Efficient Chemoenzymatic Synthesis of an N-glycan Isomer Library

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Supporting Information

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I. Materials and enzymes

Neu5Gc and CTP were purchased from Carbosynth Limited. β1,4-galactosyltransferase from bovine milk (B4GALT1) was purchased from Sigma. Thermosensitive Alkaline Phosphatase from shrimp (FastAP) was purchased from Thermo Scientific. Recombinant human FUT8 was purchased from Fisher Scientific. Other enzymes including double mutant E271F/R313Y from *Pasteurella multocida* α2,3-sialyltransferase 1 (PmST1m) [1], α2,6-sialyltransferase from *Photobacterium damslae* (Pd2,6ST) [2], C-terminal 66 amino acids truncated *Helicobacter pylori* α1,3-fucosyltransferase (Hpα1,3FT) [3], CMP-sialic acid synthetase from *N. meningitidis* (NmCSS)[4] were expressed and purified as previously described. Enzymes were then desalted against 50 mM Tris-HCl, 100 mM NaCl, and 50% glycerol, and stored at -20 °C for long term use. Sugar nucleotides uridine 5'-diphospho-galactose (UDP-Gal) [5], cytidine 5'-monophospho-N-acetylneuraminic acid (CMP-Neu5Ac)[4] and guanoside 5'-diphospho-L-fucose (GDP-Fuc)[6] were prepared as described previously.

II. General methods for enzyme treatment

A) β1,4-galactosylation catalyzed by B4GALT1

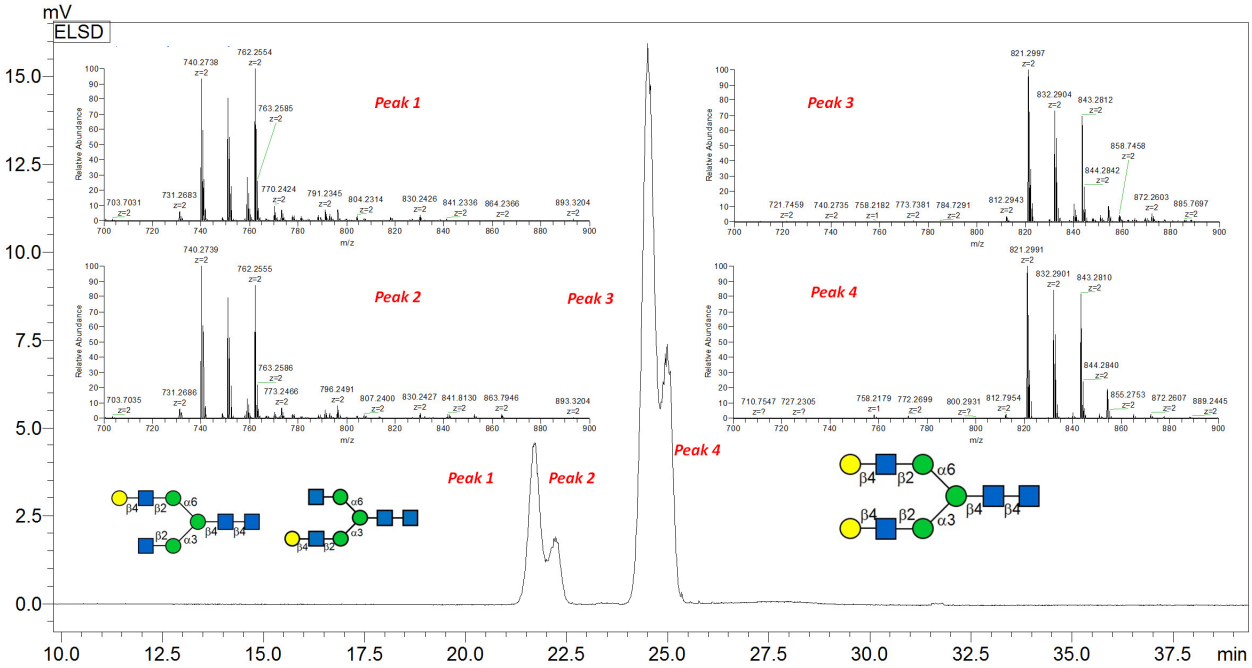


Figure S1. HILIC-ELSD analysis of **N001** glycans yielded from P2. Waters XBridge BEH amide column was used (130 Å, 5 μm, 4.6 mm × 250 mm) under a gradient running condition (solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 70-50% within 50 min).

Reactions contain 50 mM Tris-HCl (pH 8.0), 4 mM of acceptor glycans, 8 mM of UDP-Gal, 5 mM of $MnCl_2$, and varying amounts of B4GALT1. FastAP (1 U/200 μL) was also added to digest the reaction byproduct UDP to drive reaction forward. Reactions incubated at 37 °C for 2-12 h, and monitored by HILIC-ELSD (amide column, 4.6 mm × 250 mm under a gradient running condition (solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min)). After over 90% acceptor converted, the reaction was quenched by been put in -80 °C for 30 min, followed concentration by lyophilization. HPLC-A_{210nm} was then used to purify target glycans using a semi-preparative amide column (130 Å, 5 μm, 10 mm × 250 mm). The running conditions are solvent A: 100 mM ammonium formate (for glycans with Sia residues) or water (for glycans without Sia residues), pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min.

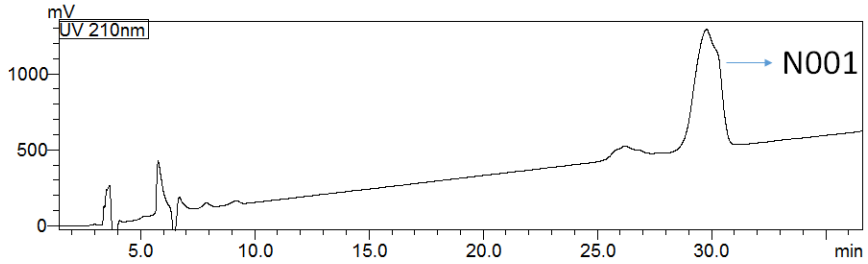


Figure S2. HILIC-$_{210nm}$ purification of **N001** yielded from P2. Waters XBridge BEH amide column was used (130 Å, 5 μm, 10 mm × 250 mm) under a gradient condition (solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 4 mL/min; B%: 70-50% within 50 min). The peak corresponding to **N001** was pooled and lyophilized twice to remove ammonium formate.

B) α2,3-sialylation catalyzed by PmST1m

Reactions contain 100 mM Tris-HCl (pH 8.0), 4 mM of acceptor glycans, 8 mM of CMP-Neu5Ac, and of PmST1m (5 μg/mL). Reactions were incubated at 37 °C for 30 min and quenched by been put in -80 °C for 30 min, followed concentration by lyophilization. HPLC-A_{210nm} was then used to purify target glycans using a semi-preparative amide column (130 Å, 5 μm, 10 mm × 250 mm). The running conditions are solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min. For the synthesis of Neu5Gc containing glycans, CMP-Neu5Ac was simply substituted by reagents for CMP-Neu5Gc synthesis (8 mM Neu5Ac, 8 mM CTP, 5 mM $MgCl_2$, and excessive amounts of NmCSS).

C) α2,6-sialylation catalyzed by Pd2,6ST

Reactions contain 100 mM Tris-HCl (pH 8.0), 4 mM of acceptor glycans, 8 mM of CMP-Neu5Ac, and varying amounts of Pd2,6ST. 1 U/200 μL) was also added to digest the reaction

byproduct UDP to drive reaction forward. Reactions incubated at 37 °C for 2-12 h, and monitored by HILIC-ELSD (amide column, 4.6 mm × 250 mm under a gradient running condition (solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min). HPLC-A_{210nm} was then used to purify target glycans using a semi-preparative amide column (130 Å, 5 μm, 10 mm × 250 mm). The running conditions are solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min. **Supplementary Figure 3** shows that only MS detectable product was found when Pd26ST was used to synthesized Neu5Ac6Le^X-OBn (a unnatural glycan). For the synthesis of Neu5Gc containing glycans, CMP-Neu5Ac was simply substituted by reagents for CMP-Neu5Gc synthesis (8 mM Neu5Ac, 8 mM CTP, 5 mM $MgCl_2$, and excessive amounts of NmCSS).

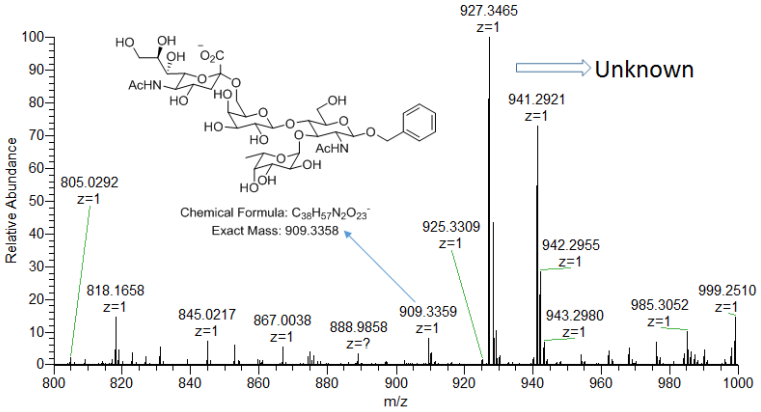


Figure S3. MS analysis of Pd2,6ST catalyzed formation of Neu5Ac6Le^X-OBn.

D) α1,3-fucosylation catalyzed by Hpα1,3FT

Reactions contain 50 mM Tris-HCl (pH 8.0), 4 mM of acceptor glycans, 8 mM of GDP-Fuc, 5 mM of $MnCl_2$, and varying amounts of Hpα1,3FT. FastAP (1 U/200 μL) was also added to digest the reaction byproduct GDP to drive reaction forward. Reactions incubated at 37 °C for 4-24 h, and monitored by HILIC-ELSD (amide column, 4.6 mm × 250 mm under a gradient running condition (solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min)). After over 90% acceptor converted, the reaction was quenched by been put in -80 °C for 30 min, followed concentration by lyophilization. HPLC-A_{210nm} was then used to purify target glycans using a semi-preparative amide column (130 Å, 5 μm, 10 mm × 250 mm). The running conditions are solvent A: 100 mM ammonium formate (for glycans with Sia residues) or water (for glycans without Sia residues), pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min.

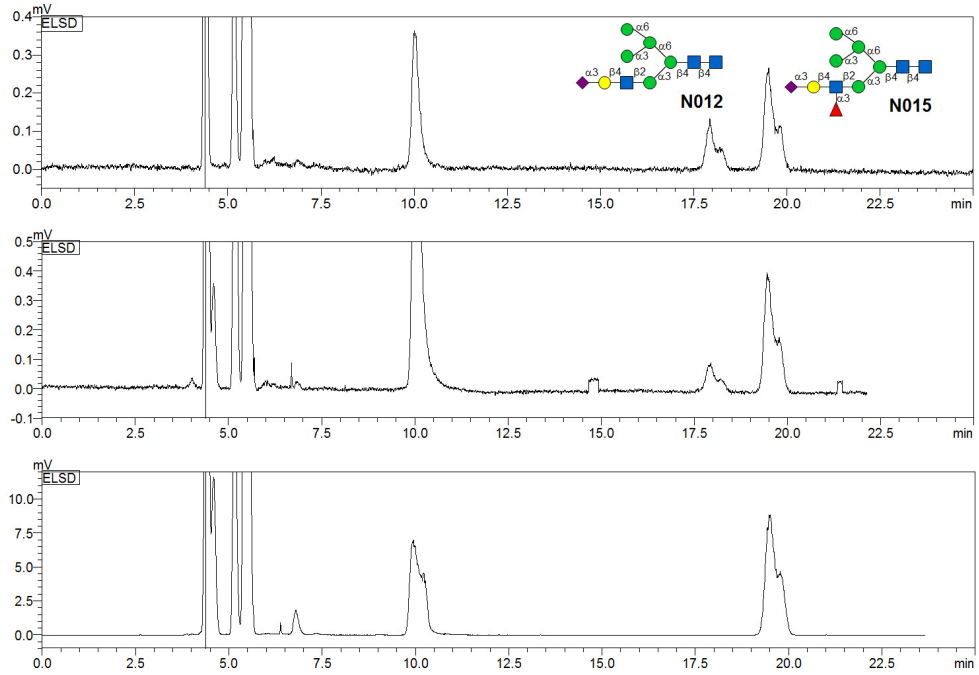


Figure S4. HILIC-ELSD analysis of Hpα1,3FT catalyzed fucosylation of **N012**.

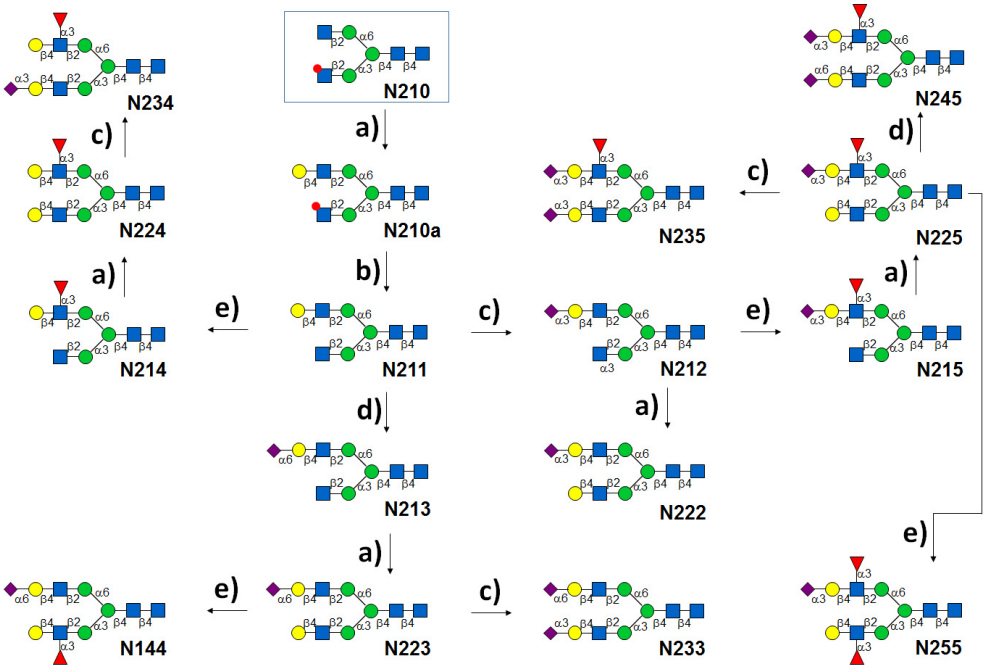


Figure S5. Synthetic scheme of glycans **N2XX** and **N144** by enzymatic extension. a) B4GALT1; b) 30% ammonium hydroxide treatment for 6 h; c) PmST1m; d) Pd2,6ST; e) Hpα1,3FT. Each N-glycan was purified into 98% pure by HPLC with a semi-preparative amide column (10 × 250 mm).

D) Substrate specificity study of Hpα1,3FT towards various acceptors

Reactions contain 50 mM Tris-HCl (pH 8.0), 2 mM of acceptor glycans, 4 mM of GDP-Fuc, 5 mM of $MnCl_2$, and 1 μg of Hpα1,3FT. FastAP (1 U/200 μL) was also added to digest the reaction byproduct GDP to drive reaction forward. Reactions incubated at 37 °C for 1 h, and analyzed by HILIC-ELSD (or UV210) (amide column, 4.6 mm × 250 mm under a gradient running condition (solvent A: 100 mM ammonium formate, pH 3.4; solvent B: acetonitrile; flow rate: 1 mL/min; B%: 65-50% within 25 min).

It was found that Hpα1,3FT has a strict requirement of terminal glycans (e.g., requires LacNAc or Sia3LacNAc for activity), but a very relaxed requirement of glycans linked to the reducing end of GlcNAc (e.g., it showed similar activity towards LacNAc-OBn, **N011**, **N021**, **N211**, etc.). The enzyme showed reduced activity towards N125 and N225 (highlighted), possibly due to the α1,3-fucose located on the other antennary of N-glycans. Also, as expected core-fucosylation did not affect the activity of Hpα1,3FT (N211, 82.4%; N6211, 78.9%).

Table S1 Substrate specificity of Hpα1,3FT towards various acceptors

Substrate	Terminal glycan of substrate	**Product**	**Yield (%)**
GlcNAc-OBn	GlcNAc		ND
N010			ND
N020			ND
N040			ND
N110			ND
N210			ND
LacNAc-OBn	LacNAc	Le^X-OBn	100
N011		N014	90.6
N021		N024	100
N031		N034	93.8
N041		N044	97.6
N051		N054	95.4
N111		N114	88.9
N123		N244	86.7
N125		N155	41.0
N211		N214	82.4
N223		N144	89.1
N225		N255	57.4
N6211		N6214	78.9
N012G	Neu5Gc3LacNAc	N015G	34.2
S3LacNAc-OBn	Neu5Ac3LacNAc	SLe^X-OBn	34.2
N012		N015	30.5
N022		N025	40.2
N032		N035	38.6
N042		N045	40.0
N052		N055	33.7
N112		N115	26.9
N212		N215	23.0
S6LacNAc-OBn	Neu5Ac6LacNAc	$S6Le^X$-OBn	ND
N013			ND
N023			ND
N033			ND
N043			ND
N053			ND

III. General methods for HPLC analysis and purification of N-glycans

A) General methods for HILIC-ELSD analysis of N-glycans

Column: Waters XBridge BEH amide column, 130 Å, 5 μm, 4.6 mm × 250 mm
Solvent A: 100 mM ammonium formate, pH 3.4
Solvent B: Acetonitrile
Temperature: 40 °C

Gradient elution:	Time	B%	Flow rate
	0	65	1
	25	50	1
	26	0	0.5
	27	0	0.5
	28	65	1
	30	65	1

Monitor: Evaporative light scattering detector, 60 °C (Shimadzu ELSD-LTII)

B) General methods for HILIC-UV210 purification of N-glycans

Column: Waters XBridge BEH amide column, 130 Å, 5 μm, 10 mm × 250 mm
Solvent A: Water or 100 mM ammonium formate, pH 3.4
Solvent B: Acetonitrile
Temperature: 40 °C

Gradient elution:	Time	B%	Flow rate
	0	65	4
	25	50	4
	26	0	2
	27	0	2
	28	65	4
	30	65	4

Monitor: A_{210nm}

C) Test of different solvents for HILIC separation of N-glycans

Column: Waters XBridge BEH amide column, 130 Å, 5 μm, 4.6 mm × 250 mm
Solvent A1: 100 mM Ammonium Formate, pH 3.4
Solvent A2: Water
Solvent A3: 10 mM Formic Acid
Solvent B: Acetonitrile
Temperature: 40 °C

Gradient elution:	Time	B%	Flow rate
	0	70	1
	50	50	1
	52	0	0.5

54	0	0.5
56	70	1
60	70	1

Monitor: Evaporative light scattering detector, 60 °C (Shimadzu ELSD-LTII)

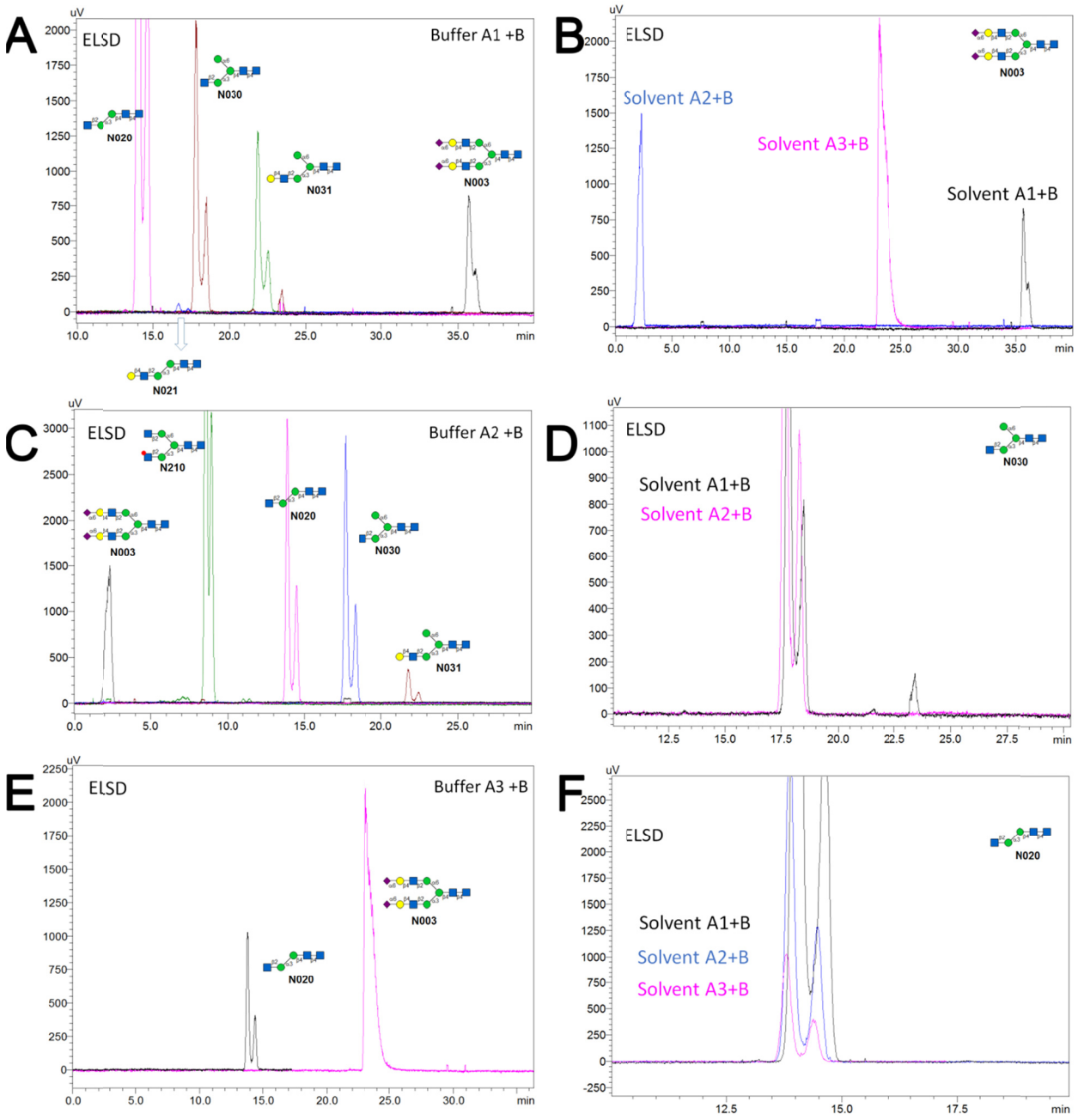


Figure S6. Separation of N-glycans using different solvent combinations. Results showed that 100 mM of ammonium formate gave best separation of all tested N-glycans (B), and solvent does not matters then separating non-sialylated N-glycans (C, D, F). In addition, the use of water yielded rapid elution of sialylated N-glycans (B, C).

IV. Groups of synthesized N-glycan isomers

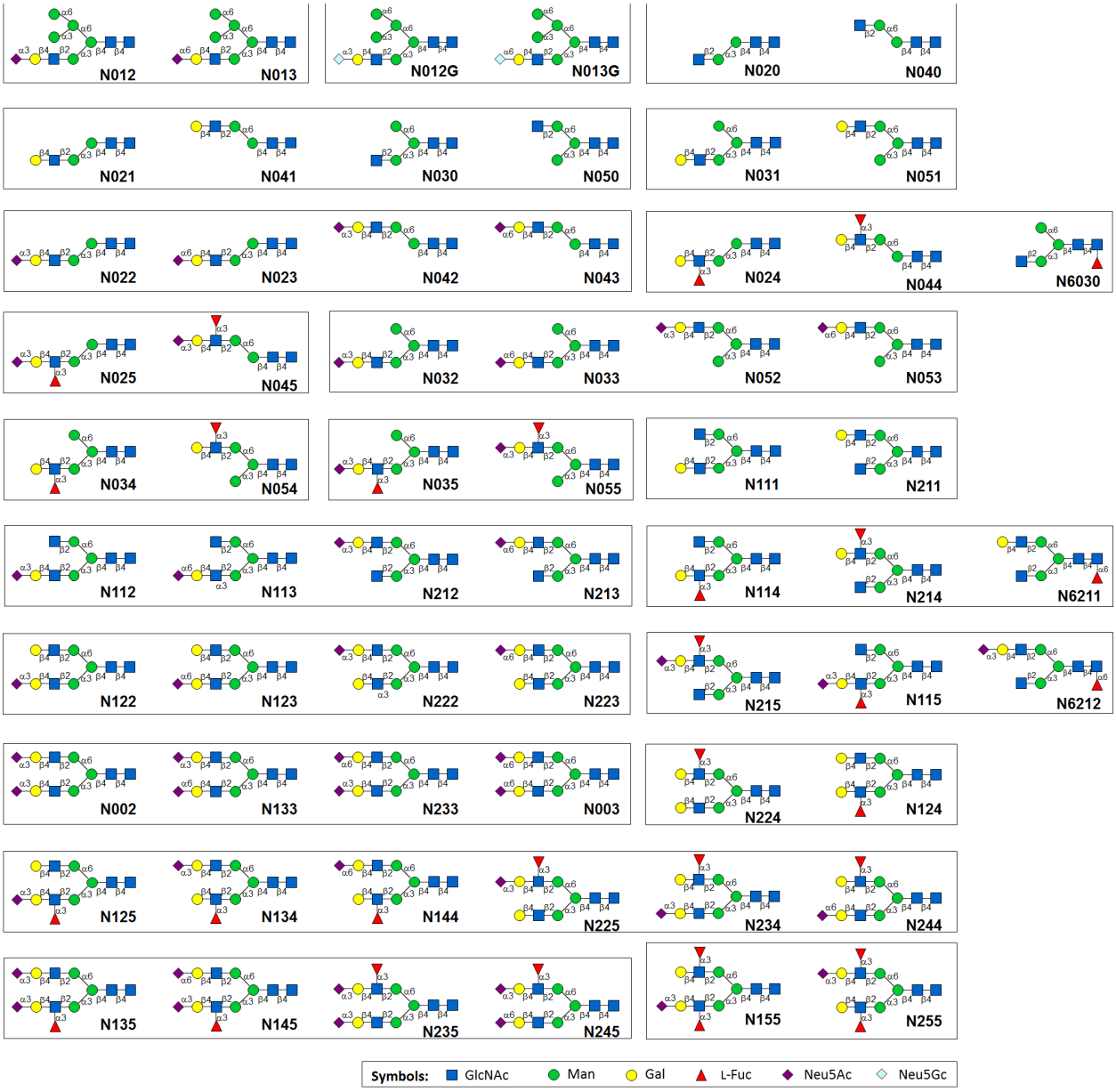


Figure S7. Groups of synthesized N-glycan isomers. Each group contains 2 to 6 distinct structures.

V. General methods for mass spectrum analysis

A) ESI-MS and MS^2 analysis of N-glycans

In this study, HPLC-MS experiments were performed on an LTQ-Orbitrap Elite mass spectrometer (Thermo Fisher) equipped with EASY-spray source and nano-LC UltiMate 3000 high performance liquid chromatography system (Thermo Fisher). Samples were transmitted into MS with a silica column. LTQ-Orbitrap Elite mass spectrometer was operated in the data-dependent mode. A full-scan survey MS experiment (m/z range from 375 to 1600; automatic gain control target, 1,000,000 ions; resolution at 400 m/z, 240,000; maximum ion accumulation time, 200 ms) was acquired by the Orbitrap mass spectrometer. CID fragmentation ion spectra were acquired in ion-trap spectrometer (automatic gain control target, 10,000 ions; maximum ion accumulation time, 100 ms), and Normal Collision Energy (NCE) of CID is set to 35.

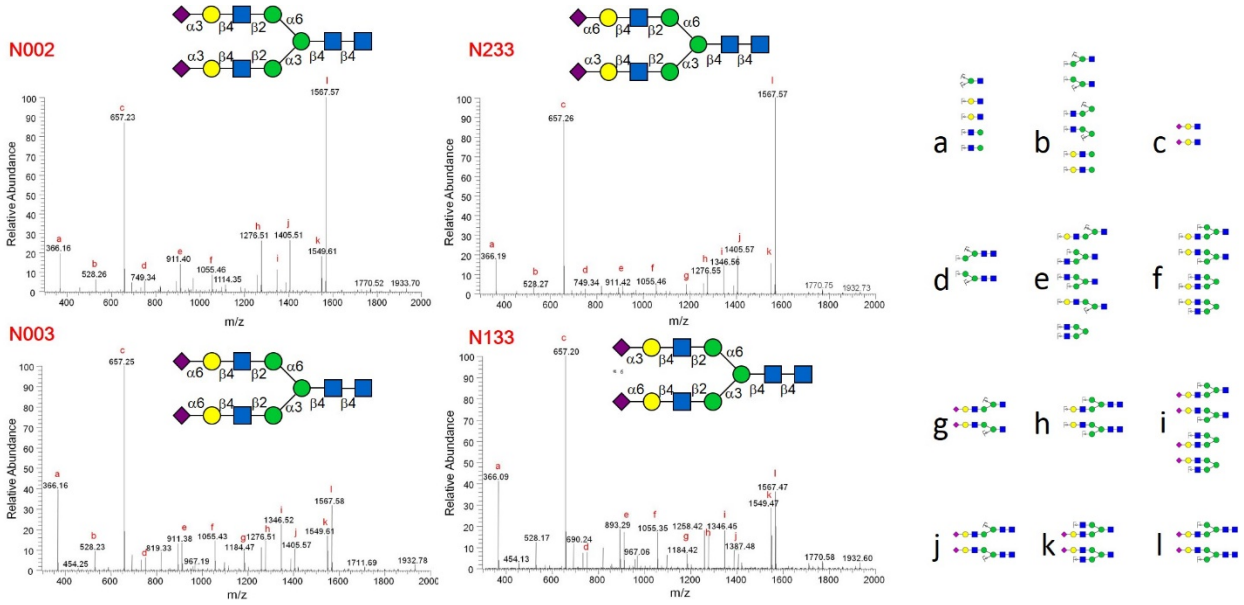


Figure S8. MS2 analysis of 4 N-glycan isomers (**N002**, **N003**, **N133** and **N233**).

B) MALDI-MS running conditions

MALDI-MS experiments were performed on UltrafleXtreme MALDI TOF/TOF Mass Spectrometer (Bruker). Scan range of MS^1 was according to the molecular weight of N-glycans, and reflector mode was used for N-glycan analysis. Mass spectra were obtained in both positive and negative extraction mode with the following voltage settings: ion source 1 (19.0 kV), ion source 2 (15.9 kV), and lens (9.3 kV). The reflector voltage was set to 20 kV. The laser was pulsed at 7 Hz and the pulsed ion extraction time was set to 400 ns. The laser power was kept in the 25–40% range.

VI. Chemical Synthesis

Materials: All chemicals were purchased as reagent grade and used without further purification. Anhydrous dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), tetrahydrofuran (THF), *N,N*-dimethyl formamide (DMF), toluene, and methanol (MeOH) were purchased from a commercial source without further distillation. Pulverized Molecular Sieves MS-4 Å (Aldrich) for glycosylation was activated by heating at 350 ^oC for 3 h. Reactions were monitored by analytical thin-layer chromatography (TLC) in EM silica gel 60 F254 plates and visualized under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate or *p*-anisadehyde. Flash chromatography was performed on silica gel (Merck) of 40-63μm particle size and P2 gel (Biorad). ^1H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz), and Bruker AVANCE 500 (500 MHz) spectrometer at 25 ^oC. All ^1H Chemical shifts (in ppm) were assigned according to $CDCl_3$ (δ= 7.24 ppm) and D_2O (δ = 4.79 ppm). ^{13}C NMR spectra were obtained with Bruker AVANCE 600 spectrometer and calibrated with $CDCl_3$ (δ = 77.00 ppm). Coupling constants (*J*) are reported in hertz (Hz). Splitting patterns are described using the following abbreviations: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; m, multiplet. 1H NMR spectra are reported in the following order: chemical shift, multiplicity, coupling constant(s), and number(s) of protons. All NMR signals were assigned on the basis of ^1H NMR, COSY, HSQC, HMQC, and ^{13}C NMR experiments. High resolution MALDA mass spectra were recorded on a Bruker Ultraflextreme spectrometer.

General Procedures.

A) Glycosylation procedure: A mixture of donor (1.3 mmol), acceptor (1 mmol) and 4 Å molecular sieves in dry Et_2O (or CH_2Cl_2) was stirred at room temperature under argon for 2 h. NIS (1.5 mmol) and AgOTf (0.2 mmol) were added at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h before it was quenched with a few drops of triethylamine. The resulting mixture was filtered. The filtrate was diluted with CH_2Cl_2 and washed with 5% $Na_2S_2O_3$, aqueous $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. The residue was purified on a silica gel column to produce the product.

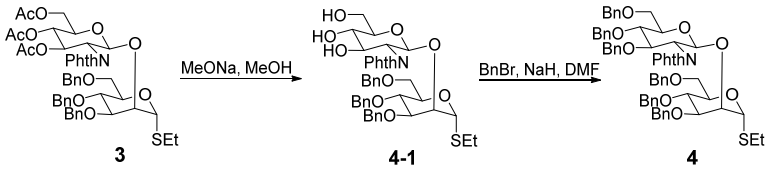
B) Benzylidene opening procedure: A mixture of oligosaccharide (1 mmol) and 4 Å molecular sieves in dry CH_2Cl_2 was stirred at room temperature under argon for 2 h. $PhBCl_2$ (2 mmol) and Et_3SiH (2 mmol) were added at -78 °C. The reaction mixture was stirred at -78 ^oC for 3 h before it was quenched with a few drops of triethylamine. The resulting mixture was filtered. The filtrate was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. The residue was purified on a silica gel column to afford the product.

C) Transformation of N-Phth to NHAc procedure: A mixture of N-Phth protected oligosaccharide was dissolved in *n*BuOH at room temperature, followed by addition of ethylenediamine (*n*BuOH: ethylenediamine = 2:1). After being stirred at 90 °C for 12 h, the mixture was evaporated *in vacuo* to give a residue for the next step without further purification. To a solution of the residue in pyridine was added Ac_2O. After being stirred at room temperature for 12 h, the solution was diluted with EtOAc and washed with aqueous HCl (1 M), saturated aqueous $NaHCO_3$, and brine solution. The organic layer was dried over Na_2SO_4, filtered, and evaporated *in vacuo* to give a residue, which was purified by silica gel column chromatography to give N-NHAc compound.

D) Deacetylation procedure: Ac-protected oligosaccharide was dissolved in MeOH, and NaOMe in MeOH was added until pH was 10. After stirring at room temperature for 2 h, the solution was neutralized with ion-exchange resin (H+), and then filtered. The residue was purified on a silica gel column to afford the desired deacetylated product

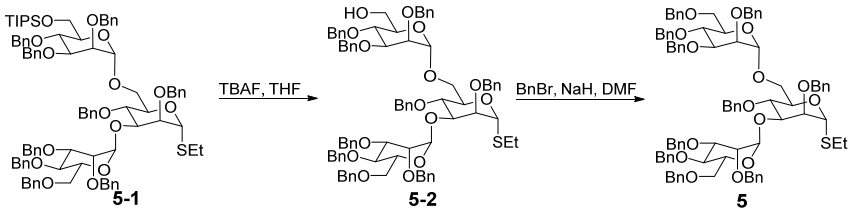
E) Global deprotection procdure: $Pd(OH)_2$ on carbon was added to a solution of protected oligosaccharide in $MeOH/H_2O$ (10/1). The mixture was stirred under 1 atmosphere of hydrogen. After being stirred for 24 h, the mixture was filtered through a PTFE syringe filter and concentrated in *vacuo.* The residue was purified by Bio-Gel P-2 (BIO-RAD) column chromatography using water as eluent. The product was then lyophilized to get target compound, as white powder.

Ethanethiol 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranoside (4):



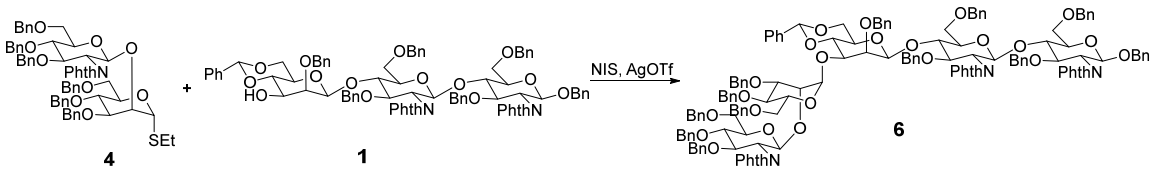
Compound **3**[7] (1 g, 1.1 mmol) was dissolved in MeOH, and NaOMe in MeOH was added until pH was 10. After stirring at room temperature for 2 h, the solution was neutralized with ion-exchange resin (H^+), and then filtered. The residue was dried under *vacuo* without further purification for next step, and then the residue was dissolved in dry DMF (10 mL). NaH (238 mg, 5.94 mmol), Bu_4NI (221 mg, 0.6 mmol), followed by BnBr (588 μL, 4.95 mmol) were added at 0 °C, the reaction mixture was stirred under argon for 4 h. The solvent was evaporated, and the residue was diluted with ethyl acetate and washed with water and a brine solution. After dried over Na_2SO_4, the organic layer was evaporated. The residue was purified on a silica gel column (Hexanes: EtOAc = 5:1) to afford the desired product **4** (929 mg, 80% over two steps) as colorless oil. $[\alpha]_D^{20}$ -1.68 (c 1, CH_2Cl_2);^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.57 (m, 2 H), 7.30-7.40 (m, 23 H), 7.19-7.21 (m, 2 H), 7.13-7.15 (m, 2 H), 7.07-7.08 (m, 2 H), 6.89-6.95 (m, 3 H), 5.36 (d, J = 8.1 Hz, 1 H), 5.05 (s, 1 H), 4.82-4.94 (m, 4 H), 4.70 (d, J = 11.5 Hz, 1 H), 4.62 (d, J = 14.1 Hz, 1 H), 4.63 (d, J = 16.2 Hz, 1 H), 4.59 (d, J = 12.5 Hz, 1 H), 4.56 (d, J = 13.1 Hz, 1 H), 4.53 (d, J = 12.1 Hz, 1 H), 4.37-4.45 (m, 3 H), 4.21 (brs, 1 H), 4.05 (brs, 2 H), 3.92 (t, J = 10.6 Hz, 1 H), 3.77-3.79 (m, 2 H), 3.55 (t, J = 5.2 Hz, 1 H), 3.43 (d, J = 10.6 Hz, 1 H), 3.01 (d, J = 10.7. 6.8 Hz, 1 H), 2.37-2.53 (m, 2 H), 1.18 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.5, 138.5 (2 C), 138.0 (2 C), 133.6, 131.8, 128.6, 128.5, 128.4 (2 C), 128.3, 128.2 (2 C), 128.1, 128.0 (2 C), 127.9, 127.8, 127.7, 127.5, 127.4 (3 C), 123.1, 96.6, 92.3, 80.9, 79.7, 79.2, 78.1, 75.5, 75.2, 75.1, 75.0, 74.9, 74.8, 73.7, 72.8, 71.9, 70.9, 69.9, 69.2, 55.8, 25.3, 14.7. MALDI-MS: [M+Na]+ $C_{64}H_{65}NO_{11}SNa$ calcd for 1078.4176, found 1078.4147

Ethanethiol 2,3,4,6-O-tetra-benzyl-α-D-Mannopyranosyl-(1→3)-[2,3,4,6-O-tetra-benzyl-α-D-Mannopyranosyl-(1→6)]-2,4-O-di-benzyl-α-D-Mannopyranoside (5):



To the solution of compound **5-1**[8] (2 g, 1.32 mmol) in THF (20 mL) was added TBAF (1.98 mL, 1.98 mmol) at room temperature. After being stirred for 2 h, the mixture was concentrated, purified by flash chromatography to give the compound **5-2**. The residue was dissolved in dry DMF (20 mL). NaH (95 mg, 2.38 mmol), Bu_4NI (74 mg, 0.2 mmol), followed by BnBr (235 μL, 1.98 mmol) were added at 0 °C, and the reaction mixture was stirred under argon for 4 h. The solvent was evaporated, and the residue was diluted with ethyl acetate and washed with water and a brine solution. After dried over Na_2SO_4, the organic layer was evaporated. The residue was purified on a silica gel column (Hexanes: EtOAc = 9:1) to afford the desired product **5** (1.63 g, 85% over two steps) as colorless oil. $[\alpha]_D^{20}$ -6.68 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26-7.41 (m, 46 H), 7.19-7.22 (m, 4 H), 5.38 (d, J = 1.5 Hz, 1 H, H-1), 5.34 (d, J = 1.5 Hz, 1 H, H-1), 5.11 (d, J = 1.1 Hz, 1 H, H-1), 4.93 (d, J = 11.0 Hz, 1 H, $PhCH_2$-), 4.88 (d, J = 10.6 Hz, 1 H, $PhCH_2$-), 4.68-4.73 (m, 5 H), 4.65-4.67 (m, 1 H), 4.59-4.64 (m, 3 H), 4.54-4.58 (m, 2 H), 4.51-4.53 (m, 2 H), 4.47-4.50 (m, 2 H), 4.33-4.35 (m, 3 H), 4.04-4.15 (m, 4 H), 3.81-3.97 (m, 9 H), 3.73-3.77 (m, 4 H), 2.58-2.65 (m, 1 H, $SC\underline{H}_2CH_3$), 2.47-2.56 (m, 1 H, $SC\underline{H}_2CH_3$), 1.23 (t, J = 7.4 Hz, 3 H, $SCH_2C\underline{H}_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.0, 138.8 (2 C), 138.7 (3 C), 138.5 (2 C), 137.9 (2 C), 128.5, 128.4 (4 C), 128.3 (3 C), 128.2 (2 C), 128.1, 127.9, 127.8 (5 C), 127.7, 127.6 (4 C), 127.4 (2 C), 127.2, 127.1, 100.0, 97.6, 81.1, 80.4, 80.3, 80.0, 77.3, 75.9, 75.5, 75.3, 75.1, 75.0, 74.8, 74.7, 73.4, 73.3, 73.1, 72.7, 72.5, 72.1, 72.0, 71.8, 71.7, 71.2, 71.1, 69.2, 66.5, 25.3, 15.0; MALDI-MS: [M+Na]+ $C_{90}H_{96}O_{15}SNa$ calcd for 1471.6368, found 1471.6454

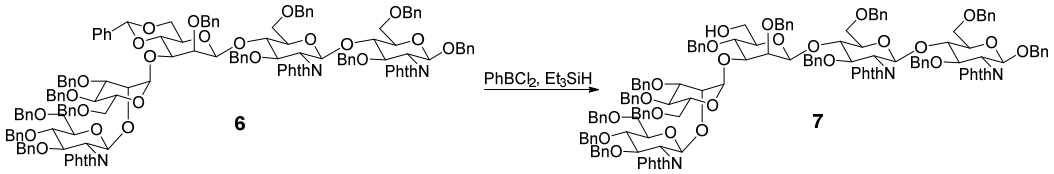
Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-Mannopyranosyl-(1→3)-2-O-benzyl-4,6-O-benzylidene-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (6):



Compound **1** (800 mg, 0.58 mmol) was glycosylated with **4** (789 mg, 0.75 mmol) by following general procedure **A** to get the desired compound **6 (**1.48 g, 93%) as colorless oil. $[\alpha]_D^{20}$ 18.8 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90-7.92 (m, 1 H), 7.57-7.77 (m, 11 H), 6.90-7.50 (m, 62 H), 6.77-6.83 (m, 3 H), 5.36 (s, 1 H, benzylidene), 5.32 (d, J = 7.6 Hz, H-1), 5.08 (s, 1 H, Man H-1), 5.01 (d, J = 8.2 Hz, 1 H, H-1), 4.83-4.93 (m, 6 H), 4.73-4.77 (m, 4 H), 4.60-4.67 (m, 2 H), 4.51-4.58 (m, 5 H), 4.38-4.49 (m, 7 H), 4.16-4.32 (m, 9 H), 4.03-4.10 (m, 4 H), 3.93-3.96 (m, 1 H), 3.82-3.88 (m, 2 H), 3.55-3.68 (m, 7 H), 3.35-3.51 (m, 7 H), 3.28 (dd, J = 10.8, 2.0 Hz, 1 H), 3.17-3.20 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.5, 167.7, 138.9, 138.8 (2 C), 138.7,

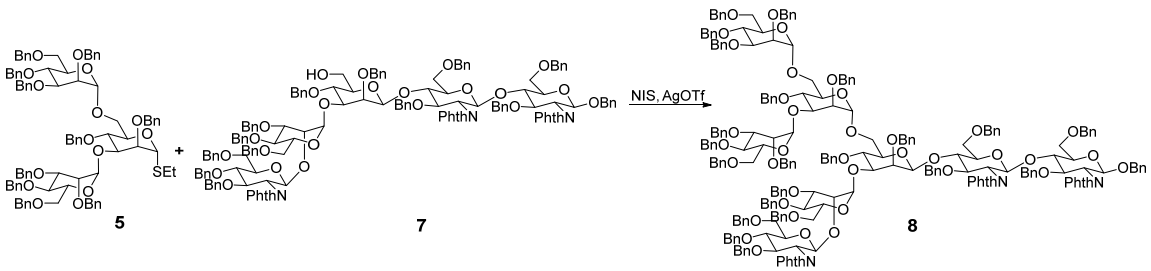
138.5, 138.4 (3 C), 138.3, 138.1, 138.0, 137.6, 137.2, 133.5, 132.0, 131.7, 129.0, 128.4 (2 C), 128.3, 128.2 (3 C), 128.1 (2 C), 127.9 (2 C), 127.8, 127.7, 127.6 (2 C), 127.5 (2 C), 127.4, 126.9 (2 C), 126.8, 123.2, 102.1, 100.9, 97.5, 97.2, 97.1, 95.5, 79.7, 79.0, 78.8, 78.3, 78.2, 77.6, 77.3, 76.2, 76.0, 75.2, 74.9, 74.6, 74.5, 74.4, 74.3, 74.1, 73.2, 73.1, 72.9, 72.7, 72.1, 71.2, 70.6, 70.2, 69.1, 68.6, 68.2, 67.7, 66.5, 56.6, 55.8, 55.7; MALDI-MS: [M+Na]+ $C_{145}H_{137}N_3O_{29}Na$ calcd for 2406.9235, found 2406.9355.

Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-Mannopyranosyl-(1→3)-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (7):



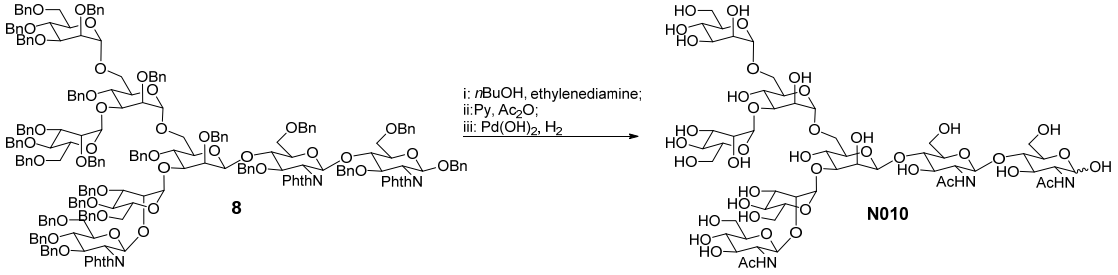
Compound **6** (800 mg, 0.335 mmol) was selectively opened the benzylidene ring by following general procedure **B** to get the desired title compound **7** (768 mg, 96%) as white foam. $[\alpha]_D^{20}$ -3.5 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67-7.75 (m, 6 H), 7.50-7.58 (m, 4 H), 7.35-7.44 (m, 15 H), 7.25-7.35 (m, 18 H), 7.15-7.25 (m, 11 H), 6.95-7.10 (m, 12 H), 6.85-6.95 (m, 8 H), 6.75-6.82 (m, 3 H), 5.28 (d, J = 7.3 Hz, 1 H), 5.07 (d, J = 7.7 Hz, 1 H), 4.98-5.00 (m, 2 H), 4.86-4.94 (m, 3 H), 4.78-4.83 (m, 3 H), 4.69-4.74 (m, 3 H), 4.60-4.66 (m, 3 H), 4.56-4.63 (m, 2 H), 4.54-4.56 (m, 3 H), 4.49-4.52 (m, 3 H), 4.44-4.47 (m, 3 H), 4.41-4.43 (m, 1 H), 4.37-4.39 (m, 2 H), 4.33-4.35 (m, 1 H), 4.13-4.30 (m, 10 H), 3.94-4.07 (m, 4 H), 3.84-3.86 (m, 1 H), 3.68-3.73 (m, 2 H), 3.63-3.67 (m, 1 H), 3.37-3.63 (m, 2 H), 3.50-3.56 (m, 4 H), 3.40-3.47 (m, 3 H), 3.32-3.40 (m, 3 H), 3.25-3.30 (m, 2 H), 3.15-3.17 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.9, 167.8, 138.9 (2 C), 138.8, 138.6, 138.5 (2 C), 138.4 (2 C), 138.3, 138.2, 138.0, 137.3, 133.6, 132.0, 131.8, 129.0, 128.7, 128.5 (2 C), 128.4, 128.3 (2 C), 128.2 (2 C), 128.1 (2 C), 128.0, 127.9 (2 C), 127.8, 127.7 (2 C), 127.6 (2 C), 127.5 (3 C), 127.2 (2 C), 127.0, 126.8, 123.2, 100.6, 98.8, 97.4, 97.3, 96.2, 80.8, 79.7, 79.0, 78.4, 78.1, 77.6, 76.9, 76.2, 75.4, 74.8, 74.7 (2 C), 74.5, 74.0, 73.5, 73.2, 73.0, 72.9, 72.6, 70.8, 70.6, 69.2, 68.3, 67.7, 61.9, 60.5, 56.6, 55.9, 55.8, 53.7; MALDI-MS: [M+Na]+ $C_{145}H_{139}N_3O_{29}Na$ calcd for 2408.9392, found 2408.9255

Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-[2,3,4,6-O-tetra-benzyl-α-D-Mannopyranosyl-(1→3)-[2,3,4,6-O-tetra-benzyl-α-D-Mannopyranosyl-(1→6)]-O-2,4-di-benzyl-α-D-Mannopyranosyl-(1→6)]-O-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (8):



Compound **7** (300 mg, 0.126 mmol) was glycosylated with **5** (237 mg, 0.164 mmol) by following general procedure A to get the desired title compound **8** (404 mg, 85%) as colorless oil. $[\alpha]_D^{20}$ 20.9 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.79 (m, 1 H), 7.62-7.68 (m, 4 H), 7.54-7.56 (m, 3 H), 7.36-7.41 (m, 8 H), 7.01-7.39 (m, 100 H), 6.92-6.95 (m, 3 H), 6.85-6.87 (m, 2 H), 6.78-6.79 (m, 3 H), 6.65-6.67 (m, 3 H), 5.35 (s, 1 H), 5.23-5.25 (m, 1 H), 5.11 (d, J = 7.8 Hz, 1 H), 5.03-5.04 (m, 2 H), 4.96-5.00 (m, 2 H), 4.78-4.93 (m, 8 H), 4.73-4.76 (m, 2 H), 4.70-4.71 (m, 2 H), 4.67-4.68 (m, 2 H), 4.63-4.65 (m, 2 H), 4.58-4.61 (m, 3 H), 4.41-4.56 (m, 18 H), 4.37-4.39 (m, 3 H), 4.32-4.34 (m, 2 H), 4.30-4.31 (m, 3 H), 4.24-4.27 (m, 4 H), 4.17-4.22 (m, 4 H), 4.12-4.16 (m, 4 H), 4.01-4.11 (m, 7 H), 3.95-3.98 (m, 2 H), 3.75-3.92 (m, 14 H), 3.68-3.71 (m, 6 H), 3.63-3.65 (m, 2 H), 3.48-3.59 (m, 7 H), 3.30-3.45 (m, 6 H), 3.12-3.14 (m, 1 H), 2.90-2.93 (m, 1 H), 2.74-2.78 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.8, 171.2, 171.0, 170.6, 170.5, 168.6, 139.0, 138.9, 138.8 (3 C), 138.7 (2 C), 138.6, 138.5, 138.4, 138.3 (2 C), 138.2 (3 C), 137.9, 137.8, 128.9, 128.7, 128.6 (2 C), 128.5, 128.4 (2 C), 128.3, 128.2, 128.1 (2 C), 128.0 (2 C), 127.9 (2 C), 127.8 (3 C), 127.6 (2 C), 127.5 (3 C), 127.4 (2 C), 127.3, 127.2, 127.1, 126.5, 101.8, 100.1, 100.0, 99.9, 99.6, 98.4, 98.3, 98.0, 81.2, 80.3, 80.2, 79.7, 78.9, 78.7, 78.5, 78.1, 77.5, 77.4, 75.9, 75.1, 75.0, 74.6, 74.5, 74.4, 73.5, 73.4 (2 C), 73.3, 73.2, 72.6, 72.4, 72.2, 72.0, 71.6, 71.0, 70.5, 70.2, 70.0, 69.8, 69.6, 69.3, 69.2, 68.5, 66.6, 66.1, 60.4, 57.8, 54.8, 53.9, 50.3; MALDI-MS: [M+Na]+ $C_{233}H_{229}N_3O_{44}Na$ calcd for 3795.5672, found 3795.5482

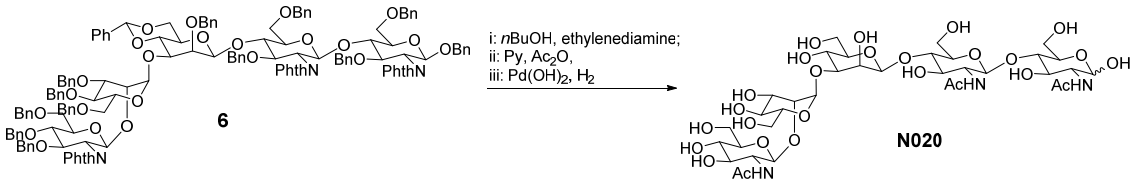
2-deoxy-acetamido-β-D-glucopyranosyl-(1→2)-α-D-Mannopyranosyl-(1→3)-[α-D-Mannopyranosyl-(1→3)-[α-D-Mannopyranosyl-(1→6)]-O-α-D-Mannopyranosyl-(1→6)]-O-β-D-Mannopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranoside (N010):



Following the general procedure **C,** and **E**, compound **8** (150 mg, 0.04 mmol) yielded the compound **N010** (35 mg, 63% over three steps). $[\alpha]_D^{20}$ 10.1 (c 0.5, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.22 (s, 1 H, Man5 H-1), 5.17 (d, J = 2.5 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.09 (s, 1 H, Man2 H-1), 4.92 (s, 1 H, Man3 H-1), 4.87 (s, 1 H, Man4 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.60 (d, J = 7.7 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.58 (d, J = 7.7 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.54 (d, J = 8.4 Hz, 1 H,

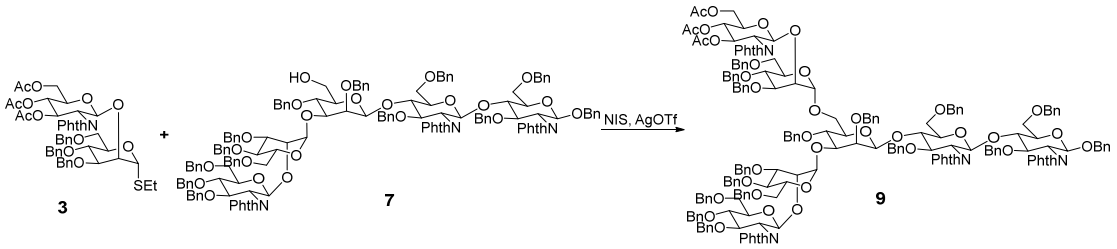
GlcNAc-3 H-1), 4.23 (d, J = 2.4 Hz, 1 H), 4.19 (d, J = 1.7 Hz, 1 H), 4.02-4.04 (m, 1 H), 3.83-3.96 (m, 15 H), 3.58-3.82 (m, 26 H), 3.47-3.55 (m, 2 H), 3.41-3.44 (m, 2 H), 2.06 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac); ^{13}C NMR (D_2O, 125 MHz): δ 174.7, 174.5, 174.4, 101.2 ($J_{C,H}$ = 174.8, 167.3 Hz, 2 C, Man5 C-1, GlcNAc-2 C-1), 100.3 ($J_{C,H}$ = 163.6 Hz, Manβ C-1), 99.5 ($J_{C,H}$ = 174.3, 173.1, 165.2 Hz, 3 C, Man2 C-1, Man4 C-1, GlcNAc-3 C-1), 99.1 ($J_{C,H}$ = 176.2 Hz, Man3 C-1), 94.7 (GlcNAc-1 C-1 of β anomer), 90.3 (GlcNAc-1 C-1 of α anomer), 80.4, 79.6, 79.3, 79.1, 76.3, 75.7, 74.5, 74.3, 73.7, 73.5, 73.2, 72.7, 72.4, 71.8, 70.7, 70.5, 70.1, 70.0, 69.9, 69.6, 69.3, 69.1, 67.2, 66.6, 66.4, 66.3, 65.5, 65.3, 61.6, 60.9, 60.8, 60.6, 60.0, 59.9, 56.0, 55.2, 54.9, 53.5, 22.2, 22.1, 21.8; ESI-MS: [M+H]+ $C_{54}H_{92}N_3O_{41}$ calcd for 1438.5206, found 1438.5187

2-dexoy-acetamido-β-D-glucopyranosyl-(1→2)-α-Mannopyranosyl-(1→3)-β-D-Mannopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranoside (N020):



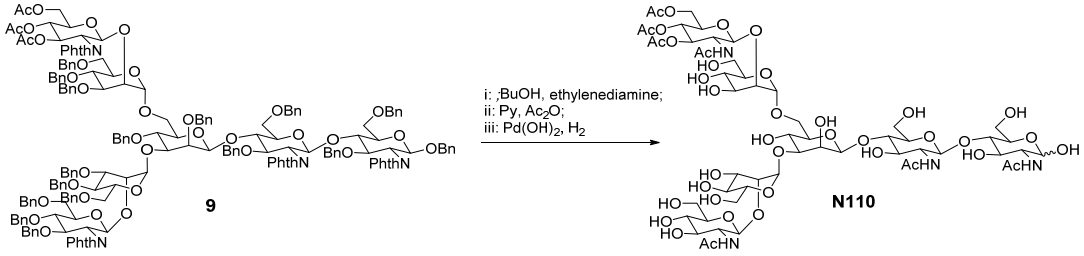
Following the general procedure **C** and **E**, compound **6** (150 mg, 0.063 mmol) yielded the compound **N020** (40 mg, 67% over three steps). $[\alpha]_D^{20}$ 1.8 (c 0.5, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.18 (d, J = 2.0 Hz, 0.54 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.9 Hz, 0.46 H, GlcNAc-1 H-1 of β anomer), 4.59 (d, J = 7.6 Hz, 0.54 H, GlcNAc-2 H-1 of α anomer), 4.58 (d, J = 7.6 Hz, 0.46 H, GlcNAc-2 H-1 of β anomer), 4.54 (d, J = 8.4 Hz, 1 H, GlcNAc-3 H-1), 4.22 (d, J = 2.8 Hz, 1 H), 4.18 (d, J = 1.7 Hz, 1 H), 3.86-3.93 (m, 7 H), 3.64-3.80 (m, 13 H), 3.57-3.64 (m, 3 H), 3.55 (t, J = 8.3 Hz, 1 H), 3.48-3.52 (m, 2 H), 3.41-3.47 (m, 3 H), 2.06 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac); ^{13}C NMR (D_2O, 125 MHz): δ 174.8, 174.7, 174.5, 174.4, 101.4 (GlcNAc-2 C-1), 99.9 ($J_{C,H}$ = 173.3 Hz, Man_2 C-1), 99.6 (GlcNAc-3 C-1), 99.5 ($J_{C,H}$ = 164.4 Hz, Manβ C-1), 94.8 (GlcNAc-1 C-1 of β anomer), 90.4 (GlcNAc-1 C-1 of α anomer), 80.4, 79.7, 79.2, 78.8, 76.4, 76.2, 75.8, 74.5, 73.5, 73.2, 72.4, 72.0, 70.3, 70.0, 69.9, 69.6, 69.3, 69.2, 67.3, 65.9, 61.7, 60.8, 60.6, 60.1, 60.0, 56.1, 55.3, 55.0, 53.6, 22.3, 22.2, 22.1, 21.9; ESI-MS: [M+H]+ $C_{36}H_{62}N_3O_{26}$ calcd for 952.3622, found 974.3637.

Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-[3,4,6-O-tri-acetyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→6)]-O-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (9):



Compound **7** (300 mg, 0.126 mmol) was glycosylated with **3** (149 mg, 0.164 mmol) by following general procedure **A** to get the desired compound **9 (**338 mg, 83%) as colorless oil. $[\alpha]_D^{20}$ 15.9 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 7.3 Hz, 1 H), 7.74 (t, J = 7.6 Hz, 1 H), 7.63-7.70 (m, 4 H), 7.33-7.41 (m, 8 H), 7.20-7.32 (m, 32 H), 7.12-7.19 (m, 15 H), 7.04-7.10 (m, 8 H), 6.95-7.02 (m, 8 H), 6.88-6.92 (m, 5 H), 6.76-6.82 (m, 5 H), 6.64 (t, J = 7.4 Hz, 1 H), 5.40 (t, J = 9.4 Hz, 1 H), 5.21 (d, J = 7.7 Hz, 1 H), 4.93-5.01 (m, 5 H), 4.82-4.91 (m, 5 H), 4.76-4.79 (m, 2 H), 4.68-4.74 (m, 3 H), 4.61-4.68 (m, 3 H), 4.32-4.54 (m, 15 H), 4.26-4.31 (m, 1 H), 4.09-4.24 (m, 10 H), 4.04-4.06 (m, 1 H), 3.95-4.00 (m, 3 H), 3.88-3.91 (m, 2 H), 3.68-3.83 (m, 8 H), 3.60-3.62 (m, 1 H), 3.42-3.56 (m, 6 H), 3.25-3.40 (m, 6 H), 3.20-3.24 (m, 1 H), 3.11-3.17 (m, 2 H), 2.91 (dd, J = 11.5, 5.7 Hz, 1 H), 2.79 (d, J = 9.5 Hz, 1 H), 2.63-2.67 (m, 1 H), 2.37-2.40 (m, 1 H), 2.29-2.32 (m, 1 H), 2.00 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 1.83 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2, 170.7, 170.1, 169.2, 168.1, 167.6, 167.4, 139.1, 139.0, 138.9, 138.8, 138.7, 138.6, 138.4 (2 C), 138.3, 138.1 (2 C), 137.8, 137.2, 133.4, 131.9, 131.7, 131.4, 129.1, 128.8, 128.6, 128.4, 128.3 (3 C), 128.2, 128.1 (3 C), 128.0 (2 C), 127.9 (2 C), 127.8, 127.7, 127.5 (2 C), 127.4 (3 C), 127.2, 126.8, 126.0, 123.1, 101.9, 98.6, 97.7, 97.1, 96.9, 96.7, 95.8, 80.7, 80.0, 79.4, 78.8, 78.3, 77.7, 77.2, 76.7, 75.8, 75.1, 74.8, 74.7, 74.6 (2 C), 74.5, 74.4 (2 C), 74.1, 74.0, 73.9, 73.5, 73.4, 72.9 (2 C), 72.6, 72.4 (2 C), 72.3, 71.9, 71.7 (2 C), 71.1, 71.0, 70.7, 70.5, 70.4 (2 C), 70.0, 69.5, 69.2, 68.7, 68.6, 68.4, 68.1, 67.6, 66.8, 63.8, 61.9, 61.8, 61.4, 60.4, 56.7, 55.8, 55.7, 54.2, 53.8, 20.7, 20.6, 20.5; MALDI-MS: [M+Na]+ $C_{192}H_{186}N_4O_{43}Na$ calcd for 3258.2389, found 3258.2169

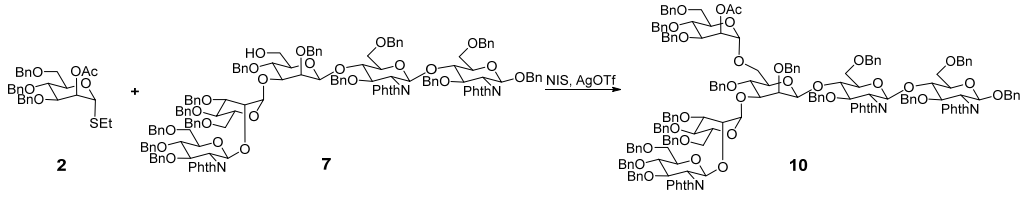
2-deoxy-acetamido-β-D-glucopyranosyl-(1→2)-α-D-Mannopyranosyl-(1→3)-[3,4,6-O-tri-acetyl-2-deoxy-acetamido-β-D-glucopyranosyl-(1→2)-α-D-Mannopyranosyl-(1→6)]-β-D-Mannopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranoside (N110):



Following the general procedure **C,** and **E**, compound **9** (150 mg, 0.046 mmol) yielded the compound **N110** (45 mg, 69% over three steps). $[\alpha]_D^{20}$ 4.9 (c 0.5, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.22 (t, J = 10.2 Hz, 1 H), 5.16 (d, J = 1.4 Hz, 0.6 H, GlcNAc-1H1 of α anomer), 5.09

(s, 1 H, Man2 H-1), 5.05 (t, J = 9.3 Hz, 1 H), 4.92 (s, 1 H, Man3 H-1), 4.77 (overlapped with D_2O, 1 H, GlcNAc-4 H-1), 4.74 (s, 1 H, Manβ H-1), 4.67 (d, J = 6.2 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.59 (d, J = 7.5 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.58 (d, J = 7.5 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.53 (d, J = 8.4 H, 1 H, GlcNAc-3 H-1), 4.40 (dd, J = 12.8, 3.3 Hz, 1 H), 4.22 (d, J = 1.5 Hz, 1 H), 4.16 (d, J = 1.9 Hz, 1 H), 4.10-4.11 (m, 1 H), 3.91-3.97 (m, 3 H), 3.82-3.90 (m, 8 H), 3.69-3.80 (m, 10 H), 3.65-3.68 (m, 2 H), 3.56-3.64 (m, 7 H), 3.53 (t, J = 7.9 Hz, 1 H), 3.49 (t, J = 5.5 Hz, 1 H), 3.47 (t, J = 4.2 Hz, 1 H), 3.44-3.46 (m, 1 H), 3.40-3.42 (m, 2 H), 2.10 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.97 (s, 3 H, Ac); ^{13}C NMR (D_2O, 125 MHz): δ 176.5, 174.6 (2 C), 174.5, 174.3, 173.6, 100.3 (GlcNAc-2 C-1), 99.5 ($J_{C,H}$ = 161.9 Hz, Manβ C-1), 99.0 ($J_{C,H}$ = 172.3, 165.5 Hz, Man2 C-1, GlcNAc-3 C-1), 98.8 (GlcNAc-4 C-1), 96.8 ($J_{C,H}$ = 171.9 Hz, Man3 C-1), 94.7 (GlcNAc-1 C-1 of β anomer), 90.3 (GlcNAc-1 C-1 of α anomer), 80.3, 79.6, 79.3, 79.1, 76.6, 76.3, 75.7, 74.5, 74.3, 74.2, 73.4, 73.3, 73.2, 72.8, 72.6, 72.3, 71.9, 71.2, 71.0, 70.1, 69.9, 69.8, 69.5, 69.3, 69.1, 68.9, 68.3, 67.2, 65.7, 65.5, 61.6 (2 C), 61.5, 61.4, 60.5, 60.0, 59.9, 59.8, 59.7, 56.0, 55.2, 54.8, 53.5, 53.4, 22.2, 22.1, 22.0, 21.8, 20.3, 20.0, 19.9; ESI-MS: [M+H]+ $C_{56}H_{91}N_4O_{39}$ calcd for 1443.5260, found 1443.5231

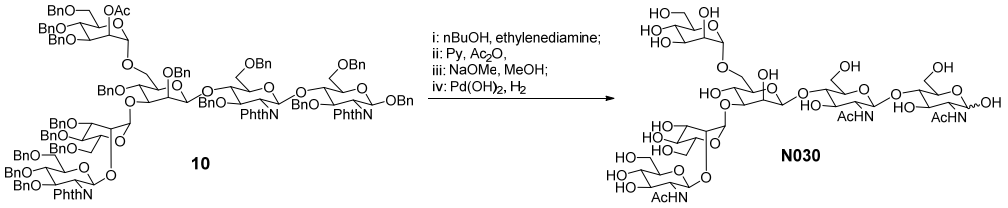
Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-[2-O-acetyl-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl (1→6)]-O-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (10):



Compound **7** (300 mg, 0.126 mmol) was glycosylated with **2** (88 mg, 0.16 mmol) by following general procedure **A** to get the desired title compound **10 (**327 mg, 91%) as colorless oil. $[\alpha]_D^{20}$ -10.7 (c 0.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.86 (m, 1 H), .7.56-7.76 (m, 7 H), 7.46-7.50 (m, 5 H), 7.12-7.45 (m, 61 H), 7.05-7.10 (m, 7 H), 6.90-6.98 (m, 5 H), 6.70-6.85 (m, 6 H), 5.38 (s, 1 H), 5.29 (d, J = 5.5 Hz, 1 H), 5.01-5.10 (m, 3 H), 4.86-4.97 (m, 6 H), 4.72-4.84 (m, 4 H), 4.37-4.69 (m, 20 H), 4.16-4.37 (m, 10 H), 4.05-4.15 (m, 3 H), 3.96-4.04 (m, 3 H), 3.91-3.94 (m, 1 H), 3.76-3.89 (m, 5 H), 3.66-3.74 (m, 4 H), 3.50-3.64 (m, 6 H), 3.41-3.47 (m, 2 H), 3.30-3.36 (m, 2 H), 3.15 (d, J = 9.6 Hz, 1 H), 2.97 (d, J = 9.4 Hz, 1 H), 2.79 (t, J = 8.0 Hz, 1 H), 1.89 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 171.2, 170.1, 169.8, 168.2, 167.7, 167.5, 139.0, 138.9, 138.8, 138.6 (2 C), 138.5 (2 C), 138.3 (3 C), 138.2, 138.1, 138.0, 137.9 (2 C), 137.3, 133.5, 132.0, 131.8, 128.9, 128.6, 128.5 (2 C), 128.4 (2 C), 128.3, 128.2, 128.1, 128.0 (3 C), 127.9 (3 C), 127.8 (2 C), 127.7, 127.6 (2 C), 127.5 (2 C), 127.4 (3 C), 126.9 (2 C), 126.4, 123.1, 101.5, 98.7, 98.3, 97.2 (2 C), 96.1, 81.1, 79.5, 79.3, 79.0, 78.3, 77.8, 77.7, 77.5, 76.8, 76.6, 76.5, 76.2, 76.1, 75.2, 74.9, 74.8, 74.7 (2 C), 74.6, 74.5, 74.3 (2 C), 74.2 (2 C), 73.9, 73.5, 73.4,

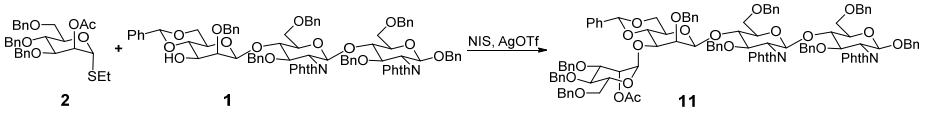
73.3, 73.0, 72.7 (2 C), 72.6, 72.5, 71.7, 71.2, 70.8, 70.6, 70.5, 69.0, 68.9, 68.8, 68.2, 67.8, 66.5, 60.4, 56.6, 55.9, 55.8, 20.8; MALDI-MS: [M+Na]+ $C_{174}H_{169}N_3O_{35}Na$ calcd for 2883.1434, found 2883.1833

2-deoxy-acetamido-β-D-glucopyranosyl-(1→2)-α-D-Mannopyranosyl-(1→3)-[α-D-Mannopyranosyl (1→6)]-O-β-D-Mannopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranoside (N030):



Following the general procedure **C, D** and **E**, compound **10** (150 mg, 0.05 mmol) yielded the compound **N030** (31 mg, 53% over four steps). $[\alpha]_D^{20}$ 20.6 (c 0.5, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.0 Hz, 0.6 H, GlcNAc-1 H1 of α anomer), 5.10 (s, 1 H, Man2 H-1), 4.90 (s, 1 H, Man3 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.8 Hz, 1 H, GlcNAc-1 H-1 of β anomer), 4.59 (d, J = 7.9 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.58 (d, J = 7.9 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.53 (d, J = 8.4 Hz, 1 H, GlcNAc-3 H-1), 4.24 (brs, 1 H), 4.17-4.18 (m, 1 H), 3.95-3.97 (m, 1 H), 3.84-3.92 (m, 9 H), 3.70-3.80 (m, 11 H), 3.67-3.69 (m, 1 H), 3.65-3.66 (m, 1 H), 3.58-3.64 (m, 7 H), 3.54 (t, J = 8.4 Hz, 1 H), 3.48 (t, J = 9.8 Hz, 1 H), 3.41-3.44 (m, 2 H), 2.06 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac); ^{13}C NMR (D_2O, 125 MHz): δ 174.7, 174.6, 174.3, 101.2 (GlcNAc-2, C-1), 100.3 ($J_{C,H}$ = 161.6 Hz, Manβ, C-1), 99.5 ($J_{C,H}$ = 174.4, 172.7, 161.6 Hz, 3 C, Man2 C-1, Man3 C-1, GlcNAc-3 C-1), 94.7 (GlcNAc-1 C-1 of β anomer), 90.3 (GlcNAc-1 C-1 of α anomer), 80.3, 79.5, 79.1, 76.3, 75.7, 74.5, 74.2, 74.0, 73.4, 73.1, 72.6, 72.3, 71.9, 70.3, 70.0, 69.9, 69.8, 69.3, 69.1, 67.2, 66.6, 65.8, 61.6, 60.8, 60.5, 59.8, 56.0, 55.2, 54.8, 53.5, 22.2, 22.1, 21.7; ESI-MS: [M+H]+ $C_{42}H_{72}N_3O_{31}$ calcd for 1114.4150, found 1114.4170

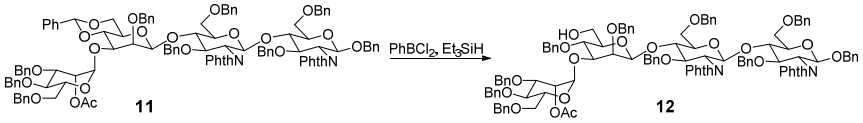
Benzyl 2-O-acetyl-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-2-O-benzyl-4,6-benzylidene-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (11):



Compound **1** (300 mg, 0.22 mmol) was glycosylated with **2** (150 mg, 0.28 mmol) by following general procedure **A** to get the desired compound **11** (382 mg, 95%) as colorless oil. $[\alpha]_D^{20}$ 7.68 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 6.7 Hz, 1 H), 7.75-7.78 (m, 4 H), 7.67-7.69 (m, 2 H), 7.48-7.50 (m, 4 H), 7.30-7.45 (m, 28 H), 7.23-7.28 (m, 4 H), 7.09-7.13 (m, 1 H), 7.03-7.07 (m, 5 H), 6.98-7.01 (m, 3 H), 6.94-6.96 (m, 3 H), 6.80-6.83 (m, 3 H), 5.67 (t, J = 2.0 Hz, 1 H), 5.56 (s, 1 H), 5.40 (d, J = 1.1 Hz, 1 H), 5.37 (d, J = 8.0 Hz, 1 H), 5.04 (d, J = 8.2 Hz, 1 H), 4.98 (d, J = 12.3 Hz, 1 H), 4.96 (d, J = 10.8 Hz, 1 H), 4.92 (d, J = 1.0 Hz, 12.1 Hz, 1

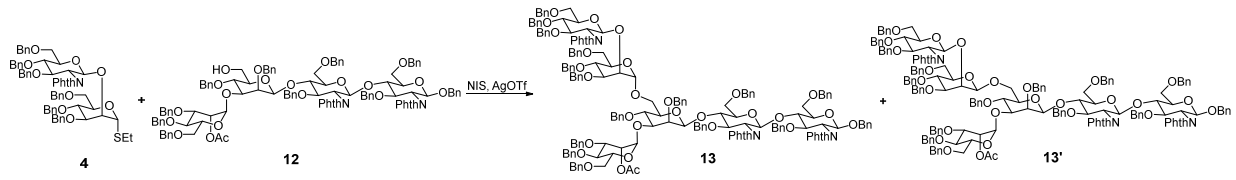
H), 4.88 (d, J = 12.8 Hz, 1 H), 4.77 (d, J = 12.4 Hz, 1 H), 4.76 (d, J = 11.1 Hz, 1 H), 4.71 (d, J = 12.7 Hz, 1 H), 4.68 (d, J = 8.4 Hz, 1 H), 4.61-4.64 (m, 3 H), 4.55-4.58 (m, 3 H), 4.52 (d, J = 6.0 Hz, 1 H), 4.48-4.49 (m, 2 H), 4.44-4.47 (m, 2 H), 4.25-4.35 (m, 4 H), 4.18-4.23 (m, 2 H), 4.14-4.16 (m, 1 H), 4.12 (t, J = 9.5 Hz, 1 H), 4.05 (dd, J = 8.5, 3.2 Hz, 1 H), 3.91-3.94 (m, 2 H), 3.82-3.88 (m, 3 H), 3.69-3.75 (m, 2 H), 3.64-3.67 (m, 1 H), 3.51-3.58 (m, 2 H), 3.46 (dd, J = 11.5, 2.6 Hz, 1 H), 3.39 (dd, J = 9.8, 2.4 Hz, 1 H), 3.26-3.29 (m, 1 H), 3.12-3.18 (m, 1 H), 2.16 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.6, 170.1, 167.7, 138.9, 138.7, 138.6, 138.5, 138.4, 138.2, 137.9 (2 C), 137.4, 137.3, 133.5, 131.8, 128.8, 128.7, 128.5 (2 C), 128.4 (2 C), 128.3, 128.2, 128.1 (3 C), 127.9 (3 C), 127.8, 127.7, 127.6 (3 C), 127.5, 127.4 (2 C), 127.0, 126.9, 126.1, 123.2, 101.6, 101.1, 98.8, 97.2, 97.1, 79.0, 78.8, 78.5, 78.1, 77.4, 77.1, 76.6, 76.5, 76.1, 75.8, 75.5 (2 C), 74.9, 74.8, 74.7, 74.6, 74.4, 74.3, 73.6, 73.3, 72.8, 72.7, 72.5, 72.3, 71.7, 70.6, 69.0, 68.9, 68.4, 67.8, 67.0, 56.7, 55.8, 21.1; MALDI-MS: [M+Na]+ $C_{112}H_{108}N_2O_{24}Na$ calcd for 1887.7190, found 1887.7325

Benzyl 2-O-acetyl-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (12):



Compound **11** (300 mg, 0.16 mmol) was treated by following general procedure **B** to get the desired title compound **12 (**276 mg, 92%) as white foam. $[\alpha]_D^{20}$ 3.68 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.96 (m, 1 H), 7.75-7.78 (m, 3 H), 7.67-7.69 (m, 2 H), 7.48-7.50 (m, 2 H), 7.28-7.45 (m, 33 H), 7.23-7.26 (m, 3 H), 7.04-7.08 (m, 6 H), 6.97-7.01 (m, 5 H), 6.82-6.84 (m, 3 H), 5.57-5.58 (m, 1 H), 5.39 (d, J = 7.8 Hz, 1 H, H-1), 5.27 (d, J = 0.9 Hz, 1 H, Man H-1), 5.02-5.07 (m, 3 H), 4.87-4.97 (m, 3 H), 4.77-4.82 (m, 2 H), 4.67-4.73 (m, 3 H), 4.56-4.66 (m, 5 H), 4.51-4.55 (m, 3 H), 4.44-4.50 (m, 3 H), 4.23-4.36 (m, 5 H), 4.12-4.18 (m, 1 H), 4.05 (dd, J = 9.1, 3.2 Hz, 1 H), 3.98-4.01 (m, 1 H), 3.83-3.95 (m, 3 H), 3.71-3.80 (m, 5 H), 3.65-3.68 (m, 1 H), 3.46-3.57 (m, 3 H), 3.40-3.43 (m, 1 H), 3.31-3.33 (m, 1 H), 3.15-3.18 (m, 1 H), 2.18 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 170.1, 167.7, 138.8, 138.7, 138.6, 138.1, 138.0, 137.9, 137.8, 137.3, 133.6, 131.8, 128.7, 128.5 (3 C), 128.4 (2 C), 128.3 (2 C), 128.2 (3 C), 128.1, 128.0, 128.0, 127.9 (3 C), 127.8 (3 C), 127.6 (2 C), 127.5, 127.2, 127.1, 126.9, 123.2, 100.9, 99.7, 97.2, 80.7, 78.5, 78.3, 78.0, 77.1, 76.7, 76.0, 75.6, 75.1, 75.0 (2 C), 74.7, 74.6, 74.5, 73.6, 73.3, 72.8, 72.7, 72.5, 72.4, 71.9, 70.6, 69.2, 68.8, 68.3, 67.8, 67.6, 62.1, 56.6, 55.9, 21.1; MALDI-MS: [M+Na]+ $C_{112}H_{110}N_2O_{24}Na$ calcd for 1889.7346, found 1889.7427

Benzyl 2-O-acetyl-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-[3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→6)]-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (13):

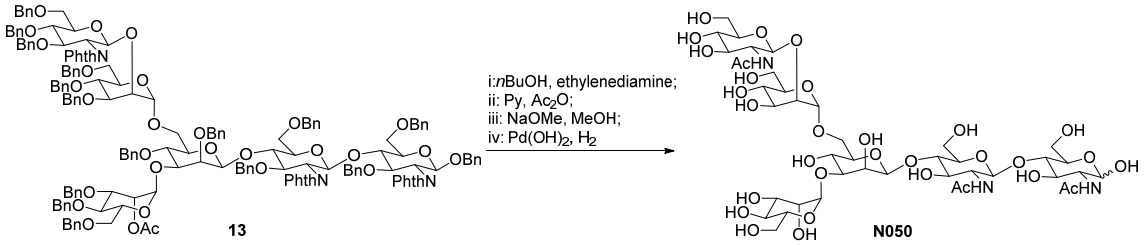


Compound **12** (300 mg, 0.16 mmol) was glycosylated with **4** (220 mg, 0.21 mmol) by following general procedure **A** to get the desired α anomer **13 (**347 mg, 76%) and β-anomer **13'** (69 mg, 15%) as colorless oil. $[\alpha]_D^{20}$ 13.7 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, J = 7.3 Hz, 1 H), 7.69 (t, J = 7.3 Hz, 1 H), 7.60-7.64 (m, 3 H), 7.49-7.52 (m, 3 H), 7.39-7.43 (m, 4 H), 7.06-7.43 (m, 59 H), 6.99-7.03 (m, 2 H), 6.90-6.98 (m, 11 H), 6.85-6.89 (m, 5 H), 6.69-6.74 (m, 3 H), 6.61 (t, J = 7.5 Hz, 1 H), 6.53 (t, J = 7.3 Hz, 1 H), 5.47 (s, 1 H), 5.19 (d, J = 7.8 Hz, 1 H), 5.11 (s, 1 H), 4.99 (d, J = 12.0 Hz, 1 H), 4.91 (d, J = 8.5 Hz, 1 H), 4.87 (d, J = 13.0 Hz, 1 H), 4.85 (d, J = 15.5 Hz, 1 H), 4.74-4.80 (m, 4 H), 4.62-4.69 (m, 4 H), 4.54-4.62 (m, 4 H), 4.40-4.55 (m, 10 H), 4.32-4.36 (m, 4 H), 4.26 (dd, J = 11.4, 4.4 Hz, 1 H), 4.10-4.19 (m, 6 H), 4.05-4.09 (m, 2 H), 3.98-4.02 (m, 3 H), 3.90-3.97 (m, 2 H), 3.80-3.88 (m, 4 H), 3.73-3.80 (m, 2 H), 3.63-3.71 (m, 4 H), 3.56-3.62 (m, 4 H), 3.47-3.52 (m, 2 H), 3.29-3.42 (m, 6 H), 3.22-3.26 (m, 1 H), 3.12-3.19 (m, 2 H), 3.08-3.10 (m, 1 H), 2.74 (dd, J = 11.1, 6.2 Hz, 1 H), 2.59-2.63 (m, 1 H), 2.05 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 177.2, 169.9, 167.9, 167.5, 167.3, 138.9, 138.8, 138.6, 138.5 (2 C), 138.4, 138.2, 137.9, 137.7, 133.4, 131.8, 131.7, 131.4, 128.6, 128.5, 128.3, 128.2 (2 C), 128.1 (2 C), 128.0, 127.9, 127.8, 127.7 (2 C), 127.5 (2 C), 127.4, 127.2, 127.1, 127.0 (2 C), 126.8, 123.4, 123.0, 102.3 ($J_{C,H}$ = 157.9Hz), 99.5 ($J_{C,H}$ = 176.2 Hz), 97.8 ($J_{C,H}$ = 170.2 Hz), 97.0 ($J_{C,H}$ = 164.5 Hz), 96.8 ($J_{C,H}$ = 166.2 Hz), 96.7 ($J_{C,H}$ = 169.8 Hz), 81.0, 80.2, 79.2, 78.8, 78.1, 77.9, 76.5, 75.6, 74.9, 74.7, 74.6, 74.5, 74.4, 74.3, 74.1, 74.0, 73.9, 73.4 (2 C), 73.0, 72.6, 72.4, 72.3, 72.1, 71.7, 70.4, 69.6, 68.9, 68.7, 68.1, 67.4, 66.9, 56.6, 55.7, 55.5, 20.9; MALDI-MS: [M+Na]+ $C_{174}H_{169}N_3O_{35}Na$ calcd for 2883.1434, found 2883.1873

Benzyl 2-O-acetyl-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-[3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-β-D-Mannopyranosyl-(1→6)]-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (13'): $[\alpha]_D^{20}$11. 8 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61-7.63 (m, 1 H), 7.50-7.56 (m, 4 H), 7.35-7.45 (m, 10 H), 7.10-7.33 (m, 54 H), 7.02-7.06 (m, 3 H), 6.93-7.01 (m, 9 H), 6.71-6.623 (m, 7 H), 6.65-6.68 (m, 2 H), 6.59-6.62 (m, 2 H), 5.44 (d, J = 8.8 Hz, 1 H), 5.43 (s, 1 H), 5.34 (d, J = 7.8 Hz, 1 H), 5.15 (s, 1 H), 4.98-5.02 (m, 2 H), 4.95 (d, J = 8.4 Hz, 1 H), 4.81-4.87 (m, 3 H), 4.67-4.75 (m, 7 H), 4.57-4.64 (m, 4 H), 4.49-4.55 (m, 4 H), 4.30-4.48 (m, 16 H), 4.22-4.28 (m, 2 H), 4.15-4.21 (m, 3 H), 4.13 (dd, J = 14.3, 7.2 Hz, 1 H), 4.02-4.08 (m, 2 H), 4.00 (t, J = 9.2 Hz, 1 H), 3.94-3.97 (m, 2 H), 3.80-3.91 (m, 7 H), 3.75-3.77 (m, 1 H), 3.60-3.70 (m, 3 H), 3.52-3.59 (m, 3 H), 3.35-3.47 (m, 5 H), 3.23-3.28 (m, 1 H), 3.10-3.14 (m, 1 H), 2.98-3.02 (m, 1 H), 2.05 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.9, 168.3, 168.2, 167.9, 167.5, 167.2, 139.4, 139.3, 139.0, 138.7, 138.6, 138.5, 138.2, 138.0, 137.8, 137.2, 136.8, 133.8, 133.5, 132.9, 132.0, 131.7 (2 C), 131.5, 128.9, 128.7, 128.5, 128.4, 128.3 (2 C), 128.1, 128.0, 127.8 (2 C), 127.7, 127.5, 127.4, 127.3, 127.1, 127.0, 126.8, 126.7, 123.3, 123.0, 122.5, 100.6

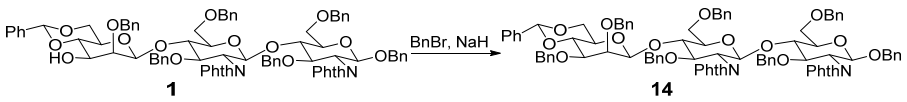
($J_{C,H}$ = 160.7 Hz), 100.3 ($J_{C,H}$ = 159.2 Hz), 99.5 ($J_{C,H}$ = 174.7 Hz), 99.1 ($J_{C,H}$ = 170.1 Hz), 98.1 ($J_{C,H}$ = 168.8 Hz), 97.0 ($J_{C,H}$ = 166.0 Hz), 81.0, 79.4, 78.9, 78.0, 77.7, 76.4, 75.9, 75.6, 74.6, 74.5, 74.4, 74.2, 74.1,73.5, 73.4, 73.3, 73.2, 72.7, 72.6, 72.3, 71.4, 69.6, 69.3, 68.8, 68.6, 67.8, 67.1, 66.8, 56.4, 56.2, 55.8, 54.6, 20.9; MALDI-MS: [M+Na]+ $C_{174}H_{169}N_3O_{35}Na$ calcd for 2883.1434, found 2883.2833

α-D-Mannopyranosyl-(1→3)-[2-deoxy-acetamido-β-D-glucopyranosyl-(1→2)-α-D-Mannopyranosyl-(1→6)]-O-β-D-Mannopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranoside (N050):



Following the general procedure **C, D** and **E**, compound **13** (150 mg, 0.05 mmol) yielded the compound **N050** (32 mg, 55% over four steps). $[\alpha]_D^{20}$ 6.78 (c 0.5, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.3 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.08 (s, 1 H, Man_2 H-1), 4.90 (s, 1 H, Man_3 H-1), 4.75 (s, 1 H, Manβ H-1), 4.67 (d, J = 8.0 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.59 (d, J = 7.8 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.58 (d, J = 7.8 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.53 (d, J = 8.4 Hz, 1 H, GlcNAc-3 H-1), 4.23 (d, J = 1.6 Hz, 1 H), 4.09 (d, J = 1.8 Hz, 1 H), 4.04 (dd, J = 3.1, 1.6 Hz, 1 H), 3.94 (dd, J = 11.0, 5.5 Hz, 1 H), 3.84-3.91 (m, 7 H), 3.65-3.80 (m, 14 H), 3.57-3.65 (m, 7 H), 3.51 (t, J = 8.5 Hz, 1 H), 3.42-3.49 (m, 2 H), 3.40-3.42 (m, 1 H), 2.06 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac); ^{13}C NMR (D_2O, 125 MHz): δ 174.7, 174.6, 174.5, 174.4, 102.4 ($J_{C,H}$ = 173.6 Hz, Man2 C-1), 101.3 (GlcNAc-2 C-1), 100.3 ($J_{C,H}$ = 161.9 Hz, Manβ C-1), 99.5 (GlcNAc-3 C-1), 96.9 ($J_{C,H}$ = 171.9 Hz, Man3 C-1), 94.7 (GlcNAc-1 C-1 of β anomer), 90.3 (GlcNAc-1 C-1 of α anomer), 80.5, 79.6, 79.4, 79.1, 76.1, 75.7, 74.5, 74.3, 74.2, 73.3, 73.2, 72.7, 72.4, 71.9, 70.2, 70.0, 69.9, 69.8, 69.5, 69.3, 69.1, 67.2, 66.7, 65.7, 65.5, 61.5, 61.0, 60.5, 60.0, 59.9, 56.0, 55.2, 54.8, 53.5, 22.2, 22.1, 22.0, 21.8; ESI-MS: [M+H]+ $C_{42}H_{72}N_3O_{31}$ calcd for 1114.4150, found 1114.4105

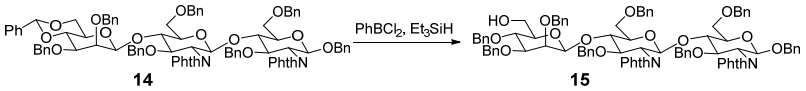
Benzyl 2,3-O-di-benzyl-4,6-O-benzylidene-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (14):



Compound **1** (500 mg, 0.36 mmol) was dissolved in dry DMF (10 mL). NaH (26 mg, 0.65 mmol), Bu_4NI (15 mg, 0.04 mmol), followed by BnBr (64 μL, 0.54 mmol) were added at 0 °C,

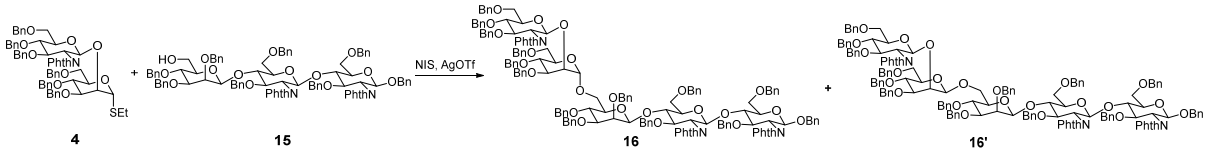
and the reaction mixture was stirred under argon for 4 h. The solvent was evaporated, and the residue was diluted with ethyl acetate and washed with water and a brine solution. After dried over Na_2SO_4, the organic layer was evaporated. The residue was purified on a silica gel column (Hexanes: EtOAc = 3:1) to afford the product **14** (479 mg, 90%) as colorless oil. $[\alpha]_D^{20}$ 19.2 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, J = 6.8 Hz, 1 H), 7.66-7.76 (m, 5 H), 7.48-7.50 (m, 4 H), 7.21-7.41 (m, 26 H), 7.05-7.08 (m, 1 H), 6.96-7.02 (m, 6 H), 6.89-6.91 (m, 3 H), 6.77-6.80 (m, 2 H), 5.53 (s, 1 H), 5.32 (d, J = 8.0 Hz, 1 H), 4.99 (d, J = 8.2 Hz, 1 H), 4.85-4.95 (m, 4 H), 4.77 (d, J = 12.4 Hz, 1 H), 4.73 (d, J = 12.4 Hz, 1 H), 4.61 (d, J = 12.4 Hz, 1 H), 4.59 (d, J = 11.2 Hz, 2 H), 4.56 (d, J = 12.3 Hz, 2 H), 4.30 (dd, J = 7.0, 2.4 Hz, 1 H), 4.26-4.27 (m, 1 H), 4.23-4.25 (m, 1 H), 4.22 (t, J = 2.7 Hz, 1 H), 4.18-4.20 (m, 1 H), 4.13-4.16 (m, 2 H), 4.10 (t, J = 9.6 Hz, 2 H), 3.79 (d, J = 3.0 Hz, 1 H), 3.64-3.66 (m, 1 H), 3.59-3.62 (m, 1 H), 3.56 (t, J = 10.3 Hz, 1 H), 3.49 (dd, J = 8.8, 3.7 Hz, 1 H), 3.44 (dd, J = 10.4, 2.5 Hz, 1 H), 3.35 (dd, J = 9.8, 2.4 Hz, 1 H), 3.23-3.26 (m, 1 H), 3.13-3.19 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2, 167.6, 162.6, 138.9, 138.7 (2 C), 138.6 (2 C), 137.9, 137.7, 137.2, 133.5, 131.7, 128.8, 128.5, 128.4, 128.3 (2 C), 128.2 (2 C), 128.1, 127.8, 127.7 (2 C), 127.6 (2 C), 127.5 (2 C), 127.4 (2 C), 126.9 (2 C), 126.1, 123.1, 101.8, 101.3, 97.2, 97.1, 79.3, 78.7, 78.4, 77.3, 77.1, 76.6, 75.8, 75.2, 74.7, 74.6, 74.5, 74.3, 73.3, 72.7, 72.6, 70.5, 68.6, 68.2, 68.0, 67.3, 60.4, 56.6, 55.8; MALDI-MS: [M+Na]+ $C_{90}H_{84}N_2O_{18}Na$ calcd for 1503.5617, found 1503.5415

Benzyl 2,3,4-O-tri-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (15):



The compound **14** (400 mg, 0.27 mmol) was treated accordingly to the general procedure **B** to afford trisaccharide acceptor **15** (380 mg, 95%). $[\alpha]_D^{20}$ 16.2 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95-7.96 (m, 1 H), 7.76-7.79 (m, 3 H), 7.69-7.71 (m, 2 H), 7.53-7.55 (m, 2 H), 7.46-7.47 (m, 2 H), 7.28-7.43 (m, 21 H), 7.05-7.12 (m, 7 H), 6.97-7.01 (m, 5 H), 6.84-6.86 (m, 3 H), 5.41 (d, J = 8.0 Hz, 1 H), 5.07 (s, 1 H), 5.06 (d, J = 9.6 Hz, 1 H), 4.94-4.97 (m, 4 H), 4.79 (d, J = 12.3 Hz, 1 H), 4.63-4.69 (m, 5 H), 4.59-4.61 (m, 3 H), 4.54 (d, J = 3.6 Hz, 1 H), 4.51 (d, J = 3.8 Hz, 1 H), 4.47 (d, J = 12.4 Hz, 1 H), 4.24-4.41 (m, 5 H), 4.18-4.21 (m, 1 H), 4.13 (t, J = 9.1 Hz, 1 H), 3.84-3.91 (m, 2 H), 3.73-3.81 (m, 2 H), 3.68 (d, J = 10.7 Hz, 1 H), 3.53-3.58 (m, 2 H), 3.47-3.49 (m, 1 H), 3.39-3.44 (m, 2 H), 3.26-3.29 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2, 168.6, 167.7 (2C), 138.8, 138.7, 138.6, 138.4 (2 C), 138.0, 137.3, 133.6, 131.7, 128.7, 128.5 (2 C), 128.3 (2 C), 128.2 (2 C), 128.1 (2 C), 127.9, 127.8 (2 C), 127.6 (3 C), 127.4, 127.3, 127.2, 126.9, 123.2, 101.1, 97.2 (2 C), 82.6, 79.0, 77.1, 76.6, 75.9, 75.7, 75.3, 75.2, 74.9, 74.7 (2 C), 74.6, 74.5 (2 C), 73.4, 72.8, 71.9, 70.6, 68.3, 68.0, 62.4, 60.5, 56.6, 55.9; MALDI-MS: [M+Na]+ $C_{90}H_{86}N_2O_{18}Na$ calcd for 1505.5773, found 1505.5615

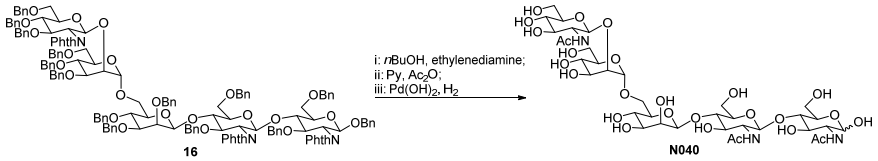
Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-Mannopyranosyl-(1→6)-2,3,4-O-tri-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (16):



Compound **15** (300 mg, 0.20 mmol) was glycosylated with **4** (277 mg, 0.26 mmol) by following general procedure **A** to get the desired α anomer compound **16 (**350 mg, 71%) and β anomer **16'** (100 mg, 20%) as colorless oil. $[\alpha]_D^{20}$ 5.9 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83 (d, J = 5.7 Hz, 1 H), 7.71 (t, J = 5.7 Hz, 1 H), 7.57-7.67 (m, 4 H), 7.46-7.49 (m, 2 H), 7.40-7.43 (m, 2 H), 7.23-7.36 (m, 30 H), 7.13-7.20 (m, 10 H), 7.07-7.12 (m, 9 H), 6.91-7.02 (m, 14 H), 6.86-6.91 (m, 3 H), 6.73-6.79 (m, 3 H), 6.68-6.71 (m, 2 H), 6.59-6.63 (m, 1 H), 5.26 (d, J = 6.7 Hz, 1 H), 4.92-5.00 (m, 4 H), 4.78-4.87 (m, 4 H), 4.68-4.75 (m, 4 H), 4.59-4.64 (m, 3 H), 4.45-4.56 (m, 9 H), 4.36-4.43 (m, 4 H), 4.24-4.30 (m, 4 H), 4.17-4.23 (m, 4 H), 4.11-4.15 (m, 3 H), 4.03-4.08 (m, 2 H), 3.91 (t, J = 7.6 Hz, 1 H), 3.84 (d, J = 1.6 Hz, 1 H), 3.81 (d, J = 2.6 Hz, 1 H), 3.70-3.77 (m, 3 H), 3.60-3.64 (m, 2 H), 3.54-3.59 (m, 2 H), 3.45-3.51 (m, 2 H), 3.39-3.44 (m, 3 H), 3.35-3.38 (m, 2 H), 3.28-3.30 (m, 2 H), 3.17-3.22 (m, 2 H), 2.88-2.92 (m, 1 H), 2.79 (dd, J = 8.8, 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.3, 168.1, 167.6, 167.5, 139.1, 139.0, 138.7, 138.6, 138.5 (2 C), 138.3, 138.2, 138.1, 138.0, 137.2, 133.8, 133.5, 133.4, 131.9, 131.7 (2 C), 131.5, 128.5, 128.4, 128.3, 128.2, 128.1 (2 C), 127.9, 128.0, 127.7, 127.6, 127.5 (2 C), 127.4, 127.3, 127.2, 127.1, 126.9, 126.8, 123.5, 123.1, 102.6 ($J_{C,H}$ = 157.5 Hz), 97.7 ($J_{C,H}$ = 171.4 Hz), 97.1 ($J_{C,H}$ = 169.2.4 Hz), 96.9 ($J_{C,H}$ = 166.0 Hz), 96.8 ($J_{C,H}$ = 170.1 Hz), 83.0, 80.4, 79.4, 79.0, 76.9, 76.4, 75.5, 75.1, 74.8, 74.6, 74.5, 74.4, 74.3, 74.0, 73.9, 73.8, 73.4, 73.2, 72.6, 72.5, 72.0, 71.8, 70.5, 69.8, 69.7, 68.9, 68.2, 68.0, 66.9, 60.4, 56.7, 55.7, 55.6; MALDI-MS: [M+Na]+ $C_{152}H_{145}N_3O_{29}Na$ calcd for 2498.9861, found 2499.1289

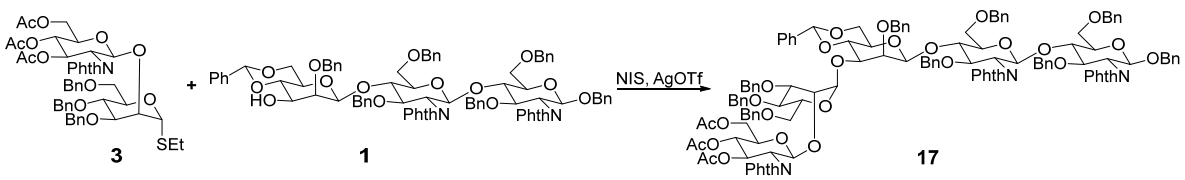
Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-β-Mannopyranosyl-(1→6)-2,3,4-O-tri-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (16'): $[\alpha]_D^{20}$ 3.9 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59-7.63 (m, 2 H), 7.51-7.57 (m, 5 H), 7.47-7.49 (m, 1 H), 7.40-7.42 (m, 5 H), 7.35-7.38 (m, 5 H), 7.21-7.33 (m, 26 H), 7.14-7.20 (m, 12 H), 7.09-7.12 (m, 3 H), 7.03-7.05 (m, 2 H), 6.94-6.98 (m, 8 H), 6.78-6.85 (m, 7 H), 6.64-6.70 (m, 4 H), 6.57-6.60 (m, 2 H), 5.43 (d, J = 6.8 Hz, 1 H), 5.33 (d, J = 6.6 Hz, 1 H), 5.01 (d, J = 9.0 Hz, 1 H), 4.92-4.98 (m, 3 H), 4.87 (d, J = 10.0 Hz, 1 H), 4.81-4.84 (m, 2 H), 4.79 (d, J = 3.3 Hz, 1 H), 4.74 (d, J = 8.8 Hz, 1 H), 4.67-4.71 (m, 2 H), 4.65 (d, J = 3.7 Hz, 1 H), 4.61 (d, J = 12.2 Hz, 1 H), 4.56 (d, J = 9.6 Hz, 1 H), 4.51-4.53 (m, 1 H), 4.44-4.46 (m, 2 H), 4.39-4.42 (m, 6 H), 4,36-4.37 (m, 2 H), 4.32-4.34 (m, 2 H), 4.29-4.31 (m, 1 H), 4.24-4.26 (m, 1 H), 4.21-4.22 (m, 1 H), 4.15-4.16 (m, 1 H), 4.14-4.15 (m, 2 H), 4.11-4.13 (m, 2 H), 4.09-4.11 (m, 1 H), 4.03-4.06 (m, 1 H), 3.95-3.98 (m, 2 H), 3.84 (t, J = 7.5 Hz, 1 H), 3.75-3.78 (m, 2 H), 3.68 (d, J = 1.4 Hz, 1 H), 3.62-3.64 (m, 1 H), 3.58-3.60 (m, 1 H), 3.55-3.57 (m, 1 H), 3.51-3.53 (m, 2 H), 3.45-3.48 (m, 2 H), 3.43-3.45 (m, 1 H), 3.36-3.42 (m, 4 H), 3.27-3.31 (m,

1 H), 3.24-3.27 (m, 1 H), 3.04-3.15 (m, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.3, 168.2, 167.6, 167.2, 139.6, 139.2, 138.9, 138.8 (2 C), 138.7, 138.6 (2 C), 138.5, 138.2, 137.9, 137.2, 133.7, 133.4, 132.9, 132.1, 131.7, 131.6, 131.5, 128.7, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8, 123.4, 123.1, 100.5 (2 C, $J_{C,H}$ = 159.8 Hz, $J_{C,H}$ = 159.0 Hz), 99.0 ($J_{C,H}$ = 170.2 Hz), 97.7 ($J_{C,H}$ = 170.1 Hz), 97.0 ($J_{C,H}$ = 166.1 Hz), 82.6, 81.1, 79.3, 78.9, 78.8, 77.5, 77.2, 75.6, 75.2, 75.0, 74.6, 74.5, 74.4, 74.2, 73.4, 73.2, 72.9, 72.6, 72.4, 71.6, 70.7, 70.4, 69.7, 69.3, 68.7, 67.9, 60.4, 56.4, 56.2, 55.8; MALDI-MS: [M+Na]+ $C_{152}H_{145}N_3O_{29}Na$ calcd for 2498.9861, found 2499.1369



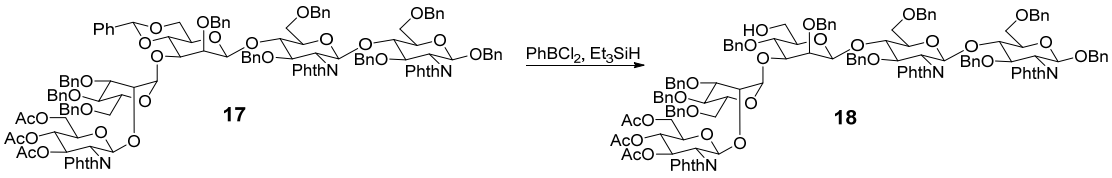
2-dexoy-acetamido-β-D-glucopyranosyl-(1→2)-α-Mannopyranosyl-(1→6)-β-D-Mannopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranoside (N040): Following the general procedure **C** and **E**, compound **16** (150 mg, 0.06 mmol) yielded the compound **N040** (37 mg, 61% over three steps). $[\alpha]_D^{20}$ 3.9 (c 0.5, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.16 (d, J = 2.4 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 4.89 (s, 1 H, Man2 H-1), 4.74 (s, 1 H, Manβ H-1), 4.67 (d, J = 8.0 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.59 (d, J = 7.8 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.57 (d, J = 7.8 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.52 (d, J = 8.4 Hz, 1 H, GlcNAc-3 H-1), 4.07-4.08 (m, 1 H), 4.05 (d, J = 1.1 Hz, 1 H), 3.83-3.93 (m, 7 H), 3.71-3.80 (m, 7 H), 3.69-3.71 (m, 1 H), 3.67-3.69 (m, 1 H), 3.65-3.66 (m, 1 H), 3.55-3.64 (m, 7 H), 3.47-3.53 (m, 2 H), 3.38-3.46 (m, 2 H), 2.05 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.01 (s, 3 H, Ac); ^{13}C NMR (D_2O, 125 MHz): δ 174.7, 174.6, 174.5, 174.4, 101.3 (GlcNAc-2 C-1), 100.5 ($J_{C,H}$ = 161.8 Hz, Manβ C-1), 99.5 (GlcNAc-3 C-1), 97.0 ($J_{C,H}$ = 172.7 Hz, Man2 C-1), 94.7 (GlcNAc-1 C-1 of β anomer), 90.3 (GlcNAc-1 C-1 of α anomer), 81.7, 79.6, 79.4, 79.1, 76.2, 75.7, 74.4, 74.3, 73.3, 72.7, 72.6, 72.4, 71.9, 70.3, 69.9, 69.8, 69.5, 69.3, 69.1, 67.3, 66.5, 66.1, 61.5, 60.5, 59.9, 56.0, 55.2, 54.8, 53.5, 22.2, 22.1, 22.0, 21.8; ESI-MS: [M+H]+ $C_{36}H_{62}N_3O_{26}$ calcd for 952.3622, found 974.3555

Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-2-O-benzyl-4,6-O-benzylidene-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (17):



Compound **1** (300 mg, 0.216 mmol) was glycosylated with **3** (256 mg, 0.28 mmol) by following general procedure **A** to get the desired compound **17 (**388 mg, 94%) as colorless oil. $[\alpha]_D^{20}$ 26.9 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 6.8 Hz, 1 H), 7.70-7.77 (m, 5 H), 7.55-7.70 (m, 6 H), 7.49-7.53 (m, 4 H), 7.30-7.40 (m, 12 H), 7.22-7.27 (m, 8 H), 7.17-7.20 (m, 1 H), 7.13-7.16 (m, 2 H), 6.99-7.08 (m, 6 H), 6.90-6.97 (m, 4 H), 6.80-6.85 (m, 3 H), 5.62 (t, J = 10.0 Hz, 1 H), 5.44 (s, 1 H), 5.33 (d, J = 7.4 Hz, 1 H), 5.12 (s, 1 H), 5.00-5.08 (m, 3 H), 4.90-4.95 (m, 3 H), 4.72-4.77 (m, 3 H), 4.68 (d, J = 11.4 Hz, 1 H), 4.53-4.60 (m, 3 H), 4.36-4.50 (m, 5 H), 4.17-4.27 (m, 6 H), 4.03-4.12 (m, 5 H), 3.93-3.99 (m, 2 H), 3.80-3.90 (m, 3 H), 3.65-3.69 (m, 1 H), 3.55-3.62 (m, 4 H), 3.42-3.47 (m, 2 H), 3.32-3.40 (m, 3 H), 3.19 (d, J = 9.8 Hz, 1 H), 2.71-2.81 (m, 2 H), 2.13 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 1.91 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 170.2, 169.3, 167.7, 138.9, 138.8, 138.7, 138.5, 138.3 (2 C), 137.9 (2 C), 137.2, 134.1, 133.9, 133.5, 131.7, 130.3, 129.1, 128.8, 128.6 (2 C), 128.4 (2 C), 128.3, 128.1 (2 C), 127.9, 127.8, 127.7 (3 C), 127.6, 127.5 (2 C), 127.4, 127.1, 127.0, 126.9, 123.1, 102.3, 100.9, 97.5, 97.2 (2 C), 95.3, 78.9, 78.2 (2 C), 77.8, 77.4, 76.6, 76.0, 75.2, 74.9, 74.6, 74.5, 74.4, 74.0, 73.2, 72.9, 72.7, 72.1, 71.8, 71.0, 70.8, 70.6, 70.4, 68.7, 68.2, 67.7, 66.4, 61.3, 56.5, 55.8, 54.2, 20.8 (2 C), 20.6; MALDI-MS: [M+Na]+ $C_{130}H_{125}N_3O_{32}Na$ calcd for 2262.8144, found 2262.7908

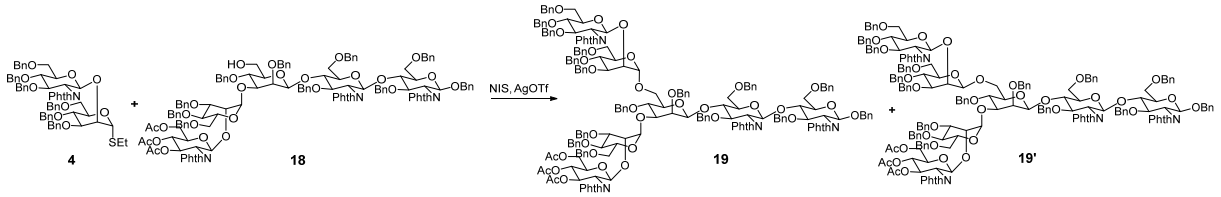
Benzyl 3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (18):



The compound **17** (350 mg, 0.156 mmol) was treated accordingly to the general procedure **B** to afford pentasaccharide acceptor **18** (326 mg, 93%). $[\alpha]_D^{20}$ 20.9 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.93 (m, 1 H), 7.60-7.80 (m, 10 H), 7.45-7.59 (m, 8 H), 7.20-7.43 (m, 26 H), 7.14-7.18 (m, 2 H), 7.00-7.10 (m, 7 H), 6.90-7.00 (m, 5 H), 6.77-6.85 (m, 3 H), 5.65 (t, J = 10.0 Hz, 1 H), 5.33 (d, J = 7.2 Hz, 1 H), 5.19 (d, J = 8.3 Hz, 1 H), 5.11 (d, J = 11.6 Hz, 1 H), 5.09 (d, J = 9.5 Hz, 1 H), 5.03 (d, J = 7.6 Hz, 1 H), 5.00 (d, J = 12.3 Hz, 1 H), 4.95 (d, J = 12.0 Hz, 1 H), 4.92 (d, J = 9.8 Hz, 1 H), 4.88 (d, J = 11.8 Hz, 1 H), 4.73-4.79 (m, 2 H), 4.63-4.69 (m, 2 H), 4.52-4.62 (m, 5 H), 4.50 (d, J = 4.5 Hz, 1 H), 4.40-4.47 (m, 3 H), 4.34-4.36 (m, 1 H), 4.22-4.30 (m, 5 H), 4.12-4.21 (m, 2 H), 4.02-4.10 (m, 3 H), 3.96-4.01 (m, 2 H), 3.87-3.93 (m, 2 H), 3.70-3.77 (m, 2 H), 3.66-3.68 (m, 1 H), 3.57-3.62 (m, 3 H), 3.46-3.53 (m, 3 H), 3.32-3.43 (m, 4 H), 3.22 (d, J = 9.6 Hz, 1 H), 2.76-2.83 (m, 2 H), 2.38-2.42 (m, 1 H), 2.10 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 1.90 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 170.2, 169.4, 167.7, 138.8 (2 C), 138.7 (2 C), 138.5, 138.1, 137.9, 137.2, 134.1, 134.0, 133.5, 131.7, 131.5, 129.0, 128.8, 128.5, 128.4, 128.3 (2 C), 128.2, 128.1 (2 C), 127.9 (3 C), 127.8, 127.7, 127.6, 127.5, 127.4 (2 C), 127.1, 126.9 (2 C), 126.0, 123.1, 100.3, 98.4, 97.3, 97.2, 95.7, 80.1, 78.3, 77.8, 77.4, 76.2, 75.1,

74.9, 74.8 (2 C), 74.6 (2 C), 74.3, 74.2, 73.0, 72.8, 71.4, 71.1, 70.6, 70.5, 70.4, 68.7, 68.2, 67.7, 61.6, 56.5, 55.8, 54.3, 20.8, 20.7, 20.6; MALDI-MS: [M+Na]+ $C_{130}H_{127}N_3O_{32}Na$ calcd for 2264.8300, found 2264.8450

Benzyl 3,4,6-O-tri-acetyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-[3,4,6-O-tri-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→6)]-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-deoxy-phthalimido-β-D-glucopyranoside (19):

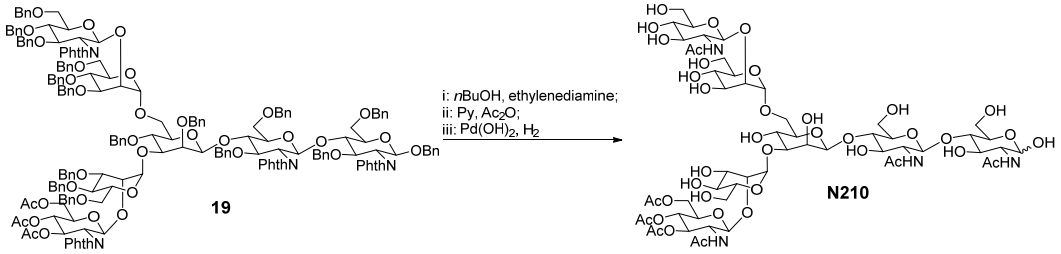


Compound **18** (400 mg, 0.178 mmol) was glycosylated with **3** (245 mg, 0.232 mmol) by following general procedure A to get the desired α anomer **19** (391 mg, 68%) and β anomer **19'** (98 mg, 17%) as colorless oil. $[\alpha]_D^{20}$ 15.4 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.88-7.90 (m, 1 H), 7.68-7.81 (m, 6 H), 7.55-7.65 (m, 5 H), 7.15-7.50 (m, 60 H), 6.95-7.10 (m, 13 H), 6.85-6.95 (m, 5 H), 6.75-6.85 (m, 3 H), 6.70-6.74 (m, 2 H), 6.62-6.64 (m, 1 H), 5.56 (t, J = 9.7 Hz, 1 H), 5.29 (s, 1 H), 5.25 (d, J = 7.0 Hz, 1 H), 5.07-5.12 (m, 2 H), 4.98-5.06 (m, 3 H), 4.85-4.95 (m, 5 H), 4.75-4.85 (m, 3 H), 4.67-4.76 (m, 6 H), 4.47-4.65 (m, 8 H), 4.32-4.45 (m, 9 H), 4.13-4.30 (m, 10 H), 3.93-4.09 (m, 7 H), 3.68-3.89 (m, 9 H), 3.46-3.61 (m, 8 H), 3.24-3.41 (m, 7 H), 3.15-3.19 (m, 2 H), 2.08 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 1.99 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.2, 170.7, 170.2, 169.3, 168.1, 167.8, 167.5, 139.0, 138.9, 138.8, 138.7 (2 C), 138.5, 138.4, 138.3, 138.3, 138.1 (2 C), 138.0 (2 C), 137.2, 133.5, 131.8, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3 (2 C), 128.2 (2 C), 128.1, 128.0 (2 C), 127.8 (2 C), 127.7, 127.6, 127.5 (2 C), 127.4, 127.3 (2 C), 127.2, 127.1, 126.9, 125.8, 123.1, 101.7 ($J_{C,H}$ = 158.4 Hz), 98.2 ($J_{C,H}$ = 171.1 Hz), 97.8 ($J_{C,H}$ = 171.4 Hz), 97.1 ($J_{C,H}$ = 165.7 Hz, $J_{C,H}$ = 165.4 Hz), 97.0 ($J_{C,H}$ = 169.2 Hz), 95.4 ($J_{C,H}$ = 165.6 Hz), 80.2, 79.6, 79.2, 79.1, 78.9, 77.9, 77.4, 77.0, 76.5, 75.9, 75.2, 74.9, 74.6 (2 C), 74.5, 74.4, 74.2 (2 C), 74.0, 73.6, 73.4, 73.3, 73.0, 72.8, 72.7, 72.5, 72.4, 72.3, 71.9, 71.3, 70.9, 70.5, 70.2, 69.7, 69.5, 68.8, 68.4, 68.1, 67.7, 66.8, 61.2, 60.4, 56.7, 55.8, 55.6, 54.3, 53.5, 21.1, 20.7, 20.5; MALDI-MS: [M+Na]+ $C_{192}H_{186}N_4O_{43}Na$ calcd for 3258.2389, found 3258.4081

Benzyl 3,4,6-O-tri-acetyl-2-deoxy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-α-D-Mannopyranosyl-(1→3)-[3,4,6-O-tri-benzyl-2-dexoy-phthalimido-β-D-glucopyranosyl-(1→2)-3,4,6-O-tri-benzyl-β-D-Mannopyranosyl-(1→6)]-2,4-O-di-benzyl-β-D-Mannopyranosyl-(1→4)-3,6-O-di-benzyl-2-dexoy-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-O-di-benzyl-2-dexoy-phthalimido-β-D-glucopyranoside (19'): $[\alpha]_D^{20}$ 23.4 (c 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.75 (m, 18 H), 7.10-7.50 (m, 56 H), 6.95-7.10 (m, 9 H), 6.72-6.92 (m, 9 H), 6.60-6.70 (m, 4 H), 5.62 (t, J = 9.4 Hz, 1 H), 5.45 (d, J = 8.4 Hz, 1 H), 5.32 (d, J = 7.5 Hz, 1 H), 5.07-5.11 (m, 3 H), 4.96-5.04 (m, 4 H), 4.84-4.91 (m, 4 H), 4.75-4.79 (m, 3 H), 4.60-4.71 (m, 6 H), 4.32-4.54 (m, 14 H), 4.25-4.29 (m, 8 H), 3.89-4.06 (m, 8 H), 3.77-3.86 (m, 5 H), 3.66-3.72 (m, 3 H), 3.53-3.61 (m, 3 H), 3.36-3.50 (m, 7 H), 3.23-3.35 (m, 5 H),

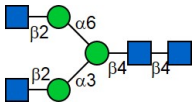
3.11-3.19 (m, 2 H), 3.04-3.07 (m, 1 H), 2.95-3.00 (m, 2 H), 2.12 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 1.91 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 170.2, 169.3, 168.4, 168.1, 167.8, 167.6, 167.2, 139.6, 139.2 (2 C), 138.9, 138.8, 138.7, 138.6 (3 C), 138.5, 138.2 (2 C), 137.5, 137.2, 133.8, 133.5, 133.4, 132.1, 131.8, 131.7, 131.5, 129.4, 129.1 (2 C), 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2 (2 C), 128.1, 128.0, 127.9 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6, 127.5, 127.4 (2 C), 127.3 (2 C), 127.2, 127.1, 127.0, 126.8, 125.7, 123.5, 123.1, 122.7, 100.5 ($J_{C,H}$ = 158.9 Hz), 99.5 ($J_{C,H}$ = 159.6 Hz), 99.2 ($J_{C,H}$ = 169.8 Hz), 98.4 ($J_{C,H}$ = 172.1 Hz), 98.2 ($J_{C,H}$ = 167.4 Hz), 97.0 ($J_{C,H}$ = 166.6 Hz), 95.9 ($J_{C,H}$ = 169.9 Hz), 81.2, 79.8, 79.3, 79.1, 78.9, 78.6, 77.9, 77.8, 77.5, 77.3 (2 C), 76.7, 75.8, 75.1, 74.8, 74.6, 74.5, 74.3, 74.1, 74.0, 73.3, 73.2, 73.0 (2 C), 72.7, 72.5 (2 C), 71.6, 70.9, 70.7, 70.6, 70.5, 70.1, 69.7, 69.3, 68.6 (2 C), 67.9, 66.7, 61.5, 56.4, 56.2, 55.9, 54.3, 20.8, 20.7, 20.6; MALDI-MS: [M+Na]+ $C_{192}H_{186}N_4O_{43}Na$ calcd for 3258.2389, found 3258.3048

3,4,6-O-tri-acetyl-2-deoxy-acetamido-β-D-glucopyranosyl-(1→2)-α-D-Mannopyranosyl-(1→3)-[2-deoxy-acetoamido-β-D-glucopyranosyl-(1→2)-α-D-Mannopyranosyl-(1→6)]-β-D-Mannopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranosyl-(1→4)-2-deoxy-acetamido-β-D-glucopyranoside (N210):

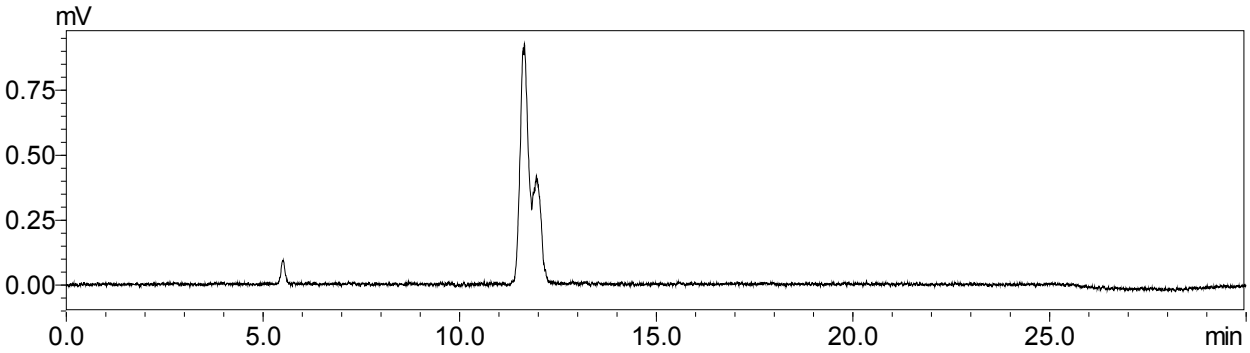


Following the general procedure **C** and **E**, compound **19** (150 mg, 0.046 mmol) yielded the compound **N210** (37 mg, 65% over three steps). $[\alpha]_D^{20}$ 7.9 (c 0.5, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.25 (dd, J = 10.4, 9.4 Hz, 1 H), 5.17 (d, J = 2 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.12 (s, 1 H, Man2 H-1), 5.08 (t, J = 9.8 Hz, 1 H), 4.91 (s, 1 H, Man3 H-1), 4.81 (overlapped with D_2O, 1 H, GlcNAc-4 H-1), 4.76 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.60 (d, J = 7.8 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.59 (d, J = 7.8 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.54 (d, J = 8.4 Hz, 1 H, GlcNAc-3 H-1), 4.40 (dd, J = 12.6, 3.5 Hz, 1 H), 4.23 (d, J = 1.3 Hz, 1 H), 4.21 (d, J = 1.5 Hz, 1 H), 4.19-4.20 (m, 1 H), 4.10 (d, J = 1.9 Hz, 1 H), 3.94-4.00 (m, 3 H), 3.84-3.92 (m, 7 H), 3.71-3.81 (m, 8 H), 3.66-3.70 (m, 3 H), 3.58-3.65 (m, 6 H), 3.45-3.54 (m, 4 H), 3.39-3.42 (m, 1 H), 2.11 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.99 (s, 3 H, Ac); ^{13}C NMR (D_2O, 125 MHz): δ 174.7, 174.6, 174.5, 174.3, 173.6, 173.1, 172.7, 101.3 (GlcNAc-2 C-1), 100.3 ($J_{C,H}$ = 162.5 Hz, Manβ C-1), 99.5 (GlcNAc-3 C-1), 99.3 ($J_{C,H}$ = 172.1 Hz, Man2 C-1), 99.0 (GlcNAc-4 C-1), 96.9 ($J_{C,H}$ = 172.3 Hz, Man3 C-1), 94.7 (GlcNAc-1 C-1 of β anomer), 90.3 (GlcNAc-1 C-1 of α anomer), 80.3, 79.5, 79.4, 79.1, 76.8, 76.2, 75.7, 74.5, 74.3, 74.2, 73.5, 73.3, 72.7, 72.4, 72.2, 71.9, 71.1, 70.0, 69.9, 69.8, 69.5, 69.4, 69.2, 69.1, 68.4, 67.2, 67.1, 65.7, 65.6, 61.7, 61.5, 60.5, 60.0, 59.9, 59.8, 56.0, 55.2, 54.8, 53.5, 53.4, 22.2, 22.1, 22.0, 21.8, 19.9, 19.8;ESI-MS: [M+H]+ $C_{56}H_{91}N_4O_{39}$ calcd for 1443.5260, found 1443.5275

VII. HPLC profiles, MS and NMR data of purified N-glycans

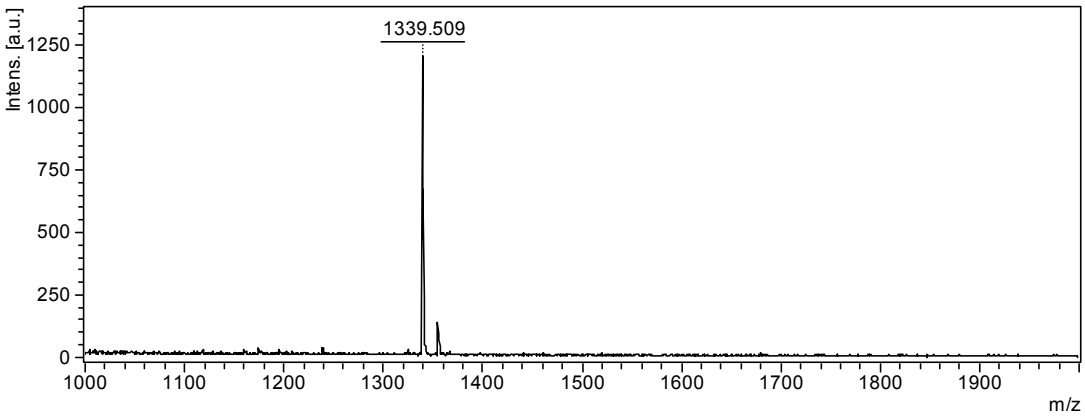
N000 

HILIC-ELSD, T_R = 11.64 min

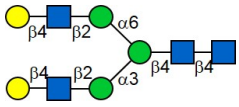


ESI-MS, calculated: 1316.4865; found $[M+2H]^{2+}$ 659.2510

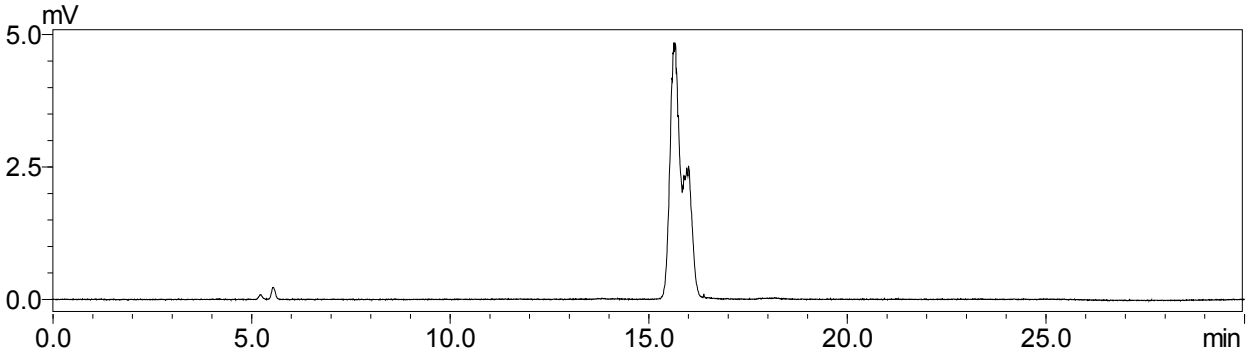
MALDI-MS,; found $[M+Na]^+$ 1339.509, $[M+K]^+$ 1355.530



^{1}H NMR (D_2O, 500 MHz): δ 5.18 (d, J = 1.9 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.92 (s, 1 H, Man3 H-1), 4.77 (s, 1 H, Manβ H-1), 4.69 (d, J = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.61 (d, J = 7.7 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.59 (d, J = 7.7 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.55 (d, J = 8.4 Hz, 2 H, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.24 (d, J = 1.9 Hz, 1 H), 4.18 (d, J = 1.4 Hz, 1 H), 4.10 (d, J = 2.2 Hz, 1 H), 3.42-3.95 (m, 39 H), 2.07 (s, 3 H, Ac), 2.04 (s, 6 H, 2 Ac), 2.03 (s, 3 H, Ac)

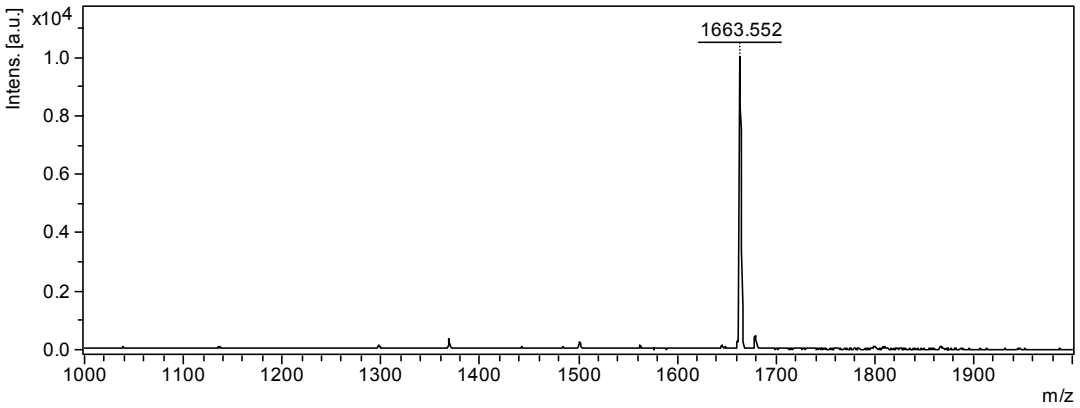
N001 

HILIC-ELSD, T_R = 15.65 min

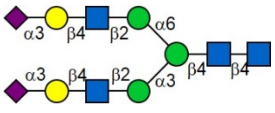


ESI-MS, calculated: 1640.5922; found $[M+2H]^{2+}$ 821.3046

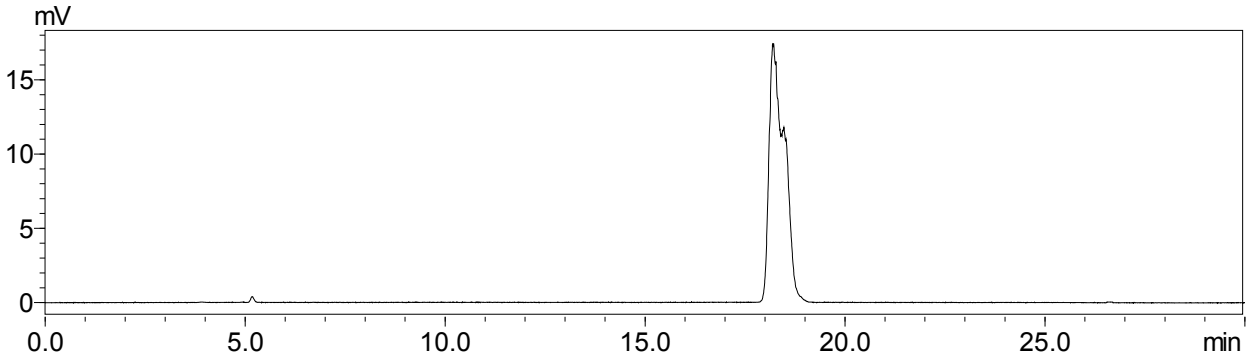
MALDI-MS, found $[M+Na]^+$ 1663.552, $[M+K]^+$ 1679.502



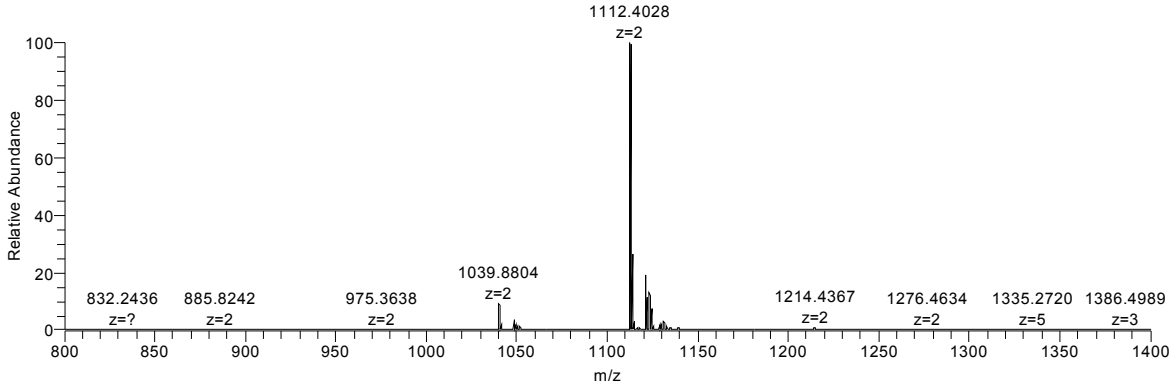
^{1}H NMR (D_2O, 500 MHz): δ 5.19 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.12 (s, 1 H, Man2 H-1), 4.93 (s, 1 H, Man3 H-1), 4.77 (s, 1 H, Manβ H-1), 4.70 (d, J = 7.5 Hz, 0.4 H, GlcNAc-1 of β anomer), 4.57-4.62 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.48 (d, J = 7.6 Hz, 1 H, Gal-1 H-1), 4.47 (d, J = 7.6 Hz, 1 H, Gal-2 H-1), 4.26 (brs, 1H), 4.19 (brs, 1 H), 4.11 (brs, 1 H), 3.47-4.00 (m, 51 H), 2.09 (s, 3 H, Ac), 2.05 (s, 6 H, 2 Ac), 2.04 (s, 3 H, Ac)

N002 

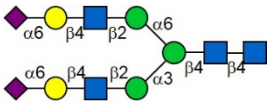
HILIC-ELSD, T_R = 18.22 min



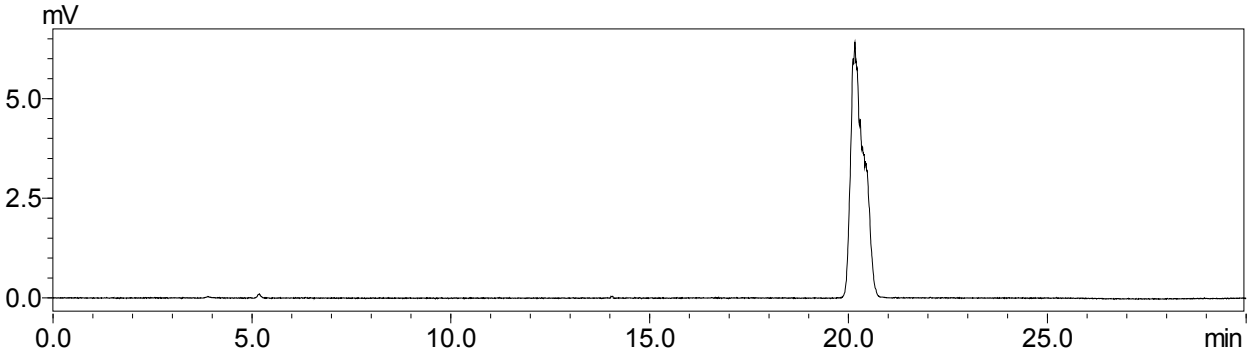
ESI-MS, calculated: 2222.7830; found $[M+2H]^{2+}$ 1112.4028



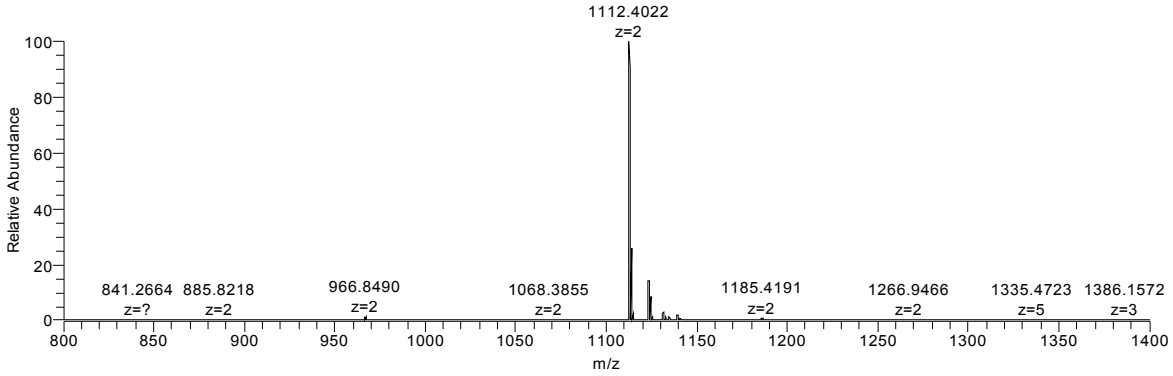
^{1}H NMR (D_2O, 500 MHz): δ 5.17 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.10 (s, 1 H, Man2 H-1), 4.77-5.00 (overlapped with D_2O, 1 H, Man3 H-1), 4.75 (s, 1 H, Manβ H-1), 4.68 (d, *J* = 7.8 Hz, 0.4 H, GlcNAc-1 of β anomer), 4.52-4.61 (m, 5 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1, Gal-1 H-1, Gal-2 H-1), 4.24 (s, 1 H), 4.18 (s, 1 H), 4.08-4.12 (m, 3 H), 3.45-4.00 (m, 63 H), 2.75 (m, *J* = 12.4, 3.5 H, 2 H, Neu5Ac H-3e), 2.07 (s, 3 H, Ac), 2.03 (s, 9 H, 3 Ac), 2.03 (s, 6 H, 2 Ac), 1.79 (t, *J* = 12.4 Hz, 2 H, Neu5Ac H-3a)

N003 

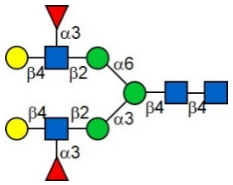
HILIC-ELSD, T_R = 20.17 min



ESI-MS, calculated: 2222.7830; found $[M+2H]^{2+}$ 1112.4022

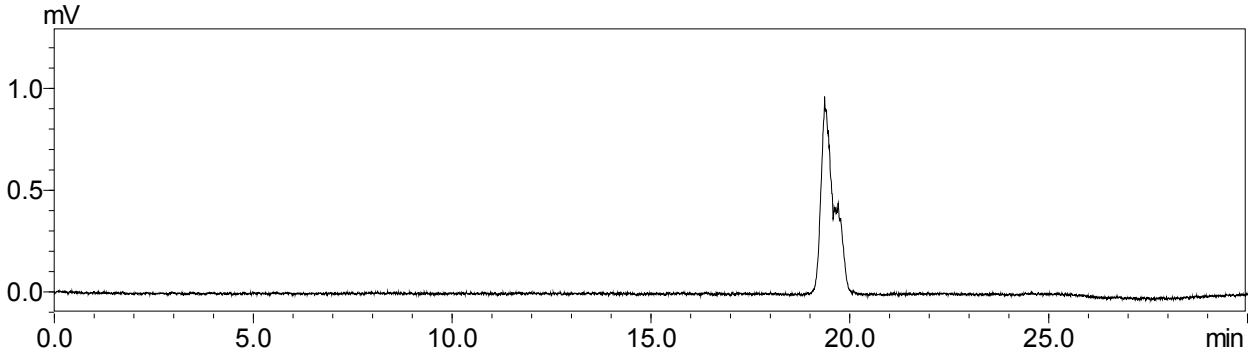


^{1}H NMR (D_2O, 500 MHz): δ 5.19 (brs, 0.7 H, GlcNAc-1 H-1 of α anomer), 5.13 (s, 1 H, Man2 H-1), 4.95 (s, 1 H, Man3 H-1), 4.76-4.94 (overlapped with D_2O, 1 H, Manβ H-1), 4.69 (d, J = 7.2 Hz, 0.3 H, GlcNAc-1 of β anomer), 4.59-4.65 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.44 (d, J = 7.2 Hz, 2 H, Gal-1 H-1, Gal-2 H-1), 4.26 (s, 1 H), 4.20 (s, 1 H), 4.12 (s, 1 H), 3.48-4.01 (m, 65 H), 2.65-2.69 (m, 2 H, Neu5Ac H-3e), 2.08 (s, 3 H, Ac), 2.07 (s, 6 H, 2 Ac), 2.03 (s, 9 H, 3 Ac), 1.72 (m, 2 H, Neu5Ac H-3a)



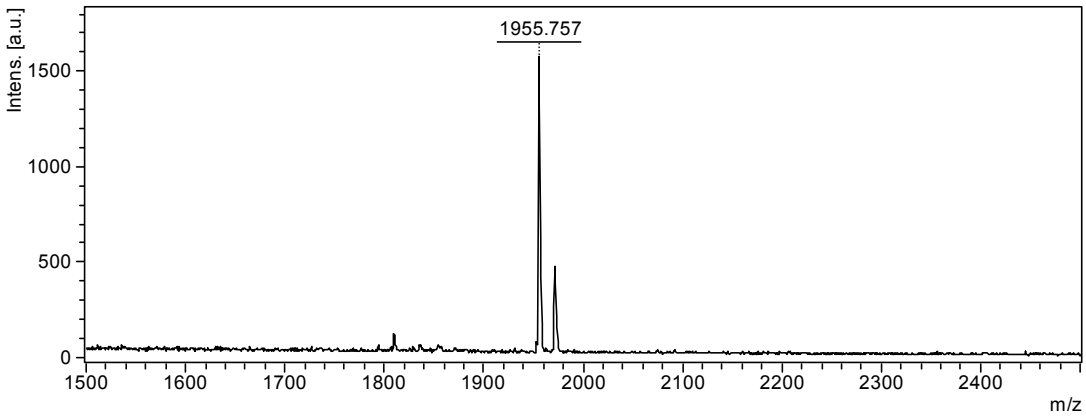
N004

HILIC-ELSD, T_R = 19.38 min

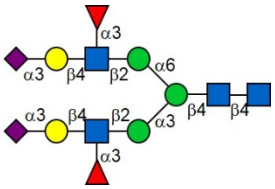


ESI-MS, calculated: 1932.7080; found $[M+2H]^{2+}$ 967.3640

MALDI-MS, found $[M+Na]^+$ 1955.757, $[M+K]^+$ 1971.753

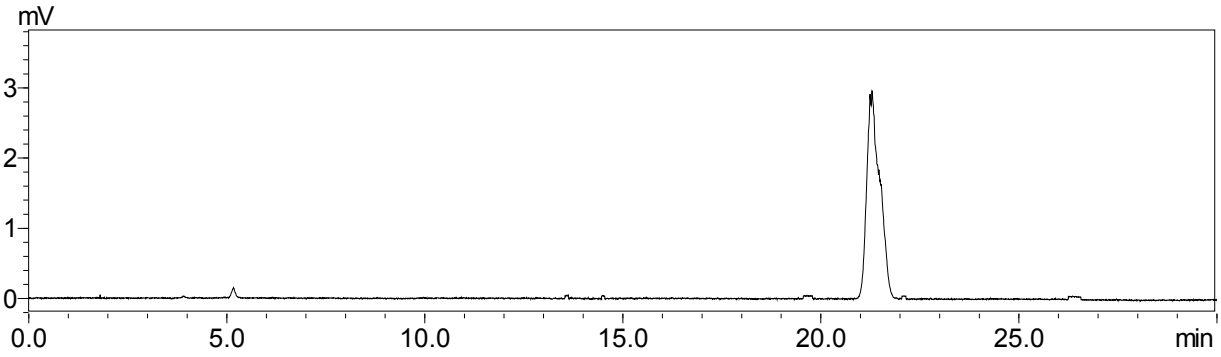


^{1}H NMR (D_2O, 500 MHz): δ 5.20 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.13-5.15 (m, 2 H, Fuc-1 H-1, Fuc-2 H-1), 5.12 (s, 1 H, Man2 H-1), 4.93 (s, 1 H, Man3 H-1), 4.75-4.87 (overlapped with D_2O, 1 H, Manβ H-1), 4.71 (d, J = 7.5 Hz, 0.4 H, GlcNAc-1 of β anomer), 4.58-4.63 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.45-4.47 (m, 2 H, Gal-1 H-1, Gla-2 H-1), 4.21 (brs, 1 H), 4.20 (brs, 1 H), 4.12 (brs, 1 H), 3.46-4.03 (m, 59 H), 2.10 (s, 3 H, Ac), 2.06 (s, 9 H, 3 Ac), 1.17-1.22 (m, 6 H, Fuc-CH_3)

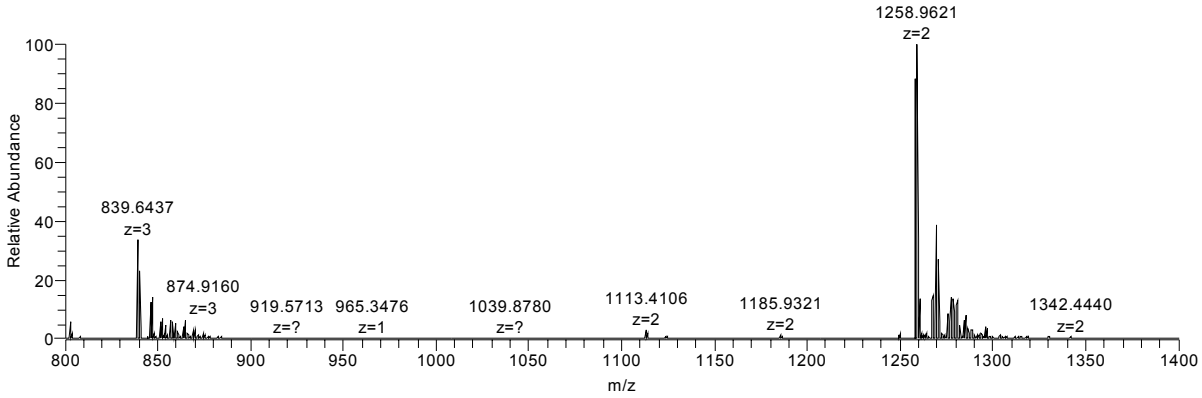


N005

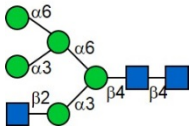
HILIC-ELSD, T_R = 21.28 min



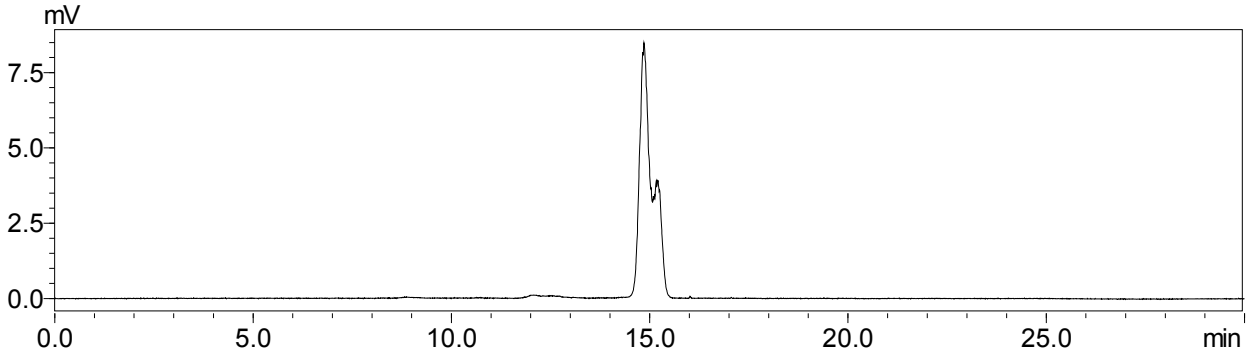
ESI-MS, calculated: 2514.8988; found $[M+2H]^{2+}$ 1258.9621, $[M+3H]^{3+}$ 839.6437



^{1}H NMR (D_2O, 500 MHz): δ4.75-5.15 (overlapped with D_2O, 6 H, Man5 H-1, Man4 H-1, Man3 H-1, Man2 H-1, Manβ H-1, GlcNAc-1 H-1), 4.55-4.62 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.50-4.53 (m, 2 H, Gal-1 H-1, Gal-2 H-1), 4.24-4.26 (m, 1 H), 4.18-4.20 (m, 2 H), 4.08-4.10 (m, 4 H), 3.45-4.03 (m, 69 H), 2.74-2.79 (m, 2 H, Neu5Ac H-3e), 2.09 (s, 3 H, Ac), 2.04 (s, 6 H, 2 Ac), 2.03 (s, 9 H, 3 Ac), 1.77-1.82 (m, 2 H, Neu5Ac H-3a), 1.15-1.19 (m, 6 H, Fuc-CH_3)

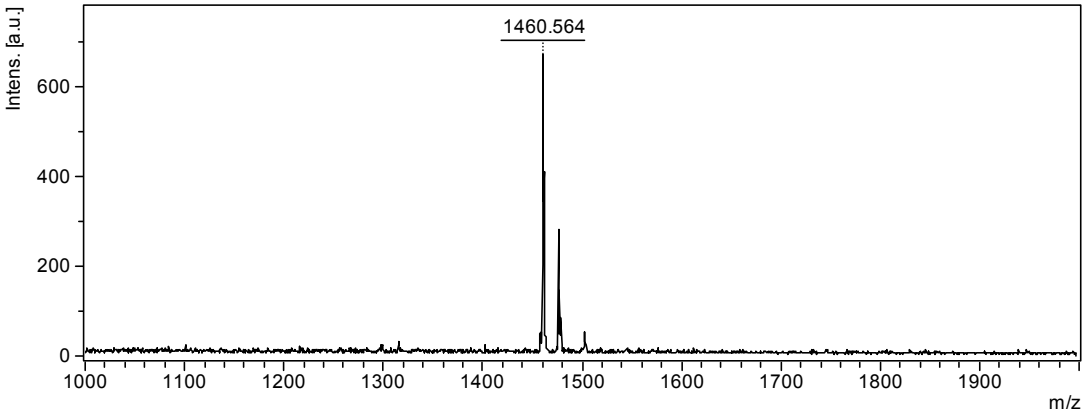
N010 

HILIC-ELSD, T_R = 14.86 min

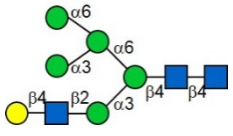


ESI-MS, calculated: 1437.5128; found $[M+2H]^{2+}$ 719.7645

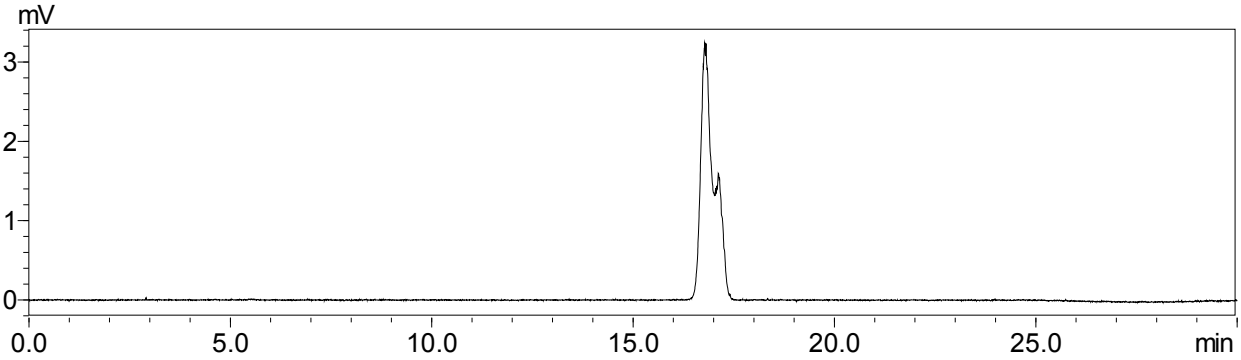
MALDI-MS, found $[M+Na]^{+}$ 1460.564, $[M+K]^{+}$ 1476.516



NMR data listed in Part VI

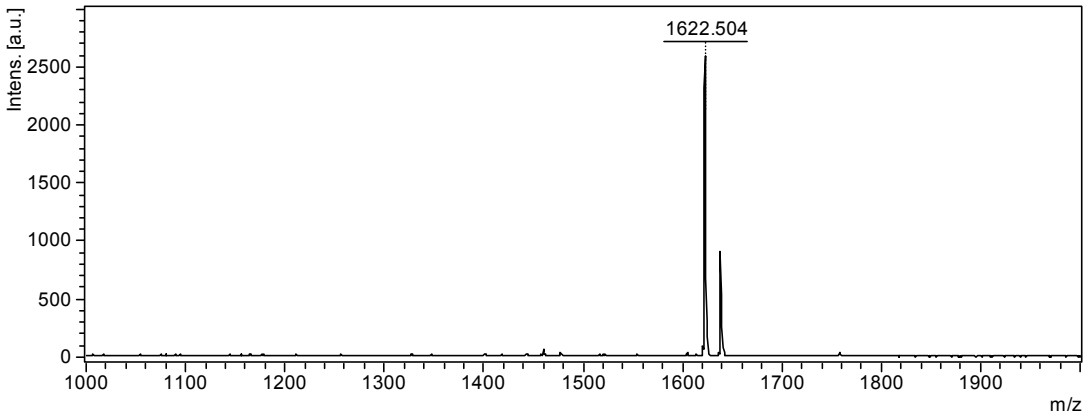
N011 

HILIC-ELSD, T_R = 16.79 min

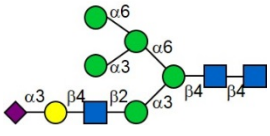


ESI-MS, calculated: 1599.5656; found $[M+2H]^{2+}$ 800.7887

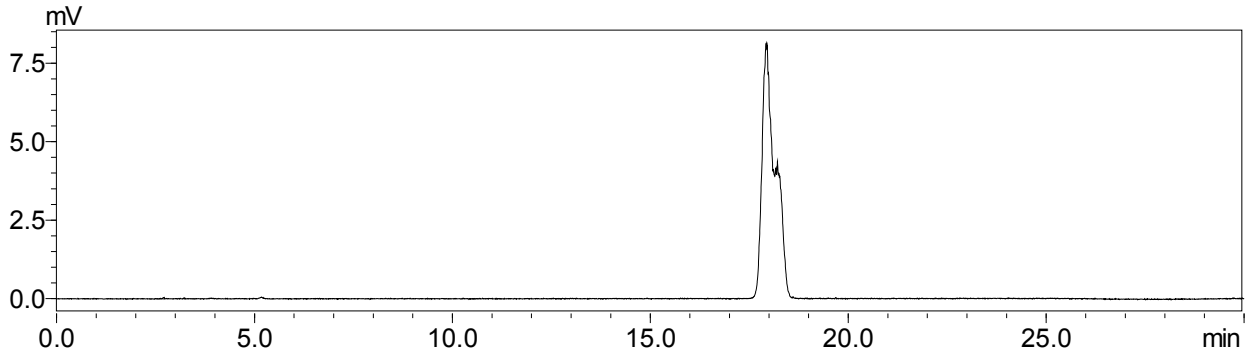
MALDI-MS, found $[M+Na]^+$ 1622.504, $[M+K]^+$ 1638.478



^{1}H NMR (D_2O, 500 MHz): δ 5.24 (s, 1 H, Man5 H-1), 5.19 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.94 (s, 1 H, Man3 H-1), 4.89 (s, 1 H, Man4 H-1), 4.77-4.88 (overlapped with D_2O, 1 H, Manβ H-1), 4.69 (d, J = 7.6 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.57-4.61 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.46 (d, J = 7.7 Hz, 1 H, , Gal H-1), 4.25 (brs, 1 H), 4.21 (brs, 1 H), 4.05 (s, 1 H), 3.48-4.02 (m, 51 H), 2.08 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.04 (s, 3 H, Ac)

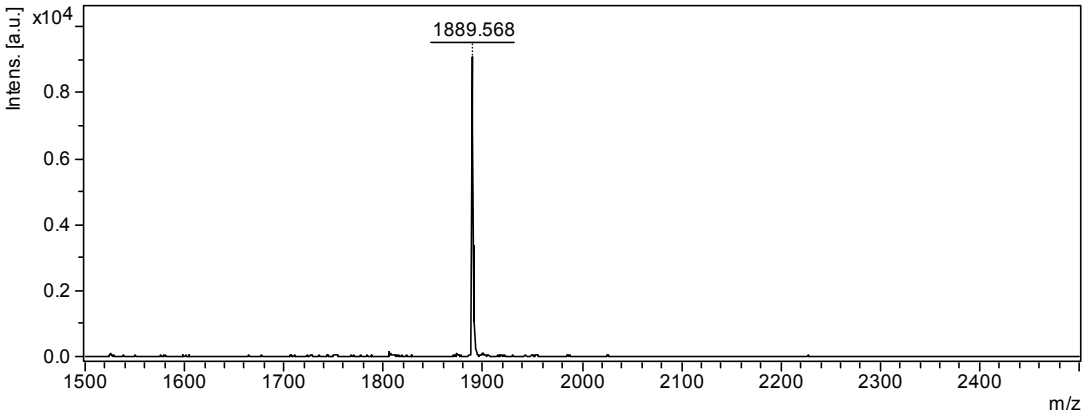
N012 

HILIC-ELSD, T_R = 17.93 min

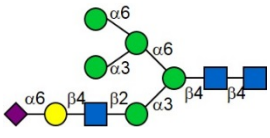


ESI-MS, calculated: 1890.6610; found $[M+2H]^{2+}$ 946.3386

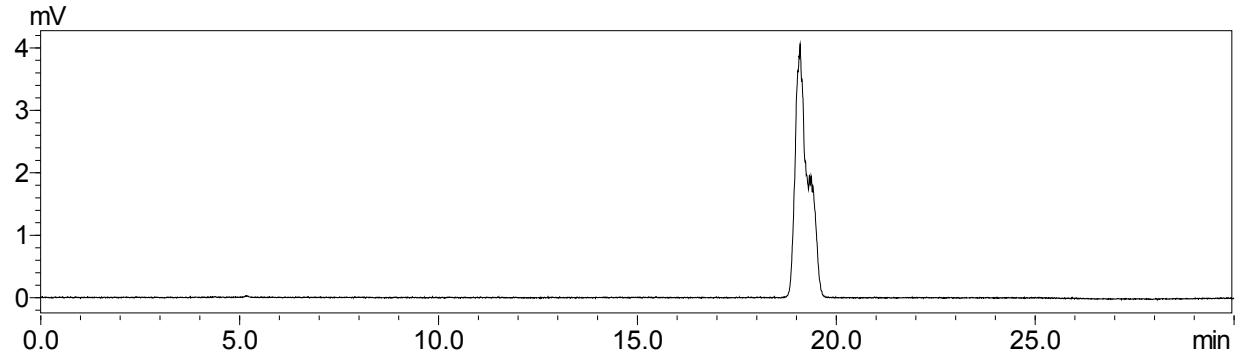
MALDI-MS, found $[M-H]^-$ 1889.568



^{1}H NMR (D_2O, 500 MHz): δ 5.23 (s, 1 H, Man5 H-1), 5.18 (brs, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.10 (s, 1 H, Man2 H-1), 4.93 (s, 1 H, Man3 H-1), 4.77-4.92 (overlapped with D_2O, 2 H, Man4 H-1, Manβ H-1), 4.68 (d, *J* = 7.8 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.52-4.61 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, Gal H-1), 4.24 (brs, 1 H), 4.20 (brs, 1 H), 4.10 (dd, *J* = 9.8, 2.1 Hz, 1 H), 3.45-4.05 (m, 58 H), 2.75 (dd, *J* = 12.2, 4.2 Hz, 1 H, Neu5Ac H-3e), 2.07 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.79 (t, *J* = 12.2 Hz, 1 H, Neu5Ac H-3a)

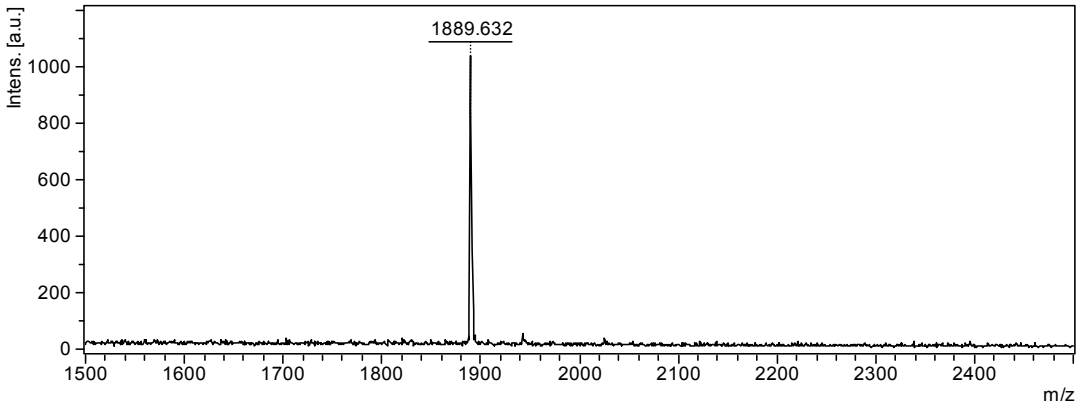
N013 

HILIC-ELSD, T_R = 19.09 min

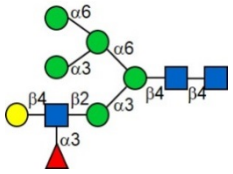


ESI-MS, calculated: 1890.6610; found $[M+2H]^{2+}$ 946.3099

MALDI-MS, found $[M-H]^-$ 1889.632

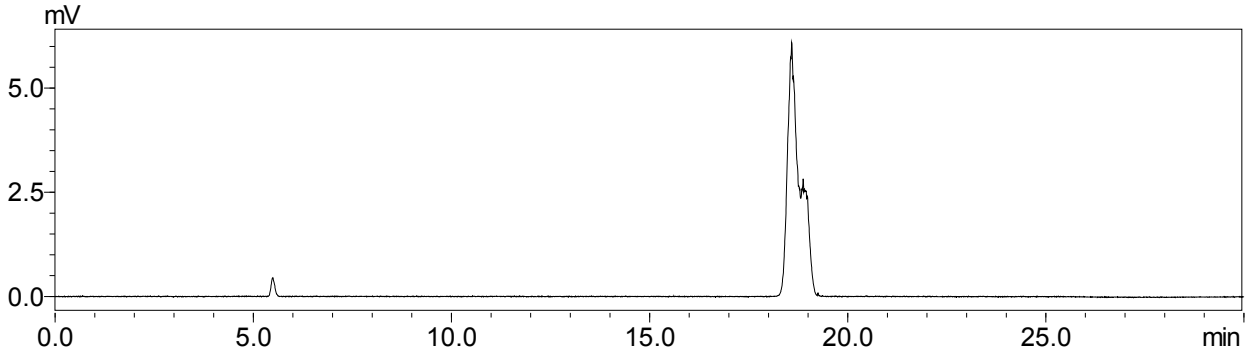


^{1}H NMR (D_2O, 500 MHz): δ 5.20 (s, 1 H, Man5 H-1), 5.15 (brs, 0.7 H, GlcNAc-1 H-1 of α anomer), 5.09 (s, 1 H, Man2 H-1), 4.90 (s, 1 H, Man3 H-1), 4.85 (s, 1 H, Man4 H-1), 4.75 (s, 1 H, Manβ H-1), 4.66 (d, *J* = 7.8 Hz, 0.3 H, GlcNAc-1 H-1 of β anomer), 4.55-4.57 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.40 (d, *J* = 7.6 Hz, 1 H, Gal H-1), 4.21 (brs, 1 H), 4.17 (brs, 1 H), 4.01 (s, 1 H), 3.45-3.96 (m, 58 H), 2.62 (dd, *J* = 12.3, 4.3 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.68 (t, *J* = 12.3 Hz, 1 H, Neu5Ac H-3a)



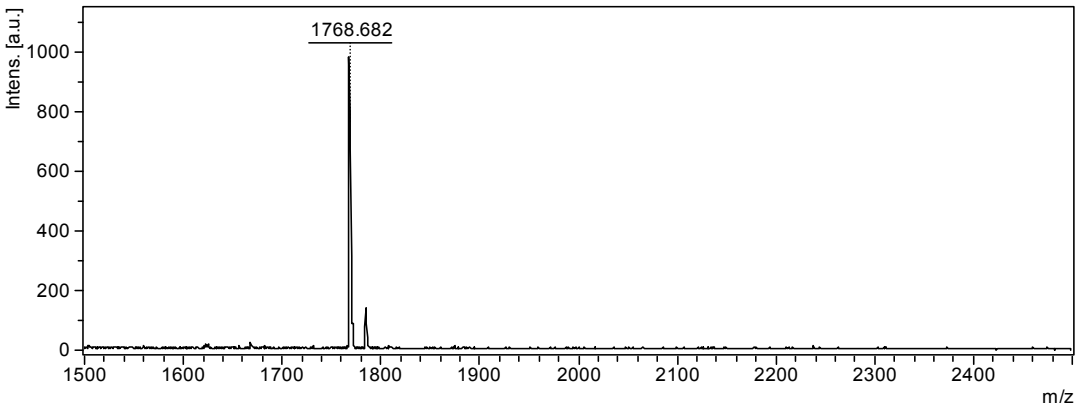
N014

HILIC-ELSD, T_R = 18.59 min

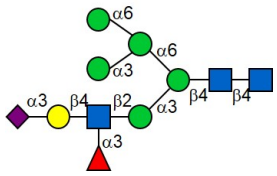


ESI-MS, calculated: 1745.6235; found $[M+2H]^{2+}$ 873.8209

MALDI-MS, found $[M+Na]^+$ 1768.682, $[M+K]^+$ 1784.669

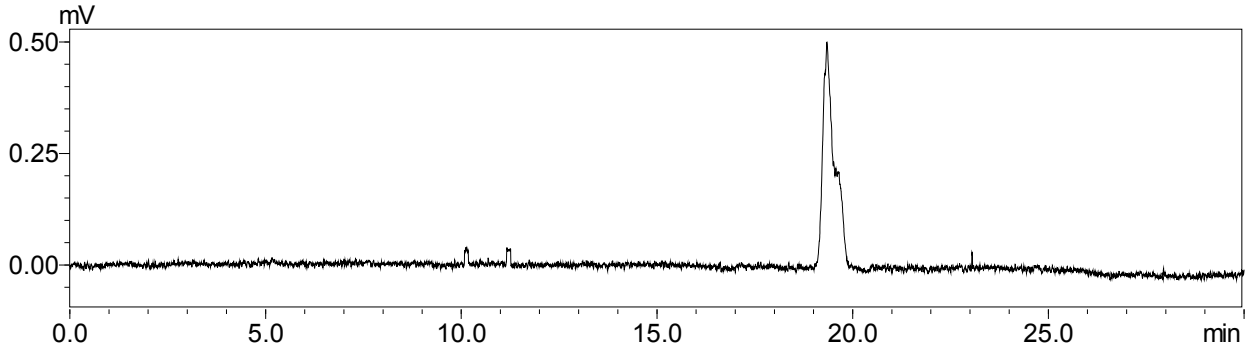


^{1}H NMR (D_2O, 500 MHz): δ 5.23 (s, 1 H, Man5 H-1), 5.17 (brs, 0.7 H, GlcNAc-1 H-1 of α anomer), 5.11 (d, J = 3.6 Hz, 1 H, Fuc H-1), 5.09 (s, 1 H, Man2 H-1), 4.94 (s, 1 H, Man3 H-1), 4.89 (s, 1 H, Man4 H-1), 4.79-4.85 (overlapped with D_2O, 1 H, Manβ H-1), 4.69 (d, J = 7.4 Hz, 0.3 H, GlcNAc-1 H-1 of β anomer), 4.57-4.61 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.43 (d, J = 7.7 Hz, 1 H, Gal H-1), 4.24 (brs, 1 H), 4.19 (s, 1 H), 4.04 (brs, 1 H), 3.44-4.00 (m, 55 H), 2.07 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.16 (d, J = 6.4 Hz, 3 H, Fuc-CH_3)



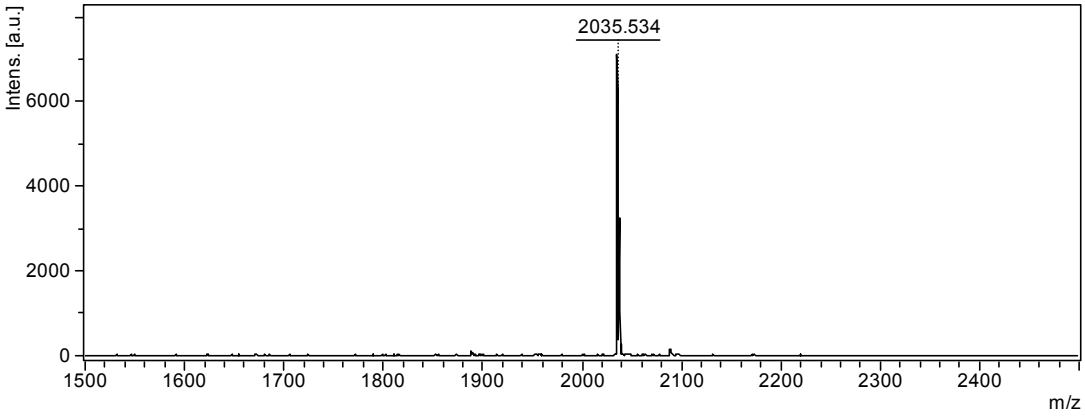
N015

HILIC-ELSD, T_R = 19.35 min

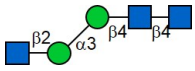


ESI-MS, calculated: 2036.7189; found $[M+2H]^{2+}$ 1019.3699

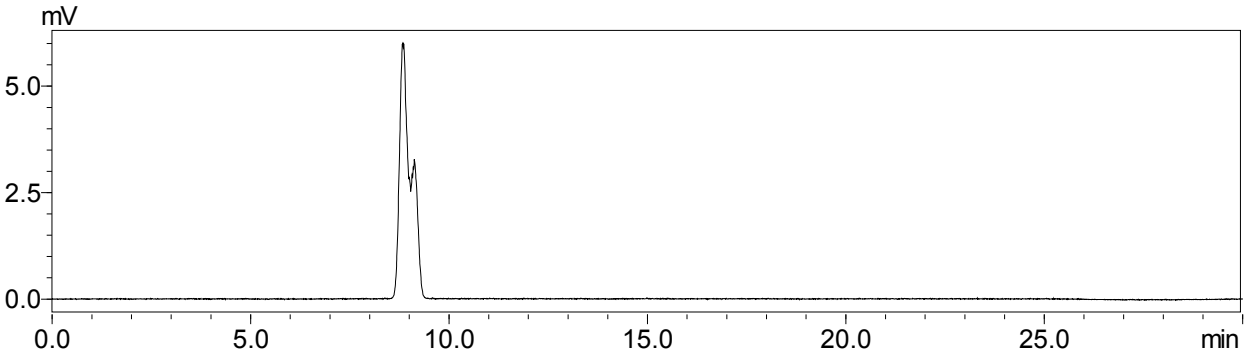
MALDI-MS, found $[M-H]^-$ 2035.534



^{1}H NMR (D_2O, 500 MHz): δ 5.13 (d, *J* = 0.8 Hz, 1 H, Man5 H-1), 5.08 (d, *J* = 2.0 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.01 (d, *J* = 3.9 Hz, 1 H, Fuc H-1), 4.99 (s, 1 H, Man2 H-1), 4.84 (s, 1 H, Man3 H-1), 4.69 (d, *J* = 1.6 Hz, 1 H, Man4 H-1), 4.68 (s, 1 H, Manβ H-1), 4.59 (d, *J* = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.47-4.52 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.40 (d, *J* = 7.8 Hz, 1 H, Gal H-1), 4.14 (d, *J* = 2.1 Hz, 1 H), 4.08-4.10 (m, 1 H), 3.36-4.00 (m, 63 H), 2.66 (dd, *J* = 12.3, 4.5 Hz, 1 H, Neu5Ac H-3e), 2.01 (s, 3 H, Ac), 1.94 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 1.69 (t, *J* = 12.3 Hz, 1 H, Neu5Ac H-3a), 1.06 (d, *J* = 6.6 Hz, 3 H, Fuc-CH_3)

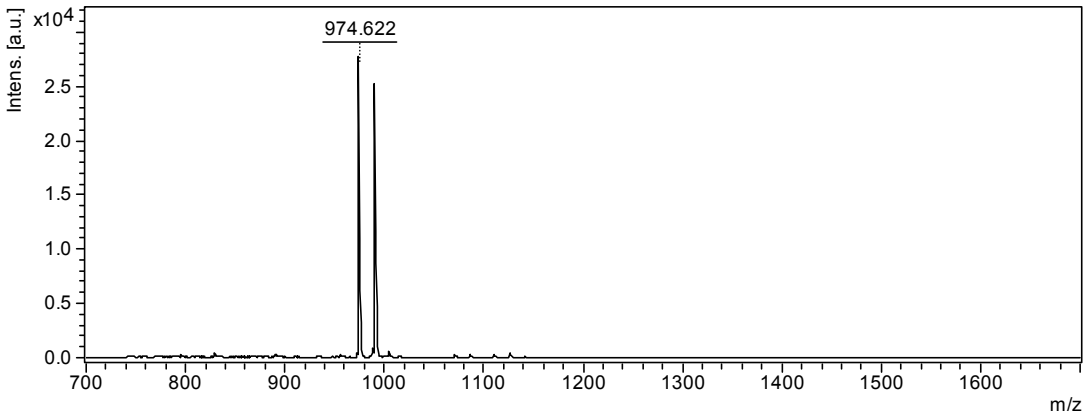
N020 

HILIC-ELSD, T_R = 8.84 min

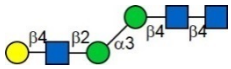


ESI-MS, calculated: 951.3543; found $[M+H]^+$ 952.3630

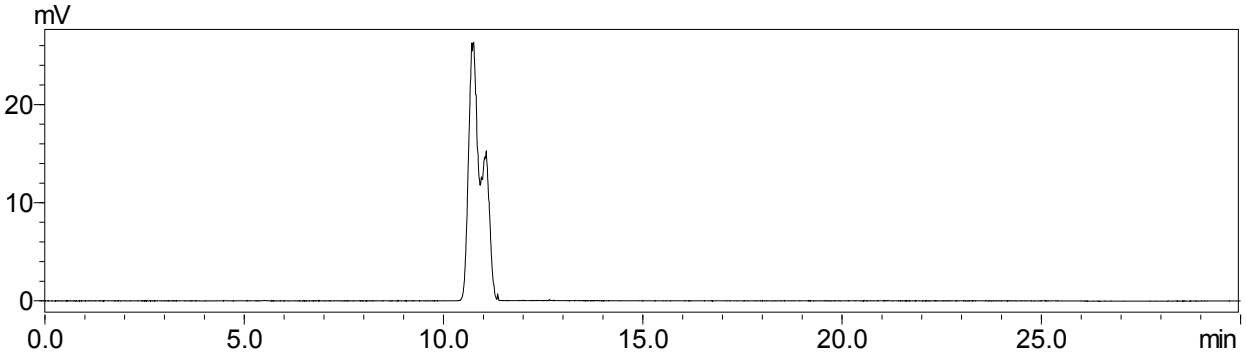
MALDI-MS, found $[M+Na]^+$ 974.622, $[M+K]^+$ 990.629



NMR data listed in Part VI

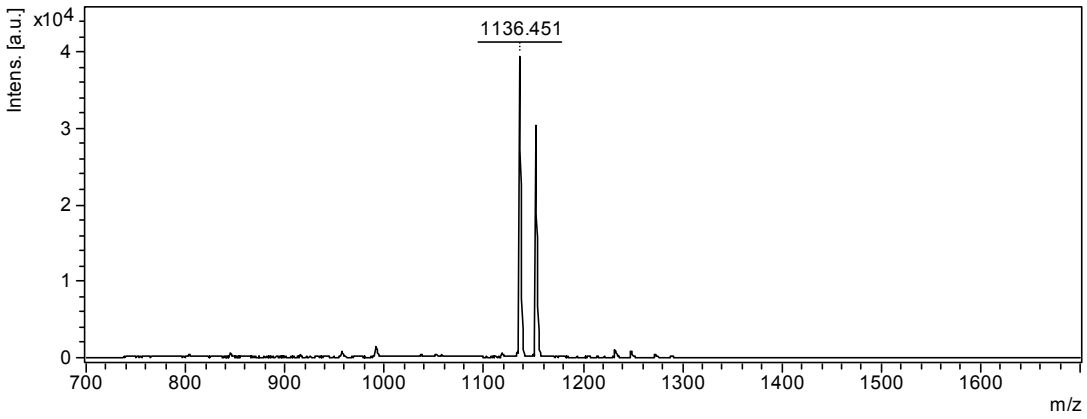
N021 

HILIC-ELSD, T_R = 10.73 min

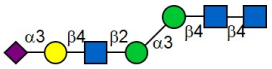


ESI-MS, calculated: 1113.4072; found $[M+H]^+$ 1114.4144

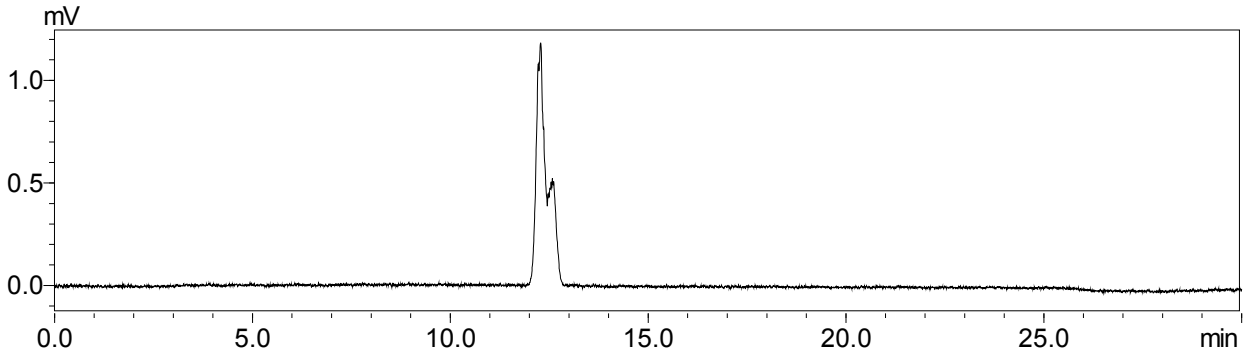
MALDI-MS, found $[M+Na]^+$ 1136.451, $[M+K]^+$ 1152.342



^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.5 Hz, 0.7 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 8.0 Hz, 0.3 H, GlcNAc-1 H-1 of β anomer), 4.59 (d, J = 7.8 Hz, 0.7 H, GlcNAc-2 H-1 of α anomer), 4.58 (d, J = 7.6 Hz, 0.3 H, GlcNAc-2 H-1 of β anomer), 4.56 (d, J = 7.7 Hz, 1 H, GlcNAc-3 H-1), 4.45 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.22 (d, J = 3.0 Hz, 1 H), 4.18 (dd, J = 3.3, 1.4 Hz, 1 H), 3.43-3.98 (m, 34 H), 2.05 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac)

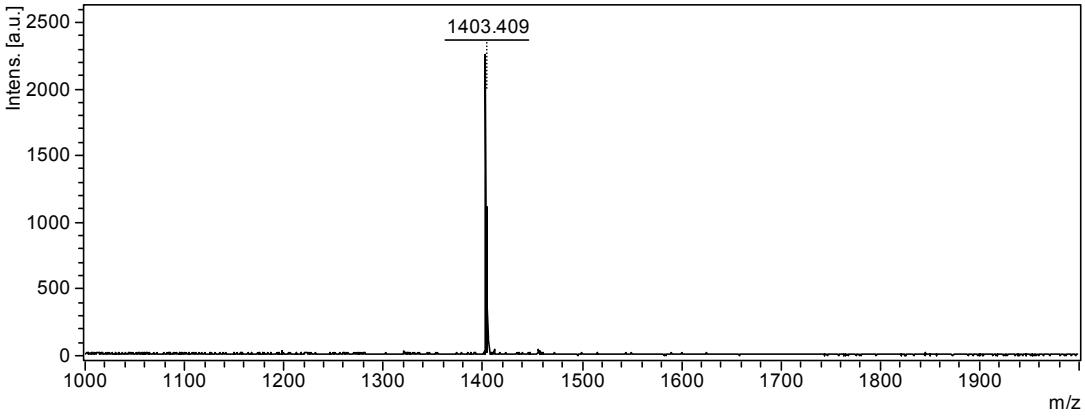
N022 

HILIC-ELSD, T_R = 12.28 min

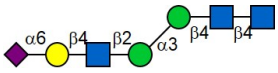


ESI-MS, calculated: 1404.5026; found $[M+2H]^{2+}$ 703.2563

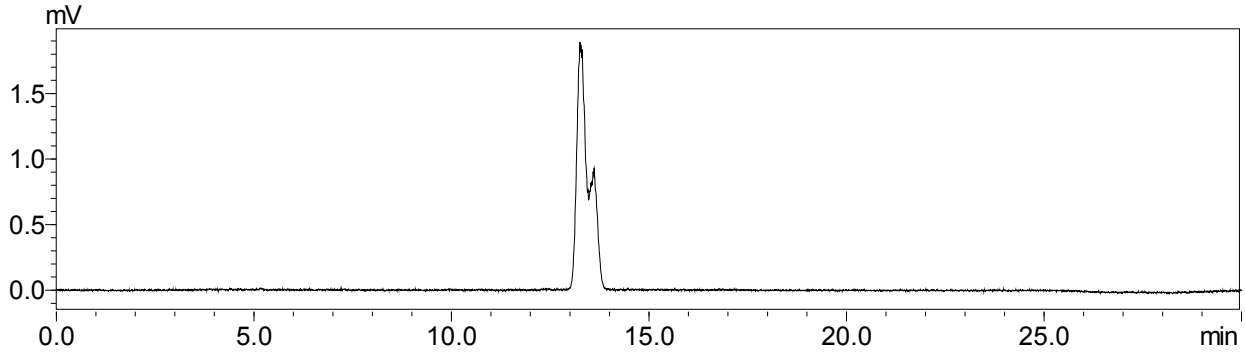
MALDI-MS, found $[M-H]^-$ 1403.409



^{1}H NMR (D_2O, 500 MHz): δ 5.18 (d, J = 2.4 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.59 (d, J = 7.6 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.58 (d, J = 7.2 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.55 (d, J = 7.8 Hz, 1 H, GlcNAc-3 H-1), 4.53 (d, J = 8.0 Hz, 1 H, Gal H-1), 4.22 (d, J = 2.5 Hz, 1 H), 4.18 (d, J = 2.9 Hz, 1 H), 4.11 (dd, J = 9.9, 2.9 Hz, 1 H), 3.81-4.00 (m, 12 H), 3.53-3.80 (m, 25 H), 3.43-3.52 (m, 3 H), 2.75 (dd, J = 12.4, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.06 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.79 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)

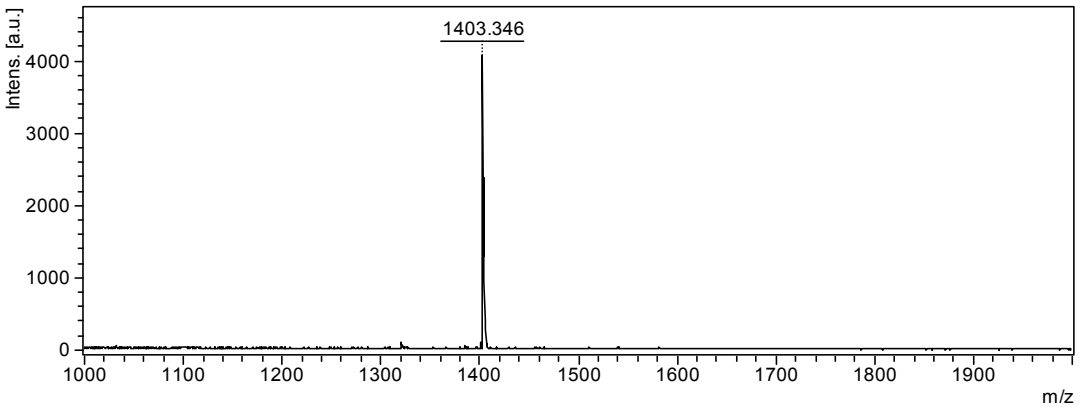
N023 

HILIC-ELSD, T_R = 13.27 min



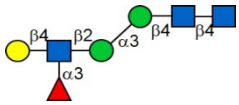
ESI-MS, calculated: 1404.5026; found $[M+2H]^{2+}$ 703.2563

MALDI-MS, found $[M-H]^-$ 1403.346

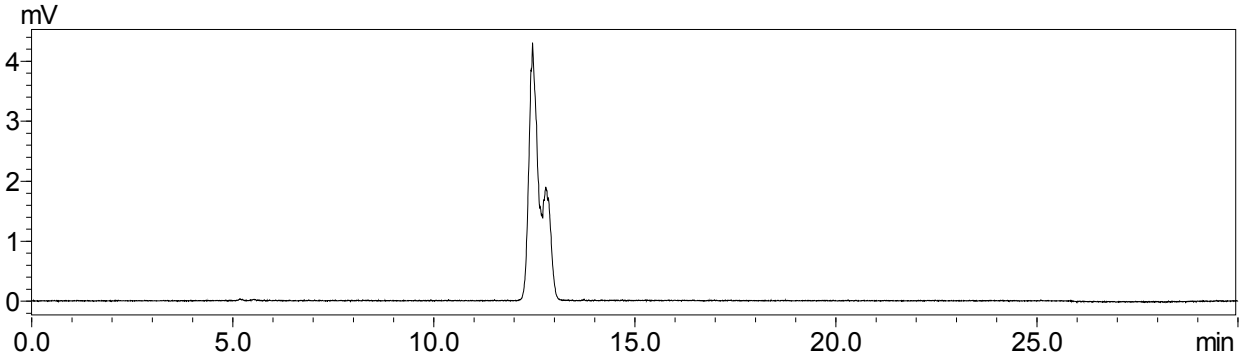


^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.7 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.13 (s, 1 H, Man2 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.57-4.60 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.43 (d, J = 7.9 Hz, 1 H, Gal H-1), 4.22 (d, J = 2.7 Hz, 1 H), 4.18 (d, J = 2.0 Hz, 1 H), 3.46-4.01 (m, 41 H), 2.65 (dd, J = 12.4, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.06 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.71 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)

N024

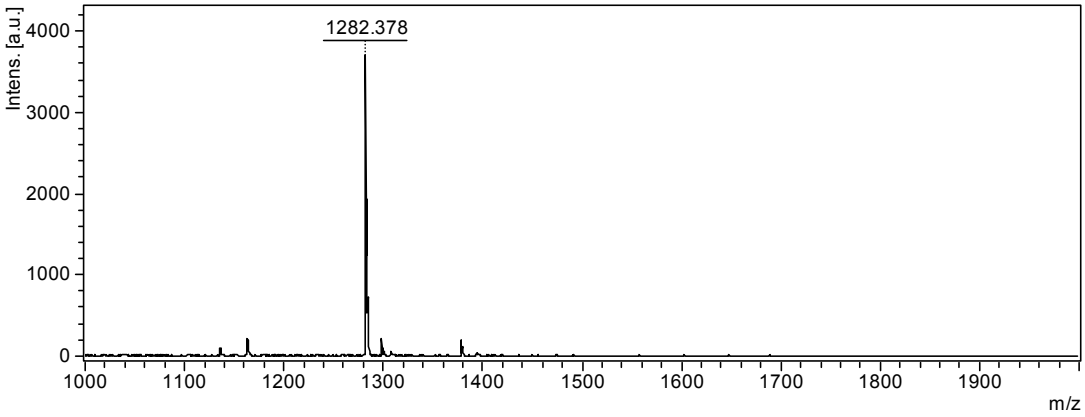


HILIC-ELSD, T_R = 12.46 min

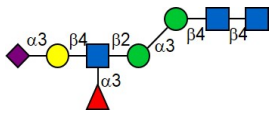


ESI-MS, calculated: 1259.4651; found $[M+2H]^{2+}$ 630.7370

MALDI-MS, found $[M+Na]^{+}$ 1282.378

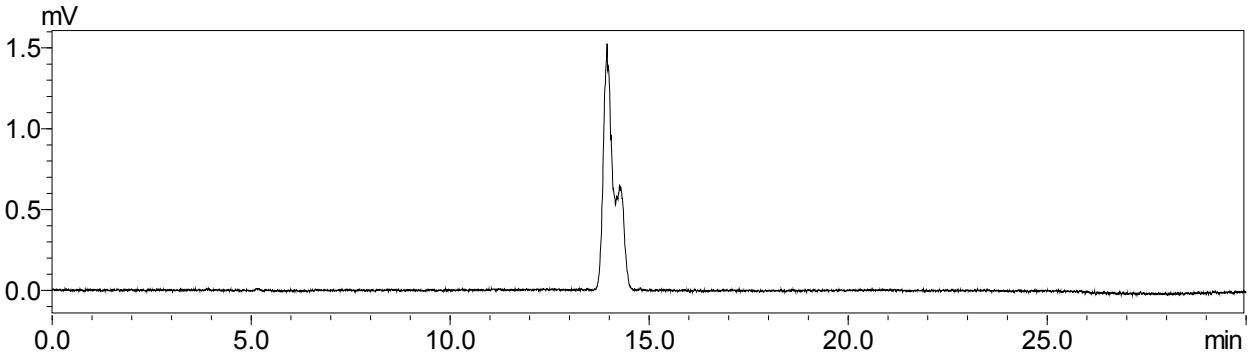


^{1}H NMR (D_2O, 500 MHz): δ 5.17 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (d, J = 4.0 Hz, 1 H, Fuc H-1), 5.10 (s, 1 H, Man2 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.8 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.56-4.60 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.43 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.22 (d, J = 2.8 Hz, 1 H), 4.17 (d, J = 2.0 Hz, 1 H), 3.83-4.02 (m, 12 H), 3.53-3.80 (m, 22 H), 3.43-3.49 (m, 4 H), 2.05 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.16 (d, J = 6.6 Hz, 3 H, Fuc-CH_3)



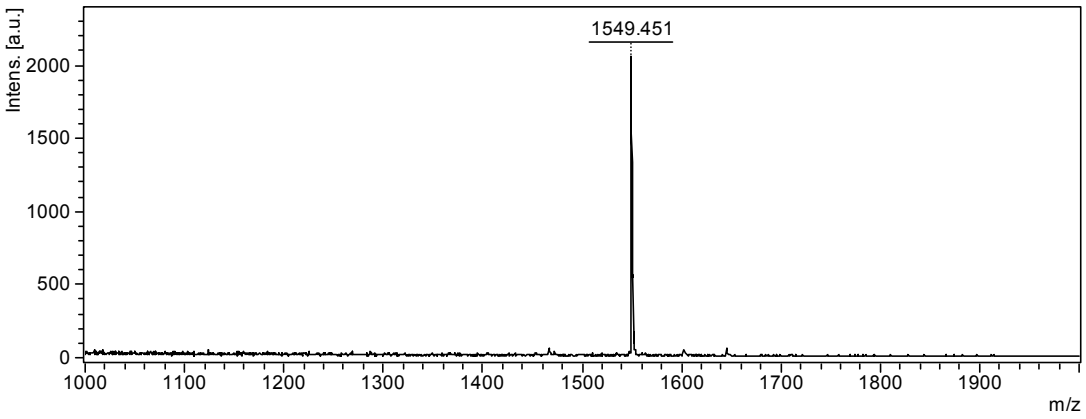
N025

HILIC-ELSD, T_R = 13.95 min

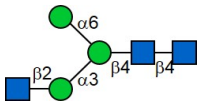


ESI-MS, calculated: 1550.5605; found $[M+2H]^{2+}$ 776.2854

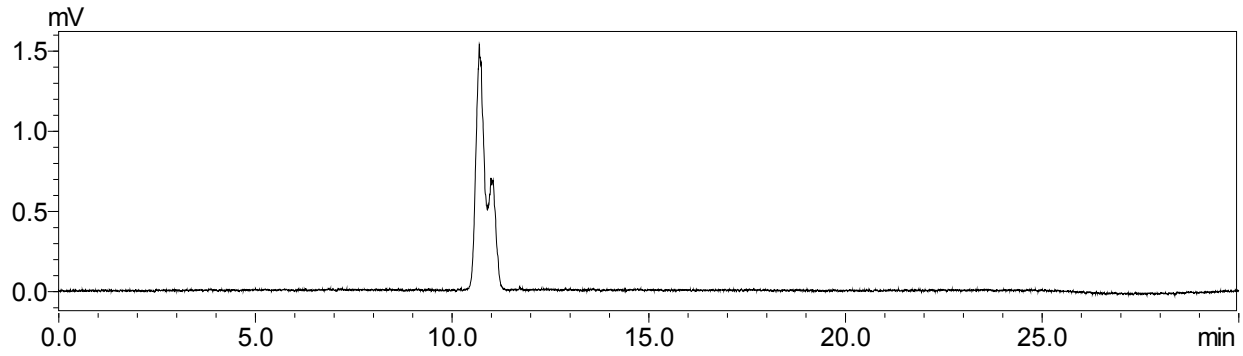
MALDI-MS, found $[M-H]^-$ 1549.451



^{1}H NMR (D_2O, 500 MHz): δ 5.18 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.10 (s, 1 H, Man2 H-1), 4.79-4.95 (overlapped with D_2O, 1 H, Man3 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, *J* = 7.0 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.55-4.60 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.50 (d, *J* = 7.5 Hz, 1 H, Gal H-1), 4.22 (brs, 1 H), 4.18 (m, 1 H), 3.45-4.03 (m, 44 H), 2.75 (dd, *J* = 12.4, 3.8 Hz, 1 H, Neu5Ac H-3e), 2.06 (s,3 H, Ac), 2.03 (s, 9 H, 3 Ac), 1.79 (t, *J* = 12.4 Hz, 1 H, Neu5Ac H-3a), 1.16 (d, *J* = 5.4 Hz, 3 H, Fuc-CH_3).

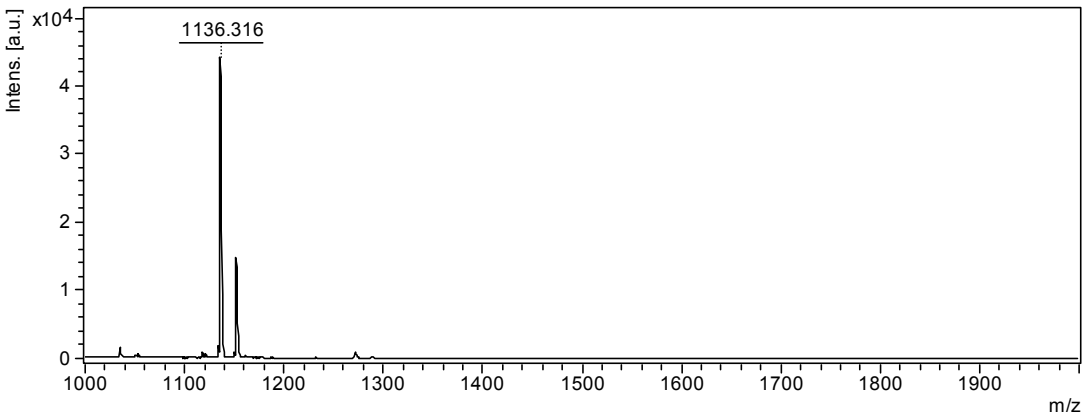
N030 

HILIC-ELSD, T_R = 10.71 min

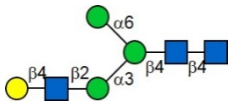


ESI-MS, calculated: 1113.4072; found $[M+H]^+$ 1114.4170

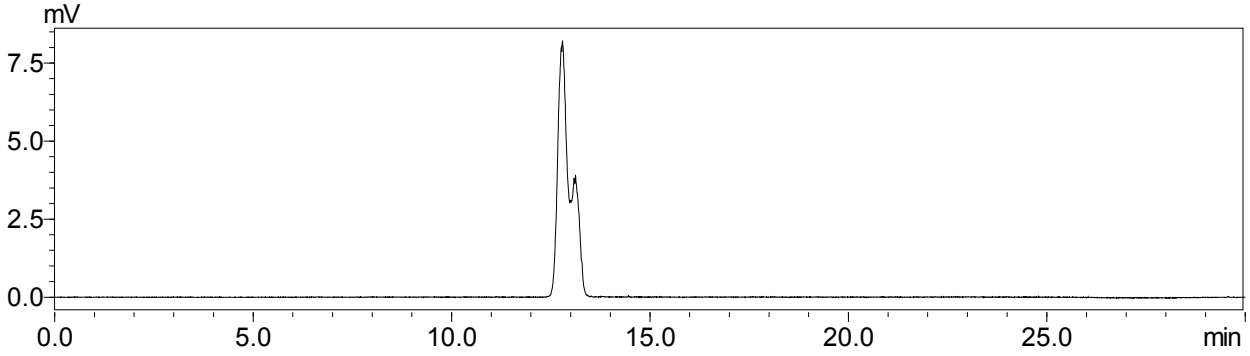
MALDI-MS, found $[M+Na]^+$ 1136.316, $[M+K]^+$ 1152.325



NMR data listed in Part VI

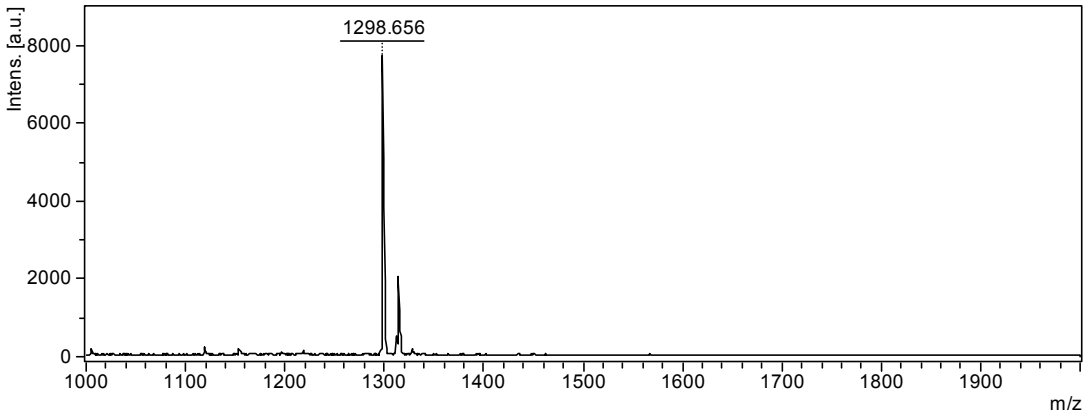
N031 

HILIC-ELSD, T_R = 12.79 min

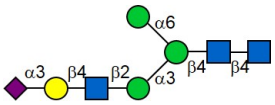


ESI-MS, calculated: 1275.4600; found $[M+2H]^{2+}$ 638.7382

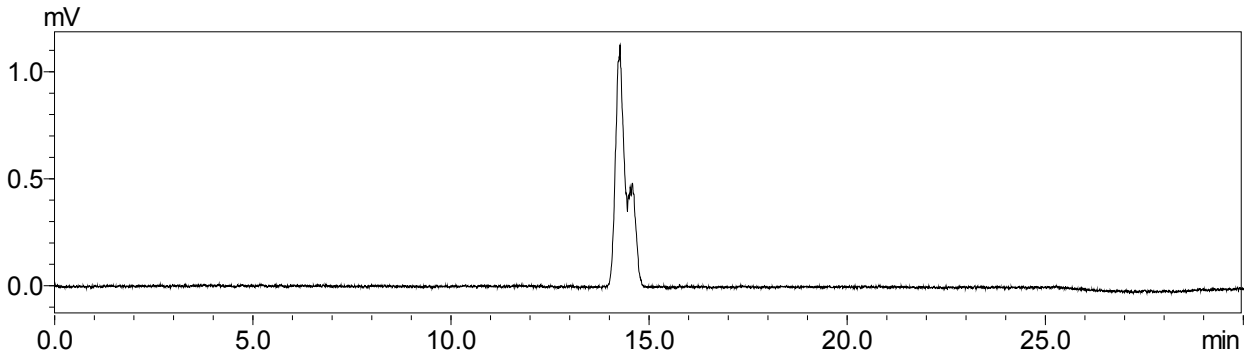
MALDI-MS, found $[M+Na]^+$ 1298.565, $[M+K]^+$ 1314.668



^{1}H NMR (D_2O, 500 MHz): δ 5.18 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.77-4.82 (overlapped with D_2O, 1 H, Manβ H-1), 4.68 (d, *J* = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.60 (d, *J* = 7.8 Hz, 1 H, GlcNAc-2 H-1 of α anomer), 4.59 (d, *J* = 7.8 Hz, 1 H, GlcNAc-2 H-1 of β anomer), 4.56 (d, *J* = 6.8 Hz, 1 H, GlcNAc-3 H-1), 4.46 (d, *J* = 6.7 Hz, 1 H, Gal H-1), 4.25 (brs, 1 H), 4.18 (brs, 1 H), 3.96-3.98 (m, 2 H), 3.47-3.95 (m, 38 H), 2.07 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac)

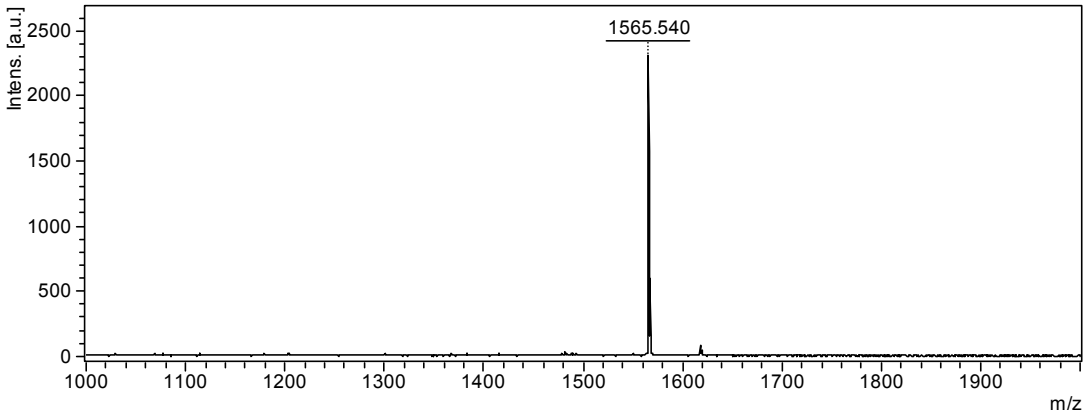
N032 

HILIC-ELSD, T_R = 14.26 min

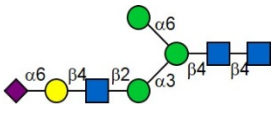


ESI-MS, calculated: 1566.5554; found $[M+2H]^{2+}$ 784.2826

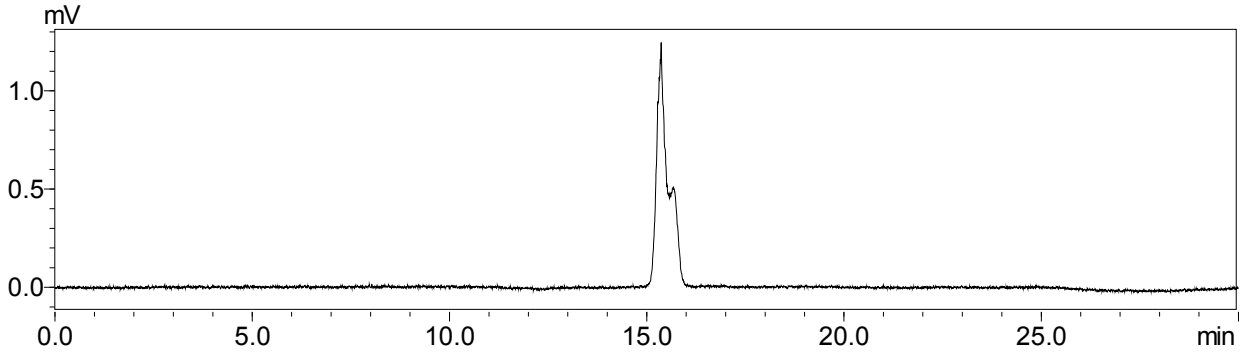
MALDI-MS, found $[M-H]^-$ 1565.540



^{1}H NMR (D_2O, 500 MHz): δ 5.18 (d, J = 1.5 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.77-4.85 (overlapped with D_2O, 1 H, Manβ H-1), 4.69 (d, J = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.53-4.61 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, Gal H-1), 4.25 (brs, 1 H), 4.18 (brs, 1 H), 4.09-4.12 (m, 1 H), 3.47-4.02 (m, 46 H), 2.75 (dd, J = 12.4, 4.6 Hz, 1 H, Neu5Ac H-3e), 2.07 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.79 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)

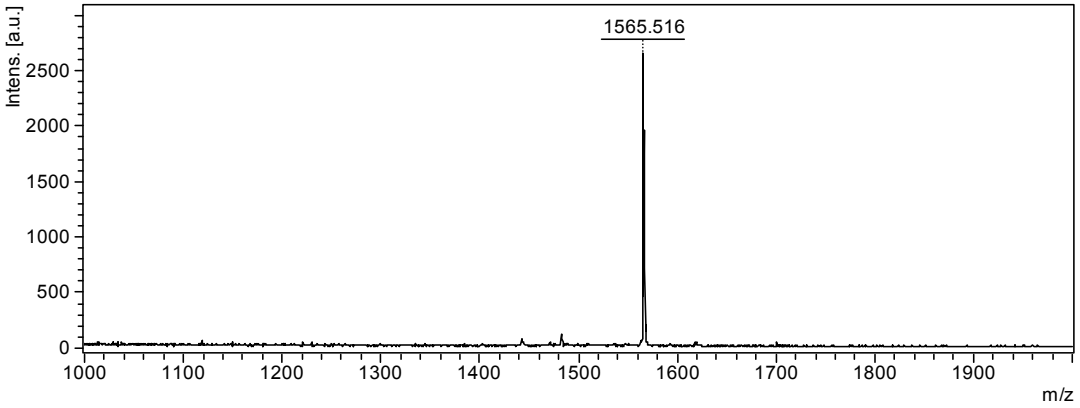
N033 

HILIC-ELSD, T_R = 15.37 min

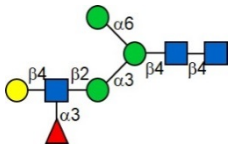


ESI-MS, calculated: 1566.5554; found $[M+2H]^{2+}$ 784.2845

MALDI-MS, found $[M-H]^-$ 1565.516

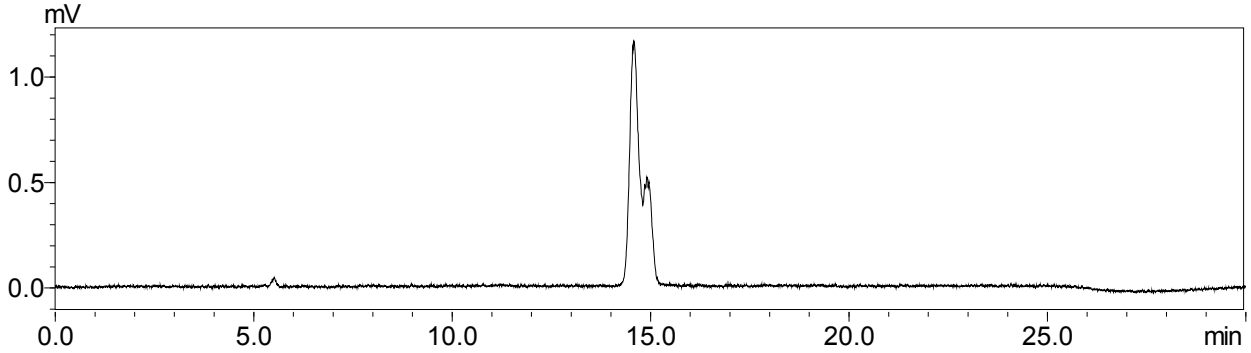


^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.5 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.12 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.77 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.9 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.58-4.61 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.43 (d, J = 8.0 Hz, 1 H, Gal H-1), 4.24 (d, J = 2.2 Hz, 1 H), 4.18-4.19 (m, 1 H), 3.95-4.01 (m, 3 H), 3.47-3.92 (m, 46 H), 2.65 (dd, J = 12.4, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.07 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.71 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)



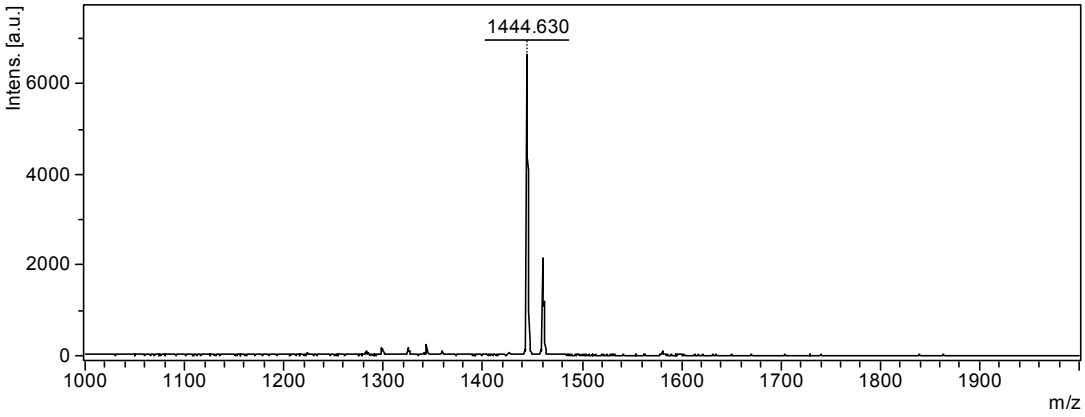
N034

HILIC-ELSD, T_R = 14.58 min



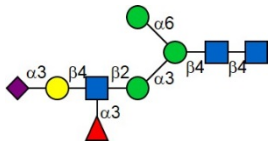
ESI-MS, calculated: 1421.5179; found $[M+2H]^{2+}$ 711.7661

MALDI-MS, found $[M+Na]^{+}$ 1444.630, $[M+K]^{+}$ 1460.599

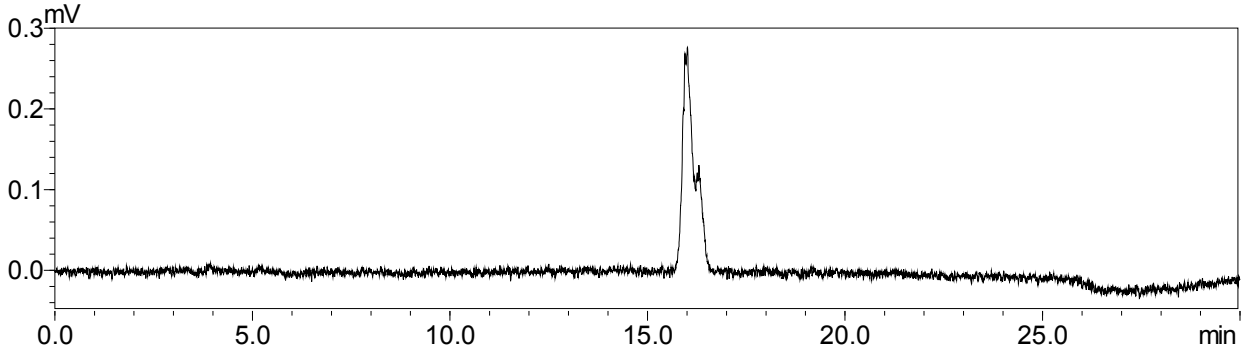


^{1}H NMR (D_2O, 500 MHz): δ 5.20 (d, J = 2.2 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.15 (d, J = 3.9 Hz, 1 H, Fuc H-1), 5.13 (s, 1 H, Man2 H-1), 4.94 (s, 1 H, Man3 H-1), 4.79-4.83 (overlapped with D_2O, 1.5 H, GlcNAc-1 H-1 of β anomer, Manβ H-1), 4.60-4.64 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.46 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.28 (brs, 1 H), 4.19-4.21 (m, 1 H), 3.47-4.03 (m, 44 H), 2.10 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 1.19 (d, J = 6.6 Hz, 3 H, Fuc-CH_3)

N035

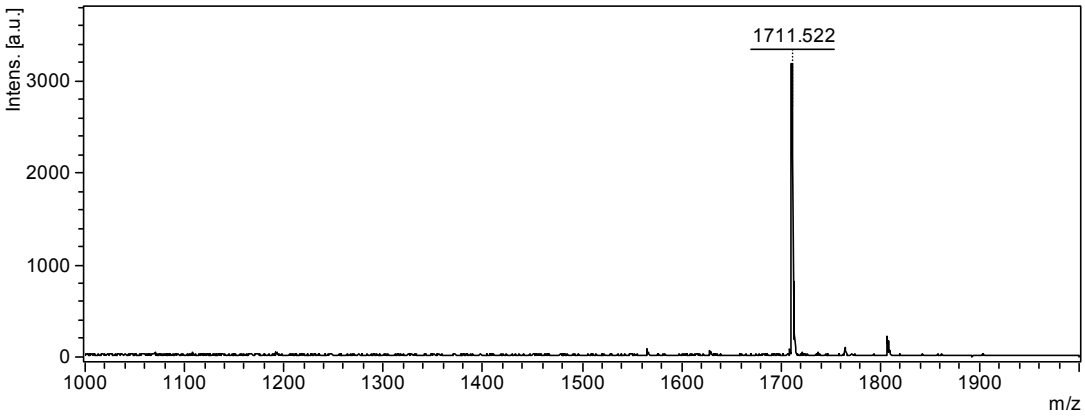


HILIC-ELSD, T_R = 15.98 min

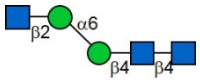


ESI-MS, calculated: 1712.6133; found $[M+2H]^{2+}$ 857.3162

MALDI-MS, found [M-H]- 1711.522

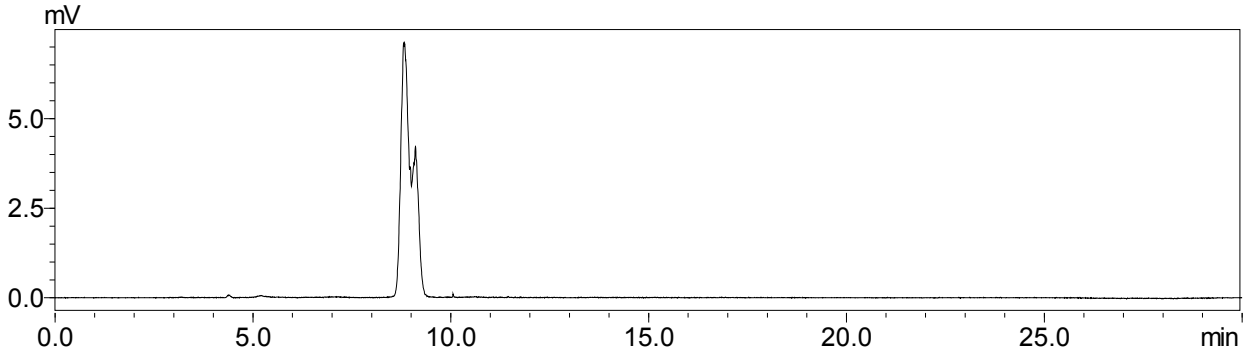


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 1.5 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.05-5.07 (m, 2 H, Fuc H-1, Man2 H-1), 4.87 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.64 (d, J = 7.2 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.52-4.56 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.46 (d, J = 7.4 Hz, 1 H, Gal H-1), 4.20-4.22 (m, 2 H), 4.12-4.14 (m, 2 H), 4.03-4.06 (m, 2 H), 3.41-3.95 (m, 47 H), 2.71 (dd, J = 12.1, 3.7 Hz, Neu5Ac H-3e), 2.03 (s, 3 H), 1.99 (s, 9 H, 3 Ac), 1.75 (t, J = 12.1 Hz, 1 H, Neu5Ac H-3a), 1.11 (d, J = 6.1 Hz, 3 H, Fuc-CH_3)



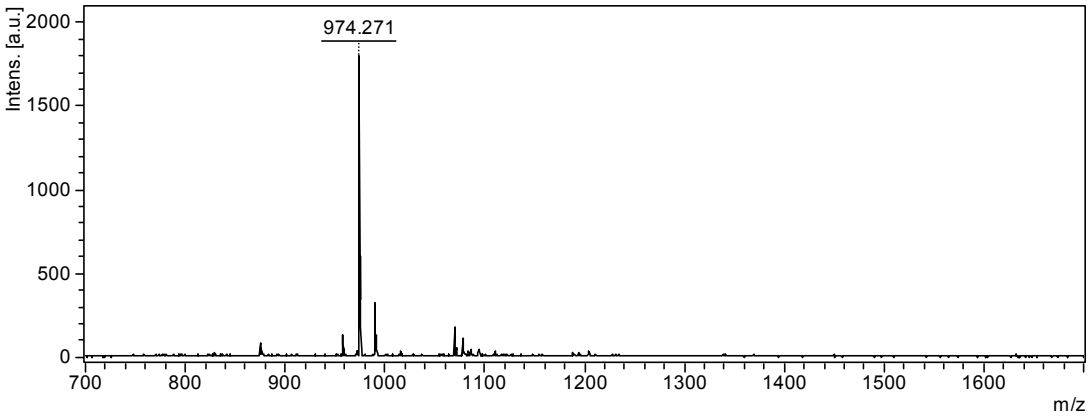
N040

HILIC-ELSD, T_R = 8.82 min

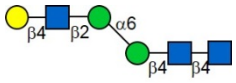


ESI-MS, calculated: 951.3543; found $[M+H]^+$ 952.3555

MALDI-MS, found $[M+Na]^+$ 974.271, $[M+K]^+$ 990.268

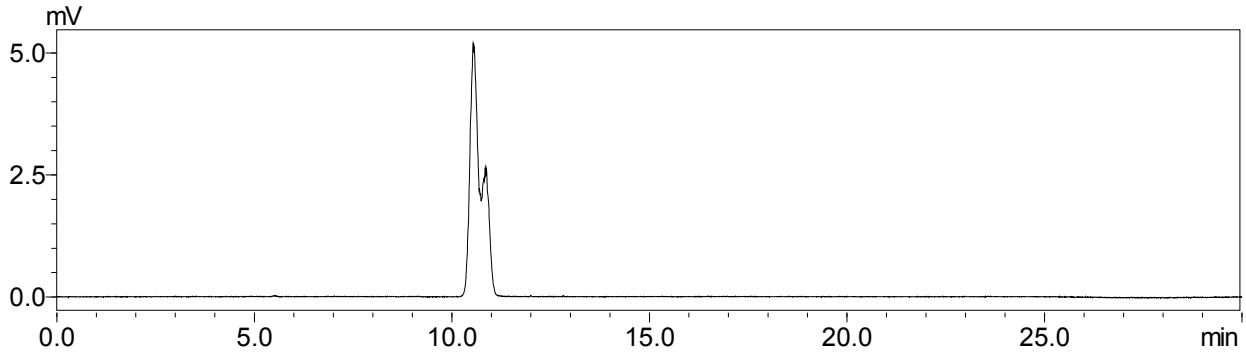


NMR data listed in Part VI



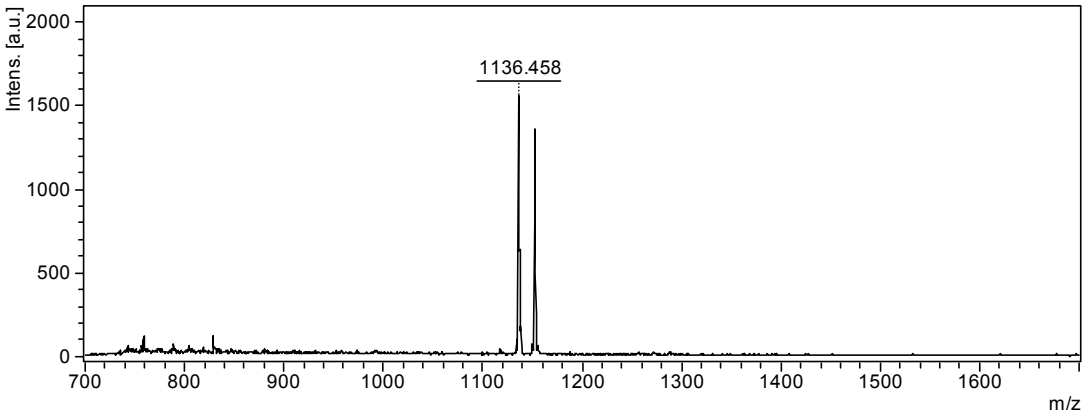
N041

HILIC-ELSD, T_R = 10.55 min

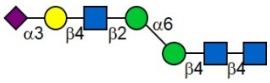


ESI-MS, calculated: 1113.4072; found $[M+H]^+$ 1114.4109

MALDI-MS, found $[M+Na]^+$ 1136.458, $[M+K]^+$ 1152.442

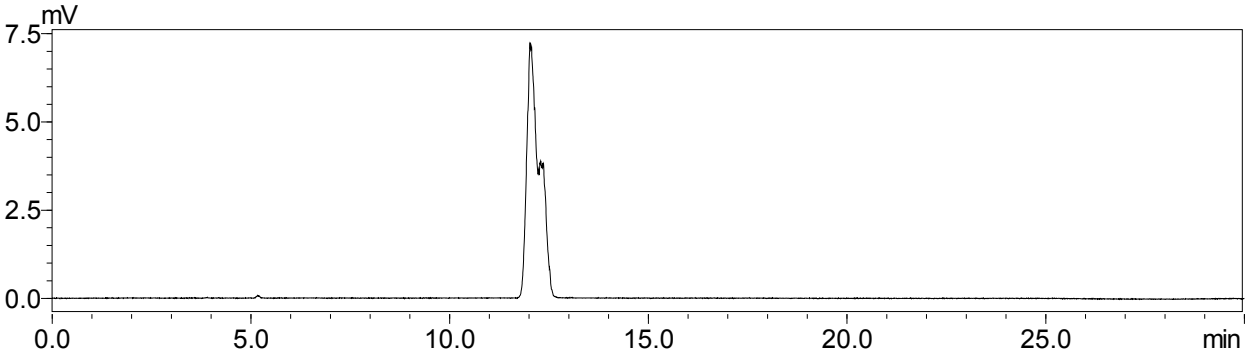


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.0 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 4.87 (s, 1 H, Man2 H-1), 4.72 (s, 1 H, Manβ H-1), 4.64 (d, J = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.56 (d, 1 H, GlcNAc-2 H-1 of α anomer), 4.55 (d, 1 H, GlcNAc-2 H-1 of β anomer), 4.53 (d, J = 8.2 Hz, 1 H, GlcNAc-3 H-1), 4.42 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.03-4.06 (m, 2 H), 3.41-3.95 (m, 40 H), 2.04 (s, 3 H, Ac), 2.00 (s, 3 H), 1.99 (s, 3 H, Ac).



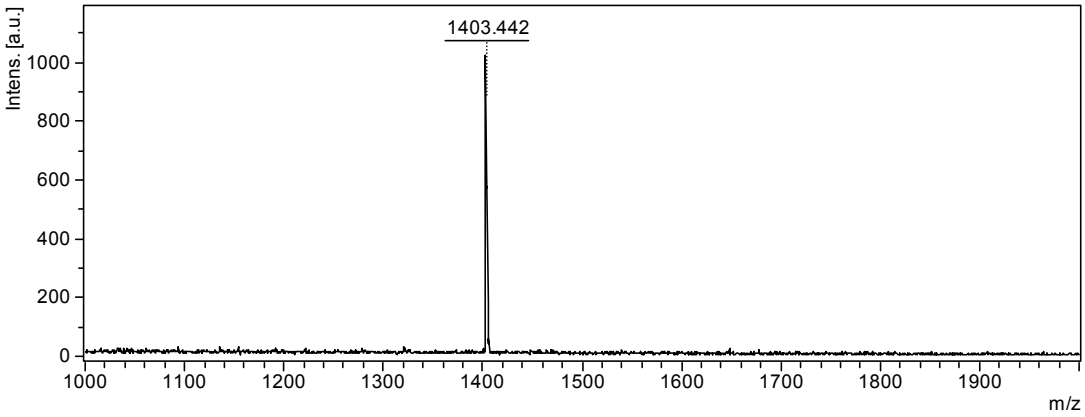
N042

HILIC-ELSD, T_R = 12.04 min

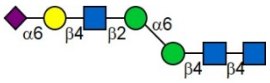


ESI-MS, calculated: 1404.5026; found $[M+2H]^{2+}$ 703.2563

MALDI-MS, found $[M-H]^-$ 1403.442

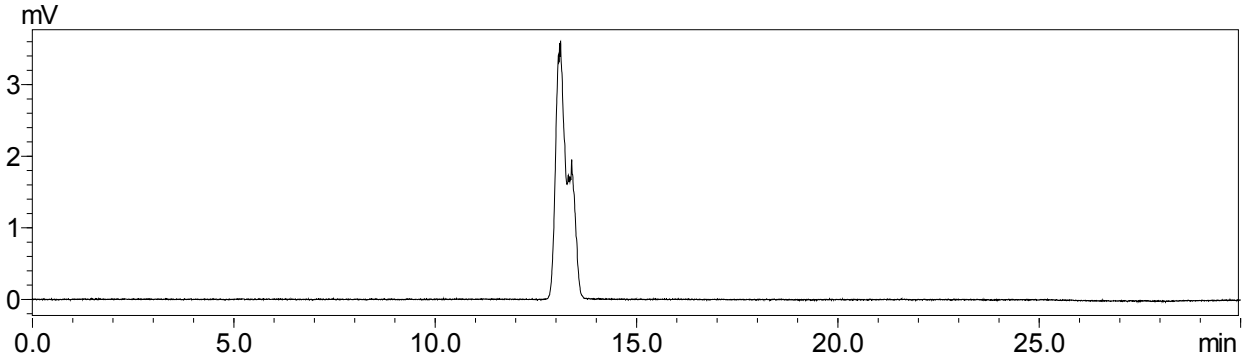


^{1}H NMR (D_2O, 500 MHz): δ 5.12 (d, J = 1.8 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 4.86 (s, 1 H, Man2 H-1), 4.69 (s, 1 H, Manβ H-1), 4.63 (d, J = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.48-4.55 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, Gal H-1), 4.01-4.06 (m, 3 H), 3.39-3.94 (m, 40 H), 2.69 (dd, J = 12.4, 3.0 Hz, 1 H, Neu5Ac H-3e), 2.02 (s, 3 H, Ac), 1.97 (s, 6 H, 2 Ac), 1.96 (s, 3 H, Ac), 1.74 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)



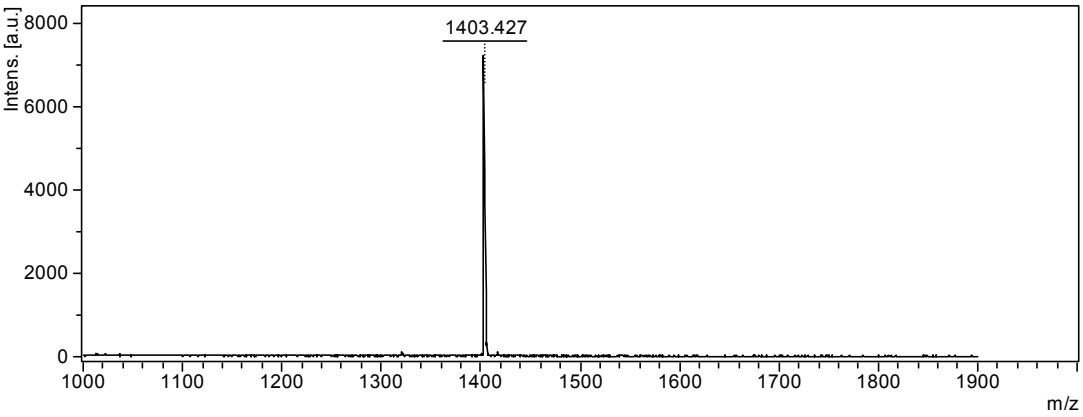
N043

HILIC-ELSD, T_R = 13.10 min

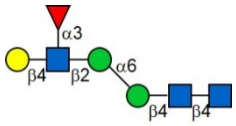


ESI-MS, calculated: 1404.5026; found $[M+2H]^{2+}$ 703.2565

MALDI-MS, found $[M-H]^-$ 1403.427

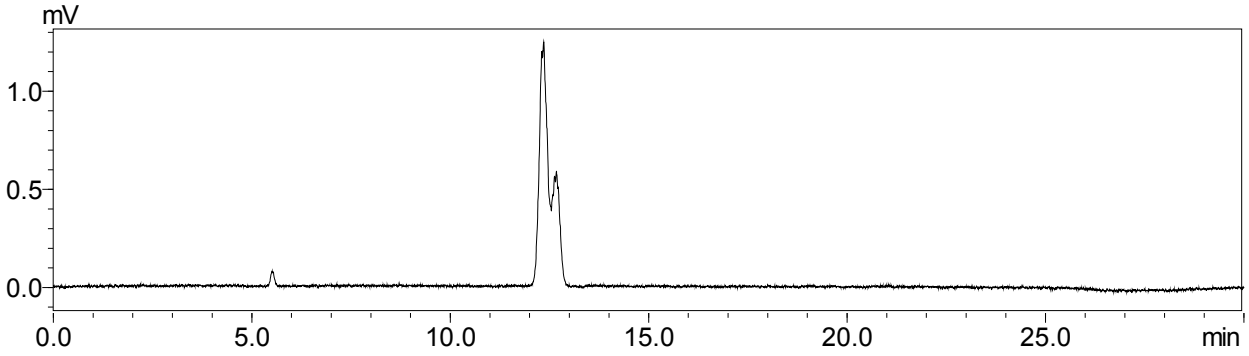


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.3 Hz, 0.7 H, GlcNAc-1 H-1 of α anomer), 4.90 (s, 1 H, Man2 H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.6 Hz, 0.3 H, GlcNAc-1 H-1 of β anomer), 4.53-4.57 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.40 (d, J = 7.9 Hz, 1 H, Gal H-1), 4.04-4.07 (m, 1 H), 4.02-4.04 (m, 1 H), 3.92-3.97 (m, 2 H), 3.43-3.90 (m, 39 H), 2.62 (dd, J = 12.4, 4.6 Hz, 1 H, Neu5Ac, H-3e), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.68 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)



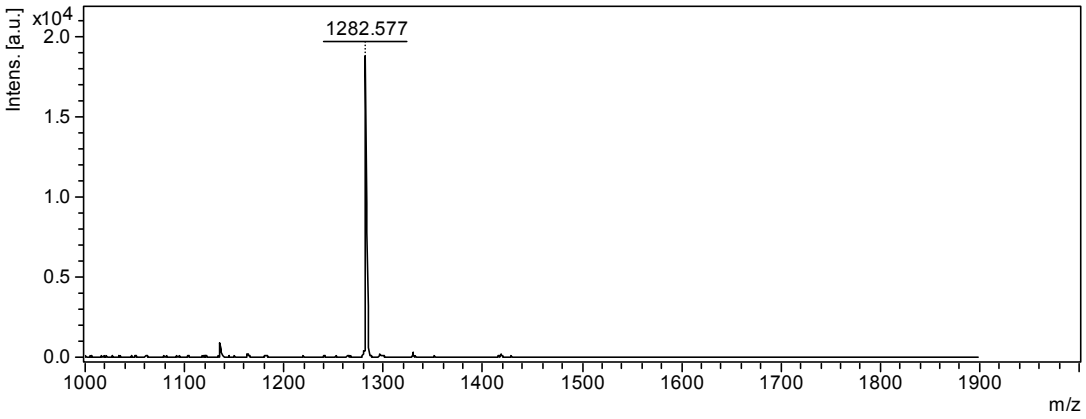
N044

HILIC-ELSD, T_R = 12.34 min

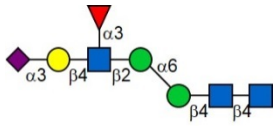


ESI-MS, calculated: 1259.4651; found $[M+2H]^{2+}$ 630.7381

MALDI-MS, found $[M+Na]^{+}$ 1282.577

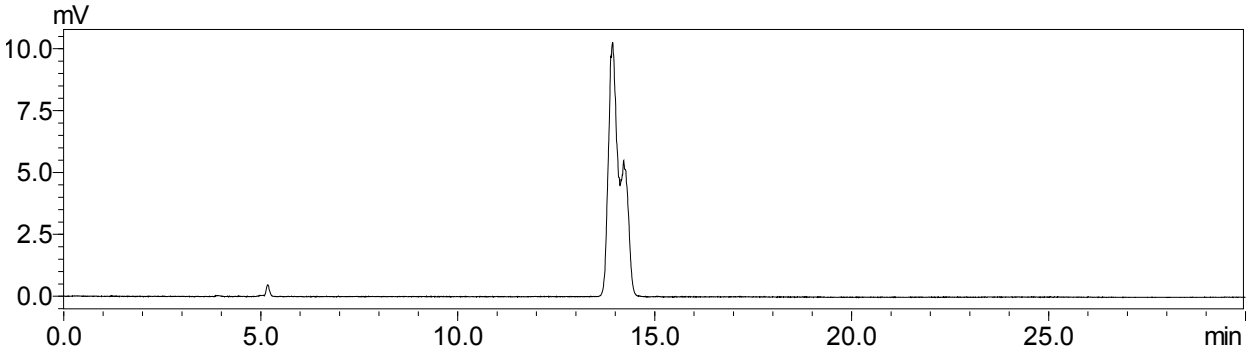


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 1.7 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, J = 3.7 Hz, 1 H, Fuc H-1), 4.87 (s, 1 H, Man2 H-1), 4.72 (s, 1 H, Manβ H-1), 4.64 (d, J = 7.8 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.52-4.57 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.40 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.03-4.06 (m, 2 H), 3.38-3.96 (m, 38 H), 2.04 (s, 3 H, Ac), 1.99 (s, 6 H), 1.13 (d, J = 6.5 Hz, 3 H, Fuc-CH_3)



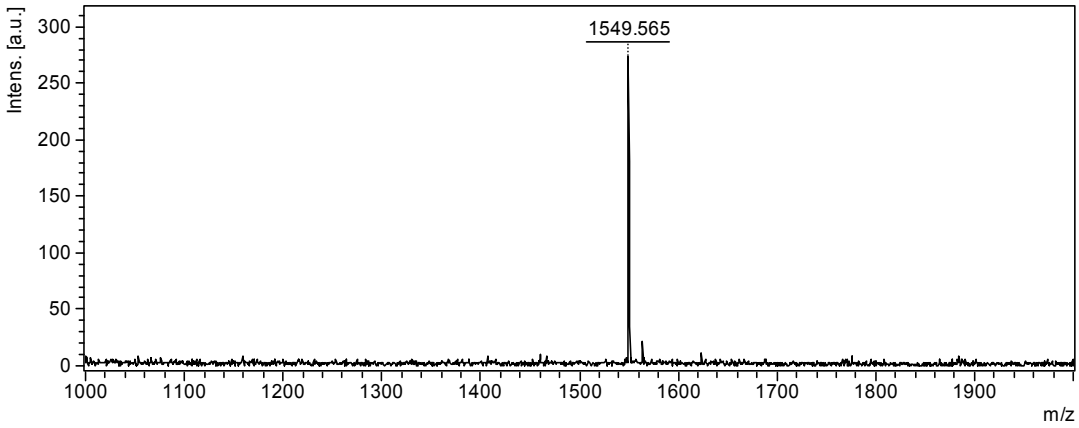
N045

HILIC-ELSD, T_R = 13.94 min

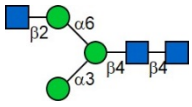


ESI-MS, calculated: 1550.5605; found $[M+2H]^{2+}$ 776.2882

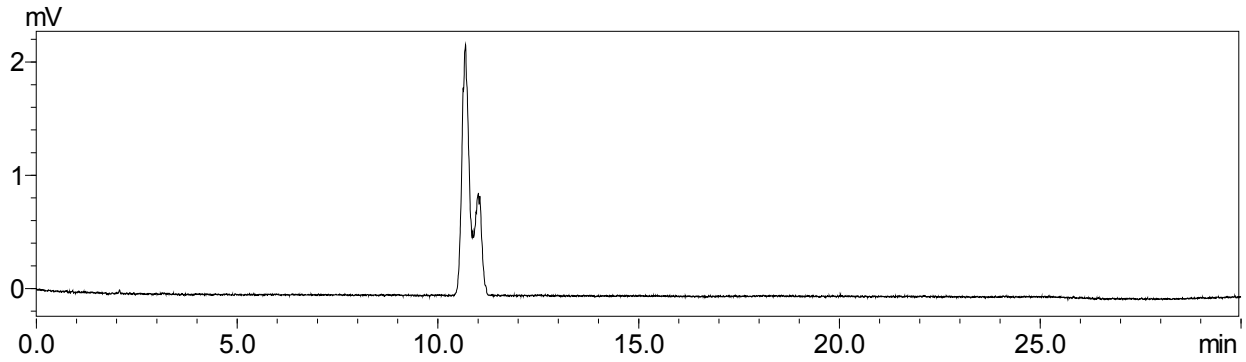
MALDI-MS, found $[M-H]^-$ 1549.565



^{1}H NMR (D_2O, 500 MHz): δ 5.15 (d, J = 2.6 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, J = 3.9 Hz, 1 H, Fuc H-1), 4.88 (s, 1 H, Man2 H-1), 4.73 (s, 1 H, Manβ H-1), 4.66 (d, J = 7.9 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.57 (d, J = 7.7 Hz, 0.5 H, GlcNAc-2 H-1 of α anomer), 4.56 (d, J = 7.7 Hz, 0.5 H, GlcNAc-2 H-1 of β anomer), 4.54 (d, J = 8.2 Hz, 1 H, H-1, GlcNAc-3 H-1), 4.48 (d, J = 7.8 Hz, 1 H, H-1, Gal H-1), 4.06 (d, J = 2.8 Hz, 1 H), 4.04 (d, J = 2.4 Hz, 1 H), 3.40-3.98 (m, 45 H), 2.72 (dd, J = 12.5, 4.6 Hz, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.76 (t, J = 12.1 Hz, 1 H, Neu5Ac H-3a), 1.13 (d, J = 6.6 Hz, Fuc-CH_3).

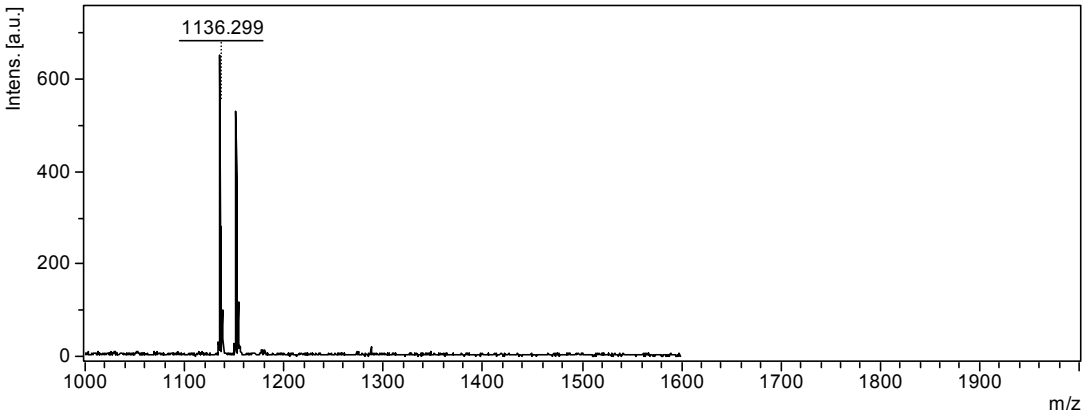
N050 

HILIC-ELSD, T_R = 10.69 min



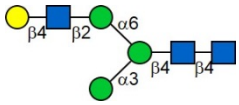
ESI-MS, calculated: 1113.4072; found $[M+H]^+$ 1114.4105

MALDI-MS, found $[M+Na]^+$ 1136.299; $[M+K]^+$ 1152.275

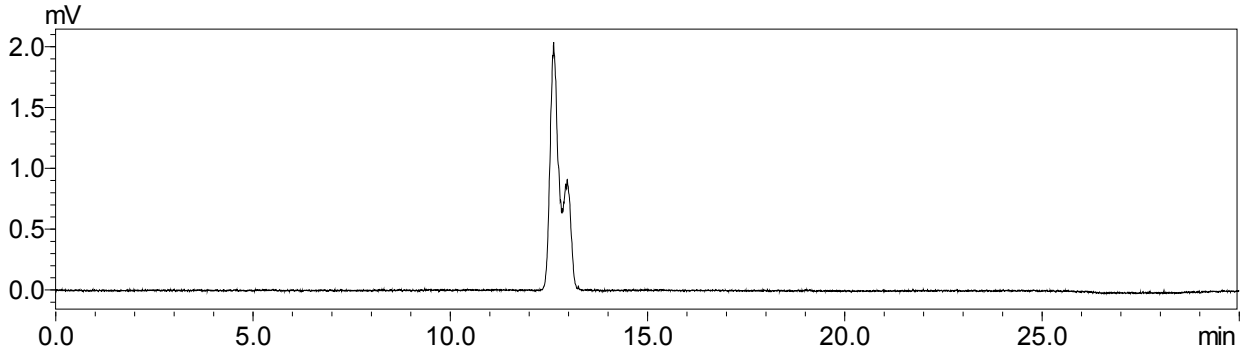


NMR data listed in Part VI

N051

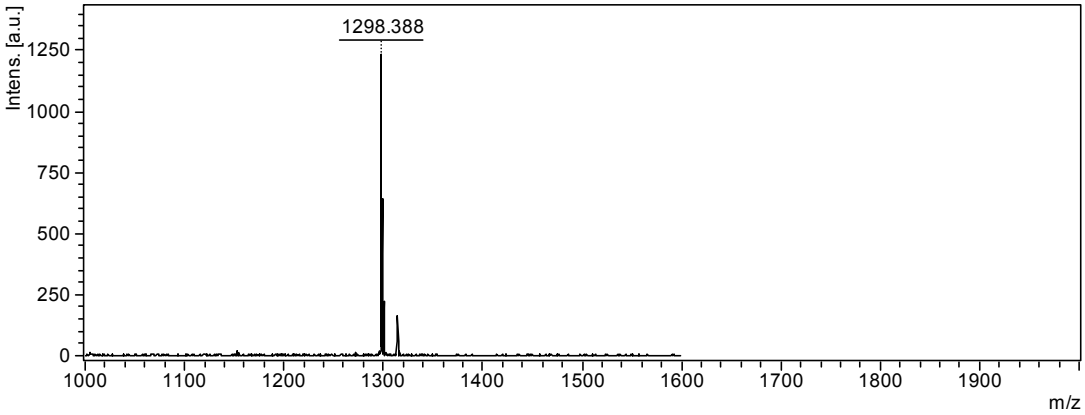


HILIC-ELSD, T_R = 12.63 min



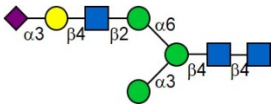
ESI-MS, calculated: 1275.4600; found $[M+2H]^{2+}$ 638.7374

MALDI-MS, found $[M+Na]^+$ 1298.388, $[M+K]^+$ 1314.366

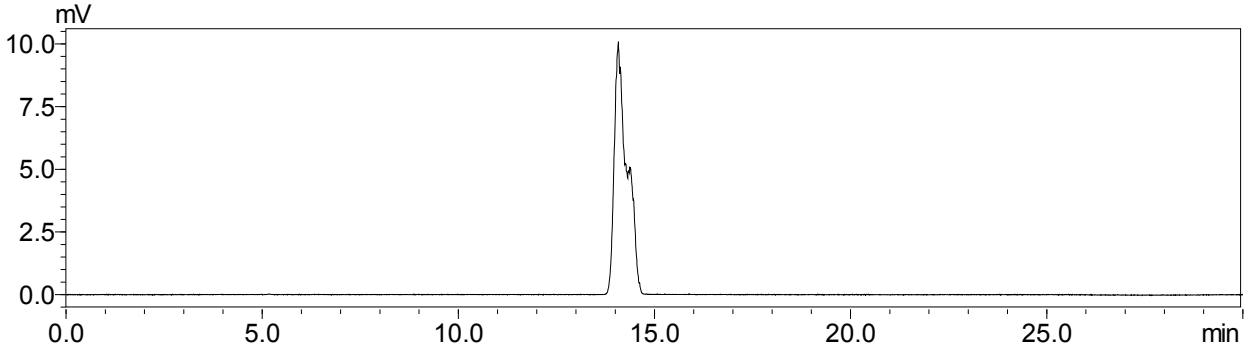


^{1}H NMR (D_2O, 500 MHz): δ 5.15 (d, J = 2.2 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.06 (s, 1 H, Man2 H-1), 4.89 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.8 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.57 (d, J = 7.8 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.56 (d, J = 7.8 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.54 (d, J = 8.3 Hz, 1 H, GlcNAc-3, H-1), 4.43 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.22 (s, 1 H), 4.06-4.08 (m, 1 H), 4.01-4.03 (m, 1 H), 3.41-3.95 (m, 39 H), 2.04 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.00 (s, 3 H, Ac)

N052

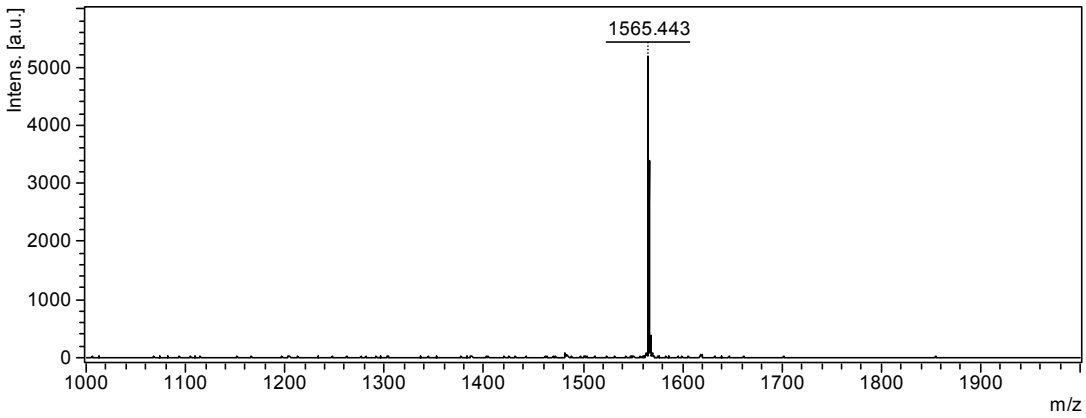


HILIC-ELSD, T_R = 14.07 min



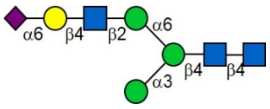
ESI-MS, calculated: 1566.5554; found $[M+2H]^{2+}$ 784.2828

MALDI-MS, found $[M-H]^-$ 1565.443

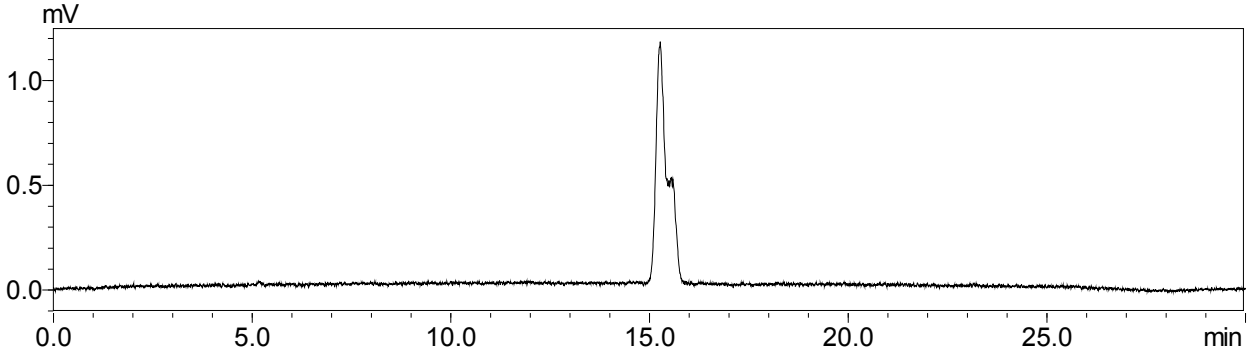


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 1.8 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.05 (s, 1 H, Man2 H-1), 4.88 (s, 1 H, Man3 H-1), 4.72 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.6 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.50-4.57 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3, Gal H-1), 4.21 (brs, 1 H), 4.06-4.08 (m, 2 H), 4.01-4.03 (m, 1 H), 3.41-3.96 (m, 45 H), 2.71 (d, J = 12.4, 4.7 Hz, 1 H, Neu5NAc H-3e), 2.04 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.98 (s, 3 H, Ac), 1.76 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a).

N053

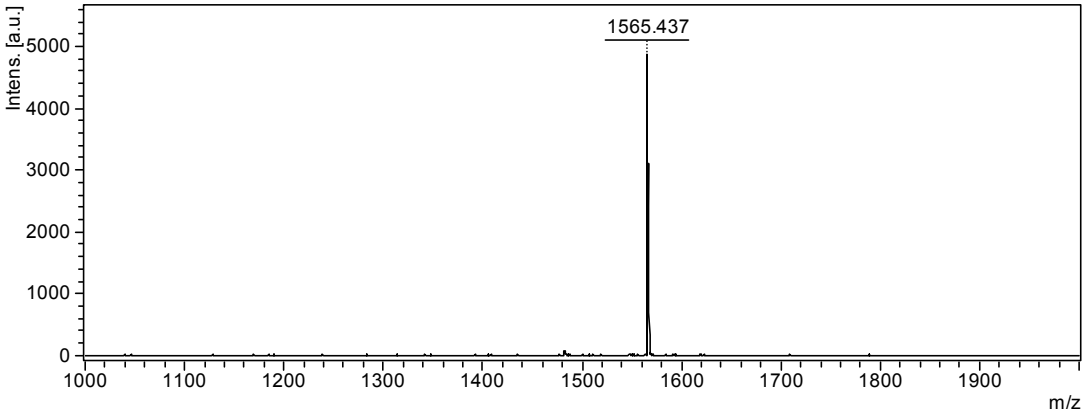


HILIC-ELSD, T_R = 15.28 min

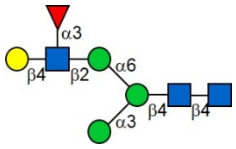


ESI-MS, calculated: 1566.5554; found $[M+2H]^{2+}$ 784.2882

MALDI-MS, found $[M-H]^-$ 1565.437

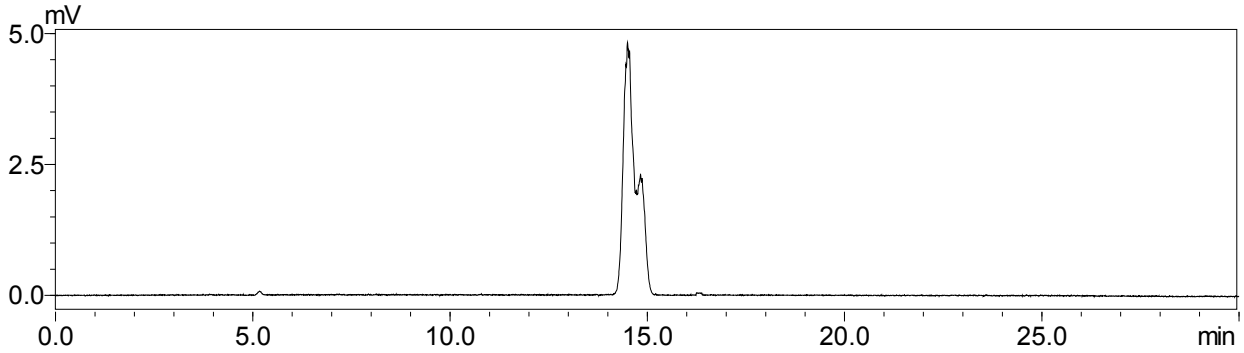


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.2 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.06 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.74 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.8 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.55-4.58 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.41 (d, J = 7.9 Hz, 1 H, Gal H-1), 4.08 (s, 1 H), 4.07-4.09 (m, 1 H), 4.02-4.04 (m, 1 H), 3.43-3.97 (m, 46 H), 4.63 (dd, J = 12.6, 4.6 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.68 (t, J = 12.6 Hz, 1 H, Neu5Ac H-3a)



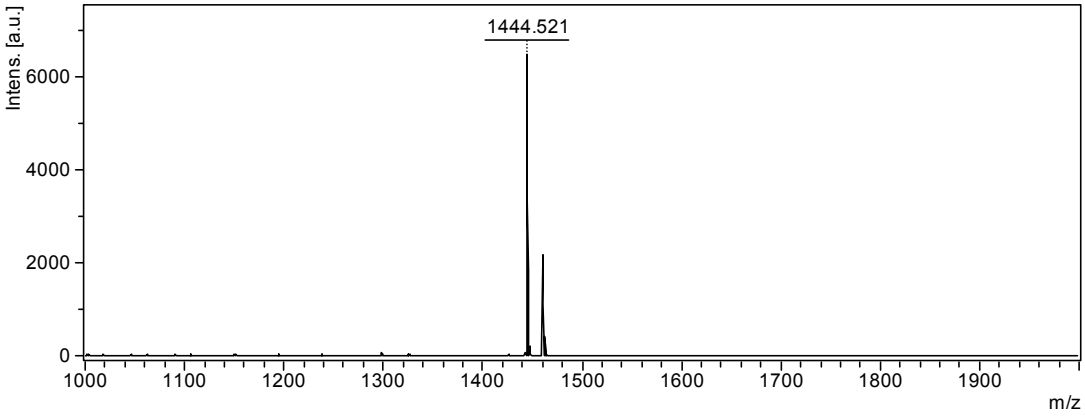
N054

HILIC-ELSD, T_R = 14.50 min



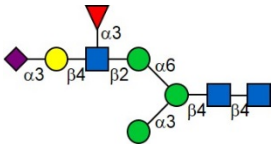
ESI-MS, calculated: 1421.5179; found $[M+2H]^{2+}$ 711.7671

MALDI-MS, found $[M+Na]^{+}$ 1444.521, $[M+K]^{+}$ 1460.499

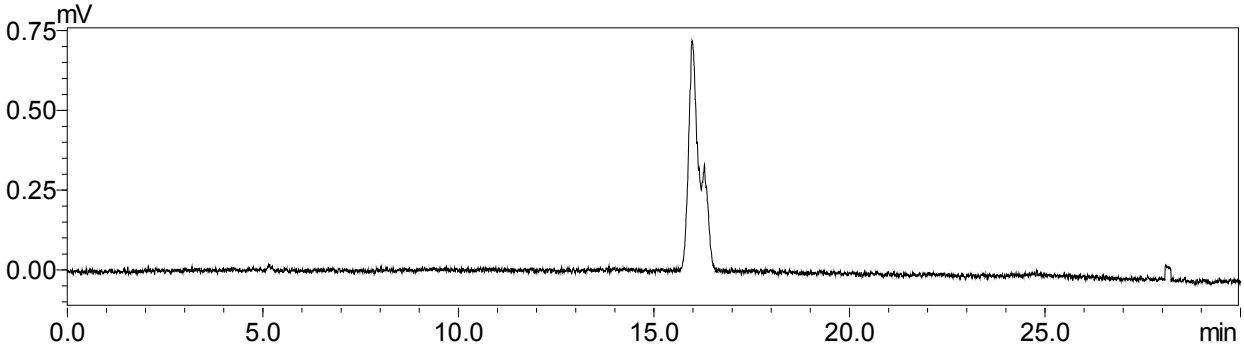


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.0 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.09 (d, J = 3.7 Hz, Fuc H-1), 5.05 (s, 1 H, Man2 H-1), 4.87 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.1 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.53-4.57 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.40 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.22 (brs, 1 H), 4.05-4.07 (m, 1 H), 4.01-4.03 (m, 1 H), 3.40-3.96 (m, 43 H), 2.04 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.13 (d, J = 6.5 Hz, 3 H, Fuc-CH_3)

N055

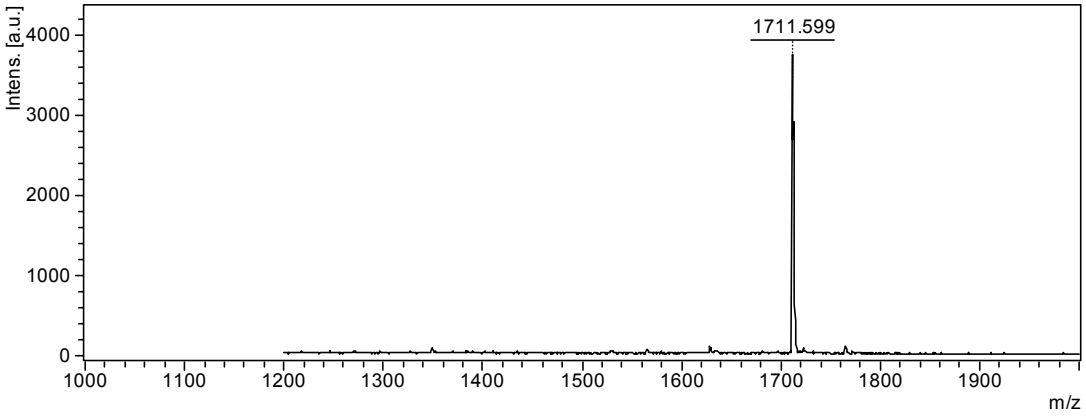


HILIC-ELSD, T_R = 15.97 min



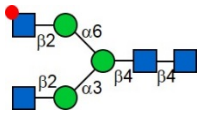
ESI-MS, calculated: 1712.6133; found $[M+2H]^{2+}$ 857.3152

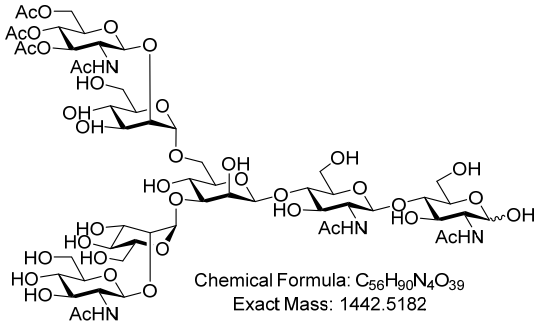
MALDI-MS, found [M-H]- 1711.599



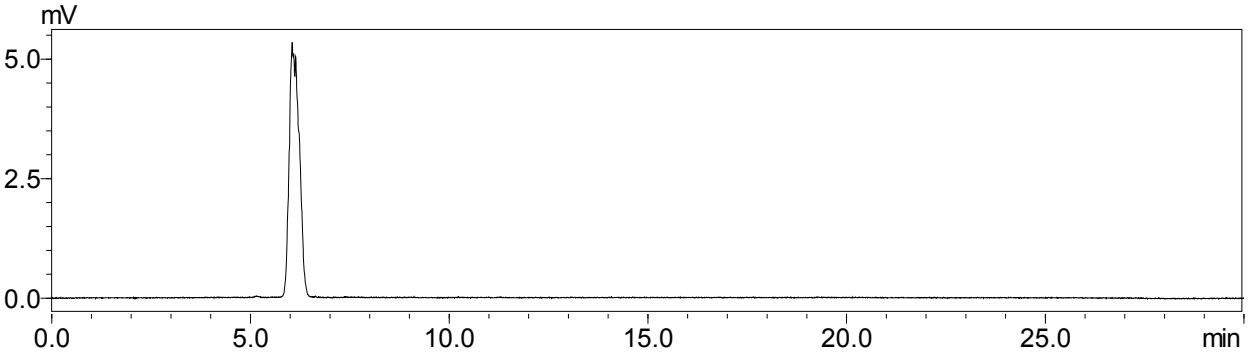
^{1}H NMR (D_2O, 500 MHz): δ 5.19 (d, J = 2.2 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.13 (d, J = 3.8 Hz, 1 H, Fuc H-1), 5.10 (s, 1 H, Man2 H-1), 4.92 (s, 1 H, Man3 H-1), 4.79-4.87 (overlapped with D_2O, 1 H, Manβ H-1), 4.70 (d, J = 7.4 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.57-4.62 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.52 (d, J = 7.7 Hz, Gal H-1), 4.21 (brs, 1 H), 4.07-4.11 (m, 3 H), 3.45-4.02 (m, 49 H), 2.77 (dd, J = 12.3, 4.4 Hz, 1 H, Neu5Ac H-3e), 2.09 (s, 3 H, Ac), 2.04 (s, 9 H, 3 Ac), 1.80 (t, J = 12.3 Hz, Neu5Ac H-3a), 1.17 (d, J = 6.5 Hz, 3 H, Fuc-CH_3)

N110



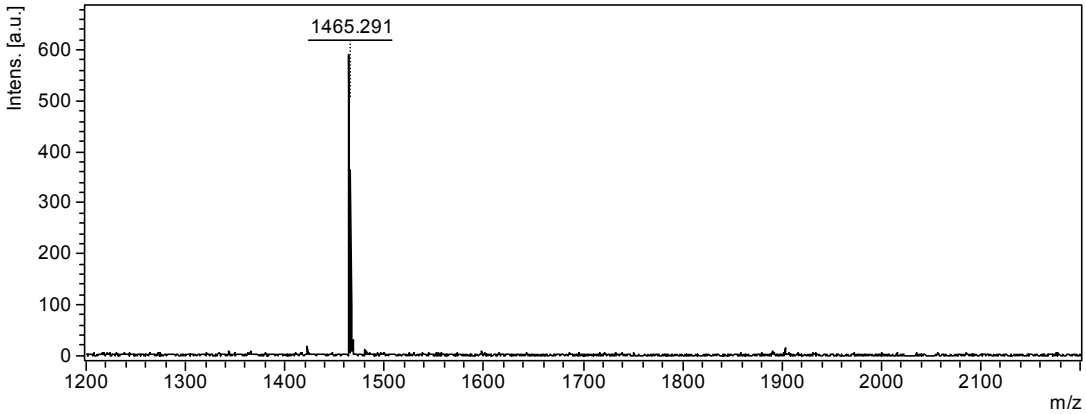


HILIC-ELSD, T_R = 6.06 min

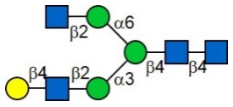


ESI-MS, calculated: 1442.5182; found $[M+2H]^{2+}$ 722.2688

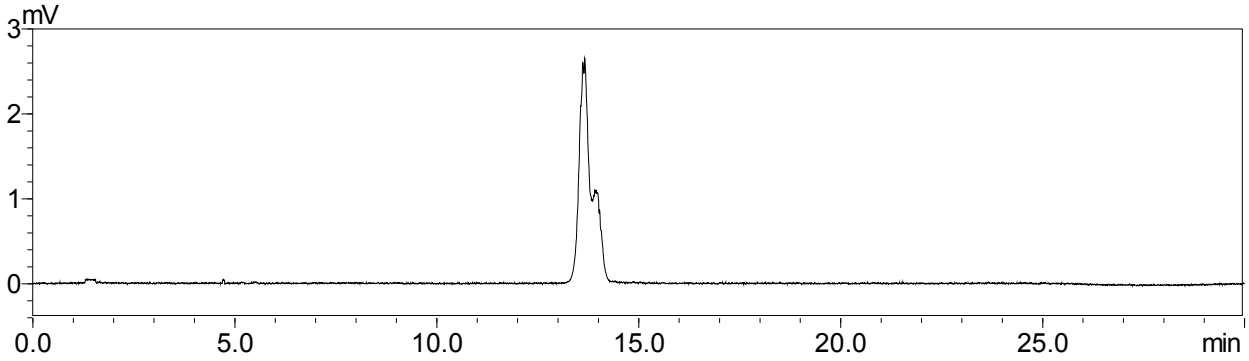
MALDI-MS, found $[M+Na]^+$ 1465.291



NMR data listed in Part VI

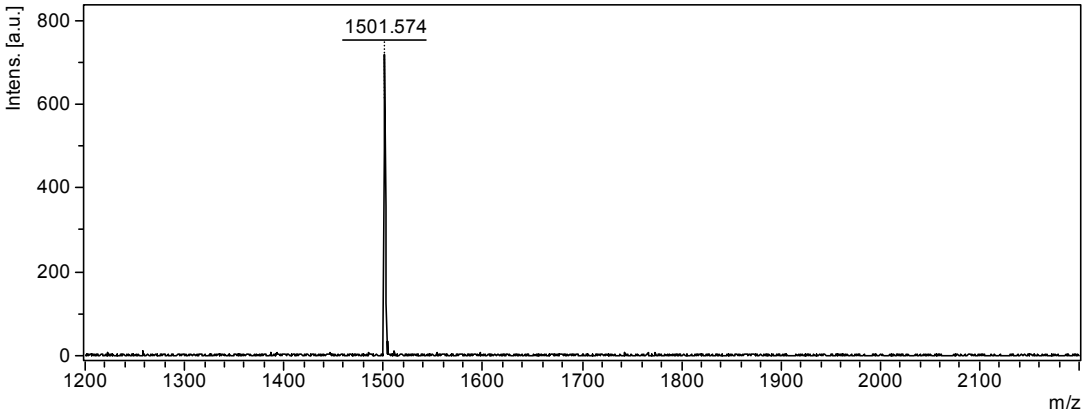
N111 

HILIC-ELSD, T_R = 13.65 min

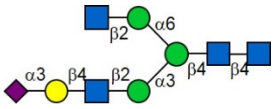


ESI-MS, calculated: 1478.5393; found $[M+2H]^{2+}$ 740.2793

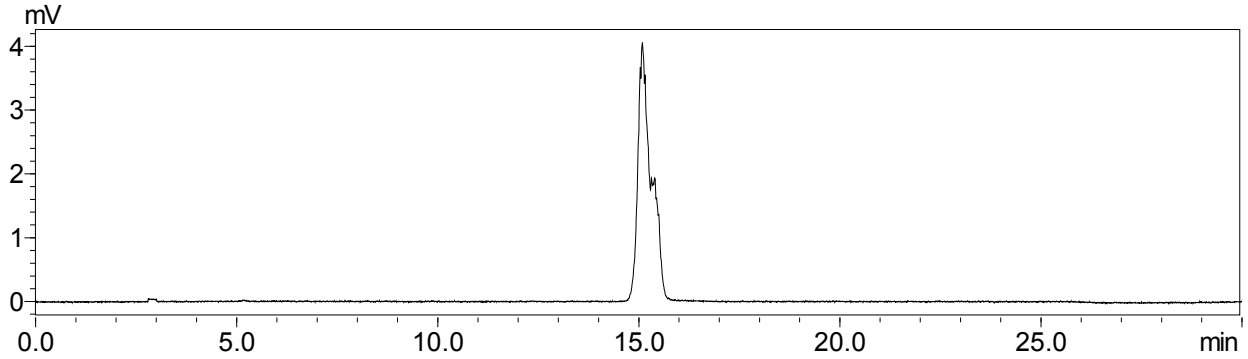
MALDI-MS, found $[M+Na]^{+}$ 1501.574



^{1}H NMR (D_2O, 500 MHz): δ 5.18 (d, J = 1.9 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.76 (s, 1 H, Manβ H-1), 4.69 (d, J = 8.0 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.60 (d, J = 7.6 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.59 (d, J = 7.5 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.57 (d, J = 7.7 Hz, 1 H, GlcNAc-3, H-1), 4.54 (d, J = 8.4 Hz, 1 H, GlcNAc-4 H-1), 4.46 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.24 (d, J = 1.4 Hz, 1 H), 4.18-4.19 (m, 1 H), 4.09-4.10 (m, 1 H), 3.40-3.97 (m, 45 H), 2.07 (s, 3 H, Ac), 2.04 (s, 6 H, 2 Ac), 2.03 (s, 3 H, Ac)

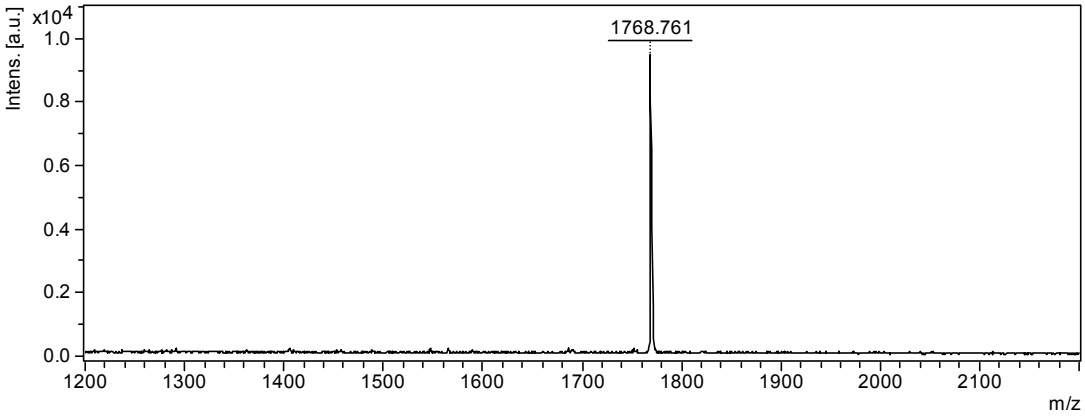
N112 

HILIC-ELSD, T_R = 15.09 min

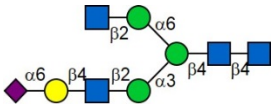


ESI-MS, calculated: 1769.6348; found $[M+2H]^{2+}$ 885.8288

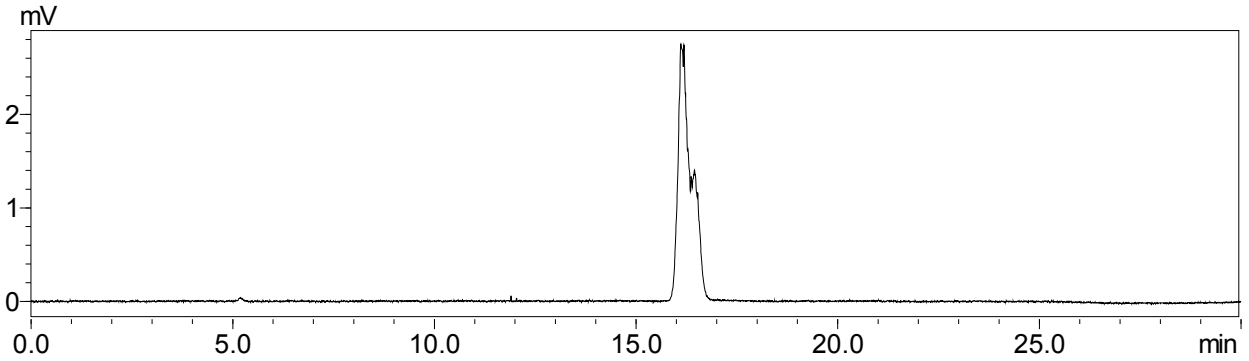
MALDI-MS, found $[M-H]^-$ 1768.761



^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.2 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.76 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.53-4.61 (m, 4 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1, Gal H-1), 4.24 (brs, 1 H), 4.18 (d, J = 1.9 Hz, 1 H), 4.09-4.12 (m, 2 H), 3.40-4.00 (m, 52 H), 2.75 (dd, J = 12.4, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.07 (s, 3 H, Ac), 2.04 (2 s, 6 H, 2 Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 1.79 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)

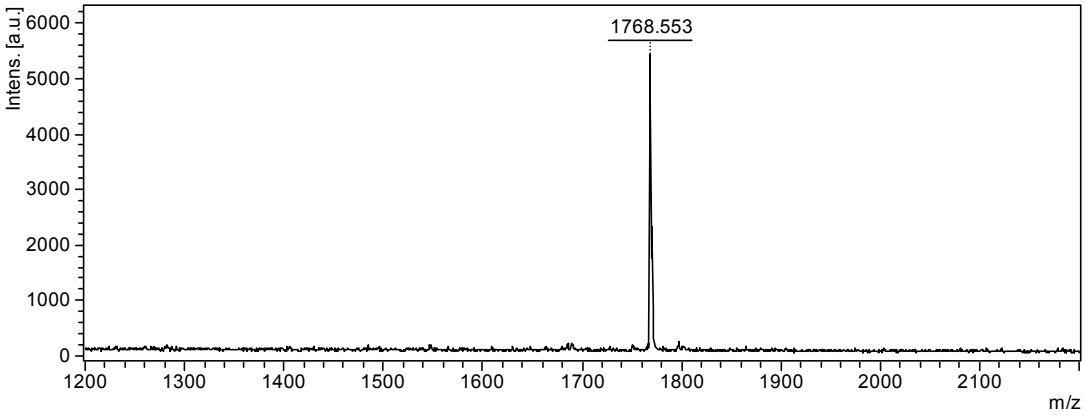
N113 

HILIC-ELSD, T_R = 16.16 min



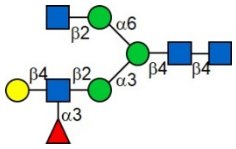
ESI-MS, calculated: 1769.6348; found $[M+2H]^{2+}$ 885.8287

MALDI-MS, found $[M-H]^-$ 1768.553

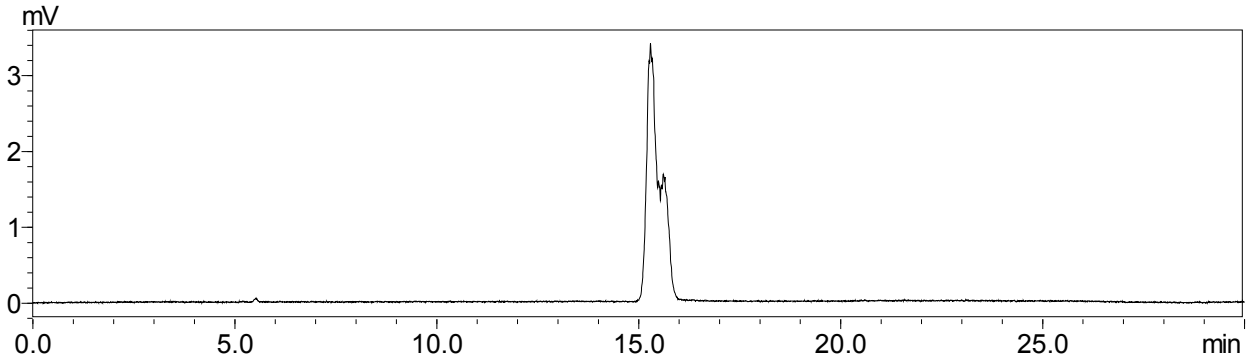


^{1}H NMR (D_2O, 500 MHz): δ 5.20 (d, J = 2.3 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.15 (s, 1 H, Man2 H-1), 4.94 (s, 1 H, Man3 H-1), 4.76-4.85 (overlapped with D_2O, 1 H, Manβ H-1), 4.71 (d, J = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.61-4.63 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.57 (d, J = 8.4 Hz, 1 H, GlcNAc-4 H-1), 4.46 (d, J = 7.9 Hz, 1 H, Gal H-1), 4.27 (brs, 1 H), 4.21-4.22 (m, 1 H), 4.11-4.13 (m, 1 H), 3.42-4.03 (m, 52 H), 2.68 (dd, J = 12.5, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.09 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 1.74 (t, J = 12.5 Hz, 1 H, Neu5Ac H-3a)

N114

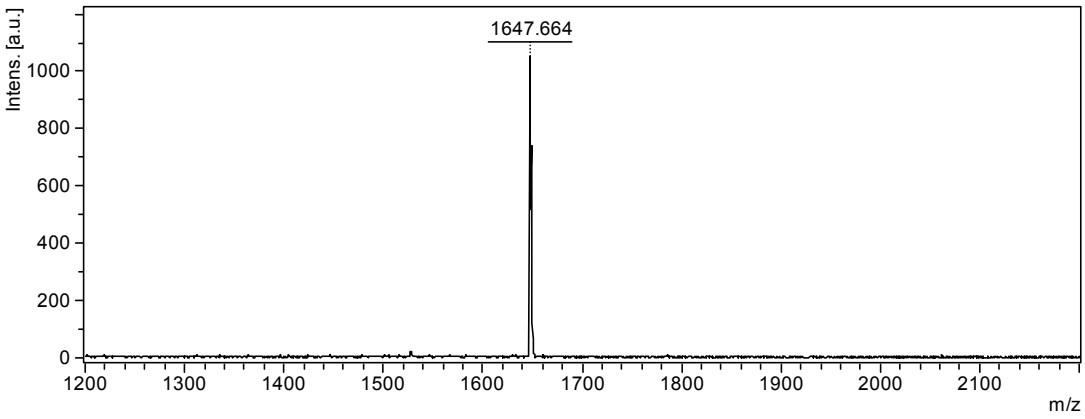


HILIC-ELSD, T_R = 15.30 min



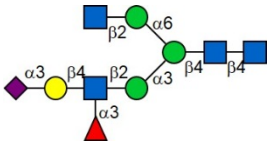
ESI-MS, calculated: 1624.5973; found $[M+2H]^{2+}$ 813.3104

MALDI-MS, found $[M+Na]^{+}$ 1647.664

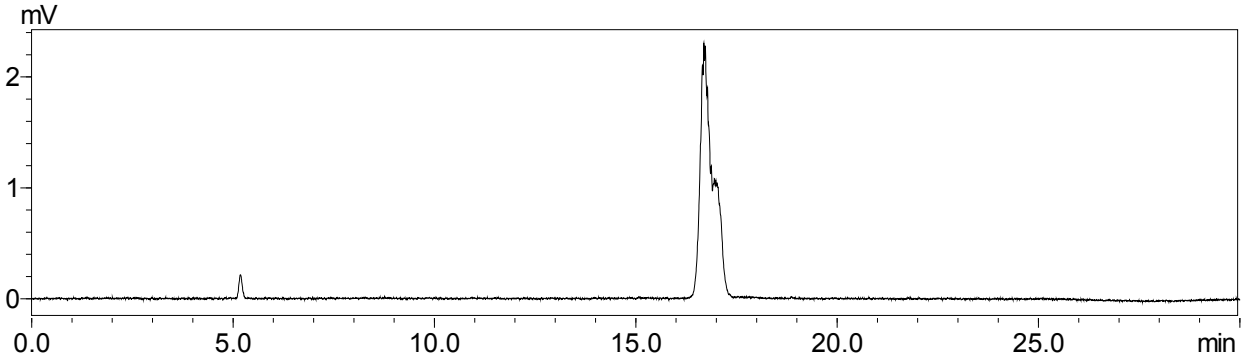


^{1}H NMR (D_2O, 500 MHz): δ 5.21 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.14 (d, J = 4.0 Hz, 1 H, Fuc H-1), 5.13 (s, 1 H, Man2 H-1), 4.94 (s, 1 H, Man3 H-1), 4.70-4.80 (overlapped with D_2O, 1 H, Manβ H-1), 4.56-4.62 (m, 3.4 H, GlcNAc-1 H-1 of β anomer, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.48 (d, J = 7.4 Hz, 1 H, Gal H-1), 4.27 (brs, 1 H), 4.20 (brs, 1 H), 4.13 (brs, 1 H), 3.45-4.01 (m, 49 H), 2.10 (s, 3 H, Ac), 2.06 (s, 9 H, 3 Ac), 1.19 (d, J = 6.0 Hz, 3 H, Fuc-CH_3)

N115

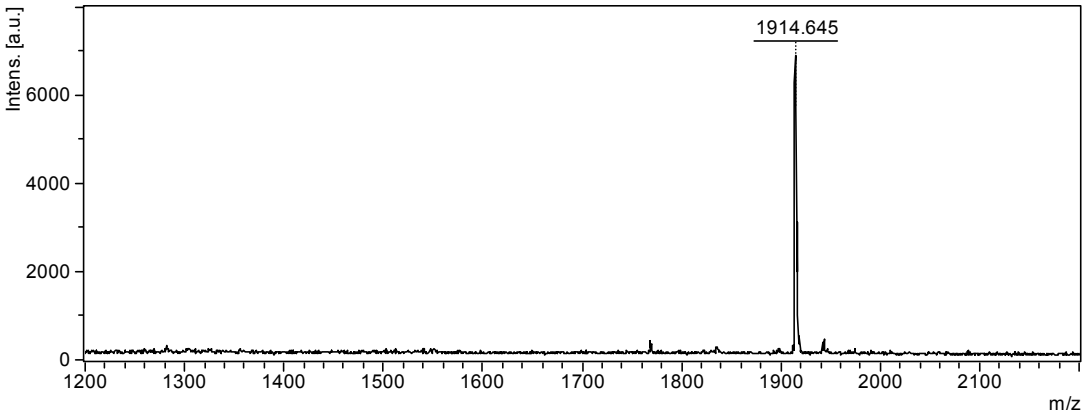


HILIC-ELSD, T_R = 16.71 min

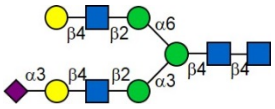


ESI-MS, calculated: 1915.6927; found $[M+2H]^{2+}$ 958.8585

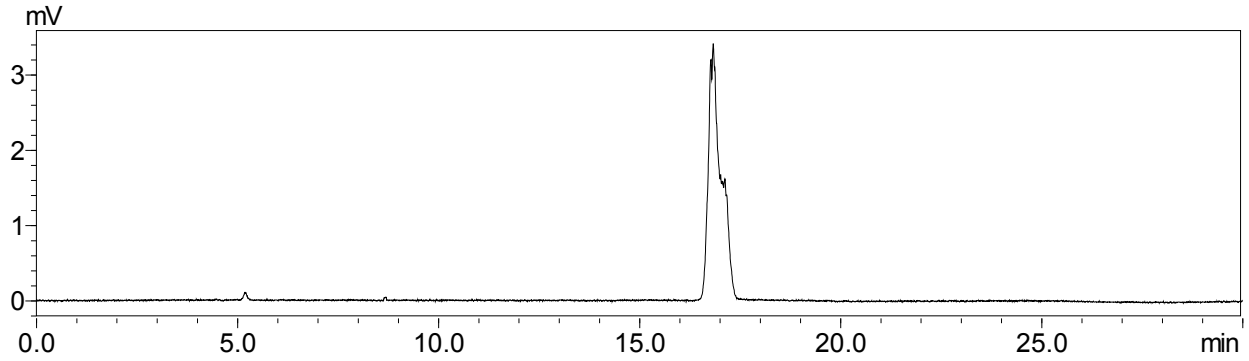
MALDI-MS, found $[M-H]^{+}$ 1914.645



^{1}H NMR (D_2O, 500 MHz): δ 5.13 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.06 (d, *J* = 4.1 Hz, 1 H, Fuc H-1), 5.05 (s, 1 H, Man2 H-1), 4.87 (s, 1 H, Man3 H-1), 4.72 (s, 1 H, Manβ H-1), 4.64 (d, *J* = 7.3 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.49-4.56 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.46 (d, *J* = 7.7 Hz, 1 H, Gal H-1), 4.20 (brs, 1 H), 4.13-4.14 (m, 1 H), 4.02-4.05 (m, 2 H), 3.35-3.96 (m, 55 H), 2.71 (dd, *J* = 12.0, 4.0 Hz, 1 H, Neu5Ac H-3e), 2.06 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.00 (s, 6 H, 2 Ac), 1.99 (s, 3 H, Ac), 1.74 (t, *J* = 12.0 Hz, 1 H, Neu5Ac H-3a), 1.11 (t, *J* = 6.3 Hz, 3 H, Fuc-CH_3)

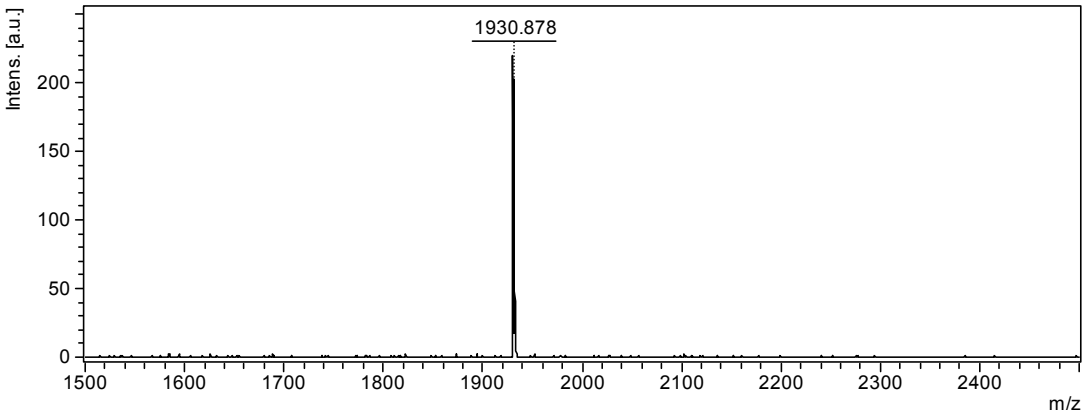
N122 

HILIC-ELSD, T_R = 16.83 min

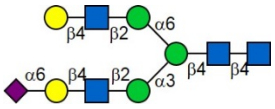


ESI-MS, calculated: 1931.6876; found $[M+2H]^{2+}$ 966.8554

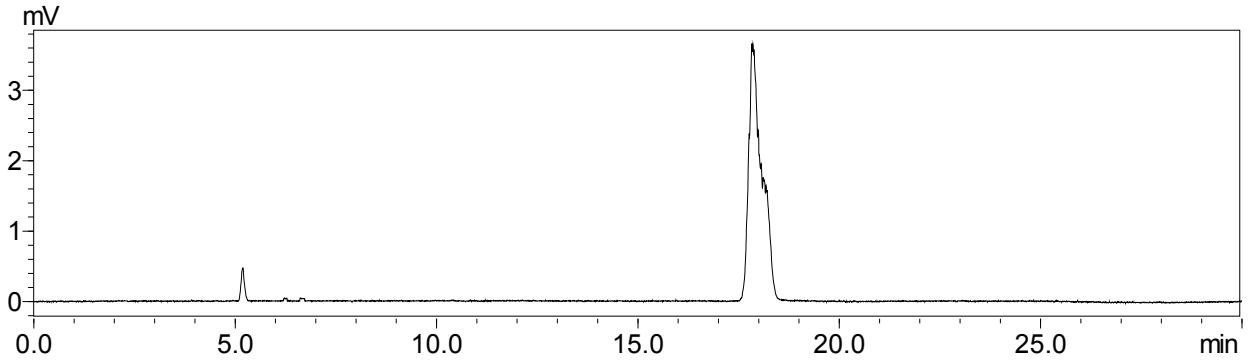
MALDI-MS, found [M-H]- 1930.878



^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 1.4 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.07 (s, 1 H, Man2 H-1), 4.88 (s, 1 H, Man3 H-1), 4.72 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.52-4.62 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.50 (d, J = 7.8 Hz, 1 H, Gal-1 H-1), 4.42 (d, J = 7.8 Hz, 1 H, Gal-2 H-1), 4.20 (brs, 1 H), 4.14 (d, J = 1.7 Hz, 1 H), 4.06-4.08 (m, 2 H), 3.41-3.95 (m, 57 H), 2.71 (dd, J = 12.3, 4.4 Hz, 1 H, Neu5Ac H-3e), 2.03 (s, 3 H, Ac), 2.00 (2 s, 3 H, 2 Ac), 1.99 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.75 (t, J = 12.3 Hz, 1 H, Neu5Ac H-3a)

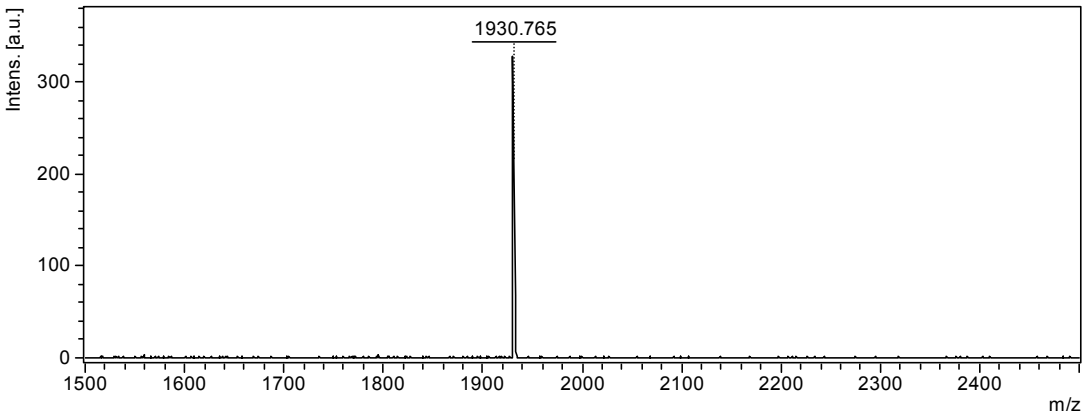
N123 

HILIC-ELSD, T_R = 17.85 min



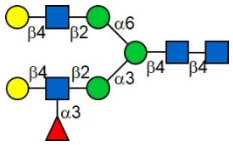
ESI-MS, calculated: 1931.6876; found $[M+2H]^{2+}$ 966.8562

MALDI-MS, found $[M-H]^-$ 1930.765

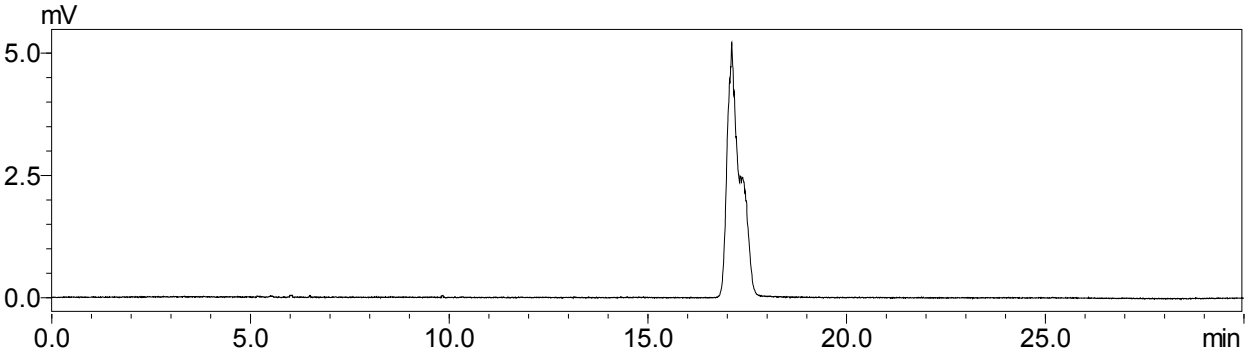


^{1}H NMR (D_2O, 500 MHz): δ 5.21 (d, J = 2.1 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.15 (s, 1 H, Man2 H-1), 4.95 (s, 1 H, Man3 H-1), 4.76-4.85 (overlapped with D_2O, 1 H, Manβ H-1), 4.72 (d, J = 7.5 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.59-4.64 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.49 (d, J = 7.9 Hz, 1 H, Gal-1 H-1), 4.46 (d, J = 7.9 Hz, 1 H, Gal-2 H-1), 4.28 (brs, 1 H), 4.21 (d, J = 1.9 Hz, 1 H), 4.13-4.14 (m, 1 H), 3.49-4.03 (m, 58 H), 2.68 (dd, J = 12.4, 4.6 Hz, 1 H, Neu5Ac H-3e), 2.10 (s, 3 H, Ac), 2.09 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 1.74 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)

N124

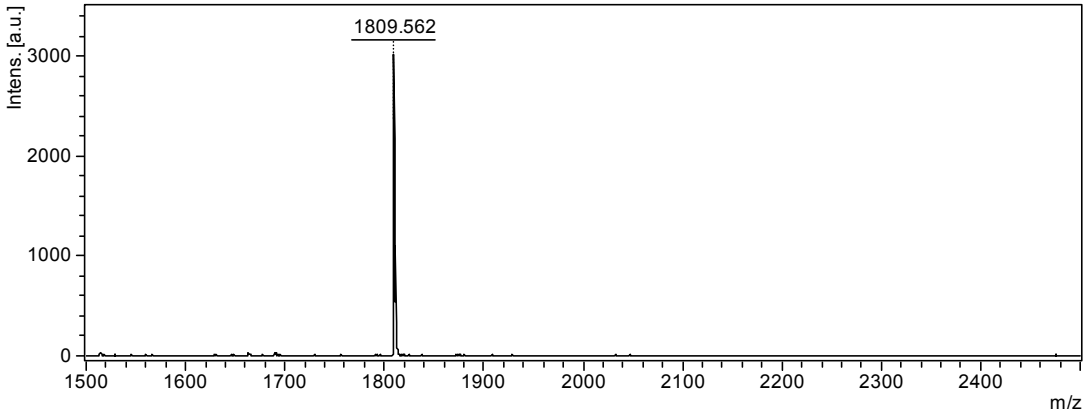


HILIC-ELSD, T_R = 17.11 min



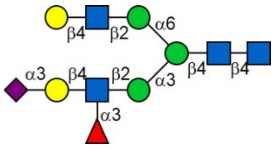
ESI-MS, calculated: 1786.6501; found $[M+2H]^{2+}$ 894.3378

MALDI-MS, found $[M+Na]^{+}$ 1809.562

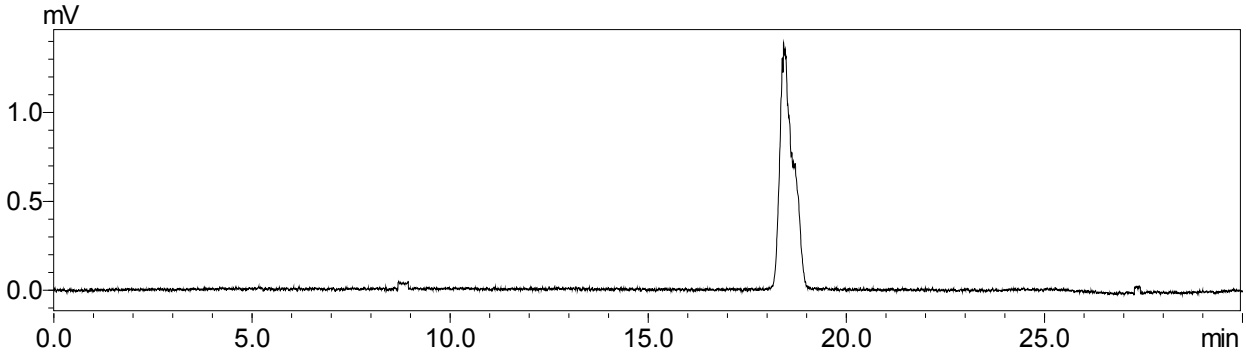


^{1}H NMR (D_2O, 500 MHz): δ 5.19 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.13 (d, *J* = 3.7 Hz, 1 H, Fuc H-1), 5.11 (s, 1 H, Man2 H-1), 4.93 (s, 1 H, Man3 H-1), 4.77 (s, 1 H, Manβ H-1), 4.70 (d, *J* = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.57-4.62 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.48 (d, *J* = 7.8 Hz, 1 H, Gal H-1), 4.45 (d, *J* = 7.9 Hz, 1 H, Gal-2 H-1), 4.24-4.25 (brs, 1 H), 4.19-4.20 (m, 1 H), 4.10-4.11 (m, 1 H), 3.47-4.03 (m, 55 H), 2.08 (s, 3 H, Ac), 2.05 (s, 9 H, 3 Ac), 1.17 (d, *J* = 6.4 Hz, 3 H, Fuc-CH_3)

N125

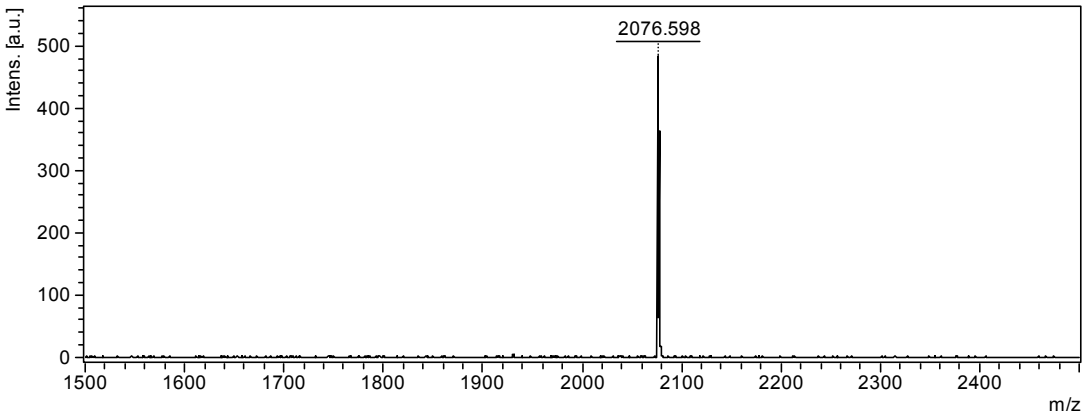


HILIC-ELSD, T_R = 18.43 min

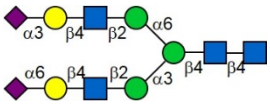


ESI-MS, calculated: 2077.7455; found $[M+2H]^{2+}$ 1039.8862

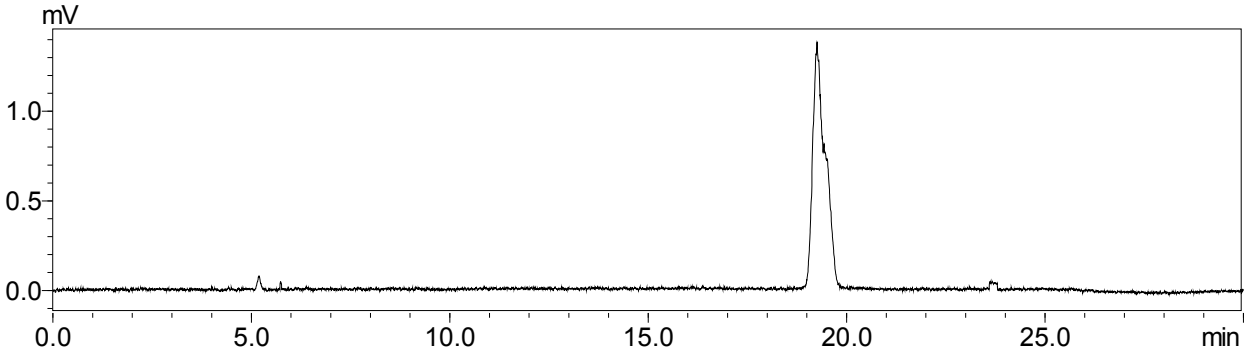
MALDI-MS, found $[M-H]^-$ 2076.598



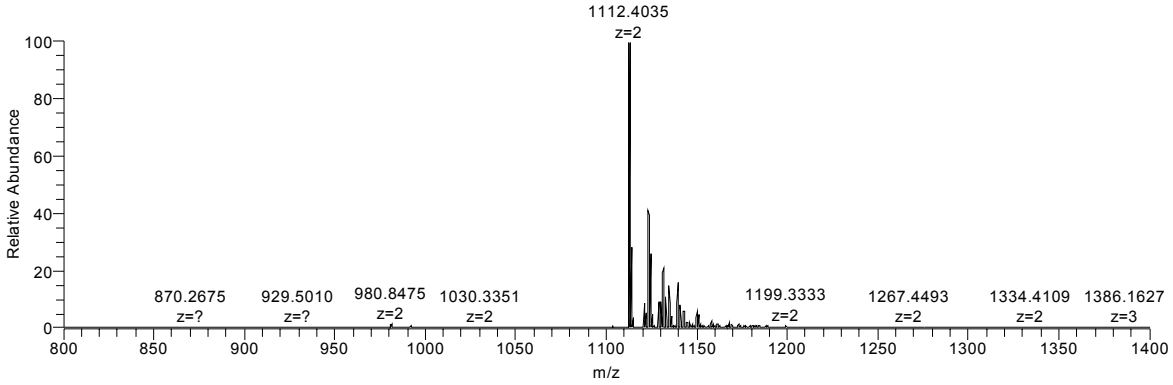
^{1}H NMR (D_2O, 500 MHz): δ 5.18 (d, J = 0.9 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.11 (d, J = 4.1 Hz, 1 H, Fuc H-1), 5.10 (s, 1 H, Man2 H-1), 4.93 (s, 1 H, Man3 H-1), 4.76 (s, 1 H, Manβ H-1), 4.69 (d, J = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.57-4.62 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.50 (d, J = 7.8 Hz, 1 H, Gal-1 H-1), 4.47 (d, J = 7.8 Hz, 1 H, Gal-2 H-1), 4.25 (brs, 1 H), 4.18 (d, J = 1.7 Hz, 1 H), 4.07-4.11 (m, 2 H), 3.46-4.01 (m, 61 H), 2.76 (dd, J = 12.5, 4.6 Hz, 1 H, Neu5Ac H-3e), 2.08 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (2 s, 6 H, 2 Ac), 2.02 (s, 3 H, Ac), 1.79 (t, J = 12.5 Hz, 1 H, Neu5Ac H-3a), 1.16 (d, J = 6.5 Hz, 3 H, Fuc-CH_3)

N133 

HILIC-ELSD, T_R = 19.25 min

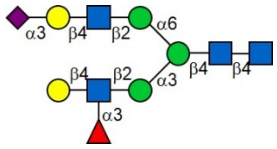


ESI-MS, calculated: 2222.7830; found $[M+2H]^{2+}$ 1112.4035

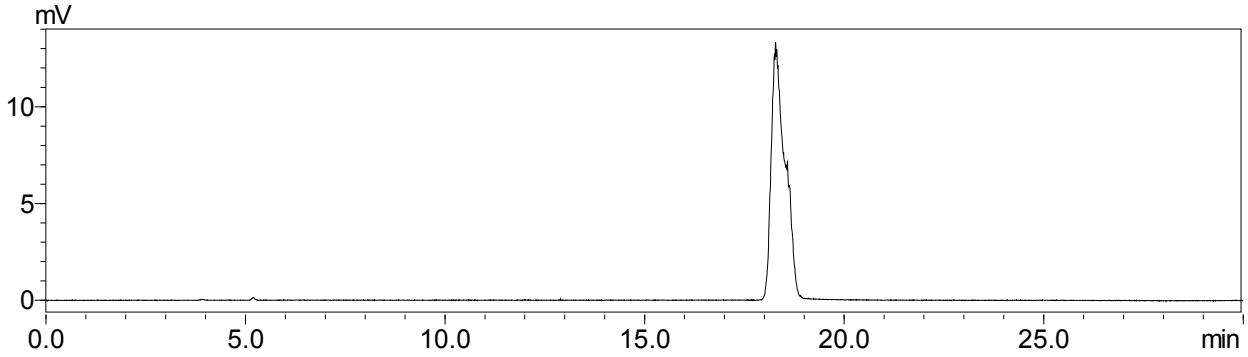


^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.6 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.10 (s, 1 H, Man2 H-1), 4.93 (s, 1 H, Man3 H-1), 4.76 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.9 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.53-4.58 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.53 (d, J = 7.9 Hz, 1 H, Gal-1 H-1), 4.43 (d, J = 7.9 Hz, 1 H, Gal-2 H-1), 4.24 (brs, 1 H), 4.15 (m, 1 H), 4.09-4.11 (m, 2 H), 3.47-4.00 (m, 64 H), 2.74 (dd, J = 12.7, 4.8 Hz, 1 H, Neu5NAc-1 H-3e), 2.64 (dd, J = 12.5, 4.6 Hz, 1 H, Neu5NAc-2 H-3e), 2.05 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.76 (t, J = 12.7 Hz, 1 H, Neu5NAc-1 H-3a), 1.69 (dd, J = 12.5 Hz, Neu5NAc-2 H-3a).

N134

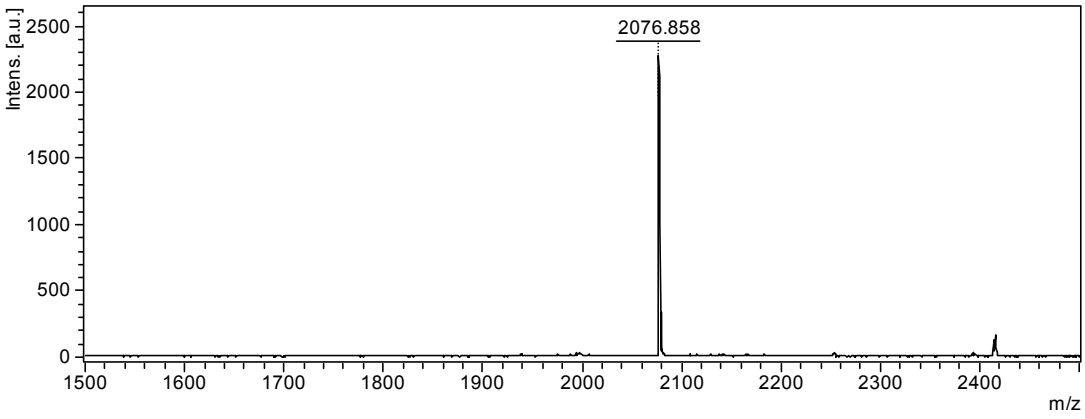


HILIC-ELSD, T_R = 18.27 min

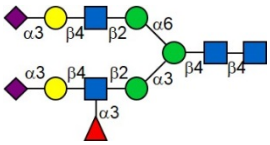


ESI-MS, calculated: 2077.7455; found $[M+2H]^{2+}$ 1039.8886

MALDI-MS, found $[M-H]^-$ 2076.858

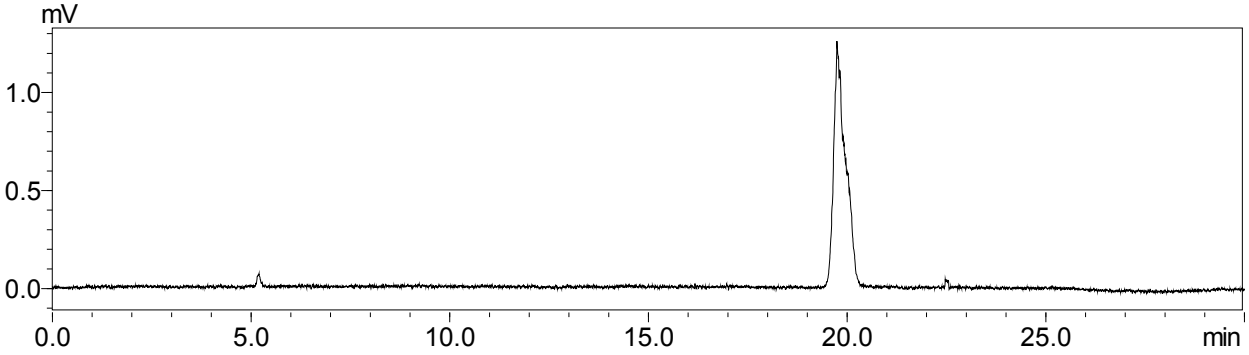


^{1}H NMR (D_2O, 500 MHz): δ 5.22 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.16 (d, J = 3.3 Hz, 1 H, Fuc H-1), 5.13 (s, 1 H, Man2 H-1), 4.96 (s, 1 H, Man3 H-1), 4.70-4.90 (overlapped with D_2O, 1 H, Manβ H-1), 4.58-4.62 (m, 4.4 H, GlcNAc-1 H-1 of β anomer, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1, Gal-1 H-1), 4.48 (d, J = 7.7 Hz, 1 H, Gal-2 H-1), 4.28 (brs, 1 H), 4.22 (brs, 1 H), 4.13-4.15 (m, 2 H), 3.47-4.03 (m, 61 H), 2.79 (dd, J = 12.0, 3.4 Hz, 1 H, Neu5Ac H-3e), 2.11 (s, 3 H, Ac), 2.07 (s, 12 H, 4 Ac), 1.83 (t, J = 12.0 Hz, 1 H, Neu5Ac H-3a), 1.20 (d, J = 6.0 Hz, 3 H, Fuc-CH_3)

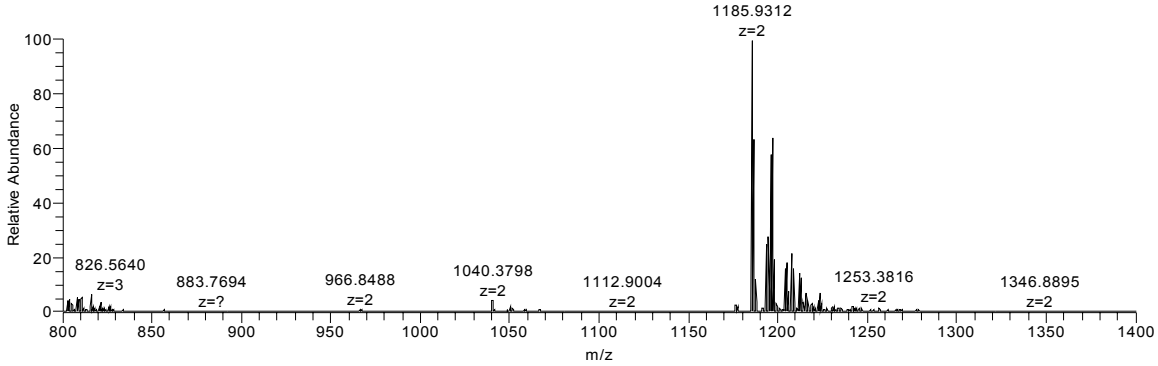


N135

HILIC-ELSD, T_R = 19.75 min

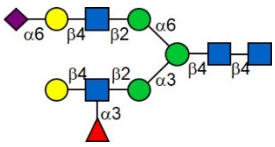


ESI-MS, calculated: 2368.8409; found $[M+2H]^{2+}$ 1185.9312

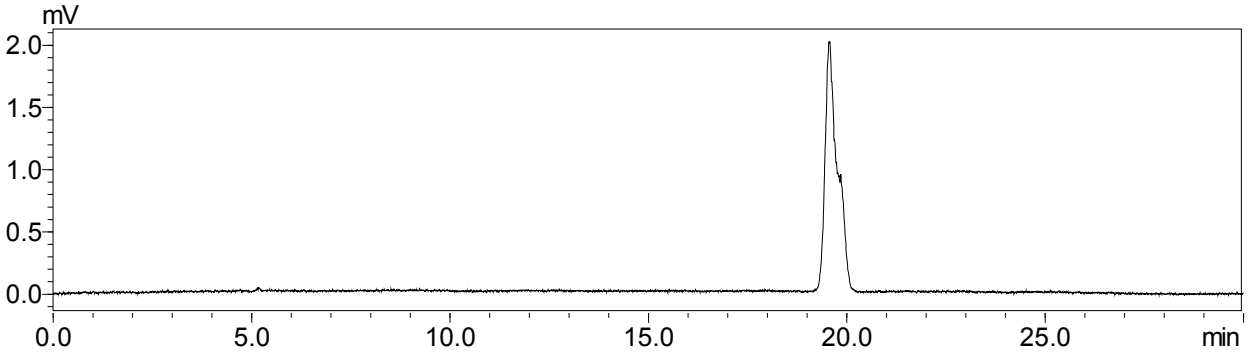


^{1}H NMR (D_2O, 500 MHz): δ 5.15 (d, *J* = 2.1 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, *J* = 4.0 Hz, 1 H, Fuc H-1), 5.07 (s, 1 H, Man2 H-1), 4.89 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.66 (d, *J* = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.51-4.58 (m, 4 H, GlcNAc-2 H-1, GlcNAc-4 H-1, Gal-1 H-1), 4.48 (d, *J* = 7.8 Hz, 1 H, Gal-2 H-1), 4.22 (brs, 1 H), 4.15-4.16 (m, 1 H), 4.04-4.10 (m, 3 H), 3.43-3.98 (m, 67 H), 2.71-2.74 (m, *2* H, Neu5Ac H-3e), 2.05 (s, 3 H, Ac), 2.01 (s, 6 H, 2 Ac), 2.00 (s, 9 H, 3 Ac), 1.77 (t, *J* = 12.0 Hz, 1 H, Neu5Ac H-3a), 1.76 (t, *J* = 12.0 Hz, Neu5Ac-2 H-3a), 1.13 (t, *J* = 6.5 Hz, 3 H, Fuc-CH_3)

N144

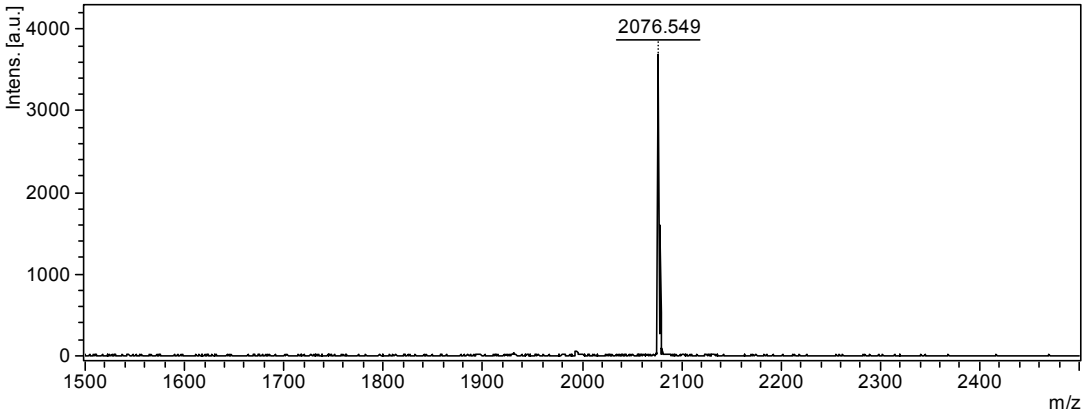


HILIC-ELSD, T_R = 19.56 min



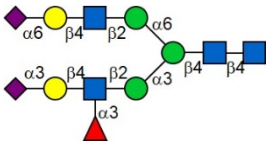
ESI-MS, calculated: 2077.7455; found $[M+2H]^{2+}$ 1039.8842

MALDI-MS, found $[M-H]^-$ 2076.549

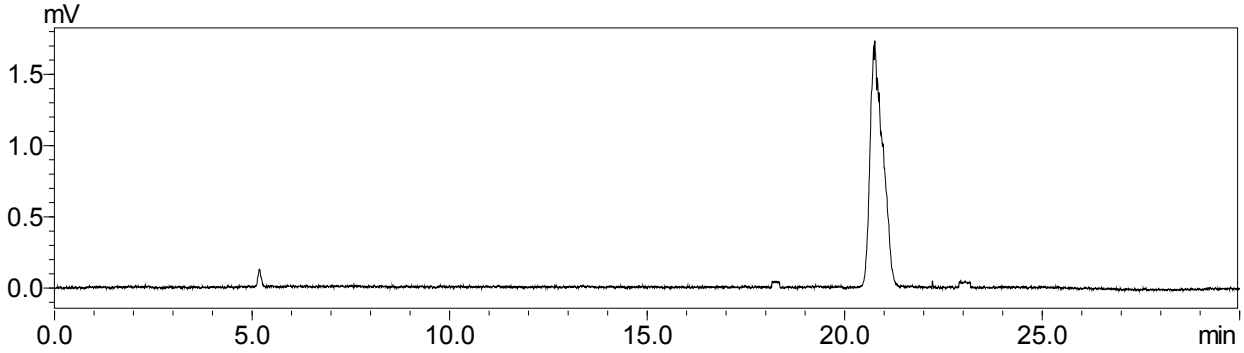


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.5 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, J = 3.9 Hz, 1 H, Fuc H-1), 5.06 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.8 Hz, 0.5 H, GlcNAc-1 H1 of β anomer), 4.53-4.57 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.41 (d, J = 7.9 Hz, 1 H, Gal-1 H-1), 4.40 (d, J = 7.7 Hz, 1 H, Gal-2 H-1), 4.21 (s, 1 H), 4.14 (d, J = 2.2 Hz, 1 H), 4.07 (d, J = 2.9 Hz, 1 H), 3.41-3.97 (m, 62 H), 2.63 (dd, J = 12.4, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.68 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a), 1.13 (s, 3 H, Fuc-CH_3);

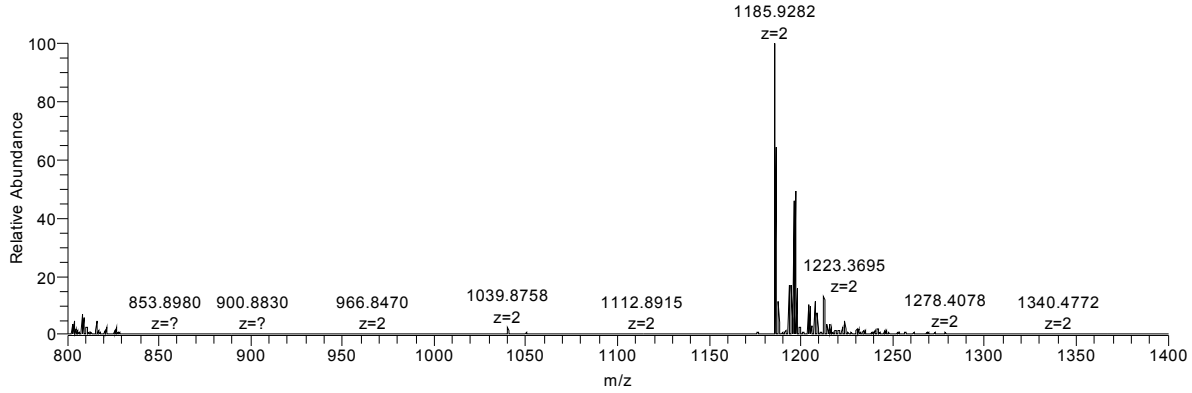
N145



HILIC-ELSD, T_R = 20.77 min

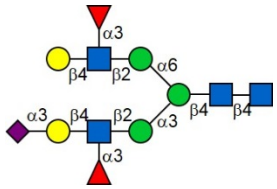


ESI-MS, calculated: 2368.8409; found $[M+2H]^{2+}$ 1185.9282



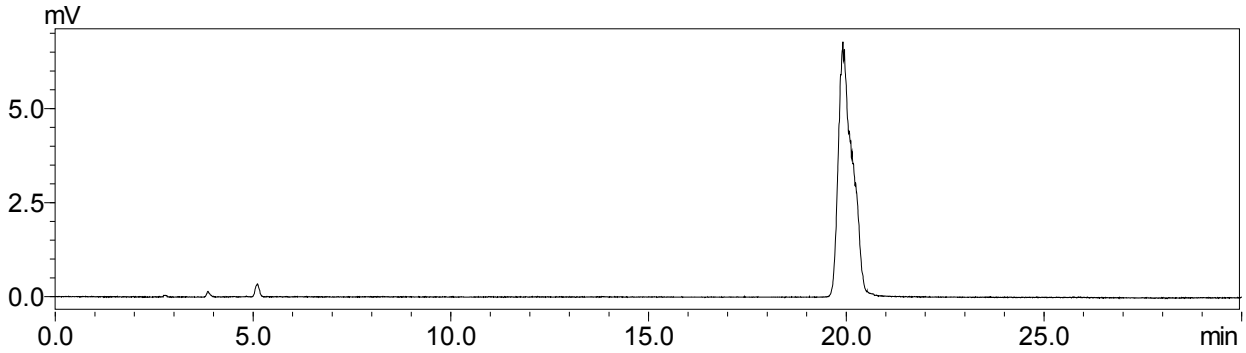
ESI-MS, found $[M+2H]^{2+}$

^{1}H NMR (D_2O, 500 MHz): δ 5.15 (d, J = 2.2 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, J = 3.8 Hz, 1 H, Fuc H-1), 5.07 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.74 (s, 1 H, Manβ H-1), 4.66 (d, J = 7.6 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.53-4.58 (m, 3 H, GlcNAc-2 H-1, GlcNAc-2 H-1, GlcNAc-4 H-1), 4.48 (d, J = 7.7 Hz, 1 H, Gal-1 H-1), 4.41 (d, J = 7.8 Hz, 1 H, Gal-2 H-1), 4.22 (brs, 1 H), 4.15 (d, J = 2.1 Hz, 1 H), 4.08 (d, J = 1.3 Hz, 1 H), 4.05 (dd, J = 9.7, 2.7 Hz, 1 H), 3.43-3.98 (m, 68 H), 2.73 (dd, J = 12.2, 4.3 Hz, 1 H, Neu5Ac-1 H-3e), 2.64 (dd, J = 12.4, 4.6 Hz, 1 H, Neu5Ac-2 H-1), 2.05 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H), 1.76 (t, J = 12.2 Hz, 1 H, Neu5Ac-1 H-3a), 1.69 (t, J = 12.4 Hz, Neu5Ac-2 H-3a), 1.13 (t, J = 6.5 Hz, 3 H, Fuc-CH_3)



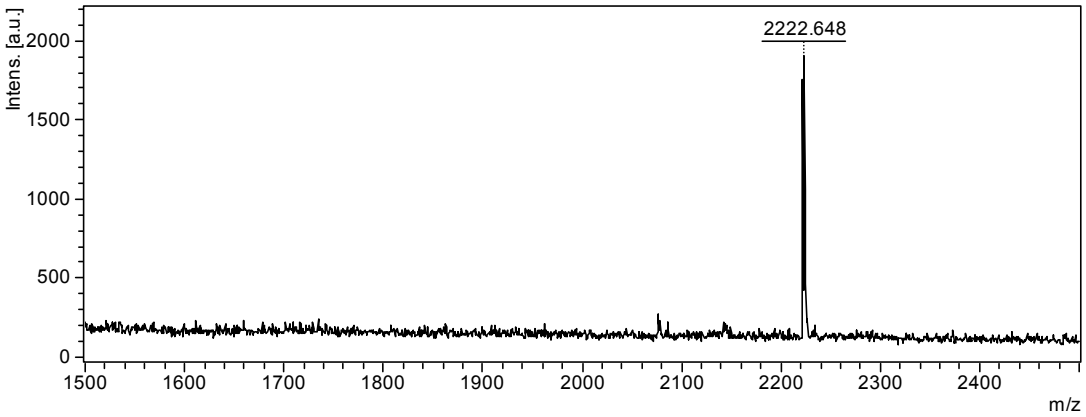
N155

HILIC-ELSD, T_R = 19.92 min



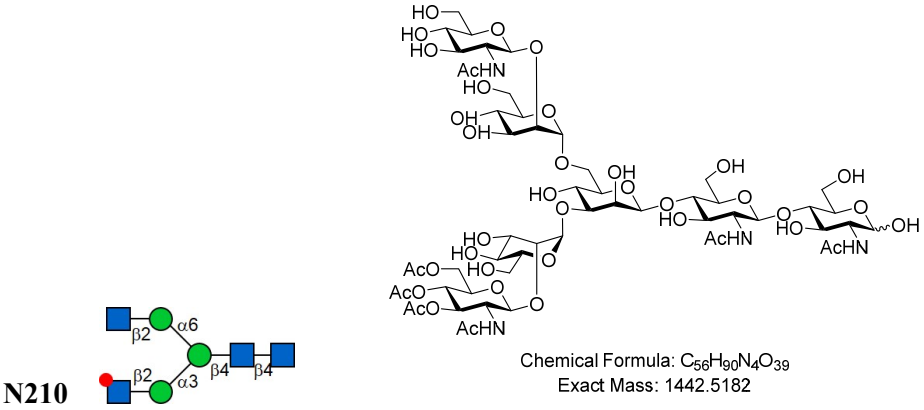
ESI-MS, calculated: 2223.8034; found $[M+2H]^{2+}$ 1112.9150

MALDI-MS, found $[M-H]^-$ 2222.648

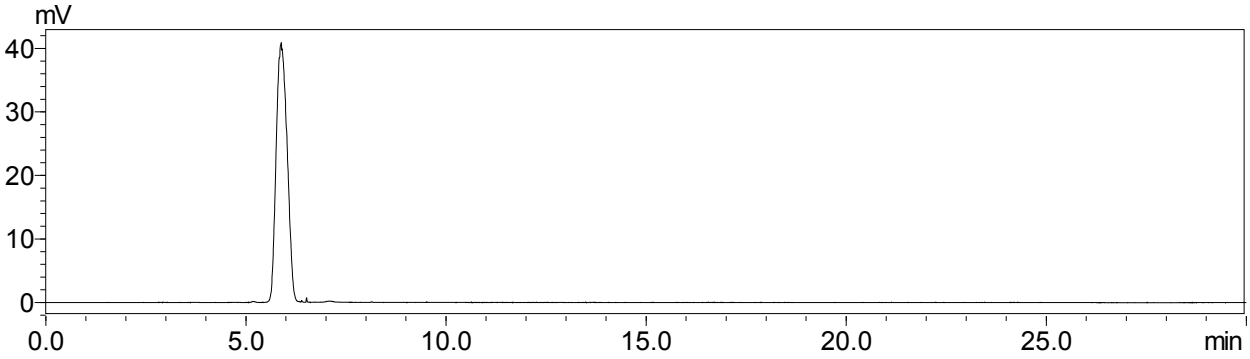


^{1}H NMR (D_2O, 500 MHz): δ 5.18 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.10-5.12 (m, 3 H, Fuc-1 H-1. Fuc-2 H-1, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.76 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.6 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.55-4.62 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.50 (d, J = 6.8 Hz, 1 H, Gal H-1), 4.44 (d, J = 8.0 Hz, 1 H, Gal-2 H-1), 4.24 (brs, 1 H), 4.18 (brs, 1 H), 4.06-4.10 (m, 3 H), 3.45-4.03 (m, 64 H), 2.75 (dd, J = 12.4, 4.0 Hz, 1 H, Neu5Ac H-3e), 2.07 (s, 3 H, Ac), 2.03 (s, 12 H, 4 Ac), 1.79 (t, J = 12.4 Hz, 1 H, Neu5Ac-H3a), 1.13-2.21 (m, 6 H, Fuc-1 CH_3, Fuc-2 CH_3)

N210

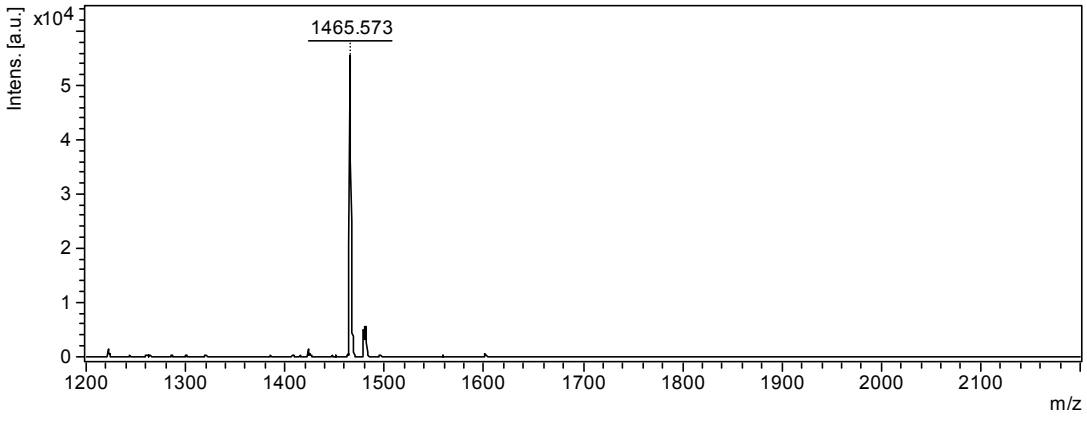


HILIC-ELSD, T_R = 5.88 min



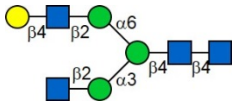
ESI-MS, calculated: 1442.5182; found $[M+2H]^{2+}$ 722.2684

MALDI-MS, found $[M+Na]^+$ 1465.573, $[M+K]^+$ 1481.534

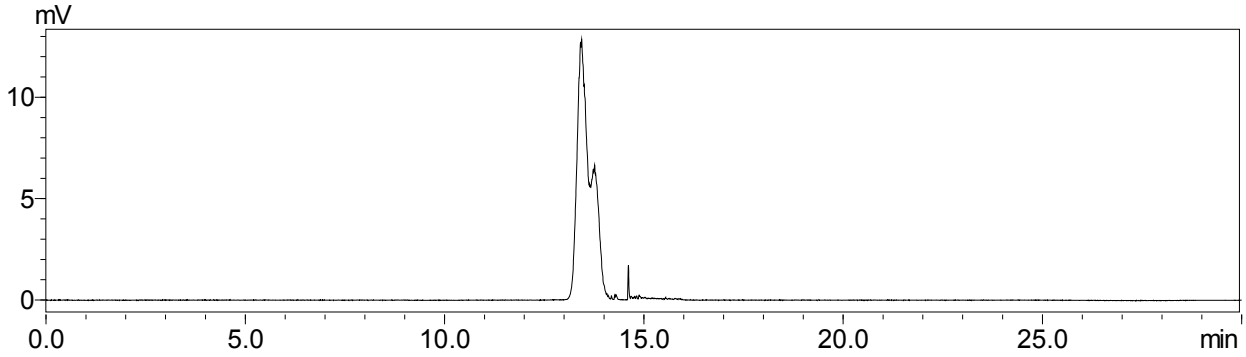


NMR data listed in Part VI

N211

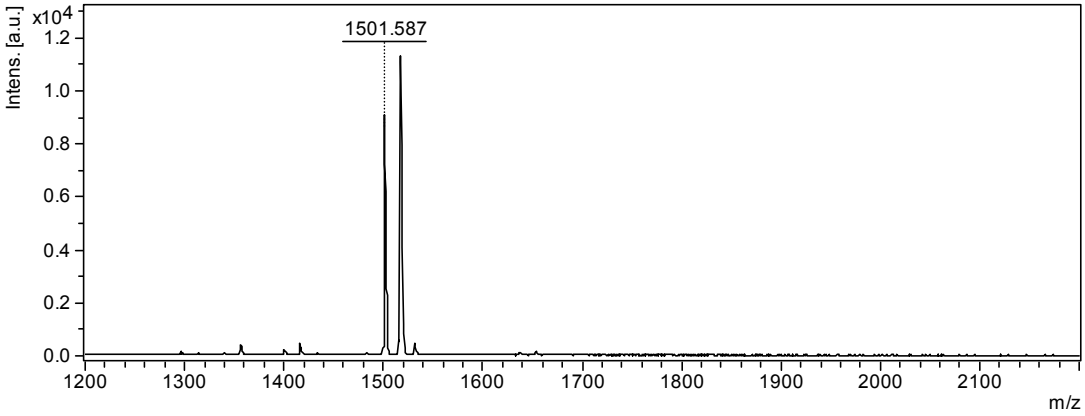


HILIC-ELSD, T_R = 13.43 min



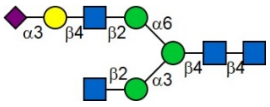
ESI-MS, calculated: 1478.5393; found $[M+2H]^{2+}$ 740.2793

MALDI-MS, found $[M+Na]^{+}$ 1501.587, $[M+K]^{+}$ 1517.677

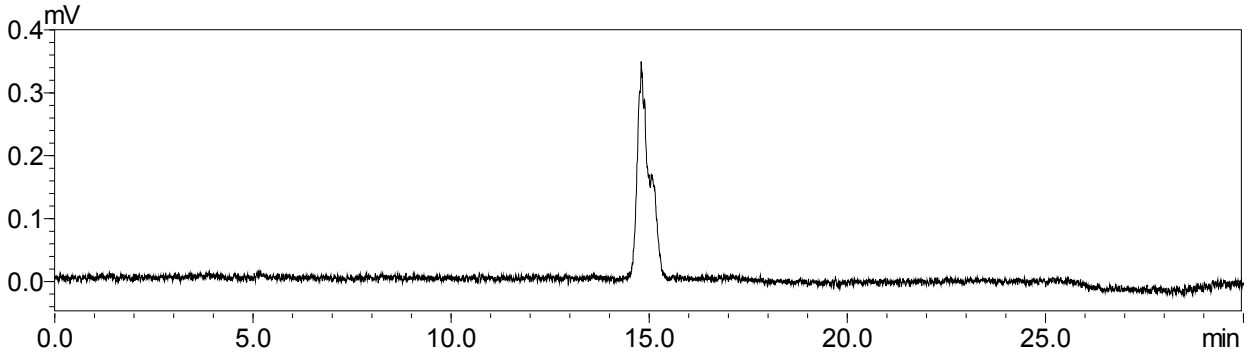


^{1}H NMR (D_2O, 500 MHz): δ 5.17 (d, J = 2.0 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.10 (s, 1 H, Man2 H-1), 4.92 (s, 1 H, Man3 H-1), 4.75 (s, 1 H, Manβ H-1), 4.68 (d, J = 7.8 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.60 (d, J = 7.8 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.59 (d, J = 7.8 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.57 (d, J = 8.3 Hz, 1 H, GlcNAc-3 H-1), 4.54 (d, J = 8.4 Hz, 1 H, GlcNAc-4 H-1), 4.46 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.24 (d, J = 2.2 Hz, 1 H), 4.17 (d, J = 1.9 Hz, 1 H), 4.10 (d, J = 2.1 Hz, 1 H), 3.40-3.98 (m, 45 H), 2.07 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac)

N212

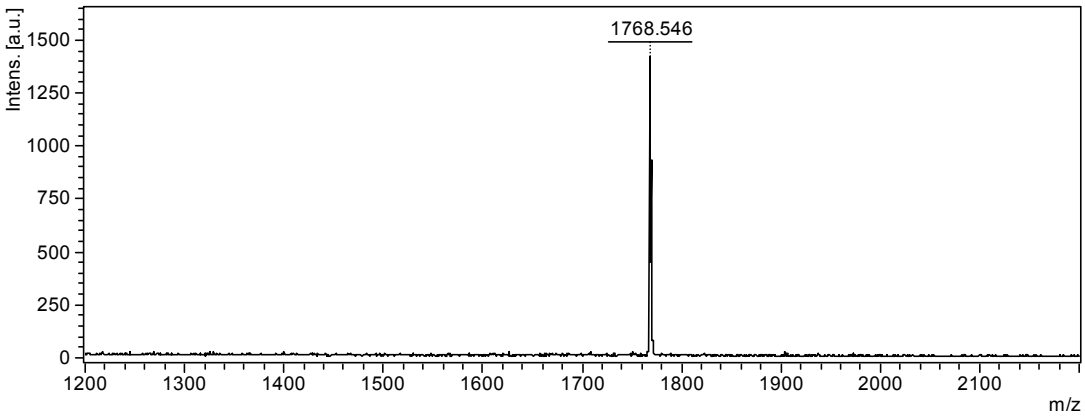


HILIC-ELSD, T_R = 14.81 min



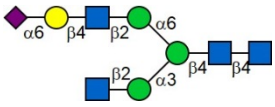
ESI-MS, calculated: 1769.6348; found $[M+2H]^{2+}$ 885.8268

MALDI-MS, found $[M-H]^-$ 1768.546

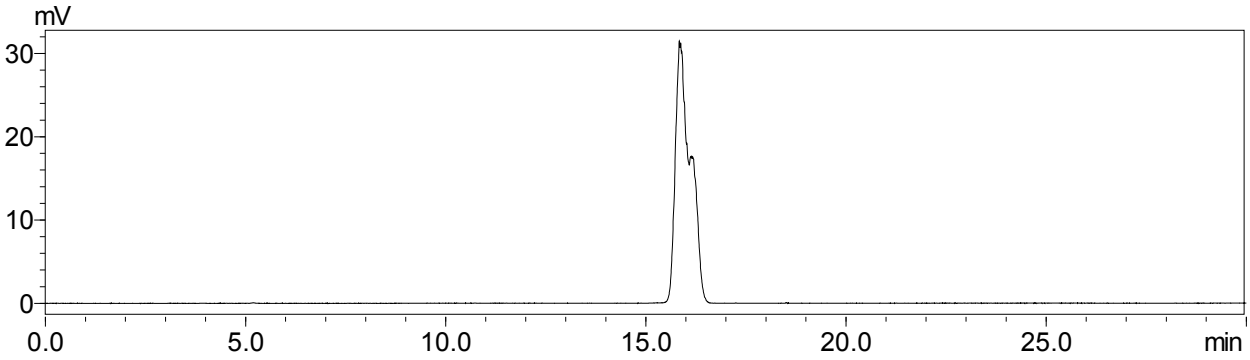


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.3 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.07 (s, 1 H, Man2 H-1), 4.88 (s, 1 H, Man3 H-1), 4.72 (s, 1 H, Manβ H-1), 4.65 (d, J = 8.0 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.50-4.57 (m, 4 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1, Gal H-1), 4.20 (d, J = 2.1 Hz, 1 H), 4.14 (d, J = 2.3 Hz, 1 H), 4.07-4.09 (m, 2 H), 3.40-3.96 (m, 51 H), 2.71 (dd, J = 12.4, 4.5 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.00 (2 s, 6 H, 2 Ac), 1.99 (s, 3 H, 2 Ac), 1.76 (d, J = 12.4 Hz, 1 H, Neu5Ac H-3a)

N213

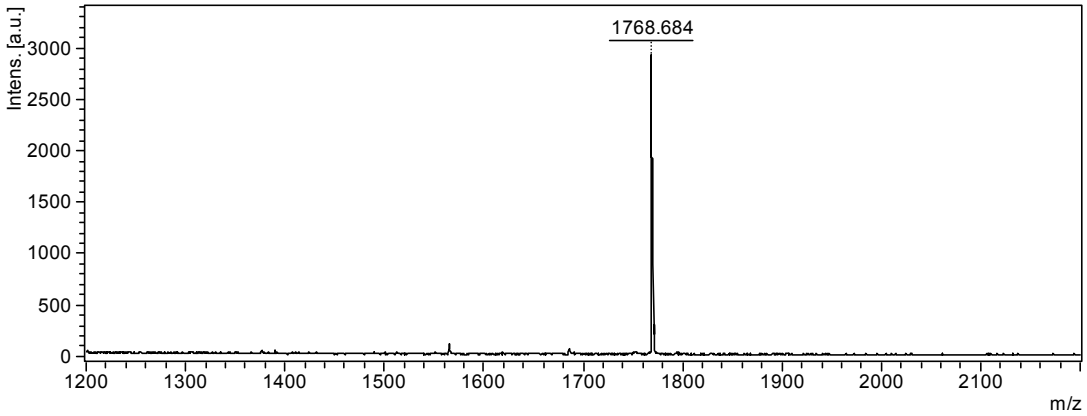


HILIC-ELSD, T_R = 15.84 min



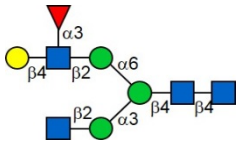
ESI-MS, calculated: 1769.6348; found $[M+2H]^{2+}$ 885.8272

MALDI-MS, found $[M-H]^-$ 1768.684

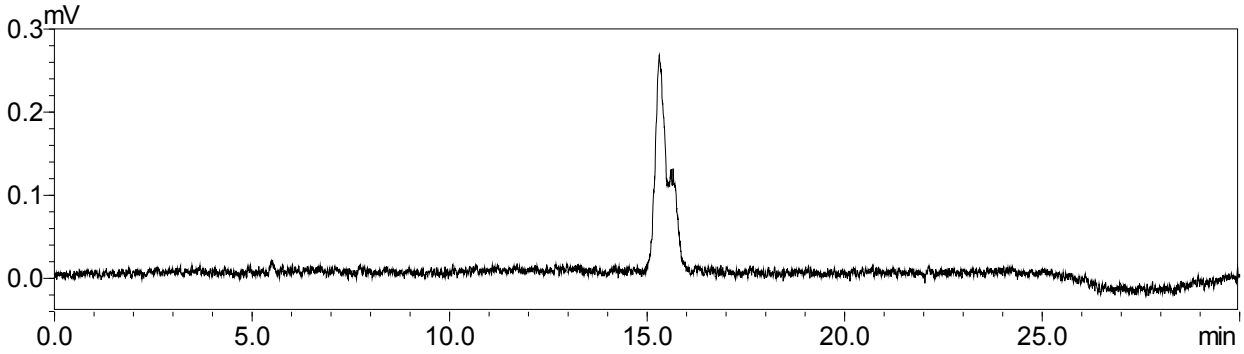


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.07 (s, 1 H, Man2 H-1), 4.90 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, *J* = 7.3 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.54-4.56 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.50 (d, *J* = 8.4 Hz, 1 H, GlcNAc-4 H-1), 4.40 (d, *J* = 8.0 Hz, 1 H, Gal H-1), 4.21 (s, 1 H), 4.14 (brs, 1 H), 4.07 (brs, 1 H), 3.38-3.96 (m, 52 H), 2.62 (dd, *J* = 12.4, 4.5 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.68 (d, *J* = 12.4 Hz, Neu5Ac H-3a)

N214

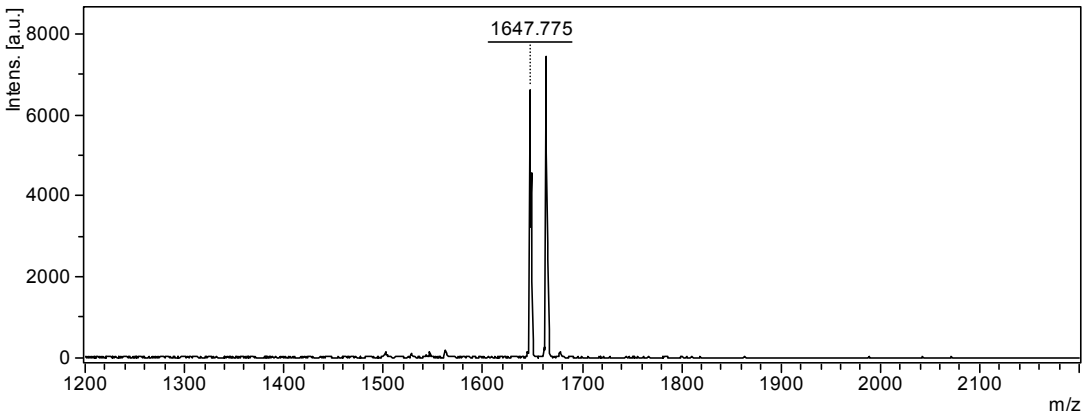


HILIC-ELSD, T_R = 15.31 min



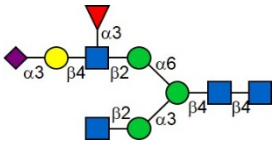
ESI-MS, calculated: 1624.5973; found $[M+2H]^{2+}$ 813.3076

MALDI-MS, found $[M+Na]^+$ 1647.775, $[M+K]^+$ 1663.773

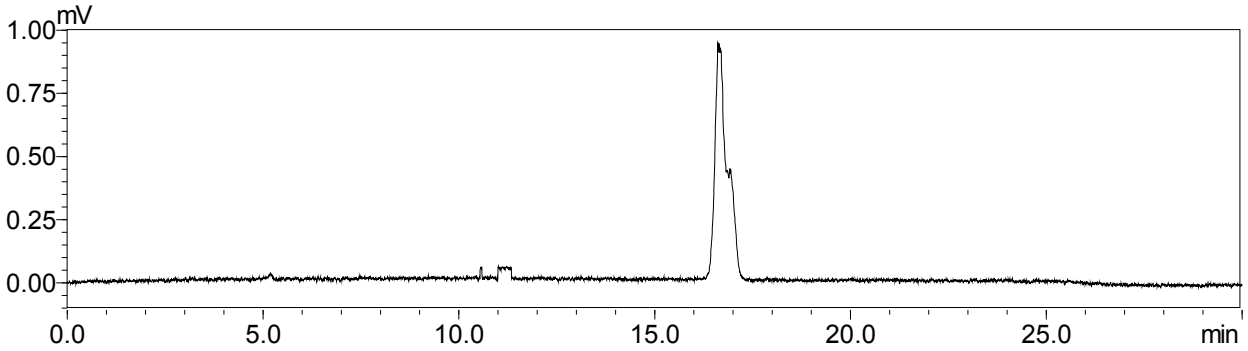


^{1}H NMR (D_2O, 500 MHz): δ 5.13 (d, J = 2.2 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.07 (d, J = 3.9 Hz, 1 H, Fuc H-1), 5.06 (s, 1 H, Man2 H-1), 4.86 (s, 1 H, Man3 H-1), 4.72 (s, 1 H, Manβ H-1), 4.64 (d, J = 7.8 Hz, 0.4 H, GlcNAc-1H1 of β anomer), 4.52-4.56 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.49 (d, J = 8.5 Hz, 1 H, GlcNAc-4 H-1), 4.39 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.20 (s, 1 H), 4.13 (d, J = 1.8 Hz, 1 H), 4.04 (d, J = 1.6 Hz, 1 H), 3.37-3.95 (m, 49 H), 2.03 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.98 (s, 6 H, 2 Ac), 1.12 (d, J = 6.6 Hz, Fuc-CH_3)

N215

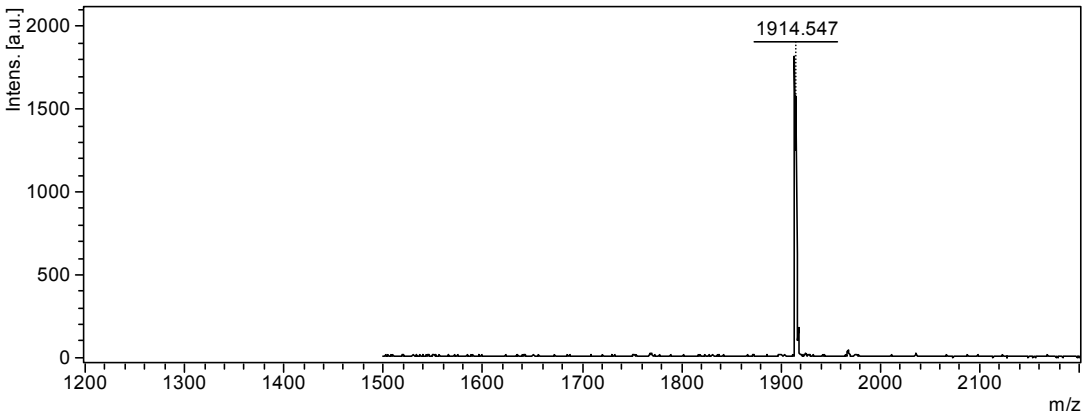


HILIC-ELSD, T_R = 16.65 min



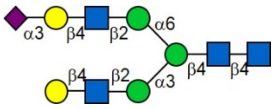
ESI-MS, calculated: 1915.6927; found $[M+2H]^{2+}$ 958.8521

MALDI-MS, found $[M-H]^{+}$ 1914.547

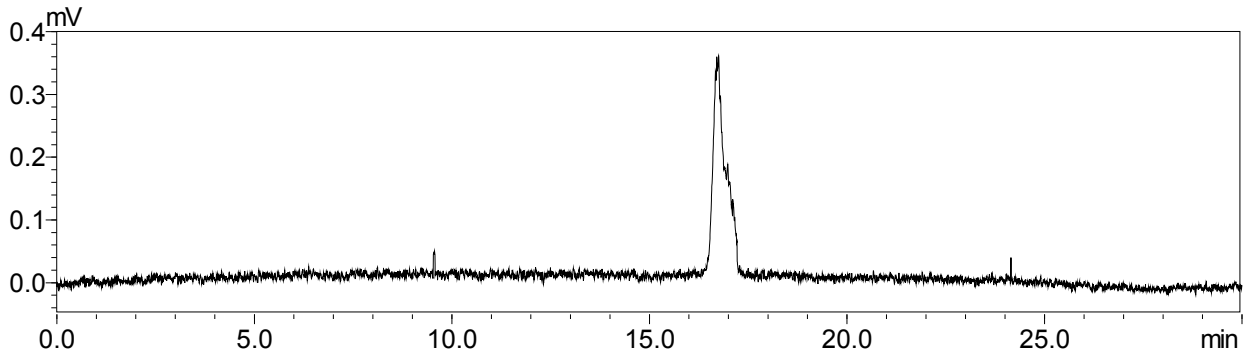


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.4 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, J = 4.0 Hz, 1 H, Fuc H-1), 5.06 (s, 1 H, Man2 H-1), 4.87 (s, 1 H, Man3 H-1), 4.73 (s, 1 H. Manβ H-1), 4.65 (d, J = 7.8 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.52-4.57 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.50 (d, J = 8.4 Hz, 1 H, GlcNAc-4 H-1), 4.47 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.21 (s, 1 H), 4.14 (d, J = 2.5 Hz, 1 H), 4.03-4.06 (m, 2 H), 3.37-3.97 (m, 55 H), 2.72 (dd, J = 12.6, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.98 (s, 3 H, Ac), 1.75 (t, J = 12.6 Hz, 1 H, Neu5Ac H-3a), 1.12 (d, J = 6.5 Hz, 3 H, Fuc-CH_3)

N222

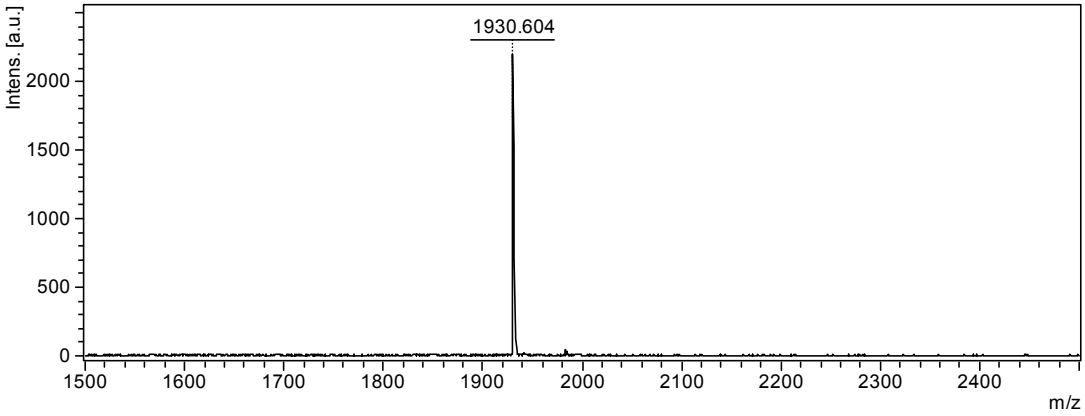


HILIC-ELSD, T_R = 16.72 min



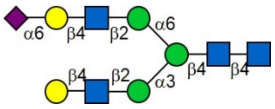
ESI-MS, calculated: 1931.6876; found $[M+2H]^{2+}$ 966.8540

MALDI-MS, found [M-H]- 1930.604

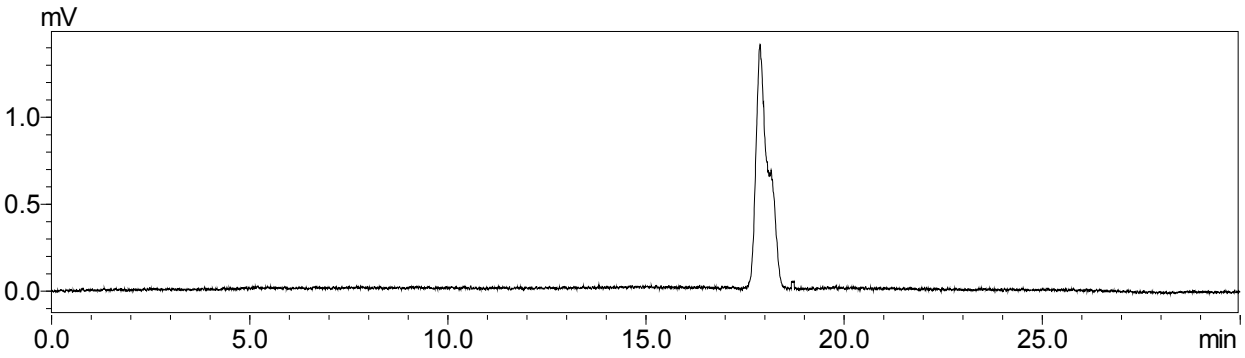


^{1}H NMR (D_2O, 500 MHz): δ 5.13 (d, J = 1.8 Hz, 0.6 H, GlcNAc-1 H1 of α anomer), 5.07 (s, 1 H, Man2 H-1), 4.88 (s, 1 H, Man3 H-1), 4.71 (s, 1 H, Manβ H-1), 4.64 (d, J = 7.6 Hz, 0.4 H, GlcNAc-1 H1 of β anomer), 4.49-4.57 (m, 4 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1, Gal-1 H-1), 4.41 (d, J = 7.9 Hz, 1 H, Gal-2 H-1), 4.20 (brs, 1 H), 4.14 (d, J = 1.6 Hz, 1 H), 4.05-4.08 (m, 2 H), 3.41-3.95 (m, 51 H), 2.71 (dd, J = 12.2, 4.2 Hz, 1 H, Neu5Ac H3e), 2.03 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.98 (s, 3 H, Ac), 1.75 (t, J = 12.2, 1 H, Neu5Ac H-3a)

N223

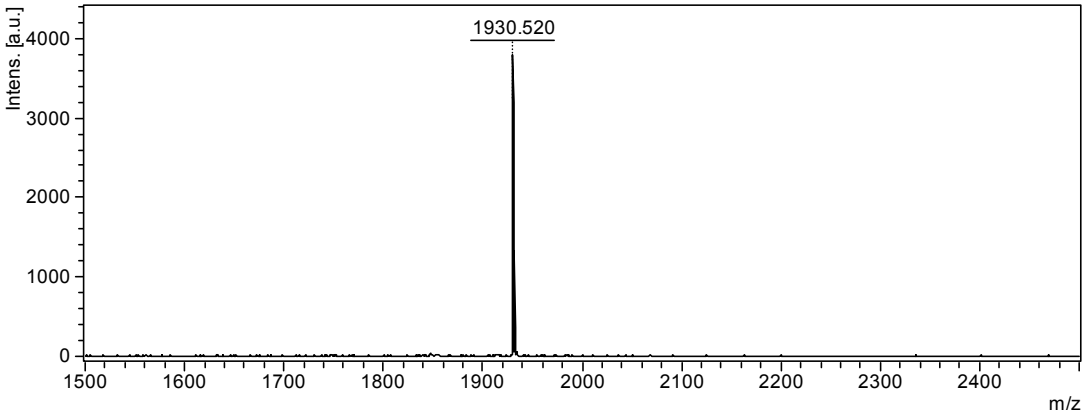


HILIC-ELSD, T_R = 17.88 min



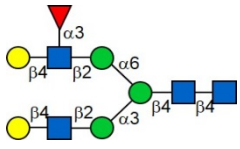
ESI-MS, calculated: 1931.6876; found $[M+2H]^{2+}$ 966.8527

MALDI-MS, found $[M-H]^-$ 1930.520

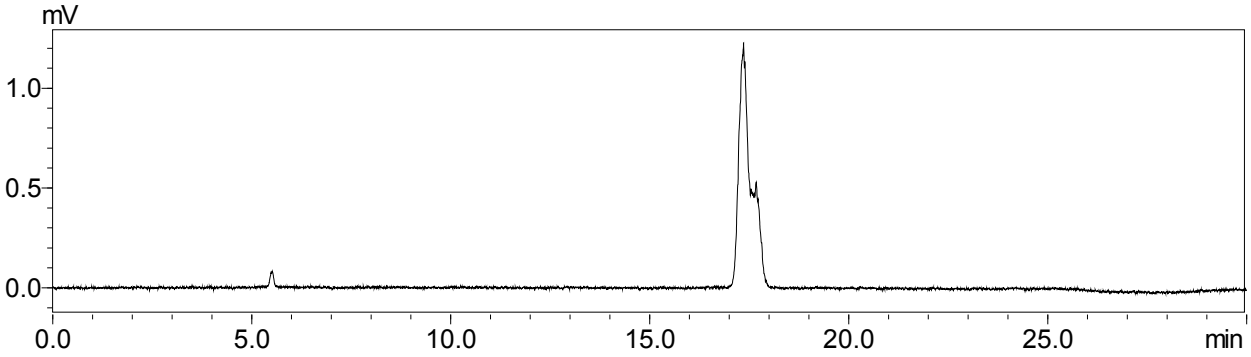


^{1}H NMR (D_2O, 500 MHz): δ 5.19 (d, J = 2.3 Hz, 0.6 H, GlcNAc-1 H1 of α anomer), 5.12 (s, 1 H, Man2 H-1), 4.95 (s, 1 H, Man3 H-1), 4.81 (s, 1 H, Manβ H-1), 4.69 (d, J = 8.0 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.57-4.62 (m, 3 H, GlcNAc-2 H-1, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.47 (d, J = 8.0 Hz, 1 H, Gal-1 H-1), 4.45 (d, J = 8.3 Hz, 1 H, Gal-2 H-1), 4.26 (s, 1 H), 4.19 (d, J = 2.2 Hz, 1 H), 4.12 (d, J = 1.7 Hz, 1 H), 3.45-4.01 (m, 58 H), 2.67 (dd, J = 12.4, 4.6 Hz, 1 H, Neu5Ac H-3e), 2.08 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 1.72 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a)

N224

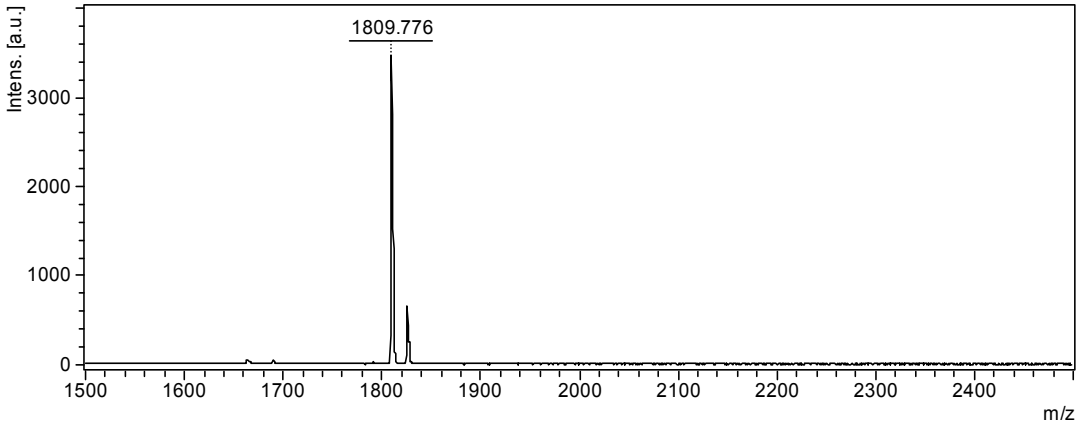


HILIC-ELSD, T_R = 17.35 min



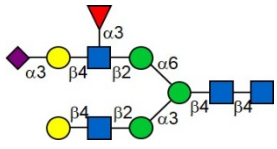
ESI-MS, calculated: 1786.6501; found $[M+2H]^{2+}$ 894.3334

MALDI-MS, found $[M+Na]^{+}$ 1809.776, $[M+K]^{+}$ 1825.755

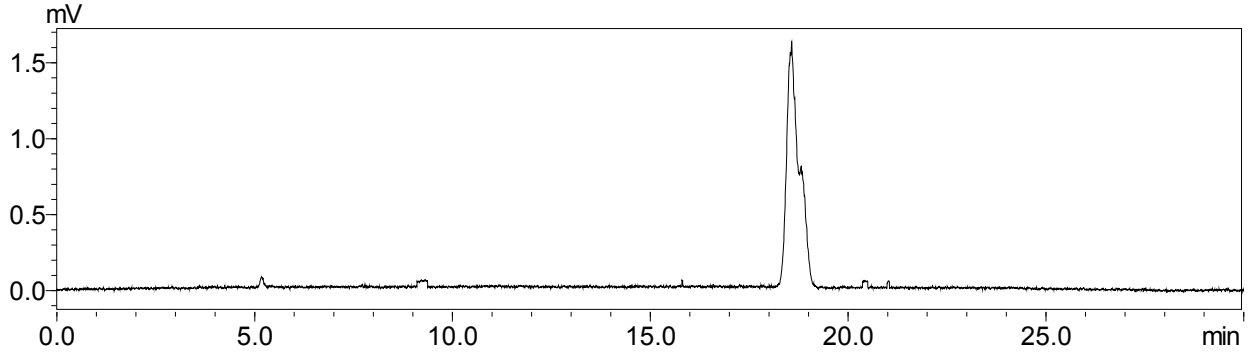


^{1}H NMR (D_2O, 500 MHz): δ 5.15 (d, J = 2.0 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.10 (d, J = 4.0 Hz, 1 H, Fuc H-1), 5.08 (s, 1 H, Man2 H-1), 4.88 (s, 1 H, Man3 H-1), 4.74 (Manβ H-1), 4.66 (d, J = 7.6 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.54-4.59 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.43 (d, J = 8.2 Hz, 1 H, Gal-1 H-1), 4.41 (d, J = 8.3 Hz, 1 H, Gal-2 H-1), 4.22 (s, 1 H), 4.16 (d, J = 2.7 Hz, 1 H), 4.07 (d, J = 2.5 Hz, 1 H), 3.42-3.98 (m, 55 H), 2.05 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.00 (s, 6 H, 2 Ac), 1.15 (d, J = 6.6 Hz, 3 H, Fuc-CH_3)

N225

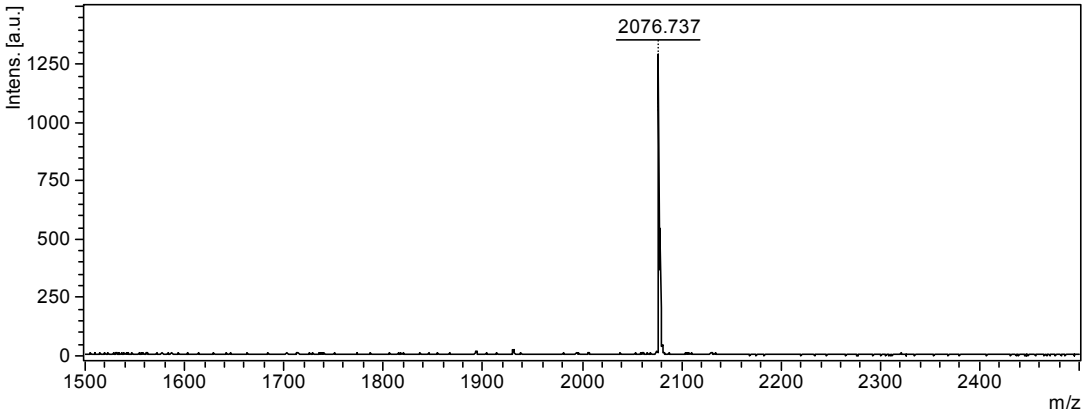


HILIC-ELSD, T_R = 18.56 min

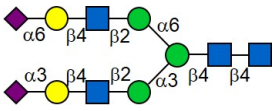


ESI-MS, calculated: 2077.7455; found $[M+2H]^{2+}$ 1039.8843

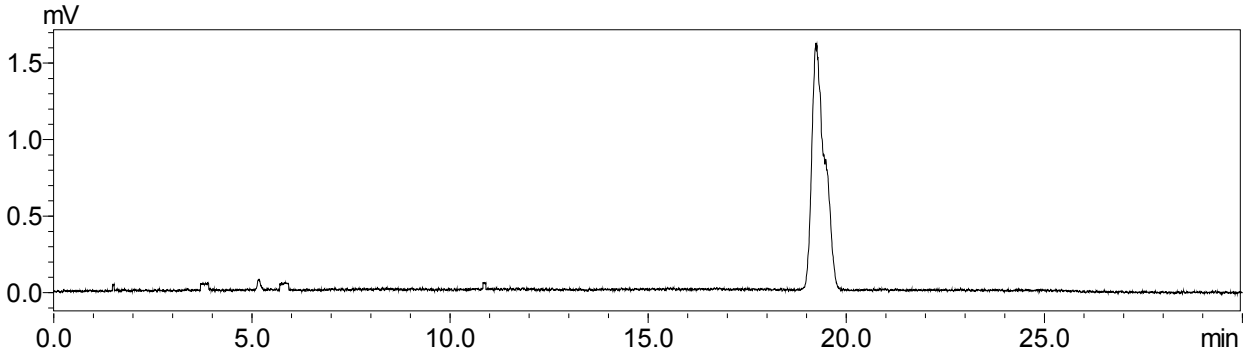
MALDI-MS, found $[M-H]^-$ 2076.737



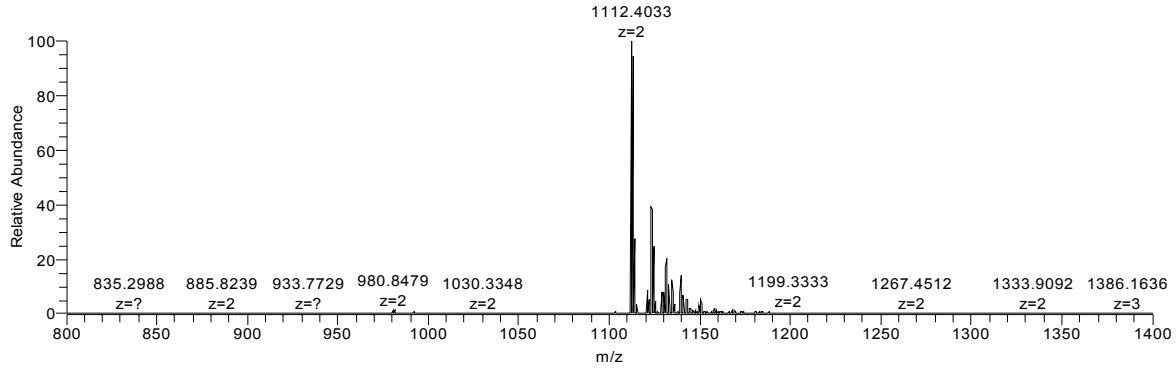
^{1}H NMR (D_2O, 500 MHz): δ 5.12 (d, J = 1.6 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.05-5.06 (d, J = 4.4 Hz, 1 H, Fuc H-1), 5.05 (s, 1 H, Man2 H-1), 4.85 (s, 1 H, Man3 H-1), 4.71 (s, 1 H, Manβ H-1), 4.63 (d, J = 7.6 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.50-4.55 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.46 (d, J = 7.8 Hz, 1 H, Gal-1 H-1), 4.40 (d, J = 7.8 Hz, 1 H, Gal-2 H-1), 4.19 (brs, 1 H), 4.13 (brs, 1 H), 4.01-4.05 (m, 2 H), 3.8-3.96 (m, 61 H), 2.70 (dd, J = 12.2, 4.2 Hz, 1 H, Neu5Ac H-3e), 2.02 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.97 (s, 6 H, 2 Ac), 1.96 (s, 3 H, Ac), 1.73 (t, J = 12.2 Hz, 1 H, Neu5Ac H-3a), 1.11 (d, J = 6.5 Hz, 3 H, Fuc-CH_3)

N233 

HILIC-ELSD, T_R = 19.24 min

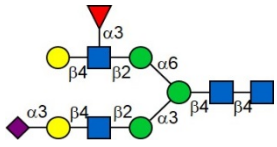


ESI-MS, calculated: 2222.7830; found $[M+2H]^{2+}$ 1112.4033

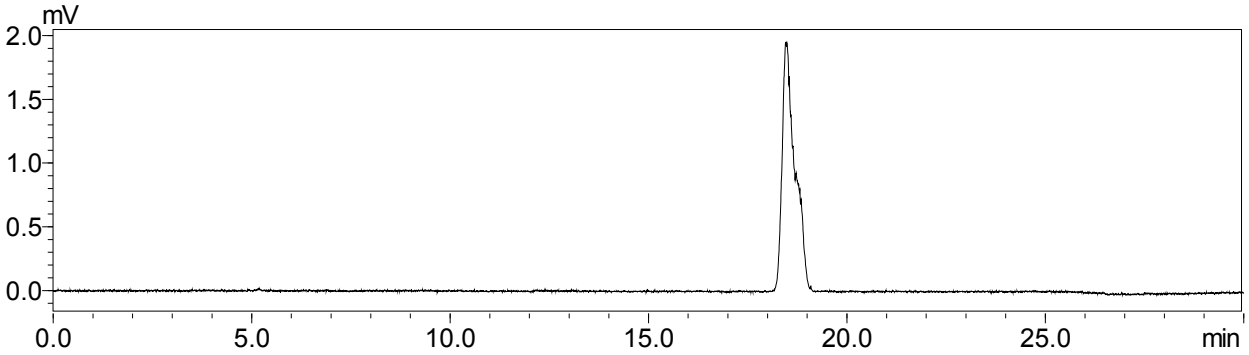


^{1}H NMR (D_2O, 500 MHz): δ 5.15 (d, J = 2.3 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.08 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.74 (s, 1 H, Manβ H-1), 4.66 (d, J = 7.5 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.53-4.58 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.51 (d, J = 7.8 Hz, 1 H, Gal-1 H-1), 4.41 (d, J = 7.8 Hz, 1 H, Gal-2 H-1), 4.22 (brs, 1 H), 4.15 (d, J = 2.1 Hz, 1 H), 4.06-4.09 (m, 2 H), 3.45-3.98 (m, 64 H), 2.72 (dd, J = 12.7, 4.7 Hz, 1 H, Neu5NAc-1 H-3e), 2.64 (dd, J = 12.5, 4.8 Hz, 1 H, Neu5NAc-2 H-3e), 2.05 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.76 (t, J = 11.5 Hz, 1 H, Neu5NAc-1 H-3a), 1.69 (dd, J = 12.7 Hz, Neu5NAc-2 H-3a)

N234

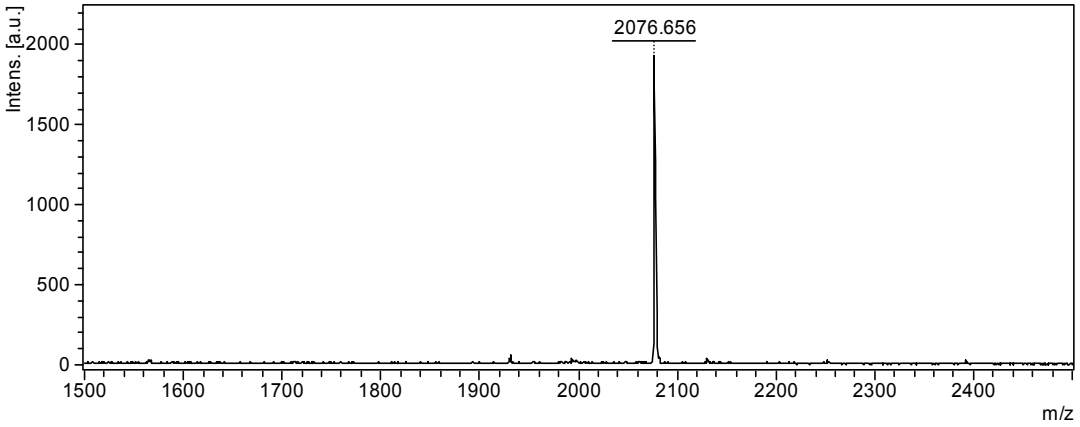


HILIC-ELSD, T_R = 18.48 min



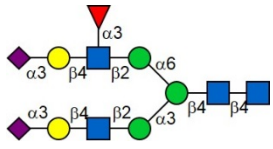
ESI-MS, calculated: 2077.7455; found $[M+2H]^{2+}$ 1039.8843

MALDI-MS, found $[M-H]^-$ 2076.656

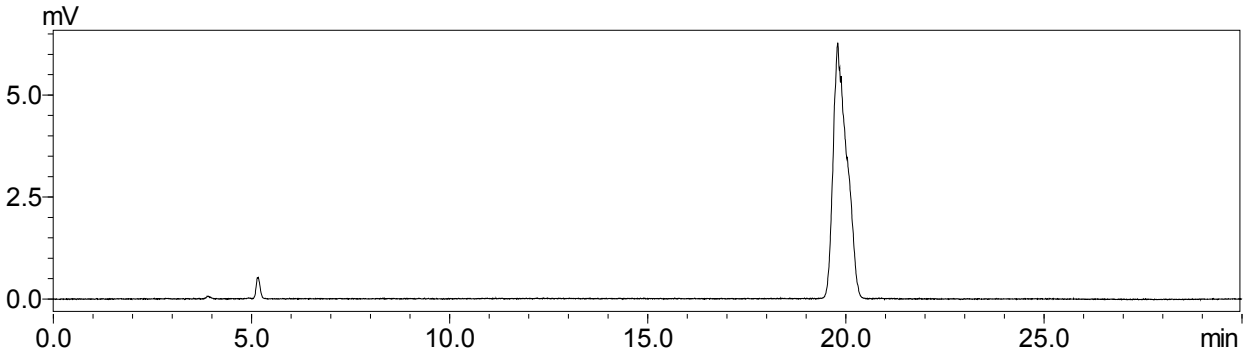


^{1}H NMR (D_2O, 500 MHz): δ 5.12 (d, J = 2.1 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.07 (d, J = 3.9 Hz, 1 H, Fuc H-1), 5.05 (s, 1 H, Man2 H-1), 4.85 (s, 1 H, Man3 H-1), 4.71 (s, 1 H, Manβ H-1), 4.63 (d, J = 7.0 Hz, 0.5 H, GlcNAc-1 H1 of β anomer), 4.47-4.55 (m, 4 H, GlcNAc-2 H-1, GlcNAC-3 H-1, GlcNAc-4 H-1,Gal-1 H-1), 4.38 (d, J = 7.7 Hz, 1 H, Gal-2 H-1), 4.19 (s, 1 H), 4.12 (d, J = 3.0 Hz, 1 H), 4.03-4.06 (m, 2 H), 3.38-3.97 (m, 61 H), 2.69 (dd, J = 12.4, 4.4 Hz, 1 H, Neu5Ac H-3e), 2.02 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.97 (s, 6 H, 2 Ac), 1.96 (s, 3 H, Ac), 1.73 (t, J = 12.4 Hz, 1 H, Neu5Ac H-3a), 1.11 (d, J = 6.6 Hz, 3 H, Fuc-CH_3)

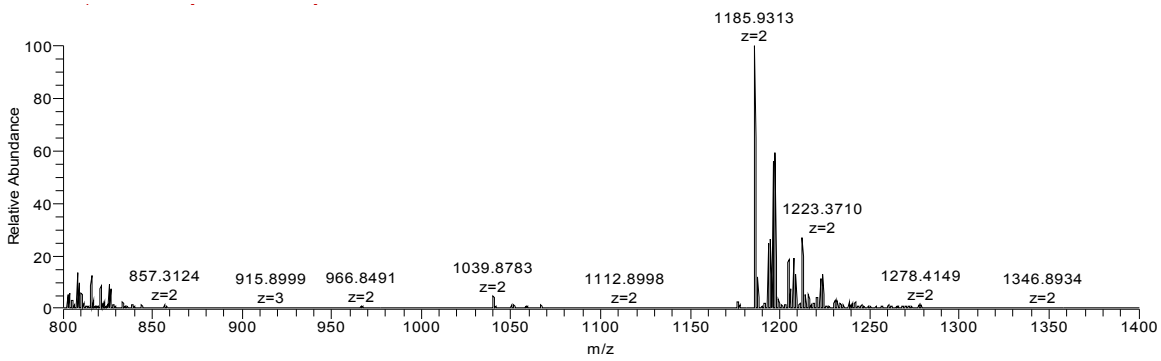
N235



HILIC-ELSD, T_R = 19.79 min



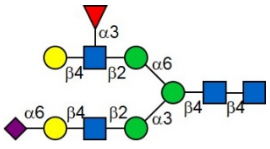
ESI-MS, calculated: 2368.8409; found $[M+2H]^{2+}$ 1185.9313



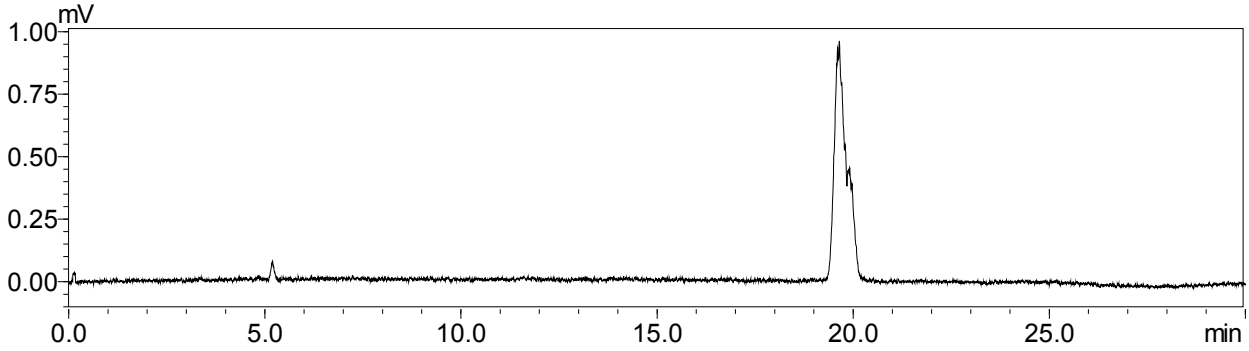
ESI-MS, found $[M+2H]^{2+}$

^{1}H NMR (D_2O, 500 MHz): δ 5.07-5.09 (m, 2 H), 4.87 (s, 1 H, Man2 H-1), 4.80 (overlapped with D_2O, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.46-4.56 (m, 5 H), 4.21 (brs, 1H), 4.14 (d, J = 2.2 Hz, 1 H), 4.03-4.07 (m, 3 H), 3.40-4.00 (m, 67 H), 2.68-2.74 (m, 2 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.98 (s, 6 H, 2 Ac), 1.76 (t, J = 12.0 Hz, 2 H, Neu5Ac H-3a), 1.13 (d, J = 6.2 Hz, 3 H, Fuc-CH_3)

N244

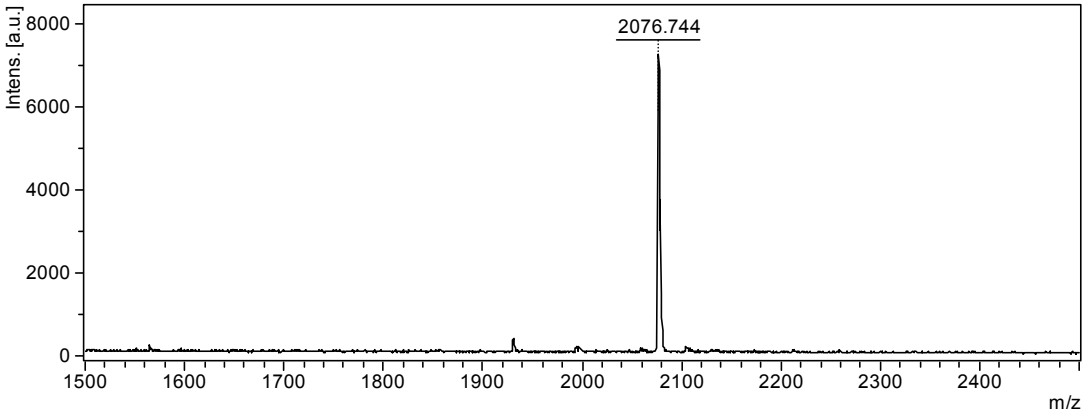


HILIC-ELSD, T_R = 19.65 min



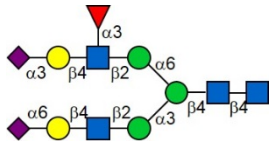
ESI-MS, calculated: 2077.7455; found $[M+2H]^{2+}$ 1039.8862

MALDI-MS, found $[M-H]^-$ 2076.744

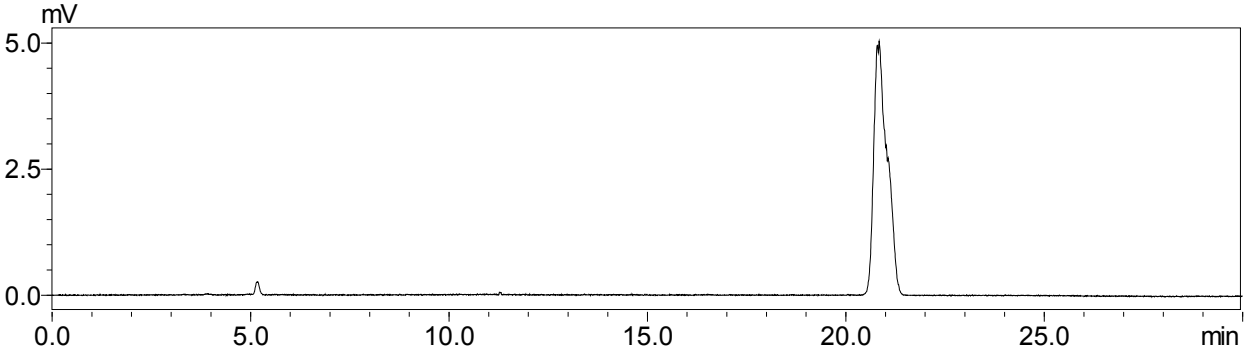


^{1}H NMR (D_2O, 500 MHz): δ 5.15 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.08-5.10 (m, 2 H, Fuc H-1, Man2 H-1), 4.89 (s, 1 H, Man3 H-1), 4.74 (s, 1 H, Manβ H-1), 4.65 (d, *J* = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.54-4.57 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.40 (d, *J* = 7.5 Hz, 2 H, Gal-1 H-1, Gal-2 H-1), 4.22 (brs, 1 H), 4.16 (brs, 1 H), 4.06 (brs, 1 H), 3.41-3.97 (m, 63 H), 2.63 (dd, *J* = 12.5, 4.9 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.00 (s, 6 H, 2 Ac), 1.99 (s, 3 H, Ac), 1.68 (t, *J* = 12.5 Hz, 1 H, Neu5Ac), 1.14 (d, *J* = 6.4 Hz, 3 H, Fuc-CH_3)

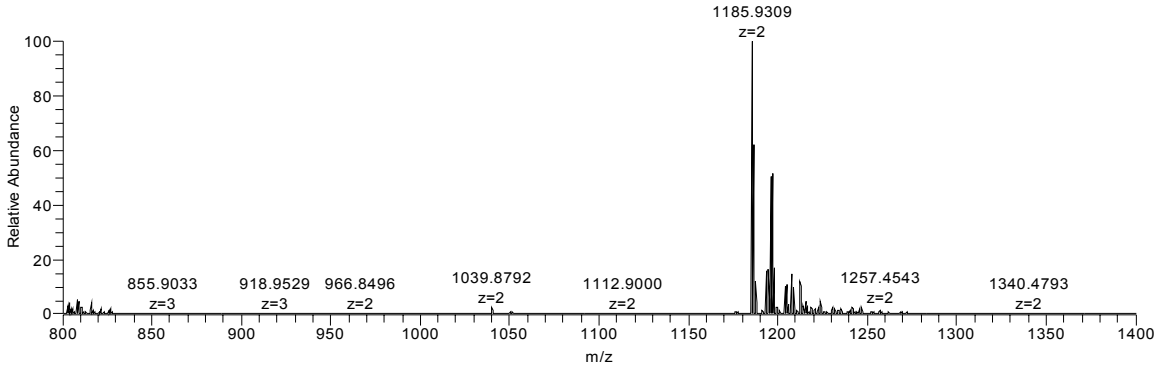
N245



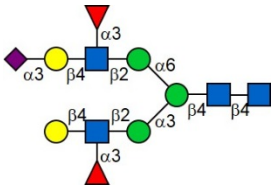
HILIC-ELSD, T_R = 20.82 min



ESI-MS, calculated: 2368.8409; found $[M+2H]^{2+}$ 1185.9309

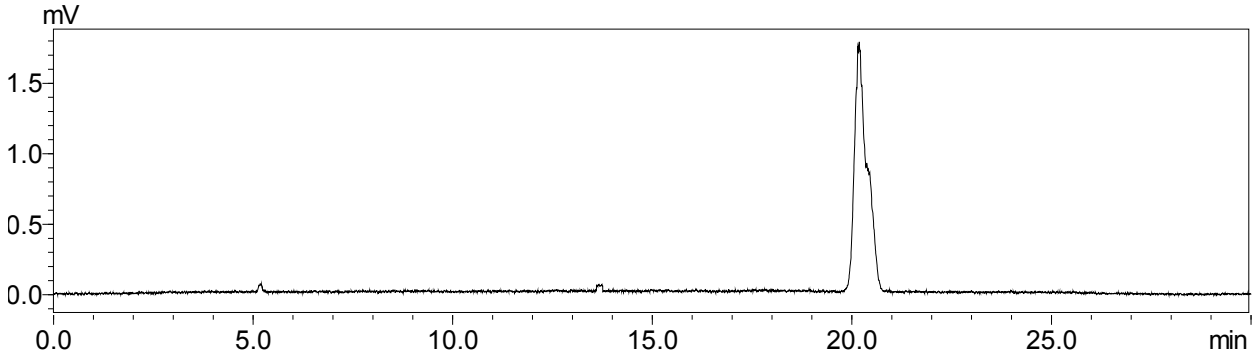


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.6 Hz, 0.4 H, GlcNAc-1 H-1 of α anomer), 5.09 (s, 1 H, Man2 H-1), 5.08 (d, J = 3.9 Hz, 1 H, Fuc H-1), 4.87 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, J = 7.8 Hz, 0.6 H, GlcNAc-1 H-1 of β anomer), 4.52-4.57 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3, GlcNAc-4), 4.48 (d, J = 7.6 Hz, 1 H, Gal-1 H-1), 4.40 (d, J = 7.9 Hz, 1 H, Gal-2 H-1), 4.22 (s, 1 H), 4.15 (d, J = 3.1 Hz, 1 H), 4.03-4.06 (m, 2 H), 3.40-3.97 (m, 68 H), 2.72 (dd, J = 12.2, 4.4 Hz, 1 H, Neu5Ac-1 H-3e), 2.62 (dd, J = 12.8, 4.8 Hz, 1 H, Neu5Ac-2 H-3e), 2.04 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.98 (s, 6 H, 2 Ac), 1.75 (t, J = 12.2 Hz, 1 H, Neu5Ac-1 H-3a), 1.68 (t, J = 12.8 Hz, 1 H, Neu5Ac-2 H-3a), 1.13 (d, J = 6.2 Hz, 3 H, Fuc-CH_3)



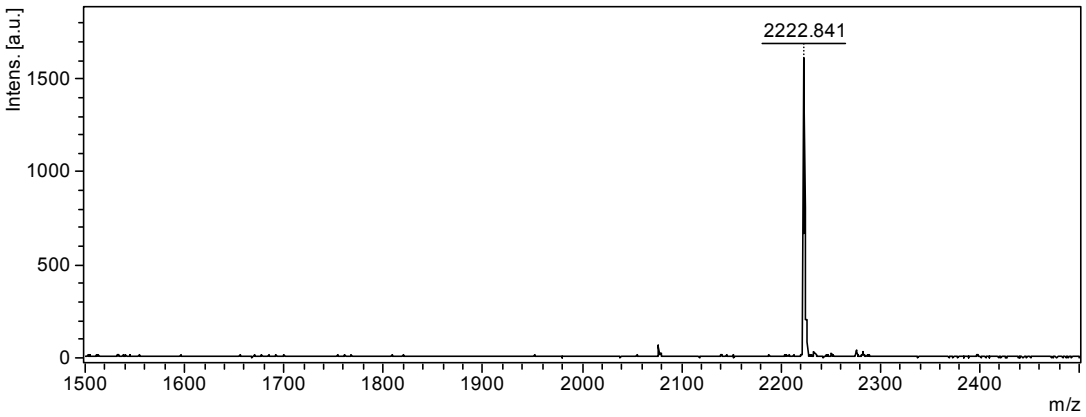
N255

HILIC-ELSD, T_R = 20.18 min

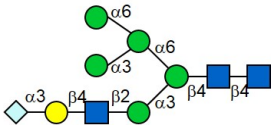


ESI-MS, calculated: 2223.8034; found $[M+2H]^{2+}$ 1112.9105

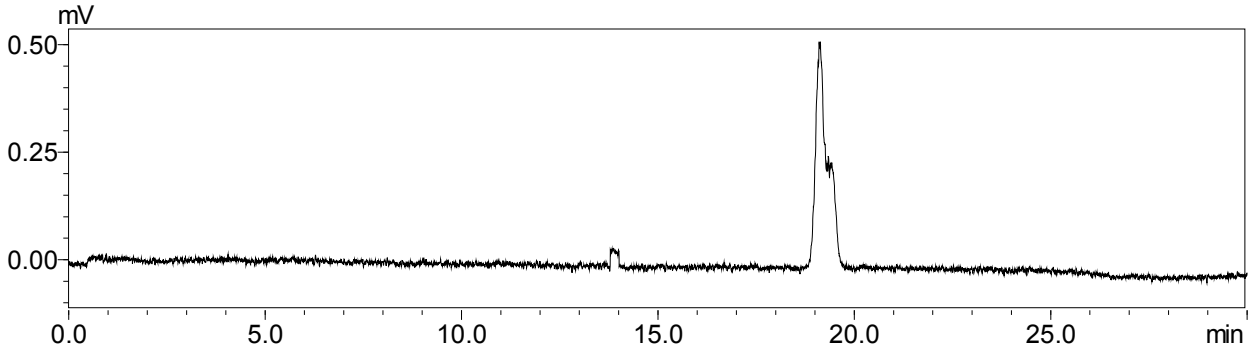
MALDI-MS, found $[M-H]^-$ 2222.841



^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 2.3 Hz, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, J = 3.9 Hz, 2 H, Fuc-1 H-1, Fuc-2 H-1), 5.06 (s, 1 H, Man2 H-1), 4.87 (s, 1 H, Man3 H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, J = 8.2 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.53-4.57 (m, 3 H, GlcNAc-2 H-1, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.47 (d, J = 7.8 Hz, 1 H, Gal-1 H-1), 4.39 (d, J = 7.8 Hz, 1 H, Gal-2 H-1), 4.21 (s, 1 H), 4.14 (d, J = 2.3 Hz, 1 H), 4.03-4.07 (m, 2 H), 3.40-3.96 (m, 65 H), 2.72 (dd, J = 12.2, 4.7 Hz, 1 H, Neu5Ac H-3e), 2.04 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.98 (s, 3 H, Ac), 1.75 (t, J = 12.2 Hz, 1 H, Neu5Ac H-3a), 1.13 (d, J = 6.6 Hz, 6 H, Fuc-1 CH_3, Fuc-2 CH_3)

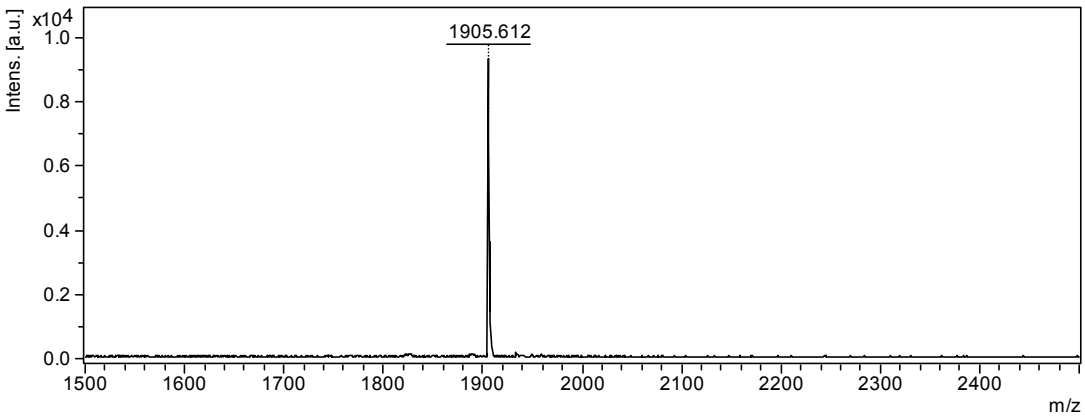
N012G 

HILIC-ELSD, T_R = 19.13 min

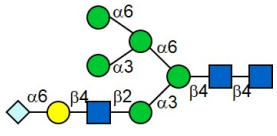


ESI-MS, calculated: 1906.6560; found $[M+2H]^{2+}$ 954.3400

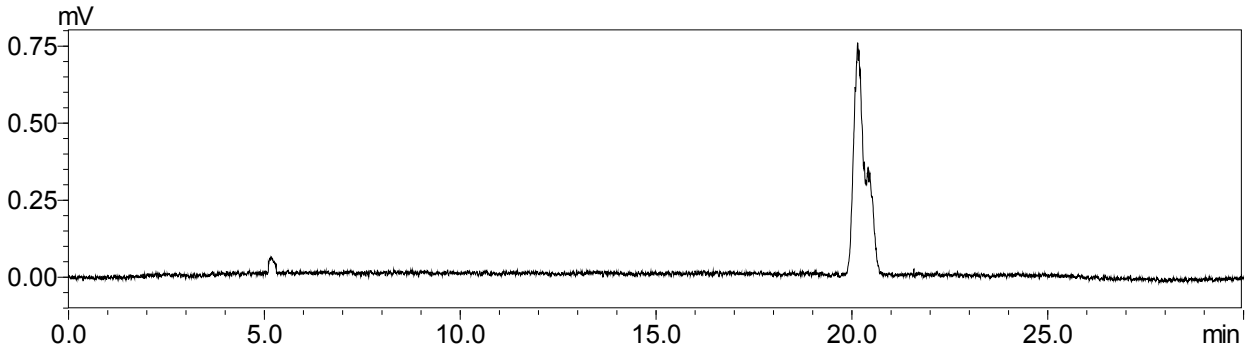
MALDI-MS, found $[M-H]^-$ 1905.612



^{1}H NMR (D_2O, 500 MHz): δ 5.20 (s, 1 H, Man5 H-1), 5.14 (d, *J* = 1.3 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.07 (s, 1 H, Man2 H-1), 4.90 (s, 1 H, Man3 H-1), 4.85 (s, 1 H, Man4 H-1), 4.74-4.83 (overlapped with D_2O, 1 H, Manβ H-1), 4.65 (d, *J* = 7.7 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.57 (d, *J* = 7.7 Hz, 0.6 H, GlcNAc-2 H-1 of α anomer), 4.56 (d, *J* = 7.7 Hz, 0.4 H, GlcNAc-2 H-1 of β anomer), 4.53 (d, *J* = 6.8 Hz, 1 H, GlcNAc-2 H-1), 4.50 (d, *J* = 7.8 Hz, 1 H, Gal H-1), 4.20 (d, *J* = 1.0 Hz, 1 H), 4.16 (d, *J* = 1.2 Hz, 1 H), 4.07-4.09 (m, 3 H), 3.43-4.01 (m, 58 H), 2.73 (dd, *J* = 12.3, 4.5 Hz, 1 H, Neu5Gc H-3e), 2.03 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.77 (t, *J* = 12.3 Hz, 1 H, Neu5Gc H-3a)

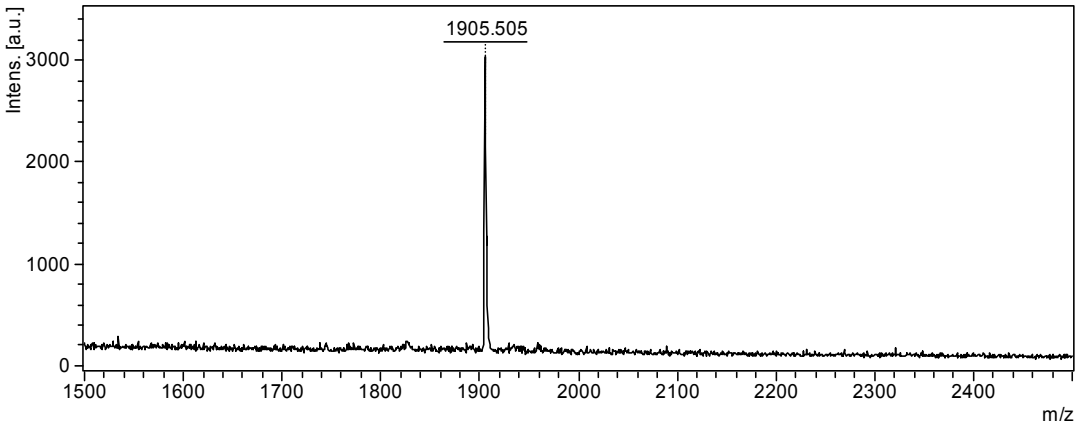
N013G 

HILIC-ELSD, T_R = 20.16 min

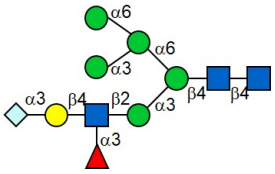


ESI-MS, calculated: 1906.6560; found $[M+2H]^{2+}$ 954.3416

MALDI-MS, found $[M-H]^-$ 1905.505

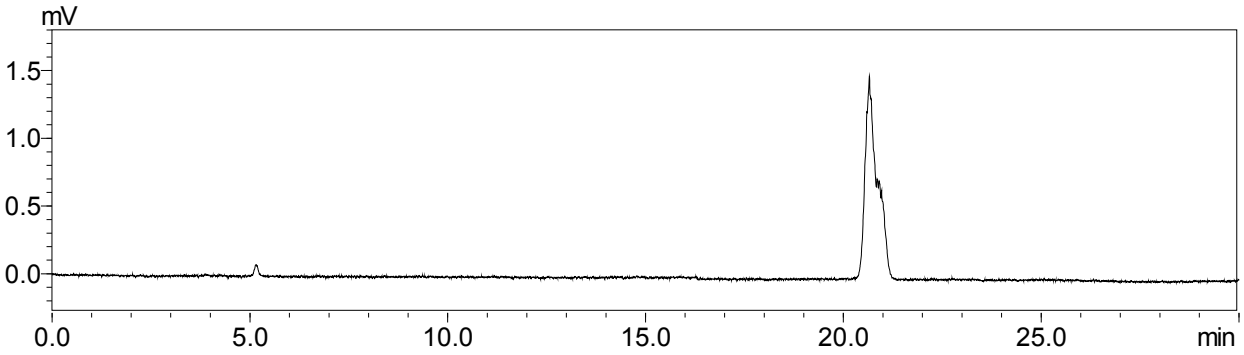


^{1}H NMR (D_2O, 500 MHz): δ 5.18 (s, 1 H, Man5 H-1), 5.13 (brs, 0.5 H, GlcNAc-1 H-1 of α anomer), 5.06 (s, 1 H, Man2 H-1), 4.88 (s, 1 H, Man3 H-1), 4.83 (s, 1 H, Man4 H-1), 4.75-4.80 (overlapped with D_2O, 1 H, Manβ H-1), 4.63 (d, J = 6.2 Hz, 0.5 H, GlcNAc-1 H-1 of β anomer), 4.53-4.56 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.38 (d, J = 7.7 Hz, 1 H, Gal H-1), 4.19 (brs, 1 H), 4.15 (brs, 1 H), 4.05 (brs, 1 H), 3.43-3.99 (m, 59 H), 2.62 (dd, J = 12.5, 3.9 Hz, 1 H, Neu5Gc H-3e), 2.01 (s, 6 H, 2 Ac), 1.98 (s, 3 H, Ac), 1.68 (t, J = 12.5 Hz, 1 H, Neu5Gc H-3a)



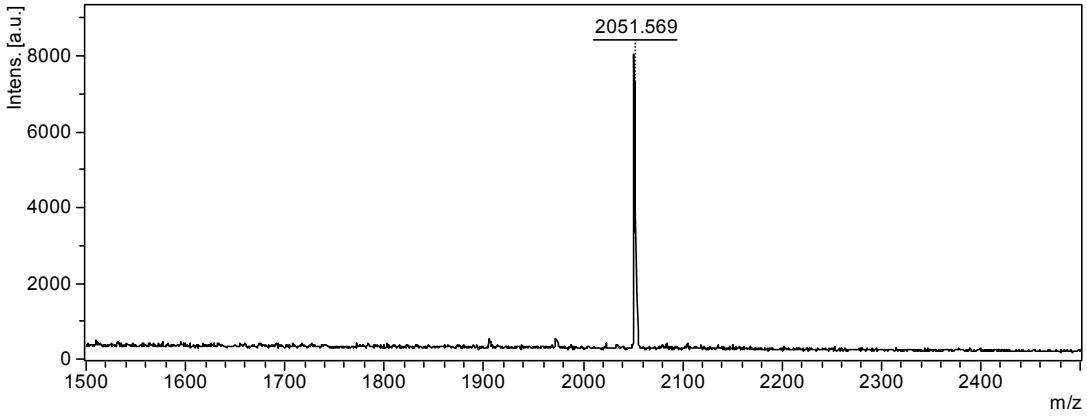
N015G

HILIC-ELSD, T_R = 20.66 min

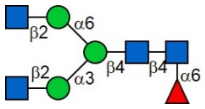


ESI-MS, calculated: 2052.7139; found $[M+2H]^{2+}$ 1027.3722

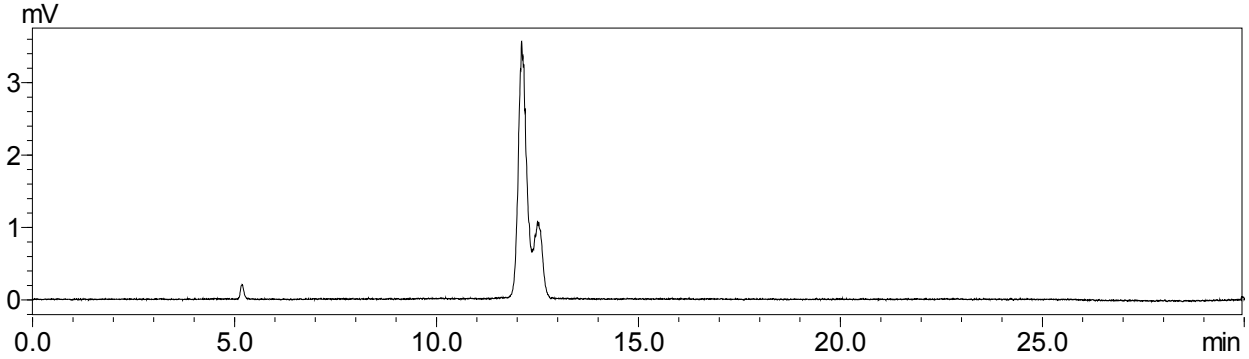
MALDI-MS, found $[M-H]^-$ 2051.569



^{1}H NMR (D_2O, 500 MHz): δ 5.20 (s, 1 H, Man5 H-1), 5.15 (brs, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.08 (d, J = 3.5 Hz, 1 H, Fuc H-1), 5.06 (s, 1 H, Man2 H-1), 4.91 (s, 1 H, Man3 H-1), 4.86 (s, 1 H, Man4 H-1), 4.75-4.83 (overlapped with D_2O, 1 H, Manβ H-1), 4.65 (d, J = 6.4 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.53-4.58 (m, 2 H, GlcNAc-2 H-1, GlcNAc-3 H-1), 4.47 (d, J = 7.7 Hz, 1 H, Gal H-1), 4.21 (brs, 1 H), 4.15-4.16 (m, 1 H), 4.05-4.08 (m, 3 H), 3.42-4.01 (m, 62 H), 2.74 (dd, J = 12.4, 4.8 Hz, 1 H, Neu5Gc H-3e), 2.04 (s, 3 H, Ac), 2.00 (s, 6 H, 2 Ac), 1.77 (t, J = 12.4 Hz, 1 H, Neu5Gc H-3a), 1.13 (t, J = 6.0 Hz, 3 H, Fuc-CH_3)

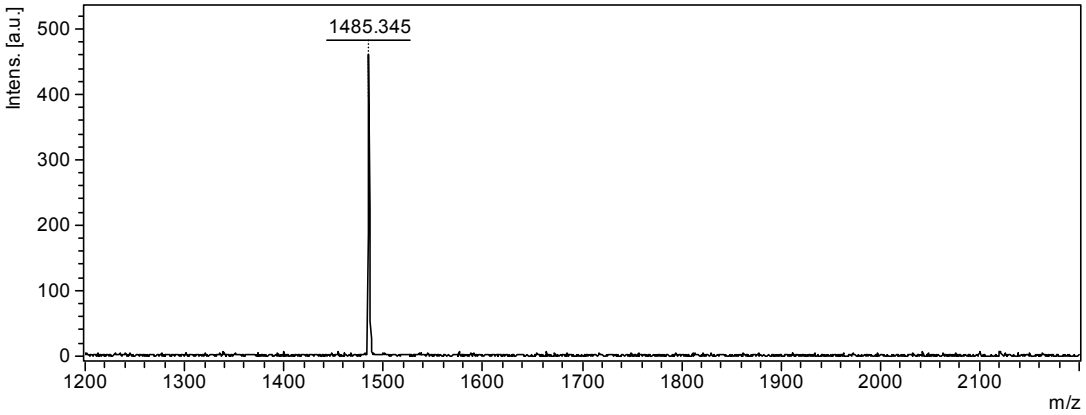
N6000 

HILIC-ELSD, T_R = 12.11 min

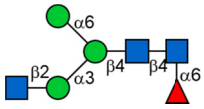


ESI-MS, calculated: 1462.5444; found $[M+2H]^{2+}$ 732.2835

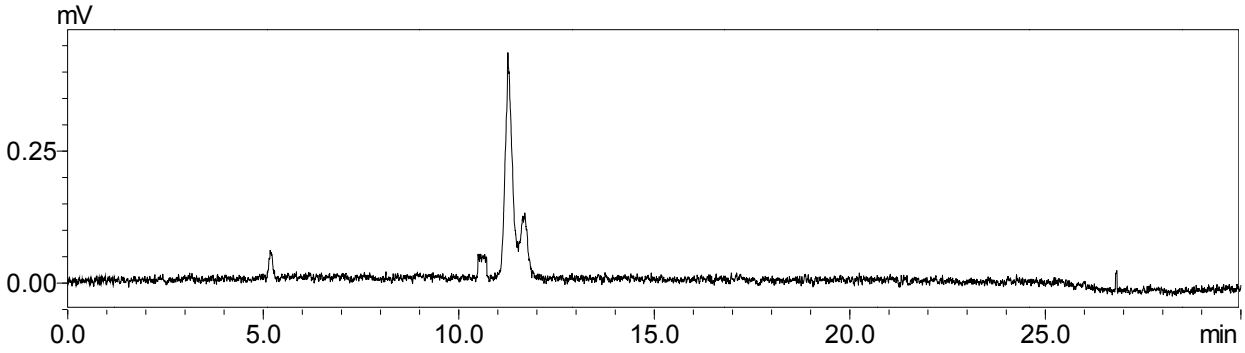
MALDI-MS, found $[M+Na]^{+}$ 1485.345



^{1}H NMR (D_2O, 500 MHz): δ 5.20 (d, J = 3.0 Hz, 0.4 H, GlcNAc-1 H-1 of α anomer), 5.13 (s, 1 H, Man2 H-1), 4.93 (s, 1 H, Man3 H-1), 4.91 (d, 0.4 H, J = 3.6 Hz, Fuc H-1 of a anomer), 4.90 (d, 0.6 H, J = 3.6 Hz, Fuc H-1 of β anomer), 4.75-4.85 (overlapped with D_2O, 1 H, Manβ H-1), 4.71 (d, J = 8.0 Hz, 0.6 H, GlcNAc-1 H-1 of β anomer), 4.69 (d, J = 8.1 Hz, 0.4 H, GlcNAc-2 H-1 of α anomer), 4.68 (d, J = 7.7 Hz, 0.6 H, GlcNAc-1 H-1 of β anomer), 4.57 (d, J = 8.4 Hz, 2 H, GlcNAc-3 H-1, GlcNAc-4 H-1), 4.27 (brs, 1 H), 4.20 (d, J = 1.8 Hz, 1 H), 4.10 (m, 2 H), 3.43-4.02 (m, 42 H), 2.11 (s, 3 H, Ac), 2.07 (s, 6 H, 2 Ac), 2.06 (s, 3 H, Ac), 1.24 (d, 1.2 H, J = 5.1 Hz, Fuc-CH_3), 1.23 (d, 1.8 H, J = 6.4 Hz, Fuc-CH_3)

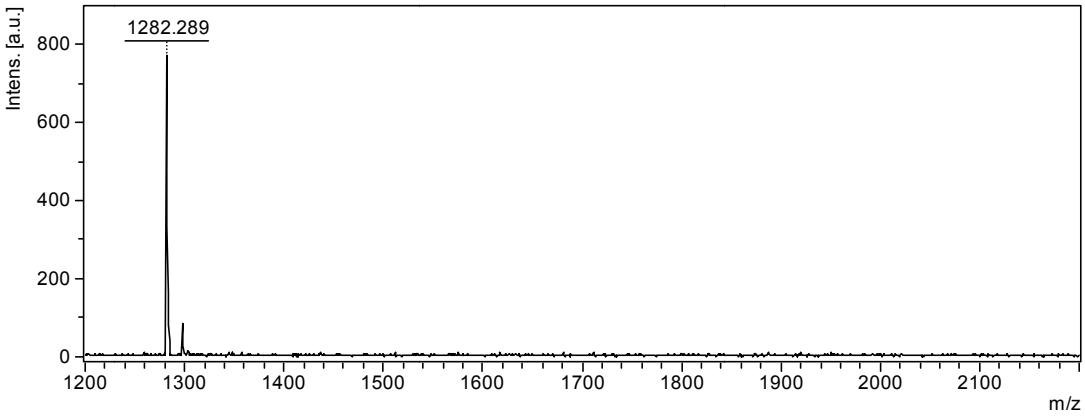
N6030 

HILIC-ELSD, T_R = 11.25 min



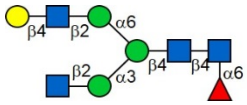
ESI-MS, calculated: 1259.4651; found $[M+2H]^{2+}$ 630.7428

MALDI-MS, found $[M+Na]^{+}$ 1282.289, $[M+K]^{+}$ 1298.266

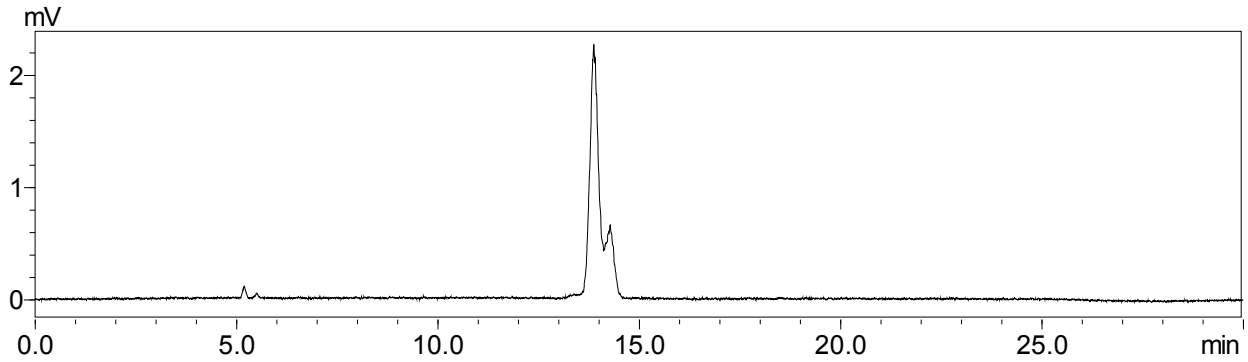


^{1}H NMR (D_2O, 500 MHz): δ 5.18 (d, J = 2.9 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.12 (s, 1 H, Man2 H-1), 4.92 (s, 1 H, Man3 H-1), 4.88-4.90 (m, 1 H, Fuc H-1), 4.77-4.83 (overlapped with D_2O, 1 H, Manβ H-1), 4.69 (d, J = 8.1 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.67 (d, J = 8.1 Hz, 0.6 H, GlcNAc-2 H-1 of β anomer), 4.66 (d, J = 7.6 Hz, 0.4 H, GlcNAc-2 H-1 of α anomer), 4.55 (d, J = 8.4 Hz, 1 H, GlcNAc-3 H-1), 4.26 (brs, 1 H), 4.17-4.19 (m, 1 H), 4.07-4.13 (m, 1 H), 3.43-4.02 (m, 37 H), 2.09 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 1.20-1.23 (m, 3 H, Fuc-CH_3)

N6211

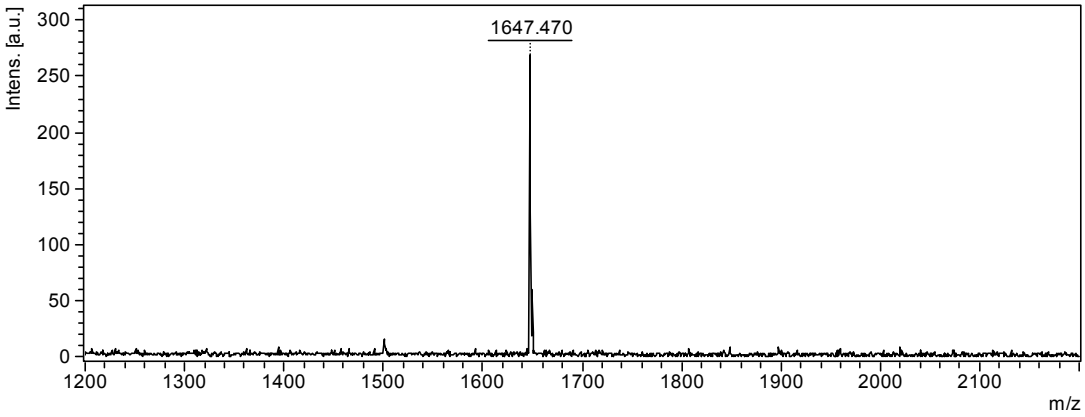


HILIC-ELSD, T_R = 13.87 min



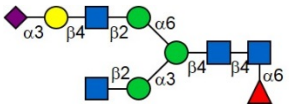
ESI-MS, calculated: 1624.5973; found $[M+2H]^{2+}$ 813.3106

MALDI-MS, found $[M+Na]^{+}$ 1647.470

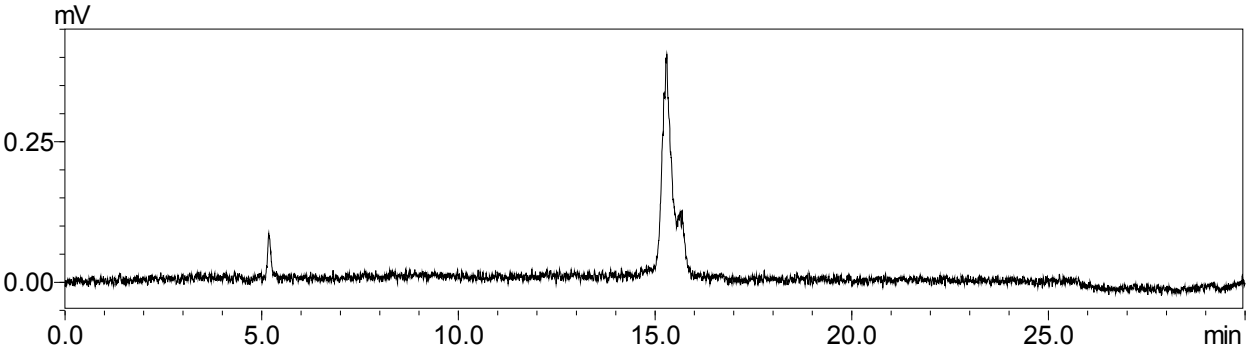


^{1}H NMR (D_2O, 500 MHz): δ 5.14 (d, J = 3.0 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.07 (s, 1 H, Man2 H-1), 4.89 (s, 1 H, Man3 H-1), 4.85-4.86 (m, 1 H, Fuc H-1), 4.73 (s, 1 H, Manβ H-1), 4.65 (d, J = 8.1 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.61-4.64 (m, 1 H, GlcNAc-2 H-1), 4.54 (d, J = 8.2 Hz, 1 H, GlcNAc-3 H-1), 4.51 (d, J = 8. 4 Hz, 1 H, GlcNAc-4 H-1), 4.43 (d, J = 7.8 Hz, 1 H, Gal H-1), 4.21 (d, J = 1.4 Hz, 1 H), 4.13-4.15 (m, 1 H), 4.05-4.10 (m, 2 H), 3.40-3.98 (m, 48 H), 2.05 (s, 3 H, Ac), 2.01 (2 s, 6 H, 2 Ac), 2.00 (s, 3 H, Ac), 1.16-1.19 (m, 3 H, Fuc-CH_3)

N6212

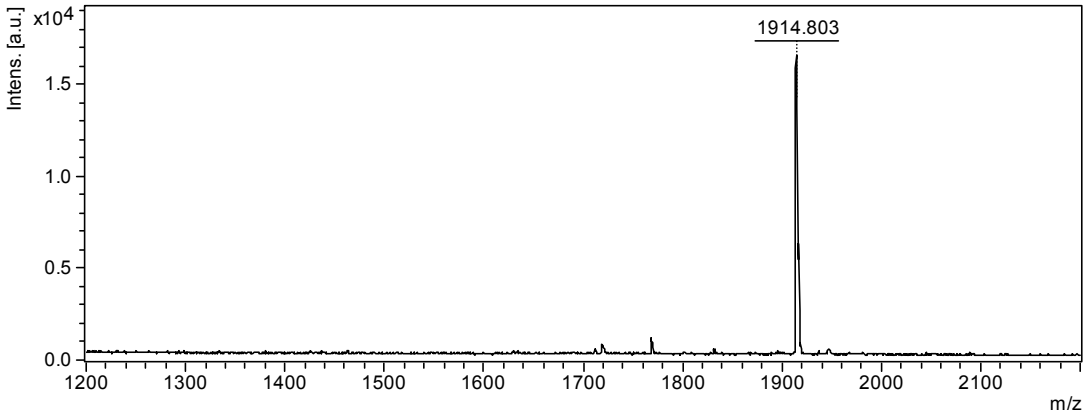


HILIC-ELSD, T_R = 15.29 min



ESI-MS, calculated: 1915.6927; found $[M+2H]^{2+}$ 958.8591

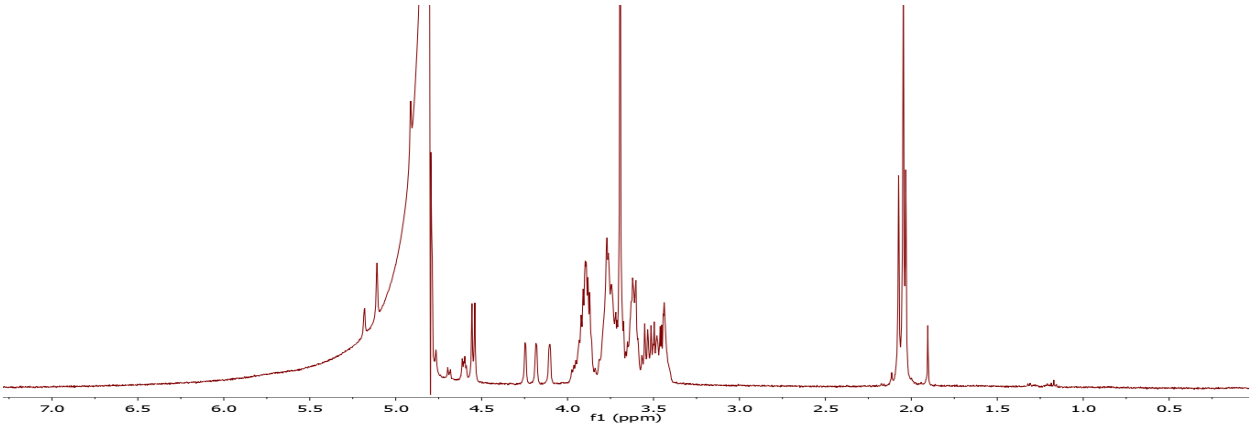
MALDI-MS, found $[M-H]^-$ 1914.803



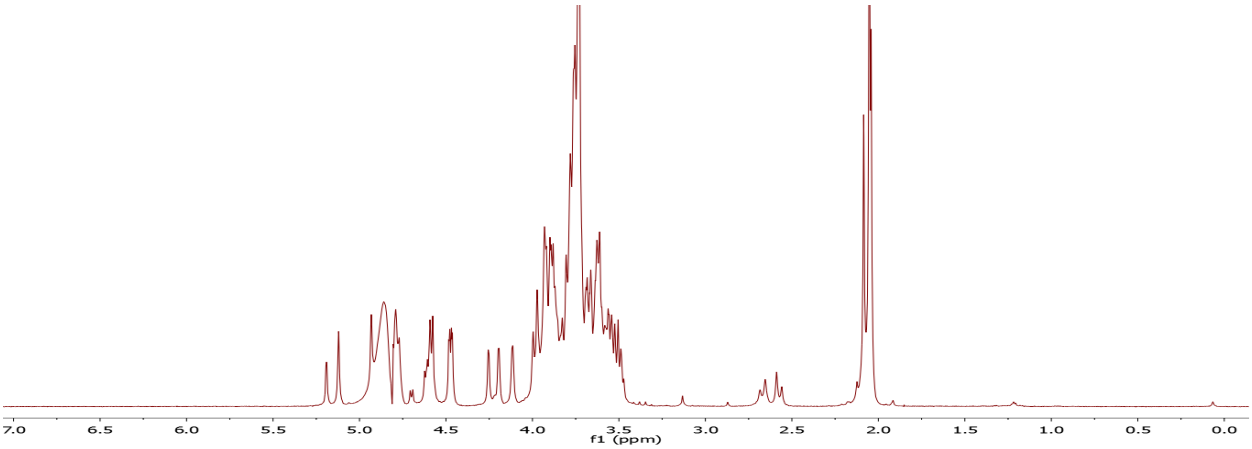
^{1}H NMR (D_2O, 500 MHz): δ 5.13 (d, J = 2.5 Hz, 0.6 H, GlcNAc-1 H-1 of α anomer), 5.06 (s, 1 H, Man2 H-1), 4.87 (s, 1 H, Man3 H-1), 4.75-4.85 (overlapped with D_2O, 1 H, Fuc H-1), 4.72 (s, 1 H, Manβ H-1), 4.64 (d, J = 8.2 Hz, 0.4 H, GlcNAc-1 H-1 of β anomer), 4.60-4.62 (m, 1 H, GlcNAc-2 H-1), 4.49-4.53 (m, 3 H, GlcNAc-3 H-1, GlcNAc-4 H-1, Gal H-1), 4.20 (brs, 1 H), 4.13-4.14 (m, 1 H), 4.05-4.08 (m, 3 H), 3.38-3.95 (m, 54 H), 2.71 (dd, J = 12.5, 4.9 Hz, 1 H, Neu5Ac H-3e), 2.05 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 6 H, 2 Ac), 1.98 (s, 3 H, Ac), 1.75 (t, J = 12.5 Hz, 1 H, Neu5Ac H-3a), 1.17 (t, J = 5.6 Hz, 3 H, Fuc-CH_3)

VIII. NMR spectra of purified N-glycans

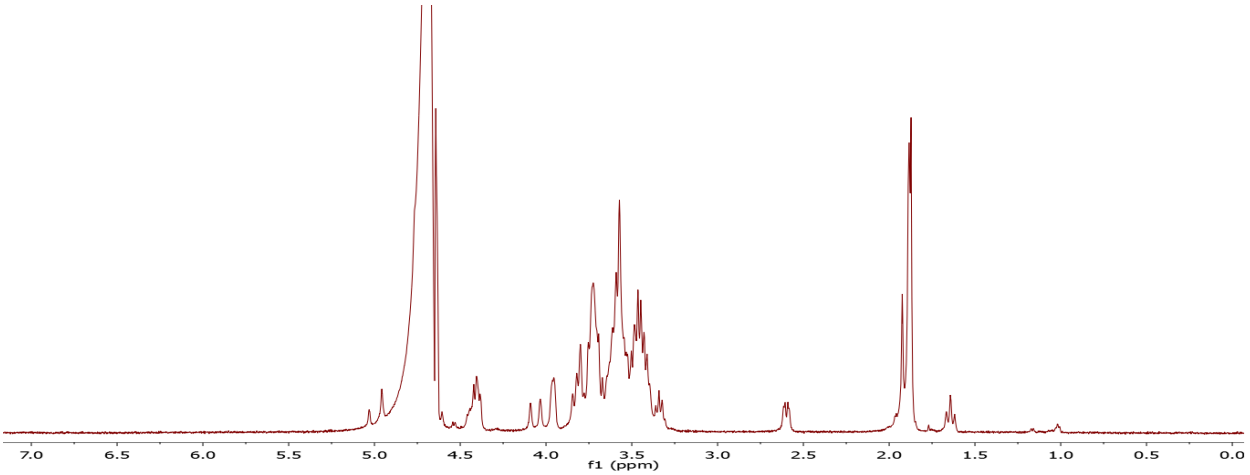
^{1}H NMR of **N000**



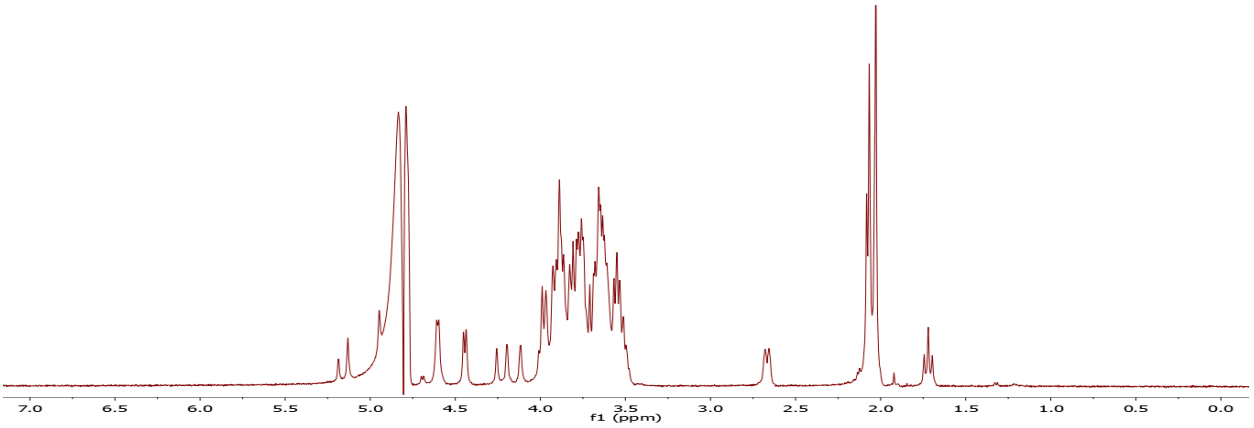
^{1}H NMR of **N001**



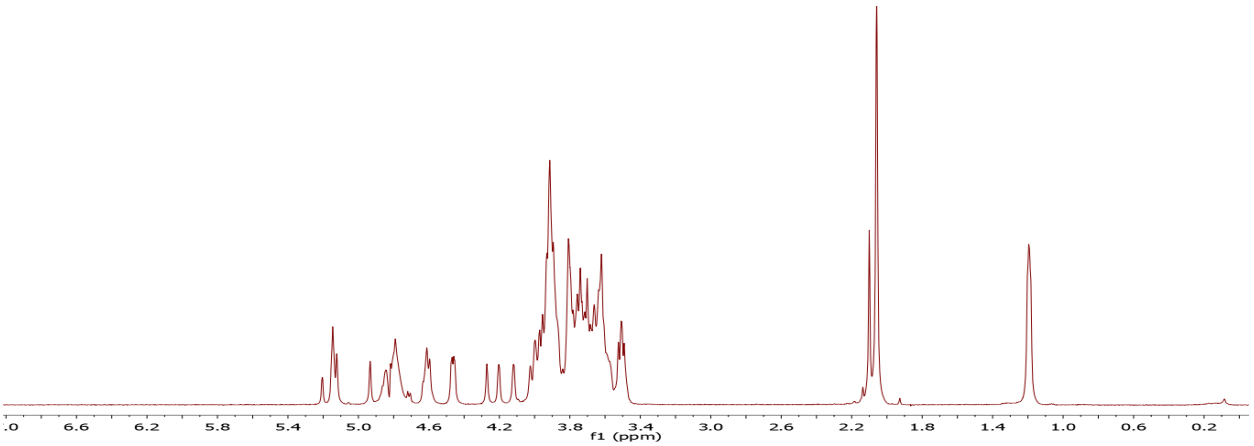
^{1}H NMR of **N002**



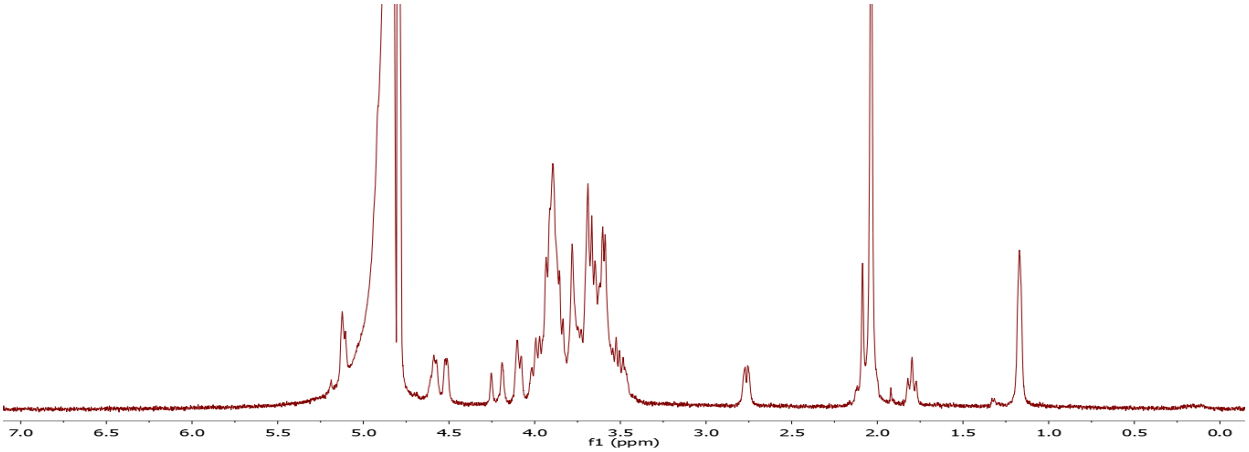
^{1}H NMR of **N003**



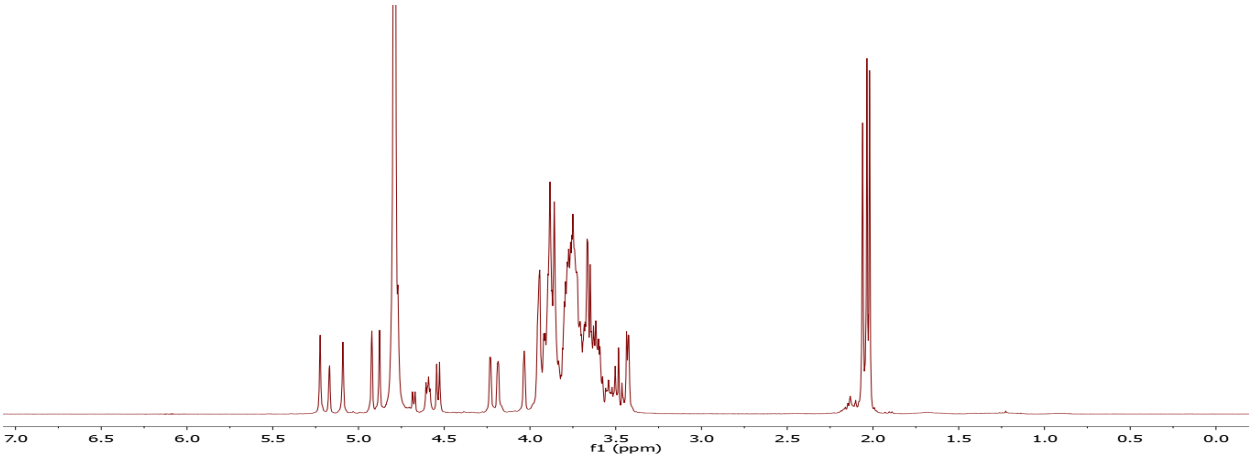
^{1}H NMR of **N004**



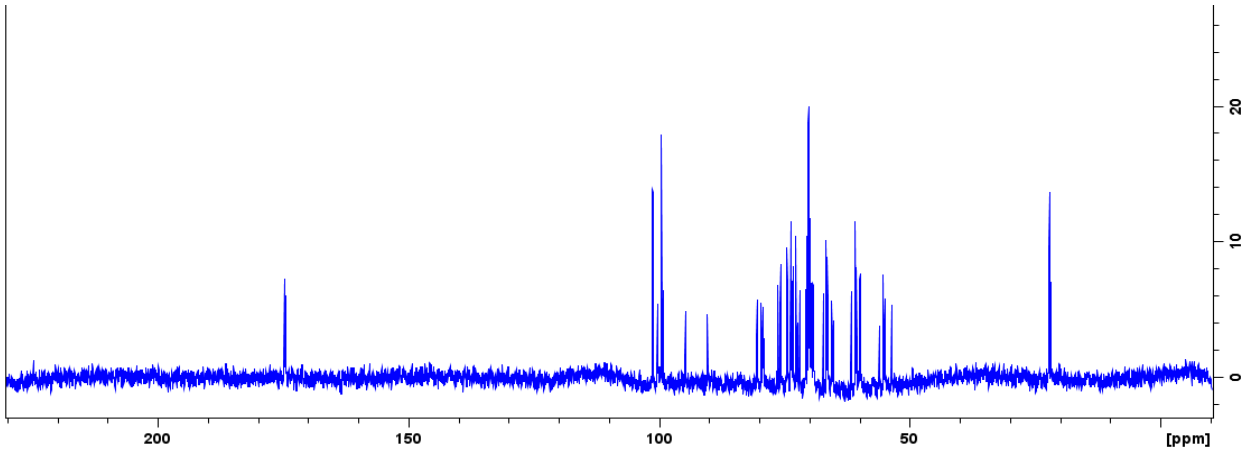
^{1}H NMR of **N005**



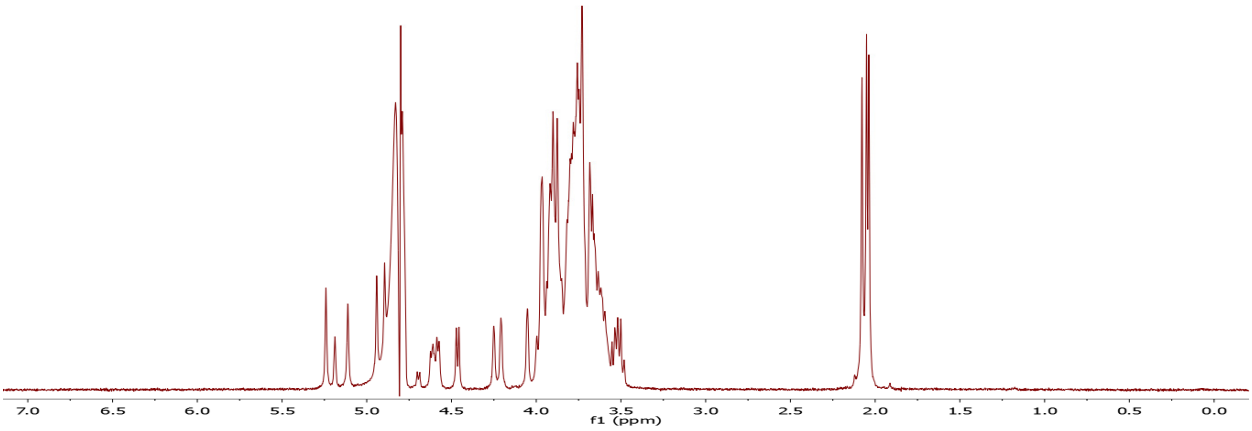
^{1}H NMR of **N010**



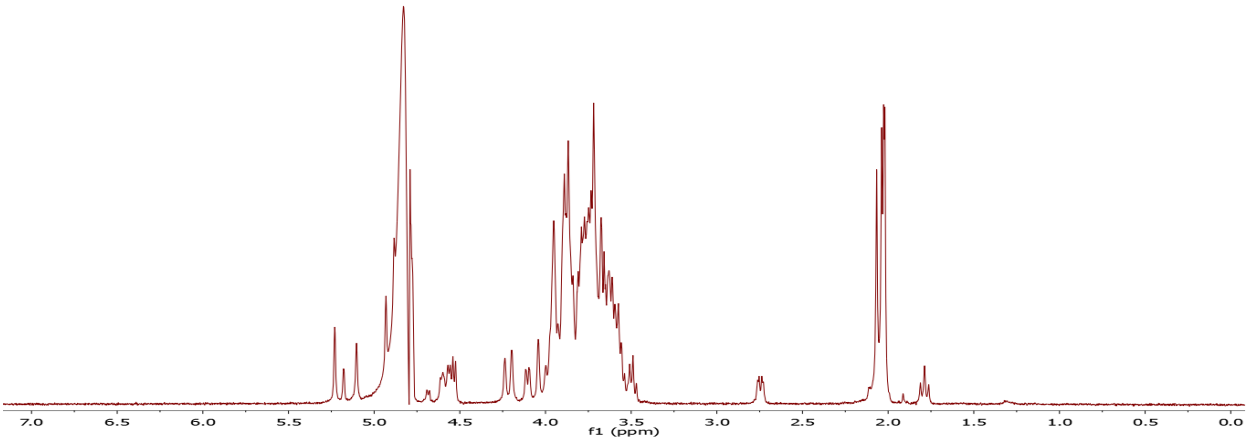
^{13}C NMR of **N010**



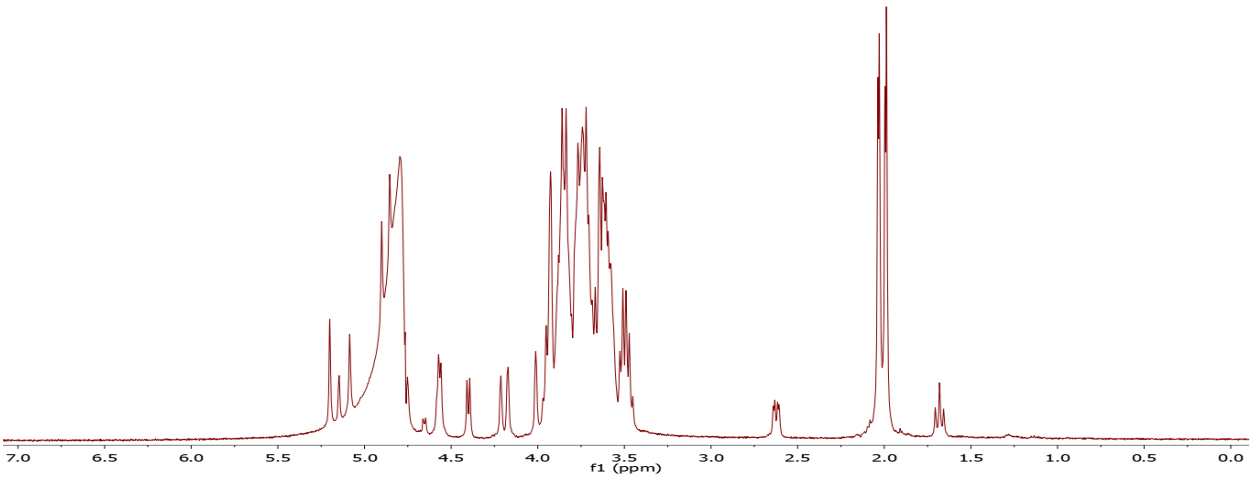
^{1}H NMR of **N011**



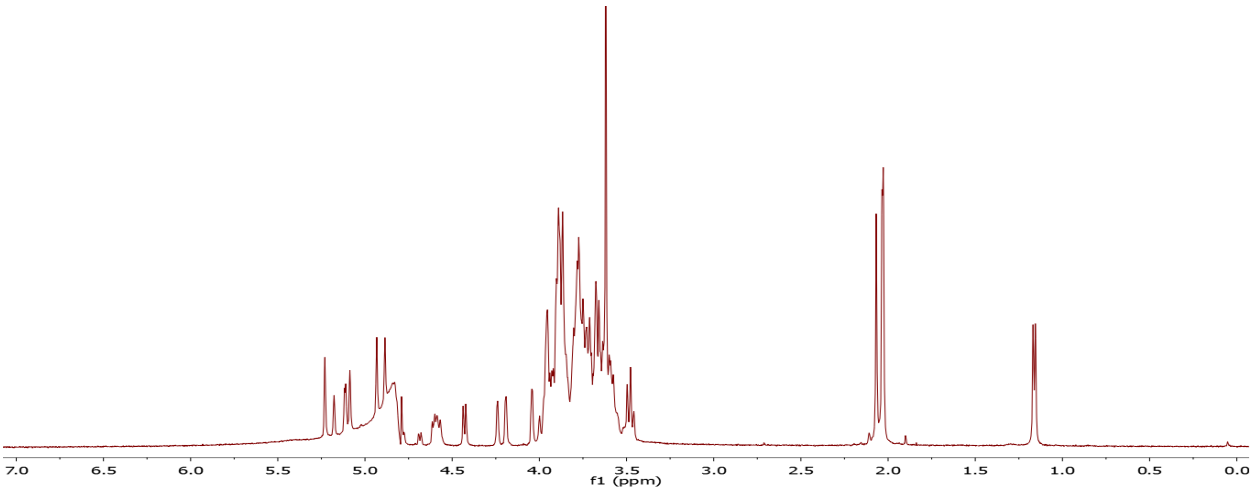
^{1}H NMR of **N012**



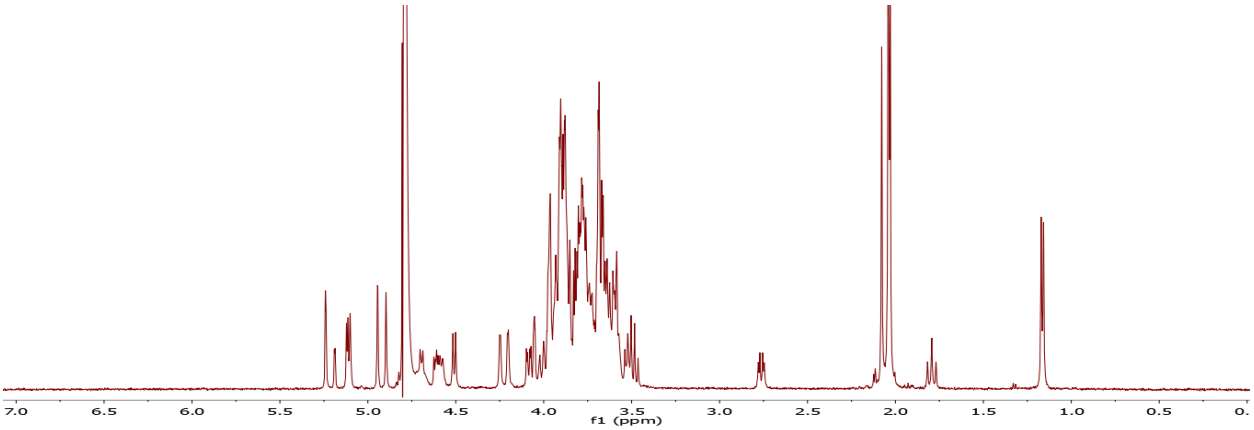
^{1}H NMR of **N013**



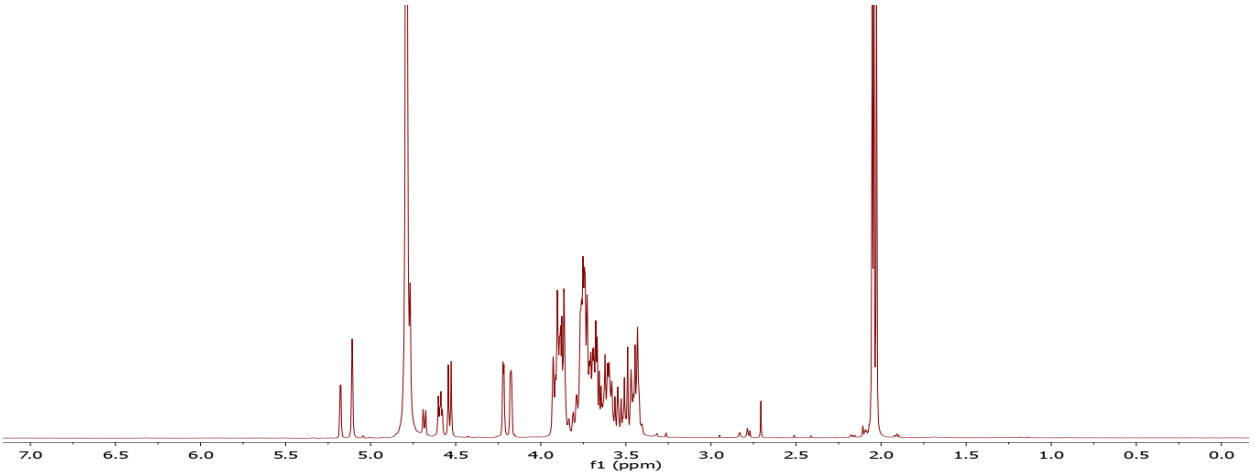
^{1}H NMR of **N014**



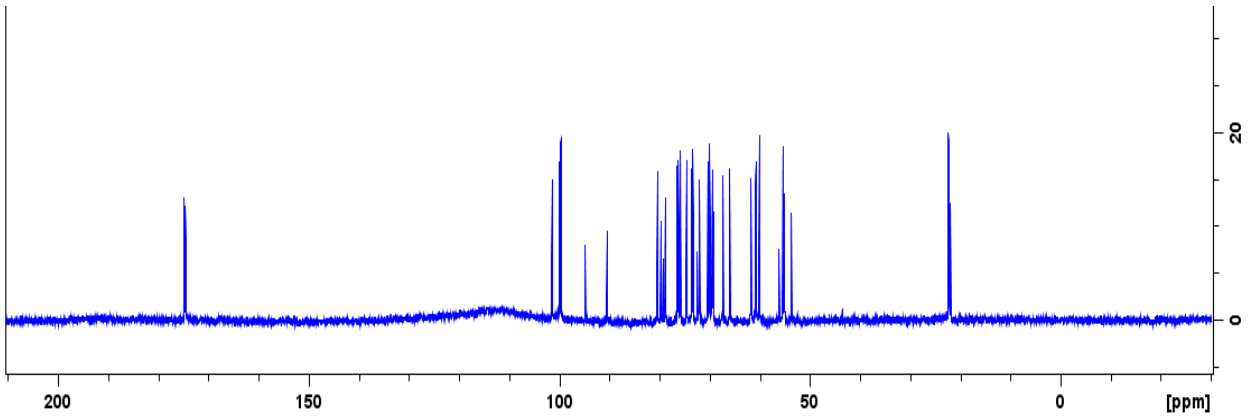
^{1}H NMR of **N015**



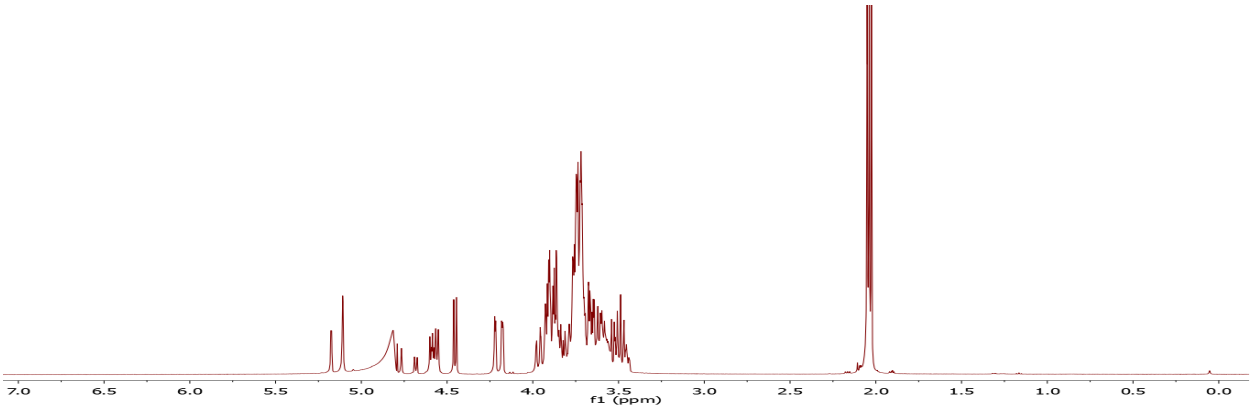
^{1}H NMR of **N020**



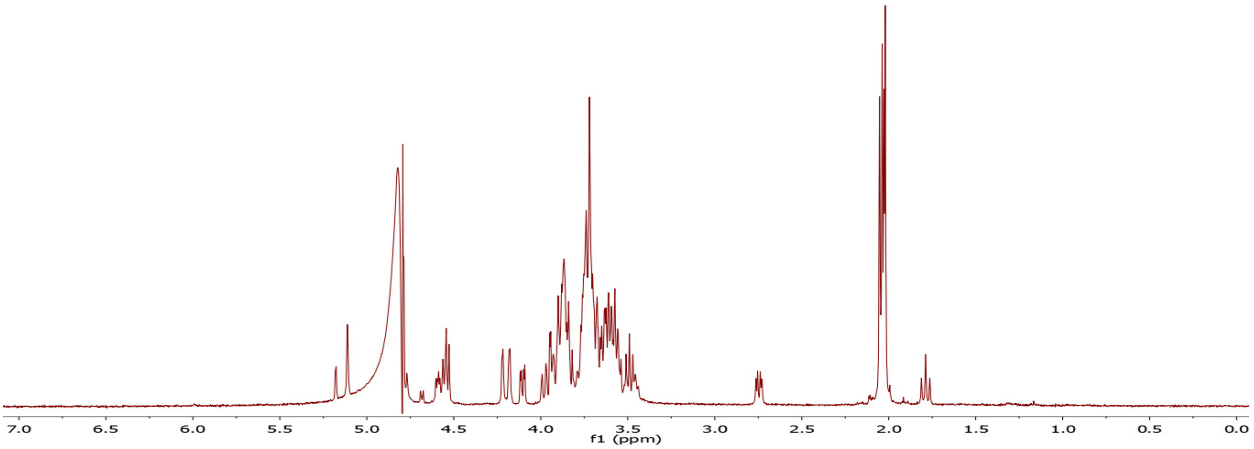
^{13}C NMR of **N020**



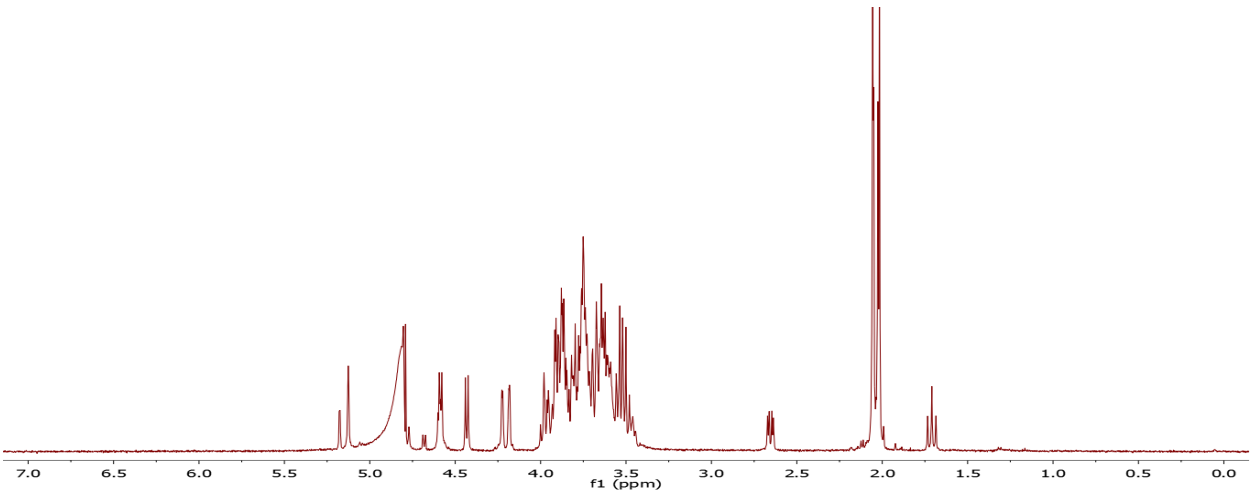
^{1}H NMR of **N021**



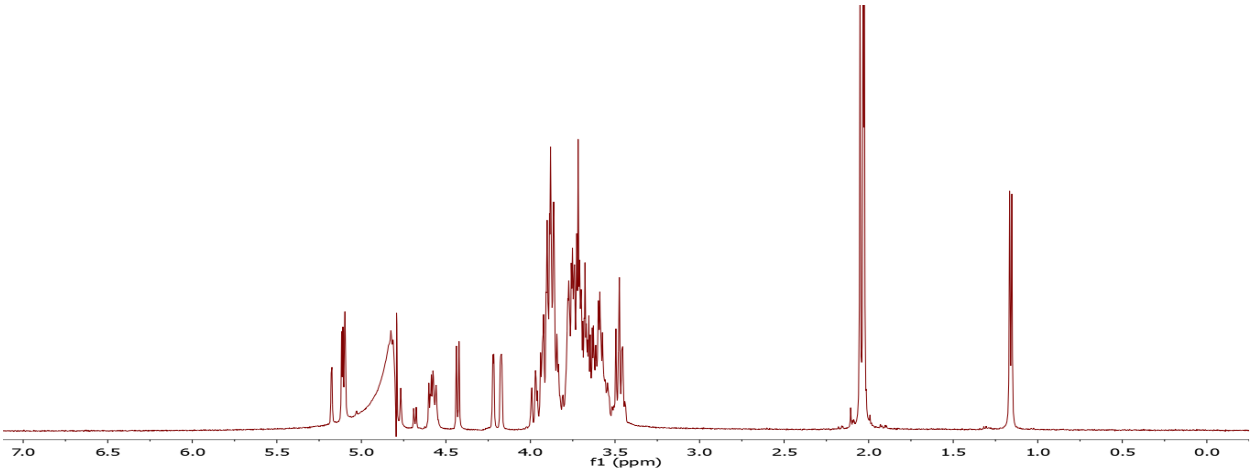
^{1}H NMR of **N022**



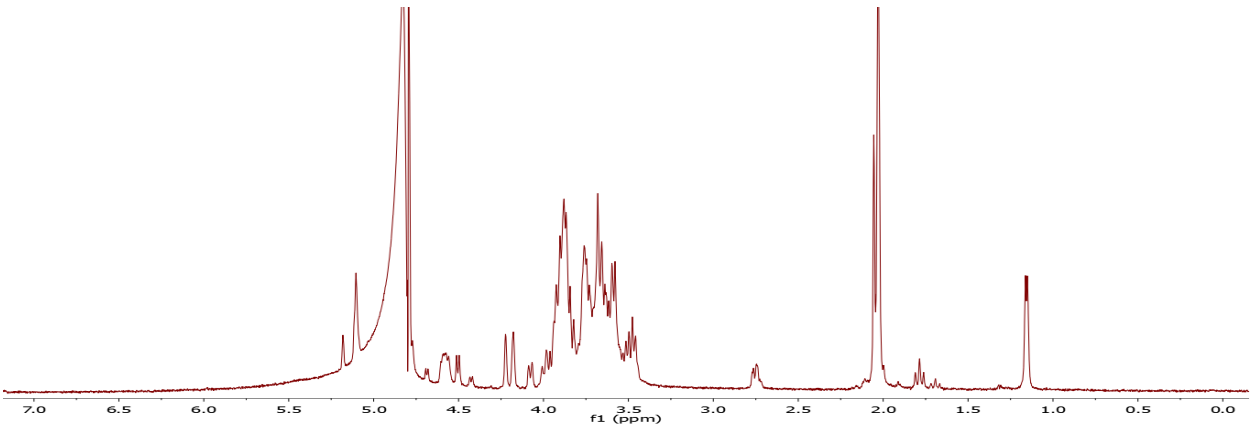
^{1}H NMR of **N023**



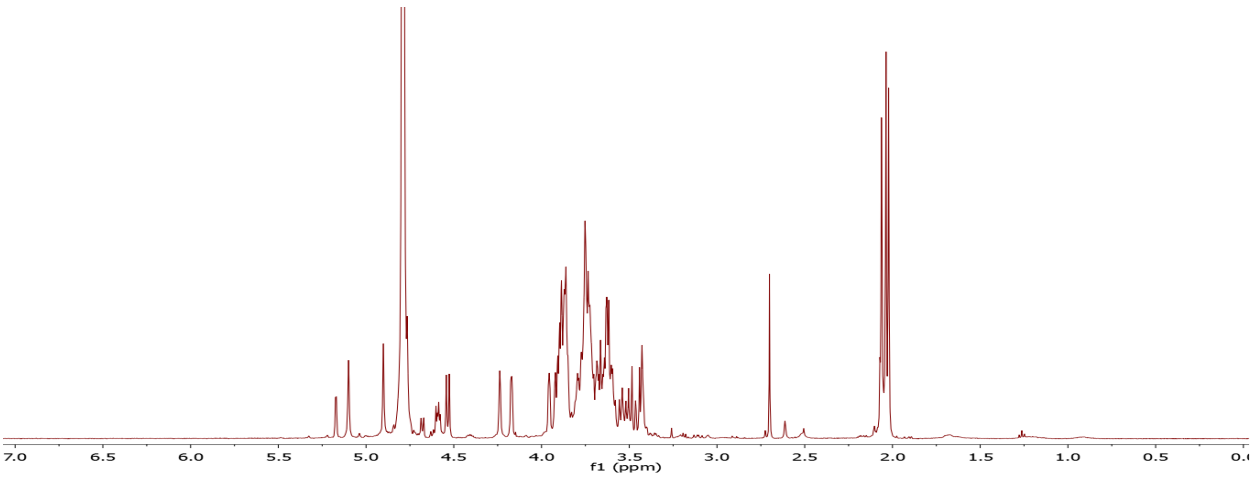
^{1}H NMR of **N024**



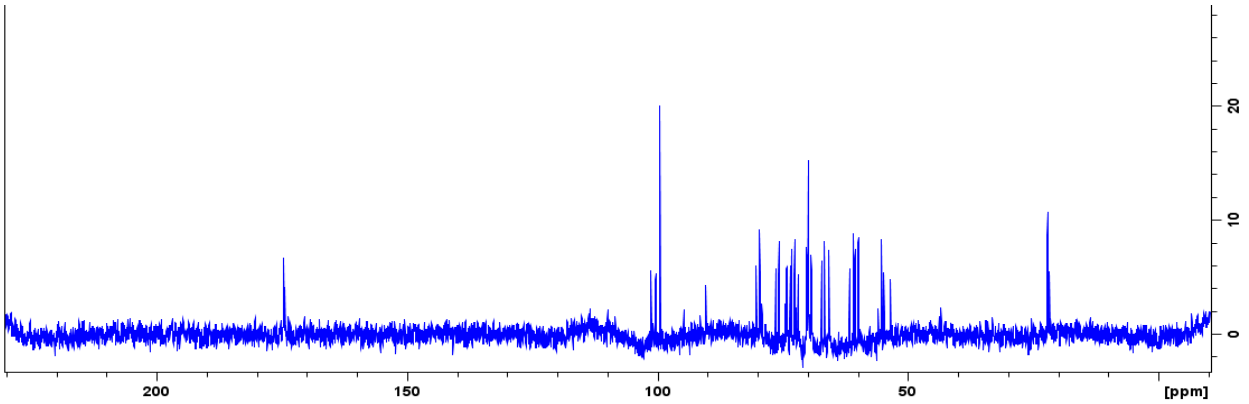
^{1}H NMR of **N025**



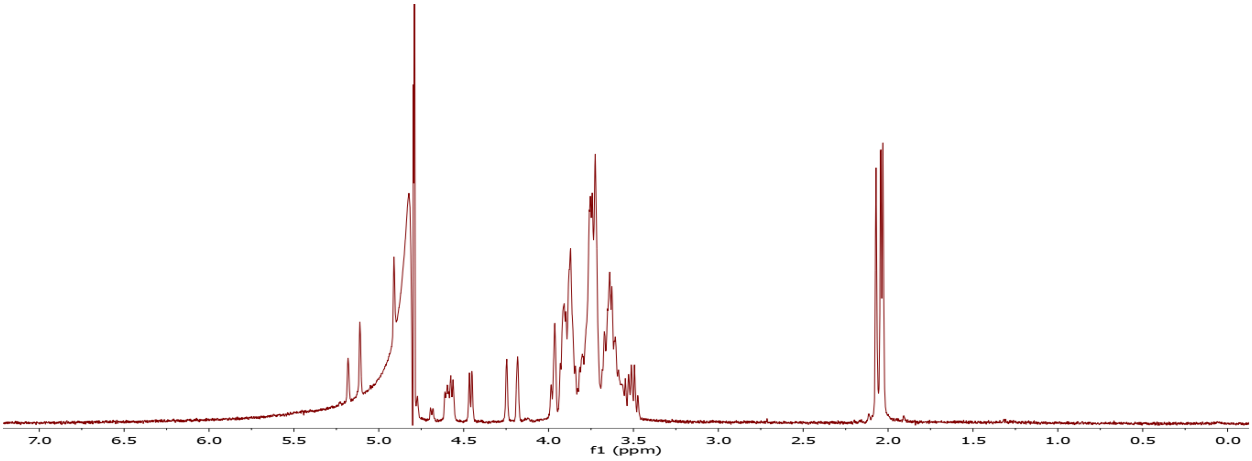
^{1}H NMR of **N030**



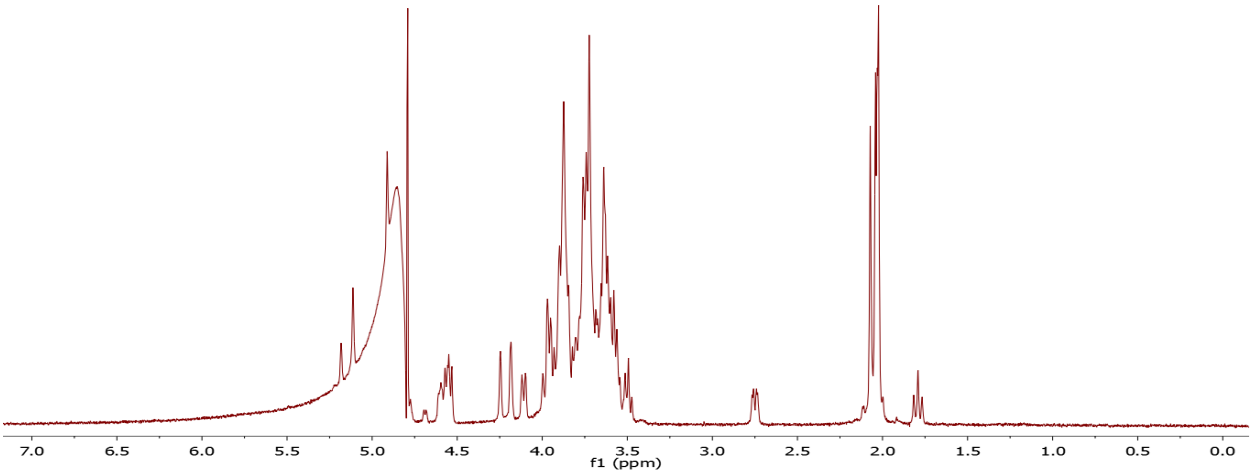
^{13}C NMR of **N030**



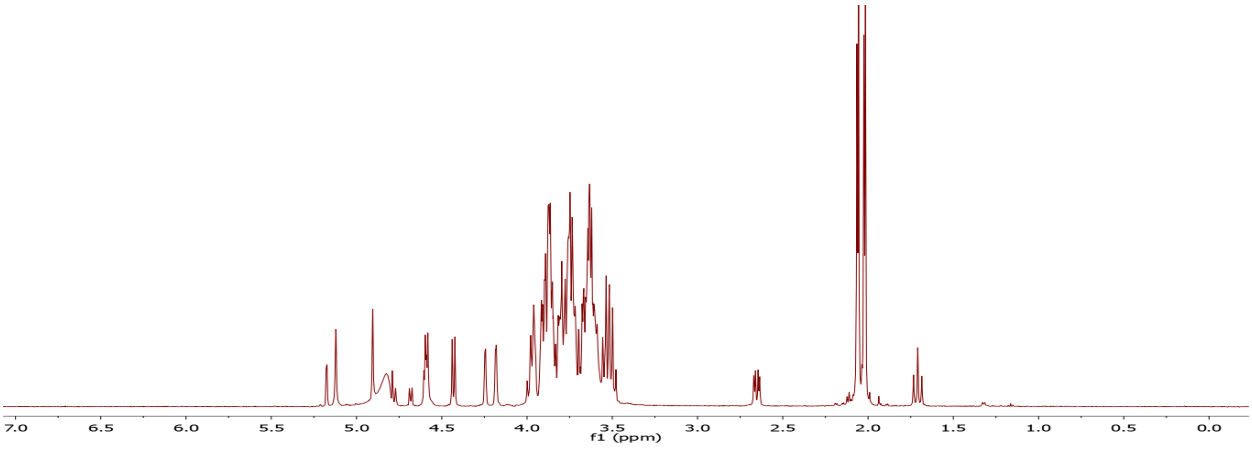
^{1}H NMR of **N031**



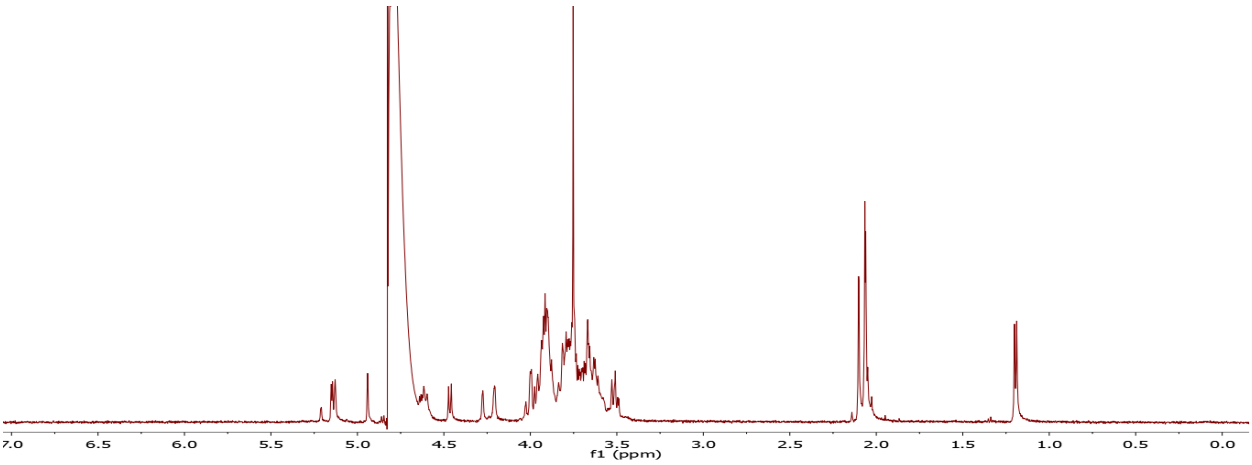
^{1}H NMR of **N032**



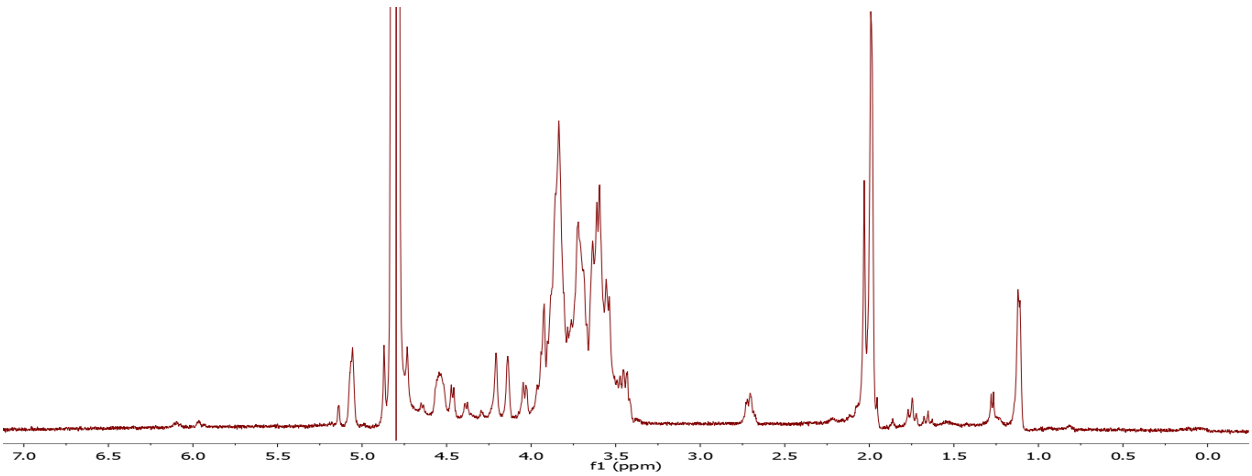
^{1}H NMR of **N033**



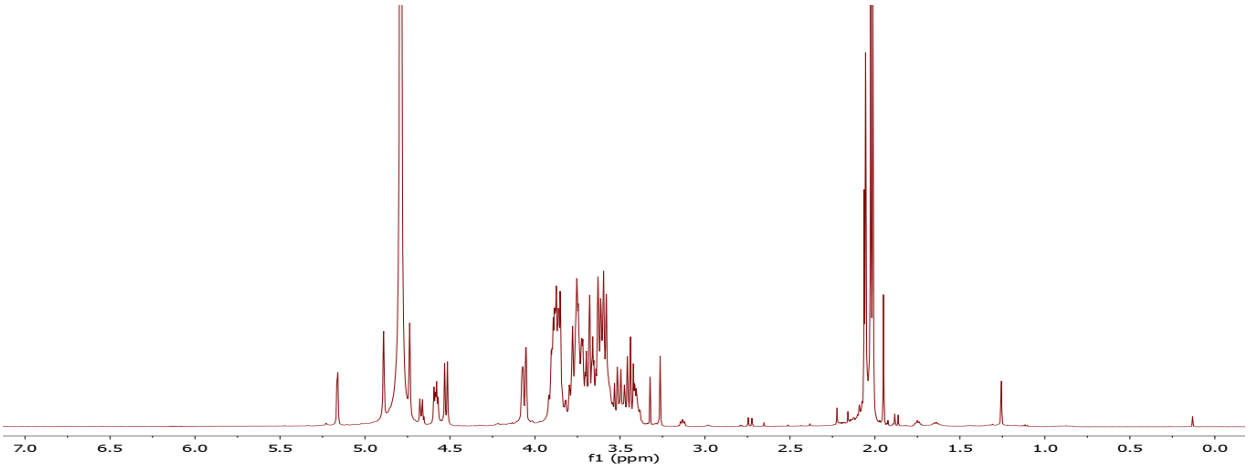
^{1}H NMR of **N034**



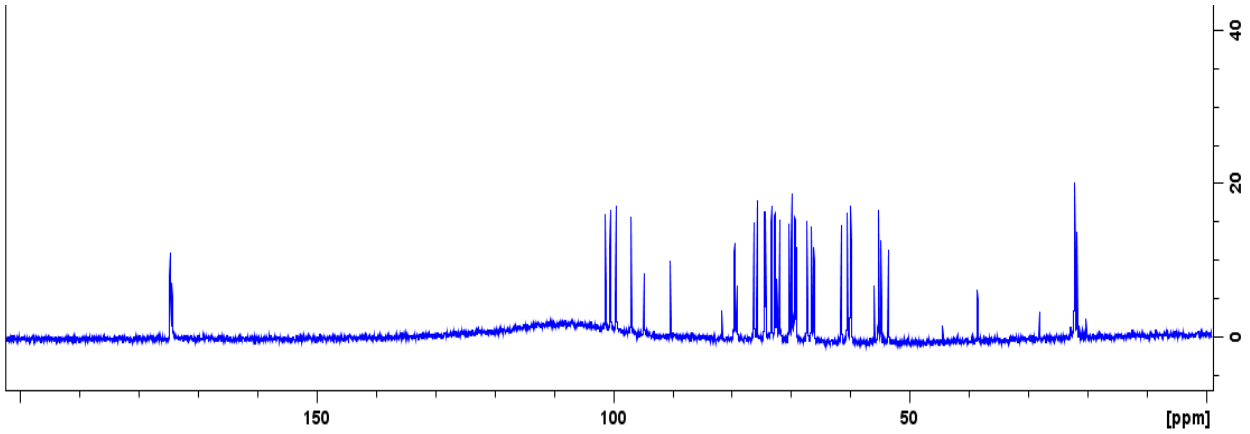
^{1}H NMR of **N035**



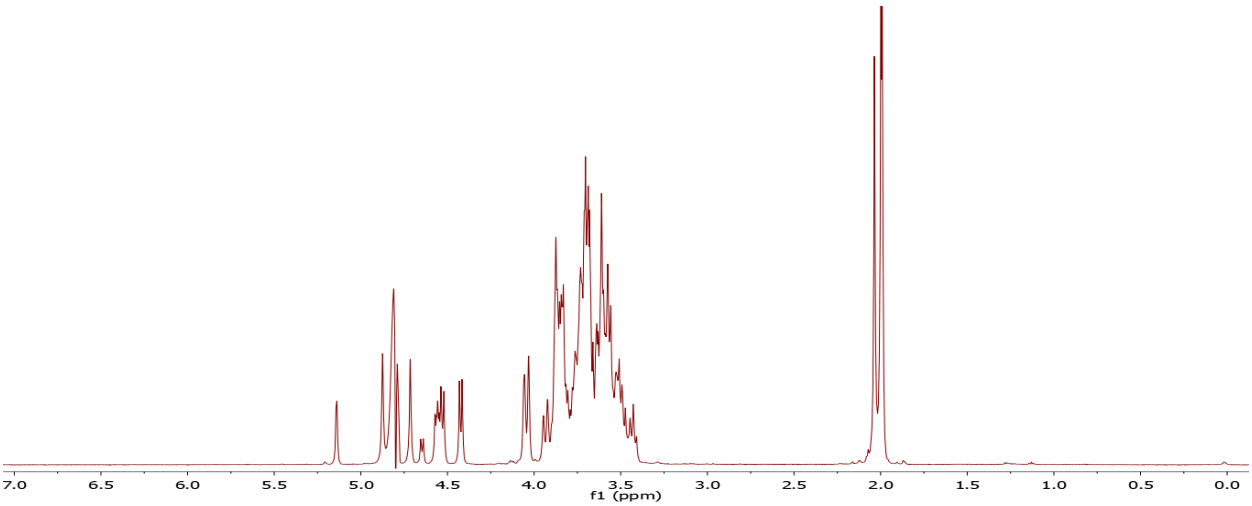
^{1}H NMR of **N040**



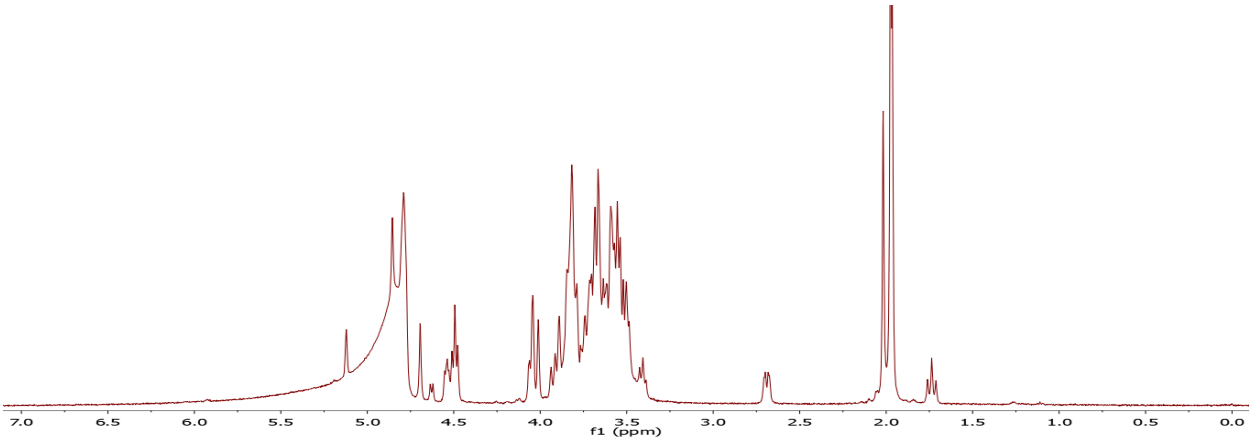
^{13}C NMR of **N040**



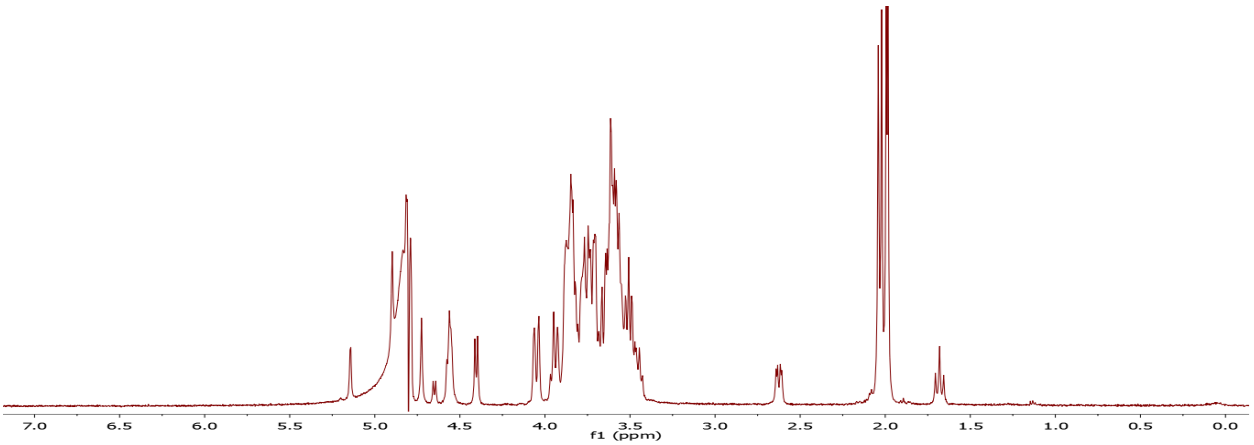
^{1}H NMR of **N041**



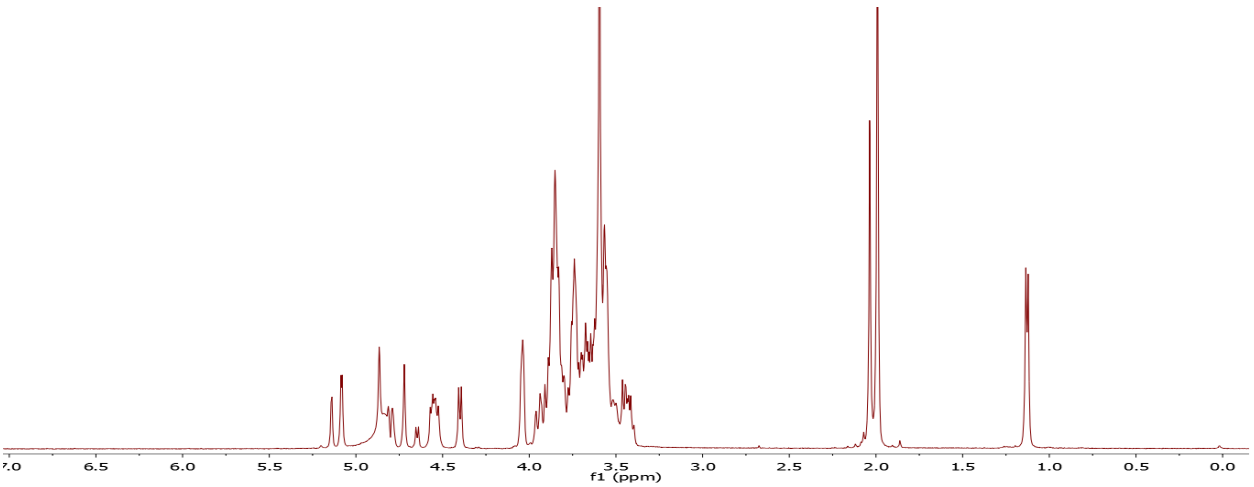
^{1}H NMR of **N042**



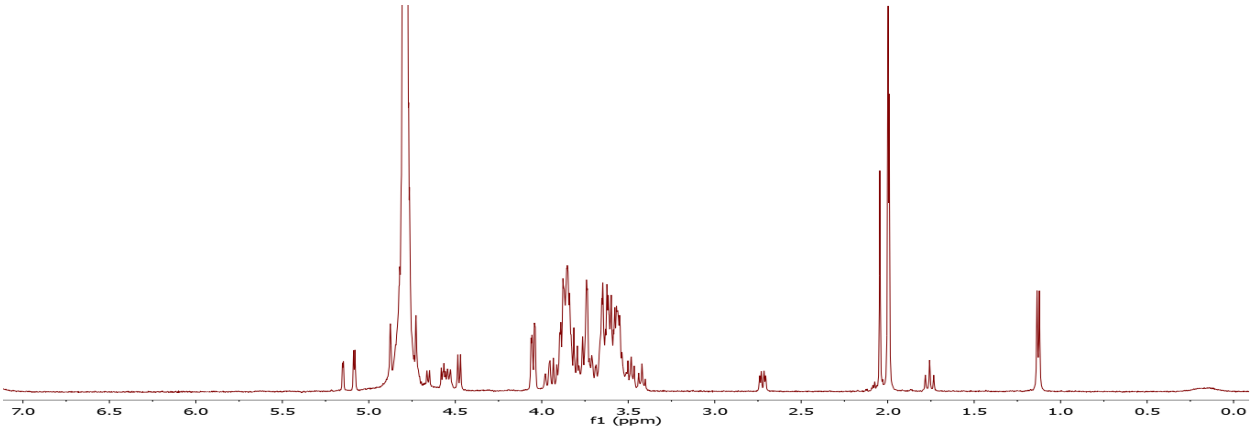
^{1}H NMR of **N043**



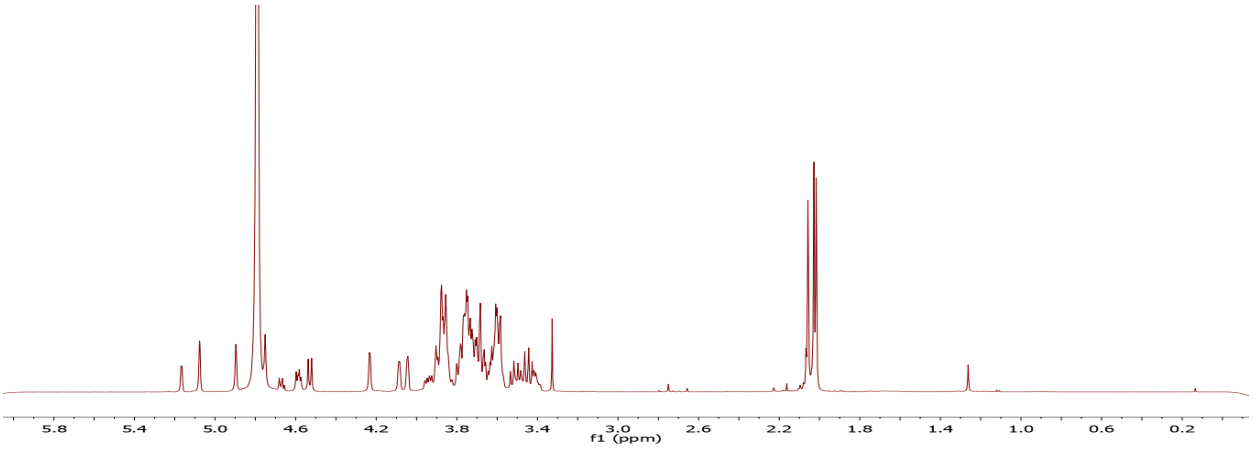
^{1}H NMR of **N044**



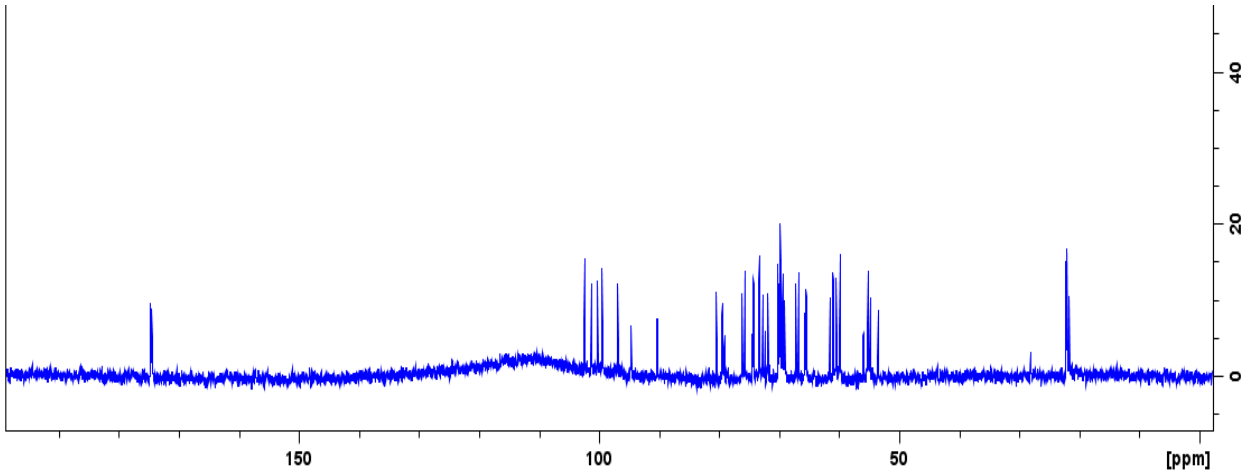
^{1}H NMR of **N045**



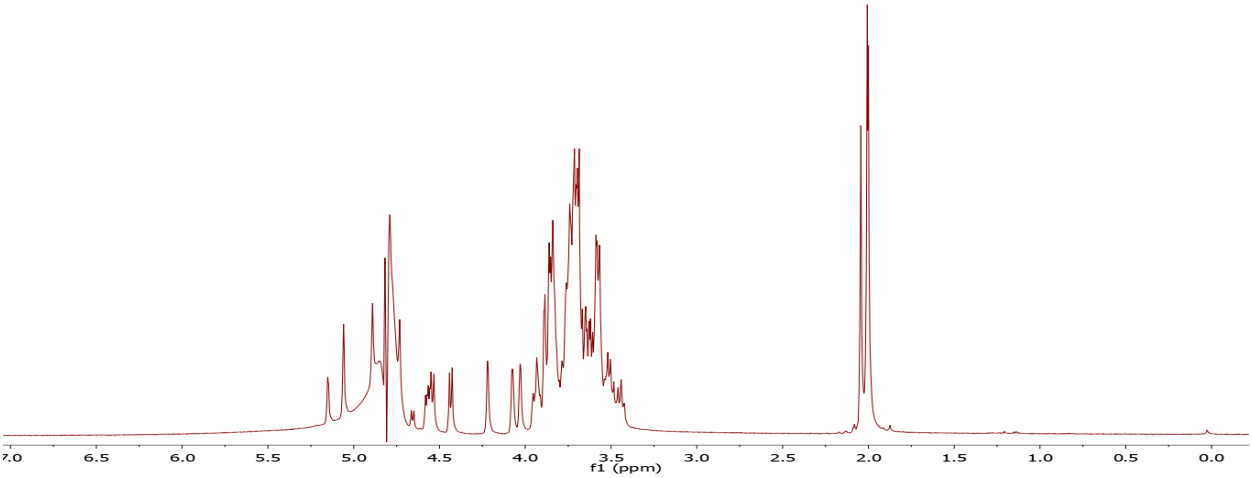
^{1}H NMR of **N050**



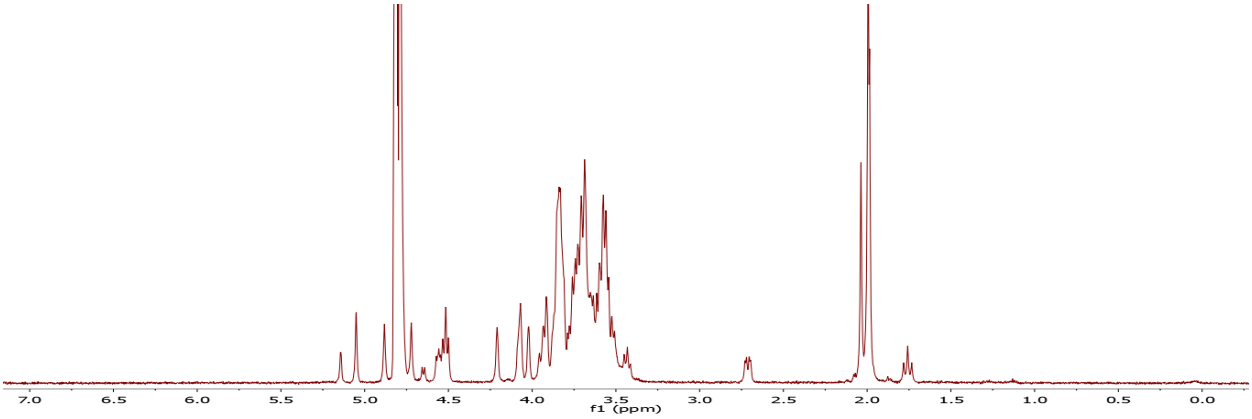
^{13}C NMR of **N050**



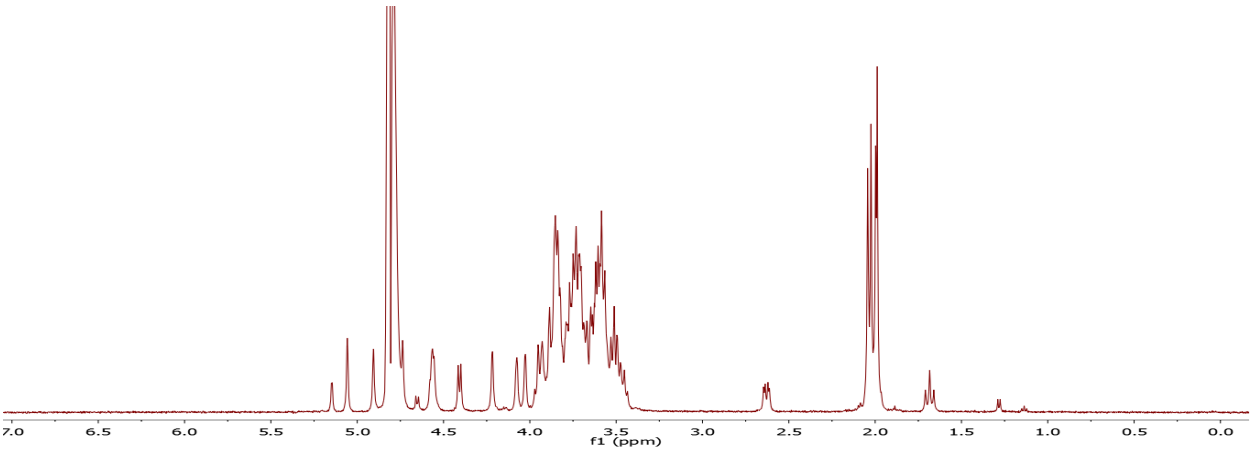
^{1}H NMR of **N051**



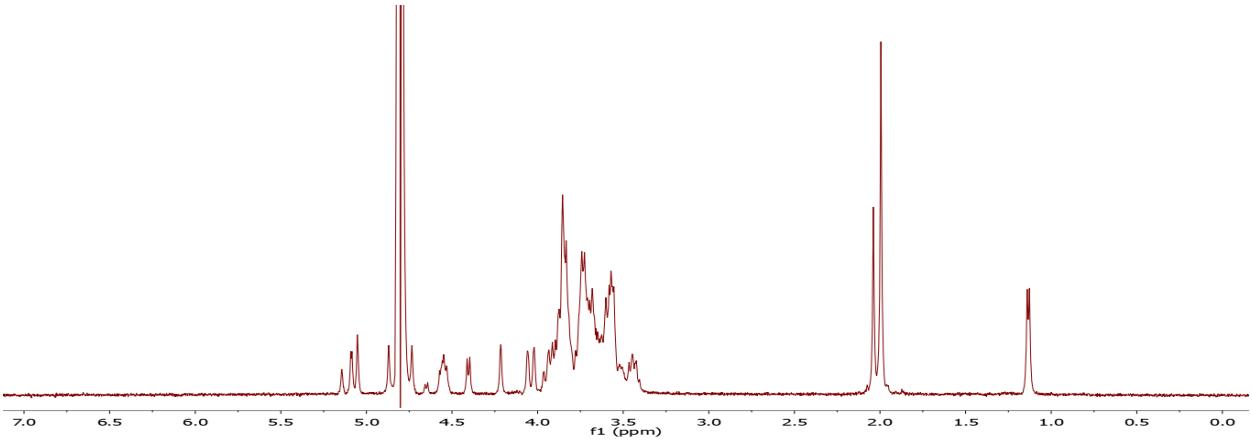
^{1}H NMR of **N052**



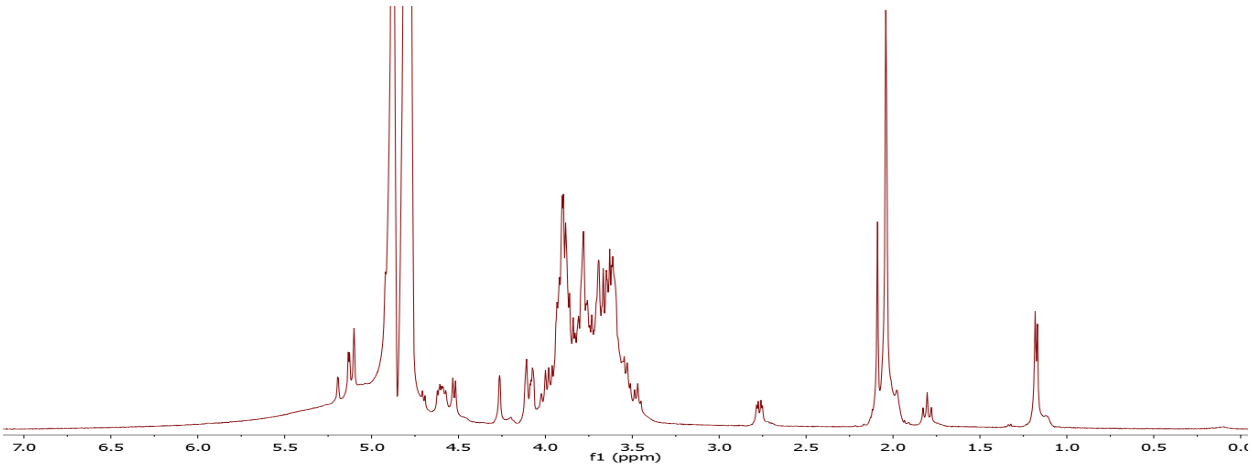
^{1}H NMR of **N053**



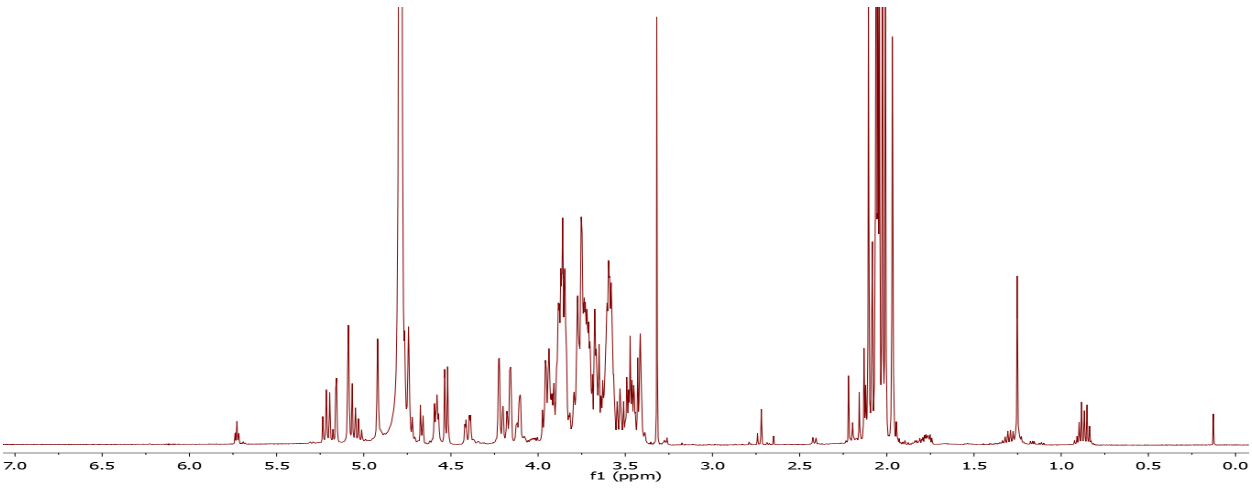
^{1}H NMR of **N054**



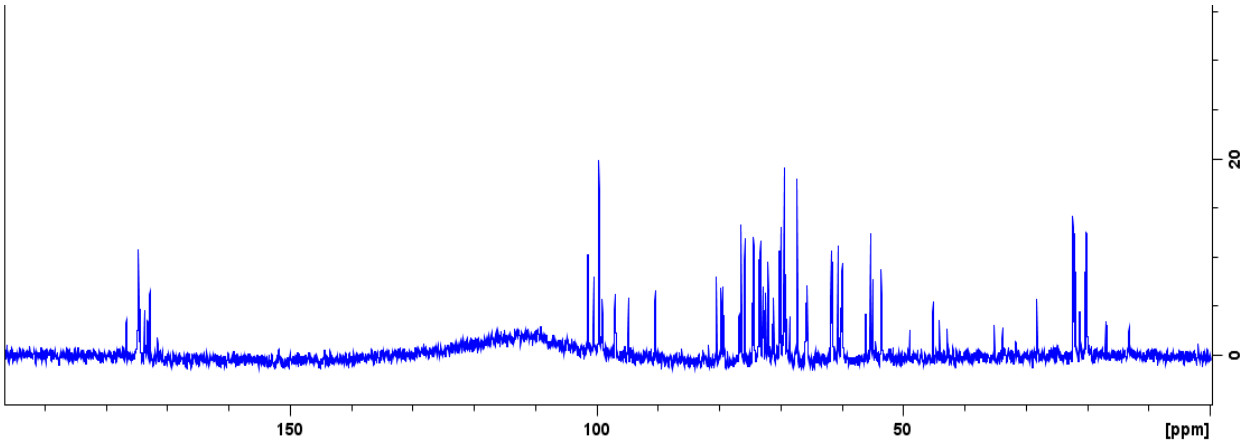
^{1}H NMR of **N055**



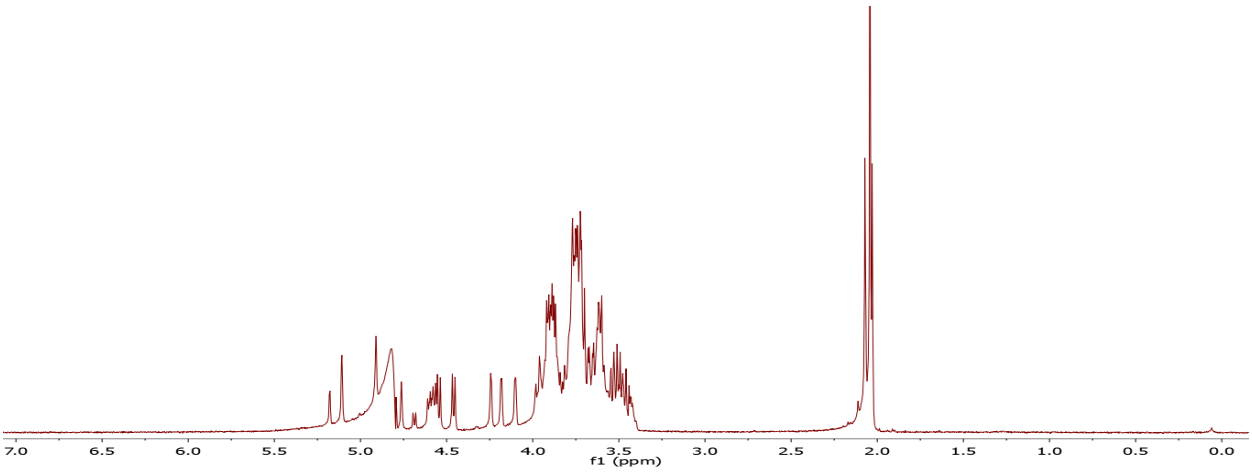
^{1}H NMR of **N110**



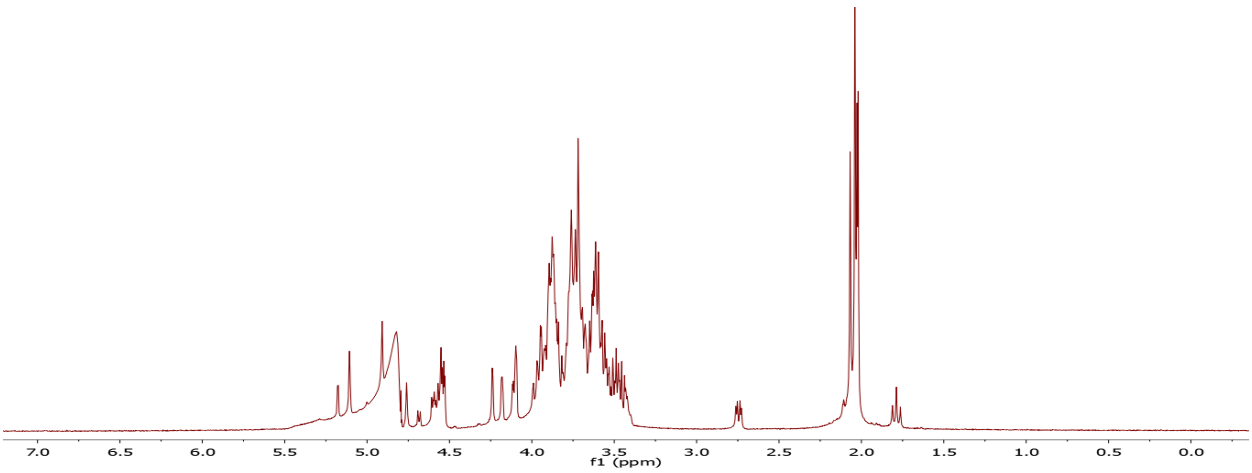
^{13}C NMR of **N110**



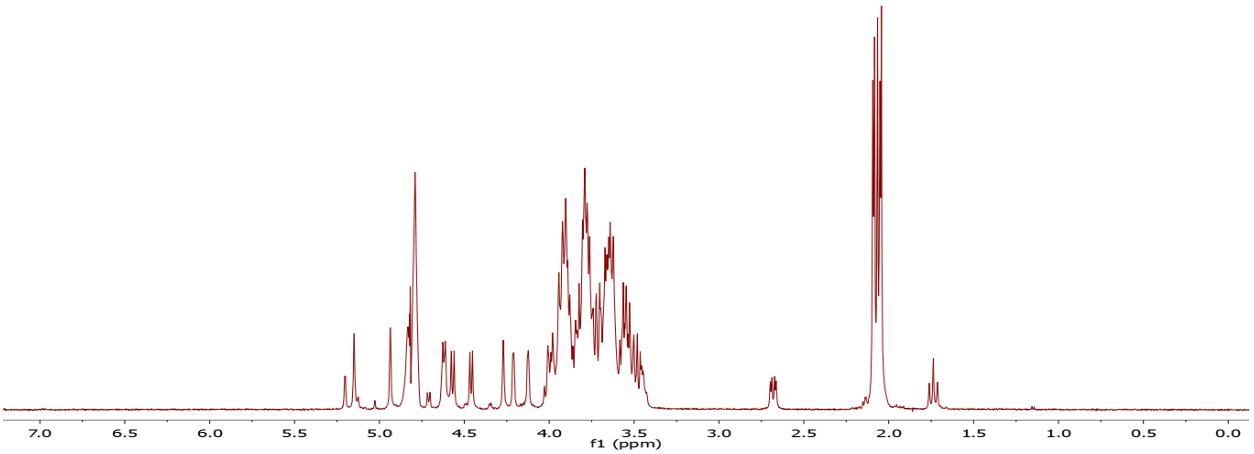
^{1}H NMR of **N111**



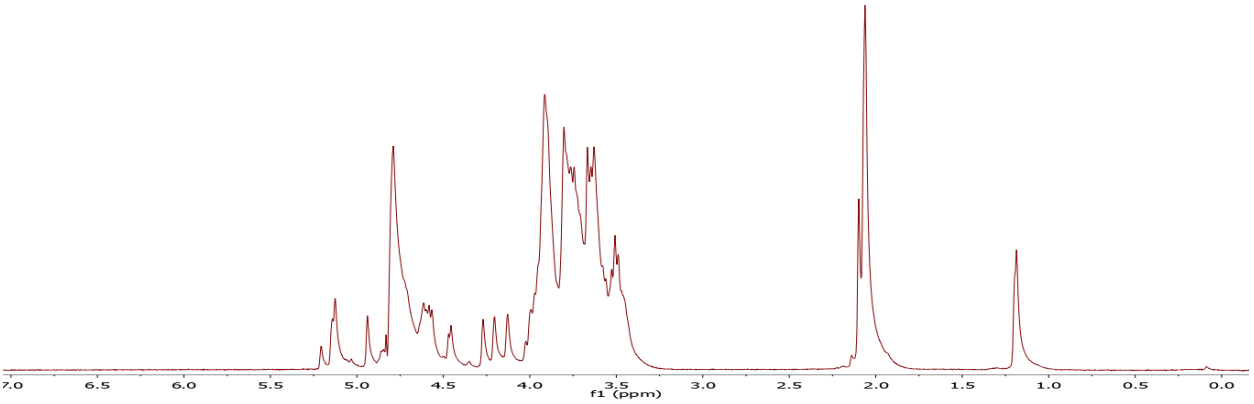
^{1}H NMR of **N112**



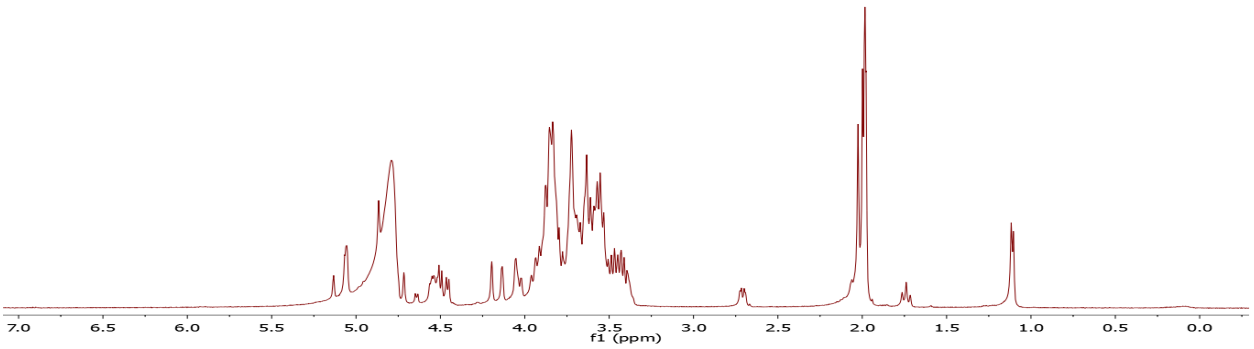
^{1}H NMR of **N113**



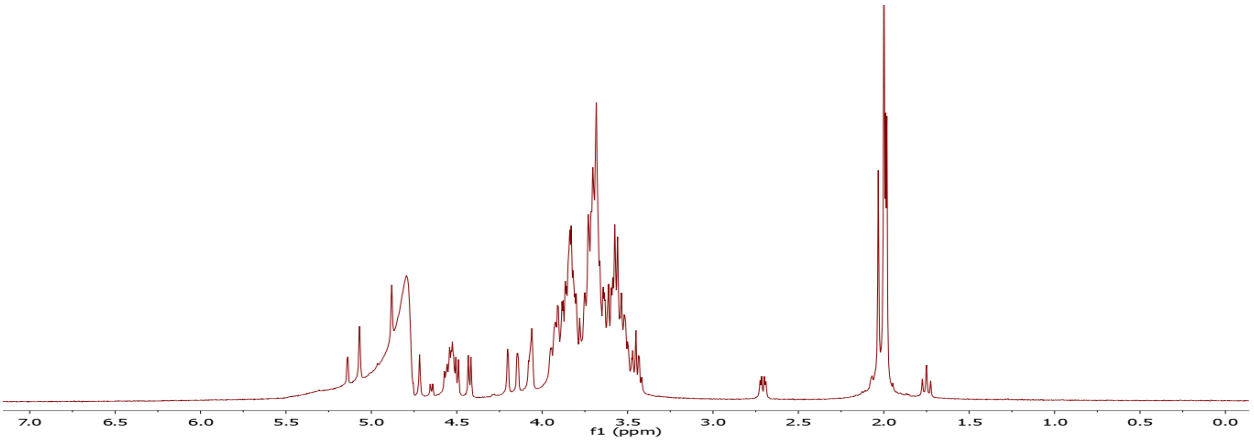
^{1}H NMR of **N114**



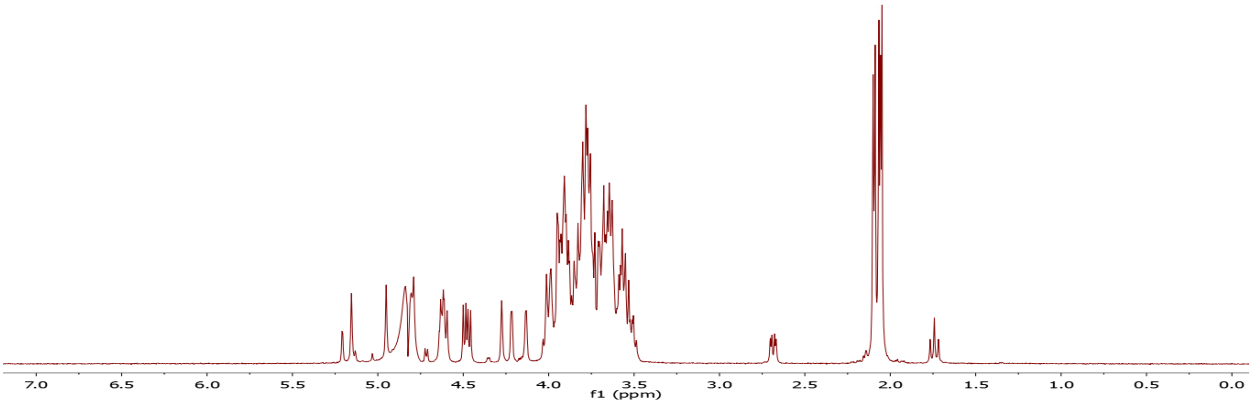
^{1}H NMR of **N115**



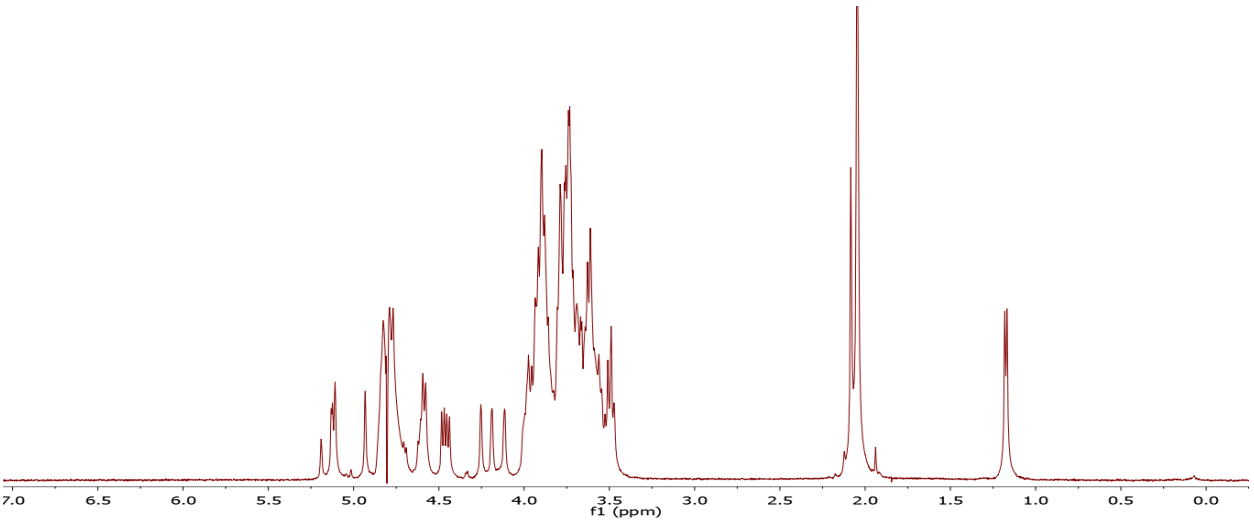
^{1}H NMR of **N122**



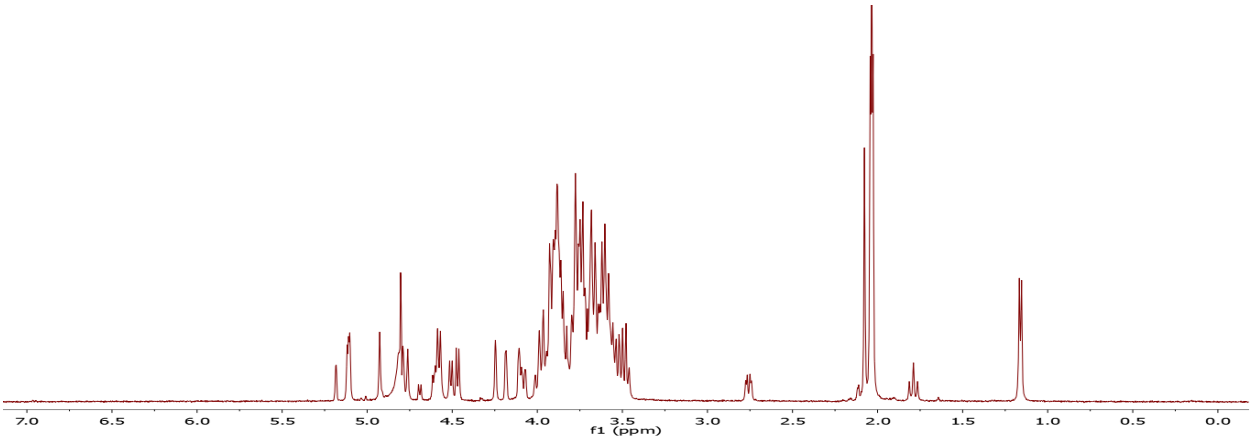
^{1}H NMR of **N123**



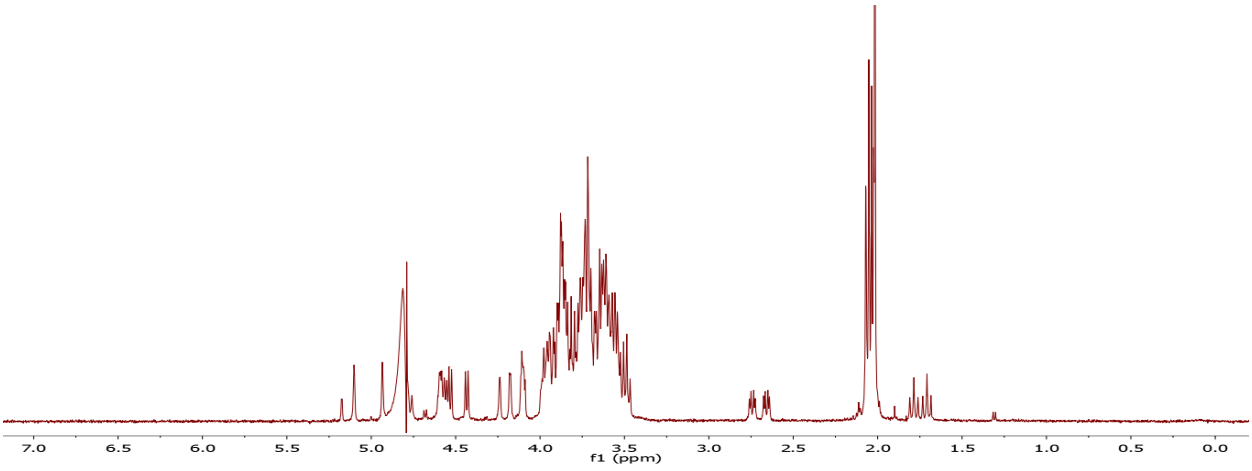
^{1}H NMR of **N124**



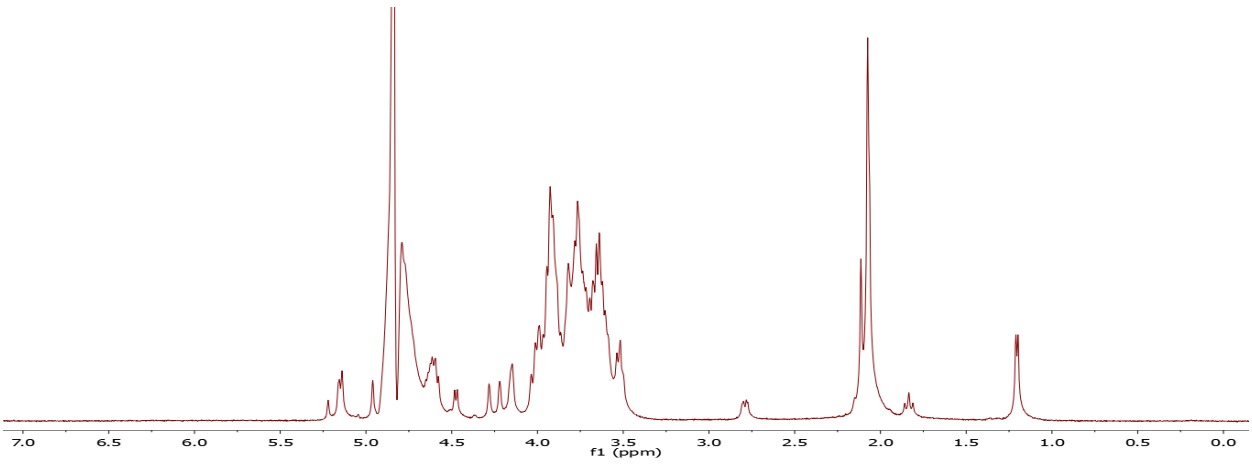
^{1}H NMR of **N125**



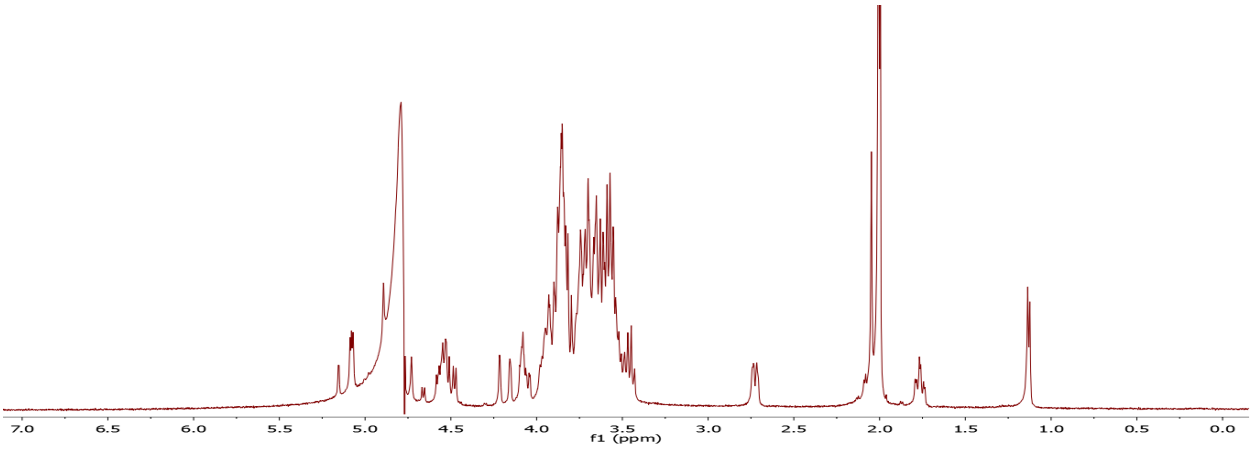
^{1}H NMR of **N133**



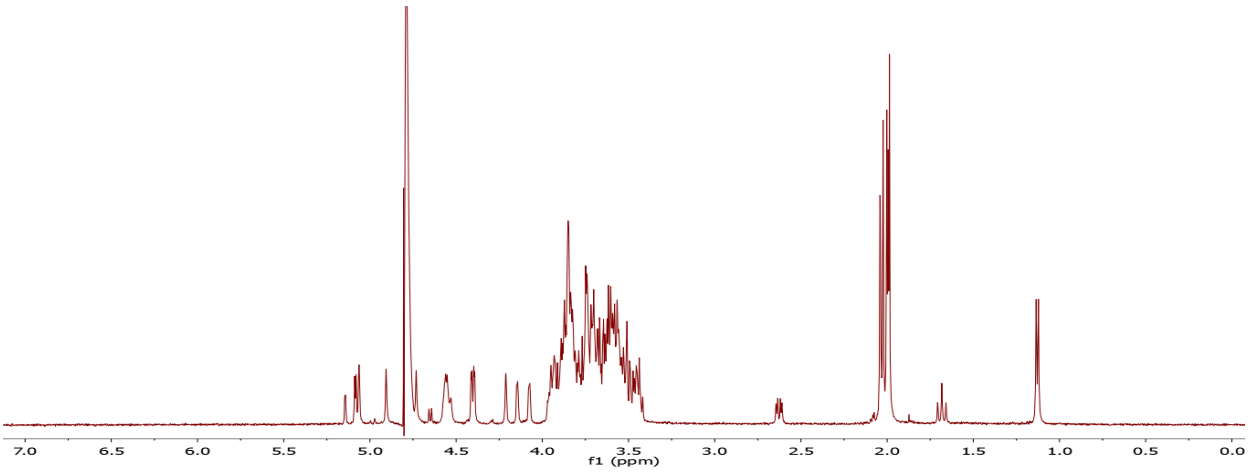
^{1}H NMR of **N134**



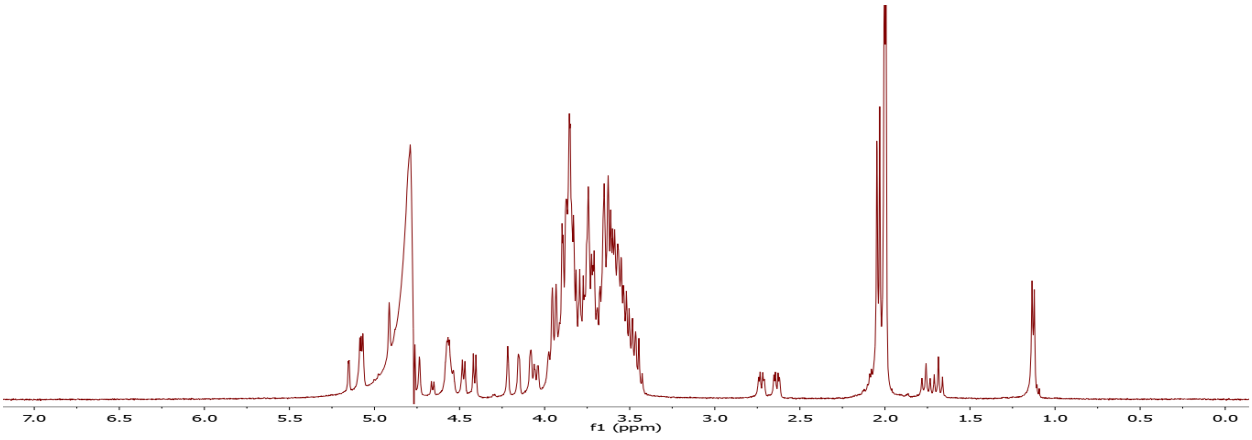
^{1}H NMR of **N135**



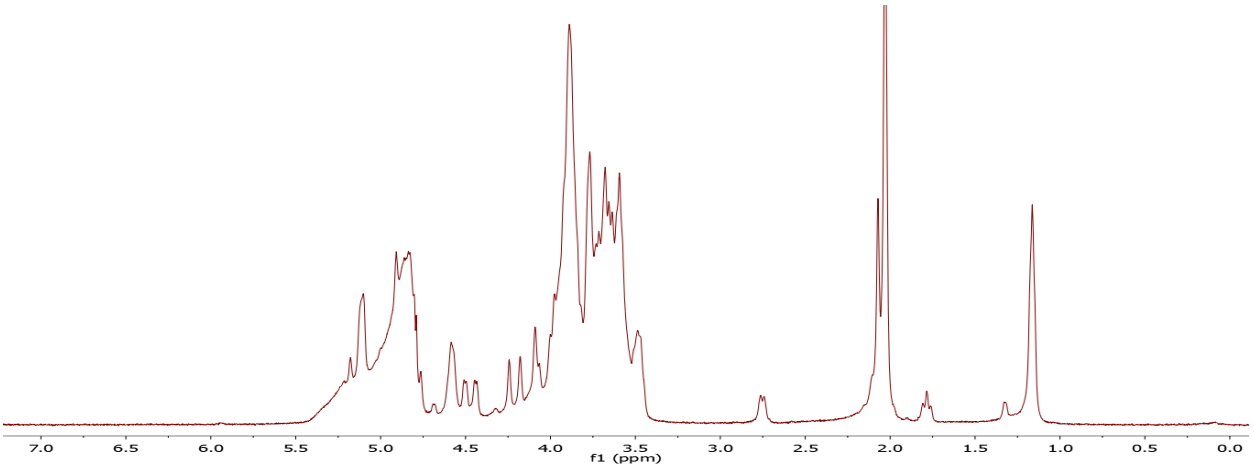
^{1}H NMR of **N144**



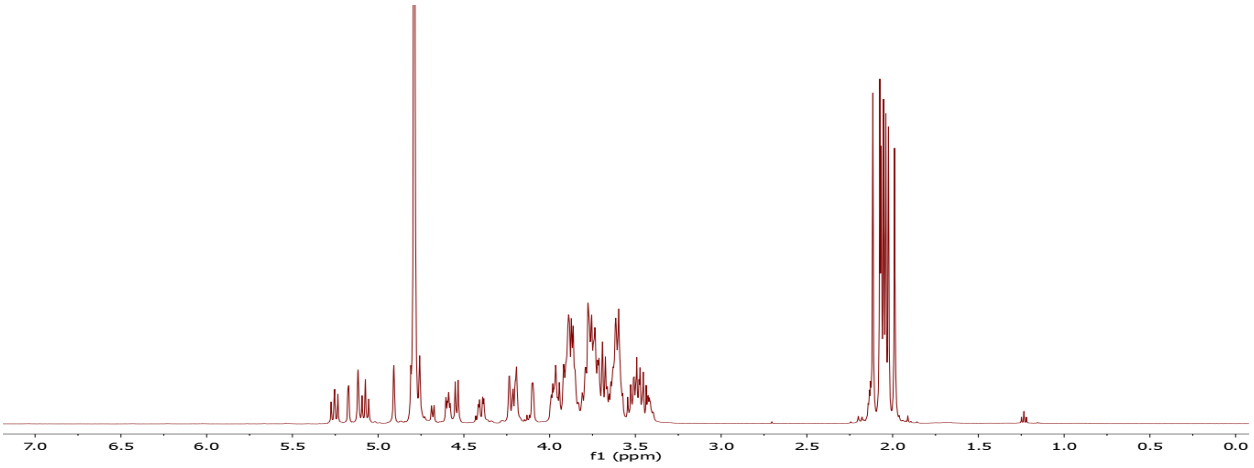
^{1}H NMR of **N145**



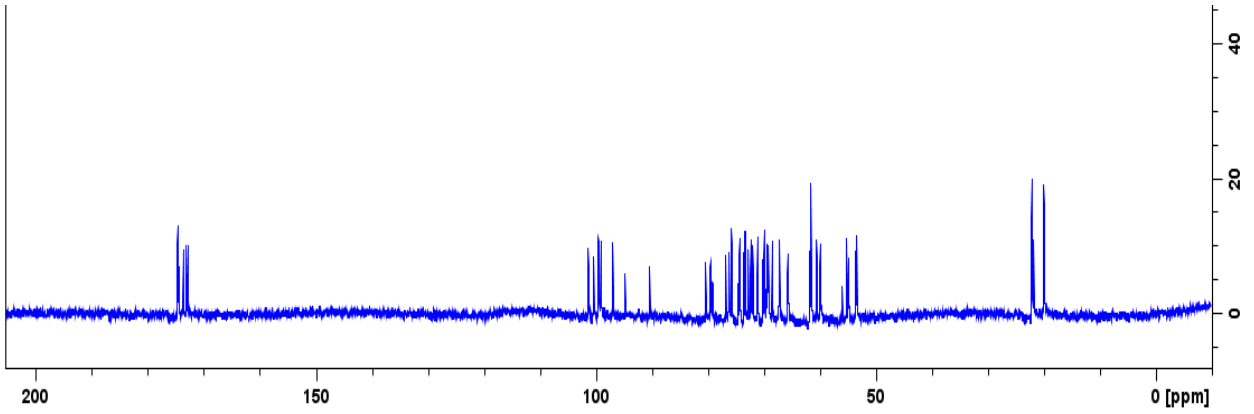
^{1}H NMR of **N155**



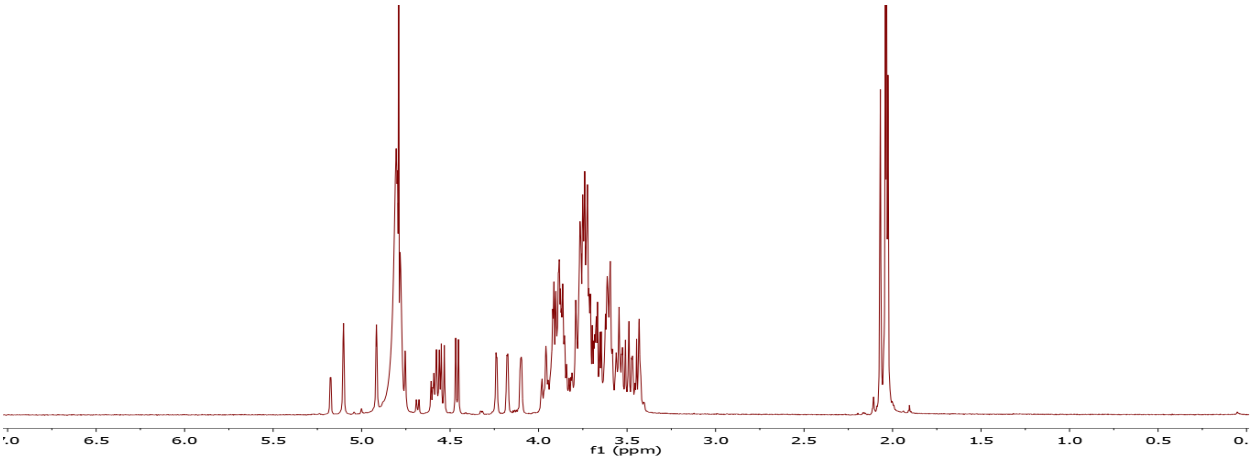
^{1}H NMR of **N210**



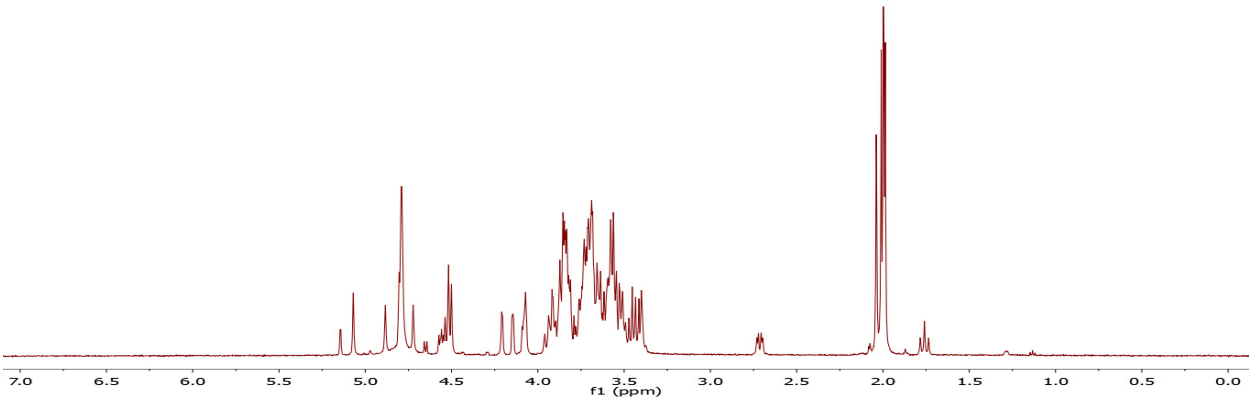
^{13}C NMR of **N210**



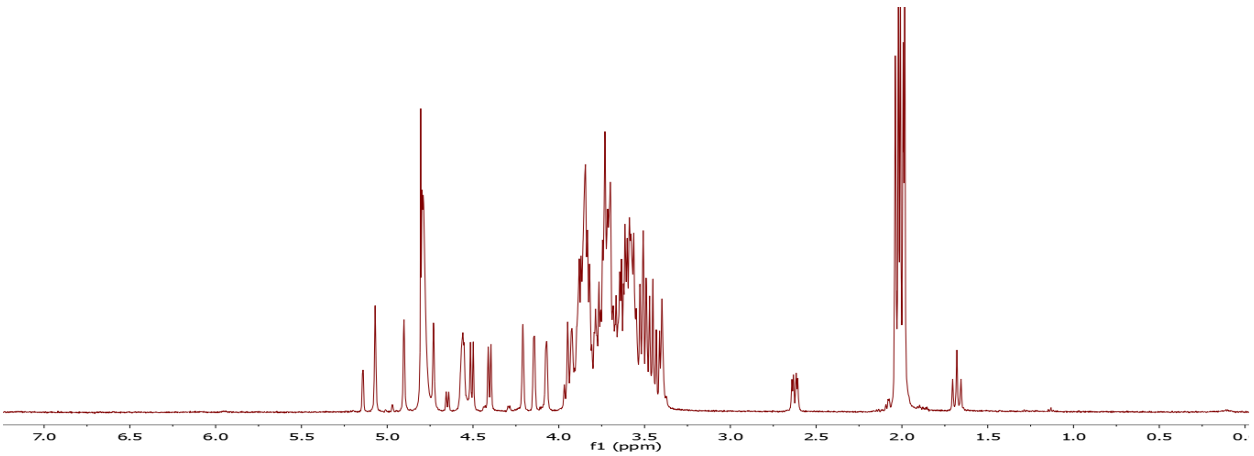
^{1}H NMR of **N211**



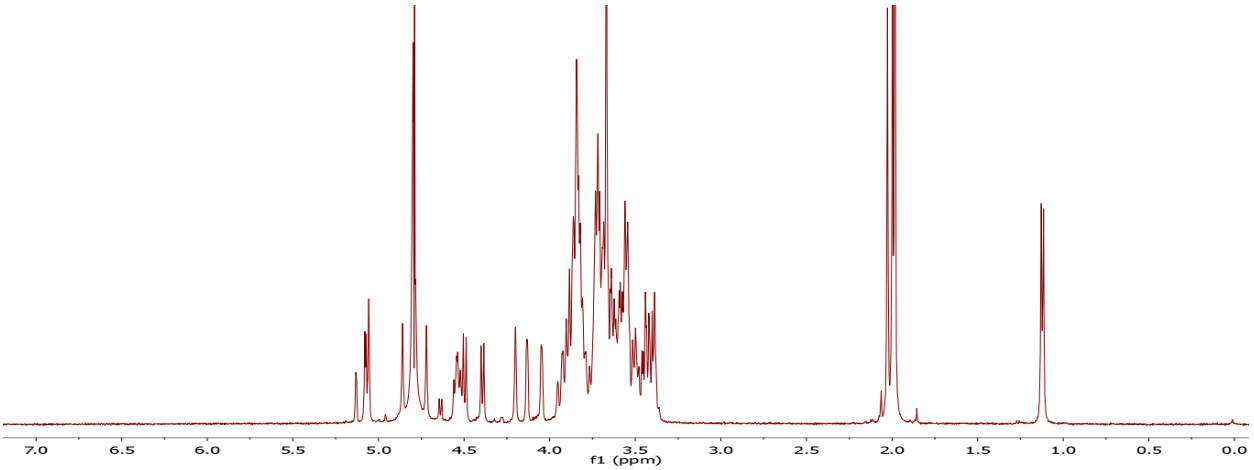
^{1}H NMR of **N212**



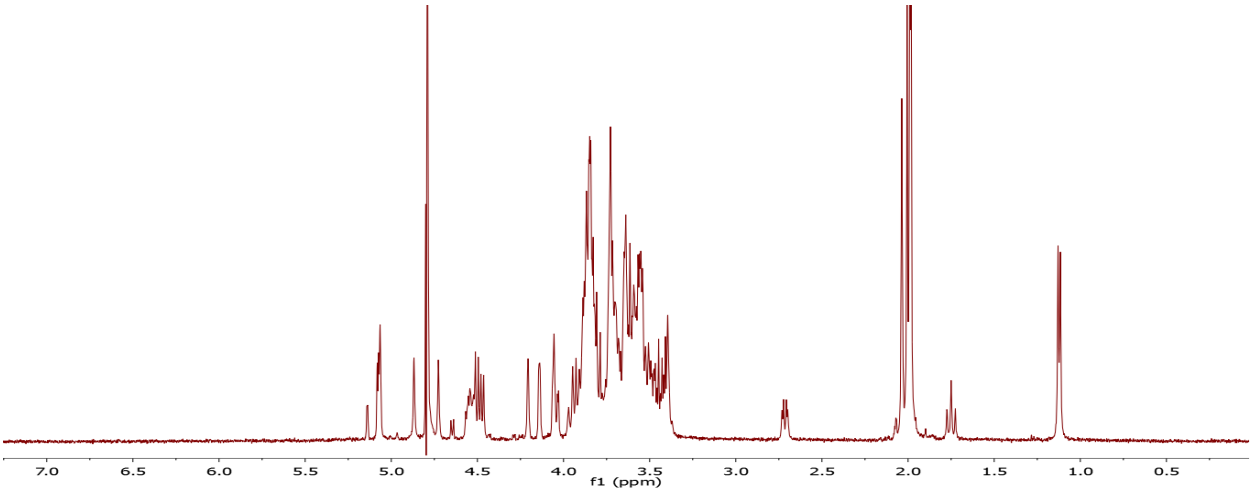
^{1}H NMR of **N213**



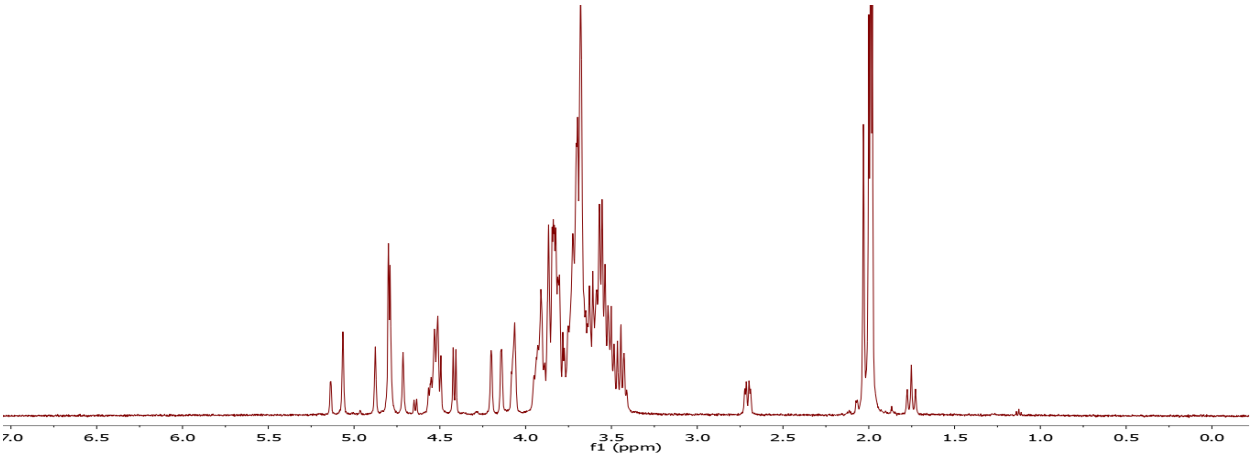
^{1}H NMR of **N214**



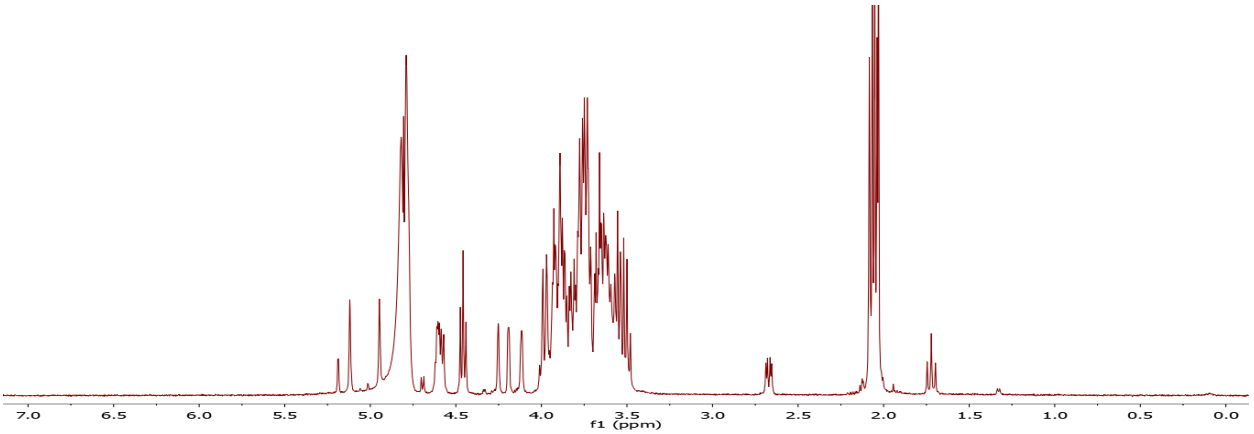
^{1}H NMR of **N215**



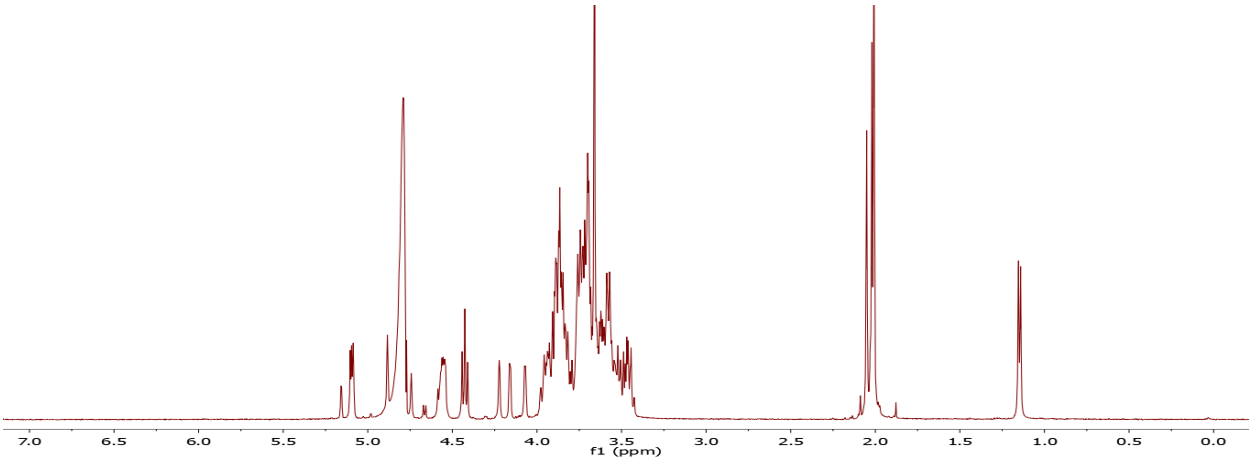
^{1}H NMR of **N222**



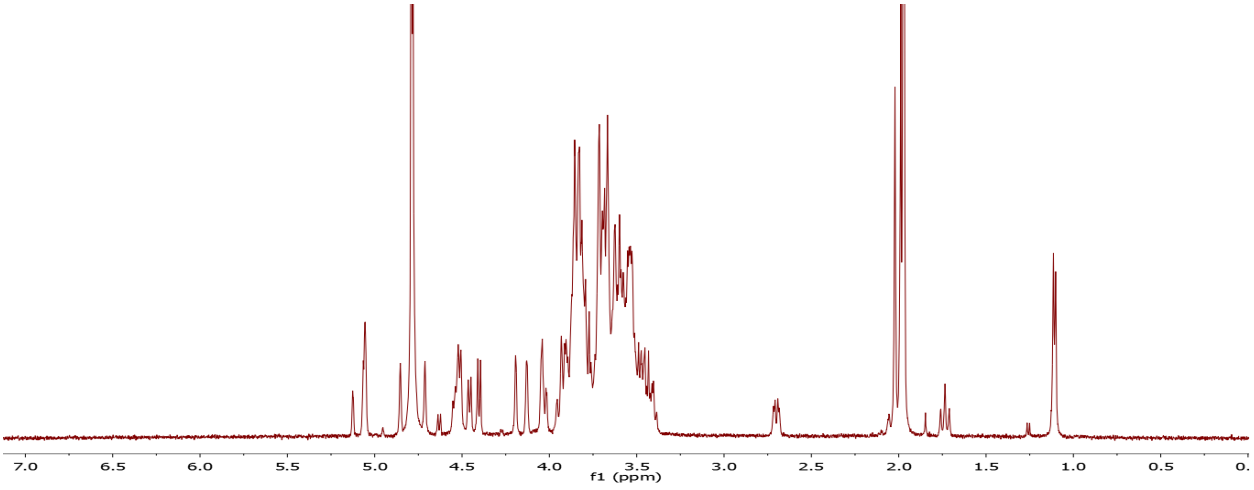
^{1}H NMR of **N223**



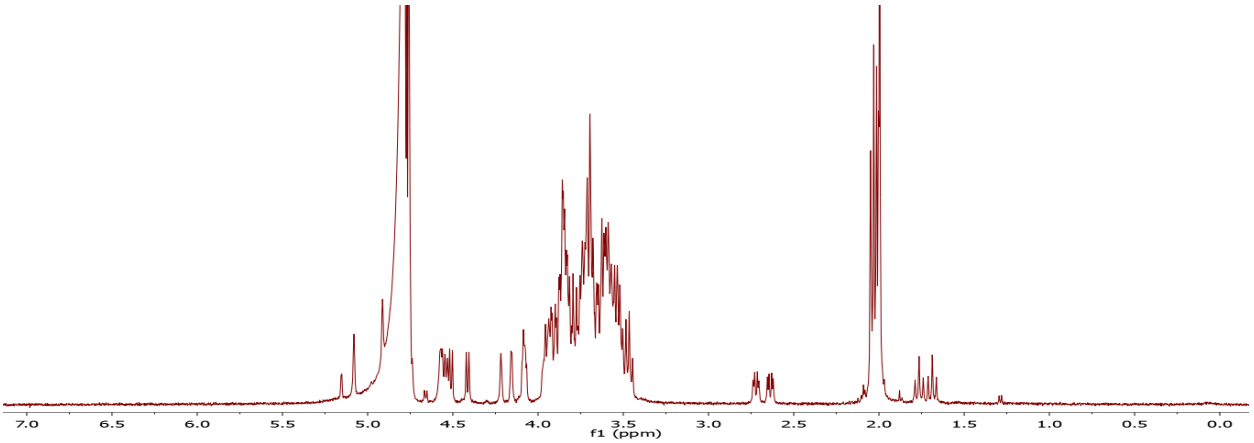
^{1}H NMR of **N224**



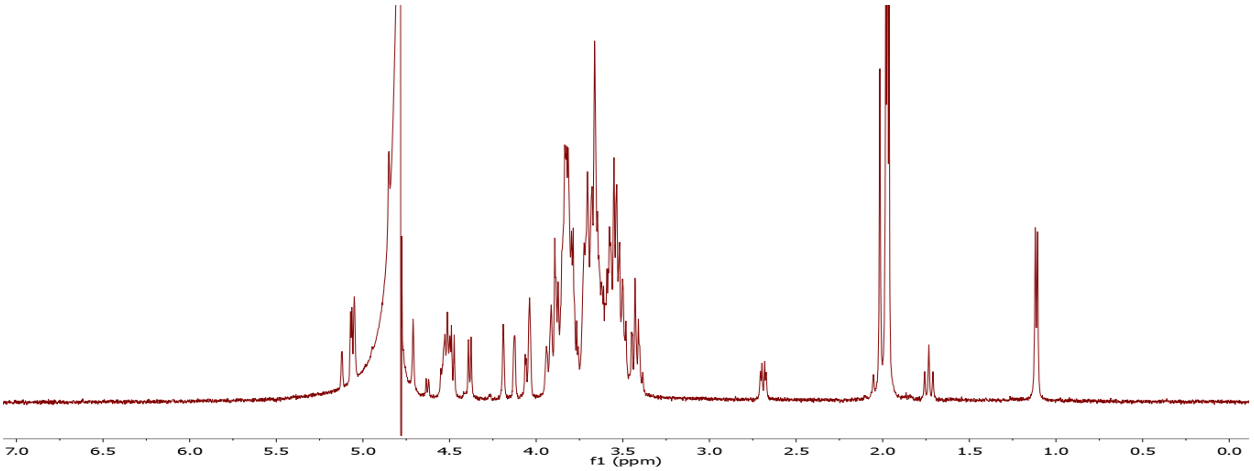
^{1}H NMR of **N225**



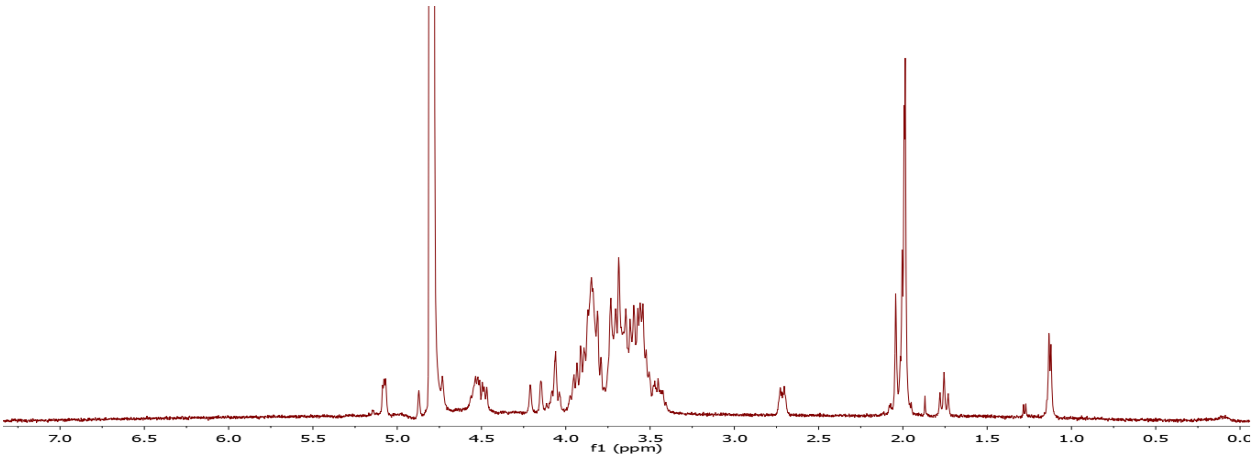
^{1}H NMR of **N233**



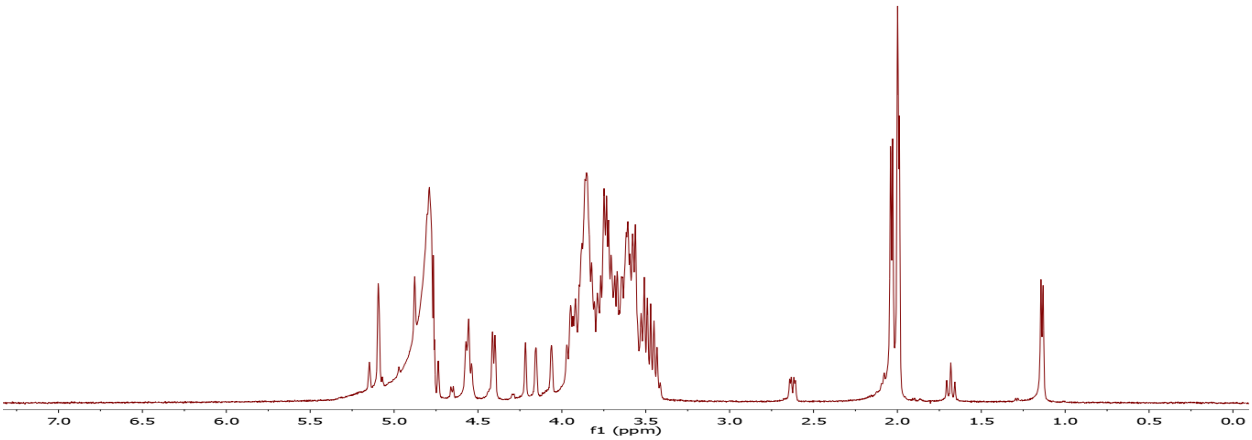
^{1}H NMR of **N234**



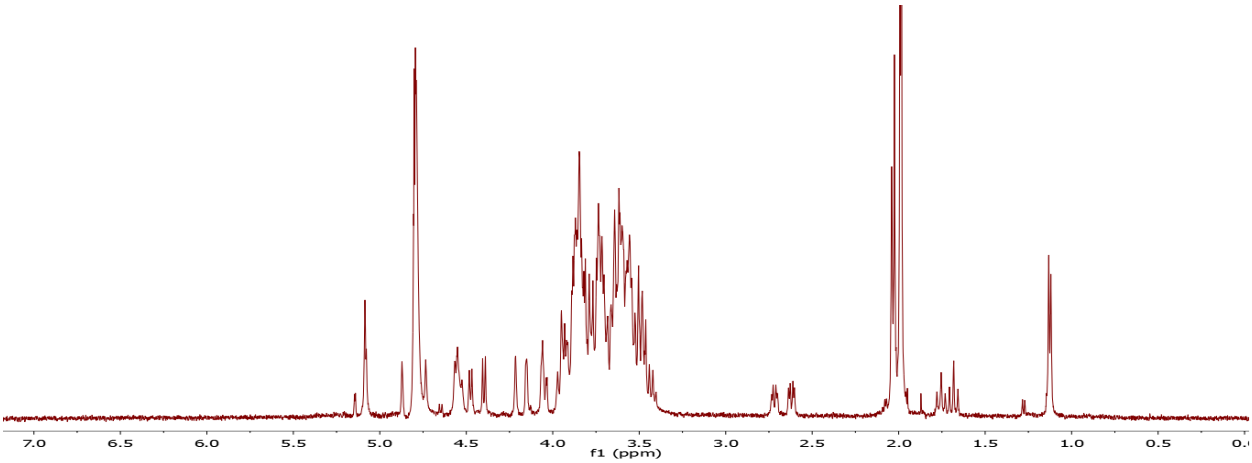
^{1}H NMR of **N235**



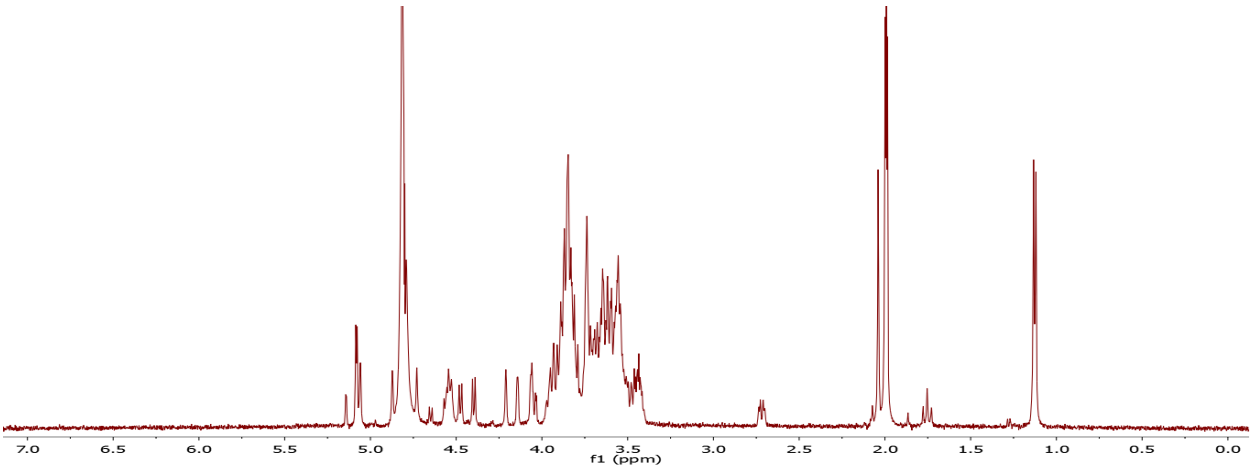
^{1}H NMR of **N244**



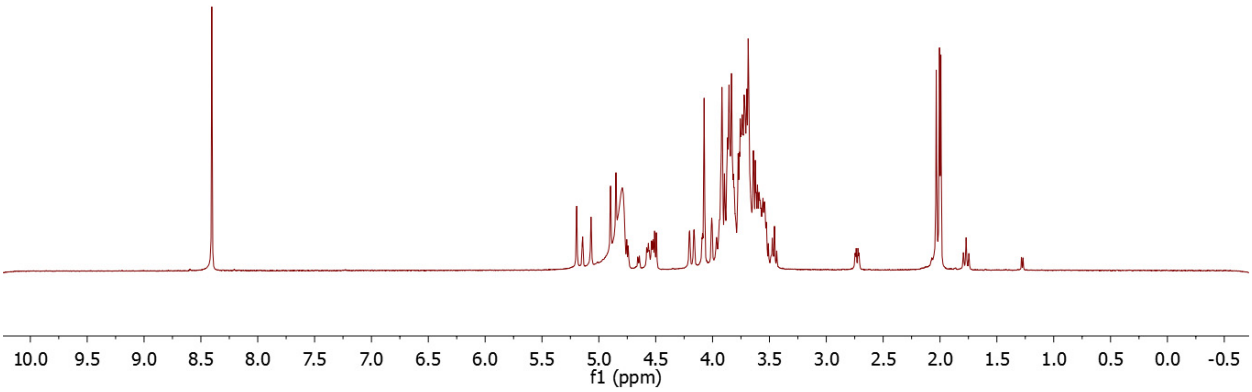
^{1}H NMR of **N245**



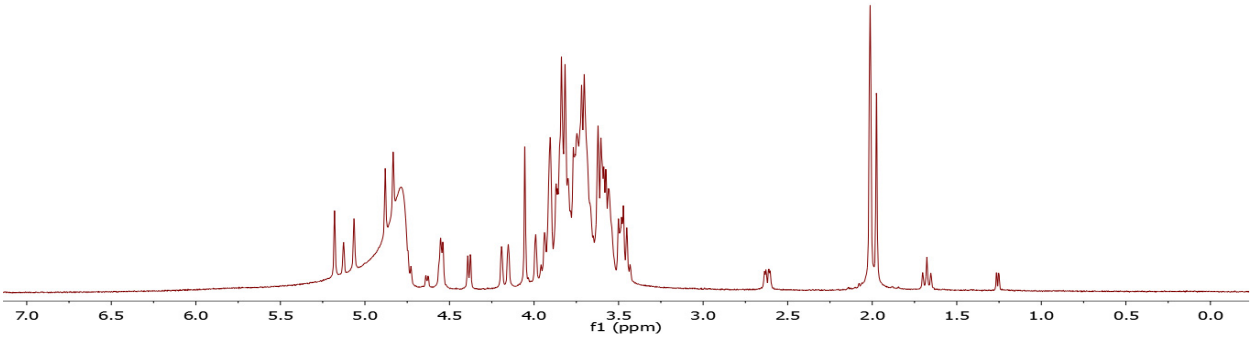
^{1}H NMR of **N255**



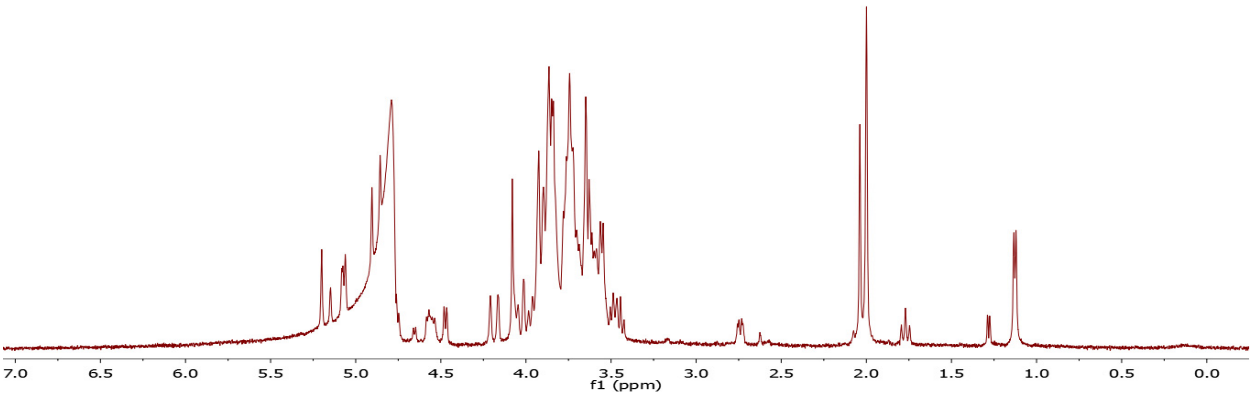
^{1}H NMR of **N012G**



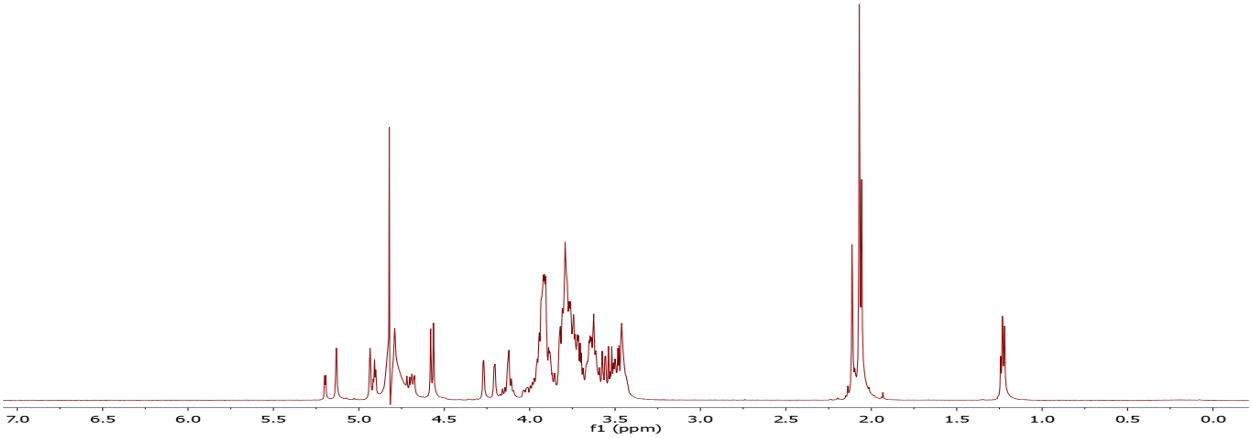
^{1}H NMR of **N013G**



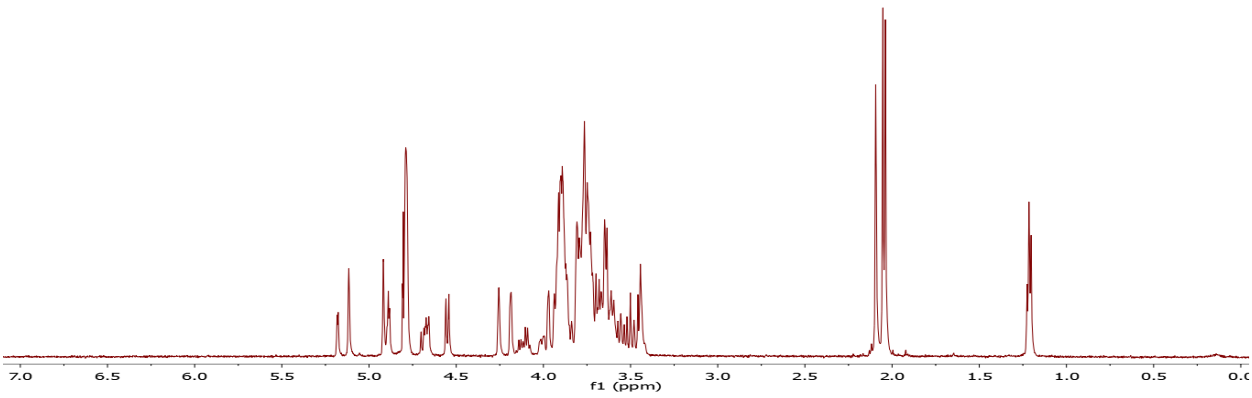
^{1}H NMR of **N015G**



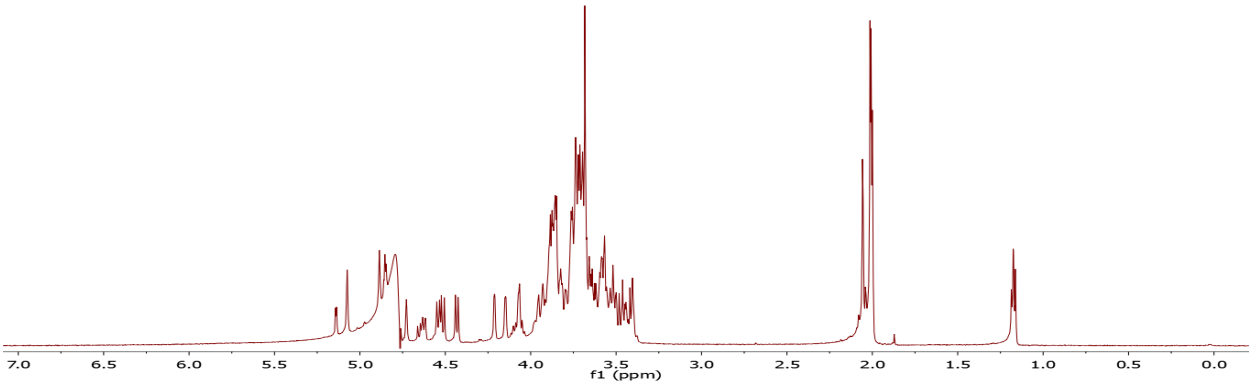
^{1}H NMR of **N6000**



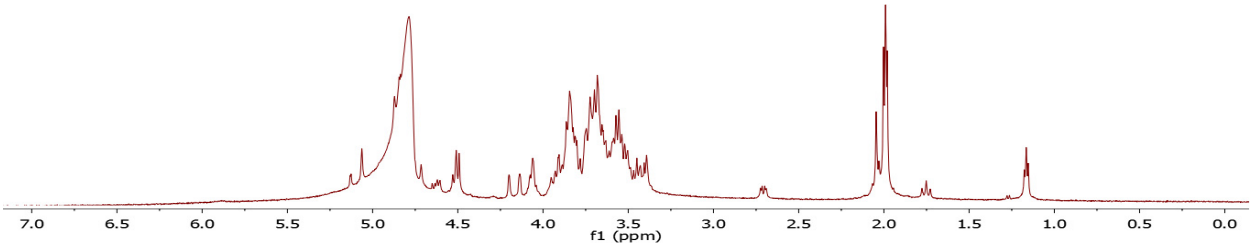
^{1}H NMR of **N6030**



^{1}H NMR of **N6211**



^{1}H NMR of **N6212**



IX. References

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