4.5. Determination of reaction temperature

In the conventional method, reactions were conducted at 75 °C by heating in an oil bath [7]. Because this reaction temperature did not seem to be optimum, we investigated it further. First, 240 μL of water and 80 μL of $[^{99m}Tc(CO)_3(H_2O)_3]^+$ were added to 240 μL of a methanol solution of **2** (0.70 mM), and then the mixture was heated at 75 °C in an oil bath or in a microwave reactor. We also conducted reactions at 90 °C and 110 °C by using microwave heating. Radiochemical yields were calculated at fixed time points of 10, 15, and 30 min.

4.6. Evaluation of effects of microwave heating on ^{99m}Tc reactions

We investigated whether ^{99m}Tc complexes can be rapidly synthesized using microwave heating or the conventional method. Several concentrations of **2**, PAMAEE, and DPA were reacted with $[^{99m}Tc(CO)_3(H_2O)_3]^+$ for 1–60 min.

4.7. Statistical test

StatView 5.0 (SAS, USA) was used for statistical analysis. A Bonferroni/Dunn test was used to assess the differences in the radiochemical yield between oil-bath heating and microwave heating. $p < 0.05$ was considered significant.

Acknowledgments

We thank FUJIFILM RI Pharma Co., Ltd., Tokyo, Japan, for providing the IsoLink™ kit. This work was supported in part by a Grant-in-Aid for General Scientific Research from the Japan Society for the Promotion of Science.

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HETEROCYCLES, Vol. 83, No. 12, 2011, pp. 2779 - 2802. © 2011 The Japan Institute of Heterocyclic Chemistry
Received, 9th August, 2011, Accepted, 30th September, 2011, Published online, 13th October, 2011
DOI: 10.3987/COM-11-12332

ALTERNATIVE SYNTHESIS OF RADIOIODINATED TRISACCHARIDE DERIVATIVES, 2-(4-^{125}IODOPHENYL)ETHYL 2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL-(1→2)-α-D-MANNO-PYRANOSYL-(1→6)-β-D-GLUCOPYRANOSIDE, AND PREPARATION OF ITS ANALOGS HAVING DIFFERENT LENGTHS OF ALKYL CHAINS INSTEAD OF ETHYL GROUP: ACCEPTOR SUBSTRATES OF *N*-ACETYLGLUCOSAMINYLTRANSFERASE V FOR *IN VIVO* IMAGING

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Abstract – A radioiodinated artificial substrate of *N*-acetylglucosaminyltransferase V (GnT-V), 2-(4-iodophenyl)ethyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-β-D-glucopyranoside ([^{125}I]**1a**), was alternatively synthesized by using the glycosylation reaction from the non-reducing end, in which a glycosyl sulfoxide and a thioglycoside were employed as the glycosyl acceptor and donor, respectively. In addition, two derivatives of [^{125}I]**1a** having different lengths of alkyl chain ([^{125}I]**1b**, [^{125}I]**1c**) were prepared in the same way to increase the permeability of the substrates through the cell membrane and into the Golgi apparatus, where GnT-V acts to modify glycoconjugates by transferring *N*-acetylglucosamine units from UDP-GlcNAc.

INTRODUCTION

Glycoconjugates on the cell surfaces play important roles in many biological events, which relate to cell adhesions. The recent development of glycosciences and cancer research revealed a close relationship between the expression of glycoconjugates carrying highly antennary sugar chains on cell surfaces and malignant transformation of tumor cells. A number of studies in the last two decades showed that *N*-acetylglucosaminyltransferase V (GnT-V) is one of the most relevant glycosyltransferases for tumor invasion and metastasis.[1-10]

Recently, we reported the synthesis of the radioiodinated trisaccharide derivative, 2-(*p*-iodophenyl)ethyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-β-D-glucopyranoside ([^{125}I]IPGMG, [^{125}I]**1a**), and its high specificity to GnT-V, which was confirmed by efficient transformation from [^{125}I]**1a** to β(1→6)GlcNAc-bearing [^{125}I]IPGMG ([^{125}I]IPGGMG, [^{125}I]**2**) *in vitro* assay (Figure 1).[11] Being proceeded via a labile intermediate of glycosyl bromide **6**, the synthetic route requires preparation each time of **6** to apply for the synthesis of analogs and derivatives of [^{125}I]**1a** even when the structural differences were quite small.

Meanwhile, increased permeability of molecules through the cell membrane and into Golgi apparatus, which depends on their hydrophobicity, is very important when designing substrates and inhibitors of glycosyltransferarses since most glycosyltransferases act in the Golgi apparatus. Thus, the derivatives ([^{125}I]**1b-c**) of [^{125}I]**1a** bearing longer alkyl chains than *p*-iodophenylethyl group, *i.e.*, *p*-iodophenyloctyl or *p*-iodophenylpentadecyl groups, are expected to behave as more reliable and useful substrates to investigate the activity of GnT-V than [^{125}I]**1a**, not only *in vitro* but also *in vivo*.

In advance of the above study, we synthesized 2-(trimethylsilyl)ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-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 (**9**) carrying the same sugar chain as [^{125}I]**1a-c** using odorless benzenethiols, such as *p*-octyloxybenzenethiol and *p*-dodecylbenzenethiol, as the activating group of glycosyl donors in the glycosylation reaction.[12,13] On the other hand, we reported a novel glycosylation method from the non-reducing end using glycosyl sulfoxides as glycosyl acceptors, which was prepared by oxidation of the *p*-octyloxyphenyl thioglycosides.[14] In this strategy, the resulting glycosyl sulfoxide was reduced to the corresponding thioglycoside, which was employed as the glycosyl donor in the following glycosylation reaction. This strategy was effective, especially when *N*-acetylglucosamine residue was presented at the non-reducing end, such as [^{125}I]**1a-c**.[14]

In the present paper, we report an alternative synthetic route of [^{125}I]**1a**, which was applicable to the synthesis of [^{125}I]**1b-c** and proceeded *via* a stable synthetic intermediate.

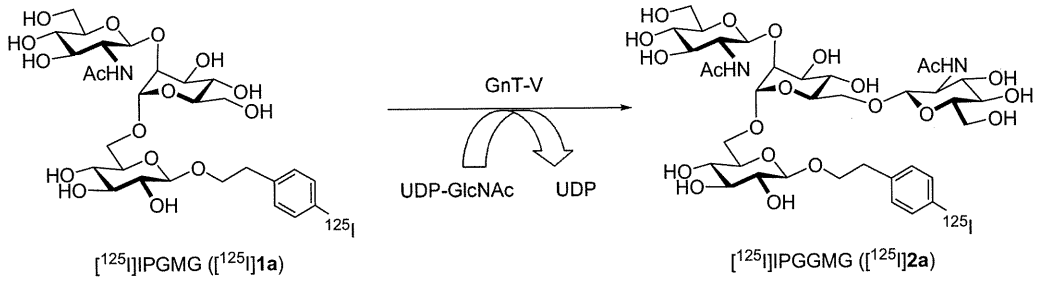
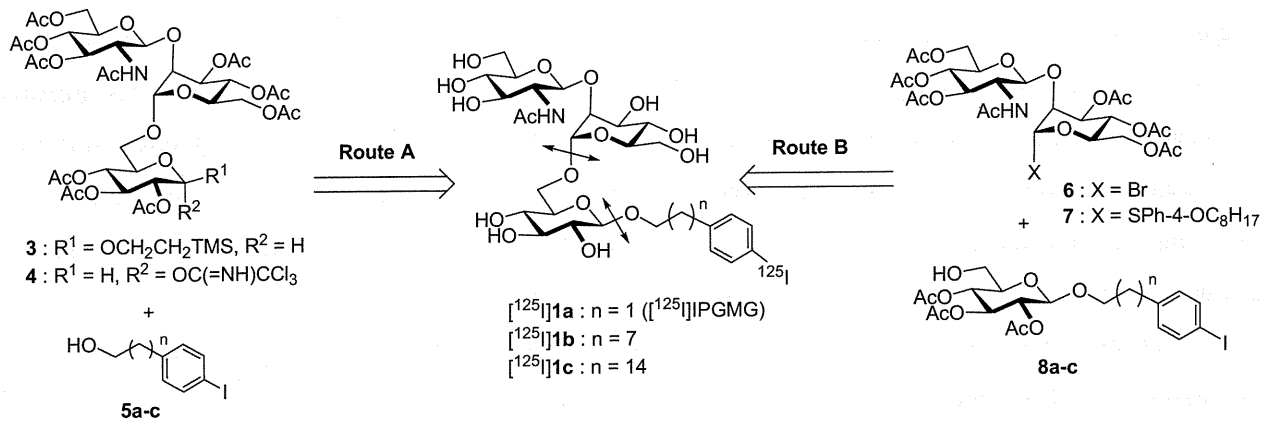


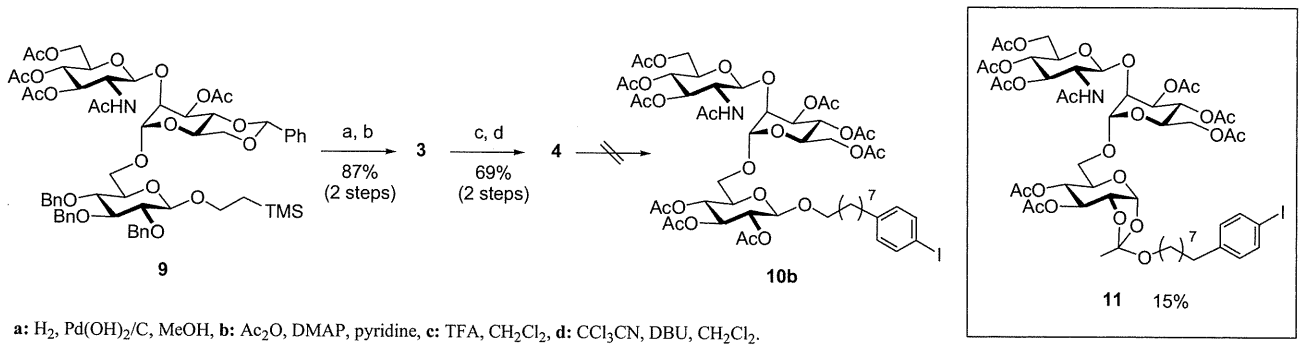
Figure 1. The transfer of a GlcNAc residue from UDP-GlcNAc to [^{125}I]**1** to form [^{125}I]**2** by GnT-V

RESULTS AND DISCUSSION

On the basis of our previous works,[11-14] two synthetic routes were attempted to obtain [^{125}I]**1a-c**, as shown in Scheme 1. One was designed by retro-synthesis that cleaved the glycosyl bond between the aglycon and the reducing end of the sugar moiety. According to this strategy, [^{125}I]**1a-c** seemed to be capable of being synthesized by the glycosylation of *p*-iodophenyl alcohols **5a-c** with the trisaccharyl donor **4** (Scheme1, route A). Herein, trichloroacetimidate **4** could be derived by cleavage of the trimethylsilylethyl group from trisaccharide **3**, for which the synthetic precursor **9** was previously synthesized as part of our glycosylation study using thioglycosides prepared from odorless benezenethiols,[12,13] followed by trichloroacetimidation using the Schmidt method; however, subsequent glycosylation of **5b** with **4** in the presence of TMSOTf did not afford the desired product **10b** but orthoester **11** (15%), recovering the intact imidate **4** (79%) (Scheme 2). The other route was retro-synthesized by the glycosylation of monoglucosides **8a-c** with disaccharyl donor **7** (Scheme 1, route B). In contrast to our recent study on the synthesis of **1a**,[11] where the labile intermediate of disaccharyl bromide **6** was chosen as the glycosyl donor for glycosylation, we herein adopted disaccharyl sulfide **7**, which could be provided by reduction of the sulfoxide group and replacement of the protecting groups in **12**.[14]



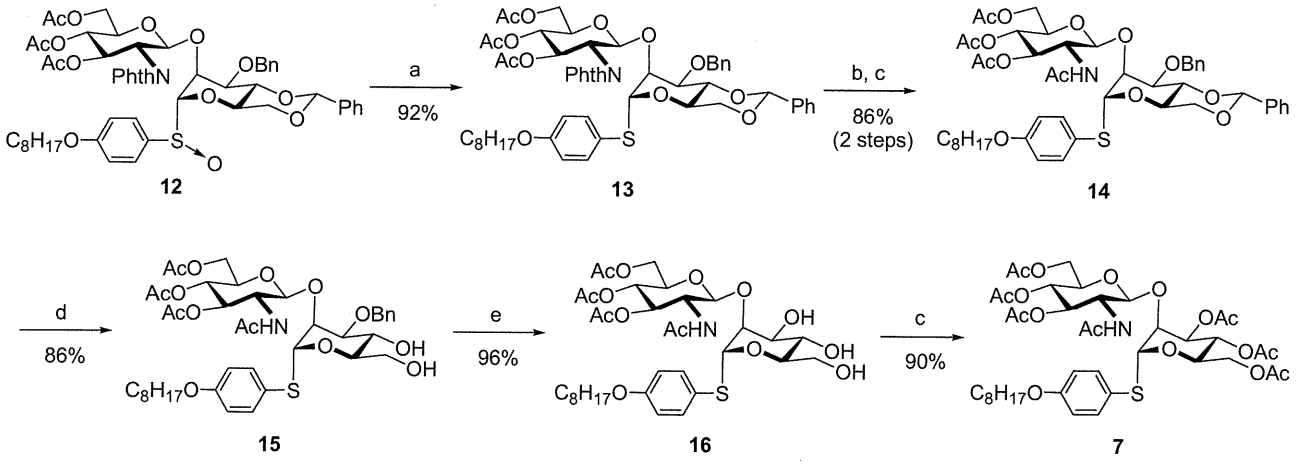
Scheme 1. Retrosynthetic strategy of [^{125}I] radiolabeled trisaccharide derivatives ([^{125}I]**1a-c**)



a: H_2, $Pd(OH)_2/C$, MeOH, **b:** Ac_2O, DMAP, pyridine, **c:** TFA, CH_2Cl_2, **d:** CCl_3CN, DBU, CH_2Cl_2.

Scheme 2. Attempted synthesis of trisaccharide **10b**

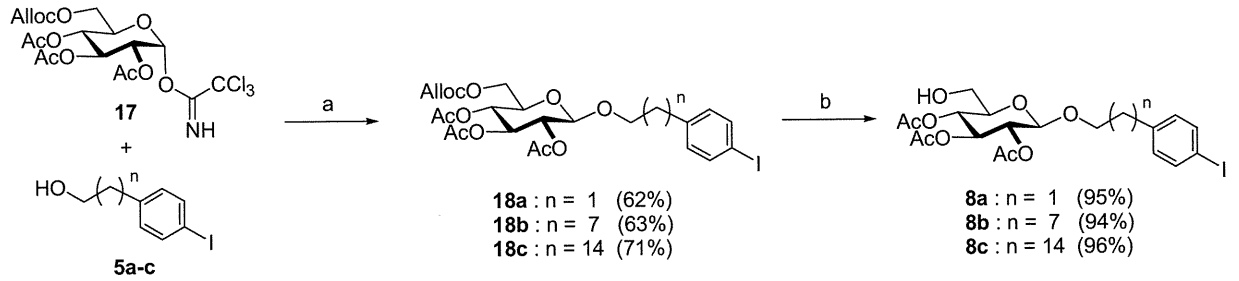
Thus, the disaccharyl sulfoxide **12**, which was prepared by our glycosylation method using glycosyl sulfoxide and thioglycoside as the acceptor and the donor, respectively,[14] was reduced with triphenylphosphine and carbon tetrachloride in MeCN to afford the thio-disaccharide **13** in good yield (92%). The phthaloyl group of **13** was removed with hydrazine hydrate, followed by acetylation to give the acetamide **14**. Since catalytic hydrogenation was not applicable for deprotection of the benzylidene and benzyl groups of **14** due to the presence of a sulfide group,[15] the benzylidene group of **14** was first cleaved by acetic acid in THF to afford diol **15**, the benzyl group of which was subsequently deprotected by treatment with trimethylsilyl chloride and lithium iodide[16] in $CHCl_3$ to afford triol **16** (96%). The disaccharide **16** was peracetylated to **7** by a conventional acetylation reaction with acetic anhydride and pyridine.



a: PPh_3, CCl_4, MeCN, **b:** $NH_2NH_2 \cdot H_2O$, EtOH-toluene, **c:** Ac_2O, DMAP, pyridine, **d:** 70 % AcOH aq., THF, **e:** TMSCl, LiI, $CHCl_3$.

Scheme 3. Synthesis of disaccharide **7**

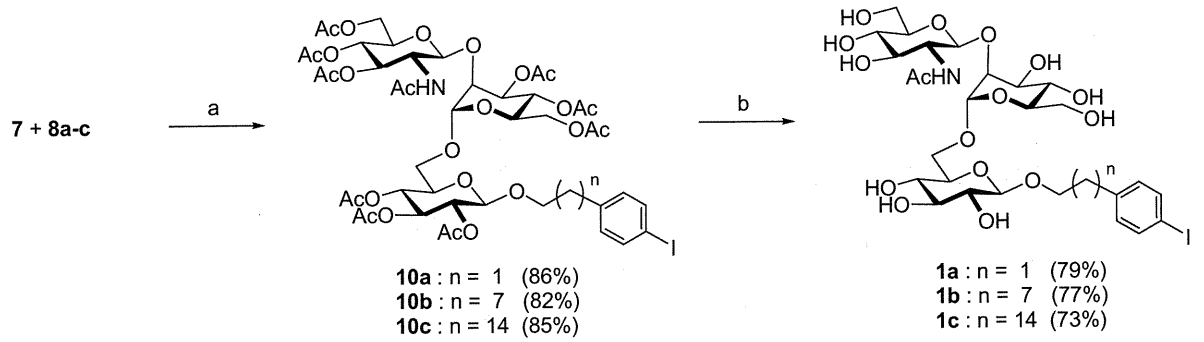
Meanwhile, 4-iodophenylalkyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosides (**8a-c**) were synthesized by glucosylation and deprotection of the allyloxycarbonyl (Alloc) group at C-6 (Scheme 4). While **5a** was commercially available, alcohol **5b** was prepared by iodination of 8-phenyl-1-octanol using triflic acid and NIS, and **5c** was synthesized by a well-established method reported by Weichert and his colleagues.[17] Glucosylation of **5a-c** with the imidate **17**[11] in the presence of $BF_3{\cdot}Et_2O$ in CH_2Cl_2 at −20 °C afforded **18a-c** in 62%, 63%, and 71%, respectively. The Alloc group at the C-6 position of the glucose residue in **18a-c** was removed with tetrakis(triphenylphosphine)palladium(0) in the presence of formic acid to afford **8a-c**,[11,18] which would be an acceptor substrate in the following glycosylation.



a: $BF_3{\cdot}Et_2O$, CH_2Cl_2, **b:** $Pd(PPh_3)_4$, PPh_3, HCO_2H, THF.

Scheme 4. Syntheses of 4-iodophenylalkyl glycosides **8a-c**

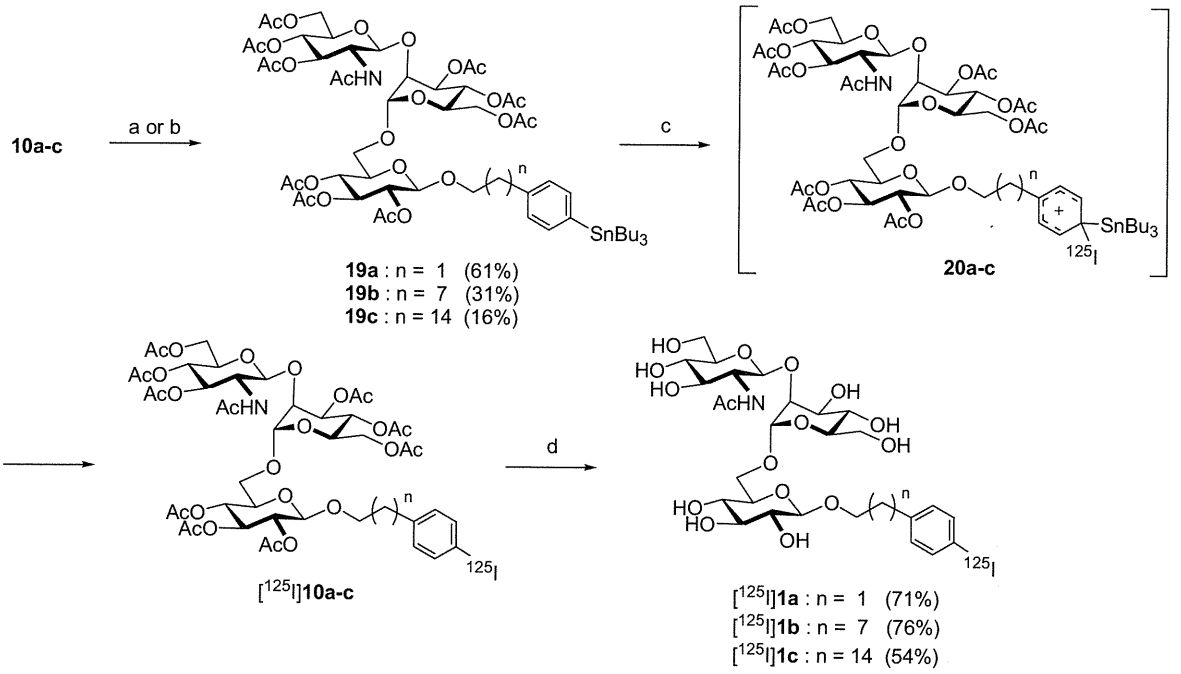
Next, glycosylation of **8a-c** with thio-disaccharide **7** was performed in the presence of triflic acid and NIS to yield **10a-c**.[19] It is noteworthy that the chemical yield was elevated from 67% to 86% by changing the bromide **6** to **7** as the glycosyl donor.[11] Subsequent deacetylation of **10a-c** with sodium methoxide in methanol afforded the non-labeled products **1a-c** (Scheme 5).



a: NIS, TfOH, MS4A, CH_2Cl_2, **b:** NaOMe, MeOH.

Scheme 5. Syntheses of trisaccharides **1a-c**

Finally, in order to synthesize the desired radioiodinated compounds [^{125}I]**1a-c**, non-labeled iodo group of **10a-c** was exchanged for a tributyltin group using a combination of $Pd(PPh_3)_4$, PPh_3, and $(Bu_3Sn)_2$ or that of $PdCl_2$(dppf), KOAc, and $(Bu_3Sn)_2$,[20] to afford **19a-c** in good yield (61%, 31%, and 16%, respectively). Replacement of the stannyl group with the radioactive iodo group was performed by iodo-destannylation reaction.[11,21] Namely, the stannylphenyl moiety of **19a-c** was reacted with $^{125}I_2$, which was prepared by a oxidation reaction of commercially available [^{125}I]NaI with H_2O_2, to afford the radioiodinated trisaccharide derivatives **10a-c** *via* iodostannyl aronium intermediates **20a-c**. The following deacetylation of [^{125}I]**10a-c** with sodium methoxide in methanol gave [^{125}I]**1a-c**. The radiochemical identity of [^{125}I]**1a-c** was verified by co-injection with nonradioactive **1a-c** by their HPLC profiles. Radioactive [^{125}I]**1a-c** showed a single radioactive peak at the same retention time as that of nonradioactive **1a-c**. Radiochemical yields of [^{125}I]**1a-c** were 71%, 76% and 54%, respectively. The radiochemical purities after purification by HPLC were >99%, >99% and >99%, respectively (Scheme 6).



a: $Pd(PPh_3)_4$, PPh_3, (n-$Bu_3Sn)_2$, toluene, **b :** $PdCl_2$(dppf), KOAc, (n-$Bu_3Sn)_2$, NMP, **c:** [^{125}I]NaI, 5 % H_2O_2 aq., 0.1 M HCl aq. MeCN, **d:** NaOMe, MeOH.

Scheme 6. Radiosyntheses of trisaccharides [^{125}I]**1a-c**

We successfully synthesized a series of trisaccharide derivatives **1a-c** having different lengths of alkyl chain with 2, 8 and, 15 carbons on the basis of our previous glycosylation method, with glycosyl sulfoxides and thioglycosides as the acceptor and the donor, respectively. Moreover, by using iodo→tin and tin→iodo exchange reactions, we succeeded in synthesizing radioiodinated [^{125}I]**1a-c**.

EXPERIMENTAL

General. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8300 diffraction grating infrared spectrophotometer and ^{1}H-NMR spectra were obtained on a JEOL JNM-AL400 spectrometer with tetramethylsilane as an internal standard in the case of $CDCl_3$. ^{13}C-NMR spectra were obtained on a JEOL JNM-AL400 spectrometer with C_5D_5N as the 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. Wakogel C-200 (silica gel) (100-200 mesh; Wako) was used for open column chromatography. Flash column chromatography was performed by using Silica Gel 60N (Kanto Chemical Co., Inc.) as a solid support in the immobile phase. Kieselgel 60 F-254 plates (Merck) were used for thin layer chromatography (TLC). Preparative TLC (PTLC) was conducted with a Kieselgel 60 F-254 plate (0.25 mm; Merck) or Silica gel 60 F-254 plate (0.5 mm; Merk). Unless purification with silica gel gave a pure enough compound, the compounds were further treated with recycling HPLC (JAI LC-908) on a GPC column (JAIGEL 1H and 2H).

Materials. Most reagents were obtained from Wako Pure Chemical Industries, Ltd., Nacalai Tesque, Inc., and Aldrich Chemical Inc. **5a** and **5c** are known compounds.

8-(*p*-Iodophenyl) octanol (5b)

N-Iodosuccinimide (1.08 g, 4.80 mmol) and triflic acid (386 μL, 4.36 mmol) were added to a solution of 8-phenyloctanol (900.1 mg, 4.36 mmol) in CH_2Cl_2 (20 mL). After stirring the reaction mixture for 8 h at room temperature, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with a saturated aqueous solution of sodium thiosulfate and a saturated aqueous solution of sodium chloride, successively, sodium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 5:1) and recrystallization ($CHCl_3$–hexane) to afford **5b** (433.0 mg, 30%). mp 57-58 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.21 (1H, br, OH), 1.31 (8H, m), 1.52-1.61 (4H, m), 2.54 (2H, t, J = 7.7 Hz), 3.63 (2H, br t, J = 5.9 Hz), 6.92 (2H, d, J = 8.4 Hz), 7.58 (2H, d, J = 8.4 Hz). ^{13}C-NMR ($CDCl_3$) δ: 25.7, 29.1, 29.3, 29.4, 31.2, 32.7, 35.4, 63.0, 90.5, 130.5 (2C), 137.2 (2C), 142.5. IR ($CHCl_3$) ν: 3445, 3007, 2932, 2858, 1638, 1485, 1400, 1061, 1007 cm^{-1}. HR-MS (EI$^+$, 70eV) *m/z*: 332.0632 (Calcd for $C_{14}H_{21}IO$: 332.0637).

2-Trimethylsilylethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (3)

Palladium hydroxide on carbon (127.4 mg) was added to a solution of **9**[12,13] (247.0 mg, 0.20 mmol) in a

mixed solvent of MeOH (6 mL) and EtOAc (4 mL), which was stirred under a hydrogen atomosphere for 21 h at room temperature. After the reaction, the reaction mixture was filtered and the filtrate was condensed *in vacuo*. The residue was treated with pyridine (5 mL) and acetic anhydride (1 mL) for 32 h. The mixture was poured into ice water, which was extracted with EtOAc. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 1:4) to afford **3** (180.4 mg, 87%, 2 steps). $[\alpha]_D$ +8.5° (*c* 0.88, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.05 (9H, s), 0.99 (1H, ddd, *J* = 5.4, 9.1, 14.1 Hz), 1.09 (1H, ddd, *J* = 7.0, 9.8, 14.1 Hz), 1.97, 1.98, 2.01, 2.06, 2.07, and 2,08 (each 3H, s), 2.088 (6H, s), 2.094 (3H, s), 2.10 (3H, s), 3.72-3.78 (2H, m, Glc-6, -OCH_2), 4.01 (1H, ddd, *J* = 2.2, 5.7, 10.3 Hz, GlcN-5), 4.03-4.17 (3H, m, GlcN-2, Glc-5, Glc-6), 4.25-4.31 (1H, m, -OCH_2), 4.27 (1H, dd, *J* = 2.2, 12.4 Hz, GlcN-6), 4.33-4.37 (1H, m, Man-5), 4.42 (1H, dd, *J* = 1.8, 12.1 Hz, Man-6), 4.53 (1H, dd, *J* = 5.3, 12.1 Hz, Man-6), 4.61 (1H, dd, *J* = 5.7, 12.4 Hz, GlcN-6), 4.79 (1H, t, *J* = 1.7 Hz, Man-2), 4.95 (1H, d, *J* = 8.1 Hz, Glc-1), 5.27 (1H, s, Man-1), 5.41 (1H, t, *J* = 9.5 Hz, GlcN-4), 5.43 (1H, t, *J* = 9.3 Hz, Glc-2), 5.46 (1H, t, *J* = 9.3 Hz, Glc-4), 5.54 (1H, d, *J* = 8.4 Hz, GlcN-1), 5.58 (1H, dd, *J* = 3.1, 10.3 Hz, Man-3), 5.76 (1H, t, *J* = 9.3 Hz, Glc-3), 5.89 (1H, t, *J* = 10.3 Hz, Man-4), 6.04 (1H, t, *J* = 9.5 Hz, GlcN-3), 9.25 (1H, d, *J* = 8.1 Hz). ^{13}C-NMR (C_5D_5N) δ: −1.32 (3C), 18.0, 20.47, 20.49, 20.52, 20.65, 20.67, 20.70, 20.8, 55.7 (GlcN-2), 62.7 (GlcN-6), 63.0 (Man-6), 66.4 (Man-4), 67.3 (Glc-6), 67.6 (-OCH_2), 69.6 (Man-5), 69.8 (GlcN-4), 70.1 (Glc-4), 71.0 (Man-3), 72.16 (Glc-2), 72.21 (GlcN-5), 72.6 (GlcN-3), 72.8 (Glc-5), 73.7 (Glc-3), 74.4 (Man-2), 98.4 (Man-1), 99.7 (GlcN-1), 100.5 (Glc-1), 169.6, 169.9, 170.0 (2C), 170.4, 170.47, 170.51, 170.6, 170.7, 171.0. IR ($CHCl_3$) ν: 3030, 3015, 1751, 1682, 1514, 1429, 1367, 1256, 1138, 1040 cm^{-1}. HR-MS (FAB^+) *m/z*: 1046.3517 (Calcd for $C_{43}H_{65}NO_{25}SiNa$: 1046.3513).

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-*O*-acetyl-α-D-manno-pyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (4)

Triflouroacetic acid (300 μL) was added to a solution of **3** (116.8 mg, 114.1 μmol) in CH_2Cl_2 (3 mL), which was stirred for 45 h at room temperature. The reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate, which was extracted with EtOAc. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over sodium sulfate, and condensed *in vacuo*. The residue was purified by silica gel chromatography ($CHCl_3$:MeOH = 50:1) to give 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1 → 6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranose trisaccharide (94.2 mg). Trichloroacetonitrile (102 μL, 1.02 mmol) and DBU (one drop with a pipet) were added to a solution of the trisaccharide (94.2 mg) in CH_2Cl_2 (3 mL), which was stirred for 30 min at room temperature. The organic solvent was evaporated and the residue

was purified by silica gel column chromatography ($CHCl_3$:MeOH = 80:1) to afford **4** (84.2 mg, 69%, 2 steps). $[\alpha]_D$ +36.5° (*c* 0.93, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.96, 1.97, 1.98, 2.03, 2.05, 2.06, 2.08, 2.09, 2.11, and 2.15 (each 3H, s, OAc), 3.74 (1H, br d, *J* = 9.3 Hz, Glc-6), 4.01-4.03 (1H, m, GlcN-5), 4.07-4.14 (2H, m, GlcN-2, Glc-6), 4.25 (1H, dd, *J* = 1.5, 12.1 Hz, GlcN-6), 4.35-4.39 (1H, m, Man-5), 4.43 (1H, br d, *J* = 12.1 Hz, Man-6), 4.54-4.60 (3H, m, Glc-5, GlcN-6, Man-6), 4.79 (1H, br s, Man-2), 5.24 (1H, br s, Man-1), 5.41 (1H, t, *J* = 9.7 Hz, GlcN-4), 5.549 (1H, dd, *J* = 3.5, 10.4 Hz, Glc-2), 5.553 (1H, d, *J* = 9.0 Hz, GlcN-1), 5.57 (1H, dd, *J* = 3.7, 10.3 Hz, Man-3), 5.67 (1H, t, *J* = 9.9 Hz, Glc-4), 5.89 (1H, t, *J* = 10.3 Hz, Man-4), 6.04 (1H, t, *J* = 9.5 Hz, GlcN-3), 6.09 (1H, t, *J* = 9.9 Hz, Glc-3), 7.02 (1H, d, *J* = 3.5 Hz, Glc-1), 9.22 (1H, d, *J* = 8.1 Hz), 10.26 (1H, s). ^{13}C-NMR (C_5D_5N) δ: 20.3, 20.48, 20.50 (2C), 20.6 (3C), 20.7, 20.8, 23.2, 55.6 (GlcN-2), 62.7 (GlcN-6), 63.0 (Man-6), 66.4 (Man-4), 66.9 (Glc-6), 69.0 (Glc-4), 69.5 (Man-5), 69.8 (GlcN-4), 70.5 (Glc-3), 70.6 (Glc-2), 71.0 (Man-3), 71.6 (Glc-5), 72.3 (GlcN-5), 72.7 (GlcN-3), 74.6 (Man-2), 79.8, 93.2 (Glc-1), 98.7 (Man-1), 100.0 (GlcN-1), 159.9, 169.87, 169.91, 170.0, 170.1, 170.3, 170.45, 170.49, 170.6, 170.8, 170.9. IR ($CHCl_3$) ν: 3344, 3044, 3026, 3015, 1751, 1676, 1514, 1429, 1367, 1256, 1074, 1040 cm^{-1}. HR-MS (FAB^+) *m/z*: 1089.1898 (Calcd for $C_{40}H_{53}Cl_3N_2O_{25}Na$: 1089.1901).

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-*O*-acetyl-α-D-manno-pyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl orthoester (11)

After stirring a suspension of **4** (34.6 mg, 32.4 μmol), **5b** (10.7 mg, 32.2 μmol), and MS4A (150 mg) in CH_2Cl_2 (2 mL) for 30 min, trimethylsilyl trifluoromethanesulfonate (0.6 μL, 3.3 μmol) was added to the mixture chilled at −40 °C. After stirring for 30 min. while maintaining the temperature, the reaction mixture was filtered through Celite. The filtrate was partitioned between EtOAc and a saturated aqueous solution of sodium bicarbonate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$: MeOH = 100:1) to afford **11** (6.0 mg, 15%). $[\alpha]_D$ +15.1° (*c* 0.44, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.18 (6H, m), 1.28 (2H, m), 1.45-1.57 (4H, m), 1.88, 1.97, 1.98, 1.99, 2.06, 2.07, 2.088, and 2.093 (each 3H, s), 2.10 (6H, s), 2.44 (2H, t, *J* = 7.9 Hz), 3.55 (2H, t, *J* = 6.6 Hz, -OCH_2), 3.81 (1H, dd, *J* = 3.0, 10.9 Hz, Glc-6), 3.91 (1H, ddd, *J* = 2.2, 5.3, 10.1 Hz, GlcN-5), 4.06 (1H, dt, *J* = 8.1, 10.4 Hz, GlcN-2), 4.15 (1H, dd, *J* = 4.9, 10.9 Hz, Glc-6), 4.22 (1H, dd, *J* = 2.2, 12.1 Hz, GlcN-6), 4.31-4.35 (1H, m, Glc-5), 4.43-4.48 (1H, m, Man-5), 4.48 (1H, dd, *J* = 2.4, 12.2 Hz, Man-6), 4.54 (1H, dd, *J* = 4.4, 12.2 Hz, Man-6), 4.56 (1H, dd, *J* = 5.3, 12.1 Hz, GlcN-6), 4.77 (1H, dd, *J* = 1.5, 3.3 Hz, Man-2), 4.81 (1H, dd, *J* = 3.1, 5.1 Hz, Glc-2), 5.32 (1H, d, *J* = 1.5 Hz, Man-1), 5.40 (1H, t, *J* = 9.7 Hz, GlcN-4), 5.49-5.52 (1H,, m, Glc-4), 5.51 (1H, d, *J* = 8.4 Hz, GlcN-1), 5.58 (1H, dd, *J* = 3.3, 10.3 Hz,

Man-3), 5.66 (1H, t, J = 2.8 Hz, Glc-3), 5.90 (1H, t, J = 10.3 Hz, Man-4), 6.04 (1H, t, J = 9.7 Hz, GlcN-3), 6.17 (1H, d, J = 5.1 Hz, Glc-1), 6.96 (2H, br d, J = 8.2 Hz), 7.71 (2H, br d, J = 8.2 Hz), 9.25 (1H, d, J = 8.1 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.48, 20.52, 20.58, 20.61, 20.65, 20.70, 20.8 (2C), 21.6, 23.2, 26.4, 29.3, 29.5, 29.6, 30.0, 31.5, 35.4, 55.7 (GlcN-2), 62.6 (GlcN-6), 63.0 (Man-6), 63.5 (-OCH_2), 66.4 (Man-4), 68.1 (Glc-6), 68.7 (Glc-5), 68.8 (Glc-4), 69.5 (Man-5), 69.8 (GlcN-4), 70.6 (Glc-3), 71.0 (Man-3), 72.2 (GlcN-5), 72.6 (GlcN-3), 73.6 (Glc-2), 74.8 (Man-2), 91.5, 97.6 (Glc-1), 98.7 (Man-1), 100.0 (GlcN-1), 122.2, 131.1 (2C), 137.7 (2C), 142.9, 169.6, 169.9, 170.0, 170.1, 170.47, 170.51, 170.6, 170.7, 171.0. IR ($CHCl_3$) ν: 3024, 2361, 1747, 1684, 1514, 1369, 1248, 1140, 1099 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 1260.3325 (Calcd for $C_{52}H_{72}INO_{25}Na$: 1260.3336).

_p_-Octyloxyphenyl 3,4,6-tri-_O_-acetyl-2-deoxy-2-phthaloylamino-β-D-glucopyranosyl-(1 → 2)-3-_O_-benzyl-4,6-_O_-benzylidene-1-_thio_-α-D-mannopyranoside (13)

A solution of triphenylphosphine (165.5 mg, 0.63 mmol) in CCl_4 (2 mL) was added to a solution of **12**[14] (127.7 mg, 0.13 mmol) in MeCN (3 mL), which was stirred for 2 h under refluxing conditions. After the reaction, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate and extracted with EtOAc. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 2:1) to afford **13** (115.2 mg, 92%). $[\alpha]_D$ +131.1° (*c* 0.86, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.85 (3H, t, J = 7.1 Hz), 1.24 (8H, m), 1.42 (2H, m), 1.75 (2H, quint., J = 6.4 Hz), 1.84, 1.99, 2.01 (each 3H, s, OAc), 3.38 (1H, t, J = 9.9 Hz, Man-6), 3.87 (1H, dd, J = 4.2, 10.3 Hz, Man-6), 3.94 (2H, t, J = 6.4 Hz, OCH_2), 4.19 (1H, ddd, J = 2.4, 4.6, 10.1 Hz, GlcN-5), 4.21 (1H, dd, J = 2.8, 9.5 Hz, Man-3), 4.37 (1H, t, J = 9.5 Hz, Man-4), 4.37-4.42 (1H, m, Man-5), 4.42 (1H, dd, J = 4.6, 12.5 Hz, GlcN-6), 4.60 (1H, dd, J = 2.4, 12.5 Hz, GlcN-6), 4.78 (1H, d, J = 11.5 Hz, OBn), 4.98 (1H, dd, J = 8.6, 10.8 Hz, GlcN-2), 5.00 (1H, d, J = 11.5 Hz, OBn), 5.02 (1H, br t, J = 2.8 Hz, Man-2), 5.57 (1H, s, PhCH<), 5.61 (1H, dd, J = 9.2, 10.1 Hz, GlcN-4), 5.71 (1H, d, J = 1.7 Hz, Man-1), 6.23 (1H, d, J = 8.6 Hz, GlcN-1), 6.47 (1H, dd, J = 9.2, 10.8 Hz, GlcN-3), 7.02 (2H, d, J = 9.0 Hz), 7.26 (1H, tt, J = 1.3, 7.3 Hz), 7.29-7.36 (7H, m), 7.54-7.56 (2H, m), 7.61 (2H, br d, J = 8.4 Hz), 7.77 (1H, br), 7.88 (1H, br). ^{13}C-NMR (C_5D_5N) δ: 14.3, 20.3, 20.4, 20.6, 22.9, 26.3, 29.48, 29.51, 29.6, 32.0, 55.4 (GlcN-2), 62.6 (GlcN-6), 65.5 (Man-5), 68.4 (OCH_2), 68.5 (Man-6), 69.7 (GlcN-4), 71.0 (GlcN-3), 71.2 (OBn), 72.5 (GlcN-5), 75.0 (Man-3), 76.7 (Man-2), 78.9 (Man-4), 87.5 (Man-1), 96.7 (GlcN-1), 102.2 (PhCH<), 115.8 (2C), 123.6, 124.2 (6C), 126.9 (2C), 127.9, 128.4, 128.6 (2C), 129.2, 132.0, 134.0 (2C), 134.6, 138.5, 139.0, 159.7, 169.8, 170.4, 170.5. IR ($CHCl_3$) ν: 2930, 1749, 1719, 1595, 1495, 1387, 1367, 1248, 1099 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 1018.3663 (Calcd for $C_{54}H_{61}NO_{15}SNa$: 1018.3660).

_p_-Octyloxyphenyl 2-acetamido-3,4,6-tri-_O_-acetyl-2-deoxy-β-D-glucopyranosyl-(1→2)-3-_O_-benzyl-4,6-_O_-benzylidene-1-_thio_-α-D-mannopyranoside (14)

Hydrazine hydrate (80% in water, 3 mL) was added to a solution of **13** (1.52 g, 1.53 mmol) in a mixed solvent of EtOH (30 mL) and toluene (15 mL), which was stirred for 5 h under refluxing conditions. After chilling the reaction mixture at room temperature, the resulting precipitates were filtered off. The filtrate was condensed *in vacuo* and the residue was treated with pyridine (20 mL) and acetic anhydride (7 mL) for 5 h. The mixture was poured into ice water, which was extracted with $CHCl_3$. The organic layer was dried over sodium sulfate and condensed *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$: EtOAc = 10:1) to afford **14** (1.19 g, 86%). $[\alpha]_D$ +70.5° (*c* 1.21, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, *J* = 7.1 Hz), 1.22 (8H, m), 1.40 (2H, m), 1.73 (2H, quint., *J* = 6.6 Hz), 1.96, 1.98, 2.00, and 2.04 (each 3H, s, Ac), 3.94 (2H, t, *J* = 6.6 Hz, OCH_2), 3.98 (1H, t, *J* = 10.1 Hz, Man-6), 4.02 (1H, ddd, *J* = 2.4, 4.9, 9.7 Hz, GlcN-5), 4.356 (1H, dd, *J* = 3.3, 9.7 Hz, Man-3), 4.361 (1H, dd, *J* = 2.4, 12.3 Hz, GlcN-6), 4.43 (1H, dd, *J* = 4.6, 10.1 Hz, Man-6), 4.52 (1H, dt, *J* = 8.4, 10.6 Hz, GlcN-2), 4.53 (1H, dd, *J* = 4.9, 12.3 Hz, GlcN-6), 4.66 (1H, t, *J* = 9.5 Hz, Man-4), 4.74 (1H, dt, *J* = 4.6, 9.5 Hz, Man-5), 4.84 (1H, d, *J* = 11.7 Hz, OBn), 5.04 (1H, t, *J* = 1.5 Hz, Man-2), 5.07 (1H, d, *J* = 11.7 Hz, OBn), 5.49 (1H, t, *J* = 9.7 Hz, GlcN-4), 5.60 (1H, d, *J* = 8.4 Hz, GlcN-1), 5.66 (1H, s, PhCH<), 5.97 (1H, dd, *J* = 9.3, 10.6 Hz, GlcN-3), 6.00 (1H, d, *J* = 1.5 Hz, Man-1), 7.03 (2H, d, *J* = 8.8 Hz), 7.25 (1H, tt, *J* = 1.3, 7.3 Hz), 7.30-7.40 (5H, m), 7.55 (2H, d, *J* = 8.8 Hz), 7.63 (2H, br d, *J* = 7.1 Hz), 7.68 (2H, br d, *J* = 8.4 Hz), 9.25 (1H, d, *J* = 8.6 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 20.5, 20.57, 20.58, 22.9, 23.3, 26.3, 29. 5 (2C), 29.6, 32.0, 55.4 (GlcN-2), 62.7 (GlcN-6), 65.9 (Man-5), 68.4 (OCH_2), 68.9 (Man-6), 69.7 (GlcN-4), 71.1 (OBn), 72.3 (GlcN-5), 73.0 (GlcN-3), 75.4 (Man-3), 76.7 (Man-2), 78.9 (Man-4), 88.1 (Man-1), 99.9 (GlcN-1), 102.2 (PhCH<), 115.9 (2C), 123.9, 126.9 (2C), 127.8, 128.3 (2C), 128.5 (2C), 128.6 (2C), 129.2, 135.5 (2C), 138.6, 139.2, 160.1, 169.8, 170.5, 170.7, 170.9. IR ($CHCl_3$) ν: 3460, 3429, 2930, 2858, 1747, 1682, 1593, 1495, 1369, 1248, 1099 cm^{-1}. HR-MS (FAB^+) *m/z*: 930.3716 (Calcd for $C_{48}H_{61}NO_{14}SNa$: 930.3710).

_p_-Octyloxyphenyl 2-acetamido-3,4,6-tri-_O_-acetyl-2-doexy-β-D-glucopyranosyl-(1→2)-3-_O_-benzyl-1-_thio_-α-D-mannopyranoside (15)

An aqueous solution of acetic acid (70%, 2 mL) was added to a solution of **14** (104.3 mg, 0.11 mmol) in THF (1 mL), it was stirred for 5 h at 55 °C. After neutralizing the mixture with an aqueous solution of sodium bicarbonate, the mixture was extracted with $CHCl_3$. The organic layer was washed with a saturated aqueous solution of sodium bicarbonate, dried over sodium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$: MeOH = 30:1) to afford **15** (81.1

mg, 86%). $[\alpha]_D$ +17.4° (*c* 1.12, $CHCl_3$). ^{1}H-NMR (C_5D_5N + D_2O) δ: 0.84 (3H, t, *J* = 7.1 Hz), 1.21 (8H, m), 1.39 (2H, m), 1.72 (2H, quint., *J* = 6.6 Hz), 1.97, 1.987, 1.990 and 2.03 (each 3H, s, Ac), 3.88, 3.91 (each 1H, dt, AB type, *J* = 6.6, 9.2 Hz, OCH_2), 4.01 (1H, ddd, *J* = 2.4, 4.9, 9.7 Hz, GlcN-5), 4.27 (1H, dd, *J* = 2.9, 9.2 Hz, Man-3), 4.35 (1H, dd, *J* = 2.4, 12.1 Hz, GlcN-6), 4.407 (1H, q, *J* = 8.6 Hz, GlcN-2), 4.412 (1H, dd, *J* = 5.5, 11.9 Hz, Man-6), 4.53 (1H, dd, *J* = 1.8, 11.9 Hz, Man-6), 4.55 (1H, dd, *J* = 4.9, 12.1 Hz, GlcN-6), 4.72 (1H, t, *J* = 9.2 Hz, Man-4), 4.77 (1H, d, *J* = 11.0 Hz, OBn), 4.85 (1H, ddd, *J* = 1.8, 5.5, 9.7 Hz, Man-5), 5.02 (1H, br t, *J* = 2.9 Hz, Man-2), 5.17 (1H, d, *J* = 11.0 Hz, OBn), 5.39 (1H, t, *J* = 9.7 Hz, GlcN-4), 5.54 (1H, d, *J* = 8.4 Hz, GlcN-1), 5.94 (1H, dd, *J* = 9.3, 10.6 Hz, GlcN-3), 6.06 (1H, d, *J* = 1.7 Hz, Man-1), 7.02 (2H, d, *J* = 9.0 Hz), 7.29 (1H, tt, *J* = 1.3, 7.3 Hz), 7.35 (2H, br t, *J* = 7.0 Hz), 7.67 (2H, br d, *J* = 7.0 Hz), 7.78 (2H, d, *J* = 9.0 Hz), 9.29 (1H, d, *J* = 8.6 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 20.47, 20.52, 20.6, 22.9, 23.3, 26.3, 29.45 (2C), 29.54, 32.0, 55.2 (GlcN-2), 62.8 (GlcN-6), 62.9 (Man-6), 67.0 (Man-4), 68.3 (OCH_2), 69.8 (GlcN-4), 70.8 (OBn), 72.2 (GlcN-5), 72.9 (GlcN-3), 76.2 (Man-2), 76.6 (Man-5), 79.6 (Man-3), 87.9 (Man-1), 100.2 (GlcN-1), 115.7 (2C), 125.3, 127.8, 128.5 (2C), 128.8 (2C), 135.3 (2C), 139.4, 159.8, 169.8, 170.5, 170.6, 171.3. IR ($CHCl_3$) ν: 3458, 3423, 3350, 2930, 2858, 1746, 1682, 1595, 1495, 1369, 1248, 1105, 1072 cm^{-1}. HR-MS (FAB^+) *m/z*: 842.3395 (Calcd for $C_{41}H_{57}NO_{14}SNa$: 842.3397).

_p_-Octyloxyphenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-1-*thio*-α-D-mannopyranoside (16)

Trimethylsilyl chloride (1.2 mL, 9.50 mmol) and lithium iodide (1.27 g, 9.50 mmol) were added to a solution of **15** (817.2 mg, 0.95 mmol) in $CHCl_3$ (15 mL) at 0 °C. After stirring the reaction mixture for 6 h at room temperature, it was poured into a saturated aqueous solution of sodium bicarbonate and extracted with $CHCl_3$. The organic layer was washed with a saturated aqueous solution of sodium thiosulfate and a saturated aqueous solution of sodium chloride, dried over sodium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$: MeOH = 30:1) to afford **16** (662.5 mg, 96%). $[\alpha]_D$ +37.4° (*c* 1.13, $CHCl_3$). ^{1}H-NMR (C_5D_5N + D_2O) δ: 0.84 (3H, t, *J* = 7.1 Hz), 1.20 (8H, m), 1.38 (2H, m), 1.70 (2H, quint., *J* = 6.6 Hz), 1.97, 1.98, 1.99, 2.03 (each 3H, s, Ac), 3.86, 3.88 (each 1H, dt, *J* = 6.6, 9.5 Hz, OCH_2), 3.96 (1H, ddd, *J* = 2.4, 4.8, 10.1 Hz, GlcN-5), 4.26 (1H, dd, *J* = 2.4, 12.3 Hz, GlcN-6), 4.39 (1H, dt, *J* = 8.8, 10.8 Hz, GlcN-2), 4.41 (1H, dd, *J* = 5.9, 11.9 Hz, Man-6), 4.516 (1H, dd, *J* = 4.8, 12.3 Hz, GlcN-6), 4.522 (1H, dd, *J* = 3.3, 9.2 Hz, Man-3), 4.55 (1H, dd, *J* = 2.2, 11.9 Hz, Man-6), 4.62 (1H, t, *J* = 9.3 Hz, Man-4), 4.86 (1H, ddd, *J* = 2.2, 5.9, 9.3 Hz, Man-5), 4.92 (1H, dd, *J* = 1.7, 3.3 Hz, Man-2), 5.37 (1H, t, *J* = 9.3 Hz, GlcN-4), 5.51 (1H, d, *J* = 8.4 Hz, GlcN-1), 5.89 (1H, dd, *J* = 9.3, 10.8 Hz, GlcN-3), 6.04 (1H, d, *J* = 1.7 Hz, Man-1), 6.97, 7.74 (each 2H, d, *J* = 8.8 Hz), 9.30 (1H, d, *J* = 8.8 Hz).

^{13}C-NMR (C_5D_5N) δ: 14.2, 20.46, 20.54, 20.6, 22.9, 23.3, 26.3, 29.45 (2C), 29.54, 32.0, 55.1 (GlcN-2), 62.5 (GlcN-6), 62.9 (Man-6), 68.3 (OCH_2), 69.2 (Man-4), 69.6 (GlcN-4), 72.2 (GlcN-5), 72.5 (Man-3), 73.1 (GlcN-3), 76.8 (Man-5), 80.4 (Man-2), 88.0 (Man-1), 100.1 (GlcN-1), 115.6 (2C), 125.3, 135.3 (2C), 159.8, 169.8, 170.5, 170.6, 171.1. IR ($CHCl_3$) ν: 3423, 3040, 2930, 2856, 1751, 1680, 1595, 1495, 1369, 1248, 1099, 1070 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 752.2932 (Calcd for $C_{34}H_{51}NO_{14}SNa$: 752.2928).

_p_-Octyloxyphenyl 2-acetamido-3,4,6-tri-_O_-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-_O_-acetyl-1-_thio_-α-D-mannopyranoside (7)

Acetic anhydride (27 μL, 0.29 mmol) and 4-dimethylaminopyridine (cat.) were added to a solution of **16** (50.9 mg, 69.7 μmol) in pyridine (3 mL) at 0 °C. After stirring the reaction mixture for 2 h at room temperature, it was extracted with EtOAc. The organic layer was washed with a saturated solution of sodium chloride, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$: EtOAc = 3:2) to afford **7** (53.7 mg, 90%). $[\alpha]_D$ +37.7° (*c* 0.92, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, *J* = 7.0 Hz), 1.22 (8H, m), 1.40 (2H, m), 1.73 (2H, quint., *J* = 6.6 Hz), 1.95, 1.97, 1.98, 2.092, 2.094, 2.11, 2.12 (each 3H, s, Ac), 3.94 (2H, t, *J* = 6.6 Hz, OCH_2), 3.97 (1H, ddd, *J* = 2.4, 5.5, 10.1 Hz, GlcN-5), 4.20-4.27 (1H, m, GlcN-2), 4.25 (1H, dd, *J* = 2.4, 12.5 Hz, GlcN-6), 4.41 (1H, dd, *J* = 2.2, 12.1 Hz, Man-6), 4.56 (1H, dd, *J* = 5.5, 12.5 Hz, GlcN-6), 4.61 (1H, dd, *J* = 6.0, 12.1 Hz, Man-6), 4.88 (1H, ddd, *J* = 2.2, 6.0, 9.7 Hz, Man-5), 5.10 (1H, br dd, *J* = 1.7, 3.1 Hz, Man-2), 5.41 (1H, t, *J* = 9.5 Hz, GlcN-4), 5.54 (1H, dd, *J* = 3.1, 10.1 Hz, Man-3), 5.62 (1H, d, *J* = 8.4 Hz, GlcN-1), 5.88 (1H, br s, Man-1), 5.94 (1H, t, *J* = 10.1 Hz, Man-4), 5.97 (1H, t, *J* = 9.7 Hz, GlcN-3), 7.05 (2H, d, *J* = 8.8 Hz), 7.59 (2H, d, *J* = 8.8 Hz), 9.21 (1H, d, *J* = 8.2 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 20.46, 20.50, 20.6, 20.65, 20.69, 20.8, 22.9, 23.1, 26.3, 29.45 (2C), 29.54, 32.0, 55.3 (GlcN-2), 62.6 (GlcN-6), 63.1 (Man-6), 66.8 (Man-4), 68.4 (OCH_2), 69.7 (GlcN-4), 70.2 (Man-5), 71.4 (Man-3), 72.2 (GlcN-5), 72.8 (GlcN-3), 76.1 (Man-2), 87.3 (Man-1), 99.7 (GlcN-1), 115.7 (2C), 124.0, 135.3 (2C), 160.2, 169.8, 170.0, 170.55 (2C), 170.61, 170.7, 170.9. IR ($CHCl_3$) ν: 3042, 2930, 2856, 1746, 1684, 1595, 1495, 1369, 1250, 1057 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 878.3249 (Calcd for $C_{40}H_{57}NO_{17}SNa$: 878.3245).

2-(_p_-Iodophenyl)ethyl 2,3,4-tri-_O_-acetyl-6-_O_-allyloxycarbonyl-β-D-glucopyranoside (18a)

$BF_3{\cdot}Et_2O$ (21 μL, 0.17 mmol) was added to a solution of **17**[11] (524.5 mg, 0.98 mmol) and **5a** (203.2 mg, 0.82 mmol) in CH_2Cl_2 (12 mL) at −20 °C. After stirring the reaction mixture for 4 h, it was poured into a saturated aqueous solution of sodium bicarbonate and extracted with $CHCl_3$. The organic layer was dried over sodium sulfate and condensed *in vacuo*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 3:1) to afford **18a** (315.9 mg, 62%). $[\alpha]_D$ −13.4° (*c* 0.96, $CHCl_3$).

^{1}H-NMR (C_5D_5N) δ: 1.969, 1.971, 2.01 (each 3H, s, OAc), 2.74 (1H, dt, *J* = 6.2, 13.8 Hz), 2.78 (1H, dt, *J* = 6.6, 13.8 Hz), 3.71 (1H, ddd, *J* = 6.6, 7.5, 9.5 Hz), 4.12 (1H, dt, *J* = 6.2, 9.5 Hz), 4.17 (1H, ddd, *J* = 2.9, 4.9, 10.1 Hz, H-5), 4.56 (1H, dd, *J* = 2.9, 11.9 Hz, H-6), 4.61 (1H, dd, *J* = 4.9, 11.9 Hz, H-6), 4.66 (2H, br dt, *J* = 1.7, 5.7 Hz), 4.90 (1H, d, *J* = 8.1 Hz, H-1), 5.15 (1H, qd, *J* = 1.3, 10.4 Hz), 5.31 (1H, qd, *J* = 1.7, 17.2 Hz), 5.42 (1H, dd, *J* = 8.1, 9.7 Hz, H-2), 5.49 (1H, t, *J* = 9.5 Hz, H-4), 5.71 (1H, t, *J* = 9.5 Hz, H-3), 5.91 (1H, ddt, *J* = 5.7, 10.4, 17.2 Hz), 6.96 (1H, d, *J* = 8.4 Hz), 7.66 (1H, d, *J* = 8.4 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.4, 20.46, 20.52, 35.6, 66.3 (C-6), 68.8, 69.3 (C-4), 70.1, 71.8 (C-2), 72.1 (C-5), 73.3 (C-3), 92.3, 101.0 (C-1), 118.6, 131.6 (2C), 132.3, 137.6 (2C), 139.0, 155.2, 169.5, 169.9, 170.3. IR ($CHCl_3$) ν: 3038, 3013, 1755, 1603, 1366, 1242, 1063 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 643.0649 (Calcd for $C_{24}H_{29}O_{11}INa$: 643.0652).

8-(*p*-Iodophenyl)octyl 2,3,4-tri-*O*-acetyl-6-*O*-allyloxycarbonyl-β-D-glucopyranoside (18b)

$BF_3{\cdot}Et_2O$ (24 μL, 0.19 mmol) was added to a solution of **17**[11] (604.1 mg, 1.13 mmol) and **5b** (311.2 mg, 0.94 mmol) in CH_2Cl_2 (12 mL) at −20 °C. After stirring the reaction mixture for 4 h, it was treated in the same manner as the synthesis of **18a**. The residue was purified by silica gel column chromatography (hexane: EtOAc = 4:1) to afford **18b** (417.1 mg, 63%). $[\alpha]_D$ −9.8° (*c* 1.22, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.16 (6H, m), 1.26 (2H, m), 1.43-1.58 (4H, m), 1.99, 2.03, 2.08 (each 3H, s, OAc), 2.44 (2H, t, *J* = 7.9 Hz), 3.55 (1H, dt, *J* = 6.6, 9.7 Hz, OCH_2), 3.93 (1H, dt, *J* = 6.4, 9.7 Hz, OCH_2), 4.20 (1H, ddd, *J* = 2.9, 4.9, 10.1 Hz, H-5), 4.57 (1H, dd, *J* = 2.9, 11.9 Hz, H-6), 4.63 (1H, dd, *J* = 4.9, 11.9 Hz, H-6), 4.67 (2H, br dt, *J* = 5.7, 1.5 Hz), 4.93 (1H, d, *J* = 7.9 Hz, H-1), 5.15 (1H, qd, *J* = 1.3, 10.4 Hz), 5.32 (1H, qd, *J* = 1.5, 17.2 Hz), 5.46 (1H, dd, *J* = 7.9, 9.9 Hz, H-2), 5.51 (1H, t, *J* = 9.5 Hz, H-4), 5.77 (1H, t, *J* = 9.5 Hz, H-3), 5.92 (1H, ddt, *J* = 17.2, 10.4, 5.7 Hz) , 6.97 (2H, d, *J* = 8.4 Hz), 7.71 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.45, 20.48, 20.6, 26.1, 29.3, 29.4, 29.6, 29.8, 31.5, 35.5, 66.4 (C-6), 68.8, 69.4 (C-4), 70.1, 72.06 (C-2), 72.09 (C-5), 73.4 (C-3), 91.4, 101.1 (C-1), 118.6, 131.1 (2C), 132.3, 137.7 (2C), 142.9, 155.2, 169.5, 169.9, 170.3. IR ($CHCl_3$) ν: 2934, 2856, 1755, 1367, 1248, 1065 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 727.1594 (Calcd for $C_{30}H_{41}O_{11}INa$: 727.1591).

15-(*p*-Iodophenyl)pentadecyl 2,3,4-tri-*O*-acetyl-6-*O*-allyloxycarbonyl-β-D-glucopyranoside (18c)

$BF_3{\cdot}Et_2O$ (16 μL, 0.13 mmol) was added to a solution of **17**[11] (278.0 mg, 0.64 mmol) and **5c** (414.0 mg, 0.77 mmol) in CH_2Cl_2 (12 mL) at −20 °C. After stirring the reaction mixture for 2.5 h, it was treated in the same manner as the synthesis of **18a**. The residue was purified by silica gel column chromatography (hexane: EtOAc = 4:1 to 3:1) to afford **18c** (369 mg, 71%). $[\alpha]_D$ −6.9° (*c* 1.18, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.22-1.31 (22H, m), 1.50-1.59 (4H, m), 1.99, 2.03, 2.09 (each 3H, s, OAc), 2.47 (2H, t, *J* =

7.9 Hz), 3.56 (1H, dt, J = 6.7, 9.6 Hz, OCH_2), 3.95 (1H, dt, J = 6.4, 9.6 Hz, OCH_2), 4.20 (1H, ddd, J = 2.8, 4.9, 10.1 Hz, H-5), 4.57 (1H, dd, J = 2.8, 11.9 Hz, H-6), 4.62 (1H, dd, J = 4.9, 11.9 Hz, H-6), 4.67 (2H, br dt, J = 1.5, 5.7 Hz), 4.93 (1H, d, J = 8.1 Hz, H-1), 5.16 (1H, qd, J = 1.3, 10.4 Hz), 5.33 (1H, qd, J = 1.5, 17.2 Hz), 5.46 (1H, dd, J = 8.1, 9.7 Hz, H-2), 5.50 (1H, dd, J = 9.5, 10.1 Hz, H-4), 5.76 (1H, t, J = 9.5 Hz, H-3), 5.93 (1H, ddt, J = 17.2, 10.4, 5.7 Hz) , 6.98 (2H, d, J = 8.4 Hz), 7.71 (2H, d, J = 8.4 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.45, 20.48, 20.6, 26.1, 29.4, 29.6, 29.7, 29.8, 29.86, 29.89 (2C), 30.0 (4C), 31.5, 35.5, 66.4 (C-6), 68.8, 69.4 (C-4), 70.1, 72.07 (C-2), 72.09 (C-5), 73.4 (C-3), 91.5, 101.1 (C-1), 118.6, 131.1 (2C), 132.3, 137.7 (2C), 143.0, 155.2, 169.5, 169.9, 170.3. IR (CHCl3) ν: 2928, 2855, 1755, 1367, 1248, 1065 cm^{-1}. HR-MS (FAB^+) *m/z*: 825.2695 (Calcd for $C_{37}H_{55}O_{11}INa$: 825.2687).

2-(*p*-Iodophenyl)ethyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (8a)

Tetrakis(triphenylphosphine)palladium(0) (12.4 mg, 10.7 μmol), triphenylphosphine (16.9 mg, 64.4 μmol), and formic acid (16.5 μL, 0.43 mmol) were added to a solution of **18a** (133.0 mg, 0.21 mmol) in THF (5 mL). After stirring the reaction mixture for 1 h, it was extracted with EtOAc, washed with distilled water and a saturated aqueous solution of sodium chloride, successively, dried over sodium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 1:1) to afford **8a** (109.0 mg, 95%). $[\alpha]_D$ −31.0° (*c* 0.91, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.98, 1.985, 1.990 (each 3H, s, OAc), 2.72 (1H, dt, J = 6.0, 13.9 Hz), 2.76 (1H, dt, J = 7.5, 13.9 Hz), 3.68 (1H, ddd, J = 6.4, 7.5, 9.7 Hz), 3.96-4.03 (2H, m, H-5 and H-6), 4.08 (1H, dt, J = 6.0, 9.7 Hz), 4.10-4.14 (1H, m, H-6), 4.88 (1H, d, J = 8.1 Hz, H-1), 5.44 (1H, dd, J = 8.1, 9.5 Hz, H-2), 5.63 (1H, t, J = 9.5 Hz, H-4), 5.72 (1H, t, J = 9.5 Hz, H-3), 6.94 (2H, d, J = 8.4 Hz), 7.66 (2H, d, J = 8.4 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.5, 20.56, 20.58, 35.6, 61.3 (C-6), 69.7 (C-4), 70.0, 72.1 (C-2), 74.0 (C-3), 75.6 (C-5), 92.3, 101.0 (C-1), 131.6 (2C), 137.6 (2C), 139.0, 169.6, 169.8, 170.4. IR ($CHCl_3$) ν: 3570, 3030, 3022, 3015, 1755, 1485, 1367, 1254, 1088, 1063, 1040 cm^{-1}. HR-MS (FAB^+) *m/z*: 559.0447 (Calcd for $C_{20}H_{25}O_9INa$: 559.0441).

8-(*p*-Iodophenyl)octyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (8b)

Tetrakis(triphenylphosphine)palladium(0) (16.0 mg, 13.8 μmol), triphenylphosphine (21.9 mg, 83.5 μmol), and formic acid (22 μL, 0.57 mmol) were added to a solution of **18b** (197.6 mg, 0.28 mmol) in THF (6 mL). After stirring the reaction mixture for 1 h, it was treated in the same manner as the synthesis of **8a**. The residue was purified by silica gel column chromatography (hexane: EtOAc = 2:1) to afford **8b** (162.8 mg, 94%). $[\alpha]_D$ −20.0° (*c* 0.91, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.16 (6H, m), 1.24 (2H, m), 1.42-1.57 (4H, m), 2.00, 2.09 (6H and 3H, s, OAc), 2.44 (2H, t, J = 7.7 Hz), 3.53 (1H, dt, J = 6.7, 9.6 Hz), 3.91 (1H, dt, J = 6.4, 9.6 Hz), 3.99-4.05 (2H, m, H-5 and H-6), 4.13 (1H, br dt, J = 4.4, 9.6 Hz, H-6), 4.91

(1H, d, J = 8.1 Hz, H-1), 5.48 (1H, dd, J = 8.1, 9.9 Hz, H-2), 5.65 (1H, t, J = 9.3 Hz, H-4), 5.77 (1H, t, J = 9.3 Hz, H-3), 6.97 (2H, d, J = 8.2 Hz), 7.71 (2H, d, J = 8.2 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.5, 20.6, 20.7, 26.1, 29.3, 29.4, 29.6, 29.8, 31.5, 35.5, 61.3 (C-6), 69.7 (C-4), 69.9, 72.3 (C-2), 74.1 (C-3), 75.6 (C-5), 91.5, 101.2 (C-1), 131.1 (2C), 137.7 (2C), 142.9, 169.6, 169.8, 170.4. IR ($CHCl_3$) ν: 3595, 3026, 2932, 2858, 1755, 1485, 1369, 1254, 1040 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 643.1384 (Calcd for $C_{26}H_{37}O_9INa$: 643.1380).

15-(*p*-Iodophenyl)pentadecyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (8c)

Tetrakis(triphenylphosphine)palladium(0) (5.2 mg, 4.5 μmol), triphenylphosphine (7.0 mg, 26.7 μmol), and formic acid (6.9 μL, 0.18 mmol) were added to a solution of **18c** (71.7 mg, 89.3 μmol) in THF (3 mL). After stirring the reaction mixture for 1 h, it was treated in the same manner as the synthesis of **8a**. The residue was purified by silica gel column chromatography (hexane : EtOAc = 3:2) to afford **8c** (61.7 mg, 96%). $[\alpha]_D$ −17.1° (*c* 0.88, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.22-1.30 (22H, m), 1.49-1.59 (4H, m), 2.00, 2.11 (6H and 3H, s, OAc), 2.47 (2H, t, J = 7.9 Hz), 3.55 (1H, dt, J = 6.7, 9.6 Hz), 3.92 (1H, dt, J = 6.4, 9.6 Hz), 3.99-4.05 (2H, m, H-5 and H-6), 4.14 (1H, br dt, J = 4.4, 9.9 Hz, H-6), 4.91 (1H, d, J = 8.1 Hz, H-1), 5.48 (1H, dd, J = 8.1, 9.7 Hz, H-2), 5.65 (1H, t, J = 9.5 Hz, H-4), 5.77 (1H, t, J = 9.5 Hz, H-3), 6.98 (2H, d, J = 8.1 Hz), 7.71 (2H, d, J = 8.1 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.5, 20.6, 20.7, 26.2, 29.4, 29.6, 29.7, 29.8, 29.86, 29.89 (2C), 30.0 (4C), 31.5, 35.5, 61.3 (C-6), 69.7 (C-4), 70.0, 72.4 (C-2), 74.1 (C-3), 75.6 (C-5), 91.5, 101.2 (C-1), 131.2 (2C), 137.7 (2C), 142.9, 169.6, 169.9, 170.4. IR ($CHCl_3$) ν: 3543, 2928, 2855, 1755, 1603, 1369, 1254, 1088, 1038 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 741.2471 (Calcd for $C_{33}H_{51}O_9INa$: 741.2476).

2-(*p*-Iodophenyl)ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (10a)

After stirring a suspension of **7** (166.0 mg, 0.19 mmol), **8a** (87.5 mg, 0.16 mmol), and MS4A (300 mg) in CH_2Cl_2 (5 mL) for 30 min, *N*-iodosuccinimide (91.8 mg, 0.41 mmol) and triflic acid (one drop with a capillary) were added to a suspension at −50 °C. After stirring the reaction mixture for 2 h while maintaining the temperature, the reaction was quenched by filtering the mixture through Celite. The filtrate was poured into a saturated aqueous solution of sodium bicarbonate, which was extracted with EtOAc. The organic layer was washed with a saturated aqueous solution of sodium thiosulfate and a saturated aqueous solution of sodium chloride, successively, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$: EtOAc = 1:1) to afford **10a** (161.8 mg, 86%). $[\alpha]_D$ +20.1° (*c* 0.60, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.96, 1.97, 1.98,

1.99, 2.00, 2.06, 2.07, 2.09, 2.097 and 2.103 (each 3H, s), 2.88 (1H, dt, J = 6.0, 14.5 Hz), 2.94 (1H, dt, J = 7.1, 14.5 Hz), 3.75-3.83 (2H, m, -OCH_2, Glc-6), 4.00-4.13 (4H, m, GlcN-2, GlcN-5, Glc-5, Glc-6), 4.28 (1H, dd, J = 2.2, 12.3 Hz, GlcN-6), 4.32-4.38 (2H, m, -OCH_2, Man-5), 4.44 (1H, dd, J = 2.7, 12.1 Hz, Man-6), 4.50 (1H, dd, J = 5.3, 12.1 Hz, Man-6), 4.63 (1H, dd, J = 5.5, 12.3 Hz, GlcN-6), 4.80 (1H, dd, J = 1.3, 3.5 Hz, Man-2), 4.90 (1H, d, J = 8.1 Hz, Glc-1), 5.29 (1H, d, J = 1.3 Hz, Man-1), 5.40 (1H, dd, J = 8.1, 9.7 Hz, Glc-2), 5.42 (1H, t, J = 9.5 Hz, GlcN-4), 5.45 (1H, t, J = 9.5 Hz, Glc-4), 5.59 (1H, d, J = 8.6 Hz, GlcN-1), 5.61 (1H, dd, J = 3.5, 10.1 Hz, Man-3), 5.72 (1H, t, J = 9.5 Hz, Glc-3), 5.87 (1H, t, J = 10.1 Hz, Man-4), 6.09 (1H, dd, J = 9.5, 10.6 Hz, GlcN-3), 7.06 (2H, br d, J = 8.2 Hz), 7.71 (2H, br d, J = 8.2 Hz), 9.29 (1H, d, J = 8.1 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.4, 20.50, 20.52, 20.54, 20.57, 20.63, 20.66, 20.67, 20.8, 23.2, 35.7, 55.8 (GlcN-2), 62.7 (GlcN-6), 63.0 (Man-6), 66.5 (Man-4), 67.1 (Glc-6), 69.6 (Glc-4), 69.87 (GlcN-4), 69.90 (Man-5), 70.5 (-OCH_2), 70.9 (Man-3), 71.9 (Glc-2), 72.2 (GlcN-5), 72.6 (GlcN-3), 73.0 (Glc-5), 73.5 (Glc-3), 74.5 (Man-2), 92.3, 98.4 (Man-1), 99.6 (GlcN-1), 101.1 (Glc-1), 131.7 (2C), 137.7 (2C), 139.1, 169.5, 169.87, 169.91, 170.0, 170.3, 170.48, 170.54, 170.6, 170.7, 171.0. IR ($CHCl_3$) ν: 3024, 1753, 1680, 1601, 1367, 1240, 1040 cm^{-1}. HR-MS (FAB^+) *m/z*: 1176.2405 (Calcd for $C_{46}H_{60}INO_{25}Na$: 1176.2397).

8-(*p*-Iodophenyl)octyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (10b)

After stirring a suspension of **7** (326.5 mg, 0.38 mmol), **8b** (195.7 mg, 0.32 mmol), and MS4A (500 mg) in CH_2Cl_2 (10 mL) for 30 min, *N*-iodosuccinimide (178.6 mg, 0.79 mmol) and triflic acid (one drop with a capillary) were added to a suspension at −50 °C. After stirring the reaction mixture for 2 h while maintaining the temperature, the reaction mixture was treated in the same manner as the synthesis of **10a**. The residue was purified by silica gel column chromatography ($CHCl_3$: EtOAc = 1:1) to afford **10b** (318.5 mg, 82%). $[\alpha]_D$ −2.4° (*c* 0.99, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.22-1.37 (8H, m), 1.47-1.68 (4H, m), 1.97, 1.99, 2.02, and 2.07 (each 3H, s), 2.09 (9H, s), 2.098, 2.103, and 2.11 (each 3H, s), 2.46 (2H, t, J = 7.9 Hz), 3.63 (1H, dt, J = 6.8, 9.7 Hz, -OCH_2), 3.75-3.80 (1H, m, Glc-6), 4.01 (1H, ddd, J = 2.2, 5.5, 10.3 Hz, GlcN-5), 4.04-4.16 (4H, m, GlcN-2, Glc-5, Glc-6, -OCH_2), 4.28 (1H, dd, J = 2.2, 12.2 Hz, GlcN-6), 4.38 (1H, ddd, J = 2.4, 5.1, 10.1 Hz, Man-5), 4.44 (1H, dd, J = 2.4, 12.1 Hz, Man-6), 4.53 (1H, dd, J = 5.1, 12.1 Hz, Man-6), 4.61 (1H, dd, J = 5.5, 12.2 Hz, GlcN-6), 4.79 (1H, dd, J = 1.5, 3.5 Hz, Man-2), 4.93 (1H, d, J = 8.1 Hz, Glc-1), 5.28 (1H, d, J = 1.5 Hz, Man-1), 5.41 (1H, t, J = 9.7 Hz, GlcN-4), 5.45 (1H, dd, J = 8.1, 9.7 Hz, Glc-2), 5.46 (1H, t, J = 9.3 Hz, Glc-4), 5.54 (1H, d, J = 8.4 Hz, GlcN-1), 5.61 (1H, dd, J = 3.5, 10.3 Hz, Man-3), 5.77 (1H, t, J = 9.7 Hz, Glc-3), 5.89 (1H, t, J = 10.3 Hz, Man-4), 6.05 (1H, t, J = 10.1 Hz, GlcN-3), 6.97 (2H, br d, J = 8.2 Hz), 7.71 (2H, br d, J = 8.2 Hz), 9.25 (1H, d, J = 8.2 Hz).

^{13}C-NMR (C_5D_5N) δ: 20.48, 20.50, 20.53, 20.7 (5C), 20.8, 23.2, 26.2, 29.4, 29.5, 29.7, 29.8, 31.5, 35.5, 55.8 (GlcN-2), 62.7 (GlcN-6), 63.0 (Man-6), 66.5 (Man-4), 67.2 (Glc-6), 69.6 (Man-5), 69.8 (GlcN-4), 70.1 (Glc-4), 70.3 (-OCH_2), 71.0 (Man-3), 72.18 (Glc-2), 72.23 (GlcN-5), 72.6 (GlcN-3), 72.9 (Glc-5), 73.6 (Glc-3), 74.5 (Man-2), 91.5, 98.4 (Man-1), 99.7 (GlcN-1), 101.1 (Glc-1), 131.1 (2C), 137.7 (2C), 142.9, 169.6, 169.9, 170.0 (2C), 170.4, 170.48, 170.54, 170.6, 170.7, 171.0. IR ($CHCl_3$) ν: 3032, 3013, 2932, 2856, 2359, 2341, 1751, 1684, 1367, 1244, 1043 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 1260.3341 (Calcd for $C_{52}H_{72}INO_{25}Na$: 1260.3336).

15-(*p*-Iodophenyl)pentadecyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1 → 2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (10c)

After stirring a suspension of **7** (88.5 mg, 103.4 μmol), **8c** (61.7 mg, 85.9 μmol), and MS4A (150 mg) in CH_2Cl_2 (3 mL) for 30 min, *N*-iodosuccinimide (48.4 mg, 215.1 μmol) and triflic acid (one drop with a capillary) were added to a suspension at −50 °C. After stirring the reaction mixture for 2 h while maintaining the temperature, the reaction mixture was treated in the same manner as the synthesis of **10a**. The residue was purified by silica gel column chromatography ($CHCl_3$: EtOAc = 1 : 1) to afford **10c** (97.5 mg, 85%). $[\alpha]_D$ −17.3° (*c* 1.10, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.26 (20H, m), 1.37-1.40 (2H, m), 1.50-1.55 (2H, m), 1.59-1.70 (2H, m), 1.97, 1.99, 2.01, 2.07, 2.09 and 2.095 (each 3H, s), 2.099 (6H, s), 2.104 (3H,s), 2.104 (3H, s), 2.47 (2H, t, *J* = 7.9 Hz), 3.64 (1H, dt, *J* = 6.8, 9.7 Hz, -OCH2), 3.75-3.79 (1H, m, Glc-6), 4.01 (1H, ddd, *J* = 2.2, 5.5, 10.1 Hz, GlcN-5), 4.05-4.16 (4H, m, -OCH_2, GlcN-2, Glc-5, Glc-6), 4.28 (1H, dd, *J* = 2.2, 12.3 Hz, GlcN-6), 4.39 (1H, ddd, *J* = 2.4, 5.3, 10.1 Hz, Man-5), 4.45 (1H, dd, *J* = 2.4, 12.1 Hz, Man-6), 4.54 (1H, dd, *J* = 5.3, 12.1 Hz, Man-6), 4.62 (1H, dd, *J* = 5.5, 12.3 Hz, GlcN-6), 4.79 (1H, dd, *J* = 1.7, 3.5 Hz, Man-2), 4.93 (1H, d, *J* = 8.1 Hz, Glc-1), 5.33 (1H, d, *J* = 1.7 Hz, Man-1), 5.41 (1H, t, *J* = 9.3 Hz, GlcN-4), 5.45 (1H, dd, *J* = 8.1, 9.7 Hz, Glc-2), 5.46 (1H, t, *J* = 9.5 Hz, Glc-4), 5.54 (1H, d, *J* = 8.4 Hz, GlcN-1), 5.61 (1H, dd, *J* = 3.5, 10.3 Hz, Man-3), 5.77 (1H, t, *J* = 9.5 Hz, Glc-3), 5.90 (1H, t, *J* = 9.5 Hz, Glc-3), 6.05 (1H, dd, *J* = 9.3, 10.4 Hz, GlcN-3), 6.98 (2H, br d, *J* = 8.2 Hz), 7.71 (2H, br d, *J* = 8.2 Hz), 9.26 (1H, d, *J* = 8.1 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.47, 20.50, 20.53, 20.6 (5C), 20.8, 23.2, 26.3, 29.4, 29.67, 29.72, 29.86 (2C), 29.94 (2C), 30.0 (4C), 31.5, 35.5, 55.7 (GlcN-2), 62.7 (GlcN-6), 63.0 (Man-6), 66.5 (Man-4), 67.2 (Glc-2), 69.6 (Man-5), 69.8 (GlcN-4), 70.1 (Glc-4), 70.3 (-OCH_2), 71.0 (Man-3), 72.17 (Glc-2), 72.22 (GlcN-5), 72.6 (GlcN-3), 72.9 (Glc-5), 73.6 (Glc-3), 74.5 (Man-2), 91.5, 98.3 (Man-1), 99.7 (GlcN-1), 101.1 (Glc-1), 131.1 (2C), 137.7 (2C), 143.0, 169.6, 169.9, 170.0 (2C), 170.4, 170.48, 170.54, 170.6, 170.7, 171.0. IR ($CHCl_3$) ν: 3036, 2928, 2855, 2359, 1753, 1682, 1367, 1244, 1042 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 1358.4437 (Calcd for $C_{59}H_{86}INO_{25}Na$: 1358.4431).

2-(*p*-Iodophenyl)ethyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-β-D-glucopyranoside (1a)

Sodium methoxide (28% in MeOH, 20 μL) was added to a solution of **10a** (30.1 mg, 26.1 μmol) in MeOH (2 mL), which was stirred for 30 min at room temperature. The reaction mixture was neutralized with Dowex 50 (H^+) (*ca.* 300 mg) and filtered. The filtrate was condensed *in vacuo*. The residue was purified by a recycle HPLC on a reversed phase column (MeOH: H_2O = 7:3) to afford **1a** (15.9 mg, 79%). $[\alpha]_D$ +27.3° (*c* 0.59, MeOH). ^{1}H-NMR (C_5D_5N+D_2O) δ: 2.20 (3H, s), 2.90 (2H, t, *J* = 7.0 Hz), 3.82-3.90 (2H, m), 3.95-4.00 (2H, m), 4.05-4.12 (2H, m), 4.19-4.56 (13H, m), 4.64 (1H, t, *J* = 9.3 Hz), 4.80 (1H, d, *J* = 7.7 Hz, Glc-1), 5.18 (1H, d, *J* = 7.1 Hz, GlcN-1), 5.53 (1H, br s, Man-1), 7.07 (2H, br d, *J* = 8.2 Hz), 7.61 (2H, br d, *J* = 8.2 Hz). ^{13}C-NMR (C_5D_5N+D_2O) δ: 23.6, 35.8, 57.8, 62.1, 62.7, 67.3, 68.5, 70.0, 71.2, 71.5, 71.9, 74.7, 75.0, 75.0, 75.3, 76.1, 78.2, 78.3, 79.4, 91.9, 98.5 (Man-1), 102.1 (GlcN-1), 104.4 (Glc-1), 131.7 (2C), 137.5 (2C), 139.2, 171.9. IR (KBr) ν: 3260, 2887, 2340, 1645, 1558, 1375, 1315, 1042 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 798.1450 (Calcd for $C_{28}H_{42}INO_{16}Na$: 798.1446).

8-(*p*-Iodophenyl)octyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)-α-D-mannopyranosyl-(1 → 6)-β-D-glucopyranoside (1b)

Sodium methoxide (28% in MeOH, 15 μL) was added to a solution of **10b** (19.1 mg, 15.4 μmol) in MeOH (1.5 mL), which was stirred for 30 min at room temperature. The reaction mixture was treated in the same manner as the synthesis of **1a**. The residue was purified by a recycle HPLC on a reversed phase column (MeOH) to afford **1b** (10.2 mg, 77%). $[\alpha]_D$ −15.0° (*c* 0.41, MeOH). ^{1}H-NMR (C_5D_5N+D_2O) δ: 1.13 (6H, m), 1.31-1.45 (4H, m), 1.59-1.66 (2H, m), 2.19 (3H, s), 2.41 (2H, t, *J* = 7.9 Hz), 3.65 (1H, dt, *J* = 6.7, 9.5 Hz), 3.88 (1H, ddd, *J* = 2.4, 5.1, 9.3 Hz), 3.96-4.02 (2H, m), 4.08-4.31 (7H, m), 4.35-4.55 (8H, m), 4.63 (1H, t, *J* = 9.3 Hz), 4.79 (1H, d, *J* = 7.7 Hz, Glc-1), 5.12 (1H, d, *J* = 9.2 Hz, GlcN-1), 5.23 (1H, br s, Man-1), 6.97 (2H, br d, *J* = 8.4 Hz), 7.70 (2H, br d, *J* = 8.4 Hz). ^{13}C-NMR (C_5D_5N+D_2O) δ: 23.8, 26.4, 29.3, 29.6, 29.7, 30.2, 31.5, 35.5, 57.9, 62.3, 62.9, 67.4, 68.8, 69.8, 71.5, 71.8, 72.1, 75.2, 75.3, 75.6, 76.3, 78.6, 78.7, 80.1, 91.4, 98.9 (Man-1), 102.6 (GlcN-1), 104.7 (Glc-1), 131.1 (2C), 137.6 (2C), 143.0, 171.6. IR (KBr) ν: 3231, 2926, 1638, 1040 cm^{-1}. HR-MS (FAB$^+$) *m/z*: 882.2389 (Calcd for $C_{34}H_{54}INO_{16}Na$: 882.2385).

15-(*p*-Iodophenyl)pentadecyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)-α-D-manno-pyranosyl-(1→6)-β-D-glucopyranoside (1c)

Sodium methoxide (28% in MeOH, 20 μL) was added to a solution of **10c** (28.9 mg, 21.6 μmol) in MeOH (2 mL), which was stirred for 30 min at room temperature. The reaction mixture was treated in the