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

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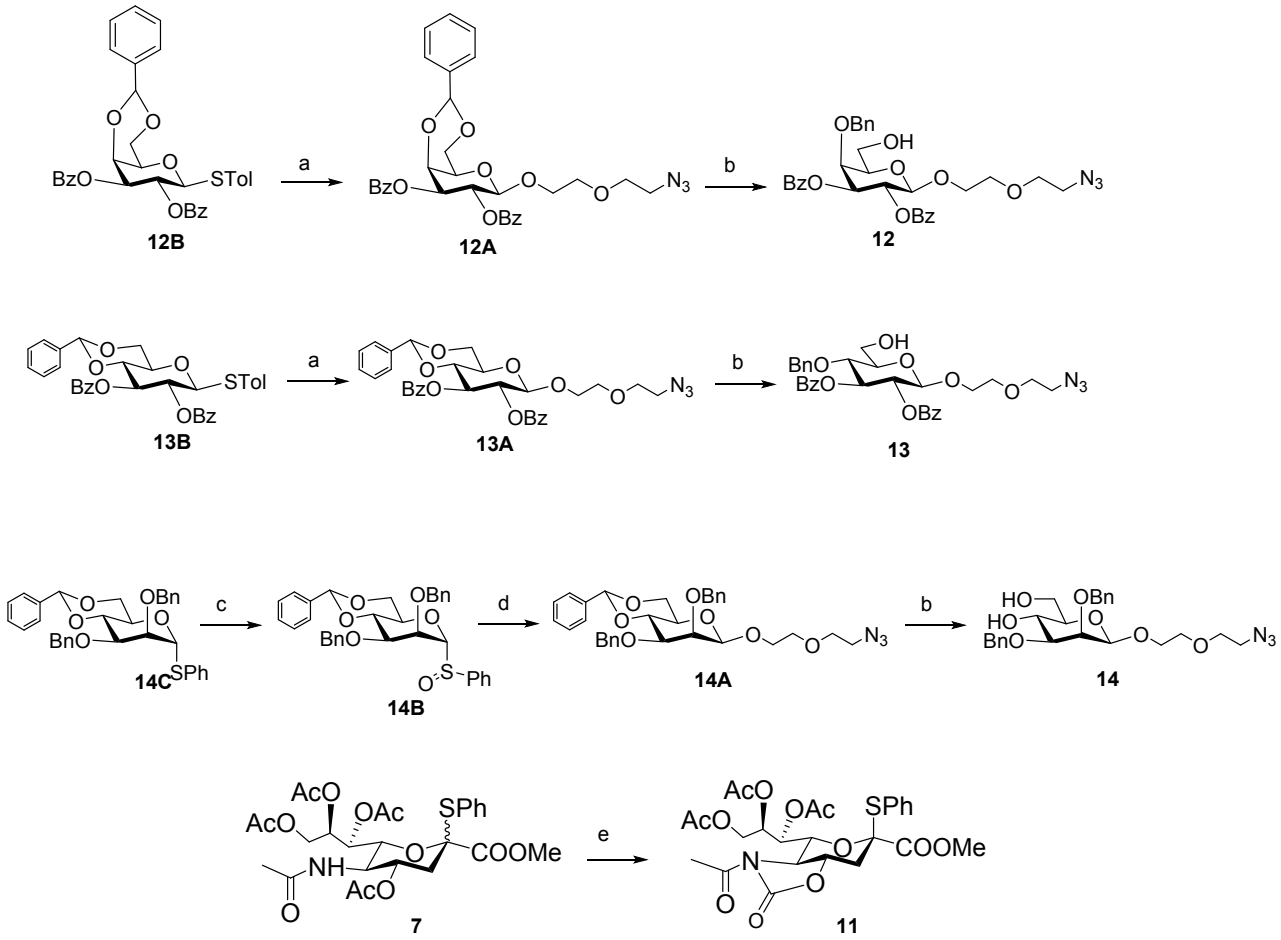
1. General information. All chemicals were reagent grade and used as supplied except where noted. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25 mmol). Compounds were visualized by UV irradiation or dipping the plate in CAM/ninhydrin solution followed by heating. Column chromatography was carried out using force flow of the indicated solvent on Fluka Kiesel gel 60 (230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Jeol 400 MHz, with cryo probe using residual solvents signals as an internal reference ($CDCl_3$ δ_H, 7.26 ppm, δ_C 77.3 ppm and CD_3OD δ_H 3.31 ppm, δ_C 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^{0}C, DCM; (b) $PhBCl_2$, Et_3SiH, -78^{0}C, DCM; (c) mCPBA,-78^{0}C, DCM; (d) 2-azidoethoxyethanol, Tf_2O, TTBP, -78^{0}C, DCM; (e) (i) MsOH, MeOH; ii) NPCC, $NaHCO_3$, CH_3CN:H_2O (2:1); (iii) AC_2O/Pyridine; (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^{0}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^{0}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 $Na_2S_2O_3$ solution, dried over Na_2SO_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 $C_{31}H_{31}N_3O_9Na$ (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^{0}C and then to the stirred solution Et_3SiH (259 µl, 1.62 mmol) and $PhBCl_2$ (147 µl, 1.38 mmol) were added successively. After being stirred for 1 h at -78^{0}C, Et_3N (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 $C_{31}H_{33}N_3O_9Na$ (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 $C_{31}H_{31}N_3O_9Na$ ($M+Na^+$): 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 $C_{31}H_{33}N_3O_9Na$ ($M+Na^+$): 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_2Cl_2(10 ml) at -78^{0}C was added Tf_2O (151 µl, 1eq) and, 5 min later, the solution of the glycosyl acceptor (78 mg, 1.2 eq) in CH_2Cl_2 (2 ml) drop wise were added. The reaction mixture was stirred at -78 ^{0}C for 2 h and then allowed to warm to 0 ^{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

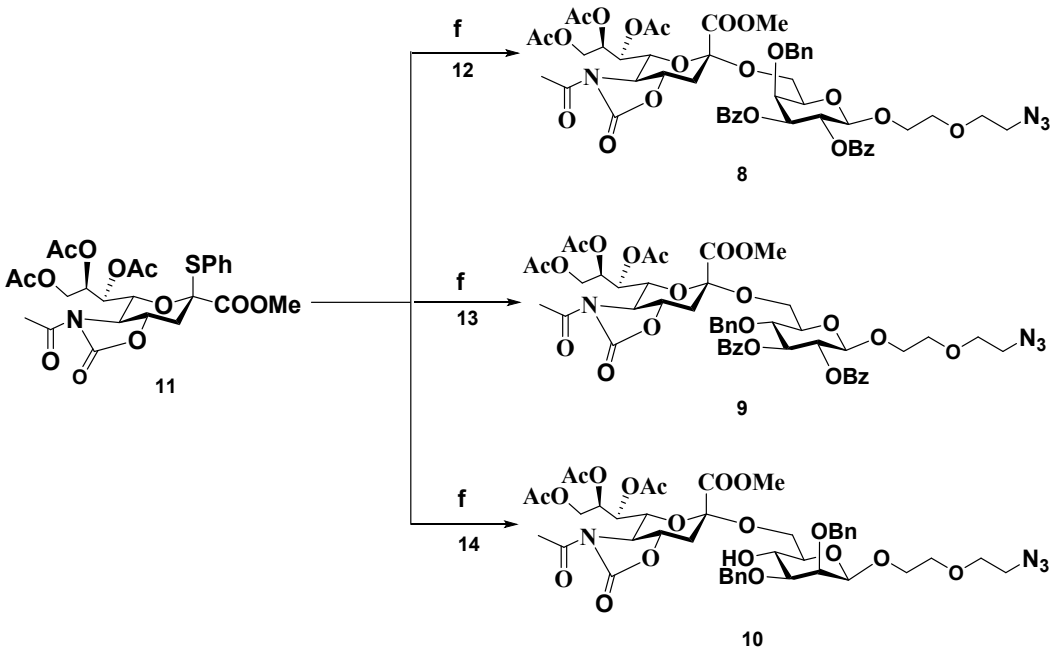
Hz, 1H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.57 (d, *J* = 12.5 Hz, 1H), 4.54 (s, 1H), 4.29 (dd, *J* = 10.4, 4.9 Hz, 1H), 4.19 (t, *J* = 9.6 Hz, 1H), 4.05–3.99 (m, 1H), 3.98 (d, *J* = 3.0 Hz, 1H), 3.92 (t, *J* = 10.3 Hz, 1H), 3.74–3.62 (m, 5H), 3.58 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.33 (dt, *J* = 9.6, 5.4 Hz, 3H). **^{13}C-NMR** (400 MHz,$CDCl_3$) δ 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 $C_{31}H_{35}N_3O_7Na$ ($M+Na^+$): 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 0^0C 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{26}H_{28}O_5S$ ($M+Na^+$): 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_3CN (30 ml) and H_2O (60 ml) and cooled to 0^0C. To the vigorously stirred mixture was added 4-nitrophenylchloroformate (4.32 g, 21.4 mmol, 2.5 equiv) in CH_3CN (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 Na_2SO_4 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 Ac_2O (24 ml) and stirred at room temperature overnight, then concentrated under reduced pressure. The residue was dissolved in anhydrous CH_2Cl_2, treated with $EtN(i\text{-}Pr)_2$ (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 $NaHCO_3$ solution, the organic layer was separated, the aqueous layer was extracted twice with CH_2Cl_2, and the combined organic phase was washed with brine, dried over Na_2SO_4, 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 recrystalization from EtOAc/Et_2O/Hex to afford white needle crystals. **^{1}H-NMR** (400 MHz, $CDCl_3$) 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). **^{13}C-NMR** (400 MHz, $CDCl_3$) 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 $C_{25}H_{29}NO_{12}SNa$ ($M+Na^+$): 590.1308; found: 590.1307.

Glycosylation of donor and acceptor:



SchemeS2: Reagents and Conditions: (f) NIS/TfOH, -40^{0}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^{0}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^{0}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 $Na_2S_2O_3$ solution, dried over Na_2SO_4, 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.

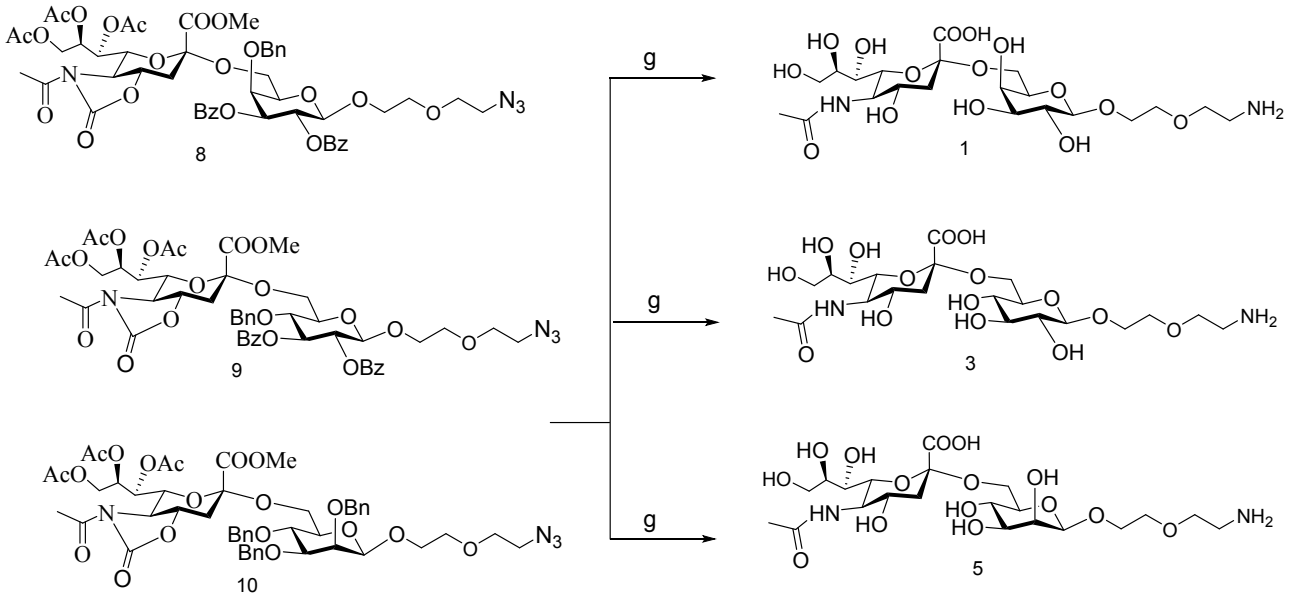
Compound 8: According to general procedure, donor **11** (200 mg) and acceptor **12** (250 mg , 1.2eq) to afford **8** (270 mg , 73%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.52–7.46 (m, 3H), 7.39–7.31 (m, 6H), 7.30–7.25 (m, 3H), 7.18-7.15 (m, 3H), 5.81 (dd, *J* = 10.5, 8.0 Hz, 1H), 5.58 (dd, *J* = 8.0, 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, 2H), 3.96-3.85 (m, 3H), 3.81–3.74 (m, 2H), 3.71(s, 3H), 3.58 (m, 2H), 3.47 (t, *J* = 5.1Hz, 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, $CDCl_3$) δ 172.03, 170.79, 170.14, 170.09, 168.39, 165.67, 165.36, 153.74, 137.44, 133.25, 133.20, 129.98, 129.98, 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 $C_{50}H_{56}N_4O_{21}$ ($M+Na^+$): 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, $CDCl_3$) δ 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 (s, 3H), 2.03 (t, *J* = 12.5 Hz, 1H), 1.90 (s, 3H). **^{13}C-NMR** (400 MHz, $CDCl_3$) δ 172.03, 170.79, 170.14, 170.09, 168.39, 165.67, 165.36, 153.74, 137.44, 133.25, 133.20, 129.85, 129.84, 129.82, 129.47, 129.44, 129.47, 129.44, 128.47, 128.43, 128.40, 128.38, 128.37, 128.33, 128.30, 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 $C_{50}H_{56}N_4O_{21}$ (M+Na): 1071.3314; found:1071.3322.

Compound 10: According to general procedure, donor **11** (200 mg) and acceptor **14** (238 mg ,1.2eq) to afford **10** (230 mg , 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{43}H_{54}N_4O_{19}$ (M+Na): 953.3279; found: 953.3292.

Global deprotection of comp 8, 9, 10 :



Scheme S3: ***Reagents and Conditions***g) i) LiOH, EtOH:H_2O (3:1), 80^0C, 12h; ii) $NaHCO_3$, Ac_2O, H_2O, rt; iii) H_2/$Pd(OH)_2$, MeOH:H_2 (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 80^0C 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 0^0C 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 hydrogenalysed 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.

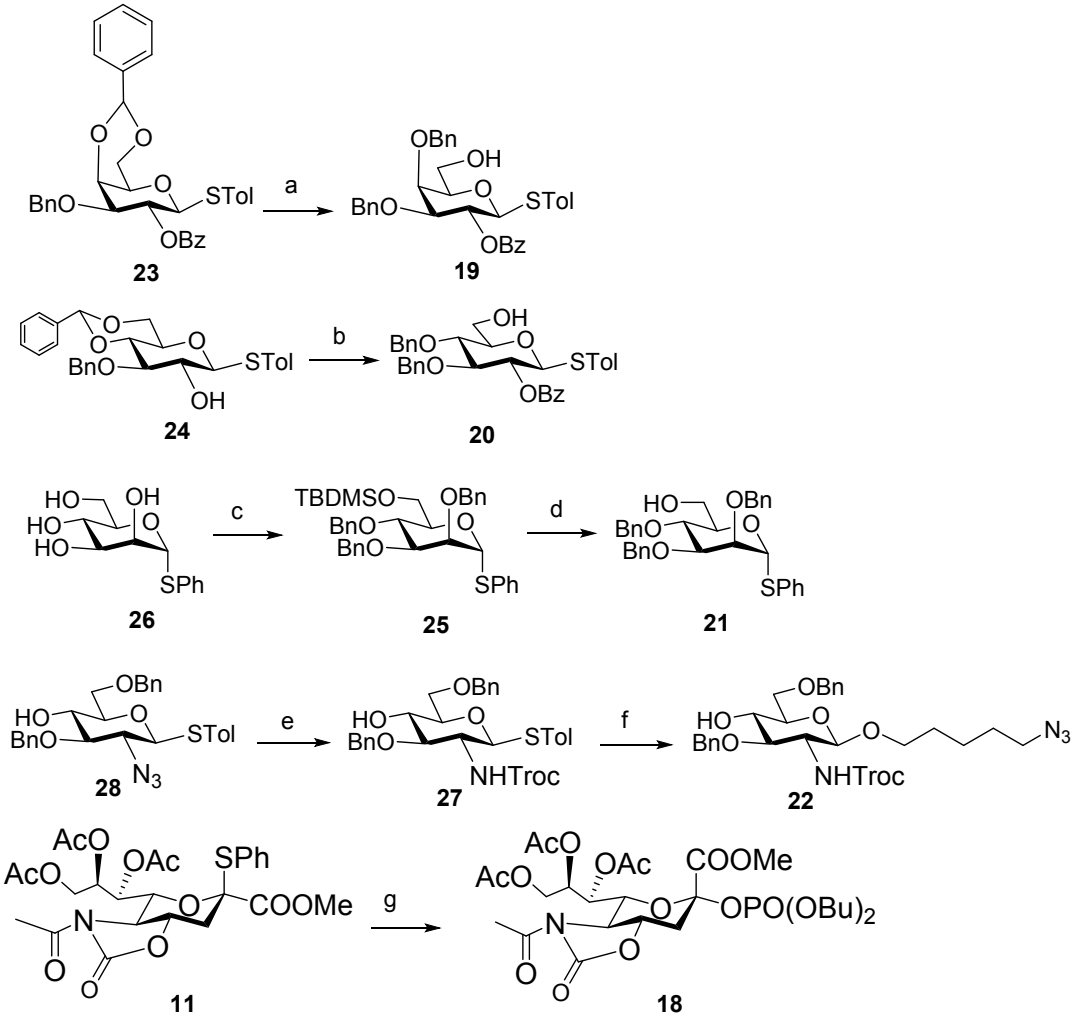
Compound 1: Synthesized from **8** by following general deprotection protocol to yield 36 mg (36%). **^{1}H-NMR** (400 MHz, D_2O) δ 4.33 (d, *J* = 7.7 Hz, 1H), 3.97 (dd, *J* = 11.8, 7.1 Hz, 1H), 3.83 (t, *J* = 8.7 Hz, 2H), 3.76 (dd, *J* = 11.5, 8.7 Hz, 4H), 3.72–3.64 (m, 5H), 3.63–3.45 (m, 7H), 3.42 (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_2O) δ 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 $C_{21}H_{38}N_2O_{15}$ (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) δ 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_2O) δ 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 $C_{21}H_{38}N_2O_{15}$ (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) δ 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, 10H), 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_2O) δ 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 $C_{21}H_{38}N_2O_{15}$ (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) $PhBCl_2$, Et_3SiH, -78^{0}C, DCM ; b) i) BzCl/Py; ii) $PhBCl_2$, Et_3SiH, -80^{0}C, DCM ; c) i) TBDMSCl, Imidazole, DMF; ii) BnBr, NaH, DMF; d) p-TSA, MeOH:DCM; e) i) 1,3-dithiopropane, DCM, 35^{0}C ; ii) TrocCl, $NaHCO_3$, THF; f) 5-Azidopentanol, NIS/TfOH, -40^{0}C, DCM; g) Dibutylphosphate, NIS/TfOH, DCM:ACN, -20^{0}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^{0}C and then to the stirred solution Et_3SiH (552 µl, 3.46 mmol) and $PhBCl_2$ (265 µl, 2.05 mmol) were added successively. After being stirred for 1 h at -78^{0}C, Et_3N (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* = 11.8 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 $C_{34}H_{34}O_6SNa$ ($M+Na^+$). 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_2SO_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^{0}C and then Et_3SiH (533 µl, 3.32 mmol) and $PhBCl_2$ (253 µl, 1.95 mmol) were added successively. After being stirred for 1 h at -78^{0}C, Et_3N (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,

9.2 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.77 (dd, *J* = 10.5, 6.1 Hz, 2H), 4.68 (d, *J* = 11.0 Hz, 2H), 3.94 (ddd, *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 (ddd, *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, $CDCl_3$) δ 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 $C_{34}H_{34}O_6SNa$ (M+Na). 593.1971; found: 593.1973.

Compound 25 : The solution of compound **26** (1.2gm, 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_2SO_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_2SO_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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 127.64, 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 $C_{39}H_{48}O_5SSiNa$ ($M+Na^+$). 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. $NaHCO_3$, brine and dried the organic layer over Na_2SO_4, concentrated. Purification of mixture by silica-gel column chromatography (Ethylacetate:Hexane) yielded compound **21** as colourless syrup (550 mg, 85%). **^{1}H-NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 138.31, 138.12, 137.84, 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, 127.67, 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 $C_{33}H_{34}O_5S$ ($M+Na^+$). 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). **^{1}H-NMR** (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (400 MHz, $CDCl_3$) 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 $C_{27}H_{29}N_3O_4S$($M+Na^+$). 514.1776; found: 514.1769.

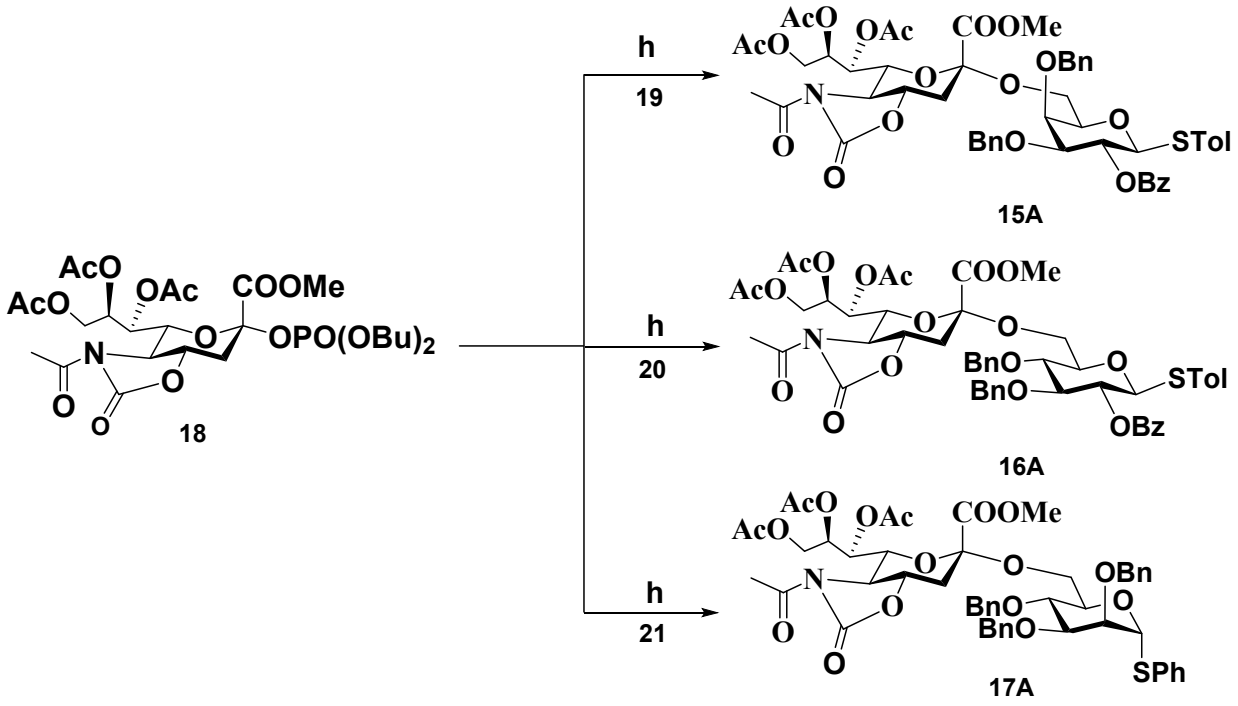
Compound 27. To compound **28** (2.5 gm, 5.09 mmol) in MeOH:DCM (1:1) was added 1,3 dithiopropane (2.5 ml, 25.45 mmol) and TEA (2.45 ml, 25.45 mmol) under Ar atmosphere. Reaction mixture was stirred at 35^0C for 18h. Then coevaporated with toluene, concentrated and purified by flash column chromatography (Ethylacetate:Hexane) to afford oily syrup. This syrup was dissolved in THF and $NaHCO_3$ (0.818 gm, 10.18 mmol) was added to it. Cooled the reaction

mixture to 4^0C 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 Na_2SO_4 and concentrated. The residue was purified on silica gel column chromatography (Ethylacetate:Hexane) to afford compound **27** as white solid (2.4 gm, 76%). **^{1}H-NMR** (400 MHz, $CDCl_3$) 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). **^{13}C-NMR** (400 MHz, $CDCl_3$) 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 $C_{30}H_{32}NCl_3O_6SNa$ ($M+Na^+$); 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 -40^0C 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 -40^0C 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 $Na_2S_2O_3$ solution, dried over Na_2SO_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 **22**(2.1 gm, 91%). **^{1}H-NMR** (400 MHz, $CDCl_3$) 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). **^{13}C-NMR** (400 MHz, $CDCl_3$) 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 $C_{28}H_{35}N_4Cl_3O_7S$ Na ($M+Na^+$); 667.1468; found: 667.1467.

Compound 18A 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^{0}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^{0}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 $Na_2S_2O_3$ solution, dried over Na_2SO_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 18(2 gm, 67%). **α-isomer ^{1}H-NMR** (400 MHz, $CDCl_3$) 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). **^{13}C-NMR** (400 MHz, $CDCl_3$) 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^{0}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^{0}C followed by addition of TMSOTf (165 μl, 0.899 mmol, 1 equiv). The reaction mixture was stirred at -78^{0}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 Na_2SO_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 sialic acid disaccharide analogues.

Compound 15A According to general procedure donor **18** and acceptor **19** to yield as white solid (700 mg, 75%). **^{1}H-NMR** (400 MHz, $CDCl_3$) 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 =

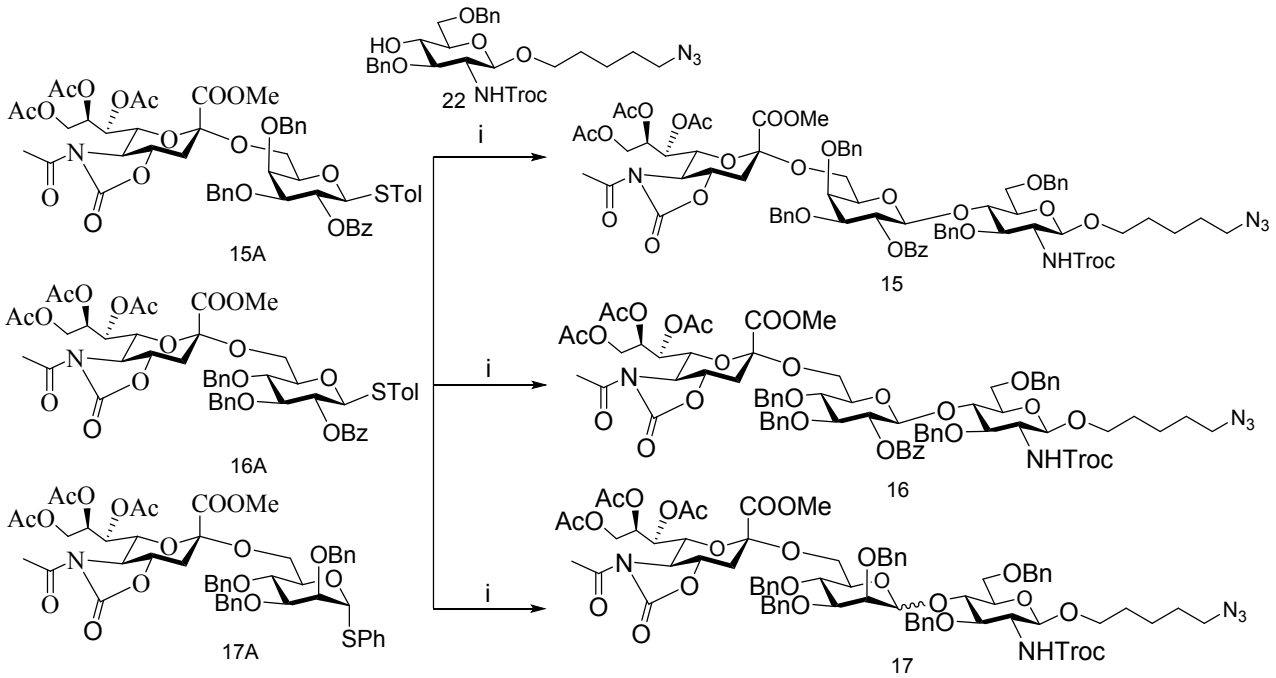
9.4 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.62 (d, *J* = 9.4 Hz, 1H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.42 (dd, *J* = 12.2, 2.3 Hz, 1H), 4.13-4.04 (m, 2H), 4.04-3.98 (m, 2H), 3.79-3.71(m, 3H), 3.69 (s, 3H), 3.66-6.59 (m, 1H), 2.90 (dd, *J* = 12.0, 3.3 Hz, 1H), 2.52 (s, 3H), 2.31 (s, 3H), 2.15(s, 3H), 2.09 (t, *J* = 12.5 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 3H). **^{13}C-NMR** (400 MHz, $CDCl_3$) δ 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, 129.42, 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, 62.95, 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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* = 1Hz, 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, $CDCl_3$) δ 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^{0}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^{0}C followed by addition of NIS (109 mg, 0.488 mmol, 1.0 equiv) and TfOH (6.46 *μl*, 0.048 mmol, 0.1 equiv) dissolved in ether. The reaction mixture was stirred at -40^{0}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.$Na_2S_2O_3$ (3:1) 20 ml solution, dried over Na_2SO_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.

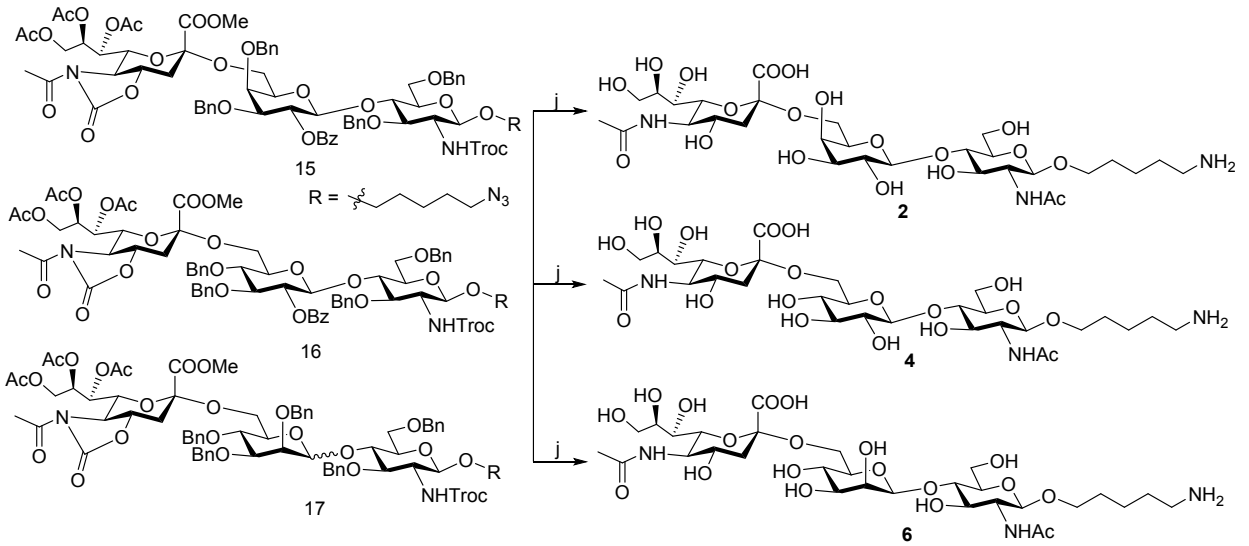
Compound 15 Synthesized from donor **15A** and acceptor **22** by following general glycosylation procedure to afford as white solid (430 mg, 57%) **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.61(t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.37-7.33 (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, $CDCl_3$) δ 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 $C_{74}H_{84}Cl_3N_5O_{25}$ (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, $CDCl_3$) δ 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 (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, 128.15, 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 $C_{74}H_{84}Cl_3N_5O_{25}$ (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 (ddd, *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 $C_{74}H_{86}Cl_3N_5O_{24}$ (M+Na). 1556.4626; found: 1556.4624.

Global Deprotection of Sialoside:



Scheme3: ***Reagents and Conditions:*****(**j) (i) LiOH, EtOH:H_2O (3:1), 80^0C, 12h; (ii) $NaHCO_3$, Ac_2O, H_2O, rt; (iii) H_2/Pd $(OH)_2$, MeOH:H_2O (1:1).

General Deprotection Procedure: Oligosaccharide (1eq) in ethanol water (3:1) 5ml at room temperature. After stirring at 80^0C 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 0^0C and Acetic-anhydride (10 eq) was added. The reaction were monitored by TLC (ethylacetate:methanol:water7:2:1), 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 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 2 Synthesized from **15** by following general deprotection protocol to afford white solid (50 mg, 50%). **^{1}H-NMR** (400 MHz, D_2O) 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). **^{13}C-NMR** (400

MHz, D_2O) 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 $C_{30}H_{51}N_5O_{19}$(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_2O) 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_2O) 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 $C_{30}H_{51}N_5O_{19}$(M+H). 760.3351; found: 760.3358.

Compoun6 Synthesized from **17** by following general deprotection protocol to afford white solid(35 mg, 30%). **^{1}H-NMR** (400 MHz, D_2O) 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_2O) 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 $C_{30}H_{51}N_5O_{19}$(M+H). 760.3351; found: 760.3344.

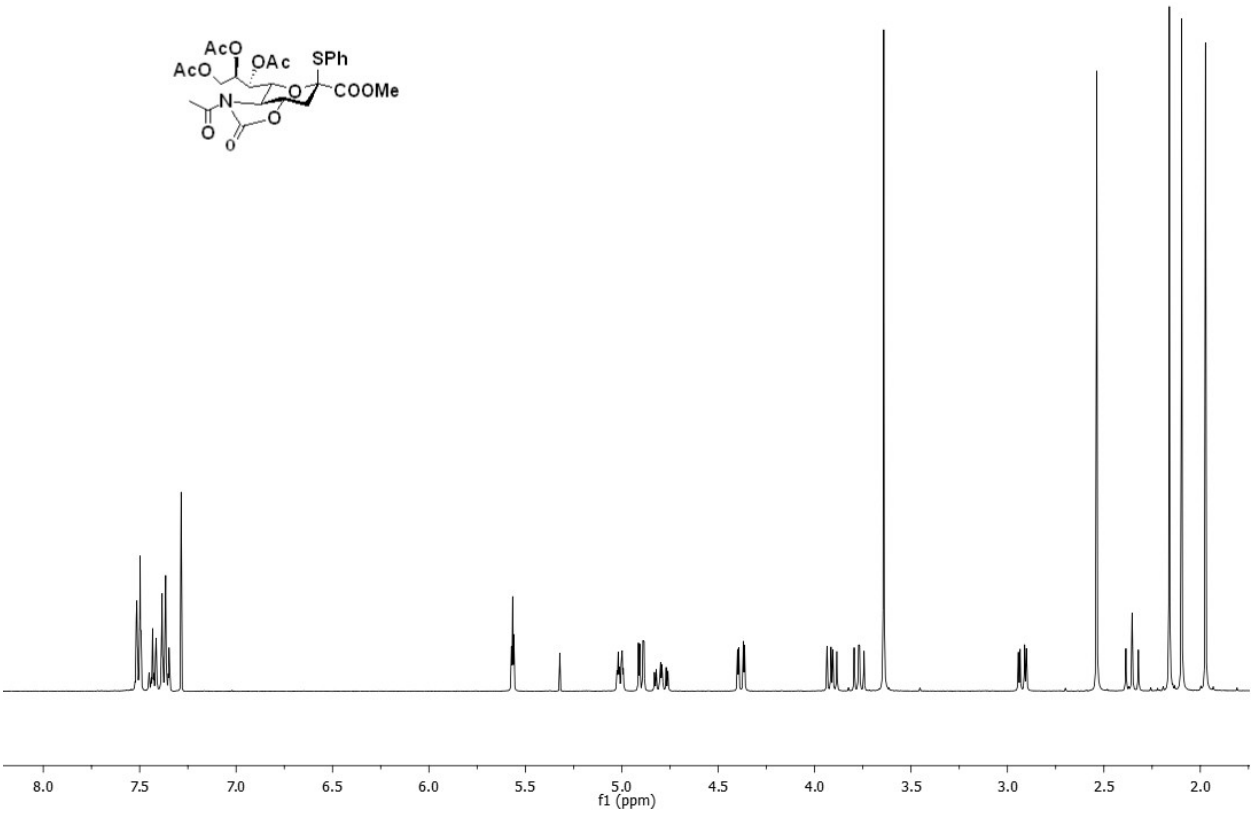
4. Glycanmicroarraydetails

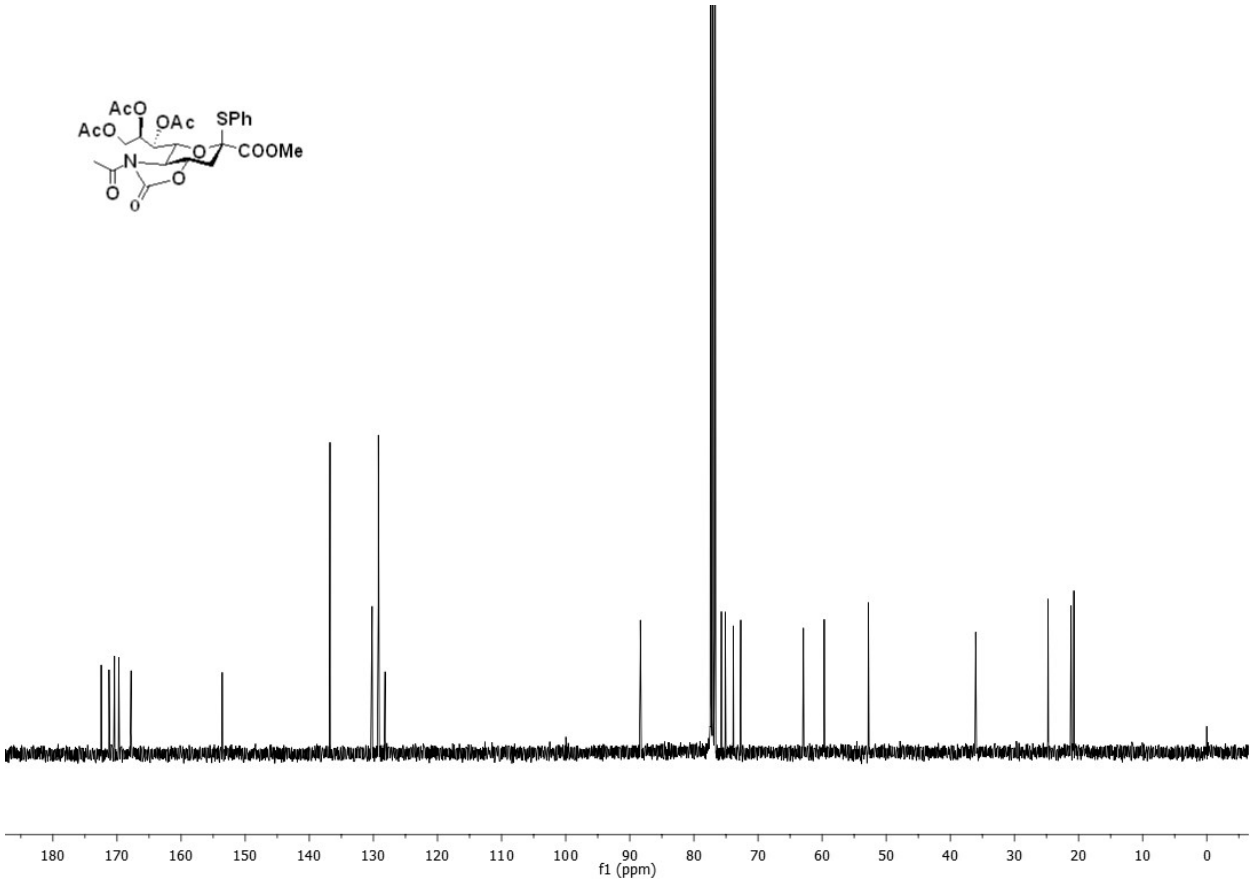
Sialoglycan microarray fabrication. Arrays were printed on Epoxide-derivatized Corning slides as described for Array 1 in Ref. {Padler-Karavani et al., 2012, J BiolChem} with some modifications. Arrays were fabricated with NanoPrint LM 60Microarray Printer (Arrayit, CA) on epoxide-derivatized slides (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.

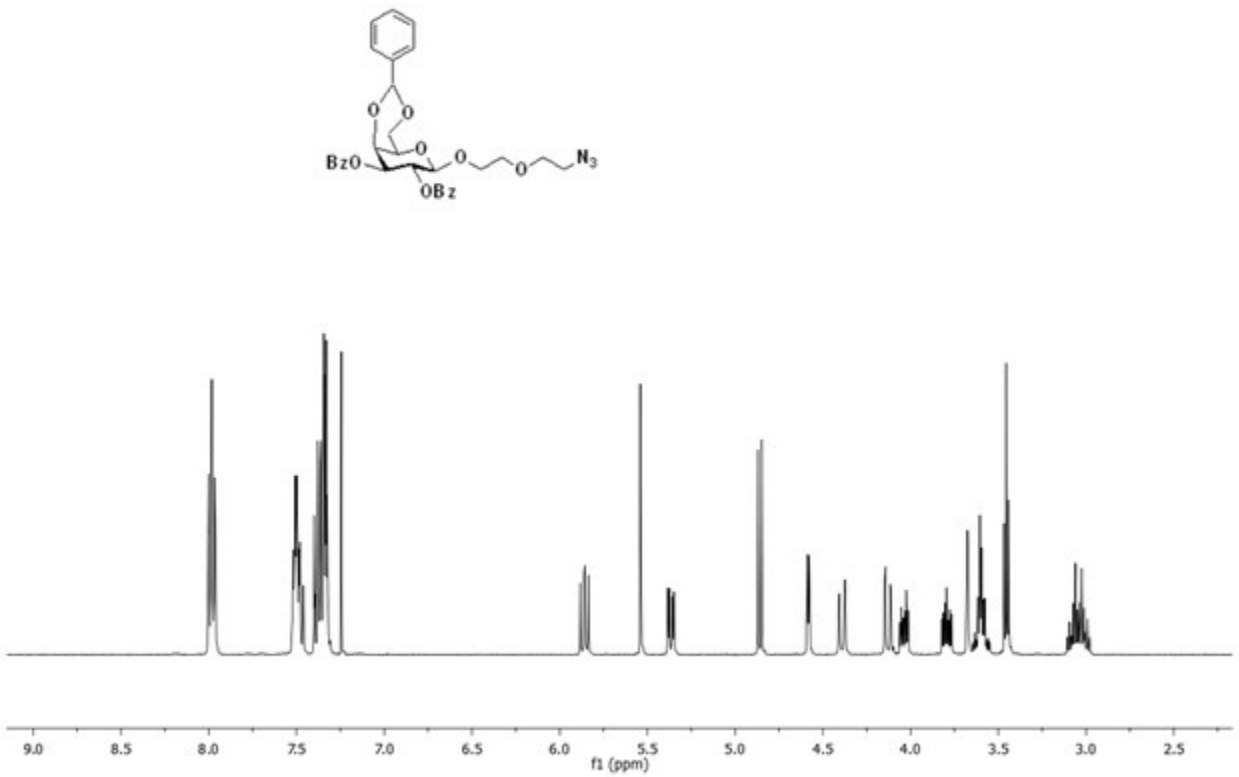
Microarray binding assay. Slides were developed {23520510} and analyzed {Padler-Karavani et al., 2012, J BiolChem} as previously described. Slides were rehydrated with dH2O and incubated for 30 min in a staining dish with 50°C pre-warmed 0.05 M ethanolamine in 0.1 M Tris, pH 9.0 to block the remaining 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 detectionwas 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.

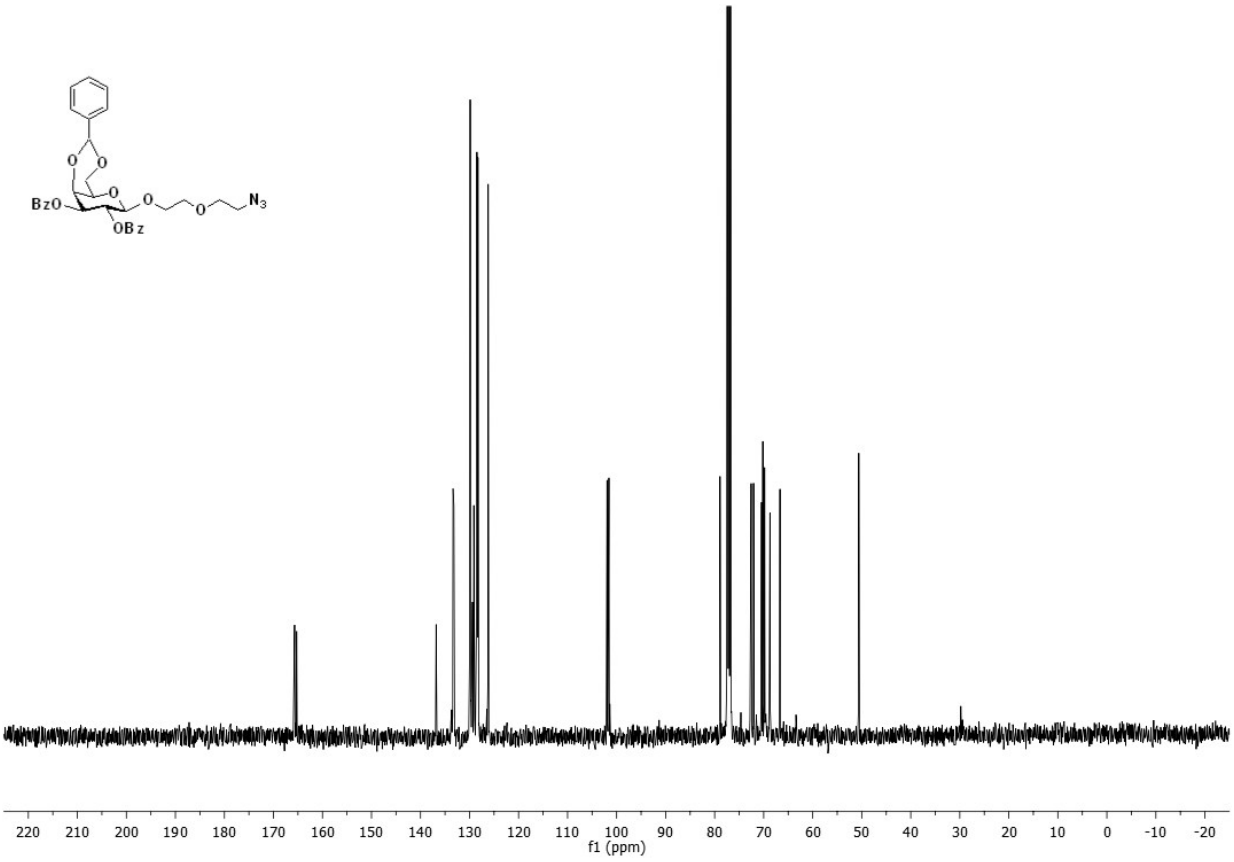
Array slide processing. Processed slides were scanned and analyzed as described {Padler-Karavani et al., 2011, Cancer Res, 71, 3352-63; Padler-Karavani et al., 2012, J BiolChem} at 10 μm resolution with a Genepix 4000B microarray scanner (Molecular Devices) using 350 gain. Image analysis was carried 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.

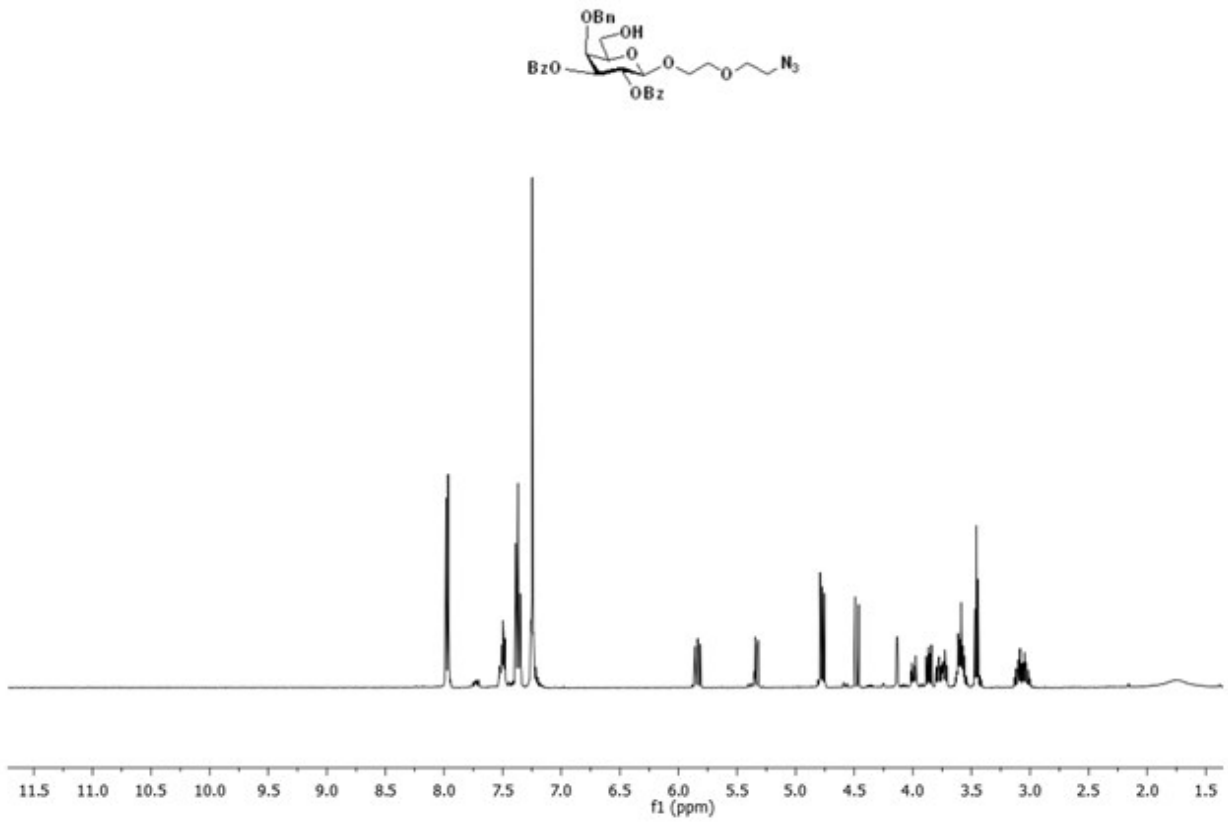
5 ^{1}H, ^{13}C-NMR, Mass Spectrometry Data of all the Compounds

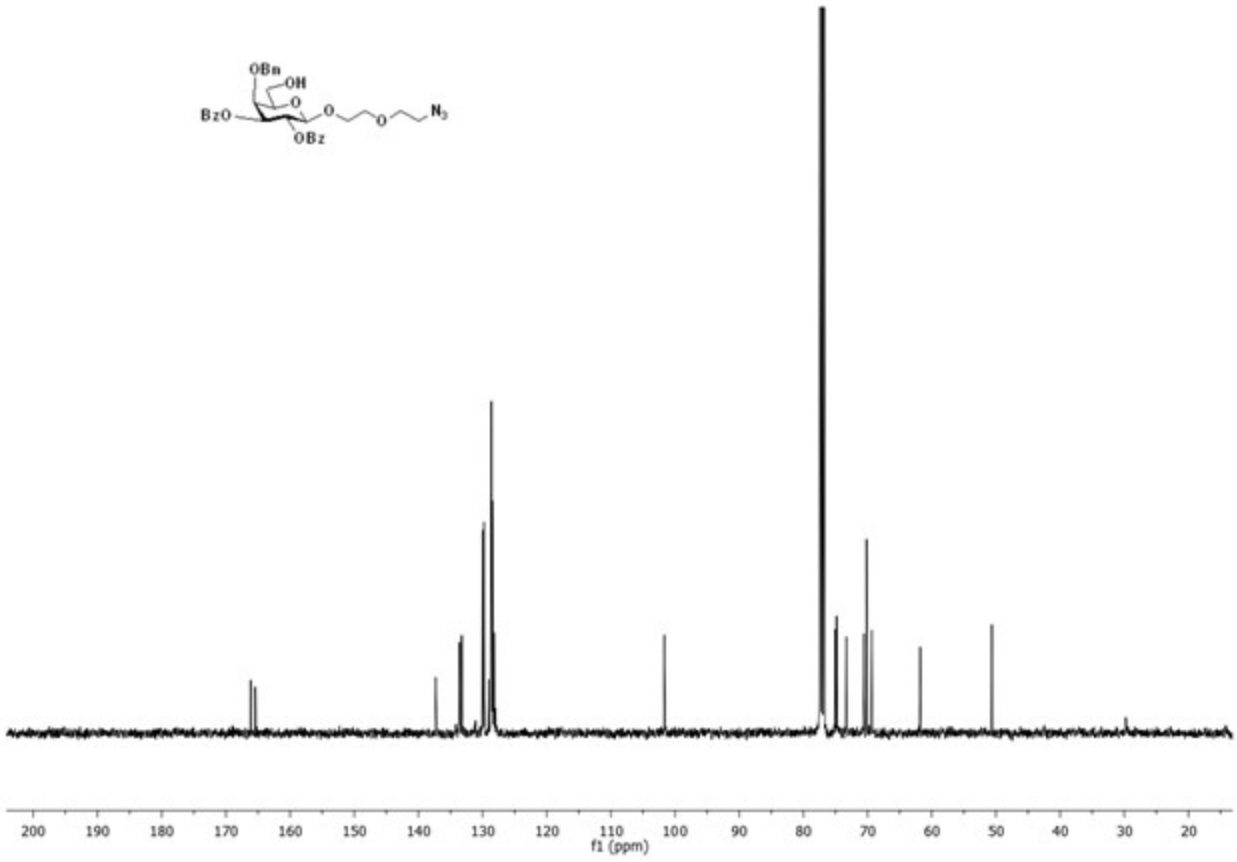

AcO
AcO
OAc
SPh
COOMe
N
O
O
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

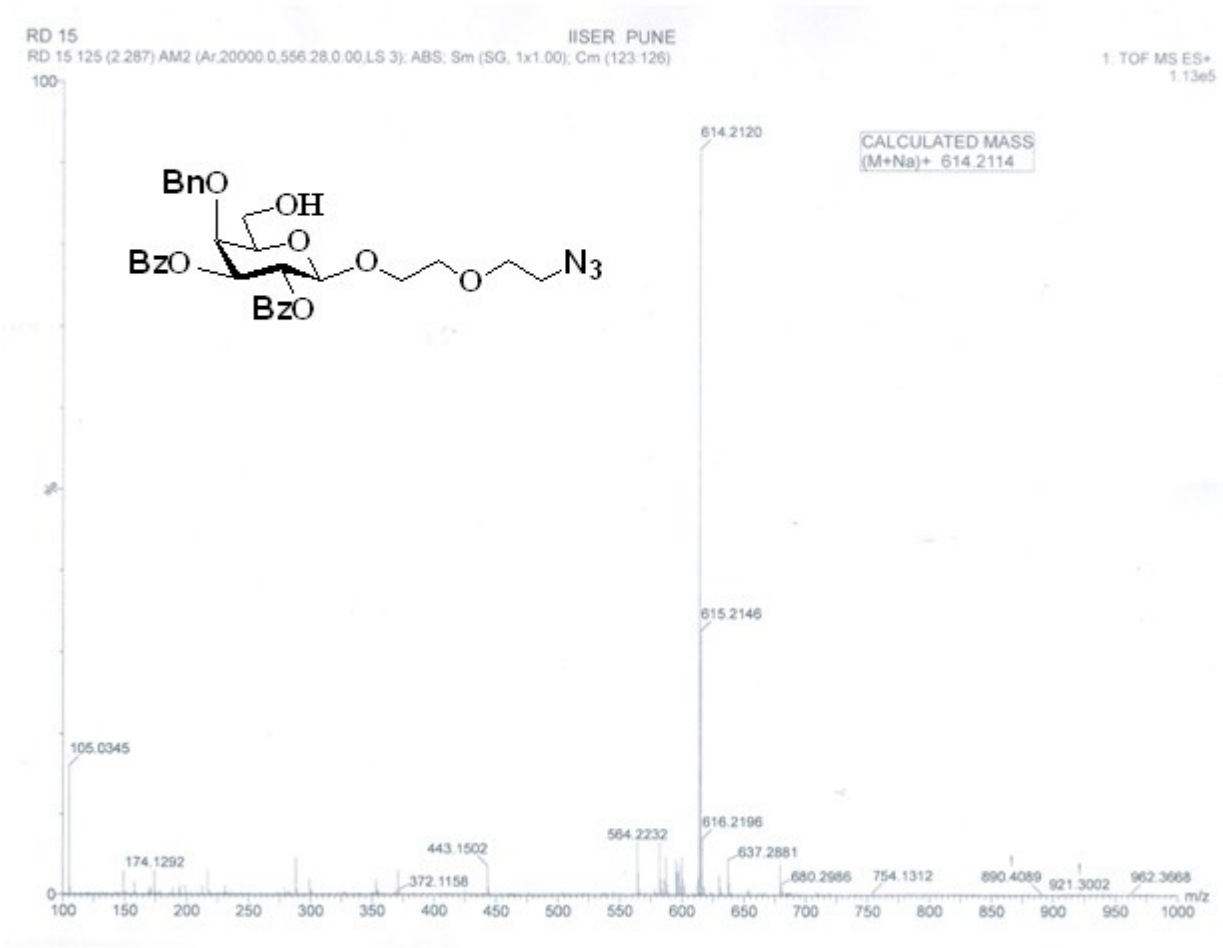

AcO
AcO
OAc
SPh
COOMe
N
O
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

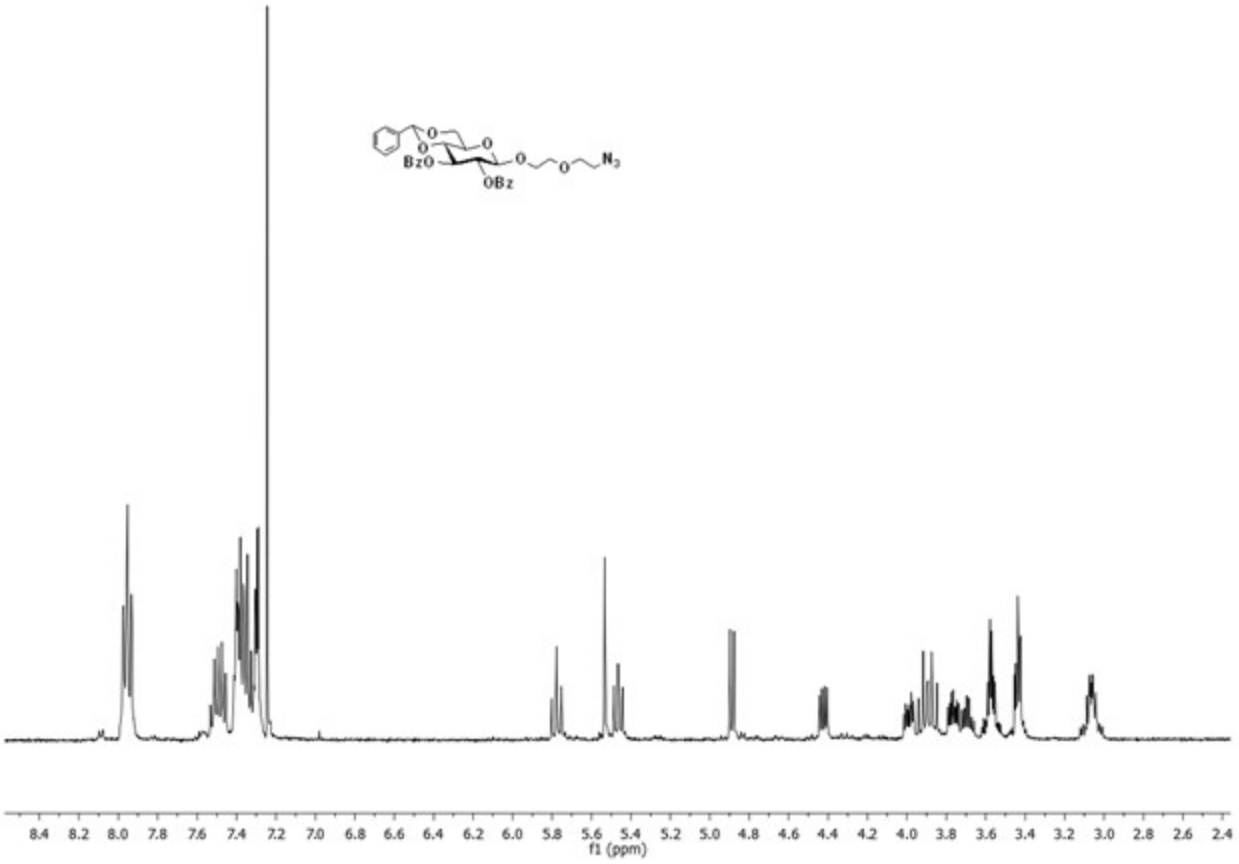

BzO
OBz
O
O
O
O
O
N3
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

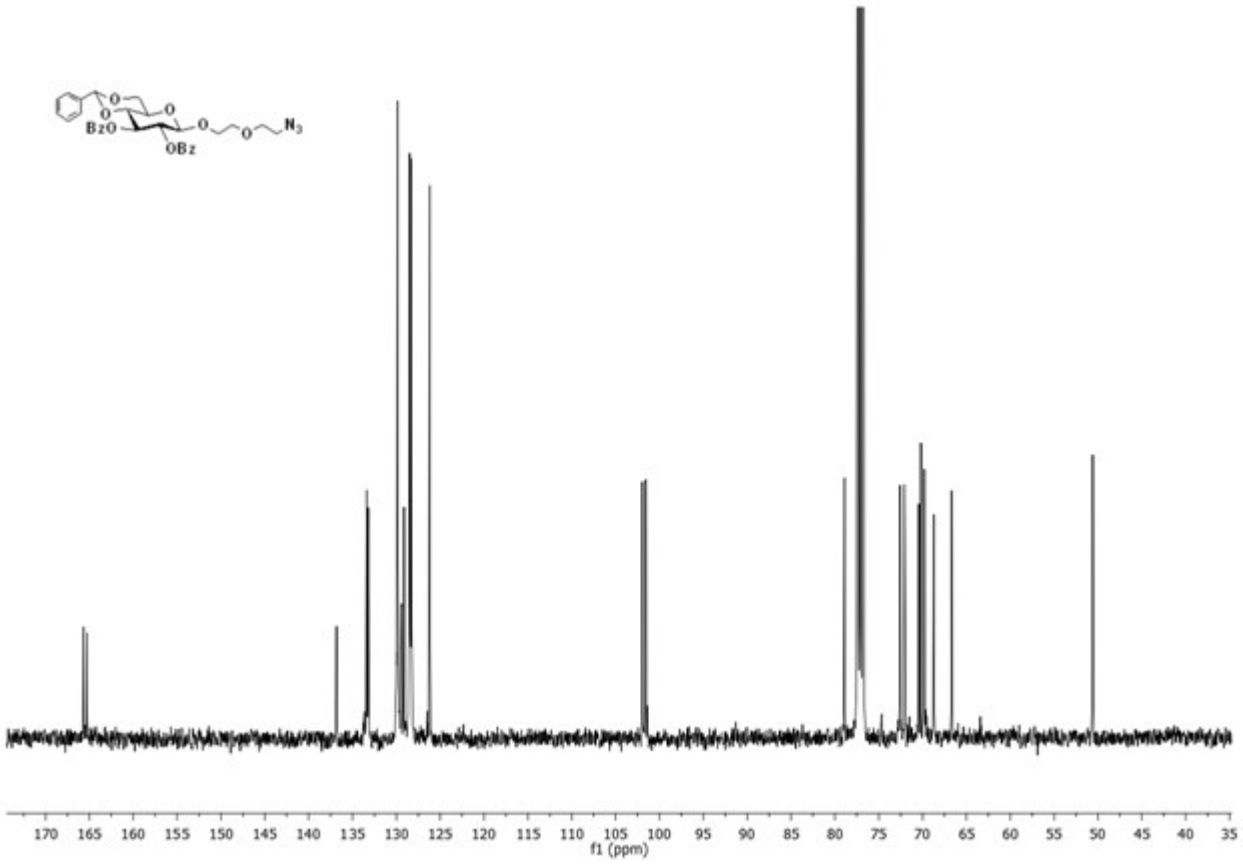

BzO
OBz
O
O
O
O
O
N3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

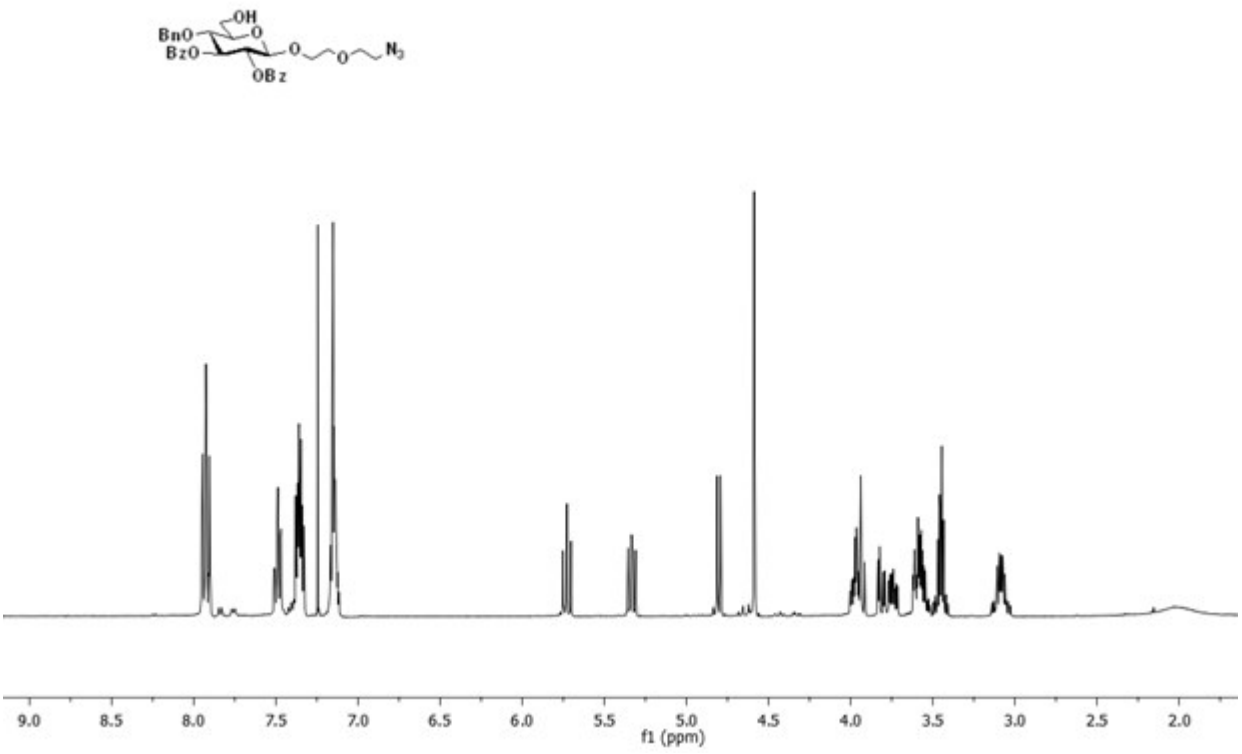

OBn
OH
O
BzO
O
O
N3
OBz
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

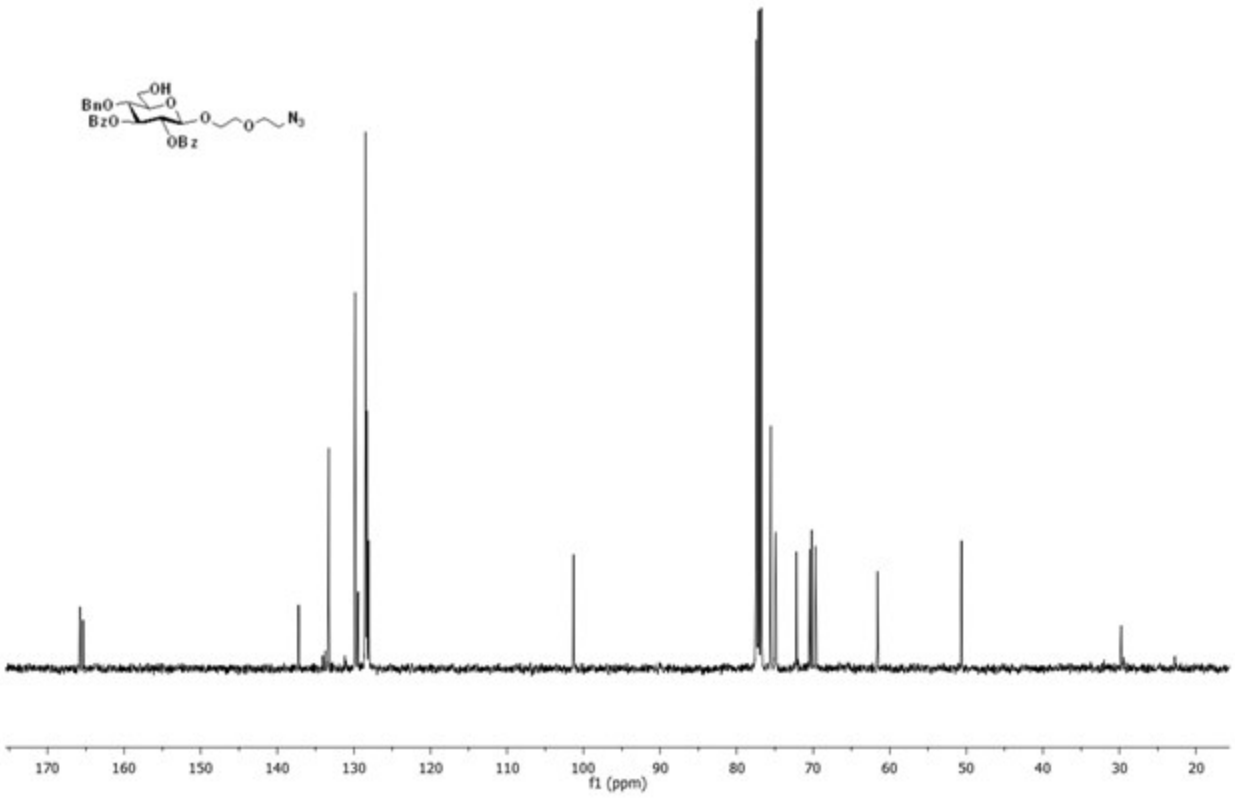

OBn
OH
O
BzO
O
O
N3
OBz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

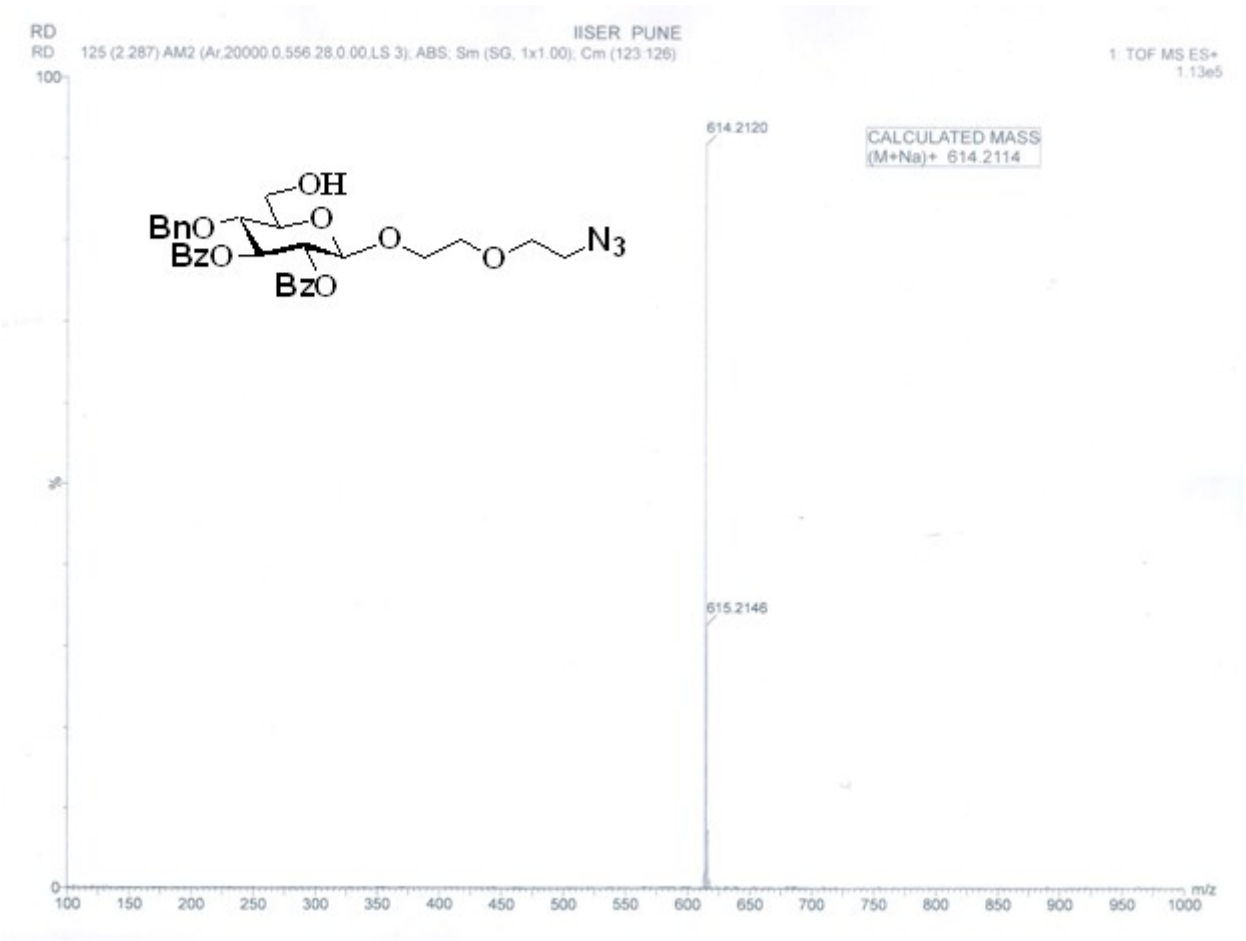

RD 15
IISER PUNE
RD 15 125 (2.287) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (123:126)
1: TOF MS ES+
1.13e5
100
%
0
614.2120
CALCULATED MASS
(M+Na)+ 614.2114
615.2146
105.0345
616.2196
564.2232
443.1502
637.2881
174.1292
372.1158
680.2986
754.1312
890.4089
921.3002
962.3668
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

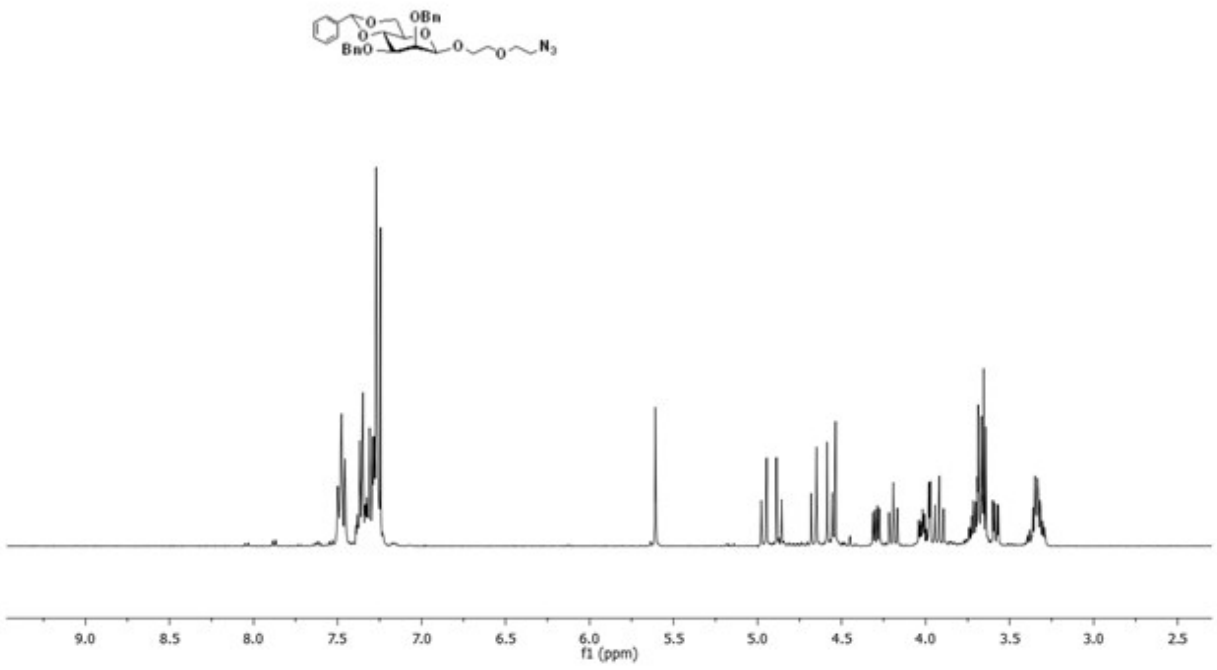

BzO
OBz
N3
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)

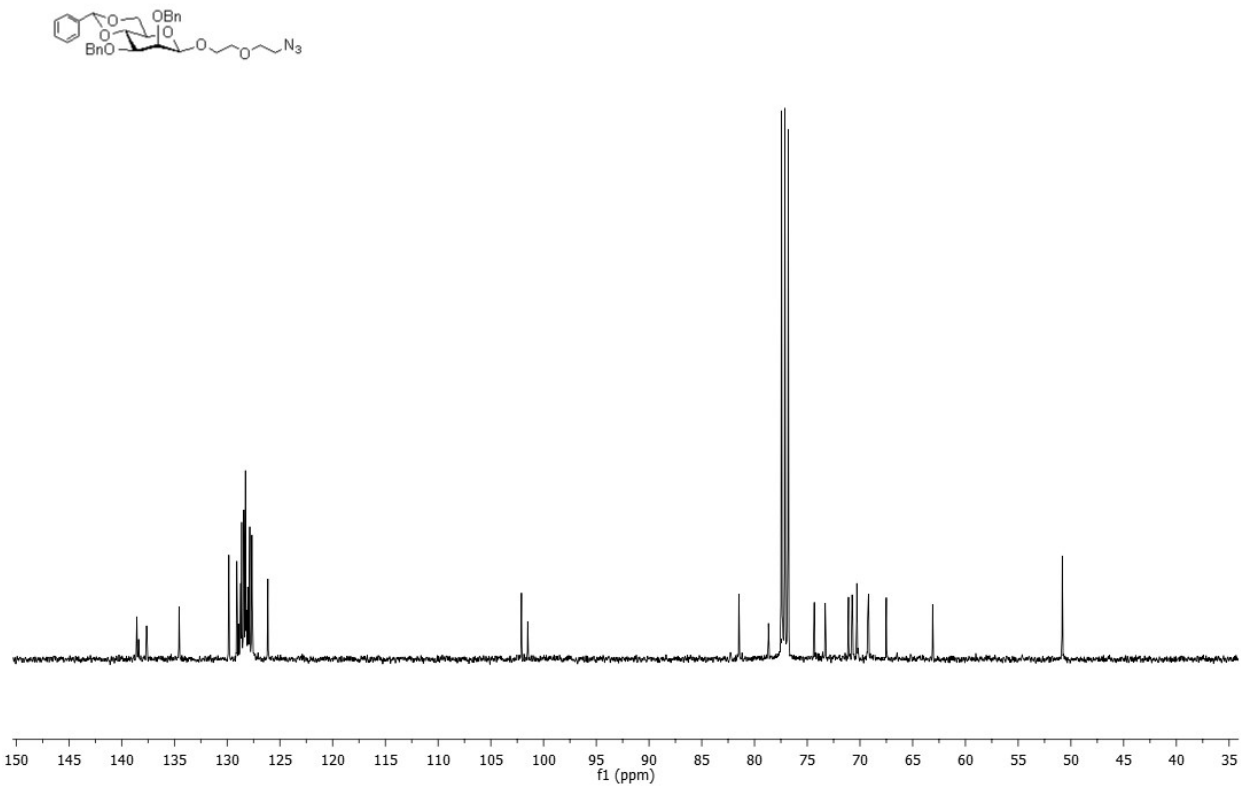

BzO
OBz
N3
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

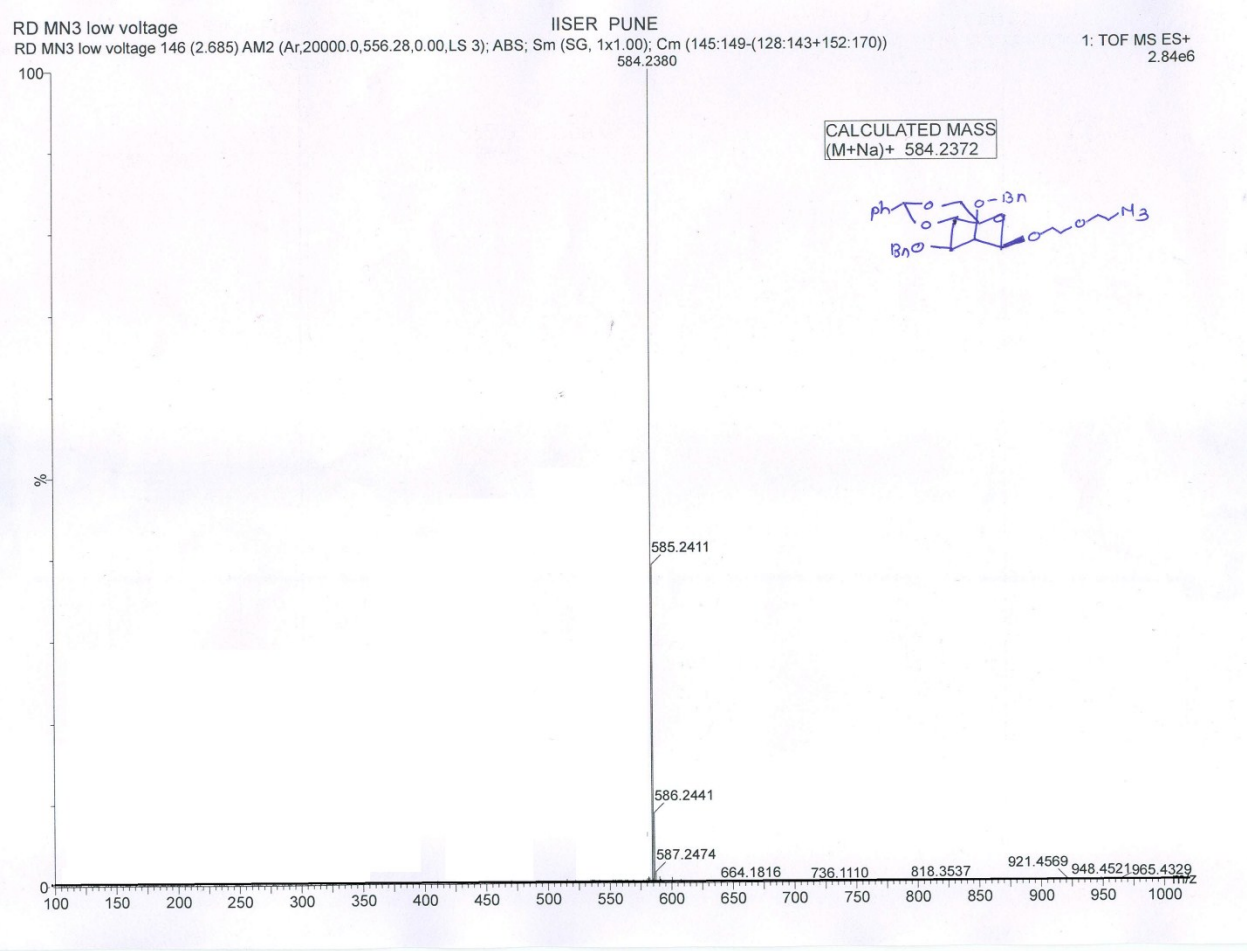

OH
BnO
O
BzO
O
O
O
N3
OBz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

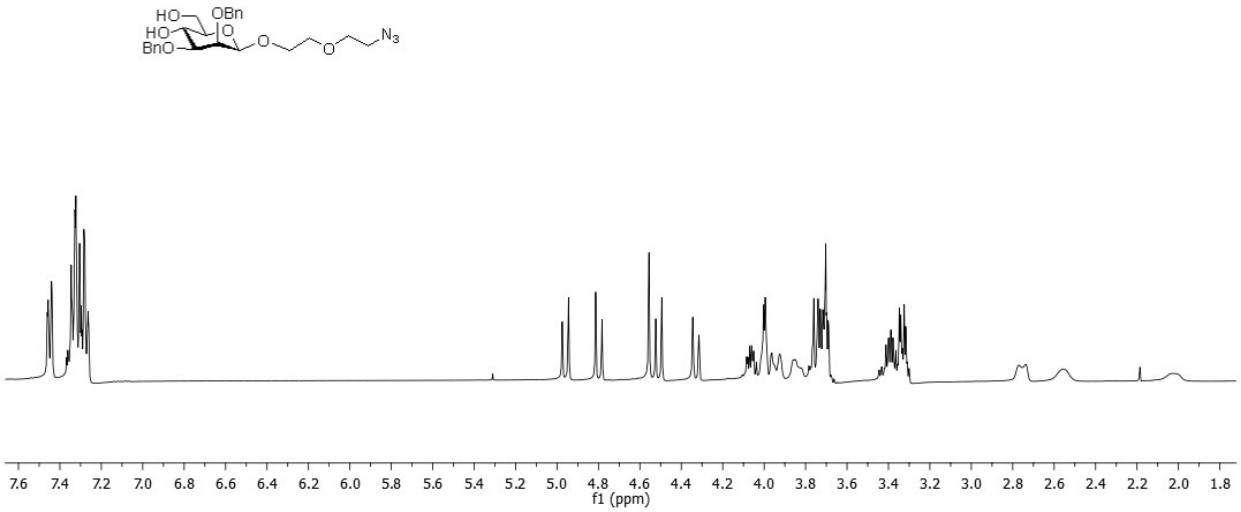

BnO
BzO
OH
O
O
O
O
N3
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

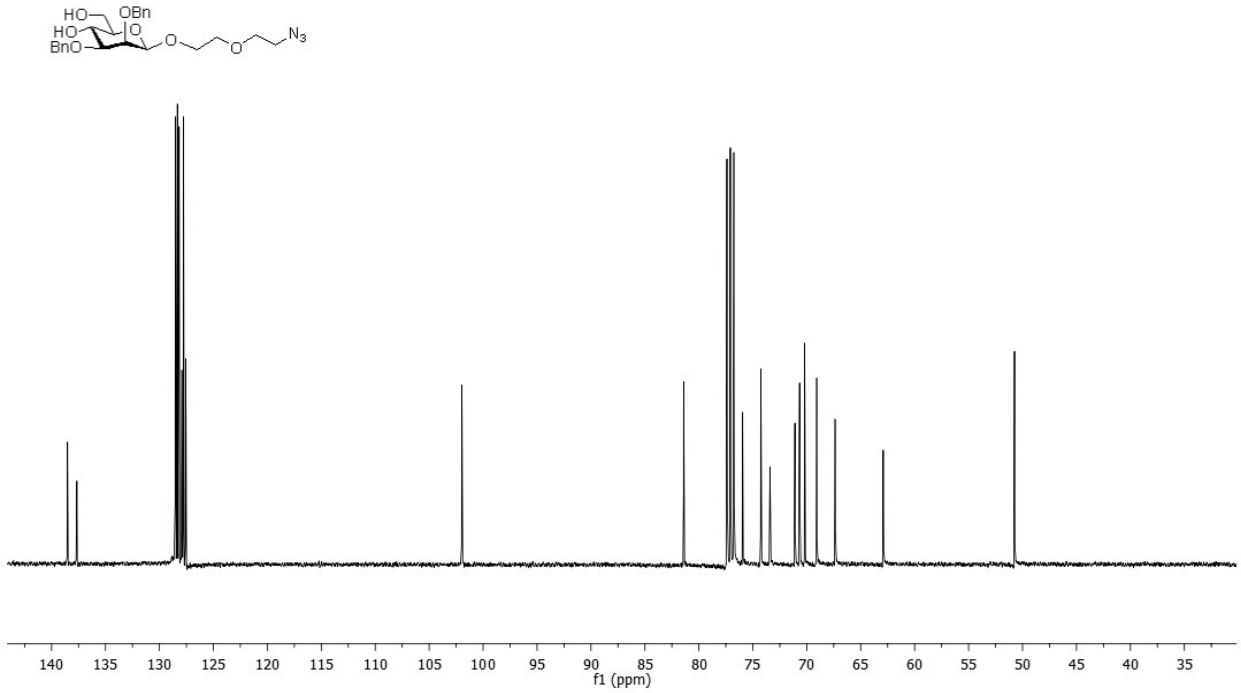

RD
IISER PUNE
RD 125 (2.287) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (123:126)
1: TOF MS ES+
1.13e5
100
%
0
614.2120
615.2146
CALCULATED MASS
(M+Na)+ 614.2114
OH
O
BnO
BzO
BzO
O
O
N3
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
m/z

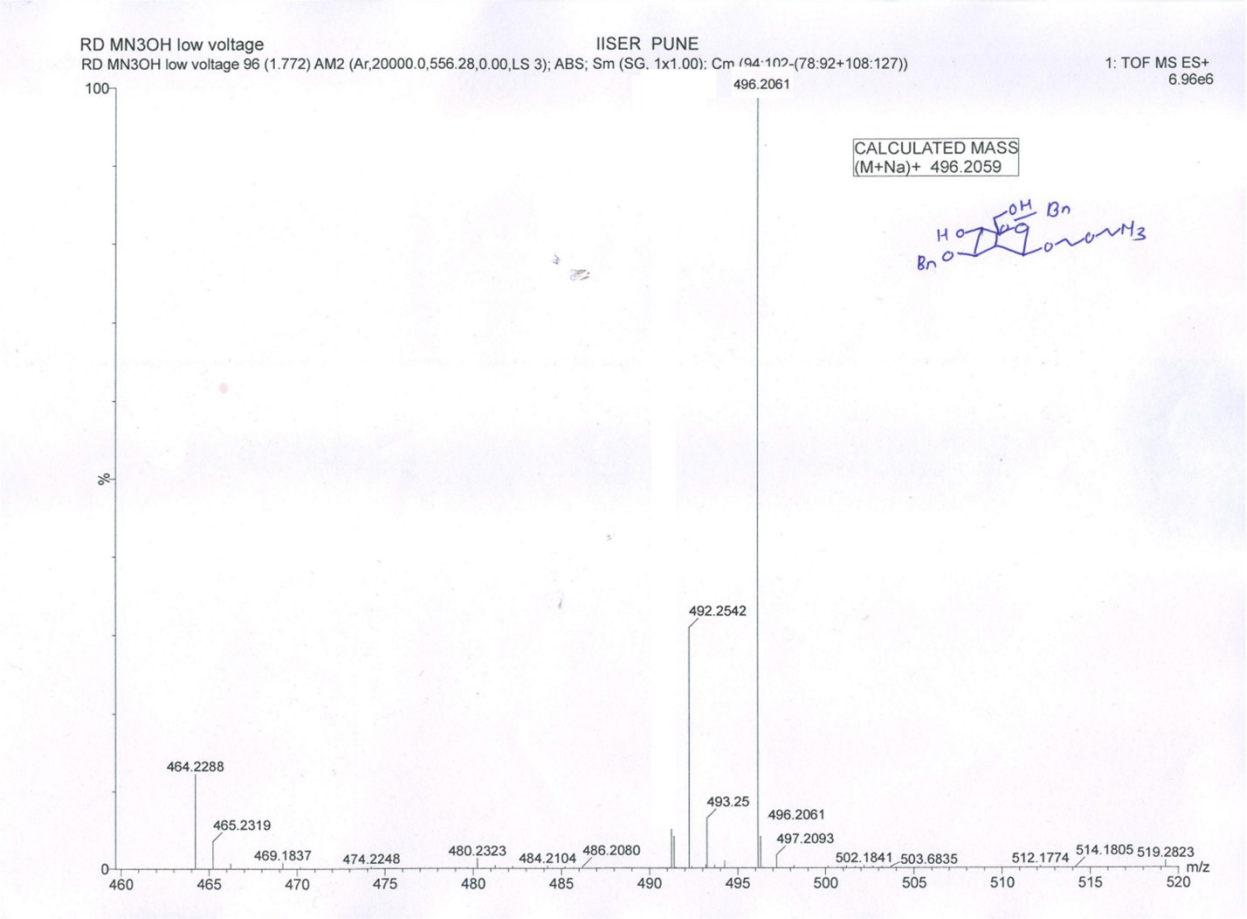

OBn
BnO
O
O
O
O
O
N3
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

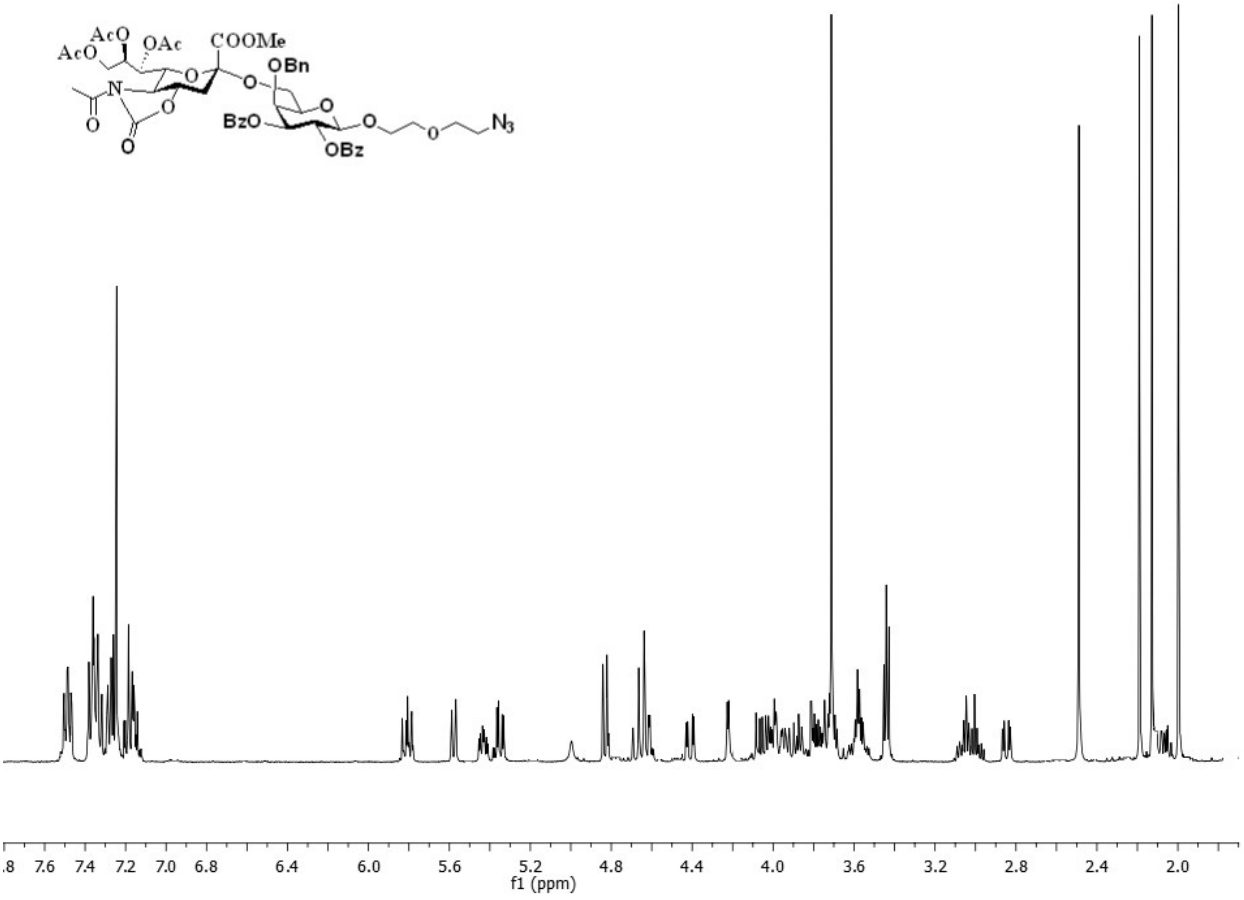

OBn
O
O
BnO
O
O
O
N3
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

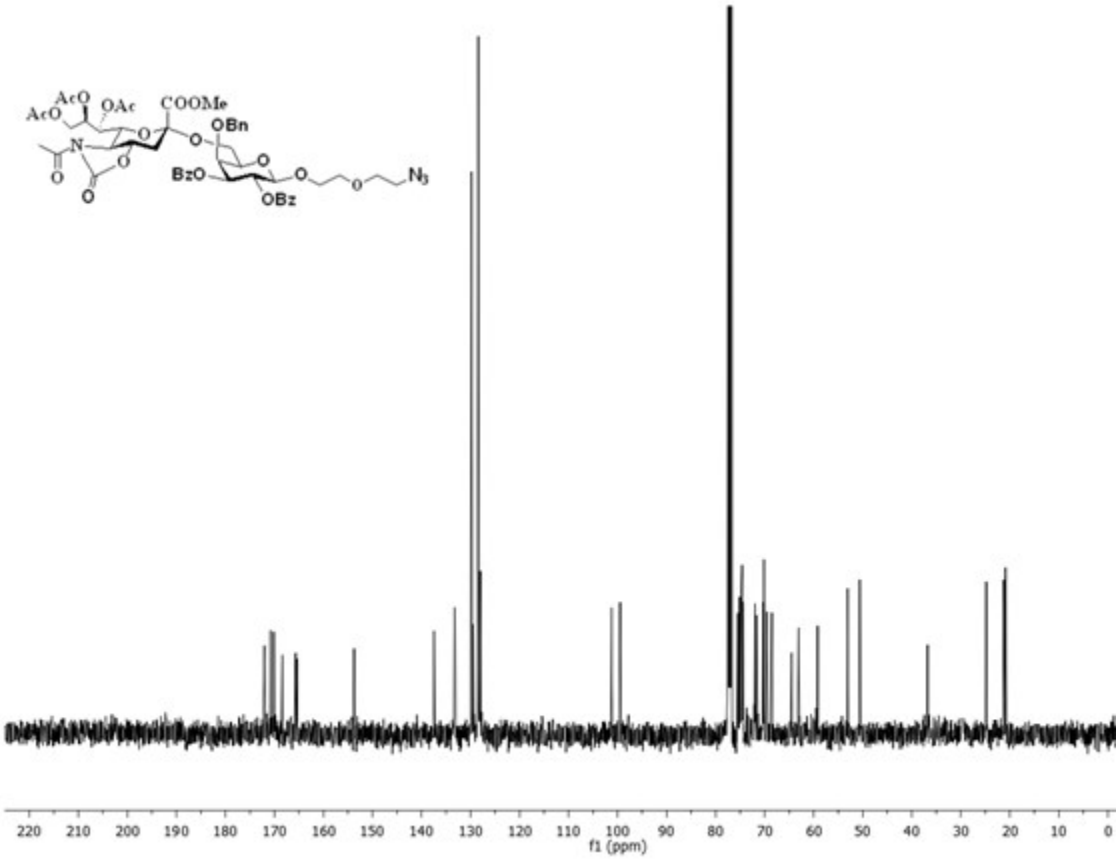

RD MN3 low voltage
IISER PUNE
RD MN3 low voltage 146 (2.685) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (145:149-(128:143+152:170))
1: TOF MS ES+
2.84e6
584.2380
CALCULATED MASS
(M+Na)+ 584.2372
585.2411
586.2441
587.2474
664.1816
736.1110
818.3537
921.4569
948.4521
965.4329
%
m/z

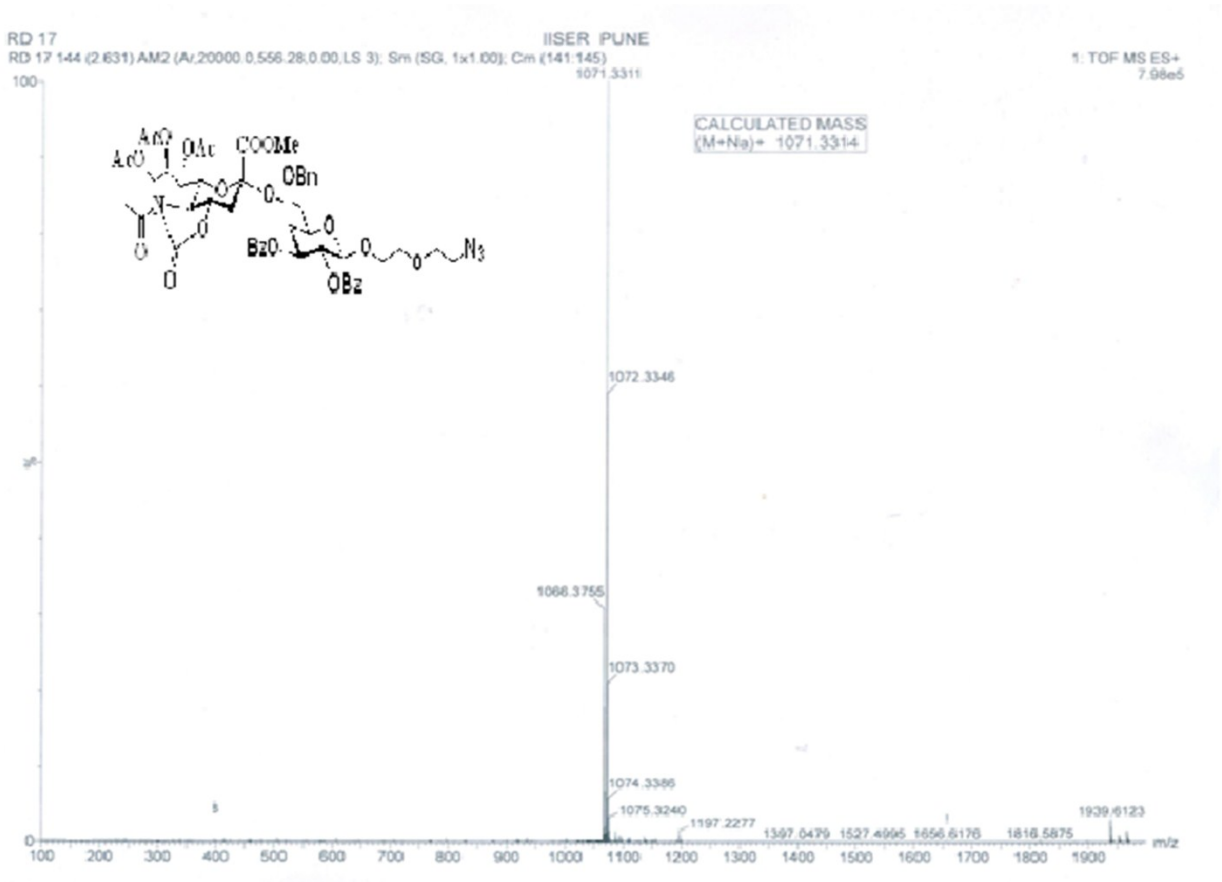

HO
OBn
HO
O
BnO
O
O
N3
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)

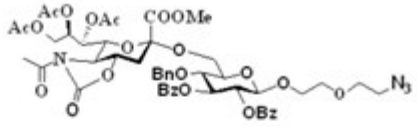

HO
OBn
HO
O
BnO
O
O
N3
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

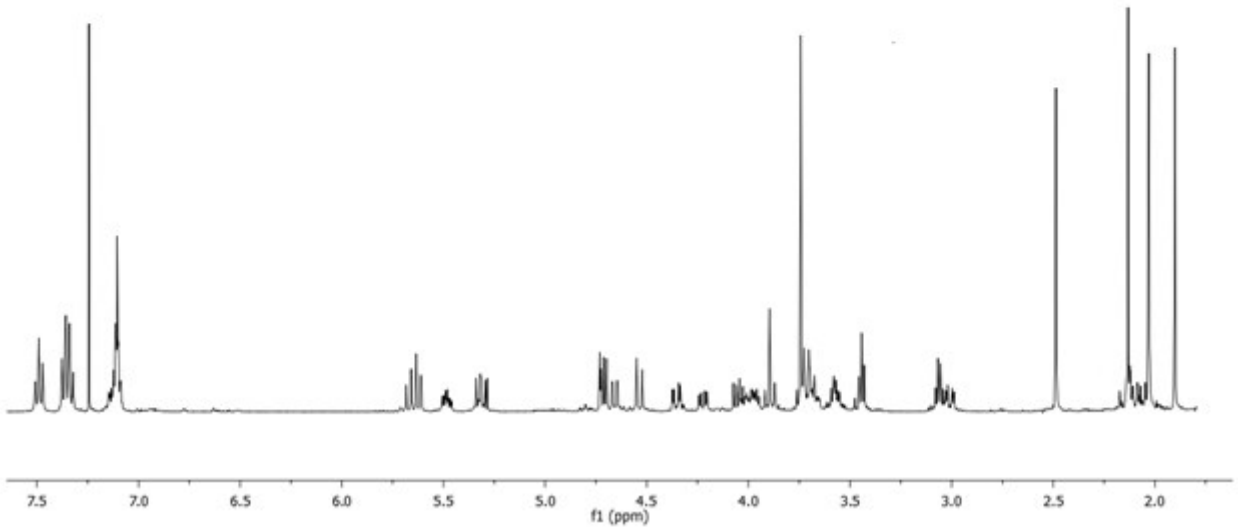

RD MN3OH low voltage
IISER PUNE
RD MN3OH low voltage 96 (1.772) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (94:102-(78:92+108:127))
1: TOF MS ES+
6.96e6
CALCULATED MASS
(M+Na)+ 496.2059
496.2061
492.2542
464.2288
465.2319
469.1837
474.2248
480.2323
484.2104
486.2080
493.25
496.2061
497.2093
502.1841
503.6835
512.1774
514.1805
519.2823
%
m/z

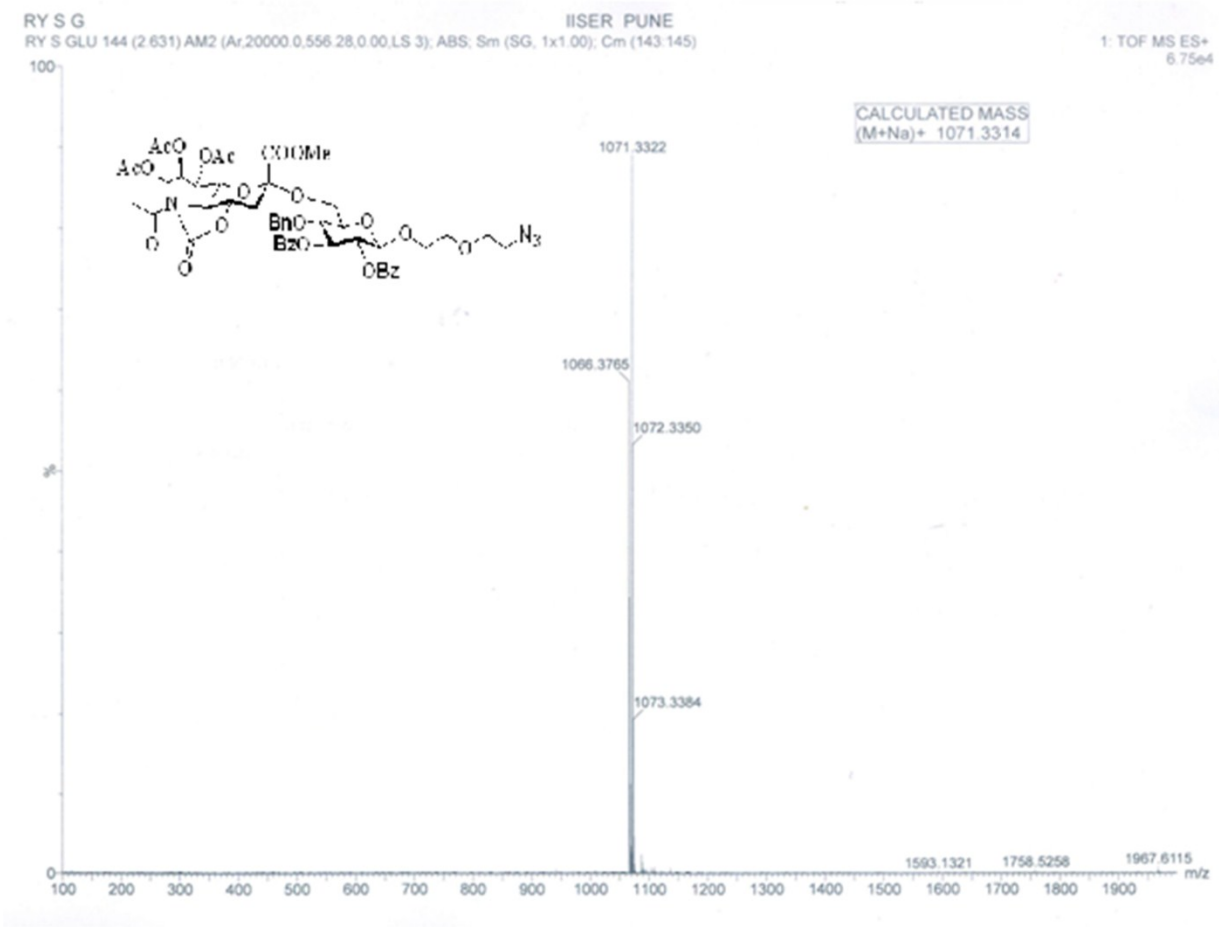

AcO
AcO
OAc
COOMe
OBn
BzO
OBz
N3
7.6
7.4
7.2
7.0
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
f1 (ppm)

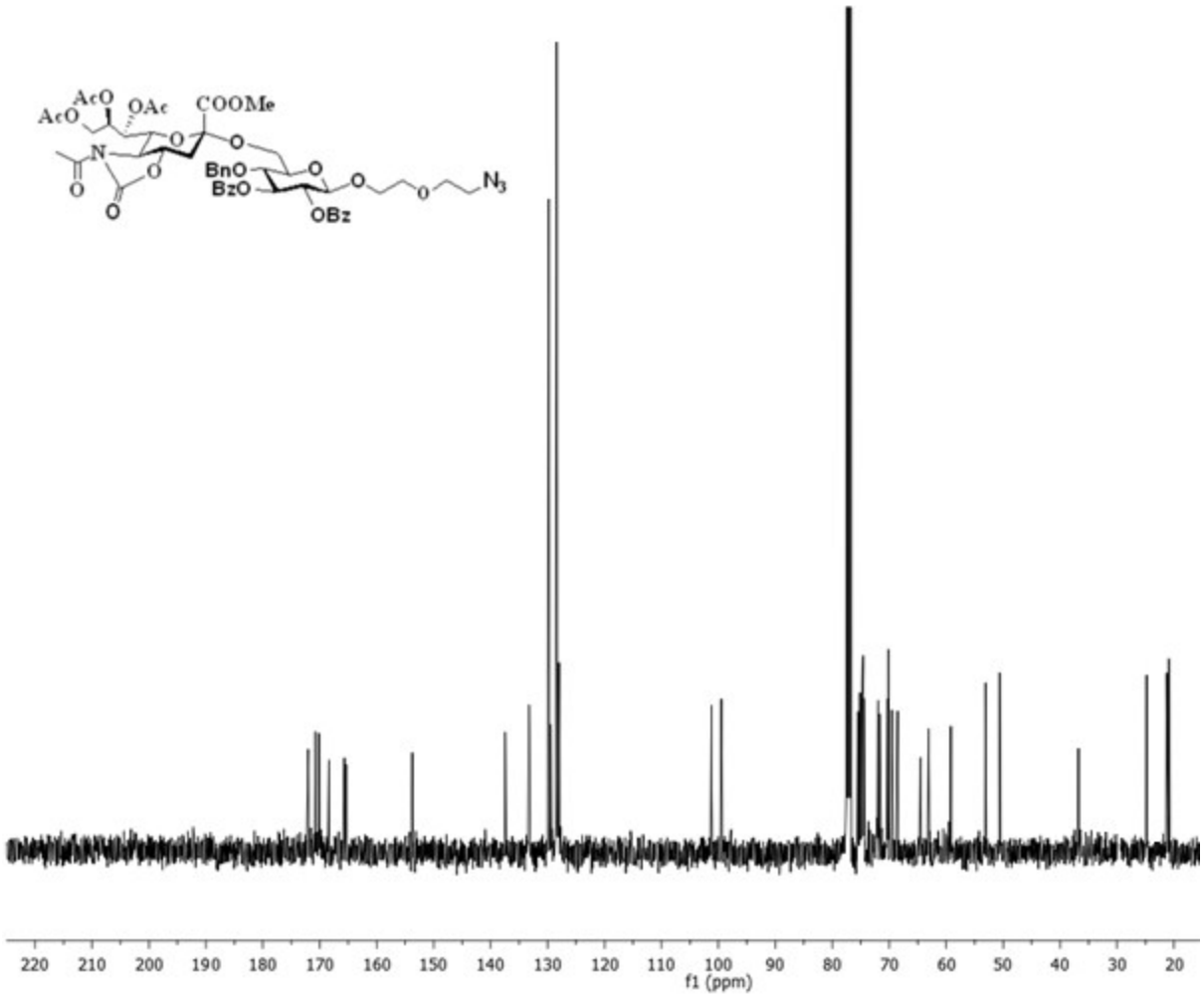

AcO
AcO
OAc
COOMe
OBn
N
O
BzO
OBz
N3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

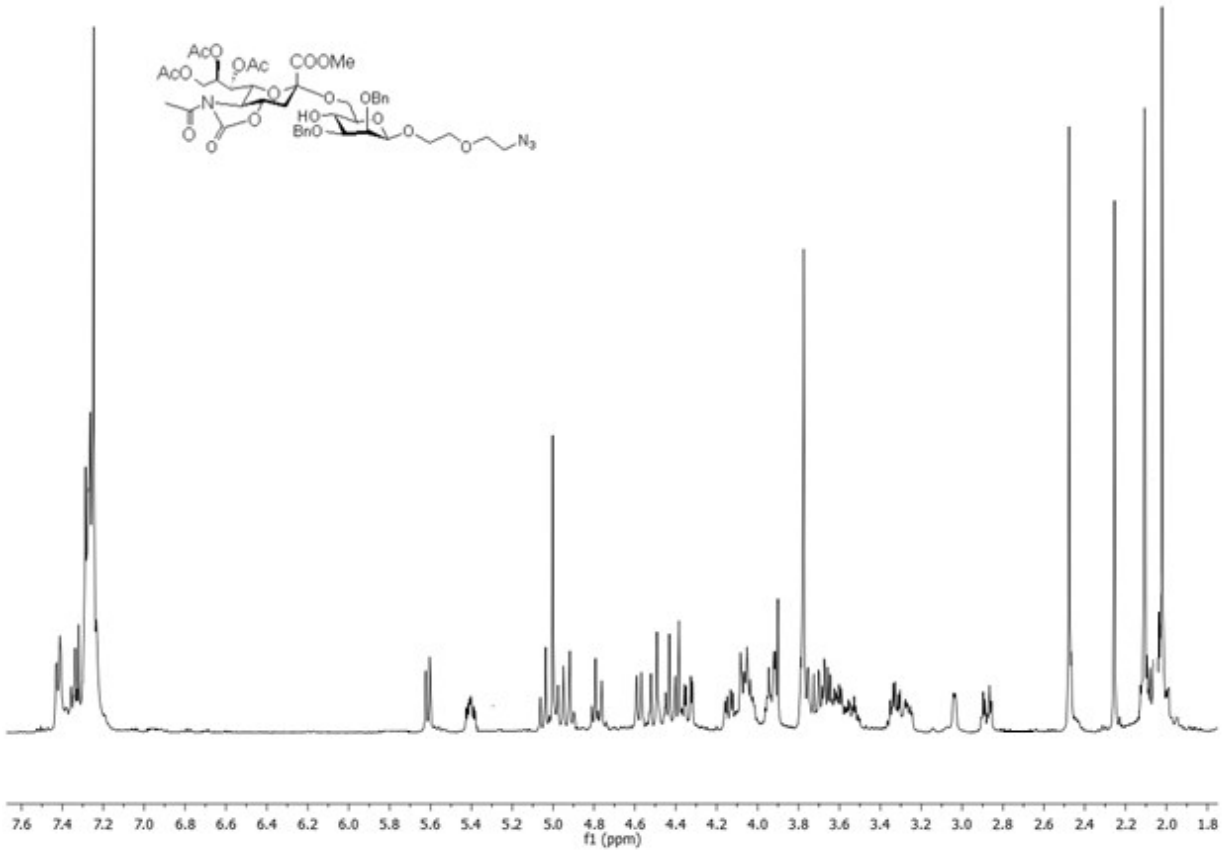

RD 17
IISER PUNE
RD 17 144 (2.631) AM2 (Ar,20000.0,556.28,0.00,LS 3); Sm (SG, 1x1.00); Cm (141:145)
1: TOF MS ES+
7.98e5
1071.3311
CALCULATED MASS
(M+Na)+ 1071.3314
1072.3346
1066.3755
1073.3370
1074.3386
1075.3240
1197.2277
1397.0479
1527.4995
1656.6176
1816.5875
1939.6123
m/z

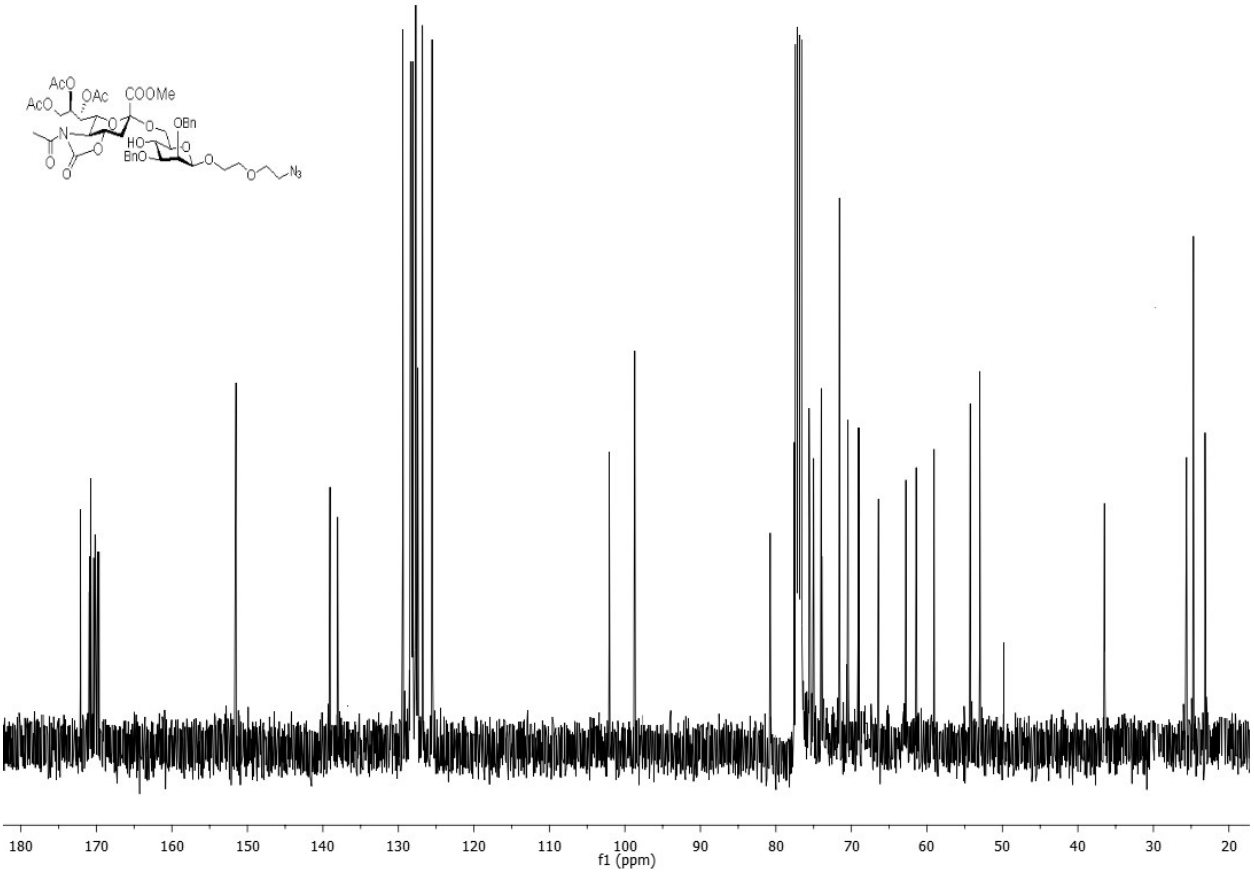

AcO
AcO
OAc
COOMe
N
O
O
O
O
BnO
BzO
OBz
O
O
N3

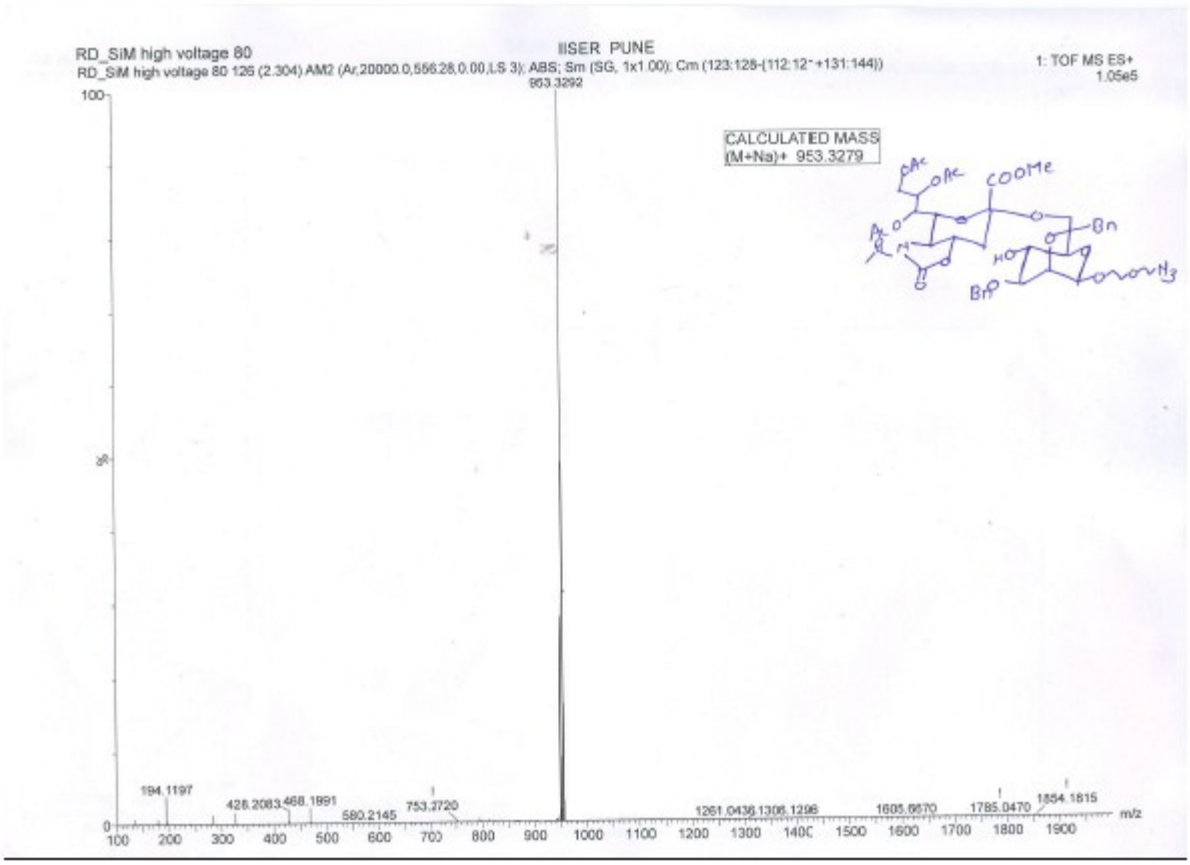

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

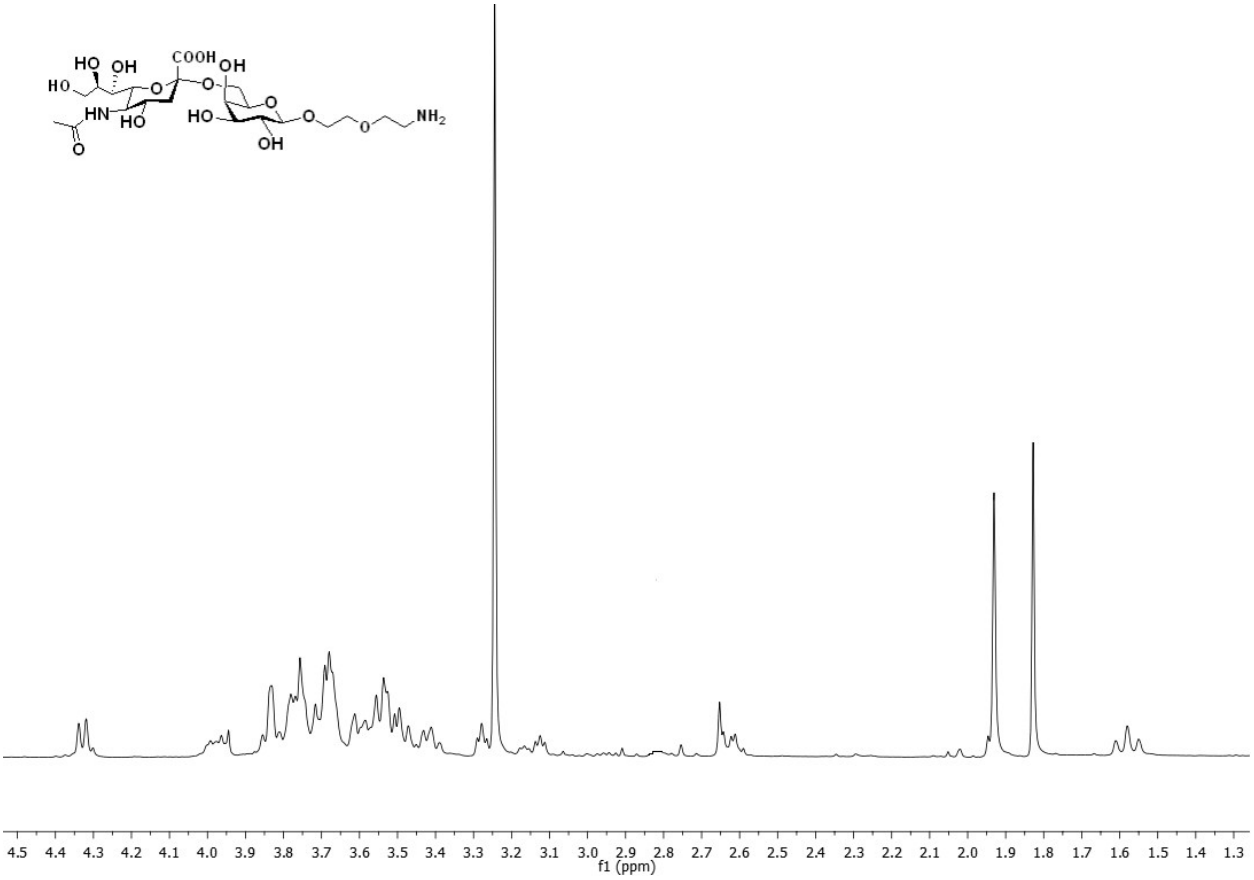

RY S G
IISER PUNE
RY S GLU 144 (2.631) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (143:145)
1: TOF MS ES+
6.75e4
100
%
0
CALCULATED MASS
(M+Na)+ 1071.3314
1071.3322
1066.3765
1072.3350
1073.3384
1593.1321
1758.5258
1967.6115
m/z
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900

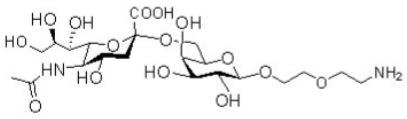

AcO
AcO
OAc
COOMe
N
O
O
O
O
BnO
BzO
O
O
O
O
N3
OBz
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

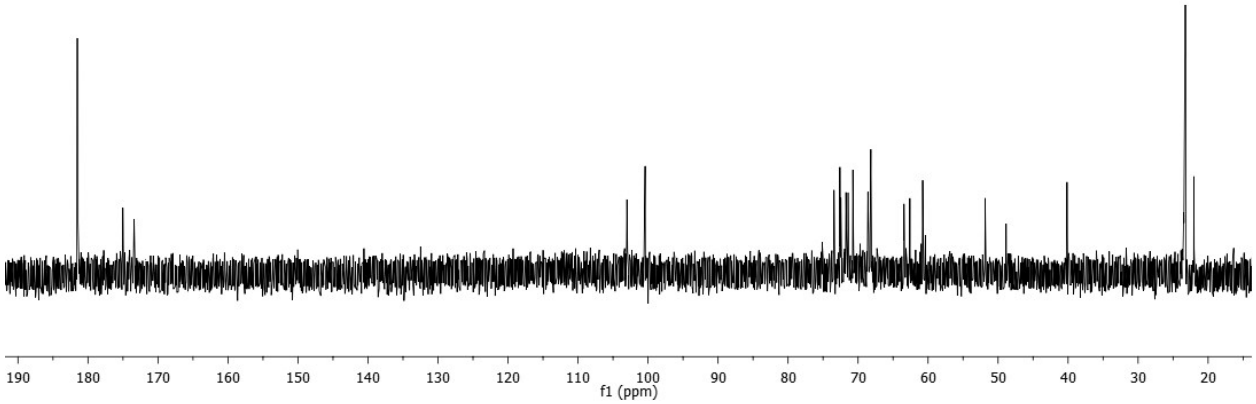

AcO
AcO
OAc
COOMe
OBn
HO
BnO
N
O
O
O
O
O
O
O
N3
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)

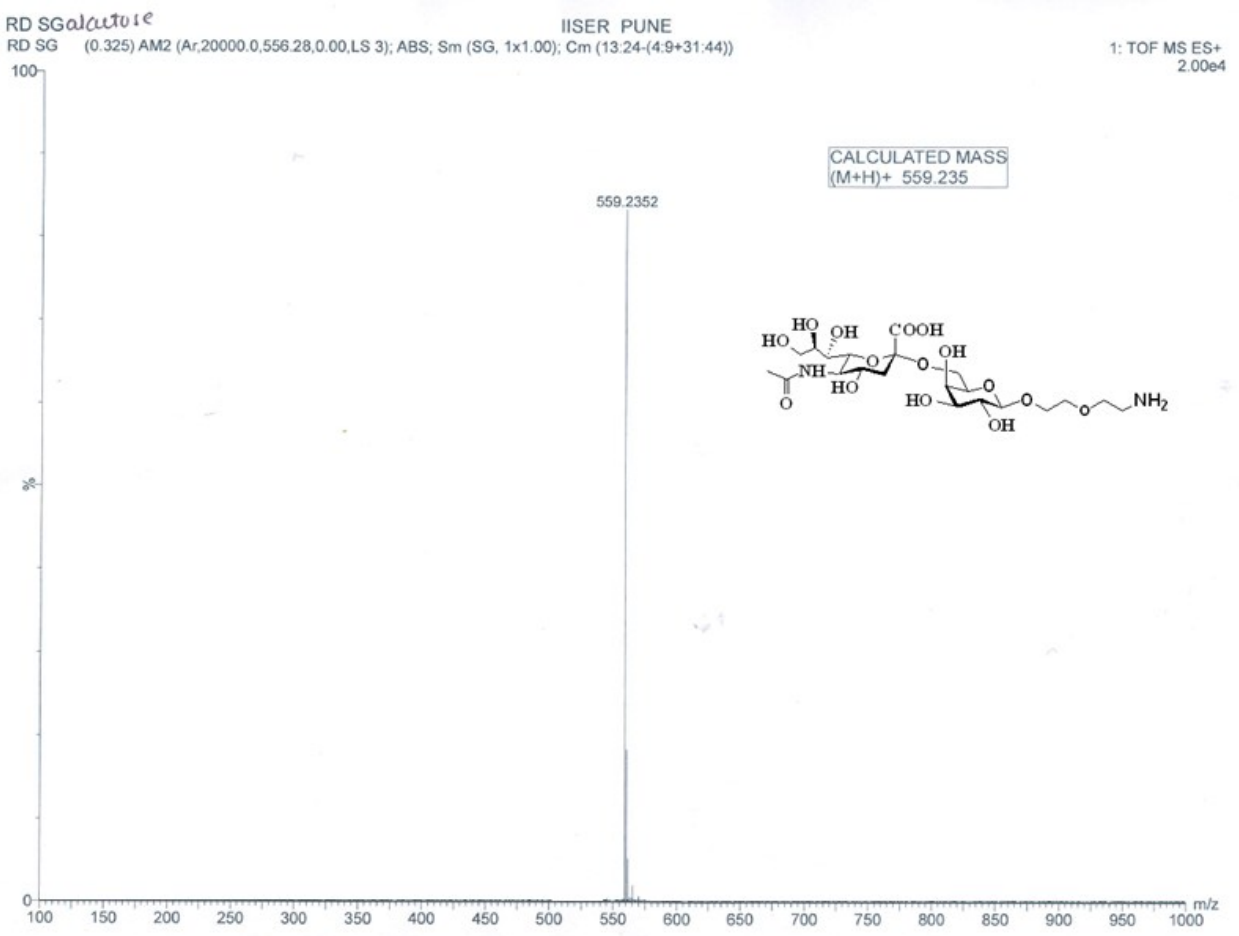

AcO
AcO
OAc
COOMe
OBn
HO
BnO
N3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

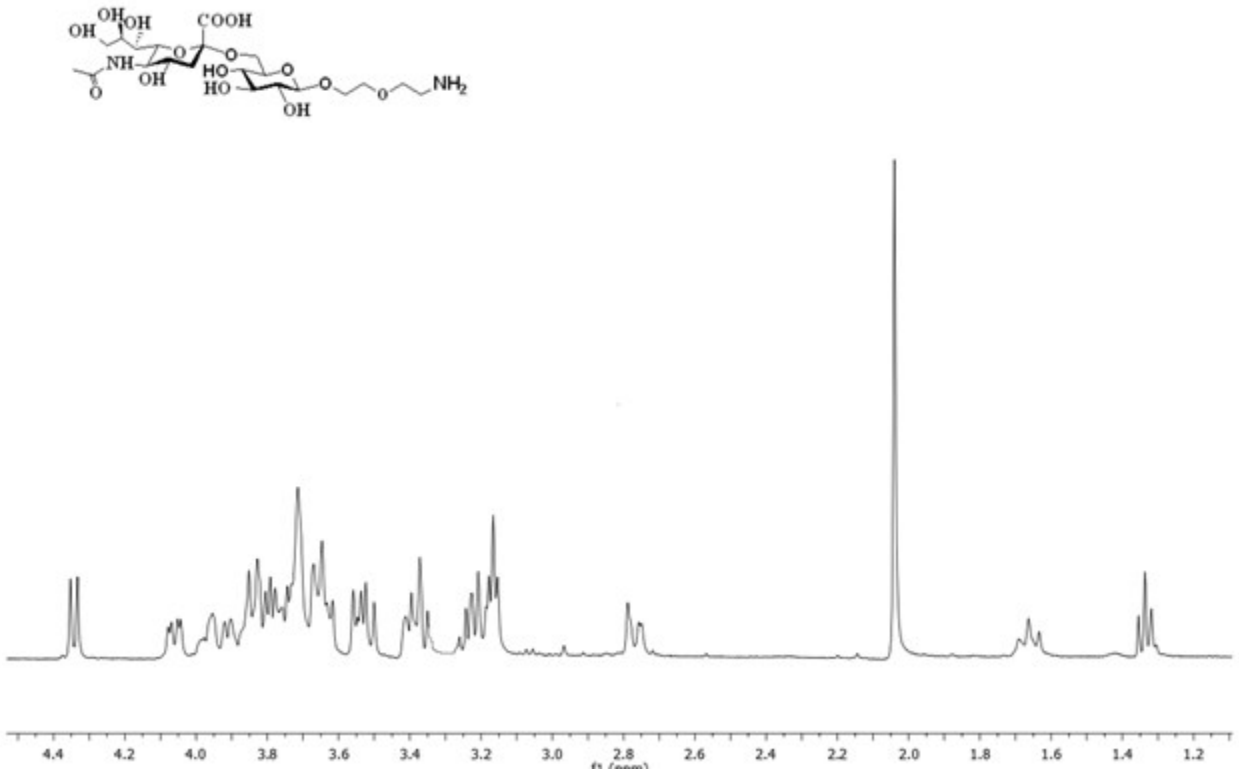

RD_SiM high voltage 80
IISER PUNE
RD_SiM high voltage 80 126 (2.304) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (123:126-(112:12"+131:144))
1: TOF MS ES+
1.05e5
953.3292
CALCULATED MASS
(M+Na)+ 953.3279
194.1197
426.2083
468.1891
580.2145
753.3720
1261.0436
1308.1296
1605.6670
1785.0470
1854.1815
m/z

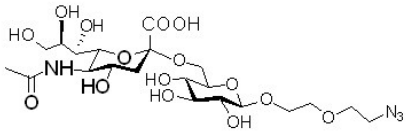

HO
OH
COOH
OH
HO
O
O
HN
HO
HO
O
O
O
O
NH2
OH
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3
f1 (ppm)

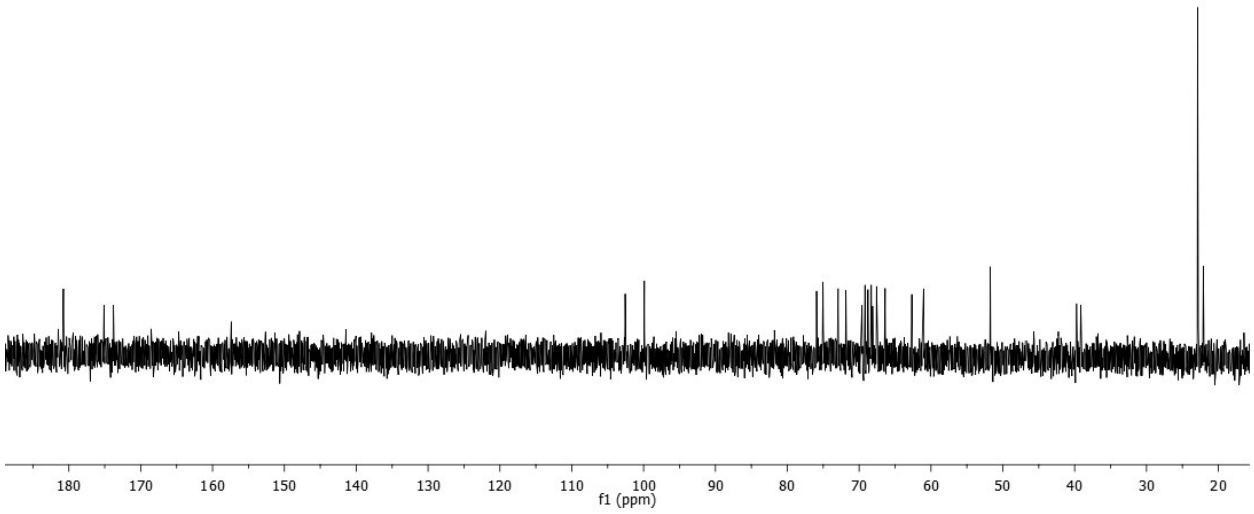

HO
OH
COOH
OH
HO
O
O
HN
HO
HO
O
O
O
NH2
OH
O

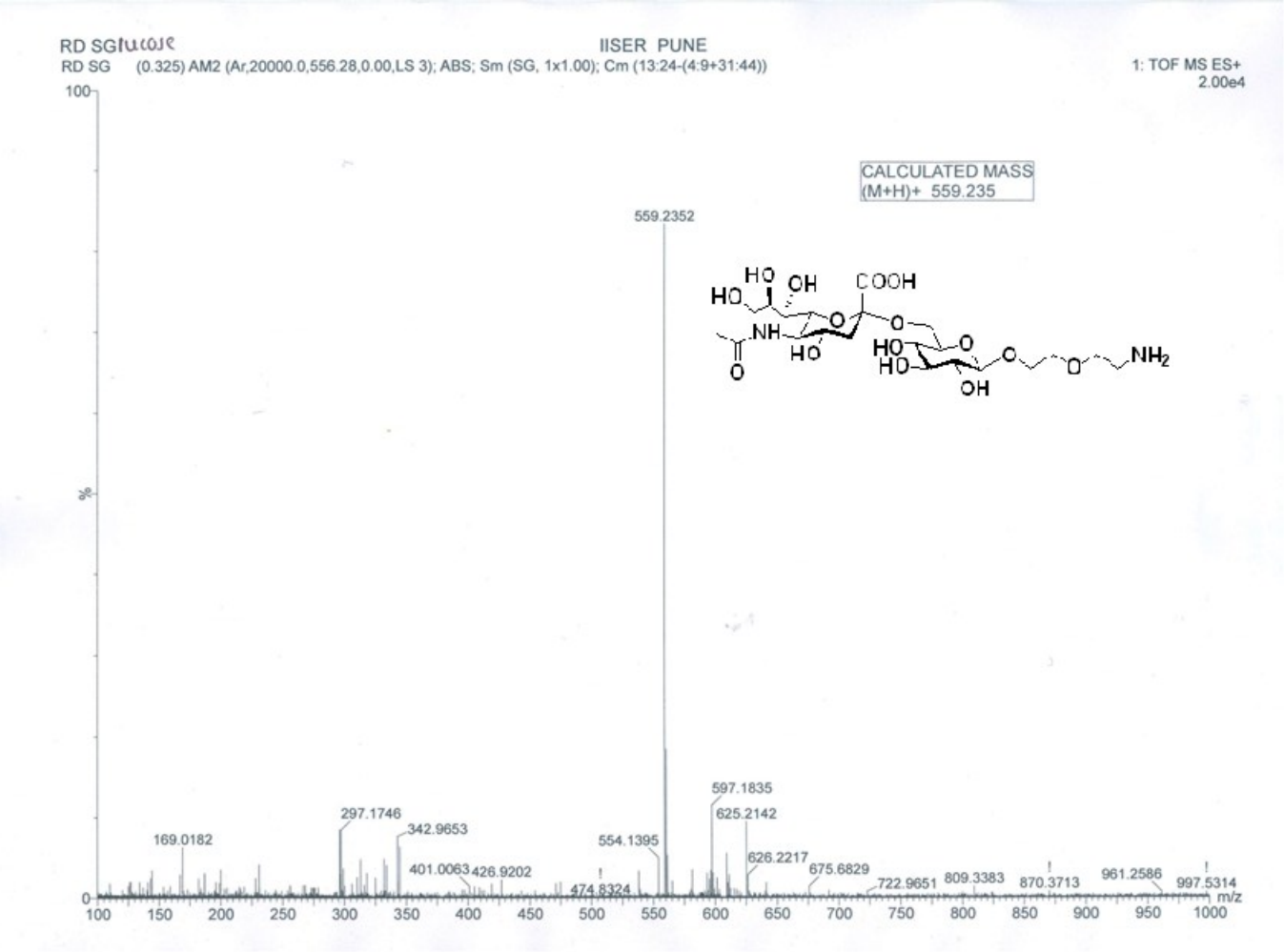

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

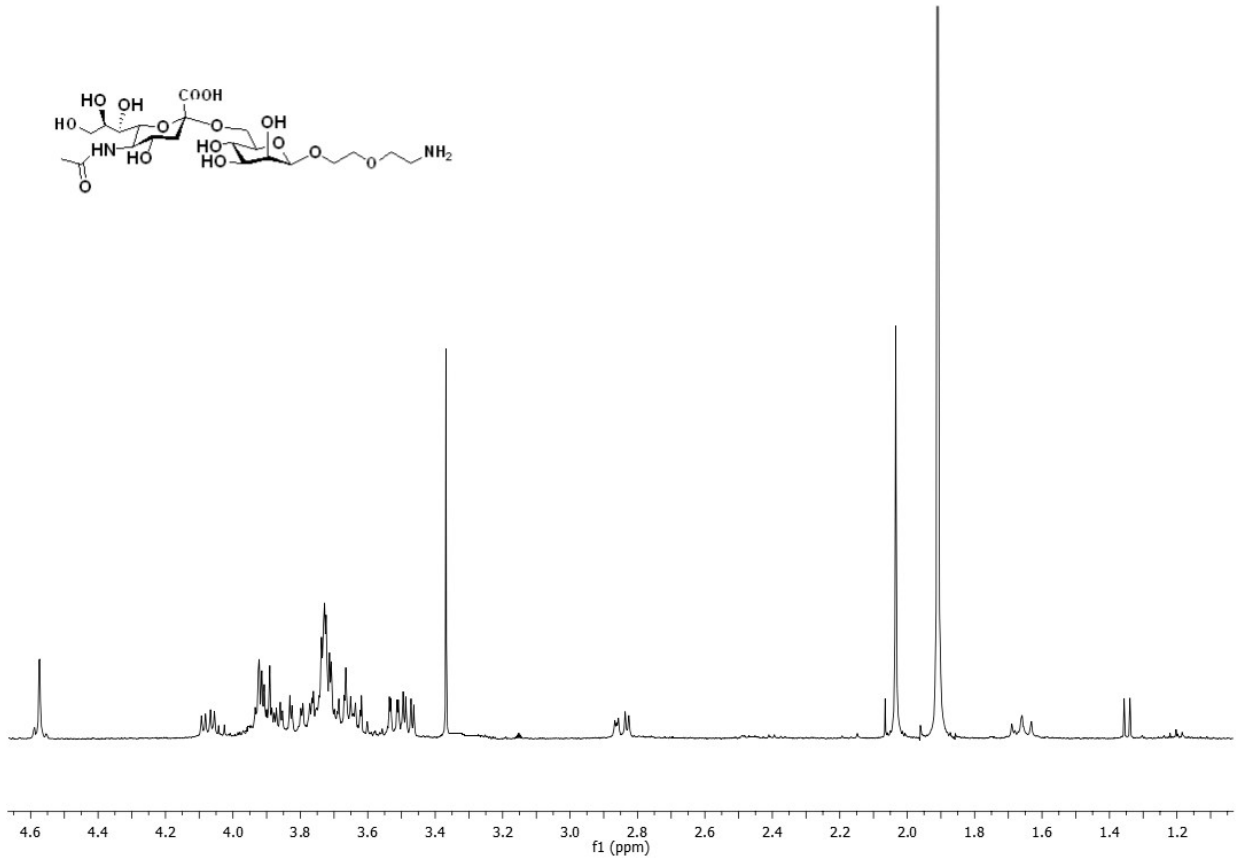

RD SGalcutoie
IISER PUNE
RD SG (0.325) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (13:24-(4:9+31:44))
1: TOF MS ES+
2.00e4
100
%
0
CALCULATED MASS
(M+H)+ 559.235
559.2352
HO
OH
COOH
NH
O
HO
OH
O
HO
OH
O
O
O
NH2
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
m/z

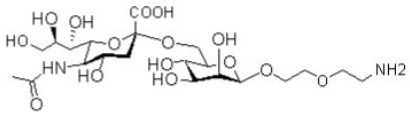

OH
OH
OH
COOH
NH
O
OH
O
HO
HO
O
OH
O
O
NH2
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2

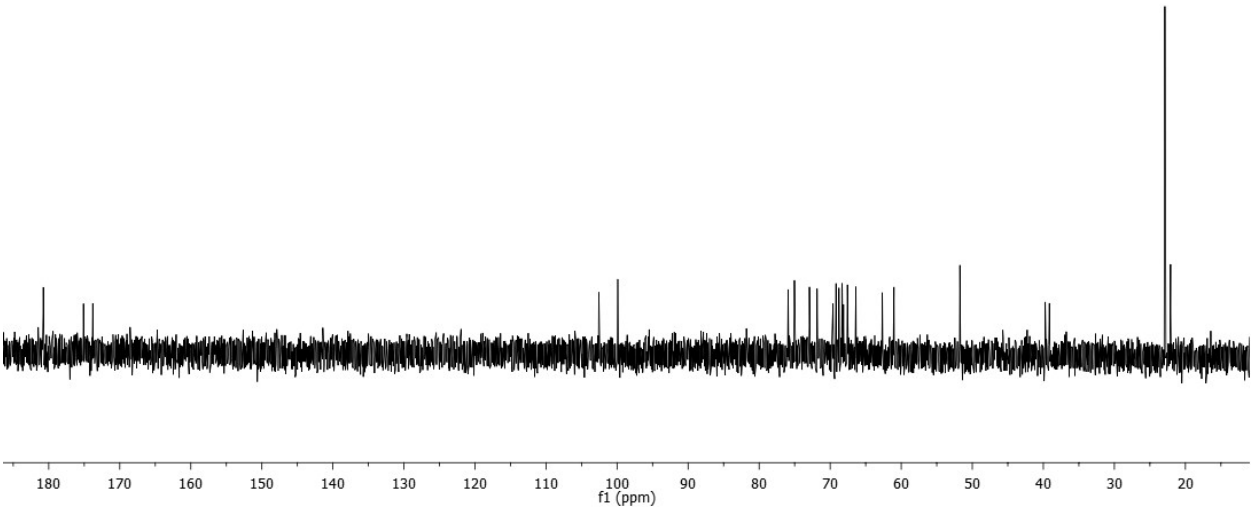

OH
HO
OH
COOH
NH
HO
O
HO
HO
O
O
OH
O
O
N3

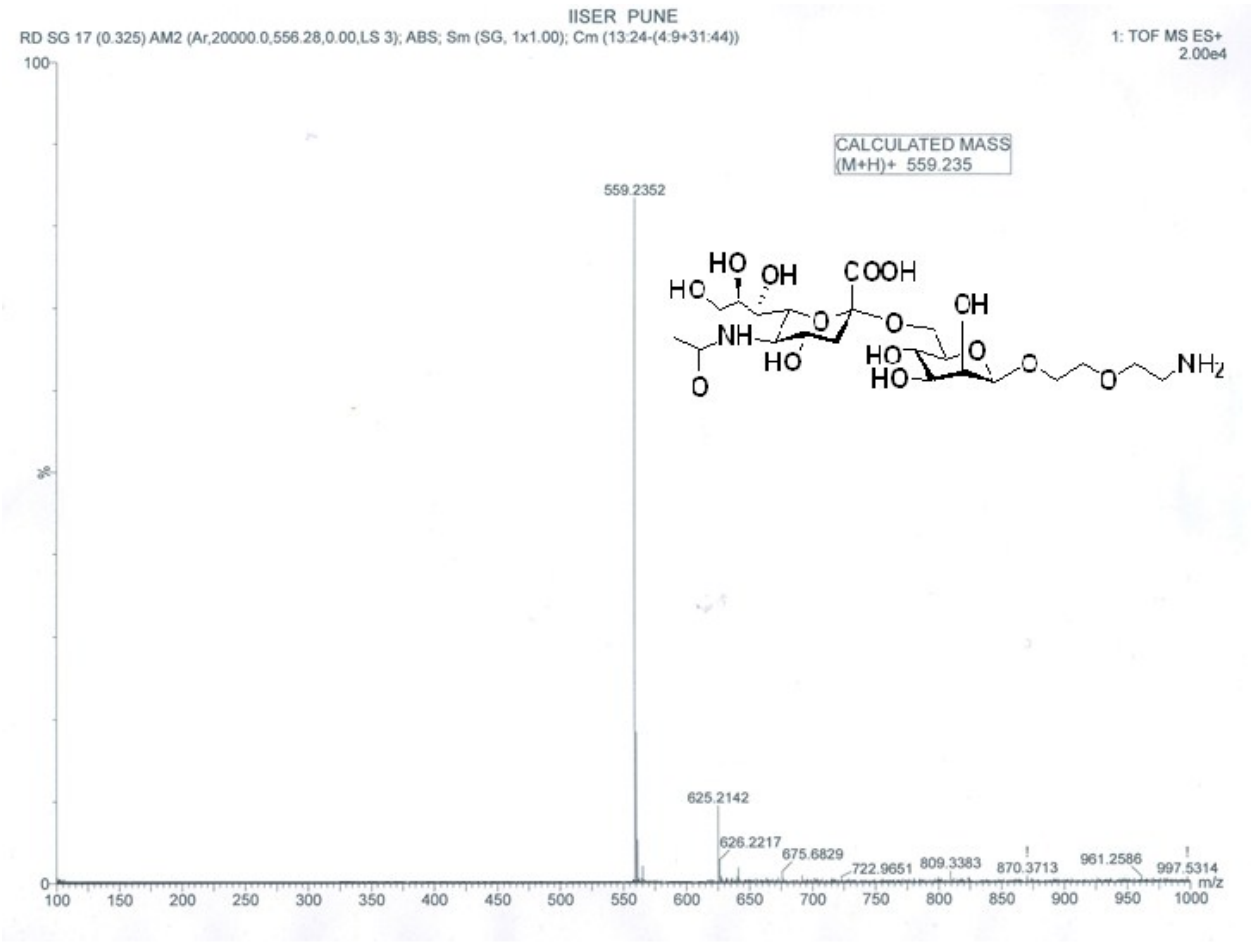

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


RD SGfucose
IISER PUNE
RD SG (0.325) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (13:24-(4:9+31:44))
1: TOF MS ES+
2.00e4
CALCULATED MASS
(M+H)+ 559.235
559.2352
597.1835
625.2142
297.1746
342.9653
169.0182
554.1395
626.2217
675.6829
401.0063
426.9202
474.8324
722.9651
809.3383
870.3713
961.2586
997.5314
%
m/z

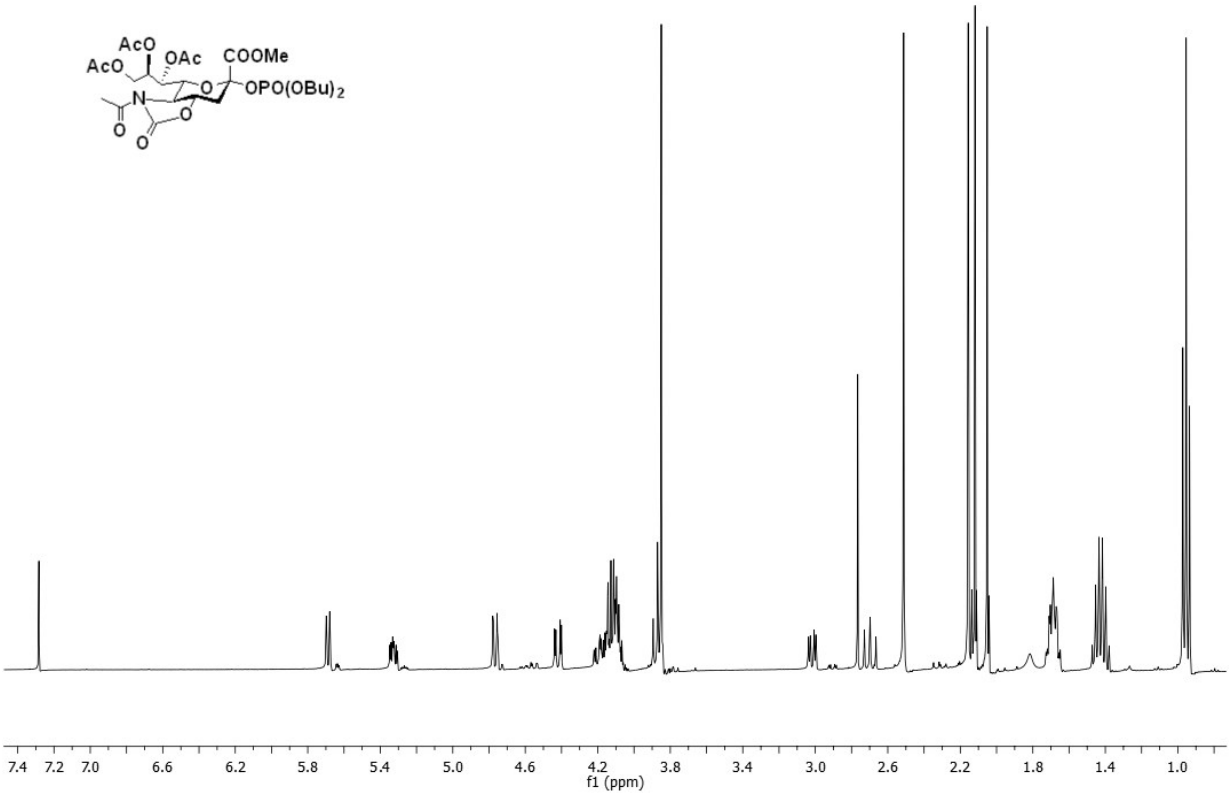

HO
OH
COOH
HO
O
O
OH
HN
HO
HO
O
HO
O
O
O
NH2
O
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f1 (ppm)

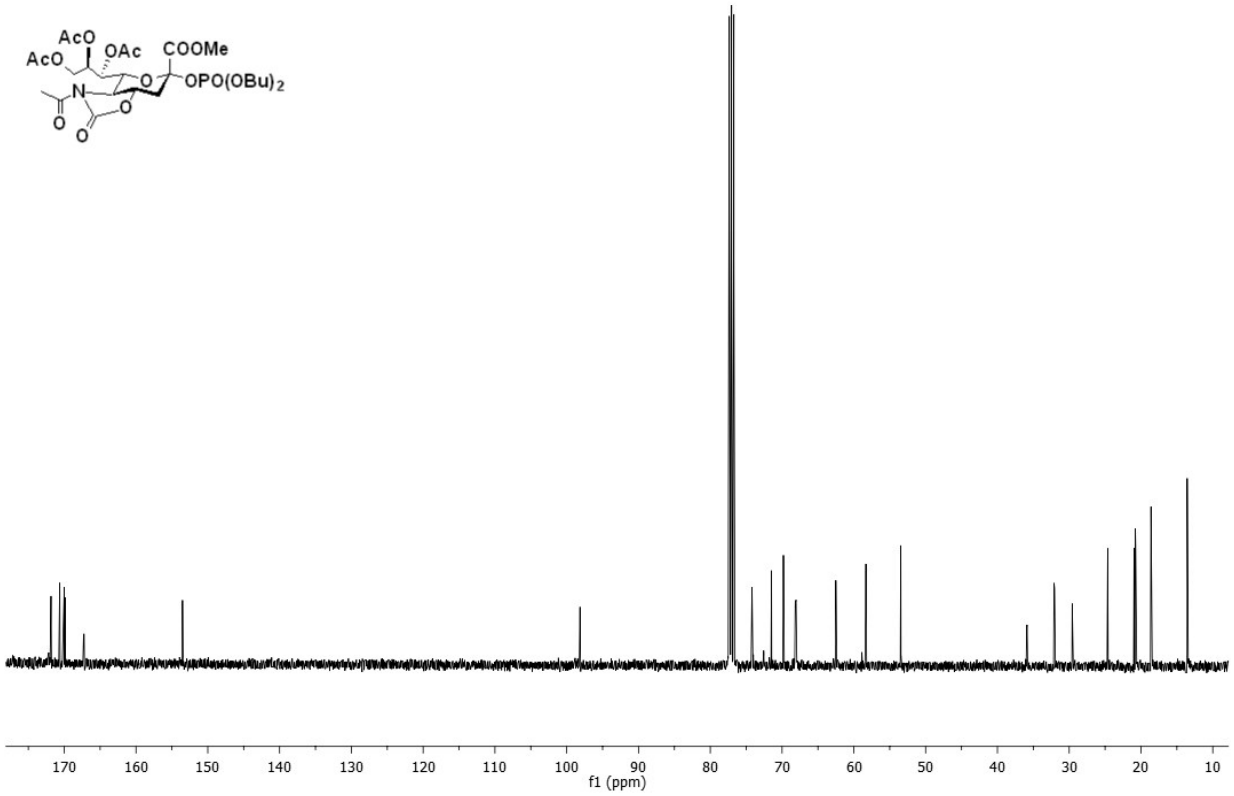

HO
OH
COOH
HO
O
O
OH
HN
HO
HO
O
HO
O
O
O
NH2
O

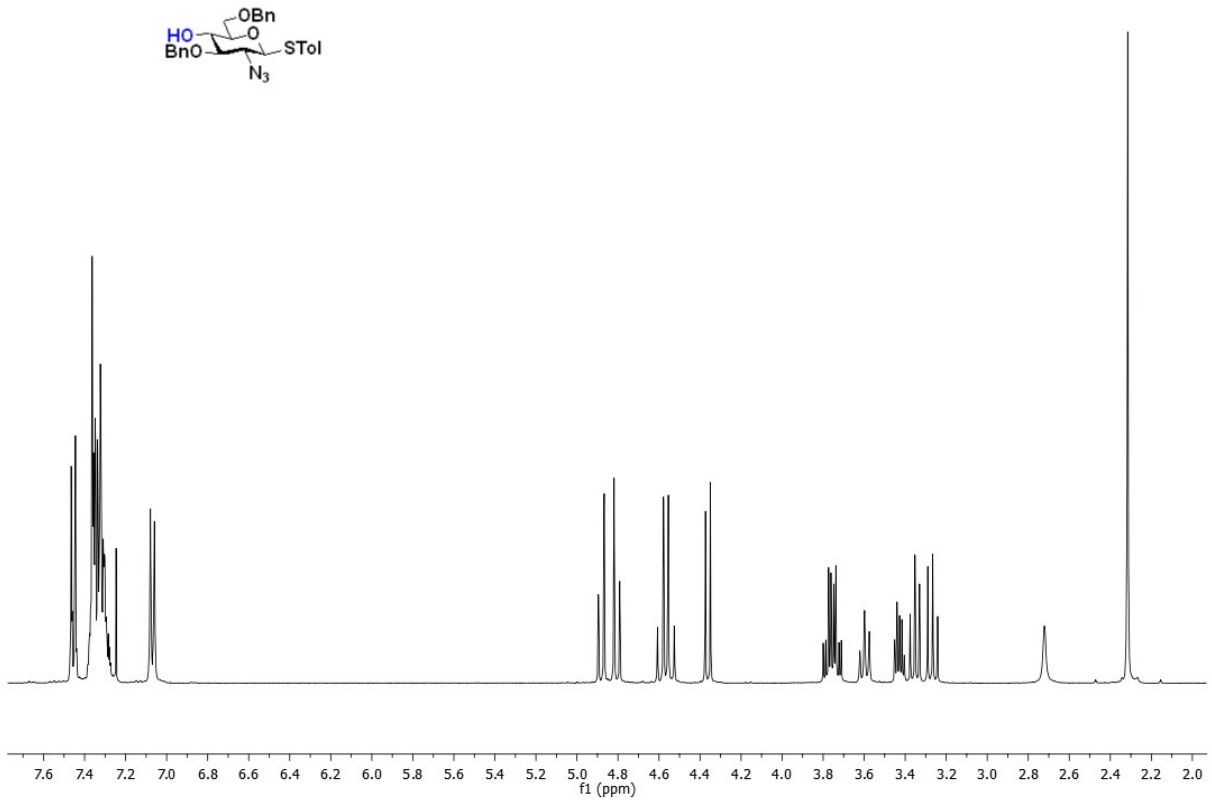

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

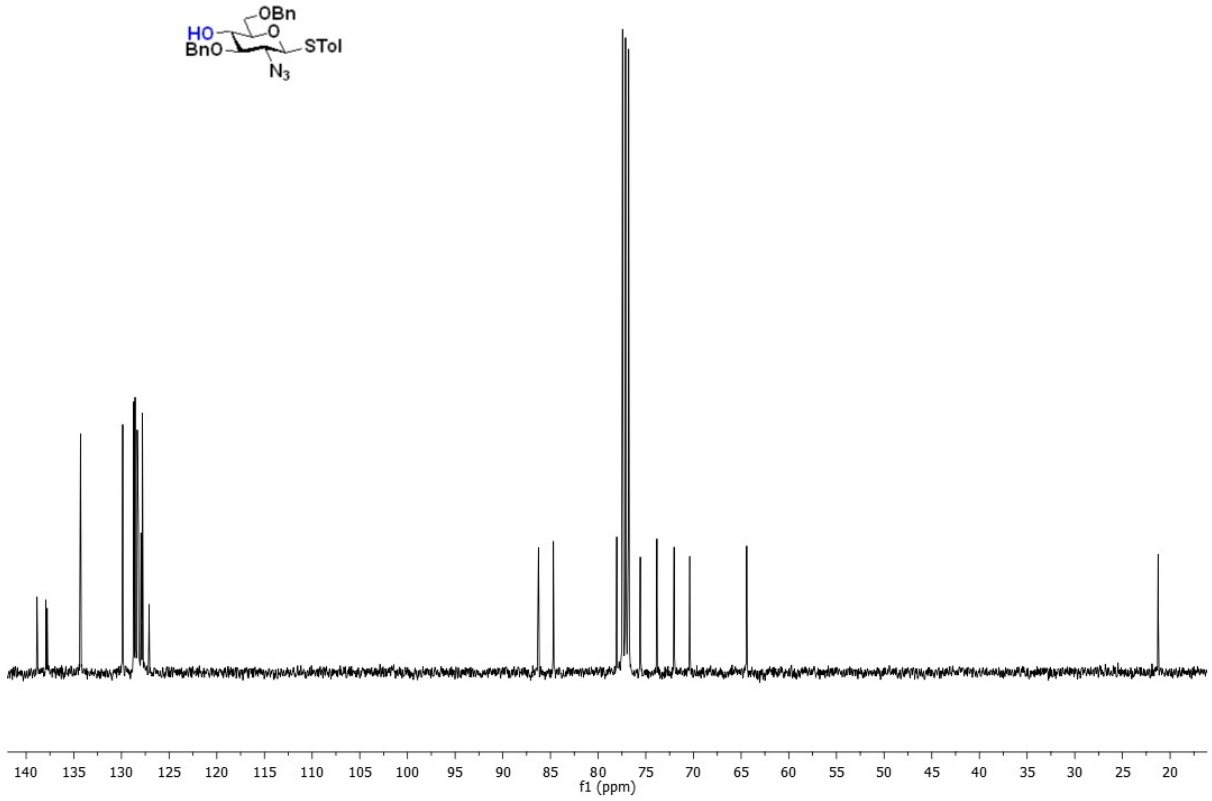

IISER PUNE
RD SG 17 (0.325) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (13:24-(4:9+31:44))
1: TOF MS ES+
2.00e4
100
%
0
CALCULATED MASS
(M+H)+ 559.235
559.2352
625.2142
626.2217
675.6829
722.9651
809.3383
870.3713
961.2586
997.5314
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

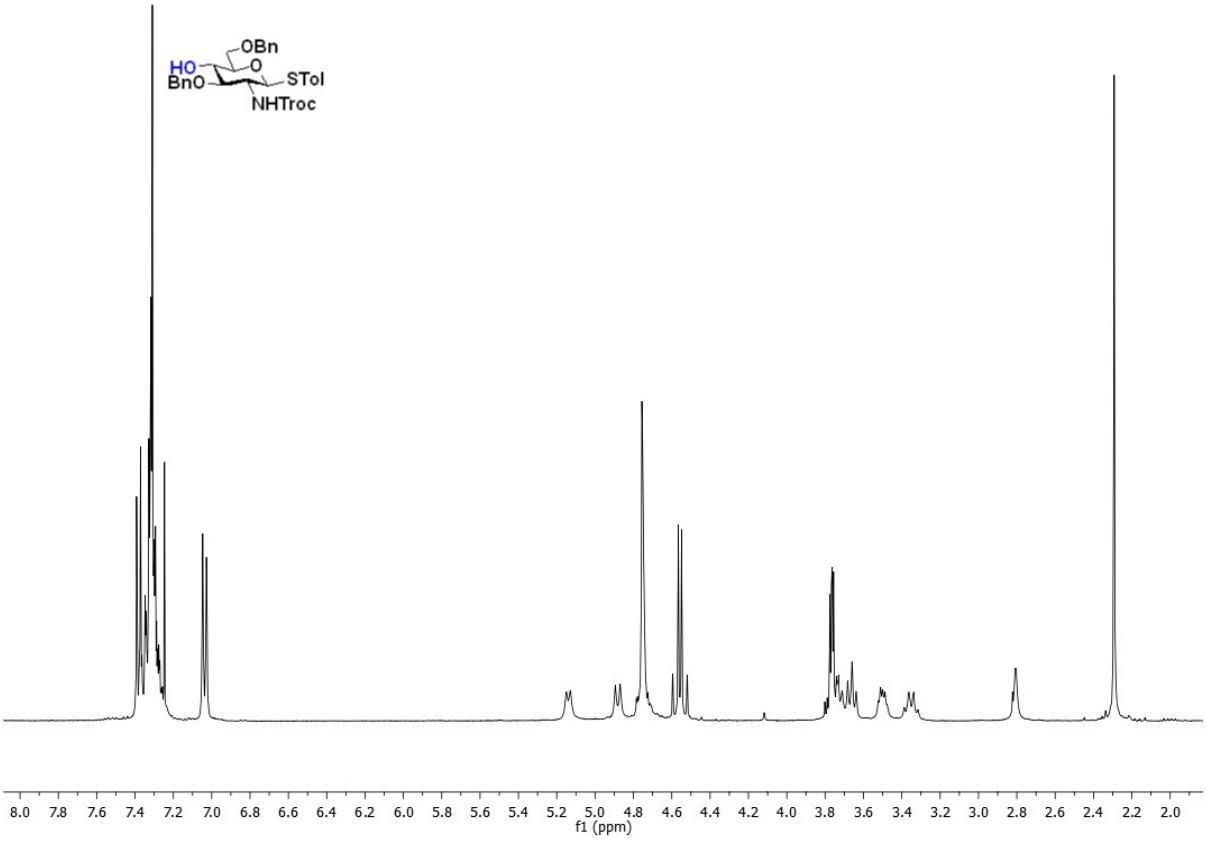
NMR For Trisaccharide Library

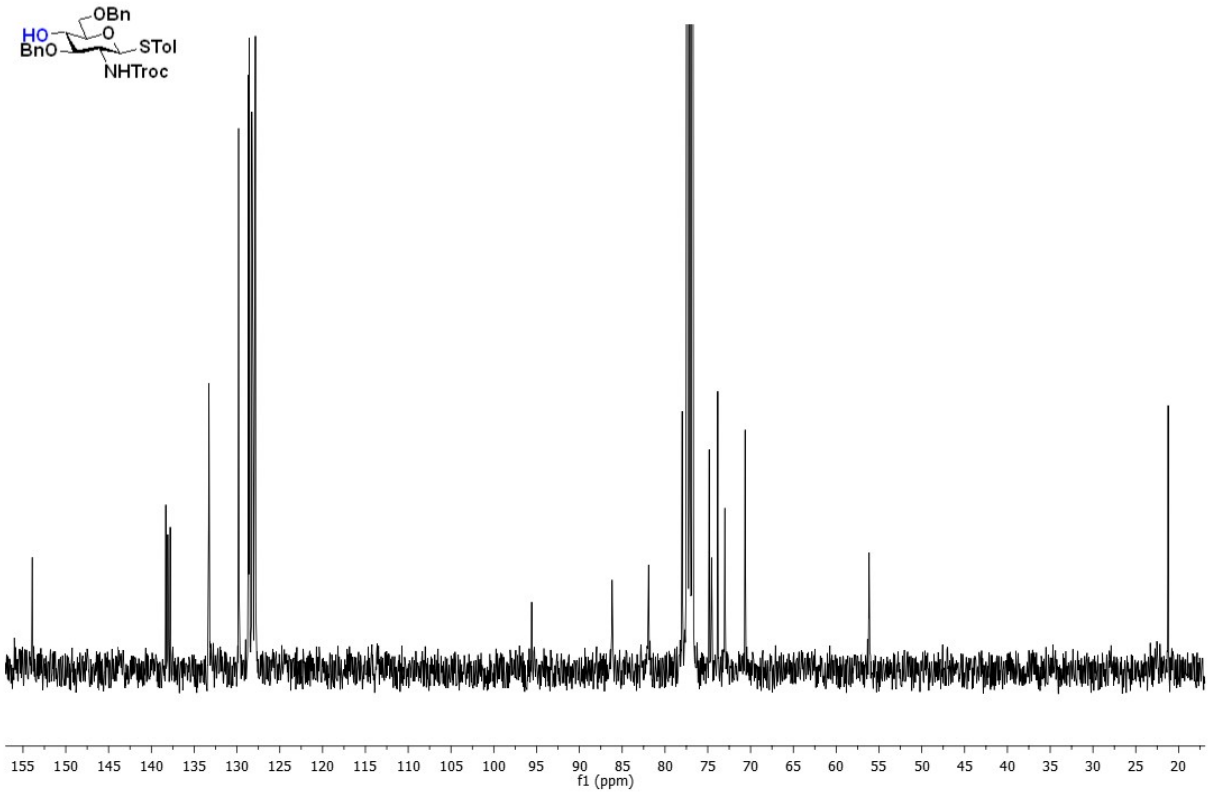

AcO
AcO
OAc
COOMe
OPO(OBu)2
N
O
O
O
O
7.4
7.2
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
f1 (ppm)

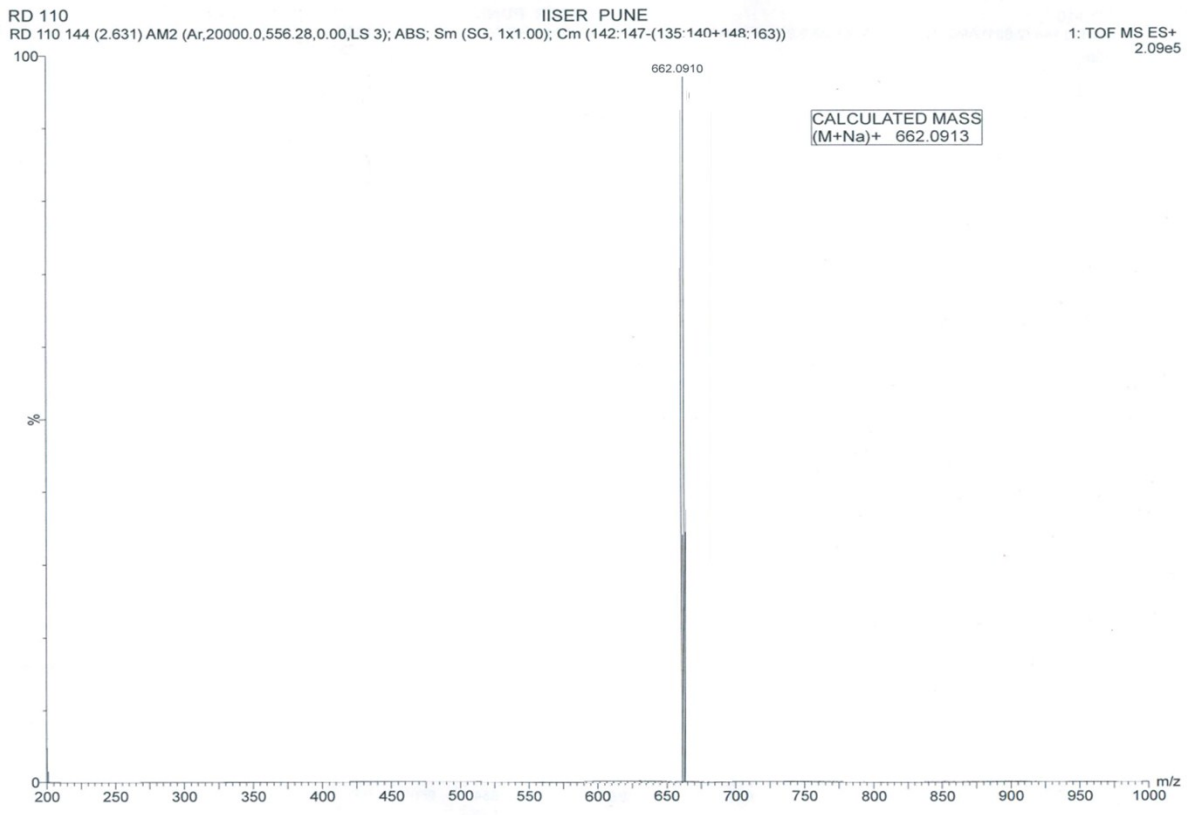

AcO
AcO
OAc
COOMe
OPO(OBu)2
N
O
O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

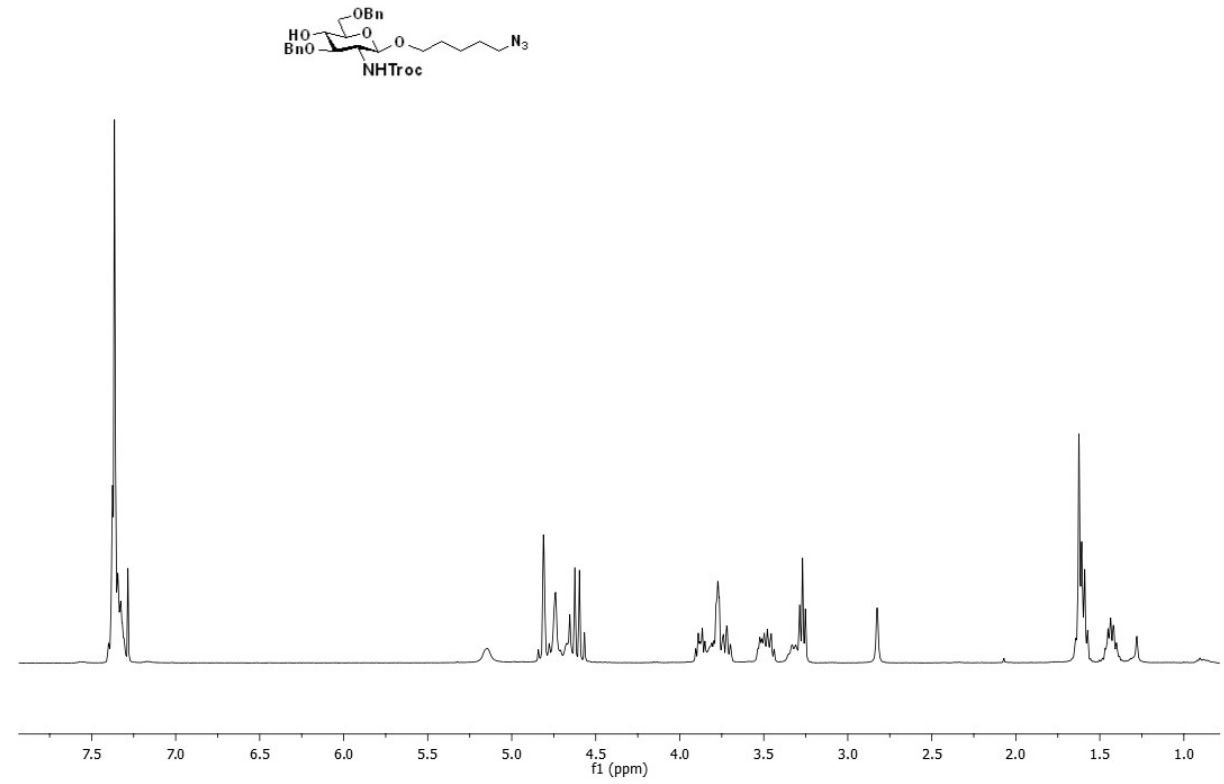

OBn
HO
O
BnO
STol
N3
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

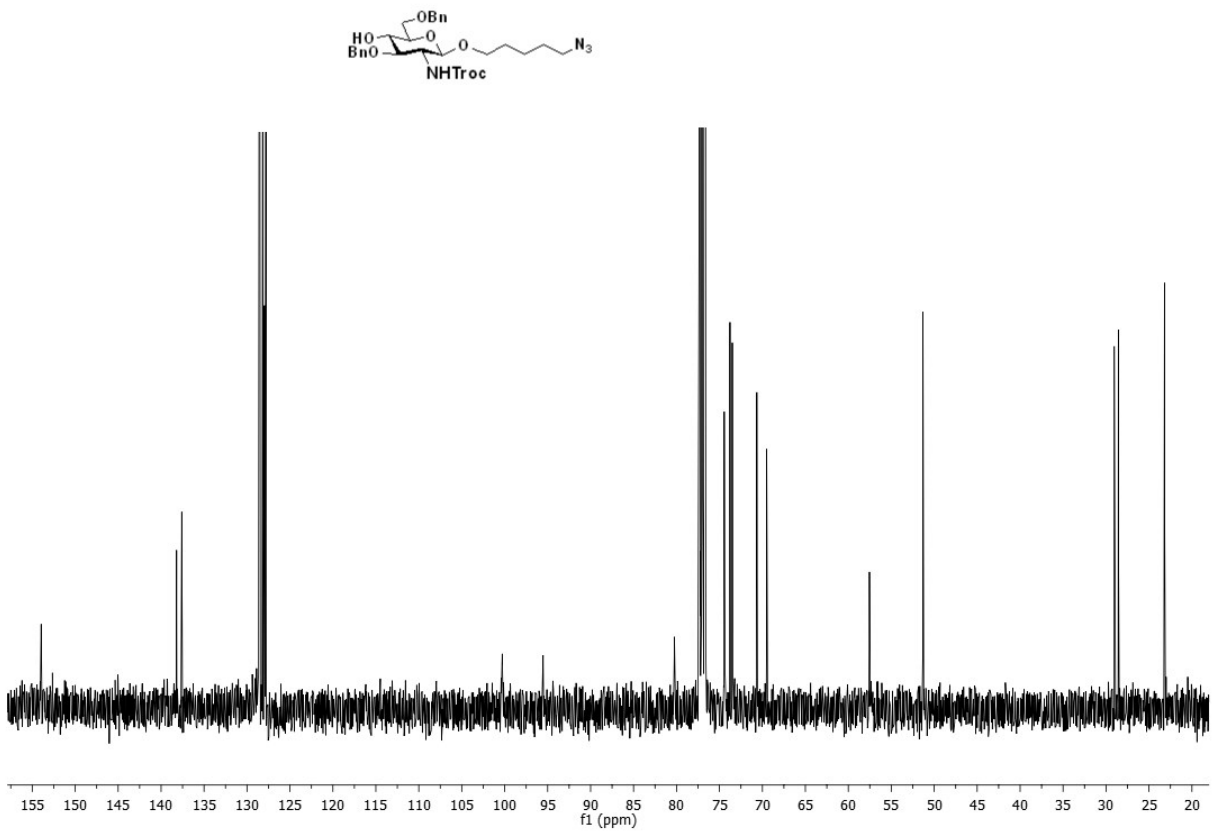

OBn
HO
O
STol
BnO
N3
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

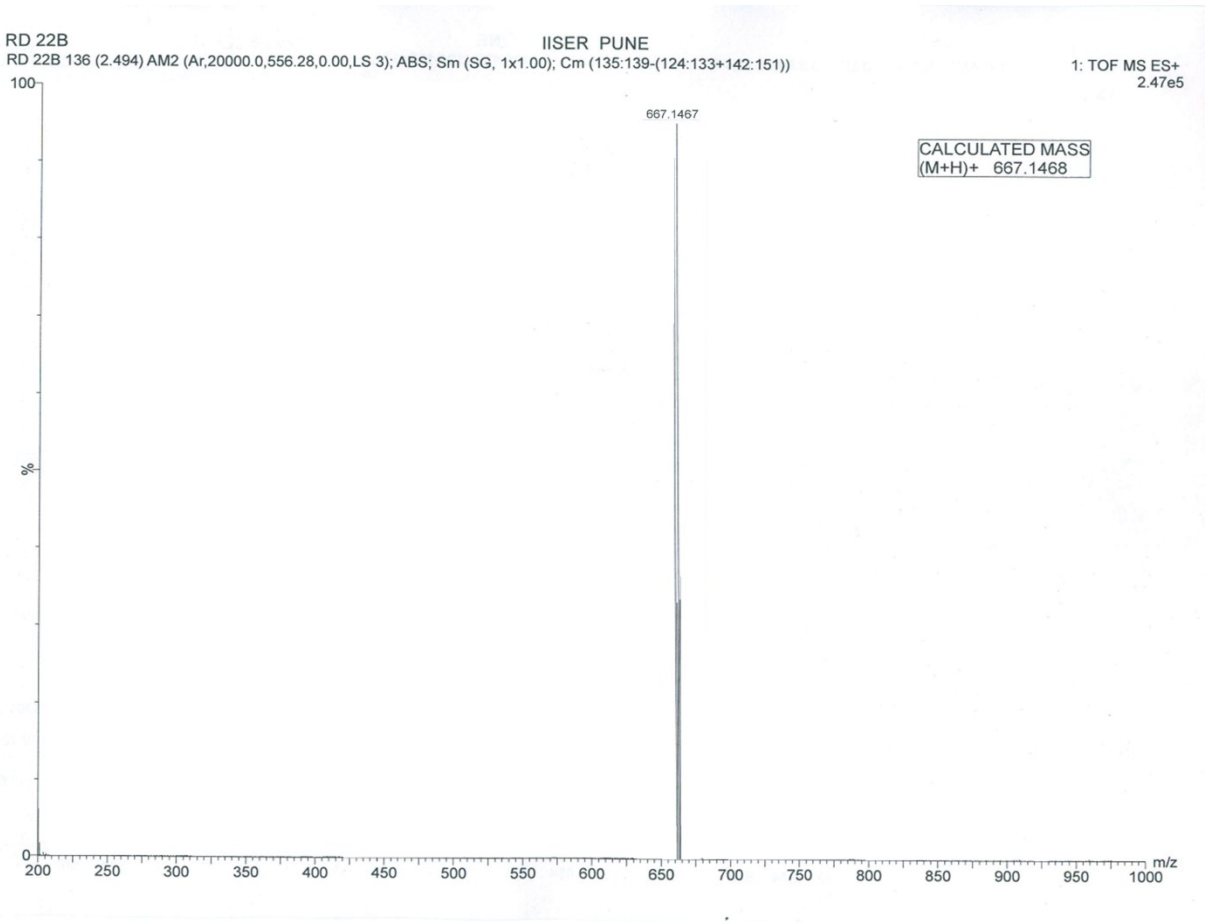

OBn
HO
O
BnO
STol
NHTroc
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

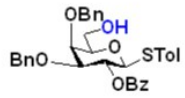

OBn
HO
O
BnO
STol
NHTroc
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

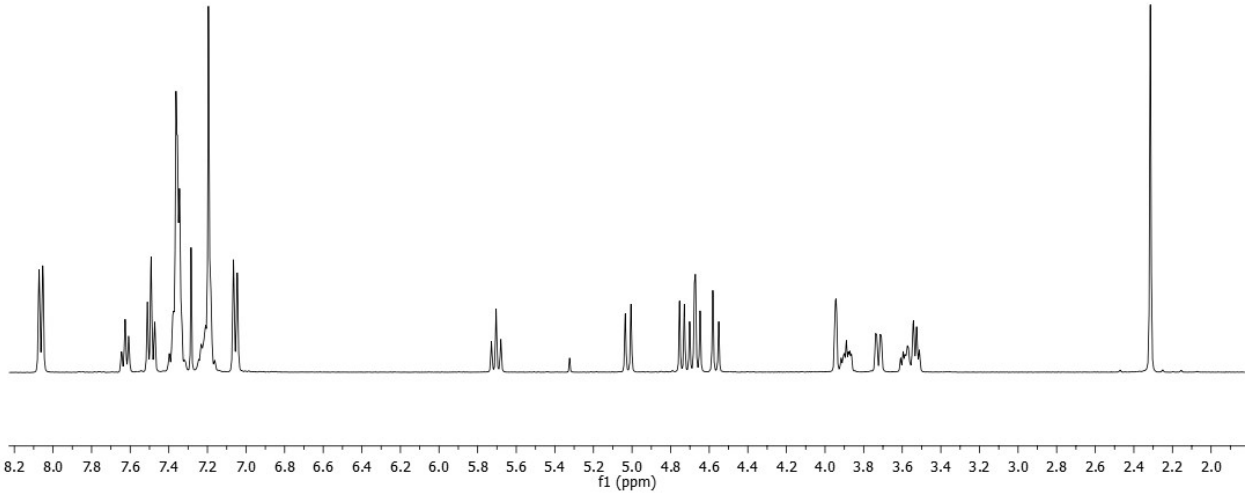

RD 110
IISER PUNE
RD 110 144 (2.631) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (142:147-(135:140+148:163))
1: TOF MS ES+
2.09e5
100
662.0910
CALCULATED MASS
(M+Na)+ 662.0913
%
0
200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
m/z

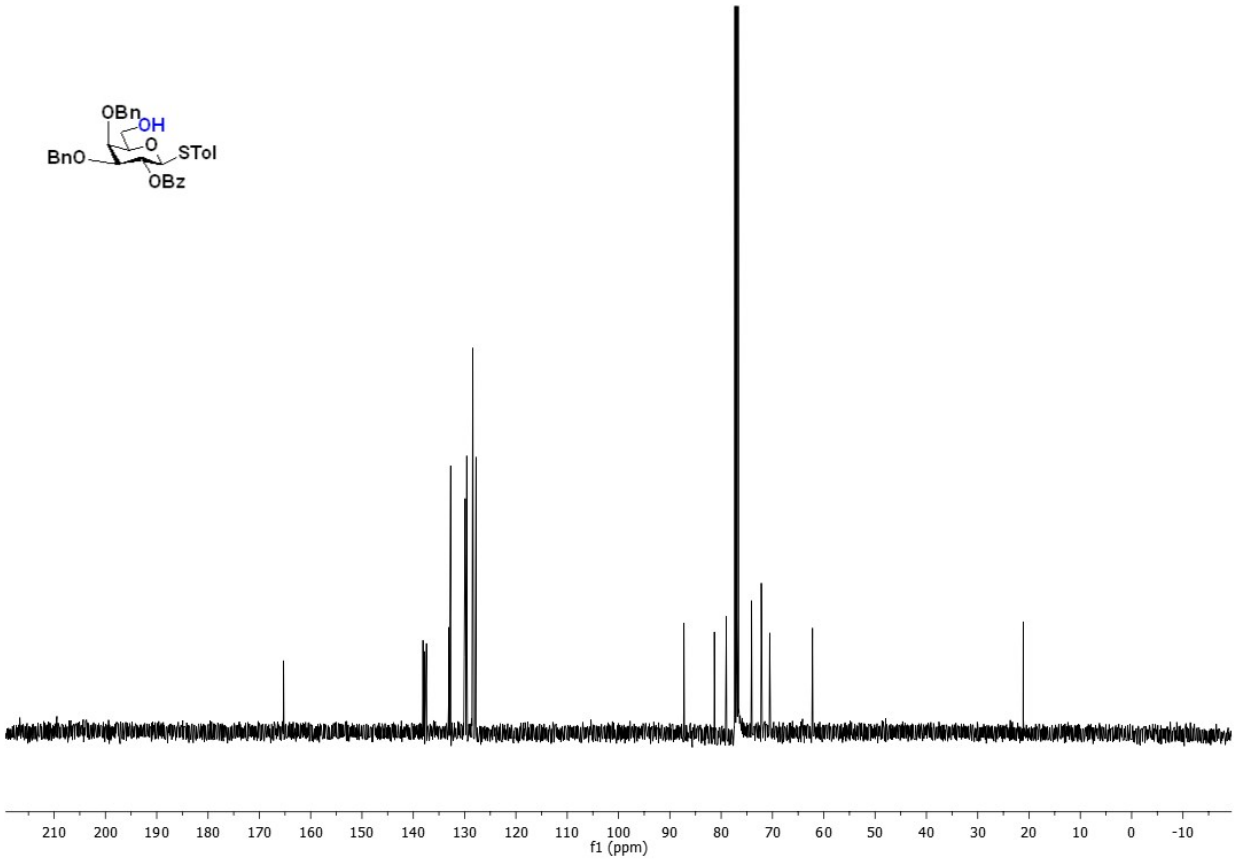

OBn
HO
BnO
O
O
N3
NHTroc
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

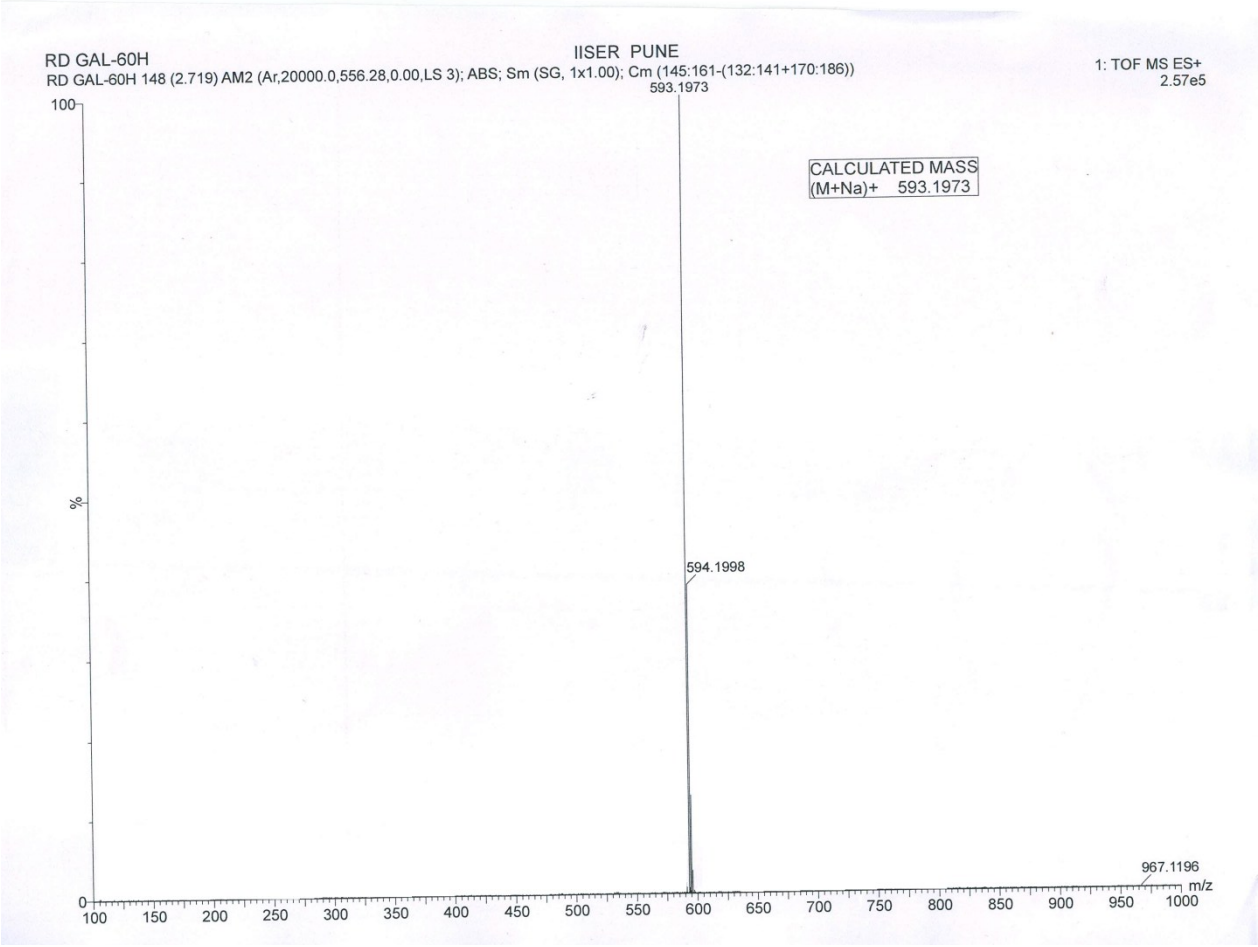

OBn
HO
BnO
O
O
N3
NHTroc
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

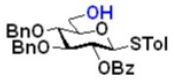

RD 22B
IISER PUNE
RD 22B 136 (2.494) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (135:139-(124:133+142:151))
1: TOF MS ES+
2.47e5
100
%
0
667.1467
CALCULATED MASS
(M+H)+ 667.1468
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
m/z

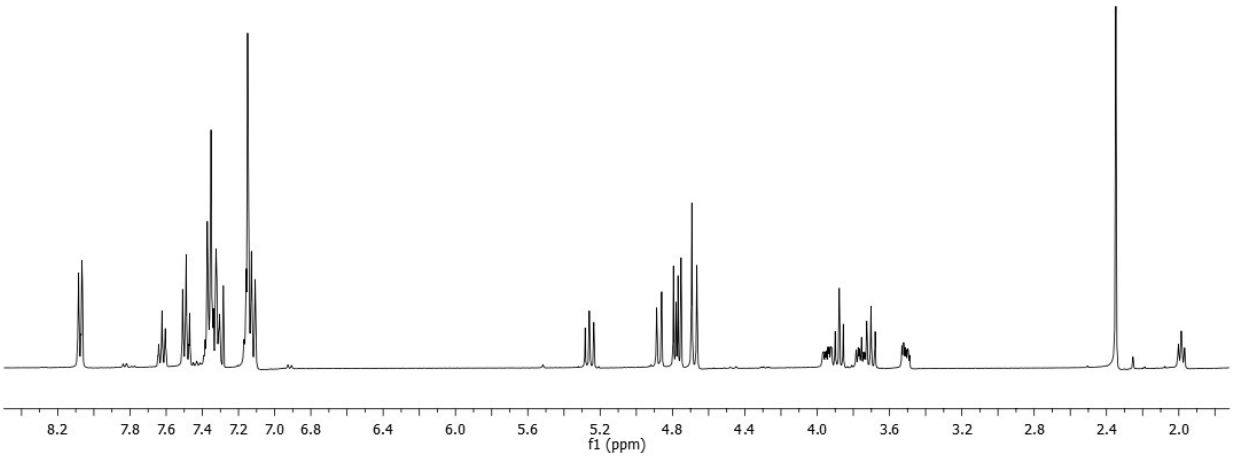

OBn
OH
O
BnO
STol
OBz

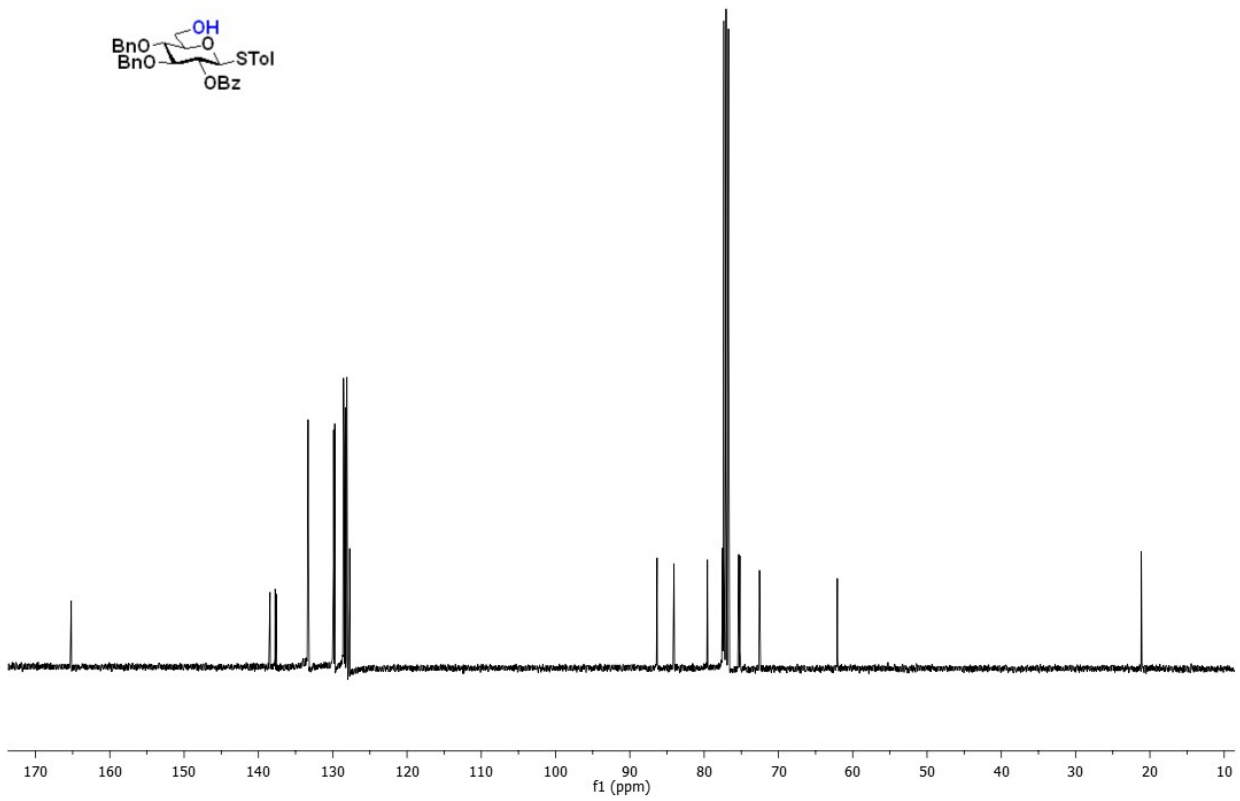

8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

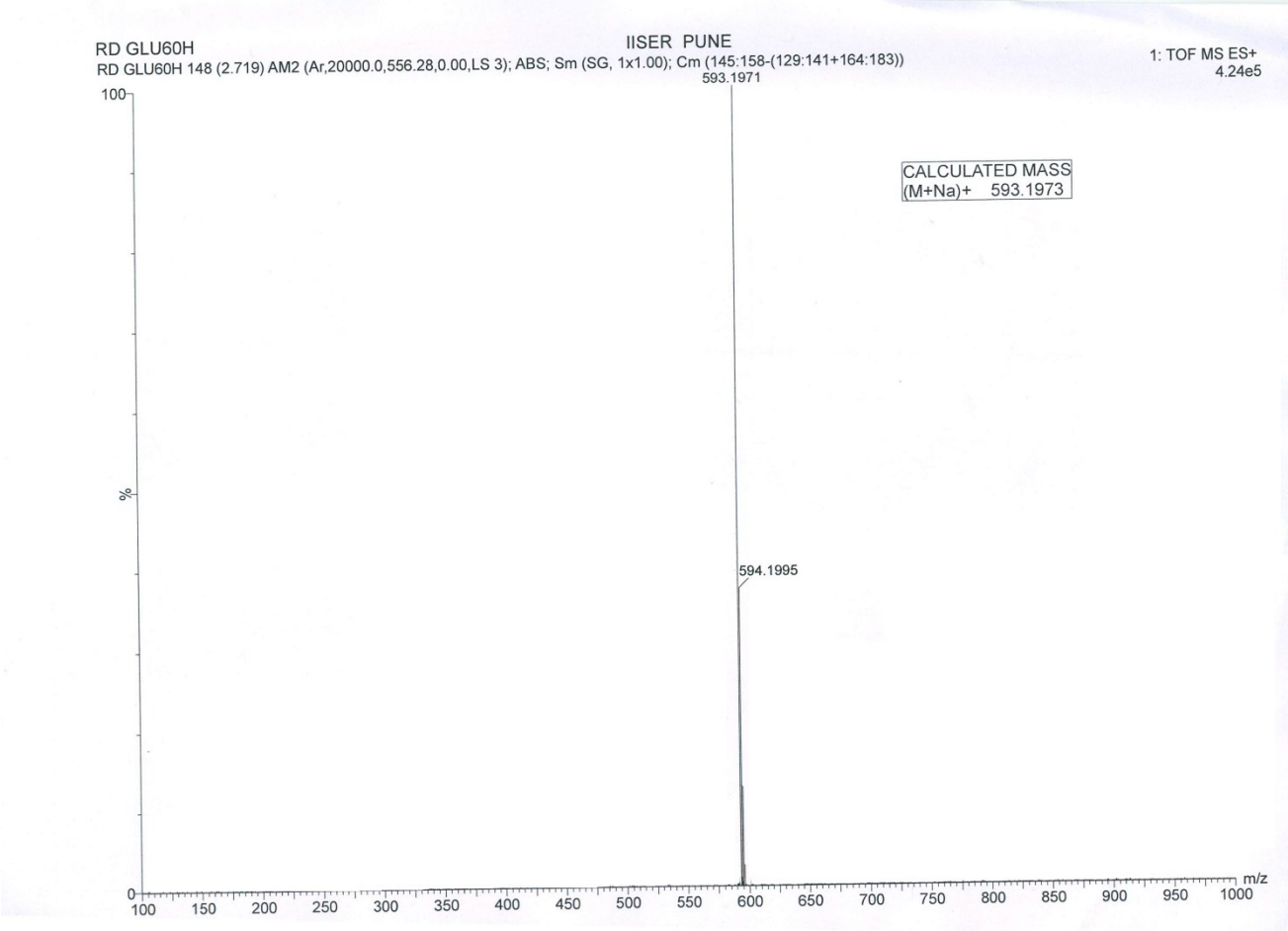

OBn
OH
O
STol
BnO
OBz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

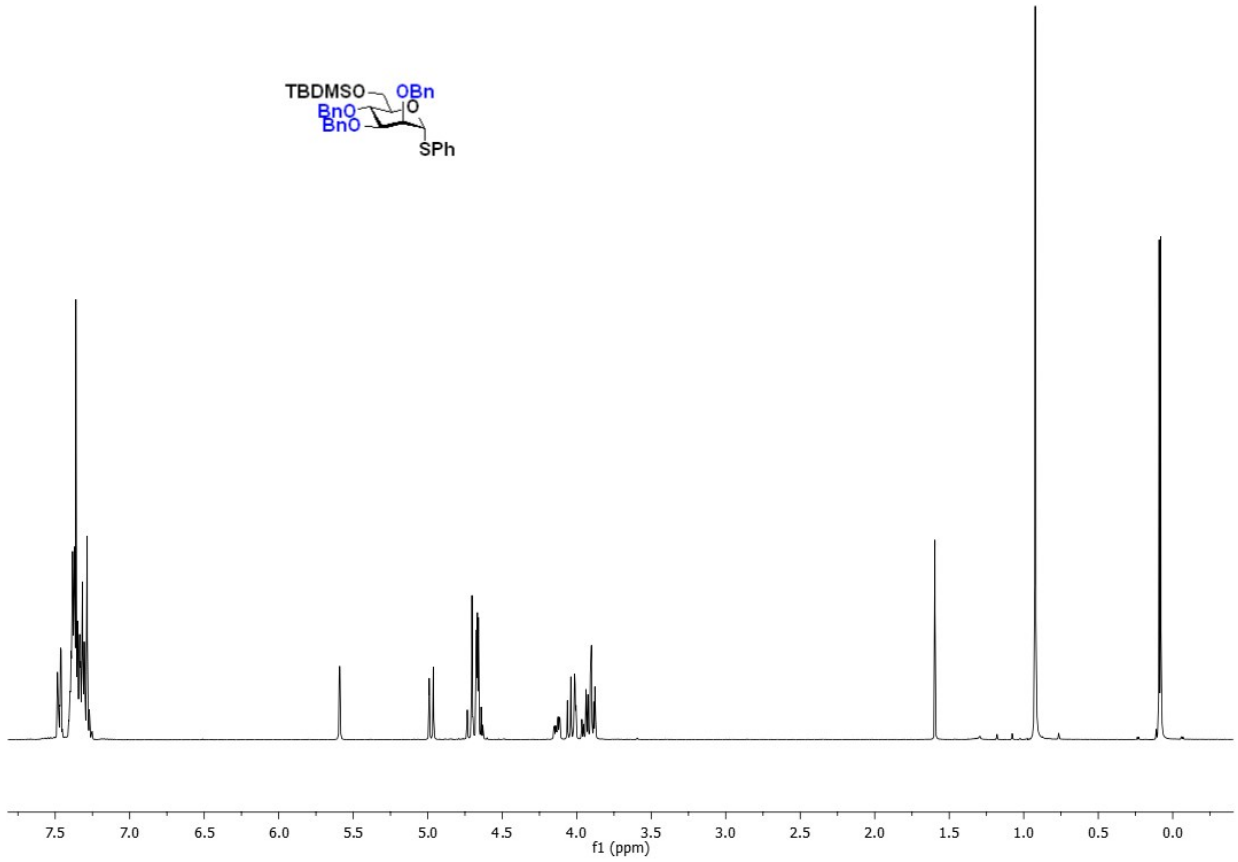

RD GAL-60H
IISER PUNE
RD GAL-60H 148 (2.719) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (145:161-(132:141+170:186))
1: TOF MS ES+
2.57e5
593.1973
CALCULATED MASS
(M+Na)+ 593.1973
594.1998
967.1196
100
%
0
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

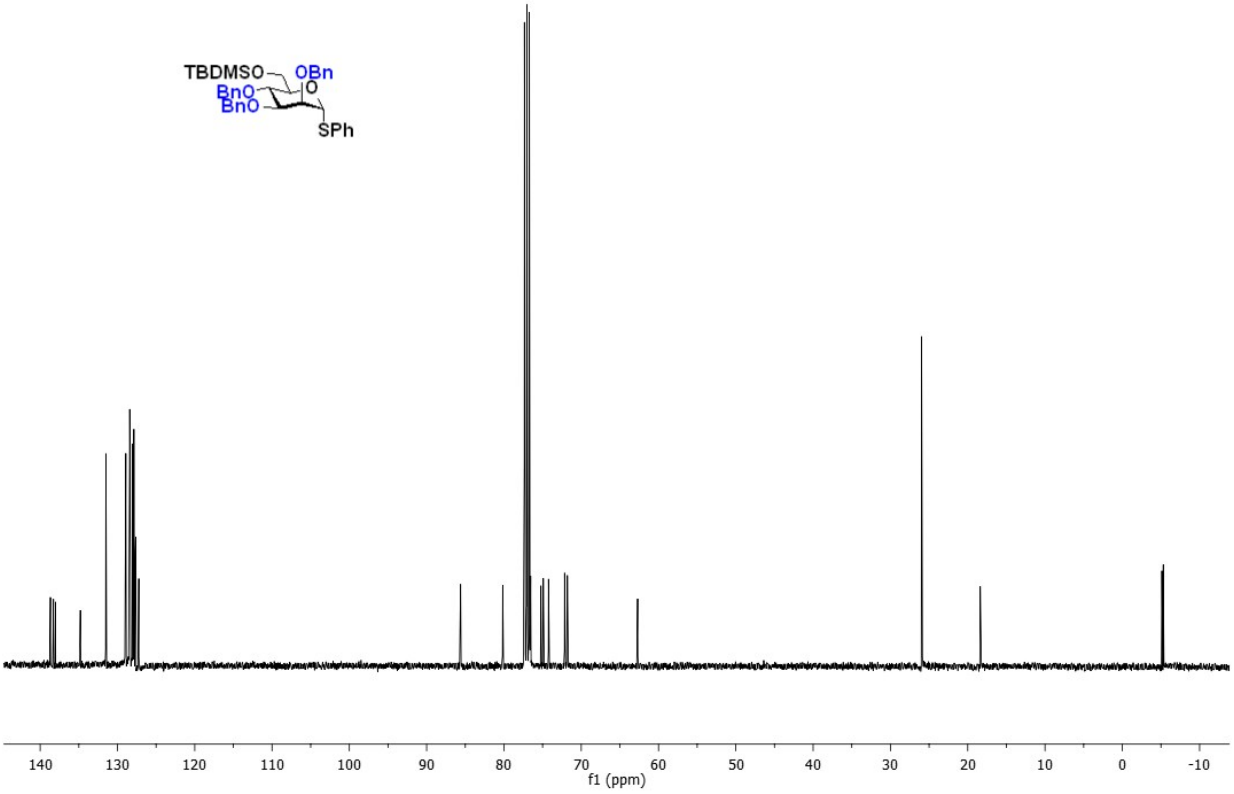

OH
BnO
O
BnO
STol
OBz

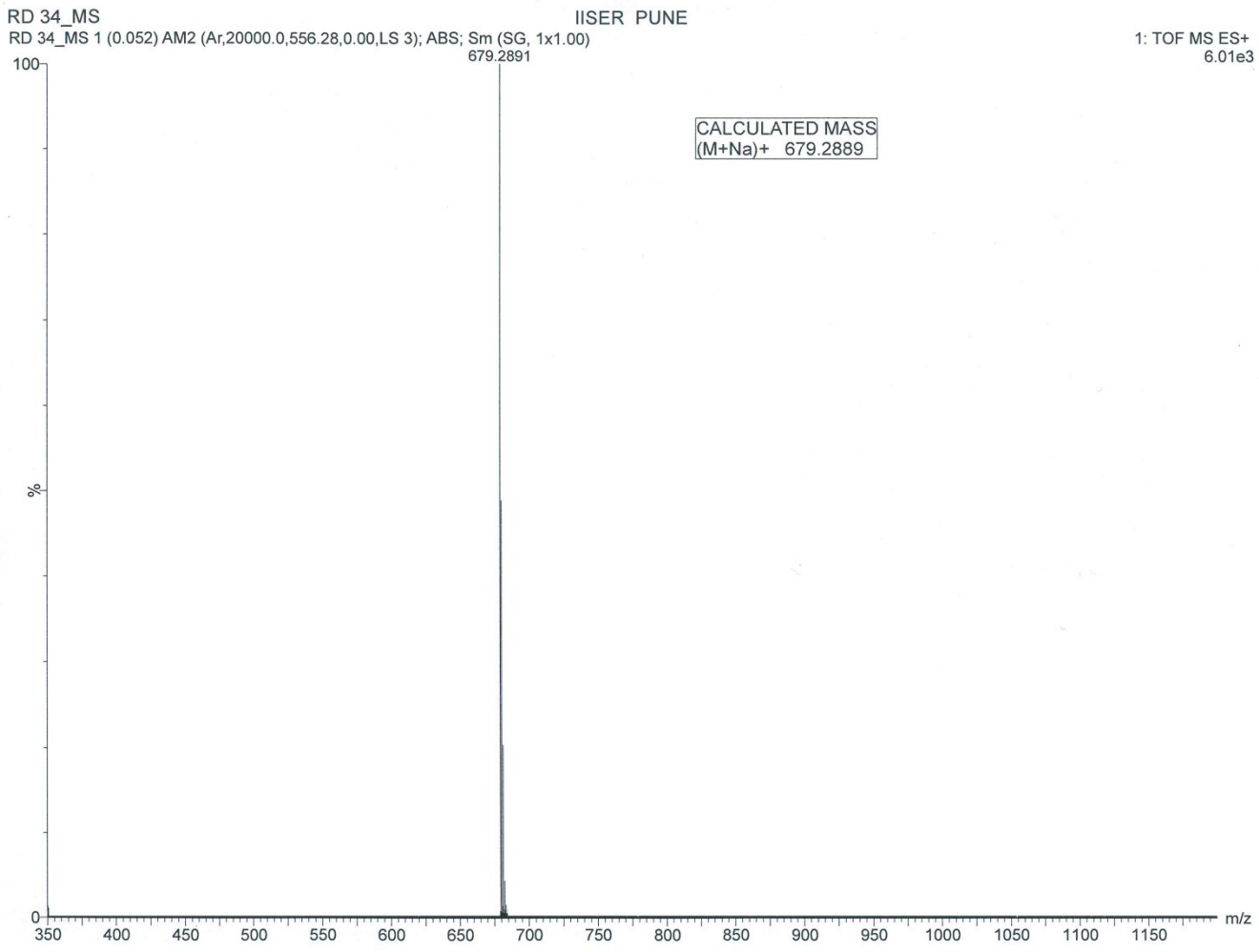

8.2
7.8
7.6
7.4
7.2
7.0
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
f1 (ppm)

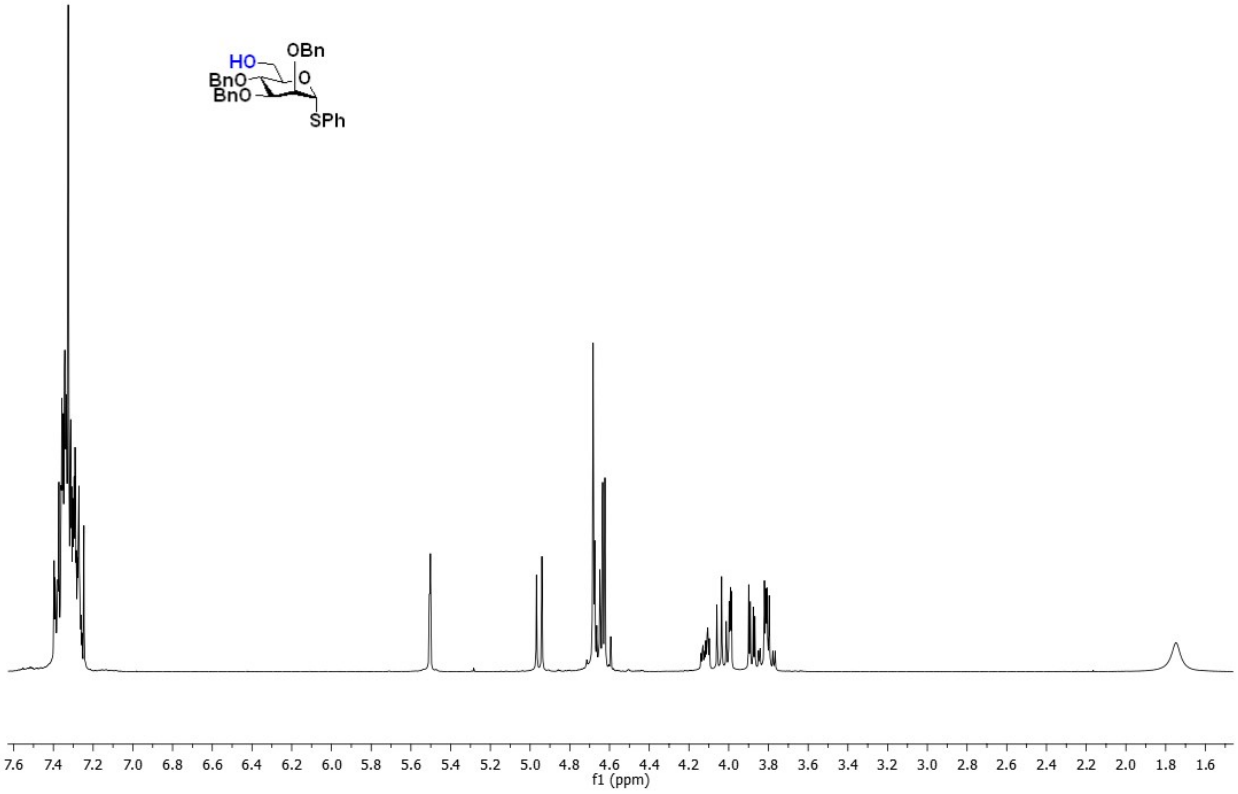

OH
BnO
O
BnO
STol
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

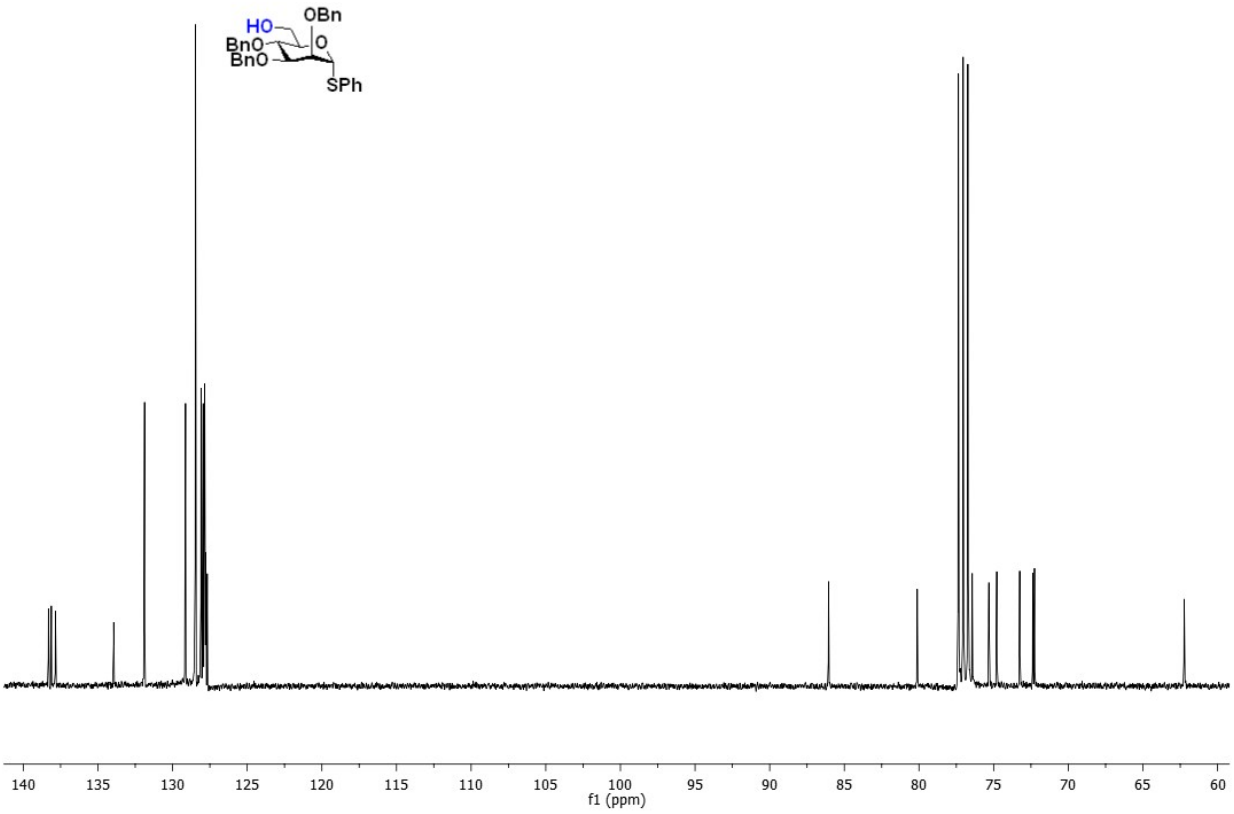

RD GLU60H
IISER PUNE
RD GLU60H 148 (2.719) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (145:158-(129:141+164:183))
1: TOF MS ES+
4.24e5
593.1971
100
%
0
CALCULATED MASS
(M+Na)+ 593.1973
594.1995
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

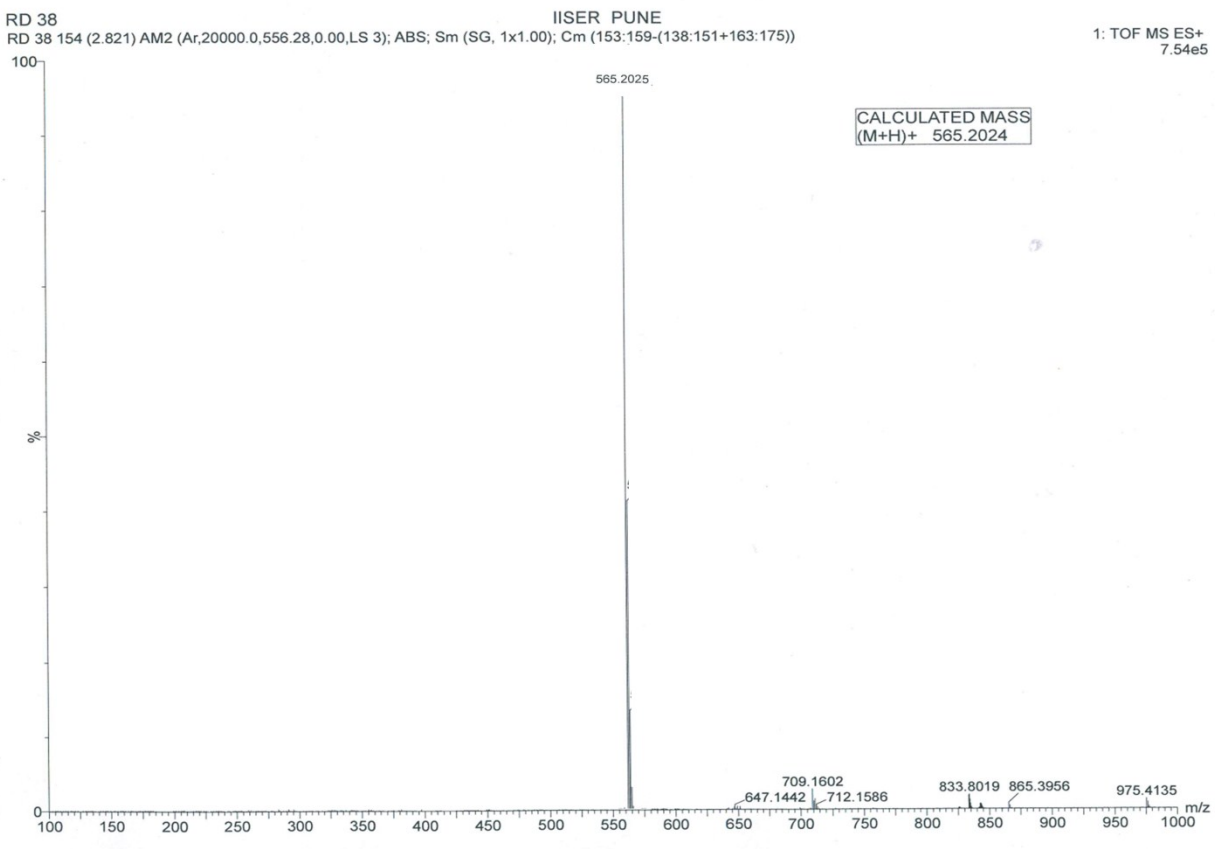

TBDMSO
OBn
BnO
BnO
O
SPh
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

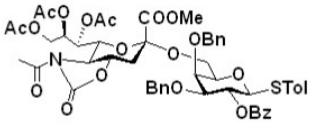

TBDMSO
OBn
BnO
O
BnO
SPh
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

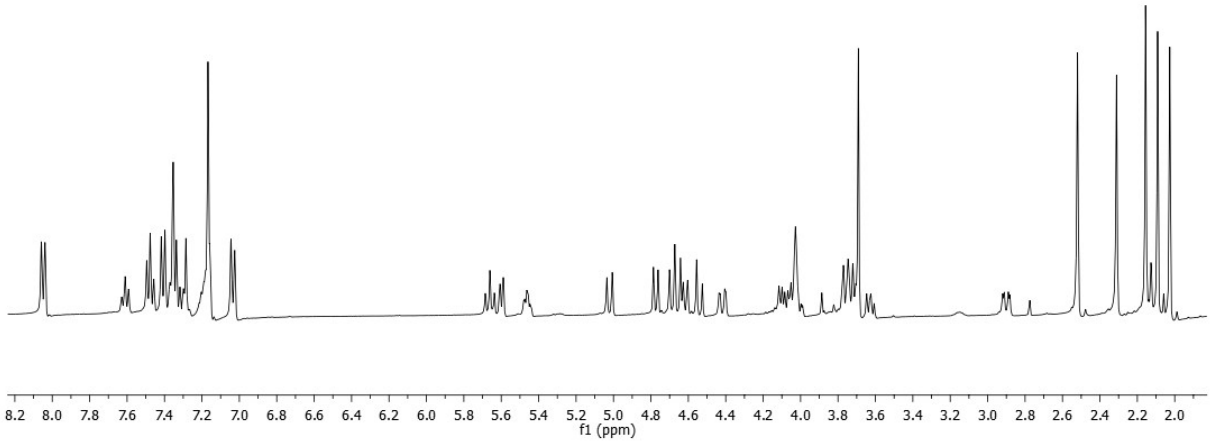

RD 34_MS
IISER PUNE
RD 34_MS 1 (0.052) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00)
1: TOF MS ES+
6.01e3
679.2891
CALCULATED MASS
(M+Na)+ 679.2889
100
%
0
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
m/z

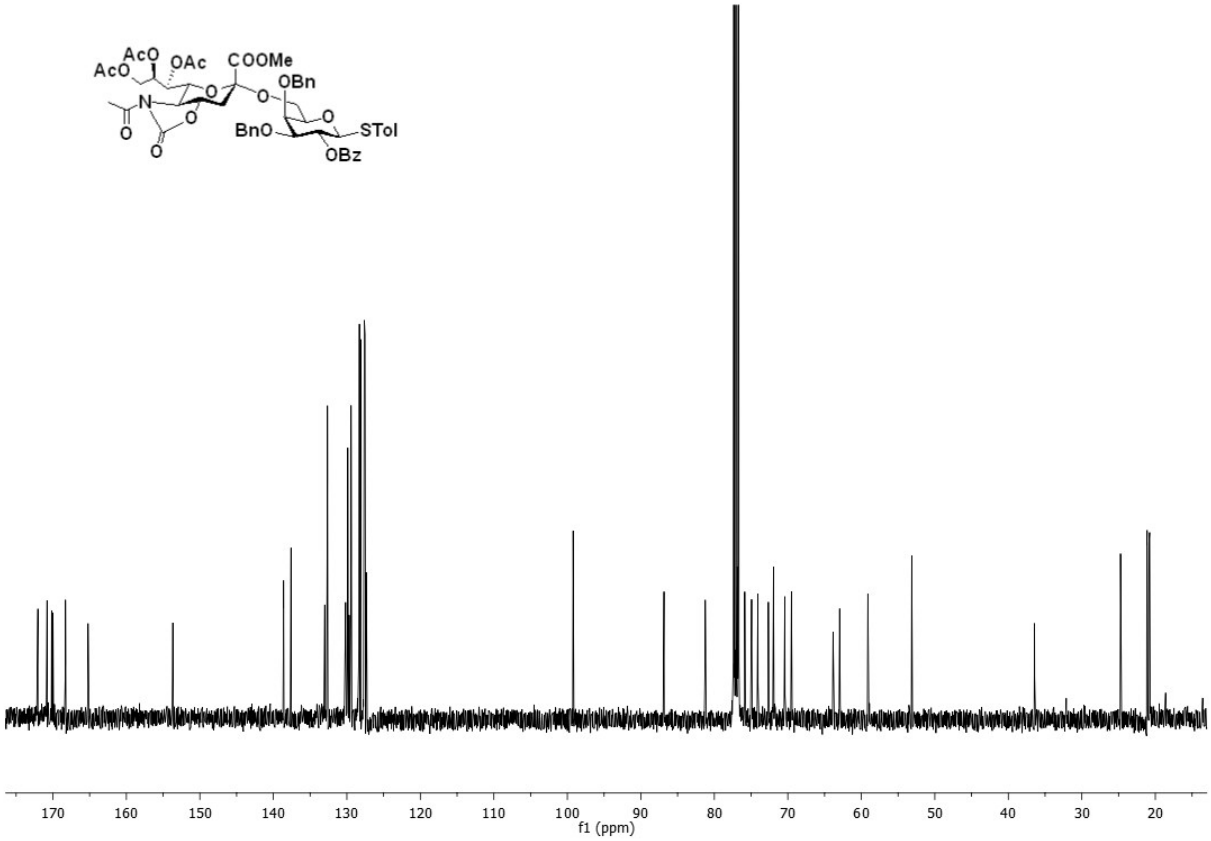

HO
OBn
BnO
O
BnO
SPh
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)

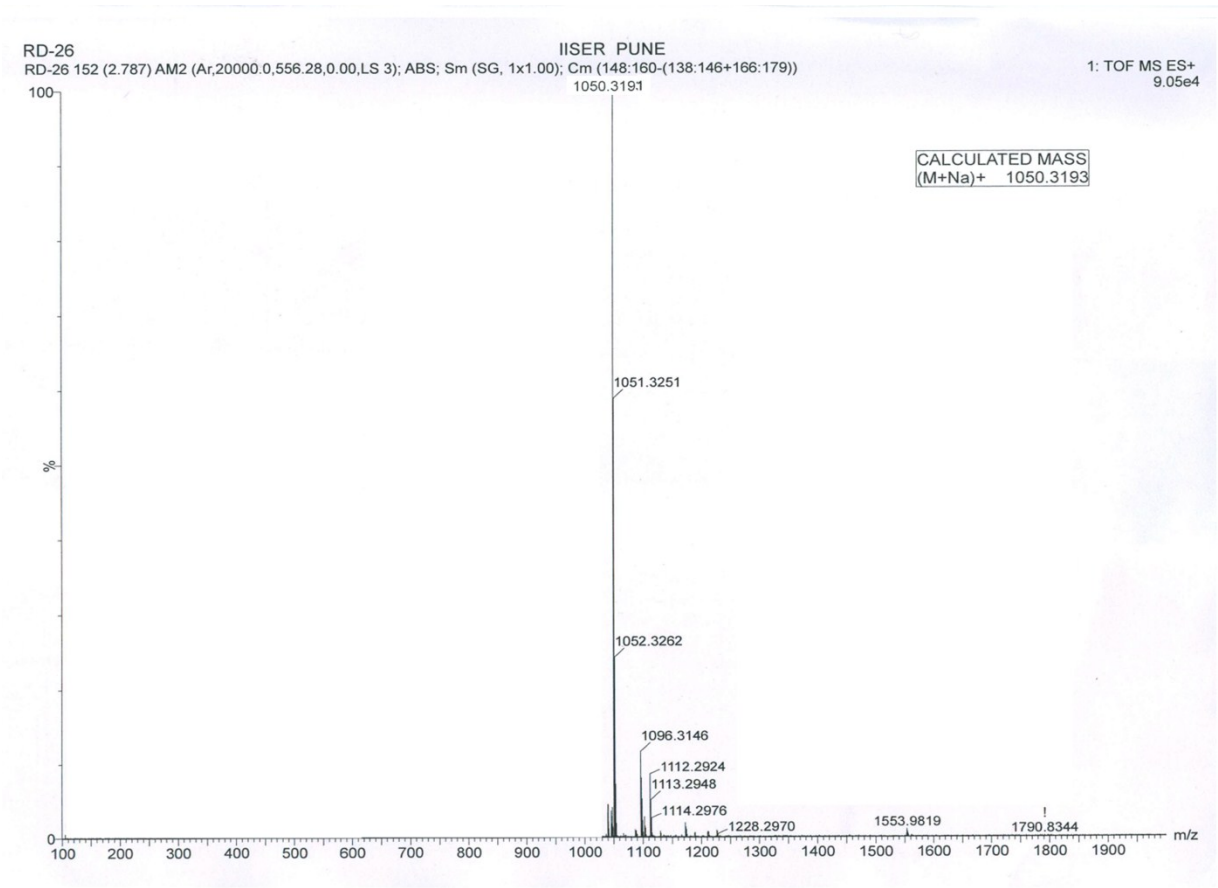

HO
OBn
BnO
BnO
O
SPh
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)

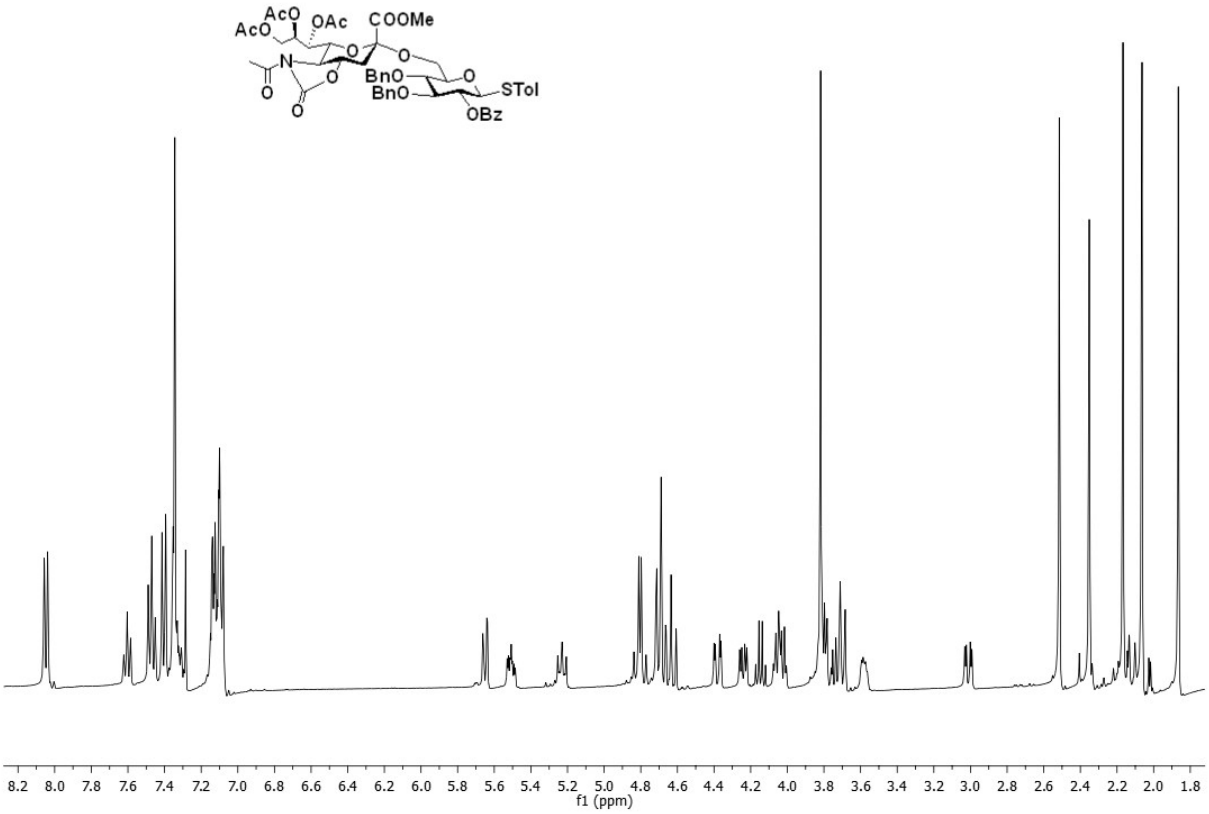

RD 38
IISER PUNE
RD 38 154 (2.821) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (153:159-(138:151+163:175))
1: TOF MS ES+
7.54e5
100
%
0
565.2025
CALCULATED MASS
(M+H)+ 565.2024
709.1602
647.1442
712.1586
833.8019
865.3956
975.4135
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

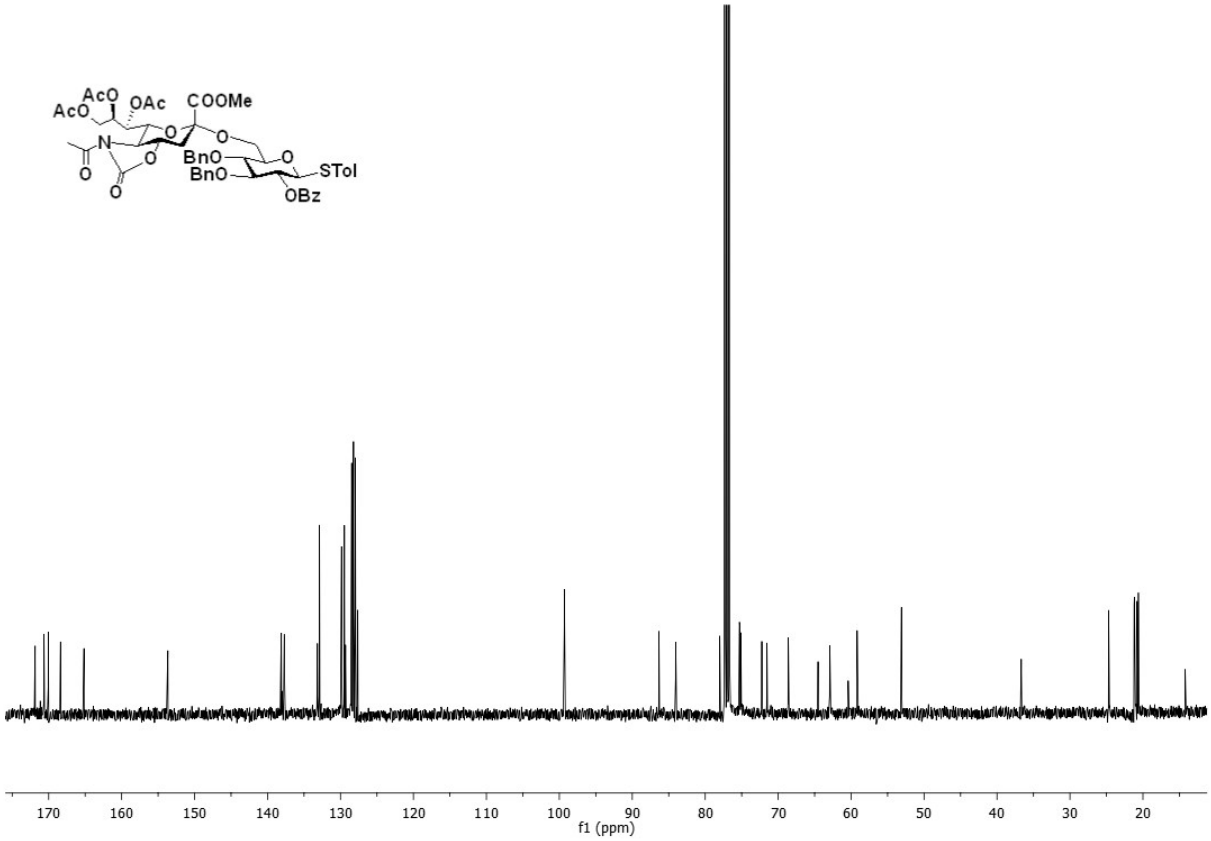

AcO
AcO
OAc
COOMe
OBn
N
O
O
O
O
O
BnO
STol
OBz

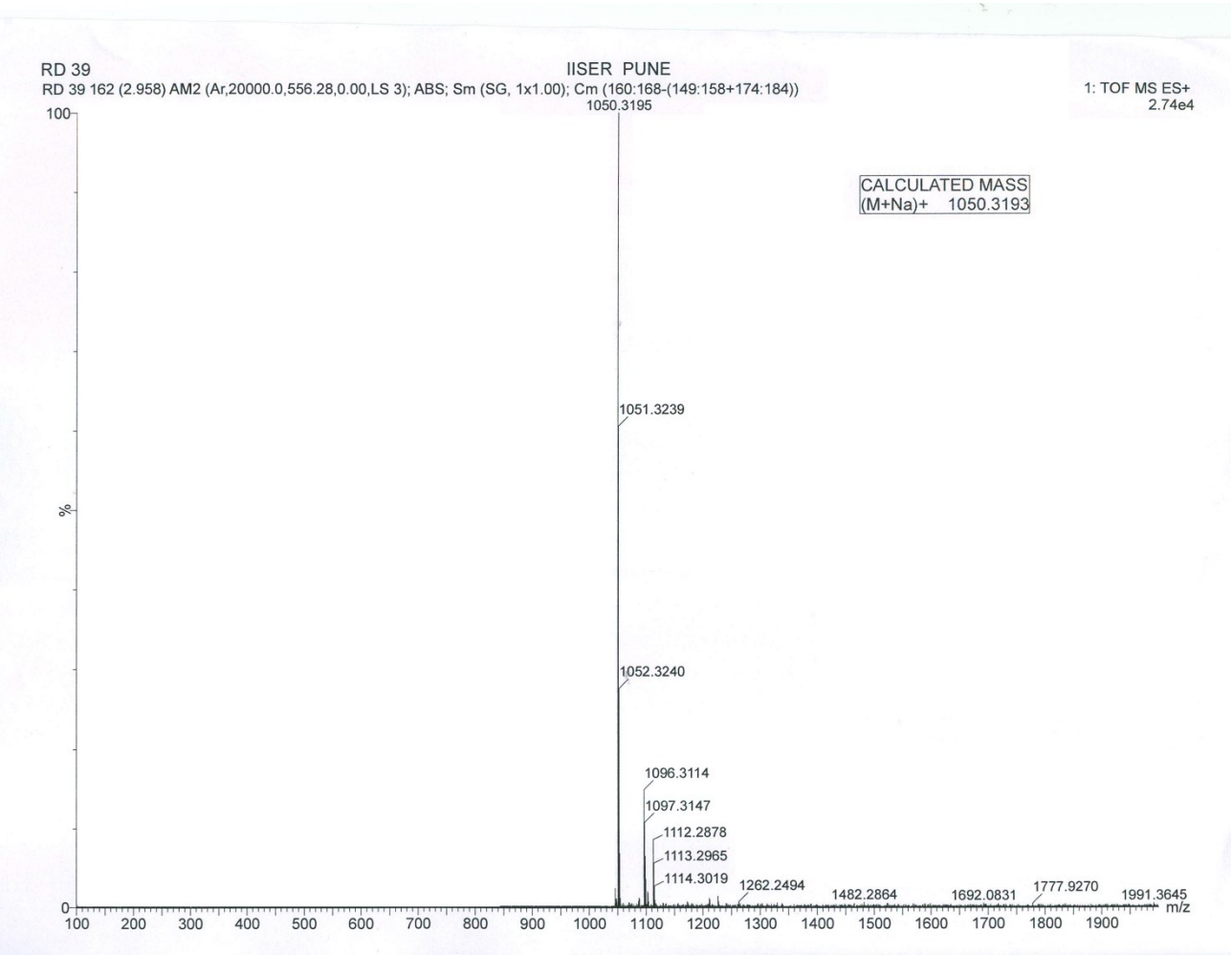

8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

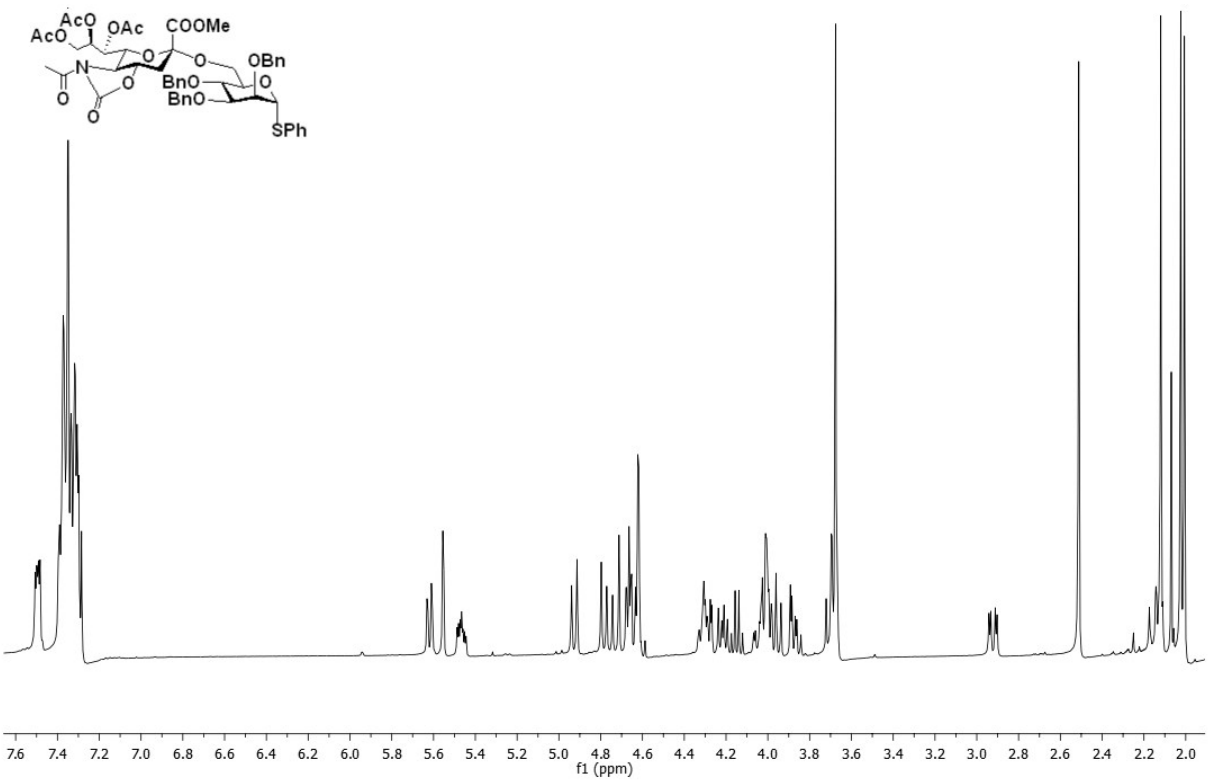

AcO
AcO
OAc
COOMe
OBn
N
O
O
O
O
O
BnO
STol
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

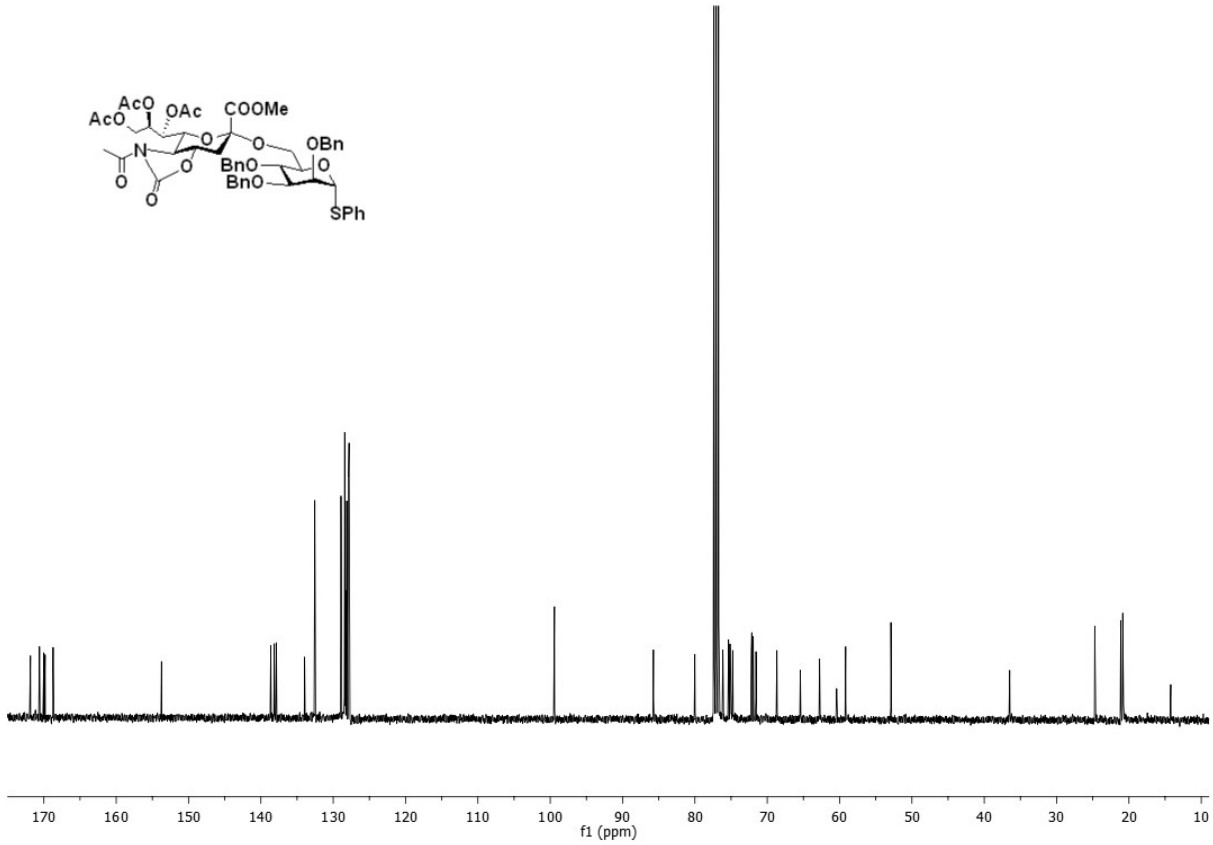

RD-26
IISER PUNE
RD-26 152 (2.787) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (148:160-(138:146+166:179))
1: TOF MS ES+
9.05e4
1050.3191
CALCULATED MASS
(M+Na)+ 1050.3193
1051.3251
1052.3262
1096.3146
1112.2924
1113.2948
1114.2976
1228.2970
1553.9819
1790.8344
%
m/z
100
0
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900

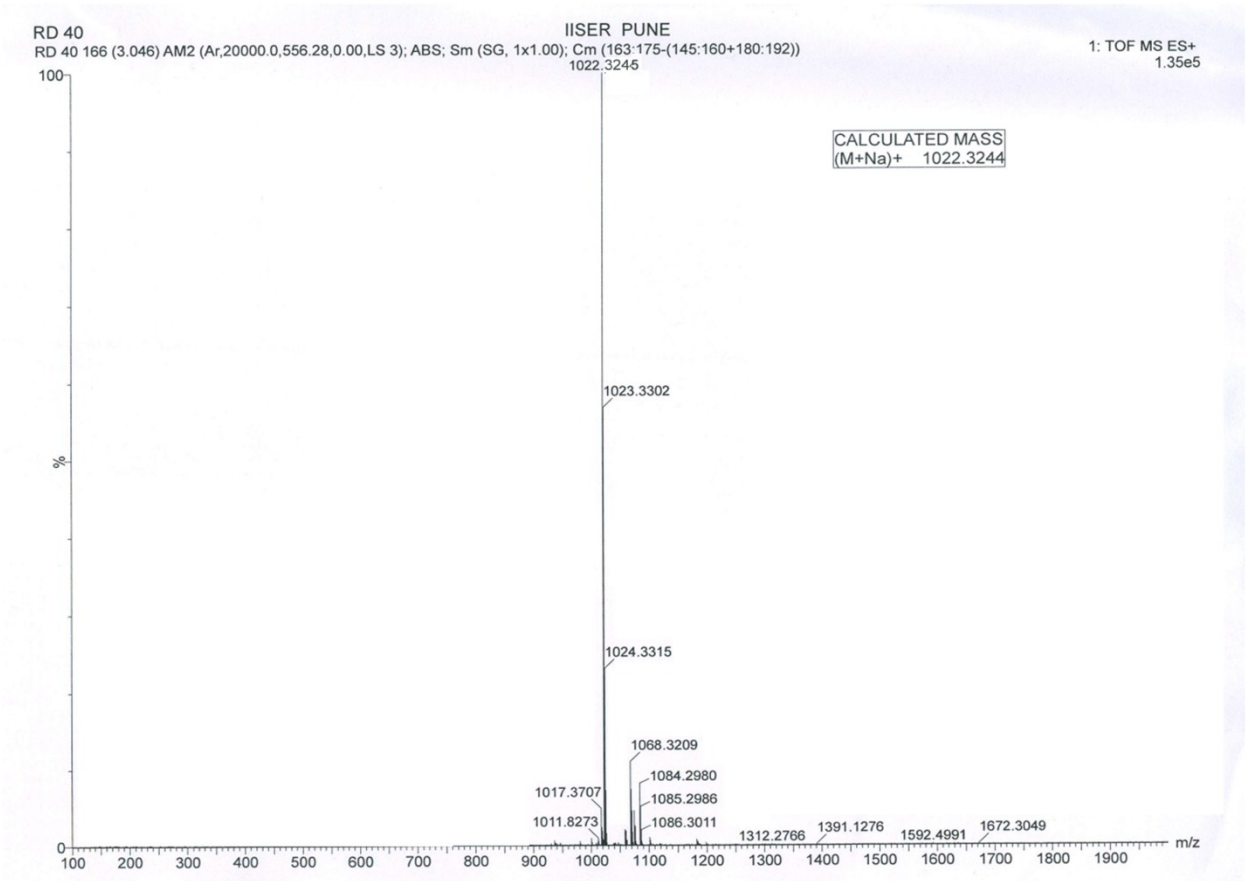

AcO
AcO
OAc
COOMe
O
N
O
O
O
BnO
BnO
O
STol
OBz
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)

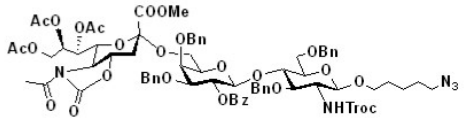

AcO
AcO
OAc
COOMe
N
O
O
O
O
O
BnO
BnO
O
STol
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

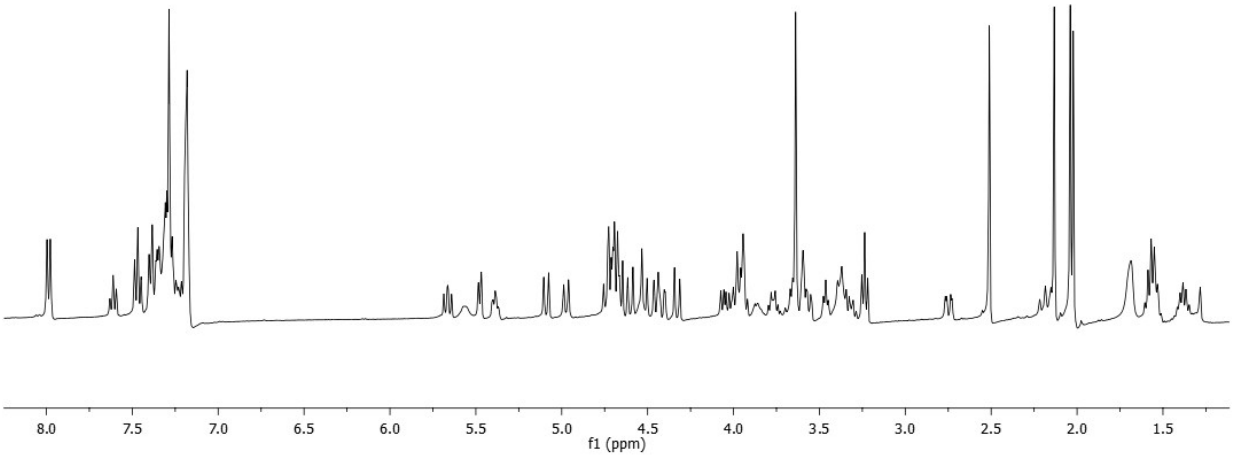

RD 39
IISER PUNE
RD 39 162 (2.958) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (160:168-(149:158+174:184))
1: TOF MS ES+
2.74e4
CALCULATED MASS
(M+Na)+ 1050.3193
1050.3195
1051.3239
1052.3240
1096.3114
1097.3147
1112.2878
1113.2965
1114.3019
1262.2494
1482.2864
1692.0831
1777.9270
1991.3645
%
m/z

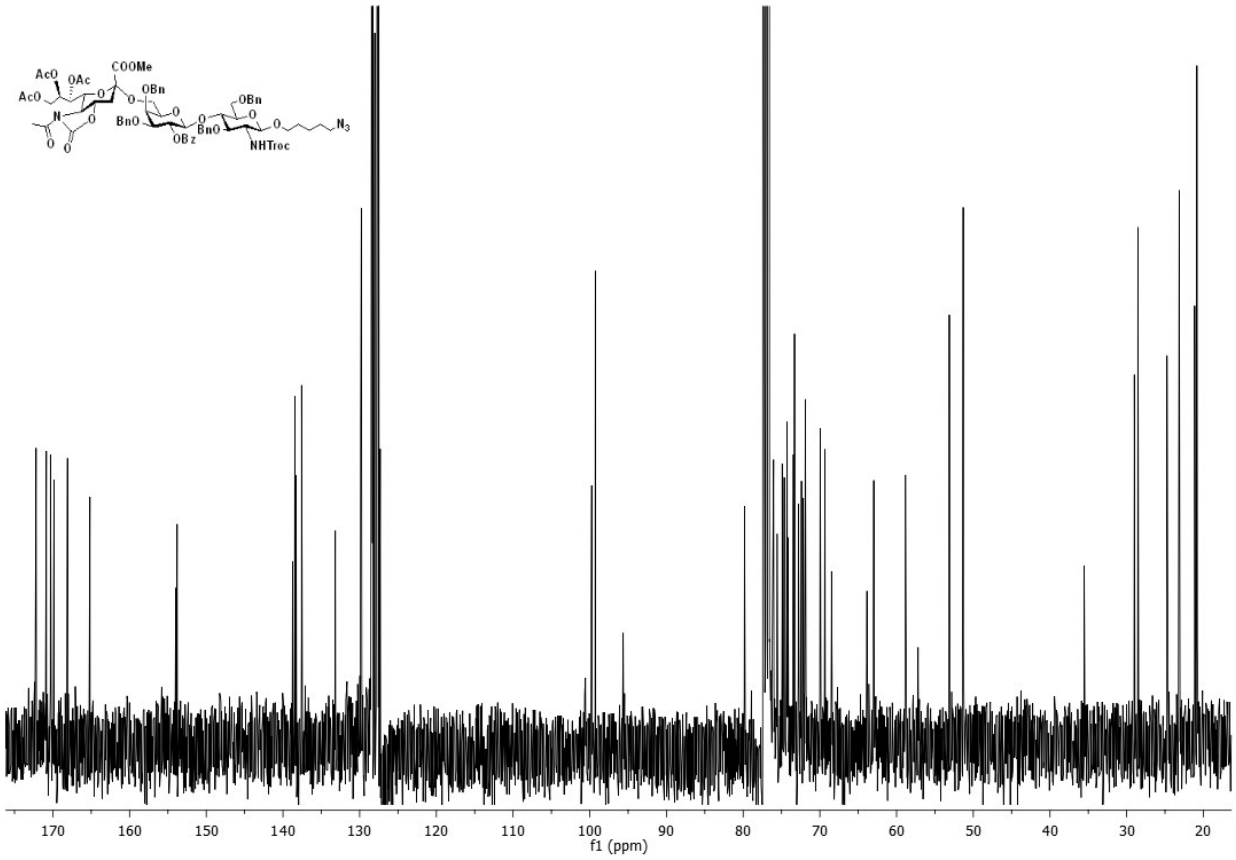

AcO
AcO
OAc
COOMe
O
N
O
O
O
O
BnO
BnO
OBn
O
SPh
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

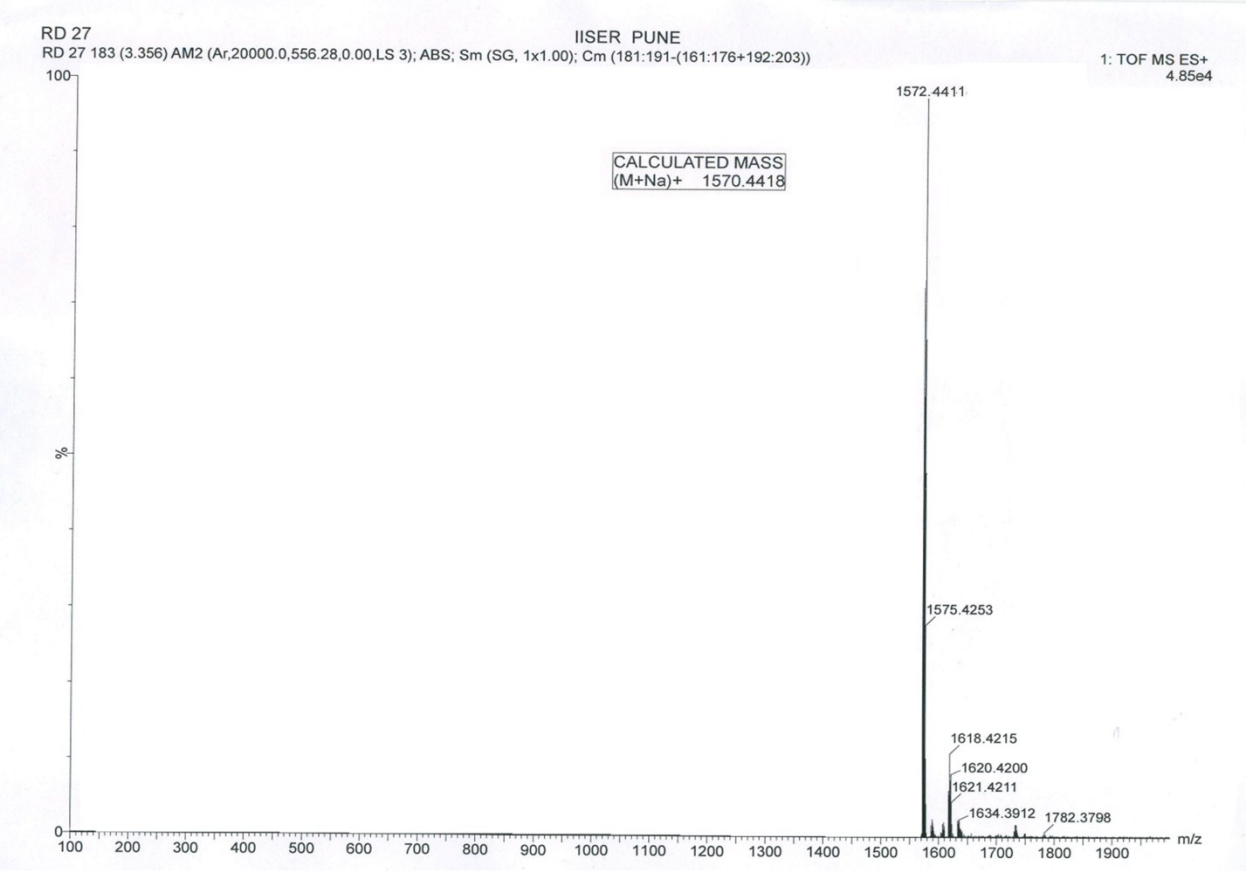

AcO
AcO
OAc
COOMe
N
O
O
O
O
O
OBn
BnO
BnO
O
SPh
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

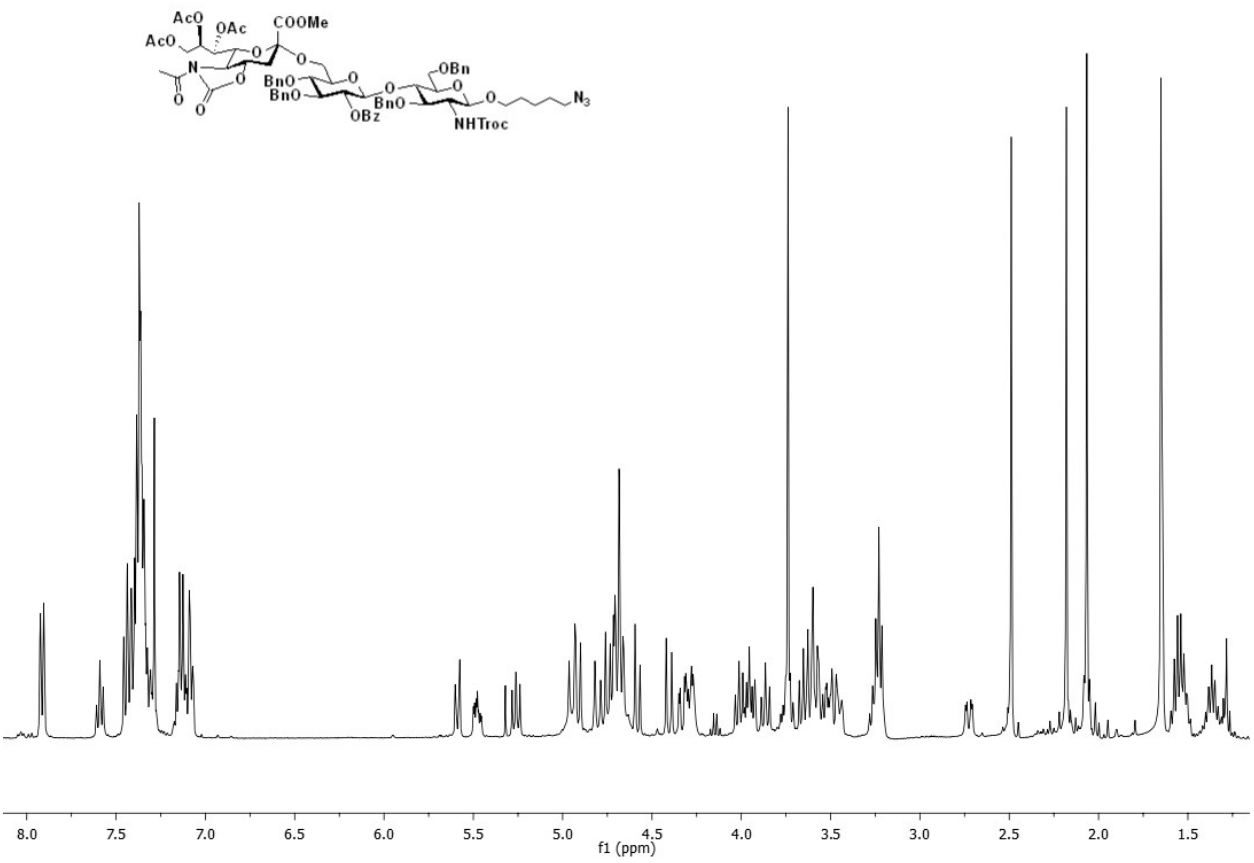

RD 40
IISER PUNE
RD 40 166 (3.046) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (163:175-(145:160+180:192))
1: TOF MS ES+
1.35e5
1022.3245
CALCULATED MASS
(M+Na)+ 1022.3244
1023.3302
1024.3315
1068.3209
1084.2980
1085.2986
1086.3011
1017.3707
1011.8273
1312.2766
1391.1276
1592.4991
1672.3049
%
m/z

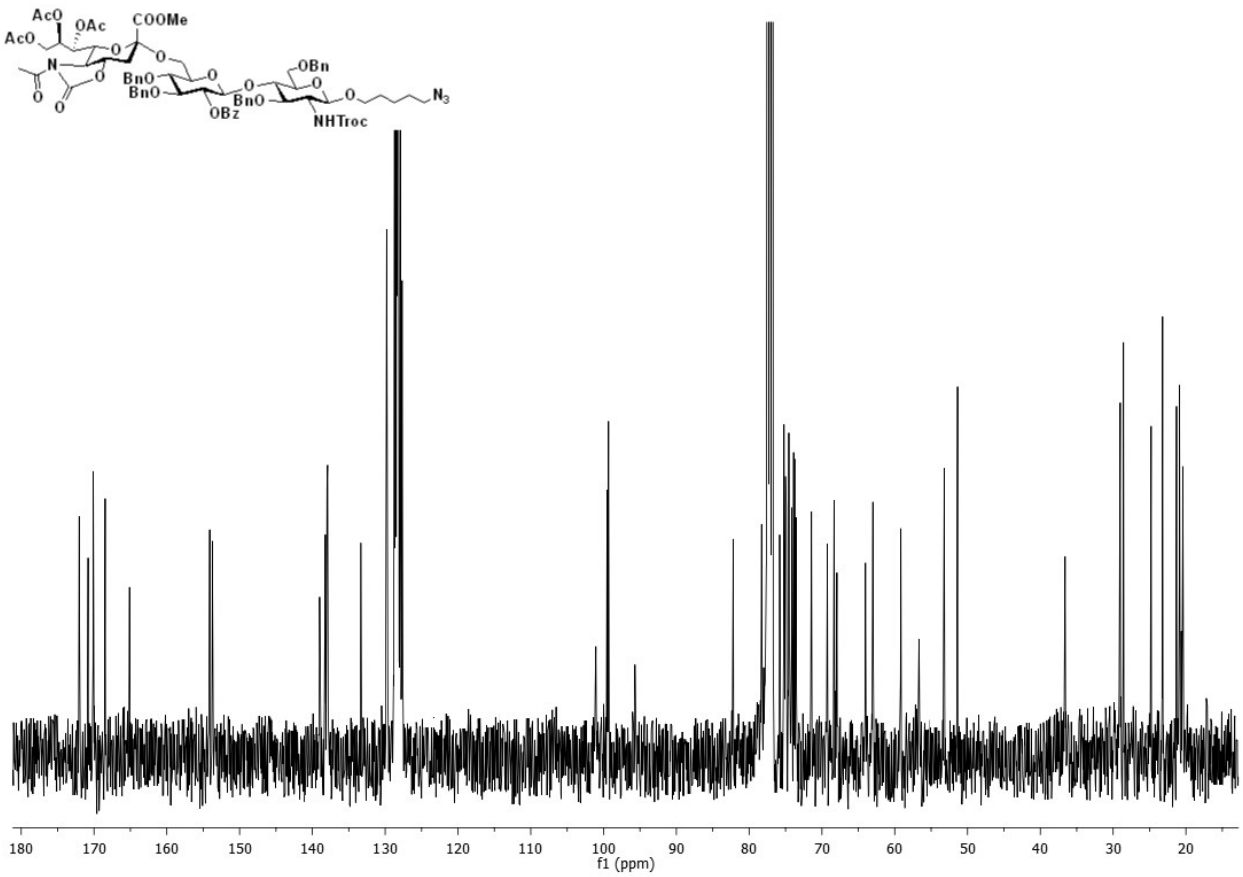

AcO
OAc
AcO
COOMe
OBn
BnO
OBz
BnO
OBn
NHTroc
N3

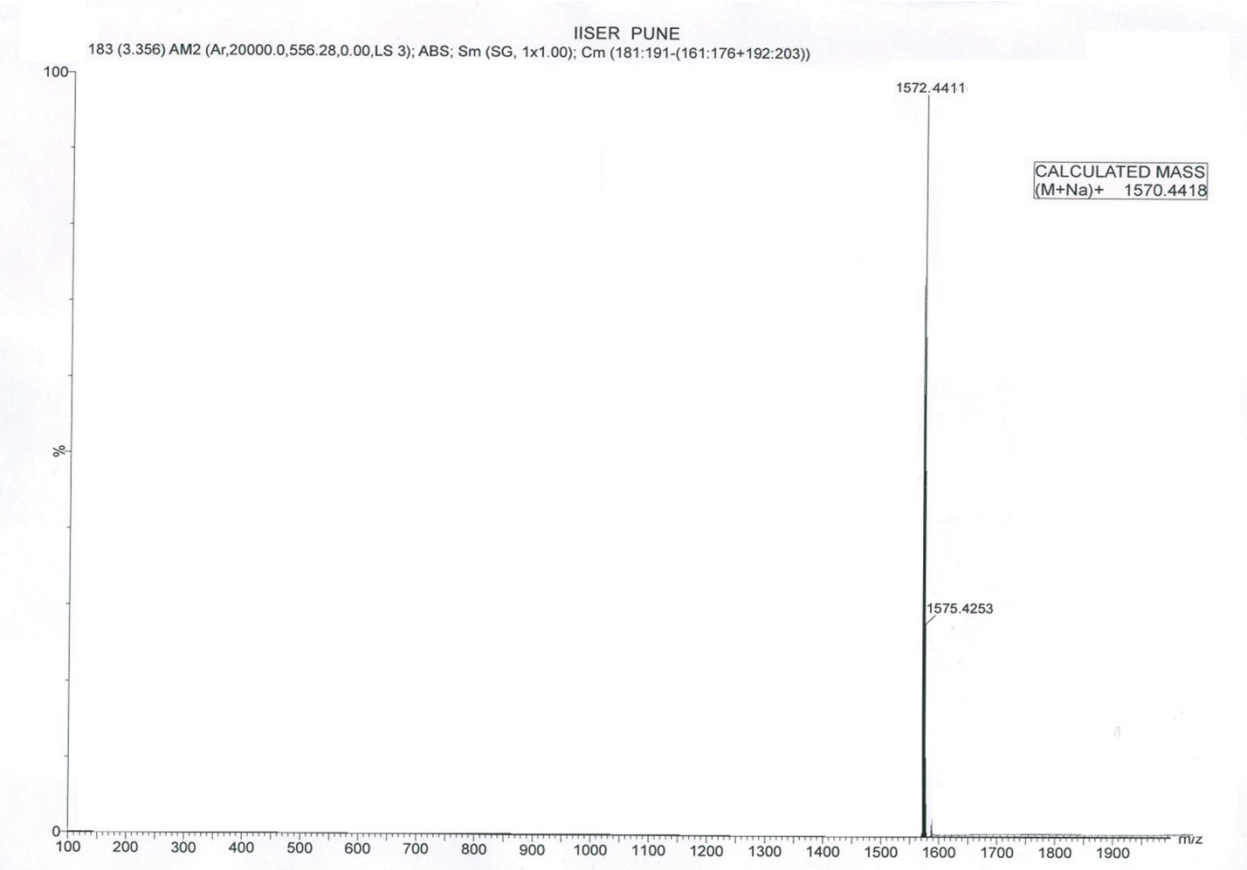

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

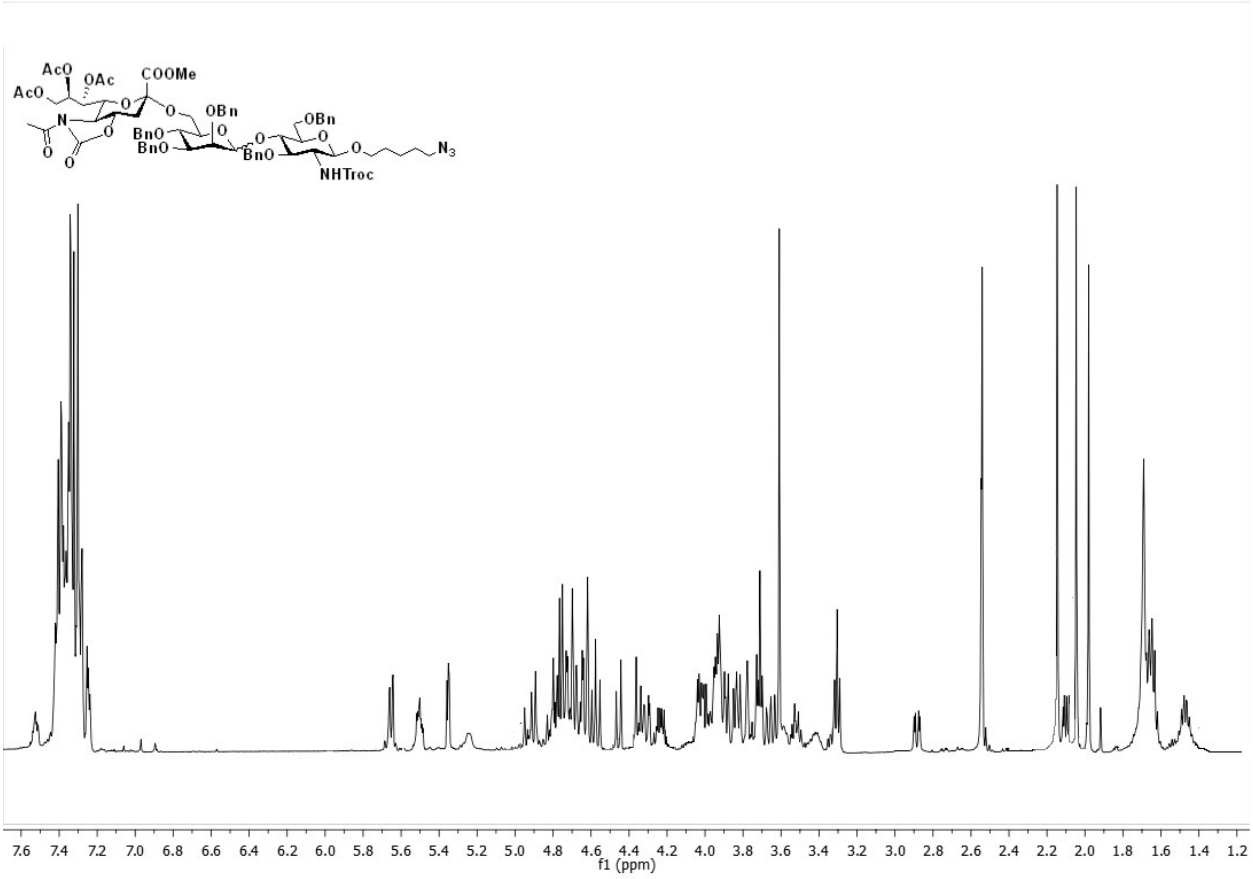

AcO
OAc
AcO
COOMe
OBn
BnO
OBz
BnO
OBn
NHTroc
N3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

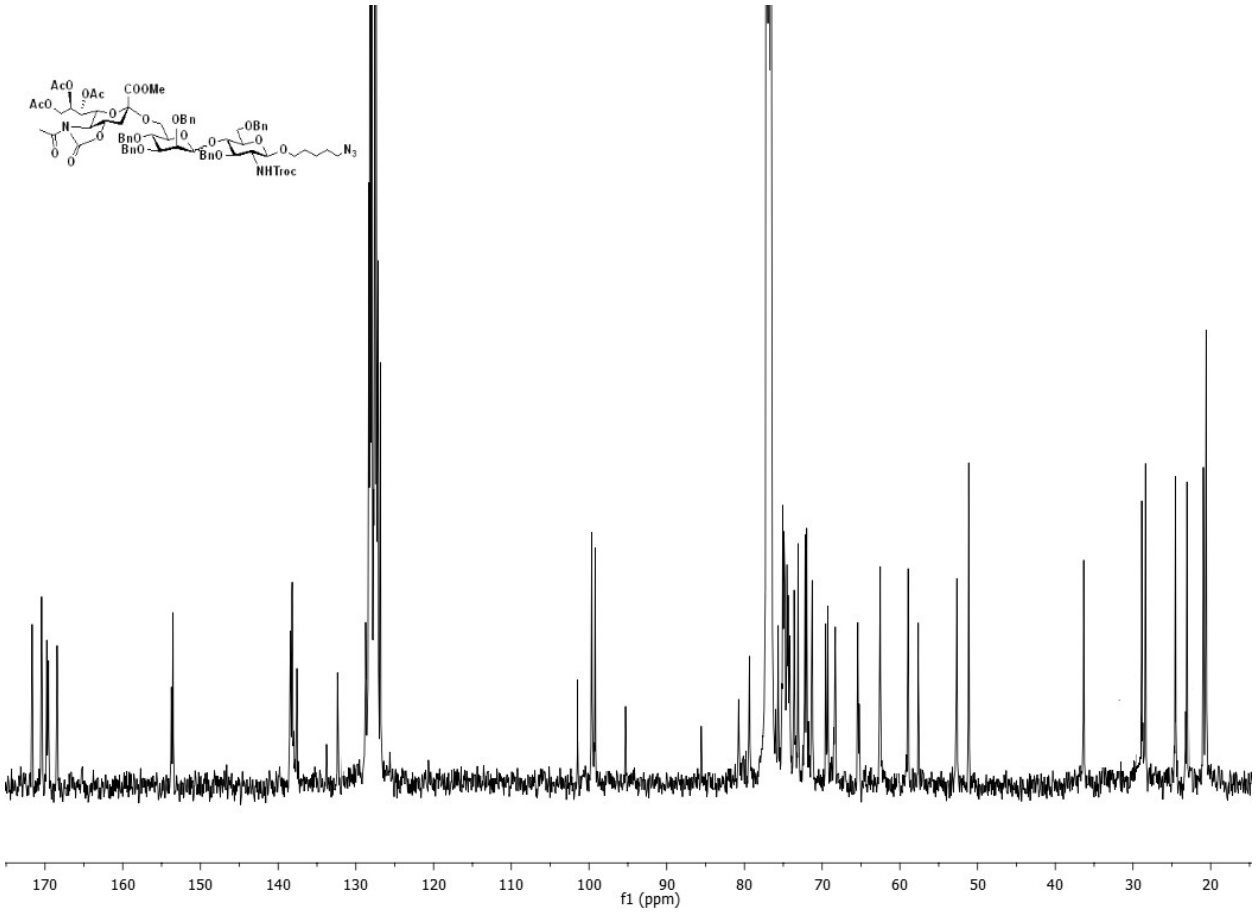

RD 27
IISER PUNE
RD 27 183 (3.356) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (181:191-(161:176+192:203))
1: TOF MS ES+
4.85e4
100
%
0
1572.4411
CALCULATED MASS
(M+Na)+ 1570.4418
1575.4253
1618.4215
1620.4200
1621.4211
1634.3912
1782.3798
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900
m/z

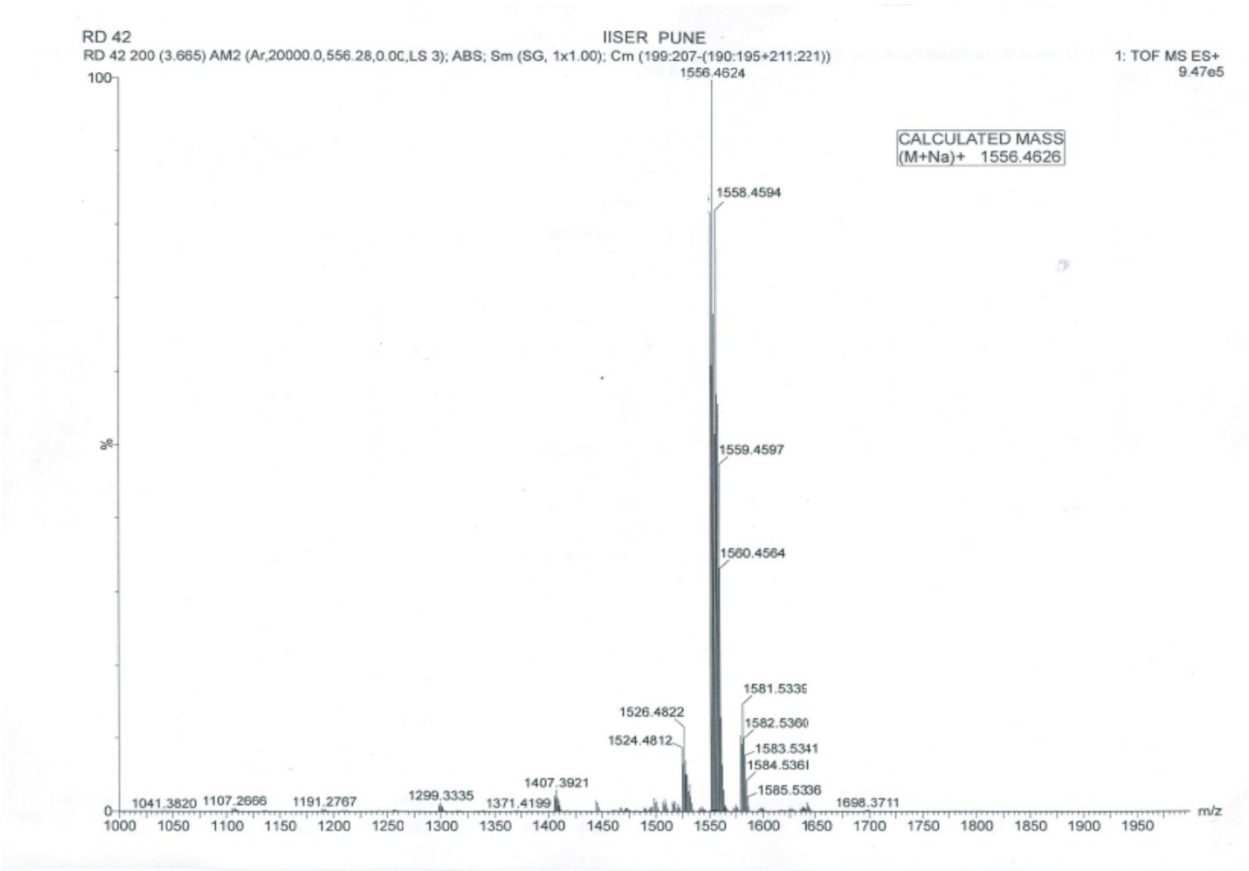

AcO
OAc
AcO
COOMe
BnO
BnO
OBz
OBn
BnO
NHTroc
N3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

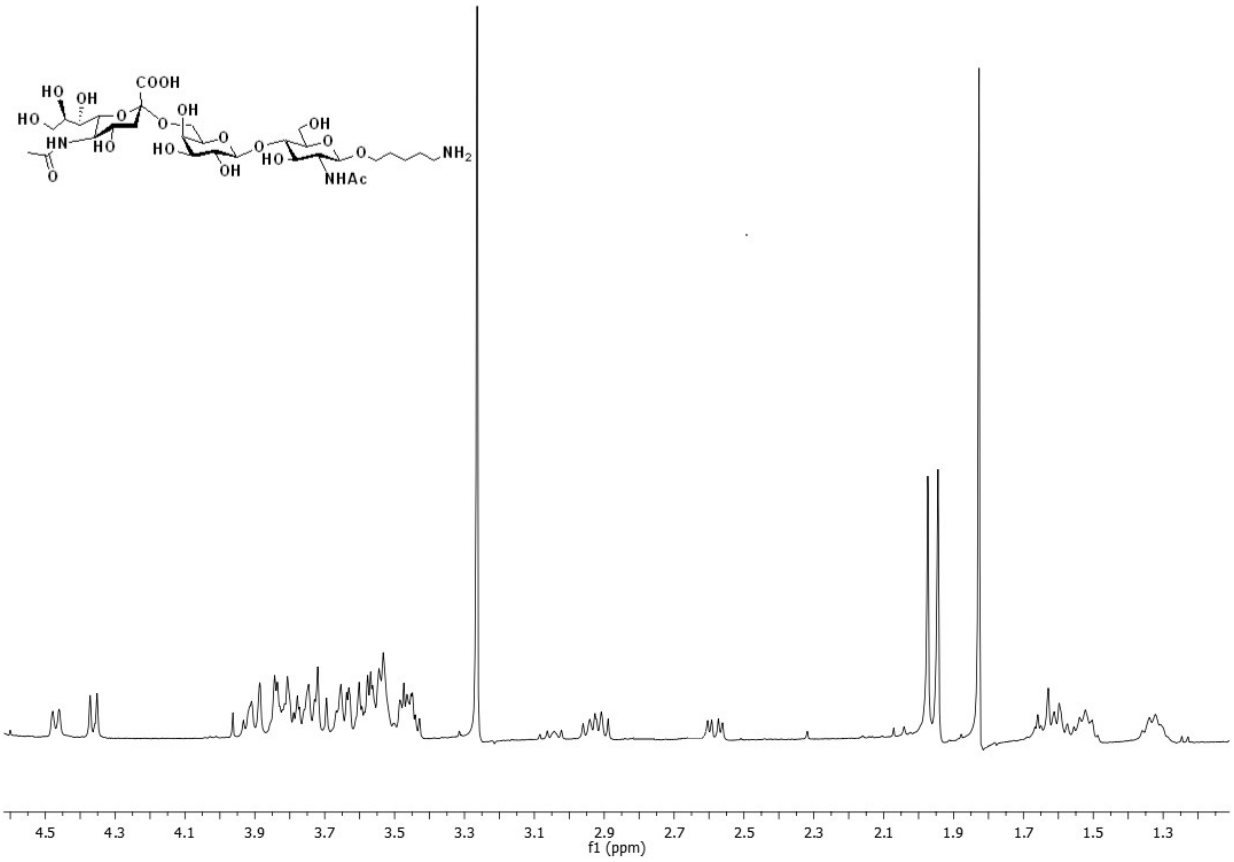

AcO
AcO
OAc
COOMe
BnO
BnO
OBz
OBn
BnO
NHTroc
N3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

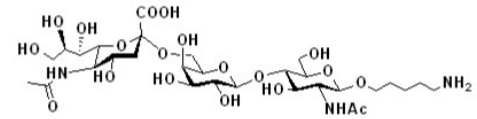

IISER PUNE
183 (3.356) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (181:191-(161:176+192:203))
100
%
0
1572.4411
1575.4253
CALCULATED MASS
(M+Na)+ 1570.4418
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900
m/z

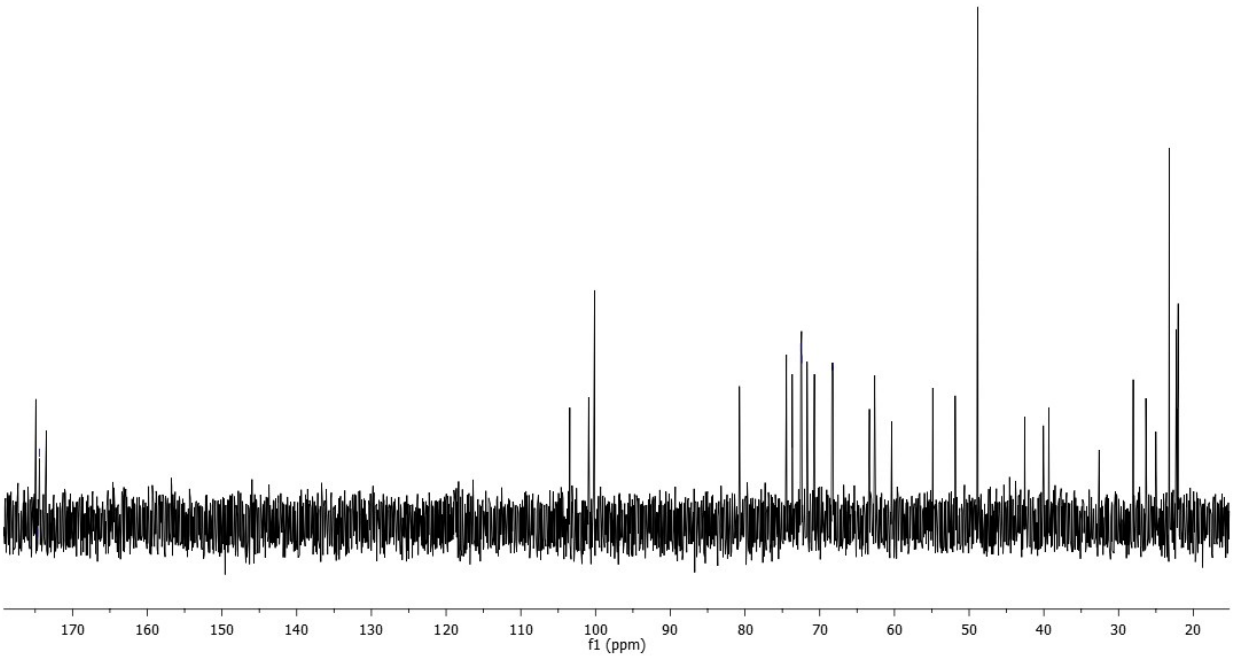

AcO
OAc
COOMe
AcO
OBn
OBn
BnO
BnO
BnO
NHTroc
N_3
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)

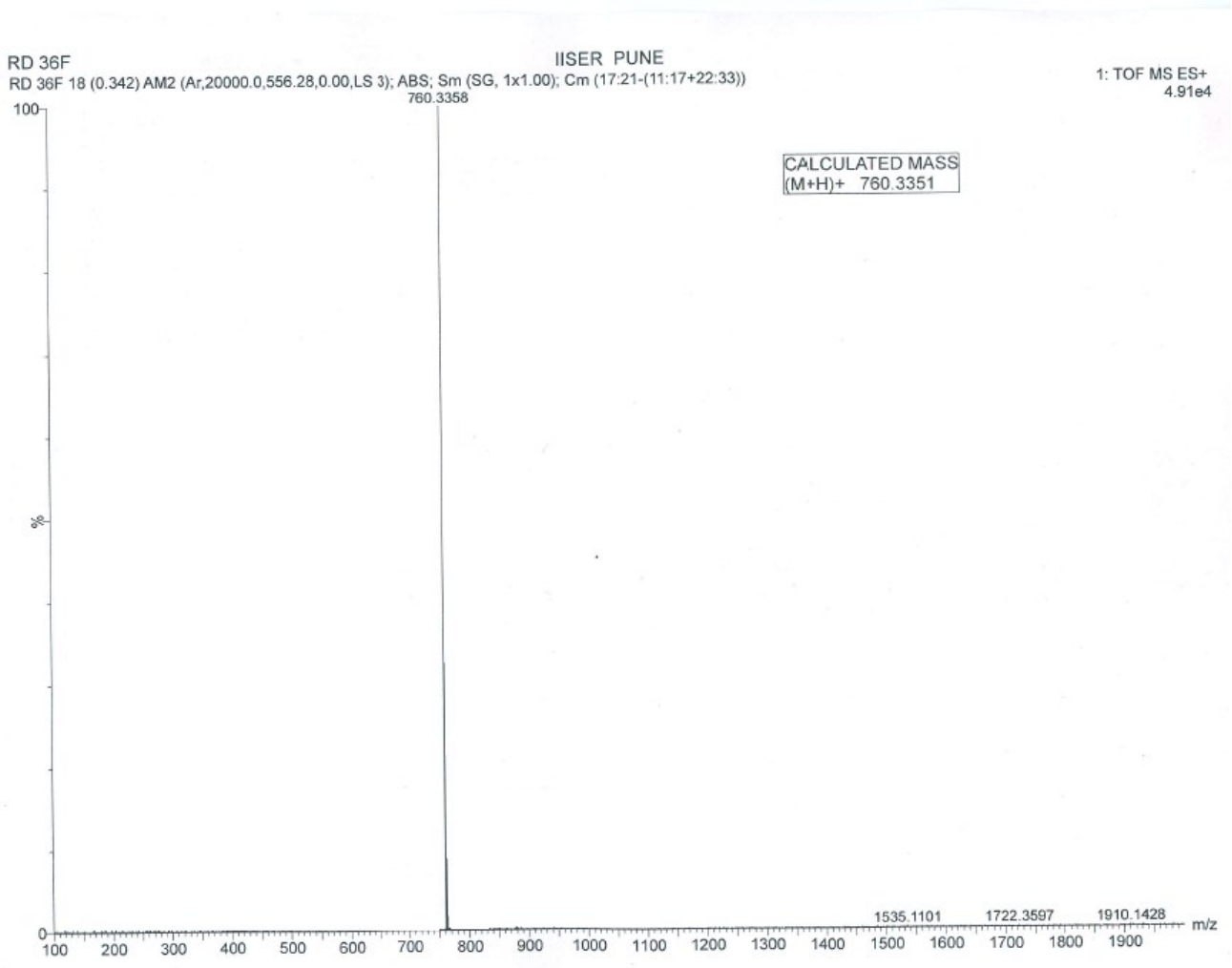

AcO
OAc
AcO
COOMe
OBn
BnO
BnO
BnO
OBn
NHTroc
N_3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

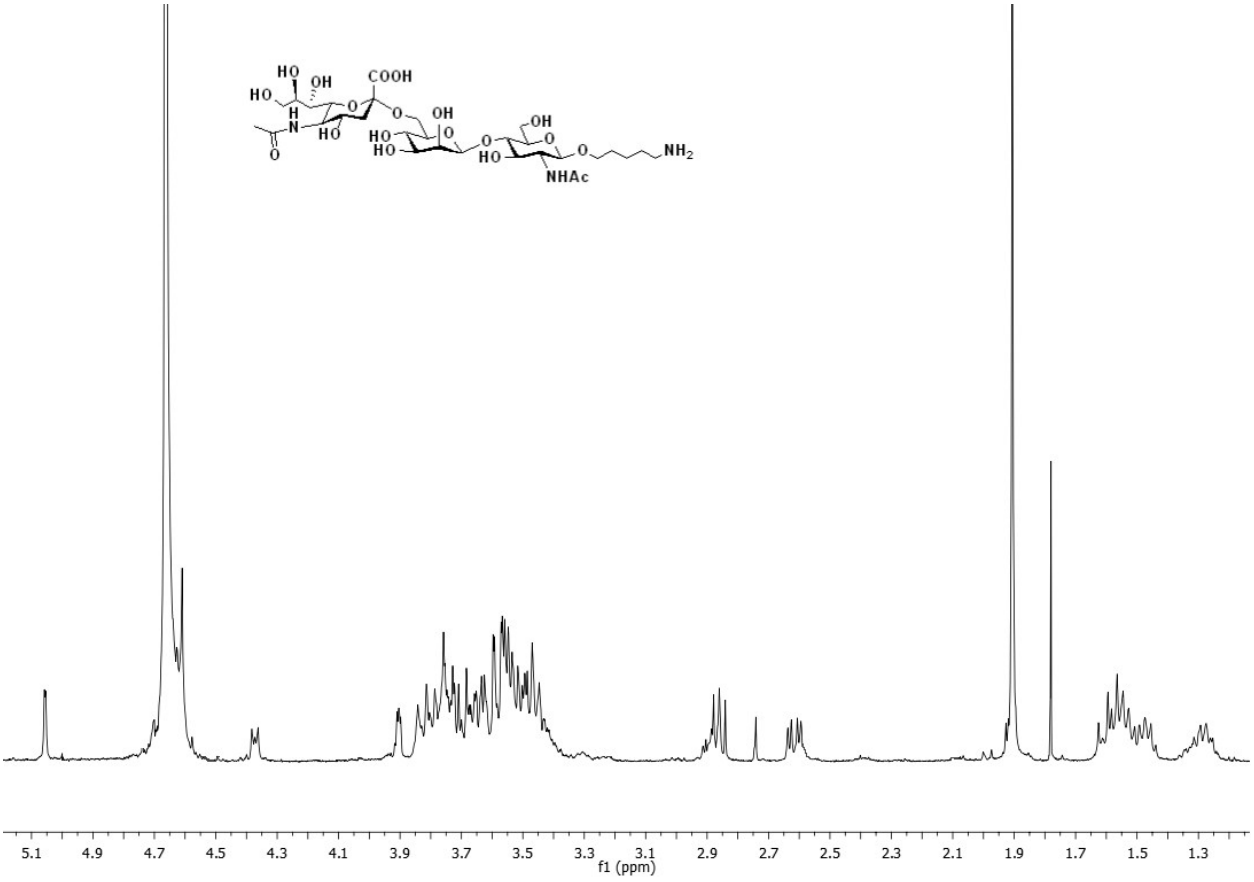

RD 42
IISER PUNE
RD 42 200 (3.665) AM2 (Ar,20000.0,556.28,0.0C,LS 3); ABS; Sm (SG, 1x1.00); Cm (199:207-(190:195+211:221))
1: TOF MS ES+
9.47e5
1556.4624
CALCULATED MASS
(M+Na)+ 1556.4626
1558.4594
1559.4597
1560.4564
1581.5335
1526.4822
1582.5360
1524.4812
1583.5341
1584.5361
1407.3921
1585.5336
1041.3820
1107.2666
1191.2767
1299.3335
1371.4199
1698.3711
100
%
0
m/z
1000 1050 1100 1150 1200 1250 1300 1350 1400 1450 1500 1550 1600 1650 1700 1750 1800 1850 1900 1950

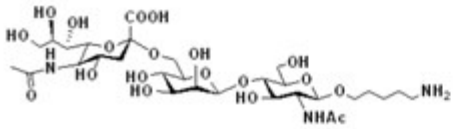

COOH
OH
HO
HO
HN
O
HO
OH
O
HO
OH
O
HO
OH
O
HO
NHAc
O
NH2
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
f1 (ppm)

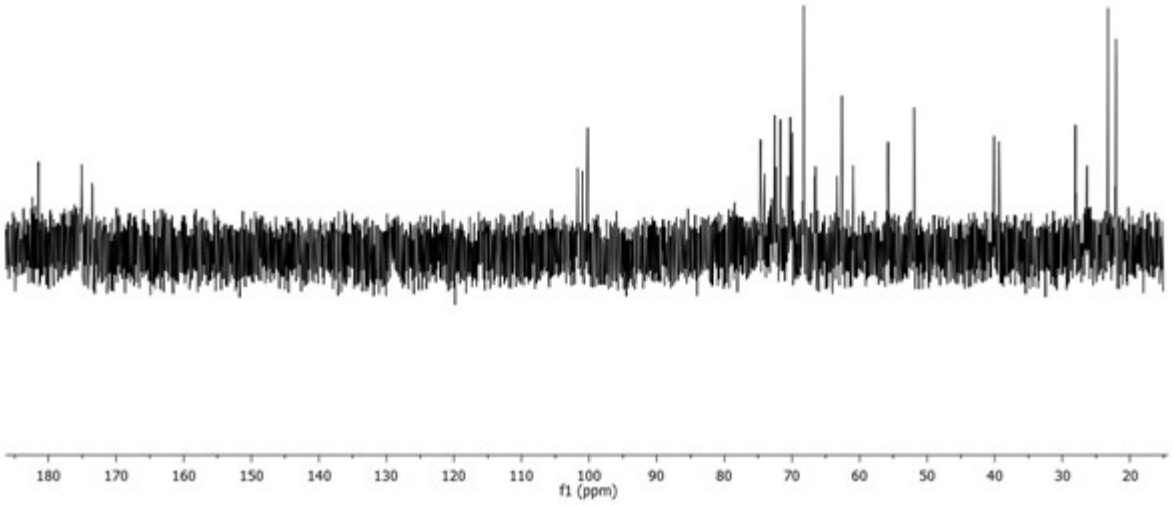

HO
OH
COOH
HO
O
OH
HN
HO
O
O
HO
OH
O
HO
O
OH
NHAc
O
NH2

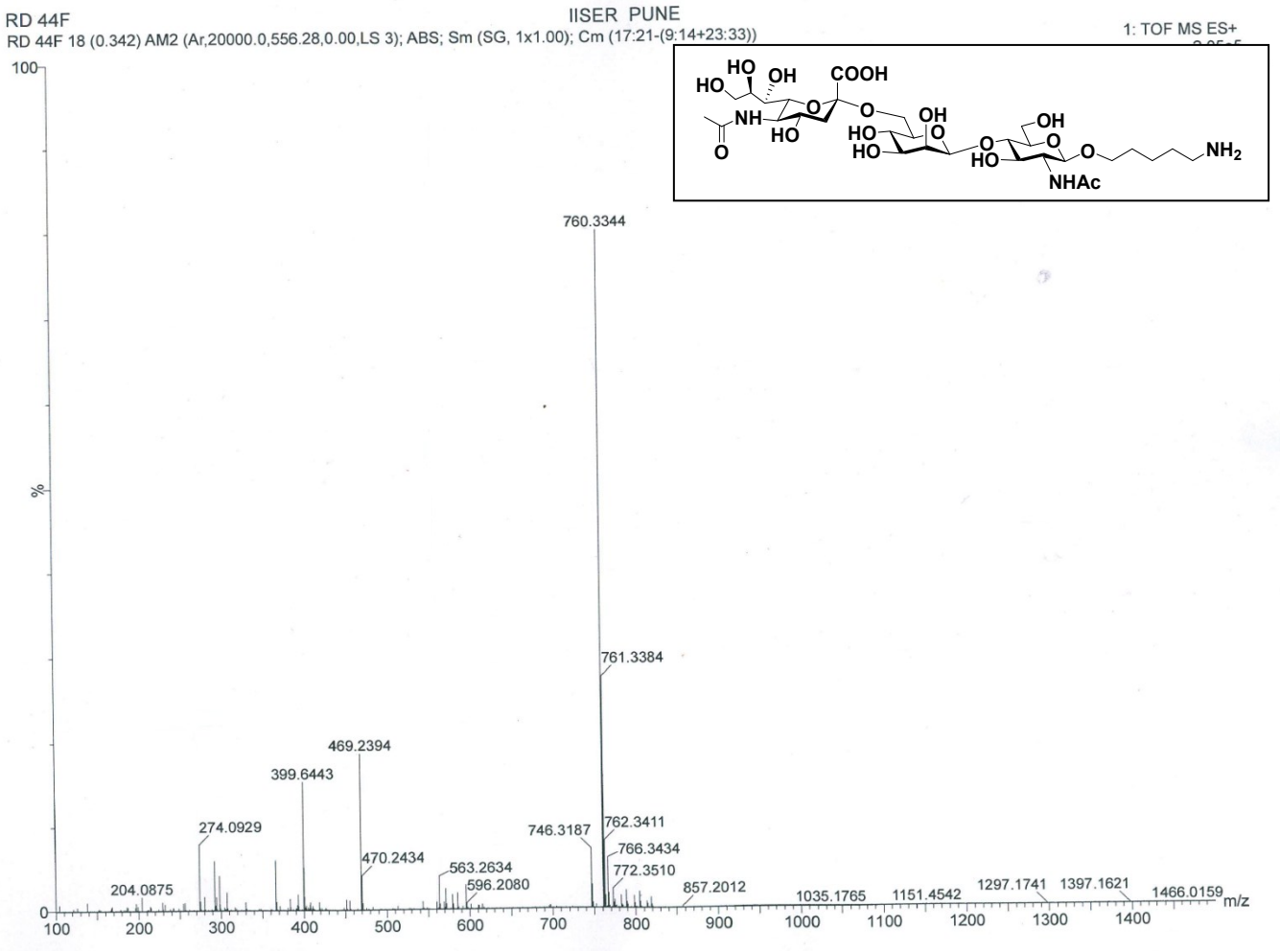

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

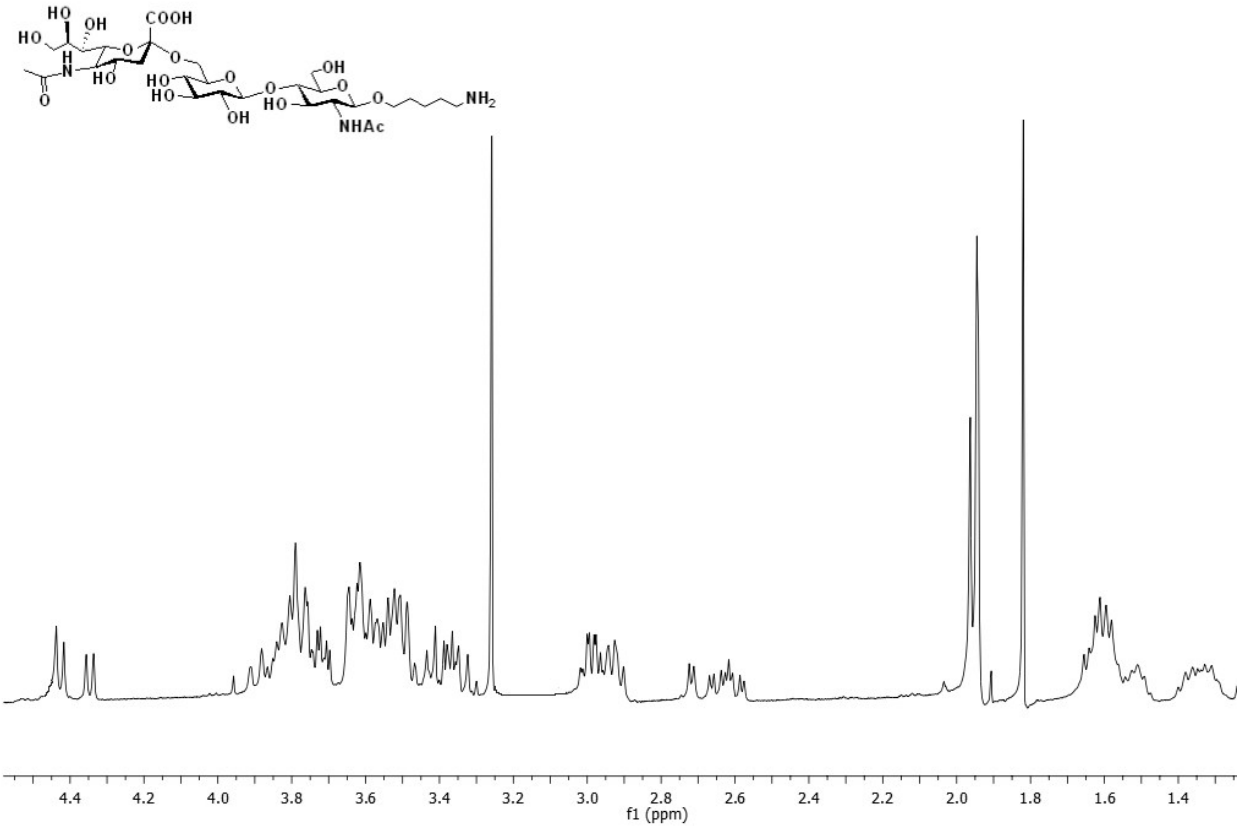

RD 36F
IISER PUNE
RD 36F 18 (0.342) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (17:21-(11:17+22:33))
1: TOF MS ES+
4.91e4
760.3358
CALCULATED MASS
(M+H)+ 760.3351
100
%
0
1535.1101
1722.3597
1910.1428
m/z
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900

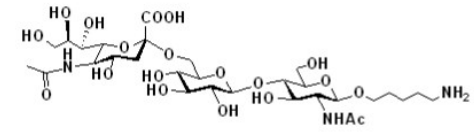

HO
OH
COOH
HO
OH
O
O
H
N
HO
O
OH
HO
HO
O
O
HO
OH
O
O
NHAc
NH2
5.1
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
f1 (ppm)

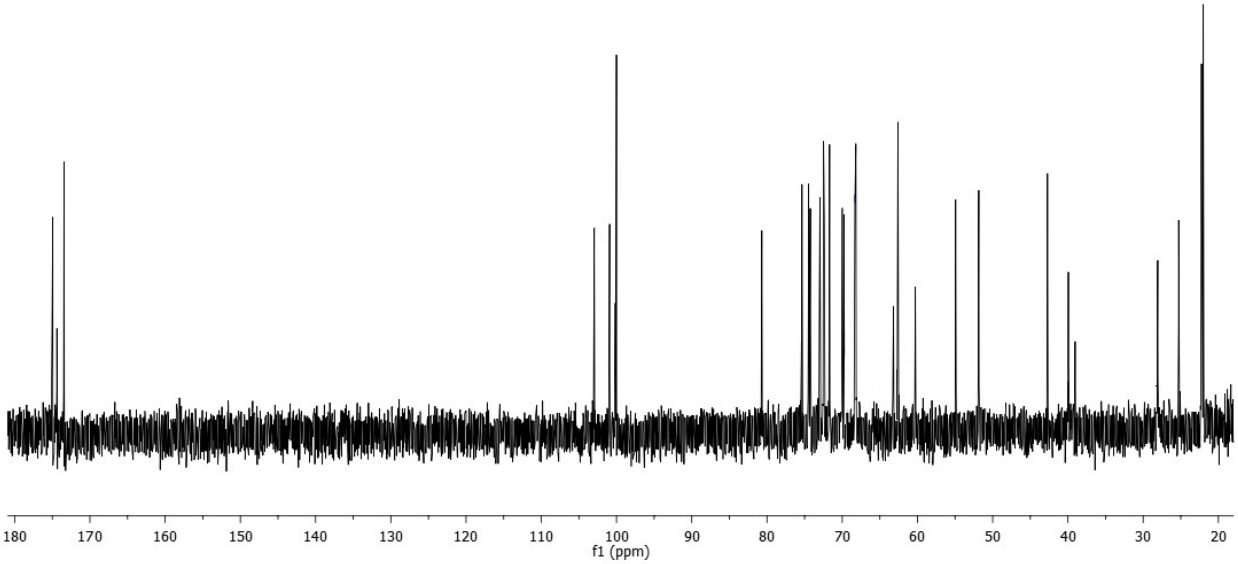

HO
OH
COOH
HO
H
N
O
HO
O
O
OH
HO
HO
O
O
HO
OH
O
O
NHAc
NH2

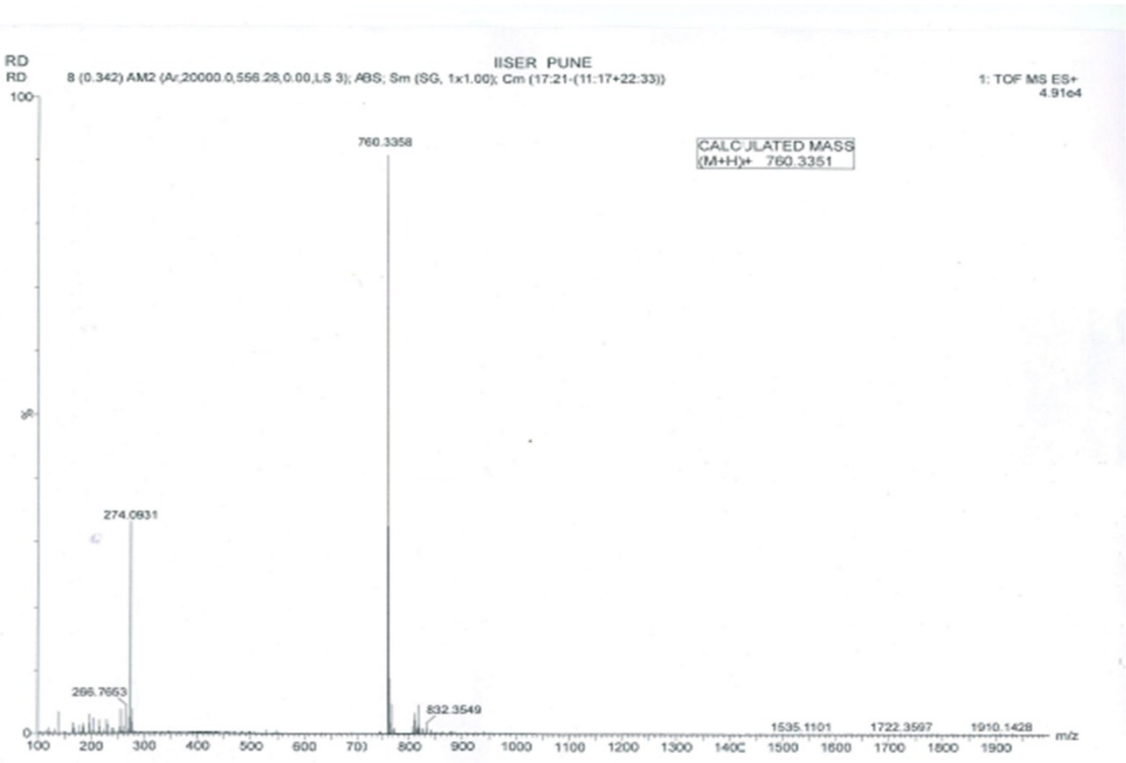

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


RD 44F
IISER PUNE
RD 44F 18 (0.342) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (17:21-(9:14+23:33))
1: TOF MS ES+
100
%
0
760.3344
761.3384
469.2394
399.6443
274.0929
746.3187
762.3411
766.3434
772.3510
470.2434
563.2634
596.2080
204.0875
857.2012
1035.1765
1151.4542
1297.1741
1397.1621
1466.0159
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
HO
OH
COOH
NH
O
NHAc
NH2


HO
OH
COOH
HO
N
HO
HO
HO
OH
OH
O
HO
NHAc
NH2
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f1 (ppm)


HO
OH
COOH
HO
O
O
H
N
HO
O
HO
HO
O
O
HO
OH
OH
O
HO
O
NHAc
NH2


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


RD
RD
IISER PUNE
8 (0.342) AM2 (Ar,20000.0,556.28,0.00,LS 3); ABS; Sm (SG, 1x1.00); Cm (17:21-(11:17+22:33))
1: TOF MS ES+
4.91e4
100
%
0
760.3358
CALCULATED MASS
(M+H)+ 760.3351
274.0831
266.7663
832.3549
1535.1101
1722.3597
1910.1428
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z