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A Facile Synthesis of Sialylated Polylactosamine Glycans from Lactose via Lafont Intermediate

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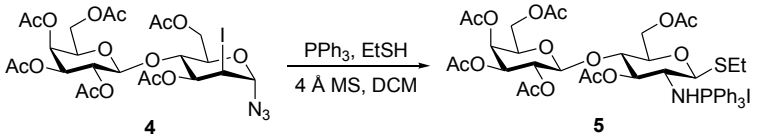
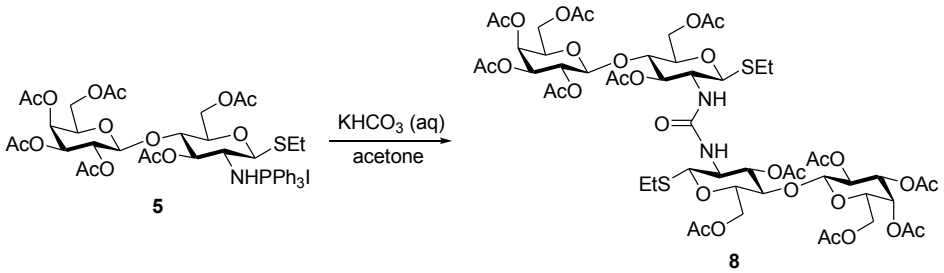
General Remarks: All reagents and solvents were dried prior to use according to standard methods. Commercial reagents were used without further purification, unless otherwise stated. ^{1}H NMR spectra were recorded on Advance DRX Bruker-300, 400, 500 and 600 MHz spectrometers at 25 ^{o}C. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in deuterated chloroform. ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High-resolution mass spectrometry was performed on a Bruker APEX IVor ABI 4800 MALDI TOF/TOF^{TM}. All reactions were performed in flame-dried modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper or rubber septa under a positive pressure of argon and away from light. Analytical TLC was performed on silica gel 60-F254 precoated on aluminium plates and glass plate (E. Merck), with detection by fluorescence and/or or by staining with acidic ceric ammonium molybdate. Column chromatography was performed employing Silica Gel 200-300 mesh.



4 **5**

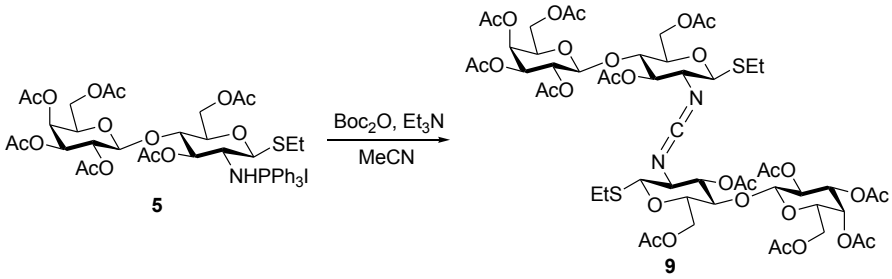
Ethyl [3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-aminotriphenylphosphonium-2-deoxy-1-thio-*β*-D-glucopyranoside] iodide (5)

Compound **4** (7.0 g, 9.60 mmol) and ethanethiol (831 μL, 11.50 mmol) and 4 Å MS were dissolved in dry 100 mL CH_2Cl_2 under argon. The reaction mixture was stirred at 0 ^{o}C for 30 min. Then a solution of PPh_3 (2.6 g 10.1 mmol) in CH_2Cl_2 (5 mL) was added dropwise**.** The reaction was warmed gradually to room temperature and further stirred for 12 h. The molecular sieves was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to give the compound **5** (9.40 g, 95%) as yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.88 (m, 7H), 7.76–7.78 (m, 3H), 7.64–7.70 (m, 6H), 5.68 (d, 1H, *J* = 10.1 Hz), 5.77 (t, 1H, *J* = 9.4 Hz), 5.33 (d, 1H, *J* = 3.1 Hz), 5.04 (dd, 1H, *J* = 7.9, 10.3 Hz), 4.93 (dd, 1H, *J* = 3.4, 10.4 Hz), 4.51 (d, 1H, *J* = 7.8 Hz), 4.41 (d, 1H, *J* =10.9 Hz), 4.04–4.12 (m, 2H), 3.95–4.00 (m, 2H), 3.88 (t, 1H, *J* = 6.8 Hz), 3.61 (t, 1H, *J* = 9.7 Hz), 3.08 (bs, 1H), 2.76–2.82 (m, 2H), 2.12 (s, 3H), 2.060 (s, 3H), 2.055 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.39 (s, 3H), 1.33 (t, 3H, *J* = 7.4 Hz). The spectroscopic data was identical with the previous report. [1]

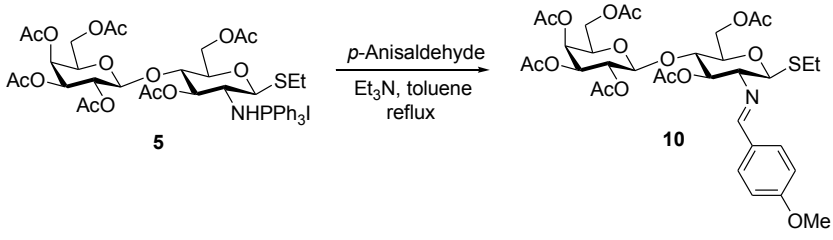


5 **8**

To the solution of compound **5** (500 mg, 0.49 mmol) in acetone (10 mL), was added $KHCO_3$ aqueous (1 mmol/mL, 0.6 mL). The reaction was stirred at room temperature for 48 h. Then the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 3) to give the compound **8** (143 mg, 45%) as foam**.** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.35 (d, 2H, *J* = 3.1 Hz), 5.10 (dd, 2H, *J* = 7.9, 10.4 Hz), 4.99 (t, 2H, *J* = 9.5 Hz), 4.96 (dd, 2H, *J* = 3.5, 10.5 Hz), 4.71 (d, 2H, *J* = 6.9 Hz), 4.50 (d, 2H, *J* = 7.9 Hz), 4.47 (dd, 2H, *J* = 1.9, 11.9 Hz), 4.37 (d, 2H, *J* = 10.1 Hz), 4.07–4.13 (m, 6H), 4.01–4.04 (m, 2H), 3.87 (t, 2H, *J* = 6.8 Hz), 3.77 (t, 2H, *J* = 9.2 Hz), 3.58–3.60 (m, 2H), 2.67–2.74 (m, 4H), 2.15 (s, 6H), 2.12 (s, 6H), 2.10 (s, 6H), 2.06 (s, 6H), 2.05 (s, 6H), 1.97 (s, 6H), 1.24 (t, 6H, *J* = 7.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.30, 170.39, 170.34, 170.14, 170.06, 169.30, 155.98, 101.10, 84.96, 76.47, 76.24, 74.42, 70.89, 70.59, 69.08, 66.54, 62.42, 60.67, 53.48, 23.78, 21.15, 20.82, 20.64, 20.62, 20.61, 20.50, 14.81. HRMS (ESI) Calcd for $C_{53}H_{76}N_2O_{31}NaS_2$ $[M+Na]^+$: 1323.3776, found: 1323.3762.

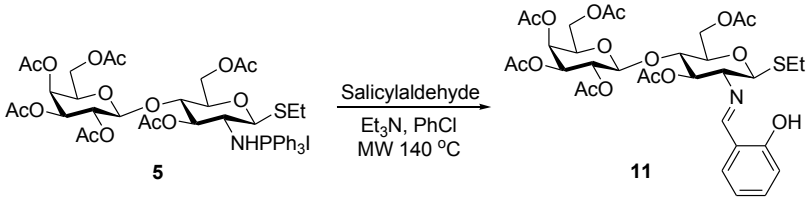


To the solution of compound **5** (334 mg, 0.33 mmol) in acetonitrile (5 mL), Boc_2O (89.6 μL, 0.39 mmol) and Et_3N (68.0 μL, 0.49 mmol) were added sequentially. The reaction mixture was stirred at room temperature for 24 h. Then the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate= 1 : 2) to give the compound **9** (110 mg, 52 %) as foam**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.36 (d, 2H, *J* = 3.5 Hz), 5.12 (t, 2H, *J* = 9.2 Hz), 5.09 (dd, 2H, *J* = 7.9, 10.4 Hz), 4.95 (dd, 2H, *J* = 3.5, 10.4 Hz), 4.45–4.48 (m, 6H), 4.17 (dd, 2H, *J* = 6.2, 11.1 Hz), 4.06–4.13 (m, 4H), 3.87 (t, 2H, *J* = 7.1 Hz), 3.64–3.71 (m, 4H), 3.45 (t, 2H, *J* = 9.9 Hz), 2.69–2.77 (m, 4H), 2.16 (s, 6H), 2.12 (s, 6H), 2.11 (s, 6H), 2.06 (s, 6H), 2.04 (s, 6H), 1.96 (s, 6H), 1.31 (t, 6 H, *J* = 7.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.30, 170.26, 170.13, 170.02, 169.66, 168.94, 138.34, 100.86, 84.71, 76.72, 76.05, 74.81, 71.03, 70.67, 69.10, 66.64, 62.38, 60.78, 59.86, 24.53, 21.05, 20.80, 20.59, 20.46, 15.00. HRMS (ESI) Calcd for $C_{53}H_{74}N_2O_{30}NaS_2$ $[M+Na]^+$: 1305.3660, found: 1305.3660.



Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*p*-methoxylbenzylideneamino-1-thio-*β*-D-glucopyranoside (10)

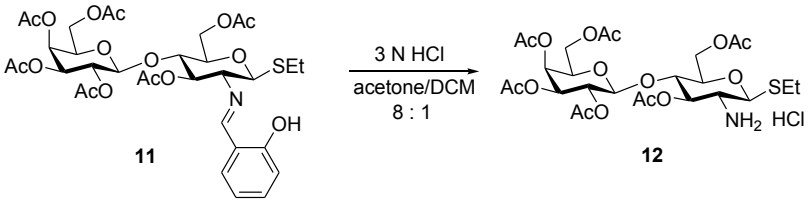
Et_3N (20 μL, 0.15 mmol) was added to a mixture of compound **5** (30 mg, 0.029 mmol) and *p*-anisaldehyde (35.2 μL, 0.29 mmol) in toluene (5 mL) in a round bottom flask. Then the mixture was refluxed for 6 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to give compound **10** (4 mg, 18 %) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 7.66 (d, 2H, *J* = 8.7 Hz), 6.91 (d, 2H, *J* = 8.7 Hz), 5.38 (t, 1H, *J* = 8.9 Hz), 5.35 (d, 1H, *J* = 3.3 Hz), 5.12 (dd, 1H, *J* = 7.9, 10.4 Hz), 4.95 (dd, 1H, *J* = 3.4, 10.4 Hz), 4.84 (d, 1H, *J* = 9.8 Hz), 4.48–4.52 (m, 2H), 4.14–4.20 (m, 2H), 4.04 (d, 1H, *J* = 7.5, 11.0 Hz), 3.87–3.90 (m, 1H), 3.84 (s, 3H), 3.75–3.81 (m, 2H), 3.24 (t, 1H, *J* = 9.6 Hz), 2.64–2.73 (m, 2H), 2.14 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H), 1.88 (s, 3H), 1.25 (t, 1H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.49, 170.33, 170.22, 170.11, 169.03, 168.99, 163.24, 162.16, 130.25, 128.43, 114.06, 100.85, 84.54, 77.20, 76.43, 74.82, 73.94, 71.11, 70.60, 69.15, 66.62, 62.88, 60.83, 55.39, 25.03, 20.90, 20.74, 20.65, 20.52, 14.97. HRMS (ESI) Calcd for $C_{34}H_{45}NO_{16}SNa$ $[M+Na]^+$: 778.2357, found: 778.2339. $C_{34}H_{46}NO_{16}SNa$ $[M+H]^+$: 756.2532, found: 756.2530.



Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*o*-hydroxylbenzylideneamino -1-thio-*β*-D-glucopyranoside (11)

Et_3N (2 mL) was added to a mixture of compound **5** (800 mg, 0.78 mmol) and salicylaldehyde (1 mL) in chlorobenzene (2 mL) in a Microwave tube (the scale was limited by the size of the microwave setup). Then the reaction was irradiated with 150 W of microwave energy at 140 °C for 30 min. The mixture was then transferred into a round bottom flask and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to give compound **11** (460 mg, 80 %) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.18 (s, 1H), 8.19 (s, 1H), 7.27 (td, 1H, *J* = 1.6, 8.8 Hz), 7.19 (dd, 1H, *J* = 2.0, 7.6 Hz), 6.90 (d, 1H, *J* = 8.3 Hz), 6.82 (td, 1H, *J* = 0.9, 5.7 Hz), 5.31 (t, 1H, *J* = 9.1 Hz), 5.29 (d, 1H, *J* = 3.0 Hz), 5.04 (dd, 1H, *J* = 3.5, 10.4 Hz), 4.89 (dd, 1H, *J* = 7.8, 10.4 Hz), 4.69 (d, 1H, *J* = 9.8 Hz), 4.42 (d, 1H, *J* = 7.8 Hz), 4.41–4.45 (m, 1H), 4.08–4.13 (m, 2H), 3.98 (dd, 1H, *J* = 7.6, 11.0 Hz) 3.79–3.82 (m, 1H), 3.68–3.77 (m, 2H), 3.21 (t, 1H, *J* = 9.6 Hz), 2.54–2.68 (m, 2H), 2.08 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H), 1.87(s, 3H), 1.19 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.37, 170.30, 170.15, 170.07, 169.02, 168.94, 167.77, 160.97, 133.11, 131.86, 118.82, 118.20, 117.32, 100.94, 84.46, 76.91, 75.90, 73.98, 73.20, 70.98, 70.65, 69.08, 66.57, 62.58, 60.76, 25.22, 20.85, 20.68, 20.63, 20.59, 20.48, 14.93. HRMS (ESI)

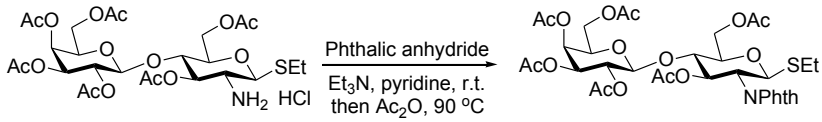
Calcd for $C_{33}H_{43}NO_{16}NaS$ $[M+Na]^+$: 764.2200, found: 764.2192.



11 12

Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-amino-1-thio-*β*-D-glucopyranoside hydrochloride (12)

Aqueous 3 N HCl (3.2 mL, 9.6 mmol) was added to a solution of compound **11** (7.0 g, 9.4 mmol) in a mixture of acetone and DCM (8 : 1, 15 mL). After being stirred at room temperature for 1 h and the material was completely consumed according to TLC analysis, the solution was diluted with toluene (10 mL). The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 20 : 1) to give compound **12** (4.50 g, 72%) as foam. ^{1}H NMR (400 MHz, CD_3OD): δ = 5.40 (d, 1H, *J* = 3.3 Hz), 5.22 (t, 1H, *J* = 10.0 Hz), 5.15 (dd, 1H, *J* = 3.4, 10.4 Hz), 5.03 (dd, 1H, *J* = 7.8, 10.1 Hz), 4.76 (dd, 1H, *J* = 3.8, 10.3 Hz), 4.72 (d, 1H, *J* = 7.9 Hz), 4.57 (d, 1H, *J* = 12.0 Hz), 4.15–4.21 (m, 4H), 3.90 (t, 1H, *J* = 9.6 Hz), 3.79–3.83 (m, 1H), 3.41 (t, 1H, *J* = 10.2 Hz), 2.76–2.84 (m, 2H), 2.20 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.08 (s, 6H), 1.96 (s, 3H), 1.35 (t, 3H, *J* =7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.33, 170.25, 170.00, 169.01, 100.74, 82.44, 75.78, 71.27, 70.94, 70.84, 68.92, 66.63, 62.01, 60.65, 54.61, 25.58, 22.01, 20.81, 20.62, 20.57, 20.45, 15.27. HRMS (ESI) Calcd for $C_{26}H_{40}NO_{15}S^+$ $[M-Cl]^+$: 638.2113, found: 638.2152.

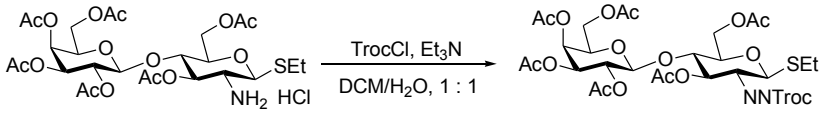


12 13

Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-1-thio-*β*-D-glucopyranoside (13)

Et_3N (247 μL, 1.85 mmol) was added to a solution of **12** (954 mg, 1.42 mmol) in pyridine (30 mL). After being stirred for 30 min, phthalic anhydride (235 mg, 1.59 mmol) was added in one portion. After 2 h, a second portion of phthalic anhydride (235 mg, 1.59 mmol) and Et_3N (247 μL, 1.85 mmol) were added, and the mixture was stirred for another 2 h. The reaction was quickly moved to an oil bath at 90 °C and Ac_2O (10 mL) was added. The mixture was stirred for another 30 min at this temperature and the solution was concentrated *in vacuo*. The residue was dissolved in DCM (100 mL) and was washed with 1 N HCl (aq.) (×3), water, $NaHCO_3$ (aq.), and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to afford compound **13** (960 mg, 86%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.81 (m, 2H), 7.64–7.70 (m, 2H), 5.71 (dd, 1H, *J* = 8.1, 10.1 Hz), 5.42 (d, 1H, *J* = 10.6 Hz), 5.27 (dd, 1H, *J* = 0.8, 3.3 Hz), 5.06 (dd, 1H, *J* = 7.9, 10.4Hz), 4.89 (dd, 1H, *J* = 3.4, 10.4 Hz), 4.42–4.48 (m,

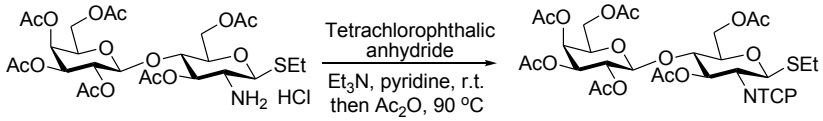
2H), 4.21 (t, 1H, *J* = 10.4 Hz), 4.08 (dd, 1H, *J* = 4.9, 11.9 Hz), 3.95–4.06 (m, 2H), 3.74–3.82 (m, 3H), 2.50–2.65 (m, 2H), 2.07 (s, 6H), 2.00 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H), 1.83 (s, 3H), 1.14 (t, 3H, *J* = 7.4 Hz). The spectroscopic data was identical with the previous report.[2]



12 **14**

Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-Troc-1-thio-*β*-D-glucopyranoside (14)

TrocCl (216 μL, 15.7 mmol) was added to a solution of **12** (100 mg, 0.16 mmol) and Et_3N (100 μL, 0.72 mmol) in DCM/H_2O (1 : 1, 10 mL). The reaction was stirred at r.t. overnight and diluted with DCM (50 mL). The mixture was washed with $NaHCO_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to afford compound **14** (93 mg, 77%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.36 (d, 1H, *J* = 3.2 Hz), 5.21 (d, 1H, *J* = 9.6 Hz), 5.09-5.14 (m, 2H), 4.96 (dd, 1H, *J* = 3.2, 10.3 Hz), 4.82 (d, 1H, *J* = 12.0 Hz), 4.67 (d, 1H, *J* = 12.4 Hz), 4.45–4.51 (m, 3H), 4.06–4.15 (m, 3H), 3.88 (t, 1H, *J* = 6.8 Hz), 3.78 (t, 1H, *J* = 9.5 Hz), 3.60–3.63 (m, 1H), 2.67–2.74 (m, 2H), 2.15 (s, 3H), 2.11 (s, 3H), 2.07 (s, 6H), 2.07 (s,3H), 1.97 (s, 3H), 1.26 (t, 1H, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6, 170.4, 170.3, 170.09, 170.01, 169.10, 154.34, 101.02, 84.59, 76.57, 76.18, 74.43, 73.60, 70.84, 70.61, 69.03, 66.55, 62.27, 60.77, 55.09, 24.35, 20.81, 20.61, 20.57, 20.46, 14.81. HRMS (ESI) Calcd for $C_{29}H_{40}Cl_3NO_{17}NaS$ $[M+Na]^+$: 834.0975, found: 834.0972.

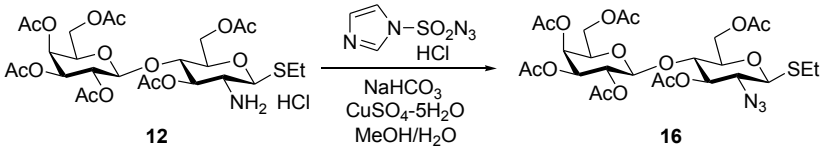


12 **15**

Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-tetrachlorophthalimido-1-thio-*β*-D-glucopyranoside (15)

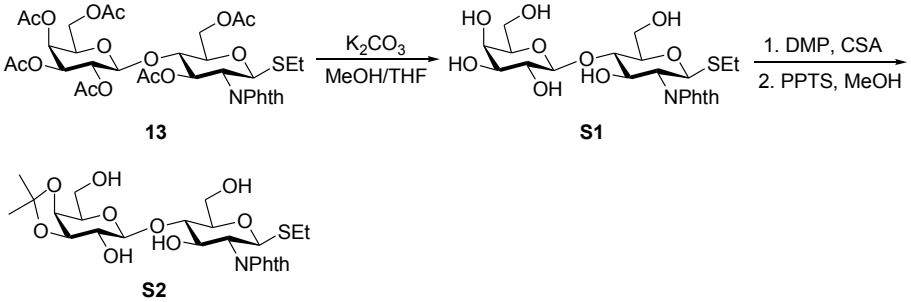
Et_3N (43 μL, 0.31 mmol) was added to the solution of **12** (100 mg, 0.16 mmol) in pyridine (2 mL). After being stirred for 30 min, tetrachlorophthalic anhydride (64.7 mg, 0.24 mmol) was added in one portion. After 2 h, a second portion of tetrachlorophthalic anhydride (64.7 mg, 0.24 mmol) and Et_3N (43 μL, 0.31 mmol) was added, and the mixture was stirred for another 2 h. The reaction was quickly moved to an oil bath at 90 °C and Ac_2O (1 mL) was added. The mixture was stirred for another 30 min at this temperature and the solution was concentrated *in vacuo*. The residue was dissolved in DCM (30 mL) and was washed with 1 N HCl (aq.) (×3), water, $NaHCO_3$ (aq.), and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to afford compound **15** (115 mg, 85%) as foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.70 (dd, 1H, *J* = 8.4, 9.9 Hz), 5.44 (d, 1H, *J* = 10.7 Hz), 5.34 (d, 1H, *J* = 3.1 Hz), 5.12

(dd, 1H, *J* = 7.8, 10.4 Hz), 4.96 (dd, 1H, *J* = 3.3, 10.4 Hz), 4.48–4.55 (m, 2H), 4.26 (t, 1H, *J* = 10.3), 4.01–4.17 (m, 3H), 3.84–3.91 (m, 2H), 3.76–3.81 (m, 1H), 2.57–2.74 (m, 2H), 2.144 (s, 3H), 2.138 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.23 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.33, 170.28, 170.23, 170.08, 170.03, 169.06, 163.01, 162.60, 140.75, 140.41, 130.09, 129.90, 127.12, 126.79, 101.01, 80.78, 76.60, 76.58, 72.03, 70.86, 70.59, 69.01, 66.49, 62.40, 60.66, 54.67, 24.72, 20.81, 20.57, 20.55, 20.46, 14.92. HRMS (ESI) Calcd for $C_{34}H_{37}Cl_4NO_{17}NaS$ $[M+Na]^+$: 926.0429, found: 926.0435.



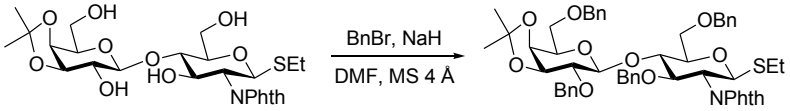
Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-azide-1-thio-*β*-D-glucopyranoside (16)

The compound **12** (100 mg, 0.16 mmol) was dissolved in the mixture of MeOH and H_2O (5 : 1, 10 mL). Then imidazole-1-sulfonyl azide hydrochloride (50 mg, 0.24 mmol), $NaHCO_3$ (200 mg, 2.38 mmol) and $CuSO_4$-$5H_2O$ (25 mg, 0.1 mmol) were added sequentially. The reaction was stirred at r.t. overnight and diluted with DCM (50 mL). The mixture was washed with water (×3) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to afford compound **16** (64 mg, 65%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.36 (dd, 1H, *J* = 0.8, 3.2 Hz), 5.06–5.12 (m, 2H), 4.95 (dd, 1H, *J* = 3.4, 10.4 Hz), 4.44–4.47 (m, 2H), 4.37 (d, 1H, *J* = 10.2 Hz), 4.18 (d, 1H, *J* = 6.3, 11.1 Hz), 4.06–4.11 (m, 2H), 3.88 (t, 1H, *J* = 6.3 Hz), 3.71 (t, 1H, *J* = 9.4 Hz), 3.57–3.61 (m, 1H), 3.41 (t, 1H, *J* = 10.0 Hz), 2.68–2.80 (m, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 2.11(s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.32 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.30, 170.28, 170.12, 170.05, 169.46, 168.94, 100.94, 84.33, 76.68, 75.89, 73.82, 70.93, 70.67, 68.99, 66.55, 63.93, 62.20, 60.80, 25.22, 20.83, 20.80, 20.61, 20.57, 20.47, 14.97. HRMS (ESI) Calcd for $C_{26}H_{37}Cl_4N_3O_{15}NaS$ $[M+Na]^+$: 686.1838, found: 686.1835.



Ethyl 4-*O*-(3:4-*O*-isopropylidene-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-1-thio-*β*-D-glucopyranoside (S2)

To a solution of compound **12** (1.32 g, 1.70 mmol) in the mixture of MeOH and THF (2 : 1, 30 mL), K_2CO_3 (80 mg) was added. The reaction was stirred for 1 h and the solution was neutralized with Amberlite HR-120 (H^+), filtered, and concentrated. The compound **S1** was used without further purification. Compound **S1** and camphorsulfonic acid (40 mg, 0.17 mmol) were dissolved in 2,2-dimethoxypropane (40 mL) and stirred at room temperature for 3 days until the reaction mixture became clear. The reaction was quenched by addition of triethylamine (1 mL), and the solvent was removed *in vacuo*. The residue was co-evaporated with toluene for three times in order to remove the trace amount of triethylamine. The residue was dissolved in 100 mL MeOH, then pyridinium *p*-toluenesulfonate (85 mg, 0.34 mmol) was added. The reaction was stirred until the TLC showed only one main product left (R_f = 0.3, *n*-hexane : ethyl acetate = 1 : 3). Then the reaction was quenched by addition of triethylamine (0.5 mL) and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to give compound **S2** (784 mg, 83%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.88 (m, 2H), 7.73–7.76 (m, 2H), 5.37 (d, 1H, *J* = 10.6 Hz), 4.56 (bs, 1H), 4.51 (t, 1H, *J* = 9.9 Hz), 4.46 (d, 1H, *J* = 8.0 Hz), 4.17–4.23 (m, 3H), 3.96–3.99 (m, 3H), 3.81–3.91 (m, 2H), 3,74 (t, 1H, *J* = 9.4 Hz), 3.57–3.66 (m, 2H), 3.54 (bs, 1H), 3.16 (bs, 1H), 2.90 (bs, 1H), 2.61–2.73 (m, 2H), 1.51 (s, 3H), 1.33 (s, 3H), 1.19 (t, 3H, *J* = 7.4 Hz). The spectroscopic data was identical with the previous report.[2]

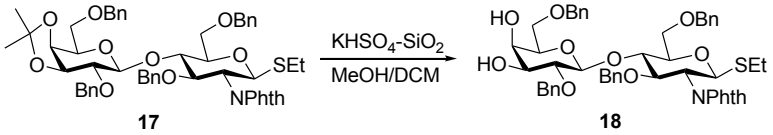


S2 **17**

Ethyl 3,6-*O*-di-benzyl-4-*O*-(3:4-*O*-isopropylidene 2,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-1-thio-*β*-D-glucopyranoside (17)

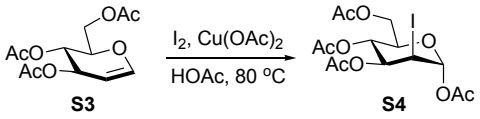
A solution of compound **S2** (580mg, 1.04 mmol) and activated powdered 4 Å molecular sieves in dry DMF (12 mL) was stirred at room temperature under an argon atmosphere for 30 min. Then the mixture was cooled to 0 ^{o}C and benzyl bromide (1.70 mL, 12.5 mmol) was added. After 10 min, NaH (60%, 251 mg, 6.27 mmol) was added portionwises. The reaction was further stirred for 3 h at this temperature and then was quenched by AcOH (0.5 mL). The reaction was diluted with DCM (200 mL) and solid was filtered off through a pad of Celite. The filtrate was washed with saturated NH_4Cl (aq.) (×3), $NaHCO_3$ (aq.) (×3), water and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 4 : 1) to afford compound **17** (620mg, 65%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, 1H, *J* = 6.5 Hz), 7.64–7.69 (m, 3H), 7.26–7.40 (m, 18H), 6.98–6.99 (m, 2H), 6.84–6.85 (m, 3H), 5.23 (d, 1H, *J* = 10.1 Hz), 4.82 (d, 2H, *J* = 12.1 Hz), 4.73 (d, 1H, *J* = 11.7 Hz), 4.59 (d, 1H, *J* = 11.9 Hz), 4.56 (d, 1H, *J* = 11.8 Hz), 4.38–4.47 (m, 4H), 4.24–4.35 (m, 2H), 4.02–4.09 (m, 3H), 3.90 (dd, 1H, *J* = 3.6, 11.0 Hz), 3.72–3.77 (m, 2H), 3,65–3,69 (m, 1H), 3.57–3.61 (m, 2H), 3.35 (t, 1H, *J* = 7.1 Hz), 2.57–2.70 (m,

2H), 1.37 (s, 3H), 1.33 (s, 3H), 1.17 (t, 3H, J = 7.4 Hz). The spectroscopic data was identical with the previous report.[3]



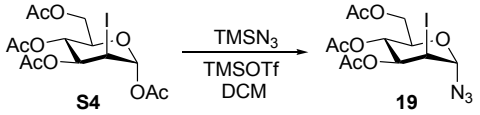
Ethyl 3,6-*O*-di-benzyl-4-*O*-(2,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-1-thio-*β*-D-glucopyranoside (18)

To a solution of compound **17** (1.20 g, 1.3 mmol) in the mixture of MeOH/DCM (1 : 1, 30 mL), $KHSO_4$-SiO_2 (100 mg) was added. After being stirred at room temperature for 4 h and the material was completely consumed according to TLC analysis, the solution was neutralized with Et_3N, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 2 : 1) to afford compound **18** (1.05 g, 92%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, 1H, J = 6.6 Hz), 7.62–7.71 (m, 3H), 7.26–7.38 (m, 18H), 6.99–7.01 (m, 2H), 6.83–6.84 (m, 3H), 5.24 (d, 1H, J = 10.1 Hz), 4.89 (d, 1H, J = 11.7 Hz), 4.86 (d, 1H, J = 12.6 Hz), 4.72 (d, 1H, J = 11.5 Hz), 4.62 (d, 1H, J = 12.0 Hz), 4.41–4.52 (m, 6H), 4.25–4.36 (m, 2H), 4.12 (t, 1H, J = 9.7 Hz), 3.95 (s, 1H), 3.89 (dd, 1H, J = 3.8, 11.0 Hz), 3.78 (d, 1H, J = 10.8 Hz), 3.66 (dd, 1H, J = 6.0, 10.1 Hz), 3.57–3.60 (m, 2H), 3.43–3.50 (m, 2H), 3.39 (t, 1H, J = 5.2 Hz), 2.55–2.72 (m, 2H), 1.18 (t, 3H, J = 7.4 Hz). The spectroscopic data was identical with the previous report.[3]



1,3,4,6-*O*-tetra-acetyl-2-deoxy-2-iodo-*α*-D-mannopyranose (S4)

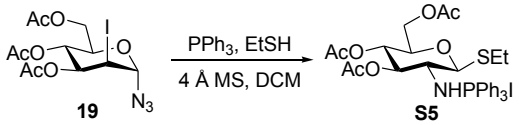
Glycal **S3** (1.00 g, 3.6 mmol), $Cu(OAc)_2$ (726 mg, 4.0 mmol), and I_2 (1.1 g, 4.3 mmol) were sequentially added into AcOH (60 mL). The mixture was stirred at 80 °C overnight under argon. The reaction was evaporated to dryness and the residue was diluted with DCM (300 mL). The organic layer was washed with $NaHCO_3$ (aq.), $Na_2S_2O_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 2 : 1) to afford compound **S4** (1.10 g, 67%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.39 (s, 1H), 5.46 (t, 1H, J = 9.6 Hz), 4.59 (dd, 1H, J = 4.4, 9.4 Hz), 4.53 (dd, 1H, J = 1.1, 4.1 Hz), 4.23 (dd, 1H, J = 4.4, 12.4 Hz), 4.10–4.18 (m, 2H), 2.17 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H). The spectroscopic data was identical with the previous report.[4]



3,4,6-*O*-tri-acetyl-2-deoxy-2-iodo-*α*-D-mannopyranosyl azide (19)

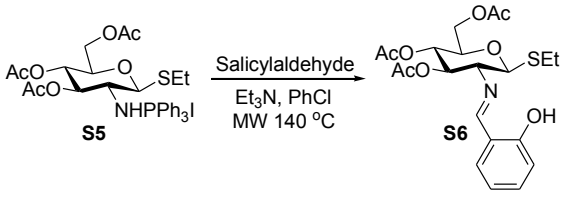
TMSOTf (94 μL, 0.52 mmol) was added to the solution of iodoacetate **S4** (1.10 g, 2.40 mmol) and

$TMSN_3$ (510 μL, 3.90 mmol) in dry DCM (20 mL) at 0 °C under argon. The reaction was gradually warmed to room temperature and stirred overnight. Then the mixture was diluted with DCM (300 mL). The organic layer was washed with $NaHCO_3$ (aq.) dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 3 : 1) to afford compound **19** (0.90 g, 82%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72 (s, 1H), 5.37 (t, 1H, *J* = 9.4 Hz), 4.50–4.53 (m, 2H), 4.20–4.25 (m, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H). The spectroscopic data was identical with the previous report.[5]



(Ethyl 3,4,6-tri-*O*-acetyl-2-aminotriphenylphosphonium-2-deoxy-1-thio-*β*-D-glucopyranoside) iodide (S5)

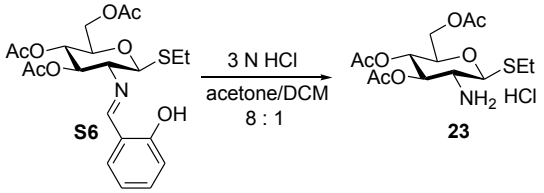
Compound **19** (400 mg, 0.91 mmol) and ethanethiol (98 μL, 1.36 mmol) and 4 Å MS were dissolved in dry DCM (10 mL) under argon. The reaction mixture was stirred at 0 °C for 30 min. Then a solution of PPh_3 (286 mg 1.10 mmol) in DCM (2 mL) was added dropwise**.** The reaction was warmed gradually to room temperature and further stirred for 12 h. The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to give the compound **S5** (556 mg, 83%) as yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.88 (m, 9H), 7.67–7.69 (m, 6H), 5.89–5.97 (m, 2H), 4.78 (t, 1H, *J* = 9.7 Hz), 4.22 (dd, 1H, *J* = 5.8, 12.9 Hz), 4.01–4.04 (m, 2H), 3.00–3.03 (m, 1H), 2.75–2.87 (m, 2H), 2.02 (s, 3H), 1.97 (s, 3H), 1.37 (t, 3H, *J* = 7.4 Hz), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.61, 170.39, 168.99, 134.94, 134.29, 134.18, 129.96, 129.83, 84.87, 76.04, 74.64, 69.63, 62.36, 57.16, 25.89, 20.70, 20.00, 15.51. ^{31}P NMR (162 MHz, $CDCl_3$): 39.83. HRMS (ESI) Calcd for $C_{32}H_{36}NO_7PS$ $[M\text{-}I]^+$: 610.1950, found: 610.2026.



Ethyl 3,4,6-*O*-tri-acetyl-2-deoxy-2-*o*-hydroxylbenzylideneamino-1-thio-*β*-D-glucopyranoside (S6)

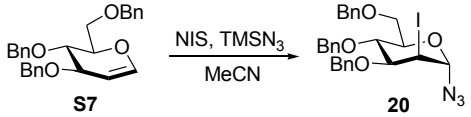
Et_3N (2 mL) was added to the mixture of compound **S5** (400 mg, 0.54 mmol) and salicylaldehyde (1 mL) in chlorobenzene (2 mL) in a Microwave tube. Then the reaction was irradiated with 150 W of microwave energy at 140 °C for 30 min. The mixture was then transferred in a round bottom flask and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to give compound **S6** (200 mg, 80 %) as foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.25 (s, 1H), 8.28 (s, 1H), 7.31–7.37 (m, 1H), 7.26–7.28 (m, 1H), 6.96 (d, 1H, *J* = 13.7

Hz), 6.87–6.92 (m, 1H), 5.37 (t, 1H, *J* = 9.4 Hz), 5.11 (t, 1H, *J* = 9.7 Hz), 4.79 (d, 1H, *J* = 9.9 Hz), 4.32 (dd, 1H, *J* = 5.2, 12.3 Hz), 4.16 (dd, 1H, *J* = 2.1, 12.3 Hz), 3.82–3.87 (m, 1H), 3.36 (t, 1H, *J* = 9.6 Hz), 2.64–2.76 (m, 2H), 2.09 (s, 3H), 2.02 (s, 3H), 1.90 (s, 3H), 1.26 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.66, 169.79, 169.55, 168.17, 160.88, 133.19, 131.95, 118.91, 118.16, 117.23, 84.53, 75.85, 74.37, 72.62, 68.28, 62.40, 25.09, 20.74, 20.64, 20.48, 14.88. HRMS (ESI) Calcd for $C_{21}H_{27}NO_8SNa$ $[M+Na]^+$: 476.1350, found: 476.1227.



Ethyl 3,4,6-*O*-tri-acetyl-2-deoxy-2-amino-1-thio-*β*-D-glucopyranoside hydrochloride (23)

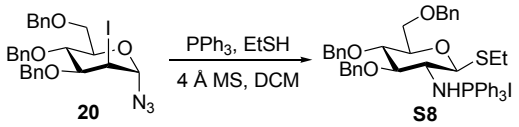
Aqueous 3 N HCl (220 μL, 0.66 mmol) was added to the solution of compound **S6** (300 mg, 0.66 mmol) in acetone (3 mL). The product precipitated from the reaction. After being stirred at room temperature for 1 h, the product **23** (227 mg, 90%) was collected via filtration and dried under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.75 (bs, 3H), 5.76 (t, 1H, *J* = 9.4 Hz), 5.09 (d, 1H, *J* = 10.4 Hz), 5.01 (t, 1H, *J* = 10.0 Hz), 4.25 (dd, 1H, *J* = 4.9, 12.5 Hz), 4.12 (dd, 1H, *J* = 1.9, 12.3 Hz), 3.84–3.89 (m, 1H), 3.43 (t, 1H, *J* = 10.1 Hz), 2.80–2.88 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.37 (d, 3H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.17, 170.53, 169.58, 81.95, 75.57, 71.43, 68.69, 61.96, 54.20, 25.04, 21.92, 20.68, 20.51, 15.16. HRMS (ESI) Calcd for $C_{14}H_{24}NO_7S$ $[M-Cl]^+$: 350.1273, found: 350.1271.



3,4,6-*O*-tri-benzyl-2-deoxy-2-iodo-*α*-D-mannopyranosyl azide (20)

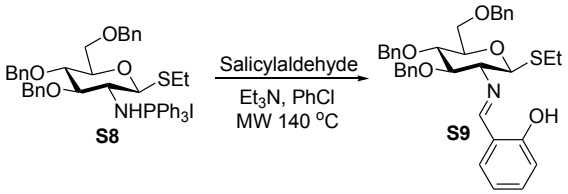
Glycal **S7** (400 mg, 0.96 mmol) was dissolved in dry MeCN (4 mL) under argon. Then NIS (220 mg, 0.96 mmol) and $TMSN_3$ (160 μL, 1.20 mmol) were added sequentially at 0 °C. The reaction was stirred at this temperature for 1 h and gradually warmed to room temperature for another 4 h. The reaction was quenched with $NaHCO_3$ (aq.) and diluted with DCM (100 mL). The organic layer was washed with $NaHCO_3$ (aq.), $Na_2S_2O_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 2 : 1) to afford compound **20** (280 mg, 50%) as oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.38 (m, 15H), 7.15–7.16 (m, 2H), 5.74 (s, 1H), 4.83 (d, 1H, *J* = 10.8 Hz), 4.71 (d, 1H, *J* = 12.0 Hz), 4.66 (d, 1H, *J* = 11.5 Hz), 4.47–4.53 (m, 3H), 4.35 (s, 1H), 3.90–4.00 (m, 2H), 3.80 (dd, 1H, *J* = 3.8, 11.1 Hz), 3.71 (d, 1H, *J* = 11.2 Hz), 3.16–3.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.09, 137.92, 137.27, 128.46, 128.32, 128.30, 128.03, 127.96, 127.73, 127.66, 127.54, 91.36, 76.32, 75.28, 75.14, 74.25,

73.39, 71.26, 68.44, 31.94. The spectroscopic data was identical with the previous report.[5]



(Ethyl 3,4,6-tri-*O*-benzyl-2-aminotriphenylphosphonium-2-deoxy-1-thio-*β*-D-glucopyranoside]) iodide (S8)

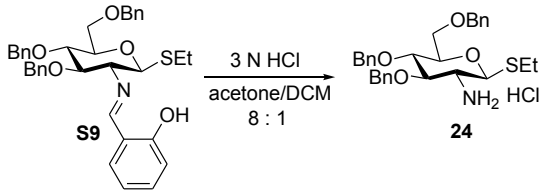
Compound **20** (450 mg, 0.77 mmol) and ethanethiol (100 μL, 1.39 mmol) and 4 Å MS were dissolved in dry DCM (10 mL) under argon. The reaction mixture was stirred at 0 ^{o}C for 30 min. Then a solution of PPh_3 (300 mg 1.15 mmol) in DCM (1 mL) was added dropwise**.** The reaction was warmed gradually to room temperature and further stirred for 12 h. The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to give the compound **S8** (440 mg, 65%) as yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.88 (m, 6H), 7.64–7.75 (m, 4H), 7.46–7.54 (m, 7H), 7.11–7.28 (m, 12H), 6.99–7.02 (m, 2H), 6.74–6.75 (m, 2H), 5.66 (d, 1H, *J* = 10.2 Hz), 5.02 (d, 1H, *J* = 11.9 Hz), 4.53–4.59 (m, 4H), 4.44 (t, 2H, *J* = 12.1 Hz), 3.76 (d, 1H, *J* = 9.9 Hz), 3.67 (d, 2H, *J* = 2.5Hz), 3.51 (t, 1H, *J* = 9.5 Hz), 2.68–2.86 (m, 3H), 1.33 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.50, 137.78, 134.39, 134.28, 129.46, 129.32, 128.28, 128.19, 127.93, 127.77, 127.60, 127.45, 127.23, 126.80, 126.16, 122.44, 121.40, 85.14, 85.08, 82.92, 79.90, 77.69, 73.82, 73.60, 73.37, 68.37, 59.31, 59.28, 25.78, 15.38. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.1. HRMS (ESI) Calcd for $C_{47}H_{49}NO_4PS$ $[M-I]^+$: 754.3114, found: 754.3115.



Ethyl 3,4,6-*O*-tri-benzyl-2-deoxy-2-*o*-hydroxylbenzylideneamino-1-thio-*β*-D-glucopyranoside (S9)

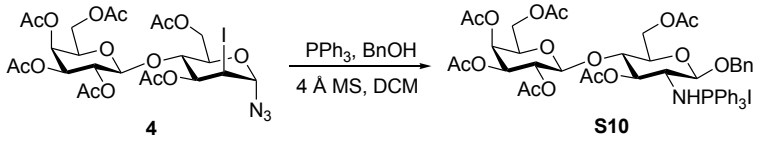
Et_3N (1 mL) was added to the mixture of compound **S8** (90 mg, 0.10 mmol) and salicylaldehyde (0.5 mL) in chlorobenzene (1 mL) in a Microwave tube. Then the reaction was irradiated with 150 W of microwave energy at 140 ^{o}C for 30 min. The mixture was then transferred into a round bottom flask and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to give compound **S9** (52 mg, 85 %) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.85 (s, 1H), 8.32 (s, 1H), 7.29–7.36 (m, 9H), 7.21–7.25 (m, 3H), 7.11–7.16 (m, 3H), 7.02–7.04 (m, 2H), 6.97 (d, 1H, *J* = 8.3 Hz), 6.90 (t, 1H, *J* = 7.4 Hz), 4.86 (d, 1H, *J* = 10.9 Hz), 4.73 (t, 2H, *J* = 9.8 Hz), 4.55–4.65 (m, 3H), 4.44 (d, 1H, *J* = 10.5 Hz), 3.70–3.81 (m, 4H), 3.63–3.64 (m, 1H), 3.27 (d, 1H, *J* = 8.7 Hz), 2.63–2.78 (m, 2H), 1.27 (t, 1H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.51, 160.89, 138.09, 137.89, 137.42, 132.71, 131.87, 128.43, 128.32, 128.29, 128.19, 127.87,

127.82, 127.79, 127.72, 127.58, 118.86, 118.58, 116.97, 84.98, 84.20, 79.41, 77.73, 75.77, 74.98, 74.71, 73.41, 68.97, 24.71, 15.00. HRMS (ESI) Calcd for $C_{36}H_{39}NO_5SNa$ $[M+Na]^+$: 620.2447, found: 620.2393.



Ethyl 3,4,6-*O*-tri-benzyl-2-deoxy-2-amino-1-thio-*β*-D-glucopyranoside hydrochloride (24)

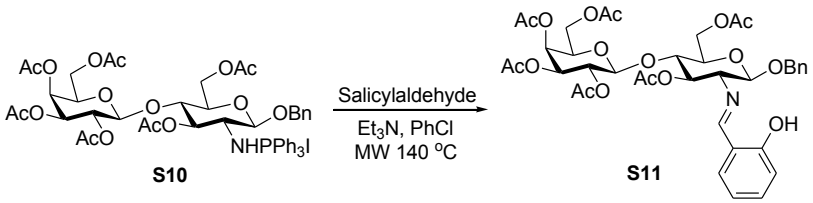
Aqueous 3 N HCl (30 μL) was added to the solution of compound **S9** (50 mg, 0.087 mmol) in acetone (2 mL) and DCM (0.25 mL). After being stirred at room temperature for 1 h and the material was completely consumed according to TLC analysis, the solution was diluted with toluene (10 mL). After the solvent was removed under vacuum, the residue was purified by column chromatography on silica gel (DCM : MeOH = 60 : 1) to give compound **24** (42 mg, 90%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.34 (m, 13 H), 7.17–7.18 (m, 2H), 4.96 (d, 1H, *J* = 11.1 Hz), 4.81 (d, 1H, *J* = 11.1 Hz), 4.76 (d, 1H, *J* = 10.9 Hz), 4.52–4.63 (m, 3H), 4.46 (d, 1H, *J* = 9.9 Hz), 3.72–3.76 (m, 2H), 3.59–3.69 (m, 2H), 3.51–3.53 (m, 1H), 3.14 (bs, 3H), 2.94 (t, 1H, *J* = 9.3 Hz), 2.71–2.76 (m, 2H), 1.30 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.11, 138.04, 137.78, 128.53, 128.41, 128.32, 127.85, 127.82, 127.80, 127.75, 127.59, 85.37, 85.19, 79.29, 78.43, 75.35, 74.72, 73.41, 68.80, 55.91, 24.52, 15.28. HRMS (ESI) Calcd for $C_{29}H_{36}NO_4S$ $[M-Cl]^+$: 494.2365, found: 494.2359.



Benzyl [3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-aminotriphenylphosphonium-2-deoxy-*β*-D-glucopyranoside] iodide (S10)

Compound **4** (500 mg, 0.69 mmol), BnOH (107 μL, 1.03 mmol) and 4 Å MS were dissolved in dry DCM (10 mL) under argon. The reaction mixture was stirred at 0 ^{o}C for 30 min. Then a solution of PPh_3 (198 mg 0.76 mmol) in DCM (1 mL) was added dropwise**.** The reaction was warmed gradually to room temperature and further stirred for 12 h. The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to afford the compound **S10** (680 mg, 92%) as yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.73 (m, 9H), 7.53–7.58 (m, 6H), 7.22–7.25 (m, 3H), 7.01–7.03 (m, 2H), 5.86 (t, 1H, *J* = 9.6 Hz), 5.79 (d, 1H, *J* = 7.9 Hz), 5.34 (d, 1H, *J* = 3.2 Hz), 5.09 (dd, 1H, *J* = 7.9, 10.2 Hz), 4.96 (dd, 1H, *J* = 3.4, 10.3 Hz), 4.82 (d, 1H, *J* = 10.8 Hz), 4.63 (d, 1H, *J* = 7.8 Hz), 4.40–4.45 (m, 2H), 4.08–4.16 (m, 2H), 3.95–4.05 (m, 3H), 3.73 (t, 1H, *J* = 9.7 Hz), 3.14 (bs, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.46,

170.34, 170.17, 169.98, 168.86, 168.83, 136.85, 134.73, 134.04, 133.93, 129.74, 129.61, 128.14, 128.08, 127.70, 121.81, 120.77, 100.26, 99.45, 76.02, 74.33, 74.28, 72.14, 71.34, 71.15, 70.63, 68.98, 66.74, 62.53, 60.71, 58.25, 20.89, 20.85, 20.67, 20.62, 20.46. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.4. HRMS (ESI) Calcd for $C_{49}H_{55}NO_{16}P$ $[M-I]^+$: 944.3253, found: 944.3250.



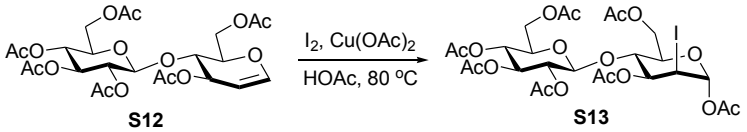
Benzyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*o*-hydroxylbenzylideneamino -*β*-D-glucopyranoside (S11)

Et_3N (2 mL) was added to the mixture of compound **S10** (800 mg, 0.78 mmol) and salicylaldehyde (1 mL) in chlorobenzene (2 mL) in a Microwave tube. Then the reaction was irradiated with 150 W of microwave energy at 140 °C for 30 min. The mixture was then transferred into a round bottom flask and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to give compound **S11** (483 mg, 82 %) as foam. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.28 (s, 1H), 8.32 (s, 1H), 7.32–7.36 (m, 1H), 7.16–7.25 (m, 6H), 6.98 (d, 1H, *J* = 8.1 Hz), 6.87–6.91 (m, 1H), 5.42 (t, 1H, *J* = 9.6 Hz), 5.36 (d, 1H, *J* = 3.4 Hz), 5.11 (dd, 1H, *J* = 7.9, 10.4 Hz), 4.97 (dd, 1H, *J* = 3.5, 10.4 Hz), 4.83 (d, 1H, *J* = 12.1 Hz), 4.66 (d, 1H, *J* = 7.8 Hz), 4.59 (d, 1H, *J* = 12.1 Hz), 4.55 (dd, 1H, *J* = 1.9, 11.9 Hz), 4.52 (d, 1H, *J* = 7.9 Hz), 4.16–4.22 (m, 2H), 4.06 (dd, 1H, *J* = 7.5, 11.1 Hz), 3.89 (t, 1H, *J* = 7.1 Hz), 3.85 (t, 1H, *J* = 9.7 Hz), 3.70–3.74 (m, 1H), 3.32 (dd, 1H, *J* = 7.8, 9.9 Hz), 2.16 (s, 3H), 2.14 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.962 (s, 3H), 1.955 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.34, 170.21, 170.10, 169.99, 169.12, 168.85, 168.63, 160.89, 136.33, 132.87, 131.79, 128.34, 127.94, 127.80, 118.65, 118.32, 117.16, 100.79, 99.76, 75.82, 73.06, 72.89, 72.83, 71.09, 70.93, 70.56, 69.05, 66.56, 62.18, 60.74, 20.81, 20.63, 20.53, 20.40. HRMS (ESI) Calcd for $C_{38}H_{46}NO_{17}$ $[M+H]^+$: 788.2760, found: 788.2757.

Benzyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-amino -*β*-D-glucopyranoside hydrochloride (25)

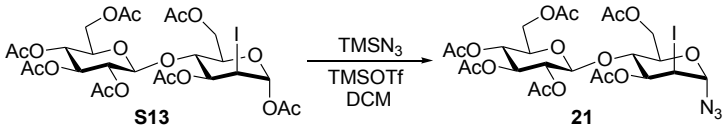
Aqueous 3 N HCl (807 μL, 2.42 mmol) was added to the solution of compound **S11** (1.9 g, 2.42 mmol) in a mixture of acetone and DCM (8 : 1, 24 mL). After being stirred at room temperature for 1 h and the material was completely consumed according to TLC analysis, the solution was diluted with toluene (10 mL). The solvent was removed under vacuum, and the residue was purified by column

chromatography on silica gel (ethyl acetate : ethanol = 20 : 1) to give compound **25** (1.38 g, 79%) as foam. ^{1}H NMR (400 MHz, CD_3OD): δ = 7.31–7.42 (m, 5H), 5.39 (d, 1H, *J* = 3.2 Hz), 5.13 (dd, 1H, *J* = 3.4, 10.4 Hz), 5.04 (dd, 1H, *J* = 7.9, 10.2 Hz), 5.00 (t, 1H, *J* = 9.2 Hz), 4.70 (d, 1H, *J* = 7.8 Hz), 4.66 (d, 1H, *J* = 11.6 Hz), 4.57 (d, 1H, *J* =11.8 Hz), 4.45 (d, 1H, *J* = 8.0 Hz), 4.12–4.24 (m, 4H), 3.79 (t, 1H, *J* = 9.7 Hz), 3.68–3.72 (m, 1H), 2.78 (dd, 1H, *J* = 8.2, 10.2 Hz), 2.166 (s, 3H), 2.158 (s, 3H), 2.153 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.24, 170.28, 170.05, 169.97, 169.10, 136.31, 132.05, 131.92, 128.43, 128.34, 127.99, 100.66, 98.63, 75.83, 72.49, 71.72, 70.86, 70.71, 68.96, 66.04, 61.69, 60.69, 55.38, 21.59, 20.77, 20.55, 20.49, 20.42. HRMS (ESI) Calcd for $C_{31}H_{42}NO_{16}^+$ $[M\text{-}Cl]^+$: 684.2498, found: 684.2318.



1-*O*-Acetyl-3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-gulcopyranosyl)-2-deoxy-2-iodo-α-D-mannopyranose (S13)

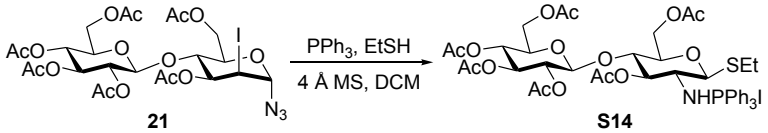
Glycal **S12** (3.0 g, 5.35 mmol), $Cu(OAc)_2$ (1.08 g, 5.89 mmol), and I_2 (1.6 g, 6.42 mmol) were sequentially added into AcOH (100 mL). The mixture was stirred at 80 ^{o}C overnight under argon. The reaction was evaporated to dryness and the residue was diluted with DCM (300 mL). The organic layer was washed with $NaHCO_3$ (aq.), $Na_2S_2O_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 2 : 1) to afford compound **S13** (2.6 g, 70%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.33 (d, 1H, *J* = 1.7 Hz), 5.19 (t, 1H, *J* = 9.5 Hz), 5.07 (t, 1H, *J* = 9.8 Hz), 4.96 (dd, 1H, *J* = 8.1, 9.2 Hz), 4.64–4.67 (m, 1H), 4.62 (d, 1H, *J* = 8.0 Hz), 4.44–4.50 (m, 2H), 4.33 (dd, 1H, *J* = 5.2, 12.4 Hz), 3.98–4.13 (m, 4H), 3.72–3.76 (m, 1H), 2.16 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.53, 170.38, 170.16, 169.50, 169.35, 169.24, 168.43, 101.06, 94.49, 75.59, 72.81, 71.86, 71.56, 68.84, 68.00, 61.96, 61.58, 27.64, 20.87, 20.81, 20.74, 20.66, 20.53. HRMS (ESI) Calcd for $C_{26}H_{35}IO_{17}Na$ $[M+Na]^+$: 769.0811, found: 769.0812.



3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-gulcopyranosyl)-2-deoxy-2-iodo-*α*-D-mannopyranosyl **azide (21)**

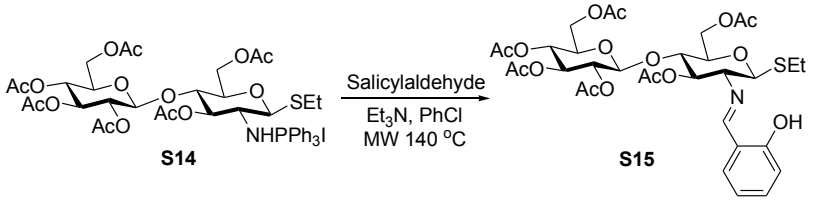
TMSOTf (116 μL, 0.64 mmol) was added to the solution of iodoacetate **S13** (2.40 g, 3.20 mmol) and $TMSN_3$ (505 μL, 3.89 mmol) in dry DCM (20 mL) at 0 ^{o}C under argon. The reaction was gradually warmed to room temperature and stirred overnight. Then the mixture was diluted with DCM (300 mL).

The organic layer was washed with $NaHCO_3$ (aq.) dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to afford compound **21** (2.20 g, 81%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (d, 1H, *J* = 2.7 Hz), 5.18 (t, 1H, *J* = 9.4 Hz), 5.06 (t, 1H, *J* = 9.9 Hz), 4.95 (dd, 1H, *J* = 8.0, 9.2 Hz), 4.66 (dd, 1H, *J* = 3.9, 7.5 Hz), 4.61 (d, 1H, *J* = 8.0 Hz), 4.49 (dd, 1H, *J* = 1.8, 12.0 Hz), 4.40 (t, 1H, *J* = 3.8 Hz), 4.31 (dd, 1H, *J* =5.2, 12.3 Hz), 4.18 (dd, 1H, *J* = 5.2, 12.0 Hz), 4.05–4.13 (m, 2H), 3.94 (dd, 1H, *J* = 7.8, 8.9 Hz), 3.71–3.76 (m, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.34, 170.18, 169.98, 169.21, 169.15, 168.95, 100.71, 90.59, 75.44, 72.58, 71.64, 71.53, 71.30, 68.78, 67.84, 61.77, 61.41, 28.03, 20.59, 20.34, 13.99. HRMS (ESI) Calcd for $C_{24}H_{32}IN_3O_{15}Na$ $[M+Na]^+$: 752.0770, found: 752.0767.



Ethyl [3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2-aminotriphenylphosphonium-2-deoxy-1-thio-*β*-D-glucopyranoside] iodide (S14)

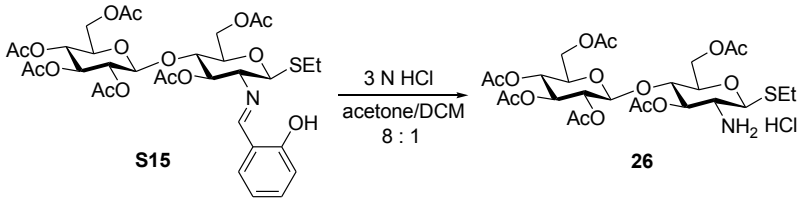
Compound **21** (2.20 g, 3.02 mmol) and ethanethiol (334 μL, 4.53 mmol) and 4 Å MS were dissolved in dry DCM (50 mL) under argon. The reaction mixture was stirred at 0 ^{o}C for 30 min. Then a solution of PPh_3 (950 mg 3.62 mmol) in CH_2Cl_2 (3 mL) was added dropwise**.** The reaction was warmed gradually to room temperature and further stirred for 12 h. The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to give the compound **S14** (2.10 g, 70%) as yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.87 (m, 9H), 7.64–7.68 (m, 6H), 5.83–5.87 (m, 2H), 5.13 (t, 1H, J = 9.4 Hz), 5.03 (t, 1H, *J* = 9.8 Hz), 4.85 (t, 1H, *J* = 8.6 Hz), 4.61 (d, 1H, *J* = 8.0 Hz), 4.27 (dd, 1H, *J* = 4.4, 12.5 Hz), 4.01–4.08 (m, 3H), 3.71–3.76 (m, 1H), 3.62 (t, 1H, *J* = 9.6 Hz), 3.09–3.11 (m, 1H), 2.74–2.80 (m, 2H), 2.058 (s, 3H), 2.055 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.36 (s, 3H), 1.32 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.47, 170.34, 170.20, 169.34, 168.88, 168.52, 134.88, 134.37, 134.26, 129.84, 129.71, 121.71, 120.68, 99.18, 85.00, 77.32, 76.41, 75.96, 75.04, 73.08, 71.82, 71.48, 67.88, 62.74, 61.67, 57.76, 26.15, 20.85, 20.73, 20.56, 20.54, 20.31, 15.47. ^{31}P (162 MHz, $CDCl_3$): δ = 39.7. HRMS (ESI) Calcd for $C_{44}H_{53}NO_{15}PS$ $[M-I]^+$: 898.2868, found: 898.2868.



Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2-deoxy-2-*o*-

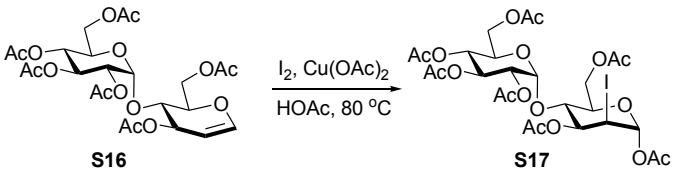
hydroxylbenzylideneamino -1-thio-*β*-D-glucopyranoside (S15)

Et_3N (2 mL) was added to the mixture of compound **S14** (210 mg, 0.20 mmol) and salicylaldehyde (1 mL) in chlorobenzene (2 mL) in a Microwave tube. Then the reaction was irradiated with 150 W of microwave energy at 140 ^oC for 30 min. The mixture was then transferred into a round bottom flask and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to give compound **S15** (460 mg, 81 %) as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 12.24 (s, 1H), 8.25 (s, 1H), 7.31–7.36 (m, 1H), 7.24–7.27 (m, 1H), 6.96 (d, 1H, *J* = 8.3 Hz), 6.87–6.91 (m, 1H), 5.37 (t, 1H, *J* = 9.0 Hz), 5.15 (t, 1H, *J* = 9.2 Hz), 5.08 (t, 1H, *J* = 9.6 Hz), 4.94 (t, 1H, *J* = 8.1 Hz), 4.75 (d, 1H, *J* = 9.9 Hz), 4.53 (d, 2H, *J* = 8.2 Hz), 4.38 (dd, 1H, *J* = 4.1, 12.4 Hz), 4.16 (dd, 1H, *J* = 5.1, 11.9 Hz), 4.05 (dd, 1H, *J* = 1.8, 12.3 Hz), 3.74–3.82 (m, 2H), 3.65–3.68 (m, 1H), 3.28 (t, 1H, *J* = 9.6 Hz), 2.63–2.72 (m, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.92(s, 3H), 1.25 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.45, 170.31, 170.22, 169.24, 169.09, 168.96, 167.76, 160.93, 133.10, 131.81, 118.79, 118.16, 117.29, 100.68, 84.46, 76.89, 76.19, 73.77, 73.07, 71.85, 71.56, 67.70, 62.45, 61.51, 25.21, 20.84, 20.62, 20.50, 20.40, 14.91. HRMS (ESI) Calcd for $C_{33}H_{43}NO_{16}SNa$ $[M+Na]^+$: 764.2195, found: 764.2075. Calcd for $C_{33}H_{44}NO_{16}S$ $[M+H]^+$: 742.2375, found: 742.2376.



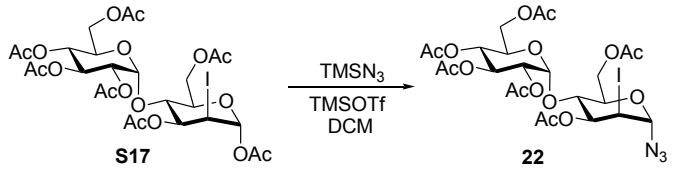
Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-2-deoxy-2-amino-1-thio-*β*-D-glucopyranoside hydrochloride (26)

Aqueous 3 N HCl (133 μL, 0.40 mmol) was added to the solution of compound **S15** (300 mg, 0.40 mmol) in the mixture of acetone and DCM (8 : 1, 3 mL). After being stirred at room temperature for 1 h and the material was completely consumed according to TLC analysis, the solution was diluted with toluene (10 mL). The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 20 : 1) to give compound **26** (210 mg, 77%) as foam. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.14 (t, 1H, *J* = 9.5 Hz), 5.08 (t, 1H, *J* = 9.5 Hz), 4.95 (t, 1H, *J* = 9.5 Hz), 4.92 (t, 1H, *J* = 8.8 Hz), 4.46–4.51 (m, 2H), 4.39 (dd, 1H, *J* = 4.3, 12.4 Hz), 4.30 (d, 1H, *J* = 10.0 Hz), 4.11 (dd, 1H, *J* = 5.6, 11.9 Hz), 4.05 (dd, 1H, *J* = 2.0, 12.4 Hz), 3.64–3.70 (m, 2H), 3.56–3.62 (m, 1H), 2.83 (t, 1H, *J* = 9.9 Hz), 2.67–2.75 (m, 2H), 2.112 (s, 3H), 2.108 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.31 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.48, 170.35, 170.22, 169.30, 169.04, 100.76, 87.76, 77.20, 75.97, 72.96, 71.88, 71.60, 67.78, 62.52, 61.58, 55.75, 24.90, 20.86, 20.88, 20.65, 20.53, 15.18. HRMS (ESI) Calcd for $C_{26}H_{40}NO_{15}S$ $[M-Cl]^+$: 638.2113, found: 638.2115.



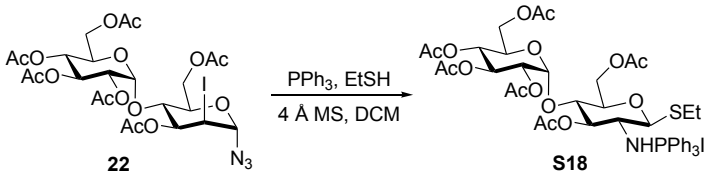
1-*O*-Acetyl-3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-D-gulcopyranosyl)-2-deoxy-2-iodo-*α*-D-mannopyranose (S17)

Glycal **S16** (1.78 g, 3.18 mmol), $Cu(OAc)_2$ (636 mg, 3.50 mmol), and I_2 (969 mg, 3.82 mmol) were sequentially added into AcOH (20 mL). The mixture was stirred at 80 °C overnight under argon. The reaction was evaporated to dryness and the residue was diluted with DCM (300 mL). The organic layer was washed with $NaHCO_3$ (aq.), $Na_2S_2O_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 2 : 1) to afford compound **S17** (2.02 g, 85%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.35 (s, 1H), 5.55 (d, 1H, *J* = 4.0 Hz), 5.40 (t, 1H, *J* = 9.8 Hz), 5.09 (t, 1H, *J* = 9.9 Hz), 4.91 (dd, 1H, *J* = 4.0, 10.5 Hz), 4.44–4.54 (m, 3H), 4.20–4.30 (m, 3H), 4.06–4.13 (m, 2H), 3.99–4.01 (m, 1H), 2.21 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 2.04 (s, 6H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.45, 170.05, 170.02, 169.81, 169.33, 168.29, 95.91, 94.17, 71.76, 71.73, 71.30, 70.10, 69.34, 68.51, 67.78, 62.49, 61.28, 26.87, 21.10, 20.87, 20.72, 20.60, 20.56, 20.51, 20.46. HRMS (ESI) Calcd for $C_{26}H_{35}IO_{17}Na$ $[M+Na]^+$: 769.0811, found: 769.0811.



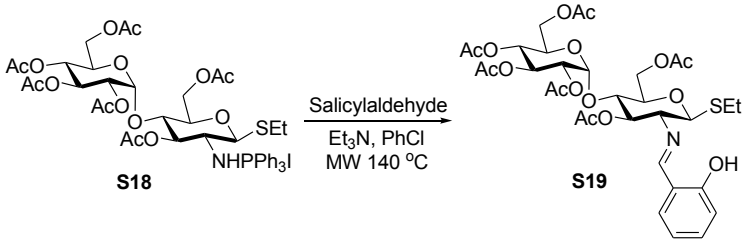
3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-D-gulcopyranosyl)-2-deoxy-2-iodo-*α*-D-mannopyranosyl **azide (22)**

TMSOTf (80 μL, 0.44 mmol) was added to the solution of iodoacetate **S17** (1.64 g, 2.19 mmol) and $TMSN_3$ (422 μL, 3.18 mmol) in dry DCM (20 mL) at 0 °C under argon. The reaction was gradually warmed to room temperature and stirred overnight. Then the mixture was diluted with DCM (300 mL). The organic layer was washed with $NaHCO_3$ (aq.) dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to afford compound **22** (1.48 g, 93%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66 (s, 1H), 5.53 (d, 1H, *J* = 4.0 Hz), 5.38 (t, 1H, *J* = 10.0 Hz), 5.07 (t, 1H, *J* = 9.9 Hz), 4.89 (dd, 1H, *J* = 4.0, 10.4 Hz), 4.45–4.52 (m, 3H), 4.25–4.31 (m, 2H), 4.12–4.20 (m, 2H), 4.09 (dd, 1H, *J* = 2.0, 12.4 Hz), 4.00–4.03 (m, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.041 (s, 3H), 2.035 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.49, 170.47, 170.15, 169.92, 169.70, 169.41, 95.82, 90.56, 71.89, 71.76, 71.26, 70.09, 69.39, 68.50, 67.86, 62.39, 61.38, 27.37, 21.07, 20.75, 20.63, 20.57, 20.54, 20.48. HRMS (ESI) Calcd for $C_{24}H_{32}IN_3O_{15}Na$ $[M+Na]^+$: 752.0770, found: 752.0770.



Ethyl [3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl)-2-aminotriphenylphosphonium-2-deoxy-1-thio-*β*-D-glucopyranoside] iodide (S18)

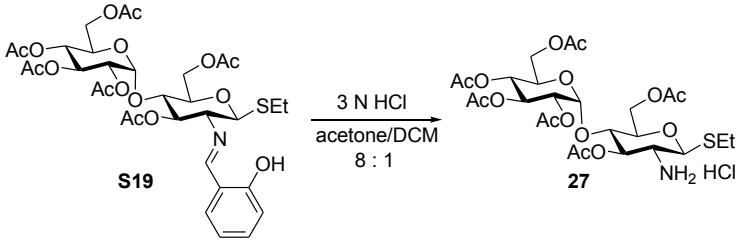
Compound **22** (1.16 g, 1.59 mmol) and ethanethiol (173 µL, 2.39 mmol) and 4 Å MS were dissolved in dry DCM (10 mL) under argon. The reaction mixture was stirred at 0 ^{o}C for 30 min. Then a solution of PPh_3 (500 mg 1.91 mmol) in DCM (3 mL) was added dropwise**.** The reaction was warmed gradually to room temperature and further stirred for 12 h. The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to give the compound **S18** (1.17 g, 72%) as yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10–8.15 (m, 1H), 7.84–7.89 (m, 6H), 7.75–7.79 (m, 3H), 7.64–7.65 (m, 6H), 5.85–5.91 (m, 2H), 5.29 (t, 1H, *J* = 9.8 Hz), 5.08 (d, 1H, *J* = 3.2 Hz), 4.99 (t, 1H, *J* = 9.7 Hz), 4.81 (dd, 1H, *J* = 3.8, 10.4 Hz), 4.39 (dd, 1H, *J* = 2.1, 12.0 Hz), 4.22 (dd, 1H, *J* = 4.6, 12.1 Hz), 4.00 (d, 2H, *J* = 10.6 Hz), 3.93 (bs, 1H), 3.66 (t, 1H, *J* = 9.3 Hz), 3.05–3.10 (m, 1H), 2.71–2.87 (m, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.41 (s, 3H), 1.30 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.60, 170.50, 170.28, 169.57, 168.49, 168.82, 134.85, 134.39, 134.28, 129.80, 129.66, 121.81, 120.77, 95.17, 84.97, 75.53, 74.82, 70.22, 69.36, 68.43, 67.98, 63.09, 61.64, 57.92, 26.20, 20.97, 20.82, 20.65, 20.57, 20.55, 15.37. ^{31}P (162 MHz, $CDCl_3$): δ = 40.3. HRMS (ESI) Calcd for $C_{44}H_{53}NO_{15}PS$ $[M\text{-}I]^{+}$: 898.2868, found: 898.2868.



Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl)-2-deoxy-2-*o*-hydroxylbenzylideneamino-1-thio-*β*-D-glucopyranoside (S19)

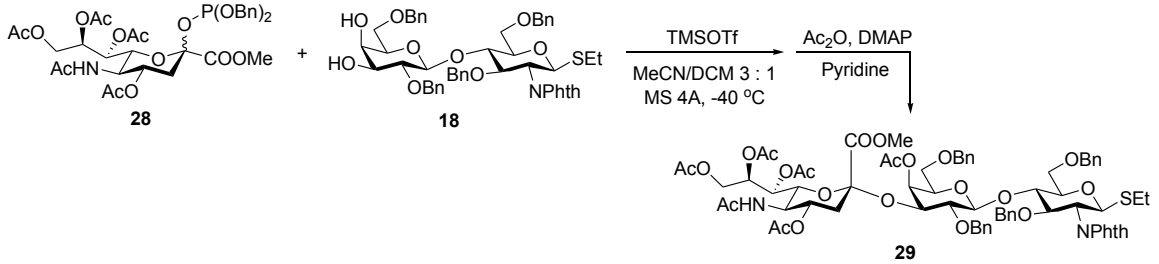
Et_3N (2.6 mL) was added to a mixture of compound **S18** (1.03 g, 1.00 mmol) and salicylaldehyde (2 mL) in chlorobenzene (2 mL) in a Microwave tube. Then the reaction was irradiated with 150 W of microwave energy at 140 ^{o}C for 30 min. The mixture was then transferred into a round bottom flask and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to give compound **S19** (546 mg, 73 %) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.19 (s, 1H), 8.22 (s, 1H), 7.31–7.35 (m, 1H), 7.24–7.27 (m, 1H), 6.97 (d, 1H, *J* = 8.6 Hz), 6.87–6.91 (m, 1H), 5.53 (t, 1H, *J* = 9.5 Hz), 5.36–5.42 (m, 2H), 5.06 (t, 1H, *J* = 9.2 Hz), 4.87

(dd, 1H, *J* = 4.7, 10.7 Hz), 4.81 (d, 1H, *J* = 9.4 Hz), 4.48 (dd, 1H, *J* = 3.2, 12.0 Hz), 4.23–4.32 (m, 2H), 3.97–4.10 (m, 3H), 3.83–3.86 (m, 1H), 3.21 (t, 1H, *J* = 9.6 Hz), 2.62–2.76 (m, 2H), 2.16 (s, 3H), 2.12 (s, 3H), 2.04 (s, 6H), 2.00 (s, 3H), 1.86 (s, 3H), 1.26 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.74, 170.54, 170.45, 169.86, 169.45, 169.31, 167.82, 160.94, 133.21, 131.83, 118.87, 118.03, 117.41, 95.45, 84.16, 76.73, 76.23, 73.96, 72.25, 69.82, 69.25, 68.53, 68.04, 63.37, 61.55, 25.11, 20.85, 20.77, 20.69, 20.65, 20.57, 14.92. HRMS (ESI) Calcd for $C_{33}H_{43}NO_{16}SNa$ $[M+Na]^+$: 764.2195, found: 764.2094. $C_{33}H_{44}NO_{16}S$ $[M+H]^+$: 742.2375, found: 742.2374.



Ethyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl)-2-deoxy-2-amino-1-thio-*β*-D-glucopyranoside hydrochloride (27)

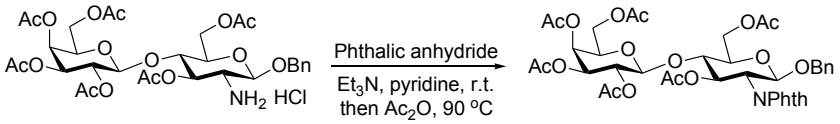
Aqueous 3 N HCl (100 μL, 0.30 mmol) was added to a solution of compound **S19** (223 mg, 0.30 mmol) in a mixture of acetone and DCM (8 : 1, 3 mL). After being stirred at room temperature for 1 h and the material was completely consumed according to TLC analysis, the solution was diluted with toluene (10 mL). The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 20 : 1) to give compound **27** (171 mg, 85%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 (d, 1H, *J* = 3.9 Hz), 5.36 (t, 1H, *J* = 9.7 Hz), 5.05 (t, 1H, *J* = 10.1 Hz), 5.04 (t, 1H, *J* = 9.5 Hz), 4.89 (dd, 1H, J = 4.0, 10.5 Hz), 4.89 (dd, 1H, J = 2.5, 12.0 Hz), 4.31 (d, 1H, *J* = 10.0 Hz), 4.24 (dd, 1H, J = 4.2, 12.6 Hz), 4.06 (d, 1H, *J* = 12.4 Hz), 3.95–3.98 (m, 1H), 3.90 (t, 1H, *J* = 9.0 Hz), 3.63–3.67 (m, 1H), 2.67–2.77 (m, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.31 (t, 1H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.97, 170.57, 170.55, 170.49, 169.91, 169.44, 95.45, 88.08, 78.65, 76.08, 72.99, 69.91, 69.41, 68.47, 68.05, 63.47, 61.56, 56.50, 24.62, 21.17, 20.85, 20.69, 20.62, 20.59, 15.19. HRMS (ESI) Calcd for $C_{26}H_{40}NO_{15}S$ $[M-Cl]^+$: 638.2113, found: 638.2114.



Sialylated lactosamine trisaccharide building block (29)

The solution of sialic acid donor **28**[3] (646 mg, 0.88 mmol), acceptor **18** (513 mg, 0.59 mmol) and

activated powdered 4 Å molecular sieves in the mixture of dry MeCN and dry DCM (3:1, 20 mL) was stirred at room temperature under an argon atmosphere for 30 min. After being cooled to -40 ^{o}C, TMSOTf (31 μL, 0.18 mmol) was added and the reaction was stirred at this temperature for 3 h (the consumption of donor was monitored by TLC). The reaction was quenched by triethylamine (0.2 mL) and diluted with DCM (50 mL). The solid was filtered off through a pad of Celite and the filtrate was washed with $NaHCO_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (DCM : MeOH = 80 : 1) to remove the sialic glycal. The crude product was dissolved in a mixture of pyridine (4 mL) and Ac_2O (2 mL) at room temperature. DMAP (32 mg) was added at 0 ^{o}C and the reaction was stirred at room temperature for 4 h. After removing the solvent *in vacuo*, the residue was finely purified by column chromatography on silica gel (toulene : acetone = 7 : 3) for 3 times to give the pure α-trisaccharide **29** (481 mg, 39% over two steps) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.81 (m, 1H), 7.68–7.70 (m, 3H), 7.47 (d, 2H, *J* = 7.5 Hz), 7.23–7.41 (m, 17H), 6.98–7.00 (m, 2H), 6.86–6.88 (m, 3H), 5.58–5.61 (m, 1H), 5.36 (dd, 1H, *J* = 2.0, 8.2 Hz), 5.18 (t, 2H, *J* = 10.3 Hz), 5.04 (d, 1H, *J* = 3.2 Hz), 4.97 (d, 1H, *J* = 12.3 Hz), 4.92 (td, 1H, *J* = 3.6, 10.7 Hz), 4.86 (d, 1H, *J* = 12.0 Hz), 4.70–4.75 (m, 2H), 4.58 (d, 1H, *J* = 12.0 Hz), 4.42–4.52 (m, 4H), 4.23–4.34 (m, 4H), 4.02–4.16 (m, 3H), 3.83 (s, 3H), 3.70–3.76 (m, 4H), 3.45–3.51 (m, 2H), 3.35 (d, 1H, *J* = 5.7, 10.0 Hz), 3.26 (d, 1H, *J* = 7.0, 9.6 Hz), 2.53–2.71 (m, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.87 (s, 3H), 1.84 (s, 3H), 1.16 (t, 3H, *J* = 7.4 Hz). The spectroscopic data was identical with the previous report.[3]

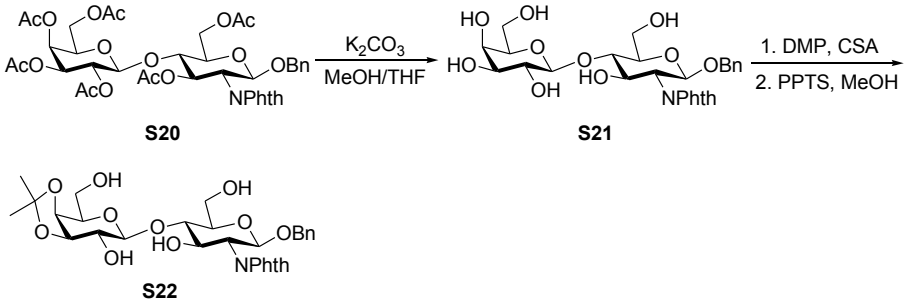


25 **S20**

Benzyl 3,6-*O*-di-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-*β*-D-glucopyranoside (S20)

Et_3N (320 μL, 2.3 mmol) was added to the solution of compound **25** (1.38 g, 1.92 mmol) in pyridine (30 mL). After stirring for 30 min, phthalic anhydride (284 mg, 1.92 mmol) was added in one portion. After 2 h, a second portion of phthalic anhydride (284 mg, 1.92 mmol) and Et_3N (320 μL, 2.3 mmol) were added and the mixture was stirred for another 2 h. The reaction was quickly moved to an oil bath at 90 ^{o}C and Ac_2O (10 mL) was added. The mixture was stirred for another 30 min at this temperature and the solution was concentrated *in vacuo*. The residue was dissolved in DCM (200 mL) and was washed with 1 N HCl (aq.) (×3), water, $NaHCO_3$ (aq.), and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane: ethyl acetate = 1 : 1) to afford compound **S20** (1.48 g, 95%) as white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.79 (m, 2H), 7.07–7.14 (m, 5H), 5.74 (dd, 1H, *J* = 8.5, 10.6 Hz), 5.37 (d, 1H, *J* = 10.5 Hz), 5.33 (d, 1H, *J* = 3.6 Hz), 5.12 (dd, 1H, *J* = 7.9, 10.5 Hz), 4.95 (dd, 1H, *J* = 3.4, 10.4 Hz), 4.82 (d, 1H,

J = 12.1 Hz), 4.49–4.58 (m, 3H), 4.26 (dd, 1H, *J* = 8.5, 10.6 Hz), 4.17 (dd, 1H, *J* = 4.7, 11.9 Hz), 4.01–4.03 (m, 2H), 3.77–3.92 (m, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H). The spectroscopic data was identical with the previous report.[6]



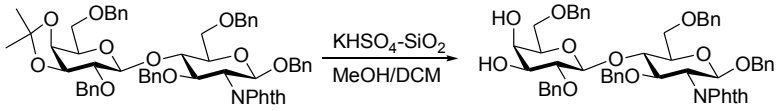
Benzyl 3,6-*O*-di-benzyl-4-*O*-(3:4-*O*-isopropylidene 2,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-*β*-D-glucopyranoside (S22)

To the solution of compound **S20** (1.07 g, 1.31 mmol) dissolved in the mixture of MeOH and THF (2 : 1, 30 mL), K_2CO_3 (35 mg) was added. The reaction was stirred for 1 h and the solution was neutralized with Amberlite HR-120 (H^+), filtered, and concentrated. The compound **S21** was used without further purification.

Compound **S21** and camphorsulfonic acid (52 mg, 0.19 mmol) were dissolved in 2,2-dimethoxypropane (20 mL) and stirred at room temperature for 3 days until the reaction mixture became clear. The reaction was quenched by addition of triethylamine (1 mL), and the solvent was evaporated. The residue was co-evaporated with toluene for three times in order to remove the trace amount of triethylamine. Then the residue was dissolved in MeOH (100 mL) and was added pyridinium *p*-toluenesulfonate (85 mg, 0.34 mmol). The reaction was stirred until the TLC showed only one main product left (R_f = 0.3, *n*-hexane : ethyl acetate = 1 : 3). Then the reaction was quenched by addition of triethylamine (0.5 mL) and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate : ethanol = 10 : 1) to give compound **S22** (653 mg, 82%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.79 (m, 4H), 7.02–7.11 (m, 5H), 5.25 (d, 1H, *J* = 8.5 Hz), 4.79 (d, 1H, *J* = 12.3 Hz), 4.45–4.55 (m, 4H), 4.17–4.23 (m, 2H), 4.10–4.12 (m, 1H), 4.02–4.04 (m, 1H), 3.99 (bs, 2H), 3.77–3.89 (m, 3H), 3.74 (bs, 1H), 3.59–3.64 (m, 2H), 3.43 (bs, 1H), 3.14 (bs, 1H), 1.49 (s, 3H), 1.30 (s, 3H). The spectroscopic data was identical with the previous report.[6]

Benzyl 3,6-*O*-di-benzyl-4-*O*-(3:4-*O*-isopropylidene 2,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-*β*-D-glucopyranoside (S23)

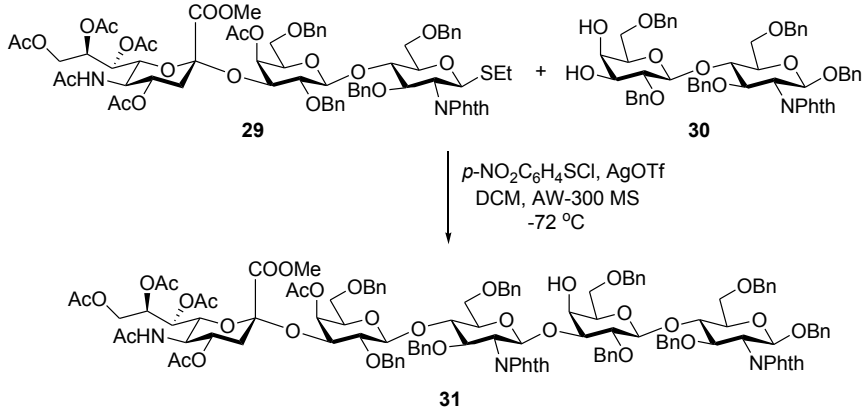
The solution of compound **S22** (400 mg, 0.67 mmol) and activated powdered 4 Å molecular sieves in dry DMF (8 mL) was stirred at room temperature under an argon atmosphere for 30 min. Then the mixture was cooled to 0 ^{o}C and the benzyl bromide (0.95 mL, 8.00 mmol) was added. After 10 min, NaH (60%, 160 mg, 4.00 mmol) was added portionwise. The reaction was further stirred for 3 h at this temperature and then was quenched by AcOH (0.5 mL). The reaction was diluted with DCM (200 mL) and solid was filtered off through a pad of Celite. The filtrate was washed with saturated NH_4Cl (aq.) (×3), $NaHCO_3$ (aq.) (×3), water and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 4 : 1) to afford compound **S23** (419 mg, 66%) as foam. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53–7.77 (m, 4H), 7.22–7.40 (m, 16H), 7.01–7.09 (m, 5H), 6.96–6.98 (m, 2H), 6.82–6.85 (m, 3H), 5.12 (d, 1H, *J* = 8.0 Hz), 4.78–4.83 (m, 3H), 4.73 (d, 1H, *J* = 11.8 Hz), 4.73 (d, 1H, *J* = 12.1Hz), 4.55 (d, 1H, *J* = 12.0 Hz), 4.48 (d, 1H, *J* = 12.4 Hz), 4.38–4.45 (m, 4H), 4.23–4.31 (m, 2H), 4.06–4.09 (m, 2H), 4.03 (t, 1H, *J* = 6.5 Hz), 3.92 (dd, 1H, *J* = 3.8, 10.9 Hz), 3.72–3.76 (m, 2H), 3.67 (dd, 1H, *J* = 6.2, 10.0 Hz), 3.55–3.61 (m, 2H), 3.35 (t, 1H, *J* = 7.7 Hz), 1.36 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.78, 167.52, 138.66, 138.36, 138.33, 138.23, 137.26, 133.50, 131.63, 128.31, 128.30, 128.19, 128.07, 128.06, 127.94, 127.84, 127.75, 127.54, 127.49, 127.44, 126.91, 123.11, 102.31, 97.30, 80.48, 79.30, 78.17, 75.10, 74.27, 73.73, 73.41, 73.36, 73.14, 72.04, 70.58, 69.06, 67.85, 55.65, 27.90, 26.35. HRMS (ESI) Calcd for $C_{58}H_{59}NO_{12}Na$ $[M+Na]^+$: 984.3935, found: 984.3924.



Benzyl 3,6-*O*-di-benzyl-4-*O*-(2,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-2-deoxy-2-*N*-phthalimido-*β*-D-glucopyranoside (30)

To the solution of compound **S23** (493 mg, 0.51 mmol) in the mixture of MeOH/DCM (1 : 1, 20 mL), $KHSO_4$-SiO_2 (100 mg) was added. After being stirred at room temperature for 4 h and the material was completely consumed according to TLC analysis, the solution was neutralized with Et_3N, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 2 : 1) to afford compound **30** (406 mg, 86%) as foam. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53–7.78 (m, 4H), 7.26–7.38 (m, 18H), 7.04–7.09 (m, 5H), 6.98–6.99 (m, 2H), 6.82–6.83 (m, 3H), 5.12 (d, 1H, *J* = 8.0 Hz), 4.88 (d, 1H, *J* = 11.6 Hz), 4.83 (d, 1H, *J* = 12.5 Hz), 4.80 (d, 1H, *J* =12.5 Hz), 4.72 (d, 1H, *J* = 11.6 Hz), 4.65 (d, 1H, *J* = 12.1 Hz), 4.41–4.50 (m, 6H), 4.23–4.31 (m, 2H), 4.12 (t, 1H, *J* = 9.6 Hz), 3.95 (s, 1H), 3.91 (dd, 1H, *J* = 3.7, 11.0 Hz), 3.66 (dd, 1H, *J* = 6.1, 10.0 Hz), 3.55–3.60 (m, 2H), 3.45–3.47 (m, 2H), 3.39 (t, 1H, *J* = 5.2 Hz), 2.66 (s, 1H), 2.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.67, 167.55, 138.58, 138.25, 138.08, 137.70, 137.08, 133.45, 131.47, 128.39, 128.31, 128.20, 128.10, 127.98, 127.86, 127.81, 127.71, 127.66, 127.54, 127.48, 127.41,

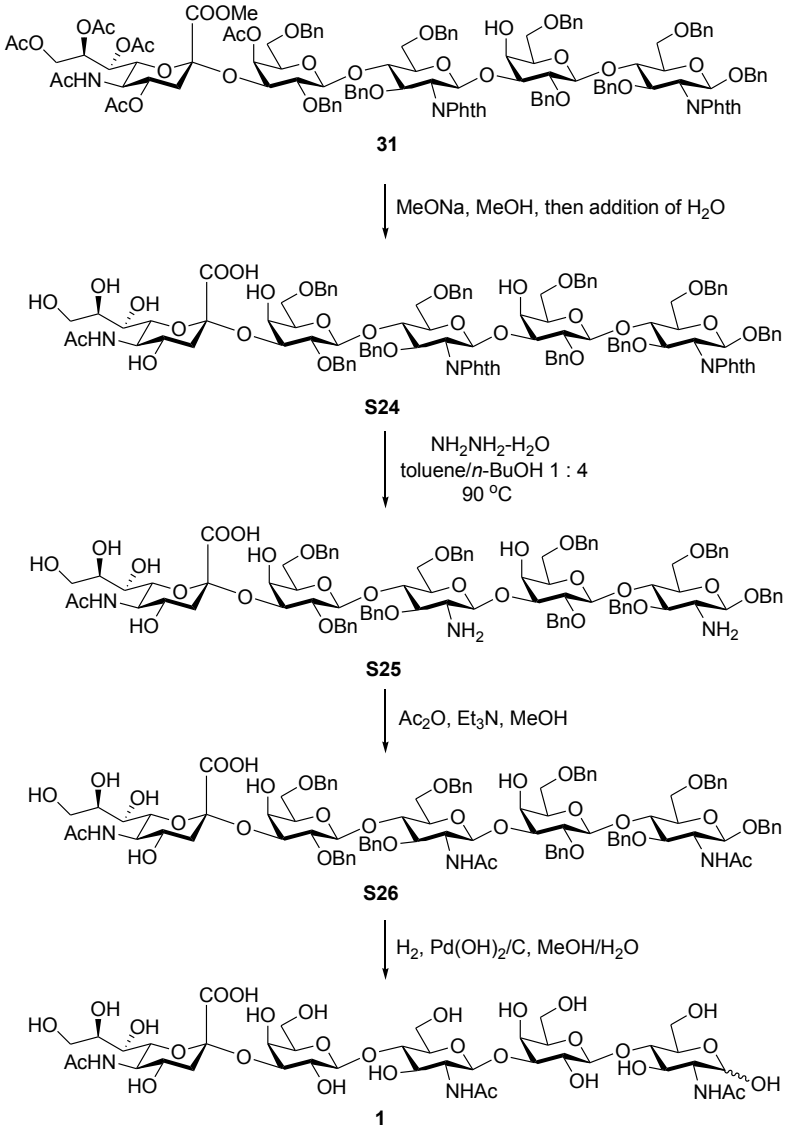
126.81, 123.01, 102.87, 97.13, 79.88, 77.99, 75.02, 74.90, 74.21, 73.37, 73.34, 73.05, 72.76, 70.50, 69.05, 69.00, 67.82, 55.54. HRMS (ESI) Calcd for $C_{55}H_{55}NO_{12}Na$ $[M+Na]^+$: 944.3622, found: 944.3609.



Pentasaccharide (31)

The solution of donor **29** (180 mg, 130 μmol, 1.0 eq), acceptor **30** (156 mg, 169 μmol, 1.3 eq), AgOTf (100 mg, 390 μmol, 3.0 eq) and activated AW 300 molecular sieves in dry DCM (4 mL) was stirred at room temperature under an argon atmosphere for 30 min. Then the mixture was cooled to -72 ^oC and the solution of *p*-nitrobenzenesulfenyl chloride (29.5 mg, 156 μmol, 1.2 eq) in dry DCM (0.5 mL) was added. The reaction was further stirred for 30 min at -72 ^oC and gradually warmed to room temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of Et_3N (0.5 mL). The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (toluene : acetone = 7 : 3) to afford compound **31** (220 mg, 75%) as foam. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (bs, 1H), 7.64 (bs, 2H), 7.46–7.52 (m, 6H), 7.39 (t, 2H, *J* = 7.4 Hz), 7.18–7.32 (m, 27H), 6.93–7.13 (m, 12H), 6.78–6.86 (m, 7H), 5.58–5.61 (m, 1H), 5.36 (dd, 1H, *J* = 2.2, 8.3 Hz), 5.29 (d, 1H, *J* = 8.3 Hz), 5.12 (d, 1H, *J* = 10.2 Hz), 5.02 (d, 1H, *J* = 3.6 Hz), 4.89–4.98 (m, 2H), 4.84 (d, 1H, *J* = 12.0 Hz), 4.78 (d, 1H, *J* = 12.3 Hz), 4.69–4.72 (m, 3H), 4.52 (dd, 1H, *J* = 3.4, 9.7 Hz), 3.91–4.47 (m, 24H), 3.83 (s, 3H), 3.72–3.74 (m, 3H), 3.66 (dd, 1H, *J* = 5.3, 10.3 Hz), 3.46–3.59 (m, 5H), 3.23–3.42 (m, 6H), 3.15–3.17 (m, 1H), 2.84 (bs, 1H), 2.60 (dd, 1H, *J* = 4.6, 12.7 Hz), 2.35 (t, 1H, *J* = 7.4 Hz), 2.10 (s, 3H), 2.02 (s, 3H), 1.96 (s, 6H), 1.87 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.81, 170.52, 170.42, 170.06, 169.94, 169.87, 167.90, 139.19, 138.85, 138.72, 138.54, 138.47, 138.30, 138.16, 137.35, 133.58, 133.45, 131.72, 131.25, 128.30, 128.27, 128.25, 128.17, 128.11, 128.01, 127.90, 127.79, 127.78, 127.66, 127.57, 127.51, 127.39, 127.36, 127.34, 127.30, 126.97, 126.83, 126.76, 126.67, 126.50, 123.11, 102.22, 98.78, 97.39, 97.26, 83.60, 79.42, 77.57, 77.52, 75.14, 74.92, 74.88, 74.36, 74.33, 74.13, 73.70, 73.39, 73.29, 73.15, 73.01, 72.96, 72.31, 71.76, 70.45, 69.50, 69.34, 68.83, 68.63, 68.40, 68.09, 67.90, 67.51, 67.14, 62.01, 55.66, 53.10, 49.26, 37.60, 23.17, 21.22, 20.79,

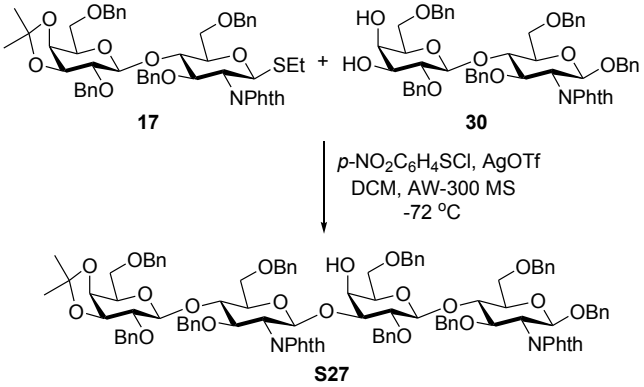
20.71, 20.64, 20.54. HRMS (MALDI) Calcd for $C_{125}H_{131}N_3O_{36}Na$ $[M+Na]^+$: 2272.8405, found: 2272.4792.



Pentasaccharide (1)

The solution of **31** (55 mg, 0.024 mmol) in anhydrous DCM (1 mL) and MeOH (1 mL) was treated with NaOMe (0.1 mL, 25% w/w in MeOH) and stirred for 18 h at room tempareture. The reaction was cooled to 0 ^oC by ice bath, and water (0.2 mL) was added. This mixture was warmed to room tempareture gradually and stirred overnight. Then the reaction was quenched with DOWEX 50W-X8 (H) resin until pH was adjusted to 6. The resin was filtered off and the filtrate was concentrated . The crude mixture **S24** was dissolved in toluene (1 mL) and *n*-BuOH (4 mL), and was treated with NH_2NH_2-H_2O (1 mL) at 90 ^oC for 72 h. The reaction mixture was concentrated and co-evaporated with toluene, then the crude free amine product **S25** was selectively acetylated with Ac_2O (0.5 mL) and Et_3N (0.5 mL) in MeOH (5 mL) at room temperature for 24 h. The acetylated mixture was

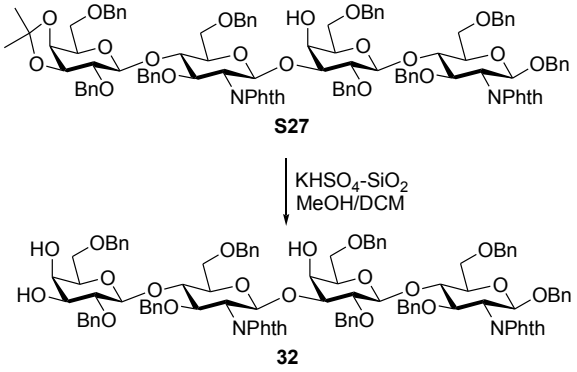
concentrated and passed through a short column with elution of DCM/MeOH to remove the excess salt. Then **S26**, $Pd(OH)_2/C$ (50 mg) in MeOH/H_2O (3 : 1, 4mL) was stirred at room tempareture under H_2 atmosphere for 3 days. The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on Bio-gel P2 (water) to afford the pentasaccharide **1** (12 mg, 47%). ^{1}H NMR (400 MHz, D_2O): δ = 5.11 (s, 1 H), 4.59–4.63 (m, 3H), 4.46 (d, 1H, *J* = 7.8 Hz), 4.37 (d, 1H, *J* = 7.8 Hz), 4.06 (d, 1H, *J* = 2.9 Hz), 4.02 (dd, 1H, *J* = 3.0, 9.9 Hz), 3.45–3.88 (m, 35 H), 2.66 (dd, 1H, *J* = 4.6, 12.4 Hz), 1.93 (s, 9H), 1.70 (t, 1H, *J* = 12.2 Hz). ^{13}C NMR (150 MHz, D_2O): δ = 174.87, 174.76, 174.32, 173.73, 102.87, 102.79, 102.68, 102.39, 99.65, 94.73, 90.37, 81.93, 81.90, 78.60, 78.20, 77.81, 75.34, 75.04, 74.76, 74.70, 74.41, 72.74, 72.36, 72.33, 72.26, 72.01, 71.63, 70.83, 70.13, 69.85, 69.25, 69.10, 68.41, 68.22, 68.19, 67.94, 67.33, 62.44, 60.91, 60.84, 60.77, 59.92, 59.79, 59.69, 56.02, 55.04, 53.55, 51.53, 39.48, 22.21, 22.02, 21.94, 21.89, 21.72. HRMS (ESI) Calcd for $C_{39}H_{64}N_3O_{29}$ $[M-H]^-$: 1038.3631, found: 1038.3629.



Tetrasaccharide (**S27)**

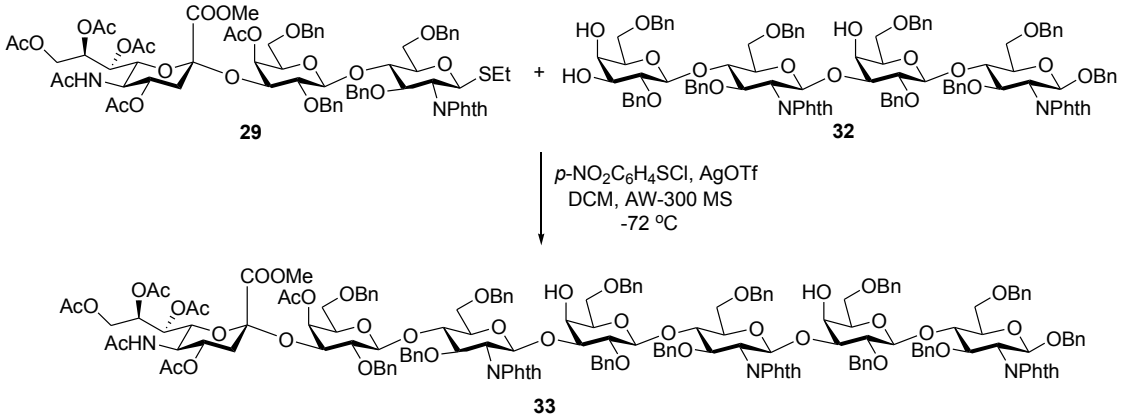
The solution of donor **17** (150 mg, 164 μmol, 1.0 eq), acceptor **30** (121 mg, 131 μmol, 0.8 eq), AgOTf (126 mg, 492 μmol, 3.0 eq) and activated powdered 4 Å molecular sieves in dry DCM (4 mL) was stirred at room temperature under an argon atmosphere for 30 min. Then the reaction mixture was cooled to -72 °C and the solution of *p*-nitrobenzenesulfenyl chloride (37.2 mg, 197 μmol, 1.2 eq) in dry DCM (0.5 mL) was added. The reaction was further stirred for 30 min at -72 °C and gradually warmed to room temperature. After the TLC analysis showed the donor was consumed completely, the reaction was quenched by addition of Et_3N (0.5 mL). The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 3 : 1) to afford compound **S27** (162 mg, 70%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.76 (m, 37H), 6.93–7.13 (m, 13 H), 6.78–6.82 (m, 8H), 5.34 (d, 1H, *J* = 8.0 Hz), 4.96 (d, 1H, *J* = 8.1 Hz), 4.69–4.85 (m, 5H), 4.54 (d, 1H, *J* = 12.0 Hz), 4.06–4.48 (m, 22H), 3.92–4.01 (m, 3H), 3.76–3.83 (m, 2H), 3.65–3.69 (m, 3H), 3.52–3.61 (m, 4H), 3.30–3.44 (m, 5H), 3.15–3.17 (m, 1H), 2.85 (s, 1H), 1.38 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.75, 167.47, 138.72, 138.41, 138.38, 138.32, 138.27, 138.20, 138.18, 137.84, 137.21, 133.47, 131.56,

131.11, 128.33, 128.28, 128.25, 128.22, 128.19, 128.13, 128.04, 127.95, 127.89, 127.83, 127.73, 127.59, 127.43, 127.34, 127.32, 126.95, 126.72, 126.62, 126.41, 123.02, 109.74, 102.42, 102.17, 98.79, 97.12, 83.57, 80.50, 79.29, 78.25, 77.90, 77.52, 76.69, 74.90, 74.72, 74.44, 74.29, 73.66, 73.38, 73.33, 73.20, 73.14, 72.90, 72.80, 72.17, 70.39, 69.05, 68.97, 67.97, 67.64, 67.35, 55.60, 55.55, 27.87, 26.30. HRMS (ESI) Calcd for $C_{106}H_{106}N_2O_{23}Na$ $[M+Na]^+$: 1797.7079, found: 1797.7077.



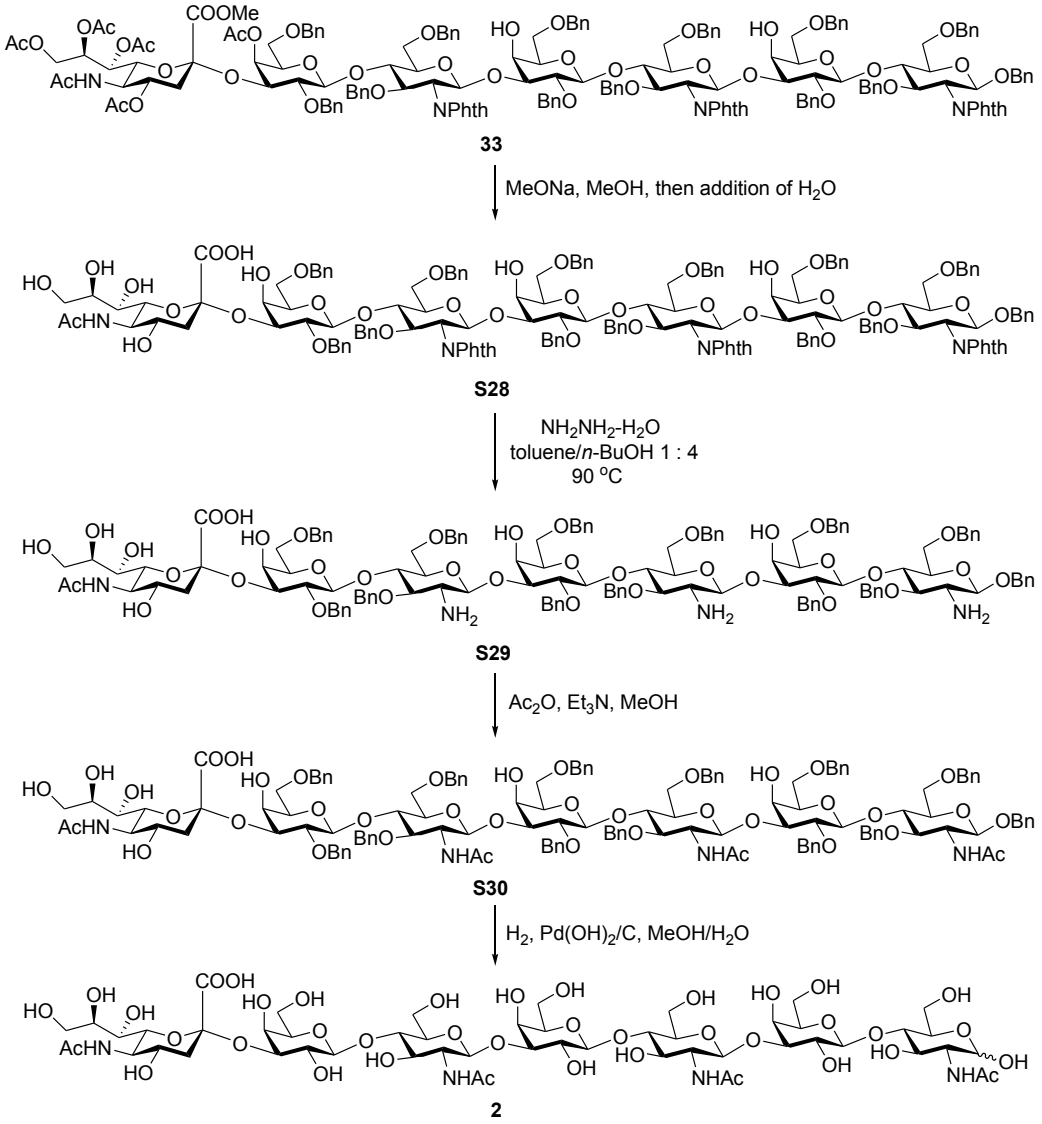
Tetrasaccharide (32)

To the solution of compound **S27** (162 mg, 91 μmol,) in the mixture of MeOH/DCM (1 : 1, 30 mL), $KHSO_4$-SiO_2 (50 mg) was added. After being stirred at room temperature for 4 h and the material was completely consumed according to TLC analysis, the solution was neutralized with Et_3N, filtered, and concentrated. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate = 2 : 1) to afford compound **32** (146 mg, 91%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.75 (m, 4H), 7.44–7.51 (m, 5H), 7.19–7.39 (m, 31H), 6.93–7.13 (m, 14H), 6.79–6.82 (m, 8H), 5.35 (d, 1H, *J* = 8.0 Hz), 4.96 (d, 1H, *J* = 8.0 Hz), 4.88 (d, 1H, *J* = 11.3 Hz), 4.85 (d, 1H, *J* = 11.0 Hz), 4.78 (d, 1H, *J* = 12.3 Hz), 4.73 (d, 1H, *J* = 11.2 Hz), 4.71 (d, 1H, *J* = 11.5 Hz), 4.02–4.51 (m, 24H), 3.92–3.97 (m, 2H), 3.81 (dd, 1H, *J* = 4.7, 10.8 Hz), 3.38–3.71 (m, 15H), 3.32 (d, 1H, *J* = 10.8 Hz), 3.15–3.17 (m, 1H), 2.81 (s, 1H), 2.66 (d, 1H, *J* = 2.9 Hz), 2.42 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.73, 167.46, 138.68, 138.44, 138.33, 138.27, 138.17, 137.76, 137.70, 137.16, 133.46, 131.52, 131.05, 128.49, 128.35, 128.31, 128.22, 128.16, 128.01, 127.93, 127.81, 127.70, 127.59, 127.56, 127.49, 127.41, 127.32, 127.31, 126.89, 126.70, 126.60, 126.35, 123.00, 103.07, 102.15, 98.78, 97.09, 83.54, 79.89, 77.86, 77.48, 76.68, 75.01, 74.88, 74.68, 74.26, 74.24, 73.41, 73.38, 73.29, 73.15, 72.93, 72.87, 72.77, 70.37, 69.14, 69.03, 68.95, 68.00, 67.66, 67.31, 55.58, 55.52. HRMS (ESI) Calcd for $C_{103}H_{102}N_2O_{23}Na$ $[M+Na]^+$: 1757.6766, found: 1757.6774.



Heptasaccharide (33)

The solution of donor **29** (98 mg, 70 μmol, 1.0 eq), acceptor **32** (146 mg, 84 μmol, 1.2 eq), AgOTf (64 mg, 252 μmol, 3.0 eq) and activated AW 300 molecular sieves in dry DCM (2 mL) was stirred at room temperature under an argon atmosphere for 30 min. Then the mixture was cooled to -72 ^{o}C and the solution of *p*-nitrobenzenesulfenyl chlorde (16 mg, 84 μmol, 1.2 eq) in dry CH_2Cl_2 (0.5 mL) was added. The reaction was further stirred for 30 min at -72 ^{o}C and gradually warmed to room temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of Et_3N (0.5 mL). The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (toluene : acetone = 7 : 3) to afford compound **33** (160 mg, 72%) as foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.75 (m, 4H), 7.37–7.47 (m, 13H), 7.21–7.26 (m, 34H), 7.05–7.11 (m, 9H), 6.98 (bs, 4H), 6.94 (bs, 6H), 6.78–6.83 (m, 12H), 5.59 (bs, 1H), 5.36 (d, 1H, *J* = 8.2 Hz), 5.30 (d, 1H, *J* = 6.9 Hz), 5.19 (d, 1H, *J* = 6.6 Hz), 5.12 (d, 1H, *J* =10.0 Hz), 4.89–5.02 (m, 4H), 4.69–4.86 (m, 6H), 3.88–4.53 (m, 39H), 3.83 (s, 3H), 3.67–3.75 (m, 5H), 3.29–3.59 (m, 20H), 3.14 (d, 1H, *J* = 8.8Hz), 2.84 (bs, 1H), 2.74 (bs, 1H), 2.60 (d, 1H, *J* = 10.2 Hz), 2.10 (s, 3H), 2.01 (s, 3H), 1.96 (s, 6H), 1.86 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.75, 170.49, 170.39, 170.05, 169.89, 169.83, 167.82, 139.10, 138.69, 138.55, 138.53, 138.39, 138.34, 138.29, 138.25, 138.16, 138.01, 137.82, 137.20, 133.42, 131.55, 131.09, 128.22, 128.17, 128.16, 128.03, 127.96, 127.94, 127.82, 127.70, 127.61, 127.58, 127.54, 127.50, 127.42, 127.41, 127.30, 127.15, 126.94, 126.78, 126.78, 126.69, 126.58, 126.38, 126.35, 102.28, 102.17, 102.14, 98.68, 98.66, 97.25, 97.10, 83.55, 83.37, 79.33, 77.89, 77.81, 77.61, 77.51, 77.20, 76.88, 73.58, 73.30, 73.26, 73.20, 72.92, 72.87, 72.18, 71.64, 70.38, 69.41, 69.06, 68.69, 68.52, 68.31, 67.98, 67.80, 67.70, 67.30, 66.99, 55.53, 53.06, 49.05, 37.50, 23.10, 21.19, 20.75, 20.67, 20.60, 20.47. HRMS (MALDI) Calcd for $C_{173}H_{178}N_4O_{47}Na$ $[M+Na]^+$: 3086.1554, found : 3086.2651.



Hepetasaccharide (2)

The solution of **33** (53 mg, 0.017 mmol) in dry DCM (1 mL) and MeOH (1 mL) was treated with NaOMe (0.1 mL, 25% w/w in MeOH) and stirred for 18 h at room tempareture. The reaction was cooled to 0 ^{o}C by ice bath, and water (0.2 mL) was added. This mixture was warmed to room tempareture gradually and was stirred overnight. Then the reaction was quenched with DOWEX 50W-X8 (H) resin until pH was adjusted to 6. The resin was filtered off and the filtrate was concentrated . The crude mixture **S28** was dissolved in toluene (1 mL) and *n*-BuOH (4 mL), and was treated with NH_2NH_2-H_2O (1 mL) at 90 ^{o}C for 72 h. The reaction mixture was concentrated and co-evaporated with toluene, then the crude free amine product **S29** was selectively acetylated with Ac_2O (0.5 mL) and Et_3N (0.5 mL) in MeOH (5 mL) at room temperature for 24 h. The acetylated mixture was concentrated and passed through a short column with elution of DCM/MeOH to remove the excess salt. Then **S30**, $Pd(OH)_2$/C (50 mg) in MeOH/H_2O (3 : 1, 4 mL) was stirred at room tempareture under

H_2 atmosphere. The solid was filtered off through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on Bio-gel P2 (water) to afford the heptasaccharide **2** (10 mg, 41%). ^{1}H NMR (600 MHz, D_2O): δ = 5.19 (s, 0.6H), 4.54 (d, 3H, *J* = 7.8 Hz), 4.44 (d, 3H, *J* = 7.8 Hz), 4.13 (bs, 2H), 4.10 (dd, 1H, *J* = 3.0, 9.9 Hz), 3.92–3.95 (m, 5H), 3.54–3.88 (m, 43H), 2.74 (dd, 1H, *J* = 4.6, 12.4 Hz), 2.01 (s, 12H), 1.78 (t, 1H, *J* = 12.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.25, 175.25, 175.06, 174.80, 174.21, 103.28, 103.22, 103.16, 103.11, 102.87, 100.14, 95.21, 90.85, 82.42, 82.39, 82.37, 79.07, 78.66, 78.48, 78.29, 75.82, 75.52, 75.22, 75.18, 74.89, 73.22, 72.81, 72.51, 72.49, 72.11, 70.61, 70.31, 69.73, 69.59, 68.70, 68.68, 68.65, 68.42, 67.81, 62.92, 61.39, 61.32, 60.39, 60.27, 60.17, 56.50, 55.52, 55.47, 54.03, 52.01, 39.97, 22.51, 22.37, 22.20. HRMS (ESI) Calcd for $C_{53}H_{87}N_4O_{39}$ $[M-H]^-$: 1403.4953, found: 1403.4947.

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