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Synthesis of the tetrasaccharide glycoside moiety of Solaradixine and rapid NMR-based structure verification using the program CASPER

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Abstract

The major glycoalkaloid in the roots of *Solanum laciniatum* is Solaradixine having the branched tetrasaccharide β -D-Glcp-(1 \rightarrow 2)- β -D-Glcp-(1 \rightarrow 3)[α -L-Rhap-(1 \rightarrow 2)]- β -D-Galp linked to O3 of the steroidal alkaloid Solasodine. We herein describe the synthesis of the methyl glycoside of the tetrasaccharide using a super-armed disaccharide as a donor molecule. A 2-(naphthyl)methyl protecting group was used in the synthesis of the donor since it was tolerant to a wide range of reaction conditions. The 6-*O*-benzylated-hexa-*O*-*tert*-butyldimethylsilyl-protected β -D-Glcp-(1 \rightarrow 2)- β -D-Glcp-SEt donor, which avoided 1,6-anhydro formation, was successfully glycosylated at O3 of a galactoside acceptor molecule. However, subsequent glycosylation at O2 by a rhamnosyl donor was unsuccessful and instead a suitably protected α -L-Rhap-(1 \rightarrow 2)- β -D-Galp-OMe disaccharide was used as the acceptor molecule together with a super-armed β -D-Glcp-(1 \rightarrow 2)- β -D-Glcp-SEt donor in the glycosylation reaction, to give a tetrasaccharide in a yield of 55%, which after deprotection resulted in the target molecule, the structure of which was verified by the NMR chemical shift prediction program CASPER.

Keywords: glycosylation, oligosaccharide, saponin, CASPER, chemical shift prediction

1. Introduction

Saponins are glycosides with one or more sugars in their structure and the aglycone is either a triterpene, a steroid or a steroidal alkaloid.¹⁻⁵ The oligosaccharide portion is typically made from a limited number of different monosaccharides, viz., D-glucose, D-galactose, D-glucuronic acid, D-xylose, L-arabinose or L-rhamnose, and linked to O3 of the aglycone (sapogenin);⁶ the number of oligosaccharides possible to form is still very large. These amphiphilic compounds are secondary metabolites widely spread in the plant kingdom and several have been found in marine animals.^{7,8} Saponins are biologically active compounds that can be used in pharmacological applications owing

to their cytotoxic effects, immunostimulatory, anti-inflammatory, antiviral and hypoglycemic activities among others.⁹⁻¹⁵

Members of the plant family *Solanaceae* include, inter alia, eggplant, tomato and potato.¹⁶ Glycoalkaloids, as well as oligosaccharides and saponins, from these plants have anticarcinogenic properties inhibiting cell growth both in culture and in vivo. *Solanum laciniatum* produces glycoalkaloids that exert various biological activities. Several different glycoalkaloids are found in the leaves, berries and roots of this species. Besides trisaccharide-containing saponins, larger glycoalkaloids are present in the roots, having Solasodine (Figure 1) as the sapogenin, viz., Solashabanine having a tetrasaccharide with a terminal β -(1 \rightarrow 6)-linked glucosyl residue, Solaradixine (**1b**) containing a tetrasaccharide but instead with a terminal β -(1 \rightarrow 2)-linked glucosyl residue (Figure 1) and Solaridine comprising a pentasaccharide with a terminal β -(1 \rightarrow 6)-linked glucosyl residue attached to the β -(1 \rightarrow 2)-linked glucosyl residue of Solaradixine.¹⁷

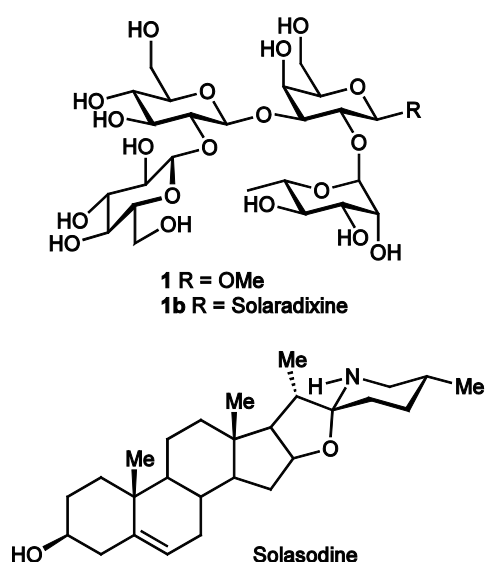


Figure 1. Schematic of methyl α -L-rhamnopyranosyl-(1 \rightarrow 2)[β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyl-(1 \rightarrow 3)]- β -D-galactopyranoside (**1**), the glycoalkaloid Solaradixine (**1b**) and Solasodine.

Synthesis of saponins and oligosaccharide glycosides¹⁸⁻²⁰ thereof facilitates corroboration of their structures, chemical modification of functional groups to study their impact and effects in biological environments as well as enabling sufficient amounts of material for in vitro as well as in vivo studies.²¹⁻²⁷ Herein we describe, to the best of our knowledge, for the first time, the synthesis of the branched tetrasaccharide β -D-Glcp-(1 \rightarrow 2)- β -D-Glcp-(1 \rightarrow 3)[α -L-Rhap-(1 \rightarrow 2)]- β -D-Galp-OMe (**1**)

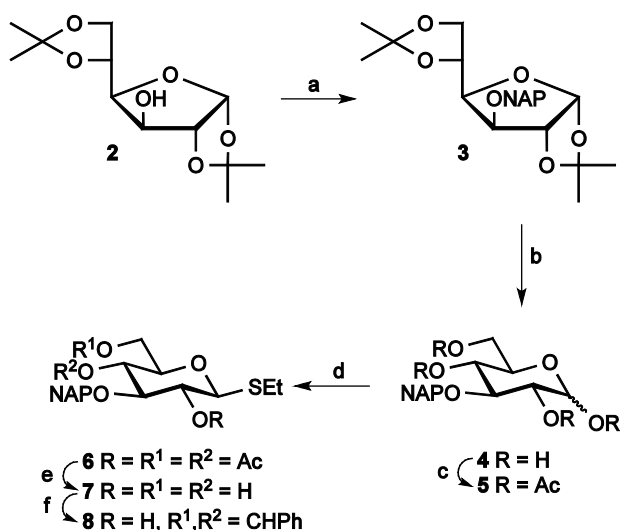
corresponding to the glycoside moiety of the glycoalkaloid Solaradixine from *S. laciniatum* and its rapid structure verification based on unassigned ^1H and ^{13}C NMR spectra as implemented in the computer program CASPER.

2. Results and Discussion

2.1 Tetrasaccharide synthesis

In the synthesis of the branched target tetrasaccharide **1** three glycosidic linkages are to be formed. Realizing that β -(1 \rightarrow 2)-linked glucosyl-containing disaccharides have been utilized as donors in glycosylation reactions with very high β -anomeric selectivity,²⁸ we envisioned that this could be a suitable donor, especially since super-armed monosaccharide donors had been used for glycosylation reactions at O4 of a protected glucosyl acceptor,²⁹ i.e., at a secondary carbon atom. If this strategy were to be chosen, a suitably protected methyl galactopyranoside could be used as an acceptor, followed by a second glycosylation reaction by a rhamnosyl donor molecule or one could use a preformed disaccharide acceptor, which had been made by glycosylation of a rhamnosyl donor to O2 of the methyl galactopyranoside.

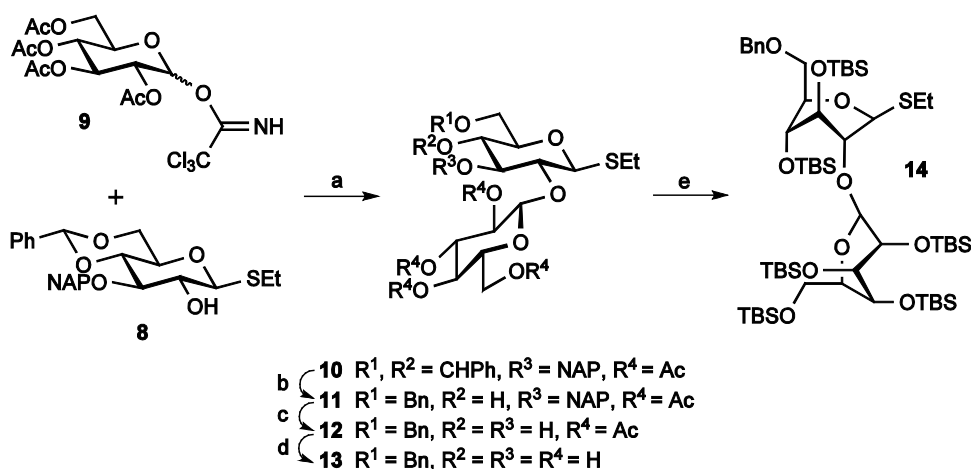
Formation of a suitably protected monosaccharide, which has a thioethyl group to be used as the leaving group in the glycosylation reaction and that can be employed as the acceptor molecule in order to form the β -(1 \rightarrow 2)-linked donor disaccharide utilized a 2-naphthylmethyl (NAP) protecting group at O3, which was introduced to diisopropylidene glucose (**2**) using sodium hydride and NAPBr (Scheme 1) to give compound **3**.



Scheme 1. Formation of thioglycoside acceptor **8**. Reagents and conditions: (a) NAPBr, NaH, DMF, 3 h, 90%; (b) 2 M HCl, EtOH, 80 °C, 4 h, 80%; (c) Ac₂O, pyridine, 90%; (d) BF₃·Et₂O, EtSH, CHCl₃, 3 h, 68%; (e) 1 M NaOMe, MeOH, 16 h, 88%; (f) PhCH(OMe)₂, CSA, CH₃CN, 2 h, 55 °C, 82%.

The NAP protecting group was chosen since it can be selectively removed in the presence of *O*-benzyl groups and that it is stable to strong acids and bases.³⁰ Subsequent removal of the isopropylidene groups by hydrochloric acid treatment gave **4**, which was *O*-acetylated using pyridine and acetic anhydride to give **5**. The donor functionality was introduced by treatment with BF₃·Et₂O and ethanethiol to give **6**, which was *O*-deacetylated under Zémlen conditions³¹ resulting in **7**, followed by protection of O4 and O6 with a 4,6-*O*-benzylidene group using benzaldehyde dimethyl acetal and camphor sulfonic acid for its installation, to give compound **8**. The different transformations from **2** to **8**³² were carried out in good to excellent yields ranging between 68% and 90% leading to a selectively protected monosaccharide having both donor and acceptor functionalities in place.

Formation of the β-(1→2)-linkage between the two orthogonally protected glucosyl donors³³ employed a glycosylation strategy in which a trimethylsilyl triflate-promoted coupling²⁸ of the known trichloroacetimidate donor **9**³⁴ with acceptor **8** gave disaccharide **10** in 75% yield (Scheme 2).

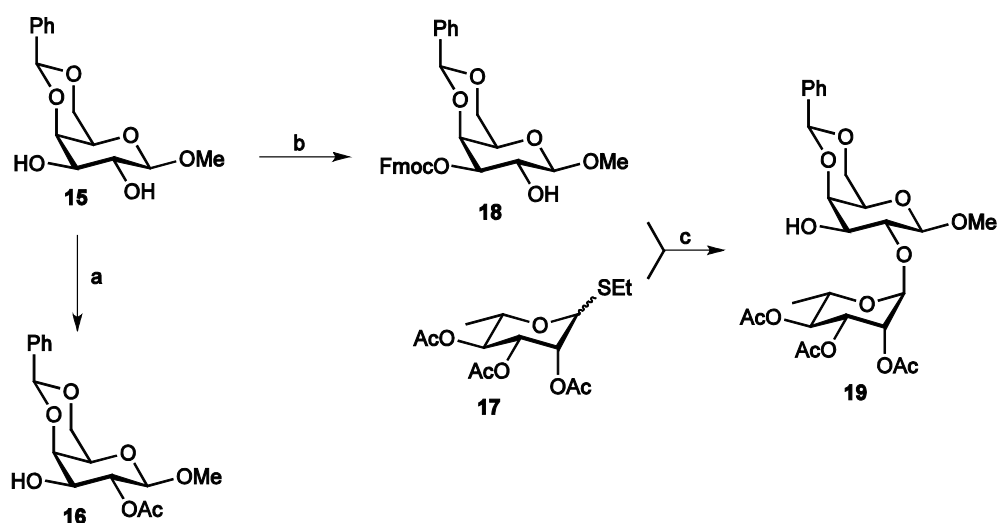


Scheme 2. Formation of armed donor **14**. Reagents and conditions: (a) TMSOTf, CH₂Cl₂/Tol 1:1, -25 °C → r.t., 2 h, 75%; (b) BH₃·NMe₃, AlCl₃, THF, 6 h, 68%; (c) DDQ, CH₂Cl₂/MeOH 4:1, 4 h, 85%; (d) 1 M NaOMe, MeOH, 16 h, 91%; (e) TBDMSOTf, DMAP, pyridine, 80 °C, 24 h, 82%.

It has been noted by Boons and co-workers that thioethyl migration from an acceptor to a donor molecule can occur.³⁵ Herein we were able to suppress this side-reaction by increasing the polarity of the solvent used, i.e., by employing a mixture of DCM and toluene in equal proportions. The 4,6-*O*-benzylidene group was regioselectively opened in a good yield (68%) using BH₃·NMe₃ and

AlCl_3 in THF ³⁶ to give **11** with a 6-*O*-benzyl group, suitably positioned to suppress 1,6-anhydro formation in the subsequent glycosylation reaction (*vide infra*). Deprotection of **11** using DDQ cleaved selectively the NAP group and furnished diol **12**³⁷ in 85% yield, followed by *O*-deacetylation using sodium methoxide in methanol to give compound **13** in 91% yield. The super-armed disaccharide donor **14** was then obtained in 82% yield from **13**, using *tert*-butyldimethylsilyl triflate as the reagent for the *O*-silylation reaction.^{29,38} The arming effect of the donor as a result of the steric crowding due to the *tert*-butyldimethylsilyl (TBS) protecting groups³⁹⁻⁴² resulted in a conformational switch from standard 4C_1 chair conformation for the pyranose rings of the two glucosyl residues to 3S_1 skew-like conformations, based on, *inter alia*, $J_{\text{H1,H2}} = 5.1$ Hz, $J_{\text{H1',H2'}} = 5.8$ Hz, $J_{\text{H2,H3}} < 2$ Hz and $J_{\text{H2',H3'}} < 2$ Hz, in good agreement with NMR data for the corresponding hepta-TBDMS-protected glucosyl-containing disaccharide donor,²⁸ and a 3,4-di-*O*-TBDPS-protected glucosyl donor.⁴⁰

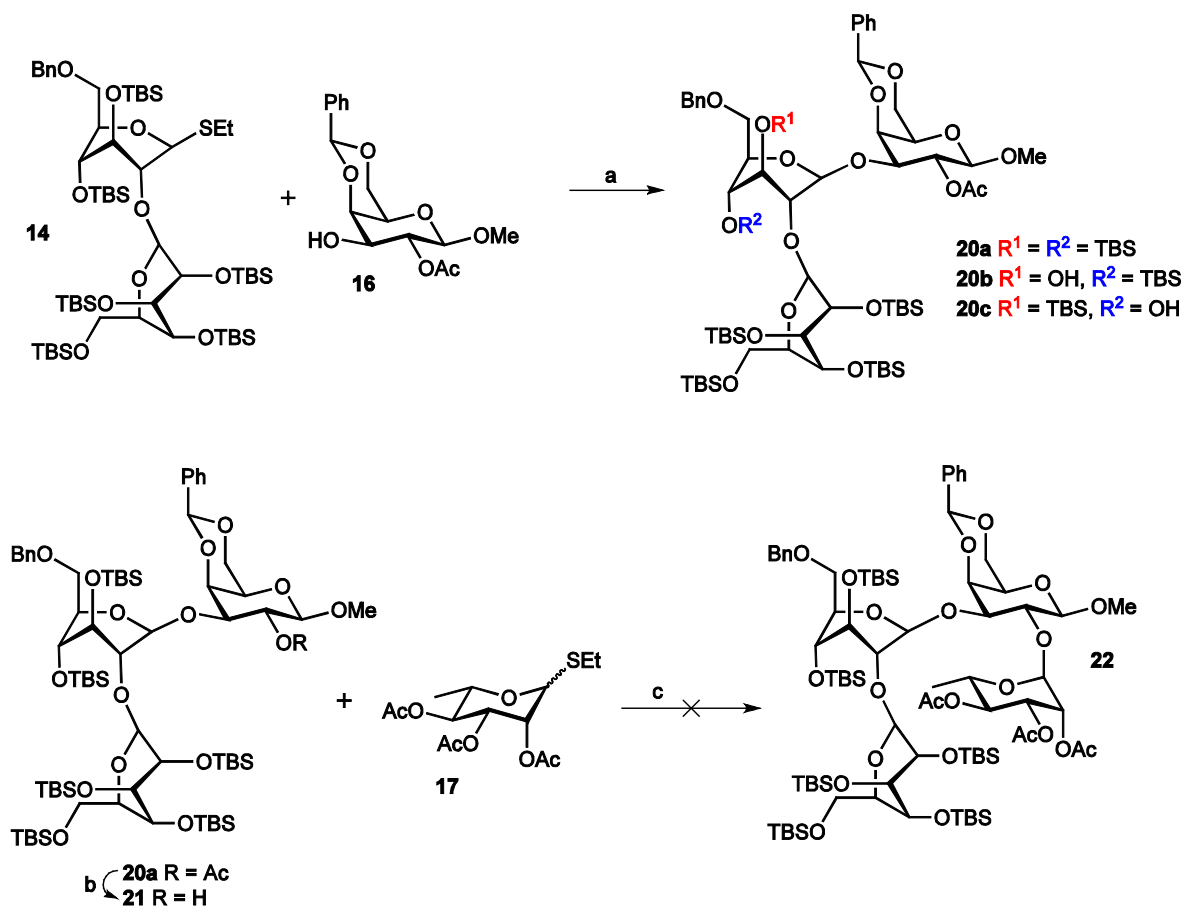
With the disaccharide donor in hand the known monosaccharide methyl 4,6-*O*-benzylidene- α -D-galactopyranoside **15**⁴³ was regioselectively protected at O2 by an *O*-acetyl group using acetic anhydride and pyridine to give compound **16**, albeit in a low yield (Scheme 3).



Scheme 3. Formation of acceptors **16** and **19**. Reagents and conditions: (a) Ac_2O , pyridine, r.t., 16 h, 22%; (b) FmocCl, DMAP, pyridine- CH_3CN , 16 h, 68%; (c) NIS, AgOTf, CH_2Cl_2 , $0\text{ }^\circ\text{C} \rightarrow$ r.t., 1 h, NEt_3 , 30 min, 82%.

The β -(1 \rightarrow 3)-linkage between the disaccharide donor **14** and the relatively unreactive acceptor **16** was facilitated by using Tf_2O -DMDS⁴⁴ as the promoter system. Several activators were tried including NIS/TfOH, NIS/AgOTf, NIS/TMSOTf and MeOTf at different temperatures, but only

Tf₂O-DPS and Tf₂O-BSP gave similar results to Tf₂O-DMDS, which was judged to be the best reagent, in the presence of the sterically hindered base DTBMP. The reaction resulted in the formation of a mixture of trisaccharides, *viz.*, the anticipated compound **20a**, but also by-products that were of lower molecular mass as indicated by mass spectroscopy (Scheme 4).

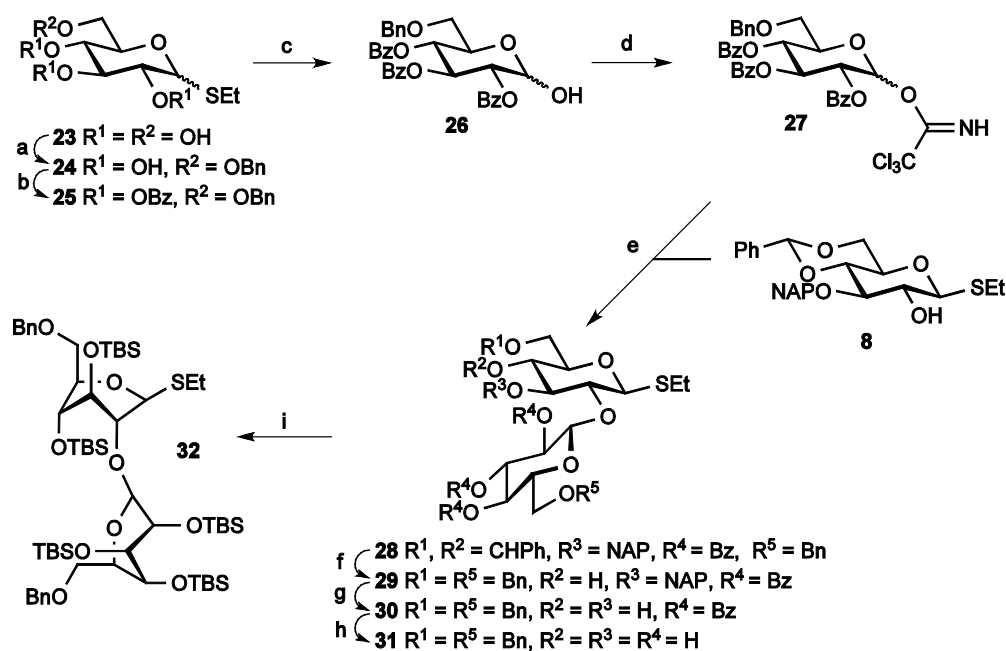


Scheme 4. Synthesis of trisaccharide acceptor **21** and attempted formation of tetrasaccharide **22**. Reagents and conditions: (a) Tf₂O-DMDS, DTBMP, CH₂Cl₂, -78 °C, 15 min, 68% (**20a** - **20c**); (b) 1 M NaOMe, MeOH, 16 h, 55%; (c) NIS, AgOTf, CH₂Cl₂, 0 °C.

¹H NMR spectroscopy revealed that the mixture contained three compounds and NMR assignments of these in the mixture showed that labile TBS ether groups, from two different ring positions, had been cleaved off during the coupling, resulting in trisaccharides **20b** and **20c**. These by-products seemed to form no matter the amount of base added or the promoter system used. It was decided to continue to aim for the target tetrasaccharide by removing the *O*-acetyl protective group in **20a** using sodium methoxide in methanol, thereby unveiling the alcohol function, to give **21** in 55%

yield. Glycosylation of acceptor **20a** with rhamnosyl donor **17**, even in large excess, under NIS/AgOTf conditions remained, however, unsuccessful and another route had to be chosen.

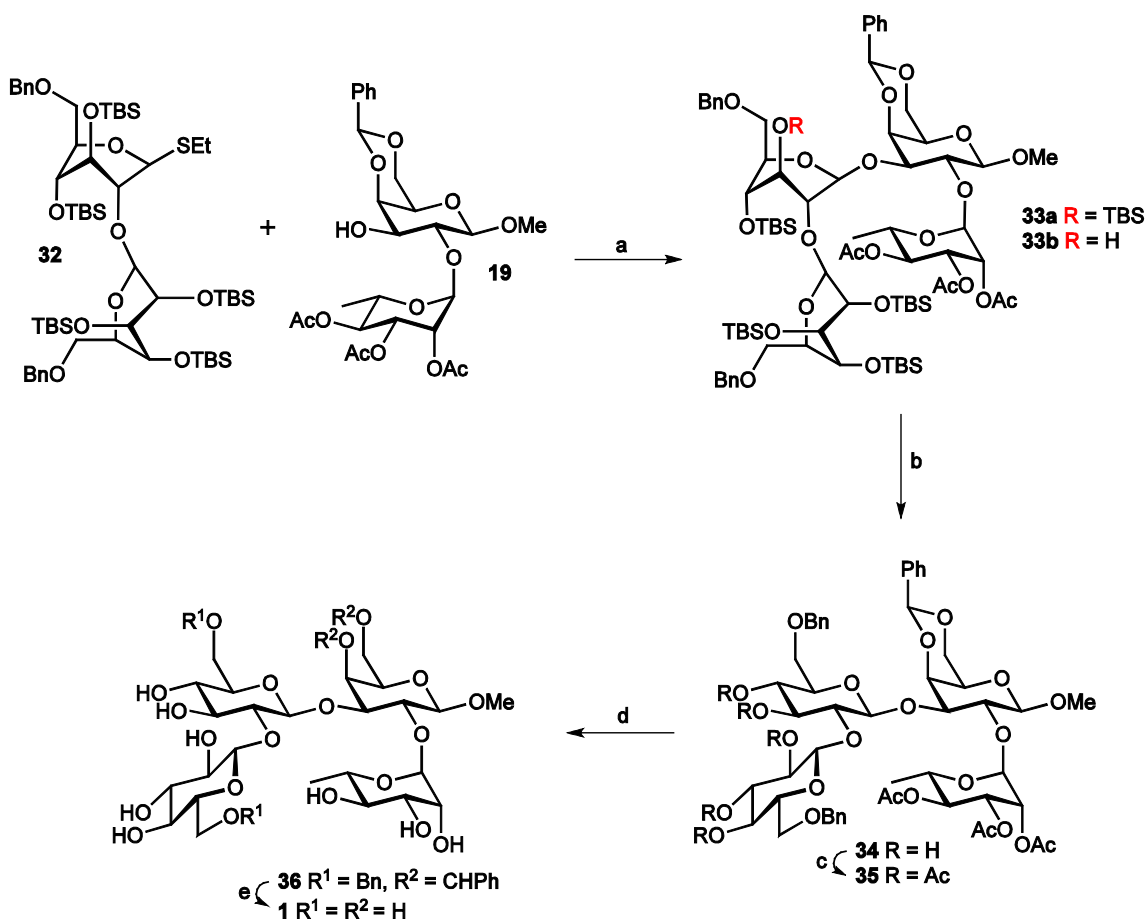
As noted above the alternative route would employ a preformed disaccharide acceptor. Diol **15** was again used but this time a regioselective protection of O3 was carried out by reacting Fmoc chloride in a mixture of pyridine and acetonitrile (2:1) to give acceptor **18** in 68% yield (Scheme 3).⁴⁵ Rhamnosyl donor **17** was glycosylated with **18** using NIS/AgOTf as the activator, followed by addition of trimethylamine to remove the Fmoc protecting group at O3,²³ which subsequently furnished disaccharide acceptor **19** in 82% yield. The correspondingly protected disaccharide methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 \rightarrow 2)-4,6-di-*O*-acetyl- β -D-galactopyranoside, in which only *O*-acetyl groups are utilized to obtain the pertinent protection scheme, was recently synthesized in order to facilitate phosphoglycerol functionalization at O-3 of the galactosyl residue.⁴⁶ The disaccharide donor for the synthesis of the tetrasaccharide was in the second strategy chosen to have 6-*O*-benzyl groups at both of the exocyclic positions, in order to suppress side-reactions such as 1,6-anhydro formation in the succeeding glycosylation reaction (Scheme 5).



Scheme 5. Formation of armed donor **32**. Reagents and conditions: (a) NaH, BnBr, DMF, 0 °C \rightarrow r.t., 6 – 8 h, 72%; (b) BzCl, pyridine, 0 °C \rightarrow r.t., 16 h, 97%; (c) NIS, H₂O, CH₂Cl₂-acetone, 8 h, 78%; (d) Cl₃CCN, K₂CO₃, CH₂Cl₂, 4 h, 85%; (e) TMSOTf, CH₂Cl₂-toluene, 16 h, -10 °C \rightarrow r.t., 84%; (f) BH₃·NMe₃, AlCl₃, H₂O, THF, 16 h, 79%; (g) DDQ, CH₂Cl₂/MeOH 4:1, 4 h, 88%; (h) 1 M NaOMe, MeOH, 16 h, 93%; (i) TBDMSOTf, DMAP, pyridine, 80 °C, 24 h, 86%.

Ethyl 1-thio- α/β -D-glucopyranoside (**23**) was selectively benzylated at O6 using sodium hydride and benzyl bromide in DMF to give **24** in 72% yield,⁴⁷ followed by treatment with benzoyl chloride in pyridine to give **25** in 97% yield, which subsequently was hydrolyzed to provide an α/β -anomeric mixture of the functionalized hemiacetal **26** that was transformed into trichloroacetimidate derivative **27** with an overall yield of 66% over two steps. Disaccharide formation was carried out by glycosylation of acceptor **8** with donor **27** using TMSOTf as promotor to give compound **28** in 84% yield. The acetal functionality in **28** was regioselectively opened, using the same conditions as for the transformation of **10**→**11** described above, to form 6-*O*-benzyl-derivatized disaccharide **29** in 79% yield. Notably, water was added to the mixture since is known to increase the rate of the reaction for electron-deficient substrates and the procedure is fully compatible with thioglycoside-derivatized sugars.⁴⁸ Using the same series of deprotection and protection reactions as for the transformations of **11**→**14** given above, compound **29** was transformed by cleavage of the NAP group (**30**, 88%), *O*-debenzoylation (**31**, 93%) and *O*-silylation to give disaccharide donor **32** in 86% yield. Like for compound **14** the super-armed donor **32** also had the pyranose rings of the two glucosyl residues in ³S₁ skew-like conformations, as deduced from *inter alia*, $J_{H1,H2} = 6.0$ Hz, $J_{H1',H2'} = 5.1$ Hz, $J_{H2,H3} < 2$ Hz and $J_{H2',H3'} < 2$ Hz.

Formation of the β -(1→3)-linkage was successful by coupling donor **32** with acceptor **19** using BSP/Tf₂O as the promoter system together with the hindered base TTBP⁴⁹ to give a tetrasaccharide product in 55% yield (Scheme 6).



Scheme 6. Formation of tetrasaccharide **1**. Reagents and conditions: (a) BSP, Tf_2O , TTBP, CH_2Cl_2 , $-78 \rightarrow -10$ °C, 30 min, 55% (**33a** and **33b**) ; (b) TBAF 1 M in THF, THF (c) Ac_2O , DMAP, pyridine, 16 h, 80% over two steps; (d) NaOMe, MeOH, 16 h, 87%; (e) 10 – 20% Pd/C, 3 atm, MeOH/ H_2O , 6 h, 89%.

The product was a mixture of the anticipated compound **33a** (50% yield) and **33b** (5% yield), which had lost its TBS group at O3' as deduced from 2D NMR experiments, inter alia, $^1\text{H}, ^1\text{H}$ -TOCSY experiments that revealed a ^1H resonance at 3.25 ppm from the HO3' hydroxyl group; the loss of the TBS group is presumably due to steric crowding during the reaction (cf. Scheme 4 above) or in the tetrasaccharide product. For the next step, deprotection of the *O*-silyl groups, the two tetrasaccharides were mixed and *O*-desilylation was carried out by treatment with a solution of TBAF in THF followed by *O*-acetylation, to facilitate purification by column chromatography, using pyridine and acetic anhydride to give compound **35** in 80% yield over two steps. Hydrogenolysis employing Palladium on carbon (loading 10 – 20%) as catalyst furnished the tetrasaccharide target compound **1** in 89%, the ^1H NMR spectrum of which is shown in Figure 2.

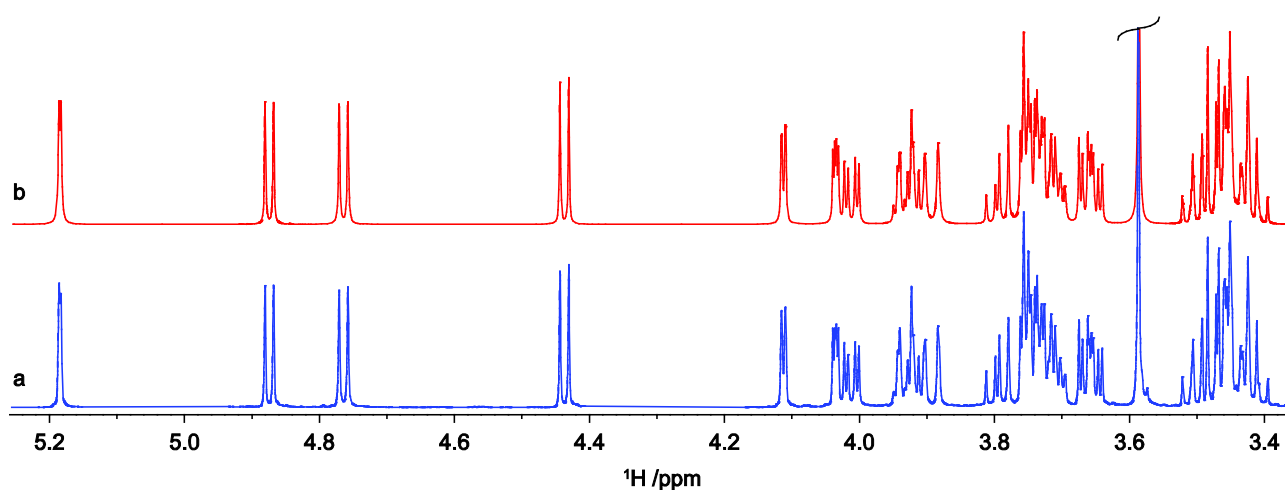


Figure 2. ^1H NMR spectrum at 600 MHz of tetrasaccharide **1** at 5 °C (a) and the corresponding spectrum simulated by total-lineshape analysis using the PERCH NMR software (b). The HDO resonance in the experimental spectrum (δ_{H} 5.02) was removed prior to the lineshape fitting procedure.

2.2 Structure verification

For structural characterization and verification of tetrasaccharide **1** an NMR-based methodology was tested to investigate if this could be carried out rapidly using *unassigned* ^1H and ^{13}C NMR chemical shift data. The computer program CASPER^{50,51} was initially developed to elucidate the primary structure of polysaccharides, but it is also possible to investigate oligosaccharide structures.^{52,53} It relies on ^1H and ^{13}C NMR chemical shift data of mono-, di- and trisaccharides and given components (or some of these, i.e., unknowns may be part of the input) and will investigate all permutations possible based on the input data. In order to speed up the structural calculations due to the potentially very large number of combinations possible, $J_{\text{H}_1,\text{H}_2}$ and $J_{\text{C}_1,\text{H}_1}$ data can be utilized as part of the input in order to limit the number of structures for which calculations are carried out. The ^1H and ^{13}C chemical shifts can also be predicted for a given structure. As input to CASPER the sugar components used in the synthesis were given, i.e., D-Galp-OMe, D-Glcp (twice) and L-Rhap together with ^1H and ^{13}C NMR data. Using only 1D NMR data in the form of ^1H and ^{13}C chemical shifts in combination with $J_{\text{H}_1,\text{H}_2}$ and $J_{\text{C}_1,\text{H}_1}$ data it was not possible to deduce the structure of **1** as given by the synthesis pathway. NMR data from 2D NMR experiments were needed, namely, correlations (unassigned) observed in $^1\text{H},^1\text{H}$ -TOCSY, $^1\text{H},^{13}\text{C}$ -HSQC and $^1\text{H},^{13}\text{C}$ -HMBC spectra. The five top-ranked structural suggestions are given in Figure 3, where the structure of the target tetrasaccharide **1** is the top-ranked one.

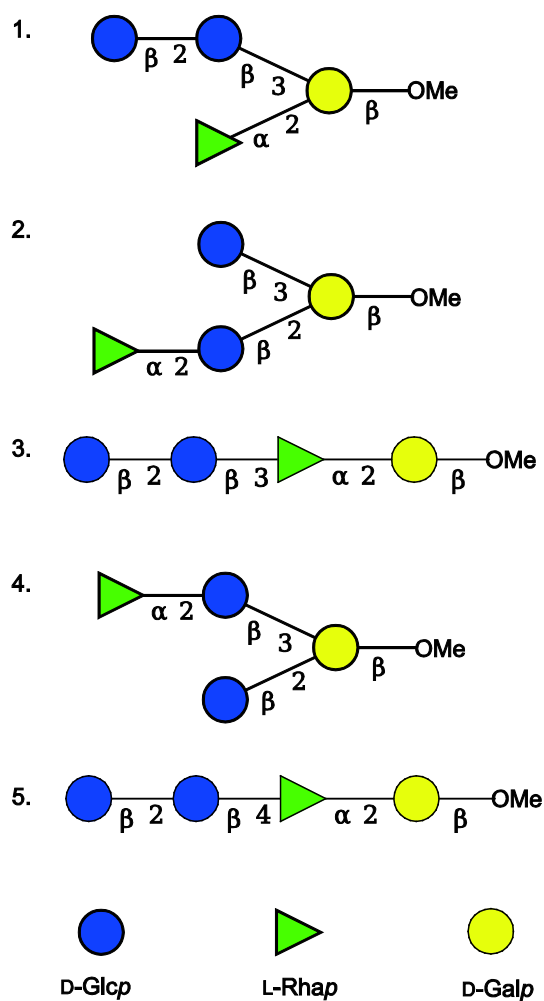


Figure 3. CASPER output of the five top-ranked structural suggestions for the synthesized tetrasaccharide presented in CFG format (blue and yellow filled circles represent D-glucopyranose and D-galactopyranose residues, respectively, and a green filled triangle represents L-rhamnopyranose). The relative deviations for structures 1 – 5 are 1.00, 1.01, 1.03, 1.03 and 1.09, respectively.

That this procedure works and that we have synthesized compound **1** was confirmed by assignment of the ^1H and ^{13}C chemical shifts (Table 1) using the NMR experiments described above. In addition, there was agreement between calculated and experimental high resolution mass spectrometry data for the pseudomolecular ion from an ESI-MS spectrum, i.e., $[\text{M} + \text{Na}]^+ m/z$ calc. for $\text{C}_{25}\text{H}_{44}\text{O}_{20}\text{Na}$ 687.2324, found 687.2326, as well as simulation of the ^1H NMR spectrum by refinement of proton chemical shifts and scalar coupling constants by an iterative total line-shape analysis employing NMR spin simulation⁵⁴ using the PERCH software.

Table 1¹H and ¹³C NMR chemical shifts (ppm) and J_{HH} (Hz) data from experiments at 5 °C and δ_H/δ_C predicted by the CASPER program.

Residue			1	2	3	4	5		6	
β -D-Glcp-(1 \rightarrow)	¹ H	Expt	4.874	3.472	3.504	3.413	3.434		3.743 ^a	3.931 ^b
		³ J_{HH}	7.99 (163) ^d	9.64	9.05	9.82	6.37 ^a	1.97 ^b	-12.31	
		Calc	4.78	3.35	3.54	3.40	3.51		3.73	3.91
	¹³ C	Expt	103.67	74.05	76.38	70.41	76.93		61.77	
		Calc	104.22	74.79	76.40	70.50	77.28		61.79	
\rightarrow 2)- β -D-Glcp-(1 \rightarrow 3)	¹ H	Expt	4.764	3.661	3.724	3.455	3.454		3.744 ^a	3.892 ^b
		³ J_{HH}	7.93 (164) ^d	9.24	9.21	9.44	4.23 ^a	0.96 ^b	-11.97	
		Calc	4.73	3.65	3.70	3.48	3.47		3.73	3.90
	¹³ C	Expt	102.74	80.33	77.31	70.16	76.49		61.08	
		Calc	103.42	82.51	76.62	70.26	76.53		61.54	
α -L-Rhap-(1 \rightarrow 2)	¹ H	Expt	5.184	4.035	3.751	3.468	3.926		1.275	
		³ J_{HH}	1.74 (176) ^d	3.25	9.66	9.93	6.27			
		Calc	4.94	4.05	3.78	3.46	3.73		1.31	
	¹³ C	Expt	101.85	71.18	71.23	72.76	69.50		17.11	
		Calc	103.46	70.93	71.09	72.83	69.87		17.56	
\rightarrow 2,3)- β -D-Galp-OMe ^c	¹ H	Expt	4.437	3.655	4.012	4.113	3.706		3.753 ^b	3.793 ^a
		³ J_{HH}	7.87 (163) ^d	9.61	3.40	0.84	8.04 ^a	4.14 ^b	-11.73	
		Calc	4.41	3.74	3.82	4.20	3.70		3.78	3.79
	¹³ C	Expt	103.44	78.56	81.26	69.94	75.37		61.69	
		Calc	103.59	79.16	84.19	69.27	75.46		61.48	

^a H6_{pro-R}; ^b H6_{pro-S}.^c CH₃ (OMe) Expt: 3.586, 57.80; Calc: 3.59, 57.49.^d ¹ $J_{H1,C1}$ at 45 °C.

Being able to simulate the ^1H spectrum, which is in excellent agreement with the experimental one (Figure 2), then facilitates extraction of highly accurate ^1H chemical shifts in conjunction with scalar coupling constants (Table1). The excellent agreement between experimental ^1H and ^{13}C NMR chemical shifts and those predicted by CASPER for tetrasaccharide **1** is illustrated Figure 4, underscoring the potential of CASPER to be used as a part of the structural verification process in chemical or chemoenzymatic synthesis of oligosaccharides.

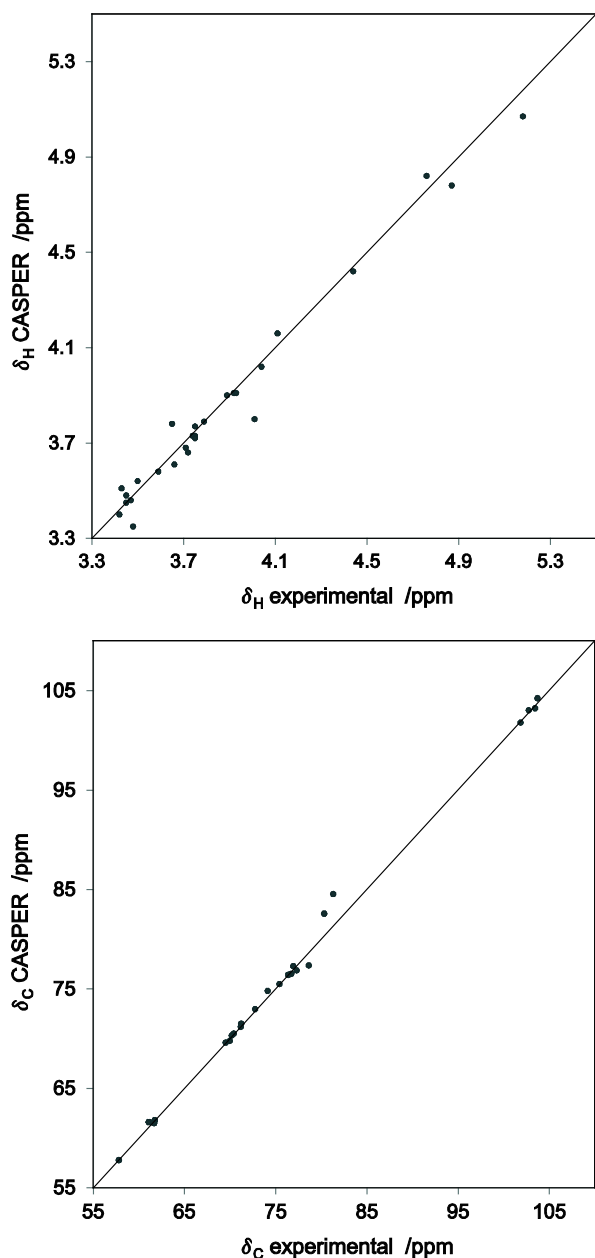


Figure 4. Comparison between experimental and CASPER-predicted ^1H and ^{13}C NMR chemical shifts (*top* and *bottom*, respectively) of tetrasaccharide **1**.

3. Conclusions

The strategy for synthesis of the oligosaccharide component of the glycoalkaloid Solaradixine from *Solanum laciniatum* was such that alternative schemes were possible prior to its execution. The order of glycosylations was of paramount importance in the synthesis of methyl lycoteraoside, a tetrasaccharide constituent of α -tomatine, where steric hindrance was the culprit in the unsuccessful pathway but could be circumvented by an alternative scheme, both of which employed a monosaccharide as the donor and a trisaccharide as an acceptor.²² Herein, the pertinently functionalized monosaccharide building blocks facilitated glycosylation to give a disaccharide donor that subsequently was super-armed by substitution with several TBS-groups enforcing sterical crowding and conformational changes of the constituent sugar residues. The successful glycosylation, with very high β -selectivity, of the hydroxyl group at a secondary carbon utilized a disaccharide acceptor molecule that facilitated formation of a tetrasaccharide, which after protection gave the branched target molecule. Furthermore, rapid structure verification of the synthesized tetrasaccharide was carried out by using unassigned ^1H and ^{13}C NMR data as input to the program CASPER, which is available to the scientific community at <http://www.casper.org.se/casper/>.⁵⁵

4. Experimental section

4.1 General

Dry solvents, including toluene (Tol), dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether (Et_2O) and acetonitrile (ACN) were obtained from a VAC solvent purifier system (Hawthorne, CA, USA). Dry *N,N*-dimethylformamide (DMF) was purchased from Acros Organics (Morris Plains, NJ, USA) and used as received. Pyridine (Pyr) was distilled over CaH_2 and dried over molecular sieves (4 Å). Methanol (MeOH) and chloroform (CHCl_3) were dried over molecular sieves (4 Å). All reagents were used as received. A nitrogen flow was used for reactions requiring inert atmosphere. Powdered molecular sieves (4 Å) were activated by heating under high vacuum. Column chromatography was performed on a Biotage Isolera flash chromatography system (Uppsala, Sweden) using KP-Sil or HP-Sil snap silica gel cartridges and purification on t-C18 Sep-pak[®] cartridges. TLC was carried out on silica gel 60 F₂₅₄ plates (20 × 20 cm, 0.2 mm thickness) and monitored with UV light 254 – 360 nm or by Ceric Ammonium Sulfate staining using 40% (2 M) sulfuric acid.

Purification of the target compound (**1**) by gel permeation chromatography was performed on an ÄKTA[™] system equipped with a Superdex[™] column (GE Healthcare, Uppsala, Sweden). The

eluent system was H₂O with 1% BuOH at a flowrate of 1 mL·min⁻¹. UV and RI detection were used to monitor elution.

NMR spectra for characterization of isolated compounds were recorded at 25 °C, except where otherwise stated, on Bruker spectrometers operating at ¹H frequencies of 400, 500 or 600 MHz. The NMR chemical shifts (δ) are reported in ppm and referenced to TMS or sodium 3-trimethylsilyl-(2,2,3,3-²H₄)-propanoate (TSP) as internal standards, $\delta_{\text{H}} = 0.0$, or to the residual solvent peaks for CDCl₃, $\delta_{\text{H}} = 7.26$, or MeOH-*d*₄ $\delta_{\text{H}} = 3.31$. ¹³C chemical shifts were referenced to external 1,4-dioxane in D₂O, $\delta_{\text{C}} = 67.40$, or internally to the CDCl₃ residual solvent peak, $\delta_{\text{C}} = 77.16$, or to the MeOH-*d*₄ residual solvent peak, $\delta_{\text{C}} = 49.00$. *J* coupling constants are reported in Hertz (Hz). All new compounds synthesized were fully characterized using 1D ¹H, 1D ¹H-decoupled ¹³C, 2D ¹H,¹H-DQF-COSY, 2D ¹H,¹³C-multiplicity-edited-HSQC proton coupled or decoupled and 2D ¹H,¹³C-HMBC NMR experiments. If required, 1D ¹H,¹H-TOCSY, 2D ¹H,¹H-TOCSY, 2D ¹H,¹³C-H2BC, 2D ¹³C,¹H-HETCOR or 2D ¹H,¹³C-HSQC-TOCSY experiments were acquired. Abbreviations for ¹H NMR multiplicity of signals: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), q (quadruplet), dt (doublet of triplet), dq (doublet of quadruplet), ddd (doublet of doublet of doublet), m (multiplet), br (broad resonance), nr (not resolved). Of the two protons constituting the hydroxymethyl group, the one resonating at higher field is denoted H-6a, and the one at lower field is denoted H-6b. The terminal glucosyl residue is denoted by G', the internal one by G, galactose by Gal and rhamnose by R. High-resolution mass spectra were recorded on Bruker Daltonics micrOTOF or micrOTOFQ spectrometers (Billerica, MA, USA) using electrospray ionization (ESI) in positive mode. Samples of 1 mg·mL⁻¹ were prepared using a solution of 1:1 ACN/H₂O containing 0.1% formic acid.

A 1D ¹H NMR spectrum of compound **1** recorded at 600 MHz and processed with an applied Gaussian function for resolution enhancement was utilized as input for the NMR spin simulation software PERCH. Accurate ¹H NMR chemical shifts and ⁿJ_{HH} coupling constants were determined by iterative fitting thereby handling strong overlaps and higher order effects. The simulated and the experimental spectra appeared highly similar according to visual inspection and the total root-mean-square value was less than 0.1%.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-naphthyl)methyl- α -D-glucopyranose (3**).**

1,2:5,6-Di-*O*-isopropylidene- α -D-glucofuranose **2** (10 g, 38 mmol) and 2-methylnaphthyl bromide (9.25 g, 1.1 eq) was introduced in a round-bottomed flask. Dry dimethylformamide (35 mL) was poured into the mixture and sodium hydride 60% in oil dispersion (1.54 g, 1.2 eq) was slowly added

at 0 °C. Then, the mixture was allowed to reach room temperature. After 6 h of stirring, excess NaH was neutralized with methanol. The product was precipitated by adding 300 mL of crushed ice. The upper layer was transferred to a separation funnel, diluted with dichloromethane and washed with water. The organic layer was dried over MgSO₄ and concentrated to dryness to give after purification by column chromatography (Toluene/EtOAc 10:1, R_f = 0.4) 13.8 g of yellow oil (90%). ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.85 – 7.80 (m, 4H, H-Ar), 7.49 – 7.45 (m, 3H, H-Ar), 5.93 (d, *J*_{H1,H2} 3.74, 1H, H-1), 4.85 (d, *J*_{gem} 12.03, 1H, NapCH₂), 4.80 (d, *J*_{gem} 12.03, 1H, NapCH₂), 4.63 (d, *J*_{H1,H2} 3.74, 1H, H-2), 4.42 (ddd, *J*_{H4,H5} 7.80, *J*_{H5,H6a} 5.86, *J*_{H5,H6b} 6.13, 1H, H-5), 4.16 (dd, *J*_{H3,H4} 3.10, *J*_{H4,H5} 7.80, 1H, H-4), 4.14 (dd, *J*_{H5,H6b} 6.13, *J*_{gem} 8.75, 1H, H-6b), 4.08 (d, *J*_{H3,H4} 3.10, 1H, H-3), 4.03 (dd, *J*_{H5,H6a} 5.86, *J*_{gem} 8.75, 1H, H-6a), 1.49, 1.43, 1.40, 1.31, (4 s, 12H, CH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 135.2, 133.4, 133.2 (3 × C-*ipso*), 128.4, 128.0, 127.9, 126.6, 126.3, 126.1, 125.8 (7 C-Ar), 112.0, 109.2 (23 × (CH₃)₂CH), 105.48 (C-1), 82.9 (C-2), 81.8 (C-3), 81.5 (C-4), 72.7 (C-5), 72.6 (NapCH₂), 67.6 (C-6), 27.0, 26.4, 25.6 (4 CH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₃H₂₈O₆Na 423.1784, found 423.1788.

3-O-(2-Naphthyl)methyl-D-glucopyranose (4).

Compound **3** (13.8 g, 34.5 mmol) was dissolved in EtOH (65 mL) and 2M HCl (33 mL) was added in a 250 mL round-bottomed flask. The mixture was heated to 80 °C and the reaction was followed by TLC (TLC: R_f = 0.2 DCM/MeOH 9:1). At completion, the mixture was neutralized with Amberlite OH⁻. The resin was filtered off and washed with methanol. The crude product was concentrated and co-evaporated with toluene to dryness. The white precipitate obtained was filtered and washed with cold ethyl acetate to give 8.8 g (80%) of compound **4** as a colorless oil. ¹H NMR (CD₃OD, 25 °C, 400 MHz) β-anomeric form: δ 7.92 – 7.41 (4 m, 7H, H-Ar), 5.06 (m, 2H, NapCH₂), 4.57 (d, *J*_{H1,H2} 7.77, 1H, H-1), 3.87 (dd, *J*_{H5,H6b} 2.40, *J*_{gem} 12.00, 1H, H-6b), 3.68 (dd, *J*_{H5,H6a} 5.88, *J*_{gem} 12.00, 1H, H-6a), 3.49 (dd, *J*_{H3,H4} 9.54, *J*_{H4,H5} 8.78, 1H, H-4), 3.43 (dd, *J*_{H2,H3} 8.88, *J*_{H3,H4} 9.54, 1H, H-3), 3.34 (ddd, *J*_{H4,H5} 8.78, *J*_{H5,H6a} 5.88, *J*_{H5,H6b} 2.40, 1H, H-5), 3.33 (m, 1H, H-2). ¹³C NMR (CD₃OD, 25 °C, 100 MHz) β-anomeric form: δ 138.0, 134.8, 134.4 (3 × C-*ipso*), 128.9, 128.8, 128.6, 127.5, 127.3, 126.9, 126.8 (7 C-Ar), 98.3 (C-1), 86.4 (C-3), 78.0 (C-5), 76.5 (C-2), 76.0 (NapCH₂), 71.6 (C-4), 62.8 (C-6). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₁₇H₂₀O₆Na 343.0260, found 343.0263.

1,2,4,6-Tetra-O-acetyl-3-O-(2-naphthyl)methyl-D-glucopyranose (5).

Compound **4** (3 g, 9.4 mmol) was dissolved in pyridine (30 mL) and acetic anhydride (7.66 mL, 75 mmol) was added at 0 °C. The mixture was left to attain room temperature and was stirred overnight. At completion, the reaction was quenched with MeOH at 0 °C. Solvents were evaporated and co-evaporation with toluene was performed. The brown oil obtained was taken up into EtOAc and washed successively with brine, 1 M HCl, brine, satd NaHCO₃ and brine. The solution was dried over MgSO₄ and solvents were evaporated to afford the desired product. The α -anomeric form could be isolated by recrystallization from cold EtOH while the residual crude was purified by chromatography (Rf = 0.6 Toluene/EtOAc 2:1) to give 4.1 g of **5** as a slightly yellow oil with an overall yield of 91%. ¹H NMR (CDCl₃, 25 °C, 400 MHz) β -anomeric form: δ 7.85 – 7.32 (4 m, 7H, H-Ar), 5.66 (d, $J_{H1,H2}$ 8.17, 1H, H-1), 5.20 (dd, $J_{H1,H2}$ 8.17, $J_{H2,H3}$ 9.39, 1H, H-2), 5.19 (dd, $J_{H3,H4}$ 9.25, $J_{H4,H5}$ 9.94, 1H, H-4), 4.78 (s, 2H, NapCH₂), 4.23 (dd, $J_{H5,H6b}$ 4.95, J_{gem} 12.53, 1H, H-6b), 4.10 (dd, $J_{H5,H6a}$ 2.33, J_{gem} 12.53, 1H, H-6a), 3.81 (dd, $J_{H2,H3}$ 9.39, $J_{H3,H4}$ 9.25, 1H, H-3), 3.73 (ddd, $J_{H4,H5}$ 9.94, $J_{H5,H6a}$ 2.33, $J_{H5,H6b}$ 4.95, 1H, H-5), 2.10, 2.08 1.94, 1.93 (4 s, 12H, CH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) β -anomeric form: δ 170.9, 169.4, 169.4, 169.2 (4 C=O), 135.1, 133.3, 133.1 (3 \times C-*ipso*), 128.4, 128.0, 127.8, 126.7, 126.4, 126.3, 125.8 (7 C-Ar), 92.2 (C-1), 80.1 (C-3), 74.4 (NapCH₂), 73.2 (C-5), 71.8 (C-2), 69.2 (C-4), 61.9 (C-6), 21.0, 20.9, 20.9, 20.8 (4 CH₃). ESI-HRMS: [M + Na]⁺ m/z calc. for C₂₅H₂₈O₁₀Na 511.1580, found 511.1583.

Ethyl 2,4,6-tri-*O*-acetyl-3-*O*-(2-naphthyl)methyl-1-thio- β -D-glucopyranoside (6**).**

1,2,4,6-Tetra-*O*-acetyl-3-*O*-(2-naphthyl)methyl-D-glucopyranose **5** (2.1 g, 4.3 mmol) previously obtained was dissolved in dry CHCl₃ (10 mL). The reaction mixture was cooled to 0 °C and ethanethiol (0.24 mL, 1.1 eq) and borontrifluoride etherate (0.59 mL, 1.1 eq) were successively added dropwise. The addition of reagents was carried out during 5 min and the mixture was stirred for 2 h at this temperature. Then, the mixture was washed twice with a satd solution of NaHCO₃ (20 mL) and with water (10 mL). The organic layer was dried over Na₂SO₄ and concentrated to dryness. The residue was purified by column chromatography (Toluene/EtOAc 4:1) to give 1.37 g of white needles in 68% yield. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.84 – 7.32 (4 m, 7H, H-Ar), 5.17 – 5.14 (m, 2H, H-2, H-4), 4.78 (m, 2H, NapCH₂), 4.40 (d, $J_{H1,H2}$ 10.02, 1H, H-1), 4.19 (dd, $J_{H5,H6b}$ 5.18, J_{gem} 12.33, 1H, H-6b), 4.12 (dd, $J_{H5,H6a}$ 2.47, J_{gem} 12.33, 1H, H-6a), 3.76 (dd, J 9.29, J 9.20, 1H, H-3), 3.63 (ddd, $J_{H4,H5}$ 10.02, $J_{H5,H6a}$ 2.47, $J_{H5,H6b}$ 5.18, 1H, H-5), 2.70 (dq, 2H, SCH₂CH₃), 2.07, 1.98, 1.92 (3 s, 9H, CH₃), 1.26 (t, 3H, SCH₂CH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 170.9, 169.5, 169.45, (3 C=O), 135.4, 133.4, 133.1 (3 \times C-*ipso*), 128.4, 128.0, 127.8, 126.6, 126.4, 126.2, 125.8 (7 C-Ar), 83.8 (C-1), 81.7 (C-3), 76.4 (C-5), 74.4 (NapCH₂), 71.4 (C-4), 69.9 (C-2),

62.6 (C-6), 24.1 (SCH₂CH₃), 21.1, 20.9, 20.9 (3 CH₃), 14.9 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₅H₃₀O₈SNa 513.1559, found 513.1556.

Ethyl 4,6-*O*-benzylidene-3-*O*-(2-naphthyl)methyl-1-thio-β-D-glucopyranoside (8).

Compound **6** (4.0g, 8.2 mmol) was dissolved in methanol (50 mL), NaOMe in MeOH was added (general procedure: 2 eq per acyl group using a 1M solution) and the mixture was stirred at room temperature overnight. TLC (R_f=0.2, DCM/MeOH 9:1) analysis indicated completion of the reaction and the solution was neutralized with Dowex-H⁺. The resin was filtered, washed with methanol and solvents were evaporated. The product ethyl 3-*O*-(2-naphthyl)methyl-1-thio-β-D-glucopyranoside **7** was obtained in 88% yield (2.6 g) as a colorless syrup. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.88 – 7.44 (2 m, 7H, H-Ar), 5.18 (d, *J*_{gem} 11.08, 1H, NapCH₂), 4.94 (d, *J*_{gem} 11.08, 1H, NapCH₂), 4.37 (d, *J*_{H1,H2} 9.54, 1H, H-1), 3.88 (dd, *J*_{H5,H6b} 3.53, *J*_{gem} 11.85, 1H, H-6b), 3.75 (dd, *J*_{H5,H6a} 5.10, *J*_{gem} 11.85, 1H, H-6a), 3.62 (dd, *J*_{H3,H4} 9.25, *J*_{H4,H5} 9.14, 1H, H-4), 3.54 (dd, *J*_{H1,H2} 9.54, *J*_{H2,H3} 8.73, 1H, H-2), 3.47 (dd, *J*_{H2,H3} 8.73, *J*_{H3,H4} 9.25, 1H, H-3), 3.39 (ddd, *J*_{H4,H5} 9.14, *J*_{H5,H6a} 5.10, *J*_{H5,H6b} 3.53, 1H, H-5), 2.73 (dq, 2H, SCH₂CH₃), 2.50, 2.10, 1.60 (3 br, 3H, OH), 1.32 (t, 3H, SCH₂CH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 135.9, 133.5, 133.2 (3 × *C-*ipso**), 128.7, 128.1, 127.9, 127.1, 126.4, 126.2, 126.0 (7 C-Ar), 86.8 (C-1), 85.1 (C-3), 79.6 (C-5), 75.0 (NapCH₂), 73.4 (C-2), 70.3 (C-4), 62.9 (C-6), 24.8 (SCH₂CH₃), 15.5 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₁₉H₂₄O₅SNa 387.1442, found 387.1446.

Ethyl 3-*O*-(2-naphthyl)methyl-1-thio-β-D-glucopyranoside **7** (2.6 g, 7.2 mmol) was dissolved in acetonitrile (20 mL) and benzaldehyde dimethyl acetal (1.45 mL, 1.5 eq) and anhydrous camphorsulfonic acid (300 mg, 0.2 eq) were successively added to the mixture. The reaction mixture was stirred for 2 h at 55 °C (TLC: R_f = 0.4 Toluene/EtOAc 4:1); it was then cooled and quenched with NEt₃ (0.175 mL). The residue obtained was concentrated to dryness and recrystallized from cold methanol. The product was filtered and dried to afford 2.7 g (82% yield) of ethyl 4,6-*O*-benzylidene-3-*O*-(2-naphthyl)methyl-1-thio-β-D-glucopyranoside **8** as a white powder. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.85 – 7.35 (5 m, 12H, H-Ar), 5.59 (s, 1H, CHPh), 5.12 (d, *J*_{gem} 11.85, 1H, NapCH₂), 4.99 (d, *J*_{gem} 11.85, 1H, NapCH₂), 4.46 (d, *J*_{H1,H2} 9.70, 1H, H-1), 4.36 (dd, *J*_{H5,H6b} 4.93, *J*_{gem} 10.50, 1H, H-6b), 3.78 (dd, *J*_{H5,H6a} 10.23, *J*_{gem} 10.50, 1H, H-6a), 3.77 – 3.69 (m, 2H, H-4, H-3), 3.61 (m, 1H, H-2), 3.50 (ddd, *J*_{H4,H5} 9.05, *J*_{H5,H6a} 10.50, *J*_{H5,H6b} 4.93, 1H, H-5), 2.75 (dq, 2H, SCH₂CH₃), 2.54 (d, 1H, OH-2), 1.31 (t, 3H, SCH₂CH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 137.4, 135.9, 133.4, 133.2 (4 × *C-*ipso**), 129.2, 3 × 128.4, 128.1, 127.8, 127.0, 3 × 126.2, 126.1, 126.0 (12 C-Ar), 101.53 (CHPh), 86.8 (C-1), 81.5 (C-3), 81.4 (C-4), 74.8 (NapCH₂), 73.3

(C-2), 71.0 (C-5), 68.8 (C-6), 24.7 (SCH₂CH₃), 15.4 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₆H₂₈O₅SNa 475.1555, found 475.1553.

Ethyl 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl-(1 \rightarrow 2)-4,6-*O*-benzylidene-3-*O*-(2-naphthyl)methyl-1-thio- β -D-glucopyranoside (10).

A solution of trichloroacetimidate **9** (720 mg, 1.41 mmol, 1.6 eq) and acceptor **8** (400 mg, 0.88 mmol) in dry CH₂Cl₂/Toluene (1:1, 14 mL) was stirred for 20 min in the presence of molecular sieves (4 Å, 0.4 g). TMSOTf (8 μ L, 0.05 eq) was then added at -25 °C. The reaction was monitored by TLC (pentane/EtOAc 2:1) and allowed to warm up to room temperature. NEt₃ was added to quench the reaction and the mixture was filtered through Celite. It was then diluted with CH₂Cl₂ and washed successively with solutions of satd NaHCO₃, brine and dried over Na₂SO₄. The solvent was removed in vacuo, and the residue obtained was purified by flash chromatography (TLC: Rf = 0.45 Pentane/EtOAc 2:1) to yield **10** in 75% yield (0.52 g) as a white powder. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.91 – 7.35 (5 m, 12H, H-Ar G), 5.60 (s, 1H, CHPh G), 5.24 – 5.13 (m, 4H, H-2, H-1, H-3, H-4 G'), 5.08 (d, *J*_{gem} 10.32, 1H, NapCH₂ G), 4.87 (d, *J*_{gem} 10.32, 1H, NapCH₂ G), 4.51 (d, *J*_{H1,H2} 9.14, 1H, H-1 G), 4.40 (dd, *J*_{H5,H6b} 5.06, *J*_{gem} 10.52, 1H, H-6b G), 4.20 (dd, *J*_{H5,H6b} 5.26, *J*_{gem} 12.25, 1H, H-6b G'), 4.10 (dd, *J*_{H5,H6a} 2.59, *J*_{gem} 12.25, 1H, H-6a G'), 3.88 – 3.80 (m, 2H, H-2, H-3 G), 3.80 – 3.72 (m, 2H, H-4, H-6a G), 3.56 (ddd, *J*_{H4,H5} 9.95, *J*_{H5,H6a} 2.59, *J*_{H5,H6b} 5.26, 1H, H-5 G'), 3.50 (m, *J*_{H5,H6b} 5.06, 1H, H-5 G), 2.72 (dq, 2H, SCH₂CH₃ G), 2.07, 2.06, 2.03, 2.00 (4 s, 12H, CH₃ G'), 1.27 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CDCl₃, 25°C, 100 MHz): δ 170.7, 170.4, 169.5, 169.3 (4 C=O G'), 137.3, 135.3, 133.5, 133.3 (4 \times C-*ipso* G), 129.2, 128.7, 3 \times 128.5, 128.3, 128.2, 127.9, 127.6, 126.6, 126.4, 3 \times 126.1 (12 C-Ar G), 101.4 (CHPh G), 100.2 (C-1 G'), 84.4 (C-1 G), 83.7 (C-2 G), 81.8 (C-4 G), 77.1 (C-3 G), 75.7 (NapCH₂ G), 73.3 (C-3 G'), 72.0 (C-2 G'), 71.9 (C-5 G'), 70.2 (C-5 G), 68.8 (C-6 G), 68.6 (C-4 G'), 62.3 (C-6 G'), 24.0 (SCH₂CH₃ G), 21.0, 20.8, 20.6, 20.6 (4 CH₃ G'), 14.7 (SCH₂CH₃ G). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₄₀H₄₆O₁₄SNa 805.2506, found 805.2510.

Ethyl 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl-(1 \rightarrow 2)-6-*O*-benzyl-3-*O*-(2-naphthyl)methyl-1-thio- β -D-glucopyranoside (11).

Disaccharide **10** (0.3 g, 0.38 mmol) was dissolved in dry THF (5 mL) at room temperature. BH₃ \cdot NMe₃ complex (336 mg, 12 eq) was added to the mixture that was let to stir for 5 min under N₂ atmosphere. Anhydrous AlCl₃ (307 mg, 6 eq) was added and after 4 h (Rf = 0.7 Pentane/EtOAc 1:1) the reaction was stopped by addition of 1mL of satd NaHCO₃. The reaction mixture was

diluted with diethylether and washed twice with a solution of satd NaHCO₃ and dried over Na₂SO₄. The residue was purified by flash chromatography to yield 0.205 g (68%) of compound **11** as a colorless oil. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.95 – 7.27 (5 m, 12H, H-Ar G), 5.23 – 5.10 (m, 4H, H-1, H-2, H-3, H-4 G'), 5.04 (d, *J*_{gem} 10.51, 1H, NapCH₂ G) 4.94 (d, *J*_{gem} 10.51, 1H, NapCH₂ G), 4.57 (2 d, *J*_{gem} 11.92, 2H, PhCH₂ G), 4.42 (d, *J*_{H1,H2} 9.69, 1H, H-1 G), 4.20 (dd, *J*_{H5,H6b} 5.14, *J*_{gem} 12.33, 1H, H-6b G'), 4.09 (dd, *J*_{H5,H6a} 2.63, *J*_{gem} 12.33, 1H, H-6a G'), 3.78 (dd, *J*_{H5,H6b} 4.94, *J*_{gem} 10.04, 1H, H-6b G), 3.74 (dd, *J*_{H1,H2} 9.69, *J*_{H2,H3} 8.74, 1H, H-2 G), 3.73 (ddd, *J*_{H3,H4} 8.77, *J*_{H4,H5} 10.06, *J*_{H4,OH-4} 2.30, 1H, H-4 G), 3.69 (dd, *J*_{H5,H6a} 5.67, *J*_{gem} 10.04, 1H, H-6a G), 3.59 (ddd, *J*_{H4,H5} 9.70, *J*_{H5,H6a} 2.63, *J*_{H5,H6b} 5.14, 1H, H-5 G'), 3.58 (dd, *J*_{H2,H3} 8.73, *J*_{H3,H4} 8.77, 1H, H-3 G), 3.46 (ddd, *J*_{H4,H5} 10.06, *J*_{H5,H6a} 5.67, *J*_{H5,H6b} 4.94, 1H, H-5 G), 2.89 (d, *J*_{H4,OH-4} 2.30, 1H, OH-4 G), 2.68 (dq, 2H, SCH₂CH₃ G), 2.07, 2.05, 2.02, 2.00 (4s, 12H, CH₃ G'), 1.25 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 170.8, 170.4, 169.5, 169.3 (4 C=O G'), 137.6, 135.7, 133.6, 133.3 (4 × C-*ipso* G), 128.8, 2 × 128.7, 128.2, 128.1, 3 × 127.9, 127.4, 2 × 126.4, 126.3, (12 C-Ar G), 100.1 (C-1 G'), 86.7 (C-3 G), 83.7 (C-1 G), 77.1 (C-5 G), 76.5 (C-2 G), 75.9 (NapCH₂ G), 74.0 (PhCH₂ G), 74.0 (C-4 G), 73.4 (C-3 G'), 72.1 (C-2 G'), 71.9 (C-5 G'), 71.1 (C-6 G), 68.6 (C-4 G'), 62.3 (C-6 G'), 24.0 (SCH₂CH₃ G), 21.0, 20.9, 20.8, 20.7 (4 CH₃ G'), 14.8 (SCH₂CH₃ G). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₄₀H₄₈O₁₄SNa 807.2662, found 807.2660.

Ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→2)-6-*O*-benzyl-1-thio-β-D-glucopyranoside (12).

Compound **11** (120 mg, 0.15 mmol) was dissolved in a mixture of CH₂Cl₂/MeOH 4/1 and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 87 mg, 2.5 eq) was added and the reaction was stirred until completion, monitored by TLC. Once complete (R_f = 0.37 Pentane/EtOAc 1:4), the reaction mixture was diluted with CH₂Cl₂ and 1mL of satd NaHCO₃ was added. The two phases were separated and the organic phase was washed twice more with the solution of satd NaHCO₃ and subsequently dried over Na₂SO₄. The residue was purified by flash chromatography to yield the desired product **12**, 84 mg (85% yield) as a colorless oil. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.37 – 7.27 (m, 5H, H-Ar G), 5.22 (dd, *J*_{H2,H3} 9.40, *J*_{H3,H4} 9.33, 1H, H-3 G'), 5.09 (dd, *J*_{H3,H4} 9.33, *J*_{H4,H5} 10.00, 1H, H-4 G'), 5.02 (dd, *J*_{H1,H2} 8.02, *J*_{H2,H3} 9.40, 1H, H-2 G'), 4.94 (d, *J*_{H1,H2} 8.02, 1H, H-1 G'), 4.57 (2 d, *J*_{gem} 12.01, 2H, PhCH₂ G), 4.44 (d, *J*_{H1,H2} 9.37, 1H, H-1 G), 4.23 (dd, *J*_{H5,H6b} 5.22, *J*_{gem} 12.18, 1H, H-6b G'), 4.16 (dd, *J*_{H5,H6a} 2.54, *J*_{gem} 12.18, 1H, H-6a G'), 3.73 (m, 2H, H-6b, H-6a G), 3.72 (ddd, *J*_{H4,H5} 10.00, *J*_{H5,H6a} 2.54, *J*_{H5,H6b} 5.22, 1H, H-5 G'), 3.63-3.51 (m, 3H, H-4, H-3, H-2 G), 3.44 (ddd, 1H, H-5 G), 3.14 (nr, 1H, OH G), 3.06 (nr, 1H, OH G), 2.70 (dq, 2H, SCH₂CH₃ G), 2.08, 2.06, 2.02, 2.00 (4s, 12H, CH₃ G'), 1.27 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ

170.9, 170.4, 169.8, 169.5 (4 C=O G'), 137.7 (C-*ipso* G), 2 × 128.6, 128.0, 2 × 127.9 (5 C-Ar G), 100.0 (C-1 G'), 83.0 (C-1 G), 79.8 (C-2 G), 77.7 (C-4 G), 77.6 (C-5 G), 73.8 (PhCH₂ G), 73.0 (C-3 G'), 72.0 (C-3 G), 72.1 (C-5 G'), 71.9 (C-2 G'), 70.6 (C-6 G), 68.5 (C-4 G'), 62.1 (C-6 G'), 24.3 (SCH₂CH₃ G), 21.0, 20.9, 2 × 20.7 (4 CH₃ G'), 14.9 (SCH₂CH₃ G). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₉H₄₀O₁₄SNa 667.2036, found 667.2034.

Ethyl β-D-glucopyranosyl-(1→2)-6-O-benzyl-1-thio-β-D-glucopyranoside (13)

For general acyl group deprotection conditions see the above reaction conditions for compound **7**. Starting from ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→2)-6-*O*-benzyl-1-thio-β-D-glucopyranoside (80 mg) **12** *O*-deacylation yielded compound **13** as a colorless oil (R_f = 0.35 DCM/MeOH 9:1) in 91% yield (57 mg). ¹H NMR (CD₃OD, 25 °C, 400 MHz): δ 7.38 – 7.24 (m, 5H, H-Ar G), 4.70 (d, *J*_{H1,H2} 7.74, 1H, H-1 G'), 4.58 (s, 2H, PhCH₂ G), 4.49 (d, *J*_{H1,H2} 9.40, 1H, H-1 G), 3.86 (dd, *J*_{H5,H6b} 2.39, *J*_{gem} 11.88, 1H, H-6b G'), 3.82 (dd, *J*_{H5,H6b} 1.89, *J*_{gem} 11.12, 1H, H-6b G), 3.70 (dd, *J*_{H5,H6a} 5.20, *J*_{gem} 11.88, 1H, H-6a G'), 3.64 (dd, *J*_{H5,H6a} 5.85, *J*_{gem} 11.12, 1H, H-6a G), 3.61 (dd, *J*_{H2,H3} 8.72, *J*_{H3,H4} 8.57, 1H, H-3 G), 3.54 (dd, *J*_{H1,H2} 9.40, *J*_{H2,H3} 8.72, 1H, H-2 G), 3.44 (ddd, *J*_{H4,H5} 9.94, *J*_{H5,H6a} 5.85, *J*_{H5,H6b} 1.89, 1H, H-5 G), 3.38 (dd, *J*_{H3,H4} 8.57, *J*_{H4,H5} 9.94, 1H, H-4 G), 3.35 – 3.34 (m, 2H, H-3, H-4 G'), 3.29 (m, *J*_{H5,H6a} 5.20, *J*_{H5,H6b} 2.39, 1H, H-5 G'), 3.25 (dd, *J*_{H1,H2} 7.74, *J*_{H2,H3} 9.25, 1H, H-2 G'), 2.74 (dq, 2H, SCH₂CH₃ G), 1.27 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CD₃OD, 25 °C, 100 MHz): G δ 139.7 (C-*ipso* G), 2 × 129.3, 2 × 128.8, 128.6 (5 C-Ar G), 104.8 (C-1 G'), 84.4 (C-1 G), 81.6 (C-2 G), 80.9 (C-5 G), 79.6 (C-3 G), 78.1 (C-5 G'), 78.0 (C-3 G'), 75.8 (C-2 G'), 74.4 (PhCH₂ G), 71.4 (C-4 G'), 71.4 (C-4 G), 70.9 (C-6 G), 62.7 (C-6 G'), 24.8 (SCH₂CH₃ G), 15.3 (SCH₂CH₃ G). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₁H₃₂O₁₀SNa 499.1614, found 499.1617.

Ethyl 2,3,4,6-tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-1-thio-β-D-glucopyranoside (14).

Ethyl 6-*O*-benzyl-2-*O*-(β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (**13**, 0.24 g, 0.5 mmol) was dissolved in dry pyridine (7.5 mL) and DMAP (12 mg, 0.2 eq) was added to the mixture. TBDMSOTf (1.46 mL, 12.6 eq) was subsequently added dropwise at 0 °C, and the reaction mixture was heated to 80 °C and was left to proceed overnight. The reaction (R_f = 0.5 Pentane/DCM 1:1) was left to cool down and then quenched by addition of MeOH. The mixture was extracted with dichloromethane and successively washed with 1 M HCl, satd aqueous NaHCO₃ and brine. The solution was dried over anhydrous Na₂SO₄ and solvents were evaporated. The resulting residue was

purified by chromatography to afford 0.48 g (82% yield) of **14** as a colorless syrup. ^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ 7.36 – 7.28 (m, 5H, H-Ar G), 5.14 (d, $J_{\text{H1,H2}}$ 5.82, 1H, H-1 G), 4.95 (d, $J_{\text{H1,H2}}$ 5.78, 1H, H-1 G'), 4.60 (d, J_{gem} 12.17, 1H, PhCH₂ G), 4.53 (d, J_{gem} 12.17, 1H, PhCH₂ G'), 3.96 (dd, $J_{\text{H2,H3}} < 2$, 1H, H-3 G), 3.90 (ddd, 1H, H-5 G), 3.94 (dd, 1H, H-4 G'), 3.89 (dd, 1H, H-4 G), 3.83 (dd, $J_{\text{H1,H2}}$ 5.82, $J_{\text{H2,H3}} < 2$, 1H, H-2 G), 3.83 (dd, 1H, H-5 G'), 3.74 (dd, $J_{\text{H2,H3}} < 2$, 1H, H-3 G'), 3.72 (dd, 1H, H-6b G'), 3.66 (dd, 1H, H-6a G'), 3.66 (dd, 1H, H-6b G), 3.60 (dd, 1H, H-6a G), 3.59 (dd, $J_{\text{H1,H2}}$ 5.78, $J_{\text{H2,H3}} < 2$, 1H, H-2 G'), 2.70 (dq, 2H, SCH₂CH₃ G), 1.26 (t, 3H, SCH₂CH₃ G), 3×0.89 , 2×0.88 , 0.85 (6 s, 54H, C(CH₃)₃), 0.13, 3×0.089 , 3×0.079 , 0.069, 0.057, 2×0.042 , 0.019 (12 s, 36H, SiCH₃). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz): δ 138.7 (C-*ipso* G), 2×128.4 , 2×127.8 , 127.5 (5 C-Ar G), 101.1 (C-1 G'), 82.3 (C-1 G), 81.2 (C-2 G), 81.0 (C-5 G'), 79.5 (C-3 G'), 79.4 (C-5 G), 77.7 (C-2 G'), 76.1 (C-3 G), 73.4 (PhCH₂ G), 71.7 (C-4 G), 71.6 (C-6 G), 70.3 (C-4 G'), 64.3 (C-6 G'), 3×26.15 , 3×26.05 (6 C(CH₃)₃), 25.3 (SCH₂CH₃ G), 18.5, 4×18.1 , 18.05 (6 C(CH₃)₃), 15.0 (SCH₂CH₃ G), -3.4, -3.7, -3.8, -3.9, -4.2, 2×-4.4 , 3×-4.5 , 2×-5.1 (12 SiCH₃). ESI-HRMS: $[\text{M} + \text{Na}]^+$ m/z calc. for C₅₇H₁₁₆O₁₀SSi₆Na 1183.6802, found 1183.6806.

Methyl 4,6-*O*-benzylidene-2-*O*-acetyl- β -D-galactopyranoside (16).

Compound **15** (0.56 g, 1.99 mmol) was dissolved in dry pyridine (10 mL) and acetic anhydride (0.375 mL, 3.99 mmol) was added at room temperature and the mixture was stirred overnight. At completion, the reaction was quenched with MeOH at 0 °C. Solvents were evaporated and co-evaporation with toluene was performed. The brown oil obtained was taken up into EtOAc and washed successively with brine, 1M HCl, brine, satd NaHCO₃ and brine. The organic phase was dried over MgSO₄ and solvents were evaporated. The residual mixture was purified by column chromatography ($R_f = 0.28$ Pentane/EtOAc 1:4) to obtain compound **16** as a white powder (142 mg, 22%). ^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ 7.55 – 7.48 (m, 2H, H-Ar), 7.42 – 7.35 (m, 3H, H-Ar), 5.56 (s, 1H, CHPh), 5.10 (dd, $J_{\text{H1,H2}}$ 8.00, $J_{\text{H2,H3}}$ 9.98, 1H, H-2), 4.38 (d, $J_{\text{H1,H2}}$ 8.00, 1H, H-1), 4.37 (dd, $J_{\text{H5,H6b}}$ 1.57, J_{gem} 12.47, 1H, H-6b), 4.22 (dd, $J_{\text{H3,H4}}$ 3.89, $J_{\text{H4,H5}}$ 1.23, 1H, H-4), 4.10 (dd, $J_{\text{H5,H6a}}$ 1.97, J_{gem} 12.47, 1H, H-6a), 3.74 (ddd, $J_{\text{H2,H3}}$ 9.98, $J_{\text{H3,H4}}$ 3.89, $J_{\text{H3,OH-3}}$ 11.24, 1H, H-3), 3.53 (s, 3H, OMe), 3.50 (ddd, $J_{\text{H4,H5}}$ 1.23, $J_{\text{H5,H6a}}$ 1.97, $J_{\text{H5,H6b}}$ 1.57, 1H, H-5), 2.44 (dd, $J_{\text{H3,OH-3}}$ 11.24, 1H, OH-3), 2.13 (s, 3H, CH₃). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz): δ 170.7 (C=O), 137.4 (C-*ipso*), 129.5, 128.4, 126.6 (5 C-Ar), 101.7 (C-1), 101.7 (CHPh), 75.7 (C-4), 72.2 (C-2), 71.9 (C-3), 69.1 (C-6), 66.7 (C-5), 56.2 (OMe), 21.2 (CH₃). ESI-HRMS: $[\text{M} + \text{Na}]^+$ m/z calc. for C₁₆H₂₀O₇Na 347.1107, found 347.1111.

Ethyl 2,3,4-tri-*O*-acetyl-1-thio- α -L-rhamnopyranose (17).

L-Rhamnopyranose (1.03 g, 6.3 mmol, 1 eq) was dissolved in pyridine (30 mL) and acetic anhydride (4.74 mL, 50.4 mmol) was added at 0 °C. The mixture was left to attain room temperature and was stirred overnight. At completion ($R_f = 0.66$ Pentane/EtOAc 1:1), the reaction was quenched with MeOH at 0 °C. Solvents were evaporated and co-evaporation with toluene was performed. The brown oil obtained was dissolved in EtOAc, washed successively with brine, 1 M HCl, brine, saturated NaHCO₃ and brine. The solution was dried over MgSO₄ and solvents were evaporated to afford the desired product. The residual anomeric mixture (α/β : 92/8) was purified by chromatography and a yellowish oil was isolated (1.85 g, 89%). ¹H NMR (CDCl₃, 25 °C, 400 MHz): α -anomer: 6.02 (d, 1H, $J_{H1,H2}$ 1.93, H-1), 5.30 (dd, $J_{H2,H3}$ 3.52, $J_{H3,H4}$ 10.08, 1H, H-3), 5.25 (dd, $J_{H1,H2}$ 1.93, $J_{H2,H3}$ 3.52, 1H, H-2), 5.12 (dd, $J_{H3,H4}$ 10.08, $J_{H4,H5}$ 9.97, 1H, H-4), 3.94 (dq, $J_{H4,H5}$ 9.97, $J_{H5,H6}$ 6.24, 1H, H-5), 2.17, 2.16, 2.06, 2.00 (4s, 12H, CH₃), 1.24 (d, $J_{H5,H6}$ 6.24, 3H, H-6). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): α -anomer: δ 170.2, 170.0, 169.9, 168.5 (4 \times C=O), 90.8 (C-1), 70.6 (C-2), 68.9 (C-4), 68.9 (C-3), 68.8 (C-5), 21.0, 20.92, 20.89, 20.8 (4 \times CH₃), 17.6 (C-6). ESI-HRMS: [M+Na]⁺ m/z calc. for C₁₄H₂₀O₉Na 355.1005, found 355.1008.

2,3,4,6-Tetra-*O*-acetyl-L-rhamnopyranose (1.75 g, 5.3 mmol) was dissolved in dry CHCl₃ (15 mL), the reaction mixture was cooled to 0 °C and ethanethiol (0.76 mL, 2 eq) and borontrifluoride diethyl etherate (3.23 mL, 5 eq) were successively added dropwise. The addition was carried out during 5 min and the mixture was stirred for 2 h at this temperature followed by 2 h more at room temperature. The mixture was then washed twice with 20 mL of a 5% NaOH solution and with 10 mL of water. The organic layer was dried over MgSO₄ and concentrated to dryness. Purification by column chromatography ($R_f = 0.72$ Pentane/EtOAc 1:1) gave 1.51 g (86%) of **17** as colorless oil (α/β -anomeric ratio 85/15). ¹H NMR (CDCl₃, 25 °C, 400 MHz): α -anomeric form: 5.34 (dd, $J_{H1,H2}$ 1.56, $J_{H2,H3}$ 3.39, 1H, H-2), 5.24 (dd, $J_{H2,H3}$ 3.39, $J_{H3,H4}$ 10.04, 1H, H-3), 5.20 (d, $J_{H1,H2}$ 1.56, 1H, H-1), 5.10 (dd, $J_{H3,H4}$ 10.04, $J_{H4,H5}$ 9.84, 1H, H-4), 4.24 (dq, $J_{H4,H5}$ 9.84, $J_{H5,H6}$ 6.26 1H, H-5), 2.64 (dq, 2H, SCH₂CH₃), 2.16, 2.06, 1.99 (3 s, 9H, CH₃), 1.30 (t, 3H, SCH₂CH₃), 1.24 (d, $J_{H5,H6}$ 6.26, 3H, H-6). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): α -anomeric form: δ 170.2, 170.1, 170.0 (3 C=O), 82.1 (C-1), 71.7 (C-2), 71.5 (C-4), 69.6 (C-3), 67.1 (C-5), 25.6 (SCH₂CH₃), 21.1, 20.9, 20.8 (3 CH₃), 17.5 (C-6), 14.9 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ m/z calc. for C₁₄H₂₂O₇NaS 357.0984, found 357.0980.

Methyl 4,6-*O*-benzylidene-3-*O*-fluorenylmethyloxycarbonyl- β -D-galactopyranoside (18).

Compound **15** (300 mg, 1.1 mmol) and DMAP (13 mg, 0.1 eq) were dissolved in a 2/1 mixture of pyridine/acetonitrile (5 mL). FMOCCl (303 mg, 1.1 eq) was added portionwise at $-10\text{ }^{\circ}\text{C}$. The mixture was left to attain room temperature and was stirred overnight. At completion (TLC: $R_f = 0.6$ Pentane/EtOAc 1:9), the reaction was quenched with MeOH at $0\text{ }^{\circ}\text{C}$. It was then diluted with EtOAc and washed successively with brine, 1 M HCl, brine, saturated NaHCO_3 and brine. The solution was dried over Na_2SO_4 . Solvents were evaporated and co-evaporation with toluene was performed. The residue obtained was purified by chromatography to give 365 mg (68% yield) of pure **18**. ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$, 400 MHz): δ 7.76 – 7.19 (m, 13H, H-Ar), 5.52 (s, 1H, CHPh), 4.73 (dd, $J_{\text{H}_2,\text{H}_3}$ 10.12, $J_{\text{H}_3,\text{H}_4}$ 3.65, 1H, H-3), 4.47 (d, $J_{\text{H},\text{CH}}$ 7.84, J_{gem} 10.37, 1H, ArCHCH₂OCO), 4.42 (d, $J_{\text{H},\text{CH}}$ 5.19, J_{gem} 10.37, 1H, ArCHCH₂OCO), 4.42 (dd, $J_{\text{H}_3,\text{H}_4}$ 3.65, $J_{\text{H}_4,\text{H}_5}$ 1.01, 1H, H-4), 4.36 (dd, $J_{\text{H}_5,\text{H}_6\text{b}}$ 1.61, J_{gem} 12.42, 1H, H-6b), 4.30 (d, $J_{\text{H}_1,\text{H}_2}$ 7.80, 1H, H-1), 4.29 (dd, $J_{\text{H},\text{CH}_2\text{a}}$ 7.84, $J_{\text{H},\text{CH}_2\text{b}}$ 5.19, 1H, ArCHCH₂OCO), 4.10 (dd, $J_{\text{H}_1,\text{H}_2}$ 7.80, $J_{\text{H}_2,\text{H}_3}$ 10.12, 1H, H-2), 4.08 (dd, $J_{\text{H}_5,\text{H}_6\text{a}}$ 1.83, J_{gem} 12.42, 1H, H-6a), 3.60 (s, 3H, OMe), 3.51 (ddd, $J_{\text{H}_4,\text{H}_5}$ 1.01, $J_{\text{H}_5,\text{H}_6\text{a}}$ 1.83, $J_{\text{H}_5,\text{H}_6\text{b}}$ 1.61, 1H, H-5), 2.44 (nr, 1H, OH₂). ^{13}C NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$, 100 MHz): δ 154.8 (ArCHCH₂OC=O), 143.5, 143.2, 2×141.4 , 137.6, (5 C-*ipso*), 129.1, 2×128.3 , 2×128.0 , 127.3, 127.3, 2×126.4 , 2×125.4 , 2×120.2 (13 C-Ar), 104.0 (C-1), 101.0 (CHPh), 77.4 (C-3), 73.3 (C-4), 70.3 (ArCHCH₂OCO), 69.1 (C-6), 68.7 (C-2), 66.5 (C5), 57.4 (OMe), 46.8 (ArCHCH₂OCO). ESI-HRMS: $[\text{M} + \text{Na}]^+$ m/z calc. for $\text{C}_{29}\text{H}_{28}\text{O}_8\text{Na}$ 527.1682, found 527.1679.

Methyl 2,3,4-tri-O-acetyl- α -L-rhamnopyranosyl-(1 \rightarrow 2)-4,6-O-benzylidene- β -D-galactopyranoside (19).

A solution of thioglycoside **17** (100 mg, 0.3 mmol, 1.5 eq) and acceptor **18** (100 mg, 0.2 mmol) in dry CH_2Cl_2 was stirred for 20 min in the presence of molecular sieves (4 Å, 0.4 g) under N_2 atmosphere. NIS (2 eq) and AgOTf (0.5 eq) were added at $0\text{ }^{\circ}\text{C}$. The reaction was monitored by TLC and left to stir at room temperature for one hour. Once the acceptor was consumed, TEA (25 eq) was added to quench the reaction and to cleave the Fmoc protecting group. After 30 min ($R_f = 0.56$ Pentane/EtOAc 1:2), the mixture was filtered through Celite. It was then diluted with CH_2Cl_2 and washed successively with solutions of satd $\text{Na}_2\text{S}_2\text{O}_3$, brine and dried over Na_2SO_4 . The solvent was removed in vacuo and the residue thus obtained was purified by flash chromatography to yield 90 mg of **19** as a white powder (82% yield). ^1H NMR (CDCl_3 , $25\text{ }^{\circ}\text{C}$, 400 MHz): δ 7.51 – 7.35 (m, 5H, H-Ar Gal), 5.54 (s, 1H, CHPh Gal), 5.36 (dd, $J_{\text{H}_1,\text{H}_2}$ 1.73, $J_{\text{H}_2,\text{H}_3}$ 3.44, 1H, H-2 R), 5.28 (dd, $J_{\text{H}_2,\text{H}_3}$ 3.44, $J_{\text{H}_3,\text{H}_4}$ 10.09, 1H, H-3 R), 5.22 (d, $J_{\text{H}_1,\text{H}_2}$ 1.73, 1H, H-1 R), 5.01 (dd, $J_{\text{H}_3,\text{H}_4}$ 10.09, $J_{\text{H}_4,\text{H}_5}$

10.02, 1H, H-4 R), 4.35 (dd, $J_{H5,H6b}$ 1.39, J_{gem} 12.45, 1H, H-6b Gal), 4.28 (d, $J_{H1,H2}$ 7.49, 1H, H-1 Gal), 4.23 (dq, $J_{H4,H5}$ 10.02, $J_{H5,H6}$ 6.29, 1H, H-5 R), 4.17 (dd, $J_{H3,H4}$ 3.61, $J_{H4,H5}$ 0.93, 1H, H-4 Gal), 4.08 (dd, $J_{H5,H6a}$ 1.81, J_{gem} 12.45, 1H, H-6a Gal), 3.82 (ddd, $J_{H2,H3}$ 9.20, $J_{H3,H4}$ 3.61, $J_{H3,OH-3}$ 10.03, 1H, H-3 Gal), 3.77 (dd, $J_{H1,H2}$ 7.49, $J_{H2,H3}$ 9.20, 1H, H-2 Gal), 3.56 (s, 3H, OMe Gal), 3.48 (ddd, $J_{H4,H5}$ 0.93, $J_{H5,H6a}$ 1.81, $J_{H5,H6b}$ 1.39, 1H, H-5 Gal), 2.50 (nr, 1H, OH-3 Gal). 2.12, 2.06, 1.98 (3 s, 9H, CH₃ R), 1.20 (d, $J_{H5,H6}$ 6.29, 3H, H-6 R). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 170.4, 2 × 170.2 (3 C=O R), 137.4 (C-*ipso* Gal), 129.4, 2 × 128.4, 2 × 126.5 (5 C-Ar Gal), 102.4 (C-1 Gal), 101.6 (CHPh Gal), 98.1 (C-1 R), 76.1 (C-2 Gal), 75.8 (C-4 Gal), 73.8 (C-3 Gal), 71.2 (C-4 R), 69.9 (C-2 R), 69.5 (C-3 R), 69.2 (C-6 Gal), 66.6 (C-5 R), 66.6 (C-5 Gal), 56.9 (OMe Gal), 21.1, 21.0, 20.9 (CH₃ R), 17.2 (C-6 R), ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₆H₃₄O₁₃Na 577.1897, found 577.1901.

Methyl 2,3,4,6-tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-acetyl-β-D-galactopyranoside (20a).

Methyl 2,3,4,6-tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl-(1→2)-4-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-acetyl-β-D-galactopyranoside (20b).

Methyl 2,3,4,6-tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl-(1→2)-3-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-acetyl-β-D-galactopyranoside (20c).

A 1 M solution of the promoter system Tf₂O-DMDS (1.1 eq) in dry CH₂Cl₂ was added to the mixture containing the armed-donor **14** (40 mg, 0.035 mmol), the acceptor **16** (1.2 eq), 2,6-DTBMP (2 eq) and activated 4 Å molecular sieves (100 mg) in dry CH₂Cl₂ (0.5 mL) at -78 °C under N₂ atmosphere. The reaction mixture was stirred for 15 min and was allowed to reach -40 °C (**20a** Rf = 0.65, **20b**, **20c** Rf = 0.45 Pentane/EtOAc 4:1). It was then quenched with NEt₃ (3 eq), diluted with CH₂Cl₂, filtered through Celite and washed with a 2 M HCl solution, aqueous NaHCO₃ and brine. The organic phase was dried over Na₂SO₄ and concentrated under vacuum. After evaporation, the resulting material was purified by chromatography to afford as white solids **20a**, **20b** and **20c** in 18, 25 and 25% yield, respectively. **20a**: ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.47 – 7.26 (m, 10H, H-Ar), 5.21 (d, $J_{H1,H2}$ 2.80, 1H, G), 5.19 (s, 1H, CHPh), 5.19 (dd, $J_{H1,H2}$ 8.04, $J_{H2,H3}$ 10.02, 1H, H-2 Gal), 4.92 (d, $J_{H1,H2}$ 6.08, 1H, H-1 G'), 4.61 (d, J_{gem} 12.04, 1H, PhCH₂ G), 4.48 (d, J_{gem} 12.04, 1H, PhCH₂ G), 4.43 (dd, $J_{H3,H4}$ 3.32, $J_{H4,H5}$ 0.79, 1H, H-4 Gal), 4.31 (d, $J_{H1,H2}$ 8.04, 1H, H-1 Gal), 4.12

(dd, $J_{H3,H4}$ 5.41, $J_{H4,H5}$ 10.71, 1H, H-4 G), 4.00 (dd, $J_{H5,H6b}$ 1.39, J_{gem} 12.16, 1H, H-6b Gal), 3.99 (dd, 1H, H-4 G'), 3.87 (ddd, $J_{H4,H5}$ 10.61, $J_{H5,H6a}$ 2.54, $J_{H5,H6b}$ 4.02, 1H, H-5 G), 3.81 (dd, 1H, H-2 G), 3.79 (dd, 1H, H-3 G), 3.78 (ddd, 1H, H-5 G'), 3.77 (dd, 1H, H-3 Gal), 3.76 (dd, 1H, H-6b G'), 3.75 (dd, 1H, H-3 G'), 3.66 (dd, $J_{H5,H6b}$ 4.02, 1H, H-6b G), 3.63 (dd, 1H, H-6a G'), 3.62 (dd, $J_{H5,H6a}$ 2.54, 1H, H-6a G), 3.58 (dd, 1H, H-2 G'), 3.46 (s, 3H, OMe Gal), 3.29 (dd, $J_{H5,H6a}$ 1.75, J_{gem} 12.16, 1H, H-6a Gal), 3.12 (ddd, $J_{H4,H5}$ 0.79, $J_{H5,H6a}$ 1.75, $J_{H5,H6b}$ 1.39, 1H, H-5 Gal), 2.05 (s, 3H, CH₃), 0.90, 0.89, 0.88, 0.87, 0.80, 0.75 (6 s, 54H, C(CH₃)₃), 0.11, 0.10 – 0.05, –0.012, –0.13, –0.14 (12 s, 36H, SiCH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 169.1 (C=O Gal), 138.6, 138.1 (2 C-*ipso*), 2 × 128.7, 2 × 128.3, 4 × 128.1, 2 × 126.7 (10 C-Ar), 102.0 (C-1 Gal), 101.9 (C-1 G'), 101.6 (C-1 G), 100.8 (CHPh Gal), 81.8 (C-5 G'), 79.9 (C-2 G), 79.7 (C-3 G'), 78.8 (C-3 G), 77.7 (C-2 G'), 77.1 (C-3 Gal), 75.7 (C-4 Gal), 73.5 (PhCH₂ G), 72.9 (C-5 G), 72.5 (C-4 G), 70.4 (C-2 Gal), 70.2 (C-6 G), 70.2 (C-4 G'), 68.7 (C-6 Gal), 66.9 (C-5 Gal), 64.1 (C-6 G'), 55.8 (OMe Gal), 26.15, 26.1 – 26.0 (6 C(CH₃)₃), 21.1 (CH₃), 18.4 – 18.1 (6 C(CH₃)₃), –2.8 to –5.2 (12 SiCH₃). **20b** and **20c**: ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.51 – 7.29 (m, 10H, H-Ar), 5.56 (s, 1H, CHPh Gal **20c**), 5.33 (dd, $J_{H1,H2}$ 8.07, $J_{H2,H3}$ 9.93, 1H, H-2 Gal **20c**), 5.30 (s, 1H, CHPh Gal **20b**), 5.25 (dd, $J_{H1,H2}$ 8.00, $J_{H2,H3}$ 10.20, 1H, H-2 Gal **20b**), 5.04 (d, $J_{H1,H2}$ 6.38, 1H, H-1 G' **20b**), 5.02 (d, $J_{H1,H2}$ 3.49, 1H, H-1 G **20c**), 4.89 (d, $J_{H1,H2}$ 5.30, 1H, H-1 G' **20c**), 4.83 (d, $J_{H1,H2}$ 5.03, 1H, H-1 G **20b**), 4.58 – 4.52 (2 d, J_{gem} 12.19, 2H, PhCH₂ G, **20b**), 4.54 – 4.49 (2 d, J_{gem} 11.68, 2H, PhCH₂ G, **20c**), 4.40 (dd, $J_{H3,H4}$ 3.35, $J_{H4,H5}$ 0.51, 1H, H-4 Gal, **20c**), 4.37 (dd, $J_{H3,H4}$ 3.53, $J_{H4,H5}$ 0.51, 1H, H-4 Gal, **20b**), 4.325 (d, $J_{H1,H2}$ 8.00, 1H, H-1 Gal, **20b**), 4.32 (dd, $J_{H5,H6b}$ 1.51, J_{gem} 12.38, 1H, H-6b Gal, **20c**), 4.30 (d, $J_{H1,H2}$ 8.07, 1H, H-1 Gal, **20c**), 4.08 (dd, $J_{H5,H6b}$ 1.52, J_{gem} 12.30, 1H, H-6b Gal, **20b**), 4.03 (dd, $J_{H5,H6a}$ 1.76, J_{gem} 12.38, 1H, H-6a Gal, **20c**), 3.96 (m, 1H, H-4 G', **20b**), 3.91 (dd, $J_{H2,H3}$ 8.81, $J_{H3,H4}$ 8.32, 1H, H-3 G, **20c**), 3.84 (dd, $J_{H2,H3}$ 9.93, $J_{H3,H4}$ 3.35, 1H, H-3 Gal, **20c**), 3.81 (ddd, 1H, H-5 G, **20c**), 3.80 (dd, $J_{H2,H3}$ 10.20, $J_{H3,H4}$ 3.53, 1H, H-3 Gal, **20b**), 3.77 (dd, 1H, H-3 G', **20b**), 3.75 (ddd, 1H, H-5 G, **20b**), 3.74 (dd, 1H, H-4 G', **20c**), 3.74 (dd, 1H, H-3 G', **20c**), 3.73 (m, 2H, H-6b G' **20c**, H-6b G **20b**), 3.71 (ddd, 1H, H-5 G', **20b**), 3.71 (dd, 1H, H-4 G, **20b**), 3.70 (m, 2H, H-6a, H-6b G', **20b**), 3.69 (ddd, 1H, H-5 G', **20c**), 3.67 (dd, 1H, H-6b G, **20c**), 3.62 (m, 2H, H-2 G **20c**, H-2 G **20b**), 3.62 (dd, 1H, H-6a G', **20c**), 3.61 (dd, 1H, H-6a G, **20b**), 3.59 (dd, 1H, H-2 G', **20c**), 3.58 (dd, 1H, H-2 G', **20b**), 3.55 (dd, 1H, H-4 G, **20c**), 3.54 (dd, 1H, H-3 G, **20b**), 3.53 (dd, 1H, H-6a G, **20c**), 3.48 (s, 3H, OMe Gal, **20b**), 3.48 (s, 3H, OMe Gal, **20c**), 3.46 (dd, $J_{H5,H6a}$ 1.83, J_{gem} 12.30, 1H, H-6a Gal, **20b**), 3.36 (ddd, $J_{H4,H5}$ 0.51, $J_{H5,H6a}$ 1.76, $J_{H5,H6b}$ 1.51, 1H, H-5 Gal, **20c**), 3.11 (ddd, $J_{H4,H5}$ 0.51, $J_{H5,H6a}$ 1.83, $J_{H5,H6b}$ 1.52, 1H, H-5 Gal, **20b**), 2.99 (nr, 1H, OH-3, **20b**), 2.22 (nr, 1H, OH-4, **20c**), 2.06 (s, 3H, CH₃, **20b**), 2.02 (s, 3H, CH₃, **20c**), 0.91 – 0.83 (10 s, 90H, C(CH₃)₃), 0.14, 0.12 – 0.05, –0.05 (20s, 60H, SiCH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 169.9 (C=O Gal, **20c**), 169.5 (C=O Gal, **20b**), 138.5, 138.2, 138.0, 137.9 (4 C-*ipso*), 129.0, 128.9, 2 × 128.7, 2 × 128.6, 8 ×

128.2, 128.1, 2×128.0 , 127.9, 2×126.6 , 2×126.5 (20 C-Ar), 103.2 (C-1 G', **20c**), 102.05 (C-1 G', **20b**), 102.0 (C-1 G, **20b**), 102.0 (C-1 Gal, **20c**), 101.9 (C-1 Gal, **20b**), 101.8 (C-1 G, **20c**), 101.1 (CHPh Gal, **20b**), 100.9 (CHPh Gal, **20c**), 82.2 (C-4 G', **20c**), 81.5 (C-5 G', **20c**), 80.3 (C-2 G, **20b**), 79.8 (C-3 Gal, **20c**), 79.6 (C-4 G', **20b**), 79.3 (C-3 G', **20c**), 79.0 (C-2 G, **20c**), 78.9 (C-2 G', **20c**), 77.9 (C-3 Gal, **20b**), 77.8 (C-2 G', **20b**), 77.4 (C-3 G, **20b**), 75.6 (C-4 Gal, **20b**), 75.3 (C-4 Gal, **20c**), 74.5 (C-3 G, **20c**), 74.4 (C-5 G', **20b**), 73.7 (PhCH₂ G, **20c**), 73.6 (PhCH₂ G, **20b**), 72.6 (2 C-4 G, **20b**, **20c**), 71.6 (C-5 G, **20b**), 70.4 (C-5 G, **20c**), 70.4 (C-2 Gal, **20c**), 70.3 (C-6 G, **20b**), 69.9 (C-3 G', **20b**), 69.6 (C-2 Gal, **20b**), 69.5 (C-6 G, **20c**), 69.0 (C-6 Gal, **20c**), 68.8 (C-6 Gal, **20b**), 67.0 (C-5 Gal, **20c**), 66.7 (C-5 Gal, **20b**), 64.6 (C-6 G', **20c**), 63.8 (C-6 G', **20b**), 56.0 (OMe Gal, **20b**), 55.9 (OMe Gal, **20c**), 26.5, 26.2 – 25.9 (10 C(CH₃)₃), 21.5 (CH₃, **20b**), 21.4 (CH₃, **20c**), 18.7 – 17.9 (10 C(CH₃)₃), –2.9 to –5.2 (10 SiCH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for **20a**: C₇₁H₁₃₀O₁₇Si₆Na 1422.7924, found 1422.7926, for **20b** and **20c**: C₆₅H₁₁₆O₁₇Si₅Na 1331.6957, found 1331.6954.

Methyl 2,3,4,6-tetra-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranoside (21).

For general acyl group deprotection conditions see the above reaction conditions for compound **7**. Starting from 20 mg of compound **20a** (TLC: R_f = 0.45 Pentane/EtOAc 4:1) *O*-deacylation yielded compound **21** in 55% yield as a colorless oil. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.47 – 7.26 (m, 10H, H-Ar), 5.21 (d, *J*_{H1,H2} 4.71, 1H, H-1 G), 5.29 (s, 1H, CHPh Gal), 4.93 (d, *J*_{H1,H2} 5.97, 1H, H-1 G'), 4.56 (d, *J*_{gem} 12.09, 1H, PhCH₂ G), 4.50 (d, *J*_{gem} 12.09, 1H, PhCH₂ G), 4.33 (dd, *J*_{H3,H4} 3.39, *J*_{H4,H5} 0.71, 1H, H-4 Gal), 4.23 (d, *J*_{H1,H2} 7.74, 1H, H-1 Gal), 4.16 (d, *J*_{H5,H6b} 1.51, *J*_{gem} 12.17, 1H, H-6b Gal), 3.96 (m, 1H, H-4 G'), 3.94 (ddd, 1H, H-5 G), 3.92 (dd, 1H, H-4 G), 3.89 (m, 2H, H-2 G, H-3 G), 3.87 (dd, 1H, H-2 Gal), 3.77 (ddd, 1H, H-5 G'), 3.76 (dd, 1H, H-3 G'), 3.72 (m, 2H, H-6a, H-6b G'), 3.71 (dd, 1H, H-6a Gal), 3.64 (dd, 1H, H-6b G), 3.59 (dd, 1H, H-2 G'), 3.55 (dd, 1H, H-6a G), 3.54 (dd, 1H, H-3 Gal), 3.54 (s, 3H, OMe Gal), 3.26 (ddd, 1H, H-5 Gal), 2.88 (nr, 1H, OH-2 Gal); 0.90, 0.885, 2×0.88 , 0.84, 0.82, (6 s, 54H, C(CH₃)₃), 0.12, 0.10 – 0.05, –0.05, –0.13, (12 s, 36H, SiCH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 138.6, 138.3 (2 C-*ipso*), 128.7, 2×128.6 , 2×128.1 , 2×128.0 , 127.8, 2×126.7 (10 C-Ar), 104.2 (C-1 Gal), 102.2 (C-1 G), 102.0 (C-1 G'), 101.0 (CHPh Gal), 82.0 (C-5 G'), 81.6 (C-3 Gal), 80.3 (C-2 G), 79.3 (C-3 G'), 78.0 (C-3 G), 77.8 (C-2 G'), 75.8 (C-5 G), 75.75 (C-4 Gal), 73.5 (PhCH₂ G), 72.5 (C-4 G), 71.2 (C-6 G), 70.3 (C-4 G'), 69.5 (C-2 Gal), 69.2 (C-6 Gal), 66.9 (C-5 Gal), 64.0 (C-6 G'), 56.9 (OMe Gal), 26.2, 26.1 – 26.0 (5

C(CH₃)₃, 18.5 – 18.1 (5 C(CH₃)₃), –3.3 to –5.1 (5 SiCH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₆₉H₁₂₈O₁₆Si₆Na 1403.7716 found 1403.7720.

Ethyl 1-thio- α/β -D-glucopyranoside (**23**).

For general acyl group deprotection conditions see the above reaction conditions for compound **7**. Starting from ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio- α/β -D-glucopyranoside⁵⁶ (3 g, 13 mmol, 90/10 α/β , TLC: R_f = 0.15 DCM/MeOH 9:1) *O*-deacylation yielded 1.58 g of compound **23** as a colorless oil (92%). ¹H NMR (CD₃OD, 25 °C, 400 MHz): α -anomeric form: δ 5.37 (d, *J*_{H1,H2} 5.48, 1H, H-1), 3.99 (ddd, *J*_{H4,H5} 9.82, *J*_{H5,H6a} 5.45, *J*_{H5,H6b} 2.35, 1H, H-5), 3.83 (dd, *J*_{H5,H6b} 2.35, *J*_{gem} 11.90, 1H, H-6b), 3.74 (dd, *J*_{H5,H6b} 5.45, *J*_{gem} 11.90, 1H, H-6a), 3.71 (dd, *J*_{H1,H2} 5.48, *J*_{H2,H3} 9.77, 1H, H-2), 3.55 (dd, *J*_{H2,H3} 9.77, *J*_{H3,H4} 8.98, 1H, H-3), 3.35 (dd, *J*_{H3,H4} 8.98, *J*_{H4,H5} 9.82, 1H, H-4), 2.64 (m, 2H, SCH₂CH₃), 1.32 (t, 3H, SCH₂CH₃). ¹³C NMR (CD₃OD, 25 °C, 400 MHz): α -anomeric form: δ 86.8 (C-1), 75.6 (C-3), 73.9 (C-5), 73.1 (C-2), 71.8 (C-4), 62.5 (C-6), 24.9 (SCH₂CH₃), 15.2 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₈H₁₆O₅SNa 247.0616, found 247.0619.

Ethyl 6-*O*-benzyl-1-thio- α/β -D-glucopyranoside (**24**).

In a 50 mL round-bottomed flask, ethyl 1-thio- α/β -D-glucopyranoside (500 mg, 2.2 mmol) was dissolved in DMF (10 mL) and 60% sodium hydride in oil dispersion (300 mg, 8.9 mmol, 4 eq) was progressively added at room temperature; 30 min later, benzyl bromide (0.4 ml, 3.3 mmol, 1.5 eq) was added dropwise at 0 °C. The reaction mixture was slowly left to attain room temperature. After disappearance of the starting material (7 h), the reaction was quenched with methanol at 0 °C. The mixture was washed with NaHCO₃ and brine, dried over Na₂SO₄, filtered and concentrated to dryness. The residue obtained was purified by column chromatography (TLC: R_f = 0.75 Acetone/Pentane 3:1) to yield 505 mg of **24** (72%) as an oil. ¹H NMR (CDCl₃, 25 °C, 400 MHz): α -anomeric form: δ 7.35 – 7.28 (m, 5H, H-Ar), 5.35 (d, *J*_{H1,H2} 5.41, 1H, H-1), 4.85 (br, 1H, OH-3), 4.56 (2d, *J*_{gem} 12.11, 2H, PhCH₂), 4.13 (br, 1H, OH-4), 4.11 (ddd, *J*_{H4,H5} 9.84, *J*_{H5,H6a} 3.10, *J*_{H5,H6b} 4.64, 1H, H-5), 3.96 (br, 1H, OH-2), 3.82 (m, 1H, H-2), 3.74 (dd, *J*_{H5,H6b} 4.64, *J*_{gem} 10.88, 1H, H-6b), 3.69 (dd, *J*_{H5,H6a} 3.10, *J*_{gem} 10.88, 1H, H-6a), 3.63 (dd, *J*_{H2,H3} 9.28, *J*_{H3,H4} 9.45, 1H, H-3), 3.55 (dd, *J*_{H3,H4} 9.45, *J*_{H4,H5} 9.84, 1H, H-4), 2.59 (m, 2H, SCH₂CH₃), 1.26 (t, 3H, SCH₂CH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): α -anomeric form: δ 138.1 (C-*ipso*), 2 × 128.5, 3 × 127.7 (5 C-Ar), 86.1 (C-1), 75.2 (C-3), 73.6 (PhCH₂), 71.2 (C-5), 71.6 (C-2), 70.9 (C-4), 69.7 (C-6), 25.2 (SCH₂CH₃), 15.1 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₁₅H₂₂O₅SNa 337.1086, found 337.1082.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-1-thio- α/β -D-glucopyranoside (25).

Compound **24** (500 mg, 1.6 mmol) was dissolved in dry pyridine (30 mL). Benzoyl chloride (0.74 mL, 6.4 mmol, 4 eq) was added slowly at 0 °C. The mixture was left to attain room temperature and was stirred overnight. At completion (TLC: R_f = 0.72 Pentane/EtOAc 3:1), the reaction was quenched with MeOH at 0 °C. Solvents were evaporated and co-evaporation with toluene was performed. The brown oil obtained was dissolved in EtOAc and washed successively with brine, 1M HCl, brine, satd NaHCO₃ and brine. The solution was dried over Na₂SO₄ and solvents were evaporated. The residue was purified by column chromatography and 968 mg (97% yield) of white solid **25** was isolated. ¹H NMR (CDCl₃, 25 °C, 400 MHz): α -anomeric form: δ 8.00 – 7.13 (m, 20H, H-Ar), 6.04 (dd, J_{H_2,H_3} 9.86, J_{H_3,H_4} 9.95, 1H, H-3), 5.97 (d, J_{H_1,H_2} 5.83, 1H, H-1), 5.68 (dd, J_{H_3,H_4} 9.95, J_{H_4,H_5} 9.72, 1H, H-4), 5.50 (dd, J_{H_1,H_2} 5.83, J_{H_2,H_3} 9.86, 1H, H-2), 4.70 (ddd, J_{H_4,H_5} 9.72, $J_{H_5,H_{6a}}$ 3.73, $J_{H_5,H_{6b}}$ 3.73, 1H, H-5), 4.55 (2d, J_{gem} 12.03, 2H, PhCH₂), 3.69 (m, 2H, H-6a, H-6b), 2.63 (m, 2H, SCH₂CH₃), 1.27 (t, 3H, SCH₂CH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): α -anomeric form: δ 165.8, 165.5, 165.3 (3 C=O), 137.7, 133.5, 133.4, 133.2 (4 C-*ipso*), 2 \times 130.1, 2 \times 129.9, 2 \times 129.8, 129.3, 129.2, 129.1, 2 \times 128.5, 2 \times 128.4, 4 \times 128.3, 2 \times 127.8, 127.7 (20 C-Ar), 82.1 (C-1), 73.7 (PhCH₂), 71.9 (C-2), 71.3 (C-4), 69.6 (C-3), 69.4 (C-5), 68.5 (C-6), 24.3 (SCH₂CH₃), 14.7 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ m/z calc. for C₃₆H₃₄O₈SNa 649.1872, found 649.1874.

2,3,4-Tri-*O*-benzoyl-6-*O*-benzyl- α/β -D-glucopyranose (26).

Compound **26** (1 g, 1.6 mmol) was dissolved in a 4:1 DCM/Acetone mixture (30 ml), NIS (719 mg, 2 eq) was added progressively at 0 °C. After 30 min, 5 eq of water were added dropwise at room temperature. At completion (TLC: R_f = 0.45 Pentane/EtOAc 3:1), the reaction was quenched with a 10% aq solution of Na₂S₂O₃. The mixture was diluted with DCM and washed three times with Na₂S₂O₃ solution (20 mL). The DCM solution was dried over Na₂SO₄, filtered and concentrated to dryness. Purification by column chromatography gave 726 mg (78% yield) of white solid **26**. ¹H NMR (CDCl₃, 25°C, 400 MHz): δ α -anomeric form: 8.00 – 7.15 (m, 20H, H-Ar), 6.20 (dd, J_{H_2,H_3} 9.94, J_{H_3,H_4} 9.88, 1H, H-3), 5.75 (dd, J_{H_1,H_2} 3.71, $J_{H_1,OH-1}$ 3.52, 1H, H-1), 5.58 (dd, J_{H_3,H_4} 9.64, J_{H_4,H_5} 10.10, 1H, H-4), 5.29 (dd, J_{H_1,H_2} 3.71, J_{H_2,H_3} 9.94, 1H, H-2), 4.54 (2d, J_{gem} 12.00, 2H, PhCH₂), 4.53 (m, 1H, H-5), 3.68 – 3.66 (m, 2H, H-6a, H-6b), 3.56 (d, $J_{H_1,OH-1}$ 3.52, 1H, OH-1). β -anomeric form: δ 5.89 (dd, J_{H_2,H_3} 9.95, J_{H_3,H_4} 9.65, 1H, H-3), 5.62 (dd, J_{H_3,H_4} 9.65, J_{H_4,H_5} 9.77, 1H, H-4), 5.33 (dd, J_{H_1,H_2} 8.02, J_{H_2,H_3} 9.95, 1H, H-2), 4.99 (dd, J_{H_1,H_2} 8.02, $J_{H_1,OH-1}$ 8.52, 1H, H-1), 4.54 (2d, J_{gem} 11.95, 2H, PhCH₂), 4.04 (d, $J_{H_1,OH-1}$ 8.52, 1H, OH-1), 3.99 (ddd, 1H, H-5), 3.68 - 3.66 (m, 2H, H-

6a, H-6b). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz): δ 166.9, 2 \times 166.00, 165.9, 165.5, 165.3 (6 C=O), 137.6, 137.5, 133.7, 2 \times 133.5, 133.4, 133.4, 133.2 (8 C-*ipso*) 2 \times 130.1, 2 \times 130.0, 6 \times 129.9, 2 \times 129.8, 129.4, 2 \times 129.2, 129.1, 129.0, 128.9, 4 \times 128.6, 10 \times 128.5, 2 \times 128.4, 2 \times 128.1, 2 \times 128.0, 2 \times 127.8 (40 C-Ar); α -anomeric form: δ 90.5 (C-1), 73.8 (PhCH₂), 72.4 (C-2), 70.4 (C-3), 69.8 (C-4), 69.0 (C-5), 68.9 (C-6). β -anomeric form: δ 96.1 (C-1), 74.4 (C-2), 74.0 (C-5), 73.9 (PhCH₂), 72.7 (C-3), 69.7 (C-4), 68.8 (C-6). ESI-HRMS: $[\text{M} + \text{Na}]^+$ m/z calc. for C₃₄H₃₀O₉Na 605.1788, found 605.1792.

2,3,4-Tri-*O*-benzoyl-6-*O*-benzyl- α/β -D-glucopyranosyl trichloroacetimidate (27).

To a solution of compound **26** (1.2 g, 2.06 mmol) and Cl₃CCN (2.06 mL, 20.6 mmol, 10 eq) in dry CH₂Cl₂ (40 mL) was added freshly dried and powdered K₂CO₃ (1.14 g, 8.24 mmol, 4 eq) at room temperature with intensive stirring. After 4 h (TLC: R_f = 0.65 Pentane/EtOAc 3:1), the mixture was diluted with CH₂Cl₂ and filtered through a Celite pad. Solvents were evaporated and the brown residue was immediately purified by flash chromatography to yield 1.27 g (85% yield) of **27** as a foam. ^1H NMR (CDCl_3 , 25 °C, 400 MHz): α -anomeric form: δ 8.62 (s, 1H, NH), 7.98 – 7.12 (m, 20H, H-Ar), 6.86 (d, $J_{\text{H1,H2}}$ 3.65, 1H, H-1), 6.25 (dd, $J_{\text{H2,H3}}$ 10.02, $J_{\text{H3,H4}}$ 9.98, 1H, H-3), 5.85 (dd, $J_{\text{H3,H4}}$ 9.98, $J_{\text{H4,H5}}$ 10.06, 1H, H-4), 5.60 (dd, $J_{\text{H1,H2}}$ 3.65, $J_{\text{H2,H3}}$ 10.02, 1H, H-2), 4.54 (2 d, J_{gem} 11.96, 2H, PhCH₂), 4.48 (ddd, $J_{\text{H4,H5}}$ 10.06, $J_{\text{H5,H6a}}$ 4.16, $J_{\text{H5,H6b}}$ 2.72, 1H, H-5), 3.74 (dd, $J_{\text{H5,H6b}}$ 2.72, J_{gem} 11.20, 1H, H-6b), 3.68 (dd, $J_{\text{H5,H6a}}$ 4.16, J_{gem} 11.20, 1H, H-6a). ^{13}C NMR (CDCl_3 , 25 °C, 100 MHz): α -anomeric form: δ 165.8, 165.4, 165.2 (3 C=O), 160.6 (C=NH), 137.5, 133.5, 133.4, 133.3 (4 C-*ipso*), 2 \times 130.0, 2 \times 129.9, 2 \times 129.8, 129.1, 129.0, 128.7, 2 \times 128.5, 2 \times 128.4, 2 \times 128.35, 2 \times 128.3, 2 \times 127.9, 127.7 (20 C-Ar), 93.5 (C-1), 90.9 (CCl₃), 73.7 (PhCH₂), 72.1 (C-5), 70.9 (C-2), 70.5 (C-3), 68.8 (C-4), 68.1 (C-6). ESI-HRMS: $[\text{M} + \text{Na}]^+$ m/z calc. for C₃₆H₃₀Cl₃NO₉Na 748.0884, found 748.0880.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl- β -D-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-(2-naphthyl)methyl-1-thio- β -D-glucopyranoside (28).

A solution of the trichloroacetimidate-containing compound **27** (1.27 g, 1.76 mmol, 2 eq) and acceptor **8** (400 mg, 0.88 mmol) in a mixture of dry CH₂Cl₂ and dry toluene 1/1 (25 mL) was stirred for 20 min in the presence of molecular sieves (4 Å, 0.6 g). TMSOTf (12.8 μL , 0.08 eq) was added dropwise at –10 °C. The reaction was monitored by TLC (pentane/EtOAc 3:1) and left to stir overnight. NEt₃ was added to quench the reaction and the mixture was filtered through Celite. It was then diluted with CH₂Cl₂ and washed successively with solutions of satd NaHCO₃, brine and

dried over Na₂SO₄. The solvent was removed in vacuo and the residue thus obtained was purified by flash chromatography to yield 895 mg of **28** (84%) as a white solid. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.98 – 7.15 (m, 32H, H-Ar), 5.86 (dd, *J*_{H₂,H₃} 9.59, *J*_{H₃,H₄} 9.53, 1H, H-3 G'), 5.63 (dd, *J*_{H₁,H₂} 7.95, *J*_{H₂,H₃} 9.59, 1H, H-2 G'), 5.61 (dd, *J*_{H₃,H₄} 9.53, *J*_{H₄,H₅} 8.61, 1H, H-4 G'), 5.53 (s, 1H, CHPh G), 5.52 (d, *J*_{H₁,H₂} 7.95, 1H, H-1 G'), 4.88 (d, *J*_{gem} 10.78, 1H, NapCH₂ G), 4.69 (d, *J*_{gem} 10.78, 1H, NAPCH₂ G), 4.59 (d, *J*_{gem} 11.95, 1H, PhCH₂ G'), 4.56 (d, *J*_{H₁,H₂} 9.48, 1H, H-1 G), 4.54 (d, *J*_{gem} 11.95, 1H, PhCH₂ G'), 4.35 (dd, *J*_{H₅,H_{6b}} 5.09, *J*_{gem} 10.51, 1H, H-6b G), 3.96 (dd, *J*_{H₁,H₂} 9.48, *J*_{H₂,H₃} 8.14, 1H, H-2 G), 3.87 (ddd, 1H, H-5 G'), 3.77 - 3.67 (m, 3H, H-6a, H-4, H-3 G), 3.70 (m, 2H, H-6a, H-6b G'), 3.43 (ddd, 1H, H-5 G), 2.77 (dq, 2H, SCH₂CH₃ G), 1.29 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 165.9, 165.4, 165.3 (3 C=O G'), 138.0, 137.2, 135.7, 133.5, 133.4, 133.3, 2 × 133.2 (8 C-*ipso*), 2 × 130.0, 6 × 129.9, 129.5, 129.2, 2 × 129.1, 4 × 128.6, 4 × 128.5, 4 × 128.4, 4 × 128.3, 128.2, 127.9, 3 × 127.8, 127.6, 126.8, 126.3, 126.2, 3 × 126.1 (40 C-Ar) 101.4 (CHPh G), 100.6 (C-1 G'), 84.6 (C-1 G), 83.6 (C-3 G), 81.8 (C-4 G), 76.9 (C-2 G), 75.3 (NapCH₂ G), 74.2 (C-5 G'), 74.0 (PhCH₂ G'), 73.6 (C-3 G'), 72.6 (C-2 G'), 70.2 (C-5 G), 70.1 (C-4 G'), 69.3 (C-6 G'), 68.8 (C-6 G), 24.5 (SCH₂CH₃ G), 14.9 (SCH₂CH₃ G). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₆₀H₅₆O₁₃SNa 1039.3339, found 1039.3335.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranosyl-(1→2)-6-*O*-benzyl-3-*O*-(2-naphthyl)methyl-1-thio-β-D-glucopyranoside (29).

Disaccharide **28** (400 mg, 0.39 mmol) was dissolved in dry THF (8 mL) at room temperature. BH₃·NMe₃ complex (114 mg, 1.56 mmol, 4 eq) was added to the mixture, which was let to stir for 5 min under N₂ atmosphere. Anhydrous AlCl₃ (327 mg, 2.34 mmol, 6 eq) was added and once it was fully dissolved, 2 eq of water was added dropwise; after 16 h (R_f = 0.6 Pentane/EtOAc 2:1) the reaction was stopped by addition of 5 mL of water. The reaction mixture was dissolved in EtOAc and washed with a solution of 1 M HCl, followed by brine and subsequently dried over Na₂SO₄. The mixture was filtered and concentrated to dryness. Purification by column chromatography yielded 317 mg (79% yield) of **29** as a colorless oil. ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.96 – 7.14 (m, 32H, H-Ar), 5.85 (dd, *J*_{H₂,H₃} 9.63, *J*_{H₃,H₄} 9.55, 1H, H-3 G'), 5.65 (dd, *J*_{H₃,H₄} 9.55, *J*_{H₄,H₅} 8.45, 1H, H-4 G'), 5.63 (dd, *J*_{H₁,H₂} 7.96, *J*_{H₂,H₃} 9.63, 1H, H-2 G'), 5.43 (d, *J*_{H₁,H₂} 7.96, 1H, H-1 G'), 4.85 (d, *J*_{gem} 11.50, 1H, NapCH₂ G), 4.75 (d, *J*_{gem} 11.50, 1H, NapCH₂ G), 4.60 (d, *J*_{gem} 12.12, 1H, PhCH₂ G'), 4.56 (d, *J*_{gem} 11.92, 1H, PhCH₂ G), 4.55 (d, *J*_{gem} 12.12, 1H, PhCH₂ G'), 4.52 (d, *J*_{gem} 11.92, 1H, PhCH₂ G), 4.47 (d, *J*_{H₁,H₂} 9.75, 1H, H-1 G), 3.91 (ddd, 1H, H-5 G'), 3.89 (dd, *J*_{H₁,H₂} 9.75, *J*_{H₂,H₃} 8.72, 1H, H-2 G), 3.74-3.62 (m, 3H, H-6a, H-6b, H-4 G), 3.72 (m, 2H, H-6a, H-6b G'), 3.47 (dd, *J*_{H₂,H₃} 8.72, *J*_{H₃,H₄} 8.77, 1H, H-3 G), 3.38 (ddd, 1H, H-5 G), 2.73 (dq, 2H, SCH₂CH₃ G), 2.56 (nr,

1H, OH-4 G), 1.28 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 165.9, 165.3, 165.2 (3 C=O G'), 138.1, 137.8, 135.9, 133.5, 133.4, 2 × 133.3, 133.2 (8 C-*ipso*), 6 × 129.9, 129.4, 129.3, 129.1, 2 × 128.7, 3 × 128.6, 4 × 128.5, 4 × 128.4, 2 × 128.2, 2 × 128.0, 2 × 127.9, 3 × 127.8, 3 × 127.7, 2 × 127.6, 126.6, 126.4, 126.15, 125.8 (40 C-Ar), 100.5 (C-1 G'), 86.9 (C-2 G), 83.9 (C-1 G), 77.4 (C-5 G), 77.0 (C-3 G), 75.5 (NapCH₂ G), 74.2 (C-2), 74.1 (C-5 G'), 74.0 (PhCH₂ G'), 73.8 (PhCH₂), 73.6 (C-3 G'), 73.1 (C-4), 72.6 (C-2 G'), 70.9 (C-6), 70.1 (C-4 G'), 69.4 (C-6 G'), 24.4 (SCH₂CH₃), 14.9 (SCH₂CH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₆₀H₅₈O₁₃SNa 1041.3496, found 1041.3498.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranosyl-(1→2)-6-*O*-benzyl-1-thio-β-D-glucopyranoside (30).

Compound **29** (150 mg, 0.15 mmol) was dissolved in a mixture of CH₂Cl₂/MeOH 4/1 and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 85 mg, 0.38 mmol, 2.5 eq) was added whereafter the reaction mixture was stirred until completion, monitored by TLC (R_f = 0.45 Pentane/EtOAc 1:1). Once complete, the reaction mixture was diluted with CH₂Cl₂ and 1 mL of satd NaHCO₃ was added. The two phases were separated and the organic phase was washed twice more with the solution of satd NaHCO₃ and then dried over Na₂SO₄. The residue was purified by flash chromatography to yield compound **30** as a white powder in 88% yield (114 mg). ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.99 – 7.14 (m, 25H, H-Ar), 5.89 (dd, *J*_{H₂,H₃} 9.55, *J*_{H₃,H₄} 9.49, 1H, H-3 G'), 5.58 (dd, *J*_{H₃,H₄} 9.49, *J*_{H₄,H₅} 9.78, 1H, H-4 G'), 5.53 (dd, *J*_{H₁,H₂} 7.82, *J*_{H₂,H₃} 9.55, 1H, H-2 G'), 5.29 (d, *J*_{H₁,H₂} 7.82, 1H, H-1 G'), 4.55 (2 d, *J*_{gem} 12.00, 2H, PhCH₂ G), 4.55 (2 d, *J*_{gem} 11.74, 2H, PhCH₂ G'), 4.45 (d, *J*_{H₁,H₂} 9.65, 1H, H-1 G), 4.02 (ddd, 1H, H-5 G'), 3.73 (m, 2H, H-6a, H-6b G'), 3.70 (m, 2H, H-6a, H-6b G), 3.65 (dd, *J*_{H₁,H₂} 9.65, *J*_{H₂,H₃} 8.81, 1H, H-2 G), 3.54 (ddd, *J*_{H₂,H₃} 8.81, *J*_{H₃,H₄} 8.74, *J*_{H₃,OH-3} 2.98, 1H, H-3 G), 3.47 (ddd, *J*_{H₃,H₄} 8.74, *J*_{H₄,H₅} 9.27, *J*_{H₄,OH-4} 1.81, 1H, H-4 G), 3.39 (ddd, 1H, H-5 G), 3.25 (d, *J*_{H₃,OH-3} 2.98, 1H, OH-3 G), 2.84 (d, *J*_{H₄,OH-4} 1.81, 1H, OH-4 G), 2.58 (dq, 2H, SCH₂CH₃ G), 1.26 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 165.9, 165.5, 165.4 (3 C=O G'), 137.9, 137.7, 133.5, 133.3, 133.3 (5 C-*ipso*), 6 × 129.9, 129.6, 129.1, 129.0, 4 × 128.6, 4 × 128.5, 2 × 128.4, 4 × 128.4, 2 × 128.0, 127.9, 4 × 127.8 (30 C-Ar), 99.8 (C-1 G'), 83.1 (C-1 G), 79.2 (C-2 G), 77.7 (C-5 G), 77.6 (C-3 G), 74.0 (PhCH₂ G'), 74.0 (PhCH₂ G), 73.7 (C-5 G'), 73.3 (C-3 G'), 72.4 (C-2 G'), 71.9 (C-4 G), 70.6 (C-6 G), 70.0 (C-4 G'), 69.3 (C-6 G'), 24.4 (SCH₂CH₃ G), 14.7 (SCH₂CH₃ G). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₄₉H₅₀O₁₃SNa 901.2870, found 901.2873.

Ethyl 6-*O*-benzyl-β-D-glucopyranosyl-(1→2)-6-*O*-benzyl-1-thio-β-D-glucopyranoside (31).

For general acyl group deprotection conditions see the above reaction conditions for compound **7**. Starting from ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl- β -D-glucopyranosyl-(1 \rightarrow 2)-6-*O*-benzyl-1-thio- β -D-glucopyranoside (**30**, 200 mg, 0.23 mmol, TLC: R_f = 0.45 DCM/MeOH 9:1) *O*-deacylation yielded compound **31** as a colorless oil in 93% yield. ¹H NMR (CD₃OD, 25 °C, 400 MHz): δ 7.39 – 7.21 (m, 10H, H-Ar), 4.71 (d, $J_{H1,H2}$ 7.76, 1H, H-1 G'), 4.64 (s, 2H, PhCH₂ G'), 4.58 (s, 2H, PhCH₂ G), 4.47 (d, $J_{H1,H2}$ 9.28, 1H, H-1 G), 3.87 - 3.79 (2 dd, 2H, H-6b G, H-6b G'), 3.72 - 3.62 (2 dd, 2H, H-6a G, H-6a G'), 3.58 (dd, $J_{H2,H3}$ 8.70, $J_{H3,H4}$ 8.43, 1H, H-3 G), 3.55 (dd, $J_{H1,H2}$ 9.28 $J_{H2,H3}$ 8.70, 1H, H-2 G), 3.44 (ddd, 1H, H-5 G), 3.42 (ddd, 1H, H-5 G'), 3.38 (dd, 1H, H-4 G'), 3.36 (dd, 1H, H-4 G), 3.35 (dd, 1H, H-3 G'), 3.27 (dd, $J_{H1,H2}$ 7.76 $J_{H2,H3}$ 9.26, 1H, H-2 G'), 2.70 (dq, 2H, SCH₂CH₃ G), 1.21 (t, 3H, SCH₂CH₃ G). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 139.8, 139.7 (2 *C*-*ipso*), 4 \times 129.3, 4 \times 128.8, 128.6, 128.5 (10 C-Ar), 104.8 (C-1 G'), 84.6 (C-1 G), 81.3 (C-2 G), 80.9 (C-5 G), 79.8 (C-3 G), 78.1 (C-3 G'), 77.5 (C-5 G'), 75.8 (C-2 G'), 74.7 (PhCH₂ G'), 74.4 (PhCH₂ G), 71.6 (C-4 G), 71.4 (C-4 G'), 70.9 (C-6 G), 70.8 (C-6 G'), 24.8 (SCH₂CH₃ G), 15.4 (SCH₂CH₃ G). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₈H₃₈O₁₀SNa 589.2083, found 589.2080.

Ethyl 2,3,4-tri-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl- β -D-glucopyranosyl-(1 \rightarrow 2)-3,4-di-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-1-thio- β -D-glucopyranoside (32**).**

Ethyl 6-*O*-benzyl-2-*O*-(6-*O*-benzyl- β -D-glucopyranosyl)-1-thio- β -D-glucopyranoside (**31**, 0.120 g, 0.21 mmol) was dissolved in dry pyridine (5 mL) and DMAP (cat) was added to the mixture. TBDMSOTf (725 μ L, 3.15 mmol, 15 eq) was added dropwise at 0 °C, the mixture was heated to 80 °C and the reaction was left to proceed overnight. The reaction mixture (R_f = 0.5 Pentane/DCM 1:1) was left to cool down and then quenched by addition of MeOH. The mixture was extracted with dichloromethane and successively washed with 1 M HCl, satd aqueous NaHCO₃ and brine. The solution was dried over anhydrous Na₂SO₄ and solvents were evaporated. The resulting residue was purified by chromatography to afford compound **32** as a colorless syrup in 86% yield (139 mg). ¹H NMR (CDCl₃, 25 °C, 400 MHz): δ 7.36 – 7.22 (m, 10H, H-Ar), 5.11 (d, $J_{H1,H2}$ 5.96, 1H, H-1 G), 4.94 (d, $J_{H1,H2}$ 5.13, 1H, H-1 G'), 4.60 (d, J_{gem} 12.16, 1H, PhCH₂ G'), 4.54 (s, 2H, PhCH₂ G), 4.53 (d, J_{gem} 12.16, 1H, PhCH₂ G'), 3.99 (ddd, 1H, H-5 G'), 3.96 (dd, $J_{H2,H3}$ < 2, 1H, H-3 G), 3.91 (ddd, 1H, H-5 G), 3.90 (dd, 1H, H-4 G), 3.89 (dd, 1H, H-4 G'), 3.87 (dd, $J_{H2,H3}$ < 2, 1H, H-2 G), 3.72 (dd, $J_{H2,H3}$ < 2, 1H, H-3 G'), 3.65 (dd, 1H, H-6b G), 3.65 (dd, 1H, H-6b G'), 3.63 (dd, $J_{H2,H3}$ < 2, 1H, H-2 G'), 3.60 (dd, 1H, H-6a G), 3.59 (dd, 1H, H-6a G'), 2.67 (dq, 2H, SCH₂CH₃ G), 1.21 (t, 3H, SCH₂CH₃ G), 2 \times 0.89, 0.88, 0.87, 0.85 (5 s, 45H, C(CH₃)₃), 0.13, 2 \times 0.095, 0.09, 0.089, 0.078, 0.056, 0.054, 0.050, 0.044, 0.019 (10 s, 30H, SiCH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 138.9,

138.75 (2 C-*ipso*), 2 × 128.4, 2 × 128.3, 2 × 127.8, 2 × 127.6, 127.5, 127.4 (10 C-Ar), 101.4 (C-1 G'), 82.2 (C-1 G), 81.0 (C-2 G), 79.5 (C-5 G), 79.0 (C-3 G'), 78.8 (C-5 G'), 77.4 (C-2 G'), 76.1 (C-3 G), 73.4 (PhCH₂ G'), 73.3 (PhCH₂ G), 71.7 (C-4 G), 71.7 (C-6 G), 71.6 (C-6 G'), 71.2 (C-4 G'), 4 × 26.1, 26.0 (5 C(CH₃)₃), 25.3 (SCH₂CH₃ G), 5 × 18.1 (5 C(CH₃)₃), 14.9 (SCH₂CH₃ G), -3.5, -3.8, -4.0, 2 × -4.1, 2 × -4.4, -4.5, 2 × -4.6 (10 SiCH₃). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₅₈H₁₀₈O₁₀SSi₅Na 1159.6407, found 1159.6404.

Methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1→2)[2,3,4-tri-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl- β -D-glucopyranosyl-(1→2)-3,4-di-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl- β -D-glucopyranosyl-(1→3)]-4,6-*O*-benzylidene- β -D-galactopyranoside (33a).

Methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1→2)[2,3,4-tri-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl- β -D-glucopyranosyl-(1→2)-4-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl- β -D-glucopyranosyl-(1→3)]-4,6-*O*-benzylidene- β -D-galactopyranoside (33b).

Donor **32** (50 mg, 0.044 mmol), BSP (9.4 mg, 0.045 mmol, 1.02 eq) and TTBP (55mg, 0.22 mmol, 5 eq) were dissolved in dry CH₂Cl₂ (2 mL) whereafter 4 Å molecular sieves (100 mg) were added under N₂ atmosphere and the mixture was cooled down to -78 °C; 1.2 eq of Tf₂O was then added dropwise, followed directly by acceptor **19** (2 eq, 4 Å molecular sieves were also present) dissolved in dry dichloromethane. The mixture was left to stir and allow to reach -10 °C and was then quenched by addition of NEt₃ (0.015 mL, 0.11 mmol, 2.5 eq). The mixture was diluted with dichloromethane and filtered through a pad of Celite. The filtrate was successively washed with water, brine and dried over Na₂SO₄. After evaporation of the solvent, the resulting material was purified by chromatography to afford a total yield of 55% of **33a** (50%) and **33b** (5%). (R_f = 0.6 **33a**, 0.3 **33b**, Pentane/EtOAc 3:1). **33a**: ¹H NMR (CDCl₃, 25°C, 400 MHz): δ 7.48 – 7.19 (m, 15H, H-Ar), 5.54 (d, *J*_{H1,H2} 1.30, 1H, H-1 G), 5.34 (dd, *J*_{H2,H3} 3.22, *J*_{H3,H4} 9.89, 1H, H-3 R), 5.32 (s, 1H, CHPh Gal), 5.22 (dd, *J*_{H1,H2} 1.70, *J*_{H2,H3} 3.22, 1H, H-2 R), 5.10 (d, *J*_{H1,H2} 4.48, 1H, H-1 G'), 5.05 (dd, *J*_{H3,H4} 9.89, *J*_{H4,H5} 10.00, 1H, H-4 R), 4.90 (d, *J*_{H1,H2} 1.70, 1H, H-1 R), 4.60 (d, *J*_{gem} 12.05, 1H, PhCH₂ G), 4.59 (s, 2H, PhCH₂ G'), 4.52 (dd, *J*_{H3,H4} 3.22, 1H, H-4 Gal), 4.49 (d, *J*_{gem} 12.05, 1H, PhCH₂ G), 4.22 (dq, *J*_{H4,H5} 10.00, *J*_{H5,H6} 6.12, 1H, H-5 R), 4.10 (dd, 1H, H-3 G'), 4.02 (dd, 1H, H-4 G), 4.01 (dd, 1H, H-4 G'), 3.96 (d, *J*_{H1,H2} 7.73, 1H, H-1 Gal), 3.94 (ddd, 1H, H-5 G), 3.91 (dd, 1H, H-6b Gal), 3.88 (dd, 1H, H-2 G), 3.80 (dd, *J*_{H1,H2} 7.73, *J*_{H2,H3} 9.97, 1H, H-2 Gal), 3.74 (dd, 1H, H-3 G), 3.72 (ddd, 1H, H-5 G'), 3.71 (dd, 1H, H-2 G'), 3.65 (dd, 1H, H-6b G), 3.62 (m, 2H, H-6a, H-6b G'), 3.54 (dd, 1H, H-6a G), 3.48 (dd, *J*_{H2,H3} 9.97, *J*_{H3,H4} 3.22, 1H, H-3 Gal), 3.42 (s, 3H, OMe Gal), 3.18 (dd, 1H, H-6a Gal), 2.84 (ddd, 1H, H-5 Gal), 2.08, 2.04, 1.83 (3s, 9H, CH₃ R), 1.13 (s, 3H, H-6

R), 0.89, 0.88, 0.85, 0.84, 0.76 (5s, 45H, C(CH₃)₃), 0.13, 0.12, 0.10, 0.09, 2 × 0.07, 0.01, -0.01, -0.27, -0.30 (10 s, 30H, SiCH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 170.4, 170.1, 169.2 (3 C=O), 139.6, 138.4, 138.3 (3 C-*ipso*), 2 × 128.7, 2 × 128.6, 128.4, 3 × 128.1, 2 × 128.0, 2 × 127.1, 126.9, 2 × 126.4 (15 C-Ar), 102.5 (C-1 Gal), 102.4 (C-1 G'), 102.2 (C-1 G), 99.9 (CHPh Gal), 98.3 (C-1 R), 81.6 (C-2 G), 80.2 (C-3 G), 80.0 (C-5 G'), 79.8 (C-3 Gal), 76.8 (C-4 G'), 76.8 (C-2 G'), 75.7 (C-4 Gal), 75.4 (C-2 Gal), 73.6 (PhCH₂ G), 72.9 (C-5 G), 72.6 (PhCH₂ G'), 72.1 (C-4 G), 72.1 (C-4 R), 71.1 (C-3 G'), 70.9 (C-6 G'), 70.7 (C-2 R), 70.4 (C-6 G), 69.3 (C-3 R), 68.7 (C-6 Gal), 66.4 (C-5 Gal), 66.3 (C-5 R), 56.1 (OMe Gal) 2 × 26.3, 26.2, 26.1, 26.0 (5 C(CH₃)₃), 2 × 21.1, 20.7 (3 CH₃ R), 18.2, 2 × 18.1, 17.9, 17.8 (5 C(CH₃)₃), 17.0 (C-6 R), -3.3, -3.4, 2 × -3.8, 2 × -4.0, 2 × -4.4, -4.5, -4.6 (10 SiCH₃). **33b**: ¹H NMR (CDCl₃, 25°C, 400 MHz): δ 7.68 - 7.65 (m, 2H, **BSP**)⁵⁷ 7.52 - 7.45 (m, 3H, **BSP**), 7.44 - 7.22 (m, 15H, H-Ar), 5.30 (dd, *J*_{H₂,H₃} 3.42, *J*_{H₃,H₄} 10.04, 1H, H-3 R), 5.30 (s, 1H, CHPh Gal), 5.22 (dd, *J*_{H₁,H₂} 1.54, *J*_{H₂,H₃} 3.42, 1H, H-2 R), 5.11 (d, *J*_{H₁,H₂} 1.54, 1H, H-1 R), 5.05 (d, *J*_{H₁,H₂} 1.23, 1H, H-1 G), 5.00 (dd, *J*_{H₃,H₄} 10.04, *J*_{H₄,H₅} 9.95, 1H, H-4 R), 5.00 (d, *J*_{H₁,H₂} 4.59, 1H, H-1 G'), 4.58 (d, *J*_{gem} 11.78, 1H, PhCH₂ G), 4.53 (s, 2H, PhCH₂ G'), 4.52 (d, *J*_{gem} 11.78, 1H, PhCH₂ G), 4.30 (dd, *J*_{H₃,H₄} 3.31, 1H, H-4 Gal), 4.21 (dq, *J*_{H₄,H₅} 9.95, *J*_{H₅,H₆} 6.21, 1H, H-5 R), 4.11 (d, *J*_{H₁,H₂} 7.70, 1H, H-1 Gal), 4.05 (dd, *J*_{H₅,H_{6b}} 1.01, *J*_{gem} 12.18, 1H, H-6b Gal), 3.94 (dd, 1H, H-2 G), 3.92 (dd, 1H, H-2 Gal), 3.915 (dd, 1H, H-3 G'), 3.84 (ddd, 1H, H-5 G'), 3.76 (dd, 1H, H-4 G), 3.73 (dd, 1H, H-6b G), 3.72 (ddd, 1H, H-5 G), 3.70 (dd, 1H, H-4 G'), 3.695 (dd, 1H, H-2 G'), 3.63 (dd, 1H, H-3 Gal), 3.63 (dd, 1H, H-6a G), 3.60 (m, 2H, H-6a, H-6b G'), 3.51 (dd, 1H, H-3 G), 3.48 (s, 3H, OMe Gal), 3.48 (dd, *J*_{gem} 12.18, 1H, H-6a Gal), 3.25 (nr, 1H, OH-3'), 3.15 - 3.10 (m, 2H, **BSP**), 3.05 (ddd, 1H, H-5 Gal), 2.99 - 2.93 (m, 2H, **BSP**), 2.06, 2.04, 1.93 (3 s, 9H, CH₃ R), 1.67 - 1.51 (m, 6H, **BSP**), 1.14 (s, 3H, H-6 R), 0.87, 0.85, 0.83, 0.82 (4s, 36H, C(CH₃)₃), 0.08, 0.06, 0.04, 0.02, 0.01, -0.01, -0.02, -0.13 (8s, 24H, SiCH₃). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 2 × 170.3, 169.6 (3 C=O), 138.9, 138.7, 138.0 (3 C-*ipso*), 128.9, 2 × 128.6, 2 × 128.3, 2 × 128.2, 2 × 128.1, 128.0, 2 × 127.5, 127.3, 2 × 126.6 (15 C-Ar), 103.6 (C-1 G'), 102.4 (C-1 Gal), 102.2 (C-1 G), 100.7 (CHPh Gal), 98.0 (C-1 R), 79.7 (C-2 G), 79.1 (C-4 G'), 78.9 (C-3 Gal), 78.1 (C-5 G'), 76.9 (C-3 G), 76.1 (C-4 Gal), 76.05 (C-2 G'), 74.4 (C-2 Gal), 74.2 (C-4 G), 73.6 (PhCH₂ G), 73.1 (PhCH₂ G'), 73.06 (C-5 G), 71.7 (C-4 R), 71.1 (C-3 G'), 70.8 (C-6 G'), 70.2 (C-2 R), 70.0 (C-6 G), 69.4 (C-3 R), 68.9 (C-6 Gal), 66.45 (C-5 Gal), 66.4 (C-5 R), 56.2 (OMe Gal) 26.2, 26.1, 2 × 26.0 (4 C(CH₃)₃), 2 × 21.0, 20.9 (3 CH₃ R), 2 × 18.2, 18.1, 18.0 (4 C(CH₃)₃), 17.1 (C-6 R), 2 × -3.9, 2 × -4.0, -4.2, -4.4, -4.8, -5.3 (8 SiCH₃). **33a**: ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₈₂H₁₃₆O₂₃Si₅Na 1651.8216, found 1651.8220. **33b**: ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₇₆H₁₂₂O₂₃Si₄Na 1537.7352, found 1537.7352.

Methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 \rightarrow 2)[2,3,4-tri-*O*-acetyl-6-*O*-benzyl- β -D-glucopyranosyl-(1 \rightarrow 2)-3,4-di-*O*-acetyl-6-*O*-benzyl- β -D-glucopyranosyl-(1 \rightarrow 3)]-4,6-*O*-benzylidene- β -D-galactopyranoside (35).

Compounds **33a/33b** (60 mg, 10:1 mixture) were dissolved altogether in dry THF and 15 eq of a 1M solution of TBAF in THF was added dropwise at room temperature. At completion, the mixture was taken into CH₂Cl₂ and washed with water. The organic phase was dried over Na₂SO₄, filtered and concentrated to dryness. The compound obtained (**34**) was dissolved in dry pyridine (3 mL). Acetic anhydride (10 eq) and DMAP were added and the reaction was left to stir overnight. The reaction was stopped by adding a few drops of MeOH and the yellow oil was washed with NaHCO₃, brine, 1M HCl and brine before being dried over Na₂SO₄, filtered and concentrated. Purification by flash chromatography (R_f = 0.55 EtOAc/Pentane 2:1) gave 38 mg of **35** as a white powder (80% yield over two steps). ¹H NMR (CDCl₃, 25°C, 400 MHz): δ 7.52 – 7.47 (m, 2H, H-Ar), 7.37 – 7.20 (m, 13H, H-Ar), 5.48 (s, 1H, CHPh Gal), 5.34 (dd, $J_{H1,H2}$ 1.62, $J_{H2,H3}$ 3.51, 1H, H-2 R), 5.30 (d, $J_{H1,H2}$ 1.62, 1H, H-1 R), 5.27 (dd, $J_{H2,H3}$ 3.51, $J_{H3,H4}$ 10.17, 1H, H-3 R), 5.21 (dd, $J_{H2,H3}$ 8.85, $J_{H3,H4}$ 8.95, 1H, H-3 G), 5.12 (dd, $J_{H3,H4}$ 9.55, $J_{H4,H5}$ 9.61, 1H, H-4), 5.08 (dd, $J_{H3,H4}$ 9.99, $J_{H4,H5}$ 10.07, 1H, H-4 R), 5.04 (dd, $J_{H3,H4}$ 9.08, $J_{H4,H5}$ 10.03, 1H, H-4 G), 5.00 (dd, $J_{H2,H3}$ 9.32, $J_{H3,H4}$ 9.48, 1H, H-3 G'), 4.86 (d, $J_{H1,H2}$ 7.03, 1H, H-1 G), 4.79 (m, 2H, H-1 G', H-2 G'), 4.58 (d, J_{gem} 12.00, 1H, PhCH₂ G), 4.47 (d, J_{gem} 12.12, 1H, PhCH₂ G'), 4.43 (d, J_{gem} 12.00, 1H, PhCH₂ G), 4.32 (d, J_{gem} 12.12, 1H, PhCH₂ G'), 4.27 (dd, $J_{H3,H4}$ 3.61, 1H, H-4 Gal), 4.27 (dd, $J_{H5,H6b}$ 1.43, J_{gem} 12.30, 1H, H-6b Gal), 4.24 (d, $J_{H1,H2}$ 7.63, 1H, H-1Gal), 4.19 (dq, $J_{H4,H5}$ 10.07, $J_{H5,H6}$ 6.22, 1H, H-5 R), 4.00 (dd, $J_{H1,H2}$ 7.63, $J_{H2,H3}$ 9.69, 1H, H-2 Gal), 3.91 (dd, $J_{H5,H6a}$ 1.62, J_{gem} 12.30, 1H, H-6a Gal), 3.91 (dd, $J_{H2,H3}$ 9.69, $J_{H3,H4}$ 3.61, 1H, H-3 Gal), 3.73 (ddd, $J_{H4,H5}$ 10.03, $J_{H5,H6a}$ 4.99, $J_{H5,H6b}$ 2.70, 1H, H-5 G), 3.71 (dd, $J_{H1,H2}$ 7.03, $J_{H2,H3}$ 8.85, 1H, H-2 G), 3.59 (dd, 1H, H-6b G'), 3.56 (dd, 1H, H-6b G), 3.52 (s, 3H, OMe Gal), 3.50 (dd, $J_{H5,H6b}$ 4.99, J_{gem} 10.73, 1H, H-6a G), 3.44 (dd, 1H, H-6a G'), 3.43 (ddd, $J_{H4,H5}$ 9.61, 1H, H-5 G'), 3.30 (ddd, $J_{H5,H6a}$ 1.62, $J_{H5,H6b}$ 1.43, 1H, H-5 Gal), 2.06, 2.05, 2.02, 1.99, 1.98, 1.96, 1.88, 1.84 (8 s, 24H, CH₃), 1.13 (d, $J_{H5,H6}$ 6.22, 3H, H-6 R). ¹³C NMR (CDCl₃, 25 °C, 100 MHz): δ 170.6, 170.5, 170.4, 2 \times 170.1, 169.9, 169.7, 169.4 (8 C=O), 138.5, 138.0, 137.8 (3 C-*ipso*), 128.9, 2 \times 128.6, 2 \times 128.4, 2 \times 128.2, 2 \times 128.1, 128.0, 2 \times 127.9, 127.5, 2 \times 126.3 (15 C-Ar), 102.9 (C-1 Gal), 101.4 (C-1 G), 100.8 (C-1 G'), 100.8 (CHPh Gal), 97.9 (C-1 R), 78.8 (C-2 G), 78.1 (C-3 Gal), 76.3 (C-4 Gal), 75.2 (C-2 Gal), 73.8 (C-3 G'), 73.6 (PhCH₂ G), 73.6 (C-3 G), 73.5 (C-5 G'), 73.4 (PhCH₂ G'), 72.9 (C-2 G'), 72.5 (C-5 G), 71.2 (C-4 R), 69.7 (C-4 G), 69.7 (C-2 R), 69.5 (C-3 R), 69.1 (C-6 Gal), 68.9 (C-4 G'), 68.8 (C-6 G), 68.5 (C-6 G'), 66.9 (C-5 R), 66.5 (C-5 Gal), 56.8 (OMe Gal), 21.0, 3 \times 20.9, 3 \times 20.8, 20.7 (8 CH₃), 17.2 (C-6 R). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₆₂H₇₆O₂₈Na 1291.4421, found 1291.4419.

Methyl α -L-rhamnopyranosyl-(1 \rightarrow 2)[6-*O*-benzyl- β -D-glucopyranosyl-(1 \rightarrow 2)-6-*O*-benzyl- β -D-glucopyranosyl-(1 \rightarrow 3)]-4,6-*O*-benzylidene- β -D-galactopyranoside (36).

For general acyl group deprotection conditions see the above reaction conditions for compound 7. Compound 35 (55 mg, 0.43 mmol) was *O*-deacylated (TLC: R_f = 0.25 DCM/MeOH 9:1) to give 35 mg of 36 (87% yield) as a colorless oil. ¹H NMR (CD₃OD, 25 °C, 400 MHz): δ 7.47 – 7.17 (m, 15H, H-Ar), 5.40 (s, 1H, CHPh Gal), 5.24 (d, $J_{H1,H2}$ 1.69, 1H, H-1 R), 4.73 (d, $J_{H1,H2}$ 7.94, 1H, H-1 G'), 4.65 (d, $J_{H1,H2}$ 7.44, 1H, H-1 G), 4.68 (d, J_{gem} 11.87, 1H, PhCH₂ G'), 4.62 (d, J_{gem} 11.87, 1H, PhCH₂ G'), 4.47 (2 d, J_{gem} 12.12, 2H, PhCH₂ G), 4.38 (dd, $J_{H3,H4}$ 3.26, 1H, H-4 Gal), 4.35 (d, $J_{H1,H2}$ 7.11, 1H, H-1 Gal), 4.12 (dd, $J_{H5,H6b}$ 1.49, J_{gem} 12.29, 1H, H-6b Gal), 4.05 (dd, $J_{H1,H2}$ 1.69, $J_{H2,H3}$ 3.26, 1H, H-2 R), 3.96 (dq, $J_{H5,H6}$ 6.20, 1H, H-5 R), 3.93 (dd, 1H, H-6b G'), 3.88 (dd, J_{gem} 12.29, 1H, H-6a Gal), 3.88 (dd, $J_{H1,H2}$ 7.11, 1H, H-2 Gal), 3.87 (dd, $J_{H3,H4}$ 3.26, 1H, H-3 Gal), 3.73 (dd, 1H, H-6b G), 3.72 (dd, 1H, H-6a G'), 3.66 (dd, $J_{H2,H3}$ 3.26, 1H, H-3 R), 3.62 (dd, $J_{H1,H2}$ 7.44, 1H, H-2 G), 3.60 (dd, 1H, H-3 G), 3.58 (dd, 1H, H-6a G), 3.56 (s, 3H, OMe Gal), 3.52 (ddd, 1H, H-5 G), 3.43 (dd, 1H, H-4 R), 3.41 (dd, 1H, H-4 G'), 3.41 (dd, $J_{H1,H2}$ 7.94, 1H, H-2 G'), 3.40 (ddd, $J_{H5,H6b}$ 1.49, 1H, H-5 Gal), 3.33 (dd, 1H, H-4 G), 3.31 (dd, 1H, H-3 G'), 3.31 (ddd, 1H, H-5 G'), 1.24 (d, $J_{H5,H6}$ 6.20, 3H, H-6 R). ¹³C NMR (CD₃OD, 25°C, 100 MHz): δ 139.8, 139.7, 139.6 (3 *C-*ipso**), 129.8, 2 \times 129.5, 2 \times 129.3, 2 \times 129.2, 2 \times 129.0, 2 \times 128.9, 128.8, 128.5, 2 \times 127.8 (15 C-Ar), 105.0 (C-1 G'), 104.4 (C-1 G), 104.3 (C-1 Gal), 102.7 (C-1 R), 102.5 (CHPh Gal), 82.1 (C-2 G), 81.9 (C-3 Gal), 78.7 (C-3 G), 78.2 (C-5 G'), 78.1 (C-4 Gal), 77.5 (C-3 G'), 77.4 (C-2 Gal), 76.7 (C-5 G), 75.2 (C-2 G'), 74.7 (PhCH₂ G'), 74.6 (PhCH₂ G), 74.1 (C-4 R), 72.5 (C-3 R), 72.2 (C-2 R), 71.6 (C-4 G), 71.4 (C-6 G'), 71.3 (C-4 G'), 70.1 (C-6 G), 70.0 (C-6 Gal), 69.8 (C-5 R), 67.7 (C-5 Gal), 56.9 (OMe Gal), 17.8 (C-6 R). ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₄₆H₆₀O₂₀Na 955.3576, found 955.3575.

Methyl α -L-rhamnopyranosyl-(1 \rightarrow 2)[β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyl-(1 \rightarrow 3)]- β -D-galactopyranoside (1).

Compound 36 (30 mg, 0.32 mmol) was dissolved in a 3/2 EtOH/EtOAc mixture (2.5 mL) and 10 – 20% Pd/C catalyst (10 mg) was added in a small pierced vial. This vial was left to stir overnight at room temperature under 3 atmospheres of H₂. Once TLC analysis indicated full conversion (R_f = 0.5 EtOAc/MeOH/H₂O 7:2:1), the mixture was filtered through a Celite pad, washed with water and concentrated to dryness. The residue was purified on an ÄKTA™ system equipped with a

Superdex™ column to give 19 mg of **1** as a white powder (89%). ¹H and ¹³C NMR data: see Table 1. ESI-HRMS: [M + Na]⁺ *m/z* calc. for C₂₅H₄₄O₂₀Na 687.2324, found 687.2326.

Supplementary data

Supplementary data associated with this article can be found in the online version.

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