Electronic Supplementary Information

Synthesis of apiose-containing oligosaccharide fragments of the plant cell wall: fragments of rhamnogalacturonan-II side chains A and B, and apiogalacturonan

Sergey A. Nepogodiev,[a,b,*] Margherita Fais,[a,b] David L. Hughes[b] and Robert A. Field[a,b,*]

[a]*Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Norwich NR4 7UH, UK*;
[b]*School of Chemistry, University of East Anglia, Norwich Research Park Norwich, NR4 7TJ, UK.*

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Crystal structure analysis of Methyl *C*-(4-*O*-acetyl-2,3-*O*-carbonyl-β-L-rhamnopyranosyl-oxymethyl)-(1→3')-(2,3-*O*-(*R*)-benzylidene-β-D-erythrofuranosyl)-(1→2)-(methyl (2-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranosid)uronate) (41)

Crystal data: $C_{32}H_{40}O_{17}$, CH_2Cl_2, M = 781.6. Orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.2799(6), b = 15.1788(9), c = 21.4815(13) Å, V = 3678.0(4) $Å^3$. Z = 4, Dc = 1.411 g cm^{-3}, F(000) = 1640, T = 140(1) K, μ(Mo-Kα) = 2.5 cm^{-1}, λ(Mo-Kα) = 0.71069 Å.

Crystals are beautiful, colourless prisms. One, *ca* 0.52 x 0.25 x 0.24 mm, was mounted in oil on a glass fibre and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3 CCD diffractometer equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Total no. of reflections recorded, to θ_{max} = 27.5°, was 49119 of which 8410 were unique (Rint = 0.045); 7002 were 'observed' with $I > 2\sigma_I$.

Data were processed using the CrysAlis-CCD and -RED (1) programs. The structure was determined by the direct methods routines in the SHELXS program (2A) and refined by full-matrix least-squares methods, on F^2's, in SHELXL (2B). The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms. At the conclusion of the refinement, wR_2 = 0.093 and R_1 = 0.049 (2B) for all 8410 reflections weighted $w = [\sigma^2(F_o^2) + (0.0556P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, R_1 = 0.037.

In the final difference map, the highest peak (*ca* 0.7 $eÅ^{-3}$) was close to Cl(2).

Scattering factors for neutral atoms were taken from reference (3). Computer programs used in this analysis have been noted above, and were run through WinGX (4) on a Dell Precision 370 PC at the University of East Anglia.

References

1. Programs CrysAlis-CCD and -RED, Oxford Diffraction Ltd., Abingdon, UK (2005).
2. G. M. Sheldrick, SHELX-97 - Programs for crystal structure determination (SHELXS) and refinement (SHELXL), *Acta Crystallogr.*, (2008), A64, 112-122.
3. *'International Tables for X-ray Crystallography'*, Kluwer Academic Publishers, Dordrecht (1992). Vol. C, pp. 500, 219 and 193.
4. L. J. Farrugia, *J. Appl. Cryst.*, (1999) **32**, 837-838 .

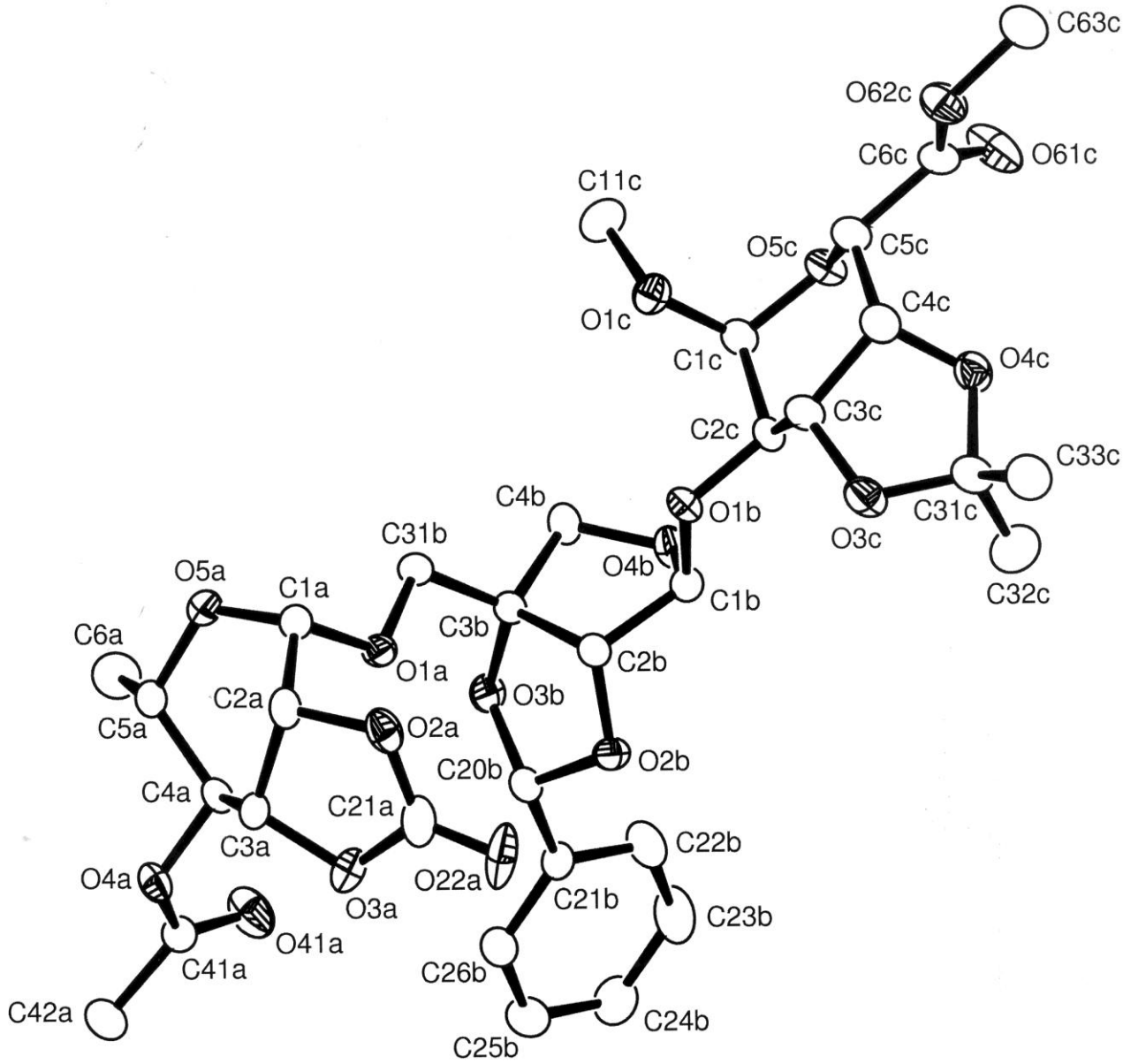

Fig. 1 X-Ray crystal structure of disaccharide derivative **41**.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data for protected saccharide derivatives and oligosaccharides 1–4

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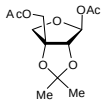

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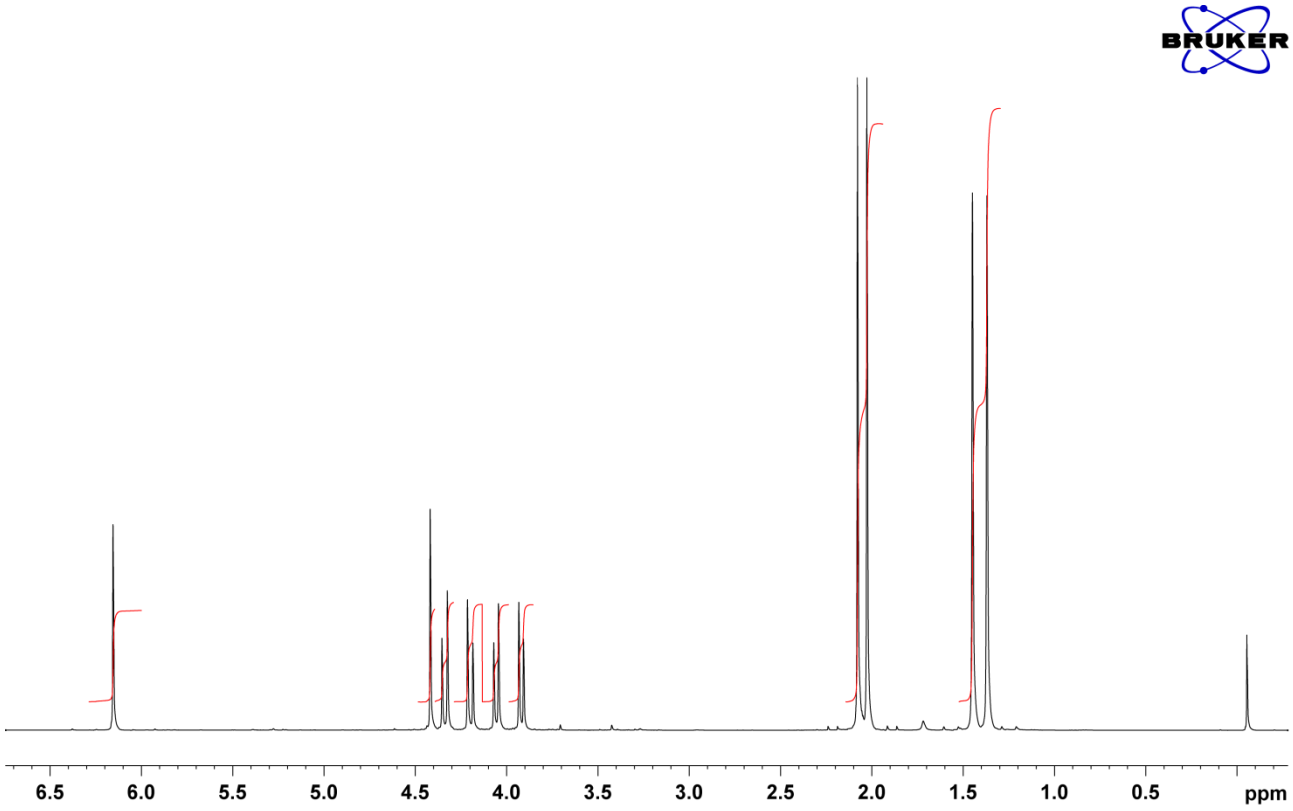

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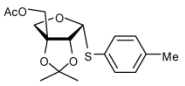

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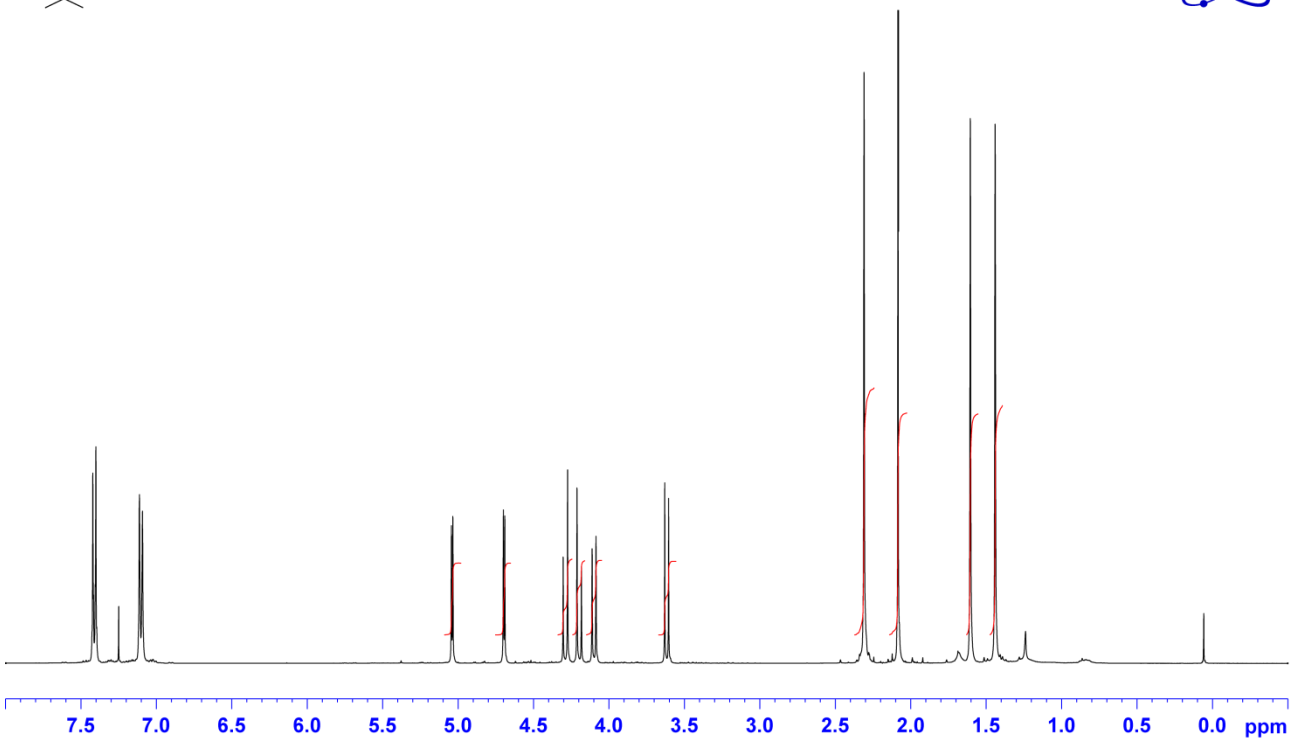

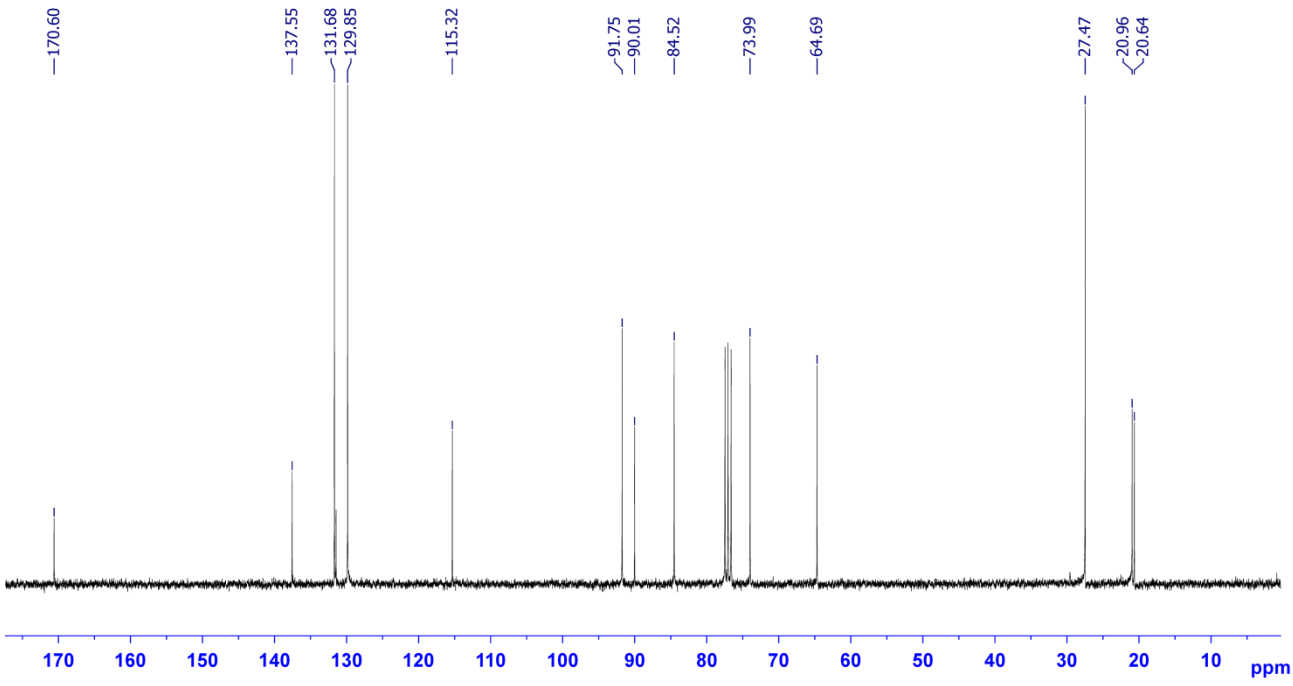

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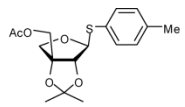

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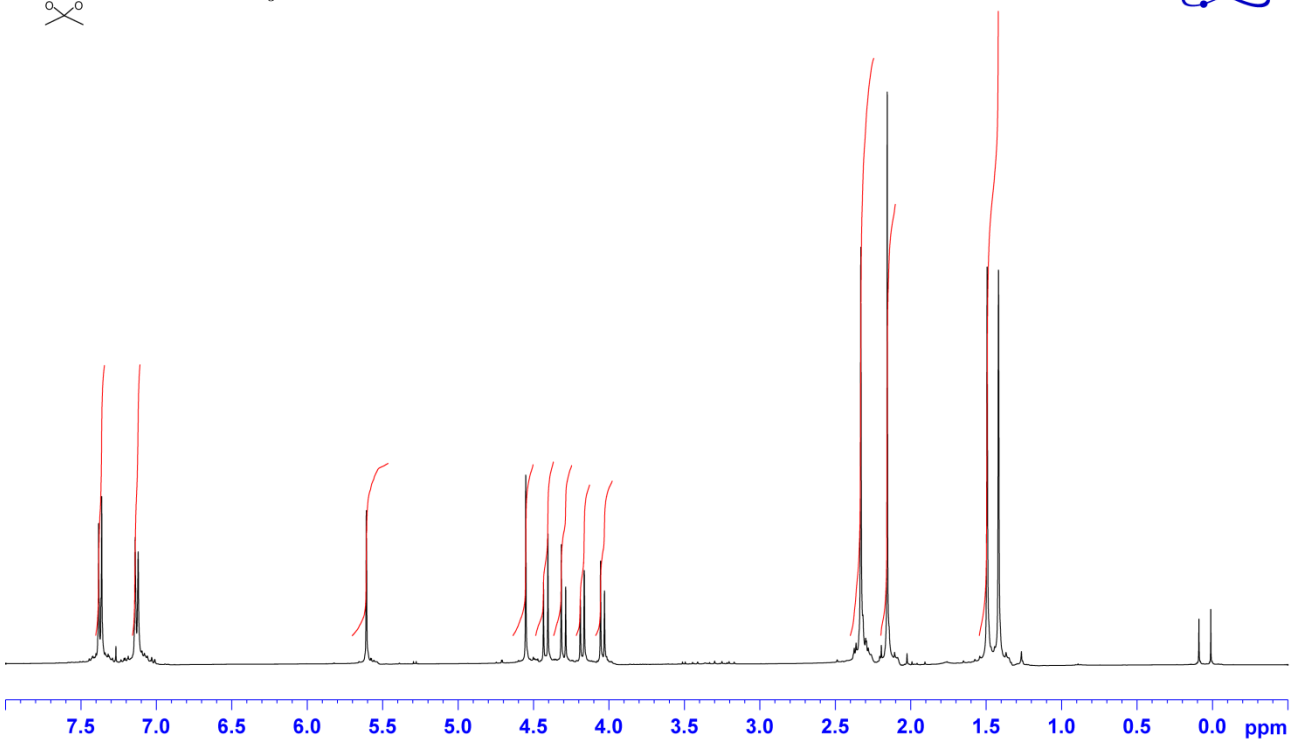

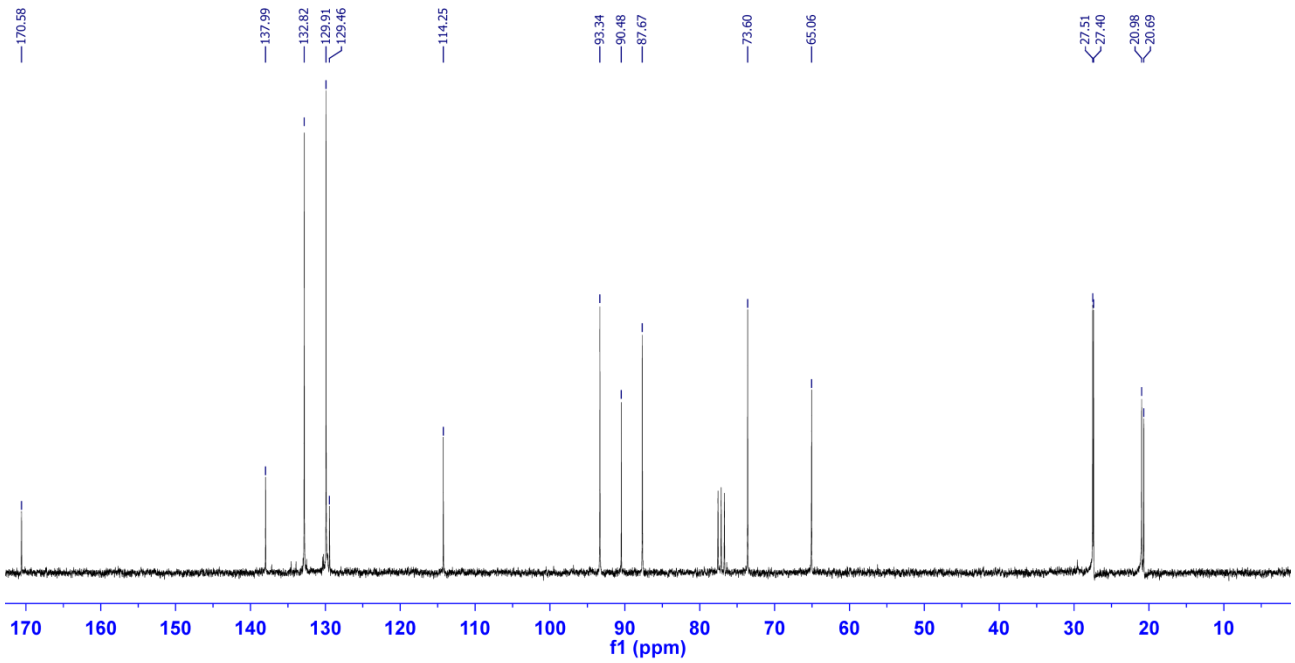

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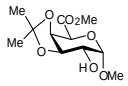

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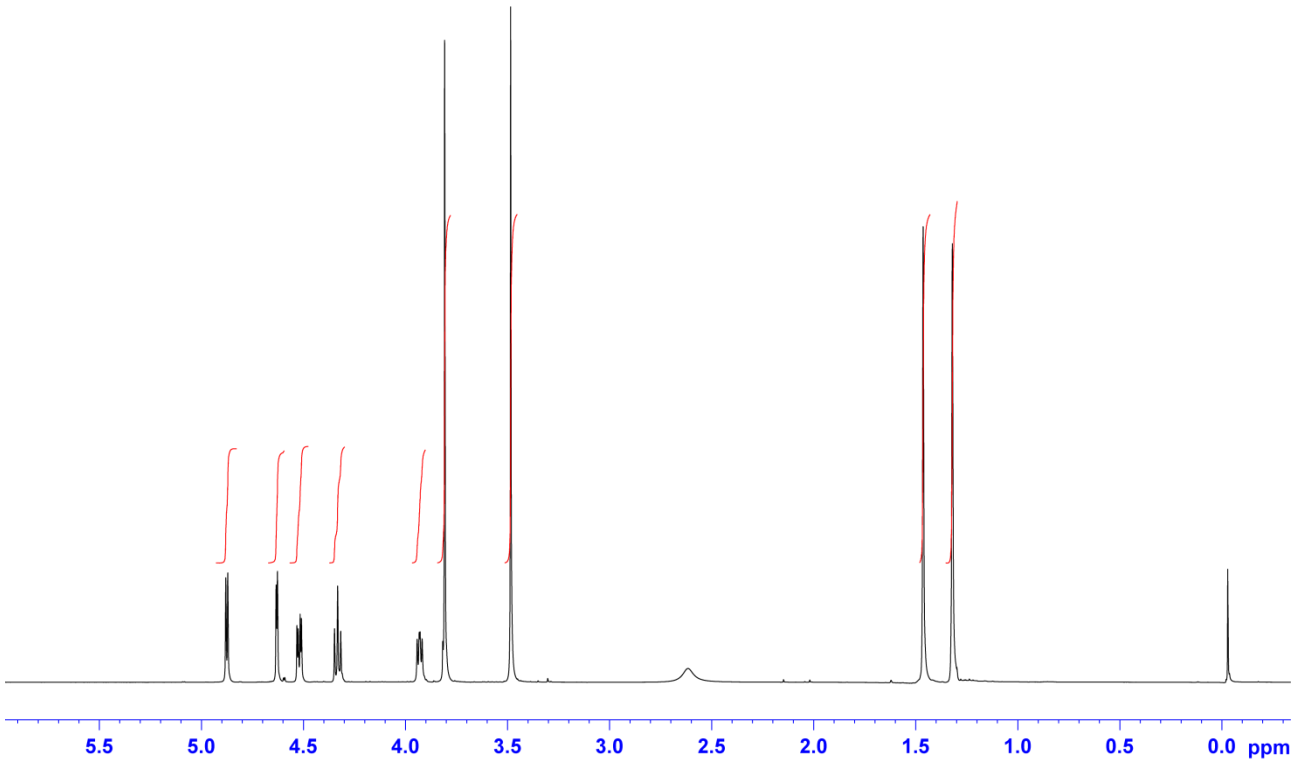

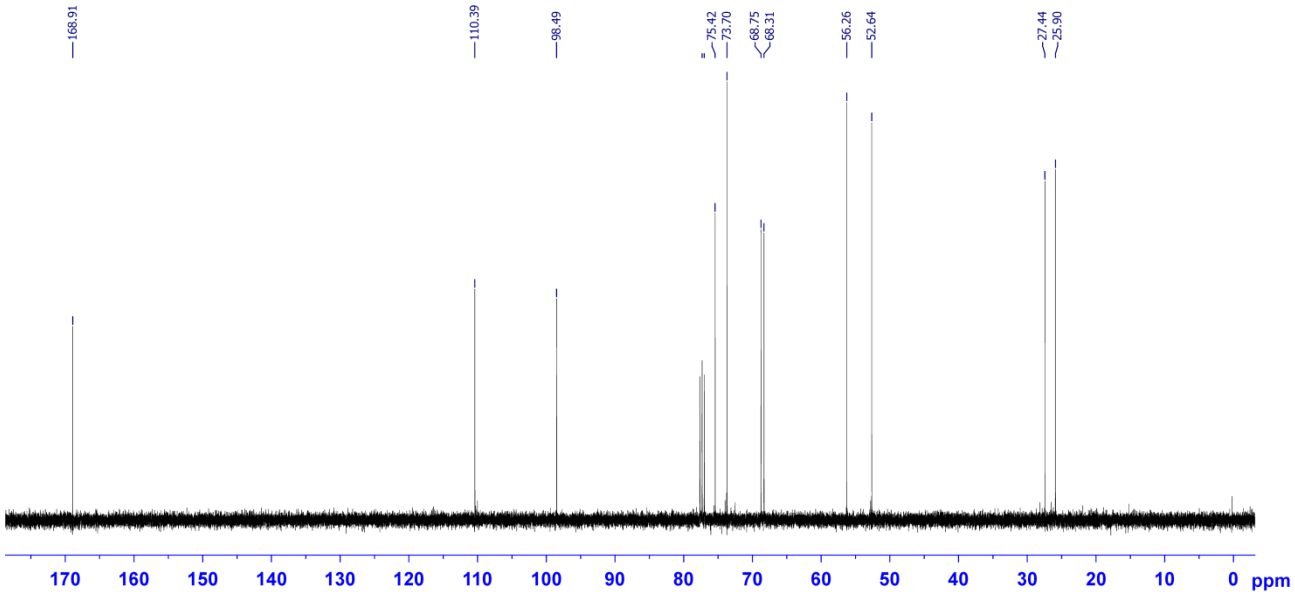

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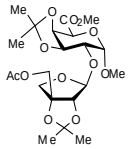

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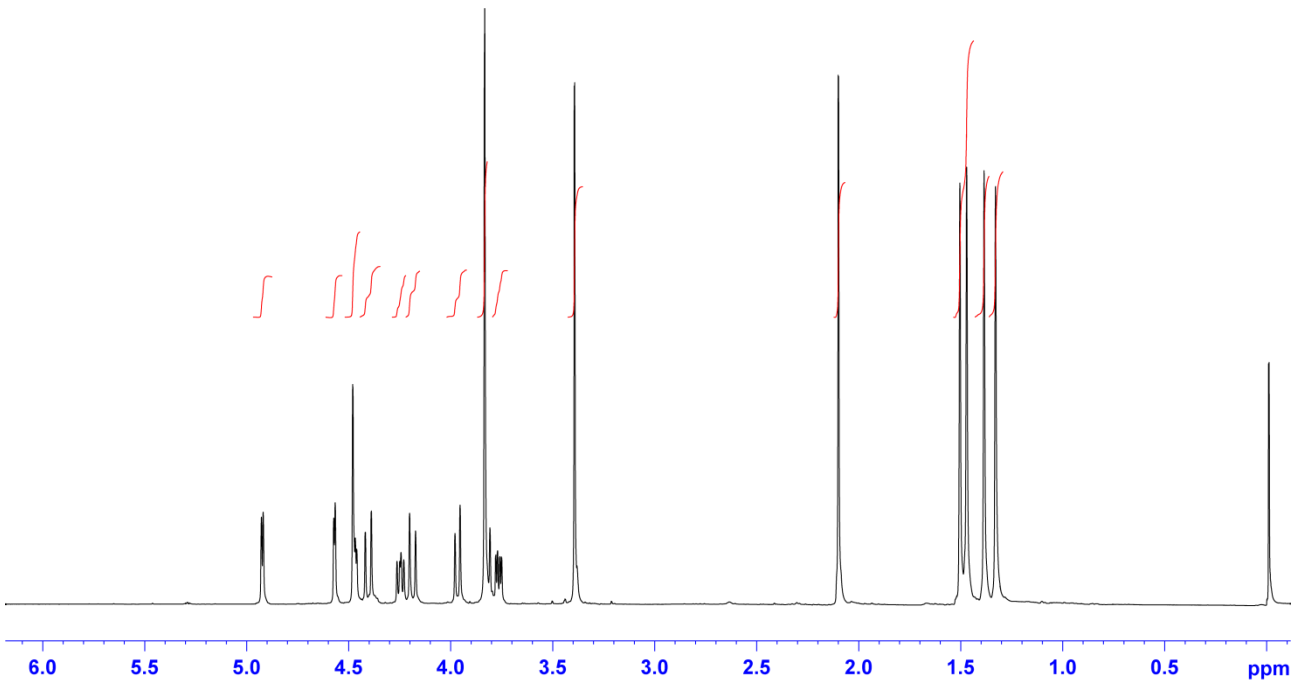

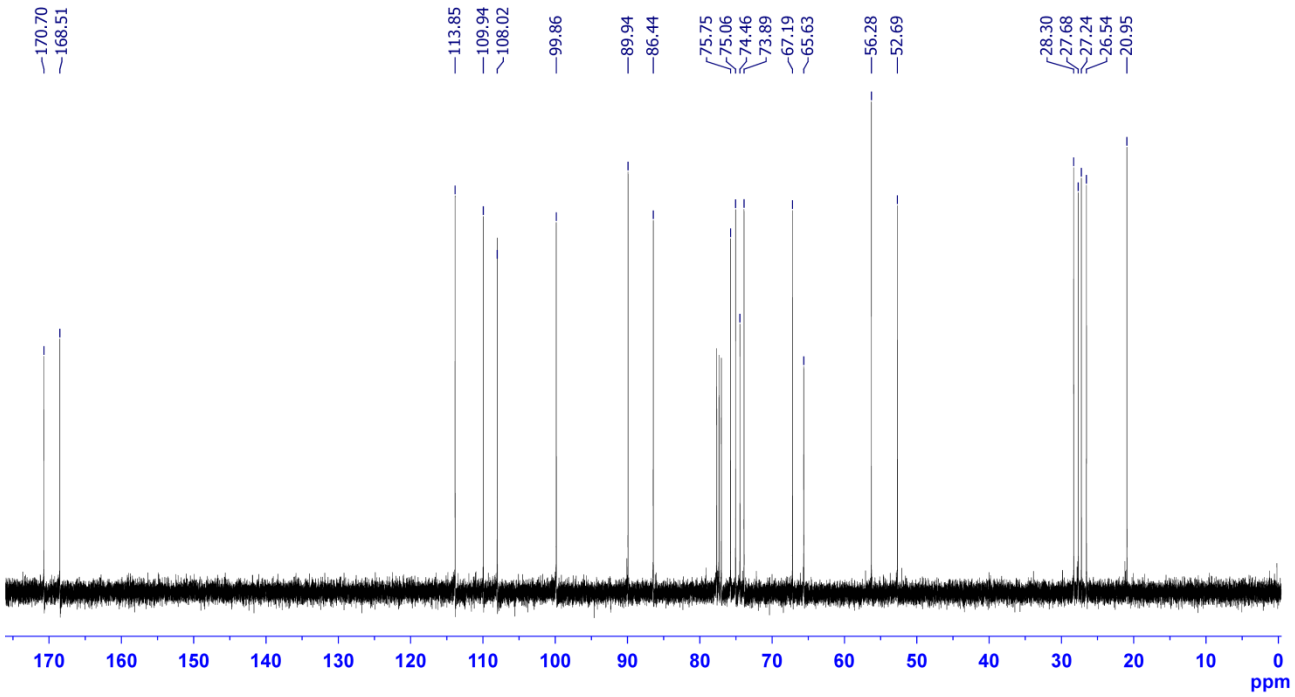

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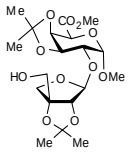

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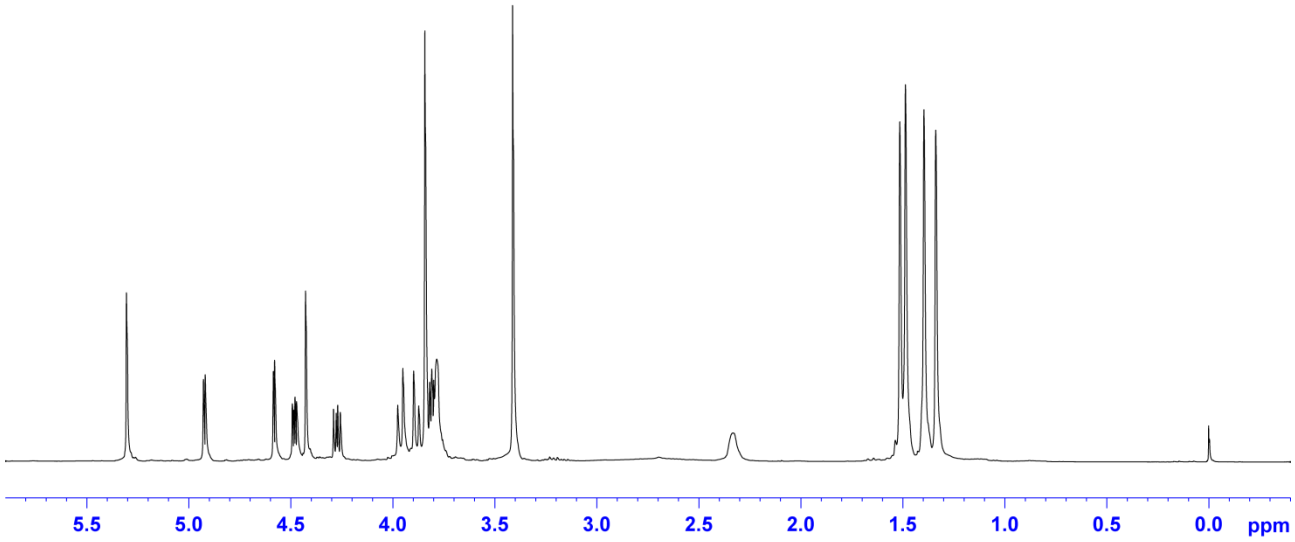

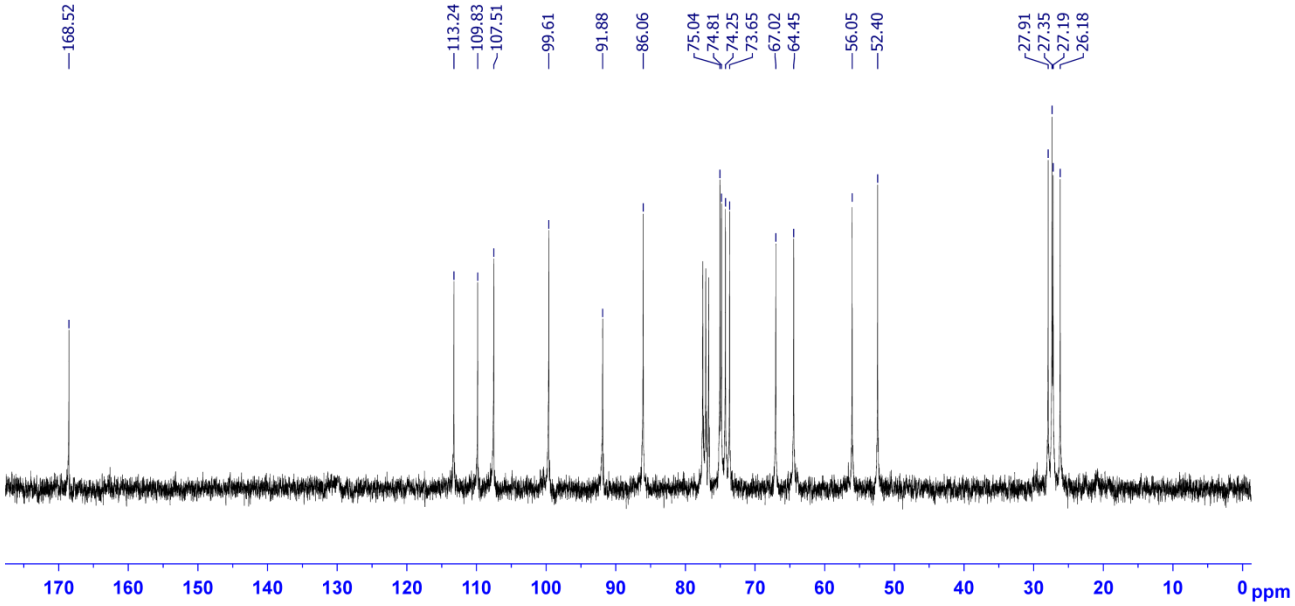

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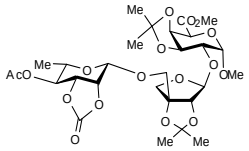

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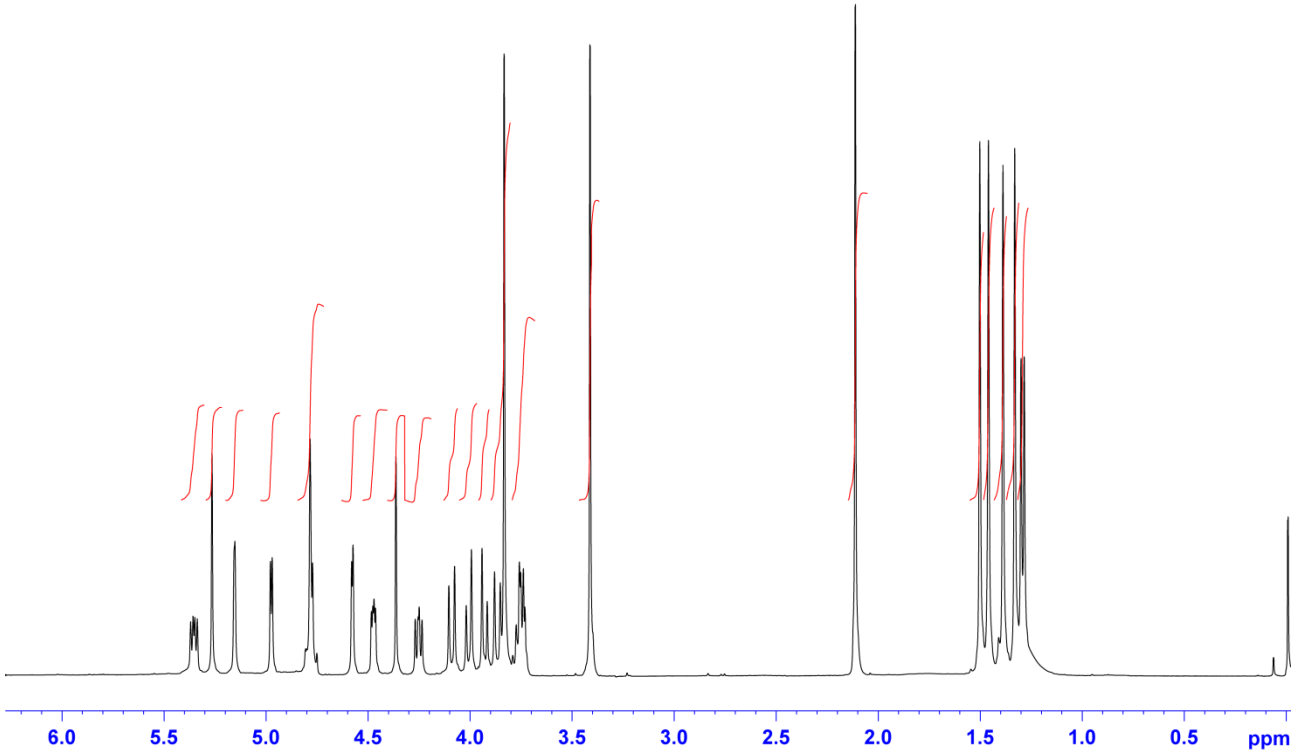

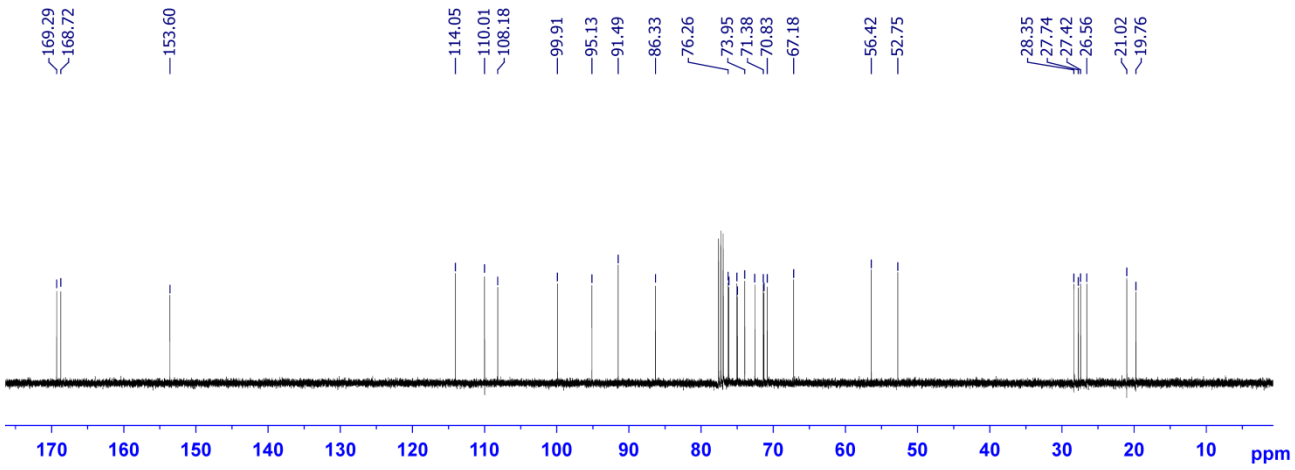

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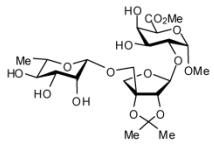

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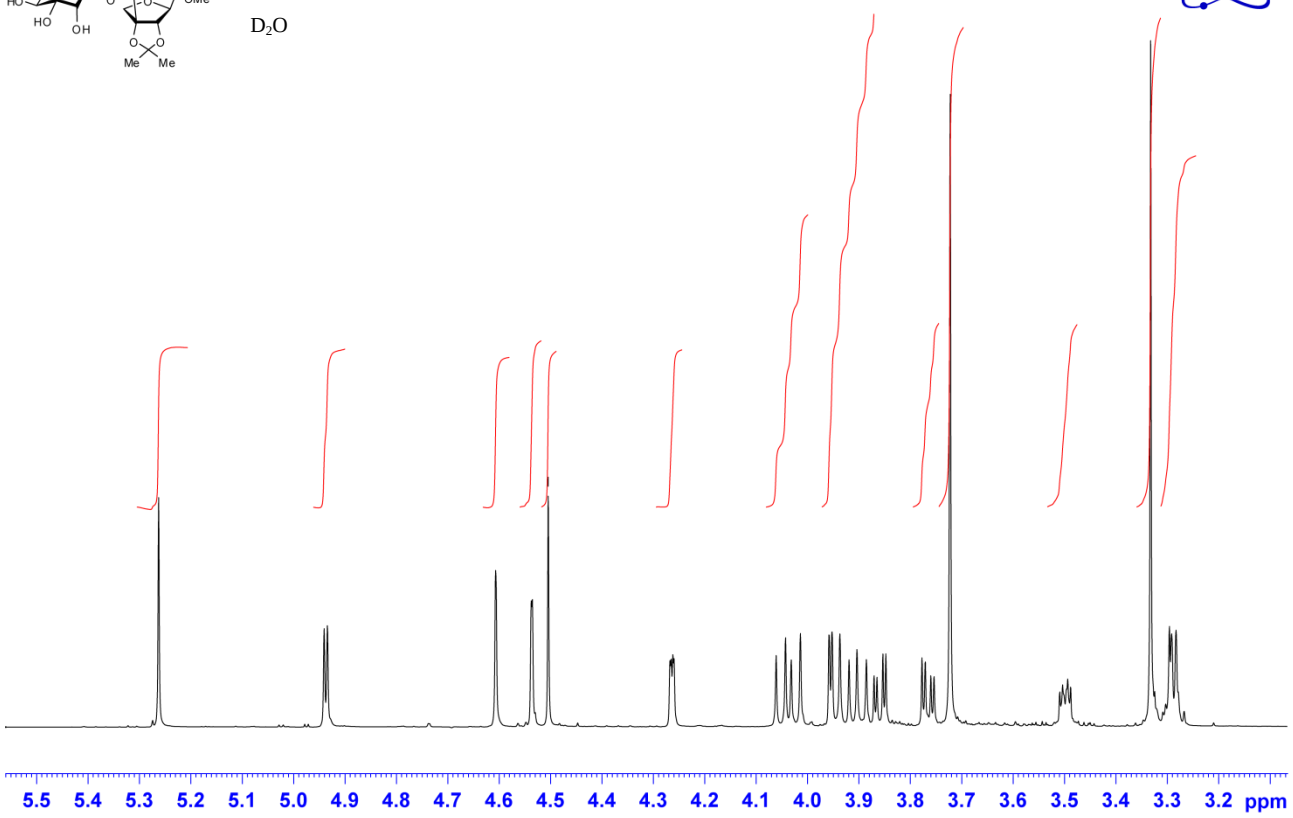

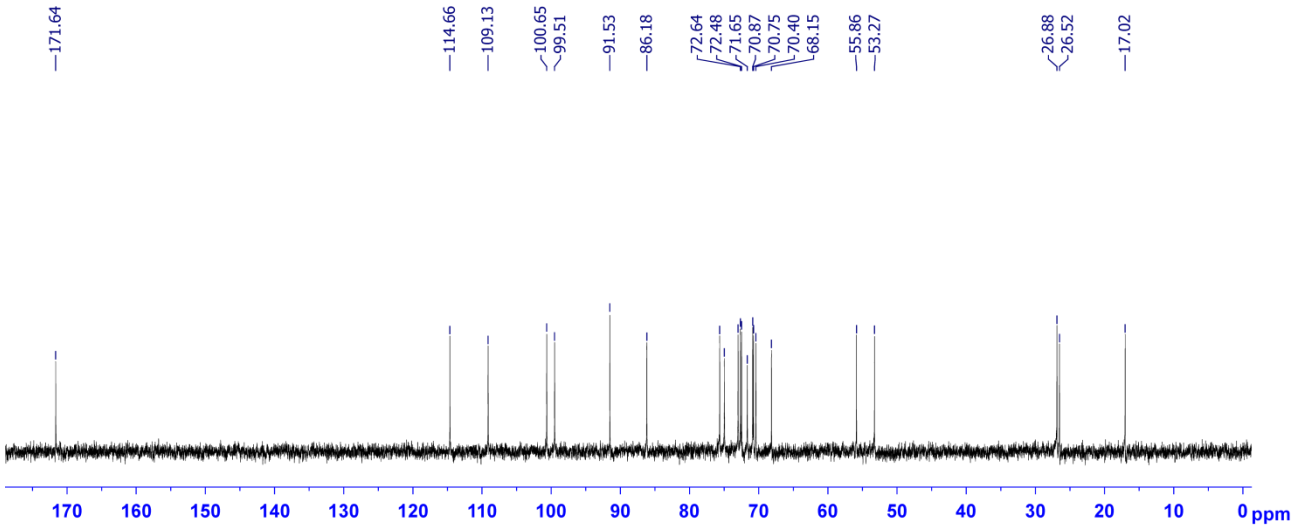

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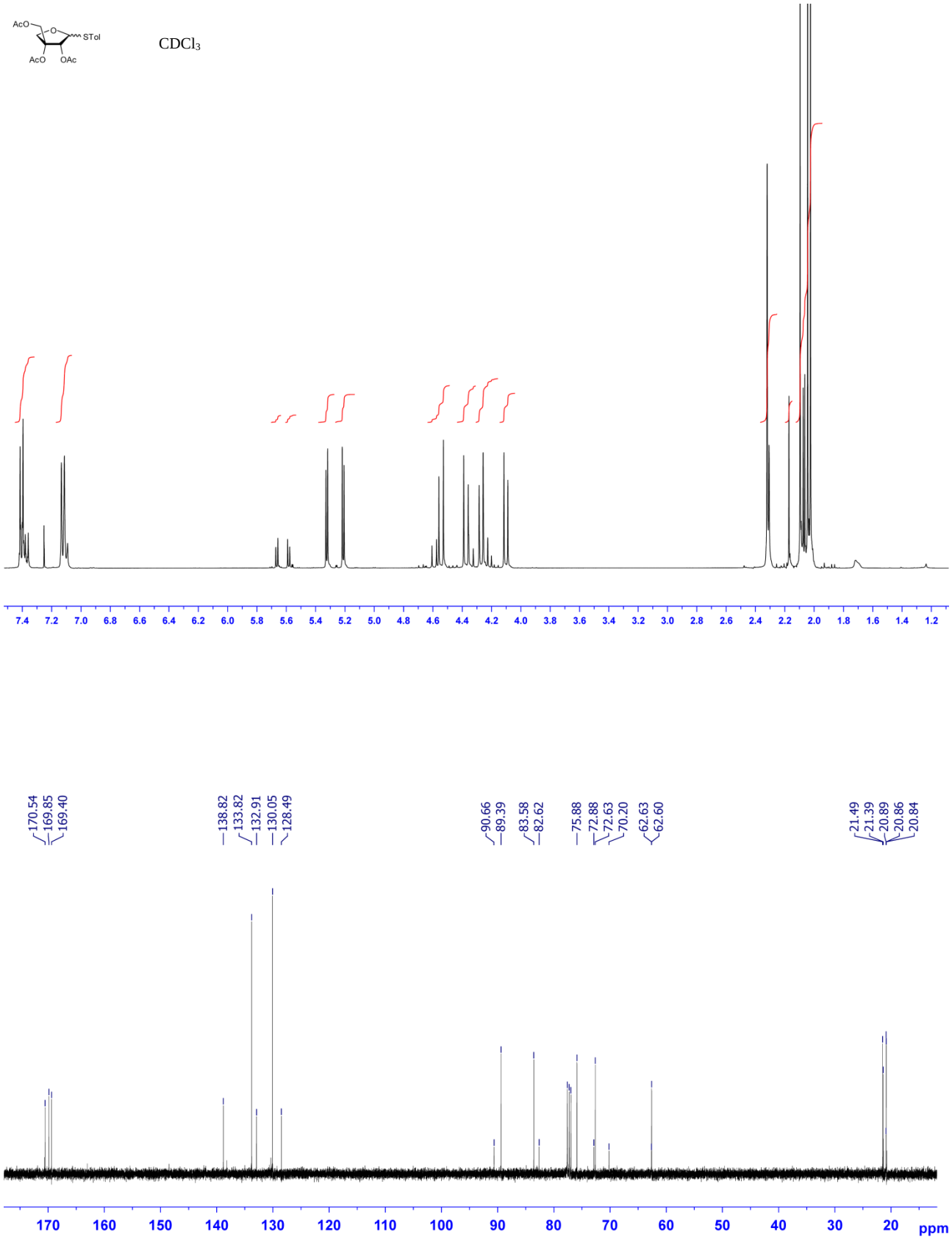

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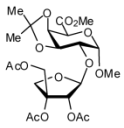

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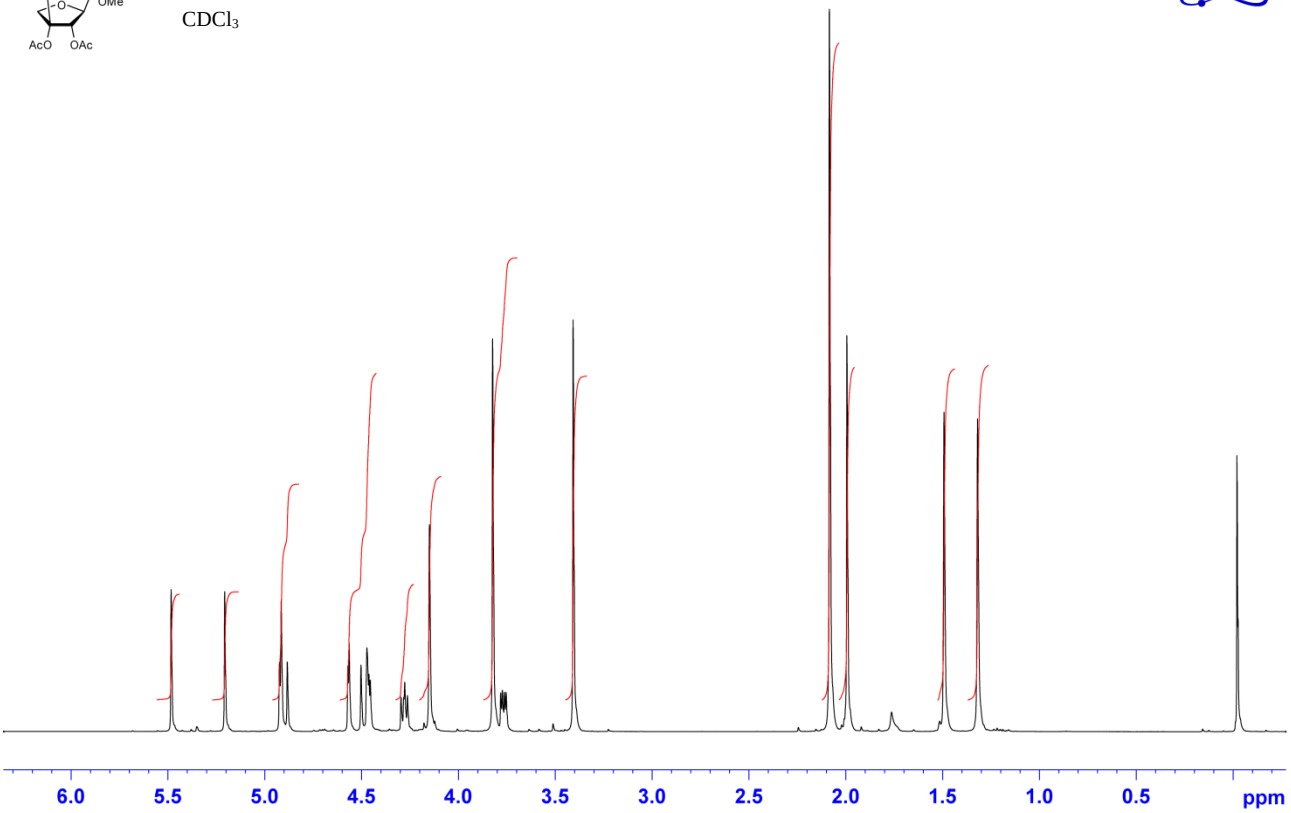

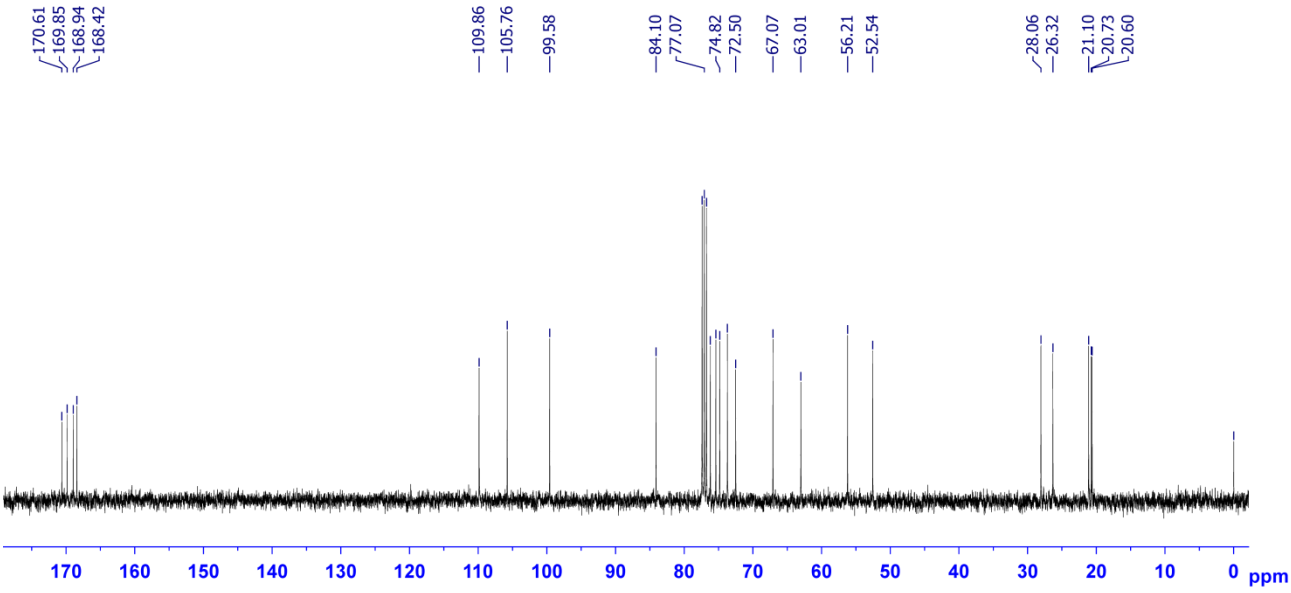

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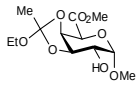

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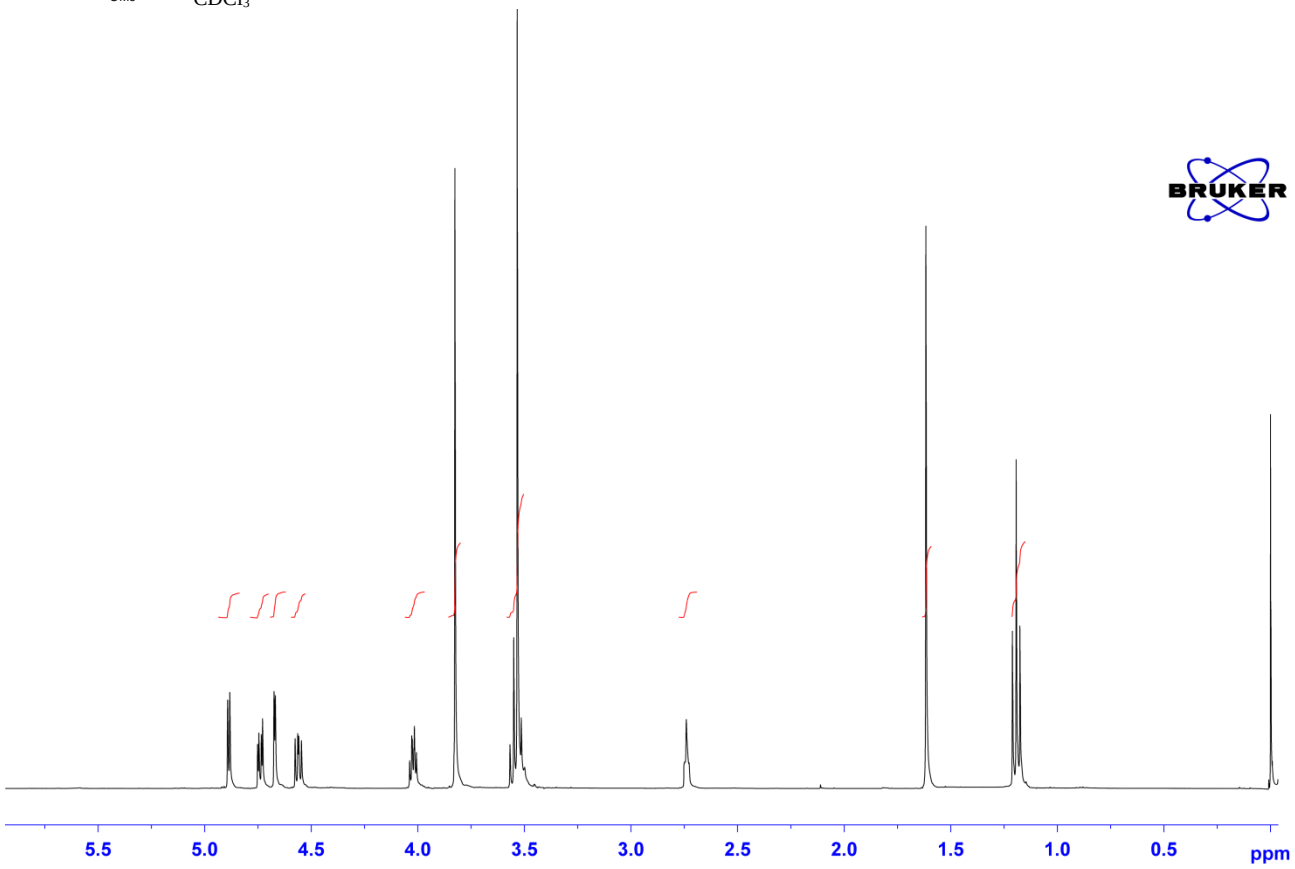

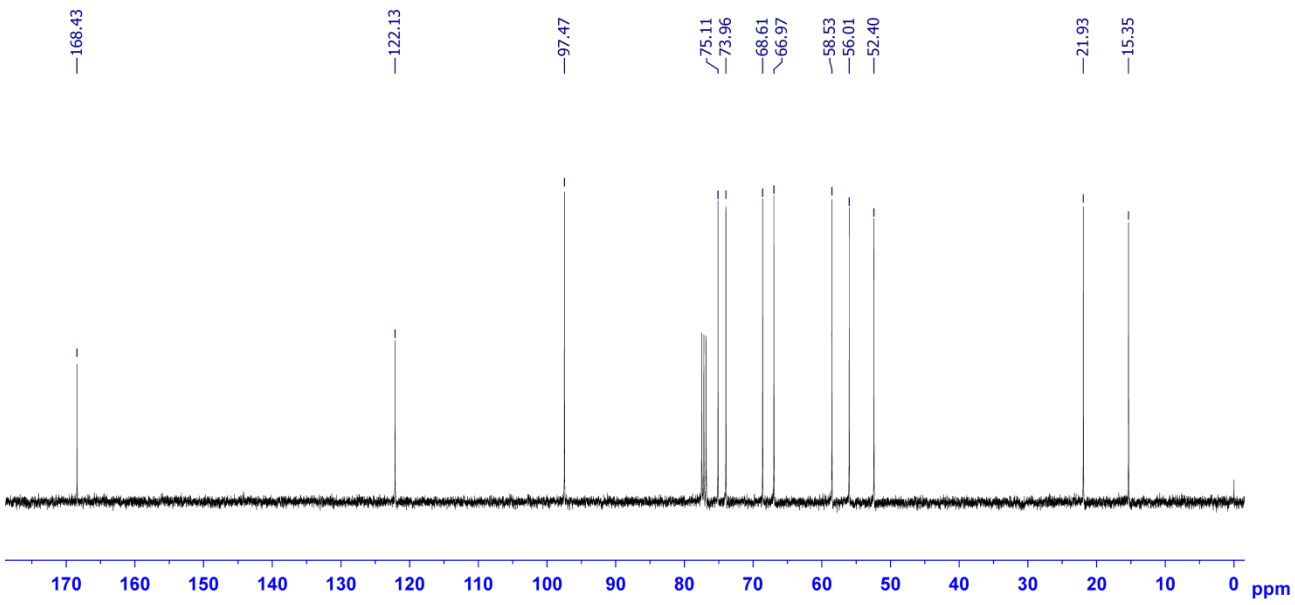

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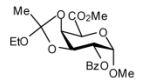

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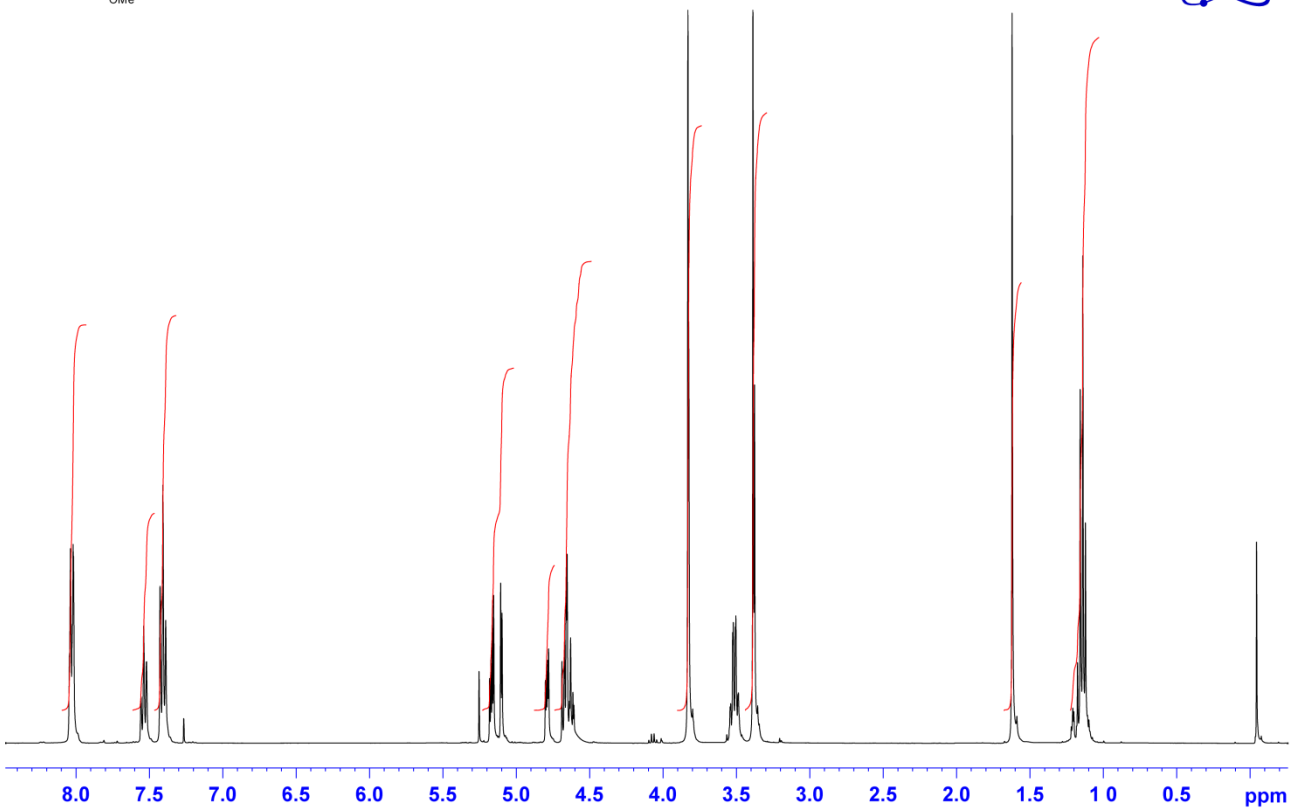

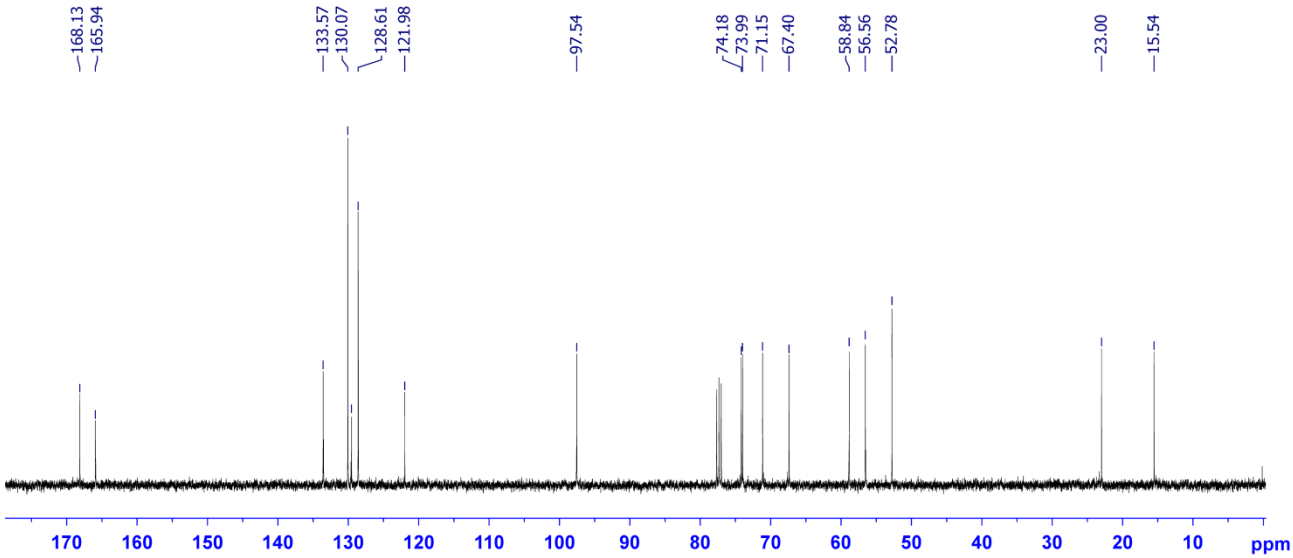

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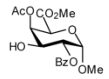

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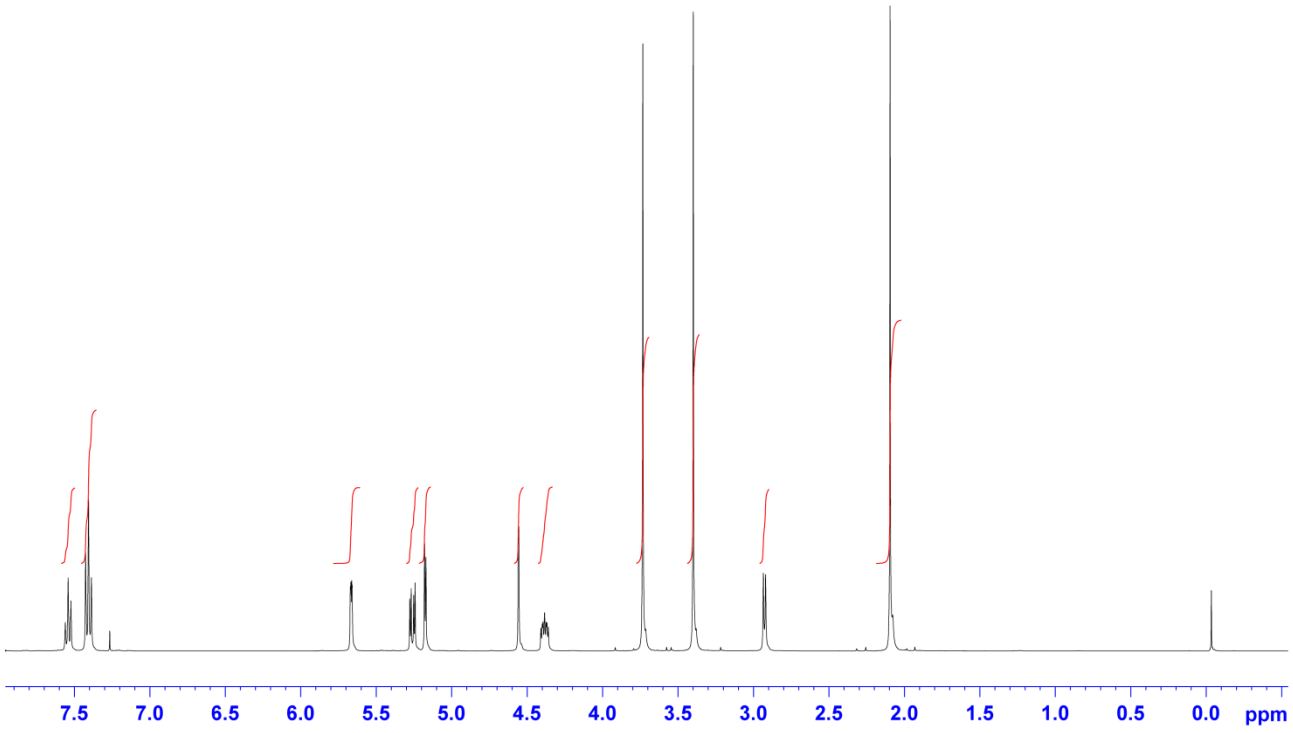

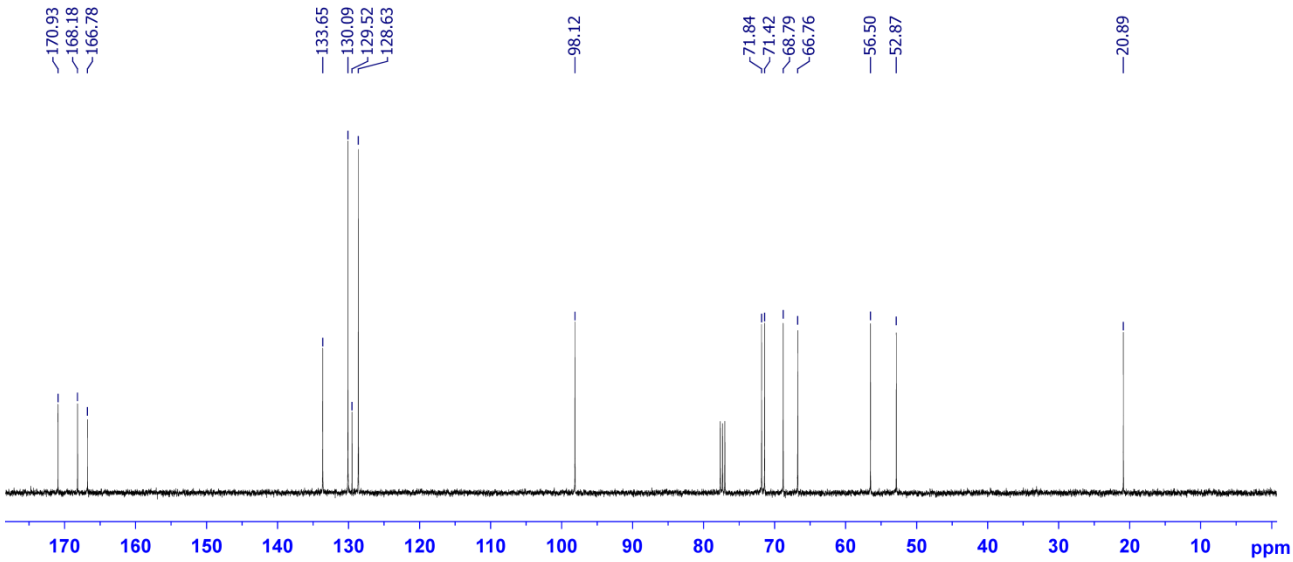

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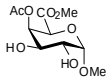

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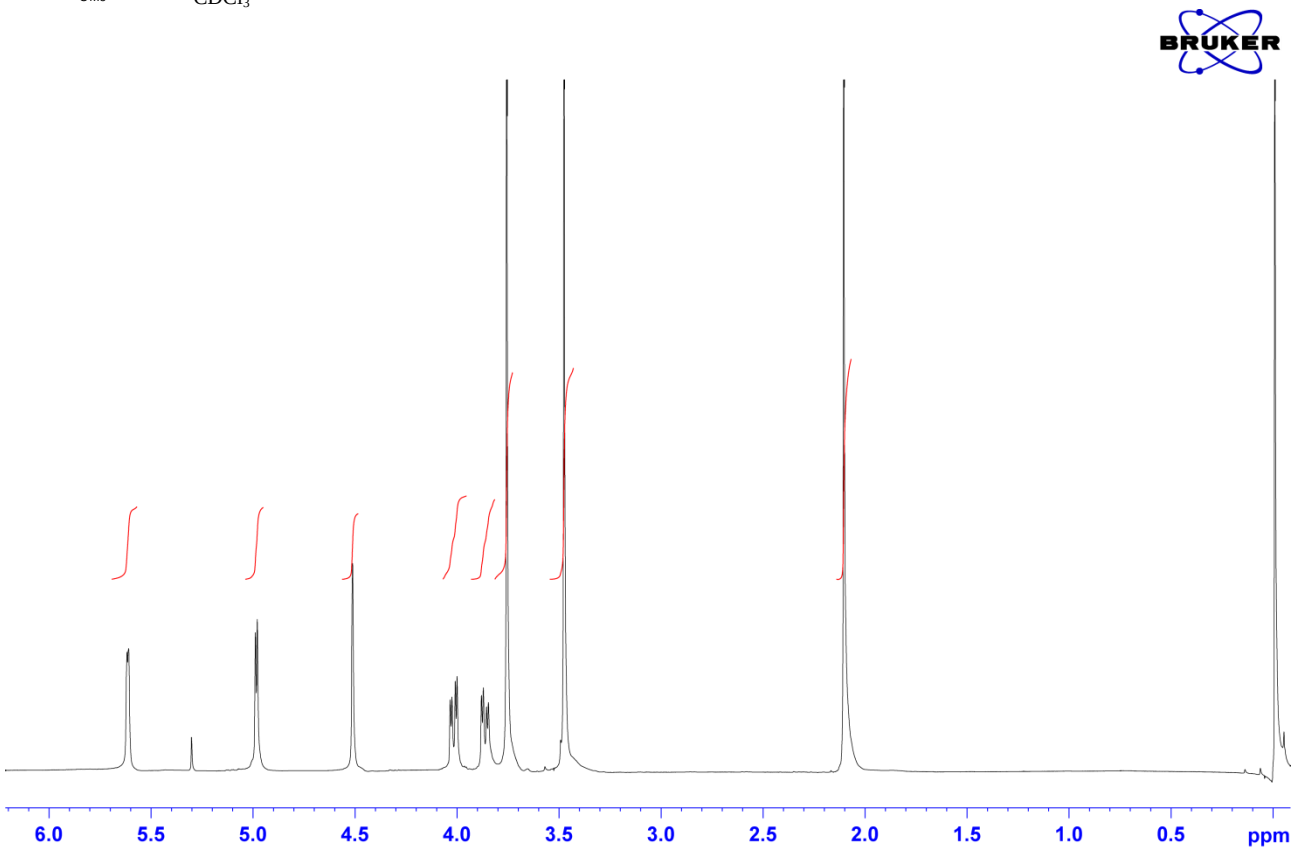

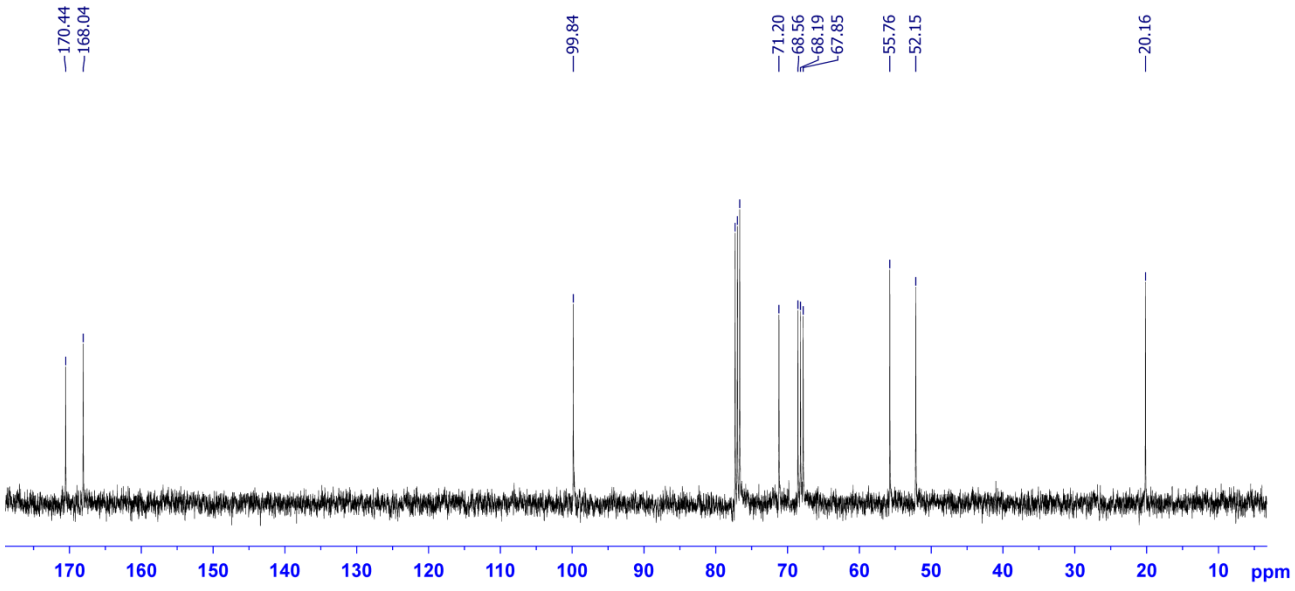

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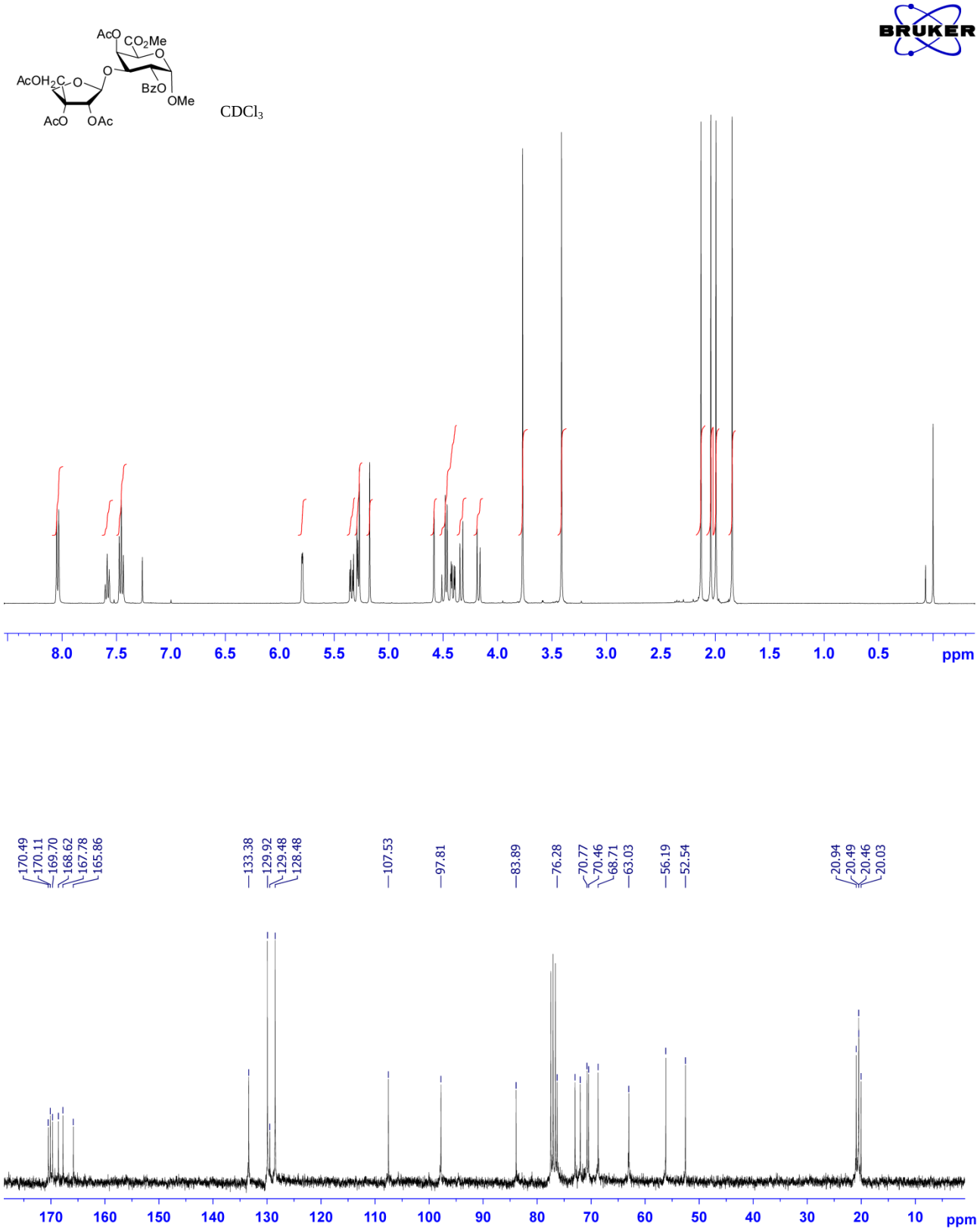
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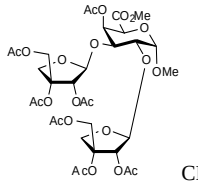

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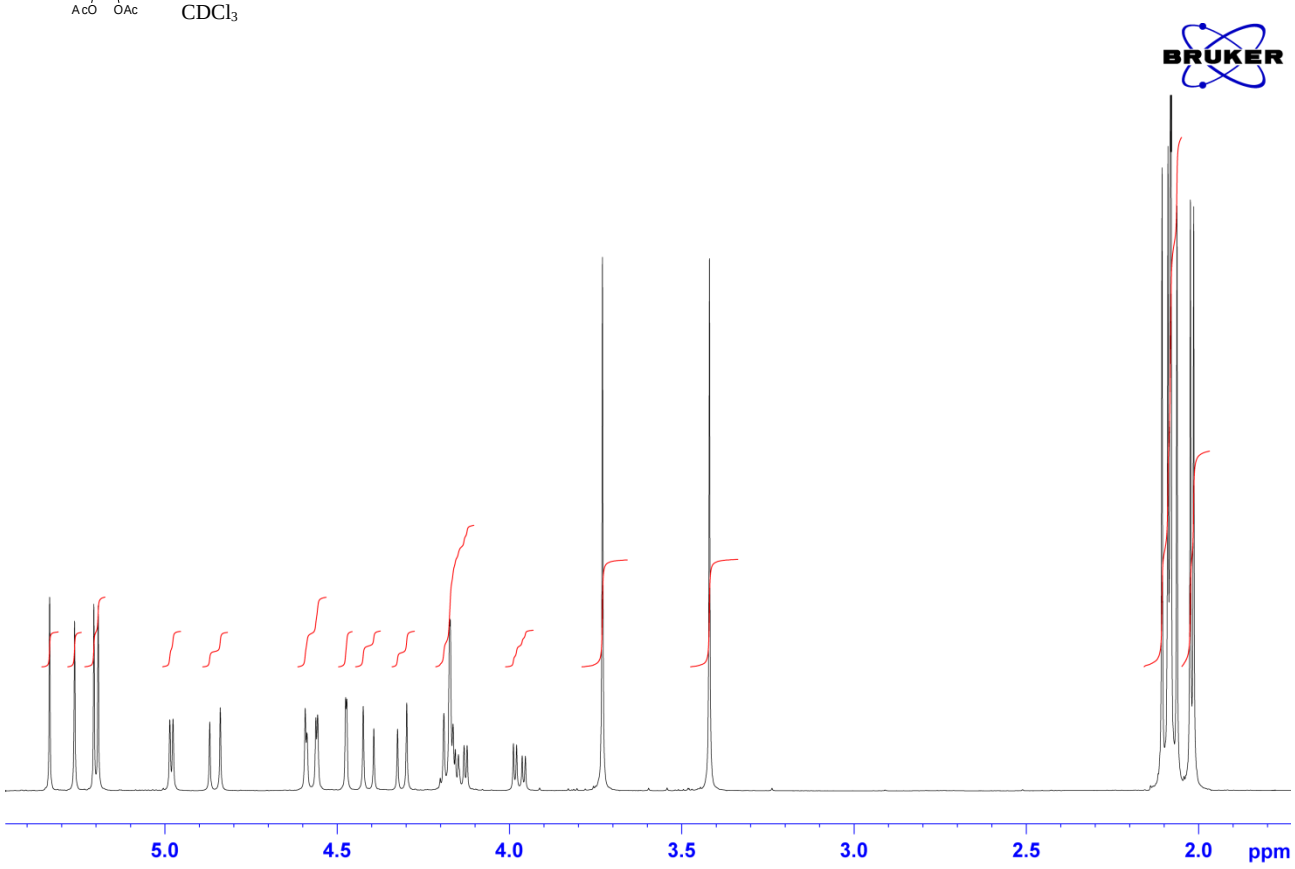

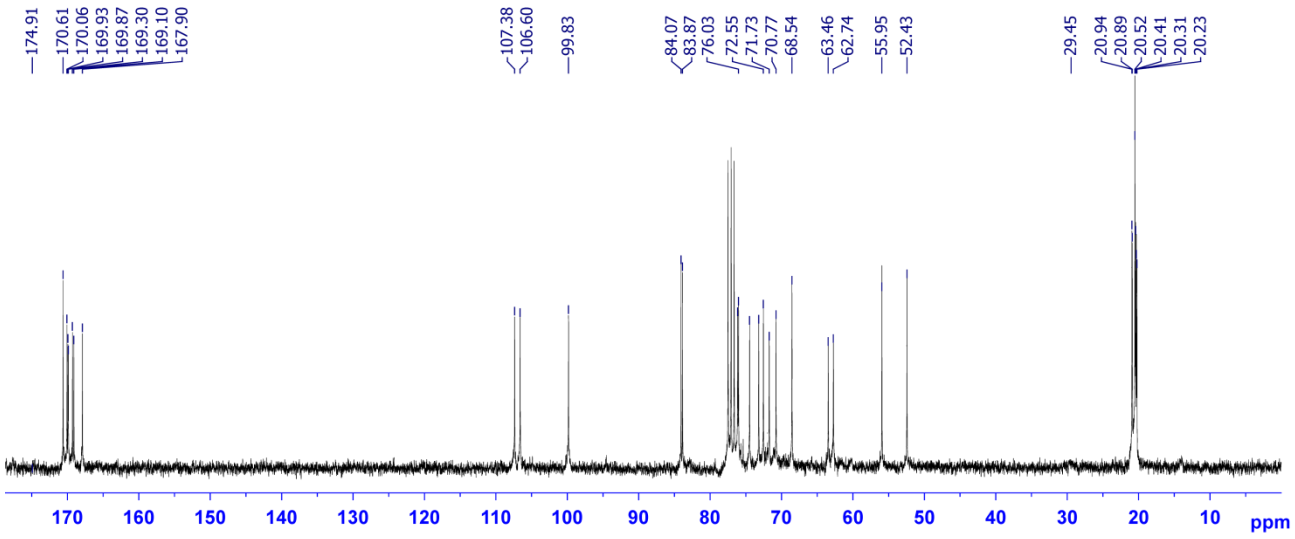

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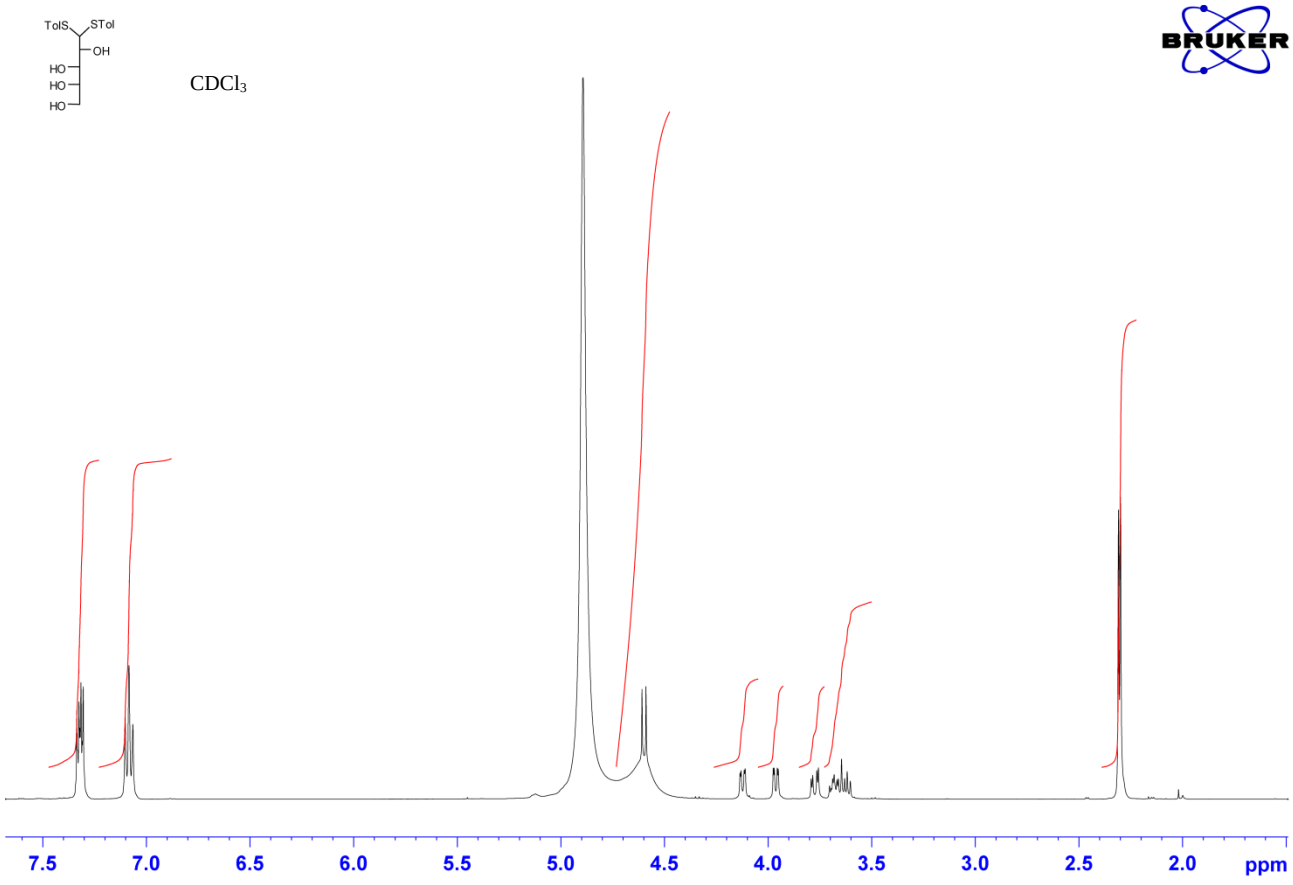
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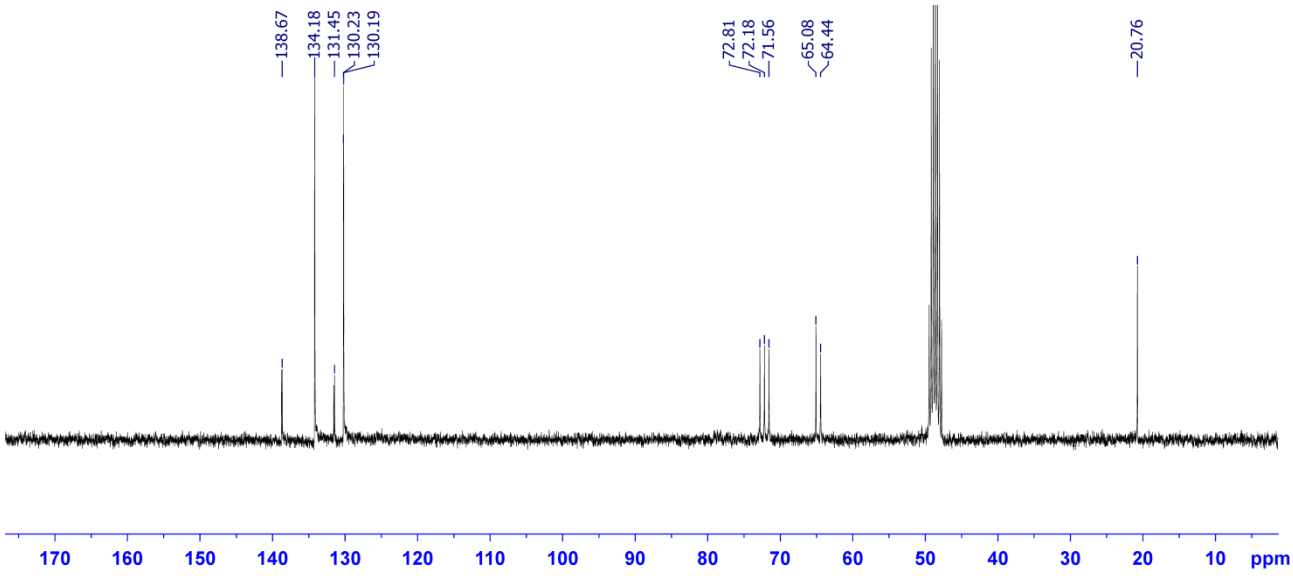
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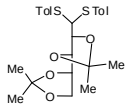

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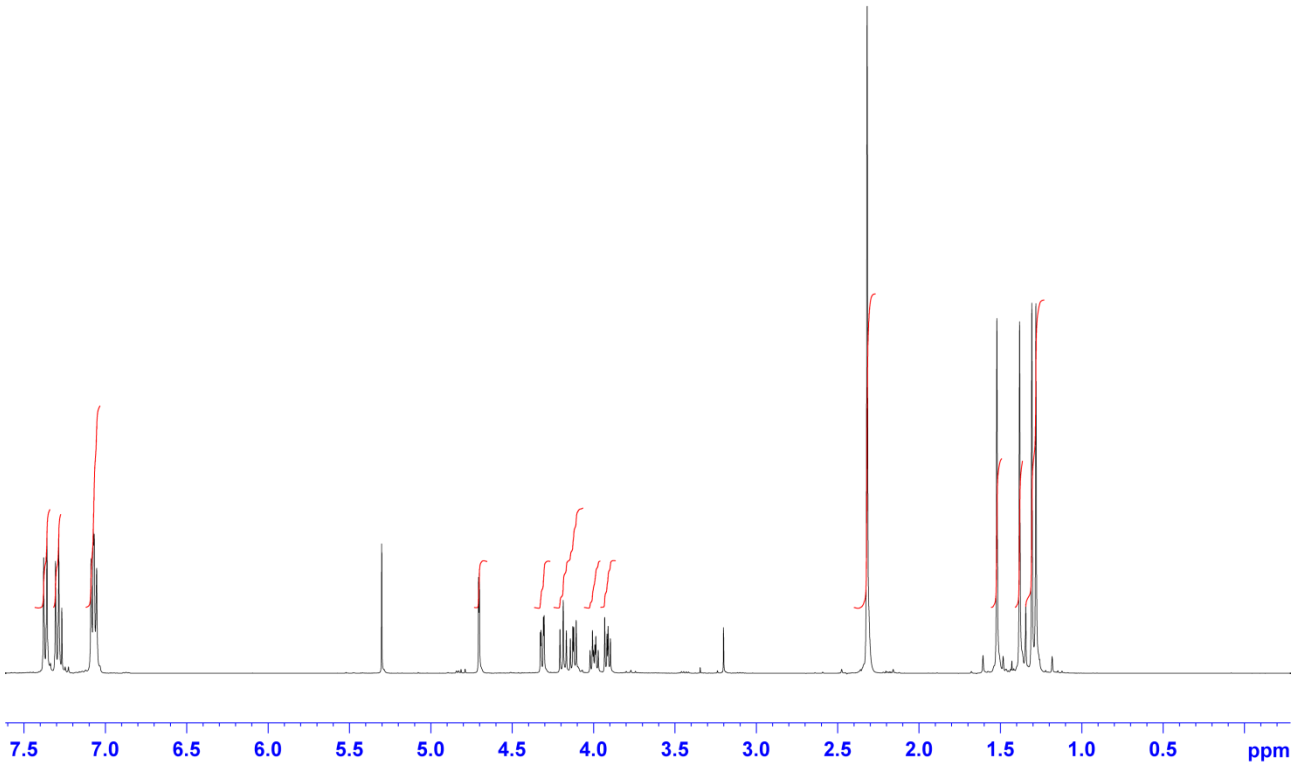
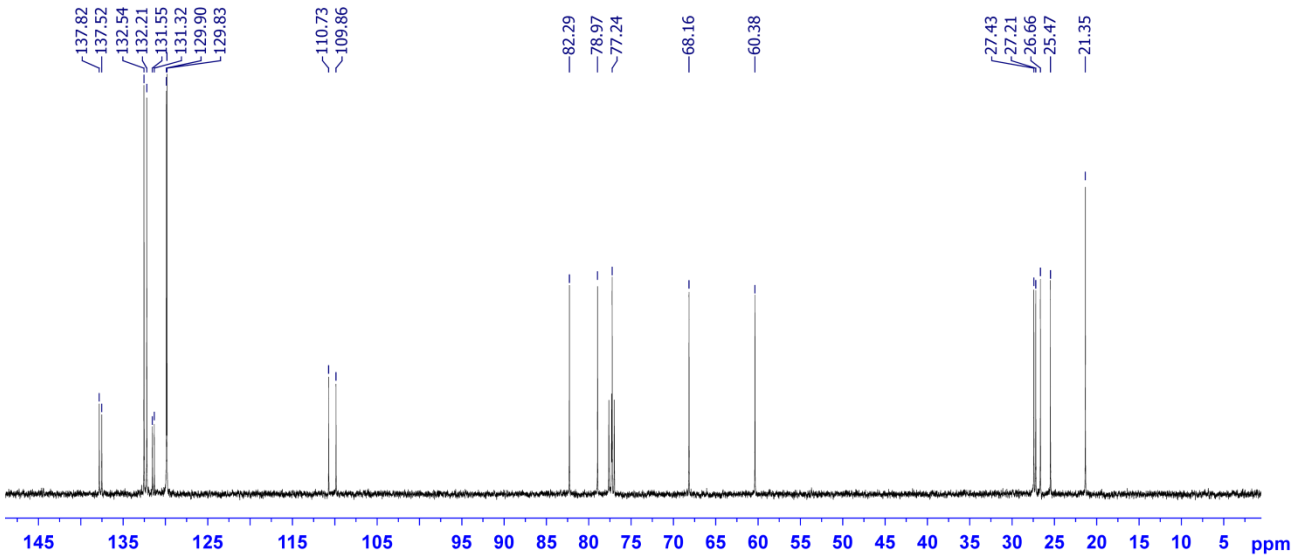
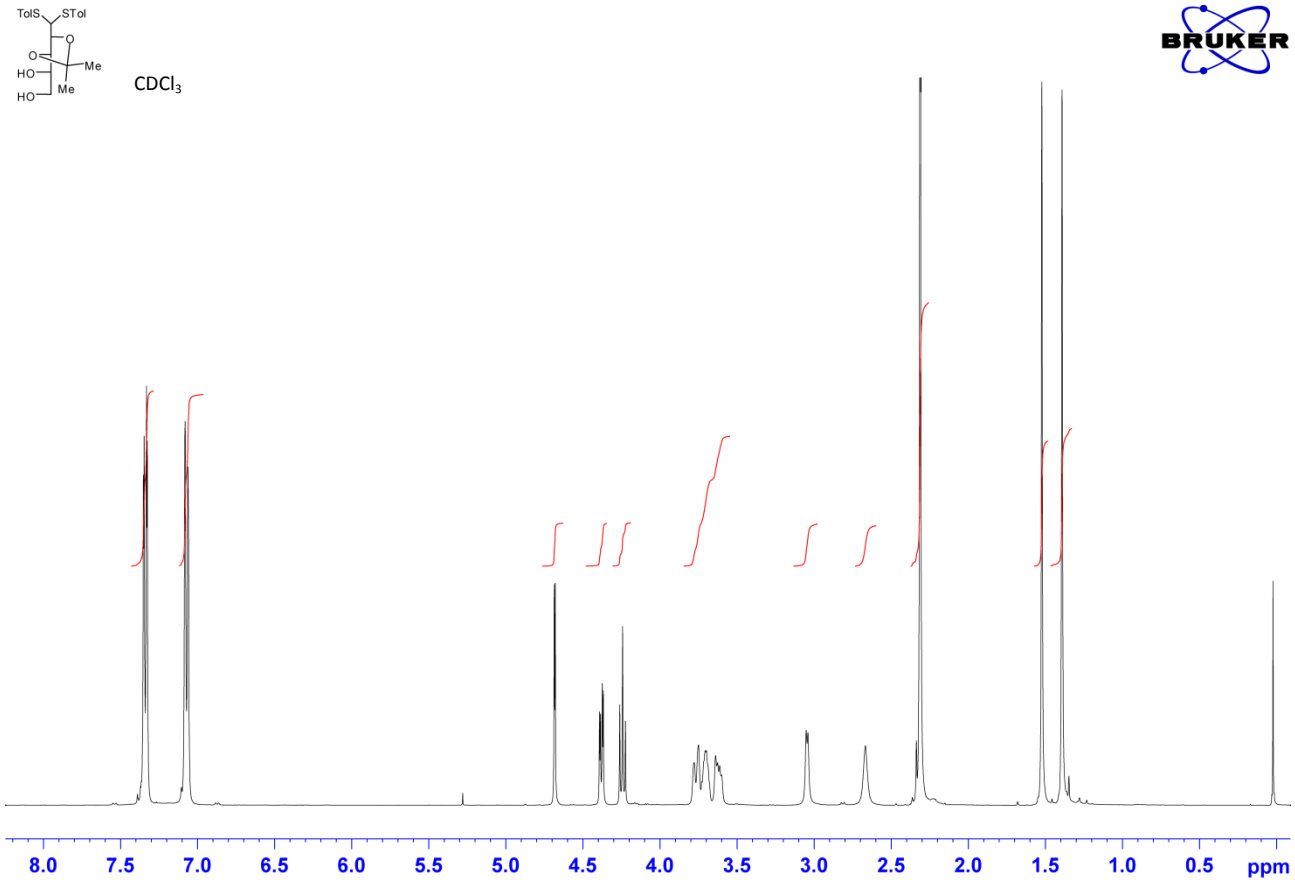
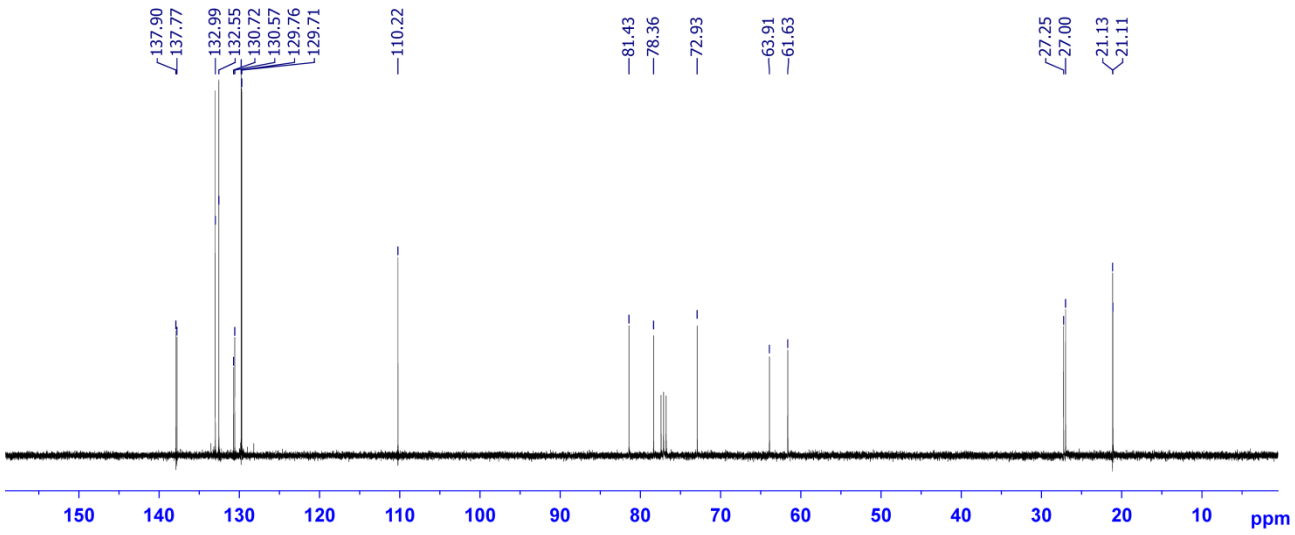




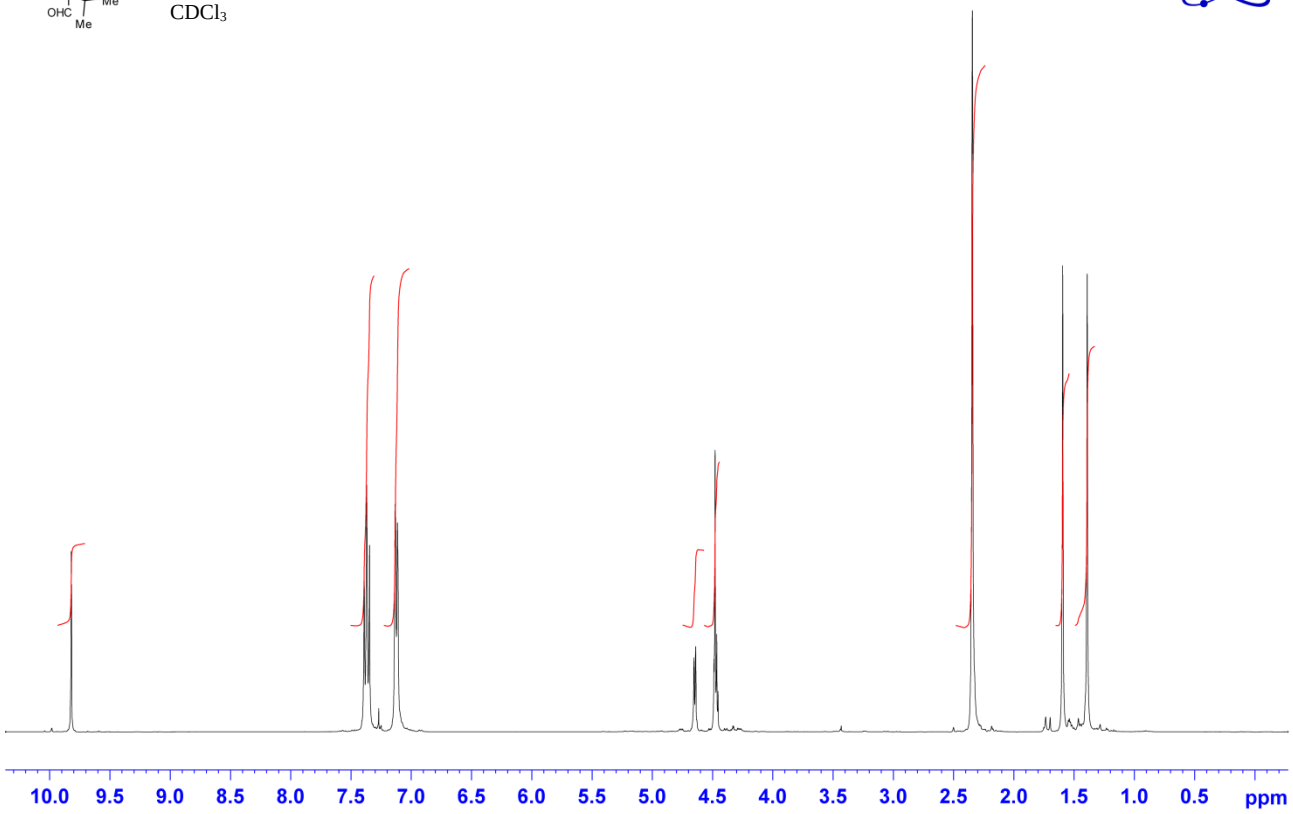
Compound **32**

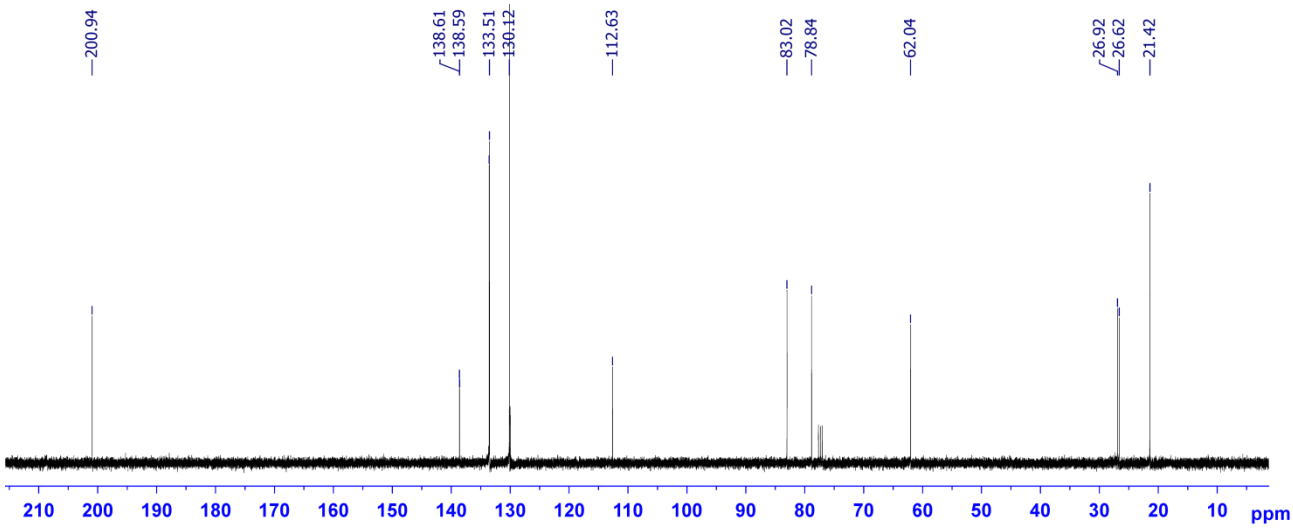

TolS
STol
O
O
HO
Me
HO
Me
CDCl3
BRUKER
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


137.90
137.77
132.99
132.55
130.72
130.57
129.76
129.71
110.22
81.43
78.36
72.93
63.91
61.63
27.25
27.00
21.13
21.11
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

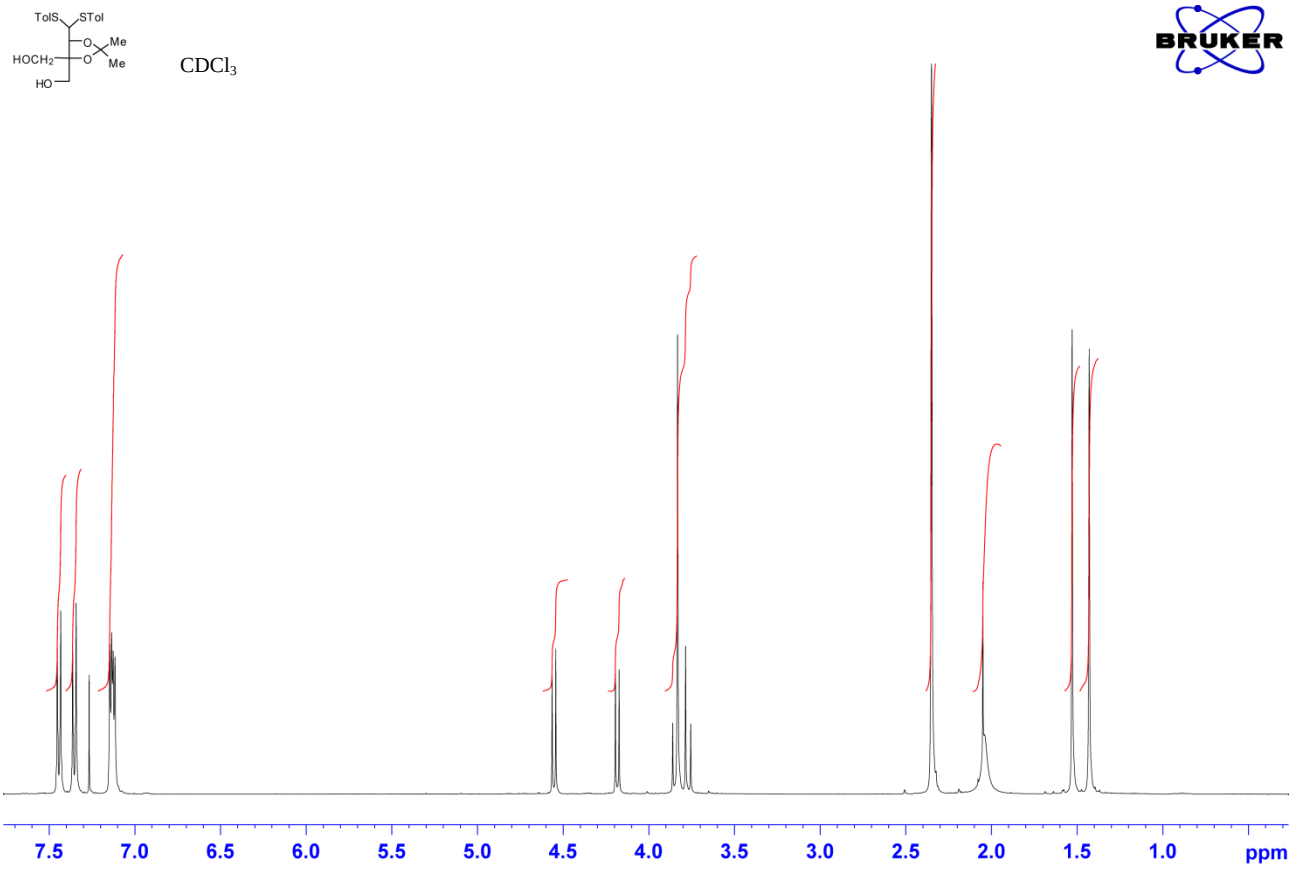
Compound **33**

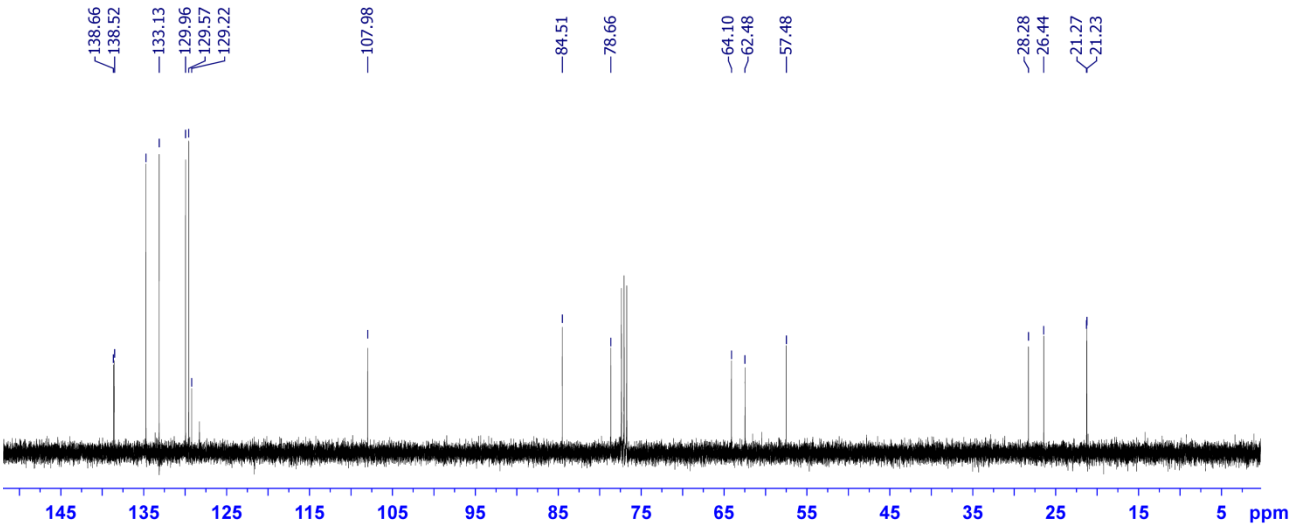
$CDCl_3$



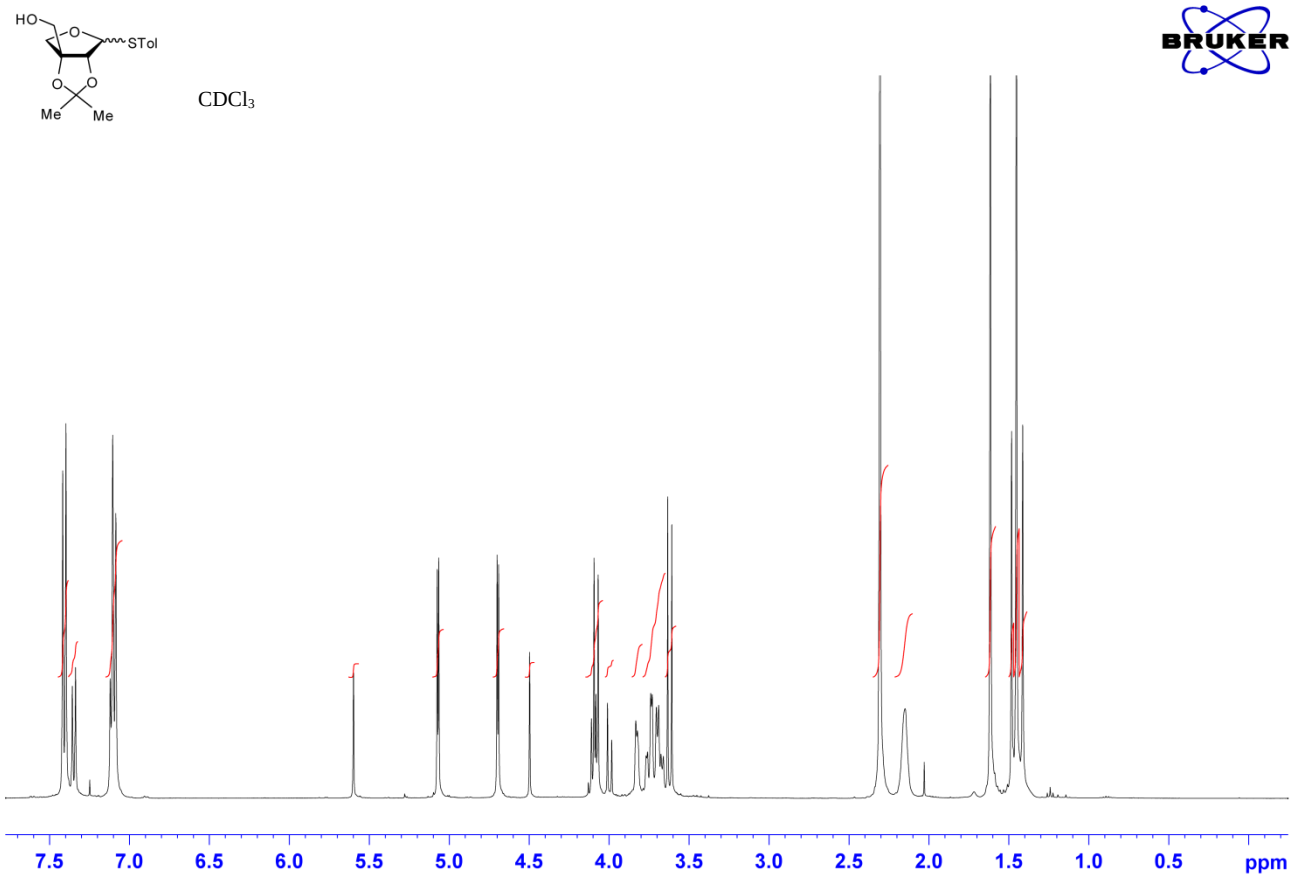


Compound **34**

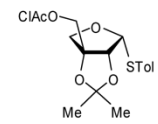

TolS
STol
Me
Me
HOCH2
HO
CDCl3
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


138.66
138.52
133.13
129.96
129.57
129.22
107.98
84.51
78.66
64.10
62.48
57.48
28.28
26.44
21.27
21.23
145
135
125
115
105
95
85
75
65
55
45
35
25
15
5
ppm

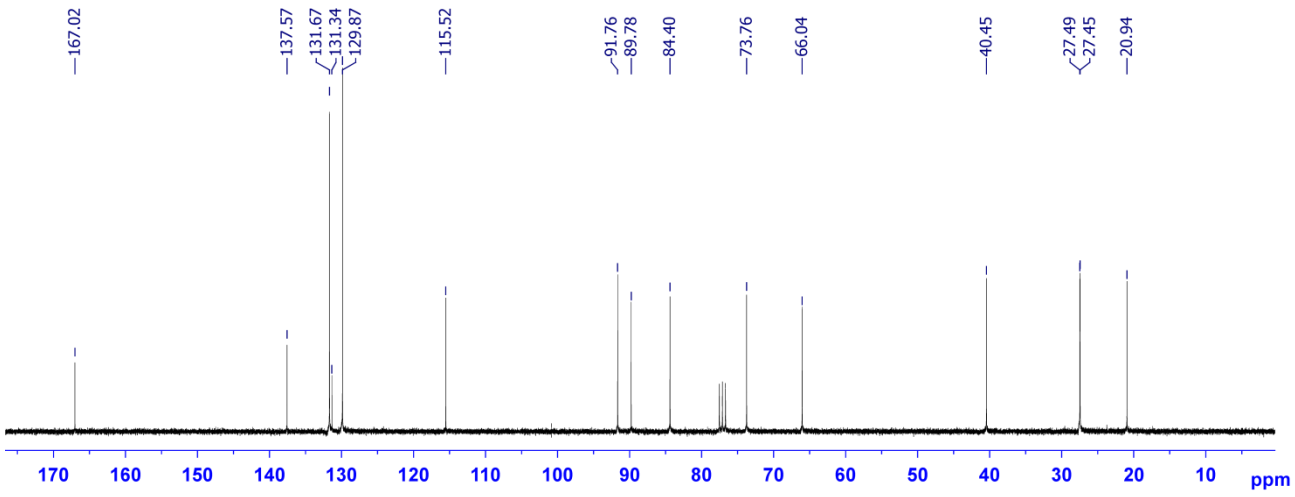
Compound **35**


HO
O
STol
O
O
Me
Me
CDCl3
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

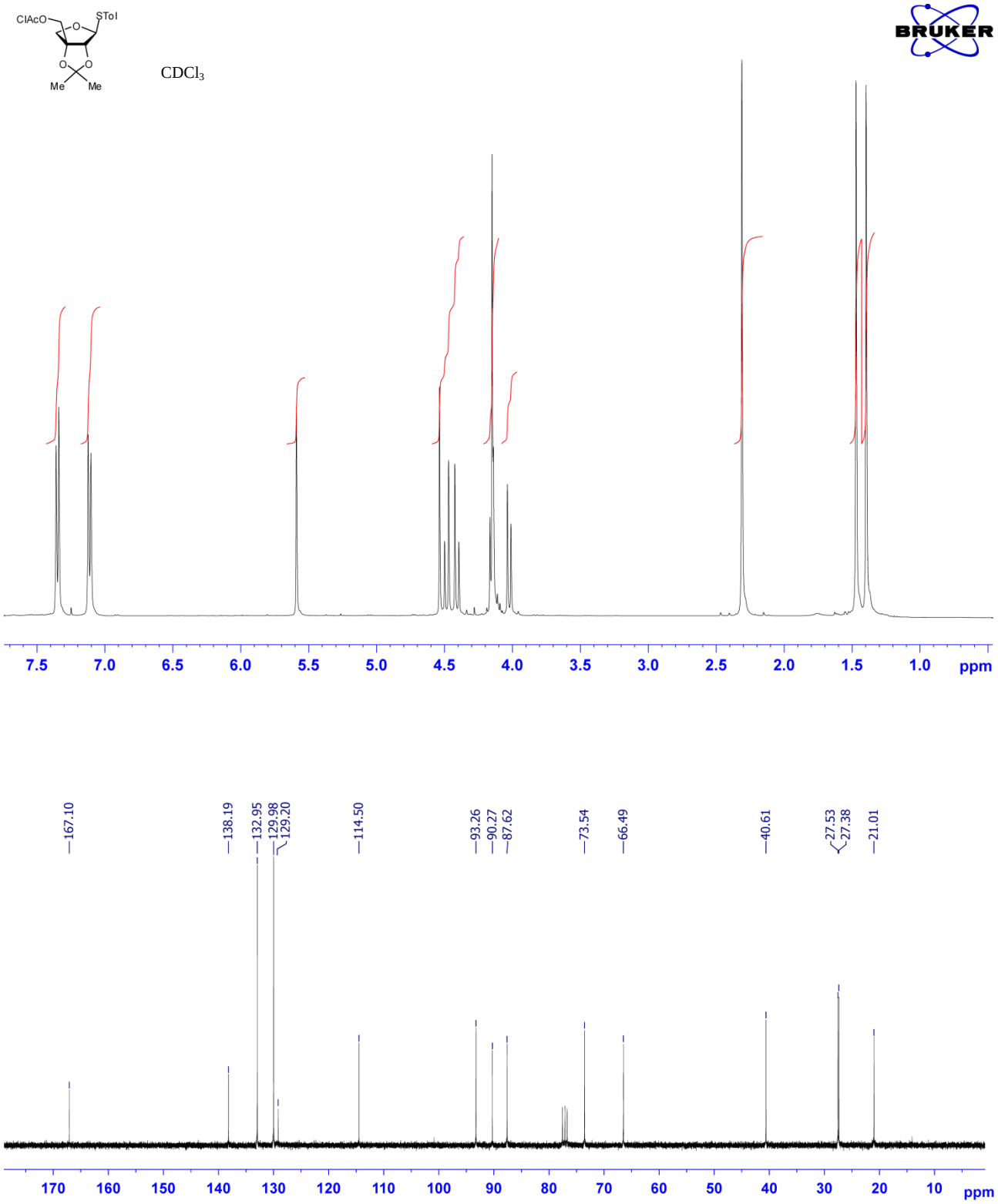
Compound **36a**



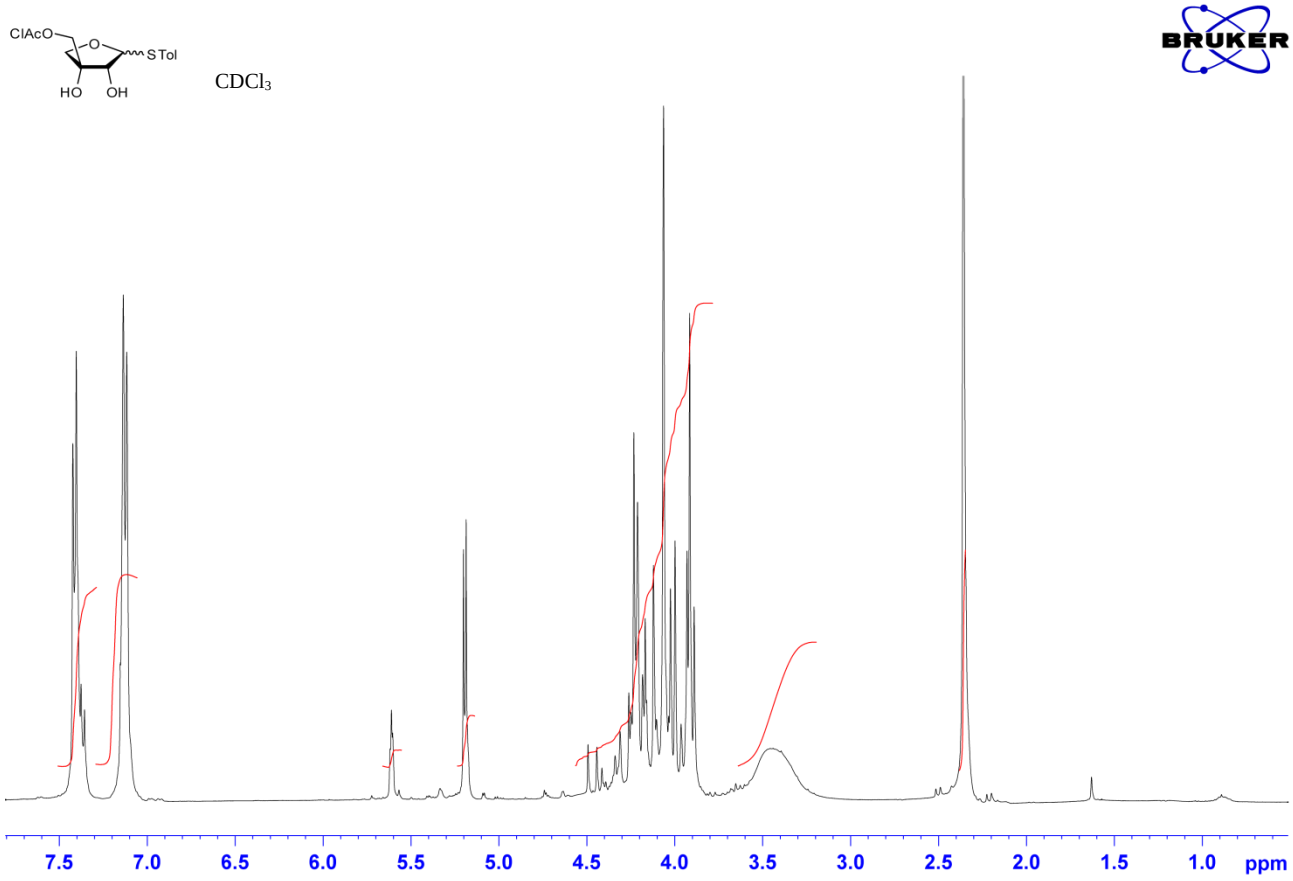
$CDCl_3$



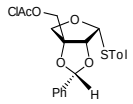
Compound **36b**



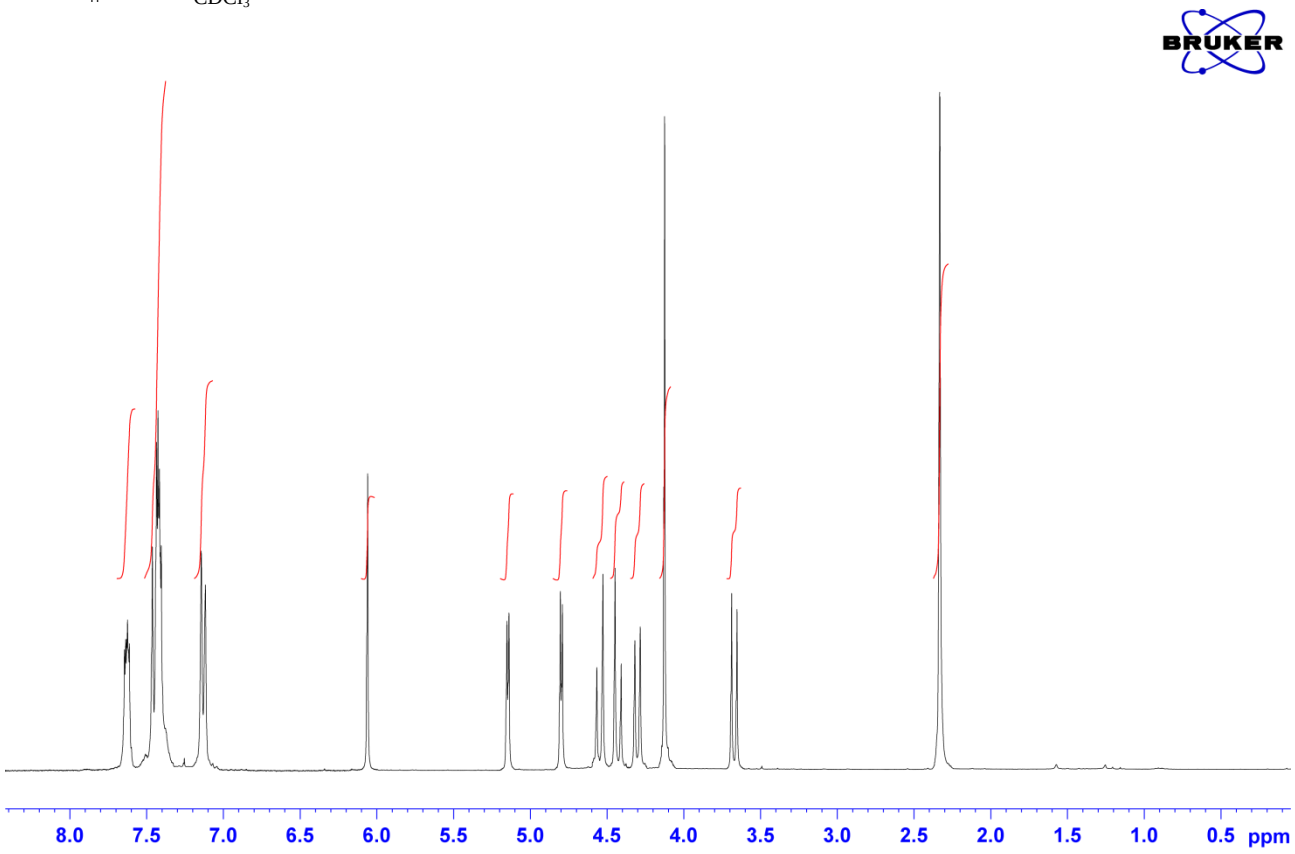
Compound **37a**,**b**

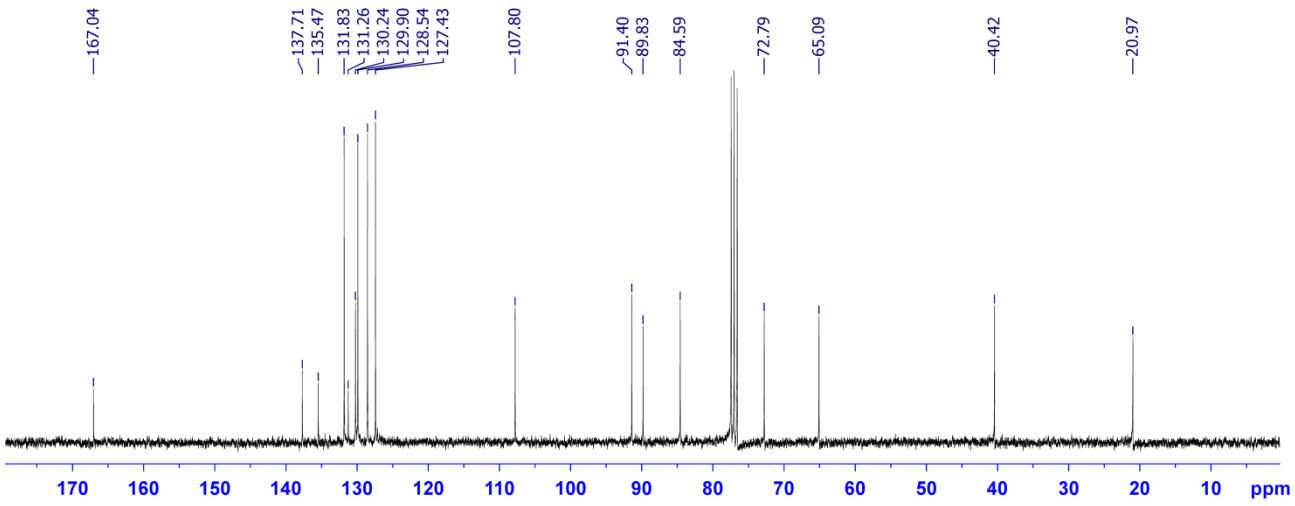


Compound **38a**

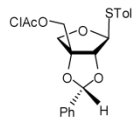


$CDCl_3$

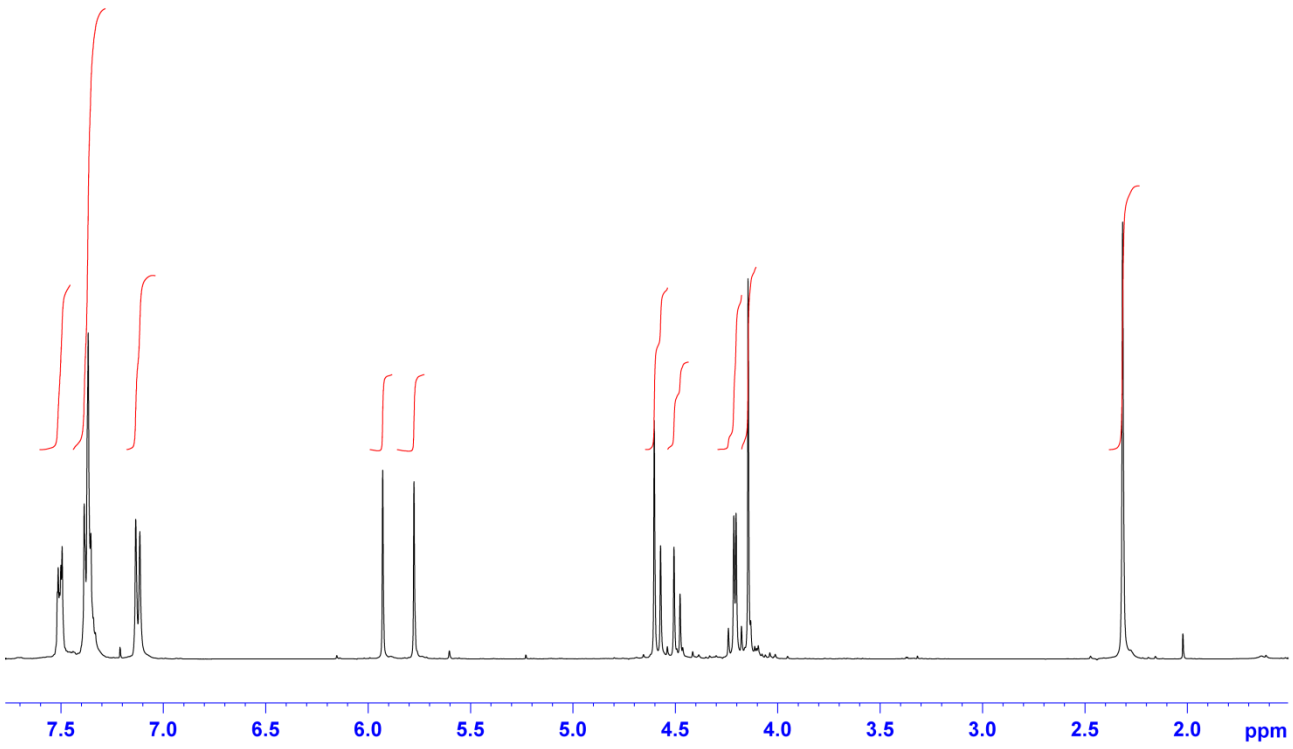


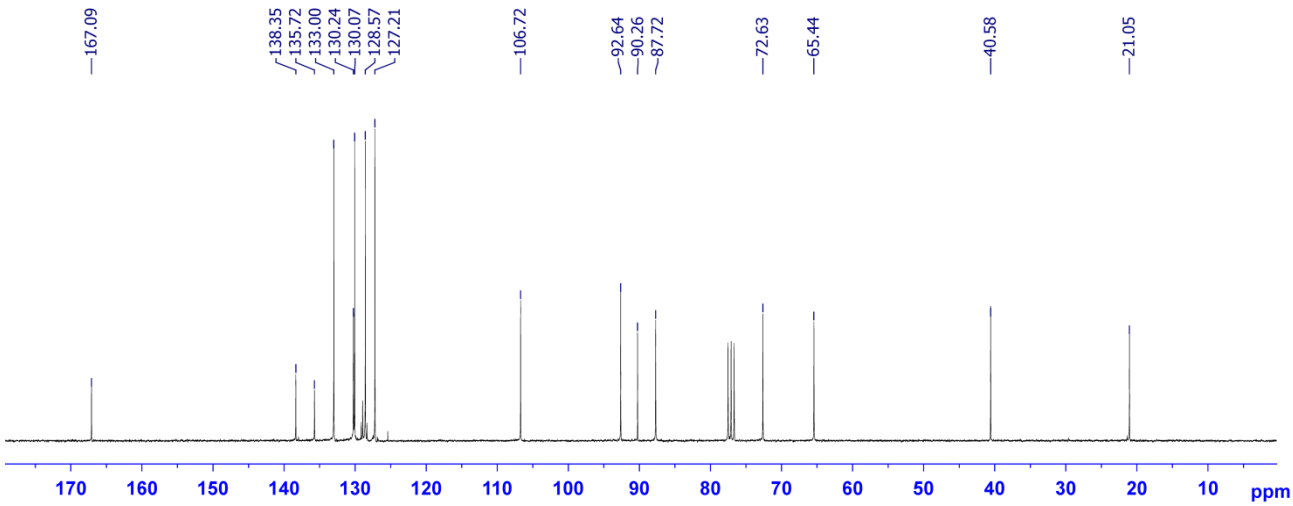


Compound **38b**

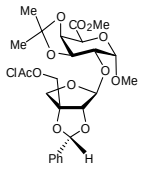


$CDCl_3$

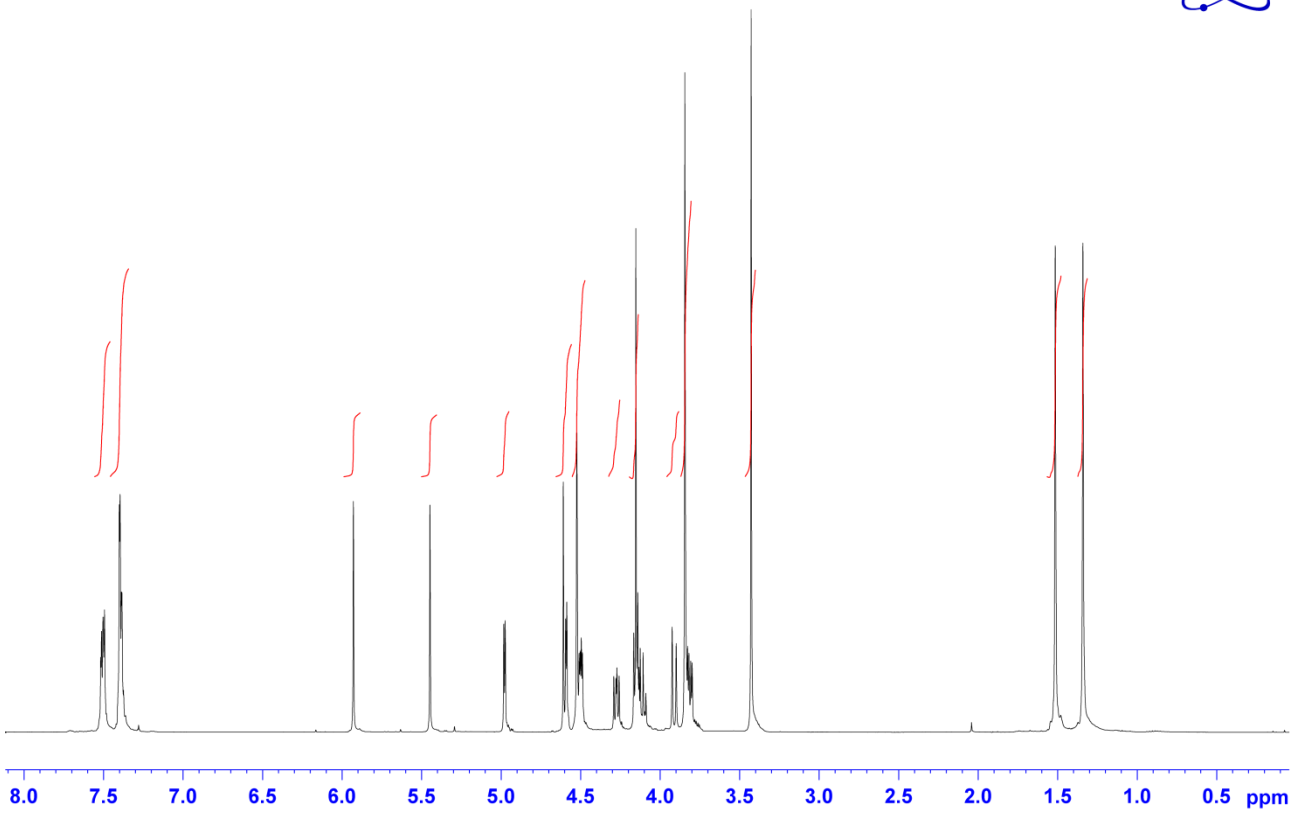


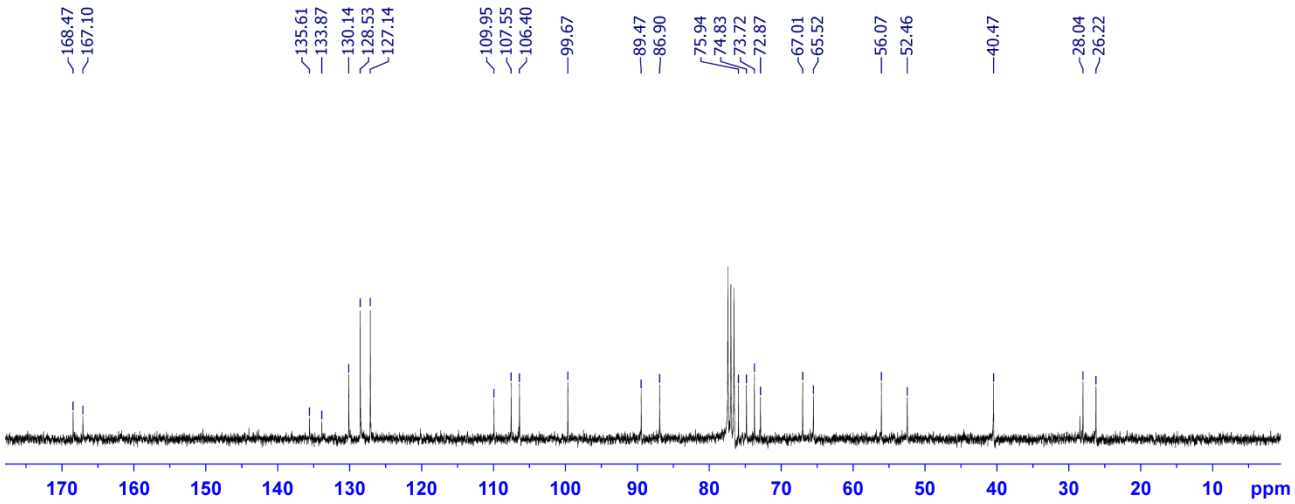


Compound **39**

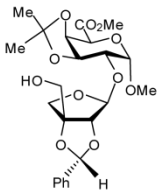


$CDCl_3$

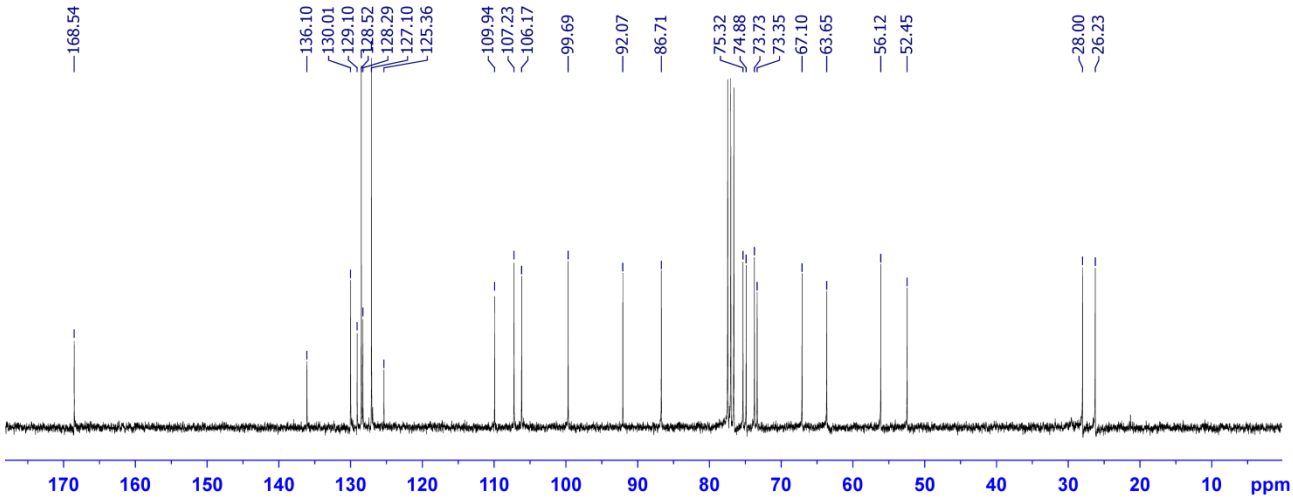




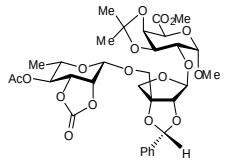
Compound **40**



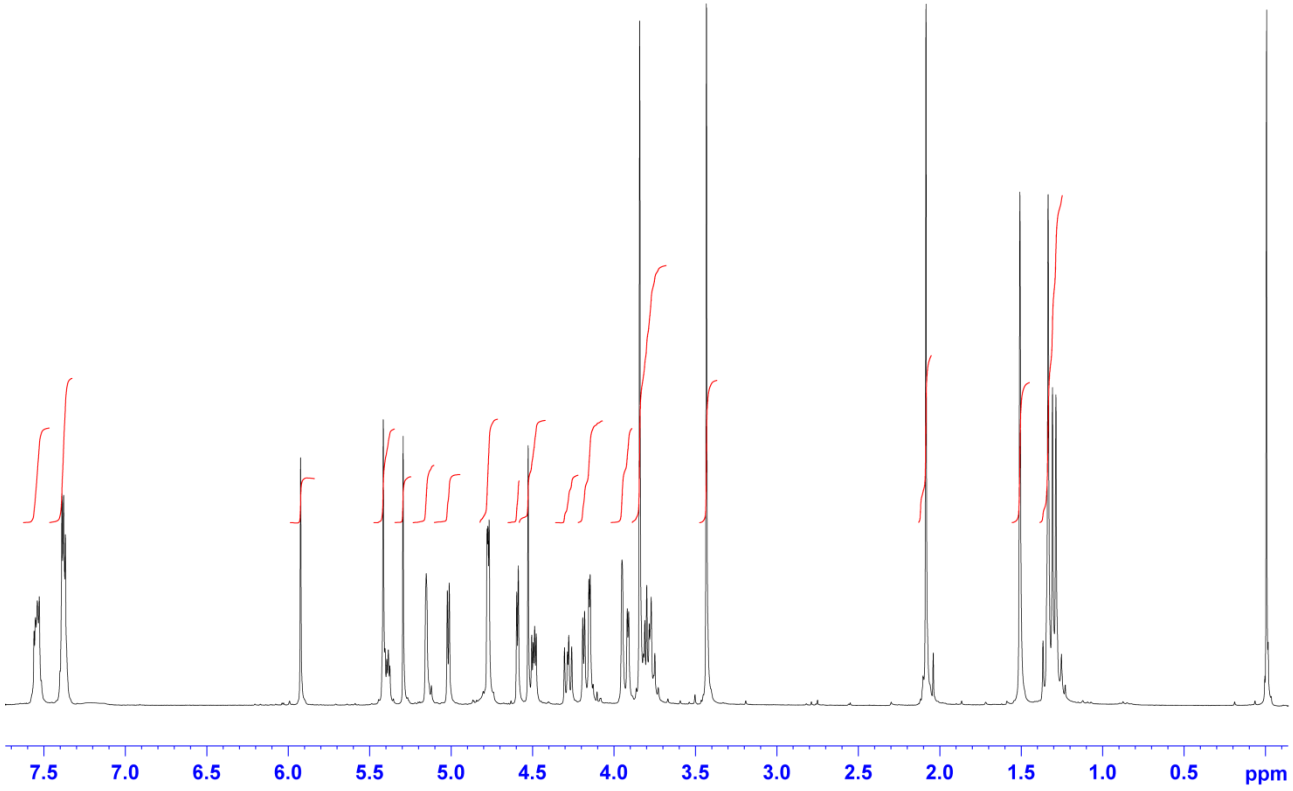
$CDCl_3$

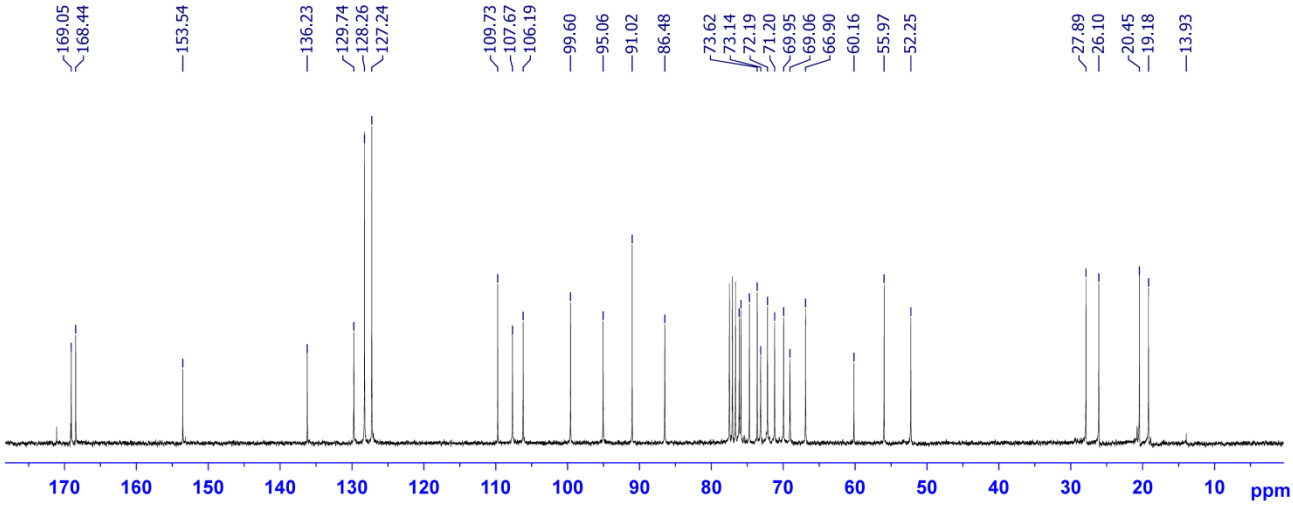


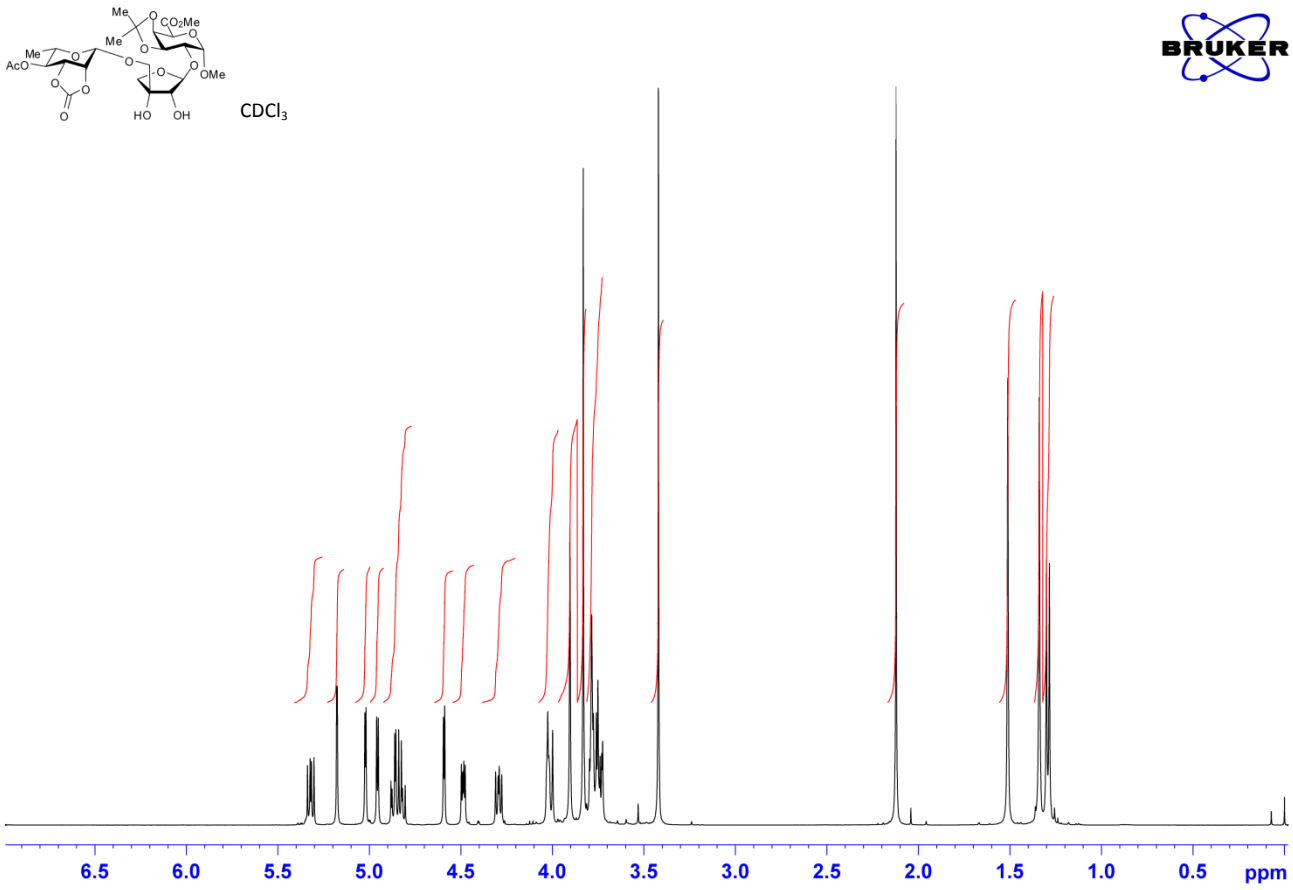
Compound **41**



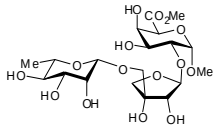
$CDCl_3$



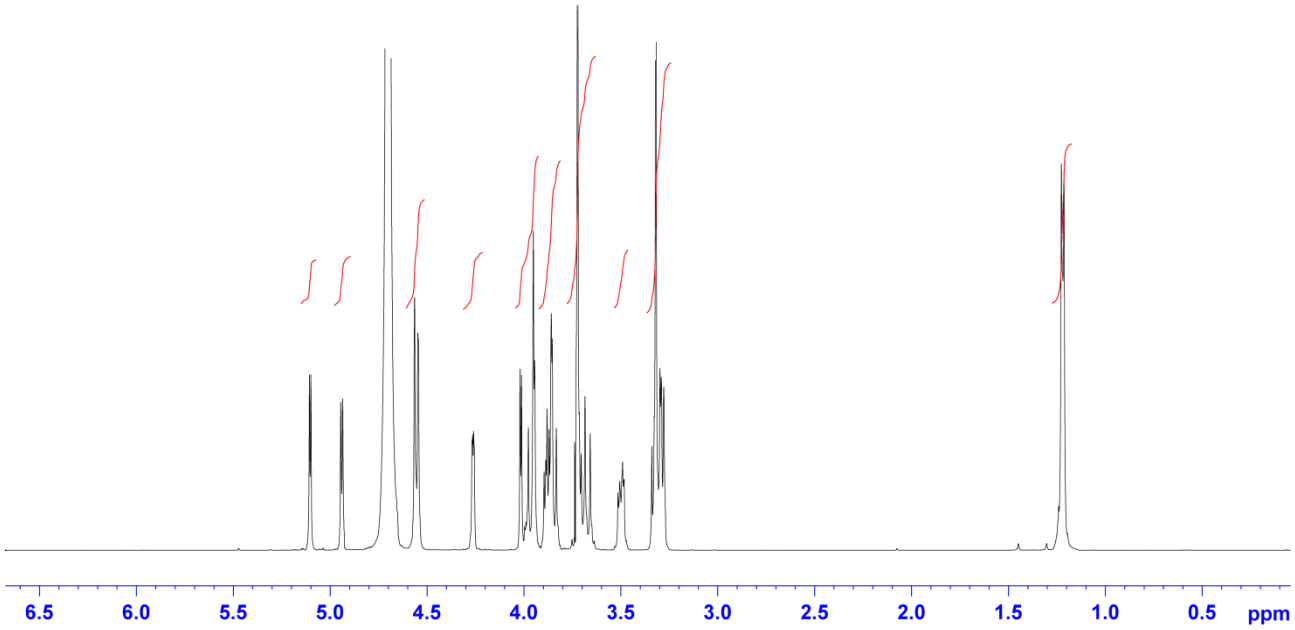


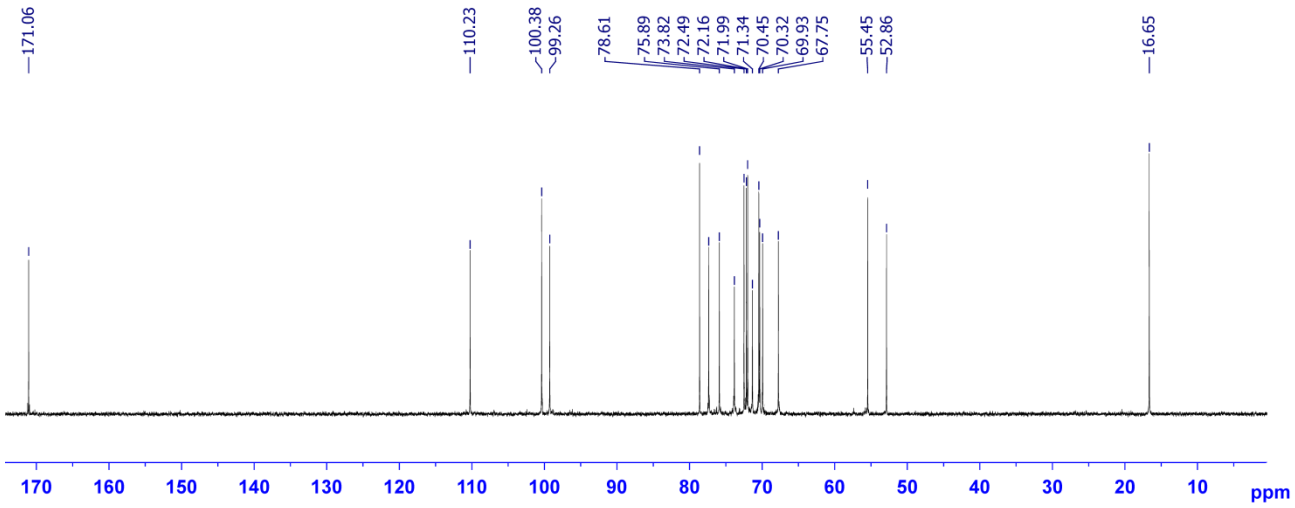

Me
CO2Me
Me
AcO
OMe
HO
OH
O
CDCl3
BRUKER
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

Compound **42**

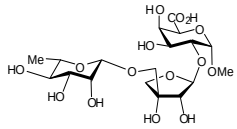


D_2O

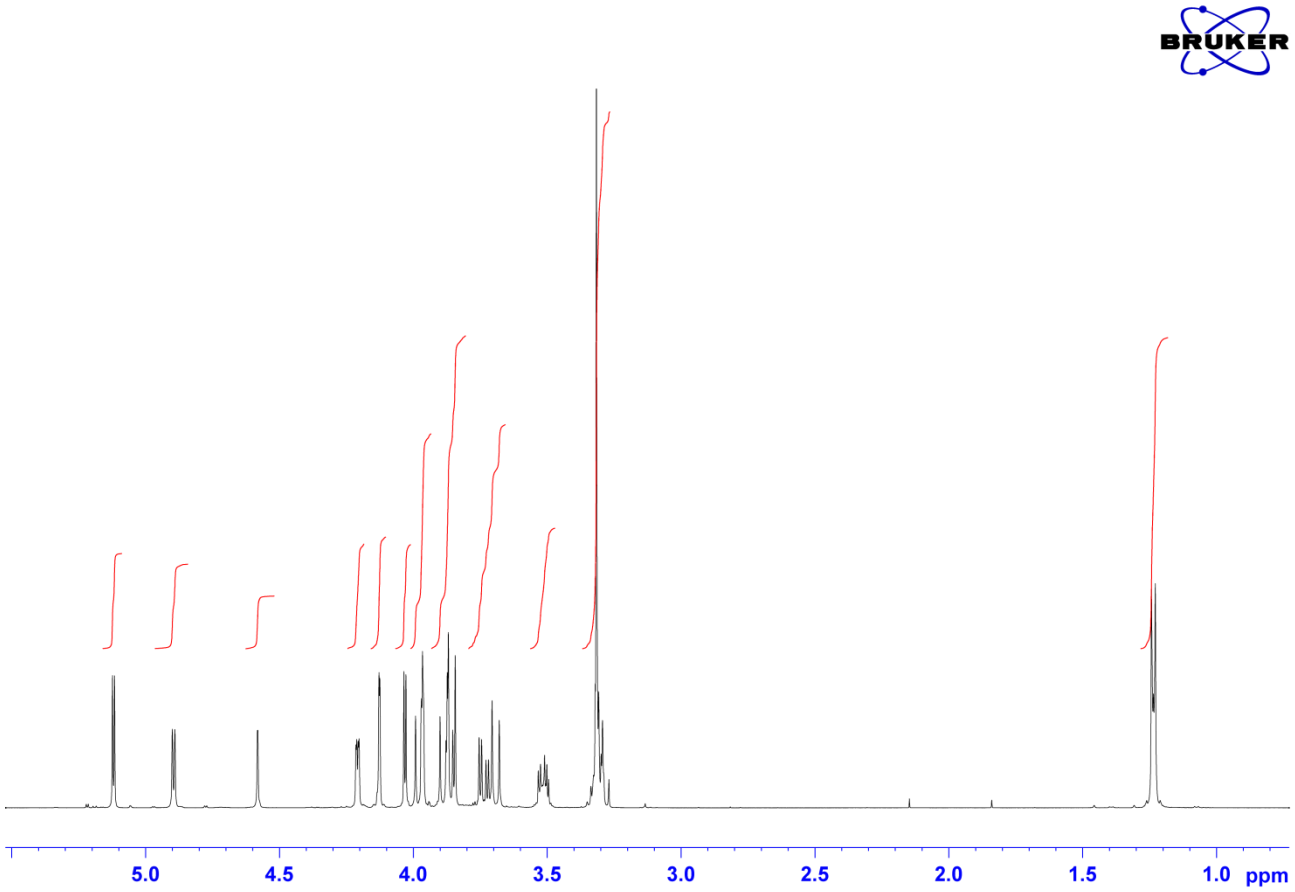


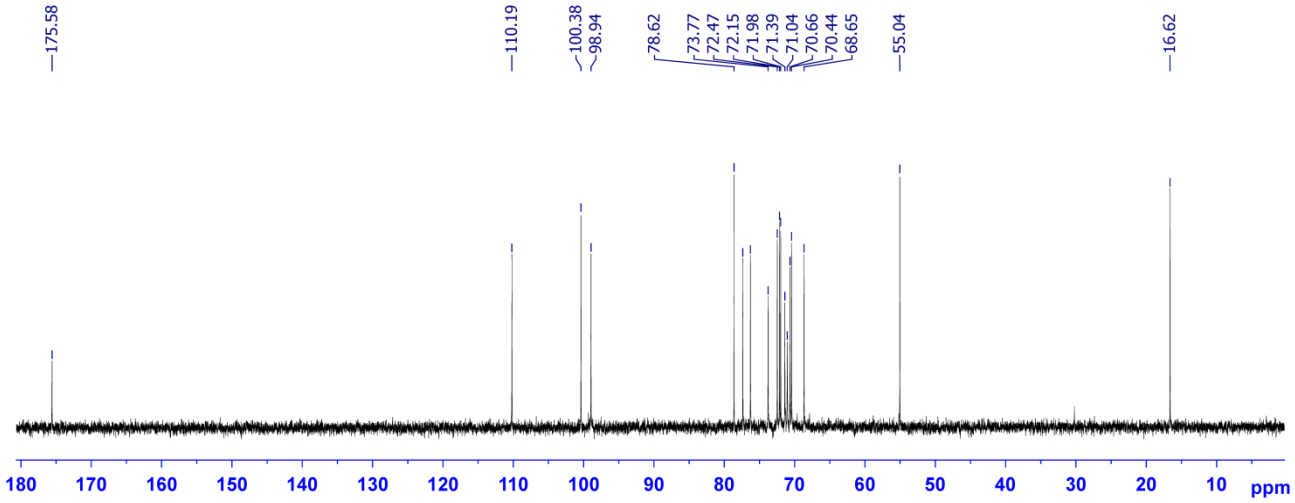


Compound **1**

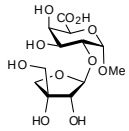


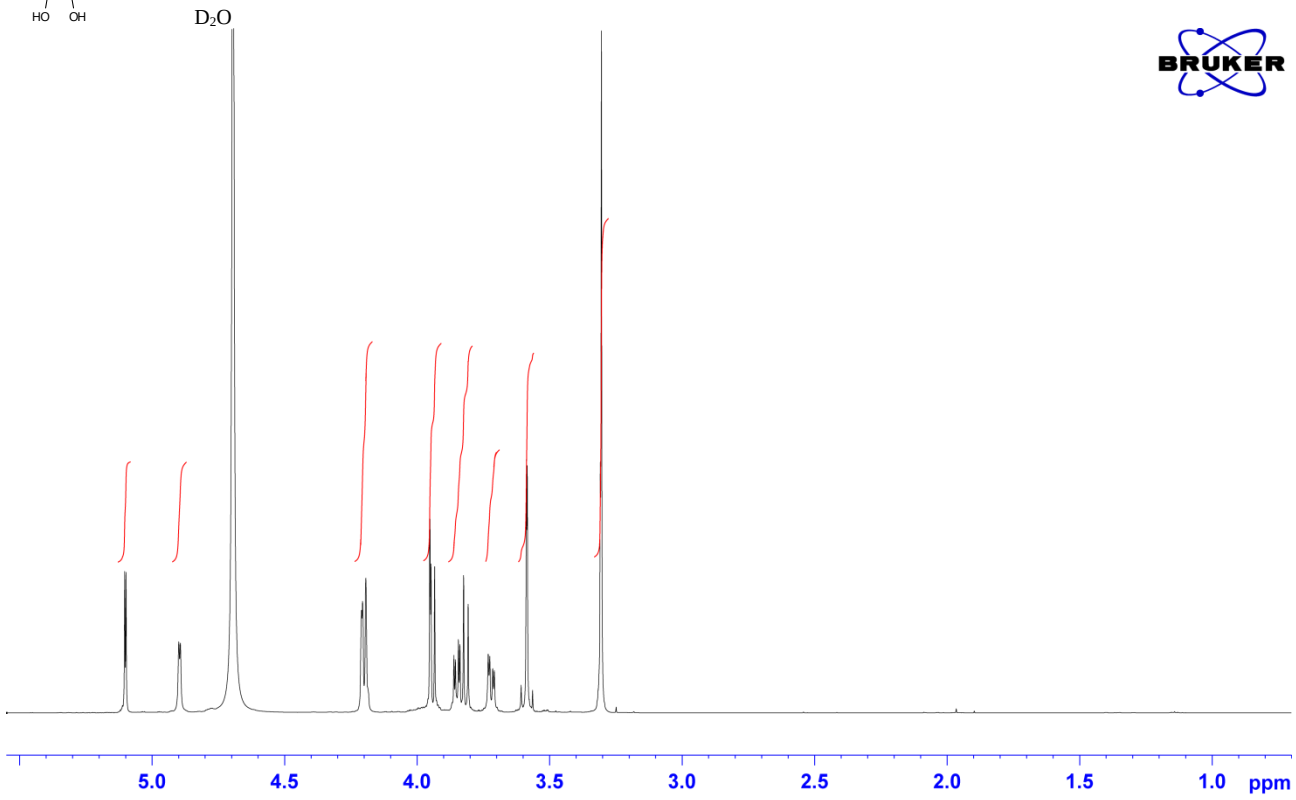
D_2O (1D NOESY presaturation)

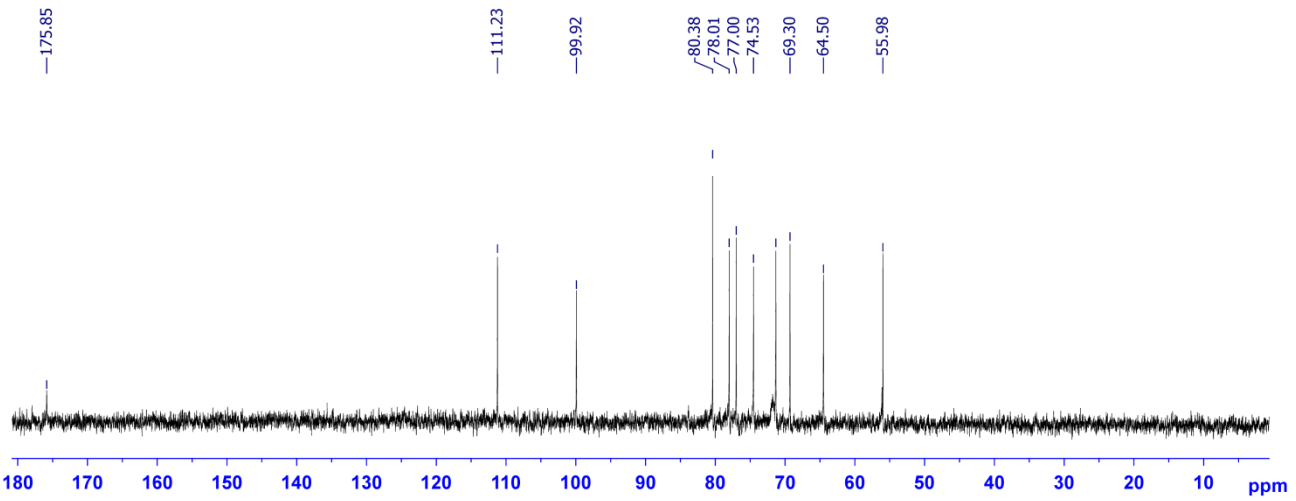




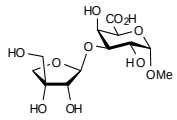
Compound **2**



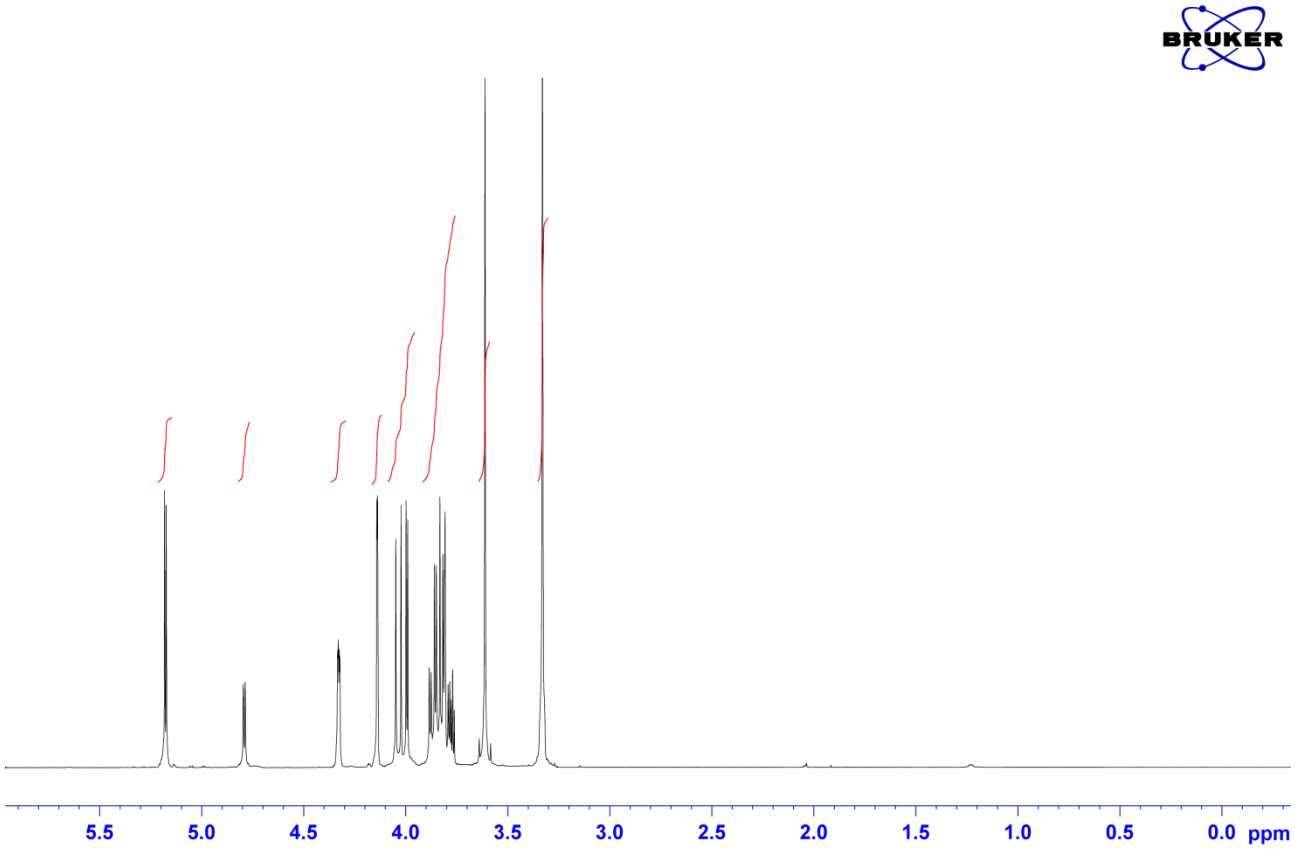


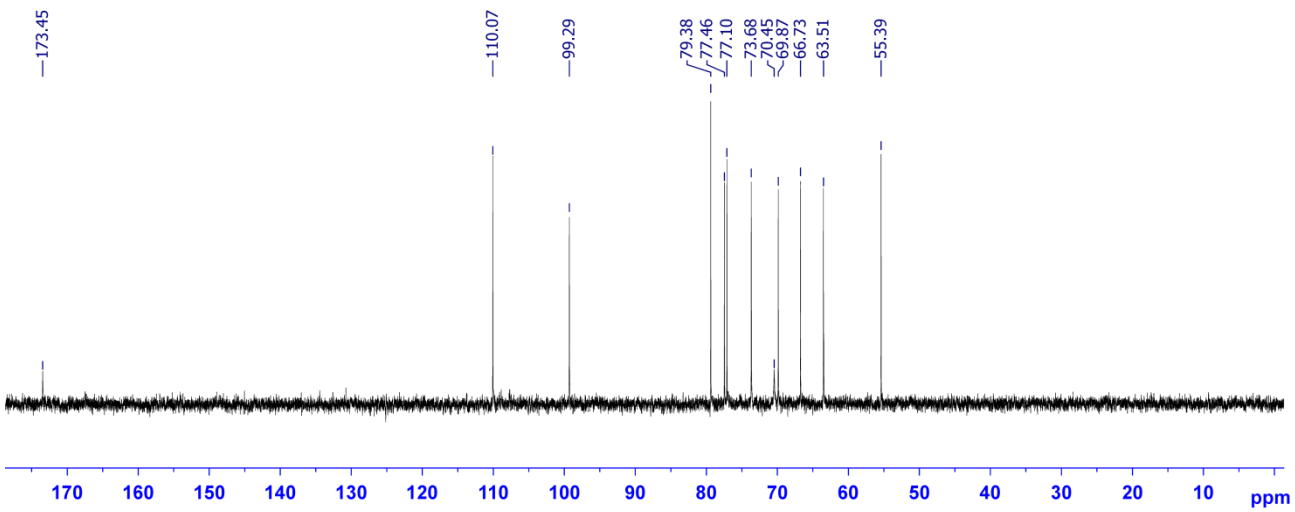


Compound **3**

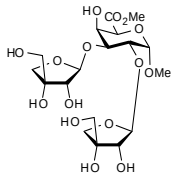


D_2O (1D NOESY presaturation)





Compound **4**



D_2O (1D NOESY presaturation)