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Article

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Introducing Oxo-Phenylacetyl (OPAc) as a Protecting Group for Carbohydrates.

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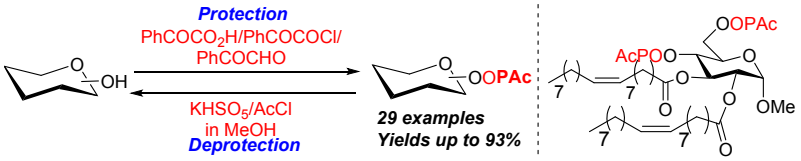
[‖] Both authors contributed equally

Supporting Information Placeholder



ABSTRACT: A series of oxo-phenylacetyl (OPAc) protected saccharides, with divergent base sensitivity profiles against benzoyl (Bz) and acetyl (Ac), were synthesized and $KHSO_5$/AcCl in methanol was identified as an easy, mild, selective and efficient deprotecting reagent for their removal in the perspective of carbohydrate synthesis. Timely monitoring of AcCl reagent was supportive in both sequential as well as simultaneous deprotecting of OPAc, Bz and Ac. The salient feature of our method is the orthogonal stability against different groups, its ease to generate different valuable acceptors using designed monosaccharides and use of OPAc as a glycosyl donar.

INTRODUCTION

Oligosaccharides, which are essential to all cellular organisms, play vital roles in cell recognition, signalling, and are involved in a broad range of biological processes.[1] They are more complex than any other biological polymers, and are frequently present as heterogeneous mixtures in nature.[2] The chemical synthesis of carbohydrates represents a

powerful tool to provide homogeneous glycans.[3] In carbohydrate synthesis, the major concern is the orthogonal protection of hydroxyl groups that can be unmasked independently.[4] Classical protecting groups include benzyl ethers (Bn), which are normally cleaved through hydrogenolysis or by means of metal reduction, and acetate (Ac), benzoate (Bz) or pivaloate esters, which are removed using base promoted hydrolysis.[5] The protecting group approaches in oligosaccharide synthesis generally rely on benzyl ethers (Bn) as the dominant protecting groups for hydroxyl functionalities.[6] However, the reaction conditions required for Bn removal are not compatible with the double bonds present in the lipid moiety of various glycolipids (Figure 1).[7] Previously, these issues were addressed through the use of benzoyl esters, PMB ethers, and napthyl ethers.[8] Despite being successful to some extent, these groups faced challenges in context to the saponification of the fatty acid esters during base mediated Bz/Ac removal, the low stability of PMB ethers under the mild acidic conditions commonly used for glycosylations, use of multiple reagent system for the removal of napthyl group and their low efficiency in the orthogonal protecting group manipulation during multistep transfo-

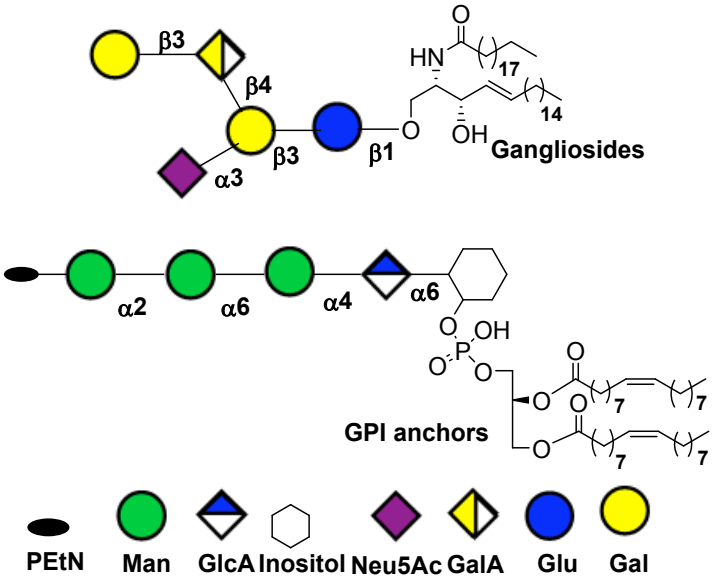
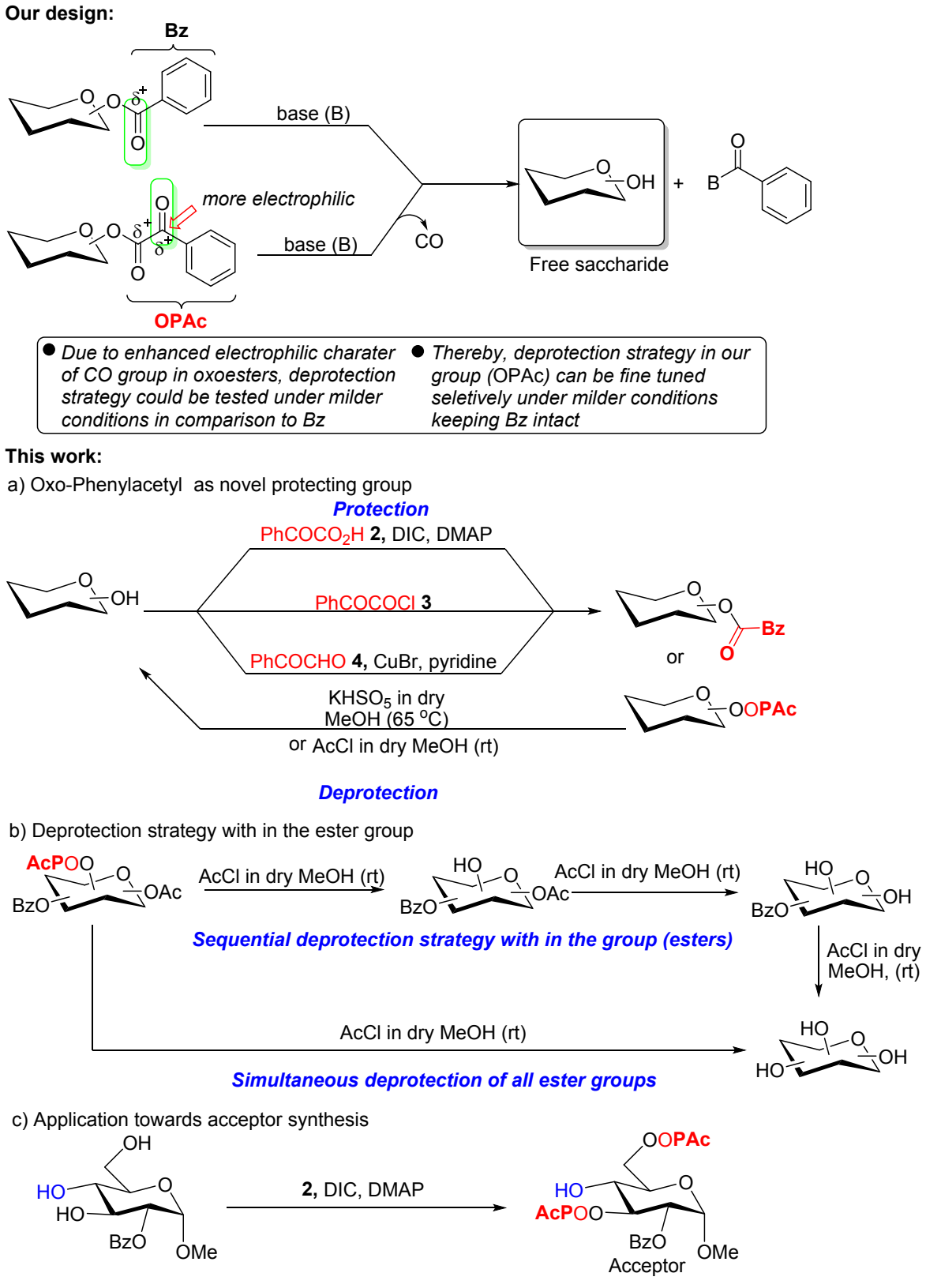


Figure 1: Representative structures of glycolipids.

rmations at the late stage of any given oligosaccharide synthesis.[9] In contrast, standardized mild, slightly labile, single-step, base-mediated deprotection procedure is widely desirable in

glycolipids (containing unsaturation) synthesis that surmounts the limitations of earlier procedures. To address this practical issue with esters, we envisage the possibility of design-

Scheme 1: Summary of this work



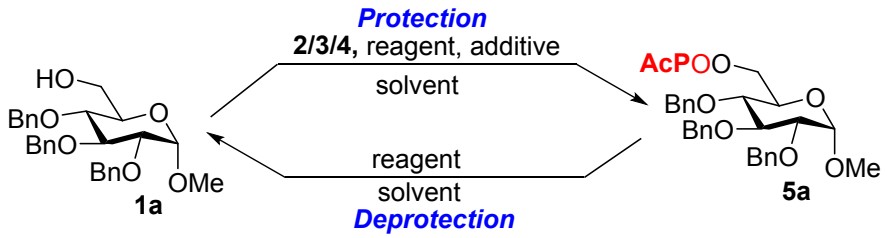
ing oxo-phenylacetyl (OPAc) as a new protecting group for carbohydrates (Scheme 1). The main inspiration behind this work is the enhanced electrophilic character of OPAc in comparison to simple Bz.[10] This type of protecting groups besides being the surrogate of benzoate, and acetate can overcome the limitations to some extent. In this communication, we synthesized different OPAc protected saccharides using phenylglyoxalic acid **2**, 2-oxo-2-phenylacetyl chloride **3** or phenylglyoxal **4** as coupling reagent and also found that $KHSO_5$ in methanol was recognized as an efficient, mild deprotecting reagent for their selective deprotection. AcCl in dry methanol was also effective in the removal of OPAc group. However, timely monitoring of AcCl reagent was helpful in establishing both sequential as well as simultaneous deprotecting of OPAc, Bz and Ac. This method further proved valuable in the synthesis of different acceptors using designed monosaccharides.

RESULTS AND DISCUSSION

Our investigation began with the coupling between Methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **1a** and phenylglyoxalic acid **2** using conventional DIC and DMAP coupling procedure in DCM (entry 1, Table 1).[11] Herein, we isolated desired product **5a** in 91% yield, when 1 mmol of **1a** was treated with 1.2 mmol of **2**, 1.2 mmol of DIC and 1.2 mmol of DMAP in 3 mL of DCM at rt for 3 h. Further, reaction was performed with 2-oxo-2-phenyl-acetyl chloride **3** (1.2 mmol) as coupling partner to **1a** (1 mmol) in pyridine:DCM (1:1) at rt for 8 h as per literature proceure[12] that led to the synthesis of **5a** in 93% yields (entry 2). In order to have diversity in coupling partners, we also performed reaction of **1a** (1 mmol) with phenylglyoxal **4** (1.2 mmol) as per Ning Jiao' procedure and successfully isolated **5a** in good yields (entry 3).[13] Next, we performed different sets of experiments to remove the OPAc groups under milder conditions (entries 4-9). Luckily, in one of our previous works, we observed that α-oxoesters are unstable in oxone environment and undergoes CO-CO cleavage to simple ester and respective alcohol.[14] Based on this finding, we performed different

experiments with varied concentrations of $KHSO_5$ at 65 °C (entries 4-7) and found that 5 mmol of oxone gave the best results in dry methanol at 65 °C (entry 7). In addition, we also tried to optimize the deprotection of OPAc group in compound **5a** using acetylchloride (AcCl) in dry methanol (entries 8-9). Interestingly, we found that 0.7 mmol of AcCl in 3 mL of dry methanol at rt completely deprotected the OPAc with in 30 min (entry 9).

Table 1. Optimization of the reaction



For protection:

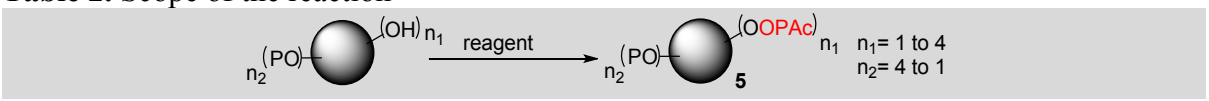
entry	**2/3/4** (mmol)	reagent (mmol)	additive (mmol)	solvent	temp (°C)	time (h)	yields (%)[g]
1[a]	2 (1.2)	DIC (1.2)	DMAP(1.2)	DCM	rt	3	91
2[b]	3 (1.2)	-	-	pyridine/DCM(1:1)	rt	8	93
3[c]	4 (1.2)	-	CuBr (0.1), pyridine (1.2)	toluene	65	8	61
For deprotection:							
4	5a (1.0)	$KHSO_5$ (1.0)	-	dry MeOH	65	8	13
5	5a (1.0)	$KHSO_5$ (2.0)	-	dry MeOH	65	8	27
6	5a (1.0)	$KHSO_5$ (4.0)	-	dry MeOH	65	8	67
7[d]	**5a** (1.0)	**$KHSO_5$ (5.0)**	-	**dry MeOH**	**65**	**8**	**92**
8	5a (1.0)	AcCl (0.5)	-	dry MeOH	rt	0.5	89
9[e]	**5a** (1.0)	**AcCl (0.7)**	-	**dry MeOH**	**rt**	**0.5**	**96**

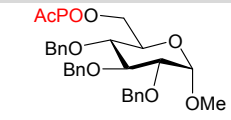
For protection: [a] Phenylglyoxalic acid **2** (1.2 mmol), DIC (1.2 mmol) and DMAP (1.2 mmol) in 3 mL of DCM at rt for 3 h, [b] 2-Oxo-2-phenylacetyl chloride **3** (1.2 mmol), in 3 mL of pyridine:DCM (1:1) at rt for 8 h, [c] Phenylglyoxal **4** (1.2 mmol), CuBr (1.2 mmol) and pyridine (1.2 mmol) in 3 mL of toluene at 65 °C for 8 h, **For deprotection**: [d] **5a** (1.0 mmol), $KHSO_5$ (5.0 mmol in 3mL of dry MeOH at 65 °C for 8 h,[e]**5a** (1.0 mmol), AcCl (0.7 mmol), in 3 mL of dry MeOH at rt for 30 min, [g] Isolated yields.

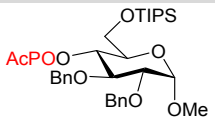
Following these optimized conditions for OPAc protections, a series of protected saccharides **5a-5ac** were synthesised (Table **2**). In one set of experiments, different mono- OPAc protected saccharides were synthesised (**5a-5r**). As depicted in Table **2**, we isolated different mono oxo-phenylacetyl protected products at different hydroxyl position in good yields. It was observed that despite change in nature of hydroxyl group (C1, C2, C3, C4 or C6), protecting groups (Bn, Me, TIPS, Bz, Ac, benzylidene, TBDMS, All, PMB, acetal, NAP,

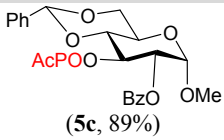
Lev, Piv etc.), and sugar/pseudosugar (mono, di/tri-saccharide), the yields of desired products **5** were appreciable. Another set of experiments were performed to generate different di OPAc

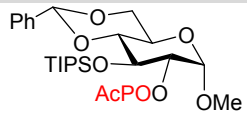
Table 2. Scope of the reaction




(**5a**, 91%)


(**5b**, 87%)


(**5c**, 89%)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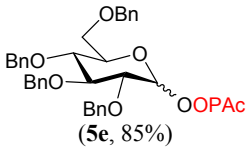
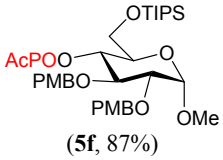

(**5e**, 85%)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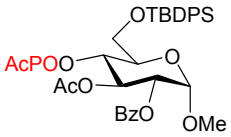
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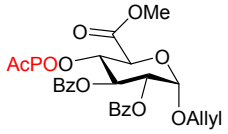
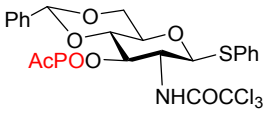

(**5h**, 81%)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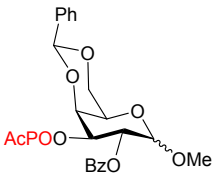
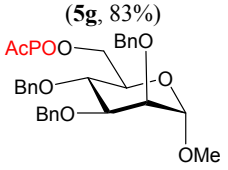
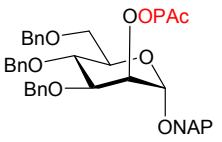
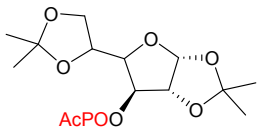
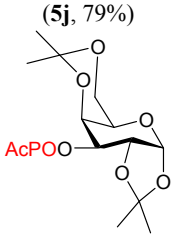
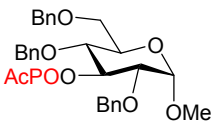

(**5j**, 79%)

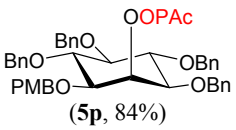

(**5k**, 83%)

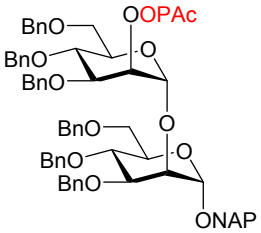

(**5l**, 88%)


(**5m**, 92%)


(**5n**, 91%)


(**5o**, 87%)


(**5p**, 84%)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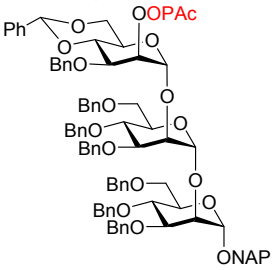
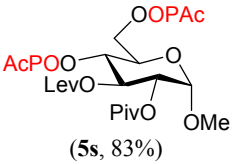

(**5r**, 78%)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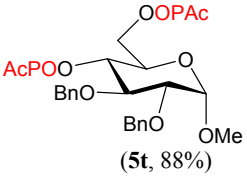
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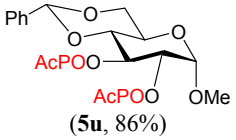
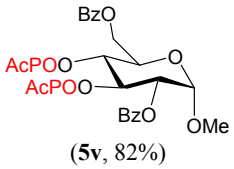
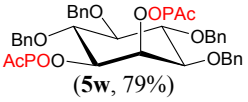
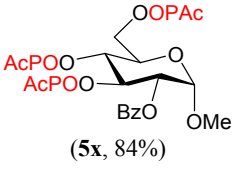
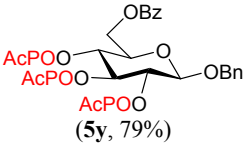
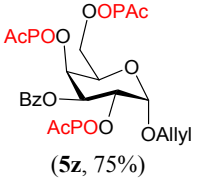

(**5u**, 86%)


(**5v**, 82%)


(**5w**, 79%)


(**5x**, 84%)


(**5y**, 79%)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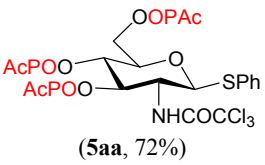
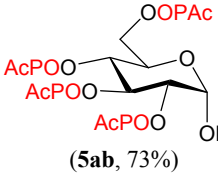
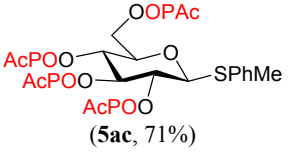

(**5aa**, 72%)


(**5ab**, 73%)

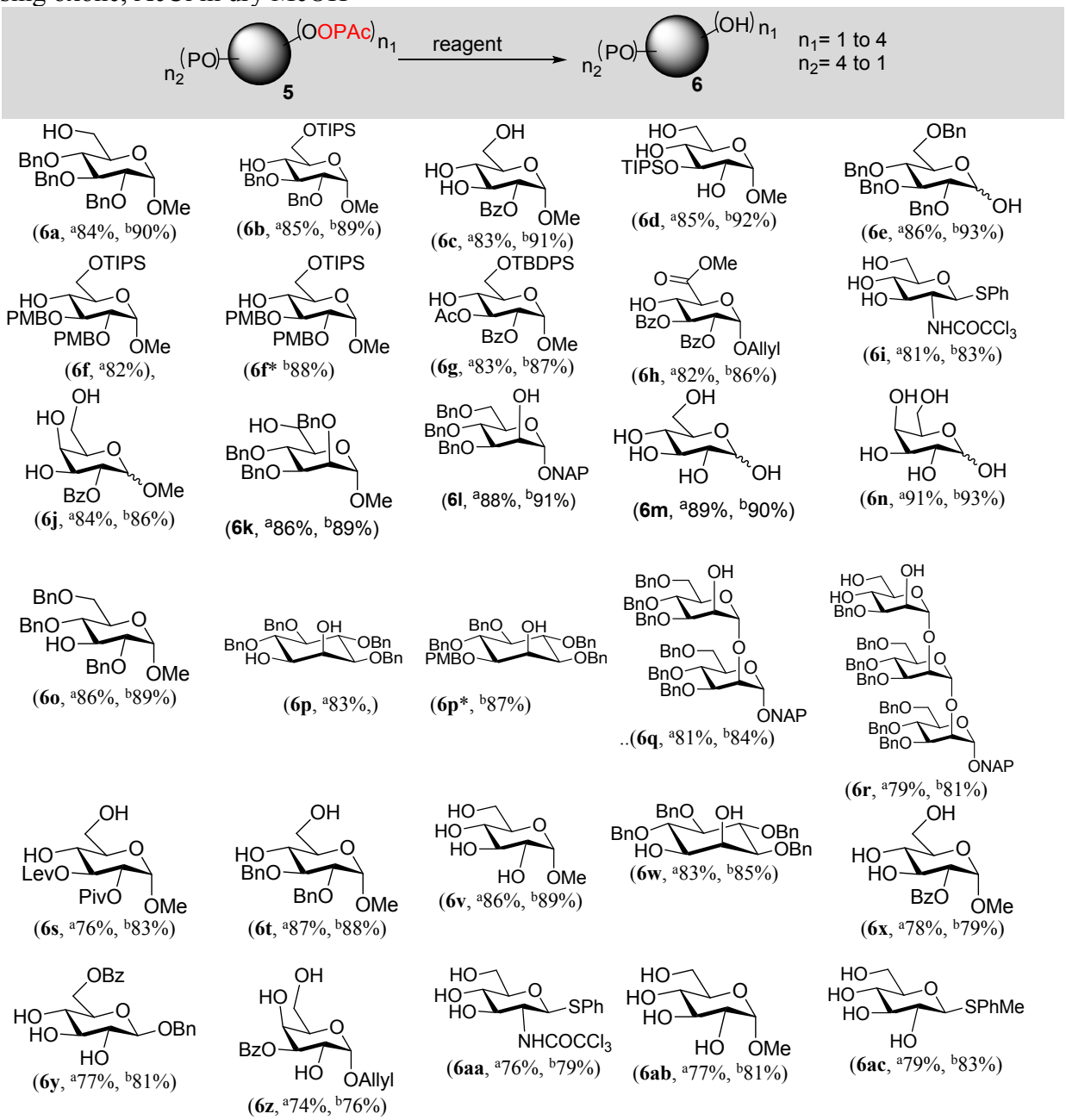

(**5ac**, 71%)

Reaction condition: (a) For mono protection; **2** (1.2 mmol), DIC (1.2 mmol) and DMAP (1.2 mmol) in 3 mL of DCM at rt for 3 h, (b) For di protection; **2** (2.4 mmol), DIC (2.4 mmol) and DMAP (2.4 mmol) in 5 mL of DCM at rt for 6 h, (c) For tri protection; **2** (3.6 mmol), DIC (3.6 mmol) and DMAP (3.6 mmol), in 8 mL of DCM at rt for 12 h, (d) For tetra protection; **2** (4.8 mmol), DIC (4.8 mmol) and DMAP (4.8 mmol), in 10 mL of DCM:DMF (1:1) at rt for 36 h.

protected saccharides (**5s-5w**). Yields were generally good for all di protected substrates as well. After having established the mono- and di- protected substrate scope, a small library of different tri- and tetra- OPAc protected saccharides were also generated (**5x-5ac**). In these cases as well, yields were good for all the reactions conducted.

Next, we performed different sets of experiments to deprotect all the OPAc protected substrates as per the optimized conditions (Table 3). Primarily, oxone based deprotection strategy was selected for further investigations against all the series of saccharides synthesized in Table 2 (**5a-5ac**). In all the reactions, we isolated the corresponding hydroxyl products in good yields. In oxone environment, we found that most of the common protecting groups such as Bn, Bz, Ac, Me, TIPS, TBDMS, All, NAP, Lev, Piv etc. (**6a-6ac**) were stable. However acetal, ketal and PMB based protections were sensitive to oxone (**6c**, **6d**, **6f**, **6i**, **6j**, **6m**, **6n**, **6p**, **6r,** & **6u**). This unstable nature of substrates containing benzylidene (**5c**, **5d**, **5i**, **5j**, **5r,** & **5u**) could be useful in the construction of branched oligosaccharides through selective ring opening, then glycosylation followed by OPAc deprotection and again glycosylation. In a similar way, different reactions were carried out under AcCl environment in dry MeOH as per the optimized conditions (**6a-6ac**) and in all cases we isolated slightly better yields of the corresponding hydroxyl products. As expected, the acetals and ketals were also found to be unstable and generated products with additional free hydroxyl groups (**6c**, **6d**, **6i**, **6j**, **6m**, **6n**, **6r** & **6u**). However, PMB group was found orthogonally stable under AcCl environment (**6f*** and **6p***). The paramount feature of both the deprotection conditions was the ease of deprotection of OPAc in presence of allyl group under milder conditions (**6h** & **6z**).

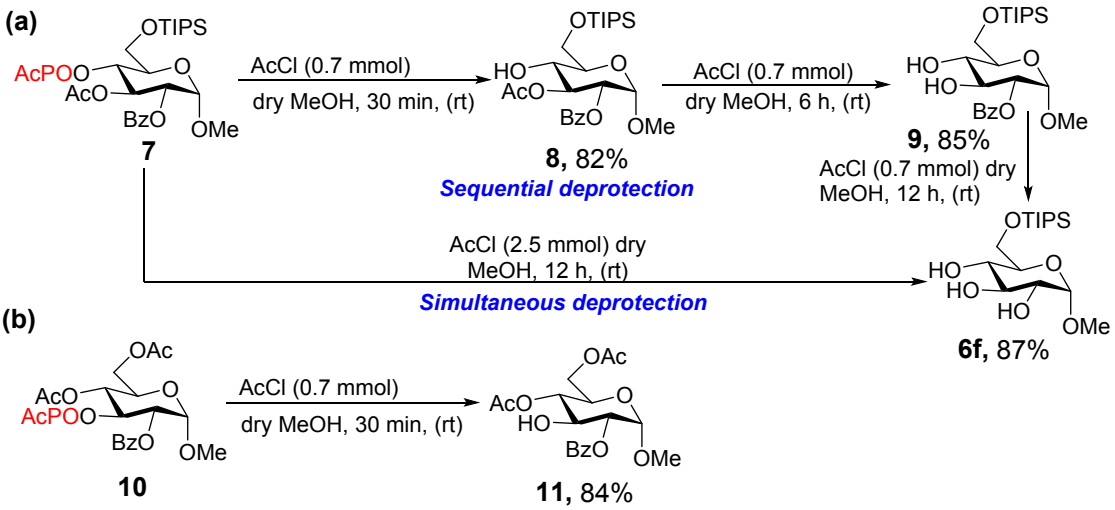
Table 3. Compatibility of OPAc removal with common protecting groups in all substrates using oxone, AcCl in dry MeOH



Reaction condition: For deprotection of each OPAc group, we employed either a5.0 mmol of $KHSO_5$ in 5 mL of dry MeOH at 65 °C or b0.7 mmol of AcCl in 5 mL of dry MeOH at rt (for details, see SI). **6f*** and **6p*** represents the deprotected compound in the presence of AcCl in MeOH condition.

Furthermore, the judicious monitoring of AcCl reagent against substrate **7** was beneficial in establishing sequential as well as simultaneous deprotecting OPAc, Bz and Ac (Scheme 2a). Compound **7** when monitored under the AcCl in dry MeOH environment for 30 min at rt selectively released OPAc (compound **8**). However, the continue stirring of **8** with AcCl reagent for 3 h removed Ac **(**compound **9**). Finally, compound **9** when stirred for 12 h

released Bz as well. The substrate **7**, when stirred continuously with the same reagent for 12 h removed all ester protections in one pot. It might be ambiguous that the sequential deprotection (OPAc, Ac, Bz) resulted whether from the properties of each protecting groups, or from the intrinsic reactivity derived from the structural factor of the employed sugar. In **Scheme 2**. a) Sequential and simultaneous deprotection. b) Validation of the concept for selective OPAc deprotection

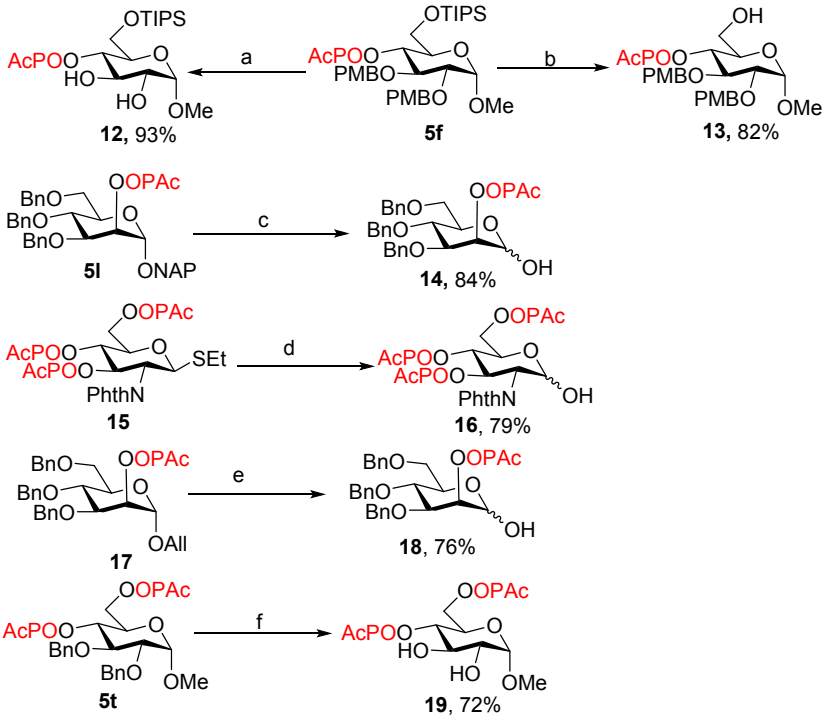


this contest, we performed a control experiment using the compound **10** where in we exchanged the positions of OPAc and Ac. It is quite evident that despite change in positions, OPAc was successfully removed (Scheme 2b). These experiments clearly highlight the advantage of using OPAc as a labile group within ester protecting groups, which could be useful for the synthesis of different oligosaccharides.

With the detailed deprotection profile revealed, we sought to examine the compatibility of OPAc with other commonly used acid labile protecting groups, SEt, Bn, and allyl groups (Scheme 3). Orthogonality between PMB, TIPS and OPAc was established using differentially protected glucoside **5f**, where in regiospecific removal of all the three groups was readily achieved. In this case, we also presented the selective removal of TIPS in presence of PMB in 2N HCl system. Furthermore, the selective cleavage of NAP in **5l** was also achieved by stirring with DDQ in DCM:MeOH. In addition, glucosides **15**, **17** and **5t**

were prepared and their orthogonality between OPAc against SEt, All and OBn were demonstrated. These observations reveal the nature of our group that are orthogonal to classical acid labile and other commonly used protecting groups, and set the stage for exploring them in the synthesis of complex glycolipids possessing unsaturation.

Scheme 3. Orthogonal stability against different groups

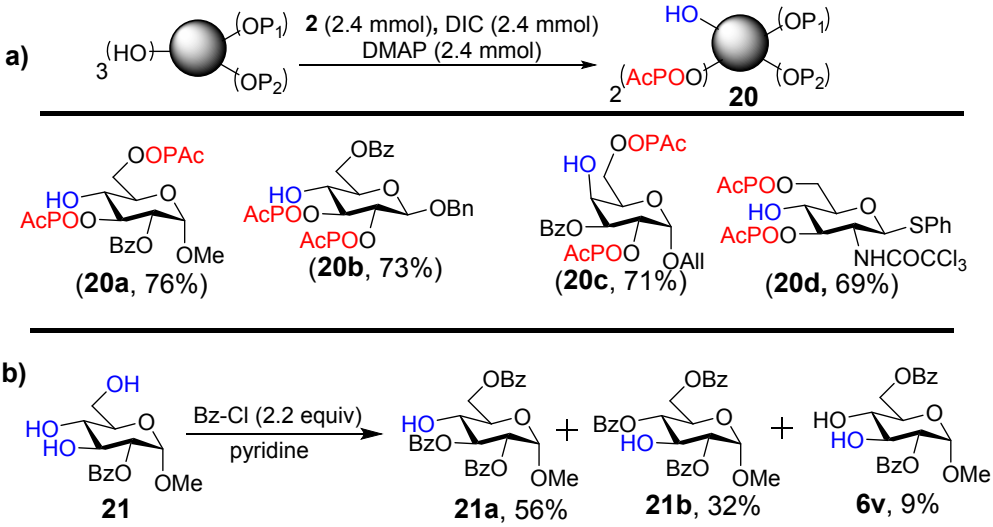


Reaction condition: a) TFA (1.0 mmol), DCM, rt. 30 min; b) 2N HCl, MeOH, rt. 15 h; c) DDQ (3 mmol), DCM, rt. 8 h; d) NBS (2.5 equiv), Acetone:H_2O (9:1), rt, 1 h; e) 1) $Rh(PPh_3)_3Cl$, DIPEA, EtOH: toluene: H_2O (7:3:1). 2) HgO/$HgCl_2$, DCM/H_2O; f) BCl_3 (5 equiv), 2 h, -78 ^oC.

The potential of the OPAc protection was next evaluated for the generation of different valuable acceptors under modified conditions (Scheme 4a, **20a-20d**). We were fortunate to observe that in different reactions of tri-OH free designer saccharides with 2.4 mmol of phenylglyoxalic acid, DIC (2.4 mmol), and DMAP (2.4 mmol), a complete regioselective OPAc protection was observed based on the expected reactivity order of different hydroxyl groups.[15] The reason behind the better selectivity of OPAc protection in comparison to Bz is assumed to be its better reactivity/steric hindrance with neighbouring OPAc group in comparison to normal acids under DIC and DMAP conditions. In order to compare, the better

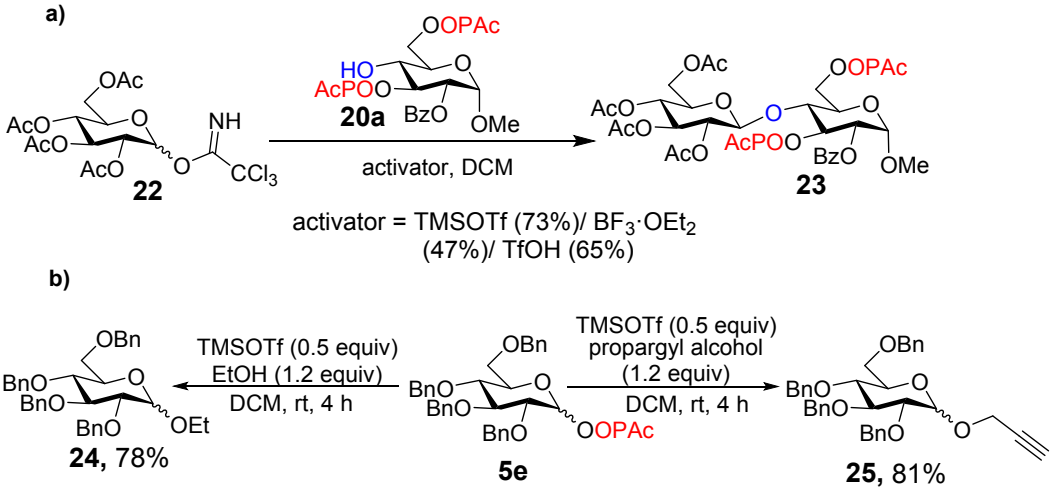
regioselective OPAc protections of the above selected sugars in comparison to Bz, we conducted the same experiment in case of the benzoylation with substrate **21** (Scheme 4b), wherein we isolated mixture of three different products (**21a**: **21b**: **6v**).

Scheme 4. a) Acceptor Synthesis b) Regioselectivity comparision between OPAc and Bz protections.



Finally, to check the compatibility of our group towards normal glycosylation conditions and the application of OPAc as a glycosylation donor, we performed two different sets of experiments (Scheme 5). On one hand, a reaction was conducted between **20a** and TCA based donor **22**[16] by using different activators (Scheme 5a) where in we isolated the expected

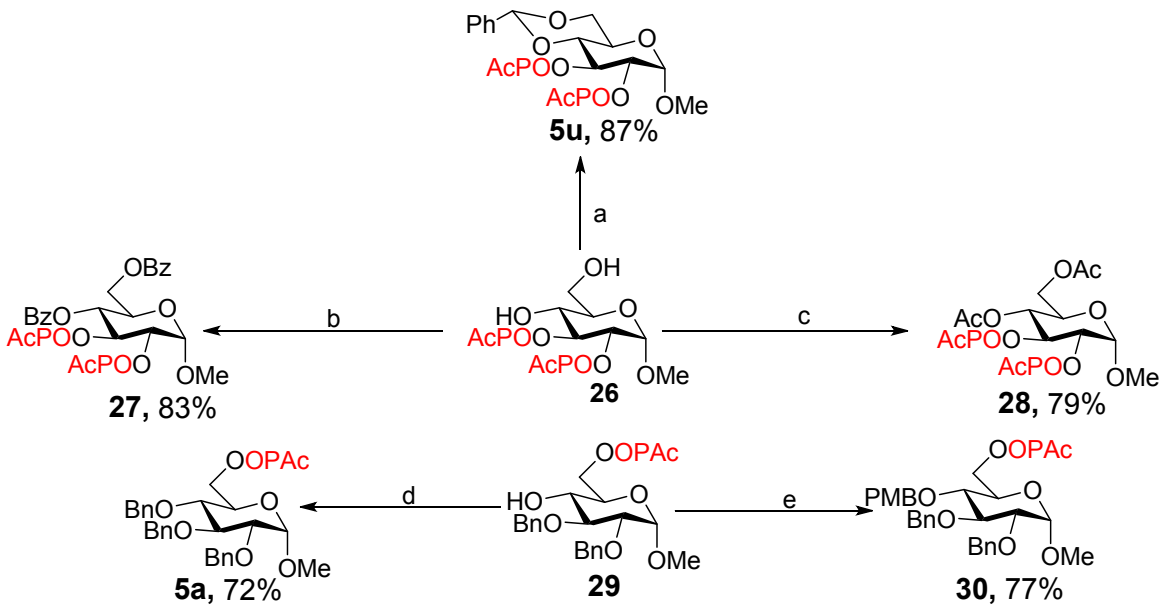
Scheme 5. Glycosylation: a) OPAc protected glycosyl acceptor b) OPAc as glycosyl donor



product **23** in all experiments in good yields. However, the best yield was observed with TMSOTf (Scheme 5a). On the other hand, two different reactions were conducted with designed donor **5e** with EtOH/propargyl alcohol as per conditions mentioned below (Scheme 5b). In both the cases, we successfully isolate the desired products in good yields.

After evaluating its glycosylation potential, we aimed to test the stability of OPAc against the post introduction of Ac, Bz, benzylidene, Bn, & PMB groups. In this context, saccharide **26** was taken as model substrate to launch benzylidene **5u**, Bz **27**, and Ac **28**. In all these reactions, we were gratified to isolate the products in appreciable yields. Being sensitive to strong basic environment, we strategically introduced Bn and PMB on saccharide **29** in moderate yields using TCA donors of Bn and PMB (scheme 6).

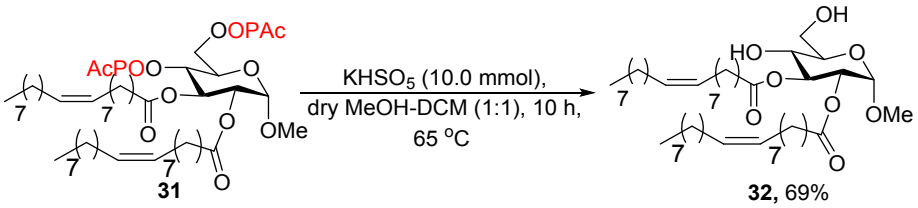
Scheme 6. Post Protection of other groups in presence of OPAc.



Reaction condition: a) $PhCH(OMe)_2$ (1.1 mmol), CSA (0.2 mmol), ACN. b) Bz-Cl (2.2 mmol), DMAP (0.5 mmol), Pyridine, rt. c) Ac_2O, pyridine (6:4), rt. d) Bn-TCA (1.2 mmol),, DCM, rt. 0 °C. e) PMB-TCA (1.2 mmol), DCM, rt. 0 °C

After establishing the flexible nature of OPAc, we tested our hypothesis on model system **31** containing two unsaturated (oleic acid) lipid esters (Scheme 7). In this case, we isolated 69% of expected product using optimized procedure with oxone in MeOH-DCM (1:1) as deprotecting reagent.

Scheme 7. Deprotection of OPAc group in model substrate containing unsaturated lipid.



CONCLUSION

In conclusion, we presented OPAc as a better, orthogonally convenient protecting group that is effective surrogate of benzoate (Bz) and acetate (Ac) and other esters. We envision that our protecting group can readily find broad applications in complex carbohydrate assemblies of glycolipids containing unsaturation. In addition, we also demonstrated the application of our protection strategy in the synthesis of different valuable acceptors under modified conditions, successfully used it as a donor and also tested our hypothesis on model substrate containing unsaturated dilipid **31**. Further, application towards the synthesis of GPI and others is in progress.

EXPERIMENTAL SECTION

A. General Information.

Solvents were purified according to standard procedures, and reagents used were of highest purity available. All reactions were performed in flame-dried glass apparatus under argon/nitrogen atmosphere unless mentioned otherwise. Anhydrous solvents like CH_2Cl_2, CH_3OH, CH_3CN, DMF, pyridine, and Et_3N were freshly dried using standard methods. NMR measurements (^1H, ^{13}C, 2D ^1H-^1H-COSY and ^1H-^{13}C HMBC, HMQC, and NOESY) were recorded on a 400 and 500 MHz spectrometer fitted with pulse-field gradient probe, and trimethylsilane (TMS) or residual resonance of deuterated solvent were used as internal reference. ^{13}C NMR spectra were broadband ^1H decoupled or inverse HMQC experiments. Chemical shifts are expressed in ppm and coupling constants *J* in Hz. High-resolution mass spectral data were obtained from Q-ToF Mass Spectrometer coupled LC system. The

following conditions were used: capillary voltage 3500 V, capillary temperature 350 ^{o}C, auxiliary gas flow rate 7.0 L/min, spray voltage 4.5 kV, mass range 100-1000 amu (maximum resolution 30000). Optical rotations were measured on a digital polarimeter. Analytical TLC was performed on 60 F254 plates, and compounds visualized by methanol-sulphuric acid/ceric-sulfate developing reagent. Silica column chromatography was carried out with silica gel 60 (60-120 mesh) or flash silica gel (230-400 mesh). Analytical and semi-preparative HPLC purification were carried out on reversed-phase (C18, 250 X 10 mm, L i.d.) column connected to an binary pump and monitored using an photodiode array detector.

B. General Procedure for protection:

For each hydroxyl present 1.2 mmol DMAP, DIC and Phenylglyoxalic acid is necessary. DIC (151.4 mg, 1.2 mmol) was added to the stirred solution of alcohol (1.0, mmol), phenylglyoxalic acid (180.1 mg, 1.2 mmol) and DMAP (146.6 mg, 1.2 mmol) in anhydrous DCM (3.0 mL) under nitrogen atmosphere, and then stirred for 3.0 h at rt. After completion of the reaction, confirmed by thin layer chromatography, the solvent was removed under reduced pressure. The reaction mass was dissolved in EtOAc and washed with 3% aqueous HCl (20 mL), followed by washed with saturated $NaHCO_3$ sloution. The organic layer was collected and dried over Na_2SO_4, and concentrated in vacuum. The products (**5a-5ac**, **7**, **10**, **12-19**, **20a-20d**, **23**, **26-30**, **31**) were purified by column chromatography on silica gel using Hexanes/EtOAc = 9:1 to 8:2 as eluent.

Procedure for Bz protected 16a, 16b and 6v.

To a solution of Methyl-2-benzoyl-α-D-glucopyranoside (1.0 equiv) in DMF 10.0 mL methanol at room temperature was added Bz-Cl (2.2 equiv) in pyridine at room temperature for 6-10 h. After 10 h, the starting materials were consumed and we got a mixture of three products. The mixture of two regioisomers (16a and 16b) was separated through HPLC and the HPLC chromatogram of the two regioisomers shown in SI.

C. General Procedure for deprotection:

Deprotection by using $KHSO_5$:

For each deprotection 5.0 mmol of $KHSO_5$ is necessary. To a solution of OPAc protected saccharide (1.0 mmol) in anhydrous 5.0 mL methanol at room temperature was added $KHSO_5$ (0.761 mg, 5.0 mmol) and the solution refluxed for 6-10 h, then cooled to rt. The mixture was filtered and washed with ethyl acetate. The filtrate was concentrated to dryness, suspended in 30 mL of water and extracted with ethyl acetate (2 × 15 mL). After which the organic layer was dried over Na_2SO_4, and concentrated in vaccum. The products (**6a-6ac**, **8**, **11**) were purified by column chromatography on silica gel using for mono deprotection Hexanes:EtOAc = 9:1, for di Hexanes:EtOAc = 7:3, for tri Chloroform:MeOH = 9.5:0.5 and for tetra Chloroform:MeOH = 8:2 as eluent.

Deprotection by using AcCl:

For each deprotection 0.7 mmol of AcCl is necessary. To a solution of OPAc protected saccharide (1.0 mmol) in anhydrous 5.0 mL methanol at room temperature was added AcCl (49.9 μL, 0.7 mmol), after stirring for 0.5-1.0 h, then the reaction mass was quenched with triethyl amine, concentrated to dryness. The crude material was suspended in 20 mL of water and extracted with ethyl acetate (2 × 20mL). After which the organic layer was dried over Na_2SO_4, and concentrated in vacuum. The products (**6a-6ac**) were purified by column chromatography on silica gel using for mono deprotection Hexanes:EtOAc = 9:1, for di Hexanes:EtOAc = 7:3, for tri Chloroform:MeOH = 9.5:0.5 and for tetra Chloroform:MeOH = 8:2 as eluent.

D. Procedure for some starting material synthesis.

1. (±)-3,4,5,6-tetra-*O*-benzyl-*myo*-inositol (Starting material of 5w)

Starting compound was synthesized from literature protocol.[28] To a solution of (±)-1,2-cyclohexylidene *myo*-inositol (10.0 g, 38.44 mmol) in anhydrous DMF (100 mL) stirring under Nitrogen at 0° C was slowly added sodium hydride (60% dispersion in mineral oil, 7.38

g, 307.54 mmol). After stirring for 30 min, benzyl bromide (21.91mL, 184.56 mmol) was added dropwise. The reaction was stirred overnight at room temperature, then quenched with ice, diluted with EtOAc, and poured into water. The aqueous layer was extracted 2x with EtOAc, after which the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vaccum. (HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{40}H_{45}O_6$ 621.3216, found: 621.3221.) The residue was dissolved in CH_2Cl_2/MeOH (2:1, 200 mL), added acetyl chloride (2.0 mL) dropwise. After 3 h, the reaction was quenched with triethylamine and concentrated in vacuum. The crude material was purified by silica gel column chromatography to give ±3,4,5,6-tetra-*O*-benzyl-*myo*-inositol(18.69 g, 90 %) as a white solid. R_f0.18 (Hexanes/EtOAc = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 20H), 4.93 (dd, *J* = 13.3, 11.0 Hz, 3H), 4.84 (dd, *J* = 10.8, 3.9 Hz, 2H), 4.73 (dd, *J* = 12.3, 6.4 Hz, 3H), 4.20 (t, *J* = 2.7 Hz, 1H), 3.97 (t, *J* = 9.5 Hz, 1H), 3.84 (t, *J* = 9.5 Hz, 1H), 3.47 (td, *J* = 9.5, 3.9 Hz, 3H), 2.54 – 2.34 (m, 2H).

2. 3,4,5,6-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-*myo*-inositol (Starting material of 5p)

Starting compound was synthesized from literature protocol.[28] A mixture of 3,4,5,6-tetra-*O*-benzyl-*myo*-inositol (2.00 g, 3.70 mmol) and dibutyltin oxide (0.925 g, 3.70 mmol) in anhydrous Methanol (60 mL) was refluxed for 4 h, until solution becomes clear. After concentration in vacuum, the residue was dissolved in anhydrous Toluene/DMF (1:1, 40 mL) and freshly activated 4 Å molecular sieves were added. And cooled to 0 ºC, after which Tetrabutyl ammonium bromide (2.37 g, 7.41 mmol) and *p*-methoxybenzyl chloride (0.60 mL, 4.4 mmol) were added to the solution. After stirring overnight under an Nitrogen atmosphere at 80^o C, reaction mixture filtered through Celite and washed with EtOAc. The organic layer was washed with water, dried over Na_2SO4, and concentrated in vacuum. This after silica gel column chromatography gave compound (2.2 g, 90 %) as a white solid. R_f0.55 (Hexanes/EtOAc = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 22H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.95 (dd, *J* = 16.8, 6.5 Hz, 3H), 4.91 – 4.83 (m, 3H), 4.71 (dd, *J* = 23.2, 11.8 Hz, 2H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 4.21 (t, *J* = 9.5 Hz, 1H), 4.11 (dd, *J* = 17.2, 7.7 Hz, 2H), 3.86 (s, 3H), 3.48 – 3.36 (m, 2H), 3.23 (dd, *J* = 9.9, 2.1 Hz, 1H).

3. Napthyl-3,4,6-tri-*O*-Benzyl-*α*-D-mannopyranoside(Starting material of 5l).

Starting compound was synthesized from literature protocol.[7b] The trichloroacetimidate donor (2.0 g, 3.16 mmol) and the acceptor (500 mg, 3.16 mmol) were first dried through co-evaporation with anhydrous toluene, further dried for 2 h under high vacuum and then dissolved in anhydrous CH_2Cl_2 (40 mL) and freshly activated 1 g of 4Å molecular sieves were added. The suspension was then stirred under Nitrogen at room temparature for 30 min. The reaction mixture was cooled at -20^{o}C and treated with TMSOTf solution (40 µL, 0.179 mmol) and then warm to room temperature. After stirring for 3 h, the reaction was neutralized with trimethylamine followed by filtration through Celite to remove molecular sieves, concentration in vacuum, the crude material was further used for next step.

To a solution of crude material from the above step in 50 mL of (1:1) mixture of DCM/MeOH, added catalytic amount of NaOMe (100 mg). The mixture was stirred at room temperature for 3 h. It was neutralized to pH 6-7 using Amberlyst H^+ resin. The solution was filtered and concentrated which after silica gel column chromatography gave compound as a colourless syrup (1.68 g, 90%).R_f0.40 (Hexanes/EtOAc = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.9, 4.4 Hz, 3H), 7.75 (s, 1H), 7.50 – 7.44 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.26 (m, 13H), 7.21 – 7.10 (m, 2H), 5.04 (d, *J* = 1.1 Hz, 1H), 4.85 (dd, *J* = 17.3, 11.4 Hz, 2H), 4.71 – 4.64 (m, 4H), 4.54 (dd, *J* = 17.5, 11.5 Hz, 2H), 4.09 (d, *J* = 1.6 Hz, 1H), 3.96 (dd, *J* = 9.1, 3.2 Hz, 1H), 3.89 (d, *J* = 5.8 Hz, 2H), 3.75 (dt, *J* = 21.4, 10.5 Hz, 2H).

4. Napthyl -(3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-*α*-D mannopyranoside (Starting material of 5q) .

Starting compound was synthesized from literature protocol.[7b] The trichloroacetimidate donor(1.29 g, 2.03mmol) and the acceptor (1.0 g, 1.69 mmol) were first dried through co-evaporation with anhydrous toluene, further dried for 2 h under high vacuum and then dissolved in anhydrous CH_2Cl_2 (30 mL) and freshly activated 1 g of 4Å molecular sieves were added. The suspension was then stirred under Nitrogen at room temparature for 30 min. The reaction mixture was cooled at -20°C and treated with TMSOTf solution (20 µL, 0.089 mmol) and then warm to room temperature. After stirring for 3 h, the reaction was neutralized with trimethylamine followed by filtration through Celite to remove molecular sieves, concentration in vacuum, the crude material was further used for next step.

To a solution of crude material from the above step in 30 mL of (1:1) mixture of DCM/MeOH, added catalytic amount of NaOMe (100 mg). The mixture was stirred at room temperature for 3 h. It was neutralized to pH 6-7 using Amberlyst H^+ resin. The solution was filtered and concentrated which after silica gel column chromatography gave compound as a colourless syrup (1.52 g, 88 %).R_f0.40 (Hexanes/EtOAc = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 3H), 7.77 (s, 1H), 7.52 – 7.43 (m, 5H), 7.41 – 7.36 (m, 4H), 7.36 – 7.20 (m, 24H), 5.61 (s, 1H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 4.87 (dd, J = 18.3, 11.3 Hz, 2H), 4.71 (m, *J* = 19.9, 14.9, 11.5 Hz, 4H), 4.61 (d, *J* = 9.9 Hz, 2H), 4.56 (t, *J* = 5.3 Hz, 3H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.22 (t, *J* = 9.6 Hz, 1H), 4.18 – 4.05 (m, 2H), 4.03 – 3.95 (m, 2H), 3.89 (m, *J* = 8.2, 3.5, 1.6 Hz, 3H), 3.85 – 3.75 (m, 4H), 3.75 – 3.68 (m, 1H).

5. Napthyl-(3-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-mannopyranosyl)(1→2)-(3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl))(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside(Starting material of 5r).

Starting compound was synthesized from literature protocol.[29] A solution of donor **6** (173 mg, 0.293 mmol), acceptor (300 mg, 0.293 mmol) BSP (88 mg, 0.421 mmol), TTBP (130.9 mg, 0.527 mmol) and freshly activated 4 Å molecular sieves (500 mg) in 10 mL CH_2Cl_2 was stirred at room temperature for 30 min, and cooled to -78 °C, which was followed by addition of Tf_2O (59.3 µL, 0.0.358 mmol) in CH_2Cl_2. The reaction mixture was stirred for further 2 h. at -78 °C, and allowed to reach room temperature. The reaction mixture was diluted with dichloromethane (10 mL) and molecular sieves were filtered off and washed with saturated $NaHCO_3$. The organic layer was separated and dried and concentrated. The crude residue was dissolved in 10 mL of (1:1) mixture of DCM/MeOH, added catalytic amount of NaOMe (20 mg). The mixture was stirred at room temperature for 3 h. It was neutralized to pH 6-7 using Amberlyst H^+ resin. The solution was filtered and concentrated which after silica gel column chromatography gave compound as a colourless syrup (0.319 g, 80 %).R_f 0.35 (Hexanes/EtOAc = 7:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 3H), 7.69 (s, 1H), 7.50 – 7.44 (m, 4H), 7.40 – 7.05 (m, 40H), 5.51 (s, 1H), 5.07 – 4.98 (m, 2H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.80 – 4.65 (m, 7H), 4.62 – 4.43 (m, 6H), 4.36 – 4.22 (m, 4H), 4.13 (m, *J* = 24.6, 14.6, 7.1 Hz, 3H), 3.96 (t, *J* = 5.5 Hz, 2H), 3.91 – 3.65 (m, 8H), 3.48 (dd, *J* = 10.6, 4.6 Hz, 1H), 3.33 (d, *J* = 3.9 Hz, 2H), 2.99 (dd, *J* = 14.4, 9.7 Hz, 1H).

E. Characterization data for Protected compounds

5a.Methyl-6-*O*-oxobenzoyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[17]. Isolated as a syrup (117 mg, 91% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.27 (m, 14H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.85 – 4.77 (m, 2H), 4.68 – 4.58 (m, 4H), 4.47 (dd, *J* = 11.7, 5.1 Hz, 1H), 4.03 (t, *J* = 9.2 Hz, 1H), 3.93 (ddd, *J* = 10.0, 5.0, 2.0 Hz, 1H), 3.54 – 3.48 (m, 2H), 3.37 (s, 3H).^{13}C NMR {1H} (101

MHz, $CDCl_3$) δ 185.9, 163.6, 138.6, 138.1, 137.9, 134.9, 132.4, 130.1, 128.9, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.7, 98.2 (C1), 81.8, 79.9, 77.6, 75.8, 75.2, 73.4, 68.6, 64.4, 55.4.; HRMS (ESI-TOF) m/z: [M + NH_4]+ Calcd for $C_{36}H_{40}NO_8$ 614.2748 found 614.2742.

5b.Methyl-4-oxobenzoyl-6-*O*-(triisopropylsilyl)-2,3,-di-*O*-benzyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[18]. Isolated as a syrup (109 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.59 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.39 – 7.26 (m, 12H), 5.27 (t, *J* = 9.7 Hz, 1H), 4.97 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.75 – 4.63 (m, 3H), 4.08 (t, *J* = 9.5 Hz, 1H), 3.92 – 3.78 (m, 3H), 3.65 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.42 (s, 3H), 1.06 (d, *J* = 4.0 Hz, 21H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.0, 162.8, 138.3, 137.9, 134.9, 132.2, 130.0, 128.9, 128.5, 128.4, 128.1, 128.0, 127.6, 127.5, 97.8 (C1), 80.0, 78.9, 75.3, 73.5, 71.9, 70.4, 62.6, 55.1, 17.9, 17.9, 12.0; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{38}H_{51}O_8Si$ 663.3348 found 663.3354.

5c. Methyl-3-*O*-oxobenzoyl-2-benzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside.

Starting material was synthesized from literature[19]. Isolated as a syrup (119 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.80 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.51 (m, *J* = 15.4, 10.7, 5.6 Hz, 5H), 7.44 – 7.37 (m, 3H), 7.09 (t, *J* = 7.9 Hz, 2H), 6.10 (t, *J* = 9.9 Hz, 1H), 5.59 (s, 1H), 5.24 (d, *J* = 3.7 Hz, 1H), 5.16 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.39 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.09 (td, *J* = 9.9, 4.8 Hz, 1H), 3.86 (td, *J* = 10.0, 2.7 Hz, 2H), 3.45 (s, 3H).^{13}C NMR {1H} (126 MHz, $CDCl_3$) δ 186.2, 165.8, 163.6, 136.8, 134.8, 133.7, 132.0, 130.1, 129.9, 129.3, 128.9, 128.7, 128.6, 128.4, 126.3, 101.9, 97.7 (C1), 78.9, 72.20, 70.7, 68.9, 62.5, 55.7; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{29}H_{26}NaO_9$ 541.1469 found 541.1453.

5d. Methyl-2-*O*-oxobenzoyl-3-*O*-(triisopropylsilyl)-4,6-*O*-benzylidene-*α*-D-glucopyranoside.

Starting material was synthesized from literature[20]. Isolated as a syrup(117 mg, 90% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.73 – 7.63 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.38 – 7.35 (m, 3H), 5.53 (s, 1H), 5.23 (d, *J* = 3.8 Hz, 1H, H1), 4.97 – 4.91 (m, 1H), 4.44 (t, *J* = 9.1 Hz, 1H), 4.32 (dd, *J* = 10.1, 4.7 Hz, 1H), 3.91 (td, *J* = 9.9, 4.7 Hz, 1H), 3.80 (dd, *J* = 12.5, 8.0 Hz, 1H), 3.58 (t, *J* = 9.3 Hz, 1H), 3.49 (s, 3H), 0.90 (d, *J* = 6.1 Hz, 21H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.4, 163.2, 137.1, 134.9, 132.7, 130.1, 129.2, 128.8, 128.1, 126.3, 102.3, 97.3 (C1), 82.3, 69.7, 68.9, 62.3, 55.5, 18.1, 18.0, 12.5; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{31}H_{43}O_8Si$ 571.2722 found 571.2744.

5e.Oxobenzoyl-2, 3,4,6-tetra-*O*-benzyl-D-glucopyranoside.

Starting material was synthesized from literature[21]. Isolated as a syrup (106 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 15.3, 7.3 Hz, 3H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.34 – 7.19 (m, 28H), 7.14 – 7.09 (m, 1H), 7.05 (dd, *J* = 6.8, 2.6 Hz, 2H), 6.64 (d, *J* = 3.3 Hz, 1H), 5.81 (d, *J* = 7.9 Hz, 1H), 4.86 (dd, *J* = 11.0, 4.7 Hz, 2H), 4.74 (dtd, *J* = 14.2, 11.0, 6.1 Hz, 6H), 4.60 – 4.40 (m, 5H), 3.94 – 3.79 (m, 2H), 3.80 – 3.58 (m, 8H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.0, 185.2, 162.6, 162.1, 138.5, 138.3, 138.0, 137.8, 137.7, 137.4, 135.1, 134.9, 132.3, 132.2, 130.2, 130.2, 129.0, 128.9, 128.6, 128.4, 128.4, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 95.7, 92.5, 84.6, 81.5, 80.6, 79.1, 77.2, 76.2, 75.8, 75.7, 75.2, 75.1, 73.8, 73.6, 73.6, 73.6, 68.3, 68.0;HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{42}H_{41}O_8$ 673.2796 found 673.2811.

5f. Methyl-4-*O*-oxobenzoyl-2,3-di-*O*-(4-methoxybenzyl)-6-*O*-(triisopropylsillyl)- *α*- D-glucopyranoside.

Starting material was synthesized from literature[18]. Isolated as a syrup (106 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.45 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 6.95 – 6.85 (m, 2H), 6.85 – 6.76 (m,

2H), 5.25 (t, *J* = 9.7 Hz, 1H), 4.88 (d, *J* = 10.7 Hz, 1H), 4.77 (d, *J* = 11.7 Hz, 1H), 4.64 (dd, *J* = 17.4, 7.8 Hz, 3H), 4.07 (t, *J* = 9.5 Hz, 1H), 3.92 – 3.79 (m, 6H), 3.77 (s, 3H), 3.63 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.42 (s, 3H), 1.12 – 1.02 (m, 21H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.9, 162.7, 159.5, 159.2, 134.9, 132.3, 130.6, 130.1, 130.1, 129.8, 129.4, 128.9, 113.9, 113.8, 97.9 (C1), 79.6, 78.6, 75.1, 73.1, 72.0, 70.4, 62.7, 55.3, 55.2, 55.1, 18.0, 17.9, 12.0; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{55}O_{10}Si$723.3559 found 723.3547.

5g.Methyl-4-*O*-oxobenzoyl-2-*O*-benzoyl-3-*O*-acetyl-6-*O*-(tert-butyldiphenylsilyl)-*α*-D-glucopyranoside.

Starting material was synthesized from literature[22]. Isolated as a syrup (102mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.90 (d, *J* = 7.3 Hz, 2H), 7.75 – 7.70 (m, 4H), 7.62 (dt, *J* = 20.8, 7.5 Hz, 2H), 7.48 – 7.37 (m, 10H), 5.87 (t, *J* = 9.8 Hz, 1H), 5.60 (t, *J* = 9.8 Hz, 1H), 5.18 (d, *J* = 3.6 Hz, 1H, H1), 5.13 (dd, *J* = 10.1, 3.6 Hz, 1H), 4.04 (ddd, *J* = 10.1, 3.7, 2.1 Hz, 1H), 3.89 (qd, *J* = 11.7, 3.0 Hz, 2H), 3.37 (s, 3H), 2.03 (s, 3H), 1.10 (s, 9H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.4, 170.0, 165.8, 162.6, 135.8, 135.7, 135.0, 133.5, 133.3, 133.0, 132.2, 130.0, 129.9, 129.8, 129.2, 129.0, 128.6, 127.8, 127.7, 96.8 (C1), 72.2, 70.1, 70.1, 69.6, 62.3, 55.3, 26.8, 20.7, 19.3; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{40}H_{43}O_{10}Si$ 711.2620 found 711.2627.

5h. Methyl (allyl-4-*O*-oxobenzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranosyluronate).

Starting material was synthesized from literature[23]. Isolated as a syrup (99 mg, 81% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.97 (m, 4H), 7.81 – 7.67 (m, 2H), 7.65 – 7.52 (m, 3H), 7.44 (dt, *J* = 17.2, 7.7 Hz, 4H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.19 (t, *J* = 9.9 Hz, 1H), 5.92 – 5.76 (m, 2H), 5.49 (d, *J* = 3.6 Hz, 1H, H1), 5.37 – 5.31 (m, 2H), 5.20 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.69 (d, *J* = 10.2 Hz, 1H), 4.32 (dd, *J* = 13.1, 5.1 Hz, 1H), 4.13 (dd, *J* = 13.0, 6.2 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR {1H} (126 MHz, $CDCl_3$) δ 185.2, 168.0, 165.7, 165.2, 162.7, 135.0, 133.6, 133.5, 132.7, 131.8, 130.0, 129.8, 129.0, 128.8, 128.6, 128.5, 118.6, 95.4 (C1), 71.4,

70.7, 69.5, 69.5, 68.0, 53.2; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{32}H_{32}NaO_9$ 583.1939 found 583.1937.

5i.Phenyl-3-*O*-oxobenzoyl-4,6-*O*-benzylidene-2-*N*-(trichloroacetyl)-amino-2-deoxy-1-deoxy-1-thio-*α*-D-glucopyranoside.

Starting material was synthesized from literature[24]. Isolated as a syrup (108 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.35 (ddd, *J* = 10.2, 7.1, 5.0 Hz, 6H), 7.26 – 7.22 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 5.92 (t, *J* = 9.8 Hz, 1H), 5.53 (s, 1H), 5.18 (d, *J* = 10.3 Hz, 1H, H1), 4.35 (dd, *J* = 10.5, 4.8 Hz, 1H), 4.02 (dd, *J* = 19.0, 10.1 Hz, 1H), 3.79 (td, *J* = 9.8, 6.4 Hz, 2H), 3.69 (dd, *J* = 9.6, 4.7 Hz, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.6, 164.0, 162.0, 136.6, 135.1, 133.4, 131.9, 131.4, 130.0, 129.4, 129.2, 128.9, 128.8, 128.4, 126.2, 101.7 (C1), 86.7, 78.5, 73.2, 70.8, 68.4, 55.2; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{29}H_{25}Cl_3NO_7S$ 636.0412 found 636.0397.

5j. Methyl-3-*O*-oxobenzoyl-2-*O*-benzoyl-4,6-*O*- benzylidene-*α*-D-galactopyranoside.

Starting material was synthesized from literature[25]. Isolated as a syrup (106 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 12.4, 5.0 Hz, 3H), 7.84 (ddd, *J* = 8.4, 3.8, 1.2 Hz, 3H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.55 (ddd, *J* = 9.4, 7.3, 2.7 Hz, 4H), 7.50 – 7.44 (m, 5H), 7.42 – 7.35 (m, 5H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.9 Hz, 2H), 5.94 (dd, *J* = 10.7, 3.5 Hz, 1H), 5.87 (dd, *J* = 10.7, 3.6 Hz, 1H), 5.70 – 5.62 (m, 2H), 5.58 (d, *J* = 5.6 Hz, 1H), 5.33 (d, *J* = 3.5 Hz, 1H), 5.27 (t, *J* = 4.0 Hz, 1H), 4.78 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 3.4 Hz, 1H), 4.38 (ddd, *J* = 12.5, 6.5, 1.4 Hz, 2H), 4.22 – 4.10 (m, 2H), 3.92 (s, 1H), 3.53 (s, 2H), 3.47 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.0, 185.8, 165.9, 165.7, 163.9, 163.5, 137.6, 137.4, 134.9, 133.5, 133.4, 132.1, 132.1, 130.0, 129.9, 129.9, 129.5, 129.5, 129.2, 129.0, 128.7, 128.7, 128.6, 128.6, 128.3, 128.2, 126.4, 126.1, 101.2, 100.8, 97.9 (C1), 97.8 (C1),

74.1, 73.8, 70.8, 69.7, 69.3, 69.2, 69.1, 68.8, 62.3, 62.1, 55.8, 55.8; HRMS (ESI-TOF) m/z: $[M + NH_4]+$ Calcd for $C_{29}H_{30}NO_9$ 536.1915 found 536.1911.

5k.Methyl-6-*O*-oxobenzoyl-2,3,4-tri-*O*-benzyl-*α*-D-mannopyranoside.

Starting material was synthesized from literature[26]. Isolated as a syrup (107 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.45 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.39 – 7.28 (m, 15H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.78 – 4.69 (m, 4H), 4.65 (d, *J* = 11.2 Hz, 3H), 4.58 (dd, *J* = 11.6, 5.5 Hz, 1H), 4.01 – 3.88 (m, 3H), 3.82 (s, 1H), 3.30 (s, 3H). ^{13}C NMR {1H} (126 MHz, $CDCl_3$) δ 186.2, 163.8, 138.3, 138.2, 138.1, 134.9, 132.4, 130.2, 128.9, 128.5, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 127.7, 99.1, 80.2, 75.3, 74.6, 74.4, 72.8, 72.1, 69.8, 65.0, 55.0; HRMS (ESI-TOF) m/z: $[M + NH_4]+$ Calcd for $C_{36}H_{40}NO_8$ 614.2748 found 614.2752.

5l. Napthy-2-*O*-oxobenzoyl-3,4,6-*O*-tri-*O*-benzyl -*α*-D-mannopyranoside.

Starting material was synthesized from literature[7b]. Isolated as a syrup (112 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.87 (t, *J* = 6.9 Hz, 3H), 7.81 (s, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 12.6, 7.5 Hz, 3H), 7.42 (d, *J* = 6.1 Hz, 2H), 7.35 (d, *J* = 6.5 Hz, 3H), 7.30 (q, *J* = 7.9 Hz, 10H), 7.18 (d, *J* = 3.0 Hz, 2H), 5.80 (s, 1H), 5.16 (s, 1H, H1), 4.97 – 4.83 (m, 3H), 4.77 – 4.61 (m, 3H), 4.51 (dd, *J* = 14.6, 11.5 Hz, 2H), 4.21 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.99 (d, *J* = 7.0 Hz, 1H), 3.83 (t, *J* = 9.6 Hz, 1H), 3.79 – 3.67 (m, 2H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.3, 163.7, 138.2, 138.1, 137.7, 134.9, 134.1, 133.3, 133.2, 132.4, 130.3, 128.8, 128.5, 128.5, 128.4, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 126.3, 126.2, 126.1, 96.6 (C1), 78.6, 75.4, 74.4, 73.5, 72.7, 72.0, 70.8, 69.7, 68.9; HRMS (ESI-TOF) m/z: $[M + NH_4]+$ Calcd for $C_{46}H_{46}NO_8$ 740.3218 found 740.3238.

5m. 1,2:5,6di-O-isopropylidene-3-*O*-oxobenzoyl-*α*-D-glucofuranoside.

Starting material was commercially available. Isolated as a syrup (138 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.97 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 5.93 (d, *J* = 3.7 Hz, 1H), 5.65 (d, *J* = 3.0 Hz, 1H, H1), 4.64 (d, *J* = 3.7 Hz, 1H), 4.27 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.17 (ddd, *J* = 8.5, 5.8, 4.6 Hz, 1H), 4.09 (dd, *J* = 8.7, 6.0 Hz, 1H), 4.01 (dd, *J* = 8.8, 4.5 Hz, 1H), 1.54 (s, 3H), 1.46 (s, 3H), 1.33 (s, 6H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.6, 162.5, 135.2, 132.3, 130.1, 128.9, 112.5, 109.6, 105.4, 83.3, 80.2, 77.3, 72.3, 67.6, 26.9, 26.7, 26.2, 25.2; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{20}H_{25}O_8$ 393.1544 found 393.1547.

5n. 1,2:4,6 di-*O*-isopropylidene-3-oxobenzoyl- *α*-D-galactopyranoside.

Starting material was commercially available. Isolated as a syrup (137 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 2H), 7.65 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 5.58 (d, *J* = 5.0 Hz, 1H, H1), 4.65 (dd, *J* = 7.8, 2.5 Hz, 1H), 4.58 – 4.53 (m, 2H), 4.36 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.29 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.25 – 4.20 (m, 1H), 1.49 (d, *J* = 7.2 Hz, 6H), 1.35 (d, *J* = 4.6 Hz, 6H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.4, 163.9, 134.9, 132.4, 130.3, 128.9, 109.9, 108.9, 96.3, 70.8, 70.7, 70.4, 65.8, 64.8, 26.0, 26.0, 24.9, 24.5; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{20}H_{24}NaO_8$ 415.1363 found 415.1355.

5o. Methyl-3-*O*-oxobenzoyl-2,4,6-tri-*O*-benzyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[27]. Isolated as a syrup (112 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.32 (m, 6H), 7.32 – 7.23 (m, 9H), 7.15 (dd, *J* = 7.0, 2.5 Hz, 2H), 5.15 (dt, *J* = 11.0, 3.7 Hz, 2H), 4.80 (dd, *J* = 18.5, 8.6 Hz, 3H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.55 (dd, *J* = 11.5, 3.5 Hz, 2H), 4.17 – 4.09 (m, 1H), 3.87 – 3.70 (m, 4H), 3.45 (s, 3H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.9, 163.4, 138.2, 138.0, 137.9, 134.9, 132.4, 130.0, 128.9, 128.8, 128.4, 128.4, 128.4, 127.9, 127.8, 127.8, 127.6, 127.6, 125.8, 96.8 (C1), 79.5, 78.0, 75.4, 75.3, 75.1, 73.6,

70.5, 68.4, 55.3. HRMS (ESI-TOF) m/z: [M + NH_4]+ Calcd for $C_{36}H_{40}NO_8$ 614.2748 found 614.2751.

5p. 2-*O*-oxobenzoyl-3,4,5,6-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-*myo*-inositol.

Starting material was synthesized from literature[28]. Isolated as a syrup (101 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 6.4 Hz, 2H), 7.39 – 7.15 (m, 22H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.94 (t, *J* = 9.9 Hz, 1H), 4.89 (ddd, *J* = 26.8, 18.3, 10.7 Hz, 5H), 4.75 (d, *J* = 10.8 Hz, 1H), 4.64 (q, *J* = 11.8 Hz, 2H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.22 (t, *J* = 9.5 Hz, 1H), 4.07 (t, *J* = 2.1 Hz, 1H), 3.81 (s, 3H), 3.60 (t, *J* = 9.4 Hz, 1H), 3.45 – 3.37 (m, 2H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.7, 163.2, 159.3, 138.7, 138.2, 134.7, 132.4, 130.2, 129.7, 129.1, 128.8, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 113.9, 81.5, 80.9, 80.7, 77.8, 75.9, 75.6, 75.3, 74.2, 73.4, 72.9, 71.9, 55.3; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{50}H_{48}NaO_9$ 815.3191 found 815.3197.

5q.Napthyl-(2-*O*-oxobenzoyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside.

Starting material was synthesized from literature[7b]. Isolated as a syrup (93 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.83 (dd, *J* = 10.8, 7.4 Hz, 3H), 7.71 (s, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 7.1, 2.3 Hz, 2H), 7.43 – 7.17 (m, 30H), 7.14 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.85 (dd, *J* = 2.7, 1.9 Hz, 1H), 5.17 (d, *J* = 1.1 Hz, 1H, H1), 5.04 (d, *J* = 1.4 Hz, 1H, H1), 4.92 (d, *J* = 10.8 Hz, 1H), 4.85 – 4.78 (m, 3H), 4.73 (dd, *J* = 19.3, 7.3 Hz, 3H), 4.62 (t, *J* = 12.3 Hz, 2H), 4.55 (dd, *J* = 11.2, 3.4 Hz, 2H), 4.44 (t, *J* = 11.8 Hz, 2H), 4.27 (d, *J* = 12.1 Hz, 1H), 4.07 (ddd, *J* = 11.7, 9.3, 3.0 Hz, 3H), 3.98 – 3.82 (m, 4H), 3.74 (dd, *J* = 19.4, 9.8 Hz, 2H), 3.55 (dd, *J* = 10.9, 4.8 Hz, 1H), 3.38 (dd, *J* = 10.7, 1.4 Hz, 1H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.4, 163.5, 138.6, 138.5, 138.3, 138.2, 138.2, 137.7, 134.7, 134.7, 133.2, 133.1, 132.4, 130.3, 128.7, 128.6, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1,

128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 126.9, 126.2, 126.0, 125.9, 99.1 (C1), 97.9 (C1[1]), 79.7, 78.4, 75.6, 75.2, 74.8, 74.3, 73.4, 73.3, 72.7, 72.2, 72.1, 70.7, 69.3, 69.2, 68.8; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{73}H_{71}O_{13}$ 1155.4889 found 1155.4903.

5r.Napthyl-(2-*O*-oxobenzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-mannopyranosyl)(1→2)-(3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl))(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside.

Starting material was synthesized from literature[29]. Isolated as a syrup (86 mg, 78% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.84 – 7.77 (m, 3H), 7.68 (s, 1H), 7.51 – 7.45 (m, 3H), 7.45 – 7.31 (m, 16H), 7.31 – 7.16 (m, 25H), 7.07 (dd, *J* = 7.6, 3.6 Hz, 2H), 5.68 (d, *J* = 3.2 Hz, 1H), 5.50 (s, 1H), 5.16 (d, *J* = 3.6 Hz, 1H, H1), 5.12 (d, *J* = 0.8 Hz, 1H, H1)., 4.91 (d, *J* = 10.4 Hz, 1H), 4.85 – 4.52 (m, 10H), 4.52 – 4.41 (m, 3H), 4.26 (m, 4H), 4.17 – 4.00 (m, 3H), 3.97 – 3.78 (m, 6H), 3.66 (m, 3H), 3.45 (dd, *J* = 10.0, 4.0 Hz, 2H), 3.34 (d, *J* = 8.8 Hz, 1H), 3.26 (s, 1H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.5, 163.5, 138.9, 138.4, 138.4, 138.3, 138.2, 138.1, 137.9, 137.5, 134.9, 134.5, 133.2, 133.0, 132.6, 130.3, 128.9, 128.8, 128.70, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 126.8, 126.8, 126.2, 126.1, 126.1, 126.0, 125.9, 101.5 (C1), 100.8 (C1), 98.6 (C1), 96.5, 80.2, 78.4, 77.2, 75.6, 75.3, 74.9, 74.3, 73.7, 73.2, 73.0, 72.9, 72.7, 72.3, 71.9, 71.6, 71.3, 69.8, 69.2, 69.1, 68.3, 66.9; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{93}H_{91}O_{18}$ 1495.6200 found 1495.6192.

5s.Methyl-4,6-di-*O*-oxobenzoyl-3-*O*-levulinyl-2-*O*-pivaloyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[35]. Isolated as a syrup (150 mg, 83% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.99 – 7.92 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 4H), 5.71 (t, *J* = 9.8 Hz, 1H), 5.30 (t, *J* = 9.8 Hz, 1H), 5.00 (d, *J* = 3.6 Hz, 1H, H1), 4.82 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.58 (qd, *J* = 12.2, 3.7 Hz, 2H), 4.24

(ddd, *J* = 10.2, 4.6, 2.7 Hz, 1H), 3.37 (s, 3H), 2.74 – 2.61 (m, 2H), 2.52 (dd, *J* = 9.9, 4.0 Hz, 2H), 2.07 (s, 3H), 1.17 (s, 9H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 205.7, 185.5, 184.8, 177.7, 171.4, 163.3, 162.4, 135.2, 135.1, 132.3, 132.1, 130.1, 130.0, 129.0, 128.9, 96.8 (C1), 70.8, 70.4, 69.5, 66.7, 63.2, 55.9, 38.8, 37.7, 29.6, 27.9, 26.8. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{33}H_{37}O_{13}$ 641.2234 found 641.2241.

5t.Methyl-4,6-di-*O*-oxobenzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[30]. Isolated as a syrup (150 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.93 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.66 – 7.57 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.23 (m, 11H), 5.32 – 5.22 (m, 1H), 4.96 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.73 – 4.57 (m, 4H), 4.49 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.66 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.40 (s, 3H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.7, 185.5, 163.4, 162.7, 138.1, 137.7, 135.1, 134.9, 132.4, 132.1, 130.2, 130.1, 128.9, 128.9, 128.6, 128.5, 128.4, 128.2, 127.6, 127.5, 98.2 (C1), 79.6, 78.4, 75.4, 73.6, 71.9, 67.0, 63.7, 55.6; HRMS (ESI-TOF) m/z: [M + NH_4]+ Calcd for $C_{37}H_{38}NO_{10}$ 656.2490 found 656.2482.

5u. Methyl-2,3-di-*O*-oxobenzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside.

Starting material was synthesized from literature[30]. Isolated as a syrup (167 mg, 86% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.94 (m, 2H), 7.89 – 7.81 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.48 (m, 5H), 7.41 (dd, *J* = 6.5, 3.6 Hz, 3H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.00 (t, *J* = 9.9 Hz, 1H), 5.56 (s, 1H), 5.31 (dd, *J* = 9.9, 3.7 Hz, 1H), 5.22 (d, *J* = 3.7 Hz, 1H, H1), 4.38 (dd, *J* = 10.4, 4.9 Hz, 1H), 4.08 (td, *J* = 9.9, 4.9 Hz, 1H), 3.83 (td, *J* = 10.0, 4.7 Hz, 2H), 3.52 (s, 3H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.0, 185.4, 163.2, 163.0, 136.7, 135.2, 134.9, 132.0, 130.1, 130.0, 129.4, 129.1, 128.8, 128.4, 126.3, 102.1, 97.3(C1), 79.2, 72.4, 70.4, 68.8, 62.5, 55.8; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{30}H_{26}NaO_{10}$ 569.1418 found 569.1413.

5v. Methyl-3,4-di-*O*-oxobenzoyl-2,6-di-*O*-benzoyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[31]. Isolated as a syrup (136 mg, 82% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 4H), 8.05 – 8.02 (m, 2H), 7.76 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 – 7.45 (m, 7H), 7.10 (dd, *J* = 8.2, 7.6 Hz, 2H), 6.21 – 6.13 (m, 1H), 5.72 (t, *J* = 9.9 Hz, 1H), 5.25 (dq, *J* = 7.3, 3.6 Hz, 2H), 4.72 (dd, *J* = 12.5, 2.3 Hz, 1H), 4.54 (dd, *J* = 12.5, 4.2 Hz, 1H), 4.39 (ddd, *J* = 10.2, 4.0, 2.3 Hz, 1H), 3.47 (s, 3H).^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 185.4, 184.9, 166.0, 165.4, 163.2, 162.1, 135.2, 134.9, 133.8, 133.3, 131.9, 131.8, 130.2, 130.1, 129.8, 129.8, 129.6, 129.1, 128.7, 128.7, 128.6, 128.5, 96.9 (C1), 71.8, 71.3, 69.5, 67.3, 62.0, 55.8; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{37}H_{31}O_{12}$ 667.1810 found 667.1804.

5w.1,2-Di-*O*-oxobenzoyl-3,4,5,6-tetra-*O*-benzyl-*myo*-inositol.

Isolated as a syrup (96 mg, 79% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.1, 5.4 Hz, 4H), 7.69 – 7.57 (m, 2H), 7.50 – 7.41 (m, 4H), 7.37 – 7.25 (m, 19H), 6.24 (s, 1H), 5.32 (dd, *J* = 10.4, 2.8 Hz, 1H), 4.90 (t, *J* = 10.4 Hz, 4H), 4.77 (m, 4H), 4.07 (t, *J* = 9.8 Hz, 1H), 3.92 (t, *J* = 9.6 Hz, 1H), 3.84 (dd, *J* = 9.7, 2.8 Hz, 1H), 3.67 (t, *J* = 9.6 Hz, 1H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.8, 185.1, 163.5, 163.0, 138.4, 138.2, 137.8, 137.2, 135.2, 135.0, 132.2, 132.1, 130.2, 130.2, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 82.7, 81.1, 78.9, 78.1, 76.2, 76.2, 75.9, 73.2, 73.1, 69.7; HRMS (ESI-TOF) m/z: [M + Na]+Calcd for $C_{50}H_{44}NaO_{10}$ 827.2827 found 827.2825.

5x.Methyl-3,4,6-tri-*O*-oxobenzoyl-2-*O*-benzoyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[19]. Isolated as a syrup (196 mg 84% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H), 8.07 – 8.00 (m, 4H), 7.73 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.67 – 7.60 (m, 3H), 7.49 (dt, *J* = 16.3, 7.8 Hz, 7H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.15 (t, *J* = 9.8 Hz, 1H), 5.56 (t, *J* = 9.8 Hz, 1H), 5.26 (d, *J* = 3.6 Hz, 1H, H1), 5.20 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.66 (qd, *J* = 12.2, 3.8 Hz, 2H), 4.38 (ddd, *J* = 10.4, 4.8, 3.2 Hz, 1H), 3.45

(s, 3H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 185.4, 184.9, 165.4, 163.2, 163.1, 162.2, 135.3, 135.1, 135.0, 133.8, 132.3, 131.8, 131.7, 130.3, 130.2, 129.8, 129.1, 128.9, 128.8, 128.7, 128.7, 96.8 (C1), 71.7, 71.0, 69.6, 67.0, 63.1, 56.0; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{38}H_{31}O_{13}$ 695.1759 found 695.1771.

5y. Benzyl-2,3,4-tri-*O*-oxobenzoyl-6-*O*-benzoyl-*β*-D-glucopyranoside.

Starting material was synthesized from literature[32]. Isolated as a syrup (163 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.01 (m, 6H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.67-7.64 (m, 3H), 7.52 (t, *J* = 7.6 Hz, 6H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.23 – 7.14 (m, 3H), 7.07 (t, *J*= 8.0 Hz, 2H), 6.21 (t, *J* = 10.0 Hz, 1H), 5.58 (t, *J* = 10.0 Hz, 1H), 5.41 (d, *J* = 3.2 Hz, 1H, H1), 5.20 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.79 (d, *J* = 12.4 Hz, 1H), 4.70 – 4.54 (m, 3H), 4.50 – 4.41 (m, 1H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 185.4, 185.0, 165.2, 163.3, 163.2, 162.3, 136.2, 135.3, 135.1, 135.0, 133.8, 132.3, 131.8, 131.7, 130.3, 130.2, 130.1, 129.8, 129.2, 129.0, 128.8, 128.7, 128.5, 128.2, 127.9, 94.9 (C1), 71.6, 71.1, 70.5, 69.6, 67.4, 63.0; HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd. for $C_{44}H_{38}NO_{13}$ 788.2338 found 788.2333.

5z. Allyl-2,4,6-tri-*O*-oxobenzoyl-3-*O*-benzoyl-*α*-D-galactopyranoside

Starting material was synthesized from literature[33]. Isolated as a syrup (167 mg, 75% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.66 – 7.56 (m, 3H), 7.53 – 7.47 (m, 4H), 7.40 (dd, *J* = 14.8, 7.5 Hz, 5H), 7.21 (t, *J* = 7.1 Hz, 2H), 6.04 (t, *J* = 9.6 Hz, 1H), 5.45 (t, *J* = 9.6 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 4.65 (qd, *J* = 12.4, 3.9 Hz, 2H), 4.26 – 4.15 (m, 1H), 4.03 (dd, *J* = 17.2, 10.0 Hz, 1H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 185.4, 185.1, 165.2, 163.4, 163.0, 163.0, 135.3, 135., 135.0, 133.8, 132.7, 132.2, 132.0, 131.9, 130.1, 130.0, 129.8, 129.1, 129.0, 128.8, 128.8, 128.7, 118.8, 95.2 (C1), 70.4, 69.3, 69.3, 68.3, 66.5, 63.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{32}NaO_{13}$ 743.1735 found 743.1731.

5aa.Phenyl-3,4,6-tri-*O*-oxobenzoyl-2-*N*-(trichloroacetyl)-amino-2-deoxy-1-deoxy-1-thio-*α*-D-glucopyranoside.

Starting material was synthesized from literature[24]. Isolated as a syrup (143 mg, 72% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.66 – 7.56 (m, 3H), 7.53 – 7.47 (m, 4H), 7.40 (dd, *J* = 14.8, 7.5 Hz, 5H), 7.21 (t, *J* = 7.1 Hz, 2H), 6.04 (t, *J* = 9.8 Hz, 1H), 5.45 (t, *J* = 9.7 Hz, 1H), 5.37 (d, *J* = 10.3 Hz, 1H, H1), 4.65 (qd, *J* = 12.2, 3.9 Hz, 2H), 4.26 – 4.15 (m, 1H), 4.03 (dd, *J* = 19.3, 9.9 Hz, 1H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 184.7, 184.3, 163.2, 163.1, 162.0, 161.6, 135.4, 135.3, 135.1, 133.5, 133.5, 132.2, 131.7, 131.6, 130.7, 130.7, 130.2, 130.0, 129.2, 129.1, 129.0, 129.0, 128.8, 128.8, 128.5, 92.0 (C1), 85.4, 75.1, 73.7, 73.6, 70.0, 63.2, 55.0; HRMS (ESI-TOF) m/z: [M + H]+ Calcd. for $C_{38}H_{29}Cl_3NO_{11}S$ 812.0521 found 812.0513.

5ab. **Methyl-2,3,4,6-tetra-*O*-oxobenzoyl-*α*-D-glucopyranoside.**

Starting material was commercially available. Isolated as a syrup (272 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 6H), 7.94 – 7.86 (m, 2H), 7.68 – 7.59 (m, 3H), 7.50 (ddd, *J* = 21.4, 13.1, 6.0 Hz, 7H), 7.40 (t, *J* = 8.0 Hz, 2H), 6.08 (t, *J*= 10.0 Hz, 1H), 5.56 (t, *J* = 10.0 Hz, 1H), 5.37 (d, *J* = 3.6 Hz, 1H, H1), 5.23 (dd, *J* = 10.0, 3.2 Hz, 1H), 4.66 (qd, *J* = 12.3, 3.7 Hz, 2H), 4.39 (ddd, *J* = 10.1, 4.5, 2.8 Hz, 1H), 3.53 (s, 3H).^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 185.1, 184.8, 184.7, 163.2, 162.7, 162.4, 162.1, 135.4, 135.3, 135.2, 132.2, 132.0, 131.7, 131.7, 130.3, 130.2, 130.1, 130.0, 129.2, 129.1, 129.0, 129.0, 96.2 (C1), 72.6, 70.5, 69.7, 67.0, 62.9, 56.1.HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{39}H_{31}O_{14}$ 723.1708 found 723.1717 .

5ac. (4-methyl)Phenyl-2,3,4,6-tetra-*O*-oxobenzoyl-1-deoxy-1-thio-*α*-D-glucopyranoside.

Starting material was synthesized from literature[34]. Isolated as a syrup (202 mg, 71% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 8.08 – 8.02 (m, 2H), 7.97 (d, *J* = 8.4 Hz, 4H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.63 (m, 7H), 7.50 (m, 2H), 7.46 – 7.37 (m, 4H), 7.28

(s, 1H), 5.92 (t, *J* = 9.6 Hz, 1H), 5.70 (t, *J* = 9.6 Hz, 1H), 5.40 (t, *J* = 10.0 Hz, 1H), 4.84 (d, *J* = 9.6 Hz 1H, H1), 4.65 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.55 (dd, *J* = 12.6, 4.4 Hz, 1H), 4.17 (ddd, *J* = 10.0, 4.2, 2.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.2, 184.4, 184.3, 184.2, 163.0, 162.0, 161.6, 161.2, 146.5, 135.5, 135.3, 135.2, 134.7, 133.9, 132.1, 132.0, 131.6, 131.6, 130.9, 130.6, 130.5, 130.3, 130.2, 129.9, 129.9, 129.2, 129.1, 129.0, 128.9, 128.3, 88.1(C1), 75.6, 73.7, 68.5, 68.1, 62.0, 21.7; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{45}H_{35}NaO_{13}S$ 838.1691 found 838.1697.

F. Characterization data for Deprotected compounds.

6a. Methyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside

White solid (66 mg and 70 mg, 84% and 90% yield), mp 89-91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 15H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.92 – 4.77 (m, 3H), 4.67 (dd, *J* = 12.0, 6.8 Hz, 2H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.03 (t, *J* = 9.2 Hz, 1H), 3.81 – 3.64 (m, 3H), 3.57 – 3.49 (m, 2H), 3.38 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 138.8, 138.2, 138.2, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 98.3, 82.0, 80.1, 77.6, 75.7, 75.0, 73.4, 70.8, 61.9, 55.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{32}NaO_6$ 487.2091 found 487.2097.

6b. Methyl-6-*O*-(triisopropylsilyl)-2,3,-di-*O*-benzyl-*α*-D-glucopyranoside.

Isolated as a syrup (68 mg and 71 mg, 85% and 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 10H), 5.01 (d, *J* = 11.6 Hz, 1H), 4.81 (dd, *J* = 18.0, 11.2 Hz, 2H), 4.66 (dd, *J* = 21.2, 12.0 Hz, 2H), 3.93 – 3.83 (m, 3H), 3.68 (m, 1H), 3.62 – 3.56 (m, 1H), 3.52 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.42 (s, 3H), 2.86 (s, 1H), 1.10 (m, 21H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 139.0, 138.2, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8, 98.0, 81.6, 79.6, 75.54, 73.2, 72.5, 70.8, 64.7, 55.1, 18.0, 11.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{47}O_6Si$ 531.3136 found 531.3149 .

6c and 6w. Methyl-2-benzoyl-*α*-D-glucopyranoside.

White solid (48 mg and 52 mg, 83% and 91% yield for **6c**), (33 mg and 34 mg, 78% and 79% yield for **6w**), mp 125-127 ^{o}C; ^{1}H NMR (400 MHz, MeOD) δ 8.04 – 7.87 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.76 – 4.72 (m, 2H), 3.90 (t, *J* = 9.2 Hz, 1H), 3.78 (dd, *J* = 11.6, 2.0 Hz, 1H), 3.65 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.53 (m, 1H), 3.37 (t, *J* = 9.2 Hz, 1H), 3.29 (s, 3H). ^{13}C NMR {1H} (101 MHz, MeOD) δ 166.4, 133.1, 129.8, 129.5, 128.2, 97.1, 74.2, 72.2, 71.1, 70.5, 61.2, 54.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_7$ 299.1125 found 299.1127.

6d. Methyl-3-*O*-(triisopropylsilyl)-*α*-D-glucopyranoside.

Isolated as a syrup (52 mg and 57 mg, 85% and 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (d, *J* = 4.0 Hz, 1H), 3.90 – 3.77 (m, 3H), 3.62 (m, 1H), 3.51 – 3.44 (m, 2H), 3.42 (s, 3H), 2.45 (s, 1H), 2.04 (d, *J* = 8.0 Hz, 1H), 1.26 – 1.12 (m, 3H), 1.09 (m, 18H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 99.8, 76.9, 72.9, 71.8, 70.9, 62.6, 55.4, 18.3, 18.2, 12.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{34}NaO_6Si$ 373.2017 found 373.2031.

6e. 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside.

White solid (69 mg and 75 mg, 86% and 93% yield), mp 145-147 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 29H), 7.10 (dd, *J* = 7.2, 2.8 Hz, 7H), 5.18 (d, *J* = 3.2 Hz, 1H), 4.90 (m, 2H), 4.81 – 4.62 (m, 6H), 4.57 – 4.39 (m, 5H), 4.04 – 3.87 (m, 2H), 3.69 – 3.40 (m,7H), 3.40 – 3.33 (m, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 138.8, 138.7, 138.5, 138.3, 138.1, 138.0, 137.9, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 97.6, 91.3, 84.7, 83.3, 81.8, 80.2, 78.0, 77.9, 75.7, 75.6, 75.0, 74.8, 74.7, 73.6, 73.5, 73.2, 70.4, 69.1, 68.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{36}NaO_6$ 563.2404 found 563.2397.

6f. Methyl-6-*O*-(triisopropylsillyl)- *α*- D-glucopyranoside.

White solid (40 mg, 82% yield), mp 76-78 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (d, *J* = 3.2 Hz, 1H), 4.68 (d, *J* = 3.6 Hz, 1H), 4.45 (d, *J* = 7.6 Hz, 1H), 4.39 (d, *J* = 3.6 Hz, 1H), 3.95 (dd,

J = 10.8, 3.2 Hz, 1H), 3.80 (m, 1H), 3.74 (m, 1H), 3.58 (m, 1H), 3.52 – 3.43 (m, 1H), 3.41 – 3.31 (m, 4H), 1.05 (m, 21H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 99.3, 74.3, 72.0, 71.8, 71.4, 64.1, 54.8, 17.9, 17.9, 11.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{35}O_6Si$ 351.2197 found 351.2199.

6f*. Methyl-2,3-di-*O*-(4-methoxybenzyl)- 6-*O*-(triisopropylsillyl)- *α*- D-glucopyranoside

Isolated as a syrup (72 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.8, 6.4 Hz, 4H), 6.92 – 6.84 (m, 4H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 2H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 3.94 – 3.85 (m, 2H), 3.84 – 3.76 (m, 7H), 3.63 (m, 1H), 3.5 (t, *J* = 8.8 Hz, 1H), 3.47 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (s, 3H), 1.13 – 1.05 (m, 21H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 159.4, 159.3, 131.2, 130.4, 129.7, 129.7, 113.9, 113.9, 98.1, 81.2, 79.2, 75.1, 72.8, 72.3, 70.9, 64.6, 55.3, 55.0, 18.0, 11.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{50}NaO_8Si$ 613.3167 found 613.3174.

6g. Methyl-2-*O*-benzoyl-3-*O*-acetyl-6-*O*-(tert-butyldiphenylsilyl)-*α*-D-glucopyranoside.

Isolated as a syrup (68 mg and 71 mg, 83% and 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 2H), 7.79 – 7.75 (m, 4H), 7.63 – 7.53 (m, 1H), 7.51 – 7.41 (m, 8H), 5.64 (dd, *J* = 10.0, 8.8 Hz, 1H), 5.18 – 5.03 (m, 2H), 4.01 (d, *J* = 4.0 Hz, 2H), 3.94 – 3.80 (m, 2H), 3.38 (s, 3H), 3.06 (s, 1H), 2.06 (s, 3H), 1.14 (s, 9H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 171.4, 166.0, 135.7, 135.7, 133.5, 133.1, 133.0, 130.0, 129.9, 129.3, 128.6, 127.9, 127.9, 96.8, 72.9, 71.9, 71.0, 70.8, 64.3, 55.2, 26.9, 21.0, 19.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{38}NaO_8Si$ 601.2228 found 601.2241.

6h. Methyl (allyl-2,3-di-*O*-benzyl-*α*-D-glucopyranosyl uronate).

Isolated as a syrup (67 mg and 70 mg , 82% and 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.87 (m, 4H), 7.52 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 4H), 5.95 – 5.79 (m, 2H), 5.40 – 5.24 (m, 3H), 5.18 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.45 (d, *J* = 10.0 Hz, 1H), 4.31 (m, 1H), 4.22 – 4.06 (m, 1H), 3.88 (s, 3H). ^{13}C NMR {1H} (126 MHz, $CDCl_3$) δ 170.3, 166.6, 165.9, 133.5, 133.4,

132.9, 129.8, 129.3, 128.9, 128.5, 128.4, 118.2, 95.5, 72.4, 71.0, 70.8, 70.6, 69.1, 53.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{25}O_9$ 457.1493 found 457.1478.

6i and 6z. Phenyl-2-*N*-trichloroacetamido-1-deoxy-1-thio-*α*-D-glucopyranoside.

White solid (52 mg and 54 mg, 81% and 83% yield for **6i**), (38 mg and 40 mg, 76% and 79% yield for **6z**) mp 189-191 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.18 (m, 3H), 4.84 (d, *J* = 10.0 Hz, 1H), 3.80 (d, *J* = 12.0 Hz, 1H), 3.71 – 3.49 (m, 3H), 3.32 – 3.10 (m, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 166.6, 138.0, 135.3, 132.5, 131.1, 90.6, 84.7, 79.2, 74.6, 65.4, 60.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}Cl_3NO_5S$ 415.9888 found 415.9892.

6j. Methyl-2-*O*-benzoyl-*α*-D-galactopyranoside.

White solid (48 mg and 49 mg, 84% and 86% yield), mp 126-128 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.39 (m, 1H), 7.33 (m, 3H), 5.15 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.83 – 4.74 (m, 1H), 4.64 (d, *J* = 4.4 Hz, 1H), 4.41 – 4.24 (m, 1H), 4.24 – 4.10 (m, 2H), 4.10 – 3.82 (m, 4H), 3.73 (m, 4H), 3.31 (s, 3H), 3.22 (s, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 166.9, 166.8, 166.8, 166.6, 133.3, 133.3, 129.9, 129.7, 129.6, 128.4, 109.0, 102.4, 99.8, 84.6, 81.7, 80.2, 77.9, 74.0, 69.7, 68.6, 68.5, 66.9, 66.0, 62.0, 57.4, 56.0, 55.4, 54.9, 54.6, 42.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_7$ 299.1125 found 299.1129.

6k. Methyl-2,3,4-tri-*O*-benzyl-*α*-D-mannopyranoside.

Isolated as a syrup (67 mg and 69 mg, 86% and 89% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 15H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.77 – 4.67 (m, 5H), 4.01 (t, *J* = 9.6 Hz, 1H), 3.94 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.89 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.84 (dd, *J* = 2.8, 2.0 Hz, 2H), 3.66 (m, 1H), 3.34 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 138.5, 138.5, 138.3, 128.5, 128.4, 128.1, 127.9, 127.8, 127.6, 99.4, 80.3, 75.2, 74.9, 74.8,

73.0, 72.3, 72.1, 62.4, 54.8; HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{28}H_{36}NO_6$ 482.2537 found 482.2543.

6l. Napthyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside.

Isolated as a syrup (69 mg and 72 mg, 88% and 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 3H), 7.75 (s, 1H), 7.50 – 7.44 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.26 (m, 13H), 7.21 – 7.10 (m, 2H), 5.04 (d, *J* = 1.2 Hz, 1H), 4.85 (dd, *J* = 18.0, 12.0 Hz, 2H), 4.71 – 4.64 (m, 4H), 4.54 (dd, *J* = 18.0, 12.0 Hz, 2H), 4.09 (m, 1H), 3.96 (m, 1H), 3.89 (d, *J* = 5.8 Hz, 2H), 3.75 (m, 2H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 134.7, 133.4, 133.2, 128.7, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.1, 126.3, 126.2, 98.7, 80.4, 75.3, 74.5, 73.6, 72.1, 71.6, 69.4, 69.1, 68.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{38}NaO_6$ 613.2561 found 613.2549.

6m. D-glucose.

White solid (41 mg and 41 mg, 89% and 90% yield); ^{1}H NMR (400 MHz, D_2O) δ 5.05 (d, *J* = 3.6 Hz, 1H), 4.46 (d, *J* = 7.6 Hz, 1H), 3.75 – 3.61 (m, 3H), 3.61 – 3.49 (m, 3H), 3.39 – 3.18 (m, 4H), 3.10 – 3.01 (m, 1H). ^{13}C NMR {1H} (101 MHz, D_2O) δ 95.8, 92.0, 75.9, 75.7, 74.1, 72.7, 71.4, 71.4, 69.6, 69.5, 60.7, 60.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_6H_{13}O_6$ 181.0707 found 181.0719.

6n. D-galactose.

White solid (42 mg and 43 mg, 91% and 93% yield); ^{1}H NMR (400 MHz, D_2O) δ 5.09 (d, *J* = 3.6 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 3.91 (t, *J* = 6.0 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.75 (d, *J* = 3.2 Hz, 1H), 3.68 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.66 – 3.51 (m, 5H), 3.48 (d, *J* = 3.5 Hz, 1H), 3.31 (m, 1H). ^{13}C NMR {1H} (101 MHz, D_2O) δ 96.4, 92.2, 75.1, 72.7, 71.8, 70.4, 69.2, 69.1, 68.7, 68.3, 61.1, 60.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_6H_{13}O_6$ 181.0707 found 181.0715.

6o. Methyl-2,4,6-tri-*O*-benzyl-*α*-D-glucopyranoside.

White solid (67 mg and 69 mg, 86% and 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 13H), 7.21 – 7.14 (m, 2H), 4.96 – 4.77 (m, 4H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.56 – 4.49 (m, 2H), 3.81 – 3.60 (m, 6H), 3.43 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 138.7, 138.3, 138.0, 128.5, 128.4, 128.4, 127.9, 127.9, 127.8, 127.7, 127.7, 99.5, 83.3, 77.6, 75.4, 74.9, 73.6, 73.0, 70.5, 68.6, 55.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{33}O_6$ 465.2272 found 465.2274.

6p and 6v. 3,4,5,6-tetra-*O*-benzyl-*myo*-inositol.

White solid (57 mg, 83% yield for **6p**),(56 mg and 57 mg, 83% and 85% yield for **6v**) mp 141-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 20H), 4.93 (m, 3H), 4.84 (dd, *J* = 10.8, 4.0 Hz, 2H), 4.73 (m, 3H), 4.20 (t, *J* = 2.4 Hz, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.84 (t, *J* = 9.6 Hz, 1H), 3.47 (m, 3H), 2.56 – 2.34 (m, 2H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 138.6, 138.5, 137.8, 128.6, 128.5, 128.4, 128.4, 127.94, 127.9, 127.8, 127.8, 127.6, 83.1, 81.6, 81.4, 80.0, 75.9, 75.7, 75.6, 72.7, 71.8, 69.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{36}NaO_6$ 563.2404 found 563.2409.

6p*. 3,4,5,6-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-*myo*-inositol.

White solid (59 mg, 87% yield) mp 65-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.26 (m, 22H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.98 – 4.85 (m, 5H), 4.83 (t, *J* = 11.6 Hz, 1H), 4.68 (q, *J* = 12.4 Hz, 2H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.19 (t, *J* = 9.6 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.84 (s, 3H), 3.46 – 3.37 (m, 2H), 3.20 (dd, *J* = 10.0, 2.4 Hz, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 159.4, 139.0, 138.9, 138.9, 138.4, 130.1, 129.4, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 114.0, 83.6, 81.5, 81.2, 79.9, 75.8, 75.3, 74.1, 73.9, 73.0, 72.9, 72.0, 55.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{42}H_{45}O_7$ 661.3160 found 661.3163.

6q. Napthyl-(3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl)(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside.

Isolated as a syrup (71 mg and 73 mg, 81% and 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 3H), 7.77 (s, 1H), 7.52 – 7.42 (m, 5H), 7.41 – 7.21 (m, 28H), 5.61 (s, 1H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 4.87 (dd, *J* = 18.8, 12.0 Hz, 2H), 4.71 (m, 4H), 4.63 – 4.47 (m, 6H), 4.22 (t, *J* = 9.6 Hz, 1H), 4.17 – 4.05 (m, 2H), 4.03 – 3.94 (m, 2H), 3.94 – 3.68 (m, 8H). ^{13}C NMR {1H} (126 MHz, $CDCl_3$) δ 138.6, 138.4, 138.4, 138.3, 138.2, 138.0, 134.7, 133.2, 133.0, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 126.9, 126.2, 126.0, 101.2, 98.0, 80.0, 79.7, 75.2, 75.0, 74.8, 74.2, 73.3, 73.3, 72.4, 72.2, 72.1, 71.4, 69.3, 69.1, 68.8, 68.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{65}H_{67}O_{11}$ 1023.4678 found 1023.4685.

6r. Napthyl-(3-*O*-benzyl-*α*-D-mannopyranosyl)(1→2)-(3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl))(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside.

Isolated as a syrup (67 mg and 68 mg, 79% and 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 3H), 7.70 (s, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.12 (m, 35H), 7.10 (dd, *J* = 7.6, 3.6 Hz, 2H), 5.06 (d, *J* = 2.0 Hz, 1H), 4.97 (s, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.70 (m, 5H), 4.64 – 4.46 (m, 6H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.36 – 4.21 (m, 4H), 4.13 (s, 1H), 4.01 – 3.87 (m, 4H), 3.87 – 3.67 (m, 8H), 3.52 (dd, *J* = 10.8 4.4 Hz, 1H), 3.34 (d, *J* = 10.0 Hz, 1H), 3.08 (dd, *J* = 9.2, 3.2 Hz, 1H), 2.99 – 2.91 (m, 1H). ^{13}C NMR {1H} (126 MHz, $CDCl_3$) δ 138.4, 138.3, 138.2, 138.2, 138.2, 138.0, 137.7, 134.6, 133.2, 133.0, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.0, 126.2, 126.0, 99.6, 97.9, 97.7, 80.1, 80.0, 77.6, 75.4, 75.2, 75.1, 74.6, 74.5, 73.5, 73.2, 72.9, 72.8, 72.0, 71.8, 71.7, 70.3, 69.2, 69.1, 68.8, 67.3, 66.5, 62.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{78}H_{82}NaO_{16}$ 1297.5495 found 1297.5487.

6s. Methyl-3-*O*-levulinyl-2-*O*-pivaloyl-*α*-D-glucopyranoside.

Isolated as a syrup (51 mg and 52 mg, 76% and 83% yield ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.27 (m, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.63 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.12 (s, 1H), 3.78 (s, 2H), 3.70 – 3.61 (m, 2H), 3.31 (s, 3H), 3.16 (s, 1H), 2.83 – 2.34 (m, 4H), 2.11 (s, 3H), 1.09 (s, 9H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 207.9, 177.9, 172.5, 96.9, 73.1, 71.2, 70.9, 68.9, 61.6, 55.4, 38.7, 38.0, 29.8, 28.0, 26.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{28}NaO_9$ 399.1626 found 399.1634.

6t. Methyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside.

White solid (51 mg and 52 mg, 87% and 88% yield) mp 69-71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 10H), 5.00 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 13.6, 12.0 Hz, 2H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 3.6 Hz, 1H), 3.82 – 3.69 (m, 3H), 3.61 – 3.54 (m, 1H), 3.54 – 3.43 (m, 2H), 3.36 (s, 3H), 2.67 (s, 1H), 2.21 (s, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 138.8, 138.1, 128.6, 128.5, 128.1, 128.0, 127.9, 127.9, 98.3, 81.4, 79.9, 75.4, 73.2, 70.8, 70.5, 62.4, 55.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_6$ 397.1622 found 397.1630.

6u and 6aa. Methyl-*α*-D-glucopyranoside.

White solid (30 mg and 31 mg, 84% and 87% yield); ^{1}H NMR (400 MHz, MeOD) δ 4.58 (d, *J* = 4.0 Hz, 1H), 3.71 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.54 (m, 2H), 3.43 (m, 1H), 3.34 – 3.28 (m, 4H), 3.23 – 3.16 (m, 1H). ^{13}C NMR {1H} (101 MHz, MeOD) δ 99.9, 73.7, 72.2, 70.4, 61.3, 54.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_7H_{15}O_6$ 195.0863 found 195.0877.

6v. Methyl-2,6-di-benzoyl-*α*-D-glucopyranoside.

White solid (52 mg and 54 mg, 86% and 89% yield)) mp 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (m, 4H), 7.58 (m, 2H), 7.45 (q, *J* = 8.4 Hz, 4H), 5.07 (d, *J* = 4.0 Hz, 1H), 4.98 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.73 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.59 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.22 (t, *J* = 9.6 Hz, 1H), 3.97 (m, 1H), 3.88 (s, 1H), 3.65 (t, *J* = 9.6 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 167.2, 166.5, 133.4, 133.4, 130.0, 129.8, 129.6, 129.5,

128.5, 128.5, 97.3, 73.7, 71.6, 70.7, 69.6, 63.8, 55.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_8$ 403.1387 found 403.1384.

6y. Benzyl-6-*O*-benzoyl-*β*-D-glucopyranoside

White solid (37 mg and 39 mg, 77% and 81% yield)) mp 117-119 °C; ^{1}H NMR (400 MHz, MeOD) δ 7.97 (m, 2H), 7.57 – 7.49 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 4.72 (d, *J* = 11.6 Hz, 2H), 4.58 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.40 (dd, *J* = 11.6, 6.0 Hz, 1H), 4.28 (d, *J* = 7.6 Hz, 1H), 3.54 – 3.44 (m, 1H), 3.36 (t, *J* = 8.8 Hz, 1H), 3.29 (t, *J* = 8.8 Hz, 1H), 3.25 – 3.15 (m, 1H). ^{13}C NMR {1H} (101 MHz, MeOD) δ 166.6, 137.3, 133.0, 129.3, 128.3, 128.0, 127.9, 127.8, 127.4, 101.7, 76.6, 74.1, 73.7, 70.5, 70.4, 63.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_7$ 375.1438 found 375.1442.

6z. Allyl-3-*O*-benzoyl-*α*-D-galactopyranoside.

Isolated as a syrup (33 mg and 34 mg, 74% and 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 2H), 5.85 (m, 1H), 5.30 – 5.13 (m, 3H), 4.95 (s, 1H), 4.24 – 4.10 (m, 3H), 3.96 (dd, *J* = 12.4, 5.6 Hz, 1H), 3.79 (m, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 166.7, 133.5, 133.4, 129.9, 129.7, 128.5, 118.1, 98.1, 74.1, 69.6, 69.2, 68.8, 67.0, 62.5, 29.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}NaO_7$ 347.1101 found 347.1094.

6ac. (4-methyl)Phenyl-1-deoxy-1-thio-*α*-D-glucopyranoside.

White solid (28 mg and 29 mg, 79% and 83% yield)) mp 146-148 °C; ^{1}H NMR (400 MHz, DMSO) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 6.0 Hz, 1H), 5.08 (d, *J* = 4.8 Hz, 1H), 4.97 (d, *J* = 5.2 Hz, 1H), 4.58 – 4.46 (m, 2H), 3.73 – 3.63 (m, 1H), 3.44 (m, 1H), 3.24 – 3.10 (m, 2H), 3.12 – 2.96 (m, 2H), 2.27 (s, 3H). ^{13}C NMR {1H} (101 MHz, MeOD) δ 137.6, 132.4, 132.2, 129.5, 129.3, 88.2, 80.5, 78.2, 72.3, 70.0, 61.5, 19.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{19}NaO_5S$ 310.0845 found 310.0854.

G. Characterization data for Remaining compounds.

7. Methyl-4-*O*-oxobenzoyl-3-Acetyl-2-benzoyl-6-*O*-(triisopropylsillyl)-*α*-D-glucopyranoside.

Starting material was synthesized from literature[22]. Isolated as a syrup (101 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.95 – 7.89 (m, 2H), 7.67 – 7.60 (m, 1H), 7.59 – 7.51 (m, 1H), 7.48 (m, 2H), 7.45 – 7.39 (m, 2H), 5.84 (t, *J* = 10.0 Hz, 1H), 5.46 (t, *J* = 9.6 Hz, 1H), 5.15 (d, *J* = 3.6 Hz, 1H, H1), 5.07 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.99 (m, 1H), 3.91 (d, *J* = 3.2 Hz, 2H), 3.37 (s, 3H), 2.00 (s, 3H), 1.07 (m, 21H) . ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 170.1, 165.8, 162.7, 135.2, 133.5, 132.1, 130.0, 129.9, 129.1, 129.0, 128.6, 96.7 (C1), 72.1, 70.2, 70.0, 69.9, 62.1, 55.3, 20.8, 18.0, 17.9, 12.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{45}O_{10}Si$ 629.2777 found 629.2769.

8. Methyl-3-Acetyl-2-benzoyl-6-*O*-(triisopropylsillyl)-*α*-D-glucopyranoside.

Isolated as a syrup (65mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 5.65 – 5.34 (m, 1H), 5.01 (d, *J* = 3.6 Hz, 1H, H1), 4.93 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.96 (m, 2H), 3.76 (d, *J* = 4.0 Hz, 2H), 3.37 (d, *J* = 20.4 Hz, 4H), 1.98 (d, *J* = 0.8 Hz, 3H), 1.05 (m, 21H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 171.2, 166.0, 133.4, 129.9, 129.3, 128.5, 96.8 (C1), 72.6, 72.0, 71.6, 70.5, 64.8, 55.2, 20.9, 17.9, 11.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{41}O_8Si$ 497.2565 found 497.2552.

9. Methyl-2-benzoyl-6-*O*-(triisopropylsillyl)-*α*-D-glucopyranoside.

Isolated as a syrup (78 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 4.98 (d, *J* = 4.0 Hz, 1H, H1), 4.89 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.14 (t, *J* = 9.2 Hz, 1H), 3.95 (dd, *J* = 5.2, 2.0 Hz, 2H), 3.79 (s, 1H), 3.71 (m, 1H), 3.64 (t, *J* = 9.6 Hz, 1H), 3.35 (s, 3H), 1.08 (m, 21H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 166.5, 133.3, 130.0, 129.6, 128.4, 97.1 (C1), 73.8, 73.4, 71.6, 70.1, 64.9, 55.2, 17.9, 11.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{39}O_7Si$ 455.2460 found 455.2453.

10. Methyl-3-*O*-oxobenzoyl-4,6-*O*-diacetyl-2-*O*-benzyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[22]. White solid, mp 136-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.04 (m, 2H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.53 – 7.39 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 2H), 5.99 (t, *J* = 10.0 Hz, 1H), 5.30 (t, *J* = 9.6 Hz, 1H), 5.23 – 5.13 (m, 2H), 4.32 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.44 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.8, 170.6, 169.4, 165.4, 163.8, 135.0, 133.8, 131.7, 130.1, 129.7, 128.9, 128.8, 128.7, 96.9 (C1), 71.8, 71.5, 68.0, 67.5, 61.9, 55.7, 20.7, 20.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{27}O_{11}$ 515.1548 found 515.1542.

11. Methyl-4,6-*O*-diacetyl-2-*O*-benzoyl-*α*-D-glucopyranoside.

Isolated as a syrup (128 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.09 – 4.97 (m, 3H), 4.34 – 4.08 (m, 3H), 3.99 (m, 1H), 3.40 (s, 3H), 2.12 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 170.8, 170.7, 166.3, 133.4, 130.0, 129.5, 128.6, 128.5, 97.2 (C1), 74.0, 71.1, 70.2, 67.3, 62.3, 55.6, 20.8, 20.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_9$ 383.1337 found 383.1332.

12. Methyl-4-*O*-oxobenzoyl-6-*O*-(triisopropylsillyl)-*α*-D-glucopyranoside.

Isolated as a syrup (62 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.69 – 7.62 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 5.22 (m, 1H), 4.82 (d, *J* = 4.0 Hz, 1H, H1), 3.99 (t, *J* = 9.2 Hz, 1H), 3.86 (m, 3H), 3.67 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.44 (s, 3H), 1.07 (m, 21H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.3, 163.2, 135.1, 132.3, 130.2, 129.0, 98.8 (C1), 72.9, 72.8, 72.1, 70.4, 62.4, 55.3, 17.9, 17.9, 12.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{39}O_8Si$ 483.2409 found 483.2421.

13. Methyl-4-*O*-oxobenzoyl-2,3-di-*O*-(4-methoxybenzyl)-*α*- D-glucopyranoside.

Isolated as a syrup (64 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69 – 7.61 (m, 1H), 7.52 – 7.45 (m, 2H), 7.29 (d, *J* = 9.2 Hz, 4H), 6.97 – 6.78 (m,

4H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.67 – 4.54 (m, 5H), 3.87 (m, 1H), 3.82 (d, *J* = 2.0 Hz, 6H), 3.76 (t, *J* = 9.2 Hz, 1H), 3.52 – 3.40 (m, 2H), 3.37 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.0, 163.7, 159.6, 159.5, 134.9, 132.4, 130.8, 130.1, 129.7, 129.7, 128.9, 114.1, 114.0, 98.3 (C1), 80.8, 79.3, 75.1, 72.8, 70.0, 68.9, 64.7, 55.4, 55.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{35}O_{10}$ 567.2225 found 567.2233.

14. 2-*O*-oxobenzoyl-3,4,6-tri-*O*-benzyl-*α*- D- mannopyranoside.

Isolated as a syrup (78 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.38 – 7.26 (m, 13H), 7.15 (dd, *J* = 6.0, 3.6 Hz, 2H), 5.72 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.40 – 5.32 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.87 (dd, *J* = 12.8, 10.8 Hz, 2H), 4.68 (d, *J* = 10.8 Hz, 1H), 4.57 – 4.49 (m, 2H), 4.47 (d, *J* = 10.8 Hz, 1H), 4.18 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.12 (m, 1H), 3.67 – 3.65 (m, 2H), 3.60 (m, 1H), 3.35 (d, *J* = 4.0 Hz, 1H) ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.3, 163.6, 138.0, 137.9, 137.6, 134.9, 132.4, 130.4, 130.3, 128.8, 128.8, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 92.1 (C1), 77.9, 77.2, 75.2, 74.5, 73.5, 72.5, 71.5, 70.8, 69.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{34}NaO_8$ 605.2146 found 605.2157.

15. Ethyl-3,4,6-Tri- *O*-oxobenzoyl-2-phthalimido-1-thio-*β*-D-glucopyranoside.

Starting compound was synthesized from literature protocol.[36] Isolated as a syrup ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.97 – 7.91 (m, 2H), 7.82 (dd, *J* = 5.6, 2.8 Hz, 2H), 7.67 (m, 4H), 7.53 (m, 5H), 7.26 (t, *J* = 8.0 Hz, 2H), 6.33 (t, *J* = 9.6 Hz, 1H), 5.62 (dd, *J* = 19.6, 10.4 Hz, 2H), 4.75 (dd, *J* = 13.6, 2.4 Hz, 1H), 4.72 – 4.67 (m, 1H), 4.63 (t, *J* = 10.4 Hz, 1H), 4.28 (m, 1H), 2.82 – 2.63 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 185.6, 184.7, 167.8, 166.8, 163.3, 162.8, 162.0, 135.4, 135.2, 135.1, 134.7, 134.6, 132.2, 131.7, 131.5, 131.3, 130.2, 130.2, 129.7, 129.1, 129.0, 128.9, 124.0, 124.0, 81.3 (C1), 75.3, 72.7, 70.1, 63.2, 53.5, 24.3, 14.9. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd $C_{40}H_{31}NNaO_{12}S$ 772.1459 found 772.1457.

16. 3,4,6-Tri-*O*-oxobenzoyl-2-phthalimido-1-D-glucopyranoside.

The thioglycoside **15** (0.1 g, 0.133 mmol) was dissolved in a mixture of acetone/water (9:1, 5 mL). Then NBS (0.059 g, 0.33mmol) was added at room temperature and the reaction mixture was stirred for the 1 h. After completion the reaction mixture was diluted with water, extracted with ether several times and the combined organic phases washed with saturated sodium bicarbonate solution and dried over sodium sulfate. After removal of the solvent, the crude product was subjected to flash chromatography (30-50 % ethyl acetate in hexane) afforded compound **16** (0.086 g, 79 %) as a colourless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 8.04 – 8.00 (m, 2H), 7.92 (m, 2H), 7.79 (m, 2H), 7.69 – 7.61 (m, 4H), 7.51 (m, 5H), 7.25 (t, *J* = 8.0 Hz, 2H), 6.34 (dd, *J* = 10.4, 9.2 Hz, 1H), 5.82 (d, *J* = 8.4 Hz, 1H), 5.64 (t, *J* = 10.0 Hz, 1H), 4.71 (m, 2H), 4.53 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.37 – 4.28 (m, 1H), 4.13 (s, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.6, 184.9, 184.8, 163.2, 162.8, 162.1, 135.4, 135.2, 135.1, 134.6, 132.1, 131.7, 131.7, 131.5, 131.3, 130.3, 130.2, 129.7, 129.1, 129.0, 128.9, 124.2, 123.9, 92.8, 71.8, 71.4, 70.1, 63.1, 55.8. HRMS (ESI-TOF) m/z: [M + H]+ Calcd $C_{38}H_{28}NO_{13}$ 706.1555 found 706.1549.

17. Allyl-2-*O*-oxobenzoyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside

Starting compound was synthesized from literature protocol.[7b] Isolated as a syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.45 (d, *J* = 6.4 Hz, 2H), 7.38 – 7.25 (m, 13H), 7.22 – 7.18 (m, 2H), 5.96 (m, 1H), 5.78 (s, 1H), 5.35 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.09 (s, 1H), 4.91 (dd, *J* = 15.2, 10.4 Hz, 2H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.52 (dd, *J* = 12.4, 7.6 Hz, 2H), 4.27 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.19 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.08 (dd, *J* = 12.8, 6,4 Hz, 1H), 3.93 (m, 1H), 3.87 – 3.66 (m, 3H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 186.4, 163.7, 138.2, 138.1, 137.7, 134.9, 133.3, 132.4, 130.3, 128.8, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7,

127.5, 118.1, 96.4 (C1), 78.5, 75.4, 74.4, 73.4, 72.6, 71.8, 70.7, 68.9, 68.3. HRMS (ESI-TOF) m/z: [M + H]+ Calcd $C_{38}H_{39}O_8$ 623.2639 found 623.2644.

18. 2-*O*-oxobenzoyl-3,4,6-tri-*O*-benzyl-D-mannopyranoside.

To a solution of the allyl ether **17** (0.2 g, 0.32 mmol) and DIPEA (10 μL) in ethanol–toluene–water (7:3:1, 5 mL) was added $(PPh_3)_3Rh(1)Cl$ (0.044 mg, 0.48 mmol) and the solution refluxed for 4 h, then cooled to rt. The mixture was filtered and washed with ethyl acetate. The filtrate was concentrated to dryness, suspended in water and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$ to give the crude propenyl ether as brown oil (mixture of geometric isomers). The residue was dissolved in 10:1 acetone-water (5 mL), and HgO (0.0318 g, 0.064 mmol) and $HgCl_2$ (0.435 g, 1.60 mmol) were added. The removal of the propenyl group occurred after 30-45 min, as shown by TLC.. The mixture was filtered and concentrated, and a solution of the residue in dichloromethane (50 mL) was washed with aq. 5% potassium iodide (2 x 20 mL), dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (30% ethyl acetate in hexane) afforded compound **18** (0.081g, 76 %) as syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.43 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.39 – 7.21 (m, 13H), 7.16 (dd, *J* = 5.6, 2.0 Hz, 2H), 5.75 – 5.72 (m, 1H), 5.37 (s, 1H), 4.88 (dd, *J* = 13.2, 10.9 Hz, 2H), 4.70 (d, *J* = 10.8 Hz, 1H), 4.58 – 4.45 (m, 3H), 4.19 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.16 – 4.10 (m, 1H), 3.71 – 3.57 (m, 3H), 3.43 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 186.4, 163.6, 137.9, 137.8, 137.6, 134.9, 132.3, 130.3, 128.8, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 92.1, 77.9, 75.3, 74.4, 73.4, 72.5, 71.4, 70.8, 69.2. HRMS (ESI-TOF) m/z: [M + H]+ Calcd $C_{35}H_{35}O_8$ 583.2326 found 583.2329.

19. Methyl-4,6-di-*O*-oxobenzoyl-*α*-D-glucopyranoside.

To a solution of the **5t** (0.2 g, 0.313 mmol) in dry DCM (5 mL) under a nitrogen atmosphere, was added slowly BCl_3 (0.183 g, 1.56 mmol, 1M solution in DCM) via a syringe at -78 ^oC, and the mixture was further stirred at this temperature. After 2 h the reaction was quenched with 1:1 MeOH-DCM (5 mL) and concentrated. Flash chromatography (30-50% ethyl acetate / hexane) afforded the diol **19** (0.050 g, 72 %) as a colourless syrup.

^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.8 Hz, 4H), 7.76 – 7.60 (m, 2H), 7.52 (t, *J* = 7.2 Hz, 4H), 6.22 (s, 1H), 5.33 (t, *J* = 9.6 Hz, 1H), 4.67 (d, *J* = 9.6 Hz, 1H), 4.59 – 4.49 (m, 2H), 4.17 (d, *J* = 7.6 Hz, 1H), 3.99 (s, 1H), 3.36 (s, 5H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.6, 185.5, 163.1, 162.6, 135.5, 135.2, 132.1, 131.9, 130.3, 130.2, 129.1, 129.0, 94.5 (C1), 72.3, 71.4, 71.0, 70.6, 62.8. HRMS (ESI-TOF) m/z: [M + H]+ Calcd $C_{23}H_{23}O_{10}$ 459.1286 found 459.1283.

20a. Methyl-3,6-di-*O*-oxobenzoyl-2-benzoyl-*α*-D-glucopyranoside.

Starting material was synthesized from literature[19]. Isolated as a syrup (143 mg, 76% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 2H), 8.07 – 8.04 (m, 2H), 7.80 – 7.77 (m, 2H), 7.71 – 7.61 (m, 2H), 7.52 (m, 5H), 7.14 (t, *J* = 8.0 Hz, 2H), 5.94 – 5.85 (m, 1H), 5.19 (d, *J* = 3.6 Hz, 1H, H1), 5.08 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.83 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.74 (dd, *J* = 12.0, 4.9 Hz, 1H), 4.14 (m, 1H), 3.96 (t, *J* = 9.6 Hz, 1H), 3.43 (s, 3H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 186.3, 185.9, 165.6, 163.78, 163.6, 135.1, 135.0, 133.7, 132.4, 131.9, 130.1, 130.1, 129.9, 129.1, 129.0, 128.8, 128.7, 97.0 (C1), 74.6, 71.6, 69.3, 68.9, 64.2, 55.7; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd $C_{30}H_{26}NaO_{11}$ 585.1367 found 585.1359.

20b. **Benzyl-2,3-di-*O*-oxobenzoyl-6-benzoyl-*β*-D-glucopyranoside.**

Starting material was synthesized from literature[32]. Isolated as a syrup (124 mg, 73% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.49 (m, 5H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.20 – 7.08 (m, 5H), 5.92 (t, *J* = 9.6 Hz, 1H), 5.31 (s, 1H), 5.06 (d, *J* = 9.2 Hz, 1H, H1), 4.73 (m, 3H), 4.56 (d, *J* =

12.4 Hz, 1H), 4.17 (d, *J* = 9.6 Hz, 1H), 3.93 (t, *J* = 9.2 Hz, 1H), 3.34 (s, 1H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 186.3, 185.9, 165.4, 163.8, 163.7, 136.6, 135.2, 135.1, 133.7, 132.4, 131.9, 130.2, 130.1, 130.0, 129.9, 129.9, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 95.1 (C1), 74.6, 71.4, 70.2, 69.6, 68.9, 64.0; HRMS (ESI-TOF) m/z: [M + NH_4]+ Calcd for $C_{36}H_{34}NO_{11}$ 656.2126 found 656.2113.

20c. Allyl-2,6-di-oxobenzoyl-3-benzoyl-*α*-D-galactopyranoside.

Starting material was synthesized from literature[24]. Isolated as a syrup (129 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.65 (m, 2H), 7.56 – 7.42 (m, 5H), 7.16 (t, *J* = 7.6 Hz, 2H), 5.94 – 5.78 (m, 2H), 5.63 (d, *J* = 10.8 Hz, 1H,), 5.36 (d, *J* = 2.4 Hz, 1H, H1), 5.30 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.73 (dd, *J* = 11.2, 7.6 Hz, 1H), 4.59 (dd, *J* = 11.6, 4.6 Hz, 1H), 4.46 (s, 1H), 4.40 (t, *J* = 6.0 Hz, 1H), 4.24 (dd, *J* = 13.2, 5.2 Hz, 1H), 4.08 (dd, *J* = 12.8, 6.0 Hz, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.7, 185.6, 165.3, 163.7, 163.3, 135.1, 135.0, 133.8, 133.0, 132.3, 132.0, 130.1, 129.9, 129.9, 129.1, 129.0, 128.8, 128.7, 118.5, 95.2 (C1), 70.9, 69.6, 68.9, 68.0, 67.7, 64.4; HRMS (ESI-TOF) m/z: [M + NH_4]+ Calcd for $C_{32}H_{32}NO_{11}$ 606.1970 found 606.1961.

20d. Phenyl-3,6-di-*O*-oxobenzoyl-2-*N*-(trichloroacetyl)-1-deoxy-1-thio-*α*-D-glucopyranoside.

Starting material was synthesized from literature[33]. Isolated as a syrup (114 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.63 (q, *J* = 7.6 Hz, 2H), 7.46 (m, 6H), 7.18 (m, 3H), 5.68 (t, *J* = 9.6 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H, H1), 4.83 (d, *J* = 12.0 Hz, 1H), 4.65 – 4.57 (m, 1H), 4.04 – 3.80 (m, 4H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 186.0, 185.7, 163.5, 163.4, 161.9, 135.5, 135.3, 133.2, 132.3, 131.8, 131.4, 130.3, 130.2, 129.3, 129.1, 129.1, 129.0, 128.6, 92.2, 85.8 (C1), 77.3, 77.2, 68.6, 64.1, 54.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{24}Cl_3NNaO_9S$ 702.0130 found 702.0126.

21a. Methyl-2,3,6-*O*-tribenzoyl-*α*-D-glucopyranoside.

Isolated as a white solid (95 mg, 56% yield),) mp 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 4H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.51 (m, 4H), 7.38 (q, *J* = 7.2 Hz, 4H), 5.85 (t, *J* = 9.6 Hz, 1H), 5.31 (dd, *J* = 10.0, 3.2 Hz, 1H), 5.19 (d, *J* = 3.2 Hz, 1H), 4.81 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.69 (dd, *J* = 12.0, 1.6 Hz, 1H), 4.22 – 4.13 (m, 1H), 3.94 (m, 1H), 3.54 (d, *J* = 4.8 Hz, 1H), 3.49 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 167.3, 166.9, 166.0, 133.4, 133.3, 129.9, 129.9, 129.8, 129.7, 129.3, 129.2, 128.5, 128.4, 128.4, 97.2 (C1), 73.9, 71.5, 70.1, 69.8, 63.6, 55.5.

21b. Methyl-2,4,6-*O*-tribenzoyl-*α*-D-glucopyranoside.

Isolated as a white solid (54 mg, 32% yield)) mp 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 7.99 (m, 6H), 7.67 – 7.54 (m, 3H), 7.46 (m, 6H), 5.41 (t, *J* = 9.6 Hz, 1H), 5.19 – 5.05 (m, 2H), 4.64 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.47 (dd, *J* = 12.0, 5.6 Hz, 2H), 4.39 – 4.27 (m, 1H), 3.48 (s, 3H), 2.71 (s, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 166.3, 166.3, 166.2, 133.6, 133.4, 133.1, 130.0, 129.7, 129.5, 129.2, 128.5, 128.5, 128.4, 97.2 (C1), 74.1, 72.3, 70.4, 67.5, 63.3, 55.6.

23. Methyl-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)(1→4)-3,6-tri-*O*-oxobenzoyl-2-*O*-benzoyl-*α*-D-glucoopyranoside.

Starting material was synthesized from literature[19]. Isolated as a syrup (116 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 4H), 7.83 – 7.78 (m, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.17 (t, *J* = 7.6 Hz, 2H), 6.02 (dd, *J* = 10.0, 8.8 Hz, 1H), 5.18 (dd, *J* = 12.8, 9.6 Hz, 2H), 5.04 – 4.96 (m, 2H), 4.94 – 4.85 (m, 2H), 4.80 (d, *J* = 8.0 Hz, 1H), 4.46 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.18 – 4.11 (m, 1H), 4.10 – 4.02 (m, 1H), 3.83 (m, 3H), 3.42 (s, 3H), 2.10 (s, 3H), 1.99 (d, *J* = 3.2 Hz, 6H), 1.87 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.8, 185.4, 170.7, 170.2, 169.5, 169.3, 165.6, 163.3, 162.1, 135.3, 135.0, 133.8, 132.2, 132.0,

130.1, 130.1, 130.0, 129.9, 129.1, 128.9, 128.7, 128.7, 100.6 (C1), 96.7 (C1), 77.2, 76.0, 73.1, 72.3, 72.0, 71.9, 71.8, 67.9, 67.9, 63.1, 61.6, 55.8, 20.7, 20.6, 20.6, 20.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{45}O_{20}$ 893.2499 found 893.2521.

24. Ethyl-2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside.

The Compound **5e** (0.1 g, 0.133 mmol) and EtOH (1.2 equiv) were dissolved in dry DCM (3 mL) at room temperature. Then TMSOTf (0.5 equiv) was added and the reaction mixture was stirred for the 4 h. After completion the reaction mixture was diluted with sodium bicarbonate solution, extracted with DCM several times and dried over sodium sulfate. After removal of the solvent, the crude product was subjected to flash chromatography (10-15% ethyl acetate / hexane) afforded compound **24** (0.066 g, 78 %) as a colourless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 18H), 7.19 (dd, *J* = 7.6, 2.8 Hz, 2H), 4.98 (t, *J* = 10.8 Hz, 2H), 4.84 (dd, *J* = 13.2, 11.2 Hz, 2H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.63 (t, *J* = 12.4 Hz, 2H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.44 (d, *J* = 8.0 Hz, 1H), 4.05 (m, 1H), 3.78 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.69 (m, 3H), 3.61 (t, *J* = 9.6 Hz, 1H), 3.50 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 138.7, 138.6, 138.3, 138.2, 128.3, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 103.5, 84.8, 82.4, 78.0, 75.7, 75.0, 74.9, 74.8, 73.5, 69.1, 65.60, 15.4. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{36}H_{41}O_6$ 569.2898 found 569.2893.

25. Propargyl-2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside.

The Compound **5e** (0.1 g, 0.133 mmol) and Propargyl alcohol (1.2 equiv) were dissolved in dry DCM (3 mL) at room temperature. Then TMSOTf (0.5 equiv) was added and the reaction mixture was stirred for the 4 h. After completion the reaction mixture was diluted with sodium bicarbonate solution, extracted with DCM several times and dried over sodium sulfate. After removal of the solvent, the crude product was subjected to flash chromatography (10-15% ethyl acetate / hexane) afforded compound **25** (0.070 g, 81 %) as a colourless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 18H), 7.17 (dd, *J* = 7.6, 2.8 Hz, 2H), 5.12 (d, *J* = 3.6 Hz, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 4.86 (t, *J* = 10.4 Hz, 2H), 4.77 (q, *J* = 12.0 Hz, 2H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.49 (d, *J* = 4.8 Hz, 1H), 4.31 (d, *J* = 2.4 Hz, 2H), 4.02 (t, *J* = 9.6 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.75 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.71 – 3.61 (m, 3H), 2.47 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR{1H} (101 MHz, $CDCl_3$) δ 138.9, 138.3, 138.1, 138.0, 128.4, 128.4, 128.4, 128.2, 128.0, 127.9, 127.9, 127.7, 127.7, 127.6, 95.3, 82.0, 79.5, 79.0, 77.6, 75.8, 75.1, 74.7, 73.6, 73.0, 70.8, 68.5, 54.4. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{37}H_{39}O_6$ 579.2741 found 579.2736.

26. Methyl-2,3-di-*O*-oxobenzoyl-*α*-D-glucopyranoside.

To a solution of the **5u** (1.0 g,) in DCM/MeOH (1:1, 20 mL), was added pTSA (0.183 g, 1.56 mmol), and the mixture was stirred at room temperature for 2 h, after completion of the reaction conformed by TLC, the reaction mixture was diluted with DCM and washed with saturated sodium bicarbonate solution. Organic layer was dried over Na2SO4and concentrated in vaccum, the crude product was subjected to flash chromatography (50 % ethyl acetate /hexane) affords the diol **26** (0.796g, 95 %) as a gummy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 4H), 7.61 (m, 2H), 7.45 (m, 4H), 5.83 (t, *J* = 9.6 Hz, 1H), 5.26 (d, *J* = 3.2 Hz, 1H, H1), 5.13 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.82 (s, 1H), 3.99 (m, 4H), 3.84 (d, *J* = 10.0 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.8, 185.4, 163.3, 163.1, 135.4, 135.2, 132.1, 131.8, 130.3, 130.0, 129.1, 96.4 (C1), 74.3, 72.8, 71.3, 68.4, 61.3, 55.5. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{23}H_{22}NaO_{10}$ 481.1105 found 481.1101.

27. Methyl-2,3-di-*O*-oxobenzoyl-4,6-di-*O*-benzoyl-*α*-D-glucopyranoside.

To a solution of diol **26** (0.2g, 0.436 mmol) in pyridine (2.0 mL), was added Benzoyl chloride (0.15, mL) and the mixture was stirred at room temperature for 10 h, the reaction mixture was diluted with EtOAc and washed with 1N HCl. Organic layer was dried over

$Na_2SO_4$and concentrated in vaccum, the crude product was subjected to flash chromatography (30 % ethyl acetate / hexane) affords compound **27** (0.115g, 83 %) as a gummy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 6H), 7.71 – 7.61 (m, 4H), 7.52 (m, 6H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 6.17 (t, *J* = 9.6 Hz, 1H), 5.67 (t, *J* = 9.6 Hz, 1H), 5.39 (dd, *J* = 10.0, 3.6 Hz, 1H), 5.34 (d, *J* = 3.6 Hz, 1H, H1), 4.65 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.50 (dd, *J* = 12.0, 5.2 Hz, 1H), 4.47 – 4.40 (m, 1H), 3.60 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.2, 185.2, 166.1, 165.0, 162.9, 162.9, 135.3, 135.0, 133.9, 133.3, 131.9, 131.6, 130.1, 130.2, 129.8, 129.7, 129.5, 129.1, 128.8, 128.7, 128.6, 128.5, 96.3 (C1), 72.2, 71.1, 69.3, 67.6, 62.7, 55.9. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{37}H_{31}O_{12}$ 667.1810 found 667.1806.

28. Methyl-2,3-di-*O*-oxobenzoyl-4,6-di-*O*-acetyl-*α*-D-glucopyranoside.

To a solution of diol **26** (0.2g, 0.436 mmol) in pyridine (2.0 mL), was added acetic anhydride (1.0, mL) and the mixture was further stirred at room temperature for 2 h, the reaction mixture was diluted with EtOAc and washed with 1N HCl. Organic layer was dried over Na2SO4and concentrated in vaccum, the crude product was subjected to flash chromatography (30% ethyl acetate in hexane) affords compound **28** (0.093g, 79 %) as a gummy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.93 – 7.89 (m, 2H), 7.70 – 7.59 (m, 2H), 7.49 (m, 4H), 5.93 (t, *J* = 10.0 Hz, 1H), 5.36 – 5.29 (m, 2H), 5.22 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.35 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.20 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.14 (m, 1H), 3.55 (s, 3H), 2.15 (s, 3H), 2.14 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 185.0, 170.6, 169.4, 163.1, 162.8, 135.3, 135.2, 132.1, 131.8, 130.0, 129.9, 129.1, 96.3 (C1), 72.4, 71.3, 68.1, 67.5, 61.7, 55.8, 20.7, 20.5. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{36}H_{37}O_8$ 597.2483 found 597.2478.

29. Methyl-6-*O*-oxobenzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside.

To a solution of **6t** (0.2 g, 0.534 mmol), Acid (0.096g, 0.640 mmol), DMAP (0.078g, 0.640 mmol) in dry DCM (10 mL) under a nitrogen atmosphere, was added DIC (0.101 µL, 0.640 mmol) via a syringe at 0°C, and the mixture was further stirred at this temperature. After 4 h the reaction was concentrated, the residue was dissolved in EtOAc and washed with 1N HCl. Organic layer was dried over $Na_2SO_4$and concentrated in vaccum, the crude product was subjected to flash chromatography (20 % ethyl acetate/hexane) affords the product **29** (0.240g, 89 %) as a gummy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.28 (m, 10H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 2H), 4.70 (m, 3H), 4.60 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.95 – 3.81 (m, 2H), 3.60 – 3.52 (m, 2H), 3.39 (s, 3H), 3.02 (s, 1H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 186.2, 163.8, 138.7, 138.0, 135.1, 132.3, 130.2, 128.9, 128.6, 128.6, 128.2, 128.1, 128.0, 127.9, 98.1 (C1), 81.3, 79.6, 75.5, 73.2, 70.03, 69.1, 64.8, 55.4. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{29}H_{31}O_8$ 507.2013 found 507.2017.

30. Methyl-6-O-oxobenzoyl-2,3-di-O-benzyl-4-O-(4-methoxybenzyl)- α-D-glucopyranoside.

To a solution of **29** (0.1g, 0.197 mmol), PMBOC(=NH)CCl3 (0.110g, 0.392 mmol) in dry DCM, was added Triflic acid (2 drops) at 0 oC. The reaction mixture was stirred at room temperature for 12 h. reaction mixture was diluted with DCM and washed with a saturated NaHCO3 solution, the organic layer was dried with MgSO4, concentrated under reduced pressure.The crude product was subjected to flash chromatography (15 % ethyl acetate in hexane) affords the product **30** (0.095g, 77 %) as a syrup

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.31 (m, 10H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.04 (d,

J = 10.8 Hz, 1H), 4.90 – 4.84 (m, 1H), 4.82 (s, 1H), 4.71 (s, 1H), 4.66 – 4.61 (m, 2H), 4.56 (d, *J* = 10.4 Hz, 1H), 4.51 – 4.47 (m, 1H), 4.06 (t, *J* = 9.2 Hz, 1H), 3.92 (m, 2H), 3.81 (s, 3H), 3.57 – 3.51 (m, 2H), 3.39 (s, 3H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.9, 163.6, 159.4, 138.6, 138.0, 135.0, 132.3, 130.1, 129.9, 129.8, 128.9, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 113.9, 98.1 (C1), 82.0, 79.7, 75.9, 74.9, 73.5, 68.6, 64.3, 55.4, 55.3, 29.7. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{37}H_{39}O_9$ 627.2589 found 627.2586.

31. Methyl-4,6-di-*O*-oxobenzoyl-2,3-di-*O*-oleoyl-*α*-D-glucopyranoside

To a solution of diol (0.2 g, 0.277 mmol), Acid (0.103g, 0.693 mmol), DMAP (0.084g, 0.693 mmol) in dry DCM (10 mL) under a nitrogen atmosphere, was added DIC (0.109 µL, 0.693 mmol) via a syringe, and the mixture was further stirred for 4h, the reaction was concentrated, and the residue was dissolved in EtOAc and washed with 1N HCl. Organic layer was dried over Na_2SO_4 and concentrated in vaccum, the crude product was subjected to flash chromatography (25 % ethyl acetate in hexane) affords the product **31** (0.085g, 91%) as a syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 2H), 7.54 (dd, *J* = 13.6, 7.2 Hz, 4H), 5.72 (t, *J* = 9.6 Hz, 1H), 5.40 – 5.31 (m, 5H), 5.04 (d, *J* = 3.6 Hz, 1H, H1), 4.95 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.67 – 4.58 (m, 2H), 4.32 – 4.25 (m, 1H), 3.43 (s, 3H), 2.38 – 2.26 (m, 4H), 2.00 (d, *J* = 14.0 Hz, 6H), 1.66 – 1.55 (m, 4H), 1.30 (d, *J* = 10.0 Hz, 42H), 0.90 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 185.5, 184.8, 172.9, 172.4, 163.3, 162.5, 135.2, 135.1, 132.3, 132.0, 130.2, 130.1, 130.0, 129.9, 129.7, 129.7, 129.1, 129.0, 96.9 (C1), 70.8, 70.5, 69.1, 66.7, 63.2, 55.7, 34.1, 34.0, 31.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 29.0, 27.2, 27.2, 24.9, 24.8, 22.7, 14.1. HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{59}H_{86}NaO_{12}$ 1009.6011 found 1009.6016.

32. Methyl-2,3-di-*O*-oleoyl-*α*-D-glucopyranoside

The compound **31** (0.1 g, 1 equiv) and oxone (0.162 g, 10 equiv) were dissolved in an equimolar concentration of Anhydrous MeOH and DCM at 65 ^{o}C for 8 h. After 8 h the reaction mixture was filtered and washed with 1N HCl. Organic layer was dried over Na_2SO_4 and concentrated in vaccum, the crude product was subjected to flash chromatography (40 % ethyl acetate in hexane) affords the product 32 (0.051g, 69 %) as a syrup.

Isolated as a syrup (51 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 – 5.27 (m, 5H), 4.92 (d, *J* = 3.6 Hz, 1H, H1), 4.84 (dd, *J* = 6.8, 3.6 Hz, 1H), 3.88 (m, 2H), 3.71 (m, 2H), 3.41 (s, 3H), 2.41 – 2.26 (m, 4H), 2.08 – 1.96 (m, 6H), 1.61 (s, 4H), 1.29 (d, *J* = 9.6 Hz, 42H), 0.90 (dd, *J* = 6.8, 4.0 Hz, 6H). ^{13}C NMR {1H} (101 MHz, $CDCl_3$) δ 174.7, 173.2, 130.0, 129.6, 96.9 (C1), 73.0, 71.3, 70.6, 69.7, 61.9, 55.3, 34.3, 34.1, 31.9, 29.8, 29.7, 29.6, 29.4, 29.3, 29.2, 29.2, 29.2, 29.1, 29.0, 27.2, 27.2, 25.6, 25.0, 24.9, 22.7, 14.1. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{43}H_{79}O_8$ 723.5769 found 723.5773.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website:

HPLC chromatogram of compound 16a and 16b, ^{1}H NMR (Precursor of 5r), ^{1}H and ^{13}C NMR spectra, and characterization of all compounds (PDF)

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REFERENCES

(1) (a) Brandley, B. K.; Schnaar, R. L. Cell-Surface Carbohydrates in Cell Recognition and Response. *J. Leuko. Biol*. **1986**, 40, 97-111. (b) Ohtsubo, K.; Marth, J. D. Glycosylation in cellular mechanisms of health and disease. *Cell,* **2006**, *126*, 855-867. (c) Varki, A. Biological roles of glycans. *Glycobiology,* **2017**, *27* , 3-49.

(2) (a) Varki A, Cummings RD, Esko JD, et al.,Essentials of Glycobiology. 3rd edition. Cold Spring Harbor (NY): Cold Spring Harbor Laboratory Press; **2015-2017**. (b) Briard, J. G.; Jiang, H.; Moremen, K. W.; Macauley, M. S.; Wu, P. Cell-based glycan arrays for probing glycan-glycan binding protein interactions. *Nat. Commun*. **2018**, *9*, 880. (c) Johannssen, T.; Lepenies, B. Glycan-Based Cell Targeting To Modulate Immune Responses. *Trends. Biotechnol.* **2017**, *35*, 334-346. (d) Murrey, H. E.; Hsieh-Wilson, L. C. The chemical neurobiology of carbohydrates. *Chem. Rev.* **2008**, *108*, 1708-1731; (e) Paulick, M. G.; Forstner, M. B.; Groves, J. T.; Bertozzi, C. R. A chemical approach to unraveling the biological function of the glycosylphosphatidylinositol anchor**.** *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 20332-20337.

(3) (a) Fernandez-Tejada, A.; Vadola, P. A.; Danishefsky, S. J. Chemical Synthesis of the β-Subunit of Human Luteinizing (hLH) and Chorionic Gonadotropin (hCG) Glycoprotein Hormones. *J. Am. Chem. Soc.* **2014**, *136*, 8450-8458. (b) Gamblin, D. P.; Scanlan, E. M.; Davis, B. G. Glycoprotein Synthesis: An Update. *Chem. Rev*. **2009**, *109*, 131-163. (c) Ito, Y.; Manabe, S., 1.09 - Polymer-Supported Oligosaccharide Synthesis A2 - Kamerling, Hans. *In Comprehensive Glycoscience*, Elsevier: Oxford, **2007**; 335-378. (d) Koeller, K. M.; Wong, C.-H. Complex carbohydrate synthesis tools for glycobiologists: enzyme-based approach and programmable one-pot strategies. *Glycobiology* **2000**, *10*, 1157-1169. (e) Payne, R. J.; Wong, C.-H. Advances in chemical ligation strategies for the synthesis of glycopeptides and glycoproteins. *Chem. Comm.* **2010**, *46*, 21-43. (f) Wang, H-Y.; Kato, A.; Kinami, K.; Li,

Y-X.; Fleet, G. W. J.; Yu,C-Y. Concise synthesis of calystegines $B_2$and B_3*via* intramolecular Nozaki–Hiyama–Kishi reaction. *Org. Biomol. Chem.*, **2016**, 14, 4885-4896.

(4) (a) Wong, C.-H.; Ye, X.-S.; Zhang, Z. Assembly of Oligosaccharide Libraries with a Designed Building Block and an Efficient Orthogonal Protection−Deprotection Strategy. *J. Am. Chem. Soc.* **1998**, *120*, 7137–7138. (b) Wunberg, T.; Kallus, C.; Opatz, T.; Henke, S.; Schmidt, W.; Kunz, H. Carbohydrates as Multifunctional Chiral Scaffolds in Combinatorial Synthesis. *Angew. Chem., Int. Ed.* **1998**, *37*, 2503–2505. (c) Zhu, T.; Boons, G.-J. A new set of orthogonal-protecting groups for oligosaccharide synthesis on a polymeric support. *Tetrahedron Asymmetry* **2000**, *11*, 199–205. (d) Arranz, E.; Boons, G.-J.The 2-(allyloxy) phenyl acetyl ester as a new relay protecting group for oligosaccharide synthesis. *Tetrahedron Lett.* **2001**, *42*, 6469–6471. (e) Tanaka, H.; Amaya, T.; Takahashi, T. Parallel synthesis of multi-branched oligosaccharides related to elicitor active pentasaccharide in rice cell based on orthogonal deprotection and glycosylation strategy. *Tetrahedron Lett.* **2003**, *44*, 3053–3057. (f) Wadzinski, T. J.; Steinauer, A.; Hie, L.; Pelletier, G.; Schepartz, A.; Miller, S. J. Rapid phenolic O-glycosylation of small molecules and complex unprotected peptides in aqueous solvent. *Nat. Chem*. **2018**, 10, 644–652. (g) Vidal, S. Protecting Groups: Strategies and application in Carbohydrate Chemistry, Wiley, **2018**.

(5) (a) Kocienski, P. J. Protecting Groups; Georg ThiemeVerlag: Stuttgart and New York, **1994**. (b) Schelhaas, M.; Waldmann, H. Protecting Group Strategies in Organic Synthesis. *Angew. Chem., Int.Ed.* **1996**, *35*, 2056–2083. (c) Wuts, P. G. M.; Greene, T. W. Greene's Protecting Groups in Organic Synthsis, John Wiley & Sons: New York, **2007**; (d) Huang, X.; Wang, Z., 1.10 - Strategies in Oligosaccharide Synthesis A2 - Kamerling, Hans. In *Comprehensive Glycoscience* Elsevier: Oxford, **2007**, 379-413; (e) Boltje, T. J.; Buskas, T.; Boons, G. J. Opportunities and challenges in synthetic oligosaccharide and glycoconjugate research. *Nat. Chem.* **2009**, *1*, 611-622.

(6) (a) Lipták, A.; Borbás, A.; Bajza, I., 1.06 - Protecting Group Manipulations in Carbohydrate Synthesis A2 - Kamerling, Hans. In *Comprehensive Glycoscience* Elsevier: Oxford **2007**; 203-259.

(7) (a) Tsai, Y. H.; Liu, X.; Seeberger, P. H. Chemical Biology of Glycosylphosphatidylinositol Anchors. *Angew. Chem., Int. Ed.* **2012**, *51* (46), 11438-11456. (b) Gannedi, V.; Ali, A.; Singh, P. P.; Vishwakarma, R. A. Intramolecular aglycon delivery for (1 → 2)-β-mannosylation: towards the synthesis of phospholipomannan of *Candida albicans*. *Tetrahedron Lett.* **2014,** *55*, 2945-2947.

(8) (a) Lee, B. Y.; Seeberger, P. H.; Varon Silva, D. Synthesis of glycosylphosphatidylinositol (GPI)-anchor glycolipids bearing unsaturated lipids. *Chemical Commun.* **2016,** *52*, 1586-1589. (b) Swarts, B. M.; Guo, Z. Synthesis of a Glycosylphosphatidylinositol Anchor Bearing Unsaturated Lipid Chains. *J. Am. Chem. Soc.* **2010**, *132*, 6648-6650. (c) Yashunsky, D. V.; Borodkin, V. S.; Ferguson, M. A. J.; Nikolaev, A. V. Recent progress in synthetic and biological studies of GPI anchors and GPI-anchored proteins. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 468-474.

(9) (a) Swarts, B. M.; Guo, Z. Chemical synthesis and functionalization of clickable glycosylphosphatidylinositol anchors. *Chem. Sci.* **2011**, *2*, 2342-2352. (b) Lloyd, D.; Bylsma, M.; Bright, D. K.; Chen, X.; Bennett, C. S. Mild Method for 2-Naphthylmethyl Ether Protecting Group Removal Using a Combination of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and β-Pinene. *J. Org. Chem*. **2017**, 82, 3926−3934.

(10) Eftekhari-Sis, B.; Zirak, M. Chemistry of α-Oxoesters: A Powerful Tool for the Synthesis of Heterocycles**.** *Chem. Rev.* **2015**, *115*, 151-264.

(11) Vishwakarma, R. A.; Vehring, S.; Mehta, A.; Sinha, A.; Pomorski, T.; Herrmann, A.; Menon, A. K. New fluorescent probes reveal that flippase-mediated flip-flop

of phosphatidylinositol across the endoplasmic reticulum membrane does *not* depend on the stereochemistry of the lipid. *Org . Biomol. Chem.* **2005**, *3*, 1275-1283.

(12) Wu, Q.; Liu, S.; Wang, F.; Li, Q.; Cheng, K.; Li, J.; Jiang, J. Amino Acid Salt Catalyzed Asymmetric Synthesis of 1,2-Diols with A Quaternary Carbon Center**.** *Synlett* **2015**, *26*, 2442-2446.

(13) Zhang, C.; Jiao, N. A Cu-catalyzed practical approach to α-ketoesters under air: an efficient aerobic oxidative dehydrogenative coupling of alcohols and α-carbonyl aldehydes. *Org. Chem. Front.* **2014**, *1*, 109-112.

14) Padala, A. K.; Saikam, V.; Ali, A.; Ahmed, Q. N. Efficient and practical approach to esters from acids/ 2-oxoacids/ 2-oxoaldehydes &/ 2-oxoesters.*Tetrahedron* **2015**, *71* (50), 9388-9395.

(15) (a) Kondo,Y. Partial tosylation of methyl α- and β-l-arabinopyranoside. *Carbohydr. Res.* **1987**,*162*, 159-165. (b) Zhang, z.; Wong, C-H. Regioselective benzoylation of sugars mediated by excessive Bu_2SnO: observation of temperature promoted migration. *Tetrahedron* 58 (**2002**) 6513–6519. (c) Williams, J. M.; Richardson, A. C. Selective acylation of pyranoside—I.: Benzoylation of methyl α-d-glycopyranosides of mannose, glucose and galactose. *Tetrahedron*. **1967**, 23, 1369-1378.

(16) Babouri, R.; Clarion, L.; Rolland, M.; Lee, A. V. d.; Kabouche, Z.; Volle, J. N.; Virieux, D.; Pirat, J. L. Synthesis of Oxaphosphinane-Based Pseudodisaccharides. *Eur. J. Org. Chem.* **2017**, *36,* 5357-5369.

(17) Agoston, K.; Agoston, A.; Dorgan, C. R.; Fugedi, P. A new method testing the orthogonality of different protecting groups. *Carbohydr. Res.* **2015**, 418, 98.

(18) Balmond, E. I.; Coe, D. M.; Galan, M. C.; McGarrigle, E. M. α-Selective organocatalytic synthesis of 2-deoxygalactosides. *Angew. Chem., Int. Ed.* **2012**, *5*1, 9152.

(19) Demizu, Y.; Kubo, Y.; Miyoshi, H.; Maki, T.; Matsumura, Y.; Moriyama, N.; Onomura, O. Regioselective Protection of Sugars Catalyzed by Dimethyltin Dichloride. *Org. Lett.* **2008**, *10*, 5075.

(20) Lee, J.; Cha, J. K. Selective cleavage of allyl ethers. *Tetrahedron Lett.* 1996, *37*, 3663.

(21) Wei, P.; Zhang, D.; Gao, Z.; Cai, W.; Xu, W.; Tang, L.; Zhao, G. Iodine Monochloride (ICl) as a Highly Efficient, Green Oxidant for the Oxidation of Alcohols to Corresponding Carbonyl Compounds. *Synth. Comm.,* **2015**, *45*, 1457.

(22) Horváth, A.; Ruttens, B.; Herdewijn, P. Stereoselective synthesis of (−)-ara-cyclohexenyl-adenine. *Tetrahedron Lett.* 2007, 48, 3621.

(23) Lin, F.; Peng, W.; Xu, W.; Han, X.; Yu, B. A facile preparation of uronates via selective oxidation with TEMPO/KBr/$Ca(OCl)_2$ under aqueous conditions. *Carbohydr. Res.* **2004**, *339*, 1219.

(24) Chassagne, P.; Raibaut, L.; Guerreiro, C.; Mulard, L. A. Concise synthesis of di- and trisaccharides related to the O-antigens from *Shigella flexneri*serotypes 6 and 6a, based on late stage mono-*O*-acetylation and/or site-selective oxidation. *Tetrahedron* **2013**, *69*, 10337.

(25) (a) Zhang, X.; Ren, B.; Ge, J.; Pei, Z.; Dong, H. A green and convenient method for regioselective mono and multiple benzoylation of diols and polyols. *Tetrahedron* **2016**, *72*, 1005. (b) Evtushenko, E. V. Regioselective Benzoylation of 4,6-*O*-Benzylidene Acetals of Glycopyranosides in the Presence of Transition Metals**.** *J. Carbohydr. Chem.* **2015**, *34*, 41.

(26) Liang, L.; Vincent, S. P. Synthesis of d-*glycero*-d-*manno*-heptose 1,7-bisphosphate (HBP) featuring a β-stereoselective bis-phosphorylation. *Tetrahedron Lett.* **2017**, *58*, 3631.

(27) Kalikanda, J.; Li, Z. Study of the stereoselectivity of 2-azido-2-deoxygalactosyl donors: relationship to the steric factors of glycosyl acceptors. *Carbohydr. Res.* **2011**, 346, 2380.

(28) Saikam, V.; Raghupathy, R.; Yadav, M.; Gannedi, V.; Singh, P. P.; Qazi, N. A.; Sawant, S. D.; Vishwakarma, R. A. Synthesis of new fluorescently labeled glycosylphosphatidylinositol (GPI) anchors *Tetrahedron Lett.* **2011**, *52*, 4277.

(29) (a) Crich, D.; Li, W.; Li, H. Direct Chemical Synthesis of the β-Mannans: Linear and Block Syntheses of the Alternating β-(1→3)-β-(1→4)-Mannan Common to *Rhodotorula glutinis*, *Rhodotorula mucilaginosa*, and *Leptospira biflexa*. *J. Am. Chem. Soc.* **2004**, *126*, 15081. (b) Crich, D.; Li, H.; Yao, Q.; Wink, D. J.; Sommer, R. D.; Rheingold, A. L. Direct Synthesis of β-Mannans. A Hexameric [→3)-β-d-Man-(1→4)-β-d-Man-(1]$_3$ Subunit of the Antigenic Polysaccharides from *Leptospira biflexa* and the Octameric (1→2)-Linked β-d-Mannan of the *Candida albicans* Phospholipomannan. X-ray Crystal Structure of a Protected Tetramer. *J. Am. Chem. Soc.* **2001**, *123*, 5826. (c) Crich, D. Mechanism of a Chemical Glycosylation Reaction. *Acc. Chem. Res.* **2010**, *43*, 1144.

(30) Wang, D.-d.; Li, X.-s.; Bao, Y.-z.; Liu, J.; Zhang, X.-k.; Yao, X.-s.; Sun, X.-L.; Tang, J.-S. Synthesis of MeON-neoglycosides of digoxigenin with 6-deoxy- and 2,6-dideoxy-d-glucose derivatives and their anticancer activity. *Bioorg. Med. Chem.* **2017**, *27*, 3359.

(31) Gathirwa, J. W.; Maki, T. Benzylation of hydroxy groups with tertiary amine as a base. *Tetrahedron* **2012**, *68*, 370.

(32) Doerschuk, A. P. Acyl Migrations in Partially Acylated, Polyhydroxylic Systems. *J. Am. Chem. Soc.* **1952**, *74*, 4202.

(33) Xia, J.; Hui, Y. A Convenient Method for Highly Selective Deprotection of Benzylidene Acetals from Sugars. *Synth. Comm.* **1996**, *26*, 881.

(34) Waschke, D.; Thimm, J.; Thiem, J. Highly Efficient Synthesis of Ketoheptoses. *Org. Lett.* **2011**, *13*, 3628.

(35) Jaipuri, F. A.; Pohl, N. L. Toward solution-phase automated iterative synthesis: fluorous-tag assisted solution-phase synthesis of linear and branched mannose oligomers. *Org. Biomol. Chem*., **2008**, 6, 2686–2691.

(36) Minuth, T.; Irmak, M.; Groschner, A.; Lehnert, T.; Boysen, M. M. K. Sweets for Catalysis – Facile Optimisation of Carbohydrate-Based Bis(oxazoline) Ligands. *Eur. J. Org. Chem*. **2009**, 997–1008.