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Threshold of Thioglycoside Reactivity Difference Is Critical for Efficient Synthesis of Type I Oligosaccharides by Chemoselective Glycosylation

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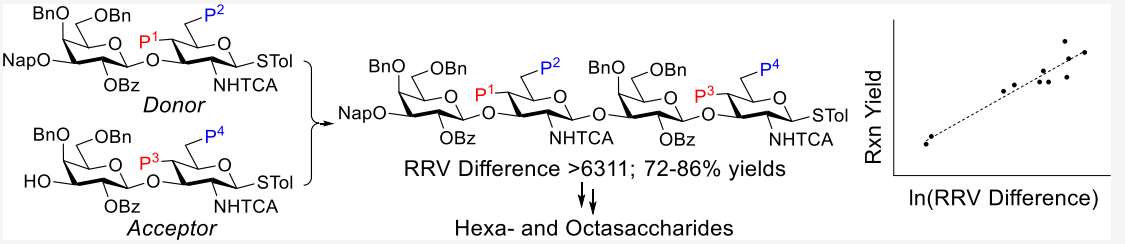

ABSTRACT: Synthesis of type I LacNAc (Galβ1 → 3GlcNAc) oligosaccharides usually suffers from low yields. We herein report the efficient synthesis of type I LacNAc oligosaccharides by chemoselective glycosylation. With 16 relative reactivity values (RRVs) measured thiotoluenyl-linked disaccharide donors and acceptors, chemoselective glycosylations were investigated to obtain optimal conditions. In these reactions, the RRV difference between the donors and acceptors had to be more than 6311 to obtain type I LacNAc tetrasaccharides in 72−86% yields, with minimal occurrence of aglycon transfer. The threshold of RRV difference was further applied to plan the synthesis of longer glycans. Because it is challenging to measure the RRVs of tetrasaccharides, anomeric proton chemical shifts were utilized to predict the corresponding RRVs, which consequently explained the outcome of glycosylations for the synthesis of type I LacNAc hexasaccharides. The result supported the idea that elongation of glycan chains has to proceed from the reducing to the nonreducing end for a better yield.

INTRODUCTION

Type I LacNAc (Galβ1 → 3GlcNAc)-repeating oligosaccharides are known as tumor-associated carbohydrate antigens, owing to the aberrant glycosylation pattern particularly in colon cancer.[1−3] For example, Hakomori *et al.* identified the dimeric Lewis antigen, Lewis a−Lewis a, on the surface of human colonic adenocarcinoma cell line Colo205.[4] Moreover, type I oligosaccharides act as a novel antigen for colon cancer cells, especially when the glycan chains are longer than octasaccharides and are decorated with additional fucose and sialic acid residues in their nonreducing end.[5] Furthermore, Lewis a-tandem repeat is known to bind with highly expressed cancer-related proteins, such as mannose-binding protein[5] and galectin 3.[6] However, biological study is limited by the availability of pure oligosaccharides. Methods leading to the accessibility of these oligosaccharides would not only help to obtain these glycans in a sufficient amount but could also pave the way for further investigations and applications. Hence, it is necessary to rapidly afford those structurally well-defined oligosaccharides.

There have been few chemical and enzymatic approaches to synthesize type I LacNAc-related oligosaccharides. For instance, Henze and co-workers applied enzymatic synthesis to assemble type I LacNAc oligomers with variable lengths.[6,7] Nevertheless, it was still a concern to yield those glycans at a milligram scale, not to mention that the work was not trivial to separate a desired product from reaction mixtures, especially for the glycans longer than a pentasaccharide. In contrast, chemical synthesis was shown to avoid the disadvantages and additionally to provide these biologically important oligosaccharides in a sufficient quantity with flexibility. Kobayashi *et al.*, for example, recently synthesized the fucosylated oligosaccharide that contained four Le^a-tandem repeats by using (*N*-phenyl) trifluoroacetimidate donors[8] with a convergent approach. These growing research efforts signify the urgency to produce type I-repeating oligomers.

At the current stage, there are several formidable barriers in chemical synthesis of type I oligosaccharides. For example, the 3-hydroxyl GlcNAc acceptor is less active than the 4-hydroxyl

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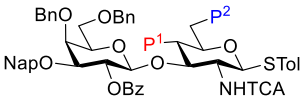
GlcNAc acceptor in glycosylation reactions.[9−12] The glycosylation with Galβ1 → 3GlcNAc donor gave a lower yield, as compared to that with Galβ1 → 4GlcNAc donor.[10] Furthermore, when the thioglycoside donor and acceptor with similar reactivity are subjected to chemoselective glycosylation, the transfer of the anomeric thiotoluenyl group usually occurs from the thioglycoside acceptor to the activated donor, leading to donor regeneration, and formation of acceptor oligomerization or/and acceptor hydrolysis. The problem, known as aglycon transfer, accounts for commonly observed low yields.[10,13,14]

In the past, different approaches were used to minimize the aglycon transfer. Mong and co-workers utilized reactivity-based [2 + 2] glycosylation between disaccharide donor and acceptor to synthesize type II LacNAc (Galβ1 → 4GlcNAc) tetrasaccharide, which was further activated to yield hexa- and octasaccharides with one-pot glycosylations.[15] Additionally, several studies developed sophisticated, less reactive sulfur-based leaving groups by using either sterically hindered or electron-withdrawing substituents on sulfur, such as 4-nitrothiophenyl,[16] dicyclohexylmethanethio,[17] 2,6-dimethyl-thiophenyl,[14] thio-*ortho*-tolyl,[18] and 2-trifluoromethyl-thiophenyl.[19] In spite of less aglycon transfer, these methods were limited to the synthesis of di- or trisaccharides.

Despite efforts of procuring similar oligosaccharides,[9,10,15,20] there is a lack of systematic study on the factors diminishing or avoiding the aforementioned problems, for example, stereoelectronic effects of protecting groups on the reactivity of type I LacNAc disaccharides. Moreover, it is equally important to know which direction for the type I glycan elongation is suited most to obtain satisfying yields. For instance, desired oligosaccharides can either be constructed from the reducing to nonreducing end or the other way around. Without in-depth understanding of associated factors, it is challenging to synthesize desirable oligosaccharides in useful quantities.

Herein, we report the chemoselective glycosylation in which various type I LacNAc thioglycoside disaccharides were first prepared with their measured relative reactivity values (RRVs). A linear correlation was found between product yields vs difference in the reactivity of disaccharide donors and acceptors. The result is useful to predict the threshold reactivity difference required for satisfying yields. The threshold RRV difference was shown applicable for preparation of longer glycan chains and useful to identify several factors to eliminate the occurrence of aglycon transfer and thus increase the reaction yields. Additionally, anomeric proton chemical shifts of glycosides were shown useful to predict the RRVs and the outcome of chemoselective glycosylation.

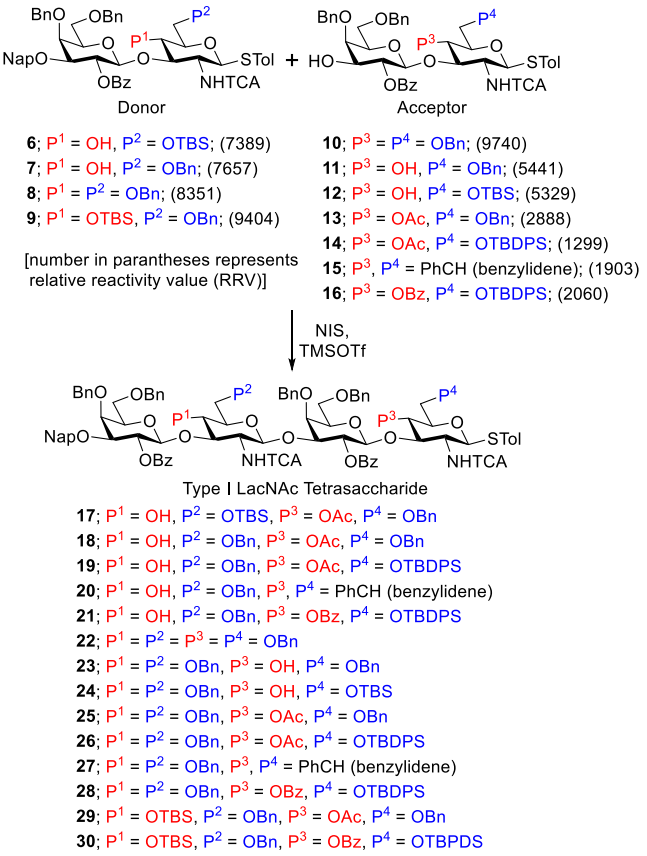
RESULTS AND DISCUSSION



1; P^1 = OBz, P^2 = OTBDPS; (1411)
2; P^1, P^2 = PhCH (benzylidene); (2239)
3; P^1 = OAc, P^2 = OTBDPS; (3202)
4; P^1 = OAc, P^2 = OBn; (3762)
5; P^1 = OH, P^2 = OTBDPS; (4433)

We first performed the synthesis of type I LacNAc tetrasaccharides by [2 + 2] glycosylation. Several Galβ1 → 3GlcNTCA thioglycoside disaccharides (**1**−**16**, see the inserted structure and Scheme 1) were prepared with protecting groups introduced at O4 and O6 positions in the GlcNTCA residue in a divergent manner (see Schemes S4−S7), including ester (OAc, OBz), ether (OBn, benzylidene), and silyl ether (OTBS and OTBDPS) groups. The purpose was to exploit their difference in steric and electronic properties to create a spectrum of thioglycoside disaccharides. For example, benzylidene was used to tortionally disarm[21] the disaccharide to generate the less reactive acceptor **15**. On the other hand, acetyl was chosen in combination with OBn to afford a moderately disarmed disaccharide donor (**4**) and acceptor (**13**). Likewise, two benzyl ethers were used to protect O4 and O6 of GlcNTCA, owing to the arming (electron-donating) behavior, to yield the reactive donor **8**. Furthermore, trichloroacetyl (TCA) was installed as the amine-protecting group to achieve β-stereoselectivity via neighboring group participation.[22]

Scheme 1. Structures of Type I LacNAc Disaccharide Donors and Acceptors Used for [2 + 2] Chemoselective Glycosylations



The reactivity of each disaccharide donor and acceptor was shown as an RRV (Scheme 1), initially established by Wong and co-workers.[23−26] Competition reactions were done between a thioglycoside with an unknown RRV and the reference thioglycoside with a known RRV in the presence of a limiting amount of promoter to determine the RRV of each disaccharide (please see Experimental Section for details). For example, compound **2a** (Figure S1) was used as a reference donor to measure the RRV of disaccharide **2**. Because tetrasaccharide products would be possibly elongated to hexasaccharides or longer glycans at a later stage, the protecting groups installed in the reducing end of tetrasaccharides appeared to be critical. To explore the possibility of

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deriving tetrasaccharide products into reactive donors or acceptors in one step, a diester combination was avoided, and rather orthogonal protecting groups were employed at O4 and O6 positions in GlcNTCA.

Four most reactive disaccharides (**6**–**9**) were chosen as donors, whereas seven disaccharide acceptors (**10**–**16**) were synthesized from their corresponding Nap-protected precursors (see Schemes S5 and S6). [2 + 2] Chemoselective glycosylations were then conducted in the presence of TMSOTf (0.2 equiv) and 3 Å molecular sieves and an equal concentration of donor and NIS in CH_2Cl_2 (Table 1). Since both the donor and acceptor are thioglycosides, it is important to selectively activate the donor STol without affecting the acceptor STol; that is, there has to be differential reactivity to obtain a satisfying yield.[27] Isolated yields were measured for the tetrasaccharide products and unreacted starting material/side product by purification with flash column chromatography on silica gel (see Experimental Section for related procedures). The structure of each tetrasaccharide was confirmed and characterized in a vigorous manner by high-resolution mass spectroscopy (HRMS) and various 1D and 2D NMR techniques. For example, a detailed assignment is shown in the Supporting Information (pages S34–S37) for the representative tetrasaccharide **27**.

Table 1. [2 + 2] Chemoselective Glycosylations to Synthesize Type I LacNAc Tetrasaccharides[a]

entry	donor (equiv), RRV	acceptor (1 equiv), RRV	$\ln(RRV_D)$[b]	temp (°C)	time (h)	product (% yield)[c]
1	**6** (1.3), 7389	**13**, 2888	8.41	−50	2.5	**17** (54)[d]
2	**7** (1.3), 7657	**13**, 2888	8.47	−50	2.5	**18** (58)
3	**7** (1.3), 7657	**14**, 1299	8.76	−50	2.5	**19** (63)
4	**7** (1.3), 7657	**15**, 1903	8.66	−50	2	**20** (60)
5	**7** (1.3), 7657	**16**, 2060	8.63	−50	2.5	**21** (67)
6	**8** (1.3), 8351	**10**, 9740	[e]	−50	2.5	**22** (19)[f]
7	**8** (1.3), 8351	**11**, 5441	7.98	−50	2.5	**23** (20)[g]
8	**8** (1.3), 8351	**12**, 5329	8.01	−50	2.5	**24** (25)[h]
9	**8** (1.3), 8351	**13**, 2888	8.61	−50	2.5	**25** (60)
10	**8** (1.3), 8351	**13**, 2888	8.61	−70	21	**25** (72)[i]
11	**8** (1.3), 8351	**13**, 2888	8.61	−60	2.5	**25** (68)
12	**8** (1.1), 8351	**13**, 2888	8.61	−60	2.5	**25** (63)
13	**8** (1.6), 8351	**13**, 2888	8.61	−60	2.5	**25** (69)[j]
14	**8** (1.3), 8351	**14**, 1299	8.86	−50	2.5	**26** (79)
15	**8** (1.3), 8351	**15**, 1903	8.77	−50	2	**27** (75)
16	**8** (1.3), 8351	**16**, 2060	8.75	−50	2.5	**28** (86)
17	**8** (1.1), 8351	**16**, 2060	8.75	−50	2.5	**28** (75)
18	**9** (1.1), 9404	**13**, 2888	8.78	−60	2.5	**29** (65)
19	**9** (1.1), 9404	**13**, 2888	8.78	−70	21	**29** (61)[i]
20	**9** (1.1), 9404	**16**, 2060	8.90	−60	4.5	**30** (52)[k]

[a]Glycosylation conditions: NIS (same as donor equiv), TMSOTf (0.2 equiv), 3 Å MS, and CH_2Cl_2 (50 mM). [b]$RRV_D = RRV_{Donor} - RRV_{Acceptor}$. [c]Isolated yield. [d]18% acceptor recovered. [e]$\ln(RRV_D)$ for this entry is not valid, as RRV_D is a negative number. [f]34%, donor recovered. [g]33%, donor recovered. [h]37% donor recovered. [i]Acceptor **13** remained after 2.5 h (entry 10)/2 h (entry 19); hence, the reactions were continued for longer time. [j]14% oxazoline recovered. [k]Donor spot disappeared with one-third acceptor remained unreacted (based on TLC).

A donor with OTBS at O6 in GlcNTCA (**6**, RRV = 7389) was found to be less reactive (entry 1, Table 1) than the corresponding O6-OBn-protected donor (**7**, RRV = 7657, entry 2). The bulkier silyl-protecting group (OTBDPS) at O6 in GlcNTCA makes donor **5** (RRV = 4433) even less reactive than donor **6**. Hence, the lowest reactivity of O6-OTBDPS plus an ester protection at O4 in GlcNTCA resulted in the less reactive acceptors **14** (RRV = 1299) and **16** (RRV = 2060), which appeared to be beneficial to [2 + 2] glycosylation (e.g., comparison of entries 2–5). For reactions with insufficient reactivity difference between the donor and acceptor, low yields were observed (entries 6–8), and about one-third of the donor was recovered (33–37%) because of aglycon transfer. The desired product and the recovered donor were also accompanied with several more polar compounds according to TLC analysis. With an increase in reactivity difference between the donor and acceptor, improved yields were observed. It was achieved by changing the reactivity of either donor or acceptor. For instance, the glycosylation of different acceptors **13**–**16** with donor **7** generated tetrasaccharides **18**–**21** (entries 2–5), respectively, while acceptors **13**–**16** reacted with donor **8** to afford products **25**–**28** (entries 9 and 14–16), respectively. Glycosylations of acceptors **14** and **16** produced the best yields, even though **16** was not the least reactive. Likewise, when the same acceptor was glycosylated with different donors (e.g., acceptor **13** reacting with different donors **6**–**8**; see entries 1, 2, and 9), the reactive donor (**8**) had the highest yield. Apparently, the presence of two OBn groups at O4 and O6 in GlcNTCA rendered **8** an excellent donor. Please also refer to entries 3 and 14, entries 4 and 15, and entries 5 and 16 for a similar comparison. Therefore, obtaining good yields has to make either donor more reactive or acceptor less reactive. High reaction yields were often in company with low/no recovery of donor and decreased decomposition of acceptor, which was easily shown by TLC analysis.

Although it is well known that the silyl protecting group increases the donor reactivity,[20,28] to the best of our knowledge, herein for the first time we found that silyl protection is decreasing the reactivity, compared to the benzyl ether protection, when the silyl group is present at O6 of GlcNTCA, for example, donor **3** (RRV = 3202) versus donor **4** (RRV = 3762), donors **5** (RRV = 4433) and **6** (RRV = 7389) versus donor **7** (RRV = 7657), acceptor **12** (RRV = 5329) versus acceptor **11** (RRV = 5441), and acceptor **14** (RRV = 1299) versus acceptor **13** (RRV = 2888). In contrast, an opposite trend was observed at O4 in GlcNTCA; TBS ether at O4 in GlcNTCA (e.g., compound **9**, RRV = 9404) appeared to increase the reactivity in comparison with **8** (RRV = 8351). However, no significant difference in yield was observed in the glycosylation of acceptor **13** with donor **9** (**29**, 65%, entry 18, Table 1) in comparison with the same acceptor glycosylation with donor **8** (**25**, 63%, entry 12, Table 1). A trace amount of

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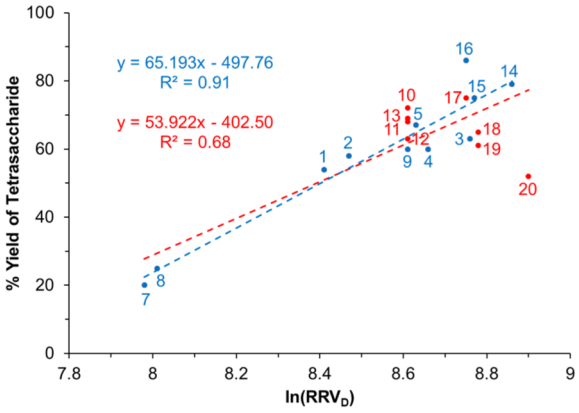
acceptor **13** remained unreacted during the reaction with donor **9**. In fact, the effort to glycosylate the less reactive acceptor **16** with donor **9** was inefficient to form product **30** in 52% yield and one-third acceptor was found unconsumed as can be seen by TLC (entry 20). Moreover, we applied a preactivation method to activate donor **9** before the addition of acceptor **13**. However, product **29** was obtained in a moderate yield (58%) even after several trials (see Scheme S8). These moderate yields from donor **9** were attributed to the oxazoline formation to a significant degree, suggesting that RRV serves as a reactivity index of glycoside donors but cannot be directly linked to reaction yield.

The RRV-based analysis also helped to identify other factors to improve reaction yields. For instance, we compared the reactions of **8** with acceptors **13** and **16**. With a relatively smaller RRV difference between donor **8** and acceptor **13**, we were able to increase the yields by either reducing the amount of donor/NIS or lowering the temperature (entries 9−13). Likewise, because there was a relatively larger RRV difference between donor **8** and acceptor **16**, increasing the amount of donor/NIS helped to improve the yield from 75 to 86% (entries 17 and 16, respectively).

To precisely delineate the required reactivity difference between glycosyl donor and acceptor, quantitative analysis becomes indispensable. To examine if the reactivity difference correlated with the yield of desired product, a graph was plotted between the yields (%) of tetrasaccharides formed in Table 1 and the corresponding ln(RRV difference) (Figure 1). The RRV difference (RRV_D) is defined as the difference in the RRVs between donor and acceptor disaccharides. As shown in Figure 1, there are red and blue lines generated by fitting different sets of data points with linear regression. The red line corresponded all entries in Table 1 (R^2 value: 0.68), except for entry 6, where $\ln(RRV_D)$ is not valid because of the negative value of RRV_D. It was noted that several entries in Table 1 were performed at a different temperature or donor equivalents (entries 10−13 and 17−20 that are shown as red numbers and data points in Figure 1). In contrast, the blue line is only corresponding to the entries that were performed under the same glycosylation conditions (−50 °C and the use of 1.3 equiv of donor), explaining a better linear correlation (R^2 value: 0.91). The following conclusions are made according to the data points of blue line (Figure 1). First, with an RRV_D of less than 3641, low yields (<25%) were observed because of aglycon transfer (entries 7 and 8, Table 1). Second, moderate to good yields (50−67%) were found when the RRV_D is in the range of 4447−6003 (entries 1, 2, and 5). Additionally, excellent yields (75−86%) of tetrasaccharides were obtained for the reactions with RRV_D > 6311 (entries 14−16).



$\ln(RRV_D)^a$	RRV_D	yield (%)^b
<8.20	<3641	<25
~8.40-8.70	4447-6003	~50-67
>8.75	>6311	>75

$^a RRV_D = RRV_{Donor} - RRV_{Acceptor}$.
^{b}Based on the blue data points.

Figure 1. Linear relationship was found between $\ln(RRV_D)$ and yields of tetrasaccharide products shown in Table 1. Blue line was generated with linear regression by fitting the blue data points that were performed under the same conditions (−50 °C and 1.3 equiv of donor). Red line was generated by fitting the red and blue data points (representing all the entries in Table 1, except for entry 6). Numbers next to data points designate the entry numbers in Table 1.

Because in this work all the acceptors were derived by removing the Nap ether from corresponding precursors, it would be interesting to use the precursors' RRVs as an estimate of the acceptors' RRVs. By this way, we could understand if Nap plays a role in affecting the RRVs. We thus plotted the graph between tetrasaccharide yields vs estimated $\ln(RRV_D)$ (Table S3 and Figure S2). The estimated RRV_D was obtained by the difference in the RRVs of donors A and B disaccharides (see Figure S2 for the definition). Interestingly, the threshold RRV_D (6634) to obtain 75−86% yields was similar to the aforementioned RRV_D (6311) derived from Figure 1. How Nap affects the RRVs is not clear because the Nap deprotection was found to increase or decrease the RRVs. The estimated RRV_D could be timesaving and applicable for cases where it is challenging to measure the RRV of every glycoside. The comparison of Figures 1 and S2 indicated that the Nap existence only marginally changed the threshold RRV difference.

Having prepared type I LacNAc tetrasaccharides in good yields (entries 13−16 in Table 1), we next proceeded with chain elongation to synthesize hexasaccharide by [2 + 4] and [4 + 2] chemoselective glycosylations. We thus selected tetrasaccharide **27** because it was readily converted in one step to either disarmed tetrasaccharide acceptor **31** by Nap deprotection or armed tetrasaccharide donor **23** by regioselective opening of the benzylidene (Scheme 2). [2 + 4] Chemoselective glycosylation was first performed between donor **8** (RRV = 8351, 1.3 equiv) and acceptor **31** (1 equiv) in the presence of NIS (1.3 equiv) and TMSOTf (0.2 equiv) at −50 °C (Scheme 2). The desired hexasaccharide **32** was obtained in 70% yield with concomitant formation of oxazoline **33** (19%). This reaction was analogous to the glycosylation of acceptor **15** (RRV = 1903, entry 15, Table 1) with **8** because both acceptors contained the identical disaccharide in the reducing end. Presumably, the RRV of **31** is smaller than that of **15** because the former one is less reactive owing to its longer chain, suggesting that the resulting RRV difference should be larger than that of the analogous [2 + 2] reaction, that is, the RRV_D of the [2 + 4] reaction should be >6448.

Although RRV is a good index to predict the reactivity in glycosylation reactions, the measurement is not trivial, especially for longer oligosaccharides. Finding another quick way is convenient and useful to determine the reactivity of glycosides. Wong and co-workers are the first to correlate the reactivity of glycosides with the H-1 chemical shift, providing

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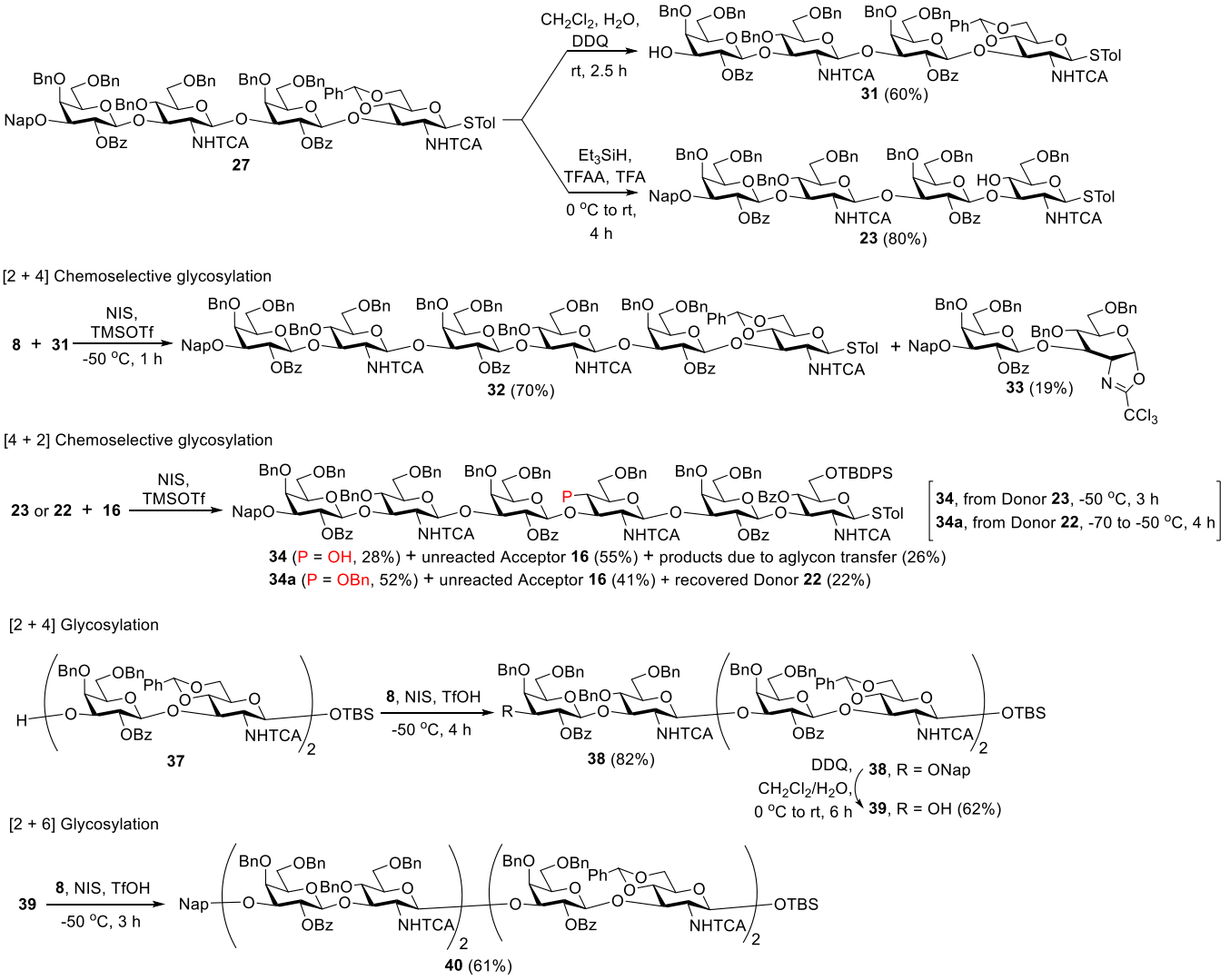
Scheme 2. Glycosylations to Synthesize Type I LacNAc Hexa- and Octasaccharides



that the glycosides contain the same protecting group at the C-2 position.[23,29] We thus plotted between the RRVs of glycosides **1**−**16** versus their H-1 chemical shifts (Table 2 and Figure 2). The resulting data points resulted in a roughly linear correlation (in correspondence to the red line in Figure 2) with an R^2 value of 0.67 because three disaccharides (**6**, **7**, and **14**) appeared to deviate more from the red line. Removal of these data points indeed led to a better linear correlation (blue line with an R^2 value of 0.92). As shown in Figure 2, disaccharides of higher reactivity (**8**−**10**) have their H-1 more upfield-shifted (4.92, 4.84, and 4.91 ppm, respectively). In contrast, less reactive disaccharides (**1**, **15**, and **16**) possess the H-1 in a relatively downfield-shifted region (5.32, 5.32, and 5.31 ppm, respectively). The RRV−chemical shift relationship helped us to explain the result of [2 + 4] and [4 + 2] glycosylation reactions. In the [2 + 4] glycosylation of tetrasaccharide acceptor **31** with donor **8** (RRV = 8351), the RRV of **31** was predicted to be 2591 because of its H-1 chemical shift ($\delta_{H\text{-}1}$ = 5.30 ppm), leading to a calculated RRV_D of 5760. On the basis of the linear correlation between $\ln(RRV_D)$ and reaction yield (blue line in Figure 1), an RRV_D of 5760 corresponded to 67% yield that is close to what we observed for this [2 + 4] reaction (70%).

Table 2. Listed RRVs of Disaccharides with the Corresponding Anomeric Proton Chemical Shifts

RRV[a] (compd)	δ (ppm)[b]
1299 (**14**)	5.17
1411 (**1**)	5.32
1903 (**15**)	5.32
2060 (**16**)	5.31
2239 (**2**)	5.36
2888 (**13**)	5.20
3202 (**3**)	5.23
3762 (**4**)	5.22
4433 (**5**)	5.23
5329 (**12**)	5.19
5441 (**11**)	5.21
7389 (**6**)	5.19
7657 (**7**)	5.22
8351 (**8**)	4.92
9404 (**9**)	4.84
9740 (**10**)	4.91

[a]Values shown in the ascending order. [b]Chemical shift of anomeric proton.

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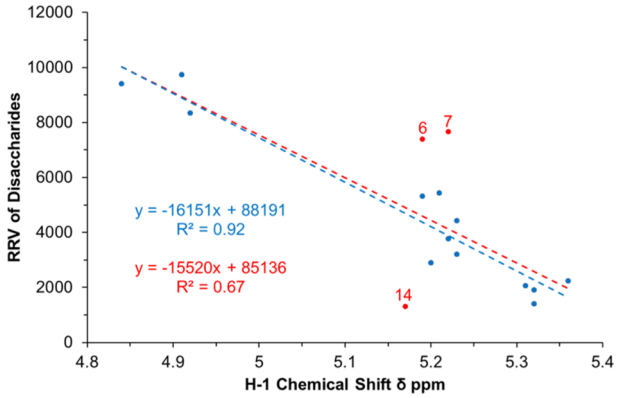

Figure 2. Linear relationship was observed between the RRVs of disaccharides vs anomeric proton chemical shifts. Red line was produced by fitting all the data points (shown in red or blue color) in Table 2. Blue line was produced by fitting the blue data points (after excluding red data points that correspond to compounds **6**, **7**, and **14**).

Meanwhile, we also examined [4 + 2] glycosylation of thioglycoside disaccharide acceptor **16** (RRV = 2060) (1.2 equiv) with tetrasaccharide donor **23** (1 equiv) in the presence of NIS (1 equiv) and TMSOTf (0.2 equiv) under −50 °C (Scheme 2). A low yield (28%) of hexasaccharide **34** was observed in addition to the recovered acceptor **16** (55%) and aglycon transfer (26%).[30] Although this reaction is comparable to the [2 + 2] glycosylation of **16** (RRV = 2060) with **7** (RRV = 7657, entry 5, Table 1), it is likely that the RRV of donor **23** became significantly smaller than that of **7**. The estimated RRV_D of this [4 + 2] glycosylation should be thus much smaller than that of entry 5; that is, the RRV_D of the [4 + 2] reaction is predicted to be <5597 (RRV_D for entry 5 from Table 1). Moreover, according to the RRV−chemical shift relationship, donor **23** ($\delta_{H\text{-}1}$ = 5.14 ppm) was predicted to have an RRV of 5175, leading to the estimated RRV_D of 3115 in the [4 + 2] glycosylation (5175 − 2060 = 3115). As a consequence, the comparison in Scheme 2 supported the idea that [2 + 4] is superior to [4 + 2] glycosylation. Our RRV-based analysis explained why it is better to elongate glycan chains from the reducing to the nonreducing end.

Notably, the predicted RRV of benzylated thioglycoside tetrasaccharide **22** (see the structure in Scheme 1) is 10343, predicted by the RRV−chemical shift relationship ($\delta_{H\text{-}1}$ of **22** = 4.82 ppm). The calculated RRV_D between the RRVs of tetrasaccharide **22** and disaccharide acceptor **16** turned out to be 8283, indicating the tendency for a possible improvement in glycosylation yield. We thus performed [4 + 2] chemoselective glycosylation of disaccharide acceptor **16** (1.2 equiv) with tetrasaccharide donor **22** (1.0 equiv) in the presence of NIS (1.0 equiv) and TMSOTf (0.2 equiv) (Scheme 2). Our initial trial to conduct this glycosylation at −50 °C did not yield any major product. Instead, the donor was decomposed in company with recovered acceptor **16** after column chromatography. Because tetrasaccharide **22** is a reactive donor, we thus lowered the temperature to −70 °C for addition of the promoter, gradually increased the temperature to −60 °C, and finally stirred the reaction for another 2 h at −50 °C to allow the glycosylation. Desired hexasaccharide **34a** was obtained in 52% yield, in conjunction with recovery of acceptor **16** (0.49 equiv recovered, with respect to the amount of acceptor **16** initially added to the reaction) and donor **22** (22%, presumably because of the aglycon transfer). The usage of donor **22** indeed gave a better yield, as compared to the [4 + 2] glycosylation of acceptor **16** with tetrasaccharide donor **23** (28% yield). Therefore, the RRV-based analysis was shown applicable to improve the [4 + 2] glycosylation.

Furthermore, the H-1 chemical shift is a direct and convenient way to index the glycoside reactivity. In the aforementioned [2 + 4] glycosylation, the H-1 chemical shifts of donor **8** and acceptor **31** are 4.92 and 5.30 ppm, respectively. In the [4 + 2] glycosylation, the H-1 chemical shifts of donor **23** and acceptor **16** are 5.14 and 5.31 ppm, respectively. With the established RRV−chemical shift relationship, judging the difference of H-1 chemical shifts is able to predict if glycosylations of interest likely afford good yields; for example, the [2 + 4] glycosylation has a higher feasibility than the [4 + 2] glycosylation. Therefore, the importance of using anomeric proton chemical shifts can be best demonstrated when measuring RRV becomes labor-intensive.

Alternatively, the synthesized di- and tetra-thioglycoside donors were available to react with acceptors that were protected with the OTBS group at the reducing-end anomeric center. The aforementioned tetrasaccharide **25** was used as the donor for the [4 + 2] glycosylation of disaccharide acceptor **35** (see Scheme S1). Hexasaccharide **36** was produced in 70% yield (Scheme S1). Additionally, [2 + 4] glycosylation was pursued by glycosylating tetrasaccharide acceptor **37** with donor **8** (see Scheme S9 for the preparation of **37**) in the presence of NIS and TfOH, leading to the formation of hexasaccharide **38** in 82% yield (Scheme 2). The resulting product was then subjected to the Nap removal (**39**, 62% yield), followed by the further [2 + 6] glycosylation with disaccharide donor **8**. The desired octasaccharide (**40**) was produced in 61% yield (Scheme 2).

CONCLUSIONS

In conclusion, with systematic investigation on the reactivity of glycosides and the direction of oligosaccharide chain elongation, we successfully accomplished the synthesis of arduous type I LacNAc hexa- and octasaccharides in good yields. Cautious and judicious protecting group design allowed us to create type I LacNAc disaccharides with varying reactivities, which were used to synthesize orthogonally protected type I tetrasaccharides. Through the graph of tetrasaccharide yields vs RRV_D, we were able to predict the threshold RRV_D required for fruitful chemoselective glycosylation. The correlation helped to access the type I LacNAc hexasaccharide **32** by [2 + 4] glycosylation and also explained the reason why reducing to nonreducing end synthesis is better than the other way. We additionally demonstrated that the H-1 chemical shifts of glycosides could be useful to predict not only their RRVs but also the feasibility of chemoselective glycosylations.

EXPERIMENTAL SECTION

General Experimental Procedure. All reactions were performed in an oven-dried glassware under the nitrogen atmosphere unless otherwise mentioned. The reaction mixtures were purified by using silica gel flash column chromatography. Anhydrous solvents and moisture-sensitive materials were transferred by using an oven-/vacuum-dried syringe or cannula through a rubber septum. Analytical TLC was performed on the precoated glass plates of TLC Silica gel 60 F_{254} from Merck and was detected by UV visualization (254 nm) and/

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or by staining with reagents that contained ceric molybdate (for general use), *para*-anisaldehyde (for carbohydrates), or ninhydrin (for amino-group-containing samples). Column chromatography was performed on silica gel (Geduran Silicagel 60, 0.040−0.063 mm, from Geduran). Purification of the bulk building blocks was performed either on a Teledyne Isco CombiFlash Rf that was equipped with a UV detector (for compounds with UV-active chromophores) or on a Grace Davison Reveleris flash system that was equipped with an evaporative light scattering detector (for compounds without UV-active chromophores). ^{1}H NMR spectra were recorded on Bruker AV-400 (400 MHz) or AVII-500 (500 MHz) spectrometers by using tetramethylsilane (δ_H = 0.00 ppm) and $CDCl_3$ (δ_H = 7.26 ppm) as internal standards. ^{13}C NMR spectra were recorded on Bruker AV-400 (100 MHz) or AVII-500 (125 MHz) spectrometers by using $CDCl_3$ (δ_C = 77.23 ppm, central line of a triplet) as an internal standard. Structural assignments were made with additional information from 2D-COSY, 2D-HMQC, and 2D-HMBC experiments using gradient pulses for coherence pathway selection, which were acquired on Bruker AV-400 or AVII-500 spectrometers. HRMS was performed on Bruker Bio-TOF III (ESI-TOF) or Bruker Ultraflex (MALDI-TOF/TOF) spectrometers and is reported as mass/charge (m/z) ratios with percentage relative abundance. Optical rotations were measured at the sodium D-line (589 nm) at 25 °C or 20.0 °C on a PerkinElmer model 341 polarimeter. Specific rotations were reported as $[\alpha]_D^{25}$ after dividing the observed values by the sample concentration (C, in g mL^{-1}) and the path length (l, in dm). The solvents for extraction and chromatography were of ACS grade. CH_2Cl_2 and CH_3CN were predried by using molecular sieves and then percolated through an active Al_2O_3 column. Anhydrous DMF and MeOH were purchased from Aldrich Chemical Co. and J-T Baker, respectively, in sealed packages. Diphenylsulfoxide (Ph_2SO) and 2,4,6-tri-*tert*-butylpyrimidine were purchased from Aldrich Chemical Co. All the chemicals were used without further purification unless otherwise specified. Celite 545 and 3 Å molecular sieves (powder < 50 μm) were purchased from Acros Co. and Alfa Aesar Co., respectively. 1,2,3,4,6-Penta-*O*-acetyl-β-D-galactopyranoside and D-glucosamine hydrochloride were purchased from Carbosynth Ltd. in a bulk package.

General Procedure to Determining RRVs of Thioglycoside Donors. In a 10 mL reaction tube, a solution of two thioglycoside donors (0.055 mmol of each, $\mathbf{D}_{ref}$ is the reference donor and $\mathbf{D}_x$ is any other donor molecule), absolute MeOH (0.275 mmol), and molecular sieves [AW-300; 2xwt ($\mathbf{D}_{ref}$ + $\mathbf{D}_x$)] in CH_2Cl_2 (1.1 mL) was stirred at rt for 10 min. An aliquot of this mixture (0.1 mL) was taken, diluted to 10.0 mL with CH_2Cl_2, and separately injected (20 μL for each injection) into the HPLC in order to determine the time = 0 absorbance $(A_x)_0$ and $(A_{ref})_0$ at 254 nm at the initial concentration of the donor molecules. The HPLC conditions must allow baseline separation of $\mathbf{D}_{ref}$ and $\mathbf{D}_x$. The NIS (0.055 mmol) and TfOH (0.005 mmol) were added to the reaction, and the reaction was kept at rt for 2 h. The mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered, washed with saturated $NaHCO_3$ aqueous and $Na_2S_2O_3$ aqueous solution, dried over $MgSO_4$, and concentrated to dryness by evaporation. The residue was redissolved in CH_2Cl_2 (1.0 mL) and diluted to 100.0 mL with CH_2Cl_2. The concentrations of the remaining unreacted donors ($[\mathbf{D}_x]$ and $[\mathbf{D}_{ref}]$) were measured by HPLC with the same conditions (20 μL for each injection) as determined for the mixture before the addition of reagents. The ratio of RRVs for $\mathbf{D}_x$ and $\mathbf{D}_{ref}$, k_x/k_{ref}, was calculated by applying the HPLC absorbance values to the formula $k_x/k_{ref} = [\ln(A_x)_t - \ln(A_x)_0]/[\ln(A_{ref})_t - \ln(A_{ref})_0]$.

General Procedure for [2 + 2] Glycosylations in Table 1. A solution of disaccharide donor (see Table 1 for the equiv) and acceptor (1 equiv) in anhydrous CH_2Cl_2 (50 mM w.r.t acceptor) was stirred with 3 Å molecular sieves (D + A, wt/wt) at rt for 30 min. After cooling to low temperature, the promoter (NIS of the same equiv as donor; and TMSOTf, 0.2 equiv) was added. After stirring for a period of time (see Table 1), the reaction was quenched by dropwise addition of Et_3N to neutralize the pH and filtered to remove insoluble. The filtrate was washed with saturated $Na_2S_2O_3$ solution, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield viscous yellow crude. The crude was subjected to column chromatography on silica gel to yield a desired tetrasaccharide product (w.r.t: with respect to).

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (1). For reaction details, please see Scheme S6. 4-DMAP (73 mg, 0.60 mmol), Et_3N (420 μL, 3.0 mmol), and BzCl (251 μL, 2.16 mmol) were sequentially added to a solution of compound **5** (1.50 g, 1.20 mmol) in anhydrous CH_2Cl_2 (12 mL). After stirring at rt for 1.5 h, the reaction was quenched by addition of MeOH (2 mL) and concentrated by evaporation to yield a pale-yellow thick crude. The crude was redissolved in CH_2Cl_2 (20 mL) and washed with saturated $NaHCO_3$ solution (20 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a thick crude that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/4, v/v) to yield the desired pure product **1** (1.62 g, 99%) as a white amorphous solid. R_f 0.26 (EtOAc/hexanes = 1/4, v/v); $[\alpha]_D^{20}$ −2.0 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.76−7.69 (m, 3H, Ar-H), 7.63 (d, *J* = 6.6 Hz, 2H, Ar-H), 7.58 (d, *J* = 6.9 Hz, 2H, Ar-H), 7.54 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.52−7.46 (m, 3H, Ar-H), 7.44−7.37 (m, 3H, Ar-H), 7.37−7.31 (m, 4H, Ar-H), 7.31−7.25 (m, 8H, Ar-H), 7.24−7.20 (m, 6H, Ar-H), 7.19−7.11 (m, 5H, Ar-H), 6.95 (d, *J* = 6.8 Hz, 1H, N−H), 6.92 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.48 (dd, *J* = 9.9, 7.9 Hz, 1H, H-2′), 5.32 (d, *J* = 10.2 Hz, 1H, H-1), 5.12 (t, *J* = 8.8 Hz, 1H, H-4), 4.89 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.74−4.63 (m, 2H, H-3, CH_2 group of Nap), 4.57 (d, *J* = 7.8 Hz, H-1′), 4.45 (m, 2H, CH_2Ph, CH_2 group of Nap), 4.25 (dd, *J* = 30.8, 11.7 Hz, 2H, 2× CH_2Ph), 3.87 (d, *J* = 2.1 Hz, 1H, H-4′), 3.79−3.68 (m, 3H, H-5, H-6a, H-6b), 3.48 (dd, *J* = 10.1, 2.4 Hz, 1H, H-3′), 3.43−3.36 (m, 1H, H-5′), 3.29−3.18 (m, 1H, H-2), 3.11−3.07 (m, 1H, H-6a′), 2.95 (t, *J* = 8.3 Hz, 1H, H-6b′), 2.25 (s, 3H, $PhCH_3$), 0.99 (s, 9H, TBDPS-*t*-Bu); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.2 (C), 165.02 (C), 161.6 (C), 138.8 (C), 138.6 (C), 137.9 (C), 135.7 (CH), 134.9 (C), 133.7 (CH), 133.3 (C), 133.19 (C), 133.16 (C), 133.1 (C), 133.0 (CH), 132.7 (CH), 130.2 (C), 130.0 (CH), 129.7 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.75 (CH), 127.72 (CH), 127.5 (CH), 126.8 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 100.1 (CH), 92.6 (C), 84.0 (CH), 79.7 (CH), 79.6 (CH), 76.4 (CH), 74.5 (CH_2), 73.5 (CH_2), 73.4 (CH), 72.5 (CH), 71.9 (CH), 71.8 (CH_2), 69.2 (CH), 67.6 (CH_2), 63.4 (CH_2), 58.2 (CH), 26.8 (CH_3), 21.3 (CH_3), 19.3 (C); HRMS (ESI-TOF) m/z: calcd for $C_{76}H_{74}Cl_3NO_{12}SSiNa$ $[M + Na]^+$, 1382.3635; found, 1382.3701.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (2). For reaction details, please see Scheme S4. A solution of **45** (3.28 g, 4.61 mmol) and **49**[9,31,32] (2.0 g, 3.85 mmol) in anhydrous CH_2Cl_2 (64 mL) was stirred with 3 Å pulverized molecular sieves (11.0 g) at rt for 30 min under the N_2 atmosphere. After cooling to −60 °C, NIS (1.04 g, 4.61 mmol) was added to the reaction mixture, followed by the addition of TMSOTf (140.0 μL, 0.77 mmol). After 4 h, the reaction was quenched by dropwise addition of Et_3N to neutralize the reaction mixture and filtered through a pad of Celite. The filtrate was washed with saturated $Na_2S_2O_3$ solution (60 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous yellow residue. The residue was purified by column chromatography on silica gel with EtOAc/hexanes (1/6 to 1/4, v/v) to yield the pure disaccharide **2** (3.39 g, 80% yield) as a white amorphous foam. R_f 0.44 (EtOAc/hexanes = 1/3, v/v); $[\alpha]_D^{25}$ +5.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.15 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.75 Hz, 1H, Ar-H), 7.55−7.47 (m, 4H, Ar-H), 7.45−7.37 (m, 5H, Ar-H), 7.36−7.27 (m, 12H, Ar-H), 7.26−7.21 (m, 4H, Ar-H), 7.14 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.06 (d, *J* = 8 Hz, 2H, Ar-H), 6.95 (d, *J* = 6.85 Hz, 1H, N−H), 5.57 (dd, *J* = 10.0, 8.1 Hz, 1H, H-2′), 5.43 (s, 1H, PhCH benzylidene), 5.36 (d, *J* = 10.4 Hz, 1H, H-1), 4.96 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.73 (d, *J* = 8.1 Hz, 1H, H-

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1′), 4.70 (d, J = 12.3 Hz, 1H, CH_2 group of Nap), 4.61 (d, J = 11.7 Hz, 1H, CH_2Ph), 4.55 (t, J = 9.1 Hz, 1H, H-3), 4.49 (d, J = 12.3 Hz, 1H, CH_2 group of Nap), 4.31 (m, 3H, H-6a, CH_2Ph), 3.94 (d, J = 2.3 Hz, 1H, H-4′), 3.67 (m, 2H, H-4, H-6b), 3.63−3.56 (m, 1H, H-6a′), 3.54 (dd, J = 10.0, 2.8 Hz, 1H, H-3′), 3.51−3.44 (m, 2H, H-5, H-6b′), 3.38 (t, J = 6.5 Hz, 1H, H-5′), 3.21−3.14 (td, J = 9.9, 7.1 Hz, 1H, H-2), 2.33 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.5 (C), 161.7 (C), 139.2 (C), 138.6 (C), 137.9 (C), 137.5 (C), 135.0 (C), 134.2 (CH), 133.2 (CH), 133.1 (C), 130.2 (CH), 130.1 (CH), 129.1 (CH), 128.7 (CH), 128.5 (CH), 128.44 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.2 (C), 126.7 (CH), 126.34 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 101.3 (CH), 100.0 (CH), 92.2 (C), 84.1 (CH), 80.2 (CH), 80.0 (CH), 76.3 (CH), 74.7 (CH_2), 73.8 (CH_2), 73.5 (CH), 72.4 (CH), 72.2 (CH), 72.0 (CH_2), 70.8 (CH), 68.8 (CH_2), 57.7 (CH), 29.9 (CH_2), 21.4 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{60}H_{56}Cl_3NO_{11}SNa$ $[M + Na]^+$, 1126.2532; found, 1126.2556.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (3). For reaction details, please see Scheme S6. A solution of compound **5** (2.60 g, 2.07 mmol) in dry CH_2Cl_2 (21 mL) was stirred with 4-DMAP (25 mg, 0.20 mmol) in an ice bath for 5 min. Then, Et_3N (0.72 mL, 5.17 mmol) and Ac_2O (488 μL, 5.17 mmol) were sequentially added, and the reaction mixture was stirred for 1.5 h. After completion of the reaction, as checked by TLC, MeOH (4 mL) was added to the mixture and concentrated by evaporation to yield a viscous white crude. The crude was redissolved in CH_2Cl_2 (20 mL) and neutralized by the addition of saturated $NaHCO_3$ solution (20 mL) under the ice bath. The organic layer was collected, washed with saturated $NaHCO_3$ solution (20 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a thick white crude. The crude was subjected to column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to obtain pure **3** (2.61 g, 97%) as a white amorphous solid. R_f 0.38 (EtOAc/hexanes = 1/4, v/v, run two times); $[\alpha]_D^{20}$ +6.0 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 7.3 Hz, 2H, Ar-H), 7.72 (d, J = 7.3 Hz, 1H, Ar-H), 7.65 (d, J = 6.9 Hz, 4H, Ar-H), 7.60−7.50 (m, 4H, Ar-H), 7.45−7.40 (m, 2H, Ar-H), 7.39−7.36 (m, 2H, Ar-H), 7.36−7.34 (m, 2H, Ar-H), 7.34−7.31 (m, 7H, Ar-H), 7.31−7.27 (m, 7H, Ar-H), 7.26−7.23 (m, 1H, Ar-H), 7.22−7.16 (m, 2H, Ar-H), 6.98 (d, J = 6.7 Hz, 1H, N−H), 6.91 (d, J = 7.8 Hz, 2H, Ar-H), 5.51 (dd, J = 9.9, 7.9 Hz, 1H, H-2′), 5.23 (d, J = 10.1 Hz, 1H, H-1), 5.00 (d, J = 11.6 Hz, 1H, CH_2Ph), 4.84 (t, J = 9.5 Hz, 1H, H-4), 4.72 (d, J = 12.2 Hz, 1H, CH_2 group of Nap), 4.63−4.40 (m, 6H, H-3, H-1′, 3× CH_2Ph, CH_2 group of Nap), 3.95 (d, J = 1.8 Hz, 1H, H-4′), 3.73−3.61 (m, 2H, H-6a, H-6b), 3.60−3.50 (m, 5H, H-5, H-3′, H-5′, H-6a′, H-6b′), 3.30−3.21 (m, 1H, H-2), 2.24 (s, 3H, $PhCH_3$), 1.56 (s, 3H, $COCH_3$), 1.02 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 169.5 (C), 165.1 (C), 161.4 (C), 138.6 (C), 138.4 (C), 137.8 (C), 135.8 (CH), 134.9 (C), 133.44 (CH), 133.38 (C), 133.3 (C), 133.2 (CH), 133.1 (C), 130.1 (CH), 130.0 (C), 129.9 (CH), 129.78 (CH), 129.76 (CH), 128.68 (CH), 128.4 (CH), 128.13 (CH), 128.11 (CH), 128.0 (CH), 127.8 (CH), 127.77 (CH), 127.7 (CH), 126.8 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 99.4 (CH), 92.7 (C), 84.5 (CH), 79.8 (CH), 79.6 (CH), 76.0 (CH), 74.6 (CH_2), 74.0 (CH), 73.8 (CH_2), 72.8 (CH), 72.1 (CH_2), 71.9 (CH), 68.4 (CH_2), 68.1 (CH), 63.4 (CH_2), 57.7 (CH), 26.9 (CH_3), 21.3 (CH_3), 20.5 (CH_3), 19.3 (C); HRMS (ESI-TOF) m/z: calcd for $C_{71}H_{72}Cl_3NO_{12}SSiNa$ $[M + Na]^+$, 1320.3478; found, 1320.3540.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (4). For reaction details, please see Scheme S5. A solution of compound **7** (0.97 g, 0.88 mmol) in dry CH_2Cl_2 (8.13 mL) was stirred with 4-DMAP (10 mg, 0.08 mmol) in an ice bath for 5 min. Then, Et_3N (227 μL, 1.75 mmol) and Ac_2O (153 μL, 1.75 mmol) were sequentially added, and the reaction mixture was stirred for 2 h. After reaction completion, as checked by TLC, MeOH (2 mL) was added, and the mixture was concentrated by evaporation to yield the viscous crude. The crude was redissolved in CH_2Cl_2 (15 mL) and neutralized by addition of saturated $NaHCO_3$ solution (15 mL) under the ice bath. Organic layer was separated, washed with saturated $NaHCO_3$ solution (15 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Pure product **4** was obtained after purification by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) in 94% yield (0.95 g) as a white amorphous foam. R_f 0.30 (EtOAc/hexanes = 1/3, v/v, run two times); $[\alpha]_D^{20}$ −2.913 (c 1.03, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, J = 7.45 Hz, 2H, Ar-H), 7.74 (d, J = 7.5 Hz, 1H, Ar-H), 7.61−7.52 (m, 4H, Ar-H), 7.48−7.4 (m, 2H, Ar-H), 7.4−7.32 (m, 5H, Ar-H), 7.31−7.30 (m, 3H, Ar-H), 7.30−7.29 (m, 5H, Ar-H), 7.29−7.23 (m, 6H, Ar-H), 7.19 (d, J = 8.55 Hz, 1H, Ar-H), 7.0 (d, J = 6.9 Hz, 1H, N−H), 6.93 (d, J = 7.85 Hz, 2H, Ar-H), 5.53 (dd, J = 9.7, 8.1 Hz, 1H, H-2′), 5.22 (d, J = 10.1 Hz, 1H, H-1), 4.99 (d, J = 11.6 Hz, 1H, CH_2Ph), 4.88 (t, J = 9.4 Hz, 1H, H-4), 4.73 (d, J = 12.25 Hz, 1H, CH_2Ph), 4.62 (d, J = 7.8 Hz, 1H, H-1′), 4.58−4.45 (m, 6H, CH_2Ph, H-3), 4.42 (d, J = 11.8 Hz, 1H, CH_2Ph), 3.95 (d, J = 1.8 Hz, 1H, H-4′), 3.64−3.46 (m, 7H, H-5, H-5′, H-6a, H-6b, H-6a′, H-6b′, H-3′), 3.27 (td, J = 9.8, 7.3 Hz, 1H, H-2), 2.25 (s, 3H, $PhCH_3$), 1.62 (s, 3H, $COCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 169.8 (C), 165.2 (C), 161.5 (C), 138.6 (C), 138.5 (C), 138.2 (C), 137.8 (C), 135.0 (C), 133.5 (CH), 133.2 (CH), 133.1 (C), 130.2 (CH), 130.0 (C), 129.9 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.3 (C), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 99.3 (CH), 92.6 (C), 84.4 (CH), 79.8 (CH), 78.0 (CH), 75.8 (CH), 74.6 (CH_2), 73.80 (CH), 73.78 (CH_2), 73.6 (CH_2), 72.8 (CH), 72.2 (CH_2), 71.9 (CH), 69.7 (CH_2), 68.6 (CH), 68.5 (CH_2), 57.6 (CH), 21.3 (CH_3), 20.6 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{62}H_{60}Cl_3NO_{12}SNa$ $[M + Na]^+$, 1172.2783; found, 1172.2801.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (5). For reaction details, please see Scheme S6. To a solution of compound **52** (1.0 g, 0.98 mmol) in DMF (10 mL), imidazole (200 mg, 2.94 mmol) and TBDPSCl (0.64 mL, 2.46 mmol) were added at rt with continuous stirring. After 1 h, the reaction was quenched by addition of MeOH (4 mL) and concentrated by evaporation to yield a viscous white crude. The crude was redissolved in EtOAc (15 mL) and washed with dd. H_2O (15 mL, two times) and saturated $NaHCO_3$ solution (15 mL, two times). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to collect the crude product. The crude product was subjected to purification by column chromatography on silica gel with EtOAc/hexanes (1/6, v/v, with 1% Et_3N) to yield pure **5** in 92% yield (1.13 g) as a white amorphous solid. R_f 0.51 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ +5.21 (c 0.96, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 7.4 Hz, 2H, Ar-H), 7.74 (d, J = 6.3 Hz, 5H, Ar-H), 7.60−7.51 (m, 4H, Ar-H), 7.48−7.42 (m, 2H, Ar-H), 7.39−7.32 (m, 10H, Ar-H), 7.31−7.24 (m, 10H, Ar-H), 7.19 (d, J = 8.1 Hz, 1H, Ar-H), 6.93 (d, J = 7.6 Hz, 2H, Ar-H), 6.70 (d, J = 6.5 Hz, 1H, N−H), 5.63 (dd, J = 9.8, 7.8 Hz, 1H, H-2′), 5.23 (d, J = 10.3 Hz, 1H, H-1), 4.95 (d, J = 11.6 Hz, 1H, CH_2Ph), 4.74 (d, J = 12.0 Hz, 1H, CH_2 group of Nap), 4.63−4.51 (m, 3H, H-1′, CH_2 group of Nap, CH_2Ph), 4.45 (d, J = 11.7 Hz, 1H, CH_2Ph), 4.41−4.29 (m, 2H, H-3, CH_2Ph), 4.05−3.93 (m, 3H, H-4′, H-6a, O−H), 3.87 (dd, J = 10.9, 4.9 Hz, 1H, H-6b), 3.69−3.41 (m, 6H, H-4, H-5, H-3′, H-5′, H-6a′, H-6b′), 3.11−3.02 (m, 1H, H-2), 2.26 (s, 3H, $PhCH_3$), 1.05 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 161.7 (C), 138.5 (C), 138.2 (C), 137.6 (C), 135.9 (CH), 134.7 (C), 133.8 (C), 133.5 (CH), 133.4 (CH), 133.2 (C), 133.17 (C), 130.2 (CH), 130.0 (CH), 129.9 (C), 129.7 (CH), 128.7 (CH), 128.6 (CH), 128.53 (CH), 128.50 (CH), 128.3 (C), 128.2 (CH), 128.1 (CH), 128.05 (CH), 128.02 (CH), 127.8 (CH), 127.0 (CH), 126.4 (CH), 126.3 (CH), 126.0 (CH), 101.2 (CH), 92.2 (C), 83.5 (CH), 81.9 (CH), 80.9 (CH), 80.0 (CH), 74.8 (CH_2), 74.2 (CH), 73.8 (CH_2), 72.5 (CH_2), 72.4 (CH), 72.0 (CH), 69.1 (CH), 68.5 (CH_2), 63.6 (CH_2), 57.3 (CH), 27.0 (CH_3), 21.3 (CH_3), 19.5 (C); HRMS (ESI-TOF) m/z:

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calcd for $C_{69}H_{70}Cl_3NO_{11}SSiNa$ $[M + Na]^+$, 1278.3365; found, 1278.3372.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (6). For reaction details, please see Scheme S5. Imidazole (155 mg, 2.27 mmol) and TBMSCl (191.4 mg, 1.27 mmol) were added to a solution of compound **52** (0.92 g, 0.91 mmol) in DMF (9 mL) at rt and stirred for 2.5 h. After complete consumption of the starting material, the reaction was quenched by adding MeOH (2 mL). The reaction mixture was concentrated by evaporation to yield the viscous white crude. The crude product was extracted with EtOAc (15 mL) and saturated $NaHCO_3$ solution (15 mL, two times). The EtOAc layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a thick crude. The crude was subjected to column chromatography on silica gel with EtOAc/hexanes (1/3, v/v, with 1% Et_3N) to yield the pure product **6** as a white amorphous solid (0.98 g, 96%). R_f 0.62 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ +4.95 (*c* 1.01, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.75 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.63−7.51 (m, 4H, Ar-H), 7.44 (td, *J* = 10.3, 5.0 Hz, 2H, Ar-H), 7.39−7.27 (m, 14H, Ar-H), 7.19 (dd, *J* = 8.2, 1.6 Hz, 1H, Ar-H), 7.00 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.68 (d, *J* = 6.7 Hz, 1H, N−H), 5.62 (dd, *J* = 9.8, 8.0 Hz, 1H, H-2′), 5.19 (d, *J* = 10.3 Hz, 1H, H-1), 4.96 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.74 (d, *J* = 12.0 Hz, 1H, CH_2 group of Nap), 4.64−4.52 (m, 3H, H-1′, CH_2 group of Nap, CH_2Ph), 4.5 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.4 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.31 (t, *J* = 9.0 Hz, 1H, H-3), 4.05−3.89 (m, 3H, H-4′, H-6a, O−H), 3.77 (dd, *J* = 11.2, 5.2 Hz, 1H, H-6b), 3.71−3.58 (m, 3H, H-3′, H-5′, H-6a′), 3.57−3.43 (m, 2H, H-4, H-6b′), 3.41−3.30 (m, 1H, H-5), 3.03 (td, *J* = 10.1, 6.8 Hz, 1H, H-2), 2.30 (s, 3H, $PhCH_3$), 0.90 (s, 9H, TBS-*t*-Bu), 0.071 (s, 3H, TBS-CH_3), 0.06 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 161.7 (C), 138.5 (C), 138.2 (C), 137.7 (C), 134.8 (C), 133.4 (CH), 133.24 (C), 133.20 (C), 130.3 (CH), 130.0 (CH), 129.9 (C), 128.7 (CH), 128.6 (CH), 128.55 (CH), 128.52 (CH), 128.4 (C), 128.2 (CH), 128.17 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 126.4 (CH), 126.3 (CH), 126.0 (CH), 101.2 (CH), 92.2 (C), 83.6 (CH), 81.9 (CH), 81.0 (CH), 80.0 (CH), 74.8 (CH_2), 74.2 (CH), 73.9 (CH_2), 72.5 (CH_2), 72.4 (CH), 72.0 (CH), 69.2 (CH), 68.7 (CH_2), 63.0 (CH_2), 57.3 (CH), 26.2 (CH_3), 21.4 (CH_3), 18.6 (C), −5.0 (2× CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{59}H_{67}Cl_3NO_{11}SSi$ $[M + H]^+$, 1132.3253; found, 1132.3252.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (7). For reaction details, please see Scheme S5. A solution of compound **2** (0.50 g, 0.45 mmol) in dry CH_2Cl_2 (4.52 mL) was stirred in an ice bath, followed by the addition of Et_3SiH (445 μL, 2.78 mmol) and TFAA (64 μL, 0.45 mmol). After stirring for 5 min, TFA (168 μL, 2.26 mmol) was added to the reaction mixture. After 3 h, the reaction was neutralized by dropwise addition of Et_3N under the ice bath. The neutralized reaction mixture was concentrated by evaporation to afford the solid residue. The residue was then redissolved in CH_2Cl_2 (10 mL) and washed with saturated $NaHCO_3$ solution (10 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation. Pure product **7** was isolated as a white solid after purification of crude by column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) in 85% yield (0.43 g). R_f 0.34 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ +10.99 (*c* 0.91, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.72 Hz, 2H, Ar-H), 7.75 (d, *J* = 7.24 Hz, 1H, Ar-H), 7.62−7.51 (m, 4H, Ar-H), 7.49−7.40 (m, 2H, Ar-H), 7.39−7.34 (m, 2H, Ar-H), 7.34−7.25 (m, 17H, Ar-H), 7.19 (dd, *J* = 8.46, 1.34 Hz, 1H, Ar-H), 6.96 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.72 (d, *J* = 6.9 Hz, 1H, N−H), 5.62 (dd, *J* = 10, 8.0 Hz, 1H, H-2′), 5.22 (d, *J* = 10.4 Hz, 1H, H-1), 4.95 (d, *J* = 11.6 Hz, 1H, CH_2), 4.74 (d, *J* = 12.1 Hz, 1H, CH_2), 4.66−4.52 (m, 5H, H-1′, CH_2), 4.46 (d, *J* = 11.8 Hz, 1H, CH_2), 4.40 (d, *J* = 11.8 Hz, 1H, CH_2), 4.34−4.26 (m, 1H, H-3), 4.12 (s, 1H, O−H), 3.94 (d, *J* = 2.5 Hz, 1H, H-4′), 3.82 (d, *J* = 11.0 Hz, 1H, H-6a), 3.70−3.60 (m, 4H, H-3′, H-6b, H-5′, H-6a′), 3.55−3.50 (m, 2H, H-4, H-5), 3.48 (dd, *J* = 4.3, 7.66 Hz, 1H, H-6b′), 3.09 (td, *J* = 10.0, 7.0 Hz, 1H, H-2), 2.28 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.6 (C), 161.6 (C), 138.7 (C), 138.6 (C), 138.1 (C), 137.6 (C), 134.7 (C), 133.5 (CH), 133.4 (CH), 133.2 (C), 133.1 (C), 130.2 (CH), 129.9 (CH), 129.8 (C), 128.6 (CH), 128.59 (CH), 128.50 (CH), 128.47 (CH), 128.41 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 127.0 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 101.1 (CH), 92.1 (C), 83.6 (CH), 81.9 (CH), 80.0 (CH), 79.8 (CH), 74.7 (CH_2), 74.1 (CH), 73.8 (CH_2), 73.5 (CH_2), 72.5 (CH_2), 72.4 (CH), 72.0 (CH), 69.9 (CH_2), 69.6 (CH), 68.7 (CH_2), 57.2 (CH), 21.3 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{60}H_{58}Cl_3NO_{11}SNa$ $[M + Na]^+$, 1130.2663; found, 1130.2670.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (8). For reaction details, please see Scheme S5. Tetrabutyl ammonium iodide (545 mg, 1.47 mmol), BnBr (525 μL, 4.42 mmol), and NaH (60% in mineral oil, 206 mg, 5.15 mmol) were sequentially added to the ice-cold solution of compound **51** (1.63 g, 1.47 mmol) in anhydrous DMF (14.75 mL) under N_2. After 2 h, the reaction was quenched by adding dd. H_2O (4 mL) under the ice bath and diluted with CH_2Cl_2 (20 mL). Solvent extraction was done to wash the CH_2Cl_2 layer with saturated $NaHCO_3$ solution (20 mL, three times). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield the pale-yellow viscous crude. The crude was purified by column chromatography on silica gel with EtOAc/hexanes (1/5, v/v) to afford the pure product **8** (1.14 g, 65%) as a white amorphous foam. R_f 0.57 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −6.62 (*c* 1.36, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.72 Hz, 2H, Ar-H), 7.73 (d, *J* = 8 Hz, 1H, Ar-H), 7.62−7.53 (m, 4H, Ar-H), 7.46−7.40 (m, 2H, Ar-H), 7.39−7.33 (m, 4H, Ar-H), 7.31−7.14 (m, 18H, Ar-H), 7.11−7.07 (m, 2H, Ar-H), 6.87 (d, *J* = 8 Hz, 2H, Ar-H), 6.82 (d, *J* = 7.85 Hz, 1H, N−H), 5.69 (dd, *J* = 10.1, 7.9 Hz, 1H, H-2′), 5.05 (d, *J* = 11.45 Hz, 1H, CH_2Ph), 4.93 (d, *J* = 10.15 Hz, 1H, CH_2Ph), 4.92 (d, *J* = 9.5 Hz, 1H, H-1), 4.76 (d, *J* = 12.4 Hz, 1H, CH_2Ph), 4.68 (d, *J* = 7.9 Hz, 1H, H-1′), 4.61 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.56 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.54−4.46 (m, 2H, CH_2Ph), 4.46−4.40 (m, 2H, H-3, CH_2Ph), 4.38 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.29 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.03 (d, *J* = 2.5 Hz, 1H, H-4′), 3.75 (dd, *J* = 10.7, 2.3 Hz, 1H, H-6a), 3.71 (d, *J* = 10.7, 4.65 Hz, 1H, H-6b), 3.60−3.52 (m, 4H, H-3′, H5, H-5′, H-6a′), 3.52−3.46 (m, 2H, H-4, H-6b′), 3.38−3.24 (m, 1H, H-2), 2.20 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.5 (C), 161.1 (C), 138.7 (C), 138.4 (C), 138.2 (C), 138.0 (C), 134.9 (C), 133.2 (CH), 133.1 (C), 133.09 (CH), 130.0 (C), 129.97 (CH), 129.7 (CH), 128.6 (CH), 128.5 (CH), 128.46 (CH), 128.4 (CH), 128.37 (CH), 128.1 (CH), 128.0 (CH), 127.97 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.66 (CH), 127.6 (CH), 127.56 (CH), 126.9 (CH), 126.2 (CH), 126.1 (CH), 126.0 (CH), 100.4 (CH), 92.7 (C), 84.4 (CH), 79.4 (CH), 78.8 (CH), 77.4 (CH), 75.9 (CH), 74.9 (CH_2), 74.8 (CH_2), 74.0 (CH), 73.7 (CH_2), 73.4 (CH_2), 73.0 (CH), 72.0 (CH), 71.8 (CH_2), 69.3 (CH_2), 68.4 (CH_2), 57.1 (CH), 21.2 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{67}H_{64}Cl_3NO_{11}SNa$ $[M + Na]^+$, 1220.3149; found, 1220.3079.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (9). For reaction details, please see Scheme S7. 2,6-Lutidine (257 μL, 2.22 mmol) and TBSOTf (170 μL, 0.74 mmol) were added to a solution of compound **7** (328 mg, 0.30 mmol) in CH_2Cl_2 (3 mL) at rt and stirred for 2.5 h. After complete consumption of the starting material, the reaction was quenched by addition of MeOH (2 mL). The reaction mixture was concentrated by evaporation, and the crude product was extracted by using CH_2Cl_2 (10 mL) and saturated $NaHCO_3$ solution (10 mL, three times). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield a thick viscous crude. The crude was purified by column chromatography on silica gel with

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EtOAc/hexanes (1/6 to 1/4, v/v, with 0.5−1% Et_3N) to obtain the pure product **9** as a white amorphous foam (257 mg, 70%). R_f 0.31 (EtOAc/hexanes = 1/4, v/v); $[\alpha]_D^{20}$ −7.14 (*c* 0.98, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.72 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.60−7.56 (m, 2H, Ar-H), 7.53 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.46−7.40 (m, 2H, Ar-H), 7.38 (t, *J* = 7.7 Hz, 2H, Ar-H), 7.35−7.31 (m, 3H, Ar-H), 7.31−7.24 (m, 11H, Ar-H), 7.23−7.19 (m, 2H, Ar-H), 7.19−7.16 (m, 2H, Ar-H), 7.00 (d, *J* = 7.7 Hz, 1H, N−H), 6.85 (d, *J* = 7.8 Hz, 2H, Ar-H), 5.72−5.58 (m, 1H, H-2′), 5.05 (d, *J* = 11.4 Hz, 1H, CH_2Ph), 4.84 (d, *J* = 8.6 Hz, 1H, H-1), 4.77 (d, *J* = 12.4 Hz, 1H, CH_2 group of Nap), 4.72 (d, *J* = 7.9 Hz, 1H, H-1′), 4.58 (d, *J* = 12.5 Hz, 1H, CH_2 group of Nap), 4.57 (d, *J* = 11.4 Hz, 1H, CH_2Ph), 4.51 (d, *J* = 11.9 Hz, 1H, CH_2Ph), 4.47−4.39 (m, 3H, 3xCH_2Ph), 4.16−4.10 (m, 1H, H-3), 3.99 (d, *J* = 1.3 Hz, 1H, H-4′), 3.81−3.73 (m, 1H, H-4), 3.67−3.48 (m, 8H, H-2, H-5, H-3′, H-5′, H-6a, H-6b, H-6a′, H6b′), 2.20 (s, 3H, PhCH_3), 0.79 (s, 9H, TBS-*t*-Bu), 0.15 (s, 3H, TBS-CH_3), −0.03 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.5 (C), 161.0 (C), 138.7 (C), 138.6 (C), 137.84 (C), 137.80 (C), 135.0 (C), 133.2 (C), 133.1 (C), 133.08 (CH), 132.4 (CH), 130.2 (C), 130.1 (CH), 129.7 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.37 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 126.2 (CH), 126.1 (CH), 126.0 (CH), 99.7 (CH), 92.8 (C), 84.9 (CH), 80.7 (CH), 79.6 (CH), 76.4 (CH), 74.8 (CH_2), 73.9 (CH), 73.8 (CH_2), 73.4 (CH_2), 73.1 (CH), 71.9 (CH_2), 71.6 (CH), 70.0 (CH_2), 69.8 (CH), 68.7 (CH_2), 56.1 (CH), 26.2 (CH_3), 21.2 (CH_3), 18.1 (C), −3.5 (CH_3), −4.7 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{66}H_{73}Cl_3NO_{11}SSi$ $[M + H]^+$, 1222.3725; found, 1222.3661.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-(1 → 3)-4,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-*β*-D-glucopyranoside (10). For reaction details, please see Scheme S5. To a solution of compound **8** (410 mg, 0.34 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (31 mL) and PBS (3.1 mL, pH = 7.4), DDQ (233 mg, 1.02 mmol) was added with continuous stirring at 0 °C under the argon atmosphere. After 6 h, the reaction mixture was quenched by addition of saturated $NaHCO_3$ solution (5 mL) under the ice bath. The organic layer was washed with saturated $NaHCO_3$ solution (30 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford the pale-yellow viscous crude. The crude was purified by column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/4, v/v) to yield the desired product **10** (228 mg, 63%) as a white amorphous solid. R_f 0.28 (EtOAc/hexanes = 1/3, v/v); $[\alpha]_D^{20}$ −20.29 (*c* 0.69, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): 8.06 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.57 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.49−7.40 (m, 2H, Ar-H), 7.36−7.24 (m, 17H, Ar-H), 7.23−7.18 (m, 3H, Ar-H), 7.17−7.13 (m, 2H, Ar-H), 7.05 (d, *J* = 8.0 Hz, 1H, N−H), 6.93 (d, *J* = 7.8 Hz, 2H, Ar-H), 5.33−5.21 (m, 1H, H-2′), 4.99−4.87 (m, 2H, H-1, CH_2Ph), 4.79 (d, *J* = 7.8 Hz, 1H, H-1′), 4.74 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.65 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.55 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.52−4.40 (m, 4H, H-3, 3× CH_2Ph), 4.34 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 3.87 (d, *J* = 2.6 Hz, 1H, H-4′), 3.80−3.67 (m, 3H, H-3′, H-6a, H-6b), 3.66−3.60 (m, 1H, H-5′), 3.59−3.44 (m, 5H, H-2, H-4, H-5, H-6a′, H-6b′), 2.56 (s, 1H, O−H), 2.24 (s, 3H, PhCH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 167.1 (C), 161.3 (C), 138.4 (C), 138.3 (C), 138.1 (C), 137.8 (C), 133.5 (CH), 133.1 (CH), 130.1 (CH), 129.8 (CH), 129.76 (C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.46 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 99.9 (CH), 92.9 (C), 85.0 (CH), 78.9 (CH), 77.7 (CH), 76.8 (CH), 76.0 (CH), 75.7 (CH_2), 74.8 (CH_2), 74.5 (CH), 74.0 (CH), 73.7 (CH_2), 73.5 (CH_2), 73.4 (CH), 69.3 (CH_2), 68.3 (CH_2), 57.0 (CH), 21.2 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{56}H_{56}Cl_3NO_{11}SNa$ $[M + Na]^+$, 1080.2506; found, 1080.2544.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-(1 → 3)-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-*β*-D-glucopyranoside (11). For reaction details, please see Scheme S5. Compound **7** (210 mg, 0.19 mmol) was stirred in a 10:1 (v/v) mixture of CH_2Cl_2 (17.2 mL) and PBS (1.72 mL, pH = 7.4) in an ice bath. Then, DDQ (129 mg, 0.57 mmol) was added and stirred continuously under the argon atmosphere. After 5 h, the reaction was quenched by addition of saturated $NaHCO_3$ solution (3 mL) under the ice bath. The organic layer was washed with saturated $NaHCO_3$ solution (15 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield the yellow viscous crude. The crude was purified by column chromatography on silica gel with EtOAc/hexanes (1/4 to 1/2, v/v) to isolate the desired product **11** as a white amorphous solid (128 mg, 70%). R_f 0.24 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ +3.66 (*c* 0.82, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.0 (d, *J* = 7.35 Hz, 2H, Ar-H), 7.63−7.54 (m, 1H, Ar-H), 7.47−7.41 (m, 2H, Ar-H), 7.38−7.27 (m, 17H, Ar-H), 6.98 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.77 (d, *J* = 7.0 Hz, 1H, N−H), 5.26 (dd, *J* = 9.6, 8.3 Hz, 1H, H-2′), 5.21 (d, *J* = 10.3 Hz, 1H, H-1), 4.68−4.65 (m, 2H, 2× CH_2Ph), 4.61 (d, *J* = 7.9 Hz, 1H, H-1′), 4.58−4.55 (m, 2H, 2× CH_2Ph), 4.51 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.45 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.37−4.30 (m, 1H, H-3), 4.04 (s, 1H, O−H), 3.88−3.81 (m, 2H, H-4′, H-6a), 3.76 (t, *J* = 6.5 Hz, 1H, H-5′), 3.73−3.64 (m, 3H, H-3′, H-6a′, H-6b), 3.60−3.50 (m, 3H, H-4, H-5, H-6b′), 3.18 (dd, *J* = 17.2, 10.1 Hz, 1H, H-2), 2.32−2.25 (m, 4H, PhCH_3, O−H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.8 (C), 161.8 (C), 138.7 (C), 138.6 (C), 137.7 (C), 137.5 (C), 133.7 (CH), 133.6 (CH), 130.2 (CH), 130.0 (CH), 129.7 (C), 128.9 (CH), 128.73 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.37 (CH), 128.29 (C), 128.2 (CH), 128.18 (CH), 127.7 (CH), 127.6 (CH), 100.6 (CH), 92.3 (C), 83.9 (CH), 81.8 (CH), 79.9 (CH), 76.5 (CH), 75.8 (CH_2), 74.1 (CH), 73.92 (CH), 73.90 (CH_2), 73.6 (CH_2), 73.2 (CH), 69.9 (CH_2), 69.6 (CH), 68.3 (CH_2), 57.3 (CH), 21.3 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{49}H_{50}Cl_3NO_{11}SNa$ $[M + Na]^+$, 990.2046; found, 990.2051.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-(1 → 3)-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-1-thio-*β*-D-glucopyranoside (12). For reaction details, please see Scheme S5. To a solution of compound **6** (298 mg, 0.26 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (24 mL) and PBS (2.4 mL, pH = 7.4), DDQ (180 mg, 0.79 mmol) was added at 0 °C under the argon atmosphere and stirred continuously. After 6 h, the reaction mixture was quenched by addition of saturated $NaHCO_3$ solution (5 mL) under the ice bath. The organic layer was washed with saturated $NaHCO_3$ solution (20 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a yellow viscous crude. The crude was purified by column chromatography on silica gel with EtOAc/hexanes (1/4 to 1/3, v/v) to yield the desired product **12** in 80% (209 mg) yield as a white amorphous solid. R_f 0.38 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −8.26 (*c* 1.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.57 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.43 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.39−7.26 (m, 12H, Ar-H), 7.02 (d, *J* = 7.7 Hz, 2H, Ar-H), 6.75 (d, *J* = 6.9 Hz, 1H, N−H), 5.31−5.23 (m, 1H, H-2′), 5.19 (d, *J* = 10.4 Hz, 1H, H-1), 4.67 (m, 2H, 2× CH_2Ph), 4.59 (d, *J* = 7.9 Hz, 1H, H-1′), 4.54 (d, *J* = 14.7 Hz, 1H, CH_2Ph), 4.46 (d, *J* = 14.7 Hz, 1H, CH_2Ph), 4.33 (t, *J* = 9.0 Hz, 1H, H-3), 3.99−3.90 (m, 2H, H-6a, O−H), 3.86 (d, *J* = 2.6 Hz, 1H, H-4′), 3.83−3.73 (m, 2H, H-6b, H-5′), 3.73−3.63 (m, 2H, H-3′, H-6a′), 3.62−3.54 (m, 1H, H-6b′), 3.49 (t, *J* = 8.9 Hz, 1H, H-4), 3.40−3.32 (m, 1H, H-5), 3.18−3.07 (m, 1H, H-2), 2.33−2.24 (m, 4H, PhCH_3, O−H), 0.91 (s, 9H, TBS-*t*-Bu), 0.086 (s, 3H, TBS-CH_3), 0.075 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.8 (C), 161.7 (C), 138.5 (C), 137.8 (C), 137.5 (C), 133.6 (CH), 133.4 (CH), 130.2 (CH), 130.0 (CH), 129.7 (C), 128.9 (CH), 128.7 (CH), 128.66 (CH), 128.5 (C), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 100.6 (CH), 92.3 (C), 83.9 (CH), 81.7 (CH), 80.9 (CH), 76.5 (CH), 75.8 (CH_2), 74.1 (CH), 73.93 (CH), 73.89 (CH_2), 73.2 (CH), 69.2 (CH), 68.2 (CH_2), 62.9 (CH_2), 57.2 (CH), 26.1 (CH_3), 21.3 (CH_3), 18.6 (C), −5.0 (2× CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{48}H_{59}Cl_3NO_{11}SSi$ $[M + H]^+$, 992.2612; found, 992.2592.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-(1 → 3)-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-trichloroacetamido-1-thio-*β*-D-glucopyranoside (13). For reaction details, please see Scheme S5. Compound **4** (0.85 g, 0.74 mmol) was stirred in a 10:1 (v/v) mixture of CH_2Cl_2 (67.20 mL) and PBS (6.72

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mL, pH = 7.4) in an ice bath. Then, DDQ (503 mg, 2.22 mmol) was added and stirred continuously under the argon atmosphere. After 5 h, the reaction was quenched by addition of saturated $NaHCO_3$ solution (8 mL) under the ice bath. The organic layer was washed with saturated $NaHCO_3$ solution (60 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a thick yellow crude. The crude was subjected to column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to afford pure **13** (0.57 g, 75% yield) as a white amorphous foam. R_f 0.31 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −9.71 (*c* 1.03, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.2 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.57 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.43 (t, *J* = 7.7 Hz, 2H, Ar-H), 7.37−7.26 (m, 17H, Ar-H), 7.08 (d, *J* = 7.2 Hz, 1H, N−H), 6.96 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.20 (d, *J* = 10.1 Hz, 1H, H-1), 5.11 (dd, *J* = 9.8, 7.8 Hz, 1H, H-2′), 4.89 (t, *J* = 9.4 Hz, 1H, H-4), 4.73 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.67 (d, *J* = 7.8 Hz, 1H, H-1′), 4.61 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.55 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.52−4.44 (m, 4H, H-3, 2× CH_2Ph), 3.84 (d, *J* = 3.3 Hz, 1H, H-4′), 3.70−3.59 (m, 4H, H3′, H5, CH_2Ph), 3.59−3.48 (m, 3H, H6a, H6b), 3.39 (td, *J* = 9.6, 7.5 Hz, 1H, H2), 2.52 (d, *J* = 8.6 Hz, 1H, OH), 2.26 (s, 3H, $PhCH_3$), 1.7 (s, 3H, $COCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 169.8 (C), 166.8 (C), 161.6 (C), 138.6 (C), 138.14 (C), 138.1 (C), 137.6 (C), 133.5 (CH), 130.2 (CH), 130.0 (CH), 129.8 (C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (C), 128.2 (CH), 128.13 (CH), 128.1 (CH), 127.95 (CH), 127.92 (CH), 127.8 (CH), 99.1 (CH), 92.7 (C), 84.8 (CH), 78.0 (CH), 76.7 (CH), 75.8 (CH), 75.6 (CH_2), 74.2 (CH), 73.8 (CH_2), 73.7 (CH), 73.6 (CH_2), 73.5 (CH), 69.6 (CH_2), 68.8 (CH), 68.3 (CH_2), 57.5 (CH), 21.3 (CH_3), 20.7 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{51}H_{52}Cl_3NO_{12}SNa$ $[M + Na]^+$, 1032.2152; found, 1032.2054.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-*β*-D-galacto-pyranosyl)-(1 → 3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-*β*-D-glucopyranoside (14). For reaction details, please see Scheme S6. To a solution of compound **3** (391 mg, 0.30 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (27 mL) and PBS (2.7 mL, pH = 7.4), DDQ (205 mg, 0.903 mmol) was added under the argon atmosphere at 0 °C. After 5 h, the reaction was completed as observed by TLC. Saturated $NaHCO_3$ solution (4 mL) was slowly added to the reaction mixture under the ice bath to quench the reaction. The organic layer was washed with saturated $NaHCO_3$ solution (20 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a thick yellow crude. The crude was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the desired pure product **14** (278 mg, 80%) as a white amorphous foam. R_f 0.35 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −4.71 (*c* 0.85, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.67 (dd, *J* = 6.3, 4.6 Hz, 4H, Ar-H), 7.57 (t, *J* = 6.8 Hz, 1H, Ar-H), 7.46−7.39 (m, 4H, Ar-H), 7.38−7.31 (m, 12H, Ar-H), 7.31−7.26 (m, 4H, Ar-H), 7.01 (d, *J* = 6.8 Hz, 1H, N−H), 6.95 (d, *J* = 7.5 Hz, 2H, Ar-H), 5.17 (d, *J* = 9.9 Hz, 1H, H-1), 5.09 (dd, *J* = 9.4, 8.0 Hz, 1H, H-2′), 4.87 (t, *J* = 9.3 Hz, 1H, H-4), 4.74 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.67−4.59 (m, 2H, H-1′, CH_2Ph), 4.56 (d, *J* = 11.7, 1H, CH_2Ph), 4.52−4.45 (m, 2H, H-3, CH_2Ph), 3.85 (d, *J* = 2.4 Hz, 1H, H-4′), 3.72−3.52 (m, 7H, H-5, H-6a, H-6b, H-3′, H-5′, H-6a′, H-6b′), 3.41−3.30 (m, 1H, H-2), 2.60−2.44 (m, 1H, O−H), 2.26 (s, 3H, $PhCH_3$), 1.66 (s, 3H, $COCH_3$), 1.03 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 169.5 (C), 166.9 (C), 161.6 (C), 138.6 (C), 138.1 (C), 137.7 (C), 135.9 (CH), 133.5 (CH), 133.47 (CH), 133.43 (C), 133.3 (C), 130.2 (CH), 130.0 (CH), 129.85 (CH), 129.82 (CH), 128.76 (CH), 128.6 (CH), 128.5 (C), 128.2 (CH), 128.1 (CH), 128.07 (CH), 127.9 (CH), 127.87 (CH), 99.3 (CH), 92.8 (C), 84.8 (CH), 79.5 (CH), 76.7 (CH), 76.1 (CH), 75.6 (CH_2), 74.3 (CH), 73.8 (CH_2), 73.7 (CH), 73.6 (CH), 68.3 (CH), 68.26 (CH_2), 63.4 (CH_2), 57.7 (CH), 26.9 (CH_3), 21.3 (CH_3), 20.7 (CH_3), 19.4 (C); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{60}H_{64}Cl_3NO_{12}SSiNa$ $[M + Na]^+$, 1180.2851; found, 1180.2802.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-*β*-D-galacto-pyranosyl)-(1 → 3)-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-*β*-D-glucopyranoside (15). For reaction details, please see Scheme S5. To a solution of compound **2** (567 mg, 0.51 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (47 mL) and PBS (4.70 mL, pH = 7.4), DDQ (349 mg, 1.54 mmol) was added under the argon atmosphere at 0 °C. After 5 h, the reaction was completed as observed by TLC. To quench the reaction, saturated $NaHCO_3$ solution (5 mL) was slowly added to the reaction mixture under the ice bath. Solvent extraction was done to wash the organic layer with saturated $NaHCO_3$ solution (40 mL, three times). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation. The residue was purified by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to yield the pure product **15** (366 mg, 74%) as a white amorphous foam. R_f 0.38 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{25}$ −0.9 (*c* 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.53 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.46−7.41 (m, 2H, Ar-H), 7.41−7.36 (m, 2H, Ar-H), 7.36−7.26 (m, 15H, Ar-H), 7.08 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.92 (d, *J* = 6.9 Hz, 1H, N−H), 5.47 (s, 1H, PhCH benzylidene), 5.32 (d, *J* = 10.4 Hz, 1H, H-1), 5.18 (dd, *J* = 9.6, 8.3 Hz, 1H, H-2′), 4.80 (d, *J* = 8.0 Hz, 1H, H-1′), 4.67 (m, 2H, 2xCH_2Ph), 4.59 (t, *J* = 9.1 Hz, 1H, H-3), 4.40 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.36−4.28 (m, 2H, H-6a, CH_2Ph), 3.80 (d, *J* = 3.1 Hz, 1H, H-4′), 3.74−3.66 (m, 2H, H-4, H-6b), 3.65−3.57 (m, 2H, H-3′, H-6a′), 3.56−3.44 (m, 3H, H-5, H-5′, H-6b′), 3.33−3.23 (m, 1H, H-2), 2.39−2.35 (m, 1H, O−H), 2.33 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.9 (C), 161.7 (C), 139.2 (C), 138.1 (C), 137.8 (C), 137.4 (C), 134.1 (CH), 133.5 (CH), 130.2 (CH), 129.8 (C), 129.2 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.4 (C), 126.3 (CH), 101.3 (CH), 99.5 (CH), 92.3 (C), 84.6 (CH), 80.1 (CH), 76.6 (CH), 76.3 (CH), 75.6 (CH_2), 74.5 (CH), 73.8 (CH_2), 73.6 (CH), 73.4 (CH), 70.8 (CH), 68.7 (CH_2), 68.5 (CH_2), 57.7 (CH), 21.4 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{49}H_{48}Cl_3NO_{11}SNa$ $[M + Na]^+$, 986.1906; found, 986.1952.

4-Methylphenyl(2-*O*-benzoyl-4,6-di-*O*-benzyl-*β*-D-galacto-pyranosyl)-(1 → 3)-4-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-*β*-D-glucopyranoside (16). For reaction details, please see Scheme S6. To a solution of compound **1** (408 mg, 0.30 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (27 mL) and PBS (2.7 mL, pH = 7.4), DDQ (204 mg, 0.90 mmol) was added at 0 °C under the argon atmosphere and stirred continuously. After 5 h, the reaction mixture was quenched by addition of saturated $NaHCO_3$ solution (4 mL) under the ice bath. The organic layer was washed with saturated $NaHCO_3$ solution (20 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford the viscous yellow crude. The crude was purified by column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the desired product **16** (273 mg, 75%) as a white amorphous foam. R_f 0.31 (EtOAc/hexanes = 1/3, v/v); $[\alpha]_D^{20}$ −24.79 (*c* 1.17, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.1 Hz, 2H, Ar-H), 7.83 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.66 (d, *J* = 6.7 Hz, 2H, Ar-H), 7.58 (d, *J* = 6.9 Hz, 2H, Ar-H), 7.52 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.46 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.41−7.37 (m, 2H, Ar-H), 7.37−7.32 (m, 5H, Ar-H), 7.31−7.27 (m, 5H, Ar-H), 7.27−7.22 (m, 5H, Ar-H), 7.21−7.13 (m, 5H, Ar-H), 7.00 (d, *J* = 7.0 Hz, 1H, N−H), 6.95 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.31 (d, *J* = 10.3 Hz, 1H, H-1), 5.17 (t, *J* = 8.8 Hz, 1H, H-4), 5.09 (dd, *J* = 9.9, 7.9 Hz, 1H, H-2′), 4.71 (t, *J* = 9.4 Hz, 1H, H-3), 4.62 (d, *J* = 7.8 Hz, 1H, H-1′), 4.54 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.46 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.30 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.24 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 3.80−3.70 (m, 4H, H, H-4′, H-5, H-6a, H-6b), 3.59−3.52 (m, 1H, H-3′), 3.47 (dd, *J* = 7.4, 6.0 Hz, 1H, H-5′), 3.37−3.28 (m, 1H, H-2), 3.13 (dd, *J* = 8.9, 5.5 Hz, 1H, H-6a′), 2.92−2.83 (m, 1H, H-6b′), 2.38 (d, *J* = 8.2 Hz, 1H, O−H), 2.26 (s, 3H, $PhCH_3$), 1.01 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.7 (C), 164.9 (C), 161.7 (C), 138.7 (C), 138.2 (C), 137.8 (C), 135.73 (CH), 135.70 (CH), 133.7 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 132.8 (CH), 130.3 (C), 130.0 (CH), 129.96 (CH), 129.9 (C), 129.7 (CH), 128.65 (CH), 128.62 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.66 (CH), 99.8 (CH), 92.7 (C), 84.2 (CH), 79.5 (CH), 76.5 (CH), 76.4 (CH), 75.3 (CH_2), 74.2 (CH), 73.4 (CH_2), 73.3 (CH), 73.2 (CH), 69.2 (CH), 67.4 (CH_2), 63.3 (CH_2), 58.1

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(CH), 26.8 (CH_3), 21.3 (CH_3), 19.3 (C); HRMS (ESI-TOF) m/z: calcd for $C_{65}H_{67}Cl_3NO_{12}SSi$ $[M + H]^+$, 1220.3189; found, 1220.3174.

Compounds 17 to 30 Are the Tetrasaccharide Products of [2 + 2] Reactions from Table 1. *4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(6-O-tert-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (17).* A solution of **6** (70 mg, 0.062 mmol) and **13** (50 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (1 mL) was stirred with 3 Å pulverized molecular sieves (120 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (14 mg, 0.062 mmol) and TMSOTf (1.8 μL, 0.01 mmol) were added to the reaction mixture. After 2.5 h, the reaction mixture was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/toluene (1/16 to 1/13, v/v) to obtain the desired product **17** (55 mg, 54%) as a white amorphous solid. R_f 0.38 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −10.49 (c 1.43, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (t, J = 7.5 Hz, 4H, Ar-H), 7.73 (d, J = 7.6 Hz, 1H, Ar-H), 7.57−7.48 (m, 5H, Ar-H), 7.46−7.37 (m, 4H, Ar-H), 7.37−7.32 (m, 6H, Ar-H), 7.31−7.26 (m, 17H, Ar-H), 7.25−7.23 (m, 1H, Ar-H), 721−7.18 (m, 2H, Ar-H), 7.18−7.13 (m, 3H, Ar-H), 7.11−7.05 (m, 1H, Ar-H), 6.93 (d, J = 7.7 Hz, 3H, Ar-H, N−H), 6.43 (d, J = 6.7 Hz, 1H, N−H), 5.61 (dd, J = 9.8, 8.1 Hz, 1H, H-2‴), 5.27 (dd, J = 9.9, 7.9 Hz, 1H, H-2′), 5.12 (d, J = 10.0 Hz, 1H, H-1), 4.94 (m, 2H, CH_2Ph, H-1″), 4.80 (t, J = 9.4 Hz, 1H, H-4), 4.70 (m, 2H, CH_2Ph, CH_2 group of Nap), 4.60−3.37 (m, 12H, H-1′, H-3, H1‴, CH_2 group of Nap, 8× CH_2Ph), 4.17 (dd, J = 9.7, 8.1 Hz, 1H, H-3″), 3.99−3.90 (m, 4H, O−H, H-6a″, H-4′, H-4‴), 3.83 (dd, J = 10.0, 2.6 Hz, 1H, H-3′), 3.71 (dd, J = 11.0, 5.8 Hz, 1H, H-6b″), 3.61−3.45 (m, 9H, H-3‴, H-5‴, H-5′, H-6a, H-6b, H-6a′, H-6b′, H-6a‴, H-6b‴), 3.43−3.34 (m, 2H, H-4″, H-5), 3.33−3.27 (m, 1H, H-5″), 3.24−3.16 (m, 1H, H-2), 2.76−2.68 (m, 1H, H-2″), 2.26 (s, 3H, $PhCH_3$), 1.58 (s, 3H, $COCH_3$), 0.86 (s, 9H, TBS-t-Bu), 0.02 (s, 3H, TBS-CH_3), 0.01 (s, 3H, TBS-CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.85 (C), 165.6 (C), 164.9 (C), 161.6 (C), 161.4 (C), 139.1 (C), 138.4 (C), 138.3 (C), 138.2 (C), 137.9 (C), 137.7 (C), 134.7 (C), 133.5 (CH), 133.4 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 130.4 (CH), 130.2 (CH), 129.9 (CH), 129.8 (C), 128.7 (CH), 128.64 (CH), 128.61 (CH), 128.59 (CH), 128.52 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.14 (CH), 128.11 (CH), 128.0 (CH), 127.96 (CH), 127.8 (CH), 127.76 (CH), 127.6 (CH), 127.0 (CH), 126.4 (CH), 126.3 (CH), 125.9 (CH), 101.0 (CH), 99.7 (CH), 98.9 (CH), 92.7 (C), 91.8 (C), 84.8 (CH), 79.7 (CH), 78.0 (CH), 77.97 (CH), 77.3 (CH), 76.6 (CH), 75.5 (CH), 75.1 (CH_2), 74.9 (CH_2), 74.0 (CH), 73.99 (CH), 73.8 (CH_2), 73.6 (CH_2), 72.58 (CH), 72.4 (CH_2), 72.2 (CH), 71.7 (CH), 69.7 (CH_2), 69.4 (CH), 68.8 (CH), 68.7 (CH_2), 68.4 (CH_2), 62.9 (CH_2), 59.4 (CH), 57.7 (CH), 26.1 (CH_3), 21.33 (CH_3), 20.54 (CH_3), 18.5 (C), −5.1 (2xCH_3); HRMS (ESI-TOF) m/z: calcd for $C_{103}H_{111}Cl_6N_2O_{23}SSi$ $[M + H]^+$, 2017.5182; found, 2017.5184.

4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (18). A solution of **7** (57 mg, 0.052 mmol) and **13** (40 mg, 0.04 mmol) in anhydrous CH_2Cl_2 (0.8 mL) was stirred with 3 Å pulverized molecular sieves (100 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (11.6 mg, 0.052 mmol) and TMSOTf (1.4 μL, 0.008 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the pure desired product **18** (46 mg, 58%) as a white amorphous foam. R_f 0.16 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −13.41 (c 1.79, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (dd, J = 6.7, 4.8 Hz, 4H, Ar-H), 7.73 (d, J = 7.7 Hz, 1H, Ar-H), 7.58−7.52 (m, 3H, Ar-H), 7.52−7.48 (m, 2H, Ar-H), 7.46−7.40 (m, 2H, Ar-H), 7.40−7.35 (m, 2H, Ar-H), 7.35−7.32 (m, 4H, Ar-H), 7.31−7.29 (m, 5H, Ar-H), 7.29−7.26 (m, 13H, Ar-H), 7.26−7.21 (m, 7H, Ar-H), 7.20−7.14 (m, 5H, Ar-H), 7.13−7.08 (m, 1H, Ar-H), 6.93 (d, J = 7.9 Hz, 2H, Ar-H), 6.89 (d, J = 7.1 Hz, 1H, N−H), 6.47 (d, J = 6.8 Hz, 1H, N−H), 5.61 (dd, J = 9.8, 8.2 Hz, 1H, H-2‴), 5.28 (dd, J = 9.9, 7.8 Hz, 1H, H-2′), 5.11 (d, J = 10.1 Hz, 1H, H-1), 4.96 (dd, J = 15.8, 9.9 Hz, 2H, H-1″, CH_2Ph), 4.79 (t, J = 9.4 Hz, 1H, H-4), 4.72 (m, 2H, CH_2Ph, CH_2 group of Nap), 4.59−4.34 (m, 14H, H-1′, H-1‴, H-3, CH_2 group of Nap, 10× CH_2Ph), 4.19 (dd, J = 9.7, 8.0 Hz, 1H, H-3″), 4.04−3.98 (m, 2H, O−H, H-4′), 3.93 (d, J = 1.8 Hz, 1H, H-4‴), 3.86−3.79 (m, 2H, H-3′, H-5‴), 3.62−3.35 (m, 13H, H-3‴, H-4″, H-5, H-5″, H-5′, H-6a, H-6b, H-6a′, H-6b′, H-6a″, H-6b″, H-6a‴, H-6b‴), 3.24−3.14 (m, 1H, H-2), 2.85−2.76 (m, 1H, H-2″), 2.26 (s, 3H, $PhCH_3$), 1.58 (s, 3H, $COCH_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.8 (C), 165.6 (C), 164.9 (C), 161.7 (C), 161.5 (C), 139.1 (C), 138.4 (C), 138.3 (C), 138.2 (C), 137.9 (C), 137.7 (C), 134.7 (C), 133.5 (CH), 133.4 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 130.4 (CH), 130.2 (CH), 129.9 (CH), 129.7 (C), 128.7 (CH), 128.6 (CH), 128.59 (CH), 128.52 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.08 (CH), 128.01 (CH), 127.96 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 126.4 (CH), 126.3 (CH), 125.9 (CH), 101.0 (CH), 99.6 (CH), 98.9 (CH), 92.7 (C), 91.7 (C), 84.7 (CH), 79.8 (CH), 79.7 (CH), 78.5 (CH), 78.0 (CH), 77.0 (CH), 75.4 (CH), 75.1 (CH), 75.0 (CH_2), 74.9 (CH_2), 74.1 (CH), 73.83 (CH), 73.8 (CH_2), 73.64 (CH_2), 73.6 (CH_2), 72.6 (CH), 72.4 (CH_2), 72.2 (CH), 71.7 (CH), 69.9 (CH_2), 69.7 (CH), 68.8 (CH), 68.7 (CH_2), 68.4 (CH_2), 59.4 (CH), 57.7 (CH), 21.3 (CH_3), 20.6 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{104}H_{103}Cl_6N_2O_{23}S$ $[M + H]^+$, 1993.4787; found, 1993.4806.

4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-acetyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (19). A solution of **7** (62 mg, 0.056 mmol) and **14** (50 mg, 0.043 mmol) in anhydrous CH_2Cl_2 (0.9 mL) was stirred with 3 Å pulverized molecular sieves (112 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (12.6 mg, 0.056 mmol) and TMSOTf (1.6 μL, 0.009 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the pure desired product **19** (58 mg, 63%) as a white amorphous solid. R_f 0.45 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −8.33 (c 1.92, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (dd, J = 11.8, 7.7 Hz, 4H, Ar-H), 7.72 (d, J = 7.5 Hz, 1H, Ar-H), 7.63 (d, J = 3.6 Hz, 4H, Ar-H), 7.58−7.47 (m, 5H, Ar-H), 7.46−7.36 (m, 6H, Ar-H), 7.35−7.27 (m, 22H, Ar-H), 7.26−7.21 (m, 6H, Ar-H), 7.20−7.13 (m, 5H, Ar-H), 7.13−7.08 (m, 1H, Ar-H), 6.98−6.86 (m, 3H, Ar-H, N−H), 6.54 (d, J = 6.5 Hz, 1H, N−H), 5.60 (dd, J = 9.7, 8.0 Hz, 1H, H-2′), 5.25 (dd, J = 9.6, 7.8 Hz, 1H, H-2‴), 5.10 (d, J = 10.1 Hz, 1H, H-1), 5.00−4.90 (m, 2H, H-1″, CH_2Ph), 4.79−4.67 (m, 3H, H-4, 2× CH_2 group of Nap), 4.59−4.35 (m, 12H, H-1′, H-1‴, H-3, 9× CH_2Ph), 4.20 (t, J = 8.7 Hz, 1H, H-3″), 4.06−3.98 (m, 2H, H-4‴, O−H), 3.94−3.90 (m, 1H, H-4′), 3.87−3.77 (m, 2H, H-3‴, H-5‴), 3.69−3.35 (m, 13H, H-3′, H-5, H-4″, H-5′, H-5″, H-6a, H-6b, H-6a′, H-6b′, H-6a″, H-6b″, H-6a‴, H-6b‴), 3.23−3.13 (m, 1H, H-2), 2.86−2.77 (m, 1H, H-2″), 2.26 (s, 3H, $PhCH_3$), 1.51 (s, 3H, $COCH_3$), 1.01 (s, 9H, TBDPS-t-Bu); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.6 (C), 165.6 (C), 164.9 (C), 161.7 (C), 161.5 (C), 139.1 (C), 138.4 (C), 138.2 (C), 137.9 (C), 137.7 (C), 135.8 (CH), 134.7 (C), 133.5 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 130.3

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(CH), 130.2 (CH), 129.9 (CH), 129.8 (CH), 129.7 (C), 128.8 (C), 128.7 (CH), 128.6 (CH), 128.57 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.09 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 101.0 (CH), 99.6 (CH), 98.9 (CH), 92.7 (C), 91.7 (C), 84.8 (CH), 79.7 (CH), 79.6 (CH), 78.6 (CH), 77.0 (CH), 75.5 (CH), 75.1 (CH), 75.0 (CH_2), 74.8 (CH_2), 74.0 (CH), 73.8 (CH_2), 73.6 (CH_2), 73.57 (CH_2), 72.6 (CH), 72.4 (CH_2), 72.2 (CH), 71.7 (CH), 69.9 (CH_2), 69.7 (CH), 68.7 (CH_2), 68.3 (CH_2), 68.2 (CH), 63.6 (CH_2), 59.3 (CH), 57.8 (CH), 26.9 (CH_3), 21.3 (CH_3), 20.5 (CH_3), 19.3 (C); HRMS (ESI-TOF) m/z: calcd for $C_{113}H_{114}Cl_6N_2O_{23}SSiNa$ $[M + Na]^+$, 2163.5319; found, 2163.5297.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**20**).* A solution of **7** (119 mg, 0.11 mmol) and **15** (80 mg, 0.083 mmol) in anhydrous CH_2Cl_2 (1.66 mL) was stirred with 3 Å pulverized molecular sieves (200 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (24.3 mg, 0.11 mmol) and TMSOTf (3 μL, 0.017 mmol) were added to the reaction mixture. After 2 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the pure desired product **20** (97 mg, 60%) as a white amorphous solid. R_f 0.23 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −5.83 (*c* 3.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.83 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.72 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.57−7.48 (m, 4H, Ar-H), 7.46−7.39 (m, 3H, Ar-H), 7.38−7.26 (m, 21H, Ar-H), 7.24−7.20 (m, 10H, Ar-H), 7.19−7.07 (m, 6H, Ar-H), 7.03 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.90 (d, *J* = 6.8 Hz, 1H, N−H), 6.41 (d, *J* = 6.7 Hz, 1H, N−H), 5.60 (dd, *J* = 9.8, 8.1 Hz, 1H, H-2‴), 5.42−5.33 (m, 2H, H-2′, PhCH benzylidene), 5.28 (d, *J* = 10.3 Hz, 1H, H-1), 4.98−4.89 (m, 2H, H-1″, CH_2Ph), 4.77−4.64 (m, 3H, H-1′, CH_2Ph), 4.59−4.35 (m, 9H, H-1‴, H-3, CH_2 group of Nap, 6× CH_2Ph), 4.31−4.20 (m, 2H, 2× CH_2Ph), 4.12 (dd, *J* = 9.5, 7.8 Hz, 1H, H-3″), 4.06 (s, 1H, O−H), 4.00 (d, *J* = 2.2 Hz, 1H, H-4′), 3.95−3.89 (m, 1H, H-4‴), 3.85 (dd, *J* = 10.0, 2.6 Hz, 1H, H-3′), 3.79 (d, *J* = 10.0 Hz, 1H, H-5‴), 3.68−3.37 (m, 14H, H-4, H-4″, H-3‴, H-5, H-5′, H-5″, H-6a, H-6b, H-6a′, H-6b′, H-6a″, H-6b″, H-6a‴, H-6b‴), 3.21−3.12 (m, 1H, H-2), 2.86−2.77 (m, 1H, H-2″), 2.31 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.5 (C), 165.1 (C), 161.6 (C), 139.1 (C), 138.9 (C), 138.4 (C), 138.2 (C), 138.0 (C), 137.6 (C), 137.4 (C), 134.7 (C), 133.9 (CH), 133.4 (CH), 133.3 (CH), 133.1 (C), 133.09 (C), 130.2 (CH), 130.1 (CH), 129.7 (C), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.47 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 126.3 (CH), 126.25 (CH), 126.2 (CH), 125.9 (CH), 100.9 (CH), 99.7 (CH), 98.7 (CH), 92.3 (C), 91.7 (C), 84.5 (CH), 80.0 (CH), 79.7 (CH), 79.1 (CH), 78.4 (CH), 76.9 (CH), 75.8 (CH), 75.1 (CH), 74.9 (CH_2), 74.8 (CH_2), 74.0 (CH), 73.74 (CH_2), 73.71 (CH_2), 73.7 (CH), 73.5 (CH_2), 72.5 (CH), 72.4 (CH_2), 72.36 (CH), 71.7 (CH), 70.8 (CH), 69.9 (CH_2), 69.7 (CH), 69.0 (CH_2), 68.5 (CH_2), 68.4 (CH_2), 59.1 (CH), 58.0 (CH), 21.3 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{102}H_{99}Cl_6N_2O_{22}S$ $[M + H]^+$, 1949.4520; found, 1949.4540.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-benzoyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**21**).* A solution of **7** (59 mg, 0.053 mmol) and **16** (50 mg, 0.041 mmol) in anhydrous CH_2Cl_2 (0.82 mL) was stirred with 3 Å pulverized molecular sieves (109 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (12 mg, 0.053 mmol) and TMSOTf (1.5 μL, 0.008 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL) and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the pure desired product **21** (61 mg, 67%) as a white amorphous solid. R_f 0.47 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −11.33 (*c* 2.03, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.78 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.74−7.71 (m, 3H, Ar-H), 7.60 (d, *J* = 6.9 Hz, 2H, Ar-H), 7.58−7.48 (m, 7H, Ar-H), 7.46−7.37 (m, 5H, Ar-H), 7.34−7.29 (m, 8H, Ar-H), 7.29−7.25 (m, 15H, Ar-H), 7.23−7.18 (m, 6H, Ar-H), 7.17−7.15 (m, 4H, Ar-H), 7.14−7.11 (m, 2H, Ar-H), 7.11−7.07 (m, 3H, Ar-H), 6.93 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.81 (d, *J* = 6.9 Hz, 1H, N−H), 6.40 (d, *J* = 6.8 Hz, 1H, N−H), 5.59 (dd, *J* = 9.9, 8.1 Hz, 1H, H-2‴), 5.28−5.22 (m, 2H, H-1, H-2′), 5.06 (t, *J* = 9.0 Hz, 1H, H-4), 4.92 (m, 2H, H-1″, CH_2Ph), 4.70 (d, *J* = 12.2 Hz, 1H, CH_2 group of Nap), 4.66−4.56 (m, 3H, H-3), 4.56−4.53 (m, 1H), 4.53−4.45 (m, 2H, H-1′), 4.45−4.41 (m, 3H), 4.40−4.33 (m, 3H, H-1‴), 4.23 (d, *J* = 12 Hz, 1H, CH_2Ph), 4.19−4.12 (m, 2H, H-3″, CH_2Ph), 3.97−3.90 (m, 3H, H-4′, H-4‴, O−H), 3.80−3.75 (m, 2H, H-3′), 3.71−3.68 (m, 2H, H-5), 3.60−3.56 (m, 2H), 3.56−3.52 (m, 1H), 3.52−3.48 (m, 2H, H-3‴), 3.45−3.40 (m, 2H, H-4″), 3.39−3.35 (m, 1H), 3.13 (td, *J* = 10, 7.1 Hz, 1H, H-2), 3.05 (dd, *J* = 9.0, 5.7 Hz, 1H, H-6a′), 2.86−2.80 (m, 1H, H-6b′), 2.71 (td, *J* = 8.6, 7.1 Hz, 1H, H-2″), 2.27 (s, 3H, $PhCH_3$), 0.98 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.5 (C), 165.0 (C), 164.8 (C), 161.7 (C), 161.6 (C), 139.3 (C), 138.4 (C), 138.3 (C), 138.1 (C), 137.7 (C), 135.7 (CH), 134.7 (C), 133.6 (CH), 133.5 (CH), 133.3 (C), 133.2 (C), 133.17 (C), 133.12 (CH), 132.7 (CH), 130.2 (CH), 130.0 (CH), 129.97 (CH), 129.9 (C), 129.7 (C), 129.68 (CH), 128.7 (CH), 128.6 (CH), 128.53 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.06 (CH), 127.98 (CH), 127.94 (CH), 127.9 (CH), 127.87 (CH), 127.8 (CH), 127.76 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 100.9 (CH), 100.2 (CH), 98.7 (CH), 92.6 (C), 91.7 (C), 84.1 (CH), 79.7 (CH), 78.1 (CH), 76.8 (CH), 75.9 (CH), 75.1 (CH), 74.82 (CH_2), 74.0 (CH), 73.8 (CH_2), 73.6 (CH_2), 73.34 (CH), 73.33 (CH_2), 72.6 (CH), 72.4 (CH_2), 72.3 (CH), 71.7 (CH), 69.9 (CH_2), 69.6 (CH), 69.1 (CH), 68.3 (CH_2), 67.7 (CH_2), 63.4 (CH_2), 59.3 (CH), 58.3 (CH), 26.9 (CH_3), 21.4 (CH_3), 19.3 (C); HRMS (ESI-TOF) m/z: calcd for $C_{118}H_{117}Cl_6N_2O_{23}SSi$ $[M + H]^+$, 2203.5659; found, 2203.5620.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**22**).* A solution of **8** (44 mg, 0.037 mmol) and **10** (30 mg, 0.028 mmol) in anhydrous CH_2Cl_2 (570 μL) was stirred with 3 Å pulverized molecular sieves (75 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (8.3 mg, 0.037 mmol) and TMSOTf (1 μL, 0.006 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the pure product **22** (11 mg, 19%) as a glassy solid and donor **8** recovered (16 mg, 34%). R_f 0.49 (EtOAc/toluene = 1/8, v/v); $[\alpha]_D^{20}$ −18 (*c* 1.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.92 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.72 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.58−7.48 (m, 4H, Ar-H), 7.46−7.35 (m, 6H, Ar-H), 7.34−7.29 (m, 10H, Ar-H), 7.29−7.26 (m, 8H, Ar-H), 7.26−7.24 (m, 3H, Ar-H), 7.22−7.18 (m, 9H, Ar-H), 7.18−7.17 (m, 3H, Ar-H), 7.16−7.14 (m, 4H, Ar-H), 7.14−7.11 (m, 3H, Ar-H), 7.10−7.05 (m, 4H, Ar-H), 6.90 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.77 (d, *J* = 7.8 Hz, 1H, N−H), 6.57 (d, *J* = 7.8 Hz, 1H, N−H), 5.63 (dd, *J* = 10.1, 8.0 Hz, 1H, H-2‴), 5.50 (dd, *J* = 10.1, 7.9 Hz, 1H, H-2′), 5.03 (d, *J* = 11.4 Hz, 1H, CH_2Ph), 4.92 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.87 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.82 (d,

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J = 9.7 Hz, 1H, H-1), 4.77 (d, J = 8.1 Hz, 1H, H-1″), 4.75−4.71 (m, 2H, CH_2 group of Nap, CH_2Ph), 4.64−4.58 (m, 3H, H-1′, H-1‴), 4.56 (d, J = 2.7 Hz, 1H), 4.54−4.49 (m, 3H), 4.47 (s, 1H), 4.45−4.41 (m, 1H), 4.41−4.35 (m, 4H, H-3), 4.35−4.30 (m, 3H, H-3″), 4.25 (d, J = 11.9 Hz, 1H, CH_2Ph), 4.22 (d, J = 11.8 Hz, 1H, CH_2Ph), 3.98−3.94 (m, 2H, H-4′, H-4‴), 3.90 (dd, J = 10.2, 2.8 Hz, 1H, H-3′), 3.73−3.62 (m, 4H), 3.55 (t, J = 6.4 Hz, 1H), 3.52−3.46 (m, 4H, H-3‴), 3.45−3.38 (m, 5H, H-4, H-4″), 3.26−3.14 (m, 2H, H-2, H-2″), 2.25 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 165.2 (C), 161.2 (C), 139.2 (C), 138.8 (C), 138.5 (C), 138.3 (C), 138.2 (C), 137.9 (C), 134.9 (C), 133.4 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 133.0 (CH), 130.1 (CH), 130.0 (CH), 129.8 (CH), 129.0 (C), 128.7 (CH), 128.6 (CH), 128.57 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.16 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 100.6 (CH), 100.3 (CH), 99.3 (CH), 92.8 (C), 92.4 (C), 84.8 (CH), 79.5 (CH), 78.9 (CH), 77.6 (CH), 76.3 (CH), 76.0 (CH), 75.2 (CH), 75.1 (CH_2), 75.0 (CH_2), 74.96 (CH_2), 74.9 (CH_2), 74.2 (CH), 73.8 (CH), 73.7 (CH_2), 73.6 (CH_2), 73.5 (CH_2), 73.2 (CH), 72.8 (CH), 72.1 (CH), 72.0 (CH_2), 69.4 (CH_2), 69.2 (CH_2), 68.6 (CH_2), 68.4 (CH_2), 59.3 (CH), 57.3 (CH), 21.3 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{116}H_{112}Cl_6N_2O_{22}SNa$ $[M + Na]^+$, 2153.5446; found, 2153.5446.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-6-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**23**).* A solution of **8** (72 mg, 0.06 mmol) and **11** (45 mg, 0.047 mmol) in anhydrous CH_2Cl_2 (0.93 mL) was stirred with 3 Å pulverized molecular sieves (117 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (13 mg, 0.06 mmol) and TMSOTf (1.7 μL, 0.009 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the product **23** (19 mg, 20%) as a white amorphous solid.

Synthesis of 23 from 27 by Regioselective Ring Opening Reaction. For reaction details, please see Scheme 2.

A solution of compound **27** (100 mg, 0.05 mmol) was stirred in anhydrous CH_2Cl_2 (490 μL) at 0 °C. Et_3SiH (47 μL, 0.29 mmol) and TFAA (21 μL, 0.15 mmol) were then added to the reaction mixture and allowed it to stir for 10 min before adding TFA (15 μL, 0.20 mmol). After complete consumption of the starting material as seen from TLC, the reaction mixture was diluted with CH_2Cl_2 (5 mL). The solvent extraction was done to wash the CH_2Cl_2 layer sequentially with dd. H_2O (5 mL) and saturated $NaHCO_3$ solution (5 mL). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield the thick white crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to yield the pure product **23** as a white amorphous solid (80.4 mg, 80%). R_f 0.40 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −7.21 (c 2.08, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (dd, J = 15.1, 7.8 Hz, 4H, Ar-H), 7.72 (d, J = 7.8 Hz, 1H, Ar-H), 7.58−7.50 (m, 3H, Ar-H), 7.49−7.38 (m, 5H, Ar-H), 7.36−7.29 (m, 13H, Ar-H), 7.29−7.26 (m, 8H, Ar-H), 7.26−7.24 (m, 4H, Ar-H), 7.23−7.20 (m, 4H, Ar-H), 7.19−7.14 (m, 7H, Ar-H), 7.14−7.11 (m, 3H, Ar-H), 7.11−7.06 (m, 2H, Ar-H), 6.95 (d, J = 7.9 Hz, 2H, Ar-H), 6.55 (d, J = 6.9 Hz, 1H, N−H), 6.45 (d, J = 8.0 Hz, 1H, N−H), 5.63 (t, J = 9.0 Hz, 1H, H-2‴), 5.38 (t, J = 8.7 Hz, 1H, H-2′), 5.14 (d, J = 10.4 Hz, 1H, H-1), 5.03 (d, J = 11.5 Hz, 1H, CH_2Ph), 4.91 (d, J = 10.3 Hz, 1H, CH_2Ph), 4.79−4.70 (m, 2H, H-1″, CH_2 group of Nap), 4.65−4.55 (m, 4H, H-1‴, 2× CH_2Ph, CH_2 group of Nap), 4.51−4.42 (m, 3H, H-1′), 4.40 (d, J = 5.4 Hz, 1H), 4.39−4.36 (m, 2H), 4.36−4.30 (m, 3H), 4.30−4.18 (m, 3H, H-3, H-3″), 4.06−3.95 (m, 2H, H-4‴, O−H), 3.91 (d, J = 10 Hz, 1H, H-3′), 3.86 (s, 1H, H-4′), 3.80 (d, J = 11.05 Hz, 1H), 3.70 (d, J = 9.9 Hz, 1H), 3.66−3.58 (m, 3H), 3.57−3.38 (m, 10H, H-4, H-4″, H-3‴), 3.30 (dd, J = 9.2, 5.3 Hz, 1H), 3.27−3.18 (m, 1H, H-2″), 3.08−2.99 (m, 1H, H-2), 2.28 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 165.0 (C), 161.7 (C), 161.1 (C), 138.8 (C), 138.5 (C), 138.2 (C), 138.1 (C), 137.9 (C), 137.7 (C), 134.9 (C), 133.6 (CH), 133.4 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 130.2 (CH), 130.0 (CH), 129.9 (CH), 129.8 (C), 128.9 (CH), 128.7 (CH), 128.66 (CH), 128.63 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.09 (CH), 128.05 (CH), 127.9 (CH), 127.8 (CH), 127.79 (CH), 127.7 (CH), 127.6 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 101.1 (CH), 100.2 (CH), 99.4 (CH), 92.4 (C), 92.1 (C), 83.8 (CH), 81.7 (CH), 79.8 (CH), 79.5 (CH), 77.2 (CH), 76.3 (CH), 76.29 (CH), 76.0 (CH), 75.4 (CH), 75.0 (CH_2), 74.9 (CH_2), 74.87 (CH_2), 74.1 (CH), 73.9 (CH), 73.74 (CH_2), 73.72 (CH_2), 73.6 (CH_2), 73.5 (CH_2), 73.1 (CH), 72.5 (CH), 72.1 (CH), 72.0 (CH_2), 70.0 (CH_2), 69.5 (CH), 69.4 (CH_2), 68.7 (CH_2), 68.5 (CH_2), 59.0 (CH), 57.3 (CH), 21.3 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{109}H_{107}Cl_6N_2O_{22}S$ $[M + H]^+$, 2041.5103; found, 2041.5178.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-6-O-tert-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**24**).* A solution of **8** (79 mg, 0.066 mmol) and **12** (50 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (1 mL) was stirred with 3 Å pulverized molecular sieves (130 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (15 mg, 0.066 mmol) and TMSOTf (1.8 μL, 0.01 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the product **24** (26 mg, 25%) as a white amorphous solid and donor **8** recovered (29 mg, 37%) as a glassy solid. R_f 0.33 (EtOAc/toluene = 1/8, v/v); $[\alpha]_D^{20}$ −13.04 (c 1.15, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (dd, J = 16.8, 7.3 Hz, 4H, Ar-H), 7.71 (d, J = 7.4 Hz, 1H, Ar-H), 7.58−7.38 (m, 8H, Ar-H), 7.37−7.31 (m, 6H, Ar-H), 7.31−7.26 (m, 13H, Ar-H), 7.24−7.14 (m, 13H, Ar-H), 7.14−7.11 (m, 2H, Ar-H), 7.11−7.07 (m, 2H, Ar-H), 6.99 (d, J = 7.6 Hz, 2H, Ar-H), 6.50 (d, J = 6.7 Hz, 1H, N−H), 6.38 (d, J = 7.8 Hz, 1H, N−H), 5.63 (t, J = 8.9 Hz, 1H, H-2‴), 5.39 (t, J = 8.7 Hz, 1H, H-2′), 5.12 (d, J = 10.3 Hz, 1H, H-1), 5.03 (d, J = 11.4 Hz, 1H, CH_2Ph), 4.91 (d, J = 10.2 Hz, 1H, CH_2Ph), 4.74 (m, 2H, H-1″, CH_2 group of Nap), 4.65−4.51 (m, 4H, H-1‴, CH_2Ph, CH_2 group of Nap), 4.50−4.19 (m, 11H, H-1′, H-3, H-3″, 8× CH_2Ph), 3.99−3.96 (m, 1H, H-4‴), 3.95−3.89 (m, 3H, H-3′, H-6a, O−H), 3.88−3.84 (m, 1H, H-4′), 3.78−3.66 (m, 2H, H-6b, H-6a″), 3.65−3.58 (m, 2H, H-5′, H-5‴), 3.57−3.37 (m, 8H, H-4, H-4″, H-3‴, H-6a′, H-6b′, H-6b″, H-6a‴, H-6b‴), 3.36−3.28 (m, 2H, H-5, H-5″), 3.24−3.16 (m, 1H, H-2″), 3.03−2.94 (m, 1H, H-2), 2.30 (s, 3H, $PhCH_3$), 0.89 (s, 9H, TBS-t-Bu), 0.062 (s, 3H, TBS-CH_3), 0.054 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 164.9 (C), 161.6 (C), 161.1 (C), 138.7 (C), 138.5 (C), 138.4 (C), 138.1 (C), 138.08 (C), 137.9 (C), 137.7 (C), 134.9 (C), 133.5 (CH), 133.2 (CH), 133.16 (C), 133.1 (C), 130.2 (CH), 130.0 (CH), 129.9 (CH), 129.8 (C), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.58 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.08 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.77 (CH), 127.7 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 101.1 (CH), 100.2 (CH), 99.3 (CH), 92.3 (C), 92.2 (C), 83.8 (CH), 81.7 (CH), 80.9 (CH), 79.5 (CH), 77.2 (CH), 76.3 (CH), 76.0 (CH), 75.5 (CH), 74.94 (CH_2), 74.9 (2× CH_2), 74.1 (CH), 73.8 (CH), 73.72 (CH_2), 73.7 (CH_2), 73.6 (CH_2), 73.1 (CH), 72.5 (CH), 72.1 (CH), 72.0 (CH_2), 69.3 (CH_2), 69.1 (CH), 68.6 (CH_2), 68.4 (CH_2), 63.1 (CH_2), 59.0 (CH), 57.3 (CH), 26.1 (CH_3), 21.3 (CH_3), 18.6 (C),

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−5.0 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{108}H_{115}Cl_6N_2O_{22}SSi$ $[M + H]^+$, 2065.5548; found, 2065.5502.

4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**25**). A solution of **8** (77 mg, 0.064 mmol) and **13** (50 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (1 mL) was stirred with 3 Å pulverized molecular sieves (127 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (14 mg, 0.064 mmol) and TMSOTf (1.8 μL, 0.01 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the product **25** (62 mg, 60%) as a white amorphous foam. R_f 0.32 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −27.5 (*c* 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.5 Hz, 4H, Ar-H), 7.71 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.6−7.5 (m, 3H, Ar-H), 7.49−7.38 (m, 4H, Ar-H), 7.37−7.28 (m, 14H, Ar-H), 7.27−7.23 (m, 15H, Ar-H), 7.21−7.13 (m, 11H, Ar-H), 7.10−7.03 (m, 2H, Ar-H), 6.98−6.87 (m, 3H, Ar-H, N−H), 6.49 (d, *J* = 7.5 Hz, 1H, N−H), 5.62 (t, *J* = 8.9 Hz, 1H, H-2‴), 5.3 (t, *J* = 8.6 Hz, 1H, H-2′), 5.14 (d, *J* = 10.0 Hz, 1H, H-1), 5.03 (d, *J* = 11.45 Hz, 1H, CH_2Ph), 4.90 (d, *J* = 10.2 Hz, 1H, CH_2Ph), 4.81 (t, *J* = 9.2 Hz, 1H, H-4), 4.77−4.70 (m, 2H, H-1″, CH_2 group of Nap), 4.66 (d, *J* = 12 Hz, 1H, CH_2Ph), 4.61−4.22 (m, 16H, H-1′, H-1‴, H-3, H-3″, CH_2 group of Nap, 11× CH_2Ph), 3.97 (s, 1H, H-4‴), 3.9−3.84 (m, 2H, H-3′, H-4′), 3.72−3.33 (m, 14H, H-3‴, H-4″, H-5, H-5′, H-5″, H-5‴, H-6a, H-6b, H-6a′, H-6b′, H-6a″, H-6b″, H-6a‴, H-6b‴), 3.24−3.11 (m, 2H, H-2, H-2″), 2.26 (s, 3H, $PhCH_3$), 1.54 (s, 3H, $COCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 169.8 (C), 165.7 (C), 164.7 (C), 161.4 (C), 161.2 (C), 138.9 (C), 138.8 (C), 138.4 (C), 138.2 (C), 138.15 (C), 137.9 (C), 137.85 (C), 134.9 (C), 133.4 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 130.2 (CH), 130.0 (CH), 129.9 (CH), 128.7 (CH), 128.6 (CH), 128.59 (CH), 128.54 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.18 (CH), 128.1 (CH), 128.07 (CH), 128.0 (CH), 127.9 (CH), 127.88 (CH), 127.85 (CH), 127.8 (CH), 127.7 (CH), 127.68 (CH), 127.6 (CH), 127.5 (CH), 126.9 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 100.2 (CH), 99.5 (CH), 99.3 (CH), 92.7 (CH), 92.3 (CH), 84.6 (CH), 79.5 (CH), 78.0 (CH), 77.7 (CH), 76.7 (CH), 76.3 (CH), 76.2 (CH), 75.6 (CH), 75.2 (CH), 74.9 (CH_2), 74.88 (CH_2), 73.9 (CH), 73.8 (CH), 73.7 (CH_2), 73.6 (CH_2), 73.58 (CH_2), 73.5 (CH_2), 73.1 (CH), 72.5 (CH), 72.1 (CH), 72.0 (CH_2), 69.6 (CH_2), 69.2 (CH_2), 68.6 (CH), 68.59 (CH_2), 68.3 (CH_2), 59.2 (CH), 57.6 (CH), 21.3 (CH_3), 20.5 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{111}H_{109}Cl_6N_2O_{23}S$ $[M + H]^+$, 2083.5260; found, 2083.5278.

4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-acetyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**26**). A solution of **8** (63 mg, 0.052 mmol) and **14** (47 mg, 0.04 mmol) in anhydrous CH_2Cl_2 (0.8 mL) was stirred with 3 Å pulverized molecular sieves (109 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (12 mg, 0.052 mmol) and TMSOTf (1.5 μL, 0.008 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the product **26** (71 mg, 79%) as a white amorphous solid. R_f 0.32 (EtOAc/toluene = 1/10, v/v); $[\alpha]_D^{20}$ −12.37 (*c* 1.94, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 12.1, 7.5 Hz, 4H, Ar-H), 7.72 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.63 (dd, *J* = 5.8, 4.4 Hz, 4H, Ar-H), 7.56−7.50 (m, 3H, Ar-H), 7.49−7.31 (m, 6H, Ar-H), 7.36−7.26 (m, 22H, Ar-H), 7.25−7.22 (m, 6H, Ar-H), 7.21−7.13 (m, 11H, Ar-H), 7.11−7.04 (m, 2H, Ar-H), 6.92 (d, *J* = 7.6 Hz, 3H, Ar-H, N−H), 6.61 (d, *J* = 7.7 Hz, 1H, N−H), 5.62 (dd, J = 9.7, 8.2 Hz, 1H, H-2‴), 5.27 (dd, *J* = 10.0, 7.8 Hz, 1H, H-2′), 5.14 (d, *J* = 10.2 Hz, 1H, H-1), 5.03 (d, *J* = 11.4 Hz, 1H, CH_2Ph), 4.91 (d, *J* = 10.2 Hz, 1H, CH_2Ph), 4.79−4.64 (m, 4H, H-4, H-1″, CH_2Ph, CH_2 group of Nap), 4.63−4.22 (m, 14H, H-1′, H-1‴, H-3, H-3″, CH_2 group of Nap, 9× CH_2Ph), 4.00−3.93 (m, 1H, H-4‴), 3.91−3.83 (m, 2H, H-3′, H-4′), 3.71−3.33 (m, 14H, H-3‴, H-4″, H-5, H-5′, H-5″, H-5‴, H-6a, H-6b, H-6a′, H-6b′, H-6a″, H-6b″, H-6a‴, H-6b‴), 3.24−3.13 (m, 2H, H-2, H-2″), 2.26 (s, 3H, $PhCH_3$), 1.47 (s, 3H, $COCH_3$), 1.01 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 169.6 (C), 165.8 (C), 164.7 (C), 161.5 (C), 161.2 (C), 139.0 (C), 138.8 (C), 138.3 (C), 138.2 (C), 138.17 (C), 137.9 (C), 135.8 (CH), 134.9 (C), 133.4 (C), 133.3 (CH), 133.2 (C), 133.1 (C), 130.2 (CH), 130.0 (CH), 129.9 (CH), 129.8 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.26 (CH), 128.22 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.66 (CH), 127.5 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 100.2 (CH), 99.6 (CH), 99.3 (CH), 92.7 (C), 92.4 (C), 84.8 (CH), 79.6 (CH), 79.5 (CH), 77.7 (CH), 76.6 (CH), 76.3 (CH), 76.2 (CH), 75.7 (CH), 75.2 (CH), 75.0 (2xCH_2), 74.9 (CH_2), 73.86 (CH), 73.8 (CH), 73.7 (CH_2), 73.6 (CH_2), 73.5 (CH_2), 73.2 (CH), 72.6 (CH), 72.1 (CH), 72.0 (CH_2), 69.3 (CH_2), 68.6 (CH_2), 68.5 (CH_2), 68.2 (CH), 63.6 (CH_2), 59.2 (CH), 57.8 (CH), 26.9 (CH_3), 21.3 (CH_3), 20.4 (CH_3), 19.4 (C); HRMS (ESI-TOF) *m/z*: calcd for $C_{120}H_{121}Cl_6N_2O_{23}SSi$ $[M + H]^+$, 2231.5973; found, 2231.6005.

4-Methylphenyl (2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**27**). A solution of **8** (240 mg, 0.20 mmol) and **15** (150 mg, 0.155 mmol) in anhydrous CH_2Cl_2 (3.1 mL) was stirred with 3 Å pulverized molecular sieves (383 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (44 mg, 0.20 mmol) and TMSOTf (5.6 μL, 0.031 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the product **27** (237 mg, 75%) as a white amorphous foam. R_f 0.43 (EtOAc/toluene = 1/8, v/v); $[\alpha]_D^{20}$ −13.08 (*c* 3.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.84 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.70 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.56−7.53 (m, 1H, Ar-H), 7.52−7.49 (m, 2H, Ar-H), 7.46−7.37 (m, 5H, Ar-H), 7.36−7.30 (m, 6H, Ar-H), 7.29−7.26 (m, 10H, Ar-H), 7.26−7.23 (m, 9H, Ar-H), 7.22−7.19 (m, 7H, Ar-H), 7.16−7.10 (m, 7H, Ar-H), 7.09−7.05 (m, 2H, Ar-H), 7.04−7.01 (m, 2H, Ar-H), 6.86 (d, *J* = 6.7 Hz, 1H, N−H), 6.37 (d, *J* = 7.8 Hz, 1H, N−H), 5.63 (dd, *J* = 10.4, 7.6 Hz, 1H, H-2‴), 5.40−5.35 (m, 2H, H-2′, PhCH benzylidene), 5.28 (d, *J* = 10.3 Hz, 1H, H-1), 5.03 (d, *J* = 11.4 Hz, 1H, CH_2Ph), 4.87 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.74−4.68 (m, 2H, H-1″, CH_2 group of Nap), 4.67−4.63 (m, 2H, H-1′, CH_2Ph), 4.60−4.53 (m, 3H, H-1‴, CH_2Ph, CH_2 group of Nap), 4.52−4.47 (m, 2H, H-3, CH_2Ph), 4.46−4.42 (m, 2H, 2× CH_2Ph), 4.41−4.38 (m, 1H, CH_2Ph), 4.37−4.31 (m, 4H, H-5‴, 3× CH_2Ph), 4.30−4.25 (m, 2H, H-5″, CH_2Ph), 4.24−4.19 (m, 2H, H-3″, H-6a), 3.99 (s, 1H, H-4‴), 3.90−3.83 (m, 2H, H-3′, H-4′), 3.67−3.62 (m, 2H, H-6a″, H-6a‴), 3.61−3.57 (m, 2H, H-4, H-6b″), 3.54−3.51 (m, 1H, H-6b), 3.51−3.48 (m, 1H, H-3‴), 3.47−3.43 (m, 3H, H-4″, H-6a′, H-6b‴) 3.43−3.40 (m, 2H, H-5, H-5′), 3.39−3.34 (m, 1H, H-6b′), 3.22−3.10 (m, 2H, H-2, H-2″), 2.30 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.6 (C), 165.0 (C), 161.5 (C), 161.1 (C), 138.9 (C), 138.8 (C), 138.7 (C), 138.1 (C), 137.9 (C), 137.4 (C), 134.9 (C), 133.9 (CH), 133.4 (CH), 133.2 (CH), 133.1 (C), 133.0 (C), 130.04 (CH), 130.0 (CH), 129.97

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(CH), 129.7 (C), 128.9 (CH), 128.6 (CH), 128.57 (CH), 128.5 (CH), 128.45 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.13 (CH), 128.11 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.78 (CH), 127.7 (CH), 127.6 (CH), 127.5 (C), 127.4 (CH), 126.8 (CH), 126.2 (CH), 126.19 (CH), 126.1 (CH), 125.9 (CH), 100.9 (CH), 100.2 (CH), 99.8 (CH), 99.1 (CH), 92.3 (C), 92.26 (C), 84.4 (CH), 79.5 (CH), 79.2 (CH), 77.6 (CH), 76.33 (CH), 76.3 (CH), 76.2 (CH), 75.9 (CH), 75.2 (CH), 74.9 (CH_2), 74.8 (CH_2), 73.7 (CH_2), 73.6 (CH_2), 73.4 (CH_2), 73.0 (CH), 72.9 (CH), 72.0 (CH), 71.9 (CH_2), 70.7 (CH), 69.2 (CH_2), 68.9 (CH_2), 68.5 (CH_2), 68.1 (CH_2), 58.9 (CH), 57.9 (CH), 21.3 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{109}H_{105}Cl_6N_2O_{22}S$ $[M + H]^+$, 2039.4997; found, 2039.5017.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-benzoyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**28**).* A solution of **8** (54 mg, 0.045 mmol) and **16** (42 mg, 0.035 mmol) in anhydrous CH_2Cl_2 (0.7 mL) was stirred with 3 Å pulverized molecular sieves (96 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (10.1 mg, 0.045 mmol) and TMSOTf (1.25 μL, 0.007 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the product **28** (68 mg, 86%) as a white amorphous foam. R_f 0.51 (EtOAc/toluene = 1/10, v/v); $[\alpha]_D^{20}$ −17.46 (*c* 1.89, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.77 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.73−7.65 (m, 3H, Ar-H), 7.62−7.58 (m, 2H, Ar-H), 7.57−7.53 (m, 3H, Ar-H), 7.52−7.49 (m, 2H, Ar-H), 7.48−7.42 (m, 2H, Ar-H), 7.42−7.40 (m, 1H, Ar-H), 7.40−7.36 (m, 2H, Ar-H), 7.33−7.31 (m, 2H, Ar-H), 7.31−7.28 (m, 9H, Ar-H), 7.27−7.25 (m, 6H, Ar-H), 7.24−7.22 (m, 5H, Ar-H), 7.22−7.21 (m, 3H, Ar-H), 7.21−7.19 (m, 3H, Ar-H), 7.19−7.17 (m, 4H, Ar-H), 7.16−7.10 (m, 9H, Ar-H), 7.09−7.03 (m, 4H, Ar-H), 6.91 (dd, *J* = 17.7, 7.3 Hz, 3H, Ar-H, N−H), 6.53 (d, *J* = 7.6 Hz, 1H, N−H), 5.60 (dd, *J* = 9.8, 8.2 Hz, 1H, H-2‴), 5.32−5.22 (m, 2H, H-1, H-2′), 5.11−4.98 (m, 2H, H-4, CH_2Ph), 4.90 (d, *J* = 10.0 Hz, 1H, CH_2Ph), 4.76−4.61 (m, 3H, H-3, H-1′, CH_2 group of Nap), 4.60−4.19 (m, 13H, H-1′, H-1‴, H-3″, CH_2 group of Nap, 9× CH_2Ph), 4.14 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 3.98−3.91 (m, 1H, H-4‴), 3.86−3.75 (m, 2H, H-3′, H-4′), 3.73−3.34 (m, 12H, H-3‴, H-4″, H-5, H-5′, H-5″, H-5‴, H-6a, H-6b, H-6a″, H-6b″, H-6a‴, H-6b‴), 3.20−3.02 (m, 3H, H-2, H-2″, H-6a′), 2.83 (t, *J* = 8.1 Hz, 1H, H-6b′), 2.27 (s, 3H, $PhCH_3$), 0.97 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.8 (C), 165.1 (C), 164.7 (C), 161.7 (C), 161.2 (C), 139.2 (C), 138.8 (C), 138.4 (C), 138.2 (C), 138.1 (C), 138.0 (C), 137.9 (C), 135.7 (CH), 134.9 (C), 133.5 (CH), 133.3 (CH), 133.2 (CH), 133.1 (C), 132.7 (CH), 130.1 (C), 130.0 (CH), 129.9 (CH), 129.7 (CH), 128.7 (CH), 128.6 (CH), 128.58 (CH), 128.4 (CH), 128.3 (C), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 126.9 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 100.2 (CH), 100.1 (CH), 99.1 (CH), 92.6 (C), 92.3 (C), 84.2 (CH), 79.7 (CH), 79.5 (CH), 77.5 (CH), 76.4 (CH), 76.3 (CH), 76.2 (CH), 76.1 (CH), 75.1 (CH), 75.0 (CH_2), 74.9 (CH_2), 74.7 (CH_2), 73.8 (CH), 73.7 (CH_2), 73.5 (CH_2), 73.4 (CH), 73.3 (CH_2), 73.2 (CH), 72.6 (CH), 72.1 (CH), 72.0 (CH_2), 69.2 (CH_2), 69.1 (CH), 68.4 (CH_2), 67.8 (CH_2), 63.4 (CH_2), 59.2 (CH), 58.2 (CH), 26.9 (CH_3), 21.4 (CH_3), 19.3 (C); HRMS (ESI-TOF) *m/z*: calcd for $C_{125}H_{123}Cl_6N_2O_{23}SSi$ $[M + H]^+$, 2293.6132; found, 2293.6093.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4-O-tert-butyldimethylsilyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**29**).* A solution of **9** (45 mg, 0.037 mmol) and **13** (34 mg, 0.033 mmol) in anhydrous CH_2Cl_2 (670 μL) was stirred with 3 Å pulverized molecular sieves (79 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −60 °C, NIS (8.3 mg, 0.037 mmol) and TMSOTf (1.21 μL, 0.0068 mmol) were added to the reaction mixture. After 2.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/toluene (1/13, v/v) to yield the pure product **29** (45 mg, 65%) as a white amorphous solid.

Synthesis of 29 by Using Preactivation Method. For reaction details, please see Scheme S8. Ph_2SO (4.9 mg, 0.024 mmol) and TTBP (10.4 mg, 0.042 mmol) were added to a solution of **9** (45 mg, 0.037 mmol) in CH_2Cl_2 (617 μL) at rt under N_2. After 30 min of stirring at rt, the reaction mixture was cooled down to −60 °C, and Tf_2O (4.1 μL, 0.024 mmol) was added to the reaction solution. After 1 h of stirring at −60 °C, a solution of **13** (34 mg, 0.034 mmol) in CH_2Cl_2 (0.5 mL) was added to the reaction mixture at −60 °C. Then, TMSOTf (2.43 μL, 0.013 mmol) was added, and the reaction was stirred for 2 h. The reaction was quenched by dropwise addition of Et_3N at −60 °C, diluted with CH_2Cl_2 (5 mL), and filtered. Solvent extraction was then done to wash the CH_2Cl_2 layer with saturated $Na_2S_2O_3$ solution (10 mL) and saturated $NaHCO_3$ solution (10 mL). The filtrate was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a yellow viscous residue that was purified by column chromatography on silica gel with EtOAc/toluene (1/14, v/v) to yield pure **29** (41 mg, 58% yield) as a white amorphous solid. R_f 0.38 (EtOAc/toluene = 1/8, v/v); $[\alpha]_D^{20}$ −10.81 (*c* 0.74, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.83 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.70 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.55−7.47 (m, 4H, Ar-H), 7.43−7.39 (m, 2H, Ar-H), 7.39−7.36 (m, 3H, Ar-H), 7.36−7.33 (m, 1H, Ar-H), 7.33−7.29 (m, 8H, Ar-H), 7.29−7.24 (m, 16H, Ar-H), 7.22−7.15 (m, 8H, Ar-H), 7.12−7.07 (m, 2H, Ar-H), 7.02 (d, *J* = 7.1 Hz, 1H, N−H), 6.93 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.44 (d, *J* = 8.1 Hz, 1H, N−H), 5.60 (dd, *J* = 9.6, 8.4 Hz, 1H, H-2‴), 5.30 (dd, *J* = 9.8, 8.0 Hz, 1H, H-2′), 5.16 (d, *J* = 10.1 Hz, 1H, H-1), 5.01 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.83 (t, *J* = 9.4 Hz, 1H, H-4), 4.76−4.68 (m, 3H, H-1″, H-1‴, CH_2 group of Nap), 4.57−4.36 (m, 12H, H-1′, H-3, CH_2 group of Nap, 9xCH_2Ph), 4.31 (d, *J* = 11.9 Hz, 1H, CH_2Ph), 4.16 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 3.94 (d, *J* = 1.5 Hz, 1H, H-4‴), 3.89 (t, *J* = 5.9 Hz, 1H, H-3″), 3.81 (dd, *J* = 10.1, 2.5 Hz, 1H, H-3′), 3.77−3.74 (m, 1H, H-4′), 3.71−3.32 (m, 14H, H-2″, H-3‴, H-4″, H-5, H-5′, H-5″, H-5‴, H-6a, H-6b, H-6a′, H-6b′, H-6a″, H-6a‴, H-6b‴), 3.27 (td, *J* = 10.1, 7.2 Hz, 1H, H-2), 3.18 (dd, *J* = 9.1, 4.9 Hz, 1H, H-6b″), 2.25 (s, 3H, $PhCH_3$), 1.49 (s, 3H, $COCH_3$), 0.76 (s, 9H, TBS-*t*-Bu), 0.05 (s, 3H, TBS-CH_3), −0.05 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 169.8 (C), 165.6 (C), 164.5 (C), 161.4 (C), 161.2 (C), 138.8 (C), 138.7 (C), 138.4 (C), 138.2 (C), 137.9 (C), 135.0 (C), 133.4 (CH), 133.3 (CH), 133.2 (C), 133.1 (C), 133.0 (CH), 130.3 (CH), 130.0 (C), 129.9 (CH), 128.7 (CH), 128.66 (CH), 128.64 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.28 (CH), 128.1 (CH), 128.07 (CH), 128.0 (CH), 127.97 (CH), 127.9 (CH), 127.8 (CH), 127.73 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 126.8 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 100.0 (CH), 99.7 (CH), 99.2 (CH), 92.7 (C), 92.2 (C), 84.9 (CH), 79.8 (CH), 78.5 (CH), 78.4 (CH), 78.0 (CH), 76.9 (CH), 76.2 (CH), 75.6 (CH), 74.8 (CH_2), 74.6 (CH_2), 74.0 (CH), 73.7 (CH_2), 73.6 (CH_2), 73.5 (CH), 73.4 (CH_2), 73.2 (CH), 72.3 (CH), 72.1 (CH_2), 71.6 (CH), 70.0 (CH_2), 69.99 (CH), 69.7 (CH_2), 68.9 (CH_2), 68.5 (CH_2), 68.47 (CH), 58.3 (CH), 57.4 (CH), 26.2 (CH_3), 21.3 (CH_3), 20.4 (CH_3), 18.0 (C), −3.7 (CH_3), −4.8 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{110}H_{117}Cl_6N_2O_{23}SSi$ $[M + H]^+$, 2107.5655; found, 2107.5675.

4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4-O-tert-butyldimethylsilyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-benzoyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-tri-

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*chloroacetamido-1-thio-β-D-glucopyranoside (**30**).* A solution of **9** (55 mg, 0.045 mmol) and **16** (50 mg, 0.041 mmol) in anhydrous CH_2Cl_2 (0.82 mL) was stirred with 3 Å pulverized molecular sieves (105 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −60 °C, NIS (10.15 mg, 0.045 mmol) and TMSOTf (1.48 μL, 0.008 mmol) were added to the reaction mixture. After 4.5 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered through filter paper. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a yellow viscous residue that was subjected to column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v, with 1% Et_3N) to yield the product **30** (49 mg, 52%) as a white amorphous solid. R_f 0.43 (EtOAc/hexanes = 1/3, v/v); $[\alpha]_D^{20}$ −10.94 (*c* 1.46, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.85−7.82 (m, 2H, Ar-H), 7.81−7.77 (m, 2H, Ar-H), 7.70 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.66−7.63 (m, 2H, Ar-H), 7.59−7.58 (m, 1H, Ar-H), 7.58−7.57 (m, 1H, Ar-H), 7.56−7.55 (m, 1H, Ar-H), 7.55−7.54 (m, 1H, Ar-H), 7.53−7.48 (m, 3H, Ar-H), 7.43−7.39 (m, 3H, Ar-H), 7.39−7.35 (m, 3H, Ar-H), 7.33−7.32 (m, 2H, Ar-H), 7.32−7.30 (m, 4H, Ar-H), 7.30−7.28 (m, 3H, Ar-H), 7.28−7.27 (m, 1H, Ar-H), 7.27−7.26 (m, 2H, Ar-H), 7.26−7.25 (m, 3H, Ar-H), 7.23−7.22 (m, 5H, Ar-H), 7.22−7.21 (m, 3H, Ar-H), 7.20−7.19 (m, 4H, Ar-H), 7.18−7.17 (m, 3H, Ar-H), 7.16−7.15 (m, 3H, Ar-H), 7.15−7.14 (m, 2H, Ar-H), 7.13−7.10 (m, 2H, Ar-H), 7.03−7.00 (m, 2H, Ar-H), 6.95−6.91 (m, 3H, Ar-H, N−H), 6.38 (d, *J* = 8.1 Hz, 1H, N−H), 5.58 (dd, *J* = 9.9, 8.0 Hz, 1H, H-2‴), 5.30−5.24 (m, 2H, H-1, H-2′), 5.05 (t, *J* = 9.2 Hz, 1H, H-4), 5.00 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.71 (d, *J* = 12.4 Hz, 1H, CH_2 group of Nap), 4.69−4.64 (m, 2H, H-1″, H-1‴), 4.64−4.60 (m, 1H, H-3), 4.56−4.49 (m, 3H, H-1′, CH_2Ph, CH_2 group of Nap), 4.47−4.35 (m, 5H, 5xCH_2Ph), 4.23 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.12 (dd, *J* = 17.7, 12.0 Hz, 2H, 2× CH_2Ph), 3.92 (d, *J* = 2.5 Hz, 1H, H-4‴), 3.86 (t, *J* = 6.4 Hz, 1H, H-3″), 3.77 (dd, *J* = 10.2, 2.9 Hz, 1H, H-3′), 3.70−3.33 (m, 13H, H-4′, H-5, H-4″, H-3″, H-2″, H-5′, H-5″, H-5‴, H-6a, H-6b, H-6a″, H-6a‴, H-6b‴), 3.21 (td, *J* = 10.0, 7.1 Hz, 1H, H-2), 3.09−3.01 (m, 2H, H-6a′, H-6b″), 2.77 (dd, *J* = 9.1, 6.9 Hz, 1H, H-6b′), 2.27 (s, 3H, $PhCH_3$), 0.97 (s, 9H, TBDPS-*t*-Bu), 0.73 (s, 9H, TBS-*t*-Bu), 0.04 (s, 3H, TBS-CH_3), −0.08 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.6 (C), 165.1 (C), 164.5 (C), 161.6 (C), 161.1 (C), 139.0 (C), 138.8 (C), 138.4 (C), 138.1 (C), 137.9 (C), 135.7 (CH), 135.1 (C), 133.5 (CH), 133.3 (C), 133.25 (C), 133.2 (C), 133.16 (CH), 133.1 (C), 133.06 (CH), 132.7 (CH), 130.1 (C), 130.0 (CH), 129.9 (C), 129.7 (CH), 128.7 (CH), 128.6 (CH), 128.57 (CH), 128.5 (CH), 128.4 (CH), 128.39 (CH), 128.37 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.05 (CH), 128.0 (CH), 127.9 (CH), 127.74 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 126.8 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 99.8 (CH), 99.7 (CH), 99.6 (CH), 92.7 (C), 92.2 (C), 84.5 (CH), 79.8 (CH), 78.2 (CH), 78.1 (CH), 76.7 (CH), 76.2 (CH), 76.1 (CH), 74.8 (CH_2), 74.6 (CH_2), 73.7 (CH_2), 73.6 (CH), 73.5 (CH), 73.4 (CH_2), 73.3 (CH_2), 73.2 (CH), 72.5 (CH), 72.1 (CH_2), 71.6 (CH), 70.1 (CH), 69.9 (CH_2), 68.9 (CH), 68.6 (CH_2), 68.0 (CH_2), 63.5 (CH_2), 58.4 (CH), 58.1 (CH), 26.9 (CH_3), 26.2 (CH_3), 21.4 (CH_3), 19.3 (C), 18.0 (C), −3.6 (CH_3), −4.8 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{124}H_{131}Cl_6N_2O_{23}SSi_2$ $[M + H]^+$, 2317.6527; found, 2317.6535.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**31**).* For reaction details, please see Scheme 2. To a solution of compound **27** (362 mg, 0.18 mmol) in a 2.4:1 (v/v) mixture of CH_2Cl_2 (3.13 mL) and dd. H_2O (1.3 mL), DDQ (60.4 mg, 0.27 mmol) was added at rt. After 1.5 h, an additional 30 mg (0.13 mmol) of DDQ was added, and let the reaction stir for another 1 h. Saturated $NaHCO_3$ solution (1 mL) was then slowly added to the reaction mixture under the ice bath to quench the reaction. Solvent extraction was done to wash the CH_2Cl_2 layer with saturated $NaHCO_3$ solution (10 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield the yellow viscous crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to yield the desired pure product **31** (203 mg, 60%) as a white amorphous foam. R_f 0.33 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −20.25 (*c* 0.79, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.88 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.43 (t, *J* = 7.3 Hz, 2H, Ar-H), 7.37−7.32 (m, 4H, Ar-H), 7.32−7.29 (m, 4H, Ar-H), 7.29−7.27 (m, 4H, Ar-H), 7.25−7.21 (m, 10H, Ar-H), 7.21−7.15 (m, 10H, Ar-H), 7.15−7.10 (m, 4H, Ar-H), 7.04 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.87 (d, *J* = 6.8 Hz, 1H, N−H), 6.50 (d, *J* = 8.0 Hz, 1H, N−H), 5.44−5.37 (m, 2H, H-2′, PhCH benzylidene), 5.30 (d, *J* = 10.3 Hz, 1H, H-1), 5.22 (t, *J* = 8.8 Hz, 1H, H-2‴), 4.85 (d, *J* = 10.2 Hz, 1H, CH_2Ph), 4.74−4.66 (m, 5H, H-1′, H-1″, H-1‴, 2× CH_2Ph), 4.62 (d, *J* = 11.6 Hz, 1H, CH_2 × Ph), 4.53−4.19 (m, 10H, H-3, H-3″, 8× CH_2Ph), 3.94−3.89 (m, 1H, H-3′), 3.89−3.83 (m, 2H, H-4′, H-4‴), 3.67−3.41 (m, 15H, H-4, H-4″, H-3‴, H-5, H-5′, H-5″, H-5‴, H-6a, H-6b, H-6a′, H-6b′, H-6a″, H-6b″, H-6a‴, H-6b‴), 3.38−3.32 (m, 1H, H-2″), 3.20−3.12 (m, 1H, H-2), 2.44 (d, *J* = 9.3 Hz, 1H, O−H), 2.31 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 167.1 (C), 165.0 (C), 161.5 (C), 161.3 (C), 138.9 (C), 138.8 (C), 138.2 (C), 138.1 (C), 138.0 (C), 137.9 (C), 137.7 (C), 137.4 (C), 133.9 (CH), 133.5 (CH), 133.4 (CH), 130.1 (CH), 130.0 (CH), 129.7 (C), 129.6 (C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.58 (CH), 128.52 (CH), 128.48 (CH), 128.40 (CH), 128.3 (CH), 128.14 (CH), 128.10 (CH), 128.0 (CH), 127.9 (CH), 127.87 (CH), 127.83 (CH), 127.75 (CH), 127.70 (CH), 127.5 (CH), 127.4 (C), 126.2 (CH), 100.9 (CH), 99.7 (CH), 99.2 (CH), 92.4 (C), 92.2 (C), 84.3 (CH), 79.2 (CH), 77.7 (CH), 76.7 (CH), 76.3 (CH), 76.1 (CH), 75.9 (CH), 75.7 (CH_2), 75.3 (CH), 74.8 (CH_2), 74.7 (CH_2), 74.4 (CH), 73.7 (CH_2), 73.6 (CH), 73.57 (CH_2), 73.5 (CH), 73.4 (CH_2), 73.3 (CH), 73.0 (CH), 70.7 (CH), 69.1 (CH_2), 68.9 (CH_2), 68.5 (CH_2), 67.9 (CH_2), 58.8 (CH), 57.9 (CH), 21.3 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{98}H_{96}Cl_6N_2O_{22}SNa$ $[M + Na]^+$, 1921.4184; found, 1921.4174.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**32**).* A solution of **8** (37 mg, 0.031 mmol) and **31** (45 mg, 0.024 mmol) in anhydrous CH_2Cl_2 (474 μL) was stirred with 3 Å pulverized molecular sieves (85 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (7 mg, 0.031 mmol) was added to the reaction mixture, followed by the addition of TMSOTf (0.9 μL, 0.005 mmol). After 1 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield the yellow residue that was purified by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to yield pure hexasaccharide **32** (49 mg, 70% yield) as a white amorphous foam and oxazoline **33** (6.1 mg, 19% w.r.t. donor **8**) as a glassy solid. R_f 0.33 (EtOAc/toluene = 1/8, v/v); $[\alpha]_D^{20}$ −32.53 (*c* 0.83, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (t, *J* = 8.1 Hz, 4H, Ar-H), 7.84 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.70 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.56−7.47 (m, 3H, Ar-H), 7.44−7.37 (m, 4H, Ar-H), 7.35−7.29 (m, 6H, Ar-H), 7.27−7.23 (m, 21 H, Ar-H), 7.22−7.21 (m, 4H, Ar-H), 7.21−7.17 (m, 11H, Ar-H), 7.17−7.12 (m, 9H, Ar-H), 7.12−7.08 (m, 5H, Ar-H), 7.08−7.01 (m, 6H, Ar-H), 6.86 (d, *J* = 6.6 Hz, 1H, N−H), 6.38 (dd, *J* = 15.0, 7.8 Hz, 2H, N−H), 5.62 (t, *J* = 8.9 Hz, 1H, H-2‴″), 5.44 (t, *J* = 9.0 Hz, 1H, H-2‴), 5.40−5.32 (m, 2H, H-2′, PhCH benzylidene), 5.31−5.23 (m, 1H, H-1), 5.02 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.88 (d, *J* = 10.1 Hz, 1H, CH_2Ph), 4.78 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.75−4.59 (m, 6H, H-1′, H-1″, H-1‴′, CH_2 group of Nap), 4.58−4.39 (m, 9H, H-1‴, H-1‴″, H-3, 5× CH_2Ph, CH_2 group of Nap), 4.37−4.32 (m, 3H), 4.32−4.21 (m, 8H, H-3‴′), 4.21−4.13 (m, 2H, H-3″), 3.97 (s, 1H, H-4‴″), 3.90 (s, 1H, H-4‴), 3.88−3.81 (m, 2H, H-3′, H-3‴), 3.79 (s, 1H, H-4′), 3.66−3.53 (m, 6H, H-4, H-5‴′), 3.52−3.38 (m, 12H, H-3‴″, H-4″, H-4‴′), 3.38−3.34 (m, 2H), 3.33−3.28 (m, 1H), 3.12 (m, 3H, H-2,

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H-2″, H-2‴′), 2.31 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 165.3 (C), 165.0 (C), 161.5 (C), 161.1 (C), 161.0 (C), 139.1 (C), 139.0 (C), 138.9 (C), 138.8 (C), 138.2 (C), 138.1 (C), 138.09 (C), 138.0 (C), 137.96 (C), 137.4 (C), 134.93 (C), 133.89 (CH), 133.4 (CH), 133.2 (CH), 133.15 (C), 133.08 (C), 130.1 (CH), 130.0 (CH), 129.98 (CH), 129.8 (C), 129.7 (C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.56 (CH), 128.5 (CH), 128.4 (CH), 128.23 (CH), 128.21 (CH), 128.17 (CH), 128.1 (CH), 128.05 (CH), 127.98 (CH), 127.9 (CH), 127.86 (CH), 127.81 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 100.9 (CH), 100.4 (CH), 100.3 (CH), 99.8 (CH), 99.2 (CH), 99.0 (CH), 92.4 (C), 92.3 (C), 92.28 (C), 84.4 (CH), 79.5 (CH), 79.2 (CH), 77.5 (CH), 76.8 (CH), 76.4 (CH), 76.37 (CH), 76.2 (CH), 75.9 (CH), 75.4 (CH), 75.2 (CH), 75.1 (CH_2), 74.94 (CH_2), 74.90 (CH_2), 74.8 (CH_2), 74.7 (CH_2), 73.8 (CH), 73.7 (CH_2), 73.66 (CH_2), 73.5 (CH_2), 73.4 (CH_2), 73.1 (CH), 73.0 (CH), 72.7 (CH), 72.1 (CH), 71.9 (CH_2), 70.8 (CH), 69.2 (CH_2), 69.0 (CH_2), 68.9 (CH_2), 68.6 (CH_2), 68.3 (CH_2), 68.2 (CH_2), 59.2 (CH), 59.0 (CH), 58.0 (CH), 21.4 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{158}H_{151}Cl_9N_3O_{33}S$ $[M - H]^{-1}$, 2970.7146; found, 2970.7103.

*2-Trichloromethyl-3-O-(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-4,6-di-O-benzyl-1,2-dideoxy-α-D-glucopyrano-[2,1-d]-2-oxazoline (**33**).* A solution of compound **8** (250 mg, 0.21 mmol) in dry CH_2Cl_2 (4.20 mL) was stirred with 3 Å powdered molecular sieves (500 mg) at rt under N_2 for 30 min. NIS (56.3 mg, 0.25 mmol) and TMSOTf (7.6 μL, 0.042 mmol) were sequentially added to the reaction mixture after cooling to −50 °C. The reaction was quenched after 30 min by dropwise addition of Et_3N at −50 °C. Thereafter, the reaction mixture was diluted with CH_2Cl_2 (5 mL), filtered, and extracted with saturated $Na_2S_2O_3$ solution (10 mL). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to afford the viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/5, v/v) to yield the pure product **33** (206 mg, 92%) as a white amorphous foam. R_f 0.35 (EtOAc/hexanes = 1/4, v/v, run two times); $[\alpha]_D^{20}$ +25.75 (*c* 1.32, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): 7.96 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.73 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.62 (s, 1H, Ar-H), 7.60−7.53 (m, 3H, Ar-H), 7.46−7.36 (m, 6H, Ar-H), 7.34−7.24 (m, 14H, Ar-H), 7.21−7.15 (m, 5H, Ar-H), 5.86 (d, *J* = 7.3 Hz, 1H, H-1), 5.66 (t, *J* = 9.0 Hz, 1H, H-2′), 5.05 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.81 (d, *J* = 12.5 Hz, 1H, CH_2 group of Nap), 4.76−4.66 (m, 3H, H-1′, 2× CH_2Ph), 4.62 (d, *J* = 12.5 Hz, 1H, CH_2 group of Nap), 4.49−4.42 (m, 3H, H-3, 2× CH_2Ph), 4.42−4.36 (m, 3H, 3× CH_2Ph), 4.19 (d, *J* = 6.0 Hz, 1H, H-2), 4.07 (d, *J* = 1.8 Hz, 1H, H-4′), 3.73 (d, *J* = 5.9 Hz, 1H, H-4), 3.69 (dd, *J* = 10.1, 2.3 Hz, 1H, H-3′), 3.66−3.50 (m, 6H, H-5, H-5′, H-6a, H-6b, H-6a′, H-6b′); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.2 (C), 162.9 (C), 138.6 (C), 138.2 (C), 138.0 (C), 137.8 (C), 135.2 (C), 133.4 (CH), 133.36 (C), 133.2 (C), 130.1 (C), 129.9 (CH), 128.7 (CH), 128.5 (CH), 128.46 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 126.8 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 104.8 (CH), 100.9 (CH), 86.5 (C), 79.8 (CH), 75.9 (CH), 74.9 (CH_2), 74.7 (CH), 74.1 (CH), 73.8 (CH_2), 73.4 (CH_2), 72.8 (CH), 72.0 (CH_2), 71.92 (CH), 71.90 (CH_2), 71.3 (CH), 69.6 (CH_2), 68.7 (CH_2), 66.6 (CH); HRMS (ESI-TOF) *m/z*: calcd for $C_{60}H_{57}Cl_3NO_{11}$ $[M + H]^+$, 1074.2981; found, 1074.2981.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-benzoyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**34**).* A solution of **23** (60 mg, 0.03 mmol) and **16** (43 mg, 0.035 mmol) in dry CH_2Cl_2 (590 μL) was stirred with 3 Å pulverized molecular sieves (103 mg) at rt for 30 min under N_2. After cooling to −50 °C, NIS (6.6 mg, 0.03 mmol) and TMSOTf (1.1 μL, 0.006 mmol) were sequentially added to the reaction mixture. After 3 h, the reaction was quenched by dropwise addition of Et_3N at −50 °C. The reaction mixture was diluted with CH_2Cl_2 (5 mL), filtered, and washed with saturated $Na_2S_2O_3$ solution (10 mL). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/3, v/v) to obtain the hexasaccharide **34** (25 mg, 28%) as a glassy solid and unreacted acceptor **16** (24 mg, 55% w.r.t the initial amount of acceptor **16** taken) as a glassy solid. R_f 0.24 (EtOAc/toluene = 1/8, v/v); $[\alpha]_D^{20}$ −16.52 (*c* 1.15, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.84 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.77 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.6 Hz, 3H, Ar-H), 7.60 (d, *J* = 7.0 Hz, 2H, Ar-H), 7.57−7.53 (m, 3H, Ar-H), 7.51 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.47−7.37 (m, 7H, Ar-H), 7.33−7.26 (m, 20H, Ar-H), 7.25−7.20 (m, 16H, Ar-H), 7.20−7.11 (m, 20H, Ar-H), 7.11−7.05 (m, 5H, Ar-H), 6.92 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.78 (d, *J* = 6.8 Hz, 1H, N−H), 6.40 (d, *J* = 8.2 Hz, 1H, N−H), 6.24 (d, *J* = 6.8 Hz, 1H, N−H), 5.61 (dd, *J* = 10.0, 8.1 Hz, 1H, H-2‴″), 5.35 (t, *J* = 8.4 Hz, 1H, H-2‴), 5.28−5.21 (m, 2H, H-1, H-2′), 5.09−5.00 (m, 2H, H-4), 4.92−4.85 (m, 2H, H-1″), 4.72 (d, *J* = 12.3 Hz, 1H), 4.67 (d, *J* = 8.0 Hz, 1H, H-1‴′), 4.65−4.59 (m, 3H, H-3), 4.59−4.53 (m, 3H, H-1‴″), 4.52−4.46 (m, 2H, H-1′), 4.45−4.41 (m, 3H), 4.40−4.36 (m, 1H), 4.36−4.32 (m, 3H), 4.32−4.30 (m, 2H), 4.30−4.27 (m, 2H, H-1‴), 4.26−4.19 (m, 2H, H-3‴′), 4.15 (d, *J* = 12.0 Hz, 1H), 4.04 (dd, *J* = 9.8, 7.9 Hz, 1H, H-3″), 3.98−3.94 (m, 2H, H-4‴″), 3.90 (d, *J* = 2.5 Hz, 1H, H-4′), 3.83−3.72 (m, 4H, H-3′, H-3‴), 3.71−3.62 (m, 4H, H-5), 3.38 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.55−3.50 (m, 2H), 3.50−3.46 (m, 3H, H-3‴″), 3.45−3.36 (m, 6H, H-4‴′), 3.36−3.29 (m, 2H, H-4″), 3.22 (td, *J* = 9.7, 6.6 Hz, 1H, H-2‴′), 3.11 (td, *J* = 9.8, 7.2 Hz, 1H, H-2), 3.04 (d, *J* = 9.0, 5.6 Hz, 1H), 2.81 (t, *J* = 8.2 Hz, 1H), 2.72 (td, *J* = 8.5, 7.0 Hz, 1H, H-2″), 2.27 (s, 3H, $PhCH_3$), 0.97 (s, 9H, TBDPS-*t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.8 (C), 165.0 (C), 164.9 (C), 164.8 (C), 161.7 (C), 161.6 (C), 161.1 (C), 139.3 (C), 138.8 (C), 138.6 (C), 138.4 (C), 138.1 (C), 137.9 (C), 137.8 (C), 135.7 (CH), 134.9 (C), 133.6 (CH), 133.3 (C), 133.2 (CH), 133.1 (CH), 132.7 (CH), 130.2 (CH), 130.1 (CH), 130.0 (CH), 129.9 (C), 129.7 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 101.0 (CH), 100.2 (CH), 99.4 (CH), 98.8 (CH), 92.6 (C), 92.4 (C), 91.7 (C), 84.1 (CH), 80.0 (CH), 79.7 (CH), 79.5 (CH), 78.3 (CH), 77.4 (CH), 77.1 (CH), 76.6 (CH), 76.3 (CH), 75.9 (CH), 75.4 (CH), 75.2 (CH), 75.0 (CH_2), 74.9 (CH_2), 74.7 (CH_2), 74.0 (CH), 73.8 (CH), 73.7 (CH_2), 73.67 (CH_2), 73.5 (CH_2), 73.3 (CH, CH_2), 73.2 (CH), 72.3 (CH), 72.1 (CH), 72.05 (CH_2), 69.9 (CH_2), 69.6 (CH), 69.3 (CH_2), 69.1 (CH), 68.5 (CH_2), 67.7 (CH_2), 63.5 (CH_2), 59.3 (CH), 58.9 (CH), 58.4 (CH), 53.6 (C), 26.9 (CH_3), 21.4 (CH_3), 19.3 (C); HRMS (ESI-TOF) *m/z*: calcd for $C_{167}H_{166}Cl_9N_3O_{34}SSi$ $[M + 2H]^{2+}$, 1568.9013; found, 1568.9015.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4-O-benzoyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**34a**).* A solution of **22** (55 mg, 0.026 mmol) and **16** (38 mg, 0.031 mmol) in dry CH_2Cl_2 (516 μL) was stirred with 3 Å pulverized molecular sieves (93 mg) at rt for 30 min under N_2. After cooling to −70 °C, NIS (5.8 mg, 0.026 mmol) and TMSOTf (0.93 μL, 0.0052 mmol) were sequentially added to the reaction mixture. After 1 h of stirring at −70 °C, the temperature was raised to −60 °C and stirred for another 1 h. This was followed by increase in temperature to −50 °C, and stirring was continued for 2 h more at −50 °C. Then, the reaction was quenched by dropwise addition of Et_3N at −50 °C. The reaction mixture was diluted with CH_2Cl_2 (5 mL), filtered, and washed with saturated $Na_2S_2O_3$ solution (10 mL). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/

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hexanes (1/5 to 1/3, v/v) to obtain the hexasaccharide **34a** (44 mg, 52%) as a glassy solid, unreacted acceptor **16** (16 mg, 41% w.r.t the initial amount of acceptor **16** taken) as a glassy solid and recovered donor **22** (12 mg, 22%) as a glassy solid. R_f 0.17 (EtOAc/hexanes = 1/3, v/v); $[\alpha]_D^{20}$ −21.88 (*c* 3.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 16.6, 7.7 Hz, 4H, Ar-H), 7.76 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.67 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.59 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.57−7.53 (m, 3H, Ar-H), 7.52−7.49 (m, 2H, Ar-H), 7.45−7.35 (m, 6H, Ar-H), 7.33−7.25 (m, 22H, Ar-H), 7.23−7.08 (m, 39H, Ar-H), 7.08−7.03 (m, 6H, Ar-H), 6.92 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.85 (d, *J* = 6.4 Hz, 1H, N−H), 6.53 (d, *J* = 7.8 Hz, 1H, N−H), 6.48 (d, *J* = 7.6 Hz, 1H, N−H), 5.64−5.57 (m, 1H, H-2‴″), 4.46−5.39 (m, 1H, H-2‴), 5.30−5.21 (m, 2H, H-1, H-2′), 5.08−4.99 (m, 2H, H-4, CH_2Ph), 4.89 (d, *J* = 10.1 Hz, 1H, CH_2Ph), 4.81 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.74−4.10 (m, 27H, H-1′, H-1″, H-1‴, H-1‴′, H-1‴″, H-3, H-3″, H-3‴′, 17× CH_2Ph, 2× CH_2 group of Nap), 3.94 (s, 1H, H-4‴″), 3.86 (s, 1H, H-4‴), 3.84−3.77 (m, 2H, H-3′, H-3‴), 3.73 (s, 1H, H-4′), 3.70−3.28 (m, 19H, H-3‴″, H-4″, H-4‴′, H-5, H-5′, H-5″, H-5‴, H-5‴′, H-5‴″, H-6a, H-6b, H-6a″, H-6b″, H-6a‴, H-6b‴, H-6a‴′, H-6b‴′, H-6a‴″, H-6b‴″), 3.24−3.17 (m, 1H, H-2‴′), 3.16−3.09 (m, 1H, H-2), 3.08−2.99 (m, 2H, H-2″, H-6a′), 2.81 (t, *J* = 8.1 Hz, 1H, H-6b′), 2.27 (s, 3H, $PhCH_3$), 0.97 (s, 9H, TBDPS-*t*-Bu); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.8 (C), 165.3 (C), 165.1 (C), 164.6 (C), 161.7 (C), 161.1 (C), 139.2 (C), 138.8 (C), 138.4 (C), 138.2 (C), 138.2 (C), 138.0 (C), 137.99 (C), 137.92 (C), 135.7 (CH), 134.95 (C), 133.5 (CH), 133.3 (C), 133.2 (CH), 133.1 (C), 132.7 (CH), 130.1 (C), 130.1 (CH), 129.99 (CH), 129.91 (CH), 129.85 (C), 129.7 (CH), 128.7 (CH), 128.64 (CH), 128.59 (CH), 128.51 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.04 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 126.9 (CH), 126.3 (CH), 126.1 (CH), 125.97 (CH), 100.4 (CH), 100.2 (CH), 100.1 (CH), 99.3 (CH), 99.1 (CH), 92.6 (C), 92.4 (C), 84.2 (CH), 79.7 (CH), 79.5 (CH), 77.5 (CH), 77.3 (CH), 76.9 (CH), 76.4 (CH), 76.2 (CH), 76.1 (CH), 75.2 (CH), 75.2 (CH), 75.1 (CH_2), 74.95 (CH_2), 74.9 (CH_2), 74.7 (CH_2), 73.9 (CH), 73.8 (CH), 73.7 (CH_2), 73.5 (CH_2), 73.4 (CH), 73.37 (CH_2), 73.2 (CH), 72.8 (CH), 72.7 (CH), 72.1 (CH), 72.0 (CH_2), 69.1 (CH_2), 69.05 (CH), 69.03 (CH_2), 68.5 (CH_2), 68.46 (CH_2), 67.7 (CH_2), 63.4 (CH_2), 59.2 (CH), 59.1 (CH), 58.3 (CH), 26.9 (CH_3), 21.4 (CH_3), 19.3 (C); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{174}H_{170}Cl_9N_3O_{34}SSiNa$ [M + Na]$^+$, 3248.8245; found, 3248.8296.

*tert-Butyldimethylsilyl(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**35**).* For reaction details, please see Scheme S4. To a solution of compound **50** (3.60 g, 3.23 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (290 mL) and dd. H_2O (29 mL), DDQ (2.20 g, 9.69 mmol) was added under the argon atmosphere at 0 °C. After 6 h, the reaction was completed as observed by TLC. To quench the reaction, saturated $NaHCO_3$ solution (20 mL) was slowly added to the reaction mixture under the ice bath. Solvent extraction was then done to wash the organic layer with saturated $NaHCO_3$ solution (250 mL, three times). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation. The resulting viscous crude was purified by column chromatography on silica gel with EtOAc/hexanes (1/6 to 1/4, v/v) to yield the desired pure product **35** (2.42 g, 77%) as a white amorphous foam. R_f 0.32 (EtOAc/hexanes = 1/3, v/v); $[\alpha]_D^{25}$ −57.1 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.50−7.41 (m, 3H, Ar-H), 7.37−7.23 (m, 15H, Ar-H), 6.88 (d, *J* = 7.2 Hz, 1H, N−H), 5.46 (s, 1H, CHPh), 5.21 (m, 2H, H-1, H-2′), 4.80 (d, *J* = 7.9 Hz, 1H, H-1′), 4.70 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.65 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.54 (t, *J* = 9.4 Hz, 1H, H-3), 4.42 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.33 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.22 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6a), 3.78 (d, *J* = 3.4 Hz, 1H, H-4′), 3.75 (t, *J* = 9.1 Hz, 1H, H-4), 3.69 (t, *J* = 10.3 Hz, 1H, H-6b), 3.66−3.58 (m, 2H, H-3′, H-6a′), 3.57−3.50 (m, 2H, H-5′, H-6b′), 3.46 (td, *J* = 9.7, 4.8 Hz, 1H, H-5), 3.33 (dt, *J* = 9.7, 7.5 Hz, 1H, H-2), 2.48 (d, *J* = 9.5 Hz, 1H, OH), 0.84 (s, 9H, TBS-*t*-Bu), 0.07 (s, 3H, TBS-CH_3), 0.04 (s, 3H, TBS-CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.9 (C), 161.8 (C), 138.2 (C), 137.8 (C), 137.6 (C), 133.4 (CH), 130.1 (CH), 129.9 (C), 129.1 (CH), 128.7 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 126.4 (CH), 101.3 (CH), 99.5 (CH), 94.3 (CH), 92.4 (C), 80.0 (CH), 76.7 (CH), 75.6 (CH_2), 75.1 (CH), 74.5 (CH), 73.8 (CH_2), 73.6 (CH), 73.4 (CH), 68.8 (CH_2), 68.5 (CH_2), 66.4 (CH), 61.8 (CH), 25.8 (CH_3), 17.9 (C), −4.1 (CH_3), −5.0 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{48}H_{56}Cl_3NO_{12}SiH$ [M + H]$^+$, 994.2530; found, 994.2538.

*tert-Butyldimethylsilyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4-O-acetyl-6-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**36**).* For reaction details, please see Scheme S1. A solution of **25** (216 mg, 0.104 mmol) and **35** (121 mg, 0.124 mmol) in dry CH_2Cl_2 (2.1 mL) was stirred with 3 Å pulverized molecular sieves (340 mg) at rt for 30 min under N_2. After cooling to −50 °C, NIS (33 mg, 0.15 mmol) and TfOH (2.7 μL, 0.031 mmol) were sequentially added to the reaction mixture. After 3 h, the reaction was quenched by dropwise addition of Et_3N at −50 °C. The neutralized reaction mixture was filtered, diluted with CH_2Cl_2 (5 mL), and washed with saturated $Na_2S_2O_3$ solution (10 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to obtain the hexasaccharide **36** (212 mg, 70%) as a white amorphous foam. R_f 0.31 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −20.34 (*c* 1.77, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95−7.88 (m, 4H, Ar-H), 7.86 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.6−7.5 (m, 3H, Ar-H), 7.48−7.39 (m, 4H, Ar-H), 7.38−7.34 (m, 3H, Ar-H), 7.33−7.25 (m, 19H, Ar-H), 7.24−7.14 (m, 28H, Ar-H), 7.14−7.1 (m, 6H, Ar-H), 7.09−7.03 (m, 2H, Ar-H), 6.81 (d, *J* = 6.7 Hz, 1H, N−H), 6.57−6.44 (m, 2H, N−H), 5.60 (dd, *J* = 9.8, 8.2 Hz, 1H, H-2‴″), 5.47−5.36 (m, 2H, H-2′, PhCH benzylidene), 5.24 (dd, *J* = 9.8, 7.9 Hz, 1H, H-2‴), 5.18 (d, *J* = 7.5 Hz, 1H, H-1), 5.02 (d, *J* = 11.4 Hz, 1H, CH_2Ph), 4.9−4.82 (m, 2H, H-1‴′, CH_2Ph), 4.75−4.15 (m, 28H, H-1″, H-1′, H-1‴″, H-3, H-1‴, H-3‴′, H-3″, 2× CH_2 group of Nap, 16× CH_2Ph, H-6a), 3.60 (s, 1H, H-4‴″), 3.9−3.83 (m, 3H, H-3′, H-4′, H-4‴), 3.78, (d, *J* = 10.0 Hz, 1H, H-3‴), 3.72−3.33 (m, 19H, H-4, H-3‴″, H-4″, H-4‴′, H-5, H-5′, H-5″, H-5‴, H-5‴′, H-5‴″, H-6b′, H-6a″, H-6b″, H-6a‴, H-6b‴, H-6a‴′, H-6b‴′, H-6a‴″, H-6b‴″), 3.17−3.06 (m, 2H, H-2, H-2″), 3.05−2.95 (m, 1H, H-2‴′), 1.62 (s, 3H, $COCH_3$), 0.8 (s, 9H, TBS-*t*-Bu), 0.02 (s, 3H, TBS-CH_3), 0.008 (s, 3H, TBS-CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.7 (C), 165.7 (C), 165.0 (C), 164.8 (C), 161.7 (C), 161.4 (C), 161.1 (C), 138.94 (C), 138.90 (C), 138.7 (C), 138.1 (C), 138.07 (C), 138.0 (C), 137.85 (C), 137.81 (C), 137.5 (C), 134.9 (C), 133.4 (CH), 133.3 (CH), 133.2 (CH), 133.1 (C), 133.0 (C), 130.07 (CH), 130.0 (CH), 129.8 (C), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.26 (CH), 128.23 (CH), 128.2 (CH), 128.1 (CH), 128.08 (CH), 128.05 (CH), 128.0 (CH), 127.9 (CH), 127.87 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.57 (CH), 127.5 (CH), 127.4 (CH), 126.8 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 100.8 (CH), 100.2 (CH), 100.0 (CH), 99.9 (CH), 99.2 (CH), 99.1 (CH), 94.0 (CH), 92.4 (C), 92.3 (C), 92.2 (C), 79.4 (CH), 79.2 (CH), 78.1 (CH), 77.6 (CH), 76.5 (CH), 76.2 (CH), 75.1 (CH), 74.9 (CH_2), 74.8 (CH), 74.76 (CH_2), 73.8 (CH), 73.7 (CH), 73.62 (CH_2), 73.6 (CH_2), 73.5 (CH_2), 73.4 (CH_2), 73.1 (CH), 72.7 (CH), 72.6 (CH), 72.0 (CH), 71.9 (CH_2), 69.5 (CH_2), 69.3 (CH), 69.1 (CH_2), 68.8 (CH_2), 68.6 (CH_2), 68.4 (CH_2), 68.3 (CH_2), 66.27 (CH), 62.3 (CH), 59.3 (CH), 59.1 (CH), 25.7 (CH_3), 20.6 (CH_3), 17.8 (C), −4.2 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{152}H_{157}Cl_9N_3O_{35}Si$ [M + H]$^+$, 2932.7550; found, 2932.7600.

*tert-Butyldimethylsilyl(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**37**).* For reaction details,

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please see Scheme S9. To a solution of compound **53** (964.4 mg, 0.49 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (45 mL) and dd. H_2O (4.5 mL), DDQ (336 mg, 1.48 mmol) was added under the argon atmosphere at 0 °C. After 5 h, the reaction was completed as observed by TLC. Saturated $NaHCO_3$ solution (5 mL) was then slowly added to the reaction mixture under the ice bath to quench the reaction. Solvent extraction was done to wash the CH_2Cl_2 layer with saturated $NaHCO_3$ solution (40 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to yield the desired pure product **37** (582 mg, 65%) as a white amorphous foam. R_f 0.31 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −21.1 (*c* 1.09, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.97−7.88 (m, 4H, Ar-H), 7.49−7.41 (m, 4H, Ar-H), 7.38 (d, *J* = 7.1 Hz, 2H, Ar-H), 7.35−7.26 (m, 20H, Ar-H), 7.25−7.23 (m, 3H, Ar-H), 7.23−7.21 (m, 5H, Ar-H), 7.20−7.16 (m, 2H, Ar-H), 6.82 (d, *J* = 6.9 Hz, 1H, N−H), 6.63 (d, *J* = 7.4 Hz, 1H, N−H), 5.48−5.42 (m, 2H, H-2′, PhCH benzylidene), 5.41 (s, 1H, PhCH benzylidene), 5.17 (d, *J* = 7.7 Hz, 1H, H-1), 5.13 (dd, *J* = 9.9, 8.0 Hz, 1H, H-2‴), 5.0 (d, *J* = 8.1 Hz, 1H, H-1″), 4.79 (d, *J* = 11.9 Hz, 1H), 4.70−4.60 (m, 4H, H-1′, H-1‴), 4.55−4.47 (m, 2H, H-3), 4.40 (d, *J* = 11.6 Hz, 1H), 4.37−4.32 (m, 2H, H-3″), 4.31−4.23 (m, 3H), 4.17 (dd, *J* = 10.3, 4.8 Hz, 1H), 3.90 (dd, *J* = 10.1, 2.7 Hz, 1H, H-3′), 3.86 (d, *J* = 2.6 Hz, 1H, H-4′), 3.76 (d, *J* = 3.3 Hz, 1H, H-4‴), 3.72−3.60 (m, 4H, H-4, H-4″), 3.59−3.49 (m, 5H, H-3‴), 3.49−3.34 (m, 4H), 3.25 (td, *J* = 9.7, 8.0 Hz, 1H, H-2″), 3.09 (td, *J* = 8.5, 6.8 Hz, 1H, H-2), 2.40 (d, *J* = 9.15 Hz, 1H, O−H), 0.8 (s, 9H, TBS-*t*-Bu), 0.016 (s, 3H, TBS-CH_3), −0.017 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.78 (C), 165.0 (C), 161.7 (C), 161.6 (C), 138.9 (C), 138.2 (C), 137.9 (C), 137.7 (C), 137.5 (C), 137.3 (C), 133.4 (CH), 130.0 (CH), 129.9 (C), 129.7 (C), 129.1 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.58 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.19 (CH), 128.11 (CH), 128.1 (CH), 128.0 (CH), 127.99 (CH), 127.9 (CH), 127.6 (CH), 126.3 (CH), 126.2 (CH), 101.1 (CH), 100.9 (CH), 100.2 (CH), 99.5 (CH), 99.4 (CH), 93.9 (CH), 92.4 (C), 91.9 (C), 79.6 (CH), 79.4 (CH), 77.9 (CH), 76.5 (CH), 76.47 (CH), 75.5 (CH_2), 75.0 (CH), 74.9 (CH_2), 74.6 (CH), 74.4 (CH), 73.6 (CH_2), 73.5 (CH), 73.4 (CH), 73.3 (CH), 72.8 (CH), 68.6 (CH_2), 68.58 (CH_2), 68.5 (CH_2), 68.4 (CH_2), 66.3 (CH), 66.2 (CH), 62.4 (CH), 59.5 (CH), 25.7 (CH_3), 17.8 (C), −4.2 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{90}H_{97}Cl_6N_2O_{23}Si$ $[M + H]^+$, 1815.4360; found, 1815.4403.

*tert-Butyldimethylsilyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**38**).* For reaction details, please see Scheme 2. A solution of **8** (225 mg, 0.19 mmol) and **37** (200 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (5 mL) was stirred with 3 Å pulverized molecular sieves (900 mg) at rt for 30 min under the N_2 atmosphere. After cooling to −50 °C, NIS (50 mg, 0.22 mmol) was added to the reaction mixture, followed by the addition of TfOH (2.91 μL, 0.033 mmol). After 4 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (12 mL), and filtered. The filtrate was washed with saturated $Na_2S_2O_3$ solution (15 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/6, v/v) to yield the pure hexasaccharide **38** (263 mg, 82%) as a white amorphous foam. R_f 0.41 (EtOAc/toluene = 1/7, v/v); $[\alpha]_D^{20}$ −21.11 (*c* 0.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.9 (d, *J* = 8.1 Hz, 4H, Ar-H), 7.81 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.54 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.53−7.49 (m, 2H, Ar-H), 7.48−7.42 (m, 3H, Ar-H), 7.41−7.37 (m, 6H, Ar-H), 7.36−7.24 (m, 24H, Ar-H), 7.24−7.23 (m, 6H, Ar-H), 7.22−7.17 (m, 11H, Ar-H), 7.17−7.10 (m, 10H, Ar-H), 7.08−7.03 (m, 2H, Ar-H), 6.80 (d, *J* = 6.85 Hz, 1H, N−H), 6.62 (d, *J* = 7.15 Hz, 1H, N−H), 6.52 (d, *J* = 8.0 Hz, 1H, N−H), 5.61 (dd, *J* = 10.0, 8.0 Hz, 1H, H-2⁗″), 5.47−5.39 (m, 3H, H-2‴, 2× PhCH benzylidene), 5.33 (dd, *J* = 9.1, 8.2 Hz, 1H, H-2′), 5.17 (d, *J* = 7.7 Hz, 1H, H-1), 5.07−4.96 (m, 2H, H-1″, CH_2Ph), 4.87 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.75 (d, *J* = 11.9 Hz, 1H, CH_2Ph), 4.72 (d, *J* = 12.4 Hz, 1H, CH_2 group of Nap), 4.69−4.61 (m, 3H, H-1⁗, H-1‴′, CH_2Ph), 4.60−4.16 (m, 21H, H-1⁗″, H-1′, H-3, H-3″, CH_2 group of Nap, 12× CH_2Ph, H-6a, H-6a″, H-3‴′), 3.95 (d, *J* = 1.7 Hz, 1H, H-4⁗″), 3.87 (dd, *J* = 10.1, 2.7 Hz, 1H, H-3‴), 3.85−3.79 (m, 3H, H-3′, H-4′, H-4‴), 3.70−3.30 (m, 19H, H-4, H-4″, H-3⁗″, H-4‴′, H-5, H-5′, H-5″, H-5‴, H-5⁗′, H-5⁗″, H-6b, H-6b″, H-6a′, H-6b′, H-6a‴, H-6b‴, H-6a⁗′, H-6b⁗′, H-6b⁗″), 3.26−3.17 (m, 1H, H-2⁗′), 3.16−3.04 (m, 2H, H-2, H-2″), 0.79 (s, 9H, TBS-*t*-Bu), 0.02 (s, 3H, TBS-CH_3), −0.012 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 165.0 (C), 161.7 (C), 161.1 (C), 139.0 (C), 138.9 (C), 138.8 (C), 138.2 (C), 138.1 (C), 138.0 (C), 137.9 (C), 137.6 (C), 137.4 (C), 134.9 (C), 133.4 (CH), 133.2 (CH), 133.16 (C), 133.1 (C), 130.0 (CH), 129.9 (C), 129.8 (C), 128.9 (CH), 128.87 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.49 (CH), 128.4 (CH), 128.37 (CH), 128.3 (CH), 128.26 (CH), 128.2 (CH), 128.16 (CH), 128.1 (CH), 128.06 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.76 (CH), 127.7 (CH), 127.4 (CH), 126.9 (CH), 126.3 (CH), 126.28 (CH), 126.1 (CH), 125.9 (CH), 100.9 (CH), 100.3 (CH), 100.1 (CH), 100.0 (CH), 99.5 (CH), 99.2 (CH), 94.0 (CH), 92.4 (C), 91.9 (C), 79.5 (CH), 79.4 (CH), 79.1 (CH), 78.0 (CH), 77.5 (CH), 76.4 (CH), 76.39 (CH), 76.23 (CH), 75.2 (CH), 74.9 (CH_2), 74.87 (CH_2), 74.84 (CH_2), 74.5 (CH), 73.8 (CH), 73.7 (CH_2), 73.66 (CH_2), 73.61 (CH_2), 73.6 (CH), 73.5 (CH_2), 73.1 (CH), 73.0 (CH), 72.8 (CH), 72.1 (CH), 72.0 (CH_2), 69.2 (CH_2), 68.9 (CH_2), 68.7 (CH_2), 68.6 (CH_2), 68.56 (CH_2), 68.4 (CH_2), 66.3 (CH), 62.4 (CH), 60.0 (CH), 59.0 (CH), 25.7 (CH_3), 17.9 (C), −4.2 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{150}H_{152}Cl_9N_3O_{34}SiNa_2$ $[M + 2Na]^{2+}$, 1466.8499; found, 1466.8500.

*tert-Butyldimethylsilyl(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**39**).* For reaction details, please see Scheme 2. To a solution of compound **38** (263 mg, 0.091 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2 (8.27 mL) and dd. H_2O (0.83 mL), DDQ (62 mg, 0.27 mmol) was added under the argon atmosphere at 0 °C. After 6 h, the reaction was completed as observed by TLC. Saturated $NaHCO_3$ solution (2 mL) was then slowly added to the reaction mixture under the ice bath to quench the reaction. Solvent extraction was done to wash the CH_2Cl_2 layer with saturated $NaHCO_3$ solution (7 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to yield the desired pure product **39** (155 mg, 62%) as a white amorphous foam. R_f 0.28 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −25.39 (*c* 3.19, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.91 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.85 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.51−7.42 (m, 3H, Ar-H), 7.42−7.37 (m, 5H, Ar-H), 7.37−7.31 (m, 7H, Ar-H), 7.31−7.30 (m, 2H, Ar-H), 7.30−7.26 (m, 9H, Ar-H), 7.25−7.24 (m, 3H, Ar-H), 7.24−7.23 (m, 6H, Ar-H), 7.23−7.18 (m, 14H, Ar-H), 7.18−7.15 (m, 6H, Ar-H), 7.14−7.09 (m, 4H, Ar-H), 6.80 (d, *J* = 6.8 Hz, 1H, N−H), 6.68 (d, *J* = 8.15 Hz, 1H, N−H), 6.63 (d, *J* = 7.1 Hz, 1H, N−H), 5.47−5.36 (m, 4H, H-2′, H-2‴, 2× PhCH benzylidene), 5.23−5.15 (m, 2H, H-1, H-2⁗″), 5.01 (d, *J* = 7.95 Hz, 1H, H-1″), 4.86 (d, *J* = 10.35 Hz, 1H), 4.78−4.15 (m, 25H, H-1⁗″, H-1‴′, H-1, H-1‴, H-3, H-3″, H-3⁗′, 15× CH_2Ph, H-6a, H-6a″), 3.93−3.86 (m, 3H, H-3′, H-3‴, H-4⁗″), 3.85−3.82 (m, 2H, H-4′, H-4‴), 3.70−3.29 (m, 20H, H-4, H-4″, H-4‴′, H-3⁗″, H-2⁗′, H-5, H-5′, H-5″, H-5‴, H-5⁗′, H-5⁗″, H-6b, H-6a′, H-6b′, H-6a⁗″, H-6b⁗″, H-6a⁗′, H-6b⁗′, H-6a⁗″, H-6b⁗″), 3.18−3.03 (m, 2H, H-2, H-2″), 2.49 (d, *J* = 4.95 Hz, 1H, O−H), 0.8 (s, 9H, TBS-*t*-Bu), 0.024 (s, 3H, TBS-CH_3), −0.01 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz,

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$CDCl_3$): δ 167.3 (C), 165.0 (C), 161.7 (C), 161.4 (C), 139.0 (C), 138.87 (C), 138.2 (C), 138.1 (C), 137.9 (C), 137.7 (C), 137.6 (C), 137.4 (C), 133.5 (CH), 133.4 (CH), 130.2 (CH), 130.0 (CH), 129.9 (C), 129.8 (C), 129.6 (C), 128.9 (CH), 128.86 (CH), 128.7 (CH), 128.63 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.09 (CH), 128.06 (CH), 128.0 (CH), 127.96 (CH), 127.8 (CH), 127.7 (CH), 127.66 (CH), 127.4 (CH), 126.3 (CH), 100.9 (CH), 100.3 (CH), 100.0 (CH), 99.6 (CH), 99.4 (CH), 99.3 (CH), 93.9 (CH), 92.5 (C), 92.4 (C), 91.9 (C), 79.3 (CH), 79.1 (CH), 78.0 (CH), 77.6 (CH), 76.8 (CH), 76.5 (CH), 76.4 (CH), 76.2 (CH), 75.7 (CH_2), 75.2 (CH), 74.9 (CH), 74.86 (CH_2), 74.8 (CH_2), 74.5 (CH), 73.7 (CH_2), 73.6 (CH_2), 73.5 (CH), 73.4 (CH_2), 73.1 (CH), 72.8 (CH), 69.1 (CH_2), 68.9 (CH_2), 68.7 (CH_2), 68.6 (CH_2), 68.55 (CH_2), 68.2 (CH_2), 66.3 (CH), 62.4 (CH), 60.0 (CH), 58.8 (CH), 25.7 (CH_3), 17.9 (C), −4.2 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{139}H_{144}Cl_9N_3O_{34}SiNa$ $[M + Na]^+$, 2770.6475; found, 2770.6435.

*tert-Butyldimethylsilyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-di-O-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-(4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**40**).* For reaction details, please see Scheme 2. A solution of **8** (80 mg, 0.066 mmol) and **39** (91 mg, 0.033 mmol) in anhydrous CH_2Cl_2 (1.6 mL) was stirred with 3 Å pulverized molecular sieves (340 mg) at rt for 30 min under the N_2 atmosphere and then cooled down to −50 °C. NIS (17.2 mg, 0.076 mmol) was added to the reaction mixture, followed by addition of TfOH (0.9 μL, 0.009 mmol). After 3 h, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/5 to 1/3, v/v) to afford octasaccharide **40** (77 mg, 61%) as a glassy solid. R_f 0.27 (EtOAc/toluene = 1/8, v/v, run two times); $[\alpha]_D^{20}$ −26.82 (*c* 2.13, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.93−7.86 (m, 6H, Ar-H), 7.81 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.56−7.50 (m, 3H, Ar-H), 7.48−7.36 (m, 9H, Ar-H), 7.35−7.25 (m, 28H, Ar-H), 7.23−7.19 (m, 18H, Ar-H), 7.18−7.12 (m, 20H, Ar-H), 7.12−7.08 (m, 6H, Ar-H), 7.07−7.02 (m, 4H, Ar-H), 6.78 (d, *J* = 6.6 Hz, 1H, N−H), 6.59 (d, *J* = 6.85 Hz, 1H, N−H), 6.55−6.45 (m, 2H, 2× N−H), 5.60 (dd, *J* = 9.7, 8.3 Hz, 1H, H-2‴″′), 5.46−5.38 (m, 4H, H-2′, H-2‴″, 2× PhCH benzylidene), 5.32 (t, *J* = 8.8 Hz, 1H, H-2‴), 5.17 (d, *J* = 7.7 Hz, 1H, H-1), 5.05−4.97 (m, 2H, H-1″, CH_2Ph), 4.88 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.79 (d, *J* = 10.4 Hz, 1H, CH_2Ph), 4.76−4.65 (m, 4H, H-1‴″″, CH_2Ph, CH_2 group of Nap), 4.64−4.12 (m, 31H, H-1‴″, H-1‴, H-1′, H-3, CH_2 group of Nap, H-3″, H-3‴″, H-3‴′, 19× CH_2Ph, H-1‴′, H-1‴″′, H-6a, H-6a″), 3.94 (s, 1H, H-4‴″′), 3.89−3.77 (m, 6H, H-3′, H-4′, H-3‴, H-4‴, H-3‴″, H-4‴″), 3.70−3.30 (m, 27H, H-4, H-4″, H-4‴″, H-4‴′, H-3‴″′, H-5, H-5′, H-5″, H-5‴, H-5‴′, H-5‴″, H-5‴‴, H-5‴″′, H-6b, H-6a′, H-6b′, H-6b″, H-6a‴, H-6b‴, H-6a‴′, H-6b‴′, H-6a‴″, H-6b‴″, H-6a‴‴, H-6b‴‴, H-6a‴″′, H-6b‴″′), 3.24−3.03 (m, 4H, H-2, H-2″, H-2‴′, H-2‴″), 0.79 (s, 9H, TBS-*t*-Bu), 0.019 (s, 3H, TBS-CH_3), −0.014 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7 (C), 165.3 (C), 165.0 (C), 161.7 (C), 161.1 (C), 139.2 (C), 139.0 (C), 138.9 (C), 138.8 (C), 138.2 (C), 138.1 (C), 138.0 (C), 137.6 (C), 137.4 (C), 134.9 (C), 133.4 (CH), 133.2 (CH), 133.1 (C), 130.0 (CH), 129.9 (C), 129.8 (C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.57 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.22 (CH), 128.2 (CH), 128.17 (CH), 128.12 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.78 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.39 (CH), 126.9 (CH), 126.3 (CH), 126.29 (CH), 126.2 (CH), 126.1 (CH), 126.0 (CH), 100.9 (CH), 100.3 (CH), 100.2 (CH), 100.1 (CH), 99.5 (CH), 99.3 (CH), 99.1 (CH), 94.0 (CH), 92.5 (C), 92.4 (C), 91.9 (C), 79.5 (CH), 79.4 (CH), 79.2 (CH), 78.0 (CH), 77.5 (CH), 77.4 (CH), 76.8 (CH), 76.4 (CH), 76.36 (CH), 76.3 (CH), 76.2 (CH), 75.3 (CH), 75.2 (CH), 75.1 (CH_2), 74.9 (CH_2), 74.89 (CH_2), 74.8 (CH_2), 74.5 (CH), 73.9 (CH), 73.8 (CH), 73.7 (CH_2), 73.6 (CH_2), 73.57 (CH), 73.52 (CH_2), 73.5 (CH_2), 73.2 (CH), 73.1 (CH), 72.8 (CH), 72.7 (CH), 72.1 (CH), 72.0 (CH_2), 69.1 (CH_2), 69.0 (CH_2), 68.9 (CH_2), 68.7 (CH_2), 68.6 (CH_2), 68.5 (CH_2), 68.4 (CH_2), 66.3 (CH), 62.5 (CH), 60.0 (CH), 59.1 (CH), 59.0 (CH), 25.7 (CH_3), 17.9 (C), −4.1 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{199}H_{200}Cl_{12}N_4O_{45}SiNa_2$ $[M + 2Na]^{2+}$, 1933.4646; found, 1933.4641.

From Compounds 42 to 45, Please See Scheme S2 for Reaction Details. *4-Methylphenyl 4,6-O-Benzylidene-3-O-(naphthalene-2-ylmethyl)-1-thio-β-D-galactopyranoside (**42**).* To a solution of compound **41**[33,34] (18.80 g, 50.2 mmol) in benzene (166 mL) was added Bu_2SnO (16.25 g, 65.0 mmol), and the resulting mixture was heated with a silicone oil bath under refluxing condition with stirring overnight. At the same time, the reaction vessel was connected with Dean−Stark apparatus to remove water. Most of the benzene was removed by distillation at 100 °C and the rest was kept under high vacuum for 2 h prior to the next step. To a solution of the resulting dried residue in DMF (166 mL) were sequentially added 2NapMeBr (16.66 g, 75.4 mmol) and CsF (12.21 g, 80.4 mmol) with stirring at room temperature (rt) for 6 h under the N_2 atmosphere. After the completion of the reaction, the solvent was removed by evaporation and the concentrated residue was partitioned by EtOAc (350 mL)/ice H_2O (350 mL). The organic layer was further washed with brine (200 mL, five times), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the crude as a white solid. The crude was purified by recrystallization in a mixture of CH_2Cl_2/hexanes (1/20, v/v) to provide the desired product **42** (23.77 g, 92%) as a white solid. R_f 0.70 (EtOAc/hexanes = 2/1, v/v); $[\alpha]_D^{25}$ 10.8 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.84−7.77 (m, 3H, Ar-H), 7.74 (m, 1H, Ar-H), 7.57 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.47 (m, 3H, Ar-H), 7.40 (dd, *J* = 7.1, 2.5 Hz, 2H, Ar-H), 7.37−7.31 (m, 3H, Ar-H), 7.05 (d, *J* = 8 Hz, 2H, Ar-H), 5.38 (s, 1H, PhCH benzylidene), 4.88 (s, 2H, CH_2 group of Nap), 4.44 (d, *J* = 9.4 Hz, 1H, H-1), 4.31 (d, *J* = 12.3 Hz, 1H, H-6a), 4.12 (d, *J* = 3.2 Hz, 1H, H-4), 3.90 (m, 2H, H-2, H-6b), 3.53 (dd, *J* = 9.3, 3.3 Hz, 1H, H-3), 3.38 (s, 1H, H-5), 2.50 (d, *J* = 1.8 Hz, 1H, O−H), 2.33 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.6 (C), 138.1 (C), 135.7 (C), 134.6 (CH), 133.4 (C), 133.3 (C), 129.9 (CH), 129.2 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 126.9 (CH), 126.8 (CH), 126.8 (C), 126.4 (CH), 126.2 (CH), 126.0 (CH), 101.4 (CH), 87.4 (CH), 80.4 (CH), 73.6 (CH), 72.1 (CH_2), 70.2 (CH), 69.6 (CH_2), 67.4 (CH), 21.4 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{31}H_{31}O_5S$ $[M + H]^+$, 515.1887; found, 515.1891.

*4-Methylphenyl 2-O-Benzoyl-4,6-O-benzylidene-3-O-(naphthalene-2-ylmethyl)-1-thio-β-D-galactopyranoside (**43**).* 4-DMAP (1.50 g, 12.3 mmol) and Bz_2O (18.55 g, 82.0 mmol) were sequentially added to a solution of compound **42** (21.11 g, 41.0 mmol) in anhydrous pyridine (205 mL) at rt. After 3 h, the reaction mixture was quenched under the ice bath by adding MeOH (15 mL) and concentrated by evaporation. The resulting residue was redissolved in CH_2Cl_2 (200 mL), washed with 1 N HCl (200 mL, three times) to completely remove the pyridine, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield the crude product as a pale-yellow-white solid. The crude was purified by recrystallization in a mixture of CH_2Cl_2/hexanes (1/20, v/v) to provide the desired product **43** (22.71 g, 89%) as a white solid. R_f 0.38 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{25}$ −36.3 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.73 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.59 (dd, *J* = 17.7, 7.5 Hz, 4H, Ar-H), 7.45 (m, 8H, Ar-H), 7.37 (s, 3H, Ar-H), 7.26 (d, *J* = 5.6 Hz, 1H, Ar-H), 7.04 (d, *J* = 7.6 Hz, 2H, Ar-H), 5.53 (t, *J* = 9.6 Hz, 1H, H-2), 5.47 (s, 1H, PhCH benzylidene), 4.81−4.66 (m, 3H, H-1, CH_2 group of Nap), 4.37 (d, *J* = 12.2 Hz, 1H, H-6a), 4.25 (s, 1H, H-4), 4.00 (d, *J* = 12.3 Hz, 1H, H-6b), 3.80 (d, *J* = 9.6 Hz, 1H, H-4), 3.46 (s, 1H, H-5), 2.32 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.2 (C), 138.4 (C), 137.9 (C), 135.4 (C), 134.6 (CH), 133.3 (C), 133.2 (CH), 130.5 (C), 130.1 (CH), 129.7 (CH), 129.3 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH),

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127.9 (CH), 127.7 (C), 126.9 (CH), 126.7 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 101.5 (CH), 85.7 (CH), 78.4 (CH), 73.4 (CH), 71.3 (CH_2), 70.2 (CH), 69.5 (CH_2), 69.4 (CH), 21.5 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{38}H_{34}O_6SNa$ $[M + Na]^+$, 641.1968; found, 641.1979.

*4-Methylphenyl 2-O-benzoyl-4-O-benzyl-3-O-(naphthalene-2-ylmethyl)-1-thio-β-D-galactopyranoside (**44**).* To a solution of compound **43** (22.71 g, 36.7 mmol) in anhydrous CH_2Cl_2 (184 mL) at 0 °C under N_2, 1 M solution of BH_3.THF complex (147 mL, 147.0 mmol) was added, followed by the addition of TMSOTf (3.32 mL, 18.4 mmol). After 2 h, the reaction was quenched by dropwise addition of Et_3N to neutralize the pH, followed by the slow addition of MeOH (20 mL) under the ice bath. After concentrating the neutralized reaction mixture by evaporation, the resulting residue was redissolved in CH_2Cl_2 (200 mL), washed with saturated $NaHCO_3$ solution (200 mL, two times), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Recrystallization was done with CH_2Cl_2/hexanes (1/20, v/v) to afford the pure product **44** (18.22 g, 80%) as a white solid. R_f 0.45 (EtOAc/hexanes = 1/1, v/v); $[\alpha]_D^{25}$ +16.3 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.73 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.58 (dd, *J* = 12.9, 8.9 Hz, 4H, Ar-H), 7.47−7.38 (m, 4H, Ar-H), 7.36−7.23 (m, 8H, Ar-H), 7.02 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.70 (t, *J* = 9.7 Hz, 1H, H-2), 5.03 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.82 (d, *J* = 12.4 Hz, 1H, CH_2 group of Nap), 4.72−4.64 (m, 3H, H-1, CH_2Ph, CH_2 group of Nap), 3.96 (d, *J* = 2.1 Hz, 1H, H-4), 3.87 (dd, *J* = 11.3, 6.9 Hz, 1H, H-6a), 3.74 (dd, *J* = 9.7, 2.5 Hz, 1H, H-3), 3.56 (dd, *J* = 11.3, 5.2 Hz, 1H, H-6b), 3.53−3.46 (m, 1H, H-5), 2.28 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.5 (C), 138.3 (C), 138.1 (C), 135.1 (C), 133.3 (CH), 133.2 (C), 132.9 (CH), 130.3 (C), 130.1 (CH), 129.8 (CH), 129.7 (C), 128.7 (CH), 128.6 (CH), 128.57 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 126.9 (CH), 126.4 (CH), 126.2 (CH), 126.0 (CH), 87.5 (CH), 81.4 (CH), 79.2 (CH), 74.3 (CH_2), 72.4 (CH_2), 72.4 (CH), 70.7 (CH), 62.4 (CH_2), 21.3 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{38}H_{36}O_6SNa$ $[M + Na]^+$, 643.2125; found, 643.2132.

*4-Methylphenyl 2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalene-2-ylmethyl)-1-thio-β-D-galactopyranoside (**45**).* BnBr (8.70 mL, 72.5 mmol) and NaH (60% in mineral oil, 1.93 g, 48.3 mmol) were added to the ice-cold solution of the starting material **44** (15.0 g, 24.2 mmol) in DMF (120.8 mL) under the N_2 atmosphere. After 3 h, the reaction was quenched by pouring dd. H_2O (15 mL) under the ice bath. Solvent extraction was then done by using CH_2Cl_2 (150 mL) and brine (150 mL, five times) to remove most of the DMF. This was followed by washing the CH_2Cl_2 layer with saturated $NaHCO_3$ solution (150 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation. The crude residue was recrystallized with CH_2Cl_2/hexanes (1/20, v/v) to yield the desired monosaccharide donor **45** (14.94 g, 87%) as a white solid. R_f 0.65 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{25}$ +43.1 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.99−7.96 (m, 2H, Ar-H), 7.71 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.58−7.52 (m, 4H, Ar-H), 7.44−7.38 (m, 4H, Ar-H), 7.36−7.22 (m, 13H, Ar-H), 6.97 (d, *J* = 8.2 Hz, 2H, Ar-H), 5.67 (t, *J* = 9.8 Hz, 1H, H-2), 5.01 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.78 (d, *J* = 12.4 Hz, 1H, CH_2 group of Nap), 4.68 (d, *J* = 9.9 Hz, 1H, H-1), 4.63 (dd, *J* = 12.0, 8.7 Hz, 2H, CH_2Ph, CH_2 group of Nap), 4.47 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.43 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.07 (d, *J* = 2.6 Hz, 1H, H-4), 3.73−3.63 (m, 4H, H-3, H-5, H-6a, H-6b), 2.26 (s, 3H, $PhCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.5 (C), 138.7 (C), 138.1 (C), 137.8 (C), 135.3 (C), 133.3 (C), 133.2 (CH), 133.0 (CH), 130.4 (C), 130.1 (CH), 129.9 (C), 129.7 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 126.7 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 87.5 (CH), 81.3 (CH), 77.9 (CH), 74.6 (CH_2), 73.8 (CH_2), 73.0 (CH), 72.0 (CH_2), 70.7 (CH), 69.1 (CH_2), 21.3 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{38}H_{34}O_6SNa$ $[M + Na]^+$, 733.2594; found, 733.2626.

From Compounds 47 and 48, Please See Scheme S3 for Reaction Details. *tert-Butyldimethylsilyl 3,4,6-Tri-O-acetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**47**).* Hydrazine acetate (2.14 g, 23.2 mmol) was added to the ice-cold solution of the starting material **46**[32,35] (10.42 g, 21.2 mmol) in anhydrous DMF (85 mL). After 1 h, the reaction was quenched by adding MeOH (15 mL) and concentrated by evaporation. The residue was redissolved in CH_2Cl_2 (100 mL), washed with saturated $NaHCO_3$ solution (100 mL, two times), dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

To the resulting solid residue solution in DMF (42 mL), imidazole (4.32 g, 63.4 mmol) and *tert*-butylchlorodimethylsilane (6.38 g, 42.3 mmol) were sequentially added at rt. After 2 h, the reaction was quenched by adding MeOH (10 mL) and concentrated *in vacuo* to dryness. The resulting crude was redissolved in CH_2Cl_2 (100 mL) and washed sequentially with dd. H_2O (100 mL, two times) and saturated $NaHCO_3$ solution (100 mL, two times). The CH_2Cl_2 layer was collected, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel with EtOAc/hexanes (1/3, v/v) to afford the desired pure product **47** (9.43 g, 79% in two steps) as an amorphous white foam. R_f 0.58 (EtOAc/hexanes = 1/1, v/v); $[\alpha]_D^{25}$ −9.6 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 6.99 (d, *J* = 9.2 Hz, 1H, N−H), 5.36 (t, *J* = 9.4 Hz, 1H, H-3), 5.09 (t, *J* = 9.7 Hz, 1H, H-4), 4.89 (d, *J* = 7.9 Hz, 1H, H-1), 4.23 (dd, *J* = 12.1, 6.2 Hz, 1H, H-6a), 4.16 (dd, *J* = 12.1, 2.5 Hz, 1H, H-6b), 3.99 (ddd, *J* = 10.8, 9.1, 8.0 Hz, 1H, H-2), 3.76 (ddd, *J* = 9.8, 6.1, 2.5 Hz, 1H, H-5), 2.08 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 0.88 (s, 9H, TBS-*t*-Bu), 0.12 (s, 3H, TBS-CH_3), 0.10 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.3 (C), 170.8 (C), 169.5 (C), 162.04 (C), 96.0 (CH), 92.6 (C), 72.2 (CH), 71.9 (CH), 69.1 (CH), 62.7 (CH_2), 58.1 (CH), 25.7 (CH_3), 20.9 (CH_3), 20.8 (2xCH_3), 18.0 (C), −4.1 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{32}Cl_3NO_9SiNa$ $[M + Na]^+$, 586.0804; found, 586.0821.

*tert-Butyldimethylsilyl 4,6-O-Benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**48**).* A catalytic amount of NaOMe (356 μL, 1.6 mmol) was added to a solution of starting material **47** (9.04 g, 16.0 mmol) in a 4:1 v/v mixture of MeOH (36 mL) and CH_2Cl_2 (9 mL) at rt. After 1 h, the reaction was quenched by neutralizing the pH by slowly adding IR-120H + Amberlite resin. The reaction solution was filtered, concentrated by evaporation, and dried under high vacuum. The resulting white solid was dissolved in CH_3CN (64 mL). Then, camphor sulfonic acid (1.86 g, 8.0 mmol) and benzaldenhyde dimethyl acetal (7.23 mL, 48.0 mmol) were added with stirring at 0 °C under the N_2 atmosphere. After 3 h, the reaction was quenched by dropwise addition of Et_3N to neutralize the pH. After concentrating *in vacuo*, the resulting white residue was redissolved in CH_2Cl_2 (70 mL), washed with saturated $NaHCO_3$ solution (70 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation. The crude product was recrystallized with CH_2Cl_2/hexanes (1/20, v/v) to afford the pure product **48** (7.08 g, 84% yield in two steps) as a white amorphous foam. R_f 0.44 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{25}$ −38.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.45 (m, 2H, Ar-H), 7.40−7.34 (m, 3H, Ar-H), 6.94 (d, *J* = 7.4 Hz, 1H, NH), 5.52 (s, 1H, PhCH benzylidene), 5.08 (d, *J* = 7.9 Hz, 1H, H-1), 4.31−4.20 (m, 2H, H-3, H-6a), 3.76 (t, *J* = 10.0 Hz, 1H, H-6b), 3.57−3.45 (m, 3H, H-2, H-4, H-5), 3.06 (d, *J* = 3.2 Hz, 1H, O−H), 0.89 (s, 9H, TBS-*t*-Bu), 0.12 (s, 1H, TBS-CH_3), 0.11 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.4 (C), 137.2 (C), 129.5 (CH), 128.5 (CH), 126.5 (CH), 102.1 (CH), 95.4 (CH), 92.7 (C), 81.8 (CH), 69.9 (CH), 68.8 (CH_2), 66.4 (CH), 61.8 (CH), 25.8 (CH_3), 18.0 (C), −4.0 (CH_3), −4.9 (CH_3); HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{30}Cl_3NO_6SiNa$ $[M + Na]^+$, 548.0800; found, 548.0802.

*tert-Butyldimethylsilyl (2-O-Benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**50**).* For reaction details, please see Scheme S4. A solution of **45** (3.23 g, 4.54 mmol) and **48** (2.0 g, 3.80 mmol) in anhydrous CH_2Cl_2 (63 mL) was stirred with 3 Å pulverized molecular sieves (10.50 g) at rt for 30 min under the N_2 atmosphere. After cooling to −60 °C, NIS (1.11 g, 4.93 mmol) was added to the reaction mixture, followed by the addition of TMSOTf (137.0 μL, 0.76 mmol). After 4 h, the reaction was

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quenched by dropwise addition of Et_3N to neutralize the reaction mixture and filtered through a pad of Celite. The filtrate was washed with saturated $Na_2S_2O_3$ solution (65 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to yield the thick yellow residue. The residue was purified by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to yield the pure disaccharide **50** (3.60 g, 85%) as a white amorphous foam. R_f 0.43 (EtOAc/hexanes = 1/5, v/v, run two times); $[\alpha]_D^{25}$ +9.2 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 8.1, 1.1 Hz, 2H, Ar-H), 7.72 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.56−7.46 (m, 4H, Ar-H), 7.46−7.38 (m, 4H, Ar-H), 7.36−7.22 (m, 15H, Ar-H), 7.17 (dd, *J* = 8.5, 1.4 Hz, 1H, Ar-H), 6.90 (d, *J* = 6.9 Hz, 1H, NH), 5.61 (dd, *J* = 10.0, 8.0 Hz, 1H, H-2′), 5.45 (s, 1H, PhCH benzylidene), 5.25 (d, *J* = 7.8 Hz, 1H, H-1), 4.98 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.75−4.69 (m, 2H, H-1′, CH_2 group of Nap), 4.62 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.58−4.49 (m, 2H, H-3, CH_2 group of Nap), 4.39 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.31 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.21 (dd, *J* = 10.4, 4.9 Hz, 1H, H-5), 3.97 (d, *J* = 2.3 Hz, 1H, H-4′), 3.74 (t, *J* = 9.1 Hz, 1H, H-4), 3.68 (t, *J* = 10.2 Hz, 1H, H-6a), 3.62 (dd, *J* = 8.8, 7.5 Hz, 1H, H-6a′), 3.56 (dd, *J* = 10.1, 2.7 Hz, 1H, H-3′), 3.51 (dd, *J* = 9.0, 5.7 Hz, 1H, H-5), 3.49−3.40 (m, 2H, H-6b, H-6b′), 3.20 (td, *J* = 9.8, 7.4 Hz, 1H, H-2), 0.81 (s, 9H, TBS-*t*-Bu), 0.04 (s, 3H, TBS-CH_3), 0.01 (s, 3H, TBS-CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.4 (C), 161.7 (C), 138.6 (C), 137.8 (C), 137.5 (C), 135.0 (C), 133.09 (C), 133.07 (CH), 133.0 (C), 130.1 (C), 130.0 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 126.7 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 125.8 (CH), 101.0 (CH), 99.9 (CH), 93.9 (CH), 92.2 (C), 79.9 (CH), 79.7 (CH), 77.4 (C), 75.1 (CH), 74.5 (2× CH_2), 73.7 (CH_2), 73.5 (CH), 72.5 (CH), 72.2 (CH), 71.8 (CH_2), 68.7 (CH_2), 66.3 (CH), 62.0 (CH), 25.7 (CH_3), 17.8 (C), −4.2 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{59}H_{64}Cl_3NO_{12}SiH$ $[M + H]^+$, 1112.3336; found, 1112.3356.

*4-Methylphenyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-4-O-benzyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**51**).* For reaction details, please see Scheme S5. To a solution of compound **2** (2.60 g, 2.35 mmol) in CH_2Cl_2 (12 mL) at 0 °C was added (1 M) BH_3.THF (9.40 mL, 9.40 mmol) solution. After 10 min, TMSOTf (213.0 μL, 1.18 mmol) was slowly added with continuous stirring. After 2 h, the reaction was quenched by dropwise addition of Et_3N to neutralize the pH. The neutralized reaction mixture was then extracted with saturated $NaHCO_3$ solution (30 mL, two times). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to afford the viscous crude. Column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) was done to purify the crude to furnish the pure product **51** (2.42 g, 93%) as a white amorphous foam. R_f 0.30 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ −6.66 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.75 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.64−7.53 (m, 4H, Ar-H), 7.48−7.42 (m, 2H, Ar-H), 7.42−7.37 (m, 2H, Ar-H), 7.36−7.32 (m, 2H, Ar-H), 7.32−7.26 (m, 7H, Ar-H), 7.25−7.22 (m, 4H, Ar-H), 7.20−7.16 (m, 3H, Ar-H), 7.15−7.1 (m, 2H, Ar-H), 6.95 (d, *J* = 7.95 Hz, 2H, Ar-H), 6.87 (d, *J* = 7.9 Hz, 1H, N−H), 5.67 (dd, *J* = 9.9, 8.0 Hz, 1H, H-2′), 5.05 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.97 (d, *J* = 10.3 Hz, 1H, CH_2Ph), 4.9 (d, *J* = 9.9 Hz, 1H, H-1), 4.78 (d, *J* = 12.3 Hz, 1H, CH_2 group of Nap), 4.69 (d, *J* = 7.9 Hz, 1H, H-1′), 4.61 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.58 (d, *J* = 12.4 Hz, 1H, CH_2 group of Nap), 4.50−4.37 (m, 3H, H-3, 2× CH_2Ph), 4.32 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.02 (d, *J* = 2.3 Hz, 1H, H-4′), 3.83 (d, *J* = 11.5 Hz, 1H, H-6a), 3.68 (d, *J* = 11.0 Hz, 1H, H-6b), 3.62−3.48 (m, 4H, H-3′, H-5′, H-6a′, H-6b′), 3.45−3.36 (m, 2H, H-4, H-5), 3.30 (m, 1H, H-2), 2.24 (s, 3H, $PhCH_3$), 2.03 (s, 1H, O−H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.6 (C), 161.2 (C), 138.7 (C), 138.6 (C), 138.1 (C), 138.0 (C), 134.9 (C), 133.3 (CH), 133.2 (C), 133.1 (CH), 130.1 (CH), 129.9 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.04 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.0 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 100.5 (CH), 92.7 (C), 84.8 (CH), 79.4 (CH), 79.3 (CH), 77.5 (CH), 76.1 (CH), 75.0 (CH_2), 74.9 (CH_2), 74.2 (CH), 73.7 (CH_2), 73.1 (CH), 72.1 (CH), 72.0 (CH_2), 68.6 (CH_2), 62.5 (CH_2), 57.4 (CH), 21.2 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{60}H_{58}Cl_3NO_{11}SNa$ $[M + Na]^+$, 1130.2677; found, 1130.2677.

*4-Methylphenyl (2-O-Benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside (**52**).* For reaction details, please see Scheme S5. A solution of compound **2** (1.50 g, 1.35 mmol) in 80% aq AcOH (64 mL) was stirred and heated at 54 °C with a silicone oil bath for 3.5 h. After completing the reaction, the reaction mixture was concentrated by evaporation to yield the viscous crude. Crude was redissolved in EtOAc (20 mL) and washed with dd. H_2O (20 mL, two times), followed by washing with saturated $NaHCO_3$ solution (20 mL, four times). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated by evaporation to yield a viscous crude. Pure product (**52**) was isolated after purification of the crude by column chromatography on silica gel with EtOAc/hexanes (1/2, v/v) in 70% yield (0.96 g) as a white amorphous solid. R_f 0.14 (EtOAc/hexanes = 1/2, v/v); $[\alpha]_D^{20}$ +9.62 (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.74 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.62−7.51 (m, 4H, Ar-H), 7.48−7.40 (m, 2H, Ar-H), 7.39−7.30 (m, 5H, Ar-H), 7.30−7.25 (m, 9H, Ar-H), 7.19 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.03 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.81 (d, *J* = 6.9 Hz, 1H, N−H), 5.68−5.58 (m, 1H, H-2′), 5.25 (d, *J* = 10.4 Hz, 1H, H-1), 4.95 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.74 (d, *J* = 12.1 Hz, 1H, CH_2 group of Nap), 4.64−4.55 (m, 3H, H-1′, CH_2Ph, CH_2 group of Nap), 4.44 (dd, *J* = 21.1, 11.7 Hz, 2H, 2× CH_2Ph), 4.38−4.21 (m, 2H, H-3, O−H), 3.99−3.90 (m, 1H, H-4′), 3.83 (dd, *J* = 11.5, 2.6 Hz, 1H, H-6a), 3.73−3.61 (m, 4H, H-3′, H-5′, H-6a′, H-6b), 3.55−3.44 (m, 2H, H-4, H-6b′), 3.43−3.33 (m, 1H, H-5), 3.22−3.05 (m, 1H, H-2), 2.35−2.10 (m, 4H, $PhCH_3$, OH); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.6 (C), 161.7 (C), 138.9 (C), 138.3 (C), 137.7 (C), 134.8 (C), 133.6 (CH), 133.4 (CH), 133.3 (C), 133.2 (C), 130.2 (CH), 130.1 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.46 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 126.9 (CH), 126.4 (CH), 126.3 (CH), 125.9 (CH), 101.2 (CH), 92.2 (C), 83.9 (CH), 81.8 (CH), 80.2 (CH), 79.8 (CH), 74.8 (CH_2), 74.3 (CH), 73.9 (CH_2), 72.7 (CH_2), 72.2 (CH), 70.6 (CH), 68.9 (CH_2), 63.4 (CH_2), 57.4 (CH), 21.3 (CH_3); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{53}H_{52}Cl_3NO_{11}SNa$ $[M + Na]^+$, 1040.2204; found, 1040.2220.

*tert-Butyldimethylsilyl(2-O-benzoyl-4,6-di-O-benzyl-3-O-(naphthalen-2-ylmethyl)-β-D-galactopyranosyl)-(1 → 3)-(4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1 → 3)-(2-O-benzoyl-4,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (**53**).* For reaction details, please see Scheme S9. A mixture of thiogalactoside **45** (164.4 mg, 0.23 mmol), compound **49** (100 mg, 0.19 mmol), and AW-300 molecular sieves (200 mg) in anhydrous CH_2Cl_2 (0.64 mL) was stirred at rt for 30 min under the N_2 atmosphere and then cooled down to −60 °C. NIS (52 mg, 0.23 mmol) and TfOH (3.4 μL, 0.04 mmol) were sequentially added to the resulting mixture and stirred at −60 °C for 2 h. The reaction was then warmed to −40 °C, followed by the addition of **35** (75 mg, 0.08 mmol). Then, NIS (34.6 mg, 0.154 mmol) and TfOH (1.36 μL, 0.02 mmol) were added to the reaction mixture. After stirring for 12 h at −40 °C, the reaction was quenched by dropwise addition of Et_3N, diluted with CH_2Cl_2 (5 mL), and filtered. The filtrate was washed with saturated $Na_2S_2O_3$ solution (10 mL, two times), dried over $MgSO_4$, filtered, and concentrated by evaporation to afford a thick yellow crude that was purified by column chromatography on silica gel with EtOAc/hexanes (1/4, v/v) to obtain tetrasaccharide **53** (93.6 mg, 0.048 mmol, 60% w.r.t compound **35**) as a white amorphous foam. R_f 0.47 (EtOAc/toluene = 1/7, v/v); $[\alpha]_D^{25}$ +4.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 7.7, 1.3 Hz, 2H, Ar-H), 7.85 (dd, *J* = 8.2, 1.2 Hz, 2H, Ar-H), 7.70 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.51−7.44 (m, 5H, Ar-H), 7.43−7.38 (m, 6H, Ar-H), 7.35−7.17 (m, 32H, Ar-H), 7.13 (dd, *J* = 8.4, 1.43 Hz, 1H, Ar-H), 6.78 (d, *J* = 6.85 Hz, 1H, NH), 6.62 (d, *J* = 5.4 Hz, 1H, NH″), 5.55 (dd, *J* = 10.05, 8.0 Hz, 1H, H-2‴), 5.45 (s, 1H, PhCH benzylidene), 5.43 (m, 2H, PhCH benzylidene, H-2′), 5.18 (d, *J* = 7.75 Hz, 1H, H-1), 5.06 (d, *J* = 8.05 Hz, 1H, H-1″), 4.95 (d, *J* = 11.7 Hz, 1H, CH_2Ph), 4.76 (d, *J* = 11.95

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Hz, 1H, CH_2Ph), 4.68 (d, J = 12.3 Hz, 1H, CH_2 group of Nap), 4.64 (d, J = 7.8 Hz, 1H, H-1′), 4.60 (t, J = 10.3 Hz, 2H, H-1‴, CH_2Ph), 4.53−4.46 (m, 3H, H-3, CH_2Ph, CH_2 group of Nap), 4.40 (d, J = 11.65 Hz, 1H, CH_2Ph), 4.37−4.22 (m, 6H, H-3, H-6a″, CH_2Ph), 4.19 (dd, J = 10.3, 4.8 Hz, 1H, H-6a), 3.93 (d, J = 2.1 Hz, 1H, H-4‴), 3.90−3.85 (m, 2H, H-3′, H-4′), 3.71−3.59 (m, 4H, H-4, H-4″, H-6b, H-6b″), 3.59−3.56 (m, 1H, H-3‴), 3.55−3.46 (m, 4H, H-5″, H-5′, H-5‴, H-6a′), 3.46−3.40 (m, 2H, H-5, H-6a‴), 3.42−3.33 (m, 2H, H-6b′, H-6b‴), 3.16−3.03 (m, 2H, H-2, H-2″), 0.79 (s, 9H, TBS-t-Bu), 0.02 (s, 3H, TBS-CH_3), −0.01 (s, 3H, TBS-CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.5 (C), 165.1 (C), 161.8 (C), 161.7 (C), 139.0 (C), 138.7 (C), 138.0 (C), 137.9 (C), 137.6 (C), 137.4 (C), 135.0 (C), 133.4 (CH), 133.2 (CH), 133.18 (C), 133.1 (C), 130.1 (CH), 130.06 (CH), 130.0 (C), 129.1 (CH), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.19 (CH), 128.15 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 126.7 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 101.1 (CH), 101.0 (CH), 100.3 (CH), 100.1 (CH), 99.3 (CH), 94.0 (CH), 92.4 (C), 91.8 (C), 80.1 (CH), 79.6 (CH), 79.4 (CH), 78.0 (CH), 76.6 (CH), 75.0 (CH_2), 75.0 (CH), 74.7 (CH), 74.7 (CH_2), 73.8 (CH_2), 73.7 (CH_2), 73.6 (CH), 73.5 (CH), 72.8 (CH), 72.6 (CH), 72.2 (CH), 72.0 (CH_2), 68.7 (CH_2), 68.6 (CH_2), 66.3 (CH), 66.28 (CH), 62.5 (CH), 59.9 (CH), 25.8 (CH_3), 17.9 (C), −4.1 (CH_3), −5.1 (CH_3); HRMS (ESI-TOF) m/z: calcd for $C_{101}H_{104}Cl_6N_2O_{23}SiNa$ $[M + Na]^+$, 1976.4827; found, 1976.4893.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02422.

Synthesis of type I LacNAc hexasaccharide **36**, donor **45**, GlcNTCA building block **48**, disaccharide building blocks **2** and **35**, type I LacNAc disaccharide donors (**4**, **6**, **7**, and **8**) and (**1**, **3**, and **5**) and acceptors (**10**−**13** and **15**) and (**14** and **16**), type I LacNAc disaccharide donor **9**, type I LacNAc tetrasaccharide acceptor **37**, and [2 + 2] chemoselective glycosylation; reference donors and linear correlation; reactivity ratio and RRV of disaccharides **1**−**9** and **10**−**16**; listed estimated ln-(RRV_D); and copies of NMR spectra of new compounds (PDF)

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