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

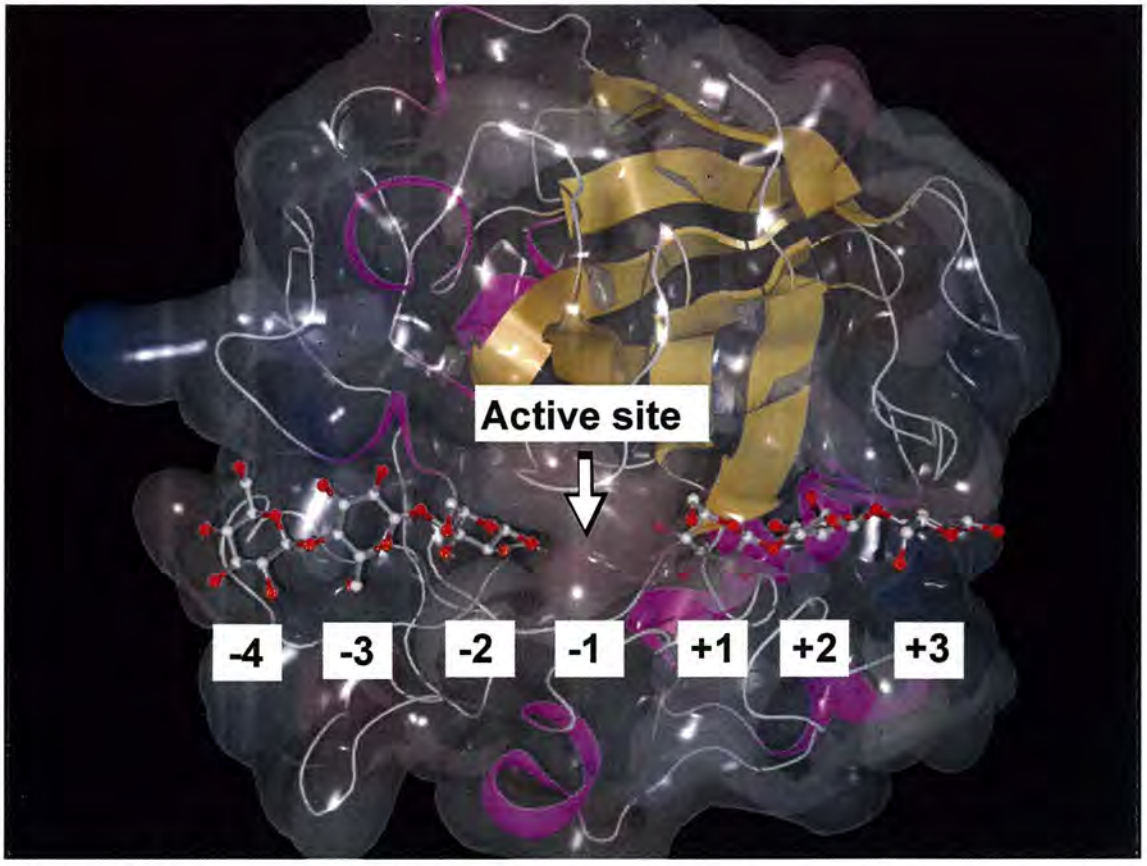
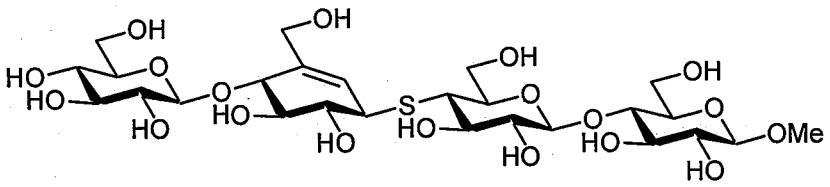


Figure iv-1. A complex of cellotrioses and endoglucanase V from *Humicola insolens*.

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 studing the effect of +2 subsite (**Figure iv-2**).



iv-1

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

Chapter4.

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_6HD_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 $^{13}C_6D_6$; 128.0 ppm). For ^{13}C-NMR spectra measured in D_2O, 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. Measurment 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 N_2 or Ar atmosphere using dried solvents except for aqueous conditions. Dichloromethane and tetrahydrfuran 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 H_2O (200 ml) and the aqueous layer was extracted with AcOEt (150 ml × 3). The combined organic layer was washed with brine (100 ml), dried over $MgSO_4$, 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; $[\alpha]_D^{24}$ +63.3 (*c* 0.94, $CHCl_3$); IR (KBr) cm^{-1}: 3400, 2930, 1490, 1445, 1150, 1075, 1045, 765; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (d, 1H, *J* = 9.5 Hz, C2O*H*), 2.46 (d, 1H, *J* = 2.7 Hz, C4O*H*), 2.58 (d, 1H, *J* = 5.3 Hz, C3O*H*), 3.38 (dd, 1H, *J* = 5.9, 9.4 Hz, C6*H*H), 3.43 (s, 3H, OCH_3), 3.43 (dd, 1H, *J* = 5.9, 9.4 Hz, C6*H*H), 3.71 (ddd, 1H, *J* = 3.7, 5.3, 9.5 Hz, C3*H*), 3.80 (dt, 1H, *J* = 3.7, 9.5 Hz, C2*H*), 3.82 (brt, 1H, *J* = 5.9 Hz, C5*H*), 4.03 (brdd, 1H, *J* = 2.7, 3.7 Hz, C4*H*), 4.82 (d, 1H, *J* = 3.7 Hz, C1*H*), 7.23 (m, 3H, *aromatic protons*), 7.30 (m, 6H, *aromatic protons*), 7.46 (m, 6H, *aromatic protons*); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 55.44 (OCH_3), 63.17 (*C*6), 69.00 (*C*5), 69.60 (*C*4), 69.88 (*C*2), 71.35 (*C*3), 87.05 ($OCPh_3$), 99.36 (*C*1), 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, $[Ph_3CO]^-$), 243 (16, $[Ph_3C]^-$), 193 (61, $[M-Ph_3C]^-$), 148 (100, $[M-Ph_3COCH_2-OCH_3]^-$); negative-FAB-HRMS: calcd. for $C_{26}H_{27}O_6$ $[M-H]^-$, 435.1808; found, *m/z* 435.1811.

A solution of the 6-*O*-triphenylmethyl ether (1.59 g, 3.64 mmol) in CH_2Cl_2 (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 H_2O (100 ml) and the aqueous layer was extracted with AcOEt (80 ml × 3). The combined organic layer was washed with brine (80 ml), dried over $MgSO_4$, 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. $[\alpha]_D^{24}$ +93.4 (*c* 0.93, $CHCl_3$); IR (film) cm^{-1}: 3500, 3060, 2935, 1725, 1450, 1280, 1105; ^1H NMR (400 MHz, C_6D_6) δ 3.11 (s, 3H, OCH_3), 3.38 (dd, 1H, *J* = 4.1, 9.9 Hz, C6*H*H), 3.56 (dd, 1H, *J* = 5.9, 9.9 Hz, C6*H*H), 3.78 (brdd, 1H, *J* = 4.1, 5.9 Hz, C5*H*), 3.96 (brd, 1H, *J* = 3.0 Hz, C4*H*), 5.29 (d, 1H, *J* = 3.6 Hz, C1*H*), 6.01 (dd, 1H, *J* = 3.0, 10.5 Hz, C3*H*), 6.12 (dd, 1H, *J* = 3.6, 10.5 Hz, C2*H*), 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*); ^{13}C NMR (100 MHz, C_6D_6) δ 54.89 (OCH_3), 64.56 (*C*6), 69.29 (*C*5), 69.67 (*C*4), 69.79 (*C*2), 71.43 (*C*3), 87.49 ($OCPh_3$), 97.97 (*C*1), 127.35, 128.53, 129.11, 130.05, 130.10, 133.02, 133.04, 144.40 (*aromatic carbons*), 165.85, 166.24 (each Ar*C*=O); FABMS (%, rel. int.) *m/z*:

667 (28, $[M+Na]^+$), 243 (100, $[CPh_3]^+$); FAB-HRMS: calcd. for $C_{26}H_{27}O_6Na$ $[M+Na]^+$, 667.2308; found, *m/z* 667.2280.

A solution of methyl 2,3-di-*O*-benzoyl-6-*O*-triphenylmethyl-α-D-galacto pyranoside (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. $[\alpha]_D^{23}$ +157 (*c* 1.02, $CHCl_3$); IR (film) cm^{-1}: 3440, 2935, 1720, 1280, 1105, 1030, 710; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (br, 1H, C6O*H*), 3.07 (br, 1H, C4O*H*), 3.44 (s, 3H, OCH_3), 4.00 (m, 3H, C6H_2, C5*H*), 4.47 (brs, 1H, C4*H*), 5.22 (d, 1H, *J* = 1.9 Hz, C1*H*), 5.70 (m, 2H, C2*H*, C3*H*), 7.36 (m, 4H, *aromatic protons*), 7.50 (m, 2H, *aromatic protons*), 7.98 (m, 4H, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.44 (OCH_3), 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 Ar*C*=*O*); negative-FABMS (%, rel. int.) *m/z*: 402 (3.7, $[M]^-$), 401 (6.0, $[M-H]^-$), 297 (9.3, $[M-PhCO]^-$), 121 (100, $[PhCOO]^-$); negative-FAB-HRMS: calcd. for $C_{21}H_{21}O_8$ $[M-H]^-$, 401.1236; found, *m/z* 401.1251.

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

A suspension of **ii-5** (1.05 g, 2.61 mmol) in a mixture of CH_2Cl_2 (10 ml) and H_2O (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 H_2O (70 ml) and the aqueous layer was extracted with AcOEt (40 ml × 3). The combined extract was washed with brine (50 ml), dried over $MgSO_4$, 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. $[\alpha]_D^{23}$ +107 (*c* 0.95, $CHCl_3$); IR (film) cm^{-1}:3940, 2955, 1725, 1450, 1280, 1100, 1025, 915, 710; ^1H NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 3H, OC*H*$_3$), 3.80 (s, 3H, C6OC*H*$_3$), 4.65 (brs, 1H, C5*H*), 4.73 (brs, 1H, C4*H*), 5.31 (d, 1H, *J* = 2.7 Hz, C1*H*), 5.71 (dd, 1H, *J* = 2.7, 10.7 Hz, C2*H*), 5.75 (dd, 1H, *J* = 1.9, 10.7 Hz, C3*H*), 7.34 (m, 4H, *aromatic protons*), 7.48 (m, 2H, *aromatic protons*), 7.98 (m, 4H, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.50 (C6O*C*H$_3$), 56.06 (O*C*H$_3$), 68.23 (*C*3), 68.88 (*C*4), 69.81 (*C*5), 70.16 (*C*2), 97.76 (*C*1), 128.16, 128.24, 128.27, 129.06, 129.64, 129.66, 133.15, 133.23 (*aromatic carbons*), 165.61, 165.83 (each Ar*C*=O), 168.59 (*C*6); FDMS (%, rel. int.) *m/z*: 431 (64, $[M+H]^+$), 398 (100, $[M-CH_3OH]^+$), 341 (26, $[MH-(COOCH_3)-CH_3O]^+$), 308 (42, $[M-PhCOOH]^+$); FD-HRMS: calcd. for $C_{22}H_{23}O_9$ $[M+H]^+$, 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 $NaHCO_3$ solution (100 ml) and the aqueous layer was extracted with AcOEt (70 ml × 3). The combined extract was washed with H_2O (50 ml) and brine (50 ml), dried over $MgSO_4$, 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; $[\alpha]_D^{23}$ -7.5 (*c* 1.50, $CHCl_3$); IR (KBr) cm^{-1}: 3410, 2910, 1615, 1515, 1250, 1165, 825; ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (brd, 1H, *J* = 9.0 Hz, C2O*H*), 2.51 (d, 1H, *J* = 1.2 Hz, C3O*H*), 3.55 (brdd, 1H, *J* = 1.4, 1.7 Hz, C5*H*), 3.69 (m, 2H, C2*H*, C3*H*), 3.82 (s, 3H, OCH_3), 4.02 (dd, 1H, *J* = 1.7, 12.4 Hz, C6*H*H), 4.20 (brd, 1H, *J* = 1.9, C4*H*), 4.37 (dd, 1H, *J* = 1.4, 12.4 Hz, C6*H*H), 4.51 (m, 1H, C1*H*), 5.47 (s, 1H, ArC*H*), 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.33 (O*C*H_3), 68.86 (*C*2), 69.25 (*C*6), 70.06 (*C*5), 73.82 (*C*3), 75.30 (*C*4), 87.00 (*C*1), 101.29 (Ar*C*$(OR)_2$), 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, $[M-CH_3]^-$), 148 (100), 109 (91, $[PhS]^-$); negative-FAB-HRMS: calcd. for $C_{20}H_{21}O_8S$ $[M-H]^-$, 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, H_2 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 PBr_3) 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 H_2O (100 ml) and the aqueous layer was extracted with AcOEt (70 ml × 3). The combined organic layer was successively washed with H_2O (50 mL), and brine (50 mL), and dried over $MgSO_4$. After concentration, the residue was purified by silica gel column chromatography (AcOEt:hexane = 25:75) to

give **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; ^1H NMR (400 MHz, $CDCl_3$) δ 3.37 (brdd, 1H, *J* = 1.3, 1.4 Hz, C5*H*), 3.57 (dd, 1H, *J* = 3.3, 9.2 Hz, C3*H*), 3.79, 3.80, 3.83 (each s, 3H, OCH_3), 3.86 (t, 1H, *J* = 9.2 Hz, C2*H*), 3.95 (dd, 1H, *J* = 1.4, 12.4 Hz, C6*H*H), 4.10 (brd, 1H, *J* = 3.3 Hz, C4*H*), 4.33 (dd, 1H, *J* = 1.3, 12.4 Hz, C6*H*H), 4.58 (d, 1H, *J* = 9.2 Hz, C1*H*), 4.62 (s, 2H, ArCH_2O), 4.63, 4.66 (each d, 1H, *J* = 12.3 Hz, ArC*H*HO), 5.43 (s, 1H, ArC*H*), 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, $CDCl_3$) δ 55.24, 55.27, 55.34 (each OCH_3), 69.37 (*C*6), 69.84 (*C*5), 71.46 (ArCH_2O), 73.79 (*C*4), 75.05 (ArCH_2O), 75.18 (*C*2), 80.95 (*C*3), 86.59 (*C*1), 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 $C_{36}H_{38}O_8S$ $[M]^+$, 630.2287; found, *m/z* 630.2276.

4.5. 2,3-di-*O*-(4-methoxyphenylmethyl)-4,6-*O*-(4-methoxyphenylmethylidene)-α-D-galactopyranosyl 2,2,2-trichloroacetimidate (ii-9)

A solution of **ii-8** (515 mg, 817.0 μmol) in a mixture of acetone (10.0 ml) and H_2O (1.0 ml) was stirred with NBS (356 mg 2.0 mmol) at 0 °C. After 5 min, 10% $Na_2S_2O_3$ (4.0 ml) was added to the mixture. After concentrating *in vacuo*, the residue was diluted with AcOEt (150 ml) and then washed with H_2O (60 ml). The aqueous solution was extracted with AcOEt (50 ml × 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; $[\alpha]_D^{22}$ +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 $CDCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 2.86 (d, 1H × 0.67, *J* = 1.2 Hz, C1O*H* (α-anomer)), 2.94 (d, 1H × 0.33, *J* = 7.4 Hz, C1O*H* (β-anomer)), 3.37 (brdd, 1H × 0.33, *J* = 1.2, 1.6 Hz, C5*H* (β-anomer)),3.54 (dd, 1H × 0.33, *J* = 3.6, 9.5 Hz, C3*H* (β-anomer)), 3.73 (dd, 1H × 0.33, *J* = 7.7, 9.5 Hz, C2*H* (β-anomer)), 3.80, 3.80, 3.80 (each s, 3H × 0.33, OCH_3 (β-anomer)), 3.81, 3.81, 3.81 (each s, 3H × 0.67, OCH_3 (α-anomer)), 3.81 (1H, m, C5*H* (α-anomer)), 3.91 (dd, 1H × 0.67, *J* = 3.6, 9.7 Hz, C3*H* (α-anomer)), 3.97-4.03 (m, 1H × 0.67, 1H × 0.33, 1H × 0.67, C6*H*H (α-anomer) , C6*H*H (β-anomer) , C2*H* (α-anomer)), 4.08 (brd, 1H × 0.33, *J* = 3.6 Hz, C4*H* (β-anomer)), 4.15 (brd, 1H × 0.67, *J* = 3.6 Hz, C4*H* (α-anomer)), 4.20 (dd, 1H × 0.67, *J* = 1.6, 12.3 Hz, C6*H*H (α-anomer)), 4.28 (dd, 1H × 0.33, *J* = 1.6, 12.5 Hz, C6*H*H (β-anomer)), 4.62 (d, 1H × 0.33, *J* = 11.2 Hz, ArC*H*HO (β-anomer)), 4.65 (d, 1H × 0.33, *J* = 7.7 Hz, C1*H* (β-anomer)), 4.68 (d, 1H × 0.67, *J* = 12.2 Hz, ArC*H*HO (α-anomer)), 4.69 (s, 2H × 0.67, ArCH_2O (α-anomer)), 4.72 (d, 1H × 0.67, *J* = 12.2 Hz, ArC*H*HO (α-anomer)), 4.78 (d, 1H × 0.33, *J* = 10.7 Hz, ArC*H*HO (β-anomer)), 4.81 (d, 1H × 0.33, *J* = 11.2 Hz, ArC*H*HO (β-anomer)), 4.82 (d, 1H × 0.33, *J* = 10.7 Hz, ArC*H*HO (β-anomer)), 5.31 (dd, 1H × 0.67, *J* = 1.2, 3.5 Hz, C1*H* (α-anomer)), 5.44 (s, 1H × 0.33, ArC*H* (β-anomer)), 5.45 (s, 1H × 0.67 ArC*H* (α-anomer)), 6.84-7.48 (12H, *aromatic protons*); FABMS (%, rel. int.) *m/z*: 561 (46, $[M+Na]^+$), 417 (61, $[M-CH_3OPhCH_2]^+$), 121 (100, $[PhCOO]^+$); FAB-HRMS: calcd. for $C_{30}H_{34}O_9Na$

$[M+Na]^+$, 561.2101; found, *m/z* 561.2108.

A solution of the product (489 mg, 908 μmol) in CH_2Cl_2 (8.0 ml) was stirred with CCl_3CN (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. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80, 3.80 (each s, 3H, OC*H*$_3$), 3.80 (m, 1H, C5*H*), 3.81 (s, 3H, OC*H*$_3$), 3.97 (dd, 1H, *J* = 1.3, 12.6 Hz, C6*H*H), 4.02 (dd, 1H, *J* = 3.3, 10.1 Hz, C3*H*), 4.19 (brd, 1H, *J* = 3.3 Hz, C4*H*), 4.24 (dd, 1H, *J* = 3.4, 10.1 Hz, C2*H*), 4.24 (dd, 1H, *J* = 1.1, 12.6 Hz, C6*H*H), 4.66 (d, 1H, *J* = 11.5 Hz, ArC*H*HO), 4.70 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.70 (d, 1H, *J* = 11.5 Hz, ArC*H*HO), 4.75 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 5.45 (s, 1H, ArC*H*), 6.59 (d, 1H, *J* = 3.4 Hz, C1*H*), 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(=N*H*)CCl_3). This sample gradually decomposed, so it was immediately used for the next step.

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

Triethylsilyl trifluoromethanesulfonate (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 CH_2Cl_2 (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. $[\alpha]_D^{23}$ +58.4 (*c* 0.60, $CHCl_3$); IR (film) cm^{-1}: 2935, 1730, 1515, 1250, 1100, 1030, 830, 710; ^1H NMR (400 MHz, $CDCl_3$) δ 3.36, 3.41 (each brd, 1H, *J* = 12.7 Hz, C6'*H*H), 3.49, 3.60, 3.76, 3.78, 3.78 (each s, 3H, OC*H*$_3$), 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, ArC*H*HO), 4.66 (brs, 1H, C5*H*), 4.66 (s, 2H, ArC*H*$_2$O), 4.71 (d, 1H, *J* = 11.4 Hz, ArC*H*HO), 4.86 (brd, 1H, *J* = 2.5 Hz, C4*H*), 4.96 (d, 1H, *J* = 3.2 Hz, C1'*H*), 5.24 (s, 1H, ArCH), 5.32 (d, 1H, *J* = 3.4 Hz, C1*H*), 5.66 (dd, 1H, *J* = 2.5, 11.0 Hz, C3*H*), 5.72 (dd, 1H, *J* = 3.4, 11.0 Hz, C2*H*), 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.39, 55.17, 55.20, 55.25, 56.16, (each O*C*H$_3$), 63.47 (*C*5'), 68.26 (*C*2), 68.94 (*C*6'), 69.73 (*C*5), 70.39 (*C*3), 71.73, 73.19 (each Ar*C*H$_2$O), 74.46 (*C*2'), 74.68 (*C*4'), 75.41 (*C*3'), 76.49 (*C*4), 97.88 (*C*1), 100,40 (*C*1'), 100.60 (Ar*C*(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 Ar*C*=O), 167.90 (*C*6); FABMS (%, rel. int.) *m/z*: 973 (1.9, $[M+Na]^+$), 829 (1.2, $[M-CH_3OPhCH]^+$), 121 (100, $[PhCOO]^+$); FAB-HRMS: calcd. for $C_{52}H_{54}O_{17}Na$ $[M+Na]^+$, 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. $[\alpha]_D^{22}$ +93.7 (*c* 0.52, $CHCl_3$); IR (film) cm^{-1}: 3450, 2935, 1730, 1510, 1250, 1095, 710; ^1H NMR (400 MHz, $CDCl_3$) δ 3.49, 3.62 (each s, 3H, OC*H*$_3$), 3.63 (dd, 1H, *J* = 3.4, 12.0 Hz, C6'*H*H), 3.69, (dd, 1H, *J* = 3.2, 10.0 Hz, C2'*H*), 3.71 (dd, 1H, *J* = 4.5, 12.0 Hz, C6'*H*H), 3.74, 3.80 (each s, 3H, OC*H*$_3$), 3.92 (dd, 1H, *J* = 3.2, 10.0 Hz, C3'*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, ArC*H*$_2$O), 4.61 (d, 1H, *J* = 11.1 Hz, ArC*H*HO), 4.69 (d, 1H, *J* = 1.8 Hz, C5*H*), 4.70 (d, 1H, *J* = 11.1 Hz, ArC*H*HO), 4.71 (brd, 1H, *J* = 1.8 Hz, C4*H*), 4.79 (d, 1H, *J* = 3.2 Hz, C1'*H*), 5.25 (brs, 1H, C1*H*), 5.75 (m, 2H, C2*H*, C3*H*), 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.43, 55.14, 55.23, 56.19 (each O*C*H$_3$), 62.95 (*C*6'), 68.20 (*C*2 or 3), 69.16 (*C*4'), 69.98 (*C*5), 70.11 (*C*2 or 3), 70.96 (*C*5'), 72.66, 73.17 (each Ar*C*H$_2$O), 75.72 (*C*2'), 76,64 (*C*3'), 76.88 (*C*4), 98.17 (*C*1), 99.98 (*C*1'), 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 Ar*C*=O), 168.01 (*C*6); FABMS (%, rel. int.) *m/z*: 855 (61, $[M+Na]^+$), 121 (100, $[CH_3OPhCH_2]^+$), 105 (96, $[PhCO]^+$); FAB-HRMS: calcd. for $C_{44}H_{48}O_{16}Na$ $[M+Na]^+$, 855.2840; found, *m/z* 855.2802.

A suspension of the diol thus obtained (70.6 mg, 84.8 μmol) in CH_2Cl_2 (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 H_2O (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 $MgSO_4$, 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 stiired for 5 min at room temperature, poured into H_2O (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 $MgSO_4$, 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. $[\alpha]_D^{23}$ + 92.7 (*c* 0.74, $CHCl_3$); IR (film) cm^{-1}: 3455, 2935, 1730, 1510, 1250, 1095, 1030, 710; ^1H NMR (400 MHz, $CDCl_3$) δ 3.41, 3.48, 3.64 (each s, 3H, OCH_3), 3.75 (dd, 1H, *J* = 3..2, 9.9 Hz, C2'*H*), 3.76, 3.80 (each s, 3H, OCH_3), 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, $ArCH_2O$), 4.62, 4.68 (each d, 1H, *J* = 10.9 Hz, $ArCH_2O$), 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, C4*H*), 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 (*C*2), 68.60 (*C*4'), 69.72 (*C*5), 69.95 (*C*3), 70.82 (*C*5'), 72.49, 73.18 (each $ArCH_2O$), 74.20 (*C*2'), 76.40 (*C*3'), 77.21 (*C*4), 97.85 (*C*1), 99.69 (*C*1'), 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 Ar*C*=O), 167.92, 168.63 (each *C*=O); FABMS (%, rel. int.) *m/z*: 883 (44, $[M+Na]^+$), 121 (100, $[CH_3OPhCH_2]^+$), 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*-methoxyphenlylmethylidene -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_2Cl_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_2O (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. $[\alpha]_D^{22}$ +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"*H*H), 3.49 (s, 3H, OCH_3), 3.57 (dd, 1H, *J* = 1.7, 12.6 Hz, C6"*H*H), 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, ArC*H*HO), 4.51 (d, 1H, *J* = 12.4 Hz, ArC*H*HO), 4.52 (s, 2H, ArCH_2O), 4.56 (d, 1H, *J* = 12.0 Hz, ArC*H*HO), 4.61 (brs, 1H, C5'*H*), 4.63, 4.67 (each d, 1H, *J* = 11.4 Hz, ArCH_2O), 4.69 (brs, 1H, C5*H*), 4.75 (d, 1H, *J* = 12.4 Hz, ArC*H*HO), 4.90 (d, 1H, *J* = 3.2 Hz, C1"*H*), 4.94 (brd, 1H, *J* = 2.4 Hz, C4*H*), 5.13 (d, 1H, *J* = 3.3 Hz, C1'*H*), 5.24 (s, 1H, ArC*H*), 5.34 (d, 1H, *J* = 2.9 Hz, C1*H*), 5.67 (dd, 1H, *J* = 2.9, 11.0 Hz, C2*H*), 5.71 (dd, 1H, *J* = 2.4, 11.0 Hz, C3*H*), 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.52, 52.52, 55.13, 55.18, 55.18, 55.21, 55.23, 56.16 (each O*C*H_3), 62.85 (*C*5"), 68.35 (*C*3), 69.12 (*C*6"), 69.57 (*C*5), 70.16 (*C*2), 71.23, 71.33, 72.30 (each Ar*C*H_2O), 72.63 (*C*5'), 72.78 (Ar*C*H_2O), 73.00 (*C*2"), 74.11 (*C*2'), 74.48 (*C*4"), 75.74 (*C*3"), 76.14 (*C*4), 76.20 (*C*3'), 76.33 (*C*4'), 97.80 (*C*1), 98.82 (*C*1'), 99.78 (*C*1"), 100.59 (Ar*C*$(OR)_2$), 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 Ar*C*=O), 167.88, 168.06 (each *C*=O); FABMS (%, rel. int.) *m/z*: 1403 (4.2, $[M+Na]^+$), 121 (100, $[CH_3OPhCH_2]^+$), 105 (82, $[PhCO]^+$); FAB-HRMS: calcd. for $C_{75}H_{80}O_{25}Na$ $[M+Na]^+$, 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. $[\alpha]_D^{23}$ +75.0 (*c* 0.84, $CHCl_3$); IR (film) cm^{-1}: 3450, 2935, 1730, 1510, 1250, 1095, 1030, 710; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (brd, 1H, *J* = 8.9 Hz, C6"O*H*), 2.51 (brs, 1H, C4"O*H*), 3.04 (s, 3H, OCH_3), 3.48 (m, 1H, C6"*H*H), 3.49 (s, 3H, OCH_3), 3.57-3.65 (m, 3H, C6"*H*H, C2"*H*, C3"*H*), 3.70, 3.73, 3.75, 3.76, 3.79 (each s, 3H, OCH_3), 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, ArC*H*HO), 4.45 (d, 1H, *J* = 10.6 Hz, ArC*H*HO), 4.51 (d, 1H, *J* = 12.1 Hz, ArC*H*HO), 4.53 (d, 1H, *J* = 10.6 Hz, ArC*H*HO), 4.59 (d, 1H, *J* = 12.1 Hz, ArC*H*HO), 4.65 (d, 1H, *J* = 0.9 Hz, C5'*H*), 4.65, 4.68 (each d, 1H, *J* = 12.1 Hz, ArCH_2O), 4.68 (brs, 1H, C5*H*), 4.70 (d, 1H, *J* = 12.1 Hz, ArC*H*HO), 4.81 (brs, 1H, C1"*H*), 4.91 (brd, 1H, *J* = 2.1 Hz, C4*H*), 5.06 (d, 1H, *J* = 3.3 Hz, C1'*H*), 5.35 (d, 1H, *J* = 2.8 Hz, C1*H*), 5.66 (dd, 1H, *J* = 2.8, 10.9 Hz, C2*H*), 5.70 (dd, 1H, *J* = 2.1, 10.9 Hz, C3*H*), 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.68, 52.54, 55.12, 55.21, 55.21, 55.25, 56.19 (each OCH_3), 62.96 (*C*6"), 68.39 (*C*3), 69.09 (*C*4"), 69.61 (*C*5), 69.70 (*C*5"), 70.23 (*C*2), 71.37 (*C*5'), 72.20, 72.57, 72.63,

73.01 (each ArCH_2O) 73.79 (*C*2'), 74.82 (*C*2" or 3"), 76.18 (*C*3'), 76.53 (*C*4), 77.20 (*C*2" or 3"), 77.81 (*C*4'), 97.82 (*C*1), 99.21 (*C*1"), 99.25 (*C*1'), 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 Ar*C*=O), 167.99, 168.02 (each *C*=O); FABMS (%, rel. int.) *m/z*: 1285 (0.6, $[M+Na]^+$), 121 (100, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{67}H_{74}O_{24}Na$ $[M+Na]^+$, 1285.4468; found, *m/z* 1285.4490.

A suspension of the product (20.0 mg, 15.8 μmol) in CH_2Cl_2 (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 H_2O (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 $MgSO_4$, 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 dihydrogenphosphate 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 H_2O (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 $MgSO_4$, 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. $[\alpha]_D^{23}$ +67.2 (*c* 0.75, $CHCl_3$); IR (film) cm^{-1}: 3450, 2935, 1730, 1510, 1250, 1100, 1030, 820, 715; ^1H NMR (400 MHz, $CDCl_3$) δ 2.92, 3.49 (each s, 3H, O*CH*$_3$), 3.54 (dd, 1H, *J* = 3.2, 10.0 Hz, C3"*H*), 3.59 (s, 3H, O*CH*$_3$), 3.62 (d, 1H,

J = 3.0, 10.0 Hz, C2"*H*), 3.70, 3.74, 3.74, 3.79, 3.80 (each s, 3H, OCH_3), 3.28 (dd, 1H, *J* = 3.3, 10.5 Hz, C2'*H*), 4.03 (dd, 1H, *J* = 2.2, 10.5 Hz, C3'*H*), 4.23 (brd, 1H, *J* = 3.2 Hz, C4"*H*), 4.25 (brd, 1H, *J* = 2.2 Hz, C4'*H*), 4.39 (d, 1H, *J* = 12.3 Hz, ArCH_2O), 4.43 (s, 2H, ArCH_2O), 4.52 (d, 1H, *J* = 12.3 Hz, ArCH_2O), 4.55 (brs, 1H, C5'*H*), 4.57 (d, 1H, *J* = 11.8 Hz, ArCH_2O), 4.62 (d, 1H, *J* = 12.7 Hz, ArCH_2O), 4.68 (brs, 1H, C5*H*), 4.73 (d, 1H, *J* = 11.8 Hz, ArCH_2O), 4.80 (d, 1H, *J* = 12.7 Hz, ArCH_2O), 4.85 (brs, 1H, C5"*H*) 4.88 (d, 1H, *J* = 3.3 Hz, C1"*H*), 4.91 (brd, 1H, *J* = 2.3 Hz, C4*H*), 5.05 (d, 1H, *J* = 3.3 Hz, C1'*H*), 5.35 (d, 1H, *J* = 3.0 Hz, C1*H*), 5.67 (dd, 1H, *J* = 3.0, 11.0 Hz, C2*H*), 5.71 (dd, 1H, *J* = 2.3, 11.0 Hz, C3*H*), 6.72 (brd, 2H, *J* = 8.4 Hz, *aromatic protons*), 6.83-6.90 (m, 6H, *aromatic protons*), 7.11 (brd, 2H, *J* = 8.5 Hz, *aromatic protons*), 7.19 (brd, 2H, *J* = 8.5 Hz, *aromatic protons*), 7.24-7.38 (m, 8H, *aromatic protons*), 7.48 (m, 2H, *aromatic protons*), 7.81 (brd, 2H, *J* = 7.5 Hz, *aromatic protons*), 7.94 (brd, 2H, *J* = 7.5 Hz, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.49, 52.08, 52.59, 55.07, 55.17, 55.20, 55.24, 56.19 (each O*C*H$_3$), 68.27 (*C*4"), 68.36 (*C*3), 69.47 (*C*5), 70.08 (*C*2), 70.42 (*C*5"), 71.08 (*C*5'), 71.82 (*C*2'), 71.94, 72.16, 72.61 , 72.63 (each Ar*C*H$_2$O), 72.96 (*C*2"), 75.74 (*C*4), 75.87 (*C*3'), 77.21 (*C*3"), 77.21 (*C*4'), 97.79 (*C*1), 98.64 (*C*1'), 99.20 (*C*1"), 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 (*aromatic carbons*), 165.75, 165.82 (each Ar*C*=O), 167.76, 168.09, 168.47 (each *C*=O); FABMS (%, rel. int.) *m/z*: 1313 (8.4, $[M+Na]^+$), 121 (100, $[CH_3OPhCH_2]^+$), 105 (76, $[PhCO]^+$); FAB-HRMS: calcd. for $C_{68}H_{74}O_{25}Na$ $[M+Na]^+$, 1313.4417; found, *m/z* 1313.4409.

4.10. Methyl α-D-galactopyranuronosyl-(1→4)-α-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 CH_2Cl_2 (1.0 ml) and H_2O (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:CH_2Cl_2 = 80:20) of the residue gave the MPM deprotected pentaol (14.9 mg, 90%) as an oil. $[\alpha]_D^{23}$ +32.4 (*c* 0.59, CH_3OH); IR (film) 3420, 2925, 1730, 1580, 1450, 1275, 1105, 1020, 715 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 3.12, 3.50 (each s, 3H, OC*H*$_3$), 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, OC*H*$_3$), 4.02 (dd, 1H, *J* = 2.9, 10.7 Hz, C3'*H*), 4.15 (dd, 1H, *J* = 1.4, 3.4 Hz, C4"*H*), 4.32 (brd, 1H, *J* = 2.9 Hz, C4'*H*), 4.74 (d, 1H, *J* = 3.8 Hz, C1"*H*), 4.76 (brs, 1H, C5'*H*), 4.84 (brs, 1H, C5*H*), 4.91 (brd, 1H, *J* = 3.0 Hz, C4*H*), 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, C1*H*), 5.58 (dd, 1H, *J* = 3.0, 11.0 Hz, C3*H*), 5.68 (dd, 1H, *J* = 3.5, 11.0 Hz, C2*H*), 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*); ^{13}C NMR (100 MHz, CD_3OD) δ 52.47, 52.59, 53.19, 56.55 (each OCH_3), 69.33 (*C*2'), 69.40 (*C*2), 69.40 (*C*3'), 69.62 (*C*2"), 70.70 (*C*3"), 70.97 (*C*5), 71.81 (*C*4"), 71.91 (*C*3), 72.48 (*C*5'), 72.81 (*C*5"), 79.00 (*C*4), 80.50 (*C*4'), 99.20 (*C*1), 102.18 (*C*1"), 102.92 (*C*1'), 129.63, 129.81, 130.35, 130.48, 130.65, 130.79, 134.65, 134.71 (*aromatic carbons*), 167.32, 167.40 (each Ar*C*=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 $C_{36}H_{42}O_{21}Na$ $[M+Na]^+$, 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_2O); ^1H NMR (400 MHz, D_2O) δ 3.25 (s, 3H, OC*H*$_3$), 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_2O) δ 58.22 (O*C*H$_3$), 70.15 (*C*2), 70.35 (*C*2"), 70.37 (*C*2'), 70.57 (*C*3'), 70.63 (*C*3), 71.24 (*C*3"), 72.03 (*C*5), 72.48 (*C*4"), 72.72 (*C*5'), 73.45 (*C*5"), 80.69 (*C*4), 80.96 (*C*4'), 102.12 (*C*1), 102.46 (*C*1"), 102.59 (*C*1'), 174.51, 174.72, 175.35 (each *C*=O); negative-FABMS (%, rel. int.) *m/z*: 599 (4.5, $[M-H]^-$), 148 (100, $[C_5H_8O_5]^-$); 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-α-D-glcopyranoside (ii-16)

A solution of methyl 4,6-*O*-(4-methoxybenzylidene)-α-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 × 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. $[\alpha]_D^{22}$ +57.7 (*c* 1.63, $CHCl_3$); IR (film) cm^{-1}: 2940, 1750, 1615, 1520, 1370, 1240, 1060, 1030; ^1H NMR (500 MH_Z, $CDCl_3$) δ 2.05, 2.09 (each s, 3H, C*H*$_3$CO), 3.41 (s, 3H, OC*H*$_3$), 3.63 (t, 1H, *J* = 9.7 Hz, C4*H*), 3.75 (t, 1H, *J* = 9.7 Hz, C6*H*H), 3.80 (s, 3H, OC*H*$_3$), 3.91 (ddd, 1H, *J* = 4.9, 9.7, 10.3 Hz, C5*H*), 4.28 (dd, 1H, *J* = 4.9, 10.3 Hz, C6*H*H), 4.90 (dd, 1H, *J* = 3.8, 9.7 Hz, C2*H*), 4.93 (d, 1H, *J* = 3.8 Hz, C1*H*), 5.46 (s, 1H, ArC*H*), 5.57 (t, 1H, *J* = 9.7 Hz, C3*H*), 6.87 (brd, 2H, *J* = 8.6 Hz, *aromatic protons*), 7.37 (brd, 2H, *J* = 8.6 Hz, *aromatic protons*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.73, 20.80 (each *C*H$_3$CO), 55.25, 55.31 (each OCH$_3$), 62.31 (*C*5), 68.75 (*C*6), 68.96 (*C*3), 71.58 (*C*2), 79.13 (*C*4), 97.57 (*C*1), 101.52 (Ar*C*), 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. $[\alpha]_D^{22}$ +105 (*c* 1.65, $CHCl_3$); IR (film) 3475, 2920, 1740, 1370, 1240, 1050, 920 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 2.09, 2.10 (each s, 3H, C*H*$_3$CO), 2.58 (br, 1H, C6O*H*), 3.41 (s, 3H, OC*H*$_3$), 3.71 (m, 2H, C4*H*, C5*H*), 3.87 (m, 2H, C6*H*$_2$), 4.82 (dd, 1H, *J* = 3.6, 10.1 Hz, C2*H*), 4.91 (d, 1H, *J* = 3.6 Hz, C1*H*), 5.31 (m, 1H, C3*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.73, 20.84 (each *C*H$_3$CO), 55.21 (OCH$_3$), 61.78 (*C*6), 69.46 (*C*5), 70.82 (*C*2), 71.17 (*C*4), 73.11 (*C*3), 96.78 (*C*1), 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, *m/z* 301.0910.

4.12. Methyl (methyl 2,3-di-*O*-acetyl-α-D-glucopyranosid)uronate (ii-17)

A suspension of **ii-16** (2.76 g, 9.92 mmol) in a mixture of CH_2Cl_2 (20 ml) and H_2O (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% $Na_2S_2O_3$ solution (5.0 ml) was added and the mixture was poured into H_2O (100 ml), 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*. To the residue in THF (10 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-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}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.08, 2.10 (each s, 3H, CH_3CO), 3.46 (s, 3H, OCH_3), 3.85 (s, 3H, $COOCH_3$), 3.91 (t, 1H, J = 9.6 Hz, C4*H*), 4.22 (d, 1H, J = 9.6 Hz, C5*H*), 4.86 (dd, 1H, J = 3.7, 10.2 Hz, C2*H*), 5.00 (d, 1H, J = 3.7 Hz, C1*H*), 5.38 (dd, 1H, J = 9.6, 10.2 Hz, C3*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.69, 20.81 (each CH_3CO), 55.88 ($COOCH_3$), 55.80 (OCH_3), 70.11 (*C*5), 70.32 (*C*2), 70.55 (*C*4), 71.55 (*C*3), 97.20 (*C*1), 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 $C_{11}H_{15}O_8$ $[M-CH_3O]^+$: 572.2860).

4.13. Methyl (methyl 2,3-di-*O*-acetyl-4-*O*-trifluoromethanesulfonyl-α-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 CH_2Cl_2 (10 ml) at 0 °C. After 10 min, the mixture was poured into H_2O (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 = 20:80) to give **ii-18** (994 mg, 94 %) as an oil. $[\alpha]_D^{23}$ +91.6 (*c* 1.00, $CHCl_3$); IR (film) 1760, 1420, 1375, 1210, 1140, 1070, 950, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.07, 2.09 (each s, 3H, C*H*$_3$CO), 3.47 (s, 3H, OC*H*$_3$), 3.84 (s, 3H, COOC*H*$_3$), 4.47 (d, 1H, *J* = 10.0 Hz, C5*H*), 4.89 (dd, 1H, *J* = 3.5, 10.0 Hz, C2*H*), 5.03 (t, 1H, *J* = 10.0 Hz, C4*H*), 5.03 (d, 1H, *J* = 3.5 Hz, C1*H*), 5.67 (t, 1H, *J* = 10.0 Hz, C3*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.39, 20.50 (each *C*H$_3$CO), 53.17 (COO*C*H$_3$), 56.27 (O*C*H$_3$), 67.92 (*C*5), 68.08 (*C*3), 70.48 (*C*2), 80.12 (*C*4), 97.05 (*C*1), 116.55, 119.72 (each *C*F$_3$), 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-acetylthio-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 H_2O (50 ml), and the aqueous layer was extracted with EtOAc (50 ml × 3). The combined organic layer was washed with H_2O (50 ml × 2), and brine (50 ml), dried over $MgSO_4$ 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:H_2O = 50:50) to provide **ii-21** (89 mg, 54%). $[\alpha]_D^{24}$ +143 (*c* 1.15, $CHCl_3$); IR (film) 1750, 1710, 1370, 1220, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00, 2.0, 2.03, 2.15 (each s, 3H, CH_3CO_2), 2.42 (s, 3H, CH_3COS), 4.06 (dd, 1H, *J* = 6.8, 11.1 Hz, C6*H*H), 4.11 (dd, 1H, *J* = 6.3, 11.1 Hz, C6*H*H), 4.17 (ddd, 1H, *J* = 1.0, 6.3, 6.8 Hz, C5*H*), 5.04 (dd, 1H, *J* = 3.3, 10.9 Hz, C3*H*), 5.44 (dd, 1H, *J* = 1.0, 3.3 Hz, C4*H*), 5.48 (dd, 1H, *J* = 5.5, 10.9 Hz, C2*H*), 6.27 (d, 1H, *J* = 5.5 Hz, C1*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.56 (CH_3CO_2 × 2), 20.60, 20.62 (each CH_3CO_2), 31.49 (CH_3COS), 61.12 (*C*6), 66.35 (*C*2), 67.24 (*C*4), 68.85 (*C*3), 70.27 (*C*5), 81.13 (*C*1), 169.57, 169.87, 170.09, 170.29 (*C*=O), 191.70 (S*C*=O); ESIMS (%, rel. int.) *m/z* 429.0834 (100, calcd. for $C_{16}H_{22}NaO_{10}S$ $[M+Na]^+$: 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 °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 $MgSO_4$, 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%). $[\alpha]_D^{24}$ +132 (*c* 0.94, $CHCl_3$); IR (film) 1745, 1375, 1220, 1090, 1060 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.83 (d, 1H, *J* = 5.0 Hz, S*H*), 2.01, 2.06, 2.09, 2.15 (each s, 3H, CH_3CO_2), 4.06 (dd, 1H, *J* = 6.8, 11.3 Hz, C6*H*H), 4.14 (dd, 1H, *J* = 6.4, 11.3 Hz, C6*H*H), 4.62 (ddd, 1H, *J* = 1.1, 6.4, 6.8 Hz, C5*H*), 5.24 (dd, 1H, *J* = 3.0, 10.7 Hz, C3*H*), 5.28 (dd, 1H, *J* = 5.0, 10.7 Hz, C2*H*), 5.47 (dd, 1H, *J* = 1.1, 3.0 Hz, C4*H*), 6.02 (d, 1H, *J* = 5.0 Hz,

C1*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.59, 20.60 20.67, 20.75 (each CH_3CO_2), 61.43 (*C*6), 67.14 (*C*5), 67.46 (*C*3), 67.52 (*C*2), 67.70 (*C*4), 77.77 (*C*1), 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-α-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 poured into H_2O (20 ml), and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with H_2O (30 ml × 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}H-NMR (400 MHz, $CDCl_3$) δ 1.99, 2.06, 2.07, 2.15 (each s, 3H, CH_3CO_2), 2.82 (4H, SCH_2CH_2), 4.12 (d, 2H, *J* = 6.5 Hz, C6*H*H× 2), 4.55 (dt, 1H, *J* = 1.1, 6.5 Hz, C5*H*), 5.19 (dd, 1H, *J* = 3.3, 10.8 Hz, C3*H*), 5.27 (dd, 1H, *J* = 5.5, 10.8 Hz, C2*H*), 5.45 (dd, 1H, *J* = 1.1, 3.3 Hz, C4*H*), 5.76 (d, 1H, *J* = 5.5 Hz, C1*H*), 9.77 (s, 1H, C*H*O).

4.17. 3-cyano-3-*O*-*tert*-butyldimethylsilylpropyl 2,3,4,6-tetra-*O*-acetyl-1-thio -α-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_3CN (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 (*c* 1.54, $CHCl_3$); IR (film) 2930, 1750, 1370, 1220, 1115, 1080, 1055, 840 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 3H, $SiCH_3$),

0.21 (each s, 3H × 0.5, SiCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 2.00 (s, 3H, CH_3CO), 2.06, 2.07, 2.08, 2.08 (each s, 3H × 0.5, CH_3CO), 2.10 (2H, SCH$_2$CH_2), 2.15 (s, 3H, CH_3CO), 2.70 (m, 2H, SCH_2CH$_2$), 4.10 (2H, C6H_2), 4.52-4.60 (2H, C5H, SCH$_2$CH$_2$CH), 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); ^{13}C NMR (100 MHz, CDCl$_3$) δ -5.37, -5.17 (each Si(CH$_3$)$_2$), 18.02 (SiC), 2.06 (CH$_3$CO × 2), 20.69, 20.71 (each CH$_3$CO × 0.5), 20.77 (CH$_3$CO), 24.37, 25.19 (each SCH$_2$ × 0.5), 25.49 (SiC(CH$_3$)$_3$), 35.87, 35.97 (each SCH$_2$CH$_2$ × 0.5), 60.27 (SCH$_2$CH$_2$$C$H), 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 $C_{24}H_{39}NO_{10}SSiNa$ $[M+Na]^+$: 584.1962), 562.2160 (30, calcd. for $C_{24}H_{40}NO_{10}SSi$ $[M+H]^+$: 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 H_2O (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%). $[\alpha]_D^{24}$ +198 (*c* 0.98, CHCl$_3$); IR (film) 3400, 2930, 1255, 1105, 1055, 840, 780 cm^{-1}; ^{1}H NMR (400 MHz, CD$_3$OD). δ 0.17, 0.18, 0.21, 0.21 (each s, 3H × 0.5, SiCH_3), 0.93 (s, 9H, SiC(CH_3)$_3$), 2.08-2.16 (2H, SCH$_2$CH_2), 2.59-2.82 (2H, SCH_2CH$_2$), 3.57, 3.60

(each dd, 1H × 0.5, J = 3.3, 10.5 Hz, C3*H*), 3.72 (d, 2H, J = 6.1 Hz, C6H_2), 3.90, 3.90 (each dd, 1H × 0.5, J = 1.5, 3.3 Hz, C4*H*), 4.08, 4.09 (each dd, 1H × 0.5, J = 5.6, 10.5 Hz, C2*H*), 4.14 (dt, 1H, J = 1.5, 6.1 Hz, C5*H*), 4.79 (dd, 1H × 0.5, J = 6.1, 7.0 Hz, SCH_2CH_2CH), 4.83 (t, 1H × 0.5, J = 6.4 Hz, SCH_2CH_2CH), 5.376, 5.381 (each d, 1H × 0.5, J = 5.6 Hz, C1*H*); ^{13}C NMR (100 MHz, CD_3OD) δ -4.64, -4.61 (each $Si(CH_3)_2$), 19.38 (Si*C*), 25.68 (SCH_2 × 0.5), 26.52 ($SiC(CH_3)_3$), 27.09 (SCH_2 × 0.5), 37.58, 37.92 (each SCH_2CH_2 × 0.5), 62.10, 62.32 (each SCH_2CH_2CH × 0.5), 63.07, 63.09 (each *C*6 × 0.5), 70.08, 70.14 (each *C*2 × 0.5), 71.32, 71.33 (each *C*4 × 0.5), 72.65, 72.71 (each *C*3 × 0.5), 73.43, 73.67 (each *C*5 × 0.5), 87.23, 88.83 (each *C*1 × 0.5), 121.68, 121.75 (each *C*N × 0.5); ESIMS (%, rel. int.) *m/z* 416.1547 (42, calcd. for $C_{16}H_{31}NO_6SSiNa$ $[M+Na]^+$: 416.1539), 394.1727 (100, calcd. for $C_{16}H_{32}NO_6SSi$ $[M+H]^+$: 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 H_2O (20 ml) and the aqueous layer was extracted with EtOAc (15 ml ×3). The combined organic solution was washed with H_2O (20 ml) and brine (15 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Silica gel column chromatography of the residue (EtOAc:hexane = 46:54) gave 3-cyano-3-*O*-*tert*-butyldimethylsilylpropyl,6-*O*-(4-methoxyphenylmethylidene)-1-thio-α-D-galactopyranoside (25.4 mg, 68%) as an oil. $[\alpha]_D^{23}$ +98.8 (*c* 1.47, $CHCl_3$); IR (film) 3430, 2930, 1615, 1520, 1250, 1095, 1065, 1035, 835, 780 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6). δ 0.02, 0.03, 0.12, 0.14 (each s, 3H × 0.5, $SiCH_3$), 0.876, 0.882 (each s, 9H × 0.5, $SiC(CH_3)_3$), 1.79-1.96 (2H, SCH_2CH_2), 2.46-2.59 (2H,

SC*H*$_2$CH$_2$), 2.63, 2.69 (each d, 1H × 0.5, *J* = 8.8 Hz, C3O*H*), 2.72, 2.83 (each d, 1H × 0.5, *J* = 3.2 Hz, C2O*H*), 3.29, 3.30 (each s, 3H × 0.5, OC*H*$_3$), 3.45, 3.48 (each dd, 1H × 0.5, *J* = 1.8, 10.4 Hz, C6*H*H), 3.52-3.56 (each 1H × 0.5, C5*H*), 3.68-3.73 (2H, C3*H*, C4*H*), 4.04, 4.06 (each dd, 1H × 0.5, *J* = 1.4, 10.4 Hz, C6*H*H), 4.19 (1H, C2*H*), 4.32 (dd, 1H × 0.5, *J* = 5.5, 7.3 Hz, SCH$_2$CH$_2$C*H*), 4.38 (dd, 1H × 0.5, *J* = 4.7, 8.0 Hz, SCH$_2$CH$_2$C*H*), 5.231, 5.235 (each s, 1H × 0.5, ArC*H*), 5.29, 5.32 (each d, 1H × 0.5, *J* = 5.3 Hz, C1*H*), 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); ^{13}C NMR (125 MHz, C_6D_6) δ -5.39, -5.38, -5.16, -5.131 (each SiCH$_3$ × 0.5), 18.10 (Si*C*), 25.17 (SCH$_2$ × 0.5), 25.59, 25.61 (each SiC(CH$_3$)$_3$ × 0.5), 25.94 (SCH$_2$ × 0.5), 36.12, 36.44 (each SCH$_2$CH$_2$ × 0.5), 54.81, 54.82 (each OCH$_3$ × 0.5), 60.40, 60.78 (each SCH$_2$CH$_2$CH × 0.5), 63.90, 63.94 (each *C*5 × 0.5), 69.13, 69.15 (each *C*6 × 0.5), 69.23, 69.33 (each *C*2 × 0.5), 70.68, 70.74 (each *C*3 × 0.5), 75.86, 75.90 (each *C*4 × 0.5), 85.99, 86.95 (each *C*1 × 0.5), 101.31, 101.33 (each Ar*C* × 0.5), 113.87, 113.90 (each *aromatic carbon* × 0.5), 119.79, 120.03 (each *C*N × 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 $C_{24}H_{37}NO_7SSiNa$ $[M+Na]^+$: 534.1958), 512.2166 (100, calcd. for $C_{24}H_{38}NO_7SSi$ $[M+H]^+$: 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 $NaHCO_3$ 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 $MgSO_4$, 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%). $[\alpha]_D^{24}$ +146 (*c* 0.92, $CHCl_3$); IR (film) 2930,

1745, 1370, 1250, 1220, 1090, 1055, 1040, 835, 780 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$). δ 0.149, 0.152, 0.20, 0.21 (each s, 3H × 0.5, SiC*H*$_3$), 0.91 (s, 9H, SiC(C*H*$_3$)$_3$), 2.07, 2.08 (each s, 3H × 0.5, C*H*$_3$CO), 2.09 (s, 3H, C*H*$_3$CO), 2.00-2.17 (2H, SCH$_2$C*H*$_2$), 2.63-2.77 (2H, SC*H*$_2$CH$_2$), 3.81 (s, 3H, OC*H*$_3$), 4.08 (2H, C5*H*, C6*H*H), 4.22 (dd, 1H, *J* = 1.5, 12.6 Hz, C6*H*H), 4.46 (t, 1H, *J* = 3.5 Hz, C4*H*), 4.55 (dd, 1H × 0.5, *J* = 5.0, 7.6 Hz, SCH$_2$CH$_2$C*H*), 4.58 (dd, 1H × 0.5, *J* = 5.6, 7.1 Hz, SCH$_2$CH$_2$C*H*), 5.17, 5.18 (each dd, 1H × 0.5, *J* = 3.5, 10.9 Hz, C3*H*), 5.47, 5.48 (each dd, 1H × 0.5, *J* = 5.6, 10.9 Hz, C2*H*), 5.487, 5.490 (each s, 1H × 0.5, ArC*H*), 5.83, 5.84 (each d, 1H × 0.5, *J* = 5.6 Hz, C1*H*), 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, $CDCl_3$) δ -5.39 (SiCH$_3$), -5.20, -5.17 (each SiCH$_3$ × 0.5), 17.99 (Si*C*), 20.79, 20.92 (each *C*H$_3$CO), 24.62, 25.19 (each SCH$_2$ × 0.5), 25.46 (SiC(*C*H$_3$)$_3$), 35.77, 35.79 (each SCH$_2$*C*H$_2$ × 0.5), 55.27 (OCH$_3$), 60.20, 60.36 (each SCH$_2$CH$_2$*C*H × 0.5), 62.62, 62.63 (each *C*5 × 0.5), 67.74 (*C*2), 69.00 (*C*3), 69.03, 69.06 (each *C*6 × 0.5), 73.56 (*C*4), 82.30, 82.87 (each *C*1 × 0.5), 100.89 (Ar*C*), 113.54 *aromatic carbon*), 119.44 (*C*N), 127.50, 129.91, 160.13 (*aromatic carbons*), 169.90 (*C*=O), 170.51, 170.53 (each *C*=O× 0.5); ESIMS (%, rel. int.) *m/z* 618.2196 (100, calcd. for $C_{28}H_{41}NO_9SSiNa$ $[M+Na]^+$: 618.2169), 596.2378 (79, calcd. for $C_{28}H_{42}NO_9SSi$ $[M+H]^+$: 596.2350).

4.19. 2,3-di-*O*-acetyl-4,6-*O*-methoxyphenylmethylidene-1-thio-α-D-galacto pyranosyl-(1→4)-[methyl(methyl 2,3-di-*O*-acetyl-α-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 NH_4Cl 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 $MgSO_4$, 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%). $[\alpha]_D^{24}$ +198 (*c* 1.12, $CHCl_3$); IR (film) 2940, 1745, 1375, 1220, 1070, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.05, 2.08, 2.09, 2.11 (each s, 3H, C*H*$_3$CO), 3.42 (s, 3H, C1OC*H*$_3$), 3.80, 3.81 (each s, 3H, OC*H*$_3$), 3.89 (dd, 1H, *J* = 1.6, 4.5 Hz, C4*H*), 4.05 (dd, 1H, *J* = 1.6, 12.5 Hz, C6'*H*H), 4.14 (dd, 1H, *J* = 1.4, 12.5 Hz, C6'*H*H), 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, C5*H*), 4.94 (dd, 1H, *J* = 3.7, 10.9 Hz, C2*H*), 5.10 (d, 1H, *J* = 3.7 Hz, C1*H*), 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, ArC*H*), 5.52 (dd, 1H, *J* = 4.5, 10.9 Hz, C3*H*), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.68, 20.74, 20.81, 20.90 (each *C*H$_3$CO), 47.99 (*C*4), 52.55, 55.27, 56.08 (each OCH$_3$), 62.65 (*C*5'), 67.45 (*C*2'), 68.24 (*C*3), 68.65 (*C*3'), 68.93 (*C*6'), 69.14 (*C*2), 69.66 (*C*5), 73.41 (*C*4'), 83.91 (*C*1'), 97.31 (*C*1), 100.82 (Ar*C*), 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 $C_{30}H_{38}O_{16}SNa$ $[M+Na]^+$: 709.1778), 687.1960 (39, calcd. for $C_{30}H_{39}O_{16}S$ $[M+H]^+$: 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, $CHCl_3$); IR (film) cm^{-1}: 3505 1745, 1370, 1220, 1070, 915, 730; ^1H NMR (500 MHz, $CDCl_3$) δ 2.08, 2.10, 2.11, 2.13 (each s, 3H, C*H*$_3$CO), 3.42 (s, 3H, C1OC*H*$_3$), 3.81 (s, 3H, CO_2CH_3), 3.81-3.90 (2H, C6'*H*$_2$), 3.91 (dd, 1H, *J* = 1.7, 4.7 Hz, C4*H*), 4.29 (2H, C4'*H*, C5'*H*), 4.77 (d, 1H, *J* = 1.7 Hz, C5*H*), 4.93 (dd, 1H, *J* = 3.7, 10.8 Hz, C2*H*), 5.10 (d, 1H, *J* = 3.7 Hz, C1*H*), 5.15 (dd, 1H, *J* = 2.7, 10.8 Hz, C3'*H*), 5.32 (dd, 1H, *J* = 5.6, 10.8 Hz, C2'*H*), 5.54 (dd, 1H, *J* = 4.7, 10.8 Hz, C3*H*), 5.65 (d, 1H, *J* = 5.6 Hz, C1'*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.67, 20.76, 20.90, 21.02 (each *C*H$_3$CO), 47.07 (*C*4), 52.61 (CO_2CH_3), 56.10 (OCH_3), 62.61 (*C*6'), 67.79 (*C*3), 67.85 (*C*2'), 68.82 (*C*4'), 69.13 (*C*2), 69.58 (*C*5), 69.62 (*C*5'), 70.05 (*C*3'), 83.03 (*C*1'), 97.33 (*C*1), 167.89, 169.89, 169.97, 170.24, 170.46 (each *C*=O); ESIMS (%, rel. int.) *m/z* 591.1373 (100, calcd. for $C_{22}H_{32}O_{15}SNa$ $[M+Na]^+$: 591.1360), 586.1819 (26, calcd. for $C_{22}H_{36}NO_{15}S$ $[M+NH_4]^+$: 586.1806).

4.21. 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-30)

A suspension of **ii-29** (139 mg, 0.24 mmol) in a mixture of CH_2Cl_2 (2.0 ml) and H_2O (1.0 ml) was stirred with $PhI(OAc)_2$ (393 mg, 1.22 mmol) and TEMPO (15.0 mg, 9.6 μmol) at room temperature for 20 min. Aqueous 10% $Na_2S_2O_3$ solution (0.2 ml) was added and the mixture was poured into H_2O (30 ml) and the aqueous layer was extracted with AcOEt (20 ml × 3). The combined extract was washed with brine (30 ml), dried over $MgSO_4$, 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 (Acetone:CH_2Cl_2 = 10:90) of the residue gave **ii-30** (95.7 mg, 67%) as an oil. $[\alpha]_D^{24}$ +186 (*c* 0.62, $CHCl_3$); IR (film) 3485, 2955, 1745, 1375, 1220, 1070, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96, 2.06, 2.10, 2.12 (each s, 3H, C*H*$_3$CO), 2.37 (d, 1H, *J* = 4.6 Hz, C4'O*H*), 3.42 (s, 3H, C1OC*H*$_3$), 3.79, 3.80 (each s, 3H, CO_2CH_3), 3.87 (dd, 1H, *J* = 1.6, 4.4 Hz, C4*H*), 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, C2*H*), 5.01 (d, 1H, *J* = 1.4 Hz, C5'*H*), 5.10 (d, 1H, *J* = 3.8 Hz, C1*H*), 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, C3*H*), 5.72 (d, 1H, *J* = 5.5 Hz, C1'*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.34, 20.64, 20.67, 20.78 (each *C*H$_3$CO), 48.57 (*C*4), 52.50, 52.59 (each CO_2CH_3), 56.13 (O*C*H$_3$), 67.24 (*C*2'), 67.54 (*C*3), 68.37 (*C*4'), 69.38 (*C*3'), 69.48 (*C*2), 69.78 (*C*5), 70.51 (*C*5'), 83.66 (*C*1'), 97.36 (*C*1), 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 $C_{23}H_{32}O_{16}SNa$ $[M+Na]^+$: 619.1309), 614.1767 (26, calcd. for $C_{23}H_{36}NO_{16}S$ $[M+NH_4]^+$: 614.1755).

4.22. Phenyl 2,3,4-tri-*O*-(4-methoxyphenylmethyl)-1-thio-6-*O*-triphenyl methyl-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 H_2O (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 $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc:hexane =

70:30) to give phenyl 1-thio-6-*O*-triphenylmethyl-β-D-galactopyranoside (3.68 g, 97 %) as an oil. $[\alpha]_D^{23}$ -11.2 (*c* 1.212, $CHCl_3$); IR (film) 3425, 2925, 1445, 1090, 1060, 1030, 910, 740, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.86 (d, 1H, *J* = 4.6 Hz, C4O*H*), 3.20 (d, 1H, *J* = 2.5 Hz, C2O*H*), 3.32 (dd, 1H, *J* = 7.2, 12.7 Hz, C6*H*H), 3.43-3.53 (4H, C3O*H*, C6*H*H, C3*H*, C5*H*), 3.66 (dt, 1H, *J* = 2.5, 9.7 Hz, C2*H*), 3.88 (brt, 1H, *J* = 4.6 Hz, C4*H*), 4.51 (d, 1H, *J* = 9.7 Hz, C1*H*), 7.18-7.28 (12H, *aromatic protons*), 7.44 (16H, *aromatic protons*), 7.58 (2H, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.55 (*C*6), 69.63 (*C*4), 69.93 (*C*2), 74.84 (*C*3), 77.62 (*C*5), 87.05 (*C*Ph_3), 88.55 (*C*1), 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, $[M+Na]^+$), 243 (100, $[CPh_3]^+$); ESI-HRMS: calcd. for $C_{31}H_{30}O_5SNa$ $[M+Na]^+$, 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 Et_3N (2.0 ml) were successively added to decompose excess reagent. After stirring for additional 30 min, the mixture was poured into H_2O (200 ml), and the aqueous layer was extracted with EtOAc (150 ml ×3). The combined organic layer was washed successively with H_2O (300 ml), and brine (200 ml), dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc:hexane = 16:84) to give **ii-31** (5.3 g, 72 %) as an oil., $[\alpha]_D^{23}$ +28.7 (*c* 0.87, $CHCl_3$); IR (film) 2930, 1610, 1510, 1250, 1085, 1030, 820, 745, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.15 (dd, 1H, *J* = 6.3, 9.7 Hz,

C6*H*H), 3.29 (brt, 1H, *J* = 6.3 Hz, C5*H*), 3.47 (dd, 1H, *J* = 2.8, 9.4 Hz, C3*H*), 3.55 (dd, 1H, *J* = 6.3, 9.7 Hz, C6*H*H), 3.78 (s, 6H, OC*H*$_3$ × 2), 3.79 (s, 3H, OC*H*$_3$), 3.79 (brd, 1H, *J* = 2.8 Hz, C4*H*), 3.85 (t, 1H, *J* = 9.4 Hz, C2*H*), 4.44 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.57 (d, 1H, *J* = 9.4 Hz, C1*H*), 4.62 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.64 (d, 1H, *J* = 10.0 Hz, ArC*H*HO), 4.66 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.70 (d, 1H, *J* = 10.0 Hz, ArC*H*HO), 4.76 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 6.74 (brd, 2H, *J* = 8.8 Hz, *aromatic protons*), 6.85 (brd, 2H, *J* = 8.7 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.24 (OCH$_3$ × 2), 55.26 (OCH$_3$), 63.20 (*C*6), 72.52 (ArCH$_2$O), 73.56 (*C*4), 73.67, 75.21 (each ArCH$_2$O), 77.12 (*C*2), 77.72 (*C*5), 83.91 (*C*3), 86.91 (*C*Ph$_3$), 87.74 (*C*1), 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, $[CPh_3]^+$); ESI-HRMS: calcd. for $C_{55}H_{54}O_8SNa$ $[M+Na]^+$, 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 H_2O (4.0 ml) was stirred with NBS (934 mg 5.3 mmol) at 0 °C. After 5 min, 10% $Na_2S_2O_3$ (4.0 ml) and saturated $NaHCO_3$ 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 H_2O (100 ml). The aqueous layer was extracted with AcOEt (100 ml × 2). Each organic layer was washed with brine

(100 ml), combined, dried over $MgSO_4$, 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. $[\alpha]_D^{23}$ +31.3 (*c* 1.08, $CHCl_3$); 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 $CDCl_3$); ^1H-NMR (400 MHz, $CDCl_3$) δ 2.86 (d, 1H × 0.8, *J* = 2.0 Hz, C1O*H* (α-anomer)), 2.93 (d, 1H × 0.2, *J* = 7.0 Hz, C1O*H* (β-anomer)), 3.16 (dd, 1H × 0.8, *J* = 7.7, 9.0 Hz, C6*H*H (α-anomer)), 3.26 (dd, 1H × 0.2, *J* = 7.4, 8.8 Hz, C6*H*H (β-anomer)), 3.37 (dd, 1H × 0.8, *J* = 5.7, 9.0 Hz, C6*H*H (α-anomer)), 3.39 (1H × 0.2, C5*H* (β-anomer)), 3.45 (1H × 0.2× 2, C3*H* (β-anomer), C6*H*H (β-anomer)), 3.62 (dd, 1H × 0.2, *J* = 7.0, 9.6 Hz, C2*H* (β-anomer)), 3.76 (s, 3H × 0.8, OCH_3 (α-anomer)), 3.76 (s, 3H × 0.2, OCH_3 (β-anomer)), 3.77 (s, 3H × 0.8, OCH_3 (α-anomer)), 3.78 (s, 3H × 0.2, OCH_3 (β-anomer)), 3.80 (s, 3H × 0.2, OCH_3 (β-anomer)), 3.80 (s, 3H × 0.8, OCH_3 (α-anomer)), 3.85 (dd, 1H × 0.8, *J* = 2.6, 10.0 Hz, C3*H* (α-anomer)), 3.88 (brd, 1H × 0.2, *J* = 2.5 Hz, C4*H* (β-anomer)), 3.91 (dd, 1H × 0.8, *J* = 3.3, 10.0 Hz, C2*H* (α-anomer)), 3.97 (brd, 1H × 0.8, *J* = 2.6 Hz, C4*H* (α-anomer)), 4.10 (brdd, 1H × 0.8, *J* = 5.7, 7.7 Hz, C5*H* (α-anomer)), 4.35 (d, 1H × 0.8, *J* = 10.8 Hz, ArC*H*HO (α-anomer)), 4.41 (d, 1H × 0.2, *J* = 10.9 Hz, ArC*H*HO (β-anomer)), 4.54 (t, 1H × 0.2, *J* = 7.0 Hz, C1*H* (β-anomer)), 4.58-4.80 (5H, ArC*H*HO× 5), 5.15 (dd, 1H × 0.8, *J* = 2.0, 3.3 Hz, C1*H* (α-anomer)), 6.69-7.40 (27H, *aromatic protons*).

A solution of the product (1.63 g, 2.08 mmol) in CH_2Cl_2 (10 ml) was stirred with CCl_3CN (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 (α:β = 5:1). The following assignment is only α-isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (dd, 1H, *J* = 6.5, 9.2 Hz, C6*H*H), 3.41 (dd, 1H, *J* = 6.5, 9.2 Hz, C6*H*H), 3.76, 3.78, 3.81 (each s, 3H, OC*H*$_3$), 3.98 (dd, 1H, *J* = 2.7, 10.0 Hz, C3*H*), 4.03 (brd, 1H, *J* = 2.7 Hz, C4*H*), 4.12 (dd, 1H, *J* = 3.6, 10.0 Hz, C2*H*), 4.19 (brt, 1H, *J* = 6.5 Hz, C5*H*), 4.42 (d, 1H, *J* = 10.8 Hz, ArC*H*HO), 4.62, 4.66 (each d, 1H, *J* = 11.2 Hz, ArC*H*$_2$O), 4.67 (d, 1H, *J* = 11.5 Hz, ArC*H*HO), 4.73 (d, 1H, *J* = 10.8 Hz, ArC*H*HO), 4.78 (d, 1H, *J* = 11.5 Hz, ArC*H*HO), 6.45 (d, 1H, *J* = 3.6 Hz, C1*H*), 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(=N*H*)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-α-D-galactopyranosyl-(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-36)

A 4.0×10^{-2} M solution of triethylsilyl trifluoromethanesulfonate in CH_2Cl_2 (0.1 ml) was added at 0 °C to a suspension of a mixture of **ii-30** (41.3 mg, 69.2 μmol), **ii-32** (77.0 mg, 83.0 μmol), and powdered 4A molecular sieves (20 mg) in CH_2Cl_2 (0.6 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 (AcOEte: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}; ^1H NMR (400 MHz, $CDCl_3$). δ 1.85, 1.97, 2.02, 2.07 (each s, 3H, CH_3CO), 3.09 (dd, 1H, *J* = 7.4, 8.5 Hz, C6"*H*H), 3.34 (dd, 1H, *J* = 5.8, 8.5 Hz, C6"H*H*), 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, C4*H*), 3.94-3.97 (2H, C3"*H*, C4"*H*), 4.15 (d, 1H, *J* = 10.4 Hz, ArC*H*HO), 4.24 (1H, C5"*H*), 4.53 (3H, C1"*H*, ArCH_2O), 4.57 (dd, 1H, *J* = 1.1, 2.8 Hz, C4'*H*), 4.61 (d, 1H, *J* = 10.4 Hz, ArC*H*HO), 4.64 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.73 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 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, $CDCl_3$) δ 20.30, 20.67, 20.79, 20.90 (each *C*H_3CO), 48.33 (*C*4), 52.32, 52.64 (each OCH_3), 55.20 (OCH_3 × 2), 55.26, 56.09 (each OCH_3), 62.30 (*C*6"), 67.60 (*C*3), 67.82 (*C*2'), 69.59 (*C*2, *C*3'), 69.84 (*C*5), 70.51 (*C*5'), 71.32 (*C*5"), 72.81, 72.99, 74.27 (each ArCH_2O), 75.32 (*C*4"), 76.04 (*C*4'), 77.20 (*C*2"), 78.30 (*C*3"), 83.78 (*C*1'), 86.63 (*C*Ph_3), 97.34 (*C*1), 100.53 (*C*1"), 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 × 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)-α-D-galactopyranosid] uronate-(1→4)-[methyl(2,3-di-*O*-acetyl-1-thio-α-D-galactopyranosid)uron ate]-(1→4)-[methyl(methyl 2,3-di-*O*-acetyl-α-D-galactopyranosid)uronate]

(ii-37)

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-α-D-galactopyranosid)uronate (23 mg, 80%) as an oil. $[\alpha]_D^{23}$ +151 (*c* 0.96, $CHCl_3$); IR(film) 3490, 2935, 1745, 1510, 1370, 1240, 1220, 1075, 1035, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.91 (dd, 1H, *J* = 3.1, 9.1 Hz, C6"O*H*), 1.95, 2.01, 2.06, 2.07 (each s, 3H, CH_3CO), 3.40 (1H, C6"*H*H), 3.41, 3.58 (each s, 3H, OCH_3), 3.60 (1H, C6"*H*H), 3.78, 3.79, 3.81, 3.82 (each s, 3H, OCH_3), 3.84-3.87 (4H, C4*H*, C2"*H*, C3"*H*, C4"*H*), 3.97 (brt, 1H, *J* = 5.6 Hz, C5"*H*), 4.52 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.55-4.63 (4H, C4'*H*, C1"*H*, ArC*H*HO × 2), 4.63 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.72 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.75 (d, 1H, *J* = 1.4 Hz, C5*H*), 4.83 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.88 (dd, 1H, *J* = 3.8, 10.8 Hz, C2*H*), 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, C1*H*), 5.32 (dd, 1H, *J* = 5.7, 11.1 Hz, C2'*H*), 5.56 (dd, 1H, *J* = 4.5, 10.8 Hz, C3*H*), 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*), 6.90 (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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.27, 20.66, 20.68, 20.76 (each *C*H_3CO), 48.87 (*C*4), 52.35, 52.46 (each OCH_3), 55.24 (OCH_3 × 2), 55.28, 56.12 (each OCH_3), 62.26 (*C*6"), 67.09 (*C*2'), 67.56 (*C*3), 69.47 (*C*2), 69.70 (*C*3'), 69.87 (*C*5), 70.79 (*C*5'), 72.06 (*C*5"), 73.19, 73.27, 73.99 (each Ar*C*H_2O),

74.51 (*C*3"), 76.08 (*C*2"), 76.81 (*C*4'), 78.56 (*C*4"), 84.37 (*C*1'), 97.37 (*C*1), 100.06 (*C*1"), 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 $C_{53}H_{66}O_{24}SNa$ $[M+Na]^+$: 1141.3562), 1136.3983 (11, calcd. for $C_{53}H_{70}NO_{24}S$ $[M+NH_4]^+$: 1136.4009).

A suspension of the product (18 mg, 16.1 μmol) in a mixture of CH_2Cl_2 (0.3 ml) and H_2O (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% $Na_2S_2O_3$ solution (0.1 ml) was added and the mixture was poured into H_2O (20 ml) and the aqueous layer was extracted with AcOEt (20 ml × 3). The combined extract was washed with brine (30 ml), dried over $MgSO_4$, 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 (AcOEte:hexane = 50:50) of the residue gave **ii-37** (18 mg, 98%) as an oil. $[\alpha]_D^{22}$ +139 (*c* 0.70, $CHCl_3$); IR (film) 2955, 1750, 1610, 1515, 1370, 1240, 1220, 1070, 1035, 915, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94, 1.96, 2.06, 2.08 (each s, 3H, CH_3CO), 3.41, 3.581, 3.585, 3.78, 3.79 (each s, 3H, OCH_3), 3.82 (s, 6H, OCH_3 × 2), 3.85 (dd, 1H, *J* = 1.5, 4.5 Hz, C4*H*), 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, ArC*H*HO), 4.608 (d, 1H, *J* = 12.0 Hz, ArC*H*HO), 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, ArC*H*HO), 4.67 (d, 1H, *J* = 12.0 Hz, ArC*H*HO), 4.72 (d, 1H, *J* = 10.9 Hz, ArC*H*HO), 4.75 (d, 1H, *J* = 1.5 Hz, C5*H*), 4.77 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.85 (d, 1H, *J* = 2.3 Hz, C1"*H*), 4.85 (dd, 1H, *J* = 3.7, 10.8 Hz, C2*H*), 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*), 7.26 (4H, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.34, 20.41, 20.65, 20.74 (each CH_3CO), 48.26 (*C*4), 52.03, 52.30, 52.52 (each OCH_3), 55.25 ($OCH_3 \times 2$), 55.26, 56.11 (each OCH_3), 67.41 (*C*2'), 67.45 (*C*3), 69.01 (*C*3'), 69.56 (*C*2), 69.83 (*C*5), 70.55 (*C*5'), 71.86 (*C*5"), 72.77, 73.26 (each $ArCH_2O$), 74.14 (*C*2"), 74.25 ($ArCH_2O$), 75.89 (*C*4"), 77.15 (*C*4'), 78.11 (*C*3"), 83.77 (*C*1'), 97.33 (*C*1), 100.98 (*C*1"), 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 $C_{54}H_{66}O_{25}SNa$ $[M+Na]^+$: 1169.3512), 1164.3949 (27, calcd. for $C_{54}H_{70}NO_{25}S$ $[M+NH_4]^+$: 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 CH_2Cl_2 (1.0 ml) and H_2O (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 H_2O (ca. 0.3 ml), the resulting solution was loaded on a ODS Sep-Pak® cartridge (5.0 g). After washing with MeOH:H_2O = 5:95, elution with MeOH:H_2O = 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, CH_3OH); IR (film) 3450, 1745, 1370, 1220, 1140, 1075 cm^{-1}; ^1H NMR (400 MHz, CD_3OD, 30 °C) δ 1.94, 1.95, 2.02, 2.05 (each s, 3H, CH_3CO), 3.40 (s, 3H, OCH_3), 3.72 (dd, 1H, *J* = 4.0, 10.3 Hz, C2"*H*), 3.75, 3.790, 3.793 (each s, 3H, CO_2CH_3), 3.80 (dd, 1H, *J* = 3.3, 10.3 Hz, C3"*H*), 3.90 (dd, 1H, *J* = 1.7, 4.5 Hz, C4*H*), 4.20 (dd, 1H, *J* = 1.7, 3.3 Hz, C4"*H*), 4.60 (dd, 1H, *J* = 1.2, 2.8 Hz, C4'*H*), 4.70 (d, 1H, *J* = 1.7 Hz, C5"*H*), 4.85 (dd, 1H, *J* = 3.8, 10.9 Hz, C2*H*), 4.90 (d, 1H, *J* = 1.7 Hz, C5*H*), 4.91 (d, 1H, *J* = 4.0 Hz, C1"*H*), 5.01 (d, 1H, *J* = 3.8 Hz, C1*H*), 5.03 (d, 1H, *J* = 1.2 Hz, C5'*H*), 5.17 (dd, 1H, *J* = 5.2, 11.0 Hz, C2'*H*), 5.23 (dd, 1H, *J* = 2.8, 11.0 Hz, C3'*H*), 5.54 (dd, 1H, *J* = 4.5, 10.9 Hz, C3*H*), 5.73 (d, 1H, *J* = 5.2 Hz, C1"*H*); ^{13}C NMR (100 MHz, CD_3OD) δ 20.94, 21.00, 21.08, 21.15 (each CH_3CO), 50.00 (*C*4), 53.14, 53.56, 53.71, 56.87 (each OCH_3), 69.60 (*C*3), 69.67 (*C*2"), 69.72 (*C*2'), 70.60 (*C*3'), 70.72 (*C*3"), 71.20 (*C*2), 71.56 (*C*5), 72.38 (*C*4"), 72.50 (*C*5'), 73.68 (*C*5"), 79.27 (*C*4'), 85.37 (*C*1'), 99.18 (*C*1), 104.18 (*C*1"), 170.14, 170.27, 171.71, 171.87, 172.00, 172.13, 172.16 (each *C*=O) ESIMS (%, rel. int.) *m/z* 809.1758 (100, calcd. for $C_{30}H_{42}O_{22}SNa$ $[M+Na]^+$: 809.1786), 804.2201 (12, calcd. for $C_{30}H_{46}NO_{22}S$ $[M+NH_4]^+$: 804.2232).

4.27. Methyl α-D-galactopyranuronosyl-(1→4)-α-D-galactopyranurono syl-(1→4)-α-D-thiogalactopyranosiduronic acid (ii-1)

A solution of **ii-38** (5.4 mg, 6.9 μmol) 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 *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, H_2O); ^1H NMR (500 MHz, D_2O) δ 3.27 (s, 3H, OCH_3), 3.43 (dd, 1H, *J* = 3.9, 10.5 Hz, C2*H*), 3.56 (dd, 1H, *J* = 1.9, 4.6 Hz, C4*H*), 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, C3*H*), 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, C5*H*), 4.74 (d, 1H, *J* = 3.9 Hz, C1*H*), 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*); ^{13}C NMR (125 MHz, D_2O) δ 58.22 (*C*4), 63.38 (OCH_3), 75.21 (*C*2'), 75.60 (*C*3), 75.61 (*C*2"), 76.51 (*C*3"), 76.65 (*C*3'), 77.15 (*C*2), 77.74 (*C*4' or *C*5), 77.78 (*C*4' or *C*5), 78.02 (*C*5'), 78.74 (*C*5"), 85.63 (*C*4'), 95.14 (*C*1'), 107.31 (*C*1), 107.80 (*C*1"), 179.67, 180.23, 180.62 (each *C*=O); ESIMS (%, rel. int.) *m/z* 615.0565 (71, calcd. for $C_{19}H_{28}O_{18}SK$ $[M+K]^+$: 615.0633), 599.0876 (100, calcd. for $C_{19}H_{28}O_{18}SNa$ $[M+Na]^+$: 599.0894).

4.28. 920-MHz NMR measurements.

Sample solutions for NMR measurements were prepared by dissolving in 99.9% D_2O, the sample pH not being adjusted. Shigemi NMR sample tubes matched with D_2O 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 ROESY[29, 30] and NOESY[51] 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}C}-^{1}H HSQC[52] spectrum was recorded without ^{13}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,[53] and the signals were assigned by Sparky 3 (Goddard, T., and Kneller, D. G., *SPARKY 3*, University of California, San Francisco, CA, USA) run under Windows XP.

4.29. Phenyl 6-*O*-benzoyl-2,3-di-*O*-(4-methoxyphenylmethyl)1-thio-β-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 *in vacuo.* Recrystallization from AcOEt:hexane (40:60) gave phenyl 2,3-di-*O*-(4-methoxyphenylmethyl)-1-thio-β-D-galactopyranoside (2.65 g, 93%) as needles. mp 154 °C; $[\alpha]_D^{24}$ +7.5 (*c* 1.24, $CHCl_3$); IR (film) 3435, 2930, 1610, 1510, 1250, 1085, 1035, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (br, 1H, C6O*H*), 2.60 (br, 1H, C4O*H*), 3.47 (ddd, 1H, *J* = 0.8, 4.2, 6.8 Hz, C5*H*), 3.55 (dd, 1H, *J* = 3.3, 8.9 Hz, C3*H*), 3.71 (t, 1H, *J* = 8.9 Hz, C2*H*), 3.77 (1H, C6*H*H), 3.80, 3.81 (each s, 3H, OCH_3), 3.96 (brdd, 1H, *J* = 6.8, 11.8 Hz, C6*H*H), 4.00 (brdd, 1H, *J* = 0.8, 3.3 Hz, C4*H*), 4.63 (d, 1H, *J* = 8.9 Hz, C1*H*), 4.64 (s, 2H, ArCH_2O), 4.67. 4.75 (each d, 1H, *J* = 10.0 Hz, ArC*H*HO), 6.87 (4H, *aromatic protons*), 7.25-7.34 (7H, *aromatic protons*), 7.55 (2H, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.27, 55.29 (each OCH_3), 62.77 (*C*6), 67.41 (*C*4), 72.00, 75.37 (each ArCH_2O), 76.69 (*C*2), 78.02 (*C*5), 82.06 (*C*3), 87.59 (*C*1), 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_2Cl_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_2O (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 $MgSO_4$, and then concentrated *in vacuo*. Recrystallization from AcOEt:hexane (30:70) gave **ii-39** (2.90 g, 80%) as a white amorphous. $[\alpha]_D^{25}$ +1.9 (*c* 1.14, $CHCl_3$); IR (film) 3500, 2905, 1705, 1510, 1295, 1250, 1120, 1090, 1050, 1030, 810, 715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.50 (dd, 1H, *J* = 1.2, 2.4 Hz, C4O*H*), 3.57 (dd, 1H, *J* = 3.4, 9.0 Hz, C3*H*), 3.72 (t, 1H, *J* = 9.0 Hz, C2*H*), 3.77 (1H, C5*H*), 3.79, 3.80 (each s, 3H, OCH_3), 4.01 (1H, C4*H*), 4.56 (dd, 1H, *J* = 7.7, 10.6 Hz, C6*H*H), 4.63 (1H, C6*H*H), 4.63 (d, 1H, *J* = 9.0 Hz, C1*H*), 4.64. 4.67 (each d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.68. 4.79 (each d, 1H, *J* = 10.0 Hz, ArC*H*HO), 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 (*C*6), 67.02 (*C*4), 72.20, 75.44 (each $ArCH_2O$), 75.82 (*C*5), 76.75 (*C*2), 81.90 (*C*3), 87.94 (*C*1), 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 $C_{35}H_{36}O_8SNa$ $[M+Na]^+$: 639.2029), 634.2464 (100, calcd. for $C_{28}H_{40}NO_8S$ $[M+NH_4]^+$: 634.2475).

4.30. Phenyl 2,3,4-tri-*O*-(4-methoxyphenylmethyl)-6-*O*-triphenylmethyl -α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-(4-methoxyphenylmeth yl)-1-thio-β-D-galactopyranoside (ii-40)

Triethylsilyl trifluoromethanesulfonate (85 μg, 0.32 μmol) 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 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 (AcOEte:hexane = 20:80) gave **ii-40** (2.06 g, 92% (α-isomer 87%, β-isomer 13%)) as an oil. $[\alpha]_D^{24}$ +13.2 (*c* 1.80, $CHCl_3$); IR (film) 2930, 1720, 1610, 1510, 1250, 1170, 1090, 1035, 820, 710 cm^{-1}; The ^1H NMR spectrum indicated that the sample consisted of a mixture of anomers (α:β = 87:13). The following assignment showed major isomer and some minor isomer. ^1H NMR (400 MHz, $CDCl_3$) δ 3.22 (t, 1H × 0.87, *J* = 8.4 Hz, C6'*H*H (α-isomer)), 3.36 (dd, 1H × 0.87, *J* = 5.1, 8.4 Hz, C6'*H*H (α-isomer)), 3.39 (dd, 1H × 0.87, *J* = 2.5, 9.4 Hz, C3*H* (α-isomer)), 3.44 (dd, 1H × 0.13, *J* = 5.3, 9.2 Hz, C6'*H*H (β-isomer)), 3.52 (dd, 1H × 0.13, *J* = 2.7, 9.3 Hz, C3*H* (β-isomer)), 3.63 (s, 3H × 0.87, OCH_3 (α-isomer)), 3.64 (1H × 0.87, C5*H* (α-isomer)), 3.709 (s, 3H × 0.13, OCH_3 (β-isomer)), 3.713 (s, 3H × 0.87, OCH_3 (α-isomer)), 3.75, 3.77 (each s, 3H × 0.13, OCH_3 (β-isomer)), 3.78 (s, 6H × 0.87, OCH_3 × 2 (α-isomer)), 3.78 (1H × 0.87, C2*H* (α-isomer)), 3.80 (s, 3H × 0.87, OCH_3 (α-isomer)), 3.81 (s, 3H × 0.13, OCH_3 (β-isomer)), 3.85 (brd, 1H × 0.87, *J* = 2.5 Hz, C4*H* (α-isomer)), 4.01 (dd, 1H × 0.87, *J* = 3.4, 10.2 Hz, C2'*H* (α-isomer)), 4.08 (dd, 1H × 0.87, *J* = 2.5, 10.2 Hz, C3'*H* (α-isomer)), 4.23 (brd, 1H × 0.87, *J* = 2.5 Hz, C4'*H*

(α-isomer)), 4.31 (brd, 1H × 0.13, J = 2.3 Hz, C4*H* (β-isomer)), 4.37 (d, 1H × 0.87, J = 10.2 Hz, ArC*H*HO (α-isomer)), 4.38, 4.42 (each d, 1H × 0.87, J = 12.3 Hz, ArC*H*HO (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, C1*H* (α-isomer)), 4.60-4.72 (5H × 0.87, C6H_2 (α-isomer), ArC*H*HO (α-isomer), ArCH_2O (α-isomer)), 4.75 (d, 1H × 0.87, J = 10.2 Hz, ArC*H*HO (α-isomer)), 4.81 (d, 1H × 0.87, J = 10.2 Hz, ArC*H*HO (α-isomer)), 4.813 (s, 2H × 0.87, ArCH_2O (α-isomer)), 4.91 (d, 1H × 0.87, J = 3.4 Hz, C1'*H* (α-isomer)), 4.94 (d, 1H × 0.13, J = 11.0 Hz, ArC*H*HO (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)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.02, 55.12, 55.23, 55.25, 55.28 (each O*C*H$_3$), 62.16 (*C*6'), 63.64 (*C*6), 70.60 (*C*5'), 71.72, 72.20, 73.51, 74.20, 75.13 (each Ar*C*H$_2$O), 75.15 (*C*4'), 75.83 (*C*2', *C*4), 76.43 (*C*5), 76.85 (*C*2), 79.14 (*C*3'), 81.11 (*C*3), 86.67 (*C*Ph$_3$), 87.86 (*C*1), 100.75 (*C*1'), 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 $C_{84}H_{84}O_{16}SNa$ $[M+Na]^+$: 1403.5378), 1398.5817 (100, calcd. for $C_{84}H_{88}NO_{16}S$ $[M+NH_4]^+$: 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 CH_2Cl_2 (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 H_2O (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 $MgSO_4$, and then concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (AcOEte: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. $[\alpha]_D^{24}$ +13.5 (*c* 0.85, $CHCl_3$); IR (film) 3430, 2935, 1610, 1510, 1250, 1085, 1035, 820, 705 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.13 (dd, 1H, *J* = 7.6, 8.6 Hz, C6'*H*H), 3.36 (dd, 1H, *J* = 5.4, 8.6 Hz, C6'*H*H), 3.43 (dd, 1H, *J* = 2.6, 9.6 Hz, C3*H*), 3.51 (1H, C5*H*), 3.66 (1H, C6*H*H), 3.725 (t, 1H, *J* = 9.6 Hz, C2*H*), 3.73 (s, 3H, OCH_3), 3.76-3.80 (11H, C6*H*H, C6O*H*, OCH_3 × 3), 3.81 (s, 3H, OCH_3), 3.99 (dd, 1H, *J* = 3.1, 9.6 Hz, C2'*H*), 4.02 (brd, 1H, *J* = 2.6 Hz, C4*H*), 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, ArC*H*HO), 4.41 (d, 1H, *J* = 9.9 Hz, ArC*H*HO), 4.46 (d, 1H, *J* = 12.3 Hz, ArC*H*HO), 4.47 (d, 1H, *J* = 9.9 Hz, ArC*H*HO), 4.49 (d, 1H, *J* = 12.3 Hz, ArC*H*HO), 4.58 (d, 1H, *J* = 11.4 Hz, ArC*H*HO), 4.62 (d, 1H, *J* = 9.6 Hz, C1*H*), 4.71 (d, 1H, *J* = 11.6 Hz, ArC*H*HO), 4.73 (d, 1H, *J* = 10.6 Hz, ArC*H*HO), 4.75 (d, 1H, *J* = 11.6 Hz, ArC*H*HO), 4.80 (d, 1H, *J* = 11.4 Hz, ArC*H*HO), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.12, 55.18 (each OCH_3),

55.24 (OCH_3× 2), 55.28 (OCH_3), 59.89 (*C*6), 62.83 (*C*6'), 71.06 (*C*5'), 72.26, 72.31, 74.25, 74.40 (each $ArCH_2O$), 74.53 (*C*4), 75.21 ($ArCH_2O$), 75.41 (*C*4'), 77.32 (*C*2'), 77.49 (*C*2), 77.74 (*C*5), 78.46 (*C*3'), 82.62 (*C*3), 86.59 (CPh_3), 88.15 (*C*1), 99.71 (*C*1'), 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_2O (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 (AcOEte:hexane = 24:76) gave **ii-41** (4.90 g, 98%) as an oil. $[\alpha]_D^{24}$ +17.5 (*c* 1.13, $CHCl_3$); IR (film) 2930, 1610, 1510, 1445, 1245, 1170, 1090, 1035, 820, 730, 705 cm^{-1}; ^1H 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'*H*H), 3.35 (dd, 1H, *J* = 5.5, 8.4 Hz, C6'*H*H), 3.65 (dd, 1H, *J* = 6.6, 11.2 Hz, C6*H*H), 3.70 (s, 3H, OCH_3), 3.73 (4H, C2*H*, OCH_3), 3.77-3.81 (11H, C6*H*H, C4*H*, OCH_3 × 3), 3.93 (2H, C2'*H*, C3'*H*), 4.09 (1H, C4'*H*), 4.32-4.38 (4H, C1*H*, ArC*H*HO × 3), 4.47 (brdd, 1H, *J* = 5.5, 8.4 Hz, C5'*H*), 4.48, 4.52 (each d, 1H, *J* = 11.9 Hz, ArC*H*HO), 4.59, 4.64 (each s, 2H, $ArCH_2O$), 4.76 (d, 1H, *J* = 10.6 Hz, ArC*H*HO), 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 = 1.1, 8.4 Hz, *aromatic protons*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.14, 55.16, 55.23, 55.24, 55.27 (each OCH_3), 62.48 (*C*6'), 63.28 (*C*6), 70.21 (*C*5'), 71.53, 72.18, 72.64 (each $ArCH_2O$), 73.71 (*C*4), 74.09, 75.03 (each $ArCH_2O$), 75.14 (*C*4'), 75.81 (*C*2'), 76.61 (*C*2), 77.59 (*C*5), 78.97 (*C*3'), 81.10 (*C*3), 86.60 (CPh_3), 87.24 (*C*1), 87.28 (CPh_3), 98.91 (*C*1'), 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 $C_{96}H_{94}O_{15}SNa$ $[M+Na]^+$: 1541.6211), 1537.6633 (100, calcd. for $C_{96}H_{99}NO_{15}S$ $[M+H+NH_4]^+$: 1537.6735), 1536.6622 (90, calcd. for $C_{96}H_{98}NO_{15}S$ $[M+NH_4]^+$: 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*-triphenyl methyl-D-galactitol (ii-42)

A solution of **ii-41** (1.5 g, 0.99 mmol) in a mixture of acetone (100 ml) and H_2O (10 ml) was stirred with NBS (445 mg 2.50 mmol) at 0°C for 15 min. Aqueous 10% $Na_2S_2O_3$ solution (5.0 ml) was added and the mixture was neutralized by the addition of saturated aqueous $NaHCO_3$ solution (15 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 H_2O (100 ml), dried over $MgSO_4$, 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 CH_2Cl_2 (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 H_2O (100 ml), and brine (100 mL) successively, dried over $MgSO_4$, 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. $[\alpha]_D^{25}$ +25.7 (*c* 1.35, $CHCl_3$); IR (film) 3465, 2935, 1610, 1510, 1450, 1250, 1175, 1080, 1035, 820, 730, 705 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.16 (dd, 1H, *J* = 5.0, 8.0 Hz, C1O*H*), 2.98 (dd, 1H, *J* = 3.7, 9.8 Hz, C6*H*H), 3.04 (t, 1H, *J* = 8.5 Hz, C6'*H*H), 3.23 (dd, 1H, *J* = 5.3, 8.5 Hz, C6'*H*H), 3.35 (dd, 1H, *J* = 4.3, 9.8 Hz, C6*H*H), 3.42 (dd, 1H, *J* = 5.3, 9.8 Hz, C2*H*), 3.57 (dd, 1H, *J* = 2.5, 5.3 Hz, C3*H*), 3.67-3.72 (8H, C1H_2, OCH_3 × 2), 3.773, 3.775, 3.785 (each s, 3H, OCH_3), 3.89 (dd, 1H, *J* = 2.3, 10.2 Hz, C3'*H*), 3.93 (dd, 1H, *J* = 3.4, 10.2 Hz, C2'*H*), 4.06 (2H, C4'*H*, ArC*H*HO), 4.13 (dddd, 1H, *J* = 3.4, 3.7, 4.3, 6.5 Hz, C5*H*), 4.20 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.21 (brdd, 1H, *J* = 5.3, 8.5 Hz, C5'*H*), 4.25 (dd, 1H, *J* = 2.5, 6.5 Hz, C4*H*), 4.31 (d, 1H, *J* = 3.4 Hz, C5O*H*), 4.32 (d, 1H, *J* = 10.5 Hz, ArC*H*HO), 4.36, 4.48 (each d, 1H, *J* = 12.1 Hz, ArC*H*HO), 4.52 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.63, 4.67 (each d, 1H, *J* = 11.4 Hz, ArC*H*HO), 4.69 (d, 1H, *J* = 10.5 Hz, ArC*H*HO), 4.72 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 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 (*C*6'), 61.74 (*C*1), 64.50 (*C*6), 70.19 (*C*5), 70.42 (*C*5'), 71.72, 72.22, 72.28, 73.94, 74.26 (each $ArCH_2O$), 74.84 (*C*4'), 75.55 (*C*2'), 77.21 (*C*3), 79.17 (*C*3'), 80.20 (*C*2), 80.77 (*C*4), 86.39, 86.70 (each CPh_3), 101.67 (*C*1'), 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. (3*S*,4*S*,5*S*)-6-(*tert*-butyldimethylsilyloxy)-4,5-di-(4-methoxybenzyloxy) -2-triphenylmethyloxymethyl-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_2O (70 ml) and the aqueous layer was extracted with EtOAc (100 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 of the residue (EtOAc:hexane = 20:80) gave 2,3,4-tri-*O*-(4-methoxyphenylmethyl)-6-*O*-triphenylmethyl-α-D-galactopyranos

yl-(1→4)-1-*O*-(*tert*-butyldimethylsilyl)-2,3-di-*O*-(4-methoxyphenylmethyl)-6-*O*-triphenylmethyl-D-galactitol (1.57 g, 98%) as an oil. $[\alpha]_D^{25}$ +24.5 (*c* 1.15, $CHCl_3$); IR (film) 3465, 2930, 1610, 1510, 1250, 1080, 1035, 830, 705 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ -0.07, -0.05 (each 3H, s, $SiCH_3$), 0.81 (9H, s, $SiC(CH_3)_3$), 2.93 (dd, 1H, *J* = 3.3, 10.0 Hz, C6'*H*H), 3.02 (t, 1H, *J* = 8.7 Hz, C6*H*H), 3.21 (dd, 1H, *J* = 5.0, 8.7 Hz, C6*H*H), 3.36 (dd, 1H, *J* = 6.0, 10.0 Hz, C6'*H*H), 3.49 (2H, C2'*H*, C3'*H*), 3.69, 3.71 (each s, 3H, OCH_3), 3.76-3.79 (10H, C1'*H*H, OCH_3 × 3), 3.87-3.91 (3H, C1'*H*H, C2*H*, C3*H*), 4.11 (2H, C4*H*, C5'*H*), 4.17, 4.24 (each d, 1H, *J* = 11.1 Hz, ArC*H*HO), 4.25-4.31 (3H, C4'*H*, C5*H*, ArC*H*HO), 4.35 (d, 1H, *J* = 12.3 Hz, ArC*H*HO), 4.41 (d, 1H, *J* = 3.3 Hz, C5'O*H*), 4.44 (d, 1H, *J* = 12.3 Hz, ArC*H*HO), 4.52 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.60, 4.63 (each d, 1H, *J* = 11.4 Hz, ArC*H*HO), 4.67 (d, 1H, *J* = 10.4Hz, ArC*H*HO), 4.71 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.90 (d, 1H, *J* = 2.8 Hz, C1*H*), 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*), 6.76 (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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.27 ($SiCH_3$ × 2), 18.25 (Si*C*), 25.98 ($SiC(CH_3)_3$), 55.12 (OCH_3 × 2), 55.21 (OCH_3), 55.22 (OCH_3 × 2), 61.47 (*C*6), 64.09 (*C*1'), 64.46 (*C*6'), 70.25 (*C*5), 70.38 (*C*5'), 71.59, 72.10, 72.89, 73.86, 74.27 (each $ArCH_2O$), 74.75 (*C*4), 75.57 (*C*2), 76.87 (*C*3'), 79.44 (*C*3), 81.18 (*C*4'), 81.62 (*C*2'), 86.26, 86.66 (each CPh_3), 101.88 (*C*1), 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 (3*S*,4*S*,5*S*)-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. $[\alpha]_D^{25}$ +21.2 (*c* 1.78, $CHCl_3$); IR (film) 2930, 1730, 1610, 1510, 1250, 1090, 1035, 830, 705 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ -0.11, -0.09 (each 3H, s, $SiCH_3$), 0.80 (9H, s, $SiC(CH_3)_3$), 2.94 (t, 1H, *J* = 7.8 Hz, C6*H*H), 3.27 (dd, 1H, *J* = 5.8, 7.8 Hz, C6*H*H), 3.59 (1H, C5'*H*), 3.65 (dd, 1H, *J* = 2.8, 10.2 Hz, C3*H*), 3.73-3.78 (18H, C6'H_2, C2*H*, OCH_3 × 5), 3.81 (brd, 1H, *J* = 2.8 Hz, C4*H*), 3.86 (dd, 1H, *J* = 3.4, 5.8 Hz, C4'*H*), 3.97 (dd, 1H, *J* = 5.8, 7.8 Hz, C5*H*), 4.19 (d, 1H, *J* = 18.2 Hz, C1'*H*H), 4.24 (d, 1H, *J* = 10.7 Hz, ArC*H*HO), 4.25 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.39 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.40 (s, 2H, $ArCH_2O$), 4.41 (d, 1H, *J* = 18.2 Hz, C1'*H*H), 4.44, 4.49 (each d, 1H, *J* = 11.6 Hz, ArC*H*HO), 4.50 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.61 (d, 1H, *J* = 3.2 Hz, C1*H*), 4.62 (d, 1H, *J* = 10.7 Hz, ArC*H*HO), 4.65 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 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, $CDCl_3$) δ -5.40, -5.38 (each Si*C*H$_3$), 18.17 (Si*C*), 25.94 (SiC(*C*H$_3$)$_3$), 55.14, 55.15 (each O*C*H$_3$), 55.17 (O*C*H$_3$ × 2), 55.21 (O*C*H$_3$), 62.35 (*C*6), 63.33 (*C*6'), 69.98 (*C*1'), 70.52 (*C*5), 71.92, 72.78, 72.95, 73.27, 74.10 (each ArCH$_2$O), 74.74 (*C*2), 75.17 (*C*4), 78.69 (*C*3), 80.08 (*C*4'), 80.69 (*C*5'), 82.01 (*C*3'), 86.61, 86.89 (each *C*Ph$_3$), 98.61 (*C*1), 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 (*C*2'); 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. $[\alpha]_D^{24}$ +45.3 (*c* 1.00, $CHCl_3$); IR (film) 2925, 1610, 1510, 1250, 1090, 1035, 830, 705 cm^{-1}; ^{1}H NMR (500 MH$_Z$, $CDCl_3$) δ -0.21, -0.20 (each 3H, s, SiC*H*$_3$), 0.71 (9H, s, SiC(C*H*$_3$)$_3$), 3.07 (dd, 1H, *J* = 7.0, 8.7 Hz, C6*H*H), 3.38 (dd, 1H, *J* = 6.1, 8.7 Hz, C6*H*H), 3.39-3.45 (3H, C6'*H*$_2$, C5'*H*), 3.48 (t, 1H, *J* = 3.8 Hz, C4'*H*), 3.71 (s, 3H, OC*H*$_3$), 3.73-3.77 (14H, C2'*H*$_2$, OC*H*$_3$ × 4), 3.90 (2H, C3*H*, C4*H*), 3.95 (dd, 1H, *J* = 3.4, 10.5 Hz, C2*H*), 4.18 (brdd, 1H, *J* = 6.1, 7.0 Hz, C5*H*), 4.30 (d, 1H, *J* = 12.0 Hz, ArC*H*HO), 4.31

(d, 1H, J = 11.2 Hz, ArC*H*HO), 4.41-4.51 (5H, ArC*H*HO × 5), 4.54 (d, 1H, J = 11.5 Hz, ArC*H*HO), 4.56 (d, 1H, J = 3.8 Hz, C3'*H*), 4.66 (d, 1H, J = 11.5 Hz, ArC*H*HO), 4.72 (d, 1H, J = 10.8 Hz, ArC*H*HO), 5.00 (d, 1H, J = 3.4 Hz, C1*H*), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.50, -5.40 (each Si*C*H$_3$), 18.04 (Si*C*), 25.84 (SiC(*C*H$_3$)$_3$), 55.10, 55.16, 55.17, 55.19, 55.21 (each O*C*H$_3$), 62.86 (*C*6), 63.36 (*C*6'), 64.51 (C2'*C*H$_2$), 70.12 (*C*5), 72.49, 72.53, 72.57, 72.87, 74.03 (each Ar*C*H$_2$O), 75.44 (*C*4), 75.86 (*C*2), 76.68 (*C*3'), 77.68 (*C*4'), 78.57 (*C*3), 78.71 (*C*5'), 86.58, 86.84 (each *C*Ph$_3$), 94.31 (*C*1), 113.35 (× 2), 113.39, 113.52, 113.60 (each *aromatic carbons*), 115.10 (*C*1'), 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 (*C*2'), 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 $C_{97}H_{106}O_{15}SiNa$ $[M+Na]^+$: 1561.7199), 1557.7636 (100, calcd. for $C_{97}H_{111}NO_{15}Si$ $[M+H+NH_4]^+$: 1557.7723), 1556.7620 (88, calcd. for $C_{97}H_{110}NO_{15}Si$ $[M+NH_4]^+$: 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-$\Delta^{5,5a}$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 H_2O (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*. Purification of the residue by silica gel column chromatography (EtOAc:hexane = 26:74) gave the corresponding alcohol (422 mg, 97%) as an oil. $[\alpha]_D^{24}$ +46.5 (*c* 1.00, $CHCl_3$); IR (film) 3500, 2930, 1610, 1510, 1250, 1090, 1035, 820, 705 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) 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, OCH_3), 3.741 (s, 6H, OCH_3 × 2), 3.77, 3.78 (each s, 3H, OCH_3), 3.78-3.83 (4H, C3*H*, C4*H*, C2'CH_2), 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, ArC*H*HO), 4.33 (d, 1H, *J* = 11.0 Hz, ArC*H*HO), 4.37 (d, 1H, *J* = 11.0 Hz, ArC*H*HO), 4.40 (d, 1H, *J* = 4.2 Hz, C3'*H*), 4.42-4.46 (each d, 1H, *J* = 11.6 Hz, ArC*H*HO), 4.50 (d, 1H, *J* = 11.0 Hz, ArC*H*HO), 4.53 (d, 1H, *J* = 11.6 Hz, ArC*H*HO), 4.65 (d, 1H, *J* = 11.6 Hz, ArC*H*HO), 4.70 (d, 1H, *J* = 11.0 Hz, ArC*H*HO), 5.00 (d, 1H, *J* = 3.6 Hz, C1*H*), 5.47 (brs, 1H, C1'*H*H), 5.81 (brd, 1H, *J* = 1.7 Hz, C1'*H*H), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.16 (OCH_3), 55.19 (OCH_3 × 4), 62.59 (*C*6'), 63.26 (*C*6), 64.25 (C2'CH_2), 70.47 (*C*5), 72.45, 72.55, 73.07, 73.89, 73.95 (each

$ArCH_2O$), 75.31 (*C*4), 75.59 (*C*2), 77.10 (*C*3'), 78.29 (*C*3), 79.32 (*C*5'), 80.22 (*C*4'), 86.65, 86.89 (each CPh_3), 93.96 (*C*1), 113.39, 113.49, 113.55, 113.61, 113.67 (each *aromatic carbons*), 115.85 (*C*1'), 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 (*C*2'), 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 $C_{91}H_{92}O_{15}Na$ $[M+Na]^+$: 1447.6334), 1443.6802 (100, calcd. for $C_{91}H_{97}NO_{15}$ $[M+H+NH_4]^+$: 1443.6858), 1442.6766 (98, calcd. for $C_{91}H_{96}NO_{15}$ $[M+NH_4]^+$: 1442.6780).

Oxalylchloride (164 mg, 1.29 mmol) was added to a solution of dimethylsulfoxide (202 mg, 2.59 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (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 H_2O (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* 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 NH_4Cl (50 ml) and 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*. Purification of the residue with silica gel column chromatography

(EtOAc:hexane = 26:74) gave 7:10 mixture of **ii-44*R*** and **ii-44*S*** (506 mg, 81%) as an oil. $[\alpha]_D^{24}$ +42.3 (*c* 1.46, $CHCl_3$); IR (film) 3485, 2930, 1610, 1510, 1250, 1090, 1035, 820, 705 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 2.26 (d, 1H × 0.4, *J* = 6.8 Hz, C6'O*H* ((*R*)-isomer)), 2.43 (d, 1H × 0.6, *J* = 7.4 Hz, C6'O*H* ((*S*)-isomer)), 2.95 (dd, 1H × 0.6, *J* = 6.0, 9.0 Hz, C6*H*H ((*S*)-isomer)), 3.03 (dd, 1H × 0.4, *J* = 6.3, 9.0 Hz, C6*H*H ((*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, C6*H*H ((*S*)-isomer)), 3.42 (1H, C6*H*H ((*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_2, C4'*H* ((*R*)-isomer), C4*H*, C3*H* ((*S*)-isomer), OCH_3 × 5), 3.85 (dd, 1H × 0.4, *J* = 2.6, 10.1 Hz, C3*H* ((*R*)-isomer)), 3.93-4.09 (3H, C2*H*, C6'*H*, C5*H*), 4.26-4.72 (11H, ArC*H*HO × 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, C1*H* ((*S*)-isomer)), 5.05 (d, 1H × 0.4, *J* = 3.6 Hz, C1*H* ((*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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.14, 55.16 (each OCH_3), 55.19 (OCH_3 × 3), 63.06 (*C*6 ((*R*)-isomer)), 63.33 (*C*6 ((*S*)-isomer)), 64.10 (C2'CH_2 ((*R*)-isomer)), 64.26 (C2'CH_2 ((*S*)-isomer)), 70.37 (*C*5 ((*R*)-isomer)), 70.58 (*C*5 ((*S*)-isomer)), 72.43, 72.47, 72.51 (each ArCH_2O), 72.55 (*C*6' ((*R*)-isomer), ArCH_2O), 73.15 (*C*6' ((*S*)-isomer)), 73.49, 73.63, 73.79, 73.84, 73.97, 74.48 (each ArCH_2O), 75.05 (*C*4 ((*S*)-isomer)), 75.32 (*C*4 ((*R*)-isomer)), 75.60 (*C*2 ((*S*)-isomer)), 75.68 (*C*2

((*R*)-isomer)), 76.88 (*C*3' ((*R*)-isomer)), 77.39 (*C*3' ((*S*)-isomer)), 78.36 (*C*3 ((*R*)-isomer)), 78.62 (*C*3 ((*S*)-isomer)), 79.32 (*C*4' ((*R*)-isomer)), 79.37 (*C*4' ((*S*)-isomer)), 80.31 (*C*5' ((*R*)-isomer)), 80.36 (*C*5' ((*S*)-isomer)), 86.58, 86.66, 86.83, 86.92 (each CPh_3), 93.86 (*C*1 ((*R*)-isomer)), 94.02 (*C*1 ((*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 (*C*1' ((*S*)-isomer)), 115.73 (*C*1' ((*R*)-isomer)), 115.89 (*C*8' ((*R*)-isomer)), 116.57 (*C*8' ((*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 (*C*7' ((*S*)-isomer)), 138.34 (*C*7' ((*R*)-isomer)), 142.60 (*C*2' ((*S*)-isomer)), 142.76 (*C*2' ((*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 $C_{93}H_{94}O_{15}Na$ $[M+Na]^+$: 1473.6490), 1469.6954 (100, calcd. for $C_{93}H_{99}NO_{15}$ $[M+H+NH_4]^+$: 1469.7015), 1468.6932 (99, calcd. for $C_{93}H_{98}NO_{15}$ $[M+NH_4]^+$: 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.

$[\alpha]_D^{25}$ +44.6 (*c* 1.34, $CHCl_3$); IR (film) 3500, 2930, 1610, 1510, 1250, 1090, 1035, 820, 705 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 2.32 (d, 1H, *J* = 5.0 Hz, C1O*H*), 3.18 (t, 1H, *J* = 8.3 Hz, C6'*H*H), 3.32 (dd, 1H, *J* = 5.6, 8.3 Hz, C6'*H*H), 3.68 (4H, C3*H*, OCH_3), 3.74, 3.76 (each s, 3H, OCH_3), 3.78 (s, 6H, OCH_3 × 2), 3.79 (1H, C3'*H*), 3.86 (dd, 1H, *J* = 3.4, 10.1 Hz, C2'*H*), 3.91 (3H, C2*H*, C6H_2), 4.05 (brs, 1H, C4'*H*), 4.23 (d, 1H, *J* = 2.9 Hz, C4*H*), 4.28 (1H, C1*H*), 4.34 (d, 1H, *J* = 10.6 Hz, ArC*H*HO), 4.35 (1H, C5'*H*), 4.36 (s, 2H, ArCH_2O), 4.39 (d, 1H, *J* = 12.6 Hz, ArC*H*HO), 4.50 (2H, ArC*H*HO× 2), 4.55, 4.59 (each d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.61 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.76 (d, 1H, *J* = 10.6 Hz, ArC*H*HO), 4.88 (d, 1H, *J* = 3.4 Hz, C1'*H*), 5.71 (brd, 1H, *J* = 3.9 Hz, C5a*H*), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.15, 55.17 (each OCH_3), 55.21 (OCH_3× 2), 55.22 (OCH_3), 62.28 (*C*6'), 64.65 (*C*6), 65.78 (*C*1), 70.29 (*C*5'), 71.95, 72.35, 72.46, 72.62 (each ArCH_2O), 73.55 (*C*4), 74.03 (ArCH_2O), 75.19 (*C*4'), 75.32 (*C*2 or *C*3), 75.36 (*C*2 or *C*3), 75.55 (*C*2'), 78.90 (*C*3'), 86.66, 87.06 (each *C*Ph_3), 98.70 (*C*1'), 113.35, 113.58, 113.62 (× 2), 113.75 (each *aromatic carbons*), 124.63 (*C*5a), 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 (*C*5), 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 $C_{91}H_{90}O_{15}Na$ $[M+Na]^+$: 1445.6177), 1441.6641 (100, calcd. for $C_{91}H_{95}NO_{15}$ $[M+H+NH_4]^+$: 1441.6702), 1440.6564 (98, calcd. for $C_{91}H_{94}NO_{15}$ $[M+NH_4]^+$: 1440.6623).

4.34.2. Pysical data for ii-45β.

$[\alpha]_D^{24}$ +32.5 (*c* 0.72, $CHCl_3$); IR (film) 3465, 2930, 1610, 1510, 1250, 1090, 1035, 820, 720 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 3.05 (dd, 1H, *J* = 6.9, 8.7 Hz, C6'*H*H), 3.36 (2H, C6'*H*H, C3*H*), 3.43 (br, 1H, C1O*H*), 3.68, 3.70 (each s, 3H, OCH_3), 3.75 (2H, $C6H_2$), 3.77, 3.782, 3.784 (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, C2*H*), 4.06 (1H, C1*H*), 4.29-4.34 (3H, C4*H*, C5'*H*, ArC*H*HO), 4.41 (d, 1H, *J* = 12.4 Hz, ArC*H*HO), 4.49, 4.55 (each d, 1H, *J* = 11.9 Hz, ArC*H*HO), 4.60 (d, 1H, *J* = 12.4 Hz, ArC*H*HO), 4.62, 4.68 (each d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.72 (d, 1H, *J* = 12.0 Hz, ArC*H*HO), 4.73 (s, 2H, $ArCH_2O$), 4.76 (d, 1H, *J* = 3.6 Hz, C1'*H*), 5.97 (brd, 1H, *J* = 4.6 Hz, C5a*H*), 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 (*C*6'), 65.42 (*C*6), 70.31 (*C*5'), 70.83 ($ArCH_2O$), 70.87 (*C*4), 71.19 (*C*1), 72.58, 72.80, 72.96, 74.02 (each $ArCH_2O$), 75.17 (*C*4'), 75.31 (*C*2'), 78.88 (*C*3'), 79.99 (*C*3), 83.13 (*C*2), 78.90 (*C*3'), 86.60, 87.05 (each CPh_3), 96.54 (*C*1'), 113.36, 113.60, 113.66, 113.68, 113.74, 126.94, 127.05 (each *aromatic carbons*), 127.74 (*C*5a, *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 (*C*5), 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 $C_{91}H_{95}NO_{15}$

$[M+H+NH_4]^+$: 1441.6702), 1440.6611 (96, calcd. for $C_{91}H_{94}NO_{15}$ $[M+NH_4]^+$: 1440.6623).

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 NH_4Cl (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 $MgSO_4$, 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. $[\alpha]_D^{25}$ -13.8 (*c* 1.33, $CHCl_3$); IR (film) 2935, 1725, 1610, 1510, 1250, 1095, 1035, 820, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.25 (2H, C6'*H*H, C3*H*), 3.40 (dd, 1H, *J* = 5.4, 8.2 Hz, C6'*H*H), 3.658, 3.663, 3.72, 3.78, 3.80 (each s, 3H, OCH_3), 3.83 (brd, 1H, *J* = 14.5 Hz, C6*H*H), 4.01 (2H, C2'*H*, C3'*H*), 4.13-4.18 (2H, C6*H*H, C2*H*), 4.19 (brs, 1H, C4'*H*), 4.24 (d, 1H, *J* = 3.3 Hz, C4*H*), 4.37 (d, 1H, *J* = 10.5 Hz, ArC*H*HO), 4.40 (d, 1H, *J* = 12.7 Hz, ArC*H*HO), 4.50 (d, 1H, *J* = 12.7 Hz, ArC*H*HO), 4.53 (1H, C5'*H*), 4.55 (s, 2H, ArCH_2O), 4.70 (d, 1H, *J* = 11.9 Hz, ArC*H*HO), 4.74 (s, 2H, ArCH_2O), 4.82 (2H, ArCH_2O × 2), 5.03 (brs, 1H, C1'*H*), 5.25 (brs, 1H, C5a*H*), 5.28 (brd, 1H, *J* = 7.7 Hz, C1*H*), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 54.99, 55.10, 55.19, 55.21, 55.24 (each OCH_3), 62.05 (*C*6'), 65.05 (*C*6), 70.28 (*C*5'), 71.59, 72.30, 72.57 (each $ArCH_2O$), 72.81 (*C*4), 73.59, 74.11 (each $ArCH_2O$), 74.82 (*C*1), 74.95 (*C*4'), 75.60 (*C*2'), 76.23 (*C*2), 77.14 (*C*3), 79.27 (*C*3'), 86.66, 87.25 (each CPh_3), 98.91 (*C*1'), 113.39, 113.54, 113.67 (× 2), 113.70 (each *aromatic carbons*), 122.12 (*C*5a), 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 (*C*5), 143.70, 144.00, 150.36, 158.91, 159.01 (× 2), 159.03 (× 2), 164.06 (each *aromatic carbons*), 203.76 (*C*=O); ESIMS (%, rel. int.) *m/z*: 1594.6276 (37, calcd. for $C_{98}H_{93}NO_{18}Na$ $[M+Na]^+$: 1594.6290), 1590.6723 (100, calcd. for $C_{98}H_{98}N_2O_{18}$ $[M+H+NH_4]^+$: 1590.6815), 1589.6686 (93, calcd. for $C_{98}H_{97}N_2O_{18}$ $[M+NH_4]^+$: 1589.6736).

The product was diluted with a mixture of MeOH (3.0 ml) and CH_2Cl_2 (3.0 ml) and stirred with 1 M NaOH aqueous solution (0.3 ml) at room temperature for 30 min. The micture was poured into H_2O (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-$\Delta^{5,5a}$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_2Cl_2 (3.0 ml) at 0 °C. After stirring at room temperature at 0°C for 1 h, the cooling bath was removed and the mixture was

stirred at room temperature for 1 h. After saturated aqueous $NaHCO_3$ solution (1.0 ml) was added at 0 °C, the mixture was poured into H_2O (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 $MgSO_4$, 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 CH_2Cl_2 (1.0 ml) and H_2O (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 H_2O (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 amorpous powder. $[\alpha]_D^{24}$ +143 (*c* 0.63, $CHCl_3$); ^{1}H NMR (500 MHz, D_2O) δ 3.51 (dd, 1H, *J* = 3.5, 10.6 Hz, C3*H*), 3.59, 3.60 (each s, 1H, C6'*H*H), 3.67 (dd, 1H, *J* = 7.3, 10.6 Hz, C2*H*), 3.69 (dd, 1H, *J* = 3.6, 8.5 Hz, C2'*H*), 3.73 (dd, 1H, *J* = 3.0, 8.5 Hz, C3'*H*), 3.86 (dd, 1H, *J* = 1.0, 3.0 Hz, C4'*H*), 3.97 (brd, 1H, *J* = 7.3 Hz, C1*H*), 4.04-4.10 (3H, C5'*H*, C6'H_2), 4.16 (d, 1H, *J* = 3.5Hz, C4*H*), 4.95 (d, 1H, *J* = 3.6Hz, C1'*H*), 5.64 (1H, C5a*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.84 (*C*6'), 62.78 (*C*6), 68.48 (*C*3'), 69.06 (*C*4'), 69.25 (*C*2'), 70.95 (*C*3), 71.33 (*C*5'), 72.01 (*C*1), 72.89 (*C*2), 77.09 (*C*4), 100.17 (*C*1'), 128.30 (*C*5a), 136.67 (*C*5); ESIMS (%, rel. int.) *m/z*: 361.1116 (100, calcd. for $C_{13}H_{22}O_{10}Na$ $[M+Na]^+$: 361.1111), 339.1317 (0.8, calcd. for $C_{13}H_{23}O_{10}$ $[M+H]^+$: 339.1291).

4.36. α-D-galactopyranosyl-(1→4)-α-$\Delta^{5,5a}$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),

CH_2Cl_2 (3.0 ml). The similar work up afforded the triol (30.0 mg, 67%) as caramel. The product (24.0 ml, 25.6 μmol) was treated enpmloying DDQ (58.0 mg, 0.26 mmol), H_2O (0.2 ml), CH_2Cl_2 (2.0 ml). The similar work up afforded **ii-46α** (6.2 mg, 71%) as a white powder. $[\alpha]_D^{24}$ +110 (*c* 0.62, H_2O); ^1H NMR (400 MHz, D_2O) δ 3.60, 3.62 (each s, 1H, C6'*H*H),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, C2*H*), 4.01-4.06 (3H, C6*H*H, C5'*H*, C3*H*), 4.11 (brd, 1H, *J* = 14.5Hz, C6*H*H), 4.29 (1H, C1*H*), 4.33 (brd, 1H, *J* = 3.8 Hz, C4*H*), 5.01 (d, 1H, *J* = 3.0 Hz, C1'*H*), 5.64 (1H, C5a*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 61.04 (*C*6'), 62.55 (*C*6), 65.56 (*C*1), 68.54 (*C*2'), 69.17 (*C*4'), 69.34 (*C*3'), 69.99 (*C*2), 70.15 (*C*3), 71.43 (*C*5'), 76.12 (*C*4), 100.84 (*C*1'), 125.93 (*C*5a), 137.37 (*C*5); ESIMS (%, rel. int.) *m/z*: 361.1112 (100, calcd. for $C_{13}H_{22}O_{10}Na$ $[M+Na]^+$: 361.1111), 356.1568 (1.8, calcd. for $C_{13}H_{26}NO_{10}$ $[M+NH^4]^+$: 356.1557), 339.1317 (0.6, calcd. for $C_{13}H_{23}O_{10}$ $[M+H]^+$: 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-acetylthio-α-$\Delta^{5,5a}$carbagalactopyranose (ii-47)

A solution of **ii-45β** (91.8 mg, 64.5 μmol) in CH_2Cl_2 (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 H_2O (20 ml) and the aqueeous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with brine (20 ml), dried over $MgSO_4$ 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 H_2O (25 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with H_2O (30 ml), and brine (30 ml) successively, dried over $MgSO_4$, 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. $[\alpha]_D^{25}$ +71.16 (*c* 1.09, $CHCl_3$); IR (film) 2930, 1690, 1610, 1510, 1250, 1090, 1035, 820, 730, 705 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 2.36 (s, 3H, $COCH_3$), 3.21 (t, 1H, *J* = 8.4 Hz, C6'*H*H), 3.31 (2H, C6'*H*H, C3*H*), 3.66 (s, 3H, OCH_3), 3.73 (1H, C3'*H*), 3.74, 3.75, 3.78, 3.79 (each s, 3H, OCH_3), 3.86 (2H, C6*H*H, C2'*H*), 3.94 (brd, 1H, *J* = 13.9 Hz, C6*H*H), 4.08 (dd, 1H, *J* = 4.9, 8.9 Hz, C2*H*), 4.14 (brs, 1H, C4'*H*), 4.17 (d, 1H, *J* = 3.1 Hz, C4*H*), 4.34 (s, 2H, $ArCH_2O$), 4.36 (d, 1H, *J* = 10.4 Hz, ArC*H*HO), 4.39-4.41 (2H, C5'*H*, ArC*H*HO), 4.45 (d, 1H, *J* = 13.0 Hz, ArC*H*HO), 4.48 (d, 1H, *J* = 12.0 Hz, ArC*H*HO), 4.56 (s, 2H, $ArCH_2O$), 4.57 (d, 1H, *J* = 12.0 Hz, ArC*H*HO), 4.64 (t, 1H, *J* = 4.9 Hz, C1*H*), 4.79 (d, 1H, *J* = 10.4 Hz, ArC*H*HO), 4.89 (d, 1H, *J* = 3.5 Hz, C1'*H*), 5.45 (brd, 1H, *J* = 4.9 Hz, C5a*H*), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.66 (CH_3CO), 44.49 (*C*1), 55.14, 55.16 (each OCH_3), 55.21 (OCH_3 × 3), 61.92 (*C*6'), 64.59 (*C*6), 70.08 (*C*5'), 71.90, 72.19, 72.30, 72.39 (each $ArCH_2O$), 73.18 (*C*2), 74.04 ($ArCH_2O$), 74.40 (*C*4), 75.06 (*C*4'), 75.27 (*C*2'), 76.44 (*C*3), 79.04 (*C*3'), 86.66, 87.19 (each CPh_3), 99.26 (*C*1'), 113.33, 113.56, 113.58, 113.60 (× 2) (each *aromatic carbons*), 122.86 (*C*5a), 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 (*C*5), 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 $C_{93}H_{92}O_{15}SNa$ $[M+Na]^+$: 1503.6055), 1499.6515 (100, calcd. for $C_{93}H_{97}NO_{15}S$ $[M+H+NH_4]^+$: 1499.6579), 1498.6508 (98, calcd. for $C_{93}H_{96}NO_{15}S$ $[M+NH_4]^+$: 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*-triphenyl methyl-1-thio-α-$\Delta^{5,5a}$carbagalactopyranose (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 H_2O (30 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed with H_2O (30 ml), and brine (30 ml) successively, dried over $MgSO_4$, 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. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ 1.64 (d, 1H, *J* = 6.7 Hz, C1S*H*), 3.21 (t, 1H, *J* = 8.4 Hz, C6'*H*H), 3.33 (dd, 1H, *J* = 5.4, 8.4 Hz, C6'*H*H), 3.63 (dd, 1H, *J* = 3.3, 9.5 Hz, C3*H*), 3.65, 3.74, 3.76 (each s, 3H, OCH_3), 3.78-3.83 (8H, C3'*H*, C1*H*, OCH_3 × 2), 3.86 (brd, 1H, *J* = 15.6 Hz, C6*H*H), 3.88 (dd, 1H, *J* = 3.5, 10.2 Hz, C2'*H*), 3.95 (dd, 1H, *J* = 4.9, 9.5 Hz, C2*H*), 3.98 (brd, 1H, *J* = 15.6 Hz, C6*H*H), 4.15 (brs, 1H, C4'*H*), 4.17 (d, 1H, *J* = 3.3 Hz, C4*H*), 4.34-4.40 (4H, ArC*H*HO × 4), 4.45 (brdd, 1H, *J* = 5.4, 8.4 Hz, C5'*H*), 4.47 (d, 1H, *J* = 12.9 Hz, ArC*H*HO), 4.57 (s, 2H, ArCH_2O), 4.59, 4.63 (each d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.77 (d, 1H, *J* = 10.4 Hz, ArC*H*HO), 4.93 (d, 1H, *J* = 3.5 Hz, C1'*H*), 5.48 (brd, 1H, *J* = 4.3 Hz, C5a*H*), 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)-α-D-glucopyranoside (ii-49)

Sodium hydride (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, 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 Et_3N (10 ml) were successively added to decompose excess reagent. After stirring for additional 30 min, the mixture was poured into H_2O (200 ml), and the aqueous layer was extracted with EtOAc (150 ml × 3). The combined organic layer was washed successively with H_2O (200 ml), and brine (200 ml), dried over $MgSO_4$, and then concentrated *in vacuo* to give the crude solid. Recrystallization from EtOAc:hexane (30:70) gave methyl 4,6-*O*-(4-methoxybenzylidene)-2,3-*O*-di-(4-methoxyphenylmethyl)-α-D-glucop yranoside (9.30 g, 81%) as needles. mp 128 °C; $[\alpha]_D^{25}$ -41.2 (*c* 1.44, $CHCl_3$); IR (film) 2910, 1615, 1515, 1370, 1250, 1085, 1045, 1035, 825 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 3.38 (s, 3H, OCH_3), 3.50 (dd, 1H, J = 3.7, 9.3 Hz, C2*H*), 3.55 (t, 1H, J = 9.3 Hz, C4*H*), 3.67 (t, 1H, J = 10.2 Hz, C6*H*H), 3.78 (1H, C5*H*), 3.79, 3.80, 3.81 (each s, 3H, OCH_3), 3.99 (t, 1H, J = 9.3 Hz, C3*H*), 4.23 (dd, 1H, J = 4.8, 10.0 Hz, C6*H*H), 4.52 (d, 1H, J = 3.7 Hz, C1*H*), 4.62 (d, 1H, J = 11.9

Hz, ArC*H*HO), 4.73-4.82 (3H, ArC*H*HO × 3), 5.49 (s, 1H, ArC*H*), 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 (*C*5), 68.98 (*C*6), 73.37, 74.97 (each ArCH_2O), 78.27 (*C*3), 78.71 (*C*2), 82.05 (*C*4), 99.31 (*C*1), 101.20 (Ar*C*H), 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 $C_{31}H_{36}O_9Na$ $[M+Na]^+$: 575.2257), 553.2455 (100, calcd. for $C_{31}H_{37}O_9$ $[M+H]^+$: 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. $[\alpha]_D^{24}$ +5.4 (*c* 1.65, $CHCl_3$); IR (film) 3465, 2930, 1610, 1510, 1250, 1090, 1050, 1035, 820 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$) δ 1.98 (dd, 1H, *J* = 6.0, 6.6 Hz, C6O*H*), 2.32 (d, 1H, *J* = 2.6 Hz, C4O*H*), 3.37 (s, 3H, O*CH*$_3$), 3.44-3.49 (2H, C2*H*, C4*H*), 3.59 (dt, 1H, *J* = 4.1, 9.7 Hz, C5*H*), 3.69-3.79 (3H, C3*H*, C6H_2), 3.796, 3.802 (each s, 3H, O*CH*$_3$), 4.54 (d, 1H, *J* = 3.5 Hz, C1*H*), 4.59 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.61 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.71 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.93 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 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 (*C*6), 70.43 (*C*4), 70.65 (*C*5), 72.77, 74.93 (each ArCH_2O), 79.42 (*C*2), 80.87 (*C*3), 98.27 (*C*1), 113.87, 114.03, 129.60, 129.69, 130.08, 130.83,

159.37, 159.45 (each *aromatic carbons*); ESIMS (%, rel. int.) *m/z*: 457.1838 (18, calcd. for $C_{23}H_{30}O_8Na$ $[M+Na]^+$: 457.1833), 453.2316 (26, calcd. for $C_{23}H_{35}NO_8$ $[M+H+NH_4]^+$: 453.2363), 452.2285 (100, calcd. for $C_{23}H_{34}NO_8$ $[M+NH_4]^+$: 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_2Cl_2 (10 ml) and H_2O (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% $Na_2S_2O_3$ solution (2.0 ml) was added and the mixture was poured into H_2O (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. $[\alpha]_D^{25}$ +7.3 (*c* 1.83, $CHCl_3$); IR (film) 3470, 2935, 1740, 1610, 1510, 1250, 1110, 1055, 820 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 3.40 (s, 3H, OCH_3), 3.48 (dd, 1H, *J* = 3.4, 9.4 Hz, C2*H*), 3.71 (dd, 1H, *J* = 8.6, 9.6 Hz, C2*H*), 3.79, 3.80 (each s, 3H, OCH_3), 3.81 (1H, C3*H*), 4.12 (d, 1H, *J* = 9.6 Hz, C5*H*), 4.57 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.60 (d, 1H, *J* = 3.4 Hz, C1*H*), 4.73 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.74 (d, 1H, *J* = 10.9 Hz, ArC*H*HO), 4.82 (d, 1H, *J* = 10.9 Hz, ArC*H*HO), 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*), 7.29 (brd, 2H, *J* = 8.7 Hz, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.22 (OCH_3 × 2), 55.95 (OCH_3), 69.66 (*C*5), 71.66 (*C*4), 73.23, 75.11 (each $ArCH_2O$), 77.97 (*C*2), 79.98 (*C*3), 98.65 (*C*1), 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 $C_{23}H_{28}O_9Na$ $[M+Na]^+$: 471.1631), 466.2087 (100, calcd. for $C_{23}H_{32}NO_9$ $[M+NH_4]^+$: 466.2077).

A solution of the product (434 mg, 0.97 mmol) in CH_2Cl_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. $[\alpha]_D^{24}$ +9.7 (*c* 0.95, $CHCl_3$); IR (film) 3490, 2920, 1740, 1610, 1510, 1240, 1030, 985, 820 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 2.77 (d, 1H, *J* = 1.9 Hz, C4O*H*), 3.42 (s, 3H, OC*H*$_3$), 3.50 (dd, 1H, *J* = 3.3, 9.1 Hz, C2*H*), 3.77-3.80 (2H, C3*H*, C4*H*), 3.800, 3.802 (each s, 3H, OC*H*$_3$), 4.15 (d, 1H, *J* = 9.6 Hz, C5*H*), 4.58 (d, 1H, *J* = 11.9 Hz, ArC*H*HO), 4.61 (d, 1H, *J* = 3.3 Hz, C1*H*), 4.68 (2H,CH_2CHCH_2O), 4.70 (d, 1H, *J* = 11.0 Hz, ArC*H*HO), 4.73 (d, 1H, *J* = 11.9 Hz, ArC*H*HO), 4.83 (d, 1H, *J* = 11.0 Hz, ArC*H*HO), 5.25 (ddd, 1H, *J* = 1.1, 2.5, 10.4 Hz, C*H*HCHCH_2O), 5.34 (ddd, 1H, *J* = 1.5, 2.5, 17.3 Hz, C*H*HCHCH_2O), 5.91 (1H, CH_2CHCH_2O), 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_2CHCH_2O), 70.76 (*C*5), 71.67 (*C*4), 73.22, 75.03 (each ArCH_2O), 78.09 (*C*2), 79.99 (*C*3), 98.75 (*C*1), 113.89, 113.93 (each *aromatic*

carbons), 119.14 (CH_2CHCH_2O), 129.59, 129.79, 130.02, 130.75 (each *aromatic carbons*), 131.26 (CH_2CHCH_2O), 159.33, 159.49 (each *aromatic carbons*), 169.79 (C=O); ESIMS (%, rel. int.) *m/z*: 511.1934 (15, calcd. for $C_{26}H_{32}O_9Na$ $[M+Na]^+$: 511.1944), 506.2378 (100, calcd. for $C_{26}H_{36}NO_9$ $[M+NH_4]^+$: 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 CH_2Cl_2 (2.0 ml) at 0 °C. After 10 min, the mixture was poured into H_2O (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 $MgSO_4$, 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. ^{1}H NMR (400 MH_Z, $CDCl_3$) δ 3.41 (s, 3H, OCH_3), 3.58 (dd, 1H, J = 3.4, 9.5 Hz, C2*H*), 3.81 (s, 6H, OCH_3 × 2), 4.02 (t, 1H, J = 9.5 Hz, C3*H*), 4.37 (d, 1H, J = 10.2 Hz, C5*H*), 4.50 (d, 1H, J = 3.4 Hz, C1*H*), 4.51 (d, 1H, J = 10.8 Hz, ArC*H*HO), 4.61, 4.71 (each ddd, 1H, J = 1.2, 6.0, 13.0 Hz, $CH_2CHCHHO$), 4.73 (d, 1H, J = 10.8 Hz, ArC*H*HO), 4.74, 4.83 (each d, 1H, J = 9.9 Hz, ArC*H*HO), 4.87 (dd, 1H, J = 9.5, 10.2 Hz, C4*H*), 5.29 (ddd, 1H, J = 1.2, 2.3, 10.3 Hz, C*H*HCHCH$_2$O), 5.36 (ddd, 1H, J = 1.2, 2.3, 17.2 Hz, C*H*HCHCH$_2$O), 5.91 (ddt, 1H, J = 6.0, 10.3, 17.2 Hz, CH_2CHCH_2O), 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-$\Delta^{5,5a}$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 H_2O (20 ml) and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was washed successively with H_2O (30 ml), and brine (30 ml), dried over $MgSO_4$, 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. $[\alpha]_D^{25}$ +49.3 (*c* 1.25, $CHCl_3$); IR (film) 2930, 1760, 1610, 1510, 1250, 1090, 1035, 820, 700 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 3.18 (t, 1H, *J* = 8.3 Hz, C6"*H*H), 3.31 (dd, 1H, *J* = 5.4, 8.3 Hz, C6"*H*H), 3.36, 3.65, 3.67 (each s, 3H, OC*H*$_3$), 3.71-3.77 (18H, C3"*H*, C3'*H*, C6'*H*H, OC*H*$_3$ × 5), 3.81 (dd, 1H, *J* = 3.4, 10.3 Hz, C2"*H*), 3.86 (brd, 1H, *J* = 13.9 Hz, C6'*H*H), 3.89 (1H, C4*H*), 3.94 (1H, C1'*H*), 4.02 (1H, C2'*H*), 4.06-4.08 (2H, C3*H*, C4"*H*), 4.11-4.14 (2H, C2*H*, C4'*H*), 4.18, 4.22 (each d, 1H, *J* = 11.9 Hz, ArC*H*HO), 4.33 (d, 1H, *J* = 10.5 Hz, ArC*H*HO), 4.38 (1H, C5"*H*), 4.41 (d, 1H, *J* = 12.4 Hz, ArC*H*HO), 4.49-4.53 (6H, $CH_2CHCHHO$, ArC*H*HO, ArC*H*$_2$O × 2), 4.56 (d, 1H, *J* = 10.8 Hz, ArC*H*HO), 4.58 (d, 1H, *J* = 11.7 Hz, ArC*H*HO), 4.60 (d, 1H, *J* = 3.6 Hz, C1*H*), 4.639 (d, 1H, *J* = 2.1 Hz, C5*H*), 4.641 (d, 1H, *J* = 11.7 Hz, ArC*H*HO), 4.75 (d, 1H, *J* = 10.5 Hz, ArC*H*HO), 4.78 (d, 1H, *J* = 10.8 Hz, ArC*H*HO), 4.83 (d, 1H, *J* = 3.4 Hz, C1"*H*), 4.86 (brdd, 1H, *J* = 5.5, 12.7 Hz, $CH_2CHCHHO$), 5.20 (brdd, 1H, *J* = 1.2, 10.4 Hz, C*H*HCH$_2$O), 5.30 (brdd, 1H, *J* = 1.2, 17.2 Hz, C*H*HCH$_2$O), 5.88 (1H, C5a'*H*), 5.94 (ddt, 1H, *J* = 5.5, 10.4, 17.2 Hz, CH_2CHCH_2O), 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, $CDCl_3$) δ 47.00 (*C*1'), 50.26 (*C*4), 55.08 (OCH_3 × 3), 55.18 (OCH_3×4), 55.95 (OCH_3), 62.07 (*C*6"), 64.51 (*C*6'), 65.88 (CH_2CHCH_2O), 70.07 (*C*5"), 70.37 (*C*5), 72.13, 72.30, 72.35, 72.42, 72.62, 73.53, 73.97 (each $ArCH_2O$), 75.08 (*C*4', *C*4"), 75.26 (*C*2"), 75.77 (*C*2), 76.19 (*C*3'), 77.37 (*C*3,-*C*2'), 78.89 (*C*3"), 86.62, 87.10 (each CPh_3), 98.93 (*C*1"), 99.58 (*C*1), 113.30, 113.49, 113.56, 113.61, 113.66, 113.77, 113.82 (each *aromatic carbons*), 118.92 (CH_2CHCH_2O), 125.04 (*C*5a'), 126.93 (×2), 127.73, 127.77, 128.57, 128.71, 128.75, 129.05, 129.13 (× 2), 129.47, 129.55, 129.85, 130.38, 130.49 (× 2), 130.93, 131.02, 131.08, 131.14 (each *aromatic carbons*), 131.92 (CH_2CHCH_2O), 135.18 (*C*5'), 143.76, 144.24, 158.81 (× 2), 158.87 (× 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-$\Delta^{5,5a}$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_2Cl_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_2O (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 $MgSO_4$, 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. $[\alpha]_D^{26}$ +96.5 (*c* 1.24, $CHCl_3$); IR (film) 3465, 2940, 1760, 1610, 1510, 1460, 1250, 1090, 1035, 820 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.67 (1H, C6"O*H*), 3.25 (ddd, 1H, *J* = 4.9, 5.1, 11.3 Hz, C6"*H*H), 3.35 (s, 3H, OCH_3), 3.48 (ddd, 1H, *J* = 1.5, 6.7, 11.3 Hz, C6"*H*H), 3.57 (2H, C5"*H*, C4*H*), 3.67 (2H, C4"*H*, C1'*H*), 3.72 (dd, 1H, *J* = 3.4, 5.6 Hz, C3'*H*), 3.75 (s, 3H, OCH_3), 3.77-3.86 (21H, C6'*H*H, C2'*H*, C3"*H*, OCH_3×6), 3.91 (dd, 1H, *J* = 3.7, 9.9 Hz, C2*H*), 3.95 (1H, C6'*H*H), 3.98 (dd, 1H, *J* = 3.6, 10.1 Hz, C2"*H*), 4.05 (dd, 1H, *J* = 4.0, 9.9 Hz, C3*H*), 4.37 (d, 1H, *J* = 11.8 Hz, ArC*H*HO), 4.40 (1H, C4'*H*), 4.42-4.48 (31H, ArC*H*HO × 2, $CH_2CHCHHO$), 4.52 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.56 (d, 1H, *J* = 11.7 Hz, ArC*H*HO), 4.58 (d, 1H, *J* = 11.7 Hz, ArC*H*HO), 4.59 (d, 1H, *J* = 3.7 Hz, C1*H*), 4.61-4.70 (5H, ArC*H*HO × 3, C5*H*, $CH_2CHCHHO$), 4.72 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 4.74 (d, 1H, *J* = 11.2 Hz, ArC*H*HO), 4.77 (d, 1H, *J* = 11.7 Hz, ArC*H*HO), 4.79 (d, 1H, *J* = 3.6 Hz, C1"*H*), 4.81 (d, 1H, *J* = 11.9 Hz, ArC*H*HO), 4.87 (d, 1H, *J* = 11.3 Hz, ArC*H*HO), 5.15 (brdd, 1H, *J* = 1.2, 10.4 Hz, C*H*HCHCH$_2$O), 5.24 (brdd, 1H, *J* = 1.4, 17.2 Hz, C*H*HCHCH$_2$O), 5.88 (2H, C5a'*H*, CH_2CHCH_2O), 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*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.78 (*C*1'), 52.47 (*C*4), 55.18, 55.19, 55.22 (each OCH$_3$), 55.24 (OCH$_3$ × 2), 55.25 (OCH$_3$ × 2), 55.95 (OCH$_3$), 62.54 (*C*6"), 64.60 (*C*6'), 65.90 (CH_2CHCH_2O), 70.76 (*C*5), 70.88 (*C*5"), 72.46, 72.73, 73.15, 73.41, 73.47, 73.85, 73.91 (each ArCH$_2$O), 74.91 (*C*4"), 75.20 (*C*2"), 76.20 (*C*3), 76.48 (*C*2 or *C*2'), 76.52 (*C*2 or *C*2'), 76.66 (*C*3'),

77.70 (*C*4'), 78.67 (*C*3"), 99.33 (*C*1), 101.08 (*C*1"), 113.67, 113.77, 113.79, 113.80, 113.82, 113.85, 113.87 (each *aromatic carbons*), 119.00 (CH_2CHCH_2O), 127.31 (*C*5a'), 129.14, 129.28, 129.49, 129.59, 129.74, 129.90, 130.00, 130.21, 130.24, 130.30, 130.31 (×2), 130.50, 130.56 (each *aromatic carbons*), 131.56 (CH_2CHCH_2O), 135.79 (*C*5'), 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 $C_{79}H_{92}O_{22}SNa$ $[M+Na]^+$: 1447.5699), 1442.5117 (100, calcd. for $C_{79}H_{96}NO_{22}S$ $[M+NH_4]^+$: 1442.6145).

4.43. α-D-galactopyranuronosyl-(1→4)-1-thio-α-$\Delta^{5,5a}$carbagalactopyranuronosyl-(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 CH_2Cl_2 (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 CH_2Cl_2 (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 H_2O (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 $MgSO_4$, 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 H_2O (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 $MgSO_4$, 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 CH_2Cl_2 (1.0 ml) and H_2O (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 H_2O (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 ^{1}H-NMR spectrum. HPLC (Inertsil® DIOL, 4.6×150 mm, H_2O:CH_3CN:TFA 10:90:0.01, 1.0 ml/min flow, t_R = 16 min) gave pure **2**. $[\alpha]_D^{24}$ +64.7 (*c* 1.60, D_2O); ^{1}H NMR (500 MH_Z, $CDCl_3$) δ 3.56 (s, 3H, OC*H*$_3$), 3.91 (2H, C2*H*, C4*H*), 3.94 (dd, 1H, *J* = 4.0, 10.3 Hz, C2"*H*), 4.06 (dd, 1H, *J* = 3.4, 10.3 Hz, C3"*H*), 4.14 (dd, 1H, *J* = 3.9, 9.1 Hz, C3'*H*), 4.23 (dd, 1H, *J* = 4.1, 5.0 Hz, C1'*H*), 4.35 (dd, 1H, *J* = 4.4, 10.2 Hz, C3*H*), 4.39 (dd, 1H, *J* = 5.0, 9.1 Hz, C2'*H*), 4.49 (dd, 1H, *J* = 1.3, 3.4 Hz, C4"*H*), 4.87 (d, 1H, *J* = 3.9 Hz, C4'*H*), 4.98 (d, 1H, *J* = 2.1 Hz, C5*H*), 5.03 (d, 1H, *J* = 4.1 Hz, C1*H*), 5.08 (d, 1H, *J* = 1.3 Hz, C5"*H*), 5.47 (d, 1H, *J* = 4.0 Hz, C1"*H*), 7.30 (d, 1H, *J* = 4.1 Hz, C5a'*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.87 (*C*1'), 54.70 (*C*4), 58.22 (O*C*H_3), 70.44 (*C*2"), 70.85 (*C*2'), 71.12 (*C*3"), 71.43 (*C*3"), 71.52 (*C*2), 71.68 (*C*3'), 72.63 (*C*4"), 72.72 (*C*5), 73.58 (*C*5"), 76.26 (*C*4'), 102.17 (*C*1", *C*1), 10.82 (*C*5a'), 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[54] solution (The quantity was determined by a peak area of HPLC at 210 nm, which was the same asthat 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 12h 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 $MgSO_4$, and then concentrated *in vacuo* to give crude thiol **iii-4**. ^1H NMR (500 MH_Z, $CDCl_3$) δ 1.98, 2.01, 2.02, 2.03, 2.07, 2.09, 2.14 (3H,

s, C*H*$_3$CO$_2$), 2.56 (1H, d, *J* = 9.6 Hz, S*H*), 3.62 (1H, ddd, *J* = 2.0, 5.3, 9.6 Hz, C5*H*), 3.65 (1H, ddd, *J* = 2.2, 5.3, 9.3 Hz, C5'*H*), 3.78 (1H, t, *J* = 9.6 Hz, C4*H*), 4.04 (1H, dd, *J* = 2.2, 12.5 Hz, C6'*H*H), 4.09 (1H, dd, *J* = 5.3, 12.1 Hz, C6*H*H), 4.37 (1H, dd, *J* = 4.5, 12.5 Hz, C6'*H*H), 4.48 (1H, dd, *J* = 2.0, 12.1 Hz, C6*H*H), 4.50 (1H, d, *J* = 8.0 Hz, C1'*H*), 4.52 (1H, t, *J* = 9.6 Hz, C1*H*), 4.89 (1H, t, *J* = 9.6 Hz, C2*H*), 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, C3*H*). 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 CH_2Cl_2 (1.0 ml) at 0 °C and the mixture was stirred at the same temperature for 20 min. The mixture was poured into H_2O (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 $MgSO_4$, 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.

^{1}H NMR (500 MH$_Z$, $CDCl_3$) δ 3.46 (3H, s, OC*H*$_3$), 4.35 (1H, dd, *J* = 7.0, 11.3 Hz, C6*H*H), 4.59 (1H, brt, *J* = 6.8 Hz, C5*H*), 4.69 (1H, dd, *J* = 6.5, 11.3 Hz, C6*H*H), 5.29 (1H, d, *J* = 3.7 Hz, C1*H*), 5.59 (1H, brd, *J* = 2.8 Hz, C4*H*), 5.60 (1H, dd, *J* = 3.7, 10.7 Hz, C2*H*), 5.95 (1H, dd, *J* = 2.8, 10.7 Hz, C3*H*), 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 tempareture, 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 $MgSO_4$, 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. $[\alpha]_D^{26}$ +23.5 (*c* 1.17, $CHCl_3$); IR (film) 2955, 1750, 1270, 1230, 1040, 715 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 1.53, 1.97, 1.99, 2.01, 2.06, 2.09, 2.11 (each 3H, s, C*H*$_3$CO$_2$ × 7), 3.29 (1H, t, *J* = 11.1 Hz, C4*H*), 3.48 (3H, s, C1OC*H*$_3$), 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'*H*H), 4.04 (1H, dd, *J* = 2.1, 12.5 Hz, C6"*H*H), 4.36 (1H, dd, *J* = 4.5, 12.5 Hz, C6"*H*H), 4.47 (1H, ddd, *J* = 2.1, 3.8, 11.1 Hz, C5*H*), 4.52 (1H, d, *J* = 7.9 Hz, C1"*H*), 4.66 (1H, dd, *J* = 2.0, 12.2 Hz, C6'*H*H), 4.76 (1H, dd, *J* = 2.1, 12.1 Hz, C6*H*H), 4.80 (1H, dd, *J* = 3.8, 12.1 Hz, C6*H*H), 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, C1*H*), 5.25 (1H, dd, *J* = 3.5, 9.6 Hz, C2*H*), 6.00 (1H, dd, *J* = 9.6, 11.1 Hz, C3*H*), 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*); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 19.90, 20.45, 20.50, 20.51, 20.55, 20.62, 20.72 (each CH_3CO_2), 46.26 (*C*4), 55.67 (OCH_3), 61.14 (*C*6'), 61.48 (*C*6"), 63.98 (*C*6), 67.24 (*C*3), 67.71 (*C*4"), 69.24 (*C*5), 70.10 (*C*2'), 71.54 (*C*2"), 71.95 (*C*5"), 72.92 (*C*3"), 73.30 (*C*3'), 73.33 (*C*2), 75.73 (*C*4'), 76.31 (*C*5'), 80.97 (*C*1'), 97.26 (*C*1), 100.54 (*C*1"), 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 $[M-C_{28}H_{25}O_8S]^+$: 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, C1*H*), 4.81 (1H, dd, *J* = 5.0, 10.3 Hz, C5*H*), 5.54 (1H, brd, *J* = 2.9 Hz, C4*H*), 5.58 (1H, dd, *J* = 2.9, 10.3 Hz, C3*H*), 5.74 (1H, dd, *J* = 7.9, 10.3 Hz, C2*H*), 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 **iii-7b** (405 mg, 67%) as an oil. $[\alpha]_D^{23}$ +3.6 (*c* 0.82, $CHCl_3$); IR (film) 2925, 1750, 1230, 1070, 715 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 1.51, 1.96, 1.99, 2.01, 2.06, 2.08, 2.10 (each 3H, s, CH_3CO_2), 3.29 (1H, t, *J* = 11.0 Hz, C4*H*), 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'*H*H), 4.04 (1H, dd, *J* = 2.2, 12.5 Hz, C6"*H*H), 4.16 (1H, ddd, *J* = 2.1, 4.3, 11.0 Hz, C5*H*), 4.34 (1H, dd, *J* = 4.5, 12.5 Hz, C6"*H*H), 4.48 (1H, d, *J* = 7.8 Hz, C1"*H*), 4.60 (1H, d, *J* = 7.9 Hz, C1*H*), 4.61 (1H, dd, *J* = 1.4, 11.9 Hz, C6'*H*H), 4.77 (1H, dd, *J* = 4.3, 12.0 Hz, C6*H*H), 4.83 (1H, dd, *J* = 9.2, 10.0 Hz, C2'*H*), 4.86 (1H, dd, *J* = 2.1, 12.0 Hz, C6*H*H), 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, C2*H*), 5.67 (1H, dd, *J* = 9.3, 11.0 Hz, C3*H*), 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, $CDCl_3$) δ 19.90, 20.45, 20.52, 20.52, 20.52, 20.64, 20.67 (each CH_3CO_2), 46.46 (*C*4), 56.91 (OCH_3), 61.54 (*C*6"), 62.05 (*C*6'), 64.02 (*C*6), 67.77 (*C*4"), 69.88 (*C*3), 70.07 (*C*2'), 71.59 (*C*2"), 72.03 (*C*5"), 72.94 (*C*3"), 73.23 (*C*2), 73.28 (*C*3'), 74.27 (*C*5), 76.29 (*C*4'), 76.54 (*C*5'), 80.87 (*C*1'), 100.72 (*C*1"), 102.06 (*C*1), 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. $[\alpha]_D^{27}$ +16.6 (*c* 1.05, H_2O), The IR spectrum was not measured because this sample was only soluble in H_2O. ^1H NMR (500 MH_Z, D_2O) δ 2.73 (1H, t, *J*= 10.8 Hz, C4*H*), 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, OCH_3), 3.27 (1H, m, C4"*H*), 3.32-3.38 (2H, C3"*H*, C5"*H*), 3.43-3.53 (4H, C2*H*, C3'*H*, C4'*H*, C5'*H*), 3.59 (1H, dd, *J*= 5.8, 12.3 Hz, C6"*H*H), 3.63 (1H, dd, *J*= 9.3, 10.8 Hz, C3*H*), 3.65 (1H, dd, *J* = 5.1, 12.5 Hz, C6'*H*H), 3.75-3.82 (3H, C5*H*, C6'*H*H, C6"*H*H), 3.83 (1H, dd, *J*= 4.5, 12.1 Hz, C6*H*H), 3.89 (1H, dd, *J*= 2.1, 12.1 Hz, C6*H*H), 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, C1*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.07 (*C*4), 55.19 (OCH_3), 60.23 (*C*6'), 60.74 (*C*6"), 61.46 (*C*6), 69.59 (*C*3), 69.61 (*C*4"), 72.07 (*C*5), 72.43 (*C*2'), 72.55 (*C*2), 73.31 (*C*2"), 75.65 (*C*3"), 75.76 (*C*4'), 76.16 (*C*5"), 78.40 (*C*3'), 78.84 (*C*5'), 83.61 (*C*1'), 99.47 (*C*1), 102.68 (*C*1"); ESIMS (%, rel. int.) *m/z*: 557.1516 (100, calcd. for $C_{19}H_{34}O_{15}SNa$ $[M+Na]^+$ 557.1516), 535.1698 (5.3, calcd. for $C_{19}H_{35}O_{15}S$ $[M+H]^+$ $[M+H]^+$ 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 H_2O. ^1H NMR (500 MH_Z, D_2O) δ 2.73 (1H, t, *J* = 10.6 Hz, C4*H*), 3.16 (1H, dd, *J* = 8.1, 9.0 Hz, C2*H*), 3.18 (1H, dd, *J* = 8.0, 9.2 Hz, C2"*H*), 3.25 (1H, dd, *J* = 8.8, 9.8 Hz, C2'*H*), 3.28 (1H, dd, *J* = 9.2, 9.7 Hz, C4"*H*), 3.35 (1H, ddd, *J* = 2.2, 5.7, 9.7 Hz, C5"*H*), 3.37 (1H, t, *J* = 9.2 Hz, C3"*H*), 3.43 (3H, s, OCH_3), 3.45 (1H, dd, *J* = 9.0, 10.6 Hz, C3*H*), 3.46 (1H, ddd, *J* = 2.2, 5.0, 9.5 Hz, C5'*H*), 3.49-3.54 (2H, C3'*H*, C4'*H*), 3.55 (ddd, 1H, *J* = 2.0, 5.3, 10.6 Hz, C5*H*), 3.60 (1H, dd, *J* = 5.7, 12.4 Hz, C6"*H*H), 3.66 (1H, dd, *J* = 5.0, 12.5 Hz, C6'*H*H), 3.78 (1H, dd, *J* = 2.2, 12.4 Hz, C6"*H*H), 3.79 (1H, dd, *J* = 5.3, 12.2 Hz, C6*H*H), 3.82 (1H, dd, *J* = 2.2, 12.5 Hz, C6'*H*H), 4.00 (1H, dd, *J* = 2.4, 12.2 Hz, C6*H*H), 4.22 (1H, d, *J* = 8.1 Hz, C1*H*), 4.37 (1H, d, *J* = 8.0 Hz, C1"*H*), 4.53 (1H, d, *J* = 9.8 Hz, C1'*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.31 (*C*4), 57.29 (O*C*H_3), 60.25 (*C*6'), 60.77 (*C*6"), 61.56 (*C*6), 69.64 (*C*4"), 72.45 (*C*2'), 73.05 (*C*3), 73.34 (*C*2"), 74.48 (*C*2), 75.68 (*C*3"), 75.74 (*C*3'), 76.18 (*C*5"), 76.61 (*C*5), 78.39 (*C*4'), 78.73 (*C*5'), 83.84 (*C*1'), 102.70 (*C*1"), 103.13 (*C*1); ESIMS (%, rel. int.) *m/z*: 557.1494 (100, calcd. for $C_{19}H_{34}O_{15}SNa$ $[M+Na]^+$ 557.1516), 535.1674 (31, calcd. for $C_{19}H_{35}O_{15}S$ $[M+H]^+$ $[M+H]^+$ 535.1697).

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

A solution of phenyl 2,3,6,2',3',4',6'-hepta-*O*-acetyl-1-thio-β-D-cellobioside (**iii-8**) (848 mg, 1.16 mmol) in a mixture of MeOH (5.0 ml) and CH_2Cl_2 (5.0 ml)

was stirred with 2M NaOH (300 μl) at room temperature for 10 min. After dilution with H_2O (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, H_2 gas was vigolously 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 PBr_3(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 H_2O (100 ml) and the aqueous layer was extracted with EtOAc (70 ml × 3). The combined organic layer was washed with H_2O (100 ml), and brine (100 ml), dried over $MgSO_4$ 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. $[\alpha]_D^{25}$ +9.80 (*c* 1.00, $CHCl_3$); IR (film) 2910, 1610, 1515, 1250, 1070, 1040, 820 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) 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'*H*H), 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'*H*H), 3.71 (1H, dd, *J* = 1.8, 10.7 Hz, C6*H*H), 3.72, 3.73, 3.76, 3.76, 3.78, 3.79, 3.80 (each 3H, s, OC*H*$_3$), 3.81 (1H, dd, *J* = 4.0, 10.7 Hz, C6*H*H), 3.99 (1H, t, *J* = 8.8 Hz, C4*H*), 4.37 (1H, d, *J* = 11.6 Hz,

ArC*H*HO), 4.37, 4.41 (each 1H, d, *J* = 11.6 Hz, ArCH_2O), 4.42 (1H, d, *J* = 7.9 Hz, C1'*H*), 4.43 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.50 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.61 (1H, d, *J* = 9.8 Hz, C1*H*), 4.62 (1H, d, *J* = 10.8 Hz, ArC*H*HO), 4.63 (1H, d, *J* = 10.3 Hz, ArC*H*HO), 4.63, 4.68 (each 1H, d, *J* = 10.3 Hz, ArCH_2O), 4.70 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.71 (1H, d, *J* = 10.3 Hz, ArC*H*HO), 4.71, 4.80 (each 1H, d, *J* = 10.6 Hz, ArCH_2O), 5.04 (1H, d, *J* = 10.8 Hz, ArC*H*HO), 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 (11H, *aromatic protons*), 7.25-7.30 (4H, *aromatic protons*), 7.55 (2H, *aromatic protons*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.13 (OCH_3 × 3), 55.16, 55.19 (each OCH_3), 55.21, 55.21 (OCH_3 × 2), 67.83 (*C*6), 68.59 (*C*6'), 72.79, 72.82, 72.85, 74.41, 74.52, 74.94, 74.98 (each ArCH_2O), 74.98 (*C*5'), 75.20 (ArCH_2O), 76.22 (*C*4), 77.68 (*C*4'), 79.30 (*C*5), 79.82 (*C*2), 82.48 (*C*2'), 84.61 (*C*3), 84.67 (*C*3'), 87.47 (*C*1), 102.44 (*C*1'), 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, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd for $C_{74}H_{82}O_{17}SNa$ $[M+Na]^+$ 1297.5170; found, *m/z* 1297.5197.

4.51. 2,3,4,6-*O*-tetra-(4-methoxyphenylmethyl)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-(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 H_2O (10 ml) was stirred with NBS (558 mg 3.10 mmol) at 0°C for 5 min. Aqueous 10% $Na_2S_2O_3$ solution (6.0 ml) was added and the mixture was

neutralized by the addition of saturated aqueous $NaHCO_3$ 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 H_2O (100 ml), dried over $MgSO_4$, 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 CH_2Cl_2 (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 H_2O (100 ml), and brine (100 ml) successively, dried over $MgSO_4$, 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. $[\alpha]_D^{26}$ +11.4 (*c* 1.11, $CHCl_3$); IR (film) 3465, 2930, 1610, 1510, 1250, 1070, 1035, 820 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 2.58 (1H, t, *J* = 6.7 Hz, C1O*H*), 2.98 (1H, t, *J* = 5.8 Hz, C5O*H*), 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'*H*H), 3.51 (1H, dd, *J* = 3.1, 9.5 Hz, C6*H*H), 3.57 (1H, dd, *J* = 1.6, 10.6 Hz, C6'*H*H), 3.65 (2H, m, C1'*H*H, C6*H*H), 3.73, 3.75 (each 3H, s, OC*H*$_3$), 3.76 (1H, m, C1*H*H), 3.77, 3.77, 3.77, 3.79, 3.79 (each 3H, s, OC*H*$_3$), 3.90 (1H, dd, *J* = 1.7, 8.1 Hz, C4*H*), 3.94-3.99 (3H, C2'*H*, C3'*H*, C5*H*), 4.27 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.28 (1H, d, *J* = 7.7 Hz, C1'*H*), 4.37 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.38 (1H, d, *J* = 10.3 Hz, ArC*H*HO), 4.38, 4.43 (each 1H, d, *J* = 11.6 Hz, ArC*H*$_2$O), 4.58 (1H, d, *J* = 11.1 Hz, ArC*H*HO), 4.59 (1H, d, *J* = 11.0 Hz,

ArC*H*HO), 4.64 (1H, d, J = 10.6 Hz, ArC*H*HO), 4.67 (1H, d, J = 11.1 Hz, ArC*H*HO), 4.69 (1H, d, J = 10.3 Hz, ArC*H*HO), 4.71 (1H, d, J = 10.7 Hz, ArC*H*HO), 4.73 (1H, d, J = 10.6 Hz, ArC*H*HO), 4.77 (1H, d, J = 11.0 Hz, ArC*H*HO), 4.83 (1H, d, J = 10.7 Hz, ArC*H*HO), 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*); ^{13}C NMR (125 MH_Z, $CDCl_3$) δ 55.15 (OCH_3 × 2), 55.19 (OCH_3 × 3), 55.23 (OCH_3 × 2), 62.69 (*C*1), 68.51 (*C*6'), 70.12 (*C*6), 70.49 (*C*5), 72.78, 72.95, 73.00 (each ArCH_2O), 74.30 (*C*5'), 74.34, 74.45, 74.51, 75.19 (each ArCH_2O), 76.85 (*C*4), 77.41 (*C*4'), 79.34, 79.62 (*C*2, *C*3), 81.74 (*C*2'), 84.44 (*C*3'),103.06 (*C*1'), 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, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{68}H_{80}O_{18}Na$ $[M+Na]^+$ 1207.5242; found, *m/z* 1207.5234.

4.52. (3*R*,4*S*,5*S*)-6-(*tert*-butyldimethylsilyloxy)-4,5-di-(4-methoxy benzyloxy)-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 H_2O (70 ml) and the aqueous layer was extracted with EtOAc (100 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 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. $[\alpha]_D^{26}$ +20.5 (*c* 1.07, $CHCl_3$); IR (film) 3470, 2930, 1610, 1510, 1250, 1070, 1035, 820 cm^{-1}; ^1H NMR (500 MH_Z, C_6D_6) δ 0.18, 0.20 (each 3H, s, SiCH_3), 1.06 (9H, s, SiC(CH_3)$_3$), 3.27, 3.27, 3.29 (each 3H, s, OCH_3), 3.31, 3.31, 3.31, 3.31 (12H, s, OCH_3 × 4), 3.40-3.43 (2H, m, C2O*H*, 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'H_2), 3.80 (1H, dd, *J* = 2.7, 10.0 Hz, C1*H*H), 4.01 (1H, dd, *J* = 3.8, 10.0 Hz, C1*H*H),4.08 (1H, dd, *J* = 3.1, 11.0 Hz, C6*H*H), 4.26 (1H, dd, *J* = 4.5, 11.0 Hz, C6*H*H), 4.30 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.31 (1H, ddd, *J* = 1.9, 3.1, 4.5 Hz, C5*H*), 4.45-4.48 (4H, C2*H*, C3*H*, ArC*H*HO × 2), 4.51 (1H, d, *J* = 11.5 Hz, ArC*H*HO), 4.52 (1H, dd, *J* = 1.9, 6.4 Hz, C4*H*), 4.58 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.74 (1H, d, *J* = 8.1 Hz, C1'*H*), 4.76, 4.81 (each 1H, d, *J* = 10.7 Hz, ArCH_2O), 4.81 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.87 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.89 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.91 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 5.01 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 5.02 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 5.06 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 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*); ^{13}C NMR (125 MH_Z, C_6D_6) δ -5.05, -4.93 (each SiCH_3), 18.58 (Si*C*), 26.27 (SiC(*C*H_3), 54.66 (O*C*H_3 × 2), 54.71 (O*C*H_3 × 4), 54.72 (O*C*H_3), 63.60 (*C*6), 69.33 (*C*6'), 70.96 (*C*1), 71.67 (*C*2), 73.09, 73.17, 73.34, 74.52, 74.57, 74.65 (each Ar*C*H_2O), 75.27 (*C*5'), 75.31 (Ar*C*H_2O), 76.60 (*C*3), 77.99 (*C*4'), 79.45 (*C*4), 80.63 (*C*5), 82.46 (*C*2'), 84.99 (*C*3'), 103.29 (*C*1'), 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, $[(CH_3)_3CSi(CH_3)_2O]^+$), 121 (100, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{74}H_{94}O_{18}SiNa$ $[M+Na]^+$ 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 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 = 30:70) of the residue afforded (3*R*,4*S*,5*S*)-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. $[\alpha]_D^{25}$ +24 (*c* 0.80, $CHCl_3$); IR (film) 2930, 1730, 1610, 1510, 1250, 1070, 1035, 820 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 0.01, 0.02 (each 3H, s, SiC*H*$_3$), 0.88 (9H, s, SiC(C*H*$_3$)$_3$), 3.31 (1H, ddd, *J* = 3.0, 3.5, 9.0 Hz, C5*H*), 3.39 (1H, dd, *J* = 7.7, 9.0 Hz, C2*H*), 3.50 (1H, t, *J* = 9.0 Hz, C4*H*), 3.54 (1H, t, *J* = 9.0 Hz, C3*H*), 3.60 (2H, m, C6*H*$_2$), 3.69-3.77 (3H, C5'*H*, C6'*H*$_2$), 3.735, 3.742, (each 3H, s, OC*H*$_3$), 3.760, (6H, s, OC*H*$_3$ × 2), 3.762, 3.78, 3.80 (each 3H, s, OC*H*$_3$), 4.03 (1H, t, *J* = 3.9 Hz, C4'*H*), 4.17 (1H, d, *J* = 11.5 Hz, ArC*H*HO), 4.19 (1H, d, *J* = 17.5 Hz, C1'*H*H), 4.21 (1H, d, *J* = 11.5 Hz, ArC*H*HO), 4.34 (1H, d, *J* = 7.7 Hz, C1*H*), 4.40 (1H, d, *J* = 17.5 Hz, C1'*H*H), 4.40-4.43 (3H, ArC*H*HO × 3), 4.43 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.47 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.48 (1H, d, *J* = 11.7 Hz, ArC*H*HO), 4.60 (1H, d, *J* = 3.9 Hz, C3'*H*), 4.61 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.69 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.70 (1H, d, *J* = 10.6 Hz,

ArC*H*HO), 4.71 (1H, d, J = 10.3 Hz, ArC*H*HO), 4.85 (1H, d, J = 10.6 Hz, ArC*H*HO), 5.07 (1H, d, J = 10.5 Hz, ArC*H*HO), 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*), 7.19-7.24 (6H, *aromatic protons*), 7.33 (2H, brd, J = 8.6 Hz, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.31, -5.28 (each Si*C*H_3), 18.23 (Si*C*), 25.95 (SiC(*C*H_3)$_3$), 55.18 (O*C*H_3 × 3), 55.20 (O*C*H_3 ×2), 55.25, 55.26 (each O*C*H_3), 62.14 (*C*6'), 68.63 (*C*6), 72.61, 72.78, 73.13, 73.90, 74.27 (each Ar*C*H_2O), 74.32 (*C*1'), 74.53 (Ar*C*H_2O), 74.97 (*C*5), 75.31 (Ar*C*H_2O), 77.42 (*C*4), 78.86 (*C*3'), 78.92 (*C*5'), 80.00 (*C*4'), 81.85 (*C*2), 84.23 (*C*3), 102.21 (*C*1), 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, $[(CH_3)_3CSi(CH_3)_2O]^+$), 121 (100, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{74}H_{92}O_{18}SiNa$ $[M+Na]^+$ 1319.5951; found, *m/z* 1319.5962.

n-Butyl lithium (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 NH_4Cl (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 $MgSO_4$, and then concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (EtOAc: hexane = 26:74) gave **iii-11** (1.37 g, 98%) as

an oil. $[\alpha]_D^{25}$ +1.5 (*c* 0.80, $CHCl_3$); IR (film) 2930, 1610, 1510, 1250, 1070, 1040, 820 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 0.02, 0.03 (each 3H, s, SiC*H*$_3$), 0.89 (9H, s, SiC(C*H*$_3$)$_3$), 3.29 (1H, ddd, *J* = 2.4, 3.9, 9.4 Hz, C5*H*), 3.36 (1H, dd, *J* = 7.9, 9.2 Hz, C2*H*), 3.52-3.57 (2H, C3*H*, C4*H*), 3.61 (1H, dd, *J* = 2.4, 11.0 Hz, C6*H*H), 3.64 (1H, dd, *J* = 3.9, 11.0 Hz, C6*H*H), 3.69 (1H, dt, *J* = 4.9, 5.2 Hz, C5'*H*), 3.74 (3H, s, OC*H*$_3$), 3.75 (6H, s, OC*H*$_3$ ×2), 3.76 (6H, s, OC*H*$_3$ × 2), 3.78, 3.79 (each 3H, s, OC*H*$_3$), 3.76-3.84 (3H, C4'*H*, C6'*H*$_2$), 3.95, 4.04 (each 1H, d, *J* = 13.5 Hz, C2'C*H*$_2$), 4.22, 4.27 (each d, 1H, *J* = 11.4 Hz, ArC*H*$_2$O), 4.37 (1H, d, *J* = 7.9 Hz, C1*H*), 4.41 (1H, d, *J* = 11.7 Hz, ArC*H*HO), 4.44 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.49 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.53 (1H, d, *J* = 11.7 Hz, ArC*H*HO), 4.58 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.61 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.64, 4.65, 4.70, 4.71 (each 1H, d, *J* = 10.6 Hz, ArC*H*HO × 4), 4.77 (1H, d, *J* = 4.6 Hz, C3'*H*), 4.84, 4.87 (each 1H, d, *J* = 10.6 Hz, ArC*H*HO × 2), 5.30, 5.40 (each 1H, brs, C1'*H*$_2$), 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*); ^{13}C NMR (125 MH_Z, $CDCl_3$) δ -5.33, (Si*C*H$_3$ × 2), 18.22 (Si*C*), 25.97 (SiC (*C*H$_3$)$_3$), 55.16 (O*C*H$_3$ × 2), 55.17 (O*C*H$_3$ × 3), 55.21, 55.23 (each O*C*H$_3$), 62.67 (*C*6'), 68.44 (*C*6), 69.80 (C2'*C*H$_2$), 71.96, 72.57, 73.06, 74.24 (each Ar*C*H$_2$O), 74.46 (Ar*C*H$_2$O × 2), 75.09 (*C*5), 75.27 (Ar*C*H$_2$O), 77.43 (*C*3'), 77.74 (*C*3), 79.85 (*C*4'), 80.36 (*C*5'), 82.02 (*C*2), 84.54 (*C*4), 99.10 (*C*1), 113.43, 113.50, 113.62, 113.64 *(aromatic carbons)*, 113.68 (*aromatic carbon* ×2), 113.73 (*aromatic carbon*), 116.52 (*C*1'), 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 (*C*2'), 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-

CH_3OPhCH_2-$CH_3OPhCH_2O]^+$), 121 (100, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{75}H_{94}O_{17}SiNa$ $[M+Na]^+$ 1317.6158; found, *m/z* 1317.6147.

4.53. (3*R*,4*S*,5*S*)-4,5-di-(4-methoxybenzyloxy)-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 H_2O (20 ml) and the aqueous layer was extracted with EtOAc (30 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 = 50:50) gave the corresponding alcohol (259 mg, 99%) as an oil. $[\alpha]_D^{25}$ +3.6 (*c* 1.28, $CHCl_3$); IR (film) 3460, 2915, 1610, 1510, 1250, 1070, 1035, 820 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) 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*H*H), 3.61 (1H, dd, *J* = 2.4, 11.0 Hz, C6*H*H), 3.75-3.86 (4H, C5'*H*, C3'*H*, C6'H_2), 3.75 (3H, s, OCH_3), 3.76 (9H, OCH_3 × 3), 3.77, 3.78, 3.79 (each 3H, s, OCH_3), 3.94, 4.06 (each 1H, brd, *J* = 13.1 Hz, C2'CH_2O), 4.24, 4.30 (each 1H, d, *J* = 11.5 Hz, ArCH_2O), 4.36 (1H, d, *J* = 7.9 Hz, C1*H*), 4.43 (1H, d, *J* = 11.7 Hz, ArC*H*HO), 4.44 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.51 (1H, d, *J* = 11.7 Hz, ArC*H*HO), 4.53 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.54, 4.58 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.67 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.67 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.69 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.69 (1H, m, C2'*H*), 4.72, 4.85 (each 1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.89 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 5.37, 5.39 (each 1H, brs, C1'H_2), 6.75 (2H, brd, *J* = 8.7 Hz, *aromatic protons*),

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*); ^{13}C NMR (125 MH_Z, $CDCl_3$) δ 55.18 (OCH_3 × 2), 55.20 (OCH_3 × 2), 55.21, 55.24, 55.25 (each OCH_3), 61.80 (*C*6'), 68.39 (*C*6), 70.52 (C2'CH_2), 71.90, 72.47, 73.08, 74.17, 74.52, 74.58 (each ArCH_2O), 74.96 (*C*5), 75.24 (ArCH_2O), 76.52 (*C*2'), 77.62 (*C*4), 79.66, 80.65 (*C*3', *C*4'), 81.90 (*C*2), 84.48 (*C*3), 99.63 (*C*1), 113.58, 113.65, 113.70, 113.73, 113.73, 113.73, 113.73 (*aromatic carbons*), 116.62 (*C*1'), 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 (*aromatic carbons*), 141.79 (*C*2'), 159.03, 159.06, 159.07, 159.07, 159.11, 159.11, 159.21 (*aromatic carbons*); FDMS (%, rel. int.) *m/z*: 1181 (20, $[M+H]^+$), 1180 (31, $[M]^+$), 1059 (46, $[M-CH_3OPhCH_2]^+$), 121 (100, $[CH_3OPhCH_2]^+$); FD-HRMS: calcd. for $C_{69}H_{80}O_{17}$ $[M]^+$ 1180.5396; 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_2Cl_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_2Cl_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_2O (30 ml). The aqueous layer was extracted with EtOAc (30 ml × 3). The combined organic layer was washed with brine (30 ml), dried over $MgSO_4$, and then concentrated *in vacuo*. Purification of the residue with silica gel column chromatography (EtOAc:hexane = 40:60) gave **iii-12** (615 mg, 99%) as an oil. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ 3.29 (1H, ddd, J = 2.7, 3.4, 9.1 Hz, C5*H*), 3.40 (1H, dd, J = 7.8, 8.3 Hz, C2*H*), 3.52-3.58 (2H, C3*H*, C4*H*), 3.62-3.67 (2H, C6H_2), 3.75 (6H, s, OCH_3 × 2),

3.76 (6H, s, OCH_3 × 3), 3.78, 3.79 (each 3H, s, OCH_3), 3.90 (1H, brd, J = 12.6 Hz, C5'C*H*HO), 3.97 (1H, dd, J = 0.9, 4.3 Hz, C2'*H*), 4.03-4.07 (2H, C3'*H*, C5'C*H*HO), 4.23, 4.28 (each 1H, d, J = 11.5 Hz, ArCH_2O), 4.33 (1H, d, J = 8.1 Hz, C1*H*), 4.42 (1H, d, J = 11.4 Hz, ArC*H*HO), 4.44 (1H, d, J = 11.6 Hz, ArC*H*HO), 4.48 (1H, d, J = 10.6 Hz, ArC*H*HO), 4.50 (1H, d, J = 11.4 Hz, ArC*H*HO), 4.54 (1H, d, J = 11.6 Hz, ArC*H*HO), 4.54, 4.58 (each 1H, d, J = 10.9 Hz, ArCH_2O), 4.65 (1H, d, J = 10.7 Hz, ArC*H*HO), 4.71, 4.72 (each 1H, d, J = 10.6 Hz, ArC*H*HO), 4.80 (1H, d, J = 10.7 Hz, ArC*H*HO), 4.82 (1H, d, J = 10.6 Hz, ArC*H*HO), 4.88 (1H, d, J = 5.0 Hz, C4'*H*), 5.32, 5.38 (each 1H, brs, C6'CH_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'C*H*O). This sample was immediately used for next step.

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

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_4Cl (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 $MgSO_4$, and then concentrated *in vacuo*. Purification of the residue with silica gel column chromatography (EtOAc:hexane = 40:60) gave 1:1 mixture of **iii-13*S*** and **iii-13*R*** (573 mg, 90%) as an oil. These were successfully separated by medium-pressured column

chromatography (EtOAc:benzene = 9:91) to provide **iii-13*R*** (286 mg, 46%) and **iii-13*S*** (280 mg, 44%).

4.54.1. Pysical data for iii-13*R*.

$[\alpha]_D^{26}$ +12 (*c* 0.64, $CHCl_3$); IR (film) 3470, 2920, 1610, 1510, 1245, 1070, 1030, 820 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 2.65 (1H, d, *J* = 7.7 Hz, C6'O*H*), 3.30 (1H, ddd, *J* = 2.7, 3.5, 9.3 Hz, C5*H*), 3.39 (1H, dd, *J* = 7.8, 9.2 Hz, C2*H*), 3.52-3.58 (2H, C3*H*, C4*H*), 3.58, 3.60 (2H, C6H_2), 3.76 (9H, s, OCH_3 × 3), 3.77 (6H, s, OCH_3 × 2), 3.78 (3H, s, OCH_3), 3.79 (1H, m, C5'*H*), 3.80 (s, 3H, OCH_3), 3.84 (1H, dd, *J* = 2.8, 7.4 Hz, C4'*H*), 3.95, 4.06 (1H, brd, *J* = 13.0 Hz, C2'C*H*HO), 4.24, 4.30 (each 1H, d, *J* = 11.6 Hz, ArCH_2O), 4.37 (1H, d, *J* = 7.8 Hz, C1*H*), 4.39 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.44 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.48 (1H, C6'*H*), 4.49 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.50 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.54 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.65 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.68 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.69 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.70 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.71 (1H, C3'*H*), 4.73, 4.86 (each 1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.92 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 5.09 (1H, dt, *J* = 1.5, 10.4 Hz, C8'*H*H), 5.33 (1H, dt, *J* = 1.5, 17.1 Hz, C8'*H*H), 5.38, 5.41 (each 1H, brs, C1'CH_2), 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 MH_Z, $CDCl_3$) δ 55.19 (O*C*H_3 × 2), 55.21 (O*C*H_3 × 3), 55.25, 55.26 (each O*C*H_3), 68.50 (*C*6), 70.55 (C2'*C*H_2), 71.80 (*C*6'), 71.93, 73.06, 74.43 (each Ar*C*H_2O), 74.53 (Ar*C*H_2O × 2), 74.53, 74.61 (each Ar*C*H_2O), 74.85 (*C*5), 75.28 (Ar*C*H_2O), 76.55 (*C*3'), 77.66 (*C*4), 80.79 (*C*4'), 81.83 (*C*5'), 81.91 (*C*2), 84.46 (*C*3), 99.69 (*C*1), 113.53, 113.63, 113.67, 113.69, 113.71, 113.74, 113.76 (*aromatic carbons*), 114.93 (*C*8'), 116.24 (*C*1'), 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 (*C*7'), 141.87 (*C*2'), 158.93, 159.10, 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, $[M-CH_3OPhCH_2]^+$), 121 (100, $[CH_3OPhCH_2]^+$); FD-HRMS: calcd. for $C_{71}H_{82}O_{17}$ $[M]^+$ 1206.5552; found, *m/z* 1206.5557.

4.54.2. Pysical data for iii-13S.

$[\alpha]_D^{26}$ –7.40 (*c* 1.13, $CHCl_3$); IR (film) 3465, 2930, 1610, 1510, 1250, 1070, 1035, 820 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$). 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, OCH_3), 3.76 (6H, s, OCH_3 × 2), 3.77, 3.78, 3.79 (each 3H, s, OCH_3), 3.82 (1H, t, *J* = 4.6 Hz, C4'*H*), 3.89, 4.02 (each 1H, brd, *J* = 13.0 Hz, C2'CH_2), 4.22, 4.30 (each 1H, d, *J* = 11.4 Hz, ArCH_2O), 4.36 (1H, d, *J* = 7.8 Hz, C1*H*), 4.43 (1H, d, *J* = 11.9 Hz, ArC*H*HO), 4.46 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.51 (2H, d, *J* = 11.9 Hz, ArC*H*HO × 2), 4.55 (1H, C6'*H*), 4.59 (1H, d, *J* = 11.9 Hz, ArC*H*HO), 4.59, 4.63, 4.68 (each 1H, d, *J* = 10.7 Hz, ArCH_2O, ArC*H*HO), 4.71 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.72 (1H, d, *J* = 10.2 Hz, ArC*H*HO), 4.82 (1H, d, *J* = 4.6 Hz, C3'*H*), 4.84 (1H, d, *J* = 10.2 Hz, ArC*H*HO), 4.87 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 5.15 (1H, brd, *J* = 10.6 Hz, C8'*H*H), 5.34, 5.36 (each 1H, brs, C1'H_2), 5.37 (1H, brd, *J* = 17.3 Hz, C8'*H*H), 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*); ^{13}C NMR (100 MH_Z, $CDCl_3$) δ 55.15, 55.17 (each OCH_3), 55.20 (OCH_3 × 3), 55.25 (each OCH_3 × 2), 68.40 (*C*6), 70.15 (C2'CH_2), 72.05

(*C*6'), 72.05, 72.75, 73.01, 73.91, 74.54, 74.58 (each Ar*C*H_2O), 75.12 (*C*5), 75.25 (Ar*C*H_2O), 77.39 (*C*3'), 77.76 (*C*4), 80.10 (*C*5'), 80.58 (*C*4'), 81.98 (*C*2), 84.59 (*C*3), 99.23 (*C*1), 113.60, 113.67, 113.67, 113.70, 113.70, 113.74, 113.74 (*aromatic carbons*), 116.02 (*C*8'), 117.44 (*C*1'), 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 (*C*7'), 141.61 (*C*2'), 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, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{71}H_{82}O_{17}Na$ $[M+Na]^+$ 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-$\Delta^{5,5a}$carbaglucopyranose (iii-14β)

A solution of **iii-13*R*** (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. $[\alpha]_D^{26}$ –20.5 (*c* 1.44, $CHCl_3$); IR (film) 3470, 2910, 1610, 1510, 1250, 1070, 1035, 820 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$). δ. 2.50 (1H, d, *J* = 7.4 Hz, C1O*H*), 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, C4*H*, C3'*H*), 3.58-3.61 (2H, C6*H*H, C2*H*), 3.64 (1H, dd, *J* = 2.0, 11.0 Hz, C6'*H*H), 3.74 (3H, s, OCH_3),3.76 (6H, s, OCH_3 × 2), 3.76 (3H, s, OCH_3), 3.77 (6H, s, OCH_3 × 2), 3.79 (6H, s, OCH_3 × 2), 3.81 (1H, brd, *J* = 12.1 Hz, C6C*H*H), 4.13 (1H, C1*H*), 4.16 (1H, dd, *J* = 4.0, 6.5 Hz, C3*H*), 4.26 (1H, d, *J* = 11.5 Hz, ArC*H*HO), 4.29 (1H, brd, *J* = 12.1 Hz, C6C*H*H), 4.36 (1H, d, *J* = 11.5 Hz,

ArC*H*HO), 4.38, 4.42 (each 1H, d, J = 11.4 Hz, ArCH_2O), 4.43-4.47 (3H, C4*H*, ArC*H*HO × 2), 4.56 (1H, d, J = 11.3 Hz, ArC*H*HO), 4.58 (1H, d, J = 10.9 Hz, ArC*H*HO), 4.63 (1H, d, J = 7.9 Hz, C1'*H*), 4.72 (1H, d, J = 10.5 Hz, ArC*H*HO), 4.71-4.76 (3H, ArC*H*HO × 3), 4.78 (1H, d, J = 11.3 Hz, ArC*H*HO), 4.83 (1H, d, J = 10.5 Hz, ArC*H*HO), 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.14 (O*C*H$_3$), 55.18 (O*C*H$_3$ × 3), 55.21 (O*C*H$_3$), 55.23(O*C*H$_3$ × 2), 68.59 (*C*1), 68.76 (*C*6'), 70.08 (*C6*), 71.33, 72.34, 72.90, 73.33, 74.45, 74.52 (Ar*C*H$_2$O × 6), 74.76 (*C*5'), 75.10 (*C*4), 75.28 (Ar*C*H$_2$O), 77.66 (*C*4'), 79.06 (*C*2), 79.26 (*C*3), 82.40 (*C*2'), 84.55 (*C*3'), 104.21 (*C*1'), 113.59, 113.64, 113.67, 113.73, 113.74, 113.74 113.79 (*aromatic carbons*), 128.10 (*C*5a), 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 (*C*5), 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, $[M\text{-}CH_3OPhCH_2]^+$), 121 (18, $[CH_3OPhCH_2]^+$); FD-HRMS: calcd. for $C_{69}H_{78}O_{17}$ $[M]^+$ 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-$\Delta^{5,5a}$carbaglucopyranose (iii-14α)

In the similar manner as described in the Section 4.55, **iii-13*S*** (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. $[\alpha]_D^{25}$ +4.6 (*c* 1.42, $CHCl_3$); IR (film) 3460, 2910, 1610, 1510, 1250,

1070, 1035, 820 cm^{-1}; ^1H NMR (500 MH_Z, $CDCl_3$) δ 2.69 (1H, d, *J* = 9.1 Hz, C1O*H*), 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'H_2), 3.65 (1H, t, *J* = 5.1 Hz, C2*H*), 3.74 (3H, s, OCH_3), 3.76 (6H, s, OCH_3 ×2), 3.77 (6H, s, OCH_3 × 2), 3.79, 3.79 (6H, s, OCH_3 × 2), 3.80 (1H, C6*H*H), 4.24 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.25 (2H, C6*H*H, C4*H*), 4.33 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.34-4.36 (2H, C1*H*, C3*H*), 4.39 (1H, d, *J* = 11.2 Hz, ArC*H*HO), 4.39, 4.43 (each 1H, d, *J* = 13.2 Hz, ArCH_2O), 4.45 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.53 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.57 (1H, d, *J* = 8.0 Hz, C1*H*), 4.57 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.68 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.73 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.73 (2H, d, *J* = 11.2 Hz, ArC*H*HO × 2), 4.73 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.76 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.84 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 5.78 (1H, brd, *J* = 1.7 Hz, C5a*H*), 6.78-6.84 (14H, *aromatic protons*), 7.08 (2H, brd, *J* = 8.7 Hz, *aromatic protons*), 7.15-7.22 (12H, *aromatic protons*); ^{13}C NMR (125 MH_Z, $CDCl_3$) δ: 55.15 (OCH_3), 55.19, 55.19 (OCH_3 × 4), 55.24, (OCH_3 × 2), 65.05 (*C*1), 68.80 (*C*6'), 70.21 (C6), 71.19, 71.43, 72.51, 72.92 (each ArCH_2O), 74.42 (*C*4), 74.50, 74.54 (each ArCH_2O), 74.70 (*C*5'), 75.17 (*C*2), 75.32 (ArCH_2O), 75.48 (*C*3), 77.66 (*C*4'), 82.47 (*C*2'), 84.54 (*C*3'), 104.76 (*C*1'), 113.60, 113.62, 113.70, 113.71, 113.71, 113.75, 113.75 (*aromatic carbons*), 128.31 (*C*5a), 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 (*C*5), 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, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{69}H_{78}O_{17}Na$ $[M+Na]^+$ 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-$\Delta^{5,5a}$carbaglucopyranosyl acetate (iii-15β)

A mixture of **iii-14β** (17.0 mg, 14.0 μmol) and acetic anhydride (300 μl) and *N*,*N*-dimetyl-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%). $[\alpha]_D^{24}$ -48 (*c* 0.62, $CHCl_3$); IR (film) 2910, 1735, 1510, 1460, 1245, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.98 (3H, s, C*H*$_3$CO), 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'*H*H), 3.64 (1H, d, *J* = 7.5, 9.6 Hz, C2*H*), 3.67 (1H, C6'*H*H), 3.75 (1H, C6*H*H), 3.74, 3.747, 3.753 (each 3H, s, ArOC*H*$_3$), 3.78 (6H, s, ArOC*H*$_3$ × 2), 3.788, 3.793 (each 3H, s, ArOC*H*$_3$), 3.81 (1H, dd, *J* = 70., 9.6 Hz, C3*H*), 4.25 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.29 (1H, brd, *J* = 11.7 Hz, C6*H*H), 4.30 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.39 (2H, s, ArC*H*$_2$O), 4.44 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.53 (1H, d, *J* = 11.2 Hz, ArC*H*HO), 4.57 (1H, brd, *J* = 7.0 Hz, C4*H*), 4.67 (1H, d, *J* = 7.7 Hz, C1'*H*), 4.68 (1H, dd, *J* = 11.1 Hz, ArC*H*HO), 4.69 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.72 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.72 (1H, d, *J* = 11.1 Hz, ArC*H*HO), 4.74 (1H, d, *J* = 11.1 Hz, ArC*H*HO), 4.74 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.85 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.96 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 5.45 (1H, brdd, *J* = 1.5, 7.5 Hz, C1*H*), 5.58 (1H, brd, *J* = 1.5 Hz, C5a*H*), 6.76-6.85 (14H, *aromatic protons*), 7.06-7.30 (14H, *aromatic protons*); ^{13}C NMR (125 MHz, C_6D_6) δ 20.70 (3H, s, $COCH_3$), 54.68, 54.69, 54.70, 54.71, 54.72, 54.74, 54.75 (ArOC*H*$_3$ × 7), 69.12 (*C*6'), 70.14 (*C*6), 72.01, 73.19 (Ar*C*H$_2$O ×2), 73.34 (*C*1), 74.34, 74.55, 74.91, 74.95, 74.34 (Ar*C*H$_2$O × 5), 75.76 (*C*5'), 77.54 (*C*4), 78.21 (C4'), 80.60 (C2), 82.62 (*C*3), 83.03 (*C*2'), 85.25 (*C*3'),

103.38 (*C*1'), 113.90, 113.93, 113.93, 114.03, 114.04, 114.05, 114.18 (*aromatic carbons*), 125.57 (*C*5a), 130.69, 131.11, 131.32, 131.35, 131.53, 131.79, 132.11 (*aromatic carbons*), 138.66 (*C*5'), 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 $C_{71}H_{86}NO_{19}$ $[M+NH_4]^+$ 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-$\Delta^{5,5a}$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*-dimetyl-4-aminopyridine (2.4 mg, 19.7 mmol) in pyridine (1.6 ml) to give **iii-15α** (23.6 mg, 96%). $[\alpha]_D^{23}$ +13 (*c* 0.59, $CHCl_3$); IR (film) 2910, 1735, 1610, 1510, 1460, 1245, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.08 (3H, s, C*H*$_3$CO), 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, C6*H*$_2$), 3.67 (1H, dd, *J* = 3.7, 7.2 Hz, C2*H*), 3.74, 3.75 (each 3H, s, ArOC*H*$_3$), 3.76 (6H, s, ArOC*H*$_3$ × 2), 3.77, 3.78, 3.79 (each 3H, s, ArOC*H*$_3$), 3.85 (1H, brd, *J* = 12.5 Hz, C6*H*H), 4.23 (1H, dd, *J* = 4.1, 7.2 Hz, C3*H*), 4.23 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.27 (1H, brd, *J* = 12.5, C6*H*H), 4.30 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.33 (1H, brd, *J* = 4.1 Hz, C4*H*), 4.35, 4.42 (each 1H, d, *J* = 11.8 Hz, ArC*H*$_2$O), 4.45 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.50, 4.58 (each 1H, d, *J* = 11.5 Hz, ArC*H*$_2$O). 4.63 (1H, d, *J* = 10.9 Hz, ArC*H*HO), 4.63 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.64 (1H, d, *J* = 10.9 Hz, C1*H*), 4.72, 4.73 (each 1H, d, *J* = 10.5, ArC*H*HO), 4.74 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.76 (1H, d, *J* = 10.9 Hz,

ArC*H*HO), 4.82 (1H, d, *J* = 10.5, ArC*H*HO), 5.57 (1H, t, *J* = 3.7 Hz, C1*H*), 5.78 (1H, brd, *J* = 3.7 Hz, C5a*H*), 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_6D_6) δ 20.78 (SCO*C*H$_3$), 54.67, 54.67, 54.69, 54.70, 54.70, 54.73 (each ArO*C*H$_3$), 67.84 (*C*1), 69.17 (*C*6'), 70.45 (*C*6), 71.99, 72.16, 73.20, 73.62, 74.56, 74.79, 75.33 (each ArC*H*$_2$O), 75.56 (*C*5'), 76.06 (*C*2), 76.79 (*C*4), 78.13 (*C*4'), 78.31 (*C*3), 82.91 (*C*2'), 85.18 (*C*3'), 104.59 (*C*1'), 113.94, 113.96, 113.96, 113.99, 114.01, 114.05, 114.17 (*aromatic carbons*), 123.60 (*C*5'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 (C*5*), 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_2O (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}; ^1H NMR (500 MHz, $CDCl_3$) δ 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_2), 3.73, 3.74, 3.756, 3.757, 3.78 (each 3H, OCH_3), 3.79 (6H, s, OCH_3 × 2), 3.81 (1H, dd, *J* = 3.8, 7.2 Hz, C2*H*), 3.91 (1H, brd, *J* = 12.7 Hz, C6*H*H), 4.25 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.27 (1H, brd, *J* = 12.7 Hz, C6*H*H), 4.31 (1H, dd, *J* = 4.2, 7.2 Hz, C3*H*), 4.32 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.37 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.39 (1H, brd, *J* = 4.2 Hz, C4*H*), 4.43 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.45 (1H, d, *J* = 10.3 Hz, ArC*H*HO), 4.49, 4.61 (each 1H, d, *J* = 11.5 Hz, ArCH_2O), 4.63 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.65 (1H, d, *J* = 7.8 Hz, C1'*H*), 4.69 (1H, d, *J* = 11.5 Hz, ArC*H*HO), 4.73 (1H, d, *J* = 10.3 Hz, ArC*H*HO), 4.74 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.74 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.78 (1H, d, *J* = 11.5 Hz, ArC*H*HO), 4.82 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 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, $CDCl_3$) δ 55.16, 55.16, 50.20 (OCH_3), 55.21, 55.21, 55.26, 55.26 (OCH_3), 68.60 (*C*6'), 69.31 (*C*1), 69.79 (*C*6), 71.74, 71.82, 72.83, 72.96, 74.51 (ArCH_2O × 5), 74.57 (*C*2), 74.84 (*C*2' or *C*5'), 74.84, 75.31 (ArCH_2O × 2), 76.37 (*C*4), 77.12 (*C*3), 77.62 (*C*3' or *C*4'), 82.44 (*C*2' or *C*5'), 84.66 (*C*3' or *C*4'), 107.24 (*C*1'), 113.57, 113.58, 113.62, 113.70, 113.77, 113.77, 113.77 (*aromatic carbons*), 123.44 (*C*5a), 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 (*C*5), 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 $C_{76}H_{81}O_{20}NK$ $[M+K]^+$: 1366.4989),

1350.5250 (50, calcd. for $C_{76}H_{81}O_{20}NNa$ $[M+Na]^+$: 1350.5929), 1345.5730 (100, calcd. for $C_{76}H_{85}N_2O_{20}$ $[M+NH_4]^+$: 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 micture was poured into H_2O (20 ml) and extracted with AcOEt (20 ml × 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-$\Delta^{5,5a}$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 × 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 × 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}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 2.31 (3H, s, SCOC*H*$_3$), 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, OC*H*$_3$), 4.12 (1H, dd, *J* = 3.9, 6.0 Hz, C3*H*), 4.23 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.28 (1H, brd, *J* = 12.6 Hz, C6*H*H), 4.32 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.36 (1H, brd, *J* = 3.9 Hz, C4*H*), 4.39 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.40 (1H, brdd, *J* = 3.8, 4.8 Hz, C1*H*), 4.42 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.44 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.48 (1H, d, *J* = 11.0 Hz, ArC*H*HO), 4.58 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.60 (1H, d, *J* = 7.7 Hz, C1'*H*), 4.67 (1H, d, *J* = 11.0 Hz, ArC*H*HO), 4.71 (1H, d, *J* = 10.5 Hz, ArC*H*HO),4.72 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.72 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.74 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.83 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 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, $CDCl_3$) δ 30.26 (SCO*C*H_3), 41.98 (*C*1), 51.15, 55.18, 55.18, 55.19, 55.19, 55.24, 55.24 (each O*C*H_3), 67.86 (*C*6'), 70.06 (*C*6), 71.26, 72.34, 72.8, 72.92 (each Ar*C*H_2O), 74.42 (*C*4), 74.43 (Ar*C*H_2O), 74.50 (*C*5'), 74.82, 75.26 (each Ar*C*H_2O), 77.41 (*C*2), 77.69 (*C*4'), 78.64 (*C*3), 82.34 (*C*2'), 84.54 (*C*3'), 104.38 (*C*1'), 113.51, 113.55, 113.59, 113.68, 113.71, 113.73 (*aromatic carbons*), 125.65 (*C*5a), 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 (*C*5), 158.93, 158.97, 159.02, 159.06, 159.07, 159.10, 159.21 (*aromatic carbon*), 195.29 (S*C*=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-*O*-di-(4-methoxyphenylmethyl)-4,6-*O*-(4-methoxyphenyl methylidene)-α-D-galactopyranoside (iii-18a)

A solution of methyl α-D-galactopyranoside (122 mg, 628 μmol) in DMF (1.0 ml) was stirred with *p*-anisaldehyde dimethylacetal (171 mg, 940 μmol) in the presence of camphorsulfonic acid (1.5 mg, 6.5 μmol) 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_2O (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)-α-D-galactopyranoside (164 mg, 83%) as an oil. $[\alpha]_D^{23}$ +130 (*c* 0.80, $CHCl_3$); IR (film) 3470, 3400, 2910, 1620, 1515, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (1H, d, *J* = 7.8 Hz, C2O*H*), 2.37 (1H, d, *J* = 9.1 Hz, C3O*H*), 3.46 (3H, s, C1OCH_3), 3.69 (1H, q, *J* = 1.5 Hz, C5*H*), 3.80 (3H, s, ArOCH_3), 3.87 (1H, ddd, *J* = 3.4, 9.1, 10.0 Hz, C3*H*), 3.93 (1H, ddd, *J* = 3.4, 7.8, 10.0 Hz, C2*H*), 4.07 (1H, dd, *J* = 1.5, 12.6 Hz, C6*H*H), 4.25 (1H, dd, *J* = 1.5, 3.4 Hz, C4*H*), 4.28 (1H, dd, *J* = 1.5, 12.6 Hz, C6*H*H), 4.93 (1H, d, *J* = 3.4 Hz, C1*H*), 5.51 (1H, s, ArC*H*), 6.90 and 7.42 (each 2H, brd, *J* = 7.4 Hz, aromatic protons); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 (Ar*C*H), 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, H_2 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 Et_3N (2.0 ml) were successively added to decompose excess reagent. After stirring for additional 30 min, the mixture was poured into H_2O (100 ml), and the aqueous layer was extracted with EtOAc (70 ml × 3). The combined organic layer was washed successively with H_2O (100 ml), and brine (100 ml), dried over $MgSO_4$, 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; $[\alpha]_D^{23}$ +61.5 (*c* 1.00, $CHCl_3$); IR (KBr) 2910, 1615, 1515, 1250, 1100, 1035, 825 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 3.37 (3H, s, OC*H*$_3$), 3.55 (1H, dt, *J* = 0.8, 1.5 Hz, C5*H*), 3.80 (6H, s, OC*H*$_3$ × 2), 3.81 (each 3H, s, OC*H*$_3$), 3.92 (1H, dd, *J* = 3.4, 10.2 Hz, C3*H*), 3.97 (1H, dd, *J* = 1.5, 12.6 Hz, C6*H*H), 4.01 (1H, dd, *J* = 3.4, 10.2 Hz, C2*H*), 4.11 (1H, dd, *J* = 0.8, 3.4 Hz, C4*H*), 4.17 (1H, dd, *J* = 1.5, 12.6 Hz, C6*H*H), 4.59 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.66 (1H, d, *J* = 11.9 Hz, ArC*H*HO), 4.69 (1H, d, *J* = 3.4 Hz, C1*H*), 4.75 (1H, d, *J* = 11.9 Hz, ArC*H*HO), 4.79 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 5.42 (1H, s, ArC*H*), 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*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.23 (OCH_3 × 2), 55.26, 55.45 (each OCH_3), 62.40 (*C*5), 69.33 (*C*6), 71.82, 73.40 (each ArCH_2O), 74.86 (*C*4), 74.98 (*C*2), 75.54 (*C*3), 99.55 (*C*1), 101.03 (Ar*C*H), 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, $[M\text{-}CH_3OPhCH_2]^+$), 121 (100, $[CH_3OPhCH_2]^+$); FAB-HRMS: calcd. for $C_{31}H_{36}O_9Na$ $[M+Na]^+$ 575.2257; found, *m/z* 575.2259.

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

In the similar manner as described in the Section 4.61, methy 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. $[\alpha]_D^{23}$ -13.2 (*c* 1.05, CH_3OH); IR (film) 3400, 2840, 1615, 1515, 1250, 1070, 1055, 990, 820 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 2.49 (1H, d, *J* = 9.6 Hz, C3O*H*), 2.50 (1H, d, *J* = 1.9 Hz, C2O*H*), 3.49 (1H, ddd, *J* = 1.3, 1.5, 1.9 Hz, C5*H*), 3.59 (3H, s, OCH_3), 3.68 (1H, dt, *J* = 3.9, 9.6 Hz, C3*H*), 3.75 (1H, ddd, *J* = 1.9, 7.6, 9.6 Hz, C2*H*), 3.81 (3H, s, OCH_3), 4.08 (1H, dd, *J* = 1.9, 12.5 Hz, C6*H*H), 4.20 (1H, dd, *J* = 1.3, 3.9 Hz, C4*H*), 4.22 (1H, d, *J* = 7.6 Hz, C1*H*), 4.35 (1H, dd, *J* = 1.5, 12.5 Hz, C6*H*H), 5.51 (1H, s, ArC*H*), 6.88, 7.43 (each brd, 2H, *J* = 8.8 Hz, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.30, 57.20 (each O*C*H_3), 66.70 (*C*5), 69.12 (*C*6), 71.90 (*C*2), 72.78 (*C*3), 75.25 (*C*4), 101.43 (Ar*C*H), 103.77 (*C*1), 113.58, 127.75, 129.97, 160.27 (*aromatic carbons*); ESIMS (%, rel. int.) *m/z*: 335.1118 (8.2, calcd. for $C_{15}H_{20}O_7Na$ $[M+Na]^+$: 335.1107), 313.1297 (100, calcd. for $C_{15}H_{21}O_7$ $[M+H]^+$: 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; $[\alpha]_D^{23}$ +57.7 (*c* 0.70, $CHCl_3$); IR (KBr) 2850, 1610,

1515, 1250, 1085, 1035, 825 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$) δ 3.29 (1H, ddd, *J* = 0.7, 1.4, 1.5 Hz, C5*H*), 3.50 (1H, dd, *J* = 3.5, 9.7 Hz, C3*H*), 3.58 (3H, s, OCH_3), 3.79 (1H, dd, *J* = 7.7, 9.7 Hz, C2*H*), 3.795 (3H, s, OCH_3), 3.801, (6H, s, OCH_3 × 2), 3.99 (1H, dd, *J* = 1.6, 12.4 Hz, C6*H*H), 4.04 (1H, dd, *J* = 0.7, 3.5 Hz, C4*H*), 4.28 (1H, d, *J* = 7.7 Hz, C1*H*), 4.28 (1H, dd, *J* = 1.4, 12.4 Hz, C6*H*H), 4.66, 4.70 (each1H, d, *J* = 12.0 Hz, ArCH_2O), 4.69 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.81 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 5.44 (1H, s, ArC*H*), 6.83, 6.86, 6.87, 7.28, 7.31, 7.47 (each 2H, brd, *J* = 8.8 Hz, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.25, 55.27, 55.29, 57.03 (each O*C*H_3), 66.38 (*C*5), 69.17 (*C*6), 71.63 (Ar*C*H_2O), 74.03 (*C*4), 74.89 (Ar*C*H_2O), 78.21 (*C*2), 78.75 (*C*3), 101.30 (Ar*C*H), 104.74 (*C*1), 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 $C_{31}H_{36}O_9K$ $[M+K]^+$:591.1996), 575.2233 (12, calcd. for $C_{31}H_{36}O_9Na$ $[M+Na]^+$: 575.2257), 570.2677 (100, calcd. for $C_{31}H_{40}O_9N$ $[M+NH_4]^+$: 570.2703), 553.2414 (25, calcd. for $C_{31}H_{37}O_9$ $[M+H]^+$: 553.2438), 431.1699 (14, calcd. for $C_{23}H_{27}O_8$ $[M-CH_3OPhCH_2]^+$: 431.1706).

4.63. Methyl 2,3,6-*O*-tri-(4-methoxyphenylmethyl)-α-D-galactopyranoside (iii-19a)

A suspension of **iii-18a** (64.1 mg, 115 μmol) 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 μmol) and $AlCl_3$ (93.0 mg, 698 μmol) 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 × 3). The

combined organic extract was washed with brine (20 ml), dried over $MgSO_4$, and then concentrated *in vacuo*. Silica gel column chromatography of the residue (EtOAc:hexane = 30:70) gave **iii-19a** (37.2 mg, 57%) as caramel. $[\alpha]_D^{23}$ +18 (*c* 0.87, $CHCl_3$); IR (film) 3500, 2910, 1610, 1510, 1460, 1250, 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.60 (1H, s, C4O*H*), 3.35 (3H, s, C1OCH_3), 3.61 (1H, dd, *J* = 6.2, 10.2 Hz, C6*H*HO), 3.68 (1H, dd, *J* = 5.4, 10.2 C6*H*HO), 3.78, 3.79 (each 3H, s, ArOCH_3), 3.80 (2H, C2*H*, C3*H*), 3.84 (1H, brdd, *J* = 5.4, 6.2 Hz, C5*H*), 3.99 (1H, brs, C4*H*), 4.47, 4.50 (each 1H, d, *J* = 11.5 Hz, ArCH_2O), 4.58 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.60 (1H, d, *J* = 2.3 Hz, C1*H*), 4.61, 4.70 (1H, dd, *J* = 11.3 Hz, ArCH_2O), 4.70 (1H, dd, *J* = 11.8 Hz, ArC*H*HO), 6.82-6.95 (6H, *aromatic protons*), 7.22-7.30 (6H, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.18 (ArO*C*H_3, and C1O*C*H_3), 55.23 (ArO*C*H_3 × 2), 68.09 (*C*4), 68.27 (*C*5), 69.23 (*C*6), 72.35, 73.09, 73.20 (each Ar*C*H_2O), 75.23 (*C*2 or *C*3), 77.22 (*C*2 or *C*3), 98.63 (*C*1), 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 $C_{31}H_{38}KO_9$ $[M+K]^+$: 593.2159), 577.2412 (18, calcd. for $C_{31}H_{38}NaO_9$ $[M+Na]^+$: 577.2414, 572.2865 (100, calcd. for $C_{31}H_{42}NO_9$ $[M+NH_4]^+$: 572.2860).

4.64. Methyl 2,3,6-*O*-tri-(4-methoxyphenylmethyl)-β-D-galactopyranoside (iii-19b)

In the similar manner as described in the Section 4.63, **iii-18b** (187 mg, 338 μmol) was treated with the finely powdered molecular sieves (60.0 mg), boran trimethylamine complex (157 mg, 2.15 mmol) and $AlCl_3$ (277 mg, 2.07 mmol) in THF (4.0 ml) to give **iii-19b** (125 mg, 66%) as caramel after work up. $[\alpha]_D^{23}$ +5.4 (*c* 0.97, $CHCl_3$); IR (film) 3490, 2910, 2835, 1610, 1510, 1460, 1250, 1095

cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.50 (1H, d, *J* = 1.7 Hz, C4O*H*), 3.44 (1H, dd, *J* = 3.3, 9.4 Hz,. C3*H*), 3.51 (1H, brdd, *J* = 5.9, 6.1 Hz, C5*H*), 3.55 (3H, C1OCH_3), 3.58 (1H, dd, *J* = 7.8, 9.4 Hz, C2*H*), 3.69 (1H, dd, *J* = 5.9, 9.9 Hz, C6*H*H), 3.76 (1H, dd, *J* = 6.1, 9.9 Hz, C6*H*H), 3.78 (9H, s, ArOCH_3 × 3), 3.96 (1H, brd, *J* = 3.3 Hz, C4*H*), 4.24 (1H, d, *J* = 7.8 Hz, C1*H*), 4.50, 4.62 (each 2H, s, ArCH_2O × 2), 4.63, 4.79 (each 1H, d, *J* = 10.6 Hz, ArCH_2O), 6.82-6.90 (6H, *aromatic protons*), 7.21-7.30 (6H, *aromatic protons*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.19 (ArOCH_3 × 3), 56.85 (C1OCH_3), 66.81 (*C*4), 66.86 (*C*6), 71.98 (ArCH_2O), 73.11 (*C*5), 73.30, 74.70 (each ArCH_2O), 78.64 (*C*2), 80.18 (*C*3), 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 $C_{31}H_{38}KO_9$ $[M+K]^+$: 593.2153), 577.2412 (16, calcd. for $C_{31}H_{38}NaO_9$ $[M+Na]^+$: 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-α-D-galactopyranoside (iii-20a)

Trifluoromethanesulfonic anhydride (259 mg, 921 μmol) was added to a mixture of **iii-19a** (335 mg, 604 μmol) and pyridine (145 mg, 1.83 μmol) in CH_2Cl_2 (2.0 ml) at 0 °C. After 20 min, the mixture was poured into H_2O (30 ml), and the aqueous layer was extracted with EtOAc (30 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 = 20:80) to give **iii-20a** (334 mg, 80 %) as an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 3.34 (3H, s, C1OCH_3), 3.53 (2H, m, C6H_2), 3.72 (1H, dd, *J* = 3.5, 10.0 Hz, C2*H*), 3.79 (9H, s, ArOCH_3 × 3), 3.93 (1H, dd, *J* =

2.6, 10.0 H, C3*H*), 4.02 (1H, brt, *J* = 4.0 Hz, C5*H*), 4.37, 4.51 (each 1H, d, *J* = 11.1 Hz, ArCH_2O), 4.54 (1H, d, *J* = 3.5 Hz, C1*H*), 4.56 (1H, d, *J* = 11.0 Hz, ArC*H*HO), 4.57, 4.74 (each 1H, d, *J* = 11.4 Hz, ArCH_2O), 4.77 (1H, d, *J* = 11.0 Hz, ArC*H*HO), 5.35 (1H, brd, *J* = 2.6 Hz, C4*H*), 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 CH_2Cl_2 (1.5 ml) to give **iii-20b** (194 mg, 84 %) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50-3.56 (2H, C2*H*, C3*H*), 3.54 (3H, s, C1OCH_3), 3.59 (1H, dd, *J* = 4.5, 10.8 Hz, C6*H*H), 3.65-3.72 (2H, C5*H*, C6*H*H), 3.78, 3.796, 3.784 (each 3H, s, ArOCH_3), 4.26, d, J = 7.1 Hz, C1*H*), 4.36 (1H, d, *J* = 11.0 Hz, ArC*H*HO), 4.51 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.56 (1H, d, *J* = 11.0 Hz, ArC*H*HO), 4.64, 4.75 (each 1H, d, *J* = 10.4 Hz, ArCH_2O), 4.78 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 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-$\Delta^{5,5a}$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 CH_2Cl_2 (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 NH_4Cl 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 $MgSO_4$, 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 H_2O (15 ml) and thw aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine (20 ml), dried over $MgSO_4$, 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. $[\alpha]_D^{23}$ -15 (*c* 0.68, $CHCl_3$); IR (film) 2900, 1610, 1460, 1250, 1070, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.86 (1H, t, *J* = 11.0 Hz, C4*H*), 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, C1OCH_3), 3.47-3.56 (7H, C2*H*, C1'*H*, C2'*H*, C3"*H*, C4"*H*, C6"*H*H), 3.59 (1H, dd, *J* = 1.6, 10.6 Hz, C6*H*H), 3.63 (2H, C3H, C6"*H*H), 3.65 '3H, s, ArOCH_3), 3.68 (1H, C5*H*), 3.69, 3.708, 3.711, 3.73, 3.75, 3.785, 3.786, 3.79, 3.792, 3.793 (each 3H, s, ArOCH_3), 3.97 (1H, d, *J* = 3.5, 10.6 Hz, C6*H*H), 4.08, 4.25 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.26 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.34 (1H, brd, *J* = 11.2 Hz, C6'*H*H), 4.34 (1H, d, *J* = 11.4 Hz, ArC*H*HO), 4.37, 4.40 (each 1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.50 (1H, brd, *J* = 6.9 Hz, C4'*H*), 4.50 (1H, d, *J* = 10.3 Hz, ArC*H*HO), 4.55 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.56 (1H, d, *J* = 3.7 Hz, C1*H*), 4.58 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.66 (1H, d, *J* = 11.2 Hz, ArC*H*HO), 4.67 (1H, d, *J* = 7.8 Hz, C1"*H*), 4.698 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.700 (1H, d, *J* = 10.4 Hz ArC*H*HO), 4.71 (1H, d, *J* = 11.8 Hz, ArC*H*HO), 4.75 (1H, d, *J* = 10.7 Hz, ArC*H*HO), 4.77 (1H, d, *J* = 10.3 Hz, ArC*H*HO), 4.82 (1H, d, *J* = 10.5 Hz,

ArC*H*HO), 4.85 (2H, s, ArCH_2O), 4.88 (1H, d, *J* = 11.2 Hz, ArC*H*HO), 5.90 (1H, brs, C5'a*H*), 6.70-6.84 (20H, *aromatic protons*), 7.06-7.32 (20H. *aromatic protons*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 48.33 (*C*1'), 49.77 (*C*4), 55.05, 55.12, 55.16, 55.16, 55.16, 55.17, 55.21, 55.24, 55.25, 55.25, 55.13 (O*C*H$_3$), 68.70 (*C*6"), 68.96 (*C*6), 70.37 (*C*6'), 71.13 (Ar*C*H$_2$O), 71.85 (*C*5), 72.62, 72.84, 72.96, 73.78, 74.21, 74.42, 74.47 (Ar*C*H$_2$O), 74.88 (*C*5"), 75.22 (Ar*C*H$_2$O), 75.95, 76.01 (Ar*C*H$_2$O, *C*4'), 77.82, 79.35, 79.96, 80.56, 84.55 (*C*2, *C*3, *C*2', *C*3", *C*4"), 81.71 (*C*3'), 82.62 (*C*2"), 98.46 (*C*1), 103.23 (*C*1"), 113.40, 113.46, 113.52, 113.63, 113.63, 113.80, 113.66, 113.70, 113.72, 113.74 (*aromatic carbons*), 129.08 (*C*5'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 (*C*5'), 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 $C_{100}H_{114}O_{24}SK$ $[M+K]^+$: 1769.7058), 1753.7450 (31, calcd. for $C_{100}H_{114}O_{24}SNa$ $[M+Na]^+$: 1753.7318), 1748.7835 (100, calcd. for $C_{104}H_{115}O_{24}SN$ $[M+NH_4]^+$ 1748.7765). 1731.7600 (95, calcd. for $C_{100}H_{115}O_{24}S$ $[M+H]^+$ 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-$\Delta^{5,5a}$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.

$[\alpha]_D^{23}$ -2.40 (*c* 1.20, $CHCl_3$); IR (film) 2910, 1610, 1460, 1250, 1070, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 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, C3*H*), 3.36 (1H, dd, *J* = 7.5, 8.5 Hz, C2*H*), 3.40 (1H, ddd, *J* = 1.8, 4.2, 10.7 Hz, C5*H*), 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*H), 3.54 (1H, m, C6'*H*H), 3.55 (3H, s, OCH_3), 3.58 (1H, m, C1'*H*), 3.63 (1H, dd, *J* = 1.5, 10.6 Hz, C6"*H*H), 3.681, 3.696, 3.706, 3.709, 3.73, 3.75, 3.782, 3.784, 3.787, 3.792 (each 3H, s, $ArOCH_3$), 3.80 (1H, C6*H*H), 3.81 (1H, dd, *J* = 5.5, 7.9 Hz, C3'*H*), 3.87 (1H, dd, *J* = 4.2, 10.5 Hz, C6*H*H), 4.09 (1H, d, *J* = 11.2 Hz, ArC*H*HO), 4.22 (1H, d, *J* = 7.5 Hz, C1*H*), 4.25 (1H, d, *J* = 11.2 Hz, ArC*H*HO), 4.31 (1H, brd, *J* = 11.5 Hz, C6'*H*H), 4.31 (1H, d, *J* = 11.5 Hz, ArC*H*HO), 4.38 (2H, s, $ArCH_2O$), 4.38 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.42, 4.47 (each 1H, d, *J* = 10.4 Hz, $ArCH_2O$), 4.48 (1H, brd, *J* = 5.5 Hz, C4'*H*), 4.56 (1H, d, *J* = 11.6 Hz, ArC*H*HO), 4.62 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.64 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 4.65 (1H, d, *J* = 7.8 Hz, C1'*H*), 4.69 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.70 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.73 (1H, d, *J* = 10.6 Hz, ArC*H*HO), 4.75 (1H, d, *J* = 10.4 Hz, ArC*H*HO), 4.82 (2H, s, $ArCH_2O$), 4.82 (1H, d, *J* = 10.5 Hz, ArC*H*HO), 4.83 (1H, d, J = 10.4 Hz, ArC*H*HO), 4.87 (1H, d, *J* = 11.3 Hz, ArC*H*HO), 5.87 (1H, brs, C5'a*H*), 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)*;^{13}C NMR (125 MHz, $CDCl_3$) δ 48.10 (*C*1'), 49.82 (*C*4), 55.09, 55.14 (each $ArOCH_3$), 55.15 ($ArOCH_3$ × 3), 55.16, 55.20 (each $ArOCH_3$), 55.24 ($ArOCH_3$ × 2), 55.25 ($ArOCH_3$), 56.95 ($C1OCH_3$), 68.70 (*C*6"), 69.24 (*C*6), 70.34 (*C*6'), 71.15, 72.66, 72.83, 73.70, 79.97, 74.42 (each $ArCH_2O$), 74.45 ($ArCH_2O$ × 2), 74.84 (C5"), 75.21, 75.80 (each $ArCH_2O$), 75.94 (*C*4'), 76.83

(*C*5), 77.81 (*C*4"), 77.84 (*C*2'), 81.45 (*C*3'), 82.54 (*C*2"), 82.70 (*C*3), 83.04 (*C*2), 84.55 (*C*3"), 103.28 (*C*1"), 104.53 (*C*1), 113.41, 113.50, 113.54, 113.62, 113.64, 113.64, 113.70, 113.72, 113.73, 113.73 (*aromatic carbons*), 128.72 (*C*5'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 (*C*5'), 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 $C_{100}H_{114}O_{24}SK$ $[M+K]^+$: 1769.7058), 1753.7411 (26, calcd. for $C_{100}H_{114}O_{24}SNa$ $[M+Na]^+$: 1753.7318), 1748.7764 (100, calcd. for $C_{104}H_{115}O_{24}SN$ $[M+NH_4]^+$ 1748.7765). 1731.7500 (96, calcd. for $C_{100}H_{115}O_{24}S$ $[M+H]^+$ 1731.7499).

4.69. Methyl β-D-glucopyranosyl-(1→4)-1-thio-β-$\Delta^{5,5a}$carbaglucopyranosyl-(1→4)-α-D-glucopyranoside (iii-2a)

A suspension of **iii-22a** (130 mg, 75 μmol) in a mixture of CH_2Cl_2 (2.0 ml) and H_2O (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 × 3) and concentrated *in vacuo*. After dilution with small amount of H_2O (ca. 0.3 ml), the resulting solution was loaded on a ODS Sep-Pak® cartridge (5.0 g). After washing with MeOH:H_2O = 5:95, elution with MeOH:H_2O = 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 amorpous powder. $[\alpha]_D^{23}$ +2.5 (*c* 0.52, H_2O); ^1H NMR (500 MHz, D_2O) δ 2.60 (1H, t, *J* = 10.9 Hz, C4*H*), 3.20 (1H, dd, *J* = 8.0, 9.2 Hz, C2"*H*), 3.26 (3H, s, OCH_3), 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, C2*H*), 3.51 (1H, dd, J = 9.0, 10.0 Hz, C2'*H*), 3.54 (1H, dd, J = 9.6, 10.9 Hz, C3*H*), 3.59 (1H, dd, J = 7.6, 10.0 Hz, C3'*H*), 3.60 (1H, dd, J = 6.1, 12.3 Hz, C6"*H*H), 3.63 (1h, ddd, J = 2.2, 4.7, 10.9 Hz, C5*H*), 3.79 (1H, dd, J = 2.1, 12.3 Hz, C6"*H*H), 3.93 (1H, dd, J = 2.2, 12.1 Hz, C6*H*H), 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, C1*H*), 5.71 (1H, brs, C5'a*H*); ^{13}C NMR (125 MHz, D_2O) 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 $C_{20}H_{34}O_{14}SK$ $[M+K]^+$: 569.1306), 553.1570 (100, calcd. for $C_{20}H_{34}O_{14}SNa$ $[M+Na]^+$: 553.1567), 531.1754 (17, calcd. for $C_{20}H_{35}O_{14}S$ $[M+H]^+$ 531.1754).

4.70. Methyl β-D-glucopyranosyl-(1→4)-1-thio-β-$\Delta^{5,5a}$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), CH_2Cl_2 (2.0 ml), and H_2O (2.0 ml). The following workup gave **iii-2b** (32 mg, 75%) as white amorpous powder. $[\alpha]_D^{23}$ -81.2 (*c* 0.65, H_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (1H, t, J = 10.8 Hz, C4*H*), 3.15 (1H, dd, J = 8.0, 9.0 Hz, C2*H*), 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, C3*H*), 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, OCH_3), 3.47 (1H, ddd, J = 2.1, 5.5, 10.8 Hz, C5*H*), 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, C6*H*H), 3.80 (1H, dd, J = 2.2, 12.5 Hz, C6*H*H), 3.83 (1H, dd, J = 5.3, 12.3 Hz, C6*H*H), 4.03 (1H, dd, J = brd, J = 13.5 Hz,

C6'*H*H), 4.05 (1H, dd, *J* = 2.1, 12.3 Hz, C6*H*H), 4.17 (1H, brd, *J* = 13.5 Hz, C6'*H*H), 4.23 (1H, d, *J* = 8.0 Hz, C1*H*), 4.28 (1H, 1H, brd, *J* = 7.4 Hz, C4'*H*), 4.61 (1H, d, *J* = 8.0 Hz, C1"*H*), 5.71 (1H, brs, C5'a*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 48.38, 48.81, 57.27, 60.80, 61.55, 61.71, 69.96, 73.60, 73.69, 74.29, 74.74, 75.05, 75.88, 76.28, 76.58, 82.31, 103.20, 103.30, 126.74, 136.51; ESIMS (%, rel. int.) *m/z* 569.1294 (10, calcd. for $C_{20}H_{34}O_{14}SK$ $[M+K]^+$: 569.1306), 553.1552 (100, calcd. for $C_{20}H_{34}O_{14}SNa$ $[M+Na]^+$: 553.1567), 531.1733 (17, calcd. for $C_{20}H_{35}O_{14}S$ $[M+H]^+$ 531.1754).

4.71. Methyl 2,3,4-6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-$\Delta^{5,5a}$carbaglucopyranosyl-(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%). $[\alpha]_D^{23}$ -52 (*c* 0.56, $CDCl_3$); IR (film) 2940, 1750, 1225, 1040 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 1.66, 1.67, 1.69, 1.77, 1.79, 1.82, 1.84, 1.89, 1.93, 1.97 (each 3H, s, OCOC*H*$_3$), 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, C1OC*H*$_3$), 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"*H*H), 4.31 (1H, dd, *J* = 4.5, 12.0 C6*H*H), 4.37 (1H, dd, *J* = 4.6, 12.4, C6"*H*H), 4.54 (1H, d, *J* = 8.1 Hz, C1"*H*), 4.58 (2H, brd, *J* = 7.8 Hz, C6'*H*$_2$), 4.63 (1H, dd, *J* = 1.9, 12.4 Hz, C6*H*H), 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*); ^{13}C NMR (125 MHz, C_6D_6) δ 20.08, 20.13, 20.28, 20.32, 20.35, 20.36, 20.41, 20.45 (each CO*C*H$_3$), 20.54 (CO*C*H$_3$ × 2), 45.24 (*C*1'), 48.64 (*C*4), 56.21 (C1O*C*H$_3$), 61.59 (*C*6"), 63.65 (*C*6), 63.97 (*C*6'), 68.29 (*C*4"), 70.00 (*C*3'), 70.61 (*C*'), 72.14 (*C*2 or *C*2'), 72.49 (*C*5"), 73.13 (*C*2 or *C*2'), 73.53 (*C*3"), 73.60 (*C*5), 74.35 (*C*3), 76.70 (*C*4'), 101.55 (*C*1), 102.35 (*C*1"), 127.10 (*C*5'a), 131.50 (*C*5'), 169.07, 169.08, 169.18, 169.53, 169.57, 169.76, 169.90 (each O*C*OCH$_3$), 170.10 (O*C*OCH$_3$ × 2); ESIMS (%, rel. int.) *m/z* 989.2341 (33, calcd. for $C_{40}H_{54}O_{24}SK$ $[M+K]^+$: 989.2362), 973.2610 (48, calcd. for $C_{40}H_{54}O_{24}SNa$ $[M+Na]^+$: 973.2610), 968.3055 (100, calcd. for $C_{40}H_{58}O_{24}SN$ $[M+NH_4]^+$ 968.3055).

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