

Supporting Information

Chemical synthesis of the dimeric repeating unit of type Ia group B *Streptococcus* capsular polysaccharide

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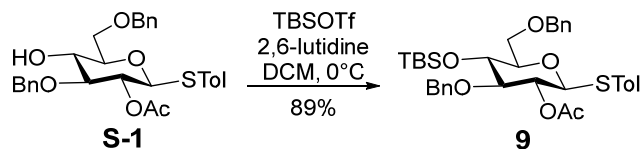
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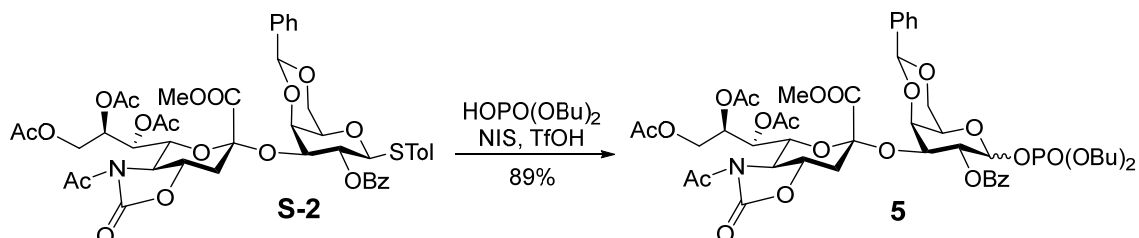
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***p*-Tolyl 2-*O*-acetyl-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-1-thio- β -D-glucopyranoside (**9**):**

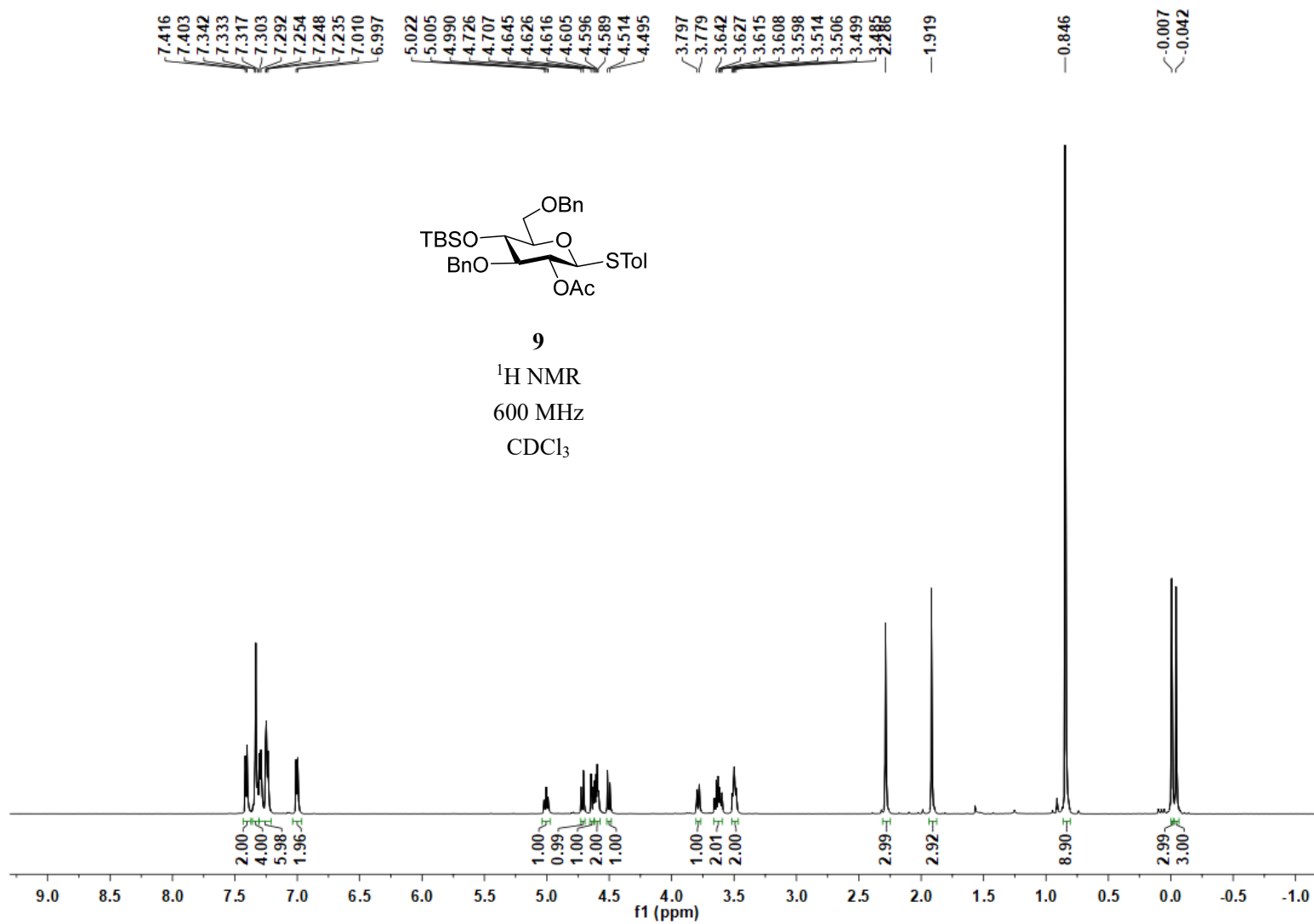


After the solution of **S-1** (500.0 mg, 0.98 mmol), which was prepared from D-glucose according to a reported procedure (see: Y. C. Ko, C. F. Tsai, C. C. Wang, V. M. Dhurandhare, P. L. Hu, T. Y. Su, L. S. Lico, M. M. L. Zulueta and S. C. Hung, *J. Am. Chem. Soc.*, 2014, **136**, 14425-14431.), in anhydrous CH_2Cl_2 (5.0 mL) was cooled to 0 °C, 2,6-lutidine (0.29 mL, 2.46 mmol) and TBSOTf (0.45 mL, 1.97 mmol) were sequentially added. The mixture was stirred under a N_2 atmosphere for overnight and then quenched with saturated NaHCO_3 solution. The reaction mixture was extracted with CH_2Cl_2 (3 \times 50 mL), and the organic layer was dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by silica gel column chromatography with EtOAc and hexanes (1:50) as the eluent to give **9** (549.9 mg, 89%) as a syrup. ^1H NMR (600 MHz, CDCl_3) δ : 7.41 (d, J = 7.8 Hz, 2H, Ph), 7.35 – 7.31 (m, 4H, Ph), 7.30 (d, J = 6.6 Hz, 2H, Ph), 7.27 – 7.22 (m, 4H, Ph), 7.00 (d, J = 7.8 Hz, 2H, Ph), 5.01 (t, J = 9.6 Hz, 1H, H-2), 4.72 (d, J = 11.4 Hz, 1H, Bn), 4.64 (d, J = 11.4 Hz, 1H, Bn), 4.61 (d, J = 12.0 Hz, 1H, Bn), 4.60 (d, J = 9.6 Hz, 1H, H-1), 4.50 (d, J = 11.4 Hz, 1H, Bn), 3.79 (d, J = 10.8 Hz, 1H, H-6a), 3.66 – 3.59 (m, 2H, H-4, H-6b), 3.52 – 3.47 (m, 2H, H-3, H-5), 2.29 (s, 3H, Ph- CH_3), 1.92 (s, 3H, - COCH_3), 0.85 (s, 9H, -*t*Bu), -0.01 (s, 3H, - SiCH_3), -0.04 (s, 3H, - SiCH_3). ^{13}C NMR (150 MHz, CDCl_3) δ : 169.5, 138.3, 138.1, 137.7, 132.5, 129.5, 129.3, 128.28, 128.27, 127.5, 127.46, 127.41, 127.2, 86.2, 84.9, 80.7, 75.2, 73.3, 72.1, 70.9, 69.3, 25.8, 21.1, 21.0, 17.9, -3.8, -4.7. HR-ESI-Orbitrap-MS (m/z): calcd for $\text{C}_{35}\text{H}_{46}\text{O}_6\text{SSiNa}$ [$\text{M} + \text{Na}$] $^+$, 645.2677; found, 645.2667.

(Methyl 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-*D*-glycero- α -*D*-galacto-non-2-ulopyranosylonate)-(2 \rightarrow 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-1-dibutylphosphoryl- α,β -*D*-galactopyranoside (5**)**



To a stirred mixture of **S-2** (100.0 mg, 0.107 mmol), which was prepared according to a reported procedure (see: C. H. Hsu, K. C. Chu, Y. S. Lin, J. L. Han, Y. S. Peng, C. T. Ren, C. Y. Wu and C. H. Wong, *Chem. - Eur. J.*, 2010, **16**, 1754-1760.), dibutyl phosphate (95.4 μ L, 0.481 mmol) and freshly activated MS 4 \AA in anhydrous CH_2Cl_2 (4.0 mL) was added NIS (60.1 mg, 0.267 mmol) and TfOH (3.8 μ L, 0.043 mmol) under a N_2 atmosphere at 0 $^\circ\text{C}$. After the mixture was stirred for another 30 min at the same temperature, it was neutralized with saturated NaHCO_3 solution, diluted with CH_2Cl_2 (50 mL), and filtered. The filtrate was washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ and NaCl, dried over Na_2SO_4 , and concentrated under a vacuum. The residue was purified by silica gel column chromatography with EtOAc and hexane (1:1) as the eluent to give **5** (97.2 mg, 89%) as a pale yellow syrup. HR-ESI-Orbitrap-MS (m/z): calcd for $\text{C}_{47}\text{H}_{64}\text{N}_2\text{O}_{22}\text{P}$ [$\text{M} + \text{NH}_4$]⁺, 1039.3683; found, 1039.3696.



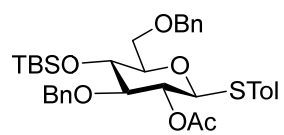
—169.58

138.37
138.18
137.70
132.54
129.54
129.38
128.28
128.27
127.54
127.46
127.41
127.23

86.26
84.94
80.78
75.23
73.39
72.17
70.90
69.39

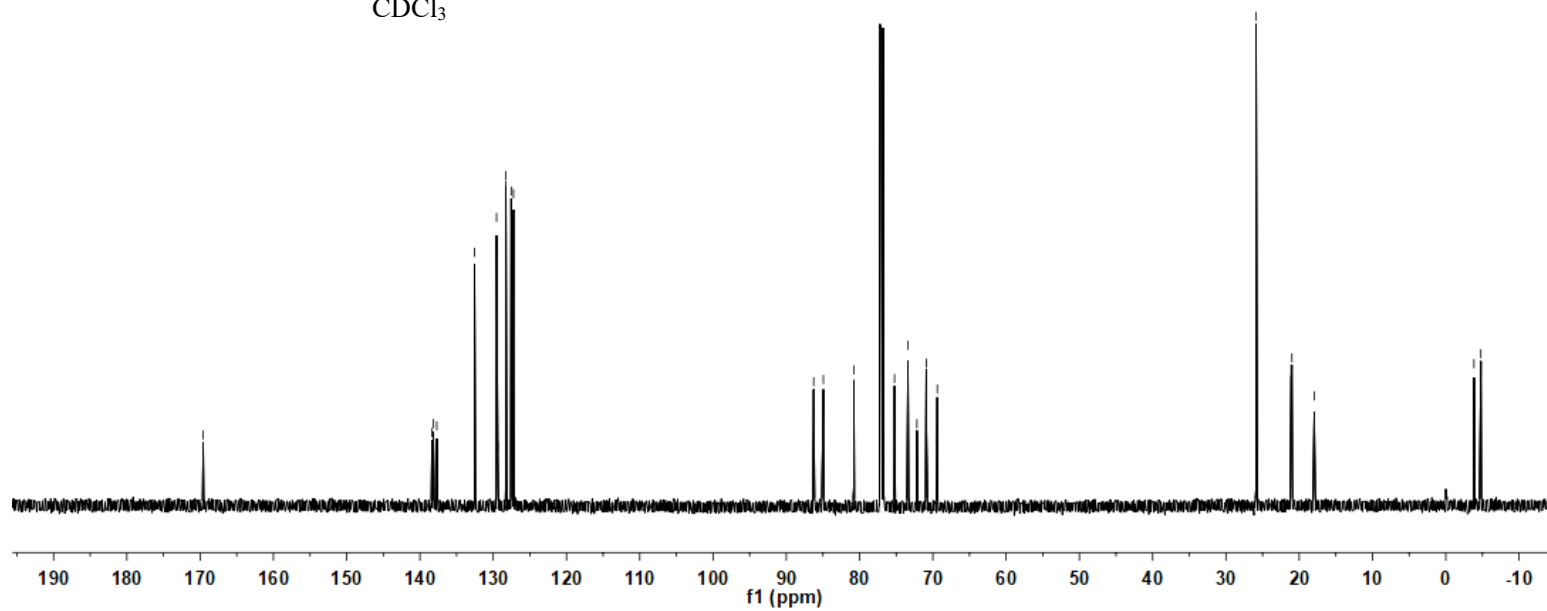
25.88
21.11
21.00
17.95

3.85
4.79

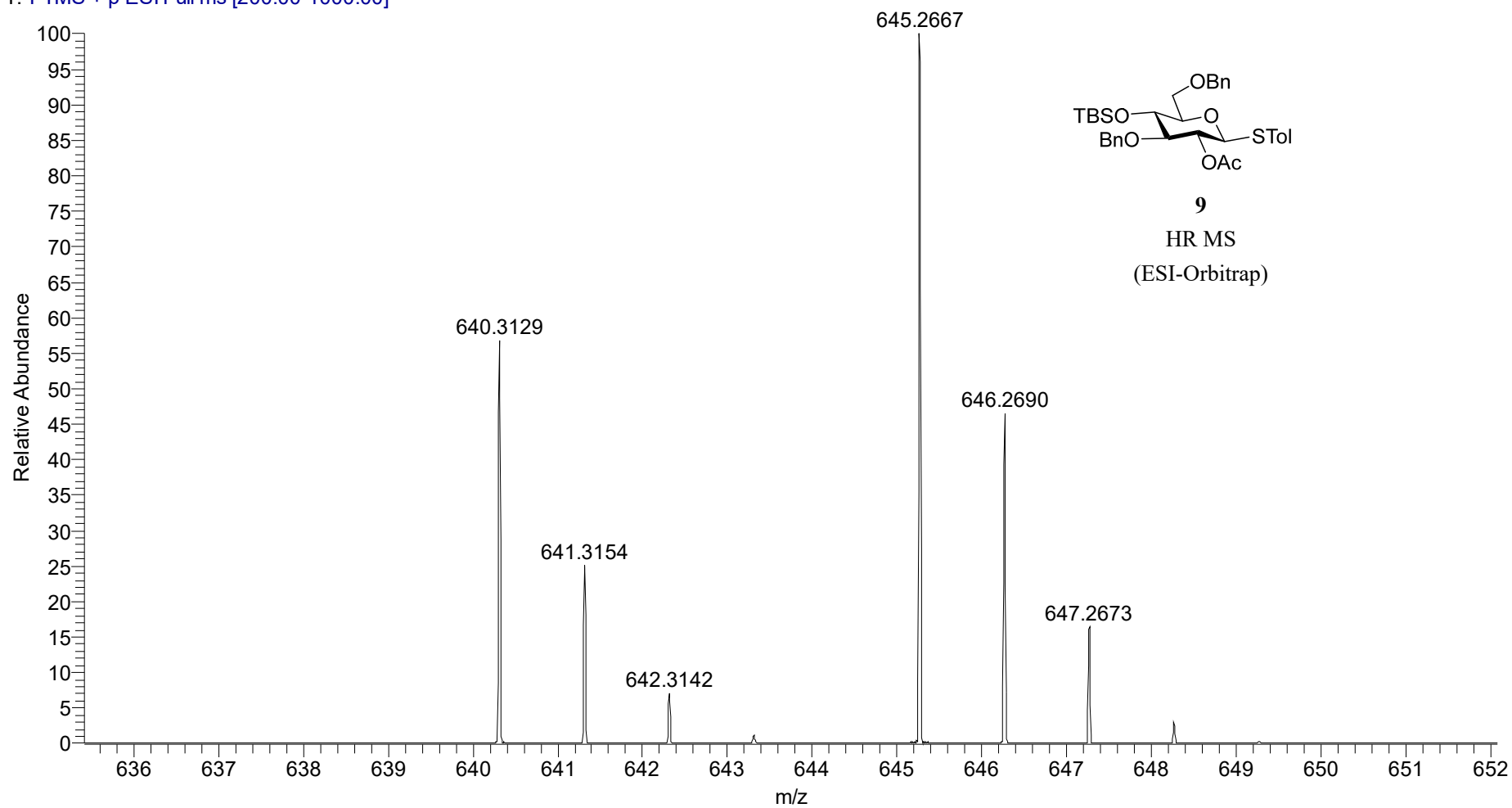


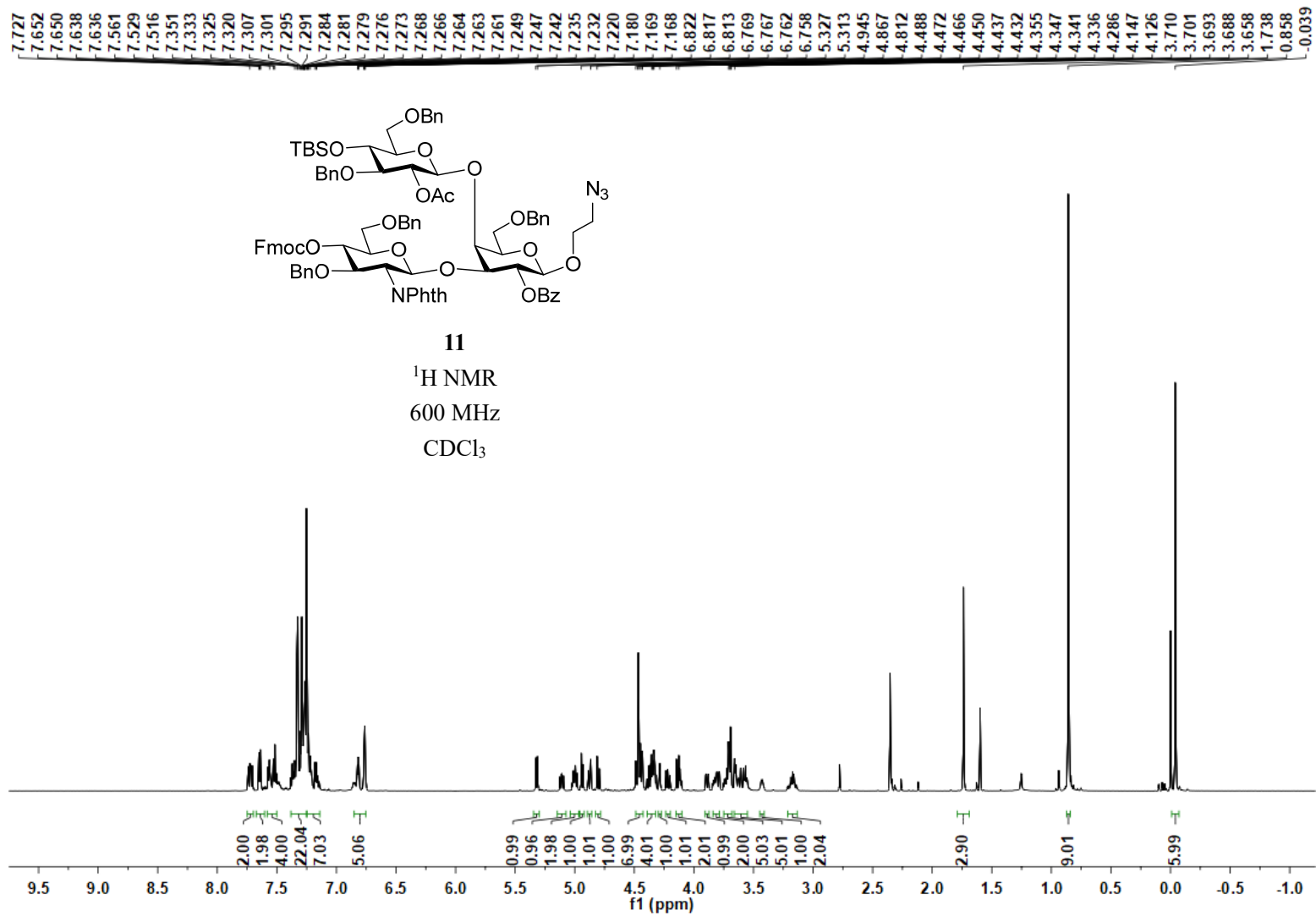
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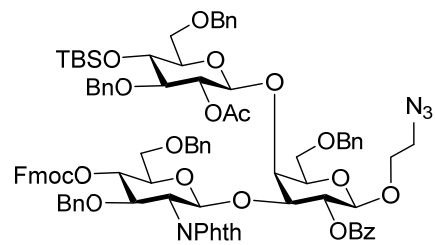
¹³C NMR
150 MHz
CDCl₃



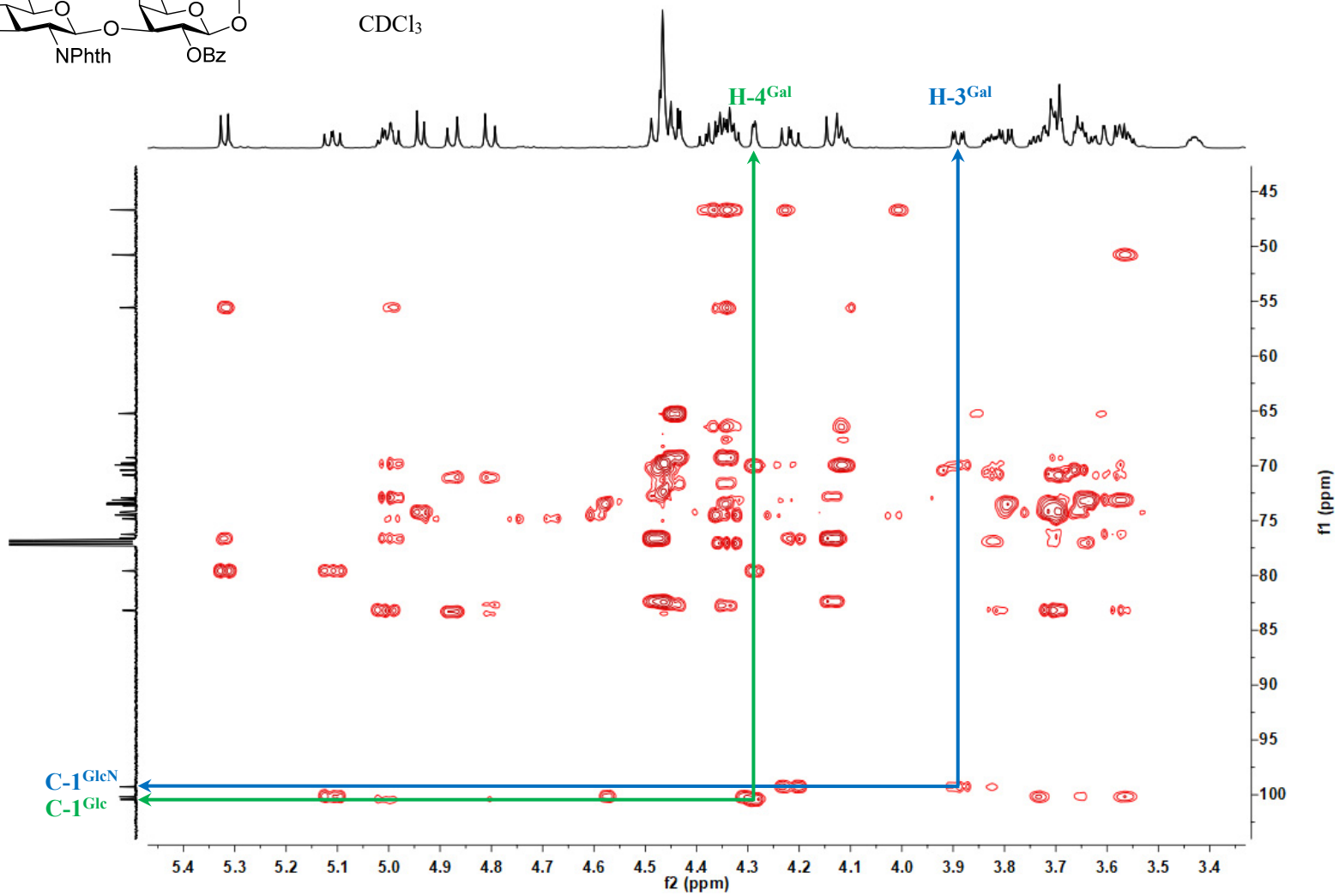
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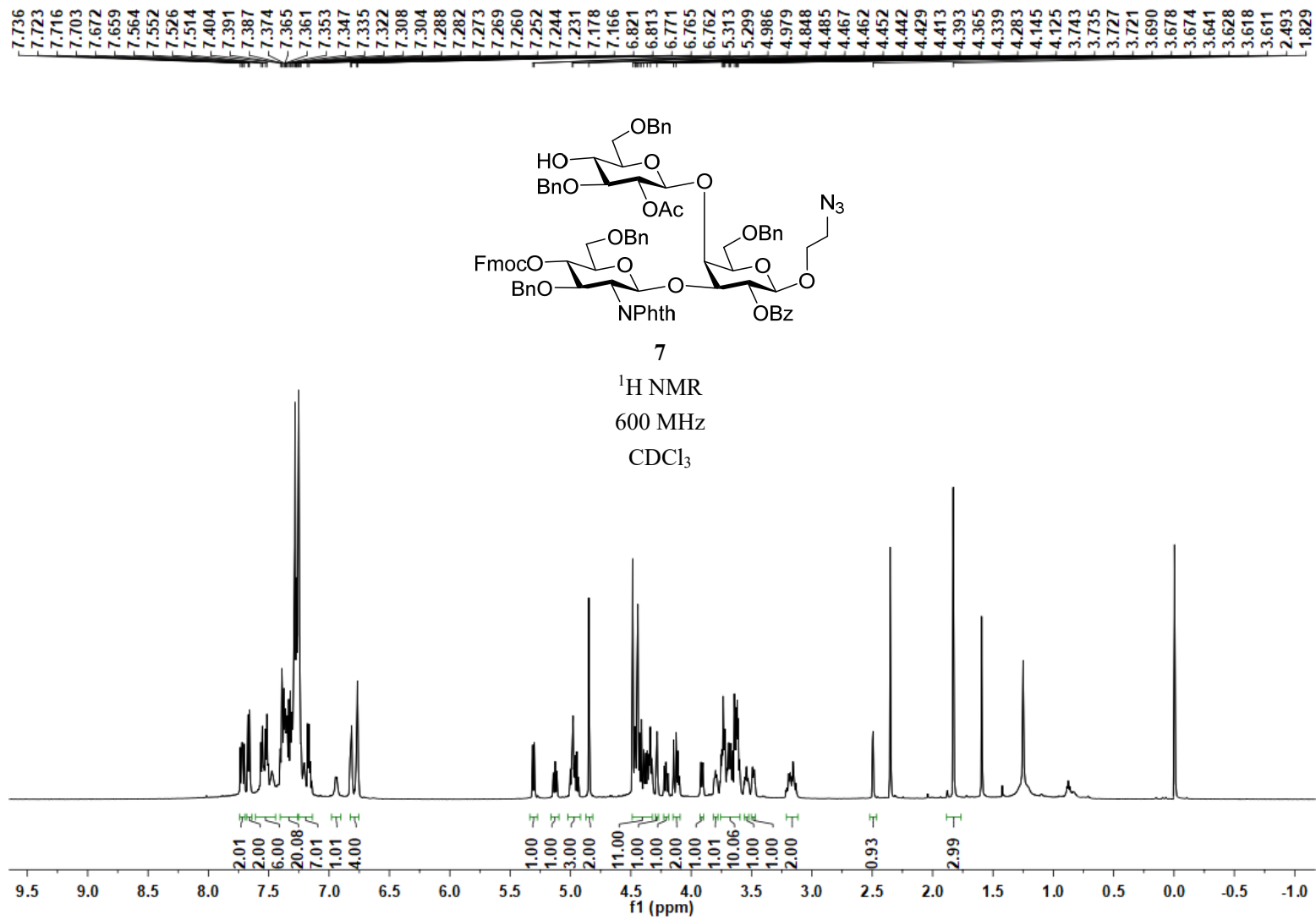




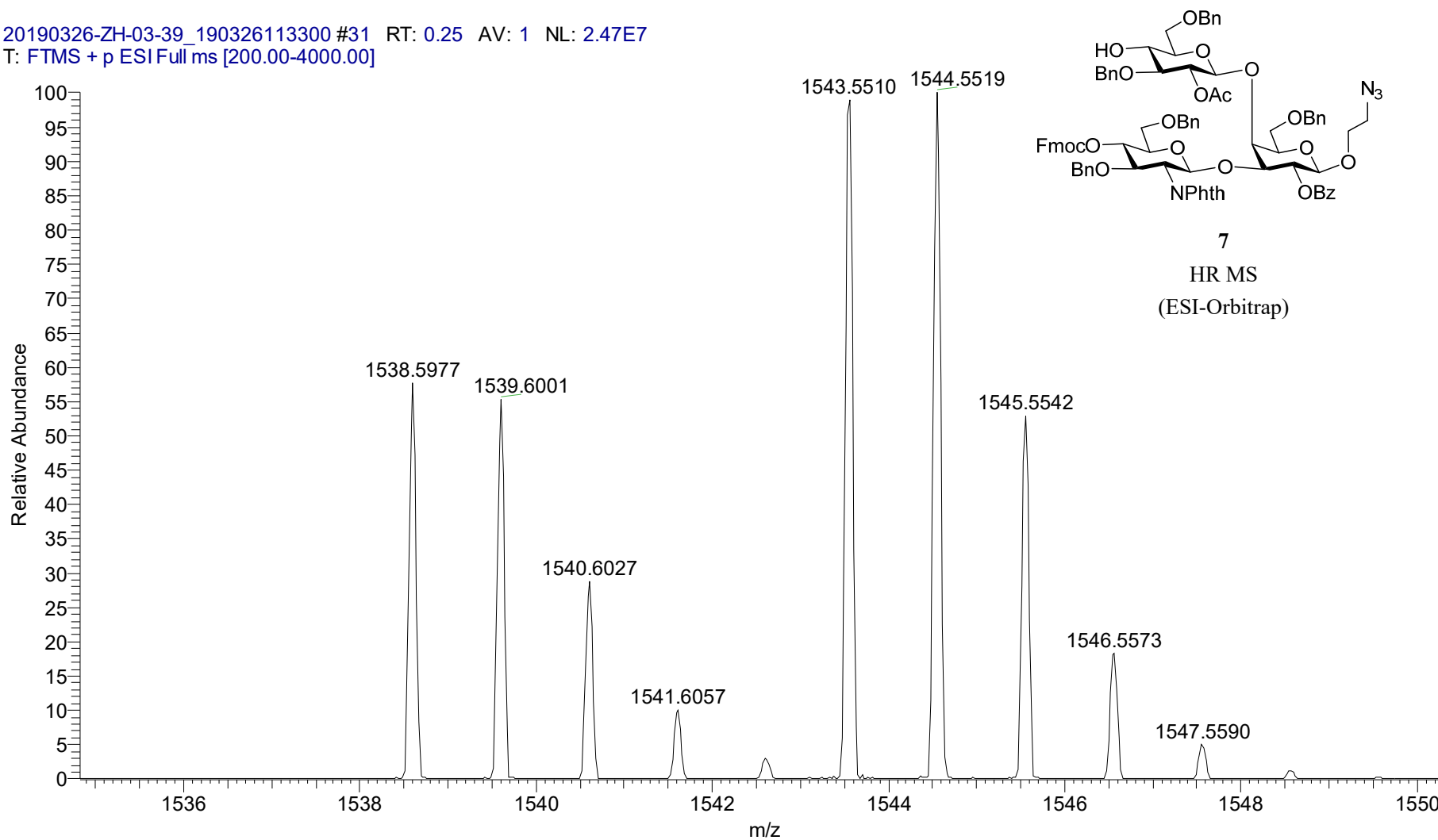


11
¹H-¹³C HMBC
 600/150 MHz
 CDCl₃

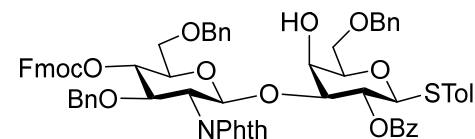
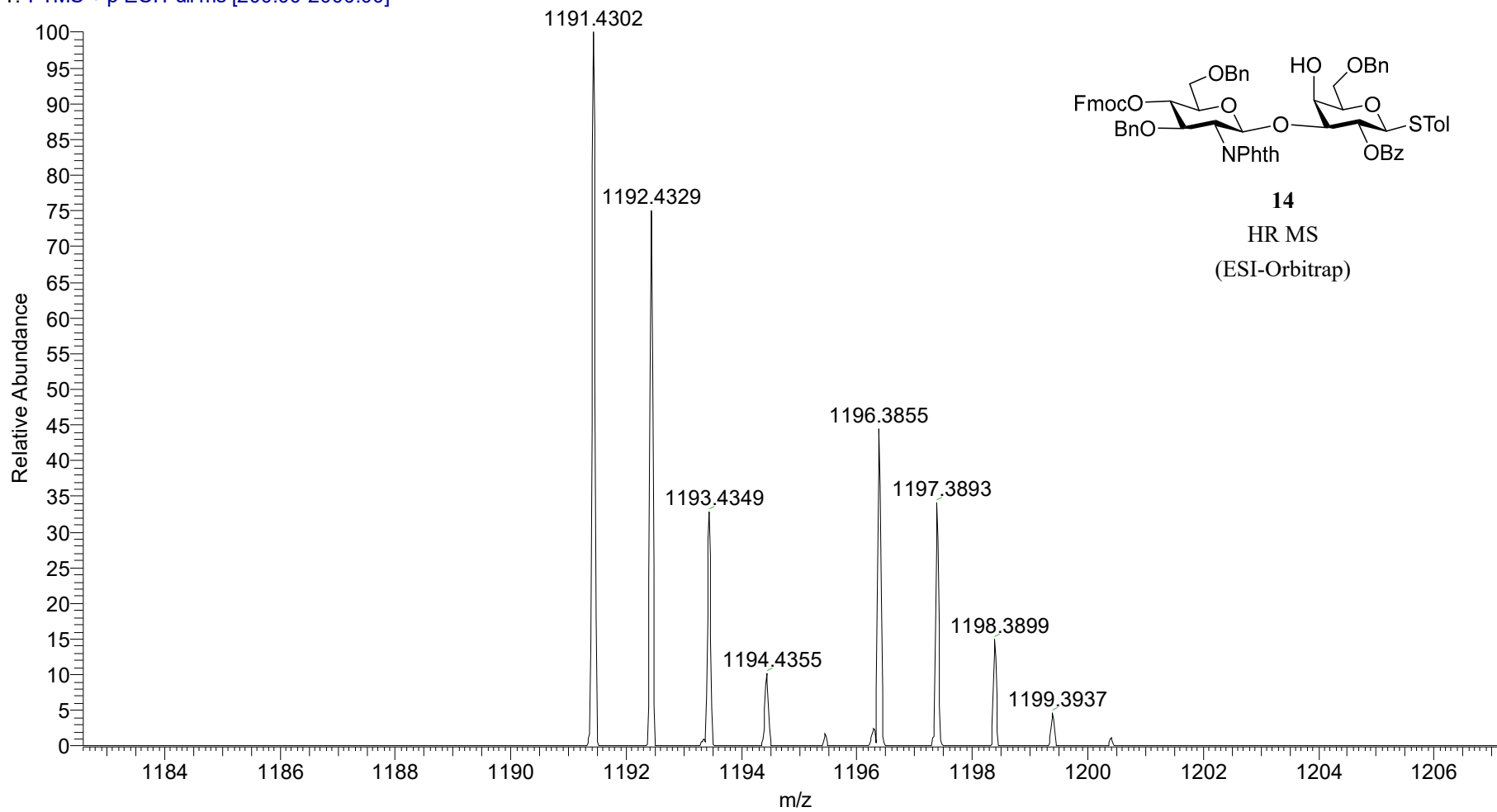




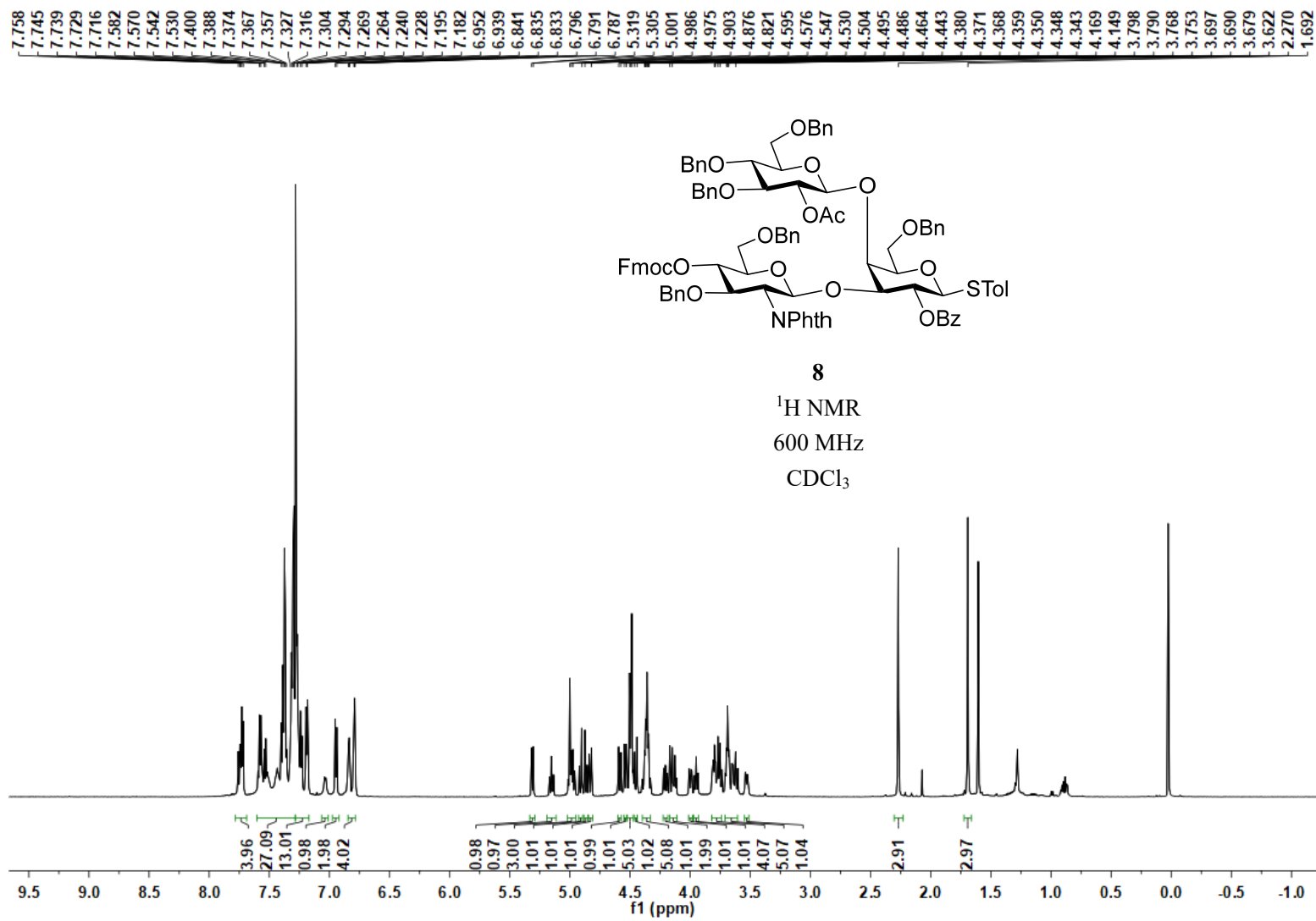
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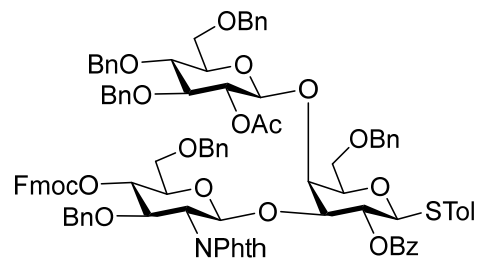


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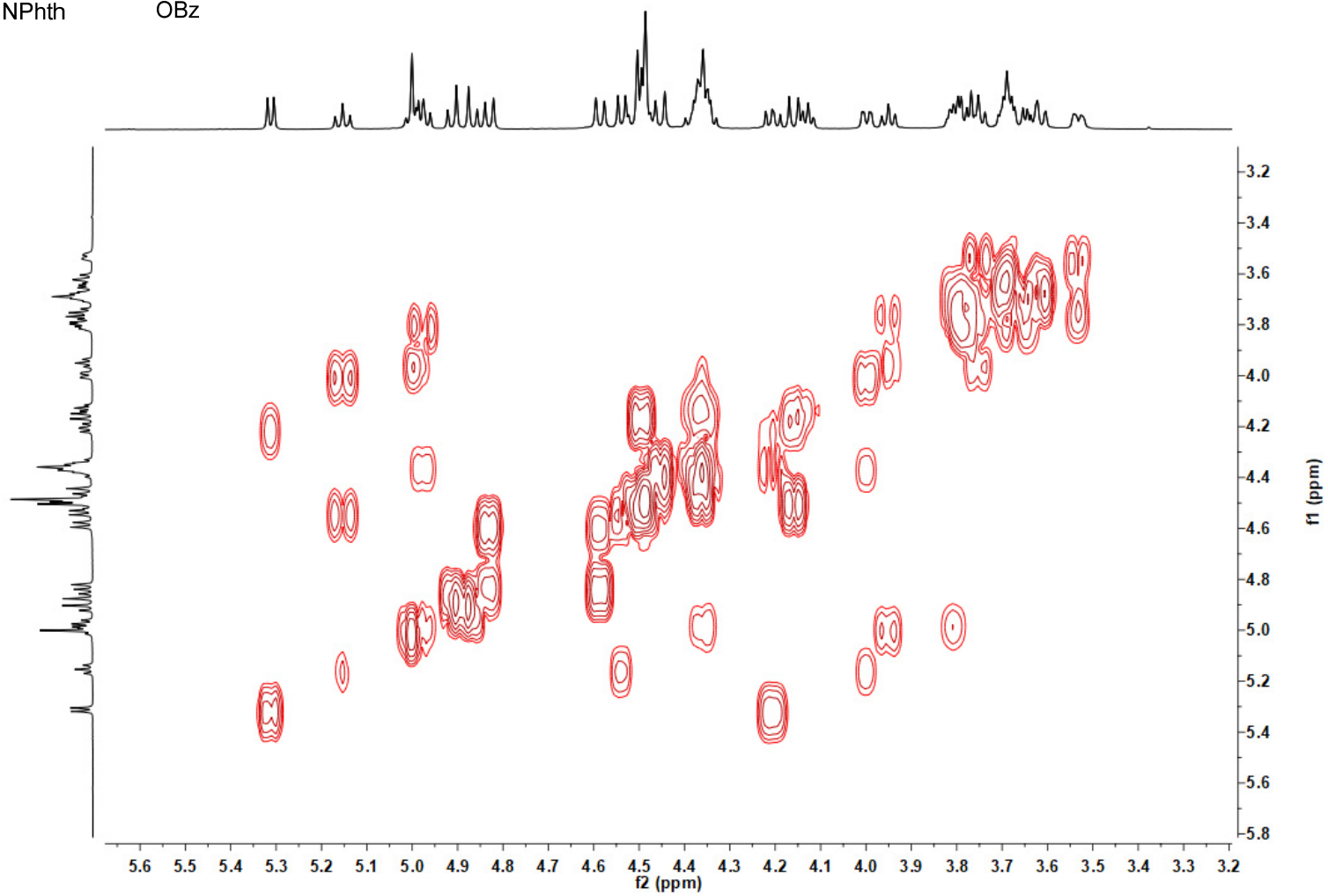


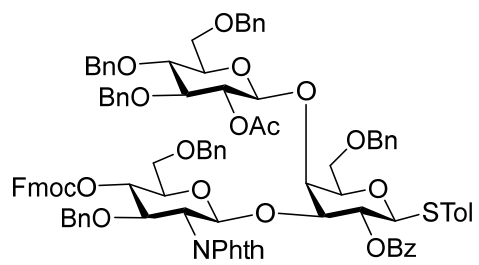
14
HR MS
(ESI-Orbitrap)





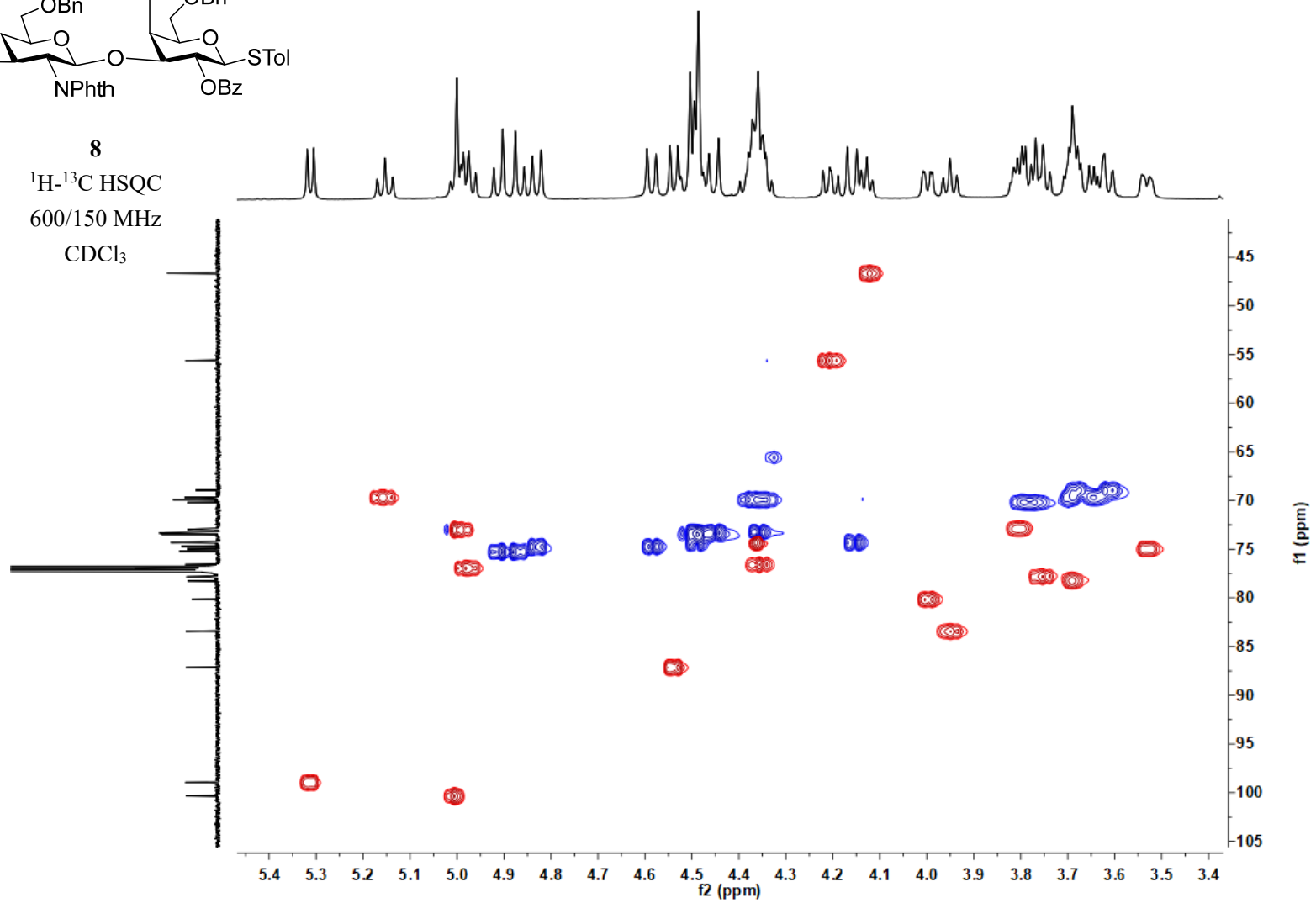
8
 ^1H - ^1H COSY
600 MHz
 CDCl_3



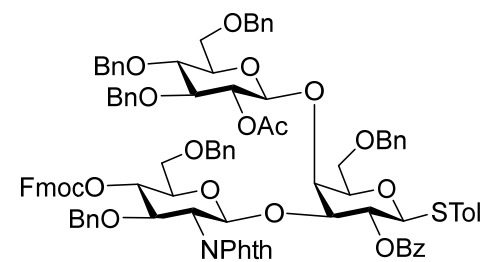
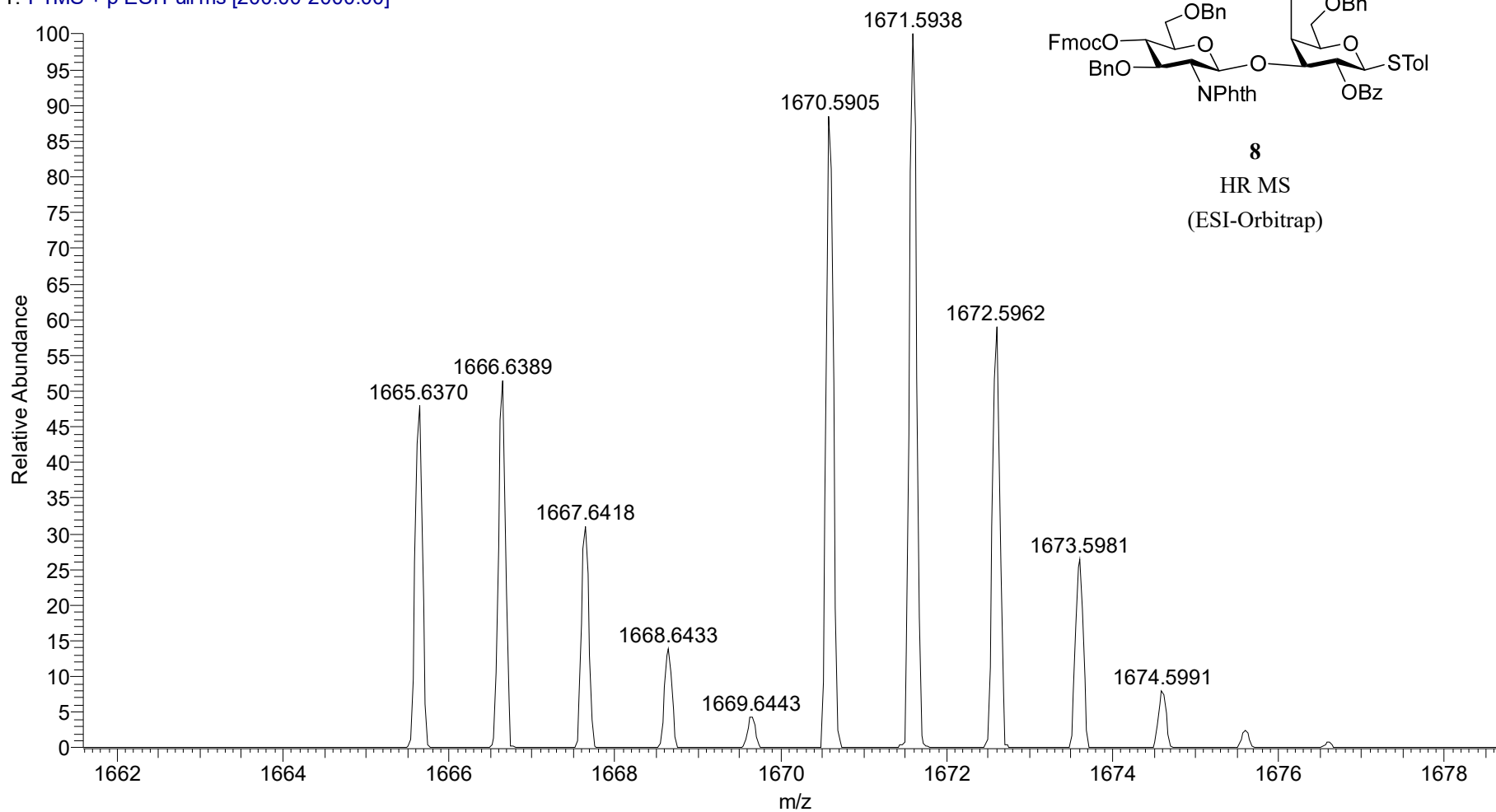


8

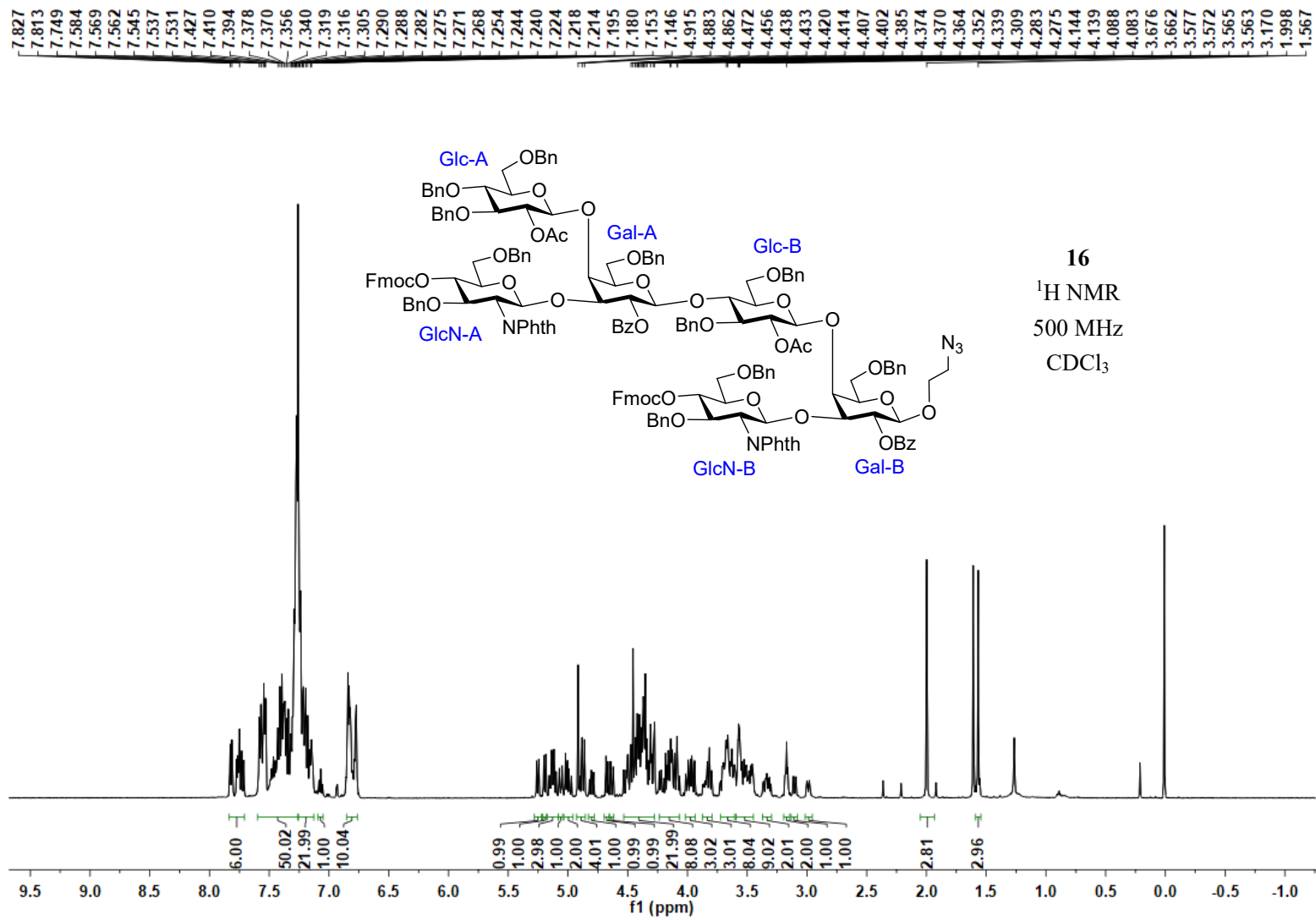
^1H - ^{13}C HSQC
600/150 MHz
 CDCl_3

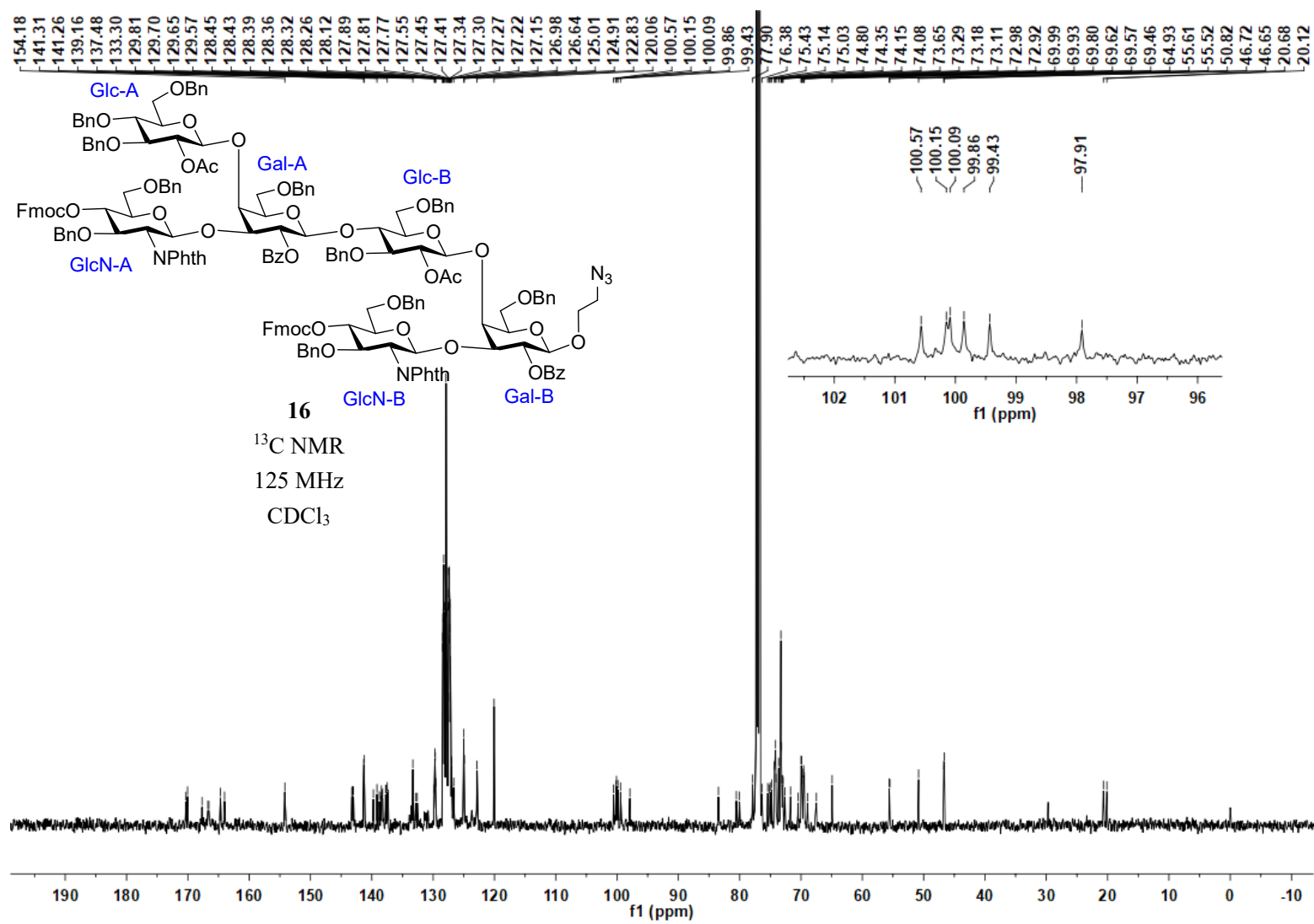


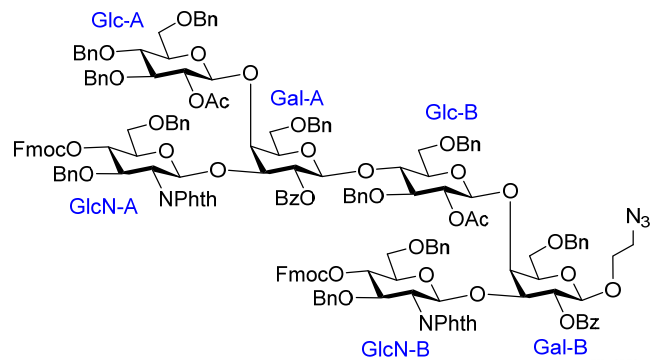
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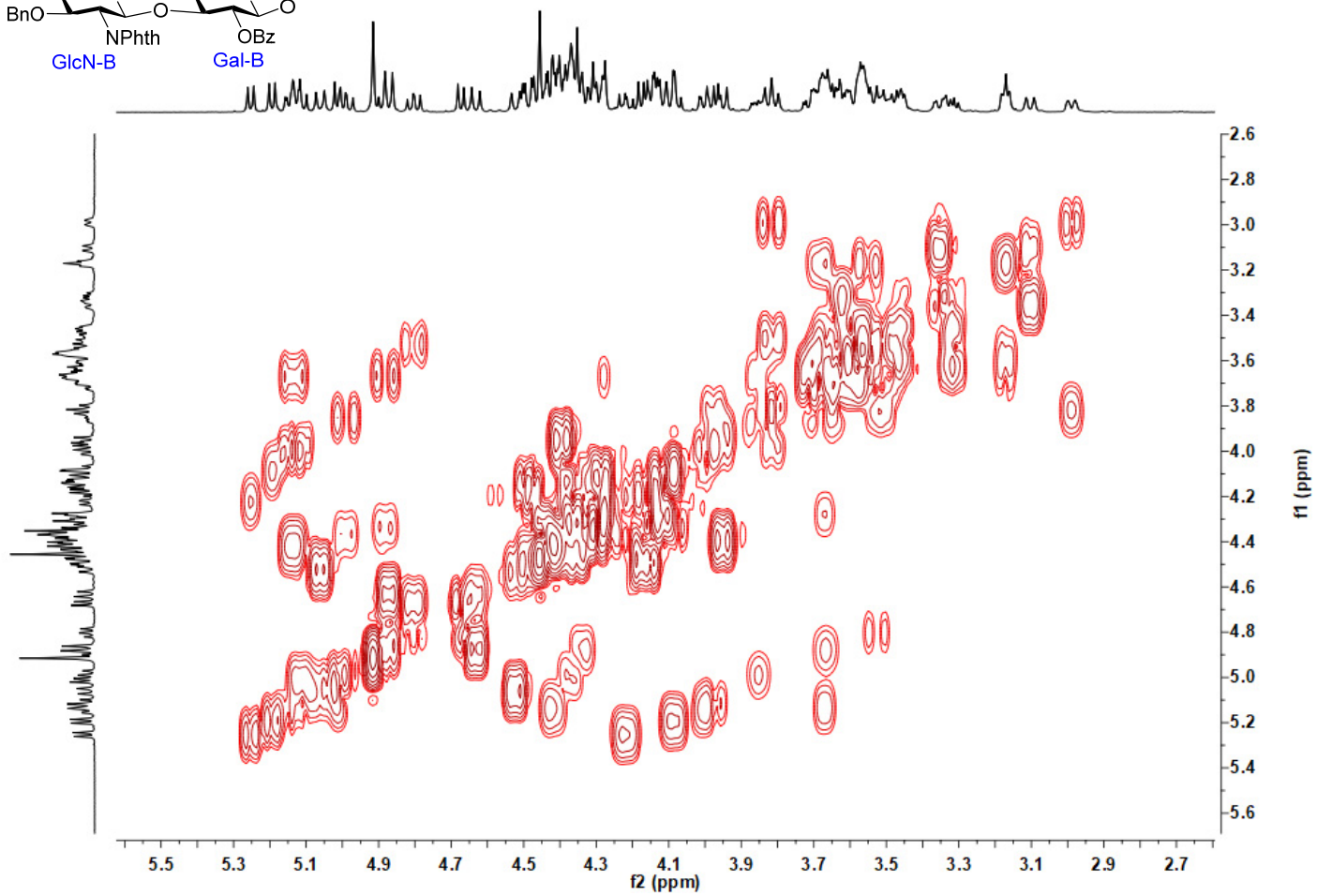
8
HR MS
(ESI-Orbitrap)

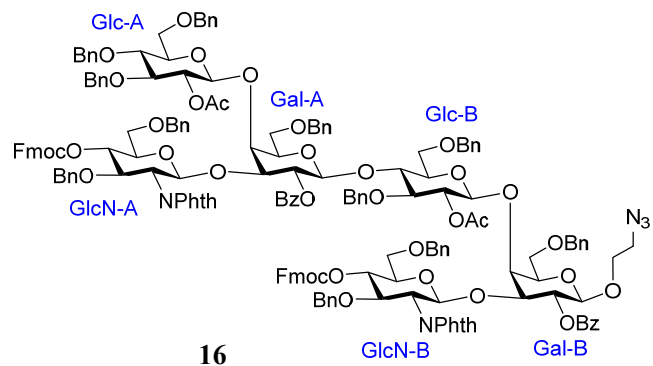




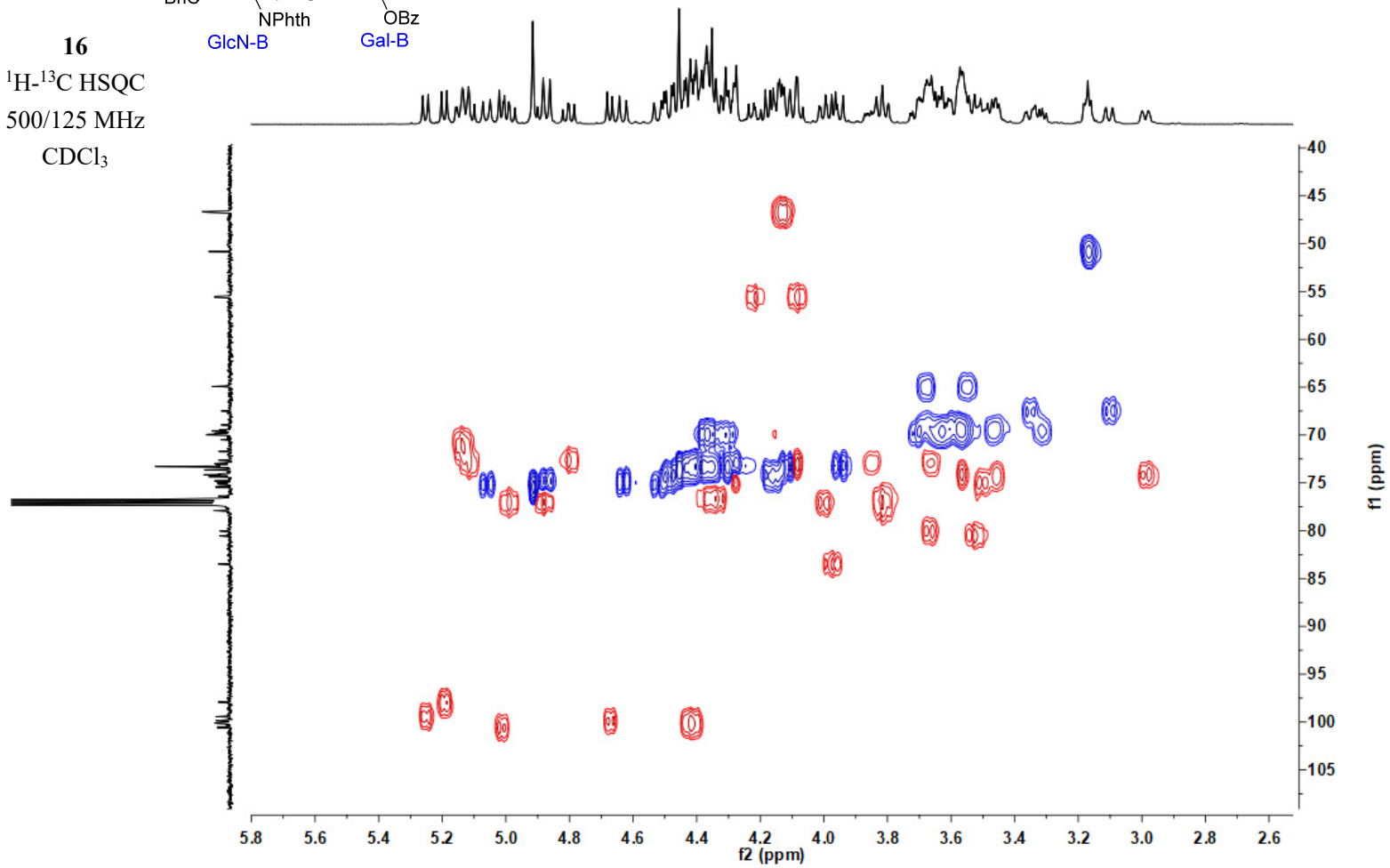


16
¹H-¹H COSY
 500 MHz
 CDCl₃

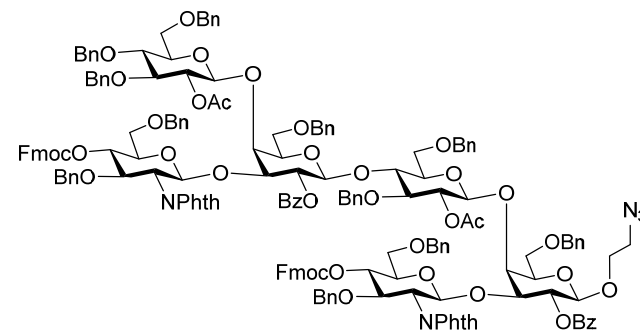




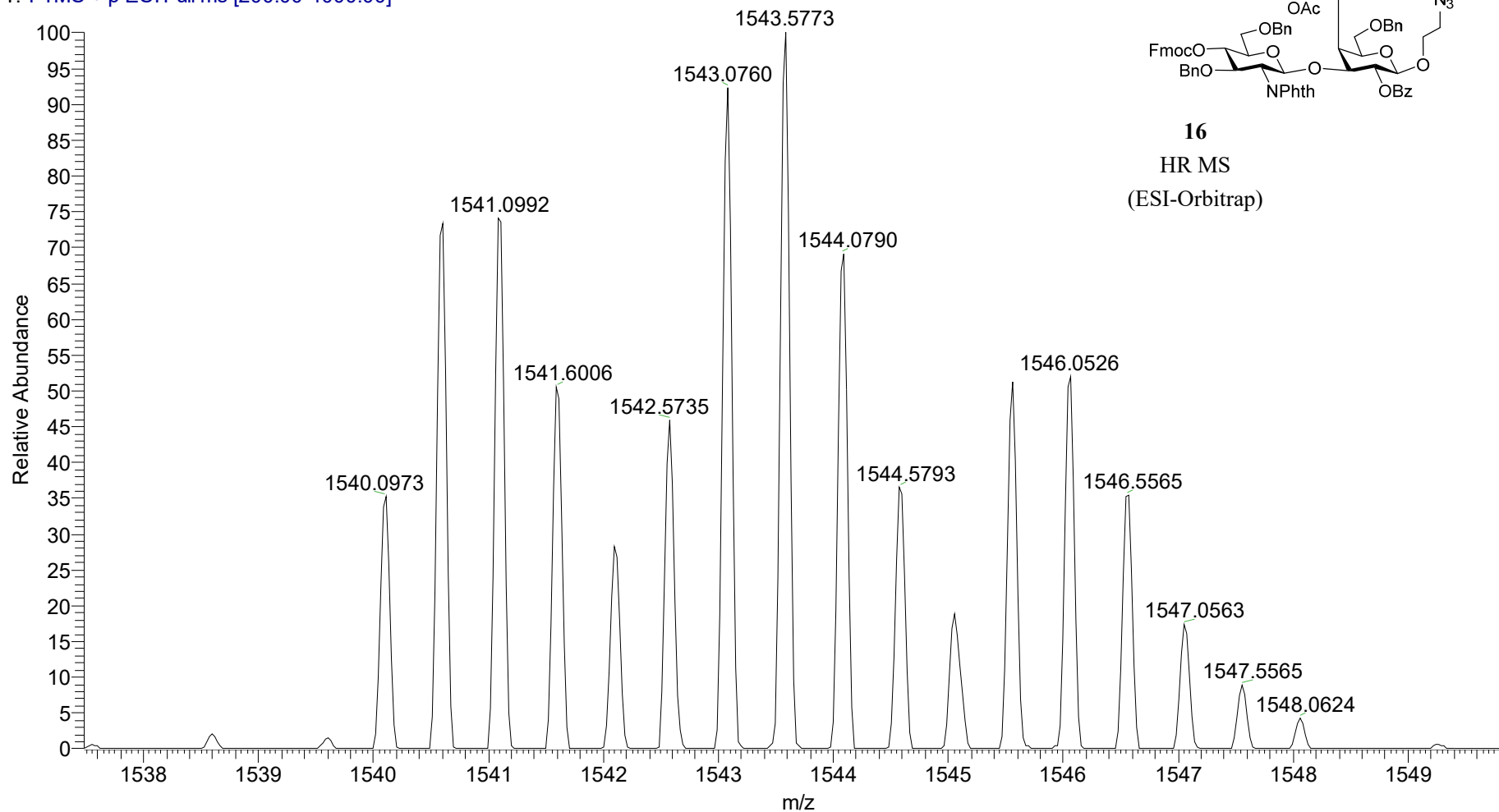
16
¹H-¹³C HSQC
 500/125 MHz
 CDCl₃

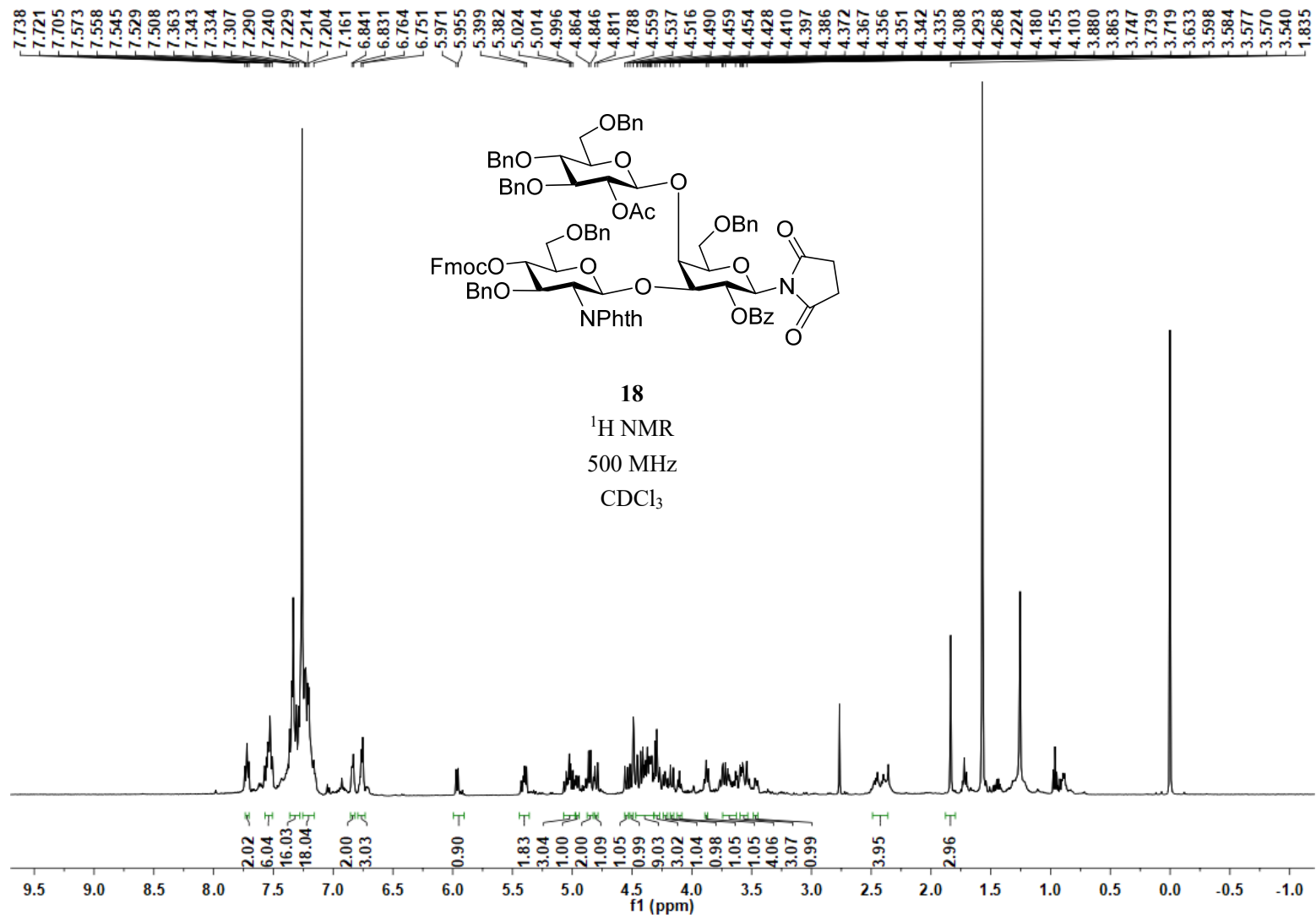


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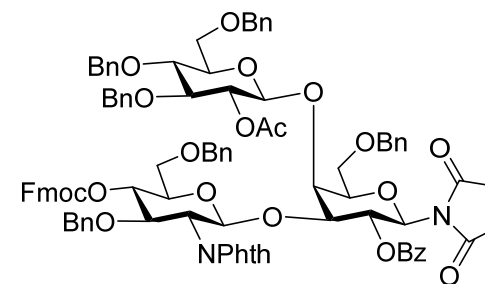
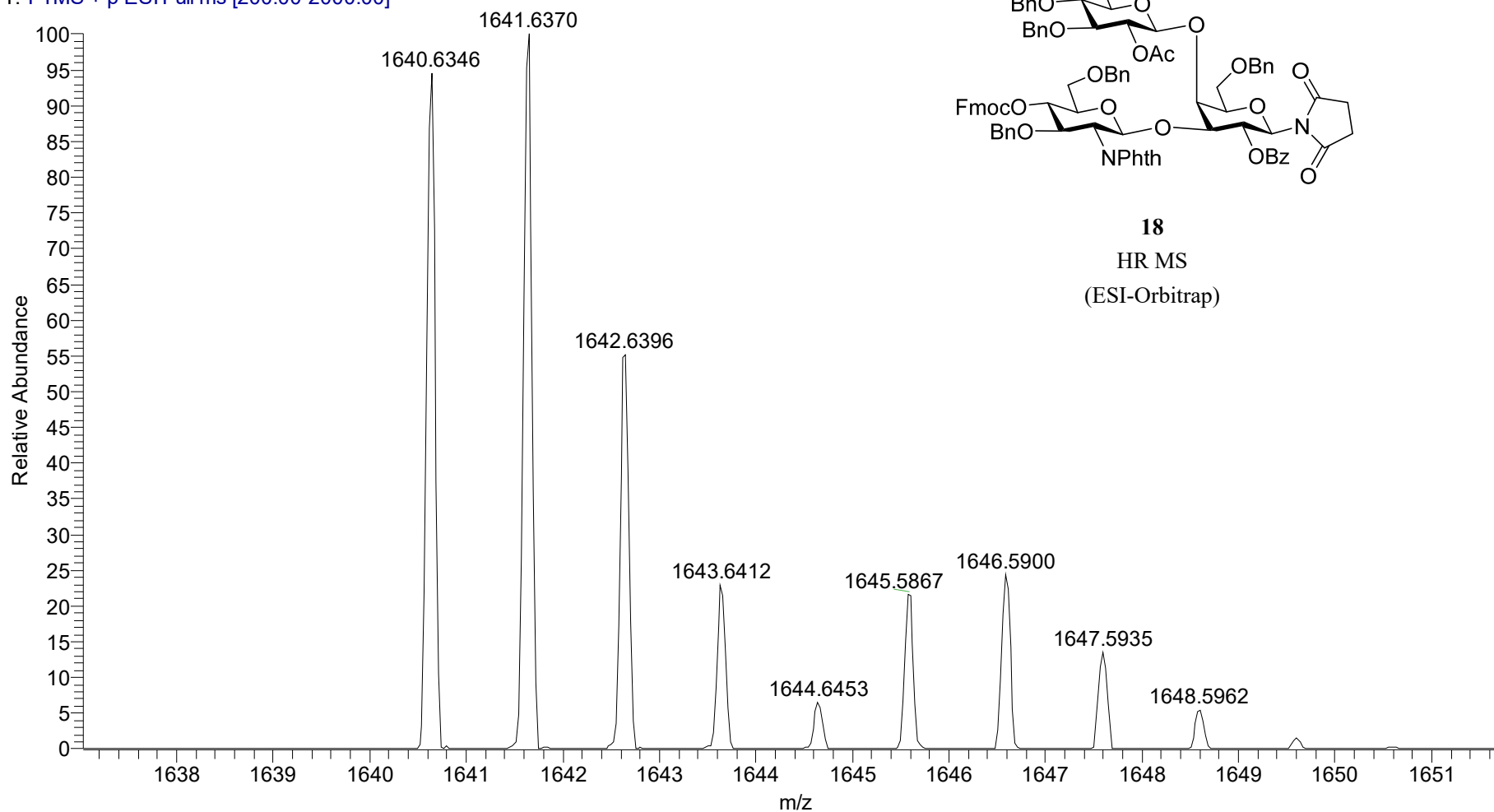


16
HR MS
(ESI-Orbitrap)

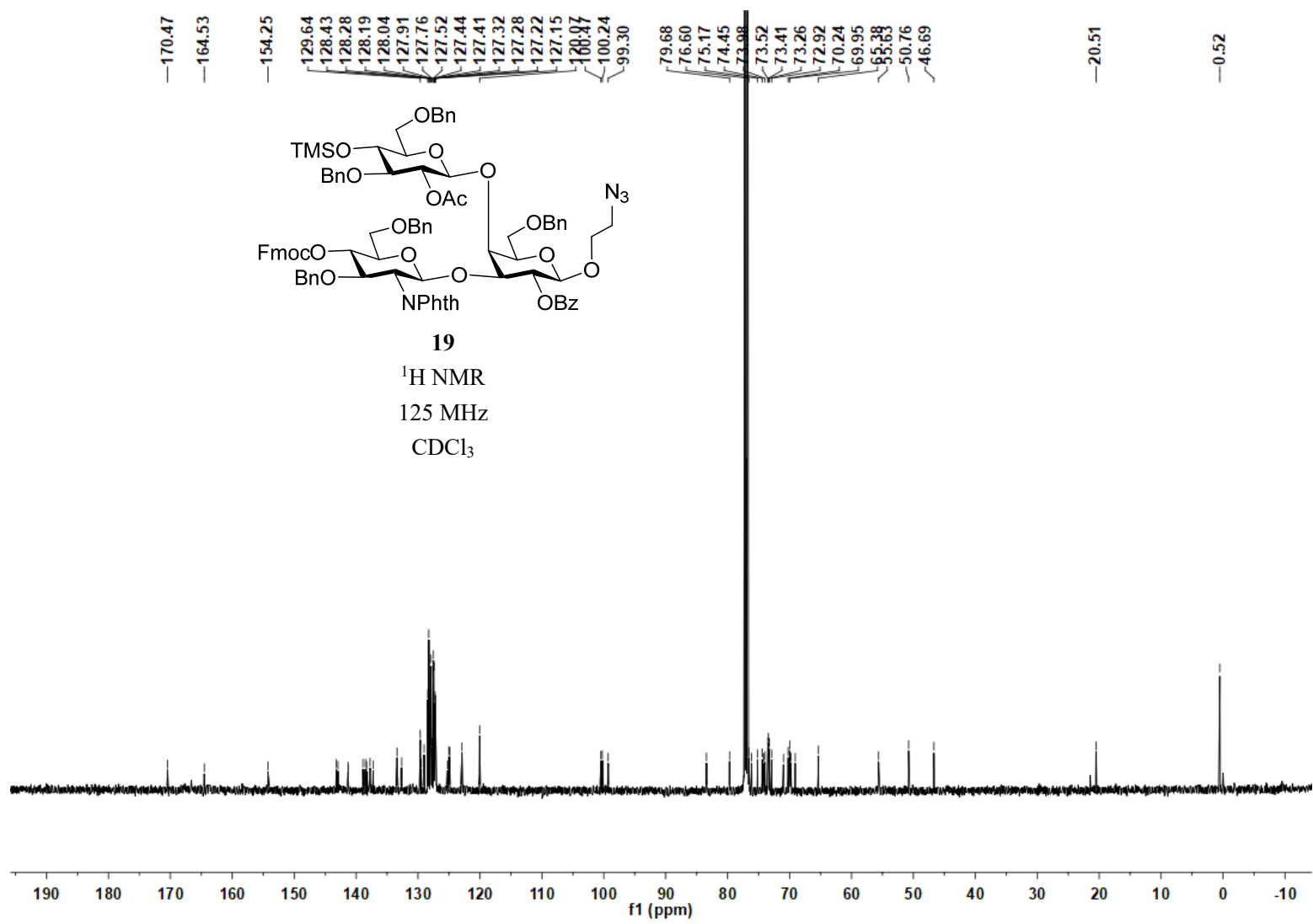


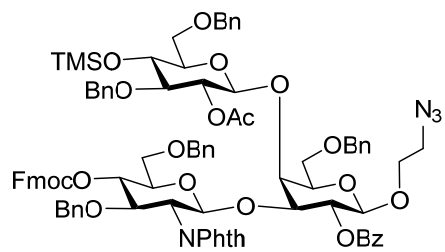


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18
HR MS
(ESI-Orbitrap)



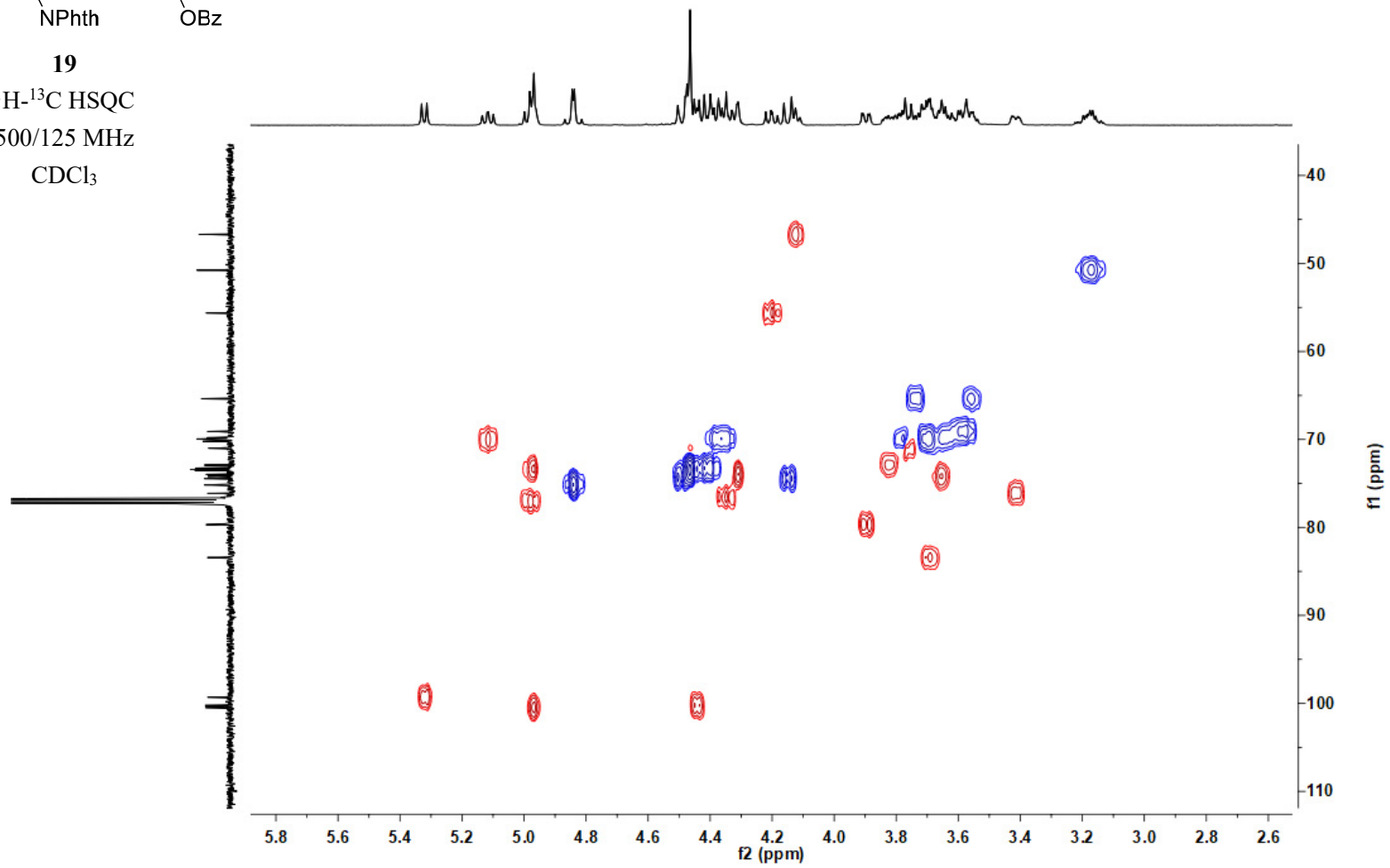


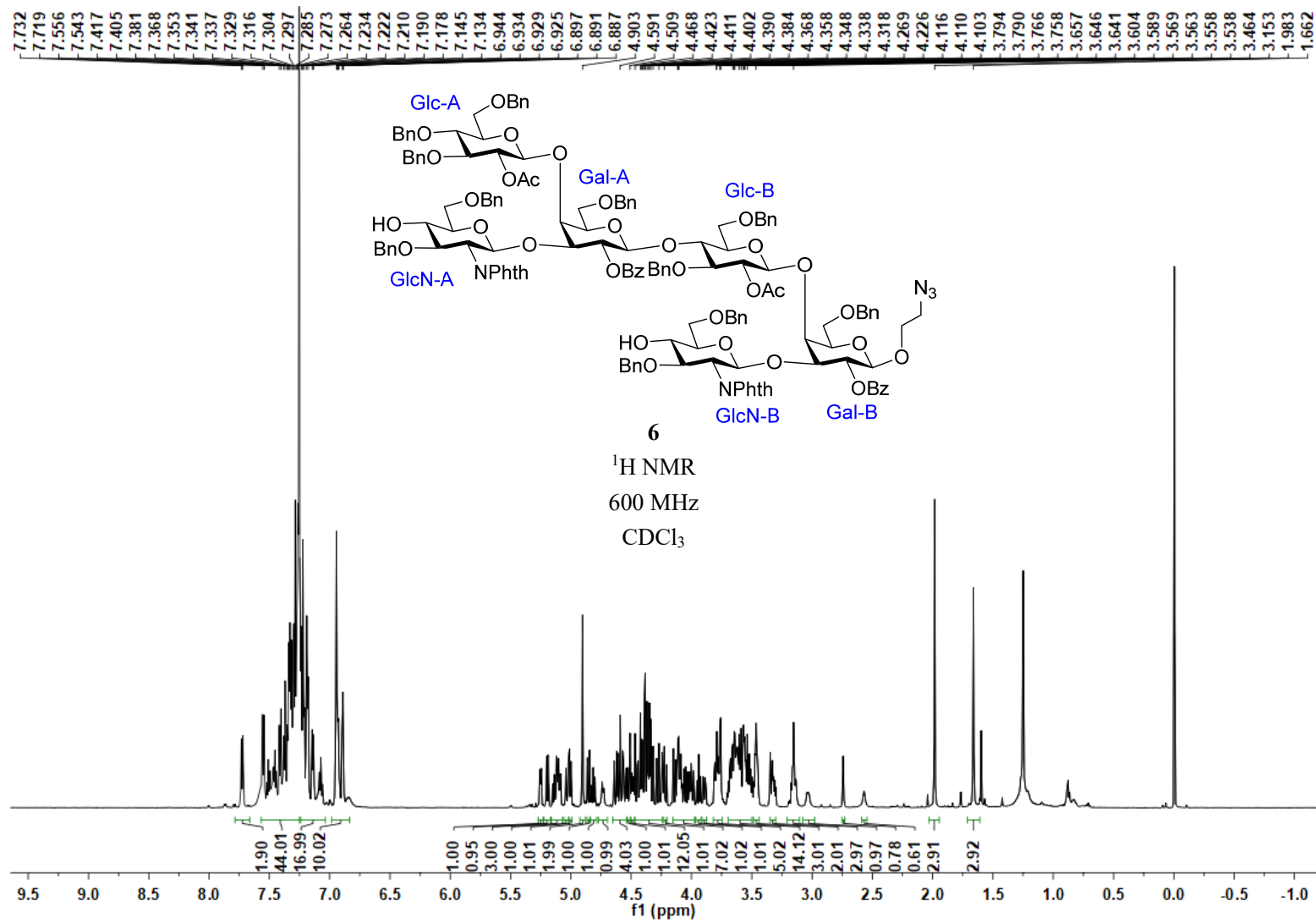
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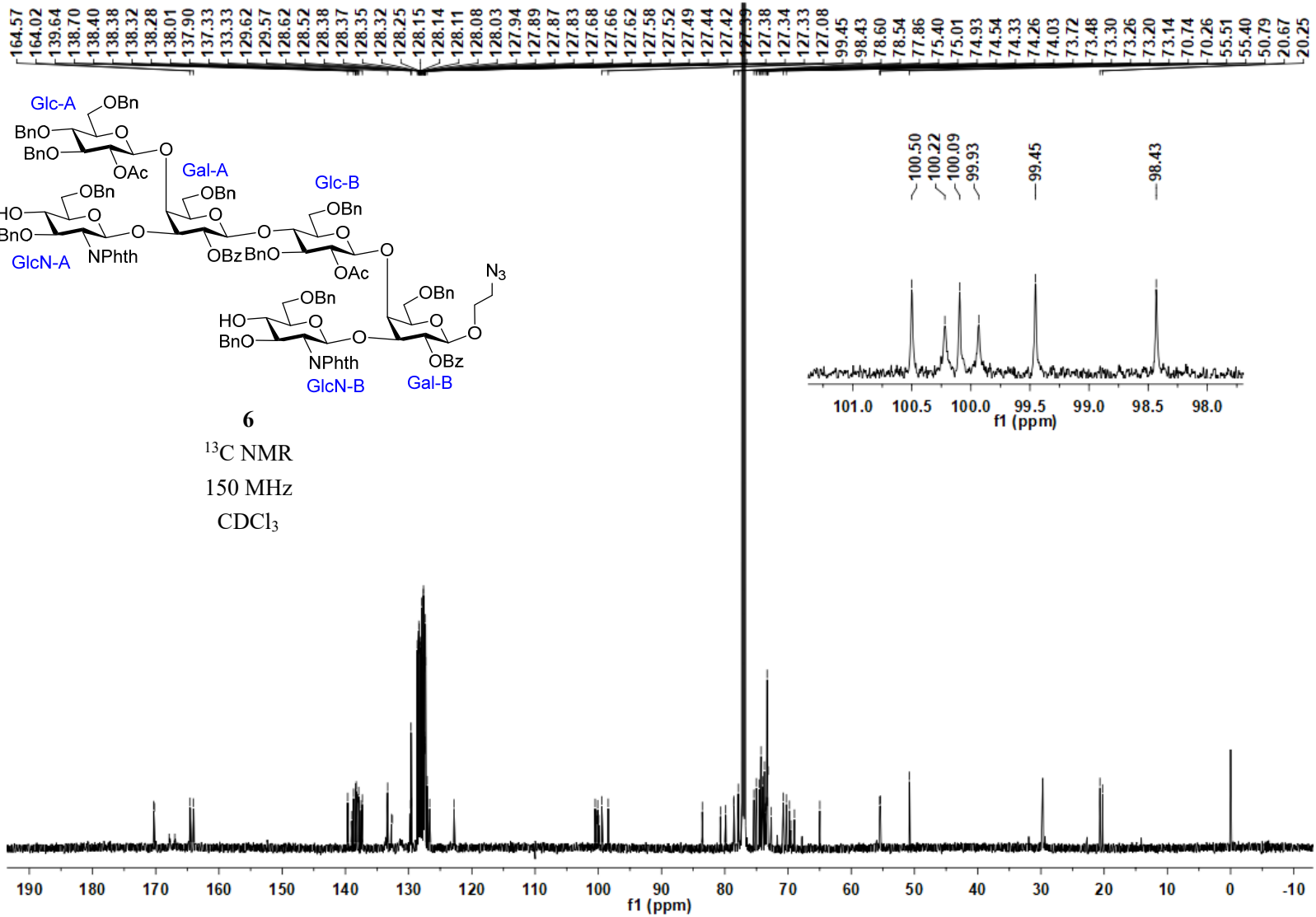
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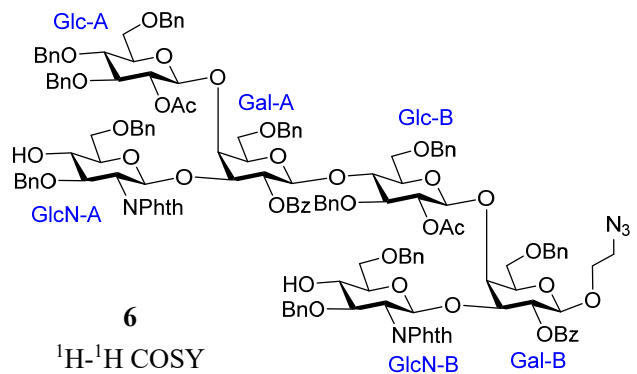
500/125 MHz

CDCl_3



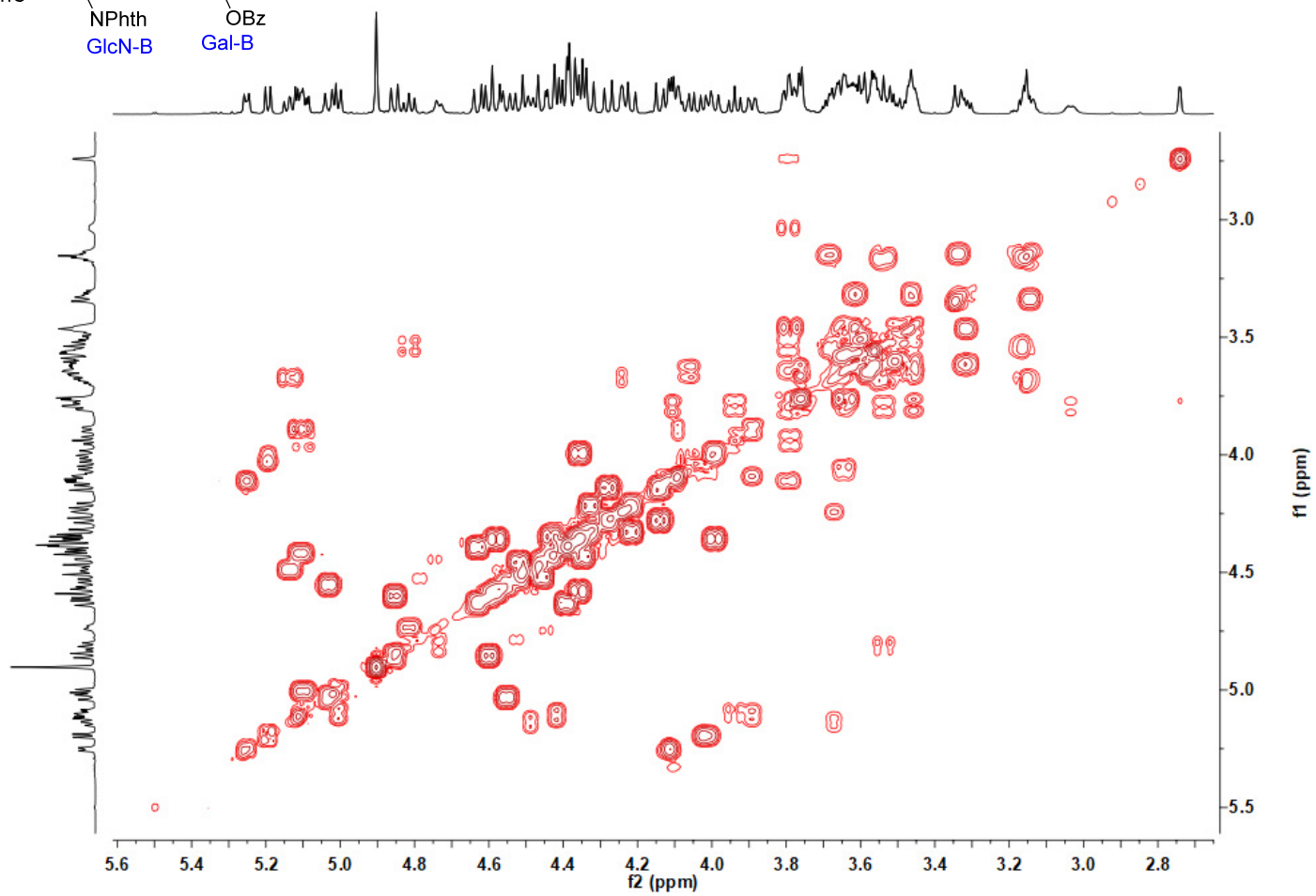


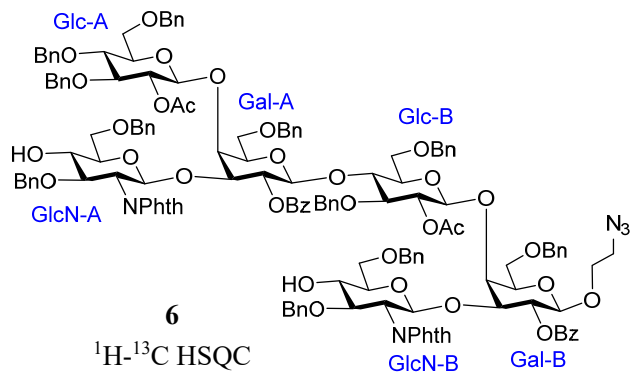




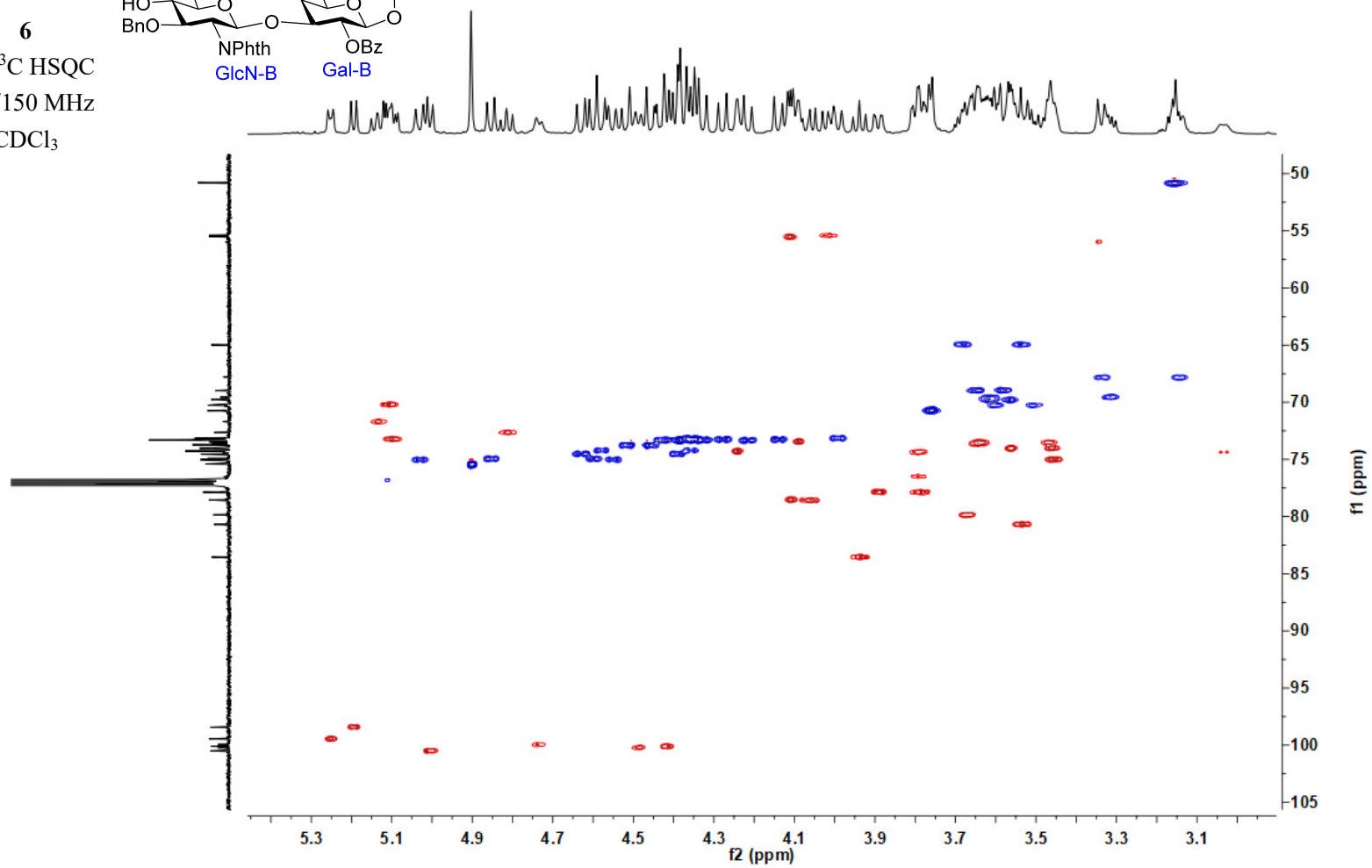
6

¹H-¹H COSY
 600 MHz
 CDCl₃

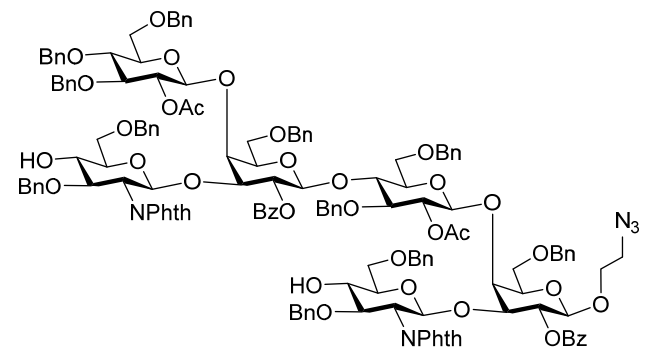




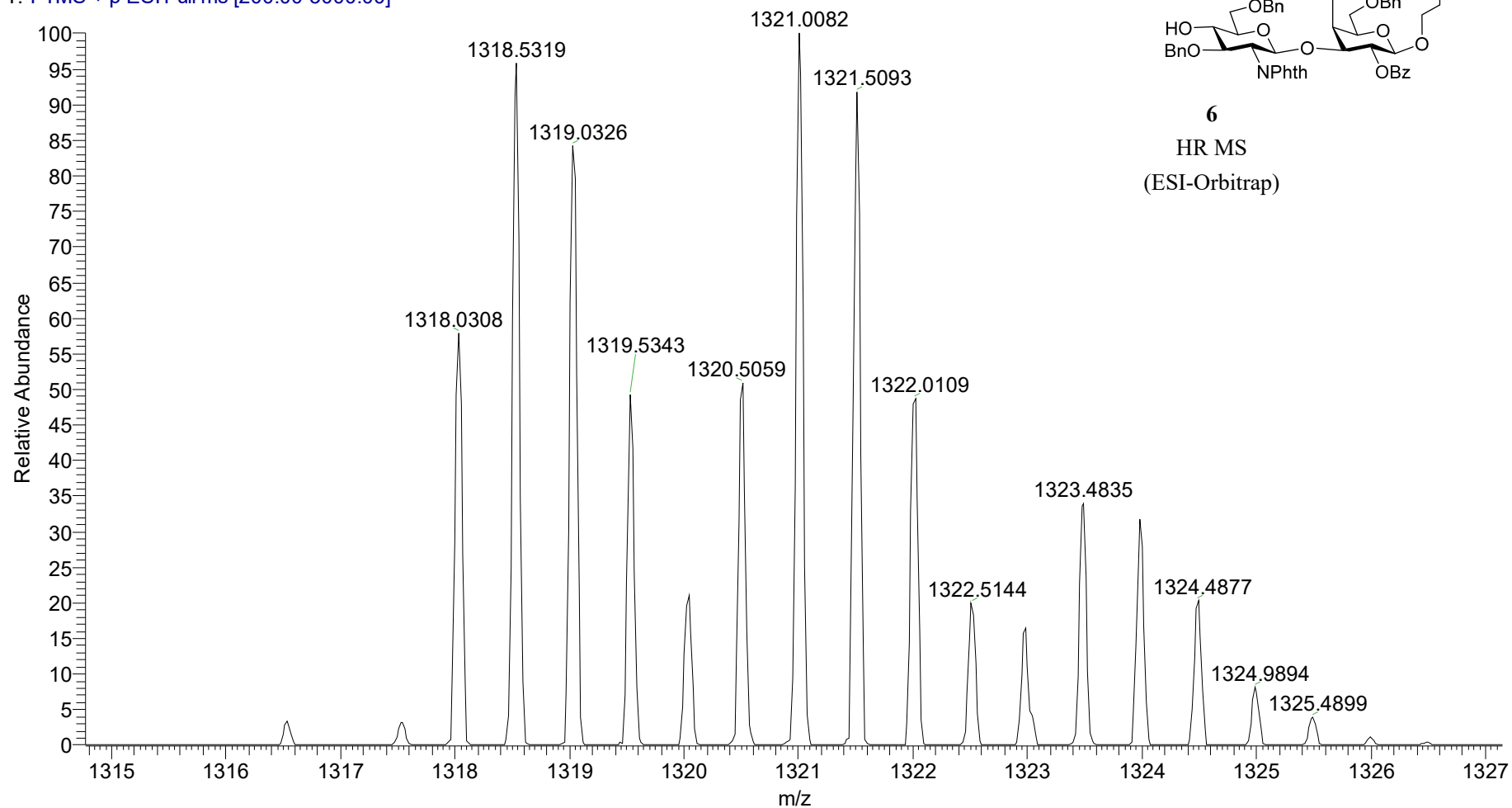
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¹H-¹³C HSQC
 600/150 MHz
 CDCl₃



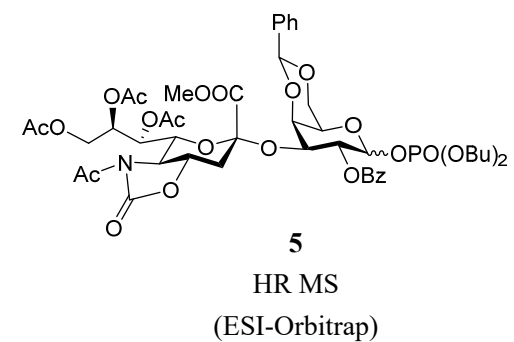
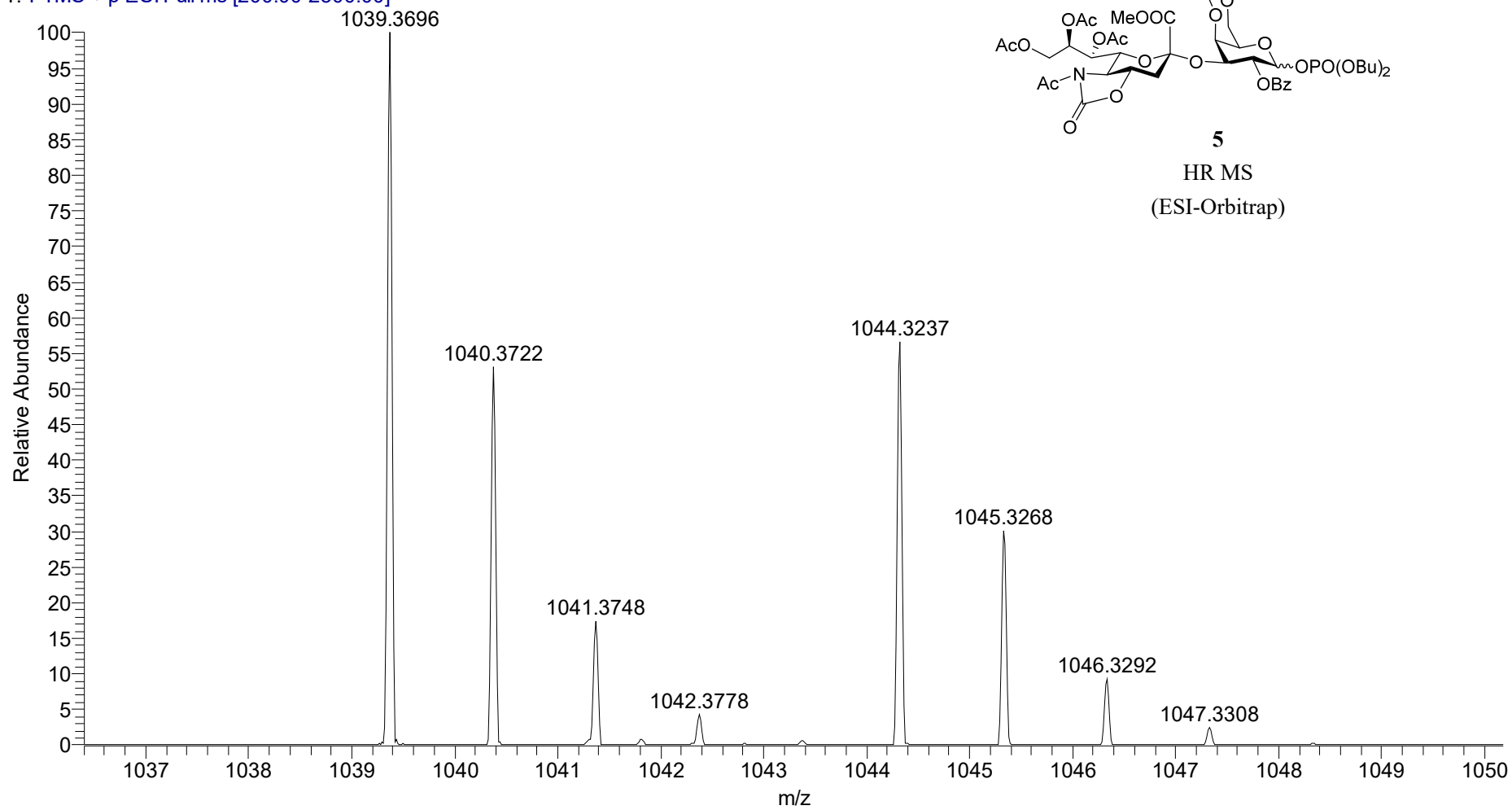
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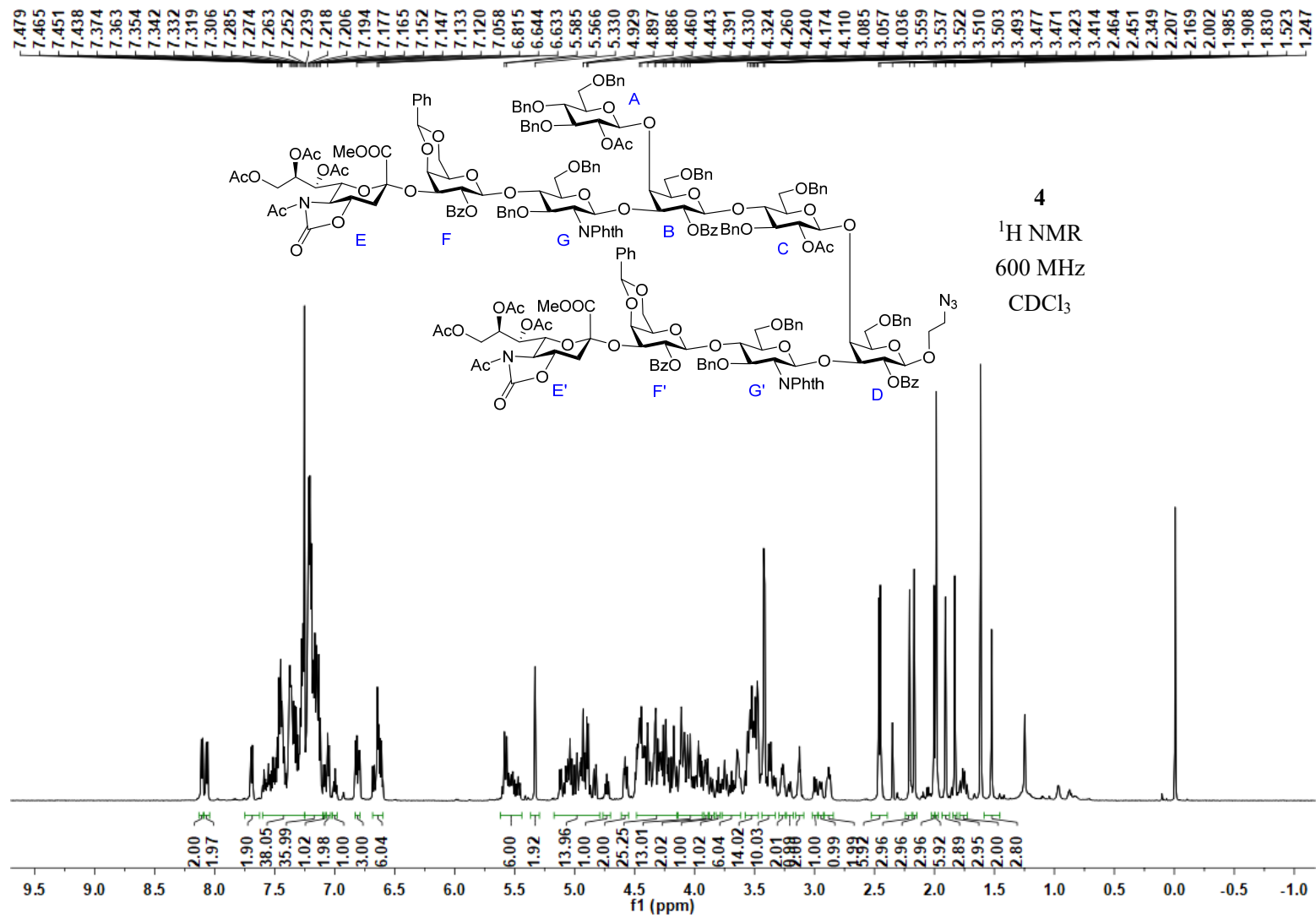


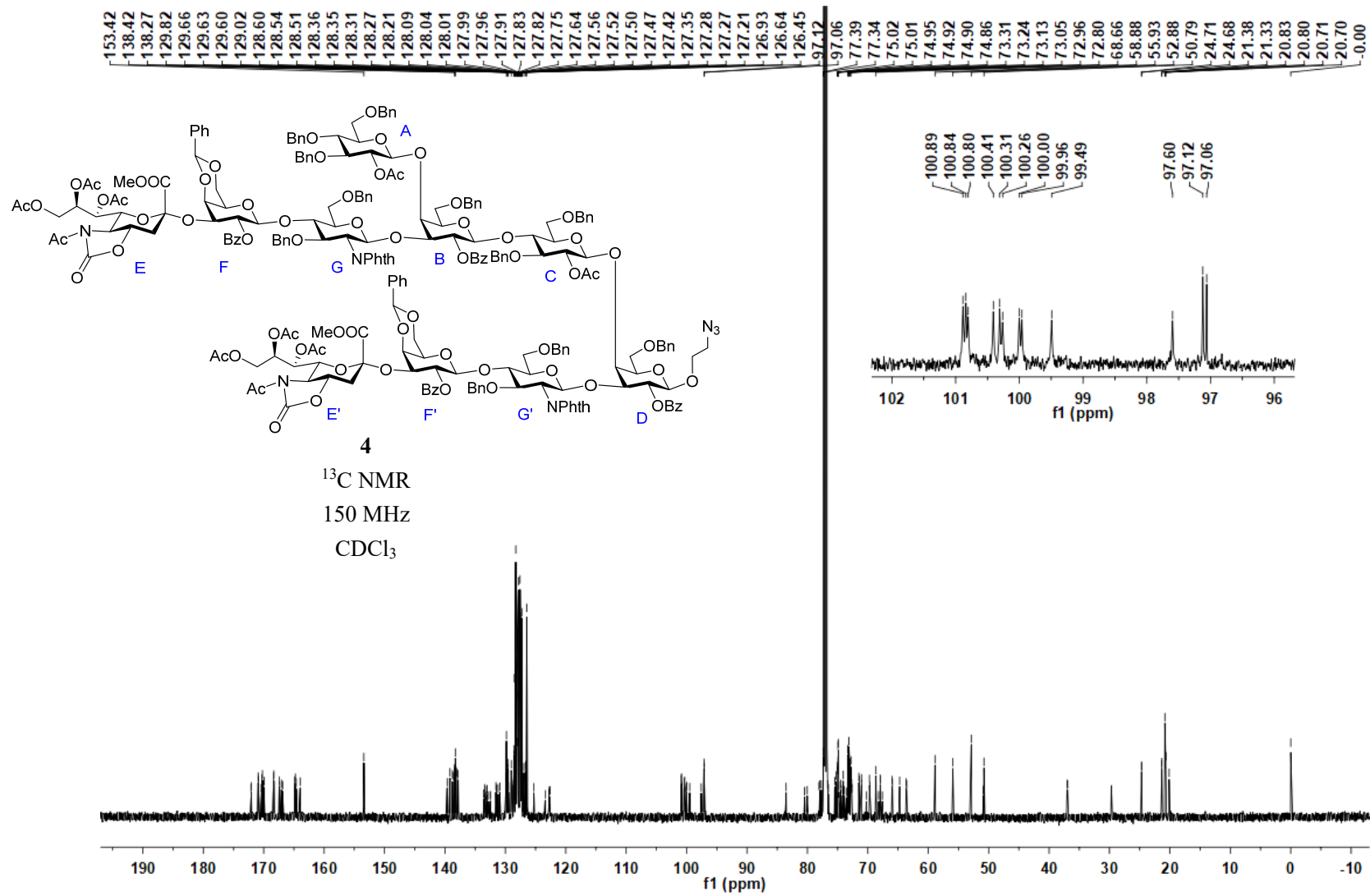
6
HR MS
(ESI-Orbitrap)

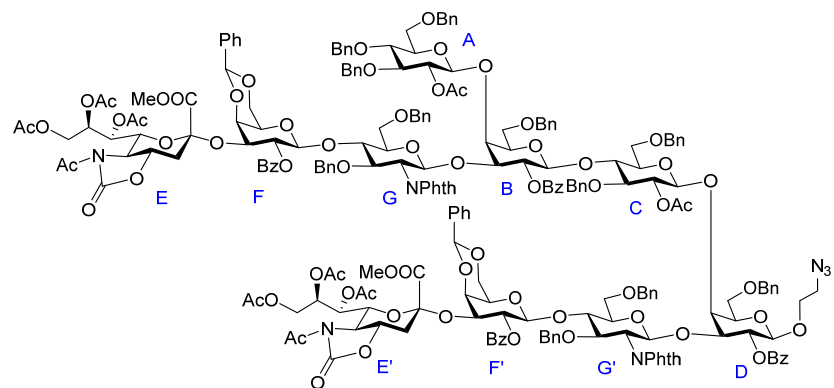


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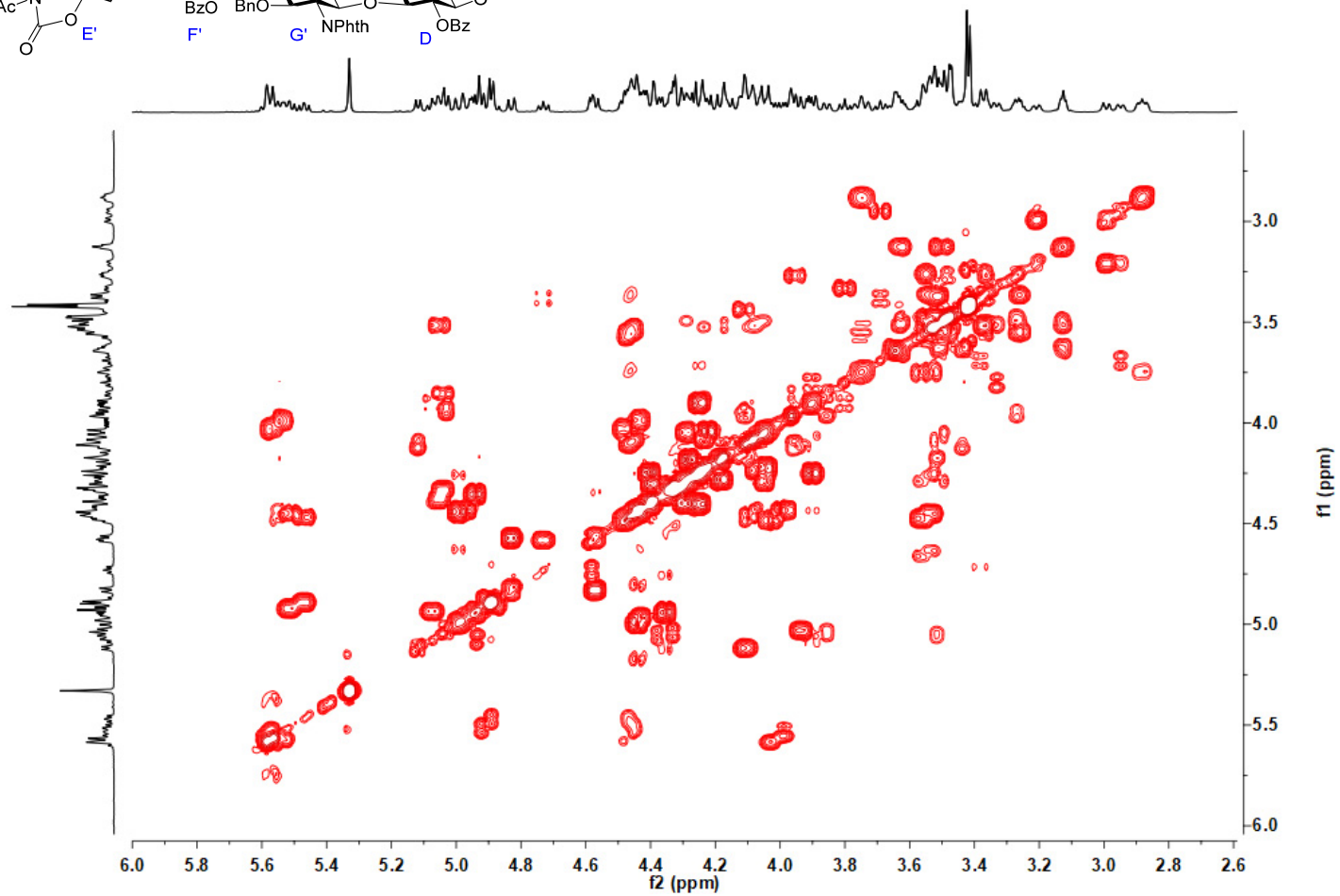


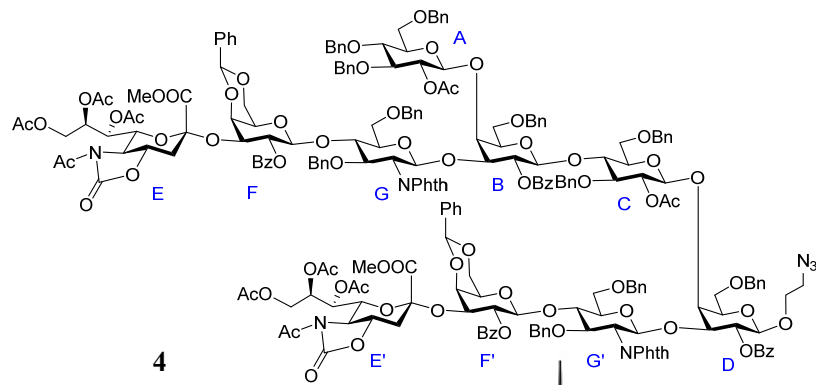




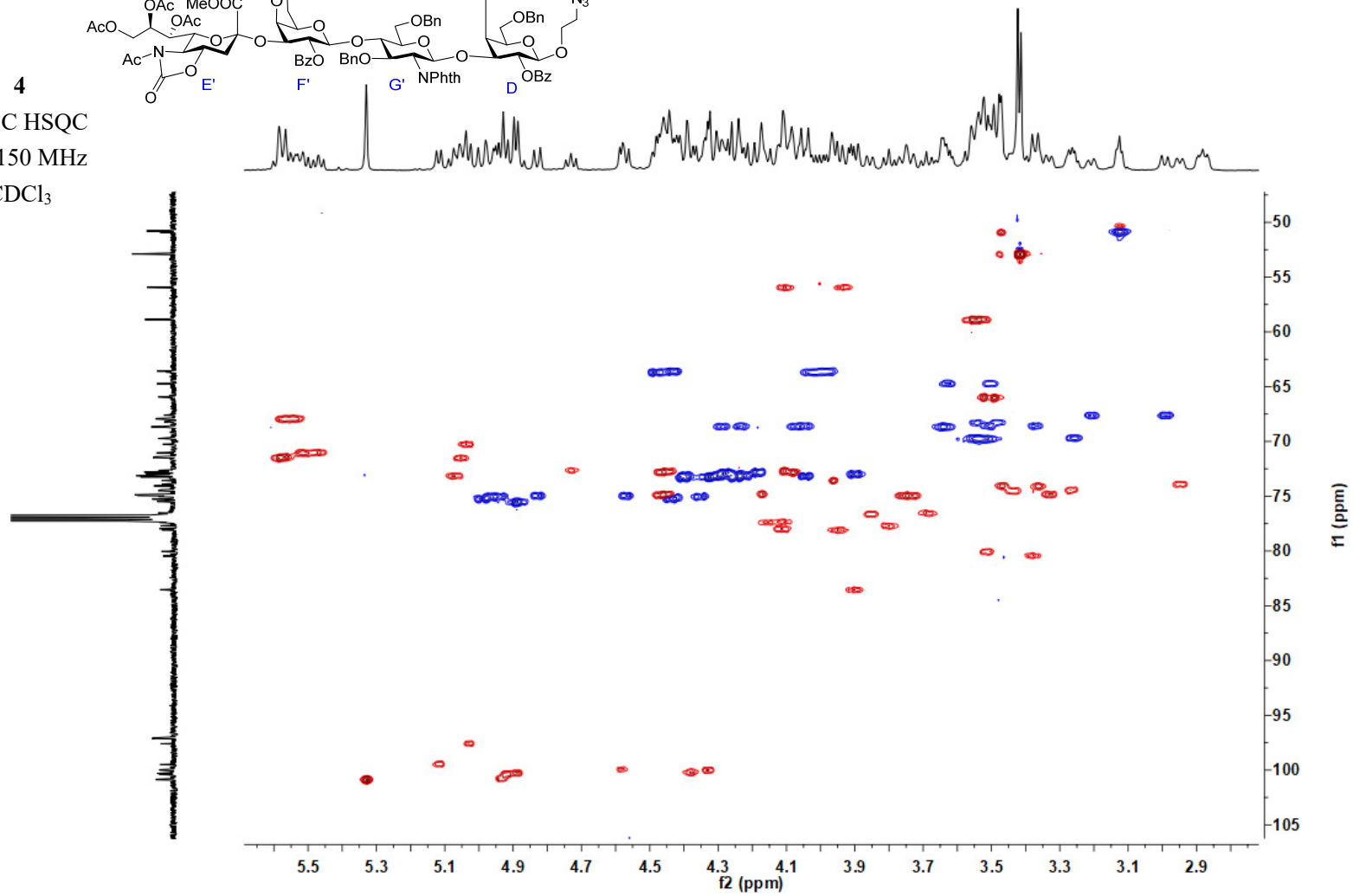


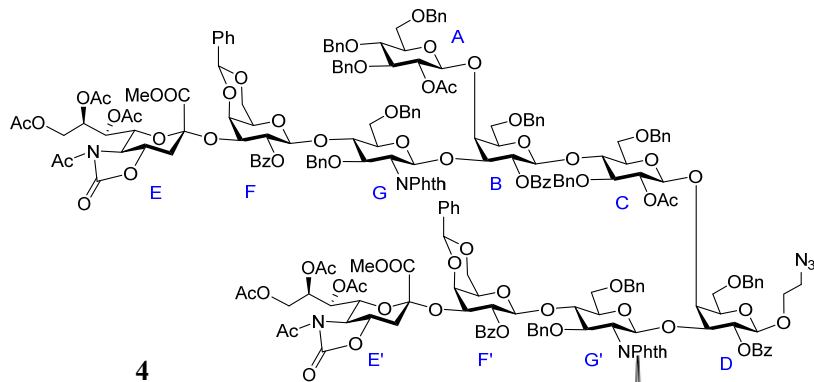
4
 ^1H - ^1H COSY
 600 MHz
 CDCl_3



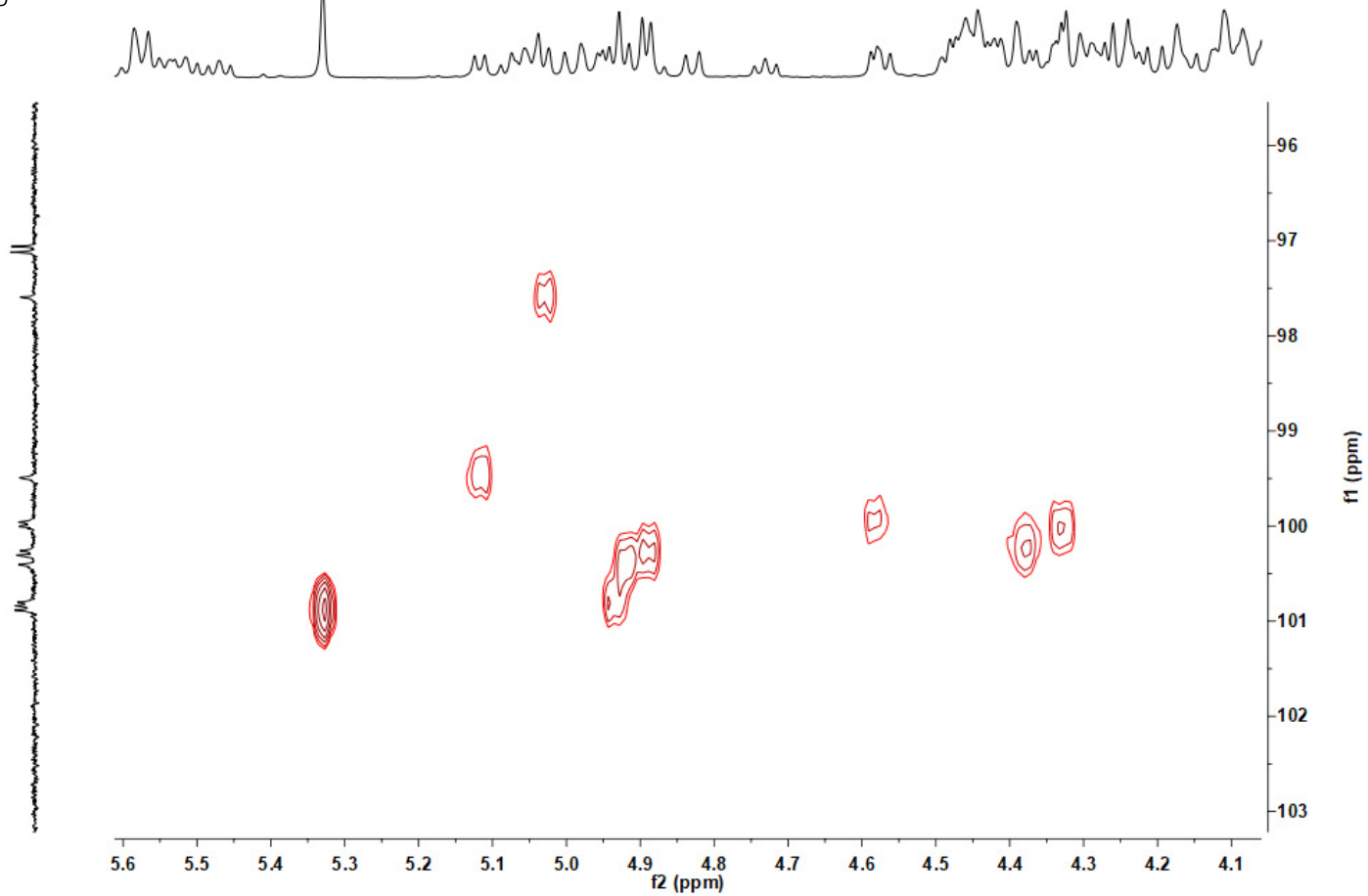


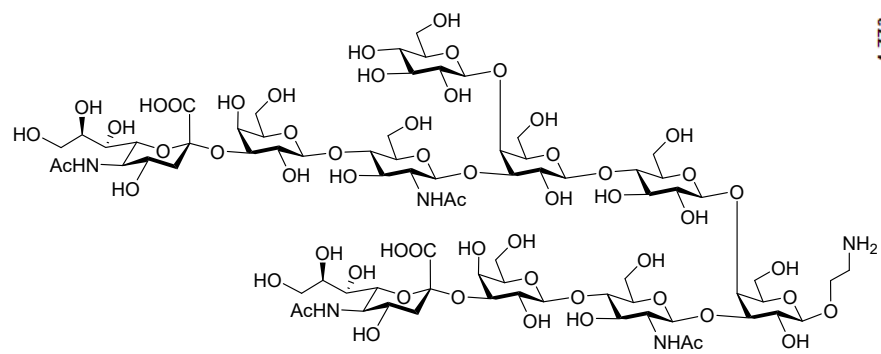
4
¹H-¹³C HSQC
 600/150 MHz
 CDCl₃





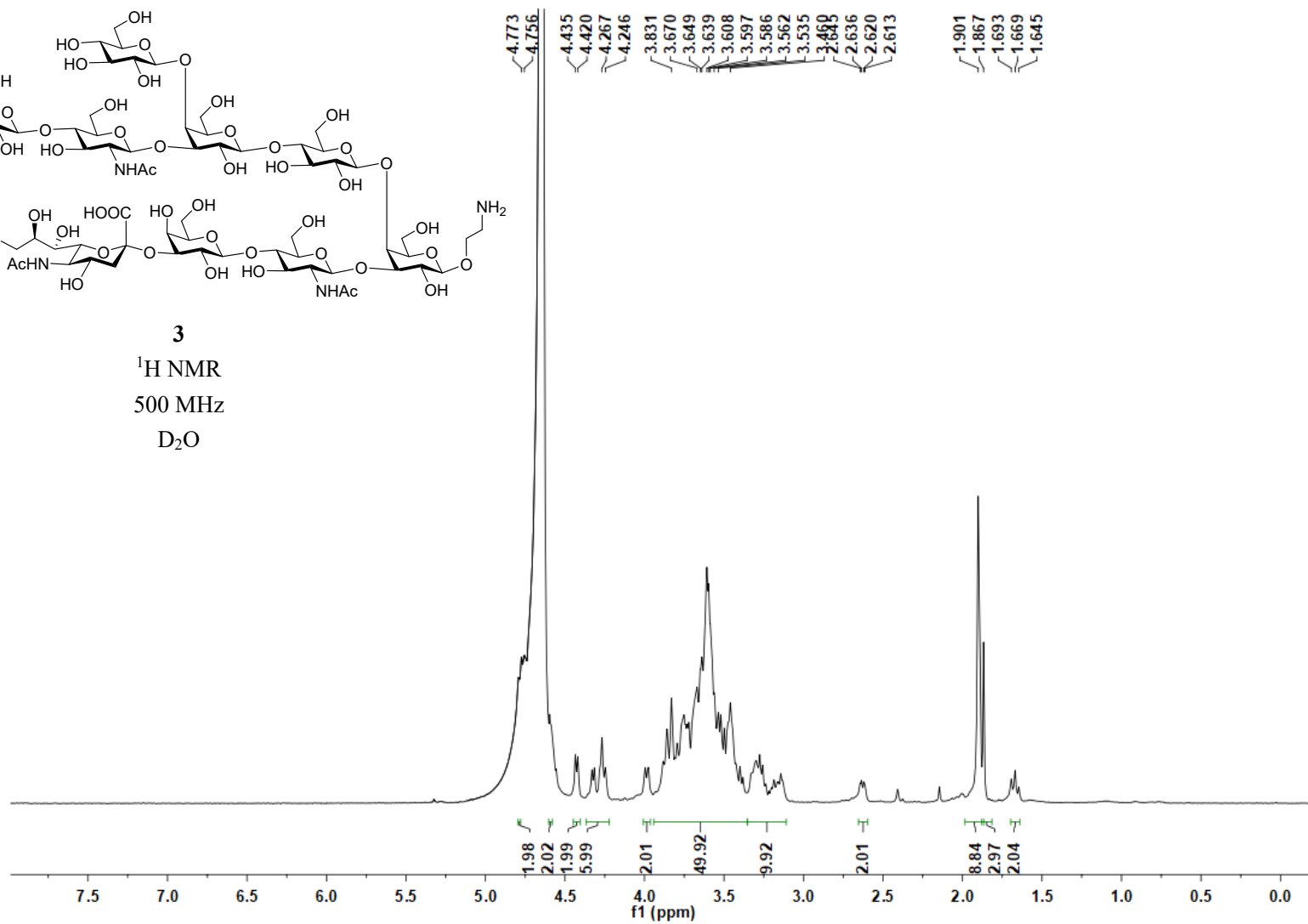
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 600/150 MHz
 CDCl_3

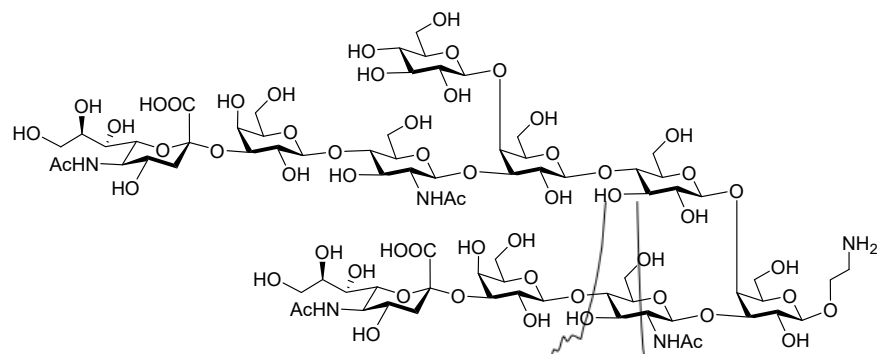




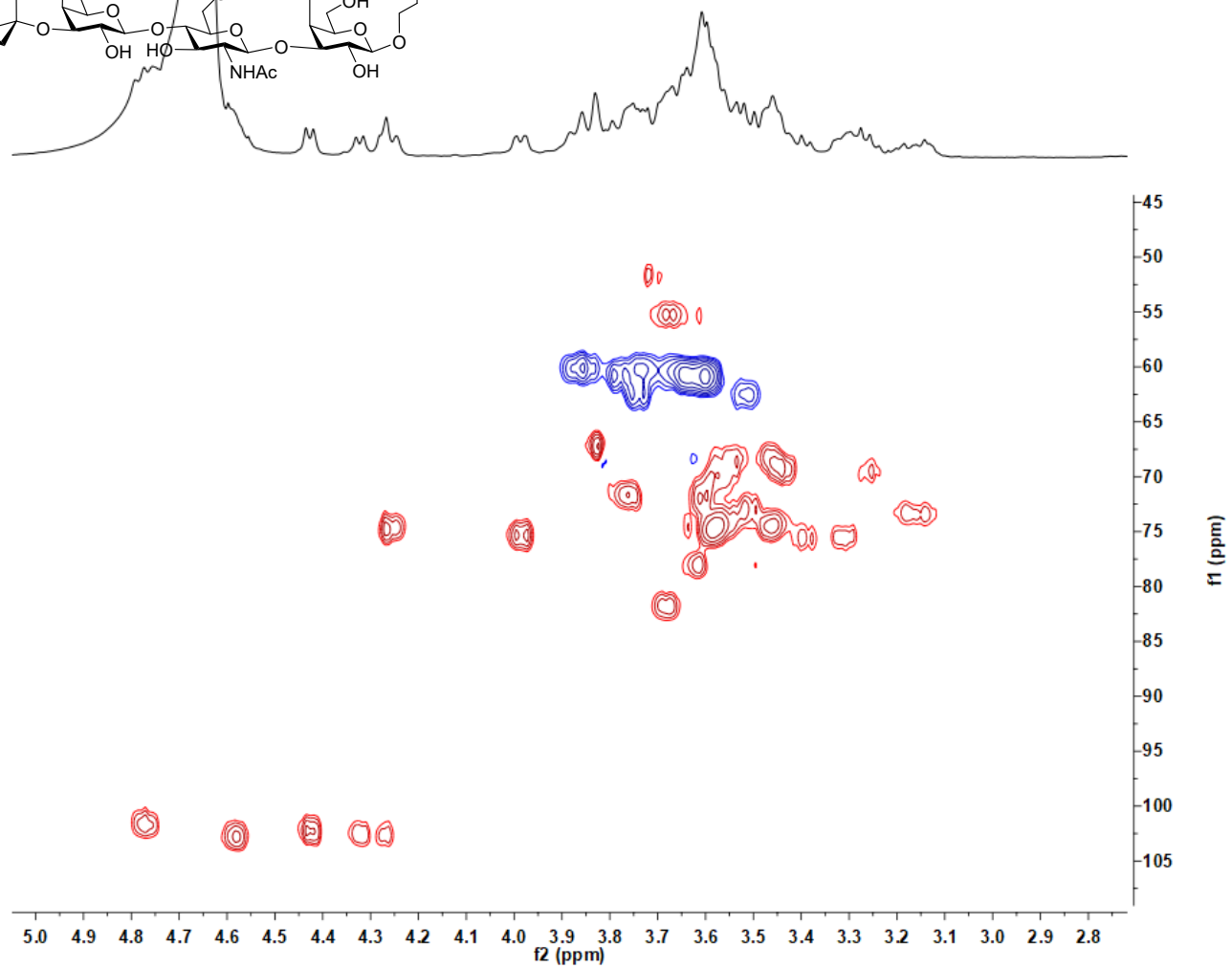
3

¹H NMR
500 MHz
D₂O

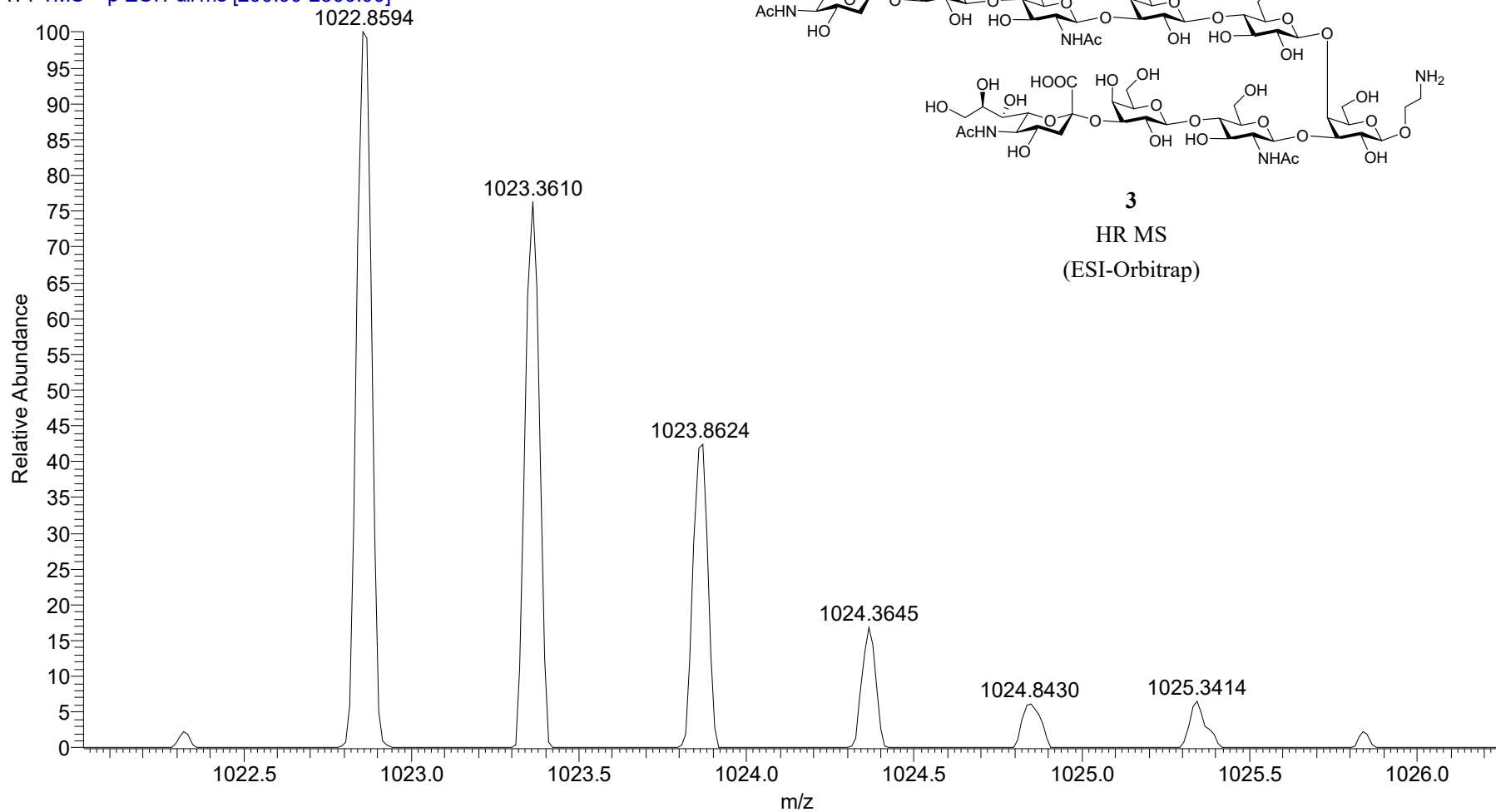


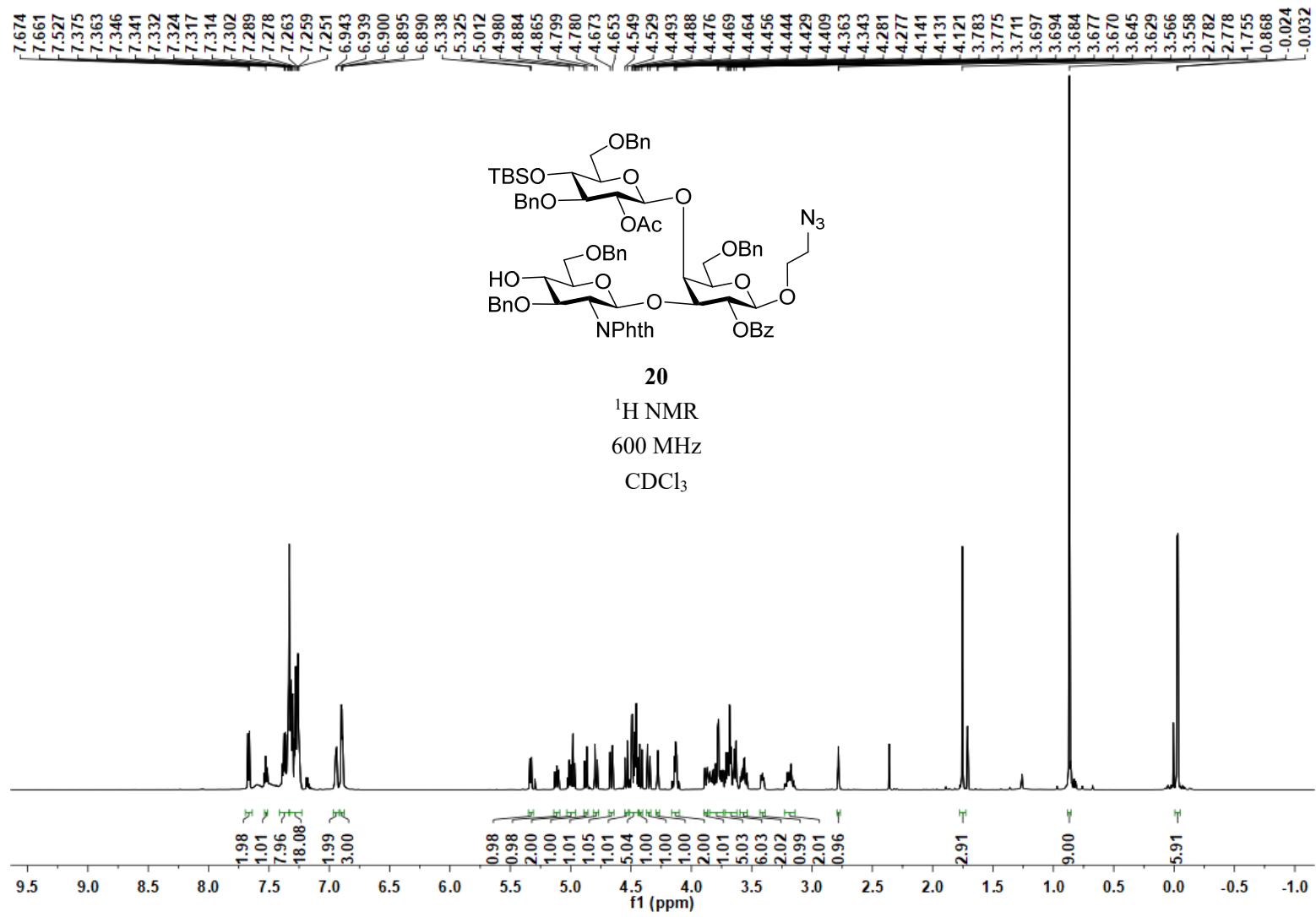


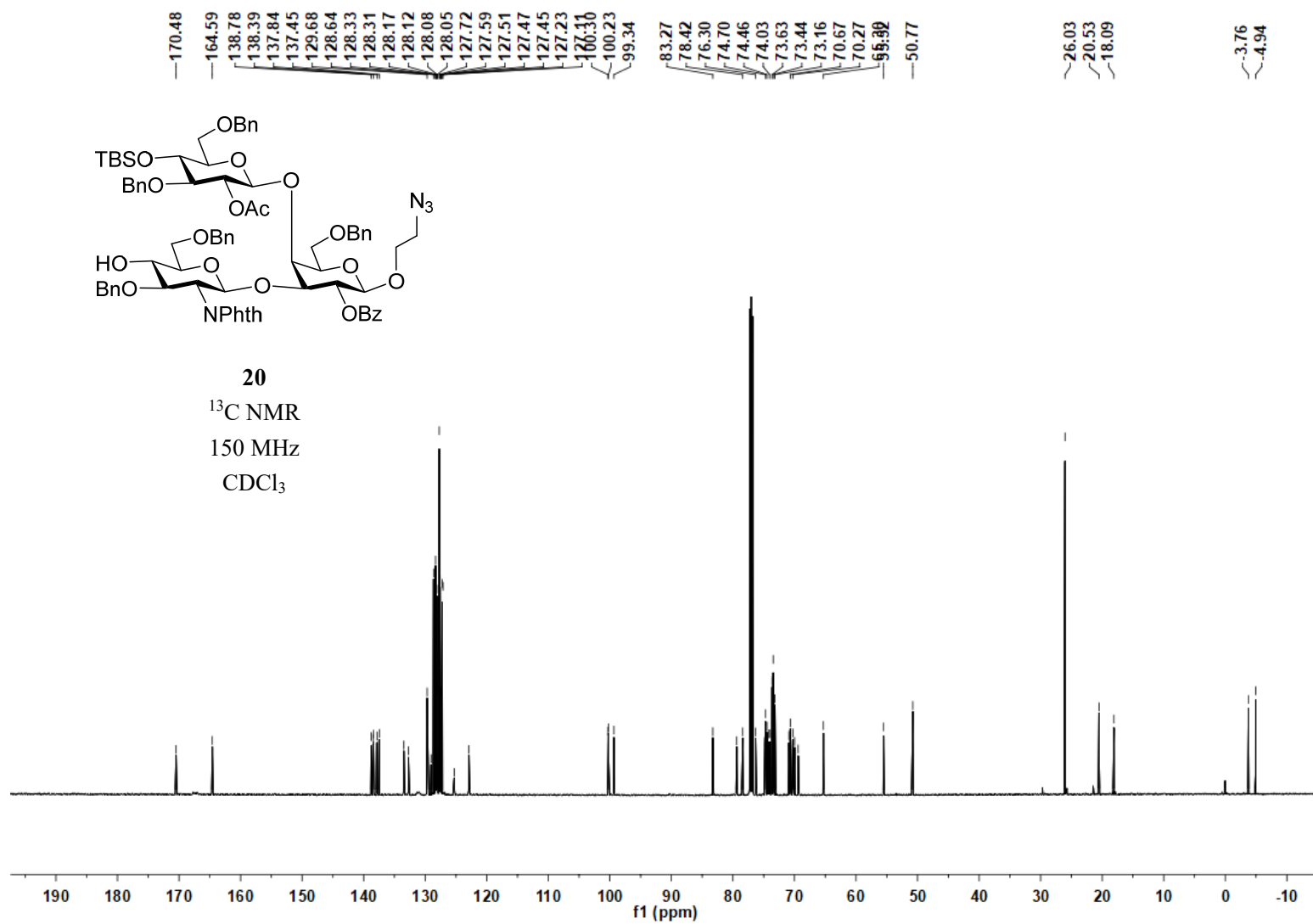
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 ^1H - ^{13}C HSQC
 500/125 MHz
 CDCl_3

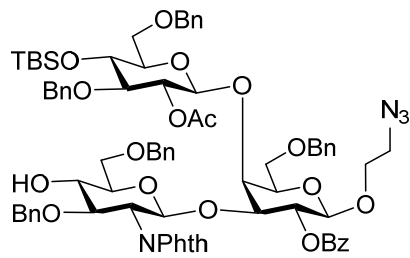


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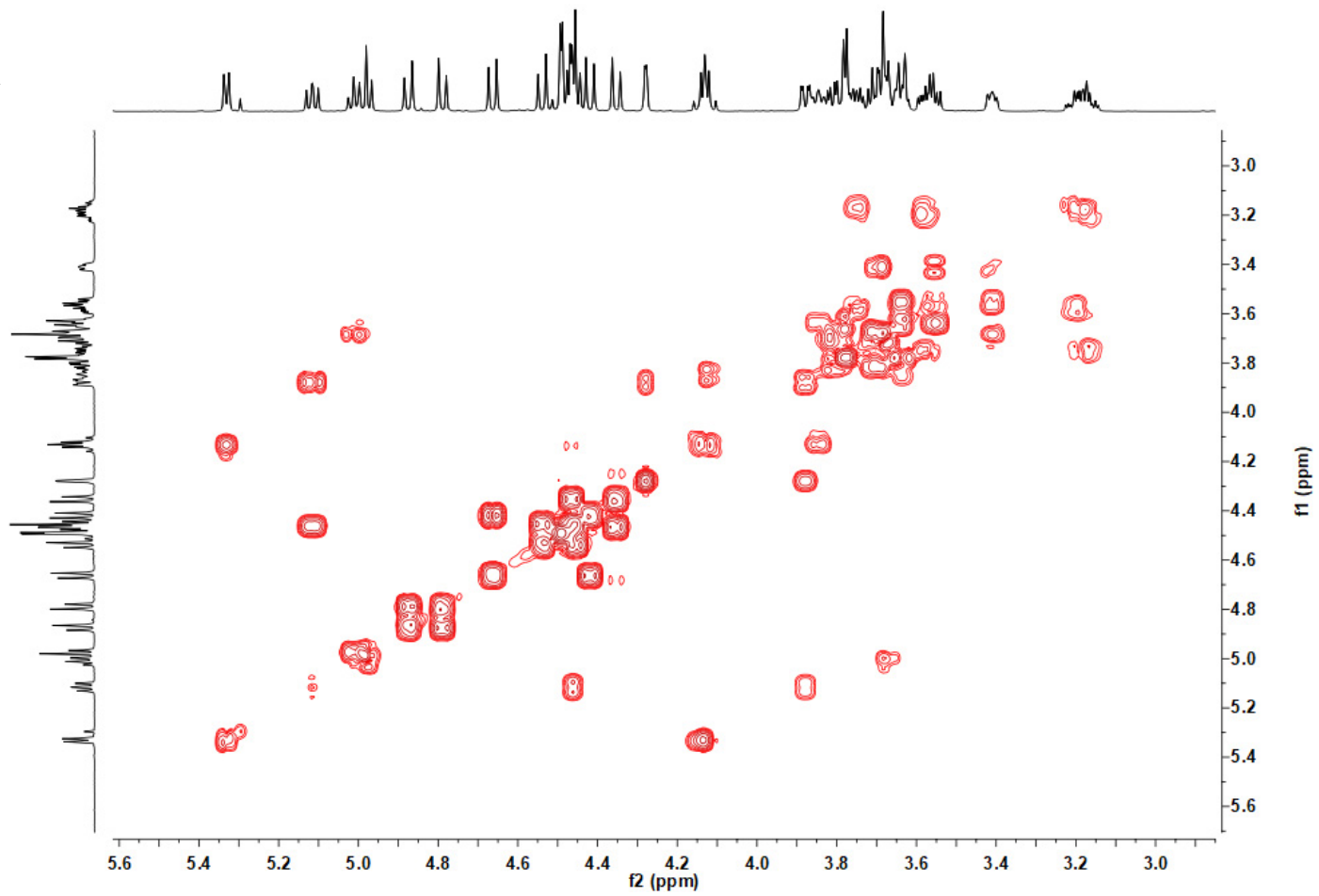


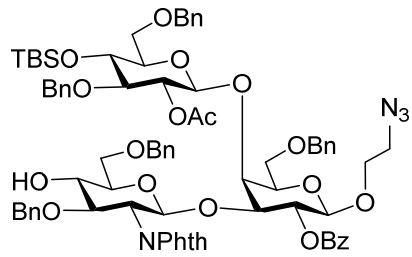




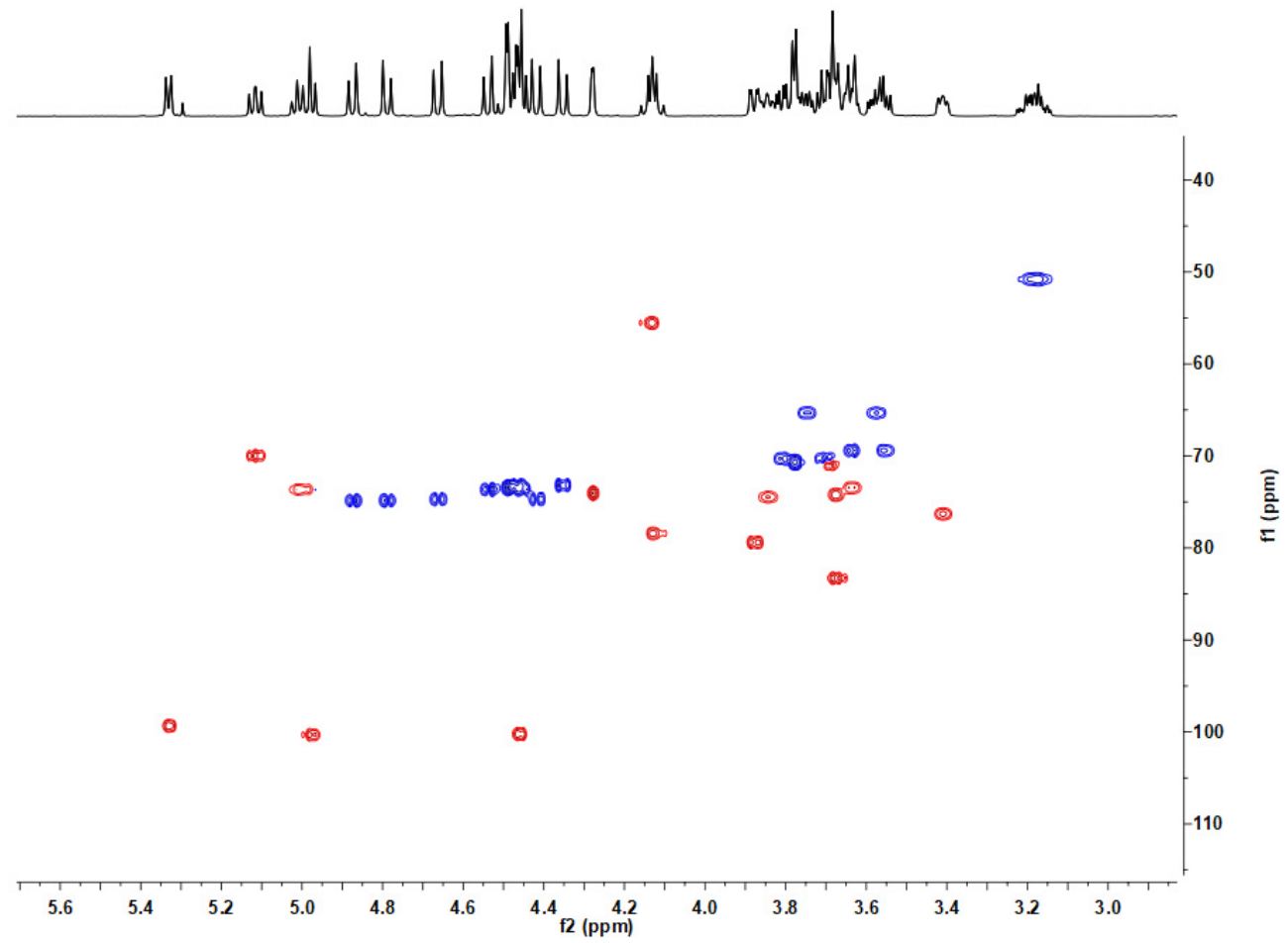


20
 ^1H - ^1H COSY
 600 MHz
 CDCl_3

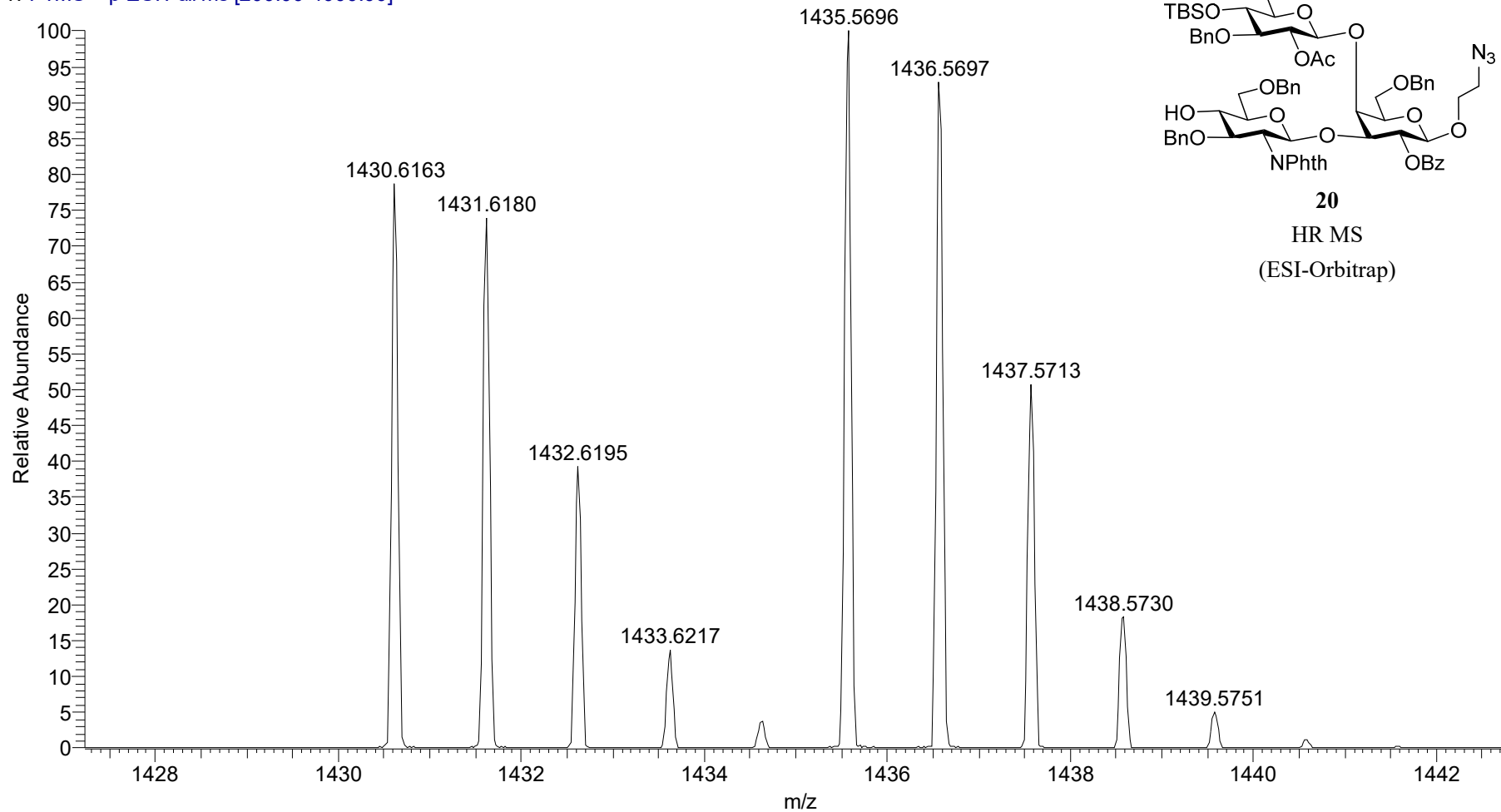


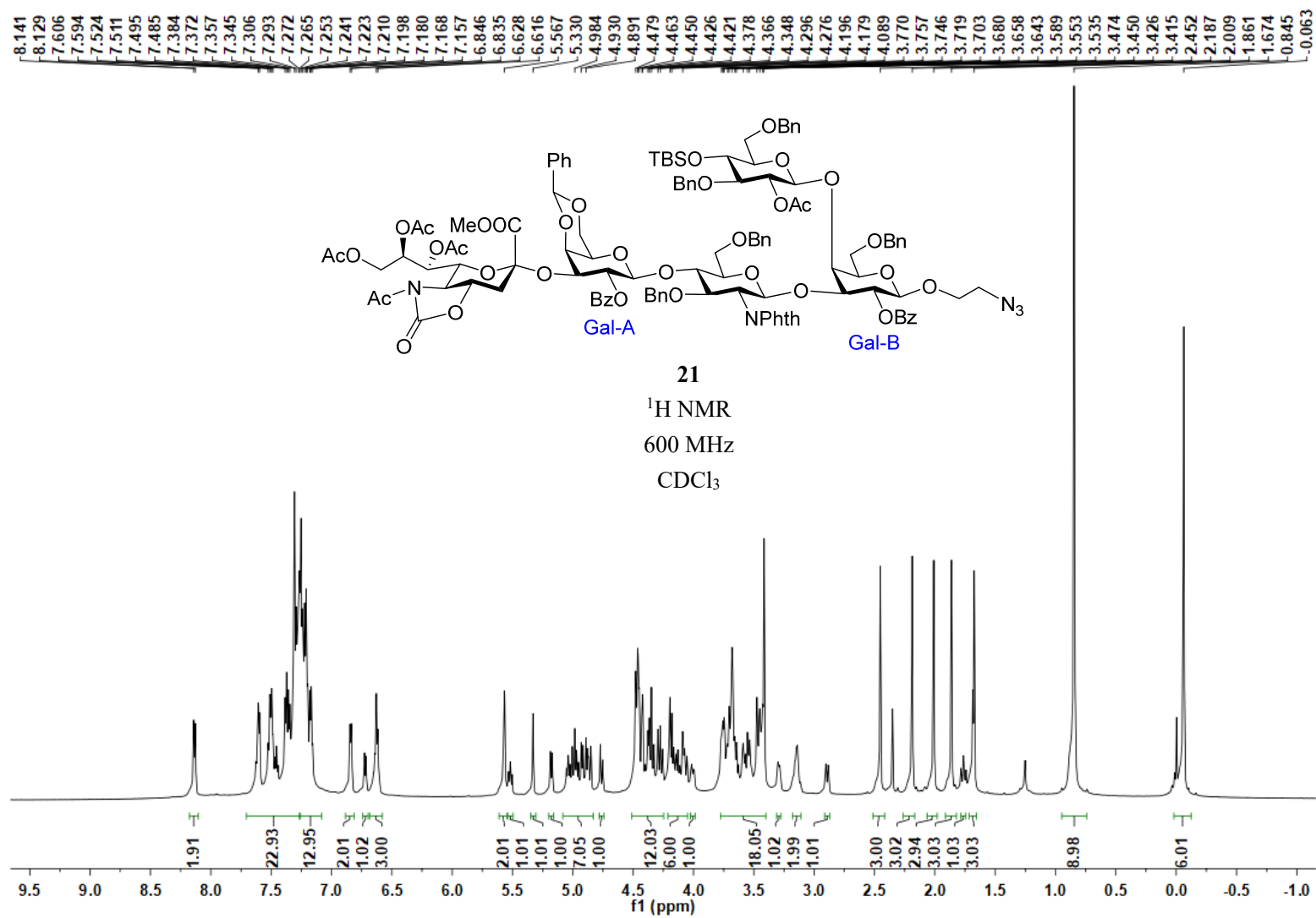


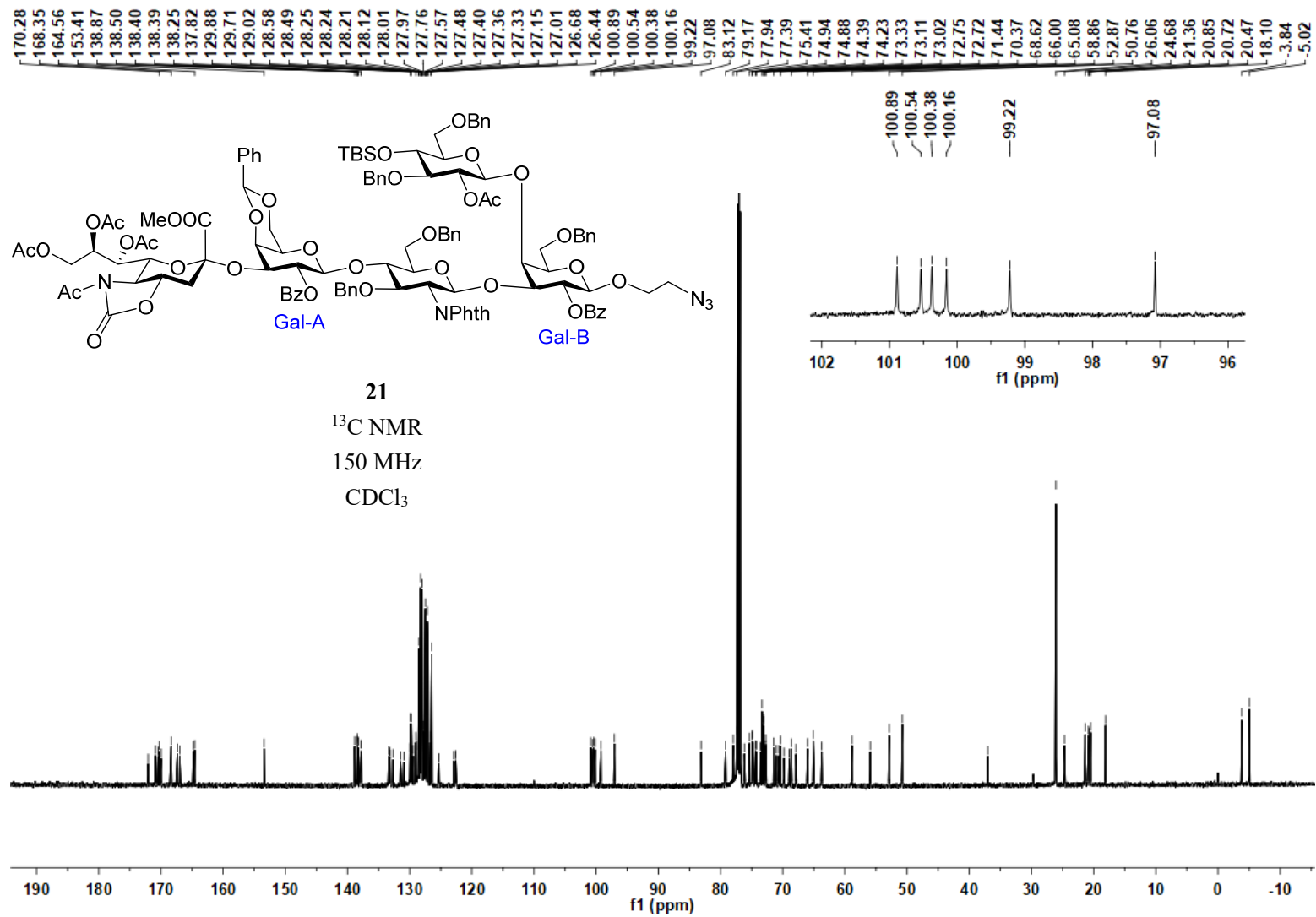
20
¹H-¹³C HSQC
 600/150 MHz
 CDCl₃

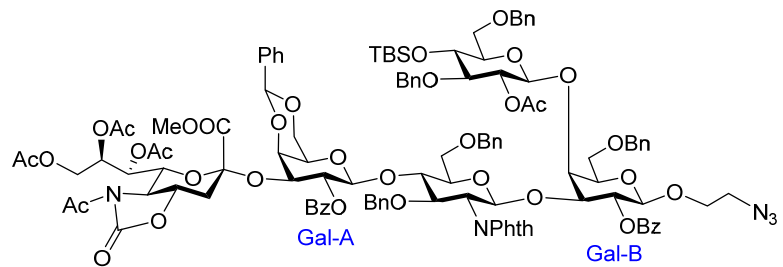


20190326-ZH-03-27_190326111508 #138 RT: 1.16 AV: 1 NL: 3.24E7
T: FTMS + p ESI Full ms [200.00-4000.00]

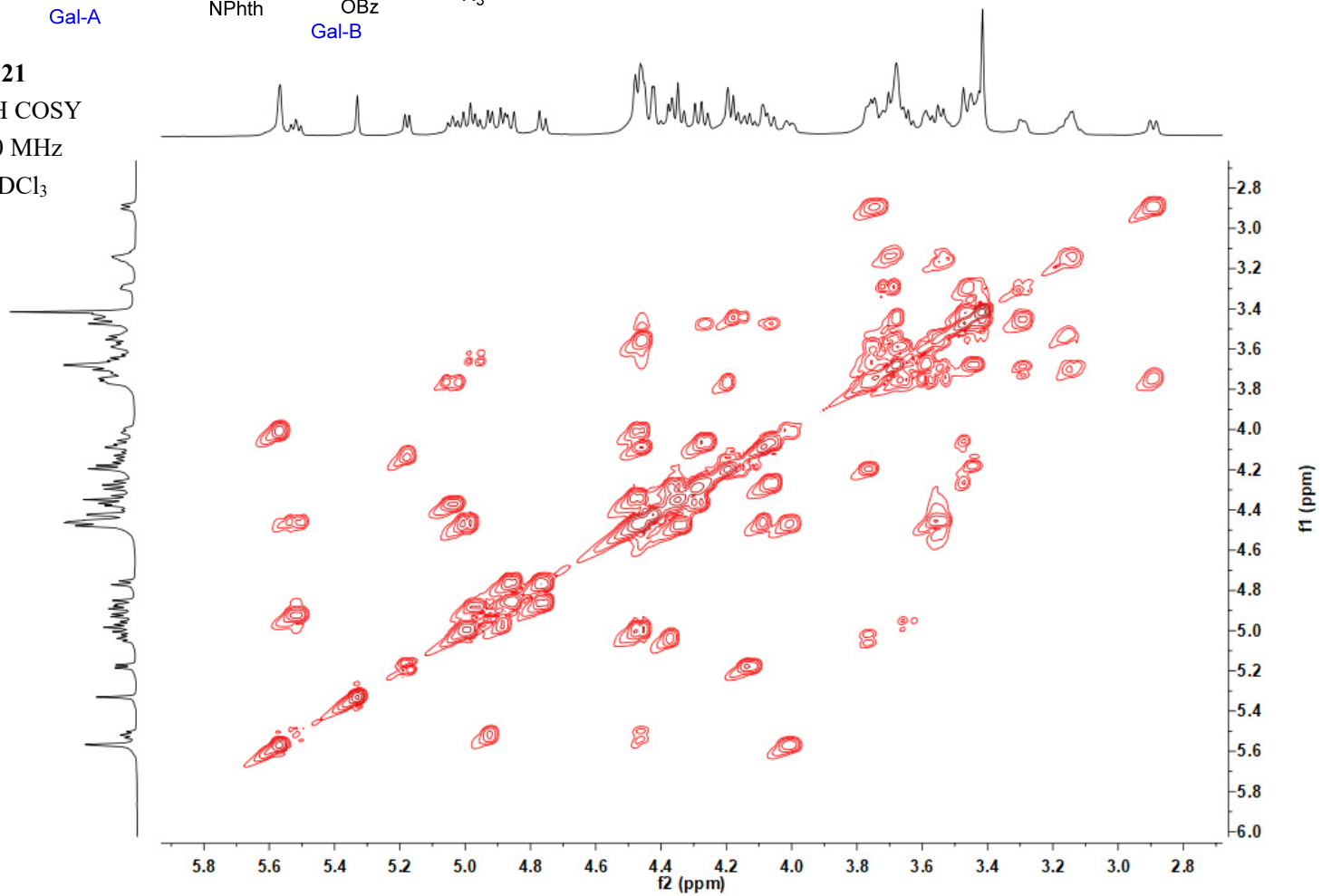


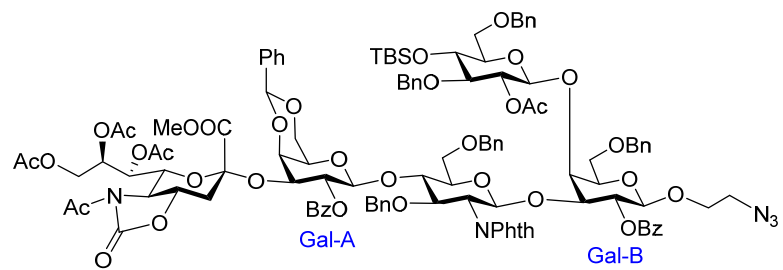






21
¹H-¹H COSY
 600 MHz
 CDCl₃





21
 ^1H - ^{13}C COSY
 600/150 MHz
 CDCl_3

