Chapter 4
Conclusion
Endoglucanase V did not recognize the sulfur substituted analogues (iii-1a and iii-1b) at all. On the other hand, the transition state analogues (iii-2a and iii-2b) formed a complex with endoglucanase V. The binding constant was 50 L/mol in calorimetric experiments. From the result, it was clarified that the introducing cyclohexene framework is important. However, the affinity between iii-2 and endoglucanase V is not enough for the further studies.

X-ray crystallographic structure shown in Figure iv-1 is a complex of cellotrioses and endoglucanase V from *Humicola insolens*, which was obtained from Protein Data Bank (PDB ID: 4eng). The sugar unit does not enter in the active site of this enzyme by the nature of endoglucanase V itself. Cellotrioses

![Figure iv-1. A complex of cellotrioses and endoglucanase V from *Humicola insolens*.](image-url)
combine selectively with +1~+3 or -2~4 subsites. The author expected that the affinity is dependent to the remote subsites from the active site. Therefore the author is synthesizing iv-1 added a sugar to the reducing end for studying the effect of +2 subsite (Figure iv-2).

**Figure iv-2.** Cellotetraose analogue iv-1.
Chapter 4.

Experimental Section
4.1. General Procedures.

Melting points were determined with a Yanako MP-J3 micro melting point apparatus and were uncorrected. Optical rotations were measured on a HORIBA SEPA300 high-sensitivity polarimeter. $^1$H-NMR spectra were measured on JEOL ALPHA 400 (400 MHz) and JNM-ECA 500 (500 MHz) spectrometers. The chemical shifts are expressed in ppm downfield from the signal of trimethylsilane (0.00 ppm) used as an internal standard in the case of CDCl$_3$. When other solvents were employed, the remained proton signals in deuterosolvents C$_6$HD$_5$ (7.15 ppm) or HDO (4.63 ppm) were used as the internal standards. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). $^{13}$C-NMR spectra were recorded also on JEOL ALPHA 400 (100 MHz) and JNM-ECA 500 (125 MHz) spectrometers. The isotope $^{13}$C in the solvents were used as the internal standard ($^{13}$CDCl$_3$; 77.0 ppm or $^{13}$C$_6$D$_6$; 128.0 ppm). For $^{13}$C-NMR spectra measured in D$_2$O, default offset was employed and did not corrected. Assignments of the signals are according to the numbering based on IUPAC nomenclature if not mentioned. For carbohydrate and cyclohexene derivatives, numberings based on carbohydrate nomenclature are employed. Measurement of IR spectra were carried out with a HORIBA FT-720 Fourier transform infrared spectrometer on a KBr cell. Measurements of field desorption (FD) and fast atom bombardment (FAB) mass spectra were performed on a JEOL JMS AX500 or JEOL JMS AX102A spectrometers. Electron spray ionization mass spectra were obtained by a HITACHI NanoFrontier LD spectrometer. MS analyses for unstable compounds such as glycosyl imidates were not performed. Analytical and preparative thin-layer chromatographies were carried out using precoated silica gel plates, Merck silica gel 60F$_{254}$ (Art. 1.05715). Silica gel used
for column chromatography was Merck silica gel 60 (Art. 1.07734). Medium-pressure column chromatographies were performed employing Yamazene ULTRA PACK ODS-SM-50B or Yamazene ULTRA PACK SI-40B equipped with FMI LAB PUMP RP-SY. All reactions were carried out under N₂ or Ar atmosphere using dried solvents except for aqueous conditions. Dichloromethane and tetrahydrofuran were freshly distilled from diphosphorus pentoxide and benzophenone-ketyl, respectively.

4.2. Methyl 2,3-di-O-benzoyl-α-D-galactopyranoside (ii-5)

Commercial available methyl α-D-galactopyranoside ii-4 (8.48 g, 43.7 mmol) was stirred with chlorotriphenylmethane (14.0 g, 50.2 mmol) in pyridine (50 ml) at 100 °C for 30 min. The mixture was poured into H₂O (200 ml) and the aqueous layer was extracted with AcOEt (150 ml x 3). The combined organic layer was washed with brine (100 ml), dried over MgSO₄, and then concentrated in vacuo. Silica gel column chromatography of the residue (AcOEt 100%) gave the corresponding 6-O-triphenylmethyl ether (14.0 g, 73%) as a white solid. Recrystallization from AcOEt:hexane (50:50) gave colorless needles. mp 122-123 °C; [α]D 24 +63.3 (c 0.94, CHCl₃); IR (KBr) cm⁻¹: 3400, 2930, 1490, 1445, 1150, 1075, 1045, 765; ¹H NMR (400 MHz, CDCl₃) δ 2.05 (d, 1H, J = 9.5 Hz, C2OH), 2.46 (d, 1H, J = 2.7 Hz, C4OH), 2.58 (d, 1H, J = 5.3 Hz, C3OH), 3.38 (dd, 1H, J = 5.9, 9.4 Hz, C6HH), 3.43 (s, 3H, OCH₃), 3.43 (dd, 1H, J = 5.9, 9.4 Hz, C6HH), 3.71 (ddd, 1H, J = 3.7, 5.3, 9.5 Hz, C3H), 3.80 (dt, 1H, J = 3.7, 9.5 Hz, C2H), 3.82 (brt, 1H, J = 5.9 Hz, C5H), 4.03 (brdd, 1H, J = 2.7, 3.7 Hz, C4H), 4.82 (d, 1H, J = 3.7 Hz, C1H), 7.23 (m, 3H, aromatic protons), 7.30 (m, 6H, aromatic protons), 7.46 (m, 6H, aromatic protons); ¹³C
NMR (100 MHz, CDCl₃) δ 55.44 (OCH₃), 63.17 (C6), 69.00 (C5), 69.60 (C4), 69.88 (C2), 71.35 (C3), 87.05 (OCPh₃), 99.36 (C1), 127.14, 127.92, 128.61, 143.69 (aromatic carbons); negative-FABMS (% rel. int.) m/z: 436 (12, [M⁺]), 435 (41, [M-H⁺]), 259 (19, [Ph₃CO⁺]), 243 (16, [Ph₃C⁺]), 193 (61, [M-Ph₃C⁺]), 148 (100, [M-Ph₃COCH₂-OCH₃⁺]); negative-FAB-HRMS: calcd. for C₂₆H₂₇O₆ [M-H⁺], 435.1808; found, m/z 435.181.

A solution of the 6-O-triphenylmethyl ether (1.59 g, 3.64 mmol) in CH₂Cl₂ (100 ml) was stirred with benzoyl chloride (1.02 g, 7.26 mmol) and pyridine (576 mg, 7.28 mmol) at 0 °C. After stirring for 5 min, the cooling bath was removed, and the mixture was stirred for additional 30 min at room temperature. The mixture was poured into H₂O (100 ml) and the aqueous layer was extracted with AcOEt (80 ml x 3). The combined organic layer was washed with brine (80 ml), dried over MgSO₄, and then concentrated in vacuo. Silica gel column chromatography of the residue (AcOEt:hexane = 10:90) gave methyl 2,3-di-O-benzoyl-6-O-triphenylmethyl-α-D-galactopyranoside (2.24 g, 95%) as a viscous oil. [α]D²⁴ +93.4 (c 0.93, CHCl₃); IR (film) cm⁻¹: 3500, 3060, 2935, 1725, 1450, 1280, 1105; ¹H NMR (400 MHz, C₆D₆) δ 3.11 (s, 3H, OCH₃), 3.38 (dd, 1H, J = 4.1, 9.9 Hz, C6HH), 3.56 (dd, 1H, J = 5.9, 9.9 Hz, C6HH), 3.78 (brdd, 1H, J = 4.1, 5.9 Hz, C5H), 3.96 (brd, 1H, J = 3.0 Hz, C4H), 5.29 (d, 1H, J = 3.6 Hz, C1H), 6.01 (dd, 1H, J = 3.0, 10.5 Hz, C3H), 6.12 (dd, 1H, J = 3.6, 10.5 Hz, C2H), 6.83-7.18 (m, 15H, aromatic protons), 7.58 (m, 6H, aromatic protons), 8.10 (brdd, 2H, J = 1.5, 8.1 Hz, aromatic protons), 8.14 (brdd, 2H, J = 1.5, 8.1 Hz, aromatic protons); ¹³C NMR (100 MHz, C₆D₆) δ 54.89 (OCH₃), 64.56 (C6), 69.29 (C5), 69.67 (C4), 69.79 (C2), 71.43 (C3), 87.49 (OCPh₃), 97.97 (C1), 127.35, 128.53, 129.11, 130.05, 130.10, 133.02, 133.04, 144.40 (aromatic carbons), 165.85, 166.24 (each ArC=O); FABMS (% rel. int.) m/z:

A solution of methyl 2,3-di-O-benzoyl-6-O-triphenylmethyl-α-D-galactopyranoside (2.24 g, 3.48 mmol) was stirred in 60% aqueous acetic acid solution (8.0 ml) at 60 °C for 30 min. After cooling, the mixture was concentrated in vacuo. Silica gel column chromatography of the residue (AcOEt:hexane = 60:40) gave ii-5 (1.05 g, 75%) as an oil. [α]D 23 +157 (c 1.02, CHCl3); IR (film) cm⁻¹: 3440, 2935, 1720, 1280, 1105, 1030, 710; ¹H NMR (400 MHz, CDCl3) δ 2.45 (br, 1H, C6OH), 3.07 (br, 1H, C4OH), 3.44 (s, 3H, OCH3), 4.00 (m, 3H, C6H2, C5H), 4.47 (brs, 1H, C4H), 5.22 (d, 1H, J = 1.9 Hz, C1H), 5.70 (m, 2H, C2H, C3H), 7.36 (m, 4H, aromatic protons), 7.50 (m, 2H, aromatic protons), 7.98 (m, 4H, aromatic protons); ¹³C NMR (100 MHz, CDCl3) δ 55.44 (OCH3), 62.73 (C6), 68.98 (C2), 69.09 (C5), 69.32 (C4), 71.02 (C3), 97.55 (C1), 128.30, 128.35, 129.23, 129.31, 129.69, 129.76, 133.22, 133.25 (aromatic carbons), 165.91, 166.21 (each ArC=O); negative-FABMS (% rel. int.) m/z: 402 (3.7, [M]), 401 (6.0, [M-H]), 297 (9.3, [M-PhCOO]), 121 (100, [PhCOO]); negative-FAB-HRMS: calcd. for C21H21O8 [M-H], 401.1236; found, m/z 401.1251.

4.3. Methyl (methyl 2,3-di-O-benzoyl-α-D-galactopyranosiduronate (ii-6)

A suspension of ii-5 (1.05 g, 2.61 mmol) in a mixture of CH2Cl2 (10 ml) and H2O (5.0 ml) was stirred with PhI(OAc)2 (4.33 g, 13.4 mmol) and TEMPO (80.0 mg, 512.0 μmol) at room temperature for 10 min. The mixture was poured into H2O (70 ml) and the aqueous layer was extracted with AcOEt (40 ml × 3). The combined extract was washed with brine (50 ml), dried over MgSO4, and then concentrated in vacuo. After the residue had been diluted with THF (8.0
ml), ethereal diazomethane was added until the yellow color did not disappear. After concentration in vacuo, silica gel column chromatography (AcOEt:hexane = 30:70) of the residue gave ii-6 (1.07 g, 95%) as an oil. [α]D 23 +107 (c 0.95, CHCl3); IR (film) cm⁻¹: 3940, 2955, 1725, 1450, 1280, 1100, 1025, 915, 710; 1H NMR (400 MHz, CDCl3) δ 3.47 (s, 3H, OCH₃), 3.80 (s, 3H, C6OCH₃), 4.65 (brs, 1H, C5H), 4.73 (brs, 1H, C4H), 5.31 (d, 1H, J = 2.7 Hz, C1H), 5.71 (dd, 1H, J = 2.7, 10.7 Hz, C2H), 5.75 (dd, 1H, J = 1.9, 10.7 Hz, C3H), 7.34 (m, 4H, aromatic protons), 7.48 (m, 2H, aromatic protons), 7.98 (m, 4H, aromatic protons); 13C NMR (100 MHz, CDCl3) δ 52.50 (C60aI3), 56.06 (OaI3), 68.23 (C3), 68.88 (C4), 69.81 (C5), 70.16 (C2), 97.76 (C1), 128.16, 128.24, 128.27, 129.06, 129.64, 129.66, 133.15, 133.23 (aromatic carbons), 165.61, 165.83 (each ArC=O), 168.59 (C6); FDMS (% rel. int.) m/z: 431 (64, [M+H]⁺), 398 (100, [M-CH₃OH]⁺), 341 (26, [MH-(COOCH₃)-CH₃OH]⁺), 308 (42, [M-PhCOOH]⁺); FD-HRMS: calcd. for C₂₂H₂₃O₉ [M+H]⁺, 431.1342; found, m/z 431.1335.

4.4. Phenyl 2,3-di-O-(4-methoxyphenylmethyl)-4,6-O-(4-methoxyphenyl methylidene)-1-thio-β-D-galactopyranoside (ii-8)

A solution of phenyl-1-thio-β-D-galactopyranoside (ii-7); (2.62 g, 9.62 mmol) in DMF (20 ml) was stirred with 4-methoxybenzaldehyde dimethylacetal (3.50 g, 19.2 mmol) and camphorsulfonic acid (22.3 mg, 96.0 μmol) at 100 °C for 10 min. After cooling, the mixture was poured into 5% aqueous NaHCO₃ solution (100 ml) and the aqueous layer was extracted with AcOEt (70 ml × 3). The combined extract was washed with H₂O (50 ml) and brine (50 ml), dried over MgSO₄, and then concentrated in vacuo to give a crude solid. Recrystallization from AcOEt:hexane (30:70) gave phenyl
4,6-O-(4-methoxyphenylmethylidene)-1-thio-β-D-galactopyranoside (2.74 g, 72%) as needles. mp 151-154°C; [α]D^23 -7.5 (c 1.50, CHCl₃); IR (KBr) cm⁻¹:
3410, 2910, 1615, 1515, 1250, 1165, 825; ^1H NMR (400 MHz, CDCl₃) δ 2.48 (brd, 1H, J = 9.0 Hz, C2OH), 2.51 (d, 1H, J = 1.2 Hz, C3OH), 3.55 (brdd, 1H, J = 1.4, 1.7 Hz, C5H), 3.69 (m, 2H, C2H, C3H), 3.82 (s, 3H, OCH₃), 4.02 (dd, 1H, J = 1.7, 12.4 Hz, C6HH), 4.20 (brd, 1H, J = 1.9, C4H), 4.37 (dd, 1H, J = 1.4, 12.4 Hz, C6HH), 4.51 (m, 1H, C1H), 5.47 (s, 1H, ArCH), 6.86 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.33 (m, 5H, aromatic protons), 7.69 (brdd, 2H, J = 2.0, 8.2 Hz, aromatic protons); ^13C NMR (100 MHz, CDCl₃) δ 55.33 (OCH₃), 68.86 (C2), 69.25 (C6), 70.06 (C5), 73.82 (C3), 75.30 (C4), 87.00 (C1), 101.29 (ArC(OR)₂), 113.57, 127.82, 128.21, 128.93, 130.14, 130.71, 133.76, 160.33 (aromatic carbons); negative-FABMS (% rel. int.) m/z: 389 (2.1, [M-H]), 375 (1.3, [M-CH₃]), 148 (100), 109 (91, [PhS]); negative-FAB-HRMS: calcd. for C₂₀H₁₉O₈S [M-H]⁻, 389.1059; found, m/z 389.1057.

Sodium hydride (washed with hexane, 3.21 g, 8.22 mmol) was slowly added to a DMF solution (20 ml) of the foregoing product (3.21 g, 8.22 mmol) at room temperature. Upon the addition of the substrate, H₂ gas was bubbled. After stirring for 30 min, 50% toluene solution of MPMBr (13.2 g, 32.8 mmol, freshly prepared from anisic alcohol and PBr₃) was added at 0 °C. After 10 min, the cooling bath was removed, and the mixture was stirred at room temperature for 30 min. Methanol (5.0 ml) and triethylamine (5.0 ml) were added to decompose the excess reagent. After stirring for an additional 30 min, the mixture was poured into H₂O (100 ml) and the aqueous layer was extracted with AcOEt (70 ml × 3). The combined organic layer was successively washed with H₂O (50 mL), and brine (50 mL), and dried over MgSO₄. After concentration, the residue was purified by silica gel column chromatography (AcOEt:hexane = 25:75) to
give \textbf{ii-8} (4.98 g, 96\%) as an oil. $[\alpha]_D^{23}$ +1.7 (c 1.25, CHCl$_3$); IR (film) cm$^{-1}$: 2860, 1610, 1515, 1250, 1170, 1100, 1035, 820; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.37 (brdd, 1H, $J = 1.3, 1.4$ Hz, C5H), 3.57 (dd, 1H, $J = 3.3, 9.2$ Hz, C3H), 3.79, 3.80, 3.83 (each s, 3H, OCH$_3$), 3.86 (t, 1H, $J = 9.2$ Hz, C2H), 3.95 (dd, 1H, $J = 1.4, 12.4$ Hz, C6HH), 4.10 (brd, 1H, $J = 3.3$ Hz, C4H), 4.33 (dd, 1H, $J = 1.3, 12.4$ Hz, C6HH), 4.58 (d, 1H, $J = 9.2$ Hz, C1H), 4.62 (s, 2H, ArCH$_2$O), 4.63, 4.66 (each d, 1H, $J = 12.3$ Hz, ArCHH), 5.43 (s, 1H, ArCH), 6.82 (brd, 2H, $J = 8.7$ Hz, aromatic protons), 6.87 (brd, 2H, $J = 8.6$ Hz, aromatic protons), 6.91 (brd, 2H, $J = 8.8$ Hz, aromatic protons), 7.16-7.27 (m, 5H, aromatic protons), 7.33 (brd, 2H, $J = 8.7$ Hz, aromatic protons), 7.44 (brd, 2H, $J = 8.6$ Hz, aromatic protons), 7.70 (brdd, 2H, $J = 2.1, 7.8$ Hz, aromatic protons); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 55.24, 55.27, 55.34 (each OCH$_3$), 69.37 (C6), 69.84 (C5), 71.46 (ArCH$_2$O), 73.79 (C4), 75.05 (ArCH$_2$O), 75.18 (C2), 80.95 (C3), 86.59 (C1), 101.24 (ArC(OR)$_2$), 113.49, 113.73, 113.76, 127.36, 127.91, 128.82, 129.37, 129.81, 130.23, 130.57, 130.76, 132.67, 132.88, 159.25, 159.27, 160.14 (aromatic carbons); FDMS (% rel. int.) $m/z$: 631 (38, [M+H]$^+$), 630 (100, [M]$^+$); FD-HRMS: calcd. for C$_{36}$H$_{38}$O$_8$S [M]$^+$, 630.2287; found, $m/z$ 630.2276.

**4.5. 2,3-di-O-(4-methoxyphenylmethyl)-4,6-O-(4-methoxyphenylmethyldiene)-\alpha-D-galactopyranosyl 2,2,2-trichloroacetimidate (ii-9)**

A solution of \textbf{ii-8} (515 mg, 817.0 $\mu$mol) in a mixture of acetone (10.0 ml) and H$_2$O (1.0 ml) was stirred with NBS (356 mg 2.0 mmol) at 0 °C. After 5 min, 10% Na$_2$S$_2$O$_3$ (4.0 ml) was added to the mixture. After concentrating \textit{in vacuo}, the residue was diluted with AcOEt (150 ml) and then washed with H$_2$O (60 ml). The aqueous solution was extracted with AcOEt (50 ml $\times$ 2). Each organic layer was washed with brine (50 ml), combined, dried over MgSO$_4$, and then
concentrated in vacuo to give a white solid. Recrystallization (from AcOEt:hexane = 50:50) gave 2,3-di-O-(4-methoxyphenylmethyl)-
4,6-O-(4-methoxyphenylmethylidene)-D-galactopyranose as needles (431 mg, 98%). mp 124-130°C; [α]_D^22 +39.8 (c 0.75, CHCl_3); IR (film) cm⁻¹: 3435, 2930, 1610, 1515, 1250, 1195, 1035, 825. The ¹H NMR spectrum indicated that the sample consisted of a mixture of anomers (α:β = 67:33 in CDCl₃); ¹H NMR (400 MHz, CDCl₃) δ 2.86 (d, 1H × 0.67, J = 1.2 Hz, C1OH (α-anomer)), 2.94 (d, 1H × 0.33, J = 7.4 Hz, C1OH (β-anomer)), 3.37 (brdd, 1H × 0.33, J = 1.2, 1.6 Hz, C5H (β-anomer)), 3.54 (dd, 1H × 0.33, J = 3.6, 9.5 Hz, C3H (β-anomer)), 3.73 (dd, 1H × 0.33, J = 7.7, 9.5 Hz, C2H (β-anomer)), 3.80, 3.80, 3.80 (each s, 3H × 0.33, OCH₃ (β-anomer)), 3.81, 3.81, 3.81 (each s, 3H × 0.67, OCH₃ (α-anomer)), 3.81 (1H, m, C5H (α-anomer)), 3.91 (dd, 1H × 0.67, J = 3.6, 9.7 Hz, C3H (α-anomer)), 3.97-4.03 (m, 1H × 0.67, 1H × 0.33, 1H × 0.67, C6HH (α-anomer), C6HH (β-anomer), C2H (α-anomer)), 4.08 (brd, 1H × 0.33, J = 3.6 Hz, C4H (β-anomer)), 4.15 (brd, 1H × 0.67, J = 3.6 Hz, C4H (α-anomer)), 4.20 (dd, 1H × 0.67, J = 1.6, 12.3 Hz, C6HH (α-anomer)), 4.28 (dd, 1H × 0.33, J = 1.6, 12.5 Hz, C6HH (β-anomer)), 4.62 (d, 1H × 0.33, J = 11.2 Hz, ArCHHO (β-anomer)), 4.65 (d, 1H × 0.33, J = 7.7 Hz, C1H (β-anomer)), 4.68 (d, 1H × 0.67, J = 12.2 Hz, ArCHHO (α-anomer)), 4.69 (s, 2H × 0.67, ArCH₂O (α-anomer)), 4.72 (d, 1H × 0.67, J = 12.2 Hz, ArCHHO (α-anomer)), 4.78 (d, 1H × 0.33, J = 10.7 Hz, ArCHHO (β-anomer)), 4.81 (d, 1H × 0.33, J = 11.2 Hz, ArCHHO (β-anomer)), 4.82 (d, 1H × 0.33, J = 10.7 Hz, ArCHHO (β-anomer)), 5.31 (dd, 1H × 0.67, J = 1.2, 3.5 Hz, C1H (α-anomer)), 5.44 (s, 1H × 0.33, ArCH (β-anomer)), 5.45 (s, 1H × 0.67 ArCH (α-anomer)), 6.84-7.48 (12H, aromatic protons); FABMS (%, rel. int.) m/z: 561 (46, [M+Na]⁺), 417 (61, [M-CH₃OPhCH₂]⁺), 121 (100, [PhCOO]⁺); FAB-HRMS: calcd. for C₃₀H₃₄O₉Na
[M+Na]+, 561.2101; found, m/z 561.2108.

A solution of the product (489 mg, 908 µmol) in CH₂Cl₂ (8.0 ml) was stirred with CCl₃CN (656 mg, 4.54 mmol) in the presence of DBU (45.6 mg, 6.94 µmol) at -15 °C for 30 min. After concentrating in vacuo, the residue was purified by silica gel column chromatography (AcOEt: hexane = 30:70) to give ii-9 (556 mg, 89%) as an oil. ¹H NMR (400 MHz, CDCl₃) δ 3.80, 3.80 (each s, 3H, OCH₃), 3.80 (m, 1H, C5H), 3.81 (s, 3H, OCH₃), 3.97 (dd, 1H, J = 1.3, 12.6 Hz, C6HH), 4.02 (dd, 1H, J = 3.3, 10.1 Hz, C3H), 4.19 (brd, 1H, J = 3.3 Hz, C4H), 4.24 (dd, 1H, J = 3.4, 10.1 Hz, C2H), 4.24 (dd, 1H, J = 1.1, 12.6 Hz, C6HH), 4.66 (d, 1H, J = 11.5 Hz, ArCHHO), 4.70 (d, 1H, J = 11.8 Hz, ArCHHO), 4.70 (d, 1H, J = 11.5 Hz, ArCHHO), 4.75 (d, 1H, J = 11.8 Hz, ArCHHO), 5.45 (s, 1H, ArCH), 6.59 (d, 1H, J = 3.4 Hz, C1H), 6.82-6.90 (m, 6H, aromatic protons), 7.25 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.29 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.44 (brd, 2H, J = 8.7 Hz, aromatic protons), 8.55 (s, 1H, C(=NH)CCl₃). This sample gradually decomposed, so it was immediately used for the next step.

4.6. 2,3-di-O-(4-methoxyphenylmethyl)-4,6-O-methoxyphenylmethylidene-α-D-galactopyranosyl-(1→4)-[methyl(methyl 2,3-di-O-benzoyl-α-D-galactopyranosid)uronate] (ii-10)

Triethylsilyl trifluoromethanesulphonate (1.8 mg, 6.8 µmol) was added to a suspension of ii-6 (30.1 mg, 69.9 µmol), ii-9 (138.7 mg, 0.2 mmol), and powdered 4A molecular sieves (43 mg) in CH₂Cl₂ (0.5 ml) at -78 °C. After stirring for 5 min, to the mixture triethylamine (50 µl) was added, and the mixture was allowed to warm to room temperature. After filtering through a cotton pad, the filtrate was concentrated in vacuo. Purification of the residue by
silica gel column chromatography (AcOEt:hexane = 25:75) gave **ii-10** (48.8 mg, 73%) as an oil. [α]D23 +58.4 (c 0.60, CHCl3); IR (film) cm⁻¹: 2935, 1730, 1515, 1250, 1100, 1030, 830, 710; ¹H NMR (400 MHz, CDCl3) δ 3.36, 3.41 (each brd, 1H, J = 12.7 Hz, C6'HH), 3.49, 3.60, 3.76, 3.78, 3.78 (each s, 3H, OCH3), 3.85 (brs, 1H, C5'H), 3.96 (dd, 1H, J = 3.2, 10.2 Hz, C2'H), 4.04 (brd, 1H, J = 3.1 Hz, C4'H), 4.08 (dd, 1H, J = 3.1, 10.2 Hz, C3'H), 4.64 (d, 1H, J = 11.4 Hz, ArCHHO), 4.66 (brs, 1H, C5H), 4.66 (s, 2H, ArCH2O), 4.71 (d, 1H, J = 11.4 Hz, ArCHHO), 4.86 (brd, 1H, J = 2.5 Hz, C4H), 4.96 (d, 1H, J = 3.2 Hz, C1'H), 5.24 (s, 1H, ArCH), 5.32 (d, 1H, J = 3.4 Hz, C1H), 5.66 (dd, 1H, J = 2.5, 11.0 Hz, C3H), 5.72 (dd, 1H, J = 3.4, 11.0 Hz, C2H), 6.80-6.88 (m, 6H, aromatic protons), 7.22-7.40 (m, 10H, aromatic protons), 7.48 (m, 2H, aromatic protons), 7.89 (brd, 2H, J = 7.3 Hz, aromatic protons), 7.99 (brd, 2H, J = 7.3 Hz, aromatic protons); ¹³C NMR (100 MHz, CDCl3) δ 52.39, 55.17, 55.20, 55.25, 56.16, (each OCH3), 63.47 (C5''), 68.26 (C2), 68.94 (C6''), 69.73 (C5), 70.39 (C3), 71.73, 73.19 (each ArCH2O), 74.46 (C2''), 74.68 (C4''), 75.41 (C3''), 76.49 (C4), 97.88 (C1), 100.40 (C1''), 100.60 (ArC(OR)₂), 113.35, 113.58, 113.63, 127.61, 127.61, 128.21, 128.45, 128.60, 129.02, 129.23, 129.26, 129.46, 129.73, 129.75, 129.80, 130.60, 130.79, 130.97, 133.38, 133.53, 159.05, 159.05, 159.91 (aromatic carbons), 165.82, 166.02 (each ArC=O), 167.90 (C6); FABMS (% rel. int.) m/z: 973 (1.9, [M+Na]+), 829 (1.2, [M-CH₃OPhCH]⁺), 121 (100, [PhCOO]+); FAB-HRMS: calcd. for C₅₂H₅₄O₁₇Na [M+Na]+, 973.3259; found, m/z 973.3230.

4.7. **Methyl[2,3-di-O-(4-methoxyphenylmethyl)-α-D-galactopyranosid]uronate-(1→4)-[methyl(methyl 2,3-di-O-benzoyl-α-D-galactopyranosid)uronate]** (ii-12)
A solution of ii-10 (348 mg, 366 µmol) in 60% aqueous acetic acid solution (8.0 ml) was stirred at 50 °C for 20 min. After cooling, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt:hexane = 50:50) to give the corresponding diol (280 mg, 92%) as a viscous oil. [α]_D^22 +93.7 (c 0.52, CHCl₃); IR (film) cm⁻¹: 3450, 2935, 1730, 1510, 1250, 1095, 710; ¹H NMR (400 MHz, CDCl₃) δ 3.49, 3.62 (each s, 3H, OCH₃), 3.63 (dd, 1H, J = 3.4, 12.0 Hz, C6'HH), 3.69, (dd, 1H, J = 3.2, 10.0 Hz, C2'H), 3.71 (dd, 1H, J = 4.5, 12.0 Hz, C6'HH), 3.74, 3.80 (each s, 3H, OCH₃), 3.92 (dd, 1H, J = 3.4, 12.0 Hz, C5'H), 4.02 (dd, 1H, J = 1.1, 3.2 Hz, C4'H), 4.16 (ddd, 1H, J = 1.1, 3.4, 4.5, Hz, C5'H), 4.51, 4.57 (each d, 1H, J = 11.7 Hz, ArCH₂O), 4.61 (d, 1H, J = 11.1 Hz, ArCHHO), 4.69 (d, 1H, J = 1.8 Hz, C5H), 4.70 (d, 1H, J = 11.1 Hz, ArCHHO); 4.71 (brd, 1H, J = 1.8 Hz, C4H), 4.79 (d, 1H, J = 3.2 Hz, C1'H), 5.25 (brs, 1H, C1H), 5.75 (m, 2H, C2H, C3H), 6.78 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.90 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.22-7.36 (m, 8H, aromatic protons), 7.48 (m, 2H, aromatic protons), 7.93-7.96 (m, 4H, aromatic protons); ¹³C NMR (100 MHz, CDCl₃) δ 52.43, 55.14, 55.23, 56.19 (each OCH₃), 62.95 (C6'), 68.20 (C2 or 3), 69.16 (C4'), 69.98 (C5), 70.11 (C2 or 3), 70.96 (C5'), 72.66, 73.17 (each ArCH₂O), 75.72 (C2'), 76.64 (C3'), 76.88 (C4), 98.17 (C1), 99.98 (C1'), 113.73, 113.88, 128.34, 128.49, 128.94, 129.08, 129.62, 129.77, 129.83, 129.87, 130.25, 130.39, 133.34, 133.42, 159.24, 159.36 (aromatic carbons), 165.90, 166.98 (each ArC=O), 168.01 (C6); FABMS (% rel. int.) m/z: 855 (61, [M+Na]^⁺), 121 (100, [CH₃OPhCH₂]^⁺), 105 (96, [PhCO]^⁺); FAB-HRMS: calcd. for C₄₄H₄₈O₁₆Na [M+Na]^⁺, 855.2840; found, m/z 855.2802.

A suspension of the diol thus obtained (70.6 mg, 84.8 µmol) in CH₂Cl₂ (2.0 ml) was stirred with PhI(OAc)$_2$ (141 mg, 437.8 µmol) and TEMPO (19.9 mg,
127.4 μmol) at room temperature for 10 min. The mixture was poured into H₂O (40 ml) and the aqueous layer was extracted with AcOEt (30 ml× 3). The combined organic layer was washed with brine (30 ml), dried over MgSO₄, and then concentrated in vacuo to give corresponding C6-aldehyde ii-11 (70.6 mg, 99%). Since this sample gradually decomposed, it was immediately used for the next step. After crude ii-11 had been dissolved in a mixture of 2-methyl-2-propanol (10 ml) and 2-methyl-2-butene (23.8 mg, 339.4 μmol), sodium dihydrogenphosphate dehydrate (79.4 mg, 508.9 μmol) and sodium chlorite (30.7 mg, 339.5 μmol) were successively added at room temperature. The mixture was stirred for 5 min at room temperature, poured into H₂O (40 ml), and the aqueous layer was extracted with AcOEt (30 ml× 3). The combined organic layer was washed with brine (30 ml), dried over MgSO₄ and then concentrated in vacuo. After diluting with THF (2.0 ml), an ethereal solution of diazomethane was added until the yellow color did not disappear. After concentrating in vacuo, silica gel column chromatography (AcOEt:hexane = 40:60) of the residue gave ii-12 (58.2 mg, 80%) as an oil. [α]D 23 + 92.7 (c 0.74, CHCl₃); IR (film) cm⁻¹: 3455, 2935, 1730, 1510, 1250, 1095, 1030, 710; ¹H NMR (400 MHz, CDCl₃) δ 3.41, 3.48, 3.64 (each s, 3H, OCH₃), 3.75 (dd, 1H, J = 3.2, 9.9 Hz, C2'H), 3.76, 3.80 (each s, 3H, OCH₃), 4.04 (dd, 1H, J = 3.3, 9.9 Hz, C3'H), 4.33 (ddd, 1H, J = 1.1, 1.6, 3.3 Hz, C4'H), 4.58, 4.62 (each d, 1H, J = 12.0 Hz, ArCH₂O), 4.62, 4.68 (each d, 1H, J = 10.9 Hz, ArCH₂O), 4.68 (brs, 1H, C5'H), 4.73 (dd, 1H, J = 1.2, 1.6 Hz, C5'H), 4.82 (brd, 1H, J = 2.7 Hz, C4H), 4.94 (d, 1H, J = 3.2 Hz, C1'H), 5.33 (d, 1H, J = 3.5 Hz, C1'H), 5.61 (dd, 1H, J = 3.5, 10.9 Hz, C2'H), 5.71 (dd, 1H, J = 2.7, 10.9 Hz, C3'H), 6.80 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.89 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.22-7.28 (m, 4H, aromatic protons), 7.32-7.37 (m, 4H, aromatic protons), 7.49
(m, 2H, aromatic protons), 7.93-7.97 (m, 4H, aromatic protons), $^{13}$C NMR (100 MHz, CDCl$_3$) δ 49.66, 52.00, 52.44, 55.21, 56.19 (each OCH$_3$), 68.44 (C2), 68.60 (C4'), 69.72 (C5), 69.95 (C3), 70.82 (C5'), 72.49, 73.18 (each ArCH$_2$O), 74.20 (C2'), 76.40 (C3'), 77.21 (C4), 97.85 (C1), 99.69 (C1'), 113.74, 113.89, 128.38, 128.48, 128.96, 129.20, 129.61, 129.69, 129.76, 129.98, 129.98, 130.25, 133.25, 133.31, 159.24, 159.39 (aromatic carbons), 165.88, 166.01 (each ArC=O), 167.92, 168.63 (each C=O); FABMS (% rel. int.) m/z: 883 (44, [M+Na]$^+$), 121 (100, [CH$_3$OPhCH$_2$]$^+$), 105 (96, [PhCO]$^+$); FAB-HRMS: calcd. for C$_{45}$H$_{48}$O$_{17}$Na [M+Na]$^+$, 883.2789; found, m/z 883.2816.

4.8. 2,3-di-O-(4-methoxyphenylmethyl)-4,6-O-methoxyphenylmethylidene-α-D-galactopyranosyl-(1→4)-{methyl[2,3-di-O-(4-methoxyphenylmethyl)-α-D-galactopyranosid]uronate}-(1→4)-{methyl(methyl 2,3-di-O-benzoyl-α-D-galactopyranosid)uronate} (ii-13)

A 0.16 M solution of triethylsilyl trifluoromethanesulfonate in CH$_2$Cl$_2$ (10 μl) was added at 0 °C to a suspension of a mixture of ii-12 (14.0 mg, 16.3 μmol), ii-9 (33.3 mg, 48.8 μmol), and powdered 4A molecular sieves (20 mg) in Et$_2$O (1.0 ml). After stirring for 10 min, triethylamine (10 μl) was added to quench the reaction. The mixture was filtered through a cotton pad, and the filtrate was concentrated in vacuo. Purification of the residue by silica gel column chromatography (benzene:AcOEt = 80:20) gave ii-13 (22.0 mg, 99%) as an oil. [α]$_D^{22}$ +69.7 (c 1.15, CHCl$_3$); IR (film) cm$^{-1}$: 2935, 1730, 1610, 1515, 1250, 1095, 1030, 825, 720; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.93 (s, 3H, OCH$_3$), 3.40 (dd, 1H, $J = 1.5, 12.6$ Hz, C6"HH), 3.49 (s, 3H, OCH$_3$), 3.57 (dd, 1H, $J = 1.7, 12.6$ Hz, C6"HH), 3.63 (brdd, 1H, $J = 1.5, 1.7$ Hz, C5"H), 3.70 (dd, 1H, $J = 3.3, 10.2$ Hz, C3"H), 3.74, 3.75, 3.76, 3.76, 3.76, 3.79 (each s, 3H, OCH$_3$), 3.83 (dd,
1H, J = 3.3, 10.3 Hz, C2’H), 3.86 (dd, 1H, J = 3.2, 10.2 Hz, C2”H), 3.89 (brd, 1H, J = 3.3 Hz, C4”H), 4.01 (dd, 1H, J = 2.3, 10.3 Hz, C3’H), 4.37 (brd, 1H, J = 2.3 Hz, C4’H), 4.50 (d, 1H, J = 12.0 Hz, ArCHHO), 4.51 (d, 1H, J = 12.4 Hz, ArCHHO), 4.52 (s, 2H, ArCH2O), 4.56 (d, 1H, J = 12.0 Hz, ArCHHO), 4.61 (brs, 1H, C5’H), 4.63, 4.67 (each d, 1H, J = 11.4 Hz, ArCH2O), 4.69 (brs, 1H, C5H), 4.75 (d, 1H, J = 12.4 Hz, ArCHHO), 4.90 (d, 1H, J = 3.2 Hz, C1’”H), 4.94 (brd, 1H, J = 2.4 Hz, C4H), 5.13 (d, 1H, J = 3.3 Hz, C1’H), 5.24 (s, 1H, ArCH), 5.34 (d, 1H, J = 2.9 Hz, C1H), 5.67 (dd, 1H, J = 2.9, 11.0 Hz, C2H), 5.71 (dd, 1H, J = 2.4, 11.0 Hz, C3H), 6.76-6.88 (m, 10H, aromatic protons), 7.18 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.25-7.37 (m, 12H, aromatic protons), 7.48 (m, 2H, aromatic protons), 7.88 (brdd, 2H, J = 1.3, 8.3 Hz, aromatic protons), 7.94 (brdd, 2H, J = 1.4, 8.6 Hz, aromatic protons); 13C NMR (100 MHz, CDCl3) δ 51.52, 52.52, 55.13, 55.18, 55.18, 55.21, 55.23, 56.16 (each OCH3), 62.85 (C5”), 68.35 (C3), 69.12 (C6”), 69.57 (C5), 70.16 (C2), 71.23, 71.33, 72.30 (each ArCH2O), 72.63 (C5’), 72.78 (ArCH2O), 73.00 (C2”), 74.11 (C2’), 74.48 (C4”), 75.74 (C3”), 76.14 (C4), 76.20 (C3’), 76.33 (C4’), 97.80 (C1), 98.82 (C1’), 99.78 (C1”), 100.59 (ArC(OR)2), 113.30, 113.45, 113.51, 113.53, 113.72, 127.61, 128.37, 128.49, 128.96, 129.00, 129.16, 129.16, 129.61, 129.72, 129.80, 129.90, 130.39, 130.40, 130.70, 130.83, 131.05, 133.24, 133.30, 158.86, 159.95, 159.07, 159.09, 159.84 (aromatic carbons), 165.87, 165.87 (each ArC=O), 167.88, 168.06 (each C=O); FABMS (% rel. int.) m/z: 1403 (4.2, [M+Na]+), 121 (100, [CH3OPhCH2]+), 105 (82, [PhCO]+); FAB-HRMS: calcd. for C75H80O25Na [M+Na]+, 1403.4886; found, m/z 1403.4907.

4.9. Methyl[2,3-di-O-(4-methoxyphenylmethyl)-α-D-galactopyranosid]
uronate-(1→4)-[methyl|2,3-di-O-(4-methoxyphenylmethyl)|α-D-galactopyranosid|uronate)-(1→4)-[methyl(methyl 2,3-di-O-benzoyl-α-D-galactopyranosid|uronate] (ii-14)

A solution of ii-13 (21.1 mg, 15.4 mmol) in 90% aqueous acetic acid solution (1.0 ml) was stirred at 50 °C for 20 min. After cooling, the mixture was concentrated in vacuo. Silica gel column chromatography of the residue (AcOEt:hexane = 70:30) gave the corresponding diol (15.4 mg, 79%) as an oil. 

[α]D23 +75.0 (c 0.84, CHCl3); IR (film) cm−1: 3450, 2935, 1730, 1510, 1250, 1095, 1030, 710; 1H NMR (400 MHz, CDCl3) δ 2.33 (brd, 1H, J = 8.9 Hz, C6"OH), 2.51 (brs, 1H, C4"OH), 3.04 (s, 3H, OCH3), 3.48 (m, 1H, C6"HH), 3.49 (s, 3H, OCH3), 3.57-3.65 (m, 3H, C6"HH, C2"H, C3"H), 3.70, 3.73, 3.75, 3.76, 3.79 (each s, 3H, OCH3), 3.83 (dd, 1H, J = 3.3, 10.3 Hz, C2'H), 3.87-3.90 (m, 2H, C4"H, C5"H), 4.03 (dd, 1H, J = 2.5, 10.3 Hz, C3'H), 4.27 (dd, 1H, J = 0.9, 2.5 Hz, C4'H), 4.43 (d, 1H, J = 12.1 Hz, ArCHHO), 4.45 (d, 1H, J = 10.6 Hz, ArCHHO), 4.51 (d, 1H, J = 12.1 Hz, ArCHHO), 4.53 (d, 1H, J = 10.6 Hz, ArCHHO), 4.59 (d, 1H, J = 12.1 Hz, ArCHHO), 4.65 (d, 1H, J = 0.9 Hz, C5'H), 4.65, 4.68 (each d, 1H, J = 12.1 Hz, ArCH2O), 4.68 (brs, 1H, C5H), 4.70 (d, 1H, J = 12.1 Hz, ArCHHO), 4.81 (brs, 1H, C1”H), 4.91 (brd, 1H, J = 2.1 Hz, C4H), 5.06 (d, 1H, J = 3.3 Hz, C1’H), 5.35 (d, 1H, J = 2.8 Hz, C1H), 5.66 (dd, 1H, J = 2.8, 10.9 Hz, C2H), 5.70 (dd, 1H, J = 2.1, 10.9 Hz, C3H), 6.78-6.81 (m, 4H, aromatic protons), 6.81-6.89 (m, 4H, aromatic protons), 7.18-7.21 (m, 4H, aromatic protons), 7.26-7.36 (m, 8H, aromatic protons), 7.48 (m, 2H, aromatic protons), 7.88 (brdd, 2H, J = 1.3, 8.3 Hz, aromatic protons), 7.95 (brdd, 2H, J = 1.3, 8.3 Hz, aromatic protons); 13C NMR (100 MHz, CDCl3) δ 51.68, 52.54, 55.12, 55.21, 55.21, 55.25, 56.19 (each OCH3), 62.96 (C6"), 68.39 (C3), 69.09 (C4”), 69.61 (C5), 69.70 (C5”), 70.23 (C2), 71.37 (C5’), 72.20, 72.57, 72.63,
73.01 (each ArCH₂O) 73.79 (C2'), 74.82 (C2" or 3'”), 76.18 (C3'), 76.53 (C4), 77.20 (C2" or 3'”), 77.81 (C4'), 97.82 (C1), 99.21 (C1”), 99.25 (C1'), 113.61, 113.61, 113.79, 113.82, 128.38, 128.46, 129.00, 129.20, 129.36, 129.56, 129.69, 129.69, 129.74, 129.88, 130.13, 130.28, 130.56, 130.59, 133.22, 133.31, 159.07, 159.09, 159.25, 159.28 (aromatic carbons), 165.86, 165.94 (each ArC=O), 167.99, 168.02 (each C=O); FABMS (% rel. int.) m/z: 1285 (0.6, [M+Na]+), 121 (100, [CH₃OPhCH₂]+); FAB-HRMS: calcd. for C₆₇H₇₄O₂₄Na [M+Na]+, 1285.4468; found, m/z 1285.4490.

A suspension of the product (20.0 mg, 15.8 µmol) in CH₂Cl₂ (1.0 ml) was stirred with PhI(OAc)₂ (26.2 mg, 81.3 µmol) and TEMPO (1.2 mg, 7.7 µmol) at room temperature for 30 min. The mixture was poured into H₂O (20 ml) and the aqueous layer was extracted with AcOEt (15 ml × 3). The combined organic layer was washed with brine (15 ml), dried over MgSO₄, and then concentrated in vacuo. After diluting with a mixture of 2-methyl-2-propanol (0.5 ml) and 2-methyl-2-butene (4.4 mg, 63.0 µmol), sodium dihydrogen phosphate dehydrate (14.8 mg, 94.9 µmol) and sodium chlorite (5.7 mg, 63.0 µmol) were successively added at room temperature. After stirring for 30 min, the mixture was poured into H₂O (20 ml) and the aqueous layer was extracted with AcOEt (15 ml × 3). The combined organic layer was washed with brine (15 ml), dried over MgSO₄, and then concentrated in vacuo. After diluting with THF (1.0 ml), an ethereal solution of diazomethane was added until the yellow color did not disappear. After concentrating in vacuo, silica gel column chromatography (AcOEt:hexane = 40:60) of the residue gave ii-14 (14.0 mg, 68%) as an oil. [α]D²3 +67.2 (c 0.75, CHCl₃); IR (film) cm⁻¹: 3450, 2935, 1730, 1510, 1250, 1100, 1030, 820, 715; ¹H NMR (400 MHz, CDCl₃) δ 2.92, 3.49 (each s, 3H, OCH₃), 3.54 (dd, 1H, J = 3.2, 10.0 Hz, C3''H), 3.59 (s, 3H, OCH₃), 3.62 (d, 1H,
\[ J = 3.0, 10.0 \text{ Hz, C2''H}, 3.70, 3.74, 3.74, 3.79, 3.80 \text{ (each s, 3H, OCH}_3) , 3.28 \text{ (dd, 1H, } J = 3.3, 10.5 \text{ Hz, C2'H)}, 4.03 \text{ (dd, 1H, } J = 2.2, 10.5 \text{ Hz, C3''H)}, 4.23 \text{ (brd, 1H, } J = 3.2 \text{ Hz, C4''H)}, 4.25 \text{ (brd, 1H, } J = 2.2 \text{ Hz, C4'H}), 4.39 \text{ (d, 1H, } J = 12.3 \text{ Hz, ArCH}_2\text{O}), 4.43 \text{ (s, 2H, ArCH}_2\text{O)}, 4.52 \text{ (d, 1H, } J = 12.3 \text{ Hz, ArCH}_2\text{O)}, 4.55 \text{ (brs, 1H, C5'H)}, 4.57 \text{ (d, 1H, } J = 11.8 \text{ Hz, ArCH}_2\text{O}), 4.62 \text{ (d, 1H, } J = 12.7 \text{ Hz, ArCH}_2\text{O}), 4.68 \text{ (brs, 1H, C5'H)}, 4.73 \text{ (d, 1H, } J = 11.8 \text{ Hz, ArCH}_2\text{O}), 4.80 \text{ (d, 1H, } J = 12.7 \text{ Hz, ArCH}_2\text{O}), 4.85 \text{ (brs, 1H, C5''H)}, 4.88 \text{ (d, 1H, } J = 3.3 \text{ Hz, C1''H}), 4.91 \text{ (brd, 1H, } J = 2.3 \text{ Hz, C4'H}), 5.05 \text{ (d, 1H, } J = 3.3 \text{ Hz, C1'H}), 5.35 \text{ (d, 1H, } J = 3.0 \text{ Hz, C1'H}), 5.67 \text{ (dd, 1H, } J = 3.0, 11.0 \text{ Hz, C2'H}), 5.71 \text{ (dd, 1H, } J = 2.3, 11.0 \text{ Hz, C3'H}), 6.72 \text{ (brd, 2H, } J = 8.4 \text{ Hz, aromatic protons)}, 6.83-6.90 \text{ (m, 6H, aromatic protons)}, 7.11 \text{ (brd, 2H, } J = 8.5 \text{ Hz, aromatic protons)}, 7.19 \text{ (brd, 2H, } J = 8.5 \text{ Hz, aromatic protons)}, 7.24-7.38 \text{ (m, 8H, aromatic protons)}, 7.48 \text{ (m, 2H, aromatic protons)}, 7.81 \text{ (brd, 2H, } J = 7.5 \text{ Hz, aromatic protons)}, 7.94 \text{ (brd, 2H, } J = 7.5 \text{ Hz, aromatic protons)}; ^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 51.49, 52.08, 52.59, 55.07, 55.17, 55.20, 55.24, 56.19 \text{ (each OCH}_3), 68.27 \text{ (C4'''}, 68.36 \text{ (C3)}, 69.47 \text{ (C5)}, 70.08 \text{ (C2)}, 70.42 \text{ (C5'')}, 71.08 \text{ (C5'''}, 71.82 \text{ (C2''), 71.94, 72.16, 72.61, 72.63 \text{ (each ArCH}_2\text{O)}, 72.96 \text{ (C2''}, 75.74 \text{ (C4)}, 75.87 \text{ (C3'''}, 77.21 \text{ (C3''}, 77.21 \text{ (C4''}, 97.79 \text{ (C1)}, 98.64 \text{ (C1''), 99.20 \text{ (C1''}, 113.58, 113.68, 113.70, 113.79, 128.39, 128.52, 128.95, 129.18, 129.35, 129.47, 129.54, 129.69, 129.72, 129.87, 130.03, 130.14, 130.26, 130.34, 133.27, 133.31, 159.01, 159.01, 159.15, 159.29 \text{ (aromatic carbons)}, 165.75, 165.82 \text{ (each ArC=O)}, 167.76, 168.09, 168.47 \text{ (each C=O); FABMS (% rel. int.) } m/z: 1313 \text{ (8.4, [M+Na]'^{+})}, 121 \text{ (100, [CH}_3\text{OPhCH}_2{]}'), 105 \text{ (76, [PhCO]'^{+}); FAB-HRMS: calcd. for C}_{68}\text{H}_{74}\text{O}_{25}\text{Na [M+Na]'^{+}}, 1313.4417; \text{ found, } m/z 1313.4409.\]

4.10. Methyl \( \alpha\)-D-galactopyranuronosyl-(1→4)-\( \alpha\)-D-galactopyranuronosyl
(1→4)-α-D-galactopyranosiduronic acid (ii-3)

A suspension of ii-14 (26.4 mg, 20.4 μmol) in a mixture of CH₂Cl₂ (1.0 ml) and H₂O (0.1 ml) was vigorously stirred with DDQ (23.2 mg, 102.2 μmol) at room temperature for 6 h. After concentrating, silica gel column chromatography (acetone:CH₂Cl₂ = 80:20) of the residue gave the MPM deprotected pentaol (14.9 mg, 90%) as an oil. [α]_D^{23} +32.4 (c 0.59, CH₃OH); IR (film) 3420, 2925, 1730, 1580, 1450, 1275, 1105, 1020, 715 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ 3.12, 3.50 (each s, 3H, OCH₃), 3.59 (dd, 1H, J = 3.8, 10.3 Hz, C2”H), 3.66 (dd, 1H, J = 3.8, 10.7 Hz, C2’H), 3.68 (dd, 1H, J = 3.4, 10.3 Hz, C3”H), 3.73, 3.84 (each s, 3H, OCH₃), 4.02 (dd, 1H, J = 2.9, 10.7 Hz, C4’H), 4.74 (d, 1H, J = 3.8 Hz, C1’”H), 4.76 (brs, 1H, C5’H), 4.84 (brs, 1H, C5H), 4.91 (brd, 1H, J = 3.0 Hz, C4H), 5.02 (d, 1H, J = 3.8, C1’H), 5.05 (d, 1H, J = 1.4 Hz, C5’”H), 5.27 (d, 1H, J = 3.5 Hz, C1H), 5.58 (dd, 1H, J = 3, 11.0 Hz, C3H), 5.68 (dd, 1H, J = 3.5, 11.0 Hz, C2H), 7.34 (m, 4H, aromatic protons), 7.52 (m, 2H, aromatic protons), 7.84 (brd, 2H, J = 7.4 Hz, aromatic protons), 7.90 (brd, 2H, J = 7.1 Hz, aromatic protons); ¹³C NMR (100 MHz, CD₃OD) δ 52.47, 52.59, 53.19, 56.55 (each OCH₃), 69.33 (C2’), 69.40 (C2), 69.40 (C3’), 69.62 (C2”), 70.70 (C3”), 70.97 (C5), 71.81 (C4”), 71.91 (C3), 72.48 (C5’), 72.81 (C5”), 79.00 (C4), 80.50 (C4’), 99.20 (C1), 102.18 (C1’”), 102.92 (C1’), 129.63, 129.81, 130.35, 130.48, 130.65, 130.79, 134.65, 134.71 (aromatic carbons), 167.32, 167.40 (each ArC=O), 169.84, 170.02, 171.67 (each C=O); FABMS (% rel. int.) m/z: 833 (50, [M+Na]⁺), 121 (86, [PhCOO]⁺), 105 (100, [PhCO]⁺); FAB-HRMS: calcd. for C₃₆H₄₂O₂₁Na [M+Na]⁺ 833.2038; found, m/z 833.2101. The product (10.3 mg, 12.7 μmol) was stirred in a mixture of THF (1.0 ml) and a 0.3% NaOH aqueous solution (1.5 ml) at room temperature for 30 min. The
mixture was passed through an ion-exchange column (DOWEX 50W, H\(^+\) form). Lyophilization of the eluent gave ii-3 (7.0 mg, 98%) as an amorphous powder. \([\alpha]_D^{24} +107.7\) (c 1.25, H\(_2\)O); \(^1\)H NMR (400 MHz, D\(_2\)O) \(\delta\) 3.25 (s, 3H, OCH\(_3\)), 3.56 (dd, 1H, \(J = 3.9, 10.3\) Hz, C2\(''\)H), 3.60 (dd, 1H, \(J = 3.9, 10.7\) Hz, C2\('\)H), 3.67 (dd, 1H, \(J = 3.8, 10.6\) Hz, C2\(\)H), 3.76 (dd, 1H, \(J = 3.4, 10.3\) Hz, C3\(''\)H), 3.82 (dd, 1H, \(J = 3.1, 10.6\) Hz, C3\(\)H) 3.87 (dd, 1H, \(J = 3.0, 10.7\) Hz, C3\(')\)H), 4.16 (dd, 1H, \(J = 1.4, 3.4\) Hz, C4\(''\)H), 4.29 (brd, 1H, \(J = 3.0\) Hz, C4\(')\)H), 4.30 (dd, 1H, \(J = 0.7, 3.1\) Hz, C4\(\)H), 4.47 (d, 1H, \(J = 0.7\) Hz, C5\(\)H), 4.77 (d, 1H, \(J = 3.8\) Hz, C1\(\)H), 4.88 (d, 1H, \(J = 3.9\) Hz, C1\(''\)H), 4.91 (d, 1H, \(J = 1.4\) Hz, C5\(''\)H), 4.93 (brs, 1H, C5\(')\)H), 4.94 (d, 1H, \(J = 3.9\) Hz, C1\(')\)H); \(^13\)C NMR (100 MHz, D\(_2\)O) \(\delta\) 58.22 (OCH\(_3\)), 70.15 (C2), 70.35 (C2\(''\)), 70.37 (C2\(')\), 70.57 (C3\(\)'), 70.63 (C3), 71.24 (C3\(''\)), 72.03 (C5), 72.48 (C4\(''\)), 72.72 (C5\(')\), 73.45 (C5\(''\)), 80.69 (C4), 80.96 (C4\(')\), 102.12 (C1), 102.46 (C1\(''\)), 102.59 (C1\(')\), 174.51, 174.72, 175.35 (each C=O); negative-FABMS (%, rel. int.) \(m/z\): 599 (4.5, [M-H]), 148 (100, [C\(_9\)H\(_{18}\)O\(_5\)]) negative-FAB-HRMS: calcd. for C\(_{19}\)H\(_{27}\)O\(_{19}\) [M-H], 559.1147; found, \(m/z\) 559.1169.

4.11. Methyl 2,3-di-O-acetyl-\(\alpha\)-D-glcopyranoside (ii-16)

A solution of methyl 4,6-O-(4-methoxybenzylidene)-\(\alpha\)-D-glucopyranoside (ii-15) (5.3 g, 17.0 mmol) in a mixture of acetic anhydride (10 ml) and pyridine (15 ml) was stirred at room temperature. After 1 h, the reaction mixture was poured into 5% aqueous NaHCO\(_3\) solution (200 ml), and the aqueous layer was extracted with AcOEt (150 ml \(\times\) 3). The combined organic layer was washed with brine (100 ml), dried over MgSO\(_4\), and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (AcOEt:hexane = 25:75) gave methyl
2,3-di-O-acetyl-4,6-O-(4-methoxybenzylidene)-α-D-glucopyranoside (6.6 g, 98%) as an oil. [α]_D^{22} +57.7 (c 1.63, CHCl_3); IR (film) cm^{-1}: 2940, 1750, 1615, 1520, 1370, 1240, 1060, 1030; ^1H NMR (500 MHz, CDCl_3) δ 2.05, 2.09 (each s, 3H, CH_3CO), 3.41 (s, 3H, OCH_3), 3.63 (t, 1H, J = 9.7 Hz, C4H), 3.75 (t, 1H, J = 9.7 Hz, C6H), 3.80 (s, 3H, OCH_3), 3.91 (ddd, 1H, J = 4.9, 9.7, 10.3 Hz, C5H), 4.28 (dd, 1H, J = 4.9, 10.3 Hz, C6H), 4.90 (dd, 1H, J = 3.8, 9.7 Hz, C2H), 4.93 (d, 1H, J = 3.8 Hz, C1H), 5.46 (s, 1H, ArCH), 5.57 (t, 1H, J = 9.7 Hz, C3H), 6.87 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.37 (brd, 2H, J = 8.6 Hz, aromatic protons); ^13C NMR (125 MHz, CDCl_3) δ 20.73, 20.84 (each CO), 55.21, 55.31 (each OCH_3), 62.31 (C5), 68.75 (C6), 68.96 (C3), 71.58 (C2), 79.13 (C4), 97.57 (C1), 101.52 (ArC), 113.55, 127.46, 129.40, 160.08 (aromatic carbons), 169.77, 170.40 (each C=O); ESIMS (% rel. int.) m/z: 419 (21, [M+Na]^+), 397 (100, [M+H]^+); ESI-HRMS: calcd. for C_{19}H_{25}O_9 [M+H]^+ 397.1499; found, m/z 397.1482.

A solution of the product (6.6 g, 16.7 mmol) in 90% aqueous acetic acid solution (100 ml) was stirred at 60 °C for 20 min. After cooling, the mixture was concentrated in vacuo. Silica gel column chromatography of the residue (AcOEt:hexane = 80:20) gave ii-16 (4.46 g, 96%) as an oil. [α]_D^{22} +105 (c 1.65, CHCl_3); IR (film) 3475, 2920, 1740, 1370, 1240, 1050, 920 cm^{-1}; ^1H NMR (500 MHz, CDCl_3) δ 2.09, 2.10 (each s, 3H, CH_3CO), 2.58 (br, 1H, C6OH), 3.41 (s, 3H, OCH_3), 3.71 (m, 2H, C4H, C5H), 3.87 (m, 2H, C6H2), 4.82 (dd, 1H, J = 3.6, 10.1 Hz, C2H), 4.91 (d, 1H, J = 3.6 Hz, C1H), 5.31 (m, 1H, C3H); ^13C NMR (125 MHz, CDCl_3) δ 20.73, 20.84 (each CH_3CO), 55.21 (OCH_3), 61.78 (C6), 69.46 (C5), 70.82 (C2), 71.17 (C4), 73.11 (C3), 96.78 (C1), 170.41, 171.67 (C=O); ESIMS (% rel. int.) m/z: 301 (15, [M+Na]^+), 279 (4.5, [M+H]^+), 247 (100, [M-CH_3O]^+); ESI-HRMS: calcd. for C_{11}H_{18}O_8Na [M+Na]^+ 301.0899;
found, \textit{m/z} 301.0910.

4.12. Methyl (methyl 2,3-di-\textit{O}-acetyl-\textalpha-\text{-D-glucopyranosid})uronate (ii-17)

A suspension of \textit{ii}-16 (2.76 g, 9.92 mmol) in a mixture of CH$_2$Cl$_2$ (20 ml) and H$_2$O (10 ml) was stirred with PhI(OAc)$_2$ (6.4 g, 19.9 mmol) and TEMPO (0.46 g, 0.83 mmol) at room temperature for 10 min. Aqueous 10\% Na$_2$S$_2$O$_3$ solution (5.0 ml) was added and the mixture was poured into H$_2$O (100 ml), the aqueous layer was extracted with AcOEt (100 ml x 3). The combined extract was washed with brine (100 ml), dried over MgSO$_4$, and then concentrated \textit{in vacuo}. To the residue in THF (10 ml) was added ethereal diazomethane until the yellow color did not disappear. After concentration \textit{in vacuo}, silica gel column chromatography (AcOEt:hexane = 50:50) of the residue gave \textit{ii}-17 (2.76 g, 91\%) as an oil. [$\alpha$]$_D^{22}$ +108 (c 1.70, CHCl$_3$); IR (film) 3485, 2940, 1745, 1440, 1375, 1240, 1050, 895 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.08, 2.10 (each s, 3H, CH$_3$CO), 3.46 (s, 3H, OCH$_3$), 3.85 (s, 3H, COOCH$_3$), 3.91 (t, 1H, $J$ = 9.6 Hz, C4H), 4.22 (d, 1H, $J$ = 9.6 Hz, C5H), 4.86 (dd, 1H, $J$ = 3.7, 10.2 Hz, C2H), 5.00 (d, 1H, $J$ = 3.7 Hz, C1H), 5.38 (dd, 1H, $J$ = 9.6, 10.2 Hz, C3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.69, 20.81 (each CH$_3$CO), 55.88 (COOCH$_3$), 55.80 (OCH$_3$), 70.11 (C5), 70.32 (C2), 70.55 (C4), 71.55 (C3), 97.20 (C1), 170.20, 170.21, 170.85 (C=O); ESIMS (% rel. int.) m/z 329.0874 (18, calcd. for C$_{12}$H$_{18}$NaO$_9$ [M+Na]$^+$: 329.0849), 307.1056 (0.4, calcd. for C$_{12}$H$_{19}$O$_9$ [M+H]$^+$: 307.1029), 275.0790 (100, calcd. for C$_{11}$H$_{15}$O$_8$ [M-CH$_3$O]$^+$: 572.2860).

4.13. Methyl (methyl 2,3-di-\textit{O}-acetyl-4-\textit{O}-trifluoromethanesulfonyl-\textalpha-\text{-D-glucopyranosid})uronate (ii-18)
Trifluoromethanesulfonic anhydride (1.36 g, 4.82 mmol) was added to a mixture of ii-17 (739 mg, 2.41 mmol) and pyridine (953 mg, 12.0 mmol) in CH₂Cl₂ (10 ml) at 0 °C. After 10 min, the mixture was poured into H₂O (50 ml), and the aqueous layer was extracted with EtOAc (50 ml x 3). The combined organic layer was washed with brine (50 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 20:80) to give ii-18 (994 mg, 94 %) as an oil. [α]D23 +91.6 (c 1.00, CHCl₃); IR(film) 1760, 1420, 1375, 1210, 1140, 1070, 950, 840 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.07, 2.09 (each s, 3H, CH₃CO), 3.47 (s, 3H, OCH₃), 3.84 (s, 3H, COOCH₃), 4.47 (d, 1H, J = 10.0 Hz, C5H), 4.89 (dd, 1H, J = 3.5, 10.0 Hz, C2H), 5.03 (t, 1H, J = 10.0 Hz, C4H), 5.03 (d, 1H, J = 3.5 Hz, C1H), 5.67 (t, 1H, J = 10.0 Hz, C3H); ¹³C NMR (100 MHz, CDCl₃) δ 20.39, 20.50 (each CH₃CO), 53.17 (COOCH₃), 56.27 (OCH₃), 67.92 (C5), 68.08 (C3), 70.48 (C2), 80.12 (C4), 97.05 (C1), 116.55, 119.72 (each CF₃), 166.66, 169.23, 1169.83 (C=O). This sample was immediately used for the next step.

4.14. 2,3,4,6-tetra-O-acetyl-1-acetyltio-α-D-galactopyranose (ii-21)

A solution of 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl bromide (ii-19) (167 mg, 0.41 mmol) in DMPU (4.0 ml) was stirred with tetrabutylammonium chloride (339 mg, 1.22 mmol) at room temperature. After 30 min, potassium thioacetate (232 mg, 2.03 mmol) was added to the mixture. After the mixture was stirred for 5 h, the mixture was poured into poured into H₂O (50 ml), and the aqueous layer was extracted with EtOAc (50 ml x 3). The combined organic layer was washed with H₂O (50 ml x 2), and brine (50 ml), dried over MgSO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 22:78) to give 3:10 mixture of α-isomer:
β-isomer of ii-21 (117 mg, 71%) as an oil. These were successfully separated by medium-pressured column chromatography (MeOH:H₂O = 50:50) to provide ii-21 (89 mg, 54%). [α]D²⁴ +143 (c 1.15, CHCl₃); IR (film) 1750, 1710, 1370, 1220, 1070 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.00, 2.0, 2.03, 2.15 (each s, 3H, CH₃CO₂), 2.42 (s, 3H, CH₃COS), 4.06 (dd, 1H, J = 6.8, 11.1 Hz, C6HH), 4.11 (dd, 1H, J = 6.3, 11.1 Hz, C6HH), 4.17 (dddd, 1H, J = 1.0, 6.3, 6.8 Hz, C5H), 5.04 (dd, 1H, J = 3.3, 10.9 Hz, C3H), 5.44 (dd, 1H, J = 1.0, 3.3 Hz, C4H), 5.48 (dd, 1H, J = 5.5, 10.9 Hz, C2H), 6.27 (d, 1H, J = 5.5 Hz, C1H); ¹³C NMR (100 MHz, CDCl₃) δ 20.56 (CH₃CO₂ × 2), 20.60, 20.62 (each CH₃CO₂), 31.49 (CH₃COS), 61.12 (C6), 66.35 (C2), 67.24 (C4), 68.85 (C3), 70.27 (C5), 81.13 (Cl), 169.57, 169.87, 170.09, 170.29 (C=O), 191.70 (SC=O); ESIMS (% rel. int.) m/z 429.0834 (100, calcd. for C₁₆H₂₂NaO₁₀S [M+Na]⁺: 429.0831.

4.15. 2,3,4,6-tetra-O-acetyl-1-thio-α-D-galactopyranose (ii-22)

A solution of ii-21 (160 mg, 0.39 mmol) in MeOH (3.0 ml) was stirred with sodium methoxide (22 mg, 0.41 mmol) at -15 ºC for 30 min. The mixture was poured into aqueous HCl solution (5.0×10⁻³ M, 20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (20 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 20:80) to give ii-22 (121 mg, 85%). [α]D²⁴ +132 (c 0.94, CHCl₃); IR (film) 1745, 1375, 1220, 1090, 1060 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.83 (d, 1H, J = 5.0 Hz, SH), 2.01, 2.06, 2.09, 2.15 (each s, 3H, CH₃CO₂), 4.06 (dd, 1H, J = 6.8, 11.3 Hz, C6HH), 4.14 (dd, 1H, J = 6.4, 11.3 Hz, C6HH), 4.62 (dddd, 1H, J = 1.1, 6.4, 6.8 Hz, C5H), 5.24 (dd, 1H, J = 3.0, 10.7 Hz, C3H), 5.28 (dd, 1H, J = 5.0, 10.7 Hz, C2H), 5.47 (dd, 1H, J = 1.1, 3.0 Hz, C4H), 6.02 (d, 1H, J = 5.0 Hz,
\[ ^{13}C \text{NMR (100 MHz, CDCl}_3) \delta 20.59, 20.60, 20.67, 20.75 \text{ (each CH}_3\text{CO}_2), 61.43 (C6), 67.14 (C5), 67.46 (C3), 67.52 (C2), 67.70 (C4), 77.77 (C1), 169.87, 169.93, 170.08, 170.39 (C=O); \] 

This sample was immediately used for the next step.

4.16. 3-oxo-ethyl 2,3,4,6-tetra-O-acetyl-1-thio-\(\alpha\)-D-galactopyranoside(ii-23) A solution of ii-22 (128 mg, 0.35 mmol) in DMF (2.0 ml) was stirred with acrolein (23.5 mg, 0.42 mmol) at room temperature for 2.5 h. The mixture was poured into H\(_2\)O (20 ml), and the aqueous layer was extracted with EtOAc (20 ml x 3). The combined organic layer was washed with H\(_2\)O (30 ml x 2), and brine (20 ml), dried over MgSO\(_4\) and concentrated in vacuo to give the crude thiol ii-23, which was immediately used for the next step without purification. 

\[ ^1\text{H-NMR (400 MHz, CDCl}_3) \delta 1.99, 2.06, 2.07, 2.15 \text{ (each s, 3H, CH}_3\text{CO}_2), 2.82 (4H, SCH}_2\text{CH}_2), 4.12 (d, 2H, } J = 6.5 \text{ Hz, C6H}_2\text{Hx 2), 4.55 (dt, 1H, } J = 1.1, 6.5 \text{ Hz, C5H), 5.19 (dd, 1H, } J = 3.3, 10.8 \text{ Hz, C3H), 5.27 (dd, 1H, } J = 5.5, 10.8 \text{ Hz, C2H), 5.45 (dd, 1H, } J = 1.1, 3.3 \text{ Hz, C4H), 5.76 (d, 1H, } J = 5.5 \text{ Hz, C1H), 9.77 (s, 1H, CHO).} \]

4.17. 3-cyano-3-\(O\)-tert-butyldimethylsilylpropyl 2,3,4,6-tetra-O-acetyl-1-thio-\(\alpha\)-D-galactopyranoside (ii-24) Potassium cyanide (6.8 mg, 0.1 mmol) was added to a mixture of ii-23 and tert-butyldimethylsilyl cyanide (59 mg, 0.4 mmol) in CH\(_3\)CN (2.0 ml) at 0 °C. After 20 min, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 20:80) to give ii-24 (181 mg, 91%). \([\alpha]_D^{24} +128 \text{ (c 1.54, CHCl}_3\); IR (film) 2930, 1750, 1370, 1220, 1115, 1080, 1055, 840 cm\(^{-1}\); \(^1\text{H NMR (400 MHz, CDCl}_3) \delta 0.16 \text{ (s, 3H, SiCH}_3), \]

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0.21 (each s, 3H × 0.5, SiCH₃), 0.92 (s, 9H, SiC(CH₃)₃), 2.00 (s, 3H, CH₃CO), 2.06, 2.07, 2.08, 2.08 (each s, 3H × 0.5, CH₃CO), 2.10 (2H, SCH₂CH₂), 2.15 (s, 3H, CH₃CO), 2.70 (m, 2H, SCH₂CH₂), 4.10 (2H, C₆H₄), 4.52-4.60 (2H, C₅H, SCH₂CH₂CH), 5.19, 5.20 (each dd, 1H × 0.5, J = 3.2, 10.9 Hz, C₃H), 5.27, 5.28 (each dd, 1H × 0.5, J = 5.5, 10.9 Hz, C₂H), 5.45 (dd, 1H, J = 1.2, 3.2 Hz, C₄H), 5.73, 5.74 (each d, 1H × 0.5, J = 5.5 Hz, C₁H); ¹³C NMR (100 MHz, CDCl₃) δ -5.37, -5.17 (each Si(CH₃)₂), 18.02 (Si(CH₃)₂), 18.02 (Si(CH₃)₂), 20.69, 20.71 (each Si(CH₃)₂), 20.77 (CH₃CO), 24.37, 25.19 (each SCH₂ × 0.5), 25.49 (SiC(CH₃)₃), 35.87, 35.97 (each SCH₂CH₂ × 0.5), 60.27 (SCH₂CH₂CH), 61.73, 61.85 (each C₆ × 0.5), 66.81, 66.83 (each C₅ × 0.5), 67.79, 67.83 (each C₄ × 0.5), 67.87 (C₂), 68.03, 68.06 (each C₃ × 0.5), 81.98, 82.89 (each C₁ × 0.5), 119.41, 119.45 (each CN × 0.5), 169.83 (C=O), 170.08 (C=O × 2), 170.36, 170.41 (each C=O × 0.5); ESIMS (% rel. int.) m/z 584.1975 (100, calcd. for C₂₄H₃₉NO₁₀SSiNa [M+Na]+: 584.1962), 562.2160 (30, calcd. for C₂₄H₄₀NO₁₀SSi [M+H]+: 562.2142).

4.18. 3-cyano-3-O-tert-butyldimethylsilylpropyl 2,3-di-O-acetyl-4,6-O-(4-methoxyphenylmethylidene)-1-thio-α-D-galactopyranoside (ii-25)

A solution of ii-24 (176 mg, 0.31 mmol) in MeOH (3.0 ml) was stirred with sodium methoxide (17 mg, 0.31 mmol) at room temperature for 20 min. After dilution with H₂O (50 ml), the mixture was passed through an ion-exchange column (DOWEX 50W, H⁺ form). Concentration of the eluent gave the corresponding crude tetraol (115 mg, 97%). [α]D₂⁰ +198 (c 0.98, CHCl₃); IR (film) 3400, 2930, 1255, 1105, 1055, 840, 780 cm⁻¹; ¹H NMR (400 MHz, CD₃OD), δ 0.17, 0.18, 0.21, 0.21 (each s, 3H × 0.5, SiCH₃), 0.93 (s, 9H, SiC(CH₃)₃), 2.08-2.16 (2H, SCH₂CH₂), 2.59-2.82 (2H, SCH₂CH₂), 3.57, 3.60
(each dd, 1H x 0.5, J = 3.3, 10.5 Hz, C3H), 3.72 (d, 2H, J = 6.1 Hz, C6H2), 3.90, 3.90 (each dd, 1H x 0.5, J = 1.5, 3.3 Hz, C4H), 4.08, 4.09 (each dd, 1H x 0.5, J = 5.6, 10.5 Hz, C2H), 4.14 (dt, 1H, J = 1.5, 6.1 Hz, C5H), 4.79 (dd, 1H x 0.5, J = 6.1, 7.0 Hz, SCH2CH2CH), 4.83 (t, 1H x 0.5, J = 6.4 Hz, SCH2CH2CH), 5.376, 5.381 (each d, 1H x 0.5, J = 5.6 Hz, ClH); 13C NMR (100 MHz, CD3OD) δ -4.64, -4.61 (each Si(CH3)2), 19.38 (SiC), 25.68 (SCH2 x 0.5), 26.52 (SiC(CH3)3), 27.09 (SCH2 x 0.5), 37.58, 37.92 (each SCH2CH2 x 0.5), 62.10, 62.32 (each SCH2CH2CH x 0.5), 63.07, 63.09 (each C6 x 0.5), 70.08, 70.14 (each C2 x 0.5), 71.32, 71.33 (each C4 x 0.5), 72.65, 72.71 (each C3 x 0.5), 73.43, 73.67 (each C5 x 0.5), 87.23, 88.83 (each Cl x 0.5), 121.68, 121.75 (each CN x 0.5); ESIMS (% rel. int.) m/z 416.1547 (42, calcd. for C16H31NO6SSiNa [M+Na]+: 416.1539), 394.1727 (100, calcd. for C16H32NO6SSi [M+H]+: 394.1720).

A solution of the tetraol (27.8 mg, 73.2 µmol) in DMF (1.5 ml) was stirred with p-anisaldehyde dimethylacetal (26.7 mg, 52.2 µmol) in the presence of camphorsulfonic acid (0.2 mg, 0.9 µmol) at room temperature for 30 min. Triethylamine (50 µl) were added in order to neutralize. The mixture was poured into H2O (20 ml) and the aqueous layer was extracted with EtOAc (15 ml x3). The combined organic solution was washed with H2O (20 ml) and brine (15 ml), dried over MgSO4 and concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 46:54) gave 3-cyano-3-O-tert-butylidimethylsilylpropyl,6-O-(4-methoxyphenylmethylidene)-1-thio-α-D-galactopyranoside (25.4 mg, 68%) as an oil. [α]D23 +98.8 (c 1.47, CHCl3); IR (film) 3430, 2930, 1615, 1520, 1250, 1095, 1065, 1035, 835, 780 cm−1; 1H NMR (500 MHz, CD3OD), δ 0.02, 0.03, 0.12, 0.14 (each s, 3H x 0.5, SiCH3), 0.876, 0.882 (each s, 9H x 0.5, SiCH3), 1.79-1.96 (2H, SCH2CH2), 2.46-2.59 (2H,
SCH₂CH₂, 2.63, 2.69 (each d, 1H × 0.5, J = 8.8 Hz, C3OH), 2.72, 2.83 (each d, 1H × 0.5, J = 3.2 Hz, C2OH), 3.29, 3.30 (each s, 3H × 0.5, OCH₃), 3.45, 3.48 (each dd, 1H × 0.5, J = 1.8, 10.4 Hz, C6HH), 3.52-3.56 (each 1H × 0.5, C5H), 3.68-3.73 (2H, C3H, C4H), 4.04, 4.06 (each dd, 1H × 0.5, J = 1.4, 10.4 Hz, C6HH), 4.19 (1H, C2H), 4.32 (dd, 1H × 0.5, J = 5.5, 7.3 Hz, SCH₂CH₂CH), 4.38 (dd, 1H × 0.5, J = 4.7, 8.0 Hz, SCH₂CH₂CH), 5.231, 5.235 (each s, 1H × 0.5, ArCH), 5.29, 5.32 (each d, 1H × 0.5, J = 5.3 Hz, C1H), 6.86, 6.87 (each brd, 2H × 0.5, J = 8.7 Hz, aromatic protons), 7.55, 7.57 (each brd, 2H × 0.5, J = 8.7 Hz, aromatic protons); ¹³C NMR (125 MHz, C₆D₆) δ -5.39, -5.38, -5.16, -5.131 (each SiCH₃ × 0.5), 18.10 (SiC), 25.17 (SCH₂ × 0.5), 25.59, 25.61 (each SiC(CH₃)₃ × 0.5), 25.94 (SCH₂ × 0.5), 36.12, 36.44 (each SCH₂CH₂ × 0.5), 54.81, 54.82 (each OCH₃ × 0.5), 60.40, 60.78 (each SCH₂CH₂CH × 0.5), 63.90, 63.94 (each C5 × 0.5), 69.13, 69.15 (each C6 × 0.5), 69.23, 69.33 (each C2 × 0.5), 70.68, 70.74 (each C3 × 0.5), 75.86, 75.90 (each C4 × 0.5), 85.99, 86.95 (each C1 × 0.5), 101.31, 101.33 (each ArC × 0.5), 113.87, 113.90 (each aromatic carbon × 0.5), 119.79, 120.03 (each CN × 0.5), 128.29, 131.17 (aromatic carbons), 160.70, 160.72 (each aromatic carbon × 0.5); ESIMS (% rel. int.) m/z 534.1986 (86, calcd. for C₂₄H₃₇NO₇SSiNa [M+Na]⁺: 534.1958), 512.2166 (100, calcd. for C₂₄H₃₈NO₇SSi [M+H]⁺: 512.2138).

A mixture of the diol (614 mg, 1.2 mmol) in a mixture of pyridine (5.0 mL) and acetic anhydride (5.0 ml) at room temperature for 3 hours. The mixture was poured into saturated aqueous NaHCO₃ solution (50 ml) and the aqueous layer was extracted with EtOAc (70 ml × 3). The combined organic layer was washed with brine (70 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 22:78) to give ii-25 (660 mg, 93%). [α]D 24 +146 (c 0.92, CHCl₃); IR (film) 2930,
1745, 1370, 1250, 1220, 1090, 1055, 1040, 835, 780 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)), \(\delta\) 0.149, 0.152, 0.20, 0.21 (each s, 3H \times 0.5, SiCH\(_3\)), 0.91 (s, 9H, SiC(CH\(_3\))\(_3\)), 2.07, 2.08 (each s, 3H \times 0.5, CH\(_3\)CO), 2.09 (s, 3H, CH\(_3\)CO), 2.00-2.17 (2H, SCH\(_2\)CH\(_2\)), 2.63-2.77 (2H, SCH\(_2\)CH\(_2\)), 3.81 (s, 3H, OCH\(_3\)), 4.08 (2H, C5H, C6HH), 4.22 (dd, 1H, \(J = 1.5, 12.6\) Hz, C6HH), 4.46 (t, 1H, \(J = 3.5\) Hz, C4H), 4.55 (dd, 1H \times 0.5, \(J = 5.0, 7.6\) Hz, SCH\(_2\)CH\(_2\)CH), 4.58 (dd, 1H \times 0.5, \(J = 5.6, 7.1\) Hz, SCH\(_2\)CH\(_2\)CH), 5.17, 5.18 (each dd, 1H \times 0.5, \(J = 5.6, 10.9\) Hz, C3H), 5.47, 5.48 (each dd, 1H \times 0.5, \(J = 5.6, 10.9\) Hz, C2H), 5.487, 5.490 (each s, 1H \times 0.5, ArCH), 5.83, 5.84 (each d, 1H \times 0.5, \(J = 5.6\) Hz, C1H), 6.90 (brd, 2H, \(J = 8.8\) Hz, aromatic protons), 7.43 (brd, 2H, \(J = 8.8\) Hz, aromatic protons);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) -5.39 (SiCH\(_3\)), -5.20, -5.17 (each SiCH\(_3\) \times 0.5), 17.99 (SiC), 20.79, 20.92 (each CH\(_3\)CO), 24.62, 25.19 (each SCH\(_2\) \times 0.5), 25.46 (SiC(CH\(_3\))\(_3\)), 35.77, 35.79 (each SCH\(_2\)CH\(_2\) \times 0.5), 55.27 (OCH\(_3\)), 60.20, 60.36 (each SCH\(_2\)CH\(_2\)CH \times 0.5), 62.62, 62.63 (each C5 \times 0.5), 67.74 (C2), 69.00 (C3), 69.03, 69.06 (each C6 \times 0.5), 73.56 (C4), 82.30, 82.87 (each C1 \times 0.5), 100.89 (ArC), 113.54 (aromatic carbon), 119.44 (CN), 127.50, 129.91, 160.13 (aromatic carbons), 169.90 (C=O), 170.51, 170.53 (each C=O \times 0.5); ESIMS (% rel. int.) \(m/z\) 618.2196 (100, calcd. for C\(_{28}\)H\(_{41}\)NO\(_9\)SSiNa [M+Na]\(^+\): 618.2169), 596.2378 (79, calcd. for C\(_{28}\)H\(_{42}\)NO\(_9\)S [M+H]\(^+\): 596.2350).

4.19. 2,3-di-O-acetyl-4,6-O-methoxyphenylmethylidene-1-thio-\(\alpha\)-D-galactopyranosyl-(1\(\rightarrow\)4)-[methyl(methyl 2,3-di-O-acetyl-\(\alpha\)-D-galactopyranosid) uronate] (ii-26)

A solution of ii-25 (248 mg, 0.43 mg) in THF (2.0 ml) was added at room temperature to a suspension of a mixture of tetrabutylammonium fluoride 1M THF solution (0.64 ml) and powdered 4A molecular sieves (100 mg) in THF
(1.0 ml). After 5 min, a solution of ii-18 (277 mg, 0.63 mg) in THF (2.0 ml) was added to the mixture. After 10 min, the mixture was poured into saturated aqueous NH₄Cl solution (50 ml) and the aqueous layer was extracted with EtOAc (50 ml × 3). The combined organic layer was washed with brine (70 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 46:54) to give ii-26 (276 mg, 95%). [α]D²⁴ +198 (c 1.12, CHCl₃); IR (film) 2940, 1745, 1375, 1220, 1070, 1030 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.05, 2.08, 2.09, 2.11 (each s, 3H, CH₃CO), 3.42 (s, 3H, C1OCH₃), 3.80, 3.81 (each s, 3H, OCH₃), 3.89 (dd, 1H, J = 1.6, 4.5 Hz, C4H), 4.05 (dd, 1H, J = 1.6, 12.5 Hz, C6'HH), 4.14 (dd, 1H, J = 1.4, 12.5 Hz, C6'HH), 4.20 (1H, C5'H), 4.48 (dd, 1H, J = 0.7, 3.4 Hz, C4'H), 4.77 (d, 1H, J = 1.6 Hz, C5H), 4.94 (dd, 1H, J = 3.7, 10.9 Hz, C2H), 5.10 (d, 1H, J = 3.7 Hz, C1H), 5.15 (dd, 1H, J = 3.4, 11.0 Hz, C3'H), 5.40 (dd, 1H, J = 5.5, 11.0 Hz, C2'H), 5.48 (s, 1H, ArCH), 5.52 (dd, 1H, J = 4.5, 10.9 Hz, C3H), 5.72 (d, 1H, J = 5.5 Hz, C1'H), 6.89 (brd, 1H, J = 8.9 Hz, aromatic protons), 7.42 (brd, 1H, J = 8.9 Hz, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 20.68, 20.74, 20.81, 20.90 (each CH₃CO), 47.99 (C4), 52.55, 55.27, 56.08 (each OCH₃), 62.65 (C5'), 67.45 (C2'), 68.24 (C3), 68.65 (C3'), 68.93 (C6'), 69.14 (C2), 69.66 (C5), 73.41 (C4'), 83.91 (C1'), 97.31 (C1), 100.82 (ArC), 113.55, 127.43, 129.74, 160.15 (each aromatic carbons), 167.54, 169.30, 169.92, 170.30, 170.45 (each C=O); ESIMS (% rel. int.) m/z 709.1780 (100, calcd. for C₃₀H₃₈O₁₆SNa [M+Na]⁺: 709.1778), 687.1960 (39, calcd. for C₃₀H₃₉O₁₆S [M+H]⁺: 687.1959).

4.20. 2,3-di-O-acetyl-1-thio-α-D-galactopyranosyl-(1→4)-[methyl (methyl 2,3-di-O-acetyl-α-D-galactopyranosid)uronate (ii-29)
A solution of ii-26 (270 mg, 0.4 mmol) in 90% aqueous acetic acid solution (10 ml) was stirred at 60 °C for 20 min. After cooling, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt:hexane = 20:80) to give ii-29 (206 mg, 90%) as an oil. 

$[\alpha]_D^{24} +271 \,(c\,1.14,\,CHCl_3);\text{IR (film) cm}^{-1}: 3505\,\text{1745, 1370, 1220, 1070, 915, 730;}^1\text{H NMR (500 MHz, CDCl}_3)\delta 2.08, 2.10, 2.11, 2.13\,(\text{s, 3H, CH}_3\text{CO}), 3.42\,(\text{s, 3H, C1OCH}_3), 3.81\,(\text{s, 3H, CO}_2\text{CH}_3), 3.81-3.90\,(2\text{H, C6}'\text{H}_2), 3.91\,(\text{dd, 1H, } J = 1.7, 4.7\text{ Hz, C4H}), 4.29\,(2\text{H, C4}'\text{H, C5}'\text{H}), 4.77\,(\text{d, 1H, } J = 1.7\text{ Hz, C5H}), 4.93\,(\text{dd, 1H, } J = 3.7, 10.8\text{ Hz, C2H}), 5.10\,(\text{d, 1H, } J = 3.7\text{ Hz, C1H}), 5.15\,(\text{dd, 1H, } J = 2.7, 10.8\text{ Hz, C3}'\text{H}), 5.32\,(\text{dd, 1H, } J = 5.6, 10.8\text{ Hz, C2}'\text{H}), 5.54\,(\text{dd, 1H, } J = 4.7, 10.8\text{ Hz, C3H}), 5.65\,(\text{d, 1H, } J = 5.6\text{ Hz, C1}'\text{H});^{13}\text{C NMR (125 MHz, CDCl}_3)\delta 20.67, 20.76, 20.90, 21.02\,(\text{each CH}_3\text{CO}), 47.07\,(C4), 52.61\,(\text{CO}_2\text{CH}_3), 56.10\,(\text{OCH}_3), 62.61\,(C6') , 67.79\,(C3), 67.85\,(C2'), 68.82\,(C4'), 69.13\,(C2), 69.58\,(C5), 69.62\,(C5'), 70.05\,(C3'), 83.03\,(C1'), 97.33\,(C1), 167.89, 169.89, 169.97, 170.24, 170.46\,(\text{each C=O});\text{ESIMS (%, rel. int.) m/z 591.1373 (100, calcd. for C}_{22}\text{H}_{32}\text{O}_{15}\text{SNa [M+Na]}^+: 591.1360), 586.1819 (26, calcd. for C}_{22}\text{H}_{36}\text{NO}_{15}\text{S [M+NH}_4]^+: 586.1806).
vacuo. To the residue in THF (2.0 ml) was added ethereal diazomethane until the yellow color did not disappear. After concentration in vacuo, silica gel column chromatography (Acetone:CH₂Cl₂ = 10:90) of the residue gave ii-30 (95.7 mg, 67%) as an oil. [α]D²⁴ +186 (c 0.62, CHCl₃); IR (film) 3485, 2955, 1745, 1375, 1220, 1070, 1025 cm⁻¹;¹H NMR (400 MHz, CDCl₃) δ 1.96, 2.06, 2.10, 2.12 (each s, 3H, CH₃CO), 2.37 (d, 1H, J = 4.6 Hz, C4'OH), 3.42 (s, 3H, C1OCH₃), 3.79, 3.80 (each s, 3H, CO₂CH₃), 3.87 (dd, 1H, J = 1.6, 4.4 Hz, C4H), 4.53 (1H, C4'H), 4.76 (d, 1H, J = 1.6 Hz, C5'H), 4.89 (dd, 1H, J = 3.8, 10.9 Hz, C2H), 5.01 (d, 1H, J = 1.4 Hz, C5'H), 5.10 (d, 1H, J = 3.8 Hz, C1H), 5.17 (dd, 1H, J = 3.0, 10.8 Hz, C3'H), 5.30 (dd, 1H, J = 5.5, 10.8 Hz, C2'H), 5.58 (dd, 1H, J = 4.4, 10.9 Hz, C3H), 5.72 (d, 1H, J = 5.5 Hz, C1'H);¹³C NMR (100 MHz, CDCl₃) δ 20.34, 20.64, 20.67, 20.78 (each CH₃CO), 48.57 (C4), 52.50, 52.59 (each CO₂CH₃), 56.13 (OCH₃), 67.24 (C2'), 67.54 (C3), 68.37 (C4'), 69.38 (C3'), 69.48 (C2), 69.78 (C5), 70.51 (C5'), 83.66 (C1'), 97.36 (C1), 167.55, 168.41, 169.44, 169.55, 169.93, 170.22 (each C=O); ESIMS (% rel. int.) m/z 619.1323 (100, calcd. for C₂₃H₃₂O₁₆SNa [M+Na]⁺: 619.1309), 614.1767 (26, calcd. for C₂₃H₃₆NO₁₆S [M+NH₄]⁺: 614.1755).

4.22. Phenyl 2,3,4-tri-O-(4-methoxyphenylmethyl)-1-thio-6-O-triphenylmethyl-β-D-galactopyranoside (ii-31)

A solution of phenyl-1-thio-β-D-galactopyranoside (ii-7) (2.0g, 7.34 mmol) in pyridine (10 mL) was stirred with triphenylchloromethane at 100°C for 30 min. The mixture was poured into H₂O (100 ml), and the aqueous layer was extracted with EtOAc (70 ml × 3). The combined organic layer was washed with brine (100 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane =
70:30) to give phenyl 1-thio-6-\(\beta\)-D-galactopyranoside (3.68 g, 97\%) as an oil. \([\alpha]_D^{23} -11.2 (c 1.212, \text{CHCl}_3)\); IR (film) 3425, 2925, 1445, 1090, 1060, 1030, 910, 740, 705 cm\(^{-1}\); \(^1\)H NMR (400 MHz, \text{CDCl}_3) \(\delta 2.86 (d, 1H, J = 4.6 \text{ Hz}, \text{C4OH}), 3.20 (d, 1H, J = 2.5 \text{ Hz}, \text{C2OH}), 3.32 (dd, 1H, J = 7.2, 12.7 \text{ Hz}, \text{C6HH}), 3.43-3.53 (4H, \text{C3OH}, \text{C6HH}, \text{C3H}, \text{C5H}), 3.66 (dt, 1H, J = 2.5, 9.7 \text{ Hz}, \text{C2H}), 3.88 (brt, 1H, J = 4.6 \text{ Hz}, \text{C4H}), 4.51 (d, 1H, J = 9.7 \text{ Hz}, \text{C1H}), 7.18-7.28 (12H, aromatic protons), 7.44 (16H, aromatic protons), 7.58 (2H, aromatic protons); \(^{13}\)C NMR (100 MHz, \text{CDCl}_3) \(\delta 63.55 (\text{C6}), 69.63 (\text{C4}), 69.93 (\text{C2}), 74.84 (\text{C3}), 77.62 (\text{C5}), 87.05 (\text{CPh}_3), 88.55 (\text{C1}), 127.11, 127.72, 127.90, 128.63, 128.93, 132.11, 132.80, 143.64 (each aromatic carbons); ESIMS (% rel. int.) \(m/z: 537 (70, [\text{M+Na}]^+)\), 243 (100, [\text{CPh}_3]^{+}); ESI-HRMS: calcd. for C\(_{31}\)H\(_{30}\)O\(_5\)SNa [M+Na]\(^+\), 537.1712; found, \(m/z\) 537.1740.

Sodium hydride (washed with hexane, 1.2 g, 50 mmol) slowly was added to a DMF solution (40 ml) of the triol (4.4 g, 8.5 mmol) at room temperature. Upon the addition of the substrate, H\(_2\) gas was bubbled. After stirring for 10 min, to the mixture was added 4-methoxybenzyl bromide (14.6 g, 72.6 mmol) at 0 °C. After stirring at 0 °C for 10 min, the cooling bath was removed and the mixture was stirred at room temperature for 1 h. Methanol (4.0 ml) and \(\text{Et}_3\text{N}\) (2.0 ml) were successively added to decompose excess reagent. After stirring for additional 30 min, the mixture was poured into H\(_2\)O (200 ml), and the aqueous layer was extracted with \(\text{EtOAc}\) (150 ml \(\times\) 3). The combined organic layer was washed successively with H\(_2\)O (300 ml), and brine (200 ml), dried over MgSO\(_4\), and then concentrated \textit{in vacuo}. The residue was purified by silica gel column chromatography (\(\text{EtOAc}:\text{hexane} = 16:84\)) to give \textit{ii-31} (5.3 g, 72\%) as an oil., \([\alpha]_D^{23} +28.7 (c 0.87, \text{CHCl}_3)\); IR (film) 2930, 1610, 1510, 1250, 1085, 1030, 820, 745, 705 cm\(^{-1}\); \(^1\)H NMR (400 MHz, \text{CDCl}_3) \(\delta 3.15 (dd, 1H, J = 6.3, 9.7 \text{ Hz}, \text{C1H}), 7.18-7.28 (12H, aromatic protons), 7.44 (16H, aromatic protons), 7.58 (2H, aromatic protons); \(^{13}\)C NMR (100 MHz, \text{CDCl}_3) \(\delta 63.55 (\text{C6}), 69.63 (\text{C4}), 69.93 (\text{C2}), 74.84 (\text{C3}), 77.62 (\text{C5}), 87.05 (\text{CPh}_3), 88.55 (\text{C1}), 127.11, 127.72, 127.90, 128.63, 128.93, 132.11, 132.80, 143.64 (each aromatic carbons); ESIMS (% rel. int.) \(m/z: 537 (70, [\text{M+Na}]^+)\), 243 (100, [\text{CPh}_3]^{+}); ESI-HRMS: calcd. for C\(_{31}\)H\(_{30}\)O\(_5\)SNa [M+Na]\(^+\), 537.1712; found, \(m/z\) 537.1740.
C6HH) 3.29 (brt, 1H, J = 6.3 Hz, C5H), 3.47 (dd, 1H, J = 2.8, 9.4 Hz, C3H), 3.55 (dd, 1H, J = 6.3, 9.7 Hz, C6HH), 3.78 (s, 6H, OCH3 x 2), 3.79 (s, 3H, OCH3), 3.79 (brd, 1H, J = 2.8 Hz, C4H), 3.85 (t, 1H, J = 9.4 Hz, C2H), 4.44 (d, 1H, J = 11.3 Hz, ArCHHO), 4.57 (d, 1H, J = 9.4 Hz, C1H), 4.62 (d, 1H, J = 11.2 Hz, ArCHHO), 4.64 (d, 1H, J = 10.0 Hz, ArCHHO), 4.66 (d, 1H, J = 11.2 Hz, ArCHHO), 4.70 (d, 1H, J = 10.0 Hz, ArCHHO), 4.76 (d, 1H, J = 11.3 Hz, ArCHHO), 6.74 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.85 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.86 (brd, 2H, J = 8.8 Hz, aromatic protons), 7.03 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.14 (3H, aromatic protons), 7.20-7.31 (13H, aromatic protons), 7.39 (6H, aromatic protons), 7.54 (2H, aromatic protons); 
13C NMR (100 MHz, CDCl3) δ 55.24 (OCH3 x 2), 55.26 (OCH3), 63.20 (C6), 72.52 (ArCH2O), 73.56 (C4), 73.67, 75.21 (each ArCH2O), 77.12 (C2), 77.72 (C5), 83.91 (C3), 86.91 (CPh3), 87.74 (C1), 113.44, 113.73, 113.79, 126.69, 126.99, 127.80, 128.64, 128.72, 129.17, 129.38, 129.96, 130.51, 130.60, 130.82, 130.89, 174.68, 143.90, 158.93, 159.21, 159.27 (each aromatic carbons); ESIMS (%, rel. int.) m/z: 897 (100, [M+Na]+), 243 (27, [CPh3]+); ESI-HRMS: calcd. for C55H54O8Na [M+Na]+, 897.3437; found, m/z 897.3427.

4.23. 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-β-D-galactopyranosyl 2,2,2-trichloroacetimidate (ii-32)

A solution of ii-31 (1.85 g, 2.11 mmol) in a mixture of acetone (40 ml) and H2O (4.0 ml) was stirred with NBS (934 mg 5.3 mmol) at 0 °C. After 5 min, 10% Na2S2O3 (4.0 ml) and saturated NaHCO3 aqueous solution (20 ml) were added to the mixture. After concentrating in vacuo, the residue was diluted with AcOEt (150 ml) and then washed with H2O (100 ml). The aqueous layer was extracted with AcOEt (100 ml x 2). Each organic layer was washed with brine.
(100 ml), combined, dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 26:74) to give 2,3,4-tris-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-D-galactopyranose (1.63 g, 99%) as an oil. [α]D23° +31.3 (c 1.08, CHCl₃); IR (film) 3435, 2930, 1610, 1510, 1250, 1080, 1035, 820, 705 cm⁻¹; The ¹H NMR spectrum indicated that the sample consisted of a mixture of anomers (α:β = 80:20 in CDCl₃); ¹H-NMR (400 MHz, CDCl₃) δ 2.86 (d, 1H × 0.8, J = 2.0 Hz, C1OH (α-anomer)), 2.93 (d, 1H × 0.2, J = 7.0 Hz, C1OH (β-anomer)), 3.16 (dd, 1H × 0.8, J = 7.7, 9.0 Hz, C6HH (α-anomer)), 3.26 (dd, 1H × 0.2, J = 7.4, 8.8 Hz, C6HH (β-anomer)), 3.37 (dd, 1H × 0.8, J = 5.7, 9.0 Hz, C6HH (α-anomer)), 3.39 (1H × 0.2, C5H (β-anomer)), 3.45 (1H × 0.2 × 2, C3H (β-anomer), C6HH (β-anomer)), 3.62 (dd, 1H × 0.2, J = 7.0, 9.6 Hz, C2H (β-anomer)), 3.76 (s, 3H × 0.8, OCH₃ (α-anomer)), 3.76 (s, 3H × 0.2, OCH₃ (β-anomer)), 3.77 (s, 3H × 0.8, OCH₃ (α-anomer)), 3.78 (s, 3H × 0.2, OCH₃ (β-anomer)), 3.80 (s, 3H × 0.2, OCH₃ (β-anomer)), 3.80 (s, 3H × 0.8, OCH₃ (α-anomer)), 3.85 (dd, 1H × 0.8, J = 2.6, 10.0 Hz, C3H (α-anomer)), 3.88 (brd, 1H × 0.2, J = 2.5 Hz, C4H (β-anomer)), 3.91 (dd, 1H × 0.8, J = 3.3, 10.0 Hz, C2H (α-anomer)), 3.97 (brd, 1H × 0.8, J = 2.6 Hz, C4H (α-anomer)), 4.10 (brdd, 1H × 0.8, J = 5.7, 7.7 Hz, C5H (α-anomer)), 4.35 (d, 1H × 0.8, J = 10.8 Hz, ArCHHO (α-anomer)), 4.41 (d, 1H × 0.2, J = 10.9 Hz, ArCHHO (β-anomer)), 4.54 (t, 1H × 0.2, J = 7.0 Hz, C1H (β-anomer)), 4.58-4.80 (5H, ArCHHO × 5), 5.15 (dd, 1H × 0.8, J = 2.0, 3.3 Hz, C1H (α-anomer)), 6.69-7.40 (27H, aromatic protons).

A solution of the product (1.63 g, 2.08 mmol) in CH₂Cl₂ (10 ml) was stirred with CCl₃CN (600 mg, 4.2 mmol) in the presence of DBU (32 mg, 0.2 mmol) at -15 °C for 20 min. After concentrating in vacuo, the residue was purified by silica gel column chromatography (AcOEt: hexane = 20:80) to give ii-32 (1.9 g,
99%) as an oil. The $^1$H NMR spectrum indicated that the sample consisted of a mixture of anomers ($\alpha:\beta = 5:1$). The following assignment is only $\alpha$-isomer, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.09 (dd, 1H, $J = 6.5$, 9.2 Hz, C6H), 3.41 (dd, 1H, $J = 6.5$, 9.2 Hz, C6H), 3.76, 3.78, 3.81 (each s, 3H, OCH$_3$), 3.98 (dd, 1H, $J = 2.7$, 10.0 Hz, C3H), 4.03 (brd, 1H, $J = 2.7$ Hz, C4H), 4.12 (dd, 1H, $J = 3.6$, 10.0 Hz, C2H), 4.19 (brt, 1H, $J = 6.5$ Hz, C5H), 4.42 (d, 1H, $J = 10.8$ Hz, ArCHHO), 4.62, 4.66 (each d, 1H, $J = 11.2$ Hz, ArCH$_2$O), 4.67 (d, 1H, $J = 11.5$ Hz, ArCHHO), 4.73 (d, 1H, $J = 10.8$ Hz, ArCHHO), 4.78 (d, 1H, $J = 11.5$ Hz, ArCHHO), 6.45 (d, 1H, $J = 3.6$ Hz, C1H), 6.70 (brd, 2H, $J = 8.7$ Hz, aromatic protons), 6.81 (brd, 2H, $J = 8.7$ Hz, aromatic protons), 6.87 (brd, 2H, $J = 8.7$ Hz, aromatic protons), 6.97 (brd, 2H, $J = 8.6$ Hz, aromatic protons), 7.22-7.41 (19H, aromatic protons), 8.53 (s, 1H, C(=NH)CCl$_3$). This sample gradually decomposed, so it was immediately used for the next step.

4.24. 2,3,4-tri-$O$-(4-methoxyphenylmethyl)-6-$O$-triphenylmethyl-$\alpha$-$D$-galactopyranosyl-(1$\rightarrow$4)-[methyl(2,3-di-$O$-acetyl-1-thio-$\alpha$-$D$-galactopyranosid)uronate]-$(1\rightarrow4)$-[methyl(methyl 2,3-di-$O$-acetyl-$\alpha$-$D$-galactopyranosid)uronate] (ii-36)

A $4.0\times10^{-2}$ M solution of triethylsilyl trifluoromethanesulfonate in CH$_2$Cl$_2$ (0.1 ml) was added at 0 °C to a suspension of a mixture of ii-30 (41.3 mg, 69.2 $\mu$mol), ii-32 (77.0 mg, 83.0 $\mu$mol), and powdered 4A molecular sieves (20 mg) in CH$_2$Cl$_2$ (0.6 ml). After stirring for 10 min, triethylamine (10 $\mu$l) was added to quench the reaction. The mixture was filtered through a cotton pad, and the filtrate was concentrated in vacuo. Purification of the residue by silica gel column chromatography (AcOEt:hexane = 40:60) gave ii-36 (67.6 mg, 72%) as an oil. $[\alpha]_D^{24} +118$ (c 1.25, CHCl$_3$); IR (film) 2920, 1750, 1510, 1240, 1220,
1075, 1040, 750 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.85, 1.97, 2.02, 2.07 (each s, 3H, CH\(_3\)CO), 3.09 (dd, 1H, \(J = 7.4\), 8.5 Hz, C6'HH), 3.34 (dd, 1H, \(J = 5.8\), 8.5 Hz, C6''HH), 3.41, 3.61, 3.76, 3.78 (each s, 3H, OCH\(_3\)), 3.79 (1H, C2'H), 3.81, 3.85 (each s, 3H, OCH\(_3\)), 3.86 (1H, C4H), 3.94-3.97 (2H, C3''H, C4''H), 4.15 (d, 1H, \(J = 10.4\) Hz, ArCHHO), 4.24 (1H, C5''H), 4.53 (3H, C1''H, ArCH\(_2\)O), 4.57 (dd, 1H, \(J = 1.1\), 2.8 Hz, C4'H), 4.61 (d, 1H, \(J = 10.4\) Hz, ArCHHO), 4.64 (d, 1H, \(J = 11.2\) Hz, ArCHHO), 4.73 (d, 1H, \(J = 11.2\) Hz, ArCHHO), 4.75 (d, 1H, \(J = 1.4\) Hz, C5'H), 4.89 (dd, 1H, \(J = 3.9\), 10.8 Hz, C2'H), 5.01 (d, 1H, \(J = 1.1\) Hz, C5'H), 5.11 (d, 1H, \(J = 3.9\) Hz, C1'H), 5.12 (dd, 1H, \(J = 2.8\), 10.8 Hz, C3'H), 5.30 (dd, 1H, \(J = 5.7\), 10.8 Hz, C2'H), 5.58 (dd, 1H, \(J = 4.4\), 10.8 Hz, C3'H), 5.91 (d, 1H, \(J = 5.7\) Hz, C1'H), 6.66 (brd, 2H, \(J = 8.7\) Hz, aromatic protons), 6.79 (brd, 2H, \(J = 8.7\) Hz, aromatic protons), 6.87 (4H, aromatic protons), 7.20-7.38 (19H, aromatic protons); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 20.30, 20.67, 20.79, 20.90 (each CH\(_3\)CO), 48.33 (C4), 52.32, 52.64 (each OCH\(_3\)), 55.20 (OCH\(_3\) \(\times\) 2), 55.26, 56.09 (each OCH\(_3\)), 62.30 (C6''), 67.60 (C3), 67.82 (C2''), 69.59 (C2, C3''), 69.84 (C5), 70.51 (C5''), 71.32 (C5'''), 72.81, 72.99, 74.27 (each ArCH\(_2\)O), 75.32 (C4'''), 76.04 (C4'''), 77.20 (C2'''), 78.30 (C3'''), 83.78 (C1''), 86.63 (CPh\(_3\)), 97.34 (C1), 100.53 (C1'''), 113.34, 113.68, 113.76, 126.94, 127.78, 128.74, 128.88, 129.64, 129.86, 130.52, 130.81, 131.19, 143.80, 158.92, 158.98, 159.20 (each aromatic carbons), 167.50, 167.93, 169.54 (each C=O), 169.93 (each C=O \(\times\) 2), 170.38 (C=O); ESIMS (% rel. int.) \(m/z\) 1383.4660 (100, calcd. for C\(_{72}\)H\(_{80}\)O\(_{24}\)SNa [M+Na\(^+\)]: 1383.4658).

4.25. Methyl[2,3,4-tri-O-(4-methoxyphenylmethyl)-\(\alpha\)-D-galactopyranosid]uronate-(1\(\rightarrow\)4)-[methyl(2,3-di-O-acetyl-1-thio-\(\alpha\)-D-galactopyranosid)uronate]-(1\(\rightarrow\)4)-[methyl(methyl 2,3-di-O-acetyl-\(\alpha\)-D-galactopyranosid)uronate]
A solution of ii-36 (35 mg, 20.6 mmol) in 90% aqueous acetic acid solution (10 ml) was stirred at 60 °C for 20 min. After cooling, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt:hexane = 52:48) to give methyl 2,3,4-tri-O-(4-methoxyphenylmethyl)-α-D-galactopyranosyl-(1→4)-methyl(2,3-di-O-acetyl-1-thio-α-D-galactopyranosid)uronate-(1→4)-methyl(2,3-di-O-acetyl-1-α-D-galactopyranosid)uronate (23 mg, 80%) as an oil. [α]D23 +151 (c 0.96, CHCl3); IR(film) 3490, 2935, 1745, 1510, 1370, 1240, 1220, 1075, 1035, 820 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 1.91 (dd, 1H, J = 3.1, 9.1 Hz, C6"OH), 1.95, 2.01, 2.06, 2.07 (each s, 3H, CH3CO), 3.40 (1H, C6"HH), 3.41, 3.58 (each s, 3H, OCH3), 3.60 (1H, C6"HH), 3.78, 3.79, 3.81, 3.82 (each s, 3H, OCH3), 3.84-3.87 (4H, C4H, C2”H, C3”H, C4’H), 3.97 (brt, 1H, J = 5.6 Hz, C5”H), 4.52 (d, 1H, J = 11.3 Hz, ArCHHO), 4.55-4.63 (4H, C4’H, C1’H, ArCHHO × 2), 4.63 (d, 1H, J = 11.2 Hz, ArCHHO), 4.72 (d, 1H, J = 11.2 Hz, ArCHHO), 4.75 (d, 1H, J = 1.4 Hz, C5H), 4.83 (d, 1H, J = 11.3 Hz, ArCHHO), 4.88 (dd, 1H, J = 3.8, 10.8 Hz, C2H), 5.00 (d, 1H, J = 1.1 Hz, C5’H), 5.06 (dd, 1H, J = 2.5, 11.1 Hz, C3’H), 5.10 (d, 1H, J = 3.8 Hz, C1H), 5.32 (dd, 1H, J = 5.7, 11.1 Hz, C2’H), 5.56 (dd, 1H, J = 4.5, 10.8 Hz, C3H), 5.68 (d, 1H, J = 5.7 Hz, C1’H), 6.83 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.84 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.19 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.27 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.30 (brd, 2H, J = 8.6 Hz, aromatic protons), 13C NMR (100 MHz, CDCl3) δ 20.27, 20.66, 20.68, 20.76 (each CH3CO), 48.87 (C4), 52.35, 52.46 (each OCH3), 55.24 (OCH3 × 2), 55.28, 56.12 (each OCH3), 62.26 (C6”), 67.09 (C2’), 67.56 (C3), 69.47 (C2), 69.70 (C3’), 69.87 (C5), 70.79 (C5’), 72.06 (C5”), 73.19, 73.27, 73.99 (each ArCH2O),
74.51 (C3”), 76.08 (C2”), 76.81 (C4’), 78.56 (C4”), 84.37 (C1’), 97.37 (C1), 100.06 (C1”), 113.78, 113.81, 113.81, 129.10, 129.90, 130.20, 130.20, 130.54, 130.88, 159.15, 159.29, 159.43 (each aromatic carbons), 167.55, 167.74, 169.47, 169.92, 170.12, 170.19 (each C=O); ESIMS (% rel. int. m/z 1141.3545 (100, calcd. for C₅₃H₆₆O₂₄SNa [M+Na]+: 1141.3562), 1136.3983 (11, calcd. for C₅₃H₇₀N₂O₂₄S [M+NH₄]+: 1136.4009).

A suspension of the product (18 mg, 16.1 µmol) in a mixture of CH₂Cl₂ (0.3 ml) and H₂O (0.15 ml) was stirred with PhI(OAc)₂ (26 mg, 80.7 µmol) and TEMPO (1.2 mg, 7.7 µmol) at room temperature for 50 min. Aqueous 10% Na₂S₂O₃ solution (0.1 ml) was added and the mixture was poured into H₂O (20 ml) and the aqueous layer was extracted with AcOEt (20 ml x 3). The combined extract was washed with brine (30 ml), dried over MgSO₄, and then concentrated in vacuo. To the residue in THF (2.0 ml) was added ethereal diazomethane until the yellow color did not disappear. After concentration in vacuo, silica gel column chromatography (AcOEt:hexane = 50:50) of the residue gave ii-37 (18 mg, 98%) as an oil. [α]D²² +139 (c 0.70, CHCl₃); IR (film) 2955, 1750, 1610, 1515, 1370, 1240, 1220, 1070, 1035, 915, 825 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.94, 1.96, 2.06, 2.08 (each s, 3H, CH₃CO), 3.41, 3.581, 3.585, 3.78, 3.79 (each s, 3H, OCH₃), 3.82 (s, 6H, OCH₃×2), 3.85 (dd, 1H, J = 1.5, 4.5 Hz, C4H), 3.99 (2H, C2”H, C3”H), 4.26 (t, 1H, J = 1.6 Hz, C4”H), 4.45 (d, 1H, J = 11.2 Hz, ArCHHO), 4.608 (d, 1H, J = 12.0 Hz, ArCHHO), 4.609 (dd, 1H, J = 1.3, 2.6 Hz, C4’H), 4.63 (d, 1H, J = 1.6 Hz, C5”H), 4.66 (d, 1H, J = 10.9 Hz, ArCHHO), 4.67 (d, 1H, J = 12.0 Hz, ArCHHO), 4.72 (d, 1H, J = 10.9 Hz, ArCHHO), 4.75 (d, 1H, J = 1.5 Hz, C5H), 4.77 (d, 1H, J = 11.2 Hz, ArCHHO), 4.85 (d, 1H, J = 2.3 Hz, C1”H), 4.85 (dd, 1H, J = 3.7, 10.8 Hz, C2H), 4.98 (d, 1H, J = 1.3 Hz, C5’H), 5.10 (d, 1H, J = 3.7
Hz, C1'H), 5.12 (dd, 1H, J = 2.6, 11.2 Hz, C3'H), 5.18 (dd, 1H, J = 5.3, 11.2 Hz, C2'H), 5.59 (dd, 1H, J = 4.5, 10.8 Hz, C3'H), 5.76 (d, 1H, J = 5.3 Hz, C1'H), 6.80 (4H, aromatic protons), 6.88 (brd, 2H, J = 8.8 Hz, aromatic protons), 7.09 (brd, 2H, J = 8.7 Hz, aromatic protons); 13C NMR (100 MHz, CDCl3) δ 20.34, 20.41, 20.65, 20.74 (each CH3CO), 48.26 (C4), 52.03, 52.30, 52.52 (each OCH3), 55.25 (OCH3 × 2), 55.26, 56.11 (each OCH3), 67.41 (C2′), 67.45 (C3), 69.01 (C3′), 69.56 (C2), 69.83 (C5), 70.55 (C5′), 71.86 (C5″), 72.77, 73.26 (each ArCH2O), 74.14 (C2″), 74.25 (ArCH2O), 75.89 (C4″), 77.15 (C4′), 78.11 (C3″), 83.77 (Cl′), 97.33 (Cl), 100.98 (Cl″), 113.50, 113.73, 113.78, 129.02, 129.61, 129.81, 130.33, 130.47, 130.58, 159.12, 159.12, 159.21 (each aromatic carbons), 167.55, 167.64, 169.20, 169.37, 169.88, 169.97, 170.24 (each C=O); ESIMS (% rel. int.) m/z 1169.3497 (100, calcd. for C54H66O25SNa [M+Na]+: 1169.3512), 1164.3949 (27, calcd. for C54H70NO25S [M+NH4]+: 1164.3958).

4.26. Methyl(α-D-galactopyranosid)uronate-(1→4)-[methyl(2,3-di-O-acetyl-1-thio-α-D-galactopyranosid)uronate]-(1→4)-[methyl(methyl 2,3-di-O-acetyl-α-D-galactopyranosid)uronate] (ii-38)

A suspension of ii-37 (8.8 mg, 7.7 μmol) in a mixture of CH2Cl2 (1.0 ml) and H2O (100 μl) was stirred with 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) (10.6 mg, 46.7 mmol) at room temperature for 12 hours. The mixture was poured into water (10 ml) and the aqueous layer was washed with EtOAc (10 ml × 3), and concentrated in vacuo. After dilution with small amount of H2O (ca. 0.3 ml), the resulting solution was loaded on a ODS Sep-Pak® cartridge (5.0 g). After washing with MeOH:H2O = 5:95, elution with MeOH:H2O = 20:80 gave the fraction containing ii-38. After methanol was removed by rotary evaporator,
the resulting aqueous solution was lyophilized to give ii-1 (5.4 mg, 90%) as an oil. \([\alpha]_D^{22} +231 (c 0.50, \text{CH}_3\text{OH}); \text{IR (film)} 3450, 1745, 1370, 1220, 1140, 1075 \text{cm}^{-1}; \{^1\text{H} \text{NMR} (400 \text{MHz}, \text{CD}_3\text{OD}, 30 ^\circ \text{C}) \delta 1.94, 1.95, 2.02, 2.05 \text{(each s, 3H, CH}_3\text{CO)}, 3.40 \text{ (s, 3H, OCH}_3\text{)}, 3.72 \text{ (dd, 1H, } J = 4.0, 10.3 \text{ Hz, C}_2''\text{H)}, 3.75, 3.790, 3.793 \text{ (each s, 3H, CO}_2\text{CH}_3\text{)}, 3.80 \text{ (dd, 1H, } J = 3.3, 10.3 \text{ Hz, C}_3''\text{H)}, 3.90 \text{ (dd, 1H, } J = 1.7, 4.5 \text{ Hz, C}_4\text{H)}, 4.20 \text{ (dd, 1H, } J = 1.7, 3.3 \text{ Hz, C}_4''\text{H)}, 4.60 \text{ (dd, 1H, } J = 3.8, 10.9 \text{ Hz, C}_2\text{H)}, 4.90 \text{ (d, 1H, } J = 1.7 \text{ Hz, C}_5\text{H)}, 4.91 \text{ (d, 1H, } J = 4.0 \text{ Hz, C}_1''\text{H)}, 5.01 \text{ (d, 1H, } J = 3.8 \text{ Hz, C}_1\text{H)}, 5.03 \text{ (d, 1H, } J = 1.2 \text{ Hz, C}_5'\text{H)}, 5.17 \text{ (dd, 1H, } J = 5.2, 11.0 \text{ Hz, C}_2'\text{H)}, 5.23 \text{ (dd, 1H, } J = 2.8, 11.0 \text{ Hz, C}_3'\text{H)}, 5.54 \text{ (dd, 1H, } J = 4.5, 10.9 \text{ Hz, C}_3\text{H)}, 5.73 \text{ (d, 1H, } J = 5.2 \text{ Hz, C}_1''\text{H)}; ^{13}\text{C NMR} (100 \text{ MHz, CD}_3\text{OD}) \delta 20.94, 21.00, 21.08, 21.15 \text{ (each CH}_3\text{CO)}, 50.00 \text{ (C}_4\text{)}, 53.14, 53.56, 53.71, 56.87 \text{ (each OCH}_3\text{)}, 69.60 \text{ (C}_3\text{)}, 69.67 \text{ (C}_2''\text{), 69.72 \text{ (C}_2'\text{), 70.60 \text{ (C}_3'\text{), 70.72 \text{ (C}_3''\text{), 71.20 \text{ (C}_2\text{), 71.56 \text{ (C}_5\text{), 72.38 \text{ (C}_4''\text{), 72.50 \text{ (C}_5'\text{), 73.68 \text{ (C}_5''\text{), 79.27 \text{ (C}_4'\text{), 85.37 \text{ (C}_1'\text{), 99.18 \text{ (C}_1\text{), 104.18 \text{ (C}_1''\text{), 170.14, 170.27, 171.71, 171.87, 172.00, 172.13, 172.16 \text{ (each C=O) ESIMS (rel. int.} m/z 809.1758 \text{ (100, calcd. for C}_{30}\text{H}_{42}\text{O}_{22}\text{SNa [M+Na]}^+ : 809.1786), 804.2201 \text{ (12, calcd. for C}_{30}\text{H}_{46}\text{NO}_{22}\text{S [M+NH}_4]^+: 804.2232).}

4.27. Methyl \(\alpha\)-D-galactopyranuronosyl-(1\→4)-\(\alpha\)-D-galactopyranuronosyl(1\→4)-\(\alpha\)-D-thiogalactopyranosiduronic acid (ii-1)

A solution of ii-38 (5.4 mg, 6.9 \(\mu\)mol) in a mixture of THF (1.0 ml) and 5% NaOH aqueous solution (0.1 ml) was stirred at room temperature for 30 min. After removing THF \textit{in vacuo}, the resulting aqueous solution was passed through an ion-exchange column (DOWEX 50W, H\(^+\) form). Lyophilization of the aqueous layer gave ii-1 (3.9 mg, 99%) as an amorphous powder. \([\alpha]_D^{25} +133\)
(c 0.50, H₂O); ¹H NMR (500 MHz, D₂O) δ 3.27 (s, 3H, OCH₃), 3.43 (dd, 1H, J = 3.9, 10.5 Hz, C₂H), 3.56 (dd, 1H, J = 1.9, 4.6 Hz, C₄H), 3.60 (dd, 1H, J = 4.0, 10.5 Hz, C₂"H), 3.77 (dd, 1H, J = 3.2, 10.6 Hz, C₃'H), 3.79 (dd, 1H, J = 3.3, 10.5 Hz, C₃"H) 3.96 (dd, 1H, J = 5.5, 10.6 Hz, C₂'H), 4.01 (dd, 1H, J = 4.6, 10.5 Hz, C₃H), 4.19 (dd, 1H, J = 1.4, 3.3 Hz, C₄"H), 4.33 (dd, 1H, J = 0.9, 3.2 Hz, C₄'H), 4.72 (d, 1H, J = 1.9 Hz, C₅H), 4.74 (d, 1H, J = 3.9 Hz, C₁H), 4.92(d, 1H, J = 1.4 Hz, C₅"H), 4.93 (d, 1H, J = 4.0 Hz, C₁"H), 5.02 (d, 1H, J = 0.9 Hz, C₅'H), 5.38 (d, 1H, J = 5.5 Hz, C₁'H); ¹³C NMR (125 MHz, D₂O) δ 58.22 (C₄), 63.38 (OCH₃), 75.21 (C₂'), 75.60 (C₃), 75.61 (C₂"), 76.51 (C₃"), 76.65 (C₃'), 77.15 (C₂), 77.74 (C₄' or C₅), 77.78 (C₄' or C₅), 78.02 (C₅'), 78.74 (C₅"), 85.63 (C₄'), 95.14 (C₁'), 107.31 (C₁), 107.80 (C₁"), 179.67, 180.23, 180.62 (each C=O); ESIMS (%), rel. int.) m/z 615.0565 (71, calcd. for C₁₉H₂₈O₁₈SK [M+K]⁺: 615.0633), 599.0876 (100, calcd. for C₁₉H₂₈O₁₈SNa [M+Na]⁺: 599.0894).

4.28. 920-MHz NMR measurements.

Sample solutions for NMR measurements were prepared by dissolving in 99.9% D₂O, the sample pH not being adjusted. Shigemi NMR sample tubes matched with D₂O were used. 920-MHz NMR spectra were measured by a Jeol spectrometer at Institute for Molecular Science, Okazaki, Japan. The sample was not spun, and the spectra were recorded at a temperature of 298 K. The water signal was suppressed by DANTE (Delay Alternating with Nutation for Tailored Exitation) method.⁵¹ One-dimensional ¹H-NMR experiments were performed with a spectral width of 11,510.12891 Hz, 64K data points and 8 scans. Both the two-dimensional ROESY²⁹, ³⁰ and NOESY⁵¹ spectra were recorded in the phase-sensitive mode, with a mixing time of 300 msec. and with
2048 x 512 data points, and were zero-filled to yield 2048 x 2048 data matrices. The two-dimensional \(^{13}\text{C})\text{-}^1\text{H} \text{HSQC}\) spectrum was recorded without \(^{13}\text{C}\) decoupling during the acquisition period and with 2048 x 128 data points. The number of scans for all spectra was 8. Time domain data in both dimensions were multiplied by a sine bell squared function. All 2D NMR spectra were processed by NMRPipe software, and the signals were assigned by Sparky 3 (Goddard, T., and Kneller, D. G., \textit{SPARKY 3}, University of California, San Francisco, CA, USA) run under Windows XP.

4.29. Phenyl 6-\textit{O}-benzoyl-2,3-di-\textit{O}-(4-methoxyphenylmethyl)1-thio-\textit{D}-galactopyranoside (ii-39)

A solution of ii-8 (3.50 g, 5.55 mmol) in 90% aqueous acetic acid solution (100 ml) was stirred at 60 °C for 10 min. After cooling, the mixture was concentrated \textit{in vacuo}. Recrystallization from AcOEt:hexane (40:60) gave phenyl 2,3-di-\textit{O}-(4-methoxyphenylmethyl)-1-thio-\textit{D}-galactopyranoside (2.65 g, 93%) as needles. mp 154 °C; [\(\alpha\)]\textsubscript{D}\textsuperscript{24} +7.5 (c 1.24, CHCl\textsubscript{3}); IR (film) 3435, 2930, 1610, 1510, 1250, 1085, 1035, 820 cm\textsuperscript{-1}; \(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}\textsubscript{3}) \delta 2.14 (br, 1H, C6OH), 2.60 (br, 1H, C4OH), 3.47 (ddd, 1H, \(J = 0.8, 4.2, 6.8 \text{ Hz}, \text{C5H}\)), 3.55 (dd, 1H, \(J = 3.3, 8.9 \text{ Hz}, \text{C3H}\)), 3.71 (t, 1H, \(J = 8.9 \text{ Hz}, \text{C2H}\)), 3.77 (1H, C6HH), 3.80, 3.81 (each s, 3H, OCH\textsubscript{3}), 3.96 (brdd, 1H, \(J = 6.8, 11.8 \text{ Hz}, \text{C6HH}\)), 4.00 (brdd, 1H, \(J = 0.8, 3.3 \text{ Hz}, \text{C4H}\)), 4.63 (d, 1H, \(J = 8.9 \text{ Hz}, \text{C1H}\)), 4.64 (s, 2H, ArCH\textsubscript{2}O), 4.67. 4.75 (each d, 1H, \(J = 10.0 \text{ Hz}, \text{ArCHHO}\)), 6.87 (4H, \textit{aromatic protons}), 7.25-7.34 (7H, \textit{aromatic protons}), 7.55 (2H, \textit{aromatic protons}); \(^{13}\text{C} \text{NMR} (100 \text{ MHz, CDCl}\textsubscript{3}) \delta 55.27, 55.29 (each OCH\textsubscript{3}), 62.77 (C6), 67.41 (C4), 72.00, 75.37 (each ArCH\textsubscript{2}O), 76.69 (C2), 78.02 (C5), 82.06 (C3), 87.59 (C1), 113.80, 113.98, 127.42, 128.93, 129.55, 129.64, 129.89,
130.33, 131.77, 133.71, 159.38, 159.52 (each aromatic carbons); ESIMS (% rel. int.) m/z: 535.1756 (21, calcd. for C_{28}H_{32}O_7SNa [M+Na]^+: 535.1766), 530.2199 (100, calcd. for C_{28}H_{36}NO_7S [M+NH_4]^+: 530.2212).

Benzoyl chloride (829 mg, 5.90 mmol) was added to a mixture of the diol (3.00 g, 5.85 mmol) and pyridine (933 mg, 11.8 mmol) in CH$_2$Cl$_2$ (7.0 ml) at 0 °C and the mixture was stirred at the same temperature for 1 h. The mixture was poured into H$_2$O (100 ml), and the aqueous layer was extracted with EtOAc (70 ml x 3). The combined organic layer was washed with brine (100 ml), dried over MgSO$_4$, and then concentrated in vacuo. Recrystallization from AcOEt:hexane (30:70) gave ii-39 (2.90 g, 80%) as a white amorphous. [α]$_D^{25}$ +1.9 (c 1.14, CHCl$_3$); IR (film) 3500, 2905, 1705, 1510, 1295, 1250, 1120, 1090, 1050, 1030, 810, 715 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.50 (dd, 1H, J = 1.2, 2.4 Hz, C4OH), 3.57 (dd, 1H, J = 3.4, 9.0 Hz, C3H), 3.72 (t, 1H, J = 9.0 Hz, C2H), 3.77 (1H, C5H), 3.79, 3.80 (each s, 3H, OCH$_3$), 4.01 (1H, C4H), 4.56 (dd, 1H, J = 7.7, 10.6 Hz, C6HH), 4.63 (1H, C6HH), 4.63 (d, 1H, J = 9.0 Hz, C1H), 4.64, 4.67 (each d, 1H, J = 11.3 Hz, ArCHH), 4.68, 4.79 (each d, 1H, J = 10.0 Hz, ArCHH), 6.87 (4H, aromatic protons), 7.15 (3H, aromatic protons), 7.26 (brd, 2H, J = 8.8 Hz, aromatic protons), 7.34 (brd, 2H, J = 8.8 Hz, aromatic protons), 7.48 (brt, 3H, J = 7.5 Hz, aromatic protons), 7.53-7.61 (3H, aromatic protons), 8.02 (brdd, 2H, J = 1.3, 8.4 Hz, aromatic protons); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 55.25, 55.28 (each OCH$_3$), 64.01 (C6), 67.02 (C4), 72.20, 75.44 (each ArCH$_2$O), 75.82 (C5), 76.75 (C2), 81.90 (C3), 87.94 (C1), 113.80, 113.98, 127.23, 128.38, 128.77, 129.55, 129.64, 129.74, 129.84, 129.92, 130.30, 131.56, 133.13, 134.13, 159.39, 159.53 (each aromatic carbons); ESIMS (% rel. int.) m/z: 639.2020 (15, calcd. for C$_{35}$H$_{36}$O$_8$SNa [M+Na]$^+$: 639.2029), 634.2464 (100, calcd. for C$_{28}$H$_{40}$NO$_8$S [M+NH$_4$]$^+$: 634.2475).
4.30. Phenyl 2,3,4-tri-\(O\)-(4-methoxyphenylmethyl)-6-\(O\)-triphenylmethyl-\(\alpha\)-\(D\)-galactopyranosyl-(1→4)-6-\(O\)-benzoyl-2,3-di-\(O\)-(4-methoxyphenylmethyl)-1-thio-\(\beta\)-\(D\)-galactopyranoside (ii-40)

Triethylsilyl trifluoromethanesulfonate (85 \(\mu\)g, 0.32 \(\mu\)mol) was added at -20 °C to a suspension of a mixture of ii-39 (1.00 g, 1.62 mmol), ii-32 (3.00 g, 3.24 mmol), and powdered 4A molecular sieves (100 mg) in THF (30 ml). After stirring for 5 min, triethylamine (50 \(\mu\)l) was added to quench the reaction. The mixture was filtered through a cotton pad, and the filtrate was concentrated \textit{in vacuo}. Purification of the residue by silica gel column chromatography (AcOEt:hexane = 20:80) gave ii-40 (2.06 g, 92% (\(\alpha\)-isomer 87%, \(\beta\)-isomer 13%)) as an oil. \([\alpha]_D^{24} +13.2 (c 1.80, \text{CHCl}_3); \text{IR (film)} 2930, 1720, 1610, 1510, 1250, 1170, 1090, 1035, 820, 710 \text{ cm}^{-1}; \text{The } ^1\text{H NMR spectrum indicated that the sample consisted of a mixture of anomers (\(\alpha:\beta = 87:13\)). The following assignment showed major isomer and some minor isomer.} \text{\(^1\text{H NMR (400 MHz, CDCl}_3\)} \text{\(\delta 3.22 \ (t, 1H \times 0.87, J = 8.4 \text{ Hz, C6'HH (\(\alpha\)-isomer)), 3.36 \ (dd, 1H \times 0.87, J = 5.1, 8.4 \text{ Hz, C6'HH (\(\alpha\)-isomer)), 3.39 \ (dd, 1H \times 0.87, J = 2.5, 9.4 \text{ Hz, C3H (\(\alpha\)-isomer)), 3.44 \ (dd, 1H \times 0.13, J = 5.3, 9.2 \text{ Hz, C6'HH (\(\beta\)-isomer)), 3.52 \ (dd, 1H \times 0.13, J = 2.7, 9.3 \text{ Hz, C3H (\(\beta\)-isomer)), 3.63 \ (s, 3H \times 0.87, OCH}_3 \text{ (\(\alpha\)-isomer)), 3.64 \ (1H \times 0.87, C5H (\(\alpha\)-isomer)), 3.709 \ (s, 3H \times 0.13, OCH}_3 \text{ (\(\beta\)-isomer)), 3.713 \ (s, 3H \times 0.87, OCH}_3 \text{ (\(\alpha\)-isomer)), 3.75, 3.77 \ (each s, 3H \times 0.13, OCH}_3 \text{ (\(\beta\)-isomer)), 3.78 \ (s, 6H \times 0.87, OCH}_3 \times 2 \ (\(\alpha\)-isomer)), 3.78 \ (1H \times 0.87, C2H (\(\alpha\)-isomer)), 3.80 \ (s, 3H \times 0.87, OCH}_3 \text{ (\(\alpha\)-isomer)), 3.81 \ (s, 3H \times 0.13, OCH}_3 \text{ (\(\beta\)-isomer)), 3.85 \ (brd, 1H \times 0.87, J = 2.5 \text{ Hz, C4H (\(\alpha\)-isomer)), 4.01 \ (dd, 1H \times 0.87, J = 3.4, 10.2 \text{ Hz, C2'H (\(\alpha\)-isomer)), 4.08 \ (dd, 1H \times 0.87, J = 2.5, 10.2 \text{ Hz, C3'H (\(\alpha\)-isomer))}, 4.23 \ (brd, 1H \times 0.87, J = 2.5 \text{ Hz, C4'H.}}

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(α-isomer)), 4.31 (brd, 1H × 0.13, J = 2.3 Hz, C4H (β-isomer)), 4.37 (d, 1H × 0.87, J = 10.2 Hz, ArCHHO (α-isomer)), 4.38, 4.42 (each d, 1H × 0.87, J = 12.3 Hz, ArCHHO (α-isomer)), 4.46 (brdd, 1H × 0.87, J = 5.1, 8.4 Hz, C5'H (α-isomer)), 4.60 (d, 1H × 0.87, J = 9.7 Hz, C1H (α-isomer)), 4.60-4.72 (5H × 0.87, C6H2 (α-isomer), ArCHHO (α-isomer), ArCH2O (α-isomer)), 4.75 (d, 1H × 0.87, J = 10.2 Hz, ArCHHO (α-isomer)), 4.81 (d, 1H × 0.87, J = 3.4 Hz, C1'H (α-isomer)), 4.94 (d, 1H × 0.13, J = 11.0 Hz, ArCHHO (β-isomer)), 6.66-7.59 (43H, aromatic protons), 7.96 (brdd, 2H × 0.87, J = 1.3, 8.1 Hz, aromatic protons (α-isomer)), 7.99 (brdd, 2H × 0.13, J = 1.3, 8.1 Hz, aromatic protons (β-isomer)); 13C NMR (100 MHz, CDCl3) δ 55.02, 55.12, 55.23, 55.25, 55.28 (each OCH3), 62.16 (C6'), 63.64 (C6), 70.60 (C5'), 71.72, 72.20, 73.51, 74.20, 75.13 (each ArCH2O), 75.15 (C4'), 75.83 (C2', C4), 76.43 (C5), 76.85 (C2), 79.14 (C3'), 81.11 (C3), 86.67 (CPh3), 87.86 (C1), 100.75 (C1'), 113.39, 113.62, 113.67, 113.71, 113.79, 126.99, 127.79, 128.40, 128.76, 128.94, 129.36, 129.51, 129.65, 129.74, 129.97, 130.52, 130.60, 131.01, 131.10, 131.21, 133.04, 134.71, 143.84, 158.89, 159.02 (× 2), 159.04, 159.23 (each aromatic carbons), 166.09 (C=O); ESIMS (% rel. int.) m/z: 1403.5384 (34, calcd. for C84H84O16SNa [M+Na]+: 1403.5378), 1398.5817 (100, calcd. for C84H88NO16S [M+NH4]+: 1398.5824).

4.31. Phenyl 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranosyl-(1→4)-2,3-di-O-(4-methoxyphenylmethyl)-1-thio-6-O-triphenylmethyl-β-D-galactopyranoside (ii-41)

A solution of ii-40 (2.20 g, 1.59 mmol) in a mixture of MeOH (50 ml) and CH2Cl2 (50 ml) was stirred with 1M NaOH (4 ml) at room temperature for 5 h.
After MeOH was removed by rotary evaporator, the resulting aqueous solution was poured into H₂O (100 ml), and the aqueous layer was extracted with EtOAc (80 ml × 3). The combined organic layer was washed with brine (100 ml), dried over MgSO₄, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (AcOEt:hexane = 30:70) gave phenyl 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranosyl-(1→4)-2,3-di-O-(4-methoxyphenylmethyl)-1-thio-β-D-galactopyranoside (1.50 g, 74%) as an oil. [α]D²⁴ +13.5 (c 0.85, CHCl₃); IR (film) 3430, 2935, 1610, 1510, 1250, 1085, 1035, 820, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.13 (dd, 1H, J = 7.6, 8.6 Hz, C6’HH), 3.36 (dd, 1H, J = 5.4, 8.6 Hz, C6’HH), 3.43 (dd, 1H, J = 2.6, 9.6 Hz, C3H), 3.51 (1H, C5H), 3.66 (1H, C6HH), 3.725 (t, 1H, J = 9.6 Hz, C2H), 3.73 (s, 3H, OCH₃), 3.76-3.80 (11H, C6HH, C6OH, OCH₃ × 3), 3.81 (s, 3H, OCH₃), 3.99 (dd, 1H, J = 3.1, 9.6 Hz, C2’H), 4.02 (brd, 1H, J = 2.6 Hz, C4H), 4.03-4.06 (2H, C3’H, C4’H), 4.29 (brdd, 1H, J = 5.4, 7.6 Hz, C5’H), 4.34 (d, 1H, J = 10.6 Hz, ArCHHO), 4.41 (d, 1H, J = 9.9 Hz, ArCHHO), 4.46 (d, 1H, J = 12.3 Hz, ArCHHO), 4.47 (d, 1H, J = 9.9 Hz, ArCHHO), 4.49 (d, 1H, J = 12.3 Hz, ArCHHO), 4.58 (d, 1H, J = 11.4 Hz, ArCHHO), 4.62 (d, 1H, J = 9.6 Hz, C1H), 4.71 (d, 1H, J = 11.6 Hz, ArCHHO), 4.73 (d, 1H, J = 10.6 Hz, ArCHHO), 4.75 (d, 1H, J = 11.6 Hz, ArCHHO), 4.80 (d, 1H, J = 11.4 Hz, ArCHHO), 5.00 (d, 1H, J = 3.1 Hz, C1’H), 6.73 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.74 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.79 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.81 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.93 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.99 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.10-7.16 (8H, aromatic protons), 7.20-7.24 (10H, aromatic protons), 7.35-7.38 (8H, aromatic protons), 7.56 (brdd, 2H, J = 1.3, 8.4 Hz, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 55.12, 55.18 (each OCH₃), 101
55.24 (OCH$_3$ x 2), 55.28 (OCH$_3$), 59.89 (C6), 62.83 (C6'), 71.06 (C5'), 72.26, 72.31, 74.25, 74.40 (each ArCH$_2$O), 74.53 (C4), 75.21 (ArCH$_2$O), 75.41 (C4'), 77.32 (C2'), 77.49 (C2), 77.74 (C5), 78.46 (C3'), 82.62 (C3), 86.59 (CPh$_3$), 88.15 (C1), 99.71 (C1'), 113.41, 113.56, 113.68, 113.92, 113.98, 126.96, 127.14, 127.78, 128.76, 128.89, 129.04, 129.08, 129.35, 129.59, 129.69, 130.31(× 2), 130.55, 130.62, 130.89, 131.17, 134.59, 143.78, 158.95, 159.00, 159.09, 159.21, 159.58 (each aromatic carbons); ESIMS (% rel. int.) m/z: 1299.5126 (22, calcd. for C$_{77}$H$_{80}$O$_{15}$SNa [M+Na]$^+$: 1299.5116), 1294.5562 (100, calcd. for C$_{77}$H$_{84}$NO$_{15}$S [M+NH$_4$]$^+$: 1294.5562).

The alcohol (4.20 g, 3.29 mmol) was stirred with chlorotriphenylmethane (1.80 g, 6.46 mmol) in pyridine (30 ml) at 100 °C for 1.5 h. The mixture was poured into H$_2$O (200 ml) and the aqueous layer was extracted with AcOEt (150 ml × 3). The combined organic layer was washed with brine (150 ml), dried over MgSO$_4$, and then concentrated in vacuo. Silica gel column chromatography of the residue (AcOEt:hexane = 24:76) gave II-41 (4.90 g, 98%) as an oil.

[α]$_D^{24}$ +17.5 (c 1.13, CHCl$_3$); IR (film) 2930, 1610, 1510, 1445, 1245, 1170, 1090, 1035, 820, 730, 705 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.53 (brt, 1H, J = 6.6 Hz, C5'H), 3.10 (dd, 1H, J = 2.6, 9.3 Hz, C3'H), 3.17 (t, 1H, J = 8.4 Hz, C6'HH), 3.35 (dd, 1H, J = 5.5, 8.4 Hz, C6'HH), 3.65 (dd, 1H, J = 6.6, 11.2 Hz, C6HH), 3.70 (s, 3H, OCH$_3$), 3.73 (4H, C2'H, OCH$_3$), 3.77-3.81 (11H, C6HH, C4H, OCH$_3$ × 3), 3.93 (2H, C2'H, C3'H), 4.09 (1H, C4'H), 4.32-4.38 (4H, C1'H, ArCHHO × 3), 4.47 (brdd, 1H, J = 5.5, 8.4 Hz, C5'H), 4.48, 4.52 (each d, 1H, J = 11.9 Hz, ArCHHO), 4.59, 4.64 (each s, 2H, ArCH$_2$O), 4.76 (d, 1H, J = 10.6 Hz, ArCHHO), 4.96 (d, 1H, J = 2.5 Hz, C1'H), 6.66 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.71 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.73 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.85 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.89
(brd, 2H, J = 8.8 Hz, aromatic protons), 6.96 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.05 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.08-7.21 (24H, aromatic protons), 7.26-7.30 (4H, aromatic protons), 7.35-7.38 (11H, aromatic protons), 7.62 (brdd, 2H, J = 8.8 Hz, aromatic protons); 13C NMR (125 MHz, CDCl₃) δ 55.14, 55.16, 55.23, 55.24, 55.27 (each OCH₃), 62.48 (C6’), 63.28 (C6), 70.21 (C5’), 71.53, 72.18, 72.64 (each ArCH₂O), 73.71 (C4), 74.09, 75.03 (each ArCH₂O), 75.14 (C4’), 75.81 (C2’), 76.61 (C2), 77.59 (C5), 78.97 (C3’), 81.10 (C3), 86.60 (CPh₃), 87.24 (C1), 87.28 (CPh₃), 98.91 (C1’), 113.36, 113.51, 113.61, 113.69, 113.71, 126.54, 126.96, 127.00, 127.76, 127.85, 128.58, 128.77, 128.82, 128.85, 129.30, 129.38, 129.54, 129.82, 130.17, 130.60, 130.79, 130.95, 131.13, 131.15, 134.73, 143.82, 144.17, 158.85, 158.87, 158.94, 158.95, 159.20 (each aromatic carbons); ESIMS (% rel. int.) m/z: 1541.6208 (13, calcd. for C₉₆H₉₄O₁₅SNa [M+Na]⁺: 1541.6211, 1537.6633 (100, calcd. for C₉₆H₉₉NO₁₅S [M+H+NH₄]⁺: 1537.6735), 1536.6622 (90, calcd. for C₉₆H₉₈NO₁₅S [M+NH₄]⁺: 1536.6657).

4.32. 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranosyl-(1→4)-2,3-di-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-D-galactitol (ii-42)

A solution of ii-41 (1.5 g, 0.99 mmol) in a mixture of acetone (100 ml) and H₂O (10 ml) was stirred with NBS (445 mg 2.50 mmol) at 0°C for 15 min. Aqueous 10% Na₂S₂O₃ solution (5.0 ml) was added and the mixture was neutralized by the addition of saturated aqueous NaHCO₃ solution (15 ml). After acetone was removed by rotary evaporator, the resulting aqueous solution was extracted with EtOAc (100 ml x 3). The combined organic layer was washed with H₂O (100 ml), dried over MgSO₄, and then concentrated in vacuo. The
residue was passed through silica gel pad to give a residue, which was dissolved in a mixture of EtOH (15 ml) and CH₂Cl₂ (15 ml) and it was cooled in an ice bath. To this solution was added sodium borohydride (113 mg, 2.99 mmol) and the mixture was stirred for 30 min. The ice bath was removed and the mixture was further stirred at ambient temperature for 12 h. Aqueous 1.0 M HCl solution (2.0 ml) was added in order to decompose the excess hydride. After ethanol was removed by rotary evaporator, the resulting aqueous mixture was extracted with EtOAc (100 ml × 3). The combined organic layer was washed with H₂O (100 ml), and brine (100 mL) successively, dried over MgSO₄, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc: hexane = 28:72) gave ii-42 (1.30 g, 92%) as an oil. [α]D²⁵ +25.7 (c 1.35, CHCl₃); IR (film) 3465, 2935, 1610, 1510, 1450, 1250, 1175, 1080, 1035, 820, 730, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.16 (dd, 1H, J = 5.0, 8.0 Hz, C₁₀H), 2.98 (dd, 1H, J = 3.7, 9.8 Hz, C₆'H), 3.04 (t, 1H, J = 8.5 Hz, C₆''H), 3.23 (dd, 1H, J = 5.3, 8.5 Hz, C₆'H), 3.35 (dd, 1H, J = 4.3, 9.8 Hz, C₆''H), 3.42 (dd, 1H, J = 5.3, 9.8 Hz, C₂H), 3.57 (dd, 1H, J = 2.5, 5.3 Hz, C₃H), 3.67-3.72 (8H, C₁H), 3.77 (dd, 1H, J = 2.5, 8.5 Hz, OCH₃), 3.89 (dd, 1H, J = 10.2 Hz, C₃'H), 3.93 (dd, 1H, J = 3.4, 10.2 Hz, C₂'H), 4.06 (2H, C₄'H, ArCHHO), 4.13 (dddd, 1H, J = 3.4, 3.7, 4.3, 6.5 Hz, C₅H), 4.20 (d, 1H, J = 11.2 Hz, ArCHHO), 4.21 (brdd, 1H, J = 5.3, 8.5 Hz, C₅''H), 4.25 (dd, 1H, J = 2.5, 6.5 Hz, C₄H), 4.31 (d, 1H, J = 3.4 Hz, C₅OH), 4.32 (d, 1H, J = 10.5 Hz, ArCHHO), 4.36, 4.48 (each d, 1H, J = 12.1 Hz, ArCHHO), 4.52 (d, 1H, J = 11.2 Hz, ArCHHO), 4.63, 4.67 (each d, 1H, J = 11.4 Hz, ArCHHO), 4.69 (d, 1H, J = 10.5 Hz, ArCHHO), 4.72 (d, 1H, J = 11.2 Hz, ArCHHO), 4.93 (dd, 1H, J = 3.4 Hz, C₁'H), 6.65 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.71 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.78 (brd, 2H, J = 8.7 Hz, aromatic protons),
6.79 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.88 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.97 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.99 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.02 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.14-7.26 (20H, aromatic protons), 7.30 (8H, aromatic protons), 7.41 (6H, aromatic protons); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 55.14 (OCH$_3$ × 2), 55.23 (OCH$_3$ × 3), 61.68 (C6'), 61.74 (C1), 64.50 (C6), 70.19 (C5), 70.42 (C5'), 71.72, 72.22, 72.28, 73.94, 74.26 (each ArCH$_2$O), 74.84 (C4'), 75.55 (C2'), 77.21 (C3), 79.17 (C3'), 80.20 (C2), 80.77 (C4), 86.39, 86.70 (each CPh$_3$), 101.67 (C1'), 113.35, 113.61, 113.67, 113.74 (× 2), 126.91, 126.98, 127.79, 127.81, 128.63, 128.64, 129.02, 129.19 (× 2), 129.45, 129.79, 130.21, 130.24, 130.33, 130.82, 130.98, 143.71, 144.06, 158.88, 158.97, 159.07, 159.08, 159.28 (each aromatic carbons); ESIMS (% rel. int.) m/z: 1541.6210 (100, calcd. for C$_{90}$H$_{92}$O$_{16}$Na $[M+Na]^+$: 1541.6283), 1446.6669 (82, calcd. for C$_{90}$H$_{96}$NO$_{16}$S $[M+NH_4]^+$: 1446.6729).

4.33. (3S,4S,5S)-6-(tert-butyldimethylsilyloxy)-4,5-di-(4-methoxybenzyloxy)-2-triphenylmethylxoxymethyl-hex-1-en-3-yl 2,3,4-O-tri-(4-methoxybenzyl oxy)-6-O-triphenylmethyl-α-D-galactopyranoside (ii-43)

A solution of ii-42 (1.49 g, 1.04 mmol) in DMF (10 ml) was stirred with imidazole (212 mg, 3.12 mmol) and tert-butyldimethylchlorosilane (235 mg, 1.56 mmol) at room temperature for 30 min. The mixture was poured into H$_2$O (70 ml) and the aqueous layer was extracted with EtOAc (100 ml × 3). The combined organic layer was washed with H$_2$O (100 ml), and brine (100 ml) successively, dried over MgSO$_4$, and then concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 20:80) gave 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranos.

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yl-(1→4)-1-O-(tert-butylidemethylsilyl)-2,3-di-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-D-galactitol (1.57 g, 98%) as an oil. [α]D25 +24.5 (c 1.15, CHCl3); IR (film) 3465, 2930, 1610, 1510, 1250, 1080, 1035, 830, 705 cm-1; 1H NMR (500 MHz, CDCl3) δ -0.07, -0.05 (each 3H, s, SiCH3), 0.81 (9H, s, SiC(CH3)3), 2.93 (dd, 1H, J = 3.3, 10.0 Hz, C6′HH), 3.02 (t, 1H, J = 8.7 Hz, C6HH), 3.21 (dd, 1H, J = 5.0, 8.7 Hz, C6HH), 3.36 (dd, 1H, J = 6.0, 10.0 Hz, C6′HH), 3.49 (2H, C2′H, C3′H), 3.69, 3.71 (each s, 3H, OCH3), 3.76-3.79 (10H, C1′HH, OCH3×3), 3.87-3.91 (3H, C1′HH, C2H, C3H), 4.11 (2H, C4H, C5′H), 4.17, 4.24 (each d, 1H, J = 11.1 Hz, ArCHHO), 4.25-4.31 (3H, C4′H, C5H, ArCHHO), 4.35 (d, 1H, J = 12.3 Hz, ArCHHO), 4.41 (d, 1H, J = 3.3 Hz, C5′OH), 4.44 (d, 1H, J = 12.3 Hz, ArCHHO), 4.52 (d, 1H, J = 11.3 Hz, ArCHHO), 4.60, 4.63 (each d, 1H, J = 11.4 Hz, ArCHHO), 4.67 (d, 1H, J = 10.4 Hz, ArCHHO), 4.71 (d, 1H, J = 11.3 Hz, ArCHHO), 4.90 (d, 1H, J = 2.8 Hz, C1H), 6.62 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.71 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.75 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.88 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.96 (4H, aromatic protons), 7.02 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.14-7.32 (28H, aromatic protons), 7.42 (6H, aromatic protons); 13C NMR (125 MHz, CDCl3) δ -5.27 (SiCH3×2), 18.25 (SiC), 25.98 (SiC(CH3)3), 55.12 (OCH3×2), 55.21 (OCH3), 55.22 (OCH3×2), 61.47 (C6), 64.09 (C1′), 64.46 (C6′), 70.25 (C5), 70.38 (C5′), 71.59, 72.10, 72.89, 73.86, 74.27 (each ArCH2O), 74.75 (C4), 75.57 (C2), 76.87 (C3′), 79.44 (C3), 81.18 (C4′), 81.62 (C2′), 86.26, 86.66 (each CPh3), 101.88 (C1), 113.32, 113.41, 113.49, 113.71, 113.72, 126.83, 126.94, 127.76, 127.79, 128.61, 128.67, 128.76, 128.99, 129.01, 129.42, 129.85, 130.25, 130.57, 130.92, 131.04, 131.06, 143.75, 144.24, 158.75, 158.77, 158.84, 159.00, 159.25 (each aromatic carbons); ESIMS (% rel. int.) m/z: 1565.7178
(41, calcd. for C_{96}H_{106}O_{16}SiNa [M+Na]^+: 1565.7148), 1561.7665 (100, calcd. for C_{96}H_{111}NO_{16}Si [M+H+NH_4]^+: 1561.7672).

A solution of the product thus obtained (1.24 g, 803 μmol) in a mixture of DMSO (30 ml, 418 mmol) and acetic anhydride (15 ml, 160 mmol) was stirred at room temperature for 10 hours. The mixture was poured into H_2O (300 ml), and the aqueous layer was extracted with EtOAc (150 ml × 3). The combined organic layer was washed with H_2O (100 ml), and brine (100 ml) successively, dried over MgSO_4, and then concentrated in vacuo. Silica gel column chromatography (EtOAc:hexane = 18:82) of the residue afforded (3S,4S,5S)-6-(tert-butyldimethylsilyloxy)-4,5-di-(4-methoxyphenylmethyl)-1-O-triphenylmethyl-2-oxohexan-3-yl 2,3,4-O-tri-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranoside (1.23 g, 99%) as an oil. [α]_D^{25} +21.2 (c 1.78, CHCl_3); IR (film) 2930, 1730, 1610, 1510, 1250, 1035, 705 cm^{-1}; ^1H NMR (500 MHz, CDCl_3) δ -0.11, -0.09 (each 3H, s, SiCH_3), 0.80 (9H, s, Si(CH_3)_3), 2.94 (t, 1H, J = 7.8 Hz, C6HH), 3.27 (dd, 1H, J = 5.8, 7.8 Hz, C6HH), 3.59 (1H, C5’H), 3.65 (dd, 1H, J = 2.8, 10.2 Hz, C3H), 3.73-3.78 (18H, C6’H_2, C2H, OCH_3 × 5), 3.81 (brd, 1H, J = 2.8 Hz, C4H), 3.86 (dd, 1H, J = 3.4, 5.8 Hz, C4’H), 3.97 (dd, 1H, J = 5.8, 7.8 Hz, C5H), 4.19 (d, 1H, J = 18.2 Hz, C1’HH), 4.24 (d, 1H, J = 10.7 Hz, ArCHHO), 4.25 (d, 1H, J = 11.8 Hz, ArCHHO), 4.39 (d, 1H, J = 11.8 Hz, ArCHHO), 4.40 (s, 2H, ArCH_2O), 4.41 (d, 1H, J = 18.2 Hz, C1’HH), 4.44, 4.49 (each d, 1H, J = 11.6 Hz, ArCHHO), 4.50 (d, 1H, J = 11.2 Hz, ArCHHO), 4.61 (d, 1H, J = 3.2 Hz, C1H), 4.62 (d, 1H, J = 10.7 Hz, ArCHHO), 4.65 (d, 1H, J = 11.2 Hz, ArCHHO), 6.67 (4H, aromatic protons), 6.74 (4H, aromatic protons), 6.88 (4H, aromatic protons), 6.96 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.06 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.13-7.26 (22H, aromatic protons), 7.31 (6H, aromatic protons), 7.42 (6H,
aromatic protons; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ -5.40, -5.38 (each SiCH$_3$), 18.17 (SiC), 25.94 (SiC(CH$_3$)$_3$), 55.14, 55.15 (each OCH$_3$), 55.17 (OCH$_3 \times 2$), 55.21 (OCH$_3$), 62.35 (C6), 63.33 (C6’), 69.98 (C1’), 70.52 (C5), 71.92, 72.78, 72.95, 73.27, 74.10 (each ArCH$_2$O), 74.74 (C2), 75.17 (C4), 78.69 (C3), 80.08 (C4’), 80.69 (C5’), 82.01 (C3’), 86.61, 86.89 (each CPh$_3$), 98.61 (C1), 113.33, 113.46, 113.52, 113.62, 113.67, 126.96, 126.98, 127.80, 127.82, 128.61, 128.66, 128.79, 129.43, 129.49, 129.60, 129.69, 130.31, 130.49, 130.77, 130.86, 131.14, 143.70, 143.77, 158.87, 158.88, 158.90, 158.97, 158.98 (each aromatic carbons), 205.74 (C2’); ESIMS (% rel. int.) m/z: 1563.7013 (55, calcd. for C$_{96}$H$_{104}$O$_{16}$SiNa [M+Na$^+$: 1563.6991), 1559.7457 (100, calcd. for C$_{96}$H$_{109}$NO$_{16}$Si [M+H+NH$_4$]$^+$: 1559.7516), 1558.7428 (91, calcd. for C$_{96}$H$_{108}$NO$_{16}$Si [M+NH$_4$]$^+$: 1558.7437).

A solution of the product (2.00 g, 1.30 mmol) in a mixture of toluene (30 ml) and pyridine (0.5 ml) was stirred with Tebbe reagent 0.5M toluene solution (7.8 ml, 3.9 mmol) at -40°C for 15 min. The ice bath was removed and the mixture was further stirred at ambient temperature for 1 h. After aqueous 1.0 M NaOH solution (2.0 ml) was added to quench the reaction at 0°C, the mixture was filtered through Celite, and the filtrate was concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc: hexane = 18:82) gave ii-$^{43}$ (1.30 g, 65%) as an oil. [a]$_D$$^{24}$ +45.3 (c 1.00, CHCl$_3$); IR (film) 2925, 1610, 1510, 1250, 1090, 1035, 830, 705 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ -0.21, -0.20 (each 3H, s, SiCH$_3$), 0.71 (9H, s, SiC(CH$_3$)$_3$), 3.07 (dd, 1H, $J$ = 7.0, 8.7 Hz, C6HH), 3.38 (dd, 1H, $J$ = 6.1, 8.7 Hz, C6HH), 3.39-3.45 (3H, C6’H$_2$, C5’H), 3.48 (t, 1H, $J$ = 3.8 Hz, C4’H), 3.71 (s, 3H, OCH$_3$), 3.73-3.77 (14H, C2’H$_2$, OCH$_3 \times 4$), 3.90 (2H, C3H, C4H), 3.95 (dd, 1H, $J$ = 3.4, 10.5 Hz, C2H), 4.18 (brdd, 1H, $J$ = 6.1, 7.0 Hz, C5H), 4.30 (d, 1H, $J$ = 12.0 Hz, ArCHHO), 4.31
(d, 1H, J = 11.2 Hz, ArCHHO), 4.41-4.51 (5H, ArCHHO × 5), 4.54 (d, 1H, J =
11.5 Hz, ArCHHO), 4.56 (d, 1H, J = 3.8 Hz, C3' H), 4.66 (d, 1H, J = 11.5 Hz,
ArCHHO), 4.72 (d, 1H, J = 10.8 Hz, ArCHHO), 5.00 (d, 1H, J = 3.4 Hz, C1H),
5.50, 5.71 (each brs, 1H, C1'H), 6.64 (brd, 2H, J = 8.7 Hz, aromatic protons),
6.67 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.69 (brd, 2H, J = 8.7 Hz,
aromatic protons), 6.78 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.80 (brd, 2H, J
= 8.6 Hz, aromatic protons), 6.95 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.97
(brd, 2H, J = 8.7 Hz, aromatic protons), 7.07 (brd, 2H, J = 8.7 Hz, aromatic
protons), 7.14-7.23 (22H, aromatic protons), 7.35-7.38 (12H, aromatic protons);
13C NMR (125 MHz, CDCl3) δ -5.50, -5.40 (each SiCH3), 18.04 (SiC), 25.84
(SiC(CH3)3), 55.10, 55.16, 55.17, 55.19, 55.21 (each OCH3), 62.86 (C6), 63.36
(C6'), 64.51 (C2' CH2), 70.12 (C5), 72.49, 72.53, 72.57, 72.87, 74.03 (each
ArCH2O), 75.44 (C4), 75.86 (C2), 76.68 (C3'), 77.68 (C4'), 78.57 (C3), 78.71
(C5'), 86.58, 86.84 (each CPh3), 94.31 (C1), 113.35 (× 2), 113.39, 113.52,
113.60 (each aromatic carbons), 115.10 (C1'), 126.88, 126.91, 127.76 (× 2),
128.59, 128.73, 128.80, 129.41, 129.48, 129.54, 129.79, 130.67, 130.91, 131.00,
131.18, 131.47 (each aromatic carbons), 143.23 (C2'), 143.83, 144.25, 158.77,
158.79, 158.83, 158.88, 158.90 (each aromatic carbons); ESIMS (% rel. int.)
m/z: 1561.7184 (43, calcd. for C97H106O15SiNa [M+Na]+: 1561.7199),
1557.7636 (100, calcd. for C97H111NO15Si [M+H+NH4]+: 1557.7723),
1556.7620 (88, calcd. for C97H110NO15Si [M+NH4]+: 1556.7645).

4.34. 2,3,4-O-tri-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-
galactopyranosyl-(1→4)-2,3-di-O-(4-methoxyphenylmethyl)-6-O-triphenyl
methyl-α-Δ5,5a-carbagalactopyranose (ii-45α) and its β-isomer (ii-45β)

A solution of ii-43 (475 mg, 0.31 mmol) in THF (6.0 ml) was stirred with
tetrabutylammonium fluoride (1.0 M in THF, 0.47 ml) at room temperature for 2 h. The mixture was poured into H₂O (50 ml) and the aqueous layer was extracted with EtOAc (50 ml × 3). The combined organic layer was washed with brine (50 ml), dried over MgSO₄, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc:hexane = 26:74) gave the corresponding alcohol (422 mg, 97%) as an oil. [α]₀²⁴ +46.5 (c 1.00, CHCl₃); IR (film) 3500, 2930, 1610, 1510, 1250, 1090, 1035, 820, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.85 (dd, 1H, J = 4.8, 7.0 Hz, C6'O'H), 2.99 (dd, 1H, J = 6.2, 9.0 Hz, C6'H'H), 3.35-3.44 (3H, C6'H'H, C5'H, C6'H'H), 3.51 (ddd, 1H, J = 3.7, 7.0, 11.3 Hz, C6'H'H), 3.59 (dd, 1H, J = 4.2, 6.6 Hz, C4'H), 3.736 (s, 3H, OCH₃), 3.741 (s, 6H, OCH₃× 2), 3.77, 3.78 (each s, 3H, OCH₃), 3.78-3.83 (4H, C3'H, C4'H, C2'CH₂), 3.93 (dd, 1H, J = 3.6, 9.7 Hz, C2'H), 4.00 (brd, 1H, J = 6.3 Hz, C5'H), 4.26 (d, 1H, J = 11.3 Hz, ArCHHO), 4.33 (d, 1H, J = 11.0 Hz, ArCHHO), 4.37 (d, 1H, J = 11.0 Hz, ArCHHO), 4.40 (d, 1H, J = 4.2 Hz, C3'H), 4.42-4.46 (each d, 1H, J = 11.6 Hz, ArCHHO), 4.50 (d, 1H, J = 11.0 Hz, ArCHHO), 4.53 (d, 1H, J = 11.6 Hz, ArCHHO), 4.65 (d, 1H, J = 11.6 Hz, ArCHHO), 4.70 (d, 1H, J = 11.0 Hz, ArCHHO), 5.00 (d, 1H, J = 3.6 Hz, C1'H), 5.47 (brs, 1H, C1’HH), 5.81 (brd, 1H, J = 1.7 Hz, C1’HH), 6.65 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.68 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.74 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.77 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.78 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.94 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.02 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.08 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.12 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.14-7.21 (22H, aromatic protons), 7.34-7.37 (10H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 55.16 (OCH₃), 55.19 (OCH₃× 4), 62.59 (C₆'), 63.26 (C₆), 64.25 (C₂'CH₂), 70.47 (C₅), 72.45, 72.55, 73.07, 73.89, 73.95 (each
ArCH₂O), 75.31 (C4), 75.59 (C2), 77.10 (C3'), 78.29 (C3), 79.32 (C5'), 80.22 (C4'), 86.65, 86.89 (each CPh₃), 93.96 (C1), 113.39, 113.49, 113.55, 113.61, 113.67 (each aromatic carbons), 115.85 (C1'), 126.91, 126.96, 127.76, 127.78, 128.56, 128.68, 128.98, 129.38, 129.49, 129.59, 129.77, 130.64, 130.76, 130.77, 130.80, 130.98 (each aromatic carbons), 142.58 (C2'), 143.82, 144.17, 158.89, 158.92, 158.94 (× 2), 159.06 (each aromatic carbons); ESIMS (% rel. int.) m/z: 1447.6312 (62, calcd. for C₉₁H₉₂O₁₅Na [M+Na]⁺: 1447.6334), 1443.6802 (100, calcd. for C₉₁H₉₇NO₁₅ [M+H+NH₄]⁺: 1443.6858), 1442.6766 (98, calcd. for C₉₁H₉₆NO₁₅ [M+NH₄]⁺: 1442.6780).

Oxalylchloride (164 mg, 1.29 mmol) was added to a solution of dimethylsulfoxide (202 mg, 2.59 mmol) in CH₂Cl₂ (3.0 ml) at -78 °C and the mixture was stirred for 10 min. A solution of the alcohol (610 mg, 0.43 mmol) in CH₂Cl₂ (3.0 ml) was added to this mixture, and the resulting mixture was stirred at the same temperature for 40 min. After triethylamine (392 mg, 3.87 mmol) was added, the cooling bath was removed. The mixture was further stirred at room temperature for additional 10 min. The mixture was poured into H₂O (50 ml) and the aqueous layer was extracted with EtOAc (50 ml × 3). The combined organic layer was washed with brine (50 ml), dried over MgSO₄, and then concentrated in vacuo to give crude aldehyde. This sample was immediately used for the next step. A solution of the crude aldehyde (608 mg, 0.43 mmol) in THF (10 ml) was stirred with vinylmagnesium bromide (1.0 M in THF, 0.86 ml) at -15 °C. After the mixture was stirred for 5 min, and further stirred at 0 °C for 10 min. The mixture was poured into saturated aqueous NH₄Cl (50 ml) and extracted with EtOAc (50 ml × 3). The combined organic layer was washed with brine (50 ml), dried over MgSO₄, and then concentrated in vacuo. Purification of the residue with silica gel column chromatography
(EtOAc:hexane = 26:74) gave 7:10 mixture of ii-\textbf{44R} and ii-\textbf{44S} (506 mg, 81%) as an oil. [α]_D\textsuperscript{24} +42.3 (c 1.46, CHCl\textsubscript{3}); IR (film) 3485, 2930, 1610, 1510, 1250, 1090, 1035, 820, 705 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 2.26 (d, 1H × 0.4, J = 6.8 Hz, C6’OH ((R)-isomer)), 2.43 (d, 1H × 0.6, J = 7.4 Hz, C6’OH ((S)-isomer)), 2.95 (dd, 1H × 0.6, J = 6.0, 9.0 Hz, C6HH ((S)-isomer)), 3.03 (dd, 1H × 0.4, J = 6.3, 9.0 Hz, C6HH ((R)-isomer)), 3.24 (dd, 1H × 0.4, J = 3.5, 6.7 Hz, C5’H ((R)-isomer)), 3.37 (dd, 1H × 0.6, J = 6.6, 9.0 Hz, C6HH ((S)-isomer)), 3.42 (1H, C6HH ((R)-isomer), C5’H ((S)-isomer)), 3.60 (t, 1H × 0.6, J = 5.5 Hz, C4’H ((S)-isomer)), 3.67-3.82 (19H, C2’CH\textsubscript{2}, C4’H ((R)-isomer), C4H, C3H ((S)-isomer), OCH\textsubscript{3} × 5), 3.85 (dd, 1H × 0.4, J = 2.6, 10.1 Hz, C3H ((R)-isomer)), 3.93-4.09 (3H, C2H, C6’H, C5H), 4.26-4.72 (11H, ArCHHO × 10, C3’H), 4.91 (brd, 1H × 0.6, J = 10.5 Hz, C8’H ((S)-isomer)), 4.93 (brd, 1H × 0.4, J = 10.6 Hz, C8’H ((R)-isomer)), 4.95 (brd, 1H × 0.4, J = 17.1 Hz, C8’H ((R)-isomer)), 5.03 (d, 1H × 0.6, J = 3.7 Hz, C1H ((S)-isomer)), 5.05 (d, 1H × 0.4, J = 3.6 Hz, C1H ((R)-isomer)), 5.09 (brd, 1H × 0.6, J = 17.2 Hz, C8’H ((S)-isomer)), 5.50 (brs, 1H × 0.4, C1’H ((R)-isomer)), 5.53 (brs, 1H × 0.6, C1’H ((S)-isomer)), 5.57 (ddd, 1H × 0.4, J = 5.8, 10.6, 17.1 Hz, C7’H ((R)-isomer)), 5.72 (ddd, 1H × 0.6, J = 6.0, 10.5, 17.2 Hz, C7’H ((S)-isomer)), 5.83 (brd, 1H × 0.4, J = 1.7 Hz, C1’H ((R)-isomer)), 5.86 (brd, 1H × 0.6, J = 1.6 Hz, C1’H ((S)-isomer)), 6.63-7.38 (50H, aromatic protons); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ 55.14, 55.16 (each OCH\textsubscript{3}), 55.19 (OCH\textsubscript{3} × 3), 63.06 (C6 ((R)-isomer)), 63.33 (C6 ((S)-isomer)), 64.10 (C2’CH\textsubscript{2} ((R)-isomer)), 64.26 (C2’CH\textsubscript{2} ((S)-isomer)), 70.37 (C5 ((R)-isomer)), 70.58 (C5 ((S)-isomer)), 72.43, 72.47, 72.51 (each ArCH\textsubscript{2}O), 72.55 (C6’ ((R)-isomer), ArCH\textsubscript{2}O), 73.15 (C6’ ((S)-isomer)), 73.49, 73.63, 73.79, 73.84, 73.97, 74.48 (each ArCH\textsubscript{2}O), 75.05 (C4 ((S)-isomer)), 75.32 (C4 ((R)-isomer)), 75.60 (C2 ((S)-isomer)), 75.68 (C2
((R)-isomer), 76.88 (C3' ((R)-isomer)), 77.39 (C3' ((S)-isomer)), 78.36 (C3 ((R)-isomer)), 78.62 (C3 ((S)-isomer)), 79.32 (C4' ((R)-isomer)), 79.37 (C4' ((S)-isomer)), 80.31 (C5' ((R)-isomer)), 80.36 (C5' ((S)-isomer)), 86.58, 86.66, 86.83, 86.92 (each CPh3), 93.86 (Cl ((R)-isomer)), 94.02 (Cl ((S)-isomer)), 113.37, 113.39, 113.43, 113.49, 113.53 (× 2), 113.54, 113.56, 113.60, 113.61 (each aromatic carbons), 115.70 (Cl' ((S)-isomer)), 115.73 (Cl' ((R)-isomer)), 115.89 (C8' ((R)-isomer)), 116.57 (C8' ((S)-isomer)), 126.92, 127.78 (× 2), 128.54, 128.66, 128.70, 128.90, 128.92, 129.32, 129.35, 129.49, 129.54, 129.55, 129.74, 129.88, 129.99, 130.43, 130.72, 130.74, 130.76 (× 3), 130.81, 130.83, 130.95, 131.00 (each aromatic carbons), 137.17 (C7' ((S)-isomer)), 138.34 (C7' ((R)-isomer)), 142.60 (C2' ((S)-isomer)), 142.76 (C2' ((R)-isomer)), 143.80 (× 2), 144.14, 144.16, 158.86 (× 2), 158.88, 158.89, 158.91 (× 2), 158.92, 158.97, 158.98, 159.06 (each aromatic carbons); ESIMS (% rel. int.) m/z: 1473.6505 (62, calcd. for C93H94O15Na [M+Na]+: 1473.6490), 1469.6954 (100, calcd. for C93H98NO15 [M+H+NH4]+: 1469.7015), 1468.6932 (99, calcd. for C93H98NO15 [M+NH4]+: 1468.6936).

A solution of ii-44 (486 mg, 0.33 mmol) in toluene (25.0 ml) was stirred in the presence of Grubbs's second-generation catalyst (11.8 mg, 13.9 μmol) at 100 °C. After 10 min, the mixture was concentrated in vacuo. Purification of the residue with silica gel column chromatography (EtOAc:hexane = 28:72) gave 10:7 mixture of ii-45α and ii-45β (395 mg, 85%) as an oil. These were successfully separated by medium-pressured column chromatography (EtOAc:benzene = 6:94) to provide ii-45α (233 mg, 50%) and ii-45β (162 mg, 35%).

4.34.1. Pysical data for ii-45α.
[α]D$_{25}^{25}$ +44.6 (c 1.34, CHCl₃); IR (film) 3500, 2930, 1610, 1510, 1250, 1090, 1035, 820, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.32 (d, 1H, $J = 5.0$ Hz, C¹OH), 3.18 (t, 1H, $J = 8.3$ Hz, C6'HH), 3.32 (dd, 1H, $J = 5.6$, 8.3 Hz, C6'H'H), 3.68 (4H, C3H, OCH₃), 3.74, 3.76 (each s, 3H, OCH₃), 3.78 (s, 6H, OCH₃× 2), 3.79 (1H, C3'H), 3.86 (dd, 1H, $J = 3.4$, 10.1 Hz, C2'H), 3.91 (3H, C2H, C6H₂), 4.05 (brs, 1H, C4'H), 4.23 (d, 1H, $J = 2.9$ Hz, C4H), 4.28 (1H, C1H), 4.34 (d, 1H, $J = 10.6$ Hz, ArCHHO), 4.35 (1H, C5'H), 4.36 (s, 2H, ArCH₂O), 4.39 (d, 1H, $J = 12.6$ Hz, ArCHHO), 4.50 (2H, ArCHHO× 2), 4.55, 4.59 (each d, 1H, $J = 11.2$ Hz, ArCHHO), 4.61 (d, 1H, $J = 11.8$ Hz, ArCHHO), 4.76 (d, 1H, $J = 10.6$ Hz, ArCHHO), 4.88 (d, 1H, $J = 3.4$ Hz, C1'H), 5.71 (brd, 1H, $J = 3.9$ Hz, C5aH), 6.68-6.74 (6H, aromatic protons), 6.82 (brd, 2H, $J = 8.6$ Hz, aromatic protons), 6.86 (brd, 2H, $J = 8.7$ Hz, aromatic protons), 6.95 (brd, 2H, $J = 8.6$ Hz, aromatic protons), 7.06 (brd, 2H, $J = 8.6$ Hz, aromatic protons), 7.12-7.19 (24H, aromatic protons), 7.24 (brd, 2H, $J = 8.6$ Hz, aromatic protons), 7.33-7.36 (10H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 55.15, 55.17 (each OCH₃), 55.21 (OCH₃× 2), 55.22 (OCH₃), 62.28 (C6'), 64.65 (C6), 65.78 (C1), 70.29 (C5'), 71.95, 72.35, 72.46, 72.62 (each ArCH₂O), 73.55 (C4), 74.03 (ArCH₂O), 75.19 (C4'), 75.32 (C2 or C3), 75.36 (C2 or C3), 75.55 (C2'), 78.90 (C3'), 86.66, 87.06 (each CPh₃), 98.70 (C1'), 113.35, 113.58, 113.62 (× 2), 113.75 (each aromatic carbons), 124.63 (C5a), 126.90, 126.98, 127.75, 127.80, 128.61, 128.72, 128.84, 129.02, 129.37, 129.41, 129.49, 130.33, 130.69, 130.80, 131.04, 131.12 (each aromatic carbons), 137.55 (C5), 143.71, 144.23, 157.92, 158.85, 158.93, 158.94, 159.23 (each aromatic carbons); ESIMS (%, rel. int.) m/z: 1445.6113 (23, calcd. for C₉₁H₉₀O₁₅Na [M+Na]⁺: 1445.6177), 1441.6641 (100, calcd. for C₉₁H₉₅NO₁₅ [M+H+NH₄]⁺: 1441.6702), 1440.6564 (98, calcd. for C₉₁H₉₄NO₁₅ [M+NH₄]⁺: 1440.6623).
4.34.2. Physical data for il-45β.

[α]D$^{24}$ +32.5 (c 0.72, CHCl$_3$); IR (film) 3465, 2930, 1610, 1510, 1250, 1090, 1035, 820, 720 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.05 (dd, 1H, $J$ = 6.9, 8.7 Hz, C6'HH), 3.36 (2H, C6'H'H, C3H), 3.43 (br, 1H, C1OH), 3.68, 3.70 (each s, 3H, OCH$_3$), 3.75 (2H, C6H$_2$), 3.77, 3.78, 3.782 (each s, 3H, OCH$_3$), 3.85 (dd, 1H, $J$ = 3.6, 10.0 Hz, C2'H), 3.93 (dd, 1H, $J$ = 2.6, 10.0 Hz, C3'H), 3.96 (brd, 1H, $J$ = 2.6 Hz, C4'H), 3.98 (dd, 1H, $J$ = 3.5, 8.2 Hz, C2H), 4.06 (1H, C1H), 4.29-4.34 (3H, C4H, C5'H, ArCHHO), 4.41 (d, 1H, $J$ = 12.4 Hz, ArCHHO), 4.49, 4.55 (each d, 1H, $J$ = 11.9 Hz, ArCHHO), 4.60 (d, 1H, $J$ = 12.4 Hz, ArCHHO), 4.62, 4.68 (each d, 1H, $J$ = 11.3 Hz, ArCHHO), 4.72 (d, 1H, $J$ = 12.0 Hz, ArCHHO), 4.73 (s, 2H, ArCH$_2$O), 4.76 (d, 1H, $J$ = 3.6 Hz, C1'H), 5.97 (brd, 1H, $J$ = 4.6 Hz, C5aH), 6.64 (brd, 2H, $J$ = 8.7 Hz, aromatic protons), 6.69 (brd, 2H, $J$ = 8.6 Hz, aromatic protons), 6.74 (brd, 2H, $J$ = 8.6 Hz, aromatic protons), 6.87 (4H, aromatic protons), 6.93 (brd, 2H, $J$ = 8.7 Hz, aromatic protons), 7.09 (brd, 2H, $J$ = 8.7 Hz, aromatic protons), 7.13-7.17 (20H, aromatic protons), 7.28 (4H, aromatic protons), 7.32-7.35 (12H, aromatic protons); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 55.10, 55.14, 55.21 (× 2), 55.24 (each OCH$_3$), 62.53 (C6'), 65.42 (C6), 70.31 (C5'), 70.83 (ArCH$_2$O), 70.87 (C4), 71.19 (C1), 72.58, 72.80, 72.96, 74.02 (each ArCH$_2$O), 75.17 (C4'), 75.31 (C2'), 78.88 (C3'), 79.99 (C3), 83.13 (C2), 86.60, 87.05 (each CPh$_3$), 96.54 (C1'), 113.36, 113.60, 113.66, 113.68, 113.74, 126.94, 127.05 (each aromatic carbons), 127.74 (C5a, aromatic carbon), 127.86, 128.50, 128.71, 128.94, 129.07, 129.49, 129.52, 129.76, 130.14, 130.33, 130.80, 130.89, 130.99 (each aromatic carbons), 138.29 (C5), 143.71, 143.89, 158.87, 158.92, 158.98, 159.11, 159.12 (each aromatic carbons); ESIMS (% rel. int.) m/z: 1445.6183 (32, calcd. for C$_{91}$H$_{90}$O$_{15}$Na [M+Na]$: 1445.6177), 1441.6625 (100, calcd. for C$_{91}$H$_{95}$NO$_{15}$
4.34.3. Stereochemical inversion of C1OH group of ii-45α into ii-45β

A solution of ii-45α (104 mg, 73.1 µmol) in THF (3.5 ml) was stirred with triphenylphosphine (58.0 mg, 221 µmol), p-nitrobenzoic acid (37.0 mg, 221 µmol), and diethyl azodicarboxylate (2.2 M solution in toluene, 86.0 µl, 221 µmol) at room temperature for 40 min. The mixture was poured into saturated aqueous NH₄Cl (20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (30 ml), dried over MgSO₄, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc:hexane = 24:76) and (EtOAc:benzene = 4:96) gave p-nitrobenzoate as an oil. [α]D²⁵ -13.8 (c 1.33, CHCl₃); IR (film) 2935, 1725, 1610, 1510, 1250, 1095, 1035, 820, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.25 (2H, C6'H, C3'H), 3.40 (dd, 1H, J = 5.4, 8.2 Hz, C6’HH), 3.658, 3.663, 3.72, 3.78, 3.80 (each s, 3H, OCH₃), 3.83 (brd, 1H, J = 14.5 Hz, C6HH), 4.01 (2H, C2’H, C3’H), 4.13-4.18 (2H, C6HH, C2H), 4.19 (brs, 1H, C4’H), 4.24 (d, 1H, J = 3.3 Hz, C4H), 4.37 (d, 1H, J = 10.5 Hz, ArCHHO), 4.40 (d, 1H, J = 12.7 Hz, ArCHHO), 4.50 (d, 1H, J = 12.7 Hz, ArCHHO), 4.53 (1H, C5’H), 4.55 (s, 2H, ArCH₂O), 4.70 (d, 1H, J = 11.9 Hz, ArCHHO), 4.74 (s, 2H, ArCH₂O), 4.82 (2H, ArCH₂O × 2), 5.03 (brs, 1H, C1’H), 5.25 (brs, 1H, C5αH), 5.28 (brd, 1H, J = 7.7 Hz, C1H), 6.59 (brd, 2H, J = 8.6 Hz, aromatic protons), 6.65 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.73 (4H, aromatic protons), 6.89 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.99 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.12-7.20 (26H, aromatic protons), 7.25-7.29 (8H, aromatic protons), 7.32 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.37 (4H, aromatic protons), 7.92
(brd, 2H, J = 9.0 Hz, aromatic protons), 8.18 (brd, 2H, J = 9.0 Hz, aromatic protons); $^1$C NMR (125 MHz, CDCl$_3$) δ 54.99, 55.10, 55.19, 55.21, 55.24 (each OCH$_3$), 62.05 (C6'), 65.05 (C6), 70.28 (C5'), 71.59, 72.30, 72.57 (each ArCH$_2$O), 72.81 (C4), 73.59, 74.11 (each ArCH$_2$O), 74.82 (C1), 74.95 (C4'), 75.60 (C2'), 76.23 (C2), 77.14 (C3), 79.27 (C3'), 86.66, 87.25 (each CPh$_3$), 98.91 (C1'), 113.39, 113.54, 113.67 (× 2), 113.70 (each aromatic carbons), 122.12 (C5a), 123.23, 127.02, 127.13, 127.77, 127.90, 128.45, 128.72, 128.81, 129.09, 129.35, 129.54, 129.96, 130.31, 130.48, 130.61, 130.83, 130.96, 130.99, 135.33 (each aromatic carbons), 138.36 (C5), 143.70, 144.00, 150.36, 158.91, 159.01 (× 2), 159.03 (× 2), 164.06 (each aromatic carbons), 203.76 (C=O);

The product was diluted with a mixture of MeOH (3.0 ml) and CH$_2$Cl$_2$ (3.0 ml) and stirred with 1 M NaOH aqueous solution (0.3 ml) at room temperature for 30 min. The mixture was poured into H$_2$O (20 ml) and the aqueous layer was extracted with AcOEt (20 ml × 3). The combined organic layer was washed with brine (20 ml), dried over MgSO$_4$, and concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 30:70) gave ii-45β (91.8 mg, 92%). The $^1$H NMR spectrum and R$_f$ value in the silica gel TLC were identical to the sample ii-45β described in the Section 4.34.3.

4.35. α-D-galactopyranosyl-(1→4)-β-Δ$^{5,5a}$carbagalactopyranose (ii-46β)

90% formic acetic acid solution (0.2 ml) was added to a solution of ii-45β (67.0 mg, 47.1 mmol) in CH$_2$Cl$_2$ (3.0 ml) at 0 ºC. After stirring at room temperature at 0ºC for 1 h, the cooling bath was removed and the mixture was
stirred at room temperature for 1 h. After saturated aqueous NaHCO₃ solution (1.0 ml) was added at 0 °C, the mixture was poured into H₂O (20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (30 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was passed through silica gel pad to give the triol. A suspension of the product (25.0 mg, 26.6 μmol) in a mixture of CH₂Cl₂ (1.0 ml) and H₂O (100 μl) was stirred with 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) (60.0 mg, 0.26 mmol) at room temperature for 40 hours. The mixture was poured into water (10 ml). The aqueous solution was washed with EtOAc (10 ml × 2) and concentrated in vacuo. After dilution with small amount of H₂O (ca. 0.3 ml), the resulting solution was loaded on a ODS Sep-Pak® cartridge (5.0 g) to give ii-46β (8.7 mg, 55%) as white amorphous powder. [α]₂⁴° +143 (c 0.63, CHCl₃); ¹H NMR (500 MHz, D₂O) δ 3.51 (dd, 1H, J = 3.5, 10.6 Hz, C3'H), 3.59, 3.60 (each s, 1H, C6'HH), 3.67 (dd, 1H, J = 7.3, 10.6 Hz, C2'H), 3.69 (dd, 1H, J = 3.6, 8.5 Hz, C2'HH), 3.73 (dd, 1H, J = 3.0, 8.5 Hz, C3'H), 3.86 (dd, 1H, J = 1.0, 3.0 Hz, C4'HH), 3.97 (brd, 1H, J = 7.3 Hz, C1'H), 4.04-4.10 (3H, C5'H, C6'H₂), 4.16 (d, 1H, J = 3.5Hz, C4'H), 4.95 (d, 1H, J = 3.6Hz, C1'H), 5.64 (1H, C5aH); ¹³C NMR (125 MHz, CDCl₃) δ 60.84 (C6'), 62.78 (C6), 68.48 (C3'), 69.06 (C4'), 69.25 (C2'), 70.95 (C3), 71.33 (C5'), 72.01 (C1), 72.89 (C2), 77.09 (C4), 100.17 (C1'), 128.30 (C5a), 136.67 (C5); ESIMS (% rel. int.) m/z: 361.1116 (100, calcd. for C₁₃H₂₂O₁₀Na [M+Na]+: 361.1111), 339.1317 (0.8, calcd. for C₁₃H₂₃O₁₀ [M+H]⁺: 339.1291).

4.36. α-D-galactopyranosyl-(1→4)-α-Δ⁵⁵α-carbagalactopyranose (ii-46α)

In the similar manner as described for preparation of ii-46β, ii-45α (68.0 mg, 47.8 μmol) was treated with 90% aqueous formic acetic acid solution (0.2 ml),
CH₂Cl₂ (3.0 ml). The similar work up afforded the triq̇l (30.0 mg, 67%) as caramel. The product (24.0 ml, 25.6 μmol) was treated enpmløying DDQ (58.0 mg, 0.26 mmol), H₂O (0.2 ml), CH₂Cl₂ (2.0 ml). The similar work up afforded ii-46α (6.2 mg, 71%) as a white powder. [α]D 24° +110 (c 0.62, H₂O); 1H NMR (400 MHz, D₂O) δ 3.60, 3.62 (each s, 1H, C6’HH), 3.73 (2H, C₂’H, C₃’H), 3.86 (dd, 1H, J = 1.3, 2.6 Hz, C₄’H), 3.95 (dd, 1H, J = 4.1, 7.4 Hz, C₂H), 4.01-4.06 (3H, C6HH, C₅’H, C₃H), 4.11 (brd, 1H, J = 14.5Hz, C₆HH), 4.29 (1H, C₁H), 4.33 (brd, 1H, J = 3.8 Hz, C₄H), 5.01 (d, 1H, J = 3.0 Hz, C₁’H), 5.64 (1H, C₅aH); 13C NMR (125 MHz, CDCl₃) δ 61.04 (C₆’), 62.55 (C₆), 65.56 (C₁), 68.54 (C₂’), 69.17 (C₄’), 69.34 (C₃’), 69.99 (C₂), 70.15 (C₃), 71.43 (C₅’), 76.12 (C₄), 100.84 (C₁’), 125.93 (C₅a), 137.37 (C₅); ESIMS (% rel. int.) m/z: 361.1112 (100, calcd. for C₁₃H₂₂O₁₀Na [M+Na]⁺, 356.1568 (1.8, calcd. for C₁₃H₂₆N₂O₁₀ [M+NH₄]⁺: 356.1557), 339.1317 (0.6, calcd. for C₁₃H₂₃O₁₀ [M+H]⁺: 339.1291).

4.37. 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranosyl-(1→4)-2,3-di-O-(4-methoxyphenylmethyl)-6-O-triphenyl methyl-1-acetyltio-α-Δ⁵₅a-carbagalactopyranose (ii-47)

A solution of ii-45β (91.8 mg, 64.5 μmol) in CH₂Cl₂ (3.0 ml) was stirred with methansulfonic anhydride (45.0 mg, 258 μmol) and triethylamine (65.3 mg, 0.65 mmol) at -20°C for 10 min. After the mixture was stirred at 0°C for 10 min, the mixture was poured into H₂O (20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (20 ml), dried over MgSO₄ and the concentrated in vacuo to give crude mesylate, which was immediately diluted with DMF (3.0 ml). Potassium thioacetate (37.0 mg, 0.32 mmol) was added to the solution at room temperature for 5 h. The
mixture was poured into H₂O (25 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with H₂O (30 ml), and brine (30 ml) successively, dried over MgSO₄, and then concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 26:74) gave **ii-47** (93.8 mg, 98%) as an oil. [α]D²⁵ +71.16 (c 1.09, CHCl₃); IR (film) 2930, 1690, 1610, 1510, 1250, 1090, 1035, 820, 730, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 3H, COCH₃), 3.21 (t, 1H, J = 8.4 Hz, C6'H'H), 3.31 (2H, C6'H'H, C3'H), 3.66 (s, 3H, OCH₃), 3.73 (1H, C3'H), 3.74, 3.75, 3.78, 3.79 (each s, 3H, OCH₃), 3.86 (2H, C6HH, C2'H), 3.94 (brd, 1H, J = 13.9 Hz, C6HH), 4.08 (dd, 1H, J = 4.9, 8.9 Hz, C2H), 4.14 (brs, 1H, C4'H), 4.17 (d, 1H, J = 3.1 Hz, C4H), 4.34 (s, 2H, ArCH₂O), 4.36 (d, 1H, J = 10.4 Hz, ArCHHO), 4.39-4.41 (2H, C5'H, ArCHHO), 4.45 (d, 1H, J = 13.0 Hz, ArCHHO), 4.48 (d, 1H, J = 12.0 Hz, ArCHHO), 4.56 (s, 2H, ArCH₂O), 4.57 (d, 1H, J = 12.0 Hz, ArCHHO), 4.64 (t, 1H, J = 4.9 Hz, C1H), 4.79 (d, 1H, J = 10.4 Hz, ArCHHO), 4.89 (d, 1H, J = 3.5 Hz, C1'H), 5.45 (brd, 1H, J = 4.9 Hz, C5aH), 6.68-6.72 (6H, aromatic protons), 6.84 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.86 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.96 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.05 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.14-7.37 (36H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 30.66 (CH₃CO), 44.49 (C1), 55.14, 55.16 (each OCH₃), 55.21 (OCH₃ × 3), 61.92 (C6'), 64.59 (C6), 70.08 (C5'), 71.90, 72.19, 72.30, 72.39 (each ArCH₂O), 73.18 (C2), 74.04 (ArCH₂O), 74.40 (C4), 75.06 (C4'), 75.27 (C2'), 76.44 (C3), 79.04 (C3'), 86.66, 87.19 (each CPh₃), 99.26 (C1'), 113.33, 113.56, 113.58, 113.60 (× 2) (each aromatic carbons), 122.86 (C5a), 126.969, 126.974, 127.76, 127.77, 128.52, 128.72, 128.77, 129.01, 129.17, 129.46, 129.48, 130.49, 130.60, 130.91, 131.14, 131.16 (each aromatic carbons), 136.89 (C5), 143.75, 144.20, 158.82, 158.85, 158.88, 158.92, 158.99
(each aromatic carbons), 195.22 (C=O); ESIMS (% rel. int.) m/z: 1503.6074 (30, calcd. for C₉₃H₉₂O₁₅SNa [M+Na]⁺: 1503.6055), 1499.6515 (100, calcd. for C₉₃H₉₇NO₁₅S [M+H+NH₄]⁺: 1499.6579), 1498.6508 (98, calcd. for C₉₃H₉₆NO₁₅S [M+NH₄]⁺: 1498.6501).

4.38. 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranosyl-(1→4)-2,3-di-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-1-thio-α-Δ⁵⁵αcarbagalactopyranose (ii-48)

A solution of ii-47 (93.8 mg, 63.3 μmol) in DMF (3.0 ml) was stirred with hydrazine acetate (12.0 mg, 261 μmol) at 0°C for 30 min, then warmed to room temperature very slowly. After the mixture was stirred for 2 h, the mixture was poured into H₂O (30 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with H₂O (30 ml), and brine (30 ml) successively, dried over MgSO₄, and then concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 26:74) gave ii-48 (76.8 mg, 84%) as an oil. ¹H NMR (500 MHz, CDCl₃) δ 1.64 (d, 1H, J = 6.7 Hz, C1SH), 3.21 (t, 1H, J = 8.4 Hz, C6’HH), 3.33 (dd, 1H, J = 5.4, 8.4 Hz, C6’HH), 3.63 (dd, 1H, J = 3.3, 9.5 Hz, C3H), 3.65, 3.74, 3.76 (each s, 3H, OCH₃), 3.78-3.83 (8H, C3’H, C1H, OCH₃ × 2), 3.86 (brd, 1H, J = 15.6 Hz, C6HH), 3.88 (dd, 1H, J = 3.5, 10.2 Hz, C2’H), 3.95 (dd, 1H, J = 4.9, 9.5 Hz, C2H), 3.98 (brd, 1H, J = 15.6 Hz, C6HH), 4.15 (brs, 1H, C4’H), 4.17 (d, 1H, J = 3.3 Hz, C4H), 4.34-4.40 (4H, ArCHHO × 4), 4.45 (brdd, 1H, J = 5.4, 8.4 Hz, C5’H), 4.47 (d, 1H, J = 12.9 Hz, ArCHHO), 4.57 (s, 2H, ArCH₂O), 4.59, 4.63 (each d, 1H, J = 11.8 Hz, ArCHHO), 4.77 (d, 1H, J = 10.4 Hz, ArCHHO), 4.93 (d, 1H, J = 3.5 Hz, C1’H), 5.48 (brd, 1H, J = 4.3 Hz, C5aH), 6.67 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.71 (4H, aromatic protons), 6.85 (4H, aromatic protons).
6.96 (brd, 2H, \( J = 8.6 \) Hz, aromatic protons), 7.06 (brd, 2H, \( J = 8.5 \) Hz, aromatic protons), 7.13-7.20 (20H, aromatic protons), 7.25 (4H, aromatic protons), 7.29 (6H, aromatic protons), 7.36 (6H, aromatic protons). This sample was immediately used for the next coupling reaction with ii-50.

4.39. Methyl 2,3-di-O-(4-methoxyphenylmethyl)-\( \alpha \)-D-glucopyranoside (ii-49)

Sodium hydrde (washed with hexane 2.00 g, 83.3 mmol) slowly was added to a DMF solution (50 ml) of ii-15 (6.50 g, 20.8 mmol) at room temperature. Upon the addition of the substrate, \( \text{H}_2 \) gas was bubbled. After the mixture was stirred for 10 min, 4-methoxybenzyl bromide (16.7 g, 83.1 mmol) was added at 0 °C. After the mixture was stirred at 0°C for 10 min, the cooling bath was removed and the mixture was stirred at room temperature for 20 min. Methanol (10 ml) and \( \text{Et}_3\text{N} \) (10 ml) were successively added to decompose excess reagent. After stirring for additional 30 min, the mixture was poured into \( \text{H}_2\text{O} \) (200 ml), and the aqueous layer was extracted with \( \text{EtOAc} \) (150 ml \( \times \) 3). The combined organic layer was washed successively with \( \text{H}_2\text{O} \) (200 ml), and brine (200 ml), dried over \( \text{MgSO}_4 \), and then concentrated in vacuo to give the crude solid. Recrystallization from \( \text{EtOAc:hexane} \) (30:70) gave methyl 4,6-O-(4-methoxybenzylidene)-2,3-O-di-(4-methoxyphenylmethyl)-\( \alpha \)-D-glucopyranoside (9.30 g, 81%) as needles. mp 128 °C; \( [\alpha]_D^{25} \) -41.2 (c 1.44, CHCl₃); IR (film) 2910, 1615, 1515, 1370, 1250, 1085, 1045, 1035, 825 cm⁻¹; \(^1\text{H} \) NMR (400 MHz, CDCl₃) δ 3.38 (s, 3H, OCH₃), 3.50 (dd, 1H, \( J = 3.7, 9.3 \) Hz, C2H), 3.55 (t, 1H, \( J = 9.3 \) Hz, C4H), 3.67 (t, 1H, \( J = 10.2 \) Hz, C6HH), 3.78 (1H, C5H), 3.79, 3.80, 3.81 (each s, 3H, OCH₃), 3.99 (t, 1H, \( J = 9.3 \) Hz, C3H), 4.23 (dd, 1H, \( J = 4.8, 10.0 \) Hz, C6HH), 4.52 (d, 1H, \( J = 3.7 \) Hz, C1H), 4.62 (d, 1H, \( J = 11.9 \) Hz, C1H).
Hz, ArCHHO), 4.73-4.82 (3H, ArCHHO × 3), 5.49 (s, 1H, ArCH), 6.83 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.86 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.90 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.28 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.29 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.40 (brd, 2H, J = 8.7 Hz, aromatic protons); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 55.22, 55.23, 55.26, 55.28 (each OCH$_3$), 62.32 (C5), 68.98 (C6), 73.37, 74.97 (each ArCH$_2$O), 78.27 (C3), 78.71 (C2), 82.05 (C4), 99.31 (Cl), 101.20 (ArCH), 113.52, 113.69, 113.80, 127.31, 129.65, 129.70, 129.95, 130.27, 130.94, 159.15, 159.37, 159.96 (each aromatic carbons); ESIMS (% rel. int.) m/z: 575.2272 (3.9, calcd. for C$_{31}$H$_{36}$O$_9$Na [M+Na$^+$: 575.2257), 553.2455 (100, calcd. for C$_{31}$H$_{37}$O$_9$ [M$^+$: 553.2438).

A solution of the product (6.20 g, 11.2 mmol) in 90% aqueous acetic acid solution (100 ml) was stirred at 60 °C for 10 min. After cooling, the mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt:hexane = 70:30) to give ii-49 as an oil. [α]$_D^{24}$ +5.4 (c 1.65, CHCl$_3$); IR (film) 3465, 2930, 1610, 1510, 1250, 1090, 1050, 1035, 820 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.98 (dd, 1H, J = 6.0, 6.6 Hz, C6OH), 2.32 (d, 1H, J = 2.6 Hz, C4OH), 3.37 (s, 3H, OCH$_3$), 3.44-3.49 (2H, C2H, C4H), 3.59 (dt, 1H, J = 4.1, 9.7 Hz, C5H), 3.69-3.79 (3H, C3H, C6H$_2$), 3.796, 3.802 (each s, 3H, OCH$_3$), 4.54 (d, 1H, J = 3.5 Hz, C1H), 4.59 (d, 1H, J = 11.8 Hz, ArCHHO), 4.61 (d, 1H, J = 11.2 Hz, ArCHHO), 4.71 (d, 1H, J = 11.8 Hz, ArCHHO), 4.93 (d, 1H, J = 11.2 Hz, ArCHHO), 6.87 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.88 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.28 (4H, aromatic protons), $^{13}$C NMR (100 MHz, CDCl$_3$) δ 55.22 (OCH$_3$), 55.24 (OCH$_3$ × 2), 62.50 (C6), 70.43 (C4), 70.65 (C5), 72.77, 74.93 (each ArCH$_2$O), 79.42 (C2), 80.87 (C3), 98.27 (C1), 113.87, 114.03, 129.60, 129.69, 130.08, 130.83, 130.97.
159.37, 159.45 (each aromatic carbons); ESIMS (% rel. int.) m/z: 457.1838 (18, calcd. for C_{23}H_{30}O_{8}Na [M+Na]^+: 457.1833), 453.2316 (26, calcd. for C_{23}H_{35}NO_{6} [M+H+NH_{4}]^+: 453.2363), 452.2285 (100, calcd. for C_{23}H_{35}NO_{6} [M+NH_{4}]^+: 452.2284).

4.40. Allyl [methyl 2,3-di-O-(4-methoxyphenylmethyl)-4-O-trifluoro methanesulfonyl-α-D-glucopyranosid]uronate (ii-50)

A suspension of ii-49 (500 mg, 1.15 mmol) in a mixture of CH_{2}Cl_{2} (10 ml) and H_{2}O (5.0 ml) was stirred with PhI(OAc)_{2} (1.20 g, 3.61 mmol) and TEMPO (56.0 mg, 0.36 mmol) at room temperature for 20 min. Aqueous 10% Na_{2}S_{2}O_{3} solution (2.0 ml) was added and the mixture was poured into H_{2}O (100 ml) and the aqueous layer was extracted with AcOEt (100 ml × 3). The combined extract was washed with brine (100 ml), dried over MgSO_{4}, and then concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc 100%) gave the carboxylic acid (434 mg, 84%) as an oil. [α]_{D}^{25} +7.3 (c 1.83, CHCl_{3}); IR (film) 3470, 2935, 1740, 1610, 1510, 1250, 1110, 1055, 820 cm^{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl_{3}) δ 3.40 (s, 3H, OCH_{3}), 3.48 (dd, 1H, J = 3.4, 9.4 Hz, C2H), 3.71 (dd, 1H, J = 8.6, 9.6 Hz, C2H), 3.79, 3.80 (each s, 3H, OCH_{3}), 3.81 (1H, C3H), 4.12 (d, 1H, J = 9.6 Hz, C5H), 4.57 (d, 1H, J = 11.8 Hz, ArCHHO), 4.60 (d, 1H, J = 3.4 Hz, C1H), 4.73 (d, 1H, J = 11.8 Hz, ArCHHO), 4.74 (d, 1H, J = 10.9 Hz, ArCHHO), 4.82 (d, 1H, J = 10.9 Hz, ArCHHO), 6.86 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.87 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.26 (brd, 2H, J = 8.7 Hz, aromatic protons); \textsuperscript{13}C NMR (100 MHz, CDCl_{3}) δ 55.22 (OCH_{3} × 2), 55.95 (OCH_{3}), 69.66 (C5), 71.66 (C4), 73.23, 75.11 (each ArCH_{2}O), 77.97 (C2), 79.98 (C3), 98.65 (C1), 113.87
(× 2), 129.66, 129.76, 129.91, 130.60, 159.28, 159.46 (each aromatic carbons), 172.97 (C=O); ESIMS (% rel. int.) m/z: 471.1645 (38, calcd. for C_{23}H_{28}O_{9}Na [M+Na]^+: 471.1631), 466.2087 (100, calcd. for C_{23}H_{32}NO_{9} [M+NH4]^+: 466.2077).

A solution of the product (434 mg, 0.97 mmol) in CH_{2}Cl_{2} (10 ml) was stirred with allyl alcohol (169 mg, 2.91 mmol), 1-hydroxybenzotriazole monohydrate (148 mg, 0.97 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (558 mg, 2.91 mmol) at room temperature for 1 h. The mixture was poured into aqueous HCl solution (5.0×10^{-3} M, 50 ml) and the aqueous layer was extracted with EtOAc (50 ml × 3). The combined organic layer was washed with brine (50 ml), dried over MgSO_{4}, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 26:74) to give the allyl ester (411 mg, 68%) as an oil. [α]_{D}^{24} +9.7 (c 0.95, CHCl_{3}); IR (film) 3490, 2920, 1740, 1610, 1510, 1240, 1030, 985, 820 cm^{-1}; ^{1}H NMR (400 MHz, CDCl_{3}) δ 2.77 (d, 1H, J = 1.9 Hz, C4OH), 3.42 (s, 3H, OCH_{3}), 3.50 (dd, 1H, J = 3.3, 9.1 Hz, C2H), 3.77-3.80 (2H, C3H, C4H), 3.800, 3.802 (each s, 3H, OCH_{3}), 4.15 (d, 1H, J = 9.6 Hz, C5H), 4.58 (d, 1H, J = 11.9 Hz, ArCHHO), 4.61 (d, 1H, J = 3.3 Hz, C1H), 4.68 (2H,CH_{2}CHCH_{2}O), 4.70 (d, 1H, J = 11.0 Hz, ArCHHO), 4.73 (d, 1H, J = 11.9 Hz, ArCHHO), 4.83 (d, 1H, J = 11.0 Hz, ArCHHO), 5.25 (ddd, 1H, J = 1.1, 2.5, 10.4 Hz, CHHCHCH_{2}O), 5.34 (ddd, 1H, J = 1.5, 2.5, 17.3 Hz, CHHCHCH_{2}O), 5.91 (1H, CH_{2}CHCH_{2}O), 6.86 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.87 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.27 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.29 (brd, 2H, J = 8.6 Hz, aromatic protons); ^{13}C NMR (100 MHz, CDCl_{3}) δ 55.26 (OCH_{3} × 2), 55.85 (OCH_{3}), 66.15 (CH_{2}CHCH_{2}O), 70.76 (C5), 71.67 (C4), 73.22, 75.03 (each ArCH_{2}O), 78.09 (C2), 79.99 (C3), 98.75 (C1), 113.89, 113.93 (each aromatic
carbons), 119.14 (CH₂CHCH₂O), 129.59, 129.79, 130.02, 130.75 (each aromatic carbons), 131.26 (CH₂CHCH₂O), 159.33, 159.49 (each aromatic carbons), 169.79 (C=O); ESIMS (% rel. int.) m/z: 511.1934 (15, calcd. for C₂₆H₃₂O₉Na [M+Na]⁺: 511.1944), 506.2378 (100, calcd. for C₂₆H₃₆NO₉ [M+NH₄]⁺: 506.2390).

Trifluoromethanesulfonic anhydride (67.7 mg, 240 μmol) was added to a mixture of the product (80.0 mg, 164 μmol) and pyridine (38.0 mg, 480 μmol) in CH₂Cl₂ (2.0 ml) at 0 °C. After 10 min, the mixture was poured into H₂O (20 ml), and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (30 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 20:80) to give ii-50 (98.0 mg, 96 %) as an oil.

1H NMR (400 MHz, CDCl₃) δ 3.41 (s, 3H, OCH₃), 3.58 (d, 1H, J = 3.4, 9.5 Hz, C2H), 3.81 (s, 6H, OCH₃ × 2), 4.02 (t, 1H, J = 9.5 Hz, C3H), 4.37 (d, 1H, J = 10.2 Hz, C5H), 4.50 (d, 1H, J = 3.4 Hz, C1H), 4.51 (d, 1H, J = 10.8 Hz, ArCHHO), 4.61, 4.71 (each dd, 1H, J = 1.2, 6.0, 13.0 Hz, CH₂CHCHHO), 4.73 (d, 1H, J = 10.8 Hz, ArCHHO), 4.74, 4.83 (each d, 1H, J = 9.9 Hz, ArCHHO), 4.87 (dd, 1H, J = 9.5, 10.2 Hz, C4H), 5.29 (ddd, 1H, J = 1.2, 2.3, 10.3 Hz, CHHCHCH₂O), 5.36 (ddd, 1H, J = 1.2, 2.3, 17.2 Hz, CHHCHCH₂O), 5.91 (ddt, 1H, J = 6.0, 10.3, 17.2 Hz, CH₂CHCH₂O), 6.86 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.87 (brd, 2H, J = 8.8 Hz, aromatic protons), 7.24 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.29 (brd, 2H, J = 8.8 Hz, aromatic protons). This sample was immediately used for the next coupling reaction.

4.41. 2,3,4-tri-O-(4-methoxyphenylmethyl)-6-O-triphenylmethyl-α-D-galactopyranosyl-(1→4)-[2,3-di-O-(4-methoxyphenylmethyl)-6-O-triphenyl
methyl-1-thio-α-Δ^5,5a-carbagalactopyranosyl]- (1→4)-{Allyl [methyl 2,3-di- 
O-(4-methoxyphenylmethyl)-α-D-galactopyranosid]uronate} (ii-51)

A mixture of ii-48 (76.8 mg, 53.3 µmol) and ii-50 (66.0 mg, 106 µmol) in 
DMF (2.5 ml) was stirred with NaH (1.5 mg, 63 µmol) at room temperature for 
20 min. The mixture was poured into H2O (20 ml) and the aqueous layer was 
extracted with EtOAc (20 ml x 3). The combined organic layer was washed 
successively with H2O (30 ml), and brine (30 ml), dried over MgSO4, and then 
concentrated in vacuo Silica gel column chromatography of the residue 
(EtOAc:benzene = 6:94) gave ii-51 (36.7 mg, 36%) along with recovered ii-48 
(31.5 mg, 41%) both as oil. [α]D^25 +49.3 (c 1.25, CHCl3); IR (film) 2930, 1760, 
1610, 1510, 1250, 1090, 1035, 820, 700 cm^-1; ^1H NMR (500 MHz, CDCl3) δ 3.18 
(t, 1H, J = 8.3 Hz, C6"HH), 3.31 (dd, 1H, J = 5.4, 8.3 Hz, C6"HH), 3.36, 3.65, 
3.67 (each s, 3H, OCH3), 3.71-3.77 (18H, C3"H, C3'H, C6’HH, OCH3 x 5), 3.81 
(dd, 1H, J = 3.4, 10.3 Hz, C2"H), 3.86 (brd, 1H, J = 13.9 Hz, C6’HH), 3.89 (1H, 
C4H), 3.94 (1H, C1’H), 4.02 (1H, C2’H), 4.06-4.08 (2H, C3H, C4”H), 4.11-4.14 
(2H, C2H, C4’H), 4.18, 4.22 (each d, 1H, J = 11.9 Hz, ArCHHO), 4.33 (d, 1H, J 
= 10.5 Hz, ArCHHO), 4.38 (1H, C5”H), 4.41 (d, 1H, J = 12.4 Hz, ArCHHO), 
4.49-4.53 (6H, CH2CHCHHO, ArCHHO, ArCH2O x 2), 4.56 (d, 1H, J = 10.8 Hz, 
ArCHHO), 4.58 (d, 1H, J = 11.7 Hz, ArCHHO), 4.60 (d, 1H, J = 3.6 Hz, C1H), 
4.639 (d, 1H, J = 2.1 Hz, C5H), 4.641 (d, 1H, J = 11.7 Hz, ArCHHO), 4.75 (d, 1H, 
J = 10.5 Hz, ArCHHO), 4.78 (d, 1H, J = 10.8 Hz, ArCHHO), 4.83 (d, 1H, J = 3.4 
Hz, C1”H), 4.86 (brdd, 1H, J = 5.5, 12.7 Hz, CH2CHCHHO), 5.20 (brdd, 1H, J = 
1.2, 10.4 Hz, CHHCHCH2O), 5.30 (brdd, 1H, J = 1.2, 17.2 Hz, CHHCHCH2O), 
5.88 (1H, C5a’H), 5.94 (ddt, 1H, J = 5.5, 10.4, 17.2 Hz, CH2CHCH2O), 6.69 (6H, 
aromatic protons), 6.77 (4H, aromatic protons), 6.80 (brd, 2H, J = 8.6 Hz, 
aromatic protons), 6.85 (brd, 2H, J = 8.7 Hz, aromatic protons), 6.93 (brd, 2H, J
= 8.7 Hz, aromatic protons), 6.99 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.09-7.36 (40H, aromatic protons); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 47.00 (C1’), 50.26 (C4), 55.08 (OCH$_3 \times$ 3), 55.18 (OCH$_3 \times$4), 55.95 (OCH$_3$), 62.07 (C6’’), 64.51 (C6’), 65.88 (CH$_2$CHCH$_2$O), 70.07 (C5’’), 70.37 (C5), 72.13, 72.30, 72.35, 72.42, 72.62, 73.53, 73.97 (each ArCH$_2$O), 75.08 (C4’, C4’’), 75.26 (C2’’), 75.77 (C2), 76.19 (C3’), 77.37 (C3, C2’), 78.89 (C3’’), 86.62, 87.10 (each CPh$_3$), 98.93 (Cl’), 99.58 (Cl), 113.30, 113.49, 113.56, 113.61, 113.66, 113.77, 113.82 (each aromatic carbons), 118.92 (CH$_2$CHCH$_2$O), 125.04 (C5a’), 126.93 ($\times$2), 127.73, 127.77, 128.57, 128.71, 128.75, 129.05, 129.13 ($\times$ 2), 129.47, 129.55, 129.85, 130.38, 130.49 ($\times$ 2), 130.93, 131.02, 131.08, 131.14 (each aromatic carbons), 131.92 (CH$_2$CHCH$_2$O), 135.18 (C5’), 143.76, 144.24, 158.81 ($\times$ 2), 158.87 ($\times$ 2), 158.96, 159.00, 159.30 (each aromatic carbons), 168.15 (C=O); ESIMS (% rel. int.) m/z: 1931.7912 (21, calcd. for C$_{117}$H$_{120}$O$_{22}$SNa [M+Na]$^+$: 1931.7890), 1927.8233 (100, calcd. for C$_{117}$H$_{125}$NO$_{22}$S [M+H+NH$_4$]$^+$: 1927.8414), 1926.8204 (72, calcd. for C$_{117}$H$_{124}$NO$_{22}$S [M+NH$_4$]$^+$: 1926.8336).

4.42. 2,3,4-tri-O-(4-methoxyphenylmethyl)-α-D-galactopyranosyl-(1→4)-[2,3-di-O-(4-methoxyphenylmethyl)-1-thio-α-\(\Delta^5\)carbagalactopyranosyl]-(1→4)-\{Allyl [methyl 2,3-di-O-(4-methoxyphenylmethyl)-α-D-galactopyranosid]uronate\} (ii-52)

90% formic acetic acid solution (0.5 ml) was added to a solution of ii-51 (36.7 mg, 19.2 µmol) in a mixture of CH$_2$Cl$_2$ (2.0 ml) and MeOH (1.0 ml) at 0 °C. After stirring at 0°C for 1 h, the mixture was warmed to room temperature slowly. After the mixture was stirred for 1 h, saturated aqueous NaHCO$_3$ solution (2.0 ml) was added at 0 °C. The mixture was poured into H$_2$O (20 ml) and the aqueous layer was extracted with EtOAc (20 ml $\times$ 3). The combined organic layer was washed
with brine (30 ml), dried over MgSO₄, and then concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 50:50) gave **ii-52** (20.0 mg, 73%) as an oil. [α]D²⁶ +96.5 (c 1.24, CHCl₃); IR (film) 3465, 2940, 1760, 1610, 1510, 1460, 1250, 1090, 1035, 820 cm⁻¹; °H NMR (500 MHz, CDCl₃) δ 1.67 (1H, C6”OH), 3.25 (dd, 1H, J = 4.9, 5.1, 11.3 Hz, C6”HH), 3.35 (s, 3H, OCH₃), 3.48 (dd, 1H, J = 1.5, 6.7, 11.3 Hz, C6”HH), 3.57 (2H, C5”H, C4H), 3.67 (2H, C4”H, C1’H), 3.72 (dd, 1H, J = 3.4, 5.6 Hz, C3’H), 3.75 (s, 3H, OCH₃), 3.77-3.86 (21H, C6’HH, C2’H, C3”H, OCH₃×6), 3.91 (dd, 1H, J = 3.7, 9.9 Hz, C2H), 3.95 (1H, C6’HH), 3.98 (dd, 1H, J = 3.6, 10.1 Hz, C2”H), 4.05 (dd, 1H, J = 4.0, 9.9 Hz, C3H), 4.37 (d, 1H, J = 11.8 Hz, ArCHHO), 4.40 (1H, C4’H), 4.42-4.48 (31H, ArCHHO × 2, CH₂CHCH₂O), 4.52 (d, 1H, J = 11.3 Hz, ArCHHO), 4.56 (d, 1H, J = 11.7 Hz, ArCHHO), 4.58 (d, 1H, J = 11.7 Hz, ArCHHO), 4.59 (d, 1H, J = 3.7 Hz, C1H), 4.61-4.70 (5H, ArCHHO × 3, C5H, CH₂CHCHHO), 4.72 (d, 1H, J = 11.3 Hz, ArCHHO), 4.74 (d, 1H, J = 11.2 Hz, ArCHHO), 4.77 (d, 1H, J = 11.7 Hz, ArCHHO), 4.79 (d, 1H, J = 3.6 Hz, C1”H), 4.81 (brdd, 1H, J = 1.2, 10.4 Hz, CHHCHCH₂O), 5.24 (brdd, 1H, J = 1.4, 17.2 Hz, CHHCHCH₂O), 5.88 (2H, C5a’H, CH₂CHCH₂O), 6.77 (brd, 2H, J = 8.8 Hz, aromatic protons), 6.84-6.87 (10H, aromatic protons), 6.90 (brd, 2H, J = 8.7 Hz, aromatic protons), 7.14 (brd, 2H, J = 8.6 Hz, aromatic protons), 7.21 (4H, aromatic protons), 7.28 (6H, aromatic protons), 7.32 (brd, 2H, J = 8.8 Hz, aromatic protons); °C NMR (125 MHz, CDCl₃) δ 47.78 (C1’), 52.47 (C4), 55.18, 55.19, 55.22 (each OCH₃), 55.24 (OCH₃ × 2), 55.25 (OCH₃ × 2), 55.95 (OCH₃), 62.54 (C6”), 64.60 (C6’), 65.90 (CH₂CHCH₂O), 70.76 (C5), 70.88 (C5”), 72.46, 72.73, 73.15, 73.41, 73.47, 73.85, 73.91 (each ArCH₂O), 74.91 (C4”), 75.20 (C2”), 76.20 (C3), 76.48 (C2 or C2’), 76.52 (C2 or C2’), 76.66 (C3”), 129
77.70 (C4'), 78.67 (C3''), 99.33 (Cl), 101.08 (Cl''), 113.67, 113.77, 113.79,
113.80, 113.82, 113.85, 113.87 (each aromatic carbons), 119.00 (CH₂CHCH₂O),
127.31 (C5a'), 129.14, 129.28, 129.49, 129.59, 129.74, 129.90, 130.00, 130.21,
130.24, 130.30, 130.31 (x2), 130.50, 130.56 (each aromatic carbons), 131.56
(CH₂CHCH₂O), 135.79 (C5''), 159.09, 159.18, 159.20, 159.30, 159.35, 159.37,
159.48 (each aromatic carbons), 168.35 (C=O); ESIMS (% rel. int.) m/z:
1447.5707 (15, calcd. for C₇₉H₉₂O₂₂SNa [M+Na]: 1447.5699), 1442.5117 (100,
calcd. for C₇₉H₉₆NO₂₂S [M+NH₄]: 1442.6145).

4.43. α-D-galactopyranuronosyl-(1→4)-1-thio-α-L-5,5α-carbagalactopyranosyl-(1→4)-(methyl α-D-galactopyranosid)uronic acid (ii-2)

Oxalylchloride (24.0 mg, 189 µmol) was added to a solution of
dimethylsulfoxide (29.6 mg, 379 µmol) in CH₂Cl₂ (1.0 ml) at -78 °C and the
mixture was stirred for 10 min. A solution of ii-52 (45.0 mg, 31.6 µmol) in
CH₂Cl₂ (1.5 ml) was added to this mixture, and the resulting mixture was stirred
at the same temperature for 40 min. After triethylamine (57.6 mg, 569 µmol)
was added, the cooling bath was removed. The mixture was further stirred at
room temperature for additional 20 min. The mixture was poured into H₂O (20
ml) and the aqueous layer was extracted with EtOAc (20 ml x 3). The combined
organic layer was washed with brine (30 ml), dried over MgSO₄, and then
concentrated in vacuo. After diluting with a mixture of 2-methyl-2-propanol
(1.0 ml) and 2-methyl-2-butene (66.4 mg, 0.95 mmol), sodium
dihydrogenphosphate dehydrate (69.0 mg, 442 µmol) and sodium chlorite (29.0
mg, 321 µmol) were successively added at room temperature.
2-methyl-2-propanol (5.0 ml) was added to the mixture until solid dissolved.
After stirring for 15 min, the mixture was poured into H₂O (20 ml) and the aqueous layer was extracted with AcOEt (15 ml × 3). The combined organic layer was washed with brine (15 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was passed through silica gel pad to give a residue, which was dissolved in THF (1.4 ml). The solution was stirred with pyrrolidine (9.0 mg, 127 μmol) and tetrakis(triphenylphosphine)palladium (3.7 mg, 3.2 μmol) at room temperature. After 15 min, the mixture was concentrated in vacuo. A suspension of the residue in a mixture of CH₂Cl₂ (1.0 ml) and H₂O (100 μl) was stirred with 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) (108 mg, 476 μmol) at room temperature for 36 hours. The mixture was poured into water (10 ml) and washed with EtOAc (10 ml × 2). The aqueous solution was concentrated in vacuo. After dilution with small amount of H₂O (ca. 0.3 mL), the resulting solution was loaded on a ODS Sep-Pak® cartridge (5.0 g) to give ii-2 (16.2 mg, 90%) which contained small amount of impurities based on its ¹H-NMR spectrum. HPLC (Inertsil® DIOL, 4.6×150 mm, H₂O:CH₃CN:TFA 10:90:0.01, 1.0 ml/min flow, tᵣ = 16 min) gave pure 2. [α]D²⁴⁺64.7 (c 1.60, D₂O); ¹H NMR (500 MHz, CDCl₃) δ 3.56 (s, 3H, OCH₃), 3.91 (2H, C₂H, C₄H), 3.94 (dd, 1H, J = 4.0, 10.3 Hz, C’₂H, 4.06 (dd, 1H, J = 3.4, 10.3 Hz, C”₃H), 4.14 (dd, 1H, J = 3.9, 9.1 Hz, C’₃H), 4.23 (dd, 1H, J = 4.1, 5.0 Hz, C’₁H), 4.35 (dd, 1H, J = 4.4, 10.2 Hz, C₃H), 4.39 (dd, 1H, J = 5.0, 9.1 Hz, C₂’H), 4.49 (dd, 1H, J = 1.3, 3.4 Hz, C’₄H), 4.87 (d, 1H, J = 3.9 Hz, C’₄H), 4.98 (d, 1H, J = 2.1 Hz, C₅H), 5.03 (d, 1H, J = 4.1 Hz, C₁H), 5.08 (d, 1H, J = 1.3 Hz, C’₅H), 5.47 (d, 1H, J = 4.0 Hz, C’₁H), 7.30 (d, 1H, J = 4.1 Hz, C₅a’H); ¹³C NMR (125 MHz, CDCl₃) δ 50.87 (C’₁), 54.70 (C₄), 58.22 (OCH₃), 70.44 (C’₂), 70.85 (C’₂’), 71.12 (C’₃’), 71.43 (C’₃”), 71.52 (C₂), 71.68 (C’₃”), 72.63 (C”₄”), 72.72 (C₅), 73.58 (C’₅”), 76.26 (C’₄”), 102.17 (C’₁”, C₁), 10.82 (C₅a’), 144.41 (C’₅”), 172.01, 175.35,
175.49 (each C=O); ESIMS (%, rel. int.) m/z: 595.0954 (100, calcd. for C_{20}H_{28}O_{17}SNa [M+Na]^+: 595.0945), 590.1391 (56, calcd. for C_{20}H_{32}NO_{17}S [M+NH_{4}]^+: 590.1391).

Preliminary experiment of endo-PG1 inhibitory activity

A 62.0 μl tetragalacturonic acid solution (The quantity was determined by a peak area of HPLC at 210 nm, which was the same as that of analogue ii-2 solution. sodium acetate pH 4.7) was mixed with 38.0 μl transition state analogue ii-2 solution (0.5 mg ml⁻¹), and then incubated at 30°C for 5 min. (The control was used water in substitution for analogue ii-2 solution.) Then endo-PG1 solution (5.0 μl) was added to the mixture and incubated another 12 h at 30°C, respectively. After stop reaction through a Dowex 50W column, the mixtures were analyzed by HPLC (Shodex Sugar SH1821 Column (8×300 mm) with 0.005 N H_2SO_4 aqueous solution as eluent, flow rate of 3.0 mL/min, absorption at 210 nm.).

4.44. 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranose (iii-4)

A solution of acetyl 2,3,6-tri-O-acetyl-4-O-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl]-1-thio-β-D-glucopyranose (iii-3) (105 mg, 150 μmol) was stirred with sodium methoxide (32.6 mg 600 μmol) in a mixture of CH_2Cl_2 (2.0 ml) and MeOH (2.0 ml) at -15 °C for 30 min. The mixture was poured into aqueous HCl solution (5.0×10⁻³ M, 20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (20 ml), dried over MgSO₄, and then concentrated in vacuo to give crude thiol iii-4. ^1H NMR (500 MHz, CDCl₃) δ 1.98, 2.01, 2.02, 2.03, 2.07, 2.09, 2.14 (3H,
s, CH₃CO₂), 2.56 (1H, d, J = 9.6 Hz, SH), 3.62 (1H, ddd, J = 2.0, 5.3, 9.6 Hz, C5H), 3.65 (1H, ddd, J = 2.2, 5.3, 9.3 Hz, C5′H), 3.78 (1H, t, J = 9.6 Hz, C4H), 4.04 (1H, dd, J = 2.2, 12.5 Hz, C6′HH), 4.09 (1H, dd, J = 5.3, 12.1 Hz, C6HH), 4.37 (1H, dd, J = 4.5, 12.5 Hz, C6′HH), 4.48 (1H, dd, J = 2.0, 12.1 Hz, C6HH), 4.50 (1H, d, J = 8.0 Hz, C1′H), 4.52 (1H, t, J = 9.6 Hz, C1H), 4.89 (1H, t, J = 9.6 Hz, C2H), 4.92 (H, dd, J = 8.0, 9.3 Hz, C2′H), 5.06 (1H, t, J = 9.3 Hz, C4′H), 5.14 (1H, t, J = 9.3 Hz, C3′H), 5.18 (1H, t, J = 9.6 Hz, C3H). This sample was immediately used for the next coupling reaction with iii-6.

4.45. Methyl 2,3,6-tri-O-benzoyl-4-O-trifluoromethanesulfonyl-α-D-galactopyranoside (iii-6a)

Trifluoromethanesulfonic anhydride (42.3 mg, 150 μmol) was added to a mixture of methyl 2,3,6-tri-O-benzoyl α-D-galactopyranoside (iii-5a, 68.0 mg, 130 μmol) and pyridine (23.7 mg, 300 μmol) in CH₂Cl₂ (1.0 ml) at 0 °C and the mixture was stirred at the same temperature for 20 min. The mixture was poured into H₂O (30 ml), and the aqueous layer was extracted with EtOAc (30 ml x 3). The combined organic layer was washed with brine (30 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 10:90) to give iii-6a (74.0 mg, 92%) as an oil.

¹H NMR (500 MHz, CDCl₃) δ 3.46 (3H, s, OCH₃), 4.35 (1H, dd, J = 7.0, 11.3 Hz, C6HH), 4.59 (1H, brt, J = 6.8 Hz, C5H), 4.69 (1H, dd, J = 6.5, 11.3 Hz, C6HH), 5.29 (1H, d, J = 3.7 Hz, C1H), 5.59 (1H, brd, J = 2.8 Hz, C4H), 5.60 (1H, dd, J = 3.7, 10.7 Hz, C2H), 5.95 (1H, dd, J = 2.8, 10.7 Hz, C3H), 7.34-7.61 (9H, aromatic protons), 7.96 (1H, brdd, J = 1.2, 8.3 Hz, aromatic protons), 8.03-8.07 (4H, aromatic protons), This sample was immediately used for next step.
4.46. Methyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzoyl-4-thio-α-D-glucopyranoside (iii-7a)

Sodium hydride (washed with hexane, 5.4 mg, 225 µmol) was added to a mixture of iii-4 and iii-6a in THF (2.0 mL) at 0°C. After the mixture was stirred for 1 h at the same temperature, the mixture was poured into 500 mM aqueous HCl solution (20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (20 ml), dried over MgSO₄, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc:benzene = 22:78) gave iii-7a (120 mg, 73% in 2 steps) as an oil. [α]D²⁶ +23.5 (c 1.17, CHCl₃); IR (film) 2955, 1750, 1270, 1230, 1040, 715 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.53, 1.97, 1.99, 2.01, 2.06, 2.09, 2.11 (each 3H, s, CH₃CO₂ × 7), 3.29 (1H, t, J = 11.1 Hz, C4H), 3.48 (3H, s, C1OCH₃), 3.65 (1H, ddd, J = 2.1, 4.5, 9.4 Hz, C5′H), 3.66 (1H, ddd, J = 2.0, 4.2, 9.1 Hz, C5′H), 3.74 (1H, t, J = 9.1 Hz, C4′H), 3.97 (1H, dd, J = 4.2, 12.2 Hz, C6′HH), 4.04 (1H, dd, J = 2.1, 12.5 Hz, C6′HH), 4.36 (1H, dd, J = 4.5, 12.5 Hz, C6′HH), 4.47 (1H, ddd, J = 2.1, 3.8, 11.1 Hz, C5H), 4.52 (1H, d, J = 7.9 Hz, C1′H), 4.66 (1H, dd, J = 2.0, 12.2 Hz, C6′HH), 4.76 (1H, dd, J = 2.1, 12.1 Hz, C6HH), 4.80 (1H, dd, J = 3.8, 12.1 Hz, C6HH), 4.84 (1H, dd, J = 9.1, 10.1 Hz, C2′H), 4.93 (1H, dd, J = 7.9, 9.4 Hz, C2′H), 4.98 (1H, d, J = 10.1 Hz, C1′H), 5.07 (1H, t, J = 9.4 Hz, C4′H), 5.15 (1H, t, J = 9.4 Hz, C3′H), 5.18 (1H, t, J = 9.1 Hz, C3′H), 5.20 (1H, d, J = 3.5 Hz, C1H), 5.25 (1H, dd, J = 3.5, 9.6 Hz, C2H), 6.00 (1H, dd, J = 9.6, 11.1 Hz, C3H), 7.35-7.40 (4H, aromatic protons), 7.48-7.54 (4H, aromatic protons), 7.61 (1H, tt, J = 1.3, 8.3 Hz, aromatic protons), 7.97 (2H, brd, J = 8.5 Hz, aromatic protons), 7.99 (2H, brd, J = 8.4 Hz, aromatic protons), 8.08 (2H, brd, J = 8.3 Hz, aromatic protons); ¹³C NMR (100 MHz,
CDCl$_3$ δ 19.90, 20.45, 20.50, 20.51, 20.55, 20.62, 20.72 (each CH$_3$CO$_2$), 46.26 (C4), 55.67 (OCH$_3$), 61.14 (C6'), 61.48 (C6''), 63.98 (C6), 67.24 (C3), 67.71 (C4''), 69.24 (C5), 70.10 (C2'), 71.54 (C2''), 71.95 (C5''), 72.92 (C3''), 73.30 (C3'), 73.33 (C2), 75.73 (C4'), 76.31 (C5'), 80.97 (C1'), 97.26 (C1), 100.54 (C1''), 128.33, 128.40, 128.47, 128.97, 129.16, 129.64, 129.81, 129.86, 129.88, 133.18, 133.30, 133.38 (aromatic carbons), 165.51, 165.78, 166.11, 168.87, 169.26, 169.51, 169.55, 170.03, 170.24, 170.48 (C=O); ESIMS (% rel. int.) m/z: 1163.3041 (100, calcd. for C$_{54}$H$_{60}$O$_{25}$SNa [M+Na]$^+$: 1163.3042), 619 (41, calcd. for [M-C$_{28}$H$_{25}$O$_8$S]$: 619.1869$).

4.47. Methyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzoyl-4-thio-β-D-glucopyranoside (iii-7b)

Crude thiol iii-4 was prepared employing iii-3 (693 mg, 997 µmol) and sodium methoxide (109 mg, 2.02 µmol) in the same manner as described in the Section 4.44. Triflate iii-6b (386 mg, 604 µmol) was also prepared employing iii-5b (322 mg, 636 µmol), trifluoromethanesulfonic anhydride (268 mg, 951 µmol) and pyridine (157 mg, 1.98 mmol) in the similar manner as described in the Section 4.45. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.57 (3H, s, OCH$_3$), 4.29–4.39 (2H, m, C6H$_2$), 4.74 (1H, d, J = 7.9 Hz, C1H), 4.81 (1H, dd, J = 5.0, 10.3 Hz, C5H), 5.54 (1H, brd, J = 2.9 Hz, C4H), 5.58 (1H, dd, J = 2.9, 10.3 Hz, C3H), 5.74 (1H, dd, J = 7.9, 10.3 Hz, C2H), 7.35–7.42 (4H, aromatic protons), 7.45–7.58 (5H, aromatic protons), 7.61 (1H, brt, J = 7.6 Hz, aromatic protons), 7.96 (2H, brd, J = 7.5 Hz, aromatic protons), 8.01 (2H, brd, J = 7.3 Hz, aromatic protons), 8.05 (2H, brd, J = 8.3 Hz, aromatic protons). After iii-4 and iii-6b thus obtained were dissolved in THF (8.0 ml), the mixture was treated with sodium hydride (washed with hexane, 26
mg, 1.08 mmol) in the similar manner as described in the Section 4.31. Purification of the crude product by silica gel column chromatography (EtOAc:benzene = 20:80) gave 7b (405 mg, 67%) as an oil. \([\alpha]_D^{23} +3.6 (c 0.82, \text{CHCl}_3)\); IR (film) 2925, 1750, 1230, 1070, 715 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.51, 1.96, 1.99, 2.01, 2.06, 2.08, 2.10 (each 3H, s, CH\(_3\)CO\(_2\)), 3.29 (1H, t, \(J = 11.0\) Hz, C4H), 3.49 (3H, s, OCH\(_3\)), 3.63-3.71 (3H, m, C5”H, C4’H, C5”H), 3.95 (1H, dd, \(J = 5.7, 11.9\) Hz, C6’HH), 4.04 (1H, dd, \(J = 2.2, 12.5\) Hz, C6”HH), 4.16 (1H, ddd, \(J = 2.1, 4.3, 11.0\) Hz, C5H), 4.34 (1H, dd, \(J = 4.5, 12.5\) Hz, C6”HH), 4.48 (1H, d, \(J = 7.8\) Hz, C1”H), 4.60 (1H, d, \(J = 7.9\) Hz, C1H), 4.61 (1H, dd, \(J = 1.4, 11.9\) Hz, C6’HH), 4.77 (1H, dd, \(J = 4.3, 12.0\) Hz, C6HH), 4.83 (1H, dd, \(J = 9.2, 10.0\) Hz, C2’H), 4.86 (1H, dd, \(J = 2.1, 12.0\) Hz, C6HH), 4.93 (1H, dd, \(J = 7.8, 9.4\) Hz, C2”H), 4.93 (1H, d, \(J = 10.0\) Hz, C1’H), 5.06 (1H, t, \(J = 9.5\) Hz, C4”H), 5.13-5.17 (2H, m, C3’H, C3”H), 5.41 (1H, dd, \(J = 7.9, 9.3\) Hz, C2H), 5.67 (1H, dd, \(J = 9.3, 11.0\) Hz, C3H), 7.34-7.40 (4H, aromatic protons), 7.47-7.53 (4H, aromatic protons), 7.60 (1H, tt, \(J = 1.3, 8.3\) Hz, aromatic protons), 7.94-7.96 (4H, aromatic protons), 8.07 (brdd, 2H, \(J = 1.3, 8.3\) Hz, aromatic protons); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 19.90, 20.45, 20.52, 20.52, 20.52, 20.64, 20.67 (each CH\(_3\)CO\(_2\)), 46.46 (C4), 56.91 (OCH\(_3\)), 61.54 (C6”), 62.05 (C6”), 64.02 (C6), 67.77 (C4”), 69.88 (C3), 70.07 (C2’), 71.59 (C2”), 72.03 (C5”), 72.94 (C3”), 73.23 (C2), 73.28 (C3”), 74.27 (C5), 76.29 (C4’), 76.54 (C5’), 80.87 (C1’), 100.72 (C1”), 102.06 (C1), 128.35, 128.37, 128.51, 128.85, 129.29, 129.69, 129.81, 129.91, 129.94, 133.24, 133.24, 133.45 (aromatic carbons), 165.25, 165.59, 166.07, 168.98, 169.31, 169.51, 169.51, 169.97, 170.22, 170.49 (C=O); ESIMS (% rel. int.) m/z: 1163.3027 (34, calcd. for C\(_{54}H_{60}O_{25}SNa\) [M+Na\(^+\): 1163.3042).
4.48. Methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-4-thio-α-D-glucopyranoside (iii-1a)

A solution of iii-7a (235 mg, 206 μmol) in a mixture of MeOH (5.0 ml) and 5% NaOH aqueous solution (0.5 ml) was stirred at room temperature for 1 h. After removing methanol *in vacuo*, the resulting aqueous solution was passed through an ion-exchange column (DOWEX 50W, H⁺ form). After the eluate was concentrated until the whole volume became 30 mL, the resulting aqueous solution was washed with EtOAc (20 ml). Lyophilization of the aqueous layer gave iii-1a (109 mg, 99%) as an amorphous powder. [α]₂⁰⁺ +16.6 (c 1.05, H₂O), The IR spectrum was not measured because this sample was only soluble in H₂O.

¹H NMR (500 MHz, D₂O) δ 2.73 (1H, t, J = 10.8 Hz, C4H), 3.17 (1H, dd, J = 7.9, 9.2 Hz, C2"H), 3.25 (1H, dd, J = 8.9, 9.8 Hz, C2'H), 3.26 (3H, s, OCH₃), 3.27 (1H, m, C4"H), 3.32-3.38 (2H, C3"H, C5"H), 3.43-3.53 (4H, C2H, C3'H, C4'H, C5'H), 3.59 (1H, dd, J = 5.8, 12.3 Hz, C6"HH), 3.63 (1H, dd, J = 9.3, 10.8 Hz, C3H), 3.65 (1H, dd, J = 5.1, 12.5 Hz, C6'HH), 3.75-3.82 (3H, C5H, C6'HH, C6"HH), 3.83 (1H, dd, J = 4.5, 12.1 Hz, C6HH), 3.89 (1H, dd, J = 2.1, 12.1 Hz, C6HH), 4.36 (1H, d, J = 7.9 Hz, C1"H), 4.53 (1H, d, J = 9.8 Hz, C1'H), 4.71 (1H, d, J = 3.7 Hz, C1H); ¹³C NMR (125 MHz, CDCl₃) δ 47.07 (C4), 55.19 (OCH₃), 60.23 (C6'), 60.74 (C6'"), 61.46 (C6), 69.59 (C3), 69.61 (C4'"), 72.07 (C5), 72.43 (C2'), 72.55 (C2), 73.31 (C2'"), 75.65 (C3"'), 75.76 (C4'), 76.16 (C5''), 78.40 (C3'), 78.84 (C5'), 83.61 (C1'), 99.47 (C1), 102.68 (C1''); ESIMS (% rel. int.) m/z: 557.1516 (100, calcd. for C₁₉H₃₄O₁₅SNa [M+Na]⁺ 557.1516 ), 535.1698 (5.3, calcd. for C₁₉H₃₅O₁₅S [M+H]⁺ 535.1697).

4.49. Methyl β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-4-thio-β-D-glucopyranoside (iii-1b)
In the similar manner as described in the Section 4.48, **iii-7b** (358 mg, 314 μmol) was treated employing MeOH (5.0 ml), 5% NaOH aqueous solution (1.0 ml). The following the similar work up gave **iii-1b** (164.1 mg, 98%) as an amorphous powder. \([\alpha]_D^{23} -49\ (c \ 0.93, \ H_2O)\). The IR spectrum was not measured because this sample was only soluble in H2O. \(^1\)H NMR (500 MHz, D2O) δ 2.73 (1H, t, \(J = 10.6\ \text{Hz}, \ C4'\)), 3.16 (1H, dd, \(J = 8.1, 9.0\ \text{Hz}, \ C2'H\)), 3.18 (1H, dd, \(J = 8.0, 9.2\ \text{Hz}, \ C2''H\)), 3.25 (1H, dd, \(J = 8.8, 9.8\ \text{Hz}, \ C2'H\)), 3.28 (1H, dd, \(J = 9.2, 9.7\ \text{Hz}, \ C4''H\)), 3.35 (1H, ddd, \(J = 2.2, 5.7, 9.7\ \text{Hz}, \ C5''H\)), 3.37 (1H, t, \(J = 9.2\ \text{Hz}, \ C3''H\)), 3.43 (3H, s, OCH3), 3.45 (1H, dd, \(J = 9.0, 10.6\ \text{Hz}, \ C3'H\)), 3.46 (1H, ddd, \(J = 2.2, 5.0, 9.5\ \text{Hz}, \ C5'H\)), 3.49-3.54 (2H, C3'H, C4'H), 3.55 (ddd, 1H, \(J = 2.0, 5.3, 10.6\ \text{Hz}, \ C5'H\)), 3.60 (1H, dd, \(J = 5.7, 12.4\ \text{Hz}, \ C6''HH\)), 3.66 (1H, dd, \(J = 5.0, 12.5\ \text{Hz}, \ C6'HH\)), 3.78 (1H, dd, \(J = 2.2, 12.4\ \text{Hz}, \ C6'''HH\)), 3.79 (1H, dd, \(J = 5.3, 12.2\ \text{Hz}, \ C6'HH\)), 3.82 (1H, dd, \(J = 2.2, 12.5\ \text{Hz}, \ C6''HH\)), 4.00 (1H, dd, \(J = 2.4, 12.2\ \text{Hz}, \ C6'HH\)), 4.22 (1H, d, \(J = 8.1\ \text{Hz}, \ C1'H\)), 4.37 (1H, d, \(J = 8.0\ \text{Hz}, \ C1''H\)), 4.53 (1H, d, \(J = 9.8\ \text{Hz}, \ C1'\)); \(^1^3\)C NMR (125 MHz, CDCl3) δ 47.31 (C4), 57.29 (OCH3), 60.25 (C6'), 60.77 (C6''), 61.56 (C6), 69.64 (C4''), 72.45 (C2'), 73.05 (C3), 73.34 (C2''), 74.48 (C2), 75.68 (C3''), 75.74 (C3'), 76.18 (C5''), 76.61 (C5), 78.39 (C4'), 78.73 (C5'), 83.84 (C1'), 102.70 (C1''), 103.13 (C1); ESIMS (% rel. int.) \(m/z\): 557.1494 (100, calcd. for C19H34O15SNa \([\text{M+Na}]^+\) 557.1516), 535.1674 (31, calcd. for C19H33O15S [\text{M+H}]^+ 535.1697).

**4.50. Phenyl 2,3,4,6-tetra-O-(4-methoxyphenylmethyl)-\(\beta\)-D-glucopyranosyl-(1→4)-2,3,6-tri-O-(4-methoxyphenylmethyl)-1-thio-\(\beta\)-D-glucopyranoside (iii-9).**

A solution of phenyl 2,3,6,2',3',4',6'-hepta-O-acetyl-1-thio-\(\beta\)-D-cellobioside (iii-8) (848 mg, 1.16 mmol) in a mixture of MeOH (5.0 ml) and CH2Cl2 (5.0 ml)
was stirred with 2M NaOH (300 μl) at room temperature for 10 min. After dilution with H₂O (50 ml), the mixture was passed through an ion-exchange column (DOWEX 50W, H⁺ form). Concentration of the eluent gave the corresponding crude heptaol (494 mg, 98%). This sample was immediately used for the next step. To a suspension of sodium hydride (washed with hexane, 383 mg, 16 mmol) in DMF (20 ml), the crude heptanol (494 mg, 1.14 mmol) in DMF (10 ml) was added at room temperature. Upon the addition, H₂ gas was vigorously bubbled. After stirring for 10 min, to the mixture was added MPMBr [6.4 g, 16 mmol, freshly prepared from anisic alcohol (4.4 g) and PBr₃ (8.6 g) in diethyl ether (100 ml)] in toluene (10 ml) was added at 0 °C. After 10 min, the cooling bath was removed, and the mixture was stirred at room temperature for 40 min. Methanol (1.0 ml) and triethylamine (1.0 ml) were added successively in order to decompose the excess reagent. After stirring for an additional 30 min, the mixture was poured into H₂O (100 ml) and the aqueous layer was extracted with EtOAc (70 ml × 3). The combined organic layer was washed with H₂O (100 ml), and brine (100 ml), dried over MgSO₄ and concentrated in vacuo. Silica gel column chromatography of the residue with EtOAc:benzene = 6:94 afforded iii-9 (1.06 g, 73%) as amorphous powder. [α]D²⁵ +9.80 (c 1.00, CHCl₃); IR (film) 2910, 1610, 1515, 1250, 1070, 1040, 820 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.10 (1H, ddd, J = 1.6, 4.4, 9.7 Hz, C5'H), 3.31 (1H, dd, J = 7.9, 9.0 Hz, C2'H), 3.36 (1H, ddd, J = 1.8, 4.0, 8.8 Hz, C5'H), 3.42 (1H, dd, J = 8.8, 9.8 Hz, C2'H), 3.45 (1H, t, J = 9.0 Hz, C3'H), 3.55 (1H, dd, J = 4.4, 11.0 Hz, C6'HH), 3.56 (1H, dd, J = 9.0, 9.7 Hz, C4'H), 3.60 (1H, t, J = 8.8 Hz, C3'H), 3.69 (1H, dd, J = 1.6, 11.0 Hz, C6'HH), 3.71 (1H, dd, J = 1.8, 10.7 Hz, C6HH), 3.72, 3.73, 3.76, 3.76, 3.78, 3.79, 3.80 (each 3H, s, OCH₃), 3.81 (1H, dd, J = 4.0, 10.7 Hz, C6HH), 3.99 (1H, t, J = 8.8 Hz, C4'H), 4.37 (1H, d, J = 11.6 Hz,
ArCHHO), 4.37, 4.41 (each 1H, d, J = 11.6 Hz, ArCH₂O), 4.42 (1H, d, J = 7.9 Hz, C1'H), 4.43 (1H, d, J = 10.6 Hz, ArCHHO), 4.50 (1H, d, J = 11.6 Hz, ArCHHO), 4.61 (1H, d, J = 9.8 Hz, C1'H), 4.62 (1H, d, J = 10.8 Hz, ArCHHO), 4.63 (1H, d, J = 10.3 Hz, ArCHHO), 4.63, 4.68 (each 1H, d, J = 10.3 Hz, ArCH₂O), 4.70 (1H, d, J = 10.6 Hz, ArCHHO), 4.71 (1H, d, J = 10.3 Hz, ArCHHO), 4.71, 4.80 (each 1H, d, J = 10.6 Hz, ArCH₂O), 5.04 (1H, d, J = 10.8 Hz, ArCHHO), 6.73 (2H, brd, J = 8.6 Hz, aromatic protons), 6.79-6.85 (12H, aromatic protons), 7.07 (2H, brd, J = 8.7 Hz, aromatic protons), 7.18-7.24 (li1H, aromatic protons), 7.25-7.30 (4H, aromatic protons), 7.55 (2H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 55.13 (OCH₃ × 3), 55.16, 55.19 (each OCH₃), 55.21, 55.21 (OCH₃ × 2), 67.83 (C6), 68.59 (C6'), 72.79, 72.82, 72.85, 74.41, 74.52, 74.94, 74.98 (each ArCH₂O), 74.98 (C5'), 75.20 (ArCH₂O), 76.22 (C4), 77.68 (C4'), 79.30 (C5), 79.82 (C2), 82.48 (C2'), 84.61 (C3), 84.67 (C3'), 87.47 (C1), 102.44 (C1'), 113.43, 113.63, 113.63, 113.63, 113.66, 113.70, 113.70, 127.25, 128.55, 128.78, 129.04, 129.25, 129.28, 129.38, 129.47, 129.66, 129.76, 130.30, 130.42, 130.44, 130.50, 130.60, 130.90, 131.34, 131.83, 133.93, 158.85, 158.94, 159.02, 159.07, 159.07, 159.15, 159.18 (aromatic carbons); FABMS (% rel. int.) m/z: 1297 (12, [M+Na]⁺), 121 (100, [CH₃OPhCH₂]⁺); FAB-HRMS: calcd for C₇₄H₈₂O₁₇SNa [M+Na]⁺ 1297.5170; found, m/z 1297.5197.

4.51. 2,3,4,6-Ο-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-Ο-(4-methoxyphenylmethyl)-D-glucitol (iii-10).

A solution of iii-9 (1.60 g, 1.25 mmol) in a mixture of acetone (100 ml) and H₂O (10 ml) was stirred with NBS (558 mg 3.10 mmol) at 0°C for 5 min. Aqueous 10% Na₂S₂O₃ solution (6.0 ml) was added and the mixture was
neutralized by the addition of saturated aqueous NaHCO₃ solution (12 ml). After acetone was removed by rotary evaporator, the resulting aqueous solution was extracted with EtOAc (100 ml × 3). The combined organic layer was washed with H₂O (100 ml), dried over MgSO₄, and then concentrated in vacuo. The residue was passed through silica gel pad to give a residue, which was dissolved in a mixture of EtOH (20 ml) and CH₂Cl₂ (10 ml) and it was cooled in an ice bath. To this solution, sodium borohydride (142 mg, 3.8 mmol) was added and the mixture was stirred for 30 min. The ice bath was removed and the mixture was further stirred at ambient temperature for 12 h. Aqueous 1.0 M HCl solution (2.0 ml) was added in order to decompose the excess hydride. After ethanol was removed by rotary evaporator, the resulting aqueous mixture was extracted with EtOAc (100 ml × 3). The combined organic layer was washed with H₂O (100 ml) and brine (100 ml) successively, dried over MgSO₄, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc: hexane = 54:46) gave iii-10 (1.48 g, 99%) as caramel. [α]D<sup>26</sup> +11.4 (c 1.11, CHCl₃); IR (film) 3465, 2930, 1610, 1510, 1250, 1070, 1035, 820 cm<sup>−1</sup>; ¹H NMR (500 MHz, CDCl₃) δ 2.58 (1H, t, J = 6.7 Hz, C1OH), 2.98 (1H, t, J = 5.8 Hz, C5OH), 3.26 (1H, ddd, J = 1.6, 5.3, 8.8 Hz, C5’H), 3.30 (1H, dd, J = 7.7, 8.8 Hz, C2’H), 3.39 (1H, t, J = 8.8 Hz, C4’H), 3.43 (1H, t, J = 8.8 Hz, C3’H), 3.49 (1H, dd, J = 5.3, 10.6 Hz, C6’HH), 3.51 (1H, dd, J = 3.1, 9.5 Hz, C6HH), 3.57 (1H, dd, J = 1.6, 10.6 Hz, C6’HH), 3.65 (2H, m, C1’HH, C6HH), 3.73, 3.75 (each 3H, s, OCH₃), 3.76 (1H, m, C1HH), 3.77, 3.77, 3.79, 3.79 (each 3H, s, OCH₃), 3.90 (1H, dd, J = 1.7, 8.1 Hz, C4H), 3.94-3.99 (3H, C2’H, C3’H, C5H), 4.27 (1H, d, J = 11.6 Hz, ArCHHO), 4.28 (1H, d, J = 7.7 Hz, C1’H), 4.37 (1H, d, J = 11.6 Hz, ArCHHO), 4.38 (1H, d, J = 10.3 Hz, ArCHHO), 4.38, 4.43 (each 1H, d, J = 11.6 Hz, ArCH₂O), 4.58 (1H, d, J = 11.1 Hz, ArCHHO), 4.59 (1H, d, J = 11.0 Hz,
ArCHHO), 4.64 (1H, d, J = 10.6 Hz, ArCHHO), 4.67 (1H, d, J = 11.1 Hz, ArCHHO), 4.69 (1H, d, J = 10.3 Hz, ArCHHO), 4.71 (1H, d, J = 10.7 Hz, ArCHHO), 4.73 (1H, d, J = 10.6 Hz, ArCHHO), 4.77 (1H, d, J = 11.0 Hz, ArCHHO), 4.83 (1H, d, J = 10.7 Hz, ArCHHO), 6.78-6.85 (14H, aromatic protons), 7.04 (2H, brd, J = 8.7 Hz, aromatic protons), 7.15 (2H, brd, J = 8.7 Hz, aromatic protons), 7.19 (2H, brd, J = 8.7 Hz, aromatic protons), 7.21-7.26 (8H, aromatic protons); 13C NMR (125 MHz, CDCl₃) δ 55.15 (0ν13 X 2), 55.19 (0ν2 X 3), 55.23 (0ν3 X 2), 62.69 (C1), 68.51 (C6'), 70.12 (C6), 70.49 (C5), 72.78, 72.95, 73.00 (each Arν120), 74.99 (C5'), 75.19 (each Arν20), 76.85 (C4), 77.41 (C4'), 79.34, 79.62 (C2, C3), 81.74 (C2'), 84.44 (C3'), 103.06 (C1'), 113.62, 113.66, 113.70, 113.73, 113.74, 113.77, 113.77, 129.27, 129.56, 129.59, 129.59, 129.59, 129.59, 129.60, 129.75, 130.09, 130.21, 130.54, 130.82, 130.86, 130.88, 159.08, 159.08, 159.08, 159.10, 159.18, 159.26, 159.26 (aromatic carbons); FABMS (%, rel. int.) m/z: 1207 (37, [M+Na]⁺), 121 (100, [CH₃OPhCH₂]⁺); FAB-HRMS: calcd. for C₆₈H₈₀O₁₈Na [M+Na]⁺ 1207.5242; found, m/z 1207.5234.

4.52. (3R,4S,5S)-6-(tert-butyldimethylsilyloxy)-4,5-di-(4-methoxybenzyloxy)-2-(4-methoxybenzyloxymethyl)hex-1-en-3-yl 2,3,4,6-tetra-(4-methoxybenzyloxy)-β-D-glucopyranoside (iii-11)

A solution of iii-10 (825 mg, 696 μmol) in DMF (8.0 ml) was stirred with imidazole (95.0 mg, 1.40 mmol) and tert-butyldimethylchlorosilane (148 mg, 982 μmol) at room temperature for 1 h. The mixture was poured into H₂O (70 ml) and the aqueous layer was extracted with EtOAc (100 ml x 3). The combined organic layer was washed with H₂O (100 ml), and brine (100 ml) successively, dried over MgSO₄, and then concentrated in vacuo. Silica gel column
chromatography of the residue (EtOAc:hexane = 35:65) gave 2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl-(1→4)-1-O-(tert-butyldimethylsilyl)-2,3,6-tri-O-(4-methoxyphenylmethyl)-D-glucitol (883 mg, 97%) as caramel. [α]D26^26 +20.5 (c 1.07, CHCl₃); IR (film) 3470, 2930, 1610, 1510, 1250, 1070, 1035, 820 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 0.18, 0.20 (each 3H, s, SiCH₃), 1.06 (9H, s, SiC(CH₃)₃), 3.27, 3.27, 3.29 (each 3H, s, OCH₃), 3.31, 3.31, 3.31 (12H, s, OCH₃ × 4), 3.40-3.43 (2H, m, C₂OH, C₅’H), 3.57 (1H, dd, J = 8.1, 9.0 Hz, C₂’H), 3.62 (1H, t, J = 9.0 Hz, C₃’H), 3.68-3.74 (3H, C₄’H, C₆’H₂), 3.80 (1H, dd, J = 2.7, 10.0 Hz, C₁HH), 4.01 (1H, dd, J = 3.8, 10.0 Hz, C₁HH), 4.08 (1H, dd, J = 3.1, 11.0 Hz, C₆HH), 4.26 (1H, dd, J = 4.5, 11.0 Hz, C₆HH), 4.30 (1H, d, J = 11.8 Hz, ArCHHO), 4.31 (1H, ddd, J = 1.9, 3.1, 4.5 Hz, C₅H), 4.45-4.48 (4H, C₂H, C₃H, ArCHHO × 2), 4.51 (1H, d, J = 11.5 Hz, ArCHHO), 4.52 (1H, dd, J = 1.9, 6.4 Hz, C₄H), 4.58 (1H, d, J = 10.9 Hz, ArCHHO), 4.74 (1H, d, J = 8.1 Hz, C₁’H), 4.76, 4.81 (each 1H, d, J = 10.7 Hz, ArCH₂O), 4.81 (1H, d, J = 10.7 Hz, ArCHHO), 4.87 (1H, d, J = 10.9 Hz, ArCHHO), 4.89 (1H, d, J = 10.9 Hz, ArCHHO), 4.91 (1H, d, J = 10.9 Hz, ArCHHO), 5.01 (1H, d, J = 10.9 Hz, ArCHHO), 5.02 (1H, d, J = 10.7 Hz, ArCHHO), 5.06 (1H, d, J = 10.9 Hz, ArCHHO), 6.77-6.82 (14H, aromatic protons), 7.16 (2H, brd, J = 8.7 Hz, aromatic protons), 7.21, 7.28, 7.35 (each 2H, brd, J = 8.7 Hz, aromatic protons), 7.37-7.40 (6H, aromatic protons); ¹³C NMR (125 MHz, C₆D₆) δ -5.05, -4.93 (each SiCH₃), 18.58 (SiC), 26.27 (SiC(CH₃), 54.66 (OCH₃ × 2), 54.71 (OCH₃ × 4), 54.72 (OCH₃), 63.60 (C₆), 69.33 (C₆’), 70.96 (C₁), 71.67 (C₂), 73.09, 73.17, 73.34, 74.52, 74.57, 74.65 (each ArCH₂O), 75.27 (C₅’), 75.31 (ArCH₂O), 76.60 (C₃), 77.99 (C₄’), 79.45 (C₄), 80.63 (C₅), 82.46 (C₂’), 84.99 (C₃’), 103.29 (C₁’), 113.95, 114.02, 114.02, 114.02, 114.02, 114.14, 114.15, 129.50, 129.56, 129.57, 129.73, 129.89, 129.89, 130.11, 130.84,
130.93, 131.32, 131.32, 131.73, 131.81, 131.81, 159.56, 159.62, 159.64, 159.69, 159.72, 159.74, 159.76 (aromatic carbons); FABMS (%, rel. int.) m/z: 1321 (50, [M+Na]^+), 131 (42, [(CH₃)₃C-Si(CH₃)₂O]^+), 121 (100, [CH₃OPhCH₂]^+); FAB-HRMS: calcd. for C₇₄H₉₄O₁₈SiNa [M+Na]^+ 1321.6107; found, m/z 1321.6097.

A solution of the product thus obtained (883 mg, 679 μmol) in a mixture of DMSO (9.2 ml, 130 mmol) and acetic anhydride (6.10 ml, 637 μmol) was stirred at room temperature for 12 hours. The mixture was poured into H₂O (300 ml), and the aqueous layer was extracted with EtOAc (150 ml × 3). The combined organic layer was washed with H₂O (100 ml), and brine (100 ml) successively, dried over MgSO₄, and then concentrated in vacuo. Silica gel column chromatography (EtOAc:hexane = 30:70) of the residue afforded (3R,4S,5S)-6-(tert-butyldimethylsilyloxy)-1,4,5-tri-(4-methoxyphenylmethyl)-2-oxohexan-3-yl 2,3,5-O-tri-(4-methoxyphenylmethyl)-β-D-glucopyranoside (830 mg, 94%) as caramel. [α]D²⁵ +24 (c 0.80, CHCl₃); IR (film) 2930, 1730, 1610, 1510, 1250, 1070, 1035, 820 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.01, 0.02 (each 3H, s, SiCH₃), 0.88 (9H, s, SiC(CH₃)₃), 3.31 (1H, ddd, J = 3.0, 3.5, 9.0 Hz, C₅H), 3.39 (1H, dd, J = 7.7, 9.0 Hz, C₂H), 3.50 (1H, t, J = 9.0 Hz, C₄H), 3.54 (1H, t, J = 9.0 Hz, C₃H), 3.60 (2H, m, C₆H₂), 3.69-3.77 (3H, C₅’H, C₆’H₂), 3.735, 3.742, (each 3H, s, OCH₃), 3.760, (6H, s, OCH₃ × 2), 3.762, 3.78, 3.80 (each 3H, s, OCH₃), 4.03 (1H, t, J = 3.9 Hz, C₄’H), 4.17 (1H, d, J = 11.5 Hz, ArCHHO), 4.19 (1H, d, J = 17.5 Hz, C₁’HH), 4.21 (1H, d, J = 11.5 Hz, ArCHHO), 4.34 (1H, d, J = 7.7 Hz, C₁H), 4.40 (1H, d, J = 17.5 Hz, C₁’HH), 4.40-4.43 (3H, ArCHHO × 3), 4.43 (1H, d, J = 10.5 Hz, ArCHHO), 4.47 (1H, d, J = 10.9 Hz, ArCHHO), 4.48 (1H, d, J = 11.7 Hz, ArCHHO), 4.60 (1H, d, J = 3.9 Hz, C₃’H), 4.61 (1H, d, J = 10.5 Hz, ArCHHO), 4.69 (1H, d, J = 10.5 Hz, ArCHHO), 4.70 (1H, d, J = 10.6 Hz,
ArCHHO), 4.71 (1H, d, J = 10.3 Hz, ArCHHO), 4.85 (1H, d, J = 10.6 Hz, ArCHHO), 5.07 (1H, d, J = 10.5 Hz, ArCHHO), 6.77-6.81 (12H, aromatic protons), 6.84 (2H, brd, J = 8.6 Hz, aromatic protons), 7.04, 7.11, 7.16 (each 2H, brd, J = 8.7 Hz, aromatic protons); 13C NMR (100 MH2, CDCl3) δ -5.31, -5.28 (each SiCH3), 18.23 (SiC), 25.95 (SiC(CH3)3), 55.18 (OCH3 × 3), 55.20 (OCH3 × 2), 55.25, 55.26 (each OCH3), 62.14 (C6'), 68.63 (C6), 72.61, 72.78, 73.13, 73.90, 74.27 (each ArCH2O), 74.32 (C1'), 74.53 (ArCH2O), 74.97 (C5), 75.31 (ArCH2O), 77.42 (C4), 78.86 (C3'), 78.92 (C5'), 80.00 (C4'), 81.85 (C2), 84.23 (C3), 102.21 (C1), 113.55, 113.67, 113.69, 113.70, 113.77, (aromatic carbons), 113.78 (aromatic carbon × 2), 128.32, 129.34, 129.37, 129.46, 129.55, 129.71, 129.78, 129.95, 129.99, 130.18, 130.27, 130.36, 130.71, 130.78, 130.96, 159.06 (aromatic carbons), 159.16 (aromatic carbon × 2), 159.21, 159.23, 159.27 (aromatic carbons), 205.74 (C2'); FABMS (%, rel. int.) m/z: 1319 (33, [M+Na]+), 131 (26, [(CH3)3C-Si(CH3)2O]+), 121 (100, [CH3OPhCH2]+); FAB-HRMS: calcd. for C74H92O19SiNa [M+Na]+ 1319.5951; found, m/z 1319.5962.

n-Butyllithium (0.75 M in hexane, 4.3 ml, 3.2 mmol) was added to a suspension of methyltriphenylphosphonium bromide (1.54 g, 4.3 mmol) in THF (7.0 ml) at room temperature. Upon the addition of butyl lithium, the white suspension turned to orange suspension. After stirring for 10 min, to this mixture was added a solution of the product (1.4 g, 1.08 mmol) in THF (7.0 ml) at room temperature and the mixture was stirred for further 10 min, poured into saturated aqueous NH4Cl (50 ml), and the aqueous layer was extracted with EtOAc (80 ml × 3). The combined organic layer was washed with brine (50 ml), dried over MgSO4, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc: hexane = 26:74) gave **ii-11** (1.37 g, 98%) as
an oil. [α]_D^{25} +1.5 (c 0.80, CHCl₃); IR (film) 2930, 1610, 1510, 1250, 1070, 1040, 820 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.02, 0.03 (each 3H, s, SiCH₃), 0.89 (9H, s, SiC(CH₃)₃), 3.29 (1H, ddd, J = 2.4, 3.9, 9.4 Hz, C5H), 3.36 (1H, dd, J = 7.9, 9.2 Hz, C2H), 3.52-3.57 (2H, C3H, C4H), 3.61 (1H, dd, J = 2.4, 11.0 Hz, C6HH), 3.64 (1H, dd, J = 3.9, 11.0 Hz, C6HH), 3.69 (1H, dt, J = 4.9, 5.2 Hz, C5’H), 3.74 (3H, s, OCH₃), 3.75 (6H, s, OCH₃ × 2), 3.76 (6H, s, OCH₃ × 2), 3.78, 3.79 (each 3H, s, OCH₃), 3.82-3.84 (3H, C4’H, C6’H₂), 3.95, 4.04 (each 1H, d, J = 13.5 Hz, C2’CH₂), 4.22, 4.27 (each d, 1H, J = 11.4 Hz, ArCH₂O), 4.37 (1H, d, J = 7.9 Hz, C1H), 4.41 (1H, d, J = 11.7 Hz, ArCHH), 4.44 (1H, d, J = 10.6 Hz, ArCHHO), 4.49 (1H, d, J = 11.4 Hz, ArCHHO), 4.53 (1H, d, J = 11.7 Hz, ArCHHO), 4.58 (1H, d, J = 10.6 Hz, ArCHHO), 4.61 (1H, d, J = 11.4 Hz, ArCHHO), 4.64, 4.65, 4.70, 4.71 (each 1H, d, J = 10.6 Hz, ArCHHO × 2), 4.77 (1H, d, J = 4.6 Hz, C3’H), 4.84, 4.87 (each 1H, d, J = 10.6 Hz, ArCHHO × 2), 5.30, 5.40 (each 1H, brs, C1’H₂), 6.74-6.85 (14H, aromatic protons), 7.06, 7.15, 7.19 (each 2H, brd, J = 8.7 Hz, aromatic protons), 7.20-7.24 (8H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ -5.33, (SiCH₃ × 2), 18.22 (SiC), 25.97 (SiC (CH₃)₃), 55.16 (OCH₃ × 2), 55.17 (OCH₃ × 3), 55.21, 55.23 (each OCH₃), 62.67 (C6’), 68.44 (C6), 69.80 (C2’CH₂), 71.96, 72.57, 73.06, 74.24 (each ArCH₂O), 74.46 (ArCH₂O × 2), 75.09 (C5), 75.27 (ArCH₂O), 77.43 (C3’), 77.74 (C3), 79.85 (C4’), 80.36 (C5’), 82.02 (C2), 84.54 (C4), 99.10 (C1), 113.43, 113.50, 113.62, 113.64 (aromatic carbons), 113.68 (aromatic carbon × 2), 113.73 (aromatic carbon), 116.52 (C1’), 128.30, 128.89, 129.16, 129.32, 129.35, 129.48, 129.66, 129.70, 130.41, 130.49, 130.54, 130.74, 131.01 (aromatic carbons), 131.30 (aromatic carbon × 2), 142.03 (C2’), 158.86 (aromatic carbon × 2), 158.97 (aromatic carbon), 159.03 (aromatic carbon × 2), 159.07, 159.14 (aromatic carbons); FABMS (% rel. int.) m/z: 1317 (39, [M+Na]⁺), 1051 (24, [M-
CH₃OPhCH₂-CH₃OPhCH₂O)⁺, 121 (100, [CH₃OPhCH₂]⁺); FAB-HRMS: calcd. for C₇₅H₉₄O₁₇SiNa [M+Na]⁺ 1317.6158; found, m/z 1317.6147.

4.53. (3R,4S,5S)-4,5-di-(4-methoxybenzoyloxy)-2-(4-methoxybenzyloxy methyl)-6-oxohex-1-en-3-yl 2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranoside (iii-12)

A solution of iii-11 (288 mg, 222 μmol) in THF (5.0 ml) was stirred with tetrabutylammonium fluoride (1.0 M in THF, 400 μl) at room temperature for 1.5 h. The mixture was poured into H₂O (20 ml) and the aqueous layer was extracted with EtOAc (30 ml x 3). The combined organic layer was washed with brine (20 ml), dried over MgSO₄, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc:hexane = 50:50) gave the corresponding alcohol (259 mg, 99%) as an oil. [α]D²⁵ +3.6 (c 1.28, CHCl₃); IR (film) 3460, 2915, 1610, 1510, 1250, 1070, 1035, 820 cm⁻¹; ¹H NMR (500 MHz, CDC₃) δ 2.30 (1H, br, C6'O'H), 3.29 (1H, ddd, J = 2.4, 4.2, 9.0 Hz, C5'H), 3.39 (1H, dd, J = 7.9, 8.5 Hz, C2'H), 3.50-3.56 (2H, C3'H, C4'H), 3.58 (1H, dd, J = 4.2, 11.0 Hz, C6'HH), 3.61 (1H, dd, J = 2.4, 11.0 Hz, C6'HH), 3.75-3.86 (4H, C3'H, C4'H), 3.77, 3.78, 3.79 (each 3H, C1'H), 3.94, 4.06 (each 1H, brd, J = 13.1 Hz, C2'C'H₂O), 4.24, 4.30 (each 1H, d, J = 11.5 Hz, ArCH₂O), 4.36 (1H, d, J = 7.9 Hz, C1'H), 4.43 (1H, d, J = 11.7 Hz, ArCHH₂O), 4.44 (1H, d, J = 10.4 Hz, ArCHH₂O), 4.51 (1H, d, J = 11.7 Hz, ArCHH₂O), 4.53 (1H, d, J = 10.9 Hz, ArCHH₂O), 4.54, 4.58 (each 1H, d, J = 11.2 Hz, ArCH₂O), 4.67 (1H, d, J = 10.5 Hz, ArCHH₂O), 4.67 (1H, d, J = 10.9 Hz, ArCHH₂O), 4.69 (1H, d, J = 10.4 Hz, ArCHH₂O), 4.69 (1H, m, C2'H), 4.72, 4.85 (each 1H, d, J = 10.7 Hz, ArCHH₂O), 4.89 (1H, d, J = 10.5 Hz, ArCHH₂O), 5.37, 5.39 (each 1H, brs, C1'H₂), 6.75 (2H, brd, J = 8.7 Hz, aromatic protons), 147
6.78-6.85 (12H, aromatic protons), 7.07 (2H, brd, J = 8.7 Hz, aromatic protons), 7.16 (2H, brd, J = 8.6 Hz, aromatic protons), 7.18 (2H, brd, J = 8.7 Hz, aromatic protons), 7.21-7.24 (8H, aromatic protons); \[\text{\textsuperscript{13}C} \text{NMR (125 MHz, CDCl\textsubscript{3}) } \delta 55.18 \ (\text{OCH}_3 \times 2), 55.20 \ (\text{OCH}_3 \times 2), 55.21, 55.24, 55.25 \ (\text{each OCH}_3), 61.80 \ (C6'), 68.39 \ (C6), 70.52 \ (C2'CH_2), 71.90, 72.47, 73.08, 74.17, 74.52, 74.58 \ (\text{each ArCH}_2\text{O}), 74.96 \ (C5), 75.24 \ (\text{ArCH}_2\text{O}), 76.52 \ (C2'), 77.62 \ (C4), 79.66, 80.65 \ (C3', C4'), 81.90 \ (C2), 84.48 \ (C3), 99.63 \ (C1), 113.58, 113.65, 113.70, 113.73, 113.73, 113.73 \ (\text{aromatic carbons}), 116.62 \ (C1'), 129.02, 129.28, 129.35, 129.40, 129.59, 129.63, 129.73, 130.32, 130.35, 130.37, 130.58, 130.76, 130.85, 130.98 \ (\text{aromatic carbons}), 141.79 \ (C2'), 159.03, 159.06, 159.07, 159.07, 159.11, 159.11, 159.21 \ (\text{aromatic carbons}); \text{FDMS} (\% \ \text{rel. int.}) \ m/z: 1181 \ (20, [M+H]^+), 1180 \ (31, [M]^+), 1059 \ (46, [M-CH_3OPhCH_2]^+), 121 \ (100, [CH_3OPhCH_2]^+); \text{FD-HRMS: calcd. for } C_{69}H_{80}O_{17} [M]^+ 1180.5396; \text{found, } m/z 1180.5396.

Oxalylchloride (264 mg, 2.08 mmol) was added to a solution of dimethylsulfoxide (325 mg, 4.2 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (3.0 ml) at -78 °C and the mixture was stirred for 20 min. A solution of the alcohol (620 mg, 525 μmol) in CH\textsubscript{2}Cl\textsubscript{2} (5.0 ml) was added to this mixture, and the resulting mixture was stirred at the same temperature for 40 min. After triethylamine (526 mg, 5.21 mmol) was added, the cooling bath was removed. The mixture was further stirred at room temperature for additional 10 min and poured into H\textsubscript{2}O (30 ml). The aqueous layer was extracted with EtOAc (30 ml × 3). The combined organic layer was washed with brine (30 ml), dried over MgSO\textsubscript{4}, and then concentrated \textit{in vacuo}. Purification of the residue with silica gel column chromatography (EtOAc:hexane = 40:60) gave \textbf{iii-12} (615 mg, 99%) as an oil. \[\text{\textsuperscript{1}H} \text{NMR (500 MHZ, CDCl\textsubscript{3}) } \delta 3.29 \ (1H, ddd, J = 2.7, 3.4, 9.1 Hz, C5H), 3.40 \ (1H, dd, J = 7.8, 8.3 Hz, C2H), 3.52-3.58 \ (2H, C3H, C4H), 3.62-3.67 \ (2H, C6H\textsubscript{2}), 3.75 \ (6H, s, OCH\textsubscript{3} \times 2),

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3.76 (6H, s, OCH\textsubscript{3} × 3), 3.78, 3.79 (each 3H, s, OCH\textsubscript{3}), 3.90 (1H, brd, J = 12.6 Hz, C5'CHHO), 3.97 (1H, dd, J = 0.9, 4.3 Hz, C2'H), 4.03-4.07 (2H, C3'H, C5'CHHO), 4.23, 4.28 (each 1H, d, J = 11.5 Hz, ArCH\textsubscript{2}O), 4.33 (1H, d, J = 8.1 Hz, C1'H), 4.42 (1H, d, J = 11.4 Hz, ArCHHO), 4.44 (1H, d, J = 11.6 Hz, ArCHHO), 4.48 (1H, d, J = 10.6 Hz, ArCHHO), 4.50 (1H, d, J = 11.4 Hz, ArCHHO), 4.54 (1H, d, J = 11.6 Hz, ArCHHO), 4.58 (each 1H, d, J = 10.9 Hz, ArCH\textsubscript{2}O), 4.65 (1H, d, J = 10.7 Hz, ArCHHO), 4.71, 4.72 (each 1H, d, J = 10.6 Hz, ArCHHO), 4.80 (1H, d, J = 10.7 Hz, ArCHHO), 4.82 (1H, d, J = 10.6 Hz, ArCHHO), 4.88 (1H, d, J = 5.0 Hz, C4'H), 5.32, 5.38 (each 1H, brs, C6'CH\textsubscript{2}), 6.75-6.84 (14H, aromatic protons), 7.09 (2H, brd, J = 8.5 Hz, aromatic protons), 7.14-7.25 (12H, m, aromatic protons), 9.60 (1H, d, J = 0.9 Hz, C1’CHO). This sample was immediately used for next step.

4.54. (3R,4S,5S,6R)-6-hydroxy-4,5-di(4-methoxybenzylxy)-2-(4-methoxybenzyloxymethyl)octa-1,7-dien-3-yl 2,3,4,6-O-tetra-(4-methoxyphenyl methyl)-β-D-glucopyranoside (iii-13R) and its (3R,4S,5S,6S)-isomer (iii-13S)

A solution of iii-12 (615 mg, 0.52 mmol) in THF (3 ml) was stirred with vinylmagnesium bromide (1.0 M in THF, 1.1 ml) at -15°C for 10 min. The mixture was poured into saturated aqueous NH\textsubscript{4}Cl (30 ml) and the aqueous layer was extracted with EtOAc (30 ml × 3). The combined organic layer was washed with brine (30 ml), dried over MgSO\textsubscript{4}, and then concentrated in vacuo. Purification of the residue with silica gel column chromatography (EtOAc:hexane = 40:60) gave 1:1 mixture of iii-13S and iii-13R (573 mg, 90%) as an oil. These were successfully separated by medium-pressured column
chromatography (EtOAc:benzene = 9:91) to provide iii-13R (286 mg, 46%) and iii-13S (280 mg, 44%).

4.54.1. Physical data for iii-13R.

[α]D$^26$ +12 (c 0.64, CHCl₃); IR (film) 3470, 2920, 1610, 1510, 1245, 1070, 1030, 820 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl₃) δ 2.65 (1H, d, $J$ = 7.7 Hz, C6’OH), 3.30 (1H, ddd, $J$ = 2.7, 3.5, 9.3 Hz, C5H), 3.39 (1H, dd, $J$ = 7.8, 9.2 Hz, C2H), 3.52-3.58 (2H, C3H, C4H), 3.58, 3.60 (2H, C6H₂), 3.76 (9H, s, OCH₃ x 3), 3.77 (6H, s, OCH₃ x 2), 3.78 (3H, s, OCH₃), 3.79 (1H, m, C5’H), 3.80 (s, 3H, OCH₃), 3.84 (1H, dd, $J$ = 2.6, 7.4 Hz, C4’H), 3.95, 4.06 (1H, brd, $J$ = 13.0 Hz, C2’CHHO), 4.24, 4.30 (each 1H, d, $J$ = 11.6 Hz, ArCH₂O), 4.37 (1H, d, $J$ = 7.8 Hz, C1H), 4.39 (1H, d, $J$ = 11.6 Hz, ArCHHO), 4.44 (1H, d, $J$ = 10.5 Hz, ArCHHO), 4.48 (1H, C6’H), 4.49 (1H, d, $J$ = 11.6 Hz, ArCHHO), 4.50 (1H, d, $J$ = 10.6 Hz, ArCHHO), 4.54 (1H, d, $J$ = 10.7 Hz, ArCHHO), 4.65 (1H, d, $J$ = 10.6 Hz, ArCHHO), 4.68 (1H, d, $J$ = 10.7 Hz, ArCHHO), 4.69 (1H, d, $J$ = 10.5 Hz, ArCHHO), 4.70 (1H, d, $J$ = 10.6 Hz, ArCHHO), 4.71 (1H, C3’H), 4.73, 4.86 (each 1H, d, $J$ = 10.5 Hz, ArCHHO), 4.92 (1H, d, $J$ = 10.6 Hz, ArCHHO), 5.09 (1H, dt, $J$ = 1.5, 10.4 Hz, C8’HH), 5.33 (1H, dt, $J$ = 1.5, 17.1 Hz, C8’HH), 5.38, 5.41 (each 1H, brs, C1’CH₂), 5.96 (ddd, 1H, $J$ = 5.0, 10.4, 17.1 Hz, C7’H), 6.74-6.86 (14H, aromatic protons), 7.06 (2H, brd, $J$ = 8.7 Hz, aromatic protons), 7.16-7.26 (12H, aromatic protons); $^{13}$C NMR (100 MHz, CDCl₃) δ 55.19 (OCH₃ x 2), 55.21 (OCH₃ x 3), 55.25, 55.26 (each OCH₃), 68.50 (C6), 70.55 (C2’CH₂), 71.80 (C6’), 71.93, 73.06, 74.43 (each ArCH₂O), 74.53 (ArCH₂O x 2), 74.53, 74.61 (each ArCH₂O), 74.85 (C5), 75.28 (ArCH₂O), 76.55 (C3’), 77.66 (C4), 80.79 (C4’), 81.83 (C5’), 81.91 (C2), 84.46 (C3), 99.69 (C1), 113.53, 113.63, 113.67, 113.69, 113.71, 113.74, 113.76 (aromatic carbons), 114.93 (C8’), 116.24 (C1’), 129.04, 129.29,
129.32, 129.37, 129.56, 129.60, 129.78, 130.30, 130.41, 130.41, 130.59, 130.79, 130.99, 131.12 (aromatic carbons), 139.17 (C7'), 141.87 (C2'), 158.93, 159.10, 159.10, 159.10, 159.11, 159.21 (aromatic carbons); FDMS (% rel. int.) m/z: 1229 (7.2, [M+Na]⁺), 1207 (4.3, [M+H]⁺), 1206 (12, [M]⁺), 1085 (42, [M-CH₃OPhCH₂]⁺), 121 (100, [CH₃OPhCH₂]⁺); FD-HRMS: calcd. for C₇₁H₈₂O₁₇ [M]⁺ 1206.5552; found, m/z 1206.5557.

4.54.2. Physical data for iii-13S.

[α]D⁰ = -7.40 (c 1.13, CHCl₃); IR (film) 3465, 2930, 1610, 1510, 1250, 1070, 1035, 820 cm⁻¹; ¹H NMR (400 MHz, CDCl₃), δ. 3.27 (1H, br, C6'O'H), 3.32 (1H, ddd, J = 1.5, 4.6, 9.5 Hz, C5'H), 3.42 (1H, dd, J = 7.8, 8.5 Hz, C2'H), 3.51-3.58 (2H, C4'H, C3'H), 3.58 (1H, dd, J = 4.6, 11.3 Hz, C6'H'H), 3.63 (1H, dd, J = 1.5, 11.3 Hz, C6'H'H), 3.69 (1H, t, J = 4.6 Hz, C5'H), 3.74, 3.75 (each 3H, s, OCH₃), 3.76 (6H, s, OCH₃ x 2), 3.77, 3.78, 3.79 (each 3H, s, OCH₃), 3.82 (1H, t, J = 4.6 Hz, C4'H), 3.89, 4.02 (each 1H, brd, J = 13.0 Hz, C2’CH₂), 4.22, 4.30 (each 1H, d, J = 11.4 Hz, ArCH₂O), 4.36 (1H, d, J = 7.8 Hz, C1'H), 4.43 (1H, d, J = 11.9 Hz, ArCHHO), 4.46 (1H, d, J = 10.5 Hz, ArCHHO), 4.51 (2H, d, J = 11.9 Hz, ArCHHO x 2), 4.55 (1H, C6’H), 4.59 (1H, d, J = 11.9 Hz, ArCHHO), 4.59, 4.63, 4.68 (each 1H, d, J = 10.7 Hz, ArCH₂O, ArCHHO), 4.71 (1H, d, J = 10.5 Hz, ArCHHO), 4.72 (1H, d, J = 10.2 Hz, ArCHHO), 4.82 (1H, d, J = 4.6 Hz, C3’H), 4.84 (1H, d, J = 10.2 Hz, ArCHHO), 4.87 (1H, d, J = 10.7 Hz, ArCHHO), 5.15 (1H, brd, J = 10.6 Hz, C8’HH), 5.34, 5.36 (each 1H, brs, C1’H₂), 5.37 (1H, brd, J = 17.3 Hz, C8’HH), 5.86 (1H, ddd, J = 5.5, 10.6, 17.3 Hz, C7’H), 6.75-6.85 (14H, aromatic protons), 7.08 (2H, brd, J = 8.6 Hz, aromatic protons), 7.15-7.25 (12H, aromatic protons); ¹³C NMR (100 MHz, CDCl₃) δ 55.15, 55.17 (each OCH₃), 55.20 (OCH₃ x 3), 55.25 (each OCH₃ x 2), 68.40 (C6), 70.15 (C2’CH₂), 72.05
(C6'), 72.05, 72.75, 73.01, 73.91, 74.54, 74.58 (each ArCH2O), 75.12 (C5), 75.25 (ArCH2O), 77.39 (C3'), 77.76 (C4), 80.10 (C5'), 80.58 (C4'), 81.98 (C2), 84.59 (C3), 99.23 (C1), 113.60, 113.67, 113.67, 113.70, 113.70, 113.74, 113.74 (aromatic carbons), 116.02 (C8'), 117.44 (C1'), 129.11, 129.26, 129.29, 129.39, 129.58, 129.60, 129.85, 130.29, 130.32, 130.38, 130.58, 130.60, 130.62, 130.95 (aromatic carbons), 137.80 (C7'), 141.61 (C2'), 159.03, 159.07, 159.07, 159.07, 159.11, 159.11, 159.21 (aromatic carbons); FABMS (% rel. int.) m/z: 1229 (17, [M+Na]+), 121 (100, [CH3OPhCH2]+); FAB-HRMS: calcd. for C71H82O17Na [M+Na]+ 1229.5450; found, m/z 1229.5450.

4.55. [2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl]-(1→4)-2,3,6-tris-O-(4-methoxyphenylmethyl)-β-D-carbaglucopyranose (iii-14β)

A solution of iii-13R (56.3 mg, 46.6 μmol) in toluene (10.0 ml) was stirred in the presence of Grubbs' second-generation catalyst (1.2 mg, 1.4 μmol) at 80 °C. After 10 min, the mixture was concentrated in vacuo. Purification of the residue was performed with silica gel column chromatography (EtOAc:benzene = 14:86) to give iii-14β (52.0 mg, 95%) as a white amorphous. [α]D26° −20.5 (c 1.44, CHCl3); IR (film) 3470, 2910, 1610, 1510, 1250, 1070, 1035, 820 cm⁻¹; 1H NMR (500 MHz, CDCl3). δ, 2.50 (1H, d, J = 7.4 Hz, C1OH), 3.35 (1H, dd, J = 7.9, 8.7 Hz, C2'H), 3.38 (1H, ddd, J = 2.0, 4.7, 9.4 Hz, C5'H), 3.51-3.57 (2H, C4H, C3'H), 3.58-3.61 (2H, C6HH, C2H), 3.64 (1H, dd, J = 2.0, 11.0 Hz, C6'HH), 3.74 (3H, s, OCH3), 3.76 (6H, s, OCH3 x 2), 3.76 (3H, s, OCH3), 3.77 (6H, s, OCH3 x 2), 3.79 (6H, s, OCH3 x 2), 3.81 (1H, brd, J = 12.1 Hz, C6CHH), 4.13 (1H, C1H), 4.16 (1H, dd, J = 4.0, 6.5 Hz, C3H), 4.26 (1H, d, J = 11.5 Hz, ArCHHO), 4.29 (1H, brd, J = 12.1 Hz, C6CHH), 4.36 (1H, d, J = 11.5 Hz,
ArCHHO), 4.38, 4.42 (each 1H, d, J = 11.4 Hz, ArCH2O), 4.43-4.47 (3H, C4H, ArCHHO × 2), 4.56 (1H, d, J = 11.3 Hz, ArCHHO), 4.58 (1H, d, J = 10.9 Hz, ArCHHO), 4.63 (1H, d, J = 7.9 Hz, C1'H), 4.72 (1H, d, J = 10.5 Hz, ArCHHO), 4.71-4.76 (3H, ArCHHO × 3), 4.78 (1H, d, J = 11.3 Hz, ArCHHO), 4.83 (1H, d, J = 10.5 Hz, ArCHHO), 5.88 (1H, brd, J = 3.0 Hz, C5a'H), 6.77-6.84 (14H, aromatic protons), 7.07 (2H, brd, J = 8.7 Hz, aromatic protons), 7.16-7.24 (12H, aromatic protons); 13C NMR (100 MHz, CDCl3) δ 55.14 (OCH3), 55.18 (OCH3 × 3), 55.21 (OCH3), 55.23(OCH3 × 2), 68.59 (C1), 68.76 (C6'), 70.08 (C6), 71.33, 72.34, 72.90, 73.33, 74.45, 74.52 (ArCH2O × 6), 74.76 (C5'), 75.10 (C4), 75.28 (ArCH2O), 77.66 (C4'), 79.06 (C2), 79.26 (C3), 82.40 (C2'), 84.55 (C3'), 104.21 (C1'), 113.59, 113.64, 113.67, 113.73, 113.74, 113.74 113.79 (aromatic carbons), 128.10 (C5a), 129.20, 129.36, 129.39, 129.43, 129.51, 129.54, 129.57 (aromatic carbons), 130.21 (aromatic carbon × 2), 130.35, 130.53, 130.60, 130.73, 130.88 (aromatic carbons), 134.93 (C5), 159.03, 159.08, 159.08, 159.10, 159.11, 159.14, 159.22 (aromatic carbons); FDMS (% rel. int.) m/z: 1179 (1.6, [M+H]+), 1178 (4.3, [M]+), 1057 (100, [M-CH3OPhCH2]+), 121 (18, [CH3OPhCH2]+); FD-HRMS: calcd. for C69H78017 [M]+ 1178.5239; found, m/z 1178.5227.

4.56. [2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl]-(1→4)-2,3,6-tris-O-(4-methoxyphenylmethyl)-α-Δ55a-carbaglucopyranose (iii-14α)

In the similar manner as described in the Section 4.55, iii-13S (64.3 mg, 53.3 μmol) was treated with Grubbs’ second-generation catalyst (1.4 mg, 1.6 μmol) in toluene (10 ml) The following similar purification gave iii-14α (57.0 mg, 91%) as an oil. [α]D 25 +4.6 (c 1.42, CHCl3); IR (film) 3460, 2910, 1610, 1510, 1250,
1070, 1035, 820 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.69 (1H, d, J = 9.1 Hz, C1OH), 3.34 (1H, dd, J = 8.0, 8.9 Hz, C2' H), 3.39 (1H, ddd, J = 2.3, 4.0, 8.9 Hz, C5' H), 3.53 (1H, t, J = 8.9 Hz, C4' H), 3.56 (1H, t, J = 8.9 Hz, C3' H), 3.62-3.63 (2H, m, C6'H₂), 3.65 (1H, t, J = 5.1 Hz, C2H), 3.74 (3H, s, OCH₃), 3.76 (6H, s, OCH₃ x 2), 3.77 (6H, s, OCH₃ x 2), 3.79, 3.79 (6H, s, OCH₃ x 2), 3.80 (1H, C6HH), 4.24 (1H, d, J = 11.4 Hz, ArCHHO), 4.25 (2H, C6HH, C4H), 4.33 (1H, d, J = 11.4 Hz, ArCHHO), 4.34-4.36 (2H, C1H, C3H), 4.39 (1H, d, J = 11.2 Hz, ArCHHO), 4.39, 4.43 (each 1H, d, J = 13.2 Hz, ArCH₂O), 4.45 (1H, d, J = 10.4 Hz, ArCHHO), 4.53 (1H, d, J = 11.6 Hz, ArCHHO), 4.57 (1H, d, J = 8.0 Hz, C1H), 4.57 (1H, d, J = 11.4 Hz, ArCHHO), 4.68 (1H, d, J = 11.6 Hz, ArCHHO), 4.73 (1H, d, J = 10.4 Hz, ArCHHO), 4.73 (2H, d, J = 11.2 Hz, ArCHHO x 2), 4.73 (1H, d, J = 10.4 Hz, ArCHHO), 4.76 (1H, d, J = 11.4 Hz, ArCHHO), 4.84 (1H, d, J = 10.4 Hz, ArCHHO), 5.78 (1H, brd, J = 1.7 Hz, C5aH), 6.78-6.84 (14H, aromatic protons), 7.08 (2H, brd, J = 8.7 Hz, aromatic protons), 7.15-7.22 (12H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ: 55.15 (OCH₃), 55.19, 55.19 (OCH₃ x 4), 55.24, (OCH₃ x 2), 65.05 (C1), 68.80 (C6'), 70.21 (C6), 71.19, 71.43, 72.51, 72.92 (each ArCH₂O), 74.42 (C4), 74.50, 74.54 (each ArCH₂O), 74.70 (C5'), 75.17 (C2), 75.32 (ArCH₂O), 75.48 (C3), 77.66 (C4'), 82.47 (C2'), 84.54 (C3'), 104.76 (C1'), 113.60, 113.62, 113.70, 113.71, 113.71, 113.75, 113.75 (aromatic carbons), 128.31 (C5a), 129.21, 129.34, 129.39, 129.42, 129.43, 129.50, 129.57, 130.13, 130.19, 130.31, 130.34, 130.77, 130.83, 130.85 (aromatic carbons), 135.29 (C5), 159.01, 159.06, 159.06, 159.11, 159.12, 159.16, 159.23 (aromatic carbons); FABMS (%, rel. int.) m/z: 1201 (13, [M+Na]⁺), 121 (100, [CH₃OPhCH₂]⁺); FAB-HRMS: calcd. for C₆₉H₇₈O₁₇Na [M+Na]⁺ 1201.5137; found, m/z 1201.5162.
4.57. [2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-(4-methoxyphenylmethyl)-β-Δ5α-carbaglucopyranosyl acetate (iii-15β)

A mixture of iii-14β (17.0 mg, 14.0 μmol) and acetic anhydride (300 μl) and N,N-dimethyl-4-aminopyridine (1.7 mg, 14.0 μmol) in pyridine (1.1 ml) was stirred at room temperature for 10 min. After concentration in vacuo, the residue was purified with silica gel column chromatography (EtOAc/hexane = 60:40) to give iii-15β (16.1 mg, 92%). [α]D 24 -48 (c 0.62, CHCl₃); IR (film) 2910, 1735, 1510, 1460, 1245, 1070 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.98 (3H, s, CH₃CO), 3.32 (1H, C5'H), 3.36 (1H, dd, J = 7.7, 9.0 Hz, C2'H), 3.52-3.57 (3H, C3'H, C4'H, C6'HH), 3.64 (1H, d, J = 7.5, 9.6 Hz, C2H), 3.67 (1H, C6'HH), 3.75 (1H, C6HH), 3.74, 3.747, 3.753 (each 3H, s, ArOCH₃), 3.78 (6H, s, ArOCH₃ × 2), 3.788, 3.793 (each 3H, s, ArOCH₃), 3.81 (1H, dd, J = 70., 9.6 Hz, C3H), 4.25 (1H, d, J = 11.3 Hz, ArCHHO), 4.29 (1H, brd, J = 11.7 Hz, C6HH), 4.30 (1H, d, J = 11.3 Hz, ArCHHO), 4.39 (2H, s, ArCH₂O), 4.44 (1H, d, J = 10.5 Hz, ArCHHO), 4.53 (1H, d, J = 11.2 Hz, ArCHHO), 4.57 (1H, brd, J = 7.0 Hz, C4H), 4.67 (1H, d, J = 7.7 Hz, C1'H), 4.68 (1H, dd, J = 11.1 Hz, ArCHHO), 4.69 (1H, d, J = 10.9 Hz, ArCHHO), 4.72 (1H, d, J = 10.5 Hz, ArCHHO), 4.72 (1H, d, J = 11.1 Hz, ArCHHO), 4.74 (1H, d, J = 11.1 Hz, ArCHHO), 4.74 (1H, d, J = 10.5 Hz, ArCHHO), 4.85 (1H, d, J = 10.5 Hz, ArCHHO), 4.96 (1H, d, J = 10.9 Hz, ArCHHO), 5.45 (1H, brdd, J = 1.5, 7.5 Hz, C1H), 5.58 (1H, brd, J = 1.5 Hz, C5aH), 6.76-6.85 (14H, aromatic protons), 7.06-7.30 (14H, aromatic protons); ¹³C NMR (125 MHz, C₅D₅) δ 20.70 (3H, s, COCH₃), 54.68, 54.69, 54.70, 54.71, 54.72, 54.74, 54.75 (ArOCH₃ × 7), 69.12 (C6'), 70.14 (C6), 72.01, 73.19 (ArCH₂O × 2), 73.34 (C1), 74.34, 74.55, 74.91, 74.95, 74.34 (ArCH₂O × 5), 75.76 (C5'), 77.54 (C4), 78.21 (C4'), 80.60 (C2), 82.62 (C3), 83.03 (C2'), 85.25 (C3'), 85.75 (C2), 115.16 (C4), 124.84 (C3), 129.78 (ArCH₃), 135.36 (ArCH₃), 140.89 (ArCH₃), 147.06 (ArCH₃), 148.51 (ArCH₃), 152.14 (ArCH₃), 153.23 (ArCH₃), 162.44 (ArCH₃), 172.00 (CO).
103.38 (Cl'), 113.90, 113.93, 113.93, 114.03, 114.04, 114.05, 114.18 (aromatic carbons), 125.57 (C5a), 130.69, 131.11, 131.32, 131.35, 131.53, 131.79, 132.11 (aromatic carbons), 138.66 (C5'), 159.59, 159.60, 159.63, 159.65, 159.66, 159.77, 159.79 (aromatic carbon), 169.87 (C=O); ESIMS (% rel. int.) m/z 1259.5900 (28, calcd for C_{71}H_{80}O_{18}K [M+K]^+: 1259.4928), 1243.5282 (25, calcd. for C_{71}H_{80}O_{18}Na [M+Na]^+: 1243.5242), 1238.5698 (100, calcd. for C_{71}H_{80}NO_{19} [M+NH_{4}]^+: 1238.5688).

4.58. [2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-O-(4-methoxyphenylmethyl)-α-Δ⁵,⁶-carbaglucopyranosyl acetate (iii-15α)

In the same manner as described in the Section 4.57, iii-14α (23.2 mg, 20.0 mmol) was treated with acetic anhydride (1.0 ml) and N,N-dimethyl-4-aminopyridine (2.4 mg, 19.7 mmol) in pyridine (1.6 ml) to give iii-15α (23.6 mg, 96%). [α]_D^{23} +13 (c 0.59, CHCl₃); IR (film) 2910, 1735, 1610, 1510, 1460, 1245, 1070 cm⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 2.08 (3H, s, CH₃CO), 3.35 (1H, m, C5’H), 3.37 (1H, dd, J = 7.7, 8.7 Hz, C2’H), 3.56 (2H, C3’H, C4’H), 3.61 (2H, m, C6H₂), 3.67 (1H, dd, J = 3.7, 7.2 Hz, C2H), 3.74, 3.75 (each 3H, s, ArOCH₃), 3.76 (6H, s, ArOCH₃ × 2), 3.77, 3.78, 3.79 (each 3H, s, ArOCH₃), 3.85 (1H, brd, J = 12.5 Hz, C6HH), 4.23 (1H, dd, J = 4.1, 7.2 Hz, C3H), 4.23 (1H, d, J = 11.4 Hz, ArCHHO), 4.27 (1H, brd, J = 12.5, C6HH), 4.30 (1H, d, J = 11.4 Hz, ArCHHO), 4.33 (1H, brd, J = 4.1 Hz, C4H), 4.35, 4.42 (each 1H, d, J = 11.8 Hz, ArCH₂O), 4.45 (1H, d, J = 10.5 Hz, ArCHHO), 4.50, 4.58 (each 1H, d, J = 11.5 Hz, ArCH₂O). 4.63 (1H, d, J = 10.9 Hz, ArCHHO), 4.63 (1H, d, J = 11.3 Hz, ArCHOO), 4.64 (1H, d, J = 10.9 Hz, C1H), 4.72, 4.73 (each 1H, d, J = 10.5, ArCHHO), 4.74 (1H, d, J = 11.3 Hz, ArCHHO), 4.76 (1H, d, J = 10.9 Hz,
ArCHHO, 4.82 (1H, d, J = 10.5, ArCHHO), 5.57 (1H, t, J = 3.7 Hz, C1H), 5.78 (1H, brd, J = 3.7 Hz, C5aH), 6.77-6.84 (14H, aromatic protons), 7.07 (2H, brd, J = 8.7 Hz, aromatic protons), 7.13-7.24 (12H, aromatic protons); $^{13}$C NMR (125 MHz, C$_6$D$_6$) δ 20.78 (SCOCH$_3$), 54.67, 54.67, 54.69, 54.70, 54.70, 54.73 (each ArOCH$_3$), 67.84 (C1), 69.17 (C6'), 70.45 (C6), 71.99, 72.16, 73.20, 73.62, 74.56, 74.79, 75.33 (each ArCH$_2$O), 75.56 (C5'), 76.06 (C2), 76.79 (C4), 78.13 (C4'), 78.31 (C3), 82.91 (C2'), 85.18 (C3'), 104.59 (C1'), 113.94, 113.96, 113.96, 113.99, 114.01, 114.05, 114.17 (aromatic carbons), 123.60 (C5'a), 129.50, 129.53, 129.67, 129.68, 129.77, 129.84, 129.91, 130.84, 131.26, 131.34, 131.40, 131.75, 131.94 (aromatic carbons), 140.21 (C5), 159.60, 159.63, 159.65, 159.65, 159.67, 159.67, 159.76 (aromatic carbons), 170.04 (C=O); ESIMS (% rel. int.) m/z 1259.4909 (45, calcd. for C$_{71}$H$_{80}$O$_{18}$K [M+K]$^+$: 1259.4928), 1243.5165 (20, calcd. for C$_{71}$H$_{80}$O$_{18}$Na [M+Na]$^+$: 1243.5242), 1238.5617 (100, calcd. for C$_{71}$H$_{82}$O$_{19}$ [M+NH$_4$]$^+$ 1238.5450).

4.59. Stereochemical inversion of C1OH group of iii-14β into iii-14α

A solution of iii-14β (68.1 mg, 58.0 μmol) in THF (1.0 ml) was stirred with triphenylphosphine (46.0 mg, 175 μmol), p-nitrobenzoic acid (28.9 mg, 173 μmol), and diethyl azodicarboxylate (2.2 M solution in toluene, 79.0 μl, 174 μmol) at room temperature for 30 min. The mixture was poured into H$_2$O (20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (20 ml), dried over MgSO$_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc:hexane = 40:60) gave the oil containing the corresponding p-nitrobenzoate. Analytical sample was obtained by preparative silica gel TLC (EtOAc:hexane = 20:80). $[\alpha]_D^{23} +37$ (c 0.20, CHCl$_3$); IR (film)
2910, 1735, 1510, 1460, 1245, 1070 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.38 (1H, dd, \(J = 7.8, 9.0\) Hz, C2'H), 3.38 (1H, C5'H), 3.57 (2H, C3'H, C4'H), 3.62 (2H, m, C6'H\(_3\)), 3.73, 3.74, 3.756, 3.757, 3.78 (each 3H, OCH\(_3\)), 3.79 (6H, s, OCH\(_3\) \(\times\) 2), 3.81 (1H, dd, \(J = 3.8, 7.2\) Hz, C2'H), 3.91 (1H, brd, \(J = 12.7\) Hz, C6'H\(_3\)), 4.25 (1H, d, \(J = 11.3\) Hz, ArCH\(_{2}\)O), 4.27 (1H, brd, \(J = 12.7\) Hz, C6'H\(_3\)), 4.31 (1H, dd, \(J = 4.2, 7.2\) Hz, C3'H), 4.32 (1H, d, \(J = 11.3\) Hz, ArCH\(_{2}\)O), 4.37 (1H, d, \(J = 11.6\) Hz, ArCH\(_{2}\)O), 4.39 (1H, brd, \(J = 4.2\) Hz, C4'H), 4.43 (1H, d, \(J = 11.6\) Hz, ArCH\(_{2}\)O), 4.45 (1H, d, \(J = 10.3\) Hz, ArCH\(_{2}\)O), 4.49, 4.61 (each 1H, d, \(J = 11.5\) Hz, ArCH\(_{2}\)O), 4.63 (1H, d, \(J = 10.7\) Hz, ArCH\(_{2}\)O), 4.65 (1H, d, \(J = 7.8\) Hz, C1'H), 4.69 (1H, d, \(J = 11.5\) Hz, ArCH\(_{2}\)O), 4.73 (1H, d, \(J = 10.3\) Hz, ArCH\(_{2}\)O), 4.74 (1H, d, \(J = 10.6\) Hz, ArCH\(_{2}\)O), 4.77 (1H, d, \(J = 10.7\) Hz, ArCH\(_{2}\)O), 4.78 (1H, d, \(J = 11.5\) Hz, ArCH\(_{2}\)O), 4.81 (1H, d, \(J = 10.6\) Hz, ArCH\(_{2}\)O), 5.79 (1H, brt, \(J = 3.8\) Hz, C1'H), 5.89 (1H, brd, \(J = 3.8\) Hz, C5a'H), 6.70 (2H, brd, \(J = 8.7\) Hz, aromatic protons), 6.77-6.84 (14H, aromatic protons), 7.06-7.24 (14H, aromatic protons), 8.15, 8.24 (each 2H, brd, \(J = 8.9\) Hz, aromatic protons); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 55.16, 55.16, 50.20 (OCH\(_3\)), 55.21, 55.21, 55.26, 55.26 (OCH\(_3\)), 68.60 (C6'), 69.31 (C1), 69.79 (C6), 71.74, 71.82, 72.83, 72.96, 74.51 (ArCH\(_2\)O \(\times\) 5), 74.57 (C2), 74.84 (C2' or C5'), 74.84, 75.31 (ArCH\(_2\)O \(\times\) 2), 76.37 (C4), 77.12 (C3), 77.62 (C3' or C4'), 82.44 (C2' or C5'), 84.66 (C3' or C4'), 107.24 (C1'), 113.57, 113.58, 113.62, 113.70, 113.77, 113.77 (aromatic carbons), 123.44 (C5a), 129.27, 129.32, 129.39, 129.39, 129.40, 129.43, 129.59, 130.05, 130.15, 130.21, 130.32, 130.68, 130.80, 130.84, 130.89, 135.69 (aromatic carbons), 140.01 (C5), 150.19, 159.02, 159.04, 159.07, 159.12, 159.15, 159.15, 159.26 (aromatic carbons), 164.23 (C=O); ESIMS (% rel. int.) m/z 1366.5027 (45, calcd. for C\(_{76}H_{81}O_{26}NK [M+K]^+\): 1366.4989),
1350.5250 (50, calcd. for C_{76}H_{81}O_{20}Na [M+Na]^+; 1350.5929), 1345.5730 (100, calcd. for C_{76}H_{85}N_{2}O_{20} [M+NH_4]^+: 1345.5696).

The product was diluted with MeOH (4.0 ml) and stirred with NaOH (11.6 mg, 290 µmol) at room temperature for 2 hours. The mixture was poured into H_2O (20 ml) and extracted with AcOEt (20 ml x 3). The organic layers were washed with brine (20 ml), combined, dried over MgSO_4, and concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 30:70) gave iii-14α (30.7 mg, 44%). The 1H NMR spectrum and R_f value in the silica gel TLC were identical to the sample iii-14α described in the Section 4.58.

4.60. 2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl-(1→4)-1-acetylthio-2,3,6-tri-O-(4-methoxyphenylmethyl)-β-Δ^{5,5a}carbaglucopyranose (iii-17)

A solution of iii-14α (244 mg, 207 µmol) in CH_2Cl_2 (2.0 ml) was stirred with methansulfonic anhydride (154 mg, 885 µmol) and triethylamine (290 ml, 3.9 mmol) at -15°C for 20 min. The mixture was poured into H_2O (25 ml) and the aqueous layer was extracted with Et_2O (25 ml x 3). The combined ethereal solution was washed with brine (20 ml), dried over MgSO_4 and the concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 40:60) gave the crude mesylate (iii-16) which was immediately diluted with DMF (2.0 ml). Potassium thioacetate (240 mg, 2.11 mmol) was added to this solution at 0°C. After stirring for 30 min at the same temperature, the cooling bath was removed and the mixture was further stirred at room temperature for additional 1 h. The mixture was poured into H_2O (25 ml) and the aqueous layer was extracted with EtOAc (25 ml x 3). The combined organic solution was washed with brine (20 ml), dried over MgSO_4 and the concentrated in vacuo.
Silica gel column chromatography of the residue (EtOAc:hexane = 40:60) gave **iii-17** (223 mg, 87%) as caramel. $[\alpha]_D^{23}$ -59.5 (c 18.6, CHCl$_3$); IR (film) 2915, 2835, 1685, 1610, 1510, 1460, 1245 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.31 (3H, s, SCOCH$_3$), 2.34 (1H, dd, $J = 7.7$, 9.6 Hz, C2'H), 3.35 (1H, C5'H), 3.53 (2H, C3'H, C4'H), 3.61 (2H, C6'H$_2$), 3.67 (1H, dd, $J = 4.8$, 6.0 Hz, C2'H), 3.73, 3.748, 3.753, 3.76, 3.779, 3.788, 3.791 (each 3H, s, OCH$_3$), 4.12 (1H, dd, $J = 3.9$, 6.0 Hz, C3'H), 4.23 (1H, d, $J = 11.4$ Hz, ArCH$_2$O), 4.28 (1H, brd, $J = 12.6$ Hz, C6'H$_2$), 4.32 (1H, d, $J = 11.4$ Hz, ArCH$_2$O), 4.36 (1H, brd, $J = 3.9$ Hz, C4'H), 4.39 (1H, d, $J = 11.8$ Hz, ArCH$_2$O), 4.40 (1H, brdd, $J = 3.8$, 4.8 Hz, C1'H), 4.42 (1H, d, $J = 11.8$ Hz, ArCH$_2$O), 4.44 (1H, d, $J = 10.5$ Hz, ArCH$_2$O), 4.48 (1H, d, $J = 11.0$ Hz, ArCH$_2$O), 4.58 (1H, d, $J = 11.6$ Hz, ArCH$_2$O), 4.60 (1H, d, $J = 7.7$ Hz, C1'H), 4.67 (1H, d, $J = 11.0$ Hz, ArCH$_2$O), 4.71 (1H, d, $J = 10.5$ Hz, ArCH$_2$O), 4.72 (1H, d, $J = 11.6$ Hz, ArCH$_2$O), 4.72 (1H, d, $J = 10.5$ Hz, ArCH$_2$O), 4.74 (1H, d, $J = 10.6$ Hz, ArCH$_2$O), 4.83 (1H, d, $J = 10.5$ Hz, ArCH$_2$O), 5.67 (1H, brd, $J = 3.8$ Hz, C5a'H), 6.76-6.85 (14H, aromatic protons), 7.08, 7.14 (each 2H, brd, $J = 8.6$ Hz, aromatic protons), 7.16-7.2 (8H, aromatic protons), 7.23 (2H, brd, $J = 7.3$ Hz, aromatic protons); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 30.26 (SCOCH$_3$), 41.98 (C1), 51.15, 55.18, 55.18, 55.19, 55.19, 55.24, 55.24 (each OCH$_3$), 67.86 (C6'), 70.06 (C6), 71.26, 72.34, 72.8, 72.92 (each ArCH$_2$O), 74.42 (C4), 74.43 (ArCH$_2$O), 74.50 (C5'), 74.82, 75.26 (each ArCH$_2$O), 77.41 (C2), 77.69 (C4'), 78.64 (C3), 82.34 (C2'), 84.54 (C3'), 104.38 (C1'), 113.51, 113.55, 113.59, 113.68, 113.71, 113.73 (aromatic carbons), 125.65 (C5a), 129.17, 129.22, 129.27, 129.39, 129.50, 129.56, 129.60, 130.23, 130.32, 130.42, 130.52, 130.78, 130.93, 130.97 (aromatic carbons), 135.03 (C5), 158.93, 158.97, 159.02, 159.06, 159.07, 159.10, 159.21 (aromatic carbon), 195.29 (SC=O); ESIMS (%, rel. int.) m/z 1275.4811 (17, calcd. for C$_{71}$H$_{80}$O$_{17}$SK
[M+K]$^+$: 1366.4989), 1259.5075 (50, calcd. for C$_{71}$H$_{80}$O$_{17}$SNa [M+Na]$^+$: 
1259.5014), 1254.5507 (100, calcd. for C$_{71}$H$_{84}$O$_{17}$SN [M+NH$_4$]$^+$: 1254.5460).

4.61. Methyl 2,3-0-di-(4-methoxyphenylmethyl)-4,6-O-(4-methoxyphenyl 
methylidene)-$\alpha$-D-galactopyranoside (iii-18a)

A solution of methyl $\alpha$-D-galactopyranoside (122 mg, 628 $\mu$mol) in DMF (1.0 
ml) was stirred with $p$-anisaldehyde dimethylacetal (171 mg, 940 $\mu$mol) in the 
presence of camphorsulfonic acid (1.5 mg, 6.5 $\mu$mol) at 80°C for 30 min. The 
mixture was poured into saturated aqueous NaHCO$_3$ solution (20 ml) and the 
aqueous layer was extracted with EtOAc (15 ml × 3). The combined organic 
solution was washed with H$_2$O (20 ml) and brine (15 ml), dried over MgSO$_4$ and 
concentrated in vacuo. Silica gel column chromatography of the residue 
(MeOH:EtOAc = 10:90) gave Methyl 
4,6-O-(4-methoxyphenylmethylidene)-$\alpha$-D-galactopyranoside (164 mg, 83%) as 
an oil. [a]$_D^{23}$ +130 (c 0.80, CHCl$_3$); IR (film) 3470, 3400, 2910, 1620, 1515, 1035 
cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.13 (1H, d, 
$J$ = 9.1 Hz, C2OH), 3.37 (1H, d, 
$J$ = 9.1 Hz, C3OH), 3.46 (3H, s, C1OCH$_3$), 3.69 (1H, q, $J$ = 1.5 Hz, C5H), 3.80 
(3H, s, ArOCH$_3$), 3.87 (1H, ddd, $J$ = 3.4, 9.1, 10.0 Hz, C3H), 3.93 (1H, ddd, $J$ = 
3.4, 7.8, 10.0 Hz, C2H), 4.07 (1H, dd, $J$ = 1.5, 12.6 Hz, C6HH), 4.25 (1H, dd, $J$ = 
1.5, 3.4 Hz, C4H), 4.28 (1H, dd, $J$ = 1.5, 12.6 Hz, C6HH), 4.93 (1H, d, $J$ = 3.4 Hz, 
C1H), 5.51 (1H, s, ArCH), 6.90 and 7.42 (each 2H, brd, $J$ = 7.4 Hz, aromatic 
protons); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 55.30 (ArOCH$_3$), 55.72 (C1OCH$_3$), 
62.72 (C5), 69.30 (C6), 69.90, 69.95 (C2, C3), 75.80 (C4), 100.19 (C1), 101.26 
(ArCH), 113.62, 127.59, 130.04, 160.27 (aromatic carbons).

Sodium hydride (washed with hexane 240 mg, 10.0 mmol) slowly was added 
to a DMF solution (10 ml) of the diol (780 mg, 2.5 mmol) at room temperature.
Upon the addition of the substrate, H₂ gas was bubbled. After stirring for 10 min, 50% 4-methoxybenzyl bromide (4.0 g, 9.9 mmol) in toluene (5.0 ml) was added at 0 °C. After stirring at room temperature at 0°C for 10 min, the cooling bath was removed and the mixture was stirred at room temperature for 30 min. Methanol (2.0 ml) and Et₃N (2.0 ml) were successively added to decompose excess reagent. After stirring for additional 30 min, the mixture was poured into H₂O (100 ml), and the aqueous layer was extracted with EtOAc (70 ml × 3). The combined organic layer was washed successively with H₂O (100 ml) and brine (100 ml), dried over MgSO₄, and then concentrated in vacuo to give the crude solid. Recrystallization from EtOAc:hexane (30:70) gave **iii-18a** (1.10 g, 80%) as needles. mp 107-109 °C; [α]ᵢ²⁺ +61.5 (c 1.00, CHCl₃); IR (KBr) 2910, 1615, 1515, 1250, 1100, 1035, 825 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.37 (3H, s, OCH₃), 3.55 (1H, dt, J = 0.8, 1.5 Hz, C5H), 3.80 (6H, s, OCH₃ × 2), 3.81 (each 3H, s, OCH₃), 3.92 (1H, dd, J = 3.4, 10.2 Hz, C3H), 3.97 (1H, dd, J = 1.5, 12.6 Hz, C6HH), 4.01 (1H, dd, J = 3.4, 10.2 Hz, C2H), 4.11 (1H, dd, J = 0.8, 3.4 Hz, C4H), 4.17 (1H, dd, J = 1.5, 12.6 Hz, C6HH), 4.59 (1H, d, J = 11.8 Hz, ArCHHO), 4.66 (1H, d, J = 11.9 Hz, ArCHHO), 4.69 (1H, d, J = 3.4 Hz, C1H), 4.75 (1H, d, J = 11.9 Hz, ArCHHO), 4.79 (1H, d, J = 11.8 Hz, ArCHHO), 5.42 (1H, s, ArCH), 6.84-6.89 (6H, aromatic protons), 7.29 (2H, brd, J = 8.6 Hz, aromatic protons), 7.32 (2H, brd, J = 8.7 Hz, aromatic protons), 7.43 (2H, brd, J = 8.8 Hz, aromatic protons); ¹³C NMR (100 MHz, CDCl₃) δ 55.23 (OCH₃ × 2), 55.26, 55.45 (each OCH₃), 62.40 (C5), 69.33 (C6), 71.82, 73.40 (each ArCH₂O), 74.86 (C4), 74.98 (C2), 75.54 (C3), 99.55 (C1), 101.03 (ArCH), 113.42, 113.67, 113.70, 127.67, 129.19, 129.67, 130.50, 130.74, 130.89, 159.09, 159.22, 159.99 (aromatic carbons); FABMS (% rel. int.) m/z: 575 (8.9, [M+Na]⁺), 553 (19, [M+H]⁺), 431
(90, [M-CH₃OPhCH₂]+), 121 (100, [CH₃OPhCH₂]+); FAB-HRMS: calcd. for C₃₁H₃₆O₉Na [M+Na]+ 575.2257; found, m/z 575.2259.

4.62. Methyl 2,3-0-di-(4-methoxyphenylmethyl)-4,6-0-(4-methoxyphenyl methylidene)-β-D-galactopyranoside (iii-18b)

In the similar manner as described in the Section 4.61, methyl β-D-galactopyranoside (300 mg, 1.50 mmol) was treated with p-anicaldehyde dimethylacetal (410 mg, 2.3 mmol), camphorsulfonic acid (4.5 mg, 19.4 μmol) in DMF (2.0 ml) at 100°C for 30 min. The following similar work up gave the corresponding 4,6-O-(4-methoxyphenylmethylidene)acetal compound (337 mg, 73%) as amorphous powder. [α]D²³ -13.2 (c 1.05, CH₃OH); IR (film) 3400, 2840, 1615, 1515, 1250, 1070, 1055, 990, 820 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.49 (1H, d, J = 9.6 Hz, C3OH), 2.50 (1H, d, J = 1.9 Hz, C2OH), 3.49 (1H, ddd, J = 1.3, 1.5, 1.9 Hz, C5H), 3.59 (3H, s, OCH₃), 3.68 (1H, dt, J = 3.9, 9.6 Hz, C3H), 3.75 (1H, ddd, J = 1.9, 7.6, 9.6 Hz, C2H), 3.81 (3H, s, OCH₃), 4.08 (1H, dd, J = 1.9, 12.5 Hz, C6HH), 4.20 (1H, dd, J = 1.3, 3.9 Hz, C4H), 4.22 (1H, d, J = 7.6 Hz, C1H), 4.35 (1H, dd, J = 1.5, 12.5 Hz, C6HH), 5.51 (1H, s, ArCH), 6.88, 7.43 (each brd, 2H, J = 8.8 Hz, aromatic protons); ¹³C NMR (100 MHz, CDCl₃) δ 55.30, 57.20 (each OCH₃), 66.70 (C5), 69.12 (C6), 71.90 (C2), 72.78 (C3), 75.25 (C4), 101.43 (ArCH), 103.77 (Cl), 113.58, 127.75, 129.97, 160.27 (aromatic carbons); ESIMS (% rel. int.) m/z: 335.1118 (8.2, calcd. for C₁₅H₂₀O₇Na [M+Na]+: 335.1107), 313.1297 (100, calcd. for C₁₅H₂₁O₇ [M+H]+: 313.1287).

The obtained acetal (714 mg, 2.28 mmol mmol) was treated with NaH (110 mg, 4.58 mmol), 4-methoxybenzyl bromide (924 mg, 4.6 mmol) in DMF (16 ml) to give iii-18b (924 g, 73 %) as needles after recrystallization from EtOAc:hexane (30:70). mp 182-184 °C; [α]D²³ +57.7 (c 0.70, CHCl₃); IR (KBr) 2850, 1610,
1\textsuperscript{H} NMR (400 MHz, CDCl\textsubscript{3}) \delta 3.29 (1H, ddd, J = 0.7, 1.4, 1.5 Hz, C5\text{H}), 3.50 (1H, dd, J = 3.5, 9.7 Hz, C3\text{H}), 3.58 (3H, s, OCH\textsubscript{3}), 3.79 (1H, dd, J = 7.7, 9.7 Hz, C2\text{H}), 3.795 (3H, s, OCH\textsubscript{3}), 3.801, (6H, s, OCH\textsubscript{3} \times 2), 3.99 (1H, dd, J = 1.6, 12.4 Hz, C6\text{HH}), 4.04 (1H, dd, J = 0.7, 3.5 Hz, C4\text{H}), 4.28 (1H, d, J = 7.7 Hz, C1\text{H}), 4.28 (1H, dd, J = 1.4, 12.4 Hz, C6\text{HH}), 4.66, 4.70 (each 1H, d, J = 12.0 Hz, ArCH\textsubscript{2}O), 4.69 (1H, d, J = 10.4 Hz, ArCHH), 4.81 (1H, d, J = 10.4 Hz, ArCHHO), 5.44 (1H, s, ArCH), 6.83, 6.86, 6.87, 7.28, 7.31, 7.47 (each 2H, brd, J = 8.8 Hz, aromatic protons); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 55.25, 55.27, 55.29, 57.03 (each OCH\textsubscript{3}), 66.38 (C5), 69.17 (C6), 71.63 (ArCH\textsubscript{2}O), 74.03 (C4), 74.89 (ArCH\textsubscript{2}O), 78.21 (C2), 78.75 (C3), 101.30 (ArCH), 104.74 (C1), 113.45, 113.67, 113.70, 127.86, 129.34, 129.68, 130.51, 130.51, 131.13, 159.13, 159.18, 160.04 (aromatic carbons); ESIMS (% rel. int.) m/z 591.1971 (18, calcd. for C\textsubscript{3}lH\textsubscript{3}6O\textsubscript{9}K [M+K]\textsuperscript{+}: 591.1996), 575.2233 (12, calcd. for C\textsubscript{3}lH\textsubscript{3}6O\textsubscript{9}Na [M+Na]\textsuperscript{+}: 575.2257), 570.2677 (100, calcd. for C\textsubscript{3}lH\textsubscript{4}0O\textsubscript{9}N [M+NH\textsubscript{4}]\textsuperscript{+}: 570.2703), 553.2414 (25, calcd. for C\textsubscript{3}lH\textsubscript{3}7O\textsubscript{9} [M+H]\textsuperscript{+}: 553.2438), 431.1699 (14, calcd. for C\textsubscript{2}3H\textsubscript{2}7O\textsubscript{8} [M-CH\textsubscript{3}OPhCH\textsubscript{2}]\textsuperscript{+}: 431.1706).

4.63. Methyl 2,3,6-\textit{O}-tri-(4-methoxyphenylmethyl)-\textalpha-\textdelta-galactopyranoside (iii-19a)

A suspension of iii-18a (64.1 mg, 115 \textmu mol) and finely powdered molecular sieves (acid washed type, Fluka #69841, activated 200°C for 20 min under vacuumed condition before use, 30 mg) in THF (1.0 ml) was stirred with boran trimethylamine complex (50.0 mg, 686 \textmu mol) and AlCl\textsubscript{3} (93.0 mg, 698 \textmu mol) at room temperature for 10 min. Saturated aqueous potassium tartarate (5 ml) was added and the mixture was further stirred at room temperature for 20 min. After filtration, the aqueous layer was extracted with EtOAc (10 mL \times 3).
combined organic extract was washed with brine (20 ml), dried over MgSO₄, and then concentrated \textit{in vacuo}. Silica gel column chromatography of the residue (EtOAc:hexane = 30:70) gave \textbf{iii-19a} (37.2 mg, 57%) as caramel. \([\alpha]_D^{23} +18\) (c 0.87, CHCl₃); IR (film) 3500, 2910, 1610, 1510, 1460, 1250, 1090 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 2.60 (1H, s, C4OH), 3.35 (3H, s, C1OCH₃), 3.61 (1H, dd, \(J = 6.2, 10.2\) Hz, C6HNO), 3.68 (1H, dd, \(J = 5.4, 10.2\) C6HNO), 3.78, 3.79 (each 3H, s, ArOCH₃), 3.80 (2H, C2H, C3H), 3.84 (1H, brdd, \(J = 5.4, 6.2\) Hz, C5H), 3.99 (1H, brs, C4H), 4.47, 4.50 (each 1H, d, \(J = 11.5\) Hz, ArCH₂O), 4.58 (1H, d, \(J = 11.8\) Hz, ArCHHO), 4.60 (1H, d, \(J = 2.3\) Hz, C1H), 4.61, 4.70 (1H, dd, \(J = 11.3\) Hz, ArCH₂O), 4.70 (1H, dd, \(J = 11.8\) Hz, ArCHHO), 6.82-6.95 (6H, aromatic protons); 13C NMR (100 MHz, CDCl₃) \(\delta\) 55.18 (ArOCH₃, and C1OCH₃), 55.23 (ArOCH₃ \(\times 2\)), 68.09 (C4), 68.27 (C5), 69.23 (C6), 72.35, 73.09, 73.20 (each ArCH₂O), 75.23 (C2 or C3), 77.22 (C2 or C3), 98.63 (C1), 113.73, 113.81, 129.25, 129.39, 129.58, 130.07, 130.30, 130.50, 159.18, 159.26, 159.28 (aromatic carbons); ESIMS (% rel. int.) \(m/z\) 593.2150 (12, calcd. for C₃₁H₃₈KO₉ \([M+K]^+: 593.2159\)), 577.2412 (18, calcd. for C₃₁H₃₈NaO₉ \([M+Na]^+: 577.2414\), 572.2865 (100, calcd. for C₃₁H₄₂NO₉ \([M+NH₄]^+: 572.2860\)).

4.64. Methyl 2,3,6-\(O\)-tri-(4-methoxyphenylmethyl)-\(\beta\)-D-galactopyranoside (\textbf{iii-19b})

In the similar manner as described in the Section 4.63, \textbf{iii-18b} (187 mg, 338 \(\mu\)mol) was treated with the finely powdered molecular sieves (60.0 mg), boran trimethylamine complex (157 mg, 2.15 mmol) and AlCl₃ (277 mg, 2.07 mmol) in THF (4.0 ml) to give \textbf{iii-19b} (125 mg, 66%) as caramel after work up. \([\alpha]_D^{23} +5.4\) (c 0.97, CHCl₃); IR (film) 3490, 2910, 2835, 1610, 1510, 1460, 1250, 1095
cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 2.50\) (1H, d, \(J = 1.7\) Hz, C4OH), 3.44 (1H, dd, \(J = 3.3, 9.4\) Hz, C3H), 3.51 (1H, brdd, \(J = 5.9, 6.1\) Hz, C5H), 3.55 (3H, CI0CH\(_3\)), 3.58 (1H, dd, \(J = 7.8, 9.4\) Hz, C2H), 3.69 (1H, dd, \(J = 5.9, 9.9\) Hz, C6HH), 3.76 (1H, dd, \(J = 6.1, 9.9\) Hz, C6HH), 3.78 (9H, s, ArOCH\(_3\) \(\times 3\)) \(\), 3.96 (IH, dd, \(J = 9.9\) Hz, C2H) \(\), 4.24 (1H, d, \(J = 7.8\) Hz, C1H), 4.50, 4.62 (each 2H, s, ArCH\(_2\)O \(\times 2\)), 4.63, 4.79 (each 1H, d, \(J = 10.6\) Hz, ArCH\(_2\)O), 6.82-6.90 (6H, aromatic protons), 7.21-7.30 (6H, aromatic protons); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 55.19\) (ArOCH\(_3\) \(\times 3\)), 56.85 (C1OCH\(_3\)), 66.81 (C4), 66.86 (C6), 71.98 (ArCH\(_2\)O), 73.11 (C5), 73.30, 74.70 (each ArCH\(_2\)O), 78.64 (C2), 80.18 (C3), 113.65, 113.78, 179.37, 129.39, 129.63, 129.97, 130.05, 130.83, 159.13, 159.24, 159.30 (each aromatic carbon); ESIMS (% rel. int.) m/z 593.2150 (8.2, calcd. for C\(_{31}\)H\(_{38}\)K\(_{9}\) [M+K]+: 593.2153), 577.2412 (16, calcd. for C\(_{31}\)H\(_{38}\)Na\(_{9}\) [M+Na]+: 577.2413), 572.2865 (100, calcd. for C\(_{31}\)H\(_{42}\)NO\(_{9}\) [M+NH\(_{4}\)]+: 572.2860).

4.65. Methyl 2,3,6-O-tri-(4-methoxyphenylmethyl)-4-O-trifluoromethane sulfonyl-\(\alpha\)-D-galactopyranoside (iii-20a)

Trifluoromethanesulfonic anhydride (259 mg, 921 \(\mu\)mol) was added to a mixture of iii-19a (335 mg, 604 \(\mu\)mol) and pyridine (145 mg, 1.83 \(\mu\)mol) in CH\(_2\)Cl\(_2\) (2.0 ml) at 0 °C. After 20 min, the mixture was poured into H\(_2\)O (30 ml); and the aqueous layer was extracted with EtOAc (30 ml \(\times 3\)). The combined organic layer was washed with brine (50 ml), dried over MgSO\(_4\), and then concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:hexane = 20:80) to give iii-20a (334 mg, 80 %) as an oil. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 3.34\) (3H, s, C1OCH\(_3\)), 3.53 (2H, m, C6H\(_2\)); 3.72 (1H, dd, \(J = 3.5, 10.0\) Hz, C2H), 3.79 (9H, s, ArOCH\(_3\) \(\times 3\)), 3.93 (1H, dd, \(J =\)
2.6, 10.0 H, C3H), 4.02 (1H, brt, J = 4.0 Hz, C5H), 4.37, 4.51 (each 1H, d, J = 11.1 Hz, ArCH2O), 4.54 (1H, d, J = 3.5 Hz, C1H), 4.56 (1H, d, J = 11.0 Hz, ArCHHO), 4.57, 4.74 (each 1H, d, J = 11.4 Hz, ArCH2O), 4.77 (1H, d, J = 11.0 Hz, ArCHHO), 5.35 (1H, brd, J = 2.6 Hz, C4H), 6.80-6.90 (6H, aromatic protons), 7.20-7.35 (6H, aromatic protons). This sample was immediately used for the next step.

4.66. Methyl 2,3,6-O-tri-(4-methoxyphenylmethyl)-4-O-trifluoromethane sulfonyl-β-D-galactopyranoside (iii-20b)

In the similar manner as described in the Section 4.65, iii-19b (187 mg, 336 μmol) was treated with trifluoromethanesulfonic anhydride (142 mg, 500 μmol) and pyridine (80 mg, 1.00 mmol) in CH2Cl2 (1.5 ml) to give iii-20b (194 mg, 84 %) as an oil. 1H NMR (400 MHz, CDCl3) δ 3.50-3.56 (2H, C2H, C3H), 3.54 (3H, s, C1OCH3), 3.59 (1H, dd, J = 4.5, 10.8 Hz, C6HH), 3.65-3.72 (2H, C5H, C6HH), 3.78, 3.796, 3.784 (each 3H, s, ArOCH3), 4.26, d, J = 7.1 Hz, C1H), 4.36 (1H, d, J = 11.0 Hz, ArCHHO), 4.51 (1H, d, J = 11.4 Hz, ArCHHO), 4.56 (1H, d, J = 11.0 Hz, ArCHHO), 4.64, 4.75 (each 1H, d, J = 10.4 Hz, ArCH2O), 4.78 (1H, d, J = 11.4 Hz, ArCHHO), 6.23, 6.82, 6.89, 7.23, 7.26, 7.27 (each 2H, brd, J = 8.7 Hz, aromatic protons). This sample was immediately used for the next step.

4.67. Methyl 2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-(4-methoxyphenylmethyl)-1-thio-β-D-6Sα-carbaglucopyranosyl-(1→4)-2,3,6-O-tri-(4-methoxyphenylmethyl)-α-D-glucopyranoside (iii-22a)

A solution of iii-17 (38.0 mg, 31.0 μmol) in a mixture of methanol (2.0 ml) and CH2Cl2 (2.0 ml) was stirred with sodium methoxide (6.8 mg, 126 μmol) at room
temperature for 4 hr. The mixture was poured into saturated aqueous NH₄Cl solution (20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic solution was washed with brine (20 ml), dried over MgSO₄, and the concentrated in vacuo to give the crude thiol iii-21, which was immediately used for the next step without purification. A mixture of iii-21 thus obtained and iii-20a (21 mg, 31.0 µmol) in THF (0.4 ml) was stirred with NaH (2.7 mg, 113 µmol) at room temperature for 40 min. The mixture was poured into H₂O (15 ml) and the aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine (20 ml), dried over MgSO₄, and then concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc:hexane = 34:66) gave iii-22a (30 mg, 55%) as a caramel. [α]D²³ -15 (c 0.68, CHCl₃); IR (film) 2900, 1610, 1460, 1250, 1070, 1035 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.86 (1H, t, J = 11.0 Hz, C4H), 3.27 (1H, ddd, J = 1.7, 4.6, 9.3 Hz, C5”H), 3.31 (1H, dd, J = 7.8, 8.8 Hz, C2”H), 3.34 (3H, s, C1OCH₃), 3.47-3.56 (7H, C2H, C1’H, C2’H, C3”H, C4”H, C6”HH), 3.59 (1H, dd, J = 1.6, 10.6 Hz, C6HH), 3.63 (2H, C3H, C6”HH), 3.65 ‘3H, s, ArOCH₃), 3.68 (1H, C5H), 3.69, 3.708, 3.711, 3.73, 3.75, 3.785, 3.786, 3.79, 3.792, 3.793 (each 3H, s, ArOCH₃), 3.97 (1H, d, J = 3.5, 10.6 Hz, C6HH), 4.08, 4.25 (each 1H, d, J = 11.2 Hz, ArCH₂O), 4.26 (1H, d, J = 11.4 Hz, ArCHHO), 4.34 (1H, brd, J = 11.2 Hz, C6’HH), 4.34 (1H, d, J = 11.4 Hz, ArCHHO), 4.37, 4.40 (each 1H, d, J = 11.8 Hz, ArCHHO), 4.50 (1H, brd, J = 6.9 Hz, C4’H), 4.50 (1H, d, J = 10.3 Hz, ArCHHO), 4.55 (1H, d, J = 11.8 Hz, ArCHHO), 4.56 (1H, d, J = 3.7 Hz, C1H), 4.58 (1H, d, J = 10.7 Hz, ArCHHO), 4.66 (1H, d, J = 11.2 Hz, ArCHHO), 4.67 (1H, d, J = 7.8 Hz, C1”H), 4.698 (1H, d, J = 10.5 Hz, ArCHHO), 4.700 (1H, d, J = 10.4 Hz ArCHHO), 4.71 (1H, d, J = 11.8 Hz, ArCHHO), 4.75 (1H, d, J = 10.7 Hz, ArCHHO), 4.77 (1H, d, J = 10.3 Hz, ArCHHO), 4.82 (1H, d, J = 10.5 Hz,
ArCHHO), 4.85 (2H, s, ArCH₂O), 4.88 (1H, d, J = 11.2 Hz, ArCHHO), 5.90 (1H, brs, C5’aH), 6.70-6.84 (20H, aromatic protons), 7.06-7.32 (20H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 48.33 (C1’), 49.77 (C4), 55.05, 55.12, 55.16, 55.16, 55.17, 55.21, 55.24, 55.25, 55.25, 55.13 (OCH₃), 68.70 (C6”), 68.96 (C6), 70.37 (C6’), 71.13 (ArCH₂O), 71.85 (C5), 72.62, 72.84, 72.96, 73.78, 74.21, 74.42, 74.47 (ArCH₂O), 74.88 (C5”), 75.22 (ArCH₂O), 75.95, 76.01 (ArCH₂O, C4’), 77.82, 79.35, 79.96, 80.56, 84.55 (C2, C3, C2’, C3”, C4”), 81.71 (C3’), 82.62 (C2”), 98.46 (C1), 103.23 (C1”), 113.40, 113.46, 113.52, 113.63, 113.63, 113.80, 113.66, 113.70, 113.72, 113.74 (aromatic carbons), 129.08 (C5’a), 129.24, 129.33, 129.36, 129.43, 129.46, 129.52, 129.56, 129.74, 130.18, 130.38, 130.46, 130.50, 130.55, 130.79, 130.88, 131.09, 131.16, 131.35 (aromatic carbons), 133.73 (C5’), 158.79, 158.94, 158.97, 158.97, 158.99, 159.00, 159.06, 159.07, 159.16, 159.34 (aromatic carbons); ESIMS (%, rel. int.) m/z 1769.7165 (12, calcd. for C₁₀₀H₁₁₄O₂₄SK [M+K]+ : 1769.7058), 1753.7450 (31, calcd. for C₁₀₀H₁₁₄O₂₄SNa [M+Na]+ : 1753.7318), 1748.7835 (100, calcd. for C₁₀₄H₁₁₅O₂₄SN [M+NH₄]+ 1748.7765). 1731.7600 (95, calcd. for C₁₀₀H₁₁₅O₂₄S [M+H]+ 1731.7499).

4.68. Methyl 2,3,4,6-O-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-(4-methoxyphenylmethyl)-1-thio-β-Δ⁵⁵α-carbaglucopyranosyl-(1→4)-2,3,6-O-tri-(4-methoxyphenylmethyl)-β-D-glucopyranoside (iii-22b)

In a similar manner as described in the Section 4.67, iii-17 (173 mg, 140 µmol) was treated employing sodium methoxide (30 mg, 555 µmol), MeOH (8.0 ml), iii-20b obtained in the Section 4.66, THF (0.5 ml), and NaH (12.2 mg, 508 µmol). The following workup gave iii-22b (141 mg, 58%) as a caramel.
[α]_D^{23} -2.40 (c 1.20, CHCl₃); IR (film) 2910, 1610, 1460, 1250, 1070, cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.82 (1H, t, J = 10.7 Hz, C4H), 3.27 (1H, ddd, J = 1.5, 4.6, 9.3 Hz, C5”H), 3.31 (1H, dd, J = 7.8, 9.0 Hz, C2”H), 3.32 (1H, dd, J = 8.5, 10.7 Hz, C3H), 3.36 (1H, dd, J = 7.5, 8.5 Hz, C2H), 3.40 (1H, ddd, J = 1.8, 4.2, 10.7 Hz, C5H), 3.48 (2H, C3”H, C4”H), 3.51 (1H, t, J = 7.9 Hz, C2’H), 3.52 (1H, d, J = 11.5 Hz, C6’H), 3.54 (1H, m, C6’HH), 3.55 (3H, s, OCH₃), 3.58 (1H, m, C1’H), 3.63 (1H, dd, J = 1.5, 10.6 Hz, C6”HH), 3.681, 3.696, 3.706, 3.709, 3.73, 3.75, 3.782, 3.784, 3.787, 3.792 (each 3H, s, ArOCH₃), 3.80 (1H, C6HH), 3.81 (1H, dd, J = 5.5, 7.9 Hz, C3’H), 3.87 (1H, dd, J = 4.2, 10.5 Hz, C6HH), 4.09 (1H, d, J = 11.2 Hz, ArCHHO), 4.22 (1H, d, J = 7.5 Hz, C1H), 4.25 (1H, d, J = 11.2 Hz, ArCHHO), 4.31 (1H, brd, J = 11.5 Hz, C6’HH), 4.31 (1H, d, J = 11.5 Hz, ArCHHO), 4.38 (2H, s, ArCH₂O), 4.38 (1H, d, J = 11.3 Hz, ArCHHO), 4.42, 4.47 (each 1H, d, J = 10.4 Hz, ArCH₂O), 4.48 (1H, brd, J = 5.5 Hz, C4’H), 4.56 (1H, d, J = 11.6 Hz, ArCHHO), 4.62 (1H, d, J = 10.4 Hz, ArCHHO), 4.64 (1H, d, J = 11.3 Hz, ArCHHO), 4.65 (1H, d, J = 7.8 Hz, C1’H), 4.69 (1H, d, J = 10.5 Hz, ArCHHO), 4.70 (1H, d, J = 10.4 Hz, ArCHHO), 4.73 (1H, d, J = 10.6 Hz, ArCHHO), 4.75 (1H, d, J = 10.4 Hz, ArCHHO), 4.82 (2H, s, ArCH₂O), 4.82 (1H, d, J = 10.5 Hz, ArCHHO), 4.83 (1H, d, J = 10.4 Hz, ArCHHO), 4.87 (1H, d, J = 11.3 Hz, ArCHHO), 5.87 (1H, brs, C5’aH), 6.72 (2H, brd, J = 8.7 Hz, aromatic protons), 6.76-6.84 (18H, aromatic protons), 7.06 (2H, brd, J =8.7 Hz, aromatic protons), 7.12-7.28 (18H, aromatic protons); ¹³C NMR (125 MHz, CDCl₃) δ 48.10 (C1’), 49.82 (C4), 55.09, 55.14 (each ArOCH₃), 55.15 (ArOCH₃ × 3), 55.16, 55.20 (each ArOCH₃), 55.24 (ArOCH₃ × 2), 55.25 (ArOCH₃), 56.95 (C1OCH₃), 68.70 (C6”), 69.24 (C6), 70.34 (C6’), 71.15, 72.66, 72.83, 73.70, 79.97, 74.42 (each ArCH₂O), 74.45 (ArCH₂O × 2), 74.84 (C5”), 75.21, 75.80 (each ArCH₂O), 75.94 (C4’), 76.83
(C5), 77.81 (C4"), 77.84 (C2'), 81.45 (C3'), 82.54 (C2"), 82.70 (C3), 83.04 (C2), 84.55 (C3"), 103.28 (C1"), 104.53 (C1), 113.41, 113.50, 113.54, 113.62, 113.64, 113.64, 113.70, 113.72, 113.73, 113.73 (aromatic carbons), 128.72 (C5'a), 129.10, 129.17, 129.22, 129.33, 129.36, 129.44, 129.46, 129.52, 129.70, 129.73, 130.42, 130.46, 130.48, 130.50, 130.74, 130.76, 130.83, 130.89, 130.99 (aromatic carbons), 133.84 (C5'), 158.80, 158.93, 158.94, 158.98, 158.99, 159.01, 159.05, 159.07, 159.16, 159.16 (aromatic carbons); ESIMS (% rel. int.) m/z 1769.7074 (8, calcd. for C₁₀₀H₁₁₄O₂₄SK [M+K]⁺: 1769.7058), 1753.7411 (26, calcd. for C₁₀₀H₁₁₄O₂₄SNa [M+Na]⁺: 1753.7318), 1748.7764 (100, calcd. for C₁₀₄H₁₁₅O₂₄SN [M+NH₄]⁺ 1748.7765). 1731.7500 (96, calcd. for C₁₀₆H₁₁₅O₂₄S [M+H]⁺ 1731.7499).

4.69. Methyl β-D-glucopyranosyl-(1→4)-1-thio-β-D- rib 5,5α-carbaglucopyranosyl-(1→4)-α-D-glucopyranoside (iii-2a)

A suspension of iii-22a (130 mg, 75 µmol) in a mixture of CH₂Cl₂ (2.0 ml) and H₂O (200 µl) was stirred with 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) (332 mg, 1.46 mmol) at room temperature for 13 hours. The mixture was poured into water (10 ml) and the aqueous layer was washed with EtOAc (10 mL x 3) and concentrated in vacuo. After dilution with small amount of H₂O (ca. 0.3 ml), the resulting solution was loaded on a ODS Sep-Pak® cartridge (5.0 g). After washing with MeOH:H₂O = 5:95, elution with MeOH:H₂O = 10:90 gave the fraction containing iii-2a. After methanol was removed by rotary evaporator, the resulting aqueous solution was lyophilized to give iii-2a (34.7 mg, 87%) as white amorphous powder. [α]D²³ +2.5 (c 0.52, H₂O); ¹H NMR (500 MHz, D₄O) δ 2.60 (1H, t, J = 10.9 Hz, C4H), 3.20 (1H, dd, J = 8.0, 9.2 Hz, C2"H), 3.26 (3H, s, OCH₃), 3.27 (1H, t, J = 9.4 Hz, C4"H), 3.37 (1H, ddd, J = 2.1, 6.1, 9.4 Hz, C5"H),
3.38 (1H, dd, J = 9.2, 9.4 Hz, C3″H), 3.40 (1H, brd, J = 9.0 Hz, C1′H), 3.46 (1H, dd, J = 3.7, 9.6 Hz, C2H), 3.51 (1H, dd, J = 9.0, 10.0 Hz, C2′H), 3.54 (1H, dd, J = 9.6, 10.9 Hz, C3H), 3.59 (1H, dd, J = 7.6, 10.0 Hz, C3′H), 3.60 (1H, dd, J = 6.1, 12.3 Hz, C6″HH), 3.63 (1H, ddd, J = 2.2, 4.7, 10.9 Hz, C5H), 3.79 (1H, dd, J = 2.1, 12.3 Hz, C6″HH), 3.93 (1H, dd, J = 2.2, 12.1 Hz, C6HH), 4.01, 4.15 (each 1H, brd, J = 13.6 Hz, C6′H), 4.27 (1H, brd, J = 7.6 Hz, C4′H), 4.50 (1H, d, J = 8.0 Hz, C1″H), 4.71 (1H, 1H, d, J = 3.7 Hz, C1H), 5.71 (1H, brs, C5′aH); 13C NMR (125 MHz, D2O) δ 48.22, 48.64, 55.26, 60.83, 61.56, 61.59, 69.69, 71.45, 72.13, 72.34, 73.60, 73.71, 75.05, 75.89, 76.28, 82.35, 99.53, 103.31, 126.83, 136.44; ESIMS (%, rel. int.) m/z 569.1313 (10, calcd. for C26H34O14SK [M+K]+: 569.1306), 553.1570 (100, calcd. for C26H34O14SNa [M+Na]+: 553.1567), 531.1754 (17, calcd. for C26H35O14S [M+H]+ 531.1754).

4.70. Methyl β-D-glucopyranosyl-(1→4)-1-thio-β-Δ5,5a-carbaglucopyranosyl-(1→4)-β-D-glucopyranoside (iii-2b)

In the similar manner as described in the Section 4.69, iii-22b (139 mg, 80 μmol) was treated employing DDQ (370 mg, 1.63 mmol), CH2Cl2 (2.0 ml), and H2O (2.0 ml). The following workup gave iii-2b (32 mg, 75%) as white amorphous powder. [α]D23 -81.2 (c 0.65, H2O); 1H NMR (500 MHz, CDCl3) δ 2.59 (1H, t, J = 10.8 Hz, C4H), 3.15 (1H, dd, J = 8.0, 9.0 Hz, C2H), 3.21 (1H, dd, J = 8.0, 9.3 Hz, C2″H), 3.30 (1H, dd, J = 9.6, 9.6 Hz, C4″H), 3.38 (1H, dd, J = 9.0, 10.8 Hz, C3H), 3.39 (1H, C5″H), 3.40 (1H, t, J = 9.3 Hz, C3″H), 3.42 (1H, brd, J = 9.0 Hz, C1′H), 3.44 (1H, 3H, s, OCH3), 3.47 (1H, ddd, J = 2.1, 5.5, 10.8 Hz, C5H), 3.52 (1H, dd, J = 9.0, 10.1 Hz, C2′H), 3.60 (1H, dd, J = 7.4, 10.1 Hz, C3′H), 3.61 (1H, dd, J = 5.8, 12.5 Hz, C6HH), 3.80 (1H, dd, J = 2.2, 12.5 Hz, C6HH), 3.83 (1H, dd, J = 5.3, 12.3 Hz, C6HH), 4.03 (1H, dd, J = brd, J = 13.5 Hz,
4.71. Methyl 2,3,4-6-tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (iii-23)

A mixture of iii-2b (5.2 mg, 9.8 μmol) and 4-(dimethylamino)pyridine (200 μg, 1.6 μmol) in a mixture of pyridine (1.0 ml) and acetic anhydride (200 μl) at 60°C for 2 hours. After concentration in vacuo, silica gel column chromatography of the residue with EtOAc:hexane = 80:20 gave iii-23 (7.8 mg, 87%). [α]D23 -52 (c 0.56, CDCl3); IR (film) 2940, 1750, 1225, 1040 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 1.66, 1.67, 1.69, 1.77, 1.79, 1.82, 1.84, 1.89, 1.93, 1.97 (each 3H, s, OCOCH₃), 2.84 (1H, dd, J = 10.0, 11.0 Hz, C4'H), 2.92 (1H, ddd, J = 1.9, 4.5, 11.0 Hz, C5'H), 3.21 (3H, s, C1OCH₃), 3.46 (1H, ddd, J = 2.1, 4.6, 10.1 Hz, C5"H), 3.54 (1H, brdd, J = 3.7, 10.0 Hz, C3'H), 4.04 (1H, d, J = 7.6 Hz, C1'H), 4.05 (1H, brd, J= 4.4 Hz, C4'H), 4.09 (1H, dd, J = 2.1, 12.4 Hz, C6"HH), 4.31 (1H, dd, J = 4.5, 12.0 C6HH), 4.37 (1H, dd, J = 4.6, 12.4, C6"HH), 4.54 (1H, d, J = 8.1 Hz, C1"H), 4.58 (2H, brd, J = 7.8 Hz, C6'H₂), 4.63 (1H, dd, J = 1.9, 12.4 Hz, C6HH), 5.21 (1H, dd, J = 8.1, 9.4 Hz, C2"H), 5.21 (1H, dd, J = 7.6, 9.4 Hz, C2'H), 5.23 (1H, dd, J = 9.4, 10.1 Hz, C4"H), 5.25
(1H, dd, J = 9.4, 10.0 Hz, C3'H) 5.37 (1H, t, J = 9.4 Hz, C3''H), 5.40 (1H, dd, J = 5.0, 6.6 Hz, C2'H), 5.77 (1H, dd, J = 4.4, 6.6 Hz, C3'H), 5.92 (1H, brd, J = 3.7 Hz, C5a'H); 13C NMR (125 MHz, C6D6) δ 20.08, 20.13, 20.28, 20.32, 20.35, 20.36, 20.41, 20.45 (each COCH3), 20.54 (COCH3 × 2), 45.24 (C1''), 48.64 (C4), 56.21 (C1OCH3), 61.59 (C6''), 63.65 (C6), 63.97 (C6''), 68.29 (C4''), 70.00 (C3''), 70.61 (C'), 72.14 (C2 or C2''), 72.49 (C5''), 73.13 (C2 or C2''), 73.53 (C3''), 73.60 (C5), 74.35 (C3), 76.70 (C4''), 101.55 (C1), 102.35 (C1''), 127.10 (C5'a), 131.50 (C5''), 169.07, 169.08, 169.18, 169.53, 169.57, 169.76, 169.90 (each OCOCH3), 170.10 (OCOCH3 × 2); ESIMS (% rel. int.) m/z 989.2341 (33, calcd. for C40H54O24SK [M+K]^+: 989.2362), 973.2610 (48, calcd. for C40H54O24SNa [M+Na]^+: 973.2610), 968.3055 (100, calcd. for C40H58O24SN [M+NH4]^+: 968.3055).
References and Notes


7. Inhibitors must be incorporated to the active site of the enzyme when we use them in the mechanistic studies.


12. Private communication by Professor Miyairi.


21. We used molecular dynamic (MD) simulation program COSMOS90 developed by one of the authors of this paper (M. Saito). To perform MD simulations of endo-PG 1 with galacturonic acids, we extended COSMOS90 to make it possible to simulate sugar moieties based on the glycam force field. However, glycam did not contain the parameters for sulfur-substituted analogues. These were prepared by performing \textit{ab initio} molecular orbital calculations (HF/6-31G*), employing \( \alpha \)-1,4-linked digalacturonic acid. MD simulation of endo-PG 1 with the sulfur analogue was performed by slowly changing the force field of the carbohydrate analogue to the sulfur analogue for 40 ps and then maintaining the force field for 140 ps. The details will be reported elsewhere shortly by Saito et al.

2001, 98, 10541-10545.


43. Garegg, P. J.; Oscarson, S. 1985, 137, 270.


45. Notably, Halcomb et al employed Swern oxidation and Wittig reaction with (bromomethyl)triphenylphosphonium bromide for the corresponding transformation to give the corresponding exo-methylene derivative in 28% yield in their synthesis of monomeric carbasugar.


48. A diastereomeric mixture of ii-18 at C1 position (ca. 4:1 ratio) was obtained when methansulfonyl chloride was employed.


54. Trigalacturonic acid was not used as the natural substrate, because most of trigalacturonic acid was not hydrolyzed by endo-PG1.