 45 H, Ph). $C_{89}H_{102}O_{16}Si$ (1455.87): calcd. C 73.43, H 7.06; found C 73.45, H 7.10.

Benzyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (59): To a solution of **58** (400 mg, 0.275 mmol) in THF (12.0 mL) was added at room temp. portionwise a solution of TBAF in THF (275 μL, 1.0 M). After 20 h the reaction mixture was neutralised with acetic acid and then the mixture concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnishing **59** (294 mg, 0.224 mmol, 81%) as colourless, highly viscous oil. TKC (petroleum ether/ethyl acetate, 3:1): R_f = 0.19. $[\alpha]_D$ = +39.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.00 (m, 1 H, OH), 3.46 (dd, $^3J_{1,2}$ = 3.7, $^3J_{3,2}$ = 9.8 Hz, 1 H, 2c-H), 3.51 (dd, $^3J_{1,2}$ = 3.8, $^3J_{3,2}$ = 9.8 Hz, 1 H, 2b-H), 3.55–3.67 (m, 4 H, 2a-H, 6b-H, 4c-H, 6c-H), 3.68–3.79 (m, 4 H, 5a-H, 6a-H, 6′b-H, 5c-H), 3.82 (dd, $^3J_{3,4}$ = $^2J_{5,4}$ = 9.2 Hz, 1 H, 4a-H), 3.88 (dd, $^3J_{2,3}$ = $^2J_{4,3}$ = 9.5 Hz, 1 H, 3c-H), 3.92–4.01 (m, 3 H, 5a-H, 3b-H, 6′a-H), 4.08 (dd, $^3J_{3,4}$ = $^2J_{5,4}$ = 9.8 Hz, 1 H, 4b-H), 4.11–4.17 (m, 2 H, 3a-H, 6′c-H), 4.37–4.63 (m, 8 H, PhC*H*H), 4.64–4.80 (m, 5 H, PhC*H*H), 4.82–4.88 (m, 3 H, 1a-H, PhC*H*H), 5.08 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 5.54 (s, 1 H, PhC*H*), 5.59 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1b-H), 5.72 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1c-H), 6.99–7.55 (m, 45 H, Ph). $C_{81}H_{84}O_{16}$ (1313.55): calcd. C 74.07, H 6.44; found C 73.86, H 6.33.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-thexyldimethylsilyl-α-D-glucopyranoside (60): To a solution of **58** (100 mg, 68.7 μmol, 1.0 equiv.) in dry CH_2Cl_2 (5.0 mL) was added a solution of borane in THF (0.687 mL, 1.0 M) and then a solution of Bu_2BOTf in CH_2Cl_2 (10 μL, 1.0 M). After 24 h excess borane complex was destroyed with methanol (20 mL) and the reaction mixture neutralised with triethylamine. The reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) furnishing **60** (90 mg, 61.8 μmol, 90%) as colourless highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.45. $[\alpha]_D$ = +61.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.09, 0.11 [2s, 6 H, $Si(CH_3)_2$], 0.83–0.88 [m, 12 H, 2$C(CH_3)_2$], 1.56–1.68 [m, 1 H, $CH(CH_3)_2$], 3.39 (dd, $^3J_{1,2}$ = 3.4, $^3J_{3,2}$ = 10.6 Hz, 1 H, 2c-H), 3.46–3.56 (m, 4 H, 2a-H, 2b-H, 4c-H, 6c-H), 3.57–3.65 (m, 2 H, 6b-H, 6′c-H), 3.69 (m, 1 H, 5b-H), 3.78–3.96 (m, 7 H, 4a-H, 5a-H, 6a-H, 6′a-H, 5b-H, 6′b-H, 3c-H), 3.99–4.08 (m, 2 H, 3b-H, 4b-H), 4.15 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 8.9 Hz, 1 H, 3a-H), 4.44–4.65 (m, 10 H, PhC*H*H), 4.72–4.79 (m, 3 H, PhC*H*H), 4.80 (d, $^3J_{2,1}$ = 3.3 Hz, 1 H, 1a-H), 4.82–4.94 (m, 4 H, PhC*H*H), 5.03 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.58 (d, $^3J_{2,1}$ = 3.3 Hz, 1 H, 1c-H), 5.63 (d, $^3J_{2,1}$ = 3.3 Hz, 1 H, 1b-H), 7.04–7.48 (m, 45 H, Ph). $C_{89}H_{104}O_{16}Si$ (1457.88): calcd. C 73.32, H 7.19; found C 73.09, H 7.24.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-6-*O*-methyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-thexyldimethylsilyl-α-D-glucopyranoside (61): To a solution of **60** (150 mg, 0.103 mmol, 1.0 equiv.) in dry DMF (6.5 mL)

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was added methyl iodide (19.3 μL 43.9 mg, 0.309 mmol, 3.0 equiv.) at room temp. and then NaH (7.4 mg, 0.309 mmol, 3.0 equiv.). After 28 h methanol (10.0 mL) was added to quench the reaction and then triethylamine (0.5 mL). The reaction mixture was neutralised with acetic acid, the solvent removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 5:1) furnishing **61** (132 mg, 89.61 μmol, 87%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.68. $[\alpha]_D$ = +61.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.08, 0.10 [2s, 6 H, $Si(CH_3)_2$], 0.82–0.89 [m, 12 H, $2C(CH_3)_2$], 1.61 [hept, ^3J = 6.8 Hz, 1 H, $CH(CH_3)_2$], 3.20 (s, 3 H, OCH_3), 3.31 (dd, $^3J_{5,6}$ = 2.0, $^3J_{6,6'}$ = 9.7 Hz, 1 H, 6c-H), 3.42 (dd, $^3J_{5,6}$ = 2.4, $^3J_{6,6'}$ = 9.5 Hz, 1 H, 6′c-H), 3.45 (dd, $^3J_{1,2}$ = 3.4, $^3J_{3,2}$ = 10.4 Hz, 1 H, 2c-H), 3.48–3.55 (m, 2 H, 2a-H, 2b-H), 3.59–3.62 (m, 2 H, 6a-H, 4c-H), 3.64–3.73 (m, 1 H, 5c-H), 3.77–3.95 (m, 7 H, 4a-H, 5a-H, 6′a-H, 5b-H, 6b-H, 6′b-H, 3c-H), 3.99–4.06 (m, 2 H, 3b-H, 4b-H), 4.14 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 8.9 Hz, 1 H, 3a-H), 4.42–4.59 (m, 10 H, PhC*H*H), 4.73–4.80 (m, 4 H, 1a-H, PhC*H*H), 4.81–4.87 (m, 3 H, PhC*H*H), 4.89 (d, ^2J = 11.4 Hz, 1 H, PhC*H*H), 5.00 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.61 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1b-H), 5.67 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1c-H), 7.05–7.49 (m, 45 H, Ph). $C_{90}H_{106}O_{16}Si$ (1471.91): calcd. C 73.44, H 7.26; found C 73.39, H 7.40.

***O*-(6-*O*-Methyl-α-D-glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-α/β-D-glucopyranose (45):** To a solution of **61** (120 mg, 81.53 μmol, 1.0 equiv.) in THF (10.0 mL) at room temp. was added portionwise a solution of TBAF in THF (244.6 μL, 1.0 M, 3.0 equiv.). After 24 h the reaction mixture was neutralised with acetic acid and then concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1). The intermediate (90 mg) was then dissolved in THF/H_2O/AcOH, 300:50:1 (7.0 mL) and Pearlman catalyst[19] (15.0 mg) added. Then the argon atmosphere was completely replaced by hydrogen. After 72 h at room temp. the catalyst was separated with celite and the celite washed with methanol/water (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified by flash chromatography (H_2O 100%; *RP-18*) and lyophilised from D_2O furnishing **45** (32 mg, 61.72 μmol, 76%) as colourless lyophilisate (α/β, 2:3; D_2O). TLC *RP-18* (H_2O 100%): R_f = 0.58. ^{1}H NMR (250 MHz, D_2O): δ = 3.10 (dd, $^3J_{1,2}$ = $^3J_{3,2}$ = 8.2 Hz, 0.6 H, 2a-H_β), 3.17–3.32 (m, 4 H, 4c-H, OCH_3), 3.33–3.83 (m, 16.4 H, 2a-H_α, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, 2c-H, 3c-H, 5c-H, 6c-H, 6′c-H), 4.46 (d, $^3J_{2,1}$ = 8.0 Hz, 0.6 H, 1a-H_β), 5.04 (d, $^3J_{2,1}$ = 3.7 Hz, 0.4 H, 1a-H_α), 5.17–5.25 (m, 2 H, 1b-H, 1c-H). $C_{19}H_{34}O_{16}$·1.75H_2O (550.00): calcd. C 41.49, H 6.87; found C 41.33, H 6.62.

Benzyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-*n*-propyl-D-glucopyranoside (62): To a solution of **59** (150 mg, 0.114 mmol, 1.0 equiv.) in dry DMF (10.0 mL) was added *n*-propyl iodide (111 μL, 194 mg, 1.142 mmol, 10.0 equiv.) at room temp. and then NaH (27.4 mg, 1.142 mmol, 10.0 equiv.). After 72 h methanol (10.0 mL) was added to quench the reaction. Then the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) furnishing **62** (111 mg, 81.85 μmol, 72%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.48. $[\alpha]_D$ = +47.1 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.83 (t, ^3J = 7.4 Hz, 3 H, $OCH_2CH_2CH_3$), 1.48–1.55 (m, 2 H, $OCH_2CH_2CH_3$), 3.31–3.34 (m, 2 H, $OCH_2CH_2CH_3$), 3.46–3.54 (m, 3 H, 6a-H, 2b-H, 2c-H), 3.55–3.65 (m, 4 H, 2a-H, 6b-H, 4c-H, 6c-H), 3.75–3.92 (m, 5 H, 5a-H, 6′a-H, 6′b-H, 5c-H), 3.93–4.09 (m, 3 H, 4a-H, 3b-H, 3c-H), 4.10–4.23 (m, 3 H, 3a-H, 4b-H, 6c-H), 4.42–4.61 (m, 7 H, PhC*H*H), 4.62–4.75 (m, 5 H, PhC*H*H), 4.77–4.94 (m, 4 H, 1a-H, PhC*H*H), 5.02 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.52–5.56 (m, 2 H, 1b-H, PhC*H*H), 5.72 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1c-H), 7.03–7.52 (m, 45 H, Ph). $C_{84}H_{90}O_{16}$ (1355.63): calcd. C 74.42, H 6.69; found C 74.26, H 6.75.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-propyl-α-D-glucopyranoside (63): To a solution of **62** (110 mg, 81.14 μmol) in dry CH_2Cl_2 (5.0 mL) was added a solution of borane in THF (0.81 mL, 1.0 M) and then a solution of Bu_2BOTf in CH_2Cl_2 (20 μL, 1.0 M). After 72 h the excess borane complex was destroyed with methanol (10 mL) and the reaction mixture neutralised with triethylamine. The mixture was concentrated in vacuo and then purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnishing **63** (76 mg, 55.99 μmol, 69%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.30. $[\alpha]_D$ = +48.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.77 (t, ^3J = 7.4 Hz, 3 H, $OCH_2CH_2CH_3$), 1.44–1.53 (m, 2 H, $OCH_2CH_2CH_3$), 1.63 (br. s, 1 H, OH), 3.22–3.37 (m, 3 H, 2c-H, $OCH_2CH_2CH_3$), 3.39–3.49 (m, 4 H, 6a-H, 2b-H, 4c-H, 6c-H), 3.50–3.58 (m, 3 H, 2a-H, 6b-H, 6′c-H), 3.59–3.63 (m, 1 H, 5c-H), 3.70 (dd, $^3J_{5,6}$ = 3.4, $^2J_{6,6'}$ = 11.2 Hz, 1 H, 6′a-H), 3.74–3.82 (m, 3 H, 5a-H, 5b-H, 6′b-H), 3.83 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 8.9 Hz, 1 H, 3c-H), 3.90–4.01 (m, 3 H, 4a-H, 3b-H, 4b-H), 4.04 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 8.4 Hz, 1 H, 3a-H), 4.35–4.57 (m, 10 H, PhC*H*H), 4.63–4.70 (m, 3 H, PhC*H*H), 4.73–4.81 (m, 4 H, 1a-H, PhC*H*H), 4.84 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 4.97 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.48–5.52 (m, 2 H, 1b-H, 1c-H), 7.02–7.46 (m, 45 H, Ph). $C_{84}H_{92}O_{16}$ (1356.64): calcd. C 74.31, H 6.83; found C 73.89, H 7.15.

***O*-(α-D-Glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-6-*O*-propyl-α-D-glucopyranoside (50):** To a solution of **63** (55 mg, 40.5 μmol) in THF/H_2O, 5:1 (6.0 mL) was added Pearlman catalyst[19] (15 mg) and catalytic amounts of acetic acid (10 μL). Then the argon atmosphere was completely replaced by hydrogen. After 72 h at room temp. the catalyst was separated with celite and the celite washed with methanol/water (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified by flash chromatography (CH_3CN/H_2O, 1:50; *RP-18*) and then lyophilised from D_2O furnishing **50** (22 mg, 40.5 μmol, quant. as colourless lyophilisate (α/β, 2:3; D_2O). TLC *RP-18* (CH_3CN/H_2O, 1:50): R_f = 0.45. ^{1}H NMR (250 MHz, D_2O): δ = 0.75 (t, ^3J = 7.4 Hz, 3 H, $OCH_2CH_2CH_3$), 1.42 (qt, ^3J = $^3J'$ = 7.4 Hz, 2 H, $OCH_2CH_2CH_3$), 3.10 (dd, $^3J_{1,2}$ = $^3J_{3,2}$ = 8.5 Hz, 0.6 H, 2a-H_β), 3.20–3.91 (m, 19.4 H, 1a-H_α, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, 2c-H, 3c-H, 4c-H, 5c-H, 6c-H, 6′c-H, $OCH_2CH_2CH_3$), 4.47 (d, $^3J_{2,1}$ = 8.0 Hz, 0.6 H, 2a-H_β), 5.04 (d, $^3J_{2,1}$ = 3.6 Hz, 0.4 H, 1a-H_α), 5.21 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1c-H), 5.22–5.27 (m, 1 H, 1b-H). MALDI MS: m/z = 569 [MNa^+], 585 [MK^+]. $C_{21}H_{38}O_{16}$ (546.52).

Benzyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-methyl-α-D-glucopyranoside (64): To a solution of **56** (200 mg, 0.431 mmol, 1.0 equiv.) and **53** (598 mg, 0.646 mmol, 1.5 equiv.) in dry diethyl ether (15.0 mL) at room temp. was added *N*-iodosuccinimide (145 mg, 0.646 mmol, 1.5 equiv.). Then the reaction was started with catalytic amounts of trifluoromethanesulfonic acid (0.38 μL, 0.65 mg, 4.31 μmol, 0.01 equiv.). After 30 min the reaction mixture was washed with $NaHCO_3$ solution (5.0 mL) and Na_2SO_3 solution (3 × 10 mL) and dried with $MgSO_4$. The residue was concentrated in vacuo and purified by flash chromatography (toluene/ethyl acetate, 10:1) furnishing **64** (423 mg, 0.319 mmol, 74%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.47. $[\alpha]_D$ = +56.7 (c = 1.0,

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$CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.24 (s, 6 H, OCH_3), 3.36 (dd, $^3J_{5,6}$ = 2.0, $^2J_{6,6'}$ = 9.3 Hz, 1 H, 6a-H), 3.49 (dd, $^3J_{1,2}$ = 3.6, $^3J_{3,2}$ = 9.4 Hz, 1 H, 2c-H), 3.54 (dd, $^3J_{1,2}$ = 3.4, $^3J_{3,2}$ = 9.7 Hz, 1 H, 2b-H), 3.56–3.70 (m, 4 H, 2a-H, 6b-H, 4c-H, 6c-H), 3.74 (dd, $^3J_{5,6}$ = 2.0, $^2J_{6,6'}$ = 9.6 Hz, 1 H, 6′a-H), 3.77–3.81 (m, 1 H, 5b-H), 3.82–3.89 (m, 3 H, 5a-H, 6′b-H, 5c-H), 3.94 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.6 Hz, 1 H, 3c-H), 3.98–4.06 (m, 2 H, 4a-H, 3b-H), 4.11–4.19 (m, 3 H, 3a-H, 4b-H, 6c-H), 4.41–4.60 (m, 7 H, PhC*H*H), 4.61–4.76 (m, 5 H, PhC*H*H), 4.79 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 4.81–4.88 (m, 2 H, 1a-H, PhC*H*H), 4.94 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 5.08 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 5.55 (s, 1 H, PhC*H*), 5.65 (d, $^3J_{2,1}$ = 3.3 Hz, 1 H, 1b-H), 5.72 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1c-H), 7.01–7.53 (m, 45 H, Ph). $C_{82}H_{86}O_{16}$ (1326.59): calcd. C 74.19, H 6.53; found C 73.71, H 6.27.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-methyl-α-D-glucopyranoside (65): To a solution of **64** (400 mg, 0.301 mmol) in dry CH_2Cl_2 (15.0 mL) was added a solution of borane in THF (3.01 mL, 1.0 M) and then a solution of Bu_2BOTf in CH_2Cl_2 (100 μL, 1.0 M). After 72 h the excess borane complex was destroyed with methanol (20 mL) and the reaction mixture neutralised with triethylamine. The mixture was concentrated in vacuo and then purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) furnishing **65** (338 mg, 0.254 mmol, 84%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.10. δ = +74.2 (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.63 (br. s, 1 H, OH), 3.26 (s, 3 H, OCH_3), 3.33–3.40 (m, 2 H, 6a-H, 2c-H), 3.43–3.56 (m, 3 H, 2b-H, 4c-H, 6c-H), 3.57–3.70 (m, 4 H, 2a-H, 6b-H, 5c-H, 6′c-H), 3.71–3.77 (m, 2 H, 6′a-H, 5b-H), 3.84–3.90 (m, 3 H, 5a-H, 6′b-H, 3c-H), 3.95–4.09 (m, 3 H, 3b-H, 4b-H, 4a-H), 4.13 (dd, $^3J_{2,3}$ = $^2J_{4,3}$ = 8.8 Hz, 1 H, 3a-H), 4.41–4.63 (m, 10 H, PhC*H*H), 4.65–4.88 (m, 7 H, 1a-H, PhC*H*H), 4.91 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.07 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 5.55 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1c-H), 5.65 (d, $^3J_{2,1}$ = 3.3 Hz, 1 H, 1b-H), 7.07–7.47 (m, 45 H, Ph). $C_{82}H_{88}O_{16}$ (1329.59): calcd. C 74.08, H 6.67; found C 73.96, H 6.66.

***O*-(α-D-Glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-6-*O*-methyl-α/β-D-glucopyranose (49):** To a solution of **65** (150 mg, 0.113 mmol) in THF (10.0 mL) was added Pearlman catalyst[19] (20.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After 72 h at room temp. the catalyst was separated with celite and the celite washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified by flash chromatography (CH_3CN/H_2O, 1:100; *RP-18*) and then lyophilised from D_2O furnishing **49** (59 mg, 0.113 mmol, quant. as colourless lyophilisate (α/β, 2:3; D_2O). TLC *RP-18* (CH_3CN/H_2O, 1:100): R_f = 0.84. ^1H NMR (250 MHz, D_2O): δ = 3.10 (dd, $^3J_{1,2}$ = $^3J_{3,2}$ = 8.3 Hz, 0.6 H, 2a-H_β), 3.16–3.31 (m, 4 H, 4c-H, OCH_3), 3.32–3.91 (m, 16.4 H, 1a-H_α, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, 2c-H, 3c-H, 5c-H, 6c-H, 6′c-H), 4.48 (d, $^3J_{2,1}$ = 8.0 Hz, 0.6 H, 1a-H_β), 5.04 (d, $^3J_{2,1}$ = 3.5 Hz, 0.4 H, 1a-H_α), 5.21 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1c-H), 5.28 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1b-H). $C_{19}H_{34}O_{16}$·1.5H_2O (545.49): calcd. C 41.84, H 6.84; found C 41.65, H 6.57.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-6-*O*-methyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-methyl-α-D-glucopyranoside (66): To a solution of **65** (150 mg, 0.113 mmol, 1.0 equiv.) in dry DMF (6.0 mL) at room temp. was added methyl iodide (21.2 μL, 48.1 mg, 0.339 mmol, 3.0 equiv.) and then NaH (8.1 mg, 0.339 mmol, 3.0 equiv.). After 24 h the reaction was quenched with methanol (10.0 mL) and triethylamine (0.5 mL) and the reaction mixture neutralised with acetic acid. The solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnishing **66** (134 mg, 99.44 μmol, 88%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.35. $[\alpha]_D$ = +64.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.21 (br. s, 3 H, 6c-OCH_3), 3.28 (br. s, 3 H, 6a-OCH_3), 3.35 (dd, $^3J_{5,6}$ = 2.0, $^2J_{6,6'}$ = 10.2 Hz, 1 H, 6c-H), 3.38 (dd, $^3J_{5,6}$ = 2.0, $^2J_{6,6'}$ = 9.5 Hz, 1 H, 6a-H), 3.41–3.50 (m, 2 H, 6′c-H, 2b-H), 3.53 (dd, $^3J_{1,2}$ = 3.3, $^2J_{3,2}$ = 8.8 Hz, 1 H, 2b-H), 3.56–3.67 (m, 3 H, 2a-H, 6b-H, 4c-H), 3.69–3.80 (m, 3 H, 6′a-H, 5b-H, 5c-H), 3.82–3.92 (m, 3 H, 5a-H, 6′b-H, 3c-H), 3.96–4.06 (m, 2 H, 3b-H, 4a-H), 4.07–4.18 (m, 2 H, 3a-H, 4b-H), 4.42–4.60 (m, 10 H, PhC*H*H), 4.67–4.87 (m, 7 H, 1a-H, PhC*H*H), 4.91 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.06 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 5.63 (d, $^3J_{2,1}$ = 3.2 Hz, 1 H, 1b-H), 5.67 (d, $^3J_{2,1}$ = 3.3 Hz, 1 H, 1c-H), 7.08–7.48 (m, 45 H, Ph). $C_{83}H_{90}O_{16}$ (1343.62): calcd. C 74.20, H 6.75; found C 73.87, H 6.76.

***O*-(6-*O*-Methyl-α-D-glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-6-*O*-methyl-α/β-D-glucopyranose (48):** To a solution of **66** (150 mg, 0.112 mmol) in THF (10.0 mL) was added Pearlman catalyst[19] (20.0 mg). Then the argon atmosphere was completely replaced by hydrogen. After 72 h at room temp. the catalyst was separated with celite and the celite washed with methanol (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified by flash chromatography (CH_3CN/H_2O, 1:50; *RP-18*) and then lyophilised from D_2O furnishing **48** (53 mg, 0.101 mmol, 90%) as colourless lyophilisate (α/β, 2:3; D_2O). TLC *RP-18* (CH_3CN/H_2O, 1:50): R_f = 0.45. ^{1}HNMR (250 MHz, D_2O): δ = 3.05 (dd, $^3J_{1,2}$ = 8.0, $^3J_{3,2}$ = 8.9 Hz, 0.6 H, 2a-H_β), 3.12–3.28 (m, 7 H, 4c-H, 6a-OCH_3, 6c-OCH_3), 3.29–3.88 (m, 16.4 H, 2a-H_α, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, 2c-H, 3c-H, 5c-H, 6c-H, 6′c-H), 4.42 (d, $^3J_{2,1}$ = 8.0 Hz, 0.6 H, 1a-H_β), 4.99 (d, $^3J_{2,1}$ = 3.7 Hz, 0.4 H, 1a-H_α), 5.18 (d, $^3J_{2,1}$ = 3.6 Hz, 1 H, 1c-H), 5.22 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1b-H). $C_{20}H_{36}O_{16}$·2.5H_2O (577.53): calcd. C 41.59, H 7.16; found C 41.60, H 6.86.

Benzyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (67): To a solution of **6** (77.9 mg, 0.144 mmol, 1.0 equiv.) and **53** (200 mg, 0.216 mmol, 1.0 equiv.) in dry diethyl ether (10 mL) at room temp. was added *N*-iodosuccinimide (48.6 mg, 0.216 mmol, 1.5 equiv.). The reaction was started with catalytic amounts of trifluoromethanesulfonic acid (0.2 μL, 0.01 equiv.). After 30 min the reaction mixture was washed with $NaHCO_3$ solution (10.0 mL) and Na_2SO_3 solution (3 × 15 mL) and dried with $MgSO_4$. The reaction mixture was concentrated in vacuo and the residue purified by flash chromatography (a. toluene/ethyl acetate, 50:1; b. toluene/ethyl acetate, 20:1) furnishing **67** (113 mg, 80.64 μmol, 56%) as colourless foam. TLC (toluene/ethyl acetate, 20:1): R_f = 0.39. $[\alpha]_D$ = +52.0 (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.48–3.68 (m, 8 H, 2a-H, 6a-H, 6′a-H, 2b-H, 6b-H, 2c-H, 4c-H, 6c-H), 3.75–3.92 (m, 4 H, 5a-H, 5b-H, 6′b-H, 5c-H), 3.97 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.6 Hz, 1 H, 3c-H), 4.00–4.17 (m, 5 H, 3a-H, 4a-H, 3b-H, 4b-H, 6c-H), 4.38–4.59 (m, 10 H, PhC*H*H), 4.60–4.75 (m, 4 H, PhC*H*H), 4.77–4.87 (m, 3 H, 1a-H, PhC*H*H), 4.92 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 5.06 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.53 (s, 1 H, PhC*H*), 5.60 (d, $^3J_{2,1}$ = 3.2 Hz, 1 H, 1b-H), 5.71 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1c-H), 7.04–7.51 (m, 50 H, Ph). $C_{88}H_{90}O_{16}$ (1403.67): calcd. C 75.30, H 6.46; found C 74.89, H 6.47.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-

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glucopyranoside (68): To a solution of **67** (160 mg, 0.114 mmol) in dry CH_2Cl_2 (20.0 mL) was added a solution of borane in THF (1.14 mL, 1.0 M) and then a solution of Bu_2BOTf in CH_2Cl_2 (25 μL, 1.0 M). After 72 h the excess borane complex was destroyed with methanol (10 mL) and the reaction mixture neutralised with triethylamine. The deposit was concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnishing **68** (136 mg, 96.9 μmol, 85%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.27. $[\alpha]_D$ = +63.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.61 (br. s, 1 H, OH), 3.37 (dd, $^3J_{1,2}$ = 3.5, $^3J_{3,2}$ = 9.5 Hz, 1 H, 2c-H), 3.43–3.52 (m, 4 H, 2b-H, 6b-H, 4c-H, 6c-H), 3.53–3.65 (m, 4 H, 2a-H, 6a-H, 5c-H, 6′c-H), 3.68 (dd, $^3J_{5,6}$ = 2.2, $^3J_{6,6'}$ = 10.9 Hz, 1 H, 6′b-H), 3.81–3.93 (m, 4 H, 5a-H, 6′a-H, 5b-H, 3c-H), 3.99–4.10 (m, 3 H, 4a-H, 3b-H, 4b-H), 4.14 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.5 Hz, 1 H, 3a-H), 4.36–4.62 (m, 12 H, PhC*H*H), 4.66–4.72 (m, 2 H, PhC*H*H), 4.73–4.86 (m, 5 H, 1a-H, PhC*H*H), 4.91 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 5.06 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.56 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1c-H), 5.62 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1b-H), 7.04–7.49 (m, 50 H, Ph). $C_{88}H_{92}O_{16}$ (1405.69): calcd. C 75.19, H 6.60; found C 74.78, H 6.97.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-6-*O*-triisopropylsilyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (69): To a solution of **68** (300 mg, 0.213 mmol, 1.0 equiv.) in dry CH_2Cl_2 (10.0 mL) at room temp. was added triisopropylsilyl chloride (100.68 μL, 90.62 mg, 0.47 mmol, 2.2 equiv.) and imidazole (44 mg, 0.640 mmol, 3.0 equiv.). After 50 h (TLC monitoring) the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnishing **69** (304 mg, 0.195 mmol, 92%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.67. $[\alpha]_D$ = +55.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.95–1.04 (m, 21 H, SiC*H*(CH_3)$_2$), 3.42 (dd, $^3J_{1,2}$ = 3.5, $^3J_{3,2}$ = 9.1 Hz, 1 H, 2c-H), 3.53–3.57 (m, 3 H, 2b-H, 6b-H, 6a-H), 3.58–3.64 (m, 2 H, 2a-H, 5c-H), 3.67–3.75 (m, 3 H, 6′a-H, 4c-H, 6c-H), 3.80 (dd, $^3J_{5,6}$ = 2.5, $^3J_{6,6'}$ = 10.7 Hz, 1 H, 6′c-H), 3.84 (dd, $^3J_{5,6}$ = 2.5, $^3J_{6,6'}$ = 10.8 Hz, 1 H, 6′b-H), 3.87–3.94 (m, 3 H, 5a-H, 5b-H, 3c-H), 4.01–4.20 (m, 4 H, 3a-H, 4a-H, 3b-H, 4b-H), 4.39–4.63 (m, 11 H, PhC*H*H), 4.68–4.91 (m, 1a-H, PhC*H*H), 4.93 (d, ^2J = 11.7 Hz, 1 H, PhC*H*H), 5.06 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.63 (d, $^3J_{2,1}$ = 3.2 Hz, 1 H, 1b-H), 5.66 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1c-H), 7.10–7.48 (m, 50 H, Ph). $C_{97}H_{112}O_{16}Si$ (1562.03): calcd. C 74.59, H 7.23; found C 74.49, H 7.27.

***O*-(6-*O*-Triisopropylsilyl-α-D-glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-α/β-D-glucopyranose (47):** To a solution of **69** (200 mg, 0.128 mmol) in dioxane (8.0 mL) was added Pearlman catalyst[19] (20 mg). Then the argon atmosphere was completely replaced by hydrogen. After 5 h at room temp. the catalyst was separated with celite and the celite washed with methanol/water (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified by flash chromatography (CH_3CN/H_2O, 1:1; *RP-18*) and then lyophilised from D_2O furnishing **47** (85 mg, 0.128 mmol, quant. as colourless lyophilisate (α/β, 2:3; D_2O). TLC *RP-18* (CH_3CN/H_2O, 1:1): R_f = 0.50. ^{1}H NMR (250 MHz, D_2O): δ = 0.80–1.18 (m, 21 H, SiC*H*(CH_3)$_2$), 3.05–3.23 (m, 1.6 H, 2a-H$_\beta$, 4c-H), 3.33–3.97 (m, 16.4 H, 2a-H$_\alpha$, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, 2c-H, 3c-H, 4c-H, 5c-H, 6c-H, 6′c-H), 4.48 (d, $^3J_{2,1}$ = 8.0 Hz, 0.6 H, 1a-H$_\beta$), 5.06 (d, $^3J_{2,1}$ = 3.5 Hz, 0.4 H, 1a-H$_\alpha$), 5.16–5.28 (m, 2 H, 1b-H, 1c-H). MALDI MS: m/z = 683 [MNa^+], 699 [MK^+]. $C_{27}H_{52}O_{16}Si{\cdot}2H_2O$ (696.81): calcd. C 46.54, H 8.10; found C 46.35, H 7.72.

Benzyl *O*-(6-Azido-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-thexyldimethylsilyl-α-D-glucopyranoside (70): 60 (150 mg, 0.103 mmol, 1.0 equiv.) was dissolved with diisopropyl azodicarboxylate (DIAD) (29.8 μL, 31.1 mg, 0.155 mmol, 1.5 equiv.) and triphenylphosphane (41 mg, 0.155 mmol, 1.5 equiv.) in dry CH_2Cl_2 (8.0 mL). At room temp. a solution of HN_3 (6.7 mg, 0.155 mmol, 1.5 equiv.) in benzene (50 μL). After 3 h (TLC monitoring) the reaction mixture was diluted with $NaHCO_3$ solution (10 mL) and ethyl acetate (10 mL). The aqueous phase was extracted with ethyl acetate (3 × 20 mL). The solvent was removed from the combined organic phases in vacuo, then the residue purified by flash chromatography (toluene/ethyl acetate, 50:1) furnishing **70** (104 mg, 70.04 μmol, 68%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.73. $[\alpha]_D$ = +75.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.10, 0.12 (2s, 6 H, Si(CH_3)$_2$), 0.84–0.89 (m, 12 H, 2C(CH_3)$_2$), 1.62 (hept, ^3J = 6.8 Hz, 1 H, C*H*(CH_3)$_2$), 3.13 (dd, $^3J_{5,6}$ = 3.3, $^3J_{6,6'}$ = 12.5 Hz, 1 H, 6c-H), 3.29 (dd, $^3J_{5,6'}$ = 2.5, $^3J_{6,6'}$ = 12.5 Hz, 1 H, 6′c-H), 3.45 (dd, $^3J_{1,2}$ = 3.5, $^3J_{3,2}$ = 9.4 Hz, 1 H, 2c-H), 3.46–3.58 (m, 3 H, 2a-H, 2b-H, 4c-H), 3.66 (dd, $^3J_{5,6}$ = 2.0, $^3J_{6,6'}$ = 10.9 Hz, 1 H, 6b-H), 3.78–3.95 (m, 8 H, 4a-H, 5a-H, 6a-H, 6′a-H, 5b-H, 6′b-H, 3c-H, 5c-H), 4.03 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.2 Hz, 1 H, 3b-H), 4.09 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.3 Hz, 1 H, 4b-H), 4.16 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.2 Hz, 1 H, 3a-H), 4.43–4.61 (m, 10 H, PhC*H*H), 4.70–4.78 (m, 3 H, PhC*H*H), 4.81 (d, $^3J_{2,1}$ = 3.3 Hz, 1 H, 1a-H), 4.82–4.95 (m, 4 H, PhC*H*H), 5.04 (d, ^2J = 11.5 Hz, 1 H, PhC*H*H), 5.62–5.67 (m, 2 H, 1b-H, 1c-H), 7.05–7.49 (m, 45 H, Ph). $C_{89}H_{103}N_3O_{15}Si$ (1482.90): calcd. C 72.09, H 7.00, N 2.83; found C 71.88, H 7.07, N 2.45.

Benzyl *O*-(6-Azido-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (71): To a solution of **70** (70 mg, 47.21 μmol, 1.0 equiv.) in THF (5.0 mL) at room temp. was added portionwise a solution of TBAF in THF (94.4 μL, 1 M, 2.0 equiv.). After 40 h the reaction mixture was neutralised with acetic acid and the deposit concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) furnishing **71** (58 mg, 43.26 μmol, 92%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.18. $[\alpha]_D$ = +76.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.00 (br. s, 1 H, OH), 3.16 (dd, $^3J_{5,6}$ = 3.4, $^3J_{6,6'}$ = 12.6 Hz, 1 H, 6c-H), 3.26 (dd, $^3J_{5,6'}$ = 2.5, $^3J_{6,6'}$ = 12.6 Hz, 1 H, 6′c-H), 3.36–3.44 (m, 2 H, 2c-H, 4c-H), 3.55 (dd, $^3J_{1,2}$ = 3.6, $^3J_{3,2}$ = 8.8 Hz, 1 H, 2b-H), 3.58–3.65 (m, 3 H, 2a-H, 6b-H, 5c-H), 3.66–3.75 (m, 2 H, 6a-H, 6′b-H), 3.76–3.83 (m, 3 H, 5a-H, 4b-H, 3c-H), 3.93–4.01 (m, 3 H, 6′a-H, 3b-H, 5b-H), 4.07 (dd, $^3J_{3,4}$ = $^3J_{5,4}$ = 9.5 Hz, 1 H, 4a-H), 4.17 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.7 Hz, 1 H, 3a-H), 4.41–4.63 (m, 10 H, PhC*H*H), 4.67 (d, ^2J = 11.4 Hz, 1 H, PhC*H*H), 4.69–4.76 (m, 3 H, PhC*H*H), 4.77–4.88 (m, 4 H, 1a-H, PhC*H*H), 5.08 (d, ^2J = 11.8 Hz, 1 H, PhC*H*H), 5.47 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1c-H), 5.71 (d, $^3J_{2,1}$ = 3.8 Hz, 1 H, 1b-H), 7.01–7.48 (m, 45 H, Ph). $C_{81}H_{85}N_3O_{15}$ (1339.60): calcd. C 72.57, H 6.39, N 3.13; found C 72.11, H 6.36, N 2.75.

***O*-(6-Amino-6-deoxy-α-D-glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-α/β-D-glucopyranoside (46):** To a solution of **71** (175 mg, 0.132 mmol) in THF/H_2O, 7:1 (17.0 mL) was added Pearlman catalyst[19] (15 mg) and catalytic amounts of acetic acid (20 μL). Then the argon atmosphere was completely replaced by hydrogen. After 72 h at room temp. the catalyst was separated with celite and the celite washed with methanol/water (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified by flash chromatography (EtOH/H_2O/HCl, 10:1000:1; *RP-18*) and then lyophilised as hydrochloride from D_2O furnishing **46** (35 mg, 66 μmol, 50%) as colourless lyo-

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philisate (α/β, 2:3; D_2O). TLC *RP-18* (H_2O/AcOH, 100:1): R_f = 0.81. ^1H NMR (250 MHz, D_2O): δ = 2.93–4.92 (m, 18 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, 2c-H, 3c-H, 4c-H, 5c-H, 6c-H, 6′c-H), 4.48 (d, $^3J_{2,1}$ = 7.9 Hz, 0.6 H, 1a-H_β), 5.05 (d, $^3J_{2,1}$ = 3.4 Hz, 0.4 H, 1a-H_α), 5.26–5.32 (m, 1 H, 1b-H), 5.45 (d, $^3J_{2,1}$ = 3.7 Hz, 1 H, 1c-H). MALDI MS: *m*/*z* = 526 [MNa^+], 542 [MK^+]. $C_{18}H_{33}NO_{15}$·HCl (539.92). The physical data are in accordance with the literature.[37]

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-6-bromo-6-deoxy-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (72): To a solution of **68** (110 mg, 78.25 μmol, 1.0 equiv.) and tetrabromomethane (39 mg, 0.117 mmol, 1.5 equiv.) in dry CH_2Cl_2 (10.0 mL) at room temp. was added triphenyl phosphane (31 mg, 0.117 mmol, 1.5 equiv.). After 6 h the solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) furnishing **72** (101 mg, 68.9 μmol, 88%) as colourless, highly viscous oil. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.59. $[\alpha]_D$ = +57.0 (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.37 (dd, $^3J_{5,6}$ = 2.0, $^3J_{6,6'}$ = 11.0 Hz, 1 H, 6c-H), 3.43–3.50 (m, 2 H, 2c-H, 6′c-H), 3.52–3.69 (m, 5 H, 2a-H, 6a-H, 2b-H, 6b-H, 4c-H), 3.74 (dd, $^3J_{5,6}$ = 2.5, $^3J_{6,6'}$ = 10.9 Hz, 1 H, 6′a-H), 3.77–3.83 (m, 1 H, 5c-H), 3.85–3.99 (m, 4 H, 5a-H, 5b-H, 6′b-H, 3c-H), 4.02–4.12 (m, 3 H, 4a-H, 3b-H, 4b-H), 4.17 (dd, $^3J_{2,3}$ = $^3J_{4,3}$ = 9.8 Hz, 1 H, 3a-H), 4.43–4.64 (m, 11 H, PhC*H*H), 4.67–4.79 (m, 4 H, PhC*H*H), 4.81–4.90 (m, 3 H, 1a-H, PhC*H*H), 4.91–4.96 (m, 2 H, PhC*H*H), 5.09 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 5.64 (d, $^3J_{2,1}$ = 3.4 Hz, 1 H, 1b-H), 5.67 (d, $^3J_{2,1}$ = 3.5 Hz, 1 H, 1c-H), 7.03–7.50 (m, 50 H, Ph). $C_{88}H_{91}BrO_{15}$ (1468.59): calcd. C 71.97, H 6.25; found C 71.77, H 6.34.

***O*-(6-Bromo-6-deoxy-α-D-glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-α/β-D-glucopyranose (51):** To a solution of **72** (244 mg, 0.166 mmol) in dioxane (15.0 mL) was added Pearlman catalyst[19] (20 mg). Then the argon atmosphere was completely replaced by hydrogen. After 8 h at room temp. the catalyst was separated with celite and the celite washed with methanol/water (3 × 10 mL). Filtrate and wash solution were combined and the solvent removed in vacuo. The residue was purified by flash chromatography (CH_3CN/H_2O, 1:100; *RP-18*) and then lyophilised from D_2O furnishing **51** (71 mg, 0.125 mmol, 75%) as colourless lyophilisate (α/β, 2:3; D_2O). TLC *RP-18* (CH_3CN/H_2O, 1:100): R_f = 0.52. ^1H NMR (250 MHz, D_2O): δ = 3.10 (dd, $^3J_{1,2}$ = $^3J_{3,2}$ = 8.2 Hz, 0.6 H, 2a-H_β), 3.24–3.89 (m, 17.4 H, 2a-H_α, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H, 6′b-H, 2c-H, 3c-H, 4c-H, 5c-H, 6c-H, 6′c-H), 4.49 (d, $^3J_{2,1}$ = 8.0 Hz, 0.6 H, 1a-H_β), 5.10 (d, $^3J_{2,1}$ = 3.6 Hz, 0.4 H, 1a-H_α), 5.19–5.30 (m, 2 H, 1b-H, 1c-H). MALDI MS: *m*/*z* = 589, 591 [MNa^+], 605, 507 [MK^+]. $C_{18}H_{31}BrO_{15}$ (567.34).

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