Tetrahedron 72 (2016) 912–927

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

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

Thibault Angles d'Ortoli, Göran Widmalm *

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 9 September 2015
Received in revised form 9 December 2015
Accepted 21 December 2015
Available online 23 December 2015

Keywords:
Glycosylation
Oligosaccharide
Saponin
CASPER
Chemical shift prediction

ABSTRACT

The major glycoalkaloid in the roots of *Solanum laciniatum* is Solaradixine having the branched tetrasaccharide β-D-Glc*p*-(1→2)-β-D-Glc*p*-(1→3)[α-L-Rha*p*-(1→2)]-β-D-Gal*p* 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-Glc*p*-(1→2)-β-D-Glc*p*-SEt donor, which avoided 1,6-anydro 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-Rha*p*-(1→2)-β-D-Gal*p*-OMe disaccharide was used as the acceptor molecule together with a super-armed β-D-Glc*p*-(1→2)-β-D-Glc*p*-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.

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 as well as their 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 (Fig. 1) as the sapogenin, viz., Solashabanine having a tetrasaccharide with a terminal β-(1→6)-linked glucosyl residue, Solaradixine (**1b**) containing a tetrasaccharide but instead with a terminal β-(1→2)-linked glucosyl residue (Fig. 1) and Solaridine comprising a pentasaccharide with a terminal β-(1→6)-linked glucosyl residue attached to the β-(1→2)-linked glucosyl residue of Solaradixine.[17]

Synthesis of saponins and oligosaccharide glycosides[18–20] 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-Glc*p*-(1→2)-β-D-Glc*p*-(1→3)[α-L-Rha*p*-(1→2)]-β-D-Gal*p*-OMe (**1**) corresponding to the glycoside moiety of the glycoalkaloid Solaradixine from *S. laciniatum* and its rapid structure verification based on unassigned ^{1}H and ^{13}C NMR spectra as implemented in the computer program CASPER.

* Corresponding author. E-mail address: goran.widmalm@su.se (G. Widmalm).

http://dx.doi.org/10.1016/j.tet.2015.12.042
0040-4020/

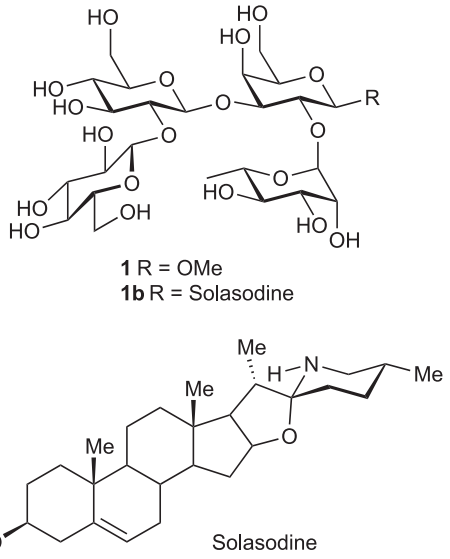
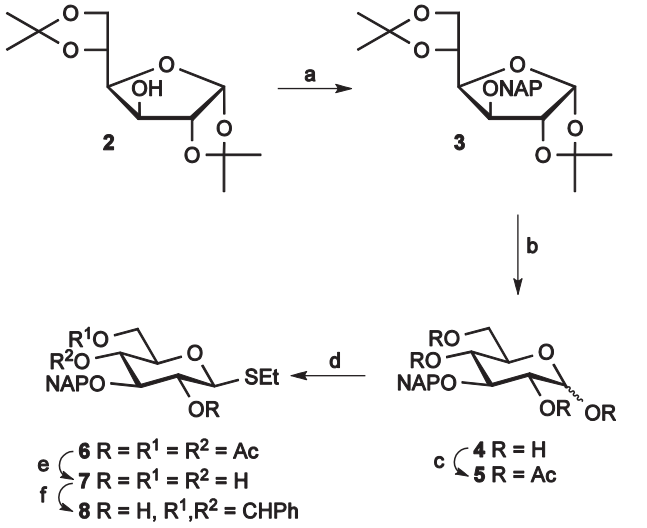


Fig. 1. Schematic of methyl α-L-rhamnopyranosyl-(1→2)[β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→3)]-β-D-galactopyranoside (**1**), the glycoalkaloid Solaradixine (**1b**) and Solasodine.



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) Ac_2O, pyridine, 90%; (d) $BF_3{\cdot}Et_2O$, EtSH, $CHCl_3$, 3 h, 68%; (e) 1 M NaOMe, MeOH, 16 h, 88%; (f) $PhCH(OMe)_2$, CSA, CH_3CN, 2 h, 55 °C, 82%.

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→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→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**.

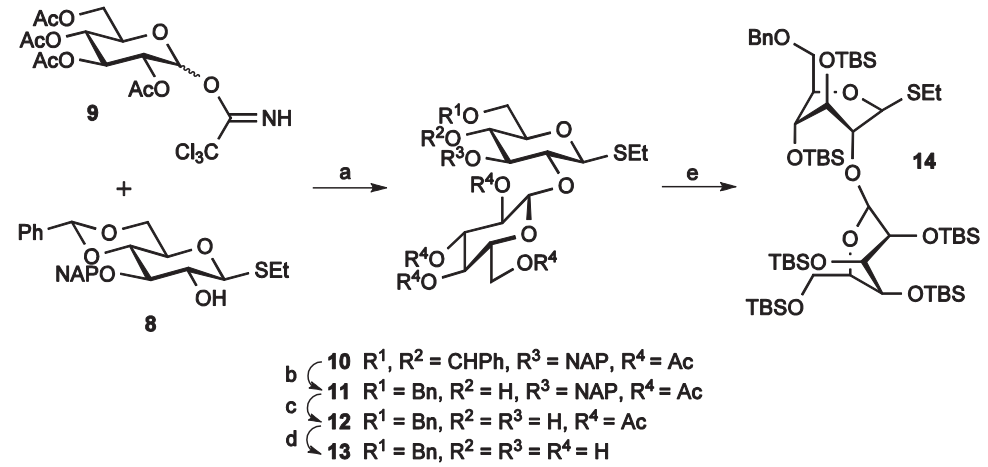
The NAP protecting group was chosen since it can be selectively removed in the presence of *O*-benzyl groups and that it is stable to strong acids and bases.[30] Subsequent removal of the isopropylidene groups by hydrochloric acid treatment gave **4**, which was *O*-acetylated using pyridine and acetic anhydride to give **5**. The donor functionality was introduced by treatment with $BF_3{\cdot}Et_2O$ and ethanethiol to give **6**, which was *O*-deacetylated under Zémplen conditions[31] resulting in **7**, followed by protection of O4 and O6 with a 4,6-*O*-benzylidnene 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 donors[33] employed a glycosylation strategy in which a trimethylsilyl triflate-promoted coupling[28] of the known trichloroacetimidate donor **9**[34] with acceptor **8** gave disaccharide **10** in 75% yield (Scheme 2).

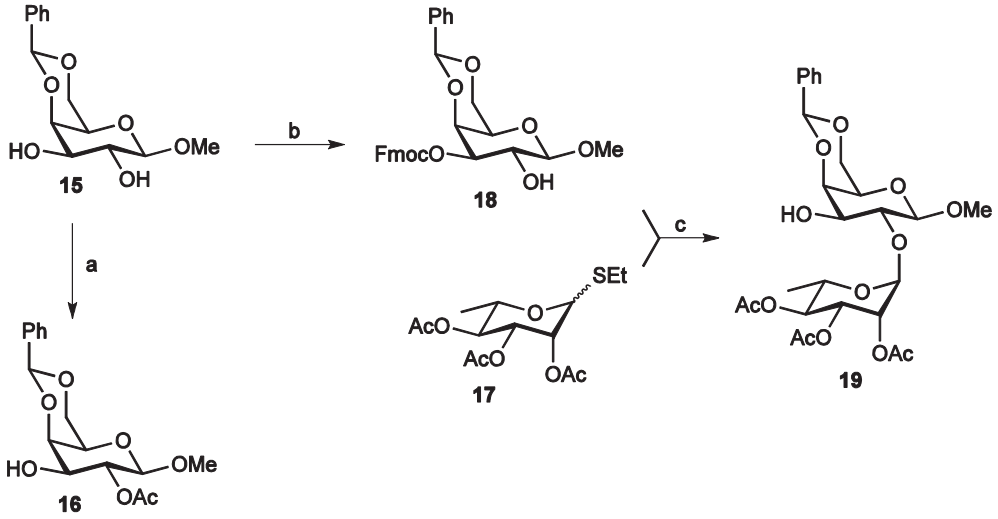
It has been noted by Boons and co-workers that thioethyl migration from an acceptor to a donor molecule can occur.[35] Herein we were able to suppress this side-reaction by increasing the polarity of the solvent used, i.e., by employing a mixture of DCM and toluene in equal proportions. The 4,6-*O*-benzylidene group was regioselectively opened in a good yield (68%) using $BH_3{\cdot}NMe_3$ 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[37] and furnished diol **12** 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 groups[39–42] 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*, $J_{H1,H2}$=5.1 Hz, $J_{H1',H2'}$=5.8 Hz, $J_{H2,H3}$<2 Hz and $J_{H2',H3'}$<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).

The β-(1→3)-linkage between the disaccharide donor **14** and the relatively unreactive acceptor **16** was facilitated by using Tf_2O-DMDS[44] as the promoter system. Several activators were tried including NIS/TfOH, NIS/AgOTf, NIS/TMSOTf and MeOTf at different temperatures, but only Tf_2O-DPS and Tf_2O-BSP gave similar results to Tf_2O-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



Scheme 2. Formation of armed donor **14**. Reagents and conditions: (a) TMSOTf, CH_2Cl_2/Tol 1:1, −25 °C → rt, 2 h, 75%; (b) $BH_3 \cdot NMe_3$, $AlCl_3$, THF, 6 h, 68%; (c) DDQ, CH_2Cl_2/MeOH 4:1, 4 h, 85%; (d) 1 M NaOMe, MeOH, 16 h, 91%; (e) TBDMSOTf, DMAP, pyridine, 80 °C, 24 h, 82%.



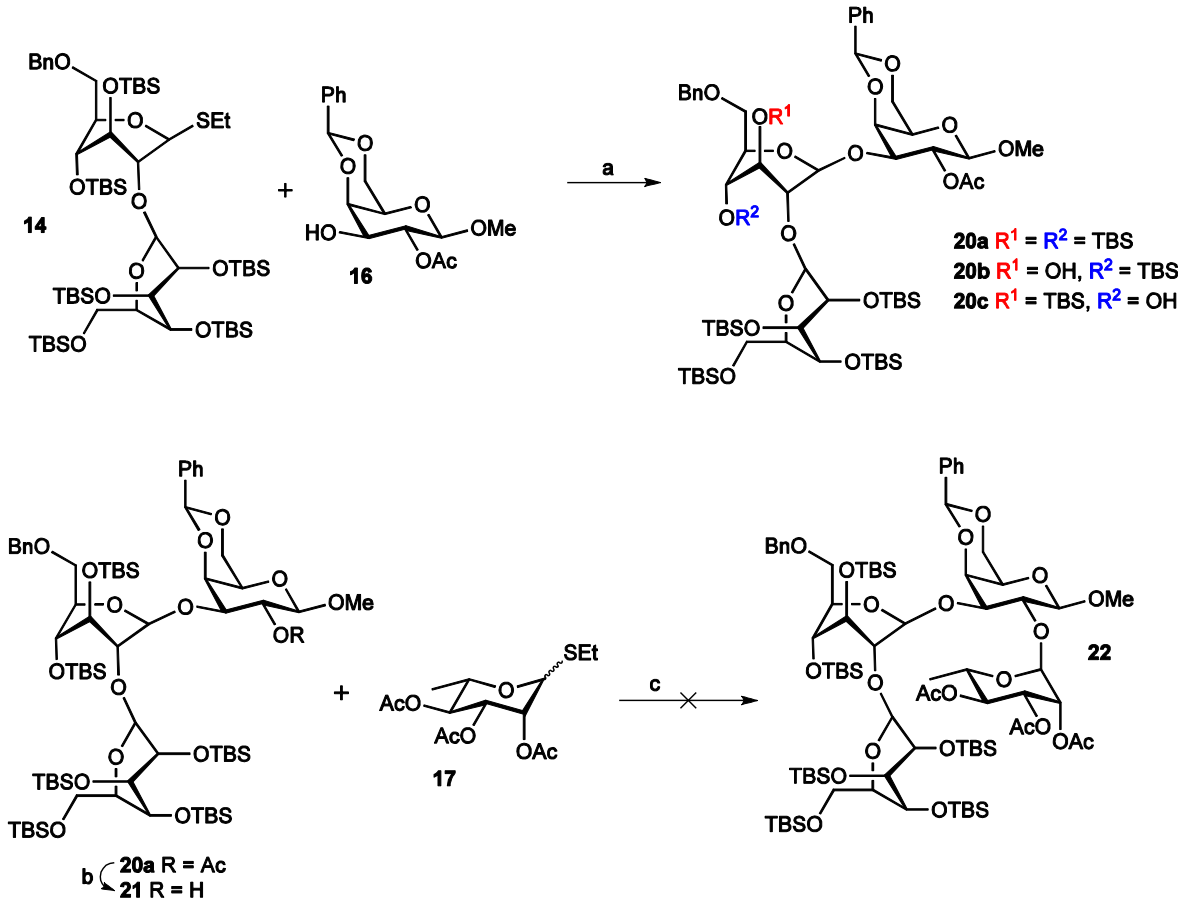
Scheme 3. Formation of acceptors **16** and **19**. Reagents and conditions: (a) Ac_2O, pyridine, rt, 16 h, 22%; (b) FmocCl, DMAP, pyridine-CH_3CN, 16 h, 68%; (c) NIS, AgOTf, CH_2Cl_2, 0 °C→rt, 1 h, NEt_3, 30 min, 82%.

anticipated compound **20a**, but also by-products that were of lower molecular mass as indicated by mass spectroscopy (Scheme 4).

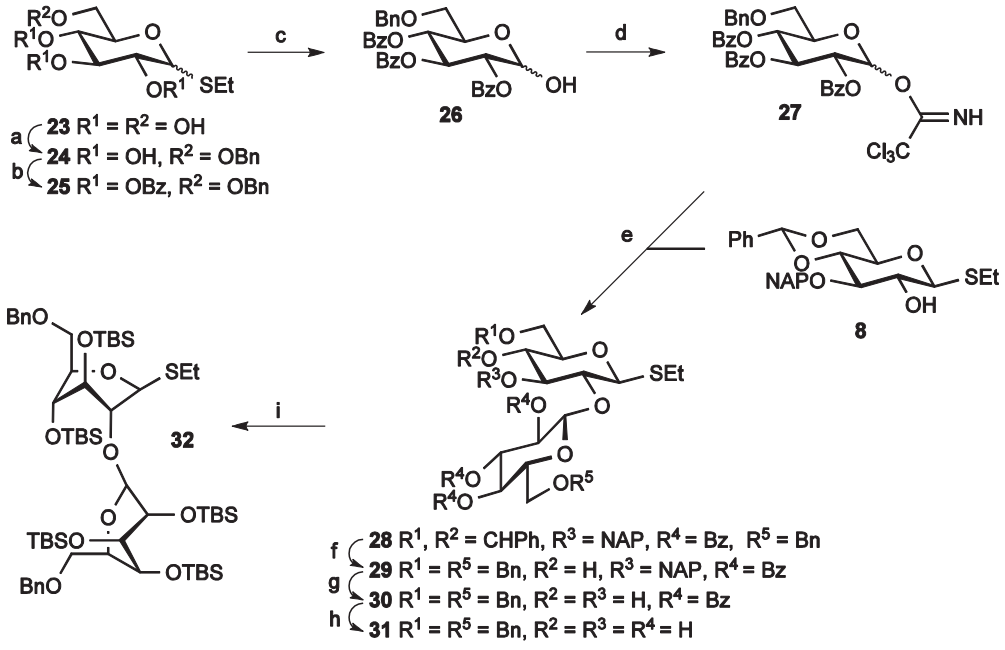
^{1}H NMR spectroscopy revealed that the mixture contained three compounds and NMR assignments of these in the mixture showed that labile TBS ether groups, from two different ring positions, had been cleaved off during the coupling, resulting in trisaccharides **20b** and **20c**. These by-products seemed 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→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).

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



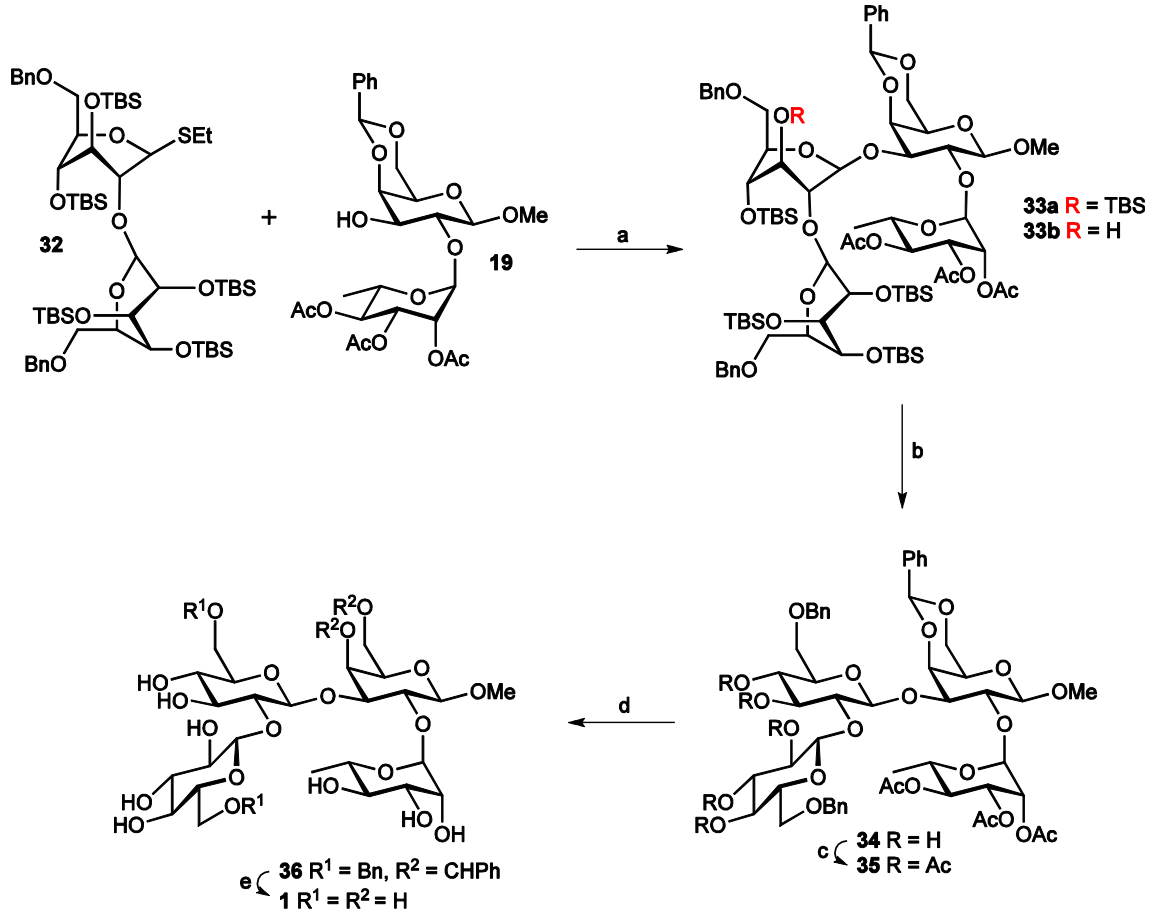
Scheme 4. Synthesis of trisaccharide acceptor **21** and attempted formation of tetrasaccharide **22**. Reagents and conditions: (a) Tf_2O-DMSO, DTBMP, CH_2Cl_2, −78 °C, 15 min, 68% (**20a**–**20c**); (b) 1 M NaOMe, MeOH, 16 h, 55%; (c) NIS, AgOTf, CH_2Cl_2, 0 °C.



Scheme 5. Formation of armed donor **32**. Reagents and conditions: (a) NaH, BnBr, DMF, 0 °C→rt, 6–8 h, 72%; (b) BzCl, pyridine, 0 °C→rt, 16 h, 97%; (c) NIS, H_2O, CH_2Cl_2-acetone, 8 h, 78%; (d) Cl_3CCN, K_2CO_3, CH_2Cl_2, 4 h, 85%; (e) TMSOTf, CH_2Cl_2-toluene, 16 h, −10 °C→rt, 84%; (f) $BH_3{\cdot}NMe_3$, $AlCl_3$, H_2O, THF, 16 h, 79%; (g) DDQ, CH_2Cl_2/MeOH 4:1, 4 h, 88%; (h) 1 M NaOMe, MeOH, 16 h, 93%; (i) TBDMSOTf, DMAP, pyridine, 80 °C, 24 h, 86%.

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 $^3S_1$ 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/Tf_2O as the promoter system together with the hindered base TTBP[49] 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→−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}H,^{1}H-TOCSY experiments that revealed a ^{1}H 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 ^{1}H NMR spectrum of which is shown in Fig. 2.

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* ^{1}H 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 ^{1}H 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, $J_{H1,H2}$ and $J_{C1,H1}$ data can be utilized as part of the input in order to limit the number of structures for which calculations are carried out. The ^{1}H 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-Gal*p*-OMe, D-Glc*p* (twice) and L-Rha*p* together with ^{1}H and ^{13}C NMR data. Using only 1D NMR data in the form of ^{1}H and ^{13}C chemical shifts in combination with $J_{H1,H2}$ and $J_{C1,H1}$ 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}H,^{1}H-TOCSY, ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC spectra. The five top-ranked structural suggestions are given in Fig 3, where the structure of the target tetrasaccharide **1** is the top-ranked one.

That this procedure works and that we have synthesized compound **1** was confirmed by assignment of the ^{1}H 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., $[M+Na]^+$ *m/z* calcd for $C_{25}H_{44}O_{20}Na$ 687.2324, found 687.2326, as well as simulation of the ^{1}H NMR spectrum by refinement of proton chemical shifts and scalar coupling constants by an iterative total line-shape

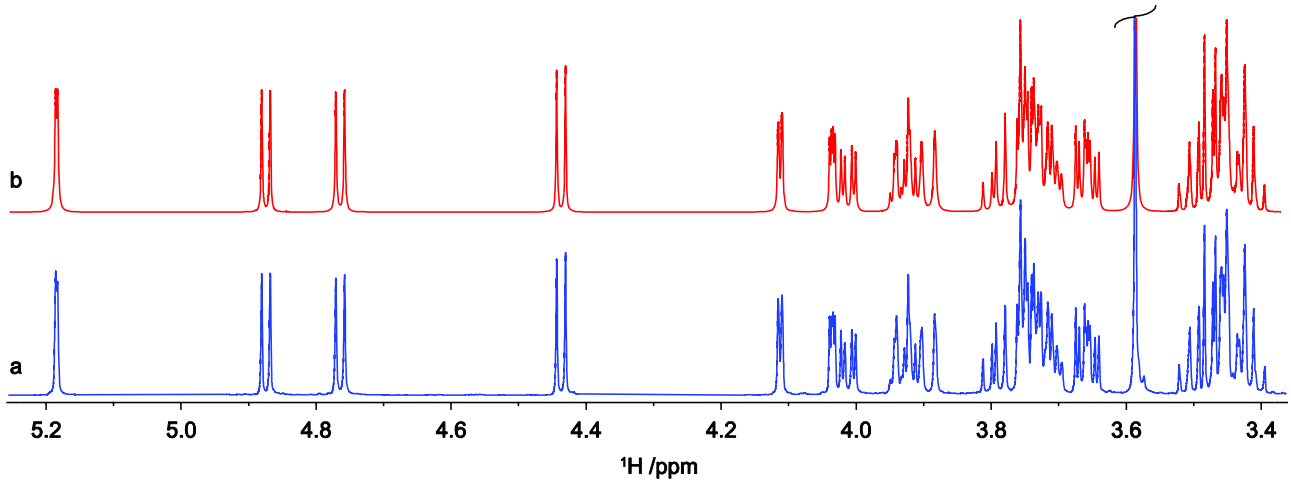


Fig. 2. ^{1}H NMR spectrum at 600 MHz of tetrasaccharide **1** at 5 °C (a) and the corresponding spectrum simulated by total-lineshape analysis using the PERCH NMR software (b). The HDO resonance in the experimental spectrum (δ_H 5.02) was removed prior to the lineshape fitting procedure.

analysis employing NMR spin simulation[54] using the PERCH software.

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

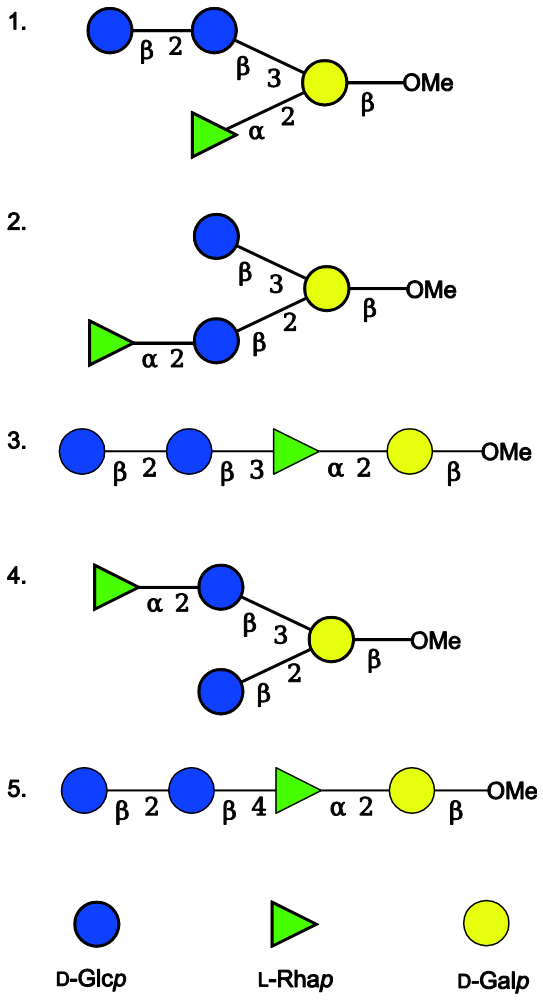


Fig. 3. CASPER output of the five top-ranked structural suggestions for the synthesized tetrasaccharide presented in CFG format (blue and yellow filled circles represent D-glucopyranose and D-galactopyranose residues, respectively, and a green filled triangle represents L-rhamnopyranose). The relative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

3. Conclusions

The strategy for synthesis of the oligosaccharide component of the glycoalkaloid Solaradixine from *S. 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 ^{1}H and ^{13}C NMR data as input to the program CASPER, which is available to the scientific community at http://www.casper.organ.su.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.

Table 1
^{1}H and ^{13}C 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-Glc*p*-(1→	^{1}H	Expt	4.874	3.472	3.504	3.413	3.434		3.743[a]	3.931[b]
		$^3J_{HH}$	7.99 (163)[d]	9.64	9.05	9.82	6.37[a]	1.97[b]	−12.31	
		calcd	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	
		calcd	104.22	74.79	76.40	70.50	77.28		61.79	
→2)-β-D-Glc*p*-(1→3)	^{1}H	Expt	4.764	3.661	3.724	3.455	3.454		3.744[a]	3.892[b]
		$^3J_{HH}$	7.93 (164)[d]	9.24	9.21	9.44	4.23[a]	0.96[b]	−11.97	
		calcd	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	
		calcd	103.42	82.51	76.62	70.26	76.53		61.54	
α-L-Rha*p*-(1→2)	^{1}H	Expt	5.184	4.035	3.751	3.468	3.926		1.275	
		$^3J_{HH}$	1.74 (176)[d]	3.25	9.66	9.93	6.27			
		calcd	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	
		calcd	103.46	70.93	71.09	72.83	69.87		17.56	
→2,3)-β-D-Gal*p*-OMe[c]	^{1}H	Expt	4.437	3.655	4.012	4.113	3.706		3.753[b]	3.793[a]
		$^3J_{HH}$	7.87 (163)[d]	9.61	3.40	0.84	8.04[a]	4.14[b]	−11.73	
		calcd	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	
		calcd	103.59	79.16	84.19	69.27	75.46		61.48	

[a] $H6_{pro\text{-}R}$.
[b] $H6_{pro\text{-}S}$.
[c] CH_3 (OMe) Expt: 3.586, 57.80; calcd: 3.59, 57.49.
[d] $^1J_{H1,C1}$ at 45 °C.

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 F_{254} plates (20×20 cm, 0.2 mm thickness) and monitored with UV light 254–360 nm or by a staining solution prepared from Ceric Ammonium Sulfate (2 g) in ethanol (40 mL) and 2 M sulfuric acid (40 mL).

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 H_2O 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 ^{1}H 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-$^2H_4$)-propanoate (TSP) as internal standards, δ_H=0.0, or to the residual solvent peaks for $CDCl_3$, δ_H=7.26, or MeOH-d_4 δ_H=3.31. ^{13}C chemical shifts were referenced to external 1,4-dioxane in D_2O, δ_C=67.40, or internally to the $CDCl_3$ residual solvent peak, δ_C=77.16, or to the MeOH-d_4 residual solvent peak, δ_C=49.00. *J* coupling constants are reported in Hertz (Hz). All new compounds synthesized were fully characterized using 1D ^{1}H, 1D ^{1}H-decoupled ^{13}C, 2D ^{1}H,^{1}H-DQF-COSY, 2D ^{1}H,^{13}C-multiplicity-edited-HSQC proton coupled or decoupled and 2D ^{1}H,^{13}C-HMBC NMR experiments. If required, 1D ^{1}H,^{1}H-TOCSY, 2D ^{1}H,^{1}H-TOCSY, 2D ^{1}H,^{13}C-H2BC, 2D ^{13}C,^{1}H-HETCOR or 2D ^{1}H,^{13}C-HSQC-TOCSY experiments were acquired. Abbreviations for ^{1}H 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/H_2O containing 0.1% formic acid.

A 1D ^{1}H 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 ^{1}H 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%.

*4.1.1. 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-methylnaphtyl bromide (9.25 g, 1.1 equiv) 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 equiv) 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 $MgSO_4$ 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%). ^{1}H NMR ($CDCl_3$, 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, NapCH_2), 4.80 (d, J_{gem} 12.03, 1H, NapCH_2), 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, CH_3). ^{13}C NMR ($CDCl_3$, 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 (2×$(CH_3)_2$CH), 105.48 (C-1), 82.9 (C-2), 81.8 (C-3), 81.5 (C-4), 72.7 (C-5), 72.6 (NapCH_2), 67.6 (C-6), 27.0, 26.4, 25.6 (4 CH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{23}H_{28}O_6Na$ 423.1784, found 423.1788.

*4.1.2. 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

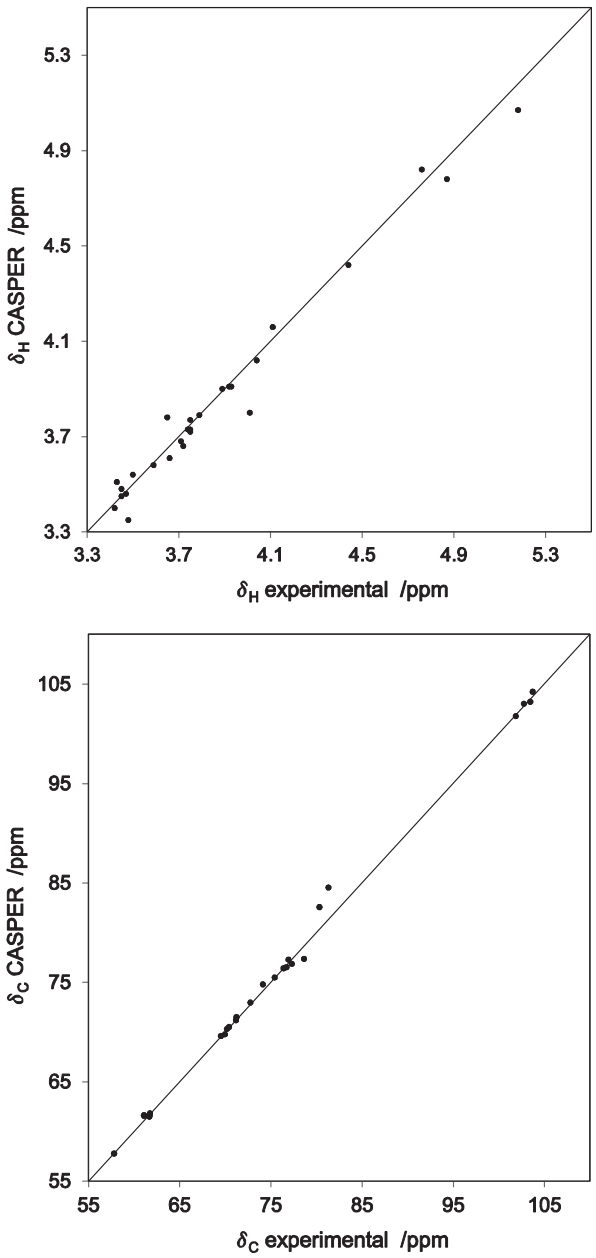


Fig. 4. Comparison between experimental and CASPER-predicted ^{1}H and ^{13}C NMR chemical shifts (*top* and *bottom*, respectively) of tetrasaccharide **1**.

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. ^{1}H NMR (CD_3OD, 25 °C, 400 MHz) β-anomeric form: δ 7.92–7.41 (4 m, 7H, H–Ar), 5.06 (m, 2H, $NapCH_2$), 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). ^{13}C NMR (CD_3OD, 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 ($NapCH_2$), 71.6 (C-4), 62.8 (C-6). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{17}H_{20}O_6Na$ 343.0260, found 343.0263.

*4.1.3. 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 $NaHCO_3$ and brine. The solution was dried over $MgSO_4$ 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 (R_f=0.6 Toluene/EtOAc 2:1) to give 4.1 g of **5** as a slightly yellow oil with an overall yield of 91%. ^{1}H NMR ($CDCl_3$, 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, $NapCH_2$), 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, CH_3). ^{13}C NMR ($CDCl_3$, 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×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 ($NapCH_2$), 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 CH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{28}O_{10}Na$ 511.1580, found 511.1583.

*4.1.4. 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 $CHCl_3$ (10 mL). The reaction mixture was cooled to 0 °C and ethanethiol (0.24 mL, 1.1 equiv) and borontrifluoride etherate (0.59 mL, 1.1 equiv) 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 $NaHCO_3$ (20 mL) and with water (10 mL). The organic layer was dried over Na_2SO_4 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. ^{1}H NMR ($CDCl_3$, 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, $NapCH_2$), 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, SCH_2CH_3), 2.07, 1.98, 1.92 (3 s, 9H, CH_3), 1.26 (t, 3H, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 170.9, 169.5, 169.45, (3 C=O), 135.4, 133.4, 133.1 (3×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 ($NapCH_2$), 71.4 (C-4), 69.9 (C-2), 62.6 (C-6), 24.1 (SCH_2CH_3), 21.1, 20.9, 20.9 (3 CH_3), 14.9 (SCH_2CH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{30}O_8SNa$ 513.1559, found 513.1556.

*4.1.5. Ethyl 4,6-O-benzylidene-3-O-(2-naphthyl)methyl-1-thio-β-D-glucopyranoside (**8**).* Compound **6** (4.0 g, 8.2 mmol) was dissolved in methanol (50 mL), NaOMe in MeOH was added (general procedure: 2 equiv 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. ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 7.88–7.44 (2 m, 7H, H–Ar), 5.18 (d, J_{gem} 11.08, 1H, $NapCH_2$), 4.94 (d, J_{gem} 11.08, 1H, $NapCH_2$), 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, SCH_2CH_3), 2.50, 2.10, 1.60 (3 br, 3H, OH), 1.32 (t, 3H,

SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 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 ($NapCH_2$), 73.4 (C-2), 70.3 (C-4), 62.9 (C-6), 24.8 (SCH_2CH_3), 15.5 (SCH_2CH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{19}H_{24}O_5SNa$ 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 equiv) and anhydrous camphor sulfonic acid (300 mg, 0.2 equiv) 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 NEt_3 (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 ($CDCl_3$, 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, $NapCH_2$), 4.99 (d, J_{gem} 11.85, 1H, $NapCH_2$), 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, SCH_2CH_3), 2.54 (d, 1H, OH-2), 1.31 (t, 3H, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 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), 101.5 (CHPh), 86.8 (C-1), 81.5 (C-3), 81.4 (C-4), 74.8 ($NapCH_2$), 73.3 (C-2), 71.0 (C-5), 68.8 (C-6), 24.7 (SCH_2CH_3), 15.4 (SCH_2CH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{28}O_5SNa$ 475.1555, found 475.1553.

*4.1.6. Ethyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→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 equiv) and acceptor **8** (400 mg, 0.88 mmol) in dry CH_2Cl_2/Toluene (1:1, 14 mL) was stirred for 20 min in the presence of molecular sieves (4 Å, 0.4 g). TMSOTf (8 μL, 0.05 equiv) was then added at −25 °C. The reaction was monitored by TLC (pentane/EtOAc 2:1) and allowed to warm up to room temperature. NEt_3 was added to quench the reaction and the mixture was filtered through Celite. It was then diluted with CH_2Cl_2 and washed successively with solutions of satd $NaHCO_3$, brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue obtained was purified by flash chromatography (TLC: R_f=0.45 Pentane/EtOAc 2:1) to yield **10** in 75% yield (0.52 g) as a white powder. ^1H NMR ($CDCl_3$, 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, $NapCH_2$ G), 4.87 (d, J_{gem} 10.32, 1H, $NapCH_2$ 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, SCH_2CH_3 G), 2.07, 2.06, 2.03, 2.00 (4 s, 12H, CH_3 G′), 1.27 (t, 3H, SCH_2CH_3 G). ^{13}C NMR ($CDCl_3$, 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×C-*ipso* G), 129.2, 128.7, 3×128.5, 128.3, 128.2, 127.9, 127.6, 126.6, 126.4, 3×126.1 (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 ($NapCH_2$ 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 (SCH_2CH_3 G), 21.0, 20.8, 20.6, 20.6 (4 CH_3 G′), 14.7 (SCH_2CH_3 G). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{40}H_{46}O_{14}SNa$ 805.2506, found 805.2510.

*4.1.7. Ethyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→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. $BH_3 \cdot NMe_3$ complex (336 mg, 12 equiv) was added to the mixture that was let to stir for 5 min under N_2 atmosphere. Anhydrous $AlCl_3$ (307 mg, 6 equiv) was added and after 4 h (R_f=0.7 Pentane/EtOAc 1:1) the reaction was stopped by addition of 1 mL of satd $NaHCO_3$. The reaction mixture was diluted with diethyl ether and washed twice with a solution of satd $NaHCO_3$ and dried over Na_2SO_4. The residue was purified by flash chromatography to yield 0.205 g (68%) of compound **11** as a colorless oil. ^1H NMR ($CDCl_3$, 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, $NapCH_2$ G) 4.94 (d, J_{gem} 10.51, 1H, $NapCH_2$ G), 4.57 (2 d, J_{gem} 11.92, 2H, $PhCH_2$ 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, SCH_2CH_3 G), 2.07, 2.05, 2.02, 2.00 (4s, 12H, CH_3 G′), 1.25 (t, 3H, SCH_2CH_3 G). ^{13}C NMR ($CDCl_3$, 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 ($NapCH_2$ G), 74.0 ($PhCH_2$ 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 (SCH_2CH_3 G), 21.0, 20.9, 20.8, 20.7 (4 CH_3 G′), 14.8 (SCH_2CH_3 G). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{40}H_{48}O_{14}SNa$ 807.2662, found 807.2660.

*4.1.8. 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 CH_2Cl_2/MeOH 4/1 and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 87 mg, 2.5 equiv) 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 CH_2Cl_2 and 1 mL of satd $NaHCO_3$ was added. The two phases were separated and the organic phase was washed twice more with the solution of satd $NaHCO_3$ and subsequently dried over Na_2SO_4. The residue was purified by flash chromatography to yield the desired product **12**, 84 mg (85% yield) as a colorless oil. ^1H NMR ($CDCl_3$, 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, $PhCH_2$ 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, SCH_2CH_3 G), 2.08, 2.06, 2.02, 2.00 (4s, 12H, CH_3 G′), 1.27 (t, 3H, SCH_2CH_3 G). ^{13}C NMR ($CDCl_3$, 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 ($PhCH_2$ 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 (SCH_2CH_3 G), 21.0, 20.9, 2×20.7 (4 CH_3 G′), 14.9 (SCH_2CH_3 G). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{29}H_{40}O_{14}SNa$ 667.2036, found 667.2034.

*4.1.9. 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 (CD_3OD, 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, $PhCH_2$ 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, S$CH_2$$CH_3$ G), 1.27 (t, 3H, SCH_2CH_3 G). ^{13}C NMR (CD_3OD, 25 °C, 100 MHz): G δ 139.7 (C-*ipso* G), 2×129.3, 2×128.8, 128.6 (5 C–Ar G), 104.8 (C-1 G′), 84.4 (C-1 G), 81.6 (C-2 G), 80.9 (C-5 G), 79.6 (C-3 G), 78.1 (C-5 G′), 78.0 (C-3 G′), 75.8 (C-2 G′), 74.4 ($PhCH_2$ G), 71.4 (C-4 G′), 71.4 (C-4 G), 70.9 (C-6 G), 62.7 (C-6 G′), 24.8 (S$CH_2$$CH_3$ G), 15.3 (SCH_2CH_3 G). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{21}H_{32}O_{10}SNa$ 499.1614, found 499.1617.

*4.1.10. 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 equiv) was added to the mixture. TBDMSOTf (1.46 mL, 12.6 equiv) 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 $NaHCO_3$ and brine. The solution was dried over anhydrous Na_2SO_4 and solvents were evaporated. The resulting residue was purified by chromatography to afford 0.48 g (82% yield) of **14** as a colorless syrup. ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 7.36–7.28 (m, 5H, H–Ar G), 5.14 (d, $J_{H1,H2}$ 5.82,1H, H-1 G), 4.95 (d, $J_{H1,H2}$ 5.78,1H, H-1 G′), 4.60 (d, J_{gem} 12.17, 1H, $PhCH_2$ G), 4.53 (d, J_{gem} 12.17, 1H, $PhCH_2$ G), 3.96 (dd, $J_{H2,H3}$<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, $J_{H1,H2}$ 5.82, $J_{H2,H3}$<2, 1H, H-2 G), 3.83 (dd, 1H, H-5 G′), 3.74 (dd, $J_{H2,H3}$<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, $J_{H1,H2}$ 5.78, $J_{H2,H3}$<2, 1H, H-2 G′), 2.70 (dq, 2H, S$CH_2$$CH_3$ G), 1.26 (t, 3H, SCH_2CH_3 G), 3×0.89, 2×0.88, 0.85 (6 s, 54H, $C(CH_3)_3$), 0.13, 3×0.089, 3×0.079, 0.069, 0.057, 2×0.042, 0.019 (12 s, 36H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 138.7 (C-*ipso* G), 2×128.4, 2×127.8, 127.5 (5 C–Ar G), 101.1 (C-1 G′), 82.3 (C-1 G), 81.2 (C-2 G), 81.0 (C-5 G′), 79.5 (C-3 G′), 79.4 (C-5 G), 77.7 (C-2 G′), 76.1 (C-3 G), 73.4 ($PhCH_2$ G), 71.7 (C-4 G), 71.6 (C-6 G), 70.3 (C-4 G′), 64.3 (C-6 G′), 3×26.15, 3×26.05 (6 $C(CH_3)_3$), 25.3 (S$CH_2$$CH_3$ G), 18.5, 4×18.1, 18.05 (6 $C(CH_3)_3$), 15.0 (SCH_2CH_3 G), −3.4, −3.7, −3.8, −3.9, −4.2, 2×−4.4, 3×−4.5, 2×−5.1 (12 $SiCH_3$). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{57}H_{116}O_{10}SSi_6Na$ 1183.6802, found 1183.6806.

*4.1.11. 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 $NaHCO_3$ and brine. The organic phase was dried over $MgSO_4$ and solvents were evaporated. The residual mixture was purified by column chromatography (R_f=0.28 Pentane/EtOAc 1:4) to obtain compound **15** as a white powder (142 mg, 22%). ^{1}H 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, $J_{H1,H2}$ 8.00, $J_{H2,H3}$ 9.98, 1H, H-2), 4.38 (d, $J_{H1,H2}$ 8.00, 1H, H-1), 4.37 (dd, $J_{H5,H6b}$ 1.57, J_{gem} 12.47, 1H, H-6b), 4.22 (dd, $J_{H3,H4}$ 3.89, $J_{H4,H5}$ 1.23, 1H, H-4), 4.10 (dd, $J_{H5,H6a}$ 1.97, J_{gem} 12.47, 1H, H-6a), 3.74 (ddd, $J_{H2,H3}$ 9.98, $J_{H3,H4}$ 3.89, $J_{H3,OH-3}$ 11.24, 1H, H-3), 3.53 (s, 3H, OMe), 3.50 (ddd, $J_{H4,H5}$ 1.23, $J_{H5,H6a}$ 1.97, $J_{H5,H6b}$ 1.57, 1H, H-5), 2.44 (dd, $J_{H3,OH-3}$ 11.24, 1H, OH-3), 2.13 (s, 3H, CH_3). ^{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 (CH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{16}H_{20}O_7Na$ 347.1107, found 347.1111.

*4.1.12. Ethyl 2,3,4-tri-O-acetyl-1-thio-α/β-L-rhamnopyranose (**17**).* L-Rhamnopyranose (1.03 g, 6.3 mmol, 1 equiv) 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 $NaHCO_3$ and brine. The solution was dried over $MgSO_4$ 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%). ^{1}H NMR ($CDCl_3$, 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, CH_3), 1.24 (d, $J_{H5,H6}$ 6.24, 3H, H-6). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): α-anomer: δ 170.2, 170.0, 169.9, 168.5 (4×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×CH_3), 17.6 (C-6). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{14}H_{20}O_9Na$ 355.1005, found 355.1008.

2,3,4,6-Tetra-*O*-acetyl-L-rhamnopyranose (1.75 g, 5.3 mmol) was dissolved in dry $CHCl_3$ (15 mL), the reaction mixture was cooled to 0 °C and ethanethiol (0.76 mL, 2 equiv) and borontrifluoride diethyl etherate (3.23 mL, 5 equiv) 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 $MgSO_4$ 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). ^{1}H NMR ($CDCl_3$, 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, S$CH_2$$CH_3$), 2.16, 2.06, 1.99 (3 s, 9H, CH_3), 1.30 (t, 3H, SCH_2CH_3), 1.24 (d, $J_{H5,H6}$ 6.26, 3H, H-6). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): α-anomeric form: δ 170.2, 170.1, 170.0 (3 C=O), 82.1 (C-1), 71.7 (C-2), 71.5 (C-4), 69.6 (C-3), 67.1 (C-5), 25.6 (S$CH_2$$CH_3$), 21.1, 20.9, 20.8 (3 CH_3), 17.5 (C-6), 14.9 (SCH2CH3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{14}H_{22}O_7NaS$ 357.0984, found 357.0980.

*4.1.13. 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 equiv) were dissolved in a 2/1 mixture of pyridine/acetonitrile (5 mL). FMOCCl (303 mg, 1.1 equiv) was added portionwise at −10 °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 °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**. ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 7.76–7.19 (m, 13H, H–Ar), 5.52 (s, 1H, CHPh), 4.73 (dd, $J_{H2,H3}$ 10.12, $J_{H3,H4}$ 3.65, 1H, H-3), 4.47 (d, $J_{H,CH}$ 7.84, J_{gem} 10.37, 1H, ArCHCH_2OCO), 4.42 (d, $J_{H,CH}$ 5.19, J_{gem} 10.37, 1H, ArCHCH_2OCO), 4.42 (dd, $J_{H3,H4}$ 3.65, $J_{H4,H5}$ 1.01, 1H, H-4), 4.36 (dd,

$J_{H5,H6b}$ 1.61, J_{gem} 12.42, 1H, H-6b), 4.30 (d, $J_{H1,H2}$ 7.80, 1H, H-1), 4.29 (dd, $J_{H,CH2a}$ 7.84, $J_{H,CH2b}$ 5.19, 1H, ArC*H*CH_2OCO), 4.10 (dd, $J_{H1,H2}$ 7.80, $J_{H2,H3}$ 10.12, 1H, H-2), 4.08 (dd, $J_{H5,H6a}$ 1.83, J_{gem} 12.42, 1H, H-6a), 3.60 (s, 3H, OMe), 3.51 (ddd, $J_{H4,H5}$ 1.01, $J_{H5,H6a}$ 1.83, $J_{H5,H6b}$ 1.61, 1H, H-5), 2.44 (nr, 1H, OH-2). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 154.8 (ArCHCH_2OC=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 (ArCH*C*H_2OCO), 69.1 (C-6), 68.7 (C-2), 66.5 (C5), 57.4 (OMe), 46.8 (ArCHCH_2OCO). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{29}H_{28}O_8Na$ 527.1682, found 527.1679.

*4.1.14. Methyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl-(1→2)-4,6-O-benzylidene-β-D-galactopyranoside (**19**).* A solution of thioglycoside **17** (100 mg, 0.3 mmol, 1.5 equiv) 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 equiv) and AgOTf (0.5 equiv) were added at 0 °C. The reaction was monitored by TLC and left to stir at room temperature for one hour. Once the acceptor was consumed, TEA (25 equiv) 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 $Na_2S_2O_3$, 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). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 7.51–7.35 (m, 5H, H–Ar Gal), 5.54 (s, 1H, CHPh Gal), 5.36 (dd, $J_{H1,H2}$ 1.73, $J_{H2,H3}$ 3.44, 1H, H-2 R), 5.28 (dd, $J_{H2,H3}$ 3.44, $J_{H3,H4}$ 10.09, 1H, H-3 R), 5.22 (d, $J_{H1,H2}$ 1.73, 1H, H-1 R), 5.01 (dd, $J_{H3,H4}$ 10.09, $J_{H4,H5}$ 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, CH_3 R), 1.20 (d, $J_{H5,H6}$ 6.29, 3H, H-6 R). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 170.4, 2×170.2 (3C=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 (CH_3 R), 17.2 (C-6 R), ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{34}O_{13}Na$ 577.1897, found 577.1901.

*4.1.15. 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 Tf_2O-DMDS (1.1 equiv) in dry CH_2Cl_2 was added to the mixture containing the armed-donor **14** (40 mg, 0.035 mmol), the acceptor **16** (1.2 equiv), 2,6-DTBMP (2 equiv) and activated 4 Å molecular sieves (100 mg) in dry CH_2Cl_2 (0.5 mL) at −78 °C under N_2 atmosphere. The reaction mixture was stirred for 15 min and was allowed to reach −40 °C (**20a** R_f=0.65, **20b**, **20c** R_f=0.45 Pentane/EtOAc 4:1). It was then quenched with NEt_3 (3 equiv), diluted with CH_2Cl_2, filtered through Celite and washed with a 2 M HCl solution, aqueous $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4 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**: ^{1}H NMR ($CDCl_3$, 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, $PhCH_2$ G), 4.48 (d, J_{gem} 12.04, 1H, $PhCH_2$ 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, CH_3), 0.90, 0.89, 0.88, 0.87, 0.80, 0.75 (6 s, 54H, C(CH_3)$_3$), 0.11, 0.10–0.05, −0.012, −0.13, −0.14 (12 s, 36H, SiCH_3). ^{13}C NMR ($CDCl_3$, 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 ($PhCH_2$ 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(CH_3)$_3$), 21.1 (CH_3), 18.4–18.1 (6 *C*(CH_3)$_3$), −2.8 to −5.2 (12 SiCH_3). **20b** and **20c**: ^{1}H NMR ($CDCl_3$, 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, $PhCH_2$ G, **20b**), 4.54–4.49 (2 d, J_{gem} 11.68, 2H, $PhCH_2$ 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, CH_3, **20b**), 2.02 (s, 3H, CH_3, **20c**), 0.91–0.83 (10 s, 90H, C(CH_3)$_3$), 0.14, 0.12–0.05, −0.05 (20s, 60H, SiCH_3). ^{13}C NMR ($CDCl_3$, 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 ($PhCH_2$ G, **20c**), 73.6 ($PhCH_2$ 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(CH_3)$_3$), 21.5 (CH_3, **20b**), 21.4 (CH_3, **20c**), 18.7–17.9 (10 C(CH_3)$_3$), −2.9 to −5.2 (10 SiCH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for **20a**: $C_{71}H_{130}O_{17}Si_6Na$ 1445.7821, found 1445.7823, for **20b** and **20c**: $C_{65}H_{116}O_{17}Si_5Na$ 1331.6957, found 1331.6954.

*4.1.16. 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. ^{1}H NMR ($CDCl_3$, 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, PhCH_2 G), 4.50 (d, J_{gem} 12.09, 1H, PhCH_2 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(CH_3)$_3$), 0.12, 0.10–0.05, −0.05, −0.13, (12 s, 36H, SiCH_3). ^{13}C NMR ($CDCl_3$, 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 (PhCH_2 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 (5C(CH3)3), 18.5–18.1 (5 C(CH_3)$_3$), −3.3 to −5.1 (5 SiCH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{69}H_{128}O_{16}Si_6Na$ 1403.7716 found 1403.7720.

*4.1.17. 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-glucopyranoside[56] (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%). ^{1}H NMR (CD_3OD, 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, SCH_2CH$_3$), 1.32 (t, 3H, SCH$_2$$CH_3$). ^{13}C NMR ($CD_3OD$, 25 °C, 400 MHz): α-anomeric form: δ 86.8 (C-1), 75.6 (C-3), 73.9 (C-5), 73.1 (C-2), 71.8 (C-4), 62.5 (C-6), 24.9 (SCH_2CH$_3$), 15.2 (SCH$_2$$CH_3$). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_8H_{16}O_5SNa$ 247.0616, found 247.0619.

*4.1.18. 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 equiv) was progressively added at room temperature; 30 min later, benzyl bromide (0.4 ml, 3.3 mmol, 1.5 equiv) 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 $NaHCO_3$ and brine, dried over Na_2SO_4, 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. ^{1}H NMR ($CDCl_3$, 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, PhCH_2), 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, SCH_2CH$_3$), 1.26 (t, 3H, SCH$_2$$CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): α-anomeric form: δ 138.1 (C-*ipso*), 2×128.5, 3×127.7 (5 C–Ar), 86.1 (C-1), 75.2 (C-3), 73.6 (PhCH_2), 71.6 (C-2), 71.2 (C-5), 70.9 (C-4), 69.7 (C-6), 25.2 (SCH_2CH$_3$), 15.1 (SCH$_2$$CH_3$). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{15}H_{22}O_5SNa$ 337.1086, found 337.1082.

*4.1.19. 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 equiv) 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 $NaHCO_3$ and brine. The solution was dried over Na_2SO_4 and solvents were evaporated. The residue was purified by column chromatography and 968 mg (97% yield) of white solid **25** was isolated. ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): α-anomeric form: δ 8.00–7.13 (m, 20H, H–Ar), 6.04 (dd, $J_{H2,H3}$ 9.86, $J_{H3,H4}$ 9.95, 1H, H-3), 5.97 (d, $J_{H1,H2}$ 5.83, 1H, H-1), 5.68 (dd, $J_{H3,H4}$ 9.95, $J_{H4,H5}$ 9.72, 1H, H-4), 5.50 (dd, $J_{H1,H2}$ 5.83, $J_{H2,H3}$ 9.86, 1H, H-2), 4.70 (ddd, $J_{H4,H5}$ 9.72, $J_{H5,H6a}$ 3.73, $J_{H5,H6b}$ 3.73, 1H, H-5), 4.55 (2d, J_{gem} 12.03, 2H, PhCH_2), 3.69 (m, 2H, H-6a, H-6b), 2.63 (m, 2H, SCH_2CH$_3$), 1.27 (t, 3H, SCH$_2$$CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): α-anomeric form: δ 165.8, 165.5, 165.3 (3C=O), 137.7, 133.5, 133.4, 133.2 (4 C-*ipso*), 2×130.1, 2×129.9, 2×129.8, 129.3, 129.2, 129.1, 2×128.5, 2×128.4, 4×128.3, 2×127.8, 127.7 (20 C–Ar), 82.1 (C-1), 73.7 (PhCH_2), 71.9 (C-2), 71.3 (C-4), 69.6 (C-3), 69.4 (C-5), 68.5 (C-6), 24.3 (SCH_2CH$_3$), 14.7 (SCH$_2$$CH_3$). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{36}H_{34}O_8SNa$ 649.1872, found 649.1874.

*4.1.20. 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 equiv) was added progressively at 0 °C. After 30 min, 5 equiv 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 $Na_2S_2O_3$. The mixture was diluted with DCM and washed three times with $Na_2S_2O_3$ solution (20 mL). The DCM solution was dried over Na_2SO_4, filtered and concentrated to dryness. Purification by column chromatography gave 726 mg (78% yield) of white solid **26**. ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ α-anomeric form: 8.00–7.15 (m, 20H, H–Ar), 6.20 (dd, $J_{H2,H3}$ 9.94, $J_{H3,H4}$ 9.88, 1H, H-3), 5.75 (dd, $J_{H1,H2}$ 3.71, $J_{H1,OH-1}$ 3.52, 1H, H-1), 5.58 (dd, $J_{H3,H4}$ 9.64, $J_{H4,H5}$ 10.10, 1H, H-4), 5.29 (dd, $J_{H1,H2}$ 3.71, $J_{H2,H3}$ 9.94, 1H, H-2), 4.54 (2d, J_{gem} 12.00, 2H, PhCH_2), 4.53 (m, 1H, H-5), 3.68–3.66 (m, 2H, H-6a, H-6b), 3.56 (d, $J_{H1,OH-1}$ 3.52, 1H, OH-1). β-anomeric form: δ 5.89 (dd, $J_{H2,H3}$ 9.95, $J_{H3,H4}$ 9.65, 1H, H-3), 5.62 (dd, $J_{H3,H4}$ 9.65, $J_{H4,H5}$ 9.77, 1H, H-4), 5.33 (dd, $J_{H1,H2}$ 8.02, $J_{H2,H3}$ 9.95, 1H, H-2), 4.99 (dd, $J_{H1,H2}$ 8.02, $J_{H1,OH-1}$ 8.52, 1H, H-1), 4.54 (2d, J_{gem} 11.95, 2H, PhCH_2), 4.04 (d, $J_{H1,OH-1}$ 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, 2×166.0, 165.9, 165.5, 165.3 (6 C=O), 137.6, 137.5, 133.7, 2×133.5, 133.4, 133.4, 133.2 (8 C-*ipso*) 2×130.1, 2×130.0, 6×129.9, 2×129.8, 129.4, 2×129.2, 129.1, 129.0, 128.9, 4×128.6, 10×128.5, 2×128.4, 2×128.1, 2×128.0, 2×127.8 (40 C–Ar); α-anomeric form: δ 90.5 (C-1), 73.8 (PhCH_2), 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 (PhCH_2),72.7 (C-3),

69.7 (C-4), 68.8 (C-6). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{34}H_{30}O_9Na$ 605.1788, found 605.1792.

*4.1.21. 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 Cl_3CCN (2.06 mL, 20.6 mmol, 10 equiv) in dry CH_2Cl_2 (40 mL) was added freshly dried and powdered K_2CO_3 (1.14 g, 8.24 mmol, 4 equiv) at room temperature with intensive stirring. After 4 h (TLC: R_f=0.65 Pentane/EtOAc 3:1), the mixture was diluted with CH_2Cl_2 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. ^{1}H 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, $J_{H1,H2}$ 3.65, 1H, H-1), 6.25 (dd, $J_{H2,H3}$ 10.02, $J_{H3,H4}$ 9.98, 1H, H-3), 5.85 (dd, $J_{H3,H4}$ 9.98, $J_{H4,H5}$ 10.06, 1H, H-4), 5.60 (dd, $J_{H1,H2}$ 3.65, $J_{H2,H3}$ 10.02, 1H, H-2), 4.54 (2 d, J_{gem} 11.96, 2H, $PhCH_2$), 4.48 (ddd, $J_{H4,H5}$ 10.06, $J_{H5,H6a}$ 4.16, $J_{H5,H6b}$ 2.72, 1H, H-5), 3.74 (dd, $J_{H5,H6b}$ 2.72, J_{gem} 11.20, 1H, H-6b), 3.68 (dd, $J_{H5,H6a}$ 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*), 2×130.0, 2×129.9, 2×129.8, 129.1, 129.0, 128.7, 2×128.5, 2×128.4, 2×128.35, 2×128.3, 2×127.9, 127.7 (20 C–Ar), 93.5 (C-1), 90.9 (CCl_3), 73.7 ($PhCH_2$), 72.1 (C-5), 70.9 (C-2), 70.5 (C-3), 68.8 (C-4), 68.1 (C-6). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{36}H_{30}Cl_3NO_9Na$ 748.0884, found 748.0880.

*4.1.22. 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 equiv) and acceptor **8** (400 mg, 0.88 mmol) in a mixture of dry CH_2CL_2 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 equiv) was added dropwise at −10 °C. The reaction was monitored by TLC (pentane/EtOAc 3:1) and left to stir overnight. NEt_3 was added to quench the reaction and the mixture was filtered through Celite. It was then diluted with CH_2Cl_2 and washed successively with solutions of satd $NaHCO_3$, 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 895 mg of **28** (84%) as a white solid. ^{1}H NMR ($CDCl_3$, 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, $NapCH_2$ G), 4.69 (d, J_{gem} 10.78, 1H, $NAPCH_2$ G), 4.59 (d, J_{gem} 11.95, 1H, $PhCH_2$ G′), 4.56 (d, $J_{H1,H2}$ 9.48, 1H, H-1 G), 4.54 (d, J_{gem} 11.95, 1H, $PhCH_2$ G′), 4.35 (dd, $J_{H5,H6b}$ 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, SCH_2CH_3 G), 1.29 (t, 3H, SCH_2CH_3 G). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 165.9, 165.4, 165.3 (3C=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 ($NapCH_2$ G), 74.2 (C-5 G′), 74.0 ($PhCH_2$ 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 (SCH_2CH_3 G), 14.9 (SCH_2CH_3 G). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{60}H_{56}O_{13}SNa$ 1039.3339, found 1039.3335.

*4.1.23. 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. $BH_3{\cdot}NMe_3$ complex (114 mg, 1.56 mmol, 4 equiv) was added to the mixture, which was let to stir for 5 min under N_2 atmosphere. Anhydrous $AlCl_3$ (327 mg, 2.34 mmol, 6 equiv) was added and once it was fully dissolved, 2 equiv 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 Na_2SO_4. The mixture was filtered and concentrated to dryness. Purification by column chromatography yielded 317 mg (79% yield) of **29** as a colorless oil. ^{1}H NMR ($CDCl_3$, 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, $NapCH_2$ G), 4.75 (d, J_{gem} 11.50, 1H, $NapCH_2$ G), 4.60 (d, J_{gem} 12.12, 1H, $PhCH_2$ G′), 4.56 (d, J_{gem} 11.92, 1H, $PhCH_2$ G), 4.55 (d, J_{gem} 12.12, 1H, $PhCH_2$ G′), 4.52 (d, J_{gem} 11.92, 1H, $PhCH_2$ 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, SCH_2CH_3 G), 2.56 (nr, 1H, OH-4 G), 1.28 (t, 3H, SCH_2CH_3 G). ^{13}C NMR ($CDCl_3$, 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 ($NapCH_2$ G), 74.2 (C-2), 74.1 (C-5 G′), 74.0 ($PhCH_2$ G′), 73.8 ($PhCH_2$), 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 (SCH_2CH_3), 14.9 (SCH_2CH_3). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{60}H_{58}O_{13}SNa$ 1041.3496, found 1041.3498.

*4.1.24. 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 CH_2Cl_2/MeOH 4/1 and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 85 mg, 0.38 mmol, 2.5 equiv) 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 CH_2Cl_2 and 1 mL of satd $NaHCO_3$ was added. The two phases were separated and the organic phase was washed twice more with the solution of satd $NaHCO_3$ and then dried over Na_2SO_4. The residue was purified by flash chromatography to yield compound **30** as a white powder in 88% yield (114 mg). ^{1}H NMR ($CDCl_3$, 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, $PhCH_2$ G), 4.55 (2 d, J_{gem} 11.74, 2H, $PhCH_2$ 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, SCH_2CH_3 G), 1.26 (t, 3H, SCH_2CH_3 G). ^{13}C NMR ($CDCl_3$, 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, 6×128.4, 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 ($PhCH_2$ G′), 74.0 ($PhCH_2$ 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 (SCH_2CH_3 G), 14.7 (SCH_2CH_3 G). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{49}H_{50}O_{13}SNa$ 901.2870, found 901.2873.

*4.1.25. 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→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. ^{1}H NMR (CD_3OD, 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, $PhCH_2$ G′), 4.58 (s, 2H, $PhCH_2$ 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, SCH_2CH$_3$ G), 1.21 (t, 3H, SCH$_2$CH_3 G). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 139.8, 139.7 (2 C-*ipso*), 4×129.3, 4×128.8, 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 ($PhCH_2$ G′), 74.4 ($PhCH_2$ G), 71.6 (C-4 G), 71.4 (C-4 G′), 70.9 (C-6 G), 70.8 (C-6 G′), 24.8 (SCH_2CH$_3$ G), 15.4 (SCH$_2$CH_3 G). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{28}H_{38}O_{10}SNa$ 589.2083, found 589.2080.

*4.1.26. Ethyl 2,3,4-tri-O-tert-butyldimethylsilyl-6-O-benzyl-β-D-glucopyranosyl-(1→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 μL, 3.15 mmol, 15 equiv) 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 $NaHCO_3$ and brine. The solution was dried over anhydrous Na_2SO_4 and solvents were evaporated. The resulting residue was purified by chromatography to afford compound **32** as a colorless syrup in 86% yield (139 mg). ^{1}H NMR ($CDCl_3$, 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, $PhCH_2$ G′), 4.54 (s, 2H, $PhCH_2$ G), 4.53 (d, J_{gem} 12.16, 1H, $PhCH_2$ 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, SCH_2CH$_3$ G), 1.21 (t, 3H, SCH$_2$CH_3 G), 2×0.89, 0.88, 0.87, 0.85 (5 s, 45H, C(CH_3)$_3$), 0.13, 2×0.095, 0.09, 0.089, 0.078, 0.056, 0.054, 0.050, 0.044, 0.019 (10 s, 30H, SiCH_3). ^{13}C NMR ($CDCl_3$, 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 ($PhCH_2$ G′), 73.3 ($PhCH_2$ 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 (5C(CH_3)$_3$), 25.3 (SCH_2CH$_3$ G), 5×18.1 (5 C(CH$_3$)$_3$), 14.9 (SCH$_2$CH_3 G), −3.5, −3.8, −4.0, 2×−4.1, 2×−4.4, −4.5, 2×−4.6 (10 SiCH$_3$). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{58}H_{108}O_{10}SSi_5Na$ 1159.6407, found 1159.6404.

*4.1.27. 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 equiv) and TTBP (55 mg, 0.22 mmol, 5 equiv) were dissolved in dry CH_2Cl_2 (2 mL) whereafter 4 Å molecular sieves (100 mg) were added under N_2 atmosphere and the mixture was cooled down to −78 °C; 1.2 equiv of Tf_2O was then added dropwise, followed directly by acceptor **19** (2 equiv, 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 NEt_3 (0.015 mL, 0.11 mmol, 2.5 equiv). The mixture was diluted with dichloromethane and filtered through a pad of Celite. The filtrate was successively washed with water, brine and dried over Na_2SO_4. 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**: ^{1}H NMR ($CDCl_3$, 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, $PhCH_2$ G), 4.59 (s, 2H, $PhCH_2$ G′), 4.52 (dd, $J_{H3,H4}$ 3.22, 1H, H-4 Gal), 4.49 (d, J_{gem} 12.05, 1H, $PhCH_2$ 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, CH_3 R), 1.13 (s, 3H, H-6 R), 0.89, 0.88, 0.85, 0.84, 0.76 (5s, 45H, C(CH_3)$_3$), 0.13, 0.12, 0.10, 0.09, 2×0.07, 0.01, −0.01, −0.27, −0.30 (10 s, 30H, SiCH_3). ^{13}C NMR ($CDCl_3$, 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 ($PhCH_2$ G), 72.9 (C-5 G), 72.6 ($PhCH_2$ 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(CH_3)$_3$), 2×21.1, 20.7 (3 CH_3 R), 18.2, 2×18.1, 17.9, 17.8 (5 C(CH$_3$)$_3$), 17.0 (C-6 R), −3.3, −3.4, 2×−3.8, 2×−4.0, 2×−4.4, −4.5, −4.6 (10 SiCH_3). **33b**: ^{1}H NMR ($CDCl_3$, 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, $PhCH_2$ G), 4.53 (s, 2H, $PhCH_2$ G′), 4.52 (d, J_{gem} 11.78, 1H, $PhCH_2$ 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, $J_{H5,H6b}$ 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, CH_3 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(CH_3)$_3$), 0.08, 0.06, 0.04, 0.02, 0.01, −0.01, −0.02, −0.13 (8s, 24H, SiCH_3). ^{13}C NMR ($CDCl_3$, 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 ($PhCH_2$ G), 73.1 ($PhCH_2$ 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 (4C(CH_3)$_3$), 2×21.0, 20.9 (3 CH_3 R), 2×18.2, 18.1, 18.0 (4 C(CH$_3$)$_3$), 17.1 (C-6 R), 2×−3.9, 2×−4.0, −4.2, −4.4, −4.8, −5.3 (8 SiCH$_3$). **33a**: ESI-HRMS: $[M+Na]^+$ *m/z* calcd for

$C_{82}H_{136}O_{23}Si_5Na$ 1651.8216, found 1651.8220. **33b**: ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{76}H_{122}O_{23}Si_4Na$ 1537.7352, found 1537.7352.

*4.1.28. Methyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl-(1→2)[2,3,4-tri-O-acetyl-6-O-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-O-acetyl-6-O-benzyl-β-D-glucopyranosyl-(1→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 equiv of a 1M solution of TBAF in THF was added dropwise at room temperature. At completion, the mixture was taken into CH_2Cl_2 and washed with water. The organic phase was dried over Na_2SO_4, filtered and concentrated to dryness. The compound obtained (**34**) was dissolved in dry pyridine (3 mL). Acetic anhydride (10 equiv) 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 $NaHCO_3$, brine, 1M HCl and brine before being dried over Na_2SO_4, 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). ^{1}H NMR ($CDCl_3$, 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, $PhCH_2$ G), 4.47 (d, J_{gem} 12.12, 1H, $PhCH_2$ G′), 4.43 (d, J_{gem} 12.00, 1H, $PhCH_2$ G), 4.32 (d, J_{gem} 12.12, 1H, $PhCH_2$ 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-1 Gal), 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, CH_3), 1.13 (d, $J_{H5,H6}$ 6.22, 3H, H-6 R). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 170.6, 170.5, 170.4, 2×170.1, 169.9, 169.7, 169.4 (8C=O), 138.5, 138.0, 137.8 (3 C-*ipso*), 128.9, 2×128.6, 2×128.4, 2×128.2, 2×128.1, 128.0, 2×127.9, 127.5, 2×126.3 (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 ($PhCH_2$ G), 73.6 (C-3 G), 73.5 (C-5 G′), 73.4 ($PhCH_2$ 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, 3×20.9, 3×20.8, 20.7 (8 CH_3), 17.2 (C-6 R). ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{62}H_{76}O_{28}Na$ 1291.4421, found 1291.4419.

*4.1.29. Methyl α-L-rhamnopyranosyl-(1→2)[6-O-benzyl-β-D-glucopyranosyl-(1→2)-6-O-benzyl-β-D-glucopyranosyl-(1→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. ^{1}H NMR (CD_3OD, 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, $PhCH_2$ G′), 4.62 (d, J_{gem} 11.87, 1H, $PhCH_2$ G′), 4.47 (2 d, J_{gem} 12.12, 2H, $PhCH_2$ 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). ^{13}C NMR (CD_3OD, 25 °C, 100 MHz): δ 139.8, 139.7, 139.6 (3 C-*ipso*), 129.8, 2×129.5, 2×129.3, 2×129.2, 2×129.0, 2×128.9, 128.8, 128.5, 2×127.8 (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 ($PhCH_2$ G′), 74.6 ($PhCH_2$ 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* calcd for $C_{46}H_{60}O_{20}Na$ 955.3576, found 955.3575.

*4.1.30. Methyl α-L-rhamnopyranosyl-(1→2)[β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→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 atm of H_2. Once TLC analysis indicated full conversion (R_f=0.5 EtOAc/MeOH/H_2O 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%). ^{1}H and ^{13}C NMR data: see Table 1. ESI-HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{44}O_{20}Na$ 687.2324, found 687.2326.

Acknowledgements

This work was supported by grants from the Swedish Research Council and the Knut and Alice Wallenberg Foundation.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.12.042.

References and notes

1. Chen, Z.; Miller, A. R. In *Horticultural Reviews*; Janick, J., Ed.; John Wiley & Sons: New York, USA, 2001; Vol. 25, pp 171–196.
2. Güçlü-Üstündağ, Ö.; Mazza, G. *Crit. Rev. Food Sci. Nutr.* **2007**, *47*, 231–258.
3. Osbourn, A.; Goss, R. J. M.; Field, R. A. *Nat. Prod. Rep.* **2011**, *28*, 1261–1268.
4. Schwarz, S.; Xavier, N. M.; Csuk, R.; Rauter, A. M. *Carbohydr. Chem.* **2012**, *37*, 326–373.
5. Munafo, J. P., Jr.; Gianfanga, T. J. *Nat. Prod. Rep.* **2015**, *32*, 454–477.
6. Francis, G.; Kerem, Z.; Makkar, H. P. S.; Becker, K. *Br. J. Nutr.* **2002**, *88*, 587–605.
7. Lorent, J. H.; Quetin-Leclercq, J.; Mingeot-Leclercq, M.-P. *Org. Biomol. Chem.* **2014**, *12*, 8803–8822.
8. Williams, J. R.; Gong, H. *Lipids* **2007**, *42*, 77–86.
9. de Paula Barbosa, A. *Afr. J. Pharm. Pharmcol.* **2014**, *8*, 1049–1057.
10. Cham, B. E. *Res. J. Biol. Sci.* **2007**, *2*, 503–514.
11. Punjabi, S.; Cook, L. J.; Kersey, P.; Marks, R.; Cerio, R. *Int. J. Dermatol* **2008**, *47*, 78–82.
12. Podolak, I.; Galanty, A.; Sobolewska, D. *Phytochem. Rev.* **2010**, *9*, 425–474.
13. Cham, B. E. *Int. J. Clin. Med.* **2011**, *2*, 473–477.
14. Cmoch, P.; Korda, A.; Rárová, L.; Oklešťková, J.; Strnad, M.; Luboradzki, R.; Pakulski, Z. *Tetrahedron* **2014**, *70*, 2717–2730.
15. Sidoryk, K.; Korda, A.; Rárová, L.; Oklešťková, J.; Strnad, M.; Cmoch, P.; Pakulski, Z.; Gwardiak, K.; Karczewski, R.; Luboradzki, R. *Tetrahedron* **2015**, *71*, 2004–2012.
16. Friedman, M. *J. Agric. Food Chem.* **2015**, *63*, 3323–3337.
17. Neszmelyi, A.; Machytka, D.; Shabana, M. M. *Phytochemistry* **1988**, *27*, 603–605.
18. Nigudkar, S. S.; Demchenko, A. V. *Chem. Sci.* **2015**, *6*, 2687–2704.
19. Frihed, T. G.; Bols, M.; Pedersen, C. M. *Chem. Rev.* **2015**, *115*, 4963–5013.
20. Thorsheim, K.; Siegbahn, A.; Johnsson, R. E.; Stålbrand, H.; Manner, S.; Widmalm, G.; Ellervik, U. *Carbohydr. Res.* **2015**, *418*, 65–88.
21. Gu, G.; Du, Y.; Linhardt, R. J. *J. Org. Chem.* **2004**, *69*, 5497–5500.

22. Jones, N. A.; Nepogodiev, S. A.; Field, R. A. *Org. Biomol. Chem.* **2005**, *3*, 3202–3206.
23. Gao, J.; Gu, G.; Sun, B.; Cui, M.; Ji, M.; Lou, H.-X. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 622–627.
24. Verma, P.; Kumar Kabra, V.; Mukhopadhyay, B. *Carbohydr. Res.* **2011**, *346*, 2342–2347.
25. Xiong, J.; Lu, Z.; Ding, N.; Ren, S.; Li, X. *Eur. J. Org. Chem.* **2013**, 6158–6166.
26. Adak, S.; Emmadi, M.; Kulkarni, S. S. *RSC Adv.* **2014**, *4*, 7611–7616.
27. Liu, Q.-C.; Guo, T.-T.; Zhao, C.; Sun, J.; Li, W.-H. *Helv. Chim. Acta* **2014**, *97*, 361–368.
28. Okada, Y.; Nagata, O.; Taira, M.; Yamada, H. *Org. Lett.* **2007**, *9*, 2755–2758.
29. Pedersen, C. M.; Nordstrøm, L. U.; Bols, M. *J. Am. Chem. Soc.* **2007**, *129*, 9222–9235.
30. Xia, J.; Alderfer, J. L.; Piskorz, C. F.; Matta, K. L. *Chem.—Eur. J.* **2001**, *7*, 356–367.
31. Zemplén, G.; Pacsu, E. *Ber. Dtsch. Chem. Ges. B* **1929**, *62*, 1613–1614.
32. Jamois, F.; Ferrières, V.; Guégan, J.-P.; Yvin, J.-C.; Plusquellec, D.; Vetvicka, V. *Glycobiology* **2005**, *15*, 393–407.
33. Kanie, O.; Ito, Y.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 12073–12074.
34. Schmidt, R. R.; Michel, J.; Roos, M. *Liebigs Ann. Chem.* **1984**, 1343–1357.
35. Zhu, T.; Boons, G.-J. *Carbohydr. Res.* **2000**, *329*, 709–715.
36. Johnsson, R.; Ohlin, M.; Ellervik, U. *J. Org. Chem.* **2010**, *75*, 8003–8011.
37. Xia, J.; Abbas, S. A.; Locke, R. D.; Piskorz, C. F.; Alderfer, J. L.; Matta, K. L. *Tetrahedron Lett.* **2000**, *41*, 169–173.
38. Pedersen, C. M.; Marinescu, L. G.; Bols, M. *Comptes Rendus Chim.* **2011**, *14*, 17–43.
39. Walford, C.; Jackson, R. F. W.; Rees, N. H.; Clegg, W.; Heath, S. L. *Chem. Commun.* **1997**, 1855–1856.
40. Yamada, H.; Tanigakiuchi, K.; Nagao, K.; Okajima, K.; Mukae, T. *Tetrahedron Lett.* **2004**, *45*, 5615–5618.
41. Yamada, H.; Tanigakiuchi, K.; Nagao, K.; Okajima, K.; Mukae, T. *Tetrahedron Lett.* **2004**, *45*, 9207–9209.
42. Broddefalk, J.; Bergquist, K.-E.; Kihlberg, J. *Tetrahedron* **1998**, *54*, 12047–12070.
43. Rich, J. R.; McGavin, R. S.; Gardner, R.; Reimer, K. B. *Tetrahedron Asym.* **1999**, *10*, 17–20.
44. Fügedi, P.; Tatai, J. *Org. Lett.* **2007**, *9*, 4647–4650.
45. Roussel, F.; Knerr, L.; Grathwohl, M.; Schmidt, R. R. *Org. Lett.* **2000**, *2*, 3043–3046.
46. Dasgupta, S.; Nitz, M. *Carbohydr. Res.* **2010**, *345*, 2282–2286.
47. Sawada, Y.; Nanboku, N.; Yanase, E.; Nakatsuka, S.-i *Heterocycl. Commun.* **2010**, *16*, 21–24.
48. Sherman, A. A.; Mironov, Y. V.; Yudina, O. N.; Nifantiev, N. E. *Carbohydr. Res.* **2003**, *338*, 697–703.
49. Picard, S.; Crich, D. *Tetrahedron* **2013**, *69*, 5501–5510.
50. Jansson, P.-E.; Kenne, L.; Widmalm, G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 508–516.
51. Stenutz, R.; Jansson, P.-E.; Widmalm, G. *Carbohydr. Res.* **1998**, *306*, 11–17.
52. Jansson, P.-E.; Kenne, L.; Widmalm, G. *Anal. Biochem.* **1991**, *199*, 11–17.
53. Rönnols, J.; Pendrill, R.; Fontana, C.; Hamark, C.; Angles d'Ortoli, T.; Engström, O.; Ståhle, J.; Zaccheus, M. V.; Säwén, E.; Hahn, L. E.; Iqbal, S.; Widmalm, G. *Carbohydr. Res.* **2013**, *380*, 156–166.
54. Pauli, G. F.; Chen, S.-N.; Lankin, D. C.; Bisson, J.; Case, R. J.; Chadwick, L. R.; Gödecke, T.; Inui, T.; Krunic, A.; Jaki, B. U.; McAlpine, J. B.; Mo, S.; Napolitano, J. G.; Orjala, J.; Lehtivarjo, J.; Korhonen, S.-P.; Niemitz, M. *J. Nat. Prod.* **2014**, *77*, 1473–1487.
55. Jansson, P.-E.; Stenutz, R.; Widmalm, G. *Carbohydr. Res.* **2006**, *341*, 1003–1010.
56. Olsson, U.; Serianni, A. S.; Stenutz, R. *J. Phys. Chem. B* **2008**, *112*, 4447–4453.
57. Crich, D.; Smith, M. *J. Am. Chem. Soc.* **2001**, *123*, 9015–9020.