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Studies on the Selectivity Between Nickel-Catalyzed 1,2-*cis*-2-Amino Glycosylation of Hydroxyl Groups of Thioglycoside Acceptors with C(2)-Substituted Benzylidene *N*-Phenyl Trifluoroacetimidates and Intermolecular Aglycon Transfer of the Sulfide Group

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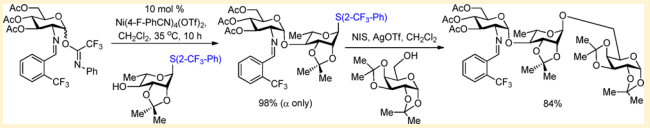
Supporting Information

ABSTRACT: The stereoselective synthesis of saccharide thioglycosides containing 1,2-*cis*-2-amino glycosidic linkages is challenging. In addition to the difficulties associated with achieving high α-selectivity in the formation of 1,2-*cis*-2-amino glycosidic bonds, the glycosylation reaction is hampered by undesired transfer of the anomeric sulfide group from the glycosyl acceptor to the glycosyl donor. Overcoming these obstacles will pave the way for the preparation of oligosaccharides and glycoconjugates bearing the 1,2-*cis*-2-amino glycosidic linkages because the saccharide thioglycosides obtained can serve as donors for another coupling iteration. This approach streamlines selective deprotection and anomeric derivatization steps prior to the subsequent coupling event. We have developed an efficient approach for the synthesis of highly yielding and α-selective saccharide thioglycosides containing 1,2-*cis*-2-amino glycosidic bonds, via cationic nickel-catalyzed glycosylation of thioglycoside acceptors bearing the 2-trifluoromethylphenyl aglycon with *N*-phenyl trifluoroacetimidate donors. The 2-trifluoromethylphenyl group effectively blocks transfer of the anomeric sulfide group from the glycosyl acceptor to the C(2)-benzylidene donor and can be easily installed and activated. The current method also highlights the efficacy of the nickel catalyst selectively activating the C(2)-benzylidene imidate group in the presence of the anomeric sulfide group on the glycosyl acceptors.



INTRODUCTION

Alkyl and aryl thioglycosides have been widely utilized as both the acceptors and donors in the multistep synthesis of oligosaccharides and glycoconjugates.[1] They are versatile in that their anomeric sulfide groups are easy to install and stable under many reaction conditions.[2] As a result, the sulfide groups not only serve as efficient protecting groups of anomeric centers but also act as glycosyl acceptors in combination with a variety of glycosyl donors such as trichloroacetimidates, halides and sulfoxides.[3] The resulting saccharide thioglycosides can be subsequently activated for another coupling iteration to generate the corresponding oligosaccharides or glycoconjugates.[3,4] Despite the widespread synthetic utility of thioglycosides, intermolecular aglycon transfer can be a serious side reaction. When an unreactive thioglycoside acceptor is employed in the coupling process, the anomeric sulfide group can be transferred from the glycosyl acceptor to the glycosyl donor to give another thioglycoside.[6] To prevent aglycon transfer, Li and Gildersleeve have recently reported the use of 2,6-dimethylphenyl (DMP) group as an efficient aglycon for thioglycoside acceptors.[5] This bulky group effectively blocks intermolecular aglycon transfer[6] of the anomeric sulfur atom in the glycosylation reaction.

We recently developed a novel strategy for the synthesis of 1,2-*cis*-2-aminosugars via nickel-catalyzed coupling with the C(2)-*N*-substituted benzylidene trichloroacetimidates (Scheme 1a).[7,8] This method utilizes the nature of the nickel-ligand complex and metal-bound functional group at the C(2)-position of glycosyl donors to control the α-selectivity and provide high yielding oligosaccharides and glycoconjugates from a wide variety of glycosyl donors and acceptors.

In an effort to expand the capabilities of this method, we targeted the development of a variant proceeding via chemoselective coupling to the hydroxyl groups of thioglycosides, as depicted in Scheme 1b. A number of challenges have to be addressed in developing such a chemoselective glycosylation process. For instance, the nickel catalyst could fail to promote the coupling due to the displacement of metal-bound benzonitrile ligand by the anomeric sulfide group, producing an inactive nickel catalyst.[9] Second, the trihaloacetimidate group could undergo [1,3]-rearrangement to provide the corresponding glycosyl trihaloacetamide.[10] Third, intermolecular aglycon transfer of the anomeric sulfide group from the glycosyl acceptor to the glycosyl donor provides undesired thioglycoside.[6] We report herein an efficient approach for the preparation of saccharides containing 1,2-*cis*-2-amino glycosidic linkages via nickel-catalyzed α-chemoselective glycosylation of the hydroxyl groups of thioglycoside acceptors with C(2)-benzylidene *N*-phenyl trifluoroacetimidates (Scheme 1b). This strategy overcomes the challenges associated with intermolecular aglycon transfer of the anomeric sulfide group from the acceptors to the C(2)-benzylidene imidate donors and retains the unique features

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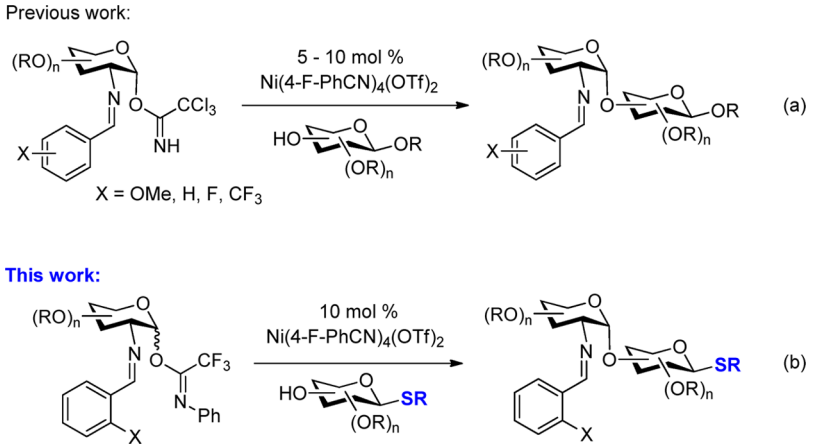
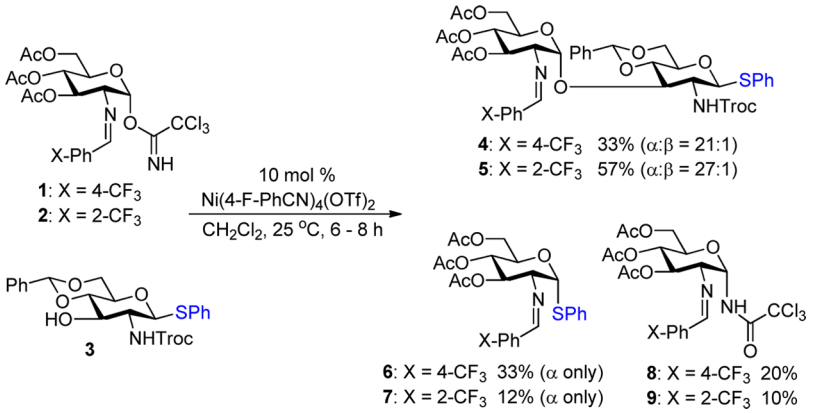
Scheme 1. Nickel-Catalyzed 1,2-*cis*-2-Amino Glycosylation



Scheme 2. Initial Studies with Trichloroacetimidate Donors



of the nickel catalyst to control the α-selectivity at the newly formed glycosidic bond.

RESULTS AND DISCUSSION

Optimization Studies. We initially explored the nickel-catalyzed glycosylation of *N*-Troc protected thioglycoside **3**[6f,g] with the C(2)-*N*-*p*-trifluoromethyl-benzylidene trichloroacetimidate **1** (Scheme 1) to probe issues of both aglycon transfer and selectivity. Under previous nickel conditions (10 mol % Ni(4-F-PhCN)$_4$(OTf)$_2$ at 25 °C in CH_2Cl_2),[7] disaccharide **4** (Scheme 2) was isolated in 33% along with aglycon transfer product **6** (33%) and [1,3]-rearrangement trichloroacetamide **8** (20%). Switching to C(2)-*N*-*o*-trifluoromethyl-benzylidene donor **2** improved both the yield and α-selectivity of disaccharide **5** (57%) and decreased the amount of transfer product **11** (12%) and trichloroacetamide **9** (10%). Formation of the rearrangement products **8** and **9** indicate the disadvantage of utilizing trichloroacetimidates as glycosyl donors.

To prevent [1,3]-rearrangement of the imidate group, the *N*-phenyl trifluoroacetimidate donor **10** (Table 1) was chosen due to its attenuated reactivity in comparison to trichloroacetimidates **1** and **2** (Scheme 2).[11] Accordingly, coupling of thioglycoside **3** (Table 1) with **10** was first examined at 25 °C, and the reaction was sluggish. Warming the reaction to 35 °C accelerated the coupling process and provided **5** (entry 1) in 58% yield as a single α-isomer. The undesired rearrangement acetamide (e.g., **9**) was not observed. In this experiment, both α- and β-isomers of donor **10** reacted, highlighting another advantage of using this glycosyl donor.[12] A significant amount of aglycon transfer product **7** (14%, entry 1), however, was still obtained in the reaction.

Thus, the key to the optimization is to minimize aglycon transfer. Unfortunately, we were unable to install the DMP group[5] onto the anomeric center of *N*-Troc glucosamine. We then systematically examined the steric and electronic nature of the substituents on the phenyl ring of a number of thioglycosides **12**−**17** (Table 1) in the coupling with imidate **10**. While the electron-rich 4-methoxyphenyl aglycon **14** (entry 5) significantly increased the amount of transfer product **28**, the electron-poor groups **15**−**17** (entries 6−8) nearly blocked transfer. The most efficient acceptor was 2-trifluoromethylphenyl thioglycoside **17** (entry 8), which completely prevented transfer and provided disaccharide **24** (entry 8) in 61% yield and exclusively as the α-isomer. Even with two equivalents of donor **10**, no aglycon transfer product **31** (entry 9) was observed in the reaction. Overall, the 2-trifluoromethylphenyl group is an excellent alternative aglycon for thioglycoside acceptor. In addition, the nickel catalyst not only selectively activates the C(2)-benzylidene imidate **10** in the presence of the anomeric sulfide group on the glycosyl acceptor **17** but also effectively controls the α-anomeric selectivity in the synthesis of disaccharide thioglycoside **24** containing 1,2-*cis*-2-amino glycosidic bond.

To evaluate the unique features of the nickel catalyst as the effective activating agent to promote the glycosylation reaction, a number of catalysts (Table 2) were screened in the coupling of 2-trifluoromethylphenyl thioglycoside **3** with imidate donor **10**. Using TMSOTf (entry 1) resulted in 13% of disaccharide **5** with α:β = 10:1 and 40% of transfer product **7**. Similar results were

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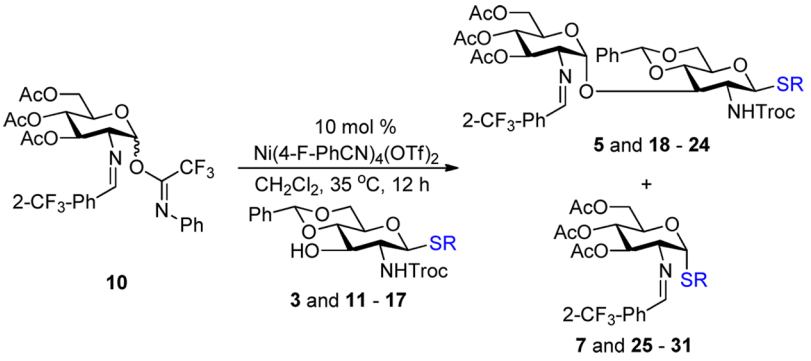
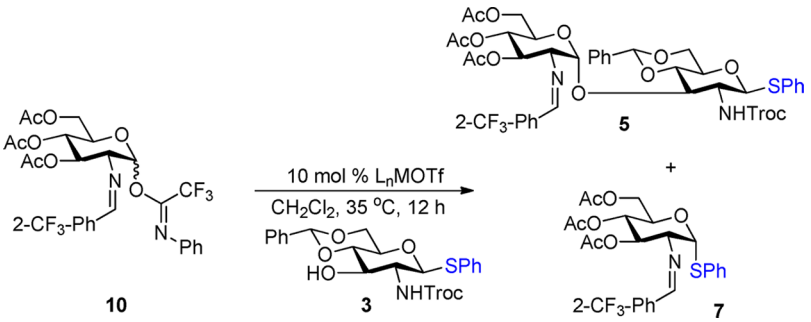
Table 1. Studies with *N*-Phenyl Trifluoroacetimidate[a]



entry	acceptors	donor/acceptor ratio	disaccharides yield (%)[b] (α:β)[c]	thioglycosides yield (%)
1	**3**: R = Ph	1/2	**5**: 58 (α only)	**7**: 14
2	**11**: R = Et	1/2	**18**: 43(10:1)	**25**:22
3	**12**: R = 1-Naphthyl	1/2	**19**: 59 (α only)	**26**: 10
4	**13**: R = 4-Me-Ph	1/2	**20**: 38(11:1)	**27**: 20
5	**14**: R = 4-MeO-Ph	1/2	**21**:37(11:1)	**28**: 30
6	**15**: R = 4-F-Ph	1/2	**22**: 58(20:1)	**29**: 9
7	**16**: R = 2-F-Ph	1/2	**23**: 60 (α only)	**30**: 4
8	**17**: R = 2-CF_3-Ph	1/2	**24**: 61 (α only)	**31**: 0
9	**17**: R = 2-CF_3-Ph	2/1	**24**: 58 (α only)	**31**: 0

[a]All reactions were run in 10 mol % $Ni(4\text{-F-PhCN})_4(OTf)_2$ at 35 °C for 12 h. [b]Isolated Yield. [c]^{1}H NMR ratio.

Table 2. Activation of Glycosyl Imidate with Various Catalysts[a]



entry	catalysts	disaccharide **5** yield (%)[b] (α:β)[c]	thioglycoside **7** yield (%)
1	TMSOTf	13(10:1)	40
2	$Cu(OTf)_2$	26(10:1)	30
3	$Rh(COD)_2OTf$	43(6:1)	20
4	$Ir(COD)_2OTf$	45(8:1)	26
5	$Pd(4\text{-F-PhCN})_2(OTf)$	36(20:1)	23
6	$Ph_3PAuOTf$	43 (α only)	21
7	$Fe(OTf)_2$	11(11:1)	1

[a]All reactions were run in 10 mol % catalyst at 35 °C for 12 h. [b]Isolated yield. [c]^{1}H NMR ratio.

obtained with a milder Lewis acid, $Cu(OTf)_2$ (entry 2). Use of both $Rh(COD)_2OTf$ and $Ir(COD)_2OTf$ catalysts (entries 3 and 4) provided **5** in lower yield (43−45%) and α-selectivity (α:β = 6:1−8:1) in comparison to the nickel catalyst whereas **7** was obtained in 58% yield and as a single α-isomer (Table 1, entry 1). In addition, employing iridium as the activating agent significantly increased the amount of transfer product **7** (14%→26%). The palladium catalyst (entry 5), $Pd(4\text{-F-PhCN})_2OTf_2$, decreased the yield of disaccharide **5** (40%) but increased the yield of transfer product **7** (14%→24%). Gold catalyst, $Ph_3PAuOTf$ (entry 6), provided exclusive α-disaccharide **5** in 43% yield, but a significant amount of sulfide transfer **7** (21%) was still obtained in the reaction. Although less than 1% of transfer product **7** was observed in the reaction using $Fe(OTf)_2$ as the catalyst (entry 7), the desired disaccharide **5** was only isolated in 11% yield.

Substrate Scope. We next examined the scope of the glycosylation of a variety of thioglycosides with armed and disarmed imidates **10**, **32**, and **33** (Table 3). In contrast to disarmed donor **10** (Table 1, entry 1), coupling of armed donor **33** (Table 3, entry 1) with phenyl thioglycoside **3** resulted in no transfer product **47**; disaccharide **39** (entry 1) was isolated in 70% yield, albeit in lower α-selectivity (α:β = 6:1). Similarly, coupling of phenyl D-galactosyl thioglycoside **34** with both

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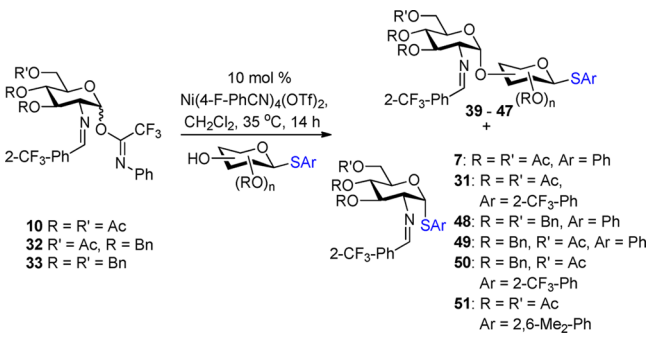
Table 3. Coupling of Thioglycosides with Glucosamine Donors[a]



entry	donors	acceptors	disaccharides yield[d] (α:β)[e]	thioglycosides (yield)[f]
1	33	3	**39**: 64% (6:1)[b]	**48**: 0%
2	10	34	**40**: R = Ac 55% (α only)[b]	**7**: 24%
3	32	34	**41**: R = Bn 61% (α only)[b]	**49**: 8%
4	10	35	**42**: 71% (α only)[c]	**31**: 0%
5	10	36	**43**: R = Ac 81% (α only)[b]	**7**:15%
6	32	36	**44**: R = Bn 72% (α only)[b]	**49**: 9%
7	10	37	**45**: R = Ac 98% (α only)[b]	**31**: 0%
8	32	37	**46**: R = Bn 78% (α only)[b]	**50**: 0%
9	10	38	**47**: 74% (α only)[b]	**51**: 0%

[a]All reactions were conducted with 10 mol % $Ni(4\text{-F-PhCN})_4(OTf)_2$ for 14 h. [b]Donor/Acceptor = 1:2. [c]Donor/Acceptor = 2:1. [d]Isolated yields. [e]^1H NMR ratio. [f]Transfer products were obtained as single α-isomers.

donors **10** and **32** (entries 2 and 3) provided a large quantity of sulfide transfer products **7** and **49**, respectively. The armed donor **32** provided less aglycon transfer than the disarmed donor **10** (8 vs 24%). The 2-trifluoromethylphenyl aglycon was then incorporated into D-galactosyl thioglycoside **35** (entry 4).[6] No trace amount of transfer product **31** (entry 4) was observed, and exclusive α-disaccharide **42** was isolated in 71% yield. The efficacy of the nickel method was further evaluated with L-rhamnose acceptors **36** and **37** (entries 5 and 8). As anticipated, although glycosylation of the phenyl thioglycoside acceptor **36** with both disarmed donor **10** (entry 5) and armed donor **32** (entry 6) provided disaccharides **43** and **44**, respectively, in good yields (72−81%) and with complete α-selectivity, a significant amount of transfer products **7** (15%) and **49** (9%) was still observed in the coupling process. On the other hand, the electron deficient 2-trifluoromethylphenyl thioglycoside **37** completely blocked sulfide transfer (entries 7 and 8), providing disaccharides **45** and **46** in high yield (78−98%) and as single α-isomers. To further compare, the DMP group was incorporated into L-rhamnose thioglycoside **38** (entry 9). In agreement with previous studies,[5] no transfer product **51** was obtained in the reaction. The modified disaccharide **47** (entry 9), however, was obtained in lower yield than disaccharide **45** (entry 5) bearing the 2-trifluoromethylphenyl aglycon. Overall, the results clearly illustrate that the electron-withdrawing 2-trifluoromethylphenyl aglycon completely prevents transfer of the anomeric sulfide group from thioglycoside acceptors to both disarmed and armed *N*-phenyl trifluoroacetimidate donors.

The utility of the current method was further explored with galactosamine donors **52** and **53** (Table 4). Coupling of phenyl thioglycoside **3** with both disarmed and armed galactosamine donors **52** and **53** (entries 1 and 2) provided disaccharides **54** and **55**, respectively, in moderate yield (56 − 67%) and with excellent α-selectivity (α:β = 14:1 to >20:1). As expected, a significant amount of transfer products **60** and **61** (6−16%) was also isolated in the reaction. On the other hand, employing 2-trifluoromethylphenyl thioglycoside **17** (entry 3) as a glycosyl acceptor completely blocked formation of transfer product **62** and provided α-disaccharide **56** (entry 3) in 73% yield. Derivative of disaccharides **54**−**56** (entries 1−3), GalNAc-α-(1→3)-GlcNAc, is a part of the *O*-polysaccharide present in the outer membrane of Gram-negative bacteria such as *Salmonella enterica*[13] and *Providencia rustigianii*.[14] *S. enterica* is a major pathogen of humans and animals.[11] *P. rustigianii* invades human intestinal mucosa and causes stomach infection particularly in children.[12] Next, phenyl thioglycoside **34** (entries 4 and 5) was investigated with both glycosyl donors **52** and **53**, and a significant amount of transfer products **60** and **61** were obtained in the glycosylation reaction. Under nickel conditions, the higher amount of transfer product **61** (40%, entry 5) was obtained with partially armed donor **53** than that of transfer product **60** (24%, entry 4) with disarmed donor **52**. Thioglycoside **35** (entry 6) bearing the 2-trifluoromethylphenyl aglycon was then explored with this problematic reaction. As expected, the modified disaccharide **59** (entry 6) was isolated in 62% yield and with exclusively α-selectivity. Again, transfer product **62** was not observed with this 2-trifluoromethylphenyl acceptor **35**. Disaccharides **57**−**59** (entries 4−6), derivatives of GalNAc-α-(1→3)-Gal, are vital disaccharide units of human blood group A antigens.[15]

One of the key concerns in reducing the reactivity of the sulfide aglycon to prevent intermolecular transfer is that the modified arylthiol group cannot be efficiently activated. To illustrate that the 2-trifluoromethylphenyl aglycon can be sufficiently activated with thiophilic reagents (Scheme 3), disaccharide thioglycoside donor **45** was treated with the reagent combination of NIS and AgOTf.[16,17] Subsequent addition of a galactosyl acceptor **63** provided trisaccharide **64** in 84% yield, validating the ability of the 2-trifluoromethylphenyl group as an excellent alternative aglycon for thioglycosides. Encouraged by this result, we further explored the glycosylation of glycosyl acceptor **63** with less reactive disaccharide thioglycoside donor **24** (Scheme 3b) under similar nickel conditions. Gratifyingly, the coupling process

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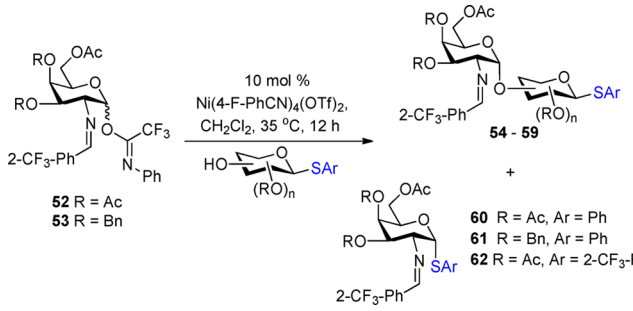
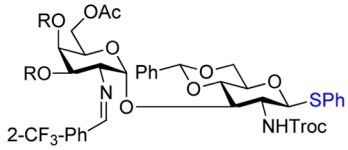
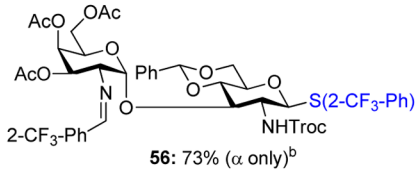
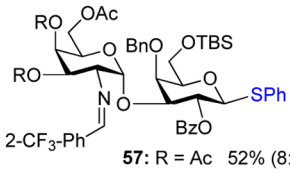
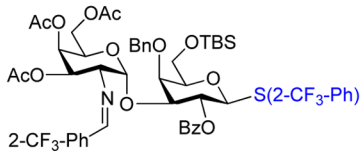
Table 4. Coupling of Thioglycosides with Galactosamine Donors[a]



entry	donors	acceptors	disaccharides yield[d] (α:β)[e]	thioglycosides (yield)[f]
				
1	**52**	**3**	**54:** R = Ac 67% (α only)[b]	**60**: 16%
2	**53**	**3**	**55:** R = Bn 56% (14:1)[b]	**61**: 6%
				
3	**52**	**17**	**56:** 73% (α only)[b]	**62**: 0%
				
4	**52**	**34**	**57:** R = Ac 52% (8:1)[b]	**60**: 24%
5	**53**	**34**	**58:** R = Bn 51% (α only)[b]	**61**: 40%
				
6	**52**	**35**	**59:** 62% (α only)[b]	**62**: 0%

[a]All reactions were conducted with 10 mol % Ni(4-F-PhCN)$_4$(OTf)$_2$ for 14 h. [b]Donor/Acceptor = 1:2. [c]Donor/Acceptor = 2:1. [d]Isolated yields. [e]^{1}H NMR ratio. [f]Transfer products were obtained as single α-isomers.

proceeded smoothly to provide the desired trisaccharide **65** in 81% yield and with exclusive β-selectivity. The results obtained in Scheme 3 also illustrate the ability of the C(2)-*N*-substituted benzylidene functionality to act as the efficient protecting group. Next, it is essential to determine that these benzylidene groups could be converted to the corresponding *N*-acetyl or other functional groups. Accordingly, treatment of **65** with HCl, acetone/CH_2Cl_2 at 25 °C for less than 5 min provided the corresponding amine salt along with the concomitant removal of the benzylidene protecting group. To ease the purification process, the resulting amine salt intermediate was acetylated to afford the fully protected trisaccharide **66** (Scheme 3b) in 99% yield over two steps.

Currently, the most common method for the synthesis of 1,2-*cis*-2-aminosugars employs glycosyl donors bearing the C(2)-azido functionality.[18] To compare the ability of the nickel catalyst to efficiently activate the C(2)-azido donor, a series of glycosylations were performed with glycosyl *N*-phenyl trifluoroacetimidate **67** (Scheme 4).[11,19] Accordingly, coupling of phenyl thioglycoside acceptor **3** with imidate **67** in the presence of 10 mol % Ni(4-F-PhCN)$_4$(OTf)$_2$ provided sulfide transfer product **69** (40%) as the major product (Scheme 4a). The desired disaccharide **68** was obtained in 18% yield, albeit with excellent α-selectivity. Although transfer product was not detected in the reaction with the 2-trifluoromethyl-phenyl thioglycoside acceptor **17**, only 13% of the desired disaccharide **67** was isolated (Scheme 4b).[20] When L-rhamnoside **36** was employed as the glycosyl donors in the reaction with C(2)-azido donor **67** (Scheme 4c), higher amount of transfer product **69** (28 vs 15%) and lower yield of the desired disaccharide **71** (49 vs 81%) were obtained than those with C(2)-benzylidene donor **10** (Table 3, entry 5). Overall, these results suggest that the nickel catalyst, Ni(4-F-PhCN)$_4$(OTf)$_2$, is the more efficient activating

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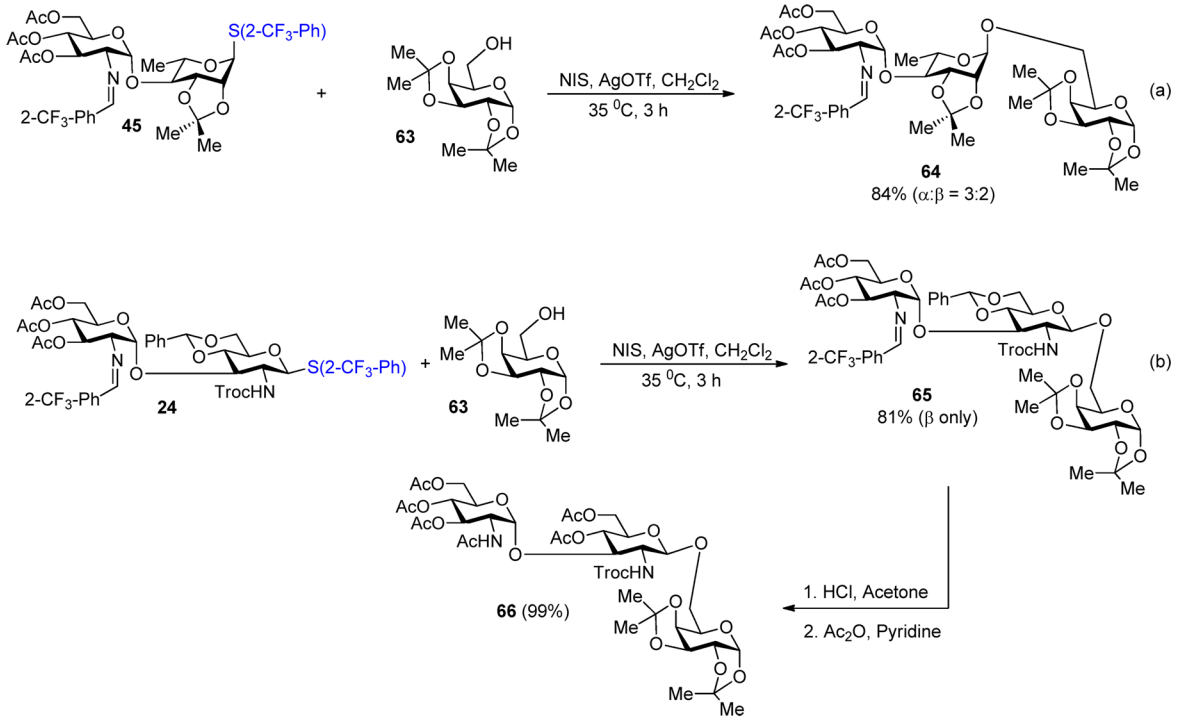
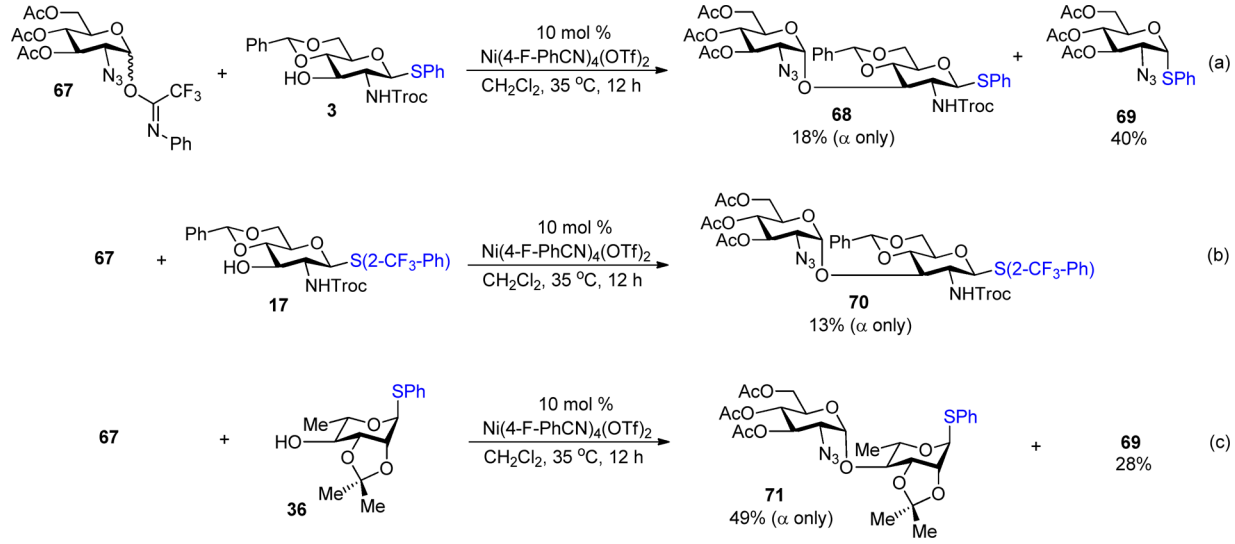
Scheme 3. Activation of 2-Trifluoromethylphenyl Thiolglycosides



Scheme 4. Glycosylation with C(2)-Azido Imidate Donor



reagent for C(2)-*N*-substituted benzylideneamino donors than that for C(2)-azido donors.

CONCLUSION

In summary, we have developed an efficient strategy to chemoselective glycosylation for the preparation of various saccharide thioglycoside building blocks in moderate to good yields and with excellent levels of α-selectivity. This approach employs a method of nickel-catalyzed 1,2-*cis*-2-amino glycosylation of thioglycoside acceptors bearing the 2-trifluoromethylphenyl aglycon with armed and disarmed C(2)-substituted *N*-phenyl trifluoroacetimidate donors. The resulting saccharide thioglycosides serve as glycosyl donors for another coupling iteration to generate oligosaccharides. Overall, the 2-trifluoromethylphenyl functionality is a more efficient aglycon than its phenyl counterpart to completely prevent transfer of the sulfide group from the glycosyl acceptor to the C(2)-benzylidene *N*-phenyl trifluoroacetimidate donors. In addition, it can be easily introduced onto the glycosyl acceptor and subsequently activated. This approach to the stereoselective synthesis of saccharide thioglycosides also highlights the ability of the C(2)-*N*-substituted benzylidene functionality as the efficient protecting group. Efforts are underway in our group to adapt this strategy for the preparation of biologically active oligosaccharides and glycoconjugates.

EXPERIMENTAL SECTION

General Procedure for the Preparation of Glycosyl Donors: 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-glucopyranosyl *N*-Phenyl Trifluoroacetimidate 10. A 100 mL RBF was charged with triacetyl D-glucosamine hemiacetal **10A**

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(4.9 g, 10.6 mmol, 1.0 equiv.),[7b] 2,2,2-Trifluoro-*N*-phenyl-ethanimidoyl chloride (6.66 g, 31.9 mmol, 3.0 equiv), K_2CO_3 (2.93 g, 21.2 mmol, 2.0 equiv) and acetone (30.0 mL). The solution was stirred at room temperature overnight. When the reaction was complete as monitored by TLC (hexane/ethyl acetate = 3/1), the reaction mixture was filtered, evaporated, and purified by flash chromatography on silica gel (hexane/ethyl acetate = 5/1 → 3/1 with 1% Et_3N) to afford **10** (5.26 g, 80%, α:β = 1:4) as a viscous oil. **10*α***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.68 (s, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 7.73−7.52 (m, 3 H), 7.25−7.13 (m, 2 H), 7.12−6.98 (m, 1 H), 6.88−6.65 (m, 2 H), 6.44 (brs, 1 H), 6.65 (t, J = 10.0 Hz, 1 H), 5.23 (app t, J = 10.0 Hz, 1 H), 4.48−4.27 (m, 2 H), 4.22−4.08 (m, 1 H), 3.88−3.77 (m, 1 H), 2.10 (s, 3 H), 2.05 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.4, 169.7, 169.5, 161.5, 143.2, 133.1, 132.1, 131.0, 129.4 (q, J_{C-F} = 30.5 Hz), 128.64, 128.59, 125.6 (q, J_{C-F} = 5.6 Hz), 124.3, 124.0 (d, J_{C-F} = 272 Hz), 119.4, 94.7, 71.1, 70.5, 68.0, 61.7, 20.55, 20.50, 20.2; IR (film, cm^{-1}): ν = 2963, 1752, 1644, 1367, 1315, 1212; HRMS (ESI): calcd for $C_{28}H_{26}F_6N_2O_8Na$ (M + Na): 655.1491; found: 655.1497. **10*β***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.68 (d, J = 2.4 Hz, 1 H), 8.11 (d, J = 7.6 Hz, 1 H), 7.71 (d, J = 7.2 Hz, 1 H), 7.68−7.51 (m, 2 H), 7.38−7.27 (m, 2 H), 7.19−7.07 (m, 1 H), 6.82 (d, J = 7.6 Hz, 2 H), 6.02 (brs, 1 H), 5.46 (t, J = 10.0 Hz, 1 H), 5.19 (app t, J = 10.0 Hz, 1 H), 4.34 (dd, J = 12.4, 4.8 Hz, 1 H), 4.17 (dd, J = 12.4, 2.0 Hz, 1 H), 3.93−3.76 (m, 1 H), 3.71 (t, J = 8.8 Hz, 1 H), 2.10 (s, 3 H), 2.04 (s, 3 H), 1.93 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.4, 169.5, 143.2, 133.3, 132.1, 130.9, 129.3 (q, J_{C-F} = 31.0 Hz), 128.7, 128.6, 125.6 (q, J_{C-F} = 5.5 Hz), 124.4, 124.0 (d, J_{C-F} = 272 Hz), 119.2, 95.7, 73.3, 72.9, 72.7, 68.0, 61.7, 20.53, 20.47, 20.2; IR (film, cm^{-1}): ν = 2887, 1752, 1645, 1489, 1315, 1231; HRMS (ESI): calcd for $C_{28}H_{26}F_6N_2O_8Na$ (M + Na) 655.1491; found 655.1511.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-galactopyranosyl *N*-Phenyl Trifluoroacetimidate 52. Viscous oil: 276 mg, 94%, α:β = 1:4; **52*α***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.70 (s, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 7.70 (d, J = 7.6 Hz, 1 H), 7.65−7.52 (m, 2 H), 7.31−7.18 (m, 2 H), 7.10−7.02 (m, 1 H), 6.89−6.66 (m, 2 H), 6.50 (brs, 1 H), 5.68−5.56 (m, 1 H), 5.51 (dd, J = 10.4, 2.8 Hz, 1 H), 4.53 (app t, J = 6.0 Hz, 1 H), 4.34−4.11 (m, 2 H), 4.09−3.93 (m, 1 H), 2.20 (s, 3 H), 2.08 (s, 3 H), 1.90 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.3, 170.0, 169.7, 161.6, 143.3, 133.3 132.1, 130.9, 129.2 (q, J_{C-F} = 31.0 Hz), 128.7, 128.5, 125.6 (q, J_{C-F} = 5.5 Hz), 124.6, 124.1 (d, J_{C-F} = 272 Hz), 119.4, 95.3, 69.4, 68.1, 66.3, 66.2, 61.6, 20.7, 20.6, 20.3; IR (film, cm^{-1}): ν = 2968, 1750, 1713, 1645, 1488, 1314; HRMS (ESI): calcd for $C_{28}H_{26}F_6N_2O_8Na$ (M + Na) 655.1491; found 655.1502. **52*β***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.71 (s, 1 H), 8.10 (d, J = 7.6 Hz, 1 H), 7.69 (d, J = 7.6 Hz, 1 H), 7.66−7.48 (m, 2 H), 7.37−7.20 (m, 2 H), 7.17−7.02 (m, 1 H), 6.89−6.71 (m, 2 H), 6.00 (brs, 1 H), 5.53−5.41 (m, 1 H), 5.38−5.12 (m, 1 H), 4.42−4.16 (m, 2 H), 4.11−3.98 (m, 1 H), 3.84 (t, J = 8.4 Hz, 1 H), 2.20 (s, 3 H), 2.02 (s, 3 H), 1.91 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.2, 170.1, 169.6, 162.5, 143.2, 133.4, 132.1, 130.8, 129.2 (q, J_{C-F} = 31.0 Hz), 128.7, 128.5, 125.6 (q, J_{C-F} = 5.7 Hz), 124.4, 124.0 (d, J_{C-F} = 272 Hz), 119.1, 96.0, 71.9, 70.9, 69.1, 65.5, 61.2, 20.6, 20.5, 20.2; IR (film, cm^{-1}): ν = 2932, 1747, 1721, 1646, 1488, 1371, 1314, 1209; HRMS (ESI): calcd for $C_{28}H_{26}F_6N_2O_8Na$ (M + Na) 655.1491; found 655.1501.

1,6-Di-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-*p*-methoxybenzylideneamino-D-galactopyranoside 53B. A 250 mL oven-dried RBF was charged with **53A** (3.36 g, 11.3 mmol, 1 equiv),[7b] TBSCl (3.58 g, 23.7 mmol, 2.1 equiv), imidazole (1.69 g, 24.9 mmol, 2.2 equiv) and THF/DMF (40 mL/10 mL). The solution was stirred at room temperature overnight. The solution was diluted with CH_2Cl_2/MeOH (20:1), washed with brine (2 × 50 mL). The aqueous phase was then extracted with CH_2Cl_2/MeOH (20:1, 2 × 100 mL). The organic phase was combined, concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography (hexane/ethyl acetate = 10/1 → 5/1 → 1/1 with 1% Et_3N) to afford **53B** (1.94 g, 35%) as a viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.26 (s, 1H), 7.67 (d, J = 9.2 Hz, 2H), 6.91 (d, J = 9.2 Hz, 2H), 4.79 (d, J = 7.2 Hz, 1 H), 4.06 (app t, J = 3.6 Hz, 1 H), 3.94 (dd, J = 10.4, 6.0 Hz, 1 H), 3.88 (dd, J = 10.4, 4.8 Hz, 1 H), 3.90−3.80 (m, 1 H), 3.85 (s, 3 H), 3.60 (t, J = 5.6 Hz, 1 H), 3.24 (dd, J = 9.6, 7.6 Hz, 1 H), 2.78 (d, J = 4.8 Hz, 1 H), 4.27 (brs, 1 H), 0.92 (s, 9 H), 0.78 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.07 (s, 3 H), −0.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.9, 161.7, 131.9, 130.2, 113.7, 96.6, 75.6, 74.8, 72.6, 68.0, 62.8, 55.3, 25.8, 25.5, 18.2, 17.9, −4.3, −5.3, −5.45, −5.51; IR (film, cm^{-1}): ν = 3419, 2927, 1644, 1605, 1577, 1512, 1249.

3,4-Di-*O*-benzyl-1,6-di-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-*p*-Methoxybenzylideneamino-D-galactopyranoside 53C. A 250 mL RBF was charged with diol **53B** (1.17 g, 2.2 mmol, 1.0 equiv), benzyl bromide (0.78 mL, 6.6 mmol, 3.0 equiv) and DMF (10 mL). The solution was cooled to −20 °C, and NaH (60%, 0.22 g, 5.5 mmol, 2.5 equiv.) was added in several portions. The reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with ethyl acetate, washed with brine (2 × 50 mL), dried over Na_2SO_4, concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (hexane/ethyl acetate = 20/1 → 10/1 with 1% Et_3N) to afford **53C** (1.158 g, 75%) as a viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (s, 1 H), 7.70 (d, J = 8.8 Hz, 2 H), 7.45−7.15 (m, 10 H), 6.94 (d, J = 8.8 Hz, 2 H), 4.97 (d, J = 11.6 Hz, 1 H), 4.82 (d, J = 7.2 Hz, 1 H), 4.56 (d, J = 11.6 Hz, 1 H), 4.62−4.53 (m, 2 H), 3.87 (s, 3 H), 3.88−3.83 (m, 1 H), 3.80−3.64 (m, 3 H), 3.60 (dd, J = 10.0, 7.2 Hz, 1 H), 3.49 (t, J = 6.4 Hz, 1 H), 0.91 (s, 9 H), 0.79 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 6 H), 0.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.2, 161.4, 138.9, 138.5, 129.8, 129.5, 128.2, 128.1, 128.0, 127.7, 127.4, 113.8, 97.2, 81.3, 75.7, 74.9, 74.3, 72.3, 72.3, 62.3, 55.3, 25.9, 25.6, 18.2, 18.0, −4.1, −5.2, −5.4, −5.5; IR (film, cm^{-1}): ν = 2928, 1847, 1606, 1512, 1248.

3,4-Di-*O*-benzyl-2-deoxy-2-amino-D-galactopyranose 53D. A 25 mL RBF was charged with **53C** (105 mg, 0.15 mmol, 1.0 equiv), 6N HCl (0.2 mL, 1.2 mmol, 8.0 equiv) and acetone (1.0 mL). The solution was stirred at 50 °C overnight, concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography (CH_2Cl_2/MeOH = 20/1 → 5/1) to afford 56 mg (95%) of **53D** as a viscous oil. ^{1}H NMR (CD_3OD, 400 MHz): δ = 7.51−7.24 (m, 10 H), 5.33 (d, J = 3.6 Hz, 1 H), 4.65−4.61 (m, 2 H), 4.59−4.52 (m, 2 H), 4.23−4.18 (m, 1 H), 4.11−4.02 (m, 2 H), 3.72−3.62 (m, 2 H), 3.57 (dd, J = 10.8, 3.6 Hz, 1 H); ^{13}C NMR (CD_3OD, 100 MHz): δ = 139.6, 138.6, 129.2, 129.1, 128.9, 128.8, 128.7, 128.4, 91.2, 77.1, 75.6, 73.5, 72.2, 72.1, 61.9, 52.1

1,6-Di-*O*-acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-galactopyranoside 53E. A 25 mL RBF was charged with **53D** (40 mg, 0.1 mmol, 1.0 equiv), 1 M NaOH (0.12 mL, 0.12 mmol, 1.2 equiv), and CH_2Cl_2 (0.5 mL). To this pale-yellow solution was then added 2-trifluoromethylbenzylaldehyde (0.02 mL, 0.12 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature overnight. Then the mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, concentrated *in vacuo*. The crude residue was used directly without further purification. A 25 mL RBF was charged with the crude residue, acetic anhydride (0.15 mL), and pyridine (0.30 mL). After the reaction mixture was stirred at room temperature overnight, it was azeotroped with toluene for three times (3 × 15 mL). The residue was then purified by silica gel flash chromatography (hexane/ethyl acetate = 5/1 → 2/1 with 1% Et_3N) to afford **53E** (45 mg, 75%) as a viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.76 (d, J = 2.4 Hz, 1 H), 8.11 (d, J = 7.6 Hz, 1 H), 7.70 (d, J = 7.6 Hz, 1 H), 7.62−7.47 (m, 2 H), 7.34−7.23 (m, 10 H), 5.85 (d, J = 7.2 Hz, 1 H), 4.99 (d, J = 11.6 Hz, 1 H), 4.67−4.53 (m, 3 H), 4.23 (dd, J = 11.2, 6.8 Hz, 1 H), 4.15 (dd, J = 11.2, 6.4 Hz, 1 H), 3.96−3.88 (m, 4 H), 1.99 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 169.1, 161.5, 138.0, 137.7, 133.9, 132.0, 130.4, 129.3, 129.0, 128.4, 128.3, 127.83, 127.77, 127.7, 125.6 (q, J_{C-F} = 5.7 Hz), 124.0 (d, J_{C-F} = 272 Hz), 93.3, 80.7, 74.4, 73.5, 72.6, 71.4, 63.1, 20.8, 20.6; IR (film, cm^{-1}): ν = 2936, 1749, 1644, 1368, 1228.

6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-galactopyranose 53F. A 50 mL oven-dried Schlenk flask was charged with **53E** (500 mg, 0.83 mmol, 1.0 equiv) and THF (5.0 mL). The solution was cooled to 0 °C, and a solution of NH_3 in methanol (7 N, 3.6 mL, 25.0 mmol, 30 equiv) was added. The resulting mixture was warmed to room temperature and stirred. When the reaction was complete as monitored by TLC, the mixture was evaporated and purified by flash chromatography on silica gel (hexane/ethyl acetate = 2/1 → 1/2 with 1% Et_3N) to afford **53F** (300 mg, 65%) as a viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.77 (d, J = 2.4 Hz, 1 H),

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6.19 (d, J = 8.0 Hz, 1 H), 7.70 (d, J = 7.2 Hz, 1 H), 7.63−7.52 (m, 2H), 7.38−7.21 (m, 10 H), 4.99 (d, J = 11.6 Hz, 1 H), 4.94 (d, J = 7.2 Hz, 1 H), 4.68−4.50 (m, 3 H), 4.32−4.11 (m, 2 H), 3.84−3.68 (m, 4 H), 2.02 (s, 3 H); IR (film, cm^{-1}): ν = 3423, 2894, 1742, 1644, 1455, 1314.

6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-galactopyranosyl *N*-Phenyl Trifluoroacetimidate 53. Viscous oil: 377 mg, 99%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.82 (d, J = 1.2 Hz, 1 H), 8.16 (d, J = 7.6 Hz, 1 H), 7.73 (d, J = 7.6 Hz, 1 H), 7.64−7.53 (m, 2 H), 7.37−7.21 (m, 12 H), 7.06 (t, J = 3.6 Hz, 1 H), 6.76 (d, J = 7.6 Hz, 2 H), 5.91 (brs, 1 H), 5.01 (d, J = 11.6 Hz, 1 H), 4.73−4.57 (m, 3 H), 4.28 (dd, J = 11.2, 6.8 Hz, 1 H), 4.17 (dd, J = 11.2, 5.6 Hz, 1 H), 4.07−4.01 (m, 1 H), 3.90−3.62 (m, 3 H), 1.97 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 161.9, 143.6, 137.9, 137.6, 133.9, 131.9, 130.5, 128.5 (q, J_{C-F} = 31.0 Hz), 128.6, 128.41, 128.38, 128.36, 127.9, 127.8, 127.7, 125.7 (q, J_{C-F} = 5.6 Hz), 124.1, 124.0 (d, J_{C-F} = 272 Hz), 119.2, 96.3, 80.5, 74.5, 73.6, 72.6, 71.5, 71.3, 63.0, 20.7; IR (film, cm^{-1}): ν = 2890, 1744, 1598, 1368, 1315; HRMS (ESI): calcd for $C_{38}H_{35}F_6N_2O_6$ (M + H): 729.2399; found: 729.2405.

6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-glucopyranosyl *N*-Phenyl Trifluoroacetimidate 32. Viscous oil: 7.76 g, 98%, β only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.76 (s, 1 H), 8.20 (d, J = 7.6 Hz, 1 H), 7.73 (d, J = 7.6 Hz, 1 H), 7.63−7.54 (m, 2 H), 7.37−7.06 (m, 13 H), 6.83−6.74 (m, 2 H), 5.92 (brs, 1 H), 4.86 (d, J = 10.8 Hz, 1 H), 4.73−4.57 (m, 3 H), 4.40−4.26 (m, 2 H), 4.06−3.94 (m, 1 H), 3.75−3.58 (m, 3 H), 2.05 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 161.7, 143.3, 137.5, 137.4, 133.4, 132.0, 130.7, 128.6, 128.5, 128.3, 128.14, 128.09, 127.9, 127.8, 126.2, 125.7 (q, J_{C-F} = 5.6 Hz), 124.3, 124.0 (d, J_{C-F} = 272 Hz), 119.2, 95.6, 83.2, 76.1, 75.2, 75.1, 73.9, 73.0, 62.6, 20.8. IR (film, cm^{-1}): ν = 3032, 2978, 1738, 1719, 1644, 1488, 1313. HRMS (ESI): calcd for $C_{38}H_{34}F_6N_2O_6Na$ (M + Na): 751.2219; found: 751.2217.

3,4,6-Tri-*O*-acetyl-1-*tert*-butyldimethylsilyl-2-deoxy-2-*p*-methoxybenzylideneamino-D-glucopyranoside 33B. A 250 mL oven-dried RBF was charged with **33A** (13.0 g, 30.7 mmol, 1.0 equiv),[2] TBSCl (5.10 g, 33.8 mmol, 1.1 equiv.), imidazole (4.2 g, 61.4 mmol, 2.0 equiv) and DMF (120 mL). The resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with ethyl acetate, washed with brine (2 × 50 mL), concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (hexane/ethyl acetate =5/1 → 3/1 with 1% Et_3N) to afford **33B** (16.4 g, 99%) as a viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.13 (s, 1 H), 7.63 (d, J = 8.8 Hz, 2 H), 6.89 (d, J = 8.8 Hz, 2 H), 5.45 (t, J = 9.6, 1 H), 5.06 (app t, J = 9.6 Hz, 1 H), 4.93 (d, J = 7.6 Hz, 1 H), 4.28 (dd, J = 12.0, 6.0 Hz, 1 H), 4.18−3.97 (m, 2 H), 3.84 (s, 3 H), 3.24 (dd, J = 7.6, 10.0 Hz, 1 H), 2.08 (s, 3 H), 2.03 (s, 3 H), 1.88 (s, 3 H), 0.79 (s, 9 H), 0.06 (s, 3 H), 0.00 (s, 3 H).

1-*tert*-Butyldimethylsilyl-2-deoxy-2-*p*-methoxybenzylideneamino-D-glucopyranoside 33C. A 250 mL oven-dried RBF was charged with **33B** (6.5 g, 12.0 mmol, 1.0 equiv), sodium methoxide (0.52 g, 9.6 mmol, 0.8 equiv), and CH_2Cl_2/MeOH (50 mL/100 mL). The resulting solution was stirred at room temperature. When the reaction mixture was complete as monitored by TLC, it was evaporated and then purified by flash chromatography on silica gel (ethyl acetate → CH_2Cl_2/MeOH = 5/1) to afford **33C** (4.80 g, 96%) as a viscous oil. ^{1}H NMR (CD_3OD, 400 MHz): δ = 8.21 (s, 1 H), 7.72 (d, J = 8.8 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 4.88 (d, J = 7.2 Hz, 1 H), 3.92−3.86 (m, 1 H), 3.85 (s, 3 H), 3.76−3.72 (m, 1 H), 3.47−3.38 (m, 2 H), 2.97 (dd, J = 9.6, 7.2 Hz, 1 H), 0.78 (s, 9 H), 0.09 (s, 3 H), 0.02 (s, 3 H).

3,4,6-Tri-*O*-benzyl-1-*tert*-butyldimethylsilyl-2-deoxy-2-*p*-methoxybenzylideneamino-D-glucopyranoside 33D. A 250 mL RBF was charged with **33C** (12.3 g, 30.0 mmol, 1.0 equiv), benzyl bromide (16.2 mL, 135 mmol, 4.5 equiv) and DMF (100 mL). The solution was cooled to −20 °C, and NaH (60%, 5.40 g, 135 mmol, 4.5 equiv) was added in several portions. The mixture was warmed to room temperature and stirred overnight. The reaction mixture was diluted with ethyl acetate (100 mL), washed with brine (2 × 30 mL), dried over Na_2SO_4, concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (hexane/ethyl acetate = 20/1 → 10/1 → 5/1 with 1% Et_3N) to afford **33D** (15.6 g, 76%) as a viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.24 (s, 1 H), 7.68 (d, J = 8.8 Hz, 2 H), 7.36−7.27 (m, 12 H), 7.17−7.09 (m, 3 H), 6.94 (d, J = 8.8 Hz, 1 H), 4.91−4.87 (m, 2 H), 4.68−4.55 (m, 5 H), 3.93 (t, J = 9.2 Hz, 1 H), 3.86 (s, 3 H), 3.80−3.62 (m, 4 H), 3.23 (dd, J = 9.2, 7.2 Hz, 1 H), 0.81 (s, 9 H), 0.10 (s, 3 H), 0.02 (s, 3 H).

3,4,6-Tri-*O*-benzyl-2-deoxy-2-amino-D-glucopyranose 33E. A 250 mL RBF was charged with **33D** (15.1 g, 22.2 mmol, 1.0 equiv), 6N HCl (18.5 mL, 110 mmol, 5.0 equiv) and acetone (200 mL). The solution was stirred at 40 °C. When the reaction mixture was complete as monitored by TLC, it was then evaporated and purified by flash chromatography on silica gel (hexane/ethyl acetate = 2/1 → CH_2Cl_2/MeOH = 10/1) to afford **33E** (8.17 g, 82%) as a viscous oil. ^{1}H NMR ($CDCl_3$ + CD_3OD, 400 MHz): δ = 7.25−7.18 (m, 13 H), 7.03−6.98 (m, 2 H), 5.38 (s, 1 H), 4.86 (d, J = 10.4 Hz, 1 H), 4.69 (d, J = 10.4 Hz, 1 H), 4.62 (d, J = 10.4 Hz, 1 H), 4.47−4.36 (m, 2 H), 3.70−3.53 (m, 4 H), 3.10 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$ + CD_3OD, 100 MHz): δ = 137.3, 137.1, 137.0, 128.21, 128.17, 127.8, 127.7, 127.5, 127.4, 86.9, 78.5, 74.9, 74.5, 73.2, 69.9, 67.8, 54.0; IR (film, cm^{-1}): ν = 3435, 2978, 1585, 1487.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-glucopyranose 33F. A 250 mL RBF was charged with **33E** (4.50 g, 10.0 mmol, 1.0 equiv), 2-trifluoromethylbenzylaldehyde (1.5 mL, 11.0 mmol, 1.1 equiv), pyridine (8.1 mL, 100 mmol, 100 equiv) and CH_2Cl_2 (100 mL). The resulting solution was stirred under reflux overnight. The reaction mixture was azeotroped with toluene and purified by flash chromatography on silica gel (Hexane/ethyl acetate = 2/1−1/2) to afford 3.11 g (52%) of **33F** as a viscous oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.71 (d, J = 2.0 Hz, 1 H), 8.21 (d, J = 6.0 Hz, 1 H), 7.69 (d, J = 6.0 Hz, 1 H), 7.58−7.47 (m, 2 H), 7.35−7.05 (m, 15 H), 5.01 (d, J = 8.0 Hz, 1 H), 4.82 (d, J = 10.8 Hz, 1 H), 4.70−4.47 (m, 5 H), 3.92 (t, J = 8.0 Hz, 1 H), 3.83−3.65 (m, 3 H), 3.60 (dd, J = 9.6, 3.6 Hz, 1 H), 3.34 (dd, J = 8.0, 9.6 Hz, 1 H); IR (film, cm^{-1}): ν = 3403, 2820, 1640, 1454, 1359, 1312.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-D-glucopyranosyl *N*-Phenyl Trifluoroacetimidate 33.[21] Viscous oil: 3.95 g, 98%, α:β = 1:3; **33α**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.77 (s, 1 H), 8.35 (d, J = 7.6 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 1 H), 7.67−7.55 (m, 2 H), 7.43−6.55 (m, 20 H), 6.49 (brs, 1 H), 4.89 (d, J = 10.8 Hz, 1 H), 4.77−4.68 (m, 2 H), 4.65−4.53 (m, 3 H), 4.32−4.20 (m, 2 H), 3.96−3.85 (m, 2 H), 3.83−3.72 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.6, 137.9, 137.8, 137.7, 133.4, 132.0, 130.7, 129.4 (q, J_{C-F} = 31.0 Hz), 128.5, 128.44, 128.38, 128.3, 128.2, 128.0, 127.92, 127.88, 127.85, 127.7, 127.6, 125.6 (q, J_{C-F} =5.6 Hz), 123.9 (d, J_{C-F} = 273 Hz), 95.7, 80.2, 75.3, 74.2, 73.8, 73.5, 60.4; IR (film, cm^{-1}): ν = 2876, 1667, 1594, 1488, 1313; HRMS (ESI): calcd for $C_{43}H_{38}F_6N_2O_5Na$ (M + Na): 799.2583; found: 799.2598. **33β**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.79 (s, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 1 H), 7.63−7.54 (m, 2 H), 7.43−7.05 (m, 18 H), 6.85−6.74 (m, 2 H), 6.07 (brs, 1 H), 4.89 (d, J = 10.8 Hz, 1 H), 4.77−4.56 (m, 5 H), 4.10−3.63 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.5, 137.9, 137.8, 137.7, 135.2, 133.5, 131.9, 130.6, 129.5 (q, J_{C-F} = 31.0 Hz), 129.3, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 126.2, 125.7 (q, J_{C-F} = 5.5 Hz), 124.1, 123.9 (d, J_{C-F} = 273 Hz), 95.8, 83.0, 76.2, 76.0, 75.2, 75.1, 73.4, 60.4; IR (film, cm^{-1}): ν = 3031, 2865, 1644, 1597, 1488, 1314; HRMS (ESI): calc. for $C_{43}H_{38}F_6N_2O_5Na$ (M + Na): 799.2584; found: 799.2598.

General Glycosylation Procedure Using Ni(4-F-PhCN)$_4$(OTf)$_2$: Formation of Disaccharide 5 and Transfer Product 7. A 10 mL oven-dried Schlenk flask was charged with donor **10** (31 mg, 0.05 mmol, 1.0 equiv), thioglycoside acceptor **3** (53 mg, 0.10 mmol, 2.0 equiv), and CH_2Cl_2 (0.3 mL). Then a 0.25 mL of preformed solution of Ni(4-F-PhCN)$_4$(OTf)$_2$, which was generated *in situ* from a reaction of Ni(4-F-PhCN)$_4$Cl$_2$ (12 mg, 0.02 mmol, 10 mol %) and AgOTf (11 mg, 0.4 mmol, 20 mol %) in dichloromethane (1.0 mL) for 30 min, was added to the solution. The resulting mixture was stirred at 35 °C overnight. When the reaction was complete as monitored by TLC (toluene/acetonitrile = 4/1), the mixture was evaporated, and purified by flash chromatography on silica gel (hexane/ethyl acetate = 9/1 → 5/1 → 3/2 with 1% Et_3N) to afford disaccharide **5** (28 mg, 58%, α only) and thioglycoside **7** (4 mg, 14%, α only) as viscous oil.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 5. $[\alpha]^{24}_D$ = 28.2 (c = 2.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$,

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400 MHz): δ = 8.43 (d, J = 2.0 Hz, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 7.62 (d, J = 7.6 Hz, 1 H), 7.56−7.33 (m, 7 H)., 7.23−7.16 (m, 1 H), 7.14−7.03 (m, 2 H), 6.93 (d, J = 7.2 Hz, 2 H), 5.65−5.51 (m, 2 H), 5.37 (d, J = 3.6 Hz, 1 H), 5.19 (s, 1 H), 5.09 (t, J = 5.6 Hz, 2 H), 4.98 (d, J = 12.0 Hz, 1 H), 4.61 (d, J = 12.0 Hz, 1 H), 4.38−4.26 (m, 4 H), 4.06 (dd, J = 12.0, 2.0 Hz, 1 H), 3.92−3.65 (m, 3 H), 3.62 (dd, J = 10.4, 3.6 Hz, 1 H), 3.56−3.49 (m, 1 H), 2.11 (s, 3 H), 2.02 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.7, 169.6, 160.4, 153.8, 136.3, 132.4, 131.9, 130.7, 129.1, 128.9, 128.3, 128.2, 127.9, 126.3, 125.5, 101.5, 99.0, 95.2, 87.1, 82.0, 76.7, 74.6, 72.3, 70.7, 70.0, 68.7, 68.5, 67.8, 62.1, 55.7, 20.8, 20.7, 20.3; IR (film, cm^{-1}): ν = 3335, 2872, 1746, 1643, 1523, 1368, 1314, 1226; HRMS (ESI): calcd for $C_{42}H_{43}Cl_3F_3N_2O_{13}S$ (M + H): 977.1504; found: 977.1505.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 7. ^{1}H NMR ($CDCl_3$, 400 MHz):[22] δ = 8.66 (d, J = 2.0 Hz, 1 H), 8.27 (d, J = 7.6 Hz, 1 H), 7.70−7.47 (m 5 H), 7.33 −7.22 (m, 2 H), 5.72−5.62 (m, 2 H), 5.14 (app t, J = 9.6 Hz, 1 H), 4.72−4.65 (m, 1 H), 4.30 (dd, J = 5.6, 12.0 Hz, 1 H), 4.02 (dd, J = 5.6, 10.0 Hz, 1 H), 3.97 (dd, J = 2.0, 12.0 Hz, 1 H), 2.05 (s, 3 H), 2.00 (s, 3 H), 1.89 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.6, 169.9, 169.7, 160.3, 133.2, 132.3, 131.7, 130.9, 129.2, 129.0, 127.3, 125.4, 86.3, 72.2, 71.7, 68.6, 68.4, 62.1, 20.7, 20.6, 20.4. IR (film, cm^{-1}): ν = 2932954, 1744, 1643, 1366, 1314, 1221. HRMS (ESI): calcd for $C_{26}H_{27}F_3NO_7S$ (M + H): 554.1460; found: 554.1473.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*p*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 4. Viscous oil: 16 mg, 33%, α:β = 21:1; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (s, 1 H), 7.48−7.31 (m, 11 H), 7.16−7.14 (m, 2 H), 6.63−6.60 (m, 1 H), 5.65 (t, J = 9.6 Hz, 1 H), 5.55 (app t, J = 9.2 Hz, 1 H), 5.36 (d, J = 4.0 Hz, 1 H), 5.18−4.94 (m, 4 H), 4.60 (d, J = 12.0 Hz, 1 H), 4.42−4.03 (m, 5 H), 3.72−3.45 (m, 5 H), 2.12 (s, 3 H), 2.04 (s, 3 H), 1.83 (s, 3 H);^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 170.8, 170.7, 132.7, 132.5, 129.2, 128.4, 128.0, 126.0, 125.7, 100.5, 99.6, 95.2, 77.2, 74.6, 71.0, 70.1, 70.0, 68.6, 68.5, 20.9, 20.7, 20.6; IR (film, cm^{-1}): ν = 3343, 2824, 1744, 1648, 1532, 1368, 1323, 1230; HRMS (ESI): calcd for $C_{42}H_{43}Cl_3F_3N_2O_{13}S$ (M + H): 977.1504; found: 977.1512.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*p*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 6. Viscous oil: 9 mg, 33%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.34 (s, 1 H), 7.90 (d, J = 8.0 Hz, 2 H), 7.69 (d, J = 8.0 Hz, 2 H), 7.48−7.45 (m, 2 H), 7.33−7.24 (m, 3 H), 5.72−5.64 (m, 2 H), 5.13 (app t, J = 10.0 Hz, 1 H), 4.75−4.67 (m, 1 H), 4.32 (dd, J = 12.0, 5.2 Hz, 1 H), 4.00−3.93 (m, 2 H), 2.06 (s, 3 H), 2.00 (s, 3 H), 1.88 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.6, 170.2, 169.5, 162.4, 133.1, 131.8, 131.7, 129.0, 127.4, 125.7 (q, J_{C-F} = 5.5 Hz), 86.5, 72.1, 71.9, 68.8, 68.4, 62.1, 20.74, 20.70, 20.6; IR (film, cm^{-1}): ν = 2923, 1748, 1647, 1454, 1370, 1324, 1234; HRMS (ESI): calcd for $C_{26}H_{27}F_3NO_7S$ (M + H): 554.1460; found: 554.1463.

Ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 18. Viscous oil: 32 mg, 43%, α:β = 10:1; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.42 (d, J = 2.0 Hz, 1 H), 8.23 (d, J = 7.6 Hz, 1 H), 7.64−7.33 (m, 4 H), 7.22−7.07 (m, 1 H), 7.11−7.04 (m, 2 H), 6.91 (d, J = 7.2 Hz, 2 H), 5.76 (t, J = 10.0 Hz, 1 H), 5.49 (d, J = 8.8 Hz, 1 H), 5.18 (s, 1 H), 5.09 (app t, J = 10.0 Hz, 2 H), 5.02 (d, J = 12.0 Hz, 1 H), 4.57 (d, J = 12.0 Hz, 1 H), 4.40−4.23 (m, 3 H), 4.19 (t, J = 9.2 Hz, 1 H), 4.10 (dd, J = 12.0, 2.0 Hz, 1 H), 3.85−3.73 (m, 2 H), 3.71 (t, J = 10.0 Hz, 1 H), 3.62 (dd, J = 10.0, 4.0 Hz, 1 H), 3.51 (td, J = 9.6, 4.8 Hz, 1 H), 2.76 (q, J = 7.2 Hz, 2 H), 2.12 (s, 3 H), 2.03 (s, 3 H), 1.83 (s, 3 H), 1.27 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.8, 169.6, 160.4, 153.9, 136.3, 131.9, 130.8, 129.0, 128.3, 128.0, 126.2, 125.5, 101.5, 99.1, 95.2, 85.1, 82.2, 77.2, 74.6, 72.3, 70.7, 70.1, 68.6, 67.8, 62.3, 55.6, 24.3, 20.9, 20.8, 20.4, 14.8; IR (film, cm^{-1}): ν = 3332, 2872, 1746, 1643, 1527, 1368, 1314, 1227; HRMS (ESI): calcd for $C_{38}H_{43}Cl_3F_3N_2O_{13}S$ (M + H): 929.1504; found: 929.1516.

Ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 25. Viscous oil: 11 mg, 22%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz):[22] δ = 8.61 (d, J = 2.0 Hz, 1 H), 8.21 (d, J = 7.6 Hz, 1 H), 7.67 (d, J = 7.6 Hz, 1 H), 7.62−7.53 (m, 2 H), 5.58 (t, J = 9.6 Hz, 1 H), 5.41 (d, J = 5.6 Hz, 1 H), 5.13 (app t, J = 10.0 Hz, 1 H), 4.64−4.57 (m, 1 H), 4.38 (dd, J = 12.0, 4.8 Hz, 1 H), 4.12 (dd, J = 12.0, 2.0 Hz, 1 H), 3.95 (dd, J = 10.0, 5.6 Hz, 1 H), 2.66−2.48 (m, 2 H), 2.11 (s, 3 H), 2.04 (s, 3 H), 1.86 (s, 3 H), 1.30 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 170.0, 169.7, 160.0, 133.2, 132.3, 130.8, 129.1, 125.4 (q, J_{C-F} = 5.5 Hz), 83.5, 72.2, 71.8, 68.8, 67.7, 62.2, 23.6, 20.8, 20.7, 20.4, 14.4; IR (film, cm^{-1}): ν = 2930, 1748, 1644, 1453, 1368, 1315, 1227; HRMS (ESI): calcd for $C_{22}H_{26}F_3NO_7S$ (M + H): 506.1460; found: 506.1456.

Naphthyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 19. Viscous oil: 30 mg, 59%, α only; $[\alpha]^{24}_D$ = 6.1 (c = 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.53−8.47 (m,1 H), 8.40 (d, J = 2.0 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 1 H), 7.92−7.83 (m, 3 H), 7.64−7.43 (m, 5 H), 7.18−7.13 (m, 1 H), 7.08−7.03 (m, 2 H), 6.89 (d, J = 7.2 Hz, 2 H), 5.63 (d, J = 8.4 Hz, 1 H), 5.54 (t, J = 9.6 Hz, 1 H), 5.34 (d, J = 4.0 Hz, 1 H), 5.17 (s, 1 H), 5.13−5.05 (m, 2 H), 4.99 (d, J = 12.0 Hz, 1 H), 4.62 (d, J = 12.0 Hz, 1 H), 4.34−4.23 (m, 4 H), 4.08−4.02 (m, 1 H), 3.81−3.65 (m, 3 H), 3.60 (dd, J = 10.4, 4.0 Hz, 1 H), 3.46 (td, J = 9.6, 4.8 Hz, 1 H), 2.10 (s, 3 H), 2.02 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.8, 169.7, 160.5, 153.7, 136.3, 134.1, 133.2, 131.9, 130.8, 129.7, 128.9, 128.7, 128.3, 127.9, 126.9, 126.4, 125.7, 125.5, 101.5, 99.1, 95.1, 82.1, 77.2, 74.7, 72.3, 70.6, 70.0, 68.6, 67.8, 62.1, 55.8, 20.8, 20.7, 20.4; IR (film, cm^{-1}): ν = 3335, 2965, 1744, 1643, 1532, 1368, 1314, 1225; HRMS (ESI): calcd for $C_{46}H_{45}Cl_3F_3N_2O_{13}S$ (M + H): 1027.1660; found: 1027.1650.

Naphthyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 26. Viscous oil: 3 mg, 10%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz):[22] δ = 8.71 (d, J = 2.0 Hz, 1 H), 8.57−8.46 (m, 2 H), 7.86−7.26 (m, 9 H), 5.77 (t, J = 9.6 Hz, 1 H), 5.65 (d, J = 5.6 Hz, 1 H), 4.83−4.74 (m, 1 H), 4.29 (dd, J = 12.0, 4.8 Hz, 1 H), 4.05 (dd, J = 10.0, 5.6 Hz, 1 H), 3.90−3.83 (m, 1 H), 3.63−3.52 (m, 1 H), 2.07 (s, 3 H), 1.94 (s, 3 H), 1.92 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.6, 169.8, 147.8, 134.1, 133.1, 132.3, 130.9, 129.14, 129.09, 128.9, 128.3, 127.2, 126.8, 126.2, 125.1, 124.1, 87.0, 74.1, 72.2, 71.8, 68.8, 62.1, 20.7, 20.5; IR (film, cm^{-1}): ν = 2924, 1745, 1644, 1439, 1369, 1313, 1221; HRMS (ESI): calcd for $C_{30}H_{29}F_3NO_7S$ (M + H): 604.1617; found: 604.1615.

4-Methyphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 20. Viscous oil: 37 mg, 38%, α:β =11:1; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.42 (d, J = 2.0 Hz, 1 H), 8.20 (d, J = 7.2 Hz, 1 H), 7.63−7.52 (m, 3 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.18−7.13 (m, 3 H), 7.07−7.04 (m, 2 H), 6.91 (d, J = 8.0 Hz, 2 H), 5.60−5.53 (m, 2 H), 5.36 (d, J = 4.0 Hz, 1 H), 5.17 (s, 1 H), 5.15−5.04 (m, 2 H), 5.00 (d, J = 12.0 Hz, 1 H), 4.59 (d, J = 12.0 Hz, 1 H), 4.36−4.23 (m, 4 H), 4.07−4.04 (m, 1 H), 3.78−3.66 (m, 2 H), 3.61 (dd, J = 10.4, 4.0 Hz, 1 H), 3.54−3.48 (m, 1 H), 2.36 (s, 3 H), 2.11 (s, 3 H), 2.02 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.8, 169.7, 160.5, 153.7, 138.6, 136.3, 133.2, 130.8, 129.9, 129.0, 128.3, 128.0, 125.5, 101.5, 99.0, 95.2, 82.1, 77.2, 74.6, 72.3, 70.6, 70.0, 68.6, 67.8, 62.1, 55.6, 21.2, 20.8, 20.7, 20.4; IR (film, cm^{-1}): ν = 3383, 2958, 1746, 1642, 1539, 1368, 1314, 1224; HRMS (ESI): calcd for $C_{43}H_{45}Cl_3F_3N_2O_{13}S$ (M + H): 991.1660; found: 991.1673.

4-Methylphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 27. Viscous oil: 11 mg, 20%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.65 (d, J = 2.0 Hz, 1 H), 8.28 (d, J = 8.0 Hz, 1 H), 7.69 (d, J = 8.0 Hz, 1 H), 7.64−7.53 (m, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 5.66 (t, J = 9.6 Hz, 1 H), 5.62 (d, J = 5.6 Hz, 1 H), 5.14 (app t, J = 10.0 Hz, 1 H), 4.73−4.68 (m, 1 H), 4.30 (dd, J = 12.0, 4.8 Hz, 1 H), 4.01 (dd, J = 10.0, 5.6 Hz, 1 H), 3.97 (dd, J = 12.0, 2.0 Hz, 1 H), 2.32 (s, 3 H), 2.06 (s, 3 H), 2.01 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.6, 170.0, 169.7, 137.6, 132.5, 130.9, 129.8, 129.2, 129.1, 86.7, 72.2, 71.7, 68.8, 68.2, 62.2, 21.1, 20.8, 20.7, 20.4; IR (film, cm^{-1}): ν = 2924, 1748, 1643, 1492, 1369, 1315, 1228; HRMS (ESI): calcd for $C_{27}H_{29}F_3NO_7S$ (M + H): 568.1617; found: 568.1616.

4-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 21. Viscous oil: 37 mg, 38%, α:β =11:1; ^{1}H NMR

($CDCl_3$, 400 MHz): δ = 8.41 (d, J = 2.0 Hz, 1 H), 8.20 (d, J = 7.2 Hz, 1 H), 7.63−7.44 (m, 5 H), 7.18−7.13 (m, 1 H), 7.09−7.04 (m, 2 H), 6.92−6.84 (m, 4 H), 5.62−5.52 (m, 2 H), 5.35 (d, J = 4.0 Hz, 1 H), 5.17 (s, 1 H), 5.10 (app t, J = 10.0 Hz, 1 H), 5.03−4.93 (m, 2 H), 4.62 (d, J = 12.0 Hz, 1 H), 4.35−4.22 (m, 4 H), 4.09−4.02 (m, 1 H), 3.83 (s, 3 H), 3.81−3.67 (m, 3 H), 3.61 (dd, J = 4.0, 10.4 Hz, 1 H), 3.53−3.44 (m, 1 H), 2.11 (s, 3 H), 2.02 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.8, 169.7, 160.2, 136.3, 135.9, 131.8, 130.7, 128.9, 128.3, 127.9, 127.1, 125.5, 121.6, 114.7, 101.5, 99.0, 95.2, 87.1, 82.0, 77.2, 76.4, 74.6, 72.3, 70.6, 70.0, 68.6, 67.8, 62.1, 55.5, 55.3, 20.8, 20.7, 20.4; IR (film, cm^{-1}): ν = 3342, 2958, 1745, 1642, 1539, 1493, 1368, 1314, 1226; HRMS (ESI): calcd for $C_{43}H_{45}Cl_3F_3N_2O_{14}S$ (M + H): 1007.1609; found: 1007.1597.

4-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 28. Viscous oil: 17 mg, 30%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz):[22] δ = 8.65 (d, J = 2.0 Hz, 1 H), 8.32−8.25 (m, 1 H), 7.72−7.54 (m, 3 H), 7.42 (d, J = 8.8 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 5.65 (t, J = 9.6 Hz, 1 H), 5.52 (d, J = 5.6 Hz, 1 H), 5.14 (app t, J = 6.0 Hz, 1 H), 4.77−4.71 (m, 1 H), 4.31 (dd, J = 12.0, 4.8 Hz, 1 H), 4.03−3.95 (m, 2 H), 3.79 (s, 3 H), 2.06 (s, 3 H), 2.03 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.9, 169.7, 160.2, 159.6, 134.9, 133.2, 132.3, 130.9, 129.2, 129.0, 125.4 (q, J_{C-F} = 5.5 Hz), 124.1, 123.0, 114.6, 87.3, 72.2, 68.8, 68.1, 63.1, 60.9, 55.3, 20.7, 20.5, 20.4; IR (film, cm^{-1}): ν = 2934, 1747, 1644, 1494, 1369, 1315, 1227; HRMS (ESI): calcd for $C_{27}H_{29}F_3NO_8S$ (M + H): 584.1566; found: 584.1567.

4-Fluorophenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 22. Viscous oil: 23 mg, 58%, α:β =20:1; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.44 (d, J = 2.0 Hz, 1 H), 8.21 (d, J = 7.2 Hz, 1 H), 7.62−7.50 (m, 5 H), 7.21−7.17 (m, 1 H), 7.10−7.02 (m, 4 H), 6.92 (d, J = 7.2 Hz, 2 H), 5.69 (d, J = 8.4 Hz, 1 H), 5.58 (t, J = 9.6 Hz, 1 H), 5.37 (d, J = 3.6 Hz, 1 H), 5.19 (s, 1 H), 5.11 (app t, J = 10.0 Hz, 1 H), 5.04−4.93 (m, 2 H), 4.64 (d, J = 12.0 Hz, 1 H), 4.36−4.18 (m, 4 H), 4.10−4.04 (m, 1 H), 3.77−3.59 (m, 4 H), 3.51 (td, J = 9.6, 4.8 Hz, 1 H), 2.13 (s, 3 H), 2.04 (s, 3 H), 1.84 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.8, 169.7, 163.0 (d, J_{C-F} = 248 Hz), 160.5, 153.7, 136.2, 135.7, 135.6, 133.1, 131.8, 130.8, 129.0, 128.2, 127.9, 125.5, 116.3, 116.1, 101.5, 99.0, 95.2, 87.0, 81.9, 77.2, 74.6, 72.3, 70.6, 70.0, 68.6, 68.4, 67.8, 62.1, 55.5, 20.8, 20.7, 20.3; IR (film, cm^{-1}): ν = 3382, 2958, 1744, 1643, 1490, 1368, 1314, 1223; HRMS (ESI): calcd for $C_{42}H_{41}Cl_3F_4N_2O_{13}S$ (M + H): 995.1409; found: 995.1434.

4-Fluorophenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 29. Viscous oil: 2 mg, 9%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz):[22] δ = 8.65 (d, J = 2.0 Hz, 1 H), 8.27 (d, J = 8.0 Hz, 1 H), 7.69 (d, J = 8.0 Hz, 1 H), 7.64−7.53 (m, 2 H), 7.50−7.45 (m, 2 H), 7.03−6.97 (m, 2 H), 5.64 (t, J = 10.0 Hz, 1 H), 5.60 (d, J = 5.6 Hz, 1 H), 5.14 (app t, J = 10.0 Hz, 1 H), 4.71−4.63 (m, 1 H), 4.30 (dd, J = 12.4, 5.2 Hz, 1 H), 4.03−3.94 (m, 2 H), 2.06 (s, 3 H), 2.02 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.6, 169.9, 169.7, 161.2, 160.4, 134.5, 134.4, 133.1, 132.3, 131.0, 129.1, 129.0, 127.9, 125.5 (q, J_{C-F} = 5.7 Hz), 116.3, 116.0, 86.8, 72.1, 71.6, 68.7, 68.3, 62.2, 20.72, 20.69, 20.4; IR (film, cm^{-1}): ν = 2922, 1748, 1644, 1491, 1368, 1315, 1227; HRMS (ESI): calcd for $C_{26}H_{26}F_4NO_7S$ (M + H): 572.1366; found: 572.1368.

2-Fluorophenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 23. Viscous oil: 30 mg, 60%, α only; $[\alpha]^{24}_D$ = 21.9 (c = 1.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.41 (d, J = 2.0 Hz, 1 H), 8.21 (d, J = 7.6 Hz, 1 H), 7.63−7.33 (m, 5 H), 7.20−7.03 (m, 5 H), 6.89 (d, J = 7.6 Hz, 2 H), 5.69 (d, J = 8.4 Hz, 1 H), 5.57 (t, J = 10.0 Hz, 1 H), 5.35 (d, J = 3.6 Hz, 1 H), 5.17 (s, 1 H), 5.14−4.97 (m, 3 H), 4.59 (d, J = 12.0 Hz, 1 H), 4.42−4.24 (m, 4 H), 4.14−4.05 (m, 1 H), 3.82−3.54 (m, 3 H), 3.63 (dd, J = 10.0, 3.6 Hz, 1 H), 3.52−3.44 (m, 1 H), 2.12 (s, 3 H), 2.03 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.8, 169.7, 162.0 (d, J_{C-F} = 245 Hz), 160.5, 153.9, 136.2, 135.8, 131.9, 130.9, 130.8, 129.0, 128.35. 128.27, 127.9, 125.5, 124.8, 124.7, 116.2, 116.0, 101.6, 99.1, 95.1, 86.6, 82.0, 76.3, 74.7, 72.3, 70.7, 70.1, 68.6, 68.4, 67.9, 62.3, 55.9, 20.81, 20.76, 20.4; IR (film, cm^{-1}): ν = 3332, 2965, 1743, 1642, 1474, 1368, 1314, 1224; HRMS (ESI): calcd for $C_{42}H_{42}Cl_3F_4N_2O_{13}S$ (M + H): 995.1409; found: 995.1409.

2-Fluorophenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 30. Viscous oil: 1.3 mg, 4%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.67 (d, J = 2.0 Hz, 1 H), 8.29 (d, J = 8.0 Hz, 1 H), 7.74−7.53 (m, 5 H), 7.13−7.06 (m, 2 H), 5.76 (d, J = 6.0 Hz, 1 H), 5.70 (t, J = 9.6 Hz, 1 H), 5.18−5.02 (m, 2 H), 4.70−4.63 (m, 1 H), 4.27 (dd, J = 12.0, 4.8 Hz, 1 H), 4.03 (dd, J = 9.6, 5.6 Hz, 1 H), 3.85 (dd, J = 12.0, 2.0 Hz, 1 H), 2.06 (s, 3 H), 1.97 (s, 3 H), 1.90 (s, 3 H); IR (film, cm^{-1}): ν = 2925, 1749, 1644, 1474, 1370, 1315, 1228; HRMS (ESI): calcd for $C_{26}H_{26}F_4NO_7S$ (M + H): 572.1366; found: 572.1368.

2-Trifluoromethylphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 24. Viscous oil: 31 mg, 61%, α only; $[\alpha]^{24}_D$ = 19.8 (c = 3.3, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.42 (d, J = 2.0 Hz, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 7.70 (d, J = 7.6 Hz, 1 H), 7.70 (d, J = 7.6 Hz, 1 H), 7.63 (d, J = 7.6 Hz, 1 H), 7.60−7.48 (m, 3 H), 7.46−7.40 (m, 1 H), 7.22−7.15 (m, 1 H), 7.10−7.03 (m, 2 H), 6.90 (d, J = 7.6 Hz, 2 H), 5.65−5.53 (m, 2 H), 5.34 (d, J = 4.0 Hz, 1 H), 5.20 (s, 1 H), 5.14−4.94 (m, 3 H), 4.53 (d, J = 12.0 Hz, 1 H), 4.44−4.37 (m, 1 H), 4.33−4.22 (m, 3 H), 4.13−4.05 (m, 2 H), 3.85 (t, J = 4.8 Hz, 2 H), 3.77 (t, J = 6.4 Hz, 1 H), 3.61 (dd, J = 10.0, 3.6 Hz, 1 H), 3.50 (td, J = 9.6, 4.8 Hz, 1 H), 2.11 (s, 3 H), 2.02 (s, 3 H), 1.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.8, 169.6, 160.5, 154.0, 136.2, 135.5, 132.3, 131.9, 130.8, 128.9, 128.3, 128.0, 125.5, 101.6, 99.2, 95.0, 81.9, 77.2, 74.8, 72.3, 70.7, 70.0, 68.6, 68.4, 67.9, 62.5, 55.6, 20.77, 20.75, 20.4; IR (film, cm^{-1}): ν = 3382, 2987, 1748, 1642, 1521, 1441, 1369, 1313, 1226; HRMS (ESI): calcd for $C_{43}H_{42}Cl_3F_6N_2O_{13}S$ (M + H): 1045.1377; found: 1045.1379.

Phenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 39. Viscous oil: 36 mg, 64%, α:β = 6:1; ^{1}H NMR ($CDCl_3$, 400 MHz):[23] δ = 8.53 (d, J = 2.0 Hz, 1 H), 8.33 (d, J = 7.6 Hz, 1 H), 7.62−7.13 (m, 26 H), 6.92 (d, J = 7.6 Hz, 2 H), 5.82 (d, J = 9.2 Hz, 1 H), 5.22 (d, J = 4.0 Hz, 1 H), 5.18 (s, 1 H), 4.87−4.04 (m, 13 H), 3.81−3.36 (m, 8 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.8, 154.1, 138.1, 138.0, 136.3, 133.6, 132.2, 132.9, 132.0, 131.8, 130.4, 128.9, 128.4, 128.3, 128.23, 128.18, 128.14, 128.10, 127.92, 127.91, 127.89, 127.8, 127.7, 127.5, 126.1, 125.5 (q, J_{C-F} = 5.6 Hz), 125.4, 123.8 (d, J_{C-F} = 273 Hz), 101.4, 99.5, 95.3, 87.8, 81.9, 80.9, 77.8, 77.2, 75.7, 75.6, 75.0, 74.6, 73.7, 70.9, 70.0, 68.5, 55.2; IR (film, cm^{-1}): ν = 3389, 2867, 1743, 1640, 1454, 1368, 1314; HRMS (ESI): calcd for $C_{57}H_{55}Cl_3F_3N_2O_{10}S$ (M + H): 1121.2595; found: 1121.2575.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thiol-β-D-galactopyranoside 40. Viscous oil: 25 mg, 55%, α only; $[\alpha]^{24}_D$ = 73.9 (c = 1.8, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.62 (s, 1 H), 8.08 (d, J = 7.6 Hz, 2 H), 7.95 (d, J = 7.6 Hz, 1 H), 7.63−7.54 (m, 2 H), 7.50−7.15 (m, 14 H), 5.87−5.76 (m, 1 H), 5.49 (t, J = 9.6 Hz, 1 H), 5.18 (d, J = 11.2 Hz, 1 H), 5.12 (d, J = 3.2 Hz, 1 H), 4.99 (t, J = 9.6 Hz, 1 H), 4.82−4.75 (m, 1 H), 4.47 (d, J = 11.2, Hz, 1 H), 4.18−4.02 (m, 3 H), 3.94−3.55 (m, 6 H), 2.01 (s, 3 H), 1.79 (s, 3 H), 1.74 (s, 3 H), 0.85 (s, 9 H), 0.01 (s, 3 H), −0.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 168.7, 168.3, 164.9, 161.3, 138.8, 133.1, 132.9, 132.1, 131.3, 130.7, 130.1, 129.8, 128.7, 128.6, 128.4, 128.0, 127.6, 127.5, 127.1, 125.4 (q, J_{C-F} = 5.7 Hz), 98.2, 86.6, 81.0, 79.3, 77.2, 74.7, 72.8, 72.7, 70.5, 68.1, 67.9, 61.5, 61,4, 25.8, 20.6, 20.5, 20.3, 18.2, −5.4, −5.5; IR (film, cm^{-1}): ν = 2928, 1728, 1668, 1602, 1365, 1314, 1263; HRMS (ESI): calcd for $C_{52}H_{61}F_3NO_{13}SSi$ (M + H): 1024.3585; found: 1024.3585.

Phenyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thiol-β-D-galactopyranoside 41. Viscous oil: 33 mg, 61%, α only; $[\alpha]^{24}_D$ = 30.4 (c = 0.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.69 (d, J = 2.0 Hz, 1 H), 8.02 (d, J = 6.8 Hz, 2 H), 7.95 (d, J = 7.6 Hz, 1 H), 7.60 (d, J = 7.6 Hz, 1 H), 7.48−7.32 (m, 7 H), 7.26−7.17 (m, 8 H), 7.14−7.07 (m, 6 H), 6.99−6.93 (m, 4 H), 5.92−5.76 (m, 1 H), 5.14 (d, J = 7.2 Hz, 1 H), 5.05

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(d, J = 3.2 Hz, 1 H), 4.80 (d, J = 9.6 Hz, 1 H), 4.62 (d, J = 11.6 Hz, 1 H), 4.48 (d, J = 11.2 Hz, 1 H), 4.40 (d, J = 10.8 Hz, 1 H), 4.33 (d, J = 11.6 Hz, 1 H), 4.27 (d, J = 10.8 Hz, 1 H), 4.02−3.97 (m, 3 H), 3.92−3.88 (m, 1 H), 3,81 (dd, J = 12.0, 3.2 Hz, 1 H), 3.77−3.63 (m, 2 H), 3.49 (m, 3 H), 3.46 (t, J = 9.6 Hz, 1 H), 1.98 (s, 3 H), 0.83 (s, 9 H), 0.03 (s, 3 H), −0.03 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 165.1, 160.5, 138.9, 138.1, 137.8, 133.1, 132.1, 132.0, 130.3, 130.0, 129.7, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.60, 127.57, 127.52, 127.47, 127.4, 127.1, 97.3, 86.8, 80.1, 79.2, 79.0, 77.2, 75.5, 75.0, 74.6, 74.3, 71.9, 69.6, 62.4, 61.3, 25.8, 20.8, 18.1, −5.4, −5.6; IR (film, cm^{-1}): ν = 2925, 1735, 1642, 1454, 1362, 1314; HRMS (ESI): calcd for $C_{62}H_{69}F_3NO_{11}SSi$ (M + H): 1120.4313; found: 1120.4309.

Phenyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-glucopyranoside 49. Viscous oil: 5 mg, 8%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.75 (d, J = 2.0 Hz, 1 H), 8.39 (d, J = 8.0 Hz, 1 H), 7.73−7.52 (m, 3 H), 7.48−7.44 (m, 2 H), 7.37−7.08 (m, 13 H), 5.55 (d, J = 5.2 Hz, 1 H), 4.88 (d, J = 10.8 Hz, 1 H), 4.69 (d, J = 10.4 Hz, 1 H), 4.63−4.52 (m, 3 H), 4.34−4.26 (m, 2 H), 4.17 (dd, J = 12.0, 2.0 Hz, 1 H), 3.95 (dd, J = 10.0, 5.6 Hz, 1 H), 3.65 (dd, J = 9.6, 8.8 Hz, 1 H), 3.35−3.26 (m, 1 H), 1.95 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 159.5, 137.81, 137.75, 133.7, 132.2, 131.8, 130.7, 128.91, 128.85, 128.5, 128.3, 128.1, 128.0, 127.7, 127.1, 125.6 (q, J_{C-F} = 5.7 Hz), 87.0, 81.8, 77.5, 75.23, 75.18, 75.1, 70.0, 63.1, 20.8; IR (film, cm^{-1}): ν = 2923, 1742, 1641, 1454, 1364, 1314; HRMS (ESI): calcd for $C_{36}H_{35}F_3NO_5S$ (M + H): 650.2188; found: 650.2195.

2-Trifluorophenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thiol-β-D-galactopyranoside 42. Viscous oil: 38 mg, 71%, α only; $[\alpha]^{24}_D$ = 30.4 (c = 0.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.62 (d, J = 2.0 Hz, 1 H), 8.04 (d, J = 7.2 Hz, 2 H), 7.98 (d, J = 7.6 Hz, 2 H), 7.94 (d, J = 7.6 Hz, 1 H), 7.62−7.52 (m, 3 H), 7.47−7.38 (m, 3 H), 7.32−7.10 (m, 8 H), 5.99−5.87 (m, 1 H), 5.48 (t, J = 9.6 Hz, 1 H), 5.22 (d, J = 10.8 Hz, 1 H), 5.13 (d, J = 3.2 Hz, 1 H), 4.82−4.74 (m, 1 H), 4.79 (d, J = 8.8 Hz, 1 H), 4.15−4.02 (m, 3 H), 3.89−3.71 (m, 4 H), 3.65 (dd, J = 10.0, 3.2 Hz, 1 H), 3.58 (t, J = 6.4 Hz, 1 H), 2.01 (s, 3 H), 1.78 (s, 3 H), 1.73 (s, 3 H), 0.85 (s, 9 H), 0.02 (s, 3 H), −0.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 169.7, 169.2, 164.8, 161.4, 138.7, 134.0, 133.0, 132.1, 132.0, 130.7, 129.9, 129.8, 128.5, 128.3, 128.1, 128.0, 127.3, 127.1, 126.4 (q, J_{C-F} = 5.6 Hz), 125.4 (q, J_{C-F} = 5.8 Hz), 98.1, 86.3, 80.9, 79.3, 77.2, 74.8, 72.6, 70.4, 68.1, 67.8, 61.5, 61,3, 25.8, 20.7, 20.5, 20.4, 18.2, −5.4, −5.5; IR (film, cm^{-1}): ν = 2930, 1738, 1640, 1452, 1366, 1312, 1224; HRMS (ESI): calcd for $C_{53}H_{60}F_6NO_{13}SSi$ (M + H): 1092.3459; found: 1092.3451.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-1-thiol-α-L-rhamnopyranoside 43. Viscous oil: 30 mg, 81%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.66 (d, J = 2.0 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 1 H), 7.69 (d, J = 7.6 Hz, 1 H), 7.63−7.52 (m, 2 H), 7.48−7.44 (m, 2 H), 7.33−7.23 (m, 3 H), 5.76 (s, 1 H), 5.66 (t, J = 9.6 Hz, 1 H), 5.24 (app t, J = 9.6 Hz, 1 H), 5.02 (d, J = 3.6 Hz, 1 H), 4.53−4.44 (m, 2 H), 4.38−4.25 (m, 3 H), 4.15−4.06 (m, 2 H), 3.71 (dd, J = 10.0, 3.6 Hz, 1 H), 3.47 (dd, J = 10.0, 7.6 Hz, 1 H), 2.12 (s, 3 H), 2.04 (s, 3 H), 1.89 (s, 3 H), 1.55 (s, 3 H), 1.37 (s, 3 H), 1.17 (d, J = 6.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 170.0, 169.8, 161.3, 133.6, 132.2, 131.7, 131.4, 130.8, 130.0, 128.3, 127.4, 125.6 (q, J_{C-F} = 5.4 Hz), 109.4, 100.0, 83.7, 82.1, 76.7, 76.5, 72.7, 70.8, 68.3, 67.7, 66.5, 61.5, 28.2, 26.5, 20.8, 20.7, 20.4, 16.9; IR (film, cm^{-1}): ν = 2932, 1747, 1641, 1578, 1379, 1314, 1220; HRMS (ESI): calcd for $C_{35}H_{41}F_3NO_{11}S$ (M + H): 740.2352 ; found: 740.2351.

Phenyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-1-thiol-α-L-rhamnopyranoside 44. Viscous oil: 30 mg, 72%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.78 (d, J = 2.0 Hz, 1 H), 8.36 (d, J = 7.6 Hz, 1 H), 7.30 (d, J = 7.6 Hz, 1 H), 7.67−7.53 (m, 2 H), 7.49−7.45 (m, 2 H), 7.38−7.13 (m, 13 H), 5.77 (s, 1 H), 4.94−4.87 (m, 2 H), 4.73 (d, J = 10.4 Hz, 1 H), 4.65−4.57 (m, 2 H), 4.51 (dd, J = 12.0, 2.0 Hz, 1 H), 4.40−4.25 (m, 6 H), 3.38 (dd, J = 10.0, 8.8 Hz, 1 H), 3.64 (dd, J = 10.0, 3.6 Hz, 1 H), 3.45 (dd, J = 10.0, 7.6 Hz, 1 H), 2.08 (s, 3 H), 1.56 (s, 3 H), 1.36 (s, 3 H), 1.13 (d, J = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 160.6, 138.0, 137.9, 133.7, 133.5, 132.1, 131.4, 130.6, 129.0, 128.5, 128.29, 128.27, 128.2, 128.0, 127.9, 127.6, 127.4, 125.7 (q, J_{C-F} = 5.6 Hz), 109.4, 100.8, 83.8, 81.8, 80.8, 76.5, 76.0, 75.1, 69.2, 66.7, 62.7, 28.2, 26.5, 21.0, 16.8; IR (film, cm^{-1}): ν = 2926, 1739, 1638, 1455, 1381, 1314; HRMS (ESI): calcd for $C_{45}H_{49}F_3NO_9S$ (M + H): 836.3080; found: 836.3088.

2-Trifluorophenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-1-thiol-α-L-rhamnopyranoside 45. Viscous oil: 40 mg, 98%, α only; $[\alpha]^{24}_D$ = −48.9 (c = 0.8, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.66 (d, J = 2.0 Hz, 1 H), 8.21 (d, J = 7.6 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 1 H), 7.68 (d, J = 7.6 Hz, 2 H), 7.61−7.46 (m, 3 H), 7.37−7.32 (m, 1 H), 5.79 (s, 1 H), 5.66 (t, J = 10.0 Hz, 1 H), 5.24 (t, J = 9.6 Hz, 1 H), 5.03 (d, J = 3.6 Hz, 1 H), 4.53−4.41 (m, 3 H), 4.24 (dd, J = 10.0, 6.0 Hz, 1 H), 4.28−4.20 (m, 1 H), 4.14 (dd, J = 10.0, 2.0 Hz, 1 H), 3.71 (dd, J = 10.0, 3.6 Hz, 1 H), 3.48 (dd, J = 10.0, 7.6 Hz, 1 H), 2.12 (s, 3 H), 2.04 (s, 3 H), 1.88 (s, 3 H), 1.55 (s, 3 H), 1.37 (s, 3 H), 1.17 (d, J = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.8, 170.0, 169.8, 161.1, 133.6, 133.3, 133.2, 132.2, 130.8, 129.4, 129.1, 128.4, 127.3, 126.8 (q, J_{C-F} = 5.6 Hz), 125.6 (q, J_{C-F} = 5.6 Hz), 125.4, 123.6 (d, J_{C-F} = 275 Hz), 109.5, 100.0, 84.4, 81.9, 76.7, 76.5, 72.6, 70.9, 68.4, 67.8, 67.0, 61.6, 28.2, 26.6, 20.8, 20.7, 20.4, 16.9; IR (film, cm^{-1}): ν = 2937, 1749, 1642, 1577, 1381, 1312, 1222; HRMS (ESI): calcd for $C_{36}H_{40}F_6NO_{11}S$ (M + H): 808.2226; found: 808.2228.

2-Trifluorophenyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-1-thiol-α-L-rhamnopyranoside 46. Viscous oil: 35 mg, 78%, α only; $[\alpha]^{24}_D$ = −7.6 (c = 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.76 (d, J = 2.0 Hz, 1 H), 8.35 (d, J = 7.6 Hz, 1 H), 7.76−7.44 (m, 6 H), 7.37−7.26 (m, 6 H), 7.21−7.12 (m, 5 H), 5.80 (s, 1 H), 4.93−4.87 (m, 2 H), 4.72 (d, J = 10.4 Hz, 1 H), 4.63−4.57 (m, 2 H), 4.61 (dd, J = 10.4, 6.0 Hz, 1 H), 4.43−4.18 (m, 6 H), 3.77 (t, J = 9.6 Hz, 1 H), 3.61 (dd, J = 10.0, 3.2 Hz, 1 H), 3.45 (dd, J = 10.0, 7.6 Hz, 1 H), 2.06 (s, 3 H), 1.55 (s, 3 H), 1.35 (s, 3 H), 1.12 (d, J = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.8, 160.4, 138.0, 137.9, 133.5, 133.3, 132.2, 132.1, 130.9, 130.6, 129.3, 128.5, 128.3, 128.2, 127.9, 127.8, 127.6, 127.1, 126.7 (q, J_{C-F} = 5.8 Hz), 125.7 (q, J_{C-F} = 5.5 Hz), 120.4, 109.5, 100.7, 84.5, 81.5, 80.8, 76.7, 76.5, 75.9, 75.1, 69.3, 67.2, 62.7, 28.1, 26.5, 20.9, 16.8; IR (film, cm^{-1}): ν = 2935, 1740, 1641, 1454, 1381, 1312; HRMS (ESI): calcd for $C_{46}H_{48}F_6NO_9S$ (M + H): 904.2954; found: 904.2957.

2,6-Dimethylphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-1-thiol-α-L-rhamnopyranoside 47. Viscous oil: 28 mg, 74%, α only; $[\alpha]^{24}_D$ = −70.8 (c = 4.8, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.66 (d, J = 2.0 Hz, 1 H), 8.21 (d, J = 8.0 Hz, 1 H), 7.69 (d, J = 7.6 Hz, 1 H), 7.63−7.53 (m, 2 H), 7.17−7.05 (m, 2 H), 5.67 (t, J = 10.0 Hz, 1 H), 5.40 (s, 1 H), 5.24 (app t, J = 9.6 Hz, 1 H), 5.02 (d, J = 3.6 Hz, 1 H), 4.55−4.42 (m, 3 H), 4.36 (dd, J = 7.2, 5.6 Hz, 1 H), 4.22−4.05 (m, 3 H), 3.72 (dd, J = 10.0, 3.6 Hz, 1 H), 3.43 (dd, J = 10.0, 7.6 Hz, 1 H), 2.53 (s, 6 H), 2.12 (s, 3 H), 2.05 (s, 3 H), 1.89 (s, 3 H), 1.53 (s, 3 H), 1.36 (s, 3 H), 1.15 (d, J = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 170.0, 169.9, 161.2, 143.0, 133.2, 132.1, 131.5, 130.8, 128.8, 128.31, 128.28, 125.6 (q, J_{C-F} = 5.6 Hz), 123.9 (d, J_{C-F} = 263 Hz), 109.4, 99.9, 84.4, 81.9, 77.6, 76.5, 72.6, 70.8, 68.3, 67.72, 67.68, 61.6, 28.2, 26.6, 22.1, 20.8, 20.7, 20.4, 17.0; IR (film, cm^{-1}): ν = 2936, 1746, 1641, 1459, 1378, 1314, 1220; HRMS (ESI): calcd for $C_{37}H_{45}F_3NO_{11}S$ (M + H): 768.2665; found: 768.2668.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 54. Viscous oil: 65 mg, 67%, α only; $[\alpha]^{24}_D$ = 15.1 (c = 4.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.47 (d, J = 2.0 Hz, 1 H), 8.17 (d, J = 7.2 Hz, 1 H), 7.63 (d, J = 7.2 Hz, 1 H), 7.57−7.46 (m, 4 H), 7.39−7.30 (m, 3 H), 7.23−7.18 (m, 1 H), 7.14−7.08 (m, 2 H), 6.97 (d, J = 7.2 Hz, 2 H), 5.66 (d, J = 8.4 Hz, 1 H), 5.47−5.38 (m, 3 H), 5.19 (s, 1 H), 5.09−5.03 (m, 1 H), 5.00 (d, J = 12.0 Hz, 1 H), 4.63 (d, J = 12.0 Hz, 1 H), 4.54 (t, J = 6.4 Hz, 1 H), 4.31 (dd, J = 10.4, 4.8 Hz, 1 H), 4.38−4.24 (m, 1 H), 4.20−4.05 (m, 2 H), 3.85 (dd, J = 10.4, 3.6 Hz, 1 H), 3.77−3.68 (m, 2 H), 3.57−3.48 (m, 1 H), 2.15 (s, 3 H), 2.09 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 170.1, 169.7, 160.5, 153.9, 136.4, 132.4, 131.8, 130.6, 129.1, 128.9, 128.4, 128.2, 128.0, 125.5, 101.5,

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99.7, 95.3, 87.5, 82.2, 76.1, 74.6, 70.0, 68.5, 68.2, 67.3, 66.8, 66.7, 62.3, 55.8, 20.9, 20.7, 20.3; IR (film, cm^{-1}): ν = 3340, 2937, 1745, 1644, 1528, 1374, 1314, 1220; HRMS (ESI): calcd for $C_{42}H_{43}Cl_3F_3N_2O_{13}S$ (M + H): 977.1504 ; found: 977.1509.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-galactopyranoside 60. Viscous oil: 10 mg, 16%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz):[22] δ = 8.69 (d, *J* = 2.0 Hz, 1 H), 8.30−8.26 (m, 1 H), 7.72−7.47 (m, 5 H), 7.33−7.22 (m, 3 H), 5.75 (d, *J* = 5.6 Hz, 1 H), 5.58−5.47 (m, 2 H), 4.84 (t, *J* = 6.4 Hz, 1 H), 4.19 (dd, *J* = 10.4, 5.6 Hz, 1 H), 4.13−4.04 (m, 2 H), 2.19 (s, 3 H), 1.92 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.4, 170.1, 169.7, 160.3, 132.3, 131.9, 130.7, 129.2, 128.9, 127.2, 125.5, 86.8, 77.2, 69.6, 67.4, 66.9, 62.0, 20.7, 20.62, 20.55; IR (film, cm^{-1}): ν = 2927, 1748, 1642, 1439, 1372, 1314, 1227; HRMS (ESI): calcd for $C_{26}H_{27}F_3NO_7S$ (M + H): 554.1460; found: 554.1460.

Phenyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 55. Viscous oil: 30 mg, 56%, α:β = 14:1; ^{1}H NMR ($CDCl_3$, 400 MHz):[23] δ = 8.59 (d, *J* = 2.0 Hz, 1 H), 8.26 (d, *J* = 7.2 Hz, 1 H), 7.64−7.45 (m, 4 H), 7.36−7.17 (m, 14 H), 7.12−7.06 (m, 2 H), 6.95 (d, *J* = 7.6 Hz, 2 H), 5.60 (d, *J* = 8.8 Hz, 1 H), 5.36 (d, *J* = 3.6 Hz, 1 H), 5.20 (s, 1 H), 4.94 (t, *J* = 12.0 Hz, 2 H), 4.82 (d, *J* = 10.0 Hz, 1 H), 4.64−4.52 (m, 4 H), 4.33−4.25 (m,2 H), 4.20−3.96 (m, 6 H), 3.84−3.72 (m, 3 H), 3.53−3.46 (m, 1 H), 2.05 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.4, 160.4, 154.2, 138.2, 138.0, 136.3, 134.0, 133.1, 132.1, 131.7, 130.3, 129.0, 128.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.5, 127.4, 125.6 (q, J_{C-F} = 5.6 Hz), 125.5, 123.9 (d, J_{C-F} = 273 Hz), 101.4, 100.1, 95.5, 81.9, 77.2, 76.1, 74.6, 73.2, 72.6, 70.3, 69.0, 68.5, 64.8, 55.5, 21.0; IR (film, cm^{-1}): ν = 3350, 2924, 1741, 1640, 1524, 1370, 1313, 1234; HRMS (ESI): calcd for $C_{52}H_{51}Cl_3F_3N_2O_{11}S$ (M + H): 1073.2231 ; found: 1073.2237.

Phenyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-1-thiol-α-D-galactopyranoside 61. Viscous oil: 2 mg, 6%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.54 (d, *J* = 2.0 Hz, 1 H), 8.20 (d, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.63−7.45 (m, 4 H), 7.35−7.15 (m, 13 H), 4.95−4.99 (m, 2 H), 4.60 (d, *J* = 11.6 Hz, 1 H), 4.54 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 4.33 (dd, *J* = 11.2, 6.8 Hz, 1 H), 4.17 (dd, *J* = 11.2, 5.2 Hz, 1 H), 3.87−3.83 (m, 2 H), 3.77−3.72 (m, 2 H), 2.02 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.6, 160.6, 138.3, 137.7, 132.8, 132.2, 130.3, 129.7, 129.4, 129.1, 128.64, 128.59, 128.2, 128.0, 127.7, 127.6, 127.3, 125.6 (q, J_{C-F} = 5.6 Hz), 124.0 (d, J_{C-F} = 273 Hz), 86.3, 81.6, 76.4, 74.2, 72.4, 71.7, 70.4, 63.8, 20.8; IR (film, cm^{-1}): ν = 2924, 1740, 1642, 1439, 1314, 1234; HRMS (ESI): calcd for $C_{36}H_{35}F_3NO_5S$ (M + H): 650.2188 ; found: 650.2181.

2-Trifluoromethylphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 56. Viscous oil: 38 mg, 73%, α only; $[\alpha]^{24}_D$ = 12.3 (*c* = 1.7, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.46 (d, *J* = 2.0 Hz, 1 H), 8.18 (d, *J* = 7.2 Hz, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 7.2 Hz, 1 H), 7.64 (d, *J* = 7.2 Hz, 1 H), 7.59−7.34 (m, 4 H), 7.23−7.18 (m, 1 H), 7.13−7.07 (m, 2 H), 6.94 (d, *J* = 7.2 Hz, 2 H), 5.64 (d, *J* = 8.8 Hz, 1 H), 5.48−5.36 (m, 3 H), 5.20 (s, 1 H), 5.08 (d, *J* = 12.0 Hz, 1 H), 4.92−4.83 (m, 1 H), 4.64−4.60 (m, 1 H), 4.56 (d, *J* = 12.0 Hz, 1 H), 4.28 (dd, *J* = 10.4, 4.8 Hz, 1 H), 4.21−4.03 (m, 3 H), 3.95−3.73 (m, 4 H), 3.52−3.44 (m, 1 H), 2.15 (s, 3 H), 2.12 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 170.1, 169.7, 160.6, 154.1, 136.3, 132.2, 131.8, 130.6, 129.0, 128.45, 128.36, 128.0, 126.9 (q, J_{C-F} = 5.6 Hz), 125.5, 101.6, 99.8, 95.1, 82.0, 77.2, 76.1, 74.7, 70.0, 68.4, 68.2, 67.2, 67.0, 66.9, 60.4, 55.5, 21.0, 20.8, 20.4; IR (film, cm^{-1}): ν = 3339, 2927, 1745, 1644, 1526, 1374, 1312, 1225; HRMS (ESI): calcd for $C_{43}H_{42}Cl_3F_6N_2O_{13}S$ (M + H): 1045.1377; found: 1045.1367.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-galactopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thiol-β-D-galactopyranoside 57. Viscous oil: 46 mg, 52%, α:β = 8:1; ^{1}H NMR ($CDCl_3$, 400 MHz):[23] δ = 8.66 (d, *J* = 2.0 Hz, 1 H), 8.12−8.07 (m, 2 H), 7.95 (d, *J* = 7.6 Hz,1 H), 7.66−7.18 (m, 18 H), 5.79 (t, *J* = 9.6 Hz, 1 H), 5.41 (dd, *J* = 3.2, 10.8 Hz, 1 H), 4.83−4.77 (m, 1 H), 4.44 (d, *J* = 11.6 Hz, 1 H), 4.20 (t, *J* = 8.0 Hz, 1 H), 4.11−4.03 (m, 2 H), 3.94−3.85 (m, 2 H), 3.80−3.67 (m, 3 H), 3.62−3.57 (m, 1 H), 2.08 (s, 3 H), 1.96 (s, 3 H), 1.82 (s, 3 H), 0.86 (s, 9 H), 0.02 (s, 3 H), −0.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.1, 169.9, 169.2, 165.0, 161.3, 138.8, 133.1, 132.8, 132.5, 132.2, 132.1, 131.9, 130.5, 130.0, 129.7, 128.7, 128.5, 128.0, 127.5, 127.1, 125.4 (q, J_{C-F} = 5.7 Hz), 98.8, 86.7, 80.9, 79.3, 77.2, 74.7, 73.0, 68.1, 67.9, 67.0, 66.7, 61.5, 61.0, 25.8, 20.7, 20.6, 20.3, 18.2, −5.4, −5.5; IR (film, cm^{-1}): ν = 2929, 1747, 1642, 1453, 1371, 1314, 1249; HRMS (ESI): calcd for $C_{52}H_{61}F_3NO_{13}SSi$ (M + H): 1024.3585; found: 1024.3581.

Phenyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-galactopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thiol-β-D-galactopyranoside 58. Viscous oil: 29 mg, 51%, α only; $[\alpha]^{24}_D$ = 116.3 (*c* = 0.3, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.73 (d, *J* = 2.0 Hz, 1 H), 8.03−7.94 (m, 3 H), 7.61−7.56 (m, 2 H), 7.46−7.05 (m, 24 H), 5.82 (t, *J* = 9.6 Hz, 1 H), 5.13−5.07 (m, 2 H), 4.83−4.74 (m, 2 H), 4.42−4.34 (m, 3 H), 4.26 (d, *J* = 11.2 Hz, 1 H), 4.10−3.93 (m, 8 H), 3.75−3.66 (m, 2 H), 3.57 (t, *J* = 10.8 Hz, 1 H), 1.91 (s, 3 H), 0.84 (s, 9 H), 0.00 (s, 3 H), −0.02 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.1, 164.9, 160.9, 138.9, 138.1, 133.5, 133.2, 132.1, 131.9, 130.1, 130.0, 129.7, 128.7, 128.4, 128.29, 128.27, 128.2, 127.9, 127.7, 127.5, 127.4, 125.3 (q, J_{C-F} = 5.3 Hz), 97.6, 86.9, 79.3, 78.5, 77.2, 74.6, 74.4, 73.3, 72.7, 71.9, 70.4, 69.1, 63.0, 61.4, 25.8, 20.8, 18.2, −5.4, −5.6; IR (film, cm^{-1}): ν = 2927, 1733, 1638, 1454, 1314, 1261; HRMS (ESI): calcd for $C_{62}H_{69}F_3NO_{11}SSi$ (M + H): 1120.4313; found: 1120.4311.

2-Trifluoromethylphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-galactopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thiol-β-D-galactopyranoside 59. Viscous oil: 34 mg, 62%, α only; $[\alpha]^{24}_D$ = 85.5 (*c* = 1.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.64 (d, *J* = 2.0 Hz, 1 H), 8.07−7.92 (m, 4 H), 7.63−7.54 (m, 3 H), 7.46−7.38 (m, 3 H), 7.32−7.15 (m, 8 H), 5.90 (t, *J* = 9.6 Hz, 1 H), 5.38 (dd, *J* = 3.2, 10.8 Hz, 1 H), 5.16−5.10 (m, 2 H), 5.03 (d, *J* = 2.0 Hz, 1 H), 4.78 (d, *J* = 10.0 Hz, 1 H), 4.44 (d, *J* = 10.8 Hz, 1 H), 4.18 (t, *J* = 7.2 Hz, 1 H), 4.10−4.02 (m, 2 H), 3.88−3.67 (m, 5 H), 3.58 (t, *J* = 6.4 Hz, 1 H), 2.07 (s, 3 H), 1.95 (s, 3 H), 1.80 (s, 3 H), 0.85 (s, 9 H), 0.02 (s, 3 H), −0.01 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.2, 170.0, 169.2, 165.0, 161.4, 138.6, 134.1, 133.1, 132.1, 132.0, 130.5, 130.3, 129.7, 129.6, 129.1, 128.7, 128.5, 128.3, 128.1, 127.8, 127.3, 127.1, 126.4 (q, J_{C-F} = 5.8 Hz), 125.4 (q, J_{C-F} = 5.8 Hz), 122.7, 122.3 (d, J_{C-F} = 272 Hz), 98.7, 86.3, 80.7, 79.3, 77.2, 74.8, 72.7, 68.0, 67.8, 67.0, 66.6, 61.5, 61.1, 25.8, 20.68, 20.66, 20.3, 18.2, −5.4, −5.5; IR (film, cm^{-1}): ν = 2929, 1746, 1641, 1452, 1372, 1312, 1249; HRMS (ESI): calcd for $C_{53}H_{60}F_6NO_{13}SSi$ (M + H): 1092.3459; found: 1092.3456.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-azido-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)-amino-1-thiol-β-D-glucopyranoside 68. Viscous oil: 15 mg, 18%, α only; $[\alpha]^{24}_D$ = 60.8 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52−7.45 (m, 4 H), 7.37−7.32 (m, 6 H), 5.65−5.57 (m, 2 H), 5.45−5.36 (m, 2 H), 5.13−5.01 (m, 2 H), 4.90 (d, *J* = 12.0 Hz, 1 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.40 (dd, *J* = 10.4, 4.8 Hz, 1 H), 4.34−4.23 (m, 2 H), 4.16−4.11 (m, 1 H), 4.01 (dd, *J* = 12.0, 3.2 Hz, 1 H), 3.85−3.77 (m, 2 H), 3.60−3.47 (m, 2 H), 3.19 (dd, *J* = 10.8, 4.0 Hz, 1 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 170.0, 169.5, 153.7, 136.8, 132.5, 132.0, 129.2, 128.34, 128.32, 125.9, 101.4, 98.9, 95.1, 86.8, 74.6, 70.0, 69.7, 68.5, 68.4, 67.6, 62.0, 60.5, 55.9, 20.8, 20.7, 20.6; IR (film, cm^{-1}): ν = 2923, 2108, 1748, 1453, 1367, 1215; HRMS (ESI): calcd for $C_{34}H_{37}Cl_3N_4O_{13}SK$ (M + K): 885.0781; found: 885.0792.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-azido-1-thiol-α-D-glucopyranoside 69. Viscous oil: 16 mg, 40%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53−7.46 (m, 2 H), 7.38−7.29 (m, 3 H), 5.64 (d, *J* = 5.6 Hz, 1 H), 5.34 (dd, *J* = 10.4, 9.2 Hz, 1 H), 5.04 (dd, *J* = 10.4, 9.6 Hz, 1 H), 4.67−4.56 (m, 1 H), 4.30 (dd, *J* = 12.4, 4.8 Hz, 1 H), 4.09 (dd, *J* = 10.4, 5.6 Hz, 1 H), 4.03 (dd, *J* = 12.4, 2.0 Hz, 1 H), 2.11 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 169.8, 134.1, 132.2, 129.2, 128.1, 86.4, 72.0, 68.6, 68.4, 61.9, 61.6, 20.7, 20.6; IR (film, cm^{-1}): ν = 2918, 2109, 1748, 1367, 1227; HRMS (ESI): calcd for $C_{18}H_{21}N_3O_7NaS$ (M + Na): 446.0998; found: 446.0997.

2-Trifluoromethylphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-azido-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-1-thiol-β-D-glucopyranoside 70. Viscous oil: 6 mg, 13%, α only; $[\alpha]^{24}_D$ = 28.0 (*c* = 0.1, CH_2Cl_2); ^{1}H

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NMR ($CDCl_3$, 400 MHz): δ = 7.79 (d, J = 7.6 Hz, 1 H), 7.71 (d, J = 7.6 Hz, 1 H), 7.55−7.35 (m, 7 H), 5.65−5.60 (m, 2 H), 5.44−5.36 (m, 2 H), 5.01 (app t, J = 10.0 Hz, 1 H), 4.93 (d, J = 12.0 Hz, 1 H), 4.57 (d, J = 12.0 Hz, 1 H), 4.39 (dd, J = 10.8, 4.8 Hz, 1 H), 4.28−4.17 (m, 2 H), 4.07−4.03 (m, 1 H), 3.93−3.81 (m, 3 H), 3.70−3.52 (m, 3 H), 317 (dd, J = 10.8, 3.6 Hz, 1 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.5, 170.0, 169.5, 154.0, 136.7, 132.3, 129.2, 128.5, 128.3, 125.9, 101.5, 99.0, 94.9, 81.3, 77.2, 74.8, 69.7, 68.4, 67.7, 62.2, 60.4, 20.74, 20.68, 20.65; IR (film, cm^{-1}): ν = 3346, 2923, 2108, 1745, 1536, 1371, 1314, 1260; HRMS (ESI): calcd for $C_{35}H_{36}Cl_3F_3N_4O_{13}NaS$ (M + Na): 937.0915; found: 937.0922.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-azido-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-1-thiol-α-L-rhamnopyranoside 71. Viscous oil: 17 mg, 49%, α only; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52−7.43 (m, 2 H), 7.36−7.27 (m, 3 H), 5.75 (s, 1 H), 5.50 (t, J = 9.6 Hz, 1 H), 5.15 (app t, J = 10.0 Hz, 1H), 5.08 (d, J = 4.0 Hz, 1 H), 4.47−4.31 (m, 3 H), 4.26−4.17 (m, 2 H), 4.05 (dd, J = 2.0, 10.0 Hz, 1 H), 3.52−3.38 (m, 2 H), 2.104 (s, 3 H), 2.096 (s, 3 H), 2.05 (s, 3 H), 1.53 (s, 3 H), 1.35 (s, 3 H), 1.28 (d, J = 6.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 170.0, 169.7, 133.1, 131.9, 129.1, 127.7, 109.5, 98.5, 83.5, 82.2, 76.6, 76.3, 70.6, 67.9, 67.5, 66.0, 61.3, 61.1, 28.2, 26.5, 20.8, 20.7, 20.6, 17.2; IR (film, cm^{-1}): ν = 2982, 2108, 1749, 1380, 1221; HRMS (ESI): calcd for $C_{27}H_{35}N_3O_{11}NaS$ (M + Na): 632.1890; found: 632.1888.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-isopropylidene-L-rhamnopyranosyl-(1→6)-1,2,3,4-bis-(di-*O*-isopropylidene)-α-D-galactopyranoside 64. After the solution of disaccharide thioglycoside **45** (16 mg, 0.02 mmol), galactosyl acceptor **63** (10 mg, 0.04 mmol) and 4 Å MS (100 mg) in 2.0 mL of dry CH_2Cl_2 under argon was stirred at room temperature for 1 h and then cooled to −78 °C, NIS (14 mg, 0.06 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 20 min and was then cooled to −78 °C. AgOTf (3 mg, 0.01 mg) was added to the reaction, and the resulting mixture was warmed to 0 °C for 1 h and then slowly to room temperature overnight. TLC showed that the reaction was not complete, an additional amount of NIS (10 mg, 0.04 mmol) and AgOTf (3 mg, 0.01 mg) were added. The solution was stirred at 35 °C for 3 h. The reaction mixture was filtered through a Celite pad, evaporated, and purified by flash chromatography on silica gel (hexane/ethyl acetate = 3/1 →2/1 → 3/2) to afford trisaccharide **64** (15 mg, 85%, α:β = 3:2). **α,α-64**: $[\alpha]^{24}_D$ = 29.8 (c = 0.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.65 (d, J = 2.0 Hz, 1 H), 8.18−8.15 (m, 1 H), 7.72−7.67 (m, 1 H), 7.58−7.51 (m, 2 H), 5.64 (t, J = 9.6 Hz, 1 H), 5.54 (d, J = 4.8 Hz, 1 H), 5.23 (app t, J = 9.6 Hz, 1 H), 5.02−4.98 (m, 2 H), 4.63 (dd, J = 8.0, 2.4 Hz, 1 H), 4.53−4.42 (m, 2 H), 4.32 (dd, J = 10.0, 2.8 Hz, 1 H), 4.26−4.20 (m, 3 H), 4.14−4.08 (m, 1 H), 3.87−3.80 (m, 2 H), 3.70 (dd, J = 10.0, 3.2 Hz, 1 H), 3.57 (dd, J = 10.0, 6.8 Hz, 1 H), 3.37 (dd, J = 10.0, 7.6 Hz, 1 H), 2.12 (s, 3 H), 2.03 (s, 3 H), 1.88 (s, 3 H), 1.57 (s, 3 H), 1.53 (s, 3 H), 1.41 (s, 3 H), 1.34 (s, 6 H), 1.32 (s, 3 H), 1.20 (d, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 170.0, 169.9, 161.2, 133.3, 132.0, 130.8, 129.3, 128.2, 125.6 (q, J_{C-F} = 5.6 Hz), 124.0 (d, J_{C-F} = 275 Hz), 109.3, 109.1, 108.7, 99.9, 96.9, 96.2, 81.7, 77.2, 76.0, 75.6, 72.7, 71.1, 70.9, 70.6, 70.4, 68.3, 67.6, 66.5, 65.7, 64.9, 61.6, 28.2, 26.4, 26.2, 26.0, 24.9, 24.5, 20.8, 20.7, 20.5, 16.9; IR (film, cm^{-1}): ν = 2934, 1752, 1640, 1455, 1381, 1314, 1242; HRMS (ESI): calcd for $C_{41}H_{55}F_3NO_{17}$ (M + H): 890.3422; found: 890.3420. **α,β-64**: $[\alpha]^{24}_D$ = 25.5 (c = 0.2, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.65 (d, J = 2.0 Hz, 1 H), 8.16 (d, J = 7.2 Hz, 1 H), 7.60 (d, J = 7.2 Hz, 1 H), 7.62−7.51 (m, 2 H), 5.63 (t, J = 10.0 Hz, 1 H), 5.49 (d, J = 4.8 Hz, 1 H), 5.22 (t, J = 9.6 Hz, 1 H), 5.02 (d, J = 3.6 Hz, 1 H), 4.82 (d, J = 2.0 Hz, 1 H), 4.61 (dd, J = 10.0, 2.0 Hz, 1 H), 4.49−4.43 (m, 2 H), 4.35−4.22 (m, 4 H), 4.12−3.98 (m, 3 H), 3.77 (dd, J = 9.6, 8.8 Hz, 1 H), 3.71 (dd, J = 12.0, 3.2 Hz, 1 H), 3.57−3.44 (m, 2 H), 2.12 (s, 3 H), 2.03 (s, 3 H), 1.88 (s, 3 H), 1.57 (s, 3 H), 1.51 (s, 3 H), 1.44 (s, 3 H), 1.38 (s, 3 H), 1.35 (s, 3 H), 1.31 (s, 3 H), 1.25 (d, J = 6.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.9, 170.0, 161.3, 130.8, 128.3, 110.7, 109.1, 108.6, 99.9, 98.8, 96.2, 81.5, 77.2, 74.6, 72.5, 70.7, 70.6, 70.5, 68.4, 67.8, 67.7, 65.5, 61.6, 28.0, 26.5, 26.1, 26.0, 24.8, 24.5, 20.8, 20.7, 20.5, 17.6; IR (film, cm^{-1}): ν = 2927, 1752, 1644, 1456, 1381, 1315, 1223; HRMS (ESI): calcd for $C_{41}H_{55}F_3NO_{17}$ (M + H): 890.3422; found: 890.3428.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*o*-trifluoromethylbenzylideneamino-α-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethyl)amino-β-D-glucopyranosyl-(1→6)-1,2,3,4-bis-(di-*O*-isopropylidene)-α-D-galactopyranoside 65. Viscous oil: 5 mg, 81%, β only; **α,β-65**: $[\alpha]^{24}_D$ = −5.9 (c = 1.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.44 (d, J = 2.0 Hz, 1 H), 8.24 (d, J = 7.2 Hz, 1 H), 7.64−7.52 (m, 3 H), 7.21−7.16 (m, 1 H), 7.09 (t, J = 7.6 Hz, 1 H), 6.93 (d, J = 7.6 Hz, 2 H), 5.64 (d, J = 4.8 Hz, 1 H), 5.60 (t, J = 9.6 Hz, 1 H), 5.53 (d, J = 4.8 Hz, 1 H), 5.36 (d, J = 4.0 Hz, 1 H), 5.18 (s, 1 H), 5.12 (d, J = 7.2 Hz, 1 H), 5.09 (d, J = 9.6 Hz, 1 H), 4.82 (d, J = 8.4 Hz, 1 H), 4.61 (dd, J = 8.0, 2.4 Hz, 1 H), 4.53−4.14 (m, 7 H), 4.07−3.95 (m, 2 H), 3.82−3.40 (m, 7 H), 2.14 (s, 3 H), 2.03 (s, 3 H), 1.84 (s, 3 H), 1.58 (s, 3 H), 1.46 (s, 3 H), 1.35 (s, 3 H), 1.34 (s, 3 H);^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.7, 169.9, 169.6, 160.3, 136.4, 133.2, 131.9, 130.7, 129.0, 128.9, 128.3, 127.9, 125.5, 109.4, 108.6, 102.1, 101.5, 99.1, 96.2, 95.4, 83.3, 77.2, 75.5, 74.6, 72.3, 71.1, 70.8, 70.6, 70.3, 68.9, 68.6, 67.8, 65.8, 62.3, 59.3, 56.5, 26.2, 26.0, 24.3, 22.7, 20.9, 20.8, 20.4; IR (film, cm^{-1}): ν = 3468, 2926, 1747, 1634, 1586, 1455, 1375, 1314; HRMS (ESI): calcd for $C_{48}H_{57}Cl_3F_3N_2O_{19}$ (M + H): 1127.2573; found: 1127.2569.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-*N*-acetyl-α-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2 Deoxy-2-(2,2,2-trichloroethyl)amino-β-D-glucopyranosyl-(1→6)-1,2,3,4-bis-(di-*O*-isopropylidene)-α-D-galactopyranoside 66. A 25 mL RBF was charged with **65** (5 mg, 0.0044 mmol, 1.0 equiv), 6N HCl (4.5 μL, 0.027 mmol, 6.0 equiv) and acetone (1.0 mL). The solution was stirred under reflux for 5 min, concentrated *in vacuo*. The crude amine salt was used directly without further purification. To another A 25 mL RBF was charged with this crude amine intermediate, acetic anhydrate (0.5 mL), and pyridine (1.0 mL). After the reaction mixture had been stirring at room temperature overnight, it was azeotroped with toluene for three times. The resulting residue was purified by silica gel flash chromatography (hexane/ethyl acetate = 1/2 → 1/3) to afford trisaccharide **66** (5 mg, 99%) as a viscous oil. **66:** $[\alpha]^{24}_D$ = 12.3 (c = 0.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.75 (d, J = 8.4 Hz, 1 H), 5.66 (d, J = 9.6 Hz, 1 H), 5.20−4.99 (m, 5 H), 4.66 (d, J = 8.4 Hz, 1 H), 4.60 (dd, J = 8.0, 2.4 Hz, 1 H), 4.51 (d, J = 12.0 Hz, 1 H), 4.39 (dt, J = 10.0, 4.0 Hz, 1 H), 4.32 (dd, J = 5.2, 2.4 Hz, 1 H), 4.23−4.16 (m, 4 H), 4.09−3.94 (m, 4 H), 3.76−3.52 (m, 3 H), 2.14 (s, 3 H), 2.11 (s, 3 H), 2.04 (s, 3 H), 2.014 (s, 3 H), 2.009 (s, 3 H), 1.97 (s, 3 H), 1.56 (s, 3 H), 1.44 (s, 3 H), 1.34 (s, 3 H), 1.33 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.0, 170.8, 170.6, 109.4, 108.7, 98.4, 96.2, 95.3, 77.2, 74.7, 71.6, 71.2, 71.1, 70.9, 70.6, 70.2, 69.2, 68.1, 68.0, 67.7, 61.9, 56.4, 51.2, 26.2, 25.0, 24.3, 23.0, 22.7, 20.84, 20.82, 20.74, 20.69, 20.6; IR (film, cm^{-1}): ν = 3347, 2924, 1747, 1669, 1539, 1455, 1374, 1231; HRMS (ESI): calcd for $C_{39}H_{55}Cl_3N_2O_{22}Na$ (M + Na): 1031.2210; found: 1031.2197.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and characterization data, including ^{1}H NMR and ^{13}C NMR spectra for all new compounds, are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(23) The desired α-disaccharide contained a small amount of β-isomer because we were unable to cleanly separate the minor β-isomer from the desired α-disaccharide by flash chromatography.