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# Efficient activation of thioglycosides with *N*-(*p*-methylphenylthio)-ε-caprolactam-TMSOTf

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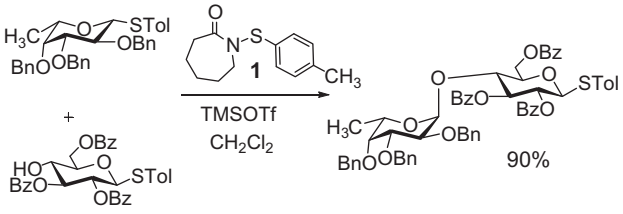
ABSTRACT




*N*-(*p*-Methylphenylthio)-ε-caprolactam (**1**) in combination with trimethylsilyl trifluoromethanesulfonate (TMSOTf) provides an efficient thiophilic promoter system, capable of activating different thioglycosides. Both 'armed' and 'disarmed' thioglycosyl donors were activated for glycosidic bond formation. Notably, this reagent combination works well in reactivity-based one-pot oligosaccharide assembly strategy.



## 1. Introduction

Owing to the multifaceted biological significance and remarkable therapeutic potential of complex oligosaccharides and glycoconjugates in life processes,[1] the synthesis of oligosaccharides has been the subject of research for many years. Glycosylation method is considered to be the most crucial step for the synthesis of oligosaccharides and glycoconjugates.[2] In spite of many reports on glycosylations[3] since several of them are not devoid of limitations toward synthesis of oligosaccharides, development of a general, convenient, and efficient methodology for the assembly of a variety of oligosaccharides is still desirable.

Among the various classes of glycosyl donors, thioglycosides have several advantages[4] like their stability and accessibility. Moreover, these are compatible with many protection and deprotection sequences and thus can be used for the preparation of various glycosyl donors and glycosyl acceptors.[4,5] These versatile features of thioglycosides allow them to be used for the preparation of oligosaccharides in greatly simplified manner and also for the assembly of oligosaccharide library.

So far there are many promoter systems available for the activation of thioglycosides toward glycosylation. The widely-used promoters for thioglycoside activation include NIS/TfOH,[6] DMTST,[7] IDCP,[8] MeOTf,[9] MeSOTf,[10] PhSeOTf,[11] and its related sulfur analog.[12] Sulfinamide-type activators in combination with Lewis acids such as EtSNphth-TrB$(C_6F_5)_4$[13] and *N*-(phenylthio)-ε-caprolactam-$Tf_2O$[14] systems have also been described. Recently various kinds of organosulfur reagents, which include *S*-(4-methoxyphenyl) benzenethiosulfinates,[15] BSP/$Tf_2O$,[16] DPSO/$Tf_2O$,[17] BSM/$Tf_2O$,[18] $Me_2S_2$/$Tf_2O$,[19] BDMS/AgOTf[20] and DMTPSB/AgOTf[21] have been utilized for glycosylation. It is known that benzenesulfinyl or benzenesulfenyl derived promoter systems are an extremely powerful thiophilic reagent that can be used to couple thioglycosides with various acceptors at low temperature only. While available promoters are convenient to construct oligosaccharides, but, numerous drawbacks and limitations have also been noticed which mainly includes reagent stability, solubility, and most importantly, side reactions with by-products resulting from the promoters.[18,22] These issues prompted us to search for a more convenient and powerful

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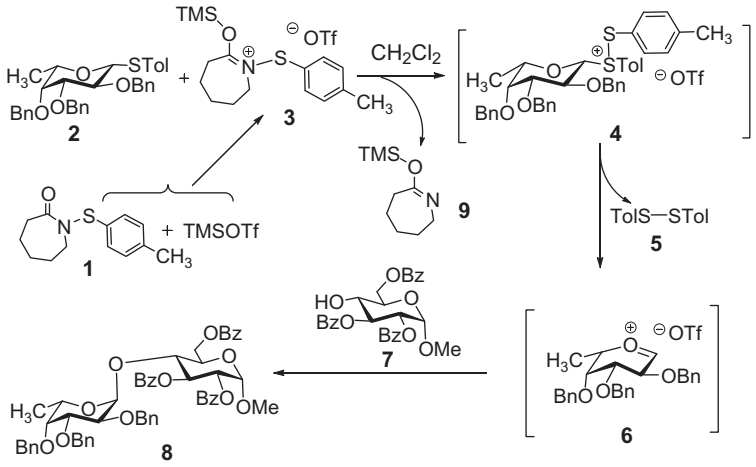



**Scheme 1.** Plausible mechanism for thioglycoside activation.

**Table 1**
Screening of the reaction conditions for the synthesis of **8**

| Entry | Promoter system | Yield[a]/yield[b] |
|---|---|---|
| 1 | *N*-(*p*-Methylphenylthio)-ε-caprolactam | — |
| 2 | *N*-(*p*-Methylphenylthio)-ε-caprolactam/$Tf_2O$ | 90%/85% |
| 3 | *N*-(*p*-Methylphenylthio)-ε-caprolactam/TMSOTf | 92%/89% |
| 4 | TMSOTf | —/<5% |
| 5 | N-(Phenylthio)-ε-caprolactam/$Tf_2O$ | 90%/84% |

[a] Condition: 1.1:1.0:1.1 donor/acceptor/promoter, −45 °C to ambient temperature, 30 min.
[b] Condition: 1.1:1.0:1.1 donor/acceptor/promoter, room temperature, 15 min. All reactions were carried out in $CH_2Cl_2$.

promoter system for the activation of thioglycosides that will reduce the existing problem associated with glycosylation reactions as well as can also be used in one-pot oligosaccharide assembly.

*N*-(*p*-Methylphenylthio)-ε-caprolactam (**1**), a white crystalline, easy to prepare, cost effective, and new shelf-stable compound, is a convenient 'soft' electrophilic reagent. In continuation of our research on carbohydrates[23] including oligosaccharide syntheses,[24] we report herein, **1** with TMSOTf as a new promoter system for the activation of thioglycosides and its application in the reactivity-based one-pot oligosaccharide synthesis.

## 2. Results and discussion

At the outset, to test the activating capability of **1** in conjugation with TMSOTf, the glycosylation reaction of benzylated thioglycoside donor **2** with glucoside acceptor **7** was investigated (Scheme 1). Through a preliminary screening of reactions (Table 1), we found that **1** in combination with TMSOTf furnished the best result (performing the reaction in $CH_2Cl_2$ at −45 °C to ambient temperature, entry 3, Table 1). Thus, **1**—TMSOTf combo system was able to activate glycosyl donor **2** even at low temperature. It is worthy to mention here that the use of sub-stoichiometric amount of TMSOTf in the combo reagent system resulted in incomplete conversion of the starting materials.

That the reaction does not proceed via activation of the thioglycoside donor with *p*TolSOTf formed (if any) in situ from the reaction of **1** with TMSOTf is evidenced from the following sets of experiments. The glycosyl donor **10** in reaction (following the condition reported by Yamago et al.[25]) with *p*TolSCl and AgOTf at −60 °C got activated within 5 min, which then on treatment with the glycosyl acceptor **11** at −60 °C followed by increasing the temperature to 25 °C resulted in the formation of the corresponding disaccharide **12**[26] (Fig. 1). When **10** was treated with a mixture of **1** and TMSOTf at −60 °C, and then the mixture was subjected to react with **11**, after increasing the temperature to 25 °C, **10** remained intact and could be recovered in 98% yield from the reaction mixture even after 24 h, but, the glycosyl acceptor **11** was fully consumed producing a mixture of self coupled products.

Si of TMSOTf being a soft center is likely to react preferentially with the softer amide carbonyl O rather than the hydroxyl O of the glycosyl acceptor. Thus, we propose that, *N*-(*p*-methylphenylthio)-ε-caprolactam (**1**) may react with TMSOTf to provide a strong electrophilic reagent **3**, which is then exposed to be attacked by the 'soft' nucleophile **2**, producing activated sugar derived complex **4**. The activated species may then liberate disulfide **5** to produce oxacarbenium ion intermediate **6**, which then reacts with acceptor **7**, yielding the desired disaccharide **8** in 92% yield (Scheme 1).

Under the present activation condition a variety of glycosyl donors and acceptors were employed to evaluate the efficacy and scope of this promoter system (Table 2). The glycosylations of different 'armed' thioglycosides with various glycosyl acceptors, having a secondary hydroxyl group exposed proceeded smoothly (Table 2, entries 1–5). As shown, the 'armed' thioglycoside **13** activated by **1**-TMSOTf, reacted readily with the glucoside acceptor **7**, affording the desired disaccharide **14** in high yield (entry 2). The other 'armed' thioglycoside donors, such as **15** (entry 3) and **17** (entry 4), were also activated quickly and efficiently at low-temperature, and the coupling products were obtained in high yields. The latter entry also demonstrates the compatibility with several protecting groups including TBDPS, benzyl, and acyl. As shown, a number of 4-O-linked disaccharides, which suffered from side

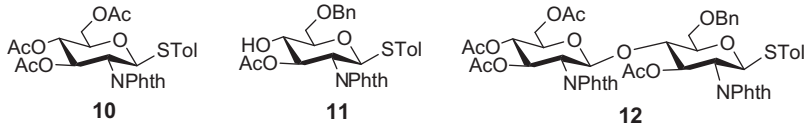
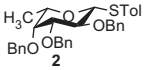
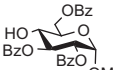
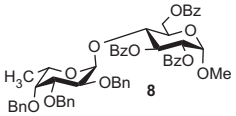
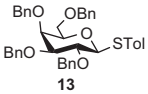
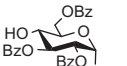
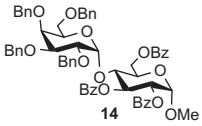
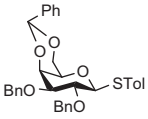
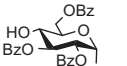
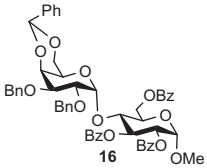
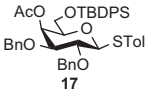
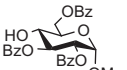
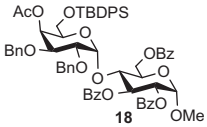
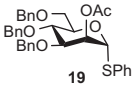
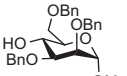
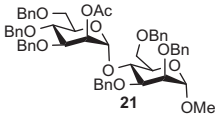
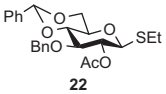
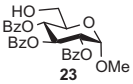
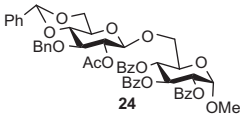
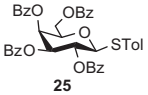
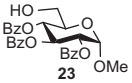
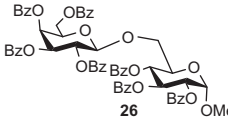
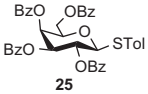
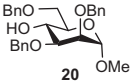
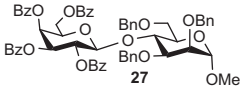
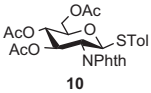
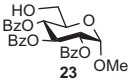
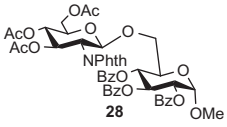
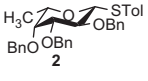
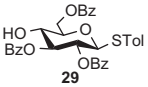
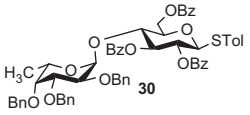
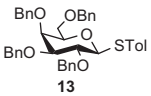
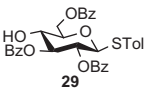
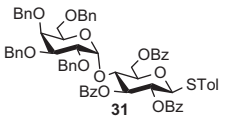
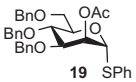
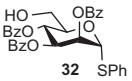
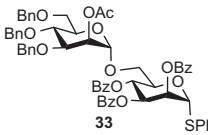
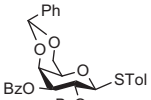
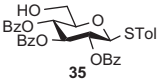
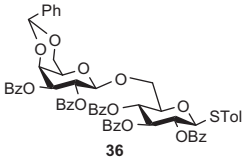
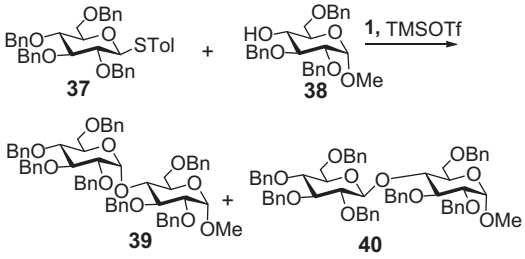



**Figure 1.**

**Table 2**
Glycosylations with *N*-(*p*-methylphenylthio)-ε-caprolactam (**1**) and trimethylsilyl trifluoromethane sulfonate[a]

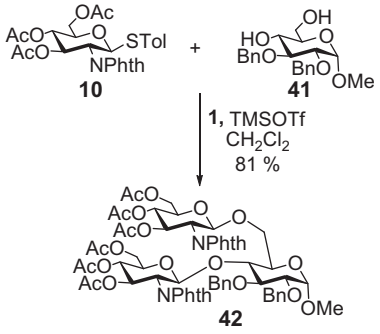
| Entry | Glycosyl donor | Glycosyl acceptor | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  **2** |  **7** |  **8** | 92 |
| 2 |  **13** |  **7** |  **14** | 90 |
| 3 |  **15** |  **7** |  **16** | 89 |
| 4 |  **17** |  **7** |  **18** | 91 |
| 5 |  **19** |  **20** |  **21** | 95 |
| 6 |  **22** |  **23** |  **24** | 88 |
| 7 |  **25** |  **23** |  **26** | 95 |
| 8 |  **25** |  **20** |  **27** | 93 |
| 9 |  **10** |  **23** |  **28** | 95 |
| 10 |  **2** |  **29** |  **30** | 90 |
| 11 |  **13** |  **29** |  **31** | 93 |
| 12 |  **19** |  **32** |  **33** | 94 |
| 13 |  **34** |  **35** |  **36** | 87 |

[a] All reactions were carried out in $CH_2Cl_2$.
[b] Isolated yield.




| entry | solvent | isolated yield | |
|---|---|---|---|
| | | 39 | 40 |
| 1 | $CH_2Cl_2$ | 45% | 42% |
| 2 | $Et_2O$-$CH_2Cl_2$ | 72% | 19% |
| 3 | MeCN-$CH_2Cl_2$ | 21% | 68% |

**Scheme 2.** Solvent effects on the stereoselectivity of glycosylations.




**Scheme 3.** Double glycosylation.

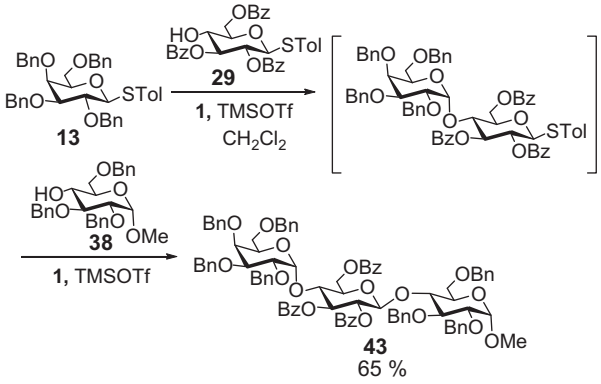
products at the glycosylation step when promoted by NIS-TfOH[22a] using 'armed' thioglycoside donors were prepared in high yields when relatively low reactive acceptor **7** was used.

It is noteworthy that, the 'disarmed' thioglycosides also reacted very easily and efficiently. As shown, the 'disarmed' thioglycosides **25** activated by **1**-TMSOTf, reacted readily with the acceptor **23**, affording the desired disaccharide in high yield (Table 2, entry 7). The low-reactive benzoyl-protected acceptor **23**[21] also coupled smoothly with **10** to obtain disaccharide **28** in 95% isolated yield (entry 9). In all cases, the 'disarmed' thioglycosides in Table 2, invariably afforded 1,2-*trans*-linked disaccharides as a result of neighboring group participation; no orthoesters were detected.

In a different experiment, the solvent effects on the stereoselectivity of glycosylation were also examined. A high combined yield but low stereoselectivity was observed when perbenzylated thioglucoside **37**, was reacted with **38** in dichloromethane affording the corresponding anomeric mixture of **39** and **40** (Scheme 2). The selectivity could be shifted significantly toward the α-anomer by using ether or toward the β-anomer by using acetonitrile as cosolvent. This can be explained by the participation of the solvents.[27]

Next, we apply this reagent combination in a reactivity-based oligosaccharide synthesis. In fact, this reagent combination works well, as we were able to synthesize various disaccharides using thioglycosides as acceptors in excellent yields (Table 2, entries 10–13). Disaccharide **31**, which suffered from by-products when using NIS/TfOH as promoter,[22a] was also obtained in high yield.

To investigate the power of the new reagent combination, we turned to the double glycosylation of carbohydrate diols. Union of a 4,6-glucopyranosyl diol **41** and phthalimide protected glucosamine donor **10**, resulted in the isolation of the desired trisaccharide **42** in 81% yield (Scheme 3).




**Scheme 4.** Reactivity-based one-pot glycosylation of **43**.

As a final demonstration of the reagent combination, we apply this in the reactivity-based one-pot synthesis of oligosaccharide. A one-pot synthesis of a trisaccharide derivative, **43** as outlined in Scheme 4, was carried out in satisfactory yield and with good stereoselectivity, supporting that this new reagent combination can be used in reactivity-based one-pot assembly of oligosaccharides.

## 3. Conclusion

In summary, the combination of a cost-effective and stable thiophilic reagent [*N*-(*p*-methylphenylthio)-ε-caprolactam] and TMSOTf works as an efficient promoter system for the activation of thioglycosides toward glycosylation reactions. Both 'disarmed' and 'armed' glycosyl donors can be triggered smoothly at low-temperature, and the coupling reactions proceed very well with a variety of glycosyl acceptors in high yields. This reagent overcomes limitations of some reported methods and can be employed in the reactivity-based one-pot oligosaccharide assembly.

## 4. Experimental section

### 4.1. General

All reactions were performed in flame-dried flasks fitted with rubber septa under a positive pressure of argon, unless otherwise stated. Dichloromethane was refluxed with $P_2O_5$ and distilled before use. Diethyl ether (Merck, India) and acetonitrile (Merck, India) were distilled over $P_2O_5$, and stored over 4 Å molecular sieves before use. Trimethylsilyl trifluoromethanesulfonate was purchased from Aldrich and used without further purification. Triethylamine was purchased from Merck (India) and distilled over potassium hydroxide before use. *N*-(*p*-Methylthiophenyl)-ε-caprolactam (**1**) was synthesized. Traces of water in the donor and acceptor glycosides were removed by co-evaporation with toluene. Molecular sieves (4 Å) were flame dried before use. Flash column chromatography was performed employing Silica Gel 60 Sorbent (40–63 μm, 230–400 mesh). Thin-layer chromatography (analytical and preparative) was performed using Merck silica gel plates (60-$F_{254}$) to monitor the reactions and visualized under UV (254 nm) and/or by charring with 5% ethanolic solution of sulfuric acid. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DPX-300 (300 MHz), a Bruker DPX-400 (400 MHz), a Bruker DPX-500 (500 MHz), or a Bruker DPX-600 (600 MHz) spectrometer at ambient temperature in $CDCl_3$, and assigned using 2D-methods (COSY, HSQC). Chemical shifts were expressed in parts per million ($\delta$ scale). Optical rotations were measured using Jasco P-1020 digital polarimeter. High Resolution Mass Spectra (HRMS) were measured

in a QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface on Micro (YA-263) mass spectrometer (Manchester, UK).

### 4.2. Preparation of *N*-(*p*-methylphenylthio)-ε-caprolactam (1)

A solution of freshly prepared *p*-toluenesulfenyl chloride[12] (5.0 g, 31.6 mmol), in $CCl_4$ (20 mL) was added drop wise with stirring, at 0–5 °C and under anhydrous conditions, to a solution of caprolactam (6.85 g, 31.6 mmol) and $Et_3N$ (5.3 mL, 38 mmol) in $CCl_4$ (30 mL). The reaction mixture was stirred at ambient temperature for 3 h, and then filtered to remove the precipitate. The precipitate was washed with $CCl_4$ (2 × 10 mL). The combined filtrate and washings were washed with water. The organic phase was dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc, 15:1) to give *N*-(*p*-methylphenylthio)-ε-caprolactam as white solid (6.56 g, 88%). Crystallization from hexane–EtOAc afforded white needle shaped crystal; mp 70–72 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.28–7.26 (m, 2H, ArH), 7.13–7.11 (m, 2H, ArH), 3.86–3.83 (m, 2H), 2.70–2.67 (m, 2H), 2.31 (s, 3H), 1.72–1.65 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 178.1 (C═O), 137.9, 134.4, 130.0, 128.4, 58.3, 37.3, 29.8, 29.2, 23.5, 21.3; HRMS (ESI-TOF) calcd for $C_{13}H_{17}NOSNa$ $[M+Na]^+$ 258.0929, found 258.0926.

### 4.3. Methyl (2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-1-thio-α-D-glucopyranoside (8)

A mixture of **2**[28] (46.9 mg, 0.0869 mmol), **7**[29] (40.0 mg, 0.0791 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (22.0 mg, 0.0932 mmol), and flame activated 4 Å MS were stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (19 μL, 0.105 mmol) was added to the reaction mixture via a micro-syringe. The reaction was further stirred for 10 min and then warmed gradually to ambient temperature over 30 min. The reaction was quenched with $Et_3N$ (150 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 6:1) to afford **8** (67.2 mg, 92%) as a white foam. $R_f$ 0.24 (25% EtOAc in hexane); $[\alpha]_D^{26}$ +46.2 (*c* 1.06, $CHCl_3$); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.12–8.11 (m, 2H, ArH), 7.96–7.93 (m, 4H, ArH), 7.62 (m, 1H, ArH), 7.52–7.22 (m, 23H, ArH), 6.02 (t, 1H, *J* = 9.6 Hz), 5.14–5.12 (m, 2H, H-1), 4.96 (dd, 1H, *J* = 12.0, 1.8 Hz), 4.93 (d, 1H, *J* = 3.0 Hz, H-1′), 4.89–4.82 (m, 3H), 4.79–4.76 (m, 2H), 4.73 (d, 1H, *J* = 12.0 Hz), 4.54 (d, 1H, *J* = 12.0 Hz), 4.20 (dd, 1H, *J* = 9.6, 2.4 Hz), 4.05 (t, 1H, *J* = 9.6 Hz), 4.01 (dd, 1H, *J* = 10.8, 3.6 Hz), 3.97 (dd, 1H, *J* = 10.2, 2.4 Hz), 3.83 (q, 1H, *J* = 6.6 Hz, H-5), 3.54 (br s, 1H), 3.42 (s, 3H), 0.67 (d, 1H, *J* = 6.0 Hz); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 166.1 (C═O), 166.0 (C═O), 165.9 (C═O), 138.6, 138.4, 138.0, 133.2, 133.1, 132.9, 130.0, 129.8, 129.73, 129.68, 129.66, 129.0, 128.42, 128.41, 128.35, 128.31, 128.27, 128.2, 128.1, 127.7, 127.5, 127.44, 127.36, 100.6 (C-1′), 96.6 (C-1), 79.3, 77.6, 76.7, 75.6, 74.8, 74.3, 72.6, 72.4, 71.7, 69.0, 67.6, 63.0, 55.3, 16.0; HRMS (ESI-TOF) calcd for $C_{55}H_{54}O_{13}Na$ $[M+Na]^+$ 945.3462, found 945.3455.

### 4.4. Methyl (2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (14)

A mixture of **13**[22a] (56.2 mg, 0.087 mmol), **7** (40.0 mg, 0.0791 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (22.6 mg, 0.0958 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (19 μL, 0.105 mmol) was added to reaction mixture via a micro-syringe. The reaction was further stirred for 10 min and then warmed gradually to ambient temperature over 30 min. The reaction was then quenched with $Et_3N$ (180 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 6:1) to afford **14**[14] (72.9 mg, 90%) as a white foam. $R_f$ 0.22 (20% EtOAc in hexane); $[\alpha]_D^{24}$ +79.2 (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, 2H, *J* = 8.0 Hz), 8.02–8.00 (m, 2H, ArH), 7.63–7.14 (m, 29H, ArH), 6.24 (t, 1H, *J* = 9.5 Hz), 5.26 (dd, 1H, *J* = 11.0, 3.5 Hz), 5.20 (d, 1H, *J* = 3.5 Hz), 5.17 (d, 1H, *J* = 3.5 Hz), 4.86–4.83 (m, 2H), 4.70–4.64 (m, 3H), 4.47 (d, 1H, *J* = 11.0 Hz), 4.38–4.27 (m, 4H), 4.21 (d, 1H, *J* = 12.0 Hz), 4.10 (d, 1H, *J* = 12.0 Hz), 4.05 (t, 1H, *J* = 6.8 Hz), 3.96–3.93 (m, 2H), 3.86 (dd, 1H, *J* = 10.0, 4.0 Hz), 3.49–3.47 (m, 1H), 3.46 (s, 3H), 3.41 (dd, 1H, *J* = 9.0, 6.0 Hz). The spectral data were consistent with those in the literature.[14]

### 4.5. Methyl (2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galacto-pyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (16)

A mixture of **15**[22a,30] (60.2 mg, 0.1087 mmol), **7** (50.0 mg, 0.0988 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (28.2 mg, 0.1195 mmol) and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (2 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −5 °C. After stirring for 5 min, TMSOTf (24 μL, 0.1326 mmol) was added via a micro-syringe. The reaction mixture was further stirred for 30 min at −5 °C and then warmed gradually to ambient temperature. The reaction was then quenched with $Et_3N$ (220 μL), filtered off through a pad of Celite, and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 4:1) to afford **16**[14] (82.5 mg, 89%) as a white foam. $R_f$ 0.22 (20% EtOAc in hexane). $[\alpha]_D^{26}$ +117.4 (*c* 1.07, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 8.13–8.11 (m, 2H, ArH), 8.02–7.99 (m, 4H, ArH), 7.63–7.14 (m, 24H, ArH), 6.24 (t, 1H, *J* = 10.0 Hz), 5.40 (s, 1H, PhC*H*), 5.32 (d, 1H, *J* = 3.5 Hz), 5.23 (dd, 1H, *J* = 10.0, 3.5 Hz), 5.18 (d, 1H, *J* = 3.5 Hz), 4.84 (dd, 1H, *J* = 12.0, 3.5 Hz), 4.67 (d, 1H, *J* = 12.0 Hz, PhC$H_aH_b$), 4.63 (d, 1H, *J* = 12.0 Hz, PhC$H_aH_b$), 4.51 (dd, 1H, *J* = 12.0, 4.0 Hz), 4.36–4.32 (m, 2H), 4.26 (m, 1H), 4.21–4.17 (m, 2H), 4.00–3.91 (m, 3H), 3.82 (dd, 1H, *J* = 12.5, 1.5 Hz), 3.67 (s, 1H), 3.44 (s, 3H). The spectral data were consistent with those in the literature.[14]

### 4.6. Methyl (4-*O*-acetyl-2,3-di-*O*-benzyl-6-*O*-*tert*-butyldi-phenylsilyl-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (18)

A mixture of **17** (48.6 mg, 0.0651 mmol), **7** (30.0 mg, 0.0593 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (17.0 mg, 0.072 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −45 °C, stirred for 5 min followed by addition of TMSOTf (14 μL, 0.0774 mmol). The reaction mixture was warmed gradually to −10 °C over 30 min. The reaction was then quenched with $Et_3N$ (130 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc,) to afford **18** (60.9 mg, 91%) as a white foam. $R_f$ 0.32 (20% EtOAc in hexane). $[\alpha]_D^{26}$ +77.7 (*c* 1.0 , $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 8.04–7.97 (m, 6H, ArH), 7.65–7.10 (m, 29H, ArH), 6.15 (m, 1H), 5.65 (d, 1H, *J* = 2.0 Hz), 5.24 (dd, 1H, *J* = 10.5, 3.5 Hz, H-1), 5.15 (d, 1H, *J* = 3.5 Hz), 4.98 (d, 1H, *J* = 3.5 Hz, H-1′), 4.79 (d, 1H, *J* = 12.0 Hz), 4.71 (d, 1H, *J* = 10.5 Hz), 4.57 (dd, 1H, *J* = 12.0, 2.5 Hz), 4.37 (d, 1H, *J* = 10.5 Hz), 4.25–4.20 (m, 2H), 4.16–4.13 (m, 2H), 3.96–3.93 (m, 2H), 3.67 (dd, 1H, *J* = 10.0, 6.5 Hz), 3.57 (dd, 1H, *J* = 10.0, 7.0 Hz), 3.51 (dd, 1H, *J* = 10.0, 3.5 Hz), 3.46 (s, 3H, OC$H_3$), 1.88 (s, 3H, COC$H_3$), 1.07 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 169.9 (C═O), 166.2 (C═O), 166.0 (C═O), 165.8 (C═O), 138.6, 138.4, 135.8, 135.7, 133.4, 133.3, 133.2, 133.1, 132.9, 130.3, 130.1,

130.07, 129.92, 129.87, 129.8, 129.3, 128.6, 128.51, 128.41, 128.32, 128.29, 128.25, 127.94, 127.88, 127.6, 127.5, 99.9 (C-1′), 96.9 (C-1), 76.6, 74.7, 73.1, 72.5, 72.2, 71.7, 70.8, 69.2, 67.9, 63.5, 62.1, 55.6, 26.9, 20.9, 19.2. HRMS (ESI-TOF) calcd for $C_{66}H_{68}O_{15}SiNa$ $[M+Na]^+$ 1151.4225, found 1151.4214.

### 4.7. Methyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (21)

A mixture of **19**[31] (49.0 mg, 0.0839 mmol), **20**[32] (35.5 mg, 0.0765 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (22.0 mg, 0.0932 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (18 μL, 0.0995 mmol) was injected into the reaction mixture via a micro-syringe. The reaction mixture was warmed gradually to ambient temperature over 30 min. The reaction was then quenched with $Et_3N$ (170 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 4:1) to afford **21** (68.2 mg, 95%) as a white foam. $R_f$ 0.28 (25% EtOAc in hexane). $[\alpha]_D^{26}$ +28.2 (*c* 1.0, $CHCl_3$); $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ 7.34–7.13 (m, 30H, ArH), 5.47 (br s, 1H), 5.42 (br s, 1H, H-1′), 4.80 (d, 1H, *J* = 10.8 Hz), 4.76 (s, 1H, H-1), 4.67 (d, 1H, *J* = 10.8 Hz), 4.65–4.60 (m, 4H), 4.58–4.53 (m, 3H), 4.43 (br s, 1H), 4.41 (br s, 1H), 4.35 (d, 1H, *J* = 12.0 Hz), 4.16 (t, 1H, *J* = 9.0 Hz), 3.85–3.84 (m, 3H), 3.77–3.70 (m, 5H), 3.63 (dd, 1H, *J* = 10.8, 3.0 Hz), 3.43 (d, 1H, *J* = 10.8 Hz), 3.35 (s, 3H, $OCH_3$), 2.01 (s, 3H, $COCH_3$); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ 169.9 (C=O), 138.51, 138.48, 138.3, 138.2, 138.1, 137.9, 128.29, 128.27, 128.2, 128.0, 127.9, 127.82, 127.76, 127.61, 127.57, 127.52, 127.45, 127.4, 127.3, 99.4 (C-1), 98.7 (C-1′), 80.1, 78.4, 75.0, 74.0, 73.9, 73.4, 73.2, 72.5, 72.3, 71.7, 71.4, 71.1, 69.9, 68.6, 68.5, 54.9, 21.0; HRMS (ESI-TOF) calcd for $C_{57}H_{62}O_{12}Na$ $[M+Na]^+$ 961.4139, found 961.4131.

### 4.8. Methyl (2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (24)

A mixture of **22**[33] (40.0 mg, 0.0901 mmol), **23**[34] (41.4 mg, 0.0818 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (23.4 mg, 0.0992 mmol), and flame activated 4 Å MS were stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to 0 °C. After stirring for 5 min, TMSOTf (20 μL, 0.1105 mmol) was injected via a micro-syringe. The reaction mixture was further stirred for 30 min at the same temperature, and then the reaction was quenched with $Et_3N$ (190 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 3:1) to afford **24** (64.1 mg, 88%) as a white foam. $R_f$ 0.30 (25% EtOAc in hexane); mp 185–186 °C; $[\alpha]_D^{26}$ +29.6 (*c* 1.0, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.99–7.94 (m, 4H, ArH), 7.88–7.85 (m, 2H, ArH), 7.54–7.49 (m, 4H, ArH), 7.42–7.35 (m, 8H, ArH), 7.31–7.26 (m, 7H, ArH), 6.15 (t, 1H, *J* = 9.3 Hz), 5.55 (s, 1H, PhC*H*), 5.45 (t, 1H, *J* = 9.8 Hz), 5.27–5.23 (m, 1H), 5.23 (br s, 1H, H-1), 5.08 (dt, 1H, *J* = 7.6, 2.4 Hz), 4.88 (d, 1H, *J* = 12.1 Hz), 4.69 (d, 1H, *J* = 12.1 Hz), 4.54 (d, 1H, *J* = 7.9 Hz, H-1′), 4.31 (dd, 1H, *J* = 10.5, 4.9 Hz), 4.25 (m, 1H), 4.06 (dd, 1H, *J* = 10.8, 1.5 Hz), 3.77–3.71 (m, 3H), 3.68 (dd, 1H, *J* = 10.8, 6.7 Hz), 3.46 (s, 3H, $OCH_3$), 3.42 (m, 1H), 2.07 (s, 3H, $COCH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 169.4 (C=O), 165.8 (C=O), 165.7 (C=O), 165.3 (C=O), 138.2, 137.1, 133.5, 133.3, 133.0, 129.9, 129.8, 129.6, 129.03, 128.99, 128.87, 128.43, 128.40, 128.3, 128.2, 127.8, 127.6, 126.0, 101.8 (C-1′), 101.2, 96.7 (C-1), 81.4, 78.4, 74.1, 72.6, 72.0, 70.5, 69.4, 68.5, 68.3, 66.2, 55.4, 20.9; HRMS (ESI-TOF) calcd for $C_{50}H_{48}O_{15}Na$ $[M+Na]^+$ 911.2891, found 911.2889.

### 4.9. Methyl (2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D glucopyranoside (26)[6]

A solution of **25**[21,22a] (53.7 mg, 0.0763 mmol), **23** (35.1 mg, 0.0694 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (19.8 mg, 0.0839 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −45 °C, stirred for 5 min followed by the addition of TMSOTf (17 μL, 0.0939 mmol). The reaction mixture was warmed gradually to ambient temperature over 30 min. The reaction was then quenched with $Et_3N$ (160 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 6:1) to afford **26**[6] (71.8 mg, 95%) as a white foam. $R_f$ 0.22 (20% EtOAc in hexane); $[\alpha]_D^{24}$ +77.2 (*c* 1.1, $CHCl_3$); Lit.[6] $[\alpha]_D^{20}$ +78.1 (*c* 1.0, $CDCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.03–8.01 (m, 2H, ArH), 7.97–7.95 (m, 4H, ArH), 7.90–7.84 (m, 4H, ArH), 7.76–7.73 (m, 4H, ArH), 7.57–7.17 (m, 21H, ArH), 6.04 (t, 1H, *J* = 10.0 Hz), 5.95 (d, 1H, *J* = 3.0 Hz), 5.80 (dd, 1H, *J* = 10.0, 8.0 Hz), 5.60 (dd, 1H, *J* = 10.0, 3.0 Hz), 5.29 (t, 1H, *J* = 10.0 Hz), 5.02 (dd, 1H, *J* = 10.0, 3.5 Hz), 4.91 (d, 1H, *J* = 7.5 Hz), 4.87 (d, 1H, *J* = 3.5 Hz), 4.56 (m, 1H), 4.36 (dd, 1H, *J* = 11.0, 7.0 Hz), 4.28 (t, 1H, *J* = 7.0 Hz), 4.21 (t, 1H, *J* = 9.0, 8.5 Hz), 4.13 (d, 1H, *J* = 11.0 Hz), 3.76 (dd, 1H, *J* = 11.0, 7.5 Hz), 3.06 (s, 3H, $OCH_3$). The spectral data were consistent with those in the literature.[6,21]

### 4.10. Methyl (2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D mannopyranoside (27)

A solution of **25** (54.4 mg, 0.0773 mmol), **20** (32.6 mg, 0.0703 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (20.0 mg, 0.0847 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (2 mL) for 0.5 h at ambient temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (17 μL, 0.0939 mmol) was injected into the reaction mixture via a micro-syringe. The reaction mixture was then warmed gradually to ambient temperature. The reaction was then quenched with $Et_3N$ (160 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 4:1) to afford **27** (68.3 mg, 93%) as a white foam. $R_f$ 0.21 (25% EtOAc in hexane). $[\alpha]_D^{26}$ +59.5 (*c* 1.06, $CHCl_3$); $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ 7.97 (d, 2H, *J* = 7.2 Hz, ArH), 7.94 (d, 2H, *J* = 7.8 Hz, ArH), 7.89 (d, 2H, *J* = 7.8 Hz, ArH), 7.76 (d, 2H, *J* = 7.2 Hz, ArH), 7.57–7.17 (m, 27H, ArH), 5.87 (d, 1H, *J* = 3.6 Hz), 5.72 (dd, 1H, *J* = 10.2, 8.4 Hz), 5.40 (dd, 1H, *J* = 10.8, 3.6 Hz), 4.99 (d, 1H, *J* = 8.4 Hz, H-1′), 4.92 (d, 1H, *J* = 12.0 Hz), 4.73–4.67 (m, 3H, H-1), 4.61 (d, 1H, *J* = 12.0 Hz), 4.40 (apparent t, 1H, *J* = 6.0, 4.8 Hz), 4.37 (apparent t, 1H, *J* = 9.6, 9.0 Hz), 4.26 (dd, 1H, *J* = 12.0, 8.0 Hz), 3.94 (t, 1H, *J* = 6.6 Hz), 3.90 (dd, 1H, *J* = 3.0 Hz), 3.76 (t, 1H, *J* = 2.4 Hz), 3.64–3.60 (m, 2H), 3.39 (d, 1H, *J* = 9.6 Hz), 3.25 (s, 3H, $OCH_3$); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ 166.0 (C=O), 165.7 (C=O), 165.6 (C=O), 165.3 (C=O), 139.3, 138.6, 133.5, 133.4, 133.30, 133.26, 130.0, 129.9, 129.7, 129.4, 129.3, 129.0, 128.7, 128.57, 128.55, 128.4, 128.0, 127.9, 127.6, 127.4, 127.0, 101.2 (C-1′), 99.5 (C-1), 78.5, 75.6, 73.5, 73.0, 72.7, 72.1, 71.2, 70.7, 68.8, 61.8, 54.9; HRMS (ESI-TOF) calcd for $C_{62}H_{58}O_{15}Na$ $[M+Na]^+$ 1065.3673, found 1065.3665.

### 4.11. Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (28)

A solution of **10**[35] (46.6 mg, 0.0884 mmol), **23** (40.7 mg, 0.0804 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (23.0 mg, 0.0975 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (2 mL) for 30 min at room temperature. The reaction mix-

ture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (19 μL, 0.105 mmol) was added via a micro-syringe. The reaction mixture was warmed gradually to ambient temperature over 30 min. The reaction was then quenched with $Et_3N$ (180 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 11:9) to afford **28**[36] (70.7 mg, 95%) as a white foam. $R_f$ 0.20 (40% EtOAc in hexane). $[\alpha]_D^{24}$ +45.3 (*c* 1.65, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.92–7.85 (m, 4H, ArH), 7.80–7.73 (m, 6H, ArH), 7.49–7.46 (m, 2H, ArH), 7.40–7.32 (m, 5H, ArH), 7.25–7.22 (m, 2H, ArH), 6.00 (t, 1H, *J* = 10.0 Hz), 5.81 (t, 1H, *J* = 10.0 Hz), 5.41 (d, 1H, *J* = 8.0 Hz), 5.26 (t, 1H, *J* = 10.0 Hz), 5.15 (t, 1H, *J* = 9.5 Hz), 5.06 (dd, 1H, *J* = 10.0, 3.5 Hz), 4.72 (d, 1H, *J* = 3.5 Hz), 4.36 (t, 1H, *J* = 10.0, 9.0, Hz), 4.31 (dd, 1H, *J* = 12.5, 4.5 Hz), 4.12–4.10 (m, 2H), 4.05 (d, 1H, *J* = 10.5 Hz), 3.87 (d, 1H, *J* = 7.5 Hz), 3.61 (dd, 1H, *J* = 10.0, 7.5 Hz), 3.08 (s, 3H, $OCH_3$), 2.05 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 1.86 (s, 3H, $COCH_3$). The spectral data were consistent with those in the literature.[36]

### 4.12. *p*-Methylphenyl (2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (30)

A solution of **2** (40.7 mg, 0.0754 mmol), **29**[22a] (45.0 mg, 0.0753 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (19.6 mg, 0.0831 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (17 μL, 0.0939 mmol) was injected into the reaction mixture via a micro-syringe. The reaction mixture was warmed gradually to ambient temperature over 30 min. The reaction was then quenched with $Et_3N$ (160 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 5:1) to afford **30**[14,37] (68.7 mg, 90%) as a white foam. $R_f$ 0.30 (25% EtOAc in hexane). $[\alpha]_D^{24}$ −8.2 (*c* 0.98, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.08–8.07 (m, 2H, ArH), 7.90–7.89 (m, 2H, ArH), 7.85–7.83 (m, 2H, ArH), 7.64 (m, 1H, ArH), 7.52–7.19 (m, 25H, ArH), 6.87–6.85 (m, 2H), 5.69 (apparent t, 1H, *J* = 9.5, 9.0 Hz), 5.24 (t, 1H, *J* = 9.5 Hz), 5.06 (dd, 1H, *J* = 12.0, 1.5 Hz), 4.86–4.82 (m, 4H), 4.79 (d, 1H, *J* = 12.0 Hz), 4.73 (d, 1H, *J* = 12.0 Hz), 4.68 (d, 1H, *J* = 11.5 Hz), 4.64 (dd, 1H, *J* = 12.0, 4.5 Hz), 4.50 (d, 1H, *J* = 11.5 Hz), 3.97–3.93 (m, 2H), 3.91–3.87 (m, 2H), 3.71 (q, 1H, *J* = 6.0 Hz), 3.45 (br s, 1H), 2.23 (s, 3H), 0.60 (d, 3H, *J* = 6.0 Hz). The spectral data were consistent with those in the literature.[37]

### 4.13. *p*-Methylphenyl (2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (31)

A solution of **13** (43.3 mg, 0.067 mmol), **29** (40.0 mg, 0.0669 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (17.4 mg, 0.0737 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at room temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (15 μL, 0.0829 mmol) was injected via a micro-syringe. The reaction mixture was warmed gradually to room temperature over 30 min. The reaction was quenched with $Et_3N$ (140 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 5:1) to afford **31**[14] (69.8 mg, 93%) as a white foam. $R_f$ 0.30 (25% EtOAc in hexane); $[\alpha]_D^{26}$ +30.6 (*c* 1.02, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.06–8.04 (m, 2H, ArH), 7.97–7.92 (m, 4H, ArH), 7.64 (t, 1H, *J* = 7.5 Hz, ArH), 7.53–7.07 (m, 30H, ArH), 6.90 (d, 2H, *J* = 8.0 Hz, ArH), 5.86 (t, 1H, *J* = 9.0 Hz), 5.37 (t, 1H, *J* = 10.0 Hz), 5.00 (d,1H, *J* = 3.5 Hz), 4.96 (dd, 1H, *J* = 12.0, 2.0 Hz), 4.89 (d, 1H, *J* = 9.5 Hz), 4.79 (d, 1H, *J* = 11.0 Hz), 4.64–4.61 (m, 2H), 4.58 (dd, 1H, *J* = 12.0, 5.0 Hz), 4.44 (d, 1H, *J* = 11.0 Hz), 4.31 (d, 1H, *J* = 12.0 Hz), 4.25 (d, 1H, *J* = 12.5 Hz), 4.24–4.16 (m, 2H), 4.01–3.94 (m, 3H), 3.90 (s, 1H), 3.86 (dd, 1H, *J* = 10.5, 2.5 Hz), 3.78 (dd, 1H, *J* = 10.0, 3.5 Hz), 3.45–3.37 (m, 2H), 2.26 (s, 3H). The spectral data were consistent with those in the literature.[14]

### 4.14. Phenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-α-D-mannopyranoside (33)

A solution of **19** (40.0 mg, 0.0685 mmol), **32**[38] (40.1 mg, 0.0685 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (17.8 mg, 0.0754 mmol), and flame activated 4 Å MS were stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at room temperature. The reaction mixture was then cooled to −10 °C. After stirring for 5 min, TMSOTf (15 μL, 0.0829 mmol) was injected via a micro-syringe. The reaction mixture was warmed gradually to ambient temperature over 1 h. The reaction was then quenched with $Et_3N$ (130 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 3:1) to afford **33** (68.2 mg, 94%) as a white foam. $R_f$ 0.25 (30% EtOAc in hexane); $[\alpha]_D^{26}$ +16.3 (*c* 1.34, $CHCl_3$); $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ 8.07 (d, 2H, *J* = 7.2 Hz, ArH), 8.00 (d, 2H, *J* = 7.2 Hz, ArH), 7.85 (d, 2H, *J* = 7.2 Hz, ArH), 7.57–7.41 (m, 9H, ArH), 7.35–7.22 (m, 19H, ArH), 7.16–7.13 (m, 3H, ArH), 5.99 (t, 1H, *J* = 10.2 Hz), 5.94 (m, 1H), 5.81 (dd, 1H, *J* = 9.6, 3.0 Hz), 5.73 (d, 1H, *J* = 1.2 Hz, H-1), 5.36 (dd, 1H, *J* = 3.0, 1.8 Hz), 4.87 (d, 1H, *J* = 1.3 Hz, H-1′), 4.84 (d, 1H, *J* = 10.8 Hz), 4.81 (m, 1H), 4.58 (d, 1H, *J* = 12.0 Hz), 4.50 (d, 1H, *J* = 10.8 Hz), 4.44 (d, 1H, *J* = 10.8 Hz), 4.36 (d, 1H, *J* = 12.0 Hz), 4.32 (d, 1H, *J* = 10.8 Hz), 4.00 (dd, 1H, *J* = 10.8, 5.4 Hz), 3.95 (dd, 1H, *J* = 9.6, 3.6 Hz), 3.87 (t, 1H, *J* = 9.6 Hz), 3.75 (dd, 1H, *J* = 10.2, 3.0 Hz), 3.69 (m, 1H), 3.68 (m, 1H), 3.53 (d, 1H, *J* = 9.6 Hz), 2.10 (s, 3H, $COCH_3$); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ 170.3 (C═O), 165.44 (C═O), 165.36 (C═O), 138.5, 138.0, 137.9, 133.6, 133.5, 133.25, 133.22, 132.1, 131.5, 129.92, 129.89, 129.8, 129.74, 129.71, 129.4, 129.3, 129.2, 128.9, 128.6, 128.54, 128.47, 128.4, 128.32, 128.27, 128.23, 128.18, 128.0, 127.90, 127.88, 127.7, 127.51, 127.50, 98.0 (C-1′), 86.0 (C-1), 78.4, 75.1, 74.0, 73.2, 72.0, 71.8, 71.5, 70.48, 70.45, 68.46, 68.44, 67.3, 66.6, 21.0, HRMS (ESI-TOF) calcd for $C_{62}H_{58}O_{14}SNa$ $[M+Na]^+$ 1081.3445, found 1081.3441.

### 4.15. *p*-Methylphenyl (2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (36)

A solution of **34**[39] (48.7 mg, 0.0837 mmol), **35**[34c] (50.0 mg, 0.0836 mmol), *N*-(*p*-methylphenylthio)-ε caprolactam (21.7 mg, 0.0919 mmol) and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (2 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −5 °C. After stirring for 5 min, TMSOTf (18 μL, 0.0995 mmol) was injected into the reaction mixture via a micro-syringe. The reaction mixture was further stirred for 1 h at −5 °C and then warmed gradually to ambient temperature. The reaction mixture was then quenched with $Et_3N$ (170 μL), filtered off through a pad of Celite, and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 2:1) to afford **36**[21] (76.8 mg, 87%) as a white foam. $R_f$ 0.28 (30% EtOAc in hexane); $[\alpha]_D^{24}$ +51.2 (*c* 1.1, $CHCl_3$); Lit.[21] $[\alpha]_D^{27}$ +50.0 (*c* 1.0, $CDCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.93–7.90 (m, 2H, ArH), 7.87–7.84 (m, 4H, ArH), 7.78–7.60 (m, 2H, ArH), 7.66 (d, 2H, *J* = 8.0 Hz, ArH), 7.45–7.23 (m, 20H, ArH), 7.17–7.14 (m, 2H, ArH), 7.02 (d, 2H, *J* = 8.0 Hz, ArH), 5.80 (dd, 1H, *J* = 10.5, 8.0 Hz), 5.68 (t, 1H, *J* = 9.5 Hz), 5.45 (s, 1H, PhC*H*), 5.27–5.19 (m, 3H), 4.87 (d, 1H, *J* = 8.0 Hz), 4.72 (d, 1H, *J* = 10.0 Hz), 4.52 (d, 1H, *J* = 3.5 Hz), 4.22 (d, 1H, *J* = 12.5 Hz), 4.03–3.92 (m, 3H), 3.86 (dd,

1H, $J$ = 11.5, 7.5 Hz), 3.56 (s, 1H), 2.22 (s, 3H). The spectral data were consistent with those in the literature.[21]

### 4.16. Glycosylation method for 39 and 40

A mixture of **37**[40] (0.0825 mmol), **38**[41] (0.075 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (0.091 mmol), and flame activated 4 Å MS was stirred in dry solvent (3 mL) for 30 min at room temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (0.10 mmol) was injected via a micro-syringe. The reaction mixture was warmed gradually to ambient temperature over 30 min. The reaction was then quenched with $Et_3N$, filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography ($CH_2Cl_2$/hexane, 3:2) to afford the title compounds.

Procedure *A*: solvent: $CH_2Cl_2$.

Procedure *B*: solvent: $Et_2O$–$CH_2Cl_2$ (3:1).

Procedure *C*: solvent: $CH_3CN$–$CH_2Cl_2$ (3:1).

#### 4.16.1. Methyl (2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (39) and Methyl (2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (40)[43]

Reaction of **37** with 38 following the procedure *A*, afforded **39** and **40** in 45% and 42% yields, respectively. Following the procedure *B*, the corresponding yields were 72% and 19%, whereas procedure *C* provided **39** and **40** in 21% and 68% yields.

Compound **39**:[42] syrupy oil; $R_f$ 0.43 (80% $CH_2Cl_2$ in hexane); $[\alpha]_D^{24}$ +46.2 (*c* 1.0, $CHCl_3$); Lit.[42a] $[\alpha]_D^{20}$ +40 (*c* 1.1, $CHCl_3$), Lit.[19] $[\alpha]_D$ +46 (*c* 0.6, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.34–7.10 (m, 35H, ArH), 5.69 (d, 1H, $J$ = 3.0 Hz), 5.03 (d, 1H, $J$ = 11.5 Hz), 4.88 (d, 1H, $J$ = 10.5 Hz), 4.80 (d, 1H, $J$ = 11.0 Hz), 4.78 (d, 1H, $J$ = 10.0 Hz), 4.77 (d, 1H, $J$ = 11.0 Hz), 4.70 (d, 1H, $J$ = 12.0 Hz), 4.60 (d, 1H, $J$ = 3.0 Hz), 4.58–4.55 (m, 3H), 4.51 (d, 1H, $J$ = 12.0 Hz), 4.49 (s, 2H), 4.42 (d, 1H, $J$ = 10.5 Hz), 4.28 (d, 1H, $J$ = 12.0 Hz), 4.09 (t, 1H, $J$ = 9.0 Hz), 4.04 (t, 1H, $J$ = 9.0 Hz), 3.90 (t, 1H, $J$ = 9.5 Hz), 3.86–3.81 (m, 2H), 3.72 (d, 1H, $J$ = 10.0 Hz), 3.66–3.62 (m, 2H), 3.59 (dd, 1H, $J$ = 9.0, 3.5 Hz), 3.50 (d, 1H, $J$ = 3.0 Hz), 3.48 (d, 1H, $J$ = 3.0 Hz), 3.40 (br s, 1H), 3.38 (s, 3H, OC$H_3$). The spectral data were consistent with those in the literature.[42a]

Compound **40.**[42] White solid; $R_f$ 0.33 (80% $CH_2Cl_2$ in hexane); mp 84–85 °C (hexanes), Lit.[41a] mp 88–89 °C, Lit.[19] mp 79–81 °C (ether–hexanes); $[\alpha]_D^{24}$ +22.8 (*c* 1.15, $CHCl_3$); Lit.[42a] $[\alpha]_D^{20}$ +20 (*c* 1.0, $CHCl_3$), Lit.[19] $[\alpha]_D$ +22 (*c* 0.4, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.26–7.18 (m, 35H, ArH), 5.09 (d, 1H, $J$ = 11.5 Hz), 4.87 (d, 1H, $J$ = 11.0 Hz), 4.80 (d, 1H, $J$ = 12.5 Hz), 4.80 (d, 1H, $J$ = 11.5 Hz), 4.79 (s, 1H), 4.75 (d, 1H, $J$ = 11.5 Hz), 4.75 (d, 1H, $J$ = 9.5 Hz), 4.74 (d, 1H, $J$ = 11.5 Hz), 4.60 (d, 1H, $J$ = 12.5 Hz), 4.57 (d, 1H, $J$ = 11.5 Hz), 4.57 (d, 1H, $J$ = 4.0 Hz), 4.55 (d, 1H, $J$ = 10.0 Hz), 4.44 (d, 1H, $J$ = 12.0 Hz), 4.39 (d, 1H, $J$ = 12.0 Hz), 4.38 (d, 1H, $J$ = 8.0 Hz), 4.38 (d, 1H, $J$ = 12.5 Hz), 3.96 (t, 1H, $J$ = 9.5 Hz), 3.84 (t, 1H, $J$ = 9.5 Hz), 3.83 (dd, 1H, $J$ = 10.5, 3.5 Hz), 3.71 (dd, 1H, $J$ = 10.5, 1.5 Hz), 3.59 (t, 1H, $J$ = 9.5 Hz), 3.54 (dd, 1H, $J$ = 11.0, 5.0 Hz), 3.50–3.46 (m, 3H), 3.36 (m, 1H), 3.36 (s, 3H, OC$H_3$), 3.29 (m, 1H). The spectral data were consistent with those in the literature.[42a]

### 4.17. Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phathalimido-β-D-glucopyranosyl)-(1→4)-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phathalimido-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzyl-α-D-glucopyranoside (42)

A solution of **10** (85.9 mg, 0.163 mmol), **41**[43] (25.4 mg, 0.0679 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (42.4 mg, 0.1797 mmol), and flame activated 4 Å MS were stirred in dry $CH_2Cl_2$ (3 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to 0 °C. After stirring for 5 min, TMSOTf (36 μL, 0.1989 mmol) was injected into the reaction mixture via a micro-syringe. The reaction mixture was further stirred for 30 min and then warmed gradually to ambient temperature. The reaction was then quenched with $Et_3N$ (400 μL), filtered off through a pad of Celite, and concentrated. The crude residue was directly purified by silica gel flash column chromatography (hexane/EtOAc, 1:2) to afford **42**[16] (66.2 mg, 81%) as a white foam. $R_f$ 0.31 (60% EtOAc in hexane). $[\alpha]_D^{24}$ +24.6 (*c* 1.0, $CHCl_3$); Lit.[16] $[\alpha]_D^{20}$ +23.9 (*c* 0.8, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.88–7.87 (m, 2H, ArH), 7.79–7.75 (m, 4H, ArH), 7.67–7.65 (m, 2H, ArH), 7.33–7.32 (m, 4H, ArH), 7.26–7.21 (m, 4H, ArH), 7.16–7.15 (m, 2H, ArH), 5.69 (dd, 1H, $J$ = 10.5, 9.5 Hz), 5.52 (dd, 1H, $J$ = 10.5, 9.5 Hz), 5.47 (d, 1H, $J$ = 8.5 Hz), 5.12–5.05 (m, 3H), 4.90 and 4.82 (d, each 1H, $J$ = 12.0 Hz, PhC$H_2$), 4.53 and 4.41 (d, each 1H, $J$ = 12.0 Hz, PhC$H_2$), 4.34 (dd, 1H, $J$ = 12.5, 5.0 Hz), 4.20–4.11 (m, 4H), 4.08 (dd, 1H, $J$ = 12.5, 4.0 Hz), 3.84 (dd, 1H, $J$ = 12.5, 2.5 Hz), 3.76 (apparent t, 1H, $J$ = 9.5, 8.5 Hz), 3.68–3.66 (m, 2H), 3.59–3.52 (m, 2H), 3.40 (apparent t, 1H, $J$ = 10.0, 9.0 Hz), 3.19–3.17 (m, 2H), 3.06 (s, 3H, OC$H_3$), 2.12 (s, 3H, COC$H_3$), 2.03 (s, 3H, COC$H_3$), 1.99 (s, 3H, COC$H_3$), 1.97 (s, 3H, COC$H_3$), 1.84 (s, 3H, COC$H_3$), 1.80 (s, 3H, COC$H_3$). The spectral data were consistent with those in the literature.[16]

### 4.18. Methyl (2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (43)

A solution of **13** (54.0 mg, 0.0836 mmol), **29** (50.0 mg, 0.0836 mmol), *N*-(*p*-methylphenylthio)-ε-caprolactam (21.7 mg, 0.092 mmol), and flame activated 4 Å MS was stirred in dry $CH_2Cl_2$ (2 mL) for 30 min at ambient temperature. The reaction mixture was then cooled to −45 °C. After stirring for 5 min, TMSOTf (18 μL, 0.0995 mmol) was injected via a micro-syringe and then allowed to warm to ambient temperature. The formation of **31** was monitored by TLC (hexanes/EtOAc 3:1). After the starting materials were consumed, **38** (35.2 mg, 0.0759 mmol) and *N*-(*p*-methylphenylthio)-ε-caprolactam (22.0 mg, 0.0932 mmol) were added to the reaction mixture and stirred for 30 min. The solution was cooled to −45 °C and then TMSOTf (19 μL, 0.105 mmol) was injected into the reaction mixture, the mixture was stirred for 5 min at −45 °C, and then for 2 h at ambient temperature. The reaction was then quenched with $Et_3N$ (380 μL), filtered off through a pad of Celite, and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (toluene/EtOAc, 10:1) to afford **43** (72.1 mg, 65%) as a colorless oil. $R_f$ 0.56 (10% EtOAc in toluene); $[\alpha]_D^{26}$ +32.5 (*c* 1.22, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, 2H, $J$ = 7.6 Hz, ArH), 7.95 (d, 2H, $J$ = 7.5 Hz, ArH), 7.87 (d, 2H, $J$ = 7.2 Hz, ArH), 7.45–7.08 (m, 44H, ArH), 5.67 (t, 1H, $J$ = 9.3 Hz), 5.43 (dd, 1H, $J$ = 8.1, 1.8 Hz), 5.10 (d, 1H, $J$ = 11.4 Hz), 4.94 (d, 1H, $J$ = 3.6 Hz, H-1), 4.81–4.75 (m, 3H, H-1′), 4.71–4.65 (m, 5H), 4.55–4.52 (m, 2H, H-1″), 4.46–4.42 (m, 2H), 4.37 (br s, 1H), 4.33 (br s, 1H), 4.28–4.16 (m, 3H), 3.97–3.86 (m, 6H), 3.76 (dd, 1H, $J$ = 9.9, 2.4 Hz), 3.66 (dd, 1H, $J$ = 9.6, 1.5 Hz), 3.56 (br s, 1H), 3.51 (br s, 1H), 3.48–3.36 (m, 4H), 3.26 (s, 3H, OC$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 165.8 (C═O), 165.5 (C═O), 165.1 (C═O), 139.3, 138.8, 138.5, 138.4, 138.1, 137.8, 133.2, 132.9, 130.0, 129.79, 129.75, 129.3, 128.8, 128.4, 128.3, 128.19, 128.13, 128.11, 128.08, 127.95, 127.92, 127.85, 127.7, 127.6, 127.52, 127.48, 127.43, 127.37, 127.3, 127.0, 100.3 (C-1′), 99.6 (C-1), 98.1 (C-1″), 80.6, 78.8, 78.6, 77.5, 75.5, 75.3, 75.2, 75.0, 74.8, 74.7, 73.6, 73.5, 73.4, 73.3, 73.1, 72.9, 62.7, 63.6, 55.3. HRMS (ESI-TOF) calcd for $C_{89}H_{88}O_{19}Na$ $[M+Na]^+$ 1483.5818, found 1483.5812.

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## Supplementary data

Supplementary data (preparation of compound **17**; **c**opies of spectra ($^1$H, $^{13}$C NMR) of compounds **1** and **17**; copies of spectra ($^1$H NMR) of compounds **12**, **39** and **40**; copies of $^1$H-, $^{13}$C- and 2D-NMR spectra of compounds **8**, **18**, **21**, **24**, **27**, **33** and **43**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.03.024.

## References

1. (a) Varki, A. *Glycobiology* **1993**, *3*, 97–130; (b) Dwek, R. A. *Chem. Rev.* **1996**, *96*, 683–720.
2. (a) Fraser-Reid, B.; Madsen, R.; Campbell, A. S.; Roberts, C. S.; Merritt, J. R. In *Bioorganic Chemistry: Carbohydrates*; Hecht, S. M., Ed.; Oxford University Press: Oxford, 1999; pp 89–133; (b) Fügedi, P. In *The Organic Chemistry of Sugars*; Levy, D. E., Fügedi, P., Eds.; CRC Press: Boca Raton, FL, 2005; pp 89–179.
3. (a) Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503–1531; (b) Codée, J. D. C.; Litijens, R. E. J. N.; van den Bos, L. J.; Overkleeft, H. S.; van der Marel, G. A. *Chem. Soc. Rev.* **2005**, *34*, 769–782; (c) Kaeothip, S.; Demchenko, A. V. *Carbohydr. Res.* **2011**, *346*, 1371–1388.
4. (a) Fügedi, P.; Garegg, P. J.; Lönn, H.; Norberg, T. *Glycoconjugate J.* **1987**, *4*, 97–108; (b) Garegg, P. J. *Adv. Carbohydr. Chem. Biochem.* **1997**, *52*, 179–205.
5. Oscarson, S. In *Glycoscience: Chemistry and Chemical Biology*; Tatsuta, K. T., Fraser-Reid, B. O., Thiem, J., Eds.; Springer-Verlag: Berlin, Heidelberg, 2001; pp 643–671.
6. Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 1331–1334.
7. Fügedi, P.; Garegg, P. J. *Carbohydr. Res.* **1986**, *149*, C9–C12.
8. Veenenman, G. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 275–278.
9. Lönn, H. *Carbohydr. Res.* **1985**, *139*, 105–113.
10. Dasgupta, F.; Garegg, P. J. *Carbohydr. Res.* **1988**, *177*, C13–C17.
11. Ito, Y.; Ogawa, T. *Tetrahedron Lett.* **1988**, *29*, 1061–1064.
12. Martichonok, V.; Whitesides, G. M. *J. Org. Chem.* **1996**, *61*, 1702–1706.
13. Jona, H.; Takeuchi, K.; Saitoh, T.; Mukaiyama, T. *Chem. Lett.* **2000**, 1178–1179.
14. Durón, S. G.; Polat, T.; Wong, C.-H. *Org. Lett.* **2004**, *6*, 839–841.
15. Crich, D.; Smith, M. *Org. Lett.* **2000**, *2*, 4067–4069.
16. Crich, D.; Smith, M. *J. Am. Chem. Soc.* **2001**, *123*, 9015–9020.
17. Codée, J. D. C.; Litjens, R. E. J. N.; den Heeten, R.; Overkleeft, H. S.; van Boom, J. H.; van der Marel, G. A. *Org. Lett.* **2003**, *5*, 1519–1522.
18. Wang, C.; Wang, H.; Huang, X.; Zhang, L.-H.; Ye, X.-S. *Synlett* **2006**, 2846–2850.
19. Tatai, J.; Fügedi, P. *Org. Lett.* **2007**, *9*, 4647–4650.
20. Xiong, D.-C.; Zhang, L.-H.; Ye, X.-S. *Adv. Synth. Catal.* **2008**, *350*, 1696–1700.
21. Peng, P.; Ye, X.-S. *Org. Biomol. Chem.* **2011**, *9*, 616–622.
22. (a) Zhang, Z.; Ollmann, I. R.; Ye, X.-S.; Wischnat, R.; Baasov, T.; Wong, C.-H. *J. Am. Chem. Soc.* **1999**, *121*, 734–753; (b) Ercegovic, T.; Meijer, A.; Magnusson, G.; Ellervik, U. *Org. Lett.* **2001**, *3*, 913–915.
23. (a) Ghosh, R.; De, D.; Shown, B.; Maiti, S. B. *Carbohydr. Res.* **1999**, *321*, 1–3; (b) Ghosh, R.; Chakraborty, A.; Maiti, D. K. *Synth. Commun.* **2003**, *33*, 1623–1632; (c) Ghosh, R.; Chakraborty, A.; Maiti, S. *Arkivoc* **2004**, *xiv*, 1–9; (d) Ghosh, R.; Chakraborty, A.; Maiti, D. K.; Puranik, V. G. *Tetrahedron Lett.* **2005**, *46*, 8047–8050; (e) Ghosh, R.; Chakraborty, A.; Maiti, D. K.; Puranik, V. G. *Org. Lett.* **2006**, *8*, 1061–1064; (f) Das Sarma, M.; Ghosh, R.; Patra, A.; Chowdhury, R.; Chaudhuri, K.; Hazra, B. *Org. Biomol. Chem.* **2007**, *5*, 3115–3125; (g) Roy, S.; Chakraborty, A.; Ghosh, R. *Carbohydr. Res.* **2008**, *343*, 2523–2529; (h) Roy, S.; Chakraborty, A.; Chattopadhaya, S.; Bhattacharya, A.; Mukherjee, A. K.; Ghosh, R. *Tetrahedron* **2010**, *66*, 8512–8521; (i) Basu, N.; Maity, S. K.; Singha, S.; Ghosh, R. *Carbohydr. Res.* **2011**, *346*, 534–539.
24. (a) Maity, S. K.; Maiti, S.; Patra, A.; Ghosh, R. *Tetrahedron Lett.* **2008**, *49*, 5847–5849; (b) Maity, S. K.; Patra, A.; Ghosh, R. *Tetrahedron* **2010**, *66*, 2809–2814.
25. Yamago, S.; Yamada, T.; Maruyama, T.; Yoshida, J. I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2145–2148.
26. Compound **12**: $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.84–7.83 (m, 4H, ArH), 7.74–7.72 (m, 4H, ArH), 7.38–7.14 (m, 10H, ArH), 5.73–5.67 (m, 2H), 5.59 (d, 1H, $J$ = 11.0 Hz), 5.45 (d, 1H, $J$ = 8.5 Hz), 5.10 (t, 1H, $J$ = 9.5 Hz), 4.50 (d, 1H, $J$ = 11.5 Hz), 4.44 (d, 1H, $J$ = 12.0 Hz), 4.36 (dd, 1H, $J$ = 12.5, 4.0 Hz), 4.25–4.18 (m, 2H), 4.12 (t, 1H, $J$ = 9.5 Hz), 3.94 (dd, 1H, $J$ = 11.5, 1.0 Hz), 3.60–3.54 (m, 3H), 3.47 (dd, 1H, $J$ = 11.0, 3.0 Hz), 2.03 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 1.89 (s, 3H, $COCH_3$), 1.82 (s, 3H, $COCH_3$).
27. (a) Lemieux, R. U. *Pure Appl. Chem.* **1971**, *25*, 527–548; (b) Lönn, H. *J. Carbohydr. Chem.* **1987**, *6*, 301–306.
28. (a) Wang, Z.; Zhou, L.; El-Boubbou, K.; Ye, X.-S.; Huang, X. *J. Org. Chem.* **2007**, *72*, 6409–6420; (b) Lee, J.-C.; Greenberg, W. A.; Wong, C.-H. *Nat. Protocols* **2006**, *1*, 3143–3152.
29. (a) Zhang, Z.; Wong, C.-H. *Tetrahedron* **2002**, *58*, 6513–6519; (b) Stévenin, A.; Boyer, F.-D.; Beau, J.-M. *J. Org. Chem.* **2010**, *75*, 1783–1786.
30. Chen, C.-T.; Weng, S.-S.; Kao, J.-Q.; Lin, C.-C.; Jan, M.-D. *Org. Lett.* **2005**, *7*, 3343–3346.
31. (a) Zhang, Y.-M.; Mallet, J.-M.; Sinaÿ, P. *Carbohydr. Res.* **1992**, *236*, 73–88; (b) Peters, T. *Liebigs Ann. Chem.* **1991**, 135–141.
32. Madiyalakan, R.; Chowdhary, M. S.; Rana, S. S.; Matta, K. L. *Carbohydr. Res.* **1986**, *152*, 183–194.
33. Misra, A. K.; Roy, N. *J. Carbohydr. Chem.* **1998**, *17*, 1047–1056.
34. (a) Ziegler, T.; Kováč, P.; Glaudemans, C. P. J. *Carbohydr. Res.* **1989**, *194*, 185–198; (b) Verduyn, R.; Douwes, M.; van der Klein, P. A. M.; Mösinger, E. M.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron* **1993**, *49*, 7301–7316; (c) Zhang, F.; Zhang, W.; Zhang, Y.; Curran, D. P.; Liu, G. *J. Org. Chem.* **2009**, *74*, 2594–2597.
35. Das, S. K.; Roy, J.; Reddy, K. A.; Abbineni, C. *Carbohydr. Res.* **2003**, *338*, 2237–2240.
36. Takeuchi, K.; Tamura, T.; Mukaiyama, T. *Chem. Lett.* **2000**, 124–125.
37. Mong, T. K.-K.; Lee, H.-K.; Durón, S. G.; Wong, C.-H. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 797–802.
38. Christensen, M. K.; Meldal, M.; Bock, K. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1453–1460.
39. (a) Vargas-berenguel, A.; Meldal, M.; Paulsen, H.; Jensen, K. J.; Bock, K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3287–3294; (b) Wang, C.; Li, Q.; Wang, H.; Zhang, L.-H.; Ye, X.-S. *Tetrahedron* **2006**, *62*, 11657–11662.
40. France, R. R.; Rees, N. V.; Wadhawan, J. D.; Fairbanks, A. J.; Compton, R. G. *Org. Biomol. Chem.* **2004**, *2*, 2188–2194.
41. (a) Garegg, P. J.; Hultberg, H. *Carbohydr. Res.* **1981**, *93*, C10–C11; (b) Dasgupta, F.; Anderson, L. *Carbohydr. Res.* **1990**, *202*, 239–255.
42. (a) Garcia, B. A.; Gin, D. Y. *J. Am. Chem. Soc.* **2000**, *122*, 4269–4279; (b) Jona, H.; Mandai, H.; Chavasiri, W.; Takeuchi, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 291–309.
43. (a) Vatèle, J.-M. *Tetrahedron* **2007**, *63*, 10921–10929; (b) Tiwari, P.; Misra, A. K. *J. Carbohydr. Chem.* **2007**, *26*, 239–248; (c) Davis, N. J.; Flitsch, S. L. *J. Chem. Soc., Perkin Trans. 1* **1994**, 359–368.