Anomeric Reactivity-Based One-Pot Oligosaccharide Synthesis: A Rapid Route to Oligosaccharide Libraries

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The assembly of an oligosaccharide library has been achieved in a practical and efficient manner employing a one-pot sequential approach. With the help of the anomeric reactivity values of thioglycosides, using a thioglycoside (mono- or disaccharide) with one free hydroxyl group as acceptor and donor coupled with another fully protected thioglycoside, a di- or trisaccharide is selectively formed without self-condensation and subsequently reacted in situ with an anomerically inactive glycoside (mono- or disaccharide) to form a tri- or tetrasaccharide in high overall yield. The approach enables the rapid assembly of 33 linear or branched fully protected oligosaccharides using designed building blocks. These fully protected oligosaccharides have been partially or completely deprotected to create 29 more structures to further increase the diversity of the library.

Introduction

Carbohydrates contain an evolutionary potential of information content several orders of magnitude higher in a short sequence than any other biological oligomer due to their monomers capable of more than one linkage position, anomerity, and branching.[1] For example, the number of all possible linear and branched isomers of a hexasaccharide was calculated and found to be $>1.05 \times 10^{12}$. It has been well-documented that the structural diversity of sugar oligomers leads to their involvement in many key inter- and intracellular events.[2,3] Cells, bacteria, viruses, and toxins often use cell-surface carbohydrates as points of attachment.[4] These and other important discoveries in molecular glycobiology have stimulated intense research in oligosaccharides, focusing on both their synthesis and structure−function relationship study.

Unlike peptide and nucleotide synthesis, oligosaccharide synthesis is not a facile process. It is complicated by the issues of anomeric stereochemistry and protecting group manipulation. Therefore, the need for rapid access to oligosaccharides for the better understanding of biological processes is still a formidable challenge. Major advances[5] have been made in this field using strategies such as glycal assembly,[6] random-glycosylation,[7] latent-active glycosylation,[8] enzyme-assisted synthesis,[9] armed/disarmed glycosylation,[10] and solid-phase approach.[11] Recently, a new chemoselective glycosylation strategy, "the one-pot sequential glycosylation",[12] has received considerable interest as it provides a rapid route to oligosaccharides. This strategy is, however, not generally applicable due to the lack of precise reactivity values of useful glycosyl donors and acceptors. To tackle this problem, the relative reactivity values of a number of glycosylation reagents have been established recently,[13] and a computer program has been developed to guide the

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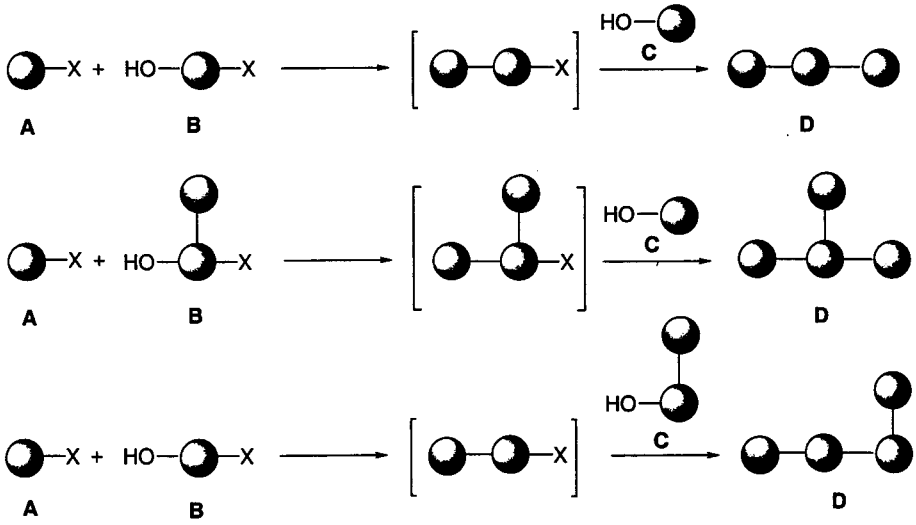
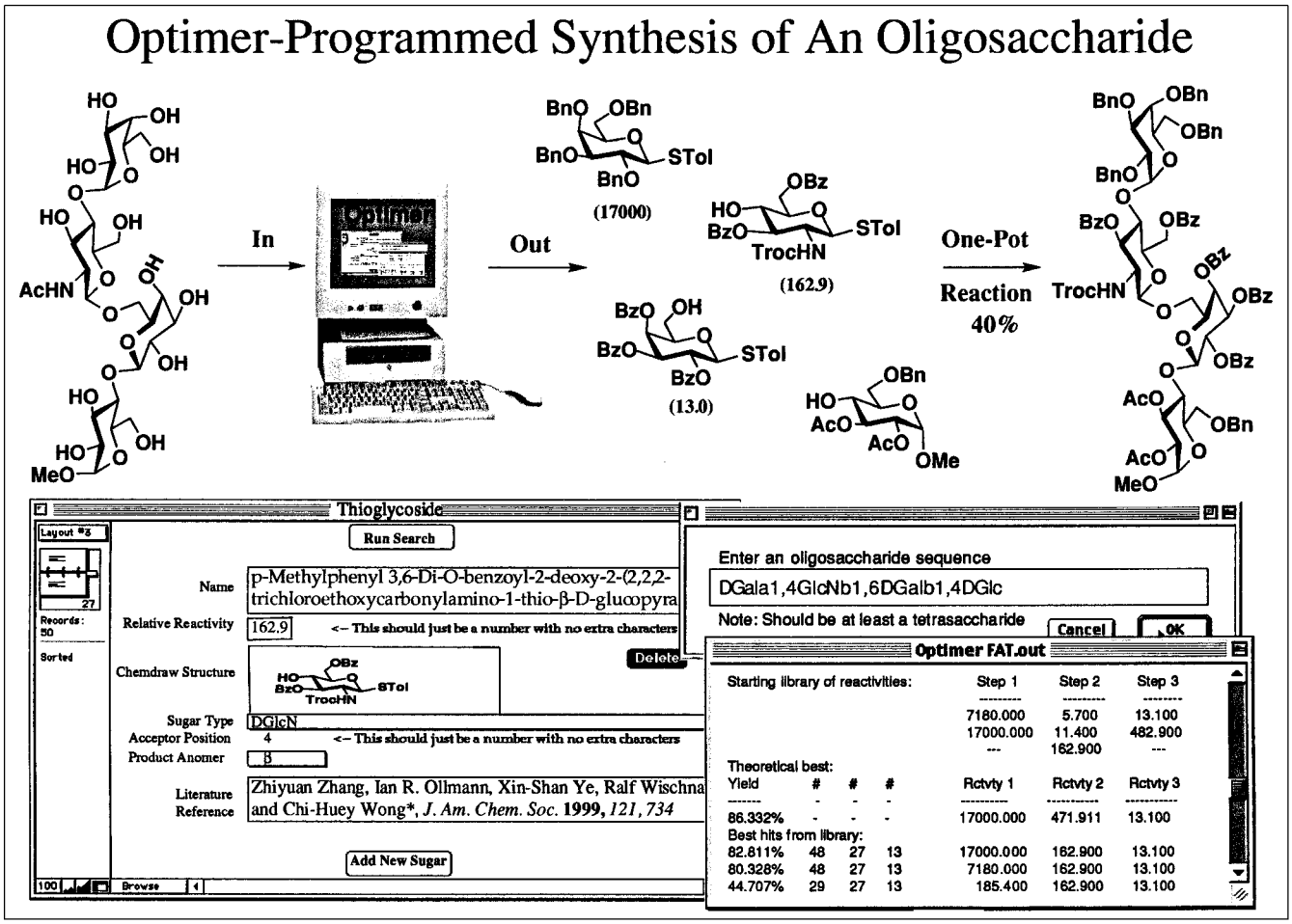
Scheme 1. Strategy for One-Pot Assembly of Linear and Branched Oligosaccharides



A representative computer-based synthesis of a tetrasaccharide (for details, see Ref. 13b)



selection of building blocks for sequential one-pot oligosaccharide synthesis.[13b] On the other hand, an orthogonal protection−deprotection strategy for the synthesis of a highly branched oligosaccharide library has also been developed.[14] With the aid of the anomeric relative reactivity values, we report here a rapid and practical assembly of a small tri- and tetrasaccharide library based on the combination of orthogonal protection−deprotection and one-pot sequential glycosylation strategies using thioglycosides[15] as glycosylation reagents.

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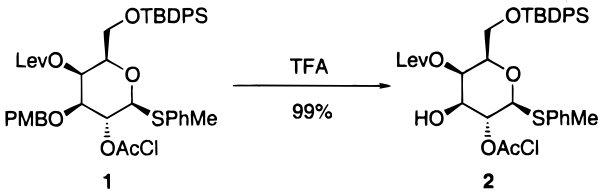
Scheme 2



1 2

Results and Discussion

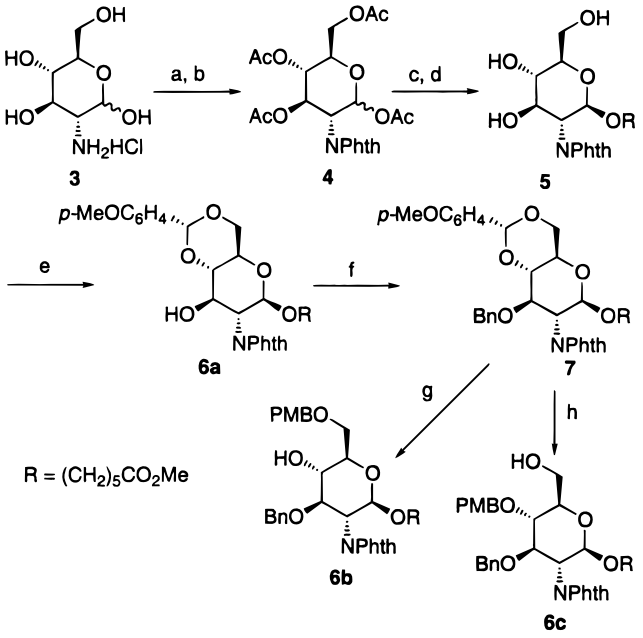
The principle of the one-pot sequential glycosylation is illustrated in Scheme 1. If the difference in the reactivity between glycosyl donor A (X = leaving group) and acceptor as well as donor B is large enough to be distinguished by a promotor, the donor A can be selectively activated to react with B to give the disaccharide intermediate, which upon activation and coupling with the glycosyl acceptor C (the third component) will provide the trisaccharide D in one pot without contamination of byproducts derived from self-condensation of B and other undesirable coupling. Here, B functions as both an acceptor for the first glycosylation and a donor for the second glycosylation (we call B acceptor−donor). In this way, two glycosidic linkages are sequentially constructed in a one-pot reaction. If B is a disaccharide acceptor−donor, a branched tetrasaccharide will be formed. Similarly, if a disaccharide acceptor C is used, a tetrasaccharide will also be produced. We envisaged that this strategy would provide a powerful tool for the assembly of oligosaccharide libraries. For instance, if six donors (A^{1-6}), seven acceptor−donors (B^{1-7}), and four acceptors (C^{1-4}) are employed, 672 ($6 \times 7 \times 4 \times 2 \times 2 = 672$) oligosaccharides ($A^{1-6}B^{1-7}C^{1-4}$) (including anomeric isomers) will be formed in principle, and a computer program[13b] can be used as a guide for selection of appropriate building blocks for the assembly of a large number of oligosaccharides (Scheme 1). To verify the proposed strategy, a relatively small library of 33 oligosaccharides has been prepared.

To realize this goal and enhance the diversity of the library, suitably protected building blocks have to be designed carefully. Our previous paper[14] indicated that the four protecting groups—chloroacetyl (ClAc), *p*-methoxybenzyl (PMB), levulinyl (Lev), and *tert*-butyldiphenylsilyl (TBDPS)—on a galactoside can be selectively removed. The same result was obtained from thiogalactodide **1** as shown in Scheme 2. Selective deprotection of the PMB group in **1** using trifluoroacetic acid (TFA) gave acceptor−donor **2** in high yield (99%).

Synthesis of glucosamine acceptors **6a**−**c** was performed as depicted in Scheme 3. Treatment of glucosamine hydrogen chloride (**3**) with phthalic anhydride and subsequent O-acetylation afforded **4**. Glycosylation of **4** and methyl 6-hydroxyhexanate followed by O-deacetylation gave **5** (72%). 4,6-*O*-*p*-Methoxybenzylidenation of **5** provided acceptor **6a** with the 3-hydroxyl group exposed. Benzylation of **6a** gave saccharide **7** in 54% yield. Regioselective reductive ring-opening[16] of 4,6-*O*-*p*-methoxybenzylidene acetal of **7** produced acceptor **6b** and **6c** with the 4- and 6-hydroxyl groups exposed, respectively.

Our initial one-pot trisaccharide assembly was performed with thioglycoside donor **1a** (RRV = 1.7×10^4),[14] acceptor−donor **2** (RRV = 57.0), and glycosyl acceptor

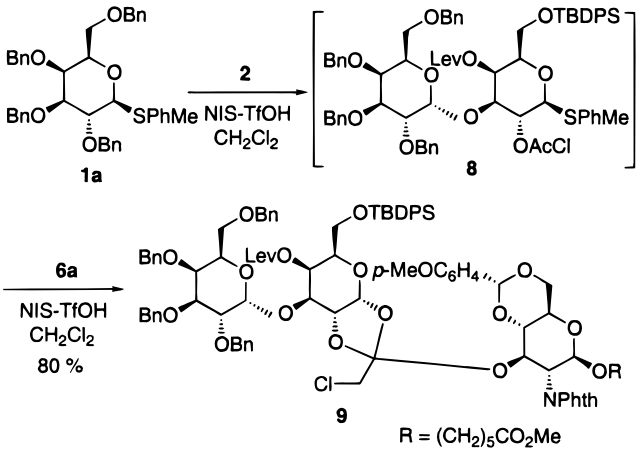
Scheme 3[a]



3 4 5 6a 7 6b 6c

[a] Key: (a) *N*,*N*-diisopropylethylamine, MeOH; then phthalic anhydride; (b) Ac_2O, pyridine, DMAP, 52%; (c) methyl 6-hydroxyhexanate, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 73%; (d) NaOMe, MeOH, 99%; (e) anisaldehyde dimethyl acetal, 10-camphorsulfonic acid, MeCN, 81%; (f) BnBr, NaH, DMF, 54%; (g) $NaCNBH_3$, CF_3CO_2H, DMF, 90%; (h) $NaCNBH_3$, Me_3SiCl, MeCN, 51%.

Scheme 4



6a. As illustrated in Scheme 4, glycosylation of **1a** and **2** gave the intermediate disaccharide **8** in α-glycosidic linkage, which was then coupled with acceptor **6a** to provide **9** in high yield (80%). Both two glycosylation steps were activated by *N*-iodosuccinimide and triflic acid (NIS−TfOH).[17] Unfortunately, compound **9** is not our desired trisaccharide, but an ortho ester. When promotor (dimethylthio)methylsulfonium triflate (DMTST)[14,15] was employed instead of NIS−TfOH, the same product was isolated. The ortho ester was evident from the coupling constant of the anomeric proton at δ 5.48 ppm (J = 5.5 Hz).

To avoid the formation of ortho esters, the chloroacetyl protecting group of **2** was simply changed to the benzoyl

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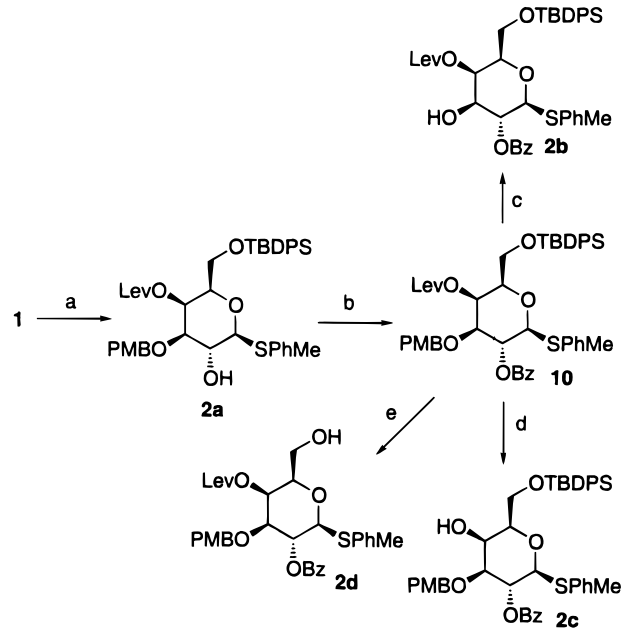
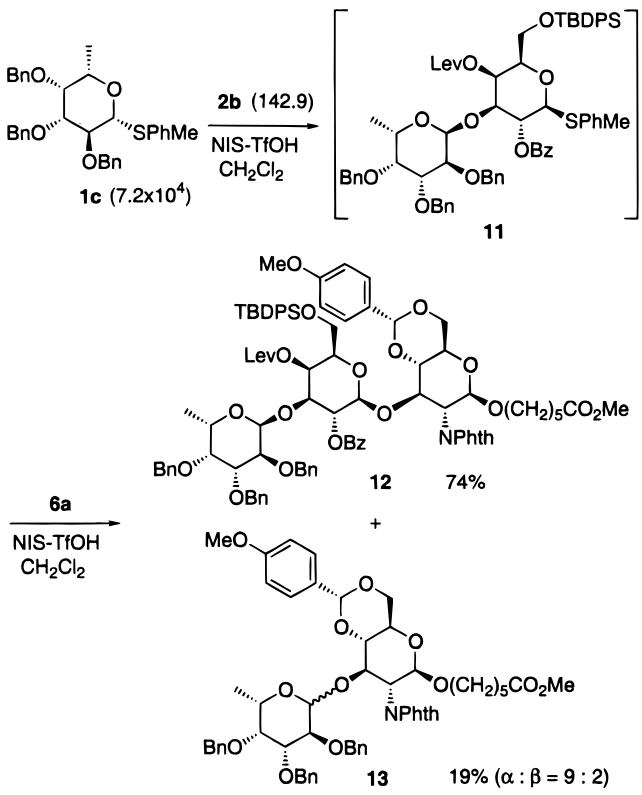
Scheme 5[a]



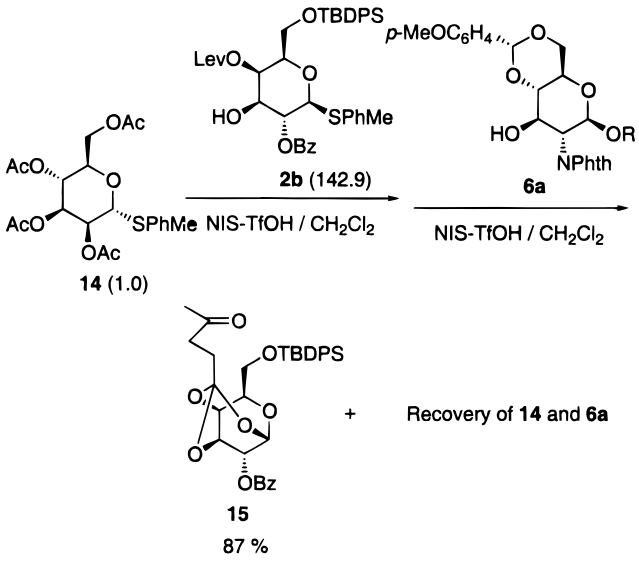
[a] Key: (a) $NaHCO_3$, $MeOH/H_2O$, 100%; (b) BzCl, pyridine, 100%; (c) TFA, CH_2Cl_2, 58%; (d) hydrazine, AcOH, 92%; (e) HF−pyridine, 100%.

Scheme 6

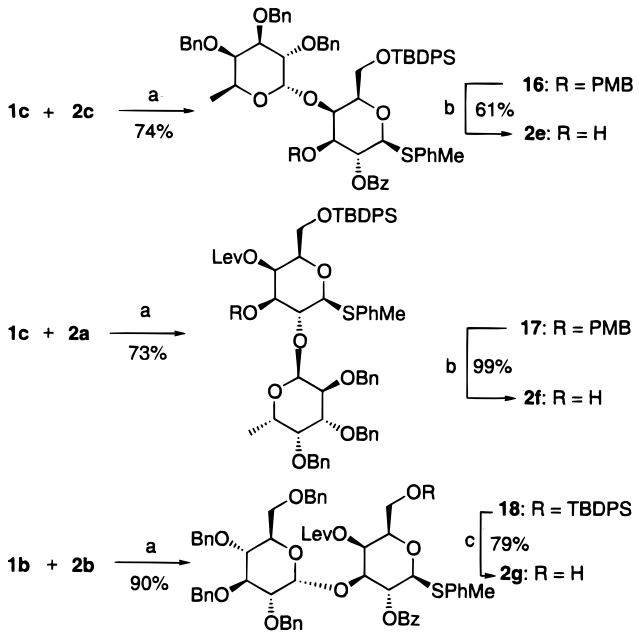


protecting group. The transformation of thioglycoside **1** to acceptor−donors **2a**−**d** is outlined in Scheme 5. Selective removal of chloroacetyl group on saccharide **1** with $NaHCO_3$ afforded the 2-hydroxyl group exposed acceptor−donor **2a** in quantitative yield. Benzoylation of **2a** gave fully protected saccharide **10**. Selective deprotection of **10** with trifluoroacetic acid, hydrazine, and hydrogen fluoride−pyridine provided acceptor−donors

Scheme 7



Scheme 8.[a] **Synthesis of Disaccharide Acceptor−Donors 2e−g**

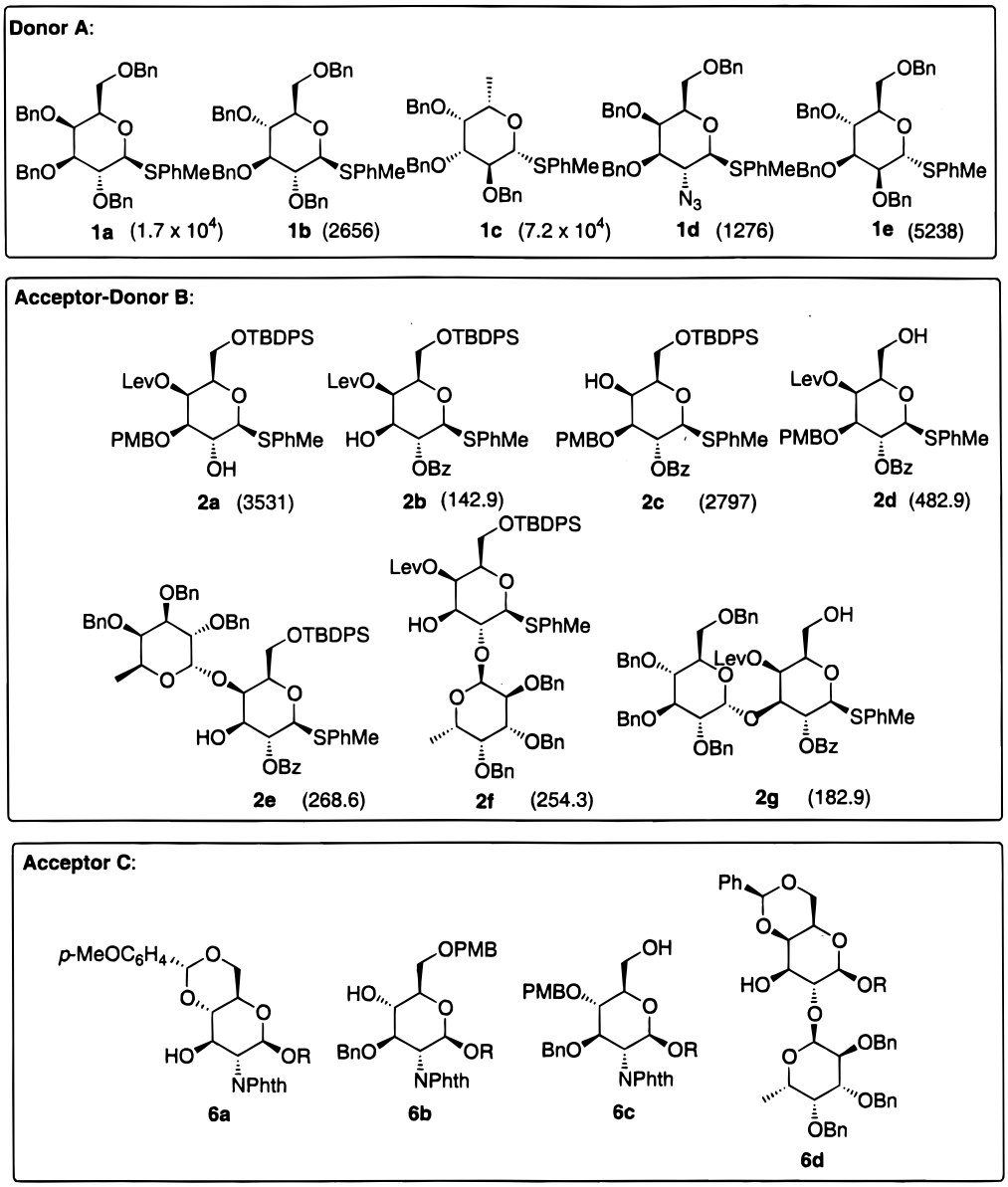


[a] Key: (a) NIS, TfOH, molecular sieves, CH_2Cl_2; (b) TFA, CH_2Cl_2; (c) HF−pyridine.

2b, **2c**, and **2d** with one free hydroxyl group at the 3, 4, and 6-positions, respectively.

After the benzoyl group was introduced instead of the chloroacetyl group, we continued to perform the one-pot trisaccharide assembly. The highly reactive thioglycoside donor **1c** (RRV = 7.2×10^4), acceptor−donor **2b** (RRV = 142.9), and acceptor **6a** were chosen. As shown in Scheme 6, **1c** and **2b** were coupled in the presence of *N*-iodosuccinimide and a catalytic amount of triflic acid to generate the intermediate disaccharide **11** in α-1,3-glycosidic linkage, which was activated by the same promotor (NIS−TfOH) followed by addition of the third coupling component **6a** to the reaction mixture to give the trisaccharide **12** in 74% overall isolated yield. This constitutes an average of over 85% conversion per glycosylation. The reaction process was monitored by TLC. Because excess amounts of **6a** (3 equiv) and **1c** (1.5 equiv)

Scheme 9. Building Blocks for the Assembly of Oligosaccharides[a,b]



[a] PMB = *p*-methoxybenzyl, TBDPS = *tert*-butyldiphenylsilyl, Lev = Levulinyl, NPhth = *N*-Phthaloyl, R = $(CH_2)_5CO_2Me$. [b] The relative reactivity value (RRV) is shown in parentheses.

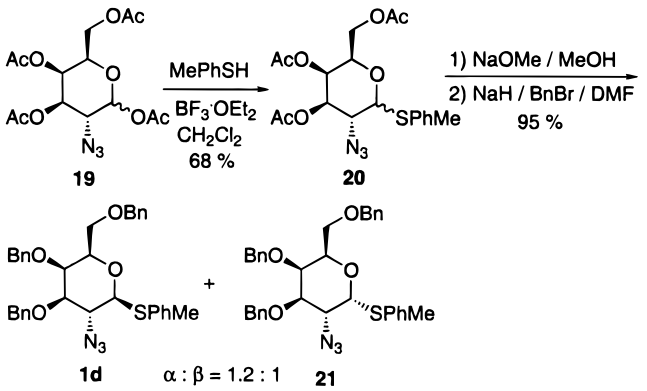
were used, a 1,3-component coupling product disaccharide **13** as an anomeric mixture (α/β = 9:2 from NMR analysis, 19%) and a recovery of **6a** were also isolated.

We also tried to assemble a trisaccharide with mannose thioglycoside **14**, benzoyl protected acceptor−donor **2b**, and acceptor **6a** under the same conditions as mentioned above. As shown in Scheme 7, no disaccharide or trisaccharide was detected. Interestingly, the starting material **2b** was converted to **15** in 87% isolated yield, and the other two reactants **14** and **6a** were recovered. This result perhaps can be explained by the relative reactivity values.[13b] Donor **14** (RRV = 1.0) is less reactive than **2b** (RRV = 142.9), so **2b** should be activated more easily than **14**. Actually, donor **14** is too unreactive to be activated by NIS−TfOH for glycosylation.

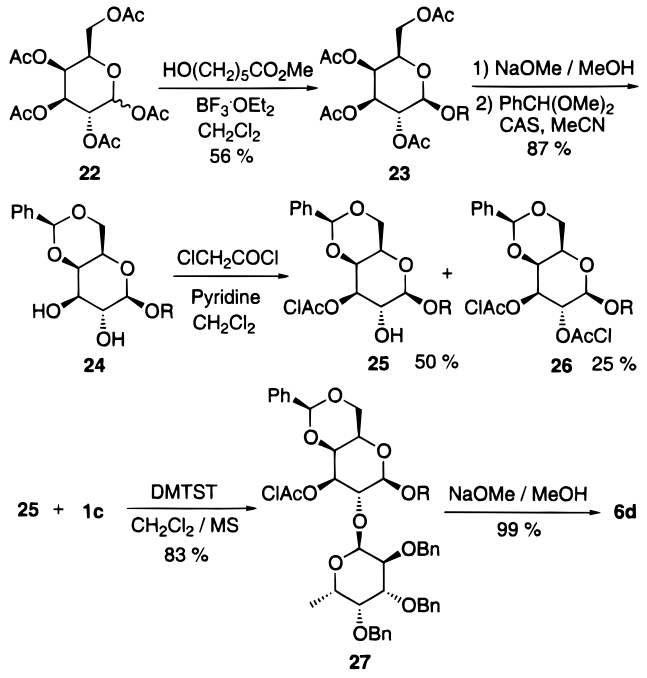
To increase the diversity of acceptor−donors, some disaccharide acceptor−donors **2e**−**g** were prepared (Scheme 8). The coupling reaction of **1c** and **2c** in the presence of NIS−TfOH afforded disaccharide **16** in 74% yield with complete stereochemistry control. Selective removal of PMB group in **16** with TFA furnished **2e** in 61% yield. In a similar way, disaccharides **2f** and **2g** were obtained in 72% and 71% overall yield, respectively. Thus, a galactose moiety with a free hydroxyl group at the 2-, 3-, 4-, or 6-position (**2a**−**d**) and three orthogonally protected disaccharide thioglycosides with one hydroxyl group exposed (**2e**−**g**) were prepared as the central part (acceptor−donor B) to build oligosaccharides. For the preparation of acceptor−donors **2a**−**g**, the key feature is the use of an orthogonal protection−deprotection strategy. Starting from a monosaccharide core, a di-, tri-, or tetrasaccharide carrying one free hydroxyl group can be made in a combinatorial fashion in principle. These structures can then be subjected to the one-pot assembly of oligosaccharides.

In our method for the one-pot glycosylation, five thioglycoside donors **1a**−**e** (donor A) were employed. Similarly, for acceptor C, we used three differently protected glucosamines **6a**−**c** and one disaccharide **6d** as acceptors for the construction of oligosaccharides.

Scheme 10



Scheme 11



Building blocks for the assembly of oligosaccharides are listed in Scheme 9.

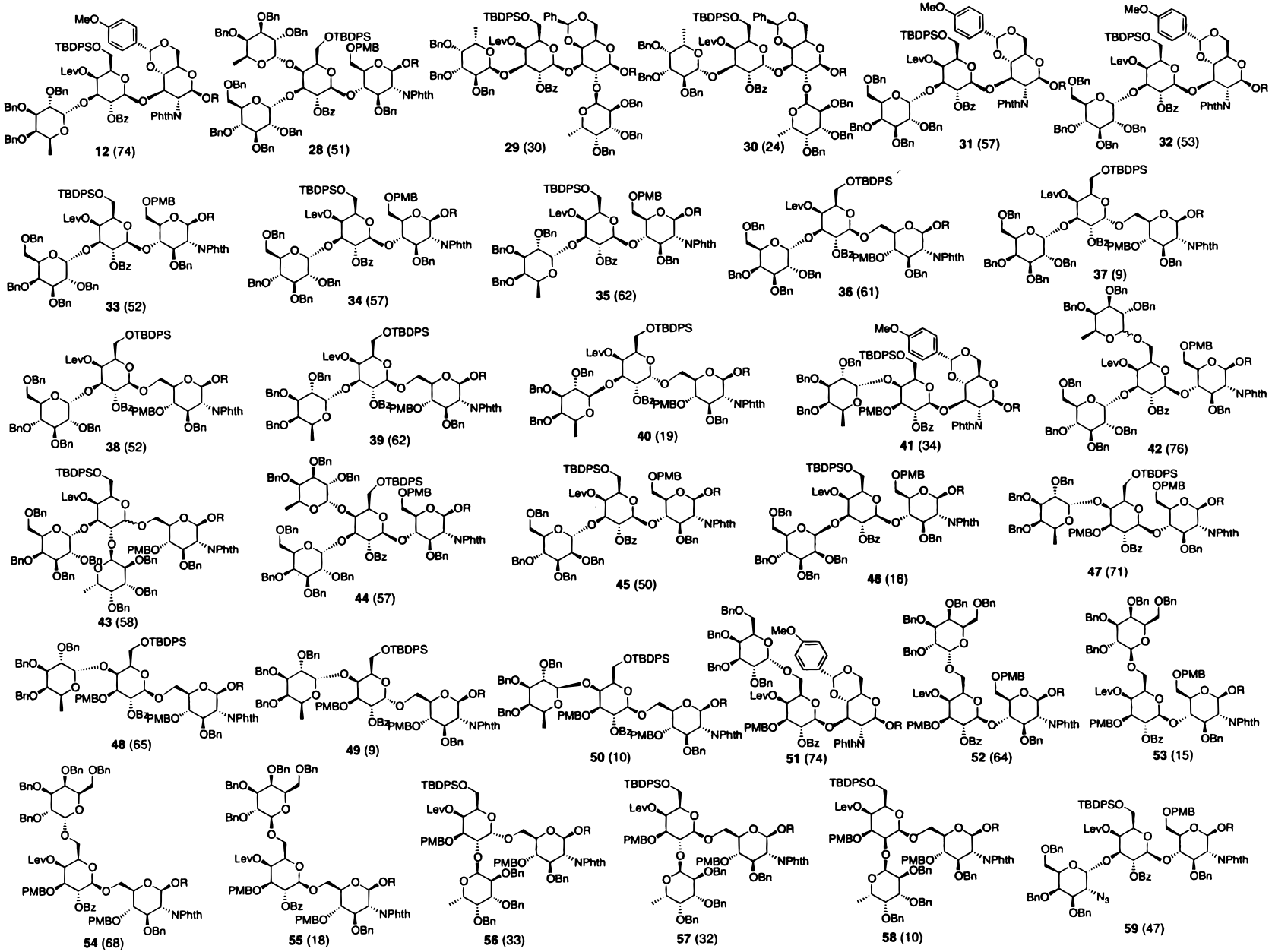
The preparation of some monosaccharide building blocks is summarized in Scheme 10. Thus, manipulation of galactosamine derivative **19**[18] with *p*-thiocresol in the presence of boron trifluoride etherate gave thioglycoside **20** (68% yield). Treatment of **20** with sodium methoxide followed by benzylation gave chromatographically separatable anomeric isomers **1d** and **21** (95% yield). Similarly, mannose derivative **14** was converted to thioglycoside **1e** in 76% yield.

The synthesis of disaccharide acceptor **6d** was shown in Scheme 11. The synthesis was started from the commerically available galactose pentaacetate (**22**), which was directly glycosylated with methyl 6-hydroxy hexanate in the presence of boron trifluoride etherate in CH_2Cl_2 (0 °C to rt) to afford **23** (56%). The stereochemical assignment was confirmed by ^{1}H NMR, where the $J_{1,2}$ value of 7.9 Hz for H-1 indicated the β-D-configuration for the side chain. Deacetylation of **23** followed by 4,6-*O*-benzylidene protection produced saccharide **24** (87%, two steps). Interestingly, when **24** was treated with chloroacetyl chloride in pyridine−Et_3N−CH_2Cl_2 at −20 °C, the desired 3-chloroacetyl saccharide **25** was isolated as the major product (50%), but the 2,3-dichloroacetyl saccharide **26** was also isolated (25%). With the suitably protected galactoside **25** in hand, the glycosylation with thioglycoside **1c** promoted by (dimethylthio)methylsulfonium triflate in CH_2Cl_2 (0 °C to rt) was achieved to afford disaccharide **27** (83%). The α-configuration of the newly formed glycosidic linkage was evident from the coupling constant of the anomeric proton at δ 5.23 ppm (J = 3.5 Hz). Deprotection of chloroacetyl group on disaccharide **27** finally gave **6d** (99%).

With all these building blocks in hand, under the guidance of the relative reactivity values, a one-pot approach to oligosaccharide libraries was attempted. In a representative synthesis of the branched tetrasaccharide **28**, DMTST was used as a promotor for the first-step coupling between donor **1b** and disaccharide acceptor−donor **2e**. The reaction proceeded smoothly under these conditions, and the product, without the isolation, was further treated with acceptor **6b** in situ in the presence of NIS−TfOH to afford **28** in 51% yield (Scheme 12). In this case, NIS−TfOH is too reactive to be used as an effective reagent for the coupling of **1b** (RRV = 2656) and **2e** (RRV = 268.6). In fact, we found that the reaction proceeded with very fast consumption of **1b** to give exclusively the succinimide glucoside when NIS−TfOH was used as an initial promotor. We assume that the elevated reactivity of donor **1b** coupled with high steric hindrance of the secondary hydroxyl group in **2e** leads to a very efficient competition of succinimide to provide the byproduct. For the assembly of tetrasaccharides **29** and **30**, we found that DMTST is an efficient coupling reagent for both the first-step and the second-step glycosylation. The highly reactive donor **1c** (RRV = 7.2 × 10^4) was coupled with acceptor−donor **2b** (RRV = 142.9) followed by addition of acceptor **6d** in the presence of DMTST to afford separatable tetrasaccharides **29** and **30** in 30% and 24% isolated yield, respectively. It seems that NIS−TfOH is generally a more efficient promotor than DMTST. If a highly reactive donor such as **1c** was coupled with a sterically hindranced acceptor, DMTST should be employed instead of the NIS−TfOH system to avoid the formation of a succinimide derivative. In this way, a small fully protected oligosaccharide library (33 tri- or tetrasaccharides) in which the central galactose moiety can be linked at any position was assembled, and the results are summarized in Chart 1. The linear and branched structures are biologically relevent. Most of the constructed oligosaccharides were isolated in pure isomer in 50−80 mg, and all these structures were characterized by their ^{1}H and ^{13}C NMR and further confirmed by high-resolution mass analysis. People may think the separation of the products could be a tough task. According to our experience, the isolation of products is not very difficult. Actually, all the separation work was accomplished by a routine column chromatography technique. Thus, good separation of unreacted acceptor, major side-product 1,3-component coupling product, and desired

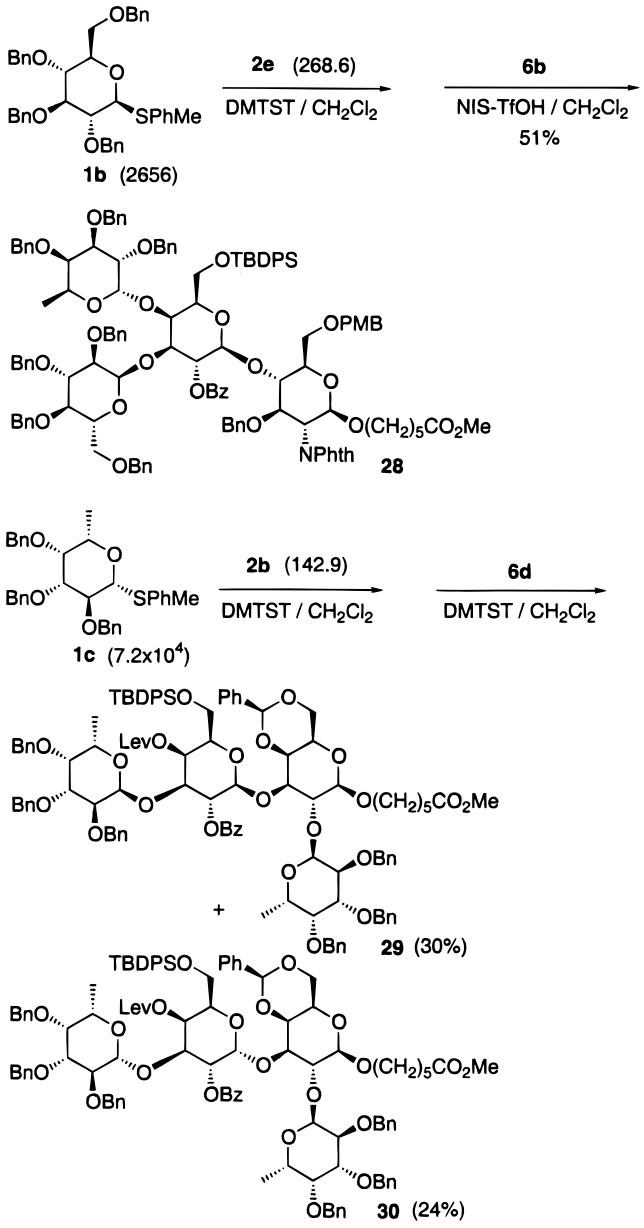
(18) Alper, P. B.; Hung, S.-C.; Wong, C.-H. *Tetrahedron Lett.* **1996**, *37*, 6029−6032.

Chart 1. A Small Library of 33 Oligosaccharides



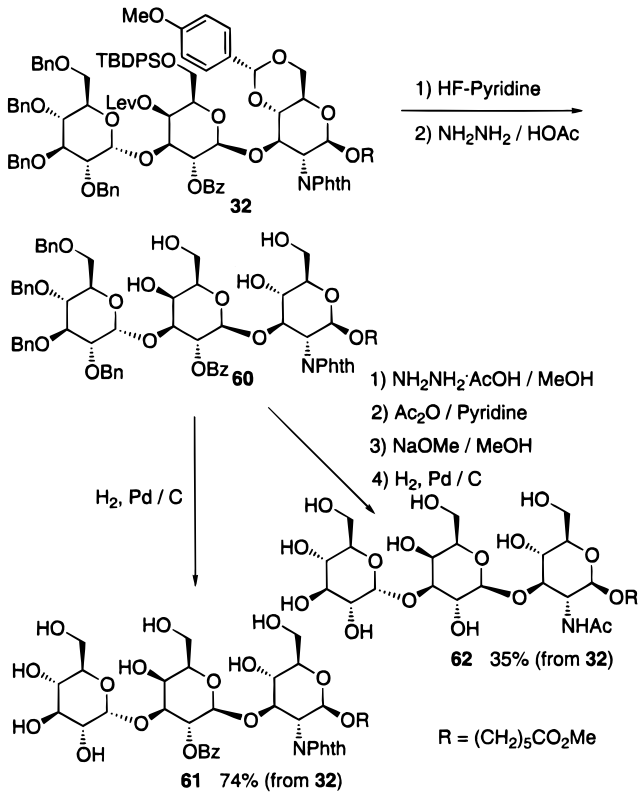
[a] R = $(CH_2)_5CO_2Me$. [b] The isolated yield (%) is shown in the parentheses.

Scheme 12



oligosaccharide (usually in form of a pure isomer, in some case in form of an anomeric mixture) was achieved (see the Experimental Section).These protected oligosaccharides can be partially and fully deprotected to generate a larger library. From some point of view, an oligosaccharide that retains one or two hydrophobic groups in it may probably have stronger binding affinity due to the hydrophobic interaction. As examplified in Scheme 13, trisaccharide **32** was successively treated with hydrogen fluoride−pyridine, hydrazine, and hydrogen over Pd on charcoal to afford the partially deprotected saccharide **61** (74% yield, three steps). A complete deprotection of compound **32** was accomplished as follows: the *tert*-butyldiphenylsilyl and *p*-methoxybenzylidine functionalities were removed by hydrogen fluoride−pyridine, the levulinyl functionality was removed by hydrazine, the phthalimido functionality was converted into an NHAc moiety by treatment with hydrazine acetate and reacetylation with acetic anhydride in pyridine, the benzoyl functionality was removed by methanolic sodium methoxide, and the benzyl protecting groups were cleaved by

Scheme 13



catalytic hydrogenolysis over 10% Pd−C to give trisaccharide **62** (35% yield from **32**). The final products **61** and **62** were purified by C-18 reversed-phase column chromatography. In this manner, most of fully protected oligosaccharides assembled from one-pot access were partially deprotected. Their structures (29 partially or fully deprotected oligosaccharides) are listed in Chart 2. All structures were identified by their ^{1}H NMR, ^{13}C NMR, and mass spectral analysis.

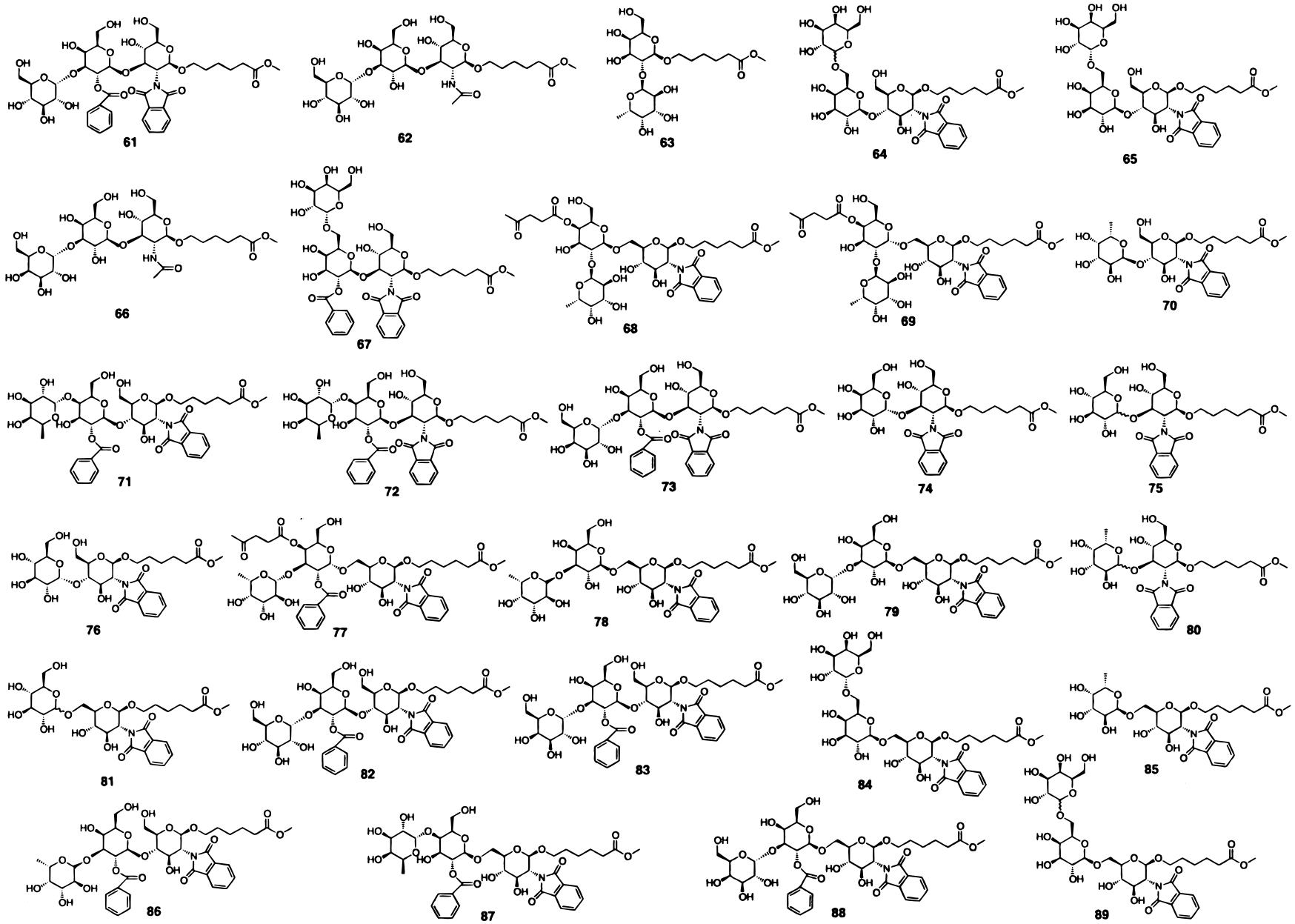
Conclusion

The strategy disclosed here for the construction of saccharide libraries is very efficient, and only a small number of building blocks is employed to generate a relatively large number of oligosaccharides. To our knowledge, this is the first oligosaccharide library created by one-pot assembly. Furthermore, the described principle points out a possible route to the assembly of more complex and biologically significant oligosaccharides in a rapid fashion if combined with the use of the computer program Optimer[13b] and possibly forms the basis for automated carbohydrate synthesis. As interest in the database increases, the computer program for the selection of building blocks will receive more interest. Work is in progress to enlarge the size of the building blocks for preparation of a larger library and to screen for binders to certain proteins and nucleic acids.

Experimental Section

General Methods. Tetrahydrofuran (THF), toluene, and diethyl ether (Et_2O) were distilled over sodium/benzophenone, methylene chloride (CH_2Cl_2), and acetonitrile (CH_3CN) over calcium hydride. Reagents of commercial quality were purchased and used without further purification unless otherwise stated. Compounds **1a**−**c**, **2a**−**g**, **6a**,**b**, **7**, and **14** were prepared

Chart 2. Partially and Fully Deprotected Oligosaccharides



previously.[13,14] All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted.

***p*-Methylphenyl 2-*O*-Chloroacetyl-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-galactopyranoside (2).** To a stirred solution of *p*-methylphenyl 2-*O*-chloroacetyl-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-galactopyranoside[14] (104 mg, 0.127 mmol) in CH_2Cl_2 (8 mL) was added trifluoroacetic acid (1.5 mL) at − 20 °C. After the mixture was stirred for 20 min at this temperature, methanol (2 mL) and CH_2Cl_2 (20 mL) were then added to the reaction mixture, and the mixture was washed with saturated $NaHCO_3$ and brine and then dried over Na_2SO_4. After removal of the solvent, the residue was purified by chromatography on a silica gel column (hexanes−EtOAc 2.5:1) to yield **2** (87.9 mg, 99%) as a syrup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.66 (m, 4H), 7.35−7.45 (m, 8H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.54 (d, *J* = 3.1 Hz, 1H), 4.94 (t, *J* = 9.8 Hz, 1H), 4.60 (d, *J* = 10.0 Hz, 1H), 4.16 (s, 1H), 4.15 (s, 1H), 3.83 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.71−3.78 (m, 2H), 3.64 (dd, *J* = 9.0, 5.7 Hz, 1H), 2.63−2.79 (m, 2H), 2.35−2.50 (m, 2H), 2.32 (s, 3H), 2.13 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.33, 171.96, 166.54, 138.20, 135.58, 135.55, 133.09, 129.80, 129.76, 129.60, 127.71, 86.30, 77.71, 72.54, 72.34, 70.30, 61.77, 40.84, 38.38, 29.61, 28.14, 26.69, 21.08, 19.05; HRMS (M + Na) calcd for $C_{36}H_{43}O_8SSiClNa$ 721.2034, found 721.2005.

5-Methoxycarbonylpentyl 3-*O*-Benzyl-4-*O*-*p*-methoxybenzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (6c). To a mixture of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-β-D-glucopyranoside (**7**) (2.90 g, 4.5 mmol), $NaCNBH_3$ (1.80 g, 27.0 mmol), and 3 Å molecular sieves (6.0 g, powder) in CH_3CN (anhydrous, 80 mL), was added dropwise a solution of Me_3SiCl (2.99 g, 27.0 mmol) in CH_3CN (27 mL) at 0 °C. The mixture was stirred for 24 h at room temperature. Then more Me_3SiCl, as a solution of Me_3SiCl (0.86 g, 7.9 mmol) in CH_3CN (9 mL), was added at 0 °C, and the reaction mixture was stirred for 8 h at room temperature. The solids were filtered off through Celite, and the cake was washed with CH_2Cl_2. The filtrate was poured into ice-cold saturated $NaHCO_3$. The aqueous phase was repeatedly extracted with CH_2Cl_2. The combined extracts were washed with saturated $NaHCO_3$ and brine. The extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 2:1) to give **6c** (1.83 g, 63%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (br s, 1H), 7.61−7.69 (m, 3H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.84−6.92 (m, 5H), 5.15 (d, *J* = 8.5 Hz, 1H), 4.83 (d, *J* = 12.5 Hz, 1H), 4.82 (d, *J* = 10.5 Hz, 1H), 4.67 (d, *J* = 11.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.34 (dd, *J* = 10.5, 8.5 Hz, 1H), 4.10 (dd, *J* = 11.0, 8.5 Hz, 1H), 3.90−3.94 (m, 1H), 3.80 (s, 3H), 3.69−3.79 (m, 3H), 3.60 (s, 3H), 3.51−3.54 (m, 1H), 3.37 (dt, *J* = 9.5, 6.5 Hz, 1H), 2.10 (dd, *J* = 7.0, 6.5 Hz, 1H), 1.92−2.03 (m, 2H), 1.31−1.44 (m, 4H), 1.01−1.13 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 159.4, 138.0, 133.7, 130.0, 129.8, 128.0, 127.9, 127.3, 123.2, 113.9, 98.3, 79.10, 79.05, 75.20, 74.76, 74.76, 69.39, 61.82, 55.92, 55.26, 51.40, 33.67, 28.90, 25.23, 24.28; HRMS (M + Cs) calcd for $C_{36}H_{41}O_{10}NCs$ 780.1781, found 780.1803.

Ortho Ester 9. To a solution of **1a** (69.5 mg, 0.1074 mmol) and **2** (50.0 mg, 0.07158 mmol) in CH_2Cl_2 (5 mL) was added 4 Å molecular sieves (600 mg), and the mixture was stirred for 30 min at room temperature and then cooled to − 20 °C. NIS (25.5 mg, 0.1077 mmol) and TfOH (45 μL, 0.3 M etheral solution) were added to the mixture, and this mixture was stirred for 20 min at −20 °C. To the reaction mixture was added a solution of **6a** (119.0 mg, 0.2147 mmol) in CH_2Cl_2 (2 mL), NIS (25.5 mg, 0.1077 mmol), and TfOH (50 μL, 0.3 M etheral solution). The reaction mixture was stirred for 30 min at −20 °C. The course of the reaction was monitored by TLC. Et_3N (0.5 mL) was then added to the mixture. The precipitate was filtered off, and the filtrate was successively washed with saturated aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 4:1 to 3:1) to give **9** (94.8 mg, 80%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67−7.84 (m, 2H), 7.56 (t, *J* = 6.5 Hz, 4H), 7.22−7.42 (m, 30H), 6.89 (d, *J* = 9.0 Hz, 2H), 5.50 (s, 1H), 5.48 (d, *J* = 5.5 Hz, 1H), 5.43 (d, *J* = 2.5 Hz, 1H), 5.20 (d, *J* = 8.5 Hz, 1H), 5.16 (d, *J* = 3.0 Hz, 1H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.76−4.82 (ABq, 2H), 4.69 (t, *J* = 9.5 Hz, 1H), 4.62−4.68 (ABq, 2H), 4.56 (d, *J* = 11.0 Hz, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.35 (dd, *J* = 11.0, 4.5 Hz, 1H), 4.20 (dd, *J* = 10.0, 9.0 Hz, 1H), 3.99−4.13 (m, 4H), 3.91 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.76−3.82 (m, 3H), 3.64 (s, 3H), 3.59 (s, 3H), 3.37−3.67 (m, 10H), 2.06−2.38 (m, 4H), 1.99 (s, 3H), 1.93−2.01 (m, 2H), 1.30−1.42 (m, 4H), 1.01−1.11 (m, 2H), 0.98 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 173.8, 170.9, 160.0, 139.0, 138.8, 138.7, 137.7, 135.6, 135.5, 134.4, 133.2, 133.1, 129.7, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 127.6, 127.4, 127.4, 123.5, 118.3, 113.7, 101.5, 98.8, 98.6, 93.1, 80.74, 78.89, 76.07, 75.44, 74.92, 74.78, 73.64, 73.19, 72.57, 72.12, 72.06, 70.22, 69.66, 69.12, 68.67, 68.34, 66.28, 63.19, 61.42, 55.91, 55.12, 51.32, 45.79, 37.85, 33.70, 29.58, 28.98, 27.72, 26.77, 25.32, 24.39, 19.07; HRMS (M + Cs) calcd for $C_{92}H_{102}O_{23}NSiClCs$ 1784.5355, found 1784.5486.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-galactopyranosyl]-4,6-*O*-*p*-methoxybenzylidene-β-D-glucopyranoside (12). To a solution of **1c** (58.0 mg, 0.107 mmol) and **2b** (52.0 mg, 0.072 mmol) in CH_2Cl_2 (5 mL) was added 4 Å molecular sieves (600 mg), and the mixture was stirred for 30 min at room temperature and then cooled to − 20 °C. NIS (25.0 mg, 0.107 mmol) and TfOH (35 μL, 0.3 M etheral solution) were added to the mixture, and this mixture was stirred for 15 min at − 20 °C. To the reaction mixture were added a solution of **6a** (119.0 mg, 0.215 mmol) in CH_2Cl_2 (3 mL), NIS (25.0 mg, 0.107 mmol), and TfOH (45 μL, 0.3 M etheral solution). The reaction mixture was stirred for 30 min at −20 °C. The course of the reaction was monitored by TLC. Et_3N (1.5 mL) was then added to the mixture. The precipitate was filtered off, and the filtrate was successively washed with saturated aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 3:1 to 2:1) to give **12** (83.0 mg, 74%) as a thick oil and the 1,3-component coupling product **13** (19.8 mg, 19%) as a thick oil that was recently deprotected to form compound **80** (see the preparation of saccharide **80**). For compound **12**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.04−7.44 (m, 30H), 6.79−6.82 (m, 4H), 5.45 (d, *J* = 3.0 Hz, 1H), 5.37 (s, 1H), 5.29 (dd, *J* = 8.0, 10.0 Hz, 1H), 5.00 (d, *J* = 8.5 Hz, 1H), 4.91 (d, *J* = 2.5 Hz, 1H), 4.81 (d, *J* = 11.5 Hz, 1H), 4.70 (d, *J* = 8.5 Hz, 1H), 4.68 (dd, *J* = 9.0, 10.0 Hz, 1H), 4.56−4.63 (ABq, *J* = 12.0 Hz, 2H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.28 (dd, *J* = 4.5, 10.5 Hz, 1H), 4.22 (dd, *J* = 8.5, 10.0 Hz, 1H), 4.17 (q, *J* = 6.5 Hz, 1H), 4.02 (dd, *J* = 3.5, 10.5 Hz, 1H), 3.87−3.94 (ABq, *J* = 12.0 Hz, 2H), 3.72−3.80 (m, 3H), 3.71(s, 3H), 3.68−3.70 (m, 1H), 3.66 (s, 3H), 3.59−3.64 (m, 2H), 3.58 (s, 3H), 3.53 (q, *J* = 4.5 Hz, 1H), 3.27 (dt, *J* = 9.5, 6.5 Hz, 1H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.31−2.48 (m, 2H), 1.98 (s, 3H), 1.82−1.92 (m, 2H), 1.19−1.34 (m, 4H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.99 (s, 9H), 0.89−0.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 173.8, 171.8, 163.9, 160.0, 138.8, 138.4, 138.3, 135.8, 135.5, 133.6, 133.0, 132.5, 132.5, 129.9, 129.8, 129.6, 129.3, 129.2, 128.4, 128.2, 128.1, 128.1, 127.7, 127.7, 127.6, 127.5, 127.3, 127.2, 127.2, 127.1, 127.1, 126.8, 113.6, 100.8, 100.5, 98.6, 98.5, 80.95, 78.49, 77.41, 75.43, 74.66, 73.58, 73.07, 72.82, 72.59, 71.59, 69.39, 68.77, 68.47, 67.13, 66.28, 64.30, 60.58, 55.29, 55.12, 51.32, 38.29, 33.56, 29.57, 28.77, 28.36, 26.72, 25.13, 24.20, 18.91, 16.42; HRMS (M + Cs) calcd for $C_{90}H_{99}O_{22}NSiCs$ 1706.5482, found 1706.5604.

Compound 15. To a solution of **14** (46.9 mg, 0.1033 mmol) and **2b** (50.0 mg, 0.06887 mmol) in CH_2Cl_2 (5 mL) was added 4 Å molecular sieves (600 mg), and the mixture was stirred for 30 min at room temperature and then cooled to −20 °C. NIS (24.5 mg, 0.1033 mmol) and TfOH (50 μL, 0.3 M etheral solution) were added to the mixture, and this mixture was stirred for 40 min at −20 °C. To the reaction mixture was added a solution of **6a** (114.7 mg, 0.2066 mmol) in CH_2Cl_2 (3

mL), NIS (24.5 mg, 0.1033 mmol), and TfOH (45 μL, 0.3 M etheral solution). The reaction mixture was stirred for 30 min at −20 °C. Et_3N (0.5 mL) was then added to the mixture. The precipitate was filtered off, and the filtrate was successively washed with saturated aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 4:1 to 3:1) to give **15** (36.1 mg, 87%) as a syrup and recovery of **14** (46.3 mg) and **6a** (114.0 mg): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.5 Hz, 2H), 7.62−7.67 (m, 5H), 7.49 (t, J = 8.0 Hz, 2H), 7.33−7.44 (m, 6H), 5.44 (t, J = 2.5 Hz, 1H), 5.29 (t, J = 2.5 Hz, 1H), 4.87 (d, J = 6.5 Hz, 1H), 4.76 (dt, J = 6.5, 2.0 Hz, 1H), 4.28 (dd, J = 8.5, 5.5 Hz, 1H), 3.89 (t, J = 9.0 Hz, 1H), 3.85 (dd, J = 9.5, 5.5 Hz, 1H), 2.64−2.73 (m, 2H), 2.25 (t, J = 7.5 Hz, 2H), 2.17 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 165.0, 135.6, 135.5, 137.7, 133.3, 133.0, 129.8, 129.8, 128.9, 128.6, 127.7, 118.4, 93.8, 72.64, 72.00, 69.78, 67.33, 62.98, 37.86, 29.88, 27.19, 26.89, 19.22; HRMS (M + Cs) calcd for $C_{34}H_{38}O_8SiCs$ 735.1390, found 735.1410.

***p*-Methylphenyl 2-Deoxy-2-azido-3,4,6-tri-*O*-acetyl-1-thio-D-galactopyranoside (20).** To a mixture of 2-deoxy-2-azido-1,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (**19**)[18] (3.5 g, 9.38 mmol) and *p*-thiocresol (1.75 g, 14.07 mmol) in CH_2Cl_2 (60 mL) was added boron trifluoride diethyl etherate (1.54 mL, 12.19 mol) at 0 °C. The mixture was then stirred overnight at room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromotography on silica gel (hexanes/EtOAc 3:1) to give **20** (2.78 g, 68%) as a syrup and recovery of **19** (0.69 g): ^{1}H NMR (500 MHz, $CDCl_3$) (α/β = 1.2:1), δ 7.50 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.12−7.16 (m, 4H), 5.61 (d, J = 5.5 Hz, 1H, H-1 of α-isomer), 5.48 (dd, J = 3.0, 1.0 Hz, 1H), 5.34 (dd, J = 3.5, 1.0 Hz, 1H), 5.17 (dd, J = 11.0, 3.5 Hz, 1H), 4.85 (dd, J = 10.0, 3.0 Hz, 1H), 4.77 (t, J = 6.5 Hz, 1H), 4.46 (d, J = 10.0 Hz, 1H, H-1 of β-isomer), 4.29 (dd, J = 11.0, 5.5 Hz, 1H), 4.16 (dd, J = 11.0, 6.5 Hz, 1H), 4.07−4.12 (m, 3H), 3.86 (dt, J = 1.0, 6.5 Hz, 1H), 3.63 (t, J = 10.0 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H); HRMS (M + Cs) calcd for $C_{19}H_{23}O_7N_3SCs$ 570.0311, found 570.0326.

***p*-Methylphenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-azido-1-thio-β-D-galactopyranoside (1d) and *p*-Methylphenyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-azido-1-thio-α-D-galactopyranoside (21).** Compound **20** (926.0 mg, 2.12 mmol) was treated with NaOMe/MeOH (25 wt %, 0.5 mL) in MeOH (18 mL) at room temperature. After 3 h, the mixture was neutralized (IRC-50 resin, weak acid) and concentrated to give semisolids. To a solution of above semisolids in dry DMF (15 mL) was added NaH (95%, 0.32 g, 12.7 mmol) in portions. After the mixture was stirred for 10 min, benzyl bromide (2.2 g, 12.7 mmol) was then added at 0 °C. The reaction mixture was stirred for 3 h at room temperature. MeOH (4 mL) was then added to the mixture. The reaction mixture was poured to ice−water and extracted with EtOAc. The combined organic liquid was dried over Na_2SO_4. The solvent was removed, and the residue was subjected to a column chromatography on silica gel (hexanes/EtOAc 8:1) to give **1d** (532.6 mg, 43%) and its α-anomeric isomer **21** (641.4 mg, 52%) as thick oils. Compound **1d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.19−7.39 (m, 15H), 7.00 (dd, J = 8.4, 0.6 Hz, 2H), 4.86 (d, J = 11.4 Hz, 1H), 4.71 (d, J = 11.6 Hz, 1H), 4.65 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.47 (d, J = 11.7 Hz, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.33 (d, J = 10.1 Hz, 1H), 3.93 (d, J = 2.2 Hz, 1H), 3.79 (t, J = 9.9 Hz, 1H), 3.63 (d, J = 6.7 Hz, 1H), 3.62 (s, 1H), 3.55 (dt, J = 0.6, 6.7 Hz, 1H), 3.40 (dd, J = 9.8, 2.7 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.41, 138.02, 137.69, 137.36, 133.34, 129.57, 128.46, 128.39, 128.09, 127.92, 127.87, 127.79, 127.58, 127.40, 86.45, 82.42, 77.22, 74.30, 73.50, 72.31, 71.99, 68.36, 61.34, 21.11; HRMS (M + Cs) calcd for $C_{34}H_{35}O_4N_3SCs$ 714.1403, found 714.1429. Its α-anomeric isomer **21**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.43 (m, 17H), 7.02 (d, J = 7.9 Hz, 2H), 5.53 (d, J = 5.4 Hz, 1H), 4.89 (d, J = 11.3 Hz, 1H), 4.75 (s, 2H), 4.54 (d, J = 11.3 Hz, 1H), 4.49 (t, J = 6.5 Hz, 1H), 4.39−4.46 (m, 3H), 4.04 (d, J = 1.6 Hz, 1H), 3.78 (dd, J = 10.6, 2.7 Hz, 1H), 3.61 (dd, J = 9.4, 6.9 Hz, 1H), 3.53 (dd, J = 9.4, 6.1 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.19, 137.85, 137.78, 137.36, 132.84, 129.73, 129.49, 128.53, 128.37, 128.28, 127.99, 127.96, 127.82, 127.74, 127.66, 87.93, 79.11, 74.84, 73.42, 73.42, 72.38, 70.38, 68.63, 60.36, 21.08; HRMS (M + Cs) calcd for $C_{34}H_{35}O_4N_3SCs$ 714.1403, found 714.1429.

***p*-Methylphenyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-mannopyranoside (1e).** Compound **14** (1.82 g, 4.01 mmol) was treated with NaOMe/MeOH (25 wt %, 0.6 mL) in MeOH (35 mL) at room temperature. After 3 h, the mixture was neutralized (IRC-50 resin, weak acid) and concentrated to give solids. To a solution of the above solids in dry DMF (35 mL) was added NaH (95%, 0.61 g, 24.06 mmol) in portions. After the mixture was stirred for 15 min, benzyl bromide (4.2 g, 24.06 mmol) was then added at 0 °C. The reaction mixture was stirred for 6 h at room temperature. MeOH (6 mL) was then added to the mixture. The reaction mixture was poured to ice−water and extracted with EtOAc. The combined organic liquid was dried over Na_2SO_4. The solvent was removed, and the residue was subjected to a column chromatography on silica gel (hexanes/EtOAc 8:1) to give **1e** (1.97 g, 76%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22−7.37 (m, 20H), 7.20 (dd, J = 7.5, 1.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 5.55 (d, J = 1.5 Hz, 1H), 4.91 (d, J = 11.0 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.57−4.65 (m, 4H), 4.53 (d, J = 11.0 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.28−4.31 (m, 1H), 4.05 (t, J = 9.5 Hz, 1H), 3.99 (dd, J = 2.5, 2.0 Hz, 1H), 3.87 (dd, J = 9.5, 3.5 Hz, 1H), 3.84 (dd, J = 11.0, 5.0 Hz, 1H), 3.75 (dd, J = 11.0, 1.5 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.4, 138.2, 137.9, 137.5, 132.1, 130.5, 129.7, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 85.95, 80.11, 76.08, 75.16, 75.00, 73.23, 72.66, 72.02, 71.76, 69.20, 21.08; HRMS (M + Cs) calcd for $C_{41}H_{42}O_5SCs$ 779.1807, found 779.1828.

5-Methoxycarbonylpentyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranoside (23). To a mixture of D-galactose pentaacetate (**22**) (8.0 g, 20.49 mmol), methyl 6-hydroxylhexate (4.49 g, 30.74 mmol), and 4 Å molecular sieves (5 g) in CH_2Cl_2 (200 mL) was added $BF_3{\cdot}OEt_2$ (7.8 mL, 61.47 mmol) at 0 °C. The reaction mixture was then stirred for 6 h at room temperature. Water (1.6 mL) was added to the mixture, and the mixture was stirred for 15 min. The reaction mixture was filtered through Celite, and the filtrate was diluted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ and brine and dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography on silica gel (hexanes/EtOAc 2.5:1) to give product (5.51 g, 56%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (dd, J = 3.4, 1.0 Hz, 1H), 5.20 (dd, J = 10.5, 8.0 Hz, 1H), 5.01 (dd, J = 10.4, 3.5 Hz, 1H), 4.45 (d, J = 7.9 Hz, 1H), 4.10−4.21 (m, 2H), 3.85−3.92 (m, 2H), 3.67 (s, 3H), 3.48 (dt, J = 9.5, 6.5 Hz, 1H), 2.31 (t, J = 7.6 Hz, 2H), 2.15 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.54−1.67 (m, 4H), 1.30−1.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 170.4, 170.3, 170.2, 169.4, 101.3, 70.93, 70.57, 69.84, 68.87, 67.00, 61.26, 51.48, 33.91, 29.06, 25.35, 24.55, 20.71, 20.66, 20.58; HRMS (M + Cs) calcd for $C_{21}H_{32}O_{12}Cs$ 609.0948, found 609.0967.

5-Methoxycarbonylpentyl 4,6-*O*-Benzylidene-β-D-galactopyranoside (24). Compound **23** (5.2 g, 10.92 mmol) was treated with NaOMe/MeOH (25 wt %, 0.4 mL) in MeOH (140 mL) at room temperature. After 4 h, the mixture was neutralized (IRC-50 resin, weak acid) and concentrated to give white solids. To a mixture of above white solids, benzaldehyde dimethyl acetal (2.34 g, 15.6 mmol), and dry acetonitrile (70 mL) was added 10-camphorsulfonic acid (49.3 mg) at room temperature. The mixture was stirred for 4 h, and Et_3N (2 mL) was then added. The solvent was removed to give white solids. The crude product was subjected to recrystallization (EtOAc/hexanes) to give **24** (3.76 g, 87%) as a solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.52 (m, 2H), 7.34−7.39 (m, 3H), 5.56 (s, 1H), 4.34 (dd, J = 12.5, 1.5 Hz, 1H), 4.27 (d, J = 7.5 Hz, 1H), 4.22 (dd, J = 3.5, 1.0 Hz, 1H), 4.09 (dd, J = 12.5, 2.0 Hz, 1H), 3.99 (dt, J = 9.0, 6.5 Hz, 1H), 3.76 (dt, J = 1.5, 8.5

Hz, 1H), 3.71 (dd, J = 8.5, 3.5 Hz, 1H), 3.67 (s, 3H), 3.51 (dt, J = 9.5, 6.5 Hz, 1H), 3.48 (d, J = 1.0 Hz, 1H), 2.77 (br. s, 1H), 2.57 (d, J = 8.5 Hz, 1H), 2.34 (t, J = 7.5 Hz, 2H), 1.61−1.73 (m, 4H), 1.37−1.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 137.5, 129.2, 128.2, 126.4, 102.8, 101.4, 75.30, 72.68, 71.73, 69.50, 69.15, 66.64, 51.54, 33.79, 28.89, 25.42, 24.44; HRMS (M + Na) calcd for $C_{20}H_{28}O_8Na$ 419.1682, found 419.1669.

5-Methoxycarbonylpentyl 3-*O*-Chloroacetyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (25) and 5-Methoxycarbonylpentyl 2,3-Di-*O*-chloroacetyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (26). To a cold (−20 °C) solution of compound **24** (500 mg, 1.26 mmol) in pyridine (0.8 mL), Et_3N (0.8 mL), and CH_2Cl_2 (10 mL) was added slowly chloroacetyl chloride (160 mg, 1.39 mmol). The mixture was stirred for 2 h at − 20 °C. The reaction mixture was then diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine. The dried organic solvent (Na_2SO_4) was concentrated. The residue was subjected to a column chromatography on silica gel (hexanes/EtOAc 2:1) to give **25** (295.1 mg, 50%) as a thick oil and **26** (173.8 mg, 25%) as a syrup. For compound **25**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.51 (m, 2H), 7.32−7.38 (m, 3H), 5.49 (s, 1H), 4.92 (dd, J = 10.0, 3.5 Hz, 1H), 4.39 (d, J = 3.5 Hz, 1H), 4.32 (d, J = 7.5 Hz, 1H), 4.30 (d, J = 12.5 Hz, 1H), 4.17 (ABq, J = 15.5 Hz, 2H), 4.05 (dd, J = 12.5, 1.5 Hz, 1H), 3.94−4.00 (m, 2H), 3.65 (s, 3H), 3.51 (dt, J = 9.0, 7.0 Hz, 1H), 3.48 (s, 1H), 2.32 (t, J = 7.5 Hz, 2H), 2.04 (d, J = 2.0 Hz, 1H), 1.58−1.69 (m, 4H), 1.35−1.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 167.2, 137.4, 128.9, 128.1, 126.2, 102.8, 100.7, 75.28, 73.03, 69.42, 68.84, 68.16, 66.05, 51.44, 40.84, 33.63, 28.63, 25.16, 24.15; HRMS (M + Cs) calcd for $C_{22}H_{29}O_9ClCs$ 605.0554, found 605.0579. For compound **26**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.52 (m, 2H), 7.34−7.40 (m, 3H), 5.50 (s, 1H), 5.42 (dd, J = 10.5, 8.0 Hz, 1H), 5.06 (dd, J = 10.5, 4.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.43 (d, J = 3.5 Hz, 1H), 4.33 (dd, J = 12.5, 1.5 Hz, 1H), 4.08 (dd, J = 12.0, 1.5 Hz, 1H), 4.07 (s, 2H), 4.05 (s, 2H), 3.93 (dt, J = 9.5, 6.0 Hz, 1H), 3.66 (s, 3H), 3.53 (d, J = 1.0 Hz, 1H), 3.47 (dt, J = 9.5, 6.5 Hz, 1H), 2.30 (t, J = 7.5 Hz, 2H), 1.52−1.66 (m, 4H), 1.31−1.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.0, 167.1, 165.9, 137.1, 129.1, 128.1, 126.2, 101.0, 100.4, 73.32, 73.06, 70.14, 69.23, 68.72, 66.11, 51.42, 40.54, 40.47, 33.83, 28.94, 25.36, 24.49; HRMS (M + Cs) calcd for $C_{24}H_{30}O_{10}Cl_2Cs$ 681.0270, found 681.0240.

5-Methoxycarbonylpentyl 2-*O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-chloroacetyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (27). To a solution of **25** (1.01 g, 2.14 mmol), *p*-methylphenyl 2,3,4,-tri-*O*-benzyl-1-thio-*β*-L-fucopyranoside (**1c**) (1.73 g, 3.21 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (672 mg, 3.21 mmol) in CH_2Cl_2 (40 mL) was added 4 Å molecular sieves (4.0 g), and the mixture was stirred for 20 min at room temperature. At the same time, methyl disulfide (610 mg, 6.41 mmol) and methyl trifluoromethanesulfonate (1.06 g, 6.41 mmol) were mixed in a vial to form solids. The solids in CH_2Cl_2 (10 mL) were then added to the above stirred mixture at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 1 h. Et_3N (2.5 mL) was then added to the mixture. The precipitate was filtered off, and the filtrate was diluted with CH_2Cl_2 and washed with $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 4:1) to give product **27** (1.19 g, 83%) as a thick oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.5, 1.5 Hz, 2H), 7.22−7.40 (m, 18H), 5.50 (s, 1H), 5.23 (d, J = 3.5 Hz, 1H), 5.12 (dd, J = 10.0, 4.0 Hz, 1H), 4.99 (d, J = 12.0 Hz, 1H), 4.79 (d, J = 11.5 Hz, 1H), 4.77 (d, J = 10.0 Hz, 1H), 4.72 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.46 (d, J = 7.5 Hz, 1H), 4.37 (d, J = 4.0 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 4.22 (q, J = 6.5 Hz, 1H), 4.12 (dd, J = 9.5, 7.5 Hz, 1H), 4.03−4.08 (m, 2H), 3.91 (dt, J = 9.0, 7.0 Hz, 1H), 3.86 (dd, J = 10.5, 3.0 Hz, 1H), 3.76 (d, J = 15.5 Hz, 1H), 3.69 (d, J = 15.5 Hz, 1H), 3.66 (dd, J = 6.0, 4.0 Hz, 1H), 3.65 (s, 3H), 3.48 (s, 1H), 3.45 (dt, J = 9.0, 7.0 Hz, 1H), 2.29 (t, J = 7.5 Hz, 2H), 1.57−1.63 (m, 4H), 1.31−1.37 (m, 2H), 1.10 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 167.0, 138.8, 138.7, 138.3, 137.5, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.5, 127.5, 127.4, 126.2, 102.2, 100.8, 98.0, 79.65, 77.69, 76.64, 76.07, 74.78, 73.81, 73.34, 73.05, 72.83, 69.84, 68.99, 66.79, 65.94, 51.48, 40.66, 33.94, 29.19, 25.56, 24.70, 16.66; HRMS (M + Cs) calcd for $C_{49}H_{57}O_{13}ClCs$ 1021.2542, found 1021.2582.

5-Methoxycarbonylpentyl 2-*O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-4,6-*O*-benzylidene-*β*-D-galactopyranoside (6d). Compound **27** (1.18 g, 1.33 mmol) was treated with NaOMe/MeOH (25 wt %, 0.5 mL) in MeOH (50 mL) at room temperature. After 3 h, the mixture was neutralized (IRC-50 resin, weak acid) and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 2:1) to give **6d** (1.07 g, 99%) as a thick oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.5, 2.0 Hz, 2H), 7.22−7.40 (m, 18H), 5.54 (s, 1H), 5.25 (d, J = 3.6 Hz, 1H), 4.97 (d, J = 11.6 Hz, 1H), 4.73−4.83 (m, 4H), 4.66 (d, J = 11.6 Hz, 1H), 4.27−4.37 (m, 2H), 4.19 (br. s, 1H), 4.17 (q, J = 6.5 Hz, 1H), 4.03−4.09 (m, 2H), 3.97 (dd, J = 10.1, 2.7 Hz, 1H), 3.88 (dt, J = 9.2, 7.0 Hz, 1H), 3.82−3.84 (m, 2H), 3.75 (br. s, 1H), 3.68 (d, J = 2.0 Hz, 1H), 3.64 (s, 3H), 3.44 (dt, J = 9.2, 6.9 Hz, 1H), 3.39 (br. s, 1H), 2.28 (t, J = 7.4 Hz, 2H), 1.54−1.64 (m, 4H), 1.28−1.40 (m, 2H), 1.12 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.07, 138.76, 138.64, 137.78, 137.68, 129.06, 128.37, 128.27, 128.16, 128.13, 127.79, 127.53, 127.48, 127.35, 126.53, 101.77, 101.39, 99.25, 79.70, 77.72, 77.61, 75.54, 74.76, 73.71, 73.58, 72.88, 69.24, 69.12, 66.78, 66.54, 51.46, 33.94, 29.33, 25.54, 24.73, 16.69; HRMS (M + Cs) calcd for $C_{47}H_{56}O_{12}Cs$ 945.2826, found 945.2856.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (28). To a solution of *p*-methylphenyl 2-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (**2e**) (20.0 mg, 0.01916 mmol) and *p*-methylphenyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranoside (**1b**) (18.6 mg, 0.02874 mmol) in CH_2Cl_2 (2 mL) was added 4 Å molecular sieves (300 mg), and the mixture was stirred for 20 min at room temperature under argon. At the same time, methyl disulfide (10.9 mg, 115.0 μmol) and methyl trifluoromethanesulfonate (19.1 mg, 115.0 μmol) were mixed in a vial to form solids. The solids in CH_2Cl_2 (0.5 mL) were then added to the above stirred mixture at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 1 h. To the reaction mixture was added a solution of 5-methoxycarbonylpentyl 3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (**6b**) (37.2 mg, 0.05748 mmol) in CH_2Cl_2 (0.5 mL), NIS (6.8 mg, 0.02874 mmol), and TfOH (25 μL, 0.3 M etheral solution). The reaction mixture was stirred for 30 min at room temperature. The course of the reaction was monitored by TLC. Et_3N (0.6 mL) was then added to the mixture. The precipitate was filtered off, and the filtrate was successively washed with saturated aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 3:1 to 2:1) to give **28** (20.4 mg, 51%) as a thick oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55−7.98 (m, 63H), 3.15−6.02 (m, 52H), 1.85−1.93 (m, 2H), 1.22−1.32 (m, 4H), 1.08 (s, 9H), 0.99−1.03 (m, 2H), 0.96 (d, J = 6.5 Hz, 3H); HRMS (M + Cs) calcd for $C_{126}H_{135}O_{25}NSiCs$ 2222.8147, found 2222.8286.

5-Methoxycarbonylpentyl 2-*O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-4,6-*O*-benzylidene-*β*-D-galactopyranoside (29) and 5-Methoxycarbonylpentyl 2-*O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzyl-*β*-L-fucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranosyl]-4,6-*O*-benzylidene-*β*-D-galactopyranoside (30). To a solution of **2b** (28.0 mg, 0.03857 mmol) and **1c** (31.2 mg, 0.05785 mmol) in CH_2Cl_2 (2 mL) were added 4 Å molecular sieves (400 mg) and 2,6-di-*tert*-butyl-4-methylpyridine (12.1 mg, 0.05785 mmol), and the mixture was stirred for 20 min

at room temperature under argon. At the same time, methyl disulfide (22.0 mg, 0.2314 mmol) and methyl trifluoromethanesulfonate (38.4 mg, 0.2314 mmol) were mixed in a vial to form solids. The solids in CH_2Cl_2 (0.8 mL) were then added to the above stirred mixture at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 1.5 h. To the reaction mixture, after the addition of a solution of **6d** (93.9 mg, 0.1157 mmol) in CH_2Cl_2 (0.5 mL), the solids formed by mixing methyl disulfide (22.0 mg, 0.2314 mmol) and methyl trifluoromethanesulfonate (38.4 mg, 0.2314 mmol) were added. The reaction mixture was stirred overnight. Et_3N (0.6 mL) was then added to the mixture. The precipitate was filtered off, and the cake was washed with CH_2Cl_2. The filtrate was washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc 4:1 to 3:1) to give **29** (21.2 mg, 30%) and **30** (16.9 mg, 24%) as thick oils. For compound **29**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.1, 1.0 Hz, 2H), 7.59−7.63 (m, 4H), 7.51 (t, J = 7.5 Hz, 1H), 7.09−7.44 (m, 41H), 6.93 (dd, J = 8.1, 1.5 Hz, 2H), 5.77 (s, 1H), 5.53 (d, J = 3.6 Hz, 1H), 5.50 (dd, J = 10.1, 8.0 Hz, 1H), 5.40 (d, J = 3.6 Hz, 1H), 5.14 (d, J = 3.4 Hz, 1H), 4.94 (d, J = 11.6 Hz, 1H), 4.88 (d, J = 11.4 Hz, 1H), 4.85 (d, J = 11.0 Hz, 1H), 4.74 (d, J = 11.8 Hz, 1H), 4.70 (d, J = 12.5 Hz, 2H), 4.67 (d, J = 8.5 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 11.6 Hz, 1H), 4.59 (d, J = 11.6 Hz, 1H), 4.57 (d, J = 8.0 Hz, 1H), 4.32 (t, J = 6.4 Hz, 1H), 4.07−4.21 (m, 7H), 4.02 (dd, J = 6.2, 2.2 Hz, 1H), 4.00 (dd, J = 10.0, 3.6 Hz, 1H), 3.65−3.87 (m, 10H), 3.64 (s, 3H), 3.61 (d, J = 1.9 Hz, 1H), 3.37 (dt, J = 9.6, 5.8 Hz, 1H), 2.98 (dt, J = 9.6, 5.6 Hz, 1H), 2.46−2.68 (m, 4H), 2.17 (t, J = 7.5 Hz, 2H), 1.99 (s, 3H), 1.41−1.49 (m, 2H), 1.20−1.30 (m, 2H), 1.15 (d, J = 6.5 Hz, 3H), 1.04−1.11 (m, 2H), 1.01 (s, 9H), 1.00 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.03, 174.00, 172.02, 164.55, 139.02, 138.90, 138.59, 138.52, 138.35, 138.30, 136.51, 135.60, 135.49, 133.16, 132.97, 132.85, 129.85, 129.81, 129.67, 129.61, 129.30, 128.52, 128.45, 128.28, 128.21, 128.14, 128.12, 128.04, 127.86, 127.77, 127.74, 127.56, 127.51, 127.35, 127.26, 127.23, 126.99, 126.92, 105.09, 101.66, 100.67, 98.52, 95.37, 79.79, 79.32, 78.65, 77.82, 77.40, 76.39, 76.16, 75.57, 75.02, 74.79, 74.75, 73.76, 73.42, 73.31, 72.82, 72.70, 72.46, 72.17, 71.83, 69.17, 68.77, 68.54, 67.25, 66.03, 60.96, 51.47, 38.35, 33.89, 29.68, 29.21, 28.42, 26.68, 25.74, 24.71, 19.02, 16.53, 16.39; HRMS (M + Cs) calcd for $C_{108}H_{122}O_{24}SiCs$ 1963.7150, found 1963.7269. For compound **30**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 7.5, 1.5 Hz, 2H), 7.65−7.68 (m, 4H), 7.55 (d, J = 7.0 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.05−7.46 (m, 38H), 6.91 (d, J = 7.0 Hz, 2H), 5.45 (s, 1H), 5.44 (dd, J = 10.0, 8.0 Hz, 1H), 5.20 (d, J = 12.0 Hz, 1H), 5.10 (d, J = 4.0 Hz, 1H), 5.05 (d, J = 4.0 Hz, 1H), 5.04 (d, J = 4.0 Hz, 1H), 4.94 (d, J = 11.0 Hz, 1H), 4.88 (d, J = 11.5 Hz, 1H), 4.83 (d, J = 8.0 Hz, 1H), 4.81 (d, J = 13.0 Hz, 1H), 4.78 (d, J = 11.5 Hz, 1H), 4.72 (d, J = 11.5 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 11.0 Hz, 1H), 4.22 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 12.0 Hz, 1H), 4.17 (q, J = 6.5 Hz, 1H), 4.11 (d, J = 11.5 Hz, 1H), 4.07 (d, J = 12.0 Hz, 1H), 4.01 (q, J = 6.5 Hz, 1H), 3.98 (d, J = 4.0 Hz, 1H), 3.97 (dd, J = 10.0, 2.5 Hz, 1H), 3.88 (dd, J = 9.5, 7.5 Hz, 1H), 3.65−3.84 (m, 8H), 3.64 (s, 3H), 3.58−3.61 (m, 2H), 3.51 (dd, J = 10.0, 6.0 Hz, 1H), 3.33 (dt, J = 9.0, 7.0 Hz, 1H), 2.95 (s, 1H), 2.89 (t, J = 6.5 Hz, 1H), 2.47−2.68 (m, 3H), 2.32−2.40 (m, 1H), 2.26 (t, J = 7.5 Hz, 2H), 1.95 (s, 3H), 1.54−1.60 (m, 2H), 1.46−1.52 (m, 2H), 1.25−1.32 (m, 2H), 1.14 (d, J = 6.5 Hz, 3H), 1.07 (s, 9H), 0.95 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 174.0, 171.9, 164.4, 139.4, 139.3, 138.9, 138.6, 138.3, 138.0, 135.5, 135.4, 133.6, 133.0, 132.9, 129.9, 129.8, 129.7, 129.4, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.3, 127.2, 127.0, 127.0, 126.2, 101.5, 100.9, 100.1, 98.9, 97.0, 80.00, 79.09, 78.79, 78.21, 77.45, 76.56, 75.77, 74.74, 74.70, 74.70, 73.91, 73.67, 73.61, 72.66, 72.34, 72.09, 72.09, 71.61, 69.67, 68.77, 68.45, 67.16, 66.23, 65.99, 61.83, 51.46, 38.01, 33.93, 29.68, 29.35, 28.40, 26.76, 25.63, 24.75, 19.31, 16.62, 16.42; HRMS (M + Cs) calcd for $C_{108}H_{122}O_{24}SiCs$ 1963.7150, found 1963.7267.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside (31). This trisaccharide was prepared from **1a** (17.4 mg, 0.0268 mmol), **2b** (13.0 mg, 0.0179 mmol), and **6a** (29.8 mg, 0.0537 mmol) as described in the preparation of **12**, yielding product (17.1 mg, 57%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.0, 1.5 Hz, 2H), 7.47 (dd, J = 8.0, 1.5 Hz, 2H), 7.18−7.42 (m, 31H), 7.14 (dd, J = 8.0, 2.5 Hz, 2H), 7.05 (m, 2H), 6.99 (t, J = 8.0 Hz, 2H), 6.79 (m, 2H), 5.62 (d, J = 3.0 Hz, 1H), 5.37 (s, 1H), 5.23 (dd, J = 10.5, 8.0 Hz, 1H), 5.18 (d, J = 3.5 Hz, 1H), 5.07 (d, J = 8.5 Hz, 1H), 4.86 (d, J = 8.0 Hz, 1H), 4.74 (dd, J = 10.5, 8.5 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.32 (dd, J = 10.5, 5.0 Hz, 1H), 4.28 (d, J = 5.0 Hz, 1H), 4.25 (dd, J = 8.0, 1.5 Hz, 1H), 4.18 (d, J = 10.5 Hz, 1H), 4.16 (d, J = 10.5 Hz, 1H), 3.90 (dd, J = 10.5, 3.0 Hz, 1H), 3.73−3.82 (m, 3H), 3.68−3.72 (m, 4H), 3.56−3.64 (m, 8H), 3.35 (dd, J = 9.5, 7.5 Hz, 1H), 3.30 (dt, J = 10.0, 6.5 Hz, 1H), 3.23 (dd, J = 10.0, 2.5 Hz, 1H), 2.97 (dd, J = 9.5, 5.0 Hz, 1H), 2.82 (d, J = 1.5 Hz, 1H), 2.24−2.37 (m, 3H), 2.13−2.22 (m, 1H), 1.92 (s, 3H), 1.81−1.94 (m, 2H), 1.19−1.41 (m, 6H), 1.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 173.8, 171.2, 164.1, 160.0, 138.8, 138.7, 138.3, 138.0, 135.8, 135.6, 133.5, 133.0, 132.6, 132.5, 129.8, 129.7, 129.5, 129.5, 129.0, 128.4, 128.2, 128.1, 128.0, 128.0, 127.8, 127.6, 127.4, 127.4, 127.2, 127.2, 126.9, 113.7, 100.8, 100.2, 98.6, 93.2, 81.50, 78.59, 75.91, 75.83, 74.48, 74.33, 73.25, 73.11, 73.07, 72.97, 71.51, 71.43, 69.45, 69.36, 69.01, 68.47, 66.29, 64.35, 61.14, 55.13, 55.00, 51.32, 37.96, 33.57, 29.51, 28.79, 28.10, 26.82, 25.15, 24.23, 19.01; HRMS (M + Cs) calcd for $C_{97}H_{105}O_{23}NSiCs$ 1812.5901, found 1812.5773.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside (32). This trisaccharide was prepared from **1b** (80.1 mg, 0.1240 mmol), **2b** (60.0 mg, 0.08264 mmol), and **6a** (137.6 mg, 0.2479 mmol) as described in the preparation of **12**, yielding product (73.1 mg, 53%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.0, 1.5 Hz, 2H), 7.48 (dd, J = 8.0, 1.5 Hz, 2H), 7.10−7.43 (m, 33H), 6.97 (t, J = 8.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 6.73 (dd, J = 7.5, 1.5 Hz, 2H), 5.65 (d, J = 3.0 Hz, 1H), 5.34 (s, 1H), 5.23 (dd, J = 10.0, 8.0 Hz, 1H), 5.11 (d, J = 3.5 Hz, 1H), 5.06 (d, J = 8.5 Hz, 1H), 4.86 (d, J = 8.0 Hz, 1H), 4.65−4.71 (m, 3H), 4.53 (d, J = 12.0 Hz, 1H), 4.44 (d, J = 11.0 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 11.0 Hz, 1H), 4.30 (dd, J = 10.0, 5.0 Hz, 1H), 4.28 (d, J = 12.0 Hz, 1H), 4.24 (dd, J = 10.0, 8.5 Hz, 1H), 4.05−4.08 (m, 1H), 3.88 (dd, J = 10.5, 3.0 Hz, 1H), 3.76−3.82 (m, 2H), 3.74 (s, 3H), 3.61−3.73 (m, 3H), 3.52−3.59 (m, 5H), 3.40 (t, J = 9.5 Hz, 1H), 3.28−3.35 (m, 4H), 3.24 (q, J = 9.0 Hz, 1H), 3.16 (dd, J = 10.5, 4.0 Hz, 1H), 2.27−2.35 (m, 3H), 2.17−2.25 (m, 1H), 1.93 (s, 3H), 1.80−1.92 (m, 2H), 1.19−1.40 (m, 4H), 1.03 (s, 9H), 0.99−1.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 173.8, 171.2, 164.4, 160.0, 138.6, 138.5, 138.4, 137.7, 135.8, 135.6, 133.5, 133.0, 132.5, 129.8, 129.7, 129.6, 129.3, 128.9, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 127.4, 127.3, 127.1, 127.0, 113.7, 100.7, 100.1, 98.5, 93.3, 81.36, 81.31, 79.26, 77.09, 75.73, 75.31, 74.27, 73.31, 73.22, 73.13, 72.40, 71.10, 70.24, 69.42, 68.45, 67.84, 66.25, 64.43, 61.25, 55.15, 55.03, 51.32, 37.91, 33.56, 29.56, 28.78, 28.03, 26.84, 25.10, 24.22, 19.04; HRMS (M + Cs) calcd for $C_{97}H_{105}O_{23}NSiCs$ 1812.5901, found 1812.6013.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (33). This trisaccharide was prepared from **1a** (66.7 mg, 0.1033 mmol), **2b** (50.0 mg, 0.06887 mmol), and **6b** (133.7 mg, 0.2066 mmol) as described in the preparation of **12**, yielding product (63.2 mg, 52%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.0, 1.0 Hz, 2H), 7.56−7.74 (m, 7H), 7.49 (t, J = 7.5 Hz, 1H), 7.17−7.41 (m, 29H), 7.10−

7.12 (m, 2H), 6.91−6.93 (m, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.74−6.77 (m, 3H), 5.72 (d, J = 3.0 Hz, 1H), 5.49 (dd, J = 10.5, 8.0 Hz, 1H), 5.29 (d, J = 3.0 Hz, 1H), 4.95 (d, J = 8.5 Hz, 1H), 4.78 (d, J = 8.0 Hz, 1H), 4.75 (d, J = 12.5 Hz, 1H), 4.74 (d, J = 11.5 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.37 (d, J = 12.0 Hz, 1H), 4.33 (d, J = 12.0 Hz, 1H), 4.31 (d, J = 12.0 Hz, 1H), 4.29 (d, J = 11.5 Hz, 1H), 4.22 (dd, J = 10.5, 8.5 Hz, 1H), 4.03−4.08 (m, 2H), 3.99 (dd, J = 10.0, 8.5 Hz, 1H), 3.93 (dd, J = 10.0, 3.0 Hz, 1H), 3.91 (t, J = 6.0 Hz, 1H), 3.73 (s, 3H), 3.63−3.69 (m, 3H), 3.45−3.59 (m, 8H), 3.35−3.38 (m, 1H), 3.21−3.28 (m, 3H), 2.21−2.45 (m, 4H), 1.88−1.96 (m, 2H), 1.86 (s, 3H), 1.25−1.39 (m, 4H), 1.03 (s, 9H), 0.98−1.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 173.8, 171.2, 164.6, 159.1, 138.8, 138.6, 138.4, 138.3, 138.1, 135.6, 135.5, 133.6, 133.2, 133.0, 132.9, 130.2, 129.8, 129.7, 129.6, 129.3, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 127.4, 127.3, 127.2, 126.8, 113.6, 100.6, 98.1, 93.6, 78.73, 77.99, 77.20, 77.10, 75.70, 74.73, 74.70, 74.45, 73.42, 73.07, 73.02, 72.80, 72.12, 71.65, 69.71, 69.23, 68.99, 67.50, 64.70, 60.89, 55.60, 55.15, 51.27, 37.84, 33.61, 29.36, 28.76, 27.98, 26.74, 25.20, 24.28, 19.02; HRMS (M + Cs) calcd for $C_{104}H_{113}O_{23}NSiCs$ 1904.6527, found 1904.6796.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (34). This trisaccharide was prepared from **1b** (66.7 mg, 0.1033 mmol), **2b** (50.0 mg, 0.06887 mmol), and **6b** (113.7 mg, 0.2066 mmol) as described in the preparation of **12**, yielding product (70.1 mg, 57%) as a thick oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.0 Hz, 2H), 7.58−7.74 (m, 8H), 7.19−7.42 (m, 27H), 7.14−7.17 (m, 2H), 6.91−6.94 (m, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.74−6.79 (m, 5H), 5.74 (d, J = 3.0 Hz, 1H), 5.49 (dd, J = 10.5, 8.5 Hz, 1H), 5.21 (d, J = 3.0 Hz, 1H), 4.94 (d, J = 8.5 Hz, 1H), 4.79 (d, J = 10.5 Hz, 1H), 4.75 (d, J = 12.5 Hz, 1H), 4.74 (d, J = 8.5 Hz, 1H), 4.73 (d, J = 11.0 Hz, 1H), 4.62 (d, J = 12.5 Hz, 1H), 4.57 (d, J = 11.0 Hz, 1H), 4.54 (d, J = 10.5 Hz, 1H), 4.52 (d, J = 11.5 Hz, 1H), 4.49 (d, J = 12.5 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.38 (d, J = 12.0 Hz, 1H), 4.30 (d, J = 11.5 Hz, 1H), 4.22 (d, J = 11.5 Hz, 1H), 4.20 (dd, J = 10.5, 8.5 Hz, 1H), 3.97−4.08 (m, 3H), 3.75 (s, 3H), 3.61−3.70 (m, 5H), 3.56 (s, 3H), 3.48−3.59 (m, 4H), 3.44 (dd, J = 9.5, 3.0 Hz, 1H), 3.40 (d, J = 9.5 Hz, 1H), 3.32−3.38 (m, 2H), 3.25 (dt, J = 9.5, 6.5 Hz, 1H), 2.28−2.42 (m, 3H), 2.19−2.27 (m, 1H), 1.87−1.98 (m, 2H), 1.84 (s, 3H), 1.24−1.42 (m, 4H), 1.05 (s, 9H), 0.96−1.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 173.8, 171.2, 164.7, 159.2, 138.6, 138.6, 138.5, 137.8, 135.6, 135.5, 133.6, 133.1, 133.1, 132.9, 130.3, 129.7, 129.4, 129.3, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.7, 127.3, 127.1, 126.9, 113.7, 100.6, 98.1, 93.7, 81.37, 79.31, 77.73, 77.35, 76.96, 75.41, 74.68, 74.41, 74.28, 73.51, 73.42, 73.13, 72.97, 72.90, 71.52, 70.67, 69.02, 68.24, 67.47, 64.89, 60.98, 55.60, 55.20, 51.30, 37.83, 33.60, 29.39, 28.79, 27.95, 26.79, 25.26, 24.31, 19.07; HRMS (M + Cs) calcd for $C_{104}H_{113}O_{23}NSiCs$ 1904.6527, found 1904.6680.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (35). This trisaccharide was prepared from **1c** (55.8 mg, 0.1033 mmol), **2b** (50.0 mg, 0.06887 mmol), and **6b** (113.7 mg, 0.2066 mmol) as described in the preparation of **12**, yielding product (71.6 mg, 62%) as a thick oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.2, 1.2 Hz, 2H), 7.54−7.75 (m, 8H), 7.33−7.44 (m, 8H), 7.20−7.30 (m, 13H), 7.09−7.16 (m, 3H), 6.91−6.97 (m, 6H), 6.74−6.78 (m, 3H), 5.54 (d, J = 3.2 Hz, 1H), 5.49 (dd, J = 10.1, 8.0 Hz, 1H), 5.11 (d, J = 3.2 Hz, 1H), 4.93 (d, J = 8.4 Hz, 1H), 4.90 (d, J = 11.5 Hz, 1H), 4.76 (d, J = 12.2 Hz, 1H), 4.68 (ABq, J = 11.9 Hz, 2H), 4.62 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 7.4 Hz, 1H), 4.59 (d, J = 11.7 Hz, 1H), 4.41 (d, J = 12.1 Hz, 1H), 4.24−4.31 (m, 2H), 4.11−4.20 (m, 3H), 4.02−4.09 (m, 3H), 3.99 (dd, J = 9.8, 8.7 Hz, 1H), 3.78−3.86 (m, 2H), 3.75 (s, 3H), 3.66 (dt, J = 9.8, 6.0 Hz, 2H), 3.57 (s, 3H), 3.53−3.56 (m, 2H), 3.39−3.44 (m, 2H), 3.24 (dt, J = 9.8, 6.4 Hz, 2H), 2.39−2.66 (m, 4H), 1.95 (s, 3H), 1.85−1.93 (m, 2H), 1.27−1.39 (m, 4H), 1.21 (d, J = 6.5 Hz, 3H), 1.03 (s, 9H), 0.98−1.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.85, 173.83, 171.80, 164.28, 159.40, 138.87, 138.57, 138.54, 138.25, 135.60, 135.46, 133.60, 133.58, 133.26, 132.98, 132.79, 130.14, 129.79, 129.75, 129.62, 129.57, 129.42, 128.59, 128.31, 128.16, 128.09, 127.79, 127.77, 127.70, 127.65, 127.46, 127.32, 127.18, 126.93, 126.82, 113.78, 100.81, 98.63, 98.11, 78.71, 77.65, 77.46, 76.57, 74.78, 74.67, 74.50, 74.34, 73.58, 73.33, 72.98, 72.86, 72.60, 71.88, 69.02, 67.20, 67.10, 60.26, 55.52, 55.31, 51.30, 38.22, 33.63, 29.48, 28.75, 28.30, 26.72, 25.20, 24.29, 18.98, 16.51; HRMS (M + Cs) calcd for $C_{97}H_{107}O_{22}NSiCs$ 1798.6108, found 1798.6230.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (36) and 5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranosyl]-*β*-D-glucopyranoside (37). These two trisaccharides were prepared from **1a** (66.7 mg, 0.1033 mmol), **2b** (50.0 mg, 0.06887 mmol), and **6c** (133.7 mg, 0.2066 mmol) as described in the preparation of **12**, yielding **36** (75.0 mg, 61%) as a syrup and **37** (10.5 mg, 9%) as a syrup. For compound **36**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.5 Hz, 2H), 7.57−7.75 (m, 8H), 7.19−7.43 (m, 25H), 7.08−7.11 (m, 4H), 7.03 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 6.79−6.87 (m, 3H), 6.72 (d, J = 8.5 Hz, 2H), 5.66(d, J = 3.0 Hz, 1H), 5.56 (dd, J = 10.5, 8.5 Hz, 1H), 5.26 (d, J = 3.5 Hz, 1H), 4.95 (d, J = 8.5 Hz, 1H), 4.71 (d, J = 11.5 Hz, 1H), 4.68 (d, J = 5.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.61 (d, J = 8.0 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.43 (ABq, J = 10.5 Hz, 2H), 4.36 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 4.31 (d, J = 12.0 Hz, 1H), 4.27 (d, J = 11.5 Hz, 1H), 4.19−4.23 (m, 2H), 4.02−4.09 (m, 2H), 3.88−3.92 (m, 2H), 3.73−3.81 (m, 2H), 3.72 (s, 3H), 3.65−3.71 (m, 2H), 3.58−3.63 (m, 2H), 3.57 (s, 3H), 3.52 (dd, J = 10.5, 3.0 Hz, 1H), 3.38−3.48 (m, 3H), 3.16−3.22 (m, 2H), 3.00−3.04 (m, 1H), 2.32−2.47 (m, 4H), 1.98 (s, 3H), 1.75−1.87 (m, 2H), 1.16−1.27 (m, 4H), 1.05 (s, 9H), 1.02−1.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.33, 173.77, 171.56, 164.57, 159.15, 138.77, 138.60, 138.31, 138.17, 137.92, 135.58, 135.51, 133.61, 133.24, 132.93, 132.92, 129.85, 129.77, 129.75, 129.66, 129.40, 128.34, 128.27, 128.20, 128.12, 128.07, 127.92, 127.77, 127.73, 127.69, 127.62, 127.55, 127.47, 127.29, 127.25, 127.17, 113.65, 101.13, 97.85, 93.40, 79.38, 79.13, 78.75, 75.70, 74.64, 74.56, 74.42, 74.40, 74.24, 73.90, 73.36, 73.08, 73.00, 71.93, 70.62, 69.70, 69.39, 68.74, 67.82, 64.94, 61.74, 55.74, 55.16, 51.30, 37.94, 33.58, 29.55, 28.54, 28.14, 26.70, 25.16, 24.26, 19.08; HRMS (M + Cs) calcd for $C_{104}H_{113}O_{23}NSiCs$ 1904.6527, found 1904.6670. For compound **37**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.3 Hz, 2H), 6.99−7.79 (m, 39H), 6.79−6.93 (m, 7H), 5.66 (d, J = 3.0 Hz, 1H), 5.47 (dd, J = 10.5, 3.6 Hz, 1H), 5.41 (d, J = 3.6 Hz, 1H), 5.24 (d, J = 3.4 Hz, 1H), 4.94 (d, J = 8.5 Hz, 1H), 4.76 (d, J = 11.2 Hz, 1H), 4.60−4.72 (m, 4H), 4.59 (d, J = 11.7 Hz, 1H), 4.49 (dd, J = 10.5, 3.2 Hz, 1H), 4.45 (d, J = 11.7 Hz, 1H), 4.40 (d, J = 11.9 Hz, 1H), 4.33 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 11.3 Hz, 1H), 4.28 (d, J = 12.3 Hz, 1H), 4.26 (dd, J = 10.5, 8.5 Hz, 1H), 4.18 (t, J = 6.5 Hz, 1H), 4.08 (t, J = 6.5 Hz, 1H), 3.96 (dd, J = 10.0, 3.2 Hz, 1H), 3.41−3.93 (m, 19H), 3.14 (dt, J = 9.8, 6.5 Hz, 1H), 2.29−2.50 (m, 4H), 1.94 (s, 3H), 1.82−1.93 (m, 2H), 1.12−1.25 (m, 4H), 1.05 (s, 9H), 0.98−1.03 (m, 2H); HRMS (M + Cs) calcd for $C_{104}H_{113}O_{23}NSiCs$ 1904.6527, found 1904.6678.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (38). This trisaccharide was prepared from **1b** (66.7 mg, 0.1033 mmol), **2b** (50.0 mg, 0.06887 mmol), and **6c** (133.7 mg, 0.2066 mmol) as described in the preparation of **12**, yielding product (63.6 mg, 52%) as a syrup: ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 2H), 7.13−7.76 (m, 33H), 7.08 (t, J = 7.5 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 6.80−6.88 (m, 3H), 6.77 (d, J = 7.0 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 5.70 (d, J = 3.0 Hz, 1H), 5.55 (dd, J = 10.0, 8.0 Hz, 1H), 5.20 (d, J = 3.0 Hz, 1H), 4.93 (d, J = 8.5 Hz, 1H), 4.79 (d, J = 11.0 Hz, 1H), 4.71 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 8.0 Hz, 1H), 4.61 (d, J = 11.5 Hz, 1H), 4.56 (d, J = 11.0 Hz, 1H), 4.53 (d, J = 11.5 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 10.5 Hz, 1H), 4.38 (d, J = 12.0 Hz, 1H), 4.36 (d, J = 12.5 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 4.17−4.22 (m, 3H), 4.05 (dd, J = 10.5, 3.5 Hz, 1H), 4.03 (dd, J = 11.0, 8.5 Hz, 1H), 3.76 (dd, J = 12.5, 3.5 Hz, 1H), 3.73 (s, 3H), 3.72 (dd, J = 6.5, 3.5 Hz, 1H), 3.68 (d, J = 9.0 Hz, 1H), 3.67 (d, J = 9.0 Hz, 1H), 3.61 (dd, J = 10.5, 6.5 Hz, 1H), 3.58 (s, 3H), 3.56 (dd, J = 11.0, 6.5 Hz, 1H), 3.33−3.45 (m, 7H), 2.99 (m, 1H), 2.34−2.45 (m, 4H), 1.98 (s, 3H), 1.75−1.86 (m, 2H), 1.18−1.35 (m, 4H), 1.06 (s, 9H), 0.98−1.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 173.7, 171.5, 164.9, 159.2, 138.6, 138.5, 138.4, 137.9, 137.8, 135.6, 135.5, 133.6, 133.2, 132.9, 132.8, 129.8, 129.8, 129.7, 129.6, 129.5, 129.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.4, 127.4, 127.3, 127.2, 127.1, 123.2, 113.7, 101.3, 97.8, 93.5, 81.34, 79.42, 79.32, 79.13, 77.32, 75.38, 74.53, 74.47, 74.43, 74.27, 73.97, 73.36, 73.10, 72.84, 70.56, 68.70, 68.20, 67.76, 65.14, 61.75, 55.72, 55.16, 51.28, 37.90, 33.57, 29.63, 29.56, 28.59, 28.09, 26.72, 25.18, 24.26, 19.09; HRMS (M + Cs) calcd for $C_{104}H_{113}O_{23}NSiCs$ 1904.6527, found 1904.6654.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (39) and 5-Methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4-tri-*O*-benzyl-*β*-L-fucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranosyl]-*β*-D-glucopyranoside (40). These two trisaccharides were prepared from **1c** (55.8 mg, 0.1033 mmol), **2b** (50.0 mg, 0.06887 mmol), and **6c** (133.7 mg, 0.2066 mmol) as described in the preparation of **12**, yielding **39** (71.4 mg, 62%) as a syrup and **40** (22.2 mg, 19%) as a syrup. For compound **39**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 2H), 7.10−7.75 (m, 30H), 7.03 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 7.0 Hz, 2H), 6.94 (d, J = 7.0 Hz, 2H), 6.81−6.88 (m, 3H), 6.74 (d, J = 8.5 Hz, 2H), 5.57 (dd, J = 10.0, 8.5 Hz, 1H), 5.55 (d, J = 3.5 Hz, 1H), 5.15 (d, J = 3.5 Hz, 1H), 4.91 (d, J = 8.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.71 (d, J = 12.0 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 8.0 Hz, 1H), 4.59 (d, J = 11.5 Hz, 1H), 4.46 (d, J = 11.0 Hz, 1H), 4.36 (d, J = 10.5 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 4.14−4.23 (m, 5H), 4.11 (d, J = 12.0 Hz, 1H), 4.01−4.08 (m, 1H), 3.75−3.85 (m, 4H), 3.73 (s, 3H), 3.69−3.72 (m, 2H), 3.60 (dd, J = 11.0, 6.5 Hz, 1H), 3.57 (s, 3H), 3.52−3.56 (m, 1H), 3.37−3.45 (m, 2H), 3.00−3.04 (m, 1H), 2.70 (t, J = 7.0 Hz, 2H), 2.49−2.61 (m, 2H), 2.02 (s, 3H), 1.80−1.91 (m, 2H), 1.21−1.31 (m, 4H), 1.16 (d, J = 6.5 Hz, 3H), 1.05 (s, 9H), 0.99−1.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 173.7, 171.9, 164.4, 159.2, 138.9, 138.5, 138.2, 137.9, 135.6, 135.5, 133.6, 133.1, 133.0, 132.8, 129.8, 129.7, 129.7, 129.6, 129.3, 128.4, 128.1, 128.1, 127.9, 127.8, 127.5, 127.5, 127.4, 127.2, 127.2, 126.9, 123.0, 113.6, 101.5, 98.5, 97.9, 79.33, 79.13, 78.59, 77.41, 74.98, 74.68, 74.57, 74.47, 74.35, 73.85, 73.61, 72.67, 72.30, 71.81, 69.18, 68.74, 67.72, 67.19, 61.08, 55.68, 55.10, 51.26, 38.27, 33.57, 29.56, 28.62, 28.45, 26.65, 25.28, 24.32, 19.00, 16.48; HRMS (M + Cs) calcd for $C_{97}H_{107}O_{22}NSiCs$ 1798.6108, found 1798.6261. For compound **40**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.5, 1.0 Hz, 2H), 7.24−7.76 (m, 30H), 7.20 (t, J = 7.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 7.0 Hz, 2H), 6.81−6.89 (m, 3H), 6.75 (d, J = 8.5 Hz, 2H), 5.78 (dd, J = 10.5, 8.0 Hz, 1H), 5.24 (d, J = 3.5 Hz, 1H), 5.14 (dd, J = 10.5, 2.5 Hz, 1H), 4.94 (d, J = 8.5 Hz, 1H), 4.91 (d, J = 11.5 Hz, 1H), 4.83 (d, J = 11.5 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 4.75 (d, J = 13.0 Hz, 1H), 4.72 (d, J = 8.0 Hz, 1H), 4.69 (d, J = 11.5 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.44 (d, J = 10.5 Hz, 1H), 4.38 (d, J = 10.5 Hz, 1H), 4.33 (d, J = 12.5 Hz, 1H), 4.20−4.26 (m, 3H), 4.06 (dd, J = 11.0, 8.5 Hz, 1H), 4.00 (dd, J = 10.0, 3.5 Hz, 1H), 3.86−3.94 (m, 2H), 3.75 (s, 3H), 3.69−3.74 (m, 3H), 3.64 (q, J = 7.0 Hz, 1H), 3.58 (s, 3H), 3.50−3.57 (m, 2H), 3.43−3.64 (m, 2H), 3.02−3.07 (m, 1H), 2.14−2.33 (m, 4H), 1.83 (s, 3H), 1.78−1.90 (m, 2H), 1.18−1.30 (m, 4H), 1.06 (s, 9H), 1.01−1.04 (m, 2H), 0.81 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 173.8, 172.2, 164.9, 159.2, 139.0, 138.8, 138.6, 138.0, 135.6, 135.5, 133.6, 133.2, 133.2, 132.9, 130.0, 129.8, 129.8, 129.3, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.3, 127.2, 123.0, 113.7, 101.7, 98.0, 97.7, 79.55, 79.21, 78.81, 77.55, 76.34, 75.72, 74.75, 74.69, 74.56, 74.46, 74.13, 73.29, 72.99, 71.83, 69.81, 68.93, 67.64, 67.20, 63.32, 55.81, 55.22, 51.32, 37.61, 33.66, 29.68, 28.67, 27.86, 26.84, 25.28, 24.35, 19.20, 16.44; HRMS (M + Cs) calcd for $C_{97}H_{107}O_{22}NSiCs$ 1798.6108, found 1798.6256.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside (41). This trisaccharide was prepared from **1c** (72.2 mg, 0.1337 mmol), **2c** (50.0 mg, 0.06684 mmol), and **6a** (111.3 mg, 0.2005 mmol) as described in the preparation of **12**, yielding product (36.2 mg, 34%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.61 (m, 8H), 7.46 (d, J = 8.5 Hz, 2H), 7.01−7.39 (m, 26H), 6.82 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 9.0 Hz, 2H), 5.56 (d, J = 3.5 Hz, 1H), 5.53 (s, 1H), 5.47 (dd, J = 10.0, 7.5 Hz, 1H), 5.08 (d, J = 8.5 Hz, 1H), 4.84 (d, J = 8.0 Hz, 1H), 4.82 (d, J = 12.0 Hz, 2H), 4.76 (dd, J = 10.0, 8.5 Hz, 1H), 4.71 (d, J = 13.0 Hz, 1H), 4.55 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 11.5 Hz. 1H), 4.40 (d, J = 11.5 Hz, 1H), 4.38 (d, J = 12.5 Hz, 1H), 4.30 (dd, J = 10.5, 8.5 Hz, 1H), 4.30 (dd, J = 10.5, 5.5 Hz, 1H), 4.23 (d, J = 11.5 Hz, 1H), 4.17 (d, J = 1.5 Hz, 1H), 3.86−3.90 (m, 2H), 3.83 (dd, J = 10.0, 3.5 Hz, 1H), 3.73−3.80 (m, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.61 (dd, J = 10.5, 2.5 Hz, 1H), 3.58 (s, 3H), 3.56 (dd, J = 10.0, 5.0 Hz, 1H), 3.49−3.52 (m, 2H), 3.42 (q, J = 6.5 Hz, 1H), 3.30 (dt, J = 9.5, 6.5 Hz, 1H), 3.22 (d, J = 2.0 Hz, 1H), 1.83−1.96 (m, 2H), 1.22−1.37 (m, 4H), 1.04 (s, 9H), 0.95−1.02 (m, 2H), 0.77 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 164.5, 159.8, 159.1, 139.5, 139.0, 138.7, 135.6, 135.5, 133.5, 133.1, 132.4, 131.3, 130.2, 130.1, 129.8, 129.8, 129.7, 129.4, 129.3, 128.6, 128.2, 128.1, 128.0, 128.0, 127.8, 127.8, 127.6, 127.4, 127.3, 127.2, 127.0, 126.7, 113.5, 113.4, 100.5, 100.3, 98.8, 96.1, 80.98, 80.23, 78.52, 75.26, 74.94, 74.77, 74.35, 73.47, 72.71, 71.57, 71.31, 69.43, 68.49, 67.83, 66.66, 66.48, 64.06, 55.60, 55.16, 55.08, 51.32, 33.62, 29.66, 28.86, 27.07, 25.20, 24.28, 19.19, 16.65; HRMS (M + Cs) calcd for $C_{93}H_{101}O_{21}NSiCs$ 1728.5690, found 1728.5598.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-levulinyl-6-*O*-(2,3,4-tri-*O*-benzyl-L-fucopyranosyl)-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (42). This tetrasaccharide was prepared from **1c** (21.4 mg, 0.0396 mmol), **2g** (20.0 mg, 0.0198 mmol), and **6b** (38.4 mg, 0.0594 mmol) as described in the preparation of **12**, yielding product (29.3 mg, 76%) as a syrup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78−8.21 (m, 53H), 3.23−5.64 (m, 52H), 2.31−2.42 (m, 4H), 1.90−1.97 (m, 2H), 1.87 (s, 3H), 1.15−1.25 (m, 4H), 1.06 (d, J = 6.5 Hz, 3H), 0.93−1.01 (m, 2H); HRMS (M + Cs) calcd for $C_{115}H_{123}O_{27}NCs$ 2082.7337, found 2082.7462.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-6-*O*-[2-*O*-(2,3,4-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-D-galactopyranosyl]-*β*-D-glucopyranoside (43). This tetrasaccharide was prepared from **1a** (19.6 mg, 0.03035 mmol), **2f** (21.0 mg, 0.02023 mmol), and **6c** (39.3 mg, 0.06069 mmol) as described in the preparation of **12**, yielding product (22.9 mg, 58%) as a syrup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83−7.86 (m, 54H), 3.24−5.73 (m, 48H), 2.25−2.43 (m, 3H), 2.05 (s, 3H), 1.91−2.02 (m, 3H), 1.25−1.39 (m, 4H), 1.18 (d, J = 6.5 Hz, 3H), 1.06 (s, 9H), 0.96−1.01 (m, 2H); ESI-MS (pos) (M + H) calcd for $C_{116}H_{129}O_{25}NSiH$ 1965, found 1965.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-

benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (44) This tetrasaccharide was prepared from **1a** (13.9 mg, 0.02155 mmol), **2e** (15.0 mg, 0.01437 mmol), and **6b** (27.9 mg, 0.04311 mmol) as described in the preparation of **28**, yielding product (17.2 mg, 57%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.08−7.77 (m, 46H), 6.96−6.97 (m, 4H), 6.81−6.85 (m, 6H), 6.76 (d, J = 6.0 Hz, 2H), 6.64 (t, J = 7.5 Hz, 1H), 6.55 (t, J = 7.5 Hz, 2H), 5.98 (d, J = 3.5 Hz, 1H), 5.90 (dd, J = 10.0, 7.5 Hz, 1H), 5.28 (d, J = 3.5 Hz, 1H), 4.94 (d, J = 8.0 Hz, 1H), 4.88 (d, J = 12.5 Hz, 1H), 4.83 (d, J = 7.5 Hz, 1H), 4.81 (d, J = 11.5 Hz, 1H), 4.78 (d, J = 11.5 Hz, 1H), 4.64−4.71 (m, 2H), 4.59 (d, J = 11.0 Hz, 1H), 4.55 (d, J = 12.5 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 11.0 Hz, 2H), 4.43 (d, J = 12.0 Hz, 1H), 4.27−4.36 (m, 6H), 4.17 (d, J = 12.0 Hz, 1H), 3.98−4.09 (m, 5H), 3.93 (d, J = 12.0 Hz, 1H), 3.85−3.90 (m, 2H), 3.73−3.80 (m, 5H), 3.57−3.68 (m, 5H), 3.56 (s, 3H), 3.51 (q, J = 6.5 Hz, 1H), 3.36−3.42 (m, 3H), 3.19−3.27 (m, 4H), 1.84−1.96 (m, 2H), 1.25−1.35 (m, 4H), 1.10 (s, 9H), 0.95−1.03 (m, 2H), 0.90 (d, J = 6.5 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 164.43, 159.11, 139.45, 139.42, 139.17, 138.78, 138.66, 138.51, 138.17, 137.88, 135.69, 135.48, 133.53, 133.47, 133.00, 130.40, 129.82, 129.74, 129.33, 128.70, 128.53, 128.45, 128.38, 128.33, 128.24, 128.19, 128.15, 128.00, 127.87, 127.74, 127.69, 127.66, 127.51, 127.48, 127.22, 126.84, 126.58, 113.71, 100.44, 98.15, 94.78, 94.29, 78.72, 78.28, 77.22, 77.17, 76.51, 75.59, 74.97, 74.83, 74.69, 74.65, 74.50, 74.22, 73.44, 73.34, 73.03, 72.84, 72.07, 71.46, 69.75, 69.06, 68.97, 67.90, 66.64, 64.92, 63.76, 55.74, 55.24, 51.35, 33.69, 29.70, 28.83, 27.02, 25.27, 24.37, 22.69, 19.25, 16.84, 14.13; HRMS (M + Cs) calcd for $C_{126}H_{135}O_{25}NSiCs$ 2222.8147, found 2222.8294.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (45) and 5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (46). These two trisaccharides were prepared from **1e** (33.4 mg, 0.05165 mmol), **2b** (25.0 mg, 0.03444 mmol), and **6b** (66.8 mg, 0.1033 mmol) as described in the preparation of **29**, yielding **45** (30.4 mg, 50%) as a syrup and **46** (9.7 mg, 16%) as a syrup. For compound **45**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 6.75−7.74 (m, 46H), 5.68 (d, J = 2.9 Hz, 1H), 5.33 (dd, J = 10.0, 8.2 Hz, 1H), 5.29 (s, 1H), 4.94 (d, J = 8.4 Hz, 1H), 4.67−4.76 (m, 4H), 4.64 (d, J = 11.5 Hz, 1H), 4.58 (d, J = 12.1 Hz, 1H), 4.54 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 11.6 Hz, 1H), 4.47 (d, J = 11.8 Hz, 2H), 4.38 (d, J = 12.1 Hz, 1H), 4.28 (d, J = 11.6 Hz, 1H), 4.24 (d, J = 11.6 Hz, 1H), 4.19 (dd, J = 10.6, 8.5 Hz, 1H), 4.07 (d, J = 8.8 Hz, 1H), 4.05 (dd, J = 10.0, 6.5 Hz, 1H), 3.98 (t, J = 9.1 Hz, 1H), 3.76−3.81 (m, 1H), 3.75 (s, 3H), 3.63−3.73 (m, 5H), 3.57 (s, 3H), 3.51−3.56 (m, 4H), 3.46 (t, J = 9.1 Hz, 1H), 3.39 (dd, J = 10.3, 5.1 Hz, 1H), 3.33 (d, J = 9.6 Hz, 1H), 3.25 (dt, J = 9.5, 6.5 Hz, 1H), 2.45−2.59 (m, 3H), 2.32−2.40 (m, 1H), 2.01 (s, 3H), 1.88−1.97 (m, 2H), 1.26−1.37 (m, 4H), 1.04 (s, 9H), 0.83−0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.53, 173.85, 171.46, 164.80, 159.25, 138.99, 138.96, 138.70, 138.46, 138.23, 135.61, 135.49, 133.65, 133.14, 132.86, 132.84, 130.23, 129.79, 129.41, 129.20, 128.28, 128.10, 128.00, 127.77, 127.73, 127.66, 127.49, 127.16, 127.10, 126.92, 126.80, 113.78, 100.50, 98.12, 94.14, 79.31, 77.76, 77.06, 74.70, 74.66, 74.41, 74.06, 74.00, 73.42, 72.87, 72.73, 72.52, 71.96, 71.96, 71.74, 71.14, 69.27, 69.07, 67.45, 64.94, 60.51, 55.60, 55.22, 51.33, 37.76, 33.66, 29.67, 28.79, 27.79, 26.77, 25.24, 24.32, 19.05; HRMS (M + Cs) calcd for $C_{104}H_{113}O_{23}NSiCs$ 1904.6527, found 1904.6638. For compound **46**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64−7.97 (m, 48H), 3.20−5.72 (m, 41H), 2.28−2.49 (m, 4H), 1.88−1.96 (m, 2H), 1.80 (s, 3H), 1.25−1.36 (m, 4H), 1.09 (s, 9H), 0.83−0.89 (m, 2H); HRMS (M + Cs) calcd for $C_{104}H_{113}O_{23}NSiCs$ 1904.6527, found 1904.6638.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (47). This trisaccharide was prepared from **1c** (54.1 mg, 0.1003 mmol), **2c** (50.0 mg, 0.06684 mmol), and **6b** (129.7 mg, 0.2005 mmol) as described in the preparation of **12**, yielding product (80.0 mg, 71%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.5 Hz, 2H), 7.54−7.78 (m, 10H), 7.49 (t, J = 7.5 Hz, 2H), 7.12−7.74 (m, 20H), 7.04 (d, J = 8.5 Hz, 2H), 6.87−6.90 (m, 6H), 6.67−6.72 (m, 3H), 6.62 (t, J = 7.5 Hz, 2H), 5.79 (dd, J = 10.0, 7.5 Hz, 1H), 5.70 (d, J = 4.0 Hz, 1H), 4.96 (d, J = 8.0 Hz, 1H), 4.87 (d, J = 12.5 Hz, 1H), 4.81 (d, J = 11.5 Hz, 1H), 4.72 (d, J = 13.0 Hz, 1H), 4.61 (d, J = 8.0 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.55 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.39 (d, J = 11.5 Hz, 2H), 4.28 (d, J = 11.5 Hz, 2H), 4.02−4.09 (m, 4H), 3.85−3.89 (m, 2H), 3.78 (dd, J = 10.5, 4.0 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.67 (dt, J = 9.5, 6.5 Hz, 1H), 3.54−3.64 (m, 3H), 3.56 (s, 3H), 3.44−3,51 (m, 4H), 3.32−3.34 (m, 1H), 3.23−3.27 (m, 2H), 1.86−1.97 (m, 2H), 1.28−1.38 (m, 4H), 1.11 (s, 9H), 0.97−1.02 (m, 2H), 0.81 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 167.7, 167.5, 164.6, 159.2, 139.2, 139.1, 138.9, 138.6, 135.7, 135.4, 133.6, 133.5, 133.4, 133.1, 132.9, 130.4, 130.2, 129.9, 129.7, 129.7, 129.5, 129.4, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 126.9, 126.9, 126.8, 126.7, 123.1, 123.0, 113.8, 113.7, 100.2, 98.2, 95.8, 80.44, 78.70, 77.74, 76.05, 75.47, 75.33, 74.61, 74.48, 74.04, 73.47, 72.97, 72.73, 71.67, 71.58, 69.03, 67.46, 66.59, 63.49, 55.70, 55.23, 55.15, 51.29, 33.63, 29.66, 28.80, 27.00, 25.21, 24.38, 19.27, 16.66; HRMS (M + Cs) calcd for $C_{100}H_{109}O_{21}NSiCs$ 1820.6316, found 1820.6439.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (48), 5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranosyl]-*β*-D-glucopyranoside (49), and 5-Methoxycarbon*yl*pentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-(2,3,4-tri-*O*-benzyl-*β*-L-fucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (50). These three trisaccharides were prepared from **1c** (72.2 mg, 0.1337 mmol), **2c** (50.0 mg, 0.06684 mmol), and **6c** (129.7 mg, 0.2005 mmol) as described in the preparation of **12**, yielding **48** (73.3 mg, 65%) as a syrup, **49** (10.3 mg, 9%) as a syrup, and **50** (11.3 mg, 10%) as a syrup. For compound **48**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.5, 1.0 Hz, 2H), 7.15−7.78 (m, 27H), 7.06 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 7.0 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 6.87−6.91 (m, 2H), 6.85 (d, J = 7.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 5.81 (dd, J = 10.0, 8.0 Hz, 1H), 5.58 (d, J = 3.5 Hz, 1H), 5.06−5.11 (m, 1H), 4.99−5.03 (m, 1H), 4.96 (d, J = 8.5 Hz, 1H), 4.94 (d, J = 12.0 Hz, 1H), 4.88 (d, J = 11.5 Hz, 1H), 4.85 (d, J = 12.0 Hz, 1H), 4.84 (d, J = 12.5 Hz, 1H), 4.80 (dd, J = 10.0, 4.0 Hz, 1H), 4.64−4.76 (m, 3H), 4.57 (d, J = 11.5 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 7.5 Hz, 1H), 4.43−4.47 (m, 1H), 4.39 (d, J = 11.0 Hz, 1H), 4.29−4.34 (m, 1H), 4.23 (dd, J = 11.0, 8.5 Hz, 1H), 4.19 (d, J = 1.5 Hz, 1H), 4.05−4.08 (m, 1H), 3.95 (dd, J = 10.5, 7.5 Hz, 1H), 3.91 (dd, J = 10.0, 3.5 Hz, 1H), 3.77−3.88 (m, 4H), 3.74 (s, 3H), 3.71 (s, 3H), 3.54−3.66 (m, 4H), 3.45−3.51 (m, 2H), 3.33 (d, J = 1.0 Hz, 1H), 3.03−3.09 (m, 1H), 1.80−1.97 (m, 2H), 1.24−1.35 (m, 4H), 1.06 (s, 9H), 0.97−1.03 (m, 2H), 0.78 (d, J = 6.5 Hz, 3H); HRMS (M + Cs) calcd for $C_{100}H_{109}O_{21}NSiCs$ 1820.6316, found 1820.6419. For compound **49**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 4H), 7.58 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.24−7.43 (m, 23H), 7.19 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 6.81−6.87 (m, 3H), 6.69 (d, J = 8.5 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 5.52 (dd, J = 10.0, 8.0 Hz,

1H), 5.15 (d, J = 11.0 Hz, 1H), 4.99 (d, J = 11.5 Hz, 1H), 4.89 (s, 1H), 4.87 (d, J = 3.0 Hz, 1H), 4.78 (d, J = 10.5 Hz, 1H), 4.77 (d, J = 3.0 Hz, 1H), 4.75 (d, J = 8.5 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 7.0 Hz, 1H), 4.56 (d, J = 11.0 Hz, 1H), 4.48 (d, J = 11.0 Hz, 2H), 4.40 (d, J = 10.5 Hz, 1H), 4.31 (d, J = 12.5 Hz, 1H), 4.26 (t, J = 9.5 Hz, 1H), 4.14−4.20 (m, 2H), 4.07 (t, J = 6.5 Hz, 1H), 3.94−4.01 (m, 2H), 3.74−3.80 (m, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 3.54−3.57 (m, 3H), 3.49 (d, J = 3.0 Hz, 1H), 3.29−3.43 (m, 4H), 2.92−2.96 (m, 1H), 1.77−1.87 (m, 2H), 1.18−1.25 (m, 4H), 1.15 (d, J = 6.5 Hz, 3H), 1.03 (s, 9H), 0.97−1.00 (m, 2H); HRMS (M + Cs) calcd for $C_{100}H_{109}O_{21}NSiCs$ 1820.6316, found 1820.6418. For compound **50**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.5, 1.4 Hz, 2H), 7.16−7.76 (m, 32H), 7.06 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 6.79−6.94 (m, 5H), 6.75 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 5.80 (dd, J = 10.1, 8.0 Hz, 1H), 5.58 (d, J = 3.8 Hz, 1H), 5.00 (d, J = 11.6 Hz, 1H), 4.96 (d, J = 8.4 Hz, 1H), 4.94 (d, J = 11.8 Hz, 1H), 4.87 (dd, J = 11.5, 4.7 Hz, 1H), 4.83 (d, J = 12.1 Hz, 1H), 4.76 (d, J = 11.8 Hz, 1H), 4.64−4.70 (m, 4H), 4.57 (dd, J = 9.7, 3.1 Hz, 1H), 4.56 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 11.7 Hz, 1H), 4.48 (d, J = 11.5 Hz, 1H), 4.37−4.46 (m, 3H), 4.32 (d, J = 12.2 Hz, 1H), 4.27−4.31 (m, 1H), 4.22 (dd, J = 10.8, 8.5 Hz, 1H), 4.19 (d, J = 1.6 Hz, 1H), 4.04−4.09 (m, 2H), 3.89−3.95 (m, 1H), 3.58−3.80 (m, 12H), 3.44−3.50 (m, 2H), 3.33 (d, J = 2.2 Hz, 1H), 3.04−3.08 (m, 1H), 1.77−1.89 (m, 2H), 1.17−1.35 (m, 4H), 1.06 (s, 9H), 0.98−1.04 (m, 2H), 0.77 (d, J = 6.4 Hz, 3H); HRMS (M + Cs) calcd for $C_{100}H_{109}O_{21}NSiCs$ 1820.6316, found 1820.6418.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside (51). This trisaccharide was prepared from **1a** (79.7 mg, 0.1234 mmol), **2d** (50.0 mg, 0.08224 mmol), and **6a** (136.9 mg, 0.2467 mmol) as described in the preparation of **12**, yielding product (95.0 mg, 74%) as a syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21−7.42 (m, 31H), 6.83 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 8.5 Hz, 2H), 6.39 (d, J = 8.5 Hz, 2H), 5.50 (d, J = 3.5 Hz, 1H), 5.43 (s, 1H), 5.10 (dd, J = 10.0, 8.0 Hz, 1H), 5.06 (d, J = 8.5 Hz, 1H), 4.91 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 11.5 Hz, 1H), 4.65−4.72 (m, 6H), 4.60 (d, J = 11.5 Hz, 1H), 4.54 (d, J = 11.5 Hz, 1H), 4.49 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.33 (d, J = 12.0 Hz, 1H), 4.23−4.28 (m, 2H), 4.06 (t, J = 6.5 Hz, 1H), 3.99 (d, J = 12.0 Hz, 1H), 3.95 (dd, J = 10.0, 3.5 Hz, 1H), 3.84 (d, J = 2.5 Hz, 1H), 3.63−3.75 (m, 3H), 3.64 (s, 3H), 3.63 (s, 3H), 3.57 (s, 3H), 3.48−3.55 (m, 3H), 3.43 (dd, J = 9.0, 5.0 Hz, 1H), 3.38 (dd, J = 10.0, 3.0 Hz, 1H), 3.37 (s, 1H), 3.33 (dd, J = 10.5, 3.5 Hz, 1H), 3.26−3.31 (m, 1H), 2.57−2.70 (m, 4H), 2.08 (s, 3H), 1.81−1.94 (m, 2H), 1.21−1.38 (m, 4H), 0.95−1.03 (m, 2H); HRMS (M + Cs) calcd for $C_{89}H_{95}O_{24}NCs$ 1694.5298, found 1694.5398.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (52) and 5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl)-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (53). These two trisaccharides were prepared from **1a** (79.7 mg, 0.1234 mmol), **2d** (46.3 mg, 0.07615 mmol), and **6b** (159.6 mg, 0.2467 mmol) as described in the preparation of **12**, yielding **52** (80.3 mg, 64%) as a syrup and **53** (18.9 mg, 15%) as a syrup. For compound **52**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2H), 7.66−7.78 (m, 3H), 7.61 (t, J = 7.5 Hz, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.43 (d, J = 7.0 Hz, 2H), 7.40 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 7.0 Hz, 2H), 7.22−7.32 (m, 14H), 7.20 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 6.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.81−6.87 (m, 5H), 6.58 (d, J = 8.5 Hz, 2H), 5.57 (d, J = 3.5 Hz, 1H), 5.32 (dd, J = 9.5, 8.0 Hz, 1H), 4.97 (d, J = 8.5 Hz, 1H), 4.95 (d, J = 10.0 Hz, 1H), 4.93 (d, J = 3.5 Hz, 1H), 4.86 (d, J = 12.5 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.79 (d, J = 10.0 Hz, 1H), 4.77 (d, J = 12.0 Hz, 1H), 4.70 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 8.0 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.5 Hz, 1H), 4.50 (d, J = 13.0 Hz, 1H), 4.48 (d, J = 11.5 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 4.27 (d, J = 12.0 Hz, 1H), 4.20 (dd, J = 10.5, 8.5 Hz, 1H), 4.17 (d, J = 12.0 Hz, 1H), 4.04−4.12 (m, 4H), 4.01 (q, J = 6.5 Hz, 1H), 3.94 (dd, J = 10.0, 2.5 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.54−3.68 (m, 6H), 3.57 (s, 3H), 3.46−3.51 (m, 3H), 3.34 (d, J = 10.0 Hz, 1H), 3.26 (dt, J = 9.5, 6.5 Hz, 1H), 2.54−2.67 (m, 4H), 2.02 (s, 3H), 1.86−1.97 (m, 2H), 1.26−1.42 (m, 4H), 0.97−1.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 173.8, 171.9, 164.9, 159.2, 159.0, 138.9, 138.8, 138.7, 138.5, 138.0, 133.6, 133.1, 130.3, 129.8, 129.8, 129.6, 129.4, 129.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4, 127.4, 127.3, 127.0, 123.1, 113.8, 113.5, 100.5, 98.3, 98.1, 78.96, 77.83, 76.68, 76.55, 76.38, 74.94, 74.76, 74.62, 74.43, 73.56, 72.95, 72.93, 72.83, 71.89, 71.76, 70.62, 69.66, 69.14, 69.03, 67.34, 66.25, 65.85, 55.77, 55.20, 55.08, 51.29, 38.03, 33.61, 29.53, 28.79, 28.04, 25.19, 24.32; HRMS (M + Cs) calcd for $C_{96}H_{103}O_{24}NCs$ 1786.5924, found 1786.6022. For compound **53**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.17−7.59 (m, 27H), 7.09 (d, J = 9.0 Hz, 2H), 7.02 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.77−6.82 (m, 5H), 6.64 (d, J = 8.5 Hz, 2H), 5.46 (d, J = 3.5 Hz, 1H), 5.27 (dd, J = 9.5, 8.0 Hz, 1H), 5.00 (d, J = 8.0 Hz, 1H), 4.97 (d, J = 10.5 Hz, 1H), 4.90 (d, J = 12.0 Hz, 1H), 4.87 (d, J = 13.0 Hz, 1H), 4.85 (d, J = 10.0 Hz, 2H), 4.84 (d, J = 8.0 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.39 (d, J = 8.0 Hz, 1H), 4.37 (d, J = 11.5 Hz, 1H), 4.28 (d, J = 11.5 Hz, 1H), 4.21 (d, J = 11.5 Hz, 1H), 3.95−4.18 (m, 7H), 3.86 (dd, J = 10.0, 2.5 Hz, 1H), 3.74−3.83 (m, 3H), 3.73 (s, 6H), 3.58−3.71 (m, 5H), 3.56 (s, 3H), 3.39−3.44 (m, 3H), 3.23−3.29 (m, 1H), 2.54−2.69 (m, 4H), 2.01 (s, 3H), 1.87−1.94 (m, 2H), 1.26−1.40 (m, 4H), 0.97−1.02 (m, 2H); HRMS (M + Cs) calcd for $C_{96}H_{103}O_{24}NCs$ 1786.5924, found 1786.6030.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (54) and 5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-benzoyl-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (55). These two trisaccharides were prepared from **1a** (79.7 mg, 0.1234 mmol), **2d** (46.3 mg, 0.07615 mmol), and **6c** (159.6 mg, 0.2467 mmol) as described in the preparation of **12**, yielding **54** (86.0 mg, 68%) and **55** (22.1 mg, 18%) as syrups. For compound **54**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.0 Hz, 2H), 7.59−7.75 (m, 4H), 7.50 (t, J = 7.5 Hz, 1H), 7.44 (d, J = 7.0 Hz, 2H), 7.39 (d, J = 7.0 Hz, 2H), 7.22−7.36 (m, 18H), 7.06 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.82−6.88 (m, 3H), 6.79 (d, J = 8.5 Hz, 2H), 6.56 (d, J = 8.5 Hz, 2H), 5.60 (d, J = 3.0 Hz, 1H), 5.40 (dd, J = 10.0, 8.0 Hz, 1H), 5.00 (d, J = 3.5 Hz, 1H), 4.94 (d, J = 8.5 Hz, 1H), 4.93 (d, J = 11.5 Hz, 1H), 4.84 (d, J = 11.5 Hz, 1H), 4.76 (d, J = 12.0 Hz, 1H), 4.72 (d, J = 11.5 Hz, 1H), 4.71 (d, J = 11.5 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 8.0 Hz, 1H), 4.54 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 11.5 Hz, 1H), 4.45 (d, J = 10.5 Hz, 1H), 4.41 (d, J = 10.5 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.31 (d, J = 12.0 Hz, 1H), 4.21 (d, J = 12.0 Hz, 1H), 4.20 (d, J = 11.0 Hz, 1H), 4.18 (d, J = 11.0 Hz, 1H), 4.01−4.08 (m, 3H), 3.97 (d, J = 1.5 Hz, 1H), 3.93 (dd, J = 10.0, 3.0 Hz, 1H), 3.85 (t, J = 6.0 Hz, 1H), 3.74−3.81 (m, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 3.54−3.65 (m, 8H), 3.40−3.45 (m, 2H), 3.02−3.06 (m, 1H), 2.64−2.78 (m, 4H), 2.13 (s, 3H), 1.79−1.90 (m, 2H), 1.19−1.32 (m, 4H), 1.04−1.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 173.8, 172.0, 165.0, 159.2, 159.0, 138.8, 138.6, 138.0, 133.6, 132.8, 129.9, 129.9, 129.7, 129.4, 129.3, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.7, 127.7, 127.5, 127.5, 127.4, 127.3, 127.2, 113.7, 113.5, 101.2, 98.4, 97.8, 79.42, 79.09, 78.82, 76.52, 76.11, 75.09, 74.70, 74.59, 74.49, 74.37, 73.40, 73.04, 72.96, 72.05, 71.06, 70.46, 69.73, 69.24, 68.72, 67.90, 66.78, 66.55, 55.71, 55.17, 55.04, 51.28, 38.12, 33.58, 29.68, 28.61, 28.23, 25.21, 24.27; HRMS (M + Cs) calcd

for $C_{96}H_{103}O_{24}NCs$ 1786.5924, found 1786.6008. For compound **55**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.5 Hz, 2H), 7.59−7.76 (m, 4H), 7.48 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 7.0 Hz, 2H), 7.22−7.36 (m, 20H), 6.98 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 7.0 Hz, 2H), 6.81−6.88 (m, 3H), 6.77 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 8.5 Hz, 2H), 5.51 (d, J = 3.0 Hz, 1H), 5.38 (dd, J = 9.5, 8.5 Hz, 1H), 4.96 (d, J = 11.5 Hz, 1H), 4.92 (d, J = 11.5 Hz, 1H), 4.88 (d, J = 8.0 Hz, 1H), 4.78 (d, J = 11.0 Hz, 1H), 4.65 (d, J = 11.5 Hz, 2H), 4.60 (d, J = 12.5 Hz, 2H), 4.47 (d, J = 12.5 Hz, 1H), 4.46 (d, J = 7.5 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.29 (d, J = 10.5 Hz, 1H), 4.25 (d, J = 11.0 Hz, 1H), 4.21 (d, J = 12.0 Hz, 1H), 4.14 (d, J = 10.5 Hz, 1H), 4.13 (d, J = 8.5 Hz, 1H), 4.06 (t, J = 6.5 Hz, 1H), 4.01 (d, J = 11.0 Hz, 1H), 3.99 (d, J = 11.0 Hz, 1H), 3.92−3.96 (m, 1H), 3.90 (d, J = 2.5 Hz, 1H), 3.75−3.85 (m, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.55−3.62 (m, 9H), 3.41−3.47 (m, 3H), 3.30 (t, J = 8.5 Hz, 1H), 2.98−3.03 (m, 1H), 2.66−2.75 (m, 4H), 2.15 (s, 3H), 1.79−1.91 (m, 2H), 1.22−1.31 (m, 4H), 1.04−1.17 (m, 2H); HRMS (M + Cs) calcd for $C_{96}H_{103}O_{24}NCs$ 1786.5924, found 1786.6012.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-(2,3,4-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-galactopyranosyl]-*β*-D-glucopyranoside (56), 5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-(2,3,4-*O*-benzyl-α-L-fucopyranosyl)-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (57), and 5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-[2-*O*-(2,3,4-*O*-benzyl-*β*-L-fucopyranosyl)-3-*O*-*p*-methoxybenzyl-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (**58**)**.** These three trisaccharides were prepared from **1c** (54.6 mg, 0.1011 mmol), **2a** (50.0 mg, 0.06738 mmol), and **6c** (130.8 mg, 0.2021 mmol) as described in the preparation of **12**, yielding **56** (37.5 mg, 33%), **57** (36.1 mg, 32%), and **58** (11.1 mg, 10%) as syrups. For compound **56**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80−7.68 (m, 38H), 6.70 (d, J = 7.0 Hz, 2H), 6.65 (d, J = 8.5 Hz, 2H), 5.55 (d, J = 2.5 Hz, 1H), 5.32 (d, J = 3.5 Hz, 1H), 5.22 (d, J = 4.0 Hz, 1H), 5.10 (d, J = 11.5 Hz, 1H), 5.03 (d, J = 11.5 Hz, 1H), 4.98 (d, J = 8.5 Hz, 1H), 4.83 (d, J = 12.5 Hz, 2H), 4.80 (d, J = 12.0 Hz, 1H), 4.67−4.73 (m, 4H), 4.49 (d, J = 12.5 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.42 (d, J = 2.5 Hz, 1H), 4.32 (d, J = 12.5 Hz, 1H), 4.25−4.29 (m, 2H), 4.12 (dd, J = 10.0, 3.5 Hz, 1H), 4.01−4.06 (m, 2H), 3.95 (dd, J = 10.5, 3.5 Hz, 1H), 3.84−3.91 (m, 3H), 3.65−3.79 (m, 4H), 3.64 (s, 3H), 3.62 (s, 3H), 3.56 (s, 3H), 3.47−3.54 (m, 2H), 3.25 (dt, J = 9.5, 7.0 Hz, 1H), 2.54−2.68 (m, 4H), 2.11 (s, 3H), 1.82−1.94 (m, 2H), 1.24−1.34 (m, 4H), 1.21 (d, J = 6.5 Hz, 3H), 1.05 (s, 9H), 0.93−1.01 (m, 2H); HRMS (M + Cs) calcd for $C_{98}H_{111}O_{22}NSiCs$ 1814.6421, found 1814.6524. For compound **57**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16−7.77 (m, 30H), 7.10 (d, J = 8.5 Hz, 4H), 6.93 (d, J = 7.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 6.78 (d, J = 7.0 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 5.69 (d, J = 3.5 Hz, 1H), 5.60 (d, J = 3.0 Hz, 1H), 5.07 (d, J = 8.5 Hz, 1H), 5.05 (d, J = 12.0 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.83 (d, J = 11.0 Hz, 1H), 4.80 (d, J = 10.5 Hz, 1H), 4.78 (d, J = 11.0 Hz, 1H), 4.72 (d, J = 8.5 Hz, 1H), 4.71 (d, J = 12.5 Hz, 1H), 4.65 (d, J = 8.5 Hz, 1H), 4.64 (s, 2H), 4.53 (q, J = 6.5 Hz, 1H), 4.38 (d, J = 12.0 Hz, 1H), 4.35 (dd, J = 10.0, 8.0 Hz, 1H), 4.30 (d, J = 10.5 Hz, 1H), 4.20 (d, J = 8.0 Hz, 1H), 4.14 (s, 1H), 3.95−4.13 (m, 5H), 3.76 (s, 3H), 3.72−3.75 (m, 2H), 3.71 (s, 3H), 3.59−3.69 (m, 5H), 3.57 (s, 3H), 3.52 (t, J = 7.0 Hz, 1H), 3.29 (dt, J = 9.5, 6.5 Hz, 1H), 2.52−2.58 (m, 4H), 2.08 (s, 3H), 1.82−1.93 (m, 2H), 1.25 (d, J = 6.5 Hz, 3H), 1.17−1.24 (m, 4H), 1.06 (s, 9H), 0.95−0.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 173.7, 171.8, 159.4, 159.0, 139.3, 139.2, 138.9, 137.8, 135.6, 135.5, 133.7, 133.3, 133.0, 130.1, 129.8, 129.7, 129.6, 128.9, 128.2, 128.1, 128.0, 127.7, 127.6, 127.3, 127.2, 127.1, 127.0, 123.2, 114.1, 113.6, 102.3, 98.0, 96.9, 81.43, 80.14, 80.05, 79.44, 78.18, 75.67, 75.24, 75.08, 74.84, 74.71, 73.67, 72.64, 72.37, 71.36, 70.91, 69.04, 66.71, 66.53, 66.38, 61.75, 56.11, 55.21, 55.21, 51.27, 38.20, 33.63, 29.66, 28.87, 28.21, 26.75, 25.27, 24.38, 19.10, 16.53; HRMS (M + Cs) calcd for $C_{98}H_{111}O_{22}NSiCs$ 1814.6421, found 1814.6525. For compound **58**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17−7.77 (m, 30H), 7.08 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 7.0 Hz, 2H), 6.83−6.90 (m, 4H), 6.75 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 5.62 (d, J = 3.0 Hz, 1H), 5.00 (d, J = 8.5 Hz, 1H), 4.98 (d, J = 12.5 Hz, 1H), 4.93 (d, J = 7.5 Hz, 1H), 4.92 (d, J = 11.0 Hz, 1H), 4.65−4.78 (m, 6H), 4.62 (d, J = 11.0 Hz, 2H), 4.54 (d, J = 11.0 Hz, 1H), 4.46 (d, J = 10.5 Hz, 1H), 4.40 (d, J = 8.0 Hz, 1H), 4.38 (d, J = 12.5 Hz, 1H), 4.26 (dd, J = 11.0, 8.5 Hz, 1H), 3.98−4.10 (m, 4H), 3.71 (s, 3H), 3.69 (s, 3H), 3.59−3.81 (m, 6H), 3.57 (s, 3H), 3.44−3.53 (m, 3H), 3.28 (q, J = 6.0 Hz, 1H), 3.21 (dt, J = 9.5, 6.5 Hz, 1H), 2.51−2.57 (m, 4H), 2.04 (s, 3H), 1.80−1.88 (m, 2H), 1.17−1.25 (m, 4H), 1.12 (d, J = 6.5 Hz, 3H), 1.05 (s, 9H), 0.93−1.01 (m, 2H); HRMS (M + Cs) calcd for $C_{98}H_{111}O_{22}NSiCs$ 1814.6421, found 1814.6314.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-[2-*O*-benzoyl-3-*O*-(2-deoxy-2-azido-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (59). This trisaccharide was prepared from **1d** (24.0 mg, 0.04132 mmol), **2b** (20.0 mg, 0.02755 mmol), and **6b** (53.5 mg, 0.08264 mmol) as described in the preparation of **29**, yielding product (22.1 mg, 47%) as a syrup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.1, 1.2 Hz, 2H), 7.56−7.74 (m, 8H), 7.51 (t, J = 7.4 Hz, 1H), 7.22−7.42 (m, 21H), 7.20 (d, J = 8.6 Hz, 2H), 7.10−7.13 (m, 2H), 6.91−6.94 (m, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.75−6.79 (m, 3H), 5.72 (d, J = 3.1 Hz, 1H), 5.46 (dd, J = 10.1, 8.0 Hz, 1H), 5.23 (d, J = 3.4 Hz, 1H), 4.95 (d, J = 8.5 Hz, 1H), 4.75 (d, J = 7.9 Hz, 1H), 4.74 (d, J = 13.0 Hz, 1H), 4.70 (d, J = 11.4 Hz, 1H), 4.50 (d, J = 11.7 Hz, 2H), 4.48 (d, J = 11.2 Hz, 1H), 4.38 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 11.0 Hz, 1H), 4.33 (d, J = 11.8 Hz, 1H), 4.29 (d, J = 11.6 Hz, 1H), 4.25 (d, J = 11.6 Hz, 1H), 4.21 (dd, J = 10.7, 8.5 Hz, 1H), 4.06 (dd, J = 10.7, 8.5 Hz, 1H), 3.95−4.02 (m, 2H), 3.84 (t, J = 6.5 Hz, 1H), 3.77 (dd, J = 10.6, 3.3 Hz, 1H), 3.75 (s, 3H), 3.63−3.71 (m, 3H), 3.57 (s, 3H), 3.49−3.55 (m, 4H), 3.47 (dt, J = 9.5, 6.5 Hz, 1H), 3.22−3.38 (m, 4H), 2.70−2.81 (m, 1H), 2.57−2.69 (m, 3H), 2.09 (s, 3H), 1.86−1.97 (m, 2H), 1.28−1.37 (m, 4H), 1.02 (s, 9H), 0.83−0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.05, 173.87, 171.57, 164.54, 159.23, 138.41, 138.04, 137.91, 137.50, 135.65, 135.50, 133.68, 133.39, 133.03, 132.76, 130.23, 129.81, 129.74, 129.42, 129.28, 128.61, 128.44, 128.20, 128.06, 127.87, 127.83, 127.73, 127.65, 126.94, 113.72, 100.50, 98.14, 94.08, 78.02, 77.55, 77.19, 74.70, 74.57, 74.53, 73.48, 73.17, 73.14, 72.88, 72.59, 72.50, 71.57, 69.92, 69.07, 68.95, 67.47, 64.58, 60.65, 59.38, 55.63, 55.22, 51.35, 37.95, 33.67, 29.68, 28.81, 27.84, 26.74, 25.25, 24.34, 19.03; HRMS (M + Cs) calcd for $C_{97}H_{106}O_{22}N_4SiCs$ 1839.6122, found 1839.6251.

5-Methoxycarbonylpentyl 2-Deoxy-2-phthalimido-3-*O*-(2-*O*-benzoyl-3-*O*-α-D-glucopyranosyl-*β*-D-galactopyranosyl)-*β*-D-glucopyranoside (61). A mixture of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-[2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-4-*O*-levulinyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-galactopyranosyl]-4,6-*O*-*p*-methoxybenzylidne-*β*-D-glucopyranoside (73.1 mg, 0.0435 mmol), HF−pyridine complex (0.6 mL), acetic acid (1.2 mL), and dry THF (6 mL) was stirred overnight under argon. The reaction mixture was diluted with EtOAc, washed with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. The dried organic layer was concentrated under reduced pressure, and the residue was purified by chromatography on a silica gel column (EtOAc) to yield a syrup.

To a stirred solution of above syrup in THF−MeOH (10:1 v/v, 5.5 mL), 1 M hydrazine−acetic acid (1:2.5 v/v) in THF−MeOH (5:1 v/v) (1 mL) was added. The reaction mixture was stirred overnight. The solvent was then removed, and the residue was diluted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ and brine and dried over Na_2SO_4. The dried organic layer was concentrated under reduced pressure, and the residue was purified by chromatography on a silica gel column (EtOAc) to give **60** (47.0 mg, 88%) as a thick oil.

A mixture of **60** (18.0 mg, 0.01469 mmol), 10% Pd−C (7.0 mg) in HOAc (2.0 mL), THF (1.0 mL), and H_2O (0.5 mL) was stirred overnight under H_2 atmosphere. The catalyst was then

removed by filtration, and the filtrate was concentrated. The residue was subjected to a C-18 reversed-phase column chromatography (H_2O, H_2O−MeOH) to give **61** (10.7 mg, 84%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 7.18−7.56 (m, 9H), 5.29 (dd, J = 9.7, 8.0 Hz, 1H), 4.96 (d, J = 8.6 Hz, 1H), 4.87 (d, J = 3.8 Hz, 1H), 4.70 (d, J = 8.0 Hz, 1H), 4.50 (dd, J = 10.8, 8.0 Hz, 1H), 4.04 (d, J = 3.2 Hz, 1H), 4.01 (dd, J = 10.8, 8.5 Hz, 1H), 3.89−3.95 (m, 2H), 3.88 (dd, J = 11.0, 8.0 Hz, 1H), 3.69−3.78 (m, 4H), 3.60 (dd, J = 9.8, 8.0 Hz, 1H), 3.56 (s, 3H), 3.41−3.46 (m, 1H), 3.26−3.38 (m, 3H), 3.16 (t, J = 9.0 Hz, 1H), 3.02 (dd, J = 11.8, 3.3 Hz, 1H), 2.97 (dt, J = 9.9, 3.0 Hz, 1H), 2.79 (dd, J = 11.8, 2.0 Hz, 1H), 1.72−1.89 (m, 2H), 1.10−1.33 (m, 4H), 0.80−0.96 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.49, 166.51, 163.20, 157.86, 135.57, 134.26, 132.18, 130.67, 130.48, 129.61, 124.35, 123.89, 102.45, 99.42, 98.15, 83.00, 79.26, 77.77, 76.59, 74.59, 73.68, 73.06, 72.53, 71.52, 70.13, 70.09, 66.70, 62.66, 62.32, 60.96, 56.46, 51.90, 34.42, 29.88, 26.40, 25.29; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{20}NCs$ 998.2059, found 998.2020.

5-Methoxycarbonylpentyl 2-Deoxy-2-acetylamino-3-*O*-(3-*O*-α-D-glucopyranosyl-β-D-galactopyranosyl)-β-D-glucopyranoside (62). A mixture of **60** (28.0 mg, 0.0228 mmol) and hydrazine acetate (21.0 mg, 0.228 mmol) in dry MeOH (4 mL) was boiled under reflux for 36 h. The solvent was then evaporated. A solution of the residue in pyridine (1 mL) and acetic anhydride (1 mL) was kept for 16 h at room temperature, methanol (1 mL) was added at 0 °C, the solvent was evaporated, and toluene (2 × 10 mL) was evaporated from the residue. A solution of the residue in CH_2Cl_2 (20 mL) was washed with saturated $NaHCO_3$ and cold water and then concentrated. Column chromatography (silica gel, hexanes/EtOAc 1:1) of the residue gave a syrup.

The above syrup was treated with NaOMe/MeOH (25 wt %, 0.1 mL) in MeOH (4 mL) at room temperature. After 24 h, the mixture was neutralized (IRC-50 resin, weak acid) and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/MeOH 4:1) to give a thick oil.

A mixture of above thick oil and 10% Pd−C (5.0 mg) in HOAc (2.0 mL), THF (1.0 mL), and H_2O (0.5 mL) was stirred overnight under H_2 atmosphere. The catalyst was then removed by filtration through Celite, and the filtrate was concentrated. The residue was subjected to a C-18 reversed-phase column chromatography (H_2O, H_2O−MeOH) to give **62** (5.4 mg, 35%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 4.96 (d, J = 3.7 Hz, 1H), 4.41 (d, J = 8.2 Hz, 1H), 4.34 (d, J = 7.7 Hz, 1H), 4.02 (d, J = 3.0 Hz, 1H), 3.32−3.85 (m, 22H), 2.26 (t, J = 7.4 Hz, 2H), 1.87 (s, 3H), 1.37−1.51 (m, 4H), 1.16−1.25 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.90, 174.18, 105.62, 102.41, 97.67, 85.01, 79.91, 77.55, 76.69, 75.04, 73.55, 73.41, 71.50, 70.66, 70.52, 70.33, 66.74, 62.69, 62.46, 62.42, 56.21, 51.99, 34.77, 30.25, 26.65, 25.72, 23.19; HRMS (M + Na) calcd for $C_{27}H_{47}O_{18}NNa$ 696.2691, found 696.2660; ESI-MS (pos) (M + Na) calcd 696, found 696; ESI-MS (neg) (M − H) calcd 672, found 672.

Saccharide 63. This compound was prepared from hydrogenolysis of **6d** (46.0 mg, 0.05665 mmol) as described in the preparation of **61**, yielding **63** (25.6 mg, 99%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 5.06 (d, J = 3.8 Hz, 1H), 4.28 (d, J = 7.8 Hz, 1H), 4.14 (q, J = 6.5 Hz, 1H), 3.44−3.75 (m, 13H), 3.39 (dd, J = 9.2, 8.0 Hz, 1H), 2.21 (t, J = 7.4 Hz, 2H), 1.40−1.47 (m, 4H), 1.13−1.21 (m, 2H), 1.02 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ 179.95, 103.90, 101.76, 78.94, 77.40, 76.25, 74.31, 72.67, 71.96, 71.39, 70.72, 69.19, 63.33, 54.50, 36.03, 31.03, 27.27, 26.52, 17.85; HRMS (M + Na) calcd for $C_{19}H_{34}O_{12}Na$ 477.1948, found 477.1939.

Saccharide 64. This compound was prepared from the corresponding fully protected saccharide **53** (36.0 mg, 0.02178 mmol) as described in the preparation of **62**, yielding **64** (6.1 mg, 37%) as a solid after lyophilization. For the β-isomer: ^{1}H NMR (400 MHz, D_2O) δ 7.68−7.80 (m, 4H), 5.10 (d, J = 8.5 Hz, 1H), 4.31 (d, J = 7.7 Hz, 1H), 4.30 (dd, J = 9.7, 8.0 Hz, 1H), 4.29 (d, J = 8.0 Hz, 1H), 3.32−3.87 (m, 21H), 3.24 (dd, J = 10.0, 8.0 Hz, 1H), 1.51−1.72 (m, 2H), 1.14−1.25 (m, 2H), 0.91−1.07 (m, 2H), 0.69−0.80 (m, 2H); HRMS (M + Cs) calcd for $C_{33}H_{47}O_{19}NCs$ 894.1797, found 894.1830.

Saccharide 65. This compound was prepared from the corresponding fully protected saccharide **52** (45.0 mg, 0.02722 mmol) as described in the preparation of **62**, yielding **65** (7.5 mg, 36%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 7.69−7.80 (m, 4H), 5.12 (d, J = 8.6 Hz, 1H), 4.69 (d, J = 2.6 Hz, 1H), 4.32 (d, J = 7.8 Hz, 1H), 4.29 (dd, J = 10.9, 8.0 Hz, 1H), 3.32−3.84 (m, 20H), 3.16 (dd, J = 11.6, 4.5 Hz, 1H), 3.12 (m, 1H), 1.66−1.74 (m, 1H), 1.53−1.61 (m, 1H), 1.16−1.26 (m, 2H), 0.92−1.13 (m, 2H), 0.72−0.83 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 179.39, 172.24, 172.04, 137.97, 132.95, 132.85, 126.73, 126.09, 105.73, 101.13, 100.22, 83.20, 77.14, 76.27, 74.75, 73.29, 73.08, 72.57, 72.01, 71.45, 71.45, 71.11, 70.82, 70.05, 63.29, 62.61, 58.32, 54.41, 35.71, 30.49, 27.20, 26.01; ESI-MS (pos) (M + Na) calcd for $C_{33}H_{47}O_{19}NNa$ 784, found 784; ESI-MS (neg) (M − H) calcd 760, found 760.

Saccharide 66. This compound was prepared from the corresponding fully protected saccharide **31** (22.5 mg, 0.01340 mmol) as described in the preparation of **62**, yielding **66** (2.4 mg, 27%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 5.01 (d, J = 2.4 Hz, 1H), 4.44 (d, J = 8.4 Hz, 1H), 4.33 (d, J = 7.4 Hz, 1H), 4.29 (t, J = 5.8 Hz, 1H), 3.29−4.01 (m, 22H), 2.32 (t, J = 7.4 Hz, 2H), 1.96 (s, 3H), 1.31−1.65 (m, 4H), 0.81−0.95 (m, 2H); ESI-MS (pos) (M + Na) calcd for $C_{27}H_{47}O_{18}NNa$ 696, found 696; ESI-MS (neg) (M − H) calcd 672, found 672.

Saccharide 67. This compound was prepared from the corresponding fully protected saccharide **51** (67.7 mg, 0.04337 mmol) as described in the preparation of **62**, yielding **67** (18.8 mg, 50%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 7.14−7.43 (m, 7H), 7.04 (t, J = 7.8 Hz, 2H), 4.90 (dd, J = 10.0, 8.0 Hz, 1H), 4.88 (d, J = 8.6 Hz, 1H), 4.82 (d, J = 4.0 Hz, 1H), 4.66 (d, J = 8.1 Hz, 1H), 4.40 (dd, J = 10.9, 8.0 Hz, 1H), 3.44−3.94 (m, 17H), 3.39 (s, 3H), 3.20−3.25 (m, 1H), 1.52−1.60 (m, 1H), 1.36−1.44 (m, 1H), 0.40−1.10 (m, 6H); ^{13}C NMR (100 MHz, D_2O) δ 179.27, 172.51, 171.88, 169.45, 137.94, 137.92, 136.57, 131.97, 131.63, 131.33, 130.14, 126.18, 125.77, 103.57, 101.10, 100.31, 84.15, 77.69, 76.22, 75.36, 73.60, 73.29, 72.42, 72.34, 71.67, 71.67, 70.89, 70.80, 69.29, 63.61, 63.12, 57.39, 54.37, 35.59, 30.43, 27.04, 25.80; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{20}NCs$ 998.2059, found 998.2022.

Saccharide 68. This compound was prepared from the corresponding fully protected saccharide **57** (35.0 mg, 0.02082 mmol) as described in the preparation of **62**, yielding **68** (12.8 mg, 73%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 7.66−7.74 (m, 4H), 5.12 (d, J = 3.8 Hz, 1H), 5.09 (d, J = 3.5 Hz, 1H), 5.02 (d, J = 8.6 Hz, 1H), 4.50 (d, J = 7.8 Hz, 1H), 4.20 (q, J = 6.5 Hz, 1H), 4.15 (dd, J = 10.7, 8.8 Hz, 1H), 4.02 (dd, J = 10.8, 1.5 Hz, 1H), 3.90 (dd, J = 9.7, 3.5 Hz, 1H), 3.82 (dd, J = 12.5, 5.5 Hz, 1H), 3.73 (dd, J = 10.7, 8.5 Hz, 1H), 3.54−3.71 (m, 6H), 3.51 (dd, J = 9.6, 7.8 Hz, 1H), 3.42−3.47 (m, 2H), 3.41 (s, 3H), 3.30−3.37 (m, 2H), 2.75 (t, J = 6.0 Hz, 2H), 2.52 (t, J = 6.5 Hz, 2H), 2.06 (s, 3H), 1.66−1.74 (m, 1H), 1.52−1.61 (m, 1H), 1.13−1.24 (m, 2H), 1.10 (d, J = 6.5 Hz, 3H), 1.00−1.07 (m, 1H), 0.87−0.98 (m, 1H), 0.66−0.83 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 215.98, 179.32, 177.03, 172.49, 172.30, 137.76, 133.05, 126.41, 126.06, 104.46, 101.69, 100.46, 78.63, 77.93, 76.20, 74.67, 74.31, 73.95, 72.99, 72.94, 72.38, 71.95, 70.67, 70.51, 69.38, 62.70, 59.26, 54.42, 40.12, 35.71, 31.58, 30.56, 30.32, 27.23, 26.03, 18.03; HRMS (M + Cs) calcd for $C_{38}H_{53}O_{20}NCs$ 976.2215, found 976.2247.

Saccharide 69. This compound was prepared from the corresponding fully protected saccharide **56** (36.0 mg, 0.02142 mmol) as described in the preparation of **62**, yielding **69** (12.6 mg, 70%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 7.67−7.75 (m, 4H), 5.21 (d, J = 3.4 Hz, 1H), 5.04 (d, J = 8.6 Hz, 1H), 4.99 (d, J = 3.6 Hz, 1H), 4.89 (d, J = 4.0 Hz, 1H), 4.14 (dd, J = 10.7, 8.9 Hz, 1H), 4.07 (dd, J = 10.2, 3.4 Hz, 1H), 4.02 (q, J = 6.5 Hz, 1H), 3.97 (t, J = 6.3 Hz, 1H), 3.87 (dd, J = 11.1, 4.9 Hz, 1H), 3.78 (dd, J = 10.8, 8.7 Hz, 1H), 3.75 (dd, J = 11.2, 3.3 Hz, 1H), 3.33−3.71 (m, 13H), 2.75 (t, J = 6.2 Hz, 2H), 2.50−2.54 (m, 2H), 2.05 (s, 3H), 1.66−1.75 (m, 1H), 1.53−1.61 (m, 1H), 1.12−1.24 (m, 2H), 1.08 (d, J = 6.5 Hz, 3H), 1.02−1.07 (m, 1H), 0.87−0.98 (m, 1H), 0.65−0.83 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 215.98, 179.33, 176.95, 172.52, 172.30, 137.74, 133.06, 126.39,126.04, 103.96, 100.46,

100.35, 80.05, 77.10, 74.32, 74.20, 73.22, 72.79, 72.36, 72.11, 71.82, 70.71, 69.71, 69.38, 68.36, 62.78, 59.26, 54.42, 40.10, 35.71, 31.54, 30.56, 30.32, 27.22, 26.04, 18.17; HRMS (M + Cs) calcd for $C_{38}H_{53}O_{20}NCs$ 976.2215, found 976.2249.

Saccharide 70. This compound was prepared from hydrogenolysis of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (53.0 mg, 0.04986 mmol) isolated as a side product like the formation of **13** in the assembly of oligosaccharides, yielding **70** (23.3 mg, 80%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 7.81−7.88 (m, 4H), 5.14 (d, J = 8.6 Hz, 1H), 5.00 (d, J = 3.7 Hz, 1H), 4.36 (dd, J = 10.7, 8.6 Hz, 1H), 4.28 (q, J = 6.5 Hz, 1H), 4.02 (dd, J = 10.7, 8.6 Hz, 1H), 3.62−3.97 (m, 7H), 3.59 (s, 3H), 3.55 (dt, J = 9.7, 3.1 Hz, 1H), 3.39−3.46 (m, 1H), 1.86−2.00 (m, 2H), 1.25−1.46 (m, 4H), 1.14 (d, J = 6.6 Hz, 3H), 1.01−1.12 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.54, 169.92, 169.48, 135.64, 132.96, 124.38, 124.16, 101.66, 99.62, 80.45, 77.05, 73.70, 71.46, 71.34, 70.17, 69.98, 68.24, 61.95, 58.75, 51.92, 34.40, 29.98, 26.50, 25.34, 16.50; HRMS (M + Cs) calcd for $C_{27}H_{37}O_{13}NCs$ 716.1319, found 716.1342.

Saccharide 71. This compound was prepared from the corresponding fully protected saccharide **47** (75.0 mg, 0.04446 mmol) as described in the preparation of **62**, yielding **71** (22.4 mg, 59%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 8.00 (dd, J = 8.2, 1.0 Hz, 2H), 7.69−7.75 (m, 4H), 7.52 (tt, J = 7.4, 1.2 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 5.21 (dd, J = 9.8, 8.1 Hz, 1H), 4.98 (d, J = 8.5 Hz, 1H), 4.86 (d, J = 3.4 Hz, 1H), 4.69 (d, J = 8.1 Hz, 1H), 4.26 (dd, J = 10.8, 8.5 Hz, 1H), 4.01 (q, J = 6.5 Hz, 1H), 3.88 (dd, J = 10.9, 8.6 Hz, 1H), 3.86 (d, J = 3.7 Hz, 1H), 3.82 (dd, J = 9.8, 3.3 Hz, 1H), 3.58−3.76 (m, 8H), 3.46−3.53 (m, 2H), 3.45 (s, 3H), 3.19−3.29 (m, 2H), 1.73−1.87 (m, 2H), 1.15−1.29 (m, 4H), 1.09 (d, J = 6.5 Hz, 3H), 0.88−0.97 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.57, 169.73, 169.41, 167.31, 135.68, 134.49, 132.89, 131.16, 130.80, 129.67, 124.41, 124.20, 104.44, 102.57, 99.50, 81.73, 81.19, 77.33, 76.54, 74.97, 73.70, 73.50, 71.62, 70.98, 70.65, 70.20, 68.82, 62.80, 61.25, 57.87, 51.93, 34.48, 29.94, 26.47, 25.38, 16.62; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{19}NCs$ 982.2110, found 982.2139.

Saccharide 72. This compound was prepared from the corresponding fully protected saccharide **41** (35.0 mg, 0.02194 mmol) as described in the preparation of **62**, yielding **72** (12.7 mg, 68%) as a solid after lyophilization: ^{1}H NMR (500 MHz, CD_3OD) δ 7.41−7.43 (m, 4H), 7.35 (t, J = 7.5 Hz, 1H), 7.30 (m, 1H), 7.18 (m, 1H), 7.08 (t, J = 7.5 Hz, 2H), 5.04 (dd, J = 9.5, 8.0 Hz, 1H), 4.87 (d, J = 8.5 Hz, 1H), 4.80 (d, J = 3.5 Hz, 1H), 4.56 (d, J = 8.0 Hz, 1H), 4.37 (dd, J = 10.5, 8.0 Hz, 1H), 4.04 (q, J = 6.5 Hz, 1H), 3.91 (dd, J = 10.5, 8.5 Hz, 1H), 3.82 (dd, J = 11.5, 1.5 Hz, 1H), 3.79 (d, J = 3.0 Hz, 1H), 3.75 (dd, J = 10.5, 3.5 Hz, 1H), 3.62−3.69 (m, 8H), 3.50 (dd, J = 9.5, 8.0 Hz, 1H), 3.46 (s, 3H), 3.32−3.35 (m, 1H), 3.19−3.24 (m, 1H), 1.63−1.76 (m, 2H), 1.14 (d, J = 6.5 Hz, 3H), 1.04−1.23 (m, 4H), 0.74−0.84 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 175.5, 170.0, 168.9, 166.8, 135.5, 134.1, 132.1, 130.7, 130.4, 129.5, 124.3, 123.8, 104.5, 102.5, 99.4, 83.31, 81.49, 77.77, 76.94, 75.12, 73.70, 73.53, 71.57, 71.50, 70.64, 70.11, 68.87, 62.62, 62.59, 56.42, 51.90, 34.42, 29.88, 26.40, 25.29, 16.66; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{19}NCs$ 982.2110, found 982.2141.

Saccharide 73. This compound was prepared from the corresponding fully protected saccharide **31** (33.0 mg, 0.01965 mmol) as described in the preparation of **62**, yielding **73** (11.1 mg, 65%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 7.59 (dd, J = 8.2, 1.1 Hz, 2H), 7.45−7.54 (m, 4H), 7.24−7.28 (m, 2H), 7.21 (t, J = 8.0 Hz, 2H), 5.35 (dd, J = 10.0, 8.0 Hz, 1H), 4.98 (d, J = 8.6 Hz, 1H), 4.96 (d, J = 3.8 Hz, 1H), 4.73 (d, J = 8.0 Hz, 1H), 4.49 (dd, J = 10.8, 8.0 Hz, 1H), 4.10 (d, J = 2.9 Hz, 1H), 3.98−4.04 (m, 2H), 3.93 (dd, J = 12.0, 2.0 Hz, 1H), 3.87 (dd, J = 11.2, 8.2 Hz, 1H), 3.58−3.79 (m, 6H), 3.56 (s, 3H), 3.28−3.47 (m, 4H), 3.24 (dd, J = 10.1, 3.3 Hz, 1H), 3.11 (dd, J = 11.0, 4.0 Hz, 1H), 3.06−3.07 (m, 1H), 1.72−1.88 (m, 2H), 1.10−1.34 (m, 4H), 0.81−0.97 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.49, 170.01, 168.85, 166.44, 135.55, 134.33, 132.18, 130.70, 130.27, 129.67, 124.31, 123.85, 102.50, 99.40, 96.26, 83.25, 77.74, 76.82, 76.53, 72.40, 72.05, 71.59, 71.03, 70.86, 70.09, 69.71, 65.55, 62.72, 62.67, 62.34, 56.43, 51.89, 34.42, 29.88, 26.41, 25.29; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{20}NCs$ 998.2059, found 998.2030.

Saccharide 74. This compound was prepared from hydrogenolysis of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside (70.0 mg, 0.06500 mmol) isolated as a side product like the formation of **13** in the assembly of oligosaccharides, yielding **74** (26.7 mg, 69%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 7.79−7.92 (m, 4H), 5.14 (d, J = 8.4 Hz, 1H), 4.90 (d, J = 3.8 Hz, 1H), 4.37 (dd, J = 10.8, 8.6 Hz, 1H), 4.07 (dd, J = 10.8, 8.5 Hz, 1H), 3.91 (dd, J = 12.0, 2.1 Hz, 1H), 3.60−3.87 (m, 6H), 3.59 (s, 3H), 3.40−3.54 (m, 3H), 3.14 (dd, J = 10.4, 8.1 Hz, 1H), 2.67 (dd, J = 10.4, 4.8 Hz, 1H), 1.84−1.99 (m, 2H), 1.24−1.44 (m, 4H), 1.02−1.15 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.54, 170.04, 169.45, 135.78, 132.92, 124.64, 124.35, 104.03, 99.68, 83.95, 77.67, 72.56, 72.37, 71.17, 70.71, 70.22, 70.22, 62.39, 60.84, 56.93, 51.92, 34.48, 29.96, 26.50, 25.40; HRMS (M + Cs) calcd for $C_{27}H_{37}O_{14}NCs$ 732.1268, found 732.1244.

Saccharide 75. This compound was prepared from hydrogenolysis of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranoside (36.0 mg, 0.03343 mmol) isolated as a side product like the formation of **13** in the assembly of oligosaccharides, yielding **75** (18.4 mg, 92%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) α/*β* = 3:1, for α-isomer, δ 7.85−7.91 (m, 4H), 5.14 (d, J = 8.4 Hz, 1H), 4.92 (d, J = 3.7 Hz, 1H), 4.37 (dd, J = 10.8, 8.6 Hz, 1H), 3.01−4.13 (m, 15H), 2.53 (dd, J = 11.8, 2.2 Hz, 1H), 1.84−1.99 (m, 2H), 1.24−1.46 (m, 4H), 1.00−1.13 (m, 2H); HRMS (M + Cs) calcd for $C_{27}H_{37}O_{14}NCs$ 732.1268, found 732.1245.

Saccharide 76. This compound was prepared from hydrogenolysis of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-6-*O*-*p*-methoxybenzyl-*β*-D-glucopyranoside (11.0 mg, 0.00941 mmol) isolated as a side product like the formation of **13** in the assembly of oligosaccharides, yielding **76** (4.6 mg, 82%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 7.81−7.89 (m, 4H), 5.24 (d, J = 3.8 Hz, 1H), 5.16 (d, J = 8.5 Hz, 1H), 4.51 (dd, J = 10.9, 8.6 Hz, 1H), 4.01 (dd, J = 11.1, 8.5 Hz, 1H), 3.24−3.96 (m, 15H), 1.84−2.00 (m, 2H), 1.25−1.45 (m, 4H), 1.02−1.13 (m, 2H); ESI-MS (pos) (M + Na) calcd for $C_{27}H_{37}O_{14}NNa$ 622, found 622; ESI-MS (neg) (M − H) calcd 598, found 598.

Saccharide 77. This compound was prepared from the corresponding fully protected saccharide **40** (22.0 mg, 0.01321 mmol) as described in the preparation of **62**, yielding **77** (8.2 mg, 66%) as a solid after lyophilization: ^{1}H NMR (500 MHz, CD_3OD) δ 7.99 (dd, J = 8.5, 1.0 Hz, 2H), 7.80−7.86 (m, 4H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 5.54 (dd, J = 10.5, 8.0 Hz, 1H), 5.28 (dd, J = 10.5, 3.0 Hz, 1H), 5.16 (d, J = 4.0 Hz, 1H), 4.95 (d, J = 8.5 Hz, 1H), 4.92 (d, J = 7.5 Hz, 1H), 4.29 (s, 1H), 4.28 (dd, J = 9.5, 1.0 Hz, 1H), 4.14 (dd, J = 10.5, 7.5 Hz, 1H), 4.07 (q, J = 6.5 Hz, 1H), 3.72−3.87 (m, 8H), 3.59 (s, 3H), 3.40−3.52 (m, 2H), 3.19 (dd, J = 9.5, 8.5 Hz, 1H), 3.06−3.10 (m, 1H), 2.64−2.67 (m, 2H), 2.46−2.52 (m, 1H), 2.37−2.43 (m, 1H), 1.95 (s, 3H), 1.85−1.94 (m, 2H), 1.24−1.31 (m, 2H), 1.22 (d, J = 6.5 Hz, 3H), 1.13−1.20 (m, 2H), 0.91−0.97 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 208.9, 175.6, 173.4, 167.1, 135.6, 134.6, 133.0, 131.1, 130.9, 129.7, 124.3, 124.1, 103.0, 101.6, 99.3, 77.60, 76.84, 75.35, 74.18, 73.60, 72.93, 72.51, 71.75, 71.65, 70.51, 70.51, 69.86, 68.65, 62.06, 58.43, 51.96, 38.54, 24.60, 29.84, 29.41, 29.04, 26.47, 25.42, 16.66; HRMS (M + Cs) calcd for $C_{45}H_{57}O_{21}NCs$ 1080.2477, found 1080.2448.

Saccharide 78. This compound was prepared from the corresponding fully protected saccharide **39** (40.4 mg, 0.02426 mmol) as described in the preparation of **62**, yielding **78** (7.1 mg, 39%) as a solid after lyophilization: ^{1}H NMR (500 MHz, D_2O) δ 7.73−7.80 (m, 4H), 5.13 (d, J = 8.5 Hz, 1H), 5.03 (d, J = 4.0 Hz, 1H), 4.40 (d, J = 7.5 Hz, 1H), 4.21 (dd, J = 10.5, 9.5 Hz, 1H), 4.15 (d, J = 11.5 Hz, 1H), 4.05 (q, J = 6.5 Hz, 1H),

3.41−3.89 (m, 18H), 1.70−1.76 (m, 1H), 1.56−1.63 (m, 1H), 1.16−1.28 (m, 2H), 1.07−1.13 (m, 1H), 1.06 (d, J = 6.5 Hz, 3H), 0.94−1.01 (m, 1H), 0.74−0.86 (m, 2H); ^{13}C NMR (125 MHz, D_2O) δ 177.7, 170.8, 170.7, 136.1, 131.4, 124.7, 124.4, 104.0, 101.7, 98.9, 81.52, 75.94, 75.88, 72.55, 71.32, 71.13, 70.93, 70.93, 70.19, 69.44, 69.40, 69.25, 67.98, 61.69, 57.59, 52.76, 34.04, 28.88, 25.54, 24.35, 16.12; HRMS (M + Cs) calcd for $C_{33}H_{47}O_{18}NCs$ 878.1847, found 878.1868.

Saccharide 79. This compound was prepared from the corresponding fully protected saccharide **38** (36.6 mg, 0.02067 mmol) as described in the preparation of **62**, yielding **79** (6.6 mg, 42%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 7.71−7.79 (m, 4H), 5.12 (d, J = 8.6 Hz, 1H), 4.96 (d, J = 3.6 Hz, 1H), 4.37 (d, J = 7.7 Hz, 1H), 4.20 (dd, J = 10.0, 9.5 Hz, 1H), 4.14 (d, J = 11.5 Hz, 1H), 4.02 (d, J = 2.4 Hz, 1H), 3.38−3.87 (m, 19H), 3.31 (t, J = 9.5 Hz, 1H), 1.68−1.76 (m, 1H), 1.53−1.62 (m, 1H), 1.16−1.28 (m, 2H), 1.03−1.14 (m, 1H), 0.90−1.01 (m, 1H), 0.68−0.87 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 179.37, 173.58, 172.71, 137.75, 133.03, 126.40, 126.05, 105.86, 100.52, 97.84, 79.88, 77.54, 77.31, 75.26, 74.14, 73.78, 72.96, 72.71, 72.57, 71.74, 71.61, 71.09, 67.44, 63.38, 62.64, 59.23, 54.41, 35.69, 30.53, 27.19, 26.00; HRMS (M + Cs) calcd for $C_{33}H_{47}O_{19}NCs$ 894.1797, found 894.1766.

Saccharide 80. This compound was prepared from hydrogenolysis of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-(2,3,4-tri-*O*-benzyl-L-fucopyranosyl)-4,6-*O*-*p*-methoxybenzylidene-β-D-glucopyranoside (**13**) (58.0 mg, 0.05973 mmol), yielding **80** (23.2 mg, 67%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) α/β = 9:2, for α-isomer, δ 7.79−7.87 (m, 4H), 5.10 (d, J = 8.5 Hz, 1H), 4.65 (d, J = 4.0 Hz, 1H), 4.36 (dd, J = 10.8, 8.2 Hz, 1H), 4.20 (q, J = 6.5 Hz, 1H), 4.11 (dd, J = 10.8, 8.5 Hz, 1H), 3.33−3.95 (m, 12H), 1.84−1.99 (m, 2H), 1.24−1.46 (m, 4H), 1.15 (d, J = 6.6 Hz, 3H), 0.99−1.10 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.55, 170.36, 169.58, 135.49, 133.31, 124.49, 124.19, 102.07, 99.72, 81.32, 78.11, 73.47, 71.41, 71.17, 70.23, 69.29, 68.49, 62.54, 56.83, 51.93, 34.50, 29.99, 26.51, 25.41, 16.51; HRMS (M + Cs) calcd for $C_{27}H_{37}O_{13}NCs$ 716.1319, found 716.1343.

Saccharide 81. This compound was prepared from hydrogenolysis of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-β-D-glucopyranoside (30.4 mg, 0.02601 mmol) isolated as a side product like the formation of **13** in the assembly of oligosaccharides, yielding **81** (8.5 mg, 55%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) α/β = 1:1, δ 7.81−7.88 (m, 8H), 5.17 (d, J = 8.6 Hz, 1H), 5.15 (d, J = 8.6 Hz, 1H), 4.88 (d, J = 3.8 Hz, 1H), 4.41 (d, J = 7.7 Hz, 1H), 3.60−4.28 (m, 18H), 3.59 (s, 6H), 3.22−3.56 (m, 10H), 1.85−2.00 (m, 4H), 1.24−1.48 (m,8H), 1.01−1.13 (m, 4H); HRMS (M + Cs) calcd for $C_{27}H_{37}O_{14}NCs$ 732.1268, found 732.1245.

Saccharide 82. This compound was prepared from the corresponding fully protected saccharide **34** (69.1 mg, 0.03902 mmol) as described in the preparation of **62**, yielding **82** (25.2 mg, 75%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD-$CDCl_3$ v/v = 1:1) δ 8.06 (d, J = 7.5 Hz, 2H), 7.74−7.83 (m, 4H), 7.59 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 5.43 (dd, J = 9.8, 8.1 Hz, 1H), 5.06 (d, J = 8.5 Hz, 1H), 4.93 (d, J = 3.8 Hz, 1H), 4.81 (d, J = 8.0 Hz, 1H), 4.37 (dd, J = 10.9, 8.6 Hz, 1H), 4.07 (d, J = 2.8 Hz, 1H), 3.97−4.03 (m, 2H), 3.84 (dd, J = 10.8, 6.7 Hz, 1H), 3.44−3.79 (m, 10H), 3.21−3.38 (m, 6H), 3.19 (dd, J = 11.4, 9.8 Hz, 1H), 1.86−1.99 (m, 2H), 1.26−1.39 (m, 4H), 0.97−1.09 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD-$CDCl_3$ v/v = 1:1) δ 175.59, 169.23, 168.92, 166.54, 134.99, 134.23, 132.20, 130.37, 129.90, 129.21, 124.01, 123.78, 101.50, 98.81, 97.34, 79.40, 78.08, 76.24, 75.65, 73.99, 73.02, 72.35, 71.75, 70.20, 69.89, 69.79, 66.35, 62.08, 60.88, 60.44, 56.89, 51.86, 34.18, 29.38, 25.84, 24.85; ESI-MS (pos) (M + Na) calcd for $C_{40}H_{51}O_{20}NNa$ 888, found 888; ESI-MS (neg) (M − H) calcd 864, found 864.

Saccharide 83. This compound was prepared from the corresponding fully protected saccharide **33** (30.9 mg, 0.01745 mmol) as described in the preparation of **62**, yielding **83** (12.8 mg, 85%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 8.16 (d, J = 7.5 Hz, 2H), 7.80−7.86 (m, 4H), 7.66 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 5.49 (dd, J = 9.5, 8.1 Hz, 1H), 5.08 (d, J = 8.5 Hz, 1H), 5.06 (d, J = 3.7 Hz, 1H), 4.88 (d, J = 8.0 Hz, 1H), 4.38 (dd, J = 10.8, 8.6 Hz, 1H), 4.15 (s, 1H), 4.14 (dd, J = 11.5, 3.0 Hz, 1H), 3.99 (dd, J = 10.9, 8.6 Hz, 1H), 3.84 (dd, J = 12.3, 8.8 Hz, 1H), 3.57−3.78 (m, 8H), 3.56 (s, 3H), 3.45−3.51 (m, 2H), 3.31−3.40 (m, 4H), 1.84−1.98 (m, 2H), 1.22−1.42 (m, 4H), 0.98−1.12 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 175.6, 169.8, 169.4, 167.0, 135.7, 134.8, 132.9, 131.0, 130.8, 129.9, 124.4, 124.2, 102.4, 99.6, 96.7, 80.74, 77.13, 76.69, 76.58, 72.40, 72.29, 71.17, 71.08, 70.97, 70.21, 69.82, 66.12, 62.86, 62.54, 61.22, 57.77, 51.91, 34.49, 29.95, 26.48, 25.39; ESI-MS (pos) (M + Na) calcd for $C_{40}H_{51}O_{20}NNa$ 888, found 888; ESI-MS (neg) (M − H) calcd 864, found 864.

Saccharide 84. This compound was prepared from the corresponding fully protected saccharide **54** (70.0 mg, 0.04235 mmol) as described in the preparation of **62**, yielding **84** (18.1 mg, 56%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) δ 7.69−7.77 (m, 4H), 5.08 (d, J = 8.6 Hz, 1H), 4.83 (d, J = 3.4 Hz, 1H), 4.33 (d, J = 7.8 Hz, 1H), 4.17 (dd, J = 10.8, 8.9 Hz, 1H), 4.08 (dd, J = 11.4, 1.5 Hz, 1H), 3.37−3.85 (m, 21H), 1.66−1.74 (m, 1H), 1.53−1.60 (m, 1H), 1.13−1.26 (m, 2H), 1.01−1.11 (m, 1H), 0.89−1.00 (m, 1H), 0.66−0.85 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 179.36, 172.50, 172.33, 137.77, 133.08, 126.41, 126.07, 105.91, 100.69, 100.54, 77.73, 75.50, 75.08, 73.42, 73.17, 73.00, 72.88, 72.62, 71.89, 71.67, 71.26, 71.12, 70.68, 68.74, 63.64, 59.23, 54.42, 35.70, 30.55, 27.21, 26.02; HRMS (M + Cs) calcd for $C_{33}H_{47}O_{19}NCs$ 894.1797, found 894.1771.

Saccharide 85. This compound was prepared from hydrogenolysis of 5-methoxycarbonylpentyl 2-deoxy-2-phthalimido-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-glucopyranoside (30.4 mg, 0.02860 mmol) isolated as a side product like the formation of **13** in the assembly of oligosaccharides, yielding **85** (8.6 mg, 52%) as a solid after lyophilization: ^{1}H NMR (500 MHz, CD_3OD) δ 7.81−7.88 (m, 4H), 5.15 (d, J = 8.5 Hz, 1H), 4.85 (d, J = 3.5 Hz, 1H), 4.25 (dd, J = 10.5, 8.5 Hz, 1H), 4.12 (q, J = 6.5 Hz, 1H), 3.77−3.99 (m, 5H), 3.75 (dd, J = 10.0, 3.5 Hz, 1H), 3.68−3.69 (m, 1H), 3.59 (s, 3H), 3.55−3.58 (m, 1H), 3.50 (dd, J = 9.5, 9.0 Hz, 1H), 3.41−3.45 (m, 1H), 1.88−2.00 (m, 2H), 1.29−1.47 (m, 4H), 1.22 (d, J = 6.5 Hz, 3H), 1.03−1.13 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 175.6, 170.0, 169.6, 135.6, 133.1, 124.4, 124.1, 100.9, 99.7, 77.09, 73.67, 72.30, 72.23, 71.75, 70.18, 70.18, 68.03, 67.62, 58.64, 51.95, 34.53, 30.04, 26.56, 25.48, 16.72; HRMS (M + Cs) calcd for $C_{27}H_{37}O_{13}NCs$ 716.1319, found 716.1341.

Saccharide 86. This compound was prepared from the corresponding fully protected saccharide **35** (69.6 mg, 0.04180 mmol) as described in the preparation of **62**, yielding **86** (26.7 mg, 75%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 8.09 (d, J = 7.5 Hz, 2H), 7.81−7.86 (m, 4H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 5.51 (dd, J = 9.4, 8.0 Hz, 1H), 5.08 (d, J = 8.5 Hz, 1H), 4.92 (d, J = 4.0 Hz, 1H), 4.85 (d, J = 8.0 Hz, 1H), 4.37 (dd, J = 10.9, 8.6 Hz, 1H), 4.10 (q, J = 6.5 Hz, 1H), 3.57−4.03 (m, 11H), 3.56 (s, 3H), 3.47−3.55 (m, 2H), 3.27−3.39 (m, 2H), 1.83−1.97 (m, 2H), 1.24−1.39 (m, 4H), 1.19 (d, J = 6.5 Hz, 3H), 0.98−1.11 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.57, 169.77, 169.40, 167.41, 135.69, 134.49, 132.90, 131.15, 130.88, 129.70, 124.40, 124.23, 102.51, 102.40, 99.52, 80.47, 79.76, 77.29, 76.53, 73.54, 73.44, 71.46, 70.96, 70.39, 70.20, 69.86, 68.16, 62.35, 61.14, 57.79, 51.93, 34.48, 29.94, 26.47, 25.39, 16.66; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{19}NCs$ 982.2110, found 982.2144.

Saccharide 87. This compound was prepared from the corresponding fully protected saccharide **48** (50.0 mg, 0.02964 mmol) as described in the preparation of **62**, yielding **87** (17.0 mg, 68%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 7.68−7.94 (m, 6H), 7.49 (tt, J = 7.4, 1.2 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 5.17 (dd, J = 10.0, 8.0 Hz, 1H), 4.89 (d, J = 3.8 Hz, 1H), 4.86 (d, J = 8.5 Hz, 1H), 4.64 (d, J = 8.0 Hz, 1H), 4.16 (dd, J = 11.2, 1.4 Hz, 1H), 4.09 (q, J = 6.5 Hz, 1H), 4.05 (dd, J = 10.7, 8.6 Hz, 1H), 3.91 (d, J = 3.0 Hz, 1H), 3.81 (t, J = 2.9 Hz, 1H), 3.78 (t, J = 2.9 Hz, 1H), 3.54−3.76 (m, 7H), 3.48 (s, 3H), 3.40 (t, J = 7.8 Hz, 1H), 3.28 (dt, J = 10.2, 5.9 Hz, 1H), 3.08 (dd, J = 9.8, 8.7 Hz, 1H), 2.93−2.99

(m, 1H), 1.70−1.84 (m, 2H), 1.15 (d, J = 6.5 Hz, 3H), 0.98−1.15 (m, 4H), 0.77−0.85 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.55, 169.88, 169.49, 167.55, 135.59, 134.31, 132.95, 131.59, 130.71, 129.62, 124.31, 124.14, 104.41, 102.81, 99.23, 81.84, 77.54, 76.75, 75.15, 73.66, 73.58, 73.00, 72.49, 71.68, 70.78, 70.36, 69.74, 68.87, 62.54, 58.42, 51.96, 34.49, 29.80, 26.45, 25.35, 16.69; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{19}NCs$ 982.2110, found 982.2088.

Saccharide 88. This compound was prepared from the corresponding fully protected saccharide **36** (70.0 mg, 0.03952 mmol) as described in the preparation of **62**, yielding **88** (24.9 mg, 73%) as a solid after lyophilization: ^{1}H NMR (400 MHz, CD_3OD) δ 8.10 (dd, J = 8.5, 1.4 Hz, 2H), 7.78−7.86 (m, 4H), 7.62 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.9 Hz, 2H), 5.47 (dd, J = 10.0, 8.0 Hz, 1H), 5.08 (d, J = 3.7 Hz, 1H), 4.96 (d, J = 8.5 Hz, 1H), 4.81 (d, J = 8.0 Hz, 1H), 4.29 (dd, J = 11.1, 1.3 Hz, 1H), 4.22 (d, J = 2.7 Hz, 1H), 4.12−4.18 (m, 2H), 3.65−3.89 (m, 7H), 3.58 (s, 3H), 3.32−3.53 (m, 6H), 3.20 (dd, J = 9.8, 8.8 Hz, 1H), 3.05−3.11 (m, 1H), 1.79−1.94 (m, 2H), 1.18−1.29 (m, 2H), 1.07−1.17 (m, 2H), 0.84−0.93 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.57, 169.79, 169.49, 167.24, 135.59, 134.57, 132.93, 131.11, 130.94, 129.77, 124.33, 124.12, 102.83, 99.21, 96.27, 77.43, 76.78, 76.50, 73.01, 72.46, 72.36, 72.22, 71.17, 71.10, 70.30, 69.83, 69.78, 66.04, 62.81, 62.33, 58.42, 51.96, 34.49, 29.76, 26.44, 25.34; HRMS (M + Cs) calcd for $C_{40}H_{51}O_{20}NCs$ 998.2059, found 998.2019.

Saccharide 89. This compound was prepared from the corresponding fully protected saccharide **55** (26.0 mg, 0.01573 mmol) as described in the preparation of **62**, yielding **89** (5.7 mg, 48%) as a solid after lyophilization: ^{1}H NMR (400 MHz, D_2O) α: β = 1:3, for β-isomer, δ 7.71−7.78 (m, 4H), 5.10 (d, J = 8.6 Hz, 1H), 4.33 (d, J = 7.4 Hz, 1H), 4.31 (d, J = 7.6 Hz, 1H), 4.19 (dd, J = 10.7, 8.8 Hz, 1H), 4.12 (dd, J = 11.4, 1.6 Hz, 1H), 3.35−3.86 (m, 21H), 1.67−1.75 (m, 1H), 1.53−1.61 (m, 1H), 1.14−1.27 (m, 2H), 1.03−1.10 (m, 1H), 0.89−0.97 (m, 1H), 0.70−0.82 (m, 2H); HRMS (M + Cs) calcd for $C_{33}H_{47}O_{19}NCs$ 894.1797, found 894.1771.

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Supporting Information Available: Listing of selected ^{1}H and ^{13}C NMR spectra for compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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