Supporting Information for:

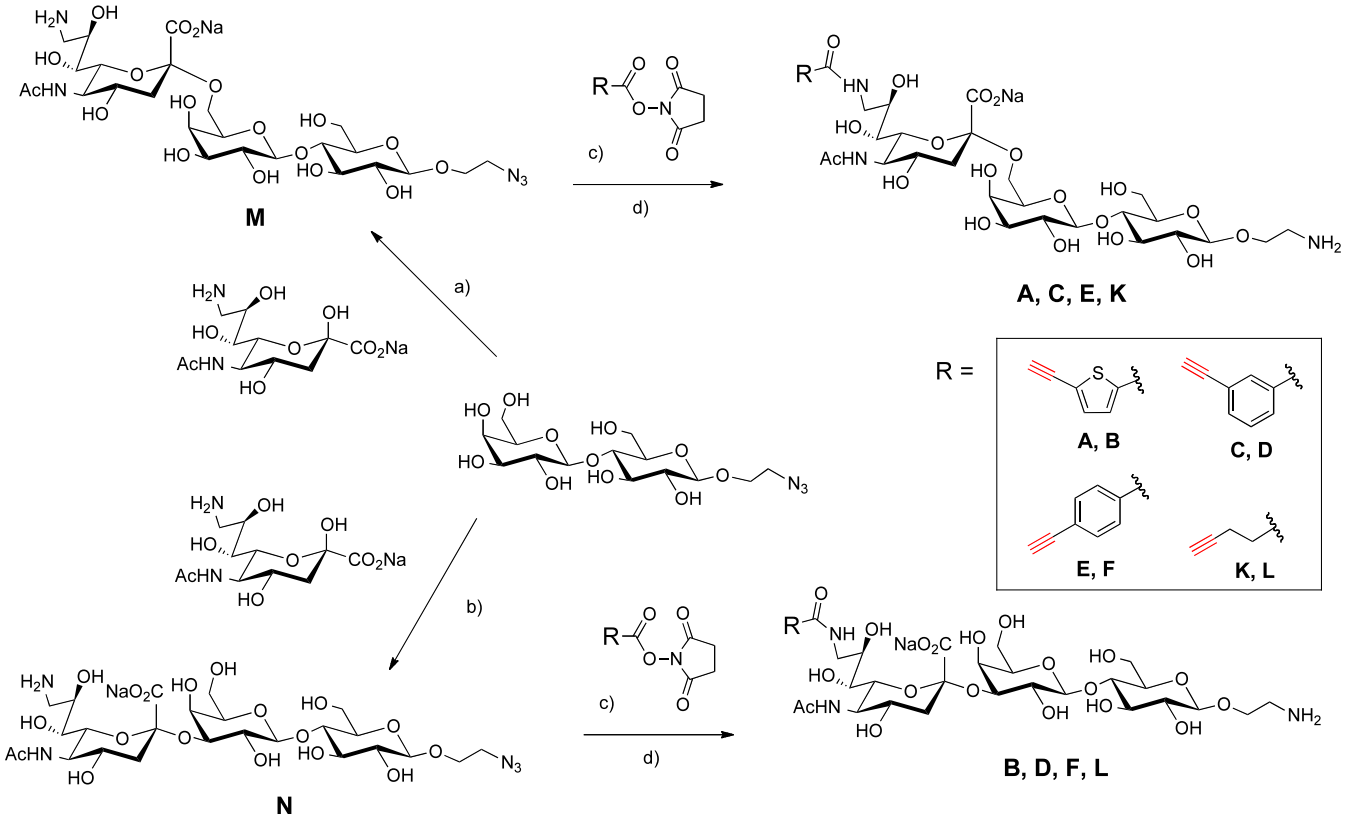
On-Chip Synthesis and Screening of a Sialoside Library Yields a High Affinity Ligand for Siglec-7

Cory D. Rillahan, Erik Schwartz, Christoph Rademacher, Ryan McBride, Janani Rangarajan, Valery V. Fokin, and James C. Paulson

Supplementary Methods

General Methods for Synthesis. All chemicals were obtained from Sigma Aldrich or Acros Chemical Companies unless otherwise stated. CuI (99.99%) was purchased from Strem Chemicals. NHS-activated-PEGylated-lipid (**Supplementary Scheme 4**) was purchased from NOF Corporation. C_{18} columns were obtained from Waters Corp. Reactions were monitored by thin-layer chromatography on 60F pre-coated TLC plates (EMD Chemicals, Inc.). Compounds were visualized by UV light and/or dipping in 5% sulfuric acid in EtOH followed by charring on a hot plate. NMR spectra were obtained on a Bruker DRX-600 MHz instrument at 25°C. Spectra obtained in D_2O were referenced to external acetone (^1H δ 2.225 and ^{13}C δ 29.9). ESI-TOF high-accuracy mass spectrometry was recorded with an LC MSD TOF (Agilent Technologies). Silica gel column chromatography was performed with 60-200 mesh silica gel or Iatrobeads (Mitsubishi Kagaku Iatron Inc.), as indicated below, under medium pressure. Gel filtration was carried out with P-2 resin (Bio-Rad) as previously described with solvents degassed prior to use. Dialysis cassettes, used for the purification of the **G35**-lipid, **I35**-lipid, and **K35**-lipid, were obtained from Pierce. Tris((1-*tert*-butyl-1H-1,2,3-triazolyl)methyl)amine (TTTA) and tris(3-hydroxypropyltriazolylmethyl)amine (THPTA) was synthesized according to literature.[1-3]

Synthesis of the Alkyne-Sialoside Library – Synthesis of Sialosides A-F, K-L



Supplementary Scheme 1 | a) CTP, *N. Meningitidis* CMP-NeuAc Synthetase, *P. Damsella* ⟨2,6 Sialyltransferase (91% yield). b) CTP, *N. Meningitidis* CMP-NeuAc Synthetase, *P. Multocida* ⟨2,3 Sialyltransferase (72% yield). c) CH_2Cl_2:MeOH (1:1, v/v), NEt_3. d) PMe_3, THF:H_2O (1:1) (~70% yield over 2 steps)

Synthesis of Compound **M**

(β-O-ethylazide)-lactoside[4] (50 mg, 121.5 μmol, 1 eq.), 9-amino NeuAc[5] (45 mg, 146 μmol, 1.2 eq.), CTP (99.4 mg, 182 μmol, 1.5 eq) were combined in 10 mls of 100 mM Tris, 20 mM $MgCl_2$ (pH 9.0) to which *N. Meningitidis* CMP-NeuAc Synthetase[6] (12.5 U) and *P. Damsella* α2,6 sialyltransferase[7] (1.1 U) were added and the reaction was left to proceed at 37°C at 220 rpm. After 4 hrs the reaction was complete and was immediately frozen and lyophilized. The material was then taken up in 4 mls of H_2O, centrifuged to remove insoluble precipitate, and loaded onto a Biogel P-2 column (2.5 x 100 cm) running in 100 mM NH_4CO_3. Fractions containing the product were then pooled, lyophilized, and repurified once more to yield Compound **M** (80 mg, 110.6 μmol, 91% yield),

HRMS: $C_{25}H_{43}N_5O_{18}$, $[M+H]^+$: Expected: 702.2676, Found: 702.2679.

^1H NMR (600 MHz, D_2O) δ 4.40 (d, J = 8.0 Hz, 1H), 4.30 (d, J = 7.9 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.88 – 3.78 (m, 3H), 3.75 – 3.61 (m, 5H), 3.57 – 3.36 (m, 10H), 3.30 – 3.21 (m, 2H), 2.86 (dd, J = 13.1, 9.5 Hz, 1H), 2.57 (dd, J = 12.4, 4.6 Hz, 1H), 1.89 (s, 3H), 1.60 (dd, J = 12.2 Hz, 12.2 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.75, 174.20, 104.00, 102.84, 101.16, 80.32, 75.43, 75.37, 74.44, 73.47, 73.10, 73.07, 71.56, 71.11, 69.33, 69.31, 69.06, 68.96, 64.44, 60.97, 52.48, 51.30, 43.12, 40.86, 22.83.

Synthesis of Compound **N**

The reaction was carried out essentially as described above, however, *P. Multocida* α2,3 sialyltransferase[8] (1.1 U) was used as the sialyltransferase. After ~ 3hrs, the reaction was frozen and lyophilized. Purification as above yielded Compound **N** (63 mg, 87.5 μmol, 72% yield).

HRMS: $C_{25}H_{43}N_5O_{18}$, $[M+H]^+$: Expected: 702.2676, Found: 702.2674.

^1H NMR (600 MHz, D_2O) δ 4.402 (d, J = 7.9, 1H), 4.399 (d, J = 7.9, 1H) 3.96 (dd, J = 9.8, 3.1 Hz, 1H), 3.95 – 3.89 (m, 2H), 3.86 (dd, J = 12.4, 2.2 Hz, 1H), 3.83 (d, J = 3.1 Hz, 1H), 3.74 – 3.66 (m, 3H), 3.66 – 3.39 (m, 12H), 3.25 (dd, J = 13.1, 2.9 Hz, 1H), 3.22 – 3.18 (m, 1H), 2.86 (dd, J = 13.2, 9.5 Hz, 1H), 2.62 (dd, J = 12.5, 4.6 Hz, 1H), 1.89 (s, 3H), 1.67 (dd, J = 12.1,12.1 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.85, 174.62, 103.40, 102.97, 100.82, 79.05, 76.32, 75.88, 75.54, 75.12, 73.54, 73.35, 70.75, 70.26, 69.35, 69.02, 68.99, 68.20, 61.77, 60.88, 52.40, 51.31, 42.99, 40.36, 22.81.

Synthesis of NHS-Esters

4-ethynylbenzoic acid (Alfa Aesar), 3-ethynylbenzoic acid (Chem Impex), and 4-pentynoic acid (Acros) were purchased commercially. 5-ethynylthiophene-2-carboxylic acid was synthesized as previously described.[9] These acids (1 eq.) were then dissolved in EtOAc to which *N*-Hydroxysuccinimide (1 eq.) was added and the solution was cooled to O°C. Then, dicyclohexylcarbodimide (1 eq.) was added (as a solid, in portions) and the solution was left to stir overnight and warm to room temperature. After filtration, these were purified by silica gel column chromatography and obtained in good yields (>70%).

General Procedure for Synthesis of Alkyne-Sialosides **A, C, E, K**

Compound **M** (7.5 mgs, 10.4 μmol, 1 eq.), was dissolved in MeOH (750 μl), NEt_3 was added (2 drops), and the desired NHS-ester (20.4 μmol, 2 eq.) dissolved in CH_2Cl_2 (750 μl) was added. Reactions were left to proceed for 30 min-1 hr after which time reactions were typically complete. The solvent was evaporated, the residue redissolved in H_2O (1 ml), and purified on a C18 column (2g, Waters Corp) by first washing with H_2O, and then eluting the desired material with MeOH/H_2O mixtures in the range of

15-20% MeOH in H_2O. The azido-intermediates were then dissolved in THF/H_2O (1 ml, 1:1 v/v) to which a 1M PMe_3 solution in THF (1.5 eq.) was added. Reactions were left to proceed for 2 hrs at room temperature at which time TLC indicated the conversion to be complete. The solvent was evaporated and the crude material was taken up in H_2O (500 μl), and loaded onto a P-2 column (0.625 x 42.5 cm) eluting with 100 mM NH_4CO_3 to afford Sialosides **A**, **C**, **E**, **K** in ~70% yields over two steps.

Compound **A**: HRMS: $C_{32}H_{47}N_3O_{19}S$, $[M+H]^+$: Expected: 810.2597, Found: 810.2590.

^{1}H NMR (600 MHz, D_2O) δ 7.46 (d, J = 4.0 Hz, 1H), 7.21 (d, J = 4.0 Hz, 1H), 4.37 (d, J = 7.9 Hz, 1H), 4.27 (d, J = 7.8 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.92 – 3.87 (m, 1H), 3.85 – 3.71 (m, 5H), 3.68-3.57 (m, 4H), 3.54 – 3.45 (m, 6H), 3.43 – 3.36 (m, 3H), 3.23 (t, J = 8.4 Hz, 1H), 3.05 (t, J = 5.0 Hz, 2H), 2.58 (d, J = 1.0 Hz, 1H), 2.57 (dd, J = 12.4, 4.6 Hz), 1.86 (s, 3H), 1.60 (dd, J = 12.2, 12.1 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.66, 174.24, 164.53, 139.35, 135.01, 129.97, 127.05, 103.97, 102.65, 101.13, 80.33, 76.41, 75.44, 75.29, 74.55, 73.41, 73.20. 73.13, 71.52, 70.94, 70.91, 69.32, 69.09, 67.77, 64.57, 60.95, 52.54, 43.51, 40.89, 40.34, 39.49, 22.81.

Compound **C**: HRMS: $C_{34}H_{49}N_3O_{19}$, $[M+H]^+$: Expected: 804.3033, Found: 804.3042.

^{1}H NMR (600 MHz, D_2O) δ 7.80-7.76 (m, 1H), 7.69 – 7.63 (m, 1H), 7.63 – 7.58 (m, 1H), 7.39 (t, J = 7.8 Hz, 1H), 4.36 (d, J = 8.0 Hz, 1H), 4.27 (d, J = 7.9 Hz, 1H), 3.98 – 3.90 (m, 2H), 3.85 – 3.72 (m, 5H), 3.69 – 3.63 (m, 4H), 3.56 – 3.37 (m, 10H), 3.23 (dd, J = 9.1, 8.2 Hz, 1H), 3.06-2.98 (m, 2H), 2.59 (s, 1H), 2.57 (dd, J = 12.4, 4.6 Hz, 1H), 1.87 (s, 3H), 1.61 (dd, J = 12.2, 12.2 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.66, 174.27, 171.10, 136.09, 134.97, 131.52, 129.82, 128.51, 122.81, 103.97, 102.65, 101.15, 83.18, 80.33, 75.42, 75.29, 74.56, 73.42, 73.20, 73.14, 71.52, 70.93, 70.86, 69.33, 69.10, 67.95, 64.59, 60.95, 52.56, 43.64, 40.88, 40.36, 39.48, 22.82.

Compound **E**: HRMS: $C_{34}H_{49}N_3O_{19}$, $[M+H]^+$: Expected: 804.3033, Found: 804.3019

^{1}H NMR (600 MHz, D_2O) δ 7.63 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 4.36 (d, J = 8.0 Hz, 1H), 4.27 (d, J = 7.9 Hz, 1H), 3.99 – 3.89 (m, 2H), 3.86 – 3.80 (m, 2H), 3.79-3.71 (m, 3H), 3.69 – 3.62 (m, 4H), 3.55 – 3.37 (m, 9H), 3.23 (t, J = 8.5 Hz 1H), 3.05 (t, J = 5.1 Hz, 2H), 2.57 (dd, J = 12.4, 4.6 Hz, 1H), 1.86 (s, 3H), 1.60 (dd, J = 12.4, 12.2 Hz, 1H).

Note: Terminal acetylene not seen due to deuterium exchange.

^{13}C NMR (151 MHz, D_2O) δ 175.65, 174.26, 171.20, 134.75, 133.13, 132.71, 129.56, 128.08, 125.88, 103.97, 102.64, 101.14, 83.25, 80.32, 75.43, 75.28, 74.55, 73.41, 73.19, 73.13, 71.52, 70.97, 70.87, 69.32, 69.10, 67.70, 67.69, 64.57, 60.94, 52.55, 43.67, 40.89, 40.33, 22.81.

Compound **K**: HRMS: $C_{30}H_{49}N_3O_{19}$, $[M+H]^+$: Expected: 756.3033, Found: 756.3030

^{1}H NMR (600 MHz, D_2O) δ 4.41 (d, J = 8.0 Hz, 1H), 4.29 (d, J = 7.9 Hz, 1H), 3.99 (ddd, J = 10.1, 4.7, 4.7 Hz, 1H), 3.87 – 3.78 (m, 5H), 3.72 (dd, J = 10.1, 10.1 Hz, 1H), 3.69-3.65 (m, 2H), 3.60 (dd, J = 10.5, 1.7 Hz, 1H), 3.58 – 3.44 (m, 8H), 3.40 (dd, J = 9.9, 7.9 Hz, 1H), 3.34 (dd, J = 9.1, 1.7 Hz, 1H), 3.26 (dd, J = 9.2, 8.1 Hz, 1H), 3.22 (dd, J = 14.1, 7.4 Hz, 1H), 3.11 (t, J = 5.1 Hz, 2H), 2.56 (dd, J = 12.4, 4.7 Hz, 1H), 2.40 – 2.32 (m, 4H), 2.25 (t, J = 2.3 Hz, 1H), 1.89 (s, 3H), 1.59 (dd, J = 12.2, 12.2 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.79, 175.66, 174.25, 103.95, 102.62, 101.07, 84.14, 80.27, 75.44, 75.26, 74.57, 73.43, 73.16. 73.13, 71.52, 71.08, 70.82, 70.54, 69.35, 69.11, 66.95, 64.58, 60.91, 52.56, 42.77, 40.88, 40.23, 35.28, 22.89, 15.47, 15.44.

^{13}C NMR (151 MHz, D_2O) δ 175.80, 175.78, 174.66, 103.45, 102.79, 100.63, 84.16, 78.90, 76.26, 76.00, 75.58, 75.01, 73.55, 73.49, 72.50, 71.09, 70.76, 70.36, 70.20, 69.07, 68.24, 67.10, 61.85, 52.50, 42.69, 40.41, 40.26, 35.29, 22.87, 15.50, 15.47.

General Procedure for Synthesis of Alkyne-Sialosides **B, D, F, L**

These were synthesized as above with the exception that compound **N** was used instead of compound **M**.

Compound **B:** HRMS: $C_{32}H_{47}N_3O_{19}S$, $[M+H]^+$: Expected: 810.2597, Found: 810.2598.

^{1}H NMR (600 MHz, D_2O) δ 7.47 (d, J = 4.0 Hz, 1H), 7.22 (d, J = 4.0 Hz, 1H), 4.37 (d, J = 8.0 Hz, 1H), 4.34 (d, J = 7.9 Hz, 1H), 3.95 (dd, J = 9.9, 3.1 Hz, 1H), 3.94 – 3.89 (m, 1H), 3.87 (ddd, J = 8.5, 8.5, 2.9 Hz, 1H), 3.80 (d, J = 3.0 Hz, 1H), 3.77-3.69 (m, 3H), 3.69 – 3.46 (m, 9H), 3.45 – 3.39 (m, 3H), 3.36 (dd, J = 14.2, 7.8 Hz, 1H), 3.20 (t, J = 8.6 Hz, 1H), 2.99 (t, J = 5.1 Hz, 2H), 2.62 (dd, J = 12.4, 4.6 Hz, 1H), 2.59 (s, 1H), 1.87 (s, 3H), 1.66 (dd, J = 12.2, 12.2 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.77, 174.51, 164.46, 139.38, 135.04, 129.96, 127.10, 103.42, 102.84, 100.73, 78.79, 76.51, 76.41, 76.04, 75.55, 74.99, 73.65, 73.52, 71.21, 70.51, 70.10, 69.02, 68.57, 68.26, 61.83, 60.66, 52.48, 43.43, 40.56, 40.47, 39.49, 22.78.

Compound **D**: HRMS: $C_{34}H_{49}N_3O_{19}$, $[M+H]^+$: Expected: 804.3033, Found: 804.3019

^{1}H NMR (600 MHz, D_2O) δ 7.82 – 7.76 (m, 1H), 7.69 – 7.64 (m, 1H), 7.63 – 7.58 (m, 1H), 7.39 (t, J = 7.8 Hz, 1H), 4.36 (d, J = 8.0 Hz, 1H), 4.34 (d, J = 8.1 Hz, 1H), 3.96 (dd, J = 9.8, 3.1 Hz, 1H), 3.94-3.87 (m, 2H), 3.81 (d, J = 3.0 Hz, 1H), 3.73 (t, J = 10.1 Hz, 2H), 3.68 (dd, J = 13.8, 2.4 Hz, 2H), 3.63 – 3.53 (m, 6H), 3.53 – 3.46 (m, 2H), 3.46 – 3.37 (m, 4H), 3.19 (t, J = 8.4 Hz, 1H), 3.02-2.98 (m, 2H), 2.62 (dd, J = 12.4, 4.6 Hz, 1H), 1.87 (s, 3H), 1.66 (dd, J = 12.2,12.2 Hz, 1H).

Note: Terminal acetylene not seen due to deuterium exchange.

^{13}C NMR (151 MHz, D_2O) δ 175.77, 174.54, 171.02, 136.11, 134.94, 131.51, 129.84, 128.49, 122.82, 103.40, 102.81, 100.75, 83.17, 78.77, 76.51, 76.02, 75.52, 74.98, 73.64, 73.51, 71.13, 70.50, 70.13, 69.04, 68.37, 68.25, 61.82, 60.64, 52.49, 43.55, 40.54, 40.43, 22.80.

Compound **F**: HRMS: $C_{34}H_{49}N_3O_{19}$, $[M+H]^+$: Expected: 804.3033, Found: 804.3022

^{1}H NMR (600 MHz, D_2O) δ 7.69 – 7.60 (m, 2H), 7.57 – 7.48 (m, 2H), 4.36 (d, J = 8.0 Hz, 1H), 4.34 (d, J = 7.9 Hz, 1H), 3.95 (dd, J = 9.9, 3.1 Hz, 1H), 3.94 – 3.87 (m, 2H), 3.81 (d, J = 3.0 Hz, 1H), 3.78 – 3.64 (m, 4H), 3.64 – 3.37 (m, 11H), 3.20 (t, J = 8.6 Hz, 1H), 3.03 (t, J = 4.9 Hz, 2H), 2.62 (dd, J = 12.4, 4.6 Hz, 1H), 2.58 (s, 1H), 1.86 (s, 3H), 1.66 (dd, J = 12.4, 12.2 Hz, 1H).

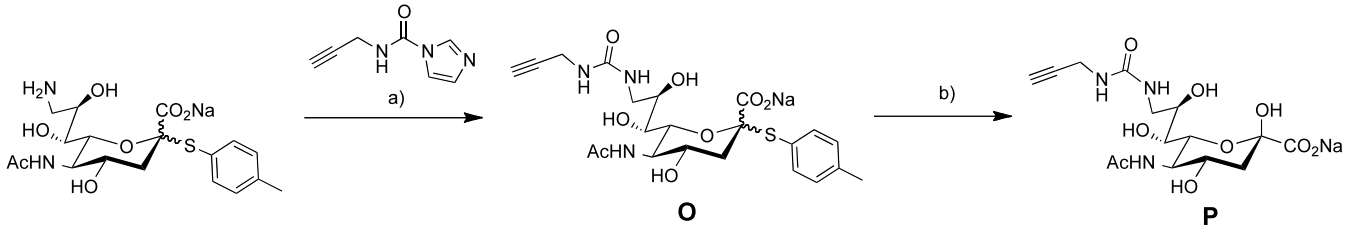
^{13}C NMR (151 MHz, D_2O) δ 175.76, 174.53, 171.09, 134.72, 133.13 (2C's), 128.07 (2C's), 125.93, 103.40, 102.79, 100.75, 83.25, 78.75, 76.50, 76.03, 75.51, 74.98, 73.62, 73.49, 71.12, 70.53, 70.13, 69.03, 68.26, 67.98, 61.83, 60.62, 52.49, 43.58, 40.53, 40.39, 39.49, 22.79.

Compound **L**: HRMS: $C_{30}H_{49}N_3O_{19}$, $[M+H]^+$: Expected: 756.3033, Found: 746.3028

^{1}H NMR (600 MHz, D_2O) δ 4.41 (d, J = 8.0 Hz, 1H), 4.38 (d, J = 7.9 Hz, 1H), 4.00 – 3.93 (m, 2H), 3.86 (dd, J = 12.3, 2.1 Hz, 1H), 3.83 – 3.77 (m, 3H), 3.73 – 3.68 (m, 2H), 3.65 – 3.41 (m, 14H), 3.38 (dd, J = 9.0, 1.8 Hz, 1H), 3.27 – 3.17 (m, 2H), 3.10 (t, J = 5.1 Hz, 2H), 2.61 (dd, J = 12.4, 4.6 Hz, 1H), 2.40-2.32 (m, 4H), 2.25 (t, J = 2.2 Hz, 1H), 1.90 (s, 3H), 1.66 (dd, J = 12.2, 12.1 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.80, 175.78, 174.66, 103.45, 102.79, 100.63, 84.16, 78.90, 76.26, 76.00, 75.58, 75.01, 73.55, 73.49, 72.50, 71.09, 70.76, 70.36, 70.20, 69.07, 68.24, 67.10, 61.85, 52.50, 42.69, 40.41, 40.26, 35.29, 22.87, 15.50, 15.47

Synthesis of the Alkyne-Sialoside Library – Synthesis of Sialosides I and J



Supplementary Scheme 2 | a) DMF, 45°C (73% Yield). b) I_2, H_2O (93% Yield)

Synthesis of ***N*^{1}-(Prop-2-yn-1-yl)-1H-imidazole-1-carboxamide**

Under N_2, propargyl amine (3.9 g, 0.07 mol) in CH_2Cl_2 (50 mL) was added dropwise to a ice-cooled solution of 1,1-carbonyldiimidazole (17.56 g, 0.11 mol, 1.5 equiv) in THF (100 mL). After complete addition of the amine, the mixture was stirred at room temperature for 16 hrs. The solvent was removed and the crude product was purified on silica (4% MeOH in $CHCl_3$) to afford the product as a white solid (8.1 g, 77 %).

HRMS: $C_7H_8NO_3$, $[M+H]^+$ Expected = 150.0662, Found = 150.0658.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.04 (br s, NH, 1H), 8.26, 7.68, 7.04 (s, imidazole H, 3H), 4.07 (d, J = 2.7 Hz, CH_2, 2H), 3.25 (tr, J = 2.4 Hz, C≡CH, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 148.7 (C=O), 136.1, 1298.8, 116.6 (imidazole C), 80.3 (C≡CH), 73.4 (C≡CH), 29.6 (CH_2).

Synthesis of Compound **O**

The 9-NH_2-NeuAc thioglycoside[5] (40 mg, 96.5 μmol, 1 eq.) was dissolved in DMF and *N*^{1}-(Prop-2-ynyl)-1H-imidazole-1-carboxamide (43.2 mg, 289.5 μmol, 3 eq.) was added, and the reaction solution was left to proceed under argon at 45°C overnight. After this time, the solvent was evaporated and the intermediate was purified on Iatrobeads eluting with EtOAc:MeOH:AcOH:H_2O (25:3:3:2, v/v/v/v) to yield a purified, but not completely pure compound **O.** This was then further purified on a P-2 column (0.625 x 42.5 cm) eluting in 100 mM NH_4CO_3 to yield pure compound **O** as a mixture of anomers (34.7 mg, 70 μmol, 73% yield)

Compound **O:** HRMS: $C_{22}H_{29}N_3O_8S$, $[M+H]^+$: Expected: 496.1746, Found: 496.1743

β-anomer:

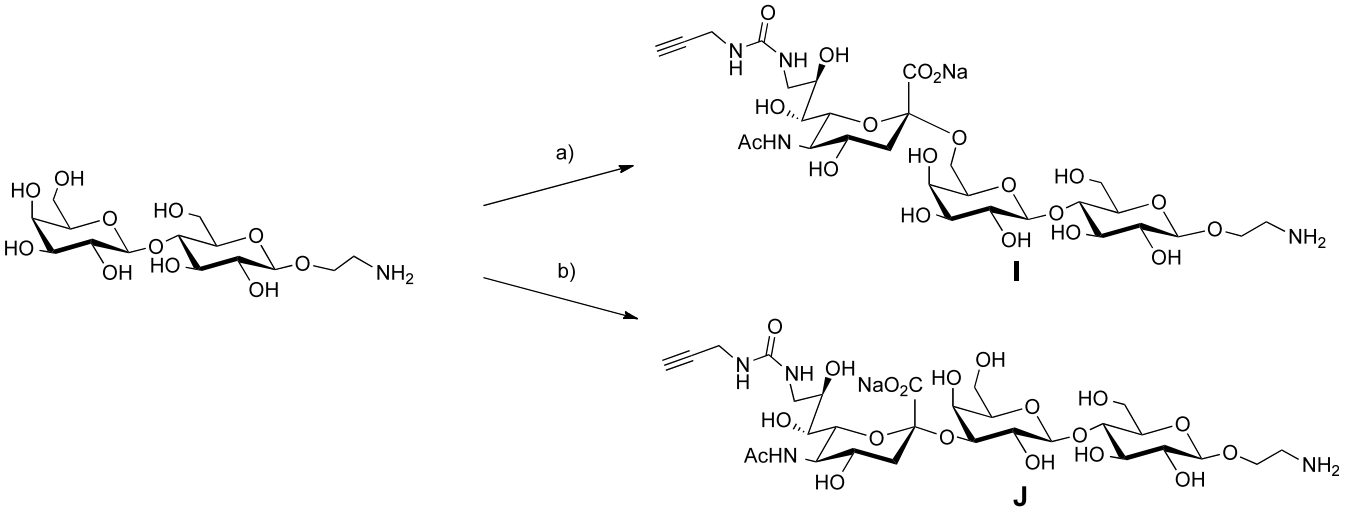
^{1}H NMR (600 MHz, D_2O) δ 7.27 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 4.23 (d, J = 10.5 Hz, 1H), 4.03 (ddd, J = 10.9, 10.9, 4.7 Hz, 1H), 3.81 – 3.76 (m, 1H), 3.76 – 3.74 (m, 2H), 3.71 (dd J = 10.4, 10.4 Hz, 1H), 3.58 – 3.54 (m, 1H), 3.34 (d, J = 8.5 Hz, 1H), 3.28
(dd, J = 13.7, 2.8 Hz, 1H), 3.03 (dd, J = 14.4, 6.5 Hz, 1H), 2.52 (dd, J = 13.7, 4.7 Hz, 1H), 2.45 (t, J = 2.3 Hz, 1H), 2.19 (s, 3H), 1.93 (s, 3H), 1.86 – 1.81 (dd, J = 12.2, 12.1 Hz, 1H).

β-anomer:

^{13}C NMR (151 MHz, D_2O) δ 175.49, 175.00, 161.09, 140.68, 135.38 (2 C's), 130.54 (2 C's), 127.31, 91.49, 81.99, 72.49, 72.12, 70.65, 70.32, 68.08, 53.16, 43.73, 41.33, 30.22, 22.95, 21.13.

Synthesis of Compound **P**

Compound **O** (34.7 mg, 70 μmol, 1 eq.) was dissolved in H_2O (5 mLs) and I_2 (27 mg, 106.2 μmol, 1.1 eq.) was added followed by vigorous stirring overnight. After repeated extraction with EtOAc (4 x 5 mLs), the aqueous layer was frozen and lyophilized. Compound **P** was obtained as a yellow solid and was used without further purification (25.3 mg, 65 μmol, 93% yield)



Supplementary Scheme 3 | a) Compound **P**, CTP, *N. Meningitidis* CMP-NeuAc Synthetase, *P. Damsella* ⟨2,6 Sialyltransferase (88% yield). b) Compound **P,** CTP, *N. Meningitidis* CMP-NeuAc Synthetase, *P. Multocida* ⟨2,3 Sialyltransferase (52% yield).

Synthesis of Compound **I**

(β-O-ethylamine)-lactoside[5] (5 mg, 13.0 μmol, 1 eq.), compound **P** (6.1 mg, 15.5 μmol, 1.2 eq.), and CTP (10.7 mg, 19.5 μmol, 1.5 eq.) were dissolved in 1 ml of 100 mM Tris, 20 mM $MgCl_2$ (pH 9.0) to which *N. Meningitidis* CMP-NeuAc Synthetase (1.25 U) and *P. Damsella* α2,6 sialyltransferase (0.1 U) were added and the reaction was left to proceed at 37°C with end-over-end rotation overnight. The reaction was then frozen, lyophilized, and the crude material redissolved in H_2O (0.5 mL). After removing the insoluble precipitate by centrifugation the supernatant was loaded onto a P-2 column (0.625 x 42.5 cm) running in 100 mM NH_4CO_3. Pure fractions were then pooled and lyophilized to afford compound **I** (8.9 mg, 11.4 μmol, 88% yield).

Compound **I**: HRMS: $C_{29}H_{48}N_4O_{19}$, $[M+H]^+$: Expected: 757.2985, Found: 757.2994

^{1}H NMR (600 MHz, D_2O) δ 4.42 (d, J = 8.0 Hz, 1H), 4.29 (d, J = 7.9 Hz, 1H), 4.00 (ddd, J = 11.6, 4.9, 4.9 Hz, 1H), 3.86-3.77 (m, 4H), 3.75 (d, J = 1.4 Hz, 2H), 3.72 (t, J = 9.9 Hz, 1H), 3.70 – 3.65 (m, 2H), 3.60 (dd, J = 10.5, 1.5 Hz, 1H) 3.58-3.54 (m, 2H) 3.54-3.48 (m, 4H), 3.46 (dd, J = 10.4, 3.4 Hz, 1H), 3.40 (ddd, J = 7.8, 4.1, 4.1 Hz, 2H), 3.33 (dd, J = 8.9, 1.5 Hz, 1H), 3.27 (dd, J = 9.0, 8.3 Hz, 1H), 3.14 (t, J = 5.1 Hz, 2H), 3.12-3.06 (m, 1H), 2.56 (dd, J = 12.4, 4.6 Hz, 1H), 2.45 (t, J = 2.4 Hz, 1H), 1.89 (s, 3H), 1.59 (dd, J = 12.2, 12.2 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.64, 174.27, 161.07, 103.94, 102.61, 101.11, 80.22, 75.45, 75.24, 74.55, 73.43, 73.22, 73.13, 72.08, 71.53, 71.30, 70.48, 69.33, 69.14, 66.56, 64.51, 60.90, 60.22, 52.56, 43.34, 40.87, 40.18, 30.23, 22.87.

Synthesis of Compound **J**

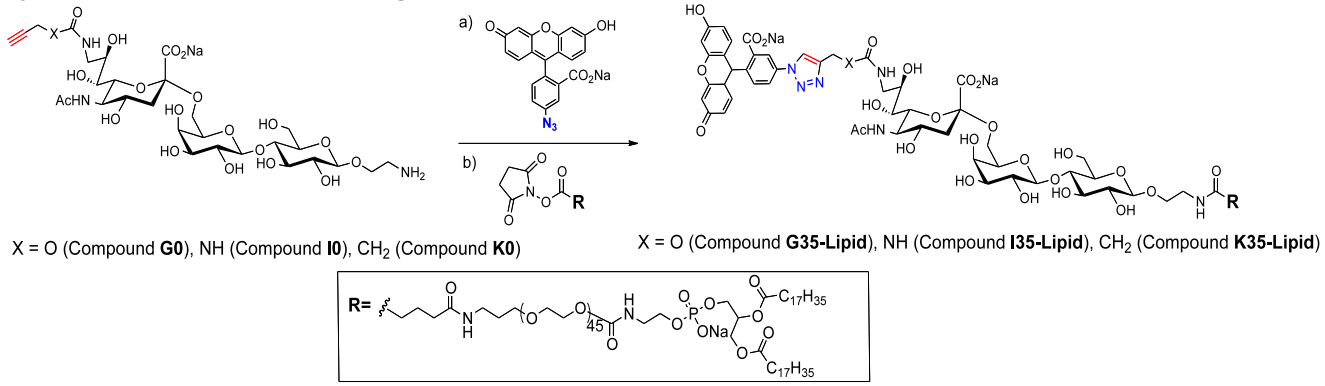
Synthesis was carried out as for compound **I**, with the exception that the *P. Multocida* α2,3 sialyltransferase[8] (0.1 U) was used as the sialyltransferase and the reaction was stopped after 4 hrs by freezing and lyophilizing. It was noted that the reaction stalled and only proceeded to ~60% completion. Two rounds of purification on a P-2 column (0.625 x 42.5 cm) yielded compound **J** (5.3 mg, 6.8 μmol, 52% yield).

Compound **J**: HRMS: $C_{29}H_{48}N_4O_{19}$, $[M+H]^+$: Expected: 757.2985, Found: 757.2994

^{1}H NMR (600 MHz, D_2O) δ 4.41 (d, J = 8.0 Hz, 1H), 4.38 (d, J = 7.8 Hz, 1H), 4.01 – 3.94 (m, 2H), 3.86 (dd, J = 12.3, 2.0 Hz, 1H), 3.84 – 3.79 (m, 2H), 3.76 (s, 2H), 3.73-3.68 (m, 2H), 3.65 – 3.59 (m, 2H), 3.59 – 3.50 (m, 5H), 3.49-3.46 (m, 1H), 3.45 – 3.39 (m, 2H), 3.37 (dd, J = 8.8, 1.4 Hz, 1H), 3.24 (t, J = 8.5 Hz, 1H), 3.15-3.07 (m, 3H), 2.61 (dd, J = 12.5, 4.6 Hz, 1H), 2.45 (t, J = 2.4 Hz, 1H), 1.89 (s, 3H), 1.65 (dd, J = 12.2, 12.1 Hz, 1H).

^{13}C NMR (151 MHz, D_2O) δ 175.74, 174.63, 161.03, 103.42, 102.77, 100.66, 78.80, 76.32, 76.01, 75.59, 74.97, 73.62, 73.49, 72.09, 71.41, 70.14, 69.08, 68.23, 66.69, 61.85, 60.65, 52.50, 43.23, 40.45, 40.21, 39.48, 30.20, 22.84.

Synthesis of Lipid-Linked Siglec-7 Hits



Supplementary Scheme 4 | a) CuI, TTTA, Ascorbate, DMF/H_2O (72-78% Yields). b) CH_2Cl_2, DMSO, DIEA (90-95% Yields)

Synthesis of Compounds **G35, K35, and I35**

G0, **K0**, or **I0** (5 mg, 6.6 μmol, 1 eq.) was dissolved in H_2O (250 μl) and added to a solution of 5-azido-fluorescein in 200 μl DMF (4.2 mg, 11.2 μmol 1.7 eq.). A precomplexed solution of CuI/TTTA[1] in DMF was added (50 μl: (0.5 mg CuI, 2.6 μmol, 0.4 eq) and (2.2 mg TTTA, 5.3 μmol, 0.8 eq)) and left to stir for 1 hr at RT. After this time, 50 μl of 100 mM sodium ascorbate (5 μmol, 0.76 eq.) was added and left to proceed for another 2 hrs after which time TLC indicated the reaction was complete and quantitative. The reaction mixture was then centrifuged and loaded directly onto a P-2 column (0.625 x 42.5 cm) running in 100 mM NH_4CO_3. Fractions containing the desired product were pooled, lyophilized, redissolved in H2O (1 ml) and centrifuged to remove insoluble precipitate. The resulting supernatant

was loaded onto a C18 column (2g) which was washed with H_2O (20 mLs) followed by eluting the desired product with 50% MeOH in H_2O. Yields ranged from 72-78%.

Compound **G35**: HRMS: $C_{49}H_{58}N_6O_{25}$, $[M+H]^+$: Expected: 1131.3524, Found: 1131.3521

^{1}H NMR (600 MHz, MeOD/D_2O) δ 8.70 (s, 1H), 8.37 (s, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 9.1 Hz, 2H), 6.86 (s, 2H), 6.78 (d, J = 9.2 Hz, 2H), 5.32 (s, 2H), 4.48 (d, J = 7.9 Hz, 1H), 4.39 (d, J = 7.7 Hz, 1H), 4.15 – 4.05 (m, 1H), 3.99 – 3.87 (m, 5H), 3.84 (t, J = 9.9 Hz, 1H), 3.79 (dd, J = 11.4, 4.1 Hz, 2H), 3.73 (d, J = 10.1 Hz, 1H), 3.67 – 3.50 (m, 8H), 3.44 (d, J = 9.0 Hz, 1H), 3.38 (t, J = 8.5 Hz, 1H), 3.29 – 3.21 (m, 3H), 2.69 (dd, J = 12.3, 4.4 Hz, 1H), 2.00 (s, 3H), 1.71 (t, J = 12.2 Hz, 1H).

^{13}C NMR (151 MHz, MeOD/D_2O) δ 173.87, 172.49, 170.43, 157.10, 156.27, 143.74, 136.83, 130.37 (2C's), 129.81, 122.73, 122.06, 119.77, 119.03 (2C's) 113.42, 102.59, 102.33 (2C's), 101.36, 99.64, 78.81, 74.13, 73.92, 73.23, 72.13, 71.98, 71.82, 70.18, 69.60, 69.55, 67.99, 67.66, 64.95, 62.99, 59.50, 56.80, 51.31, 47.80, 42.92, 39.76, 38.76, 21.20.

Compound **K35**: HRMS: $C_{50}H_{60}N_6O_{24}$, $[M+H]^+$: Expected: 1129.3732, Found: 1129.3736

^{1}H NMR (600 MHz, MeOD/D_2O) δ 8.47 (s, 1H), 8.32 (s, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.18 (d, J = 9.1 Hz, 2H), 6.71-6.66 (m, 4H), 4.43 (d, J = 7.9 Hz, 1H), 4.36 (d, J = 7.7 Hz, 1H), 4.06 (ddd, J = 11.4, 4.8, 4.8 Hz, 1H), 3.96 (t, J = 9 Hz, 1H), 3.94 – 3.85 (m, 4H), 3.83 – 3.74 (m, 3H), 3.71 (d, J = 10.5 Hz, 1H), 3.65 - 3.55 (m, 6H), 3.52 (t, J = 8.8 Hz, 2H), 3.40 (d, J = 9.3 Hz, 1H), 3.35 (t, J = 8.6 Hz, 1H), 3.29 – 3.24 (m, 1H), 3.20 (t, J = 4.9 Hz, 2H), 3.14 (t, J = 7.5 Hz, 2H), 2.74 (t, J = 7.5 Hz, 2H), 2.70 (dd, J = 12.3, 4.4 Hz, 1H), 2.01 (s, 3H), 1.69 (dd, J = 12.1, 12.1 Hz, 1H).

^{13}C NMR (151 MHz, MeOD/D_2O) δ 175.42, 174.05, 172.71, 159.22, 158.40, 148.51, 142.53, 138.24, 133.70, 132.36, 132.11 (2C's), 123.05 (3C's), 122.28, 122.16, 121.79, 114.40, 104.18, 104.16, 102.94, 101.20, 80.35, 75.68, 75.47, 74.73, 73.69, 73.54, 73.33, 71.75, 71.29, 70.88, 69.52, 69.25, 66.54, 64.48, 61.02, 52.89, 49.37, 43.28, 41.32, 40.31, 35.81, 22.79, 22.07.

Compound **I35**: HRMS: $C_{49}H_{49}N_7O_{24}$, $[M+H]^+$: Expected: 1130.3684, Found: 1130.3681

^{1}H NMR (600 MHz, MeOD/D_2O) δ 8.54 (s, 1H), 8.37 (d, J = 2.0 Hz, 1H), 8.07 (dd, J = 8.2, 2.1 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.12 (d, J = 9.1 Hz, 2H), 6.77 (d, J = 2.0 Hz, 2H), 6.73 (dd, J = 9.2, 2.2 Hz, 2H), 4.53 (s, 2H), 4.46 (d, J = 8.0 Hz, 1H), 4.37 (d, J = 7.8 Hz, 1H), 4.09 (ddd, J = 11.4, 4.8, 4.8 Hz, 1H), 3.97 (t, J = 9 Hz, 1H), 3.95 – 3.87 (m, 4H), 3.83 (t, J = 10.1 Hz, 1H), 3.81 – 3.75 (m, 2H), 3.73 (d, J = 11.8 Hz, 1H), 3.64 (t, J = 8.9 Hz, 2H), 3.62 – 3.50 (m, 6H), 3.44 (d, J = 9.2 Hz, 1H), 3.37 (dd, J = 9.0, 8.2 Hz, 1H), 3.29 – 3.24 (m, 1H), 3.23 (t, J = 5.0 Hz, 2H), 2.71 (dd, J = 12.3, 4.6 Hz, 1H), 2.00 (s, 3H), 1.70 (dd, J = 12.2, 12.1 Hz, 1H).

^{13}C NMR (151 MHz, MeOD/D_2O) δ 173.85, 172.54, 170.48, 159.47, 156.05, 146.74, 136.94, 130.29 (2C's), 129.62, 122.19, 121.13, 119.52, 118.72 (2C's), 113.25, 102.55, 102.33 (2C's), 101.33, 99.64, 78.75, 74.10, 73.87, 73.19, 72.10, 71.92, 71.83, 70.16, 69.87, 69.48, 67.97, 67.67, 64.97, 62.97, 59.45, 51.29, 47.82, 42.19, 39.70, 38.75, 38.10, 34.36, 21.23.

Synthesis of Compounds **G35-Lipid, K35-Lipid,** and **I35-Lipid**

NHS-PEG-Lipid (8.0 mg, 2.61 μmol, 1 eq.) and **G35**, **K35**, or **I35** (3.8 mg, 3.4 μmol, 1.3 eq.) were dissolved in DMSO/CH_2Cl_2 (900 μl, 5.5:3.5 v/v) to which DIEA (50 μl) was added. The reaction was left to proceed overnight and then CH_2Cl_2 was removed by rotary evaporation. The resulting solution was diluted to with H_2O (total volume 3 mLs), added to a 10,000 MWCO Dialysis Cassette (Pierce), and dialyzed against H_2O (2 x 2L). After lyophilization, a yellow solids were obtained, with yields typically

~90-95%. Due to the complexity of these molecules (and the fact that they are a mixture of compounds because of the average molecular weight PEG unit), purity and identity was confirmed by analyzing three characteristic peaks: the terminal methyl groups of the lipid chain, the N-Acetyl from the sialic acid, and the triazole peak.

G35-Lipid

^{1}H NMR (600 MHz, DMSO) δ 9.05 (triazole-H, s, 1H), 1.85 (N-Acetyl-, s, 3H), 0.82 (lipid methyl groups, t, J = 6.9 Hz, 6H).

K35-Lipid

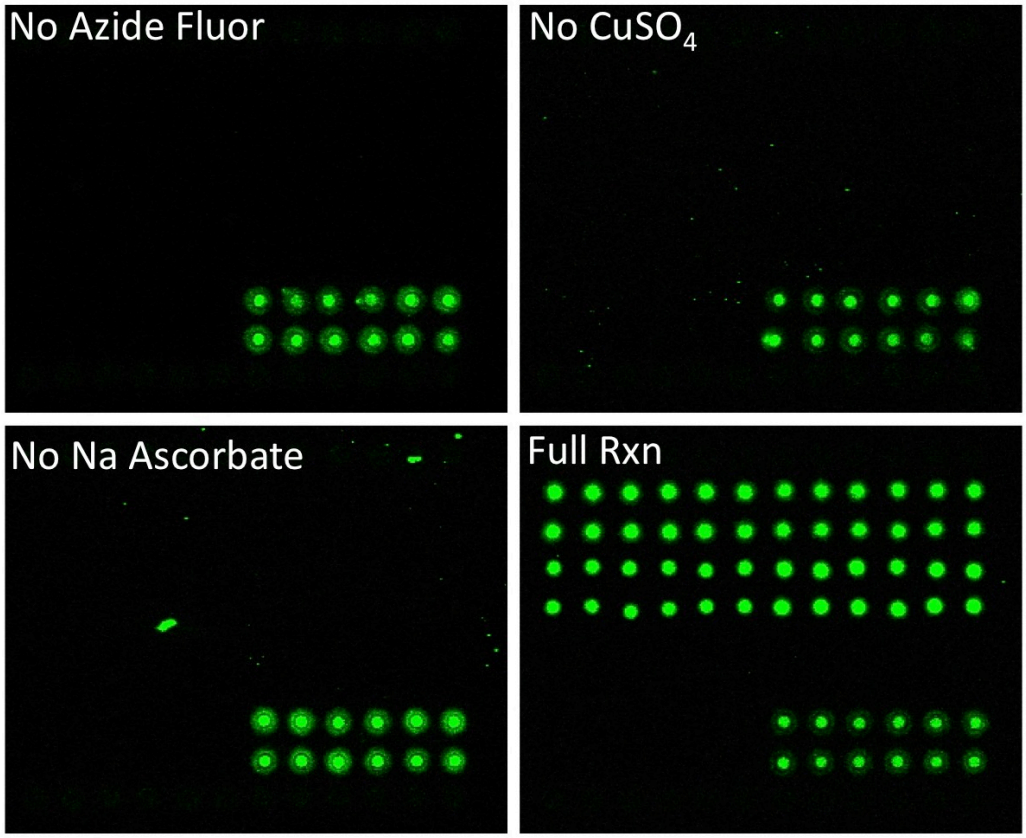
^{1}H NMR (600 MHz, DMSO) δ 8.78 (triazole-H, s, 1H), 1.85 (N-Acetyl-, s, 3H), 0.82 (lipid methyl groups, broad s, 6H).

I35-Lipid

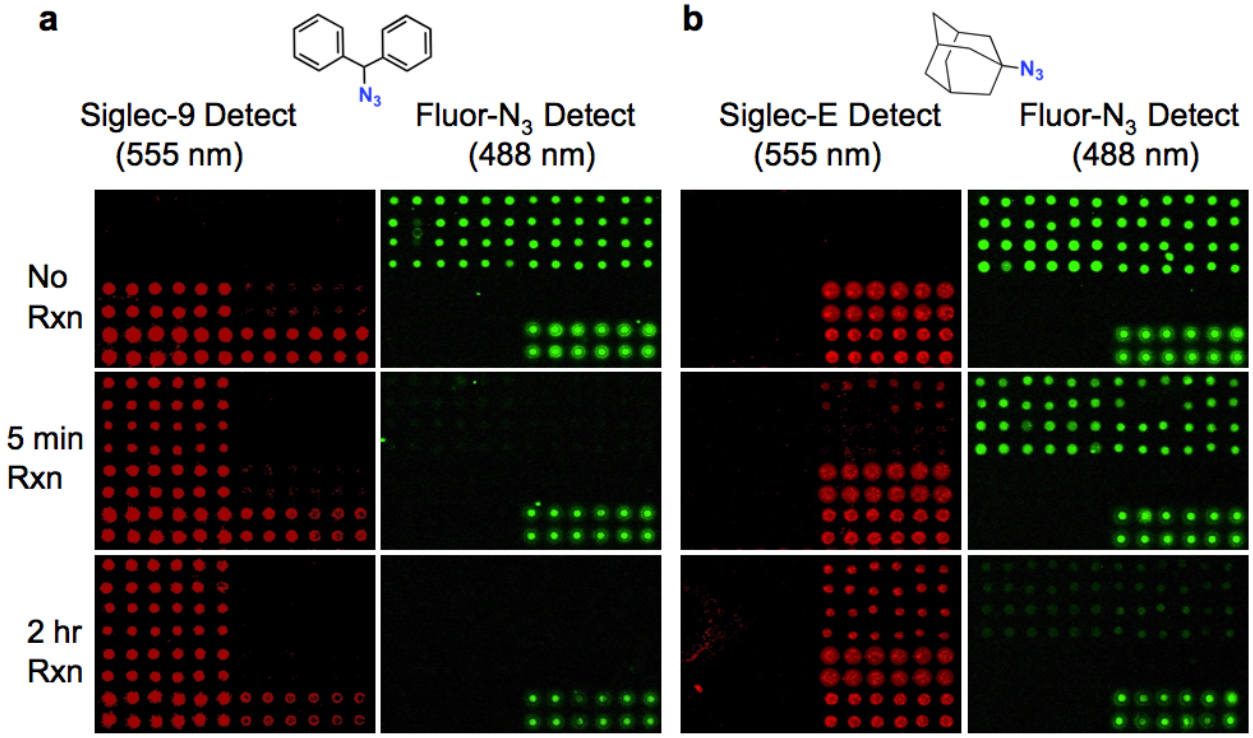
^{1}H NMR (600 MHz, DMSO) δ 8.85 (triazole-H, s, 1H), 1.83 (N-Acetyl-, s, 3H), 0.82 (lipid methyl groups, t, J = 6.9 Hz, 6H).

Supplementary Results

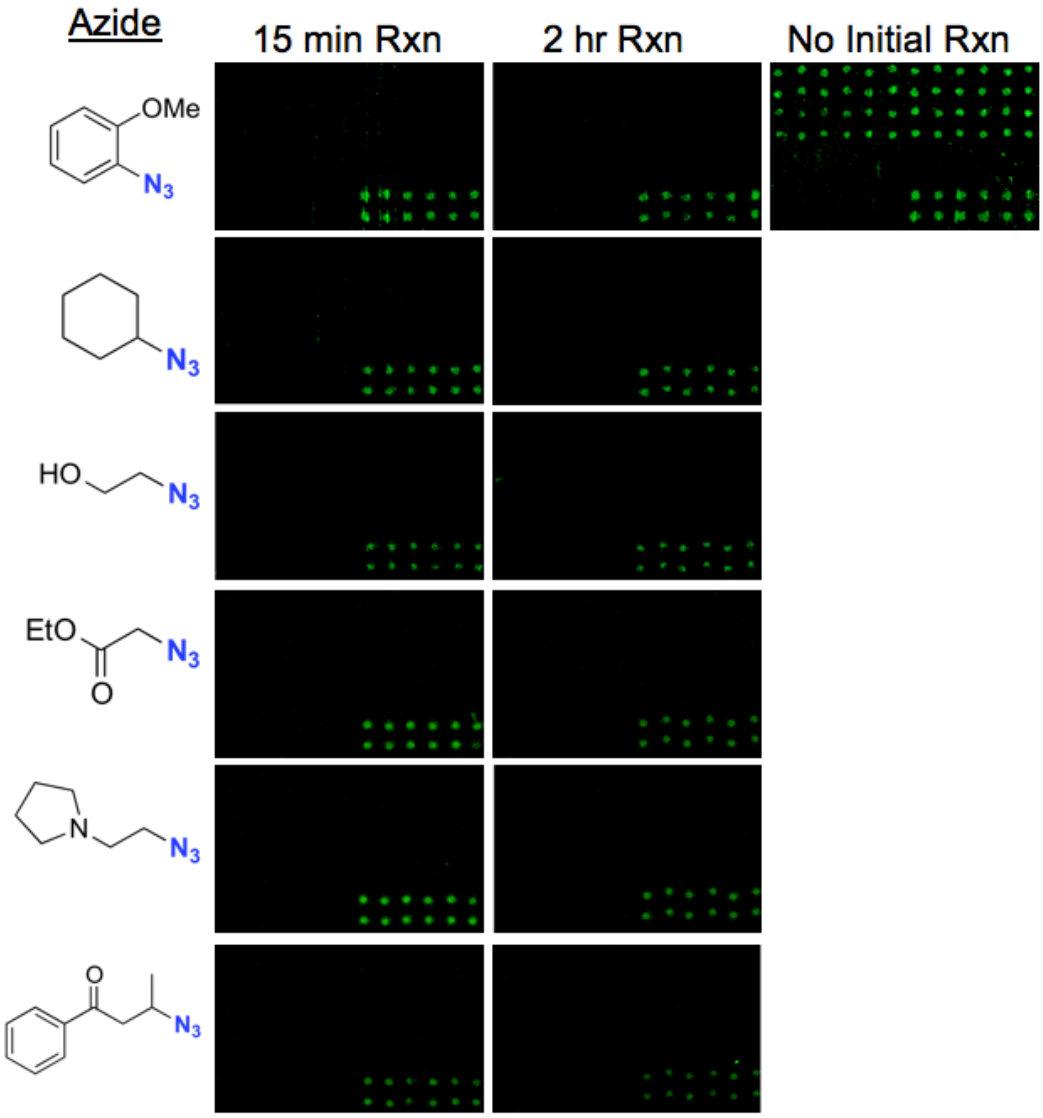
Supplementary Figure 1 - On-chip click reactions proceed via canonical Cu(I)-catalyzed click chemistry (CuAAC). The proof-of-principle array in **Figure 1** was used to show that all traditional components of CuAAC are required for the on-chip click reactions. Reactions were set up with 50 mM 5-azido-fluorescein, 10 mM Sodium Ascorbate, 1 mM $CuSO_4$, and 5 mM THPTA in DMF/H_2O (3:1 v/v) (*bottom right*), or by leaving out 5-azido fluorescein (*top left*), CuSO4 (*top right*), or sodium ascorbate (*bottom left*). After 2 hr reactions, the arrays were washed 3x each with DMF, PBS-Tween, and H_2O before being dried and scanned.



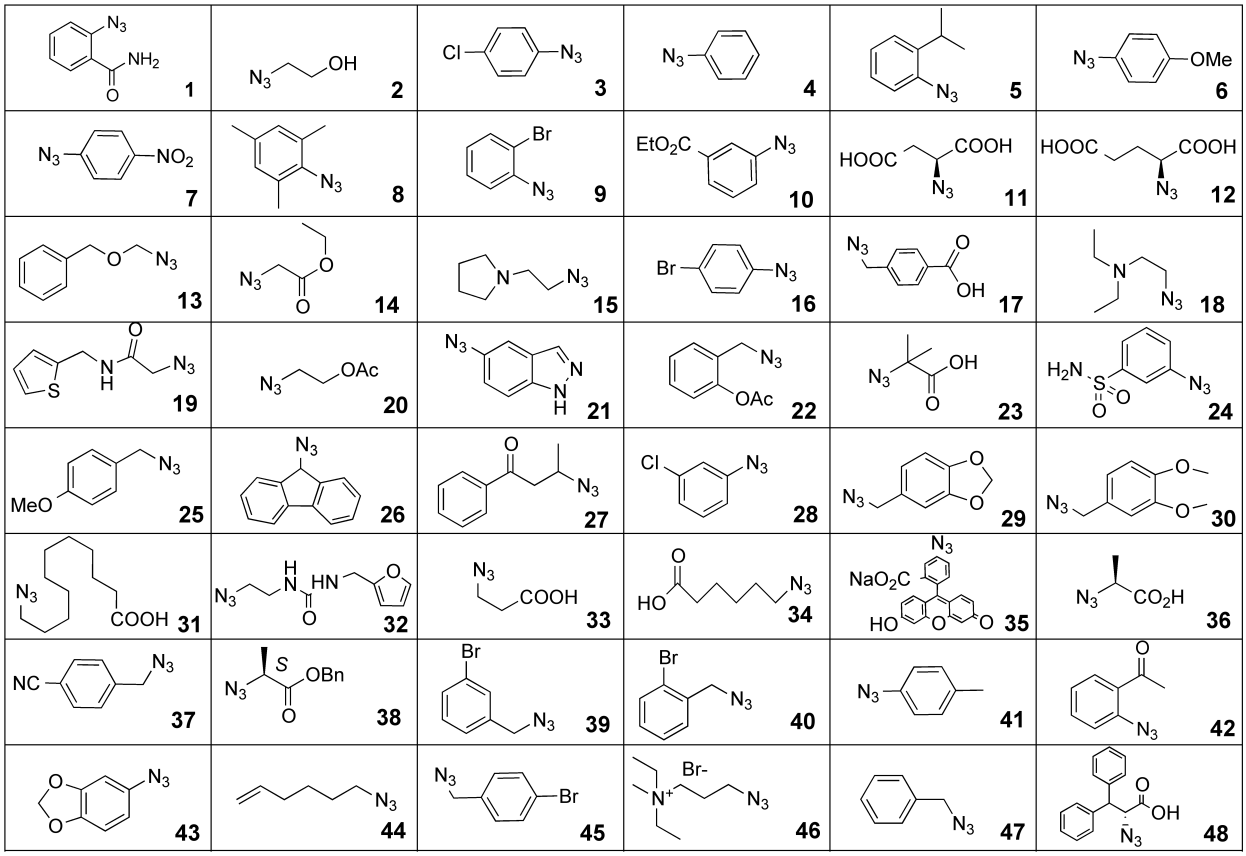
Supplementary Figure 2 – A 2-Step Click-reaction to monitor On-Chip Reaction Progress. To monitor on-chip reaction progress, the proof-of-principle array from **Figure 1** was used with two model azides: (azidomethylene)dibenzene and 1-azidoadamantane. On-chip click reactions were carried out in duplicate with 50 mM azide, 10 mM ascorbate, 1 mM $CuSO_4$, and 5 mM THPTA in DMF/H2O (3:1, v/v) for the indicated amount of time, before the arrays were washed 3x with DMF, PBS-Tween, and H_2O before being centrifuged to dry. To one set of arrays, Siglec-Fc chimeras (Siglec 9 for (azidomethylene)dibenzene, and Siglec-E for 1-azidoadamantane) were applied to read out reaction progress, since the on-chip click products would generate known high-affinity ligands for these Siglecs. To the other set of arrays, a second click reaction with 5-azido-fluorescein (using the reaction conditions above, 1 hr) was carried out to detect any remaining alkynes on the chip surface. The results show that the reaction with (azidomethylene)dibenzene (*left*) is essentially complete in 5 mins as shown by the robust binding of Siglec-9 and the lack of reaction with 5-azido-fluorescein in the second click reaction. In contrast, the much more sterically hindered 1-azidoadamantane (*right*) reacts more slowly, but reaction can be seen at 5 minutes as detected by Siglec-E detection and is nearly complete after 2 hrs as shown by both Siglec-E detection and the second click reaction.



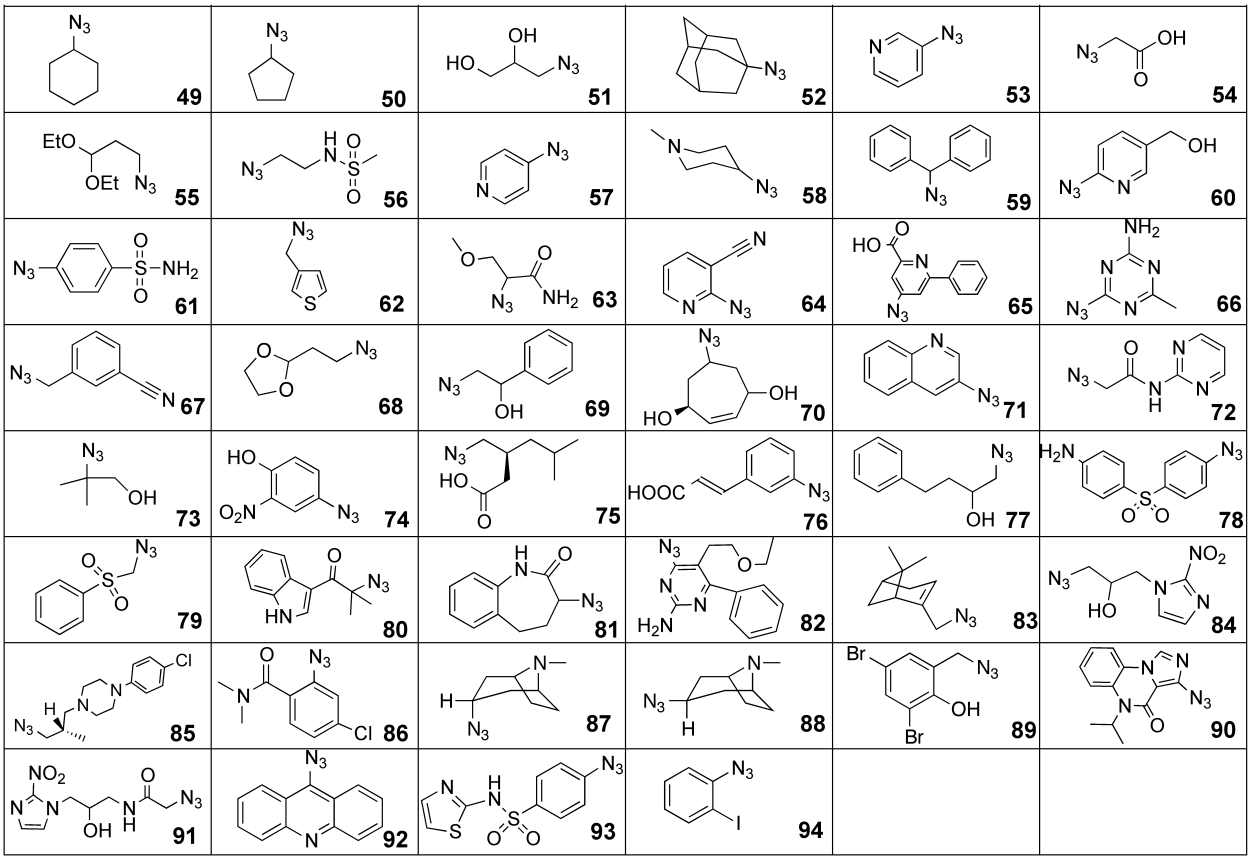
Supplementary Figure 3 – On-chip click reactions with diverse azides are rapid and quantitative as shown using the 2-Step click reaction. To show that the reaction conditions utilized lead to efficient 'on-chip' reactions for diverse azides, the experiments in Supplementary Figure 2 were repeated with a diverse set of 6 azides. Briefly, individual azides were clicked onto the proof-of-principle array (Figure 1) using the standard reactions conditions: 50 mM azide, 10 mM ascorbate, 1 mM $CuSO_4$, and 5 mM THPTA in DMF/H2O (3:1, v/v) for either 15 mins (left) or 2 hrs (right) before the arrays were washed 3x with DMF, PBS-Tween, and H_2O. 5-azido-fluorescein was then clicked onto all of the arrays (using the reaction conditions above, 1 hr) and the slides were similarly washed and then scanned. The lack of any reaction with 5-azido-fluorescein in the second step (except with the untreated slide, far right) shows that the conditions utilized give rapid reaction kinetics with quantitative coupling in 15 minutes.



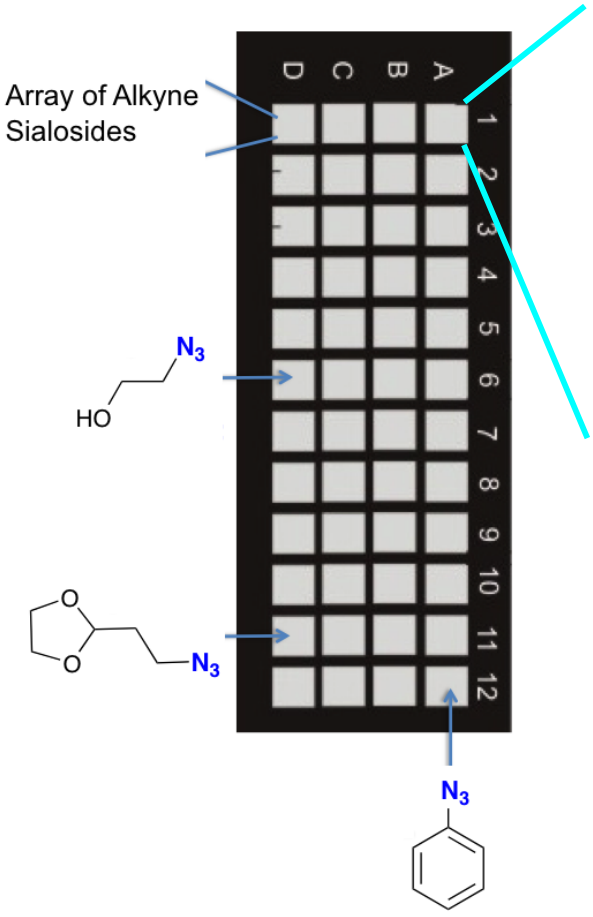
Supplementary Figure 4 – Structure of azides 1-48 used in the high-throughput on-chip synthesis.



Supplementary Figure 5 – Structure of azides 49-94 used in the high-throughput on-chip synthesis.

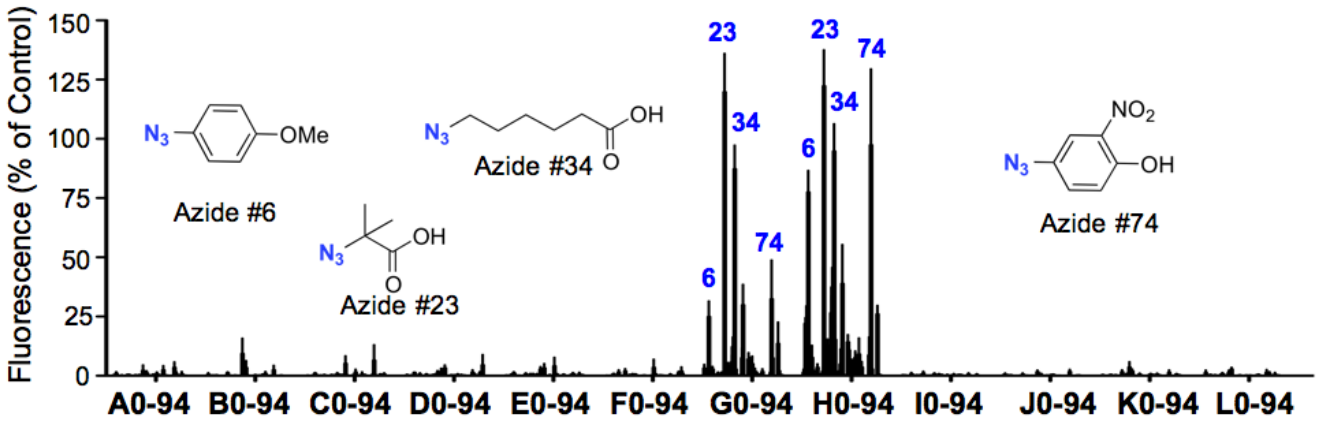


Supplementary Figure 6 – Set-up for the large scale on-chip library construction. Schott-Nexterion MPX-48 slides (see image) were used to construct the microarray. The library of 12 sialosides (Figure 2, compounds A0-L0) and a control compound (Figure 1, Compound VII), were printed into each well of the 48 wells. To facilitate alignment, 3 fluorescent grid markers (Atto-555) were printed at the top-right, and two at the bottom-left. Each individual well was then reacted with a unique azide (as depicted below). In order to construct the full library, two arrays were used wherein azides 1-47 were reacted with array 1 (one well was left unreacted) and the second array was reacted with azides 48-94 (one well was left unreacted).

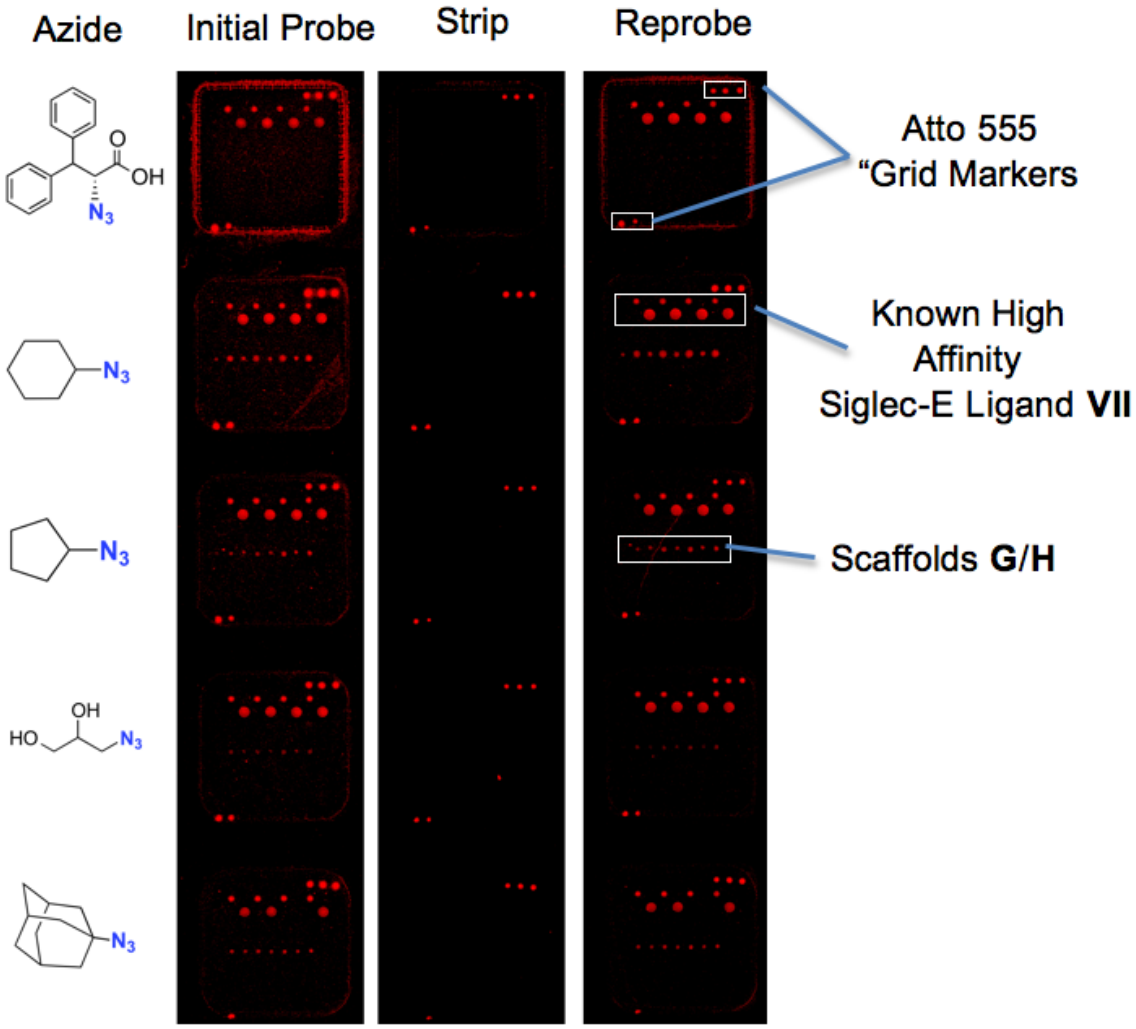


							Atto-555	Atto-555	Atto-555
	VII		VII		VII		VII		
K0	L0	VII		VII		VII		VII	
				K0	L0	K0	L0	K0	L0
I0	J0	I0	J0	I0	J0				
G0	H0	G0	H0	G0	H0	G0	H0	I0	J0
		E0	F0	E0	F0	E0	F0	E0	F0
C0	D0	C0	D0						
						C0	D0	C0	D0
A0	B0	A0	B0	A0	B0	A0	B0		
Atto-555	Atto-555								

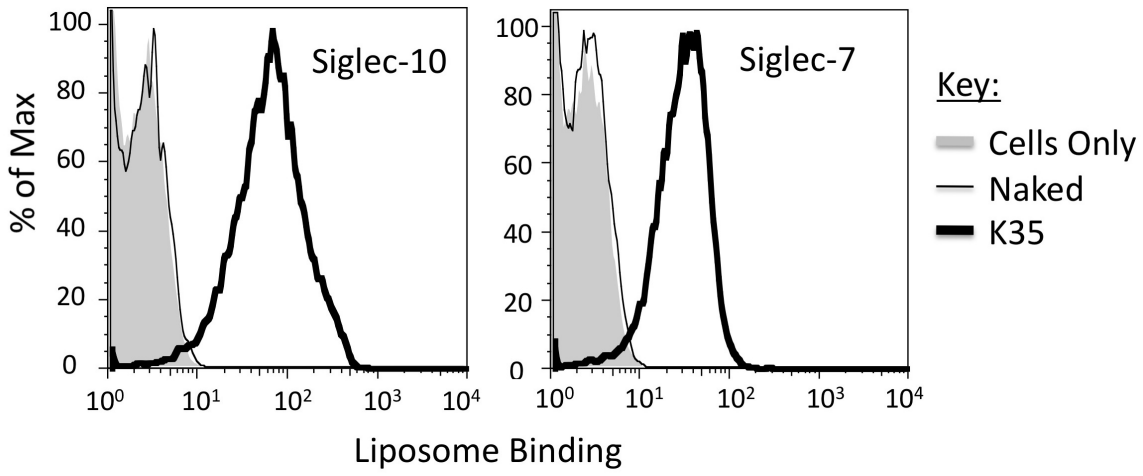
Supplementary Figure 7 – High-throughput Screening Results for Siglec-E. The arrays in **Figure 2** were probed with Siglec-E Fc chimera. The binding intensity in each well was normalized to Compound **VII** (a known high affinity ligand of Siglec-E) and the structures of various hits are shown.



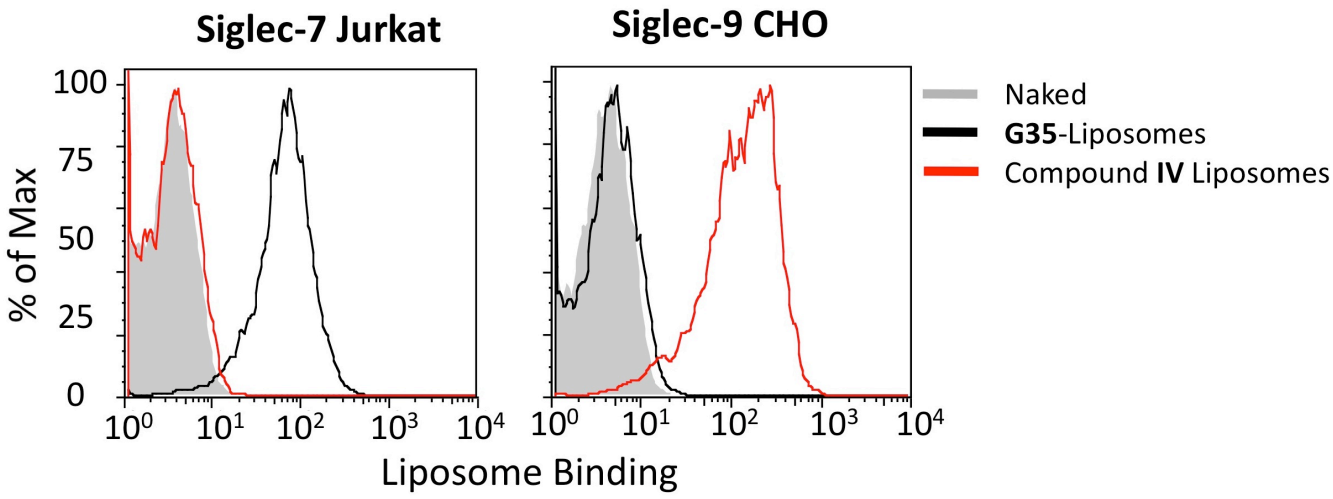
Supplementary Figure 8 – Arrays are reusable and can be stripped and reprobed without loss of signal. Array image used to create some of the data in **Supplementary Figure 7.** After probing the array with Siglec-E Fc chimera (*left*), bound protein was stripped by incubating in a 10% SDS solution in PBS for 1 hr at 37°C. The array was then extensively washed with PBS, H_2O, dried and scanned (*middle*). The array was then reprobed with Siglec-E Fc chimera (*right*). For clarity, the identities of the array signals are depicted on the far right. Each subarray, as described above **in Supplementary Figure 6**, was reacted with a different azide and the identities of these are shown on the far left.



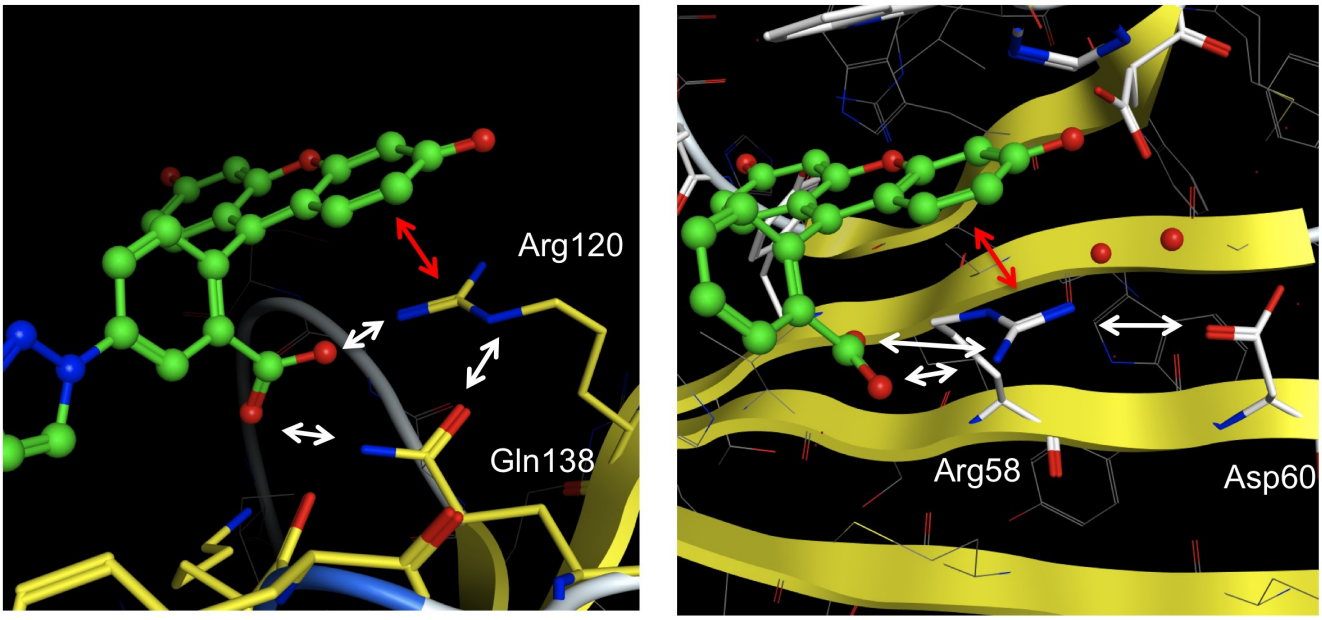
Supplementary Figure 9 – K35 is a high-affinity ligand for Siglec-10. K35, one of the top hits in the Siglec-10 screen (**Figure 2**), was coupled to a PEGylated lipid (**Supplementary Scheme 4**) and formulated into 1% ligand displaying liposomes. These liposomes showed robust binding to Siglec-10 CHO cells (*left*), but also displayed cross-reactivity to Jurkat Siglec-7 cells (*right*) as expected based on the microarray results (**Figure 2**).



Supplementary Figure 10 – G35 Liposomes do not cross-react with Siglec-9 expressing cells. **G35** was coupled to a PEGylated lipid (**Supplementary Scheme 4**) and formulated into 1% ligand displaying liposomes. These liposomes showed robust binding to Siglec-7 Jurkat cells cells (*left*), but do not bind to Siglec-9 CHO cells (*right*). As a positive control, a previously identified Siglec-9 ligand (Compound **IV**, Figure 1a)[5] was coupled to a PEGylated lipid and formulated into 2% ligand liposomes and these show selective binding to Siglec-9 CHO cells (*right*) consistent with our previous observations[5].



Supplementary Figure 11 – The proposed binding contacts of Siglec-7 with the fluorescein moiety of G35 are similar to that observed in a crystal structure of a fluorescein-binding engineered lipocalin flua protein. (*left*) The two primary proposed interactions between Siglec-7 and the fluorescein moiety include H-bonding (white arrows) to the carboxylate (Gln138 and Arg120) and the stacking interaction between the Arg and the xanthene ring (red arrow). The latter interaction is correctly oriented by hydrogen bonding (white arrows) interactions of Arg120 with the carboxylate of fluorescein and the carbonyl of Gln138. (*right*) Similarly, in the engineered lipocalin flua protein structure (PDB ID: 1NOS) one can see H-bonding (white arrows) to the carboxylate and an Arg60 stacking interaction with the xanthene ring (red arrow). Note that the Arg58 is similarly oriented in the correct way by hydrogen bonding (white arrows) interactions with the carboxylate of fluorescein and the Glu60 residue.



Supplementary Table 1 – Complete Siglec 7 Microarray Data (Normalized to Compound VII in each subarray as 100). Subarrays which showed no apparent binding (as analyzed by eye) were not processed by IMAGENE and all compounds from that subarray were assigned a 0 value.

	Sialoside Scaffold											
Azide	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
0	0	0	0	0	0	0	0	0	0	0	0	0
1	-1	-1	1	-1	3	-1	165	1	4	-2	1	1
2	-1	-1	0	1	1	-1	16	11	0	0	1	0
3	-1	6	1	-1	2	1	1330	66	2	-2	-1	-1
4	-1	-2	-2	2	1	3	1301	97	0	0	1	0
5	0	1	0	0	1	-1	17	0	0	0	-1	3
6	-1	1	1	0	1	0	998	56	-1	0	3	2
7	0	2	1	-1	1	3	205	16	1	1	-2	-2
8	2	4	-2	0	1	1	6	2	-1	1	-1	0
9	1	2	2	3	1	2	4	2	1	3	0	0
10	5	-1	1	6	1	3	1401	153	2	-1	6	0
11	0	1	0	2	1	2	1494	26	-1	1	0	0
12	-1	3	1	0	0	0	1300	60	-1	3	0	-1
13	-3	1	1	0	0	-2	281	5	-2	2	14	0
14	0	0	0	1	0	0	9	7	0	-1	-1	2
15	-2	0	0	1	1	1	17	8	-1	0	3	3
16	1	3	8	0	1	-1	726	43	0	1	5	-1
17	1	3	8	0	1	-1	726	43	0	1	5	-1
18	0	2	0	-1	1	3	1	0	2	1	4	3
19	-1	0	12	-1	4	3	4921	149	5	2	6	2
20	0	0	0	0	0	0	0	0	0	0	0	0
21	1	6	2	1	0	2	684	76	-1	0	6	2
22	0	0	0	0	1	2	71	4	-1	0	0	1
23	1	3	1	5	4	1	299	45	1	2	0	1
24	-1	2	-2	4	1	4	1276	21	10	2	2	0
25	-1	0	1	0	2	1	671	26	-1	1	0	2
26	0	0	0	0	0	0	0	0	0	0	0	0
27	3	41	0	3	2	2	767	15	4	2	1	2
28	152	-1	1	-2	2	0	1021	144	0	0	2	0
29	0	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0	0	0
31	2	1	0	-1	-1	0	2895	719	-1	3	19	2
32	-1	1	0	0	1	3	262	30	2	3	13	1
33	0	0	0	0	1	1	991	63	0	1	2	2
34	0	1	0	1	1	1	441	65	1	0	0	1
35	0	0	0	0	0	0	7309	4620	930	916	2476	1813
36	0	0	0	0	0	0	0	0	0	0	0	0
37	0	-1	0	0	-1	1	587	80	-1	1	1	4
38	0	0	1	2	0	-1	759	6	0	1	2	-1

Sialoside Scaffold

Azide	A	B	C	D	E	F	G	H	I	J	K	L
39	5	136	2	4	22	0	1336	8	0	5	1	0
40	81	81	0	-1	2	0	569	29	1	-1	1	0
41	0	1	1	1	0	1	542	59	1	0	5	0
42	0	0	0	0	0	0	0	0	0	0	0	0
43	0	0	8	11	15	6	1723	13	-2	3	-1	0
44	0	0	1	0	0	1	181	8	-1	1	1	0
45	0	0	1	-1	0	0	247	12	0	2	1	1
46	0	0	0	0	0	0	0	0	0	0	0	0
47	4	0	2	2	1	3	285	12	0	0	1	0
48	-1	-1	-2	5	-1	-2	1787	440	0	1	4	3
49	-1	-2	2	2	-2	4	431	25	-3	-1	-1	-1
50	-1	0	3	0	-1	4	309	13	-1	1	-2	0
51	0	0	0	0	0	0	0	0	0	0	0	0
52	1	1	2	0	0	1	55	10	0	2	2	0
53	0	1	5	0	0	1	65	14	1	2	3	0
54	1	2	0	2	0	5	1086	67	-1	2	1	1
55	0	0	0	0	0	0	0	0	0	0	0	0
56	0	0	0	0	0	0	0	0	0	0	0	0
57	1	0	0	0	3	3	59	3	1	2	1	0
58	0	0	0	0	0	0	0	0	0	0	0	0
59	0	0	0	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0	0	0	0
61	0	0	0	0	1	0	1359	119	0	0	1	1
62	0	-1	2	0	0	0	41	12	0	1	0	0
63	-1	-1	0	0	1	1	1549	127	1	0	-1	2
64	0	0	0	0	0	0	0	0	0	0	0	0
65	1	0	1	4	4	4	831	324	4	1	71	2
66	0	0	0	0	0	0	0	0	0	0	0	0
67	0	1	2	4	1	5	168	19	0	3	5	1
68	0	2	1	0	1	0	25	12	0	1	2	1
69	1	0	0	1	1	1	44	3	0	0	3	-1
70	0	5	1	2	1	2	157	23	-1	1	1	3
71	1	0	1	-1	-1	3	389	75	0	1	2	-1
72	-1	-2	1	0	0	1	1048	11	-1	2	5	0
73	0	0	0	0	0	0	0	0	0	0	0	0
74	-1	-1	1	1	1	2	734	45	-1	1	4	2
75	0	0	0	0	0	0	0	0	0	0	0	0
76	0	0	0	0	0	0	0	0	0	0	0	0
77	0	1	0	1	0	2	1713	751	1	0	13	1
78	4	0	0	0	-1	1	288	49	0	0	9	2
79	-1	-1	0	3	1	1	178	6	2	0	0	0
80	-1	1	-1	1	-1	6	36	11	0	1	2	0
81	1	1	1	0	2	2	1619	126	0	0	173	0

Sialoside Scaffold

Azide	A	B	C	D	E	F	G	H	I	J	K	L
82	1	0	1	3	1	1	454	47	1	0	2	1
83	0	0	0	0	0	0	0	0	0	0	0	0
84	-1	-1	0	0	0	3	661	2	1	0	11	5
85	-1	0	-1	0	1	1	972	2	0	2	1	1
86	0	0	0	0	0	0	0	0	0	0	0	0
87	0	0	0	0	0	0	0	0	0	0	0	0
88	0	0	0	0	0	0	0	0	0	0	0	0
89	0	-27	-14	-7	-19	-12	2429	625	-24	-28	-23	-23
90	0	2	0	0	-1	1	542	2	0	1	1	0
91	0	0	0	0	0	0	0	0	0	0	0	0
92	0	0	1	6	1	2	79	2	4	0	1	0
93	1	3	3	1	-1	6	1275	460	0	1	43	1
94	0	0	0	0	0	0	0	0	0	0	0	0

Supplementary Table 2 – Complete Siglec-10 Microarray Data (Normalized to Compound VII in each subarray as 100). Subarrays which showed no apparent binding (as analyzed by eye) were not processed by IMAGENE and all compounds from that subarray were assigned a 0 value.

	Sialoside Scaffold											
Azide	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
0	0	0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0	0	0
2	-17	-28	16	-1	0	0	4	8	1	0	13	2
3	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0	0	0
6	4	3	0	0	0	1	1	39	0	0	0	0
7	19	0	0	0	1	0	3	20	0	1	1	0
8	0	0	0	0	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	0	0	0	0	0
10	4	-1	0	0	0	1	0	94	0	3	0	0
11	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	-1	1	-1	1	1	0	0	1
17	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0
21	0	0	0	0	0	0	0	0	0	0	0	0
22	0	0	0	0	0	0	0	0	0	0	0	0
23	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	155	0	0	0	0
25	0	0	0	0	0	0	0	0	0	0	0	0
26	0	0	0	0	0	0	0	0	0	0	0	0
27	0	0	0	0	0	0	0	0	0	0	0	0
28	201	200	35	-2	0	0	0	7	0	0	5	3
29	0	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0	0	0
31	0	0	0	0	0	0	0	0	0	0	0	0
32	-1	0	0	1	0	1	-1	0	-1	-1	-1	-1
33	0	0	0	0	0	0	0	0	0	0	0	0
34	0	0	0	0	0	0	0	0	0	0	0	0
35	0	0	-1	0	1	3	26	84	0	2	886	858
36	0	0	0	0	0	0	0	0	0	0	0	0
37	100	55	7	0	0	0	268	304	0	0	1	3
38	0	0	0	0	0	0	0	0	0	0	0	0
39	229	278	7	17	0	0	6	65	-1	1	0	1
40	0	0	0	0	0	0	0	0	0	0	0	0
41	0	0	0	0	0	0	0	0	0	0	0	0

Sialoside Scaffold

Azide	A	B	C	D	E	F	G	H	I	J	K	L
42	0	0	0	0	0	0	0	0	0	0	0	0
43	-1	-4	0	0	0	0	1	12	1	0	0	2
44	-3	-3	-1	0	0	0	1	14	1	0	0	0
45	173	160	0	0	0	0	2	28	0	0	3	7
46	0	0	0	0	0	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0	0	0	0	0	0
48	0	0	0	0	0	0	0	0	0	0	0	0
49	0	0	0	0	0	0	0	0	0	0	0	0
50	170	148	0	12	0	0	0	0	2	0	6	0
51	0	0	0	0	0	0	0	0	0	0	0	0
52	0	0	0	0	0	0	6	45	0	0	1	0
53	7	16	-1	0	1	0	1	1	-1	1	25	22
54	5	3	0	0	0	0	0	1	-1	0	20	1
55	0	0	0	0	0	0	0	0	0	0	0	0
56	0	0	0	0	0	0	0	0	0	0	0	0
57	0	1	-1	0	0	0	0	2	0	0	12	2
58	0	0	0	0	0	0	0	0	0	0	0	0
59	0	0	0	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0	0	0	0
61	0	0	0	0	0	0	0	0	0	0	0	0
62	0	0	0	0	0	0	0	0	0	0	0	0
63	0	0	0	0	0	0	0	0	0	0	0	0
64	0	0	0	0	0	0	0	0	0	0	0	0
65	0	0	0	0	0	0	0	0	0	0	0	0
66	0	0	0	0	0	0	0	0	0	0	0	0
67	-2	-2	0	0	0	0	31	404	0	1	1	0
68	0	0	0	0	0	0	0	0	0	0	0	0
69	0	0	0	0	0	0	0	0	0	0	0	0
70	0	0	0	0	0	0	0	0	0	0	0	0
71	0	0	0	0	0	0	0	6	0	0	0	0
72	45	44	0	0	0	0	0	0	0	0	5	1
73	0	0	0	0	0	0	0	0	0	0	0	0
74	104	56	7	3	1	0	8	18	0	-1	2	0
75	0	0	0	0	0	0	0	0	0	0	0	0
76	0	0	0	0	0	0	0	0	0	0	0	0
77	0	3	0	0	0	0	0	0	0	0	1	1
78	0	0	0	0	0	0	0	0	0	0	0	0
79	0	0	0	0	0	0	0	0	0	0	0	0
80	0	0	0	0	0	0	0	0	0	0	0	0
81	-1	0	0	-1	-2	0	-2	-1	0	0	123	95
82	0	0	0	0	0	0	0	0	0	0	0	0
83	0	0	0	0	0	0	0	0	0	0	0	0
84	62	57	-1	0	0	0	0	0	0	0	3	1
85	0	0	0	0	0	0	0	0	0	0	0	0
86	0	0	0	0	0	0	0	0	0	0	0	0
87	0	0	0	0	0	0	0	0	0	0	0	0

Sialoside Scaffold

Azide	A	B	C	D	E	F	G	H	I	J	K	L
88	0	3	0	0	0	0	1	1	0	0	264	251
89	0	0	0	0	0	0	0	0	0	0	0	0
90	0	0	0	0	0	0	0	0	0	0	0	0
91	-14	-15	-1	-1	-1	0	3	9	0	0	52	42
92	0	0	0	0	0	0	0	0	0	0	0	0
93	0	0	1	1	0	0	4	6	0	0	0	1
94	0	0	0	0	0	0	0	0	0	0	0	0

Supplementary Table 3 – Complete Siglec-E Microarray Data (Normalized to Compound VII in each subarray as 100). Subarrays which showed no apparent binding (as analyzed by eye) were not processed by IMAGENE and all compounds from that subarray were assigned a 0 value.

	Sialoside Scaffold											
Azide	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
0	0	0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	3	1	0	0	0	0
2	0	1	0	0	0	0	1	3	0	0	0	0
3	0	0	0	0	0	0	2	22	0	1	0	0
4	0	0	0	0	0	0	2	22	0	1	0	0
5	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	25	78	0	0	0	1
7	0	0	0	0	0	0	2	3	0	0	0	0
8	0	0	0	0	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	1	2	0	0	0	0
10	1	0	1	1	1	1	3	8	1	0	0	0
11	0	0	0	0	1	1	1	2	1	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	1	0	2	1	4	0	0	0	0
17	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	1	1	0	0	0	0
21	0	0	0	0	0	0	0	0	0	0	0	0
22	0	0	0	0	0	0	0	2	0	0	0	0
23	0	1	0	1	1	2	120	122	1	1	2	1
24	0	0	0	0	0	0	1	2	0	0	0	1
25	0	0	0	0	0	0	0	0	0	0	0	0
26	0	0	0	0	0	0	0	0	0	0	0	0
27	0	0	0	0	0	0	4	13	0	0	0	0
28	0	0	0	0	1	0	1	1	0	0	1	0
29	0	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0	0	0
31	0	0	0	1	1	1	6	27	0	0	4	1
32	0	0	0	0	0	0	12	37	0	0	0	0
33	0	0	0	0	0	0	4	11	0	0	0	0
34	0	0	1	0	0	1	87	95	0	0	2	3
35	0	0	1	1	1	0	3	15	1	0	0	0
36	0	0	0	0	0	0	0	0	0	0	0	0
37	0	0	0	0	0	0	0	0	0	0	0	0
38	0	0	0	0	0	0	0	0	0	0	0	0
39	2	9	0	2	3	0	0	1	0	2	0	0
40	1	1	0	0	0	0	0	2	1	0	0	0
41	0	0	0	0	0	0	0	5	0	0	0	0

Sialoside Scaffold

Azide	A	B	C	D	E	F	G	H	I	J	K	L
42	0	0	0	0	0	0	8	11	0	0	1	0
43	1	3	5	3	3	0	30	39	0	1	0	0
44	1	0	0	0	0	0	0	1	0	0	0	0
45	0	0	0	0	0	0	0	0	0	0	0	0
46	0	0	0	0	0	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0	0	0	0	0	0
48	0	0	0	0	0	0	0	0	0	0	0	0
49	0	0	0	0	0	0	7	14	0	0	0	0
50	1	0	0	0	0	0	6	11	0	0	0	0
51	0	0	0	0	0	0	0	2	0	0	0	0
52	0	0	0	0	0	0	3	5	0	0	0	0
53	0	0	0	0	0	0	5	7	0	0	1	0
54	1	0	2	0	4	4	2	4	0	0	1	0
55	0	0	0	0	0	0	0	0	0	0	0	0
56	0	0	0	0	0	1	2	4	1	1	0	0
57	0	0	0	1	1	0	2	8	0	0	0	0
58	0	0	0	0	0	0	0	0	0	0	0	0
59	0	0	0	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0	0	0	0
61	2	1	1	0	0	0	1	9	0	0	1	0
62	0	0	0	0	0	0	0	0	0	0	0	0
63	0	0	0	0	0	0	0	1	0	0	0	1
64	0	1	0	0	1	0	2	4	0	0	0	0
65	0	0	0	0	0	0	0	0	0	0	0	0
66	0	0	0	0	0	0	0	0	0	0	0	0
67	0	0	0	0	0	0	0	0	0	0	0	0
68	0	0	0	0	0	0	0	0	0	0	0	0
69	0	0	0	0	0	0	0	0	0	0	0	0
70	0	0	0	0	0	0	0	0	0	0	0	0
71	0	0	0	0	0	0	0	0	0	0	0	0
72	0	0	0	0	0	1	0	9	1	0	0	1
73	4	2	1	1	0	0	1	2	0	0	0	1
74	0	0	7	1	1	0	32	97	0	2	1	0
75	1	0	0	1	1	0	7	3	0	0	0	1
76	0	0	0	0	0	0	0	0	0	0	0	0
77	0	0	0	0	0	0	0	0	0	0	0	0
78	0	0	0	0	0	0	0	0	0	0	0	0
79	0	0	0	0	0	0	0	0	0	0	0	0
80	0	0	0	0	0	0	0	0	0	0	0	0
81	1	0	1	1	1	1	14	26	1	0	0	1
82	0	0	0	1	0	0	2	1	0	0	1	0
83	0	0	0	0	0	0	0	0	0	0	0	0
84	0	0	0	5	0	2	0	0	0	0	0	0
85	0	0	1	0	0	1	0	0	0	0	0	0
86	0	0	0	0	0	0	0	0	0	0	0	0
87	0	0	0	0	0	0	0	0	0	0	0	0

	Sialoside Scaffold											
Azide	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
88	0	3	0	0	0	0	1	1	0	0	264	251
89	0	0	0	0	0	0	0	0	0	0	0	0
90	0	0	0	0	0	0	0	0	0	0	0	0
91	-14	-15	-1	-1	-1	0	3	9	0	0	52	42
92	0	0	0	0	0	0	0	0	0	0	0	0
93	0	0	1	1	0	0	4	6	0	0	0	1
94	0	0	0	0	0	0	0	0	0	0	0	0

References

(1) Hein, J. E., Krasnova, L.B., Iwasaki, M., Fokin, V.V. (2011) Cu-Catalyzed Azide-Alkyne Cycloaddition: Preparation of tris((1-Benzyl-1H-1,2,3-triazolyl)methyl)amine., *Org. Synth. 88*, 238-246.

(2) Chan, T. R., Hilgraf, R., Sharpless, K. B., and Fokin, V. V. (2004) Polytriazoles as copper(I)-stabilizing ligands in catalysis., *Org Lett 6*, 2853-2855.

(3) Hong, V., Presolski, S. I., Ma, C., and Finn, M. G. (2009) Analysis and optimization of copper-catalyzed azide-alkyne cycloaddition for bioconjugation., *Angew Chem Int Ed Engl 48*, 9879-9883.

(4) Blixt, O., Vasiliu, D., Allin, K., Jacobsen, N., Warnock, D., Razi, N., Paulson, J. C., Bernatchez, S., Gilbert, M., and Wakarchuk, W. (2005) Chemoenzymatic synthesis of 2-azidoethyl-ganglio-oligosaccharides GD3, GT3, GM2, GD2, GT2, GM1, and GD1a., *Carbohydr Res 340*, 1963-1972.

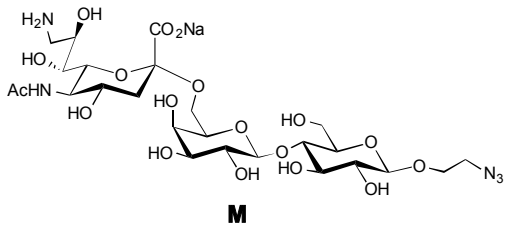
(5) Rillahan, C. D., Schwartz, E., McBride, R., Fokin, V. V., and Paulson, J. C. (2012) Click and pick: identification of sialoside analogues for siglec-based cell targeting, *Angew Chem Int Ed Engl 51*, 11014-11018.

(6) Karwaski, M. F., Wakarchuk, W. W., and Gilbert, M. (2002) High-level expression of recombinant Neisseria CMP-sialic acid synthetase in Escherichia coli., *Protein Expr Purif 25*, 237-240.

(7) Yu, H., Huang, S., Chokhawala, H., Sun, M., Zheng, H., and Chen, X. (2006) Highly efficient chemoenzymatic synthesis of naturally occurring and non-natural alpha-2,6-linked sialosides: a P. damsela alpha-2,6-sialyltransferase with extremely flexible donor-substrate specificity., *Angew Chem Int Ed Engl 45*, 3938-3944.

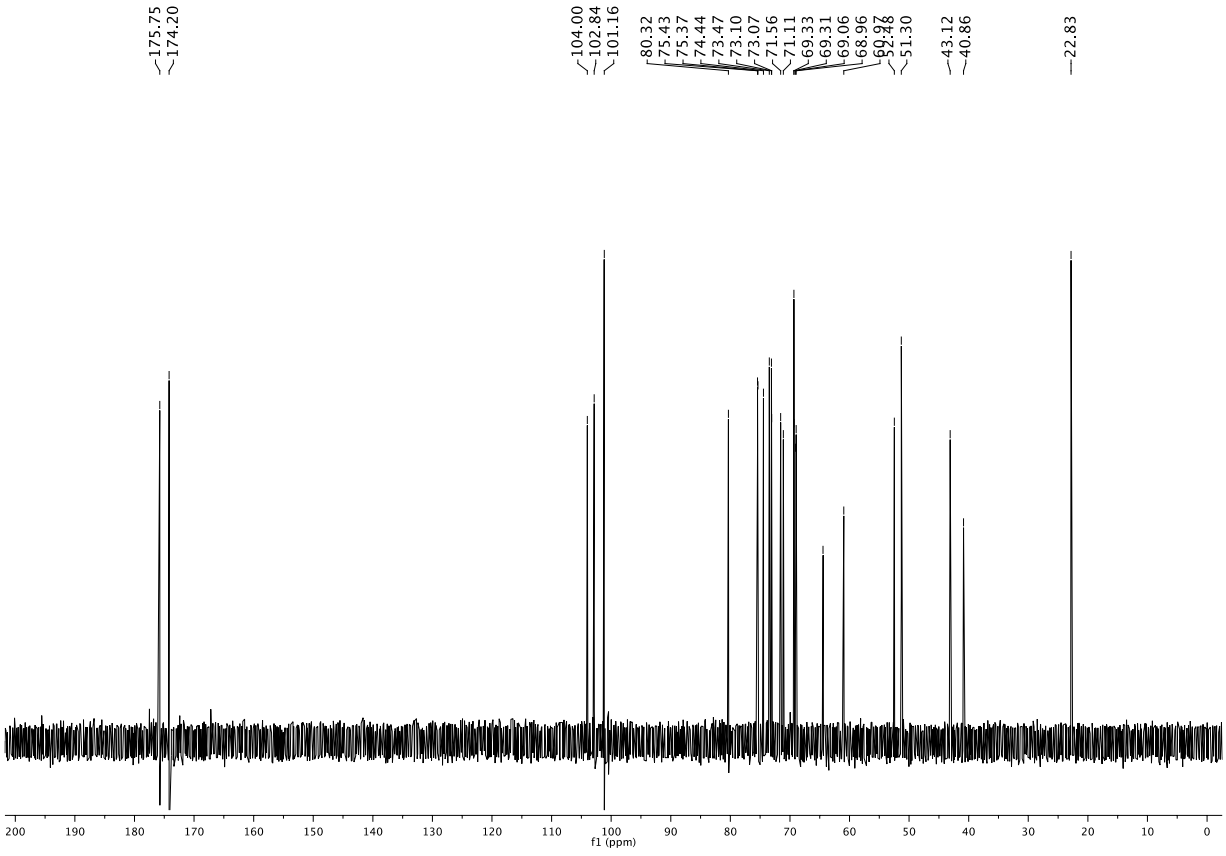
(8) Yu, H., Chokhawala, H., Karpel, R., Wu, B., Zhang, J., Zhang, Y., Jia, Q., and Chen, X. (2005) A multifunctional Pasteurella multocida sialyltransferase: a powerful tool for the synthesis of sialoside libraries., *J Am Chem Soc 127*, 17618-17619.

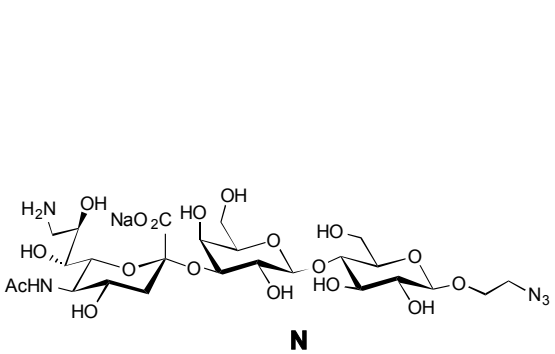
(9) Suzuki, T., Ota, Y., Kasuya, Y., Mutsuga, M., Kawamura, Y., Tsumoto, H., Nakagawa, H., Finn, M. G., and Miyata, N. (2010) An unexpected example of protein-templated click chemistry, *Angew Chem Int Ed Engl 49*, 6817-6820.


H2N
OH
CO2Na
HO
AcHN
HO
HO
HO
HO
OH
HO
HO
HO
OH
O
N3

M

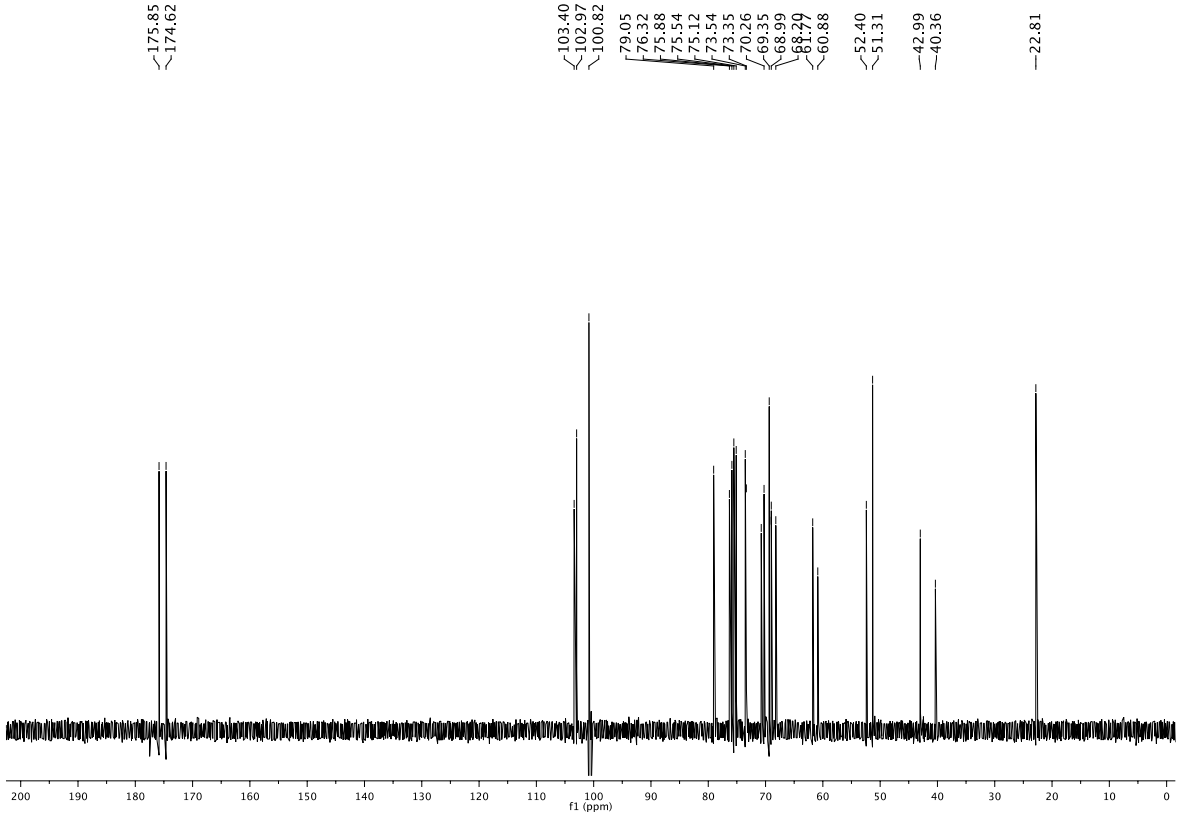
4.41
4.39
4.31
4.30
3.80
3.80
3.72
3.53
3.52
3.51
3.42
2.86
2.86
2.84
2.59
2.58
2.56
2.56
1.89
1.62
1.60
1.58
1.00
1.03
2.00
3.07
5.11
9.99
1.99
1.02
1.03
2.89
1.00
f1 (ppm)

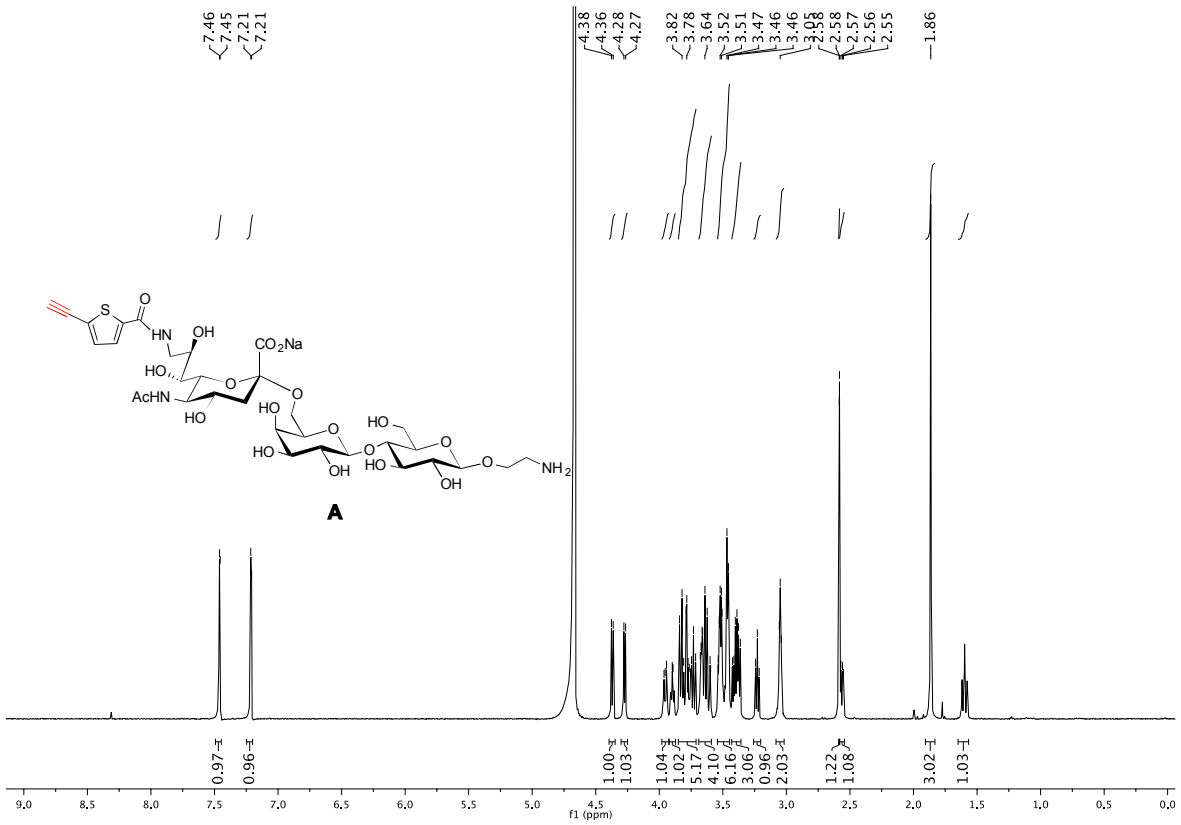

175.75
174.20
104.00
102.84
101.16
80.32
75.43
75.37
74.44
73.47
73.10
73.07
71.56
71.11
69.33
69.31
69.06
68.96
60.48
51.30
43.12
40.86
22.83
f1 (ppm)

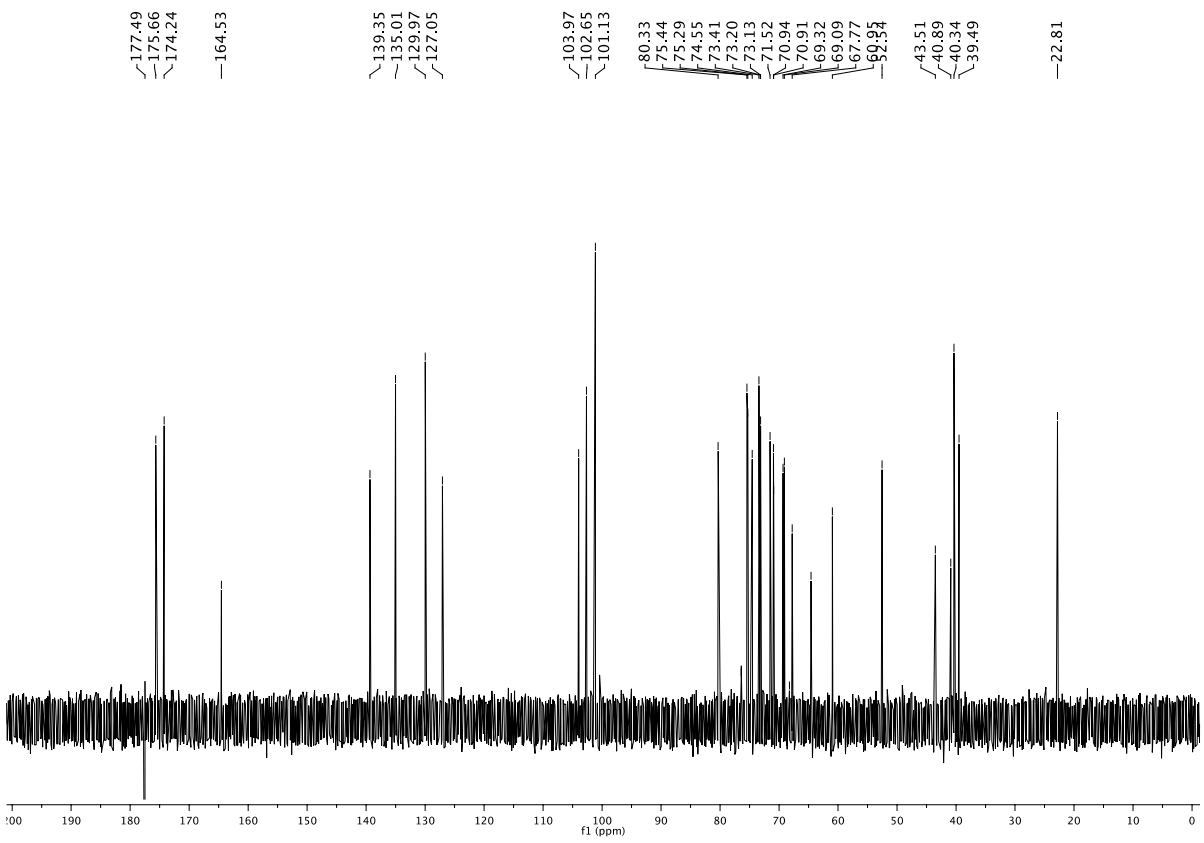

H2N
OH
NaO2C
HO
OH
HO
O
O
O
AcHN
HO
OH
HO
HO
O
HO
OH
O
N3

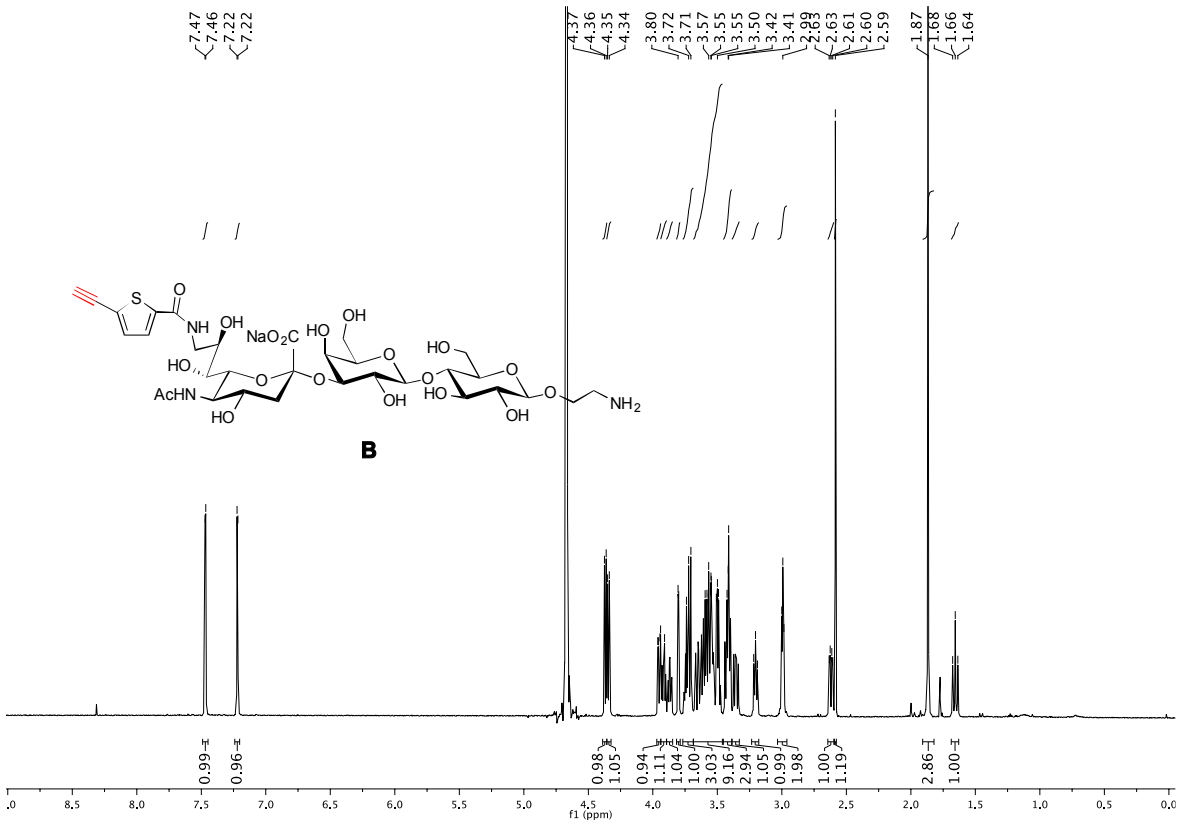
N

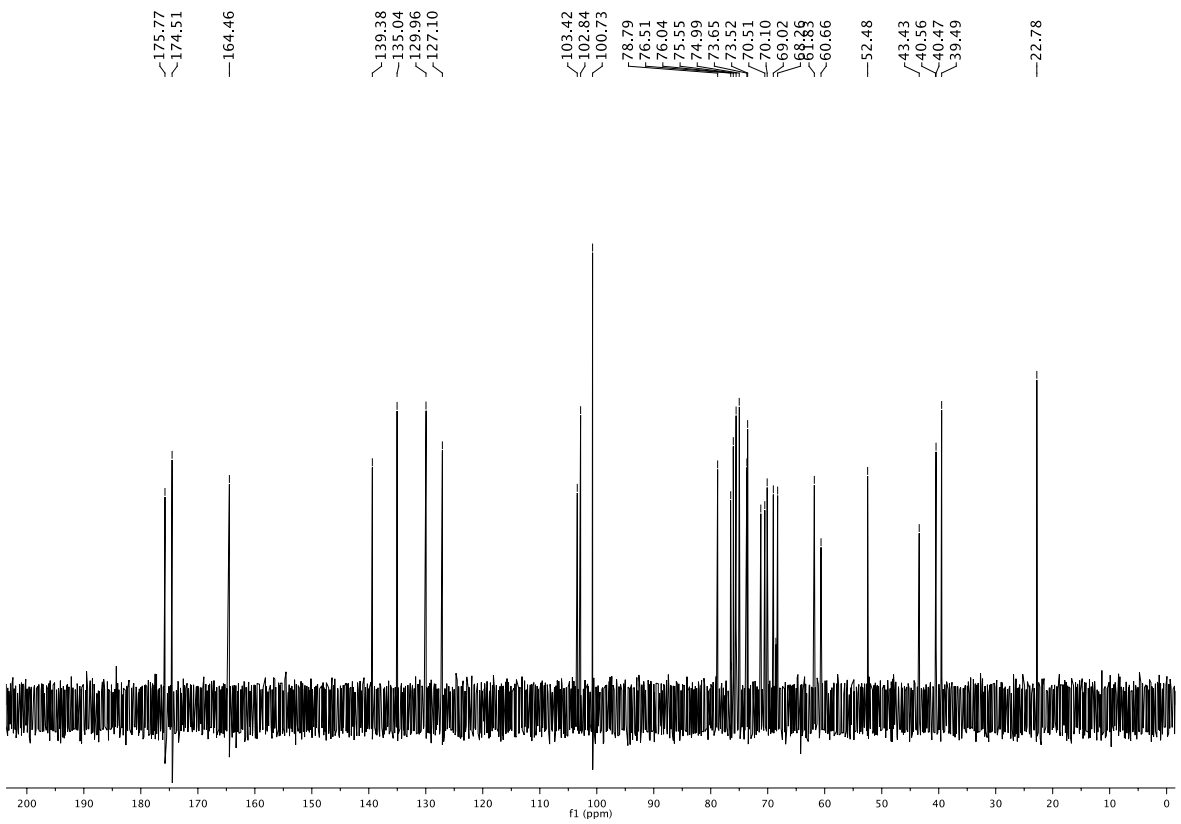
4.408
4.405
4.395
4.392
3.693
3.575
3.532
3.508
3.430
3.421
3.417
3.414
2.881
2.865
2.859
2.843
2.631
2.623
1.690
1.669
1.649
1.92
0.99
1.96
0.96
1.01
2.97
12.00
0.97
0.92
1.00
1.00
2.92
0.98
f1 (ppm)

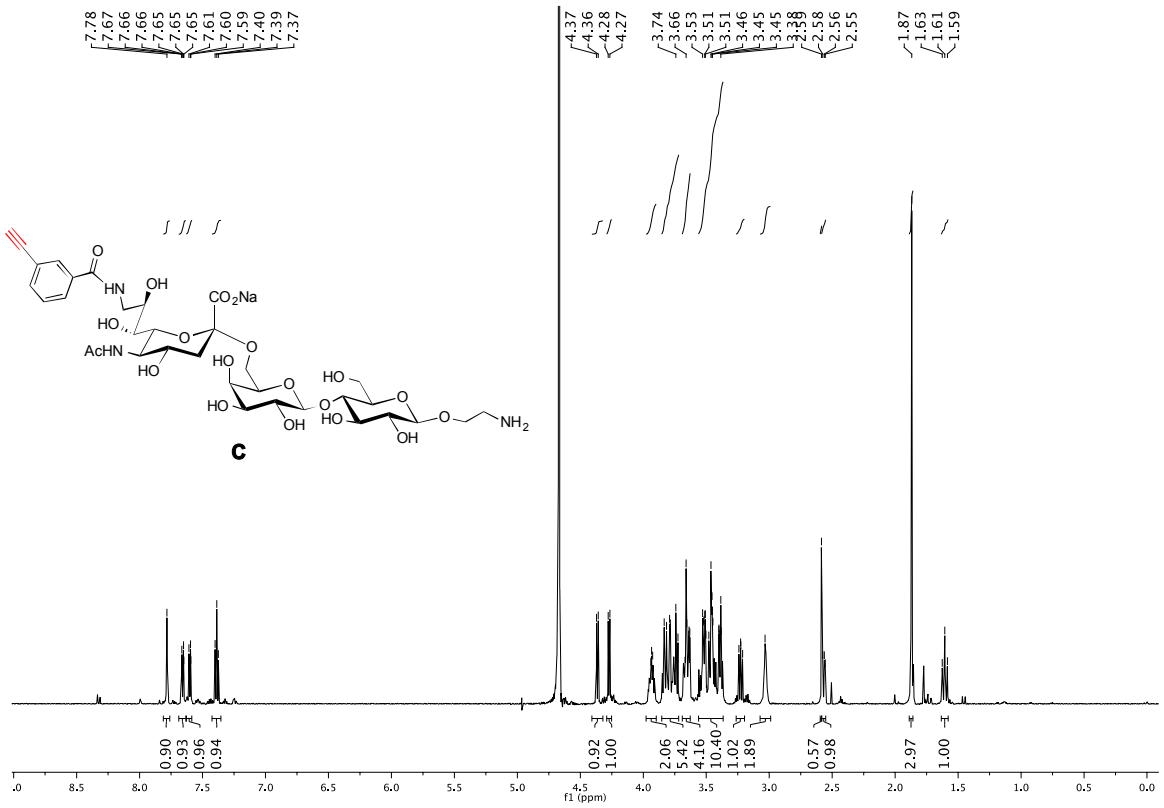

175.85
174.62
103.40
102.97
100.82
79.05
76.32
75.88
75.54
75.12
73.54
73.35
70.26
69.35
68.99
60.88
52.40
51.31
42.99
40.36
22.81
f1 (ppm)

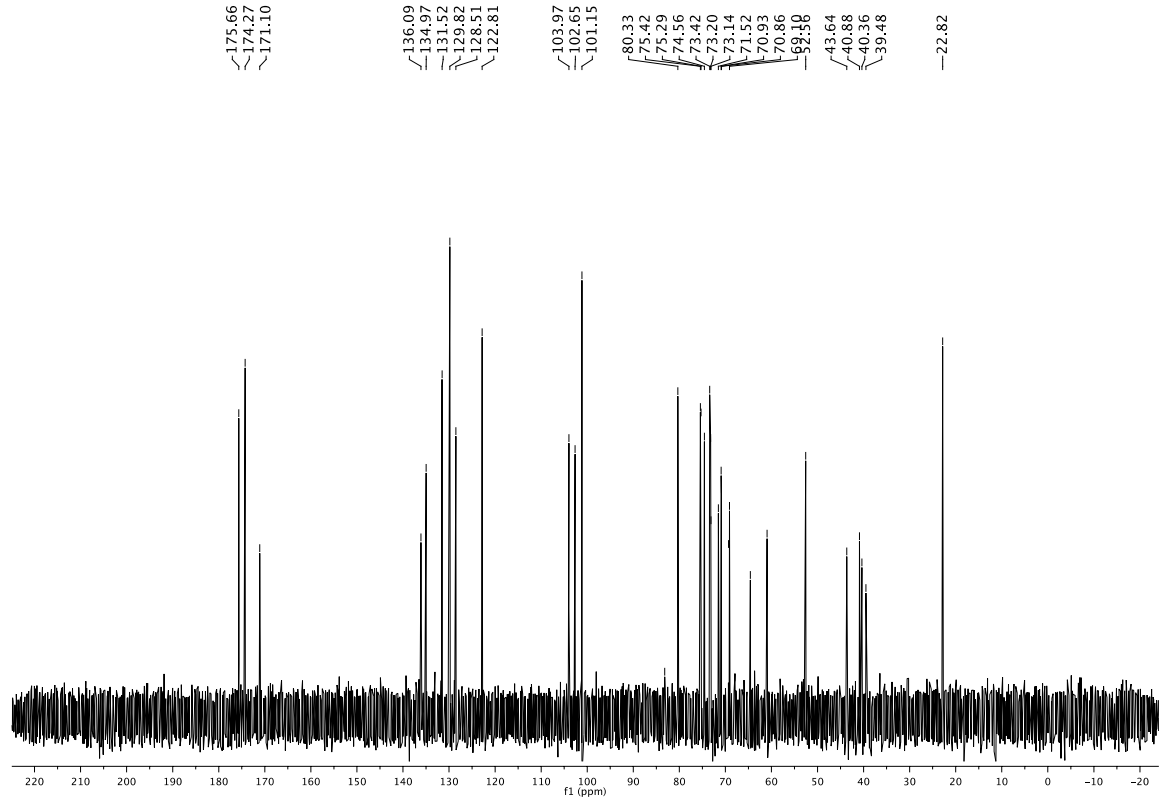

7.46
7.45
7.21
7.21
4.38
4.36
4.28
4.27
3.82
3.78
3.64
3.52
3.51
3.47
3.46
3.46
2.58
2.57
2.56
2.55
1.86
A
0.97
0.96
1.00
1.03
1.04
1.02
5.17
4.10
6.16
3.06
0.96
2.03
1.22
1.08
3.02
1.03
f1 (ppm)

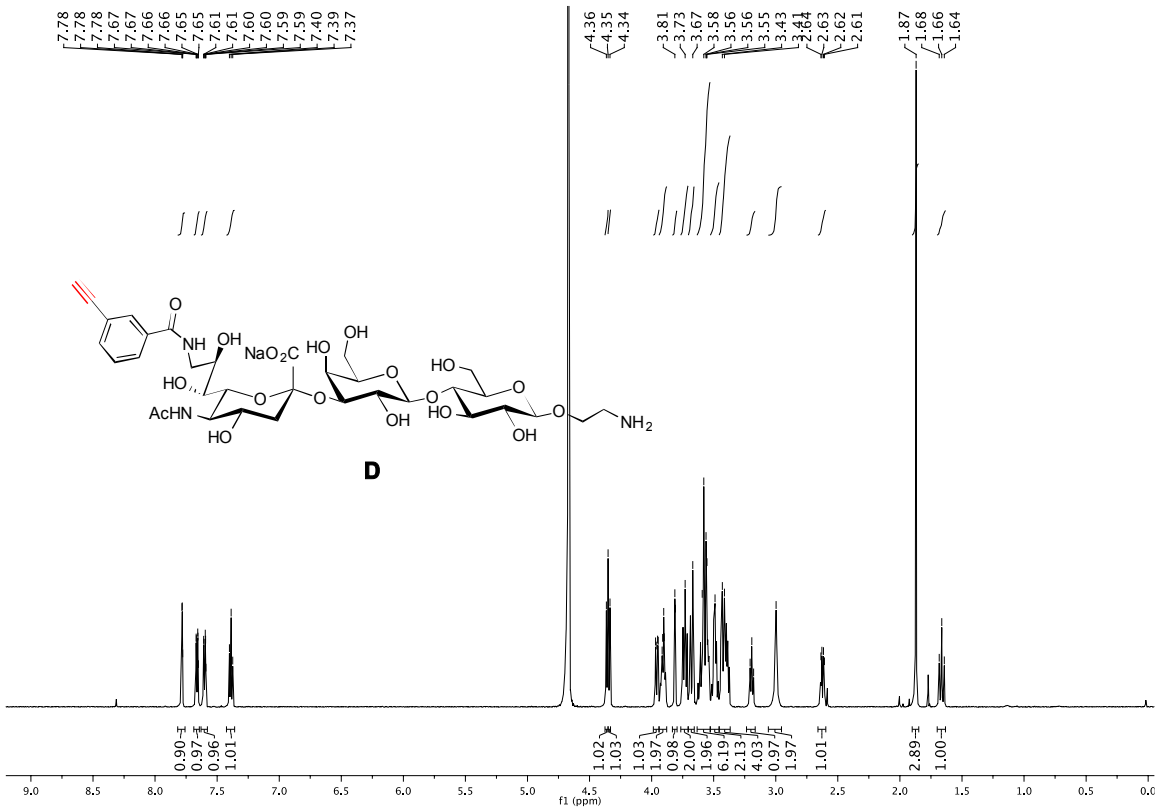

177.49
175.66
174.24
164.53
139.35
135.01
129.97
127.05
103.97
102.65
101.13
80.33
75.44
75.29
74.55
73.41
73.20
73.13
71.52
70.94
70.91
69.32
69.09
67.77
60.95
52.54
43.51
40.89
40.34
39.49
22.81
f1 (ppm)

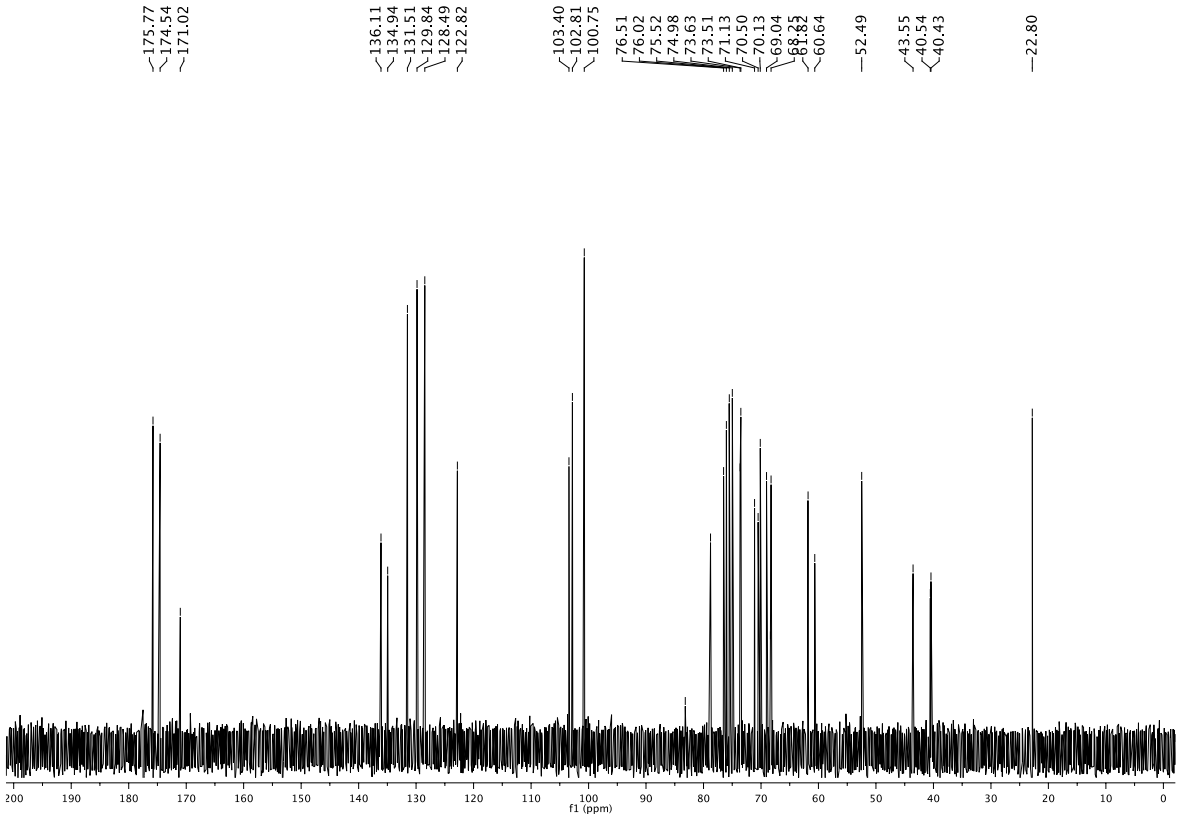

7.47
7.46
7.22
7.22
4.37
4.36
4.35
4.34
3.80
3.72
3.71
3.57
3.55
3.55
3.50
3.42
3.41
2.99
2.63
2.61
2.60
2.59
1.87
1.68
1.66
1.64
B
0.99
0.96
0.98
1.05
0.94
1.11
1.04
1.00
3.03
9.16
2.94
1.05
0.99
1.98
1.00
1.19
2.86
1.00
f1 (ppm)

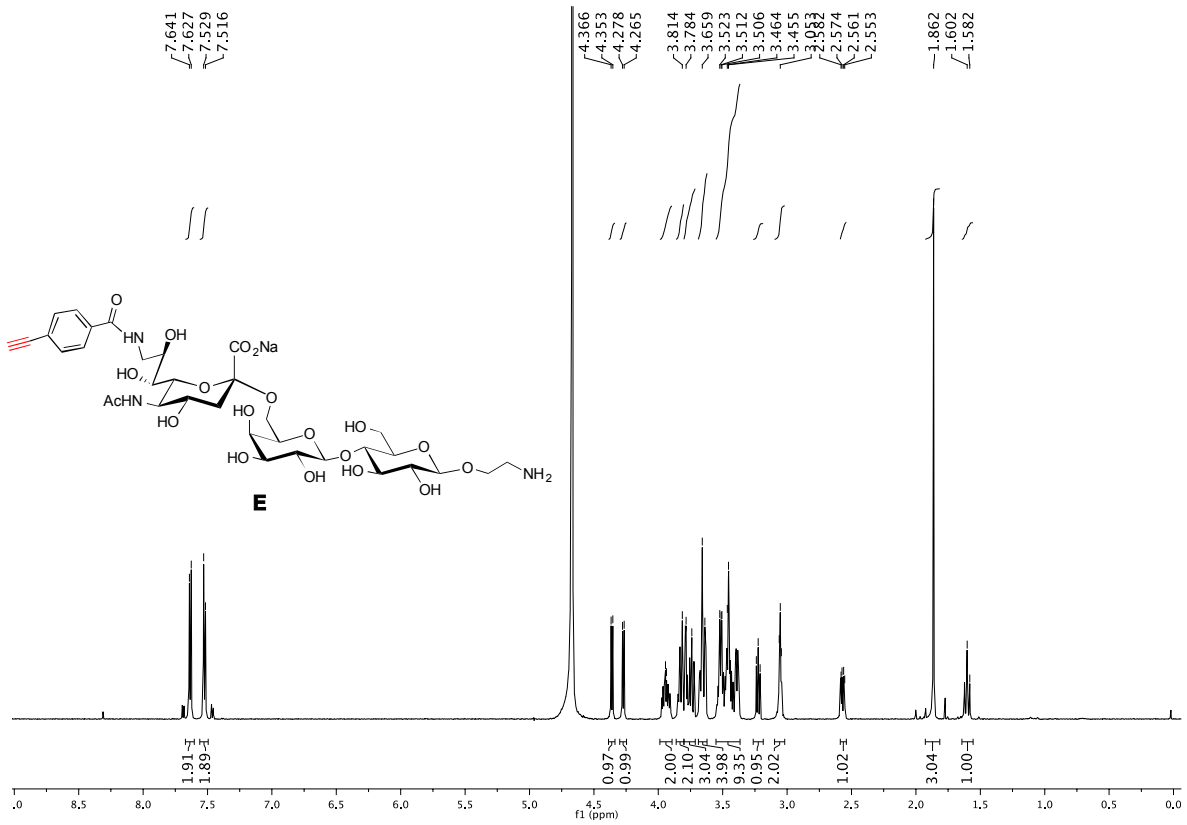

175.77
174.51
164.46
139.38
135.04
129.96
127.10
103.42
102.84
100.73
78.79
76.51
76.04
75.55
74.99
73.65
73.52
70.51
70.10
69.02
68.26
61.83
60.66
52.48
43.43
40.56
40.47
39.49
22.78
f1 (ppm)


7.78
7.67
7.66
7.66
7.65
7.65
7.65
7.61
7.60
7.59
7.40
7.39
7.37
4.37
4.36
4.28
4.27
3.74
3.66
3.53
3.51
3.51
3.46
3.45
3.45
3.38
2.59
2.58
2.56
2.55
1.87
1.63
1.61
1.59
0.90
0.93
0.96
0.94
0.92
1.00
2.06
5.42
4.16
10.40
1.02
1.89
0.57
0.98
2.97
1.00
f1 (ppm)
c

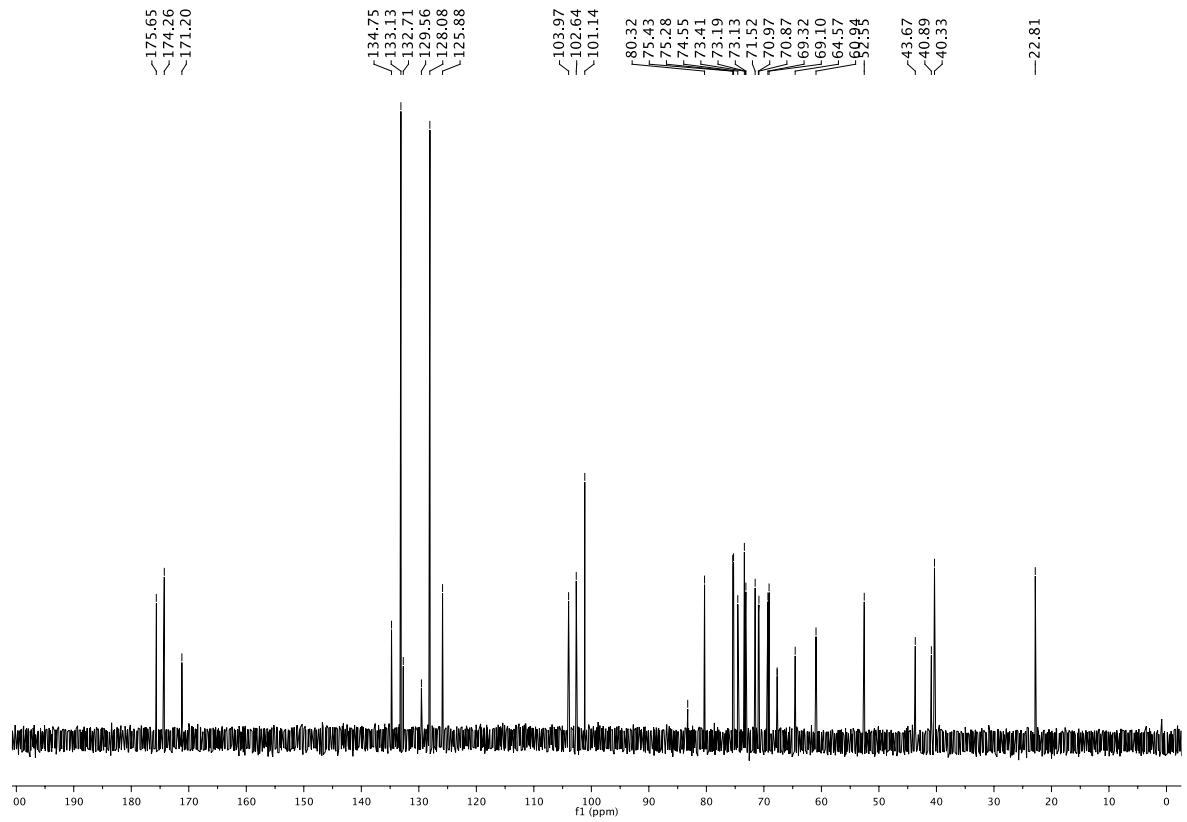

175.66
174.27
171.10
136.09
134.97
131.52
129.82
128.51
122.81
103.97
102.65
101.15
80.33
75.42
75.29
74.56
73.42
73.20
73.14
71.52
70.93
70.86
69.10
43.64
40.88
40.36
39.48
22.82
f1 (ppm)

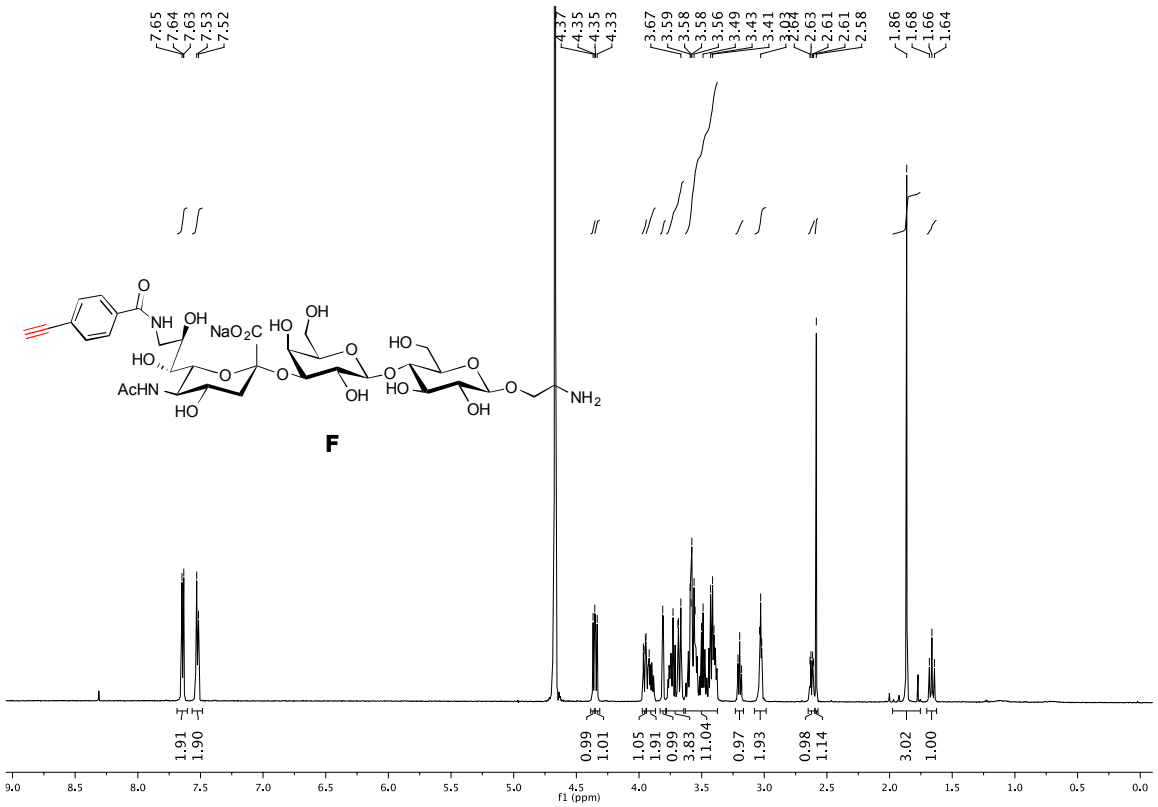

7.78
7.78
7.78
7.67
7.67
7.66
7.66
7.65
7.65
7.61
7.61
7.60
7.60
7.59
7.59
7.40
7.39
7.37
4.36
4.35
4.34
3.81
3.73
3.67
3.58
3.56
3.56
3.55
3.43
3.41
2.64
2.63
2.62
2.61
1.87
1.68
1.66
1.64
O
NH
OH
NaO2C
HO
OH
HO
O
O
O
HO
AcHN
HO
OH
HO
O
HO
OH
O
NH2
D
0.90
0.97
0.96
1.01
1.02
1.03
1.03
1.97
0.98
2.00
1.96
6.19
2.13
4.03
0.97
1.97
1.01
2.89
1.00
f1 (ppm)


175.77
174.54
171.02
136.11
134.94
131.51
129.84
128.49
122.82
103.40
102.81
100.75
76.51
76.02
75.52
74.98
73.63
73.51
71.13
70.50
70.13
69.04
60.64
52.49
43.55
40.54
40.43
22.80
f1 (ppm)

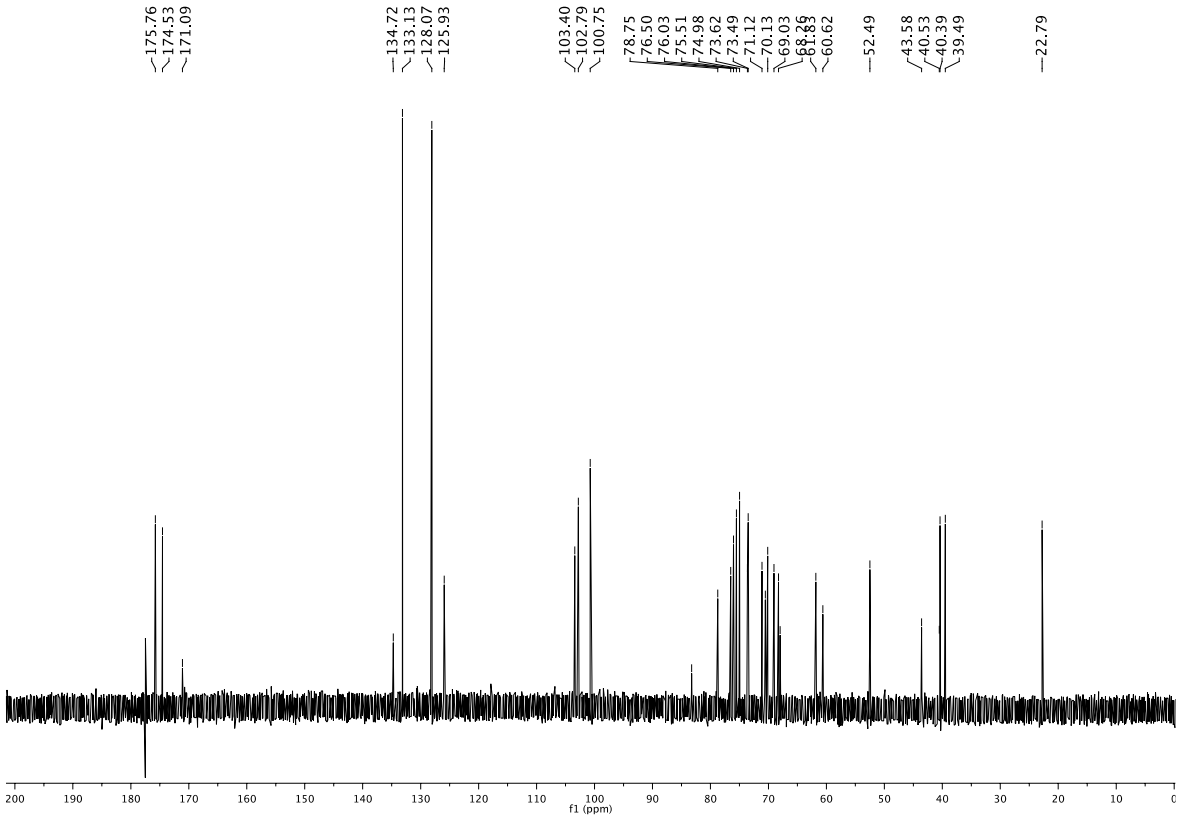

7.641
7.627
7.529
7.516
4.366
4.353
4.278
4.265
3.814
3.784
3.659
3.523
3.512
3.506
3.464
3.455
3.053
2.582
2.574
2.561
2.553
1.862
1.602
1.582
1.91
1.89
0.97
0.99
2.00
2.10
3.04
3.98
9.35
0.95
2.02
1.02
3.04
1.00
f1 (ppm)

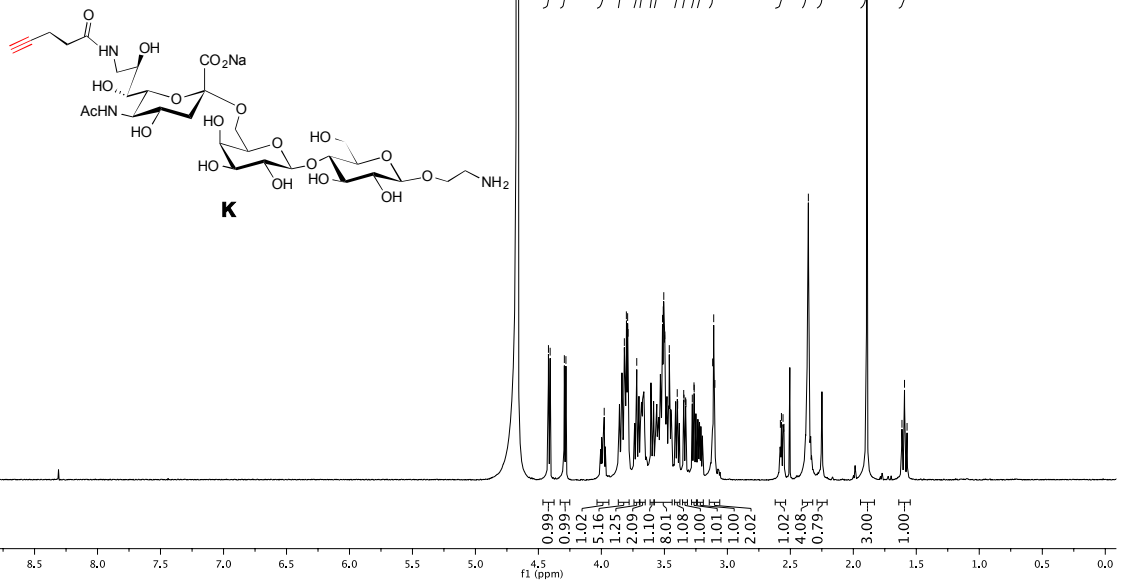
E

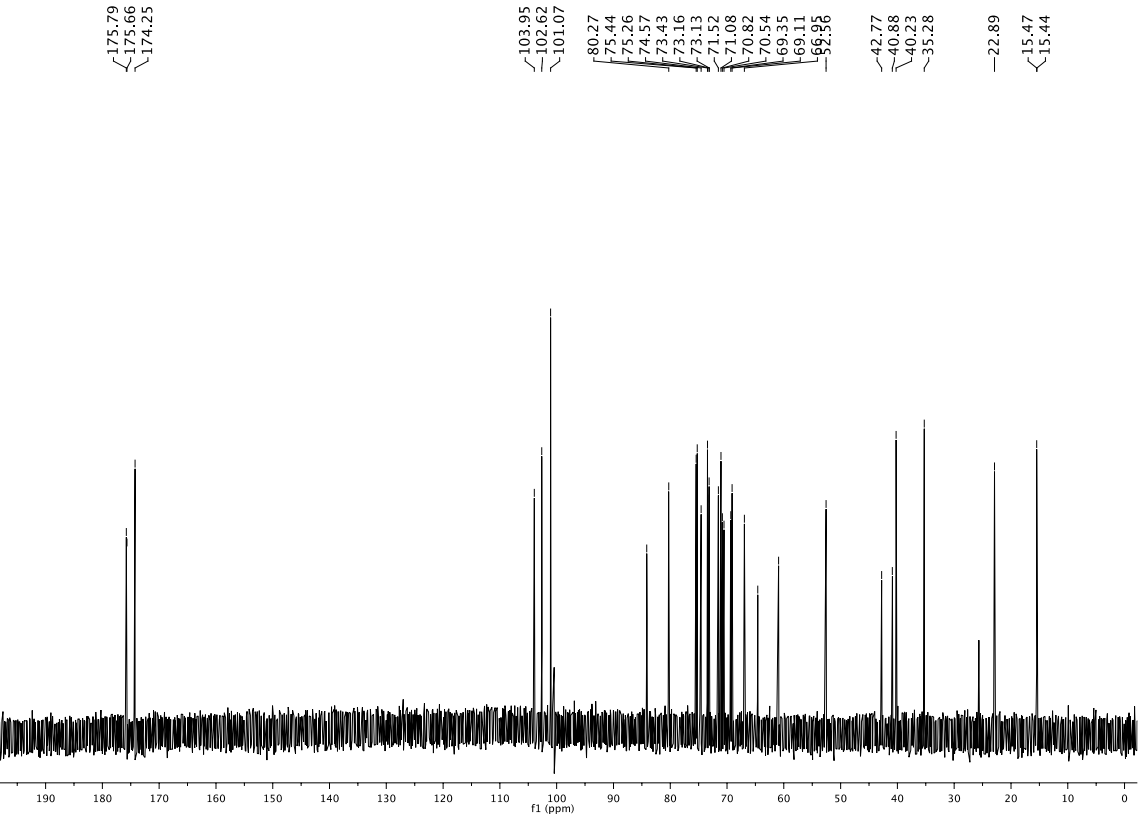

175.65
174.26
171.20
134.75
133.13
132.71
129.56
128.08
125.88
103.97
102.64
101.14
80.32
75.43
75.28
74.55
73.41
73.19
73.13
71.52
70.97
70.87
69.32
69.10
64.57
60.94
43.67
40.89
40.33
22.81
f1 (ppm)


7.65
7.64
7.63
7.53
7.52
4.37
4.35
4.35
4.33
3.67
3.59
3.58
3.58
3.56
3.49
3.43
3.41
2.63
2.61
2.61
2.58
1.86
1.68
1.66
1.64
1.91
1.90
0.99
1.01
1.05
1.91
0.99
3.83
11.04
0.97
1.93
0.98
1.14
3.02
1.00
f1 (ppm)

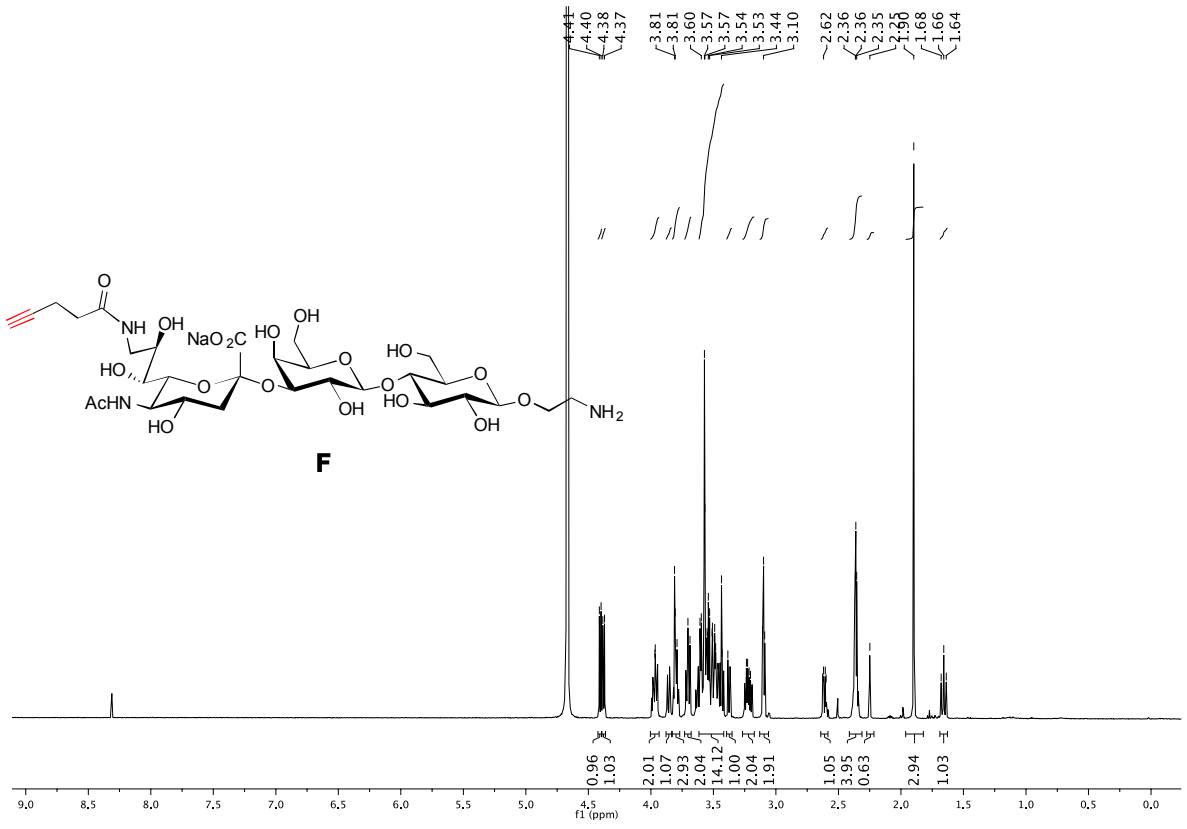
F


175.76
174.53
171.09
134.72
133.13
128.07
125.93
103.40
102.79
100.75
78.75
76.50
76.03
75.51
74.98
73.62
73.49
71.12
70.13
69.03
68.26
61.83
60.62
52.49
43.58
40.53
40.39
39.49
22.79
f1 (ppm)

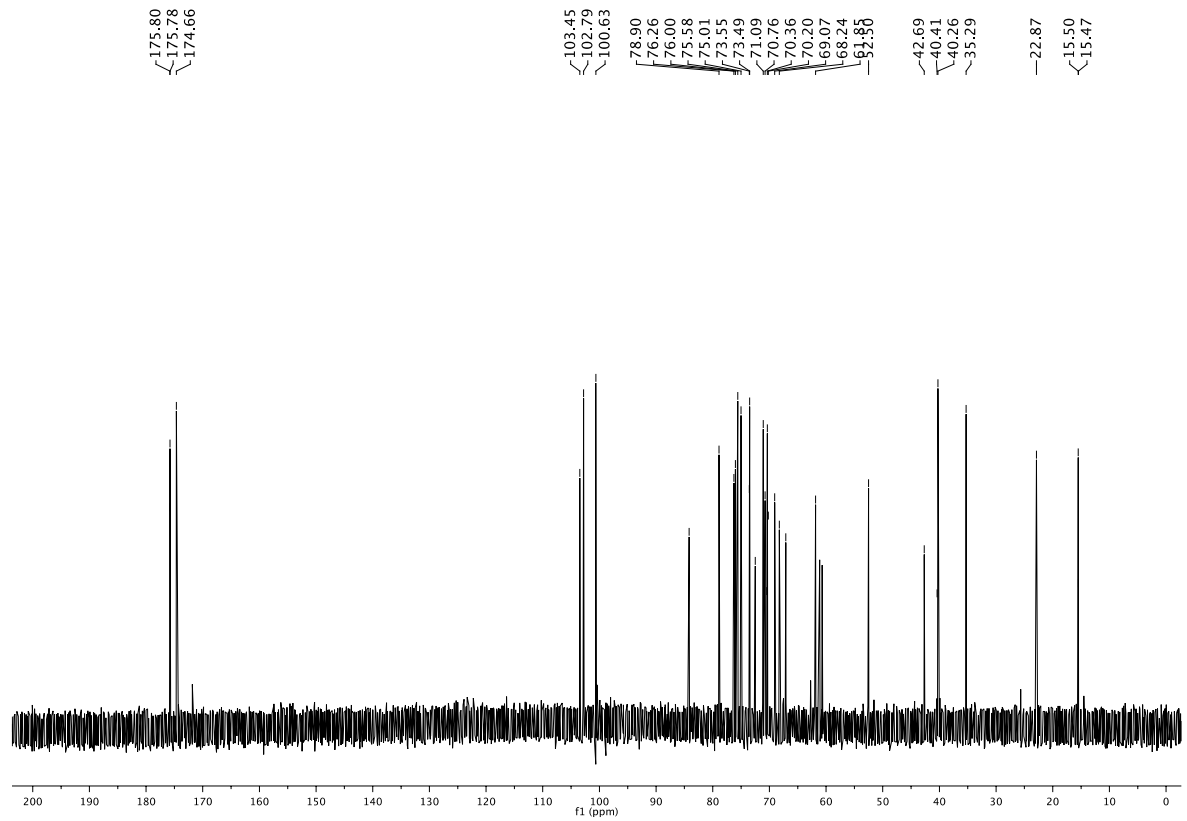

4.42
4.41
4.29
4.28
3.80
3.79
3.79
3.52
3.51
3.51
3.50
3.50
3.11
2.58
2.57
2.56
2.55
2.36
1.89
1.61
1.59
1.57
0.99
0.99
1.02
5.16
1.25
2.09
1.10
8.01
1.08
1.00
1.01
1.00
2.02
1.02
4.08
0.79
3.00
1.00
f1 (ppm)

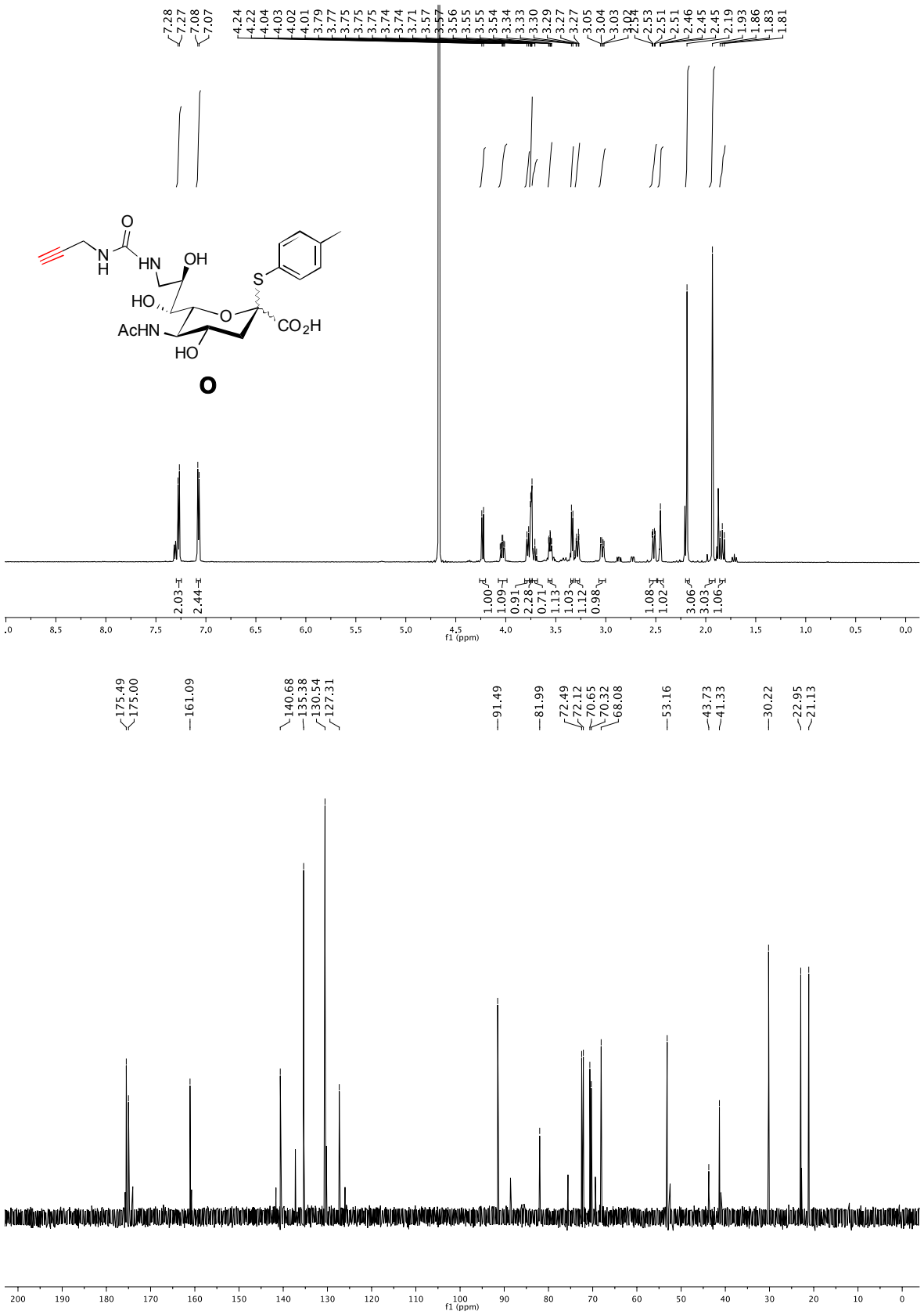

175.79
175.66
174.25
103.95
102.62
101.07
80.27
75.44
75.26
74.57
73.43
73.16
73.13
71.52
71.08
70.82
70.54
69.35
69.11
66.95
32.56
42.77
40.88
40.23
35.28
22.89
15.47
15.44
f1 (ppm)

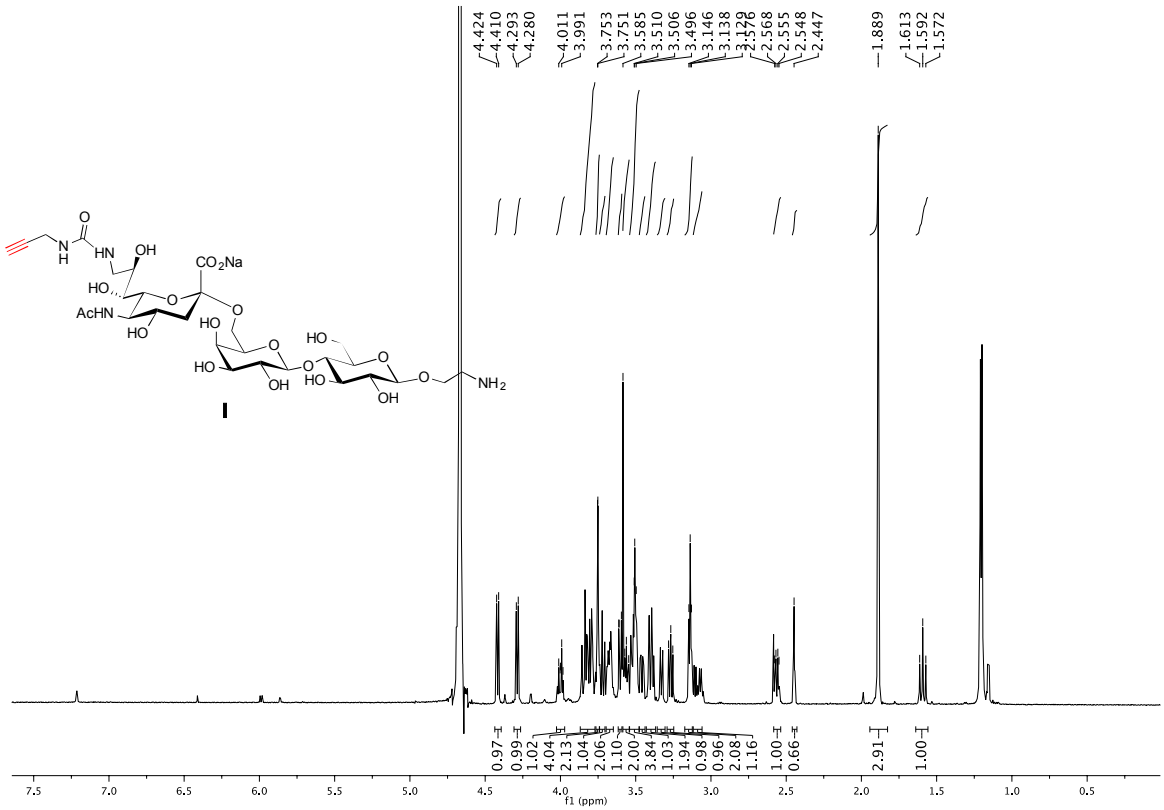
K


4.41
4.40
4.38
4.37
3.81
3.81
3.60
3.57
3.57
3.54
3.53
3.44
3.10
2.62
2.36
2.36
2.35
2.25
1.90
1.68
1.66
1.64
0.96
1.03
2.01
1.07
2.93
2.04
14.12
1.00
2.04
1.91
1.05
3.95
0.63
2.94
1.03
f1 (ppm)

F

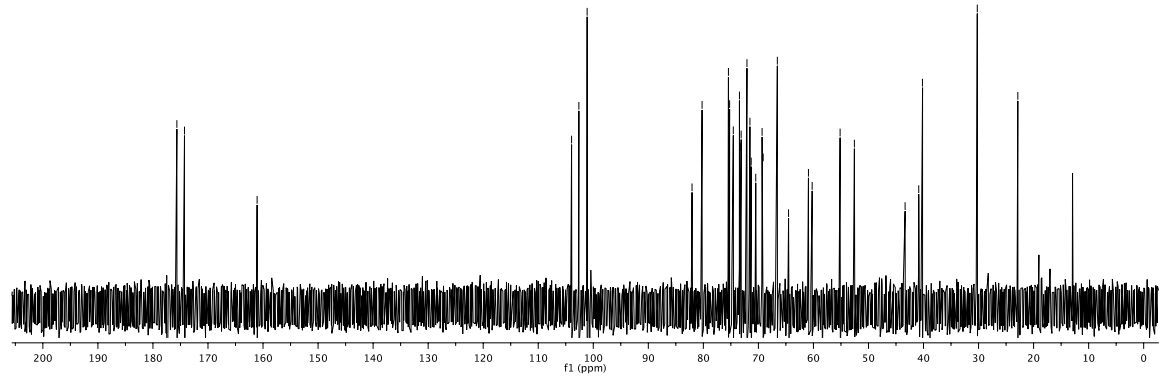

175.80
175.78
174.66
103.45
102.79
100.63
78.90
76.26
76.00
75.58
75.01
73.55
73.49
71.09
70.76
70.36
70.20
69.07
68.24
61.85
52.50
42.69
40.41
40.26
35.29
22.87
15.50
15.47
f1 (ppm)

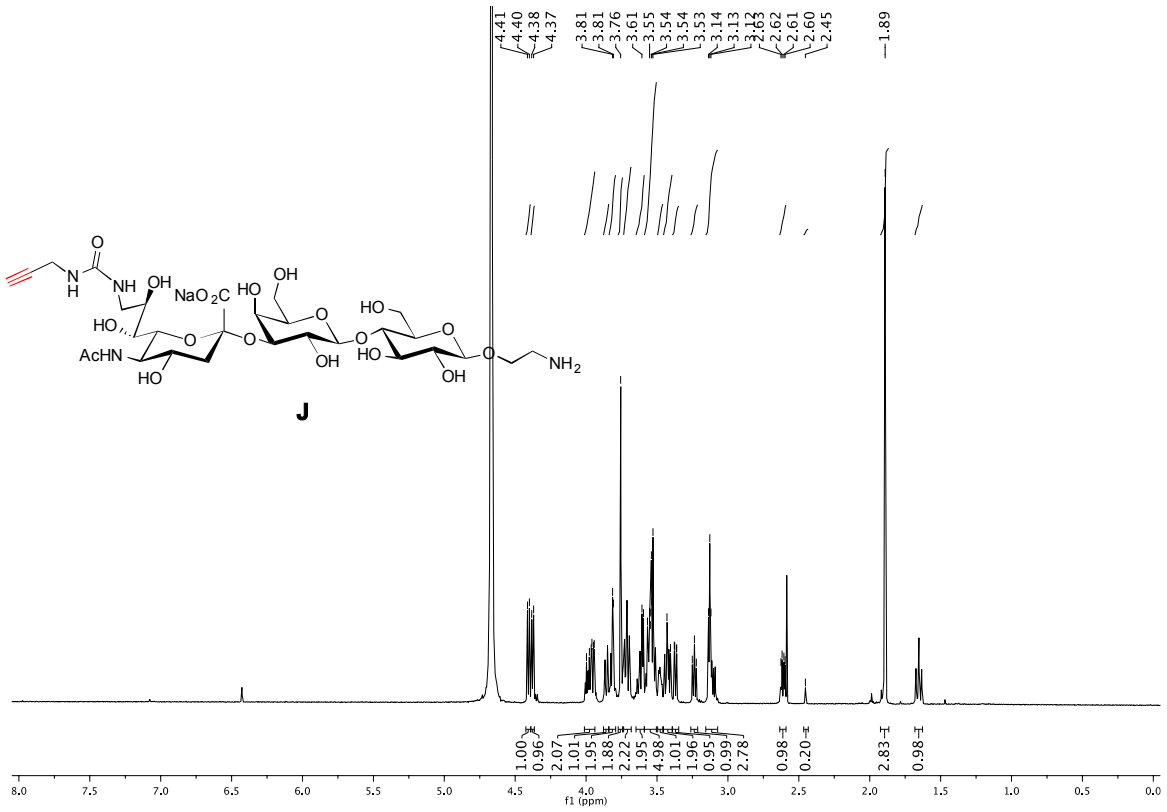

7.28
7.27
7.08
7.07
4.24
4.22
4.04
4.03
4.02
4.01
3.79
3.77
3.75
3.75
3.74
3.74
3.71
3.57
3.57
3.56
3.55
3.55
3.54
3.34
3.33
3.30
3.29
3.27
3.27
3.05
3.04
3.03
3.02
2.54
2.53
2.51
2.51
2.46
2.45
2.45
2.19
1.93
1.86
1.83
1.81
O
N
H
HN
OH
HO
O
S
AcHN
HO
CO2H
O
2.03
2.44
1.00
1.09
0.91
2.28
0.71
1.13
1.03
1.12
0.98
1.08
1.02
3.06
3.03
1.06
f1 (ppm)
175.49
175.00
161.09
140.68
135.38
130.54
127.31
91.49
81.99
72.49
72.12
70.65
70.32
68.08
53.16
43.73
41.33
30.22
22.95
21.13
f1 (ppm)

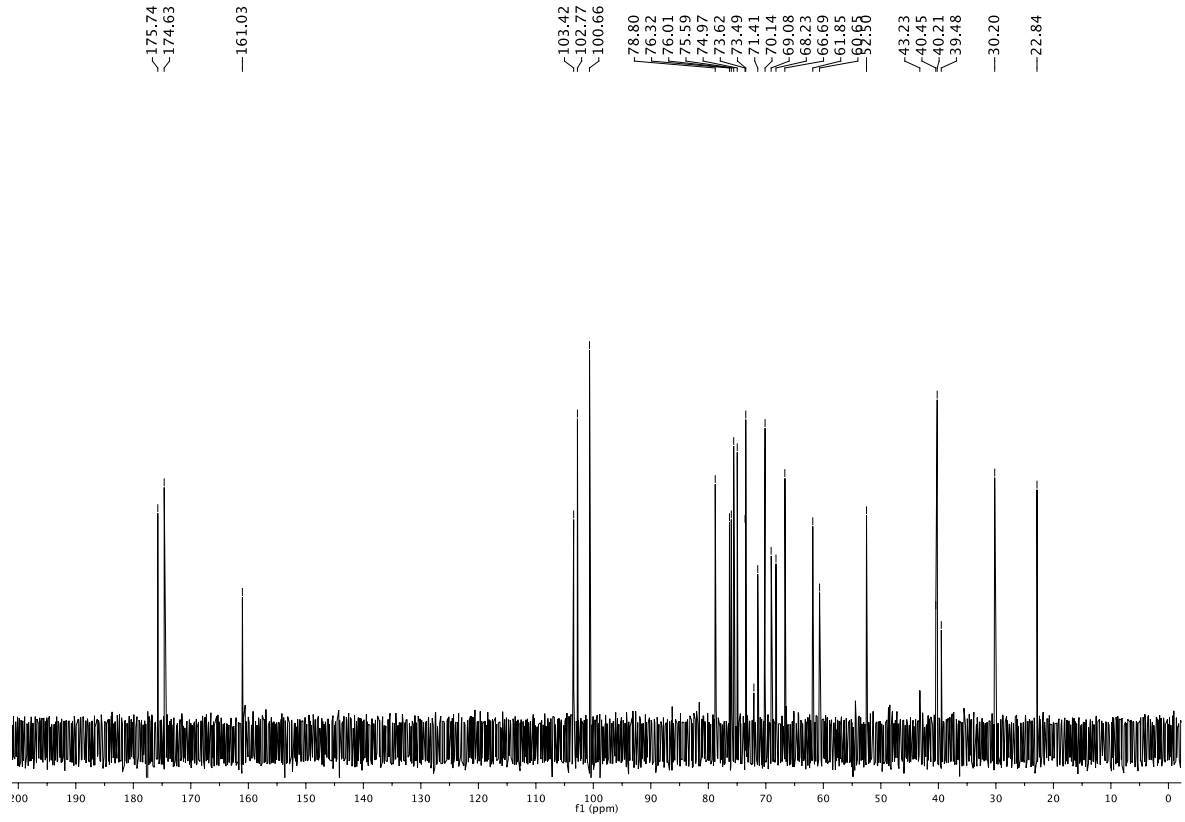

4.424
4.410
4.293
4.280
4.011
3.991
3.753
3.751
3.585
3.510
3.506
3.496
3.146
3.138
3.129
2.568
2.555
2.548
2.447
1.889
1.613
1.592
1.572
CO2Na
AcHN
HO
OH
NH2
0.97
0.99
1.02
4.04
2.13
1.04
2.06
1.10
2.00
3.84
1.03
1.94
0.98
0.96
2.08
1.16
1.00
0.66
2.91
1.00
f1 (ppm)

I

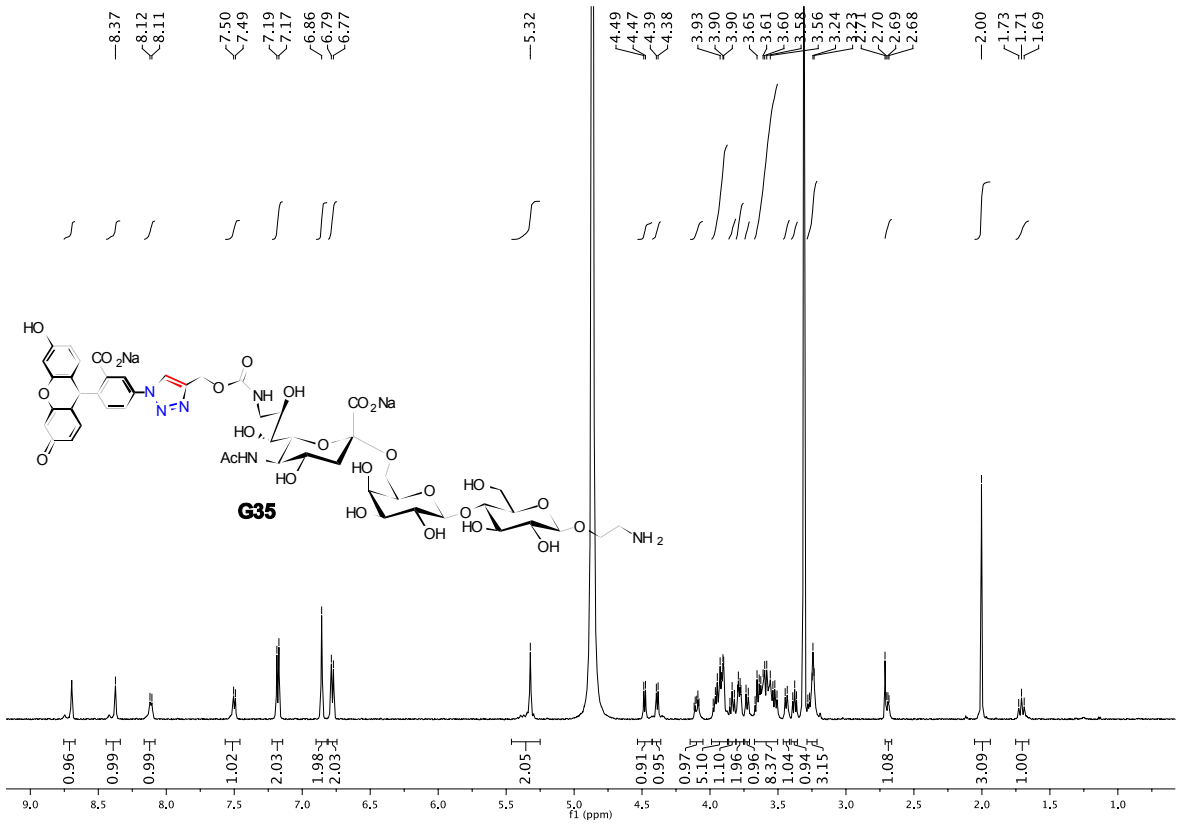

175.64
174.27
161.07
103.94
102.61
101.11
80.22
75.45
75.24
74.55
73.43
73.22
73.13
72.08
71.53
71.30
69.33
69.14
66.56
60.90
55.14
43.34
40.87
40.18
30.23
22.87

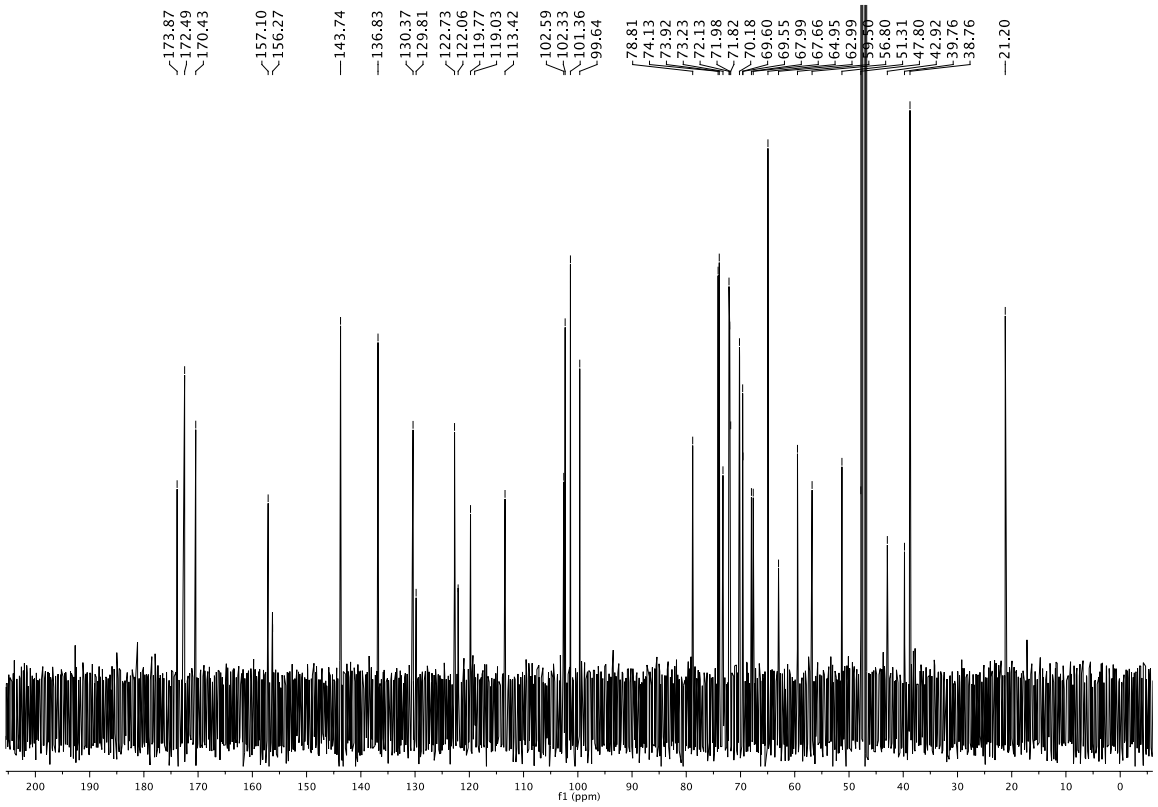

f1 (ppm)

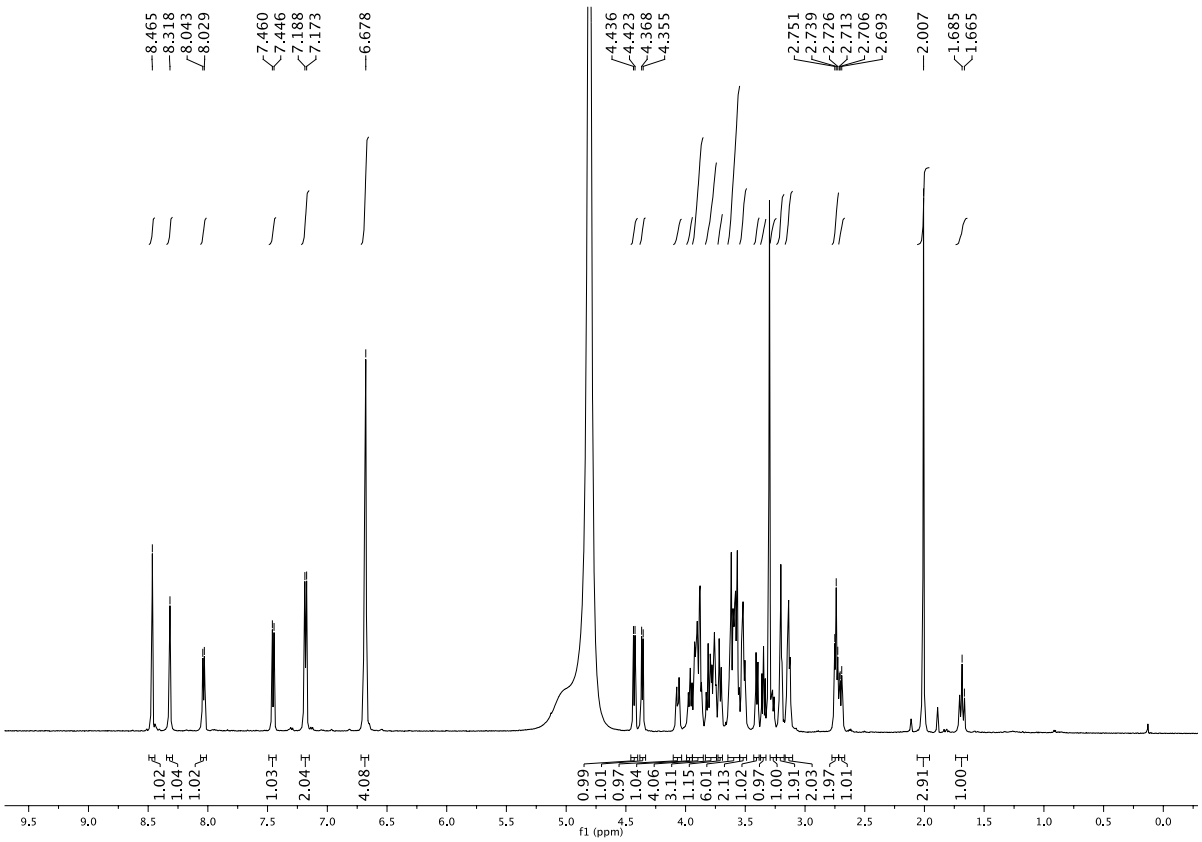

4.41
4.40
4.38
4.37
3.81
3.81
3.76
3.61
3.55
3.54
3.54
3.53
3.14
3.13
3.12
2.63
2.62
2.61
2.60
2.45
1.89
1.00
0.96
2.07
1.01
1.95
1.88
2.22
1.95
4.98
1.01
1.96
0.95
0.99
2.78
0.98
0.20
2.83
0.98
f1 (ppm)

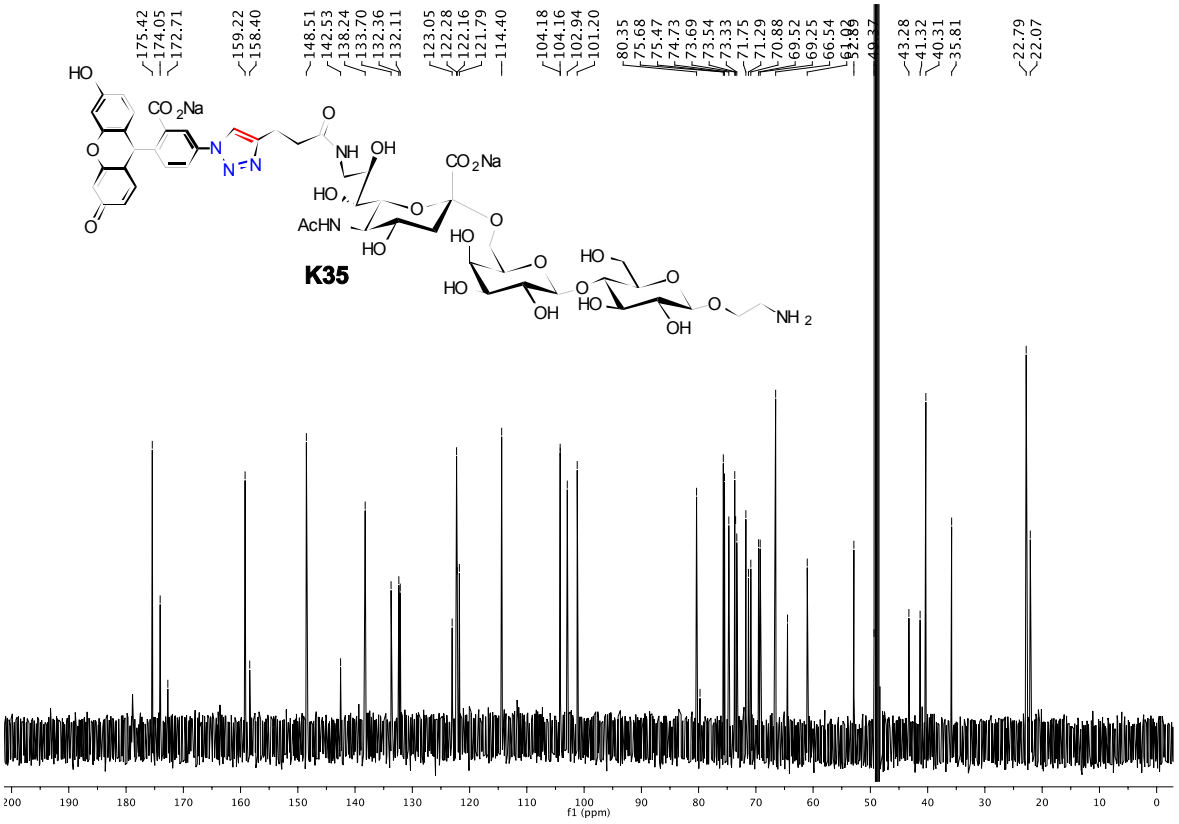

175.74
174.63
161.03
103.42
102.77
100.66
78.80
76.32
76.01
75.59
74.97
73.62
73.49
71.41
70.14
69.08
68.23
66.69
61.85
52.50
43.23
40.45
40.21
39.48
30.20
22.84
f1 (ppm)

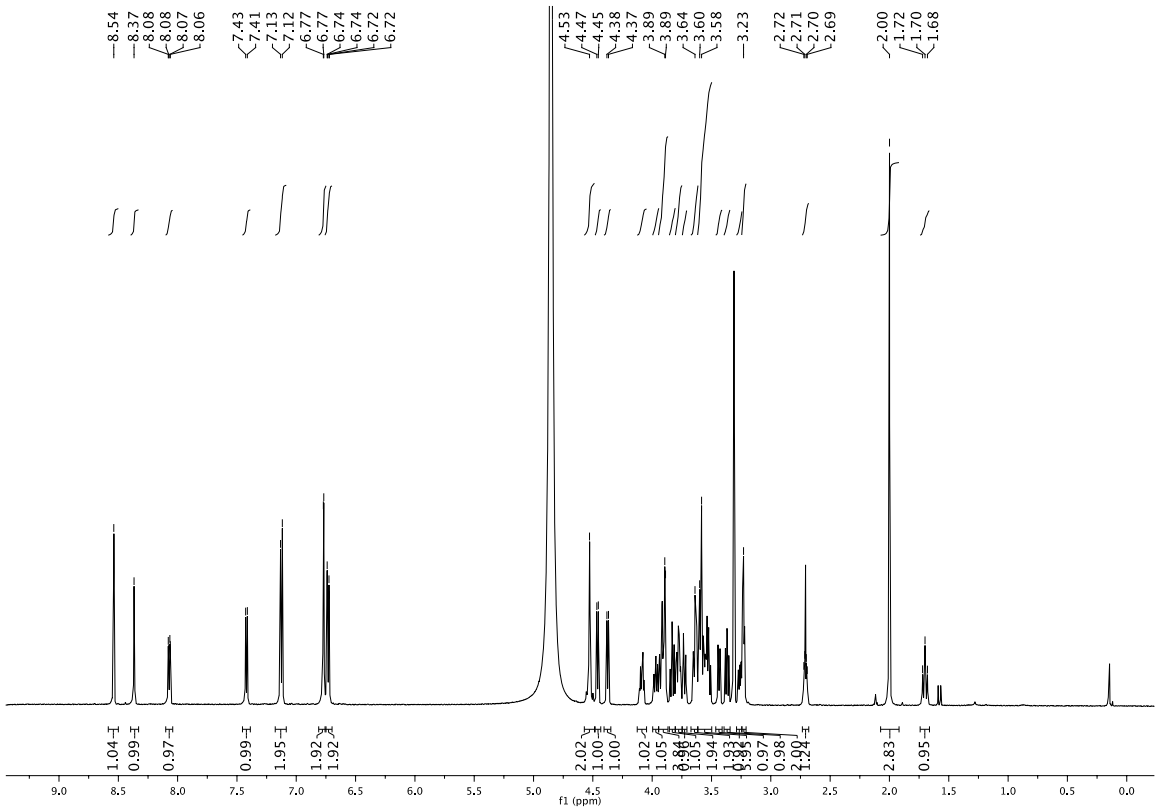
J

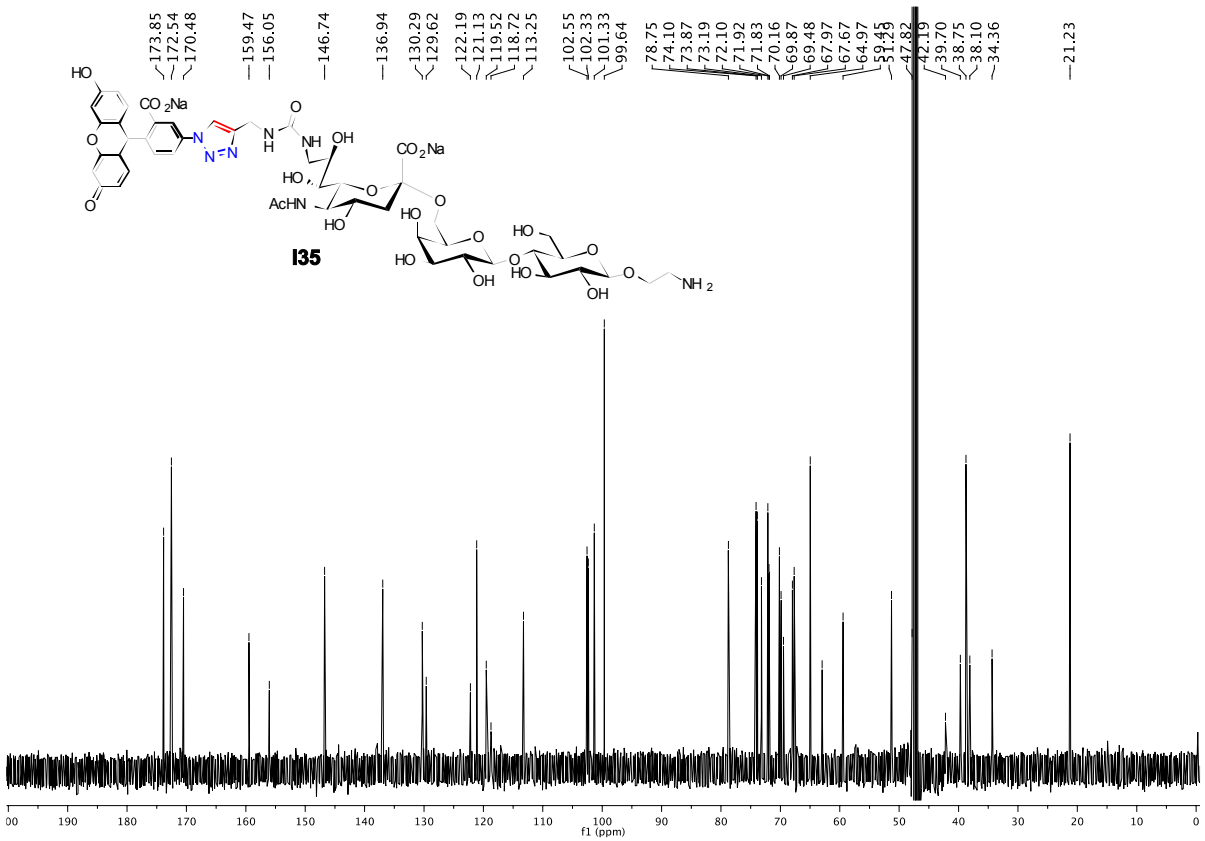

8.37
8.12
8.11
7.50
7.49
7.19
7.17
6.86
6.79
6.77
5.32
4.49
4.47
4.39
4.38
3.93
3.90
3.90
3.65
3.61
3.60
3.58
3.56
3.24
2.70
2.69
2.68
2.00
1.73
1.71
1.69
HO
CO2Na
O
N
N=N
O
NH
OH
HO
AcHN
HO
O
CO2Na
HO
O
HO
O
HO
OH
HO
O
HO
OH
O
NH2
G35
0.96
0.99
0.99
1.02
2.03
1.98
2.03
2.05
0.91
0.95
0.97
5.10
1.10
1.96
0.96
8.37
1.04
0.94
3.15
1.08
3.09
1.00
f1 (ppm)


173.87
172.49
170.43
157.10
156.27
143.74
136.83
130.37
129.81
122.73
122.06
119.77
119.03
113.42
102.59
102.33
101.36
99.64
78.81
74.13
73.92
73.23
72.13
71.98
71.82
70.18
69.60
69.55
67.99
67.66
64.95
62.99
56.80
51.31
47.80
42.92
39.76
38.76
21.20
f1 (ppm)

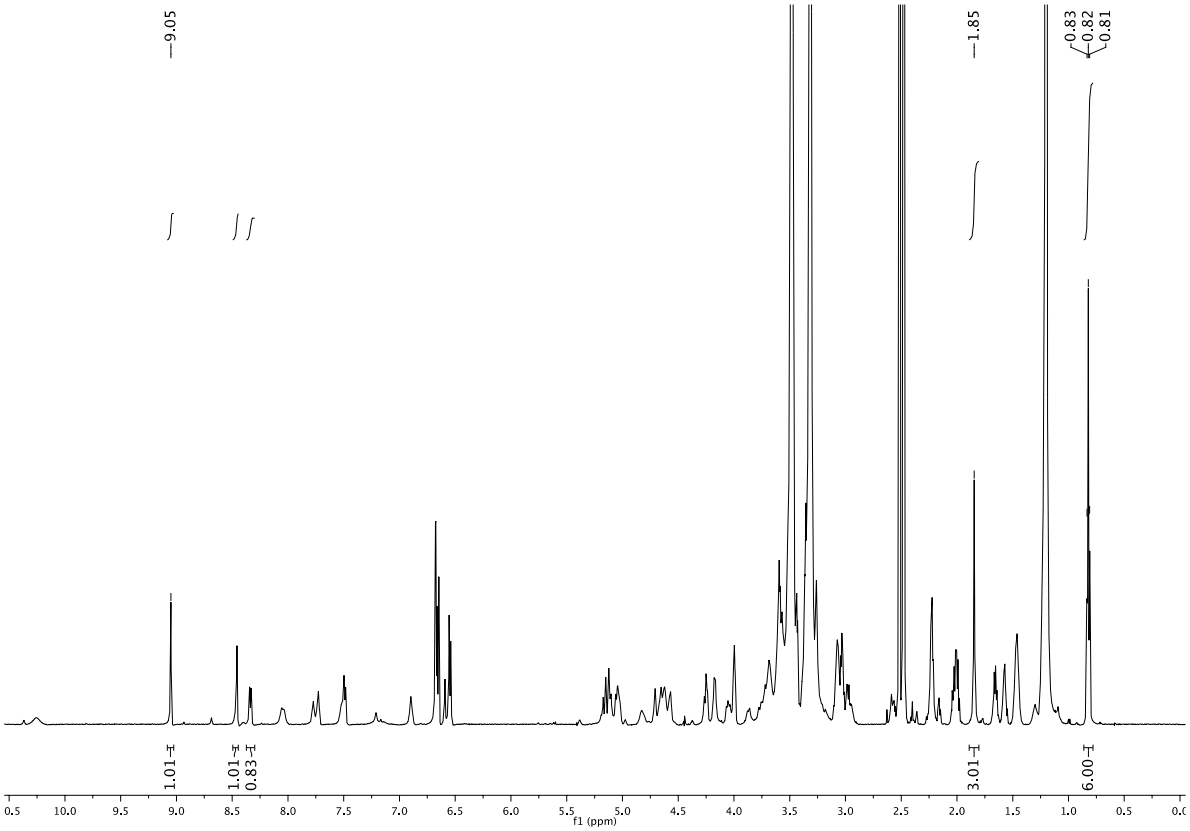

8.465
8.318
8.043
8.029
7.460
7.446
7.188
7.173
6.678
4.436
4.423
4.368
4.355
2.751
2.739
2.726
2.713
2.706
2.693
2.007
1.685
1.665
f1 (ppm)

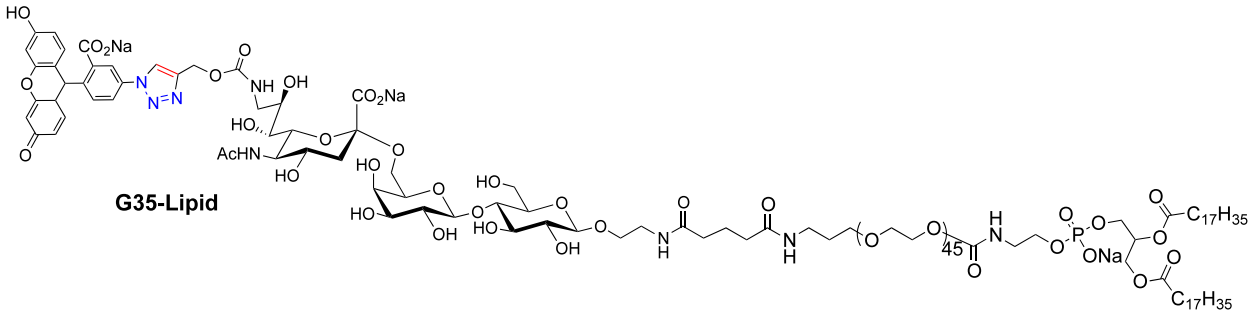

175.42
174.05
172.71
159.22
158.40
148.51
142.53
138.24
133.70
132.36
132.11
123.05
122.28
122.16
121.79
114.40
104.18
104.16
102.94
101.20
80.35
75.68
75.47
74.73
73.69
73.54
73.33
71.75
71.29
70.88
69.52
69.25
66.54
43.28
41.32
40.31
35.81
22.79
22.07
HO
CO2Na
O
N
N=N
NH
OH
HO
AcHN
HO
CO2Na
HO
O
HO
OH
HO
O
HO
OH
O
NH2
K35
f1 (ppm)


8.54
8.37
8.08
8.08
8.07
8.06
7.43
7.41
7.13
7.12
6.77
6.74
6.74
6.72
6.72
4.53
4.47
4.45
4.38
4.37
3.89
3.89
3.64
3.60
3.58
3.23
2.72
2.71
2.70
2.69
2.00
1.72
1.70
1.68
f1 (ppm)

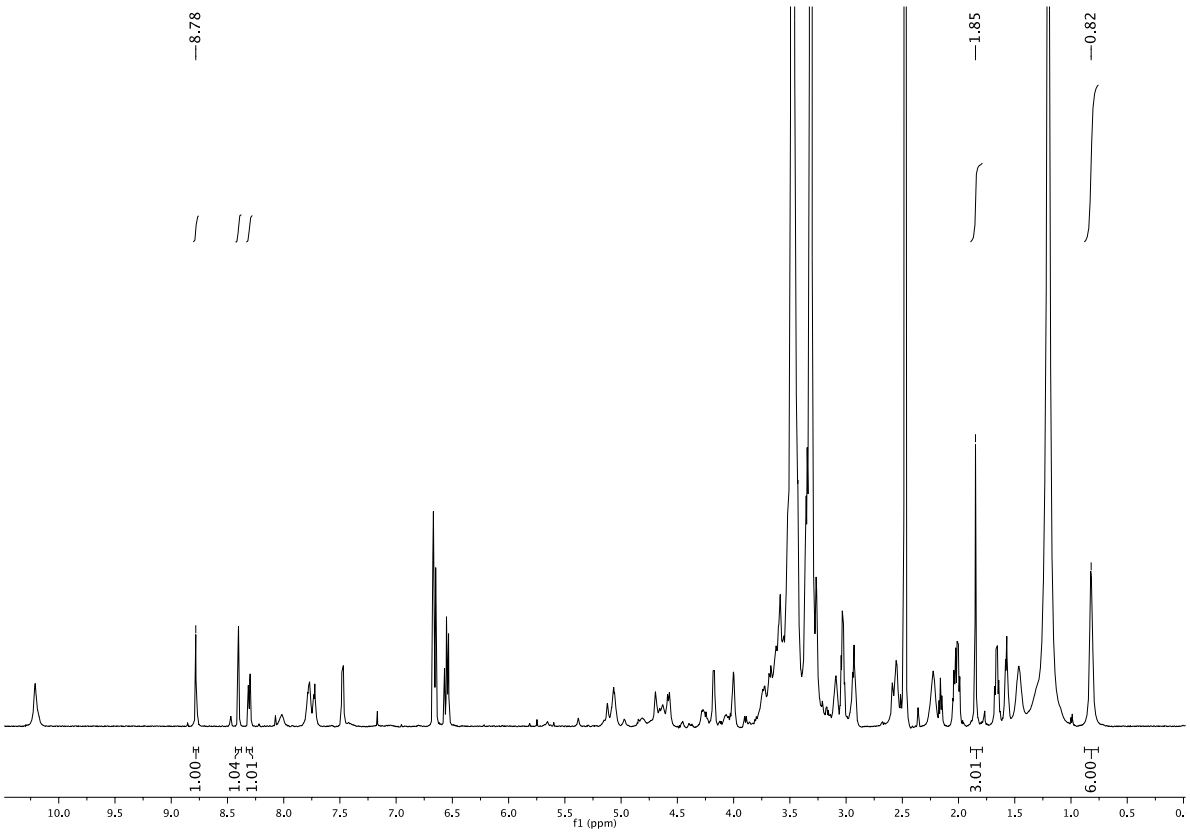

173.85
172.54
170.48
159.47
156.05
146.74
136.94
130.29
129.62
122.19
121.13
119.52
118.72
113.25
102.55
102.33
101.33
99.64
78.75
74.10
73.87
73.19
72.10
71.92
71.83
70.16
69.87
69.48
67.97
67.67
64.97
51.45
47.82
42.19
39.70
38.75
38.10
34.36
21.23
f1 (ppm)

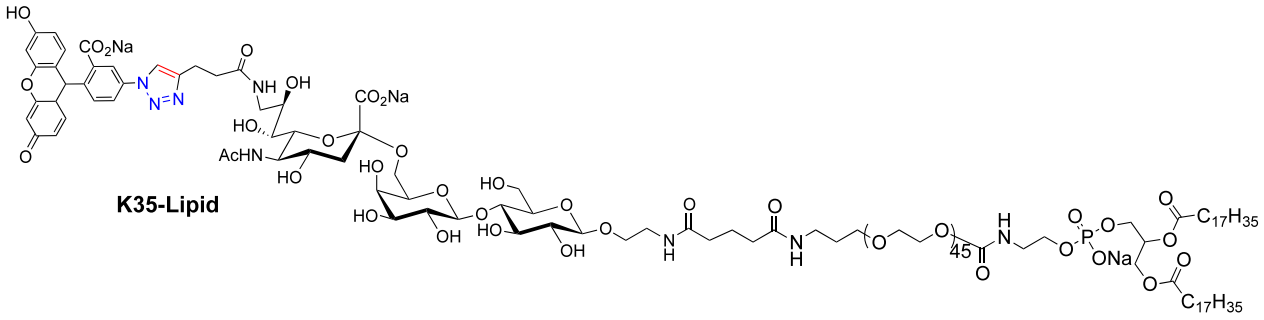
I35


9.05
1.85
0.83
0.82
0.81
1.01
1.01
0.83
3.01
6.00
f1 (ppm)

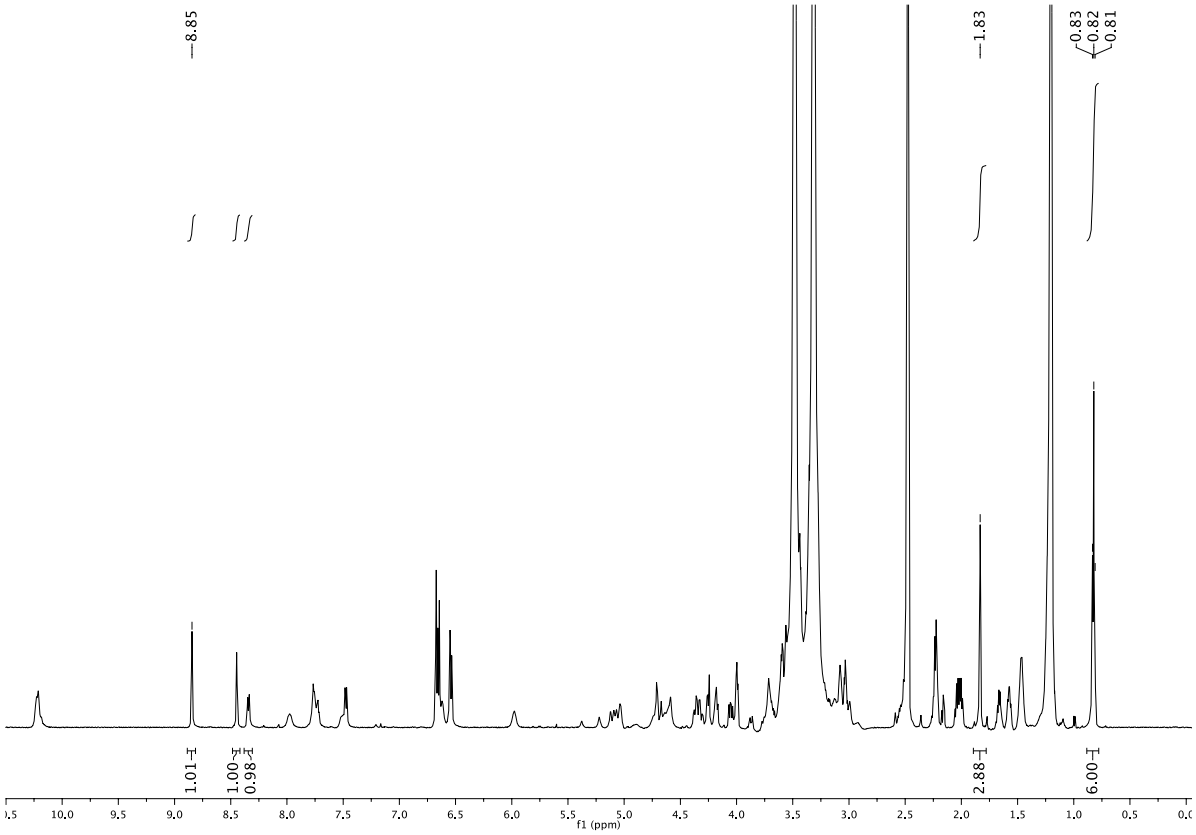

HO
CO2Na
O
NH
OH
HO
AcHN
HO
CO2Na
HO
HO
HO
OH
HO
OH
N
H
O
O
N
H
O
O
45
O
H
N
O
P
O
ONa
O
O
C17H35
O
O
C17H35

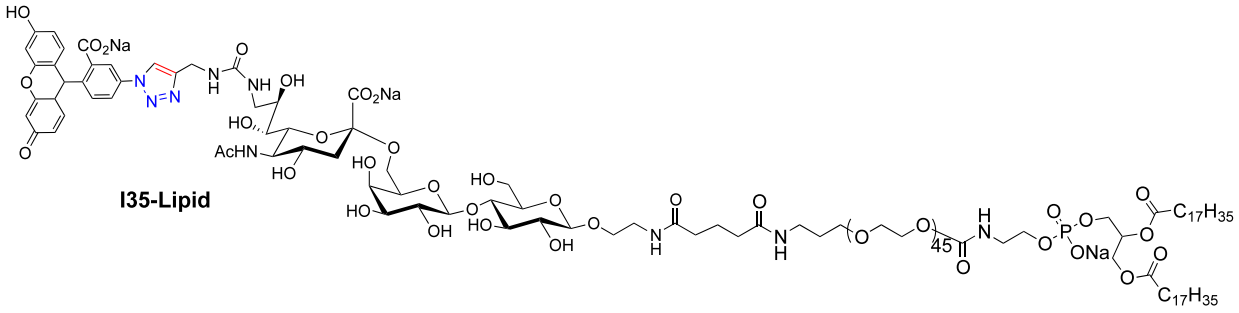
G35-Lipid





K35-Lipid





I35-Lipid