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Acylation of carbohydrates over Al_2O_3: preparation of partially and fully acylated carbohydrate derivatives and acetylated glycosyl chlorides☆

Pallavi Tiwari and Anup Kumar Misra*

Medicinal and Process Chemistry Division, Central Drug Research Institute, Chattar Manzil Palace, Lucknow 226 001, UP, India

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Abstract—Selective and per-O-acylation of carbohydrate derivatives using acyl chlorides and Al_2O_3, a solid support reagent, is reported. This protocol does not require the addition of any base or activator. This methodology has been further extended to the selective acylation of carbohydrate diols and the one-pot preparation of acetylated glycosyl chlorides direct from free reducing sugars. The yields obtained in most of the cases are excellent.

Keywords: Carbohydrates; Acylation; Al_2O_3; Regioselectivity; Chemoselectivity

Acylation of hydroxyl groups of carbohydrates is one of the most commonly used functional group protection techniques in the synthesis of oligosaccharides. Per-O-acetylated sugars are inexpensive and useful intermediates for the synthesis of naturally occurring glycosides, oligosaccharides, and other glycoconjugates.[1–7] The acetylation reaction has also been employed for structural elucidation of many natural products containing carbohydrates. The most commonly used acyl protecting groups used in the carbohydrate syntheses are acetyl, benzoyl, chloroacetyl, and pivaloyl, which are prepared by using acetyl chloride, acetic anhydride, benzoyl chloride, chloroacetyl chloride, pivaloyl chloride, respectively, in the presence of a base.[8] Acetylation of sugar alcohols is often carried out using a large excess of acetic anhydride with pyridine serving as the solvent and base, despite its toxicity and unpleasant odor.[9,10] Sometimes, pyridine derivatives such as 4-(*N*,*N*-dimethylamino)pyridine and 4-(pyrrolidino)pyridine are added as a cocatalyst to speed up the acylation.[11,12] A variety of other catalysts in combination with excess acetic anhydride and solvent have been employed in the acetylation of carbohydrate derivatives, including sodium acetate,[13] sulfuric acid,[14] perchloric acid,[15] and a number of Lewis acid catalysts such as, iodine,[16] $Sc(OTf)_3$,[17] $Cu(OTf)_2$,[18] $CoCl_2$,[19] $ZnCl_2$,[20] $BiOCl–SOCl_2$,[21] $LiClO_4$,[22] $FeCl_3$,[23] $BiCl_3$,[24] and a series of heterogeneous catalysts such as, montmorillonite K-10,[25] zeolites,[26] nafion-H.[27] Recently, a $ZnCl_2$–sodium acetate combination[28] or $InCl_3$[29] with acetic anhydride under microwave condition has been reported for the acetylation of carbohydrates. A few reports have also appeared on the acetylation of carbohydrates using ionic liquids as solvents and catalysts.[30,31] In most cases, acetic anhydride is used in excess, which sometimes causes troublesome workup during the neutralization process and thereby makes the protocol tedious. Despite the number of available methods, there is a need to develop a fast clean reaction protocol for the acetylation of sugars particularly over solid surfaces, which reduces conventional workup and purification procedures. In this context, we recently reported a fast per-O-acetylation of carbohydrates using $HClO_4–SiO_2$ as a solid catalyst and stoichiometric quantity of acetic anhydride to minimize workup.[32] While applying this methodology for the acetylation of carbohydrate derivatives containing acid labile functional groups such as,

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* Corresponding author. Tel.: +91 522262411; fax: +91 5222623405; e-mail: akmisra69@rediffmail.com

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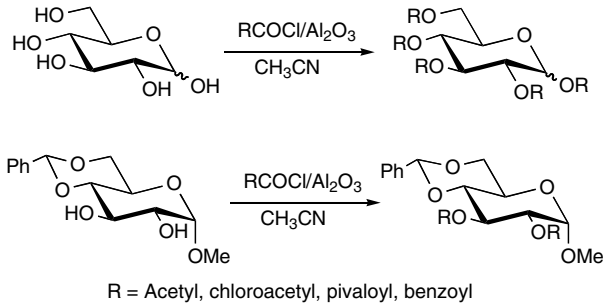
benzylidene acetals, isopropylidene acetals, and triphenylmethyl (trityl) groups, it was observed that some acid labile functional groups were cleaved during the reaction. To overcome this unwanted side reaction, we have been interested in developing economical methods for a general acylation of carbohydrate derivatives, that avoids the use of an acid or a base, such as pyridine or its derivatives, in addition to a reaction protocol that would be easy to perform for scaling up without the requirement of workup or tedious chromatographic purifications. Reactions on solid supports are always welcome because of the possibility of recycling the solid support and the exclusion of conventional workup procedures. Recently, a few reports[33–35] appeared involving the use of Al_2O_3 as a solid support for the acylation of alcohols, phenols, amine, thiols, which have excluded the addition of a base or acid as catalyst. Prompted by this work, we envisioned that acylation of carbohydrate derivatives containing acid labile functional groups could be best performed over basic Al_2O_3 as a solid support using a minimum quantity of the acylating agents. Although previously Al_2O_3 has been used in carbohydrate chemistry to promote transesterification of sugar alcohols with ethyl acetate, the yields were poor and the reaction required long reaction times and a large amount of Al_2O_3.[36–38] We disclose here an efficient and economical method for the selective and complete acylation of carbohydrate derivatives and those with acid-susceptible functional groups using acyl chlorides and basic Al_2O_3 as a solid support in a solvent or under solvent-free conditions.

To evaluate the potential of basic Al_2O_3 in acetylating carbohydrate derivatives, a series of preliminary experiments were carried out using a variable quantity of acetyl chloride and basic Al_2O_3 with CH_3CN as the solvent (Scheme 1). It was observed that use of 1.2 M equiv of acetyl chloride and 2.0 equiv of basic Al_2O_3 per hydroxyl group in CH_3CN produced an excellent yield of per-O-acetylated carbohydrate derivatives, even those containing acid labile functionalities. Increasing the quantity of acetyl chloride and Al_2O_3 did not increase the yield or reduce the reaction time significantly; rather it reduced the selectivity of the acylation between two hydroxyl groups. With the satisfactory yields with acetyl chloride, the same reaction was done using acetic anhydride as acetylating



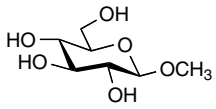
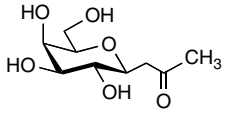
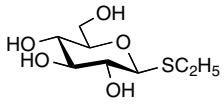
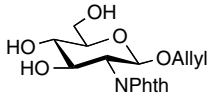
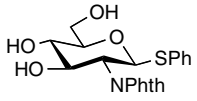
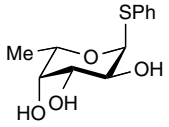
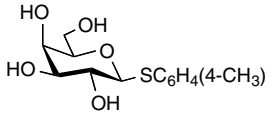
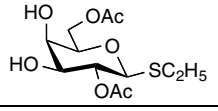
Scheme 1.

agent. However, the reaction did not proceed well and even after 48 h only ~30% of the product was obtained. The same reaction was performed without addition of CH_3CN, but the reaction time was only reduced by a few minutes and the yield was comparable. Using the similar molar ratio of the substrates and reagents, a series of other acyl chlorides (chloroacetyl chloride, pivaloyl chloride, benzoyl chloride) were allowed to react with carbohydrate derivatives containing acid labile functional groups in the presence of basic Al_2O_3. In every case, excellent yields of the corresponding acylated products were isolated (Tables 1 and 2). It was observed that acid chlorides react more efficiently than the corresponding acid anhydride and that benzoyl chloride reacts much more slowly than acetyl or chloroacetyl chlorides. Many acid labile functional groups such as benzylidene acetals, isopropylidene acetals, TBDMS ethers are stable under these reaction conditions.

The methodology has also been applied to the selective acylation of carbohydrate derivatives. The primary hydroxyl groups of the carbohydrate derivatives were acylated very efficiently, while leaving the secondary hydroxyl groups unacylated. The slow reactivity of benzoyl chloride as found earlier provided the possibility of selective benzoylation of primary alcohols in the presence of secondary alcohols. In earlier reports, selective benzoylation of primary alcohols over secondary alcohols of carbohydrate derivatives has been carried out using benzoyl chloride and pyridine at low temperature[39] through the use of highly toxic benzoyl cyanide[40] or through stannylidene acetal derivatives.[41] In our hands, selective acetylations of primary alcohol of carbohydrate derivatives were also achieved by using a limited quantity of acetyl chloride under controlled reaction conditions. Thus, selective acetylation of primary alcohols of the carbohydrate diols has been achieved by using 1.2 M equiv acetyl chloride and 2.0 M equiv basic Al_2O_3 from 0 to 10 °C. In the case of pivaloylations, no secondary alcohol protected products were observed, even after prolonged reaction times (Table 3). It is worth noting that among the solvents most frequently used for acylation reactions, for example, dichloromethane, CH_3CN, dichloroethane, THF, that CH_3CN was the most effective, producing both high product yields and cleaner reactions (Table 4).

After selective and complete acylation of a wide range of partially protected carbohydrate derivatives, the methodology was extended to the acylation of unprotected reducing sugars. Thus, a series of unprotected sugars were reacted with acetyl chloride (1.2 equiv per OH group) and benzoyl chloride (1.5 equiv per OH group) over basic Al_2O_3 (2.0 equiv per OH group) either in CH_3CN or under solvent-free conditions. In the case of acetylation, complete reaction was observed in a few hours. While the formation of the per-O-acetylated sugar derivatives, a faster moving spot on TLC was also

Table 1. Per-O-acylation of carbohydrate derivatives over basic Al_2O_3 (2.0 equiv per OH) as a solid support at room temperature

Entry	Substrate (**1**)	% Yield of per-O-acylated product (time in h)			
		AcCl[a] (**2**)	BzCl[b] (**3**)	CACl[b] (**4**)	Ac_2O[c]
a		98 (1.0)[48] [99][d]	90 (2.5) [92][d]	—	30 (48.0)
b		95 (1.0) [98][d]	—	—	20 (48.0)
c		96 (1.0)[49] [95][d]	92 (2.5)	—	—
d		94 (0.5)[50]	—	—	—
e		98 (0.5)[51] [98][d]	—	—	40 (48.0)
f		95 (0.5)[52]	—	—	—
g		98 (1.0)[18]	—	—	—
h		—	—	88 (0.5)	—

AcCl: Acetyl chloride; BzCl: benzoyl chloride; CACl: chloroacetyl chloride; Ac_2O: acetic anhydride. The numbered superscripts correspond to literature references of the products.

[a] 1.2 equiv per OH.

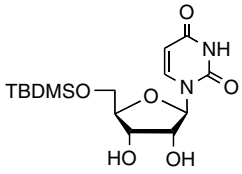
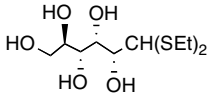
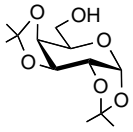
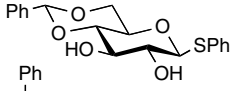
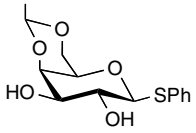
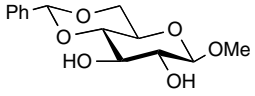
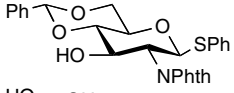
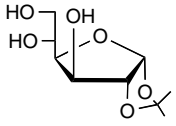
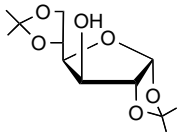
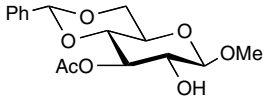
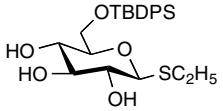
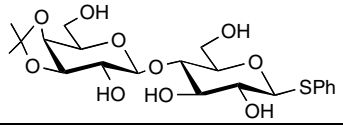
[b] 1.5 equiv per OH.

[c] 2.0 equiv per OH.

[d] Yields obtained under solvent-free conditions.

noticed, whose formation increased with time. After some experimentation, it was confirmed that the faster moving compounds were per-O-acetylated glycopyranosyl chlorides. To isolate the acetylated glycosyl chlorides, similar acetylation reactions were carried out using an excess of acetyl chloride (2.5 equiv per OH group) and the reaction times were extended to allow for complete conversion of initially formed per-O-acetylated sugars to the acetylated sugar chlorides. Acetylated glycosyl chlorides are important intermediates in oligosaccharide syntheses, as well as in the generation of anomeric carbocations and radicals. Although, the preparation of acetylated glycosyl chlorides has been reported earlier, most have used per-O-acetylated glycopyranoses as the starting materials.[21,24,42–47] Using the present protocol, the preparation of acetylated glycosyl chlorides can be achieved directly from unprotected sugars. The results of acetylation and conversion to the glycosyl chlorides using a series of unprotected sugars are presented in Table 5. The same protocol was applied to the case of benzoylation of free sugars using benzoyl chloride over basic Al_2O_3 and it took significantly longer for the reaction to furnish per-O-benzoylated sugars. Further addition of benzoyl chloride or longer reaction time did not produce benzoylated glycosyl chlorides. It was observed that the time required for acylation of unprotected sugars was much more than the partially protected carbohydrate derivatives. To extend this protocol, D-glucose was treated with acetyl

Table 2. Per-O-acylation of carbohydrate derivatives containing acid labile functional groups over basic Al_2O_3 (2.0 equiv per OH) as a solid support at room temperature

Entry	Substrate (**5**)	% Yield of per-O-acylated product (time in min)			
		AcCl[a] (**6**)	BzCl[b] (**7**)	CACl[b] (**8**)	Ac_2O[c]
a		98 (30)	—	—	—
b		96 (60) [95][d]	—	—	30 (48.0)
c		98 (20)[22] [98][d]	95 (45)	90 (20)	—
d		92 (40)	92 (90)	—	—
e		95 (40)	90 (90)	—	—
f		96 (40)[53] [95][d]	92 (90)	—	—
g		98 (25)	—	90 (45)	20 (48.0)
h		98 (20)	—	—	—
i		98 (30)	98 (45)	96 (20)	30 (48.0)
j		—	88 (60)	—	—
k		—	90 (120)	—	—
l		92 (90)	—	—	—

AcCl: Acetyl chloride; BzCl: benzoyl chloride; CACl: chloroacetyl chloride; Ac_2O: acetic anhydride. The numbered superscripts correspond to literature references of the products.

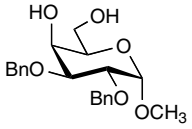
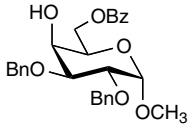
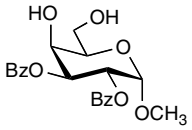
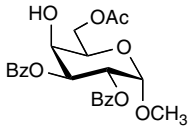
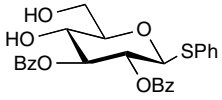
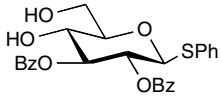
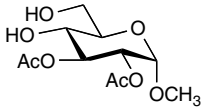
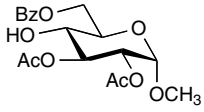
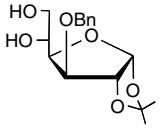
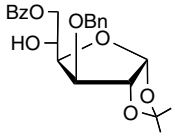
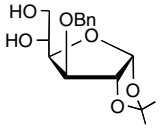
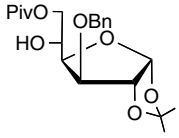
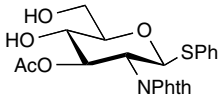
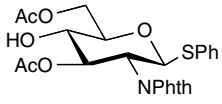
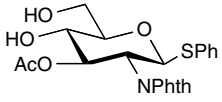
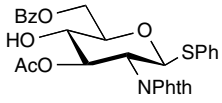
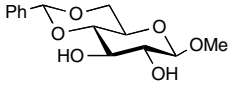
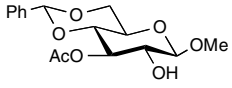
[a] 1.2 equiv per OH.

[b] 1.5 equiv per OH.

[c] 2.0 equiv per OH.

[d] Yields obtained under solvent-free conditions.

Table 3. Selective acylation of carbohydrate diols over basic Al_2O_3 (2.0 M equiv) using acyl chlorides[a]

Entry	Sugar diol (**9**)	Product (**10**)	Time (h)	Acyl chloride (equiv)	Yield (%)
a			4.0	Benzoyl chloride (1.5)	92
b			1.5	Acetyl chloride (1.2)	90
c			2.0	Acetyl chloride (1.2)	90
d			4.0	Benzoyl chloride (1.5)	85
e			4.5	Benzoyl chloride (1.5)	92
f			8.0	Pivaloyl chloride (1.2)	88
g			1.0	Acetyl chloride (1.2)	95
h			2.0	Benzoyl chloride (1.5)	92
i			45 min[b]	Acetyl chloride (1.2)	65

[a] Reaction conditions: Sugar diol (1.0 mmol), basic Al_2O_3 (2.0 mmol), and acyl chloride (1.2 mmol) in CH_3CN (5.0 mL) was stirred at 5–10 °C.
[b] Reaction carried out at 0 °C; a small amount of 2-O-acetylated product (~20%) was also isolated.

Table 4. Comparison of solvents in the acetylation of carbohydrates using acetyl chloride over Al_2O_3 as a solid support

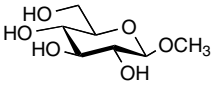
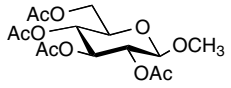
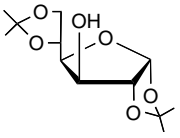
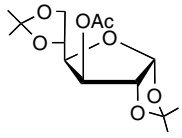
Entry	Substrate	Product	Solvent	Time (h)	Yield (%)
1			CH_3CN	1.0	98
			THF	2.5	95
			CH_2Cl_2	5.0	85
			$ClCH_2CH_2Cl$	5.0	90
2			CH_3CN	0.5	98
			THF	1.5	92
			CH_2Cl_2	1.0	95
			$ClCH_2CH_2Cl$	1.0	95

Table 5. Acylation of unprotected carbohydrates over basic Al_2O_3 (2.0 equiv per OH group) using acyl chlorides[a]

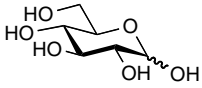
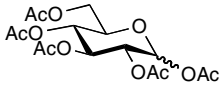
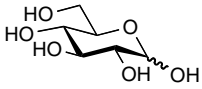
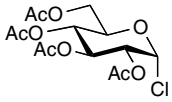
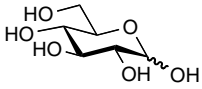
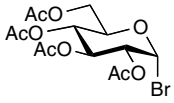
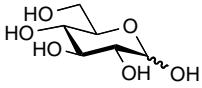
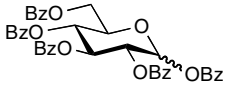
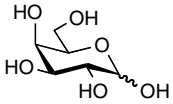
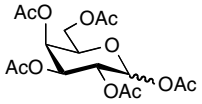
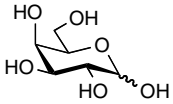
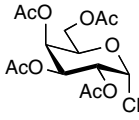
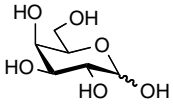
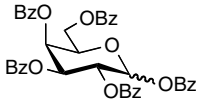
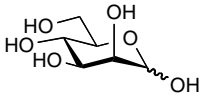
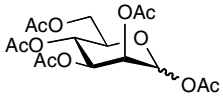
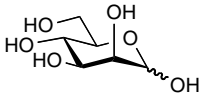
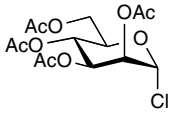
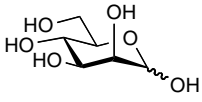
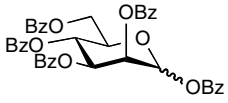
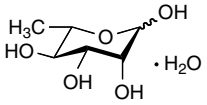
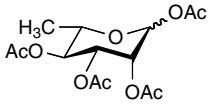
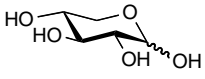
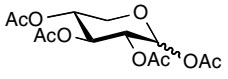
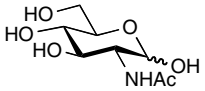
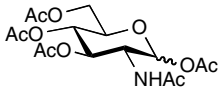
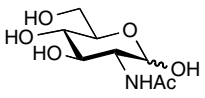
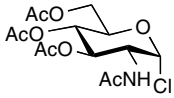
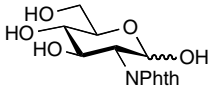
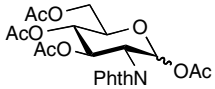
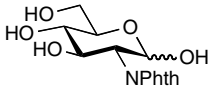
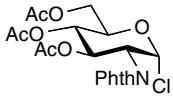
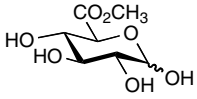
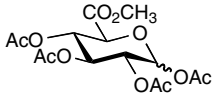
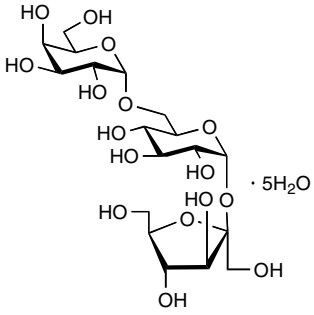
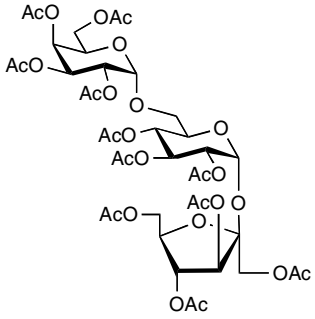
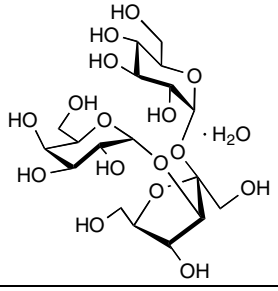
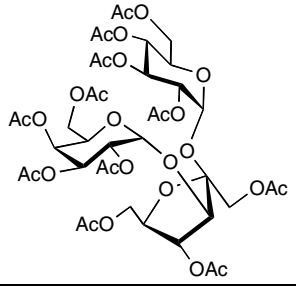
Entry	Sugars (**11**)	Products (**12**)	Time (h)	Acyl chloride (equiv)	Yield (%)[b]	α/β[c]	Ref.
a			1.5	Acetyl chloride (6.0)	97	5.9:1	18
b			5	Acetyl chloride (12.5)	90	α	24
c			4	Acetyl bromide	20	α	—
d			12	Benzoyl chloride (7.5)	92	α	54
e			1.5	Acetyl chloride (6.0)	95	6.2:1	18
f			4.5	Acetyl chloride (12.5)	87	α	24
g			12	Benzoyl chloride (7.5)	92	3.4:1	54
h			1.5	Acetyl chloride (6.0)	92	4:1	18
i			4.5	Acetyl chloride (12.5)	85	α	24
j			10	Benzoyl chloride (7.5)	95	2.2:1	54
k			2	Acetyl chloride (6.0)	85	α	18
l			1	Acetyl chloride (4.8)	92	4.5:1	55
m			1	Acetyl chloride (4.8)	90	10:1	30
n			2.5	Acetyl chloride (10.0)	86	α	56

Table 5 (*continued*)

Entry	Sugars (**11**)	Products (**12**)	Time (h)	Acyl chloride (equiv)	Yield (%)[b]	α/β[c]	Ref.
o			1.5	Acetyl chloride (4.8)	92	1:1.3	57
p			2.5	Acetyl chloride (10.0)	85	1:1	58
q			2	Acetyl chloride (4.8)	90	β	59
r			1.5	Acetyl chloride (20.0)	92	—	32
s			1.5	Acetyl chloride (15.0)	95	—	32

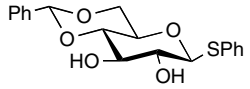
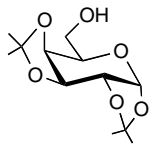
[a] All reactions were carried out at room temperature.
[b] Isolated yield.
[c] α/β ratio was determined from the ^{1}H NMR spectra of the inseparable mixture.

bromide in the presence of Al_2O_3 in an identical molar ratio of reagents as used in the case of acetyl chloride. As expected, acetobromoglucose was formed; however, the isolated product was mostly the corresponding hemiacetal because of the instability of acetobromoglucose compared to acetochloroglucose. In both the case of acetylation and benzoylation, formation of per-O-acylated furanosyl glycoses was not observed, which was confirmed from the NMR spectra of the products. From the above-mentioned observations it is evident that though the use of this one-pot reaction protocol that per-O-acylated sugar derivatives and acetylated glycosyl chlorides can be prepared efficiently directly from unprotected reducing sugars by controlling the acylating agents and reaction time.

To further prove the efficacy of this method, a comparison study with previously reported methods for acylation of carbohydrates was carried out (Table 6). Most of the previously reported protocols either (1) take a longer reaction time for completion; (2) require prior preparation of the catalyst; (3) use hazardous chemicals as an activator; or (4) cannot be used with acid labile functional groups. From the comparison in Table 6, it is clear that the present protocol has significant advantages over previously reported methods. Although in some cases, the yield is comparable to the earlier reports (e.g., use of iodine or $HClO_4$–SiO_2), the most notable advantage is that it can acylate carbohydrate derivatives containing acid labile functional groups very efficiently without any side reactions.

In conclusion, a simple, efficient, and economical protocol for the acylation of carbohydrates has been devised using Al_2O_3, which avoids the use of any acid or base as an activator. This methodology has been further extended to the selective acylation of carbohydrate derivatives and also the one-pot preparation of acetylated glycosyl chlorides directly from free sugars. In most of the cases, yields were good to excellent. This

Table 6. Comparative study of acetylation using different reported catalysts

Substrate	Reagent (equiv)	Catalyst	Time (min)	Yield (%)	Ref.
	Ac_2O (5.0)	Pyridine (excess)	60.0	95	9 and 10
	Ac_2O (4.0)	I_2	30.0	30 (with degraded product)	16
	Ac_2O (2.2)	$Cu(OTf)_2$	300.0	90	18
	Ac_2O (3.0)	$InCl_3$	2.0	20 (with degraded product)	29[a]
	Ac_2O (2.2)	$HClO_4$–SiO_2	20.0	10 (with degraded product)	32
	Ac_2O (3.0)	Al_2O_3 (2.0 equiv)	12.0 h	20 (reaction not completed)	33
	AcCl (2.4)	Al_2O_3 (2.0 equiv)	40.0	92	This work[b]
	Ac_2O (2.5)	Pyridine (excess)	45	95	9 and 10
	Ac_2O (2.0)	I_2	20	40 (with degraded product)	16
	Ac_2O (1.1)	$Cu(OTf)_2$	300	80	18
	Ac_2O (1.5)	$InCl_3$	2.0	35 (with degraded product)	29[a]
	Ac_2O (1.2)	$HClO_4$–SiO_2	30.0	No desired product isolated	32
	Ac_2O (1.5)	Al_2O_3	12.0 h	30 (reaction not completed)	33
	AcCl (1.2)	Al_2O_3	20	98	This work[b]

[a] Microwave irradiation.
[b] Reaction conditions: Diol (1.0 mmol), basic Al_2O_3 (2.0 mmol), and acyl chloride in CH_3CN (5.0 mL) was stirred at room temperature.

method is operationally simple and does not require any aqueous workup, which therefore reduces purification of the products. Along with these features, this method may be considered as an attractive alternative to the existing methodologies for the acylation of carbohydrates particularly those containing acid-susceptible functionalities.

1. Experimental

1.1. General

All reactions were monitored by thin-layer chromatography using silica gel coated TLC plates. Spots on TLC were visualized by warming ceric sulfate (2% $CeSO_4$ in 2 N H_2SO_4) sprayed plates in hot plate at ~150 °C. Silica gel 100–200 mesh (SRL, India) was used for column chromatography. ESI-MS mass spectra were recorded on Micromass Quattro II. ^1H and ^{13}C NMR was recorded on Bruker Advance DPX 200 MHz using TMS as the internal reference. Chemical shift values are expressed in δ parts per million. Elemental analysis was carried out on Carlo ERBA-1108 analyzer. Optical rotations were measured at 25 °C on a Rudolf Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity were used in reactions.

1.2. General procedure for complete acylation of partially protected carbohydrate derivatives

To a stirred suspension of the sugar alcohol (1.0 mmol) and basic Al_2O_3 (204.0 mg, 2.0 mmol) in distilled CH_3CN (5.0 mL) was added acid chloride (1.20 mmol; in the case of benzoyl chloride 1.5 mmol) in one portion at rt and the reaction mixture was allowed to stir for appropriate time as mentioned in Tables 1 and 2. After completion of the reaction as monitored by TLC (hexane–EtOAc 2:1), the reaction mixture was filtered through Celite and evaporated followed by coevaporation twice with toluene under reduced pressure. Although in most of the cases, considerably pure products were obtained, analytical samples were prepared by passing the reaction product through a column over SiO_2 using hexane–EtOAc as the eluant.

1.3. General procedure for complete acylation of partially protected carbohydrate derivatives under solvent-free conditions

The molar ratio of substrate and reagents were exactly as mentioned above for the complete acylation procedure, except the reaction was performed without using any solvent. After completion of the reaction, the mixture was diluted with CH_2Cl_2 and filtered through Celite and the filtrate was removed under reduced pressure to furnish the product.

1.4. General procedure for selective acylation of partially protected carbohydrate derivatives

An acid chloride (acetyl chloride (1.20 mmol), benzoyl chloride (1.50 mmol), pivaloyl chloride (1.2 mmol)) was added to a stirred solution of carbohydrate derivative (1.0 mmol) and basic Al_2O_3 (204.0 mg, 2.0 mmol) in CH_3CN (5.0 mL) at 15–20 °C. After allowing the mixture to stir for appropriate time (Table 3), the mixture was filtered through Celite and the filtrate was removed to furnish selectively acylated product.

1.5. General procedure for complete acylation of unprotected reducing sugars

To a suspension of carbohydrate (1.0 mmol) and basic Al_2O_3 (2.0 equiv per OH) in CH_3CN (5.0 mL) was added an acid chloride (acetyl chloride (1.2 equiv per

OH), benzoyl chloride (1.5 equiv per OH)) in one portion and the reaction mixture was allowed to stir at rt for appropriate time (Table 5). After completion of the reaction, the mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was evaporated to furnish per-O-acylated carbohydrate derivatives.

1.6. General procedure for the one-pot preparation of acetylated glycosyl chlorides from unprotected reducing sugars

To a suspension of carbohydrate (1.0 mmol) and basic Al_2O_3 (2.0 equiv per OH) in CH_3CN (5.0 mL) was added acetyl chloride (2.5 equiv per OH) in one portion and the reaction mixture was allowed to stir at rt for the appropriate time (Table 5). After completion of the reaction, the mixture was diluted with CH_2Cl_2 and filtered through a Celite. The filtrate was evaporated to furnish the acylated glycosyl chloride.

1.7. Spectral data for new compounds

1.7.1. 5,6,7,9-Tetra-*O*-acetyl-4,8-anhydro-1,3-dideoxy-D-*glycero*-L-*gluco*-nonulose (2b). White solid; mp 91–92 °C; $[\alpha]_D^{25}$ +5.6 (*c* 1.5, $CHCl_3$); IR (KBr): 2941, 2884, 1746, 1704, 1383, 1227, 1097, 1038, 908 cm^{-1}; ^1H NMR: δ 5.34 (br s, 1H, H-7), 5.01–4.98 (m, 2H, H-5 and H-6), 4.05–3.98 (m, 2H, H-$9_{a,b}$), 3.96–3.85 (m, 2H, H-4, H-8), 2.81–2.68 (dd, $J = 16.3$, 8.5 Hz, 1H, H-3_a), 2.50–2.40 (dd, $J = 16.4$, 3.4 Hz, 1H, H-3_b), 2.16, 2.15, 2.02, 2.01, 1.96 (5s, 15H, 5COCH_3); ^{13}C NMR ($CDCl_3$): δ 204.5, 169.9 (2C), 169.7, 169.6, 74.4, 74.3, 71.9, 69.3, 67.9, 61.6, 45.6, 30.9, 20.7, 20.6 (2C), 20.5; ESI-MS (M+Na): 411; Anal. Calcd for $C_{17}H_{24}O_{10}$: C, 52.57; H, 6.23. Found: C, 52.48; H, 6.30.

1.7.2. 2,3-Di-*O*-acetyl-5-*O*-*tert*-butyldimethylsilyl uridine (6a). White solid; mp 83.5 °C; $[\alpha]_D$ −2.6 (*c* 1.5, $CHCl_3$); IR (KBr): 3202, 3072, 2929, 2858, 1749, 1715, 1460, 1380, 1241, 1125, 1101, 1046, 834, 813, 778, 757 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.18 (br s, 1H, NH), 7.72 (d, $J = 9.0$ Hz, 1H), 6.15 (d, $J = 6.0$ Hz, 1H), 5.62 (d, $J = 9.0$ Hz, 1H), 5.20–5.18 (m, 2H), 4.09 (br s, 1H), 3.85–3.73 (m, 2H), 2.04, 1.98 (2s, 6H, 2COCH_3), 0.85 (s, 9H, C(CH_3)$_3$), 0.06 (s, 6H, 2CH_3Si); ^{13}C NMR ($CDCl_3$): δ 169.3, 169.0, 163.0, 150.6, 139.0, 103.0, 85.0, 83.4, 73.1, 71.4, 63.0, 25.7 (2C), 25.4, 20.4, 20.1, 18.1, −5.8 (2C); ESI-MS (M+Na): 465; Anal. Calcd for $C_{19}H_{30}N_2O_8Si$: C, 51.57; H, 6.83. Found: C, 51.31; H, 7.02.

1.7.3. 2,3,4,5,6-Penta-*O*-acetyl-D-glucose diethyl dithioacetal (6b). White solid; mp 47 °C; $[\alpha]_D$ +13.2 (*c* 1.5, $CHCl_3$); IR (KBr): 2971, 2932, 1752, 1432, 1372, 1219, 1069, 1033, 967, 758 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.76 (dd, $J = 7.5$, 2.7 Hz, 1H), 5.43 (dd, $J = 8.1$, 2.7 Hz, 1H), 5.28 (dd, $J = 7.5$, 4.2 Hz, 1H), 5.06 (m, 1H), 4.27 (dd, $J = 16.8$, 3.0 Hz, 1H), 4.13 (dd, $J = 17.0$, 4.8 Hz, 1H), 4.07 (d, $J = 4.2$ Hz, 1H, H-1), 2.80–2.72 (m, 2H), 2.62–2.54 (m, 2H), 2.14, 2.09, 2.08, 2.06, 2.05 (5s, 15H, 5COCH_3), 1.31 (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 1.22 (t, $J = 7.2$ Hz, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.5, 170.2 (2C), 169.9, 72.5, 70.4, 68.8 (2C), 61.8, 51.2, 25.9, 25.3, 21.0 (2C), 20.9 (3C), 14.8, 14.6; ESI-MS (M+Na): 519; Anal. Calcd for $C_{20}H_{32}O_{10}S_2$: C, 48.37; H, 6.50. Found: C, 48.20; H, 6.75.

1.7.4. Phenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (6d). White solid; mp 119 °C; $[\alpha]_D$ −2.1 (*c* 1.2, $CHCl_3$); IR (Neat): 2956, 2893, 1748, 1586, 1481, 1439, 1373, 1225, 1089, 1041, 912, 744, 686. ^1H NMR ($CDCl_3$): δ 7.46–7.25 (m, 10H, aromatic), 5.49 (s, 1H, PhCH), 5.33 (dd, $J = 8.9$, 9.1 Hz, 1H, H-2), 5.04–4.96 (dd, $J = 9.8$, 8.9 Hz, 1H, H-3), 4.80 (d, $J = 9.9$ Hz, 1H, H-1), 4.39 (m, 1H, H-5), 3.79 (dd, $J = 10.0$, 9.4 Hz, 1H, H-40), 3.71–3.56 (m, 2H, H-6_{ab}), 2.10, 2.03 (2s, 6H, 2COCH_3); ESI-MS (M+Na): 467; Anal. Calcd for $C_{23}H_{24}O_7S$: C, 62.15; H, 5.44. Found: C, 61.94; H, 5.60.

1.7.5. Phenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (6e). Oil; $[\alpha]_D$ −19 (*c* 1.5, $CHCl_3$); IR (Neat): 2887, 1734, 1630, 1586, 1441, 1403, 1375, 1295, 1250, 1225, 1180, 1092, 1052, 999, 933, 745, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.62–7.25 (m, 10H, aromatic), 5.46 (s, 1H, PhC*H*), 5.34 (t, $J = 9.8$ Hz, 1H, H-2), 5.00 (dd, $J = 9.9$, 3.4 Hz, 1H, H-3), 4.69 (d, $J = 9.7$ Hz, 1H, H-1), 4.36 (m, 2H, H-4, H-6_a), 4.00 (dd, $J = 12.4$, 1.4 Hz, 1H, H-6_b), 3.59–3.56 (m, 1H, H-5), 2.08, 2.02 (2s, 6H, 2COCH_3); ESI-MS (M+Na): 467; Anal. Calcd for $C_{23}H_{24}O_7S$: C, 62.15; H, 5.44. Found: C, 61.90; H, 5.65.

1.7.6. Phenyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (6g). White solid; mp 115 °C; $[\alpha]_D$ +18 (*c* 1.2, $CHCl_3$); IR (KBr): 2934, 2829, 2367, 1715, 1595, 1366, 1228, 1105, 1030, 966, 719 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.85–7.71 (m, 4H, aromatic), 7.42–7.25 (m, 10H, aromatic), 5.84 (dd, $J = 9.5$, 9.0 Hz, 1H, H-3), 5.80 (d, $J = 10.6$ Hz, 1H, H-1), 5.50 (s, 1H, PhC*H*), 4.41 (d, $J = 5.9$ Hz, 1H, H-4), 4.30 (dd, $J = 10.2$, 10.1 Hz, 1H, H-2), 3.82–3.70 (m, 3H, H-5 and H-6_{ab}), 1.87 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 17.5, 168.2, 167.6, 137.3–124.1 (aromatic), 102.1, 84.3, 79.4, 70.9, 69.0, 54.7, 20.9; ESI-MS (M+Na): 554; Anal. Calcd for $C_{29}H_{25}NO_7S$: C, 65.52; H, 4.74. Found: C, 65.70; H, 4.96.

1.7.7. 3,5,6-Tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (6h). White solid; mp 78 °C; $[\alpha]_D$ +23.8 (*c* 1.2, $CHCl_3$); IR (KBr): 2994, 2364, 1741, 1595, 1378, 1244,

1166, 1079, 1026 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.93 (d, $J = 3.5$ Hz, 1H), 5.35 (d, $J = 2.8$ Hz, 1H), 5.27–5.13 (m, 1H), 4.60 (dd, 2.2, 16.3 Hz, 1H), 4.48 (d, $J = 3.6$ Hz, 1H), 4.39 (dd, $J = 2.0$, 14.0 Hz, 1H), 4.17–4.03 (m, 1H), 2.06 (s, 6H, 2COCH_3), 2.01 (s, 3H, COCH_3), 1.52, 1.32 (2s, 6H, C(CH_3)$_2$); ESI-MS (M+Na): 369; Anal. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40. Found: C, 51.83; H, 6.62.

1.7.8. Phenyl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (6i). Oil; $[\alpha]_D$ +5.4 (*c* 1.2, $CHCl_3$); IR (KBr): 2923, 2855, 2363, 1730, 1461, 1218, 769 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.52–7.20 (m, 5H, aromatic), 5.30–5.16 (dd, $J = 10.8$, 8.1 Hz, 1H, H-2), 4.92 (t, $J = 9.5$ Hz, 1H, H-2′), 4.87–4.80 (m, 1H), 4.68 (d, $J = 9.8$ Hz, 1H, H-1), 4.53 (d, $J = 11.2$ Hz, 1H, H-1′), 4.35–4.20 (m, 3H), 4.19–4.02 (m, 3H), 3.95–3.90 (m, 1H), 3.80–3.55 (m, 2H), 2.08, 2.04 (2s, 15H, 5COCH_3), 1.52, 1.31 (2s, 6H, C(CH_3)$_2$); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.4, 170.0, 169.4, 169.3, 133.2–128.4 (aromatic), 111.0, 100.6, 85.7, 78.1, 77.2, 76.2, 73.8, 73.4, 72.9, 71.2, 70.6, 63.4, 62.7, 27.7, 26.5, 21.0 (3C), 20.9 (2C); ESI-MS (M+Na): 707; Anal. Calcd for $C_{31}H_{40}O_{15}S$: C, 54.38; H, 5.89. Found: C, 54.03; H, 6.10.

1.7.9. Phenyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (6j). White solid; mp 211 °C; $[\alpha]_D$ −43 (*c* 1.2, $CHCl_3$); IR (KBr): 2930, 1729, 1598, 1453, 1352, 1270, 1094, 1025, 995, 706 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.95–7.89 (m, 4H, aromatic), 7.49–7.25 (m, 16H, aromatic), 5.75 (t, $J = 9.3$ Hz, 1H, H-2), 5.48 (s, 1H, PhCH), 5.41 (t, $J = 9.3$ Hz, 1H, H-3), 4.99 (d, $J = 9.9$ Hz, 1H, H-1), 4.42 (dd, $J = 9.9$, 4.5 Hz, 1H, H-4), 3.88–3.74 (m, 2H, H-6_{ab}), 3.73–3.67 (m, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 165.3, 164.9, 136.7–126.2 (aromatic), 101.5, 86.9, 78.6, 73.3, 71.0, 70.9, 68.5; ESI-MS (M+Na): 591; Anal. Calcd for $C_{33}H_{28}O_7S$: C, 69.70; H, 4.96. Found: C, 69.45; H, 5.22.

1.7.10. Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (6k). White solid; mp 187 °C; $[\alpha]_D$ −10.8 (*c* 1.2, $CHCl_3$); IR (KBr): 3021, 2929, 2365, 1715, 1571, 1218, 769, 672 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.12–7.30 (m, 15H, aromatic), 5.47 (s, 1H, PhC*H*), 5.32 (t, $J = 9.3$ Hz, 1H, H-2), 4.95 (t, $J = 8.0$ Hz, 1H, H-3), 4.48 (d, $J = 7.8$ Hz, 1H, H-1), 4.36 (dd, $J = 10.4$, 5.6 Hz, 1H, H-4), 3.77–3.63 (m, 2H, H-6_{ab}), 3.55–3.53 (m, 1H, H-5), 3.49 (s, 3H, CH_3); ESI-MS (M+Na): 513; Anal. Calcd for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.78; H, 5.50.

1.7.11. 3-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (7i). White solid; mp 66 °C; $[\alpha]_D$ −60 (*c* 1.2, $CHCl_3$); IR (KBr): 2926, 2365, 1724, 1657, 1584, 1437, 1352, 1219, 771, 676 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.08–7.99 (m, 2H, aromatic), 7.61–7.40 (m, 3H, aromatic), 5.91 (dd, $J = 3.5$, 1.7 Hz, 1H), 5.47 (br s, 1H), 4.60 (dd, $J = 3.5$, 1.1 Hz, 1H), 4.38–4.22 (m, 2H), 4.10–4.01 (m, 2H), 1.55, 1.42, 1.31, 1.26 (4s, 12H, C(CH_3)$_2$); ^{13}C NMR ($CDCl_3$): δ 165.1, 133.6–128.6 (aromatic), 112.5, 109.6, 105.4, 83.8, 80.3, 76.7, 72.9, 67.6, 27.3, 27.2, 26.7, 25.6; ESI-MS (M+Na): 387; Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.40; H, 6.90.

1.7.12. Methyl 3-*O*-acetyl-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (7j). Oil; $[\alpha]_D$ −68 (*c* 1.2, $CHCl_3$); IR (Neat): 2937, 1735, 1600, 1459, 1367, 1278, 1100, 1020, 990, 716 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.03–7.99 (m, 2H, aromatic), 7.53–7.27 (m, 8H, aromatic), 5.60 (t, $J = 9.4$ Hz, 1H, H-2), 5.51 (s, 1H, PhC*H*), 5.20 (dd, $J = 7.8$, 9.4 Hz, 1H, H-3), 4.58 (d, $J = 7.8$ Hz, 1H, H-1), 4.44–4.36 (dd, $J = 4.6$, 10.3 Hz, 1H, H-4), 3.84 (t, $J = 9.4$ Hz, 2H, H-6_{ab}), 3.63 (dd, $J = 4.8$, 9.3 Hz, 1H, H-5), 3.53 (s, 3H, CH_3), 1.97 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 169.9, 166.0, 137.2, 133.6, 130.3 (2C), 129.9, 129.4, 128.8 (2C), 128.6 (2C), 126.5 (2C), 102.8, 101.8, 79.2, 72.7, 72.4, 69.0, 66.9, 57.6, 21.1; ESI-MS (M+Na): 451; Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.15; H, 5.82.

1.7.13. Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (7k). White solid; mp 117 °C; $[\alpha]_D$ +18.6 (*c* 1.5, $CHCl_3$); IR (KBr): 2372, 1722, 1596, 1352, 706 cm^{-1}; ^1H NMR: δ 7.97 (d, $J = 7.5$ Hz, 2H), 7.90–7.84 (m, 4H), 7.74–7.72 (m, 2H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.56–7.49 (m, 2H), 7.45–7.29 (m, 11H), 7.22–7.18 (m, 2H), 5.84 (dd, $J = 9.3$, 9.6 Hz, 1H, H-2), 5.70 (dd, $J = 9.6$, 9.9 Hz, 1H, H-3), 5.57 (t, $J = 9.6$ Hz, 1H, H-4), 4.81–4.78 (d, $J = 9.9$ Hz, 1H, H-1), 3.87–3.84 (m, 3H, H-5, H-6_{ab}), 2.91–2.76 (dq, 2H, CH_2CH_3), 1.34 (t, $J = 7.5$ Hz, 3H, CH_2CH_3), 1.08 (s, 9H, C(CH_3)$_3$); ESI-MS (M+Na): 797; Anal. Calcd for $C_{45}H_{46}O_8SSi$: C, 69.74; H, 5.98. Found: C, 69.93; H, 6.25.

1.7.14. 3-*O*-Chloroacetyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (8i). Yellow oil; $[\alpha]_D$ −78.6 (*c* 1.2, $CHCl_3$); IR (Neat): 2990, 2930, 1754, 1378, 1256, 1218, 1162, 1077, 1025, 847, 759 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.84 (d, $J = 3.6$ Hz, 1H), 5.28 (d, $J = 1.5$ Hz, 1H), 4.48 (d, $J = 3.6$ Hz, 1H), 4.17 (m, 2H), 4.11–4.04 (m, 3H), 3.96 (m, 1H), 1.50, 1.39 (2s, 6H, C(CH_3)$_2$), 1.29 (s, 6H, C(CH_3)$_2$); ESI-MS (M+Na): 359; Anal. Calcd for $C_{14}H_{21}ClO_7$: C, 49.93; H, 6.29. Found: C, 49.75; H, 6.55.

1.7.15. Methyl 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (10a). Oil; $[\alpha]_D$ +306 (*c* 1.2, $CHCl_3$); IR (Neat): 3449, 3018, 2926, 2371, 1720, 1454, 1275, 1218,

1101, 1049, 766, 711 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.06–7.96 (m, 2H, aromatic), 7.54–7.24 (m, 13H, aromatic), 4.81 (dd, $J = 11.6$, 2.9 Hz, 2H, PhCH_2), 4.72 (br s, 1H, H-1), 4.68–4.62 (dd, $J = 1.6$, 12.0 Hz, 2H, PhCH_2), 4.57–4.46 (m, 2H, H-6_{ab}), 4.00–3.97 (m, 2H, H-2, H-3), 3.86–3.85 (m, 2H, H-4, OH), 3.46–3.44 (m, 1H, H-5), 3.36 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$): δ 166.3, 138.7–128.2 (aromatic), 98.8, 77.7, 76.2, 73.8, 73.4, 68.2, 67.9, 64.3, 55.7; ESI-MS (M+Na): 501; Anal. Calcd for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32. Found: C, 70.03; H, 6.55.

1.7.16. Methyl 6-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-glucopyranoside (10b). Oil; $[\alpha]_D$ +232 (*c* 1.2, $CHCl_3$); IR (Neat): 3428, 3021, 2373, 1724, 1217, 1033, 764, 670 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.02–7.96 (m, 4H, aromatic), 7.55–7.33 (m, 6H, aromatic), 5.74 (t, $J = 8.5$, 9.6 Hz, 1H, H-2), 5.25 (dd, $J = 10.1$, 2.5 Hz, 1H, H-3), 5.13 (br s, 1H, H-1), 4.45 (dq, $J = 12.1$, 3.7 Hz, 2H, H-6_{ab}), 4.01–3.96 (m, 1H, H-5), 3.80 (t, $J = 9.6$, 9.1 Hz, 1H, H-4), 3.43 (s, 3H, OCH_3), 2.15 (s, 3H, COCH_3); ESI-MS (M+Na): 467; Anal. Calcd for $C_{23}H_{24}O_9$ (444): C, 62.16; H, 5.44. Found: C, 62.37; H, 5.68.

1.7.17. Phenyl 6-*O*-acetyl-2,3-di-*O*-benzoyl-1-thio-β-D-glucopyranoside (10c). Oil; $[\alpha]_D$ +93.4 (*c* 1.2, $CHCl_3$); IR (Neat): 3427, 3020, 2926, 2855, 2374, 1722, 1656, 1525, 1460, 1218, 771, 671 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.97–7.90 (m, 4H, aromatic), 7.53–7.48 (m, 4H, aromatic), 7.39–7.25 (m, 7H, aromatic), 5.48 (dd, $J = 9.0$, 8.4 Hz, 1H, H-2), 5.40 (dd, $J = 9.6$, 9.3 Hz, 1H, H-3), 4.95 (d, $J = 9.6$ Hz, 1H, H-1), 4.51–4.39 (m, 2H, H-6_{ab}), 3.84–3.77 (m, 2H, H-4, OH), 3.48–3.47 (m, 1H, H-5), 2.10 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 171.3, 167.3, 165.3, 133.5–128.2 (aromatic), 86.0, 78.2, 77.8, 70.1, 69.4, 63.2, 20.8; ESI-MS (M+Na): 545; Anal. Calcd for $C_{28}H_{26}O_8S$: C, 64.36; H, 5.01. Found: C, 64.12; H, 5.25.

1.7.18. Methyl 2,3-di-*O*-acetyl-6-*O*-benzoyl-α-D-glucopyranoside (10d). Oil; $[\alpha]_D$ +110 (*c* 1.2, $CHCl_3$); IR (Neat): 3486, 3022, 2371, 1724, 1449, 1373, 1277, 1218, 1054, 762, 714, 669 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.07–8.03 (m, 2H, aromatic), 7.61–7.40 (m, 3H, aromatic), 5.34 (dd, $J = 9.6$, 9.4 Hz, 1H, H-2), 4.92–4.90 (d, $J = 3.4$ Hz, 1H, H-1), 4.88–4.81 (dd, $J = 10.0$, 3.5 Hz, 1H, H-3), 4.76–4.68 (dd, $J = 12.1$, 4.3 Hz, 1H, H-6_a), 4.56–4.49 (dd, $J = 12.0$, 1.7 Hz, 1H, H-6_b), 3.97–3.92 (m, 1H, H-5), 3.62 (dd, $J = 9.4$, 9.3 Hz, 1H, H-4), 3.40 (s, 3H, OCH_3), 31.6 (br s, 1H, OH), 2.08 (s, 6H, 2COCH_3); ^{13}C NMR ($CDCl_3$): δ 171.5, 170.5, 167.0, 133.5–128.8 (aromatic), 97.2, 73.2, 71.2, 70.2, 69.7, 63.8, 55.5, 21.2, 21.0; ESI-MS (M+Na): 405; Anal. Calcd for $C_{18}H_{22}O_9$: C, 56.54; H, 5.80. Found: C, 56.30; H, 6.01.

1.7.19. 6-*O*-Benzoyl-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (10e). Oil; $[\alpha]_D$ +55 (*c* 1.2, $CHCl_3$); IR (Neat): 3449, 2925, 2854, 2370, 1721, 1276, 1219, 1075, 771 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.07–8.03 (m, 2H, aromatic), 7.56–7.26 (m, 8H, aromatic), 5.97 (br s, 1H, H-1), 4.77–4.55 (m, 5H), 4.48–4.39 (m, 1H), 4.35–4.24 (m, 2H), 4.20–4.15 (m, 1H), 1.48, 1.32 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$): δ 166.9, 137.2, 127.8, 111.7, 105.2, 82.2, 81.6, 79.6, 72.3, 68.0, 67.3, 26.9, 26.4; ESI-MS (M+Na): 437; Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.43; H, 6.55.

1.7.20. 3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-trimethylacetyl-α-D-glucofuranose (10f). Oil; $[\alpha]_D$ −49 (*c* 1.2, $CHCl_3$); IR (Neat): 3470, 2926, 2855, 1722, 1458, 1377, 1287, 1218, 1166, 1078, 1027, 763 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.36–7.25 (m, 5H, aromatic), 5.87–5.86 (d, $J = 3.3$ Hz, 1H, H-1), 4.71–4.57 (AB q, $J = 12.0$, 11.7 Hz, 2H, PhCH_2), 4.54 (d, $J = 3.6$ Hz, 1H), 4.37 (d, $J = 9.9$ Hz, 1H), 4.16 (dd, $J = 16.2$, 4.8 Hz, 2H), 4.09–4.05 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 178.9, 137.4–127.8 (aromatic), 111.6, 105.2, 105.0, 82.3, 81.7, 79.4, 72.3, 67.8, 66.6, 27.2 (3C), 26.9, 26.4; ESI-MS (M+Na): 417; Anal. Calcd for $C_{23}H_{26}O_7$: C, 63.94; H, 7.67. Found: C, 63.70; H, 7.90.

1.7.21. Phenyl 3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (10g). Oil; $[\alpha]_D$ +14 (*c* 1.2, $CHCl_3$); IR (Neat): 3434, 2922, 2854, 2369, 1720, 1380, 1222, 1082, 1034, 769 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.84–7.47 (m, 4H, aromatic), 7.41–7.24 (m, 5H, aromatic), 5.73–5.69 (d, $J = 10.5$ Hz, 1H, H-1), 5.63 (dd, $J = 9.6$, 9.3 Hz, 1H, H-3), 4.47–4.37 (m, 2H, H-6_{ab}), 4.21 (dd, $J = 10.5$, 10.2 Hz, 1H, H-4), 3.77–3.73 (m, 1H, H-5), 3.57 (dd, $J = 9.6$, 9.3 Hz, 1H, H-2), 2.12, 1.89 (2s, 6H, 2COCH_3); ESI-MS (M+Na): 508; Anal. Calcd for $C_{24}H_{23}NO_8S$: C, 59.35; H, 4.77. Found: C, 59.58; H, 5.00.

1.7.22. Phenyl 3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (10h). Oil; $[\alpha]_D$ +7.8 (*c* 1.2, $CHCl_3$); IR (Neat): 3475, 3020, 2926, 1777, 1719, 1385, 1276, 1219, 1082, 1042, 766, 717 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.05–8.02 (m, 2H, aromatic), 7.83–7.78 (m, 2H, aromatic), 7.70–7.45 (m, 3H, aromatic), 7.45–7.40 (m, 4H, aromatic), 7.19–7.07 (m, 3H, aromatic), 5.86 (d, $J = 10.5$ Hz, 1H, H-1), 5.73 (dd, $J = 9.6$, 9.3 Hz, 1H, H-3), 4.720 (d, $J = 11.4$ Hz, 1H, H-6_a), 4.59 (d, $J = 12.0$ Hz, 1H, H-6_b), 4.25 (dd, $J = 10.5$, 10.2 Hz, 1H, H-4), 3.97–3.95 (m, 1H, H-5), 3.66 (t, $J = 9.3$ Hz, 1H, H-2), 1.86 (s, 3H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 171.5, 168.2, 167.3, 166.8, 134.7–123.9 (aromatic), 83.0, 78.5, 74.6, 69.9, 64.2, 54.1, 20.9; ESI-MS (M+Na): 570; Anal. Calcd for $C_{29}H_{25}NO_8S$: C, 63.61; H, 4.60. Found: C, 63.38; H, 4.85.

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