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C-2 auxiliaries for stereoselective glycosylation based on common additive functional groups†

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The stereoselective introduction of the glycosidic bond is one of the main challenges in chemical oligosaccharide synthesis. Stereoselective glycosylation can be achieved using neighbouring group participation of a C-2 auxiliary or using additives, for example. Both methods aim to generate a defined reactive intermediate that reacts in a stereoselective manner with alcohol nucleophiles. This inspired us to develop new C-2 auxiliaries based on commonly used additive functionalities such as ethers, phosphine oxides and tertiary amides. Good 1,2-*trans*-selectivity was observed for the phosphine oxide and amide-based auxiliaries expanding the toolbox with new auxiliaries for stereoselective glycosylation reactions.

Introduction

Carbohydrates play an essential role in biological systems. A major challenge in relating carbohydrate structure to function is the limited availability of structurally well-defined oligosaccharides and glycoconjugates. Such well-defined oligosaccharides can be obtained by chemical synthesis. The major challenge in oligosaccharide synthesis is the stereoselective introduction of the glycosidic bonds.[1,2] Stereoselective glycosylation can be achieved using neighbouring group participation (NGP) of a C-2 auxiliary or using additives, for example. Both methods aim to generate a defined reactive intermediate that reacts in a stereoselective manner with alcohol nucleophiles (Fig. 1A). For example, NGP of C-2 auxiliaries such as esters, picolyl ethers,[3] aryl nitriles[4] and ethers[5] mainly leads to 1,2-*trans*-glycosides, whilst other C-2 auxiliaries based on esters, thioethers[6–11] and selenoethers[12] mainly lead to 1,2-*cis*-glycosides. Alternatively, the use of additives for stereoselective glycosylations requires a non-assisting functionality at C-2.[13] A Lewis base additive, such as nitriles,[14] ethers,[15,16] sulfides,[17] phosphine oxides,[18–20] iodide based reagents[21,22] and (form) amides,[19,20,23] is added to stabilize the glycosyl cation and introduce facial selectivity in the subsequent nucleophilic displacement by the glycosyl acceptor. Inspired by both these approaches we set out to develop new C-2 auxiliaries based on recently reported additives. To this end, new C-2 auxiliaries based on linear and cyclic ethers, phosphine oxides, and amide functionalities were prepared (Fig. 1B). Their glycosylation properties were established with a number of glycosyl acceptors. The ether-based auxiliaries showed very modest stereoselectivity whilst the phosphine oxide and amide based auxiliaries lead to the stereoselective formation of 1,2-*trans* glycosides.

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Results and discussion

Six auxiliaries based on ethers, phosphine oxide and amides were designed and installed on the C-2 position of glucose and galactose leading to a set of 12 glycosyl donors (**3–14**, Table 1). All glycosyl donors were prepared starting from benzyl protected D-glucal and D-galactal.[11] Oxidation of the glycal led to the corresponding α-1,2-anhydro sugar[24] which was reacted with sodium thiophenolate to yield corresponding β-thioglycosides **1** and **2** in moderate yields (55–65%).[25] The C-2 auxiliary was introduced using sodium hydride and subsequent addition of the appropriate bromide or tosylate (**15–20**) resulted in moderate to good yields of coupled products **3–14** (54–86%, Table 1).

Donors **3–14** were glycosylated with glycosyl acceptor (**21**) under premix condition using the commonly employed *N*-iodosuccinimide (NIS) triflic acid (TfOH) promotor system.[26] The glycosylation reactions were carried out in CH_2Cl_2 at −15 °C and the stereoselectivity was determined using NMR analysis of the crude reaction mixtures after work-up. The corresponding purified disaccharides (**22–33**) were obtained in moderate to excellent yields with α/β-selectivities ranging from non-selective to high β-selectivity (Table 2). Donors containing ether-based auxiliaries (**3–6**) were unselective and no clear change in selectivity over the different donors was observed (entries 1–4 and 7–10). Chiral auxiliaries have shown to induce more stereoselectivity in glycosylation reactions.[8,27] Therefore, better stereoselectivities were expected for chiral THF-based

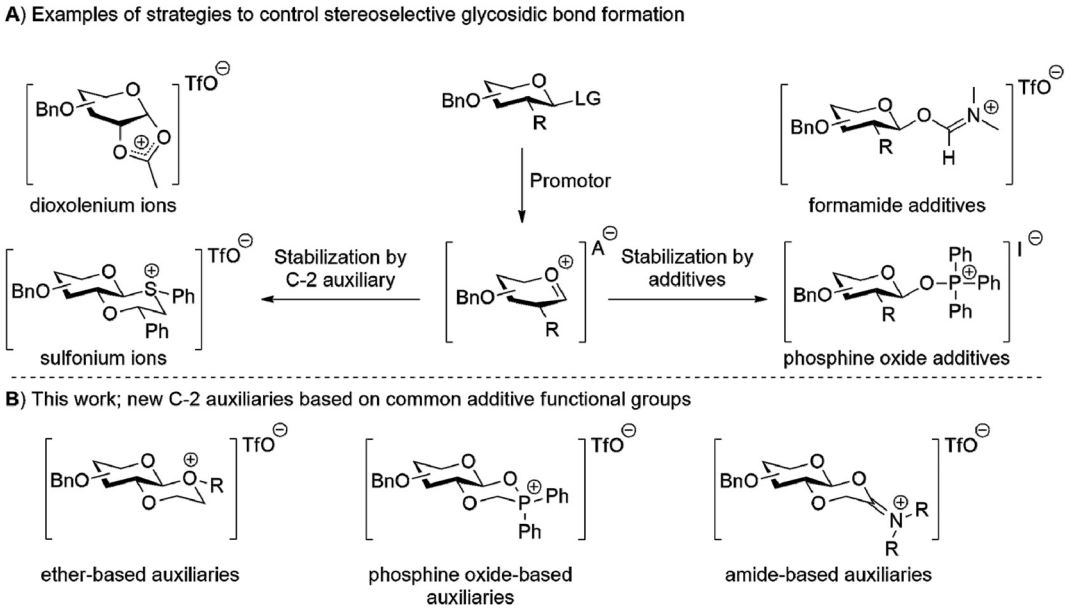
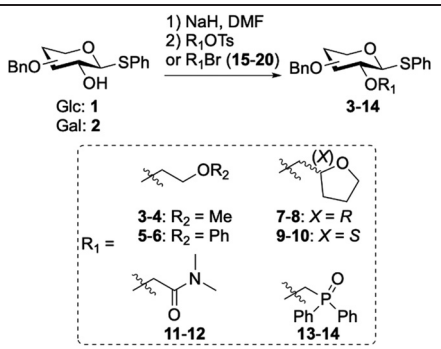


Fig. 1 (A) The two main strategies for stereoselecitve glycosylation. The oxocarbenium ion is trapped either by a C-2 auxiliary or additive to control the structure of the reactive intermediate. (B) Newly developed C-2 auxiliaries based on common additive functional groups.

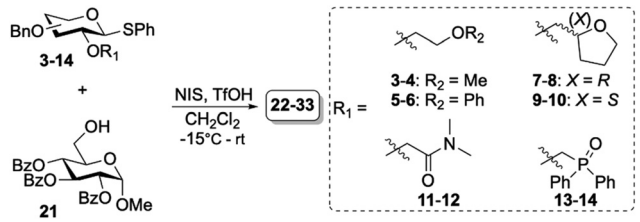
Table 1 Synthesis of glycosyl donors equipped with ether, phosphine oxide and *N*,*N*-dimethylamide auxiliaries (**3–14**)



Entry	Product	Type	Yield [%]
1	**3**	Glc	59
2	**4**	Gal	73
3	**5**	Glc	86
4	**6**	Gal	69
5	**7**	Glc	54
6	**8**	Gal	83
7	**9**	Glc	72
8	**10**	Gal	66
9	**11**	Glc	58
10	**12**	Gal	65
11	**13**	Glc	45
12	**14**	Gal	41

Reagents and conditions: 1-Bromo-2-methoxyethane (**15**), (2-bromoethoxy)benzene (**16**), 2-bromo-*N*,*N*-dimethylacetamide (**17**), (bromomethyl)diphenylphosphine oxide (**18**) or (*R*)- or (*S*)-(tetrahydrofuran-2-yl)methyl 4-methylbenzenesulfonate (**19–20**) (4 eq.), NaH (2–4 eq.), DMF, 0 °C to rt, 16 h.

Table 2 Glycosylation results of glycosyl donors **3–14** with glycosyl acceptor **21**



Entry	Donor	Type	α/β[a]	Yield[b] [%]	Product
1	**3**	Glc	50/50	96	**22**
2	**5**	Glc	50/50	54	**24**
3	**7**	Glc	37/63	85	**26**
4	**9**	Glc	37/63	55	**28**
5	**11**	Glc	0/100	57	**30**
6	**13**	Glc	11/89	67	**32**
7	**4**	Gal	60/40	95	**23**
8	**6**	Gal	60/40	77	**25**
9	**8**	Gal	45/55	81	**27**
10	**10**	Gal	55/45	73	**29**
11	**12**	Gal	20/80	43	**31**
12	**14**	Gal	17/83	68	**33**

[a] α/β ratios were determined by NMR spectroscopy[29,30] of the crude reaction mixture. [b] Isolated yields.

auxiliaries (**7–10**). Nevertheless, donors **7–10** did not show any stereoselectivity (entries 3–4 and 9–10). In contrast, the *N*,*N*-dimethylamide auxiliary proved the be β-selective for glucose and moderately β-selective (α/β = 20/80) for galactose (entries 5 and 11, respectively). This β-selectivity was surprising compared to findings by Mong and coworkers, where DMF as additive induced α-selectivity.[23] Similarly, phosphine oxide auxili-

aries **13–14** induced high β-selectivity (entries 6 and 12), in contrast to the α-selectivity observed when an additive combination of triphenylphosphine oxide/TMSI was used.[19] Generally, the galacto-series were more α-selective compared to the gluco-series counterparts consistent with earlier observed trends.[6,11,28]

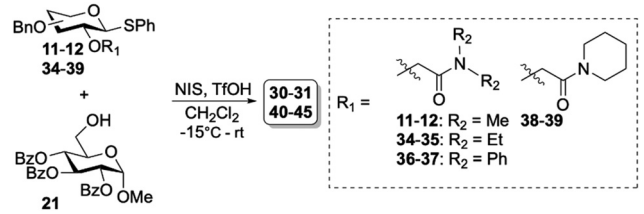
The high β-selectivity observed for glycosyl donor **11**, led us to further investigate the amide containing auxiliaries. The amide functionality is more amendable for easy alteration in substitution pattern and holds better prospects for removal compared to the phosphine oxide auxiliaries which also demonstrated good selectivity. Hence, we set out to further optimize the amide auxiliaries starting with exploring the influence of the amide substitution pattern on the stereoselectivity. To this end, we prepared diethyl- (**34–35**), diphenyl- (**36–37**) and cyclic amide derivatives (**38–39**) according to the protocol described in Table 1. These syntheses resulted in moderate to good yields (32–77%) of glycosyl donors **34–39**. Glycosylations of **34–39** also showed excellent β-selectivity for the gluco-type donors (Table 3, entries 1–4). For the galacto-type donors, β-selectivity was moderate and increased with the introduction of bulky substituents on the amide (Table 3, entries 5–7). The piperidine derived amide auxiliary gave selectivity comparable to the dimethyl auxiliary (Table 3, entries 8).

In addition to the amide substituents we investigated the glycosyl acceptor scope using a broader range of glycosyl acceptors for both gluco- and galacto-type glycosyl donors containing the dimethylamide auxiliary. Glycosylation with primary alcohols (21, 46 and 47) resulted moderate to good yield (39% to 61%) with excellent β-selectivity for gluco-type donors (Table 4, entries 1–3). However, secondary and tertiary alcohols gave poorer to no selectivity (α/β = 33/67 and 50/50 respectively) and resulted in moderate yields (Table 4, entries 4 and 5). Glycosylations with galacto-type donors were less β-selective compared to their gluco-type counterparts (Table 4). These glycosylations resulted in low to moderate yield (22 to 56%) and moderate to non-selective for the β-anomer (α/β = 20/80 to 50/50). Again, glycosylation with secondary and tertiary alcohols gave poorer selectivity compared to primary alcohols (Table 4, entries 6–10).

To identify reaction intermediates for gluco-type donors **11** and **13**, variable temperature (VT) NMR experiments were performed. Glycosyl donor **11** was reacted with Ph_2SO and Tf_2O in presence of TTBP at −80 °C in CD_2Cl_2 (Fig. 2). In a control experiment using glycosyl donor **11** and this promotor system (Tf_2O, Ph_2SO) no significant changes in yields or selectivity were observed indicating that the promotor system does not influence the glycosylation outcome. Directly after the addition of Tf_2O the α-iminium intermediate (**11α**) was formed (Fig. 2b–f). In addition, a small amount of β-iminium ion (**11β**) was observed (α/β = 5/1). The ratio of intermediate **11α** and **11β** did not change even upon heating to room temperature and remained stable at this temperature (Fig. 2d).

Additionally, we performed VT NMR experiments under the same conditions for glycosyl donor **13** starting at −20 °C (Fig. 3a and c). After addition of Tf_2O, the expected α- (**13α**) and β-phosphonium ions (**13β**) were observed in a α/β-ratio of 5/2 (Fig. 3). Both reaction intermediates were stable at 10 °C and decomposed slowly at room temperature. Again, the ratio of **13α** and **13β** did not change upon heating. Based on these VT NMR results, the α-intermediates predominate for both the amide and phosphine oxide auxiliaries and may be reactive

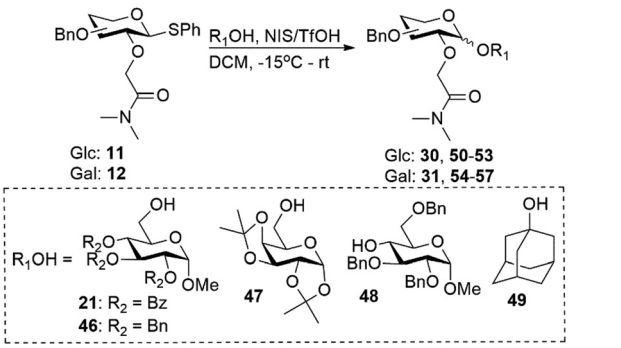
Table 3 Glycosylation results using a series of amide-based auxiliaries



Entry	Donor	Type	α/β[a]	Yield[b] [%]	Product
1	**11**	Glc	0/100	57	**30**
2	**34**	Glc	0/100	42	**40**
3	**36**	Glc	0/100	86	**42**
4	**38**	Glc	3/97	40	**44**
5	**12**	Gal	20/80	43	**31**
6	**35**	Gal	17/83	44	**41**
7	**37**	Gal	11/89	71	**43**
8	**39**	Gal	20/80	42	**45**

[a] α/β ratios were determined by NMR spectroscopy[29,30] of the crude reaction mixture. [b] Isolated yields.

Table 4 Glycosylation results for glycosyl donors **11** and **12** using a broader range of glycosyl acceptors



Entry	Donor type	R_1OH	α/β[a]	Yield[b] [%]	Product
1	Glc	**21**	0/100	57	**30**
2	Glc	**46**	0/100[c]	39	**50**
3	Glc	**47**	10/90	61	**51**
4	Glc	**48**	33/67	30	**52**
5	Glc	**49**	50/50	34	**53**
6	Gal	**21**	0/100	43	**31**
7	Gal	**46**	25/75[c]	40	**54**
8	Gal	**47**	20/80	56	**55**
9	Gal	**48**	50/50	22	**56**
10	Gal	**49**	40/60	28	**57**

[a] α/β ratios were determined by NMR spectroscopy[29,30] of the crude reaction mixture. [b] Isolated yields. [c] α/β ratios were determined by NMR spectroscopy after removal of the acceptor residues by silica gel flash column chromatography (30 to 80% EtOAc in *n*-heptane).

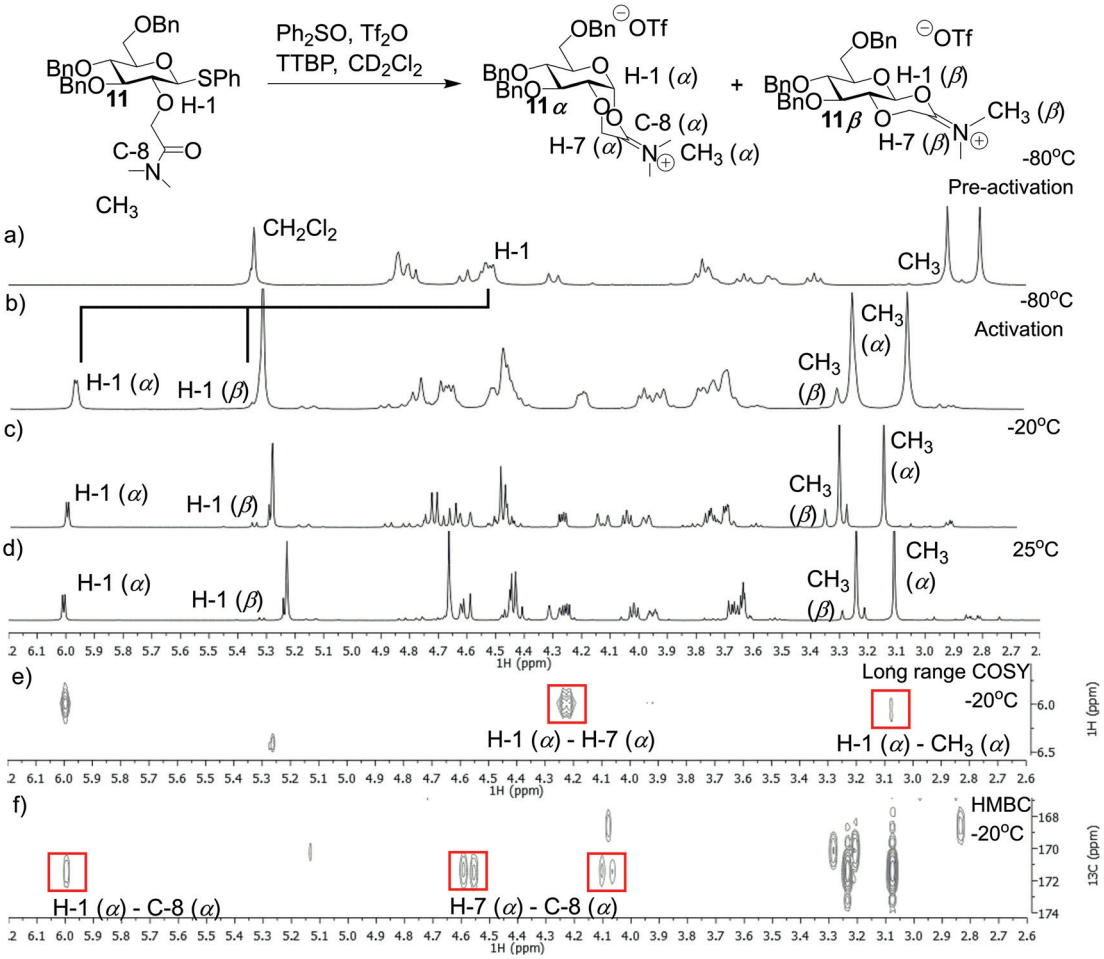


Fig. 2 VT-NMR spectra of the iminium ion derived from **11** (a) ^{1}H NMR spectrum of **11** at −80 °C in CD_2Cl_2. (b) ^{1}H NMR of **11** at −78 °C after the addition of Tf_2O. (c) ^{1}H NMR of **11** at −20 °C. (d) ^{1}H NMR at 25 °C. (e) Long range COSY at −20 °C. (f) ^{1}H/^{13}C HMBC at −20 °C.

intermediates with strong nucleophiles. However, the erosion of stereoselectivity when glycosylating with secondary and tertiary alcohols suggests that other reactive intermediates such as the oxocarbenium ion may be responsible for disaccharide formation in these cases.

Finally, we explored the removal of amide auxiliaries. Using disaccharide **50** as a model substrate, the tertiary amide was hydrolysed to yield the carboxylic acid.[31,32] After a simple workup the carboxylic acid was converted to the acyl azide, heated to form the isocyanate and reacted with *t*-BuOH at 100 °C to yield the Boc-protected amine. After a short workup the Boc group was removed and the amine was subsequently treated with 1.0 M NaOH in which it was eliminated to yield the unprotected 2-OH (**58**) in 50% overall yield from **50** (Scheme 1).[33]

In conclusion, we prepared a series glycosyl donor containing new C-2 auxiliaries based on commonly used additives for stereoselective glycosylation. The ether based auxiliaries gave rather unselective glycosylation reactions whilst tertiary amides and our phosphine oxide based auxiliaries showed good to absolute β-selectivity with reactive glycosyl acceptors. VT-NMR experiments confirmed the formation of reaction intermediates resulting from NGP of the C-2 auxiliaries. Potentially, chiral auxiliaries based on these functional groups can be developed to obtain even better stereoselectivity.

Experimental section

General conditions

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 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 (*J*) in hertz (Hz), integration. All NMR signals were assigned on the basis of ^{1}H NMR, ^{13}C NMR, ^{31}P 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. Automatic flash column chromatography was performed using Biotage Isolera Spektra

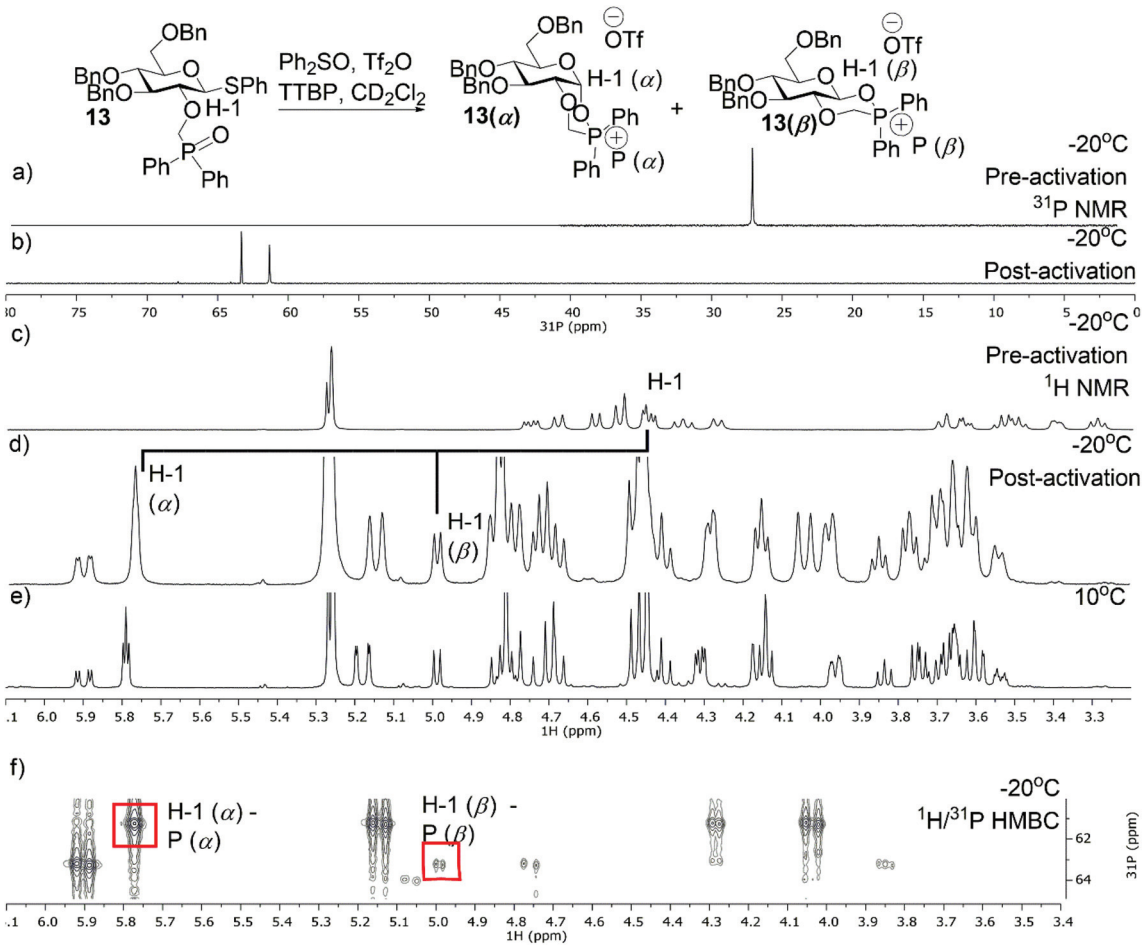
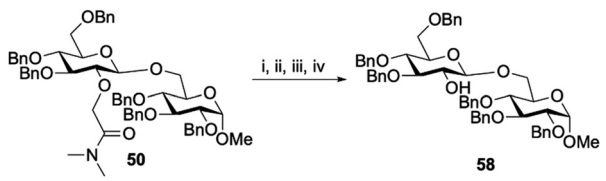


Fig. 3 VT-NMR spectra of the phosphonium ion derived from **13** (a) ^{31}P NMR spectrum of **13** at −20 °C in CD_2Cl_2. (b) ^{31}P NMR of **13** at −20 °C after the addition of Tf_2O. (c) ^{1}H NMR spectrum of **13** at −20 °C in CD_2Cl_2. (d) ^{1}H NMR of **13** at −20 °C after the addition of Tf_2O. (e) ^{1}H NMR of **13** at 10 °C. (f) ^{1}H/^{31}P HMBC at −20 °C.



Scheme 1 Removal of the auxiliary. Reagents and conditions (i) H_2O (2.2 eq.), *t*-BuOK (5.9 eq.), THF, rt; (ii) DIPEA (1.2 eq.), DPPA (1.1 eq.), DMF, 0 °C – rt; (iii) *t*-BuOH, DMF, 100 °C; (iv) NaOH, THF, EtOH, 60 °C.

One, using SNAP cartridges (Biotage, 30–100 μm, 60 Å), 4–50 g. TLC analysis was conducted on silica gel F254 (Merck KGaA) with detection by UV absorption (254 nm) where applicable; by spraying with 10% sulfuric acid in methanol followed by charring at ≈300 °C or by spraying with $KMnO_4$ stain consisting of (0.06 M $KMnO_4$, 0.5 M K_2CO_3 and 0.02 M NaOH in water) after gently heating of the plate. DCM, THF, and toluene were freshly distilled. Molecular sieves (4 Å) were flame-activated under a vacuum prior to use. All inert reactions were carried out under an argon atmosphere using flame-dried flasks.

General procedure A

5.0 grams (0.035 mol, 1.0 eq.) D-glucal or D-galactal was dissolved in dry DMF (170 mL). 7.0 grams (0.18 mol, 5.0 eq.) NaH (60% dispersion in paraffin oil) was added on ice. The reaction was stirred for 15 minutes and 21 mL (0.18 mol, 5.0 eq.) benzyl bromide was added. The reaction was stirred at room temperature until TLC indicated full consumption of starting material (16 hours). The reaction was quenched with methanol and the solution was concentrated *in vacuo*. The resulting oil was taken up in ethyl acetate and washed with water (3 × 100 mL) and brine (1 × 100 mL). The organic layer was dried over $MgSO_4$ (anhydrous), filtrated and evaporated *in vacuo* to result the crude product. The benzylated products were obtained by purification of the crude product through silica gel flash column chromatography.

General procedure B

To a cooled (0 °C) solution of 4.0 grams (9.6 mmol, 1.0 eq.) benzylated glycal in DCM (40 mL) were added acetone (4 mL) and saturated aqueous $NaHCO_3$ (68 mL). The mixture was

stirred vigorously, and a solution of oxone (19.2 mmol, 2 eq.) in H_2O (24 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 × 40 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was dissolved in dry THF (80 mL). The solution was cooled to −78 °C. MS (4 Å) and 2.2 grams (15 mmol, 1.6 eq.) sodium thiophenolate (90%) were added under an inert atmosphere. 1.0 mL (0.096 mmol, 0.1 eq.) $ZnCl_2$ (1.0 M in Et_2O) was added and the mixture was stirred for 3 days allowing it to warm up to room temperature. An aqueous solution of 1.0 M NaOH (80 mL) was added to quench the reaction. The mixture was filtrated and the organic layer was separated from the aqueous layer. The organic layer was washed with brine (80 mL), dried over Na_2SO_4 (anhydrous), filtrated and evaporated *in vacuo*. The crude product was purified with silica gel flash column chromatography to obtain the pure product. If the product was strongly coloured, the product was dissolved in DCM, norrit was added, filtrated over Celite and evaporated *in vacuo* to yield the product.

General procedure C

An anomeric thioether with free 2-OH (**1** or **2**, 1.0 eq.) was dissolved in dry DMF (0.1 M) under an inert atmosphere at 0 °C. 60% NaH dispersion in paraffin oil was added (2.0 eq. for the preparation of **11–14** and **34–39**, 4.0 eq. for **3–10**). After stirring for 15 minutes, ice was removed and the corresponding bromide or tosylate (4.0 eq.) was added. The reaction was stirred for overnight after which the reaction was quenched with methanol and the solvent was evaporated *in vacuo*. The donors were obtained by purification through silica gel flash column chromatography.

General procedure D

The corresponding glycosyl donor (1.0 eq.) and the corresponding glycosyl acceptor (2.0 eq.) were dissolved in dry DCM (0.02 M and 0.04 M respectively). MS (4 Å) were added and the mixture was cooled to −15 °C. NIS (1.1 eq.) was added followed by the addition of a catalytic amount TfOH (0.1 eq.). The reaction was stirred for 2 h allowing it to slowly reach room temperature. The reaction was quenched with TEA and taken up in EtOAc (20 mL). The solution was filtrated, washed with aqueous thiosulfate solution (10%, 20 mL) and washed with brine (20 mL). The organic layer was dried over $MgSO_4$ (anhydrous), filtrated and the solvent was evaporated *in vacuo* to yield the crude product. The crude product was dissolved in $CDCl_3$ and analysed by quantitative HSQC to determine the selectivity. After analysis the crude product was purified by flash column chromatography to obtain the product.

VT-NMR studies procedure

Glycosyl donor (15 mg, 1.0 eq.), Ph_2SO (1.2 eq.) and TTBP (2.5 eq.) were dissolved in DCM-d_2 (1 mL) under inert atmosphere. MS (4 Å) were added and the solution was stirred for 1.5 h. In a second vial under inert atmosphere was stirred 1.0 mL of DCM-d_2 for 1.5 h over molecular sieves (4 Å). The donor solution was transferred to an NMR tube and was analysed at low temperature by NMR. To the DCM-d_2 was added Tf_2O (1.1 eq.) and the solution was added at −78 °C to the tube. The tube was quickly shaken and transferred to the NMR. The reaction was first analysed by NMR at low temperature and was measured at increasing temperatures.

3,4,6-Tri-*O*-benzyl-D-glucal. Using general procedure A starting from D-glucal (5.14 g, 35.2 mmol), the crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane), affording 3,4,6-tri-*O*-benzyl-D-glucal (14.1 g, 98%) as white solid. **TLC:** R_f = 0.61 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.50–7.13 (m, 15H), 6.42 (dd, J = 6.1, 1.4 Hz, 1H, H-1), 4.87 (dd, J = 6.2, 2.7 Hz, 1H, H-2), 4.83 (d, J = 11.3 Hz, 1H), 4.66–4.62 (m, 2H), 4.61–4.54 (m, 3H), 4.21 (ddd, J = 6.1, 2.7, 1.4 Hz, 1H, H-3), 4.06 (ddd, J = 8.3, 5.1, 2.8 Hz, 1H, H-5), 3.86 (dd, J = 8.7, 6.2 Hz, 1H, H-4), 3.83–3.74 (m, 2H, H-6). **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 144.9 (CH, C-1), 138.5, 138.3, 138.2 (all quaternary), 128.6, 128.5, 128.5, 128.1, 127.9, 127.9, 127.8 (all aromatic), 100.1 (CH, C-2), 77.0 (CH, C-5) 75.9 (CH, C-3), 74.6 (CH, C-4), 73.9 (CH_2), 73.7 (CH_2), 70.6 (CH_2), 68.7 (CH_2, C-6). **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{27}H_{28}O_4$: 439.18853, found $[M + Na]^+$: 439.18934.

3,4,6-Tri-*O*-benzyl-D-galactal. Using general procedure A starting from D-galactal (5.02 g, 35.0 mmol), the crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane), affording 3,4,6-tri-*O*-benzyl-D-galactal (13.6 g, 96%) as white solid. **TLC:** R_f = 0.57 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.36–7.23 (m, 15H), 6.36 (dd, J = 6.2, 1.5 Hz, 1H, H-1), 4.90–4.83 (m, 2H, H-2), 4.68–4.59 (m, 3H), 4.50 (d, J = 11.9 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.19 (tdd, J = 5.2, 2.6, 1.2 Hz, 2H, H-3, H-5), 3.95 (ddd, J = 4.0, 2.5, 1.3 Hz, 1H, H-4), 3.78 (dd, J = 10.2, 7.2 Hz, 1H, H-6), 3.65 (dd, J = 10.1, 5.1 Hz, 1H, H-6). **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 144.3 (CH, C-1), 138.7, 138.5, 138.2 (all quaternary), 128.6, 128.5, 128.3, 128.0, 127.8, 127.7, 127.6 (all aromatic), 100.1 (CH, C-2), 75.8 (CH, C-5), 73.6 (CH_2), 73.5 (CH_2), 71.4 (CH, C-4), 71.0 (CH, C-3), 70.9 (CH_2), 68.6 (CH_2, C-6). **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{27}H_{28}O_4$: 439.18853, found $[M + Na]^+$: 439.18909.

3,4,6-Tri-*O*-benzyl-1-thio-β-D-glucopyranoside (1). Using general procedure B starting from **1** (4.0 gram, 9.6 mmol), the crude product was purified by silica gel flash column chromatography (0% to 15% EtOAc in *n*-heptane), affording **1** (2.9 g, 55%) as yellow/white solid. **TLC:** R_f = 0.51 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.63–7.54 (m, 2H), 7.38–7.14 (m, 18H), 4.90 (d, J = 11.2 Hz, 1H), 4.86–4.81 (m, 2H), 4.64–4.53 (m, 3H), 4.50 (d, J = 9.7 Hz, 1H, H-1), 3.79 (dd, J = 11.0, 1.9 Hz, 1H, H-6), 3.74 (dd, J = 11.0, 4.4 Hz, 1H, H-6), 3.63–3.57 (m, 2H, H-3, H-4), 3.56–3.46 (m, 2H, H-2, H-5), 2.39 (d, J = 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 138.6, 138.4, 138.2 (all quaternary), 133.1 (aromatic), 131.9 (quaternary), 129.1, 128.7, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7 (all aromatic), 88.2 (CH, C-1), 86.1 (CH, C-3), 79.6 (CH, C-5), 77.5 (CH, C-4), 75.5 (CH_2), 75.2 (CH_2), 73.6 (CH_2), 72.7

(CH, C-2), 69.2 (CH_2 C-6). **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{33}H_{34}O_5S$: 565.20246, found $[M + Na]^+$: 565.20159.

3,4,6-Tri-*O*-benzyl-1-thio-β-D-galactopyranoside (2). Using general procedure B starting from **2** (4.0 gram, 9.6 mmol), the crude product was purified by silica gel flash column chromatography (0% to 5% Et_2O in toluene), affording **2** (3.4 g, 65%) as yellow/white solid. **TLC:** R_f = 0.31 (Et_2O/toluene, 10/90 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.62–7.50 (m, 2H), 7.42–7.14 (m, 18H), 4.89 (d, *J* = 11.4 Hz, 1H), 4.76–4.65 (m, 2H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.53 (d, *J* = 9.6 Hz, 1H, H-1), 4.51–4.42 (m, 2H), 4.06–3.93 (m, 2H, H-2, H-4), 3.67–3.75 (m, 3H, H-5, H-6), 3.47 (dd, *J* = 9.2, 2.7 Hz, 1H, H-3), 2.43 (d, *J* = 2.1 Hz, 1H, OH) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.8, 138.1, 138.0, 132.7 (all quaternary), 132.3, 129.0, 128.7, 128.6, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6 (all aromatic), 88.7 (CH, C-1), 83.4 (CH, C-3), 77.8 (CH, C-5), 74.6, 73.7 (both CH_2), 73.4 (CH, C-4), 72.6 (CH_2), 69.2 (CH, C-2), 68.8 (CH_2, C-6) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{33}H_{34}O_5S$: 565.20246, found $[M + Na]^+$: 565.20265.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-methoxyethoxy)-1-thio-β-D-glucopyranoside (3). Using general procedure C starting from **1** (101 mg, 0.186 mmol) and 1-bromo-2-methoxyethane (**15**), the crude product was purified by silica gel flash column chromatography (0% to 10% EtOAc in *n*-heptane), affording **3** (65 mg, 59%) as white oil. **TLC:** R_f = 0.54 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.58–7.55 (m, 2H), 7.38–7.17 (m, 18H), 4.98 (d, *J* = 10.7 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 2H), 4.63 (d, *J* = 9.8 Hz, 1H, H-1), 4.60–4.55 (m, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.01 (ddd, *J* = 10.3, 5.6, 3.4 Hz, 1H, H-6), 3.87 (ddd, *J* = 10.1, 6.4, 3.5 Hz, 1H, H-6), 3.76 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.72–3.65 (m, 2H, H-3), 3.62–3.51 (m, 3H, H-5), 3.47 (ddd, *J* = 9.7, 4.8, 2.0 Hz, 1H, H-4), 3.36 (s, 3H), 3.34 (t, *J* = 9.0 Hz, 1H, H-2) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 138.7, 138.4, 138.2, 134.0 (all quaternary), 132.0, 129.0, 128.6, 128.6, 128.5, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5 (all aromatic), 87.5 (CH, C-1), 86.7 (CH, C-3), 81.9 (CH, C-2), 79.2 (CH, C-4), 77.8 (CH, C-5), 75.9 (CH_2), 75.2 (CH_2), 73.5 (CH_2), 72.5 (CH_2), 72.2 (CH_2), 69.2 (CH_2), 59.1 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{36}H_{40}O_6S$: 623.24433, found $[M + Na]^+$: 623.24404.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-methoxyethoxy)-1-thio-β-D-galactopyranoside (4). Using general procedure C starting from **2** (100 mg, 0.184 mmol) and 1-bromo-2-methoxyethane (**15**), the crude product was purified by silica gel flash column chromatography (0% to 15% EtOAc in *n*-heptane), affording **4** (81 mg, 73%) as white solid. **TLC:** R_f = 0.40 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.56–7.50 (m, 2H), 7.41–7.22 (m, 16H), 7.21–7.13 (m, 3H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.81–4.69 (m, 2H), 4.60 (d, *J* = 9.6 Hz, 1H, H-1), 4.57 (d, *J* = 11.6 Hz, 1H), 4.48–4.36 (m, 2H), 3.94–3.85 (m, 3H, H-5, H-6), 3.75 (t, *J* = 9.4 Hz, 1H, H-2), 3.67–3.48 (m, 6H, H-3, H-4, H-6), 3.35 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.9, 138.6, 138.0, 134.4 (all quaternary), 131.6, 128.9, 128.5, 128.5, 128.3, 128.0, 128.0, 127.9, 127.8, 127.8, 127.6, 127.1 (all aromatic), 87.8 (CH, C-1), 84.0 (CH, C-3), 78.5 (CH, C-2), 77.4 (CH, C-4), 74.6 (CH, C-5), 73.9, 73.7, 73.0, 72.6 (all CH_2), 72.3 (CH_2, C-6), 68.9 (CH_2), 59.0 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{36}H_{40}O_6S$: 623.24433, found $[M + Na]^+$: 623.24509.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-phenoxyethoxy)-1-thio-β-D-glucopyranoside (5). Using general procedure C starting from **1** (80 mg, 0.15 mmol) and (2-bromoethoxy)benzene (**16**), the crude product was purified by silica gel flash column chromatography (0% to 10% EtOAc in *n*-heptane), affording **5** (84 mg, 86%) as white solid. **TLC:** R_f = 0.55 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.57–7.53 (m, 2H), 6.92 (tt, *J* = 7.5, 1.1 Hz, 1H), 6.87–6.83 (m, 2H), 5.02 (d, *J* = 10.7 Hz, 1H), 4.84 (dd, *J* = 10.8, 3.9 Hz, 2H), 4.62 (d, *J* = 9.8 Hz, 1H, H-1), 4.60–4.57 (m, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.22–4.14 (m, 2H), 4.13–4.06 (m, 2H), 3.77 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6), 3.73–3.66 (m, 2H, H-3, H-6), 3.61 (t, *J* = 9.4 Hz, 1H, H-4), 3.49 (ddd, *J* = 9.6, 4.8, 1.9 Hz, 1H, H-5), 3.39 (dd, *J* = 9.8, 8.6 Hz, 1H, H-2) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 158.9, 138.6, 138.4, 138.2, 134.0 (all quaternary), 132.0, 129.5, 129.0, 128.6, 128.6, 128.5, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 120.9, 114.7 (all aromatic), 87.6 (CH, C-1), 86.6 (CH, C-3), 81.8 (CH, C-2), 79.2 (CH, C-5), 77.8 (CH, C-4), 76.0 (CH_2), 75.2 (CH_2), 73.6 (CH_2), 71.8 (CH_2), 69.2 (CH_2, C-6), 67.4 (CH_2) ppm. **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{41}H_{42}O_6S$: 685.25998, found $[M + Na]^+$: 685.25843.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-phenoxyethoxy)-1-thio-β-D-galactopyranoside (6). Using general procedure C starting from **2** (80 mg, 0.15 mmol) and (2-bromoethoxy)benzene (**16**), the crude product was purified by silica gel flash column chromatography (0% to 10% EtOAc in *n*-heptane), affording **6** (84 mg, 69%) as white solid. **TLC:** R_f = 0.56 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.55–7.50 (m, 2H), 7.38–7.34 (m, 2H), 7.33–7.25 (m, 13H), 7.25–7.20 (m, 2H), 7.19–7.14 (m, 3H), 6.92 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.88–6.83 (m, 2H), 4.94 (d, *J* = 11.5 Hz, 1H), 4.81–4.70 (m, 2H), 4.60 (d, *J* = 9.6 Hz, 1H, H-1), 4.58 (d, *J* = 11.5 Hz, 1H), 4.48–4.38 (m, 2H), 4.16–4.05 (m, 4H), 3.94 (dd, *J* = 2.9, 0.8 Hz, 1H, H-4), 3.81 (t, *J* = 9.4 Hz, 1H, H-2), 3.67–3.58 (m, 3H, H-5, H-6), 3.56 (dd, *J* = 9.3, 2.7 Hz, 1H, H-3) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 159.0, 138.9, 138.5, 138.0, 134.3 (all quaternary), 131.6, 129.5, 128.9, 128.6, 128.6, 128.3, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 127.2, 120.8, 114.7 (all aromatic), 87.9 (CH, C-1), 83.9 (CH, C-3), 78.4 (CH, C-2), 77.5 (CH, C-5), 74.6 (CH_2), 73.9 (CH, C-4), 73.7, 73.1, 71.9 (all CH_2), 68.9 (CH_2, C-6), 67.5 (CH_2) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{41}H_{42}O_6S$: 685.25998, found $[M + Na]^+$: 685.25861.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(((*R*)-tetrahydrofuran-2-yl)methoxy)-1-thio-β-D-glucopyranoside (7). Using general procedure C starting from **1** (99 mg, 0.18 mmol) and (*R*)-(tetrahydrofuran-2-yl)methyl 4-methylbenzenesulfonate (**19**), the crude product was purified by silica gel flash column chromatography (0% to 5% Et_2O in toluene), affording (7) (63 mg, 54%) as colourless oil. **TLC:** R_f = 0.30 (Et_2O/toluene, 10/90 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.49–7.41 (m, 2H), 7.28–7.07 (m, 18H), 4.93 (d, *J* = 10.7 Hz, 1H), 4.72 (dd, *J* = 10.8, 2.4 Hz, 2H), 4.51 (d, *J* = 9.8 Hz, 1H, H-1), 4.49–4.45 (m, 2H), 4.41 (d, *J* = 11.9 Hz, 1H), 4.06–3.98 (m, 1H), 3.74 (dt, *J* = 8.4, 6.6 Hz, 1H), 3.68–3.63

(m, 4H, H-6), 3.61–3.55 (m, 2H, H-3, H-6), 3.49 (t, J = 9.4 Hz, 1H, H-4), 3.37 (ddd, J = 9.8, 4.9, 1.9 Hz, 1H, H-5), 3.23 (dd, J = 9.8, 8.7 Hz, 1H, H-2), 1.86 (dtd, J = 12.4, 7.1, 5.9 Hz, 1H), 1.79–1.72 (m, 2H), 1.53–1.46 (m, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.7, 138.4, 138.2, 134.1 (all quaternary), 132.0, 129.0, 128.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5 (all aromatic), 87.6 (CH, C-1), 86.7 (CH, C-3), 81.7 (CH, C-2), 79.2 (CH, C-5), 78.0 (CH, C-4), 77.8 (CH), 76.2, 75.8, 75.2, 73.5 (all CH_2), 69.2 (CH_2, C-6), 68.3, 28.3, 25.6 (all CH_2) ppm. **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{38}H_{42}O_6S$: 649.25998, found $[M + Na]^+$: 649.25857.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(((*R*)-tetrahydrofuran-2-yl)methoxy)-1-thio-β-D-galactopyranoside (8). Using general procedure C starting from **2** (97 mg, 0.18 mmol) and (*R*)-(tetrahydrofuran-2-yl)methyl 4-methylbenzenesulfonate (**19**), the crude product was purified by silica gel flash column chromatography (0% to 5% Et_2O in toluene), affording (**8**) (95 mg, 83%) as white solid. **TLC:** R_f = 0.18 (Et_2O/toluene, 10/90 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.56–7.50 (m, 2H), 7.41–7.36 (m, 2H), 7.35–7.23 (m, 13H), 7.20–7.15 (m, 3H), 4.93 (d, J = 11.5 Hz, 1H), 4.81 (d, J = 11.6 Hz, 1H), 4.72 (d, J = 11.6 Hz, 1H), 4.61–4.54 (m, 2H, H-1), 4.47–4.37 (m, 2H), 4.11 (qd, J = 7.0, 4.4 Hz, 1H, H-5), 3.93 (d, J = 2.8 Hz, 1H), 3.86–3.70 (m, 4H, H-2, H-6), 3.67–3.53 (m, 5H, H-3, H-4), 1.97–1.87 (m, 1H), 1.87–1.79 (m, 2H), 1.61–1.57 (m, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 138.0, 138.6, 138.0, 134.4 (all quaternary), 131.6, 128.9, 128.5, 128.5, 128.3, 128.0, 128.0, 127.9, 127.7, 127.7, 127.6, 127.1 (all aromatic), 87.9 (CH, C-1), 84.2 (CH, C-4), 78.2 (CH, C-2), 78.0 (CH, C-5), 77.4 (CH, C-3), 76.3, 74.5 (both CH_2), 73.7 (CH), 73.0, 67.0 (both CH_2), 68.3 (CH_2, C-6), 29.8, 28.2, 25.6 (all CH_2) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{38}H_{42}O_6S$: 649.25998, found $[M + Na]^+$: 649.25849.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(((*S*)-tetrahydrofuran-2-yl)methoxy)-1-thio-β-D-glucopyranoside (9). Using general procedure C starting from **1** (85 mg, 0.16 mmol) and (*S*)-(tetrahydrofuran-2-yl)methyl 4-methylbenzenesulfonate (**20**), the crude product was purified by silica gel flash column chromatography (0% to 5% Et_2O in toluene), affording **9** (71 mg, 72%) as colourless oil. **TLC:** R_f = 0.37 (Et_2O/toluene, 10/90 v/v); **^{1}H NMR** (500 MHz, $CHCl_3$): δ_H 7.60–7.51 (m, 2H), 7.39–7.14 (m, 18H), 4.96 (d, J = 10.7 Hz, 1H), 4.82 (dd, J = 10.8, 7.9 Hz, 2H), 4.62 (d, J = 9.8 Hz, 1H, H-1), 4.60–4.54 (m, 2H), 4.52 (d, J = 12.0 Hz, 1H), 4.06 (qd, J = 6.8, 4.0 Hz, 1H), 3.93–3.84 (m, 2H), 3.75 (ddd, J = 12.7, 8.3, 1.9 Hz, 2H, H-6), 3.72–3.63 (m, 3H, H-3, H-6), 3.59 (t, J = 9.4 Hz, 1H, H-5), 3.48 (ddd, J = 9.6, 4.8, 2.0 Hz, 1H), 3.33 (dd, J = 9.7, 8.6 Hz, 1H, H-2), 1.96–1.75 (m, 3H), 1.66 (ddt, J = 11.9, 8.7, 7.3 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.7, 138.4, 138.2, 134.0 (all quaternary), 132.0, 128.9, 128.5, 128.4, 128.0, 127.9, 127.7, 127.6, 127.5 (all aromatic), 87.5 (CH, C-1), 86.7 (CH, C-3), 81.6 (CH, C-2), 79.1 (CH, C-5), 78.0 (CH), 77.8 (CH, C-4), 77.9, 75.8, 75.1, 73.5 (all CH_2), 69.2 (CH_2, C-6), 68.4, 28.0, 25.8 (all CH_2) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{38}H_{42}O_6S$: 649.25998, found $[M + Na]^+$: 649.25998.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(((*S*)-tetrahydrofuran-2-yl)methoxy)-1-thio-β-D-galactopyranoside (10). Using general procedure C starting from **2** (100 mg, 0.18 mmol) and (*S*)-(tetrahydrofuran-2-yl)methyl 4-methylbenzenesulfonate (**20**), the crude product was purified by silica gel flash column chromatography (0% to 5% Et_2O in toluene), affording **10** (76 mg, 66%) as colourless oil. **TLC:** R_f = 0.27 (Et_2O/toluene, 10/90 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.49–7.44 (m, 2H), 7.32–7.16 (m, 16H), 7.10 (p, J = 3.6 Hz, 3H), 4.86 (d, J = 11.6 Hz, 1H), 4.69 (d, J = 11.7 Hz, 1H), 4.65 (d, J = 11.7 Hz, 1H), 4.51 (t, J = 10.4 Hz, 2H, H-1), 4.38 (d, J = 11.7 Hz, 1H), 4.33 (d, J = 11.7 Hz, 1H), 3.98 (qd, J = 6.7, 4.3 Hz, 1H), 3.86 (d, J = 2.8 Hz, 1H, H-5), 3.82–3.73 (m, 2H), 3.70–3.63 (m, 2H, H-2, H-3), 3.59 (dd, J = 9.8, 4.4 Hz, 1H), 3.57–3.50 (m, 3H, H-4), 3.48 (dd, J = 9.2, 2.9 Hz, 1H), 1.85–1.69 (m, 3H), 1.57 (ddt, J = 11.3, 8.0, 7.0 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.9, 138.6, 138.0, 134.4 (all quaternary), 131.6, 128.8, 128.5, 128.5, 128.2, 128.0, 128.0, 127.0, 127.8, 127.7, 127.6, 127.1 (all aromatic), 87.8 (CH, C-1), 84.1 (CH, C-4), 78.3 (CH, C-2), 78.1 (CH), 77.5 (CH, C-3), 76.0, 74.6 (both CH_2), 73.9 (CH, C-5), 73.7, 73.0, 69.0 (all CH_2), 68.3 (CH_2, C-6), 28.0, 25.7 (both CH_2) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{38}H_{42}O_6S$: 649.25998, found $[M + Na]^+$: 649.26015.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-1-thio-β-D-glucopyranoside (11). Using general procedure C starting from **1** (101 mg, 0.19 mmol) and *N*,*N*-dimethylacetamide (**17**), the crude product was purified by silica gel flash column chromatography (0% to 10% Et_2O in DCM), affording **11** (68 mg, 58%) as white solid. **TLC:** R_f = 0.30 (Et_2O/DCM, 10/90 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.60–7.52 (m, 2H), 7.39–7.18 (m, 18H), 4.93 (d, J = 10.6 Hz, 1H), 4.88–4.80 (m, 2H), 4.68 (d, J = 9.8 Hz, 1H, H-1), 4.59 (dd, J = 12.1, 5.3 Hz, 3H), 4.53 (d, J = 11.9 Hz, 1H), 4.29 (d, J = 12.5 Hz, 1H), 3.76 (ddd, J = 10.2, 6.8, 1.4 Hz, 2H, H-3, H-6), 3.70 (ddd, J = 11.0, 4.6, 1.3 Hz, 1H, H-6), 3.65–3.58 (m, 1H, H-4), 3.52–3.46 (m, 1H, H-5), 3.39 (ddt, J = 9.9, 8.7, 1.1 Hz, 1H, H-2), 2.93 (d, J = 8.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.3, 138.5, 138.4, 138.1, 133.6 (all quaternary), 132.1, 129.0, 128.6, 128.5, 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7 (all aromatic), 86.9 (CH, C-1), 86.5 (CH, C-3), 81.5 (CH, C-2), 79.1 (CH, C-5), 77.8 (CH, C-4), 75.9, 75.2, 73.5, 72.0 (all CH_2), 69.1 (CH_2, C-6), 36.5, 35.5 (both CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{37}H_{41}NO_6S$: 650.25523, found $[M + Na]^+$: 650.25491.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-1-thio-β-D-galactopyranoside (12). Using general procedure C starting from **2** (155 mg, 0.27 mmol) and *N*,*N*-dimethylacetamide (**17**), the crude product was purified by silica gel flash column chromatography (0% to 10% Et_2O in DCM), affording **12** (185 mg, 65%) as white solid. **TLC:** R_f = 0.59 (Et_2O/DCM, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.57–7.51 (m, 2H), 7.39–7.23 (m, 15H), 7.17 (dd, J = 5.0, 1.9 Hz, 3H), 4.91 (d, J = 11.5 Hz, 1H), 4.76–4.68 (m, 3H, H-1), 4.57 (d, J = 11.5 Hz, 1H), 4.46 (d, J = 12.3 Hz, 2H), 4.40 (d, J = 11.7 Hz, 1H), 4.31 (d, J = 12.8 Hz, 1H), 3.96 (d, J = 2.6 Hz, 1H, H-4), 3.79 (t, J = 9.3 Hz, 1H, H-2), 3.70 (dd, J = 9.1, 2.7 Hz, 1H, H-3), 3.66–3.60 (m, 3H, H-5, H-6), 2.87 (s, 3H), 2.83 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.5, 138.7, 138.3, 137.8, 133.8 (all quaternary), 131.5, 128.8, 128.4, 128.4, 128.2, 127.9, 127.8,

127.8, 127.7, 127.6, 127.5, 127.2 (all aromatic), 86.9 (CH, C-1), 83.8 (CH, C-3), 78.1 (CH, C-2), 77.2 (CH, C-5), 74.5, 73.5 (both CH_2), 73.5 (CH, C-4), 72.7, 71.9 (both CH_2), 68.7 (CH_2, C-6), 36.2, 35.3 (both CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{37}H_{41}NO_6S$: 650.25523, found $[M + Na]^+$: 650.25553.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-diphenylphosphine oxide)-1-thio-β-D-glucopyranoside (13). Using general procedure C starting from **1** (90 mg, 0.17 mmol) and (bromomethyl)diphenylphosphine oxide (**18**), the crude product was purified by silica gel flash column chromatography (60% to 100% EtOAc in *n*-heptane), affording **13** (56 mg, 45%) as white sticky compound. **TLC**: R_f = 0.57 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.86 (dddd, *J* = 11.6, 8.3, 3.0, 1.3 Hz, 4H), 7.54–7.11 (m, 27H), 4.82 (dd, *J* = 12.2, 6.3 Hz, 1H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.61–4.46 (m, 6H, H-1), 4.36 (d, *J* = 10.7 Hz, 1H), 3.75 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6), 3.68 (dd, *J* = 10.9, 4.8 Hz, 1H, H-6), 3.61–3.54 (m, 2H, H-3, H-4), 3.45 (ddd, *J* = 9.3, 4.7, 2.0 Hz, 1H, H-5), 3.41–3.33 (m, 1H, H-2) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.3, 138.2, 138.0, 133.5 (all quaternary), 132.3, 132.3, 132.2, 132.2, 132.1, 132.0, 131.9 (all aromatic), 131.8 (quaternary), 131.7, 131.7 (both aromatic), 131.3, 131.0, 130.5 (all quaternary), 129.1, 128.7, 128.6, 128.5, 128.5, 128.4, 128.06, 127.9, 127.8, 127.7, 127.7, 127.7, 127.7 (all aromatic), 87.0 (CH, C-1), 86.4 (CH, C-3), 83.1, 83.0 (both CH, C-2), 79.0 (CH, C-5), 77.9 (CH, C-4), 75.4, 75.1, 73.5, 71.3, 70.6 (all CH_2), 69.0 (CH_2, C-6) ppm; **^{31}P NMR** (202 MHz, $CDCl_3$): δ_P 27.3 ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{46}H_{45}O_6PS$: 757.27527, found $[M + H]^+$: 757.27581.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-diphenylphosphine oxide)-1-thio-β-D-galactopyranoside (14). Using general procedure C starting from **2** (100 mg, 0.18 mmol) and (bromomethyl)diphenylphosphine oxide (**18**), the crude product was purified by silica gel flash column chromatography (60% to 100% EtOAc in *n*-heptane), affording **14** (63 mg, 45%) as colourless sticky compound. **TLC**: R_f = 0.49 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.83 (dddd, *J* = 11.5, 9.5, 8.2, 1.4 Hz, 4H), 7.54–7.43 (m, 2H), 7.42–7.12 (m, 26H), 4.84 (d, *J* = 11.4 Hz, 1H), 4.66 (dd, *J* = 12.3, 6.1 Hz, 1H), 4.58 (dd, *J* = 12.3, 9.5 Hz, 1H), 4.53 (d, *J* = 9.7 Hz, 1H, H-1), 4.51–4.43 (m, 3H), 4.39 (dd, *J* = 11.5, 5.3 Hz, 2H), 3.89 (d, *J* = 2.8 Hz, 1H, H-4), 3.77 (t, *J* = 9.4 Hz, 1H, H-2), 3.64–3.53 (m, 3H, H-5, H-6), 3.49 (dd, *J* = 9.1, 2.8 Hz, 1H, H-3) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.7, 138.0, 137.9, 133.8 (all quaternary), 132.2, 132.2, 132.1, 132.1, 132.1, 132.0, 131.8, 131.7 (all aromatic), 131.7 (quaternary), 131.6 (aromatic), 131.0, 130.9 (both quaternary), 129.0, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.6, 127.4 (all aromatic), 87.3 (CH, C-1), 84.3 (CH, C-3), 79.7, 79.6 (both CH, C-2), 77.3 (CH, C-5), 74.6, 73.7 (both CH_2), 73.3 (CH, C-4), 72.5, 71.3, 70.6 (all CH_2), 68.8 ppm (CH_2, C-6); **^{31}P NMR** (202 MHz, $CDCl_3$): δ_P 27.59 ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{46}H_{45}O_6PS$: 757.27527, found $[M + H]^+$: 757.27564.

Methyl 3,4,6-tribenzyl-2-*O*-(2-methoxyethoxy)-α/β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (22). Using general procedure D starting from **3** (30 mg, 0.050 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 20% EtOAc in *n*-heptane), affording **22** as an anomeric mixture (α/β = 1/1, 48 mg, 96%). **TLC:** R_f = 0.31 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CHCl_3$): δ_H 8.03–7.96 (m, 2H), 7.96–7.88 (m, 2H), 7.89–7.81 (m, 2H), 7.55–7.46 (m, 2H), 7.47–7.20 (m, 26H), 7.15 (dd, *J* = 7.4, 2.2 Hz, 2H), 6.15 (t, *J* = 9.8 Hz, 1H, H-3′), 5.47 (dd, *J* = 10.3, 9.5 Hz, 1H, H-4′), 5.26 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2′), 5.22 (d, *J* = 3.6 Hz, 1H, H-1′), 5.01 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.54–4.48 (m, 2H), 4.44 (d, *J* = 12.2 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H, H-1), 4.33 (ddd, *J* = 9.7, 7.0, 2.2 Hz, 1H, H-5′), 4.13 (ddd, *J* = 10.6, 5.5, 3.7 Hz, 1H, H-6), 4.07 (dd, *J* = 11.0, 2.2 Hz, 1H), 3.78 (qd, *J* = 6.9, 4.2 Hz, 2H, H-6, H-6′), 3.69–3.57 (m, 3H, H-3, H-6, H-6′), 3.58–3.50 (m, 3H, H-5), 3.46 (s, 3H), 3.39 (ddd, *J* = 9.7, 4.6, 2.2 Hz, 1H, H-4), 3.33 (s, 3H), 3.27 (dd, *J* = 9.0, 7.8 Hz, 1H, H-2) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 166.0, 165.9, 165.5, 139.0 (all quaternary), 139.0, 138.3, 138.3, 133.5, 133.5, 133.2, 130.0, 130.0(all aromatic), 129.8, 129.3, 129.1 (all quaternary), 128.6, 128.5, 128.5, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.7 (all aromatic), 104.0 (CH, C-1), 97.0 (CH, C-1′), 84.5 (CH, C-3), 83.4 (CH, C-2), 77.7 (CH_2), 75.7 (CH_2), 75.1 (CH_2), 75.0 (CH, C-4), 73.6 (CH_2), 72.3 (CH, C-5), 72.3 (CH, C-2′), 72.0 (CH, C-6), 70.7 (CH, C-3′), 69.9 (CH, C-4′), 69.1 (CH, C-5′), 68.9 (CH, C-6′), 59.0 (CH_3), 55.7 (CH_3) ppm. **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{58}H_{60}O_{15}$: 1019.38299. Found $[M + Na]^+$: 1019.38148.

Methyl 3,4,6-tribenzyl-2-*O*-(2-methoxyethoxy)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (23). Using general procedure D starting from **4** (40 mg, 0.067 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 15% Et_2O in toluene), affording **23** as an anomeric mixture (α/β = 3/2, 63 mg, 95%). **TLC:** R_f = 0.27 (Et_2O/toluene, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.98 (dq, *J* = 7.0, 2.1, 1.7 Hz, 2H), 7.93–7.89 (m, 2H), 7.86–7.82 (m, 2H), 7.54–7.45 (m, 3H), 7.44–7.21 (m, 29H), 6.12 (t, *J* = 9.8 Hz, 1H, H-3′), 5.53 (dd, *J* = 10.3, 9.5 Hz, 1H, H-4′), 5.25 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2′), 5.14 (d, *J* = 3.7 Hz, 1H, H-1′), 4.99 (d, *J* = 3.5 Hz, 1H, H-1), 4.92 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.9 Hz, 1H), 4.34–4.28 (m, 2H, H-5′), 4.01 (t, *J* = 6.5 Hz, 1H, H-5), 3.96 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2), 3.93–3.86 (m, 3H, H-3, H-4, H-6′), 3.85–3.79 (m, 2H), 3.69 (dd, *J* = 11.2, 2.1 Hz, 1H, H-6′), 3.55–3.50 (m, 2H), 3.49–3.43 (m, 3H, H-6), 3.37 (s, 3H), 3.32 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 165.9, 165.5, 139.1, 138.3, 133.5 (all quaternary), 133.2, 130.1, 130.0, 129.8, 129.5 (all aromatic), 129.3, 129.2, 128.5 (all quaternary), 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.5, 123.6, 119.2, 119.0 (all aromatic), 98.0 (CH, C-1), 96.9 (CH, C-1′), 78.5 (CH, C-3), 77.8 (CH, C-2), 75.3 (CH, C-4), 74.9, 73.4, 73.0, 72.3 (all CH_2), 72.3 (C-2′), 70.9 (C-3′), 70.7 (CH_2), 69.7 (CH, C-4′), 69.4 (CH, C-5), 68.9 (CH, C-6), 68.7 (CH, C-5′), 66.8 (C-6′), 59.1, 55.6 (both CH_3) ppm. **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{58}H_{60}O_{15}$: 1019.38299. Found $[M + Na]^+$: 1019.37696.

Methyl 3,4,6-tribenzyl-2-*O*-(2-phenoxyethoxy)-α/β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (24). Using general procedure D starting from **5** (40 mg, 0.060 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 20% EtOAc in *n*-heptane), affording **24** as an anomeric mixture (α/β = 1/1, 35 mg, 54%). **TLC:** R_f = 0.32 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CHCl_3$): δ_H 8.02–7.95 (m, 2H), 7.92 (dt, *J* = 8.4, 1.7 Hz, 2H), 7.84 (ddd, *J* = 8.5, 3.3, 1.4 Hz, 2H), 7.54–7.19 (m, 24H), 7.15 (ddt, *J* = 6.1, 4.2, 2.0 Hz, 2H), 6.95–6.89 (m, 1H), 6.86–6.79 (m, 1H), 6.61–6.56 (m, 1H), 6.15 (td, *J* = 9.8, 2.1 Hz, 1H, H-3′), 5.55–5.47 (m, 1H, H-4′), 5.30–5.24 (m, 1H, H-2′), 5.22 (d, *J* = 3.7 Hz, 1H, H-1′), 5.03 (d, *J* = 10.8 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.81 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.76 (dd, *J* = 10.8, 4.9 Hz, 1H), 4.57–4.43 (m, 3H), 4.42–4.36 (m, 1H, H-1), 4.32 (dtd, *J* = 12.1, 6.9, 6.1, 4.0 Hz, 2H, H-5′), 4.19–3.99 (m, 4H, H-6, H-6′), 3.78 (dt, *J* = 11.3, 6.0 Hz, 1H, H-6′), 3.70–3.52 (m, 4H, H-5, H-6, H-3), 3.45 (s, 3H), 3.41 (dt, *J* = 6.8, 2.1 Hz, 1H, H-4), 3.38–3.30 (m, 1H, H-2) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 165.9, 165.5, 158.9, 138.8 (all quaternary), 138.3 (aromatic), 138.2 (quaternary), 135.5, 133.6, 133.5, 133.2, 130.1, 130.0, 129.8, 129.5 (all aromatic), 129.4, 129.4, 129.2, 129.2, 129.1 (all quaternary), 129.0, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.7, 125.8, 120.8, 117.1, 115.7, 114.6 (all aromatic), 103.8 (CH, C-1), 97.1 (CH, C-1′), 84.4 (CH, C-3), 83.2 (CH, C-2), 82.9 (CH_2), 77.7 (CH, C-5), 75.7 (CH_2), 75.1 (CH, C-4), 75.1 (CH_2), 73.6 (CH_2), 72.2 (CH, C-2′), 71.1 (CH_2), 70.8 (CH, C-3′), 69.7 (CH, C-4′), 69.0 (CH, C-5′), 68.9 (CH_2, C-6), 67.7 (CH_2, C-6′), 55.7 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{63}H_{62}O_{15}$: 1081.39864, found $[M + Na]^+$: 1081.39610.

Methyl 3,4,6-tribenzyl-2-*O*-(2-phenoxyethoxy)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (25). Using general procedure D starting from **8** (40 mg, 0.067 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 15% Et_2O in toluene), affording **25** as an anomeric mixture (α/β = 3/2, 49 mg, 77%). **TLC:** R_f = 0.34 (Et_2O/toluene, 10/90 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.96 (m, 2H), 7.92–7.88 (m, 2H), 7.86–7.82 (m, 2H), 7.55–7.17 (m, 27H), 6.93–6.82 (m, 2H), 6.11 (t, *J* = 9.8 Hz, 1H, H-3′), 5.51 (t, *J* = 9.9 Hz, 1H, H-4′), 5.23 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2′), 5.11 (d, *J* = 3.6 Hz, 1H, H-1′), 4.99 (d, *J* = 3.6 Hz, 1H, H-1), 4.92 (d, *J* = 11.5 Hz, 1H), 4.79 (d, *J* = 11.8 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.9 Hz, 1H), 4.34–4.25 (m, 2H, H-5′), 4.13–3.96 (m, 6H, H-2, H-5, H-6), 3.95–3.83 (m, 3H, H-3, H-4, H-6′), 3.66 (dt, *J* = 11.3, 2.7 Hz, 1H, H-6′), 3.51–3.41 (m, 2H), 3.34 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 165.9, 165.5, 159.0, 139.0, 138.9 (all quaternary), 138.3 (aromatic), 138.2 (quaternary), 133.5, 133.2, 130.1, 130.0, 129.8, 129.5 (all aromatic), 129.5, 129.3, 129.2 (all quaternary), 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 127.8, 127.8, 127.7, 127.6, 127.5, 120.9, 117.2 (all aromatic), 97.9 (CH, C-1), 96.9 (CH, C-1′), 78.4 (CH, C-3), 78.0 (CH, C-2), 75.3 (CH, C-4), 74.9, 73.4, 73.0 (all CH_2), 72.3 (CH, C-2′), 70.8 (CH, C-3′), 70.2 (CH_2, C-6′), 69.8 (CH, C-4′), 69.5 (CH, C-5), 68.8 (CH_2), 68.6 (CH, C-5′), 67.5 (CH_2), 66.8 (CH_2, C-6′), 55.6 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{63}H_{62}O_{15}$: 1081.39864, found $[M + Na]^+$: 1081.39683.

Methyl 3,4,6-tribenzyl-2-*O*-(((*R*)-tetrahydrofuran-2-yl)methoxy)-α/β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (26). Using general procedure D starting from **7** (40 mg, 0.064 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 15% Et_2O in toluene), affording **26** as an anomeric mixture (α/β = 1/2, 56 mg, 85%). **TLC:** R_f = 0.26 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.95 (m, 2H), 7.94–7.89 (m, 2H), 7.87–7.83 (m, 2H), 7.55–7.47 (m, 2H), 7.45–7.20 (m, 20H), 7.17–7.13 (m, 2H), 6.15 (dd, *J* = 10.1, 9.4 Hz, 1H, H-3′), 5.47 (dd, *J* = 10.3, 9.4 Hz, 1H, H-4′), 5.25 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2′), 5.21 (d, *J* = 3.6 Hz, 1H, H-1′), 5.06 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 5.0 Hz, 1H), 4.49 (d, *J* = 3.7 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.37 (d, *J* = 7.8 Hz, 1H, H-1), 4.33 (ddd, *J* = 9.9, 7.0, 2.2 Hz, 1H, H-5′), 4.14–4.05 (m, 2H), 3.96 (dd, *J* = 9.7, 4.3 Hz, 1H), 3.83 (dt, *J* = 8.4, 6.7 Hz, 1H), 3.79–3.72 (m, 2H, H-6′), 3.69–3.58 (m, 4H, H-3, H-6), 3.53 (t, *J* = 9.3 Hz, 1H, H-4), 3.46 (s, 3H), 3.39 (ddd, *J* = 9.7, 4.6, 2.2 Hz, 1H, H-5), 3.29 (dd, *J* = 9.0, 7.8 Hz, 1H, H-2), 2.01–1.93 (m, 1H), 1.86 (dt, *J* = 9.5, 6.6 Hz, 2H), 1.62–1.57 (m, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 166.0, 165.9, 139.0, 138.3 (all quaternary), 133.5, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.5, 129.3, 129.1 (all quaternary), 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 127.7 (all aromatic), 103.9 (CH, C-1), 97.0 (CH, C-1′), 84.6 (CH, C-3), 83.3 (CH, C-2), 78.1 (CH), 77.7 (CH, C-4), 75.8, 75.7, 75.1 (all CH_2), 75.0 (CH, C-5), 73.5 (CH_2), 72.3 (CH, C-2′), 70.8 (CH, C-3′), 69.9 (CH, C-4′), 69.0 (CH, C-5′), 68.9 (CH_2, C-6), 68.8 (CH_2, C-6′), 68.2 (CH_2), 55.7 (CH_3), 28.4, 25.8 (both CH_2) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{60}H_{62}O_{15}$: 1045.39864. Found $[M + Na]^+$: 1045.39527.

Methyl 3,4,6-tribenzyl-2-*O*-(((*R*)-tetrahydrofuran-2-yl)methoxy)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (27). Using general procedure D starting from **8** (40 mg, 0.064 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 15% Et_2O in toluene), affording **27** as an anomeric mixture (α/β = 1/1, 53 mg, 81%). **TLC:** R_f = 0.27 (Et_2O/toluene, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.96 (m, 2H), 7.89 (ddd, *J* = 27.7, 8.4, 1.4 Hz, 3H), 7.55–7.19 (m, 25H), 6.12 (t, *J* = 9.9 Hz, 1H, H-3′), 5.56 (t, *J* = 9.9 Hz, 1H, H-4′), 5.25 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2′), 5.14 (d, *J* = 3.7 Hz, 1H, H-1′), 4.99 (d, *J* = 3.4 Hz, 1H, H-1), 4.92 (d, *J* = 11.5 Hz, 1H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.37 (d, *J* = 11.9 Hz, 1H), 4.32–4.24 (m, 2H, H-5′), 4.09–4.02 (m, 1H), 3.99–3.93 (m, 2H, H-2, H-5), 3.92–3.85 (m, 3H, H-3, H-4), 3.84–3.81 (m, 1H, H-6′), 3.76–3.68 (m, 2H, H-6), 3.64 (dd, *J* = 11.2, 2.0 Hz, 1H, H-6′), 3.58 (dd, *J* = 10.1, 5.1 Hz, 1H, H-6), 3.43 (d, *J* = 6.7 Hz, 2H), 3.37 (s, 3H), 1.98–1.77 (m, 3H), 1.72 (ddt, *J* = 11.3, 8.1, 6.5 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 165.8, 165.3, 139.0, 138.8, 138.1 (all quaternary), 133.3, 133.0, 129.9, 129.8, 129.7 (all aromatic), 129.4,

129.2, 129.1 (all quaternary), 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 127.6, 127.6, 127.5, 127.5, 127.4, 124.4, 123.5 (all aromatic), 97.9 (CH, C-1), 96.8 (CH, C-1′), 78.3 (CH, C-3), 77.7 (CH), 77.5 (CH, C-2), 75.1 (CH, C-4), 74.7, 73.5, 73.2, 72.9 (all CH_2), 72.2 (CH, C-2′), 70.7 (CH, C-3′), 69.4 (CH, C-4′), 69.3 (CH, C-5), 68.8 (CH_2), 68.6 (CH, C-5′), 68.3 (CH_2, C-6), 66.6 (CH_2, C-6), 55.4 (CH_3), 29.7, 28.2, 25.7 (all CH_2) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{60}H_{62}O_{15}$: 1045.39864. Found $[M + Na]^+$: 1045.39502.

Methyl 3,4,6-tribenzyl-2-*O*-(((*S*)-tetrahydrofuran-2-yl)methoxy)-α/β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (28). Using general procedure D starting from **9** (40 mg, 0.064 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 15% Et_2O in toluene), affording **28** as an anomeric mixture (α/β = 0.7/1, 35 mg, 55%). **TLC:** R_f = 0.20 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.96 (m, 2H), 7.94–7.91 (m, 2H), 7.87–7.83 (m, 2H), 7.53–7.47 (m, 2H), 7.44–7.20 (m, 20H), 7.14 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.16 (t, *J* = 9.8 Hz, 1H, H-3′), 5.45 (t, *J* = 9.9 Hz, 1H, H-5′), 5.26 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2′), 5.21 (d, *J* = 3.6 Hz, 1H, H-1′), 5.01 (d, *J* = 10.9 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.54–4.48 (m, 2H), 4.45–4.38 (m, 2H, H-1), 4.34 (ddd, *J* = 10.0, 7.3, 2.2 Hz, 1H, H-5′), 4.05 (ddt, *J* = 14.5, 9.6, 4.3 Hz, 3H, H-6′), 3.84 (dt, *J* = 8.3, 6.6 Hz, 1H, H-6), 3.81–3.69 (m, 2H, H-6, H-6′), 3.67–3.52 (m, 5H, H-3, H-4), 3.47 (s, 3H), 3.39 (ddd, *J* = 9.7, 4.3, 2.3 Hz, 1H, H-5), 3.26 (dd, *J* = 8.9, 7.7 Hz, 1H, H-2), 1.96–1.78 (m, 3H), 1.64–1.58 (m, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 166.0, 165.9, 165.6, 139.0, 138.3, 138.3 (all quaternary), 133.5, 133.5, 133.2, 130.1, 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.3, 129.1 (all quaternary), 128.5, 128.5, 128.5, 128.4, 128.4, 128.1, 128.1, 127.8, 127.7 (all aromatic), 104.1 (CH, C-1), 96.9 (CH, C-1′), 84.6 (CH, C-3), 83.4 (CH, C-2), 78.1 (CH), 77.7 (CH, C-4), 75.8, 75.6, 75.1 (all CH_2), 75.0 (CH, C-5), 73.6 (CH_2), 72.3 (CH, C-2′), 70.7 (CH, C-3′), 70.1 (CH, C-4′), 69.1 (CH, C-5′), 68.9 (CH_2, C-6′), 68.3 (CH_2, C-6), 55.7 (CH_3), 28.2, 25.9 (both CH_2) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{60}H_{62}O_{15}$: 1045.39864, found $[M + Na]^+$: 1045.39864.

Methyl 3,4,6-tribenzyl-2-*O*-(((*S*)-tetrahydrofuran-2-yl)methoxy)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (29). Using general procedure D starting from **10** (40 mg, 0.064 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (0% to 15% Et_2O in toluene), affording **29** as an anomeric mixture (α/β = 1/1, 41 mg, 73%). **TLC:** R_f = 0.30 (Et_2O/toluene, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.01–7.96 (m, 2H), 7.93–7.89 (m, 2H), 7.87–7.83 (m, 2H), 7.55–7.20 (m, 24H), 6.12 (t, *J* = 9.9 Hz, 1H, H-3′), 5.54 (t, *J* = 9.9 Hz, 1H, H-4′), 5.24 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2′), 5.14 (d, *J* = 3.7 Hz, 1H, H-1′), 5.03 (d, *J* = 3.5 Hz, 1H, H-1), 4.92 (d, *J* = 11.5 Hz, 1H), 4.81 (d, *J* = 11.9 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 11.9 Hz, 1H), 4.34–4.26 (m, 2H, H-5′), 4.05 (qd, *J* = 6.8, 5.1 Hz, 1H, H-3), 4.02–3.96 (m, 2H, H-2, H-5), 3.91–3.86 (m, 2H, H-4, H-6′), 3.81 (dt, *J* = 8.4, 6.6 Hz, 1H, H-6), 3.73–3.61 (m, 4H, H-6, H-6′), 3.44 (dd, *J* = 6.6, 2.7 Hz, 2H), 3.37 (s, 3H), 1.96–1.75 (m, 3H), 1.63 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 165.9, 165.4, 139.1, 138.9, 138.6 (all quaternary), 133.4, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.5, 129.3, 129.2 (all quaternary), 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 127.8, 127.7, 127.6, 127.6, 127.5 (all aromatic), 97.9 (CH, C-1), 96.9 (CH, C-1′), 78.6 (CH), 78.4 (CH, C-3), 77.9 (CH, C-2), 75.3 (CH, C-4), 74.9, 74.1, 73.4, 73.1 (all CH_2), 72.3 (CH, C-2′), 70.9 (CH, C-3′), 69.7 (CH, C-4′), 69.4 (CH, C-5), 68.9 (CH_2, C-6), 68.7 (CH, C-5′), 68.3 (CH_2), 66.8 (CH_2, C-6′), 55.6 (CH_3), 28.4, 25.7 (both CH_2) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{60}H_{62}O_{15}$: 1045.39864, found $[M + Na]^+$: 1045.39704.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (30). Using general procedure D starting from **11** (40 mg, 0.064 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **30** as pure β-anomer (38 mg, 57%). **TLC:** R_f = 0.18 (EtOAc/heptane, 50/50 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.96 (m, 2H), 7.91 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.86–7.83 (m, 2H), 7.54–7.47 (m, 2H), 7.44–7.21 (m, 22H), 7.18–7.12 (m, 2H), 6.15 (t, *J* = 9.8 Hz, 1H, H-3′), 5.47 (dd, *J* = 10.3, 9.5 Hz, 1H, H-4′), 5.25 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2′), 5.21 (d, *J* = 3.6 Hz, 1H, H-1′), 5.00 (d, *J* = 11.0 Hz, 1H), 4.80 (dd, *J* = 10.9, 5.7 Hz, 2H), 4.70 (d, *J* = 13.0 Hz, 1H), 4.55–4.49 (m, 2H), 4.48–4.42 (m, 2H, H-1), 4.34 (ddd, *J* = 9.9, 7.0, 2.3 Hz, 1H, H-5′), 4.26 (d, *J* = 13.0 Hz, 1H), 4.06 (dd, *J* = 11.0, 2.3 Hz, 1H, H-6′), 3.77 (dd, *J* = 11.1, 7.0 Hz, 1H, H-6′), 3.69 (t, *J* = 9.0 Hz, 1H, H-3), 3.64–3.61 (m, 2H, H-6), 3.56 (t, *J* = 9.4 Hz, 1H, H-4), 3.46 (s, 3H), 3.40 (ddd, *J* = 9.8, 4.2, 2.5 Hz, 1H, H-5), 3.33 (dd, *J* = 9.0, 7.8 Hz, 1H, H-2), 2.94 (d, *J* = 10.3 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.8, 166.0, 165.9, 165.5, 138.8, 138.2 (all quaternary), 133.5, 133.5, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.2, 129.1 (all quaternary), 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6 (all aromatic), 103.4 (CH, C-1), 97.0 (CH, C-1′), 84.2 (CH, C-3), 83.3 (CH, C-2), 77.6 (CH, C-4), 75.7, 75.1 (both CH_2), 75.0 (CH, C-5), 73.5 (CH_2), 72.2 (CH, C-2′), 71.5 (CH_2), 70.7 (CH, C-3′), 69.9 (CH, C-4′), 69.0 (CH, C-5′), 68.8 (CH_2, C-6), 68.7 (CH_2, C-6′), 55.7, 36.4, 35.5 (all CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{59}H_{61}NO_{15}$: 1024.41194, found $[M + H]^+$: 1024.41336.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (31). Using general procedure D starting from **12** (40 mg, 0.064 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **31** as an anomeric mixture (α/β = 1/4, 28.1 mg, 43%). **TLC:** R_f = 0.65 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.99–7.95 (m, 2H), 7.91–7.87 (m, 2H), 7.86–7.82 (m, 2H), 7.55–7.45 (m, 2H), 7.44–7.22 (m, 20H), 7.22–7.18 (m, 2H), 6.13 (dd, *J* = 10.1, 9.5 Hz, 1H, H-3′), 5.38 (dd, *J* = 10.4, 9.4 Hz, 1H, H-4′), 5.22 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2′), 5.18 (d, *J* = 3.6 Hz, 1H, H-1′), 4.88 (d, *J* = 11.6 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.72 (d, *J* = 11.8 Hz, 1H), 4.64 (d, *J* =

12.7 Hz, 1H), 4.56 (d, J = 11.6 Hz, 1H), 4.42 (d, J = 7.5 Hz, 1H, H-1), 4.38–4.26 (m, 4H, H-5′), 4.01 (dd, J = 10.9, 2.2 Hz, 1H, H-6′), 3.84 (d, J = 2.9 Hz, 1H, H-4), 3.73 (dd, J = 10.9, 7.9 Hz, 1H, H-6′), 3.66 (dd, J = 9.6, 7.6 Hz, 1H, H-2), 3.55 (dd, J = 9.6, 2.9 Hz, 1H, H-3), 3.53–3.45 (m, 3H, H-5, H-6), 3.44 (s, 3H), 2.92 (d, J = 9.4 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 169.0, 166.0, 165.9, 165.6, 138.7, 138.7, 138.0 (all quaternary), 133.5, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.2, 129.1 (all quaternary), 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6 (all aromatic), 103.7 (CH, C-1), 96.8 (CH, C-1′), 81.7 (CH, C-3), 80.6 (CH, C-2), 74.7, 73.6 (both CH_2), 73.6 (CH, C-4), 73.5 (CH, C-5), 73.2 (CH_2), 72.3 (CH, C-2′), 72.0 (CH_2), 70.7 (CH, C-3′), 70.1 (CH, C-4′), 69.0 (CH, C-5′), 68.9 (CH_2, C-6′), 68.7 (CH_2, C-6), 55.7, 36.5, 35.5 (all CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{49}H_{61}NO_{15}$: 1024.41194, found $[M + H]^+$: 1024.41045.

Methyl 3,4,6-tribenzyl-2-*O*-(methyldiphenylphosphine-oxide)-α/β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (32). Using general procedure D starting from **13** (40 mg, 0.053 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 80% EtOAc in *n*-heptane), affording **32** as an anomeric mixture (α/β = 1/8, 41 mg, 67%). **TLC:** R_f = 0.64 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.95 (m, 2H), 7.92–7.79 (m, 8H), 7.56 (td, J = 7.4, 1.4 Hz, 1H), 7.54–7.45 (m, 4H), 7.44–7.31 (m, 8H), 7.31–7.18 (m, 13H), 7.15–7.09 (m, 2H), 7.09–7.05 (m, 2H), 6.13 (t, J = 9.8 Hz, 1H, H-3′), 5.31 (dd, J = 10.1, 9.3 Hz, 1H, H-4′), 5.19 (dd, J = 10.2, 3.6 Hz, 1H, H-2′), 5.04 (dd, J = 12.6, 6.3 Hz, 1H), 4.98 (d, J = 3.5 Hz, 1H, H-1′), 4.71 (d, J = 10.8 Hz, 1H), 4.51–4.41 (m, 4H), 4.40–4.30 (m, 4H, H-1, H-5′), 4.01 (dd, J = 10.4, 2.2 Hz, 1H, H-6′), 3.63 (dd, J = 10.5, 8.7 Hz, 1H), 3.57 (d, J = 3.2 Hz, 2H, H-6), 3.53 (d, J = 9.4 Hz, 1H, H-4), 3.48 (t, J = 8.9 Hz, 1H, H-3), 3.33 (ddt, J = 7.8, 5.7, 2.5 Hz, 2H, H-2, H-5), 3.28 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 165.9, 165.8, 165.8, 138.5, 138.1, 138.1 (all quaternary), 133.6, 133.5, 133.2, 132.3, 132.3, 132.2, 132.2, 131.9, 131.8, 131.8, 131.7 (all aromatic), 131.0, 130.9 (both quaternary), 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.2, 128.9 (all quaternary), 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6 (all aromatic), 103.5 (CH, C-1), 96.7 (CH, C-1′), 84.8 (CH, C-2), 84.0 (CH, C-3), 77.5 (CH, C-4), 75.3, 75.0 (both CH_2), 74.9 (CH, C-5), 73.6 (CH_2), 72.1 (CH, C-2′), 70.5 (CH, C-3′), 70.3 (CH, C-4′), 69.8 (CH_2), 69.5 (CH_2, C-6′), 68.8 (CH, C-5′), 68.5 (CH_2, C-6), 55.7 (CH_3) ppm; **^{31}P NMR** (202 MHz, $CDCl_3$): δ_P 27.35 ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{68}H_{65}O_{15}P$: 1153.41393, found $[M + H]^+$: 1153.41312.

Methyl 3,4,6-tribenzyl-2-*O*-(methyldiphenylphosphine-oxide)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (33). Using general procedure D starting from **14** (48 mg, 0.063 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**33**), the crude product was purified by silica gel flash column chromatography (30% to 80% EtOAc in *n*-heptane), affording **33** as an anomeric mixture (α/β = 1/8, 50 mg, 68%). **TLC:** R_f = 0.48 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.91–7.88 (m, 2H), 7.82–7.70 (m, 9H), 7.55–7.04 (m, 29H), 6.03 (t, J = 9.8 Hz, 1H), 5.24–5.17 (m, 1H), 5.12 (dd, J = 10.2, 3.6 Hz, 1H), 4.95–4.87 (m, 2H), 4.76 (d, J = 11.6 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.41–4.33 (m, 3H), 4.27–4.21 (m, 3H), 4.17 (d, J = 11.8 Hz, 1H), 3.92 (dd, J = 10.3, 2.1 Hz, 1H), 3.68 (d, J = 2.9 Hz, 1H), 3.61 (dd, J = 9.6, 7.6 Hz, 1H), 3.50 (dd, J = 10.3, 9.0 Hz, 1H), 3.38–3.30 (m, 3H), 3.30–3.26 (m, 1H), 3.17 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 165.8, 165.8, 165.7, 138.5, 138.4, 137.9 (all quaternary), 133.5, 133.4, 133.2, 132.7, 132.7, 132.2, 132.2 (all aromatic), 131.9 (quaternary), 131.9, 131.8, 131.7, 131.6 (all aromatic), 131.1, 131.1 (both quaternary), 130.0, 130.0, 129.7 (all aromatic), 129.4, 129.2 (both quaternary), 129.0 (aromatic), 128.9 (quaternary), 128.9, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 127.9, 127.9, 127.7, 127.6, 127.5 (all aromatic), 103.7 (CH, C-1), 96.6 (CH, C-1′), 82.1 (CH, C-2), 81.4 (CH, C-3), 74.7, 73.6 (both CH_2), 73.5 (CH, C-5), 73.4 (CH, C-4), 73.0 (CH_2), 72.1 (CH, C-2′), 70.7 (CH, C-3′), 70.5 (CH_2), 70.3 (CH, C-4′), 70.0 (CH_2), 69.4 (CH_2, C-6′), 68.7 (CH, C-5′), 68.6 (CH, C-5′), 55.6 (CH_3) ppm; **^{31}P NMR** (202 MHz, $CDCl_3$): δ_P 27.73 ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{68}H_{65}O_{15}P$: 1153.41393, found $[M + H]^+$: 1153.41352.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-*N*,*N*-diethylacetamide)-1-thio-β-D-glucopyranoside (34). Using general procedure C starting from **1** (106 mg, 0.20 mmol) and 2-chloro-*N*,*N*-diethylacetamide, the crude product was purified by silica gel flash column chromatography (0% to 10% Et_2O in DCM), affording **34** (84 mg, 66%) as sticky yellowish compound. **TLC:** R_f = 0.68 (Et_2O/DCM, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.59–7.51 (m, 2H), 7.40–7.19 (m, 18H), 4.99 (d, J = 10.4 Hz, 1H), 4.84 (t, J = 10.7 Hz, 2H), 4.67 (d, J = 9.8 Hz, 1H, H-1), 4.65–4.57 (m, 3H), 4.52 (d, J = 12.0 Hz, 1H), 4.25 (d, J = 12.1 Hz, 1H), 3.80–3.74 (m, 2H, H-3, H-6), 3.71 (dd, J = 10.9, 4.7 Hz, 1H, H-6), 3.61 (t, J = 9.4 Hz, 1H, H-4), 3.50 (ddd, J = 9.9, 4.7, 1.9 Hz, 1H, H-5), 3.44–3.32 (m, 3H, H-2), 3.26 (hept, J = 7.5 Hz, 2H), 1.12 (m, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 167.3, 138.4, 138.1, 133.5 (all quaternary), 132.0, 129.0, 128.5, 128.5, 128.4, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6 (all aromatic), 86.8 (CH, C-1), 86.4 (CH, C-3), 81.6 (CH, C-2), 79.1 (CH, C-5), 77.7 (CH, C-4), 75.9, 75.1, 73.4, 72.1 (all CH_2), 69.1 (CH_2, C-6), 41.3, 40.2 (both CH_2), 14.4, 13.0 (both CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{39}H_{45}NO_6S$: 656.30458, found $[M + H]^+$: 656.30491.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-*N*,*N*-diethylacetamide)-1-thio-β-D-galactopyranoside (35). Using general procedure C starting from **2** (105 mg, 0.19 mmol) and 2-chloro-*N*,*N*-diethylacetamide, the crude product was purified by silica gel flash column chromatography (0% to 10% Et_2O in DCM), affording **35** (86 mg, 68%) as sticky white compound. **TLC:** R_f = 0.76 (Et_2O/DCM, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.58–7.49 (m, 2H), 7.42–7.07 (m, 18H), 4.93 (d, J = 11.5 Hz, 1H), 4.77 (d, J = 11.5 Hz, 1H), 4.73 (d, J = 11.5 Hz, 1H), 4.66 (d, J = 9.6 Hz, 1H, H-1), 4.57 (d, J = 11.6 Hz, 1H), 4.50 (d, J = 12.3 Hz, 1H), 4.46 (d, J = 11.7 Hz, 1H), 4.41 (d, J = 11.7 Hz, 1H), 4.29 (d, J = 12.4 Hz, 1H), 3.95 (d, J = 2.8 Hz, 1H, H-4), 3.78 (t, J = 9.3 Hz, 1H, H-2), 3.69–3.59 (m, 4H, H-3, H-5, H-6), 3.35 (q, J = 7.1 Hz, 2H), 3.21 (qd, J = 7.2, 2.9 Hz, 2H), 1.08 (dt, J = 28.1, 7.0 Hz,

6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 167.6, 138.9, 138.4, 138.0, 134.0 (all quaternary), 131.6, 128.9, 128.6, 128.5, 128.3, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 127.3 (all aromatic), 87.2 (CH, C-1), 83.8 (CH, C-3), 78.3 (CH, C-2), 77.4 (CH, C-5), 74.6 (CH_2), 73.8 (CH, C-4), 73.7, 73.0, 72.2 (all CH_2), 68.9 (CH_2, C-6), 41.2, 40.1 (both CH_2), 14.4, 13.1 (both CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{39}H_{45}NO_6S$: 656.30458, found $[M + H]^+$: 656.30448.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-*N*,*N*-diphenylacetamide)-1-thio-β-D-glucopyranoside (36). Using general procedure C starting from **1** (106 mg, 0.20 mmol) and 2-chloro-*N*,*N*-diphenylacetamide, the crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane), affording **36** (83 mg, 56%) as sticky yellow compound. **TLC:** R_f = 0.29 (EtOAc/heptane, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.43–7.38 (m, 2H), 7.36–7.06 (m, 28H), 4.99 (d, *J* = 10.7 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 9.7 Hz, 1H, H-1), 4.59–4.55 (m, 2H), 4.52–4.44 (m, 2H), 4.10 (d, *J* = 14.6 Hz, 1H), 3.80–3.73 (m, 2H, H-3, H-6), 3.70 (dd, *J* = 10.8, 4.3 Hz, 1H, H-6), 3.55 (t, *J* = 9.5 Hz, 1H, H-4), 3.47 (ddd, *J* = 9.8, 4.3, 2.0 Hz, 1H, H-5), 3.21 (t, *J* = 9.2 Hz, 1H, H-2) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.2, 138.7, 138.4, 138.1, 132.7 (all quaternary), 132.6, 128.9, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6, 127.6 (all aromatic), 86.3 (CH, C-3), 86.3 (CH, C-1), 81.3 (CH, C-2), 79.0 (CH, C-5), 77.5 (CH, C-4), 75.8, 75.1, 73.4, 72.1 (all CH_2), 69.0 (CH_2, C-6) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{47}H_{45}NO_6S$: 752.30458, found $[M + H]^+$: 752.30680.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(methyl-*N*,*N*-diphenylacetamide)-1-thio-β-D-galactopyranoside (37). Using general procedure C starting from **2** (102 mg, 0.19 mmol) and 2-chloro-*N*,*N*-diphenylacetamide, the crude product was purified by silica gel flash column chromatography (0% to 30% EtOAc in *n*-heptane), affording **37** (45 mg, 32%) as sticky white compound. **TLC:** R_f = 0.29 (EtOAc/heptane, 40/60 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.45–7.04 (m, 30H), 4.90 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.75 (d, *J* = 11.5 Hz, 1H), 4.64 (d, *J* = 9.4 Hz, 1H, H-1), 4.54 (d, *J* = 11.6 Hz, 1H), 4.48–4.37 (m, 3H), 4.11 (d, *J* = 14.7 Hz, 1H), 3.92 (d, *J* = 2.8 Hz, 1H, H-4), 3.69 (dd, *J* = 6.3, 2.8 Hz, 1H, H-3), 3.65–3.57 (m, 4H, H-2, H-5, H-6) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.6, 138.9, 138.7, 138.0, 133.4 (all quaternary), 132.0, 128.8, 128.5, 128.5, 128.3, 128.0, 127.9, 127.7, 127.7, 127.5, 127.2 (all aromatic), 86.8 (CH, C-1), 83.7 (CH, C-3), 78.4 (CH, C-5), 77.2 (CH, C-2), 74.6 (CH_2), 74.0 (CH, C-4), 73.7, 73.1, 72.2 (all CH_2), 68.7 (CH_2, C-6) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{47}H_{45}NO_6S$: 752.30458, found $[M + H]^+$: 752.30458.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-((piperidin-1-yl)ethan-1-one)-1-thio-β-D-glucopyranoside (38). Using general procedure C starting from **1** (101 mg, 0.19 mmol) and 2-chloro-1-(piperidin-1-yl) ethan-1-one, the crude product was purified by silica gel flash column chromatography (0% to 10% Et_2O in DCM), affording **38** (95 mg, 77%) as white solid. **TLC:** R_f = 0.68 (Et_2O/DCM, 20/80 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.57–7.53 (m, 2H), 7.39–7.18 (m, 18H), 4.95 (d, *J* = 10.5 Hz, 1H), 4.85 (d, *J* = 4.5 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H, H-1), 4.59 (dd, *J* = 12.0, 1.8 Hz, 3H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.79–3.74 (m, 2H, H-3, H-6), 3.70 (dd, *J* = 10.9, 4.7 Hz, 1H, H-6), 3.60 (t, *J* = 9.5 Hz, 1H, H-4), 3.57–3.47 (m, 3H, H-5), 3.41–3.30 (m, 3H, H-2), 1.62 (q, *J* = 6.2 Hz, 2H), 1.57–1.50 (m, 3H), 1.50–1.43 (m, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 166.5, 138.4, 138.2, 133.6 (all quaternary), 132.1, 129.1, 128.6, 128.6, 128.5, 128.4, 128.0, 128.0, 127.9, 127.5, 127.7, 127.7 (all aromatic), 87.0 (CH, C-1), 86.5 (CH, C-3), 81.5 (CH, C-2), 79.1 (CH, C-5), 77.8 (CH, C-4), 76.0, 75.2, 73.5, 72.3 (all CH_2), 69.1 (CH_2, C-6), 46.2, 43.0, 26.6, 25.7, 24.7 (all CH_2) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{40}H_{45}NO_6S$: 668.30458, found $[M + H]^+$: 668.30591.

Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-((piperidin-1-yl)ethan-1-one)-1-thio-β-D-galactopyranoside (39). Using general procedure C starting from **2** (120 mg, 0.22 mmol) and 2-chloro-1-(piperidin-1-yl)ethan-1-one, the crude product was purified by silica gel flash column chromatography (0% to 10% Et_2O in DCM), affording **39** (77 mg, 52%) as white solid. **TLC:** R_f = 0.78 (Et_2O/DCM, 30/70 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.59–7.49 (m, 2H), 7.42–7.22 (m, 15H), 7.22–7.13 (m, 3H), 4.92 (d, *J* = 11.5 Hz, 1H), 4.73 (s, 2H), 4.66 (d, *J* = 9.6 Hz, 1H, H-1), 4.57 (d, *J* = 11.6 Hz, 1H), 4.46 (dd, *J* = 12.0, 2.4 Hz, 2H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.33 (d, *J* = 12.2 Hz, 1H), 3.96 (d, *J* = 2.8 Hz, 1H, H-4), 3.77 (t, *J* = 9.4 Hz, 1H, H-2), 3.68–3.58 (m, 4H, H-3, H-5, H-6), 3.51 (tq, *J* = 13.2, 7.6, 5.9 Hz, 2H), 3.37–3.23 (m, 2H), 1.72–1.33 (m, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 166.8, 138.9, 138.4, 138.0, 134.0 (all quaternary), 131.7, 128.9, 128.6, 128.5, 128.3, 128.1, 127.9, 127.9, 127.9, 127.8, 127.6, 127.3 (all aromatic), 87.2 (CH, C-1), 84.0 (CH, C-3), 78.1 (CH, C-2), 77.3 (CH, C-5), 74.6, 73.7 (both CH_2), 73.6 (CH, C-4), 72.9, 72.4 (both CH_2), 68.9 (CH_2, C-6), 46.1, 42.9, 26.5, 25.6, 24.7 (all CH_2) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{40}H_{45}NO_6S$: 668.30458, found $[M + H]^+$: 668.30369.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-diethylacetamide)-β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (40). Using general procedure D starting from **34** (40 mg, 0.061 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **40** as pure β-anomer (27 mg, 43%). **TLC:** R_f = 0.53 (EtOAc/heptane, 60/40 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.96 (m, 2H), 7.93–7.89 (m, 2H), 7.87–7.82 (m, 2H), 7.54–7.47 (m, 2H), 7.45–7.21 (m, 30H), 7.15 (dd, *J* = 7.4, 2.0 Hz, 2H), 6.15 (t, *J* = 9.8 Hz, 1H, H-3′), 5.45 (t, *J* = 9.8 Hz, 1H, H-4′), 5.25 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2′), 5.20 (d, *J* = 3.6 Hz, 1H, H-1′), 5.03 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 12.8 Hz, 1H), 4.53 (d, *J* = 4.0 Hz, 1H), 4.51 (d, *J* = 2.6 Hz, 1H), 4.44 (d, *J* = 6.9 Hz, 2H, H-1), 4.34 (ddd, *J* = 9.8, 7.2, 2.3 Hz, 1H, H-5′), 4.23 (d, *J* = 12.8 Hz, 1H), 4.04 (dd, *J* = 11.1, 2.3 Hz, 1H, H-6′), 3.78 (dd, *J* = 11.1, 7.1 Hz, 1H, H-6′), 3.69 (t, *J* = 9.0 Hz, 1H, H-3), 3.64–3.62 (m, 2H, H-6), 3.55 (t, *J* = 9.3 Hz, 1H, H-4), 3.45 (s, 3H), 3.43–3.35 (m, 3H, H-5), 3.34–3.20 (m, 3H, H-2), 1.15 (dt, *J* = 16.9, 7.1 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 167.9, 166.0, 165.9, 165.5, 138.8, 138.3 (all quaternary), 133.5, 133.5, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.2, 129.1 (all quaternary), 128.6, 128.5, 128.5, 128.4,

128.4, 128.1, 127.9, 127.8, 127.7, 127.7 (all aromatic), 103.6 (CH, C-1), 97.0 (CH, C-1′), 84.2 (CH, C-3), 83.6 (CH, C-2), 77.6 (CH, C-4), 75.7, 75.1 (both CH_2), 75.0 (CH, C-5), 73.5 (CH_2), 72.2 (CH, C-2′), 71.6 (CH_2), 70.7 (CH, C-3′), 69.9 (CH, C-4′), 69.1 (CH, C-5′), 68.9 (C-6, C-6′), 55.7 (CH_3), 41.3, 40.2 (both CH_2), 14.5, 13.1 (both CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{61}H_{65}NO_{15}$: 1052.44324, found $[M + H]^+$: 1052.44311.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-diethylacetamide)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (41). Using general procedure D starting from **35** (40 mg, 0.061 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **41** as an anomeric mixture (α/β = 1/5, 28 mg, 44%). **TLC:** R_f = 0.63 (EtOAc/heptane, 60/40 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.95 (m, 2H), 7.89 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.86–7.81 (m, 2H), 7.53–7.45 (m, 2H), 7.45–7.35 (m, 5H), 7.34–7.23 (m, 19H), 7.23–7.18 (m, 2H), 6.13 (t, *J* = 9.8 Hz, 1H, H-3′), 5.38 (dd, *J* = 10.3, 9.5 Hz, 1H, H-4′), 5.23 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2′), 5.17 (d, *J* = 3.7 Hz, 1H, H-1′), 4.89 (d, *J* = 11.6 Hz, 1H), 4.81 (d, *J* = 11.8 Hz, 1H), 4.72 (d, *J* = 11.8 Hz, 1H), 4.66 (d, *J* = 12.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.42 (d, *J* = 7.6 Hz, 1H, H-1), 4.39–4.32 (m, 2H, H-5′), 4.30 (d, *J* = 11.8 Hz, 1H), 4.26 (d, *J* = 12.7 Hz, 1H), 4.00 (dd, *J* = 11.0, 2.2 Hz, 1H, H-6′), 3.84 (d, *J* = 2.9 Hz, 1H, H-4), 3.75 (dd, *J* = 11.0, 8.0 Hz, 1H, H-6′), 3.65 (dd, *J* = 9.6, 7.5 Hz, 1H, H-2), 3.55 (dd, *J* = 9.6, 3.0 Hz, 1H, H-3), 3.52–3.44 (m, 3H, H-5, H-6), 3.43 (s, 3H), 3.39–3.33 (m, 2H), 3.24 (ddq, *J* = 28.6, 14.0, 7.1, 6.7 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.1, 166.0, 165.9, 165.6, 138.8, 138.8, 138.0 (all quaternary), 133.5, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.2, 129.1 (all quaternary), 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.6, 127.6 (all aromatic), 103.8 (CH, C-1), 96.8 (CH, C-1′), 81.7 (CH, C-3), 80.7 (CH, C-2), 74.7 (CH_2), 73.7 (CH, C-4), 73.6 (CH_2), 73.5 (CH, C-5), 73.3 (CH_2), 72.3 (CH, C-2′), 72.0 (CH_2), 70.7 (CH, C-3′), 70.1 (CH, C-4′), 69.1 (CH, C-5′), 68.9 (CH_2, C-6′), 68.7 (CH, C-6), 55.7 (CH_3), 41.2, 40.1 (both CH_2), 14.5, 13.1 (both CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{61}H_{65}NO_{15}$: 1052.44324, found $[M + H]^+$: 1052.44158.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-diphenylacetamide)-β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (42). Using general procedure D starting from **36** (40 mg, 0.053 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **42** as pure β-anomer (53 mg, 86%). **TLC:** R_f = 0.31 (EtOAc/heptane, 40/60 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.03–7.98 (m, 2H), 7.89 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.87–7.78 (m, 5H), 7.62–7.57 (m, 1H), 7.54–7.46 (m, 5H), 7.42–7.19 (m, 27H), 7.18–7.14 (m, 2H), 6.14 (t, *J* = 9.9 Hz, 1H, H-3′), 5.52 (t, *J* = 9.9 Hz, 1H, H-4′), 5.26 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2′), 5.21 (d, *J* = 3.6 Hz, 1H, H-1′), 5.03 (d, *J* = 10.9 Hz, 1H), 4.80 (dd, *J* = 10.9, 2.9 Hz, 2H), 4.59 (d, *J* = 14.8 Hz, 1H), 4.56–4.46 (m, 3H), 4.36 (d, *J* = 7.8 Hz, 1H, H-1), 4.24 (ddd, *J* = 10.3, 5.4, 2.4 Hz, 1H, H-5′), 4.11 (d, *J* = 14.8 Hz, 1H), 4.01 (dd, *J* = 11.2, 2.5 Hz, 1H, H-6′), 3.81 (d, *J* = 5.8 Hz, 1H), 3.73 (dd, *J* = 11.2, 5.5 Hz, 1H, H-6′), 3.70–3.63 (m, 2H, H-3, H-6), 3.60 (dd, *J* = 10.9, 4.8 Hz, 1H, H-6), 3.50–3.44 (m, 1H, H-4), 3.43 (s, 3H), 3.37 (ddd, *J* = 9.9, 4.8, 2.0 Hz, 1H, H-5), 3.14 (dd, *J* = 9.1, 7.8 Hz, 1H, H-2) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.6, 165.9, 165.8, 165.2, 138.9, 138.2, 138.1 (all quaternary), 133.4, 133.3, 133.0, 132.6, 132.6, 131.5, 131.5 (all aromatic), 130.5 (quaternary), 130.0, 129.9 (both aromatic), 129.6 (quaternary), 129.6 (aromatic), 129.4, 129.1, 129.1 (both quaternary), 128.8, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.5 (all aromatic), 103.1 (CH, C-1), 97.0 (CH, C-1′), 84.2 (CH, C-3), 83.0 (CH, C-2), 77.4 (CH, C-4), 75.6, 74.9 (both CH_2), 74.9 (CH, C-5), 73.3 (CH_2), 72.0 (CH, C-2′), 72.0 (CH_2), 70.8 (CH, C-3′), 69.3 (CH, C-4′), 68.8 (CH_2, C-6), 68.7 (CH, C-5), 68.2 (CH_2, C-6′), 55.6 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{69}H_{65}NO_{15}$: 1148.44324, found $[M + H]^+$: 1148.44728.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-diphenylacetamide)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (43). Using general procedure D starting from **37** (20 mg, 0.027 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **43** as an anomeric mixture (α/β = 1/8, 22 mg, 71%). **TLC:** R_f = 0.76 (EtOAc/heptane, 60/40 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.02–7.97 (m, 2H), 7.86 (ddd, *J* = 16.8, 8.3, 1.4 Hz, 4H), 7.54–7.49 (m, 1H), 7.48–7.44 (m, 1H), 7.42–7.20 (m, 32H), 6.11 (t, *J* = 9.8 Hz, 1H, H-3′), 5.42 (t, *J* = 9.9 Hz, 1H, H-4′), 5.22 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2′), 5.17 (d, *J* = 3.6 Hz, 1H, H-1′), 4.88 (d, *J* = 11.6 Hz, 1H), 4.83 (d, *J* = 11.7 Hz, 1H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.56–4.48 (m, 2H), 4.40–4.31 (m, 3H, H-1), 4.25 (ddd, *J* = 9.5, 6.7, 2.3 Hz, 1H, H-5′), 4.17 (d, *J* = 14.8 Hz, 1H), 3.94 (dd, *J* = 11.2, 2.4 Hz, 1H, H-6′), 3.81 (d, *J* = 2.9 Hz, 1H, H-4), 3.72 (dd, *J* = 11.2, 6.7 Hz, 1H, H-6′), 3.56 (dd, *J* = 9.6, 3.0 Hz, 1H, H-3), 3.53–3.44 (m, 4H, H-2, H-5, H-6), 3.39 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 169.1, 166.0, 166.0, 165.5, 139.0, 138.9, 138.0 (all quaternary), 133.5, 133.4, 133.1 (all aromatic), 130.1, 130.0, 129.7 (all quaternary), 129.5, 129.3, 129.2, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.6 (all aromatic), 103.7 (CH, C-1), 96.9 (CH, C-1′), 81.9 (CH, C-3), 80.6 (CH, C-2), 74.7 (CH_2), 74.1 (CH, C-4), 73.6, 73.5 (both CH_2), 73.4 (CH, C-5), 72.3 (CH, C-2′), 72.1 (CH, C-2′), 70.9 (CH_2), 69.7 (CH, C-4′), 69.0 (CH, C-5′), 68.7 (CH_2, C-6), 68.6 (CH_2, C-6′), 55.7 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{69}H_{65}NO_{15}$: 1148.44324, found $[M + H]^+$: 1148.44155.

Methyl 3,4,6-tribenzyl-2-*O*-((piperidin-1-yl)ethan-1-one)-α/β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (44). Using general procedure D starting from **38** (40 mg, 0.060 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **44** as an anomeric mixture (α/β = 1/30, 26 mg, 40%). **TLC:** R_f = 0.56 (EtOAc/heptane, 40/60 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.95 (m, 2H), 7.93–7.90 (m, 2H), 7.84 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.54–7.47 (m, 2H), 7.44–7.20 (m, 20H), 7.18–7.13 (m, 2H),

6.15 (t, J = 9.8 Hz, 1H, H-3′), 5.46 (dd, J = 10.3, 9.5 Hz, 1H, H-4′), 5.26 (dd, J = 10.2, 3.6 Hz, 1H, H-2′), 5.21 (d, J = 3.6 Hz, 1H, H-1′), 5.00 (d, J = 10.8 Hz, 1H), 4.80 (dd, J = 12.2, 10.9 Hz, 2H), 4.72 (d, J = 12.5 Hz, 1H), 4.53–4.50 (m, 2H), 4.46–4.41 (m, 2H, H-1), 4.34 (ddd, J = 9.8, 7.0, 2.3 Hz, 1H, H-5′), 4.24 (d, J = 12.6 Hz, 1H), 4.06 (dd, J = 11.0, 2.3 Hz, 1H, H-6′), 3.77 (dd, J = 11.0, 7.1 Hz, 1H, H-6′), 3.68 (t, J = 9.0 Hz, 1H, H-3), 3.62 (t, J = 3.1 Hz, 2H), 3.59–3.51 (m, 3H, H-4, H-6), 3.46 (s, 3H), 3.40 (ddd, J = 9.9, 4.3, 2.5 Hz, 1H, H-5), 3.31 (dd, J = 9.0, 7.8 Hz, 1H, H-2), 1.75–1.57 (m, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 167.1, 166.0, 165.9, 165.5, 138.8, 138.3 (all quaternary), 133.5, 133.5, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.2, 129.1 (all quaternary), 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7 (all aromatic), 103.5 (CH, C-1), 97.0 (CH, C-1′), 84.2 (CH, C-3), 83.3 (CH, C-2), 77.4 (CH, C-4), 75.7, 75.1 (both CH_2), 75.0 (CH, C-5), 73.5 (CH_2), 72.2 (CH, C-2′), 71.8 (CH_2), 70.7 (CH, C-3′), 69.9 (CH, C-4′), 69.0 (CH, C-5′), 68.8 (CH_2, C-6), 68.8 (CH_2, C-6′), 55.7 (CH_3), 46.1, 42.9, 26.6, 25.7, 24.7 (all CH_2) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{62}H_{65}NO_{15}$: 1064.44324, found $[M + H]^+$: 1064.44448.

Methyl 3,4,6-tribenzyl-2-*O*-((piperidin-1-yl)ethan-1-one)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzoyl-α-D-glucopyranoside (45). Using general procedure D starting from **39** (30 mg, 0.045 mmol) and methyl 2,3,4 tri-*O*-benzoyl-α-D-glycopyranose (**21**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **45** as an anomeric mixture (α/β = 1/4, 20 mg, 42%). **TLC:** R_f = 0.69 (EtOAc/heptane, 60/40 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 8.00–7.93 (m, 2H), 7.91–7.86 (m, 2H), 7.86–7.81 (m, 2H), 7.53–7.45 (m, 2H), 7.43–7.35 (m, 5H), 7.34–7.22 (m, 15H), 7.22–7.17 (m, 2H), 6.13 (t, J = 9.8 Hz, 1H, H-3′), 5.38 (dd, J = 10.3, 9.5 Hz, 1H, H-4′), 5.24 (dd, J = 10.2, 3.6 Hz, 1H, H-2′), 5.18 (d, J = 3.7 Hz, 1H, H-1′), 4.88 (d, J = 11.6 Hz, 1H), 4.79 (d, J = 11.8 Hz, 1H), 4.72 (d, J = 11.8 Hz, 1H), 4.65 (d, J = 12.4 Hz, 1H), 4.55 (d, J = 11.6 Hz, 1H), 4.40 (d, J = 7.6 Hz, 1H, H-1), 4.37–4.25 (m, 4H, H-6′), 4.01 (dd, J = 10.9, 2.2 Hz, 1H, H-6′), 3.83 (d, J = 2.9 Hz, 1H, H-4), 3.73 (dd, J = 10.9, 7.9 Hz, 1H), 3.64 (dd, J = 9.6, 7.6 Hz, 1H, H-2), 3.60–3.18 (m, 11H, H-3, H-5, H-6), 1.57–1.41 (m, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 167.2, 166.0, 165.9, 165.6, 138.7, 138.7, 138.0 (all quaternary), 133.5, 133.2, 130.1, 130.0, 129.8 (all aromatic), 129.4, 129.3, 129.1 (all quaternary), 128.5, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6 (all aromatic), 103.7 (CH, C-1), 96.8 (CH, C-1′), 81.7 (CH, C-3), 80.5 (CH, C-2), 74.7, 73.6 (both CH_2), 73.6 (CH, C-5), 73.5 (CH, C-4), 73.2, 72.3 (both CH_2), 72.2 (CH, C-2′), 70.7 (CH, C-3′), 70.1 (CH, C-4′), 69.0 (CH, C-5′), 68.9 (CH_2, C-6′), 68.7 (CH_2, C-6), 55.7 (CH_3), 46.1, 42.9, 26.6, 25.7, 24.7 (all CH_2) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{62}H_{65}NO_{15}$: 1064.44324, found $[M + H]^+$: 1064.43913.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-β-D-glucopyranosyl-(1 → 6)-2,3,4-*O*-tribenzyl-α-D-glucopyranoside (50). Using general procedure D starting from **12** (50 mg, 0.080 mmol) and methyl 2,3,4 tri-*O*-benzyl-α-D-glycopyranose (**46**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **50** as pure β-anomer (30 mg, 39%). **TLC:** R_f = 0.54 (EtOAc/heptane, 60/40 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.29 (tdt, J = 18.9, 8.6, 3.4 Hz, 28H), 7.17–7.14 (m, 2H), 4.97 (dd, J = 11.0, 2.6 Hz, 2H), 4.85–4.75 (m, 5H), 4.66 (d, J = 12.2 Hz, 1H), 4.62–4.51 (m, 6H, H-1′), 4.40 (d, J = 7.8 Hz, 1H, H-1), 4.24 (d, J = 13.3 Hz, 1H), 4.11 (dd, J = 10.9, 2.1 Hz, 1H, H-6′), 3.99 (t, J = 9.2 Hz, 1H, H-4′), 3.84 (ddd, J = 10.2, 5.5, 2.0 Hz, 1H, H-5′), 3.73–3.61 (m, 4H, H-3, H-6, H-6′), 3.56 (t, J = 9.4 Hz, 1H, H-4), 3.48 (dd, J = 9.6, 3.6 Hz, 1H, H-2′), 3.45–3.33 (m, 6H, H-2, H-5, H-3′), 2.79 (s, 3H), 2.75 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.5, 138.9, 138.9, 138.4, 138.3, 138.2, 138.2 (all quaternary), 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6 (all aromatic), 103.4 (CH, C-1), 98.0 (CH, C-1′), 84.3 (CH, C-3), 83.0 (CH, C-5), 82.0 (CH, C-4′), 79.9 (CH, C-2′), 78.4 (CH, C-3′), 77.8 (CH, C-4), 75.9, 75.6 (both CH_2), 75.1 (CH, C-5), 75.0, 75.0, 73.5, 73.34, 71.3 (all CH_2), 70.0 (CH, C-5′), 69.1 (CH_2, C-6), 68.9 (CH_2, C-6′), 55.4, 36.1, 35.3 (all CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{59}H_{67}NO_{12}$: 1004.45609, found $[M + Na]^+$: 1004.45386.

3,4,6-Tribenzyl-2-*O*-(methyl-*N*,*N*-diphenylacetamide)-α/β-D-glucopyranosyl-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (51). Using general procedure D starting from **11** (30 mg, 0.048 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**47**), the crude product was purified by silica gel flash column chromatography (30% to 80% EtOAc in *n*-heptane), affording **51** as an anomeric mixture (α/β = 1/9, 23 mg, 61%). **TLC:** R_f = 0.33 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.42–7.37 (m, 2H), 7.35–7.23 (m, 11H), 7.14 (dd, J = 7.5, 2.1 Hz, 2H), 5.48 (d, J = 5.0 Hz, 1H, H-1′), 5.09 (d, J = 10.9 Hz, 1H), 4.84 (d, J = 10.8 Hz, 1H), 4.81 (d, J = 2.6 Hz, 1H), 4.78 (d, J = 5.0 Hz, 1H), 4.61–4.56 (m, 2H, H-3′), 4.50 (dd, J = 11.5, 4.7 Hz, 2H), 4.43 (d, J = 7.8 Hz, 1H, H-1), 4.29 (dd, J = 5.0, 2.4 Hz, 1H, H-2′), 4.23–4.21 (m, 1H), 4.20 (d, J = 2.1 Hz, 1H, H-4′), 4.11 (dd, J = 10.7, 2.9 Hz, 1H, H-6′), 4.01 (dt, J = 8.0, 2.4 Hz, 1H, H-5′), 3.73–3.63 (m, 4H, H-3, H-6, H-6′), 3.63–3.56 (m, 1H, H-4), 3.42 (ddd, J = 9.9, 4.4, 2.1 Hz, 1H, H-5), 3.36 (dd, J = 9.0, 7.8 Hz, 1H, H-2), 2.96 (s, 3H), 2.93 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H), 1.30 (d, J = 4.9 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 169.2, 138.9, 138.3, 138.3 (all quaternary), 128.5, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6 (all aromatic), 109.5, 108.6 (both quaternary), 103.8 (CH, C-1), 96.4 (CH, C-1′), 84.1 (CH, C-3), 83.5 (CH, C-2), 77.6 (CH, C-4), 75.6, 75.1 (both CH_2), 74.8 (CH, C-5), 73.6 (CH_2), 71.6 (CH, C-4′), 71.3 (CH_2), 70.9 (CH, C-3′), 70.5 (CH, C-2), 69.9 (CH_2, C-6′), 68.9 (CH_2, C-6), 67.6, 36.5, 35.5, 26.2, 26.1, 25.1, 24.6 (all CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{43}H_{55}NO_{12}$: 778.38025, found $[M + H]^+$: 778.38084.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-α/β-D-glucopyranosyl-(1 → 4)-2,3,6-*O*-benzyl-α-D-glucopyranoside (52). Using general procedure D starting from **12** (30 mg, 0.048 mmol) and methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**48**), the crude product was purified by silica gel flash column chromatography (30% to 80% EtOAc in *n*-heptane), affording **52** as an anomeric mixture (α/β = 1/2, 10 mg, 30%). **TLC:** R_f = 0.46 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H

7.42–7.18 (m, 28H), 7.16 (dd, J = 7.5, 2.0 Hz, 2H), 5.03 (d, J = 11.4 Hz, 1H), 4.88 (d, J = 11.1 Hz, 1H), 4.84 (d, J = 11.2 Hz, 1H), 4.79–4.74 (m, 3H), 4.63–4.60 (m, 2H), 4.59–4.50 (m, 4H, H-1′), 4.45 (d, J = 7.9 Hz, 1H, H-1), 4.41 (d, J = 7.1 Hz, 1H), 4.36 (d, J = 13.4 Hz, 1H), 4.29 (d, J = 13.1 Hz, 1H), 4.01 (t, J = 9.4 Hz, 1H, H-5′), 3.98–3.94 (m, 1H, H-6′), 3.84 (t, J = 9.2 Hz, 1H, H-3′), 3.73–3.68 (m, 2H, H-4′, H-6′), 3.66 (dd, J = 11.0, 1.9 Hz, 1H, H-6), 3.60 (t, J = 9.3 Hz, 1H, H-4), 3.55–3.47 (m, 3H, H-2′, H-3′, H-6), 3.36 (s, 3H), 3.28–3.21 (m, 2H, H-2, H-5), 2.86 (s, 3H), 2.78 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 176.1, 168.6, 139.7, 138.9, 138.6, 138.5, 138.4, 138.3 (all quaternary), 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.2, 127.2, 127.0 (all aromatic), 101.9 (CH, C-1), 98.5 (CH, C-1′), 84.6 (CH, C-3), 83.8 (CH, C-2), 80.4 (CH, C-3′), 79.2 (CH, C-2′), 78.2 (CH, C-4), 76.3 (CH, C-5′), 75.5, 75.4 (both CH_2), 75.2 (CH, C-5), 74.9, 73.8, 73.5, 73.4, 71.6 (all CH_2), 70.2 (CH, C-4′), 68.9 (CH_2, C-6), 68.6 (CH_2, C-6′), 55.6, 36.3, 35.4 (all CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{59}H_{67}NO_{12}$: 1004.45609, found $[M + Na]^+$: 1004.45235.

1-Adamantanyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-3,4,6-tri-benzyl-α/β-D-glucopyranoside (53). Using general procedure D starting from **11** (30 mg, 0.048 mmol) and adamantanol (**49**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **53** as an anomeric mixture (α/β = 1/1, 11 mg, 34%). **TLC:** R_f = 0.36 (Et_2O/toluene, 50/50 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.38–7.34 (m, 2H), 7.33–7.23 (m, 12H), 7.19 (dd, J = 7.7, 1.9 Hz, 2H), 4.99 (d, J = 11.0 Hz, 1H), 4.83 (d, J = 10.9 Hz, 2H), 4.71 (d, J = 7.8 Hz, 1H, H-1), 4.64 (d, J = 13.2 Hz, 1H), 4.60–4.50 (m, 3H), 4.28 (d, J = 13.2 Hz, 1H), 3.73–3.68 (m, 2H, H-3, H-6), 3.60 (dd, J = 10.7, 5.5 Hz, 1H, H-6), 3.50 (dd, J = 9.9, 8.6 Hz, 1H, H-4), 3.45 (ddd, J = 9.8, 5.5, 1.9 Hz, 1H, H-5), 3.30 (dd, J = 9.2, 7.8 Hz, 1H, H-2), 2.92 (s, 3H), 2.90 (s, 3H), 2.14 (p, J = 3.1 Hz, 3H), 1.92–1.87 (m, 3H), 1.81 (dp, J = 11.2, 1.9 Hz, 3H), 1.67–1.60 (m, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.9, 139.0, 138.5, 138.3 (all quaternary), 128.5, 128.4, 128.4, 128.1, 128.1, 127.9, 127.7, 127.6 (all aromatic), 96.1 (CH, C-1), 84.7 (CH, C-3), 83.6 (CH, C-2), 78.3 (CH, C-4), 75.7, 75.0 (both CH_2), 74.6 (CH, C-5), 73.5, 71.6 (both CH_2), 69.6 (CH_2, C-6), 42.9 (CH_2), 36.4 (CH_3 and CH_2), 30.9 (CH) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{41}H_{51}NO_7$: 692.35632, found $[M + Na]^+$: 692.35509.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-α/β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzyl-α-D-glucopyranoside (54). Using general procedure D starting from **12** (30 mg, 0.048 mmol) and methyl 2,3,4 tri-*O*-benzyl-α-D-glycopyranose (**46**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **54** as mixture of anomers (α/β = 1/3, 20 mg, 40%). **TLC:** R_f = 0.54 (EtOAc/heptane, 60/40 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.72 (dd, J = 5.7, 3.3 Hz, 2H), 7.53 (dd, J = 5.7, 3.3 Hz, 2H), 7.41–7.17 (m, 35H), 4.95 (d, J = 11.2 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.80–4.74 (m, 4H), 4.65 (d, J = 12.2 Hz, 1H), 4.57–4.55 (m, 3H, H-1′), 4.42 (d, J = 11.8 Hz, 1H), 4.37 (m, 4H, H-1), 4.30 (d, J = 13.1 Hz, 1H), 4.08 (dd, J = 10.8, 2.1 Hz, 1H, H-6′), 3.96 (t, J = 9.2 Hz, 1H, H-3′), 3.88 (d, J = 2.9 Hz, 1H, H-4), 3.83 (ddd, J = 10.2, 6.0, 2.1 Hz, 1H, H-5′), 3.70 (dd, J = 9.6, 7.6 Hz, 1H, H-2), 3.62–3.46 (m, 6H, H-5, H-6, H-2′, H-4′, H-6), 3.38–3.32 (m, 4H, H-3), 2.84–2.68 (m, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 168.9, 139.0, 138.8, 138.7, 138.5, 138.3, 138.0 (all quaternary), 131.1, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 128.0, 127.7, 127.7, 127.7, 127.6, 127.6 (all aromatic), 103.7 (CH, C-1′), 97.9 (CH, C-1), 82.1 (CH, C-3′), 82.0 (CH, C-5), 80.3 (CH, C-2), 80.0 (CH, C-2′), 78.6 (CH, C-3), 75.9, 75.0, 74.8 (all CH_2), 73.7 (CH, C-4), 73.4 (CH, C-4′), 73.4, 73.0, 71.7 (all CH_2), 70.0 (CH, C-5′), 69.0 (CH_2, C-6′) 68.7 (CH_2, C-6), 55.4, 36.2, 35.3 (all CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{59}H_{67}NO_{12}$: 1004.45609, found $[M + Na]^+$: 1004.45410.

3,4,6-Tribenzyl-2-*O*-(methyl-*N*,*N*-diphenylacetamide)-α/β-D-galactopyranosyl-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (55). Using general procedure D starting from **12** (40 mg, 0.063 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**47**), the crude product was purified by silica gel flash column chromatography (30% to 80% EtOAc in *n*-heptane), affording **55** as an anomeric mixture (α/β = 1/4, 28 mg, 56%). **TLC:** R_f = 0.40 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.35–7.32 (m, 2H), 7.31–7.15 (m, 18H), 5.40 (d, J = 5.0 Hz, 1H, H-1′), 4.84 (dd, J = 16.0, 11.7 Hz, 2H), 4.70 (t, J = 12.5 Hz, 2H), 4.54 (d, J = 11.7 Hz, 1H), 4.49 (dd, J = 7.9, 2.4 Hz, 1H, H-3′), 4.38–4.30 (m, 2H, H-1), 4.20 (dd, J = 5.0, 2.4 Hz, 1H, H-2′), 4.17 (d, J = 13.2 Hz, 1H), 4.10 (dd, J = 8.0, 1.9 Hz, 1H, H-4′), 4.00 (dd, J = 10.7, 2.9 Hz, 1H, H-6′), 3.92 (dt, J = 8.0, 2.5 Hz, 1H, H-5′), 3.78 (d, J = 2.9 Hz, 1H, H-4′), 3.62 (dd, J = 9.7, 7.6 Hz, 1H, H-2), 3.56–3.45 (m, 4H, H-3, H-6, H-6′), 3.45–3.40 (m, 1H, H-5), 2.87 (s, 3H), 2.85 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.22 (s, 3H), 1.22 (s, 4H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 169.4, 138.9, 138.8, 138.0 (all quaternary), 128.6, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.7, 127.6 (all aromatic), 109.5, 108.6 (both quaternary), 104.0 (CH, C-1), 96.4 (CH, C-1′), 81.3 (CH, C-3), 80.9 (CH, C-2), 74.0 (CH, C-4), 73.6, 73.5 (both CH_2), 73.4 (CH, C-5), 71.7 (CH_2), 71.7 (CH, C-4′), 70.9 (CH, C-3′), 70.5 (CH, C-2′), 69.8 (CH_2, C-6′), 68.8 (CH_2, C-6), 67.6 (CH, C-5′), 36.5, 35.5, 26.2, 26.1, 25.2 (all CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{43}H_{55}NO_{12}$: 778.38025, found $[M + H]^+$: 778.38075.

Methyl 3,4,6-tribenzyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-α/β-D-galactopyranosyl-(1 → 4)-2,3,6-*O*-benzyl-α-D-glucopyranoside (56). Using general procedure D starting from **12** (40 mg, 0.063 mmol) and methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**48**), the crude product was purified by silica gel flash column chromatography (30% to 80% EtOAc in *n*-heptane), affording **56** as an anomeric mixture (α/β = 1/1, 14 mg, 22%). **TLC:** R_f = 0.69 (EtOAc/heptane, 80/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.40–7.19 (m, 27H), 7.18–7.11 (m, 3H), 5.00 (d, J = 10.7 Hz, 1H), 4.91 (d, J = 11.4 Hz, 1H), 4.80 (d, J = 12.0 Hz, 1H), 4.75–4.70 (m, 2H), 4.67–4.58 (m, 2H), 4.57 (d, J = 3.7 Hz, 1H, H-1′), 4.54–4.51 (m, 2H), 4.50–4.46 (m, 1H), 4.43 (d, J = 7.7 Hz, 1H, H-1), 4.36 (d, J = 6.7 Hz, 1H), 4.33 (d, J = 2.2 Hz, 1H), 4.23 (d, J = 11.9 Hz, 1H), 4.02–3.97 (m, 1H, H-6′), 3.95 (d, J = 9.4 Hz,

1H, H-4′), 3.91–3.88 (m, 1H, H-4), 3.82 (t, J = 9.3 Hz, 1H, H-3′), 3.75–3.70 (m, 2H, H-5′, H-6′), 3.61 (dd, J = 9.7, 7.6 Hz, 1H, H-2), 3.52 (t, J = 8.7 Hz, 1H, H-6), 3.48 (dd, J = 9.6, 3.8 Hz, 1H, H-2′), 3.42–3.32 (m, 6H, H-3, H-6), 3.29 (dd, J = 8.6, 5.0 Hz, 1H, H-5), 2.83 (s, 3H), 2.77 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 175.9, 169.3, 168.9, 139.6, 139.1, 138.6, 138.6, 138.3, 137.6 (all quaternary), 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.1, 127.1, 126.7 (all aromatic), 102.4 (CH, C-1), 98.5 (CH, C-1′), 82.5 (CH, C-3), 80.9 (CH, C-2), 80.5 (CH, C-3′), 79.3 (CH, C-2′), 76.7 (CH, C-4′), 75.5, 74.9, 73.8 (all CH_2), 73.5 (CH, C-4), 73.4, 73.1 (both CH_2), 73.1 (CH, C-5′), 72.3, 72.0 (both CH_2), 68.7 (CH_2, C-6′), 68.2 (CH_2, C-6), 55.5, 36.6, 36.3 (all CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{59}H_{67}NO_{12}$: 982.47415, found $[M + H]^+$: 982.47593.

1-Adamantanyl-2-*O*-(methyl-*N*,*N*-dimethylacetamide)-3,4,6-tribenzyl-α/β-D-galactopyranoside (57). Using general procedure D starting from **12** (40 mg, 0.063 mmol) and adamantanol (**49**), the crude product was purified by silica gel flash column chromatography (30% to 60% EtOAc in *n*-heptane), affording **57** as an anomeric mixture (α/β = 2/3, 12 mg, 28%). **TLC:** R_f = 0.47 (EtOAc/heptane, 60/40 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.37–7.17 (m, 15H), 4.90 (d, J = 11.6 Hz, 1H), 4.77–4.70 (m, 2H), 4.67 (d, J = 7.4 Hz, 1H), 4.61 (d, J = 10.2 Hz, 1H), 4.58 (d, J = 8.8 Hz, 1H), 4.44 (d, J = 11.7 Hz, 1H), 4.39 (d, J = 11.7 Hz, 1H), 4.34 (d, J = 7.0 Hz, 1H), 3.85 (d, J = 2.8 Hz, 1H), 3.64 (dd, J = 9.7, 7.5 Hz, 1H), 3.59 (t, J = 3.1 Hz, 1H), 3.56 (d, J = 7.1 Hz, 2H), 3.52–3.50 (m, 1H), 2.90 (s, 3H), 2.89–2.88 (s, 3H), 2.11 (s, 3H), 1.87 (d, J = 12.2 Hz, 3H), 1.78 (dd, J = 11.1, 2.6 Hz, 3H), 1.64–1.59 (m, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 169.1, 138.8, 138.8, 138.3, 138.2 (all quaternary), 128.5, 128.5, 128.44, 128.3, 128.3, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5 (all aromatic), 96.3 (CH, C-1), 82.4 (CH, C-3), 80.7 (CH, C-2), 74.6 (CH_2), 73.8 (CH, C-4), 73.7 (CH_2), 73.3 (CH_2), 73.2 (CH, C-5), 72.1 (CH_2), 69.4 (CH_2, C-6), 42.8 (CH_2), 36.4 (CH_3 and CH_2), 30.8 (CH) ppm; **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calculated for $C_{41}H_{51}NO_7$: 670.37438, found $[M + H]^+$: 670.37506.

3,4,6-Tribenzyl-β-D-galactopyranosyl-(1 → 6)-2,3,4-*O*-tribenzyl-α-D-glucopyranoside (58). 25 mg (0.025 mmol, 1.0 eq.) of **50** was dissolved in THF (250 μL) and 1.0 μL (0.056 mmol, 2.2 eq.) water was added. To the mixture was added 150 μL of a 1.0 M *t*-BuOK solution (0.15 mmol, 5.9 eq.). The reaction mixture was stirred at room temperature for 18 h. The reaction was quenched with ice until two layers were formed. A solution of 2 M $KHSO_4$ was added until the pH was 1. The solution was taken up in water (5 mL). The mixture was extracted with Et_2O (5 × 10 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtrated and evaporated *in vacuo* to yield the carboxylic acid. The carboxylic acid was dissolved in dry DMF (40 μL). 5.3 μL DIPEA (0.031 mmol, 1.2 eq.) was added and the mixture was stirred on ice. To the cold solution was added 11 μL (0.027 mmol, 1.1 eq.) of a DPPA in dry DMF solution (1.1/1 v/v) and the solution was allowed to warm up to room temperature and was stirred for 2 h. The solution was cooled on ice and 1.4 μL (0.012 mmol, 0.5 eq.) of an acetic acid in dry DMF solution (1/1 v/v) was added to quench the reaction. At ambient temperature was added 21 μL (0.23 mmol, 9 eq.) of *t*-BuOH and the mixture was heated to 100 °C for 1 h. The solution was cooled on ice and 92 μL of a 2 M HCl solution was added. The mixture was taken up in water (5 mL) and extracted with toluene (3 × 10 mL). The combined toluene layers were washed with 1 M NaOH (10 mL), water (10 mL), brine (10 mL), dried over Na_2SO_4 (anhydrous), filtrated and evaporated *in vacuo*. The residue was dissolved in ethanol (10 μL), THF (30 μL) and 1 M NaOH was added (30 μL). The mixture was heated to 60 °C and for 3 h, heating was removed and the reaction was stirred for 14 h at ambient temperature. The reaction mixture was taken up in water (10 mL) and was extracted with toluene (3 × 10 mL). The combined toluene layers were washed with water (2 × 15 mL), washed with brine (15 mL), dried over Na_2SO_4 (anhydrous), filtrated and evaporated *in vacuo* to yield the crude product. The product was purified by silica gel flash column chromatography (30 to 60% EtOAc in *n*-heptane) to afford the product **58** (11.3 mg, 50%). **TLC:** R_f = 0.48 (EtOAc/heptane, 40/60 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.37–7.23 (m, 27H), 7.18–7.10 (m, 3H), 4.98 (d, J = 10.8 Hz, 1H), 4.90 (t, J = 11.7 Hz, 2H), 4.84–4.76 (m, 4H), 4.65 (d, J = 12.1 Hz, 1H), 4.63–4.60 (m, 2H, H-1′), 4.58 (d, J = 12.2 Hz, 1H), 4.54–4.50 (m, 2H), 4.22 (d, J = 6.7 Hz, 1H, H-1), 4.14 (dd, J = 11.1, 2.3 Hz, 1H, H-6′), 3.99 (t, J = 9.3 Hz, 1H, H-3), 3.82 (ddd, J = 10.1, 5.1, 2.2 Hz, 1H, H-5), 3.72 (dd, J = 10.9, 2.0 Hz, 1H, H-6), 3.67 (ddd, J = 10.9, 4.9, 2.0 Hz, 2H, H-6, H-6′), 3.59–3.47 (m, 5H, H-2, H-3, H-4, H-2′, H-4′), 3.44 (dq, J = 7.1, 2.1 Hz, 1H, H-5), 3.37 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 138.7, 138.6, 138.2, 138.2, 138.1, 138.1 (all quaternary), 129.4, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 124.4, 121.3 (all aromatic), 103.5 (CH, C-1′), 98.1 (CH, C-1), 84.5 (CH, C-2), 82.0 (CH, C-3), 79.7 (CH, C-4), 78.0 (CH, C-4′), 77.5 (CH, C-2′), 75.8 (CH_2), 75.3 (CH, C-5), 75.1, 75.0, 75.0 (all CH_2), 74.5 (CH, C-3), 73.5, 73.4 (both CH_2), 69.8 (CH, C-5′), 69.0 (CH_2, C-6), 68.8 (CH_2, C-6′), 55.3 (CH_3) ppm; **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calculated for $C_{55}H_{60}O_{11}$: 919.40333, found 919.40370.

(*R*)-(Tetrahydrofuran-2-yl)methanol. In a three neck round bottom flask equipped with cooler, thermometer and dropping funnel was dissolved 0.95 gram (25 mmol, 1.6 eq.) $LiAlH_4$ at 0 °C under an inert atmosphere in dry THF (24 mL). The $LiAlH_4$ solution was stirred for 15 minutes. 1.5 mL (15 mmol, 1.0 eq.) (2*R*)-tetrahydro-2-furancarboxylic acid was dissolved in dry THF (15 mL). The carboxylic acid in THF solution was added dropwise to the $LiAlH_4$ solution. The solution was allowed to reach a maximum temperature of 40 °C during addition of carboxylic acid solution in THF. The mixture was stirred at room temperature for 16 hours. The reaction was quenched by slow addition of saturated ammonium chloride (130 mL) at 0 °C. EtOAc (90 mL) was added to the mixture. The mixture was filtrated and the organic layer was separated from the aqueous layer. The aqueous layer was washed with EtOAc

(5 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtrated and evaporated *in vacuo* to afford the pure product as colourless liquid (300 mg, 19%). **TLC**: R_f = 0.25 (EtOH/DCM, 1/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 4.01 (qd, J = 6.8, 3.3 Hz, 1H), 3.90–3.84 (m, 1H), 3.83–3.75 (m, 1H), 3.66 (dd, J = 11.7, 3.3 Hz, 1H), 3.50 (dd, J = 11.6, 6.2 Hz, 1H), 2.60 (s, 1H), 1.98–1.85 (m, 3H), 1.70–1.60 (m, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 79.5 (CH), 68.2, 64.9, 27.1, 26.0 (all CH_2) ppm.

(*S*)-(Tetrahydrofuran-2-yl)methanol. In a three neck round bottom flask equipped with cooler, thermometer and dropping funnel was dissolved 1.13 gram (30 mmol, 1.9 eq.) $LiAlH_4$ at 0 °C under an inert atmosphere in dry THF (10 mL). The $LiAlH_4$ solution was stirred for 15 minutes. 1.24 mL (13 mmol, 1.0 eq.) (2*S*)-tetrahydro-2-furancarboxylic acid was dissolved in dry THF (5 mL). The carboxylic acid in THF solution was added dropwise to the $LiAlH_4$ solution. The solution was allowed to reach a maximum temperature of 40 °C during addition of carboxylic acid in THF. The mixture was stirred at room temperature for 16 hours. The reaction was quenched by slow addition of saturated ammonium chloride (130 mL) at 0 °C. EtOAc (90 mL) was added to the mixture. The mixture was filtrated and the organic layer was separated from the aqueous layer. The aqueous layer was washed with EtOAc (5 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtrated and evaporated *in vacuo* to obtain the pure product as yellow liquid (530 mg, 33%). **TLC**: R_f = 0.40 (EtOH/DCM, 1/20 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 4.01 (qd, J = 6.7, 3.3 Hz, 1H), 3.91–3.83 (m, 1H), 3.82–3.75 (m, 1H), 3.66 (dd, J = 11.6, 3.3 Hz, 1H), 3.50 (dd, J = 11.6, 6.2 Hz, 1H), 2.69 (s, 1H), 2.04–1.84 (m, 3H), 1.73–1.58 (m, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 79.6 (CH), 68.3 (CH_2), 64.9 (CH_2), 27.2 (CH_2), 26.1 (CH_2) ppm.

(*R*)-(Tetrahydrofuran-2-yl)methyl 4-methylbenzene-sulfonate (**19**), method based on literature.[34] To a solution of 0.88 gram (4.6 mmol, 1.6 eq.) tosylchloride and 0.7 mL (8.8 mmol, 3.0 eq.) pyridine in DCM (10 mL) was added 300 mg (2.94 mmol, 1.0 eq.) **56-(R)** in DCM (10 mL). The reaction was stirred for 16 hours. Subsequently, water (20 mL) and DCM (20 mL) were added. The organic layer was separated from the aqueous layer and the organic layer was washed with 10% HCl (40 mL) and brine (40 mL). The organic layer was dried over Na_2SO_4, filtrated and evaporated *in vacuo*. The remaining oil was purified using silica gel flash column chromatography (0% to 20% EtOAc in *n*-heptane) to yield the product **17-(R)** (545 mg, 73%). **TLC**: R_f = 0.30 (EtOAc/heptane, 3 : 7 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.83–7.77 (m, 2H), 7.37–7.33 (m, 2H), 4.11–4.06 (m, 1H), 4.04–3.96 (m, 2H), 3.81–3.70 (m, 2H), 2.45 (s, 3H), 2.02–1.93 (m, 1H), 1.87 (dddd, J = 10.0, 8.0, 6.1, 3.0 Hz, 2H), 1.66 (ddt, J = 12.1, 8.2, 6.8 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 144.9, 133.1 (both quaternary carbon), 129.9, 128.1 (both aromatic carbon), 76.0 (CH), 71.6, 68.7, 28.0, 25.7 (all CH_2), 21.8 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{12}H_{16}O_4S$: 279.06670, found $[M + Na]^+$: 279.06612.

(*S*)-(Tetrahydrofuran-2-yl)methyl 4-methylbenzene-sulfonate (**20**), method based on literature.[34] To a solution of 0.88 gram (4.6 mmol, 1.7 eq.) tosylchloride and 0.7 mL (8.7 mmol, 3.3 eq.) pyridine in DCM (10 mL) was added 271 mg (2.65 mmol, 1.0 eq.) **56-(S)** in DCM (10 mL). The reaction was stirred for 16 hours. Subsequently, water (20 mL) and DCM (20 mL) were added. The organic layer was separated from the aqueous layer and the organic layer was washed with 10% HCl (40 mL) and brine (40 mL). The organic layer was dried over Na_2SO_4, filtrated and evaporated *in vacuo*. The remaining oil was purified using silica gel flash column chromatography (0% to 20% EtOAc in *n*-heptane) to afford the product **17-(S)** (410 mg, 60%). **TLC**: R_f = 0.30 (EtOAc/heptane, 3 : 7 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.87–7.73 (m, 2H), 7.40–7.30 (m, 2H), 4.12–4.06 (m, 1H), 4.04–3.95 (m, 2H), 3.76 (ddt, J = 30.0, 8.3, 6.7 Hz, 2H), 2.45 (s, 3H), 2.04–1.94 (m, 1H), 1.87 (dtt, J = 8.0, 6.7, 3.2 Hz, 2H), 1.71–1.64 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ_C 144.91, 133.13 (both quaternary), 129.94, 128.10 (both aromatic), 76.05 (CH), 71.60, 68.75, 27.99, 25.71 (all CH_2), 21.78 (CH_3) ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + Na]^+$ calculated for $C_{12}H_{16}O_4S$: 279.06670, found $[M + Na]^+$: 279.06504.

(Hydroxymethyl)diphenylphosphine oxide, method based on literature.[35] To a solution consisting of 6.2 mL 37% aqueous formaldehyde (0.083 mmol, 25 eq.) and 6.5 mL concentrated hydrochloric acid was added 0.6 mL (0.003 mmol, 1.0 eq.) chlorodiphenylphosphine. The solution was heated to 100 °C and was stirred for 16 hours. After 16 hours the reaction mixture was neutralised using $NaHCO_3$. The neutralised solution was extracted with DCM (3 × 40 mL), dried over $MgSO_4$, filtrated and evaporated. The product was without further purification as white solid (660 mg, 85%). **TLC:** R_f = 0.57 (MeOH/EtOAc, 10/90 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.82–7.72 (m, 4H), 7.59–7.42 (m, 6H), 5.23 (s, 1H), 4.42 (dd, J = 11.0, 3.8 Hz, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C 132.2, 131.41, 131.3 (all quaternary), 130.9, 130.1 (both quaternary), 128.8, 128.7 (both aromatic), 61.67, 61.0 (both CH_2) ppm; **^{31}P NMR** (202 MHz, $CDCl_3$): δ_P 30.77 ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{13}H_{13}O_2P$: 233.07314, found $[M + H]^+$: 233.07190.

(Bromomethyl)diphenylphosphine oxide (**18**), method based on literature.[36] A suspension of 500 mg (2.15 mmol, 2.5 eq.) **56** and molecular sieves (4 Å) in benzene (2 mL) was heated to reflux. While refluxing, 0.1 mL (1.1 mmol, 1.2 eq.) PBr_3 was added dropwise and the solution started to boil heavily. After stirring for 10 minutes an orange sticky precipitate was formed. The solution was refluxed for 5 h. The solution (orange) was cooled to room temperature, chloroform (5 mL) was added, the mixture was stirred for 15 minutes and the precipitate was scratched of the flask surface, stirred for 1 h and filtrated. The organic layer was washed with water (15 mL), saturated aqueous $NaHCO_3$ solution (15 mL) and water (15 mL). The organic layer was dried over Na_2SO_4 and filtrated. The solvent was evaporated and the remaining crude product was purified by silica gel flash column chromatography (60% to 100% EtOAc in *n*-heptane) to afford **91** (375 mg, 59%). **TLC:** R_f = 0.57 (EtOAc/heptane, 90/10 v/v); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.85–7.76 (m, 4H), 7.64–7.56 (m, 2H), 7.56–7.48 (m, 4H), 3.81 (d, J = 5.8 Hz, 2H) ppm; **^{13}C NMR**

(126 MHz, $CDCl_3$): δ_C 132.8, 131.6 (both aromatic), 130.6, 129.8 (both quaternary), 128.9 (aromatic), 23.9, 23.4 (both CH_2) ppm; **^{31}P NMR** (202 MHz, $CDCl_3$): δ_P 27.05 ppm; **HRMS** (ESI-TOF) (*m*/*z*): $[M + H]^+$ calculated for $C_{13}H_{12}BrOP$: 294.98874, found $[M + H]^+$: 294.98977.

Conflicts of interest

There are no conflicts to declare.

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