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Combinatorial Synthesis of an Oligosaccharide Library by Using β-Bromoglycoside-Mediated Iterative Glycosylation of Selenoglycosides: Rapid Expansion of Molecular Diversity with Simple Building Blocks

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Abstract: A new method for constructing an oligosaccharide library composed of structurally defined oligosaccharides is presented based on an iterative glycosylation of selenoglycosides. Treatment of 2-acyl-protected selenoglycosides with bromine selectively generates β-bromoglycosides, which serve as glycosyl cation equivalents in the oligosaccharide synthesis. Thus, the coupling of the bromoglycosides with another selenoglycoside affords the corresponding glycosylated selenoglycosides, which can be directly used to next glycosylation. The iteration of this sequence allows the synthesis of a variety of oligosaccharides including an elicitor active heptasaccharide. A characteristic feature of the iterative glycosylation is that glycosyl donors and acceptors with the same anomeric reactivity can be selectively coupled by activation of the glycosyl donor prior to coupling with the glycosyl acceptor. Therefore, same selenoglycosides can be used for both the glycosyl donors and the acceptors. This feature has been exemplified by a construction of an oligosaccharide library directed to elicitor-active oligosaccharides. The library composed of stereochemically defined oligoglucosides with considerable structural diversity can be constructed starting from simple selenoglycosides.

Keywords: carbohydrates · chalcogens · combinatorial chemistry · glycosylation · oligosaccharides

Introduction

Oligosaccharides have attracted a great deal of attention due to their important biological functions.[1] They show considerable microheterogeneity in nature in terms of the branching and composition of monosaccharides as a result of complex biosynthetic pathways. Therefore, rapid access to structurally defined oligosaccharides would facilitate a better understanding of structure–function relationships with respect to biological processes.[2] However, this remains a formidable challenge.

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Oligosaccharides consist of several anomeric C–O-bond-linked monosaccharides, and their synthesis requires the iteration of glycosylation to form an anomeric bond between one sugar and the other. Therefore, reactivity control of the anomeric substituents is a major challenge in generalized oligosaccharide synthesis.[2] Several glycosylation strategies have recently been developed in order to achieve efficient high-throughput synthesis. These include the two-stage-activation method,[3] the armed–disarmed glycosylation method,[4] the one-pot synthesis based on chemoselective glycosylation,[5] the orthogonal method,[6] the programmable one-pot strategy,[7] the solid-phase synthesis[8] and the automated synthesis.[9,10] However, despite these recent developments, the rational design of oligosaccharide synthesis has been still a difficult task, because reactivities of sugar derivatives are strongly affected by structures, protecting groups and reaction conditions (for example, activating reagents and solvents). Given these considerations, the one-pot synthesis based on chemoselective or programmable glycosylations has been most effective to date, because a combination of glycosyl donors and acceptors can be rationally designed using an empirical or measurable database (Figure 1a).

However, these combinations are limited in a practical sense due to the difficulty to design a complete set of building blocks. In addition, while each glycosylation step proceeds with high efficiency in these methods, the donors and acceptors with suitable anomeric reactivities must be prepared through laborious multistep procedures. An alternative, and potentially more general, strategy for overcoming this problem is an iterative glycosylation by using a single anomeric substituent under a single set of reaction conditions (Figure 1b). However, so far this type of strategy has been limited to the glycal-assembly method.[11] New techniques have recently been reported by using C1-hydroxyl glycosides[12] and selenoglycosides[13] or thioglycosides.[14,15]

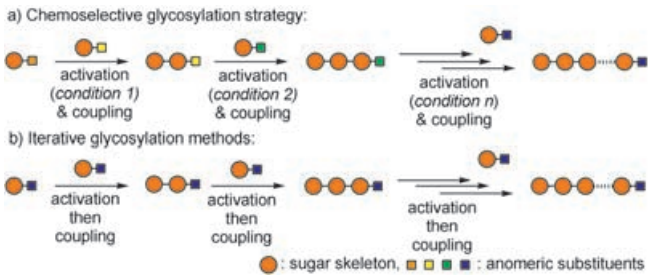


Figure 1. Strategies for oligosaccharide synthesis.

We also envisaged that an iterative glycosylation would be better adapted to enhance the structural diversity in the construction of an oligosaccharide library.[16] A key concept underlying chemoselective glycosylation is the existence of reactive and less-reactive sugar derivatives in relation to specific glycosylation conditions. Therefore, only one glycoside will form if one start from a set of two glycosides (Figure 2a). After n repetitions using a given set of combinations, a library composed of $(n + 2)$ compounds, including the starting glycosides, will be produced. Therefore, the number of starting glycosides must be increased to achieve structural diversity in the library by using conventional glycosylation methods.[17] In sharp contrast to chemoselective glycosylation, there is virtually no reactivity difference between glycosyl donors and acceptors in iterative glycosylation. Therefore, four new glycosides can be obtained from two glycosides by making arbitrary selections of the donors and acceptors (Figure 2b). As the reactivity of the starting glycosides, as well as the generated glycosides, is essentially equal, further combinatorial glycosylation among the starting and forming glycosides will dramatically increase structural diversity in the library. Therefore, a library with broad structural diversity would be constructed without increase of the number of starting glycosides. While random glycosylation has been reported to increase such structural diversity.[18] The resulting library comprises an inseparable mixture of regio- and stereoisomers. However, the iterative glycosylation approach would generate libraries composed of structurally defined oligosaccharides.

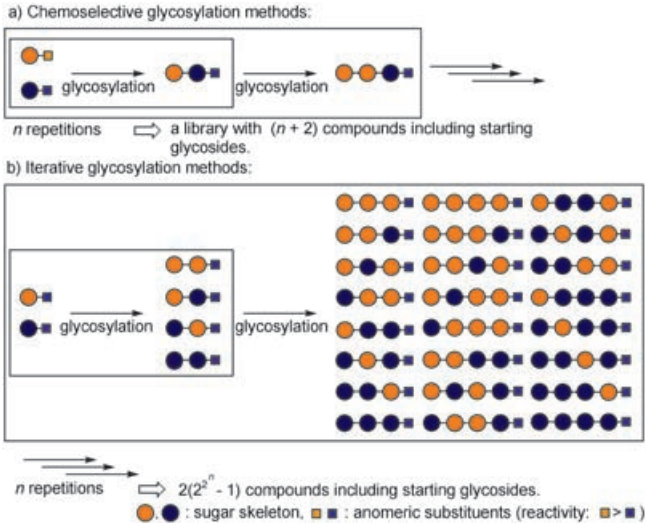
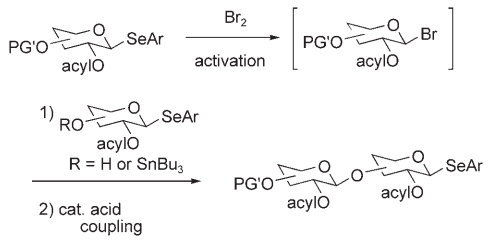


Figure 2. Strategies for construction of an oligosaccharide library: an example of starting from two glycosides.

We previously reported that chalcogenoglycosides could be selectively activated by electrochemical oxidation,[19] and that this method could be applicable to chemoselective glycosylation. During the course of developing a new glycosylation method using chalcogenoglycosides, we discovered a new iterative glycosylation using selenoglycosides as both glycosyl acceptors and donors (Scheme 1). β-Bromoglycosides generated from selenoglycosides serve as glycosyl cation equivalents, and react with selenoglycosides that possess a free hydroxyl group or equivalent without adding any activators that might react with selenoglycosides.[20] The preliminary results were reported previously[13] and the full details of the study are presented here. α-Bromoglycosides have been widely used as glycosyl donors in O-glycoside synthesis with a combination of heavy metal activators, such as silver and mercury salts.[21] However, little has been explored for the glycosylation of β-bromoglycosides. Lemieux reported that β-bromoglycosides, generated in situ from α-bromoglycosides, possessed a higher reactivity than the α-isomer and selectively reacted with glycosyl acceptors in the S_N2 manner to give α-*O*-glycosides.[22] Despite the high 1,2-*cis* selectivity observed in this glycosylation, further synthetic elaborations have been limited as a result of low coupling yields and long reaction times. Stereochemically pure β-chloro- and bromoglycosides have been reported,[23] but

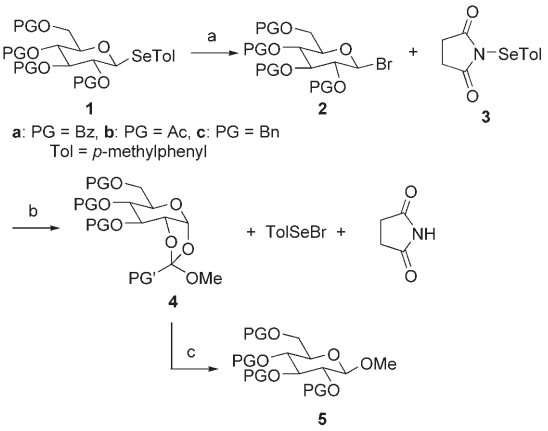


Scheme 1. β-Bromoglycoside-mediated iterative glycosylation.

little is known on their use for *O*-glycoside synthesis[22a] besides 2-deoxy-2-phthalimido-pyranosides with the combination of heavy metal activators.[24] Therefore, to our knowledge, this is the first systematic study on the syntheses and reactivities of stereochemically pure β-bromoglycosides of 2-alkoxy pyranosides.[25] In addition, we also report a new strategy for the construction of an oligosaccharide library based on iterative glycosylation.

Results and Discussion

Selective generation of β-bromoglycosides from chalcogenoglycosides: During the search for a new method for the selective activation of selenoglycosides, we found that β-**1a** (PG = Bz)[26] was selectively converted to the corresponding β-bromoglycoside **2a** upon treatment with one equivalent of *N*-bromosuccinimide (NBS) (Scheme 2 and Table 1, entry 1). The structure of **2a** was assigned on the basis of the characteristic β-coupling at the anomeric proton signal (δ 6.05 ppm; $^3J_{HH}$ = 9.6 Hz) by using ^{1}H NMR, and also by the existence of the neutral anomeric carbon (δ 79.7 ppm) and four carbonyl signals (δ = 165.25, 165.51, 165.97 and 166.39 ppm) by using ^{13}C NMR in experiments carried out in CD_2Cl_2. The tolylselenyl group in **1a** was converted to tolylselenylsuccinimide (**3**) as judged by the ^{77}Se NMR (δ 622.1 ppm) of the reaction mixture.[27] The addition of one equivalent of methanol to this mixture completely converted **2a** to orthoester **4a** (PG = Bz, PG′ = Ph), along with the formation of tolylselenylbromide (^{77}Se NMR: δ 794.4 ppm) and succinimide.[28]



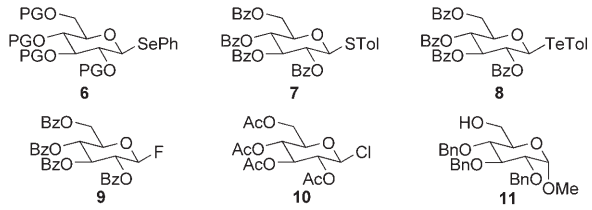
Scheme 2. Reaction of **1** with NBS. a) NBS (1.0 equiv), CD_2Cl_2, −45 °C→ RT, 0.5 h; b) MeOH (1.0 equiv), RT, 1 min; c) TMSOTf (0.2 equiv), CH_2Cl_2, 0 °C, 15 min.

Table 1. Formation of β-bromoglycoside **2** from chalcogenoglycosides.[a]

Entry	Substrate	Activator (equiv)	Yield [%]	Selectivity
1	β-**1a**	NBS (1.0)	>95	>97% β
2	β-**1a**	TolSeBr (1.0)	>95	>97% β
3	β-**1a**	Br_2 (0.5)	>95	95–98% β
4	β-**6a**	Br_2 (0.5)	>95	95–98% β
5	β-**1b**	Br_2 (0.5)	>95	95–98% β
6	β-**6b**	Br_2 (0.5)	>95	95–98% β
7	β-**1c**	Br_2 (0.5)	>95	>97% α
8	α-**1a**	Br_2 (0.5)	>95	85% β
9	β-**7**	Br_2 (0.5)	65	76% β
10	β-**8**	Br_2 (0.5)	>95	>97% β

[a] The reaction was carried out by mixing a substrate and an activator at −40 °C to room temperature for 0.5 h in CD_2Cl_2, with the exception of entry 9, in which the reaction was carried out for 3 d at room temperature.

The β-bromoglycoside **2a** was also formed by treatment of β-**1a** with one equivalent of tolylselenylbromide or with a half equivalent of bromine (entries 2 and 3). In these reactions, the tolylselenyl moiety in **1a** was converted to ditolyldiselenide, as judged by the ^{77}Se NMR (δ 206.3 ppm) analysis of the reaction mixture. The diselenide was also isolated and identified after reaction with a glycosyl acceptor. Therefore, the reaction of **1a** with Br_2 seems to involve the initial formation of **2a** and tolylselenylbromide, which subsequently reacts with the remaining **1a** to give **2a** and the diselenide.[29] The ^{1}H NMR experiments in CD_2Cl_2 revealed that the reaction was extremely β-stereoselective (95–98% selectivity) after a run of several experiments. Due to the mild reaction conditions, isomerization of β-**2a** to the thermodynamically more stable α-isomer was slow, and less than 10% of β-**2a** isomerized to α-**2a** after one day at room temperature. Phenylselenyl-substituted selenoglycoside **6a** also produced similar results (entry 4).



We next examined the factors controlling the formation of β-bromoglycosides from chalcogenoglycosides. First, the effect of the C2-protecting groups was examined: the acetyl-protected selenoglycoside **1b** and **6b** gave the corresponding β-bromoglycoside **2b**, respectively (entries 5 and 6), while the benzyl-protected **1c** gave the α-isomer as the sole product (entry 7).

Second, the effect of the stereochemistry of the starting selenoglycoside was examined; surprisingly, we found that the stereochemistry was critical for the generation of the β-bromoglycosides. Thus, treatment of α-**1a** with bromine resulted in the formation of a 15:85 mixture of α- and β-isomers in good combined yield (entry 8). These results clearly indicate the involvement of two mechanisms namely, bromination with inversion and retention of the starting selenoglycosides[29] although the detailed mechanisms are unclear. We used β-selenoglycosides as the glycosyl donors and acceptors throughout the following studies, in order to generate stereochemically pure β-bromoglycosides.

Third, the effect of the chalcogen atom was examined. The reaction of thioglycoside β-**7** with bromine was slow and gave the bromoglycoside in 65% yield with 76% β-selectivity after 3 d at room temperature (entry 9).[30] By contrast, the reaction of telluroglycoside β-**8** proceeded smoothly within 0.5 h and afforded β-**2a** with complete β-selectivity (entry 10).[31] We used the β-isomer of C2-acyl-protected selenoglycosides as glycosyl donors throughout the following investigations because telluroglycosides are slightly sensitive to oxygen.[32]

Reaction of β-bromoglycoside with glycosyl acceptors: The β-bromoglycosides generated from selenoglycosides reacted with various glycosyl acceptors. Thus, the treatment of β-**2a**, which was generated from β-**1a** or β-**6a** and bromine, with MeOH (1.0 equiv) and 2,6-lutidine (1.0 equiv) in CH_2Cl_2 afforded the orthoester **4a** in quantitative yield within 5 min at 0°C (Table 2, entry 2); by contrast, the reaction without base did not proceed (entry 1). Tributylstannyl methyl ether[33] also reacted with β-**2a** to give **4a** in quantitative yield (entry 3). Acetyl-protected β-**2b** also afforded orthoester **4b** upon treatment with methanol and 2,6-lutidine (entry 4). Although several organic bases were examined, including pyridine, 2,6-di-*tert*-butylpyridine and triethylamine, 2,6-lutidine showed the best results in terms of high conversion and short reaction time. Treatment of the isolated orthoester **4** with a catalytic amount of Me_3SiOTf resulted in the quantitative formation of the corresponding O-glycoside **5**.[34] The β-isomer of **5** formed exclusively due to the intramolecular participation of the C2 acyl-protecting groups.

Table 2. Coupling reaction of β-bromoglycosides with glycosyl acceptors.

Entry	Haloglycoside	Acceptor	Additive[a]	t [h]	Yield[b] [%]
1	β-**2a**	MeOH	none	2	0
2	β-**2a**	MeOH	2,6-lutidine	0.5	97
3	β-**2a**	$MeOSnBu_3$	none	0.5	96
4	β-**2b**	MeOH	2,6-lutidine	0.5	97
5	α-**2a**	MeOH	2,6-lutidine	240	12
6	α-**2a**	MeOH	nBu_4NI	16	78
7	β-**9**	MeOH	2,6-lutidine	12	0
8	β-**10**	MeOH	2,6-lutidine	5	31
9	β-**2a**	c-$C_6H_{11}OH$	2,6-lutidine	0.5	82[c]
10	β-**2a**	**11**	2,6-lutidine	2.5	75[c]

[a] One equivalent was added. [b] Yield of the orthoester determined by ^1H NMR in the presence of an internal standard. [c] Isolated yield of O-glycoside after isomerization of the orthoester. The β-isomer formed exclusively.

It is worth noting the effect of the stereochemistry and the halogen atom on the reactivity of haloglycosides. The α-isomer of **2a** was found to be far less reactive than β-**2a**, and the orthoester **4a** formed in only 12% after 10 d at room temperature (entry 5). We also examined the effect of ammonium salts, which facilitate the isomerization between the α- and β-halogycosides.[22a,35] The coupling of α-**2a** in the presence of Bu_4NI (1.0 equiv), however, required 16 h at room temperature to achieve a high conversion (entry 6). β-Fluoro- (**9**) and β-chloroglycosides (**10**) were also found to be less reactive than β-bromoglycosides (entries 7 and 8). In addition, we examined the coupling of β-**2a** with cyclohexanol and sugar alcohol **11**, and the desired O-glycosides were obtained in both cases after the isomerization of the orthoester intermediate (entries 9 and 10).

Iterative glycosylation of selenoglycosides: Next, we examined the use of selenoglycosides as glycosyl acceptors, as the coupling of β-bromoglycosides with glycosyl acceptors does not require chemical activators that might destroy the anomeric arylselenyl group (Scheme 1). The coupling of **2a**, generated in situ from **1a**, with C6 hydroxyl selenoglycoside **12d** proceeded smoothly in the presence of 2,6-lutidine to give orthoester **16** in 81% yield; this was isomerized to the corresponding O-glycoside **17g** ($n=1$) in 95% yield (Table 3, entry 1). The coupling of **2a** with C6 tributylstannyloxyl selenoglycoside **12e**[36] also proceeded smoothly and afforded **16** in 75% yield. One-pot synthesis from **1a** to **17g** was possible when **12e** was used as the glycosyl acceptor, and **17g** formed in 66% yield after the in situ isomerization of **16** upon treatment with trimethylsilyl triflate (entry 2). Galactose-derived selenoglycoside **14** could be used as the

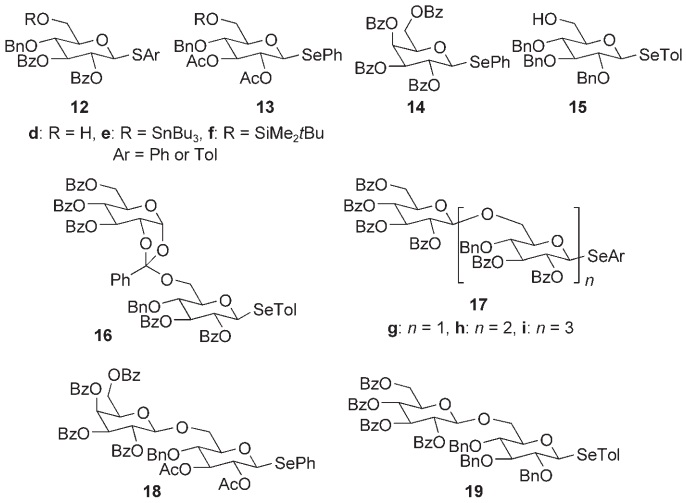


Table 3. Glycosylation of selenoglycosides.

Entry	Donor	Acceptor	Product	Yield[a] [%]
1	**1a**	**12d** (Ar=Tol)	**17g** (Ar=Tol)	77
2	**1a**	**12e** (Ar=Tol)	**17g** (Ar=Tol)	71 (66)
3	**14**	**13e**	**18**	57
4	**1a**	**15**	**19**	64
5	**17g**	**12e** (Ar=Ph)	**17h** (Ar=Ph)	81
6	**17h**	**12e** (Ar=Ph)	**17i** (Ar=Ph)	56

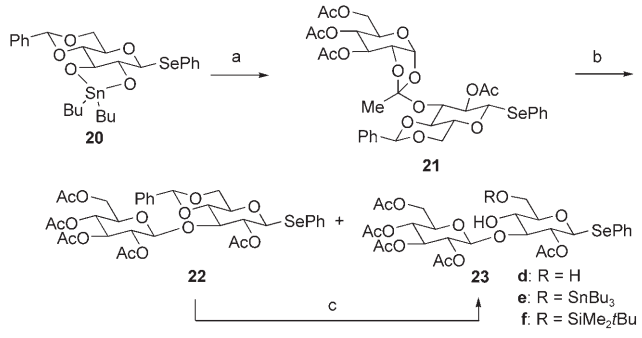
[a] The yield was based on the acceptor for entries 1, 2, and 3, in which a slight excess of the donor was used (1.5 equiv for entries 1, 2 and 3), and on the donor for the remaining entries, in which a slight excess of the acceptor was used (1.0 equiv for entry 4, and 1.5 equiv for entries 5 and 6).

glycosyl donor, and the coupling of the β-bromoglycoside derived from **14** with **13e** afforded the desired disaccharide **18** in good yield (entry 3).

A characteristic feature of the current iterative glycosylation is that less-reactive selenoglycosides can be used as the glycosyl donors and more-reactive selenoglycosides can be used as the glycosyl acceptors. For example, C2 alkyl-protected glycosides are known to be more reactive than C2 acyl-protected glycosides; thus, the former always act as donors and the latter act as acceptors in armed-disarmed glycosylation.[4] The present strategy, however, enables the use of a C2 acyl-protected glycoside **1a** as a donor and a C2 alkyl-protected glycoside **15** as an acceptor, to give **19** in good yield (entry 4). Disaccharide **19** would be used for an armed glycosyl donor in the conventional chemoselective glycosylation reactions.

The products of the current glycosylation reactions are also selenoglycosides. Thus, we could elongate the oligosaccharide chain by repeating the same reaction sequence. Tri- and tetrasaccharides **17h** and **17i** were synthesized by using **17g** and **17h** as glycosyl donors, and **12e** as a common glycosyl acceptor, respectively, in good yields (entries 5 and 6).

We also examined the coupling of the β-bromoglycosides with more sterically hindered glycosyl acceptors (Scheme 3). While the coupling reaction of β-bromoglycoside **2b**, generated from **6b**, with C3 hydroxyl glycosides was slow due to the low reactivity of **2b**, the reaction with stannylenacetal **20** proceeded smoothly to give orthoester **21** in 88% yield after acetylation of the C2 hydroxyl group. Acid-catalyzed isomerization of **21**, followed by in situ hydrolysis of the benzylidene acetal, afforded diol **23d** in 70% yield and unhydrolyzed **22** in 20% yield. The isolated **22** could be transformed to **23d** by acid-catalyzed hydrolysis in 80% yield.



Scheme 3. Synthesis of β-1,3-glycoside. a) **6b** (1.5 equiv)/Br_2 (0.75 equiv), CH_2Cl_2, 0 °C, 0.5 h, then **20** (1.0 equiv), RT, 5 h; Ac_2O (1.5 equiv), Et_3N (1.5 equiv), DMAP (0.1 equiv), RT, 0.5 h; 88%. b) Me_3SiOTf (0.1 equiv), CH_2Cl_2, 0 °C, 0.5 h, then H_2O (10 equiv), RT, 0.5 h; 20% (**22**) and 70% (**23d**). c) Me_3SiOTf (0.1 equiv), H_2O (10 equiv), CH_2Cl_2, 0 °C, 0.5 h; 80%.

Construction of an oligoglucoside library directed to elicitor-active oligosaccharides: We applied the current iterative glycosylation method to the construction of an oligosaccharide library. We targeted the library of the phytoalexin elicitor-active heptasaccharide **24**,[37] because several structurally related β-(1,3)-D-glucans possess unique activities, including elicitor, antitumor[38] and RNA-recognition abilities (Figure 3).[39] As the structure of **24** could be envisaged as a repeating β-1,6-glycosidic bond between a monosaccharide

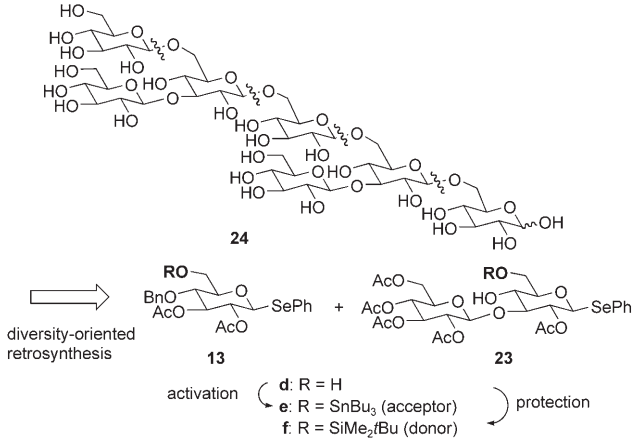
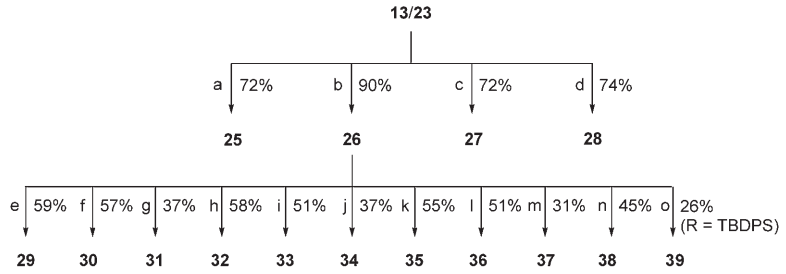


Figure 3. Diversity-oriented retrosynthetic analysis of the elicitor-active heptasaccharide **24**.

and a 1,3-linked disaccharide, the diversity-oriented retrosynthetic analysis led to the monosaccharide- and disaccharide-derived selenoglycosides **13** and **23**, respectively, as the common building blocks. When these selenoglycosides were used as glycosyl donors and acceptors, the C6 hydroxyl group was protected as the *tert*-butyldimethylsilyl ether and was activated by conversion to the tributylstannyl ether,[36] respectively.

The construction of an oligoglucoside library was initially examined with a combination of **13** and **23**. Thus, the glycosyl donors (**13f** or **23f**) were activated to the corresponding β-bromoglycosides upon treatment with bromine, followed by coupling with the glycosyl acceptors (**13e** or **23e**). In situ isomerization of the corresponding orthoesters afforded **25f**, **26f**, **27f** and **28f** depending on the donor/acceptor combinations (Scheme 4). The desired products formed in good to excellent yields in all cases. The silyl-protecting group in the products ($R = SiMe_2tBu$) was transformed to the corresponding tributylstannyl ether ($R = SnBu_3$), for use in the next glycosylation as the glycosyl acceptor, by treatment with aqueous hydrogen fluoride in acetonitrile followed by allyltributylstannane and a catalytic amount of triflic acid.

We next examined the second-generation synthesis of the library using **26** as a common scaffold. For example, two isomeric tetrasaccharides **29f** and **30f** were formed in good yield by the combination of **26** and **13**, employing **26f** and **13f** as glycosyl donors and **13e** and **26e** as acceptors, respectively. In contrast, two isomeric pentasaccharides, **31f** and **32f**, were obtained from a combination of **26** and **23**. Further combinatorial glycosylation of **26** with **25**, **26**, **27** and **28** afforded **33f**–**39f** composed of five, six and seven glucose units with different connectivity depending on the donor/ac-



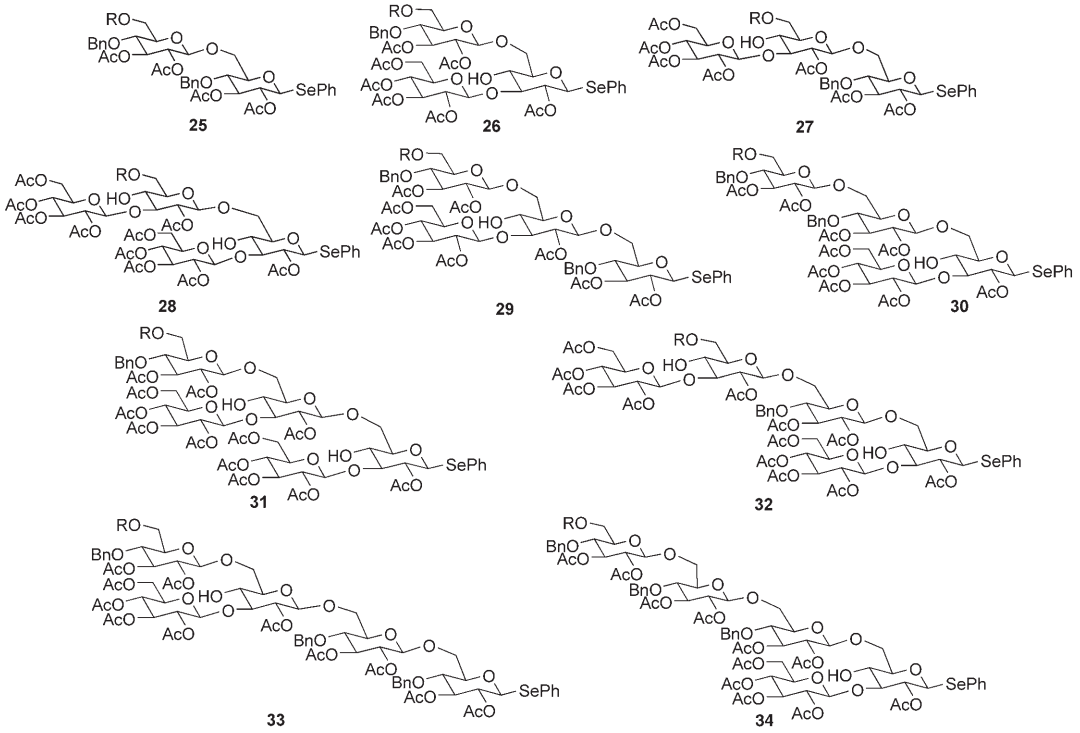
Scheme 4. Combinatorial synthesis of oligoglucosides. Glycosyl acceptor (0.8–2.0 equiv)/Br_2 (0.4–1.0 equiv), CH_2Cl_2, −23 °C→RT, 0.5 h, then glycosyl acceptor (1.0 equiv), RT, 0.1 h, Me_3SiOTf (0.1 equiv), 0 °C, 0.5 h. Glycosyl acceptor/donor: a) **13 f/13 e**, b) **13 f/23 e**, c) **23 f/13 e**, d) **23 f/23 e**, e) **26 f/13 e**, f) **13 f/26 e**, g) **26 f/23 e**, h) **23 f/26 e**, i) **26 f/25 e**, j) **25 f/26 e**, k) **26 f/26 e**, l) **26 f/27 e**, m) **27 f/26 e**, n) **26 f/28 e**, o) **28 f/26 e**. The yield was based on the donor for the synthesis of **31** and on the acceptor for all other cases. The sum of the desired O-glycoside and its desilylated product is given here (see text). See details in Experimental Section.

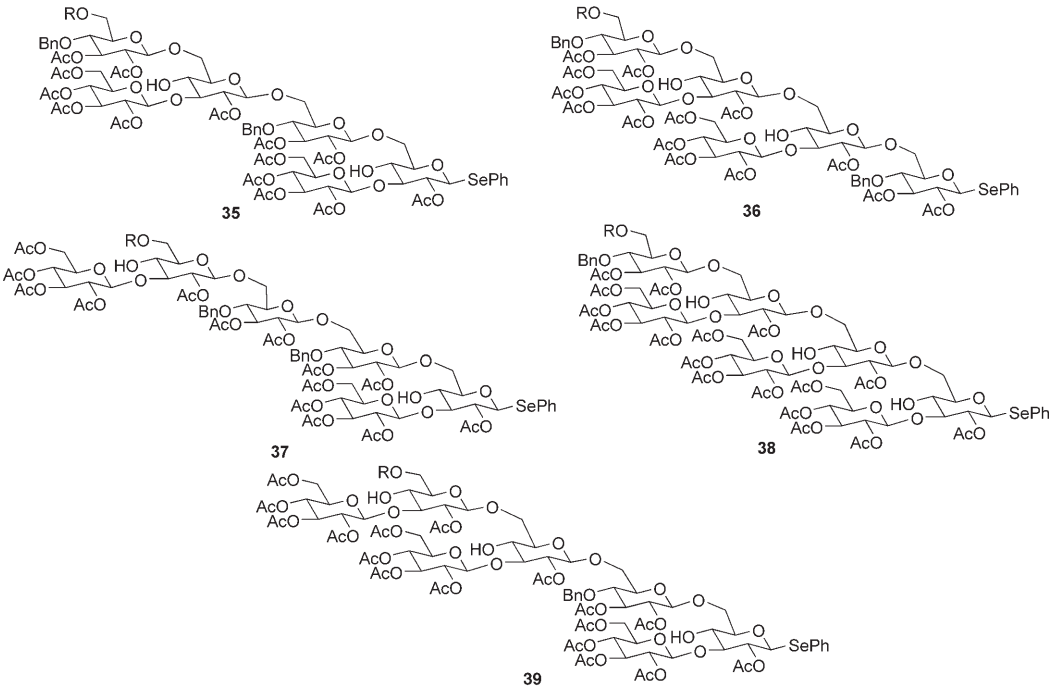
ceptor combinations. It is worth noting that all of the glycoside-bond formations were carried out under a single set of conditions, without any manipulations of the anomeric substituents. As all of the products were selenoglycosides, they could be used subsequently as glycosyl donors and acceptors to enhance the structural diversity. These results clearly demonstrate the power of iterative glycosylation for the construction of a stereochemically defined oligosaccharide library with extremely high structural diversity.

The coupling efficiencies were sometimes low. This is partly because the competitive desilylation of the glycosyl donors under the reaction conditions, and the *tert*-butyldiphenylsilyl-protecting group was used rather than the *tert*-butyldimethylsilyl group to avoid desilylation when **28 f** was used as the glycosyl donor. The low coupling efficiency could also be attributed to the low reactivity of the β-bromoglycosides compared to the conventional "glycosyl cation" intermediates, because of the strong covalent-bond character of the carbon–bromine bond. We believe that the coupling efficiency would be increased by detailed optimizations, including the use of more-reactive glycosyl cation equivalents as the intermediates.[14]

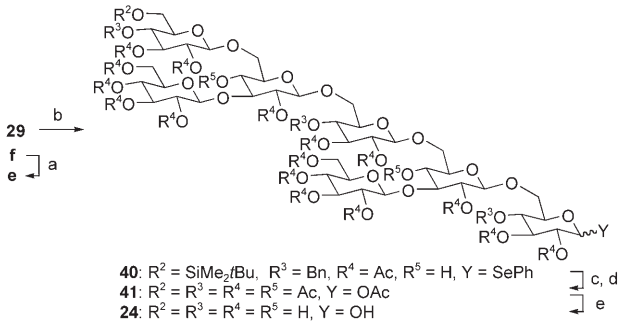
Synthesis of elicitor-active heptasaccharide: We investigated the synthesis of the elicitor-active heptasaccharide **24**.[37] Initially, we attempted the coupling of the glycosyl donor hexasaccharide **35 f** and the glycosyl acceptor monosaccharide **13 e**; however, the resulting orthoester formed in low yield (24%). The reactivities of glycosyl donors tend to decrease as the sugar moiety of the donor becomes bulkier, as quantitatively analyzed using the programmable approach.[7] Thus, the present results might have been due to the decreased reactivity of the β-bromoglycoside, which possesses six glucose units, compared with those of smaller analogues.

Next, we examined the coupling of trisaccharide donors and tetrasaccharide acceptors (Scheme 5). The silyl-protecting group in **29 f** was converted to the tributylstannyl group





(**29e**), which was coupled with the β-bromoglycoside generated from **26f** to give heptasaccharide **40** in 60% yield. The phenylselenyl group in **40** could be transformed to the reducing end sugar by the treatment of **40** with Br_2 followed by the addition of water. Hydrogenolysis of the benzyl group of the resulting hydroxyl glycoside, followed by acetylation, gave per-acetylated glycoside **41** as an approximately 1:1 mixture of α- and β-iosmers in 75% yield (three steps). Hydrolysis of the acetyl groups of **41** quantitatively afforded **24**.



Scheme 5. Synthesis of elicitor-active heptasaccharide. a) 5% aqueous HF/MeCN/CH_2Cl_2, RT, 12 h, 83%. CH_2=$CHCH_2SnBu_3$ (1.3 equiv), TfOH (0.3 equiv), CH_2Cl_2, rt, 2 h. b) **26f** (2.0 equiv)/Br_2 (1.0 equiv), CH_2Cl_2, 0°C, 0.5 h, then **29e** (1.0 equiv), RT, 1 h, then Me_3SiOTf (0.1 equiv), 0°C, 0.5 h, 60%. c) Br_2 (0.5 equiv), CH_2Cl_2, 0°C, 0.5 h, then H_2O (20 equiv), RT, 0.5 h. d) H_2 (50 atm), $Pd(OH)_2$/C, EtOH, 50°C, 16 h then Ac_2O (14 equiv), DMAP (2 equiv), Et_3N (20 equiv), CH_2Cl_2, RT, 16 h, 75% (3 steps). e) MeONa (25 equiv), MeOH, RT, 0.5 h, quant.

Summary

We have demonstrated that β-bromoglycosides serve as useful synthetic surrogates for the glycosyl cation species in the iterative glycosylation of selenoglycosides. The success of this method relies on the separation of the glycosylation reaction into two stages: activation to generate a glycosyl cation equivalent and subsequent coupling with a glycosyl acceptor. We have also shown that iterative glycosylation is suitable for the rapid synthesis of an oligosaccharide library with considerable structural diversity. Although there are several limitations to this method, such as the low reactivity of β-bromoglycosides and stereochemical control to form 1,2-*cis* glycosides, the concept presented here provides a new synthetic strategy for the generalized synthesis of oligosaccharides and their libraries.

Experimental Section

General methods: All reaction conditions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon atmosphere. ^{1}H NMR (300, 400, and 600 MHz) and ^{13}C NMR (75, 100, and 125 MHz) spectra were measured for a $CDCl_3$ solution of a sample. ^{1}H NMR spectra are reported in parts per million (δ) from internal tetramethylsilane, and ^{13}C NMR from $CDCl_3$ (77.0 ppm). IR spectra (absorption) are reported in cm^{-1}. Preparative HPLC was performed with GPC column by using $CHCl_3$ as eluent.

Materials: Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. MeCN, EtCN, CH_2Cl_2 were distilled successively from P_2O_5 and K_2CO_3 and stored over molecular sieves. DMF was dried over P_2O_5 and was distilled under reduced pressure over stored molecular sieves. Chloroform was passed through a pad of basic alumina before use.

Preparation of β-bromoglycosides

β-Bromoglycosides 2a

Bromine-promoted reaction: Bromine (8.0 mg, 0.050 mmol) at −45 °C was added to a solution of selenoglycoside **1a** (75.0 mg, 0.10 mmol) in CD_2Cl_2 (0.6 mL), and the resulting solution was slowly warmed up to room temperature over 30 min. ^{1}H NMR analysis revealed the selective formation of β-**2a** (α/β 3:97) in quantitative yield as judged by the addition of $(CHCl_2)_2$ as an internal standard. The β-bromoglycoside **2a** was sensitive toward hydrolysis, and the products were finally characterized after the reaction with glycosyl acceptors. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 4.20–4.68 (ddd, J = 9.6, 4.5, 3.0 Hz, 1H), 4.60 (dd, J = 12.9, 4.5 Hz, 1H), 4.74 (dd, J = 12.9, 3.0 Hz, 1H), 5.88–5.98 (m, 3H), 6.05 (d, J = 9.6 Hz, 1H), 7.36–7.65 (m, 17H), 7.91–8.16 (m, 8H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 62.88 (CH_2), 68.89 (CH), 73.60 (CH), 74.86 (CH), 77.26 (CH), 79.70 (CH), 128.88 128.94, 129.18, 129.30, 130.03, 130.11, 130.17, 130.23, 130.26, 130.41, 130.64, 133.73, 133.93, 134.10, 165.25 (C=O), 165.51 (C=O), 165.97 (C=O), 166.39 (C=O).

Tolylselenylbromide-promoted reaction: A solution of tolylselenylbromide (25.0 mg, 0.10 mmol) in CD_2Cl_2 (0.3 mL) was added at −45 °C to a solution of **1a** (75.0 mg, 0.10 mmol) in CD_2Cl_2 (0.3 mL), and the resulting solution was slowly warmed up to room temperature over 30 min. ^{1}H NMR analysis revealed the selective formation of β-**2a** (α/β 5:95) in quantitative yield as judged by the addition of $(CHCl_2)_2$ as an internal standard.

Methylglycoside 8a: Bromine (8.0 mg, 0.050 mmol) at −45 °C was added to a solution of **1a** (75.0 mg, 0.10 mmol) in CD_2Cl_2 (0.6 mL), and the resulting solution was slowly warmed up to room temperature over 30 min. Methanol (3.2 mg, 0.11 mmol) and 2,6-lutidine (10.8 mg, 0.10 mmol) were added, and the resulting mixture was stirred for 10 min and was quenched by addition of saturated aqueous $NaHCO_3$. The aqueous phase was extracted with Et_2O, and the combined organic extract was washed with saturated aqueous NaCl, dried over Na_2SO_4, and concentrated to give a crude oil, which was mainly consisted of orthoester **4a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.19–4.25 (ddd, J = 9.0, 4.8, 2.7 Hz, 1H), 4.44 (dd, J = 12.0, 4.8 Hz, 1H), 4.56 (dd, J = 12.0, 2.7 Hz, 1H), 4.87 (ddd, J = 3.9, 3.0, 0.9 Hz, 1H), 5.56 (d, J = 9.0 Hz, 1H), 5.83 (dd, J = 3.0, 1.5 Hz, 1H), 6.14 (d, J = 5.4 Hz, 1H), 7.48–8.17 (m, 20H).

The crude **4a** was dissolved in CD_2Cl_2 (0.6 mL), and TMSOTf (4.6 mg, 0.020 mmol) was added at 0 °C. After the resulting mixture was stirred for 15 min, saturated aqueous $NaHCO_3$ solution and Et_2O was added. The aqueous phase was extracted with Et_2O, and the combined organic extract was washed with saturated aqueous NaCl, dried over Na_2SO_4, and concentrated. Purification on silica gel afforded **8a** (58.6 mg, 96%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 4.17 (ddd, J = 9.6, 5.1, 3.3 Hz, 1H), 4.52 (dd, J = 12.0, 5.1 Hz, 1H), 4.66 (dd, J = 12.0, 3.3 Hz, 1H), 4.78 (d, J = 7.8 Hz, 1H), 5.54 (dd, J = 9.6, 7.8, Hz, 1H), 5.70 (t, J = 9.6 Hz, 1H), 5.93 (t, J = 9.6 Hz, 1H), 7.04–8.04 (m, 20H).

Iterative glycosylations

Selenoglycoside 13d: Et_3SiH (0.7 g, 6.0 mmol) and $PhBCl_2$ (1.1 g, 6.8 mmol) successively at −78 °C were added to a solution of phenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-selenoglucopyranoside[40] (985 mg, 2.0 mmol), molecular sieves 4 Å (7.5 g) and CH_2Cl_2 (25 mL), and the resulting mixture stirred for 30 min at this temperature. The reaction quenched by successive addition of Et_3N (5.0 mL) and MeOH (5.0 mL), and the resulting mixture was washed with saturated aqueous $NaHCO_3$ solution. After separation of the organic layer, the aqueous phase was extracted with ethyl acetate, and the combined organic extract was washed saturated aqueous NaCl solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a crude oil. Purification by flash chromatography (silica gel 100 g; elution with 30% ethyl acetate in hexane) afforded **13d** as a white solid (794 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (dd, J = 8.4, 5.4 Hz, 1H, OH), 1.93 (s, 3H), 2.07 (s, 3H), 3.45 (tt, J = 9.8, 4.0 Hz, 1H), 3.67 (t, J = 9.5 Hz, 1H), 3.68–3.75 (m, 1H), 3.91 (ddd, J = 12.3, 5.4, 2.4 Hz, 1H), 4.58 (d, J = 11.1 Hz, 1H), 4.63 (d, J = 11.4 Hz, 1H), 4.89–4.98 (m, 2H), 5.23 (ddd, J = 9.2, 5.8, 3.4 Hz, 1H), 7.22–7.40 (m, 8H), 7.55–7.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.73, 20.78, 61.44, 71.37, 74.75, 75.03, 75.65, 80.34, 80.83, 127.03, 127.86, 127.97, 128.46, 129.08, 134.92, 137.37, 169.63, 170.03; IR (KBr): $\tilde{\nu}$ = 3487 (m), 1748 (s), 1727 (s), 1368, 1254, 1086, 1046, 739 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{23}H_{27}O_7Se$: 495.0922; found 495.0923 $[M+H]^+$; elemental analysis calcd (%) for $C_{23}H_{26}O_7Se$: C 55.99, H 5.31; found: C 55.79, H 5.19.

Selenoglycoside 13f: A solution of selenoglycoside **13d** (2.5 g, 5.1 mmol), *t*$BuMe_2SiCl$ (1.2 g, 7.6 mmol), DMAP (65.7 mg, 0.54 mmol) and Et_3N (0.80 g, 7.9 mmol) in THF (12.0 mL) was heated at 50 °C for 12 h. To this mixture was added saturated aqueous $NaHCO_3$ solution, and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a crude mixture. Purification by flash chromatography (silica gel 100 g; elution with 17% ethyl acetate in hexane) afforded **13f** as a white powder (3.0 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10 (s, 3H), 0.12 (s, 3H), 0.94 (s, 9H), 1.89 (s, 3H), 2.04 (s, 3H), 3.37 (dt, J = 9.6, 2.3 Hz, 1H), 3.87 (dd, J = 11.7, 3.3 Hz, 1H), 3.92 (dd, J = 11.9, 2.3 Hz, 1H), 4.58 (d, J = 11.4 Hz, 1H), 4.66 (d, J = 11.4 Hz, 1H), 4.84–4.93 (m, 2H), 5.20 (tt, J = 9.4, 7.0 Hz, 1H), 7.21–7.36 (m, 8H), 7.58–7.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.45, −5.08, 18.29, 20.76, 20.82, 25. 94, 134.95, 137.85, 169.62, 170.12; IR (KBr): $\tilde{\nu}$ = 2930, 2857, 1752 (s), 1246 (s), 1065, 837, 743 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{29}H_{41}O_7SeSi$: 609.1787; found 609.1810 $[M+H]^+$; elemental analysis calcd (%) for $C_{29}H_{40}O_7SeSi$: C 57.32, H 6.63; found: C 57.32, H 6.75.

General procedures for the preparation of stannyl ethers from sugar alcohols

Preparation of stannyl ether 13e: Selenoglycoside **13d** (495 mg, 1.0 mmol) was added at room temperature to a solution of allyltributyltin (427 mg, 1.3 mmol) and TfOH (45.1 mg, 0.30 mmol) in CH_2Cl_2 (7.0 mL), and the resulting solution was stirred for 2 h at this temperature. To the solution was added 2,6-lutidine (32.2 mg, 0.30 mmol) at this temperature. This solution was used for the glycosyl-coupling reaction without further purification.

Disaccharide 17g

One-pot procedures: Bromine (23.9 mg, 0.15 mmol) was added at −25 °C to a solution of **1a** (224 mg, 0.30 mmol) in CH_2Cl_2 (0.4 mL), and the resulting solution was slowly warmed to room temperature over 30 min. To this solution was added **12e** (181 mg, 0.20 mmol) and 2,6-lutidine (6.4 mg, 0.060 mmol), and the resulting mixture was stirred for 12 h at room temperature. To this solution was added TfOH (3.1 mg, 0.020 mmol) at 0 °C, and the resulting mixture was stirred for 15 min. After the usual workup (addition of saturated aqueous $NaHCO_3$, extraction by Et_2O, washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentration), purification by flash column chromatography (elution with 25% ethyl acetate in hexane) afforded **17g** (158 mg, 0.13 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.62–3.65 (m, 1H), 3.71 (t, J = 9.3 Hz, 1H), 3.89 (dd, J = 11.6, 4.8 Hz, 1H), 4.10 (ddd, J = 9.6, 4.8, 3.3 Hz, 1H), 4.17 (dd, J = 11.6, 1.6 Hz, 1H), 4.30 (d, J = 10.8 Hz, 1H), 4.33 (d, J = 10.8 Hz, 1H),4.50 (dd, J = 12.1, 4.8 Hz, 1H), 4.73 (dd, J = 12.3, 3.3 Hz, 1H), 4.96 (d, J = 9.9 Hz, 1H), 4.96 (d, J = 8.2 Hz, 1H), 5.32 (t, J = 9.7 Hz, 1H), 5.56–5.62 (m, 2H), 5.71 (t, J = 9.7 Hz, 1H), 5.90 (t, J = 9.7 Hz, 1H), 6.92–6.96 (m, 2H), 7.09–7.14 (m, 5H), 7.27–7.57 (m, 20H), 7.81–7.95 (m, 10H), 8.03–8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.24 (CH_3), 62.94 (CH_2), 67.92 (CH_2), 69.65 (CH), 71.70 (CH), 71.95 (CH), 72.35 (CH), 72.99 (CH), 74.67 (CH_2), 75.85 (CH), 76.27 (CH), 80.01 (CH), 81.37 (CH), 101.16 (CH), 123.63 (C), 127.77, 127.79, 128.2–128.5 [128.24, 128.28, 128.32, 128.38, 128.40, 128.42], 128.85 (C), 129.26 (C), 129.39 (C), 129.43 (C), 129.62 (C), 129.7–130.0 [129.71, 129.77, 129.80, 129.84, 129.91], 133.08 (CH), 133.11 (CH), 133.19 (CH), 133.24 (CH), 133.43 (CH), 135.51 (CH), 137.12 (C), 138.52 (C), 165.03 (C=O), 165.18 (C=O), 165.20 (C=O), 165.56 (C=O), 165.83 (C=O), 166.09 (C=O); IR (KBr): $\tilde{\nu}$ = 1725, 1601, 1491, 1451, 1277 (br), 1069, 1026, 710 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{68}H_{59}O_{16}Se$: 1211.2968; found 1211.2959 $[M+H]^+$.

Stepwise procedures: Bromine (59.9 mg, 0.37 mmol) was added at −25 °C to a solution of **1a** (562 mg, 0.75 mmol) in CH_2Cl_2 (1.7 mL), and the resulting solution was slowly warmed to room temperature over 30 min. To this solution was added **12d** (316 mg, 0.50 mmol) and 2,6-lutidine (53.5 mg, 0.50 mmol), and the resulting mixture was stirred for 12 h at room temperature. After the usual workup, purification by flash column

chromatography (elution with 25% ethyl acetate in hexane) afforded orthoester **12** (484 mg, 41 mmol, 81%).

TMSOTf (1.1 mg, 0.0050 mmol) and 2,6-di-*tert*-butylpyridine (0.094 mg, 0.0050 mmol) were added at 0°C to a solution of the orthoester **12** (584 mg, 0.49 mmol) in 1,2-dichroloethane (2.5 mL). The resulting mixture was stirred for 30 min, and was quenched with saturated aqueous $NaHCO_3$. After the usual work up, purification by flash chromatography afforded **17g** (555 mg, 95%).

Disaccharide 18: Bromine (12.1 mg, 0.076 mmol) at −23°C was added to a solution of selenoglycoside **14** (110 mg, 0.15 mmol) in CH_2Cl_2 (1.5 mL), and the resulting solution was slowly warmed to room temperature over 30 min. To this solution was added 2,6-lutidine (3.2 mg, 0.030 mmol) and **13e**, which was prepared by mixing **13d** (49.4 mg, 0.10 mmol), allyltributyltin (43.0 mg, 0.13 mmol), and TfOH (4.6 mg, 0.031 mmol) in CH_2Cl_2 (0.8 mL), and the resulting mixture was stirred for 30 min at room temperature. To this mixture was added TMSOTf (2.3 mg, 0.010 mmol) at 0°C, and the resulting mixture was stirred for 15 min. Triethylamine (0.05 mL) followed by aqueous saturated $NaHCO_3$ solution were added, and organic layer was separated. The aqueous phase was extracted with ethyl acetate, and the combined organic extract was washed with aqueous saturated NaCl solution, dried over $MgSO_4$, and concentrated to give a crude mixture. Purification by flash chromatography (silica gel 10 g; elution with 30% ethyl acetate in hexane) afforded **18** (60.9 mg, 0.057 mmol, 57%) as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (s, 3H), 2.03 (s, 3H), 3.45–3.58 (m, 2H), 3.85 (dd, J=11.4, 4.5 Hz, 1H), 4.18–4.28 (m, 2H), 4.29 (d, J=11.1 Hz, 1H), 4.37 (d, J=11.1 Hz, 1H), 4.43 (dd, J=11.4, 6.6 Hz, 1H), 4.57–4.91 (m, 3H), 5.13 (br t, J= 8.1 Hz, 1H), 5.59 (dd, J=10.5, 3.6 Hz, 1H), 5.85 (dd, J=10.5, 3.6 Hz, 1H), 5.99 (br d, J=2.7 Hz, 1H), 7.00–7.08 (m, 2H), 7.20–7.67 (m, 20H), 7.77–7.83 (m, 2H), 7.87–7.94 (m, 2H), 8.01–8.06 (m, 2H), 8.09–8.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.72 (CH_3), 20.81 (CH_3), 61.89 (CH_2), 67.71 (CH_2), 68.09 (CH), 69.67 (CH), 71.20 (CH), 71.35 (CH), 71.67 (CH), 74.65 (CH_2), 75.59 (CH), 75.91 (CH), 79.75 (CH), 80.66 (CH), 101.35 (CH), 127.03 (C), 127.50 (CH), 127.88 (CH), 128.29 (CH), 128.41 (CH), 128.47 (CH), 128.653 (CH), 128.657 (C), 129.02 (C), 129.12 (CH), 129.20 (C), 129.352 (C), 129.70 (CH), 129.78 (CH), 130.02 (CH), 133.21 (CH), 133.30 (CH), 133.59 (CH), 135.12 (CH), 137.34 (C), 165.11 (C=O), 165.58 (C=O, 2C), 166.00 (C=O), 164.48 (C=O), 169.95 (C=O); IR (KBr): $\tilde{\nu}$ = 1734, 1264, 1101, 1090, 1069, 1026, 710 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{57}H_{53}O_{16}Se$: 1073.2499; found 1073.2428 $[M+H]^+$.

Disaccharide 19: Bromine (8.0 mg, 0.050 mmol) at −45°C was added to a solution of **1a** (75.0 mg, 0.10 mmol) in CD_2Cl_2 (0.6 mL), and the resulting solution was slowly warmed to room temperature over 30 min. **16** (60.4 mg, 0.10 mmol) in CD_2Cl_2 (0.6 mL) and 2,6-lutidine (10.8 mg, 0.10 mmol)were added, and the resulting mixture was stirred for 4 h at room temperature, and was quenched with saturated aqueous $NaHCO_3$. After the usual workup, a crude oil was obtained. To a solution of the crude mixture in CD_2Cl_2 (0.6 mL) was added TMSOTf (2.3 mg, 0.010 mmol) at 0°C, and the resulting mixture was stirred for 15 min, and was quenched with saturated aqueous $NaHCO_3$. After the usual workup, purification by flash chromatography afforded **19** (71.0 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (s, 3H), 2.34 (s, 3H), 3.36–3.43 (m, 3H), 3.54 (dd, J=8.8 Hz, 1H), 3.84 (dd, J=11.2, 4.3 Hz, 1H), 4.06 (ddd, J=9.7, 5.0, 3.3 Hz, 1H), 4.11–4.15 (m, 1H), 4.40 (d, J=11.0 Hz), 4.49 (dd, J=12.1, 5.0 Hz, 1H), 4.57 (d, J=11.0 Hz, 1H), 4.61–4.66 (m, 2H), 4.70 (d, J=9.7 Hz, 1H), 4.71 (d, J=11.0 Hz, 1H), 4.79 (d, J= 9.5 Hz, 1H), 4.82 (d, J=10.1 Hz, 1H), 4.94 (d, J=7.9 Hz, 1H), 5.57 (dd, J=9.7, 7.9 Hz, 1H), 5.68 (dd, J=9.7 Hz, 1H), 5.86 (dd, J=9.7 Hz, 1H), 7.07–8.03 (m, 34H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.20 (CH_3), 21.20 (CH_3), 63.15 (CH_2), 67.98 (CH_2), 69.80 (CH_2), 71.93 (CH), 72.20 (CH), 73.06 (CH), 74.85 (CH_2), 75.12 (CH_2), 75.58 (CH_2), 77.50 (CH), 79.76 (CH), 81.10 (CH), 82.70 (CH), 86.64 (CH), 101.05 (CH), 124.44, 127.51, 127.57, 127.64, 127.70, 127.75, 127.82, 127.91, 127.94, 128.12, 128.14, 128.24, 128.30, 128.35, 128.38, 128.39, 128.48, 128.81, 128.88, 128.89, 129.25, 129.62, 129.73, 129.77, 129.80, 129.83, 129.99, 133.06, 133.11, 133.20, 133.40, 135.01, 137.89, 138.06, 138.10, 138.34, 164.99 (C=O), 165.21 (C=O), 165.81 (C=O), 166.13 (C=O); IR (KBr): $\tilde{\nu}$ = 1740, 1711, 1453, 1284, 1264, 1109, 1090, 1028, 708 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{68}H_{62}O_{14}SeNa$: 1205.3202; found 1205.3225 $[M+Na]^+$.

Trisaccharide 17h: Bromine (23.9 mg, 0.15 mmol) was added at −25°C to a solution of **17g** (359 mg, 0.30 mmol) in CH_2Cl_2 (0.9 mL), and the resulting solution was slowly warmed up to room temperature over 30 min. To this solution was added **12d** (408 mg, 0.45 mmol) and 2,6-lutidine (48.2 mg, 0.45 mmol), and the resulting mixture was stirred for 12 h at room temperature. After the usual workup, purification by flash column chromatography (elution with 30% ethyl acetate in hexane) afforded the corresponding orthoester (437 mg).

To a solution of the orthoester (289 mg, 0.17 mmol) in 1,2-dichroloethane (0.85 mL) was added TfOH (2.5 mg, 0.017 mmol) at 0°C, and the resulting mixture was stirred for 10 min. After the usual workup, purification by flash chromatography afforded **17h** (272 mg, 81% overall yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52 (br ddd, J=10.0, 3.6, 1.6, Hz, 1H), 3.64–3.71 (m, 3H), 3.82 (t, J=9.3 Hz, 1H), 3.88 (dd, J=11.6, 5.9 Hz, 1H), 4.10 (br dd, J=10.0, 1.6 Hz, 1H), 4.16 (d, J=13.4 Hz, 1H), 4.20 (d, J=13.4 Hz, 1H), 4.22–4.29 (m, 2H), 4.40 (s, 2H), 4.50 (dd, J=12.1, 4.9 Hz, 1H), 4.60 (d, J=7.9 Hz, 1H), 4.68 (dd, J=12.3, 3.3 Hz, 1H), 5.03 (d, J=9.9 Hz, 1H), 5.06 (d, J=7.8 Hz, 1H), 5.28 (t, J=9.7 Hz, 1H), 5.41 (dd, J=9.7, 7.9 Hz, 1H), 5.57 (t, J=9.4 Hz, 1H), 5.60 (dd, J=9.9, 7.7 Hz, 1H), 5.66 (t, J=9.3 Hz, 1H), 5.72 (t, J=9.7 Hz, 1H), 6.0 (t, J=9.7 Hz, 1H), 6.79–6.82 (m, 2H), 7.00–7.54 (m, 41H), 7.78–7.96 (m, 15H), 7.99–8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.00 (CH_2), 67.14 (CH_2), 68.42 (CH_2), 69.53 (CH), 71.67 (CH), 72.09 (CH), 72.14 (CH), 72.29 (CH), 72.77 (CH), 74.66 (CH_2), 74.67 (CH_2), 74.97 (CH), 75.13 (CH), 75.55 (CH), 76.27 (CH), 76.33 (CH), 77.21 (CH), 79.57 (CH), 81.20 (CH), 100.57 (CH), 101.57 (CH), 123.45 (C), 127.56 (CH), 127.61 (CH), 127.85 (CH), 127.90 (CH), 128.10 (CH), 128.2–128.5 [128.21, 128.22, 128.29, 128.36, 128.44], 128.84 (C), 128.85 (C), 129.35 (C), 129.37 (C), 129.39 (C), 129.41 (C), 129.54 (C), 129.6–130.0 [129.69, 129.76, 129.82, 129.94], 132.9–133.3 [132.97, 133.04, 133.16, 133.21, 133.30], 135.58 (CH), 137.08 (C), 137.22 (C), 138.45 (C), 165.01 (C=O), 165.05 (C=O), 165.08 (C=O), 165.14 (C=O), 165.58 (C=O), 165.84 (C=O), 166.04 (C=O); IR (KBr): $\tilde{\nu}$ = 1732, 1601, 1452, 1271 (br), 1092 (br), 708 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{94}H_{80}O_{23}SeNa$: 1679.4153; found 1679.4164 $[M+Na]^+$.

Tetrasaccharide 17i: Bromine (12.1 mg, 0.075 mmol) was added at −25°C to a solution of **17h** (248 mg, 0.15 mmol) in CH_2Cl_2 (0.5 mL), and the resulting solution was slowly warmed up to room temperature over 30 min. To this solution was added **12d** (205 mg, 0.23 mmol) and 2,6-lutidine (7.3 mg, 0.068 mmol), and the resulting mixture was stirred for 12 h at room temperature. After the usual workup, purification by flash column chromatography (elution with 30% ethyl acetate in hexane) afforded the corresponding orthoester (203 mg).

To a solution of the crude orthoester (41.6 mg) in CH_2Cl_2 (0.15 mL) was added TfOH (0.33 mg, 0.0026 mmol) at 0°C, and the resulting mixture was stirred for 15 min. The reaction was quenched by addition of aqueous saturated $NaHCO_3$ solution. After the usual workup, purification by flash chromatography afforded **17i** (34.1 mg, 56% overall yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40–3.46 (m, 1H), 3.62–3.82 (m, 7H), 3.89 (dd, J=11.4, 6.4 Hz, 1H), 3.97 (d, J=10.8 Hz, 1H), 4.03 (d, J= 10.4 Hz, 1H), 4.11–4.27 (m, 5H), 4.32–4.36 (m, 3H), 4.54–4.65 (m, 3H), 4.71 (d, J=7.9 Hz, 1H), 4.32 (d, J=7.9 Hz, 1H), 5.10 (d, J=10.1 Hz, 1H), 5.31 (t, J=9.7 Hz, 1H), 5.39 (dd, J=11.0, 7.9 Hz 1H), 5.39 (t, J= 8.1 Hz, 1H), 5.62 (t, J=9.5 Hz, 1H), 5.63–5.74 (m, 3H), 5.77 (t, J= 9.7 Hz, 1H), 5.96 (t, J=9.7 Hz, 1H), 6.78 (d, J=3.6 Hz, 1H), 6.93–7.06 (m, 8H), 7.11–7.16 (m, 8H), 7.20–7.56 (m, 39H), 7.63–7.67 (m, 2H), 7.79–7.98 (m, 23H), 8.03–8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.4 (CH_2), 68.2 (CH_2), 68.4 (CH_2), 69.8 (CH), 71.6 (CH), 72.1 (CH), 72.2 (CH), 72.5 (CH), 72.5 (CH), 72.8 (CH), 74.2 (CH), 74.5 (CH_2), 74.6 ($2CH_2$), 74.9 (CH), 75.2 (CH), 75.4 (CH), 76.0 (CH), 76.2 (CH), 76.5 (CH), 76.6 (CH), 79.3 (CH), 81.1 (CH), 101.0 (CH), 101.3 (CH), 102.1 (CH), 127.4 (C), 127.6 (CH), 127.8 (CH), 127.8 (CH, 2C), 128.1 (CH, 2C), 128.2–128.3 [128.2, 128.2, 128.2, 128.3], 128.4 (CH), 128.5 (CH),128.6 (CH), 128.8 (C), 128.9 (C), 129.0 (CH), 129.4 (C), 129.5–129.6 [129.5, 129.5, 129.5, 129.5, 129.5, 129.6], 129.7–129.9 [129.7, 129.7, 129.8, 129.9, 129.9], 132.8 (CH), 132.9–133.3 [132.9, 133.0, 133.1, 133.2, 133.3,

133.3], 137.2 (C), 137.3 (C), 164.9 (C=O), 164.9 (C=O), 165.1 (C=O), 165.2 (C=O), 165.2 (C=O), 165.6 (C=O), 165.6 (C=O), 165.9 (C=O), 166.1 (C=O); IR (KBr): $\tilde{\nu}$ = 1732, 1273, 1105, 1094, 1069, 1026, 708 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{121}H_{104}O_{30}SeNa$: 2139.5675; found 2139.5637 $[M+Na]^+$.

Stannylenacetal 20: A mixture of phenyl 4,6-*O*-benzylidene-β-D-selenoglucopyranoside[40] (4.1 g, 10.0 mmol) and di-*n*-butyltin oxide (2.8 g, 11.0 mmol) in a mixture of benzene and methanol[41] (55.0 and 7.0 mL, respectively) was heated under reflux for 2 h at 90 °C. Removal of solvent under reduced pressure afforded crude **20** (6.0 g), which was used for the glycosyl-coupling reaction without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (dt, *J* = 16.6, 7.3 Hz, 6H), 1.08–1.53 (m, 8H), 3.18 (t, *J* = 8.9 Hz, 1H), 3.30 (t, *J* = 8.7 Hz, 1H), 3.41 (t, *J* = 9.2 Hz, 1H), 3.55 (distorted dt, *J* = 13.9, 4.7 Hz, 1H), 3.79 (t, *J* = 10.4 Hz, 1H), 4.33 (dd, *J* = 10.5, 5.1 Hz, 1H), 4.97 (d, *J* = 9.3 Hz, 1H), 5.38 (s, 1H), 7.20–7.43 (m, 8H), 7.60–7.68 (m, 2H).

Disaccharide 23d: Bromine (0.30 g, 1.9 mmol) was added at −23 °C to a solution of **6b**[42] (1.8 g, 3.8 mmol) in CH_2Cl_2 (10.0 mL), and the resulting solution was slowly warmed to room temperature over 30 min. To this solution was added **20** (1.6 g, 2.5 mmol), and the resulting mixture was stirred for 5 h. After the usual workup, the crude mixture was treated with DMAP (30.5 mg, 0.25 mmol), Et_3N (378 mg, 3.8 mmol) and Ac_2O (383 mg, 3.8 mmol) in CH_2Cl_2 (10.0 mL) at room temperature for 8 h, and the reaction mixture was quenched by addition of aqueous saturated $NaHCO_3$ solution. After the usual workup, purification by flash column chromatography (elution with 40% ethyl acetate in hexane) followed by recrystllization from ethyl acetate/hexane afforded **21** (1.7 g, 88%).

To a solution of **21** (0.195 g, 0.25 mmol) in CH_2Cl_2 was added TMSOTf (5.6 mg, 0.025 mmol) at 0 °C, and the resulting mixture was stirred for 30 min. To this solution was added water (45.1 mg, 2.5 mmol) and the resulting mixture was stirred for 30 min. Et_3N (0.03 mL) followed by aqueous saturated $NaHCO_3$ solution were added, and organic layer was separated. After the usual workup, purification by flash column (elution with 50% ethyl acetate in hexane) afforded **23d** (0.122 g, 0.18 mmol, 70%) and **22** (39 mg, 0.050 mmol), which was hydrolyzed to **23d** upon treatment of water (10 equiv) and TMSOTf (0.1 equiv) in CH_2Cl_2 in 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 3.37 (ddd, *J* = 8.9, 5.4, 3.5 Hz, 1H), 3.46 (s, 1H, OH), 3.55 (t, *J* = 9.0 Hz, 1H), 3.61 (t, *J* = 8.4 Hz, 1H), 3.68–3.81 (m, 3 H containing OH), 3.93 (ddd, *J* = 11.5, 6.9, 3.9 Hz, 1H), 4.19 (br d, *J* = 3.9 Hz, 2H), 4.58 (d, *J* = 8.1 Hz, 1H), 4.82 (d, *J* = 9.9 Hz, 1H), 4.96–5.10 (m, 3H), 5.20 (t, *J* = 9.3 Hz, 1H), 7.25–7.38 (m, 3H), 7.53–7.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.32 (CH_3), 20.50 (CH_3, 2C), 20.58 (CH_3), 21.07 (CH_3), 61.48 (CH_2), 62.76 (CH_2), 68.16 (CH), 68.83 (CH), 70.64 (CH), 71.50 (CH), 71.91 (CH), 72.46 (CH), 80.92 (CH), 81.40 (CH), 85.84 (CH), 100.91 (CH), 127.70 (C), 128.32 (CH), 129.12 (CH, 2C), 134.41 (CH, 2C), 169.15 (C=O), 169.25 (C=O, 2C), 170.24 (C=O), 170.56 (C=O); IR (KBr): $\tilde{\nu}$ = 3492, 1752, 1439, 1375, 1233 (br), 1038 (br), 905, 743, 695, 600 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{28}H_{37}O_{15}Se$, 693.1298; found 693.1299 $[M+H]^+$.

Disaccharide 23f: A solution of disaccharide **23d** (422 mg, 0.61 mmol), *t*$BuMe_2SiCl$ (110 mg, 0.73 mmol), DMAP (7.5 mg, 0.061 mmol), and Et_3N (74.2 mg, 0.73 mmol) in THF (1.6 mL) was heated at 50 °C for 3 h. To this mixture was added saturated aqueous $NaHCO_3$ solution, and the aqueous phase was extracted with ethyl acetate, and the combined organic extract was washed saturated aqueous NaCl solution, dried over $MgSO_4$, filtered and concentrated. Purification of the crude mixture by flash chromatography (silica gel 21.2 g; elution with 40% ethyl acetate in hexane) afforded **23f** as a white powder (456 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 2.00 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.08 (s, 3H), 2.13 (s, 3H), 3.32 (br ddd, *J* = 7.5, 5.4, 1.5 Hz, 1H), 3.37 (s, 1H), 3.53 (t, *J* = 9.0 Hz, 1H), 3.59 (t, *J* = 8.4 Hz, 1H), 3.74–3.83 (m 1H), 3.78 (dd, *J* = 11.9, 5.6 Hz, 1H), 3.99 (dd, *J* = 11.4, 1.8 Hz, 1H), 4.16 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.22 (dd, *J* = 12.6, 5.1 Hz, 1H), 4.59 (d, *J* = 7.8 Hz, 1H), 4.80 (d, *J* = 9.9 Hz, 1H), 4.98 (dd, *J* = 9.9, 7.8 Hz, 1H), 5.01 (dd, *J* = 9.6, 8.1, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 5.19 (t, *J* = 9.3 Hz, 1H), 7.22–7.35 (m, 3H), 1.56–7.63; ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.37 (CH_3), −5.31 (CH_3), 18.36 (CH_3), 20.32 (CH_3), 20.49 (CH_3), 20.56, 21.08 (CH_3), 25.09 (CH_3, 3C), 61.53 (CH_2), 62.88 (CH_2), 68.09 (CH), 68.18 (CH), 70.64 (CH), 71.53 (CH), 71.85 (CH), 72.52 (CH), 81.98 (CH, 2C), 86.05 (CH), 100.93 (CH), 127.80 (CH), 128.76 (C), 128.94 (CH, 2C), 133.83 (CH, 2C), 169.16 (C=O), 169.22 (C=O), 169.28 (C=O), 170.23 (C=O), 170.54 (C=O); IR (KBr): $\tilde{\nu}$ = 3500, 2957, 1752, 1464, 1374, 1231, 1065, 1038, 837, 779 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{34}H_{51}O_{15}SeSi$: 807.2166; found 807.2162 $[M+H]^+$.

General procedure for the construction of the oligoglucoside library

Disaccharide 25f: Bromine (120 mg, 0.75 mmol) at −23 °C was added to a solution of **13f** (911 mg, 1.5 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was slowly warmed to room temperature over 30 min. To this solution was added a CH_2Cl_2 solution of **13e**, which was prepared from **13d** (495 mg, 1.0 mmol), allyltributyltin (427 mg, 1.3 mmol), TfOH (45.1 mg, 0.30 mmol) in CH_2Cl_2 (7.0 mL), and the resulting mixture was stirred for 10 min at room temperature. To this mixture was added TMSOTf (22.2 mg, 0.10 mmol) at 0 °C, and the resulting mixture was stirred for 15 min and was quenched by addition of Et_3N (0.2 mL) and then saturated aqueous $NaHCO_3$ solution. After separation of the organic layer, the aqueous phase was extracted with ethyl acetate, and the combined organic extract was washed saturated aqueous NaCl, dried over $MgSO_4$, filtered and concentrated to give a crude oil. Purification by flash chromatography (silica gel 95 g; elution with 25% ethyl acetate in hexane) afforded **25f** as a white powder (683 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 1.90 (s, 3H), 1.91 (s, 3H), 1.93 (s, 3H), 2.02 (s, 3H), 3.29 (br dt, *J* = 9.7, 2.9 Hz, 1H), 3.52 (ddd, *J* = 9.5, 5.0, 1.5 Hz, 1H), 3.61 (t, *J* = 9.5 Hz, 1H), 3.71 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.79 (t, *J* = 9.5 Hz, 1H), 3.87 (dd, *J* = 11.9, 2.4 Hz, 1H), 3.91 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.04 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.51 (d, *J* = 8.1 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.83 (d, *J* = 10.1 Hz, 1H), 4.86–4.91 (m, 2H), 5.18 (t, *J* = 9.6 Hz, 1H), 5.18 (t, *J* = 8.8 Hz, 1H), 7.18–7.35 (m, 13H), 7.54–7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.36 (CH_3), −4.91 (CH_3), 18.34 (C), 20.75 (CH_3), 20.78 (CH_3), 20.80 (CH_3, 2C), 25.93 (CH_3, 3C), 61.63 (CH_2), 68.00 (CH_2), 71.39 (CH), 72.17 (CH), 74.72 (CH_2, 2C), 75.07 (CH), 75.30 (CH), 75.78 (CH), 75.81 (CH), 75.88 (CH), 79.84 (CH), 81.35 (CH), 100.73 (CH), 127.62 (C), 127.73 (CH, 2C), 127.85 (CH), 127.88 (CH, 2C), 127.99 (CH), 128.33 (CH), 128.46 (CH, 2C), 128.51 (CH, 2C), 129.13 (CH, 2C), 134.69 (CH, 2C), 137.4 (C), 138.00 (C), 169.57 (C=O), 169.70 (C=O), 169.97 (C=O), 170.25 (C=O); IR (KBr): $\tilde{\nu}$ = 3547, 1754, 1375, 1240, 1219, 1049 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{46}H_{61}O_{14}SeSi$: 945.2996; found 945.2971 $[M+H]^+$; elemental analysis calcd (%) for $C_{46}H_{60}O_{14}SeSi$: C 58.53, H 6.41; found: C 58.25, H 6.41.

Trisaccharide 26f: Glycosyl donor **13f** (121 mg, 0.20 mmol) and glycosyl acceptor **23d** (69.2 mg, 0.10 mmol); product **26f** (103 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 3H), 0.09 (s, 3H), 0.92 (s, 9H), 1.92 (s, 3H), 1.93 (s, 3H), 2.00 (s, 3H), 2.026 (s, 3H), 2.033 (s, 3H), 2.08 (s, 3H), 2.12 (s, 3H), 3.31–3.37 (m, 1H), 3.35 (s, 1H, OH), 3.40–3.50 (m, 2H), 3.56 (t, *J* = 8.5 Hz, 1H), 3.67 (dd, *J* = 11.6, 6.1 Hz, 1H), 3.76 (t, *J* = 9.5 Hz, 1H), 3.75–3.81 (m, 1H), 3.85–3.92 (m, 2H), 4.20–4.52 (m, 3H), 4.557 (d, *J* = 8.1 Hz, 1H), 4.563 (d, *J* = 8.1 Hz, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 10.4 Hz, 1H), 4.85 (dd, *J* = 9.6, 8.1 Hz, 1H), 4.94 (dd, *J* = 10.1, 9.0 Hz, 1H), 4.99 (dd, *J* = 9.7, 8.1 Hz, 1H), 5.05 (t, *J* = 9.7 Hz, 1H), 5.18 (t, *J* = 9.5 Hz, 1H), 5.20 (t, *J* = 9.5 Hz, 1H), 7.23–7.37 (m, 8H), 7.52–7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.41 (CH_3), −4.95 (CH_3), 18.36 (C), 20.32 (CH_3), 20.51 (CH_3, 2C), 20.61 (CH_3), 20.72 (CH_3), 20.82 (CH_3), 21.09 (CH_3), 25.93 (CH_3, 3C), 61.59 (CH_2), 61.70 (CH_2), 68.30 (CH), 68.32 (CH), 68.77 (CH_2), 70.67 (CH), 71.43 (CH), 71.98 (CH), 72.16 (CH), 72.55 (CH), 74.66 (CH_2), 74.99 (CH), 75.44 (CH), 75.72 (CH), 80.73 (CH), 81.77 (CH), 85.83 (CH), 100.93 (CH), 100.96 (CH), 127.84 (CH), 127.90 (CH, 2C), 128.12 (CH), 128.23 (C), 128.45 (CH, 2C), 129.16 (CH, 2C), 134.13 (CH, 2C), 138.00 (C), 169.05 (C=O), 169.21 (C=O), 169.23 (C=O), 169.92 (C=O), 170.21 (C=O), 170.23 (C=O), 170.54 (C=O); IR (KBr): $\tilde{\nu}$ = 3498, 2950, 2790, 1754, 1375, 1223 (br), 1048 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{51}H_{71}O_{22}SeSi$: 1143.3370; found 1143.3350 $[M+H]^+$.

Trisaccharide 27f: Glycosyl donor **23f** (322 mg, 0.40 mmol) and glycosyl acceptor **13d** (98.9 mg, 0.20 mmol); product **27f** (166 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 3H), 0.06 (s, 3H), 0.88 (s, 9H), 1.90 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.09 (s, 3H), 3.25–3.30 (m, 1H), 3.40 (s, 1H, OH), 3.52 (distorted t, J=9.2 Hz, 1H), 3.54–3.62 (m, 3H), 3.69 (dd, J=11.1, 5.4 Hz, 1H), 3.74–3.82 (m, 1H), 3.81 (dd, J=11.1, 5.3 Hz, 1H), 3.96 (dd, J=11.4, 2.2 Hz, 1H), 4.08 (dd, J=11.2, 1.5 Hz, 1H), 4.19 (dd, J=12.4, 2.8 Hz, 1H), 4.23 (dd, J=12.3, 4.8 Hz, 1H), 4.47 (d, J=8.2 Hz, 1H), 4.51 (d, J=11.4 Hz, 1H), 4.55 (d, J=11.4 Hz, 1H), 4.58 (d, J=8.1 Hz, 1H), 4.83–4.91 (m, 2H), 4.95 (br dt, J=7.6, 2.0 Hz, 1H), 5.04 (dd, J=9.6, 8.1 Hz, 1H), 5.07 (t, J=9.7 Hz, 1H), 5.189 (br t, J=8.2 Hz, 1H), 5.194 (t, J=8.6, 1H), 7.19–7.24 (m, 2H), 7.27–7.37 (m, 6H), 7.56–7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.21 (CH_3), −5.18 (CH_3), 18.43 (C), 20.39 (CH_3), 20.56 (CH_3, 2C), 20.62 (CH_3), 20.77 (CH_3), 20.82 (CH_3), 21.01 (CH_3), 25.95 (CH_3, 3C), 61.68 (CH_2), 62.68 (CH_2), 67.51 (CH_2), 68.34 (CH), 68.40 (CH), 70.79 (CH), 71.44 (CH), 71.95 (CH), 71.99 (CH), 72.62 (CH), 74.64 (CH), 75.85 (CH_2), 76.02 (CH), 76.60 (CH), 79.77 (CH), 81.14 (CH), 85.27 (CH), 100.65 (CH), 101.08 (CH), 127.63 (C), 127.73 (CH, 2C), 127.98 (CH), 128.23 (CH), 128.51 (CH, 2C), 129.10 (CH, 2C), 134.78 (CH, 2C), 137.50 (C), 168.94 (C=O), 169.27 (C=O), 169.34 (C=O), 169.57 (C=O), 169.99 (C=O), 170.28 (C=O), 170.59 (C=O); IR (KBr): $\tilde{\nu}$ = 3504, 1755, 1375, 1235, 1048 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{56}H_{81}O_{30}SeSi$: 1143.3372; found 1143.3381 $[M+H]^+$.

Tetrasaccharide 28 f: Glycosyl donor **23 f** (322 mg, 0.40 mmol) and glycosyl acceptor **23 d** (138 mg, 0.20 mmol); product **28 f** (199 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 6H), 0.88 (s, 9H), 2.00 (s, 3H), 2.00 (s, 3H), 2.03 (s, 6H), 2.03 (s, 6H), 2.04 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 3.28 (br ddd, J=7.7, 5.3, 2.0 Hz, 1H), 3.32 (br s, 1H, OH), 3.39 (t, J=9.2 Hz, 1H), 3.40 (br s, 1H, OH), 3.45–3.51 (m, 1H), 3.53 (t, J=9.9 Hz, 1H), 3.56 (t, J=9.6 Hz, 1H), 3.59 (t, J=8.9 Hz, 1H), 3.62 (dd, J=11.4, 6.8 Hz, 1H), 3.74–3.82 (m, 3H), 3.95 (dd, J=11.3, 2.1 Hz, 1H), 4.12–4.25 (m, 5H), 4.44 (d, J=8.2 Hz, 1H), 4.55 (d, J=8.1 Hz, 1H), 4.59 (d, J=8.2 Hz, 1H), 4.73 (d, J=10.3 Hz, 1H), 4.91 (t, J=8.7 Hz, 1H), 4.96 (t, J=10.0 Hz, 1H), 4.98–5.09 (m, 4H), 5.18 (t, J=9.5 Hz, 1H), 5.19 (t, J=9.5 Hz, 1H), 7.28–7.32 (m, 3H), 7.53–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.27 (CH_3), −5.19 (CH_3), 18.45 (C), 20.35 (CH_3), 20.40 (CH_3), 20.54 (CH_3, 2C), 20.56 (CH_3, 2C), 20.62 (CH_3), 20.64 (CH_3), 20.94 (CH_3), 21.10 (CH_3), 25.96 (CH_3, 3C), 61.65 (CH_2), 61.69 (CH_2), 62.79 (CH_2), 68.33 (CH), 68.35 (CH), 68.39 (CH), 68.57 (CH), 68.91 (CH_2), 70.67 (CH), 70.80 (CH), 71.52 (CH), 71.94 (CH), 72.01 (CH), 72.09 (CH), 72.57 (CH), 72.65 (CH), 76.51 (CH), 80.54 (CH), 81.82 (CH), 85.25 (CH), 85.74 (CH), 100.96 (CH), 101.10 (CH), 101.20 (CH), 128.01 (C), 128.38 (CH), 129.15 (CH), 134.16 (CH), 169.06 (C=O, 2C), 169.29 (C=O), 169.39 (C=O, 3C), 170.23 (C=O), 170.25 (C=O), 170.53 (C=O), 170.59 (C=O); IR (KBr): $\tilde{\nu}$ = 3501, 2957, 1755 (s), 1375, 1231 (s), 1169, 1063 (m), 1040 (m), 837 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{56}H_{81}O_{30}SeSi$: 1341.3747; found 1341.3763 $[M+H]^+$.

Tetrasaccharide 29 f: Glycosyl donor **26 f** (133 mg, 0.11 mmol) and glycosyl acceptor **13 d** (57.5 mg, 0.11 mmol); product **29 f** (45.5 mg, 28%) and **29 d** (46.5 mg, 31%). Compound **29 d** could be transformed quantitatively to **29 f** by standard silylation conditions. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 3H), 0.05 (s, 3H), 0.89 (s, 9H), 1.87 (s, 3H), 1.88 (s, 3H), 1.95 (s, 3H), 1.98 (s, 3H), 1.995 (s, 3H), 1.996 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 3.34–3.59 (m, 6H + OH), 3.63–3.81 (m, 4H), 3.81–3.86 (m, 2H), 4.05–4.16 (m, 2H), 4.16–4.21 (m, 2H), 4.43 (d, J=8.1 Hz, 1H), 4.47–4.66 (m, 7H), 4.79–4.93 (m, 3H), 4.99 (dd, J=9.6, 8.1 Hz, 1H), 5.04 (t, J=9.7 Hz, 1H), 5.14–5.22 (m, 3H), 7.18–7.32 (m, 13H), 7.57 (dd, J=7.9, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.41 (CH_3), −4.97 (CH_3), 18.34 (C), 20.31 (CH_3), 20.52 (CH_3, 2C), 20.63 (CH_3), 20.74 (CH_3), 20.78 (CH_3, 2C), 20.92 (CH_3), 25.93 (CH_3, 3C), 61.63 (CH_2), 61.74 (CH_2), 67.04 (CH_2), 68.35 (CH), 68.47 (CH_2), 68.71 (CH), 70.70 (CH), 71.44 (CH), 71.96 (CH), 72.01 (CH), 72.14 (CH), 72.52 (CH), 74.59 (CH_2), 74.67 (CH_2), 74.85 (CH), 75.52 (CH), 75.70 (CH), 75.82 (CH), 75.88 (CH), 75.92 (CH), 79.62 (CH), 80.71 (CH), 85.09 (CH), 100.32 (CH), 101.07 (CH), 101.11 (CH), 127.22 (C), 127.66 (CH, 2C), 127.76 (CH), 127.80 (CH, 2C), 127.93 (CH), 128.33 (CH), 128.41 (CH, 2C), 128.50 (CH, 2C), 129.05 (CH, 2C), 135.06 (CH, 2C), 137.60 (C), 138.09 (C), 168.75 (C=O), 169.20 (C=O), 169.24 (C=O), 169.46 (C=O), 169.64 (C=O), 170.00 (C=O), 170.13 (C=O), 170.23 (C=O), 170.55 (C=O); IR (KBr): $\tilde{\nu}$ = 1755 (s), 1375 (m), 1238 (s), 1156, 1048 (s), 837, 743, 700 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{68}H_{90}O_{29}SeNaSi$: 1501.4400; found 1501.4414 $[M+Na]^+$.

Tetrasaccharide 30 f: Glycosyl donor **13 f** (62.2 mg, 0.10 mmol) and glycosyl acceptor **26 d** (51.2 mg, 0.050 mmol); product **30 f** (41.9 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.88, (s, 3H), 1.89 (s, 3H), 1.92 (s, 3H), 1.97 (s, 3H), 1.97 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H), 2.05 (s, 3H), 2.08, (s, 3H), 3.28 (br dt, J=9.7, 2.7 Hz, 1H), 3.35 (br d, J=0.8 Hz, 1H, OH), 3.40 (distorted t, J=10.7 Hz, 1H), 3.40–3.46 (m, 1H), 3.49 (distorted ddd, J=9.9, 5.3, 1.3 Hz, 1H), 3.56 (t, J=8.6 Hz, 1H), 3.61 (t, J=9.5 Hz, 1H),3.67 (dd, J=29.5, 5.7 Hz, 1H), 3.67 (t, J=5.8 Hz, 1H), 3.71–3.77 (m, 1H), 3.74 (t, J=9.5 Hz, 1H), 3.83–3.88 (m, 2H), 4.01 (br dd, J=11.3, 1.3 Hz, 1H), 4.10–4.19 (m, 2H), 4.19 (br dd, J=10.1, 1.1 Hz, 1H), 4.53–4.57 (m, 2H), 4.65 (d, J=11.4 Hz, 1H), 4.71 (d, J=10.3 Hz, 1H), 4.85 (dd, J=9.5, 8.1 Hz, 1H), (dd, J=9.5, 8.1 Hz, 1H), 4.91 (dd, J=10.2, 9.1 Hz, 1H), 4.96 (dd, J=9.7, 8.2 Hz, 1H), 5.01 (t, J=9.7 Hz, 1H), 5.147 (t, J=9.6 Hz, 2H), 5.152 (t, J=9.5 Hz, 1H), 5.20 (t, J=9.5 Hz, 1H), 7.20–7.34 (m, 13H), 7.51–7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.35 (CH_3), −4.93 (CH_3), 18.36 (C), 20.34 (CH_3), 20.53 (CH_3, 2C), 20.66 (CH_3, 2C), 20.81 (CH_3, 2C), 20.82 (CH_3), 21.08 (CH_3), 25.95 (CH_3, 3C), 61.58 (CH_2), 61.68 (CH_2), 67.73 (CH_2), 68.24 (CH), 68.31 (CH), 69.14 (CH_2), 70.72 (CH), 71.47 (CH), 71.99 (CH), 72.05 (CH), 72.08 (CH), 72.63 (CH), 74.65 (CH_2), 74.69 (CH_2), 74.91 (CH), 75.02 (CH), 75.07 (CH), 75.37 (CH), 75.88 (CH), 76.17 (CH), 80.62 (CH), 81.77 (CH), 85.50 (CH), 100.78 (CH), 100.88 (CH), 101.07 (CH), 127.79 (CH, 2C), 127.85 (CH), 127.93 (CH, 2C), 128.01 (CH), 128.11 (CH), 128.25 (C), 128.46 (CH, 2C), 128.53 (CH, 2C), 129.18 (CH, 2C), 134.10 (CH, 2C), 137.53 b(C), 138.02 (C), 169.05 (C=O), 169.24 (C=O, 2C), 169.65 (C=O), 169.81 (C=O), 170.07 (C=O), 170.23 (C=O), 170.25 (C=O), 170.53 (C=O); IR (KBr): $\tilde{\nu}$ = 3495, 1755 (s), 1374 (m), 1242 (s), 1223 (s), 1049 (s), 835, 743, 698 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{68}H_{91}O_{29}SeSi$: 1479.4581; found 1479.4619 $[M+H]^+$.

Pentasaccharide 31 f: Glycosyl donor **26 f** (57.1 mg, 0.050 mmol) and glycosyl acceptor **23 d** (41.5 mg, 0.06 mmol); product **31 f** (31.0 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 3H), 0.09 (s, 3H), 0.92 (s, 9H), 1.90 (s, 3H), 1.995 (s, 3H), 1.999 (s, 3H), 2.002 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.09 (s, 3H), 3.32 (br dt, J=9.6, 2.4 Hz, 1H), 3.36–3.89 (m, 17H; containing 2 OH), 4.12–4.24 (m, 4H), 4.41 (d, J=8.1 Hz, 1H), 4.55–4.62 (m, 4H), 4.66 (d, J=11.5 Hz, 1H), 4.73 (d, J=10.3 Hz, 1H), 4.83 (dd, J=9.7, 7.9 Hz, 1H), 4.87–5.09 (m, 7H), 5.14–5.22 (m, 3H), 7.23–7.35 (m, 8H), 7.52–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.40 (CH_3), −4.94 (CH_3), 18.36 (C), 20.34 (CH_3, 2C), 20.52 (CH_3, 4C), 20.63 (CH_3), 20.65 (CH_3), 20.78 (CH_3), 20.82 (CH_3), 20.85 (CH_3), 21.06 (CH_3), 25.94 (CH_3, 3C), 61.68 (CH_2, 3C), 68.30 (CH_2), 68.35 (CH, 3C), 68.68 (CH), 69.14 (CH_2), 70.72 (CH, 2C), 71.53 (CH), 71.97 (CH, 2C), 72.20 (CH), 72.56 (CH), 72.64 (CH), 74.62 (CH_2), 74.88 (CH), 75.46 (CH), 75.72 (CH), 75.77 (CH), 77.55 (CH), 80.42 (CH), 81.84 (CH), 85.05 (CH), 85.37 (CH), 100.80 (CH), 101.01 (CH), 101.07 (CH), 101.29 (CH), 121.45 (C), 127.82 (CH), 127.92 (CH, 2C), 127.98 (CH), 128.44 (CH, 2C), 129.16 (CH, 2C), 134.02 (CH, 2C), 138.04 (C), 168.94 (C=O), 169.04 (C=O), 169.27 (C=O, 3C), 169.30 (C=O), 169.81 (C=O), 170.16 (C=O), 170.21 (C=O), 170.22 (C=O), 170.52 (C=O), 170.56 (C=O); HRMS (FAB): m/z: calcd for $C_{75}H_{100}O_{37}SeNaSi$: 1699.4776; found 1699.4816 $[M+Na]^+$.

Pentasaccharide 32 f: Glycosyl donor **23 f** (80.6 mg, 0.10 mmol) and glycosyl acceptor **26 d** (51.4 mg, 0.050 mmol); product **32 f** (26.8 mg, 32%) and **32 d** (20.3 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 3H), 0.06 (s, 3H), 0.88 (s, 9H), 1.91 (s, 3H), 1.93 (s, 3H), 1.99 (s, 3H), 2.01 (s, 3H), 2.03 (s, 9H), 2.04 (s, 3H), 2.05 (s, 3H), 2.09 (s, 6H), 2.12 (s, 3H), 3.27 (ddd, J=8.6, 5.8, 2.6 Hz, 1H), 3.33 (br s, 1H, OH), 3.40 (br t, J=9.0 Hz, 1H), 3.43 (br s, 1H, OH), 3.47–3.61 (m, 6H), 3.61–3.69 (m, 2H), 3.74–3.86 (m, 2H), 3.95 (dd, J=11.2, 2.0 Hz, 1H), 4.05 (br d, J=10.0 Hz, 1H), 4.12–4.26 (m, 5H), 4.45 (d, J=8.0 Hz, 1H), 4.50–4.60 (m, 4H), 4.75 (d, J=10.4 Hz, 1H), 4.87 (dd, J=9.6, 8.0 Hz, 1H), 4.93 (dd, J=10.0, 9.2 Hz, 1H), 4.95 (t, J=8.8 Hz, 1H), 4.99 (t, J=9.0 Hz, 1H), 5.01 (t, J=8.4 Hz, 1H), 5.07 (t, J=9.6 Hz, 2H), 5.14–5.25 (m, 3H), 7.21–7.38 (m, 8H), 7.52–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.25 (CH_3),

−5.22 (CH_3), 18.40 (C), 20.32 (CH_3), 20.38 (CH_3), 20.53 (CH_3, 4C), 20.59 (CH_3), 20.65 (CH_3), 20.68 (CH_3), 20.80 (CH_3), 20.97 (CH_3), 21.08 (CH_3), 25.92 (CH_3, 3C), 61.50 (CH_2), 61.58 (CH_2), 62.67 (CH_2), 67.40 (CH_2), 68.23 (CH, 2C), 68.35 (CH), 68.38 (CH), 69.18 (CH_2), 70.59 (CH), 70.72 (CH), 71.42 (CH), 71.82 (CH), 71.89 (CH), 71.99 (CH), 72.07 (CH), 72.55 (CH, 2C), 74.41 (CH), 74.52 (CH_2), 74.99 (CH), 76.26 (CH), 76.69 (CH), 80.47 (CH), 81.63 (CH), 85.34 (CH), 85.59 (CH), 100.64 (CH), 100.93 (CH), 101.00 (CH, 2C), 127.73 (CH, 2C), 127.96 (CH), 128.13 (CH), 128.49 (CH, 2C and C, 1 C), 129.14 (CH, 2C), 134.17 (CH, 2C), 137.51 (C), 168.89 (C=O), 169.06 (C=O), 169.26 (C=O, 4C), 169.81 (C=O), 170.06 (C=O), 170.22 (C=O, 2C), 170.57 (C=O), 170.58 (C=O); IR (KBr): $\tilde{\nu}$ = 3495, 1759, 1373, 1229, 1169, 1043 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{73}H_{101}O_{37}SeSi$: 1677.4956; found 1677.4935 $[M+H]^+$.

Pentasaccharide 33 f: Glycosyl donor **26 f** (114.2 mg, 0.10 mmol) and glycosyl acceptor **25 d** (44.6 mg, 0.054 mmol); product **33 f** (31.4 mg, 33 %) and **33 d** (16.4 mg, 18 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 3H), 0.09 (s, 3H), 0.92 (s, 9H), 1.86 (s, 3H), 1.89 (s, 3H), 1.91 (s, 3H), 1.95 (s, 3H), 1.96 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.022 (s, 3H), 2.024 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.25 (t, *J* = 9.3 Hz, 1H), 3.34 (br s, 1H, OH), 3.39–3.89 (m, 14H), 4.03–4.24 (m, 5H), 4.40 (d, *J* = 8.1 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 11.2 Hz, 1H), 4.53–4.59 (m, 3H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.65 (d, *J* = 8.1 Hz, 1H), 4.75–4.80 (m, 2H), 4.85 (dd, *J* = 9.6, 8.5 Hz, 1H), 4.88 (t, *J* = 8.3 Hz, 1H), 4.90 (dd, *J* = 9.9, 8.1 Hz, 1H), 4.97 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.04 (t, *J* = 9.7 Hz, 1H), 5.12 (dt, *J* = 9.2, 4.6 Hz, 1H), 5.16 (t, *J* = 9.1 Hz, 1H), 5.17–5.25 (m, 2H), 7.17–7.38 (m, 18H), 7.59–7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.31 (CH_3), −4.91 (CH_3), 18.42 (C), 20.30 (CH_3), 20.54 (CH_3, 2C), 20.65 (CH_3), 20.70 (CH_3), 20.75 (CH_3), 20.79 (CH_3), 20.81 (CH_3, 2C), 20.83 (CH_3), 21.01 (CH_3), 26.01 (CH_3, 3C), 61.58 (CH_2), 62.02 (CH_2), 67.03 (CH_2), 67.80 (CH_2), 68.31 (CH), 68.59 (CH), 68.89 (CH_2), 70.60 (CH), 71.24 (CH), 71.94 (CH), 71.96 (CH), 71.98 (CH), 72.17 (CH), 72.49 (CH), 73.88 (CH), 74.62 (CH_2), 74.72 (CH_2), 74.84 (CH_2), 74.88 (CH), 75.24 (CH), 75.71 (CH), 75.76 (CH), 75.90 (CH, 3C), 76.23 (CH), 79.06 (CH), 80.23 (CH), 85.23 (CH), 100.29 (CH), 100.36 (CH), 101.03 (CH), 101.48 (CH), 126.35 (C), 127.68 (CH, 2C), 127.74 (CH, 2C), 127.96 (CH, 4C), 128.04 (CH), 128.51 (CH, 2C), 125.55 (CH, 2C), 128.59 (CH,3C), 129.14 (CH, 2C), 135.66 (CH, 2C), 137.69 (C), 137.73 (C), 137.88 (C), 168.74 (C=O), 169.07 (C=O), 169.23 (C=O), 169.41 (C=O), 169.47 (C=O), 169.52 (C=O), 170.10 (C=O), 170.12 (C=O), 170.20 (C=O), 170.26 (C=O), 170.58 (C=O); IR (KBr): $\tilde{\nu}$ = 1752, 1375, 1240, 1159, 1049 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{85}H_{110}O_{16}SeNaSi$: 1837.5609; found 1837.5658 $[M+Na]^+$.

Pentasaccharide 34 f: Glycosyl donor **25 f** (94.4 mg, 0.10 mmol) and glycosyl acceptor **26 d** (51.4 mg, 0.050 mmol); product **34 f** (49.0 mg, 37 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 3H), 0.11 (s, 3H), 0.93 (s, 9H), 1.90 (s, 6H), 1.93 (s, 3H), 1.94 (s, 3H), 1.98 (s, 6H), 1.99 (, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.07 (s, 3H), 2.11 (s, 3H), 3.32 (dt, *J* = 9.7, 2.1 Hz, 1H), 3.41 (br s, 1H, OH), 3.37–3.46 (m, 2H), 3.36–3.68 (m, 5H), 3.70–3.80 (m, 5H), 3.86–3.92 (m, 2H), 4.00 (br d, *J* = 10.2 Hz, 1H), 4.12 (br d, *J* = 11.0 Hz, 1H), 4.13–4.18 (m, 2H), 4.25 (br d, *J* = 10.4 Hz, 1H), 4.53–4.62 (m, 9H), 4.65 (d, *J* = 10.0 Hz, 1H), 4.68 (d, *J* = 10.3 Hz, 1H), 4.84–4.93 (m, 4H), 4.97 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.12 (t, *J* = 9.6 Hz, 1H), 5.17 (t, *J* = 10.0 Hz, 1H), 5.18 (t, *J* = 10.0 Hz, 1H), 5.19 (t, *J* = 9.9 Hz, 1H), 5.22 (t, *J* = 9.3 Hz, 1H), 7.20–7.38 (m, 18H), 7.52–7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.30 (CH_3), −4.89 (CH_3), 18.37 (C), 20.35 (CH_3), 20.55 (CH_3, 2C), 20.66 (CH_3), 20.68 (CH_3), 20.82 (CH_3, 2C), 20.83 (CH_3, 2C), 20.85 (CH_3), 21.11 (CH_3), 25.97 (CH_3, 3C), 61.67 (CH_2, 2C), 67.50 (CH_2), 68.04 (CH_2), 68.09 (CH), 68.38 (CH), 69.22 (CH_2), 70.73 (CH), 71.51 (CH), 71.96 (CH), 72.04 (CH, 3C), 72.68 (CH), 74.69 (CH_2), 74.72 (CH_2), 74.76 (CH_2), 74.95 (CH), 75.00 (CH), 75.05 (CH), 75.07 (CH), 75.11 (CH), 75.40 (CH), 75.90 (CH), 76.15 (CH), 76.32 (CH), 80.45 (CH), 81.70 (CH), 85.44 (CH), 100.54 (CH), 100.85 (CH), 101.02 (CH), 101.11 (CH), 127.73 (CH, 2C), 127.83 (CH, 2C), 127.86 (CH), 127.95 (CH, 2C), 128.02 (CH), 128.03 (CH), 128.10 (CH), 128.28 (C), 128.49 (CH, 2C), 128.54 (CH, 2C), 128.57 (CH, 2C), 129.19 (CH, 2C), 134.06 (CH, 2C), 137.52 (C), 137.55 (C), 138.03 (C), 169.05 (C=O), 169.23 (C=O), 169.26 (C=O), 169.47 (C=O), 169.55 (C=O), 169.84 (C=O), 170.10 (C=O), 170.13 (C=O), 170.20 (C=O), 170.27 (C=O), 170.56 (C=O); IR (KBr): $\tilde{\nu}$ = 1755, 1374, 1242, 1221, 1049 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{85}H_{110}O_{36}SeNaSi$: 1837.5609; found 1837.5612 $[M+Na]^+$.

Hexasaccharide 35 f: Glycosyl donor **26 f** (343 mg, 0.30 mmol) and glycosyl acceptor **26 d** (206 mg, 0.20 mmol); product **35 f** (141 mg, 35 %) and **35 d** (75.9 mg, 20 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 3H), 0.08 (s, 3H), 0.92 (s, 9H), 1.90 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 1.99 (s, 6H), 2.00 (s, 3H), 2.029 (s, 6H), 2.033 (s, 6H), 2.05 (s, 3H), 2.088 (s, 3H), 2.09 (s, 3H), 2.12 (s, 3H), 3.28–3.92 (m, 19H; containing 2 OH), 4.15–4.27 (m, 7H), 4.47 (d, *J* = 8.2 Hz, 1H), 4.52–4.67 (m, 8H), 4.72 (d, *J* = 10.3 Hz, 1H), 4.81–5.10 (m, 7H), 5.14–4.25 (m, 5H), 7.22–7.35 (m, 13H), 7.52–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.25 (CH_3), −4.93 (CH_3), 18.37 (C), 20.35 (CH_3), 20.37 (CH_3), 20.54 (CH_3, 4C), 20.64 (CH_3), 20.66 (CH_3), 20.72 (CH_3), 20.81 (CH_3, 2C), 20.84 (CH_3), 20.99 (CH_3), 21.10 (CH_3), 25.98 (CH_3, 3C), 61.58 (CH_2, 2C), 61.80 (CH_2), 67.30 (CH_2), 68.30 (CH_2), 68.34 (CH, 2C), 68.70 (CH), 68.85 (CH_2), 69.29 (CH_2), 70.65 (CH), 70.70 (CH), 71.58 (CH), 71.92 (CH), 71.94 (CH), 72.08 (CH), 72.15 (CH), 72.17 (CH), 72.52 (CH), 72.65 (CH), 74.39 (CH), 74.63 (CH), 74.69 (CH), 74.90 (CH), 75.14 (CH), 75.56 (CH), 75.64 (CH), 75.96 (CH), 76.36 (CH), 80.39 (CH), 81.64 (CH), 85.28 (CH), 85.57 (CH), 100.50 (CH), 100.98 (CH), 101.01 (CH), 101.08 (CH), 101.34 (CH), 127.77 (CH, 2C), 127.84 (CH), 127.95 (CH, 2C), 127.99 (CH), 128.09 (CH), 128.27 (C), 128.47 (CH, 2C), 128.54 (CH, 2C), 129.16 (CH, 2C), 134.19 (CH, 2C), 137.62 (C), 138.05 (C), 168.76 (C=O), 169.10 (C=O), 169.18 (C=O), 169.25 (C=O), 169.27 (C=O), 169.29 (C=O), 169.63 (C=O), 169.87 (C=O), 170.08 (C=O), 170.13 (C=O), 170.21 (C=O), 170.24 (C=O), 170.57 (C=O), 170.60 (C=O); IR (KBr): $\tilde{\nu}$ = 1755, 1375, 1238, 1167, 1049 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{75}H_{100}O_{37}SeNaSi$: 2035.5985; found 2035.5975 $[M+Na]^+$.

Hexasaccharide 36 f: Glycosyl donor **26 f** (114 mg, 0.10 mmol) and glycosyl acceptor **27 d** (51.4 mg, 0.050 mmol); product **36 f** (32.0 mg, 34 %) and **36 d** (18.0 mg, 19 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 1.88 (s, 3H), 1.90 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.007 (s, 3H), 2.014 (s, 3H), 2.02 (s, 3H), 2.03 (s, 6H), 2.05 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 3.32–3.82 (m, 17H; containing 2 OH), 3.83–3.91 (m, 2H), 4.05–4.26 (m, 7H), 4.38 (d, *J* = 8.1 Hz, 1H), 4.44 (d, *J* = 8.1 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.55 (d, *J* = 8.8 Hz, 1H), 4.55–4.61 (m, 2H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.79–5.09 (m, 9H), 5.13–5.22 (m, 4H), 7.18–7.36 (m, 13H), 7.56–7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.36 (CH_3), −4.92 (CH_3), 18.89 (C), 20.30 (CH_3), 20.35 (CH_3), 20.55 (CH_3, 4C), 20.65 (CH_3), 20.68 (CH_3), 20.75 (CH_3), 20.80 (CH_3), 20.81 (CH_3), 20.82 (CH_3), 20.87 (CH_3), 20.95 (CH_3), 25.97 (CH_3, 3C), 61.62 (CH_2), 61.70 (CH_2), 61.77 (CH_2), 61.17 (CH_2), 68.32 (CH), 68.37 (CH, 2C), 68.42 (CH_2), 68.60 (CH and CH_2), 70.67 (CH), 70.71 (CH), 71.37 (CH), 71.85 (CH), 71.94 (CH), 71.02 (CH), 72.07 (CH), 72.17 (CH), 72.55 (CH), 72.59 (CH), 74.61 (CH_2), 74.67 (CH_2), 74.88 (CH), 75.00 (CH), 75.53 (CH), 75.70 (CH), 75.81 (CH, 2C), 75.93 (CH), 79.50 (CH), 80.63 (CH), 84.62 (CH), 85.05 (CH), 100.40 (CH), 100.92 (CH), 101.06 (CH), 101.09 (CH), 101.32 (CH), 127.00 (C), 127.74 (CH, 2C), 127.88 (CH), 127.96 (CH, 2C), 128.02 (CH), 128.41 (CH), 128.48 (CH, 2C), 128.56 (CH, 2C), 129.12 (CH, 2C), 135.17 (CH, 2C), 137.59 (C), 137.99 (C), 168.80 (C=O), 168.88 (C=O), 169.20 (C=O), 169.27 (C=O), 169.31 (C=O), 169.32 (C=O), 169.45 (C=O), 169.76 (C=O), 170.03 (C=O), 170.17 (C=O), 170.20 (C=O), 170.24 (C=O), 170.53 (C=O), 170.58 (C=O); IR (KBr): $\tilde{\nu}$ = 3499, 1755, 1373, 1236, 1163, 1045 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{90}H_{120}O_{44}SeNaSi$: 2035.5985; found 2035.5996 $[M+Na]^+$.

Hexasaccharide 37 f: Glycosyl donor **27 f** (114 mg, 0.10 mmol) and glycosyl acceptor **26 d** (51.4 mg, 0.050 mmol); product **37 f** (31.1 mg, 31 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 3H), 0.06 (s, 3H), 0.88 (s, 9H), 1.91 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 1.995 (s, 6H), 2.000 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.03 (s, 6 H9, 2.04 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 3.24–3.30 (m, 1H), 3.34–3.85 (m, 16H; containing 2 OH), 3.95 (dd, *J* = 11.4, 2.0 Hz, 1H), 4.02–4.11 (m, 2H), 4.11–4.27 (m, 6H), 4.42 (d, *J* = 8.3 Hz, 1H), 4.50–4.61 (m, 8H), 4.75 (d, *J* = 10.2 Hz, 1H), 5.84–5.04 (m, 7H), 5.07 (t, *J* = 9.7 Hz, 1H), 5.14–5.25 (m, 4H), 7.21–7.37 (m, 13H), 7.51–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.20 (CH_3), −5.18 (CH_3), 18.42 (C), 20.36 (CH_3, 2C), 20.55 (CH_3, 4C), 20.61

(CH_3), 20.66 (CH_3), 20.69 (CH_3), 20.80 (CH_3), 20.82 (CH_3), 20.85 (CH_3), 21.00 (CH_3), 21.10 (CH_3), 25.96 (CH_3, 3C), 61.65 (CH_2), 61.74 (CH_2), 62.67 (CH_2), 67.35 (CH_2), 67.55 (CH_2), 68.23 (CH), 68.32 (CH), 68.34 (CH), 68.42 (CH), 69.14 (CH_2), 70.73 (CH), 70.81 (CH), 71.51 (CH), 71.84 (CH), 71.9 (CH), 71.95 (CH), 72.01 (CH), 72.08 (CH), 72.62 (CH), 72.65 (CH), 74.41 (CH), 74.53 (CH_2), 74.65 (CH_2), 74.86 (CH), 75.01 (CH), 75.05 (CH), 76.30 (CH), 76.39 (CH), 76.71 (CH), 80.57 (CH), 81.79 (CH), 85.34 (CH), 85.42 (CH), 100.59 (CH), 100.69 (CH), 100.87 (CH), 101.00 (CH), 101.07 (CH), 127.74 (CH, 2C), 127.75 (CH, 2C), 127.96 (CH), 128.09 (CH), 128.15 (CH), 128.26 (C), 128.51 (CH, 2C), 128.62 (CH, 2C), 129.22 (CH, 2C), 134.08 (CH, 2C), 137.47 (C), 137.64 (C), 168.84 (C=O), 169.08 (C=O), 169.26 (C=O), 169.28 (C=O, 3C), 169.51 (C=O), 169.84 (C=O), 170.07 (C=O), 170.11 (C=O), 170.25 (C=O, 2C), 170.58 (C=O), 170.59 (C=O); IR (KBr): $\tilde{\nu}$ = 1755, 1375, 1235, 1167, 1049 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{90}H_{120}O_{44}SeNaSi$: 2035.5985; found 2035.5966 $[M+Na]^+$.

Heptasaccharide 38 f: Glycosyl donor **26 f** (114.2 mg, 0.10 mmol) and glycosyl acceptor **28 d** (61.3 mg, 0.050 mmol); product **38 f** (17.2 mg, 16 %) and **38 d** (30.0 mg, 34 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 1.89 (s, 3H), 1.99 (s, 3H), 2.00 (s, 6H), 2.02 (s, 6H), 2.03 (s, 3H), 2.03 (s, 9H), 2.04 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 2.085 (s, 3H), 2.090 (s, 3H), 2.11 (s, 3H), 3.31–3.65 (m, 15H; containing 3 OH), 3.67–3.84 (m, 5H), 3.86–3.91 (m, 2H), 4.11–4.26 (m, 9H), 4.39 (d, J = 7.7 Hz, 1H), 4.41 (d, J = 7.9 Hz, 1H), 4.53–4.63 (m, 5H), 4.67 (d, J = 11.4 Hz, 1H), 4.73 (d, J = 10.3 Hz, 1H), 4.80–5.09 (m, 10H), 5.14–5.23 (m, 4H), 7.23–7.36 (m, 8H), 7.53–7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.37 (CH_3), −4.92 (CH_3), 18.39 (C), 20.36 (CH_3), 20.37 (CH_3), 20.39 (CH_3), 20.56 (CH_3, 6C), 20.64 (CH_3), 20.68 (CH_3), 20.73 (CH_3), 20.81 (CH_3, 2C), 20.87 (CH_3), 20.89 (CH_3), 21.10 (CH_3), 25.97 (CH_3, 3C), 61.61 (CH_2), 61.69 (CH_2), 61.73 (CH_2, 2C), 68.31 (CH), 68.34 (CH), 68.39 (CH, 2C), 68.51 (CH and CH_2, 2C), 68.69 (CH and CH_2, 2C), 69.20 (CH_2), 70.64 (CH), 70.73 (CH, 2C), 71.54 (CH), 71.92 (CH), 71.97 (CH), 71.99 (CH), 72.06 (CH, 2C), 72.17 (CH), 72.56 (CH), 72.61 (CH), 72.65 (CH), 74.64 (CH_2), 74.86 (CH), 75.11 (CH), 75.48 (CH), 75.69 (CH), 75.73 (CH), 80.42 (CH), 81.66 (CH), 84.56 (CH), 85.12 (CH), 96.62 (CH), 100.91 (CH), 100.94 (CH), 101.07 (CH), 101.11 (CH), 101.27 (CH), 101.32 (CH), 127.86 (CH), 127.97 (CH, 2C), 128.04 (CH), 128.23 (C), 128.48 (CH, 2C), 129.16 (CH, 2C), 134.22 (CH, 2C), 138.03 (C), 169.00 (C=O, 2C), 169.05 (C=O), 169.27 (C=O), 169.32 (C=O), 169.33 (C=O, 2C), 169.38 (C=O), 169.83 (C=O), 170.17 (C=O), 170.19 (C=O, 2C), 170.22 (C=O, 2C), 170.55 (C=O), 170.59 (C=O), 170.61 (C=O); IR (KBr): $\tilde{\nu}$ = 3503, 1755, 1375, 1229, 1167, 1042 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{95}H_{130}O_{52}SeNaSi$: 2233.6360; found 2233.6409 $[M+Na]^+$.

Heptasaccharide 39 f: Glycosyl donor **28 f** (147 mg, 0.10 mmol) and glycosyl acceptor **26 d** (51.4 mg, 0.050 mmol); product **39 f** (30.3 mg, 26 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.91 (s, 3H), 1.92 (s, 3H), 1.990 (s, 3H), 1.992 (s, 3H), 1.994 (s, 3H), 2.01 (s, 3H), 2.03 (s, 12H), 2.038 (s, 3H), 2.043 (s, 6H), 2.07 (s, 3H), 2.08 (s, 6H), 2.13 (s, 3H), 3.31–3.85 (m, 19H, containing 3 OH), 3.89 (dd, J = 11.2, 5.2 Hz, 1H), 3.98 (br d, J = 9.6 Hz, 1H), 4.07 (br d, J = 10.8 Hz, 1H), 4.10–4.28 (m, 9H), 4.43 (d, J = 8.0 Hz, 1H), 4.48 (d, J = 8.4 Hz, 1H), 4.51 (d, J = 11.2 Hz, 1H), 4.53–4.64 (m, 5H), 4.76 (d, J = 10.4 Hz, 1H), 4.83–5.10 (m, 10H), 5.13–5.24 (m, 4H), 7.20–7.74 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.27 (C), 20.33 (CH_3, 3C), 20.53 (CH_3, 4C), 20.58 (CH_3, 3C), 20.64 (CH_3, 2C), 20.70 (CH_3), 20.78 (CH_3), 20.91 (CH_3), 20.96 (CH_3), 21.07 (CH_3), 26.77 (CH_3, 3C), 61.52 (CH_2), 61.60 (CH_2, 3C), 63.10 (CH_3), 67.02 (CH_2), 68.17 (CH), 68.24 (CH, 3C), 68.37 (CH), 68.53 (CH), 69.12 (CH_2), 70.56 (CH), 70.61 (CH), 70.74 (CH), 71.44 (CH), 71.71 (CH), 71.75 (CH), 71.90 (CH), 72.02 (CH), 72.06 (CH), 72.16 (CH), 72.44 (CH), 72.55 (CH), 72.60 (CH), 74.36 (CH), 74.47 (CH_2), 74.89 (CH), 75.08 (CH), 76.26 (CH), 76.47 (CH), 80.44 (CH), 81.63 (CH), 84.98 (CH), 85.31 (CH), 85.54 (CH), 100.044 (CH), 100.92 (CH, 3C), 101.00 (CH), 101.38 (CH), 127.61 (CH, 4C), 127.80 (CH, 2C), 128.04 (C), 128.12 (CH), 128.55 (CH, 2C), 129.17 (CH, 2C), 129.52 (CH, 2C), 133.46 (C), 133.49 (C), 135.59 (CH, 2C), 135.66 (CH, 2C), 137.43 (C), 168.80 (C=O), 168.97 (C=O), 169.06 (C=O), 169.25 (C=O, 3C), 169.28 (C=O), 169.30 (C=O), 169.32 (C=O), 169.83 (C=O), 170.03 (C=O), 170.16 (C=O), 170.19 (C=O, 2C), 170.51 (C=O), 170.57 (C=O, 2C); IR (KBr): $\tilde{\nu}$ = 3504, 1751, 1429, 1371, 1225, 1169, 1040, 907, 704 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{104}H_{130}O_{53}SeNaSi$: 2357.6673; found 2357.6663 $[M+Na]^+$.

General procedure for the deprotection of *t*BuMeSi group

Tetrasaccharide 29 d: An aqueous 5 % solution of hydrofluoric acid in acetonitrile (78.6 mg, 0.20 mmol, water/acetonitrile 1:20) was added to a solution of **29 f** (154 mg, 0.10 mmol) in CH_2Cl_2 (1.5 mL), and the resulting mixture was stirred for 15 h at room temperature and was quenched with aqueous saturated $NaHCO_3$ solution. After separation of the organic layer, the aqueous phase was extracted with ethyl acetate, and the combined organic extract was washed with aqueous saturated NaCl solution, dried over $MgSO_4$, and concentrated. Purification by flash chromatography afforded **29 d** (118 mg, 0.086 mmol, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 1.93 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.03 (s, 6H), 2.04 (s, 3H), 2.05 (s, 3H), 2.10 (s, 3H), 3.39–3.62 (m, 7H), 2.62–3.83 (m, 5H), 3.87 (br d, J = 11.9 Hz, 1H), 4.06–4.16 (m, 3H), 4.20 (dd, J = 12.4, 4.9 Hz, 1H), 4.24 (dd, J = 12.4, 2.6 Hz, 1H), 4.44 (d, J = 8.0 Hz, 1H), 4.53 (d, J = 11.2 Hz, 1H), 4.56 (d, J = 8.4 Hz, 1H), 4.57 (d, J = 11.2 Hz, 1H), 4.60 (d, J = 11.3 Hz, 1H), 4.64 (d, J = 11.3 Hz, 1H), 4.66 (d, J = 7.9 Hz, 1H), 4.84–4.97 (m, 4H), 5.01 (dd, J = 9.7, 8.1 Hz, 1H), 5.08 (t, J = 9.7 Hz, 1H), 5.16–5.22 (m, 2H), 5.25 (t, J = 9.5 Hz, 1H), 7.20–7.37 (m, 13H), 7.54–7.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.36 (CH_3), 20.55 (CH_3, 2C), 20.67 (CH_3), 20.76 (CH_3), 20.78 (CH_3), 20.81 (CH_3, 2C), 20.94 (CH_3), 61.44 (CH_2), 61.48 (CH_2), 67.63 (CH_2), 68.21 (CH), 68.53 (CH), 69.16 (CH_2), 70.70 (CH), 71.46 (CH), 71.93 (CH), 71.96 (CH), 72.09 (CH), 72.51 (CH), 74.75 (CH and CH_2, 2C), 75.36 (CH), 75.54 (CH), 75.85 (CH, 2C), 79.59 (CH), 80.87 (CH), 85.00 (CH), 100.66 (CH), 101.06 (CH), 101.40 (CH), 127.39 (C), 127.79 (CH, 2C), 127.91 (CH, 2C), 127.97 (CH), 127.99 (CH), 128.32 (CH), 128.51 (CH, 2C), 128.53 (CH, 2C), 129.09 (CH), 134.95 (CH, 2C), 137.58 (C), 137.66 (C), 168.78 (C=O), 169.25 (C=O, 2C), 169.60 (C=O), 169.63 (C=O), 170.05 (C=O), 170.10 (C=O), 170.27 (C=O), 170.63 (C=O); IR (KBr): $\tilde{\nu}$ = 3490, 1754, 1377, 1238, 1048 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{62}H_{76}O_{29}NaSe$: 1387.3535; found 1387.3541 $[M+Na]^+$.

Disaccharide 25 d: Substrate **25 f** (320 mg, 0.34 mmol); reaction time: 8 h; product **25 d** (241 mg, 73 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 1.95 (s, 3H), 1.96 (s, 3H), 2.05 (s, 3H), 3.40 (ddd, J = 9.7, 3.8, 2.5 Hz, 1H), 3.54 (ddd, J = 9.8, 4.8, 1.5 Hz, 1H), 3.61 (t, J = 9.5 Hz, 1H), 3.68–3.82 (m, 3H), 3.89 (ddd, J = 12.2, 5.2, 2.2 Hz, 1H), 4.02 (dd, J = 11.3, 1.4 Hz, 1H), 4.53 (d, J = 11.7 Hz, 1H), 4.57 (d, J = 7.8 Hz, 1H), 4.58 (d, J = 11.4 Hz, 1H), 4.61 (d, J = 11.4 Hz, 1H), 4.66 (d, J = 11.4 Hz, 1H), 4.86 (d, J = 10.6 Hz, 1H), 4.89–4.98 (m, 2H), 5.20 (t, J = 8.7 Hz, 1H), 5.24 (t, J = 9.5 Hz, 1H), 7.20–7.39 (m, 13H), 7.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.73 (CH_3), 20.81 (CH_3, 3C), 61.41 (CH_2), 68.19 (CH_2), 71.22 (CH), 71.93 (CH), 74.75 (CH_2), 74.80 (CH_2), 75.24 (CH, CH_2, 2C), 75.32 (CH), 75.62 (CH), 75.83 (CH), 79.63 (CH), 81.53 (CH), 100.61 (CH), 127.62 (C), 127.76 (CH, 2C), 127.99 (CH, 2C), 128.06 (CH), 128.10 (CH), 128.38 (CH), 128.56 (CH, 4C), 129.19 (CH, 2C), 134.54 (CH, 2C), 137.35 (C), 137.43 (C), 169.63 (C=O), 170.04 (C=O), 170.20 (C=O); IR (KBr): $\tilde{\nu}$ = 3489, 1752 (s), 1375, 1240, 1221, 1076, 1049, 743, 698 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{40}H_{47}O_{14}Se$: 831.2131; found 831.2122 $[M+H]^+$.

Trisaccharide 26 d: Substrate **26 f** (302 mg, 0.26 mmol); reaction time: 2 h; product **26 d** (249 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 2.11 (s, 3H), 3.40–3.50 (m, 4H), 3.57 (t, J = 8.8 Hz, 1H), 3.69–3.80 (m, 4H), 3.89 (ddd, J = 12.3, 5.0, 2.5 Hz, 1H), 4.14–4.22 (m, 3H), 4.56 (d, J = 8.2 Hz, 1H), 4.58–4.66 (m, 3H), 4.74 (d, J = 5.1 Hz, 1H), 4.90 (dd, J = 9.2, 8.0 Hz, 1H), 4.95 (dd, J = 10.1, 9.0 Hz, 1H), 4.98 (dd, J = 9.5, 8.1 Hz, 1H), 5.06 (t, J = 9.5 Hz, 1H), 5.17 (t, J = 9.6 Hz, 1H), 5.24 (t, J = 9.3 Hz, 1H), 7.23–7.37 (m, 10H), 7.54–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (CH_3), 20.5 (CH_3, 2C), 20.7 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 61.4 (CH_2), 61.5 (CH_2), 68.2 (CH), 68.3 (CH), 69.4 (CH_2), 70.7 (CH), 71.4 (CH), 72.0 (CH), 72.5 (CH), 74.8 (CH_2), 75.2 (CH), 75.5 (CH), 80.8 (CH), 81.9 (CH), 85.7 (CH), 101.0 (CH), 101.1 (CH), 128.0 (CH, 2C), 128.1 (CH), 128.2 (CH), 128.3 (C), 128.6 (CH, 2C), 129.2 (CH, 2C), 134.1 (CH, 2C), 137.5 (C), 169.1 (C=O), 169.3 (C=O, 2C), 169.9 (C=O), 170.1 (C=O), 170.3 (C=O), 170.6 (C=O); IR (KBr): $\tilde{\nu}$ = 3484 (br), 2950, 2250, 1754,

1375, 1230 (br), 1048 (br), 745 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{45}H_{57}O_{22}Se$: 1029.2507; found 1029.2512 $[M+H]^+$.

Trisaccharide 27d: Substrate **27f** (300 mg, 0.26 mmol); reaction time: 1 h; product **27d** (244 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.01 (s, 3H), 2.027 (s, 3H), 2.033 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.09 (s, 3H), 2.21 (brs, 1H, OH), 3.36 (dd, J=8.9, 5.7, 3.3 Hz, 1H), 3.48–3.63 (m, 5H containing OH), 3.71–3.84 (m, 3H), 3.93 (brd, J= 11.2 Hz, 1H), 3.95–4.01 (m, 1H), 4.15–4.26 (m, 2H), 4.49 (d, J=8.0 Hz, 1H), 4.53 (d, J=11.2 Hz, 1H), 4.56 (d, J=11.2 Hz, 1H), 4.58 (d, J= 7.6 Hz, 1H), 4.85 (d, J=10.0 Hz, 1H), 4.91 (t, J=9.4 Hz, 1H), 4.94–5.02 (m, 1H), 5.02 (dd, J=9.6, 8.0 Hz, 1H), 5.07 (t, J=9.4 Hz, 1H), 5.19 (t, J=8.8 Hz, 1H), 5.20 (t, J=9.4 Hz, 1H), 7.20–7.27 (m, 2H), 7.28–7.37 (m, 6H), 7.56–7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.34 (CH_3), 20.53 (CH_3, 2C), 20.59 (CH_3), 20.78 (CH_3, 2C), 20.92 (CH_3), 61.56 (CH_2), 62.66 (CH_2), 67.90 (CH_2), 68.23 (CH), 69.24 (CH), 70.69 (CH), 71.27 (CH), 71.84 (CH), 71.95 (CH), 72.46 (CH), 74.68 (CH_2), 75.66 (CH), 75.71 (CH), 75.83 (CH), 79.69 (CH), 81.42 (CH), 85.14 (CH), 100.71 (CH), 101.02 (CH), 127.65 (C), 127.73 (CH, 2C), 128.03 (CH), 128.28 (CH), 128.52 (CH, 2C), 129.14 (CH, 2C), 134.55 (CH, 2C), 137.45 (C), 168.86 (C=O), 169.24 (C=O, 2C), 169.54 (C=O), 170.02 (C=O), 170.25 (C=O), 170.56 (C=O); IR (KBr): $\tilde{\nu}$ = 3600, 1754, 1375, 1237, 1163, 1042 cm^-; HRMS (FAB): *m/z*: calcd for $C_{45}H_{57}O_{22}Se$: 1029.2507; found 1029.2510 $[M+H]^+$.

Tetrasaccharide 28d: Substrate **28f** (302 mg, 0.23 mmol); reaction time: 1 h; product **28d** (228 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.04 (s, 6H), 2.05 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 3.33–3.64 (m, 8 H containing 2 OH), 3.66–3.83 (m, 4H), 3.92 (ddd, J=11.2, 7.2, 3.4 Hz, 1H), 4.09–4.25 (m, 5H), 4.50 (d, J=8.0 Hz, 1H), 4.56 (d, J=8.0 Hz, 1H), 4.58 (d, J= 7.6 Hz, 1H), 4.74 (d, J=10.0 Hz, 1H), 4.91–5.02 (m, 4H), 5.06 (t, J= 9.6 Hz, 1H), 5.17 (dd, J=9.6, 8.0 Hz, 1H), 5.20 (dd, J=9.6, 8.0 Hz, 1H), 7.29–7.34 (m, 3H), 7.54–7.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.33 (CH_3), 20.37 (CH_3), 20.54 (CH_3, 4C), 20.61 (CH_3), 20.66 (CH_3), 20.90 (CH_3), 21.07 (CH_3), 61.41 (CH_2), 61.59 (CH_2), 62.62 (CH_2), 68.10 (CH), 68.24 (CH), 68.36 (CH), 69.19 (CH), 69.31 (CH_2), 70.60 (CH), 70.70 (CH), 71.37 (CH), 71.83 (CH), 71.95 (CH), 72.08 (CH), 72.50 (CH, 2C), 75.64 (CH), 80.86 (CH), 81.91 (CH), 85.15 (CH), 85.67 (CH), 100.91 (CH), 101.05 (CH), 101.35 (CH), 128.06 (CH), 128.43 (C), 129.17 (CH, 2C), 134.01 (CH, 2C), 168.97 (C=O), 169.06 (C=O), 169.25 (C=O), 169.27 (C=O), 169.28 (C=O), 169.32 (C=O), 170.23 (C=O, 2C), 170.57 (C=O), 170.63 (C=O); IR (KBr): $\tilde{\nu}$ = 3495, 1755, 1373, 1231, 1040 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{50}H_{67}O_{30}Se$: 1227.2882; found 1227.2889 $[M+H]^+$.

Heptasaccharide 40: Bromine (7.2 mg, 0.045 mmol) was added at −23 °C to a solution of **26f** (103 mg, 0.09 mmol) in CH_2Cl_2 (1.0 mL), and the resulting solution was slowly warmed to room temperature over 30 min. To this solution was added 2,6-lutidine (1.4 mg, 0.014 mmol) and **29e**, which was prepared by mixing **29d** (61.7 mg, 0.045 mmol), allyltributyltin (19.5 mg, 0.059 mmol), and TfOH (2.0 mg, 0.030 mmol) in CH_2Cl_2 (1.2 mL), and the resulting mixture was stirred for 1 h at room temperature. To this mixture was added TMSOTf (1.0 mg, 0.0045 mmol) at 0 °C, and the resulting mixture was stirred for 30 min. Triethylamine (0.03 mL) followed by aqueous saturated $NaHCO_3$ solution were added, and organic layer was separated. The aqueous phase was extracted with ethyl acetate, and the combined organic extract was washed with aqueous saturated NaCl solution, dried over $MgSO_4$, and concentrated to give a crude mixture. Purification by flash chromatography afforded **40** (26.4 mg, 0.011 mmol, 25%) and the desilylated compound (35.2 mg, 0.016 mmol, 35%), which could be transformed to **40** by standard silylation conditions. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.019 (s, 3H), 0.023 (s, 3H), 0.88 (s, 9H), 1.87 (s, 3H), 1.88 (s, 3H), 1.90 (s, 3H), 1.95 (s, 3H), 1.97 (s, 6H), 1.98 (s, 3H), 1.999 (s, 6H), 2.002 (s, 3H), 2.01 (s, 3H), 2.019 (s, 3H), 2.024 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 3.26–3.31 (m, 1H), 3.30 (brs, 1H, OH), 3.34–3.42 (m, 2H), 3.45 (brs, 1H, OH), 3.44–3.64 (m, 8H), 3.70–3.86 (m, 9H), 3.98 (d, J=9.5 Hz, 1H), 4.03–4.12 (m, 3H), 4.15–4.24 (m, 4H), 4.44 (d, J=8.0 Hz, 1H), 4.45 (d, J=8.0 Hz, 1H), 4.46–4.62 (m, 9H), 4.66 (d, J=8.0 Hz, 1H), 4.81–5.01 (m, 8H), 5.02 (t, J= 10.0 Hz, 1H), 5.07 (t, J=9.8 Hz, 1H), 5.12–5.24 (m, 5H), 7.17–7.33 (m, 18H), 7.56–7.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = −5.37 (CH_3), −5.01 (CH_3), 18.33 (C), 20.33 (CH_3, 2C), 20.49 (CH_3, 2C), 20.53 (CH_3, 2C), 20.58 (CH_3), 20.69 (CH_3), 20.75 (CH_3, 4C), 20.78 (CH_3, 2C), 20.91 (CH_3), 25.97 (CH_3, 3C), 61.39 (CH_2), 61.55 (CH_2), 61.88 (CH_2), 67.42 (CH_2), 67.98 (CH_2), 68.27 (CH), 68.31 (CH), 69.22 (CH_2), 69.31 (CH_2), 70.60 (CH), 70.66 (CH), 71.56 (CH), 71.94 (CH, 2C), 72.00 (CH), 72.06 (CH), 72.11 (CH), 72.26 (CH), 72.42 (CH), 72.59 (CH), 74.09 (CH), 74.62 (CH_2), 74.66 (CH_2), 74.72 (CH_2), 74.95 (CH), 75.01 (CH), 75.12 (CH), 75.38 (CH), 75.71 (CH), 75.90 (CH), 76.16 (CH), 76.25 (CH), 79.28 (CH), 80.69 (CH), 84.99 (CH), 85.47 (CH), 100.40 (CH), 100.71 (CH), 101.05 (CH), 101.15 (CH), 101.26 (CH), 101.56 (CH), 127.22 (C), 127.65 (CH, 2C), 127.76 (CH, 2C), 127.80 (CH), 127.87 (CH, 2C), 127.91 (CH), 128.29 (CH), 128.43 (CH, 2C), 128.45 (CH, 2C), 128.47 (CH, 2C), 129.03 (CH, 2C), 135.15 (CH, 2C), 137.71 (C), 137.78 (C), 138.04 (C), 168.67 (C=O), 168.89 (C=O), 169.07 (C=O), 169.23 (C=O), 169.28 (C=O, 2C), 169.53 (C=O), 169.58 (C=O, 2C), 170.00 (C=O), 170.13 (C=O), 170.16 (C=O), 170.20 (C=O), 170.49 (C=O), 170.57 (C=O), one sp^3 CH carbon signal and one sp^2 CH carbon signal could not be characterized due to overlapping with solvent signals for the former and other signals for the latter. HRMS (FAB): *m/z*: calcd for $C_{107}H_{140}O_{51}SeNaSi$: 2371.7194; found 2371.7290 $[M+Na]^+$.

Heptasaccharide 41: Bromine (0.11 μL, 2.2 μmol) at −23 °C was added to a solution of **40** (10.4 mg, 4.4 μmol) in CH_2Cl_2 (0.3 mL), and the resulting solution was slowly warmed to room temperature over 30 min. To this solution was added water (1.6 μL, 44 μmol), and the resulting mixture was stirred for 0.6 h at room temperature. After the usual workup, a crude mixture was passed thorough a short pad of silica gel to afford a mixture of products (13.1 mg).

To this mixture (5.0 mg) dissolving in CH_2Cl_2 (2 mL) was added 5% of hydrofluoric acid in acetonitrile (3 mg, 7.6 μmol, water/acetonitrile 1:20) room temperature, and the resulting mixture was stirred for over night. After the usual workup, a crude mixture was obtained (6.5 mg), which was used to the next step without further purification.

The crude mixture (4.1 mg) and $Pd(OH)_2$ on carbon powder (1.0 mg, 20% Pd) in ethanol (2.0 mL) was stirred under 50 $kg\,cm^{-2}$ of H_2 atmosphere for 16 h. The mixture was passed through a pad of Celite, and removal of the solvent afforded a crude mixture (6.4 mg). The crude mixture was treated with Ac_2O (2.6 μL, 27 μmol), Et_3N (5.5 μL, 39 μmol), and DMAP (0.5 mg, 4 μmol) in CH_2Cl_2 (0.5 mL) at room temperature of 16 h. After the usual workup, purification by silica gel chromatography followed by preparative GPC afforded **41** as a 1:1 mixture of α- and β-anomers (3.3 mg, total 75% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.95–2.19 (m, 69H), 3.46–5.25 (series of m, 47.5H), 5.46 (t, J=9.9 Hz, 0.5H), 5.67 (d, J=8.2 Hz, 0.5H, β-isomer), 6.23 (d, J=3.7 Hz, 0.5H, α-isomer); IR (KBr): $\tilde{\nu}$ = 1754 (s), 1375, 1225 (s), 1038 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{87}H_{114}O_{60}SeNa$: 2141.6131; found 2141.6101 $[M+Na]^+$.

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