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Using DMF as Both a Catalyst and Cosolvent for the Regioselective Silylation of Polyols and Diols

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Abstract: Highly regioselective silylation of primary hydroxyl groups of unprotected polyols and diols was obtained by the use of a mixed solvent of MeCN/DMF (10:1) in this study. DMF was discovered to be a good catalyst in this reaction, although the silylation using DMF as a solvent has been a common method for more than 40 years. The catalytic mechanism of DMF for the silylation was also proposed herein after intensive investigation of the reaction by NMR techniques. It has been demonstrated that a complex with a 1:1 ratio of the binding partners can be formed between TBSCl and DMF and has an association constant of 12/M, thus activating the silylation.

Introduction

Selective protection and semiprotection of carbohydrates for the synthesis of oligosaccharides and glycoconjugates are of great importance in carbohydrate chemistry.[1] Silyl ethers and derivatives are widely applied as protecting groups in carbohydrate synthesis due to their relative stability toward basic and acidic hydrolysis and high specificity for fluoride-mediated cleavage.[2] The most common silylation procedures involve the reaction of hydroxyl groups with silyl chlorides in the presence of an excess of a base, typically either imidazole in *N*,*N*-dimethylformamide (DMF) solvent[3] or pyridine[4] (Figure 1a). *tert*-Butyldimethylsilyl chloride (TBSCl) and *tert*-butyldiphenylsilyl chloride (TBDPSCl) have emerged as the silylation reagents of choice due to the right balance of the resulting silyl ethers between stability against acid or base. The method using imidazole in DMF is more popular likely due to the odor of pyridine being annoying. By this method, regioselective silylation of unprotected methyl pyranosides, with moderate yields for silylation of primary hydroxyl groups, has been achieved.[5] For example, the silylation of unprotected methyl α-glucopyranosides by TBSCl or TBDPSCl in the presence of imidazole in DMF usually gives the 6-monosilylated product in 75–80 % yield.[5] In order to improve the regioselectvity, the methods using equimolar amounts of dibutyltin oxide[6] and catalytic amounts of TBAF in the presence of *N*,*O*-bis(*tert*-butyldimethylsilyl)acetamide (BTBSA),[7] based on the silane alcoholysis reaction,[8] and catalyzed by Lewis acid $B(C_6F_5)_3$[9] or transition metal[10] including palladium, nickel, and ruthenium, have been developed (Figure 1b). However, all of these methods have their own shortcomings, such as long reaction times, use of toxic reagents, harsh reaction conditions, and so on. Our group has long been committed to developing environmental-friendly methods for regioselective protection of carbohydrates.[11,12] The methyl 6-monosilylated pyranosides of glucose, mannose, and galactose were often used as substrates to demonstrate the effectiveness of these methods. For example, the 3-acylated 6-

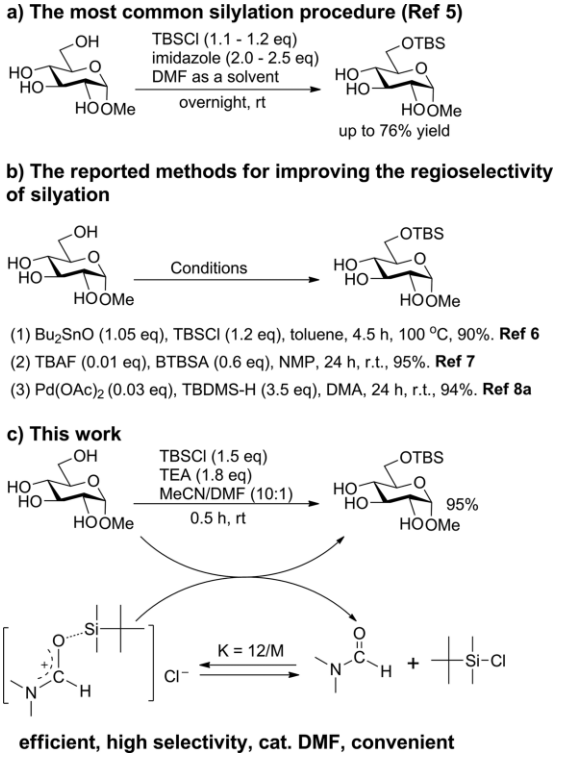

Figure 1. Comparison of this method with previously reported methods.

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O-TBS pyranosides and the 3-alkylated 6-*O*- TBS pyranosides have been obtained by our developed selective acylation,[11] and alkylation,[12] respectively. These 3-acylated-6-silylated pyranosides can be used to develop double parallel or double serial inversion strategies.[13]

In the present study (Figure 1c), we reported an efficient and convenient method for the highly regioselective silylation of primary hydroxyl groups of diols and polyols (particularly unprotected pyranosides). In this method, the treatment of a substrate with 1.5 equiv. of *tert*-butyldimethylsilyl chloride (TBSCl) and 1.8 equiv. of triethylamine (TEA) in a mixed solvent of MeCN and DMF (V_{MeCN}/V_{DMF} = 10:1) for 30 minutes at room temperature gave the primary hydroxyl group silylated product in an excellent yield in most cases. Furthermore, to our best knowledge, we first discovered that DMF was a good catalyst in addition to being a good solvent for silylation, although it had been used as a solvent in silylation for 40 years.[3a] It has been demonstrated by NMR techniques that a complex with a 1:1 ratio of the binding partners can be formed between TBSCl and DMF and has an association constant of 12/M, thus activating the silylation. We also theoretically explained why the most common silylation procedure (Figure 1a) led to relatively poor yields and was an unreasonable choice for regioselective silylation.

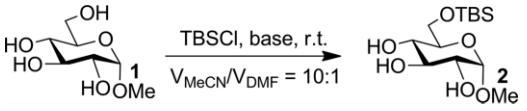
Results and Discussion

The preparation of differentially protected monosaccharide building blocks is typically achieved by the gradual introduction of each protecting group, which results in low overall yield and poor efficiency of synthesis. Therefore, the one-pot method for regioselective multistep protection is very attractive due to the absence of separation and purification of the intermediates.[14] We wondered if we could develop a one-pot method, by which the primary and the secondary hydroxyl groups of unprotected pyranosides would be serially silylated and acylated.

We have developed several regioselective protection methods where a mixed solvent of acetonitrile/DMF (V/*V* = 10:1) was often used with unprotected methyl pyranosides as substrates.[11a,11b,12b,12c] Thus, we first thought of whether the regioselective silylation of the primary hydroxyl group could be carried out in this mixed solvent (MeCN/DMF = 10:1). For this purpose, methyl-α-D-glucopyranoside **1** was tested with TBSCl in the solvent (MeCN/DMF = 10:1) in the presence of excess amounts of bases (Table 1). To our surprise, excellent isolated yields of methyl 6-*O*-TBS-α-D-glucopyranoside **2** (up to 91 %) were obtained within only half an hour in most cases (Entries 1–5 in Table 1). High regioselectivities to the primary hydroxyl group were acquired since only the product **2** and the unreacted starting material **1** were observed in all the reactions. When K_2CO_3 was used instead of organic bases, or the mixed solvent (MeCN/DMF = 10:1) was displaced with MeCN or THF, the reactivity of the silylation dramatically decreased (Entries 6–8 in Table 1).

The use of 1.5 equiv. of TBSCl and 1.8 equiv. of TEA in the mixed solvent (Entry 1 in Table 1) was applied as the optimized condition. We next examined the scope of this methodology

Table 1. Optimization of the silylation of **1** with using a mixed solvent of acetonitrile/DMF.[a]



Entry	Various conditions	Reaction time/h	Isolated yield [%]
1	1.8 equiv. TEA, 1.5 equiv. TBSCl	0.5 h	91
2	1.5 equiv. TEA, 1.5 equiv. TBSCl	0.5 h	88
3	1.8 equiv. TEA, 1.2 equiv. TBSCl	2.0 h	80
4	1.8 equiv. DIPEA, 1.5 equiv. TBSCl	0.5 h	85
5	1.8 equiv. Pyridine, 1.5 equiv. TBSCl	0.5 h	89
6	1.8 equiv. K_2CO_3, 1.5 equiv. TBSCl	3.0 h	31
7[b]	1.8 equiv. TEA, 1.5 equiv. TBSCl	3.0 h	18
8[c]	1.8 equiv. TEA, 1.5 equiv. TBSCl	0.5 h	–

[a] Reactant conditions: substrate (0.2 mmol) in 1.1 mL of solvent [MeCN/DMF = 10:1 (v/v)]. [b] MeCN alone as the solvent. [c] No or trace reaction with using THF as the solvent.

(Figure 2). Under the optimal condition, the silylation of the most substrates gave excellent yields of the desired products. Some substrates such as methyl β-D-glucopyranoside **3**, methyl α-D-galactopyranoside **4**, and α-D-thiogalactopyranoside **12** showed a little lower reactivity in the reaction. However, satisfactory yields of **3a**, **4a** and **12a** (89–91 %) were still obtained

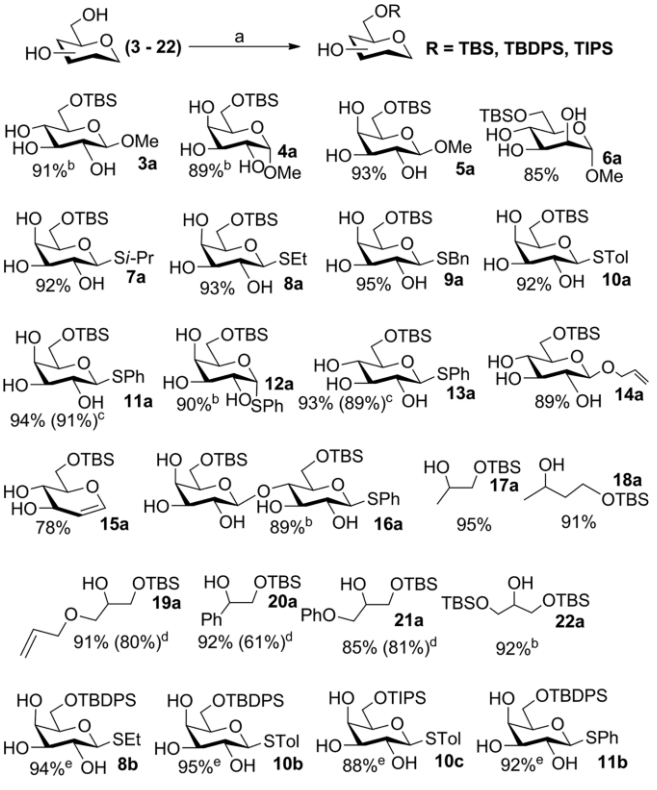


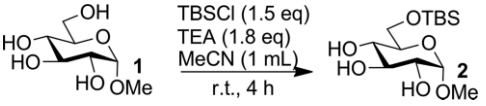
Figure 2. Regioselective silylation of varies substrates containing a primary hydroxyl group. [a]Reaction conditions: substrate (0.2 mmol), TEA (1.8 equiv.), TBSCl (1.5 equiv.), MeCN/DMF (1 mL:0.1 mL), r.t., 0.5 h. [b] The use of increased amount of TEA (2.5–5.0 equiv.) and TBSCl (2.0–4.0 equiv.). [c] Yields on a gram scale. [d] MeCN alone as the solvent, 12 h. [e] TEA (2.5 equiv.), TBDPSCl or TIPSCl (2.0 equiv.), MeCN/DMF (1 mL:0.1 mL), r.t., 8–12 h.

with the increased amounts of TBSCl and TEA. Thiophenyl pyranosides were often used as donors for glycosylation. Thus, thiophenyl β-D-galactopyranoside **11** and thiophenyl β-D-glucopyranoside **13** were silylated under the optimized conditions on a gram scale, yielding **11a** in 91 % yield and **13a** in 89 % yield, respectively. Thiophenyl lactoside **16** was silylated with 4.0 equiv. of TBSCl in the presence of 5.0 equiv. of TEA, yielding **16a** with two primary hydroxyl groups silylated in 89 % yield. All 1,2- and 1,3-diols **17–22** showed high reactivity under the optimal condition. Glycerol **22** was silylated with 2.2 equiv. of TBSCl in the presence of 3.0 equiv. of TEA, yielding **22a** with two primary hydroxyl groups silylated in 92 % yield. The silylation by *tert*-butyldiphenylsilyl chloride (TBDPSCl) or triisopropylsilyl (TIPSCl) was also explored. Thiogalactosides **8**, **10** and **11** were silylated with 2.0 equiv. of TBDPSCl/TIPSCl in the presence of 2.5 equiv. of TEA, giving **8b**, **10b**, **10c** and **11b** in 88–95 % yields.

During studies on the silylation of 1,2-diols **17–22**, we noticed that they had good solubility in acetonitrile. Thus, the silylation of **19**, **20** or **21** by TBSCl was tested in acetonitrile alone since DMF was not required to increase the solubility of the substrates. Unexpectedly, all these reactions showed low reactivities in the absence of DMF and required 12 hours' reaction (Figure 2), giving only moderate yields of **19a**, **20a**, and **21a** (61–81 %). These results inspired us to think about if DMF plays a more important role than a good solvent in the silylation. Therefore, the role of DMF was further studied through the silylation of **1** by TBSCl in the presence of TEA (Table 2). Both the conversion rate for silylation of **1** and the selectivity for **2** were 100 % (reaction proceeding for 1 h, entry 1 in Table 2) with the addition of 0.1 mL of DMF (6.5 equiv.). However, the conversion rate for silylation of **1** was 21 % (reaction proceeding for 4 h) in the absence of DMF (Entry 2 in Table 2) though the selectivity for **2** were 100 %. With the addition of 0.2 equiv. of DMF, the conversion rate for silylation of **1** increased to 40 % (reaction proceeding for 4 h) due to the increased reaction rate, indicating that DMF does catalyze this silylation. With the addition of 0.5 equiv. and 1.0 equiv. of DMF, the conversion rate for silylation of **1** increased to 69 % and 100 %, respectively (Entries 4 and 5 in Table 2). None of these silylations gave any by-products, indicating 100 % regioselectivity for **2** in the presence of DMF. However, DMSO could not improve the silylation as DMF did though DMSO was also a good solvent for glycoside **1** (Entry 6 in Table 2). It has been reported that 4-dimethylaminopyridine (DMAP) was a good catalyst for silylation.[15] The silylation of **1** was completed within four hours in the presence of 0.1 equiv. of DMAP, however, giving 7 % yield of by-products (Entry 7 in Table 2). These results indicated that DMF acted as a catalyst in the silylation as DMAP did but exhibited lower catalytic activity than DMAP. Pyridine and imidazole might have a similar catalytic mechanism to DMAP for the silylation. However, the silylation results (Entries 8, 9 and 10 in Table 2) seemed to show that either pyridine or imidazole is a worse catalyst than DMF.

In order to explore the catalytic mechanism of DMF for the silylation, an intensive investigation of the reaction by NMR techniques was performed. The signals for the protons of DMF

Table 2. Silylation of **1** under various reaction conditions.



Entry	Various condition	Conversion [%]	NMR yield [%] (**2**/by-products)
1[a]	DMF (0.1 mL)	100	100:0
2[b]	–	21	21:0
3	DMF (0.2 equiv.)	40	40:0
4	DMF (0.5 equiv.)	69	69:0
5	DMF (1.0 equiv.)	100	100:0
6	DMSO (0.1 mL)	56	30:26
7	DMAP (0.1 equiv.)	100	93:7
8	Pyridine (0.1 mL)	100	100:0
9	Pyridine (1.0 equiv.)	71	71:0
10	Imidazole (1.0 equiv.)	62	58:4
11[a,c]	Imidazole (1.8 equiv.)	90	65:25
12[c]	Imidazole (1.8 equiv.)	99	63:36
13[d]	Imidazole (2.2 equiv.)	93	85:8

[a]Reaction conditions: Reaction proceeding for 1 h. [b] MeCN (1.1 mL). [c] Without TEA. [d] The most common used condition: DMF (1 mL), TBSCl (1.1 equiv.), Imidazole (2.2 equiv.), r.t., 4 h.

were found to shift with the addition of TBSCl by NMR titration experiments using TBSCl and DMF in *d*-acetonitrile (Figure S1a). The NMR titration experiments supported the formation of a complex (**A**) between TBSCl and DMF. The association constant amounted to 12/M, and Job's analysis indicated a 1:1 ratio of the binding partners (Figure 3). The delocalization of the lone pair electrons of nitrogen to carbonyl group in the complex **A** accounts for why the signals for the protons of DMF shift to downfield. Thus, we proposed that DMF catalyzes the silylation of hydroxyl groups through the formation of the complex **A** (Figure 4). The similar mechanism was also proposed in reactions where DMF had catalyzed the reaction of oxalyl chloride with carboxylic acids to form acyl chlorides.[16] We also compared the ^{13}C NMR spectrum of TBSCl alone with the ^{13}C NMR spectrum of TBSCl in the presence of five times DMF in *d*-acetonitrile. It was observed that the signals for the carbons connecting silicon slightly shifted to downfield, likely to indicating the activation of the silicon of TBS group due to the formation of the complex **A** (Figure S1b). By the NMR experiments (Figure S2a) and gas chromatograph-mass analysis (Figure S2b), it was also observed that a small amount of TBSCl was immediately hydrolyzed to TBSOH by traces of water in the solvent once TBSCl was added into a solvent. After that, slow formation of *tert*-butyldimethylsiloxane (TBSOTBS) in the presence of DMF was observed. We proposed that the complex **A** should also play a key role during the formation of TBSOTBS (Figure 4). When TEA and methanol were subsequently added to this solvent, rapid consumption of TBSCl to form TBSOMe was observed, while both TBSOH and TBSOTBS are inactive for the silylation (Figure S3a). Interestingly, when imidazole was added to the *d*-acetonitrile solution instead of TEA, a stable intermediate formed from imidazole and TBSCl was observed (Figure S3b). With the subsequent addition of methanol, the intermediate was rapid consumed to form TBSOMe. It seemed to indicate that imidazole is a better catalyst than DMF for the silylation,

which contradicts the experimental result shown in entry 10 in Table 2.

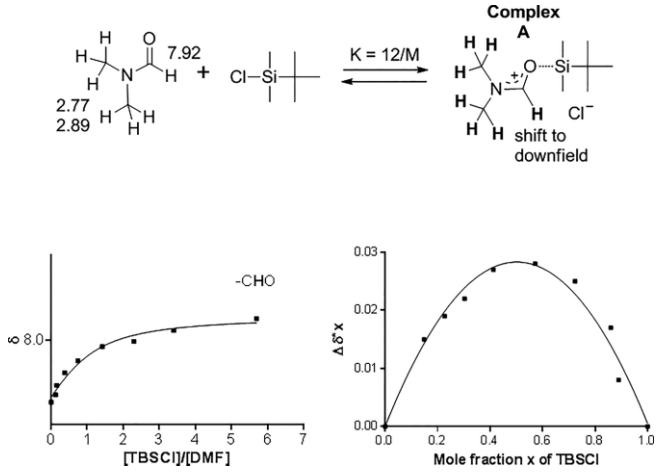


Figure 3. NMR titration and Job's plot for TBSCl with DMF in acetonitrile. K = 12/M, R^2 = 0.9774.

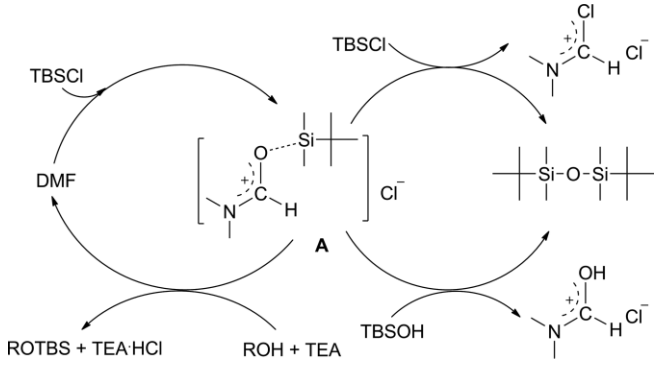


Figure 4. The proposed mechanism for silylation of hydroxyl group catalyzed by DMF.

Either imidazole, DMAP or pyridine should easily form a highly electrophilic *N*-TBS counterion (**B**, **C**, or **D** in Figure 5a) with TBSCl. The counterion **B**, **C**, or **D** then reacts with hydroxyl groups, thereby activating the silylation. The counterion **D** has been observed from the above NMR experiments. The hydrochloride salt of DMAP should be less stable than the hydrochloride salt of TEA. Thus, DMAP can be regenerated in the presence of TEA and catalyze the silylation (Figure 5b). However, for imidazole, its hydrochloride salt **E** should be more stable than the hydrochloride salt of TEA. Thus, imidazole cannot be regenerated in the presence of TEA (Figure 5c). Based on this, we guessed that using1.8 equiv. of imidazole in the absence of TEA should lead to silylation of **1** efficiently. The further experiments supported our hypothesis (Entries 11 and 12 in Table 2). The conversion rates for silylation of **1** were 90 % (reaction proceeding for 1 h) and 99 % (reaction proceeding for 4 h) with the use of 1.8 equiv. of imidazole and 1.5 equiv. of TBSCl in acetonitrile. However, 25 % (reaction for 1 h) and 36 % (reaction for 4 h) yields of other silylation by-products were also generated in these reactions. The poor regioselectivity must be caused by the high reactivity of the counterion **D** shown in Figure 5a. The silylation of **1** gave 85 % yield of **2** and 8 % yield of other silylation by-products when using the most common silylation procedure (Entry 13 in Table 2). Therefore, the formation of TBSOTBS and TBOH leads to insufficient silylation reagents and the use of imidazole leads to poor regioselectivity, which accounts for why only moderate silylation yields are obtained when using the most common silylation procedure (Figure 1a). However, the moderate reactivity of the complex **A** (Figure 4) and the less steric effect of primary hydroxyl groups lead to 100 % selectivity for the silylation of primary hydroxyl groups with DMF as a catalyst (Entries 1–5 in Table 2).

We have reported that acetate/benzoate could catalyze the regioselective acetylation/benzoylation of carbohydrates.[11a,11b] It was further found that a catalytic amount of DIPEA could trigger the catalytic process.[17] Excellent isolated yields of 3-position acylated products were obtained with using methyl 6-*O*-TBS pyranosides as substrates. Based on this result and the present silylation method, we believed that we could proceed serially the silylation and the acylation in one-pot. In the one-pot reaction, DIPEA can both act as a base for silylation and trigger the following acylation. Therefore, methyl α-D-glucopyranoside **1** was initially silylated by TBSCl in the presence of 2.0 equiv. of DIPEA, followed by the addition of 1.2 equiv. of benzoic anhydride. Consequently, methyl 3-*O*-Bz-6-*O*-TBS-α-D-glucopyranoside **2a** was isolated in 76 % yield after 12 hours' reaction at 40 °C (Entry 1 in Table 3), indicating the one-pot reaction was feasible. The use of TEA led to poor yield of **2a** (55 %) due to poor acylation (Entry 2 in Table 3). The use of 2.2 equiv. of DIPEA was the optimum condition under which

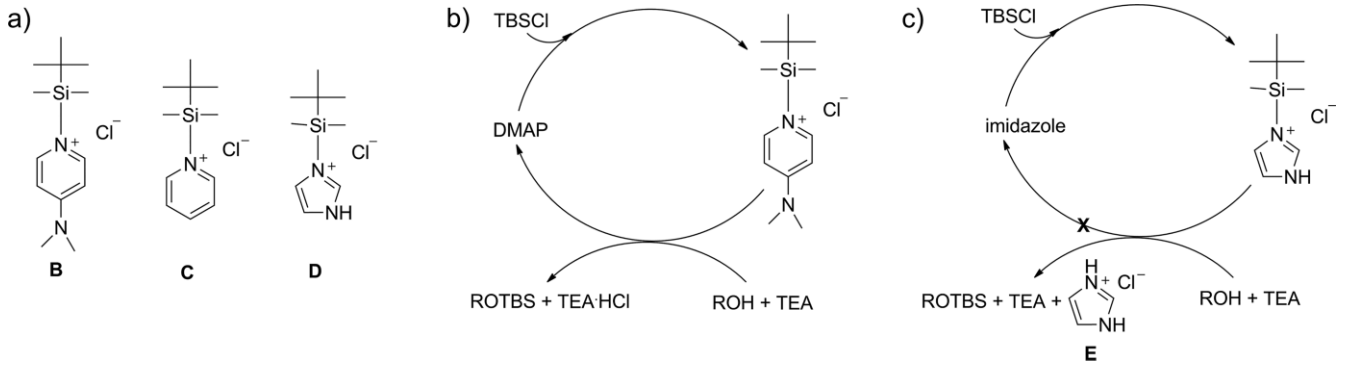
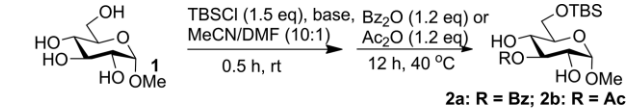


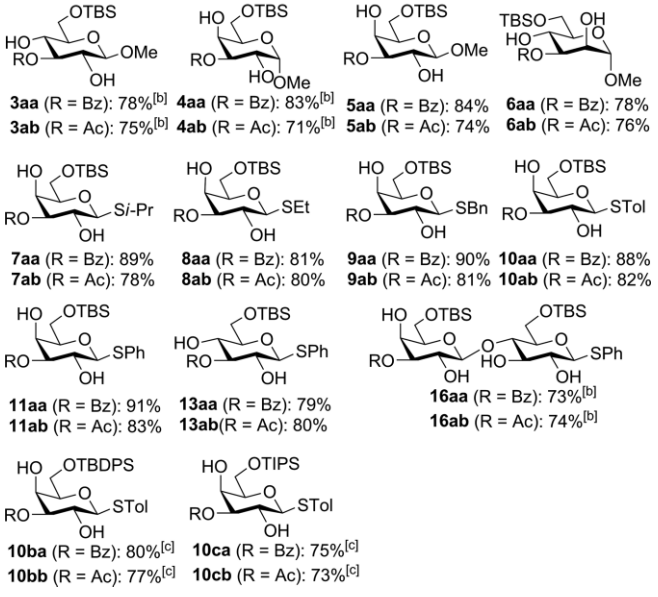
Figure 5. The proposed mechanism for silylation of hydroxyl group catalyzed by DMF.

2a was isolated in 80 % yield (Entry 3 in Table 3). Methyl 3-*O*-Ac-6-*O*-TBS-α-D-glucopyranoside **2b** was isolated in 77 % yield by the one-pot reaction when acetic anhydride was used instead of benzoic anhydride. Encouraged by this attempt, unprotected *O*-glycosides **3**, **4**, **5**, and **6** and thio-glycosides **7**, **8**, **9**, **10**, **11**, **13**, and **16** were subjected to the one-pot reaction, giving corresponding orthogonally protected glycosides in good to excellent yields (71–91 %). The one-pot reaction of methyl β-D-glucopyranoside **3**, methyl α-D-galactopyranoside **4** or thiolactoside **16** required greater amounts of TBSCl and DIPEA for the most complete silylation. TBDPSCl and TIPSCl had also been successfully applied as the silylation reagent in the one-pot reaction, giving desired products **10ba**, **10bb**, **10ca**, and **10cb** in 73–80 % yields.

Table 3. One-pot tandem silylation/acylation reactions.[a]



Entry	Reaction Conditions	Isolated Yield %
1	2.0 equiv of DIPEA	76 (**2a**)
2	2.0 equiv of TEA	55 (**2a**)
3	2.2 equiv of DIPEA	80 (**2a**), 77 (**2b**)
4	2.4 equiv of DIPEA	80 (**2a**)



[a] Reaction conditions: i) substrate (0.2 mmol), DIPEA (2.2 equiv.), TBSCl (1.5 equiv.), MeCN/DMF (1 mL:0.1 mL), r.t., 0.5 h; ii) Bz_2O/Ac_2O (1.2 equiv.), 40 °C, 8–12 h. [b] The use of increased amount of DIPEA (3.0–6.0 equiv.) and TBSCl (2.0–4.0 equiv.). [c] The use of DIPEA (2.6–3.0 equiv.) and TBDPSCl/TIPSCl (2.0 equiv.), 12 h.

Conclusions

In this study, we developed a highly regioselective silylation method for primary hydroxyl groups of diols and polyols (85–95 % yields). The method was further used in a one-pot reaction to obtain 3-acylated-6-silylated pyranosides (71–91 % yields) from unprotected pyranosides under very mild conditions. Through comprehensive mechanistic studies, DMF was first discovered to be a good catalyst in these silylation processes. NMR titration experiments demonstrated that a complex with a 1:1 ratio of the binding partners was formed between TBSCl and DMF and had an association constant of 12/M. DMF might also catalyze the formation of TBSOTBS from TBSCl and TBSOH via this complex. Imidazole was observed to form a highly active intermediate for silylation with TBSCl thus leading to poor regioselectivity. Consequently, the most common silylation procedure was theoretically demonstrated to be an unreasonable choice for regioselective silylation herein, since the formation of TBSOTBS and TBOH led to insufficient silylation reagents, and the use of imidazole and long reaction time led to poor regioselectivity.

Experimental Section

General: All commercially available starting materials and solvents were of reagent grade and used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. High resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI) and TOF detection. Flash column chromatography was performed on silica gel 60 (SDS 0.040–0.063 mm). ^{1}H NMR spectra were recorded at 298K in $CDCl_3$, CD_3OD, $(CD_3)_2SO$, CD_3CN and [D_7]DMF using the residual signals from $CDCl_3$ (^{1}H: δ = 7.26 ppm; ^{13}C: δ = 77.16 ppm), CD_3OD (^{1}H: δ = 3.31 ppm), $(CD_3)_2SO$ (^{1}H: δ = 2.49 ppm), CD_3CN (^{1}H: δ = 1.94 ppm; ^{13}C: δ = 118.26 ppm) and [D_7]DMF (δ = 8.03 ppm) as internal standard. ^{1}H peak assignments were made by first order analysis of the spectra, supported by standard ^{1}H-^{1}H correlation spectroscopy (COSY).

General Procedure A for the Silylation of Substrates: To a mixture of the substrate (0.2 mmol) in 1.1 mL of solvent (V_{MeCN}/V_{DMF} = 10:1), triethylamine (TEA) (1.8–5.0 equiv.) and *tert*-butyldimethylsilyl chloride (TBSCl)(1.5–4.0 equiv.) were added and then stirred at room temperature for 0.5 hours. The reaction mixture was directly purified by flash column chromatography, affording the pure selectively protected derivatives.

General Procedure A′ for the Silylation of Substrates 11 and 13 in Large-scale: To a mixture of the substrate (4.0 mmol) in 11.0 mL of solvent (V_{MeCN}/V_{DMF} = 10:1), triethylamine (TEA) (1.8 equiv.) and *tert*-butyldimethylsilyl chloride (TBSCl)(1.5 equiv.) were added and then stirred at room temperature for 0.5 hours. The reaction mixture was directly purified by flash column chromatography, affording the pure selectively protected derivatives.

General Procedure B for Silylation and Acylation of Substrates in One-pot: To a mixture of the substrate (0.2 mmol) in 1.1 mL of solvent (V_{MeCN}/V_{DMF} = 10:1), *N*,*N*-diisopropylethylamine (DIPEA) (2.2–6.0 equiv.) and *tert*-butyldimethylsilyl chloride (TBSCl) (1.5–4.0 equiv.) were added and then stirred at room temperature for 0.5 hours. Upon complete silylation as shown by TLC, anhydride (1.2 equiv.) was added and the mixture was left stirring at 40 °C for 8–12 h. The crude product was directly purified by flash column chromatography, affording the pure selectively protected derivatives.

Methyl 6-*O*-(*tert*-Butyldimethylsilyl)-α-D-glucopyranoside (2):[6] Following the general procedure A, the reaction was carried out

with methyl-α-D-glucopyranoside **1** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 5:1), afforded compound **2** as white solid (56.1 mg, 91 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.71 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.29 (br s, 3H, -**OH**), 3.87 (dd, *J* = 10.8 Hz and 3.2 Hz, 1H, **H-6a**), 3.81–3.73 (m, 2H, **H-6b** and **H-3**), 3.58–3.53 (m, 1H, **H-4**), 3.49 (dd, *J* = 9.6 Hz and 3.6 Hz, 1H, **H-2**), 3.43–3.37 (m, 4H, **H-5** and O**CH_3**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.07 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 6-*O*-(*tert*-Butyldimethylsilyl)-β-D-glucopyranoside (3a):[8a] Following the general procedure A, the reaction was carried out with methyl-β-D-glucopyranoside **3** (0.2 mmol), TEA (69.5 μL, 2.5 equiv.), TBSCl (61.5 mg, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 5:1), afforded compound **3a** as white solid (56.0 mg, 91 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.18 (d, *J* = 7.6 Hz, 1H, **H-1**), 3.89 (dd, *J* = 10.8 Hz and 4.0 Hz, 1H, **H-6a**), 3.82 (dd, *J* = 10.8 Hz and 5.6 Hz, 1H, **H-6b**), 3.54–3.41 (m, 5H, **H-3**, **H-4** and O**CH_3**), 3.35–3.30 (m, 2H, **H-2** and **H-5**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.08 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 6-*O*-(*tert*-Butyldimethylsilyl)-α-D-galactopyranoside (4a):[4c] Following the general procedure A, the reaction was carried out with methyl-α-D-galactopyranoside **4** (0.2 mmol), TEA (111.5 μL, 4.0 equiv.), TBSCl (92.3 mg, 3.0 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 5:1), afforded compound **4a** as white crystalline solid (54.8 mg, 89 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.81 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.09 (br s, 1H, **H-4**), 3.92–3.83 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.75–3.72 (m, 2H, **H-3** and **H-5**), 3.41 (s, 3H, O**CH_3**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.09 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 6-*O*-(*tert*-Butyldimethylsilyl)-β-D-galactopyranoside (5a):[8a] Following the general procedure A, the reaction was carried out with methyl-β-D-galactopyranoside **5** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 5:1), afforded compound **5a** as viscous colorless oil (57.3 mg, 93 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.14 (d, *J* = 7.6 Hz, 1H, **H-1**), 3.97 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.89 (dd, *J* = 10.4 Hz and 6.4 Hz, 1H, **H-6a**), 3.82 (dd, *J* = 10.4 Hz and 5.6 Hz, 1H, **H-6b**), 3.69–3.64 (m, 1H, **H-2**), 3.58–3.52 (m, 4H, **H-3** and O**CH_3**), 3.46 (t, *J* = 5.6 Hz, 1H, **H-5**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.07 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 6-*O*-(*tert*-Butyldimethylsilyl)-α-D-mannopyranoside (6a):[4c] Following the general procedure A, the reaction was carried out with methyl-α-D-mannopyranoside **6** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 4:1), afforded compound **6a** as white solid (52.4 mg, 85 %). **^{1}H NMR (400 MHz, CD_3OD)**: δ = 4.61 (br s, 1H, **H-1**), 3.98 (dd, *J* = 11.2 Hz and 1.8 Hz, 1H, **H-6a**), 3.79–3.75 (m, 2H, **H-2**, **H-6b**), 3.64 (dd, *J* = 8.8 Hz and 3.2 Hz, 1H, **H-3**), 3.56–3.64 (m, 2H, **H-4**, **H-5**), 3.36 (s, 3H, O**CH_3**), 0.92 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.10 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Isopropyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-β-D-galactopyranoside (7a):[4c]Following the general procedure A, the reaction was carried out with isopropyl-β-D-thiogalactopyranoside **7** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **7a** as viscous colorless oil (64.8 mg, 92 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 4.38 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.03 (br s, 1H, **H-4**), 3.85–3.77 (m, 2H, **H-6a** and **H-6b**), 3.71–3.47 (m, 6H, **H-2**, **H-3**, **H-5** and **OH × 3**), 3.25–3.15 (m, 1H, C**H**(CH_3)$_2$), 1.30 (dd, *J* = 6.4 Hz and 2.4 Hz, 6H, CH(**CH_3**)$_2$), 0.87 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.06 (s, 3H, Si(C(CH_3)$_3$)(**CH_3**)$_2$), 0.05 (s, 3H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Ethyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-β-D-galactopyranoside (8a): Following the general procedure A, the reaction was carried out with ethyl-β-D-thiogalactopyranoside **8** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **8a** as viscous colorless oil (62.8 mg, 93 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 4.32 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.04 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.87–3.70 (m, 6H, **H-2**, **H-6a**, **H-6b** and **OH × 3**), 3.58 (dd, *J* = 8.8 Hz and 2.8 Hz, 1H, **H-3**), 3.49 (t, *J* = 5.2 Hz, 1H, **H-5**), 2.79–2.65 (m, 2H, S**CH_2**CH_3), 1.30–1.26 (m, 3H, SCH_2**CH_3**), 0.87 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.06 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 86.0, 78.6, 75.2, 70.4, 69.4, 62.8, 25.9, 24.4, 18.3, 15.4, –5.3, –5.3 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{14}H_{30}O_5SSiNa]^+$: 361.1475, found 361.1481.

Ethyl 6-*O*-(*tert*-Butyldiphenylsilyl)-1-thio-β-D-galactopyranoside (8b): Following the general procedure A, the reaction was carried out with ethyl-β-D-thiogalactopyranoside **8** (0.2 mmol), TEA (69.5 μL, 2.5 equiv.), TBDPSCl (104.0 μL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature for 12 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 10:1), afforded compound **8b** as viscous colorless oil (86.8 mg, 94 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.71–7.66 (m, 4H, **ArH**), 7.44–7.35 (m, 6H, **ArH**), 4.30 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.10 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.93–3.85 (m, 2H, **H-6a** and **H-6b**), 3.72 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.58 (dd, *J* = 8.8 Hz and 2.8 Hz, 1H, **H-3**), 3.53 (t, *J* = 5.6 Hz, 1H, **H-5**), 3.27 (br s, 3H, **OH** × 3), 2.78–2.63 (m, 2H, S**CH_2**CH_3), 1.27 (t, *J* = 7.6 Hz, 3H, SCH_2**CH_3**), 1.05 (s, 9H, Si(C(**CH_3**)$_3$)). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 135.8, 135.7, 133.2, 133.0, 129.9, 127.9, 127.8, 86.0, 78.5, 77.4, 75.1, 70.5, 69.4, 63.4, 26.9, 24.3, 19.3, 15.4 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{24}H_{34}O_5SSiNa]^+$: 485.1788, found 485.1789.

Benzyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-β-D-galactopyranoside (9a): Following the general procedure A, the reaction was carried out with benzyl-β-D-thiogalactopyranoside **9** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **9a** as viscous colorless oil (76.0 mg, 95 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.31–7.18 (m, 5H, Ar**H**), 4.12 (d, *J* = 9.6 Hz, 1H, **H-1**), 3.98–3.91 (m, 2H, **H-4, CH**$_2$), 3.86–3.80 (m, 3H, **H-6a**, **H-6b** and **CH**$_2$), 3.70 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.44–3.35 (m, 2H, **H-3** and **H-5**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.08 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 137.7, 129.2, 128.7, 127.3, 84.3, 78.5, 75.1, 70.5, 69.4, 63.0, 33.8, 26.0, 18.4, –5.2, –5.2 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{19}H_{32}O_5SSiNa]^+$: 423.1632, found 423.1633.

***p*-Tolyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-β-D-galactopyranoside (10a):** Following the general procedure A, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **10a** as a viscous color-

less oil (73.6 mg, 92 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.44 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.07 (d, *J* = 8.0 Hz, 2H, Ar**H**), 4.47 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.04 (d, *J* = 2.4 Hz, 1H, **H-3**), 3.91–3.83 (m, 2H, **H-6a, H-6b**), 3.71 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.60–3.46 (m, 5H, **H-4**, **H-5** and **OH** × **3**), 2.31 (s, 3H, Ph**CH_3**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.08 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$), 0.07 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 138.2, 133.1, 129.8, 128.7, 89.0, 78.3, 75.1, 70.0, 69.5, 63.3, 25.9, 21.3, 18.4, –5.3, –5.3 ppm; **HRMS (ESI-TOF):** Calculated for [$C_{19}H_{32}O_5SSiNa$]$^+$: 423.1632, found 423.1630.

***p*-Tolyl 6-*O*-(*tert*-Butyldiphenylsilyl)-1-thio-β-D-galactopyranoside (10b):**[18] Following the general procedure A, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), TEA (69.5 μL, 2.5 equiv.), TBDPSCl (104.0 μL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature for 8 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 2:1), afforded compound **10b** as a white solid (99.6 mg, 95 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.73–7.68 (m, 4H, **ArH**), 7.45–7.35 (m, 8H, **ArH**), 7.05–7.03 (m, 2H, **ArH**), 4.44 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.09 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.96–3.91 (m, 2H, **H-6a, H-6b**), 3.67 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.59–3.53 (m, 2H, **H-3** and **H-5**), 2.97 (s, 3H, **OH** × **3**), 2.30 (s, 3H, Ph**CH_3**), 1.06 (s, 9H, Si(C(**CH_3**)$_3$)).

***p*-Tolyl 6-*O*-(Triisopropylsilyl)-1-thio-β-D-galactopyranoside (10c):** Following the general procedure A, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), TEA (69.5 μL, 2.5 equiv.), TIPSCl (85.5 μL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature for 16 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 2:1), afforded compound **10c** as a viscous colorless oil (77.8 mg, 88 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.45 (d, *J* = 8.0 Hz, 2H, **ArH**), 7.09 (d, *J* = 8.0 Hz, 2H, **ArH**), 4.45 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.11 (d, *J* = 2.4 Hz, 1H, **H-4**), 4.03 (dd, *J* = 10.4 Hz and 5.6 Hz, 1H, **H-6a**), 3.96 (dd, *J* = 10.4 Hz and 4.8 Hz, 1H, **H-6b**), 3.67 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.58 (dd, *J* = 9.2 Hz and 2.8 Hz, 1H, **H-3**), 3.51 (t, *J* = 4.8 Hz, 1H, **H-5**), 2.92 (br s, 3H, **OH** × **3**), 2.33 (s, 3H, SPh**CH_3**), 1.11–1.05 (m, 21H, Si(C**H**(**CH_3**)$_2$) × 3). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 138.3, 133.2, 129.8, 128.6, 88.9, 78.3, 77.4, 75.2, 70.0, 69.6, 63.7, 21.3, 18.1, 18.0, 11.9 ppm; **HRMS (ESI-TOF):** Calculated for [$C_{22}H_{38}O_5SSiNa$]$^+$: 465.2101, found 465.2102.

Phenyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-β-D-galactopyranoside (11a):[19] Following the general procedure A, the reaction was carried out with phenyl-β-D-thiogalactopyranoside **11** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **11a** as viscous colorless oil (72.6 mg, 94 %). **^{1}H NMR (400 MHz, $(CD_3)_2SO$):** δ = 7.44–7.41 (m, 2H, Ar**H**), 7.28–7.16 (m, 3H, Ar**H**), 5.16 (d, *J* = 5.6 Hz, 1H, **OH**), 4.95 (d, *J* = 5.2 Hz, 1H, **OH**), 4.59 (d, *J* = 9.2 Hz, 1H, **H-1**), 4.53 (d, *J* = 4.0 Hz, 1H, **OH**), 3.69–3.26 (m, 3H, **H-4, H-6a** and **H-6b**), 3.55–3.52 (m, 1H, **H-5**), 3.44–3.37 (m, 2H, **H-2** and **H-3**), 0.85 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.02 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$), 0.01 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$).

Phenyl 6-*O*-(*tert*-Butyldiphenylsilyl)-1-thio-β-D-galactopyranoside (11b):[18] Following the general procedure A, the reaction was carried out with phenyl-β-D-thiogalactopyranoside **11** (0.2 mmol), TEA (69.5 μL, 2.5 equiv.), TBDPSCl (104.0 μL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature for 8 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **11b** as an amorphous solid (93.8 mg, 92 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.72–7.68 (m, 4H, Ar**H**), 7.55–7.52 (m, 2H, Ar**H**), 7.43–7.33 (m, 6H, **ArH**), 7.23–7.21 (m, 3H, Ar**H**), 4.53 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.07 (d, *J* = 2.0 Hz, 1H, **H-4**), 3.93 (d, *J* = 5.2 Hz, 2H, **H-6a** and **H-6b**), 3.74 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.60–3.53 (m, 2H, **H-3** and **H-5**), 3.37 (br s, 3H, **OH** × **3**), 1.05 (s, 9H, Si(C(**CH_3**)$_3$)).

Phenyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-α-D-galactopyranoside (12a): Following the general procedure A, the reaction was carried out with phenyl-α-D-thiogalactopyranoside **12** (0.2 mmol), TEA (69.5 μL, 2.5 equiv.), TBSCl (55.3 mg, 1.8 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **12a** as viscous colorless oil (69.5 mg, 90 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.49–7.46 (m, 2H, Ar**H**), 7.33–7.24 (m, 3H, Ar**H**), 5.48 (d, *J* = 2.4 Hz, 1H, **H-1**), 4.22–4.17 (m, 2H, **H-2** and **H-3**), 4.13–4.11 (m, 1H, **H-4**), 3.91–3.86 (m, 1H, **H-5**), 3.76–3.71 (m, 1H, **H-6a**), 3.69–3.65 (m, 1H, **H-6b**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.08 (s, 6H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 133.9, 131.9, 129.2, 127.7, 92.9, 85.4, 81.6, 79.2, 72.2, 64.2, 25.9, 18.4, –5.2, –5.3 ppm; **HRMS (ESI-TOF):** Calculated for [$C_{18}H_{30}O_5SSiNa$]$^+$: 409.1475, found 409.1478.

Phenyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-β-D-glucopyranoside (13a):[20] Following the general procedure A, the reaction was carried out with phenyl-β-D-thioglucopyranoside **13** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **13a** as viscous colorless oil (71.8 mg, 93 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.52–7.50 (m, 2H, Ar**H**), 7.26–7.25 (m, 3H, Ar**H**), 4.54 (d, *J* = 9.6 Hz, 1H, **H-1**), 3.87 (d, *J* = 4.4 Hz, 2H, **H-6a** and **H-6b**), 3.60–3.47 (m, 2H, **H-3** and **H-4**), 3.39–3.31 (m, 2H, **H-2** and **H-5**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.09 (s, 6H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$).

Allyl 6-*O*-(*tert*-Butyldimethylsilyl)-β-D-glucopyranoside (14a):[21] Following the general procedure A, the reaction was carried out with allyl-β-D-glucopyranoside **14** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **14a** as viscous colorless oil (59.5 mg, 89 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 5.98–5.88 (m, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.36–4.31 (m, 2H), 4.10 (dd, *J* = 12.8 Hz and 6.4 Hz, 1H), 3.87–3.85 (m, 2H), 3.63–3.32 (m, 7H), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.09 (s, 6H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$).

6-*O*-(*tert*-Butyldimethylsilyl)-D-glucal (15a):[22] Following the general procedure A, the reaction was carried out with D-glucal **15** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 3:1), afforded compound **15a** as colorless syrup (40.6 mg, 78 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 6.31–6.29 (m, 1H), 4.71 (dd, *J* = 6.0 Hz and 2.0 Hz, 1H), 4.24 (br s, 1H), 3.99–3.89 (m, 2H), 3.80–3.75 (m, 2H), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.09 (s, 6H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$).

Phenyl 6,6′-Di-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-lactoside (16a): Following the general procedure A, the reaction was carried out with phenyl-1-thio-β-D-lactoside **16** (0.2 mmol), TEA (139.0 μL, 5.0 equiv.), TBSCl (123.0 mg, 4.0 equiv.) in dry solvent (1.1 mL) at room temperature for 3 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 10:1), afforded compound **16a** as viscous colorless oil (117.8 mg, 89 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.55–7.52 (m, 2H, Ar**H**), 7.27–7.24 (m, 3H, Ar**H**), 4.49 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.34 (d, *J* = 8.0 Hz, 1H, **H-1′**), 3.94 (d, *J* = 2.4 Hz, 1H, **H-6a′**), 3.89 (br s, 1H, **H-6b′**), 3.82–

3.75 (m, 2H, **H-6a** and **H-6b**), 3.70–3.57 (m, 4H, **H-2′**, **H-3**, **H-4′** and **H-4**), 3.50–3.45 (m, 2H, **H-3′** and **H-5′**), 3.41–3.39 (m, 1H, **H-5**), 3.33–3.28 (m, 1H, **H-2**), 0.89 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.85 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.08 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.07 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.04 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 133.3, 131.9, 128.9, 128.1, 103.3, 87.3, 79.3, 78.6, 77.4, 76.2, 75.4, 74.0, 71.5, 68.5, 62.4, 61.8, 26.1, 25.9, 18.4, 18.3, –4.9, –5.1, –5.3, –5.3 ppm; **HRMS (ESI-TOF):** Calculated for [C$_{30}$H$_{54}$O$_{10}$SSi$_2$Na]$^+$: 685.2868, found 685.2874.

1-*O*-(*tert*-Butyldimethylsilyl)propanediol (17a):[23] Following the general procedure A, the reaction was carried out with 1,2-propanediol **17** (0.177 mmol), TEA (44.5 μL, 1.8 equiv.), TBSCl (42.5 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 5 minutes. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:10), afforded compound **17a** as colorless oil (32.0 mg, 95 %). **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 3.85–3.78 (m, 1H), 3.59 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H), 3.34 (dd, *J* = 9.6 Hz and 8.4 Hz, 1H), 1.11 (d, *J* = 6.0 Hz, 3H), 0.91 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.07 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

4-*O*-(*tert*-Butyldimethylsilyl)-butan-2-ol (18a):[24] Following the general procedure A, the reaction was carried out with 1,3-butanediol **18** (0.216 mmol), TEA (54.5 μL, 1.8 equiv.), TBSCl (40.5 mg, 1.2 equiv.) in dry solvent (1.1 mL) at room temperature for 5 minutes. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:10), afforded compound **18a** as colorless oil (40.2 mg, 91 %). **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 4.05–3.96 (m, 1H), 3.89–3.75 (m, 2H), 1.70–1.56 (m, 2H), 1.17 (d, *J* = 6.0 Hz, 3H), 0.88 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.06 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

1-Allyl-3-*O*-(*tert*-Butyldimethylsilyl)-rac-glycerol (19a):[25] Following the general procedure A, the reaction was carried out with 1-allyloxy-propane-2,3-diol **19** (0.216 mmol), TEA (54.0 μL, 1.8 equiv.), TBSCl (50.0 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 5 minutes. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:8), afforded compound **19a** as colorless oil (48.5 mg, 91 %). **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 5.94–5.84 (m, 1H), 5.29–5.23 (m, 1H), 5.19–5.15 (m, 1H), 4.00 (dt, *J* = 6.0 Hz and 1.2 Hz, 2H), 3.84–3.79 (m, 1H), 3.67–3.60 (m, 2H), 3.51–3.42 (m, 2H), 0.89 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.06 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

2-*O*-(*tert*-Butyldimethylsilyl)-1-phenylethanol (20a):[26] Following the general procedure A, the reaction was carried out with 1-phenyl-1,2-ethanediol **20** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.5 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 20 minutes. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:10), afforded compound **20a** as colorless oil (46.4 mg, 92 %). **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.39–7.27 (m, 5H), 4.76 (dd, *J* = 8.4 Hz and 3.2 Hz, 1H), 3.77 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H), 3.58–3.53 (m, 1H), 0.92 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)2), 0.07 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.07 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

3-Phenoxy-1-*O*-(*tert*-butyldimethylsilyl)propane-2-ol (21a): Following the general procedure A, the reaction was carried out with 3-phenoxy-1,2-propanediol **21** (0.2 mmol), TEA (50.0 μL, 1.8 equiv.), TBSCl (46.5 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature for 20 minutes. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:8), afforded compound **21a** as colorless oil (48.0 mg, 85 %). **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.31–7.27 (m, 2H), 6.98–6.90 (m, 3H), 4.07–4.00 (m, 3H), 3.82–3.74 (m, 2H), 0.91 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.08 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 158.7, 129.6, 121.1, 114.7, 70.3, 68.5, 63.9, 26.0, 18.4, –5.3 ppm; **HRMS (ESI-TOF):** Calculated for [C$_{15}$H$_{26}$O$_3$SiNa]$^+$: 305.1543, found 305.1550.

1,3-Di-*O*-(*tert*-butyldimethylsilyl)propane-2-ol (22a):[27] Following the general procedure A, the reaction was carried out with glycerol **22** (0.212 mmol), TEA (88.5 μL, 3.0 equiv.), TBSCl (72.5 mg, 2.2 equiv.) in dry solvent (1.1 mL) at room temperature for 5 minutes. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:8), afforded compound **22a** as colorless oil (62.4 mg, 92 %). **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 3.67–3.61 (m, 5H), 0.89 (s, 18H, 2 × Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.06 (s, 12H, 2 × Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

Methyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (2a):[11b] Following the general procedure B, the reaction was carried out with methyl-α-D-glucopyranoside **1** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 10 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:5), afforded compound **2a** as a viscous colorless oil (65.9 mg, 80 %). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ = 8.09–8.06 (m, 2H, Ar**H**), 7.58–7.53 (m, 1H, Ar**H**), 7.46–7.40 (m, 2H, Ar**H**), 5.35 (t, *J* = 9.6 Hz, 1H, **H-3**), 4.81 (d, *J* = 3.6 Hz, 1H, **H-1**), 3.94–3.86 (m, 2H, **H-6a** and **H-6b**), 3.78–3.68 (m, 3H, **H-2**, **H-4** and **H-5**), 3.46 (s, 3H, O**CH$_3$**), 0.91 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.10 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

Methyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (2b):[11a]Following the general procedure B, the reaction was carried out with methyl-α-D-glucopyranoside **1** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **2b** as a viscous colorless oil (53.9 mg, 77 %). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ = 5.08 (t, *J* = 9.2 Hz, 1H, **H-3**), 4.74 (d, *J* = 3.6 Hz, 1H, **H-1**), 3.87 (dd, *J* = 10.8 Hz and 4.4 Hz, **H-6a**), 3.82 (dd, *J* = 10.8 Hz and 3.6 Hz, **H-6b**), 3.67–3.53 (m, 3H, **H-2**, **H-4** and **H-5**), 3.43 (s, 3H, O**CH$_3$**), 2.15 (s, 3H, O**Ac**), 0.89 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.08 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

Methyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranoside (3aa):[11b] Following the general procedure B, the reaction was carried out with methyl-β-D-glucopyranoside **3** (0.2 mmol), DIPEA (105.5 μL, 3.0 equiv.), TBSCl (61.5 mg, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:5), afforded compound **3aa** as a viscous colorless oil (64.3 mg, 78 %). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ = 8.11–8.07 (m, 2H, Ar**H**), 7.58–7.54 (m, 1H, Ar**H**), 7.46–7.41 (m, 2H, Ar**H**), 5.22 (t, *J* = 9.6 Hz, 1H, **H-3**), 4.33 (d, *J* = 7.6 Hz, 1H, **H-1**), 3.96 (dd, *J* = 10.4 Hz and 4.8 Hz, 1H, **H-6a**), 3.90 (dd, *J* = 10.4 Hz and 5.2 Hz, 1H, **H-6b**), 3.82 (t, *J* = 9.2 Hz, 1H, **H-4**), 3.63–3.45 (m, 5H, **H-2**, **H-5** and O**CH$_3$**), 0.89 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.10 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

Methyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranoside (3ab):[11a] Following the general procedure B, the reaction was carried out with methyl-β-D-glucopyranoside **3** (0.2 mmol), DIPEA (105.5 μL, 3.0 equiv.), TBSCl (61.5 mg, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was

directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:5), afforded compound **3ab** as a viscous colorless oil (52.5 mg, 75 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.95 (t, *J* = 9.6 Hz, 1H, **H-3**), 4.24 (d, *J* = 7.6 Hz, 1H, **H-1**), 3.92 (dd, *J* = 10.4 Hz and 4.8 Hz, 1H, **H-6a**), 3.84 (dd, *J* = 10.4 Hz and 5.2 Hz, 1H, **H-6b**), 3.65 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.53 (s, 3H, O**CH_3**), 3.45–3.37 (m, 2H, **H-4** and **H-5**), 2.16 (s, 3H, O**Ac**), 0.88 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.08 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside (4aa):[4c] Following the general procedure B, the reaction was carried out with methyl-α-D-galactopyranoside **4** (0.2 mmol), DIPEA (140.5 μL, 4.0 equiv.), TBSCl (78.8 mg, 2.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:4), afforded compound **4aa** as a viscous colorless oil (68.4 mg, 83 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.12–8.07 (m, 2H, Ar**H**), 7.61–7.53 (m, 1H, Ar**H**), 7.47–7.41 (m, 2H, Ar**H**), 5.27 (dd, *J* = 10.4 Hz and 2.4 Hz, 1H, **H-3**), 4.91 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.32 (d, *J* = 1.6 Hz, 1H, **H-4**), 4.25 (dd, *J* = 10.4 Hz and 3.6 Hz, 1H, **H-2**), 3.96–3.85 (m, 3H, **H-5**, **H-6a** and **H-6b**), 3.46 (s, 3H, O**CH_3**), 0.90 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.10 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside (4ab):[11a] Following the general procedure B, the reaction was carried out with methyl-α-D-galactopyranoside **4** (0.2 mmol), DIPEA (140.5 μL, 4.0 equiv.), TBSCl (78.8 mg, 2.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:2), afforded compound **4ab** as a viscous colorless oil (49.7 mg, 71 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 5.03 (dd, *J* = 10.0 Hz and 2.4 Hz, 1H, **H-3**), 4.85 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.19 (d, *J* = 2.0 Hz, 1H, **H-4**), 4.07 (dd, *J* = 10.0 Hz and 3.6 Hz, 1H, **H-2**), 3.94–3.86 (m, 2H, **H-6a** and **H-6b**), 3.77–3.75 (m, 1H, **H-5**), 3.43 (s, 3H, O**CH_3**), 2.17 (s, 3H, O**Ac**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.09 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside (5aa):[11b] Following the general procedure B, the reaction was carried out with methyl-β-D-galactopyranoside **5** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 10 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:4), afforded compound **5aa** as a viscous colorless oil (69.2 mg, 84 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.10–8.02 (m, 2H, Ar**H**), 7.59–7.52 (m, 1H, Ar**H**), 7.45–7.39 (m, 2H, Ar**H**), 5.07 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3**), 4.36–4.28 (m, 2H, **H-1** and **H-4**), 4.05 (dd, *J* = 9.6 Hz and 8.0 Hz, 1H, **H-2**), 3.95 (dd, *J* = 10.8 Hz and 6.0 Hz, 1H, **H-6a**), 3.89 (dd, *J* = 10.8 Hz and 4.4 Hz, 2H, **H-6b**), 3.61–3.57 (m, 4H, **H-5**, O**CH_3**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.08 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside (5ab):[11a] Following the general procedure B, the reaction was carried out with methyl-β-D-galactopyranoside **5** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:2), afforded compound **5ab** as a viscous colorless oil (51.8 mg, 74 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.80 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3**), 4.22 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.14 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.93–3.83 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.54–3.46 (m, 4H, **H-5** and O**CH_3**), 2.16 (s, 3H, O**Ac**), 0.87 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.07 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside (6aa):[11e] Following the general procedure B, the reaction was carried out with methyl-α-D-mannopyranoside **6** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 10 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:5), afforded compound **6aa** as a viscous colorless oil (64.3 mg, 78 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.11–8.08 (m, 2H, Ar**H**), 7.59–7.55 (m, 1H, Ar**H**), 7.46–7.42 (m, 2H, Ar**H**), 5.36 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.74 (d, *J* = 1.6 Hz, 1H, **H-1**), 4.16–4.10 (m, 2H, **H-2** and **H-4**), 3.98–3.89 (m, 2H, **H-6a** and **H-6b**), 3.75–3.70 (m, 1H, **H-5**), 3.42 (s, 3H, O**CH_3**), 0.91 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.11 (s, 3H, Si(C(CH_3)$_3$)(**CH_3**)$_2$), 0.11 (s, 3H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Methyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside (6ab):[11a] Following the general procedure B, the reaction was carried out with methyl-α-D-mannopyranoside **6** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:2), afforded compound **6ab** as a viscous colorless oil (53.2 mg, 76 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 5.07–5.04 (m, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3**), 4.73–4.67 (m, 1H, **H-1**), 3.98–3.84 (m, 4H, **H-2, H-4, H-6a** and **H-6b**), 3.69–3.61 (m, 1H, **H-5**), 3.37 (s, 3H, O**CH_3**), 2.15 (s, 3H, O**Ac**), 0.89 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.09 (s, 6H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Isopropyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (7aa):[4c] Following the general procedure B, the reaction was carried out with isopropylthio-β-D-galactopyranoside **7** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **7aa** as a viscous colorless oil (81.2 mg, 89 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.11–8.05 (m, 2H, Ar**H**), 7.61–7.52 (m, 1H, Ar**H**), 7.46–7.39 (m, 2H, Ar**H**), 5.12 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.52 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.34 (d, *J* = 2.0 Hz, 1H, **H-4**), 4.08 (t, *J* = 9.6 Hz, 1H, **H-2**), 3.95–3.85 (m, 2H, **H-6a** and **H-6b**), 3.63 (t, *J* = 4.4 Hz, 1H, **H-5**), 3.28–3.22 (m, 1H, SC**H**(CH_3)$_2$), 1.34 (d, *J* = 6.8 Hz, 6H, SCH(C**H_3**)**2**), 0.88 (s, 9H, Si(C(**CH_3**)$_3$)(CH_3)$_2$), 0.08 (s, 3H, Si(C(CH_3)$_3$)(**CH_3**)$_2$), 0.07 (s, 3H, Si(C(CH_3)$_3$)(**CH_3**)$_2$).

Isopropyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (7ab):[11d]Following the general procedure B, the reaction was carried out with isopropylthio-β-D-galactopyranoside **7** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatog-

raphy (ethyl acetate/petroleum ether: 1:3), afforded compound **7ab** as a viscous colorless oil (61.5 mg, 78 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.83 (dd, *J* = 9.6 Hz and 2.4 Hz, 1H, **H-3**), 4.42 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.18 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.89–3.80 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.52 (t, *J* = 4.8 Hz, 1H, **H-5**), 3.26–3.17 (m, 1H, SC**H**$(CH_3)_2$), 2.15 (s, 3H, O**Ac**), 1.31 (d, *J* = 6.8 Hz, 6H, SCH(C**H$_3$**)**2**), 0.86 (s, 9H, Si(C(**CH$_3$**)**$_3$**)$(CH_3)_2$), 0.06 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**), 0.05 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**).

Ethyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (8aa):[11d] Following the general procedure B, the reaction was carried out with ethyl-β-D-thiogalactopyranoside **8** (0.2 mmol), DIPEA (77.5 µL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **8aa** as a viscous colorless oil (71.6 mg, 81 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.12–8.10 (m, 2H, Ar**H**), 7.59–7.54 (m, 1H, Ar**H**), 7.46–7.42 (m, 2H, Ar**H**), 5.10 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.44 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.36 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.12 (t, *J* = 9.6 Hz, 1H, **H-2**), 3.96 (dd, *J* = 10.8 Hz and 5.6 Hz, 1H, **H-6a**), 3.89 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H, **H-6b**), 3.62 (t, *J* = 5.2 Hz, 1H, **H-5**), 2.85–2.70 (m, 2H, SC**H$_2$**CH_3), 1.33 (t, *J* = 7.2 Hz, 3H, SCH_2C**H$_3$**), 0.89 (s, 9H, Si(C(**CH$_3$**)**$_3$**)$(CH_3)_2$), 0.09 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**), 0.08 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**).

Ethyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (8ab):[11d] Following the general procedure B, the reaction was carried out with ethyl-β-D-thiogalactopyranoside **8** (0.2 mmol), DIPEA (77.5 µL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 µL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **8ab** as a viscous colorless oil (60.8 mg, 80 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 4.84 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.36 (d, *J* = 6.0 Hz, 1H, **H-1**), 4.23 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.97–3.85 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.53 (t, *J* = 4.4 Hz, 1H, **H-5**), 2.78–2.68 (m, 2H, SC**H$_2$**CH_3), 2.17 (s, 3H, O**Ac**), 1.33–1.28 (m, 3H, SCH_2C**H$_3$**), 0.88 (s, 9H, Si(C(**CH$_3$**)**$_3$**)$(CH_3)_2$), 0.08 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**), 0.07 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**).

Benzyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (9aa):[11d] Following the general procedure B, the reaction was carried out with benzyl-β-D-thiogalactopyranoside **9** (0.2 mmol), DIPEA (77.5 µL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **9aa** as a viscous colorless oil (90.7 mg, 90 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.11–8.06 (m, 2H, Ar**H**), 7.59–7.55 (m, 1H, Ar**H**), 7.47–7.42 (m, 2H, Ar**H**), 7.36–7.26 (m, 5H, Ar**H**), 5.03 (dd, *J* = 9.2 Hz and 2.8 Hz, 1H, **H-3**), 4.34–4.32 (m, 2H, **H-1** and **H-4**), 4.14 (t, *J* = 9.2 Hz, 1H, **H-2**), 4.03–3.88 (m, 4H, Ph**CH$_2$**, **H-6a** and **H-6b**), 3.56 (t, *J* = 4.8 Hz, 1H, **H-5**), 0.91 (s, 9H, Si(C(**CH$_3$**)**$_3$**)$(CH_3)_2$), 0.12 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**), 0.11 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**).

Benzyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (9ab):[11d]Following the general procedure B, the reaction was carried out with benzyl-β-D-thiogalactopyranoside **9** (0.2 mmol), DIPEA (77.5 µL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 µL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **9ab** as a viscous colorless oil (71.6 mg, 81 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.32–7.24 (m, 5H, Ar**H**), 4.76 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.24 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.19 (d, *J* = 2.0 Hz, 1H, **H-4**), 3.99–3.84 (m, 5H, **H-2**, Ph**CH$_2$**, **H-6a** and **H-6b**), 3.46 (t, *J* = 4.4 Hz, 1H, **H-5**), 2.15 (s, 3H, O**Ac**), 0.90 (s, 9H, Si(C(**CH$_3$**)**$_3$**)$(CH_3)_2$), 0.11 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**), 0.10 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**).

***p*-Tolyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (10aa):**[11d] Following the general procedure B, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), DIPEA (77.5 µL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **10aa** as a viscous colorless oil (88.7 mg, 88 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.09–8.05 (m, 2H, Ar**H**), 7.57–7.40 (m, 5H, Ar**H**), 7.14–7.11 (m, 2H, Ar**H**), 5.10 (dd, *J* = 9.2 Hz and 2.4 Hz, 1H, **H-3**), 4.58 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.35 (d, *J* = 2.0 Hz, 1H, **H-4**), 4.07–3.91 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.62 (t, *J* = 4.0 Hz, 1H, **H-5**), 2.35 (s, 3H, SPh**CH$_3$**), 0.91 (s, 9H, Si(C(**CH$_3$**)**$_3$**)$(CH_3)_2$), 0.12 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**), 0.10 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**).

***p*-Tolyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (10ab):**[11d] Following the general procedure B, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), DIPEA (77.5 µL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 µL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **10ab** as a viscous colorless oil (72.5 mg, 82 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 7.46 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.10 (d, *J* = 8.0 Hz, 2H, Ar**H**), 4.85 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.49 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.22 (d, *J* = 2.0 Hz, 1H, **H-4**), 3.98 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H, **H-6a**), 3.92–3.83 (m, 2H, **H-2** and **H-6b**), 3.53 (t, *J* = 4.0 Hz, 1H, **H-5**), 2.33 (s, 3H, SPh**CH$_3$**), 2.14 (s, 3H, O**Ac**), 0.90 (s, 9H, Si(C(**CH$_3$**)**$_3$**)$(CH_3)_2$), 0.12 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**), 0.10 (s, 3H, Si(C$(CH_3)_3$)(**CH$_3$**)**$_2$**).

***p*-Tolyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio-β-D-galactopyranoside (10ba):** Following the general procedure B, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), DIPEA (91.5 µL, 2.6 equiv.), TBDPSCl (104.0 µL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **10ba** as a viscous colorless oil (104.2 mg, 80 %). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 8.12–8.09 (m, 2H, Ar**H**), 7.77–7.69 (m, 4H, Ar**H**), 7.51–7.38 (m, 11H, Ar**H**), 7.10–7.08 (m, 2H, Ar**H**), 5.12 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.59 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.40 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.07 (t, *J* = 9.6 Hz, 1H, **H-2**), 4.02 (dd, *J* = 10.8 Hz and 5.2 Hz, 1H, **H-6a**), 3.95 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H, **H-6b**), 3.68 (t, *J* = 4.8 Hz, 1H, **H-5**), 2.34 (s, 3H, SPh**CH$_3$**), 1.07 (s, 9H, Si(C(**CH$_3$**)**$_3$**)). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.4, 138.5, 135.8, 135.7, 133.5, 133.4, 132.8, 132.6, 130.1, 129.8, 128.6, 128.5, 128.0, 127.9, 89.4, 77.9,

77.2, 68.9, 67.3, 64.3, 26.9, 21.3, 19.2 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{36}H_{40}O_6SSiNa]^+$: 651.2207, found 651.2207.

***p*-Tolyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio-β-D-galactopyranoside (10bb):** Following the general procedure B, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), DIPEA (91.5 μL, 2.6 equiv.), TBDPSCl (104.0 μL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **10bb** as a viscous colorless oil (90.7 mg, 77 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.76–7.68 (m, 4H, Ar**H**), 7.49–7.38 (m, 8H, Ar**H**), 7.08–7.06 (m, 2H, Ar**H**), 4.87 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.50 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.28 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.00 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H, **H-6a**), 3.94–3.86 (m, 2H, **H-2** and **H-6b**), 3.58 (t, *J* = 4.4 Hz, 1H, **H-5**), 2.32 (s, 3H, SPh**CH_3**), 2.17 (s, 3H, O**Ac**), 1.07 (s, 9H, Si(C(**CH_3**)$_3$)). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.9, 138.7, 135.8, 135.7, 133.6, 132.7, 132.4, 130.1, 129.9, 128.0, 127.9, 127.6, 89.1, 76.6, 69.0, 66.9, 64.6, 26.8, 21.3, 19.2 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{31}H_{38}O_6SSiNa]^+$: 589.2051, found 589.2049.

***p*-Tolyl 3-*O*-Benzoyl-6-*O*-(triisopropylsilyl)-1-thio-β-D-galactopyranoside (10ca):** Following the general procedure B, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), DIPEA (105.5 μL, 3.0 equiv.), TIPSCl (86.0 μL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **10ca** as a viscous colorless oil (85.4 mg, 75 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.10–8.08 (m, 2H, Ar**H**), 7.56–7.41 (m, 5H, Ar**H**), 7.12 (d, *J* = 8.0 Hz, 2H, Ar**H**), 5.11 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.58 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.39 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.13–3.99 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.63 (t, *J* = 4.4 Hz, 1H, **H-5**), 2.35 (s, 3H, SPh**CH_3**), 1.13–1.07 (m, 21H, Si(C**H**(**CH_3**)$_2$)**3**). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.5, 138.6, 133.6, 133.4, 130.1, 129.9, 129.8, 128.5, 127.8, 89.4, 77.8, 77.3, 69.0, 67.2, 64.2, 21.3, 18.1, 18.0, 11.9 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{29}H_{42}O_6SSiNa]^+$: 569.2364, found 569.2364.

***p*-Tolyl 3-*O*-Acetyl-6-*O*-(triisopropylsilyl)-1-thio-β-D-galactopyranoside (10cb):** Following the general procedure B, the reaction was carried out with *p*-tolyl-β-D-thiogalactopyranoside **10** (0.2 mmol), DIPEA (105.5 μL, 3.0 equiv.), TIPSCl (86.0 μL, 2.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **10cb** as a viscous colorless oil (74.0 mg, 73 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.48–7.46 (m, 2H, Ar**H**), 7.11–7.09 (m, 2H, Ar**H**), 4.87 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.49 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.26 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.09 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H, **H-6a**), 3.99 (dd, *J* = 10.8 Hz and 3.6 Hz, 1H, **H-6b**), 3.87 (t, *J* = 9.6 Hz, 1H, **H-2**), 3.53 (t, *J* = 4.0 Hz, 1H, **H-5**), 2.33 (s, 3H, SPh**CH_3**), 2.15 (s, 3H, O**Ac**), 1.09–1.07 (m, 21H, Si(C**H**(**CH_3**)$_2$)**3**). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 170.9, 138.7, 133.8, 129.9, 127.5, 89.1, 77.4, 76.6, 69.1, 66.9, 64.6, 21.3, 21.3, 18.1, 18.0, 11.9 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{24}H_{40}O_6SSiNa]^+$: 507.2207, found 507.2209.

Phenyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (11aa):[11d] Following the general procedure B, the reaction was carried out with phenyl-β-D-thiogalactopyranoside **11** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **11aa** as a viscous colorless oil (89.2 mg, 91 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.09–8.05 (m, 2H, Ar**H**), 7.61–7.53 (m, 3H, Ar**H**), 7.47–7.39 (m, 2H, Ar**H**), 7.32–7.30 (m, 3H, Ar**H**), 5.12 (dd, *J* = 9.2 Hz and 2.4 Hz, 1H, **H-3**), 4.66 (d, *J* = 10.0 Hz, 1H, **H-1**), 4.36 (d, *J* = 2.4 Hz, 1H, **H-4**), 4.10 (t, *J* = 9.6 Hz, 1H, **H-2**), 3.99 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H, **H-6a**), 3.93 (dd, *J* = 10.8 Hz and 4.0 Hz, 1H, **H-6b**), 3.66–3.63 (m, 1H, **H-5**), 0.91 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.12 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$).

Phenyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (11ab):[11d] Following the general procedure B, the reaction was carried out with phenyl-β-D-thiogalactopyranoside **11** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **11ab** as a viscous colorless oil (71.0 mg, 83 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.58–7.56 (m, 2H, Ar**H**), 7.30–7.28 (m, 3H, Ar**H**), 4.86 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.56 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.23 (d, *J* = 2.0 Hz, 1H, **H-4**), 3.98 (dd, *J* = 10.8 Hz and 1.2 Hz, 1H, **H-6a**), 3.93–3.88 (m, 2H, **H-2** and **H-6b**), 3.55 (t, *J* = 4.0 Hz, 1H, **H-5**), 2.15 (s, 3H, O**Ac**), 0.90 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.11 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$), 0.09 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$).

Phenyl 3-*O*-Benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-glucopyranoside (13aa): Following the general procedure B, the reaction was carried out with phenyl-β-D-thioglucopyranoside **13** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:6), afforded compound **13aa** as a viscous colorless oil (77.4 mg, 79 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.09–8.04 (m, 2H, Ar**H**), 7.58–7.56 (m, 3H, Ar**H**), 7.45–7.41 (m, 2H, Ar**H**), 7.33–7.32 (m, 3H, Ar**H**), 5.24 (t, *J* = 9.2 Hz, 1H, **H-3**), 4.65 (d, *J* = 9.6 Hz, 1H, **H-1**), 3.98 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H, **H-6a**), 3.91 (dd, *J* = 10.4 Hz and 4.8 Hz, 1H, **H-6b**), 3.82 (t, *J* = 9.2 Hz, 1H, **H-4**), 3.59 (t, *J* = 9.2 Hz, 1H, **H-2**), 3.55–3.50 (m, 1H, **H-5**), 0.91 (s, 9H, Si(C(**CH_3**)$_3$)(CH$_3$)$_2$), 0.11 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH_3**)$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 167.8, 133.6, 133.1, 131.8, 130.2, 129.6, 129.2, 128.5, 128.4, 88.5, 79.8, 79.1, 71.1, 70.6, 64.3, 26.0, 18.4, –5.3 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{25}H_{34}O_6SSiNa]^+$: 513.1738, found 513.1730.

Phenyl 3-*O*-Acetyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-glucopyranoside (13ab): Following the general procedure B, the reaction was carried out with phenyl-β-D-thioglucopyranoside **13** (0.2 mmol), DIPEA (77.5 μL, 2.2 equiv.), TBSCl (46.2 mg, 1.5 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (23.0 μL, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 8 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:3), afforded compound **13ab** as a viscous colorless oil (68.5 mg, 80 %). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.55–7.52 (m, 2H, Ar**H**), 7.32–7.30 (m, 3H, Ar**H**), 4.98 (t, *J* = 9.2 Hz, 1H, **H-3**), 4.57 (d, *J* = 9.6 Hz, 1H, **H-1**), 3.95 (dd, *J* = 10.8 Hz and

4.8 Hz, 1H, **H-6a**), 3.86 (dd, *J* = 10.8 Hz and 5.2 Hz, 1H, **H-6b**), 3.66 (t, *J* = 9.2 Hz, 1H, **H-4**), 3.47–3.39 (m, 2H, **H-2** and **H-5**), 2.15 (s, 3H, O**Ac**), 0.90 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.09 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 172.4, 133.1, 131.6, 129.2, 128.4, 88.4, 79.0, 78.9, 70.9, 70.4, 64.3, 25.9, 21.2, 18.4, –5.3 ppm; **HRMS (ESI-TOF):** Calculated for [C$_{20}$H$_{32}$O$_6$SSiNa]$^+$: 451.1581, found 451.1576.

Phenyl 6,6′-Di-*O*-(*tert*-butyldimethylsilyl)-3′-benzoyl-1-thio-β-D-lactoside (16aa):[11d] Following the general procedure **B**, the reaction was carried out with phenyl-1-thio-β-D-lactoside **16** (0.2 mmol), DIPEA (211.0 μL, 6.0 equiv.), TBSCl (123.0 mg, 4.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, benzoic anhydride (23.0 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:2), afforded compound **16aa** as a viscous colorless oil (112.0 mg, 73 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.11–8.08 (m, 2H, Ar**H**), 7.62–7.56 (m, 3H, Ar**H**), 7.49–7.43 (m, 2H, Ar**H**), 7.30–7.28 (m, 3H, Ar**H**), 5.03 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3′**), 4.56–4.49 (m, 2H, **H-1** and **H-1′**), 4.30 (d, *J* = 2.0 Hz, 1H, **H-4′**), 4.08 (dd, *J* = 9.6 Hz and 8.0 Hz, **H-2′**), 3.96–3.90 (m, 4H, **H-6a**, **H-6b**, **H-6a′** and **H-6b′**), 3.71–3.58 (m, 3H, **H-3**, **H-4** and **H-5′**), 3.45–3.36 (m, 2H, **H-2** and **H-5**), 0.90 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.88 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.09 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.08 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

Phenyl-6,6′-Di-*O*-(*tert*-butyldimethylsilyl)-3′-acetyl-1-thio-β-D-lactoside (16ab):[11d] Following the general procedure **B**, the reaction was carried out with phenyl-1-thio-β-D-lactoside **16** (0.2 mmol), DIPEA (211.0 μL, 6.0 equiv.), TBSCl (123.0 mg, 4.0 equiv.) in dry solvent (1.1 mL) at room temperature. Upon completion as shown by TLC, acetic anhydride (55.5 mg, 1.2 equiv.) was added and the reaction mixture was left stirring at 40 °C for 12 h. The crude product was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1:1), afforded compound **16ab** as a viscous colorless oil (104.2 mg, 74 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.57–7.54 (m, 2H, Ar**H**), 7.30–7.27 (m, 3H, Ar**H**), 4.77 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3′**), 4.52 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.41 (d, *J* = 8.0 Hz, 1H, **H-1′**), 4.16 (d, *J* = 2.8 Hz, **H-4′**), 3.94–3.86 (m, 5H, **H-2′**, **H-6a**, **H-6b**, **H-6a′** and **H-6b′**), 3.67–3.54 (m, 3H, **H-3**, **H-4** and **H-5′**), 3.44–3.33 (m, 2H, **H-2** and **H-5**), 2.17 (s, 3H, O**Ac**), 0.89 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.87 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.09–0.06 (m, 12H, 2 × Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**).

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