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α-Selective glycosylation with β-glycosyl sulfonium ions prepared via intramolecular alkylation

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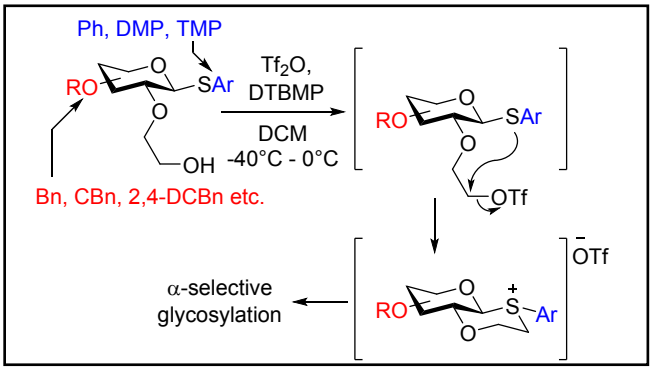


ABSTRACT: Stereoselective glycosylation remains the main challenge in the chemical synthesis of oligosaccharides. Herein we report a simple method to convert thioglycosides into β-sulfonium ions via an intramolecular alkylation reaction leading to highly α-selective glycosylations for a variety of glycosyl acceptors. The influence of the thioglycoside substituent and the protecting group pattern on the glycosyl donor was investigated and showed a clear correlation with the observed stereoselectivity.

The main challenge of chemical oligosaccharide synthesis is the stereoselective synthesis of glycosidic bonds.[1, 2] In general, 1,2-*trans* glycosides can be synthesized by exploiting neighboring group participation of a C-2-acyl group. The introduction of 1,2-*cis* glycosidic linkages is much

more challenging and requires glycosyl donors having a non-assisting functionality at C-2.[3] In general, these glycosylations are less selective and require optimization to achieve acceptable anomeric ratios. The development of methodology for stereoselective 1,2-*cis* glycosylation using a generally applicable principle is therefore highly desirable as it allows for the use of standardized monosaccharide building blocks. In this respect, the formation of glycosyl sulfonium ions holds considerable potential.[4-7] In particular, the use of C-2 auxiliaries to attain highly selective 1,2-*cis* glycosylations *via* neighboring group participation allows for careful tuning of donor reactivity and stereoselectivity.[8] First reported by Boons *et al.*, C-2 chiral auxiliaries such as the (*S*)-(phenylthiomethyl)benzyl ether can be employed for the stereoselective introduction of 1,2-*cis* glycosides such as α-glucosides and α-galactosides.[9] Neighboring group participation by the chiral auxiliary leads to a quasi-stable anomeric sulfonium ion (Figure 1) which, due to steric and electronic factors, is formed as a trans-decalin ring system. Subsequent S_N2-like displacement of the sulfonium ion then leads to the stereoselective formation of α-glycosides.[10, 11] Although this methodology is highly stereoselective in many cases, the stereoselectivity depends on the protecting groups on the glycosyl donor and the structure of the auxiliary.[10, 12-20] Since the intermediate β-sulfonium ion is in rapid equilibrium with the oxocarbenium ion, its formation alone is not a guarantee for α-selective glycosylation since it may not be a reactive intermediate in the glycosylation mechanism. [8, 13, 15, 21, 22]In addition, the preparation of glycosyl donors equipped with a C-2 auxiliary is still labor intensive.

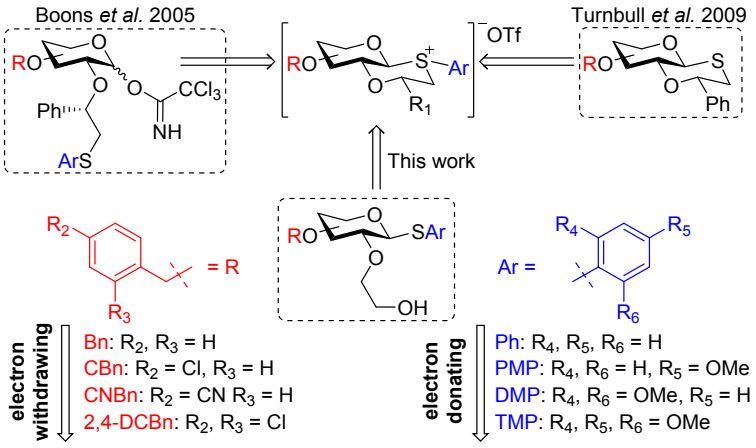


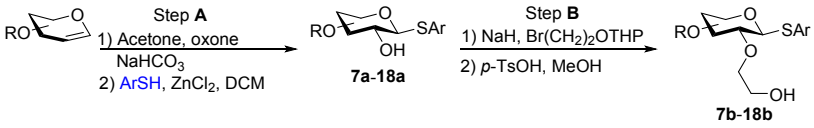
Figure 1. Retrosynthetic routes towards cyclic β-sulfonium ions.

Herein we report a simple method to prepare anomeric β-sulfonium ions from the corresponding β-thioglycosides via an intramolecular alkylation reaction. Thioglycoside precursors equipped with a C-2 2-hydroxyethyl group were prepared using a straightforward three-step procedure starting from commercially available glycal precursors. Triflation of the 2-hydroxyethyl group led to intramolecular β-sulfonium ion formation and subsequent glycosylation. The influence of the thiophenyl substituent and the nature of the protecting groups on the stereochemical outcome of the reaction were investigated. The results reveal a systematic trend of increasing α-selectivity with an increase in electron density on the sulfonium ion and decrease in electron density on the oxocarbenium ion. Hence, the most α-selective couplings were achieved with a 2,4,6-trimethoxy thiophenyl group and 2,4-dichloro benzyl protecting groups. The preactivation of the glycosyl donor allowed for the use of thioglycoside acceptors opening the possibility for iterative thioglycoside couplings.

Glycosyl donors equipped with a 2-hydroxyethyl group at C-2 were prepared from benzyl protected glucal and galactal. Oxidation of these glycals with oxone in acetone led to the formation of the α-1,2-anhydro sugars which were reacted directly with thiophenol derivatives and $ZnCl_2$ to yield the corresponding β-thioglycosides as the main product in moderate to good

yields (Table 1).[23] To investigate the effect of the thiophenyl group on the stereoselectivity, thiophenol, 4-methoxy-thiophenol (PMP), 2,6-dimethoxy thiophenol (DMP) and 2,4,6-trimethoxy thiophenol (TMP) were used yielding the corresponding thiogluco- and galactosides (Table 1, entry 1-8).[24] Next, the C-2 2-hydroxyethyl group was installed using THP-protected bromoethanol and NaH followed by THP removal catalyzed by *p*-TsOH.

Table 1: Three step synthesis of glycosyl donors 7b-18b



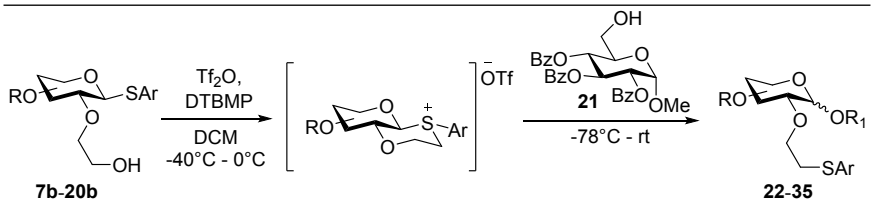
Entry	Compound	Type	R	Ar	Yield [a] 7a-18a	Yield [b] 7b-18b
1	**7**	Glc	Bn	Ph	37%	81%
2	**8**	Glc	Bn	PMP	47%	70%
3	**9**	Glc	Bn	DMP	39%	81%
4	**10**	Glc	Bn	TMP	76%	83%
5	**11**	Gal	Bn	Ph	64%	20%
6	**12**	Gal	Bn	PMP	26%	69%
7	**13**	Gal	Bn	DMP	55%	66%
8	**14**	Gal	Bn	TMP	59%	41%
9	**15**	Glc	CBn	TMP	61%	82%
10	**16**	Glc	2,4-DCBn	TMP	50%	72%
11	**17**	Gal	CBn	TMP	60%	85%
12	**18**	Gal	2,4-DCBn	TMP	50%	74%

[a] Isolated yields of the β-thioglycoside products.[b] isolated yield over two steps.

Next, we investigated the possibility to perform glycosylations with **7b-14b** by intramolecular alkylation of the thioglycoside to form intermediate β-sulfonium ions. To this end, **7b-14b** were reacted with Tf_2O and 2,6-di-tertbutyl-4-methyl-pyridine (DTBMP) in DCM at -40°C and the reactions were allowed to warm to 0°C. Subsequent addition of glycosyl acceptor **21** (-78°C to rt) led to the formation of disaccharides **22-29** in moderate to good yields (Table 2, entries 1-8). A clear trend of increasing α-stereoselectivity was observed with increasing electron donating

character of the aryl group in both the gluco and galacto series. The galacto series was more α-selective than the gluco series, consistent with earlier findings.[22]

Table 2: Glycosylation results of 7b-20b.



Entry	Type	Dono	Ar	R	α/β[a]	Yield	Product
1	Glc	**7b**	Ph	Bn	2.5/1	71%	**22**
2	Glc	**8b**	PMP	Bn	2.5/1	62%	**23**
3	Glc	**9b**	DMP	Bn	3.5/1	83%	**24**
4	Glc	**10b**	TMP	Bn	4/1	76%	**25**
5	Gal	**11b**	Ph	Bn	3/1	55%	**26**
6	Gal	**12b**	PMP	Bn	3/1	36%	**27**
7	Gal	**13b**	DMP	Bn	6/1	37%	**28**
8	Gal	**14b**	TMP	Bn	7/1	59%	**29**
9	Glc	**15b**	TMP	CBn	5/1	75%	**30**
10	Glc	**19b**	TMP	CNBn	7.5/1	65%	**31**
11	Glc	**16b**	TMP	2,4-DCBn	9/1	81%	**32**
12	Gal	**17b**	TMP	CBn	9/1	33%	**33**
13	Gal	**20b**	TMP	CNBn	12.5/1	87%	**34**
14	Gal	**18b**	TMP	2,4-DCBn	13/1	68%	**35**

[a] α/β ratios were determined using NMR spectroscopy of the crude reaction mixture after extraction.[25, 26]

However, the stereoselectivity of the TMP donor **10b** was considerably lower (α/β = 4/1) than expected based on an earlier report (α-only).[14] To investigate if the reaction indeed proceeds via a β-sulfonium ion we performed low temperature NMR studies. Glycosyl donor **10b** was reacted with Tf_2O and DTBMP in CD_2Cl_2 at -78°C (Figure 2). Upon warming to -20°C, a highly pure β-sulfonium ion was formed *via* intramolecular alkylation (Figure 2 C,D). This result does therefore not explain the discrepancy in stereoselectivity. Since our activation method is different we

reproduced the reported experiment (SI). In our hands, this reaction gave the same α/β = 4/1 ratio as obtained with our new coupling protocol (Table 2, entry 4).

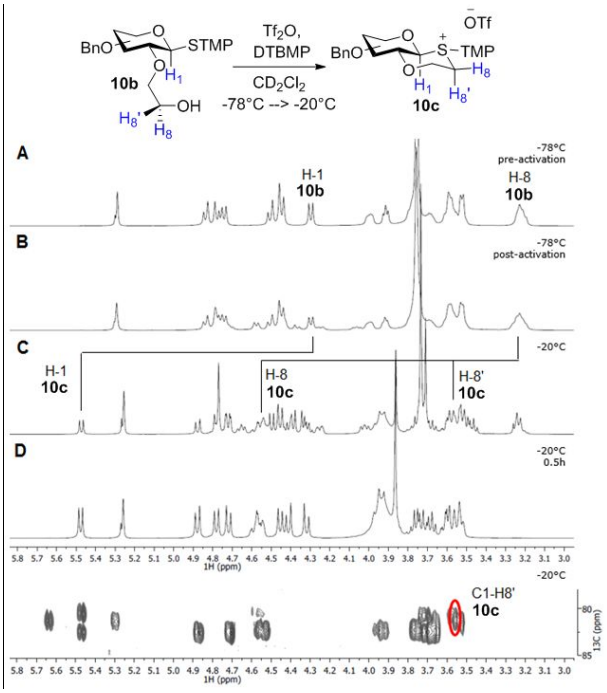


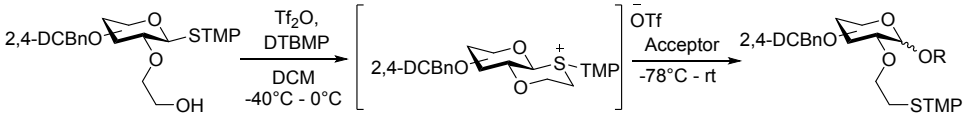
Figure 2: Low temperature NMR spectra of the sulfonium ion derived from **10b**. **A**) ^{1}H NMR spectrum of **10b** at -78°C in CD_2Cl_2. **B**) ^{1}H NMR of **10b** at -78°C after the addition of Tf_2O **C**) ^{1}H NMR at -20°C **D**) ^{1}H NMR at -20°C after 30 min. Complete conversion to sulfonium ion **10c** is observed.

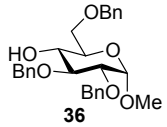
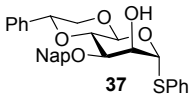
To further improve the α-selectivity, we turned our attention to the protecting groups. It is known that more electron withdrawing protecting groups improve the α-selectivity of glycosylation proceeding via β-sulfonium ions.[11, 16] To investigate the role in our system, benzyl ethers with increasingly electron withdrawing substituents were installed.[27] Benzyl ethers were used to minimize alternate reaction pathways such as neighboring group participation that may arise when using ester protecting groups. To this end, glycal precursors were prepared equipped with benzyl (Bn), *p*-chlorobenzyl (CBn) and 2,4-dichlorobenzyl (2,4-DCBn) ethers (SI).

Subsequent oxidation and reaction with 2,4,6-trimethoxy thiophenol afforded TMP thioglycosides **15a**-**18a** (Table 1, entries 9-12). Finally, installation of the 2-hydroxyethyl group as before yielded glycosyl donors **15b**-**18b**. In addition, the CBn protected donors **15b** and **17b** were converted to the *p*-cyanobenzyl (CNBn) derivatives (**19b** and **20b**) using a recently reported procedure.[28]

Next, we evaluated the glycosylation properties of **15b**-**20b** (Table 2, entry 9-14) using the aforementioned glycosylation protocol. As expected, a clear trend was observed with increasingly electron withdrawing benzyl ethers with the 2,4-DCBn giving the most α-selective results. The optimal combination for α-selective glycosylation is therefore the electron rich 2,4,6-trimethylthiophenyl group and the electron withdrawing 2,4-DCBn group to protect the C-3, 4 and 6 positions. Using this optimal combination for both glucose (**16b**) and galactose (**18b**) the glycosyl acceptor scope was investigated. To this end, two additional glycosyl acceptors **36** and **37** were evaluated (Table 3).

Table 3: Glycosyl acceptor scope of glycosyl donors 16b and 18b.



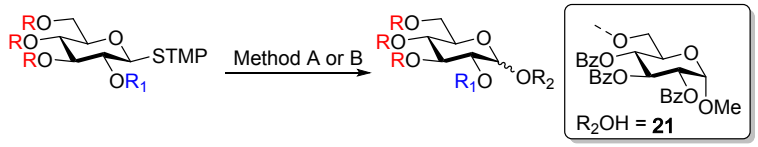
Entry	Type	Donor	Acceptor	α/β[a]	Yield	Product
1	Glc	**16b**	 **36**	3.3/1	53%	**38**
2	Gal	**18b**		21/1	48%	**39**
3	Glc	**16b**	 **37**	13/1	52%	**40**
4	Gal	**18b**		15/1	49%	**41**

[a] α/β ratios were determined using NMR spectroscopy of the crude reaction mixture after extraction.[25, 26]

From the results it is clear that the α-stereoselecitivity is maintained across different glycosyl acceptors. It is noteworthy that thioglycoside acceptors could be used (**37**) to perform chemoselective coupling of thioglycoside donors **16b** and **18b**. Hence, the developed method is amendable to iterative thioglycoside couplings.

Finally, the importance of the β-sulfonium ion as a reactive intermediate was investigated using a number of control experiments (Table 4). The effect of electron withdrawing protecting groups on the stereoselectivity can be explained by widening of the energy gap between the oxocarbenium and sulfonium ion. The inductive effect of the protecting groups is more remote from the sulfonium ion than the oxocarbenium ion and hence affect the latter intermediate to a greater extend. We prepared glycosyl donors containing a C-2 non-participating group (Bn or Pr) and benzyl or 2,4-DCBn groups at the remaining sites. Using these donors a pre-activation method was not possible at the typically used glycosylation temperature (o°C) and hence we resorted to premix conditions (NIS, TfOH). From the results it is clear that in both the C-2 OBn and OPr protected donors, the α-selectivity increased with increased electron withdrawing protecting groups (Table 4, entries 1-4).

Table 4: Control experiments to evaluate the contribution of the β-sulfonium ion intermediate in the reaction mechanism.



Entry	Donor	R	R_1 (method)	α/β[a]	Yield	Product
1	**42**	Bn	Bn (A)	1.4/1	68%	**50**
2	**43**	2,4-DCBn	Bn (A)	4/1	57%	**51**
3	**44**	Bn	Propyl (A)	1.2/1	65%	**52**
4	**45**	2,4-DCBn	Propyl (A)	3/1	51%	**53**
5	**46**	Bn	$(CH_2)_3OH$ (B)	2/1	71%	**54**
6	**47**	2,4-DCBn	$(CH_2)_3OH$ (B)	2.5/1	49%	**55**
7	**48**	Bn	Ac (A)	>1/20	83%	**56**

8	**49**	2,4-DCBn	Ac (A)	>1/20	60%	**57**

Method A: **21**, NIS, TfOH, DCM, 0°C; Method B: 1. Tf_2O, DTBMP, DCM, -40°C - 0°C. 2. **21**, -40°C - rt. [a] α/β ratios were determined using NMR spectroscopy of the crude reaction mixture after extraction.[25, 26]

This suggests that the background reaction taking place in the sulfonium ion reactions also becomes more α-selective. It is clear that the sulfonium ion intermediate is important for α-selectivity since these reactions are considerably more selective (α/β = 9/1 vs 4/1). This is highlighted by the fact that increasing the ring size by the use of a C-2 3-hydroxypropyl group led to a complete loss of stereoselectivity regardless of the protecting group used (Table 4, entry 5-6). To demonstrate that late stage switching to β-selective couplings is possible and are not affected by the protecting group pattern, compound **10a** was acetylated and coupled using NIS/TfOH (Table 4, entry 7-8). Using this synthetic route, late stage introduction of the C-2 functionality allows the synthesis of a highly α- (**10b**) and β-selective (**49**) glycosyl donor in a one-step procedure starting from a general building block (**10a**). Finally, deprotection of the auxiliary of **32** was achieved using a previously reported procedure involving methylation of the thioether followed by elimination under basic conditions to afford the corresponding C-2 OH compound (**58**).[14]

In conclusion, a novel and versatile methodology for the formation of α-glycosidic linkages was developed. Thioglycosides were activated to form β-sulfonium ions via an intramolecular alkylation reaction. The reactivity and selectivity of the β-sulfonium ions was modulated by the systematic variation of the thioglycoside substituent and the electronic nature of the protecting groups. An electron rich thioglycoside with electron withdrawing protecting groups proved to be the optimal combination. Consistent α-selectivity was observed for a number of glycosyl acceptors. In addition, chemoselective coupling of glycosyl donor thioglyocosides to thioglycoside

acceptors is possible. Mechanistic studies indicate the electron withdrawing protecting groups also improve the α-selectivity of C-2 benzyl protected donors in addition to the sulfonium ion. Late-stage modulation of donor selectivity is possible by introduction of the 2-hydroxy ethyl substituent for α-selectivity or the installation of a C-2 acetyl group for β-selective couplings.

EXPERIMENTAL SECTION

General Procedures: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS), or residual solvents as the internal standard. NMR data is presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), integration. All NMR signals were assigned on the basis of ^{1}H NMR, ^{13}C NMR, COSY, HSQC and TOCSY experiments. NMR data is presented for the major anomer. Mass spectra were recorded on an JEOL AccuTOF CS JMS-T100CS mass spectrometer. Optical rotations were measured at 589 nm using a Perkin Elmer Polarimeter Model 241 MC. Automatic flash column chromatography was performed using Biotage Isolera Spektra One, using SNAP cartridges (Biotage, 30-100 μm, 60 Å), 10-50 g. TLC-analysis was conducted on Silica gel F_{254} (Merck KGaA) with detection by UV-absorption (254nm) where applicable, and by spraying with 10% sulphuric acid in methanol followed by charring at ≈300°C. DCM, THF and toluene were freshly distilled. Molecular sieves (4Å) were flame activated under vacuum prior to use. All inert reactions were carried out under argon atmosphere using flame-dried flasks.

General procedure A: *D*-glucal or *D*-galactal was dissolved in dry DMF (0.2 M) under inert atmosphere and cooled to 0°C. NaH (8 eq; 60% dispersion in mineral oil) was added and the reaction mixture was stirred for 30 min, after which the corresponding benzylating agent (5 eq)

was added. The reaction was stirred for 16 h at ambient temperature after which it was quenched with MeOH. The mixture was concentrated under reduced pressure and taken up in DCM (100 mL) and water (100 mL). The aqueous layer was extracted with DCM (2 × 100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude product.

General procedure B: To a cooled (0°C) solution of a benzylated glycal (2.4 mmol) in DCM (10 mL) were added acetone (1 mL) and sat. aq. $NaHCO_3$ (17 mL). The mixture was stirred vigorously, and a solution of oxone (4.8 mmol) in H_2O (6 mL) was added dropwise over 15 min. The mixture was stirred vigorously at 0°C for 30 min and then at rt until TLC indicated consumption of the starting material. The organic phase was separated and the aqueous phase was extracted with DCM (2 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated *in vacuo*. The crude mixture was dissolved in dry DCM (23 mL). MS (4Å) and the corresponding thiol (3.6 mmol) were added under inert atmosphere. The mixture was cooled to -78°C and stirred for 15 min. $ZnCl_2$ (1M in Et_2O) (0.24 mmol) was added and the mixture was stirred overnight while slowly warmed up to rt. The reaction was quenched with TEA and purified with silica gel flash column chromatography to obtain the pure product.

General procedure C: An anomeric thioether with a free 2-OH (**7a** - **19a**) was dissolved in dry DMF (0.1 M) and cooled to 0°C. NaH (4 eq; 60% dispersion in mineral oil) was added and the mixture was stirred at 0°C for 15 min, after which the appropriate auxiliary ($Br(CH_2)_2OTHP$ or $Br(CH_2)_3OTHP$) was added (4 eq). The reaction was stirred for 16 h at ambient temperature, after which it was quenched with MeOH. The reaction mixture was concentrated under reduced pressure and were taken up in MeOH (25 mL). *p*-TsOH was added until a pH of 2 was reached. The reaction was stirred for 4 h and subsequently concentrated under reduced pressure. The

residue was dissolved in EtOAc (20 mL) and washed with water (3 × 20 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude product.

General procedure D: Thioglucosides **10a** or **16a** were dissolved in dry DMF (0.1 M) and cooled to 0°C. NaH (4 eq; 60% dispersion in mineral oil) was added and the mixture was stirred at 0°C for 15 min, after which benzyl- or propyl bromide was added (4 eq). The reaction was stirred for 16 h at ambient temperature, after which it was quenched with MeOH. The reaction mixture was concentrated under reduced pressure and the residue was taken up in EtOAc (20 mL). The organic layer was washed with water (3 × 20 mL), brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure yielding the crude product.

General glycosylation procedure E: the corresponding glycosyl donor (1 eq) and DTBMP (4 eq) were dissolved in dry DCM (0.05 M). MS (4Å) were added and the mixture was stirred at -40°C for 15 min. Tf_2O (1.5 eq) was added and the mixture was allowed to slowly warm up to 0°C and stirred at 0°C for 30 min. When TLC analysis indicated complete consumption of the triflated intermediate, the mixture was cooled down to -78°C and the appropriate acceptor (1.5 eq) was added. The reaction was left to warm up to rt in 16 hours and was subsequently taken up in EtOAc (20 mL) and filtered. The filtrate was washed with aq. $Na_2S_2O_3$ (20 mL, 10%), brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude product.

General glycosylation procedure F: The corresponding glycosyl donor (1 eq) and acceptor (2 eq) were dissolved in dry DCM (0.05 M). MS (4Å) were added and the mixture was cooled to -5°C. NIS (1.1 eq) and TfOH (0.2 eq) were added and the reaction was stirred for 2h. The reaction was quenched with Et_3N and taken up in EtOAc (20 mL) and filtered. The filtrate was washed with aq $Na_2S_2O_3$ sol (20 mL, 10%), brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield the crude product.

3,4,6-Tri-*O*-benzyl-*D*-glucal (1): *Via* general procedure A starting from *D*-glucal (5.13 g, 35.1 mmol) using benzyl bromide. The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) affording **1** (13.3 g, 91%). **TLC** (EtOAc/*n*-heptane, 30/70 v/v): R_f = 0.55. **^{1}H NMR:** (500 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 15H), 6.42 (dd, *J* = 6.1, 1.3 Hz, 1H, H-1), 4.87 (dd, *J* = 6.2, 2.7 Hz, 1H, H-2), 4.83 (d, *J* = 11.3 Hz, 1H), 4.66 – 4.61 (m, 2H), 4.61 – 4.53 (m, 3H), 4.21 (ddd, *J* = 6.2, 2.7, 1.3 Hz, 1H, H-3), 4.06 (ddd, *J* = 8.3, 5.1, 2.9 Hz, 1H, H-5), 3.86 (dd, *J* = 8.7, 6.2 Hz, 1H, H-4), 3.83 – 3.72 (m, 2H, H-6); **^{13}C{^{1}H} NMR:** (126 MHz, $CDCl_3$) δ 144.7 (C-1), 138.3, 138.2, 138.0, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 99.9 (C-2), 76.7 (C-5), 75.7 (C-3), 74.4 (C-4), 73.8, 73.51, 70.45, 68.5 (C-6).

3,4,6-Tri-*O*-(4-chlorobenzyl)-*D*-glucal (2): *Via* general procedure A starting from *D*-glucal (2.0 g, 13.7 mmol) using 4-chlorobenzyl chloride (11.0 g, 68 mmol). The crude product was purified by silica gel flash column chromatography (0% to 20% EtOAc in *n*-heptane) yielding **2** (6.23 g, 88%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.76. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 11H), 7.16 – 7.10 (m, 2H), 6.41 (dd, *J* = 6.1, 1.4 Hz, 1H, H-1), 4.85 (dd, *J* = 6.2, 2.6 Hz, 1H, H-2), 4.75 (d, *J* = 11.6 Hz, 1H), 4.58 (d, *J* = 11.8 Hz, 2H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.50 – 4.45 (m, 2H), 4.18 (ddd, *J* = 6.3, 2.6, 1.4 Hz, 1H, H-3), 4.01 (ddd, *J* = 8.8, 4.8, 2.7 Hz, 1H, H-5), 3.81 (dd, *J* = 8.9, 6.3 Hz, 1H, H-4), 3.77 (dd, *J* = 10.7, 4.8 Hz, 1H, H-6a), 3.72 (dd, *J* = 10.8, 2.7 Hz, 1H, H-6b). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 144.9 (C-1), 136.8, 136.6, 136.4, 133.54, 133.49, 133.46, 129.04, 129.01, 128.96, 128.60, 128.57, 99.7 (C-2), 76.7 (C-5), 76.0 (C-3), 74.5 (C-4), 72.9, 72.7, 69.6, 68.5 (C-6); **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{27}H_{25}Cl_3O_4Na$, 541.0716; found, 541.0707.

3,4,6-Tri-*O*-(2,4-dichlorobenzyl)-*D*-glucal (3): *Via* general procedure A starting from *D*-glucal (1.7 g, 11.6 mmol) using 2,4-dichloro-1-(chloromethyl)benzene. The crude product was purified by silica gel flash column chromatography (0% to 20% EtOAc in *n*-heptane) yielding **3** (6.39 g, 90%).

TLC (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.76. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.26 (m, 9H), 7.25 – 7.15 (m, 3H), 6.45 (dd, *J* = 6.1, 1.4 Hz, 1H, H-1), 4.92 (dd, *J* = 6.2, 2.5 Hz, 1H, H-2), 4.89 (d, *J* = 12.7 Hz, 1H), 4.73 (d, *J* = 12.8 Hz, 1H), 4.71 – 4.66 (m, 1H), 4.63 (d, *J* = 13.4 Hz, 1H), 4.56 (dd, *J* = 13.1, 3.7 Hz, 2H), 4.28 (ddd, *J* = 6.4, 2.6, 1.4 Hz, 1H, H-3), 4.07 (ddd, *J* = 9.1, 4.5, 2.6 Hz, 1H, H-5), 3.95 – 3.87 (m, 2H, H-4, H-6a), 3.82 (dd, *J* = 10.7, 2.7 Hz, 1H, H-6b). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 145.0 (C-1), 134.53, 134.50, 134.3, 133.94, 133.87, 133.8, 133.36, 133.33, 133.2, 130.0, 129.9, 129.8, 129.7, 129.6, 129.2, 129.07, 129.05, 129.01, 127.2, 127.10, 127.07, 127.03, 99.6 (C-2), 76.7 (C-3), 76.6 (C-5), 74.6 (C-4), 71.0, 70.2, 69.9, 69.3, 69.0 (C-6), 67.0. **HRMS (ESI-TOF) (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{27}H_{22}Cl_6O_4Na$, 642.9547; found, 642.9545.

3,4,6-tri-*O*-benzyl-*β*-D-galactal (4): *Via* general procedure A starting from *D*-galactal (5.00 g, 34.2 mmol) using benzyl bromide. Silica gel flash column chromatography (0% - 30% EtOAc in *n*-heptane) afforded **4** (12.39 g, 29.8 mmol, 87%). **TLC**: (EtOAc/n-heptane,50/50 v/v): R_f = 0.74; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 15H), 6.36 (dd, *J* = 6.2, 1.4 Hz, (H-1)), 4.85 (ddd, *J* = 8.5, 6.6, 4.1 Hz, 1H, H-2), 4.67 – 4.58 (m, 3H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.21 – 4.15 (m, H-3, H-5), 3.96 – 3.92 (m, H-4), 3.78 (dd, *J* = 10.1, 7.2 Hz, H-6a), 3.65 (dd, *J* = 10.2, 5.1 Hz, H-6b). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 144.2 (C-1), 138.5, 138.4, 138.0, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 100.0 (C-2), 75.7 (C-5), 73.44, 73.35, 71.3 (H-4), 70.9, 70.8 (C-3), 68.5 (H-6). **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{27}H_{28}O_4Na$, 439.1885; found, 439.1877.

3,4,6-tri-*O*-(4-chlorobenzyl)-*β*-D-galactal (5): *Via* general procedure A starting from *D*-galactal (72 mg, 0.492 mmol) and 4-chlorobenzyl bromide. Silica gel flash column chromatography (0% - 30% EtOAc in *n*-heptane) afforded **5** (0.12 g, 0.231 mmol, 47%). **TLC**: (EtOAc/n-heptane, 30/70 v/v): R_f = 0.37; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (m, 12H), 6.36 (dd, *J* = 6.3, 1.4 Hz, H-1), 4.84 (ddd, *J* = 6.3, 3.0, 1.2 Hz, H-2), 4.79 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H),

4.53 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.17 (m, H-3, H-5), 3.91 (m, H-4), 3.74 (dd, *J* = 10.1, 7.2 Hz, H-6a), 3.63 (dd, *J* = 10.1, 5.1 Hz, H-6b). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 144.3 (C-1), 136.8, 136.7, 136.4, 133.54, 133.52, 133.4, 132.6, 129.2, 129.1, 128.7, 128.58, 128.56, 128.50, 99.6 (C-2), 75.5 (C-5), 72.6, 72.5, 71.6 (C-4), 70.8 (C-3), 70.2, 68.2 (C-6); **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{27}H_{25}Cl_3O_4Na$, 541.0716; found, 541.0709.

3,4,6-tri-O-(2,4-dichlorobenzyl)-*β*-D-galactal (6): *Via* general procedure A starting from *D*-galactal (2.0 g, 13.7 mmol) and 2,4-dichlorobenzylchloride. Silica gel flash column chromatography (0% - 30% EtOAc in *n*-heptane) afforded **6** (3.88 g, 6.29 mmol, 46%). **TLC**: (EtOAc/n-heptane, 30/70 v/v): R_f = 0.60; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.15 (m, 9H), 6.41 (dd, *J* = 6.2, 1.3 Hz, H-1), 4.93 – 4.87 (m, 1H, H-2), 4.72 (d, *J* = 6.6 Hz, 1H), 4.69 (d, *J* = 6.6 Hz, 1H), 4.66 – 4.58 (m, 2H), 4.51 (d, *J* = 13.0 Hz, 1H), 4.32 – 4.26 (m, H-3, H-5), 4.08 – 4.04 (m, H-4), 3.87 – 3.76 (m, H-6a, H-6b). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 144.4 (C-1), 134.70, 134.65, 134.2, 134.0, 133.8, 133.6, 133.1, 133.0, 130.07, 130.01, 129.6, 129.2, 129.0, 128.9, 127.11, 127.07, 99.5 (C-2), 75.3 (C-5), 72.4 (H-4), 71.6 (C-3), 70.0, 69.9, 68.6 (C-6), 67.8; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{27}H_{22}Cl_6O_4Na$, 642.9547; found, 642.9545.

3,4,6-tri-O-benzyl-2-*O*-(2-(2,4,6-trimethoxybenzenethio)ethyl-*α*-D-glycopyranosyl)trichloroacetimidate (10d): Glucosyl donor **10b** (1 eq) and DTBMP (4 eq) were dissolved in dry DCM (2 mL). MS (4Å) were added under inert atmosphere and the mixture was stirred at -40°C for 15 min. Tf_2O (1.5 eq) was added and the mixture was allowed to slowly warm up to 0°C and stirred at 0°C for 30 min. When TLC analysis indicated complete consumption of the triflated intermediate, the mixture was quenched with H_2O, taken up in EtOAc (20 mL) and filtered. The filtrate was washed with aq. $Na_2S_2O_3$ (20 mL, 10%), brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified using silica gel

flash column chromatography (20% - 60% EtOAc in *n*-heptane) yielded the lactol (98 mg, 0.16 mmol, 63%). The lactol (1 eq) was dissolved in dry DCM (0.015M). Trichloroacetonitrile (10 eq) and DBU (4 eq) were added, and the mixture was stirred at 0°C. After 7h, TLC showed the formation of a major product. The reaction was concentrated *in vacuo* and purified using silica gel flash column chromatography (Pet ether:EtOAc (20%, with 1% TEA) to afford **10d** (51 mg, 84%). Spectral data was consistent with literature values of the reported compound by Singh *et al*.[14] Using **10d**, a glycosylation reaction under idential conditions was performed as reported by Singh *et al*. In our hands, this experiment gave 4/1, α/β ratio. This is consistent with the results obtained with **10b** but different from the report of Singh *et al*.

Phenyl 3,4,6-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (7a): *Via* general procedure B starting from **1** (0.81 g, 1.52 mmol) and thiophenol. Silica gel flash column chromatography (0% → 30% - EtOAc in *n*-heptane) afforded **7a** (0.30 g, 0.56 mmol, 37%). **TLC:** (EtOAc/n-heptane, 30/70 v/v): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.37 – 7.16 (m, 18H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.86 – 4.80 (m, 2H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 10.9 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 9.6 Hz, 1H, (H-1)), 3.79 (dd, *J* = 10.9, 2.0 Hz, 1H, (H-6)), 3.73 (dd, *J* = 11.0, 4.5 Hz, 1H, (H-6)), 3.64 – 3.46 (m, 4H, (H-2, H-3, H-4, H-5)), 2.45 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 138.4, 138.2, 138.0, 132.8, 131.7, 128.9, 128.5, 128.4, 128.3, 128.0, 127.92, 127.89, 127.7, 127.6, 127.5, 88.0(C-1), 85.9(C-3), 79.4(C-5), 77.3(C-4), 75.3, 75.0, 73.4, 72.5 (C-2), 68.9(C-6). **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{33}H_{34}O_5SNa$, 565.2025; found, 565.2022

4-Methoxyphenyl 3,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside (8a): *Via* general procedure B starting from **1** (0.185 g, 0.446 mmol) and 4-methoxythiophenol. Silica gel flash column chromatography (0% → 30% - EtOAc in *n*-heptane) afforded **8a** (0.12 g, 0.21 mmol, 47%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.7; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 1H),

7.38 – 7.15 (m, 14H), 6.76 (d, *J* = 8.8 Hz, 1H), 4.93 – 4.78 (m, 3H), 4.64 – 4.51 (m, 3H), 4.36 (d, *J* = 9.6 Hz, 1H, (H-1)), 3.80 – 3.72 (m, 5H, (H-6, H-6, OMe)), 3.61 – 3.53 (m, 2H, (H-3, H-4)), 3.50 (ddd, *J* = 7.4, 4.3, 2.1 Hz, 1H, (H-5)), 3.40 (dd, *J* = 9.6, 8.4 Hz, 1H, (H-2)), 2.41 (s, 1H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 160.2, 138.5, 138.4, 138.1, 136.0, 128.5, 128.43, 128.35, 128.01, 127.98, 127.8, 127.64, 127.56, 121.1, 114.5, 88.0(C-1), 85.9(C-3), 79.4(C-5), 77.4(C-4), 75.3, 75.1, 73.5, 72.3(C-2), 69.0(C-6), 55.3. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{34}H_{36}O_6SNa$, 595.2130; found, 595.2134

2,6-Dimethoxyphenyl 3,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside (9a): *Via* general procedure B starting from **1** (0.779 g, 1.87 mmol) and 2,6-dimethoxythiophenol. Silica gel flash column chromatography (0% → 30% - EtOAc in *n*-heptane) afforded **9a** (0.44 g, 0.731 mmol, 39%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.6; **^1H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.08 (m, 16H), 6.56 (d, *J* = 8.4 Hz, 2H), 5.04 (d, *J* = 11.1 Hz, 1H), 4.79 (dd, *J* = 11.0, 1.7 Hz, 2H), 4.57 – 4.50 (m, 2H), 4.46 (d, *J* = 11.7 Hz, 1H), 4.29 (d, *J* = 9.6 Hz, 1H, H-1), 3.83 (m, 7H), 3.79 (d, *J* = 2.7 Hz, 2H, (H-6, H-6)), 3.61 (t, *J* = 8.7 Hz, 1H, (H-3)), 3.53 (dd, *J* = 9.7, 8.7 Hz, 1H, (H-4)), 3.46 (dt, *J* = 9.7, 2.7 Hz, 1H, (H-5)), 3.32 (ddd, *J* = 9.5, 8.6, 1.9 Hz, 1H, (H-2)). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 162.2, 138.8, 138.4, 138.3, 131.6, 128.27, 128.26, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 105.0, 104.6, 88.4 (C-1), 85.6 (C-3), 80.0 (C-5), 76.9 (C-4), 75.2, 75.0, 73.6, 73.5 (C-2), 69.1 (C-6), 56.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{35}H_{38}O_7SNa$, 625.2236; found, 625.2223

2,4,6-Trimethoxyphenyl 3,4,6-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (10a): *Via* general procedure B starting from **1** (0.303 g, 0.729 mmol) and 2,4,6-trimethoxythiophenol. The crude product was purified by silica gel flash column chromatography (10% → 40% EtOAc in *n*-heptane) yielding **10a** (0.35 g, 0.554 mmol, 76%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.41. **^1H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.13 (m, 15H), 6.11 (s, 2H), 5.04 (d, *J* = 11.0 Hz, 1H), 4.79 (dd, *J* = 11.0, 2.6 Hz, 2H), 4.54 (dd, *J* = 11.2, 7.6 Hz, 2H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.20 (d, *J* = 9.4 Hz, 1H, H-1), 3.84 – 3.77

(m, 11H, H-2, H-6), 3.61 (t, *J* = 8.8 Hz, 1H, H-3), 3.54 (t, *J* = 9.3 Hz, 1H, H-4), 3.46 (ddd, *J* = 9.7, 3.2, 2.0 Hz, 1H, H-5), 3.28 (ddt, *J* = 9.5, 8.7, 2.5 Hz, 1H, H-2). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.2, 163.0, 139.0, 138.6, 138.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.49, 127.45, 96.2, 91.5, 88.5 (C-1), 85.6 (C-3), 80.0 (C-5), 76.9 (C-4), 75.2, 75.1, 73.7, 73.2 (C-2), 73.1, 69.2 (C-6), 56.4, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{40}O_8SNa$, 655.2342; found, 655.2339.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-glucopyranoside (7b): *Via* general procedure C starting from **7a** (0.137 g, 0.253mmol). Silica gel flash column chromatography (0% → 30% - EtOAc in *n*-heptane) afforded **7b** (0.12 g, 0.205 mmol, 81%). **TLC:** (EtOAc/n-heptane, 30/70 v/v): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.38 – 7.15 (m, 17H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.85 (d, *J* = 10.9 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.64 – 4.56 (m, 2H), 4.57 (d, *J* = 9.8 Hz, 1H (H-1)), 4.54 (d, *J* = 12.0 Hz, 1H), 3.89 (ddd, *J* = 10.7, 5.8, 3.0 Hz, 1H), 3.83 (ddd, *J* = 10.7, 6.0, 3.0 Hz, 1H), 3.78 (dd, *J* = 10.9, 2.0 Hz, 1H, (H-6)), 3.72 (dd, *J* = 10.9, 4.5 Hz, 1H, (H-6)), 3.70 – 3.61 (m, 4H, (H-3, H-4)), 3.50 (ddt, *J* = 6.6, 4.6, 1.9 Hz, 1H, (H-5)), 3.40 – 3.33 (m, 1H, (H-2)), 2.72 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 138.2, 137.9, 137.8, 133.2, 131.9, 128.9, 128.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.64, 127.59, 127.57, 87.5 (C-1), 86.6 (C-3), 80.6 (C-2), 79.1 (C-5), 77.9 (C-4), 77.3, 77.0, 76.8, 75.9, 75.0, 74.7, 73.4, 68.8 (C-6), 62.3. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{35}H_{38}O_6SNa$, 609.2287; found, 609.2275

4-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-1-thio-β-D-glucopyranoside (8b): *Via* general procedure C starting from **8a** (0.172 g, 0.301 mmol.) Silica gel flash column chromatography (0% → 30% - EtOAc in *n*-heptane) afforded **8b** (0.13 g, 0.211 mmol, 70%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.9 Hz, 2H), 7.30 – 7.16 (m, 13H), 7.12 (dd, *J* = 7.5, 2.1 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.72 (d, *J* = 10.9 Hz, 1H), 4.57 – 4.42 (m, 4H), 4.36 (d, *J* = 9.7 Hz, 1H), 3.83 (ddd,

J = 10.7, 5.4, 3.1 Hz, 1H), 3.76 (ddd, *J* = 10.7, 6.1, 3.1 Hz, 1H), 3.72 – 3.51 (m, 11H, (H-3, H-4, H-6, H-6)), 3.38 (ddd, *J* = 9.5, 4.3, 1.9 Hz, 1H, (H-5)), 3.22 (dd, *J* = 9.7, 8.6 Hz, 1H, (H-2)), 2.72 (s, 1H); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 159.8, 138.2, 137.90, 137.85, 135.2, 128.5, 128.4, 128.3, 127.86, 127.84, 127.6, 127.5, 122.7, 114.4, 87.8 (C-1), 86.6 (C-3), 80.5 (C-2), 79.0 (C-5), 78.0 (C-4), 75.8, 75.0, 74.7, 73.4, 73.3, 68.9 (C-6), 62.3, 55.3; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{40}O_7SNa$, 639.2392; found, 639.2382

2,6-Dimethoxyphenyl 3,4,6-tri-O-benzyl-2-O-(2-hydroxyethyl)-1-thio-β-D-glucopyranoside (9b): *Via* general procedure C starting from **9a** (0.184 g, 0.306 mmol). Silica gel flash column chromatography (0% → 30% - EtOAc in *n*-heptane) afforded **9b** (0.16 g, 0.248 mmol, 81%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.30; **^1H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 14H), 7.17 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.56 (d, *J* = 8.3 Hz, 2H), 4.87 (s, 2H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 10.9 Hz, 1H), 4.53 (d, *J* = 10.0 Hz, 1H (H-1)), 4.49 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.05 (ddd, *J* = 10.9, 5.7, 2.5 Hz, 1H), 3.95 (ddd, *J* = 10.8, 6.7, 2.4 Hz, 1H), 3.84 (m, 7H), 3.75 – 3.67 (m, 2H, (H-6)), 3.66 – 3.59 (m, 2H, (H-3, H-6)), 3.59 – 3.48 (m, 2H, (H-4)), 3.43 – 3.32 (m, 2H, (H-2, H-5)); **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 161.0, 138.4, 138.2, 137.9, 130.4, 128.5, 128.4, 128.3, 127.93, 127.88, 127.82, 127.80, 127.5, 108.6, 104.3, 87.9 (C-1), 87.2 (C-3), 81.7 (C-2), 79.6 (C-5), 78.2 (C-4), 75.8, 75.0, 74.9, 73.6, 69.4 (C-6), 61.9, 56.3; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{37}H_{42}O_8SNa$, 669.2498; found, 669.2495.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-glucopyranoside (10b): *via* general procedure C starting from **10a** (330 mg, 0.55 mmol). Silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane) afforded **10b** as a white solid (0.294 g, 0.434 mmol, 83%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.21. **^1H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.11 (m, 18H), 6.12 (s, 2H), 4.87 (s, 2H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 10.9 Hz,

1H), 4.48 (s, 2H), 4.38 (d, *J* = 9.9 Hz, 1H, H-1), 4.05 (ddd, *J* = 10.8, 5.6, 2.5 Hz, 1H), 3.94 (ddd, *J* = 10.8, 6.8, 2.5 Hz, 1H), 3.82 (s, 7H), 3.79 (s, 3H), 3.74 – 3.67 (m, 2H, H-6a), 3.64 – 3.58 (m, 3H, H-3, H-6b), 3.49 (t, *J* = 9.4 Hz, 1H, H-4), 3.39 – 3.31 (m, 2H, H-2, H-5). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.3, 162.1, 138.4, 138.3, 137.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.80, 127.79, 127.5, 100.0, 91.2, 88.7 (C-1), 87.2 (C-3), 81.6 (C-2), 79.6 (C-5), 78.2 (C-4), 75.8, 75.0, 74.9, 73.6, 69.6 (C-6), 61.9, 56.2, 55.3; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{38}H_{44}O_9SNa$, 699.2604; found, 699.2583.

Phenyl 3,4,6-tri-*O*-benzyl-1-thio-*β*-D-galactopyranoside (11a): *Via* general procedure B starting from **4** (0.682g, 1.64 mmol) and thiophenol. Silica gel flash column chromatography (0% - 30% - Et_2O in toluene) afforded **11a** (0.57 g, 1.05 mmol, 64%). **TLC**: (EtOAc/n-heptane, 30/70 v/v): R_f = 0.38; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.52 – 7.48 (m, 2H), 7.39 – 7.17 (m, 16H), 5.70 (d, *J* = 5.5 Hz), 4.89 (d, *J* = 11.4 Hz, 2H), 4.75 (dd, *J* = 13.9, 11.7 Hz, 2H), 4.70 – 4.63 (m, 2H), 4.59 - 4.56 (d, *J* = 7.0 Hz, 2H), 4.55 – 4.41 (m, 2H, H-1), 4.01 (t, *J* = 9.4 Hz, H-2), 3.98 (d, *J* = 2.7 Hz, H-4), 3.67 – 3.64 (m, 3H, H-6, H-5), 3.58 (dd, *J* = 9.4, 6.0 Hz, 1H, H-6), 3.47 (dd, *J* = 9.2, 2.8 Hz, H-3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 138.7, 138.4, 138.0, 137.9, 137.9, 137.8, 134.0, 132.6, 132.2, 132.0, 128.9, 128.8, 128.63, 128.58, 128.55, 128.45, 128.42, 128.3, 128.2, 128.02, 128.01, 127.93, 127.87, 127.84, 127.81, 127.79, 127.77, 127.74, 127.69, 127.57, 127.5, 127.3, 127.0, 88.5 (C-1), 83.2 (C-3), 77.6 (C-5), 74.8, 74.4, 73.6, 73.5, 73.2 (C-4), 72.4, 72.4, 69.1 (C-2), 68.7 (C-6); **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{33}H_{34}O_5SNa$, 565.2024; found, 565.2014.

4-methoxyphenyl 3,4,6-tri-*O*-benzyl-1-thio-*β*-D-galactopyranoside (12a): *Via* general procedure B starting from **4** (530 mg, 1.28 mmol) and 4-methoxythiophenol. Silica gel flash column chromatography (0% to 30% Et_2O in toluene) afforded **12a** (0.19 g, 0.331 mmol, 26%). **TLC**: (Et_2O/toluene, 20/80 v/v): R_f = 0.65; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.18 (m, 15H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.87 (d, *J* = 11.5 Hz, 1H), 4.69 (dd, *J* = 11.9 Hz, 2H), 4.55

(d, *J* = 11.5 Hz, 1H), 4.46 (q, *J* = 11.7 Hz, 2H), 4.40 (d, *J* = 9.5 Hz, H-1), 3.95 (d, *J* = 2.6 Hz, H-4), 3.91 (td, *J* = 9.4, 1.5 Hz, H-2), 3.74 (s, 3H), 3.69 – 3.58 (m, H-6a, H-6b, H-5), 3.45 (dd, *J* = 9.3, 2.7 Hz, H-3), 2.45 (d, *J* = 1.8 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.8, 138.7, 138.1, 137.9, 135.3, 128.54, 128.45, 128.1, 127.92, 127.85, 127.83, 127.7, 127.6, 127.4, 122.2, 114.4, 88.9 (C-1), 83.2 (C-3), 77.6 (C-5), 74.3, 73.6, 73.3 (C-4), 72.4, 69.0 (C-2), 68.7 (C-6); **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{34}H_{36}O_6SNa$, 595.2130; found, 595.2110.

2,6-dimethoxyphenyl 3,4,6-tri-*O*-benzyl-1-thio-*β*-D-galactopyranoside (13a): *Via* general procedure B starting from **4** (0.838g, 2.01 mmol and 2,6-dimethoxythiophenol. Silica gel flash column chromatography (0% - 30% Et_2O in toluene) afforded **13a** (0.667 g, 1.11 mmol, 55%). **TLC**: (Et_2O/toluene, 20/80 v/v): R_f = 0.52; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.19 (m, 15H), 7.16 – 7.11 (m, 2H), 6.59 (d, *J* = 8.4 Hz, 1H), 4.89 (d, *J* = 11.7 Hz, 1H), 4.83 (d, *J* = 12.2 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.42 (dd, *J* = 11.7 Hz, 2H), 4.26 (d, *J* = 9.4 Hz, H-1), 3.90 – 3.69 (m, 3H, H-2, H-4), 3.65 – 3.50 (m, H-5, H-6a, H-6b), 3.45 (dd, *J* = 9.4, 2.8 Hz, H-3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.0, 139.1, 138.7, 138.0, 131.3, 128.4, 128.3, 128.0, 127.9, 127.7, 127.53, 127.47, 127.3, 127.1, 104.7, 89.8 (C-1), 82.7 (C-3), 77.6 (C-5), 74.14 (C-4), 74.12, 73.5, 72.7, 70.5 (C-2), 68.5 (C-6), 56.5. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{35}H_{38}O_7SNa$, 625.2235; found, 625.2228.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-benzyl-1-thio-*β*-D-galactopyranoside (14a): *Via* general procedure B starting from **4** (0.681g, 1.64 mmol and 2,4,6-trimethoxythiophenol. Silica gel flash column chromatography (0% - 30% Et_2O in toluene) afforded **14a** (0.61 g, 0.965 mmol, 59%). **TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.44; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 - 7.10 (m, 15H), 6.16 (s, 2H), 4.89 (d, J = 11.8 Hz, 1H), 4.84 (d, J = 12.2 Hz, 1H), 4.71 (d, J = 12.2 Hz, 1H), 4.44 (dt, J = 11.5 Hz, 3H), 4.17 (d, J = 9.3 Hz, H-1), 3.87 (d, J = 2.6 Hz, H-4), 3.82 (s, 3H), 3.81 (s, 6H), 3.76 - 3.51 (m, H-2), 3.46 (dd, J = 9.5, 2.8 Hz, H-3, H-5, H-6a, H-6b). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.0, 162.8,

162.3, 139.2, 138.7, 138.0, 128.39, 128.35, 128.0, 127.9, 127.7, 127.6, 127.5, 127.2, 127.0, 97.7, 91.6, 90.6, 89.9 (C-1), 82.7 (C-3), 77.5 (C-5), 74.2 (C-4), 74.1, 73.5, 72.8, 70.2 (C-2), 68.5 (C-6), 56.4, 56.0, 55.43, 55.41. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{40}O_8SNa$, 655.2341; found, 655.2327.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-galactopyranoside (11b): *Via* general procedure C starting from **11a** (0.541g, 0.998 mmol.) Silica gel flash column chromatography (0% - 30% Et_2O in toluene) afforded **11b** (0.117 g, 0.200 mmol, 20%). **TLC**: (Et_2O/toluene, 50/50 v/v): R_f = 0.61; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 5H), 7.36 – 7.13 (m, 15H), 4.89 (d, *J* = 11.4 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.54 (d, *J* = 9.6 Hz, H-1), 4.45 (q, *J* = 11.7 Hz, 2H), 4.00 (d, *J* = 2.4 Hz, H-4), 3.86 – 3.80 (m, 2H, H-2), 3.68 – 3.58 (m, 2H, H-5, H-6a, H-6b), 3.55 (dd, *J* = 9.3, 2.7 Hz, H-3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 131.4, 129.1, 128.9, 128.6, 128.5, 128.2, 128.1, 128.0, 127.86, 127.84, 127.79, 127.6, 127.2, 125.3, 88.0 (C-1), 84.0 (C-3), 77.3 (C-5), 77.2 (C-2), 75.0, 74.5, 73.6, 72.9 (C-4), 72.2, 68.6 (C-6), 62.3, 60.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{35}H_{38}O_6SNa$, 609.2286; found, 609.2274.

4-methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-galactopyranoside (12b): *Via* general procedure C from **12a** (0.197 g, 0.344 mmol.) Silica gel flash column chromatography (0% - 40% EtOAc in *n*-heptane) afforded **12b** (0.142 g, 0.230 mmol 67%). **TLC**: (Et_2O/toluene, 50/50 v/v): R_f = 0.61; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.36 – 7.23 (m, 15H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.87 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.49 – 4.40 (m, 2H, H-1), 3.98 (d, *J* = 2.4 Hz, H-4), 3.86 (t, *J* = 4.4 Hz, 2H), 3.74 (s, 3H, H-2), 3.65 (dd, *J* = 10.4, 5.6 Hz, 2H, H-6a, H-6b), 3.59 – 3.51 (m, H-3, H-5), 3.07 (t, *J* = 6.2 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.6, 138.6, 137.8, 137.4, 134.6, 128.6, 128.4, 128.2, 128.0, 127.9, 127.84, 127.80, 127.73, 127.5, 123.4, 114.4, 88.6 (C-1), 84.0 (C-3), 77.22 (C-5), 77.17

(C-2), 75.0, 74.4, 73.6, 72.8 (C-4), 72.1, 68.6 (C-6), 62.3, 55.3. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{40}O_7SNa$, 639.2392; found, 639.2376.

2,6-dimethoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-galactopyranoside (13b): *Via* general procedure C from **13a** (0.657 g, 1.09 mmol). Silica gel flash column chromatography (0% - 50% EtOAc in *n*-heptane) afforded **13b** (0.465 g, 0.720 mmol, 66%). **TLC**: (EtOAc/n-heptane, 30/70 v/v): R_f = 0.35; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.6 Hz, 2H), 7.33 – 7.18 (m, 15H), 6.54 (d, *J* = 8.4 Hz, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.44 (d, *J* = 9.8 Hz, H-1), 4.37 (dd, *J* = 11.6 Hz, 2H), 4.06 (ddd, *J* = 11.1, 5.6, 2.3 Hz, 1H), 3.94 (ddd, *J* = 11.2, 6.3, 2.0 Hz, 1H), 3.91 (d, *J* = 2.2 Hz, H-4), 3.82 (s, 3H), 3.79 – 3.73 (m, 1H, H-2), 3.71 – 3.64 (m, 1H), 3.62 – 3.53 (m, H-6a, H-6b), 3.49 (dd, *J* = 9.2, 2.8 Hz, H-3), 3.44 (t, *J* = 6.3 Hz, H-5), 1.67 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.0, 138.7, 137.98, 137.96, 130.2, 128.5, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 109.3, 104.3, 88.9 (C-1), 84.7 (C-3), 78.3 (C-2), 77.5 (C-5), 75.1, 74.4, 73.5, 73.4 (C-4), 72.3, 69.1 (C-6), 61.8, 56.2. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{37}H_{42}O_8SNa$, 669.2498; found, 669.2484.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-galactopyranoside (14b): *Via* general procedure C starting from **14a** (0.371 g, 0.586 mmol) Silica gel flash column chromatography (0% - 20% EtOAc in toluene) afforded **14b** (0.162 g, 0.240 mmol, 41%). **TLC**: (EtOAc/n-heptane, 30/70 v/v): R_f = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 15H), 6.11 (s, 2H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.68 (dd, *J* = 28.1, 11.6 Hz, 2H), 4.55 (d, *J* = 11.7 Hz, 1H), 4.37 (q, *J* = 11.6 Hz, 2H), 4.30 (d, *J* = 9.8 Hz, H-1), 4.06 (ddd, *J* = 11.3, 5.3, 2.6 Hz, 1H), 3.99 – 3.87 (m, 1H, H-4), 3.80 (m, 10H), 3.72 (t, *J* = 9.5 Hz, 1H, H-2), 3.63 – 3.51 (m, H-6a, H-6b), 3.48 (dd, *J* = 9.2, 2.8 Hz, H-3), 3.42 (t, *J* = 6.3 Hz, H-5). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.20, 162.15, 138.7, 138.03, 138.02, 128.5, 128.4, 128.2, 127.97, 127.95, 127.8, 127.7, 127.6, 127.5, 100.8, 91.2, 89.8 (C-1), 84.7 (C-3),

78.1 (C-2), 77.4 (C-5), 75.1, 74.4, 73.6, 73.4 (C-4), 72.3, 69.2 (C-6), 61.8, 56.2, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{38}H_{44}O_9SNa$, 699.2603; found, 699.2593.

2,4,6-trimethoxyphenyl 3,4,6-Tri-*O*-(4-chlorobenzyl)-1-thio-*β*-D-glucopyranoside (15a): *via* general procedure B starting from **2** (1.0 g, 1.9 mmol). The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) to afford **15a** as white solid (0.84 g, 1.2 mmol, 61%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.52. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 8H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.11 (s, 2H), 4.99 (d, *J* = 11.4 Hz, 1H), 4.75 – 4.62 (m, 2H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.3 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.18 (d, *J* = 9.4 Hz, 1H, H-1), 3.85 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 9H), 3.77 – 3.73 (m, 2H, H-6a, H-6b), 3.56 (t, *J* = 8.7 Hz, 1H, H-3), 3.47 (t, *J* = 9.2 Hz, 1H, H-4), 3.42 (dt, *J* = 9.7, 2.5 Hz, 1H, H-5), 3.26 (td, *J* = 9.1, 2.0 Hz, 1H, H-2). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.1, 163.0, 137.3, 136.9, 136.7, 133.34, 133.26, 133.24, 129.2, 129.0, 128.9, 128.42, 128.39, 91.5, 88.4 (C-1), 85.4 (C-3), 79.9 (C-5), 76.7 (C-4), 74.2, 74.1, 73.2 (C-2), 72.9, 69.0 (C-6), 56.3, 55.4; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{37}Cl_3O_8SNa$, 757.1172; found, 757.1148.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-1-thio-*β*-D-glucopyranoside (16a): *via* general procedure B starting from **3** (2.01 g, 3.22 mmol). The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) to afford **16a** as white solid (1.35 g, 1.61 mmol, 50%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.52. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.18 – 7.13 (m, 3H), 7.09 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.12 (s, 2H), 5.08 (d, *J* = 12.8 Hz, 1H), 4.77 (m, 2H), 4.58 (d, *J* = 12.8 Hz, 1H), 4.52 (d, *J* = 12.9 Hz, 1H), 4.46 (d, *J* = 12.8 Hz, 1H), 4.20 (d, *J* = 9.5 Hz, 1H, H-1), 3.85 (d, *J* = 2.0 Hz, 1H), 3.81 (m, 11H, H-6a, H-6b), 3.62 (t, *J* = 8.7 Hz, 1H, H-3), 3.55 (dd, *J* = 9.7, 8.7 Hz, 1H, H-4), 3.46 (dt, *J* = 9.7, 2.6 Hz, 1H, H-5), 3.27 (ddd, *J* = 9.5, 8.7, 2.0 Hz, 1H, H-2). **^{13}C{^{1}H}**

NMR (126 MHz, $CDCl_3$) δ 163.2, 163.1, 135.2, 134.74, 134.73, 133.67, 133.63, 133.57, 133.4, 133.2, 133.0, 130.1, 130.0, 129.6, 128.93, 128.85, 127.0, 126.9, 96.1, 91.5, 88.4 (C-1), 85.7 (C-3), 79.4 (C-5) 76.7 (C-4), 73.2 (C-2), 71.2, 71.1, 70.0, 69.6 (C-6), 56.4, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{34}Cl_6O_8SNa$, 859.0003; found, 858.9974.

2,4,6-trimethoxyphenyl 3,4,6-tri-O-(4-chlorobenzyl)-1-thio-β-D-galactopyranoside (17a): *Via* general procedure B starting from **5** (0.97 g, 1.87 mmol) and 2,4,6-trimethoxythiophenol. Silica gel flash column chromatography (0% - 20% - Et_2O in toluene) afforded **17a** (0.85 g, 1.12 mmol, 60%). **TLC**: (Et_2O/toluene, 20/80 v/v): R_f = 0.39; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 6.98 (m, 12H), 6.17 (s, 2H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.69 – 4.63 (m, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 4.39 (d, *J* = 11.9 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 4.15 (d, *J* = 9.3 Hz, H-1), 3.86 – 3.78 (m, 9H, H-4), 3.73 – 3.65 (m, H-2), 3.61 – 3.49 (m, H-5, H-6a, H-6b), 3.43 (dd, *J* = 9.4, 2.8 Hz, H-3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.0, 162.9, 137.5, 137.2, 136.4, 133.6, 133.2, 132.7, 129.1, 128.8, 128.6, 128.5, 128.2, 128.1, 97.5, 91.5, 90.6, 89.8 (C-1), 82.6 (C-3), 77.2 (C-5), 74.4 (C-4), 73.2, 72.7, 72.1, 70.3 (C-2), 68.3 (C-6), 56.4, 56.0, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{37}Cl_3O_8SNa$, 757.1172; found, 757.1148.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-1-thio-*β*-D-galactopyranoside (18a): *Via* general procedure B starting from **6** (1.05 g, 1.70 mmol and 2,4,6-trimethoxythiophenol. Silica gel flash column chromatography (0% - 20% Et_2O in toluene) afforded **18a** (0.71g, 0.851 mmol, 50%). **TLC**: (Et_2O/toluene, 20/80 v/v): R_f = 0.49; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.00 (m, 9H), 6.19 (s, 2H), 4.92 (d, *J* = 13.3 Hz, 1H), 4.85 (d, *J* = 13.5 Hz, 1H), 4.75 (d, *J* = 13.4 Hz, 1H), 4.54 (d, *J* = 12.7 Hz, 1H), 4.48 (d, *J* = 13.5 Hz, 1H), 4.44 (d, *J* = 12.7 Hz, 1H), 4.20 (d, *J* = 9.0 Hz, H-1), 3.96 (d, *J* = 2.5 Hz, H-4), 3.89 – 3.75 (m, 9H), 3.71 – 3.56 (m, H-2, H-5, H-6a, H-6b), 3.53 (dd, *J* = 9.2, 2.5 Hz, H-3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.2, 162.9, 135.5, 135.0, 134.1, 134.0, 133.8, 133.6, 133.1,

133.0, 132.0, 130.2, 129.8, 129.2, 129.0, 128.94, 128.85, 128.4, 128.2, 127.1, 126.8, 125.3, 97.1, 91.5, 89.5 (C-1), 82.9 (C-3), 76.8 (C-5), 74.8 (C-4), 70.6, 70.1 (C-2), 69.9, 69.7, 68.4 (C-6), 56.4, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{36}H_{34}Cl_6O_8SNa$, 859.0003; found, 859.0024.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(4-chlorobenzyl)-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-glucopyranoside (15b): *via* general procedure C starting from **15a** (0.127 g ,0.172 mmol.) The crude product was purified by silica gel flash column chromatography (20% to 60% EtOAc in *n*-heptane) affording **15b** as a white solid (0.11 g, 0.141 mmol, 82%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.24. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 9H), 7.18 – 7.13 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.12 (s, 2H), 4.84 (d, *J* = 11.3 Hz, 1H), 4.75 (d, *J* = 11.3 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.49 (d, *J* = 11.3 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 9.9 Hz, 1H, H-1), 4.01 (ddd, *J* = 10.7, 5.5, 2.5 Hz, 1H), 3.93 (ddd, *J* = 10.7, 6.8, 2.5 Hz, 1H), 3.82 (s, 6H), 3.80 (s, 3H), 3.74 – 3.68 (m, 1H), 3.67 (dd, *J* = 11.4, 2.0 Hz, 1H, H-6a), 3.63 – 3.51 (m, 2H, H-3, H-6b), 3.45 (t, *J* = 9.4 Hz, 1H, H-4), 3.37 – 3.28 (m, 2H, H-2, H-5); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.4, 162.1, 136.8, 136.6, 136.3, 133.56, 133.54, 133.3, 129.1, 128.9, 128.6, 128.5, 128.4, 99.7, 91.2, 88.5 (C-1), 87.0 (C-4), 81.7 (C-2), 79.4 (C-5), 78.1 (C-3), 74.8, 74.7, 74.0, 72.8, 69.4 (C-6), 61.8, 56.2, 55.3; **HRMS (ESI-TOF)** (m/z): $[M+Na]^+$ Calcd for $C_{38}H_{41}Cl_3O_9SNa$, 801.1435; found, 801.1399.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-glucopyranoside (16b): *via* general procedure C starting from **16a** (0.593 g, 0.710 mmol.) The crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane) affording **16b** as a white solid (0.45 g, 0.511 mmol, 72%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.19 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.10 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.12 (s, 2H), 4.92 (d, *J* = 13.1 Hz, 1H), 4.81 (d, *J* = 13.1 Hz,

1H), 4.71 (d, *J* = 12.7 Hz, 1H), 4.59 (d, *J* = 12.7 Hz, 1H), 4.54 (d, *J* = 13.0 Hz, 1H), 4.47 (d, *J* = 13.0 Hz, 1H), 4.41 (d, *J* = 9.9 Hz, 1H, H-1), 4.01 – 3.87 (m, 2H), 3.83 (s, 6H), 3.80 (s, 3H), 3.79 – 3.67 (m, 5H, H-6), 3.64 (t, *J* = 8.8 Hz, 1H, H-3), 3.55 (t, *J* = 9.4 Hz, 1H, H-4), 3.49 (s, 1H), 3.41 – 3.32 (m, 2H, H-2, H-5); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.4, 162.1, 134.7, 134.6, 134.3, 133.9, 133.7, 133.4, 133.1, 132.7, 130.1, 129.7, 129.3, 129.0, 128.94, 128.92, 127.1, 127.00, 126.98, 99.7 , 91.2, 88.7 (C-1), 87.2 (C-3), 81.7 (C-2), 79.0 (C-5), 78.1 (C-4), 74.9, 71.7, 71.1, 70.0 (C-6), 61.9, 56.2, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{38}H_{38}Cl_6O_9SNa$, 903.0265; found, 903.0224.

2,4,6-trimethoxyphenyl 3,4,6-tri-O-(4-cyanobenzyl)-2-O-(2-hydroxyethyl)-1-thio-β-D-glucopyranoside (19b): 15b (0.15 g, 0.2 mmol), ^{t}BuXPhos-Pd-G3 (0.01 mmol, 5 mol%), ^{t}BuXPhos (0.01 mmol, 5 mol%) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.3 mmol) were added to a solution of 1,4-dioxane (1.3 mL) and 0.05 M KOAc in degassed water (1.3 mL) The mixture was vigorously at 100°C for 4h. The reaction was cooled to rt and diluted with EtOAc (50 mL) and brine (50 mL). The aqueous layer was further extracted with EtOAc (2 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified using silica gel flash column chromatography (0-80% EtOAc in *n*-heptane to obtain the product **19b** (0.16 g, 93%). **TLC**: (EtOAc/n-heptane, 60/40 v/v): R_f = 0.16. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.22 (m, 12H), 6.13 (s, 2H), 4.96 (d, *J* = 12.5 Hz, 1H), 4.79 (d, *J* = 12.5 Hz, 1H), 4.74 (d, *J* = 12.5 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.53 (q, *J* = 12.8 Hz, 2H), 4.45 (d, *J* = 9.9 Hz, H-1), 3.96 (dd, *J* = 5.2, 2.7 Hz, 2H), 3.82 (d, *J* = 6.5 Hz, 9H), 3.69 (m, 1H, H-6a, H-6b), 3.61 (t, *J* = 8.9 Hz, H-3), 3.51 (t, *J* = 9.4 Hz, H-4), 3.41 – 3.33 (m, H-2, H-5). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.5, 162.1, 143.8, 143.4, 143.2, 132.3, 132.2, 132.1, 127.8, 127.5, 127.4, 118.7, 118.6, 118.5, 111.64, 111.61, 111.3, 99.4, 91.2, 88.3 (C-1), 87.2 (C-3), 81.9 (C-2), 79.3 (C-5), 78.3 (C-4), 74.9, 74.4, 73.7, 72.7, 69.7 (C-6), 61.9, 56.3, 55.4. δ **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{41}H_{41}N_3O_9SNa$, 774.2461; found, 774.2465.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(4-chlorobenzyl)-2-*O*-(2-hydroxyethyl)-1-thio-β-D-galactopyranoside (17b): *Via* general procedure C starting from **17a** (0.55g, 0.748 mmol). Silica gel flash column chromatography (0% - 50% Et_2O in toluene) afforded **17b** (0.51 g, 0.634 mmol, 85%). **TLC**: (Et_2O/toluene, 30/70 v/v): R_f = 0.21; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.09 (m, 12H), 6.11 (s, 2H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.63 (m, 2H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.32 – 4.27 (m, 1H, H-1), 4.04 (ddd, *J* = 10.9, 5.6, 2.3 Hz, 1H), 3.96 – 3.89 (m, 1H), 3.81 – 3.72 (m, 10H, H-4), 3.68 (t, *J* = 9.5 Hz, 1H), 3.60 – 3.51 (m, H-6a, H-6b), 3.49 – 3.39 (m, H-3, H-5). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.3, 162.1, 137.0, 136.40, 136.39, 133.63, 133.58, 133.2, 129.2, 129.0, 128.8, 128.7, 128.5, 128.3, 100.5, 91.1, 89.8 (C-1), 84.6 (C-3), 78.2 (C-2), 77.2 (C-5), 75.1, 73.8 (C-4), 73.6, 72.7, 71.6, 69.0 (C-6), 61.8, 56.2, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{38}H_{41}Cl_3O_9SNa$, 801.1434; found, 801.1419.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-2-*O*-(2-hydroxyethyl)-1-thio-*β*-D-galactopyranoside (18b): *Via* general procedure C starting from **18a** (0.500 mg, 0.599 mmol). Silica gel flash column chromatography (0% - 20% Et_2O in toluene) afforded **18b** (0.39 g, 0.443 mmol, 74%). **TLC**: (Et_2O/toluene, 30/70 v/v): R_f = 0.37; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.10 (m, 9), 6.13 (s, 2H), 4.91 (d, *J* = 13.2 Hz, 1H), 4.75 (m, 2H), 4.55 (d, *J* = 13.2 Hz, 1H), 4.51 (d, *J* = 12.6 Hz, 1H), 4.40 (d, *J* = 12.6 Hz, 1H), 4.33 (d, *J* = 9.8 Hz, H-1), 4.05 – 3.99 (m, 1H, H-4), 3.93 – 3.87 (m, 1H), 3.86 – 3.75 (m, 10H), 3.76 – 3.64 (m, 1H, H-6a, H-2), 3.61 (dd, *J* = 9.3, 5.5 Hz, H-6b), 3.58 – 3.50 (m, H-3, H-5). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.4, 162.2, 135.0, 134.2, 134.1, 134.0, 133.9, 133.4, 133.2, 132.4, 130.4, 129.76, 129.75, 129.2, 129.1, 129.0, 128.6, 128.2, 127.3, 127.01, 127.00, 125.3, 100.3, 91.1, 90.0 (C-1), 84.9 (C-3), 78.2 (C-2), 76.7 (C-5), 75.2, 74.60(C-4), 71.1, 70.0, 69.1, 68.9 (C-6), 61.8, 56.2, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{38}H_{38}Cl_6O_9SNa$, 903.0265; found, 903.0303.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(4-cyanobenzyl)- 2-*O*-(2-hydroxyethyl)-1-thio-β-D-galactopyranoside (20b): 17b (0.178 mg, 0.222 mmol), ^{t}BuXPhos-Pd-G3 (0.01 mmol, 5 mol%), ^{t}BuXPhos (0.01 mmol, 5 mol%) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.3 mmol) were added to a solution of dioxane (1.3 mL) and 0.05 M KOAc in degassed water (1.3 mL) The mixture was vigorously at 100°C for 4h. The reaction was cooled to rt and diluted with EtOAc (50 mL) and brine (50 mL). The aqueous layer was further extracted with EtOAc (2 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified using silica gel flash column chromatography (0 - 100% EtOAc in *n*-heptane to obtain the product **20b** (0.16 g, 0.207 mmol, 93%). **TLC**: (EtOAc/n-heptane, 60/40 v/v): R_f = 0.08. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 – 7.24 (m, 12H), 6.13 (s, 1H), 4.92 (d, *J* = 12.7 Hz, 1H), 4.79 (s, 2H), 4.57 (d, *J* = 12.7 Hz, 1H), 4.50 (d, *J* = 12.7 Hz, 1H), 4.42 (d, *J* = 12.7 Hz, 1H), 4.35 (d, *J* = 9.8 Hz, H-1), 4.03 (ddd, *J* = 10.7, 5.5, 2.3 Hz, 1H), 3.97 – 3.90 (m, 1H, H-4), 3.82 (m, 10H), 3.75 – 3.58 (m, 1H, H-2, H-6a, H-6b), 3.55 – 3.48 (m, H-3, H-5). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.4, 162.2, 143.8, 143.3, 143.2, 132.4, 132.2, 132.1, 127.8, 127.5, 127.4, 118.7, 118.60, 118.55, 111.7, 111.6, 111.3, 100.1, 91.2, 89.7 (C-1), 84.7 (C-3), 78.4 (C-2), 76.9 (C-5), 75.3, 74.8 (C-4), 73.7, 72.5, 71.6, 69.3 (C-6), 61.8, 56.2, 55.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{41}H_{41}N_3O_9SNa$, 774.2461; found, 774.2448.

Methyl 3,4,6-tribenzyl-2-*O*-(2-benzenethioethyl)-α/β-D-glucopyranosyl-(1→6)- 2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (22): *Via* general procedure E and donor **7b** (53 mg, 0.090 mmol Silica gel flash column chromatography (0% → 40% - EtOAc in *n*-heptane) afforded **22** as an anomeric mixture (69 mg, 0.064 mmol, 71%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.5; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.55 – 7.44 (m, 2H), 7.44 – 7.17 (m, 24H), 7.17 – 7.05 (m, 3H), 6.14 (t, *J* = 9.9 Hz, 1H, (H-3')), 5.53 (t, *J* = 9.9 Hz, 1H, (H-4')), 5.25 (dd, *J* = 10.3, 3.7 Hz, 1H, (H-2')), 5.18 (d, *J* = 3.7 Hz, 1H, (H-1')), 4.92 (d, *J* = 3.5 Hz, 1H, (H-1)), 4.87 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 11.1 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.55 (d, *J*

= 12.1 Hz, 1H), 4.45 (d, *J* = 11.0 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.32 (ddd, *J* = 9.7, 6.6, 2.0 Hz, 1H, (H-5')), 3.93 – 3.83 (m, 3H, (H-6', H-3)), 3.83 – 3.75 (m, 2H, H-5), 3.72 – 3.59 (m, 3H, (H-6', H-4, H-6)), 3.52 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6), 3.48 – 3.39 (m, 4H, (H-2)), 3.17 – 3.00 (m, 2H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 165.82, 165.78, 165.2, 138.8, 138.5, 137.9, 133.3, 133.0, 129.91, 129.89, 129.86, 129.81, 129.6, 129.4, 129.2, 129.1, 128.9, 128.40, 128.38, 128.36, 128.31, 128.30, 128.23, 128.22, 127.88, 127.86, 127.61, 127.60, 127.5, 126.1, 97.0 (C-1), 96.7 (C-1'), 81.4 (C-3), 81.0 (C-2), 77.5 (C-4), 75.4, 74.8, 73.4, 72.2 (C-2'), 70.6 (C-3'), 70.3 (C-5), 69.9, 69.6 (C-4'), 68.5 (C-5'), 68.2 (C-6), 66.6 (C-6'), 55.6, 33.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{63}H_{62}O_{14}SNa$, 1097.3758; found, 1097.3798

Methyl 3,4,6-tribenzyl-2-*O*-(2-(4-methoxybenzenethio)ethyl)-α-D-glucopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (23): *Via* general procedure E and donor **8b** (68 mg, 0.111 mmol.) Silica gel flash column chromatography (0% → 40% - EtOAc in *n*-heptane) afforded **23** as an anomeric mixture (76 mg, 0.069 mmol 62%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.5; **^1H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.49 (dt, *J* = 16.8, 7.4 Hz, 2H), 7.44 – 7.20 (m, 22H), 7.14 – 7.05 (m, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 6.13 (t, *J* = 9.9 Hz, 1H, (H-3')), 5.53 (t, *J* = 9.9 Hz, 1H, (H-4')), 5.25 (dd, *J* = 10.2, 3.7 Hz, 1H, (H-2')), 5.18 (d, *J* = 3.7 Hz, 1H, (H-1')), 4.92 (d, *J* = 3.5 Hz, 1H, (H-1)), 4.86 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.32 (ddd, *J* = 9.8, 6.8, 2.2 Hz, 1H, (H-5')), 3.92 – 3.81 (m, 3H, (H-6', H-3, H-5)), 3.81 – 3.66 (m, 6H, (H-6')), 3.66 – 3.56 (m, 2H, (H-4, H-6)), 3.52 (dd, *J* = 10.7, 2.0 Hz, 1H, (H-6)), 3.46 – 3.37 (m, 4H, (H-2)), 3.07 – 2.88 (m, 2H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 165.82, 165.78, 165.3, 159.0, 138.8, 138.5, 137.9, 133.5, 133.3, 133.0, 129.91, 129.89, 129.7, 129.2, 129.1, 128.9, 128.38, 128.36, 128.32, 128.29, 128.24, 128.22, 127.91, 127.87, 127.62, 127.60, 127.5, 125.8, 114.6, 97.1 (C-1), 96.7 (C-1'), 81.4 (C-3), 80.9 (C-2), 77.5 (C-4), 75.4, 74.8, 73.4, 72.2 (C-2'), 70.6 (C-3'), 70.3 (C-5), 70.1, 69.6 (C-4'), 68.5

(C-5'), 68.2 (C-6), 66.6 (C-6'), 55.6, 55.3, 35.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{64}H_{64}O_{15}SNa$, 1127,3864; found, 1127,3879.

Methyl 3,4,6-tribenzyl-2-*O*-(2-(2,6-dimethoxybenzenethio)ethyl)-α-D-glucopyranosyl-(1→6)- 2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (24): *Via* general procedure E and donor **9b** (35 mg, 0.054 mmol.) Silica gel flash column chromatography (0% → 40% - EtOAc in *n*-heptane) afforded **24** (51 mg, 0.045 mmol, 83%) as an α/β mixture. **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.95 – 7.89 (m, 2H), 7.85 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.55 – 7.44 (m, 2H), 7.39 (dt, *J* = 18.0, 7.7 Hz, 3H), 7.35 – 7.17 (m, 20H), 7.11 (dd, *J* = 7.7, 1.9 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 2H), 6.12 (t, *J* = 9.8 Hz, 1H, (H-3')), 5.49 – 5.41 (m, 1H, (H-4')), 5.23 (dd, *J* = 10.2, 3.7 Hz, 1H, (H-2')), 5.16 (d, *J* = 3.8 Hz, 1H, (H-1')), 4.92 (d, *J* = 3.4 Hz, 1H, (H-1)), 4.84 (d, *J* = 10.9 Hz, 1H), 4.78 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 10.9 Hz, 1H), 4.44 (d, *J* = 11.1 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.33 (ddd, *J* = 9.9, 7.3, 2.1 Hz, 1H, (H-5')), 3.93 – 3.76 (m, 9H, (H-6', H-3, H-5)), 3.72 – 3.63 (m, 4H, (H-6', H-6)), 3.60 (dd, *J* = 10.1, 8.9 Hz, 1H, (H-4)), 3.53 (dd, *J* = 10.7, 2.0 Hz, 1H, (H-6)), 3.50 – 3.36 (m, 4H, (H-2)), 3.01 (dt, *J* = 12.9, 7.3 Hz, 1H), 2.97 – 2.87 (m, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.8, 165.7, 165.3, 161.1, 138.8, 138.6, 138.0, 133.3, 133.0, 129.9, 129.8, 129.6, 129.2, 129.1, 128.9, 128.37, 128.35, 128.30, 128.25, 128.22, 128.19, 128.0, 127.9, 127.6, 127.5, 127.41, 127.40, 109.4, 104.0, 97.1 (C-1), 96.6 (C-1'), 81.5 (C-3), 81.0 (C-2), 77.4 (C-4), 75.3, 74.7, 73.4, 72.2 (C-2'), 71.0, 70.6 (C-3'), 70.3 (C-5), 69.7 (C-4'), 68.4 (C-5'), 68.3 (C-6), 66.8 (C-6'), 56.1, 55.6, 33.4; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{65}H_{66}O_{16}SNa$, 1157.3969; found, 1157.3954.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-(2,4,6-trimethoxyphenylthio)ethyl)-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (25): *via* general procedure E starting from glucosyl donor **10b** (48 mg; 0.071 mmol). The crude product was purified by silica gel flash column chromatography (10% to 40% EtOAc in *n*-heptane) affording **25** as an anomeric mixture

(63 mg, 76%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.35. **^{1}H NMR ^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.92 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.85 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.53 – 7.44 (m, 2H), 7.43 – 7.34 (m, 3H), 7.34 – 7.22 (m, 17H), 7.11 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.11 (m, 3H, (H-3')), 5.45 (dd, *J* = 10.3, 9.5 Hz, 1H, (H-4')), 5.23 (dd, *J* = 10.2, 3.7 Hz, 1H, (H-2')), 5.16 (d, *J* = 3.7 Hz, 1H, (H-1')), 4.93 (d, *J* = 3.4 Hz, 1H, (H-1)), 4.84 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 10.9 Hz, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.43 (d, *J* = 11.1 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.34 (ddd, *J* = 10.0, 7.4, 2.1 Hz, 1H, (H-5')), 3.92 – 3.86 (m, 2H, (H-6', H-5)), 3.79, m, 10H, (H-3)), 3.72 – 3.58 (m, 5H, (H-6', H-4, H-6)), 3.53 (dd, *J* = 10.7, 2.0 Hz, 1H, (H-6)), 3.44 – 3.36 (m, 4H, (H-2)), 2.91 (ddd, *J* = 12.9, 8.3, 6.5 Hz, 1H), 2.82 (ddd, *J* = 12.9, 8.4, 7.0 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.8, 165.7, 165.3, 162.0, 161.8, 138.8, 138.6, 138.0, 133.3, 133.0, 129.9, 129.6, 129.2, 129.1, 128.9, 128.36, 128.33, 128.29, 128.23, 128.21, 128.17, 128.0, 127.9, 127.6, 127.5, 127.40, 127.38, 100.8, 97.1 (C-1), 96.6 (C-1'), 90.93 81.5 (C-3), 81.0 (C-2), 77.4 (C-4), 75.3, 74.7, 73.4, 72.2 (C-2'), 71.0, 70.6 (C-3'), 70.3 (C-5), 69.7 (C-4'), 68.4 (C-5'), 68.3 (C-6), 66.8 (C-6'), 56.0, 55.6, 55.3, 33.9; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{66}H_{68}O_{17}SNa$, 1187.4075; found, 1187.4118.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-(benzenethio)ethyl)-α/β-D-galactopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (26): *Via* general procedure E starting from galactosyl donor **11b** (65 mg, 0.112 mmol.) Silica gel flash column chromatography (0% - 20% Et_2O in toluene) afforded **26** as an anomeric mixture (61 mg, 0.062 mmol, 55%). **TLC**: (Et_2O/toluene, 30/70 v/v): R_f = 0.50; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 – 7.79 (m, 6H), 7.54 – 7.06 (m, 29H), 6.12 (t, *J* = 9.8 Hz, 1H), 5.52 (t, *J* = 9.9 Hz, 1H), 5.28 – 5.22 (m, 1H), 5.13 (d, *J* = 3.5 Hz, H-1'), 4.94 – 4.86 (m, H, H-1), 4.76 (dd, *J* = 11.9, 3.6 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.55 (t, *J* = 11.3 Hz, 1H), 4.34 (dt, *J* = 12.0 Hz, 3H), 3.99 (t, *J* = 6.4 Hz, 1H), 3.86 (m, 6H), 3.65 (d, *J* = 11.1 Hz, 1H), 3.52 – 3.39 (m, 2H), 3.36 (m, 3H), 3.11 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.8, 165.3, 138.73, 138.66, 138.1, 133.3, 133.0, 129.9, 129.8, 129.7, 129.29, 129.27, 129.1, 129.0, 128.9, 128.39, 128.36, 128.33, 128.29, 128.25, 128.21, 127.7,

127.6, 127.54, 127.50, 127.45, 97.7 (C-1), 96.8 (C-1'), 78.2, 77.4, 75.0, 74.8, 73.2, 72.8, 72.1, 70.7, 70.1, 69.6, 69.3, 68.6, 68.4, 66.7, 55.5. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{63}H_{62}O_{15}SNa$, 1113.3707; found, 1113.3652.

Methyl 3,4,6-tri-O-benzyl-2-*O*-(2-(4-methoxybenzenethio)ethyl)-α/*β*-D-galactopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (27): *Via* general procedure E and galactosyl donor **12b** (50 mg, 0.081 mmol.) Silica gel flash column chromatography (0% - 25% Et_2O in toluene) afforded **27** as an anomeric mixture (32 mg, 0.029 mmol 36%). **TLC**: (Et_2O/toluene, 50/50 v/v): R_f = 0.64; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.81 (m, 6H), 7.55 – 7.10 (m, 26H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.13 (m, 1H), 5.53 (t, *J* = 9.9 Hz, 1H), 5.24 (td, *J* = 10.2, 3.5 Hz, 2H), 5.13 (d, *J* = 3.5 Hz, H-1'), 4.95 – 4.85 (m, 1H, H-1), 4.76 (m, 1H), 4.67 (m, 1H), 4.54 (d, *J* = 11.3 Hz, 1H), 4.43 – 4.24 (m, 3H), 3.99 (t, *J* = 6.4 Hz, 1H), 3.93 – 3.84 (m, 4H), 3.84 – 3.71 (m, 6H), 3.67 (d, *J* = 10.3 Hz, 2H), 3.45 (m, 2H), 3.38 (m, 3H), 3.00 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.8, 165.4, 159.0, 138.8, 138.7, 138.1, 133.4, 133.3, 133.0, 132.7, 129.9, 129.8, 129.7, 129.30 129.1, 129.0, 128.40, 128.36, 128.32, 128.26, 128.21, 128.20, 127.7, 127.6, 127.54, 127.49, 127.4, 114.6, 97.8 (C-1), 96.8 (C-1'), 78.2, 77.3, 75.1, 74.8, 73.2, 72.8, 72.1, 70.7, 70.2, 69.6, 69.3, 68.7, 68.4, 66.7, 55.5, 55.3, 35.3. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{64}H_{64}O_{15}SNa$, 1127.3863; found, 1127.3816.

Methyl 3,4,6-tri-O-benzyl-2-*O*-(2-(2,6-dimethoxybenzenethio)ethyl)-α-D-galactopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (28): *Via* general procedure E and galactosyl donor **13b** (60 mg, 0.092 mmol.) Silica gel flash column chromatography (0% - 25% Et_2O in toluene) afforded **28** as an anomeric mixture (39 mg, 0.034 mmol 37%). **TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.68; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.81 (m, 6H), 7.53 – 7.12 (m, 25H), 6.47 (d, *J* = 8.4 Hz, 2H), 6.11 (t, *J* = 9.8 Hz, H-3'), 5.45 (t, *J* = 9.9 Hz, H-4'), 5.23 (dd, *J* = 10.2, 3.6 Hz, H-2'), 5.11 (d, *J* = 3.5 Hz, H-1'), 4.92 (d, *J* = 3.2 Hz, H-1), 4.87 (d, *J* = 11.4 Hz, 1H), 4.74

(d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 11.3 Hz, 1H), 4.42 – 4.32 (dd, 2H), 4.30 (t, *J* = 9.3 Hz, H-5'), 4.01 (t, *J* = 6.5 Hz, H-5), 3.92 – 3.83 (m, H-2, H-4, H-6a'), 3.83 – 3.62 (m, 8H, H-3, H-6b'), 3.45 (t, *J* = 6.1 Hz, H-6a, H-6b), 3.33 (s, 3H), 3.06 – 2.87 (m, 2H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 165.8, 165.4, 161.1, 138.9, 138.7, 138.1, 133.3, 133.0, 129.93, 129.86, 129.6, 129.3, 129.2, 128.9, 128.40, 128.37, 128.27, 128.25, 128.20, 128.18, 127.7, 127.6, 127.5, 127.43, 127.35, 104.0, 97.7 (C-1), 96.7 (C-1'), 78.2 (C-3), 77.5 (C-2), 75.2 (C-4), 74.8, 73.2, 72.8, 72.1 (C-2'), 71.2, 70.7 (C-3'), 69.7 (C-4'), 69.2 (C-5), 68.6 (C-6), 68.3 (C-5'), 66.7 (C-6'), 56.1, 55.4, 33.4. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{65}H_{66}O_{16}SNa$, 1157.3969; found, 1157.3926.

Methyl 3,4,6-tri-O-benzyl-2-*O*-(2-(2,4,6-trimethoxybenzenethio)ethyl)-α-D-galactopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (29): *Via* general procedure E and galactosyl donor **14b** (44 mg, 0.065 mmol.) Silica gel flash column chromatography (0% - 30% EtOAc in *n*-heptane) afforded **29** (45 mg, 0.039 mmol, 59%). **TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.64; **^1H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.80 (m, 6H), 7.54 – 7.21 (m, 24H), 6.14 – 6.01 (m, 2H, H-3'), 5.48 – 5.41 (m, H-4'), 5.23 (dd, *J* = 10.2, 3.7 Hz, H-2'), 5.12 (t, *J* = 3.8 Hz, H-1'), 4.94 (d, *J* = 3.3 Hz, H-1), 4.88 (d, *J* = 11.4 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.43 – 4.27 (m, 2H, H-5'), 4.01 (t, *J* = 6.7 Hz, H-5), 3.91 – 3.77 (m, 3H, H-2, H-3, H-4, H-6'), 3.77 – 3.63 (m, 8H, H2-6'), 3.45 (dd, *J* = 6.5, 3.4 Hz, H2-6), 3.32 (s, 3H), 3.02 – 2.71 (m, 2H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ 165.79, 165.76, 165.4, 162.1, 161.8, 138.9, 138.8, 138.1, 133.3, 133.0, 130.0, 129.9, 129.7, 129.3, 129.2, 128.9, 128.41, 128.38, 128.28, 128.26, 128.24, 128.20, 127.7, 127.6, 127.51, 127.45, 127.36, 97.8 (C-1), 96.7 (C-1'), 90.9, 78.2 (C-3), 77.6 (C-2), 75.2 (C-4), 74.8, 73.2, 72.8, 72.1 (C-2'), 71.2, 70.7 (C-3'), 69.7 (C-4'), 69.2 (C-5), 68.7 (C-6), 68.3 (C-5'), 66.7 (C-6'), 56.0, 55.41, 55.35. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{66}H_{68}O_{17}SNa$, 1187.4074; found, 1187.4038.

Methyl 3,4,6-tri-*O*-(4-chlorobenzyl)-2-*O*-(2-(2,4,6-trimethoxyphenylthio)ethyl)-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (30): *via* general procedure E starting from glucosyl donor **15b** (67 mg, 0.086 mmol). The crude product was purified by silica gel flash column chromatography (20% to 60% EtOAc in *n*-heptane) yielding **30** as an anomeric mixture (α/β = 7.5/1, 82 mg, 75%). **TLC** (Et_2O/toluene 20/80 v/v): R_f = 0.61; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.93 – 7.90 (m, 2H), 7.87 – 7.83 (m, 2H), 7.55 – 7.14 (m, 22H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.16 – 6.07 (m, 3H, H-3'), 5.47 (dd, *J* = 10.3, 9.5 Hz, 1H, H-4'), 5.23 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2'), 5.17 (d, *J* = 3.6 Hz, 1H, H-1'), 4.93 (d, *J* = 3.4 Hz, 1H, H-1), 4.82 (d, *J* = 11.3 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 11.3 Hz, 1H), 4.51 (d, *J* = 12.3 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.34 – 4.29 (m, 1H, H-5'), 4.32 (d, *J* = 12.4 Hz, 1H), 3.91 – 3.74 (m, 12H, H-3, H-5, H-6a'), 3.72 – 3.55 (m, 4H, H-6a, H-6b'), 3.53 (dd, *J* = 10.1, 8.9 Hz, 1H, H-4), 3.48 (dd, *J* = 10.7, 2.1 Hz, 1H, H-6b), 3.42 (s, 3H), 3.38 (dd, *J* = 9.7, 3.5 Hz, 1H, H-2), 2.90 (ddd, *J* = 12.9, 9.0, 5.8 Hz, 1H), 2.81 (ddd, *J* = 13.0, 9.1, 5.9 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.8, 165.7, 165.3, 162.1, 161.8, 137.3, 136.9, 136.3, 133.5, 133.4, 133.20, 133.16, 133.0, 129.90, 129.87, 129.6, 129.21, 129.17, 129.14, 129.0, 128.8, 128.51, 128.48, 128.39, 128.38, 128.37, 128.36, 128.2, 100.8, 96.9 (C-1), 96.7 (C-1'), 91.0, 81.3 (C-3), 81.0 (C-2), 77.3 (C-4), 74.4, 73.7, 72.6, 72.2 (C-2'), 70.8, 70.5 (C-3'), 70.1 (C-5), 69.6 (C-4'), 68.4 (C-5'), 68.3 (C-6), 66.7 (C-6'), 56.1, 55.5, 55.4, 34.0; **HRMS (ESI-TOF)** (*m*/*z*): $[M+Na]^+$ Calcd for $C_{66}H_{65}Cl_3O_{17}SNa$, 1289.2906; found, 1289.2888.

Methyl 3,4,6-tri-O-(4-cyanobenzyl)-2-*O*-(2-(2,4,6-trimethoxybenzenethio)ethyl)-α-D-glucopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (31): *Via* general procedure E starting from glucosyl donor **19b** (56 mg, 0.078 mmol). Silica gel flash column chromatography (0% - 60% EtOAc in *n*-heptane) afforded product **31** (64 mg, 0.05 mmol, 65%). **TLC**: (Et_2O/toluene, 40/60 v/v): R_f = 0.36; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.18 (m, 27H), 6.12 (d, *J* = 12.3 Hz, 2H, H-3'), 5.51 (t, *J* = 9.9 Hz, H-4'), 5.23 (dd, *J* = 10.2, 3.7 Hz, H-2'), 5.19 (d, *J* = 3.6 Hz, H-1'),

5.00 (d, *J* = 12.5 Hz, 1H), 4.97 (d, *J* = 3.4 Hz, H-1), 4.82 (d, *J* = 12.8 Hz, 1H), 4.67 (d, *J* = 12.6 Hz, 1H), 4.56 (d, *J* = 13.6 Hz, 2H), 4.44 (d, *J* = 13.2 Hz, 1H), 4.35 – 4.29 (m, H-5'), 3.95 – 3.84 (m, H-3, H-5, H-6a'), 3.80 (d, *J* = 20.3 Hz, 9H), 3.75 – 3.52 (m, 2H, H-4, H-6b', H-6a, H-6b)), 3.44 (s, H-2), 2.92 – 2.78 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.9, 165.8, 165.3, 162.0, 161.9, 144.2, 143.8, 143.4, 133.5, 133.1, 132.2, 132.14, 132.05, 129.9, 129.8, 129.6, 129.2, 129.0, 128.9, 128.45, 128.41, 128.3, 127.8, 127.6, 127.2, 118.8, 118.7, 118.6, 111.5, 111.4, 111.2, 100.9, 96.82 (C-1'), 96.81 (C-1), 91.0, 81.6 (C-3), 81.0 (C-2), 77.7 (C-4), 74.1, 73.5, 72.4, 72.1 (C-2'), 70.6, 70.5 (C-3'), 69.9 (C-5), 69.5 (C-4'), 69.0 (C-6), 68.5 (C-5'), 66.7 (C-6'), 60.4, 56.1, 55.6, 55.4, 34.2. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{69}H_{65}N_3O_{17}SNa$, 1262.3932; found, 1262.3966.

Methyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-2-*O*-(2-(2,4,6-trimethoxyphenylthio)ethyl)-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (32): *via* general procedure E starting from glucosyl donor **25b** (51 mg, 0.058 mmol). The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) yielding **32** as an anomeric mixture (α/β = 9/1, 69 mg, 81%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.40. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.94 – 7.89 (m, 2H), 7.88 – 7.83 (m, 2H), 7.54 – 7.45 (m, 2H), 7.45 – 7.27 (m, 12H), 7.25 – 7.08 (m, 6H), 6.14 (t, *J* = 9.8 Hz, 1H, H-3'), 6.09 (s, 2H), 5.48 (dd, *J* = 10.3, 9.5 Hz, 1H, H-4'), 5.24 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2'), 5.19 (d, *J* = 3.7 Hz, 1H, H-1'), 4.96 (d, *J* = 3.4 Hz, 1H, H-1), 4.90 (d, *J* = 12.9 Hz, 1H), 4.76 (d, *J* = 13.1 Hz, 1H), 4.67 (d, *J* = 12.9 Hz, 1H), 4.59 (d, *J* = 13.2 Hz, 1H), 4.52 (d, *J* = 13.1 Hz, 1H), 4.42 (d, *J* = 13.3 Hz, 1H), 4.35 (ddd, *J* = 9.8, 7.2, 2.0 Hz, 1H, H-5'), 3.94 – 3.82 (m, 3H, H-5, H-3, H-6a'), 3.81 (s, 3H), 3.78 (s, 6H), 3.71 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6b'), 3.69 – 3.52 (m, 5H, H-4, H-6), 3.46 (s, 3H), 3.42 (dd, *J* = 9.7, 3.4 Hz, 1H, H-2), 2.84 (dddd, *J* = 40.2, 12.9, 9.2, 5.8 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.9, 165.8, 165.3, 162.0, 161.9, 135.1, 134.9, 134.3, 133.8, 133.47, 133.46, 133.41, 133.38, 133.35, 133.2, 133.1, 132.6, 130.0, 129.93, 129.89, 129.86, 129.7, 129.2, 129.1, 129.04, 129.03, 128.83, 128.81, 128.80, 128.42, 128.40, 128.3, 127.0, 126.87, 126.86, 100.7,

96.9 (C-1), 96.8 (C-1'), 91.0, 81.6 (C-3), 81.0 (C-2), 77.5 (C-4), 72.2 (C-2'), 71.4, 71.0, 70.9, 70.6 (C-3'), 70.0 (C-5), 69.8, 69.6 (C-4'), 68.9 (C-6), 68.5 (C-5'), 66.8 (C-6'), 56.1, 55.6, 55.4, 33.9. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{66}H_{62}Cl_6O_{17}SNa$, 1391.1737; found, 1391.1701.

Methyl 3,4,6-tri-O-(4-chlorobenzyl)-2-*O*-(2-(2,4,6-trimethoxybenzenethio)ethyl)-α-D-galactopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (33): *Via* general procedure E starting from galactosyl donor **17b** (50 mg, 0.064 mmol.) Silica gel flash column chromatography (0% - 40% EtOAc in *n*-heptane) afforded **33** (27 mg, 0.021 mmol, 33%). **TLC**: (EtOAc/n-heptane, 60/40 v/v): R_f = 0.75; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 7.82 (m, 6H), 7.55 – 7.05 (m, 21H), 6.10 (m, 2H, H-3'), 5.49 (t, *J* = 9.9 Hz, H-4'), 5.23 (dd, *J* = 10.2, 3.7 Hz, H-2'), 5.15 (d, *J* = 3.6 Hz, H-1'), 4.95 (d, *J* = 3.3 Hz, H-1), 4.79 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 12.1 Hz, 1H), 4.33 – 4.24 (m, 1H, H-5'), 3.99 (t, *J* = 6.7 Hz, H-5), 3.89 – 3.73 (m, 9H, H-2, H-3, H-4, H-6a'), 3.72 – 3.63 (m, 2H, H-6b'), 3.46 – 3.37 (m, H-6a, H-6b), 2.94 – 2.78 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.82, 165.75, 165.4, 162.1, 161.8, 137.3, 137.1, 136.5, 133.44, 133.35, 133.32, 133.12, 133.05, 129.9, 129.8, 129.6, 129.32, 129.25, 129.1, 129.03, 128.92, 128.88, 128.7, 128.6, 128.43, 128.38, 128.36, 128.3, 128.2, 125.3, 97.7 (C-1), 96.8 (C-1'), 90.9, 78.1 (C-3), 77.6 (C-2), 75.5 (C-4), 74.0, 72.5, 72.2, 72.1 (C-2'), 71.0, 70.6 (C-3'), 69.6 (C-4'), 69.0 (C-5), 68.6 (C-6), 68.3 (C-5'), 66.7 (C-6'), 56.1, 55.41, 55.36, 34.1. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{66}H_{65}Cl_3O_{17}SNa$, 1289.2905; found, 1289.2852.

Methyl-3,4,6-tri-O-(4-cyanobenzyl)-2-*O*-(2-(2,4,6-trimethoxybenzenethio)ethyl)-α-D-galactopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (34): *Via* general procedure E starting from galactosyl donor **20b** (60 mg, 0.08 mmol). Silica gel flash column chromatography (0% - 40% - EtOAc in *n*-heptane) afforded **34** as an anomeric mixture (86 mg, 0.069 mmol, 87%). **TLC**: (EtOAc/n-heptane, 60/40 v/v): R_f = 0.51; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 7.78 (m, 6H),

7.66 – 7.24 (m, 21H), 6.11 (m, 2H, H-3'), 5.54 (t, *J* = 9.9 Hz, H-4'), 5.24 (dd, *J* = 10.2, 3.6 Hz, H-2'), 5.17 (d, *J* = 3.6 Hz, H-1'), 5.02 (d, *J* = 2.9 Hz, H-1), 4.95 (m, 2H), 4.72 (d, *J* = 13.1 Hz, 1H), 4.56 (d, *J* = 12.6 Hz, 1H), 4.44 (d, *J* = 13.1 Hz, 1H), 4.37 (d, *J* = 13.1 Hz, 1H), 4.29 (ddd, *J* = 10.1, 6.1, 2.0 Hz, H-5'), 4.07 (t, *J* = 6.6 Hz, H-5), 3.96 – 3.86 (m, H-2, H-3, H-4, H-6a'), 3.82 (s, 3H), 3.77 (s, 6H), 3.75 – 3.60 (m, 2H, H-6b'), 3.56 – 3.45 (m, H-6a, H-6b). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.9, 165.8, 165.4, 162.0, 161.9, 144.3, 143.9, 143.4, 133.43, 133.42, 133.1, 132.3, 132.14, 132.10, 129.9, 129.8, 129.6, 129.2, 129.0, 128.9, 128.5, 128.4, 128.3, 127.8, 127.5, 127.4, 118.8, 118.7, 111.5, 111.4, 111.2, 100.9, 97.6 (C-1), 96.9 (C-1'), 91.0, 78.5 (C-3), 77.7 (C-2), 76.7 (C-4), 74.0, 72.5, 72.2, 72.0 (C-2'), 70.58, 70.55 (C-3'), 69.5 (C-4'), 69.1 (C-6), 68.9 (C-5), 68.3 (C-5'), 66.7 (C-6'), 56.1, 55.5, 55.4, 34.3. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{69}H_{65}N_3O_{17}SNa$, 1262.3932; found, 1262.3873.

Methyl 3,4,6-tri-O-(2,4-dichlorobenzyl)-2-*O*-(2-(2,4,6-trimethoxythiophenyl)ethyl)-α-D-galactopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (35): *Via* general procedure E starting from galactosyl donor **18b** (50 mg, 0.057 mmol). Silica gel flash column chromatography (0% - 40% EtOAc in *n*-heptane) afforded **35** as an anomeric mixture (53 mg, 0.039 mmol, 68%). **TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.5; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 – 7.72 (m, 6H), 7.48 – 6.93 (m, 18H), 6.11 – 5.99 (m, 2H, H-3'), 5.33 (t, *J* = 9.9 Hz, H-4'), 5.16 (dd, *J* = 10.2, 3.7 Hz, H-2'), 5.12 (d, *J* = 9.9 Hz, 1H), 5.04 (d, *J* = 3.6 Hz, H-1'), 4.98 (d, *J* = 10.6 Hz, 1H), 4.81 (s, H-1), 4.72 – 4.49 (m, 4H), 4.31 – 4.20 (m, H-5'), 4.04 (t, *J* = 6.3 Hz, H-5), 3.94 (s, H-4), 3.83 – 3.60 (m, 10H, H-2, H-3, H-6a', H-6b', H-6a), 3.54 (td, *J* = 10.1, 6.0 Hz, 1H), 3.42 (dd, *J* = 9.3, 5.4 Hz, H-6b), 2.91 – 2.64 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.74, 165.71, 165.4, 162.1, 161.8, 137.2, 136.9, 136.8, 134.2, 134.1, 133.5, 133.30, 133.28, 133.0, 129.92, 129.88, 129.86, 129.7, 129.6, 129.5, 129.3, 129.2, 128.9, 128.4, 128.3, 128.24, 128.23, 128.1, 100.9, 97.9 (C-1), 96.7 (C-1'), 90.9, 79.6 (C-3), 77.5 (C-2), 75.9 (C-4), 72.1 (C-2'), 71.6, 70.7 (C-3'), 69.9 (C-4'), 69.6 (C-5), 68.8, 68.7(C-6), 68.5 (C-5'), 68.3, 67.4, 67.2 (C-6'),

56.4, 55.5, 55.4, 33.29. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{66}H_{62}Cl_6O_{17}SNa$, 1391.1736; found, 1391.1805.

Methyl 3,4,6-Tri-*O*-(*o*,*p*-dichlorobenzyl)-2-*O*-(2-(2,4,6-trimethoxyphenylthio)ethyl)-*α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside (38): via general procedure E starting from glucosyl donor **16b** (50 mg; 0.057 mmol) using acceptor **36** The crude product was purified by silica gel flash column chromatography (15% to 35% EtOAc in *n*-heptane) yielding **38** (39.6 mg; 0.025 mmol; 53%) as a mixture of isomers. **TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.6. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.00 (m, 57H, C*H* Ar), 6.09 (s, 1H) 6.01 (s, 2H), 5.70 (d, *J* = 3.7 Hz, 1H, H-1, 5.34 (dt, *J* = 5.9, 4.5 Hz, 1H), 5.01 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 13.4 Hz, 1H), 4.79 – 4.73 (m, 1H), 4.73 – 4.61 (m, 5H), 4.61 – 4.41 (m, 9H, H-1'), 4.38 – 4.23 (m, 3H,), 4.08 – 3.99 (m, 2H), 3.93 (t, *J* = 9.6 Hz, 1H), 3.90 – 3.72 (m, 12H), 3.69 (s, 6H), 3.67 – 3.47 (m, 5H), 3.47 – 3.41 (m, 2H), 3.41 – 3.31 (m, 7H), 3.27 (t, *J* = 9.0 Hz, 0H), 3.18 (dd, *J* = 9.6, 3.8 Hz, 0H), 3.13 – 3.06 (m, 0H), 2.86 – 2.69 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.9, 139.34 – 131.95 (m), 131.36 – 125.97 (m), 102.4, 97.8 (C-1'), 96.2 (C-1), 91.0, 90.9, 82.0, 81.9, 80.83, 80.29, 77.5, 74.5, 73.4, 73.2, 71.6, 71.5, 71.4, 71.1, 70.5, 69.8, 69.4, 69.0, 68.7, 56.71 – 54.63 (m), 33.7, 31.9, 30.2, 22.7, 14.1. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{66}H_{68}O_{14}SCl_6Na$, 1349.2359; found, 1349.2361.

Methyl 3,4,6-Tri-*O*-(*o*,*p*-dichlorobenzyl)-2-*O*-(2-(2,4,6-trimethoxyphenylthio)ethyl)-*α*-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside (39): via general procedure E starting from galactosyl donor **18b** (25 mg; 0.028 mmol) using acceptor **36** The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) yielding **39** (18 mg; 0.014 mmol; 48%). **TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.6. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.04 (m, 24H), 6.01 (s, 2H), 5.75 (d, *J* = 3.8 Hz, 1H (H-1)), 4.98 (d, *J* = 11.1 Hz, 1H), 4.83 (d, *J* = 12.9 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.68 (dd, *J* = 12.6, 5.9 Hz, 2H), 4.62 (d, *J* = 13.6 Hz,

1H), 4.59 – 4.52 (m, 4H (H-1')z), 4.47 (d, *J* = 12.3 Hz, 1H), 4.28 (d, *J* = 12.8 Hz, 1H), 4.21 (d, *J* = 12.9 Hz, 1H), 4.05 (t, *J* = 9.0 Hz, 1H), 3.98 – 3.91 (m, 2H), 3.90 – 3.66 (m, 17H), 3.66 – 3.57 (m, 2H), 3.56 – 3.49 (m, 2H), 3.44 – 3.39 (m, 1H), 3.36 (s, 3H), 2.79 (dddd, *J* = 35.0, 12.8, 9.9, 5.7 Hz, 2H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 161.9, 161.7, 138.8, 138.2, 138.0, 134.9, 134.8, 134.2, 133.9, 133.7, 133.51, 133.48, 133.1, 132.8, 130.1, 129.9, 129.5, 129.1, 128.9, 128.4, 128.3, 128.22, 128.16, 127.9, 127.5, 127.4, 127.2, 127.1, 126.93, 126.91, 100.9, 97.7 (C-1'), 97.0 (C-1), 90.9, 81.9, 80.3, 79.0, 75.6, 74.4, 73.3, 73.2, 72.2, 72.0, 71.2, 69.7, 69.4, 69.3, 68.6, 56.0, 55.3, 55.1, 33.8. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{66}H_{68}O_{14}SCl_6Na$, 1351.2362; found, 1351.2329

Phenyl 3,4,6-Tri-(o,p-dichlorobenzyl)-2-O-(2-(2,4,6-trimethoxyphenylthio)ethyl)-α-D-glucopyranosyl-(1→2)-4,6-O-benzylidene-3-O-(2-methylnaphthyl)-1-thio-α-D-mannopyranoside (40):via general procedure E starting from glucosyl donor **16b** (39 mg; 0.045 mmol) using acceptor **37** The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) yielding **40** (31 mg; 0.023 mmol; 52%).**TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.7. **^1H NMR** (500 MHz, $CDCl_3$) δ 7.89 – 7.69 (m, 4H), 7.57 – 7.33 (m, 12H), 7.32 – 7.19 (m, 7H), 7.19 – 7.08 (m, 3H), 6.03 (s, 2H), 5.72 (s, 1H), 5.63 (d, *J* = 1.5 Hz, 1H, H-1'), 5.42 (d, *J* = 3.7 Hz, 1H, H-1), 5.03 (d, *J* = 12.8 Hz, 1H), 4.92 (d, *J* = 12.4 Hz, 1H), 4.85 (d, *J* = 12.3 Hz, 1H), 4.78 (dd, *J* = 12.7, 4.6 Hz, 2H), 4.59 – 4.46 (m, 2H), 4.46 – 4.36 (m, 2H, H-4'), 4.37 – 4.25 (m, 2H, H-2', H-5'), 4.22 (ddd, *J* = 9.3, 4.9, 2.1 Hz, 1H, H-6a'), 4.04 (dd, *J* = 9.8, 2.9 Hz, 1H, H-3'), 3.94 (m, 2H, H-3, H-6b'), 3.89 – 3.78 (m, 2H, H-5), 3.74 (s, 3H), 3.71 – 3.63 (m, 7H, H-6a), 3.59 – 3.50 (m, 3H, H-4, H-6b), 3.45 (dd, *J* = 9.6, 3.7 Hz, 1H, H-2), 2.87 (ddd, *J* = 13.6, 7.8, 6.1 Hz, 1H), 2.80 (ddd, *J* = 13.3, 7.9, 6.0 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 161.9, 161.7, 137.7, 135.6, 135.3, 134.5, 134.3, 133.8, 133.71, 133.65, 133.5, 133.3, 133.2, 133.02, 133.00, 131.6, 130.2, 129.8, 129.7, 129.1, 129.0, 128.94, 128.88, 128.8, 128.2, 128.1, 128.0, 127.7, 127.03, 126.97, 126.9, 126.7, 126.24, 126.16, 126.0, 125.9, 125.8,

101.6, 101.4, 98.4 (C-1), 91.0, 88.2 (C-1'), 81.3 (C-3), 81.0(C-2), 79.0 (C-4'), 77.9 (C-2'), 77.6 (C-4), 75.7 (C-3'), 72.8, 71.5, 71.3, 70.6 (C-5), 70.0, 69.7, 69.1 (C-6), 68.5 (C-6'), 65.6 (C-5'), 56.0, 55.3, 34.5. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{68}H_{64}O_{13}S_2Cl_6Na$, 1387.1849; found, 1387.1788.

Phenyl 3,4,6-Tri-(o,p-dichlorobenzyl)-2-O-(2-(2,4,6-trimethoxyphenylthio)ethyl)-α-D-galactopyranosyl-(1→2)-4,6-O-benzylidene-3-O-(2-methylnaphthyl)-1-thio-α-D-mannopyranoside (41):via general procedure E starting from galactosyl donor **18b** (44 mg; 0.050 mmol) using acceptor **38** The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) yielding **41** (33 mg; 0.024 mmol; 48%). **TLC**: (EtOAc/n-heptane, 50/50 v/v): R_f = 0.7. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.71 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.54 – 7.41 (m, 6H), 7.38 (m, 3H), 7.36 – 7.27 (m, 6H), 7.23 – 7.16 (m, 5H), 7.13 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.09 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.03 (s, 2H), 5.71 (s, 1H), 5.68 (d, *J* = 1.5 Hz, 1H, H-1'), 5.45 (d, *J* = 3.5 Hz, 1H, H-1), 4.97 – 4.75 (m, 5H), 4.58 (d, *J* = 12.9 Hz, 1H), 4.45 – 4.36 (m, 2H, H-4'), 4.35 – 4.27 (m, 3H, H-2', H-5'), 4.24 – 4.15 (m, 1H, H-6a'), 4.08 (t, *J* = 6.2 Hz, 1H, H-5), 4.03 (dd, *J* = 9.8, 2.9 Hz, 1H, H-3'), 3.99 – 3.87 (m, 4H, H-2, H-3, H-4, H-6b'), 3.87 – 3.78 (m, 1H), 3.74 (s, 4H), 3.68 (s, 6H), 3.60 (ddd, *J* = 9.9, 7.4, 6.2 Hz, 1H), 3.53 (dt, *J* = 8.9, 5.7 Hz, 1H, H-6a), 3.51 – 3.44 (m, 1H, H-6b), 2.95 – 2.84 (m, 1H), 2.80 (ddd, *J* = 13.0, 7.4, 6.0 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.98, 161.68, 137.7, 135.7, 135.1, 134.8, 134.2, 133.8, 133.7, 133.7, 133.6, 133.4, 133.3, 133.0, 131.5, 130.4, 130.3, 129.6, 129.0, 128.93, 128.88, 128.2, 128.1, 128.0, 127.7, 127.5, 127.1, 126.9, 126.6, 126.2, 126.0, 125.9, 125.8, 101., 101.44, 99.2 (C-1), 94.7, 91.0, 88.2 (C-1'), 79.0 (C-4'), 78.2 (C-3), 77.9 (C-2'), 77.5 (C-2), 76.0 (C-4), 75.8 (C-3'), 72.7, 71.2, 70.0, 69.93, 69.86 (C-5), 69.62, 69.59 (C-6), 68.5 (C-6'), 65.6 (C-5'), 56.0, 55.3, 34.7. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{68}H_{64}O_{13}S_2Cl_6Na$, 1385.1864; found, 1385.1842.

2,4,6-trimethoxyphenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-*β*-D-glucopyranoside (42): *via* general procedure D starting from **10a** (98 mg, 0.155 mmol) using BnBr as the benzylation agent. The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) affording **42** as a white solid (81 mg, 73%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.53. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.38 – 7.14 (m, 19H), 6.10 (s, 2H), 5.15 (d, *J* = 10.3 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.84 – 4.76 (m, 3H), 4.69 (d, *J* = 9.7 Hz, 1H, H-1), 4.56 (d, *J* = 10.9 Hz, 1H), 4.46 – 4.32 (m, 2H), 3.78 (s, 6H), 3.75 (s, 3H), 3.74 – 3.55 (m, 4H, H-2, H-3, H-6), 3.52 (dd, *J* = 9.8, 8.9 Hz, 1H, H-4), 3.37 (ddd, *J* = 9.8, 5.6, 1.7 Hz, 1H, H-5). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 162.2, 162.0, 138.67, 138.65, 138.6, 138.2, 128.42, 128.39, 128.3, 128.24, 128.21, 128.0, 127.87, 127.86, 127.7, 127.63, 127.60, 127.5, 99.8, 91.2, 86.9 (C-3), 86.8 (C-1), 82.6 (C-2), 79.8 (C-5), 78.2 (C-4), 75.8, 75.2, 75.0, 73.6, 69.6 (C-6), 56.2, 55.3. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{43}H_{46}O_8SNa$, 745.2811; found, 745.2783.

Methyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-*α*/*β*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (50): *via* general procedure F starting from glucosyl donor **42** (0.40 g; 0.059 mmol). The crude product was purified by silica gel flash column chromatography (10% to 40% EtOAc in *n*-heptane) yielding **50** as a mixture of isomers (46.7 mg, 0.045 mmol, 68%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.57. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.89 (m, 8H), 7.87-7.83 (m, 4H), 7.52 – 7.45 (m, 4H), 7.45 – 7.08 (m, 46H), 6.21 – 6.16 (m, 1H), 6.14 (t, *J* = 8.5 Hz, 1H), 5.53 (dd, *J* = 10.3, 9.5 Hz, 1H), 5.48 (dd, *J* = 10.3, 9.5 Hz, 1H), 5.28 – 5.19 (m, 4H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 2H), 4.84 – 4.71 (m, 6H, *α*-H-1), 4.69 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.56 – 4.42 (m, 6H, *β*-H-1), 4.41 – 4.34 (m, 2H), 4.32 (ddd, *J* = 10.4, 6.6, 2.2 Hz, 1H), 4.13 (dd, *J* = 11.0, 2.2 Hz, 1H), 3.96 (t, *J* = 9.3 Hz, 1H), 3.89 – 3.78 (m, 3H), 3.68 – 3.40 (m, 13H), 3.38 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.81, 165.80, 165.75, 165.4, 165.2, 138.9, 138.59, 138.56, 138.5, 138.4, 138.10, 138.07, 137.9, 133.4, 133.3, 133.04, 133.03, 129.91, 129.88, 129.66, 129.64, 129.3, 129.2, 129.08,

129.06, 129.0, 128.9, 128.4 – 128.3 (m), 128.3 – 128.15 (m), 127.9, 127.91, 127.89, 127.85, 127.8, 127.72, 127.65, 127.62, 127.56, 127.54, 127.47, 127.46, 104.0 (*β*-C-1), 97.2 (*α*-C-1), 96.8, 96.7, 84.5, 82.3, 81.7, 80.0, 77.7, 77.6, 75.7, 75.7, 75.5, 75.00, 74.96, 74.9, 74.80, 74.77, 73.5, 73.42, 73.39, 73.3, 73.1, 72.2, 72.1, 70.6, 70.5, 70.2, 69.9, 69.6, 69.0, 68.9 , 68.64, 68.56, 68.3, 66.6, 55.6, 55.5. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{62}H_{60}O_{14}Na$, 1051.3881; found, 1051.3851.

2,4,6-trimethoxyphenyl 2-O-benzyl-3,4,6-tri-*O*-(2,4-dichlorobenzyl)-1-thio-*β*-D-glucopyranoside (43): *via* general procedure D starting from **16a** (0.074 g, 0.088 mmol) using BnBr as the benzylation agent. The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) yielding **43** as a white solid (49 mg, 60%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.57. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.02 (m, 18H), 6.09 (s, 2H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.94 (d, *J* = 13.1 Hz, 1H), 4.80 – 4.67 (m, 5H, H-1), 4.59 (d, *J* = 12.7 Hz, 1H), 4.48 (d, *J* = 12.9 Hz, 1H), 4.39 (d, *J* = 12.9 Hz, 1H), 3.79 (s, 7H), 3.76 (s, 3H), 3.75 – 3.64 (m, 3H, H-6, H-3), 3.63 – 3.53 (m, 2H, H-2, H-4), 3.38 (ddd, *J* = 9.9, 5.3, 1.9 Hz, 1H, H-5). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.1, 162.0, 138.2, 135.4, 135.0, 134.7, 134.5, 133.8, 133.6, 133.5, 133.3, 133.0, 132.7, 130.4, 130.1, 129.7, 129.4, 128.90, 128.88, 128.8, 128.5, 128.4, 128.3, 128.23, 128.17, 127.7, 126.96, 126.95, 99.5, 91.1, 86.7 (C-1, C-3), 82.4 (C-2), 79.1 (C-5), 78.1 (C-4), 75.1, 71.7, 71.0, 70.0, 56.2, 55.3; **HRMS (ESI-TOF)** (*m*/*z*): $[M+Na]^+$ Calcd for $C_{43}H_{40}O_8SCl_6Na$, 949.0473; found, 949.0464.

Methyl 2-*O*-benzyl-3,4,6-tri-*O*-(2,4-dichlorobenzyl)-1-thio-*α*-D-glucopyranosyl-(1→6)- 2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (51): *via* general procedure F starting from glucosyl donor **43** (0.489 g; 0.053 mmol). The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) yielding **51** as a mixture of isomers (*α*/*β* = 4/1, 37 mg, 57%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.62. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.76 (m, 8H), 7.57 – 7.07 (m, 30H), 6.21 – 6.11 (m, 1H, H-3'), 5.60 – 5.54 (m, 1H, H-4'), 5.28 – 5.19 (m, 2H,

H-1', H-2'), 5.05 (d, *J* = 10.9 Hz, 1H), 4.98 (d, *J* = 12.9 Hz, 1H), 4.94 (d, *J* = 13.0 Hz, 1H), 4.83 – 4.66 (m, 5H, H-1), 4.66 – 4.48 (m, 4H), 4.45 (d, *J* = 13.4 Hz, 1H), 4.39 (d, *J* = 13.3 Hz, 1H), 4.33 (ddd, *J* = 10.3, 6.3, 2.0 Hz, 1H, H-5'), 4.13 (dd, *J* = 11.0, 2.2 Hz, 1H), 3.99 (t, *J* = 9.2 Hz, 1H, H-3), 3.91 – 3.83 (m, 2H, H-5, H-6a'), 3.83 – 3.73 (m, 1H), 3.72 – 3.69 (m, 1H), 3.67 – 3.50 (m, 6H, H-2, H-4, H-6, H-6b'), 3.47 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.84, 165.81, 165.7, 165.5, 165.2, 138.12, 138.05, 135.1, 135.0, 134.9, 134.5, 134.4, 134.2, 133.8, 133.74, 133.67, 133.52, 133.50, 133.44, 133.37, 133.30, 133.25, 133.22, 133.1, 132.7, 130.2, 129.5, 129.4, 127.7, 127.1, 126.8, 97.0 (C-1), 96.9 (C-1'), 84.5, 82.0, 81.6 (C-3), 80.0 (C-2), 77.6, 77.5 (C-4), 74.7, 74.6, 73.0, 72.2 (C-2'), 72.1, 71.6, 71.5, 71.1, 71.0, 70.6 (C-3'), 70.4, 70.0 (C-5), 69.9, 69.8, 69.7, 69.5 (C-4'), 69.2, 69.0, 68.9 (C-6), 68.6 (C-5'), 66.6 (C-6'), 55.60, 55.57; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{62}H_{54}O_{14}Cl_6Na$, 1257.1513; found, 1257.1537.

2,4,6-Trimethoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-propyl-1-thio-*β*-D-glucopyranoside (44): *via* general procedure D starting from **10a** (99 mg, 0.156 mmol) using propyl bromide as the alkylating agent. The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) yielding **44** (91 mg, 87%) as a white solid. **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.54. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 19H), 7.21 – 7.12 (m, 4H), 6.10 (s, 2H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.87 – 4.75 (m, 2H), 4.63 (d, *J* = 9.8 Hz, 1H, H-1), 4.53 (d, *J* = 11.0 Hz, 1H), 4.43 – 4.29 (m, 2H), 4.03 – 3.92 (m, 1H), 3.81 (s, 6H), 3.74 (s, 4H), 3.71 (dd, *J* = 11.6, 1.8 Hz, 1H, H-6a), 3.64 – 3.54 (m, 2H, H-3, H-6b), 3.49 – 3.43 (m, 1H, H-4), 3.41 – 3.30 (m, 2H, H-2, H-5), 1.68 (h, *J* = 7.1 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 162.1, 128.39, 128.35, 128.2, 127.9, 127.83, 127.82, 127.7, 127.6, 127.4, 91.2, 86.9 (C-3), 86.3 (C-1), 82.7 (C-2), 79.9 (C-5), 78.1 (C-4), 75.7, 75.0, 74.9, 73.6, 69.6 (C-6), 56.2, 55.24 23.6, 10.6; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{39}H_{46}O_8SNa$, 697.2811; found, 697.2786.

Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-propyl-1-thio-*α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (52): *via* general procedure F starting from glucosyl donor **44** (40 mg, 0.059 mmol). The crude product was purified by silica gel flash column chromatography (0% to 40% EtOAc in *n*-heptane) affording **52** as a mixture of anomers (37 mg, 62%); **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.32. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 – 7.81 (m, 13H), 7.62 – 7.10 (m, 38H), 6.14 (t, *J* = 9.8 Hz, 1H, H-3'), 5.56 – 5.50 (m, 1H, H-4'), 5.24 (dd, *J* = 10.1 Hz, 3.7 Hz, 1H, H-2'), 5.18 (d, *J* = 3.6 Hz, 1H, H-1'), 4.97 (d, *J* = 3.4 Hz, 1H, H-1), 4.85 – 4.77 (m, 2H), 4.74 (d, *J* = 11.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 11.1 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.36 – 4.31 (m, 1H, H-5'), 3.94 – 3.84 (m, 4H, H-3, H-6a), 3.71 (dd, *J* = 11.2, 2.1 Hz, 1H, H-6a'), 3.68 – 3.49 (m, 5H, H-4, H-6b', H-6, H-7), 3.48 – 3.41 (m, 6H), 1.67 – 1.56 (m, 2H), 0.98 – 0.81 (m, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.4, 167.0, 166.0, 165.9, 165.9, 165.3, 139.0, 138.7, 138.0, 133.43, 133.40, 133.35, 133.33, 133.0, 130.1, 129.8, 129.7, 129., 129.20, 129.12, 129.10, 129.0, 128.50, 128.46, 128.2, 128.0, 127.9, 127.6, 127.47, 127.45, 97.1 (C-1), 96.8 (C-1'), 81.6 (C-3), 80.7 (C-2), 77.5 (C-4), 75.4, 74.8, 72.9 (C-2'), 72.2 (C-7), 70.7 (C-3), 70.4, 70.1 (C-4), 69.73 (C-4'), 69.65, 68.7 (C-5'), 68.4 (C-6), 66.6 (C-6'), 55.6, 55.5, 23.3, 10.6. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{58}H_{60}O_{14}Na$, 1003.3881; found, 1003.3837.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-2-*O*-propyl-1-thio-*β*-D-glucopyranoside (45): *via* general procedure D starting from **16a** (0.10 g, 0.12 mmol) and 1-bromopropane as the alkylating agent. The crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane) yielding **45** as a white solid (88 mg, 84%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.02 (m, 8H), 6.08 (s, 2H), 4.98 (d, *J* = 13.2 Hz, 1H), 4.78 (d, *J* = 13.3 Hz, 1H), 4.73 (d, *J* = 12.7 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H, H-1), 4.57 (d, *J* = 12.7 Hz, 1H), 4.44 (d, *J* = 12.9 Hz, 1H), 4.34 (d, *J* = 12.9 Hz, 1H), 3.97 (dt, *J* = 8.5, 7.0 Hz, 1H), 3.82 (s, 6H), 3.75 (s, 3H), 3.71 (dd, *J* = 11.4, 1.9 Hz, 1H, H-6a), 3.66 – 3.60 (m, 3H, H-3, H-6b), 3.51 (t, *J* = 9.4 Hz, 1H, H-4), 3.40 (dd, *J* = 9.8, 8.7 Hz, 1H, H-2), 3.35

(ddd, *J* = 9.9, 5.5, 1.8 Hz, 1H, H-5), 1.66 – 1.53 (m, 2H), 0.93 – 0.85 (m, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.0, 161.9, 135.1, 134.8, 134.5, 133.7, 133.6, 133.4, 133.3, 133.0, 132.7, 130.1, 129.7, 129.3, 128.90, 128.87, 128.8, 127.0, 126.94, 126.92, 91.2, 86.8 (C-3), 86.2 (C-1), 82.7 (C-2), 79.2 (C-5), 78.0 (C-4), 75.0, 71.6, 70.0 (C-6), 69.9, 56.20, 56.18, 56.15, 55.25, 55.22, 23.5, 10.5. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{39}H_{40}Cl_6O_8SNa$, 901.0472; found, 901.0439.

Methyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-2-*O*-propyl-1-thio-*α*/*β*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (53): V*ia* general procedure F starting from glucosyl donor **45** (50 mg; 0.057 mmol). The crude product was purified by silica gel flash column chromatography (10% to 60% EtOAc in *n*-heptane) yielding **53** as an anomeric mixture (α/β = 3/1, 35 mg, 51%) **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.8. *α*-Anomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 – 7.71 (m, 6H), 7.51 – 6.93 (m, 15H), 6.08 (t, *J* = 9.8 Hz, 1H, H-3'), 5.48 (t, *J* = 9.9 Hz, 1H, H-4'), 5.18 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2'), 5.14 (d, *J* = 3.7 Hz, 1H, H-1'), 4.94 – 4.89 (m, 2H, H-1), 4.72 (d, *J* = 13.1 Hz, 1H), 4.67 (d, *J* = 13.1 Hz, 1H), 4.53 (d, *J* = 13.4 Hz, 1H), 4.46 (d, *J* = 13.1 Hz, 1H), 4.35 (d, *J* = 13.2 Hz, 1H), 4.30 – 4.22 (m, 1H, H-5'), 3.91 – 3.78 (m, 3H, H-3, H-5, H-6'a), 3.71 – 3.32 (m, 10H, H-6a, H-6'b, H-6b, H-4, H-2), 1.57 – 1.45 (m, 2H), 0.87 – 0.76 (m, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.9, 165.8, 165.2, 135.3, 134.9, 134.3, 133.7, 133.48, 133.46, 133.43, 133.39, 133.30, 133.2, 133.1, 132.7, 129.95, 129.94, 129.86, 129.84, 129.82, 129.75, 129.67, 129.64, 129.61, 129.59, 129.3, 129.2, 129.04, 129.01, 128.96, 128.95, 128.92, 128.86, 128.81, 128.5, 128.43, 128.42, 128.32, 128.28, 128.25, 127.02, 126.95, 126.88, 126.86, 96.88 (C-1), 96.85 (C-1'), 81.5 (C-3), 80.7 (C-2), 77.4 (C-4), 72.8, 72.2 (C-2'), 71.4, 71.0, 70.6 (C-3'), 70.1 (C-5'), 69.8, 69.5 (C-4'), 69.0, 68.7(C-5), 66.6, 55.6, 23.3, 10.5. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{58}H_{54}Cl_6O_{14}Na$, 1207.1504; found, 1207.1568.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(benzyl)-2-*O*-(3-hydroxypropyl)-1-thio-*β*-D-glucopyranoside (46): *via* general procedure C starting from **10a** (124 mg; 0.192 mmol) using

$Br(CH_2)_3OTHP$ as the alkylating agent. The crude product was purified by silica gel flash column chromatography (10% to 60% EtOAc in *n*-heptane) yielding **46** as a white solid (84 mg, 62%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.08 (m, 15H), 6.11 (s, 2H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 10.9 Hz, 1H), 4.57 – 4.52 (m, 2H, H-1), 4.41 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.97 – 3.89 (m, 1H), 3.83 (s, 6H), 3.76 (s, 3H), 3.70 (dd, *J* = 11.6, 1.7 Hz, 1H, H-6a), 3.62 (t, *J* = 8.9 Hz, 1H, H-3), 3.57 (dd, *J* = 11.6, 5.8 Hz, 1H, H-6b), 3.46 (t, *J* = 9.4 Hz, 1H, H-4), 3.34 (dd, *J* = 10.0, 8.8 Hz, 1H, H-2), 3.32 – 3.28 (m, 1H, H-5), 3.09 (t, *J* = 6.9 Hz, 1H), 1.96 – 1.84 (m, 1H), 1.82 – 1.73 (m, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.29, 162.25, 138.51, 138.48, 138.0, 128.43, 128.35, 128.2, 127.9, 127.8, 127.71, 127.69, 127.4, 98.8, 91.2, 87.0 (C-1), 86.7 (C-3), 82.1 (C-2), 79.8 (C-5), 78.0 (C-4), 75.7, 74.9, 73.6, 71.4, 69.6 (C-6), 60.6, 56.2, 55.3, 32.7. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{39}H_{46}O_9SNa$, 713.2728; found, 713.2760.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-(2,4,6-trimethoxyphenylthio)propyl)-1-thio-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (54): *via* general procedure E starting from glucosyl donor **46** (56 mg, 0.081 mmol). The crude product was purified by silica gel flash column chromatography (10% to 40% EtOAc in *n*-heptane) yielding **54** as an anomeric mixture (α/β = 2/1, 68 mg, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 – 7.71 (m, 10H), 7.50 – 6.97 (m, 48H), 6.05 (s, 1H), 6.02 (s, 2H), 5.41 (t, *J* = 9.9 Hz, 1H), 5.35 (t, *J* = 9.9 Hz, 1H), 5.19 – 5.13 (m, 2H), 5.11 (d, *J* = 3.6 Hz, 1H, α-H-1'), 5.10 (d, *J* = 3.7 Hz, 1H, β-H-1'), 4.86 (d, *J* = 3.4 Hz, 1H, α-H-1), 4.83 – 4.66 (m, 4H), 4.67 – 4.57 (m, 2H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.45 – 4.39 (m, 2H), 4.37 (d, *J* = 11.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.30 – 4.22 (m, 2H, β-H-1), 3.98 – 3.90 (m, 1H), 3.86 – 3.75 (m, 4H), 3.74 (s, 2H), 3.72 (s, 3H), 3.70 (s, 3H), 3.70 (s, 9H), 3.69 – 3.49 (m, 7H), 3.49 – 3.39 (m, 3H), 3.37 – 3.28 (m, 2H) 3.35 (s, 3H), 3.34 (s, 3H), 3.14 (ddd, *J* = 7.6, 6.3, 2.4 Hz, 1H), 2.77 – 2.63 (m, 2H), 1.77 – 1.56 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.75, 165.71, 165.3, 165.2, 162.07, 162.05, 161.57,

161.55, 138.8, 138.6, 138.10, 138.05, 138.0, 133.30, 133.26, 133.21, 132.97, 132.96, 129.85, 129.80, 129.76, 129.6, 129.21, 129.19, 129.1, 128.9, 128.4, 128.33, 128.28, 128.27, 128.24, 128.20, 128.19, 128.15, 127.93, 127.91, 127.84, 127.83, 127.80, 127.65, 127.63, 127.61, 127.55, 127.54, 127.48, 127.46, 127.37, 127.35, 103.9 (*β*-C-1), 101.6, 101.3, 96.9 (*α*-C-1), 96.7 (*β*-C-1'), 96.6 (*α*-C-1), 90.94, 90.90, 84.5, 82.5, 81.4, 80.7, 77.5, 77.42, 77.3, 77.0, 76.8, 75.5, 75.3, 74.84, 74.77, 74.7, 73.33, 73.31, 72.2, 72.1, 71.7, 70.6, 70.5, 70.3, 69.8, 69.6, 69.4, 69.0, 68.8, 68.7, 68.4, 68.3, 66.7, 56.04, 56.01, 55.5, 55.4, 55.3, 31.8, 31.3, 30.90, 30.87, 30.4, 29.7, 22.6. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{67}H_{70}O_{17}SNa$, 1201.4231; found, 1201.4233.

2,4,6-trimethoxyphenyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-2-*O*-(3-hydroxypropyl)-1-thio-*β*-D-glucopyranoside (47): *via* general procedure C starting from **16a** (0.100 g, 0.119 mmol) using $Br(CH_2)_3OTHP$ as the alkylating agent. The crude product was purified by silica gel flash column chromatography (20% to 50% EtOAc in *n*-heptane) affording **47** as a white solid (78 mg, 73%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 1H), 7.31 (dd, *J* = 14.1, 2.1 Hz, 2H), 7.28 – 7.23 (m, 5H), 7.22 – 7.09 (m, 6H), 6.09 (s, 2H), 4.97 (d, *J* = 13.0 Hz, 1H), 4.79 (d, *J* = 13.0 Hz, 1H), 4.74 (d, *J* = 12.8 Hz, 1H), 4.61 – 4.54 (m, 2H, H-1), 4.47 (d, *J* = 12.8 Hz, 1H), 4.38 (d, *J* = 12.9 Hz, 1H), 4.10 – 4.00 (m, 1H), 3.96 – 3.85 (m, 2H), 3.85 -3.75 (m, 10H), 3.70 (dd, *J* = 11.4, 2.0 Hz, 1H, H-6a), 3.68 – 3.59 (m, 2H, H-3, H-6b), 3.51 (t, *J* = 9.4 Hz, 1H, H-4), 3.42 – 3.29 (m, 2H, H-2, H-5), 2.99 (t, *J* = 6.9 Hz, 1H), 1.92 – 1.79 (m, 1H), 1.79 – 1.65 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.4, 162.2, 134.9, 134.7, 134.4, 133.8, 133.66, 133.64, 133.4, 133.0, 132.8, 130.2, 129.6, 129.5, 128.93, 128.92, 127.1, 126.98, 126.95, 98.6, 91.2, 86.9 (C-1), 86.7 (C-3), 82.1 (C-2), 79.2 (C-5), 78.1 (C-4), 71.6, 71.3, 71.1, 70.02 (C-6), 70.01, 60.4, 56.2, 55.3, 32.7; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{39}H_{40}O_9SCl_6Na$, 917.0422; found, 917.0403.

Methyl 3,4,6-tri-*O*-(2,4-dichlorobenzyl)-2-*O*-(2-(2,4,6-trimethoxyphenylthio)propyl)-*α*/*β*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (55): *via* general procedure E starting from glucosyl donor **47** (51 mg, 0.058 mmol). The crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) affording **55** as a mixture of anomers (α/β = 2.5/1, 39 mg, 49%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.43. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.83 (m, 7H), 7.55 – 7.08 (m, 22H), 6.18 – 6.10 (m, 1H, H-3'), 6.09 (s, 2H), 5.52 (t, *J* = 10.0 Hz, 1H, H-4'), 5.25 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2'), 5.21 (d, *J* = 3.7 Hz, 1H, H-1'), 4.97 (d, *J* = 3.4 Hz, 1H, H-1), 4.90 (d, *J* = 13.0 Hz, 1H), 4.77 (d, *J* = 13.0 Hz, 1H), 4.69 (d, *J* = 13.1 Hz, 1H), 4.59 (d, *J* = 13.3 Hz, 1H), 4.56 – 4.50 (m, 1H), 4.42 (d, *J* = 13.3 Hz, 1H), 4.34 (ddd, *J* = 10.4, 6.7, 2.0 Hz, 1H, H-5'), 3.96 – 3.84 (m, 3H, H-3, H-5, H-6a'), 3.79 (m, 9H), 3.77 – 3.52 (m, 6H, H-4, H-6, H6b', H-7), 3.46 (s, 3H), 3.44 – 3.38 (m, 1H, H-2), 2.84 – 2.62 (m, 2H), 1.83 – 1.62 (m, 2H).**^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.9, 165.8, 165.3, 162.1, 161.7, 135.2, 134.9, 134.4, 133.7, 133.5, 133.41, 133.38, 133.3, 133.12, 133.08, 132.7, 129.99, 129.94, 129.85, 129.67, 129.65, 129.3, 129.1, 128.9, 128.84 – 128.75 (m), 128.42, 128.38, 128.2, 127.0, 126.88, 126.85, 101.2, 96.8 (C-1'), 96.7 (C-1), 91.0, 81.4 (C-3), 80.7 (C-2), 77.4 (C-4), 72.2 (C-2'), 71.3, 71.0, 70.6 (C-3'), 70.1 (C-5), 69.8, 69.6 (C-4'), 69.3, 69.0 (C-6), 68.5 (C-5), 66.7 (C-6'), 56.1, 55.6, 55.3, 30.8, 29.6. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{67}H_{64}Cl_6O_{17}SNa$, 1405.1893; found, 1405.1883.

2,4,6-Trimethoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-acetyl-1-thio-*β*-D-glucopyranoside (48): To a solution of **10a** (58 mg, 0.092 mmol) in pyridine (2 ml), was added acetic anhydride (1 mL). The solution was stirred for 4 h at rt before it was concentrated *in vacuo*. Silica gel flash column chromatography (0% → 30% - EtOAc in *n*-heptane) of the residue afforded **48** (56 mg, 91%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.4; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 13H), 7.18 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.09 (s, 2H), 5.04 (dd, *J* = 10.0, 8.7 Hz, 1H, (H-2)), 4.77 (dd, *J* = 11.0, 4.2 Hz, 2H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.57 – 4.54 (m, 2H, (H-1)), 4.48 (d, *J* = 11.8 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 1H),

3.77 (d, *J* = 9.6 Hz, 1oH, (H-6)), 3.69 – 3.58 (m, 3H, (H-3, H-4, H-6)), 3.41 (ddd, *J* = 9.5, 5.3, 1.8 Hz, 1H, H-5); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.5, 162.2, 138.4, 138.2, 137.9, 128.39, 128.37, 128.2, 128.0, 127.85, 127.81, 127.77, 127.7, 127.5, 99.2, 91.2, 85.8 (C-1), 84.7 (C-3), 80.0 (C-5), 78.0 (C-4), 75.2, 75.0, 73.6, 72.9 (C-2), 69.3 (C-6), 56.1, 55.2, 21.1. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{38}H_{42}O_9SNa$, 697.2447; found, 697.2445

Methyl 3,4,6-tribenzyl-2-*O*-acetyl-*β*-D-glucopyranosyl-(1→6)-2,3,4-*O*-tribenzoyl-*α*-D-glucopyranoside (56): *Via* general procedure F using glycosyl donor **48** (36 mg, 0.52 mmol). Silica gel flash column chromatography (0% → 40% - EtOAc in *n*-heptane) afforded **56** (42 mg, 0.0428 mmol) 83%). **TLC:** (EtOAc/n-heptane, 40/60 v/v): R_f = 0.5; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.87 – 7.82 (m, 2H), 7.77 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.36 – 7.12 (m, 20H), 7.08 (dd, *J* = 7.4, 2.2 Hz, 2H), 6.06 (t, *J* = 9.7 Hz, 1H, H-3'), 5.34 (dd, *J* = 10.3, 9.4 Hz, 1H, H-4'), 5.15 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2'), 5.12 (d, *J* = 3.6 Hz, 1H, H-1'), 4.96 (dd, *J* = 9.2, 7.9 Hz, 1H, H-2), 4.70 (dd, *J* = 11.1, 7.8 Hz, 2H), 4.60 (d, *J* = 11.4 Hz, 1H), 4.47 (d, *J* = 2.8 Hz, 1H), 4.44 (d, *J* = 1.5 Hz, 1H), 4.37 (d, *J* = 12.2 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H, H-1), 4.19 (ddd, *J* = 9.7, 7.3, 1.9 Hz, 1H, H-5'), 3.99 (dd, *J* = 10.9, 1.9 Hz, 1H, H-6'), 3.65 – 3.54 (m, 5H, H-6', H-6, H-6, H-3, H-4), 3.43 – 3.34 (m, 4H, H-5), 1.93 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.5, 165.8, 165.7, 165.3, 138.1, 138.0, 137.8, 133.4, 133.3, 133.0, 129.9, 129.8, 129.6, 129.2, 129.0, 128.8, 128.39, 128.37, 128.3, 128.2, 128.0, 127.81, 127.78, 127.70, 127.67, 127.5, 101.3, 96.6 (C-1'), 82.8 (C-3), 77.8 (C-4), 75.2 (C-5), 75.02, 74.99, 73.4, 73.0 (C-2), 72.1 (C-2'), 70.5 (C-3'), 69.5 (C-4'), 68.7 (C-5'), 68.42 (C-6), 68.36 (C-6'), 55.3, 20.9. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{57}H_{56}O_{12}Na$, 980.3619; found, 980.3578.

2,4,6-trimethoxyphenyl 2-O-acetyl-3,4,6-tri-*O*-(*o*,*p*-dichlorobenzyl)-1-thio-*β*-D-glucopyranoside (49): 10a (0.105 g; 0.125 mmol) was dissolved in pyridine (2 mL) and Ac_2O (1 ml). The reaction mixture was stirred at ambient temperature 4h, before it was concentrated *in*

vacuo. Silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane) afforded **49** as a white solid (76 mg, 69%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.43; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.22 – 7.10 (m, 4H), 6.09 (s, 2H), 5.07 (dd, *J* = 10.0, 8.7 Hz, 1H, H-2), 4.78 (d, *J* = 13.1 Hz, 1H), 4.75 (d, *J* = 12.7 Hz, 1H), 4.69 (d, *J* = 13.0 Hz, 1H), 4.65 – 4.57 (m, 2H, H-1), 4.52 (d, *J* = 13.0 Hz, 1H), 4.44 (d, *J* = 13.0 Hz, 1H), 3.80 (s, 6H), 3.78 (s, 3H), 3.77 – 3.63 (m, 4H, H-3, H-4, H-6), 3.43 (ddd, *J* = 9.6, 4.9, 2.1 Hz, 1H, H-5), 2.02 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.5, 162.2, 162.1, 134.6, 134.5, 134.2, 134.0, 133.71, 133.66, 133.3, 132.6, 130.1, 129.9, 129.7, 129.0, 128.9, 128.8, 127.2, 127.0, 99.2, 91.2, 85.8 (C-1), 85.1 (C-3), 79.4 (C-5), 77.94 (C-4), 72.88 (C-2), 71.3, 71.2, 70.0, 69.7 (C-6), 56.2, 55.3, 21.1; **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{38}H_{36}Cl_6O_9SNa$, 901.0109; found, 901.0103.

Methyl 2-*O*-acetyl-3,4,6-tri-*O*-(2,4-dichlorobenzyl)-1-thio-*β*-D-glucopyranosyl-(1→6)- 2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (57): *via* general procedure F starting from glucosyl donor **49** (51 mg; 0.058 mmol). The crude product was purified by silica gel flash column chromatography (10% to 30% EtOAc in *n*-heptane) affording **57** (41 mg, 60%). **TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.57. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.95 – 7.88 (m, 2H), 7.87 – 7.81 (m, 2H), 7.54 – 7.47 (m, 2H), 7.44 – 7.23 (m, 16H), 7.22 – 7.10 (m, 5H), 6.13 (t, *J* = 9.7 Hz, 1H, H-3'), 5.42 (dd, *J* = 10.3, 9.4 Hz, 1H, H-4'), 5.26 – 5.16 (m, 2H, H-1', H-2'), 5.10 – 5.02 (m, 1H, H-2), 4.78 (d, *J* = 13.0 Hz, 1H), 4.76 (d, *J* = 12.5 Hz, 1H), 4.70 (d, *J* = 12.9 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.54 (d, *J* = 13.4 Hz, 1H), 4.46 (d, *J* = 7.9 Hz, 1H, H-1), 4.45 (d, *J* = 13.4 Hz, 1H), 4.25 (ddd, *J* = 10.3, 7.0, 2.0 Hz, 1H, H-5'), 4.07 (dd, *J* = 11.0, 2.0 Hz, 1H, H-6a'), 3.77 – 3.68 (m, 4H, H-3, H-4, H-6), 3.65 (dd, *J* = 10.9, 7.0 Hz, 1H, H-6b'), 3.53 – 3.47 (m, 1H, H-5), 3.45 (s, 3H), 2.05 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.5, 165.8, 165.7, 165.4, 134.4, 134.3, 134.2, 134.1, 133.8, 133.7, 133.5, 133.4, 133.3, 133.2, 133.1, 132.8, 129.9, 129.8, 129.71, 129.69, 129.6, 129.2, 129.08, 129.05, 129.0, 128.9, 128.8, 128.44, 128.41, 128.3, 101.3 (C-1), 96.7 (C-1'), 83.3 (C-3), 77.7 (C-4), 74.9 (C-5), 73.0 (C-2), 72.1 (C-2'),

71.3, 71.2, 70.5 (C-3'), 69.8, 69.5 (C-4'), 69.0 (C-6), 68.7 (C-5'), 68.3 (C-6'), 55.4, 21.0. **HRMS (ESI-TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{57}H_{50}Cl_6O_{15}Na$, 1207.1179; found, 1207.1173.

Methyl 3,4,6-Tri-*O*-(*o*,*p*-dichlorobenzyl)-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (58): 32 (35.9 mg; 0.026 mmol) was dissolved in dry DCM (10 mL). MeOTf (4.6 µL; 0.041 mmol) and TTBP (14 mg; 0.055 mmol) were added and the reaction mixture was refluxed for 4 h at 40°C, after which the mixture was allowed to cool down to RT. KOtBu (6.8 mg; 0.041 mmol) was added and the mixture was stirred at rt for 1 h, after which the mixture was diluted with DCM (15 mL) and washed with water (20 mL), sat aq $NaHCO_3$ sol (20 mL) and brine (20 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (20% to 40% EtOAc in *n*-heptane) yielding **58** (22 mg; 0.019 mmol; 73%).**TLC** (EtOAc/*n*-heptane 40/60 v/v): R_f = 0.24. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H, C*H* Ar), 7.96 – 7.90 (m, 2H, C*H* Ar), 7.90 – 7.84 (m, 2H, C*H* Ar), 7.56 – 7.27 (m, 15H, C*H* Ar), 7.23 – 7.09 (m, 4H, C*H* Ar), 6.15 (t, *J* = 9.9 Hz, 1H, H-3'), 5.67 (t, *J* = 9.9 Hz, 1H, H-4'), 5.28 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2'), 5.23 (d, *J* = 3.7 Hz, 1H, H-1'), 5.08 – 5.03 (m, 1H, H-1), 5.01 (d, *J* = 12.8 Hz, 1H, CH_2PhCl$_2$), 4.83 (d, *J* = 12.8 Hz, 1H, CH_2PhCl$_2$), 4.80 (d, *J* = 12.9 Hz, 1H, CH_2PhCl$_2$), 4.57 (d, *J* = 13.0 Hz, 1H, CH_2PhCl$_2$), 4.55 (d, *J* = 13.3 Hz, 1H, CH_2PhCl$_2$), 4.41 (d, *J* = 13.3 Hz, 1H, CH_2PhCl$_2$), 4.28 (ddd, *J* = 10.3, 4.6, 2.2 Hz, 1H, H-5'), 3.93 (dd, *J* = 11.8, 4.6 Hz, 1H, H-6a'), 3.84 – 3.71 (m, 4H, H-2, H-3, H-5, H-6b'), 3.67 (dd, *J* = 10.7, 3.6 Hz, 1H, H-6a), 3.65 – 3.60 (m, 1H, H-4), 3.54 (dd, *J* = 10.6, 1.9 Hz, 1H, H-6b), 3.47 (s, 3H, O*Me*), 2.65 (s, 1H, O*H*). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.83, 165.80, 165.4, 135.0, 134.7, 134.3, 133.7, 133.64, 133.58, 133.4, 133.22, 133.20, 133.14, 132.9, 130.2, 130.0, 129.9, 129.8, 129.7, 129.5, 129.1, 128.99, 128.98, 128.90, 128.88, 128.81, 128.5, 128.4, 128.3, 127.05 – 126.99 (m), 126.9, 98.6 (C-1), 97.1 (C-1'), 83.4 (C-3), 77.2 (C-4), 73.3 (C-2), 72.1 (C-2'), 71.4, 71.0, 70.5 (C-5), 70.4 (C-3'), 69.7, 69.2 (C-4), 68.9 (C-6), 68.6 (C-5'), 65.6 (C-6'), 55.8 (O*Me*). **HRMS (ESI–TOF)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{55}H_{48}O_{14}Cl_6Na$, 1165.1073; found, 1165.1048.

ASSOCIATED CONTENT

Supporting Information

Analytical data for compounds **1-58**. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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