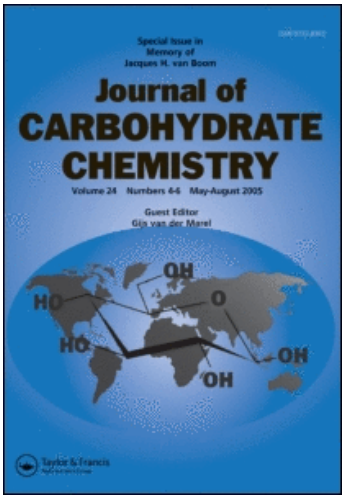

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Application of Novel Glycosides Prepared with Odorless Benzenethiols in Glycosylation Reaction

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p-Dodecylbenzenethiol (**1**) and *p*-octyloxybenzenethiol (**2**) were synthesized as new odorless benzenethiols. Moreover, preparation of novel 1-thioglycosides using **1** and **2** as well as their application for glycosylation reactions was performed. As a result, it was found that these 1-thio-glycosides were excellent glycosyl donors, and especially 2-thio-sialoside prepared from **1** and **2** afforded the best result to date in terms of α- and β-selectivity in the sialylation where only the single C-3 hydroxyl group of acceptor D-galactopyranoside was free. All procedures from the preparation of thioglycosides to glycosylation reaction were attainable under completely odorless conditions.

Keywords Odorless, *p*-Dodecylbenzenethiol, *p*-Octyloxybenzenethiol, Thioglycoside, Glycosylation, Sialylation

INTRODUCTION

1-Thioglycosides have been widely used as excellent glycosyl donors in glycosylation reaction, not only in the solution phase, but also on solid or polymer supports.[1,2] However, malodorous smells generated during the synthesis of the thioglycosides and glycosylation reactions are unavoidable due to the volatile property of commonly available thiols, such as ethanethiol and benzenethiol. Recently, Sakairi, Matsuoka, and their colleagues showed the utility of

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lauryl thioglycosides,[3] including thiosialoside,[4] as substitutes of the corresponding alkyl or phenyl thioglycosides on the basis of the fact that lauryl mercaptan is an odorless thiol. In addition, Kobayashi and Nishida's group also reported an interesting method for the synthesis of galacto- and fuco-oligosaccharides by using faintly smelling methyl thiosalicylate, of which the methoxycarbonyl group played an important role to control the stereochemistry in glycosylation.[5] Furthermore, Huang and his colleagues developed polyfluoronated thiols for the synthesis of novel thioglycosides to facilitate isolation of oligosaccharides from the residue of the glycosylation reactions by taking advantage of fluorous technology.[6] Meanwhile, we have developed odorless organosulfur reagents and exhibited their utility in organic reactions (e.g., Corey-Kim oxidation and demethylation of methyl esters).[7] In addition, we recently published the synthesis of thiopentofuranosides, in which the ring oxygen was replaced with a sulfur atom, by using odorless *p*-octylphenylmethanethiol as the sulfur source.[8]

On the basis of this background, we embarked on studies for the synthesis of phenyl 1-thioglycoside derivatives by using new odorless benzenethiols and their application as glycosyl donors in glycosylation. According to our strategy for designing odorless organosulfur reagents (i.e., the higher molecular weight reagents are less malodorous), benzenethiol derivatives carrying a dodecyl or octyloxy group on the *p*-position of phenyl groups (**1**, **2**) were initially synthesized.[8,9] Then, we found that *p*-dodecylphenyl 1-thioglycosides and *p*-octyloxyphenyl 1-thioglycosides were excellent glycosyl donors in glycosylation reactions, especially in sialylation reaction to the secondary alcohol at the C-3 position of D-galactose. Herein, we would like to report the details of the procedures, of which some partial results obtained in the early study were shown before in a communication for quick publication.[9]

RESULTS AND DISCUSSION

We chose β-D-*N*-acetylglucosaminyl-(1 → 2)-β-D-mannopyranosyl-(1 → 6)-α-D-glucopyranoside (**3a**) as a target oligosaccharide because it was reported that a neo-glycoconjugate (**3b**) carrying a same glycosyl moiety was a good substrate of *N*-acetylglucosaminyltransferase V (GnTase V),[10] of which the activity is reported to be involved in metastatic potency of tumor cells,[11] and *O*-methylated and deoxygenated derivatives (**3c**, **3d**) are potent inhibitors against GnTase V (Fig. 1).[12]

First, 1,2,3,4,6-penta-*O*-acetyl-α-D-mannopyranose (**4**) and 2-deoxy-2-acetamido-1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (**5**) were treated with **1** or **2** in the presence of boron trifluoride etherate to prepare the glycosyldonors. As mentioned in the previous report[9] and the general experimental, *p*-alkylbenzenethiol (**1**) employed here was prepared by the reduction of *p*-dodecylbenzenesulfonyl chloride for industrial use. Therefore, it should contain analogues of

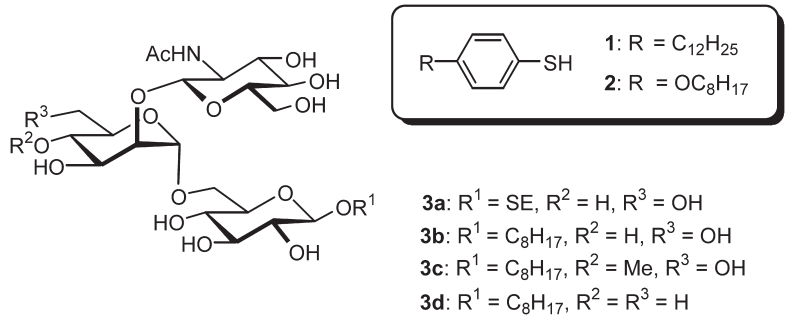
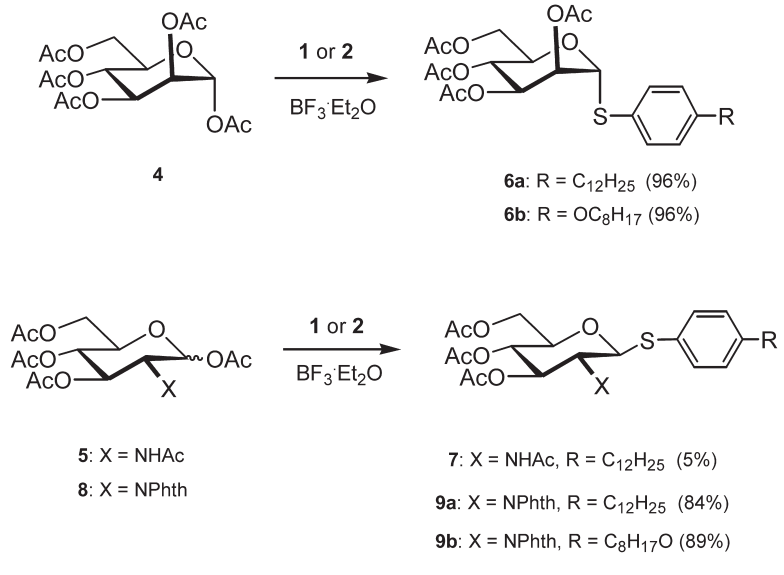


Figure 1: Structures a new odorless benzene thiols (**1**,**2**), target trisaccharide (**3a**), and its related compounds (**3b**–**d**).

1 having a linear alkyl chain comprising one more or less carbon atom than the dodecyl group. Thus, the ^{1}H- and ^{13}C-NMR spectra of compounds carrying the *p*-dodecylphenylmercaptan group as a partial structure were often too complicated to be assigned. While the former (**4**) was effectively converted to phenyl 1-thio-D-mannoside derivatives (**6a**, **6b**) (96% and 95%, respectively), the latter (**5**) was transformed to **7** in quite low yield (5%). Thus, 2-deoxy-2-phthalimido-1,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**8**) was employed as a substrate in the same reaction as above, which afforded the desired 1-thioglycosides (**9a**, **9b**) in good yields (84% and 89%, respectively) (Sch. 1).

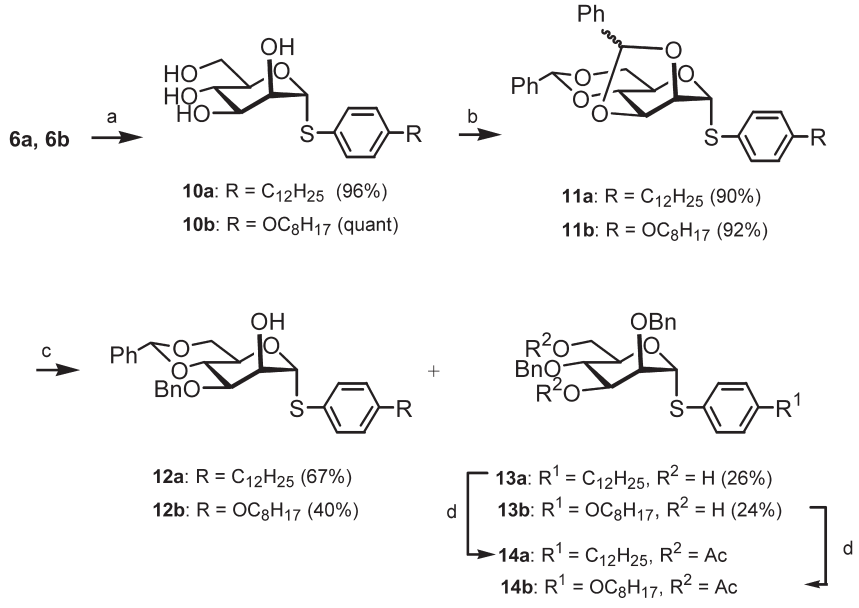


Scheme 1: Synthesis of thioglycosides (**6**, **9**) using odorless benzenethiols.

Next, transformation of the 1-thiomannosides (**6a**, **6b**) to 2,3:4,6-dibenzylidene-1-thio-D-mannoside (**10a**, **10b**) and the following reductive ring opening of the 2,3-benzylidene acetals were performed. The acetyl groups of **6a** and **6b** were cleaved by saponification with 0.5% potassium hydroxide in methanol, and the hydroxyl groups of the obtained aryl 1-thio-D-mannosides (**10a**, **10b**) were protected with α,α-dichlorotoluene to give **11a** and **11b** (86% and 92% in 2 steps, respectively). According to Liptak's procedure, dibenzylidene-1-thio-D-mannosides (**11a**, **11b**) were respectively treated with lithium aluminum hydride in the presence of aluminum chloride to attain reductive cleavage of the protecting group at the C-2 position with high selectivity. Although it was reported that the hydroxyl group at the C-2 position was selectively regenerated from mannose derivatives having an (*R*)-configurated benzylidene group while the hydroxyl group at the C-3 position was revived from the epimer, of which the corresponding benzylidene had (*S*)-configuration,[13] mixtures of (*R*)- and (*S*)-isomers of **11a** and **11b** were subjected to the reaction because neither separation of the two isomers nor stereoselectively controlled protection of 2,3-dihydroxyl groups of **10a** and **10b** was successful. The reaction of **11a** afforded the desired product **12a** in higher yield (67%) than the conversion from **11b** to **12b** (40%). It was in good contrast with the report by Liptak that the products, in which only the hydroxyl group on the C-3 position was deprotected,[13] were not obtained but instead aryl 2,4-di-*O*-benzyl-1-thio-D-mannosides (**13a**, **13b**) were obtained as minor products in both cases (Sch. 2). The structures of **13a** and **13b** were secured by the down-field shift of signals assigned to C-2 and C-4 carbons in the ^{13}C NMR spectra on comparing with those of the corresponding nonprotected 1-thio-D-mannosides (**10a**, **10b**). Furthermore, the fact that signals assigned to the protons on C-3 and C-6 in the ^{1}H NMR spectra of **13a** and **13b** were shifted to lower field by acetylation into **14a** and **14b** also supports the identification (Sch. 2)

Herein, a pretest of mannosylation with **12a** was attempted by using allyl 2,3,4-tri-*O*-benzyl-α-D-glucoside (**15a**)[14] as a glycosyl acceptor, which was activated by $BF_3 \cdot Et_2O$ and *N*-iodosuccinimide (NIS);[8,15] however, the desired product was not obtained but the reaction afforded 1-fluoro-D-mannoside (**16**). The structure of **16** was incorrectly reported in the previous publication.[9] Herein, we would like to revise it as shown in Figure 2. (31%) (Fig. 2).

Each acetate was then employed as a glycosyl donor in mannosylation of trimethylsilylethyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**15b**)[16] in the presence of silver triflate and NIS,[17] a milder activator than the combination of $BF_3 \cdot Et_2O$ and NIS. As expected, both of the reactions afforded disaccharide **18** in good yield (90% from **17a**, 83% from **17b**). After cleavage of the acetyl group in **18** with sodium methoxide, the obtained α-D-mannopyranosyl-$(1 \rightarrow 6)$-β-D-glucopyranoside derivative (**19**) was subjected to glycosylation with **9a** and **9b**, respectively, in the same way as the above to afford a fully



Scheme 2: Synthesis of 1-arylthiomannoside derivatives. **a**: KOH, MeOH; **b**: $PhCHCl_2$, pyr.; **c**: $LiAlH_4$, $AlCl_3$; **d**: Ac_2O, pyr.

protected trisaccharide (**20**) in excellent yield (92% from **9a**, 93% from **9b**). The phthaloyl group of **20** was removed with hydrazine hydrate, followed by acetylation with acetic anhydride and pyridine to yield **21**. Finally, treatment of **21** with sodium methoxide to afford **22** and successive hydrogenation on palladium-carbon in acidic medium gave the desired trisaccharide (**3a**) (Sch. 3).

In order to exhibit further application of the odorless benzenethiols (**1**, **2**) to glycosylation reactions, we adopted our method in the synthesis of sialylosides. Methyl *N*-acetyl-2,4,7,8,9-penta-*O*-acetyl-neuraminate (**23**) was treated with *p*-dodecylbenzenethiol (**1**) and *p*-octyloxybenzenethiol (**2**) in the presence of $BF_3 \cdot Et_2O$ to afford *p*-dodecylphenyl 2-thiosialoside (**24a**) and *p*-octyloxyphenyl 2-thiosialoside (**24b**), respectively, in satisfactory yield (84% and 74%). At first, sialylation reactions of primary alcohol in methyl 2,3,4-tri-*O*-acetyl-α-D-

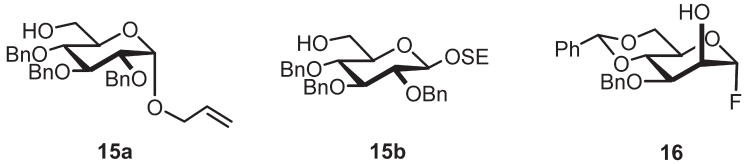
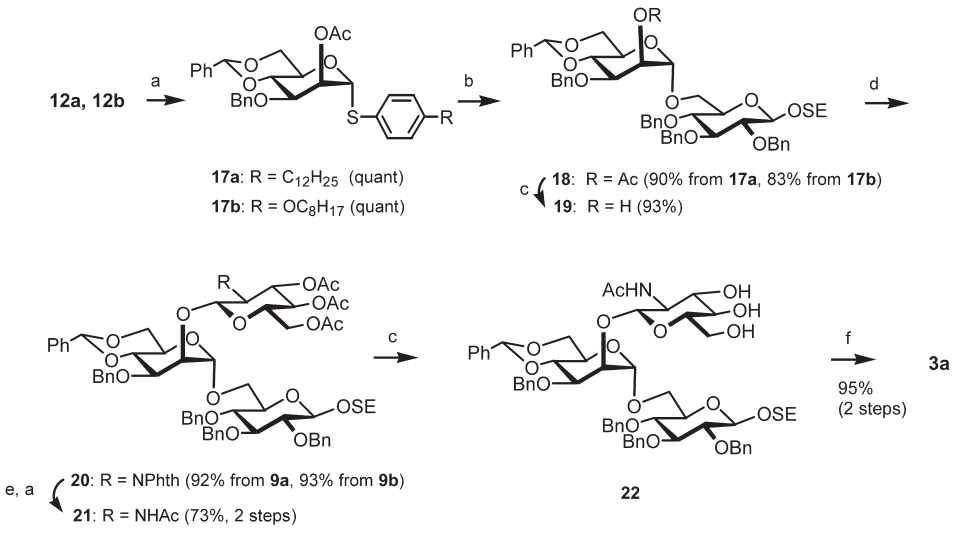


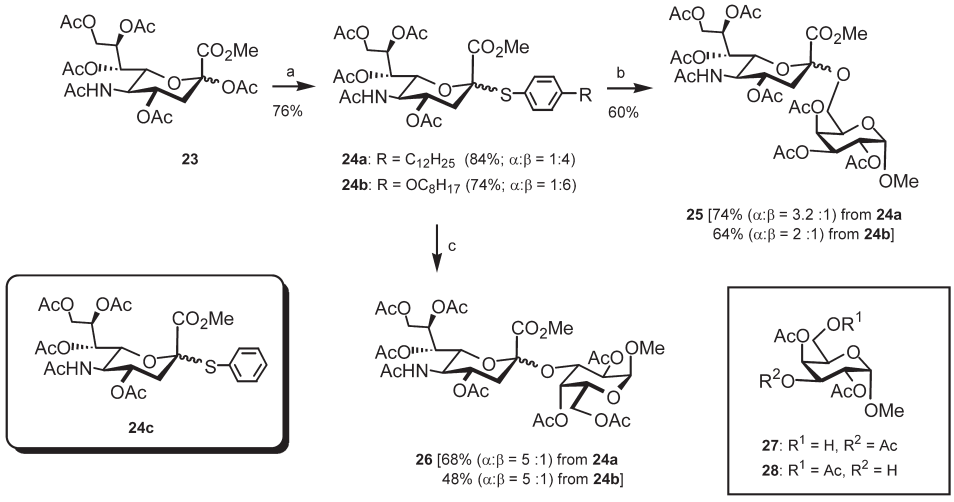
Figure 2: Employed acceptor subtrates (**15a**, **15b**) of mannosylation with **12a**, **12b** and undesired product (**16**) from **12a** in the presence of $BF_3 \cdot Et_2O$.



Scheme 3: Synthesis of trisaccharide (3a). **a**: Ac_2O, pyr.; **b**: **15b**, NIS (2.5 eq.), AgOTf, − 50 °C; **c**: NaOMe; **d**: **9a** or **9b**, NIS (2.5 eq.), AgOTf, − 50 °C; **e**: NH_2NH_2; **f**: Pd-C/H_2, HCO_2H.

galactopyranoside (**27**) were performed with **24a** and **24b** in acetonitrile in the presence of triflic acid and NIS.[18] The results to afford sialyl $\alpha(2 \rightarrow 6)$galactoside **25** (74% and 64%, respectively) were as good as that in a similar reaction using phenyl 2-thiosilaloside (**24c**) as glycosyl donor.[18b]

Surprisingly, silaylation of secondary alcohol (i.e., the hydroxyl group at the C-3 position of methyl 2,4,6-tri-*O*-acetyl-α-D-galactopyranoside (**28**)),



Scheme 4: Synthesis of sialosides (**25**, **26**).**a**: **1** or **2**, $BF_3 \cdot Et_2O$; **b**: **27**, TfOH (cat.), NIS (2 eq), CH_3CN − 40°C; **c**: **28**, TfOH (cat.), NIS (2 eq.), CH_3CN − 40°C

with **24a** and **24b** under the same conditions gave sialyl $\alpha(2 \rightarrow 3)$galactoside **26** (68% and 48%, respectively), which was a much better result in terms of α- to β-selectivity in comparison with sialylation in the literature. Namely, sialylation of galactopyranoside derivatives, where the hydroxyl groups except for one at the C-3 position of the galactose were protected, with phenyl 2-thio-sialoside (**24c**) generally proceeded with low selectivity.[19] Ogawa's and Hasegawa's groups independently developed novel methods, where less protected galactopyranosides were utilized as acceptor glycosides, to avoid the defect.[20,21] Because of no possibility of forming undesired isomers, such as sialyl $\alpha(2 \rightarrow 4)$galactoside, and requirement of only an equimolecular amount of the thiosialosides to the acceptor substrates, our method could provide an alternative method for sialylation (Sch. 4).

CONCLUSION

In conclusion, we have succeeded in developing a new practical method of glycosylation reaction, including sialylation, where odorless benzenethiols (**1**, **2**) were used as novel reagents for the synthesis of thioglycosides and no malodor was generated during preparation of the thioglycosides and synthesis of saccharides. It is noteworthy that surprisingly better results were obtained in the sialylation of a galactose derivative, of which the hydroxyl groups except for one at the C-3 position were protected, than those in the literature to date. Our method would be widely feasible for large-scale synthesis of biologically active oligosaccharides either in liquid phase or solid phase.

EXPERIMENTAL

General

Infrared (IR) spectra were recorded on a JASCO IR-810 or a Shimadzu FTIR-8300 diffraction grating infrared spectrophotometer and ^{1}H NMR spectra were obtained on a JEOL JNM-AL300, a Varian XL-300, and a Varian Unity INOVA-400 spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained on a Varian Unity INOVA-400 spectrometer with $CDCl_3$ as an internal standard. Mass spectra (MS) were determined on a JEOL JMS-SX 102A QQ or a JEOL JMS-GC-mate mass spectrometer. Specific rotations were recorded on a Horiba SEPA-200 automatic digital polarimeter. Kiesel gel Art-7734 (70–230 mesh), Art-9385 (230–400 mesh) (Merck), and ODS gel (100–200 mesh; Chromatorex ODS DM1020T) (Fuji Silysia Chemical Ltd.) were used for open column chromatography. Kieselgel 60 F-254 plates (Merck) were used for thin-layer chromatography (TLC). Preparative TLC (PTLC) was conducted with Kieselgel 60 F-254 plate (0.25 mm, Merck) or Silica gel 60 F-254 plate (0.5 mm, Merck). Unless purification with

silica gel gave sufficiently pure compound, the compounds were further treated with a recycled HPLC (JAI LC-908) on GPC column (JAIGEL 1H and 2H). In the case it was possible, diastereomeric mixtures were also separated by a recycled HPLC (JAI LC-908) on silica gel column (Kusano Si-10) after the purification mentioned above. Within the chemicals, *p*-dodecylbenzenethiol (1) used in the present study contained undecyl- and tridecylbenzenethiols as minor components (ca. each 30%) as described in the literature,[9] which could be confirmed in ^{13}C NMR and MS spectra.

p-Dodecylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (6a)

Boron trifluoride etherate complex (0.60 mL, 4.92 mmol) was added to a solution of **4** (1.28 g, 3.28 mmol) and **1** (1.37 g, 4.92 mmol) in dichloromethane (15 mL) at 0°C and the mixture was stirred for 15 h at rt. After the reaction, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 7:2) to afford **6a** (1.75 g, 89%) as a colorless syrup. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.82 (t, $J = 7.0$ Hz, 3H), 2.02 (s, 3H), 2.07 (s, 6H, 2 × Ac), 2.15 (s, 3H), 4.10 (br d, $J = 12.0$ Hz, 1H), 4.33 (dd, $J = 5.4$, 12.0 Hz, 1H), 4.58 (br s, 1H), 5.34 (m, 2H), 5.44, 5.50 (each br s, 1H), 7.07, 7.39 (each d, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 11.6, 13.5, 13.6, 19.8, 19.9, 20.0, 21.7, 22.2 (2C), 22.3, 26.8, 27.2, 28.9, 29.2, 29.3, 31.3, 31.4, 36.0, 36.4, 37.8, 38.6, 39.2, 45.0, 45.3, 47.0, 62.2 (C-6), 66.2 (C-4), 69.6 (C-3), 70.6 (C-2), 79.2 (C-5), 85.6 (C-1), 127.7, 128.4 (2C), 129.3 (2C), 146.5, 169.4 (2C), 169.5, 169.7; IR ($CHCl_3$): 2959, 2928, 2856, 1747, 1489, 1456, 1369 cm^{-1}; MS FAB(+) *m/z*: 631 $[M + Na]^+$; HRMS calcd for $C_{32}H_{48}O_9SNa$ $[M + Na]^+$: 631.2917, found: 631.2913.

p-Octyloxyphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (6b)

Boron trifluoride etherate complex (95 μL, 0.75 mmol) was added to a solution of **4** (96.7 mg, 0.25 mmol) and **2** (178.8 mg, 0.75 mmoL) in dichloromethane (2 mL) at 0°C and mixture was stirred for 19 h at rt. After the reaction, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 5:1) to afford **6b** (136.2 mg, 96%) as a colorless syrup. $[\alpha]D^{25}$ +85.8° ($c = 1.35$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, $J = 7.0$ Hz, 3H), 1.77 (quint, $J = 6.6$ Hz, 2H), 2.01 (s, 3H), 2.07 (s, 6H, 2 × Ac), 2.13 (s, 3H), 3.93

(t, $J = 6.6$ Hz, 2H, -OCH_2-), 4.10 (dd, $J = 2.2$, 12.3 Hz, A part of AB, 1H), 4.29 (dd, $J = 5.9$, 12.3 Hz, B part of AB, 1H), 4.56 (m, 1H), 5.32 (m, 3H), 5.48 (t, $J = 1.8$ Hz, 1H, H-2), 6.82, 7.40 (each d, $J = 8.8$ Hz, 2H); ^{13}C NMR (50 MHz, C_5D_5N) δ: 13.8, 20.0 (2C), 20.1, 20.2, 22.4, 25.8, 28.95, 29.04, 31.5, 62.4 (C-6), 66.4 (C-4), 67.8 (-OCH_2), 69.7 (C-3), 70.6 (C-2), 79.2 (C-5), 86.3 (C-1), 115.2 (2C), 122.1, 135.2 (2C), 159.6, 169.4, 169.5 (2C), 169.7; IR ($CHCl_3$): 3030, 3020, 3010, 1747, 1595, 1495, 1369 cm^{-1}; MS FAB(+) m/z: 591 $[M + Na]^+$; HRMS calcd for $C_{28}H_{50}O_{10}SNa$ $[M + Na]^+$: 591.2240, found: 591.2234.

p-Dodecylphenyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-glucopyranoside (7)

Boron trifluoride etherate complex (106 μL, 0.84 mmol) was added to a solution of **5** (108 mg, 0.28 mmol) and **1** (155 mg, 0.56 mmol) in dichloromethane (2 mL) at 0°C and the mixture was stirred for 14 h at rt. After the reaction, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:1) to afford recovered **5** (77.6 mg, 71%) and **7** (9.1 mg, 5%) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.84 (m, 6H), 1.98, 2.02, 2.03, 2.12 (each s, 3H), 3.72 (m, 1H), 3.95–4.30 (m, 3H), 4.83 (br t, $J = 9.0$ Hz, 1H), 5.06 (br t, $J = 9.0$ Hz, 1H), 5.22 (br t, $J = 9.0$ Hz, 1H), 5.53 (br d, $J = 9.0$ Hz, 1H), 7.09 (m, 2H), 7.38 (m, 2H); MS FAB(+) m/z: 630 $[M + Na]^+$; HRMS calcd for $C_{32}H_{49}O_8NSNa$ $[M + Na]^+$: 630.3077, found: 630.3071.

p-Dodecylphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (9a)

Boron trifluoride etherate complex (1.4 mL, 11.0 mmol) was added to a solution of **8** (2.10 g, 4.4 mmol) and **1** (3.06 g, 11.0 mmoL) in dichloromethane (30 mL) at 0°C and the mixture was stirred for 20 h at rt. After the reaction, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 6:1) to afford **9a** (2.56 g, 84%) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.83 (t, $J = 7.0$ Hz, 3H), 1.86, 2.02, 2.10 (each s, 3H, OAc), 3.90 (ddd, $J = 2.4$, 5.3, 10.0 Hz, 1H H-5) 4.20 (dd, $J = 2.4$, 12.3 Hz, Apart of AB, 1H, H-6), 4.29 (dd, $J = 5.3$, 12.3 Hz, B part of AB, 1H, H-6), 4.38 (t, $J = 10.0$ Hz, 1H), 5.15 (t, $J = 10.0$ Hz, 1H), 5.67 (dd, $J = 3.5$, 10.0 Hz, H-1) 7.01, 7.30 (each d, $J = 8.0$ Hz, 2H), 7.75 (dd, $J = 3.0$, 5.5 Hz, 2H) 7.86 (dd, $J = 3.0$, 5.5 Hz, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 13.6, 19.47 19.52, 19.67, 19.73, 19.95, 20.00, 21.6, 22.1,

22.20, 22.23, 22.3, 27.2, 27.3, 28.76, 28.87, 28.95, 29.06, 29.12, 29.2, 29.3, 31.3, 31.4, 36.1, 36.3, 37.8, 38.5, 38.6, 39.1, 45.2, 53.7, 53.8 (C-2), 61.9 (C-6), 68.6 (C-4), 71.5 (C-5), 75.8 (C-5), 83.2 (C-1), 123.2, 127.6, 128.3, 128.5, 130.9, 131.2, 132.2, 132.6, 134.2, 146.1, 146.4, 146.5, 148.0, 166.8, 167.7, 169.0, 169.7; IR ($CHCl_3$): 2959, 2928, 2856, 1778, 1747, 1719, 1470, 1456 cm^{-1}; MS FAB(+) m/z: 718 $[M + Na]^+$: HRMS calcd. for $C_{38}H_{49}O_9SNa$ $[M + Na]^+$: 718.3026, found: 718.3029.

p-Octyloxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (9b)

Boron trifluoride etherate complex (268 μL, 2.12 mmol) was added to a solution of **8** (676 mg, 1.41 mmol), and **2** (506 mg, 2.12 mmol) in dichloromethane (5 mL) at 0°C and the mixture was stirred for 20 h at rt. After the reaction, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 2:1) to afford **9b** (829 mg, 89%) as a colorless syrup. $[\alpha]D^{25}$ +17.3° ($c = 3.57$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, $J = 7.0$ Hz, 3H), 1.78 (quint, $J = 7.0$ Hz, 2H), 1.83, 2.01, 2.10 (each s, 3H, OAc), 3.86 (dq, $J = 2.4$, 10.0 Hz, 1H, H-5), 3.93 (t, $J = 6.6$ Hz, 2H, OCH_2), 4.20 (dd, $J = 2.4$, 12.3 Hz, A part of AB, H-6), 4.26 (dd, $J = 5.0$, 12.3 Hz, 1H, H-6), 4.28 (t, $J = 10.0$ Hz, H-4), 5.09 (t, $J = 10.0$ Hz, 1H, H-3), 5.56 (d, $J = 10.0$ Hz, 1H, H-1), 5.76 (t, $J = 10.0$ Hz, H-2), 6.78, 7.33 (each d, $J = 8.8$ Hz, 2H), 7.76 (dd, $J = 3.0$, 5.3 Hz, 2H), 7.88 (dd, $J = 3.0$, 5.3 Hz, 2H); ^1H NMR (300 MHz, C_5D_5N) δ: 0.84 (t, $J = 7.0$ Hz, 3H), 1.21 (m, 8H), 1.37 (m, 2H), 1.69 (sextet, $J = 7.0$ Hz, 8H), 1.81, 1.97, 2.06 (each s, 3H, Ac), 3.86 (t, $J = 7.0$ Hz, 2H, -OCH_2), 4.16 (ddd, $J = 2.4$, 5.0, 10.3 Hz, 1H, H-5), 4.43 (dd, $J = 2.4$, 12.3 Hz, A part of AB, 1H, H-6), 4.55 (dd, $J = 5.0$, 12.3 Hz, B part of AB, 1H, H-6), 4.85 (t, $J = 10.3$ Hz, 1H, H-2), 5.52 (dd, $J = 9.3$, 10.3 Hz, 1H. H-4), 6.18 (d, $J = 10.3$ Hz, 1H, H-1), 6.30 (dd, $J = 9.3$, 10.3 Hz, 1H, H-3), 6.97 (d, $J = 8.8$ Hz, 2H), 7.61 (m, 2H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.89 (m, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 13.6, 19.5, 19.7, 20.0, 22.2, 25.8, 28.7, 28.76, 28.85, 31.3, 53.8 (C-2), 61.9 (C-6), 67.6 (-OCH_2), 68.6 (C-4), 71.6 (C-3), 75.9 (C-5), 83.2 (C-1), 114.9 (2C), 120.5, 122.3, 130.9, 131.3, 134.2, 134.3, 135.8 (2C), 159.7, 166.9, 167.8, 169.0, 169.7, 169.8; IR ($CHCl_3$): 2930, 2856, 1778, 1747, 1719, 1593, 1495, 1470 cm^{-1}; MS FAB(+) m/z: 678 $[M + Na]^+$; HRMS calcd for $C_{34}H_{50}O_{10}NSNa$ $[M + Na]^+$: 678.2349, found: 678.2343.

p-Dodecylphenyl 1-Thio-α-D-mannopyranoside (10a)

A solution of 0.5% potassium hydroxide in methanol (6.0 mL) was added to a solution of **6a** (636 mg, 1.04 mmol) in methanol (12 mL) and the mixture was

stirred for 15 h at rt. After the reaction, the reaction mixture was partitioned between *n*-butanol and water. The organic layer was washed with a small amount of water and evaporated. The residue was purified by silica gel column chromatography (chloroform/methanol/water = 9:1:0.08) to afford **10a** (439 mg, 96%) as a colorless syrup. ^{1}H NMR (300 MHZ, CD_3OD) δ: 0.84 (t, $J = 7.0$ Hz, 3H), 1.54 (m, 2H), 3.69–3.80 (m, 4H), 4.07 (m, 2H), 5.37 (br s, 1H), 7.10, 7.43 (each d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 11.7, 13.5, 13.6, 13.7, 20.30. 21.7, 21.8, 22.2, 22.26, 22.29, 22.4, 26.9, 27.22, 27.27, 27.34, 28.8, 28.92, 29.03, 29.13, 29.19, 29.23, 29.30, 29.34, 29.42, 29.78, 31.3, 31.45, 31.48, 31.52, 36.1, 36.2, 36.5, 37.9, 38.6, 39.1, 45.0 45.2, 47.0, 49.0, 62.1 (C-6′), 68.6 (C-4′), 73.05, 73.13 (C-2′, 3′), 76.00 (C-5′) 90.0, 90.1 (C-1′), 127.5, 128.1, 128.2, 131.5, 131.8, 132.9, 132.2, 132.3, 144.8, 145.1, 145.2, 146.8; MS FAB(+) m/z: 463 $[M + N]^+$; HRMS calcd for $C_{24}H_{50}O_5SNa$ $[M + Na]^+$: 463.2494, found: 463.2499.

p-Octyloxyphenyl 1-Thio-α-D-mannopyranoside (10b)

A solution of 0.5% potassium hydroxide in methanol (1.0 mL) was added to a solution of **6b** (20.7 mg, 0.036 mmol) in methanol (1 mL) and the mixture was stirred for 16 h at rt. After the reaction, the reaction mixture was partitioned between *n*-butanol and water. The organic layer was washed with a small amount of water and evaporated. The residue was purified by silica gel column chromatography (chloroform/methanol/water = 9:1:0.08) to afford **10b** (14.5 mg, 100%) as a colorless syrup. $[\alpha]D^{25}$ +150.7° ($c = 0.77$, MeOH) ^{1}H NMR (400 MHz, C_5D_5N) δ: 0.83 (t, $J = 7.0$ Hz, 3H), 1.32 (m, 2H), 1.66 (quint, J= 7.0 Hz, 2H), 3.80 (m, 2H), 4.43 (dd, $J = 5.9$, 12.0 Hz, 1H, A part of AB, H-6), 4.58 (t, $J = 12.0$ Hz, 1H, B part of AB, H-6), 4.60 (dd, $J = 3.0$, 9.5 Hz, H-3), 4.74 (t, $J = 9.5$ Hz, 2H, H-4), 4.84 (dd, $J = 1.2$, 3.0 Hz, 1H, H-2), 4.92 (m, H-5), 6.03 (d, $J = 1.2$ Hz, H-1), 6.92, 7.75 (each d, $J = 9.0$ Hz, 2H); ^{13}C NMR (50 MHz, C_5D_5N) δ: 13.8, 22.4, 25.8, 29.0 (2C), 29.1, 31.5, 62.3 (C-6), 67.6 (OCH_2), 68.8 (C-4), 73.0, 73.1 (C-2, 3), 76.0 (C-5), 91.0 (C-1), 115.0 (2C), 123.2, 134.8 (2C), 158.9; MS FAB(+) m/z: 423 $[M + Na]^+$; HRMS calcd for $C_{20}H_{40}O_6SNa$ $[M + Na]^+$: 423.1817, found: 423.1814.

p-Dodecylphenyl 2,3:4,6-di-*O*-benzylidene-1-thio-α-D-mannopyranoside (11a)

Dichlorotouluene (1.3 mL, 10.2 mmol) was added to a solution of **10a** (1.5 g, 3.4 mmol) in pyridine (30 mL) and the mixture was stirred for 13 hours at 130°C. After the reaction, the organic solvent was removed in vacuo and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 50:1) to afford **11a** (1.87 g, 90%) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.83 (t, $J = 7.0$ Hz, 3H), 2.46

(m, 0.7H), 2.65 (m, 0.3H), 3.69 (t, $J = 9.9$ Hz, 0.3H), 3.76 (m, 1H), 3.98 (t, $J = 9.0$ Hz, 0.7H), 4.17–4.33 (m, 2H), 4.37 (d, $J = 5.1$ Hz, 0.6H), 4.50 (m, 0.6H), 4.67 (dd, $J = 5.1$, 8.0 Hz, 0.6H), 5.05 (s, 0.3H), 5.64 (s, 0.7H), 5.81 (d, $J = 3.3$ Hz, 0.7H), 5.88 (d, $J = 3.3$ Hz, 0.3H), 5.99 (s, 0.3H), 6.30 (s, 0.7H), 7.10 (m, 2H), 7.34–7.56 (m, 12H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 11.7, 13.57, 13.63, 13.7, 20.3, 21.7, 22.17, 22.26, 22.30, 22.39, 26.9, 27.3, 28.85, 28.93, 29.0, 29.2, 29.4, 29.5, 31.3, 31.4, 31.5, 36.0, 36.2, 36.4, 36.5, 47.9, 38.6, 39.2, 61.7, 68.0, 68.1, 73.9, 75.5, 75.7, 76.2, 76.7, 77.0, 78.6, 80.8, 84.2, 84.5, 84.8, 101.4, 101.5, 102.9, 103.3, 103.8, 126.0, 126.3, 126.4, 126.6, 127.8, 127.9, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 129.0, 129.2, 129.5, 129.7, 132.6, 132.9, 137.2, 137.71, 137.74, 138.9, 146.1, 146.5; MS FAB(+) m/z: 639 $[M + Na]^+$; HRMS calcd for $C_{38}H_{50}O_5SNa$ $[M + Na]^+$: 639.3120, found: 639.3127.

p-Octyloxyphenyl 2,3:4,6-di-*O*-benzylidene-1-thio-α-D-mannopyranoside (11b)

Dichlorotouluene (0.9 mL, 7.13 mmol) was added to a solution of **10b** (952 mg, 2.73 mmol) in pyridine (20 mL) and the mixture was stirred for 11 hours at 130°C. After the reaction, the organic solvent was removed in vacuo and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 10:1) to afford **11b** (1.26 g, 92%) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, $J = 7.0$ Hz, 3H), 1.77 (quint, $J = 7.0$ Hz, 2H), 3.69 (t, $J = 10.0$ Hz, 0.5H), 3.79 (t, $J = 9.5$ Hz, 0.5H), 3.80 (dd, $J = 7.5$, 9.7 Hz, 0.5H), 3.94 (t, $J = 7.0$ Hz, 2H), 3.96 (m, 1H), 4.19–4.36 (m, 2.5H), 4.50 (m, 1H), 4.66 (dd, $J = 8.0$, 5.5 Hz, 0.5H), 5.51, 5.64, 5.69, 5.75, 5.97, 6.23 (each s, 0.5H), 6.84, 6.85 (each, d, $J = 9.0$ Hz, 1H), 7.29–7.57 (m, 12H); MS FAB(+) m/z: 599 $[M + Na]^+$; HRMS calcd for $C_{34}H_{50}O_6SNa$ $[M + Na]^+$: 599.2443, found: 599.2451.

Reductive Cleavage of Benzylidene Protecting Group of 11a

A solution of **11a** (1.02 g, 1.65 mmol) in diethyl ether (10 mL) and dichloromethane (10 mL) was added to a suspension of lithium aluminum hydride (125.5 mg, 3.30 mmol) and aluminum chloride (440.9 mg, 3.30 mmol) in diethyl ether (10 mL). After stirring the mixture for 30 min at room temperature, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 10:1) to afford **12a** (657 mg, 64%) and **13a** (261 mg, 26%) as a colorless syrup, respectively.

12a: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.83 (m, 6H), 2.79 (d, $J = 1.0$ Hz, 1H), 3.85 (t, $J = 10.2$ Hz, 1H, H-6), 3.96 (dd, $J = 9.6$, 3.4 Hz, 1H, H-3), 4.17 (t, $J = 9.6$ Hz, 1H, H-4), 4.21 (dd, $J = 4.5$, 10.2 Hz, 1H, H-6), 4.29 (br d, $J = 3.4$ Hz, H-2), 4.34 (ddd, $J = 4.5$, 9.6, 10.2, 2H, H-5), 4.74 (d, $J = 12.0$ Hz, A part of AB type, 1H), 4.90 (d, $J = 12.0$ Hz, B part of AB type, 1H), 5.55 (br s, 1H), 5.62 (s, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.29–7.40 (m, 10H), 7.49–7.60 (m, 2H); ^{13}C NMR (50 MHz, C_5D_5N) δ: 12.2, 14.2, 22.2, 22.6, 22.7, 27.3, 27.6, 27.7, 29.3, 29.4, 29.6, 29.7, 31.8, 31.9, 32.0, 36.4, 36.6, 36.9, 38.3, 39.1, 39.6, 45.4, 45.7, 47.5, 64.5 (C-5), 68.6 (C-6), 71.4 (C-2), 73.2 (OCH_2Ph), 75.7 (C-3), 79.0 (C-4), 88.0 (C-1), 101.6, 126.0, 127.8, 127.9, 128.1, 128.4, 128.9, 129.7, 131.9, 132.1, 137.3, 137.6, 146.1, 146.3, 146.4, 147.9; IR ($CHCl_3$): 2959, 2928, 2872, 2856, 1601, 1490, 1456, 1375 cm^{-1}; MS FAB(+) m/z: 641 $[M + Na]^+$; HRMS calcd for $C_{38}H_{50}O_5SNa$ $[M + Na]^+$: 641.3277, found: 641.3273.

13a: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.88 (m, 6H), 2.40 (m, 2H), 3.76 (t, $J = 9.5$ Hz, 1H), 3.85 (m, 2H), 4.01 (br s, 2H), 4.15 (dt, $J = 3.5$, 10.0 Hz, 1H), 4.55 (d, $J = 11.0$ Hz, A part of AB, 1H), 4.63 (d, $J = 11.0$ Hz, A′ part of A′B′, 1H), 4.67 (d, $J = 11.0$ Hz, B′ part of A′B′, 1H), 4.93 (d, $J = 11.0$ Hz, B part of AB, 1H), 5.55 (br s, 1H), 7.10 (d, $J = 9.0$ Hz, 2H), 7.35 (m, 12H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 11.7, 13.5, 13.56, 13.60, 20.3, 21.7, 22.1, 22.22, 22.24, 22.3, 26.9, 27.17, 27.24, 27.3, 28.8, 28.9, 28.99, 29.09, 29.18, 19.25, 29.30, 29.4, 31.3, 31.39, 31.43, 31.48, 36.0, 36.2, 36.4, 37.8, 38.7, 39.1, 44.9, 45.2, 47.0, 61.4, 63.6, 72.2, 72.4, 74.4, 74.7, 76.8, 81.3, 86.4, 86.5, 126.4, 126.5, 127.0, 127.2, 127.4, 127.5, 127.9, 128.0, 128.16, 128.22, 131.6, 131.83, 131.86, 131.88, 138.6, 139.2, 143.1, 145.1, 145.4, 145.5, 147.0; MS FAB(+) m/z: 643 $[M + Na]^+$; HRMS calcd for $C_{38}H_{52}O_5SNa$ $[M + Na]^+$: 643.3433, found: 643.3427.

p-Dodecylphenyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-1-thio-α-D-mannopyranoside (14a)

Acetic anhydride (0.2 mL) was added to a solution of **13a** (4.8 mg) in pyridine (0.3 mL) and the mixture was stirred at room temperature for 30 min. After the reaction, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel preparative thin layer chromatography (hexane:ethyl acetate = 9:2) to afford **14a** (4.3 mg) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.85 (m, 6H), 1.98, 2.05 (each s, 3H, Ac), 3.98 (t, $J = 9.4$ Hz, 1H, H-4), 4.12 (br s, 1H, H-2), 4.34 (br s, 1H, H-6), 4.40 (m, 1H, H-5), 4.48 (d, $J = 12.0$ Hz, A part of AB), 4.59 (d, $J = 11.2$ Hz, A′ part of A′B′), 4.70 (m, 2H, B and B′ parts of AB and A′B′), 5.20 (dd, $J = 3.0$, 9.4 Hz, 1H, H-3), 5.50 (br s, 1H, H-1), 7.07 (m, 2H), 7.30 (m, 12H); MS FAB(+) m/z: 727 $[M + Na]^+$; HRMS calcd for $C_{42}H_{56}O_7SNa$ $[M + Na]^+$: 727.3644, found: 727.3640.

Reductive Cleavage of Benzylidene Protecting Group of 11b

A solution of **11b** (83.9 mg, 0.15 mmol) in diethyl ether (2 mL) and dichloromethane (2 mL) was added to a suspension of lithium aluminum chloride (11.0 mg, 0.29 mmol) and aluminum chloride (38.8 mg, 0.29 mmol) in diethyl ether (1 mL). After stirring the mixture for 30 min at room temperature, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 4:1) to afford **12b** (34.8 mg, 40%) and **13b** (21.0 mg, 24%) as a colorless syrup, respectively.

12b: $[\alpha]D^{26}$ +203.9° ($c = 0.89$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ: 0.86 (t, $J = 7.0$ Hz, 3H), 1.77 (quint, $J = 7.0$ Hz, 2H), 2.80 (s, 1H), 3.84 (t, $J = 10.2$ Hz, 1H, H-6), 3.93 (t, $J = 6.6$ Hz, 2H, OCH_2), 3.96 (dd, $J = 3.3$, 10.2 Hz, 1H, H-3), 4.16 (t, $J = 9.5$ Hz, 1H, H-4), 4.21 (dd, $J = 5.0$, 10.2 Hz, 1H, H-6), 4.26 (d, $J = 3.3$ Hz, 1H, H-2), 4.35 (ddd, $J = 5.0$, 9.5, 10.2 Hz, 1H, H-5), 4.74 (d, $J = 12.0$ Hz, A part of AB, 1H), 4.89 (d, $J = 12.0$ Hz, B part of AB, 1H), 5.42, 5.62 (each s, 1H), 6.83 (d, $J = 8.8$ Hz, 2H), 7.29–7.40 (m, 10H), 7.50–7.53 (m, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 13.6, 22.2, 25.6, 28.8 (2C), 28.9, 31.3, 65.2 (C-5), 67.6 ($O\underline{C}H_2C_7H_{15}$), 68.3 (C-6), 70.6 (C-2), 72.1 ($O\underline{C}H_2Ph$), 76.7 (C-3), 79.2 (C-4), 90.9 (C-1), 101.4 ($Ph\underline{C}H<$), 115.1 (2C), 123.3, 126.2 (2C), 127.2, 127.6 (2C), 127.9 (2C), 128.0 (2C), 128.5, 134.8 (2C), 138.2, 138.7, 159.2; MS FAB(+) m/z: 579 $[M + H]^+$; HRMS calcd for $C_{34}H_{43}O_6S$ $[M + H]^+$: 579.2780, found: 579.2776.

13b: $[\alpha]D^{25}$ +104.4° ($c = 1.17$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, $J = 7.0$ Hz, 3H), 1.77 (quint, $J = 7.0$ Hz, 2H), 2.38 (d, $J = 9.2$ Hz, 1H), 3.73 (t, $J = 9.2$ Hz, 1H), 3.81 (m, 2H), 3.93 (t, $J = 6.5$ Hz, 2H, OCH_2), 3.99 (br s, 1H), 4.03 (dd, $J = 3.5$, 9.0 Hz, 1H), 4.16 (ddd, $J = 3.5$, 9.0, 9.2 Hz, 1H), 4.54 (d, $J = 12.0$ Hz, A part of AB, 1H), 4.67 (d, $J = 11.5$ Hz, A′ part of A′B′, 1H), 4.70 (d, $J = 11.5$ Hz, B′ part of A′B′, 1H), 4.92 (d, B part of AB, 1H), 6.83 (d, $J = 8.5$ Hz, 2H), 7.27–7.39 (m, 12H); ^1H NMR (400 MHz, C_5D_5N) δ: 0.84 (t, $J = 6.9$ Hz, 3H), 1.36 (m, 2H), 1.68 (m, 2H), 3.85 (dt, $J = 2.8$, 6.4 Hz, 2H, OCH_2), 4.28 (dd, $J = 5.0$, 12.0 Hz, A part of AB, 1H, H-6), 4.35 (dd, $J = 2.0$, 12.0 Hz, B part of AB, 1H, H-6), 4.30 (dd, $J = 1.5$, 3.3 Hz, 1H, H-2), 4.51 (t, $J = 9.2$ Hz, 1H, H-4), 4.65 (dd, $J = 3.3$, 9.2 Hz, 1H, H-3), 4.70 (ddd, $J = 2.0$, 5.0, 9.2 Hz, 1H, H-5), 4.87, 4.92 (each d, $J = 12.0$ Hz, AB type, 1H, $PhC\underline{H}_2O$), 4.98, 5.31 (each d, $J = 11.4$ Hz, AB type, 1H, $PhC\underline{H}_2O$), 5.94 (d, $J = 1.5$ Hz, 1H, H-1), 6.97 (d, $J = 8.7$ Hz, 2H), 7.28 (m, 6H), 7.49, 7.53 (each d, $J = 6.9$ Hz, 2H), 7.71 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 13.6, 22.2, 25.6, 28.8 (2C), 28.9, 31.3, 61.4 (C-6), 67.6 (OCH_2), 72.3 ($Ph\underline{C}H_2O$), 72.4 (C-3), 74.4 ($Ph\underline{C}H_2O$), 74.6 (C-5), 76.9 (C-4), 81.1 (C-2), 87.3

(C-1), 115.0 (2C), 124.5, 127.0, 127.2, 127.4 (2C), 127.6 (2C), 127.9 (2C), 128.0 (2C), 134.7 (2C), 138.6, 139.3, 159.0; MS FAB(+) m/z: 579 $[M+H]^+$; HRMS calcd for $C_{34}H_{43}O_6S$ $[M+H]^+$: 579.7778, found: 579.2780.

p-Octyloxyphenyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-1-thio- α-D-mannopyranoside (14b)

Acetic anhydride (0.2 mL) and *N*,*N*-dimethylaminopyridine (1 mg) were added to a solution of **13b** (20.7 mg) in pyridine (0.3 mL) and the mixture was stirred at room temperature for 30 min. After the reaction, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel preparative thin layer chromatography (hexane:ethyl acetate = 5:1) to afford **14b** (22.1 mg, 93%) as a colorless syrup. $[\alpha]D^{24}$ +67.3° ($c = 0.62$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, $J = 6.7$ Hz, 3H), 1.77 (m, 2H), 1.99, 2.05 (each s, 3H), 3.93 (t, $J = 6.7$ Hz, 2H, OCH_2-), 3.96 (t, $J = 9.3$ Hz, 1H, H-4), 4.10 (dd, $J = 2.0$, 3.0 Hz, 1H, H-2), 4.32 (m, 2H), 4.40 (m, 1H, H-5), 4.47 (d, $J = 12.0$ Hz, A part of AB, 1H), 4.58 (d, $J = 11.2$ Hz, A′ part of A′B′, 1H), 4.66 (d, $J = 11.2$ Hz, B′ part of A′B′, 1H), 4.72 (d, $J = 12.0$ Hz, B part of AB, 1H), 5.22 (dd, $J = 3.0$, 9.3 Hz, 1H, H-3), 5.38 (d, $J = 2.0$ Hz, 1H, H-1), 6.82 (d, $J = 8.8$ Hz, 2H), 7.30 (m, 12H); MS FAB(+) m/z: 687 $[M+Na]^+$; HRMS calcd for $C_{38}H_{48}O_8SNa$ $[M+Na]^+$: 687.2968, found: 687.2972.

3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl Fluoride (16)

N-Iodosuccinimide (14.2 mg, 0.063 mmol) and boron trichloride etherate complex (8 μL, 0.063 mmol) were added to a suspension of allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**15a**) (20.6 mg, 0.042 mmol), **12a** (26.0 mg, 0.042 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (2 mL) at 0°C. After stirring the mixture for 30 hours while keeping the temperature, the reaction mixture was filtered through Hiflro super® which was washed with ethyl acetate. The filtrate was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel thin layer chromatography (*n*-hexane/ethyl acetate = 3:1) to afford **16** (5.0 mg, 31%) as a syrup.

^1H NMR (300 MHz, $CDCl_3$) δ: 3.84 (t, $J = 9.9$ Hz, 1H, H-6), 3.93 (d, $J = 8.5$ Hz, 1H, H-3), 3.96 (dt, $J = 4.8$, 9.9 Hz, 1H, H-5), 4.14 (t, $J = 8.5$ Hz, 1H, H-4), 4.14 (s, 1H, H-2), 4.33 (dd, $J = 4.8$, 9.9 Hz, H-6), 4.73 (d, $J = 11.7$ Hz, A part of AB, 1H), 4.90 (d, $J = 11.7$ Hz, B part of AB, 1H), 5.61 (d, $J = 49.0$ Hz, 1H, H-1), 5.62 (s, 1H, PhCH); MS FAB(+) m/z:

361 $[M+H]^+$; HRMS calcd for $C_{20}H_{21}FO_5$ $[M+H]^+$: 383.1271, found: 383.1275.

p-Dodecylphenyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (17a)

Acetic anhydride (20 μL, 0.2 mmol) was added to a solution of **12a** (88.8 mg, 0.144 mmol) in pyridine (5 mL) and the mixture was stirred for 30 min at room temperature. After the reaction, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was successively washed with water and a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexene/ethyl acetate = 6:1) to afford **17a** (95 mg, 100%) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.82 (m, 6H), 2.15 (s, 3H, OAc), 3.86 (t, J = 10.2 Hz, 1H, H-6), 4.00 (dd, J = 3.2, 9.8 Hz, 1H, H-3), 4.14 (t, J = 9.8 Hz, 1H, H-4), 4.23 (dd, J = 5.0, 10.2 Hz, 1H, H-6), 4.37 (ddd, J = 5.0, 9.8, 10.2 Hz, H-5), 4.68 (d, J = 12.0 Hz, A part of AB, 1H), 4.72 (d, J = 12.0 Hz, B part of AB, 1H), 5.40 (br s, 1H, H-1), 5.62 (dd, J = 1.3, 3.2 Hz, 1H, H-2), 5.64 (s, 1H, PhC<u>H</u>); 7.07 (d, J = 8.2 Hz, 2H), 7.27–7.42 (m, 10H), 7.50–7.54 (m, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 11.6, 13.47, 13.53, 13.6, 20.1, 20.3, 21.7, 22.1, 22.19, 22.22, 22.3, 26.9, 27.22, 27.23, 28.77, 28.85, 28.95, 29.06, 29.14, 29.3, 29.4, 31.3, 31.36, 31.41, 37.8, 38.6, 39.1, 44.9, 45.2, 47.0, 65.2, 67.9, 71.2, 71.8, 74.4, 78.5, 86.9, 101.3, 126.2, 127.3, 127.4, 127.7, 127.9, 128.0, 128.4, 128.6, 132.1, 137.9, 138.1, 169.3; MS FAB(+) m/z: 683 $[M+Na]^+$; HRMS calcd for $C_{40}H_{52}O_6SNa$ $[M+Na]^+$: 683.3382, found: 683.3390.

p-Octylphenyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (17b)

Acetic anhydride (5 μL) was added to a solution of **12b** (24.3 mg, 0.042 mmol) in pyridine (0.3 mL) and the mixture was stirred for 30 min at room temperature. After the reaction, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was successively washed with water and a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel preparative thin layer chromatography (*n*-hexene/ethyl acetate = 4:1) to afford **17b** (26 mg, 100%) as a colorless syrup. $[\alpha]D^{24}$ +106.3° (c = 2.94, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, J = 7.0 Hz, 3H), 1.77 (quint, J = 7.0 Hz, 2H), 2.14 (s, 3H, OAc), 3.85 (t, J = 9.9 Hz, 1H, H-6), 3.93 (t, J = 6.6 Hz, 2H, OCH_2), 4.01 (dd, J = 3.5, 9.9 Hz, 1H, H-3), 4.12 (t, J = 9.9 Hz, 1H, H-4), 4.23 (dd, J = 5.0, 9.9 Hz, 1H, H-6), 4.38 (dt, J = 5.0, 9.9 Hz, 1H, H-5), 4.68 (d, J = 12.3 Hz, A part of AB, 1H), 4.73

(d, $J = 12.3$ Hz, B part of AB, 1H), 5.28 (d, $J = 1.5$ Hz, 1H, H-1), 5.60 (dd, $J = 1.5$, 3.5 Hz, 1H, H-2), 5.64 (s, 1H, PhC<u>H</u>), 6.83 (d, $J = 8.8$ Hz, 2H), 7.25–7.43 (m, 10H), 7.50–7.54 (m, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: 13.6, 20.1, 22.2, 25.6, 28.7, 28.8, 28.9, 31.3, 65.0, 67.6, 67.9, 71.0, 71.8, 74.4, 78.6, 87.6, 101.4, 115.2 (2C), 126.2 (2C), 127.3, 127.4 (2C), 127.9 (2C), 128.0 (2C), 128.6, 135.1 (2C), 137.9, 138.2, 159.5, 169.4; IR ($CHCl_3$): 2930, 2858, 1743, 1595, 1495, 1468, 1456, 1373 cm^{-1}; MS FAB(+) m/z: 643 $[M + Na]^+$; HRMS calcd for $C_{36}H_{44}O_7SNa$ $[M + Na]^+$: 643.2705, found: 643.2700.

2-(Trimethylsilyl)ethyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (18) from 15b and 17a

N-Iodosuccinimide (133 mg, 0.59 mmol) and silver triflate (60.9 mg, 0.24 mmol) were added to a suspension of **15** (157 mg, 0.24 mmol), **17a** (131 mg, 0.24 mmol), and molecular sieves 4A (MS 4A) (200 mg) in dichloromethane (5 mL). After stirring the mixture for 2 hours at room temperature, the reaction mixture was filtered through Hiflro super® which was washed with chroroform. The filtrate was condensed in vacuo and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 6:1) to afford **18** (199 mg, 90%). $[\alpha]D^{24}$ +14.4° ($c = 1.05$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ: − 0.01 (s, 9H), 1.00 (m, 2H), 2.16 (s, 3H, OAc), 3.42 (m, 3H), 3.46 (t, $J = 10.3$ Hz, 1H), 3.55–3.72 (m, 3H), 3.77–3.88 (m, 3H), 3.93–4.07 (m, 3H), 4.20 (br d, $J = 6.0$ Hz, 1H), 4.37 (d, $J = 7.5$ Hz, 1H), 4.50 (d, $J = 11.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, A part of AB, 1H), 4.70 (d, $J = 12.0$ Hz, B part of AB, 1H), 4.73 (d, $J = 11.0$, A' part of A′B′, 1H), 4.78 (d, $J = 11.0$ Hz, A′ part of A′B′, 1H), 4.84 (d, $J = 7.5$ Hz, 1H), 4.86 (d, $J = 1.6$ Hz, 1H), 4.95 (d, $J = 11.0$ Hz, B′ part of AB, 1H), 4.97 (d, $J = 11.0$ Hz, B′ part of A′B′, 1H), 5.46 (dd, $J = 1.6$, Hz, 1H, H-2), 5.61 (s, 1H), 7.18–7.37 (m, 23H), 7.45–7.48 (m, 2H); ^{1}H NMR (400 MHz, C_5D_5N) δ: 0.03 (s, 9H), 1.07 (t, $J = 8.0$ Hz, 3H), 2.08 (s, 3H), 3.73 (dd, $J = 8.0$, 9.0 Hz, 1H, Glc-2), 3.80 (m, 3H, Glc-4, 5, and a part of OCH_2), 3.96 (br t, $J = 10.0$ Hz, 2H, Man-6 and Glc-3), 4.03 (br d, $J = 11.0$ Hz, A part of AB, 1H, Glc-6), 4.14 (dd, $J = 4.0$, 11.0 Hz, B part of AB, 1H, Glc-6), 4.20 (t, $J = 9.5$ Hz, 1H, a part of OCH_2), 4.25 (dt, $J = 4.5$, 9.5 Hz, 1H, Man-5), 4.37, (dd, $J = 5.5$, 10.0 Hz, Man-6), 4.38 (dd, $J = 3.5$, 9.5 Hz, 1H, Man-3), 4.47 (t, $J = 9.5$ Hz, 1H, Man-4), 4.73 (d, $J = 8.0$ Hz, 1H, Glc-1), 4.79 (d, $J = 11.5$ Hz, 2H, A and A′ parts of AB and A′B′), 4.86 (d, $J = 11.5$ Hz, B part of AB, 1H), 4.96 (d, $J = 11.5$ Hz, A′ part of A′B′, 1H), 4.97 (d, $J = 11.5$ Hz, A′part of A′B′, 1H), 5.09 (d, $J = 11.5$ Hz, B′ part of A′B′ 1H), 5.15 (d, $J = 11.5$ Hz, B′ part of A′B′, 1H), 5.21 (d, $J = 11.5$ Hz, B′part of A′B‘, 1H), 5.27 (d, $J = 1.5$ Hz, 1H, Man-1), 5.84 (s, 1H, PhC<u>H</u><),

5.89 (dd, $J = 1.5$, 3.5 Hz, 1H, Man-2), 7.15–7.40 (m, 15H), 7.48 (m, 6H), 7.56 (d, $J = 7.0$ Hz, 2H), 7.71 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: − 2.0 (3C), 17.8, 20.1, 64.1 (Man-5), 66.4 (Glc-6), 66.6 (OCH_2-), 68.3 (Man-6), 69.4 (Man-2), 71.6 ($O\underline{C}H_2Ph$), 73.6 (Glc-4), 74.1, 74.0 (Man-3, $O\underline{C}H_2Ph$), 74.3 ($O\underline{C}H_2Ph$), 74.9 ($O\underline{C}H_2Ph$), 77.7 (Glc-5), 78.3 (Man-4), 82.2 (Glc-2), 84.5 (Glc-3), 98.8 (Man-1), 101.3 ($Ph\underline{C}H<$), 102.8 (Glc-1), 126.2 (2C), 127.1, 127.2, 127.30, 127.34 (2C), 127.5 (4C), 127.6 (2C), 127.8 (2C), 127.93 (2C), 127.97 (2C), 127.99 (3C), 128.1 (2C), 128.5, 138.0, 138.3, 138.4, 138.9, 139.0, 169.2; IR ($CHCl_3$): 3007, 2952, 2912, 2875, 1747, 1456 cm^{-1}; MS FAB(+) m/z: 955 $[M + Na]^+$; HRMS calcd for $C_{54}H_{64}O_{12}SiNa$ $[M + Na]^+$: 955.4065, found: 955.4060.

2-(Trimethylsilyl)ethyl 2-*O*-acetyl-3-*O*-benzyl-4,6-benzylidene-α-D-mannopyranosyl-(1 → 6)2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (18) from 15b and 17b

N-Iodosuccinimide (31.4 mg, 0.14 mmol) and silver triflate (14.4 mg, 0.056 mmol) were added to a suspension of **15** (30.8 mg, 0.056 mmol), **17b** (34.7 mg, 0.056 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (2 mL) at − 50°C. After stirring the mixture for 2 hours at room temperature, the reaction mixture was filtered through Hiflrosuper® which was washed with chroroform. The filtrate was condensed in vacuo and the residue was purified by silica gel preparative thin layer chromatography (*n*-hexane/ethyl acetate = 3:1) to afford **18** (42.1 mg, 81%).

2-(Trimethylsilyl)ethyl 3-*O*-benzyl-4,6-benzylidene-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-Obenzyl-β-D-glucopyranoside (19)

28% Sodium methoxide in methanol (4 mL, 0.08 mmol) was added to a solution of **18** (65 mg, 0.07 mmol) in methanol (3 mL) and the mixture was stirred for 30 min at room temperature. After the reaction, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel preparative thin layer chromatography (*n*-hexane/ethyl acetate = 3:1) to afford **19** (57.5 mg, 92%). $[\alpha]D^{24}$ +28.6° ($c = 1.33$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.00 (s, 9H), 1.00 (t, $J = 7.5$ Hz, 2H), 2.61 (br s, 1H), 3.35–3.70 (m, 6H), 3.77–3.88 (m, 4H), 3.92–4.15 (m, 4H), 4.20 (br d, 5.1 Hz, 1H), 4.37 (d, $J = 7.7$ Hz, 1H), 5.53 (d, $J = 11.0$ Hz, 1H), 4.68 (d, $J = 11.0$ Hz, 1H), 4.73 (d, $J = 11.0$ Hz, 1H), 4.78 (d, $J = 11.0$ Hz, 1H), 4.83 (d, $J = 11.0$ Hz, 1H), 4.86 (d, $J = 11.0$ Hz,

1H), 4.95 (d, $J = 11.0$ Hz, 1H), 4.96 (d, $J = 11.0$ Hz, 1H), 5.87 (br s, 1H), 7.24–7.33 (m, 23H), 7.45–7.46 (m, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: − 2.0 (3C), 17.9, 64.4 (Man-5), 66.1 (Glc-6), 66.6 (-OCH_2), 68.6 (Man-6), 69.2 (Man-2), 72.1 (O$\underline{C}H_2$Ph), 73.9 (Glc-4), 74.0 (Man-3), 74.3 (O$\underline{C}H_2$Ph), 74.9 (O$\underline{C}H_2$Ph), 76.3 (Glc-5), 77.7 (Man-4), 79.1 (O$\underline{C}H_2$Ph), 82.3 (Glc-2), 84.6 (Glc-3), 101.3 (Man-1), 102.1 (Ph$\underline{C}$H<), 102.8 (Glc-1), 126.2, 127.1, 127.2, 127.3, 127.5 (2C), 127.6, 127.8, 127.9, 128.0 (2C), 128.1, 128.4, 138.3, 138.5, 138.8, 139.0 (2C); IR ($CHCl_3$): 3691, 3571, 3067, 3049, 3016, 2954, 2927, 2880, 1602, 1454 cm^{-1}; MS FAB(+) m/z: 913 $[M + Na]^+$; HRMS calcd for $C_{52}H_{62}O_{11}SiNa$ $[M + Na]^+$: 913.3953, found: 913.3959.

2-(Trimethylsilyl)ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (20) from 19 and 9a

N-Iodosuccinimide (22.8 mg, 0.11 mmol) and silver triflate (10.0 mg, 0.041 mmol) were added to a suspension of **19** (36.2 mg, 0.041 mmol), **9a** (28.3 mg, 0.041 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (2 mL) at −50°C. After stirring the mixture for 2 hours while keeping the temperature, the reaction mixture was filtered through Hiflo super® which was washed with chroroform. The filtrate was condensed in vacuo and the residue was purified by silica gel preparative thin layer chromatography (*n*-hexane/ethyl acetate = 3:1, 3 times) to afford **20** (48.6 mg, 92%). $[\alpha]D^{24}$ +6.3° ($c = 1.62$, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.06 (s, 9H), 1.06 (dt, $J = 5.0$, 13.5 Hz, 1H), 1.16 (dt, $J = 5.0$, 13.5 Hz, 1H), 1.89, 2.04, 2.07 (each s, 3H, OAc), 2.91 (t, $J = 10.0$ Hz, 1H), 3.31–3.36 (m, 3H), 3.40–3.85 (m, 8H), 3.94 (t, $J = 6.6$ Hz, 2H), 4.07 (dt, $J = 2.0$, 9.0 Hz, 1H), 4.13–4.41 (m, 5H), 4.48 (dd, $J = 8.5$, 10.5 Hz, 1H), 4.65 (br s, 1H), 4.69 (d, $J = 8.5$ Hz, 1H), 4.71 (d, $J = 8.5$ Hz, 1H), 4.74 (d, $J = 8.0$ Hz, 1H), 4.78 (d, $J = 8.0$ Hz, 1H), 4.97 (t, $J = 11.0$ Hz, 2H), 5.21 (t. $J = 9.0$ Hz, 1H), 5.39 (s, 1H), 5.48 (d, $J = 8.4$ Hz, 1H), 5.89 (dd, $J = 9.0$, 10.5 Hz, 1H), 6.83 (d, $J = 8.8$ Hz, 2H), 7.08–7.38 (m, 25H), 7.74 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: − 2.0 (3C), 18.2, 19.6, 19.8, 20.0, 54.6 (GlcN-2), 62.1 (GlcN-6), 63.8 (Man-5), 66.9 (Glc-6), 67.6 (OCH_2-), 68.1 (Man-6), 69.4 (GlcN-4), 70.1 (O$\underline{C}H_2$Ph), 70.4 (GlcN-3), 71.7 (GlcN-5), 72.9 (Glc-4), 73.6 (Man-3), 74.0 (O$\underline{C}H_2$Ph), 74.2 (O$\underline{C}H_2$Ph), 74.3 (Man-2), 75.1 (O$\underline{C}H_2$Ph), 77.0 (Glc-5), 78.1 (Man-4), 82.6 (Glc-2), 84.4 (Glc-3), 95.8 (GlcN-1), 98.6 (Man-1), 101.4 (Ph$\underline{C}$H<), 103.2 (Glc-1), (2C), 127.17, 127.24, 127.26, 127.34, 127.38 (3C), 127.56 (3C), 127.65 (3C), 127.66 (3C), 127.68 (3C), 128.0 (6C), 128.1 (3C), 128.4, 134.0, 137.8, 138.4, 138.8, 139.0, 167.4,

168.4, 169.1, 169.6, 169.9; MS FAB(+) m/z: 1330 $[M + Na]^+$; HRMS calcd for $C_{72}H_{81}O_{20}NSiNa$ $[M + Na]^+$: 1330.5019, found: 1330.5015.

2-(Trimethylsilyl)ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (20) from 19 and 9b

N-Iodosuccinimide (18.3 mg, 0.08 mmol) and silver triflate (8.4 mg, 0.033 mmol) were added to a suspension of **19** (29.0 mg, 0.033 mmol), **9b** (21.3 mg, 0.033 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (2 mL) at −50°C. After stirring the mixture for 2 hours while keeping the temperature, the reaction mixture was filtered through Hiflro super® which was washed with chloroform. The filtrate was condensed in vacuo and the residue was purified by silica gel preparative thin layer chromatography (*n*-hexane/ethyl acetate = 3:1, 3 times) to afford **20** (39.6 mg, 93%).

2-(Trimethylsilyl)ethyl 3,4,6-Tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (21)

Hydrazine hydrate (1 drop with a pipette) was added to a solution of **20** (61.4 mg, 0.047 mmol) in ethanol (2 mL) and the mixture was stirred for 1.5 hours at room temperature. After the reaction, the reaction mixture was filtered through filtrating paper which was washed with ethanol and the filtrate was evaporated. The obtained residue was treated with acetic anhydride (1 drop with a pipette) and pyridine (1 mL) in the presence of a catalytic amount of *N*,*N*-dimethyl-4-aminopyridine. After stirring the mixture for 1.5 hours at room temperature, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:1) and GPC to afford **21** (41.3 mg, 73%) as an amorphous powder. $[\alpha]D^{24}$ −2.2° (c = 1.26, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.02 (s, 9H), 1.05 (dt, J = 3.3, 7.5 Hz, 2H), 1.83 (s, 3H, NHAc), 2.01, 2.02, 2.03 (each s, 3H, OAc), 3.37 (t, J = 8.5 Hz, 1H), 3.44 (t, J = 8.5 Hz, 1H), 3.30–3.50 (m, 1H), 3.55–3.75 (m, 6H), 3.76–3.92 (m, 3H), 4.00–4.21 (m, 5H), 4.27 (dd, J = 5.0, 12.0 Hz, 1H), 4.40 (d, J = 8.0 Hz, 1H), 4.44 (d, J = 10.5 Hz, 1H), 4.63–4.89 (m, 6H), 4.93–5.08 (m, 4H), 5.45–5.65 (m, 3H), 7.14–7.37 (m, 23H), 7.43–7.46 (m, 2H); ^{13}C NMR (100 MHz, C_5D_5N) δ: −1.9 (3C), 18.0, 19.89, 19.94, 20.0, 20.1, 22.7, 24.4, 55.1 (GlcNAc-2), 62.2 (GlcNAc-6), 64.4 (Man-5), 66.9 (Glc-6), 67.2 (OCH_2), 68.5

(Man-6), 69.3 (GlcNAc-4), 70.2 (O$\underline{C}H_2$Ph), 71.6 (GlcNAc-5), 72.2 (GlcNAc-3), 73.8 (Glc-4), 73.9 (Man-3), 74.0 (Man-2), 74.3 (Ph$\underline{C}H_2$O-), 74.4 (Ph$\underline{C}H_2$O-), 75.1 (O$\underline{C}H_2$Ph), 77.4 (Glc-5), 78.1 (Man-4), 82.4 (Glc-2), 84.6 (Glc-3), 99.0 (Man-1), 99.3 (GlcNAc-1), 101.4 (Ph$\underline{C}$H<), 103.0 (Glc-1), 126.3, 127.18, 127.21, 127.27, 127.36, 127.47, 127.51, 127.60, 127.62, 127.74, 127.96, 128.04, 128.12, 128.45, 138.0, 138.4, 138.6, 138.8, 139.0, 169.2, 169.86, 169.90, 169.99, 170.3, 171.3; MS FAB(+) m/z: 1242 $[M + Na]^+$; HRMS calcd for $C_{66}H_{81}O_{19}NSiNa$ $[M + Na]^+$: 1242.5070, found: 1242.5065.

2-(Trimethylsilyl)ethyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (22)

Sodium methoxide (28% solution in methanol, 58 μL) was added to a solution of **21** (352.3 mg, 0.289 mmol) in methanol (5 mL) and the mixture was stirred for 30 min at room temperature. After the reaction, the reaction mixture was neutralized with Dowex 50 (H^+) and filtered. The filtrate was condensed in vacuo and the residue was purified by silica gel column chromatography (chloroform:methanol = 10:1) to afford **22** (310.4 mg, 98%) as amorphous powder. $[\alpha]D^{24}$ +1.3° (c = 1.34, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.01 (s, 9H), 1.04 (t, J = 8.0 Hz, 2H), 1.76 (s, 3H, NHAc), 3.36–3.50 (m, 6H), 3.57–4.22 (m, 16H), 4.39 (d, J = 7.8 Hz, 1H), 4.45 (br d, J = 10.5 Hz, 1H), 4.72–4.84 (m, 6H), 4.96 (s, 2H), 5.00 (s, 1H), 5.64 (s, 1H), 7.14–7.36 (m, 23H), 7.45–7.48 (m, 2H); ^{1}H NMR (400 MHz, C_5D_5N) δ: 0.01 (s, 9H), 1.10 (t, J = 8.0 Hz, 2H), 2.18 (s, 3H), 3.76 (br t, J = 8.0 Hz, 4H), 3.96 (br t, J = 10.0 Hz, 4H), 4.20 (m, 4H), 4.30–4.55 (m, 7H), 4.65 (br t, J = 9.5 Hz, 1H), 4.75 (m, 2H), 4.83 (br dd, J = 5.0, 6.0 Hz, 2H), 4.98 (br t, J = 13.0 Hz, 1H), 5.08 (br d, J = 11.5 Hz, 1H), 5.16 (br d, J = 11.0 Hz, 1H), 5.26 (br d, J = 11.5 Hz, 1H), 5.35 (br d, J = 7.5 Hz, 1H), 5.51 (br s, 1H), 5.61 (br s, 1H), 6.04 (br, 1H), 7.14 (br t, J = 7.0 Hz, 1H), 7.20–7.40 (m, 16H), 7.48 (m, 3H), 7.60 (m, 5H), 8.82 (br d, J = 7.8 Hz, 1H); ^{13}C NMR (C_5D_5N, 100 MHz) δ: −1.9 (3C), 17.9, 23.2, 57.7 (GlcNAc-2), 62.3 (GlcNAc-6), 64.5 (Man-5), 66.7 (Glc-6), 66.8 (OCH_2), 68.5 (Man-6), 70.3 (O$\underline{C}H_2$Ph), 71.9 (GlcNAc-4), 73.7 (GlcNAc-5), 74.0 (GlcNAc-3), 74.1 (Glc-4), 74.3 (Man-3), 74.4 (O$\underline{C}H_2$Ph), 74.9 (O$\underline{C}H_2$Ph), 75.0 (O$\underline{C}H_2$Ph), 77.5 (Man-2), 77.7 (Glc-5), 78.1 (Man-4), 82.3 (Glc-2), 84.6 (Glc-3), 99.2 (Man-1), 100.7 (GlcNAc-1), 101.4 (Ph$\underline{C}$H<), 102.9 (Glc-1), 126.3 (2C), 127.0, 127.16, 127.20, 127.3, 127.4 (2C), 127.5 (2C), 127.6 (4C), 127.7 (2C), 127.9 (2C), 128.00 (2C), 128.03 (2C), 128.1 (2C), 128.4, 135.1, 138.1, 138.5, 138.8, 138.9, 170.1; MS FAB(+) m/z: 1116 $[M + Na]^+$; HRMS calcd for $C_{60}H_{75}O_{16}NSiNa$ $[M + Na]^+$: 1116.4753, found: 1116.4757; Anal.

Calcd for $C_{60}H_{75}O_{16}NSi$: C, 64.95; H, 6.69; N, 1.15. Found: C, 64.71; H, 6.66; N, 1.16.

2-(Trimethylsilyl)ethyl 2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-β-D-glucopyranoside (3a)

Palladium-carbon (15.3 mg) and formic acid (15 μL) were added to a solution of **22** (17.3 mg, 0.016 mmol) in methanol (1 mL) and the mixture was stirred under hydrogen atmosphere for 12 hours at room temperature. After the reaction, the reaction mixture was filtered and the filtrate was condenced in vacuo to afford **3a** (10.0 mg, 99%). ^{1}H NMR (400 MHz, C_5D_5N) δ: − 0.02 (s, 9H), 1.05 (m, 2H), 2.19 (3H, s, NHAc), 3.79 (dt, J = 6.5, 10.0 Hz, 1H), 3.87 (br, 1H), 3.99 (br t, J = 8.0 Hz, 2H), 4.11 (br t, J = 9.0 Hz, 2H), 4.18–4.30 (m, 4H), 4.34–4.46 (m, 6H), 4.48–4.56 (m, 3H), 4.64 (br t, J = 9.3 Hz, 1H), 4.81 (d, J = 7.5 Hz, 1H, Glc-1), 5.13 (d, J = 7.5 Hz, 1H, GlcNAc-1), 5.49 (br s, 1H, Man-1), 9.07 (br d, J = 7.0 Hz, 1H, NH); ^{13}C NMR (100 MHz, C_5D_5N) δ: − 2.0 (3C), 17.8 ($\underline{C}H_2SiMe_3$), 23.1 ($\underline{C}H_3CO$), 57.0 (GlcNAc-2), 61.4, 61.9 (GlcNAc-6, Man-6), 66.3 (Glc-6), 66.9 ($O\underline{C}H_2CH_2Si$), 67.9 (Man-4), 70.5, 71.0, 71.2 (Man-2 and 3, Glc-4), 74.5 (2C), 74.8 (GlcNAc-3 and 4, Man-5), 75.6 (Glc-2), 77.8, 78.1 (GlcNAc-5, Glc-5), 79.5 (Glc-3), 98.3 (Man-1), 102.1 (GlcNAc-1), 103.6 (Glc-1), 171.2 (CH_3CO); MS FAB(+) m/z: 668 $[M + Na]^+$; HRMS calcd for $C_{25}H_{47}O_{16}NSiNa$ $[M + Na]^+$: 668.2562, found: 668.2558.

Methyl (*p*-Dodecylphenyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (24a)

Boron trifluoride etherate complex (377 μL, 2.98 mmol) was added to a solution of **23** (529 mg, 0.99 mmol) and **1** (553 mg, 1.98 mmol) in dichloromethane (5 mL) at 0°C and mixture was stirred for 16 hours at room temperature. After the reaction, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:2) to afford **24a** (550.6 mg, 74%). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.1, 14.0, 14.1, 20.6, 20.7, 20.8, 21.0, 22.0, 22.5, 22.6, 23.2, 27.2, 27.6, 27.7, 29.3, 29.6, 29.7, 31.8, 36.6, 36.8, 37.6, 38.2, 38.9, 39.8, 45.6, 45.8, 47.6, 49.3, 49.5, 52.4, 62.0, 62.5, 67.7, 67.7, 67.8, 72.8, 72.9,73.1, 125.8, 127.77, 127.81, 128.4, 128.5, 135.9, 136.1, 148.5, 148.8, 150.2, 170.21, 170.25, 170.28, 170.9, 171.0; IR ($CHCl_3$): 3028, 3008, 2956, 2927, 2856, 1739, 1685, 1508, 1456, 1436 cm^{-1}; MS FAB(+) m/z: 753 $[M + H]^+$; HRMS calcd for $C_{38}H_{58}O_{12}NS$ $[M]^+$: 752.3680, found: 752.3676.

Methyl (*p*-Octyloxyphenyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (24b)

Boron trifluoride etherate complex (340 μL, 2.64 mmol) was added to a solution of **23** (469 mg, 0.88 mmol) and **2** (419 mg, 1.76 mmol) in dichloromethane (10 mL) at 0°C and mixture was stirred for 13 hours at room temperature. After the reaction, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (chloroform/methanol = 50:1) to afford **24b** (462 mg, 74%), which was further purified by silica gel preparative thin layer chromatography (ethyl acetate) for data collection. $[\alpha]D^{24}$ −108.0° ($c = 0.68$, $CHCl_3$); ^1H NMR of the major (β) isomer (400 MHz, $CDCl_3$) δ: 0.88 (m, 3H), 1.90 (s, 3H, NHAc), 2.03 (s, 6H, 2 × OAc), 2.07, 2.12 (each s, 3H, OAc), 2.45 (m, 1H, H-3ax), 2.66 (dd, $J = 5.7$, 13.7 Hz, 1H, H-3eq), 3.50 and 3.51 (s, 3H, CO_2Me), 3.95–4.25 (m, 2H), 4.50–4.65 (m, 2H), 4.80–5.00 (m, 1H), 5.25–5.50 (m, 3H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H).

Several signals in the ^1H NMR of the minor (α) isomer (400 MHz, $CDCl_3$) δ: 2.38 (m, 1H), 2.82 (dd, $J = 5.0$, 13.0 Hz, 1H, H-3eq), 3.55 and 3.57 (s, 3H, CO_2Me), 7.13 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 20.6, 20.7, 20.8, 21.1, 22.6, 23.1, 26.0, 29.1, 29.2, 29.3, 31.8, 37.1, 49.5, 52.6, 62.7, 68.1, 68.8, 69.1, 73.0, 73.2, 88.7, 115.1 (2C), 118.8, 138.0 (2C), 160.7, 168.4, 170.21, 170.25, 170.31, 170.9, 171.1. MS FAB(+) m/z: 712 $[M + H]^+$; HRMS calcd for $C_{34}H_{50}O_{13}NS$ $[M + H]^+$: 712.3003, found: 712.2999.

Methyl (Methyl (5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate)-(2 → 6)-2,3,4-tri-*O*-acetyl-α-D-galactopyranoside (25) from 27 and 24a

N-Iodosuccinimide (41.8 mg, 0.19 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of methyl 2,3,4-tri-*O*-acetyl-1-*O*-α-D-galactopyranoside (**27**) (29.8 mg, 0.093 mmol), **24a** (69.9 mg, 0.093 mmol), and molecular sieves 4A (MS 4A) (150 mg) in acetonitrile (3 mL) at −40°C. After stirring the mixture for 1 hour while keeping the temperature, the reaction mixture was filtered through Hiflro super® which was washed with chroroform. The filtrate was condensed in vacuo and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:4) to afford **25** (54.3 mg, 74%) as an amorphous powder, which was further purified by the preparative HPLC (JAI LC-908: ethyl acetate) to obtain a sample for data collection. $[\alpha]D^{25}$ +33.0° ($c = 1.52$, $CHCl_3$); ^1H NMR of the major (α) isomer (400 MHz, $CDCl_3$) δ: 1.88 (s, 3H, NHAc), 1.92 (t, $J = 13.0$ Hz, 1H,

H-3ax), 1.98, 2.02, 2.04, 2.09, 2.12, 2.15, 2.17 (each s, 3H, OAc), 2.54 (dd, $J = 4.6$, 13.0 Hz, 1H, H-3eq), 3.30 (dd, $J = 6.6$, 10.3 Hz, 1H), 3.44 (s, 3H, OMe), 3.79 (s, 3H, CO_2Me), 3.85 (dd, $J = 6.4$, 10.3 Hz, 1H), 3.98–4.22 (m, 4H), 4.26 (dd, $J = 2.6$, 12.5 Hz, 1H), 4.87 (ddd, $J = 4.6$, 10.3, 13.0 Hz, 1H), 4.99 (d, $J = 3.5$ Hz, 1H), 5.14 (dd, $J = 3.6$, 10.8 Hz, 1H), 5.17 (m, 1H), 5.30–5.42 (m, 3H), 5.44 (br d, $J = 2.6$ Hz, 1H); Several signals in ^{1}H NMR of the minor (β) isomer (400 MHz, $CDCl_3$) δ: 2.45 (dd, $J = 4.8$, 13.0 Hz, 1H, H-3eq), 3.40 (s, 3H, OMe), 3.50 (dd, $J = 5.3$, 13.7 Hz, 1H), 3.81 (s, 3H, CO_2Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.66, 20.69, 20.82, 20.88, 21.05, 21.11, 23.1 (minor; m), 23.2 (Major; M), 61.1 (m), 62.3 (M), 63.0 (M), 66.5 (m), 67.1 (M), 67.2 (M), 67.6 (m), 68.0 (m), 68.1 (M), 68.2 (M), 68.3 (M), 68.5 (m), 68.8 (M), 68.9 (M), 71.8 (m), 71.9 (m), 72.5 (M), 97.1 (M), 97.2 (m), 98.5 (m), 98.6 (M), 166.9 (m), 167.9 (M), 169.6 (m), 169.7 (M), 170.1 (m), 170.18 (M), 170.23 (M, 2C), 170.3 (m), 170.4 (M), 170.5 (m), 170.56 (m), 170.57 (M), 170.9 (M), 171.6 (m), 171.7 (M); MS FAB(+) m/z: 794 $[M + H]^+$; HRMS calcd for $C_{33}H_{47}O_{21}N$ $[M + H]^+$: 794.2719, found: 794.2723.

Methyl (Methyl (5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate)-(2 → 6)-2,3,4-tri-*O*-acetyl-α-D-galactopyranoside (25) from 27 and 24b

N-Iodosuccinimide (27.8 mg, 0.12 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of methyl 2,3,4-tri-*O*-acetyl-1-*O*-α-D-galactopyranoside (**27**) (19.8 mg, 0.062 mmol), **24b** (44.0 mg, 0.062 mmol), and molecular sieves 4A (MS 4A) (150 mg) in acetonitrile (3 mL) at −40°C. After stirring the mixture for 1 hour while keeping the temperature, the reaction mixture was filtered through Hiflro super® which was washed with chroroform. The filtrate was condensed in vacuo and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:4) to afford **25** (31.2 mg, 64%).

Methyl (Methyl (5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate)-(2 → 3)-2,3,4-tri-*O*-acetyl-α-D-galactopyranoside (26) from 28 and 24a

N-Iodosuccinimide (44.7 mg, 0.20 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of methyl 2,3,6-tri-*O*-acetyl-1-*O*-α-D-galactopyranoside (**28**) (31.8 mg, 0.099 mmol), **24a** (74.7 mg, 0.099 mmol), and molecular sieves 4A (MS 4A) (150 mg) in acetonitrile (3 mL) at −40°C. After stirring the mixture for 1 hour while keeping the temperature, the reaction mixture was filtered through Hiflro super® which was washed

with chroroform. The filtrate was condensed in vacuo and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:2) to afford **26** (53.5 mg, 68%) as a amorphous powder, which was further purified by the preparative HPLC (JAI LC-908: ethyl acetate) to obtain a sample for data collection. $[\alpha]D^{27}$ +42.7° (c = 1.51, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.89 (s, 3H, NHAc), 2.01, 2.05, 2.08, 2.086, 2.093, 2.13, 2.21 (each s, 3H, OAc), 2.57 (dd, J = 4.7, 12.5 Hz, 1H), 3.38 (s, 3H, OMe), 3.71 (dd, J = 2.1, 10.5 Hz, 1H), 3.85 (s, 3H, CO_2Me), 3.88–4.20 (m, 4H), 4.22 (dd, J = 5.4, 12.5 Hz, 1H), 4.48 (dd, J = 2.5, 12.5 Hz, 1H), 4.80 (dd, J = 3.5, 10.5 Hz, 1H), 4.87 (d, J = 3.5 Hz, 1H), 4.86 (m, 1H), 5.07 (dd, J = 3.5, 10.5 Hz, 1H), 5.20–5.30 (m, 1H), 5.30–5.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 20.7 (2C), 20.78, 20.81, 20.96, 21.12, 23.2, 37.7, 49.4, 53.1, 55.2, 62.0, 62.5, 66.6, 67.9, 68.2, 68.4, 69.0, 69.2, 69.8, 73.0, 97.1, 97.6, 168.0, 169.7, 170.2, 170.3, 170.4 (2C), 170.45, 170.54, 170.9; MS FAB(+) m/z: 794 $[M + H]^+$; HRMS calcd for $C_{33}H_{47}O_{21}N$ $[M + H]^+$: 794.2719, found: 794.2712.

Methyl (Methyl (5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galcto*-2-nonulopyranosid)onate)-(2 → 3)-2,3,4-tri-*O*-acetyl-α-D-galactopyranoside (26) from 28 and 24b

N-Iodosuccinimide (43.2 mg, 0.19 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of methyl 2,3,6-tri-*O*-acetyl-1-*O*-α-D-galactopyranoside (**28**) (30.8 mg, 0.096 mmol), **24b** (68.4 mg, 0.096 mmol), and molecular sieves 4A (MS 4A) (150 mg) in acetonitrile (3 mL) at −40°C. After stirring the mixture for 1 hour while keeping the temperature, the reaction mixture was filtered through Hiflro super® which was washed with chroroform. The filtrate was condensed in vacuo and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:2) to afford **27** (36.7 mg, 48%).

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