Supporting Online Information for

Differential Receptor Binding Affinities of Influenza Hemagglutinins on Glycans Arrays

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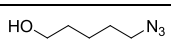
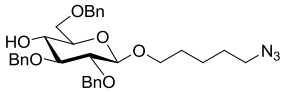
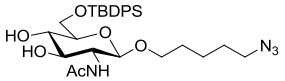
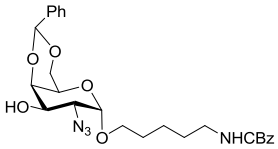
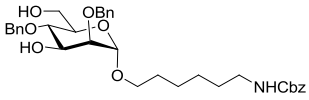
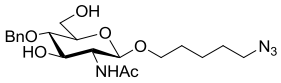
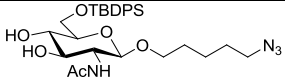
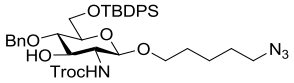
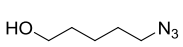
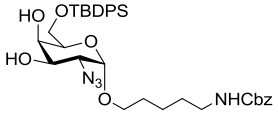
General. All chemicals were purchased as reagent grade and used without further purification. Anhydrous dichloromethane (CH_2Cl_2) and acetonitrile (CH_3CN) were purchased from a commercial source without further distillation. Pulverized Molecular Sieves MS-4Å (Aldrich) for glycosylation was activated by heating at 350 ^oC for 10 h. Reactions were monitored by analytical thin-layer chromatography (TLC) in EM silica gel 60 F254 plates and visualized under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate or *p*-anisadehyde. Flash chromatography was performed on silica gel (Merck) of 40-63 μm particle size. ^1H NMR spectra were recorded on a Bruker AVANCE 600 (600 MHz) spectrometer at 25 ºC. Chemical shifts (in ppm) were assigned according to $CDCl_3$ (δ = 7.24 ppm) and D_2O (δ = 4.80 ppm). ^{13}C NMR spectra were obtained with Bruker AVANCE 600 spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Coupling constants (*J*) are reported in hertz (Hz). Splitting patterns are described by using the following abbreviations: s, singlet; brs, broad singlet; d doublet; brd, broad doublet; t, triplet; q, quartet; dt, triplet of doublet; tt, triplet of triplet; qt, triplet of quartet; m, multiplet. High resolution ESI mass spectra were recorded on a Bruker Daltonics spectrameter.

Synthesis of α2,3 and α2,6 Sialosides by using compound B or C as a building block.

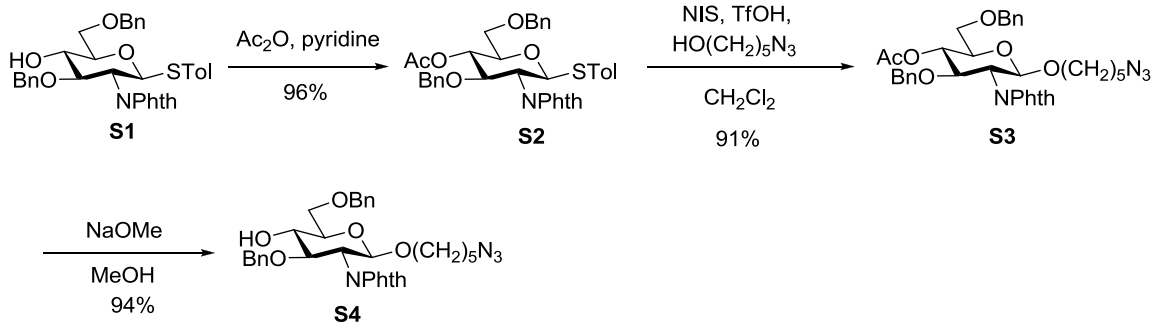
Trisaccharide compounds **1-9**, **13-14**, **22**, **24**, **26-28** can be synthesized by using disaccharides **A** or **B** as a donor and different kind of acceptors in TMSOTf (disaccharide **A**) and NIS/TfOH (disaccharide **B**) promoted glycosylation under different conditions. Their glycosylation conditions and yields are listed in table S1.

Table S1. Synthesis of Sialosides from Sialylated Disaccharide **A** and **B**.

D[a]	Acceptor	Promoter/ Solvent	T(°C)		Yield[b]	No.[c]
A		TMSOTf/CH_2Cl_2	0		83%	**1**
		TMSOTf/CH_2Cl_2	-45→0		82%	**2**
		TMSOTf/CH_2Cl_2	-10→5	C4	32%	**3**, **4, 5**
				C3	35%	**6**, **7**
		TMSOTf/CH_2Cl_2	-45→0		75%	**8**
		TMSOTf/CH_2Cl_2	-45→0	C6[d]	21%	**9**
				C6 and C3 42%		**14**
		TMSOTf/CH_2Cl_2	-45→0	C3 and C6 58%		**13**
B		NIS/TfOH/CH_2Cl_2	-30	C3	53%[e]	**27**
				C4	6%	**24, 28**
		NIS/TfOH/CH_2Cl_2	-30		71%	**27**
		NIS/TfOH/CH_2Cl_2	-30		86%	**22**
		NIS/TfOH/CH_2Cl_2	-30		58%	**26**

[a]Disaccharide donor [b]Isolated yields [c]The numbering of representative glycans in the libray [d]The position of free hydroxyls that are glycosylated by disaccharide [e]With 32% simultaneously C-3 and C-4 glycosylated product

Scheme S1. Synthesis of general acceptor compound S4.



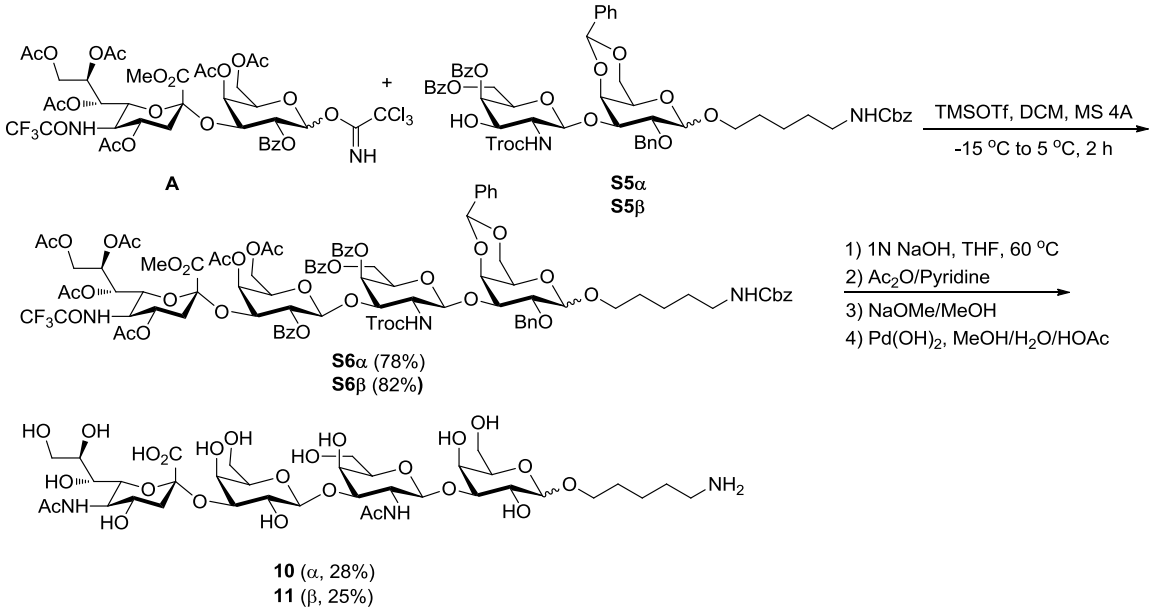
Synthesis of 5-Azidopentyl-*O*-(*p*-tolyl-2,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalimido-α-D-glucopyranoside) (S**4**)

To a solution of *p*-tolyl-2,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalimido-1-thio-α-D-glucopyranoside **S1**[1] (1.0 g, 1.68 mmol) in pyridine (10 mL) was added acetic anhydride (10 mL) at 0 ^{o}C. After being stirred at room temperature for 2 h, the reaction mixture was directly concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc/Hexane 1 : 3), to give **S2** (1.0 g, 96%) as white foam.

A solution of **S2** (500 mg, 0.78 mmol), 5-azido-pentanol (373 mg, 1.55 mmol) and pulverized activated molecular sieves (MS 4Å , 2 gmmol^{-1}) in dry CH_2Cl_2 (10 mL) was stirred under argon at room temperature for 2 h. The reaction mixture was then cooled to -40 ^{o}C followed by addition of NIS (420 mg, 1.2 mmol) and 0.5 M TfOH solution in dry Et_2O (3 mL, 0.3 mmol). After being stirred for 3 h, the reaction mixture was diluted with dichloromethane and filtered through a pad of celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc/Hexane 1 : 2), to give **S3** (456.3 mg, 92%).

To a solution of **S3** (400 mg, 0.67 mmol) in dry MeOH (5 mL) was added NaOMe (25.3 mg, 0.47 mmol). After being stirred for 1 h, the reaction mixture was neutralized by the addition of Amberlite IR 120 (H^+) resin and kept stirred for 10 min. The residue was then filtered, concentrated *in vacuo*, and purified by silica gel column chromatography (EtOAc/Hexane 1 : 1), to give **S4** (378.3 mg, 94%) as white foam.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.8-6.9 (m, 14H), 5.11 (dd, *J* = 8.9, 0.6 Hz, 1H), 4.72 (d, *J* = 12.2 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.20 (dd, *J* = 10.7, 8.4 Hz, 1H), 4.12 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.82-3.73 (m, 4H), 3.63-3.60 (m, 1H), 3.36-3.32 (m, 1H), 3.19-3.10 (m, 1H), 1.51-1.03 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 167.6, 138.1, 137.5, 133.8, 133.8, 131.5, 131.5, 128.5, 128.1, 127.9, 127.8, 127.8, 127.4, 123.4, 123.1, 98.2, 78.6, 74.6, 74.3, 73.7, 73.3, 70.7, 69.1, 69.1, 55.3, 51.0, 44.6, 32.0, 28.7, 28.4, 28.2, 23.2, 23.0; HRMS (ESI-TOF, MNa^+) calcd for $C_{33}H_{36}N_4O_7Na$ 623.2482, found 623.2474.

Scheme S2. Synthesis of compounds **10** and **11**.



To a solution of acceptor **S5**β (158 mg, 0.14 mmol) and imidate **A** (200 mg, 0.19 mmol) in 10 mL of dichloromethane (CH_2Cl_2) was added powdered molecular sieves (MS 4Å , 500 mg). The mixture was stirred at room temperature for 2 h. After cooling to -15 ^oC, TMSOTf (5 μL, 0.03 mmol) was added, and the mixture was stirred at 0 to 5 ^oC for 2 h. The reaction mixture was quenched by the addition of triethylamine (0.2 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated sodium bicarbonate ($NaHCO_3$) aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (50-100% EtOAc in Hexane) to afford tetrasaccharide **S6**β (230 mg, 82%). In the same manner, the reaction of **S5**α and imidate **A** afforded **S6**α in 78% yield

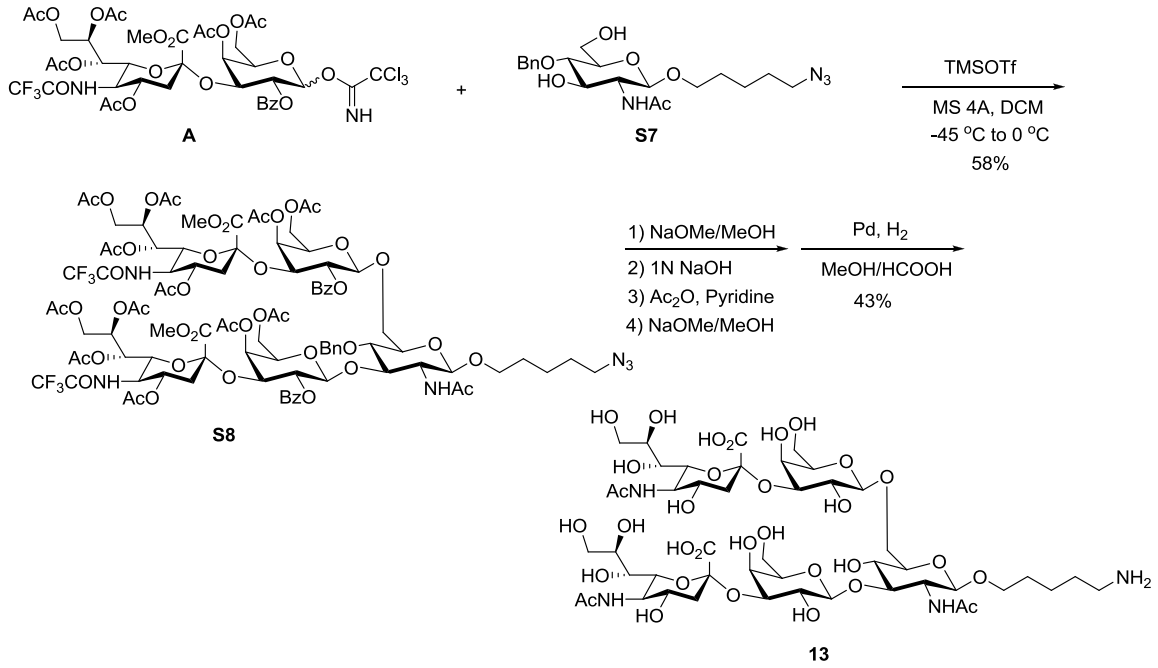
To a solution of **S6**β (230 mg, 0.115 mmol) in THF (5 mL) was added an aqueous solution of 1N NaOH (5 mL, 5.0 mmol), and the mixture was stirred at 50-60 ^oC for 24 h.

The reaction solution was concentrated to dryness under reduced pressure, and the residue was treated with pyridine (4 mL), AcOH (1 mL), and Ac_2O (2 mL). After stirred for 16 h, the mixture was diluted with EtOAc (50 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was dissolved in dry MeOH (5 mL), treated with NaOMe (28 mg), and stirred for 6 h. The reaction solution was neutralized with Amberlite IR-120, filtered, and concentrated. The residue was purified by reverse phase C-18 column chromatography to give diacetamide as colorless foam (74 mg, 52%).

To a solution of the diacetamide in a mixture of methanol, water and acetic acid (7 : 2 : 1, 10 mL) was added 20% $Pd(OH)_2$ in Carbon (110 mg), and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 16 h. After reaction was complete, the reaction mixture was filtered through a pad of Celite and concentrated. The residue was neutralized with ammonium hydroxide in water (28-30%), concentrated, and purified by reverse phase column chromatography (RP-18) to afford free amine compound **11**β (27 mg, 48%). In the same manner, compound **10**α were obtained in 28% yield from **S6**α.

Compound 12 was synthesized by reported procedures.[2]

Scheme S3. Synthesis of compound **13**

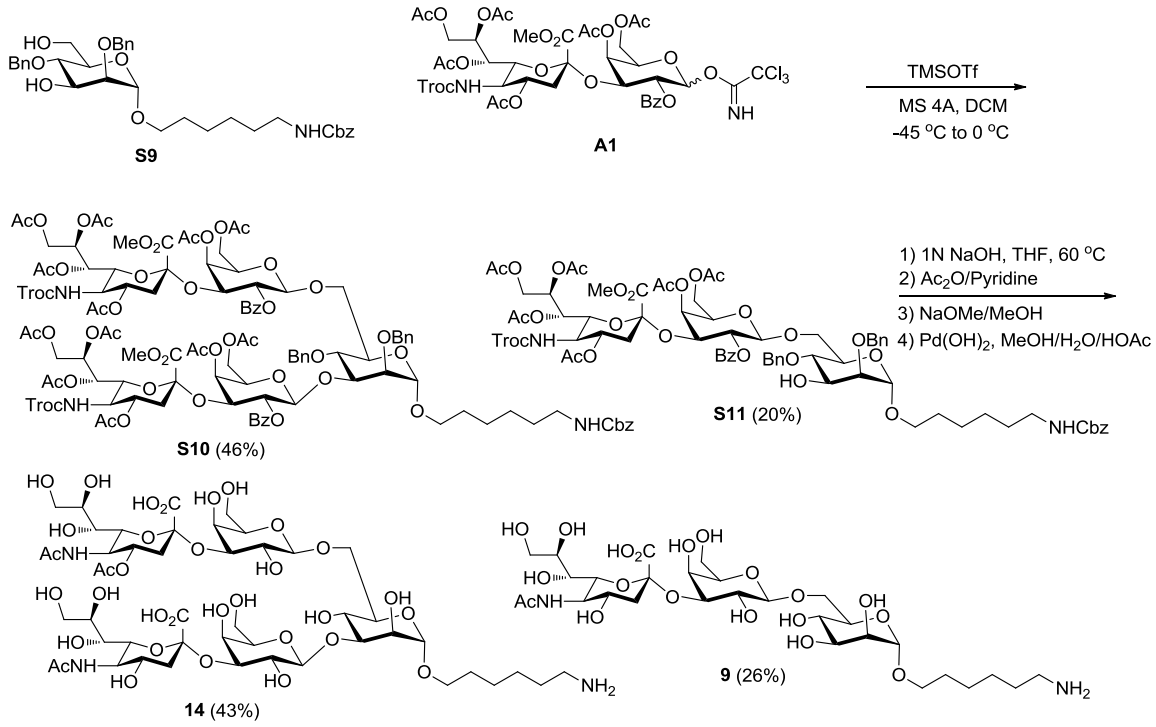


To a solution of acceptor **S7** (100 mg, 0.24 mmol) and imidate donor **A** (500 mg, 0.48 mmol) in 10 mL of dichloromethane (CH_2Cl_2) was added powdered molecular sieves (MS 4Å , 660 mg). The mixture was stirred at room temperature for 2 h. After cooling to -45 ^oC, TMSOTf (10 μL, 0.06 mmol) was added, and the mixture was allowed to slowly warm to 0 ^oC. A second portion of imidate (250 mg, 0.24 mmol) in 1.5 mL of dry CH_2Cl_2 was then added, and the reaction solution was stirred at 0 ^oC overnight. The reaction mixture was quenched by the addition of triethylamine (0.5 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated sodium bicarbonate ($NaHCO_3$) aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (50-100% EtOAc in Hexane) to afford pentasaccharide **S8** (300 mg, 57%).

To a solution of pentasaccharide **S8** (300 mg, 0.138 mmol) in anhydrous methanol (10.0 mL) was added NaOMe (18 mg), and the mixture was stirred for 3 h. The solvent and volatile products were removed under reduced pressure. The residue was dissolved in aqueous NaOH (1 N, 2.0 mL), stirred for 24 h, and concentrated. The residue was treated with pyridine (2.0 mL) and acetic anhydride (2.0 mL), and the solution was stirred for 16 h. The reaction mixture was diluted with ethyl acetate (50 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated. The acylated mixture was dissolved in anhydrous MeOH (5.0 mL) and treated with NaOMe (15 mg). The resulting mixture was stirred for 16 h, neutralized with Amberlite IR-120, filtered, and concentrated. The residue was purified by reverse phase chromatography (RP-18).

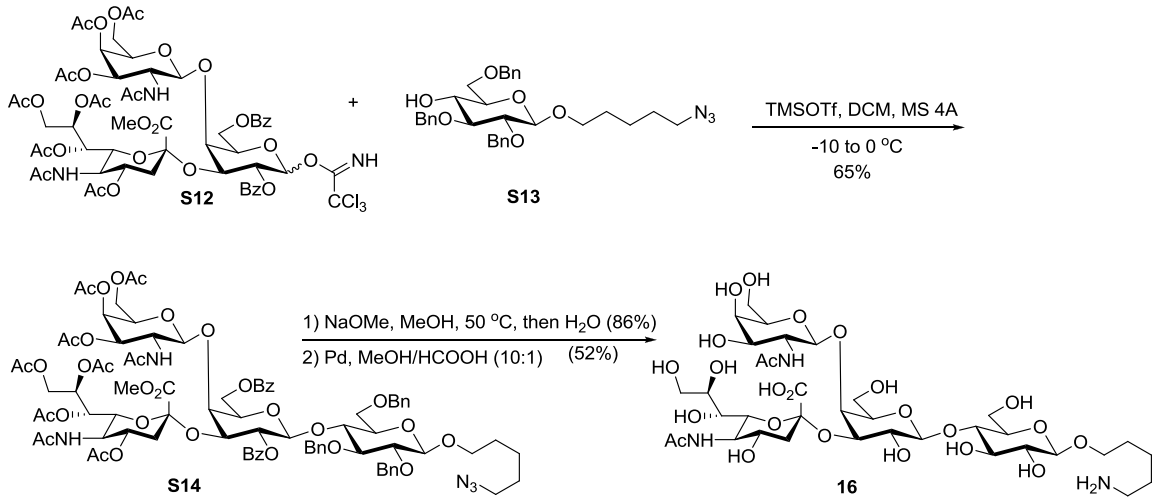
To a solution of the triacetamide in a mixture of methanol and formic acid (10 : 1, 10 mL) was added palladium black (50 mg), and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 16 h. After reaction was complete, the reaction mixture was filtered through a pad of Celite and concentrated. The residue was neutralized with ammonium hydroxide in water (28-30%), concentrated, and further purified by reverse phase column chromatography (RP-18) to afford free amine compound **13** (72 mg, 43%).

Scheme S4. Synthesis of Compounds 9 and 14.



To a solution of acceptor **S9** (103 mg, 0.17 mmol) and imidate donor **A1** (390 mg, 0.35 mmol) in 10 mL of dichloromethane (CH_2Cl_2) was added powdered molecular sieves (MS 4Å , 820 mg). The mixture was stirred at room temperature for 2 h. After cooling to -45 ^oC, TMSOTf (10 μL, 0.06 mmol) was added, and the mixture was allowed to slowly warm to 0 ^oC and stirred overnight. The reaction mixture was quenched by the addition of triethylamine (0.5 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated sodium bicarbonate ($NaHCO_3$) aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (50-100% EtOAc in Hexane) to afford pentasaccharide **S10** (202 mg, 46%) and trisaccharide **S11** (55 mg, 20%). Following the same deprotection procedures as described in compound **S6**β, compounds **9** and **14** were obtained in 26% and 43% yield, respectively.

Scheme S5. Synthesis of GM1 compound 16[3-4].



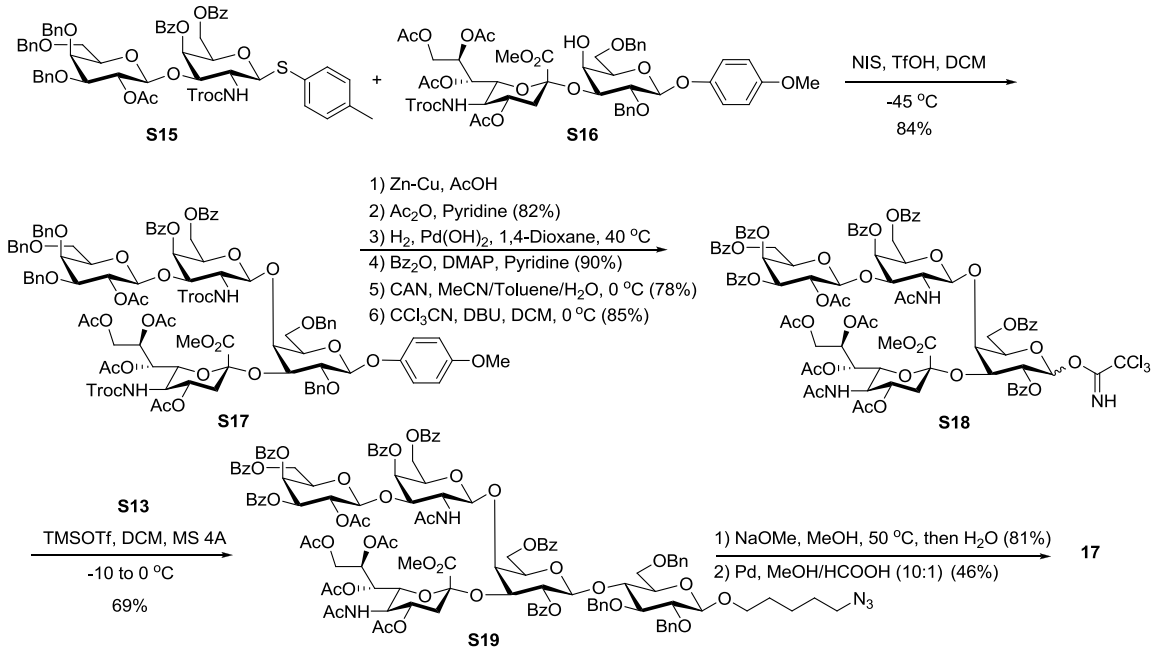
To a solution of the known imidate **S12** (227 mg, 0.17 mmol) and **S13** (146 mg, 0.26 mmol) in 6 mL of dichloromethane (CH_2Cl_2) was added powdered molecular sieves (MS 4Å , 780 mg). The mixture was stirred at room temperature for 2 h. After cooling to -10 ^oC, TMSOTf (5 μL, 0.03 mmol) was added, and the mixture was stirred at 0 ^oC for 3 h. The reaction mixture was quenched by the addition of triethylamine (0.5 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated sodium bicarbonate ($NaHCO_3$) aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (50-100% EtOAc in Hexane) to afford **S14** (192 mg, 65%).

To a solution of **S14** (192 mg, 0.111 mmol) in anhydrous methanol (5.0 mL) was added NaOMe (38 mg), and the mixture was stirred at 50 ^oC for 16 h. The solvent and volatile products were removed under reduced pressure. The residue was dissolved in aqueous NaOH (1N, 2.0 mL), stirred for 16 h, neutralized with Amberlite IR-120, filtered,

and concentrated. The residue was purified by reverse phase C-18 column chromatography to give intermediate as colorless foam (107 mg, 86%).

To a solution of the triacetamide (107 mg, 0.095 mmol) in a mixture of methanol and formic acid (10 : 1, 10 mL) was added palladium black (64 mg), and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 16 h. After reaction was complete, the reaction mixture was filtered through a pad of Celite and concentrated. The residue was neutralized with ammonium hydroxide in water (28-30%), concentrated, and further purified by reverse phase column chromatography (RP-18) to afford free amine compound **16** (30 mg, 34%).

Scheme S6. Synthesis of GM2 compound 17[3,5]**.**



To a solution of acceptor **S15** (110 mg, 0.10 mmol) and donor **S16** (165 mg, 0.14 mmol) in 5 mL of dichloromethane (CH_2Cl_2) was added powdered molecular sieves (MS

4Å , 500 mg). The mixture was stirred at room temperature for 2 h. After cooling to -45 ^{o}C, N-Iodosuccinimide (NIS; 51 mg, 0.23 mmol) and TfOH (5 μL, 0.06 mmol) was added, and the mixture was stirred at -45 ^{o}C for 2 h. The reaction mixture was quenched by the addition of triethylamine (0.2 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated $NaHCO_3$ and $Na_2S_2O_3$ aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (50-100% EtOAc in Hexane) to afford tetrasaccharide **S17** (176 mg, 84%).

To a solution of **S17** (176 mg, 0.084 mmol) in acetic acid (2.0 mL) was added Zn-Cu complex (2.1 g), and the mixture was stirred for 5 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered through celite. The filtrate was washed with saturated $NaHCO_3$ aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. Without purification the residue was treated with pyridine (2.0 mL) and acetic anhydride (1.0 mL), and the solution was stirred for 16 h. The reaction mixture was diluted with ethyl acetate (50 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash silica get chromatography (50-100% EtOAc in Hexane) to afford diacetamide (126 mg, 82%).

To a solution of the diacetamide (126 mg, 0.069 mmol) in 1,4-Dioxane (10.0 mL) was added 20% $Pd(OH)_2$ in Carbon (155 mg), and the reaction mixture was stirred at 40 ^{o}C under a positive pressure of hydrogen for 16 h. After reaction was complete, the reaction mixture was filtered through a pad of Celite and concentrated. The residue was

treated with pyridine (3.0 mL), benzoic anhydride (323 mg, 1.43 mmol), and DMAP (5 mg, 0.041 mmol), and the solution was stirred for 24 h. The reaction was quenched by the slow addition of methanol (0.6 mL) at 0 ^{o}C, and the volatile materials were removed under reduced pressure. The residue was extracted with dichloromethane (40 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash silica get chromatography (50-100% EtOAc in Hexane) to afford heptabenzoate (118 mg, 90%).

To a solution of heptabenzoate (118 mg, 0.062 mmol) in a mixture of toluene (4 mL), acetonitrile (3 mL), and water (3 mL) at 0 ^{o}C was added Ceric ammonium nitrate (CAN; 350 mg, 0.64 mmol), and the mixture was stirred at the same temperature for 1.5 h. The resulting dark solution was then diluted with EtOAc (50 mL), successively washed with water, saturated NaHCO3, and brine. The organic layer was dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (2-10% MeOH in CH_2Cl_2) to afford alcohol as an anomeric mixture (86 mg, 78%).

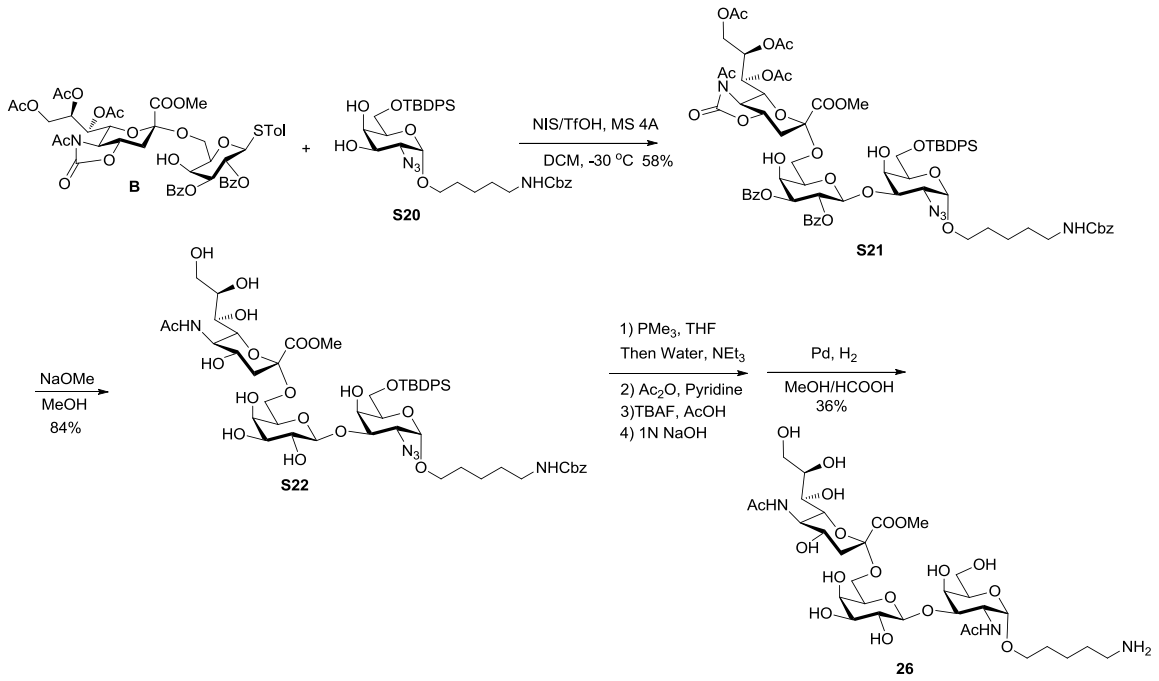
To a solution of anomeric alcohol (179 mg, 0.10 mmol) in dry CH_2Cl_2 (5 mL) was added trichloroacetonitrile (1.0 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 10 μL, 0.07 mmo). The mixture was stirred at 0 ^{o}C for 1 h, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (60-100% EtOAc in CH_2Cl_2) to afford product **S18** as an anomeric mixture (164 mg, 85%).

To a solution of the imidate **S18** (164 mg, 0.085 mmol) and **S13** (73 mg, 0.13 mmol) in 6 mL of dichloromethane (CH_2Cl_2) was added powdered molecular sieves (MS 4Å, 780 mg). The mixture was stirred at room temperature for 2 h. After cooling to -10 ^oC, TMSOTf (5 μL, 0.03 mmol) was added, and the mixture was stirred at 0 ^oC for 3 h. The reaction mixture was quenched by the addition of triethylamine (0.5 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated sodium bicarbonate ($NaHCO_3$) aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (50-100% EtOAc in Hexane) to afford **S19** (137 mg, 69%).

To a solution of **S19** (137 mg, 0.059 mmol) in anhydrous methanol (5.0 mL) was added NaOMe (38 mg), and the mixture was stirred at 50 ^oC for 16 h. The solvent and volatile products were removed under reduced pressure. The residue was dissolved in aqueous NaOH (1N, 2.0 mL), stirred for 16 h, neutralized with Amberlite IR-120, filtered, and concentrated. The residue was purified by reverse phase C-18 column chromatography to give intermediate as colorless foam (62 mg, 81%).

To a solution of the triacetamide (62 mg, 0.048 mmol) in a mixture of methanol and formic acid (10 : 1, 6 mL) was added palladium black (50 mg), and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 16 h. After reaction was complete, the reaction mixture was filtered through a pad of Celite and concentrated. The residue was neutralized with ammonium hydroxide in water (28-30%), concentrated, and further purified by reverse phase column chromatography (RP-18) to afford free amine compound **17** (24 mg, 46%).

Scheme S7. Synthesis of α(2,6)-linked compound **26**.



To a solution of acceptor **S20** (93 mg, 0.14 mmol) and thioglycoside **B** (143 mg, 0.15 mmol) in 5 mL of dichloromethane (CH_2Cl_2) was added powdered molecular sieves (MS 4Å , 400 mg). The mixture was stirred at room temperature for 2 h. After cooling to -30 ^oC, NIS (68 mg, 0.30 mmol) was added following by the addition of TfOH (0.2 mmol), and the mixture was stirred for 2 h until the donor was consumed. The reaction mixture was quenched by the addition of triethylamine (0.5 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated aq. $Na_2S_2O_3$ (10 mL) and aq. $NaHCO_3$ (10 mL), dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica get chromatography (EtOAc/Hexane 2:3) to afford trisaccharide **S21** (121 mg, 58%).

To a solution of trisaccharide **S21** (121 mg, 0.08 mmol) in anhydrous methanol (4.0 mL) was added NaOMe (15 mg), and the mixture was stirred for 5 h. The reaction

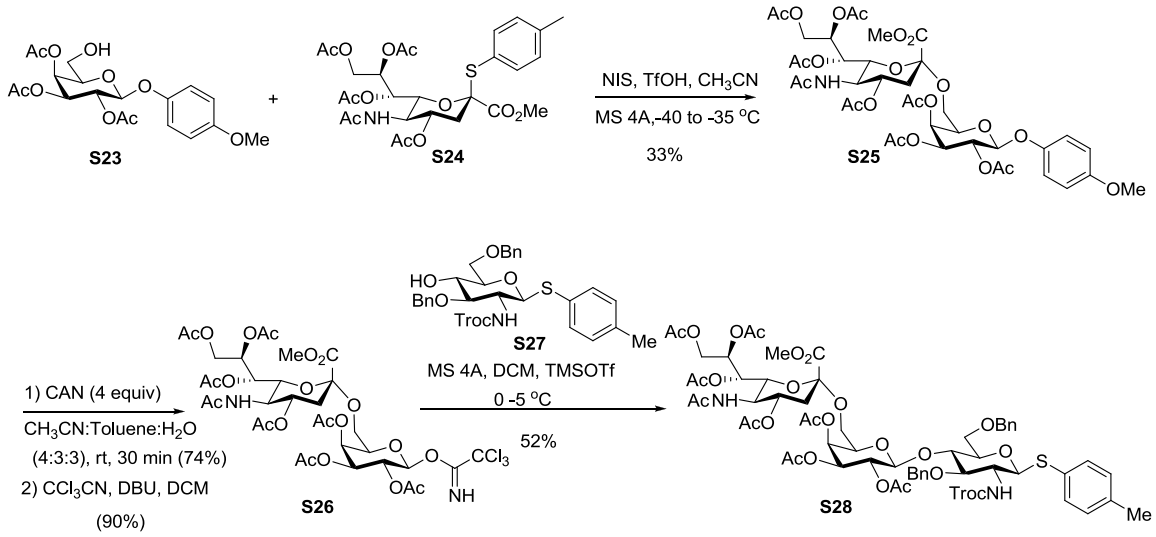
mixture was neutralized by the addition of Amberlite IR 120 (H^+) resin and kept stirring for 10 min. The residue was filtered, concentrated *in vacuo*, and purified by silica gel column chromatography (CH_2Cl_2/MeOH 8 : 1) to afford product **S22** (76 mg, 84%).

The trisaccharide **S22** (76 mg, 0.067 mmol) was dissolved in 1.0 mL of anhydrous THF and cooled to 0 ^oC. A solution of PMe_3 (1.0 mL, 1.0 M in THF) was added, and the resulting mixture was warmed to room temperature. After being stirred for 1 h, water (0.2 mL) and triethylamine (0.5 mL) was added, and the mixture was stirred for 16 h. The solvent and excess reagents were removed under reduced pressure. The residue was diluted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude was dissolved in a mixture of pyridine (2.0 mL) and acetic anhydride (1.0 mL), and the solution was stirred for 1 h. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated. To a flask containing the residue, AcOH (35 μL, 0.06 mmol) was added. The mixture was cooled to 0 ℃, and a 1 M solution of TBAF in THF (0.035 mL) was added. The reaction was stirred for 24 h until the starting material was consumed. The residue was diluted with ethyl acetate (10 mL) and washed with aqueous $NaHCO_3$ and brine. The organic layer was dried over MgSO4, filtered, and concentrated. The residue was dissolved in aqueous NaOH (1 N, 2.0 mL), stirred for 24 h, and concentrated. The residue was purified by reverse phase chromatography (RP-18).

To a solution of trisaccharide in a mixture of methanol and formic acid (10 : 1, 10 mL) was added palladium black (20 mg), and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 16 h. After the reaction was complete, the reaction mixture was filtered through a pad of celite and concentrated. The

residue was neutralized with ammonium hydroxide in water (28-30%), concentrated, and further purified by reverse phase column chromatography to afford free amine compound **16** (18.4 mg, 36%).

Scheme S8. Synthesis of α(2,6)-linked trisaccharide donor S28.



To a solution of acceptor **S23** (2.31g, 5.60 mmol) and thioglycoside donor **S24** (4.00 g, 6.69 mmol) in 40 mL of dry acetonitrile was added powdered molecular sieves (MS 4Å , 4.2 g). The mixture was stirred at room temperature for 2 h. After cooling to -40 ^{o}C, N-Iodosuccinimide (NIS; 1.55 g, 6.89 mmol) and TfOH (10 μL, 0.12 mmol) was added, and the mixture was stirred at -35 ^{o}C for 1 h. The reaction mixture was quenched by the addition of triethylamine (0.2 mL), filtered through celite, and washed with ethyl acetate. The filtrate was concentrated, and the resulting residue was dissolved in 200 mL of EtOAc, washed with saturated $NaHCO_3$ and $Na_2S_2O_3$ aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash

silica gel column chromatography (5-10% Ethanol in Toluene) to afford disaccharide **S25** as a colorless foam (1.66 g, 33%).

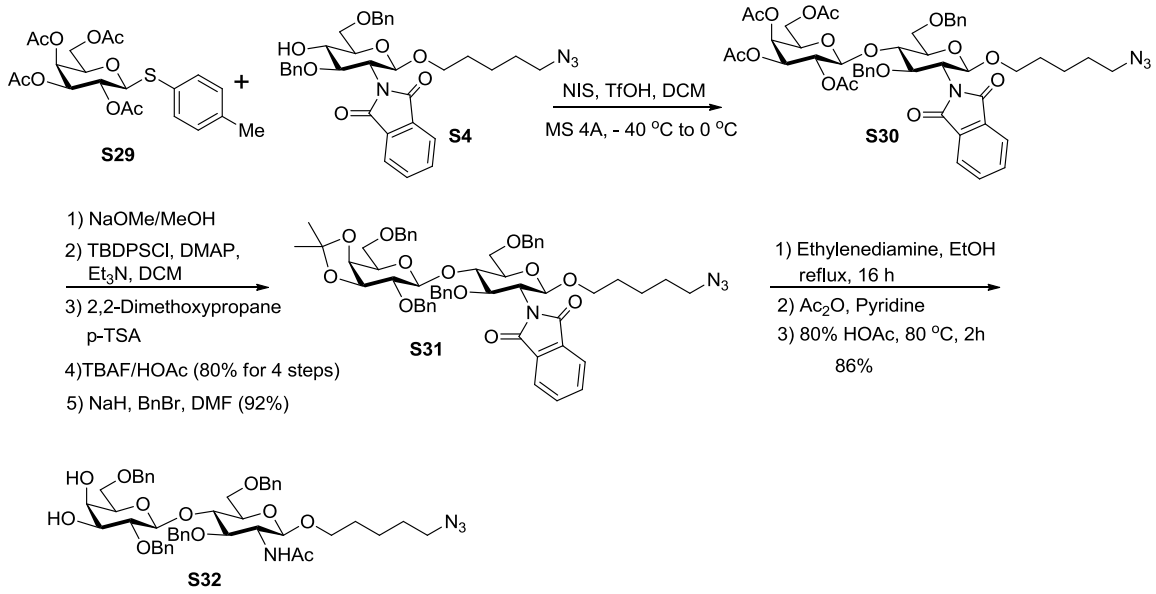
To a solution of disaccharide **S25** (288 mg, 0.32 mmol) in a mixture of toluene (8 mL), acetonitrile (6 mL), and water (6 mL) was added ceric ammonium nitrate (CAN; 350 mg, 0.64 mmol), and the mixture was stirred for 10 min at room temperature. A second portion of CAN (350 mg, 0.64 mmol) was added, and the mixture was stirred for another 10 min. The dark solution was then diluted with EtOAc (50 mL), successively washed with water, saturated NaHCO3, and brine. The organic layer was dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (60-100% EtOAc in CH_2Cl_2, then 10% MeOH in CH_2Cl_2) to afford alcohols as an anomeric mixture (188 mg, 74%).

To a solution of alcohols (188 mg, 0.24 mmol) in dry CH_2Cl_2 (5 mL) was added trichloroacetonitrile (1.0 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 10 uL, 0.07 mmo). The mixture was stirred at room temperature for 1 h, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (60-100% EtOAc in CH_2Cl_2) to afford product **S26** as an anomeric mixture (200 mg, 90%).

To a solution of acceptor **S27** (128 mg, 0.20 mmol) and imidate donor **S26** (203 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was added powdered molecular sieves (MS 4Å , 390 mg), and the mixture was stirred at room temperature for 2 h. After cooling to 0 ^oC in an ice-bath, TMSOTf (10 μL, 0.06 mmol) was added, and the resulting mixture was stirred at 0-5 ^oC overnight. The reaction solution was quenched by the addition of triethylamine

(0.5 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated sodium bicarbonate ($NaHCO_3$) aqueous solution, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified[6] by flash silica gel column chromatography (50-100% EtOAc in CH_2Cl_2) to afford trisaccharide **S28** (145 mg, 52%).

Scheme S9. Synthesis of LacNAc- acceptor S32.



To a solution of acceptor **S4** (4.51g, 7.51 mmol) and thioglycoside **S29** (5.10 g, 11.0 mmol) in 40 mL of dry CH_2Cl_2 was added powdered molecular sieves (MS 4Å , 4.88 g). The mixture was stirred at room temperature for 2 h. After cooling to -40 ^oC, N-Iodosuccinimide (NIS; 2.51 g, 11.2 mmol) and TfOH (65 μL, 0.78 mmol) was added, and the mixture was stirred at -40 ^oC for 1 h, and slowly warmed to 0 ^oC. The reaction mixture was quenched by the addition of triethylamine (0.5 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated aq. $Na_2S_2O_3$ (10 mL) and aq. $NaHCO_3$ (10 mL), dried over sodium sulfate (Na_2SO_4), filtered, and concentrated.

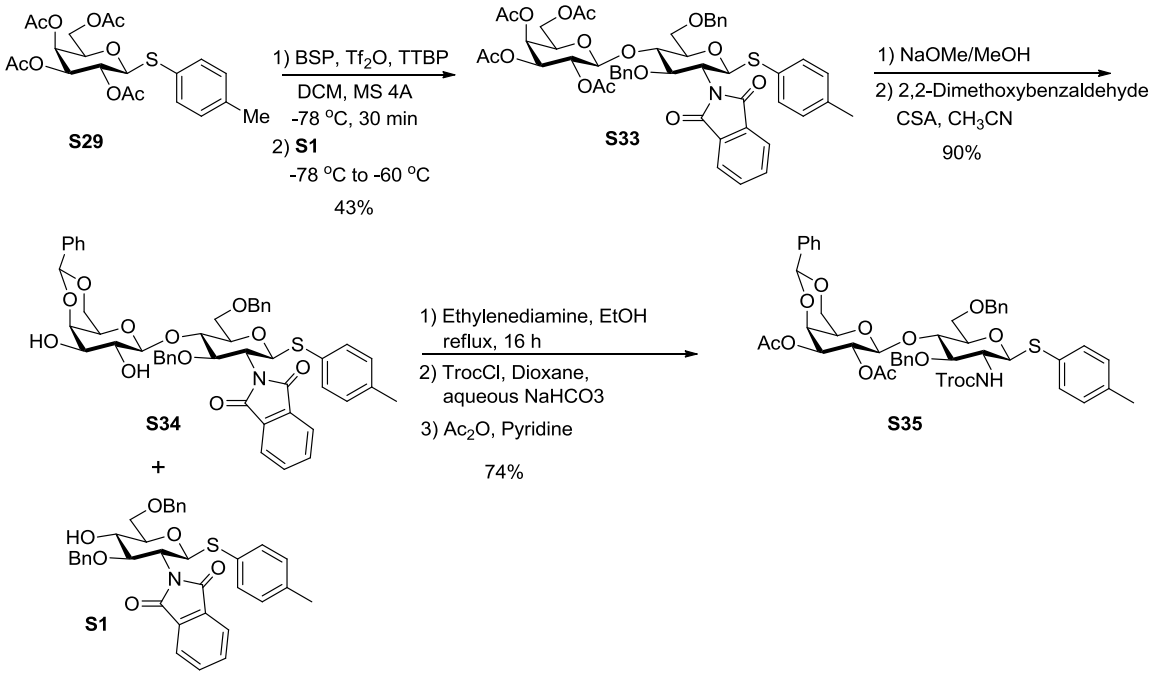
The residue was purified by flash silica gel column chromatography (30-70% EtOAc in Hexane) to afford disaccharide **S30** (5.96 g, 85%).

To a solution of **S30** (5.96 g, 6.40 mmol) in dry MeOH (60 mL) was added NaOMe (41 mg, 0.76 mmol). After being stirred for 3 h, the reaction mixture was neutralized by the addition of Amberlite IR 120 (H^+) resin, filtered through a pad of celite, and concentrated. The residue was dissolved in CH_2Cl_2 (40 mL), and treated with Et_3N (1.78 mL, 12.8 mmol), DMAP (122 mg, 1.0 mmol), and tert-Butylchlorodiphenylsilane (2.0 mL, 7.71 mmol). The mixture was stirred for 16 h, poured into 1N HCl aqueous solution, and extracted with CH_2Cl_2 (30 mL x 2). The combined organic layers were washed with water and brine, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. To the residue was added 2,2-dimethoxypropane (5.0 mL, 40.33 mmol) and DL-10-camphorsulfonic acid (100 mg, 0.43 mmol). The mixture was stirred for 1 h, poured into saturated aqueous NaHCO3 solution, and extracted with EtOAc /Hexane (1 : 1, 40 mL x 2). The organic layers were washed with brine, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. To the residue was added AcOH (0.74 mL, 12.9 mmol) and a 1M solution of TBAF in THF (12.9 mL, 12.9 mmol), and the resulting solution was stirred for 24 h. The reaction mixture was diluted with 100 mL of EtOAc, washed with saturated aqueous NaHCO3, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (20-80% EtOAc in Hexane) to afford diol (4.12 g, 80%) as a white foam. To a solution of diol (4.12 g, 5.13 mmol) in 20 mL of dry DMF was added NaH (60%, 820 mg, 20.52 mmol) and benzyl bromide (2.40 mL, 20.06 mmol). The mixture was stirred for 6 h, poured into water, and extracted with EtOAc /Hexane (1 : 1, 120 mL). The organic layer

was washed with water (40 mL x 3), dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (10-50% EtOAc in Hexane) to afford disaccharide **S31** (4.63 g, 92%) as a white foam.

To a solution of disaccharide **S31** (4.63 g, 4.71 mmol) in dry ethanol (80 mL) was added ethylenediamine (15.0 mL, 224.13 mmol). The mixture was refluxed for 16 h, cooled to room temperature, and concentrated under reduced pressure. The residue was diluted with EtOAc (50 mL), neutralized with 1N HCl until the PH value ~7.5, and extracted the aqueous layer with a second portion of EtOAc (50 mL) after layer separation. The combined organic layers were washed with water and brine, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. To the crude product was added pyridine (10.0 mL) and acetic anhydride (2.0 mL, 21.29 mmol), and the mixture was stirred for 1 h. The reaction mixture was concentrated, diluted with EtOAc (100 mL), and washed with cold 1N HCl, water, and aqueous NaHCO3 successively. The organic layer was dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. To the residue was added 80% HOAc (20 mL), and the mixture was stirred at 80 ^oC for 2-3 h. After cooled to room temperature, the solution was poured into saturated aqueous $NaHCO_3$ solution, and extracted with EtOAc (100 mL x 2). The combined organic layers were washed with water and brine, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (50-100% EtOAc in Hexane) to afford diol **S32** (3.45 g, 85.7%).

Scheme S10. Synthesis of LacNAc donor



To a solution of thioglycoside **S29** (500 mg, 1.10 mmol), 1-benzenesulfinyl piperidine (BSP; 250 mg, 1.19 mmol), and TTBP (534 mg, 2.15 mmol) in dry CH_2Cl_2 (15 mL) was added powdered molecular sieves (MS 4Å, 900 mg). The mixture was stirred at room temperature for 2 h. After cooling to -78 ^oC, trifluoromethanesulfonic anhydride (Tf_2O; 240 μL, 1.43 mmol) was added. The mixture was stirred at -78 ^oC for 30 min, a solution of acceptor **S1** (988 mg, 1.66 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise via a cannula. After stirring at -78 ^oC for 1 h, the solution was slowly warmed to -60 ^oC over 1 h, quenched by the addition of triethylamine (1.0 mL), diluted with CH_2Cl_2 (50 mL), filtered through celite, and washed with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over sodium sulfate

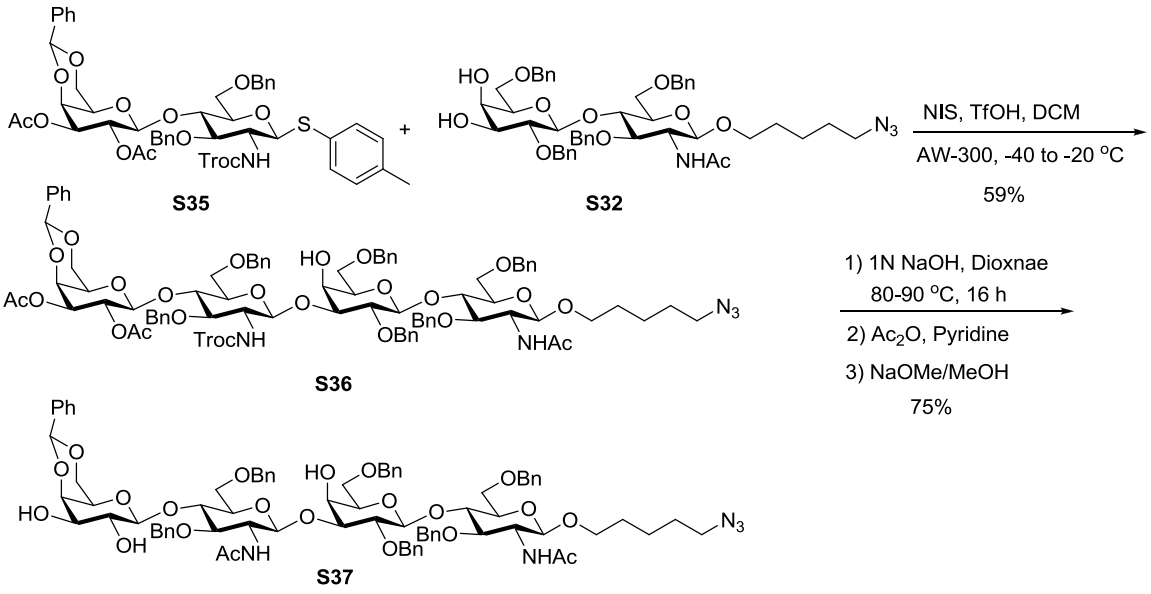
(Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (20-100% EtOAc in Hexane) to afford product **S33** (436 mg, 43%).

To a solution of **S33** (1.54 g, 1.66 mmol) in dry MeOH (20 mL) was added NaOMe (23 mg, 0.43 mmol). After being stirred for 16 h, the reaction mixture was neutralized by the addition of Amberlite IR 120 (H^+) resin, filtered through a pad of celite, and concentrated. The residue was dissolved in CH_3CN (40 mL), and treated with benzaldehyde dimethyl acetal (330 μL, 2.19 mmol) and DL-10-camphorsulfonic acid (40 mg, 0.17 mmol). The mixture was stirred for 3 h, poured into saturated aqueous NaHCO3, and extracted with EtOAc (120 mL). The organic layer was washed with brine, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (20-80% EtOAc in Hexane) to afford diol **S34** (1.27 g, 90%).

To a solution of **S34** (1.27 g, 1.50 mmol) in dry ethanol (20 mL) was added ethylenediamine (5.0 mL, 74.71 mmol). The mixture was refluxed for 16 h, cooled to room temperature, and concentrated under reduced pressure. The residue was diluted with EtOAc (20 mL), neutralized with 1N HCl until the PH value ~7.5, and extracted the aqueous layer with a second portion of EtOAc (50 mL) after layer separation. The combined organic layers were washed with water and brine, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. To a solution of crude product in 1,4-Dioxane (10.0 mL) and 1M $NaHCO_3$ (5.0 mL) was added 2,2,2-trichloroethyl chloroformate (0.42 mL, 3.05 mmol), and the mixture was stirred vigorously for 3 h. The reaction mixture was concentrated, diluted with EtOAc (100 mL), and washed with aqueous $NaHCO_3$. The

organic layer was dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. To the crude product was added pyridine (5.0 mL) and acetic anhydride (2.0 mL, 21.29 mmol), and the mixture was stirred for 16 h. The reaction mixture was concentrated, diluted with EtOAc (100 mL), and washed with cold 1N HCl, water, and aqueous $NaHCO_3$ successively. The organic layer was dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (20-60% EtOAc in Hexane) to afford **S35** (1.08 g, 74%).

Scheme S11. Synthesis of di-LacNAc acceptor S37.

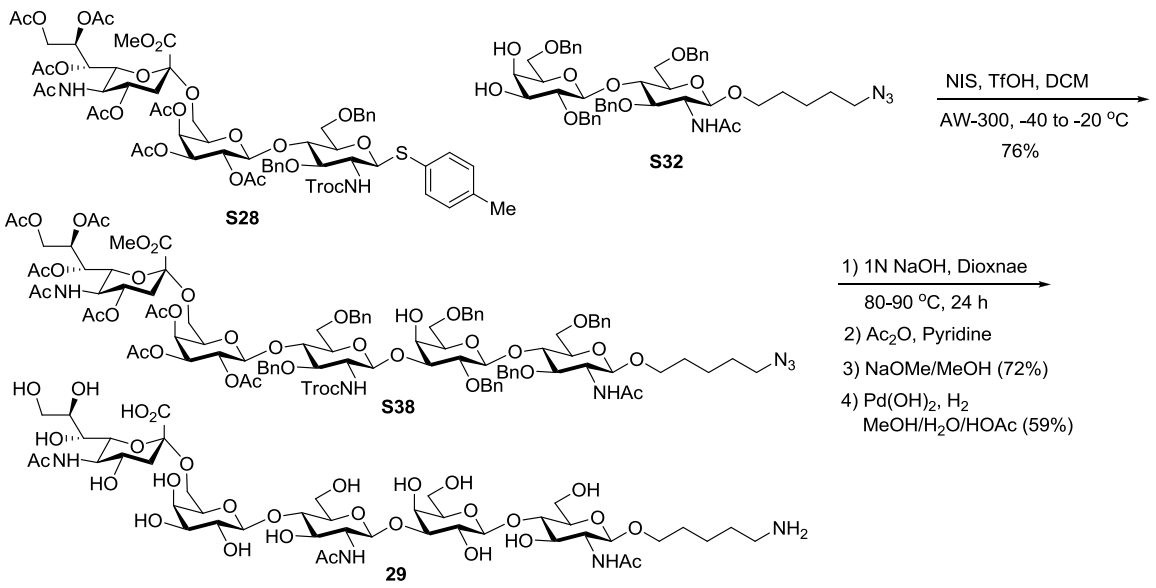


To a solution of acceptor **S32** (174 mg, 0.20 mmol) and thioglycoside **S35** (211 mg, 0.22 mmol) in 10 mL of dry dichloromethane (CH_2Cl_2) was added powdered molecular sieves (AW-300, 500 mg). The mixture was stirred at room temperature for 2 h. After cooled to -40 ^oC, NIS (70 mg, 0.30 mmol) and TfOH (5 μl, 0.06 mmol) was added successively. The mixture was stirred at -40 ^oC for 30 min, and then allowed to slowly

warm to -20 ^{o}C over 1 h. The reaction mixture was quenched by the addition of triethylamine (0.2 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (EtOAc/Hexane/DCM=1 : 1 : 1) to afford tetrasaccharide **S36** (211 mg, 59%).

To a solution of tetrasaccharide **S36** (211 mg, 0.124 mmol) in 1,4-Dioxane (6.0 mL) and 1N NaOH (1.5 mL) was heated at 80 ^{o}C for 24 h. The solvent and volatile products were removed under reduced pressure. The residue was treated with pyridine (2.0 mL) and acetic anhydride (1.0 mL), and the solution was stirred for 3 h. The excess reagents were removed under reduced pressure. The residue was diluted with EtOAc (50 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated. To the solution of crude in dry methanol (5.0 mL) was added NaOMe (45 mg, 0.83 mmol). After being stirred for 3 h, the reaction mixture was neutralized by the addition of Amberlite IR 120 (H^+) resin, filtered through a pad of celite, and concentrated. The residue was purified by flash silica gel column chromatography to afford di-LacNAc **S37** (134 mg, 75%).

Scheme S12. Synthesis of α(2→6) sialyl di-LacNAc compound 29.

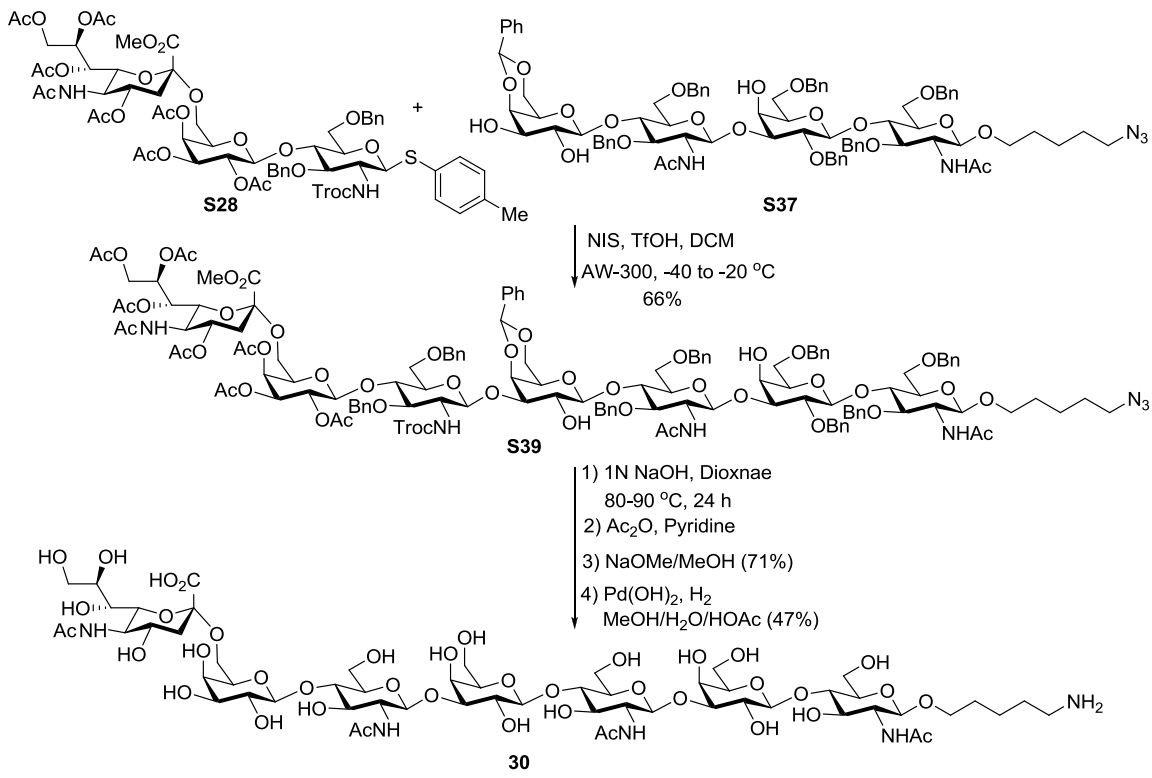


To a solution of acceptor **S32** (128 mg, 0.15 mmol) and thioglycoside donor **S28** (154 mg, 0.11 mmol) in 10 mL of dry dichloromethane (CH_2Cl_2) was added powdered molecular sieves (AW-300, 500 mg). The mixture was stirred at room temperature for 2 h. After cooled to -40 ^oC, NIS (45 mg, 0.20 mmol) and TfOH (5 ul, 0.06 mmol) was added successively. The mixture was stirred at -40 ^oC for 30 min, and then allowed to slowly warm to -20 ^oC over 1 h. The reaction mixture was quenched by the addition of triethylamine (0.2 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash silica gel column chromatography (60-100% EtOAc in Hexane) to afford pentasaccharide **S38** (178 mg, 76%).

To a solution of pentasaccharide **S38** (178 mg, 0.08 mmol) in 1,4-Dioxane (6.0 mL) and 1N NaOH (5.0 mL) was heated at 80-90 ^{o}C for 24 h. The solvent and volatile products were removed under reduced pressure. The residue was treated with pyridine (2.0 mL) and acetic anhydride (2.0 mL), and the solution was stirred for 16 h. The excess reagents were removed under reduced pressure. The residue was diluted with EtOAc (50 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated. To the solution of crude in dry methanol (5.0 mL) was added NaOMe (45 mg, 0.83 mmol). After being stirred for 3 h, the reaction mixture was neutralized by the addition of Amberlite IR 120 (H^+) resin, filtered through a pad of celite, and concentrated. The residue was purified by reverse phase column chromatography (10-80% MeOH in water) to afford all deprotective azido pentasaccharide (101 mg, 72%) as white foam.

To a solution of azido pentasaccharide (101 mg, 0.06 mmol) in a mixture of methanol (7.0 mL), water (3.0 mL) and Acetic acid (0.2 mL) was added palladium hydroxide (20% on Carbon, 114 mg), and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 16 h. The reaction mixture was filtered through a pad of celite and concentrated. The residue was neutralized with ammonium hydroxide in water (28-30%), concentrated, and further purified by reverse phase column chromatography (0-10% MeOH in water) to afford free amine **29** (40 mg, 59%).

Scheme S13. Synthesis of α(2→6) sialyl tri-LacNAc compound 30.



To a solution of acceptor **S37** (230 mg, 0.154 mmol) and thioglycoside donor **S28** (240 mg, 0.171 mmol) in 10 mL of dry dichloromethane (CH_2Cl_2) was added powdered molecular sieves (AW-300, 500 mg). The mixture was stirred at room temperature for 2 h. After cooled to -40 ^oC, NIS (45 mg, 0.20 mmol) and TfOH (5 μL, 0.06 mmol) was added successively. The mixture was stirred at -40 ^oC for 30 min, and then allowed to slowly warm to -20 ^oC over 1 h. The reaction mixture was quenched by the addition of triethylamine (0.2 mL), diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated. The residue was purified by flash

silica gel column chromatography (EtOAc/Hexane/DCM = 1 : 1 : 1) to afford heptasaccharide **S39** (280 mg, 66%).

To a solution of heptaasaccharide **S39** (280 mg, 0.101 mmol) in 1,4-Dioxane (6.0 mL) and 1N NaOH (5.0 mL) was heated at 80-90 ^{o}C for 24 h. The solvent and volatile products were removed under reduced pressure. The residue was treated with pyridine (2.0 mL) and acetic anhydride (2.0 mL), and the solution was stirred for 16 h. The excess reagents were removed under reduced pressure. The residue was diluted with EtOAc (50 mL), washed with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, filtered, and concentrated. To the solution of crude in dry methanol (5.0 mL) was added NaOMe (45 mg, 0.83 mmol). After being stirred for 3 h, the reaction mixture was neutralized by the addition of Amberlite IR 120 (H^+) resin, filtered through a pad of celite, and concentrated. The residue was purified by reverse phase column chromatography (30-100% MeOH in water) to afford intermediate (166 mg, 71%) as white foam.

To a solution of intermediate (166 mg, 0.071 mmol) in a mixture of methanol (7 .0 mL), water (3.0 mL) and acetic acid (0.2 mL) was added palladium hydroxide (20% on Carbon, 162 mg), and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 40 h. The reaction mixture was filtered through a pad of celite and concentrated. The residue was neutralized with ammonium hydroxide in water (28-30%), concentrated, and further purified by reverse phase column chromatography (0-10% MeOH in water) to afford free amine compound **30** (50 mg, 47%).

^{1}H & ^{13}C NMR data for compounds 1-17, 21-30.

Compound No.1

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.45 (d, *J* = 7.98 Hz, 1H), 4.07 (dd, *J* = 9.78, 3.24 Hz, 1H), 3.94-3.90 (m, 2H), 3.87-3.81 (m, 3H), 3.75-3.57 (m, 8H), 3.52 (dd, *J* = 9.72, 8.04 Hz, 1H), 2.98 (t, *J* = 7.44 Hz, 2H), 2.74 (dd, *J* = 12.48, 4.68 Hz, 1H), 2.01 (s, 3H), 1.78 (dd, *J* = 12.18 Hz, 1H), 1.70-1.63 (m, 4H), 1.47-1.42 (m, 2H); 13C (150 MHz, $CDCl_3$) δ 174.98, 173.80, 102.38, 99.76, 75.84, 74.85, 72.79, 71.72, 69.77, 69.09, 68.27, 67.99, 67.44, 62.51, 60.89, 51.60, 39.57, 39.28, 28.06, 26.36, 22.03, 21.96; HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{22}H_{39}N_2O_{14}Na_2$ 601.2178, found 601.2191.

Compound No.2

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.51 (d, *J* = 7.86 Hz, 1H), 4.47 (d, *J* = 8.04 Hz, 1H), 4.10 (dd, *J* = 9.84, 3.06 Hz, 1H), 3.97 (dd, *J* = 12.18, 2.1 Hz, 1H), 3.94-3.79 (m, 6H), 3.76-3.54 (m, 12 H), 3.28 (t, *J* = 8.58 Hz, 1H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.74 (dd, *J* = 12.48, 4.68 Hz, 1H), 2.01 (s, 3H), 1.78 (dd, *J* = 12.12, 12.12 Hz, 1H), 1.70-1.63 (m, 4H), 1.47-1.42 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.96, 173.83, 102.57, 101.96, 99.73, 78.18, 75.43, 75.14, 74.73, 74.37, 72.82, 72.76, 71.72, 70.01, 69.31, 68.29, 68.02, 67.38, 62.51, 60.98, 59.98, 51.61, 39.57, 39.29, 28.08, 26.35, 22.01, 21.96. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{28}H_{49}N_2O_{19}Na_2$ 763.2520, found 763.2719.

Compound No.3

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.54 (d, *J* = 7.86 Hz, 1H), 4.50 (d, *J* = 8.1 Hz, 1H), 4.10 (dd, *J* = 9.84, 3.12 Hz, 1H), 3.99 (dd, *J* = 12.36, 2.22 Hz, 1H), 3.93 (d, *J* = 3.12 Hz, 1H),

3.89-3.81 (m, 5H), 3.75-3.53 (m, 13H), 2.96 (t, *J* = 7.56 Hz, 1H), 2.74 (dd, *J* = 12.48, 4.68 Hz, 1H), 2.01 (brs, 6H), 1.78 (dd, *J* = 12.48 Hz, 1H), 1.66-1.62 (m, 2H), 1.66-1.56 (m, 2H), 1.40-1.35 (m, 2H); ^{13}C (150 MHz, $CDCl_3$) δ 174.96, 174.36, 173.82, 102.49, 101.09, 99.74, 78.20, 75.41, 75.13, 74.71, 72.82, 72.32, 71.71, 70.02, 69.32, 68.28, 67.39, 62.51, 60.98, 55.01, 51.60, 39.55, 39.28, 28.0, 26.42, 22.07, 22.04, 21.96. ; HRMS (ESI-TOF, M2Na$^+$) calcd for $C_{30}H_{52}N_3O_{19}Na_2$ 804.2985, found 804.2956.

Compound No.4

^{1}H NMR (400 MHz, D_2O) δ 4.64 (d, *J* = 7.9 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.46 (d, *J* = 10.9 Hz, 1H), 4.40 – 4.30 (m, 1H), 4.16 (dd, *J* = 9.9, 2.9 Hz, 1H), 4.02 – 3.56 (m, 18H), 2.97-2.87 (m, 2H), 2.79 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.07 (brs, 6H), 1.84 (t, *J* = 12.2 Hz, 1H), 1.71 – 1.56 (m, 4H), 1.43 (dd, *J* = 12.2, 7.1 Hz, 2H); ^{13}C NMR (151 MHz, D_2O) δ 174.88, 174.40, 173.94, 102.10, 101.15, 99.68, 77.24, 75.27, 75.04, 72.79, 72.45, 72.29, 71.46, 70.21, 69.40, 68.41, 68.00, 67.39, 66.32, 62.45, 61.01, 55.02, 51.63, 39.52, 39.38, 28.05, 26.59, 22.09, 21.99. HRMS (ESI-TOF, MNa$^+$) calcd for $C_{30}H_{51}N_3O_{22}SNa$ 860.2577, found 860.2549.

Compound No.5

^{1}H NMR (600 MHz, D_2O) δ 5.09 (d, *J* = 3.9 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 2H), 4.07 (dd, *J* = 9.8, 3.1 Hz, 1H), 4.00 (d, *J* = 10.4 Hz, 1H), 3.95 – 3.80 (m, 10H), 3.76 (d, *J* = 3.1 Hz, 1H), 3.71 – 3.55 (m, 11H), 3.51 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.98 – 2.92 (m, 2H), 2.75 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.78 (t, *J* = 12.2 Hz, 1H), 1.68 – 1.62 (m, 2H), 1.61 – 1.55 (m, 2H), 1.41 – 1.35 (m, 2H), 1.15 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150

MHz, D_2O) δ 175.04, 174.16, 173.84, 101.61, 101.00, 99.65, 98.59, 75.67, 75.28, 74.92, 74.83, 73.35, 72.91, 71.86, 70.15, 69.24, 69.17, 68.27, 68.10, 67.70, 67.30, 66.68, 62.60, 61.48, 59.65, 55.81, 51.68, 39.78, 39.35, 28.08, 26.55, 22.20, 22.11, 22.01, 15.25. ; HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{36}H_{62}N_3O_{23}Na_2$ 950.3564, found 950.3522.

Compound No.6

^1H NMR (600 MHz, D_2O) δ 4.54 (d, *J* = 8.3 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.07 (dd, *J* = 9.8, 3.1 Hz, 1H), 3.94 – 3.78 (m, 7H), 3.78 – 3.57 (m, 10H), 3.54 – 3.50 (m, 2H), 3.48 – 3.43 (m, 1H), 3.00 – 2.94 (m, 2H), 2.74 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.77 (t, *J* = 12.2 Hz, 1H), 1.70 – 1.62 (m, 2H), 1.62 – 1.56 (m, 2H), 1.43 – 1.34 (m, 2H);

^{13}C NMR (150 MHz, D_2O) δ 174.93, 174.42, 173.84, 103.40, 100.86, 99.58, 82.48, 75.57, 75.34, 75.05, 72.74, 71.79, 70.02, 69.02, 68.66, 68.31, 67.98, 67.17, 62.41, 60.97, 60.67, 54.39, 51.59, 39.71, 39.27, 27.99, 26.33, 22.22, 22.07, 21.97; HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{30}H_{52}N_3O_{19}Na_2$ 804.2985, found 804.2979.

Compound No.7

^1H NMR (600 MHz, D_2O) δ 4.56 (d, *J* = 8.4 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.36 (dd, *J* = 11.2, 2.1 Hz, 1H), 4.19 (dd, *J* = 11.3, 6.0 Hz, 1H), 4.07 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.92 (d, *J* = 3.3 Hz, 1H), 3.90 – 3.80 (m, 5H), 3.77 (dd, *J* = 10.3, 8.5 Hz, 1H), 3.74 – 3.50 (m, 11H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.75 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.77 (t, *J* = 12.2 Hz, 1H), 1.69 – 1.63 (m, 2H), 1.63 – 1.57 (m, 2H), 1.46 – 1.34 (m, 2H);

^{13}C NMR (150 MHz, D_2O) δ 174.92, 174.45, 173.86, 103.46, 100.90, 99.57, 82.23, 75.57, 75.06, 73.21, 72.73, 71.78, 70.24, 69.03, 68.54, 68.34, 67.99, 67.22, 67.19, 62.39, 60.98, 54.38, 51.58, 39.71, 39.30, 28.02, 26.23, 22.23, 21.97. HRMS (ESI-TOF, MNa^+) calcd for $C_{30}H_{51}N_3O_{22}SNa$ 860.2577, found 860.2556.

Compound No.8

^{1}H NMR (600 MHz, D_2O) δ 4.90 (d, *J* = 3.8 Hz, 1H), 4.53 (d, *J* = 7.9 Hz, 1H), 4.29 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.23 (d, *J* = 2.8 Hz, 1H), 4.06 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.02 (dd, *J* = 11.1, 3.0 Hz, 1H), 3.99 – 3.95 (m, 1H), 3.91 (d, *J* = 3.1 Hz, 1H), 3.89 – 3.80 (m, 3H), 3.77 – 3.56 (m, 10H), 3.53 (dd, *J* = 9.7, 7.9 Hz, 1H), 3.48 (dt, *J* = 10.0, 6.2 Hz, 1H), 2.98 – 2.94 (m, 2H), 2.74 (dd, *J* = 12.5, 4.7 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 2H), 1.77 (t, *J* = 12.2 Hz, 1H), 1.70 – 1.59 (m, 4H), 1.50 – 1.40 (m, 2H). ^{13}C NMR (150 MHz, D_2O) δ 175.01, 174.51, 173.88, 104.44, 99.71, 96.99, 77.45, 75.67, 74.81, 72.80, 71.84, 70.59, 69.06, 68.55, 68.34, 68.07, 67.66, 67.38, 62.54, 61.26, 61.00, 51.65, 48.73, 39.74, 39.45, 28.00, 26.82, 22.33, 22.02.; HRMS (ESI-TOF, MNa^+) calcd for $C_{30}H_{52}N_3O_{19}Na$ 782.3165, found 782.3109.

Compound No.9

^{1}H NMR (600 MHz, D_2O) δ 4.84 (d, *J* = 1.4 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 1H), 4.21 – 4.17 (m, 1H), 4.09 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.93 (d, *J* = 3.4 Hz, 1H), 3.92 (dd, *J* = 3.1, 1.7 Hz, 1H), 3.88 – 3.81 (m, 4H), 3.79 – 3.51 (m, 13H), 2.99 – 2.96 (m, 2H), 2.75 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.02 (s, 3H), 1.78 (t, *J* = 12.2 Hz, 1H), 1.68-1.57 (m, 4H), 1.35-1.25 (m, 4H); ^{13}C NMR (150 MHz, D_2O) δ 174.96, 173.81, 102.86, 99.78, 99.73, 75.68, 74.89, 72.80, 71.76, 71.65, 70.42, 69.94, 69.21, 68.42, 68.29, 67.96, 67.91, 67.43, 66.40, 62.47,

61.01, 51.60, 39.62, 39.38, 28.15, 26.64, 25.25, 24.77, 21.97. HRMS (ESI-TOF, MNa^+) calcd for $C_{29}H_{52}N_2O_{19}Na$ 755.3056, found 755.2917.

Compound No.10

^{1}H NMR (600 MHz, D_2O) δ 4.80 (d, *J* = 3.7 Hz, 1H), 4.59 (d, *J* = 8.5 Hz, 1H), 4.40 (d, *J* = 7.8 Hz, 1H), 4.07 (dd, *J* = 9.0, 3.1 Hz, 2H), 3.97 – 3.92 (m, 2H), 3.85 – 3.39 (m, 23H), 2.91 – 2.86 (m, 2H), 2.64 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.92 (s, 3H), 1.91 (s, 3H), 1.67 (t, *J* = 12.1 Hz, 1H), 1.62 – 1.51 (m, 4H), 1.40 – 1.30 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 175.10, 174.93, 173.90, 104.53, 102.73, 99.60, 98.33, 79.75, 78.89, 75.51, 74.74, 74.63, 72.72, 71.78, 70.46, 69.20, 68.93, 68.33, 67.99, 67.82, 67.66, 67.27, 67.23, 62.42, 61.12, 60.94, 51.59, 51.33, 39.68, 39.34, 28.01, 26.62, 22.34, 22.30, 21.97. HRMS (ESI-TOF, MNa^+) calcd for $C_{36}H_{63}N_3O_{24}Na$ 944.3694, found 944.3659.

Compound No.11

^{1}H NMR (600 MHz, D_2O) δ 4.68 (d, *J* = 8.5 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 8.0 Hz, 1H), 4.15 (dd, *J* = 18.8, 3.3 Hz, 2H), 4.07 – 4.01 (m, 2H), 3.95 – 3.51 (m, 23H), 3.00 – 2.96 (m, 2H), 2.74 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.01 (s, 2H), 2.01 (s, 2H), 1.77 (t, *J* = 12.1 Hz, 1H), 1.66 (tt, *J* = 14.1, 7.1 Hz, 4H), 1.48 – 1.41 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 175.07, 174.94, 173.90, 104.52, 102.82, 102.71, 99.61, 82.03, 79.71, 75.49, 74.75, 74.63, 72.73, 71.77, 69.90, 69.75, 68.94, 68.34, 68.00, 67.77, 67.27, 62.43, 60.94, 60.84, 51.59, 51.31, 39.67, 39.32, 28.12, 26.51, 22.27, 22.04, 21.97. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{36}H_{63}N_3O_{24}Na_2$ 966.3513, found 966.3500.

Compound No.12

^{1}H NMR (600 MHz, D_2O) δ 4.94 (d, *J* = 3.9 Hz, 1H), 4.72 (d, *J* = 8.4 Hz, 1H), 4.57 – 4.49 (m, 3H), 4.41 (t, *J* = 6.4 Hz, 1H), 4.27 (d, *J* = 2.0 Hz, 1H), 4.20 (d, *J* = 2.8 Hz, 1H), 4.13 – 3.54 (m, 35H), 3.36 – 3.30 (m, 1H), 3.05 – 2.98 (m, 2H), 2.78 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.05 (m, 6H), 1.81 (t, *J* = 12.1 Hz, 1H), 1.75 – 1.65 (m, 4H), 1.53 – 1.44 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 175.08, 174.98, 173.93, 104.56, 103.29, 102.93, 101.94, 100.37, 99.66, 79.76, 78.81, 78.71, 77.13, 75.56, 75.45, 74.81, 74.78, 74.61, 74.56, 72.92, 72.78, 72.11, 71.82, 70.88, 70.28, 70.06, 68.99, 68.90, 68.37, 68.06, 67.84, 67.56, 67.33, 62.48, 60.98, 60.37, 60.30, 60.07, 51.65, 51.34, 39.74, 39.36, 28.14, 26.50, 22.33, 22.07, 22.02. HRMS (ESI-TOF, M2Na^{+}) calcd for $C_{48}H_{83}N_3O_{34}Na_2$ 1290.4570, found 1290.4549.

Compound No.13

^{1}H NMR (600 MHz, D_2O) δ 4.55 (d, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.24 (d, *J* = 10.6 Hz, 1H), 4.07 (td, *J* = 9.6, 3.1 Hz, 2H), 3.95 – 3.50 (m, 31H), 2.99 – 2.95 (m, 2H), 2.74 (dd, *J* = 12.4, 4.5 Hz, 2H), 2.01 (brs, 9H), 1.81-1.74 (m, 2H), 1.69-1.56 (m, 4H), 1.42 – 1.36 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.94, 174.42, 173.85, 103.43, 102.99, 100.85, 99.79, 99.57, 82.17, 75.67, 75.57, 75.04, 74.88, 74.54, 72.79, 72.73, 71.78, 71.74, 70.22, 69.12, 69.02, 68.72, 68.33, 67.98, 67.42, 67.18, 62.48, 62.39, 60.97, 60.91, 54.39, 51.59, 39.72, 39.56, 39.29, 28.01, 26.37, 22.23, 22.05, 21.97.

Compound No.14

^{1}H NMR (600 MHz, D_2O) δ 4.80 (d, *J* = 1.7 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 7.9 Hz, 1H), 4.11 (d, *J* = 10.7 Hz, 1H), 4.05 – 4.04 (m, 1H), 4.00 (m, 2H), 3.92 (dd, *J* = 9.3, 3.1 Hz, 1H), 3.84 (t, *J* = 3.1 Hz, 2H), 3.80 – 3.42 (m, 27H), 2.90 – 2.86 (m, 2H), 2.65 (dt, *J* = 12.3, 4.8 Hz, 2H), 1.92 (m, 6H), 1.69 (t, *J* = 12.1 Hz, 2H), 1.59 – 1.49 (m, 4H), 1.33-1.27 (m, 4H); ^{13}C NMR (150 MHz, D_2O) δ 174.95, 173.86, 173.80, 102.92, 100.31, 99.74, 99.42, 77.78, 75.64, 75.04, 74.86, 72.79, 71.76, 69.20, 69.10, 68.62, 68.33, 68.03, 67.98, 67.93, 67.43, 64.96, 62.52, 62.47, 61.04, 61.00, 51.60, 39.64, 39.59, 39.39, 28.17, 26.63, 25.27, 24.82, 21.97. HRMS (ESI-TOF, MNa^+) calcd for $C_{46}H_{79}N_3O_{32}Na$ 1208.4544, found 1208.4885.

Compound No.15

^{1}H NMR (600 MHz, D_2O) δ 4.47 (t, *J* = 8.0 Hz, 2H), 4.18 (d, *J* = 3.3 Hz, 1H), 4.05 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.98 (dd, *J* = 10.8, 8.6 Hz, 1H), 3.95 – 3.55 (m, 24H), 3.52 (dd, *J* = 9.8, 7.9 Hz, 1H), 3.00 – 2.95 (m, 2H), 2.72 (m, 2H), 2.03 – 1.98 (m, 9H), 1.77 (t, *J* = 12.2 Hz, 1H), 1.66 (m, 3H), 1.59 (dt, *J* = 13.6, 6.7 Hz, 2H), 1.43 – 1.36 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.98, 174.92, 174.57, 173.90, 173.36, 104.62, 101.44, 100.36, 99.62, 80.09, 75.53, 74.71, 73.12, 72.72, 72.57, 71.75, 71.67, 70.11, 68.93, 68.35, 68.15, 68.00, 67.71, 67.32, 63.44, 62.58, 62.42, 60.91, 51.78, 51.59, 51.02, 40.15, 39.66, 39.28, 28.03, 26.30, 22.21, 22.00, 21.97. HRMS (ESI-TOF, MNa^+) calcd for $C_{41}H_{70}N_4O_{27}Na$ 1073.4120, found 1073.4119.

Compound No.16

^{1}H NMR (600 MHz, D_2O) δ 4.62 (d, *J* = 8.6 Hz, 1H), 4.42 (d, *J* = 7.9 Hz, 1H), 4.38 (d, *J* = 8.0 Hz, 1H), 4.04 (dd, *J* = 9.8, 3.1 Hz, 1H), 4.00 (d, *J* = 3.0 Hz, 1H), 3.87 (dd, *J* = 12.2, 1.8 Hz, 1H), 3.85 – 3.46 (m, 21H), 3.37 (dd, *J* = 10.2, 2.1 Hz, 1H), 3.25 (dd, *J* = 9.7, 8.0 Hz, 1H), 3.20 – 3.16 (m, 1H), 2.89 – 2.83 (m, 2H), 2.55 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.92 (s, 3H), 1.90 (s, 3H), 1.81 (t, *J* = 11.9 Hz, 1H), 1.61 – 1.52 (m, 4H), 1.38 – 1.30 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.94, 174.77, 174.03, 102.70, 102.52, 101.92, 101.55, 78.53, 77.06, 74.69, 74.65, 74.40, 74.25, 73.96, 73.00, 72.68, 72.22, 71.16, 70.01, 69.95, 68.64, 67.92, 67.68, 62.76, 61.10, 60.48, 60.03, 52.26, 51.51, 39.34, 36.86, 28.09, 26.62, 22.53, 22.03, 21.97. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{36}H_{62}N_3O_{24}Na_2$ 966.3513, found 966.3507.

Compound No.17

^{1}H NMR (600 MHz, D_2O) δ 4.76 (d, *J* = 8.5 Hz, 1H), 4.54 – 4.50 (m, 2H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.16 – 4.10 (m, 3H), 4.02 (dd, *J* = 10.8, 8.6 Hz, 1H), 3.97 (dd, *J* = 12.2, 1.8 Hz, 1H), 3.95 – 3.89 (m, 2H), 3.86 (dd, *J* = 12.0, 2.2 Hz, 1H), 3.83 – 3.55 (m, 21H), 3.52 – 3.47 (m, 2H), 3.34 (dd, *J* = 9.5, 7.9 Hz, 1H), 3.30 – 3.26 (m, 1H), 3.00 – 2.96 (m, 2H), 2.64 (dd, *J* = 12.6, 4.6 Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.94 – 1.89 (t, *J* = 12.2 Hz, 1H), 1.70 – 1.63 (m, 4H), 1.47 – 1.42 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.95, 174.72, 174.06, 104.68, 102.50, 102.43, 101.92, 101.56, 80.23, 78.53, 77.04, 74.81, 74.68, 74.40, 74.28, 74.25, 74.00, 73.01, 72.67, 72.41, 72.21, 70.60, 69.99, 69.95, 68.65, 68.50, 67.92, 67.81, 62.74, 61.04, 60.86, 60.54, 60.03, 51.51, 51.12, 39.31, 36.84, 28.07, 26.44, 22.51, 22.01, 21.97. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{42}H_{72}N_3O_{29}Na_2$ 1128.4041, found 1128.4232.

Compound No.21

^{1}H NMR (600 MHz, D_2O) δ 3.68 (m, 2H), 3.63 (t, *J* = 10.1 Hz, 1H), 3.58 (dt, *J* = 9.5, 6.3 Hz, 1H), 3.53 – 3.43 (m, 3H), 3.41 (dd, *J* = 8.9, 1.9 Hz, 1H), 3.28 (dt, *J* = 9.4, 6.6 Hz, 1H), 2.83 – 2.78 (m, 2H), 2.56 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.85 (s, 3H), 1.52 – 1.40 (m, 5H), 1.25 (dt, *J* = 7.8, 6.9 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.81, 173.52, 100.34, 72.34, 71.57, 68.02, 67.80, 64.02, 62.24, 51.60, 40.20, 39.06, 27.97, 26.05, 21.85, 21.71. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{16}H_{29}N_2O_9Na_2$ 439.1663, found 439.1668.

Compound No.22

^{1}H NMR (600 MHz, D_2O) δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.78 – 3.73 (m, 3H), 3.72 – 3.68 (m, 2H), 3.65 (t, *J* = 10.1 Hz, 1H), 3.59 (dd, *J* = 7.6, 4.9 Hz, 1H), 3.55 – 3.39 (m, 7H), 3.30 (dd, *J* = 9.8, 8.0 Hz, 1H), 2.84 – 2.81 (m, 2H), 2.55 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.85 (s, 3H), 1.56 – 1.47 (m, 5H), 1.32 – 1.25 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.77, 173.26, 102.60, 100.13, 73.16, 72.37, 71.54, 70.41, 70.04, 68.29, 67.97, 67.85, 63.15, 62.32, 51.55, 39.97, 39.08, 27.99, 26.22, 21.80, 21.74. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{22}H_{39}N_2O_{14}Na_2$ 601.2191, found 601.2207.

Compound No.23

^{1}H NMR (600 MHz, D_2O) δ 4.81 (d, *J* = 3.8 Hz, 1H), 4.06 (dd, *J* = 11.1, 3.8 Hz, 1H), 3.96 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.92 (d, *J* = 3.3 Hz, 1H), 3.86 – 3.79 (m, 4H), 3.75 (t, *J* = 10.1 Hz, 1H), 3.69 – 3.55 (m, 5H), 3.51 (dd, *J* = 8.8, 1.7 Hz, 1H), 3.42 (dt, *J* = 10.2, 6.3 Hz, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.65 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.96 (brs, 6H), 1.66 – 1.54 (m, 5H), 1.38 (p, *J* = 7.7 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.97, 174.45, 173.38, 100.28, 96.90, 72.49, 71.72, 69.46, 68.48, 68.20, 68.15, 67.84, 67.52, 63.82,

62.55, 51.79, 49.91, 40.08, 39.36, 27.89, 26.45, 22.21, 21.96, 21.84. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{24}H_{42}N_3O_{14}Na_2$ 642.2457, found 642.2425.

Compound No.24

^{1}H NMR (600 MHz, D_2O) δ 4.54 (d, *J* = 8.1 Hz, 1H), 4.43 (d, *J* = 7.9 Hz, 1H), 3.98 (m, 2H), 3.88 (m, 4H), 3.83 – 3.76 (m, 3H), 3.76 – 3.57 (m, 9H), 3.56 – 3.50 (m, 3H), 3.00 – 2.95 (m, 2H), 2.65 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.04 (s, 3H), 2.01 (s, 3H), 1.73 – 1.54 (m, 5H), 1.43 – 1.35 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.86, 174.39, 173.49, 103.43, 100.87, 100.07, 80.76, 74.41, 73.65, 72.48, 72.39, 72.36, 71.64, 70.66, 69.98, 68.34, 68.29, 68.17, 63.31, 62.58, 60.31, 54.80, 51.80, 40.02, 39.27, 27.99, 26.31, 22.21, 22.07, 21.97. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{30}H_{52}N_3O_{19}Na_2$ 804.2985, found 804.2959.

Compound No.25

^{1}H NMR (600 MHz, D_2O) δ 4.38 (d, *J* = 8.1 Hz, 1H), 4.31 (d, *J* = 7.9 Hz, 1H), 3.90 – 3.66 (m, 9H), 3.62 – 3.38 (m, 11H), 3.24 – 3.18 (m, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.60 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.92 (s, 3H), 1.66 – 1.52 (m, 5H), 1.39 – 1.31 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.85, 173.44, 103.14, 101.81, 100.20, 79.62, 74.63, 74.58, 73.66, 72.67, 72.45, 72.29, 71.74, 70.71, 69.97, 68.44, 68.31, 63.57, 62.56, 60.20, 51.70, 40.03, 39.31, 28.06, 26.39, 22.05, 21.99. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{28}H_{49}N_2O_{19}Na_2$ 763.2719, found 763.2708.

Compound No.26

^{1}H NMR (600 MHz, D_2O) δ 4.87 (d, *J* = 3.7 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.29 (dd, *J* = 11.0, 3.7 Hz, 1H), 4.23 (d, *J* = 2.6 Hz, 1H), 4.05 – 3.96 (m, 2H), 3.93 – 3.84 (m, 4H), 3.81 (t, *J* = 10.1 Hz, 1H), 3.77 (d, *J* = 6.0 Hz, 2H), 3.73 – 3.55 (m, 8H), 3.49 (m, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.72 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.71 – 1.59 (m, 5H), 1.51 – 1.40 (m, 2H). ^{13}C NMR (150 MHz, D_2O) δ 175.06, 174.48, 173.42, 104.53, 100.45, 97.05, 77.19, 73.23, 72.59, 72.39, 71.75, 70.72, 70.49, 68.74, 68.53, 68.25, 68.19, 67.65, 63.54, 62.62, 61.47, 51.87, 48.77, 40.18, 39.45, 28.04, 26.69, 22.33, 22.01, 21.97. HRMS (ESI-TOF, M2Na^{+}) calcd for $C_{30}H_{52}N_3O_{19}Na_2$ 804.2985, found 804.2946.

Compound No.27

^{1}H NMR (600 MHz, D_2O) δ 4.54 (d, *J* = 8.5 Hz, 1H), 4.36 (d, *J* = 7.8 Hz, 1H), 4.00 – 3.45 (m, 21H), 3.00 – 2.91 (m, 2H), 2.68 (dd, *J* = 12.4, 4.6 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 3H), 1.71 – 1.54 (m, 5H), 1.38 (dt, *J* = 7.8, 6.8 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.85, 174.48, 173.45, 103.83, 100.85, 100.04, 83.94, 75.43, 73.54, 72.38, 72.34, 71.76, 70.45, 70.01, 68.84, 68.37, 68.33, 68.23, 63.47, 62.55, 60.81, 54.25, 51.74, 40.07, 39.27, 27.99, 26.31, 22.13, 22.03, 21.99. HRMS (ESI-TOF, M2Na^{+}) calcd for $C_{30}H_{52}N_3O_{19}Na_2$ 804.2985, found 804.2981.

Compound No.28

^{1}H NMR (600 MHz, D_2O) δ 4.47 (d, *J* = 8.2 Hz, 1H), 4.36 (d, *J* = 7.9 Hz, 1H), 4.34 (dd, *J* = 11.1, 2.0 Hz, 1H), 4.15 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.89 (dd, *J* = 10.0, 9.2 Hz, 1H), 3.81

(d, *J* = 3.9 Hz, 1H), 3.80 – 3.66 (m, 7H), 3.64 (m, 2H), 3.60 – 3.50 (m, 6H), 3.46 – 3.39 (m, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.55 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.95 (s, 3H), 1.91 (s, 3H), 1.62 – 1.48 (m, 5H), 1.36 – 1.25 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.84, 174.43, 173.50, 103.41, 100.93, 100.06, 80.47, 73.61, 72.47, 72.44, 72.32, 72.24, 71.62, 70.67, 70.19, 68.35, 68.29, 68.19, 66.84, 63.26, 62.58, 54.73, 51.81, 40.02, 39.31, 28.02, 26.25, 22.22, 21.97. HRMS (ESI-TOF, MNa^+) calcd for $C_{30}H_{51}N_3O_{22}Na$ 860.2577, found 860.2569.

Compound No.29

^{1}H NMR (600 MHz, D_2O) δ 4.71 (d, *J* = 7.8 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 1H), 4.44 (dd, *J* = 7.9, 4.4 Hz, 2H), 4.15 (d, *J* = 3.2 Hz, 1H), 4.01 – 3.50 (m, 32H), 2.99 – 2.95 (m, 2H), 2.65 (dd, *J* = 12.3, 4.6 Hz, 1H), 2.04 (s, 3H), 2.02 (m, 6H), 1.74 – 1.54 (m, 5H), 1.43 – 1.35 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.85, 174.37, 173.51, 103.42, 102.84, 102.54, 101.06, 100.06, 81.98, 80.45, 78.39, 74.83, 74.71, 74.19, 73.65, 72.48, 72.35, 72.18, 71.65, 70.66, 70.03, 69.90, 68.33, 68.29, 68.22, 68.16, 63.30, 62.58, 60.92, 60.06, 59.96, 54.97, 54.86, 51.81, 40.02, 39.25, 28.00, 26.31, 22.22, 22.07, 22.05, 21.96. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{44}H_{75}N_4O_{29}Na_2$ 1169.4307, found 1169.4327.

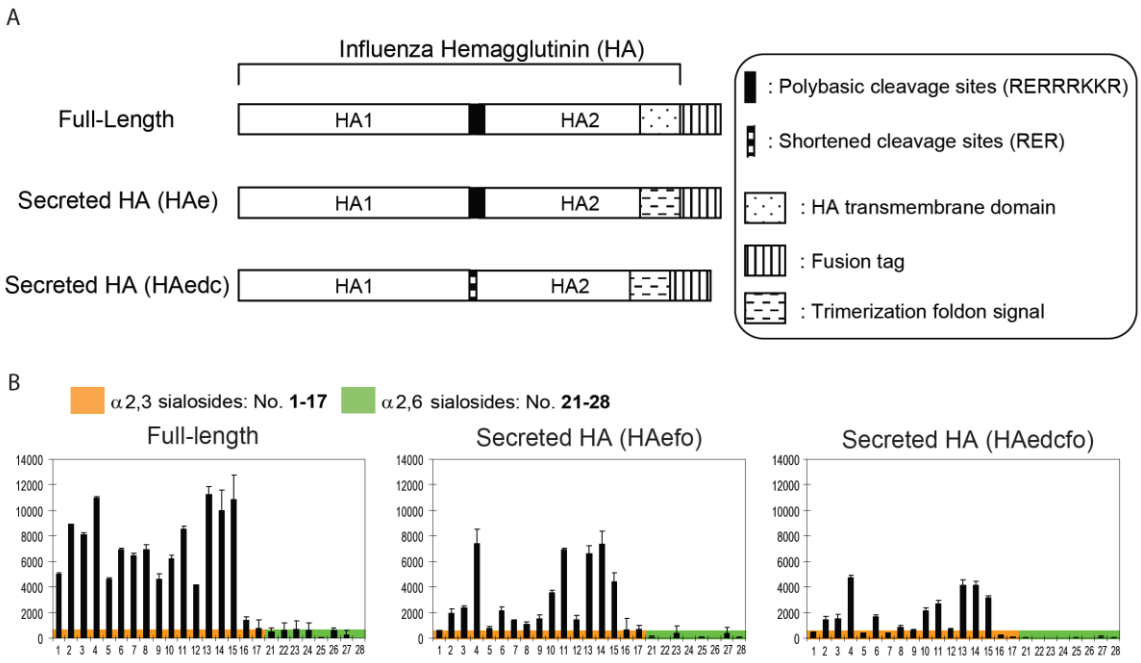
Compound No.30

^{1}H NMR (600 MHz, D_2O) δ 4.71 (d, *J* = 7.7 Hz, 1H), 4.68 (d, *J* = 8.3 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.45 (t, *J* = 7.8 Hz, 3H), 4.15 (brs, 2H), 4.00 – 3.50 (m, 43H), 2.99 – 2.95 (m, 2H), 2.65 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.04 (s, 3H), 2.02 (brs, 9H), 1.74 – 1.55 (m, 5H), 1.42 – 1.35 (m, 2H); ^{13}C NMR (150 MHz, D_2O) δ 174.85, 174.37, 173.52, 103.42,

102.83, 102.73, 102.55, 101.05, 100.06, 82.00, 80.44, 78.38, 78.06, 74.82, 74.70, 74.49, 74.19, 73.64, 72.47, 72.34, 72.17, 72.11, 71.65, 70.66, 70.04, 69.90, 68.33, 68.28, 68.23, 68.16, 63.29, 62.57, 60.91, 60.06, 59.97, 59.74, 55.05, 54.98, 54.86, 51.81, 40.01, 39.25, 28.01, 26.31, 22.21, 22.05, 21.96. HRMS (ESI-TOF, $M2Na^+$) calcd for $C_{58}H_{98}N_5O_{39}Na_2$ 1534.5629, found 1534.5610.

Determination of Glycosylation Sites and Deglycosylation of Glycosylation Mutants. Purified HA proteins dissolved in trifluoroethanol/100 mM ammonia bicarbonate (pH 8.5) (1:1 (v:v)) were reduced with 10 mM dithiothreitol for 1 h at 37℃, alkylated with 20 mM iodoacetamide for another 1h in the dark at 37℃, and subsequently digested with modified trypsin (sequencing grade, Promega) for overnight at 37 ℃. All of the reagents were prepared in 50 mM ammonium bicarbonate buffer, pH 8.5. After stopping the trypsin digestion by heating at 95℃ for 10 min, the glycans were removed by incubating with 500U PNGase F (glycerol free, New England Biolabs) overnight at 37℃. All the samples were dried *in vacuo*, redissolved in 0.1% formic acid and injected into nano-LC/ESI LTQ FT linear ion trap mass spectrometer (Bruker Daltonics). MS/MS spectra were acquired in a data-dependent acquisition mode that automatically selects and fragments the five most intense peaks from each MS spectrum generated. The MS and MS/MS raw data were processed by Raw2msm software and searched against an in-house generated NCBI database comprising WT HA and various glycosylation mutants, using Mascot Daemon searching engine. Search criteria were trypsin digestion and variable modifications such as carbamidomethyl (C), oxidation (M), deamidation (D) and N-glycosylation (Gly-Asn). Up to 1 missed cleavage, mass accuracy of 3 ppm on the parent ion and 0.60 Da on the fragment ions were allowed to be included for data analysis. All significant protein hits from Mascot ($p < 0.05$) thus obtained contained no false positive hits from the reverse database.

Figure S1. The sialoside binding intensities of HA in various forms. (A) Full-length and secreted HA were prepared with a C-terminal tag composed of a strep and a $(His)_6$ tag from human 293T cells. To prepare the secreted HA, the transmembrane domain was replaced with a trimerization signal. Polybasic cleavage site or shortened cleavage site was used. (B) Purified HA proteins were incubated with SA-Cy3 and the complexes were incubated with a sialosides array containing α 2,3-silosides **1-17** and α 2,6-sialoside **21-28**.



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