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Journal Name

ARTICLE

Efficient one-pot per-*O*-acetylation–thioglycosidation of native sugars, 4,6-*O*-arylidenation and one-pot 4,6-*O*-benzylidenation–acetylation of *S*-/*O*-glycosides catalyzed by $Mg(OTf)_2$

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A sequential one-pot per-*O*-acetylation– *S*-/*O*-glycosidation of native mono and disaccharides under solvent free condition using 0.5 mole% of $Mg(OTf)_2$ as non hygroscopic, recyclable catalyst is reported. Regioselective 4,6-*O*-arylidenation of glycosides and thioglycosides with benzaldehyde or *p*-methoxybenzaldehyde dimethyl acetal is catalyzed by 10 mole% of $Mg(OTf)_2$ to produce the corresponding 4,6-*O*-arylidenated product in high yields. $Mg(OTf)_2$ can also mediate sequential one-pot benzylidenation–acetylation of mono and disaccharides based glycosides and thioglycosides in high yield.

Introduction

The central principle of the atom economy and green chemistry is the design of synthetic strategies that minimise waste by using stoichiometric reagent and catalytic promoters.[1a-d] Advancement of synthetic carbohydrate chemistry demands extensive functional group transformation by means of suitable protection and deprotection of hydroxy groups.[1e] In this context, per-*O*-acetylation of native sugars is the most commonly utilised functional group transformation as these readily made per-*O*-acetylated sugars can be easily activated by Lewis acid and transformed towards other glycosyl donors like glycosyl halides or thioglycosides.[2] The classical method for carrying out per-*O*-acetylation is via excess reagent like acetic anhydride or acetyl chloride in large excess of pyridine as base as well as solvent in spite of its well documented toxicity.[3] The poor nucleophilicity of hydroxy groups in carbohydrates sometimes necessitates addition of pyridine derivatives like 4-dimethylaminopyridine (DMAP) or 4-pyrrolidino pyridine as co catalyst to activate the acetylating agents or accelerate the reaction.[4] So far many reports have been made in this direction utilising acid or bases which include (i) bases like NaOAc,[5a] NaOH/TBAB,[5b] imidazole[5c] and DABCO;[5d] (ii) Lewis Acids such as $ZnCl_2$,[6a] $FeCl_3$,[6b] $BF_3.Et_2O$,[6c] $Cu(OTf)_2$,[6d] $Sc(OTf)_3$,[6e] $In(OTf)_3$,[6f] $Ce(OTf)_3$,[6g] $SnCl_4$,[6h] $LiClO_4$[6i] and $Fe_2(SO_4)_3$;[6j] (iii) protic acids such as H_2SO_4,[7a] H_3BO_3/H_2SO_4[7b] and *p*-TSA;[7c] (iv) heterogeneous catalysts like montmorillonite K-10,[8a] H-β-Zeolite,[8b] H_2SO_4-SiO_2,[8c] $HClO_4$-SiO_2,[8d] molecular sieves,[8e] Al_2O_3,[8f] sulphonic acid functionalised γ-Al_2O_3[8g] and sulfamic acid.[8h] Beside these few other catalysts like I_2,[9a,b] *N*-bromosuccinimide,[9c] $Cu(ClO_4)_2.6H_2O$[9d] and even ionic liquids[9e] and microwave condition[9f] were also used. A few among the above catalysts such as $Cu(OTf)_2$,[6d] $SnCl_4$,[6h] *p*-TSA,[7c] I_2,[9a,b] and $Cu(ClO_4)_2.6H_2O$[9d] have been employed previously in conjugation with $BF_3.Et_2O$ for the one-pot sequential per-*O*-acetylation – thioglycosidation reaction. In spite of their effectiveness on many instances these catalysts even suffer from many flaws like use of large excess of acetic anhydride, environmentally hazardous volatile organic solvents (VOSs), expensive catalysts, moisture intolerance, requirement of catalyst preparation or incompatibility with carbohydrate derivatives carrying acid sensitive protecting group. In some instances, isomerized product mixture of furanose and pyranose are obtained during acetylation of native sugars.[6j, 8i] Therefore, there is strong need to search an effective catalyst that is mild, non-toxic, and economically viable yet allows just stoichiometric amount of the reagent and avoids use of toxic VOSs. Moreover that can be employed for undertaking more than one steps in one-pot in order to develop more efficient and expeditious transformations.

After smooth preparation of *S*- and/or *O*-glycosides, 4,6-*O*-benzylidene protection is of immense importance in the synthesis of complex carbohydrates[2g,h] as these can be selectively transformed to the corresponding 6-deoxy sugars under oxidative condition.[10a-e] These benzylidene acetals can either be selectively transformed under reductive conditions[11a-c] to their corresponding 4-*O*-benzylated or 6-*O*-benzylated analogue leaving the alternate hydroxy group free to be used further as glycosyl acceptor during oligosaccharide synthesis or to produce the corresponding 4,6-diol.[11d-11f] In earlier days when benzaldehyde was employed as electrophile for 4,6-*O*-benzylidene protection, most of such transformations were catalysed by $ZnCl_2$,[12a] H_2SO_4[12b] or

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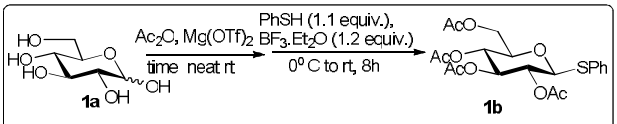
TsOH[12c] and later when benzaldehyde dimethylacetal was proved to be a better reagent, transacetalations were carried out with Lewis acids $[VO(OTf)_2]$[13a] or Brønsted acids like HBF_4,[13b] CSA[13c,d] and TfOH[13e] including silica supported reagents ($NaHSO_4$-SiO_2,[14a] H_2SO_4-SiO_2[14b] and $HClO_4$-SiO_2,[14c]) or other reagents like I_2[15a-c] or 2,4,6 trichloro-1,3,5-triazine.[15d] However some of these catalysts suffer from limitations too like those having short shelf life, or often being corrosive and expensive or tough to handle due to moisture sensitivity.

In continuation of our research on complex oligosaccharide synthesis[16] we needed to prepare a number of *S*- and *O*-glycosides and 4,6-*O*-benzylidenated carbohydrate derivatives and we sought to modify even our own developed method based on $FeCl_3$[16h] with a more efficient, non-hygroscopic and recyclable one. Recently $Mg(OTf)_2$ has been used as highly stable, non-hygroscopic and recyclable catalyst[17a] for many organic transformations like silylation of α-hydroxyphosphonates,[17b] tetrahydroquinolene synthesis,[17c] and 1,3-dipolar cycloaddition reaction.[17d] For time and cost effectiveness and also due to environmental reasons minimisation of overall isolated steps during a total target synthesis is advisable. Sometimes this is managed by undertaking two or more reactions sequentially in one-pot. In this context we report herein $Mg(OTf)_2$ as an inexpensive, recyclable, eco-friendly and multi-functional potent catalyst for the extensive functional group manipulations of carbohydrate derivatives: For one-pot per-*O*-acetylation–*S*-/-*O*-glycosidation of native sugars, for 4,6-*O*-arylidenation and also for one-pot 4,6-*O*-benzylidenation – acetylation of mono and disaccharide derivatives.

Result and discussion

For optimisation of reaction condition for one-pot acetylation – *S*-/*O*-glycosidation, D-glucose **1a** was initially allowed to react with a varied quantity of acetic anhydride (1.5 to 1.0 equivalent per hydroxy group) in the presence of catalytic amount of $Mg(OTf)_2$ (0.1 to 0.001 equivalent) at room temperature under neat condition for acetylation step; and this was followed by in situ addition of 1.1 equivalent of thiophenol and 1.2 equivalent of $BF_3.Et_2O$ at 0 °C for thiophenylation step. An exothermic reaction started immediately and a clear reaction mixture was obtained within few minutes resulting in a complete consumption of the starting material (checked by TLC). Proceeding through a number of such experiments 1.0 equivalent acetic anhydride per hydroxy group with 0.5 mol% (0.005 equivalent) of the catalyst at room temperature was found to be most effective for the per *O*-acetylation reaction in terms of time of per *O*-acetylation step (Table 1); then to this reaction mixture thiophenol followed by lowering of the temperature to 0 °C, BF_3. Et_2O was added and the reaction mixture was kept for 8 hours at room temperature to produce phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyanoside **1b.** The resulting thioglycoside was obtained as a single β anomer, due to neighbouring group participation by C-2 acetate.

Table 1 Optimisation of reaction condition of one-pot acetylation – thioglycosidation



Entry	Catalyst (mol%)	Ac_2O equiv.	Time (min)[a]	Yield[b] (%)
1	10	1.5 per OH	1 to 2	90
2	5	1.2 per OH	1 to 2	92
3	1	1.1 per OH	1 to 2	92
4	**0.5**	**1.0 per OH**	**3**	**95**
5	0.1	1.1 per OH	15	93
6	0.05	1.1 per OH	45	90

[a] Time corresponds to acetylation step
[b] Isolated yield over two steps

In order to extend the scope of this reaction a series of native mono and disaccharides were subjected to per-*O*-acetylation followed by one pot *S*-/*O*-glycosidation, and the results are summarised in Table 2. Per *O*-acetylation of glucose **1a** under this condition was completed at room temperature within 3 minutes (checked by TLC) and then sequential one-pot thioglycosidation separately with thiophenol, ethanethiol and thiocresol produced the corresponding thioglycosides **1b, 1c** and **1d** in 95%, 89% and 87% respective yields (entries 1, 2 and 3, Table 2). Scale up reaction using 5 g **1a** produced 91% of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyanoside **1b**; the yield is comparable with that of the pilot reaction (entry 1, Table 2). Similar sequential one-pot *O*-glycosidation using 4-methoxyphenol afforded the corresponding *O*-glycoside **1e** in 85% yield (entry 4, Table 2).

Reaction sequence akin to the previous one with D-galactose **2a** produced the corresponding *S*- and *O*-glycosides **2b, 2c** and **2d** in 94%, 84% and 86% yield, respectively (entries 5, 6 and 7, Table 2). The preparative scale reaction with 5 g of **2a** produced phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyanoside **2b** in 89% yield (entry 5, Table 2). Per *O*-acetylation of D-mannose **3a** underwent smoothly at room temperature within 3 minutes (checked by TLC) and then its sequential one-pot thioglycosidation separately using thiophenol and ethanethiol generated the corresponding α-thioglycosides in 93% and 91% yields, respectively (entries 8 and 9, Table 2). Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyanoside **3b** was prepared in 87% yield starting from 5 g of D-mannose (entry 8, Table 2).

After successful per-*O*-acetylation followed by in situ stereoselective *S*- aryl/alkyl or *O*-aryl glycoside preparation of native hexoses we turned our attention to similar reactions of commonly used pentose sugars. Reaction of D-xylose **4a** with 3 equivalent of Ac_2O, 0.5 mole% $Mg(OTf)_2$ followed by in situ addition of thiophenol and $BF_3.Et_2O$ produced the corresponding phenyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside **4b** in 86% yield (entry 10, Table 2). L-Rhamnose **5a** after robust per-*O*-acetylation, in reaction separately with thiophenol and 4-methoxyphenol produced the corresponding *S*- and *O*-glycosides **5b** and **5c** in 84% and 87% respective yields (entries 11 and 12, Table 2). The efficiency of this protocol was

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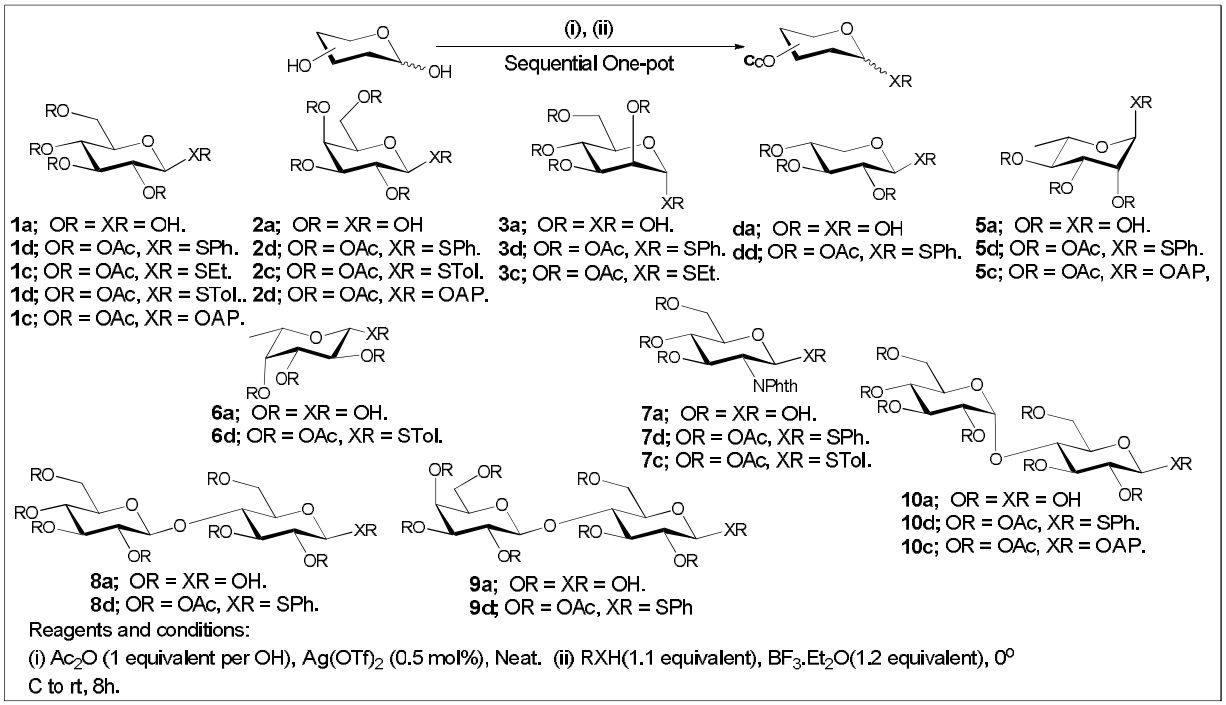

Scheme 1 Per-*O*-acetylation and their one-pot conversion to *S*-aryl/alkyl or *O*-aryl glycoside of native sugars

Table 2 Sequential one-pot acetylation-*S*-or-*O*-glycosidation of native sugars

Entry	Product	Time (min)[a]	temperature[a]	yield (%)[b]	Entry	Product	Time (min)[a]	temperature[a]	yield (%)[b]
1	**1b**	3	rt	95, 91[c]	11	**5b**	3	rt	84, 80[c]
2	**1c**	3	rt	89	12	**5c**	3	rt	87
3	**1d**	3	rt	87	13	**6b**	3	rt	86
4	**1e**	3	rt	85	14	**7b**	15	80 °C	78
5	**4b**	3	rt	94, 89[c]	15	**7c**	15	80 °C	73
6	**4c**	3	rt	84	16	**8b**	5	80 °C	77
7	**4d**	3	rt	86	17	**9b**	5	80 °C	85, 83[b]
8	**3b**	3	rt	93, 87[c]	18	**10b**	5	80 °C	91, 87[b]
9	**3c**	3	rt	91	19	**10c**	5	80 °C	83
10	**4b**	3	rt	86					

[a] Time and temperature corresponds to per-*O*-acetylation step. [b] Isolated yield over two steps [c] Reaction was carried out in 5 g scale.
[b] Reaction was carried out in 2 g scale.

supported by preparative scale reaction with 5 g of **5a** which produced phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyanoside **5b** in 80% yield, comparable with the pilot reaction (entry 11, Table 2). p-Tolyl 2,3,4-tri-O-acetyl-1-thio-β-L-fucopyranoside **6b** was prepared from L-fucose **6a** via sequential one-pot per-O-acetylation–thioglycosidation in 86% overall yield (entry 13, Table 2). The reaction with 2-deoxy-2-phthalimidoglucopyranoside **7a** was carried out at 80 °C for 15 minutes, and then sequential in situ thioglycosidation separately with thiophenol and thiocresol produced the corresponding β-D-thioglycosides **7b** and **7c** in 78% and 73% respective yields (entries 14 and 15, Table 2).

This per *O*-acetylation followed by in situ *S*- or *O*-glycoside preparation was also successful for the disaccharides like cellobiose **8a**, lactose **9a** and maltose **10a**. The per-*O*-acetylation for these native disaccharides were performed at 80 °C for 5 minutes and after full consumption of free sugar (checked by TLC); sequential one-pot thioglycosidation then produced the corresponding phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside **8b** in 77% yield (entry 16, Table 2). Similarly lactose produced the corresponding phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-galactopyranoside **9b** in 85% overall yield, and its preparative scale reaction based on 2 g of **9a** produced **9b** in 83% overall yield (entry 17, Table 2). In case of maltose the corresponding *S*-/ *O*-glycosides **10b** and **10c** were obtained in 91% and 83% overall yields, respectively (entries 18 and 19, Table 2). Preparative scale reaction with 2 g of native maltose produced phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-

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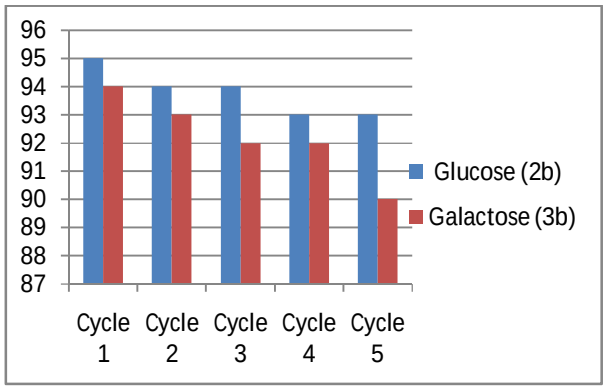
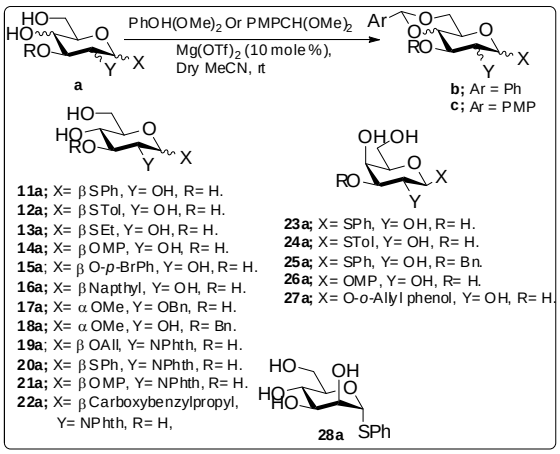


Figure 1 Recyclability of catalyst

tri-*O*-acetyl-1-thio-α-D-glucopyranoside **10b** in 87% overall yield (entry 18, Table 2). All these products were characterized by melting point (mp) and spectral analysis; the data corresponded well with the literature values.

After completion of sequential one-pot per-*O*-acetylation – thioglycosidation the reaction mixture was poured into water. The aqueous phase was evaporated under reduced pressure and the Mg(II) salt was recovered as a white solid and reused after drying overnight over P_2O_5. This recycle protocol was repeated five times, and the percentage of the catalyst recovery was always more than 90% while the yields of the phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside **2b** and phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside **3b** were always more than 93% and 90%, respectively (Figure 1).

After efficient sequential one-pot per-*O*-acetylation-*S*-/*O*-glycosidation of native mono and disaccharides we turned our attention towards employment of $Mg(OTf)_2$ for preparation of 4,6-*O*-arylidinated carbohydrate derivatives. At the outset, phenyl 1-thio-β-D-glucopyranoside **11a** was chosen as the substrate for optimization of reaction condition. **11a** was treated with benzaldehyde dimethylacetal in the presence of $Mg(OTf)_2$ using CH_3CN as solvent (Table 3). After several trial experiments optimum reaction condition was established as **11a** (1.0 equivalent) and benzaldehyde dimethylacetal (1.1 equivalent) in the presence of $Mg(OTf)_2$ (10 mol%) in dry



Scheme 2 4,6-*O*-arylidenation of monosaccharides

CH_3CN at ambient temperature, which produced the corresponding 4,6-*O*-benzylidene acetal **11b** in 87% yield. The reaction retains its productivity even after scale up based on 2 g of substrate. (entry 1, Table 3).

Under similar reaction condition, other phenyl thioglycosides of 2-NPhth-β-D-Glc, β-D-Gal and α-D-Man furnished the corresponding 4,6-*O*-benzylidene derivatives (**20b**, **23b, 25b** and **28b**) in 82%, 88% (for scale up 82%), 84% (for scale up 82%) and 68% respective yields (entries 11, 14, 16 and 19 respectively, Table 3). Efficient 4,6-*O*-benzylidenation was also possible for *p*-tolyl 1-thio-β-D-glycopyranosides **12a** and **24a** which produced **12b** and **24b** (entries 2 and 15, Table 3) and for ethyl 1-thio-β-D-glucopyranoside **13a** that afforded **13b** (entry 3, Table 3), in high yields. The efficacy of the present process was further established under scale-up condition for the preparation of **12b, 13b** and **24b** using 2 g starting material (77%, 79% and 80% yields, respectively; entries 2, 3 and 15, Table 3).

Among other substrates while methyl α-D-glucopyranoside derivatives **17a** and **18a** generated the corresponding 4,6-*O*-benzylidene glucopyranosides (**17b** and **18b**) in 83% and 85% respective yields (entries 8 and 9, Table 3), *p*-methoxyphenyl, *p*-bromophenyl and 2-napthyl β-D-glucopyranosides furnished

Table 3 4,6-*O*-arylidination of monosaccharides

Entry	Product	Time(h)	yield (%)[a]	Entry	Product	Time(h)	yield (%)[a]
1	**11b**	3	87, 82[b]	11	**20b**	2.5	82
2	**12b**	3	80, 77[b]	12	**21b**	3	85, 81[b]
3	**13b**	3	82, 79[b]	13	**22b**	2	87
4	**11c**	3	78	14	**23b**	3	88, 82[b]
5	**14b**	3	82	15	**24b**	3	86, 80[b]
6	**15b**	2.5	81	16	**25b**	2.5	84, 82[b]
7	**16b**	3	83	17	**26b**	3.5	77
8	**17b**	3	83	18	**27b**	3.5	76
9	**18b**	3	85	19	**28b**	3	68
10	**19b**	2	88	[a] Isolated yield [b] Reaction was carried out in 2 g scale			

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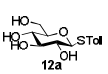
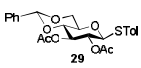
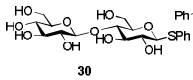
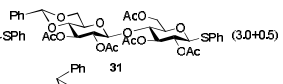
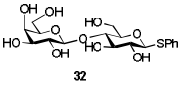
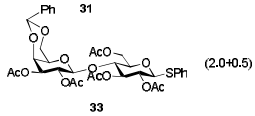
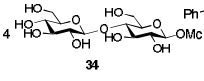
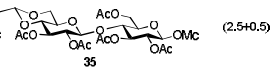
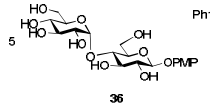
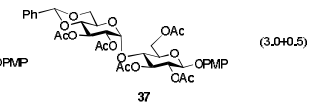
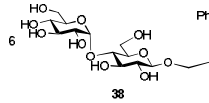
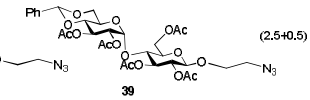
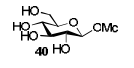
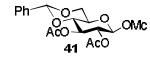
the corresponding desired products (**14b, 15b** and **16b**) in high yields (82%, 81% and 83%, respectively, entries 5, 6 and 7, Table 3). Similarly preparation of 4,6-*O*-benzylidene of allyl, *p*-methoxyphenyl and 3-(*N*-benzoyloxycarbonyl)propyl 2-deoxy-2-phthalimido glucosides was also found to be very efficient, and the desired derivatives **19b, 21b** and **22b** were obtained in 88%, 85% (81% for scale-up condition) and 87% respective yields (entries 10, 12 and 13, Table 3). Under similar condition *p*-methoxyphenyl and *o*-allylphenyl β-D-galactopyranosides **26a** and **27a** were converted to their corresponding 4,6-*O*-benzylidene products **26b** and **27b** in high yields (77% and 76%, respectively, entries 16 and 17, Table 3). The present arylidenation protocol was further applied for the synthesis of phenyl 4,6-*O*-(4-methoxybenzylidene)-1-thio-β-D-glucopyranoside **11c** in 78% yield (entry 4, Table 3) using *p*-methoxybenzaldehyde dimethylacetal as the electrophile.

For further elaboration of the efficacy of $Mg(OTf)_2$ towards synthesis of some glycosyl acceptors and thioglycoside donors we set out for an one-pot benzylidenation-acetylation of some *S*-/*O*-glycosides based on mono and disaccharides. Using $Mg(OTf)_2$, preparation of 4,6-*O*-benzylidene acetal followed by one-pot acetylation of 2- and 3- hydroxy group of *p*-tolyl 1-thio-β-D-glucopyranoside **12a** produced *p*-tolyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside **29** in 77% overall yield at ambient temperature (entry 1, Table 4). 4,6-*O*-Benzylidenation followed by one pot acetylation of β-D-glucopranoside **40** produced methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopranoside **41** in 77% overall yield (entry 7, Table 4).

Table 4 Benzylidenation acetylation of carbohydrates

Entry	Starting material	Product	Time (x+y)(h)	Yield[a] (%)
1	 12a	 29	0.5+0.5	77%
2	 30	 31	(3.0+0.5)	73%
3	 32	 33	(2.0+0.5)	84%
4	 34	 35	(2.5+0.5)	78%
5	 36	 37	(3.0+0.5)	79%
6	 38	 39	(2.5+0.5)	79%
7	 40	 41	(0.5+0.5)	77%

[a] Isolated yield over two steps

Lactose, maltose and cellobiose are common disaccharide units of many biologically important polysaccharides and glycoconjugates in which chain elongation of these units occur via their C-4′ or C-6′ hydroxy group.[18] With this end in view *S*- and *O*-glycosides of cellobiose, lactose and maltose were next 4′,6′-*O*-benzylidenated followed by acetylation in one-pot reaction. High combined yields (over two steps) of the final products (**31**, **33**, **35**, **37** and **39** in 73%, 84%, 78%, 79%, and 79% respective yields, entries 2 to 6, Table 4) indicate that the yields of the individual steps are quite high.

Conclusions

In summary, we have demonstrated $Mg(OTf)_2$ as a mild, non-hygroscopic, recyclable and inexpensive bench-top catalyst for robust and convenient one-pot per-*O*-acetylation – *S*-/*O*-glycosidation of native mono and disaccharides. The catalyst retains its efficacy even after several cycles of reactions. Similarly the $Mg(OTf)_2$ catalyzed selective 4,6-*O*-arylidenation of monosaccharides and disaccharides was high yielding. These reactions are equally applicable under scale-up condition also. Moreover $Mg(OTf)_2$ is also able to mediate one-pot 4,6-*O*-benzylidenation-acetylation of various mono and disaccharide based *S*- / *O*-glycosides in high yields. Unlike many of the reported procedures glycosides or thioglycosides are not anomerized.

Experimental

Column chromatography was performed employing silica gel 60-120 (60-120 mesh). Thin-layer chromatography (analytical and preparative) was performed using Merck silica gel plates (60-F254) to monitor the reactions and visualized under UV (254 nm) and/or by charring with 5% ethanolic solution of sulfuric acid. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 (300 MHz), a Bruker DPX-400 (400 MHz), a Bruker DPX-500 (500 MHz). Optical rotations were measured using Jasco P-1020 digital polarimeter.

General experimental procedure for sequential one-pot per-*O*-acetylation–*S*/*O*-glycosidation of native sugars

To a suspension of sugar (500 mg scale) and stoichiometric acetic anhydride (1.0 equivalent per -OH of sugar) was added $Mg(OTf)_2$ (0.5 mole % of sugar), and the reaction mixture was allowed to stir at ambient temperature (for disaccharides the same was carried out at 80 ^oC) for appropriate time as mentioned in Table 1. When the reaction was completed (checked by TLC), reaction mixture was cooled in ice bath, and to this thiol/thiophenol/phenol (1.1 equivalent) followed by $BF_3.Et_2O$ (1.2 equivalent) were added, and the reaction mixture was kept on stirring for overnight (8 hours). When TLC showed complete conversion of starting material, the reaction mixture was diluted with ethyl acetate, and the mixture was washed subsequently with cold 5% NaOH solution followed by brine solution. The organic layer was dried over anhydrous

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Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was passed through a short pad of silica to give pure *S*- or *O*-glycosides.

Compound characterization data

Typical procedure for phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (1b)[19]

To a suspension of D-glucose **1a** (500 mg, 2.8 mmol), and acetic anhydride (5 equivalent, 14.0 mmol, 143 mg), was added $Mg(OTf)_2$ (0.005 equivalent, 0.014 mmol, 4.5 mg), and the reaction mixture was allowed to stir at ambient temperature for 3 minutes. After the reaction was completed (checked by TLC), the mixture was cooled in ice bath and to this thiophenol (1.1 equivalent, 3.08 mmol, 0.4 ml) followed by $BF_3.Et_2O$ (1.2 equivalent, 3.36 mmol, 0.44 ml) were added, and the reaction mixture was kept on stirring for overnight for completion (8 hours). The reaction mixture was then worked up as described under the general procedure. The crude product was passed through a short pad of silica to give pure product as white solid following elution of the column with 25% EA/PE; Yield 1.16 g, 95% (scale up yield 11.1 g, 91% starting with **1a**, 5 g, 27.8 mmol).; mp (EA/PE) 122 ^oC, $[\alpha]^{25}_D$ -102.6 (*c* 1.00, $CHCl_3$), lit[19] mp 124 °C and $[\alpha]^{23}_D$ -101.5 (*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.98 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 3.74 (m, 1H, H_5), 4.15-4.21 (m, 2H, H_6, H_6), 4.70 (d, *J* = 9.9 Hz, 1H, H_1), 4.94-5.07 (m, 2H, H_2, H_3), 5.22 (apparent t, *J* = 9.1, 9.2 Hz, 1H, H_4), 7.32-7.49 (m, 5H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.6 (CH_3CO), 20.7 (CH_3CO), 62.1, 68.2, 69.9, 73.9, 75.7, 85.6 (C_1), 128.4, 128.9, 131.6, 133.1, 169.2 (*C*=O), 169.3 (*C*=O), 170.1 (*C*=O), 170.5 (*C*=O).

Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (1c)[20]

Pure product **1b** was isolated as white solid following elution of the column with 25% EA/PE.; Yield 0.97 g, 89% (starting from **1a**, 500 mg, 2.8 mmol).; mp (EA/PE) 82-84 ^oC, $[\alpha]^{25}_D$ -26.7 (*c* 1.3, $CHCl_3$) lit[20] mp 84-86 °C and $[\alpha]^{23}_D$ -27.3 (*c* 2.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.22-1.27 (m, 3H, CH_3), 1.98 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.64-2.75 (m, 2H, CH_2), 3.69 (m, 1H, H_5), 4.09-4.25 (m, 2H, H_6, H_6), 4.47 (d, *J* = 9.9 Hz, 1H, H_1), 4.97-5.09 (m, 2H, H_2, H_3), 5.19 (t, 1H, *J* = 9.3 Hz, H_4).

***p*-Tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (1d)[21]**

Pure product was isolated as white solid following elution of the column with 20% EA/PE.; Yield 1.09 g, 87% (starting from **1a**, 500 mg, 2.8 mmol).; mp (EA/PE) 114 ^oC, $[\alpha]^{25}_D$ -116.8 (*c* 1.00, $CHCl_3$), lit[21] mp 116 °C and $[\alpha]^{23}_D$ -114.3(*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.98 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.35 (s, 3H, CH_3), 3.70 (m, 1H, H_5), 4.19-4.20 (m, 2H, H_6, H_6), 4.62 (d, *J* = 10.0 Hz, 1H, H_1), 4.92 (t, *J* = 9.9 Hz, 1H, H_2), 5.01 (t, *J* = 9.8 Hz, 1H, H_3), 5.20 (t, *J* = 9.3 Hz, 1H, H_4), 7.01-7.14 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.37-7.39 (d, *J* = 7.9 Hz, 2H, Ar*H*).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (1e)[22]**

Pure product was isolated as white solid following elution of the column with 33% EA/PE.; Yield 1.07 g, 85% (starting from **1a**, 500 mg, 2.8 mmol).; mp 104-105 °C, $[\alpha]^{25}_D$ -9.3 (*c* 1.00, $CHCl_3$), lit[22] mp 106-107 ^0C and $[\alpha]^{25}_D$ -8.4(*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.08 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.13 (s, 3H, $COCH_3$), 3.81 (bs, 4H, OCH_3, H_5), 4.21 (d, *J* = 10.4 Hz, 1H, H_6), 4.34 (dd, *J* = 5.0, 12.2 Hz, 1H, H_6), 5.00 (d, *J* = 7.2 Hz, 1H, H_1), 5.21-5.33 (m, 3H, H_2, H_3, H_4), 6.84-6.88 (d, *J* = 8.9 Hz, 2H, Ar*H*), 6.98-7.01 (d, *J* = 8.9 Hz, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.60(CH_3CO), 20.62 (CH_3CO), 20.66 (CH_3CO), 20.7(CH_3CO), 55.6 (OCH_3), 61.9, 68.3, 71.2, 71.9, 72.7, 100.3 (C_1), 114.5, 118.7, 150.9, 155.8, 169.3 (*C*=O), 169.4 (*C*=O), 170.3 (*C*=O), 170.6 (*C*=O).

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (2b)[23]

Pure product was isolated as white solid following elution of the column with 30% EA/PE.; Yield 1.14 g, 94% (starting from **2a**, 500 mg, 2.8 mmol), scale up yield 10.8 g, 89% (starting with **2a**, 5 g, 27.8 mmol).; mp (EA/PE) 80-82 ^oC, $[\alpha]^{25}_D$ -82.9 (*c* 1.05, $CHCl_3$), lit[23] mp 81 °C and $[\alpha]^{25}_D$ -84 (*c* 1.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.97 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 3.94 (apparent t, *J* = 6.3, 6.4 Hz, 1H, H_5), 4.08-4.22 (m, 2H, H_6, H_6'), 4.71 (d, *J* = 9.9 Hz, 1H, H_1), 5.04 (dd, *J* = 3.2, 9.9 Hz, 1H, H_3), 5.24 (t, *J* = 9.9 Hz, 1H, H_2), 5.41 (d, *J* = 2.5 Hz, 1H, H_4), 7.31-7.51 (m, 5H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.5 (CH_3CO), 20.60 (CH_3CO), 2.63 (CH_3CO), 20.8 (CH_3CO), 61.6, 67.2, 71.9, 74.4, 76.7, 86.5 (C_1), 128.1, 128.9, 132.4, 132.5, 169.4 (*C*=O), 169.9 (*C*=O), 170.1 (*C*=O), 170.3 (*C*=O).

***p*-Tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (2c)[21]**

Pure product was isolated as white solid following elution of the column with 30% EA/PE.; Yield 1.05 g, 84% (starting from **2a**, 500 mg, 2.8 mmol); mp (EA/PE) 110-112 ^oC, $[\alpha]^{25}_D$ -125.5 (*c* 1.05, $CHCl_3$). Lit[21] mp 112 °C and $[\alpha]^{22}_D$ -127.0 (*c* 1.05, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.97 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.35 (s, 3H, CH_3), 3.92 (bt, *J* = 6.5 Hz, 1H, H_5), 4.12-4.19 (m, 2H, H_6, H_6), 4.65 (d, *J* = 9.9 Hz, 1H, H_1), 5.04 (dd, *J* = 3.2, 9.9 Hz, 1H, H_3), 5.22 (t, *J* = 9.9 Hz, 1H, H_2), 5.41 (d, *J* = 2.7 Hz, 1H, H_4), 7.12-7.14 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.40-7.43 (d, *J* = 8.0 Hz, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.58 (CH_3CO), 20.60 (CH_3CO), 20.63 (CH_3CO), 20.8 (CH_3CO), 21.1 (CH_3) 61.6, 67.2, 67.3, 72.0, 74.4, 86.9 (C_1), 128.6, 129.6, 133.1, 138.4, 169.4 (*C*=O), 170.0 (*C*=O), 170.2 (*C*=O), 170.3 (*C*=O).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (2d)[22]**

Pure product was isolated as white solid following elution of the column with 33% EA/PE.; Yield 1.08 g, 86% (starting from **2a**, 500 mg, 2.8 mmol).; mp 112-114 °C, $[\alpha]^{25}_D$ +3.5 (*c* 1.00, $CHCl_3$), lit[22] 109-110 °C and $[\alpha]^{25}_D$ +3.2 (*c* 0.9, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.99 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.17 (s, 3H, $COCH_3$), 3.76 (s, 3H, OCH_3), 4.00 (apparent t, *J* = 6.4, 6.6 Hz, 1H, H_5), 4.11-4.25 (m, 2H, H_6, H_6), 4.91 (d, *J* = 7.9 Hz, 1H, H_1), 5.07 (dd, *J* = 3.2, 10.5 Hz, 1H, H_3), 5.42-5.47 (m, 2H, H_2, H_4), 6.79-6.82 (d, *J* = 8.9 Hz, 2H, Ar*H*), 6.92-6.96 (d, *J* = 8.9 Hz, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.58 (CH_3CO), 20.65 (CH_3CO), 20.7 (CH_3CO), 55.6 (OCH_3), 61.3, 66.9, 68.8, 70.8, 100.8 (C_1), 114.5, 118.6, 151.0, 155.7, 169.4 (*C*=O), 170.1 (*C*=O), 170.27 (*C*=O), 170.3 (*C*=O).

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (3b)[6c]

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Pure product was isolated as white solid following elution of the column with 22.5% EA/PE.; Yield 1.13 g, 93% (starting from **3a**, 500 mg, 2.8 mmol), scale up yield 10.6 g, 87% (starting from **3a**, 5 g, 27.8 mmol).; mp (EA/PE) 84-86 ^{o}C, $[\alpha]^{25}_{D}$+77.1 (*c* 1.2, $CHCl_3$), lit[6c] mp 87 °C (Et_2O/PE) and $[\alpha]^{22}_{D}$ +74.4 (*c* 1.5, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.02 (s, 3H, COC*H*$_3$), 2.05 (s, 3H, COC*H*$_3$), 2.07 (s, 3H, COC*H*$_3$), 2.15 (s, 3H, COC*H*$_3$), 4.10 (dd, *J* = 2.0, 12.2 Hz, 1H, H_6), 4.30 (dd, *J* = 5.9, 12.2 Hz, 1H, H_6), 4.54 (m, 1H, H_5), 5.32-5.34 (m, 2H, H_3, H_4), 5.49 (m, 2H, H_1, H_2), 7.29-7.50 (m, 5H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.6 (*C*H$_3$CO), 20.7 (*C*H$_3$CO), 20.8 (*C*H$_3$CO), 62.5, 66.4, 69.4, 69.5, 70.9, 85.7 (C_1), 128.1, 129.2, 132.1, 132.6, 169.7 (*C*=O), 169.8 (*C*=O), 169.9 (*C*=O), 170.5 (*C*=O).

Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (3c)[24]

Pure product was isolated as white solid following elution of the column with 22.5% EA/PE.; Yield 0.99 g, 91% (starting from **3a**, 500 mg, 2.8 mmol).; mp (EA/PE) 160-162 ^{o}C, $[\alpha]^{25}_{D}$ -64.8 (*c* 1.00, $CHCl_3$), lit[24] mp 162-164 °C and $[\alpha]^{23}_{D}$ -64.3 (*c* 0.90, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.25 (bs, 3H, C*H*$_3$), 1.92 (s, 3H, COC*H*$_3$), 1.99 (s, 3H, COC*H*$_3$), 2.02 (s, 3H, COC*H*$_3$), 2.09 (s, 3H, COC*H*$_3$), 2.59 (bs, 2H, C*H*$_2$), 4.04 (bs, 1H), 4.32 (bs, 2H), 5.22 (bs, 4H).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 14.7, 20.5 (*C*H$_3$CO), 20.6 (*C*H$_3$CO), 20.8 (*C*H$_3$CO), 25.3, 62.4, 66.3, 68.8, 69.4, 71.1, 82.2 (C_1), 169.6 (*C*=O), 169.7 (*C*=O), 169.8 (*C*=O), 170.4 (*C*=O).

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside (4b)[25]

Pure product was isolated as white solid following elution of the column with 20% EA/PE.; Yield 1.06 g, 86% (starting from **4a**, 500 mg, 3.3 mmol).; mp (EA/PE) 78-80 ^{o}C, $[\alpha]^{25}_{D}$-56.8 (*c* 1.00, $CHCl_3$), lit[25] mp 74-76 °C and $[\alpha]^{23}_{D}$ -55.3 (*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.04 (s, 3H, COC*H*$_3$), 2.05 (s, 3H, COC*H*$_3$), 2.09 (s, 3H, COC*H*$_3$), 3.43 (t, *J* = 11.5 Hz, 1H, H_{5a}), 4.27 (dd, *J* = 4.8, 11.6 Hz, 1H, H_{5e}), 4.79 (d, *J* = 8.3 Hz, 1H, H_1), 4.88-4.96 (m, 2H, H_3, H_4), 5.18 (apparent t, *J* = 7.9, 8.1 Hz, 1H, H_2) 7.31-7.32(m, 3H, Ar*H*), 7.46-7.48 (m, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.7 (*C*H$_3$CO), 20.8 (*C*H$_3$CO), 65.2, 69.8, 72.0, 86.2 (C_1), 128.2, 129.0, 132.2, 132.7, 169.3 (*C*=O), 169.7 (*C*=O), 169.9 (*C*=O).

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (5b)[26]

Pure product was isolated as white solid following elution of the column with 30% EA/PE.; Yield 0.97 g, 84% (starting from **5a**, 500 mg, 3.05 mmol), scale up yield 9.30 g, 80% (starting from **5a**, 5 g, 30.5 mmol).; mp (EA/PE) 120-122 ^{o}C, $[\alpha]^{25}_{D}$-110.0 (*c* 1.5, $CHCl_3$), lit[26] mp 118 °C and $[\alpha]^{25}_{D}$ -107.0 (*c* 2.4, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.22 (d, *J* = 6.1 Hz, 3H, C*H*$_3$), 1.99 (s, 3H, COC*H*$_3$), 2.05 (s, 3H, COC*H*$_3$), 2.11 (s, 3H, COC*H*$_3$), 4.34 (m, 1H, H_5), 5.12 (t, 1H, *J* = 9.7 Hz, H_4), 5.26 (dd, *J* = 3.0, 9.9 Hz, 1H, H_3), 5.39 (s, 1H, H_1), 5.48 (bs, 1H, H_2), 7.27-7.46 (m, 5H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 17.3 (*C*H$_3$), 20.6 (*C*H$_3$CO), 20.8 (*C*H$_3$CO), 20.9 (*C*H$_3$CO), 67.8, 69.4, 71.1, 71.3, 85.7 (C_1), 127.9, 129.1, 131.8, 133.2, 169.8 (*C*=O), 169.9 (*C*=O), 170.2 (*C*=O).

***p*-Methoxyphenyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (5c)[27]**

Pure product was isolated as white solid following elution of the column with 30% EA/PE.; Yield 1.05 g, 87% (starting from **5a**, 500 mg, 3.05 mmol).; mp (EA/PE) 116-118 ^{o}C, $[\alpha]^{25}_{D}$ -64.0 (*c* 1.5, $CHCl_3$), lit[27] mp 120 °C and $[\alpha]^{25}_{D}$ -65.0 (*c* 1.5, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.19 (d, *J* = 6.2 Hz, 3H, C*H*$_3$), 2.01 (s, 3H, COC*H*$_3$), 2.05 (s, 3H, COC*H*$_3$), 2.17 (s, 3H, COC*H*$_3$), 3.73 (s, 3H, OC*H*$_3$), 4.00 (m, 1H, H_5), 5.13 (t, *J* = 9.9 Hz, 1H, H_4), 5.33 (bs, 1H, H_1), 5.41 (bs, 1H, H_2), 5.48 (dd, *J* = 3.3, 10.0 Hz, 1H, H_3), 6.79-6.83 (d, *J* = 8.9 Hz, 2H, Ar*H*), 6.97-7.00 (d, *J* = 8.9 Hz, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 17.4 (*C*H$_3$), 20.7 (*C*H$_3$CO), 20.8 (*C*H$_3$CO), 20.9 (*C*H$_3$CO), 55.6 (OCH$_3$), 66.9, 68.9, 69.8, 71.0, 96.5 (C_1), 114.6, 117.6, 149.9, 155.2, 170.01 (*C*=O), 170.02 (*C*=O), 170.07 (*C*=O).

***p*-tolyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-fucopyranoside (6b)[6h]**

Pure product was isolated as white solid following elution of the column with 20% EA/PE.; Yield 1.04 g, 86% (starting from **5a**, 500 mg, 3.05 mmol).; mp (EA/PE) 110-112 ^{o}C, $[\alpha]^{25}_{D}$ -125.5 (*c* 1.05, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.3 Hz, 3H, C*H*$_3$), 1.95 (s, 3H, COC*H*$_3$), 2.06 (s, 3H, COC*H*$_3$), 2.11 (s, 3H, COC*H*$_3$), 2.32 (s, 3H, C*H*$_3$), 3.78 (m, 1H, H_5), 4.61 (d, *J* = 9.8 Hz, 1H, H_1), 5.01 (dd, *J* = 3.2, 9.8 Hz, 1H, H_3), 5.14-5.23 (m, 2H, H_2, H_4), 7.09-7.12 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.38-7.40 (d, *J* = 7.9 Hz, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 16.5 (*C*H$_3$), 20.62 (*C*H$_3$CO), 20.63 (*C*H$_3$CO), 20.9 (*C*H$_3$CO), 21.1 (*C*H$_3$), 67.4, 70.4, 72.5, 73.1, 86.8 (C_1), 129.1, 129.6, 132.9, 138.2, 169.5 (*C*=O), 170.1 (*C*=O), 170.6 (*C*=O).

Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (7b)[28]

To a suspension of **7a** (500 mg, 1.6 mmol) and acetic anhydride (4 equivalent, 6.5 mmol, 0.62 ml) was added $Mg(OTf)_2$ (0.005 equivalent, 0.008 mmol, 2.6 mg), and the reaction mixture was allowed to stir at 80 ^{o}C for 15 minutes. After the reaction was completed (checked by TLC), reaction mixture was cooled in ice bath and to this thiophenol (1.1 equivalent, 1.78 mmol, 0.19 ml) followed by $BF_3.Et_2O$ (1.2 equivalent, 1.94 mmol, 0.25 ml) were added, and the reaction mixture was kept on stirring for overnight (8 hours) for complete conversion of starting material. The reaction mixture was then worked up as described under the general procedure. The crude product was passed through a short pad of silica to give pure product as white solid following elution of the column with 35% EA/PE; Yield 0.67 g, 78%.; mp (EA/PE) 144-146 ^{o}C, $[\alpha]^{25}_{D}$ +53.9 (*c* 1.00, $CHCl_3$), lit[28] mp 145-146 °C and $[\alpha]^{25}_{D}$ +53.0 (*c* 1.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.84 (s, 3H, COC*H*$_3$), 2.04 (s, 3H, COC*H*$_3$), 2.10 (s, 3H, COC*H*$_3$), 3.91 (m, 1H, H_5), 4.18-4.30 (m, 2H, H_6, H_6'), 4.35 (t, *J* = 3.4 Hz, 1H, H_2) 5.14 (apparent t, *J* = 9.6, 9.8 Hz, 1H, H_4), 5.71 (d, *J* = 10.6 Hz, 1H, H_1), 5.79 (d, *J* = 7.9 Hz, 1H, H_3), 7.26-7.88 (m, 9H, Ar*H*).

***p*-Tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (7c)[9d]**

Pure product was isolated as white solid following elution of the column with 33% EA/PE; Yield 0.64 g, 73% (starting from **7a**, 500 mg, 1.6 mmol).; mp (EA/PE) 162-164 ^{o}C, $[\alpha]^{25}_{D}$ +40.9 (*c* 0.70, $CHCl_3$), lit[9d] mp 160-162 °C and $[\alpha]^{25}_{D}$ +40.0 (*c* 0.60, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.83 (s, 3H, COC*H*$_3$), 2.01 (s, 3H, COC*H*$_3$), 2.09 (s, 3H, COC*H*$_3$), 2.32 (s, 3H, C*H*$_3$), 3.87 (m, 1H, H_5), 4.18-4.35 (m, 3H, H_2, H_6, H_6'), 5.11 (t, *J* = 9.8 Hz, 1H, H_4), 5.64 (d, *J* = 10.5 Hz, 1H, H_1), 5.77 (apparent t, *J* = 9.5, 9.9 Hz, 1H, H_3), 7.06-7.08 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.28-7.31 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.74-7.88 (m, 4H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.4 (*C*H$_3$CO), 20.6 (*C*H$_3$CO), 20.7 (*C*H$_3$CO), 21.2 (*C*H$_3$),

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53.6, 62.2, 68.7, 71.7, 75.8, 83.1 (C_1), 123.7, 126.9, 129.7, 131.2, 131.6, 133.9, 134.3, 134.5, 138.7, 166.9 (*C*=O), 167.8 (*C*=O), 169.4 (*C*=O), 170.1 (*C*=O), 170.6 (*C*=O).

Typical procedure for phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (8b)[29]

To a suspension of D-cellobiose **8a** (500 mg, 1.46 mmol) and acetic anhydride (8 equivalent, 11.7 mmol, 1.1 ml) was added $Mg(OTf)_2$ (0.005 equivalent, 0.007 mmol, 2.4 mg) and the reaction mixture was allowed to stir at 80 ^oC for 5 minutes. After the reaction was completed (checked by TLC), reaction mixture was cooled in ice bath and to this thiophenol (1.1 equivalent, 1.6 mmol, 0.16 ml), followed by $BF_3.Et_2O$ (1.2 equivalent, 1.75 mmol, 0.22 ml) were added, and the reaction mixture was kept on stirring for overnight (8 hours). When TLC showed complete conversion of starting material, the reaction mixture was diluted with ethyl acetate, and the mixture was washed subsequently with cold 5% NaOH solution followed by brine solution. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was passed through a short pad of silica to give the product. Pure product was isolated as white solid following elution of the column with 33% EA/PE.; Yield 0.82 g, 77%.; mp (EA/PE) 214-216 ^oC, $[\alpha]^{25}_D$ -16.8 (*c* 1.00, $CHCl_3$), lit[29] mp 217 °C and $[\alpha]^{20}_D$ -13.2(*c* 1.05, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.96 (s, 3H, COCH_3), 1.99 (s, 6H, COCH_3), 2.00 (s, 3H, COCH_3), 2.05 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 3.62-3.74 (m, 3H, H_4, H_5, H_5'), 3.99-4.18 (m, 2H, H_6, H_6), 4.36 (dd, *J* = 3.7, 12.3 Hz, 1H, H_6'), 4.47-4.56 (m, 2H, H_2', H_6'), 4.65 (d, *J* = 10.0 Hz, 1H, H_1), 4.86-4.92 (m, 2H, H_2, H_1'), 5.01-5.21 (m, 3H, H_3, H_3', H_4'), 7.26-7.29 (m, 3H, Ar*H*), 7.44-7.66 (m, 2*H*, ArH).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.5 (CH_3CO), 20.6 (CH_3CO), 20.7 (CH_3CO), 20.8 (CH_3CO), 61.5, 62.0, 67.8, 70.2, 71.6, 71.9, 72.9, 73.6, 76.3, 85.5 (C_1), 100.7 (C_1'), 128.3, 128.9, 129.1, 131.7, 133.1, 168.9 (*C*=O), 169.3 (*C*=O), 169.5 (*C*=O), 169.7 (*C*=O), 170.1 (*C*=O), 170.2 (*C*=O), 170.4 (*C*=O).

Phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (9b)[29]

Pure product was isolated as white solid following elution of the column with 33% EA/PE.; Yield 0.90 g, 85% (from D-lactose **9a**, 500 mg, 1.46 mmol), scale up yield 3.5 g, 83% (from **9a**, 2 g, 5.84 mmol).; mp (EA/PE) 168-170 °C, $[\alpha]^{25}_D$ -15.3 (*c* 1.00, $CHCl_3$), lit[29] mp 169-170 ^{0}C and $[\alpha]^{25}_D$ -12.7 (*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.95 (s, 3H, COCH_3), 2.03 (s, 9H, COCH_3), 2.08 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 2.14 (s, 3H, COCH_3), 3.65 (m, 1H, H_5), 3.74 (t, *J* = 9.3 Hz, 1H, H_4), 3.85 (bt, *J* = 6.7 Hz, 1H, H_5'), 4.02-4.12 (m, 3H, H_6, H_6/H_6', H_6'), 4.45-4.54 (m, 2H, H_3, H_6/H_6'), 4.66 (d, *J* = 10.0 Hz, 1H, H_1), 4.86-4.96 (m, 2H H_1', H_3'), 5.08 (apparent t, *J* = 9.3 Hz, 1H, H_2), 5.21 (t, *J* = 9.0 Hz, 1H, H_2'), 5.33 (d, *J* = 2.5 Hz, 1H, H_4'), 7.31-7.48 (m 5H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.5 (CH_3CO), 20.6 (CH_3CO), 20.7 (CH_3CO), 20.8 (CH_3CO), 60.8, 62.1, 66.6, 69.1, 70.2, 70.7, 70.9, 73.8, 76.1, 85.5 (C_1), 101.0 (C_1'), 128.3, 128.9, 131.7, 133.0, 162.3, 169.4 (*C*=O), 169.6 (*C*=O), 169.7 (*C*=O), 170.0 (*C*=O), 170.1 (*C*=O), 170.2 (*C*=O), 170.3 (*C*=O).

Phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (10b)[29]

Pure product was isolated as white solid following elution of the column with 33% EA/PE.; Yield 0.96 g, 91% (from D-maltose **10a**, 500 mg, 1.46 mmol), scale up yield 3.7 g, 87% (from **10a**, 2 g, 5.84 mmol).; mp 90-92 °C, $[\alpha]^{25}_D$ +56.3 (*c* 1.00, $CHCl_3$), lit[29] mp 92-94 ^{0}C and $[\alpha]^{25}_D$ +57.0 (*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.98 (s, 3H, COCH_3), 2.01 (s, 3H, COCH_3), 2.02 (s, 6H, COCH_3), 2.05 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 2.11 (s, 3H, COCH_3), 3.72 (m, 1H, H_5), 3.89-3.93 (m, 2H, H_4, H_5'), 4.03 (m, 1H, H_6/H_6'), 4.17-4.24 (m, 2H, H_6/H_6', H_6'), 4.53 (m, 1H, H_6), 4.69-4.85 (m, 3H, H_1, H_2', H_3'), 5.03 (t, *J* = 9.8 Hz, 1H, H_2), 5.24-5.33 (m, 2H, H_3, H_4'), 5.37 (d, *J* = 4.1 Hz, 1H, H_1'), 7.17-7.47 (m 5H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.57 (CH_3CO), 20.66 (CH_3CO), 20.7 (CH_3CO), 20.8 (CH_3CO), 20.9 (CH_3CO), 61.5, 62.8, 68.0, 68.5, 69.3, 69.9, 70.7, 72.5, 76.1, 76.4, 85.0 (C_1), 95.4 (C_1'), 128.5, 128.9, 129.0, 131.2, 133.4, 169.4 (*C*=O), 169.5 (*C*=O), 169.9 (*C*=O), 170.1 (*C*=O), 170.3 (*C*=O), 170.5 (*C*=O).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (10c)[30]**

Pure product was isolated as white solid following elution of the column with 40% EA/PE.; Yield 0.89 g, 83% (from D-maltose **10a**, 500 mg, 1.46 mmol).; mp 130-132 °C, $[\alpha]^{25}_D$ +54.3 (*c* 1.00, $CHCl_3$), lit[30] mp 130-132 °C and $[\alpha]^{24}_D$ +49.8 (c 1.0, $CHCl_3$).; ^{1}H-NMR (400 MHz, $CDCl_3$); δ 2.00 (s, 3H, COCH_3), 2.02 (s, 3H, COCH_3), 2.03 (s, 3H, COCH_3), 2.04 (s, 3H, COCH_3), 2.05 (s, 3H, COCH_3), 2.10 (s, 3H, COCH_3), 2.11 (s, 3H, COCH_3), 3.77 (s, 3H, OCH_3), 3.80 (m, 1H, H_5), 3.96 (m, 1H, H_5'), 4.05 (dd, *J* = 1.6, 12.0 Hz, 1H, H_6), 4.18 (t, *J* = 9.2Hz, 1H, H_4), 4.23-4.28 (m, 2H, H_6', H_6'), 4.48 (dd, *J* = 2.8, 12.0 Hz, 1H, H_6), 4.86 (dd, *J* = 3.8, 10.6 Hz, 1H, H_2'), 4.98 (d, *J* = 7.6 Hz, 1H, H_1), 5.02-5.08 (m, 2H, H_2, H_3'), 5.30 (m, 1H, H_4'), 5.36 (t, *J* = 10.0 Hz, 1H, H_3), 5.43 (d, *J* = 4.0 Hz, 1H, H_1'), 6.81-6.94 (m, 4H, Ar*H*).

General procedure for 4,6-*O*-arylidenation of monosaccharides

To a solution of unprotected monosaccharide glycosides (200 mg) and benzaldehyde dimethylacetal or *p*-methoxybenzaldehyde dimethylacetal (1.1 equivalent with respect to sugr) in dry acetonitrile (10 ml), 10 mole % $Mg(OTf)_2$ was added at ambient temperature. After completion of reaction (indicated by TLC), the reaction mixture was diluted with ethyl acetate, and the mixture was washed subsequently with saturated $NaHCO_3$ followed by brine solution; finally the organic extract was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was either crystallized or passed through a short pad of silica to give pure arylidenated product.

Typical procedure for phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (11b)[31]

To a solution of **11a** (200 mg, 0.74 mmol) and benzaldehyde dimethylacetal (1.1 equivalent, 0.81 mmol, 0.12 ml) in dry acetonitrile (10 ml), $Mg(OTf)_2$ (0.1 equivalent, 0.074 mmol, 23.8 mg) was added at ambient temperature. After completion of reaction (indicated by TLC), the reaction mixture was diluted with ethyl acetate, and the mixture was washed subsequently with saturated $NaHCO_3$ followed by brine solution; finally the organic extract was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude material was crystallized from EtOH to isolate pure product as white solid.

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Yield 230 mg, 87% (2.17 g, 82%).; mp (EtOH) 172-174 °C, $[\alpha]^{22}_{D}$ -28.1 (*c* 1.00, $CHCl_3$), lit[31] 174 °C and $[\alpha]^{25}_{D}$ -26.9.; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.17 (bs, 2H, O*H*), 3.45-3.54 (m, 3H, H_2, H_3, H_5), 3.75-3.88 (m, 2H, H_4, H_{6a}), 4.38 (m, 1H, H_{6e}), 4.62 (d, *J* = 9.7 Hz, 1H, H_1), 5.54 (s, 1H, PhC*H*), 7.33-7.56 (m, 10H, Ar*H*).

4-Tolyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (12b)[32]

The crude product was crystallized from EtOH to isolate pure product as white solid. Yield 209 mg, 80% (starting from **12a**, 200 mg, 0.699 mmol), scale up yield, 2.0 g, 77% (starting from **12a**, 2.09 g, 6.99 mmol).; mp 170-172 °C, $[\alpha]^{25}_{D}$ -40.1 (*c* 1.0, $CHCl_3$), lit[32] mp 171-172 °C and $[\alpha]^{25}_{D}$ -34.4 (*c* 1.0, $CHCl_3$).; ^{1}H-NMR (500 MHz, $CDCl_3$); δ 2.28 (s, 3H, CH_3), 2.61 (s, 1H, O*H*), 2.76 (s, 1H, O*H*), 3.35 (t, *J* = 9.0 Hz, 1H, H_3), 3.39-3.44 (m, 2H, H_2, H_5), 3.69 (m, 1H, H_{6a}), 3.75 (t, *J* = 8.5 Hz, 1H, H_4), 4.29 (dd, *J* = 4.3, 10.3 Hz, 1H, H_{6e}), 4.48 (d, *J* = 10 Hz, 1H, H_1), 5.44 (s, 1H, PhC*H*), 7.07-7.08 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.28-7.31 (m, 3H, Ar*H*), 7.35 -7.40 (m, 4H, Ar*H*).; ^{13}C-NMR (125 MHz, $CDCl_3$); δ 21.2, 68.6, 70.6, 72.5, 74.6, 80.2, 88.7 (C_1), 101.9 (PhCH), 126.3, 127.2, 128.4, 129.3, 129.9, 133.7, 136.9, 138.9.

Ethyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (13b)[33]

The crude product was crystallized from EtOH to isolate pure product as white solid. Yield 228 mg, 82% (starting from **13a**, 200 mg, 0.89 mmol), scale up yield, 2.2 g, 79% (starting from **13a**, 2.09 g, 8.9 mmol).; mp 146-148 °C, $[\alpha]^{22}_{D}$ -64.0 (*c* 1.4, $CHCl_3$), lit[33] 145 °C, and $[\alpha]^{25}_{D}$ -65.0 (*c* 1.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.33-1.38 (t, *J* = 7.4 Hz, 3H, CH_3), 2.75-2.82 (q, *J* = 7.4 Hz, 3H, SCH_2, O*H*), 2.93 (bs, 2H, O*H*), 3.49-3.63 (m, 3H, H_2, H_3, H_5), 3.76-3.88 (m, 2H, H_4, H_{6a}), 4.37 (m, 1H, H_{6e}), 4.48 (d, *J* = 9.7 Hz, 1H, H_1), 5.56 (s, 1H, PhC*H*), 7.28-7.52 (m, 5H, Ar*H*).

Phenyl 4,6-*O*-(4-methoxybenzylidene)-1-thio-β-D-glucopyranoside (11c)[34]

11c was isolated as white solid following elution of the column with 45% EA/PE; Yield 224 mg, 78% (starting from **11a**, 200 mg, 0.74 mmol).; mp (EtOH) 170-172 °C, $[\alpha]^{25}_{D}$ -31.5 (*c* 1.0, $CHCl_3$), lit[34] mp(EtOH) 173-176 °C and $[\alpha]^{25}_{D}$ -38.8 (*c* 0.19, $CHCl_3$).; ^{1}H-NMR (500 MHz, $CDCl_3$); δ 2.66 (s, 1H, O*H*), 2.82 (s, 1H, O*H*), 3.36-3.44 (m, 3H, H_2, H_3, H_5), 3.66-3.76 (m, 5H, OCH_3, H_4, H_{6a}), 4.27 (m, 1H, H_{6e}), 4.54 (d, *J* = 9.5 Hz, 1H, H_1), 5.40 (s, 1H, PhC*H*), 6.79-6.81 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.26 (bs, 3H, Ar*H*), 7.31-7.33 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.46 (bs, 2H, Ar*H*).; ^{13}C-NMR (125 MHz, $CDCl_3$); δ 55.3 (OCH_3), 68.6, 70.6, 72.6, 74.6, 80.2, 88.6 (C_1), 101.9 (PhCH), 113.8, 127.6, 128.5, 129.1, 129.4, 131.3, 133.4.

4-Methoxyphenyl 4,6-*O*-benzylidene-β-D-glucopyranoside (14b)[35]

The crude material was crystallized from MeOH to isolate pure product as white solid. Yield 214 mg, 82% (starting from **14a**, 200 mg, 0.699 mmol).; mp 212 °C, $[\alpha]^{25}_{D}$ -28.1 (*c* 1.0, $CH_3OH/CHCl_3$ 1:1), lit[35] mp 213-214 °C and $[\alpha]^{25}_{D}$ -35.0 (*c* 1.0, DMF).; ^{1}H-NMR (300 MHz, D_6-DMSO); δ 3.48 (d, *J* = 8.9 Hz, 1H), 3.57 (bs, 2H), 3.70 (s, 4H), 4.20 (d, *J* = 5.2 Hz, 1H), 4.97 (d, *J* = 7.3 Hz, 1H, H_1), 5.44 (d, *J* = 3.7 Hz, 1H), 5.59 (s, 1H, PhC*H*), 6.85-6.87 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.98-7.00 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.37-7.45 (m, 5H, Ar*H*).; ^{13}C-NMR (75 MHz, D_6-DMSO); δ 55.8 (OCH_3), 66.2, 68.3, 73.3, 74.7, 80.9 (C_1), 101.2 (PhCH), 102.2 (C_1), 114.9, 118.3, 126.8, 128.5, 129.3, 138.2, 151.5, 154.9.

4-Bromophenyl 4,6-*O*-benzylidene-β-D-glucopyranoside (15b)[16g]

The crude mass was crystallized from EtOH to isolate pure product as white solid. Yield 205 mg, 81% (starting from **15a**, 200 mg, 0.66 mmol).; mp 180-182 °C, $[\alpha]^{25}_{D}$ -38.7 (*c* 1.00, $CHCl_3$), lit[16g] mp 182-184 °C and $[\alpha]^{25}_{D}$ -38.8 (*c* 0.89, $CHCl_3$).; ^{1}H-NMR (400 MHz, $CDCl_3$); δ 2.71 (bs, 1H, O*H*), 2.84 (bs, 1H, O*H*), 3.49-3.67 (m, 2H, H_2/H_3, H_5), 3.77-3.84 (m, 2H, H_3/H_2, H_{6a}), 3.92 (m, 1H, H_4), 4.37 (m, 1H, H_{6e}), 4.99 (d, *J* = 7.6 Hz, 1H, H_1), 5.57 (s, 1H, PhC*H*), 6.93-6.95 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.38-7.51 (m, 7H, Ar*H*).

2'-Napthyl 4,6-*O*-benzylidene-β-D-glucopyranoside (16b)[36]

The crude product was crystallized from EtOH to isolate pure product as white solid. Yield 214 mg, 83% (starting from **16a**, 200 mg, 0.65 mmol).; mp 202-204 °C, $[\alpha]^{25}_{D}$ -36.0 (*c* 1.00, $CHCl_3$), lit[36] mp 202-205 °C and $[\alpha]^{25}_{D}$ -37.1 (*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.83 (bs, 1H, O*H*), 2.92 (bs, 1H, O*H*), 3.68-3.90 (m, 4H, H_2, H_3, H_5, H_{6a}), 3.95 (m, 1H, H_4), 4.44 (m, 1H, H_{6a}), 5.19 (d, *J* = 7.5 Hz, 1H, H_1), 5.59 (s, 1H, PhC*H*), 7.28-7.52 (m, 9H, Ar*H*), 7.75-7.82 (m, 3H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 66.6, 68.6, 73.2, 74.4, 80.3, 101.3, 102.0, 111.6, 118.8, 124.7, 126.3, 126.6, 127.2, 127.7, 128.4, 129.4, 129.8, 130.2, 134.1, 136.8.

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (17b)[37]

The pure product was isolated as white solid following elution of the column with 22.5% EA/PE.; Yield 217 mg, 83% (starting from **17a**, 200 mg, 0.7 mmol).; mp 126-128 °C, $[\alpha]^{25}_{D}$ +35.5 (*c* 5.0, $CHCl_3$), lit[37] mp 129-130 °C and $[\alpha]^{25}_{D}$ +35.0 (*c* 5.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 3.37 (s, 3H, OCH_3), 3.44-3.52 (m, 2H, H_2, H_3), 3.69 (apparent t, *J* = 10.1, 10.2 Hz, 1H, H_{6a}), 3.80 (m, 1H, H_5), 4.16 (t, *J* = 9.3 Hz, 1H, H_4), 4.26 (dd, *J* = 4.9, 9.9 Hz, 1H, H_{6e}), 4.61 (d, *J* = 3.1 Hz, 1H, H_1), 4.67-4.81 (m, 2H, Bn*H*), 5.51 (s, 1H, PhC*H*), 7.30-7.39 (m, 8H, Ar*H*), 7.49-7.53 (m, 2H, ArH).

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (18b)[37]

The pure product was isolated as white solid following elution of the column with 22.5% EA/PE.; Yield 222 mg, 85% (starting from **18a**, 200 mg, 0.7 mmol).; mp 184-186 °C, $[\alpha]^{25}_{D}$ +77.8 (*c* 5.0, $CHCl_3$), lit[37] mp 185-187 °C and $[\alpha]^{25}_{D}$ +80.0 (*c* 5.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 3.46 (s, 3H, OCH_3), 3.58-3.89 (m, 5H, H_2, H_3, H_4, H_{6a}, H_{6e}), 4.33 (m, 1H, H_5), 4.80 (d, *J* = 3.7 Hz, 1H, H_1), 4.80-4.84 (m, 1H, Bn*H*), 4.98 (dd, *J* = 3.1, 11.6 Hz, 1H, Bn*H*), 5.59 (s, 1H, PhC*H*), 7.29-7.41 (m, 8H, Ar*H*), 7.51-7.54 (m, 2H, Ar*H*).

Allyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (19b)[38]

Pure product was isolated as white solid following elution of the column with 33% EA/PE and crystallized from DCM and PE.; Yield 220 mg, 88% (starting from **19a**, 200 mg, 0.57 mmol).; mp 182-184 °C, $[\alpha]^{25}_{D}$ -39.0 (*c* 1.0, $CHCl_3$), lit[38] mp 185-187 °C and $[\alpha]^{25}_{D}$ -40.0 (*c* 1.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.89 (bs, 1H, O*H*), 3.58-3.60 (m, 2H), 3.81 (m, 1H, H_3), 4.00 (m, 1H, H_6), 4.23-4.39 (m, 3H, H_2, H_4, H_6), 4.61 (m, 1H, H_5), 5.02-5.16 (m, 2H, AllCH_2), 5.28 (d, *J* = 8.4 Hz, 1H, H_1), 5.56 (s, 1H, PhC*H*), 5.69 (m, 1H, AllC*H*), 7.36-7.37 (d, *J* = 3.0 Hz, 3H, Ar*H*), 7.49-7.50 (d, *J* = 3.3 Hz, 2H, Ar*H*), 7.69-7.71 (d, *J* = 2.9 Hz, 2H, Ar*H*), 7.82-7.84 (m, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 56.7, 66.2, 68.6, 68.7, 70.1, 82.2, 98.0 (C_1), 101.9 (PhCH),

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117.6, 123.5, 126.4, 128.4, 129.3, 131.6, 133.4, 137.1, 168.1 (*C*=O), 168.2 (*C*=O).

Phenyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (20b)[39]

Pure product was isolated as foam following elution of the column with 40% EA/PE.; Yield 200 mg, 82% (starting from **20a**, 200 mg, 0.5 mmol).; $[\alpha]^{25}_{D}$ +30.7 (*c* 1.0, $CHCl_3$), lit[39] $[\alpha]^{25}_{D}$ +34.2 (*c* 1.3, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 3.61 (m, 1H, H_3), 3.70 (m, 1H, H_{6a}), 3.83 (apparent t, *J* = 9.8, 10.1 Hz, 1H, H_2), 4.30-4.43 (m, 2H, H_4, H_{6e}), 4.64 (m, 1H, H_5), 5.56 (s, 1H, PhC*H*), 5.69 (d, *J* = 10.3 Hz, 1H, H_1), 7.17-7.89 (m, 14H, Ar*H*).

4-Methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (21b)[40]

Pure product was isolated as foam following elution of the column with 33% EA/PE.; Yield 206 mg, 85% (starting from **21a**, 200 mg, 0.48 mmol), scale up yield, 1.96 g, 81% (starting from **21a**, 2.0 g, 4.8 mmol).; $[\alpha]^{25}_{D}$ +12.3 (*c* 1.0, $CHCl_3$), lit[40] $[\alpha]^{20}_{D}$ +11.4 (*c* 0.67, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 3.67-3.69 (m, 2H), 3.72 (s, 3H, OCH_3), 3.87 (m, 1H), 4.39 (m, 1H), 4.50 (m, 1H), 4.70 (m, 1H), 5.59 (s, 1H, PhC*H*), 5.80 (d, *J* = 8.4 Hz, 1H, H_1), 6.72-6.75 (d, *J* = 9.0 Hz, 2H, Ar*H*), 6.83-6.86 (d, *J* = 9.1 Hz, 2H, Ar*H*), 7.37-7.86 (m, 9H, Ar*H*).

3-(*N*-Carboxybenzyl)propyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (22b)[16e]

Pure product was isolated as foam following elution of the column with 50% EA/PE.; Yield 205 mg, 87% (starting from **22a**, 200 mg, 0.4 mmol).; $[\alpha]^{25}_{D}$ -38.7 (*c* 1.2, $CHCl_3$), lit[16e] $[\alpha]^{20}_{D}$ -39.8 (*c* 1.48, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 1.62-1.69 (m, 2H, CH_2), 2.87 (bs, 1H, O*H*), 3.02-3.12 (m, 2H, NCH_2), 3.47 (m, 1H), 3.59 - 3.65 (m, 3H, OCH_2, H_6), 3.75-3.87 (m, 2H, H_3, H_5), 4.23 (dd, *J* = 8.5, 10.4 Hz, 1H, H_2), 4.35 (dd, *J* = 3.7, 10.6 Hz, 1H, H_6), 4.60 (apparent t, *J* = 8.9, 9.1 Hz, 1H, H_4), 4.94 (m, 1H, N*H*), 5.01 (bs, 2H, Bn*H*), 5.24 (d, *J* = 8.5 Hz, 1H, H_1), 5.54 (s, 1H, PhC*H*), 7.34-7.81 (m, 14H, Ar*H*).

Phenyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (23b)[41]

The crude product was crystallized from EtOH to isolate pure product as white solid.; Yield 233 mg, 88% (starting from **23a**, 200 mg, 0.74 mmol), scale up yield, 2.25 g, 82% (starting from **23a**, 2.0 g, 7.4 mmol).; mp 116-118 °C, $[\alpha]^{25}_{D}$ -41.2 (*c* 1.0, $CHCl_3$), lit[41] mp 118°C and $[\alpha]^{25}_{D}$ -34.5 (*c* 1.2, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 3.55 (s, 1H, O*H*), 3.68-3.72 (m, 3H, H_2, H_3, H_5), 4.03 (d, *J* = 10.6 Hz, 1H, H_6), 4.21(s, 1H, H_4), 4.38 (d, *J* = 12.4 Hz, 1H, H_6), 4.51 (d, *J* = 8.8 Hz, 1H, H_1), 5.51 (s, 1H, PhC*H*), 7.27-7.31 (m, 3H, Ar*H*), 7.38 (bs, 5H, Ar*H*), 7.68-7.70 (d, *J* = 6.3 Hz, 2H, Ar*H*).

4-Tolyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (24b)[32]

The crude mass was crystallized from EtOH to isolate pure product as white solid.; Yield 225 mg, 86% (starting from **24a**, 200 mg, 0.699 mmol), scale up yield, 2.09 g, 80% (starting from **24a**, 2.0 g, 6.9 mmol).; mp 152-154 °C, $[\alpha]^{25}_{D}$ -65.1 (*c* 1.0, $CHCl_3$), lit[32] mp 154-155 °C and $[\alpha]^{25}_{D}$ -72.8 (*c* 1.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.36 (s, 3H, CH_3), 2.96 (bs, 2H, O*H*), 3.44 (bs, 1H), 3.63-3.65 (m, 2H), 3.95 (d, *J* = 12.4 Hz, 1H, H_6), 4.12 (bs, 1H, H_4), 4.33 (d, *J* = 12.4 Hz, 1H, H_1), 4.43 (m, 1H, H_6), 5.47 (s, 1H, PhC*H*), 6.98-7.12 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.37-7.39 (m, 5H, Ar*H*), 7.58 (d, *J* = 7.9 Hz, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 21.3, 68.7, 69.3, 69.9, 73.7, 75.5, 87.1 (C_1), 101.9 (PhCH), 126.6, 126.9, 128.2, 129.0, 129.3, 129.7, 129.8, 134.2, 134.5, 136.4, 137.7, 138.4.

Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (25b)

The crude mass was crystallized from DCM and PE to isolate pure product as white solid.; Yield 209 mg, 84% (starting from **25a**, 200 mg, 0.55 mmol), scale up yield, 2.04 g, 82% (starting from **25a**, 2.0 g, 5.5 mmol).; mp 159-160 °C and $[\alpha]^{25}_{D}$ +13.1 (*c* 1.0, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.51 (bs, 1H, O*H*), 3.45 (bs, 1H, H_5), 3.52 (dd, *J* = 3.3, 9.3 Hz, 1H, H_3), 3.91-4.00 (m, 2H, H_2, H_{6a}), 4.15 (d, *J* = 3.2 Hz, 1H, H_4), 4.35 (dd, *J* = 1.4, 12.4 Hz, 1H, H_{6e}), 4.52 (d, *J* = 9.5 Hz, 1H, H_1), 4.72-4.77 (m, 2H, Bn*H*), 5.43 (s, 1H, PhC*H*), 7.20-7.43 (m, 13H, Ar*H*), 7.66-7.69 (m, 2H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 67.2, 69.4 70.1, 71.7, 73.3, 80.3, 87.1 (C_1), 101.1 (PhCH), 126.5, 127.9, 128.0, 128.1, 128.5, 128.9, 129.1, 129.8, 130.8, 132.6, 133.7, 137.9, 138.0.

4-Methoxyphenyl 4,6-*O*-benzylidene-β-D-galactopyranoside (26b)[42]

The crude mass was crystallized from MeOH to isolate pure product as white solid.; Yield 201 mg, 77% (starting from **26a**, 200 mg, 0.699 mmol).; mp 230-232 °C, $[\alpha]^{25}_{D}$ -79.8 (*c* 1.0, $CH_3OH/CHCl_3$ 1:1), lit[42] mp 230-232 °C and $[\alpha]^{25}_{D}$ -80.4 (*c* 1.0, CH_3OH / $CHCl_3$ 1:1).; ^{1}H-NMR (300 MHz, D_6-DMSO); δ 3.59 (bs, 2H, O*H*), 3.69 (s, 4H), 4.05 (bs, 2H), 4.12 (s, 1H), 4.83 (d, *J* = 5.9 Hz, 1H), 5.05 (s, 1H), 5.27 (s, 1H), 5.57 (s, 1H, PhC*H*), 6.84-6.87 (d, *J* = 8.9 Hz, 2H, Ar*H*), 6.99-7.02 (d, *J* = 8.9 Hz, 2H, Ar*H*), 7.36-7.46 (m, 5H, Ar*H*).; ^{13}C-NMR (75 MHz, D_6-DMSO); δ 55.8 (OCH_3), 66.5, 68.9, 70.2, 72.2, 76.3, 101.2 (PhCH), 102.0 (C_1), 114.9, 118.1, 126.7, 128.4, 129.1, 139.1, 151.8, 154.8.

2-Allylphenyl 4,6-*O*-benzylidene-β-D-galactopyranoside (27b)

The crude mass was crystallized from MeOH to isolate pure product as white solid. Yield 197 mg, 76% (starting from **27a**, 200 mg, 0.68 mmol).; mp 230-232 °C.; ^{1}H-NMR (300 MHz, D_6-DMSO); δ 3.59-3.68 (m, 2H), 3.72 (bs, 2H, O*H*), 4.06 (s, 2H), 4.15 (s, 1H), 4.90 (d, *J* = 7.3 Hz, 1H, H_1), 4.99 (d, *J* = 9.9 Hz, 1H), 5.06-5.12 (m, 2H), 5.26 (d, *J* = 5.0 Hz, 1H), 5.58 (s, 1H, PhC*H*), 5.97-6.06 (m, 1H), 6.95 (m, 1H, Ar*H*), 7.11-7.16 (m, 3H, Ar*H*), 7.36-7.48 (m, 5H, Ar*H*).; ^{13}C-NMR (75 MHz, D_6-DMSO); δ 66.5, 68.9, 70.4, 72.3, 76.3, 100.3 (C_1), 101.9 (PhCH), 115.6, 116.1, 122.4, 126.7, 127.7, 128.4, 129.1, 129.7, 129.9, 137.7, 139.1, 155.5.

Phenyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (28b)[43]

Isolated as white solid following elution of the column with EA and crystallized from CH_3OH.; Yield 180 mg, 68% (starting from **28a**, 200 mg, 0.74 mmol).; mp 210-212 °C, $[\alpha]^{25}_{D}$ +281.0 (*c* 1.0, $CH_3OH/CHCl_3$ 1:1), lit[43] mp 213-214 °C and $[\alpha]^{20}_{D}$ -289.0 (*c* 0.50, $CH_3OH/CHCl_3$ 1:1).; ^{1}H-NMR (300 MHz, D_6-DMSO); δ 3.77-3.81 (m, 2H, 2O*H*), 3.93-4.08 (m, 4H, H_4, H_5, H_{6a}, H_{6e}), 5.24 (d, *J* = 6.0 Hz, 1H, H_3), 5.47 (s, 1H, H_2), 5.57 (d, *J* = 3.8 Hz, 1H, H_1), 5.63 (s, 1H, PhC*H*), 7.30-7.49 (m, 10H, Ar*H*).; ^{13}C-NMR (75 MHz, D_6-DMSO); δ 65.8, 68.1, 68.6, 72.9, 78.9, 89.7 (C_1), 101.7 (PhCH), 126.9, 127.9, 128.5, 129.3, 129.7, 131.8, 134.1, 138.3.

General procedure for one-pot 4,6-*O*-benzylidation acetylation of carbohydrates

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To a solution of unprotected glycosides (100 mg) and benzaldehyde dimethylacetal (1.1 mmol) in dry acetonitrile (5 ml), 10 mole % $Mg(OTf)_2$ was added at room temperature. After completion of reaction (indicated by TLC), solvent was concentrated in vacuum and in the same reaction vessel acetic anhydride (1.0 equivalent per hydroxyl group) was added. After completion of the reaction (indicated by TLC), the reaction mixture was diluted with ethyl acetate, and the mixture was washed subsequently with saturated $NaHCO_3$ followed by brine solution; the organic extract was finally dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was either crystallized or passed through a short pad of silica to give pure product.

Typical procedure for 4-tolyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (29)[44]

To a solution of glycoside **12a** (100 mg, 0.35 mmol) and benzaldehyde dimethylacetal (1.1 equivalent, 0.39 mmol, 0.06 ml) in dry acetonitrile (5 ml), $Mg(OTf)_2$ (0.1 equivalent, 0.4 mmol, 12.8 mg) was added at ambient temperature. After completion of reaction (indicated by TLC), solvent was concentrated in vacuum and in the same reaction vessel acetic anhydride (2.0 equivalent, 0.7 mmol, 0.06 ml) was added. After completion of the reaction (indicated by TLC), the reaction mixture was worked up as described under the general procedure, and the crude product was crystallized from EA and PE to isolate **29** as white solid.; Yield 123.4 mg, 77%.; mp 170-172 °C, $[\alpha]^{25}_D$ -38.0 (*c* 1.00, $CHCl_3$), lit[44] mp 172-174 °C and $[\alpha]^{25}_D$ -34.1 (*c* 1.00, $CHCl_3$).; ^{1}H-NMR (500 MHz, $CDCl_3$); δ 1.95 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 2.28 (s, 3H, CH_3), 3.48 (m, 1H, H_5), 3.56 (t, *J* = 9.5 Hz, 1H, H_{6a}), 3.70 (t, *J* = 10.0 Hz, 1H, H_4), 4.29 (dd, *J* = 5.0, 10.5 Hz, 1H, H_{6e}), 4.65 (d, *J* = 10.0 Hz, 1H, H_1), 4.89 (apparent t, *J* = 9.0, 10.0 Hz, 1H, H_2), 5.25 (apparent t, *J* = 9.0, 9.5 Hz, 1H, H_3), 5.42 (s, 1H, PhC*H*), 7.06-7.07 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.26-7.35 (m, 7H, Ar*H*).;^{13}C-NMR (125 MHz, $CDCl_3$); δ 20.7 (CH_3CO), 20.8 (CH_3CO), 21.2 (CH_3), 68.5, 70.6, 70.8, 72.9, 78.1, 86.8 (C_1), 101.5 (PhCH), 126.2, 127.7, 128.3, 129.2, 133.7, 136.8, 138.8, 169.5 (*C*=O), 170.1 (*C*=O).

Phenyl 2,3-di-*O*-acetyl-4,6-*O*-benzyledene-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (31)[45]

The crude product was crystallized from EA and PE to isolate pure product as white solid.; Yield 123.2 mg, 73% (starting from **30**, 100 mg, 0.23 mmol).; mp 264-266 °C, $[\alpha]^{25}_D$ -42.5 (*c* 0.50, $CHCl_3$), lit[45] mp 267 °C and $[\alpha]^{25}_D$ -45.3 (*c* 1.00, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.01 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.11 (s, 3H, $COCH_3$), 3.47 (m, 1H, H_5), 3.62-3.77 (m, 4H, H_4, H_6', H_5', H_6'), 4.07 (dd, *J* = 5.0, 11.8 Hz, 1H, H_6), 4.33 (dd, *J* = 4.5, 10.0 Hz, 1H, H_6'), 4.48-4.59 (m, 2H, H_3, H_4'), 4.66 (d, *J* = 10.0 Hz, 1H, H_1) 4.85-4.94 (m, 2H, H_1', H_2), 5.16-5.28 (m, 2H, H_2', H_3'), 5.47 (s, 1H, PhC*H*), 7.26-7.48 (m, 10H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.6 (CH_3CO), 20.7 (CH_3CO), 20.8 (CH_3CO), 20.9 (CH_3CO), 30.9 (CH_3CO), 61.9, 62.2, 62.3, 66.4, 68.5, 69.2, 70.2, 70.3, 71.7, 71.9, 72.6, 74.2, 74.4, 75.8, 76.1, 76.3, 76.8, 77.9, 85.3, 100.5, 101.5, 126.1, 128.3, 128.9, 129.0, 129.8, 133.0, 133.3, 134.5, 136.6, 169.4 (*C*=O), 169.5 (*C*=O), 170.2 (*C*=O), 170.3 (*C*=O), 171.5 (*C*=O).

Phenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (33)[45]

The crude product was crystallized from EA and PE to isolate pure product as white solid.; Yield 141.7 mg, 84% (starting from **32**, 100 mg, 0.23 mmol).; mp 254-256 °C, $[\alpha]^{25}_D$ +23.5 (*c* 0.50, $CHCl_3$), lit[45] mp 257 °C and $[\alpha]^{25}_D$ +24.5 (*c* 0.70, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.03 (s, 9H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 3.45 (s, 1H), 3.65-3.77 (m, 2H), 4.01-4.14 (m, 2H), 4.26-4.33 (m, 2H), 4.44 (d, *J* = 7.8 Hz, 1H, H_1), 4.56 (m, 1H), 4.68 (d, *J* = 10.0 Hz, 1H), 4.85-4.96 (m, 2H, H_1'), 5.19-5.28 (m, 2H,), 5.46 (s, 1H, PhC*H*), 7.29-7.31 (m, 3H, Ar*H*), 7.36-7.38 (m, 3H, Ar*H*), 7.41-7.49 (m, 4H, Ar*H*).; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 20.6 (CH_3CO), 20.7 (CH_3CO), 20.8 (CH_3CO), 22.7 (CH_3CO), 29.7 (CH_3CO), 62.1, 62.4, 66.5, 68.1, 68.4, 69.0, 69.7, 70.1, 70.4, 72.1, 73.1, 73.4, 73.6, 74.4, 75.9, 76.9, 85.5, 101.1, 101.4, 126.5, 128.2, 128.9, 129.0, 129.2, 129.7, 131.9, 133.0, 134.5, 137.4, 168.9 (*C*=O), 169.4 (*C*=O), 169.6 (*C*=O), 170.2 (*C*=O), 170.3 (*C*=O), 170.4 (*C*=O), 170.7 (*C*=O).

Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (35)[46]

The crude product was purified by column chromatography on silica gel and the white solid mass was crystallized from EtOH to give **35.;** Yield 78% (starting from **34**, 100 mg, 0.28 mmol).; mp 220–222 °C, $[\alpha]^{25}_D$ +36.5 (c 1.46, $CHCl_3$), lit[32] mp 225 °C and $[\alpha]^{25}_D$ +36.5 (*c* 0.70, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.03 (s, 12H, 4×$COCH_3$), 2.11 (s, 3H, $COCH_3$), 3.45 (s, 1H), 3.47 (s, 3H, OCH_3), 3.59-3.63 (m, 1H), 3.79 (t, *J* = 9.5 Hz, 1H), 4.03 (d, *J* = 12.4 Hz, 1H), 4.12 (dd, *J* = 4.8,11.9 Hz, 1H), 4.27-4.33 (m, 2H), 4.39 (d, *J* = 7.9 Hz, 1H), 4.45-4.54 (m,2H), 4.85-4.93 (m, 2H), 5.26 (d, *J* = 10.5 Hz 1H), 5.19 (d, *J* = 9.7 Hz, 1H), 5.46 (s, 1H, CHPh), 7.36-7.38 (m, 3H, Ar*H*), 7.44-7.46 (m, 2H, Ar*H*).

4-Methoxyphenyl 2,3-di-O-acetyl-4,6-O-benzylidene-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (37)[16g]

The crude product was purified by column chromatography on silica gel and the white solid mass was crystallized from EtOH to give **37.;** Yield 131.5 mg, 79% (starting from **36**, 100 mg, 0.35 mmol).; mp 180-182 °C, $[\alpha]^{25}_D$ +25.5 (c 0.49, $CHCl_3$), lit[16g] mp 182–184 °C and $[\alpha]^{25}_D$ +24.5 (*c* 0.60, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.04 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 3.64 (t, *J* = 9.5 Hz, 1H, H_4), 3.70-3.77 (m, 4H, OCH_3, H_4'), 3.80-3.91 (m, 2H, H_5', H_6'), 4.08 (t, *J* = 9.4 Hz, 1H, H_3), 4.24-4.32 (m, 2H, H_5, H_2'), 4.54 (dd, *J* = 2.7, 12.5 Hz, 1H, H_6'), 4.89 (dd, *J* = 4.1, 10.1 Hz, 1H, H_6), 4.97 (d, *J* = 7.6 Hz, 1H, H_1), 5.06 (t, *J* = 7.7 Hz, 1H, H_2), 5.31 (t, *J* = 8.8 Hz, 1H, H_6), 5.38 (d, *J* = 4.1 Hz, 1H, H_1'), 5.43–5.50 (m, 2H, H_3', PhC*H*), 6.79-6.84 (m, 2H, Ar*H*), 6.90-6.95 (m, 2H, Ar*H*), 7.33-7.36 (m, 3H, Ar*H*), 7.40-7.44 (m, 2H, Ar*H*).;

2'-Azidoethyl 2,3-di-O-acetyl-4,6-O-benzylidene-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (39)[16g]

The crude product was purified by column chromatography on silica gel and the white solid mass was crystallized from EtOH to give **39**.; Yield 135.8 mg, 79% (starting from **38**, 100 mg, 0.24 mmol).; mp 184-186 °C, $[\alpha]^{25}_D$ +2.3 (c 2.25, $CHCl_3$), lit[16g] mp 186-188 °C and $[\alpha]^{25}_D$ +2.0 (c 2.25, $CHCl_3$).; ^{1}H-NMR (400

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MHz, $CDCl_3$); δ 2.01 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.11 (s, 3H, $COCH_3$), 3.26 (m, 1H, NC*H*), 3.47 (m, 1H, NC*H*), 3.60-3.76 (m, 4H), 3.83-3.89 (m, 1H), 3.97-4.05 (m, 2H), 4.22-4.27 (m, 2H, H_6), 4.57-4.61 (m, 2H, H_6, H_3'), 4.82-4.89 (m, 2H, H_1, H_2'), 5.26 (apparent t, J = 8.8, 9.2 Hz, 1H, H_2), 5.36 (d, J = 4.0 Hz, 1H, H_1'), 5.44 (d, J = 9.6 Hz, 1H, H_3), 5.48 (s, 1H, PhC*H*), 7.33-7.42 (m, 5H, Ar*H*).

Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (41)[47]

The crude product was crystallized from EA and PE to isolate pure product as white solid.; Yield 145 mg, 77% (starting from **40**, 100 mg, 0.52 mmol).; mp 106-108 ˚C, $[\alpha]^{28}_D$ -100.6 (*c* 2.10, $CHCl_3$), lit[47] mp 110-112 ˚C and $[\alpha]^{24}_D$ -95.2 (*c* 5.24, $CHCl_3$).; ^{1}H-NMR (300 MHz, $CDCl_3$); δ 2.05 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 3.52 (s, 3H, OCH_3), 3.56 (m, 1H, H_5), 3.70 (t, J = 9.5 Hz, 1H, H_4), 3.80 (t, J = 10.2 Hz, 1H, H_6), 3.83 (dd, J = 4.9, 10.5 Hz, 1H, H_6), 4.51 (d, J = 7.8 Hz, 1H, H_1), 4.99 (apparent t, J = 8.0, 9.0 Hz, 1H, H_2), 5.32 (apparent t, J = 9.4, 11.5 Hz, 1H, H_3), 5.51 (s, 1H, C*H*Ph), 7.35-7.44 (m, 5H, Ar*H*).

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