Screening of Neu5Acα(2-6)Gal Isomers Preferences of Siglec with Sialic acid Microarray.

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1. General information. All chemicals were reagent grade and used as supplied except where noted. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25 mmol). Compounds were visualized by UV irradiation or dipping the plate in CAM/ninhydrin solution followed by heating. Column chromatography was carried out using force flow of the indicated solvent on Fluka Kiesel gel 60 (230–400 mesh). 1H and 13C NMR spectra were recorded on Jeol 400 MHz, with cryo probe using residual solvents signals as an internal reference (CDCl3 δH, 7.26 ppm, δC 77.3 ppm and CD3OD δH 3.31 ppm, δC 49.0 ppm). The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. UV-visible measurements were performed with Evolution 300 UV-visible spectrophotometer (Thermo Fisher Scientific, USA). Fluorescence spectra were recorded in FluoroMax-4 spectrofluorimeter (Horiba Scientific, U.S.A.).
2. Synthesis of disaccharide library

Scheme S1: Reagents and conditions: (a) 2-azidoethoxyethanol, NIS/TfOH, -40°C, DCM; (b) PhBCl$_2$, Et$_3$SiH, -78°C, DCM; (c) mCPBA, -78°C, DCM; (d) 2-azidoethoxyethanol, Tf$_2$O, TTBP, -78°C, DCM; (e) (i) MsOH, MeOH; ii) NPCC, NaHCO$_3$, CH$_3$CN:H$_2$O (2:1); (iii) AC$_2$O/Pyrindine; (iv) AcCl, DIPEA, DCM.

Synthetic procedure for comp 12A: A solution of 12B (500 mg, 1.08 mmol, 1.0 equiv), 2-azidoethoxyethanol (1.28 mmol, 1.2 equiv), and activated 4Å powdered molecular sieves (1.5 gm) in anhydrous dichloromethane (5 ml) was stirred for 2h at room temperature under an argon atmosphere, and then cooled to -40°C followed by addition of NIS (290 mg, 1.28 mmol, 1.2
equiv) and TfOH (9.58 μl, 0.108 mmol, 0.1 equiv). The reaction mixture was stirred at -40°C for 0.5 h to 3 h until the disappearance of donor on TLC, then quenched with triethylamine (81 μl, 0.81 mmol, 0.75 equiv) and warmed to room temperature. The mixture was diluted with dichloromethane, filtered through celite, washed with 20% aqueous NaS$_2$O$_3$ solution, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethylacetate/hexane (1:1) system to afford the compound 12A (450 mg, 70%). $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.04–7.92 (m, 4H), 7.55–7.43 (m, 4H), 7.43–7.29 (m, 7H), 5.86 (dd, $J$ = 10.4, 8.0 Hz, 1H), 5.54 (s, 1H), 5.37 (dd, $J$ = 10.4, 3.6 Hz, 1H), 4.86 (d, $J$ = 8.0 Hz, 1H), 4.58 (dd, $J$ = 3.6, 1.6 Hz, 1H), 4.39 (dd, $J$ = 12.4, 1.2 Hz, 1H), 4.13 (dd, $J$ = 11.3, 1.6 Hz, 1H), 4.04 (dt, $J$ = 11.3, 3.6 Hz, 1H), 3.79 (ddd, $J$ = 11.3, 7.4, 3.6 Hz, 1H), 3.68 (s, 1H), 3.60 (dt, $J$ = 7.4, 3.6 Hz, 2H), 3.45 (t, $J$ = 5.1 Hz, 2H), 3.04 (m, 2H). $^{13}$C-NMR (400 MHz, CDCl$_3$) δ 165.68, 165.27, 136.82, 133.37, 133.19, 130.08, 130.04, 129.99, 129.90, 129.87, 129.46, 129.40, 129.12, 128.57, 128.49, 128.40, 128.44, 128.38, 128.28, 126.20, 101.95, 101.57, 78.90, 72.56, 72.07, 70.44, 70.18, 69.81, 68.72, 66.68, 50.60. Maldi-ToF m/z calc’d for C$_{31}$H$_{31}$N$_3$O$_9$Na (M+Na$^+$): 612.1958; found: 612.1951.

**Synthetic procedure for comp 12:** A solution of compound 12A (300 mg, 0.509 mmol) and activated 4Å powdered molecular sieves 1.5 g were stirred 1h at room temperature. The mixture was cooled to -78°C and then to the stirred solution Et$_3$SiH (259 μl, 1.62 mmol) and PhBCl$_2$ (147 μl, 1.38 mmol) were added successively. After being stirred for 1 h at -78°C, Et$_3$N (1 ml) and MeOH (1 ml) were added successively, and the mixture was diluted with CHCl$_3$ and washed with aqueous NaHCO$_3$, dried over MgSO$_4$, filtered and concentrated. The crude product was purified by silica gel column hexane:ethylacetate (1:1) to afford comp 12 (260 mg, 86%). $^1$H NMR (400 MHz,CDCl$_3$) δ 8.00–7.94 (m, 4H), 7.54–7.47 (m, 2H), 7.36 (dd, $J$ = 10.5, 4.8 Hz, 4H), 7.28 – 7.21 (m, 5H), 5.84 (dd, $J$ = 10.5, 7.9 Hz, 1H), 5.34 (dd, $J$ = 10.5, 3.0 Hz, 1H), 4.79 (d, $J$ = 7.9 Hz, 1H), 4.78 (d, $J$ = 11.7 Hz, 1H), 4.48 (d, $J$ = 11.7 Hz, 1H), 4.13 (d, $J$ = 2.5 Hz, 1H), 3.99 (ddd, $J$ = 11.4, 4.5, 3.3 Hz, 1H), 3.86 (dd, $J$ = 11.4, 6.9 Hz, 1H), 3.81 – 3.69 (m, 2H), 3.64 – 3.53 (m, 3H), 3.46 (t, $J$ = 5.1 Hz, 2H), 3.14 – 2.99 (m, 2H), 1.76 (bs, 1H). $^{13}$C NMR (400 MHz,CDCl$_3$)δ 166.11, 165.43, 137.30, 133.60, 133.24, 129.98, 129.98, 129.78, 129.78, 129.72, 129.02, 128.62, 128.61, 128.60, 128.59, 128.44, 128.38, 128.23, 128.08, 127.95, 101.65, 77.31, 75.03, 74.81, 74.78, 73.32, 70.56, 70.15, 69.35, 61.79, 50.64. Maldi-ToF m/z calc’d for C$_{31}$H$_{33}$N$_3$O$_9$Na (M+Na$^+$): 614.2114; found: 614.2120.
Synthetic procedure for comp 13A: Compound was synthesized from 13B by following synthetic procedure mentioned above 13A (420 mg, 65%). $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.99–7.91 (m, 4H), 7.55–7.27 (m, 11H), 5.78 (t, J = 9.6 Hz, 1H), 5.53 (s, 1H), 5.47 (dd, J = 9.6, 7.9 Hz, 1H), 4.89 (d, J = 7.9 Hz, 1H), 4.42 (dd, J = 10.5, 4.9 Hz, 1H), 3.99 (ddd, J = 11.3, 4.9, 3.5 Hz, 1H), 3.92 (t, J = 8.4 Hz, 1H), 3.90–3.85 (m, 1H), 3.79–3.73 (m, 1H), 3.69 (td, J = 9.6, 4.9 Hz, 1H), 3.62–3.52 (m, 2H), 3.48–3.39 (m, 2H), 3.12–3.00 (m, 2H).

$^{13}$C-NMR (400 MHz, CDCl$_3$) δ 165.68, 165.27, 136.82, 133.37, 133.19, 130.08, 129.99, 129.90, 129.87, 129.54, 129.46, 129.40, 129.22, 129.12, 128.57, 128.49, 128.38, 128.32, 128.28, 126.20, 101.95, 101.57, 78.90, 72.56, 72.07, 70.44, 70.18, 69.81, 68.72, 66.68, 50.60. Maldi-ToF m/z calc’d for C$_{31}$H$_{31}$N$_3$O$_9$Na (M+Na$^+$): 612.1958; found: 612.1955.

Synthetic procedure of comp 13: Compound synthesized from 13A by same procedure mentioned for 12 to give 13 (240 mg, 80%). $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.96–7.89 (m, 4H), 7.53–7.45 (m, 2H), 7.39–7.32 (m, 4H), 7.18–7.11 (m, 5H), 5.73 (t, J = 9.6 Hz, 1H), 5.33 (dd, J = 9.6, 8.0 Hz, 1H), 4.80 (d, J = 8.0 Hz, 1H), 4.59 (s, 2H), 4.01–3.90 (m, 3H), 3.81 (dd, J = 11.2, 3.9 Hz, 1H), 3.74 (ddd, J = 11.2, 4.8, 3.2 Hz, 1H), 3.63–3.54 (m, 3H), 3.45 (m, 2H), 3.08 (m, 2H), 2.01(bs, 1H). $^{13}$C NMR (400 MHz, CDCl$_3$) δ 165.78, 165.38, 137.22, 133.30, 133.28, 129.85, 129.84, 129.82, 129.47, 129.44, 128.47, 128.40, 128.38, 128.37, 128.35, 128.34, 128.32, 128.30, 128.28, 128.07, 101.31, 77.33, 75.55, 74.96, 74.91, 72.20, 70.46, 70.19, 69.69, 61.59, 50.61. Maldi-ToF m/z calc’d for C$_{31}$H$_{33}$N$_3$O$_9$Na (M+Na$^+$): 614.2114; found: 614.2120.

Synthesis of compound 14A: To a stirred solution of sulfoxide 14B (500 mg, 0.900 mmol, 1eq) and TTBP (468 mg, 2.1 eq) in CH$_2$Cl$_2$ (10 ml) at -78°C was added Tf$_2$O (151 μl, 1eq) and, 5 min later, the solution of the glycosyl acceptor (78 mg, 1.2 eq) in CH$_2$Cl$_2$ (2 ml) drop wise were added. The reaction mixture was stirred at -78°C for 2 h and then allowed to warm to 0°C over 2 h and maintained for further 0.5 h before quenching with saturated aqueous NaHCO$_3$, washing with brine, drying, concentrating, and purified by chromatography on silica gel Hexane:Ethylacetate to give compound 14A (320 mg, 64%); $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.51–7.44 (m, 2H), 7.40–7.25 (m, 13H), 5.61 (s, 1H), 4.96 (d, J = 12.2 Hz, 1H), 4.87 (d, J = 12.2
Hz, 1H), 4.66 (d, J = 12.5 Hz, 1H), 4.57 (d, J = 12.5 Hz, 1H), 4.54 (s, 1H), 4.29 (dd, J = 10.4, 4.9 Hz, 1H), 4.19 (t, J = 9.6 Hz, 1H), 4.05–3.99 (m, 1H), 3.98 (d, J = 3.0 Hz, 1H), 3.92 (t, J = 10.3 Hz, 1H), 3.74–3.62 (m, 5H), 3.58 (dd, J = 9.6, 3.1 Hz, 1H), 3.33 (dt, J = 9.6, 5.4 Hz, 3H).

$^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 138.56, 138.39, 137.64, 134.56, 129.84, 129.09, 128.93, 128.72, 128.63, 128.42, 128.38, 128.27, 128.18, 128.05, 127.86, 127.65, 127.60, 126.14, 102.09, 101.50, 81.48, 78.67, 74.92, 73.29, 71.09, 70.69, 70.30, 69.19, 67.50, 63.10, 50.82. Maldi-ToF m/z calc’d for C$_{31}$H$_{35}$N$_3$O$_7$Na (M+Na$^+$): 584.2372; found: 584.2380.

Synthesis of compound 14: A solution of compound 14A (350 mg 534 mmol) was dissolved in dichloromethane (7 ml) and stirred for 1h at room temperature. The mixture was cooled to 0°C and then catalytic amount of p-TsOH were added to it. Allowed this reaction to stir at RT till complete disappearance of starting material on TLC. Then quenched the mixture by TEA and diluted with DCM followed by extraction with sat.NaHCO$_3$. The organic layer were concentrated and purified by silica gel column chromatography (DCM:MeOH) to afford colourless syrup (250 mg, 85%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49–7.41 (m, 2H), 7.36–7.24 (m, 8H), 4.96 (d, J = 12.3 Hz, 1H), 4.80 (d, J = 12.3 Hz, 1H), 4.56 (s, 1H), 4.51 (d, J = 11.8 Hz, 1H), 4.33 (d, J = 11.8 Hz, 1H), 4.10–4.03 (m, 1H), 4.02–3.98 (m, 1H), 3.97–3.91 (m, 1H), 3.89–3.80 (m, 1H), 3.78–3.67 (m, 5H), 3.39 (ddd, J = 9.6, 5.5, 4.4 Hz, 2H), 3.37–3.29 (m, 2H), 2.75 (d, J = 3.8 Hz, 1H), 2.55 (s, 1H), 2.03 (s, 1H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 138.52, 137.66, 128.56, 128.54, 128.36, 128.34, 128.20, 128.18, 127.92, 127.79, 127.77, 127.56, 101.97, 81.41, 75.94, 74.26, 73.41, 71.10, 70.66, 70.20, 69.08, 67.37, 62.91, 50.74. Maldi-ToF m/z calc’d for C$_{26}$H$_{28}$O$_5$S (M+Na$^+$): 496.2059; found: 496.2061.

Synthesis of compound 11: A stirred solution of 7 (5.00 g, 8.57 mmol, 1.00 equiv) in methanol (80 ml) was treated with methanesulfonic acid (1.68 ml, 25.7 mmol, 3.0 equiv) at room temperature, and then refluxed under Ar for 24 h. After being cooled to room temperature, the reaction mixture was quenched with excess triethylamine, and then concentrated. The concentrate and NaHCO$_3$ (3.60 g, 42.8 mmol, 5.0 equiv) were dissolved in CH$_3$CN (30 ml) and H$_2$O (60 ml) and cooled to 0°C. To the vigorously stirred mixture was added 4-nitrophenylchloroformate (4.32 g, 21.4 mmol, 2.5 equiv) in CH$_3$CN (30 ml) slowly through a
dropping funnel, after which stirring was continued for 3 h at 0°C. The resulting mixture was extracted with ethylacetate, and the combined extracts were washed with brine, and then dried over Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography, eluting with EtOAc then EtOAc/MeOH from 10/1 to 5/1 to give the title residue as white foam. A solution of residue (2.67 gm) in pyridine (20 ml) was treated with Ac₂O (24 ml) and stirred at room temperature overnight, then concentrated under reduced pressure. The residue was dissolved in anhydrous CH₂Cl₂, treated with EtN(i-Pr)₂ (11.6 ml, 66.8 mmol, 10 equiv), and cooled to 0°C before acetyl chloride (3.87 ml, 53.4 mmol, 8 equiv) was added dropwise, then the mixture stirred at 0°C for 1 h. After warming to room temperature, the resulting solution was poured into saturated aqueous NaHCO₃ solution, the organic layer was separated, the aqueous layer was extracted twice with CH₂Cl₂, and the combined organic phase was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel eluting with EtOAc/Hex (1:1) to give donor 1 as a yellowish solid (2.8 g, 82%), which can be further purified by recrystallization from EtOAc/ Et₂O/ Hex to afford white needle crystals.

**¹H-NMR** (400 MHz, CDCl₃) δ 7.55–7.32 (m, 5H), 5.57 (t, J = 2.3 Hz, 1H), 5.01 (dt, J = 8.2, 2.3 Hz, 1H), 4.90 (dd, J = 9.1, 2.5 Hz, 1H), 4.80 (ddd, J = 12.8, 11.4, 2.5 Hz, 1H), 4.38 (dd, J = 12.1, 2.5 Hz, 1H), 3.91 (dd, J = 12.1, 8.3 Hz, 1H), 3.77 (dd, J = 11.3, 9.2 Hz, 1H), 3.64 (s, 3H), 2.92 (dd, J = 13.0, 3.7 Hz, 1H), 2.54 (s, 3H), 2.35 (t, J = 13.0 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H). **¹³C-NMR** (400 MHz, CDCl₃) δ 172.46, 171.24, 170.38, 169.72, 167.80, 153.58, 136.77, 136.70, 130.20, 129.23, 129.20, 128.18, 88.35, 75.72, 75.11, 73.85, 72.69, 62.92, 59.67, 52.79, 36.05, 24.76, 21.17, 20.82, 20.73. Maldi-ToF m/z calc’d for C₂₅H₂₉NO₁₂SNa (M+Na⁺): 590.1308; found: 590.1307.
Glycosylation of donor and acceptor:

Scheme S2: Reagents and Conditions: (f) NIS/TfOH, -40°C, DCM.

General procedure for glycosylation. A solution of donor 11 (200 mg, 0.11 mmol, 1.0 equiv), acceptor (1.2 equiv), and activated 4 Å powdered molecular sieves (216 mg, 2.0 g/mmol) in anhydrous dichloromethane (2 ml) was stirred overnight under an argon atmosphere, and then cooled to -40°C followed by addition of NIS (172 mg, 0.26 mmol, 2.4 equiv) and TfOH (9.5 μl, 0.11 mmol, 1.0 equiv). The reaction mixture was stirred at -40°C for 20 min to 2 h until the disappearance of the donor on TLC, then quenched with triethylamine (22.6 μl, 0.16 mmol, 1.5 equiv) and warmed to room temperature. The mixture was diluted with dichloromethane, filtered through celite, washed with 20% aqueous Na₂S₂O₃ solution, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with THF/Hex system to afford the sialic acid disaccharide.
**Compound 8:** According to general procedure, donor 11 (200 mg) and acceptor 12 (250 mg, 1.2 eq) to afford 8 (270 mg, 73%). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.52–7.46 (m, 3H), 7.39–7.31 (m, 6H), 7.30–7.25 (m, 3H), 7.18–7.15 (m, 3H), 5.81 (dd, $J = 10.5$, 8.0 Hz, 1H), 5.58 (dd, $J = 8.0$, 1.6 Hz, 1H), 5.43 (td, $J = 7.1$, 3.1 Hz, 1H), 5.35 (dd, $J = 10.5$, 3.1 Hz, 1H), 4.83 (d, $J = 8.0$ Hz, 1H), 4.70–4.60 (m, 3H), 4.41 (dd, $J = 12.3$, 3.0 Hz, 1H), 4.22 (d, $J = 3.0$ Hz, 1H), 4.06 (dd, $J = 12.3$, 7.0 Hz, 1H), 4.03–3.97 (m, 3H), 3.81–3.74 (m, 2H), 3.71 (s, 3H), 3.58 (m, 2H), 3.47 (t, $J = 5.1$ Hz, 2H), 3.08–2.96 (m, 2H), 2.85 (dd, $J = 12.1$, 3.5 Hz, 1H), 2.49 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H), 2.05 (t, $J = 12.1$ Hz, 1H), 2.00 (s, 3H). $^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 172.03, 170.79, 170.14, 170.09, 168.39, 165.67, 165.36, 153.74, 137.44, 133.25, 133.20, 129.98, 129.82, 129.78, 129.72, 129.47, 129.02, 128.62, 128.61, 128.60, 128.59, 128.43, 128.33, 128.23, 127.99, 101.21, 99.47, 75.52, 75.36, 75.13, 74.81, 74.60, 74.45, 71.98, 71.63, 70.34, 70.15, 69.53, 68.54, 64.53, 63.10, 59.19, 53.08, 50.60, 36.76, 24.79, 21.28, 20.88, 20.79. HRMS m/z calc’d for C$_{50}$H$_{56}$N$_4$O$_21$ (M+Na$^+$): 1071.3314; found: 1071.3311.

**Compound 9:** According to general procedure, donor 11 (200 mg) and acceptor 13 (250 mg, 1.2 eq) to afford 9 (255 mg, 69%). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.51–7.46 (m, 4H), 7.37–7.32 (m, 5H), 7.15–7.08 (m, 6H), 5.69–5.60 (m, 2H), 5.48 (ddd, $J = 9.0$, 6.3, 3.0 Hz, 1H), 5.35–5.28 (m, 2H), 4.72 (dd, $J = 9.4$, 3.9 Hz, 2H), 4.66 (dd, $J = 9.4$, 1.6 Hz, 1H), 4.54 (d, $J = 10.8$ Hz, 1H), 4.35 (dd, $J = 12.3$, 2.9 Hz, 1H), 4.22 (dd, $J = 11.4$, 4.4 Hz, 1H), 4.05 (dd, $J = 12.3$, 6.4 Hz, 1H), 4.02–3.94 (m, 2H), 3.90 (dd, $J = 12.3$, 6.6 Hz, 1H), 3.74 (s, 3H), 3.73–3.64 (m, 3H), 3.57 (m, 2H), 3.45–3.43 (m, 2H), 3.07–3.04 (m, 2H), 3.01 (dd, $J = 12.0$, 3.4 Hz, 1H), 2.49 (s, 3H), 2.13 (s, 3H), 2.03 (t, $J = 12.5$ Hz, 1H), 1.90 (s, 3H). $^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 172.03, 170.79, 170.14, 170.09, 168.39, 165.67, 165.36, 153.74, 137.44, 133.25, 133.20, 129.98, 129.82, 129.47, 129.02, 128.62, 128.61, 128.60, 128.59, 128.43, 128.33, 128.23, 127.99, 101.21, 99.47, 75.52, 75.36, 75.13, 74.81, 74.60, 74.45, 71.98, 71.63, 70.34, 70.15, 69.53, 68.54, 64.53, 63.10, 59.19, 53.08, 50.60, 36.76, 24.79, 21.28, 20.88, 20.79. HRMS m/z calc’d for C$_{50}$H$_{56}$N$_4$O$_{21}$ (M+Na): 1071.3314; found: 1071.3322.

**Compound 10:** According to general procedure, donor 11 (200 mg) and acceptor 14 (238 mg, 1.2 eq) to afford 10 (230 mg, 64%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45–7.20 (m, 10H), 5.61 (dd, $J = 8.2$, 1.2 Hz, 1H), 5.46–5.32 (m, 1H), 5.05 (dd, $J = 10.5$, 3.1 Hz, 1H), 5.00 (s, 1H), 4.93 (d, $J = 12.3$ Hz, 1H), 4.78 (d, $J = 12.3$ Hz, 1H), 4.58 (d, $J = 9.3$ Hz, 1H), 4.51 (d, $J = 11.3$ Hz,
1H), 4.42 (d, \( J = 11.3 \) Hz, 1H), 4.34 (dd, \( J = 12.3, 3.2 \) Hz, 1H), 4.14 (dd, \( J = 9.2, 4.5 \) Hz, 1H), 4.10 – 4.01 (m, 4H), 3.98-3.90 (m, 3H), 3.78 (s, 3H), 3.76–3.52 (m, 4H), 3.39–3.23 (m, 4H), 3.03 (s, 1H), 2.88 (dd, \( J = 12.3, 3.6 \) Hz, 1H), 2.48 (s, 3H), 2.25 (s, 3H), 2.11 (s, 3H), 2.05 (t, dd, \( J = 12.4 \) Hz, 1H), 2.02 (s, 3H).

\(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \( \delta \) 172.12, 170.76, 170.16, 169.81, 168.99, 151.45, 139.06, 138.05, 129.42, 128.39, 128.33, 128.29, 128.25, 128.09, 127.70, 127.43, 126.82, 125.52, 102.08, 98.69, 80.76, 75.61, 75.51, 75.01, 73.99, 73.71, 71.58, 70.46, 69.11, 68.97, 66.42, 64.35, 62.78, 61.41, 59.05, 54.26, 53.00, 50.74, 36.48, 24.70, 21.19, 20.89, 20.85.

HRMS m/z calc’d for C\(_{43}\)H\(_{54}\)N\(_4\)O\(_{19}\) (M+Na): 953.3279; found: 953.3292.

Global deprotection of comp 8, 9, 10:

\[ \text{Reagents and Conditions:} \]
- i) LiOH, EtOH:H\(_2\)O (3:1), 80\(^{\circ}\)C, 12h;
- ii) NaHCO\(_3\), Ac\(_2\)O, H\(_2\)O, rt;
- iii) H\(_2\)/Pd(OH)\(_2\), MeOH:H\(_2\)O (1:1), 12h.

LiOH (30 eq) was added to a stirred solution of protected oligosachharide (1 eq) in ethanol water (3:1) 5 ml at room temperature. After stirring at 80\(^{\circ}\)C for 12h, the reaction mixture cooled to room temperature and carefully neutralized by IR-120H\(^+\) resin to pH-7, diluted with methanol, filtered and concentrated. Crude residue was dissolved in water and NaHCO\(_3\) (15 eq) were added to it. Cooled the reaction mixture to 0\(^{\circ}\)C and Acetic-anhydride (10 eq) was added. The reaction were monitored by TLC (ethylacetate:methanol:water 7:2:1), after 3h, LiOH (10 eq)
were added and stirred for another 5-6h at room temperature, then reaction mixture carefully neutralized by IR-120H resin to pH-7, diluted concentrated and purified by reverse-phase column chromatography (Bond Elu-C18). The Pd(OH)$_2$ (1 mmole) was added to the above residue in methanol water (1:1) 4ml. The reaction mixture was hydrogenasled under H$_2$ atmosphere for 12h, filtered and concentrated. The residue was purified by reverse phase column chromatography (Bond Elu-C18) to give deprotected sialic acid analogues.

**Compound 1:** Synthesized from 8 by following general deprotection protocol to yield 36 mg (36%). $^1$H-NMR (400 MHz, D$_2$O) $\delta$ 4.33 (d, $J = 7.7$ Hz, 1H), 3.97 (dd, $J = 11.8$, 7.1 Hz, 1H), 3.83 (t, $J = 8.7$ Hz, 2H), 3.76 (dd, $J = 11.5$, 8.7 Hz, 4H), 3.72–3.64 (m, 5H), 3.63–3.45 (m, 7H), 3.42 (dd, $J = 16.3$, 8.3 Hz, 1H), 3.28 (t, $J = 5.0$ Hz, 1H), 3.15–3.10 (m, 1H), 2.63 (dd, $J = 12.5$, 3.6 Hz, 1H), 1.93 (s, 3H), 1.58 (t, $J = 12.0$ Hz, 1H). $^{13}$C-NMR (400 MHz, D$_2$O) $\delta$ 175.02, 173.42, 103.01, 100.41, 73.44, 72.59, 72.46, 71.72, 71.42, 70.74, 68.59, 68.22, 68.17, 63.44, 62.60, 60.77, 60.37, 51.84, 40.15, 39.74, 22.03. HRMS m/z calc’d for C$_{21}$H$_{38}$N$_2$O$_{15}$ (M+H): 559.2350; found: 559.2352.

**Compound 3:** Synthesized from 9 by following general deprotection protocol to yield 20 mg (20%). $^1$H-NMR (400 MHz, MeOD) $\delta$ 4.34 (d, $J = 7.8$ Hz, 1H), 4.06 (dd, $J = 10.4$, 3.5 Hz, 1H), 3.95 (t, $J = 9.5$ Hz, 1H), 3.93–3.88 (m, 1H), 3.88–3.60 (m, 10 H), 3.58–3.48 (m, 2H), 3.38 (dd, $J = 16.2$, 6.8 Hz, 2H), 3.27–3.11 (m, 4H), 2.76 (dd, $J = 12.0$, 3.7 Hz, 1H), 2.04 (s, 3H), 1.66 (t, $J = 12.0$ Hz, 1H). $^{13}$C-NMR (400 MHz, D$_2$O) $\delta$ 174.90, 173.86, 102.37, 99.79, 75.92, 75.03, 72.92, 71.84, 69.60, 69.18, 68.77, 68.31, 68.12, 67.57, 66.38, 62.67, 61.02, 51.75, 39.73, 39.15, 22.17. HRMS m/z calc’d for C$_{21}$H$_{38}$N$_2$O$_{15}$ (M+H): 559.2350; found: 559.2352.

**Compound 5:** Synthesized from 10 by following general deprotection protocol to yield 27 mg (25%). $^1$H-NMR (400 MHz, MeOD) $\delta$ 4.57 (d, $J = 0.8$ Hz, 1H), 4.11–4.02 (m, 2H), 3.94–3.81 (m, 6H), 3.81–3.59 (m, 10 H), 3.55–3.45 (m, 4H), 2.85 (dd, $J = 12.4$, 4.3 Hz, 1H), 2.03 (s, 3H), 1.66 (t, $J = 12.4$ Hz, 1H). $^{13}$C-NMR (400 MHz, D$_2$O) $\delta$ 175.11, 173.80, 102.52, 99.35, 75.92, 75.03, 72.92, 71.84, 69.60, 69.18, 68.77, 68.31, 68.12, 67.57, 66.38, 62.67, 61.02, 51.75, 39.73, 39.15, 21.84. HRMS m/z calc’d for C$_{21}$H$_{38}$N$_2$O$_{15}$ (M+H): 559.2350; found: 557.2352.
3. Synthesis of trisaccharide library of compounds:

Synthesis of donor and acceptors

Scheme S4: Reagents and conditions: a) PhBCl₂, Et₃SiH, -78°C, DCM; b) i) BzCl/Py; ii) PhBCl₂, Et₃SiH, -80°C, DCM; c) i) TBDMSCl, Imidazole, DMF; ii) BnBr, NaH, DMF; d) p-TSA, MeOH:DCM; e) i) 1,3-dithiopropane, DCM, 35°C; ii) TrocCl, NaHCO₃, THF; f) 5-Azidopentanol, NIS/TfOH, -40°C, DCM; g) Dibutylphosphate, NIS/TfOH, DCM:ACN, -20°C.
Synthetic procedure:

**Compound 19:** A solution of compound 23 (600 mg, 1.08 mmol) and activated 4Å powdered molecular sieves 1.1 g in dichloromethane were stirred 1h at room temperature. The mixture was cooled to -78°C and then to the stirred solution Et$_3$SiH (552 μl, 3.46 mmol) and PhBCl$_2$ (265 μl, 2.05 mmol) were added successively. After being stirred for 1 h at -78°C, Et$_3$N (1 ml) and MeOH (1 ml) were added successively, and the mixture was diluted with CHCl$_3$ and washed with aqueous NaHCO$_3$, dried over MgSO$_4$, filtered and concentrated. The crude product was purified by silica gel column hexane:ethylacetate (2:1) to afford white solid (545 mg, 91%).

$^1$H- NMR (400 MHz, CDCl$_3$) δ 8.06 (d, $J = 7.6$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.42 – 7.31 (m, 7H), 7.27–7.14 (m, 5H), 7.06 (d, $J = 7.8$ Hz, 2H), 5.70 (t, $J = 9.7$ Hz, 1H), 5.02 (d, $J = 11.3$ Hz, 1H), 4.74 (d, $J = 9.7$ Hz, 1H), 4.67 (t, $J = 10.8$ Hz, 2H), 4.57 (d, $J = 12.2$ Hz, 1H), 3.94 (s, 1H), 3.93–3.85 (m, 1H), 3.72 (dd, $J = 9.0$, 2.2 Hz, 1H), 3.59 (dd, $J = 9.0$, 5.2 Hz, 1H), 3.56–3.50 (m, 1H), 2.31 (s, 3H), 1.67 (dd, $J = 8.5$, 3.7 Hz, 1H).

$^{13}$C-NMR (400 MHz, CDCl$_3$) δ 165.28, 138.11, 137.85, 137.43, 133.08, 132.71, 132.69, 130.08, 129.90, 129.88, 129.58, 129.51, 128.47, 128.44, 128.45, 128.41, 128.40, 128.39, 128.37, 128.35, 127.92, 127.86, 127.84, 127.79, 127.77, 87.25, 81.32, 78.99, 77.23, 74.07, 72.18, 70.54, 62.20, 21.14; HRMS m/z calc’d for C$_{34}$H$_{34}$O$_6$SNa (M+Na$^+$). 593.1973; found: 593.1971.

**Compound 20:** To solution of compound 24 (700 mg, 1.5 mmol) in dry pyridine (10 ml) benzoyl chloride (440 ml, 3.7mmol) were added dropwise. Allowed the reaction mixture to stir for 12h at room temperature. After completion quenched the reaction by methanol 2ml and diluted with DCM. Extracted with dilute HCl (5%), dried over Na$_2$SO$_4$ and concentrated. Crude residue was purified through silica gel column to afford the white solid. This white solid (575 mg, 1.03 mmol) dissolved in dry dichloromethane (10 ml) containing 4Å M.S. and stirred at room temperature for 1h. Reaction mixture was cooled to -78°C and then Et$_3$SiH (533 μl, 3.32 mmol) and PhBCl$_2$ (253 μl, 1.95 mmol) were added successively. After being stirred for 1 h at -78°C, Et$_3$N (1 ml) and MeOH (1 ml) were added successively, and the mixture was diluted with CHCl$_3$ and washed with aqueous NaHCO$_3$, dried over MgSO$_4$, filtered and concentrated. The crude product was purified by silica gel column hexane:ethylacetate (1:1) to afford white solid(530 mg, 88%).

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.08 (dd, $J = 8.3$, 1.3 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.49 (dd, $J = 8.2$, 4.7 Hz, 2H), 7.40–7.29 (m, 7H), 7.18–7.09 (m, 7H), 5.26 (dd, $J = 9.9$, 5.2 Hz, 1H), 3.94–3.85 (m, 1H), 3.72 (dd, $J = 9.0$, 2.2 Hz, 1H), 3.59 (dd, $J = 9.0$, 5.2 Hz, 1H), 3.56–3.50 (m, 1H), 2.31 (s, 3H), 1.67 (dd, $J = 8.5$, 3.7 Hz, 1H).
9.2 Hz, 1H), 4.87 (d, J = 10.5, 6.1 Hz, 2H), 4.68 (d, J = 11.0 Hz, 2H), 3.94 (dd, J = 12.0, 6.0, 2.6 Hz, 1H), 3.88 (t, J = 9.0 Hz, 1H), 3.79–3.73 (m, 1H), 3.73–3.67 (m, 1H), 3.51 (dd, J = 9.7, 4.7, 2.6 Hz, 1H), 2.35 (s, 3H), 1.99 (t, J = 6.8 Hz, 1H).\(^{13}\)C-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 165.20, 138.44, 137.75, 137.60, 133.32, 133.31, 133.25, 129.88, 129.86, 129.85, 129.75, 129.73, 128.54, 128.52, 128.50, 128.45, 128.30, 128.28, 128.12, 128.10, 128.08, 128.05, 128.03, 127.70, 127.72, 86.34, 84.06, 79.56, 77.51, 75.34, 75.19, 72.55, 62.07, 21.16. HRMS m/z calc’d for C\(_{34}\)H\(_{34}\)O\(_6\)SNa (M+Na). 593.1971; found: 593.1973.

**Compound 25**: The solution of compound 26 (1.2 gm, 4.41 mmol) in dry DMF (10 ml) cooled to -20\(^{0}\)C and then imidazole (0.6 gm, 8.82 mmol) were added to it. After 10 minutes TBDMSCl (0.79 gm, 5.29 mmol) were added portion wise and allowed the reaction mixture to stir for 2h. After completion of reaction, evaporated the solvent and then diluted with DCM and extracted with 1N HCl. The organic layer dried over Na\(_2\)SO\(_4\). This crude residue was purified by flash silica gel column chromatography in DCM:MeOH (9:1) to afford as colorless syrup (0.7 gm, 40%). This syrup was dissolved in dry THF (10 ml) followed by addition of tetrabutylammonium iodide(2 gm, 5.44 mmol). Cooled this reaction mixture to 0\(^{0}\)C and then sodium hydride(60%, 450 mg) was added. After 5 minutes benzyl bromide (1.0 ml, 9 mmol) was added dropwise and allowed the reaction mixture to stir for 12h at room temperature. After completion, reaction was quenched with methanol and diluted with ether. The organic layer was extracted with NaHCO3, brine and dried over Na\(_2\)SO\(_4\), concentrated. Purification by silica gel column chromatography (Ethylacetate:Hexane) afforded compound 25 as oily syrup (0.9 gm, 76%).\(^{1}\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (m, 20H), 5.59 (d, J = 1.5 Hz, 1H), 4.98 (d, J = 10.9 Hz, 1H), 4.74–4.62 (m, 5H) 4.13 (ddd, J = 9.6, 4.8, 1.7 Hz, 1H), 4.05 (d, J = 9.3 Hz, 1H), 4.01(dd, J = 3.1, 1.6 Hz, 1H) 3.97–3.87 (m, 3H), 0.92 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H).\(^{13}\)C-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 138.67, 138.28, 138.02, 134.80, 131.50, 131.48, 128.92, 128.90, 128.43, 128.41, 128.39, 128.37, 128.33, 128.31, 128.03, 128.01, 127.87, 127.86, 127.84, 127.82, 127.69, 127.64, 127.24, 85.61, 80.16, 76.54, 75.21, 74.91, 74.23, 72.15, 71.79, 62.70, 25.97, 25.97, 25.97, 18.38, -5.12, -5.30. HRMS m/z calc’d for C\(_{39}\)H\(_{48}\)O\(_5\)SSiNa (M+Na\(^{+}\)). 679.2889; found: 679.2891.
Compound 21  Compound 25 (0.750 gm, 1.14 mmol) was dissolved in dry methanol and dichloromethane mixture (10 ml). To it catalytic amount of *p*-TSOH (110 mg) were added and stirred this reaction mixture for 2h at room temperature. Quenched the reaction mixture with triethylamine and extracted with sat. NaHCO₃, brine and dried the organic layer over Na₂SO₄, concentrated. Purification of mixture by silica-gel column chromatography (Ethylacetate:Hexane) yielded compound 21 as colourless syrup (550 mg, 85%). ¹H-NMR (400 MHz, CDCl₃) δ 7.41-7.25 (m, 20H), 5.50 (d, *J* = 1.6 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.67-4.59 (m, 2H), 4.64 (d, *J* = 5.1 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.15-4.09 (m, 1H), 4.04 (t, *J* = 9.4 Hz, 1H), 3.99 (dd, *J* = 2.9, 1.8 Hz, 1H), 3.88 (dd, *J* = 9.2, 3.1 Hz, 1H), 3.83 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.79 (dd, *J* = 8.7, 4.4 Hz, 1H), 1.75 (bs, 1H). ¹³C NMR (400 MHz, CDCl₃) δ 138.31, 138.12, 137.94, 133.94, 131.87, 131.85, 129.13, 129.12, 128.48, 128.47, 128.46, 128.45, 128.09, 128.07, 127.95, 127.93, 127.86, 127.85, 127.83, 127.81, 127.80, 127.78, 127.76, 127.67, 127.65, 86.06, 80.12, 76.43, 75.32, 74.79, 73.25, 72.38, 72.26, 62.24. HRMS m/z calc’d for C₃₃H₃₄O₅S (M+Na⁺). 565.2024; found: 565.2025.

Compound 28: was synthesized by following synthetic reported protocol (C. H. Wang, K. Tony, K. Mong, C. Y. Huang, *J. Org. Chem.*, 2003, 68, 2135-2142). ¹H-NMR (400 MHz, CDCl₃) δ 7.50-7.40 (m, 2H), 7.39-7.21 (m, 11H), 7.07 (d, *J* = 7.9 Hz, 1H ), 4.88 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 9.9 Hz, 1H), 3.78 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.73 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.60 (t, *J* = 9.0 Hz, 1H), 3.43 (dt, *J* = 9.4, 4.4 Hz, 1H), 3.35 (t, *J* = 9.0 Hz, 1H), 3.30-3.23 (m, 1H), 2.72 (s, 1H), 2.32 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) δ 138.86, 137.92, 137.79, 134.30, 129.87, 128.80, 128.72, 128.66, 128.57, 128.40, 128.34, 128.30, 128.22, 127.93, 127.95, 127.78, 127.80, 127.11, 86.25, 84.69, 78.04, 75.58, 73.83, 72.03, 70.39, 64.42, 21.26. HRMS m/z calc’d for C₂₇H₂₉N₃O₄S(M+Na⁺). 514.1776; found: 514.1769.

Compound 27. To compound 28 (2.5 gm, 5.09 mmol) in MeOH:DCM (1:1) was added 1,3 dithiopropane (2.5 ml, 25.45 mmol) and TEA (2.45 ml, 25.45 mmol) under Ar atmosphere. Reaction mixture was stirred at 35°C for 18h. Then coevaporated with toluene, concentrated and purified by flash column chromatography (Ethylacetate:Hexane) to afford oily syrup. This syrup was dissolved in THF and NaHCO₃ (0.818 gm, 10.18 mmol) was added to it. Cooled the reaction
mixture to 4°C and Troc-chloride (1 ml, 7.63 mmol) added dropwise. Stirred this reaction mixture at room temperature under argon for 6h. Filtered the reaction mixture and filtrate was concentrated. The residue was dissolved in DCM and washed with water, brine and the organic layer was dried over Na₂SO₄ and concentrated. The residue was purified on silica gel column chromatography (Ethylacetate:Hexane) to afford compound 27 as white solid (2.4 gm, 76%).

**1H-NMR** (400 MHz, CDCl₃) δ 7.42-7.24 (m, 12H), 7.04 (d, J = 7.9 Hz, 2H), 5.14 (d, J = 8.1 Hz, 1H), 4.88 (d, J = 10.2 Hz, 1H), 4.75 (m, 4H), 4.58 (d, J = 11.8 Hz, 1H), 4.53 (d, J = 11.8 Hz, 1H), 3.77 (dd, J = 4.7, 3.0 Hz, 2H), 3.67 (t, J = 9.3, 10.2 Hz, 2H), 3.45-3.55 (m, 1H), 3.35 (dd, J = 9.1, 4.2 Hz, 1H), 2.81 (s, 1H), 2.29 (s, 3H).

**13C-NMR** (400 MHz, CDCl₃) δ 153.91, 138.31, 138.08, 137.80, 133.30, 133.28, 129.81, 129.79, 128.68, 128.66, 128.56, 126.54, 128.26, 128.24, 128.11, 127.95, 127.93, 127.85, 127.83, 95.57, 86.18, 81.91, 77.99, 74.83, 74.55, 73.83, 73.00, 70.64, 56.15, 21.22. HRMS m/z calc’d for C₃₀H₃₂NCl₃O₆SNa (M+Na⁺); 662.0913 found: 662.0910.

**Compound 22:** A solution of 27 (2.3 gm, 3.59 mmol, 1.0 equiv), 5-azidopentanol (4.31 mmol, 1.2 equiv), and activated 4Å powdered molecular sieves (1.5 gm) in anhydrous dichloromethane (12 ml) was stirred for 2h at room temperature under an argon atmosphere, and then cooled to -40°C followed by addition of NIS (0.96 gm, 4.31 mmol, 1.2 equiv) and TfOH (32 μl, 0.359 mmol, 0.1 equiv). The reaction mixture was stirred at -40°C for 0.5 h to 3 h until the disappearance of the donor on TLC, then quenched with triethylamine (270μl, 2.69 mmol, 0.75 equiv) and warmed to room temperature. The mixture was diluted with dichloromethane, filtered through Celite, washed with 20% aqueous Na₂S₂O₃ solution, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Ethylacetate/Hexane (1:1) system to afford the compound 22 (2.1 gm, 91%).

**1H-NMR** (400 MHz, CDCl₃) δ 7.44-7.33 (m, 10H), 5.15 (s, 1H), 4.85-4.70 (m, 3H), 4.72 (d, J = 11.7 Hz, 2H), 4.64 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 3.91-3.84 (m, 2H), 3.83-3.75 (m, 2H), 3.72 (t, J = 8.3 Hz, 1H), 3.55-3.43 (m, 2H), 3.27 (t, J = 6.8 Hz, 3H), 2.83 (s, 1H), 1.66-1.57 (m, 4H), 1.43 (m, 2H). **13C-NMR** (400 MHz, CDCl₃) δ 153.96, 138.19, 137.59, 128.58, 128.56, 128.51, 128.49, 128.16, 128.18, 127.97, 127.92, 127.80, 127.78, 100.29, 95.53, 80.24, 77.23, 74.44, 73.77, 73.50, 73.49, 70.65, 69.50, 57.54, 51.31, 29.04, 28.56, 23.19. HRMS m/z calc’d for C₂₈H₃₅N₄Cl₃O₆S Na (M+Na⁺); 667.1468; found: 667.1467.
**Compound 18**

A solution of 11 (3 gm, 4.62 mmol, 1.0 equiv), dibutylphosphate (6.94 mmol, 1.5 equiv), and activated 4Å powdered molecular sieves (2.2 gm) in anhydrous dichloromethane (20 ml) and acetonitrile (10 ml) was stirred for 2h at room temperature under an argon atmosphere, and then cooled to -20°C followed by addition of NIS (2 gm, 9.28 mmol, 2 equiv) and TfOH (200 μl, 2.31 mmol, 0.5 equiv). The reaction mixture was stirred at -20°C for 12 h until the disappearance of the donor on TLC, then quenched with triethylamine (81μl, 0.81 mmol, 0.75 equiv) and warmed to room temperature. The mixture was diluted with dichloromethane, filtered through celite, washed with 20% aqueous Na₂S₂O₃ solution, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Ethylacetate/Hexane (1:1) system to afford the compound 18(2 gm, 67%).

**α-isomer** ¹H-NMR (400 MHz, CDCl₃) δ 5.69 (dd, J = 7.5, 1.5 Hz, 1H), 5.33 (ddd, J = 7.5, 6.2, 2.8 Hz, 1H), 4.77 (dd, J = 9.5, 1.5 Hz, 1H), 4.42 (dd, J = 12.3, 2.8 Hz, 1H), 4.26-4.05 (m, 6H), 3.91-3.83 (m, 4H), 3.02 (dd, J = 12.2, 4.0 Hz, 1H), 2.74 (t, J = 12.7 Hz, 1H), 2.51 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 1.74-1.64 (m, 4H), 1.43 (dq, J = 14.7, 7.4 Hz, 4H), 0.95 (t, J = 7.4 Hz, 6H).

¹³C-NMR (400 MHz, CDCl₃) δ 171.84, 170.62, 169.99, 169.89, 167.30, 167.23, 153.52, 98.22, 98.15, 74.19, 71.48, 69.81, 68.16, 68.10, 68.05, 67.99, 62.51, 58.32, 53.46, 35.91, 35.87, 32.14, 32.10, 32.07, 24.63, 20.96, 20.79, 20.74, 18.63, 18.60, 13.56. HRMS m/z calc’d for C_{27}H_{42}NO_{16}P (M+Na) 690.2139; found: 690.2134.

**Glycosylation of Donor and Acceptors:**
Scheme 2: Reagents and condition: h) TMSOTf, M.S 4Å, DCM, -78°C.

General procedure of glycosylation: The mixture of donor 18 (0.899 mmol, 1eq), acceptor(0.674 mmol, 0.75 eq) and activated 4Å powdered molecular sieves (1.5 gm) in anhydrous dichloromethane(10 ml) and was stirred for 3h at room temperature under an argon atmosphere, and then cooled to -78°C followed by addition of TMSOTf (165 μl, 0.899 mmol, 1 equiv). The reaction mixture was stirred at -78°C for 1-3 h until the disappearance of the donor on TLC, then quenched with triethylamine warmed to room temperature. The mixture was diluted with dichloromethane, filtered through celite, washed brine solution, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Ethylacetate/Hexane (1:1) system to afford the sialic acid disaccharide analogues.

Compound 15A According to general procedure donor 18 and acceptor 19 to yield as white solid (700 mg, 75%). ¹H-NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 7.33 (dt, J = 7.8, 3.6 Hz, 5H ), 7.24 – 7.14 (m, 5H), 7.03 (d, J = 7.8 Hz, 2H), 5.66 (t, J = 9.7 Hz, 1H), 5.60 (d, J = 7.0 Hz, 1H), 5.46 (ddd, J = 8.7, 6.7, 3.1, Hz, 1H), 5.02 (d, J = 11.3 Hz, 1H), 4.77 (d, J = 11.3 Hz, 1H), 4.71 (J =
9.4 Hz, 1H), 4.66 (d, J = 11.3 Hz, 1H), 4.62 (d, J = 9.4 Hz, 1H), 4.54 (d, J = 12.2 Hz, 1H), 4.42 (dd, J = 12.2, 2.3 Hz, 1H), 4.13-4.04 (m, 2H), 4.04-3.98 (m, 2H), 3.79-3.71 (m, 3H), 3.69 (s, 3H), 3.66-6.59 (m, 1H), 2.90 (dd, J = 12.0, 3.3 Hz, 1H), 2.52 (s, 3H), 2.31 (s, 3H), 2.15 (s, 3H), 2.09 (t, J = 12.5 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 3H).  

$^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 172.04, 170.79, 170.17, 169.99, 168.28, 165.21, 153.68, 138.61, 137.99, 137.60, 133.01, 132.64, 130.17, 129.89, 129.87, 129.69, 129.44, 128.33, 128.32, 128.29, 128.27, 128.16, 128.14, 127.66, 127.64, 127.62, 127.55, 127.58, 127.53, 127.35, 99.21, 86.85, 81.23, 76.85, 75.86, 74.93, 74.07, 72.65, 72.02, 71.95, 70.41, 69.51, 63.85, 59.11, 53.13, 36.43, 24.73, 21.15, 21.11, 20.87, 20.77.

HRMS m/z calc'd for C$_{53}$H$_{57}$NO$_{18}$S (M+Na) 1050.3193; found: 1050.3191.

**Compound 16A**  According to general procedure donor 18 and acceptor 20 gave as white solid (765 mg, 83%).  

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (t, J = 6.3 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.38-7.30 (m, 5H), 7.17-7.06 (m, 7H), 5.65 (dd, J = 8.6, 1.4 Hz, 1H), 5.51 (ddd, J = 8.8, 6.3, 2.8 Hz, 1H), 5.22 (dd, J = 9.9, 9.2 Hz, 1H), 4.80 (d, J = 10.5 Hz, 1H), 4.78 (d, J = 10.5 Hz, 1H), 4.73-4.65 (m, 3H), 4.64-4.60 (m, 1H), 4.38 (dd, J = 12.4, 2.8 Hz, 1H), 4.24 (dd, J = 11.0, 4.5 Hz, 1H), 4.08-4.00 (m, 2H), 3.82 (m, 4H), 3.77 (m, 1H), 3.71 (t, J = 10.2 Hz, 2H), 3.58 (dd, J = 8.6, 3.4 Hz, 1H), 3.01 (dd, J = 12.0, 3.4 Hz, 1H), 2.52 (s, 3H), 2.35 (s, 3H), 2.17 (s, 3H), 2.13 (t, J = 12.3 Hz, 1H), 2.07 (s, 3H), 1.87 (s, 3H).  

$^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 171.86, 170.65, 170.05, 170.03, 168.37, 165.16, 153.66, 138.11, 138.01, 137.70, 133.16, 132.90, 132.88, 129.92, 129.85, 129.83, 129.48, 129.46, 129.44, 129.31, 128.46, 128.43, 128.41, 128.24, 128.22, 128.20, 128.18, 127.99, 127.96, 127.95, 127.63, 99.31, 86.34, 84.05, 78.01, 77.27, 75.31, 75.24, 75.11, 75.00, 72.24, 71.54, 68.61, 64.53, 62.92, 59.18, 53.09, 36.68, 24.70, 21.20, 21.16, 20.80, 20.62. HRMS m/z calc'd for C$_{53}$H$_{57}$NO$_{18}$S (M+Na) 1050.3193; found: 1050.3195.

**Compound 17A:** According to general procedure donor 18 and acceptor 21 to afford as white solid (830 mg, 90%).  

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (dd, J = 6.4, 3.0 Hz, 2H), 7.33 (m, 18H), 5.62 (dd, J = 8.3, 1.5 Hz, 1H), 5.55 (d, J = 1 Hz, 1H), 5.47 (ddd, J = 8.5, 6.0, 2.9 Hz, 1H), 4.93 (d, J = 10.4 Hz, 1H), 4.78 (d, J = 10.4 Hz, 1H), 4.70 (dd, J = 13.1, 6.9 Hz, 2H), 4.67-4.60 (m, 3H), 4.30 (dt, J = 9.1, 6.3 Hz, 2H), 4.21 (dd, J = 10.8, 6.6 Hz, 1H), 4.07-3.99 (m, 3H), 3.96 (t, J = 9.3 Hz, 1H), 3.88 (dd, J = 9.3, 3.0 Hz, 1H), 3.73-3.68 (m, 2H), 3.68 (s, 3H), 2.92 (dd, J = 12.0, 3.5 Hz, 1H), 2.51 (s, 3H), 2.14 (t, J = 12.6 Hz, 1H), 2.12 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H).
$^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 171.85, 170.60, 169.99, 169.82, 168.71, 153.74, 138.63, 138.13, 137.85, 133.95, 132.54, 132.52, 128.92, 128.43, 128.41 128.40, 128.39, 128.37, 128.30, 128.28, 128.13, 128.10, 127.90, 127.88, 127.83, 127.81, 127.80, 127.79, 127.72, 127.70, 99.41, 85.73, 80.01, 76.13, 75.34, 75.14, 75.05, 74.77, 72.21, 72.13, 71.93, 71.55, 68.66, 65.43, 62.76, 59.16, 52.90, 36.48, 24.72, 21.12, 20.86, 20.77. HRMS m/z calc’d for C$_{52}$H$_{57}$NO$_{17}$SNa (M+Na ). 1022.3244; found: 1022.3245.

Synthesis of trisaccharide from disaccharide:

Scheme S5: Reagents and condition: i) NIS/TfOH, M.S. 4Å, DCM or ACN, -40°C.

General Glycosylation Procedure: A solution of donor 15A/16A/17A (500 mg, 0.488 mmol, 1.0 equiv), acceptor 22 (0.585 mmol, 1.2 equiv), and activated 4Å powdered molecular sieves(976 mg, 2.0 g/mmol) in anhydrous dichloromethane (10 ml) was stirred overnight under an argon atmosphere, and then cooled to -40°C followed by addition of NIS (109 mg, 0.488 mmol, 1.0 equiv) and TfOH (6.46 $\mu$l, 0.048 mmol, 0.1 equiv) dissolved in ether. The reaction mixture was stirred at -40°C for 20 min to 2 h until the disappearance of the donor on TLC and warmed to room temperature. The mixture was diluted with dichloromethane, filtered through
celite, washed with sat. Na$_2$S$_2$O$_3$ (3:1) 20 ml solution, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Ethylacetate/Hexane system to afford the sialic acid trisaccharide.

**Compound 15** Synthesized from donor 15A and acceptor 22 by following general glycosylation procedure to afford as white solid (430 mg, 57%) $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 7.7$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.39 (d, $J = 7.4$ Hz, 2H), 7.37-7.33 (m, 3H), 7.33-7.22 (m, 10H), 7.21-7.14 (m, 5H), 5.70-5.63 (m, 1H), 5.57 (s, 1H), 5.48 (d, $J = 6.5$ Hz, 1H), 5.39 (td, $J = 6.9$, 2.3 Hz, 1H), 5.09 (d, $J = 11.4$ Hz, 1H), 4.97 (d, $J = 11.1$ Hz, 1H), 4.75-4.63 (m, 5H), 4.60 (d, $J = 12.2$ Hz, 1H), 4.52 (d, $J = 12.2$ Hz, 2H), 4.47-4.39 (m, 2H), 4.33 (d, $J = 12.2$ Hz, 2H), 4.05 (dd, $J = 12.2$, 7.2 Hz, 1H), 4.01-3.91 (m, 4H), 3.87 (d, $J = 6.3$ Hz, 2H), 3.76 (m, 2H), 3.68-3.65 (m, 1H), 3.64 (s, 3H), 3.60 (d, $J = 3.1$ Hz 1H), 3.56 (dd, $J = 10.1$, 2.1 Hz, 1H), 3.45 (dd, $J = 12.9$, 7.1 Hz, 1H), 3.34 (m, 3H), 3.24 (t, $J = 6.9$ Hz, 2H), 2.73 (dd, $J = 12.3$, 3.7 Hz, 1H), 2.51 (s, 3H), 2.17 (t, $J = 12.6$, Hz, 1H), 2.13 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.62-1.50 (m, 4H), 1.38 (m, 2H). $^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 172.19, 170.85, 170.31, 169.85, 168.09, 165.17, 153.98, 153.80, 138.75, 138.44, 138.29, 137.57, 133.20, 133.17, 135.15, 129.87, 129.78, 129.76, 129.77, 128.46, 128.44, 128.42, 128.39, 128.40, 128.37, 128.36, 128.34, 128.32, 128.30, 128.03, 127.75, 127.71, 127.69, 127.68, 127.63, 127.60, 127.52, 127.32, 100.50, 99.75, 99.23, 95.65, 79.82, 77.24, 76.03, 75.57, 74.91, 74.64, 74.35, 74.26, 74.15, 73.45, 73.30, 72.80, 72.40, 72.16, 71.89, 69.96, 69.34, 68.47, 63.86, 62.97, 58.83, 57.20, 53.12, 51.31, 35.54, 29.00, 28.53, 24.74, 23.15, 21.13, 20.84, 20.73. HRMS m/z calc’d for C$_{74}$H$_{84}$Cl$_3$N$_5$O$_{25}$ (M+Na). 1570.4418; found: 1570.4411.

**Compound 16** Synthesized from donor 16A and acceptor 22 by following general glycosylation procedure to afford as white solid (340 mg, 45%) $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.4$ Hz 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.48-7.30 (m, 17H), 7.18-7.05 (m, 5H), 5.59 (dd, $J = 9.0$, 1.4 Hz, 1H), 5.48 (ddd, $J = 8.9$, 6.2, 2.7 Hz, 1H), 5.26 (dd, $J = 9.4$, 8.2 Hz, 1H), 4.98-4.88 (m, 4H), 4.80 (d, $J = 12.9$ Hz, 2H), 4.75 (d, $J = 10.5$ Hz, 1H), 4.71 (d, $J = 3.4$ Hz, 2H), 4.68(s, 2H), 4.66 (d, $J = 1.4$ Hz, 1H), 4.58 (d, $J = 11.2$ Hz, 2H), 4.40 (d, $J = 12.2$ Hz, 2H), 4.33 (dd, $J = 12.2$, 2.7 Hz, 1H), 4.30-4.25 (m, 3H), 4.01 (dd, $J = 11.5$, 6.2 Hz, 2H), 3.95 (dd, $J = 12.5$, 6.2 Hz, 2H), 3.86 (t, $J = 9.4$ Hz, 1H), 3.73(s, 3H), 3.68-3.62 (m, 3H), 3.56-3.47(m, 4H), 3.25 (m, 4H), 2.73
(dd, $J = 12.0$, 3.3 Hz, 1H), 2.49 (s, 3H), 2.18 (s, 3H), 2.07 (t, $J = 12.3$ Hz, 1H), 1.60-1.48 (m, 4H), 1.41-1.26 (m, 2H). $^{13}$C-NMR (400 MHz, CDCl$_3$) δ 171.90, 170.69, 170.00, 169.94, 168.38, 165.03, 154.03, 153.65, 138.92, 138.17, 137.94, 137.84, 133.24, 129.71, 129.63, 128.61, 128.48, 128.31, 128.27, 128.20, 128.07, 127.96, 127.71, 127.83, 127.68, 127.58, 127.56, 127.53, 100.93, 99.46, 99.26, 95.70, 82.17, 78.27, 77.23, 75.72, 75.14, 74.95, 74.92, 74.53, 74.45, 74.09, 73.85, 73.65, 73.48, 71.39, 69.18, 68.32, 67.94, 64.37, 63.96, 62.93, 59.11, 57.11, 53.11, 51.30, 36.52, 28.96, 28.51, 24.67, 23.14, 21.18, 20.79, 20.34. HRMS m/z calc’d for C$_{74}$H$_{84}$Cl$_3$N$_5$O$_{25}$ (M+Na). 1570.4418; found: 1570.4411.

**Compound 17** Synthesized from donor 17A (0.502 mmol) and acceptor 22 (0.603 mmol) by following general glycosylation procedure in DCM:ACN (1:1) solvent to afford as white solid (410 mg, 53%); α:β(1:3). β-isomer $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.47-7.21 (m, 25H), 5.65 (dd, $J = 8.6$, 1.4 Hz, 1H), 5.50 (dd, $J = 10.5$, 5.3, 2.4 Hz, 1H), 5.35 (m, 1H), 5.24 (d, $J = 7.0$ Hz, 1H), 4.90 (d, $J = 10.4$ Hz, 1H), 4.83-4.87 (m, 1H), 4.76 (d, $J = 7.8$ Hz, 2H), 4.73 (d, $J = 3.9$ Hz, 1H), 4.70 (d, $J = 3.2$ Hz, 1H), 4.68 (d, $J = 1.8$ Hz, 1H), 4.64 (d, $J = 2.9$ Hz, 1H), 4.61 (s, 1H), 4.58 (t, $J = 10.6$ Hz, 1H), 4.46 (d, $J = 12.1$ Hz, 1H), 4.35 (d, $J = 12.1$ Hz, 1H), 4.31 (dd, $J = 12.4$, 2.9 Hz, 1H), 4.29 (d, $J = 2.8$ Hz, 1H), 4.23 (dt, $J = 7.5$, 2.8 Hz, 1H), 4.04 (dd, $J = 6.2$, 3.6 Hz, 1H), 4.02-3.96 (m, 2H), 3.94 (dd, $J = 9.3$, 4.2 Hz, 2H), 3.91-3.80 (m, 4H), 3.79-3.68 (m, 3H), 3.64 (d, $J = 9.8$ Hz, 1H), 3.61 (s, 3H), 3.58 (d, $J = 9.8$, 1H), 3.55-3.49 (m, 1H), 3.45-3.38 (m, 1H), 3.30 (t, $J = 6.9$ Hz, 2H), 2.93 (dd, $J = 7.3$, 1.8 Hz, 1H), 2.88 (dd, $J = 12.0$, 3.5 Hz, 1H), 2.54 (s, 3H), 2.15 (s, 3H), 2.07 (t, $J = 12.5$ Hz, 1H), 2.05 (s, 3H), 1.98 (s, 3H), 1.69-1.59 (m, 4H), 1.45-1.41 (m, 2H). $^{13}$C-NMR (400 MHz, CDCl$_3$) δ 171.65, 170.43, 169.78, 169.55, 168.44, 153.74, 153.53, 138.41, 138.19, 138.13, 137.96, 137.59, 137.43, 133.77, 132.36, 131.69, 128.76, 128.74, 128.72, 128.70, 128.66, 128.64, 128.60, 128.59, 128.32, 128.16, 127.97, 127.80, 127.72, 127.60, 127.54, 127.46, 127.38, 127.25, 127.13, 127.08, 126.85, 101.46, 99.65, 99.20, 95.30, 85.55, 80.74, 79.35, 75.66, 75.07, 74.92, 74.75, 74.52, 74.38, 74.16, 73.60, 73.09, 72.18, 71.99, 71.27, 69.54, 69.26, 68.31, 65.41, 65.24, 62.52, 58.93, 57.63, 52.66, 51.14, 36.34, 29.18, 28.87, 24.53, 23.23, 22.52, 20.95, 20.58. HRMS m/z calc’d for C$_{74}$H$_{86}$Cl$_3$N$_5$O$_{24}$ (M+Na). 1556.4626; found: 1556.4624.
Global Deprotection of Sialoside:

Scheme 3: Reagents and Conditions: (i) LiOH, EtOH:H₂O (3:1), 80°C, 12h; (ii) NaHCO₃, Ac₂O, H₂O, rt; (iii) H₂/Pd (OH)₂, MeOH:H₂O (1:1).

General Deprotection Procedure: Oligosaccharide (1 eq) in ethanol water (3:1) 5ml at room temperature. After stirring at 80°C for 12h, the reaction mixture cooled to room temperature and carefully neutralized by IR-120H⁺ resin to pH-7, diluted with methanol, filtered and concentrated. Crude residue was dissolved in water and NaHCO₃ (15 eq) were added to it. Cooled the reaction mixture to 0°C and Acetic-anhydride (10 eq) was added. The reaction were monitored by TLC (ethylacetate:methanol:water 7:2:1), after 3h, LiOH (10 eq) were added and stirred for another 5-6h at room temperature, then reaction mixture carefully neutralized by IR-120H⁺ resin to pH-7, diluted concentrated and purified by reverse-phase column chromatography (Bond Elu-C18). The Pd(OH)₂ (1 mmole) was added to the above residue in methanol water (1:1) 4ml. The reaction mixture was hydrogenalyzed under H₂ atmosphere for 12h, filtered and concentrated. The residue was purified by reverse phase column chromatography (Bond Elu-C18) to give deprotected sialic acid analogues.

Compound 2 Synthesized from 15 by following general deprotection protocol to afford white solid (50 mg, 50%). ¹H-NMR (400 MHz, D₂O) δ 4.47 (d, J = 7.3 Hz, 1H), 4.36 (d, J = 7.9 Hz, 1H), 3.97-3.87 (m, 3H), 3.86-3.79 (m, 4H), 3.78-3.67 (m, 4H), 3.64 (dd, J = 6.3, 3.9 Hz, 3H), 3.61-3.51 (m, 4H), 3.46 (m, 3H), 2.96-2.88 (m, 2H), 2.58 (dd, J = 12.4, 4.7 Hz, 1H), 1.97 (s, 3H), 1.94 (s, 3H), 1.66-1.57 (m, 3H), 1.56-1.48 (m, 2H), 1.37-1.29 (m, 2H). ¹³C-NMR (400
MHz, D$_2$O) δ 174.68, 174.42, 173.50, 103.45, 100.91, 100.13, 80.74, 74.46, 73.68, 72.53, 72.43, 72.41, 71.69, 70.71, 68.39, 68.35, 68.21, 63.35, 62.64, 60.36, 54.87, 51.87, 42.57, 40.06, 39.33, 28.04, 26.34, 25.01, 22.27, 22.03. HRMS m/z calc’d for C$_{30}$H$_{51}$N$_5$O$_{19}$ (M+H). 760.3351; found: 760.3358.

**Compound 4** Synthesized from **16** by following general deprotection protocol to afford white solid (40 mg, 35%). $^1$H-NMR (400 MHz, D$_2$O) δ 4.43 (d, $J = 8.2$ Hz, 1H), 4.35 (d, $J = 8.0$ Hz, 1H), 3.92-3.87 (m, 1H), 3.85-3.74 (m, 5H), 3.71 (dd, $J = 10.0$, 3.4 Hz, 1H), 3.67-3.56 (m, 4H), 3.56-3.48 (m, 4H), 3.42 (d, $J = 9.2$ Hz, 2H), 3.39-3.34 (m, 1H), 3.03-2.96 (m, 2H), 2.93 (dd, $J = 7.8$, 5.3 Hz, 2H), 2.69 (dd, $J = 7.9$, 4.8 Hz, 1H), 2.60 (dd, $J = 12.3$, 4.3 Hz, 1H), 1.96 (s, 3H), 1.95 (s, 3H), 1.61-1.50 (m, 4H), 1.49-1.45 (m, 1H), 1.35 -1.21(m, 2H). $^{13}$C-NMR (400 MHz, D$_2$O) δ 174.94, 174.39, 173.44, 102.96, 100.92, 100.01, 80.69, 75.35, 74.44, 74.24, 72.96, 72.48, 71.68, 70.00, 69.78, 68.32, 68.18, 63.19, 62.59, 60.28, 54.92, 51.85, 42.72, 39.94, 39.04, 28.06, 25.27, 23.04 , 22.24, 22.01. HRMS m/z calc’d for C$_{30}$H$_{51}$N$_5$O$_{19}$ (M+H). 760.3351; found: 760.3358.

**Compound 6** Synthesized from **17** by following general deprotection protocol to afford white solid(35 mg, 30%). $^1$H-NMR (400 MHz, D$_2$O) δ 5.06 (d, $J = 0.8$ Hz, 1H), 4.37 (d, $J = 8.2$ Hz, 1H), 3.90 (m, 1H), 3.82 (dd, $J = 10.7$, 4.4 Hz, 2H), 3.79-3.72 (m, 2H), 3.73 (d, $J = 2.4$ Hz, 1H), 3.70 (d, $J = 3.5$ Hz, 1H), 3.66 (dd, $J = 7.2$, 2.2 Hz, 1H), 3.63 (d, $J = 3.7$ Hz, 2H), 3.59 (d, $J = 1.6$ Hz, 2H), 3.57 (d, $J = 1.6$ Hz, 2H), 3.55 (d, $J = 4.7$ Hz, 2H), 3.53 (d, $J = 7.6$ Hz, 2H), 3.51-3.48 (m, 2H), 3.46 (d, $J = 9.0$ Hz, 2H), 2.88-2.83 2.86 (m, 1H), 2.62 (dd, $J = 12.5$, 4.7 Hz, 1H), 1.91(s, 6H), 1.63-1.50 (m, 4H), 1.50-1.45 (m, 1H), 1.35-1.22 (m, 2H). $^{13}$C-NMR (400 MHz, D$_2$O) δ 181.55, 175.05, 173.58, 101.70, 100.96, 100.17, 74.64, 74.03, 72.61, 72.34, 71.61, 70.60, 70.20, 69.90, 68.26, 66.61, 66.53, 63.31, 62.62, 60.89, 55.74, 51.89, 51.91, 40.08, 39.36, 27.94, 26.35, 26.32, 22.06, 22.01. HRMS m/z calc’d for C$_{30}$H$_{51}$N$_5$O$_{19}$ (M+H). 760.3351; found: 760.3344.
4. Glycanmicroarraydetails

**Sialoglycan microarray fabrication.** Arrays were printed on Epoxide-derivatized Corning slides as described for Array 1 in Ref. {Padler-Karavani et al., 2012, J BiolChem} with some modifications. Arrays were fabricated with NanoPrint LM 60Microarray Printer (Arrayit, CA) on epoxide-derivatized slides (Corning) with 16 sub-array blocks on each slide. Glycoconjugates were distributed into one 384-well source plates using 4 replicate wells per sample and 8 µl per well. Each glycoconjugate was prepared at 100 µM in an optimized print buffer (300 mM phosphate buffer, pH 8.4). The arrays were printed with four 946MP3 pins (5 µm tip, 0.25 µl sample channel, ~100µm spot diameter; Arrayit, CA) with spot to spot spacing of 225 µm. The humidity level in the arraying chamber was maintained at about 66% during printing. Printed slides were left on arrayer deck over-night, allowing humidity to drop to ambient levels (40-45%). Next, slides were packed, vacuum-sealed and stored in a desiccant chamber at room temperature(RT) until used.

**Microarray binding assay.** Slides were developed {23520510} and analyzed {Padler-Karavani et al., 2012, J BiolChem} as previously described. Slides were rehydrated with dH2O and incubated for 30 min in a staining dish with 50°C pre-warmed 0.05 M ethanolamine in 0.1 M Tris, pH 9.0 to block the remaining reactive epoxy groups on the slide surface, then washed with 50°C pre-warmed dH2O. Slides were centrifuged at 200×g for 3 min then fitted with ProPlate™ Multi-Array 16-well slide module (Invitrogen) to divide into the sub-arrays (blocks). Slides were washed with PBST(PBS pH 7.4, 0.1% Tween-20), aspirated and blocked with 200 µl/sub-array of blocking buffer (PBS pH 7.4, 1% ovalbumin;PBS/OVA) for 1 hour at RT with gentle shaking. Next, the blocking solution was aspirated and 200 µl/ block of primary detection was added (Siglec-human IgGFc chimeras; R&D). Primary detections were incubated with gentle shaking for 2 hours at RT. Slides were washed three times with PBST then with PBS for 5 min/wash with shaking. Bound antibodies were detected by incubating with secondary detection diluted in PBS, 200 µl/block at RT for 1 hour: Cy3-anti–human-IgG (Jackson; 0.4μg/ml). Slides were washed three times with PBST then with PBS 5 min/wash followed by removal from ProPlate™ Multi-Array slide module and immediately dipping slide in a staining dish with dH2O for 10 min with shaking, then centrifuged at 200×g for 5 min. Dry slides were vacuum-sealed and stored in dark until scanning.
Array slide processing. Processed slides were scanned and analyzed as described {Padler-Karavani et al., 2011, Cancer Res, 71, 3352-63; Padler-Karavani et al., 2012, J BiolChem} at 10 μm resolution with a Genepix 4000B microarray scanner (Molecular Devices) using 350 gain. Image analysis was carried out with Genepix Pro 6.0 analysis software (Molecular Devices). Spots were defined as circular features with a variable radius as determined by the Genepix scanning software. Local background subtraction was performed. Data was analyzed by Excel using pivot tables.

5  $^1\text{H}, ^{13}\text{C}$-NMR, Mass Spectrometry Data of all the Compounds
CALCULATED MASS
(M+H)+ 559.235
NMR For Trisaccharide Library
RD 110
RD: 110 144 (2.631) AM2 (Ar, 20000.0, 556, 28, 0.00, LS 3); ABS: Sm (SG, 1x1.00); Om (142:147:135:140+144:163))

1: TOF MS ES+
2.09e3

CALCULATED MASS
(M+Na+) 662.0913

67
CALCULATED MASS
(M+Na)+  593.1973
Calculated Mass
(M+Na)+ 679.2889