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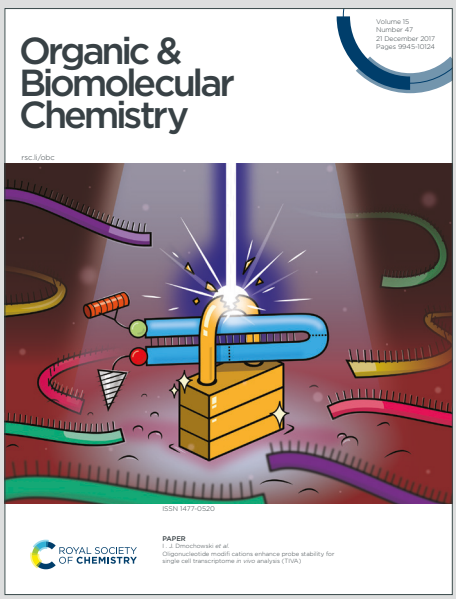

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ARTICLE

Triethylamine-Methanol Mediated Selective Removal of Oxophenylacetyl Ester in Saccharides

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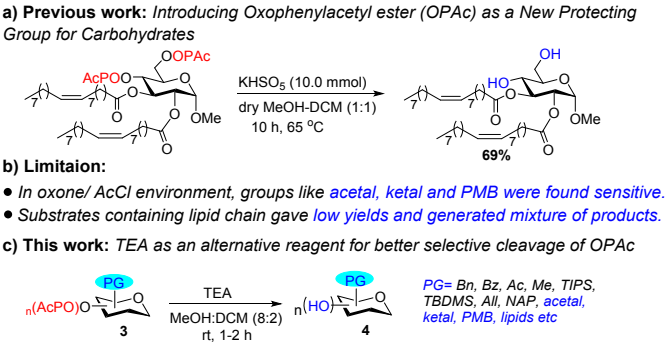
A highly selective, mild, and efficient method for the cleavage of oxophenylacetyl ester protected saccharides was developed using triethylamine in methanol at room temperature. The reagent proved successful against different labile groups like acetal, ketal, and PMB and also generated good yields of the desired saccharides bearing lipid esters. Further, we also observed DBU in methanol as an alternative reagent for the deprotection of acetyl, benzoyl, and oxophenylacetyl ester groups.

Introduction

Owing to the presence of multiple hydroxyl groups in saccharides and the need for controlled unmasking (orthogonality) of protecting groups in the chemical synthesis of oligosaccharides, careful manipulations are needed to obtain good selectivity and yield for the removal of a protecting group (PG).[1-5] The difficulty obviously arises from the presence of more groups with similar reactivity.[6-8] As a result, methods that can achieve high selectivity and good yields are indispensable.[9-12] Recently, we developed oxophenylacetyl ester (OPAc) as a new protecting group for carbohydrates and demonstrated its divergent base sensitivity profiles against benzoyl (Bz) and acetyl (Ac) groups.[13] Further, $KHSO_5$/AcCl in methanol was identified as an efficient deprotecting reagent for its removal in the presence of different protecting groups such as Bn, Bz, Ac, Me, TIPS, TBDMS, All, Nap, Levulinyl, Pivolyl, etc (Scheme 1a). However, acetal, ketal and PMB based protections were found sensitive to both reagents and, with the lipidated model saccharides, generated the desired product in lower yields with poor selectivity (Scheme 1b). To address this limitation and to improvise the better selectivity/yields, we envisage the possibility of testing different amine bases against OPAc. The key inspiration for this work is the enhanced electrophilic character of CO group in OPAc that might assist us to examine



Scheme 1: Summary of this work.

different reagents against time and concentration.[14] In this study, we established that different saccharides when treated with a fixed concentration of triethylamine in methanol selectively lead to the cleavage of OPAc in presence of other protecting groups in efficient yields (Scheme 1c). The method also proved to be very successful for the selective cleavage of OPAc against different labile groups like acetal, ketal and PMB, as well as lipidated saccharides and in our case, no unwanted ester or acyl migration was observed during the cleavage of OPAc. Further, DBU in methanol was observed as an alternative mild reagent for the efficient deprotection of acetyl, benzoyl and oxophenylacetyl ester groups.

Results and discussion

Initially, model substrate **1a** (1 mmol) was stirred with 0.3 mmol of TEA in methanol for 30 m (Table 1, entry 1) resulting in the selective cleavage of OPAc to afford the desired product **2a** in 37% yield. Further, investigation against time led to the generation of the desired product **2a** in 84% yield in 90 m with the same concentration of TEA (entry 3). However, continuous stirring for more time resulted in the mixture of other products **2c** and **2d** (entries 4-6). Further, screening of base concentration (entry 7) and solvents did not improve the selectivity and yield of the reaction

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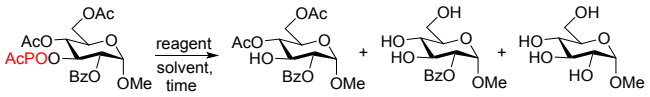
Table 1. Optimization of the reaction.



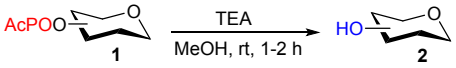
1a 2a 2c 2d

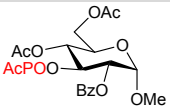
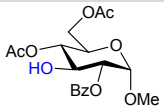
entry	reagent (mmol)	time (min)	solvent	yield (%) 2a	2c	2d
1	TEA(0.3)	30	MeOH	37	-	-
2	TEA(0.3)	60	MeOH	63	-	-
[a]3	**TEA (0.3)**	**90**	**MeOH**	**84**	**7**	**-**
4	TEA(0.3)	120	MeOH	69	22	-
5	TEA(0.3)	180	MeOH	52	33	12
6	TEA(0.3)	240	MeOH	35	21	34
7	TEA (0.5)	90	MeOH	83	14	-
8	TEA(0.3)	90	MeCN	57	-	-
9	TEA(0.3)	90	DCM	46	-	-
10	TEA(0.3)	90	Acetone: H_2O (9:1)	77	13	-
11	TEA(0.3)	90	DMF	27	-	-
12	DIPEA(0.3)	90	MeOH	71	12	7
[b]13	**DBU(0.3)**	**90**	**MeOH**	trace	9	**83**
14	TMEDA(0.3)	90	MeOH	69	23	-
15	$NH_2NH_3^+ \cdot OAc$(0.3)	60	MeOH	76	14	-
16	$BnNH_2$(0.3)	60	MeOH	79	10	-
17	NaOMe(0.3)	15	MeOH	-	-	87
18	Piperidine(0.3)	90	MeOH	43	-	-
19	PEG-400(0.3)	90	MeOH	35	-	-
20	NH_4OAc(0.3)	90	MeOH	57	-	-
21	$NH_2NH_3^+ \cdot OAc$(0.3)	90	DMF	-	-	-
22	$BnNH_2$ (0.3)	90	THF	-	-	-

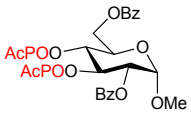
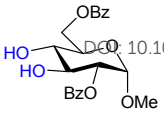
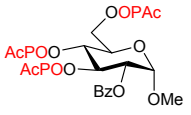
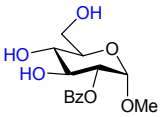
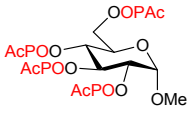
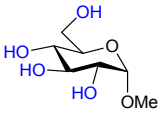
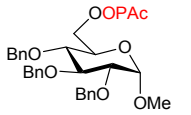
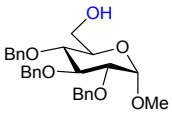
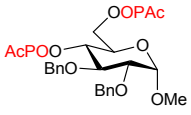
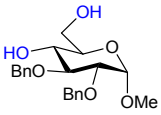
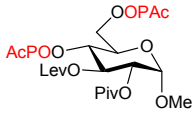
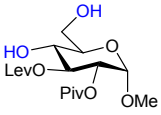
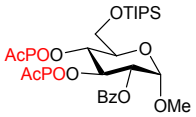
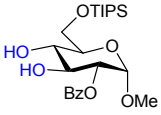
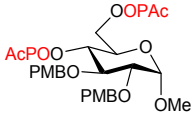
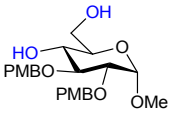
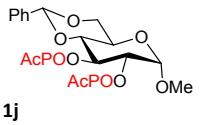
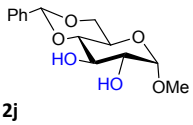
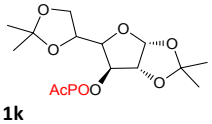
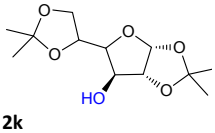
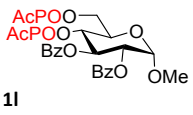
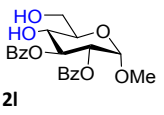
Reaction condition: a) For selective OPAc cleavage: **1a** (1 mmol), TEA (0.3 mmol) in 3 mL of MeOH at 35°C for 90 min. At rt. b) For deacylation reaction: **1a** (1 mmol), DBU (0.3 mmol) in 3 mL of MeOH at rt for 90 min. at 35°C.

(entries 8-11). Mixture of products was obtained after employing other hindered bases like DIPEA, DBU and TMEDA (entries 12-14). Meanwhile, during screening we also observed that stirring of **1a** (1 mmol) against DBU (0.3 mmol) predominantly generated **2d** in 83% yield (entry 13). The reaction was also performed with previously known reagents used for anomeric deacetylation.[15] It was found that ammonium acetate and benzylamine in methanol (entry 15 and 16) were good to some extent, however, not much improvisation in the yield was observed. Other reagents tested (entries 17-20) were found very less efficient as compared with TEA in methanol. Lastly, reaction of **1a** was performed with hydrazine acetate and benzylamines in DMF and THF respectively. However they failed to form any products (entries 21 and 22) which indicates that the reaction pathway most likely follows transesterification mechanism rather than simple aminolysis.[16]

Table 2. Scope of the reaction.



entry	substrate	product	yield(%)
1			84
	1a	2a	

2	 1b	 2b	88
3	 1c	 2c	91
4	 1d	 2d	89
5	 1e	 2e	93
6	 1f	 2f	92
7	 1g	 2g	89
8	 1h	 2h	89
9	 1i	 2i	91
10	 1j	 2j	92
11	 1k	 2k	89
12	 1l	 2l	90

Reaction condition: 1 (1 mmol), TEA (0.3 mmol) in 3 mL of MeOH at rt for 90 min.

After establishing the conditions for deprotection, we investigated the scope of the reaction by removing OPAc in presence of different protecting groups at the different positions of saccharides (Table 2). Primarily, orthogonality of OPAc was tested in presence of different acyl groups (OAc and Bz) under the optimized conditions which lead

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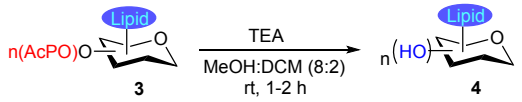
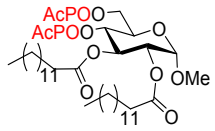
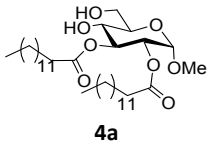
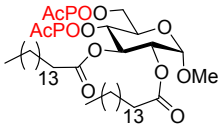
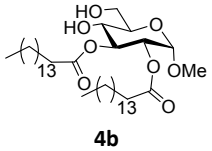
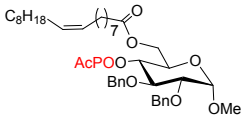
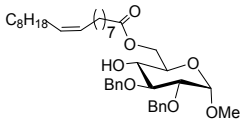
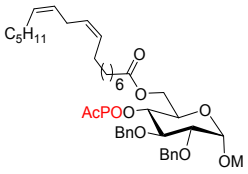
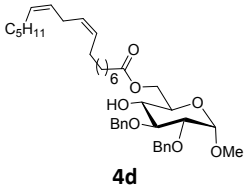
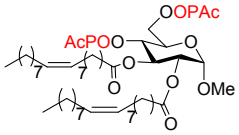
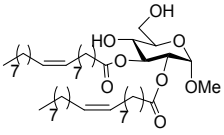
to the selective cleavage of OPAc in all of the five substrates (entries 1-3, 8 and 12). Further, a reaction with tetra-OPAc protected saccharide **1d** lead to the formation of desired product **2d** in 89% yield. The selectivity of the optimized reaction condition was further tested with different saccharides containing protecting groups like Bn, TIPS, Levulinyl and Pivaloyl. As expected, OPAc was cleaved against OBn protected saccharides to form **2e** and **2f** while as Pivolyl, Levulinyl and TIPS were found very stable and formed **2g** and **2h** respectively in appreciable yields (entries 5-8). Later on, we focused towards the acid sensitive groups like PMB, benzylidine and acetal (entries 9-11) and no interference with the aforementioned sensitive groups while employing TEA in methanol was observed. Thus, the orthogonal stability of these groups was achieved in better yields by selective removal of OPAc (entries 9-11).

Table 3. Scope against lipidated saccharides.



3 4

entry	substrate	product	yield(%)
1	 **3a**	 **4a**	93
2	 **3b**	 **4b**	89
3	 **3c**	 **4c**	91
4	 **3d**	 **4d**	94
5	 **3e**	 **4e**	93

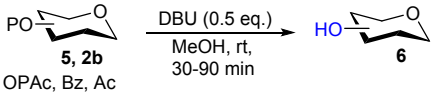
Reaction condition: **3** (1 mmol), TEA (0.3 mmol) in 3 mL of MeOH:DCM (8:2) at rt for 90 min.

With these established conditions in hand we proceeded to check the application of our reaction for the selective deprotection of OPAc in lipidated saccharides (Table 3, entries 1-5). In order to achieve better solubility we slightly modified our conditions (for details see supporting information, Page 1). For this purpose, different commonly used unsaturated lipids like mysitic acid (**3a**), palmitic acid (**3b**), oleic acid (**3c**, **3e**) and linolenic acid (**3d**) anchored saccharides through ester linkages. Interestingly, all the substrates provided the corresponding OPAc deprotected saccharides (**4a**-**4e**) between 89-94% yields (Table 3). These examples further validated our results and could serve as an asset in the total synthesis of glycolipids like glycosylphosphatidylinositol GPI and gangliosides.

The commonly encountered problem in saccharides with acyl/ester groups like OAc and OBz is their tendency to migrate towards neighbouring hydroxyl groups especially under basic conditions.[17] Thinking of this possibility, 2D-NMR analysis of **2l** and **4a** was carried out. In both the cases no acyl migration was noted (See the supporting information page: 54-58).

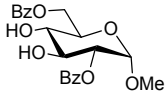
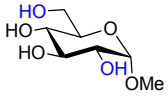
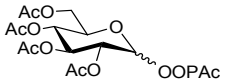
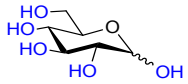
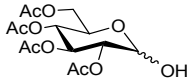
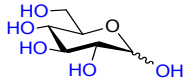
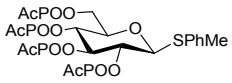
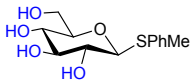
Further, as depicted in optimization table (Table 1, entry 13) DBU in methanol was found to be an alternative mild reagent that simultaneously resulted in the unmasking of all acetyl protections like OAc, OBz and OPAc in saccharide **1a** to form **2d** in 83% yield. In order to validate its generality four different reactions were carried out and deacylated products (**2d, 6a** and **6b**) were obtained in 87-93% yields (Table 4).

Table 4. Scope against DBU promoted deacylation reactions.



5, 2b **6**

P = OPAc, Bz, Ac

entry	substrate	product	yield (%)
1	 **2b**	 **2d**	91
2	 **5a**	 **6a**	93
3	 **5b**	 **6a**	87
4	 **5c**	 **6b**	89

Reaction condition: **5, 2b** (1 mmol), DBU (0.3 mmol) in 3 mL of MeOH at rt for 90 min.

Conclusion

In conclusion, TEA was demonstrated as a better, selective deprotecting reagent for the cleavage of OPAc. In addition, cleavage of OPAc with TEA was successfully established in the saccharides bearing different labile groups like acetal, ketal and PMB. Further, saccharide bearing lipid esters were obtained with improvised yields (>90%). These optimized conditions did not lead to any unwanted migration of ester or acyl groups. Meanwhile, it was observed that DBU in MeOH was an alternative reagent for the deprotection of Bz, Ac and OPAc groups. The reaction more likely

follows transesterification mechanism, a cleaner reaction than simple aminolysis.

Experimental

A. General Information.

Solvents were purified according to standard procedures, and reagents used were of highest purity available. All reactions were performed in flame-dried glass apparatus under argon/nitrogen atmosphere unless mentioned otherwise. Anhydrous solvents like CH_2Cl_2, CH_3OH, CH_3CN, DMF, pyridine, and Et_3N were freshly dried using standard methods. NMR measurements (^1H, ^{13}C, 2D ^1H-^1H-COSY and ^1H-^{13}C HMBC, HMQC, and NOESY) were recorded on a 400 and 500 MHz spectrometer fitted with pulse-field gradient probe, and trimethylsilane (TMS) or residual resonance of deuterated solvent were used as internal reference. ^{13}C NMR spectra were broadband ^1H decoupled or inverse HMQC experiments. Chemical shifts are expressed in ppm and coupling constants *J* in Hz. High-resolution mass spectral data were obtained from Q-ToF Mass Spectrometer coupled LC system. The following conditions were used: capillary voltage 3500 V, capillary temperature 350 ^oC, auxiliary gas flow rate 7.0 L/min, spray voltage 4.5 kV, mass range 100-1000 amu (maximum resolution 30000). Optical rotations were measured on a digital polarimeter. Analytical TLC was performed on 60 F254 plates, and compounds visualized by methanol-sulphuric acid/ceric-sulfate developing reagent. Silica column chromatography was carried out with silica gel 60 (60-120 mesh) or flash silica gel (230-400 mesh). Analytical and semi-preparative HPLC purification were carried out on reversed-phase (C18, 250 X 10 mm, L i.d.) column connected to an binary pump and monitored using an photodiode array detector.

B. General Procedure for oxobenzoyl protection of sugars. (Series 1)

For each of the hydroxyl group present, 1.2 mmol DIC, Phenylglyoxalic acid and DMAP was utilized. To a stirred solution of sugar alcohol (1.0 eq.) was added DIC (1.2eq.), phenylglyoxalic acid (1.2 eq.) and DMAP (1.2eq.) in dry DCM under nitrogen atmosphere and then stirred for 3 h at 35 ^oC. The reaction was monitored by thin layer chromatography. The reaction mixture was dissolved in EtOAc and washed thrice with 3% aqueous HCl (20 mL), followed by $NaHCO_3$ wash. The organic layer was collected and dried over Na_2SO4, and evaporated on vacuum. The products (**1a-1k**) were purified by column chromatography on silica gel using EtOAc and n-Hexane as eluting agents.

C. General Procedure for oxobenzoyl deprotection of sugars. (Series 2)

The oxophenylacetyl ester protected sugar was dissolved in dry MeOH and triethyl amine (TEA) was added stoichiometrically. For each hydroxyl group of the sugar 0.5 equiv of TEA was added. The reaction was carried at an ambient temperature (35 ^oC) under nitrogen atmosphere and monitored by TLC. After the reaction was completed, the reaction was quenched by 0.1 N HCl and the solvent was evaporated under reduced pressure. The resulting reaction mixture was then extracted with EtOH. The gummy solid compounds (**2a**-**2k**) thus obtained were purified through column chromatography by EtOH and n-Hexane.

D. General Procedure for oxobenzoyl protection of lipid Sugars. (Series 3). To a stirred solution of sugar alcohol (1.0 eq.) was added DIC (1.2eq.), Lipid (1.2eq.) and DMAP (1.2eq.) in dry DCM under nitrogen atmosphere. The reaction was allowed to continue for 3-4 h at 35 ^oC and monitored by thin layer chromatography. The reaction mixture was dissolved in EtOAc and washed thrice with 3% aqueous HCl followed by $NaHCO^3$ wash. The organic layer was collected and dried over Na_2SO_4, and evaporated on vacuum. The products (**3a**-**3e**) were purified by column chromatography on silica gel using EtOAc/Hexane as eluting agents.

E. General Procedure for oxobenzoyl deprotection of lipid Sugars. (Series 4). The oxobenzoyl protected lipidated saccharide was dissolved in dry MeOH/DCM (8:2) and triethyl amine (TEA) was added in stoichiometric portions. For each hydroxyl group of the saccharide 0.5 equiv of TEA was added. The reaction was carried at an ambient temperature (35^oC) under nitrogen atmosphere and monitored by TLC. After the reaction was completed, the reaction was quenched by 0.1 N HCl and the solvent were evaporated under reduced pressure. The resulting reaction mixture was then extracted with EtOH. The compounds (**4a**-**4e**) obtained were purified through column chromatography by EtOH and n-Hexane as eluting agents.

F. General Procedure for overall deprotection of OPAc, OAc, OBz and Lipid protected sugars. (Series 5). The protected saccharide was dissolved in dry MeOH and 0.5 equiv of DBU was added for each protected hydroxyl group of the sugar. The lipidated saccharides were dissolved in dry MeOH/DCM (8:2). The reaction was carried openly at an ambient temperature (30^oC) and monitored by TLC. All the reactions were completed within 1/2 to1h time scale. The reaction was quenched by 0.1 N HCl and the solvent were evaporated under reduced pressure. The resulting reaction mixture was then extracted with EtOH. The compounds (**6a**-6c) obtained were purified through column chromatography by EtOH and n-Hexane as eluting agents.

G. Procedure for some starting material synthesis.

1. General Procedure for the synthesis of starting compound of 3a, 3b and 3e.

To a solution of Methyl α-D-glucopyranoside (1.0 equiv) in anhydrous MeCN (50 mL) was added Benzaldehyde dimethyl acetal (1.1 equiv) and camphorsulfonic acid (0.2 equiv) in catalytic amount. The reaction mixture was stirred at room temperature for 4 h. After completion of the reaction confirmed by TLC, the reaction mixture was extracted with ethyl acetate after which the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vaccum. The residue was dissolved in dry DCM and added lipid acids (mysitic acid for **3a**, palmitic acid for **3b**, and oleic acid for **3e**) (2.2 equiv), DIC (2.2 equiv), and DMAP (2.2 equiv). The reaction mixture was stirred at room temperature for 4 h. After the

completion of the reaction, the reaction mixture was extracted with ethyl acetate and 2N HCl (2-3 times), dried over Na_2SO_4, and then concentrated in vaccum. In the last step the deprotection of benzylidene was carried out using catalytic amount of *P*-TSA in methanol to obtain the desired product (Methyl- 4, 6-di-O-2, 3-mesytyl-α-D-glucopyranoside, Methyl- 4, 6-di-*O*-2, 3-dipalmyl-α-D-glucopyranoside and Methyl-2, 3-di-*O*-oleoyl-α-D-glucopyranoside).

2. General Procedure for the synthesis of starting compound of 3a, 3c and 3d.

To a solution of Methyl α-D-glucopyranoside (1.0 equiv) in anhydrous MeCN (50 mL) was added benzaldehyde dimethyl acetal (1.1 equiv) and camphorsulfonic acid in catalytic amount. The reaction mixture was stirred at room temperature for 4 h. After completion of the reaction confirmed by TLC, the reaction mixture was extracted with ethylacetate after which the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vaccum. Benzyl bromide (2.2 equiv) was added to the residue in DMF and the reaction was stirred at 0 °C and NaH (4.0 equiv) was added gradually in small quantities for some time. After the addition of NaH, the reaction mixture was stirred at room temperature for 3 h to get the dibenzylated product. The reaction mixture was quenched with cold water and extracted with DCM, dried over Na_2SO_4, and concentrated in vaccum. The product was used without column chromatography for the deprotection of benzylidene group in presence of the catalytic amount of *P*-TSA to obtain Methyl-2,3-di-O-benzyl-α-D-glucopyranoside. To the solution of Methyl-2,3-di-O-benzyl-α-D-glucopyranoside in dry DCM was added lipid acid (oleic acid for **3c** and linolenic acids for **3d** in 1.1 equiv), DIC (1.1 equiv) and DMAP (1.1 equiv). The reaction was stirred at room temperature for 4 h. After completion of the reaction confirmed by TLC, the reaction mixture was extracted with ethylacetate after which the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vaccum. The product was isolated by column chromatography by using ethyl acetate and hexane as an eluent.

H. Characterization Data:

1a. Methyl-3-*O*-oxobenzoyl-2-benzoyl-4, 6- diacetyl-α-D glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 14.9, 7.4 Hz, 3H), 7.08 (t, *J* = 7.7 Hz, 2H), 5.96 (t, *J* = 9.9 Hz, 1H), 5.26 (t, *J* = 9.9 Hz, 1H), 5.18 – 5.10 (m, 2H), 4.29 (dd, *J* = 12.3, 4.6 Hz, 1H), 4.16 – 4.06 (m, 2H), 3.41 (s, 3H), 2.09 (d, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.78, 170.69, 169.44, 165.43, 163.82, 135.01, 133.80, 131.76, 130.10, 129.94, 129.69, 128.93, 128.77, 128.72, 128.59, 96.91, 71.79, 71.51, 68.04, 67.50, 61.92, 55.73, 20.74, 20.54. (ref 13)

1b. Methyl-3,4-di-*O*-oxobenzoyl-2,6-di-*O*-benzoyl-α-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.7, 6.5 Hz, 4H), 8.03 (dd, 2H), 7.76 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.64 (ddd, 2H), 7.58 – 7.55 (m, *J* = 7.8, 1.6 Hz, 1H), 7.52 – 7.45 (m, 7H), 7.12 – 7.07 (m, *J* = 8.2, 7.6 Hz, 2H), 6.18 (td, 1H), 5.72 (t, *J* = 9.9 Hz, 1H), 5.27 – 5.22 (m, *J* = 7.3, 3.6 Hz, 2H), 4.72 (dd, *J* = 12.5, 2.3 Hz, 1H), 4.54 (dd, *J* = 12.5, 4.2 Hz, 1H), 4.41 – 4.37 (m, *J* = 10.2, 4.0, 2.3 Hz, 1H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.42, 184.93, 166.05, 165.41, 163.16, 162.06, 135.19, 134.95, 133.79, 133.26, 131.93, 131.77, 130.25, 130.14, 129.81, 129.80, 129.58, 129.07, 128.74, 128.68, 128.61, 128.49, 96.87, 71.81, 71.32, 69.50, 67.35, 62.02, 55.82. (ref 13)

1c. Methyl-3, 4, 6-tri-*O*-oxobenzoyl-2-*O*-benzoyl-α-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.10 (m, 2H), 8.07 – 8.00 (m, 4H), 7.73 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.67 – 7.60 (m, 3H), 7.54 – 7.43 (m, *J* = 16.3, 7.8 Hz, 7H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.15 (t, *J* = 9.8 Hz, 1H), 5.56 (t, *J* = 9.8 Hz, 1H), 5.26 (d, *J* = 3.6 Hz, 1H), 5.20 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.71 – 4.61 (m, *J* = 12.2, 3.8 Hz, 2H), 4.41 – 4.36 (m, *J* = 10.1, 4.6, 2.9 Hz, 1H), 3.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.51, 185.36, 184.95, 165.37, 163.25, 163.12, 162.25, 135.32, 135.07, 134.98, 133.84, 132.34, 131.83, 131.74, 130.28, 130.15, 129.78, 129.14, 128.96, 128.80, 128.75, 128.71, 96.83, 71.69, 71.05, 69.65, 67.00, 63.12, 55.97. (ref 13)

1d. Methyl-2, 3, 4, 6-tetra-*O*-oxobenzoyl-α-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.95 (m, 6H), 7.92 – 7.86 (m, 2H), 7.68 – 7.60 (m, 3H), 7.56 – 7.44 (m, *J* = 21.4, 13.1, 6.0 Hz, 7H), 7.40 (t, *J* = 7.8 Hz, 2H), 6.08 (t, *J* = 9.8 Hz, 1H), 5.56 (t, *J* = 9.8 Hz, 1H), 5.37 (d, *J* = 3.5 Hz, 1H), 5.23 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.66 (qd, *J* = 12.3, 3.7 Hz, 2H), 4.43 – 4.35 (m, *J* = 10.1, 4.5, 2.8 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.49, 185.11, 184.81, 184.75, 163.20, 162.66, 162.42, 162.15, 135.42, 135.36, 135.22, 132.24, 131.99, 131.73, 131.71, 130.28, 130.18, 130.08, 130.05, 129.16, 129.10, 129.06, 129.02, 96.19, 72.60, 70.47, 69.66, 67.00, 62.93, 56.06. (ref 13)

1e. Methyl-6-*O*-oxobenzoyl-2, 3, 4-tri-*O*-benzyl-α-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.26 (m, 15H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.81 (t, 2H), 4.67 – 4.58 (m, *J* = 14.0, 10.9 Hz, 4H), 4.51 – 4.44 (m, *J* = 11.7, 5.1 Hz, 1H), 4.03 (t, *J* = 9.2 Hz, 1H), 3.96 – 3.90 (m, *J* = 10.0, 5.0, 2.0 Hz, 1H), 3.54 – 3.49 (m, *J* = 9.7, 3.2 Hz, 2H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.89, 163.55, 138.59, 138.07, 137.86, 134.91, 132.43, 130.06, 128.85, 128.51, 128.43, 128.10, 127.99, 127.96, 127.94, 127.68, 98.15, 81.84, 79.91, 77.56, 75.79, 75.16, 73.43, 68.58, 64.38, 55.38. (ref 13)

1f. Methyl-4, 6-di-*O*-oxobenzoyl-2, 3-di-*O*-benzyl-α-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.93 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.23 (m, 12H), 5.27 (t, 1H), 4.96 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.72 – 4.58 (m, 4H), 4.49 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.66 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.40 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 185.66, 185.48, 163.39, 162.70, 138.14, 137.74, 135.08, 134.96, 132.37, 132.09, 130.21, 130.10, 128.97, 128.89, 128.59, 128.47, 128.37, 128.15, 127.61, 127.55, 98.19, 79.60, 78.39, 75.44, 73.59, 71.88, 67.04, 63.69, 55.69. (ref 13)

1g. Methyl-4, 6-di-*O*-oxobenzoyl-3-*O*-levulinyl-2-*O*-pivaloyl-α-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.99 – 7.92 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 4H), 5.71 (t, *J* = 9.8 Hz, 1H), 5.30 (t, *J* = 9.8 Hz, 1H), 5.00 (d, *J* = 3.6 Hz, 1H), 4.82 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.58 (qd, *J* = 12.2, 3.7 Hz, 2H), 4.27 – 4.19 (m, *J* = 10.2, 4.6, 2.7 Hz, 1H), 3.37 (s, 3H), 2.74 – 2.61 (m, 2H), 2.52 (dd, *J* = 9.9, 4.0 Hz, 2H), 2.07 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.74, 185.56, 184.82, 177.67, 171.44, 163.31, 162.38, 135.19, 135.11, 132.27, 132.07, 130.12, 130.07, 129.03, 128.97, 96.85, 70.78, 70.43, 69.45, 66.72, 63.25, 55.90, 38.77, 37.67, 29.62, 27.88, 26.84. (ref 13)

1h. Methyl-3, 4-*O*-dioxobenzoyl-2-*O*-benzoyl-6-*O*-(triisopropylsilyl) α-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.4 Hz, 2H), 8.06 (d, *J* = 7.4 Hz, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.64 (dd, *J* = 11.8, 7.3 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 5H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.16 (s, 1H), 5.65 (t, *J* = 9.8 Hz, 1H), 5.23 (d, *J* = 1.9 Hz, 2H), 4.13 – 4.07 (m, 1H), 3.99 (d, *J* = 3.0 Hz, 2H), 3.45 (s, 3H), 1.10 (d, *J* = 5.4

Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.71, 185.51, 165.50, 163.53, 162.27, 135.20, 134.98, 133.80, 132.03, 131.81, 130.24, 130.16, 129.82, 129.10, 128.77, 128.72, 96.65, 72.14, 71.87, 70.14, 69.40, 61.94, 55.43, 17.95, 12.03. LCMS (ESI-TOF): m/z [M + H]+ Calcd for $C_{39}H_{49}O_{10}Si$, 705.31; found: 705.35

1i. Methyl-4,6-di-*O*-oxobenzoyl-2,3- di-*O*- (4-methoxybenzyl) -*α*-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 21.8, 7.4 Hz, 4H), 7.58 (t, *J* = 7.0 Hz, 2H), 7.39 (dt, *J* = 25.5, 7.8 Hz, 4H), 7.22 (d, *J* = 9.3 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 5.16 (t, *J* = 9.8 Hz, 1H), 4.79 (d, *J* = 10.7 Hz, 1H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.53 (t, *J* = 4.4 Hz, 2H), 4.12 – 4.05 (m, *J* = 7.8, 5.3 Hz, 1H), 4.01 (t, *J* = 9.4 Hz, 1H), 3.75 (d, *J* = 8.4 Hz, 3H), 3.70 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.68, 185.37, 163.39, 162.53, 159.58, 159.16, 135.11, 134.99, 132.27, 132.08, 130.28, 130.16, 129.82, 129.34, 128.98, 128.89, 113.98, 113.76, 98.27, 79.06, 78.09, 75.21, 73.27, 71.85, 66.95, 63.66, 55.69, 55.29, 55.22. LRMS (ESI-TOF): m/z [M + Na]+ Calcd for $C_{39}H_{38}NaO_{12}$, 721.2261; found: 721.10

1j. Methyl-2, 3-di-*O*-oxobenzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, 2H), 7.86 (dd, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.48 (m, 5H), 7.43 – 7.38 (m, *J* = 6.5, 3.6 Hz, 3H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.00 (t, *J* = 9.9 Hz, 1H), 5.56 (s, 1H), 5.31 (dd, *J* = 9.9, 3.7 Hz, 1H), 5.22 (d, *J* = 3.7 Hz, 1H), 4.38 (dd, *J* = 10.4, 4.9 Hz, 1H), 4.12 – 4.04 (m, *J* = 9.9, 4.9 Hz, 1H), 3.83 (td, *J* = 10.0, 4.7 Hz, 2H), 3.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.99, 185.42, 163.23, 163.03, 136.69, 135.22, 134.92, 132.05, 130.12, 130.06, 129.38, 129.15, 128.81, 128.39, 126.34, 102.10, 97.33, 79.18, 72.41, 70.39, 68.84, 62.45, 55.80. (ref 13)

1k. 1, 2:5, 6-di-O-isopropylidene-3-*O*-oxobenzoyl-*α*-D-glucofuranoside (Starting material was commercially available).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.97 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 5.93 (d, *J* = 3.7 Hz, 1H), 5.65 (d, *J* = 3.0 Hz, 1H), 4.64 (d, *J* = 3.7 Hz, 1H), 4.27 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.20 – 4.12 (m, *J* = 8.5, 5.8, 4.6 Hz, 1H), 4.12 – 4.06 (m, *J* = 8.7, 6.0 Hz, 1H), 4.05 – 3.97 (m, *J* = 8.8, 4.5 Hz, 1H), 1.54 (s, 3H), 1.46 (s, 3H), 1.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.64, 162.49, 135.16, 132.30, 130.11, 128.93, 112.47, 109.56, 105.36, 83.28, 80.20, 77.27, 72.34, 67.60, 26.92, 26.74, 26.23, 25.23. (ref 13)

1l. Methyl-2,6- di-*O*-oxobenzoyl-2, 3-di-*O*- benzoyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.8 Hz, 2H), 8.01 (dd, *J* = 15.5, 7.8 Hz, 4H), 7.68 (d, *J* = 7.5 Hz, 3H), 7.59 – 7.48 (m, 5H), 7.45 – 7.35 (m, *J* = 15.0, 7.5 Hz, 4H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.14 (t, *J* = 10.2 Hz, 1H), 5.65 (t, *J* = 9.8 Hz, 1H), 5.27 (d, *J* = 6.5 Hz, 2H), 4.68 (d, *J* = 10.6 Hz, 2H), 4.43 (d, *J* = 10.1 Hz, 1H), 3.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.59, 185.10, 165.77, 165.33, 163.31, 162.64, 135.08, 133.56, 133.50, 132.38, 131.66, 130.20, 129.99, 129.80, 129.05, 128.98, 128.88, 128.81, 128.58, 128.48, 97.10, 71.93, 70.06, 69.99, 66.93, 63.22, 55.91. LCMS (ESI-TOF): m/z [M + H_2O]+ Calcd for $C_{37}H_{32}O_{13}$, 684.18; found: 684.25

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.09 – 4.97 (m, 3H), 4.34 – 4.08 (m, 3H), 3.99 (ddd, *J* = 10.1, 4.7, 2.1 Hz, 1H), 3.40 (d, *J* = 4.6 Hz, 3H), 2.12 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.79, 170.71, 166.32, 133.44, 129.96, 129.45, 128.56, 128.47, 97.23, 73.99, 71.09, 70.24, 67.34, 62.28, 55.56, 20.85, 20.75. (ref 13)

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 4H), 7.58 (td, *J* = 7.4, 1.1 Hz, 2H), 7.45 (q, *J* = 8.0 Hz, 4H), 5.07 (d, *J* = 3.7 Hz, 1H), 4.98 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.73 (dd, *J* = 12.1, 4.8 Hz, 1H), 4.59 (dd, *J* = 12.1, 2.0 Hz, 1H), 4.22 (t, *J* = 9.4 Hz, 1H), 3.97 (ddd, *J* = 9.9, 4.7, 1.9 Hz, 1H), 3.88 (s, 1H), 3.65 (t, *J* = 9.4 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.23, 166.48, 133.40, 133.36, 129.97, 129.84, 129.61, 129.50, 128.49, 128.45, 97.30, 73.74, 71.62, 70.75, 69.56, 63.76, 55.38. (ref 13)

2c. Methyl-2-*O*-benzoyl -*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, MeOD) δ 7.98 (d, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.79 – 4.71 (m, 3H), 3.90 (t, *J* = 9.4 Hz, 1H), 3.80 – 3.76 (m, 1H), 3.67 – 3.62 (m, 1H), 3.55 – 3.51 (m, 1H), 3.38 (t, *J* = 9.1 Hz, 1H), 3.29 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 166.38, 133.07, 129.79, 129.46, 128.17, 97.11, 74.16, 72.17, 71.15, 70.51, 61.19, 54.21. (ref 13)

2d. Methyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, MeOD) δ 3.55 (s, 3H), 3.34 (d, *J* = 11.6 Hz, 1H), 2.50 (d, *J* = 11.6 Hz, 1H), 2.40 – 2.26 (m, 1H), 2.26 – 2.16 (m, 1H), 2.08 (d, *J* = 8.7, 4.6 Hz, 2H), 2.03 – 1.91 (m, *J* = 20.8, 11.3 Hz, 1H).^{13}C NMR (101 MHz, MeOD) δ 103.84, 77.73, 76.15, 76.11, 74.38, 65.29, 58.11. (ref 13)

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 15H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.92 – 4.79 (m, 3H), 4.67 (dd, *J* = 11.6, 6.2 Hz, 2H), 4.60 (d, *J* = 3.5 Hz, 1H), 4.03 (t, *J* = 9.2 Hz, 1H), 3.80 – 3.64 (m, 3H), 3.57 – 3.50 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.84, 138.24, 138.20, 128.49, 128.41, 128.13, 128.03, 127.96, 127.86, 127.61, 98.25, 82.00, 80.12, 77.57, 75.74, 75.04, 73.43, 70.77, 61.94, 55.21. (ref 13)

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 10H), 5.00 (d, *J* = 11.5 Hz, 2H), 4.73 (q, *J* = 13.5, 11.9 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 3.5 Hz, 1H), 3.82 – 3.68 (m, 3H), 3.62 – 3.55 (m, 1H), 3.55 – 3.44 (m, 2H), 3.36 (s, 3H), 2.67 (s, 1H), 2.21 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.80, 138.06, 128.61, 128.51, 128.10, 128.00, 127.96, 127.88, 98.25, 81.40, 79.90, 75.40, 73.16, 70.82, 70.49, 62.41, 55.26. (ref 13)

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (t, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.63 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.12 (s, 1H), 3.78 (s, 2H), 3.72 – 3.59 (m, 2H), 3.31 (s, 3H), 3.16 (s, 1H), 2.79 – 2.37 (m, 4H), 2.11 (s, 3H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.90, 177.95, 172.54, 96.88, 73.11, 71.19, 70.88, 68.90, 61.58, 55.35, 38.68, 37.96, 29.80, 27.97, 26.82. (ref 13)

2h. Methyl-2-*O*-benzoyl-6-*O*-triisopropylsilyl –*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 4.97 (d, *J* = 3.5 Hz, 1H), 4.87 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.12 (t, *J* = 9.2 Hz, 1H), 3.98 – 3.90 (m, 2H), 3.88 (s, 1H), 3.78 – 3.48 (m, 4H), 3.33 (s, 3H), 1.08 (t, *J* = 6.0 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.49, 133.18, 129.94, 129.73, 128.34, 97.07, 73.93, 72.96 (s), 71.70, 70.68, 64.61, 55.06. LCMS (ESI-TOF): m/z [M + H]+ Calcd for $C_{23}H_{41}O_6Si$, 441.26; found: 441.20

2i. Methyl-2, 3-di-*O*-4-methoxybenzoyl -*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.7 Hz, 4H), 6.87 (d, *J* = 6.9 Hz, 4H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.79 – 4.49 (m, *J* = 23.8, 21.2, 7.3 Hz, 4H), 3.79 (d, *J* = 2.5 Hz, 6H), 3.58 (d, *J* = 9.5 Hz, 1H), 3.51 – 3.43 (m, 2H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.47, 159.37, 130.89, 130.16, 129.72, 129.64, 114.03, 113.91, 98.30, 80.97, 79.46, 75.00, 72.80, 70.77, 70.39, 62.38, 55.27, 55.27, 55.24. LCMS (ESI-TOF): m/z [M + Na]+ Calcd for $C_{23}H_{30}NaO_8$, 457.18; found: 457.30

2j. Methyl-4, 6-*O*-benzylidine -*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.40 (d, *J* = 4.4 Hz, 3H), 5.55 (s, 1H), 4.79 (d, *J* = 3.7 Hz, 1H), 4.31 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.94 (t, *J* = 9.2 Hz, 1H), 3.83 – 3.78 (m, 2H), 3.63 (s, 1H), 3.53 (d, *J* = 9.2 Hz, 1H), 3.47 (d, 3H), 2.81 (s, 1H), 2.20 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.17, 129.25, 128.33, 126.40, 101.95, 99.94, 99.88, 81.04, 72.85, 71.53, 71.50, 68.97, 62.44, 55.53, 30.90. (ref 13)

2k. 1, 2:5, 6-di-*O*-isopropylidene-*α*-D-glucofuranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (d, *J* = 3.3 Hz, 1H), 4.54 (d, *J* = 3.3 Hz, 1H), 4.38 – 4.29 (m, *J* = 12.9, 5.1 Hz, 2H), 4.17 (t, 1H), 4.07 (d, *J* = 5.6 Hz, 1H), 3.99 (dd, *J* = 8.4, 5.4 Hz, 1H), 2.63 (d, *J* = 3.5 Hz, 1H), 1.47 (d, *J* = 21.5 Hz, 6H), 1.35 (d, *J* = 18.0 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 111.85, 109.68, 105.32, 85.13, 81.20, 75.25, 73.50, 67.70, 26.88, 26.78, 26.21, 25.17. (ref 13)

2l. Methyl- 2, 3-di-*O*- benzoyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, *J* = 7.6 Hz, 4H), 7.49 – 7.43 (m, *J* = 16.6, 7.6 Hz, 2H), 7.35 – 7.29 (m, *J* = 16.0, 8.0 Hz, 4H), 5.81 (t, ^{J} = 9.6 Hz, 1H), 5.20 (dd, *J* = 10.0, 3.3 Hz, 1H), 5.13 (d, *J* = 3.4 Hz, 1H), 4.00 (d, *J* = 9.5 Hz, 1H), 3.95 (d, *J* = 3.2 Hz, 2H), 3.89 – 3.85 (m, 1H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 167.16, 166.10, 133.35, 133.30, 129.89, 129.82, 129.43, 129.15, 128.40, 128.38, 97.17, 73.96, 71.85, 71.54, 69.56, 61.89, 55.41. LCMS (ESI-TOF): m/z [M + Na]+ Calcd for $C_{21}H_{22}NaO_8$, 425.12; found: 425.15

3a. Methyl- 4, 6-di-*O*- oxobenzoyl-2, 3-mesytyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.67 (t, 2H), 7.52 (q, *J* = 7.1 Hz, 4H), 5.69 (t, 1H), 5.30 (t, *J* = 3.4 Hz, 1H), 5.01 (d, *J* = 3.5 Hz, 1H), 4.92 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.65 – 4.54 (m, *J* = 2.6 Hz, 2H), 4.30 – 4.23 (m, *J* = 8.9 Hz, 1H), 3.41 (s, 3H), 2.38 – 2.20 (m, 5H), 2.17 (s, 2H), 1.58 (s, 5H), 1.24 (d, *J* = 11.7 Hz, 36H), 0.88 (t, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 185.53, 184.81, 172.95, 172.41, 163.30, 162.47, 135.23, 135.07, 134.44, 132.33, 132.01, 130.15, 129.98, 129.75, 129.04, 129.01, 128.96, 96.93, 70.78, 70.57, 69.07, 66.75, 63.27, 55.74, 34.14, 34.06, 31.93, 29.69, 29.66, 29.63, 29.50, 29.46, 29.36, 29.26, 29.15, 29.07, 24.89, 24.81, 22.69, 18.64, 14.10. LCMS (ESI-TOF): m/z [M + H_2O]+ Calcd for $C_{51}H_{76}O_{13}$, 896.52; found: 896.70

3b. Methyl- 4, 6-di-*O*-2, 3-dipalmyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.95 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.51 (dd, *J* = 13.8, 7.3 Hz, 4H), 5.69 (t, *J* = 9.8 Hz, 1H), 5.31 (t, *J* = 9.8 Hz, 1H), 5.01 (d, *J* = 3.4 Hz, 1H), 4.92 (dd, *J* = 10.2, 3.5 Hz, 1H), 4.65 – 4.53 (m, 2H), 4.30 – 4.21 (m, 1H), 3.40 (s, 3H), 2.34 – 2.24 (m, 4H), 1.61 – 1.50 (m, 6H), 1.24 (d, *J* = 11.3 Hz, 46H), 0.88 (t, *J* = 6.6 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 185.54, 184.82, 172.95, 172.43, 163.32, 162.48, 135.26, 135.10, 132.31, 132.00, 130.17, 129.99, 129.06, 128.98, 96.93, 70.77, 70.54, 69.06, 66.75, 63.25, 55.75, 34.14, 34.07, 31.96, 29.73, 29.70, 29.66, 29.53, 29.49, 29.40, 29.30, 29.17, 29.09, 24.91, 24.83, 22.72. LCMS (ESI-TOF): m/z [M + H]+ Calcd for $C_{55}H_{83}O_{12}$, 935.58; found: 935.70

3c. Methyl- 2, 3-dibenzyl-4-*O*-oxobenzoyl-6-oleoyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.22 (m, 12H), 5.32 (dd, *J* = 18.4, 8.5 Hz, 3H), 4.95 (d, *J* = 11.1 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 11.1 Hz, 1H), 4.70 – 4.64 (m, 2H), 4.34 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.18 (dd, *J* = 12.3, 2.2 Hz, 1H), 4.08 (dd, *J* = 16.4, 6.9 Hz, 2H), 3.67 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.41 (s, 3H), 2.37 (d, *J* = 3.3 Hz, 2H), 2.02 (d, *J* = 2.9 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.29 (d, *J* = 6.6 Hz, 22H), 0.89 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.54, 173.40, 162.51, 138.20, 137.82, 134.95, 132.22, 130.11, 129.98, 129.78, 128.92, 128.56, 128.36, 128.14, 128.11, 127.67, 127.61, 98.25, 79.64, 78.58, 75.49, 73.57, 71.80, 67.19, 62.08, 55.52, 34.03, 31.92, 29.78, 29.71, 29.53, 29.33, 29.17, 29.13, 27.24, 27.20, 25.67, 24.80, 22.69, 14.11, 11.12. LCMS (ESI-TOF): m/z [M + H]+ Calcd for $C_{47}H_{63}O_9$, 771.45; found: 771.55

3d. Methyl- 2, 3-dibenzyl-4-*O*-oxobenzoyl-6-linolyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.41 – 7.30 (m, 10H), 7.27 (d, *J* = 5.9 Hz, 2H), 5.45 – 5.28 (m, 5H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 4.67 (d, *J* = 12.3 Hz, 2H), 4.36 (dd, *J* = 12.3, 4.2 Hz, 1H), 4.17 (d, *J* = 11.0 Hz, 1H), 4.10 (t, *J* = 9.5 Hz, 1H), 4.04 (d, *J* = 9.9 Hz, 1H), 3.67 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.41 (s, 3H), 2.78 (t, *J* = 6.0 Hz,21H), 2.37 (td, *J* = 7.3, 3.6 Hz, 2H), 2.09 – 2.02 (m, 4H), 1.29 (d, *J* = 10.7 Hz, 16H), 0.90 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.04, 138.76, 138.10, 130.22, 130.03, 128.57, 128.49, 128.12, 128.08, 128.05, 127.97, 127.86, 98.23, 81.29, 79.70, 75.57, 73.22, 70.21, 69.49, 63.19, 55.22, 34.16, 31.55, 29.72, 29.62, 29.37, 29.17, 29.12, 29.11, 28.88, 27.23, 25.69, 24.91, 22.71, 22.59, 14.08. LCMS (ESI-TOF); m/z [M + H]+ Calcd for $C_{47}H_{61}O_9$, 769.43; found: 769.50

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.54 (dd, *J* = 13.9, 7.5 Hz, 4H), 5.72 (t, *J* = 9.8 Hz, 1H), 5.43 – 5.29 (m, 5H), 5.04 (d, *J* = 3.5 Hz, 1H), 4.95 (dd, *J* = 10.2, 3.5 Hz, 1H), 4.63 (qd, *J* = 12.2, 3.6 Hz, 2H), 4.33 – 4.25 (m, 1H), 3.43 (s, 3H), 2.37 – 2.27 (m, 4H), 2.02 (s, 6H), 1.59 (dd, *J* = 14.0, 6.9 Hz, 4H), 1.30 (d, *J* = 9.8 Hz, 42H), 0.90 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.52, 184.80, 172.90, 172.38, 163.30, 162.47, 135.24, 135.08, 132.31, 132.00, 130.15, 130.06, 130.02, 129.98, 129.69, 129.66, 129.05, 128.97, 96.92, 70.78, 70.54, 69.07, 66.74, 63.25, 55.74, 34.11, 34.03, 31.92, 29.78, 29.72, 29.67, 29.64, 29.54, 29.37, 29.34, 29.27, 29.18, 29.13, 29.12, 29.04, 27.24, 27.19, 24.88, 24.80, 22.69, 14.11. (ref 13)

4a. Methyl- 4, 6-di-O-2, 3-mesytyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 – 5.25 (m, 1H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.86 – 4.78 (m, 1H), 3.92 – 3.78 (m, 3H), 3.68 (d, *J* = 7.6 Hz, 2H), 3.38 (s, 3H), 2.38 – 2.24 (m, 6H), 2.16 (s, 1H), 1.58 (s, 3H), 1.24 (s, 38H), 0.87 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 96.95, 73.34, 71.36, 70.63, 70.07, 62.10, 55.29, 34.37, 34.15, 31.94, 29.70, 29.68, 29.51, 29.37, 29.30, 29.13, 29.11, 25.02, 24.97, 22.69, 14.09. LCMS (ESI-TOF): m/z [M + Na]+ Calcd for $C_{35}H_{66}NaO_8$, 637.46; found: 637.70

4b. Methyl- 4, 6-di-*O*-2, 3-dipalmyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (t, *J* = 8.6 Hz, 1H), 4.90 (s, 1H), 4.84 (d, *J* = 7.4 Hz, 1H), 3.91 – 3.78 (m, 2H), 3.70 (s, 2H), 3.39 (s, 3H), 2.31 (d, *J* = 6.0 Hz, 6H), 1.25 (s, 50H), 0.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.89, 173.10, 96.93, 73.41, 71.33, 70.58, 70.13, 62.12, 55.27, 37.11, 34.36, 34.14, 31.93, 30.04, 29.70, 29.67, 29.50, 29.49, 29.36, 29.28, 29.11, 29.09, 27.09, 25.01, 24.96, 23.44, 22.68, 19.73, 14.08. LCMS (ESI-TOF): m/z [M + H_2O]+ Calcd for $C_{39}H_{76}O_9$, 688.54; found: 688.60

4c Methyl- 2, 3-dibenzyl-4-*O*-6-oleoyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, *J* = 14.8, 7.1 Hz, 10H), 5.36 (s, 2H), 4.98 (d, 1H), 4.78 (d, *J* = 11.3 Hz, 2H), 4.69 – 4.62 (m, *J* = 12.9, 7.4 Hz, 2H), 4.38 (dd, *J* = 4.8 Hz, 1H), 4.26 (d, *J* = 11.9 Hz, 1H), 3.81 (t, 1H), 3.52 (t, 1H), 3.39 (s, 3H), 2.33 (t, *J* = 7.4 Hz, 2H), 2.03 (d, *J* = 5.2 Hz, 4H), 1.62 (s, 2H), 1.29 (s, 20H), 0.91 (t, *J* = 5.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.05, 138.74, 138.06, 129.99, 129.73, 128.53, 128.47, 128.08, 128.03, 127.96, 127.82, 98.19, 81.26, 79.62, 75.56, 73.21, 70.15, 69.46, 65.11, 63.16, 55.18, 41.89, 37.13, 34.13, 32.64, 31.94, 31.55, 29.79, 29.72, 29.70, 29.56, 29.35, 29.18, 29.12, 29.11, 28.97, 27.25, 27.20, 27.12, 24.89, 22.71, 14.15. LCMS (ESI-TOF); m/z: [M + H]+ Calcd for $C_{39}H_{59}O_7$, 639.42; found: 639.70

4d. Methyl- 2, 3-dibenzyl-4-O-6-linolyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 15.8, 5.2 Hz, 10H), 5.35 (dd, *J* = 12.2, 5.8 Hz, 4H), 4.99 (dd, *J* = 11.3, 5.6 Hz, 1H), 4.84 – 4.60 (m, 4H), 4.40 (dd, *J* = 11.9, 5.0 Hz, 1H), 4.23 (d, *J* = 12.1 Hz, 1H), 3.86 – 3.67 (m, 2H), 3.50 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.40 (dd, *J* = 13.1, 7.8 Hz, 3H), 2.77 (d, *J* = 5.3 Hz, 2H), 2.33 (dd, *J* = 9.0, 5.7 Hz, 2H), 2.17 (d, *J* = 5.9 Hz, 2H), 2.05 (d, *J* = 5.5 Hz, 4H), 1.30 (s, 14H), 0.92 – 0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.56, 173.40, 162.53, 138.21, 137.84, 134.97, 132.23, 130.23, 130.13, 130.08, 128.94, 128.58, 128.38, 128.15, 128.08, 127.98, 127.69, 127.64, 98.27, 79.73, 78.59, 75.51, 73.59, 71.80, 67.20, 62.09, 55.54, 34.04, 31.56, 29.74, 29.64, 29.38, 29.19, 29.13, 27.24, 25.69, 24.81, 22.72, 22.60, 14.09, 14.08. LCMS (ESI-TOF): m/z [M + H]+ Calcd for $C_{39}H_{57}O_7$, 637.41; found; 637.40

4e. Methyl-2,3-di-*O*-oleoyl-*α*-D-glucopyranoside.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.28 (m, 5H), 4.92 (d, *J* = 3.6 Hz, 1H), 4.84 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.92 – 3.83 (m, 2H), 3.76 – 3.68 (m, *J* = 13.6, 5.4 Hz, 2H), 3.41 (s, 3H), 2.37 – 2.28 (m, 4H), 2.06 – 2.00 (m, *J* = 12.4, 6.4 Hz, 6H), 1.61 (s, 4H), 1.29 (d, *J* = 9.6 Hz, 42H), 0.90 (t, *J* = 8.7, 4.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.69, 173.17, 130.03, 129.65, 96.85, 73.02, 71.29, 70.61, 69.73, 61.89, 55.26, 34.33, 34.09, 31.92, 29.77, 29.73, 29.55, 29.39, 29.34, 29.23, 29.22, 29.15, 29.09, 29.05, 27.23, 27.18, 25.62, 24.99, 24.92, 22.70, 14.14. (ref 13)

5a. 1-*O*-oxobenzoyl- 2, 3, 4, 6-penta-O-acetyl *α*-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.75 – 7.61 (m, 1H), 7.61 – 7.43 (m, *J* = 23.2, 7.7 Hz, 2H), 6.56 (dd, *J* = 32.3, 3.5 Hz, 1H), 5.61 – 5.42 (m, *J* = 43.3 Hz, 1H), 5.34 (dd, *J* = 3.6 Hz, 1H), 5.22 –

5.16 (m, 1H), 4.28 (td, *J* = 12.9, 3.9 Hz, 1H), 4.17 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.13 – 4.05 (m, 1H), 2.10 – 1.97 (m, 12H).

5b. 1, 2, 3, 4, 6-Penta O-acetyl *α*-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (t, *J* = 9.8 Hz, 1H), 5.39 (d, *J* = 2.5 Hz, 1H), 5.03 (t, *J* = 9.5 Hz, 2H), 4.82 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.24 – 4.17 (m, 2H), 4.07 (d, *J* = 10.6 Hz, 1H), 2.04 (d, *J* = 4.2 Hz, 6H), 1.98 (d, *J* = 7.3 Hz, 6H).

5c. (4-methyl) Phenyl-2, 3, 4, 6-tetra-*O*-oxobenzoyl-1-deoxy-1-thio-*α*-D-glucopyranoside (Starting material was synthesized from literature[13]).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, 2H), 8.08 – 8.02 (m, 2H), 7.97 (d, *J* = 8.3 Hz, 4H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.63 (m, *J* = 15.7, 12.4, 7.6, 1.4 Hz, 7H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.28 (s, 1H), 5.92 (dd, *J* = 9.4 Hz, 1H), 5.70 (t, *J* = 9.5 Hz, 1H), 5.40 (t, *J* = 9.8 Hz, 1H), 4.86 (s, 1H), 4.65 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.55 (dd, *J* = 12.6, 4.4 Hz, 1H), 4.23 – 4.12 (m, *J* = 10.0, 4.2, 2.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.23, 184.40, 184.35, 184.24, 162.99, 162.00, 161.59, 161.19, 146.53, 135.49, 135.32, 135.23, 134.72, 133.86, 132.13, 132.05, 131.65, 131.59, 130.93, 130.65, 130.52, 130.27, 130.16, 129.96, 129.88, 129.21, 129.13, 129.03, 128.94, 128.34, 88.08, 75.58, 73.73, 68.47, 68.10, 62.05, 21.74.

6a. αβ-D-Glucose

^{1}H NMR (400 MHz, D_2O) δ 5.10 (d, *J* = 3.7 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 3.78 – 3.55 (m, 6H), 3.40 (dd, *J* = 9.8, 3.7 Hz, 1H), 3.33 (D, *J* = 11.2, 5.5 Hz, 1H), 3.27 (M, *J* = 9.4, 4.4 Hz, 2H), 3.11 (t, *J* = 8.6 Hz, 1H).

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

^{1}H NMR (400 MHz, DMSO-D_6) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 6.0 Hz, 1H), 5.08 (d, *J* = 4.9 Hz, 1H), 4.97 (d, *J* = 5.3 Hz, 1H), 4.61 – 4.42 (m, 2H), 3.75 – 3.63 (m, 1H), 3.49 – 3.40 (m, *J* = 11.9, 6.0 Hz, 1H), 3.27 – 3.12 (m, *J* = 9.5, 4.0 Hz, 2H), 3.13 – 2.94 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 137.60, 132.38, 132.24, 129.52, 129.25, 88.22, 80.54, 78.20, 72.29, 69.97, 61.48, 19.78. (ref 13)

Conflicts of interest

There are no conflicts to declare.

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Triethylamine-Methanol Mediated Selective Removal of Oxophenylacetyl Ester in Saccharides

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A highly selective, mild and efficient method for the cleavage of oxophenylacetyl ester protected saccharides was developed using triethylamine in methanol at room temperature. The reagent proved successful against different labile groups like acetal, ketal and PMB and also generated good yields of the desired saccharides bearing lipid esters. Further, we also observed DBU in methanol as an alternative reagent for the deprotection of acetyl, benzoyl and oxophenylacetyl ester groups.