Supporting Information

Song et al

Part I

HPLC profiles of GGAEAB glycan **1**-**26**:

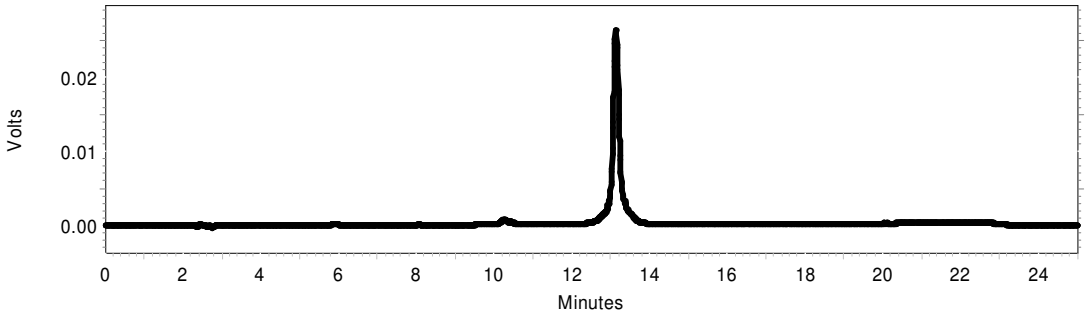
Column: Hypercarb Porous graphitized carbon (PGC) (150mm x 4.6 mm)

Solvent: Water, acetonitrile, 0.1% TFA;

Linear gradient:
0 min: 15% acetonitrile, 0.1% TFA; 20min: 35% acetonitrile, 0.1% TFA; 20.1 min: 15% acetonitrile, 0.1% TFA.

Detection: UV 330nm.

1



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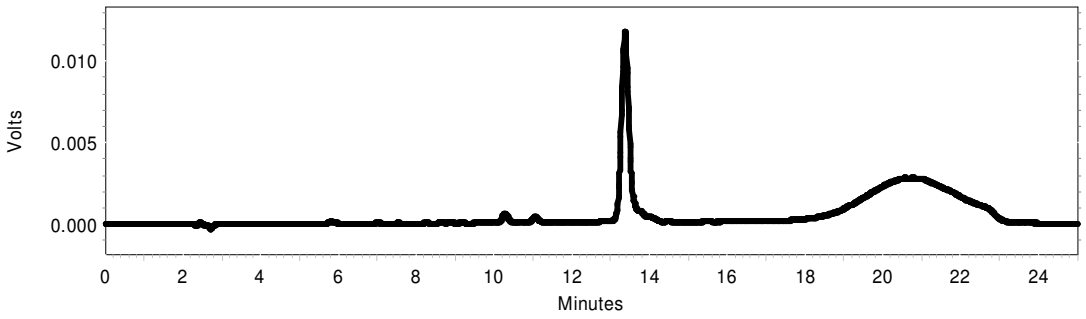

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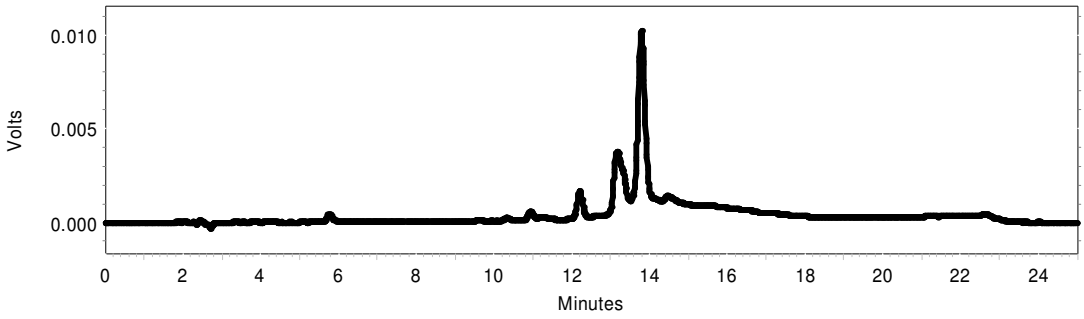
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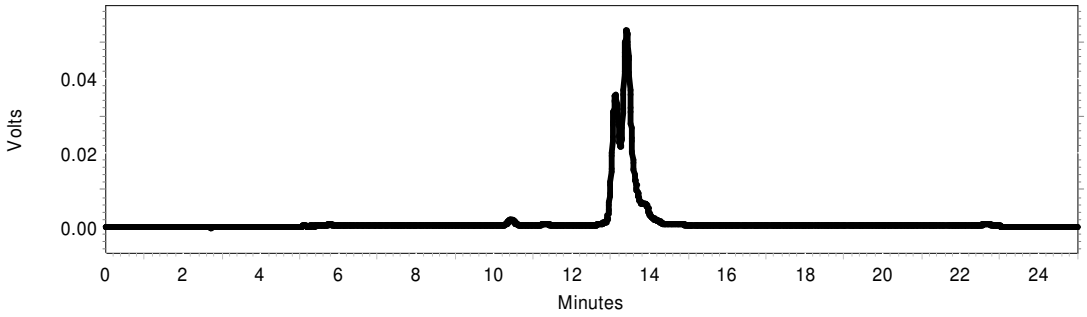
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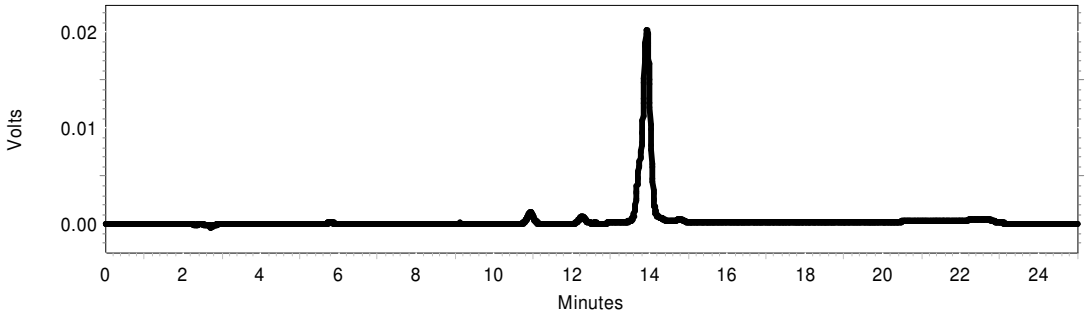
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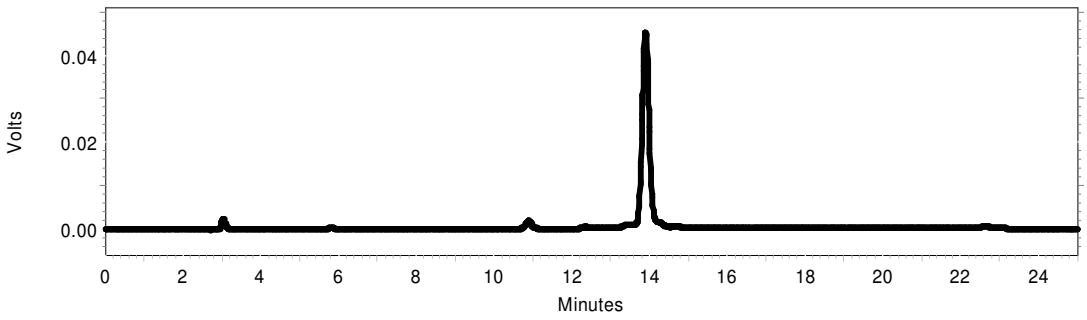
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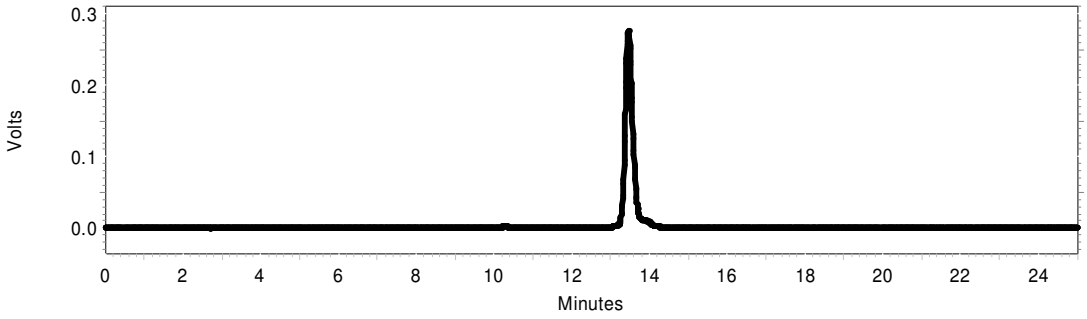
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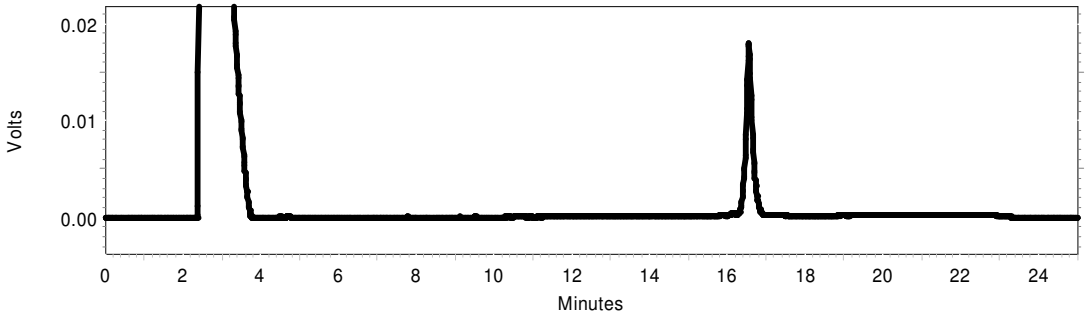
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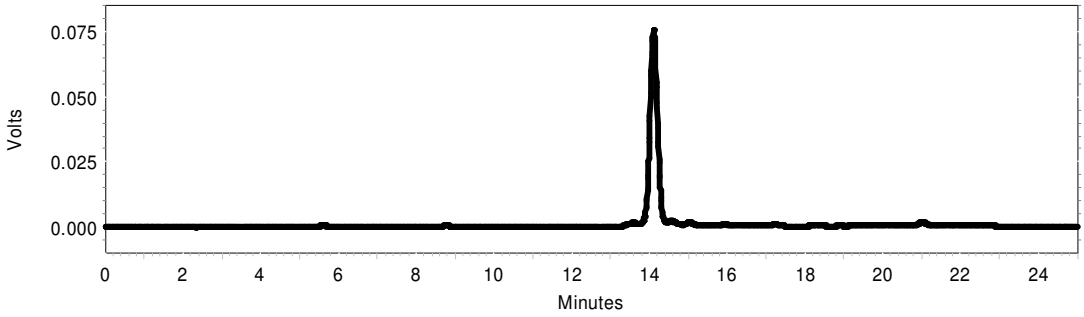
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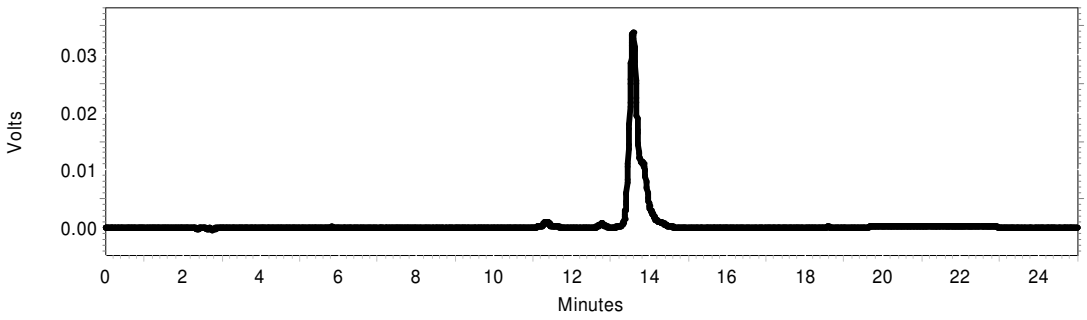
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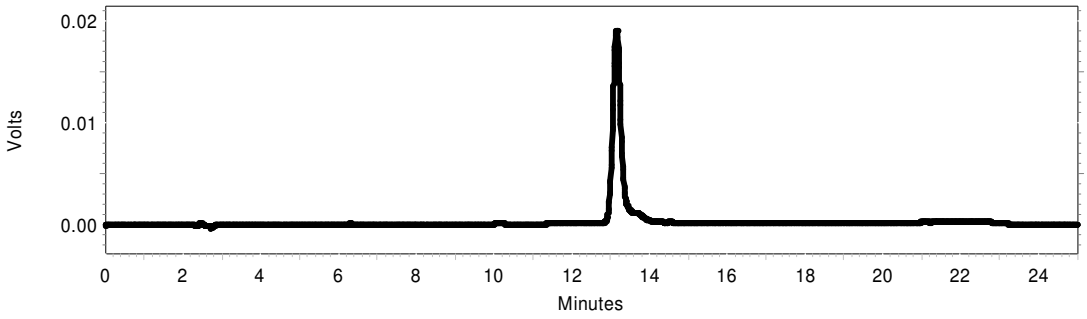
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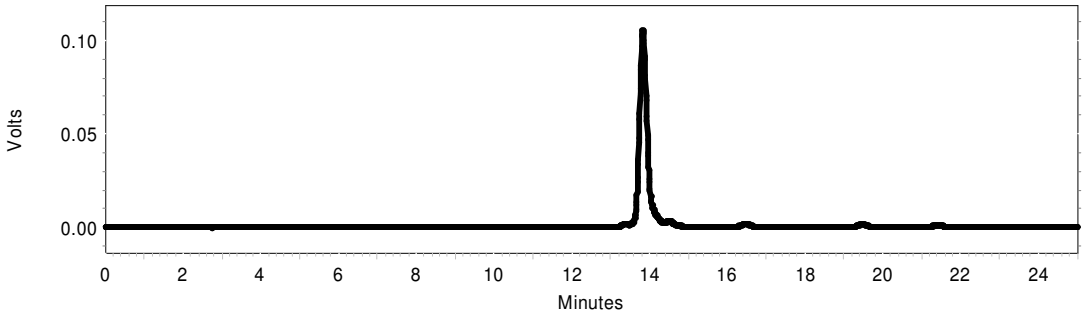
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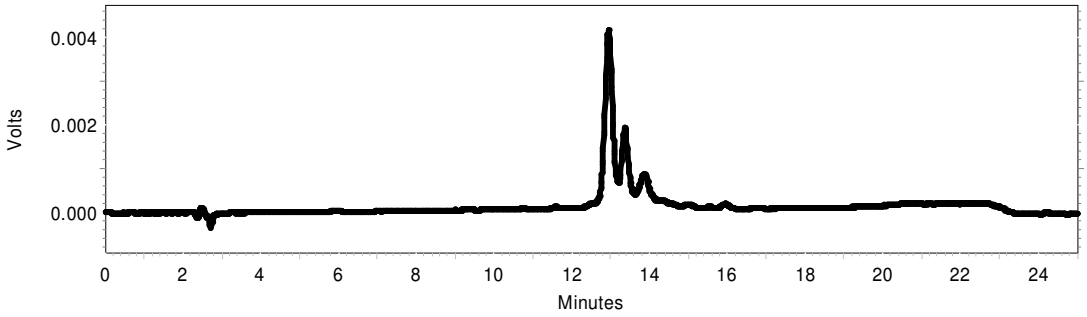
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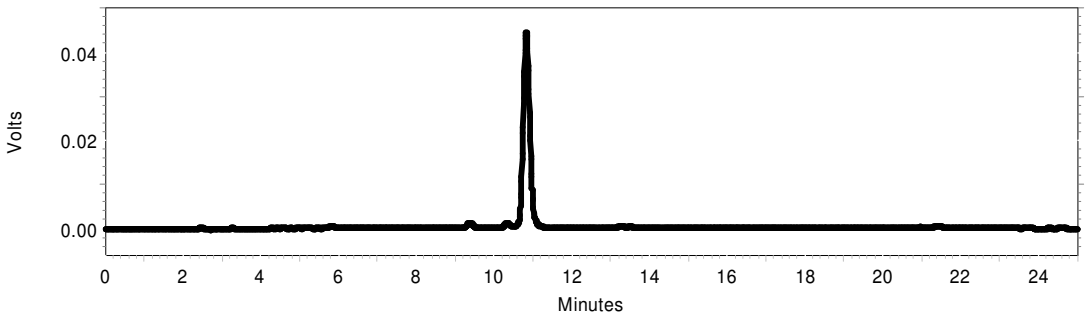
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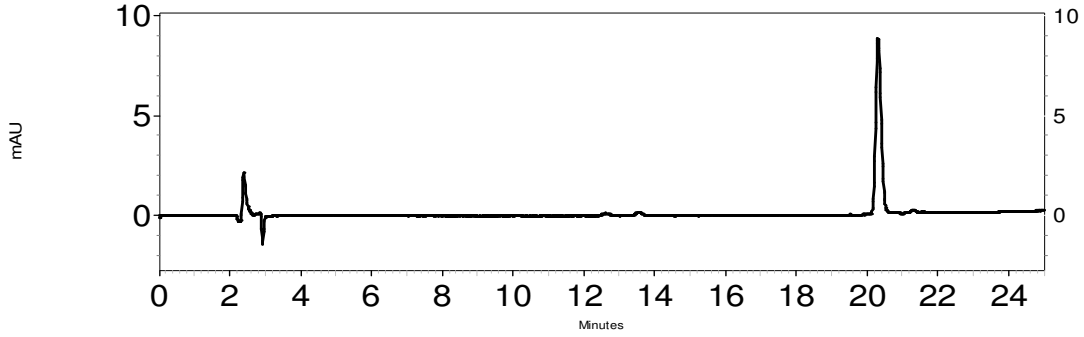
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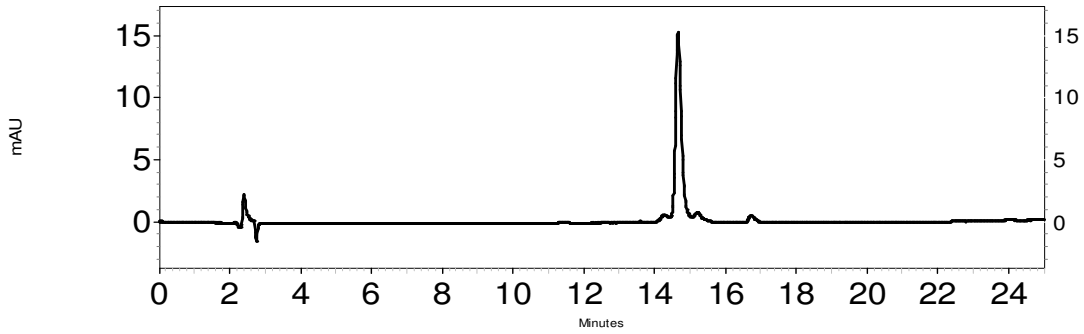
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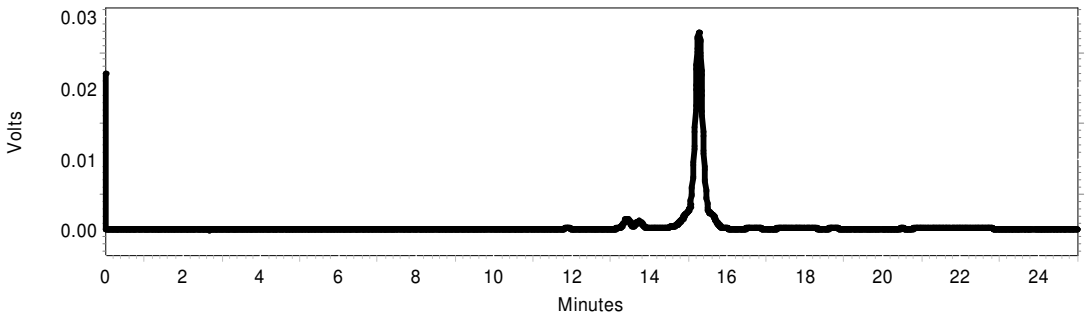
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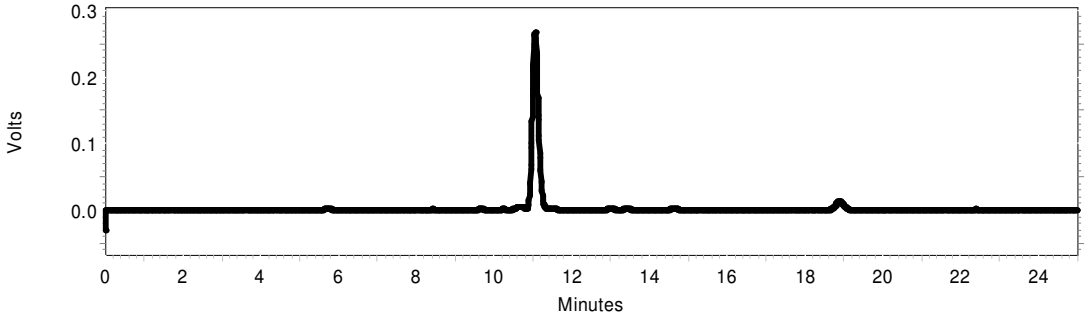
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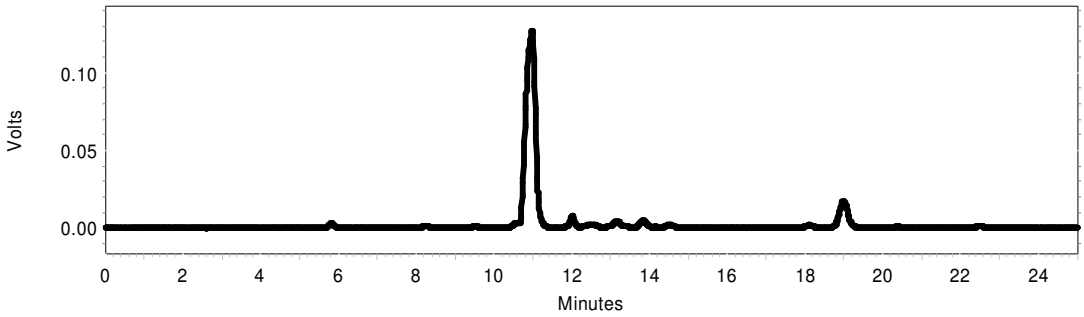
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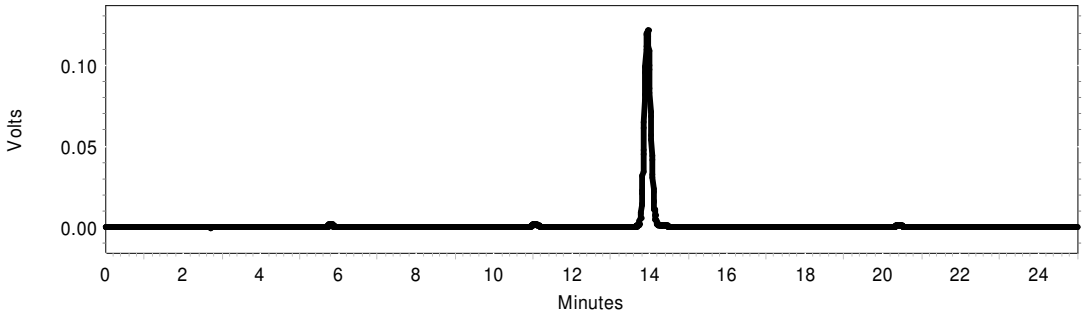
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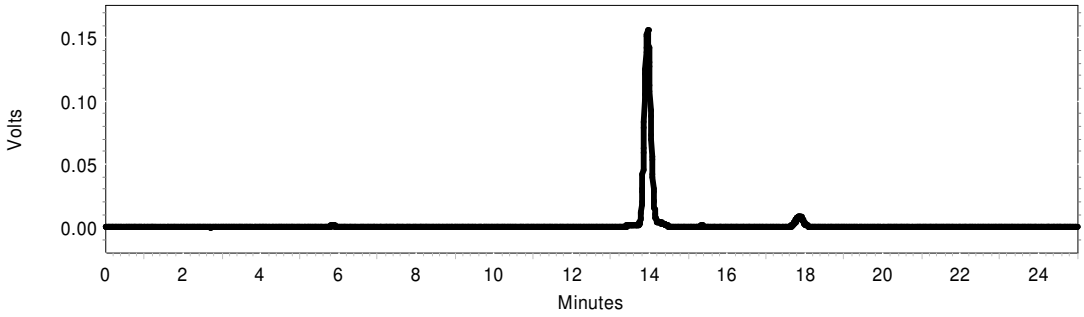
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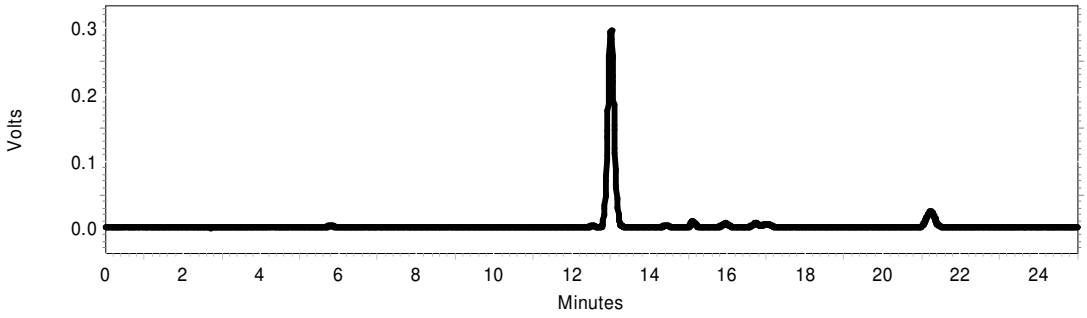
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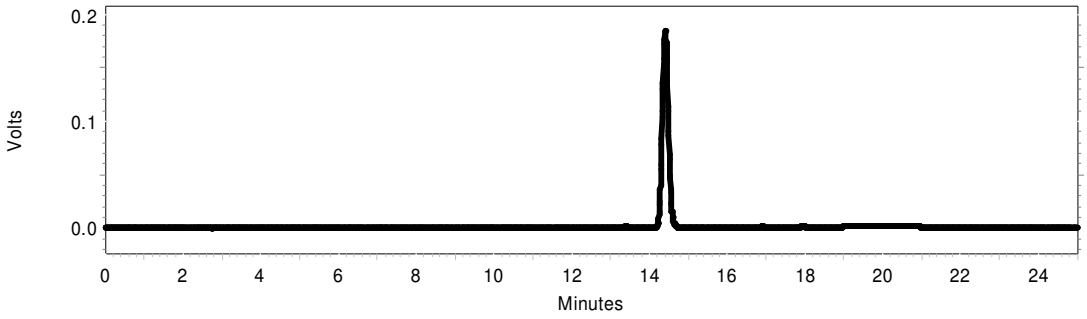
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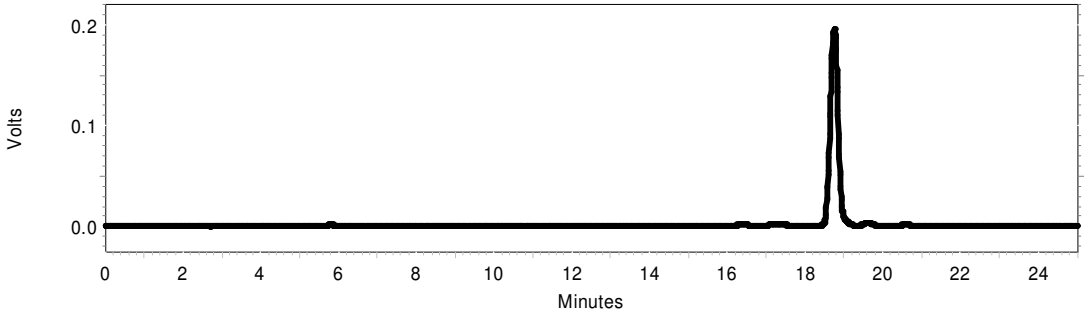
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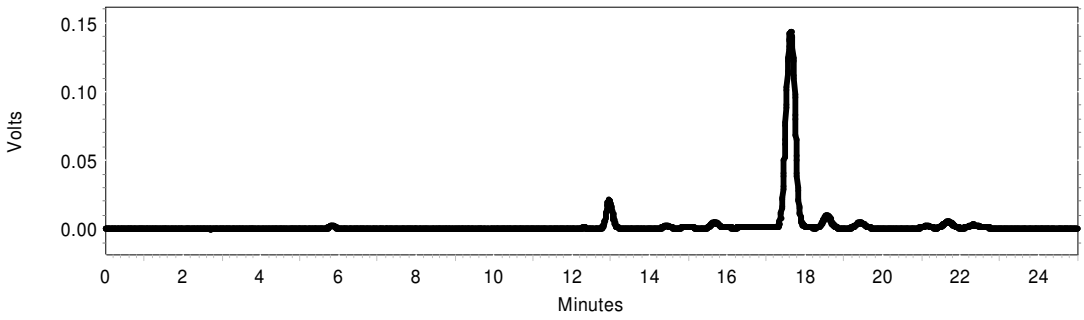
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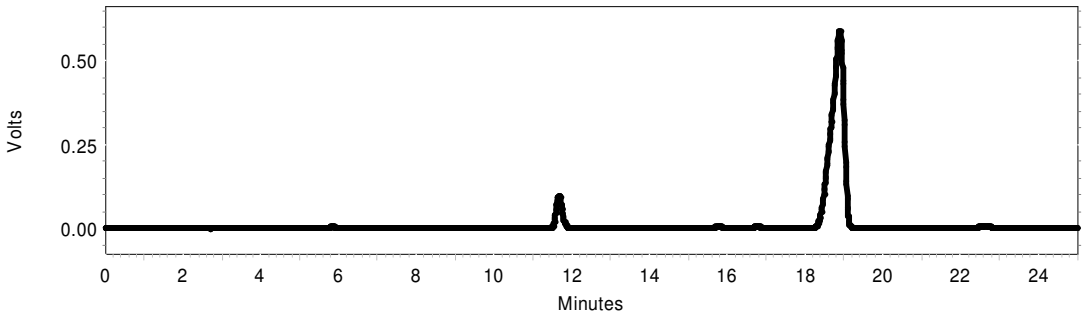
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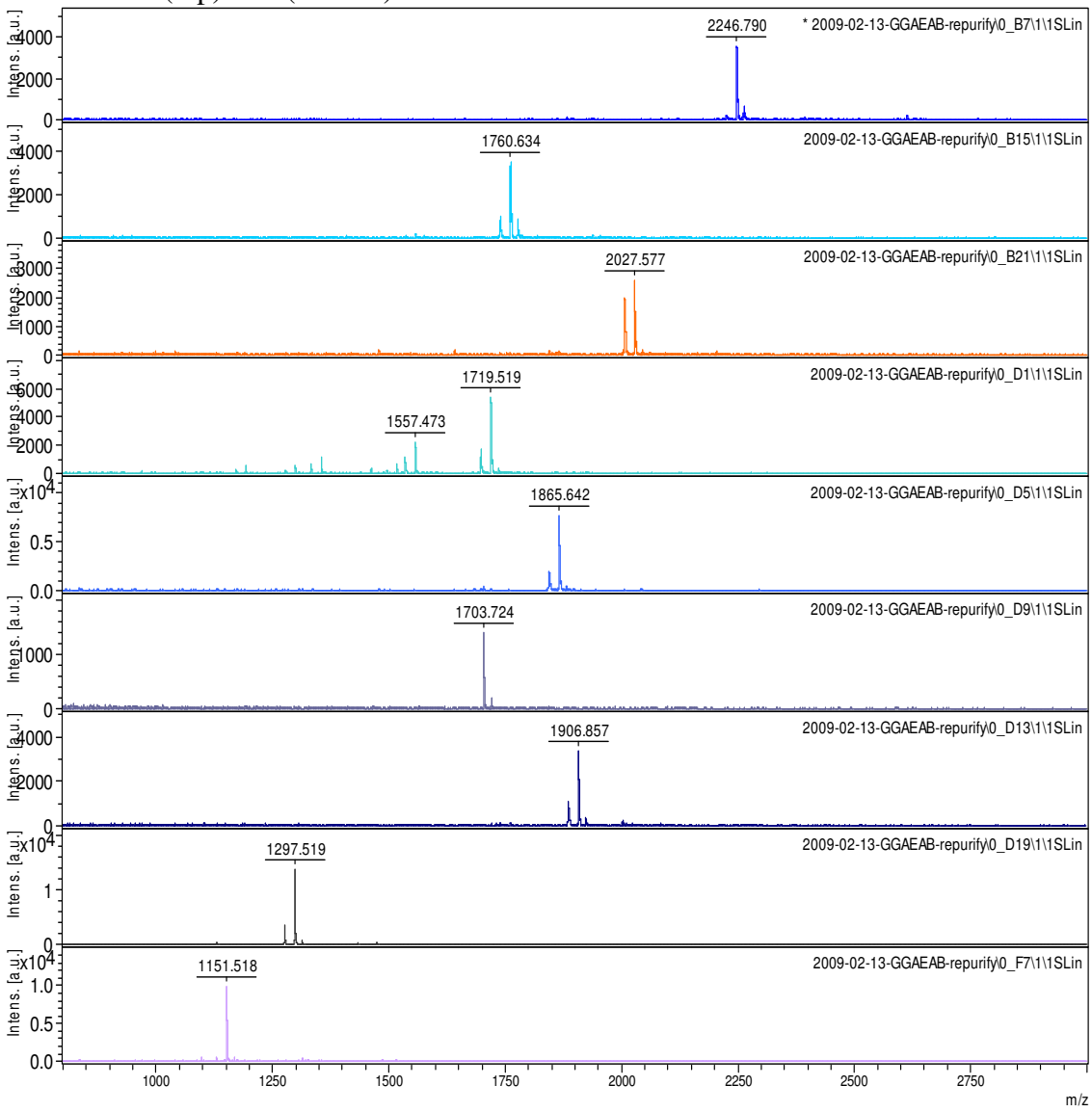
Minutes

Part II

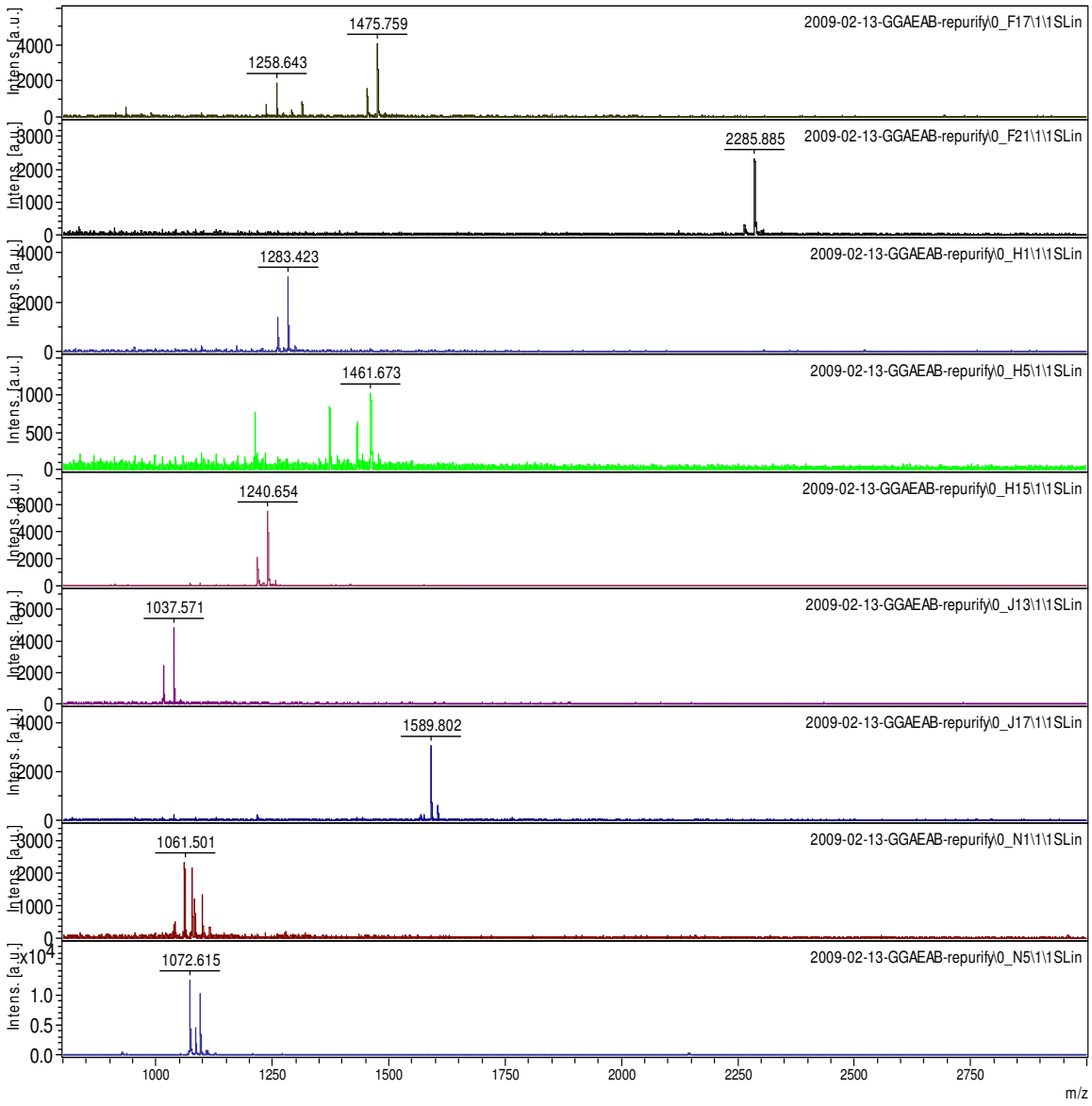
MALDI-TOF spectra of GGAEAB glycan **1-26**:

Matrix: 2,5-dihydroxybenzoic acid (DHB);
Mode: Reflective and Positive;
Protonated ion, mono- and di-sodiated ion frequently occurred in the same spectra.

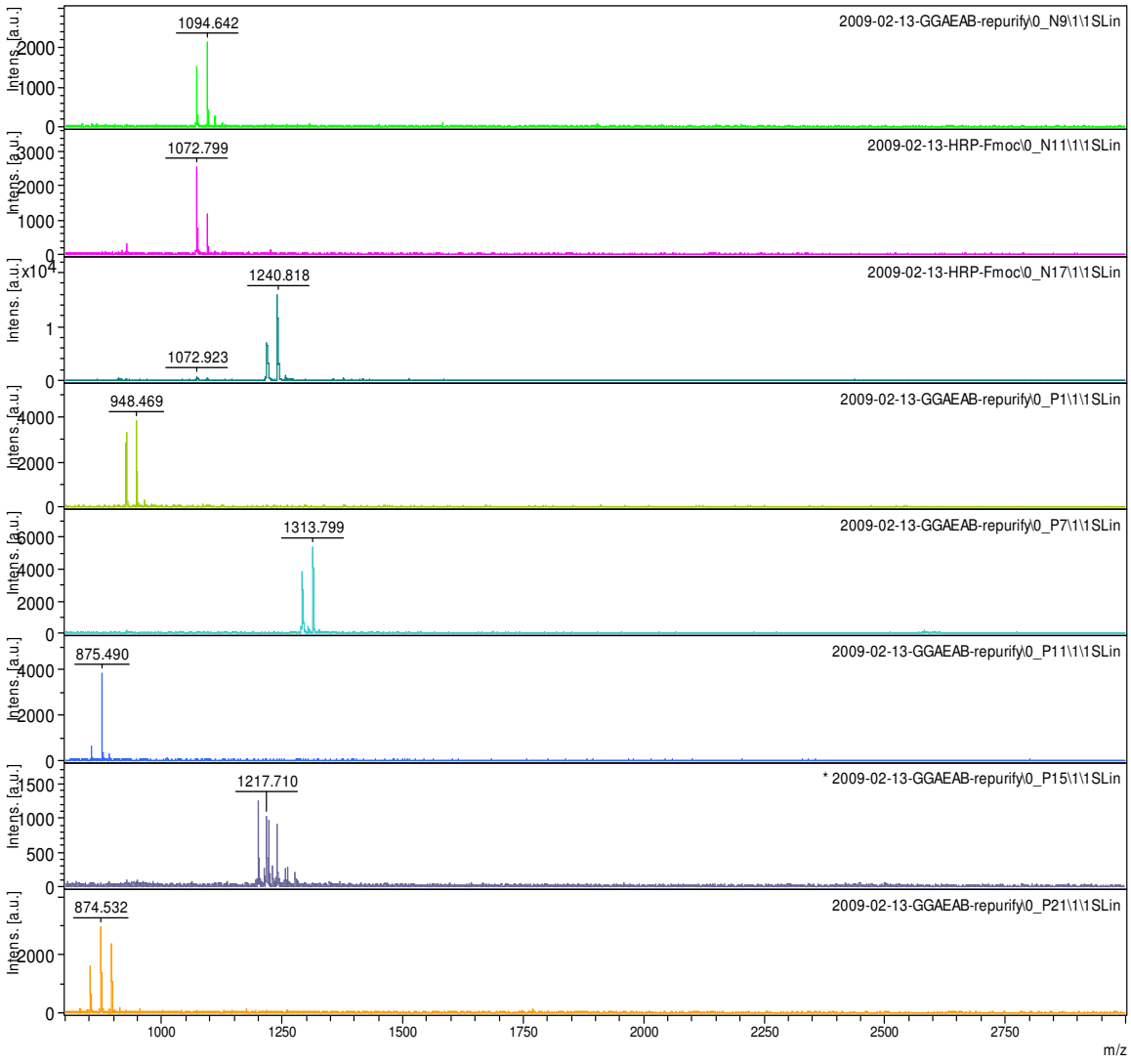
GGAEAB **1** (top) to **9** (bottom):



GGAEAB **10** (top) to **18** (bottom):



GGAEAB **19** (top) to **26** (bottom):



Part III

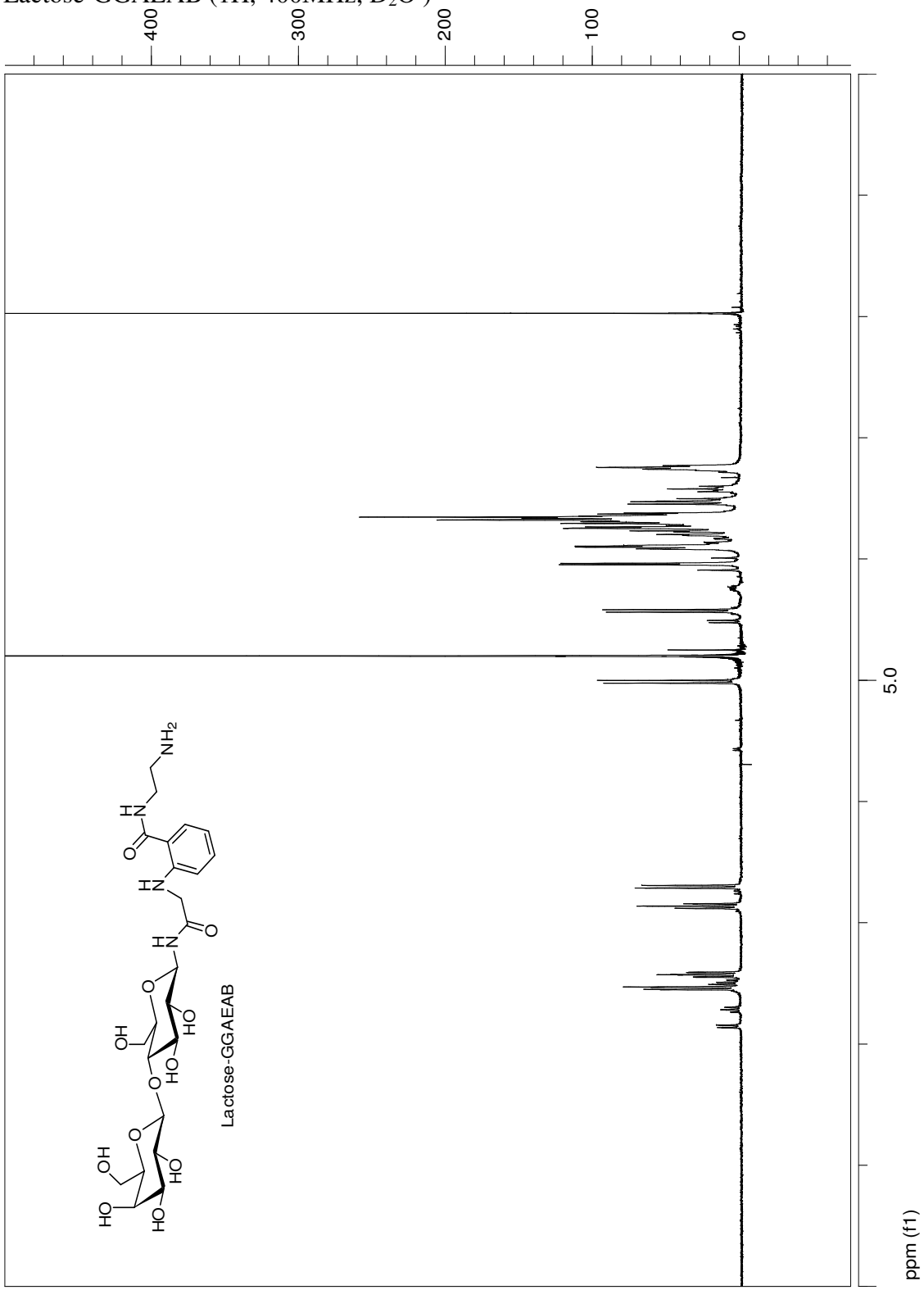
Preparation of Lactose-GGAEAB:

α-Lactose monohydrate (35mg) was mixed with ammonium bicarbonate (600 mg) and water (300 µL). The mixture was heated at 55^{o}C for 1.5 hours. Water (300 µL) was added in and the mixture was quickly filtered through a centrifuge filter with 0.22 µm nylon membrane at 5000g. The filtrate was loaded onto a Biobasic SEC-60 HPLC column and eluted with 10 mM ammonium bicarbonate. Eluent (3.5 min to 7 min) was collected and lyophilized. To the lyophilized material, sodium bicarbonate (1.0g), ice/cold water (2 mL) and acryloyl chloride (300 uL) were added quickly and stirred vigorously for 30 minutes. The mixture was filtered through a centrifuge filter with 0.22 µm nylon membrane at 5000g. The filtrate was loaded onto a Biobasic SEC-60 HPLC column and eluted with 50 mM pyridinium acetate buffer (pH 5.4). Eluent (3.5 min to 7 min) was collected and lyophilized. . To the lyophilized material, methanol (5 mL) was added. The mixture was cooled in dry ice/acetone bath. Ozone was bubbled through the solution until the blue color remains (~ 1 min). The solution was brought to room temperature and methyl sulfide (500 uL) was added. The mixture was incubated at room temperature for 8 hours and dried in a Centra-vap. To the dried material, 200 mg AEAB and 145 mg $NaCNBH_3$ were added with 4 mL DMSO/AcOH (v/v=7/3). The mixture was stirred and heated at 65^{o}C for 2 hours. Acetonitrile (40 mL) was added in and the mixture was cooled at -20^{o}C for 30 minutes. The mixture was centrifuged and the supernatant was discarded. The pellet was dried in the Centra-vap briefly and dissolved in water (1 mL). This material was again purified on a Biobasic SEC-60 HPLC column with 50 mM pyridinium acetate buffer (pH 5.4) as eluent. The eluent (4.4min to 5.5 min) was collected and lyophilized to give the product (22 mg). This is a mixture of lactose-AEAB/β-lactose-GGAEAB/α-lactose-GGAEAB (12.5/81.1/6.4 by HPLC) as shown in NMR, MS and HPLC.

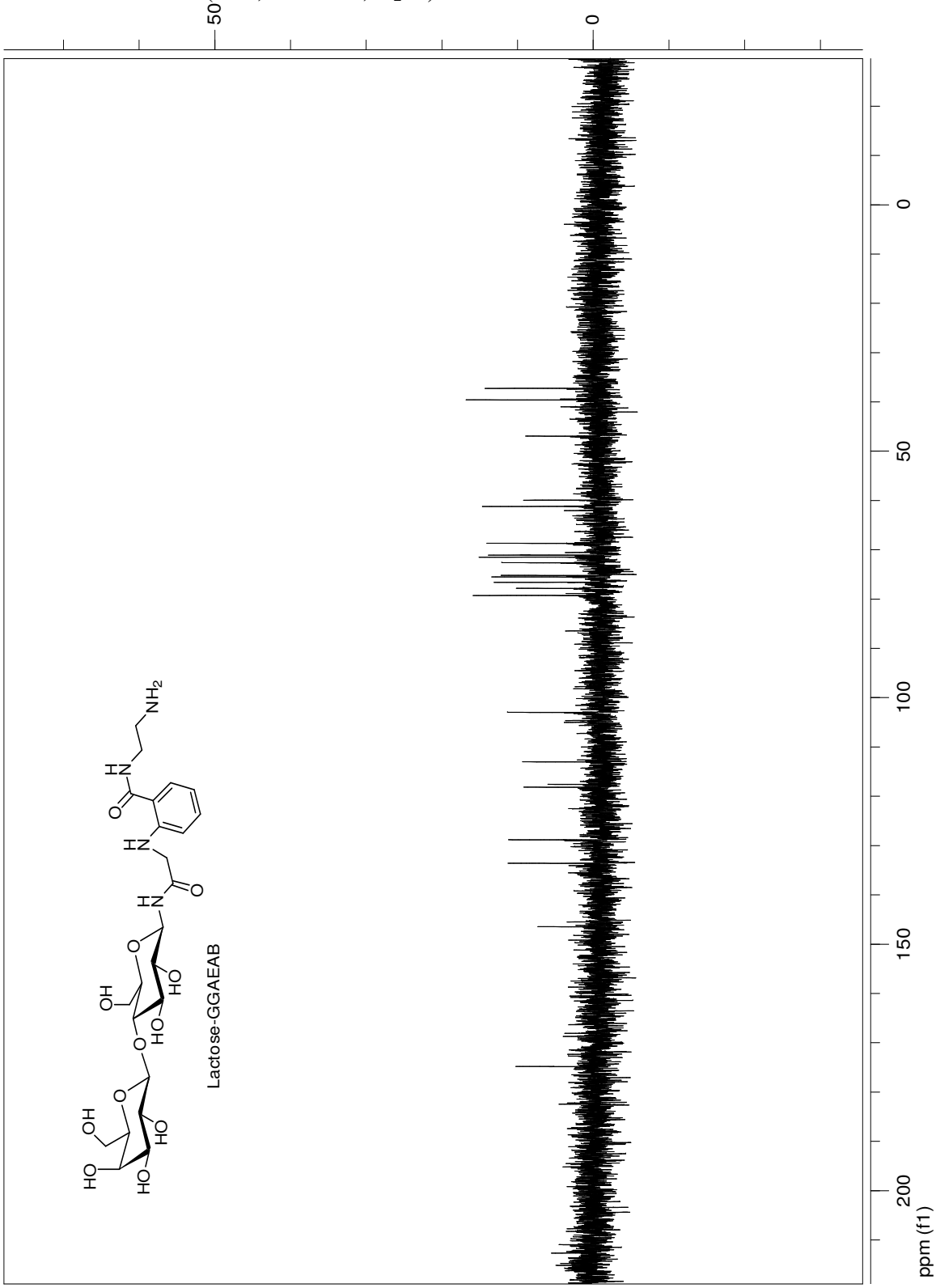
For NMR, the dried sample was dissolved in D_2O (0.5 mL) and lyophilized. This was repeated twice. The final sample was dissolved in D_2O (0.7 mL).

Lactose-AEAB conjugates were prepared by direct reductive amination with AEAB and $NaCNBH_3$ as described above.

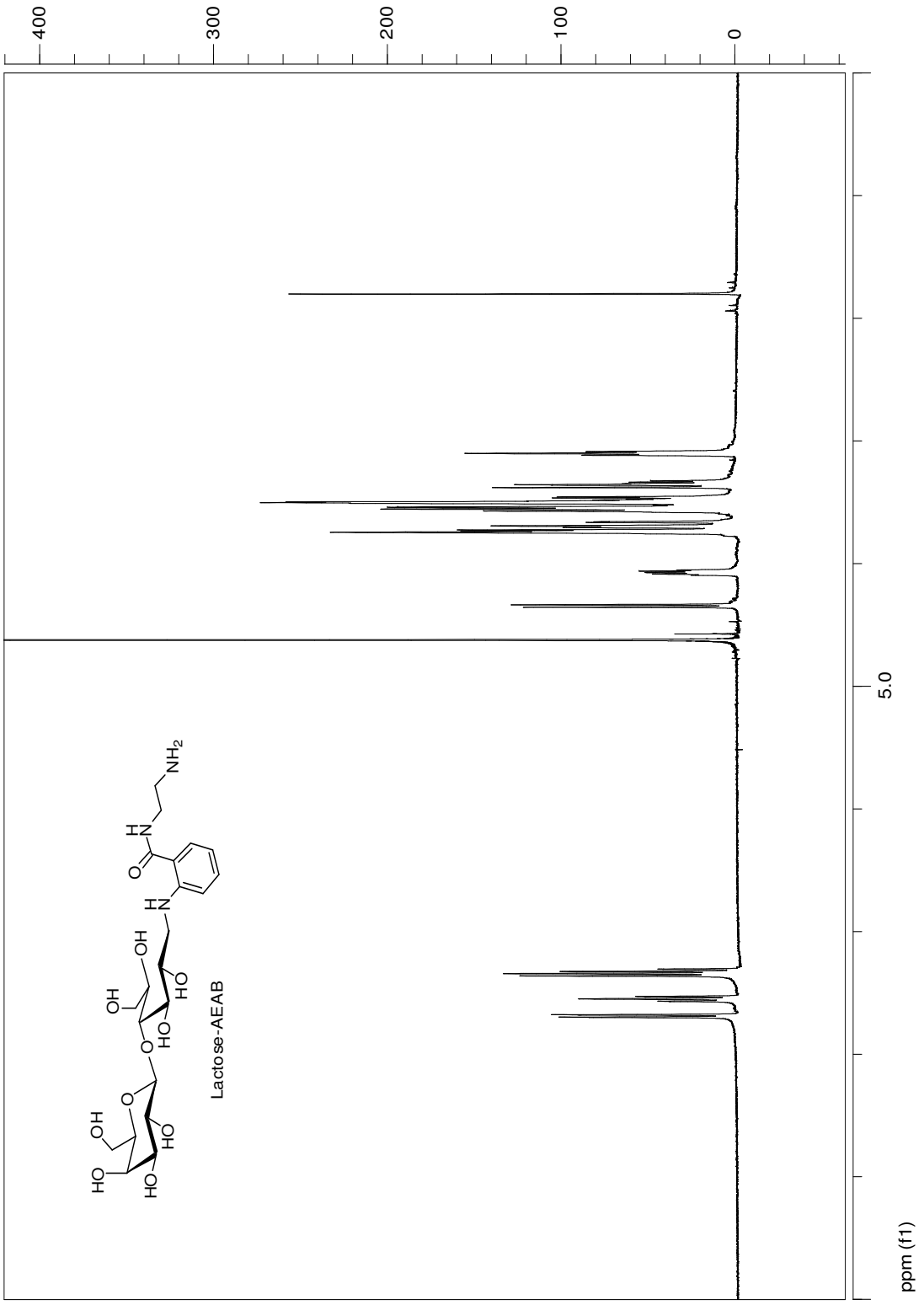
Lactose-GGAEAB (1H, 400MHz, D_2O)



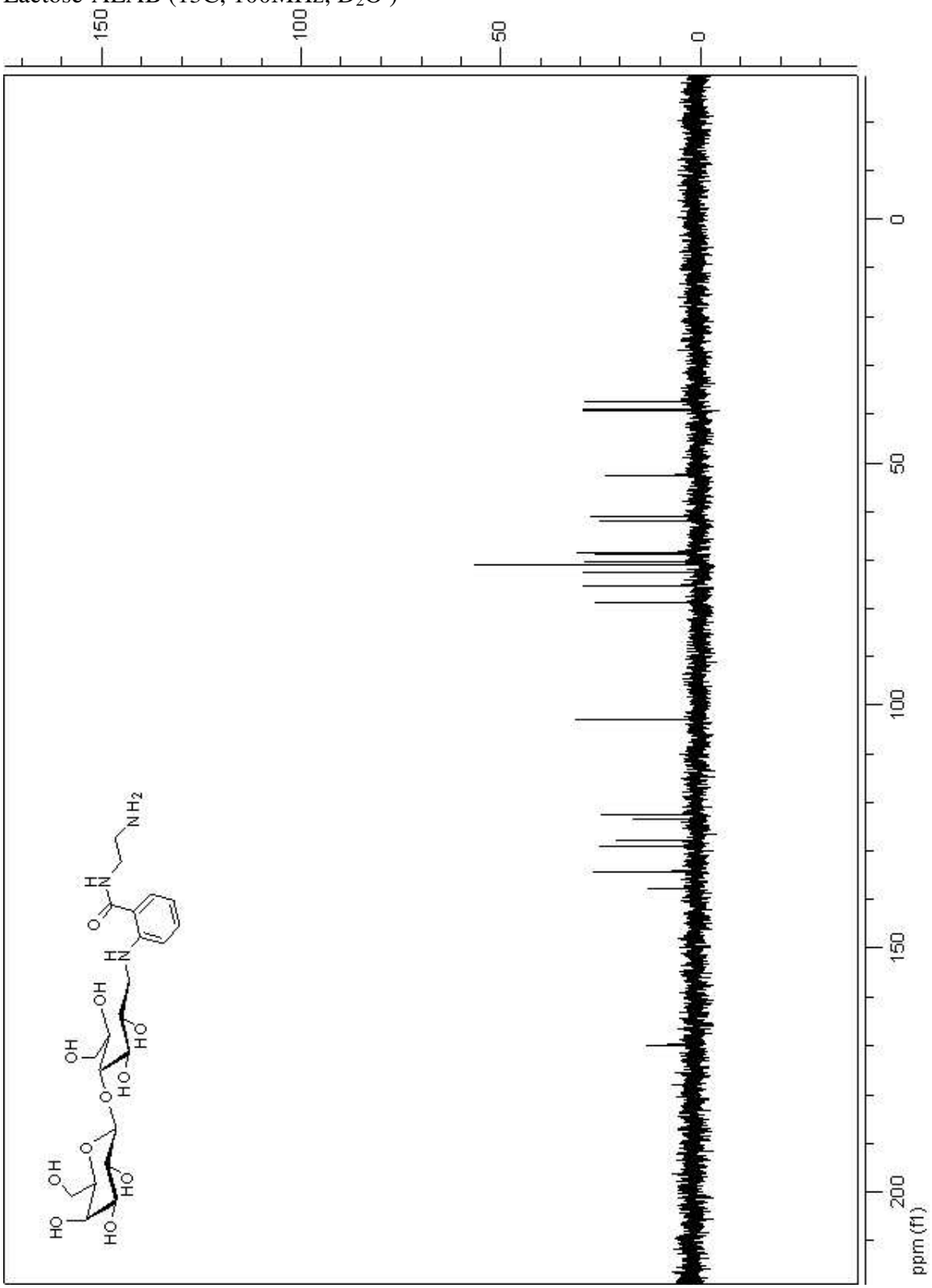
Lactose-GGAEAB (13C, 100MHz, D_2O)



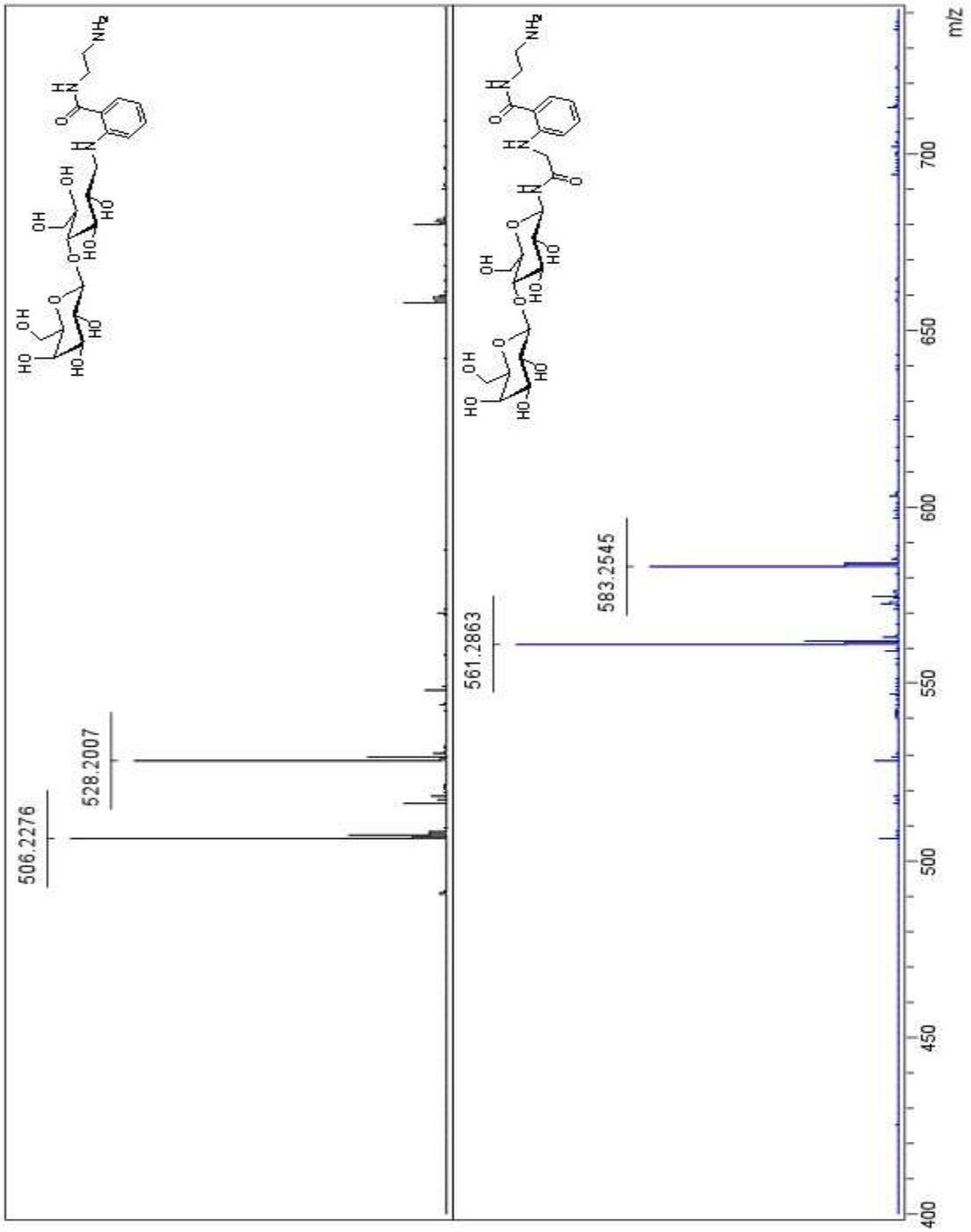
Lactose-AEAB (1H, 400MHz, D_2O):



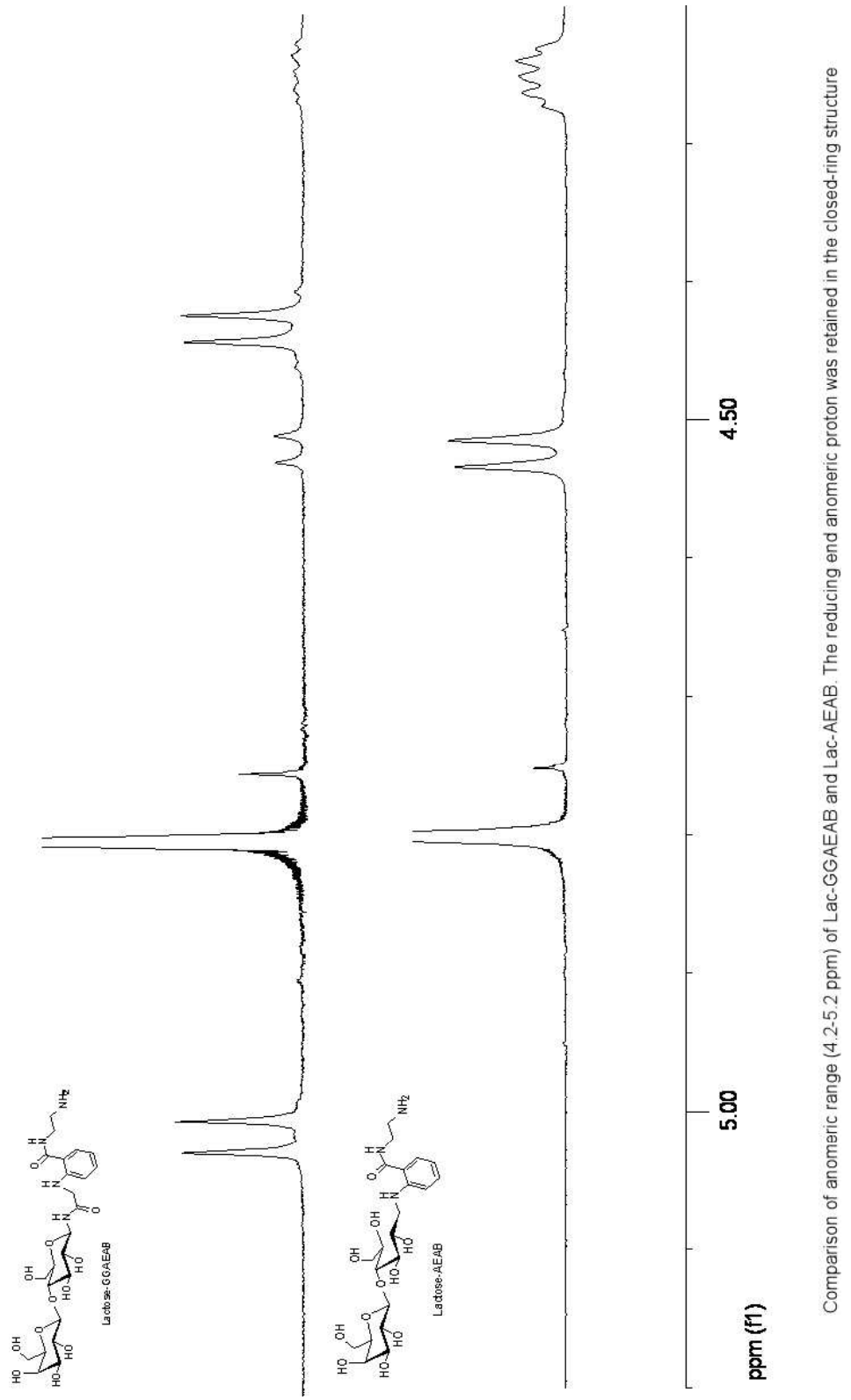
Lactose-AEAB (13C, 100MHz, D_2O)



MALDI-TOF of lactose-AEAB and lactose-GGAEAB:
Lactose-AEAB [M+H]+: Calc. 506.2344, found 506.2276;
Lactose-GGAEAB [M+H]+: Calc. 561.2402, found 561.2863.



Comparison of anomeric range (4.2-5.2 ppm) of lactose-GGAEAB and lactose-AEAB:



Comparison of anomeric range (4.2-5.2 ppm) of Lac-GGAEAB and Lac-AEAB. The reducing end anomeric proton was retained in the closed-ring structure

Comparison of PGC-HPLC profiles of lactose-GGAEAB and lactose-AEAB: