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

Peng Peng¹, Han Liu¹, Jianzhi Gong¹, John M. Nicholls² and Xuechen Li¹,³,⁴*  
E-mail: xuechenl@hku.hk

1. Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.  
2. Department of Pathology, Li Ka-Shing Faculty of Medicine, The University of Hong Kong, Hong Kong.  
3. The State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, Hong Kong.  
4. Shenzhen Institute of Research and Innovation of The University of Hong Kong, Shenzhen, P. R. China.

Table of Contents:  
General Remarks..................................................................................................................S2  
Synthesis of compound 5..................................................................................................S2  
Synthesis of compounds 8-10.........................................................................................S3-S4  
Synthesis of compound 11..............................................................................................S4-S5  
Synthesis of compound 12..............................................................................................S5  
Synthesis of compounds 13-16......................................................................................S5-S7  
Synthesis of compound 18 (via S1, S2 and 17)..............................................................S7-S9  
Synthesis of compound 23 (via S4-S6 and 19)..............................................................S9-S11  
Synthesis of compound 24 (via S8, S9 and 20)..............................................................S11-S13  
Synthesis of compound 25 (via S10 and S11)...............................................................S13-S15  
Synthesis of compound 26 (via S13-S15 and 21)........................................................S15-S17  
Synthesis of compound 27 (via S17-S19 and 22).........................................................S18-S20  
Synthesis of compound 29............................................................................................S20-S21  
Synthesis of compound 30 (via S20-S23)....................................................................S21-S24  
Synthesis of compound 31............................................................................................S24-S25  
Synthesis of compound 1 (via S24-S26).......................................................................S25-S26  
Synthesis of compound 32 (via S27)............................................................................S26-S27  
Synthesis of compound 33............................................................................................S28  
Synthesis of compound 2 (via S28-S30).......................................................................S29-S30  
Reference.........................................................................................................................S30  
Copies of ¹H, ¹³C and ³¹P NMR Spectra........................................................................S31-S117
**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 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in deuterated chloroform. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). High-resolution mass spectrometry was performed on a Bruker APEX IV or ABI 4800 MALDI TOF/TOF$^\text{TM}$. 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 by staining with acidic ceric ammonium molybdate. Column chromatography was performed employing Silica Gel 200-300 mesh.

**Ethyl [3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-ß-D-galactopyranosyl)-2-aminotriphenylphosphonium-2-deoxy-1-thio-ß-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$_2$Cl$_2$ under argon. The reaction mixture was stirred at 0 °C for 30 min. Then a solution of PPh$_3$ (2.6 g 10.1 mmol) in CH$_2$Cl$_2$ (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$_3$): $\delta = 7.83$–$7.88$ (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. $^1$
To the solution of compound 5 (500 mg, 0.49 mmol) in acetone (10 mL), was added KHCO₃ 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. ¹H NMR (600 MHz, CDCl₃): 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), 2.04 (s, 6H), 2.03 (s, 6H), 1.97 (s, 6H), 1.24 (t, 6H, J = 7.4 Hz). ¹³C NMR (150 MHz, CDCl₃): 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 C₃₅H₇₆N₂O₃₀NaS₂ [M+Na]: 1323.3776, found: 1323.3762.

To the solution of compound 5 (334 mg, 0.33 mmol) in acetonitrile (5 mL), Boc₂O (89.6 µL, 0.39 mmol) and Et₃N (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. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C NMR (150 MHz, CDCl₃): 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 C₅₃H₇₄N₂O₃₀NaS₂ [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-β-methoxylbenzylideneamino-1-thio-β-D-glucopyranoside (10)

Et$_3$N (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, 170.1, 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$_{46}$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$_3$N (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)
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. 1H NMR (400 MHz, CD3OD): 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). 13C NMR (75 MHz, CDCl3): 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 C26H44NO15S+ [M+Cl]+: 638.2113, found: 638.2152.

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)

Et3N (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 Et3N (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 Ac2O (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, NaHCO3 (aq.), and brine, dried over Na2SO4, 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. 1H NMR (400 MHz, CDCl3) 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,
at this temperature and moved to an oil bath at 90
(43 µL, 0.31 mmol) was added portion. After 2 h, a second portion of tetrachlorophthalic anhydride (64.7 mg, 0.24 mmol) and Et

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 Et₃N (100 µL, 0.72 mmol) in DCM/H₂O (1 : 1, 10 mL). The reaction was stirred at r.t. overnight and diluted with DCM (50 mL). The mixture was washed with NaHCO₃ (aq.) and brine, dried over Na₂SO₄, 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. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 C₂₀H₄₀Cl₃NO₁₇NaS [M+Na]⁺: 834.0975, found: 834.0972.

Ethyl 3,6-O-di-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-N-tetrachlorophthalalimido-1-thio-β-D-glucopyranoside (15)
Et₃N (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, tetrachlorophthalalimide (64.7 mg, 0.24 mmol) was added in one portion. After 2 h, a second portion of tetrachlorophthalalimide (64.7 mg, 0.24 mmol) and Et₃N (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 Ac₂O (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, NaHCO₃ (aq.), and brine, dried over Na₂SO₄, 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. ¹H NMR (300 MHz, CDCl₃): 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$_3$): $\delta = 170.33$, 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$_4$NO$_{17}$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$_2$O (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$_2$O (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$_2$SO$_4$, 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$_3$): $\delta = 5.36$ (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$_3$): $\delta = 170.30$, 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$_{39}$H$_{37}$Cl$_4$Na$_3$O$_{17}$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), K₂CO₃ (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 (Rf = 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. ¹H NMR (400 MHz, CDCl₃): 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]

**Ethyl 3,6-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 °C and benzyl bromide (1.70 mL, 12.5 mmol) was added. After 10 min, NaH (60%, 251 mg, 6.27 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 NH₄Cl (aq.) (×3), NaHCO₃ (aq.) (×3), water and brine, dried over Na₂SO₄, 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. ¹H NMR (400 MHz, CDCl₃): 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,
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), KHSO₄·SiO₂ (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 Et₃N, 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. ¹H NMR (400 MHz, CDCl₃): 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 I₂ (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 NaHCO₃ (aq.), Na₂S₂O₃ (aq.) and brine, dried over Na₂SO₄, 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. ¹H NMR (400 MHz, CDCl₃): 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$_2$SO$_4$, 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$_3$): $\delta$ = 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)

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$_3$): $\delta$ = 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$_3$): $\delta$ = 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$_7$PS [M-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$_3$N (2 mL) was added to the mixture of compound S5 (400 mg, 0.54 mmol) and salicyaldehyde (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$_3$): $\delta$ = 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).
The residue was purified by column chromatography on silica gel (washed with hexane), and the desired compound was obtained as a white solid. 

\[ \text{ethyl 3,4,6-O-tri-acetyl-2-deoxy-2-amino-1-thio-β-D-glucopyranoside hydrochloride (23)} \]

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. 

\[ \text{1H NMR (300 MHz, CDCl}_3\text{):} \delta = 8.75 (s, 3H), 5.76 (t, 1H, J = 9.4 Hz), 5.09 (d, 1H, J = 10.4 Hz), 5.01 (t, 1H, J = 10.0 Hz), 4.25 (dd, 1H, J = 4.9, 12.5 Hz), 4.12 (dd, 1H, J = 1.9, 12.3 Hz), 3.84–3.89 (m, 1H), 3.43 (t, 1H, J = 10.1 Hz), 2.80–2.88 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.37 (d, 3H, J = 7.4 Hz).} \]

\[ \text{13C NMR (75 MHz, CDCl}_3\text{):} \delta = 171.17, 170.53, 169.58, 81.95, 75.57, 71.43, 68.69, 61.96, 54.20, 25.04, 21.92, 20.68, 20.51, 15.16. \]


\[ \text{3,4,6-O-tri-benzyl-2-deoxy-2-iodo-α-D-mannopyranosyl azide (20)} \]

Glycal S7 (400 mg, 0.96 mmol) was dissolved in dry MeCN (4 mL) under argon. Then NIS (220 mg, 0.96 mmol) and TMSN₃ (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 NaHCO₃ (aq.) and diluted with DCM (100 mL). The organic layer was washed with NaHCO₃ (aq.), Na₂S₂O₃ (aq.) and brine, dried over Na₂SO₄, 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. 

\[ \text{1H NMR (400 MHz, CDCl}_3\text{):} \delta = 7.23–7.38 (m, 15H), 7.15–7.16 (m, 2H), 5.74 (s, 1H), 4.83 (d, 1H, J = 10.8 Hz), 4.71 (d, 1H, J = 12.0 Hz), 4.66 (d, 1H, J = 11.5 Hz), 4.47–4.53 (m, 3H), 4.35 (s, 1H), 3.90–4.00 (m, 2H), 3.80 (dd, 1H, J = 3.8, 11.1 Hz), 3.71 (d, 1H, J = 11.2 Hz), 3.16–3.19 (m, 1H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{):} \delta = 138.09, 137.92, 137.27, 128.46, 128.32, 128.30, 128.03, 127.96, 127.73, 127.66, 127.54, 91.36, 76.32, 75.28, 75.14, 74.25, \]

S11
73.39, 71.26, 68.44, 31.94. The spectroscopic data was identical with the previous report.\textsuperscript{[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 °C for 30 min. Then a solution of PPh\textsubscript{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.\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{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).\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{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.\textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}): δ = 40.1. HRMS (ESI) Calcd for C\textsubscript{47}H\textsubscript{60}NO\textsubscript{4}PS [M−I]: 754.3114, found: 754.3115.

Ethyl 3,4,6-O-tri-benzyl-2-deoxy-2-α-hydroxybenzylideneamino-1-thio-β-D-glucopyranoside (S9)

Et\textsubscript{3}N (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 mixture 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 S9 (52 mg, 85 %) as foam.\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{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).\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{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, 127.67, 127.47, 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.
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. 1H NMR (400 MHz, CDCl3): 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). 13C NMR (100 MHz, CDCl3): 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 C29H36NO8S [M+Na]+: 620.2365, found: 620.2359.

Benzyl [3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-acetaminotriphenylphosphonium-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 °C for 30 min. Then a solution of PPh3 (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. 1H NMR (400 MHz, CDCl3): 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). 13C NMR (100 MHz, CDCl3): δ = 170.46,
toluene (10 mL). The solvent was removed under vacuum, and the material was completely consumed according to TLC analysis. Aq B was removed

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

Et$_3$N (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$_3$): $\delta$ = 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$_3$): $\delta$ = 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$_3$OD): $\delta$ = 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$_3$): $\delta$ = 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-CI]$: 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 °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$_2$S$_2$O$_3$ (aq.) and brine, dried over Na$_2$SO$_4$, 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$_3$): $\delta$ = 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$_3$): $\delta$ = 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$_7$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 °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 NaHCO₃ (aq.) dried over Na₂SO₄, 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, CDCl₃): \(\delta = 5.64\) (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, CDCl₃): \(\delta = 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 C₂₃H₃₂N₃O₁₅Na [M+Na]+: 752.0770, found: 752.0767.

![Chemical structure of ethyl [3,6-di-O-acetyl-4-0-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-aminotriphenylphosphonium-2-deoxy-1-thio-β-D-glucopyranoside] iodide](image)

**Ethyl [3,6-di-O-acetyl-4-0-(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 °C for 30 min. Then a solution of PPh₃ (950 mg 3.62 mmol) in CH₂Cl₂ (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, CDCl₃): \(\delta = 7.76–7.87\) (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, CDCl₃): \(\delta = 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, CDCl₃): \(\delta = 39.7\). HRMS (ESI) Calcd for C₄₄H₆₃NO₁₅PS [M-I]+: 898.2868, found: 898.2868.

![Chemical structure of ethyl 3,6-O-di-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-deoxy-2-o-](image)

**Ethyl 3,6-O-di-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-deoxy-2-о-**
hydroxylbenzylideneamino -1-thio-β-D-glucopyranoside (S15)

Et₃N (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 °C 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, CDCl₃): 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).¹³C NMR (100 MHz, CDCl₃): δ = 170.45, 170.31, 170.22, 169.24, 169.09, 168.96, 167.76, 160.93, 131.81, 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 C₃₃H₄₂NO₁₆SNa [M+Na]⁺: 764.2195, found: 764.2075. Calcd for C₃₃H₄₂NO₁₆S [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, CDCl₃): 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).¹³C NMR (100 MHz, CDCl₃): δ = 170.48, 170.35, 169.32, 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 C₂₆H₄₀NO₁₅S [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-gulopyranosyl)-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$_2$S$_2$O$_3$ (aq.) and brine, dried over Na$_2$SO$_4$, 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$_{32}$O$_{17}$Na [M+Na]$^+$: 769.0811, found: 769.0811.

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

TMSN$_3$ (80 μL, 0.44 mmol) was added to the solution of iodoacetate S17 (1.64 g, 2.19 mmol) and TMSOTf (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$_2$SO$_4$, 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$_3$O$_{15}$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 °C for 30 min. Then a solution of PPh₃ (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. 

^1H NMR (400 MHz, CDCl₃): 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). 

^13C NMR (100 MHz, CDCl₃): δ = 170.60, 170.50, 170.28, 169.84, 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. 


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)

Et₃N (2.6 mL) was added to a mixture of compound S18 (1.03 g, 1.00 mmol) and salicyaldehyde (2 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 S19 (546 mg, 73 %) as foam. 

^1H NMR (400 MHz, CDCl₃): 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

= 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.31 (t, 1H, J = 7.4 Hz). 13C NMR (75 MHz, CDCl3): δ = 170.74, 170.54, 170.45, 169.86, 169.45, 169.31, 167.82, 160.94, 133.21, 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 C33H43NO16Na [M+Na]+: 764.2195, found: 764.2094. C33H44NO16S [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. 1H NMR (400 MHz, CDCl3): 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). 13C NMR (100 MHz, CDCl3): δ = 170.97, 170.57, 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 C26H40NO15S [M-Cl]: 638.2113, found: 638.2114.

Sialylated lactosamine trisaccharide building block (29)

The solution of sialic acid donor 28[1] (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 °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 NaHCO₃ (aq.) and brine, dried over Na₂SO₄, 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 Ac₂O (2 mL) at room temperature. DMAP (32 mg) was added at 0 °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. ¹H NMR (400 MHz, CDCl₃): 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]

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)

Et₃N (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 Et₃N (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 °C and Ac₂O (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, NaHCO₃ (aq.), and brine, dried over Na₂SO₄, 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. ¹H NMR (300 MHz, CDCl₃): 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,
\[ J = 12.1 \text{ Hz}, 4.49–4.58 (m, 3H), 4.26 (dd, 1H, \text{ } J = 8.5, 10.6 \text{ Hz}), 4.17 (dd, 1H, \text{ } J = 4.7, 11.9 \text{ Hz}), 4.01–4.03 (m, 2H), 3.77–3.92 (m, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H). \] 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-\(\beta\)-D-galactopyranosyl)-2-deoxy-2-N-phthalimido-\(\beta\)-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 (\(R_t = 0.3\), \(n\)-hexane : ethyl acetate = 1 : 3). Then the reaction was quenched by addition of triethylamine (0.5 mL) and the solvent was removed \textit{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\(_3\)): \(\delta = 7.70–7.79 (m, 4H), 7.02–7.11 (m, 5H), 5.25 (d, 1H, \text{ } J = 8.5 \text{ Hz}), 4.79 (d, 1H, \text{ } J = 12.3 \text{ 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-\(\beta\)-D-galactopyranosyl)-2-deoxy-2-N-phthalimido-\(\beta\)-D-glucopyranoside (S23)**

\(\text{S22}\)
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 °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 NH₄Cl (aq.) (×3), NaHCO₃ (aq.) (×3), water and brine, dried over Na₂SO₄, 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, CDCl₃): \(\delta = 7.53–7.77\) (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, \(J = 12.1\)Hz), 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, CDCl₃): \(\delta = 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 C₅₈H₉₁NO₁₂Na [M+Na]^+: 984.3935, found: 984.3924.

![S23](image-url)

**Benzyl 3,6-O-di-benzyl-4-O-(2,6-di-O-benzyl-\(\beta\)-D-galactopyranosyl)-2-deoxy-2-\(\beta\)-phthalamido-\(\beta\)-D-glucopyranoside (30)**

To the solution of compound S23 (493 mg, 0.51 mmol) in the mixture of MeOH/DCM (1 : 1, 20 mL), KHSO₄-SiO₂ (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 Et₃N, 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, CDCl₃): \(\delta = 7.53–7.78\) (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, CDCl₃): \(\delta = 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,
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 °C and the solution of p-nitrobenzenesulfonyl 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 °C and gradually warmed to room temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of Et3N (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, CDCl3): 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). 13C NMR (125 MHz, CDCl3): 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, 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 C55H55NO12Na [M+Na]+: 944.3622, found: 944.3609.
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 temperature. The reaction was cooled to 0 °C by ice bath, and water (0.2 mL) was added. This mixture was warmed to room temperature 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 NH₂NH₂·H₂O (1 mL) at 90 °C for 72 h. The reaction mixture was concentrated and co-evaporated with toluene, then the crude free amine product S25 was selectively acetylated with Ac₂O (0.5 mL) and Et₃N (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$_2$O (3 : 1, 4mL) was stirred at room tempature 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$_2$O): $\delta$ = 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$_2$O): $\delta$ = 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$_{30}$O$_{29}$ [M-H]: 1038.3631, found: 1038.3629.

![Tetrasaccharide (S27)](image)

**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 $^\circ$C and the solution of p-nitrobenzenesulfonyl 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 $^\circ$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$_3$N (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$_3$): $\delta$ = 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$_3$): $\delta$ = 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, 76.69, 74.90, 74.44, 74.29, 73.66, 73.38, 73.33, 73.20, 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\textsubscript{106}H\textsubscript{106}N\textsubscript{2}O\textsubscript{23}Na [M+Na]\textsuperscript{+}: 1797.7079, found: 1797.7077.

KHSO\textsubscript{4}·SiO\textsubscript{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\textsubscript{3}N, 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. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta=7.63-7.75\) (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). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta=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\textsubscript{103}H\textsubscript{102}N\textsubscript{2}O\textsubscript{23}Na [M+Na]\textsuperscript{+}: 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 °C and the solution of p-nitrobenzenesulfonyl chloride (16 mg, 84 µmol, 1.2 eq) in dry CH₂Cl₂ (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 reaction was complete, the reaction was quenched by addition of Et₂N (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.¹H NMR (400 MHz, CDCl₃): 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).¹³C NMR (100 MHz, CDCl₃): 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, 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 C₁₇₃H₁₇₈N₄O₄₇Na [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 temperature. The reaction was cooled to 0 °C by ice bath, and water (0.2 mL) was added. This mixture was warmed to room temperature gradually and was stirred overnight. Then the reaction was quenched with DOWEX 50WX8 (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$_2$NH$_2$-H$_2$O (1 mL) at 90 °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$_2$O (0.5 mL) and Et$_3$N (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$_2$O (3 : 1, 4 mL) was stirred at room temperature under
H₂ 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%). ¹H NMR (600 MHz, D₂O): 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). ¹³C NMR (150 MHz, CDCl₃): 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 C₅₃H₈₇N₄O₃₉ [M-H]: 1403.4953, found: 1403.4947.

Reference