

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,*}

^aDepartment of Biological Chemistry, John Innes Centre, Norwich Research Park, Norwich NR4 7UH, UK;

^bSchool of Chemistry, University of East Anglia, Norwich Research Park Norwich, NR4 7TJ, UK.

Table of Contents

Crystal structure analysis of methyl C-(4- <i>O</i> -acetyl-2,3- <i>O</i> -carbonyl-β-L-rhamnopyranosyloxymethyl)-(1→3')-(2,3- <i>O</i> -(<i>R</i>)-benzylidene-β-D-erythrofuranosyl)-(1→2)-(methyl (2- <i>O</i> -acetyl-3,4- <i>O</i> -isopropylidene-α-D-galactopyranosid)uronate) (41).....	S3
¹ H NMR (400 MHz) and ¹³ C NMR (100 MHz) data for protected saccharide derivatives and oligosaccharides 1–4 (in D ₂ O)	
1- <i>O</i> -Acetyl-3- <i>C</i> -acetoxymethyl-2,3- <i>O</i> -isopropylidene-β-D-erythrofurano- (8)	S5
p-Tolyl 3- <i>C</i> -acetoxymethyl-2,3- <i>O</i> -isopropylidene-1-thio-α-D-erythrofurano- (9a)	S6
p-Tolyl 3- <i>C</i> -acetoxymethyl-2,3- <i>O</i> -isopropylidene-1-thio-β-D-erythrofurano- (9b)	S7
Methyl (methyl 3,4- <i>O</i> -isopropylidene-α-D-galactopyranosid)uronate (12) .	S8
Methyl (3- <i>C</i> -acetoxymethyl-2,3- <i>O</i> -isopropylidene-β-D-erythrofuranosyl)-(1→2)-(methyl 3,4- <i>O</i> -isopropylidene-α-D-galactopyranosid)uronate (13)	S9
Methyl (2,3- <i>O</i> -isopropylidene-β-D-erythrofuranosyl)-(1→2)-(methyl 3,4- <i>O</i> -isopropylidene-α-D-galactopyranosid)uronate (14)	S10
Methyl (4- <i>O</i> -acetyl-2,3- <i>O</i> -carbonyl-β-L-rhamnopyranosyloxymethyl)-(1→3)- <i>C</i> -(2,3- <i>O</i> -isopropylidene-β-D-erythrofuranosyl)-(1→2)-(methyl 3,4- <i>O</i> -isopropylidene-α-D-galactopyranosid)uronate (16)	S11
Methyl (β-L-rhamnopyranosyloxymethyl)-(1→3)- <i>C</i> -(2,3- <i>O</i> -isopropylidene-β-D-erythrofuranosyl)-(1→2)-(methyl 3,4- <i>O</i> -isopropylidene-α-D-galactopyranosid)uronate (17)	S12
p-Tolyl 3- <i>C</i> -acetoxymethyl-2,3-di- <i>O</i> -acetyl-1-thio-α,β-D-erythrofurano- (22a and 22b)	S13
Methyl (3- <i>C</i> -acetoxymethyl-2,3-di- <i>O</i> -acetyl-β-D-erythrofuranosyl)-(1→2)-(methyl 3,4- <i>O</i> -isopropylidene-α-D-galactopyranosid)uronate (23)	S14
Methyl (methyl 3,4- <i>O</i> -(1-ethoxyethylidene)-α-D-galactopyranosid)uronate (24)	S15
Methyl (methyl 2- <i>O</i> -benzoyl-3,4- <i>O</i> -(1-ethoxyethylidene)-α-D-galactopyranosid)uronate (25)	S16
Methyl (methyl 4- <i>O</i> -acetyl-2- <i>O</i> -benzoyl-α-D-galactopyranosid)uronate (26)	S17
Methyl (methyl 4- <i>O</i> -acetyl-α-D-galactopyranosid)uronate (27)	S18
Methyl (3- <i>C</i> -acetoxymethyl-2,3,di- <i>O</i> -acetyl-β-D-erythrofuranosyl)-(1→3)-(methyl 4- <i>O</i> -acetyl-2-	S19

<i>O</i> -benzoyl- α -D-galactopyranosid)uronate (28)	S20
Methyl (3- <i>C</i> -acetoxymethyl-2,3-di- <i>O</i> -acetyl- β -D-erythrofuransyl)-(1 \rightarrow 2)-[(3- <i>C</i> -acetoxymethyl-2,3-di- <i>O</i> -acetyl- β -D-erythrofuransyl)-(1 \rightarrow 3)]-(methyl 4- <i>O</i> -acetyl- α -D-galactopyranosid)uronate (29)	S20
L-Arabinose di(<i>p</i> -tolyl)dithioacetal (30)	S21
2,3:4,5-Di- <i>O</i> -isopropylidene-L-arabinose di(<i>p</i> -tolyl)dithioacetal (31)	S22
2,3- <i>O</i> -Isopropylidene-L-arabinose di(<i>p</i> -tolyl)dithioacetal (32)	S23
2,3- <i>O</i> -Isopropylidene-L- <i>erythro</i> -tetrodialdose di(<i>p</i> -tolyl)dithioacetal (33)	S24
3- <i>C</i> -Hydroxymethyl-2,3- <i>O</i> -isopropylidene- <i>D-glycero</i> -tetrose di(<i>p</i> -tolyl)dithioacetal (34)	S25
<i>p</i> -Tolyl 3- <i>C</i> -hydroxymethyl-2,3- <i>O</i> -isopropylidene-1-thio- α,β -D-erythrofuranside (35a,b)	S26
<i>p</i> -Tolyl 3- <i>C</i> -chloroacetoxymethyl-2,3- <i>O</i> -isopropylidene-1-thio- α -D-erythrofuranside (36a)	S27
<i>p</i> -Tolyl 3- <i>C</i> -chloroacetoxymethyl-2,3- <i>O</i> -isopropylidene-1-thio- α -D-erythrofuranside (36b)	S28
<i>p</i> -Tolyl 3- <i>C</i> -chloroacetoxymethyl-1-thio- α,β -D-erythrofuranside (37)	S29
<i>p</i> -Tolyl 3- <i>C</i> -chloroacetoxymethyl-2,3- <i>O</i> -(<i>S</i>)-benzylidene-1-thio- α -D-erythrofuranside (38a) ...	S30
<i>p</i> -Tolyl 3- <i>C</i> -chloroacetoxymethyl-2,3- <i>O</i> -(<i>S</i>)-benzylidene-1-thio- β -D-erythrofuranside (38b)	S31
Methyl (2,3- <i>O</i> -(<i>S</i>)-benzylidene-3- <i>C</i> -chloroacetoxymethyl- β -D-erythrofuransyl)-(1 \rightarrow 2)-(methyl 2- <i>O</i> -acetyl-3,4- <i>O</i> -isopropylidene- β -D-galactopyranosid)uronate (39)	S32
Methyl (2,3- <i>O</i> -(<i>S</i> -benzylidene-3- <i>C</i> -hydroxymethyl- β -D-erythrofuransyl)-(1 \rightarrow 2)-(methyl 2- <i>O</i> -acetyl-3,4- <i>O</i> -isopropylidene- α -D-galactopyranosid)uronate) (40)	S33
Methyl <i>C</i> -(4- <i>O</i> -acetyl-2,3- <i>O</i> -carbonyl- β -L-rhamnopyranosyloxymethyl)-(1 \rightarrow 3')-(2,3- <i>O</i> -(<i>S</i>)-benzylidene- β -D-erythrofuransyl)-(1 \rightarrow 2)-(methyl 2- <i>O</i> -acetyl-3,4- <i>O</i> -isopropylidene- β -D-galactopyranosid)uronate (41)	S34
Methyl <i>C</i> -(4- <i>O</i> -acetyl-2,3- <i>O</i> -carbonyl- β -L-rhamnopyranosyloxymethyl)-(1 \rightarrow 3')-(β -D-erythrofuransyl)-(1 \rightarrow 2)-(methyl (2- <i>O</i> -acetyl-3,4- <i>O</i> -isopropylidene- β -D-galactopyranosid)uronate)	S35
Methyl <i>C</i> -(β -L-rhamnopyranosyloxymethyl)-(1 \rightarrow 3)- β -D-erythrofuransyl-(1 \rightarrow 2)-(methyl α -D-galactopyranosid)uronate (42)	S36
Methyl <i>C</i> -(β -L-rhamnopyranosyloxymethyl)-(1 \rightarrow 3)- β -D-erythrofuransyl-(1 \rightarrow 2)- α -D-galactopyranosiduronic acid (1)	S37
Methyl (3- <i>C</i> -hydroxymethyl- β -D-erythrofuransyl)-(1 \rightarrow 2)- α -D-galactopyranosiduronic acid (2)	S38
Methyl (3- <i>C</i> -hydroxymethyl- β -D-erythrofuransyl)-(1 \rightarrow 3)- α -D-galactopyranosiduronic acid (3)	S39
Methyl (3- <i>C</i> -hydroxymethyl- β -D-erythrofuransyl)-(1 \rightarrow 2)-[3- <i>C</i> -hydroxymethyl- β -D-erythrofuransyl-(1 \rightarrow 3)]-(α -D-galactopyranosiduronic acid) (4)	S40

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: C₃₂H₄₀O₁₇, CH₂Cl₂, M = 781.6. Orthorhombic, space group P2₁2₁2₁ (no. 19), a = 11.2799(6), b = 15.1788(9), c = 21.4815(13) Å, V = 3678.0(4) Å³. Z = 4, D_c = 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 (R_{int} = 0.045); 7002 were 'observed' with I > 2σ_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 F²'s, in SHELXL (2B). The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. At the conclusion of the refinement, wR₂ = 0.093 and R₁ = 0.049 (2B) for all 8410 reflections weighted w = [σ²(F_o²) + (0.0556P)²]⁻¹ with P = (F_o² + 2F_c²)/3; for the 'observed' data only, R₁ = 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.

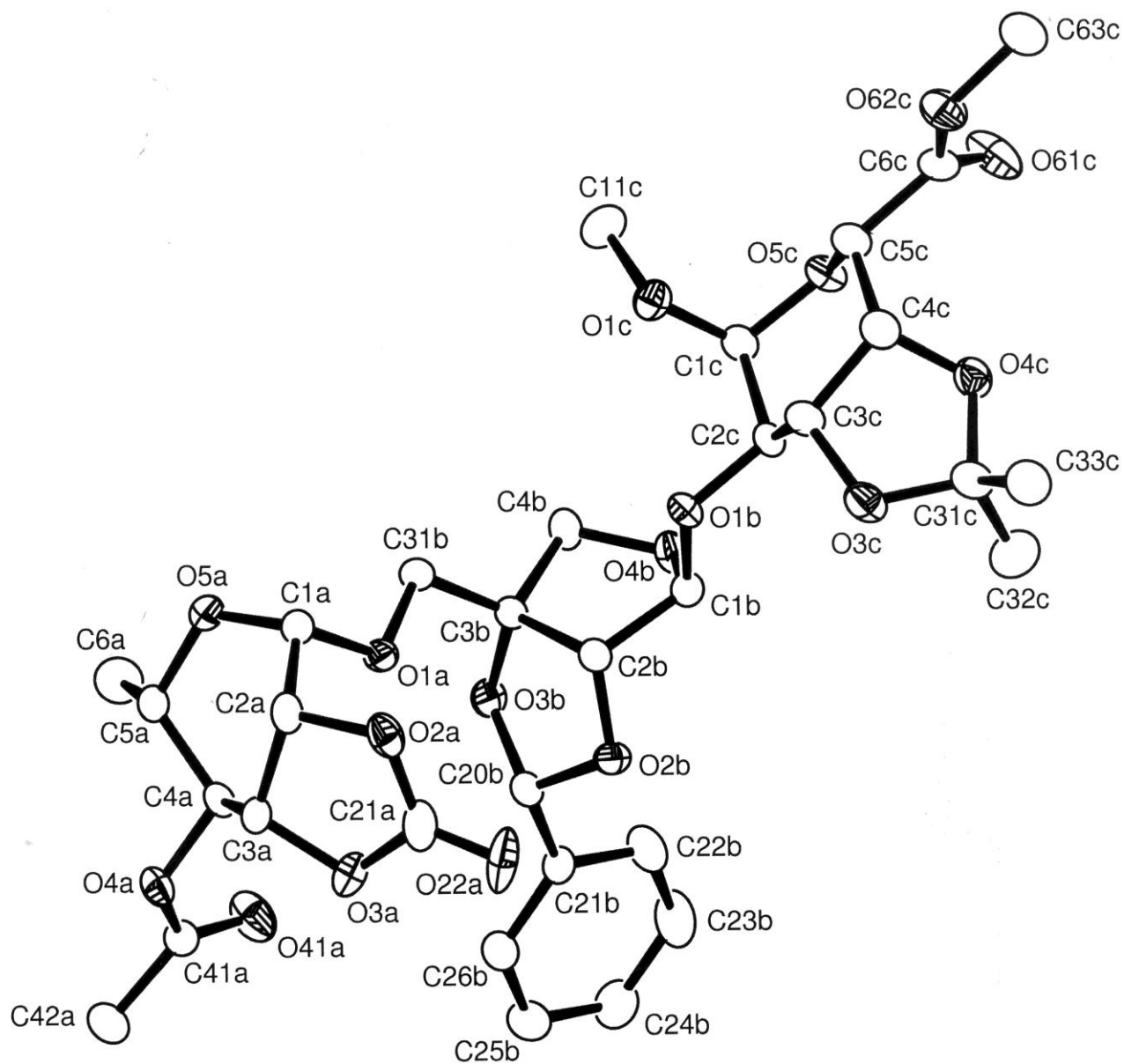
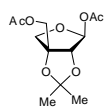


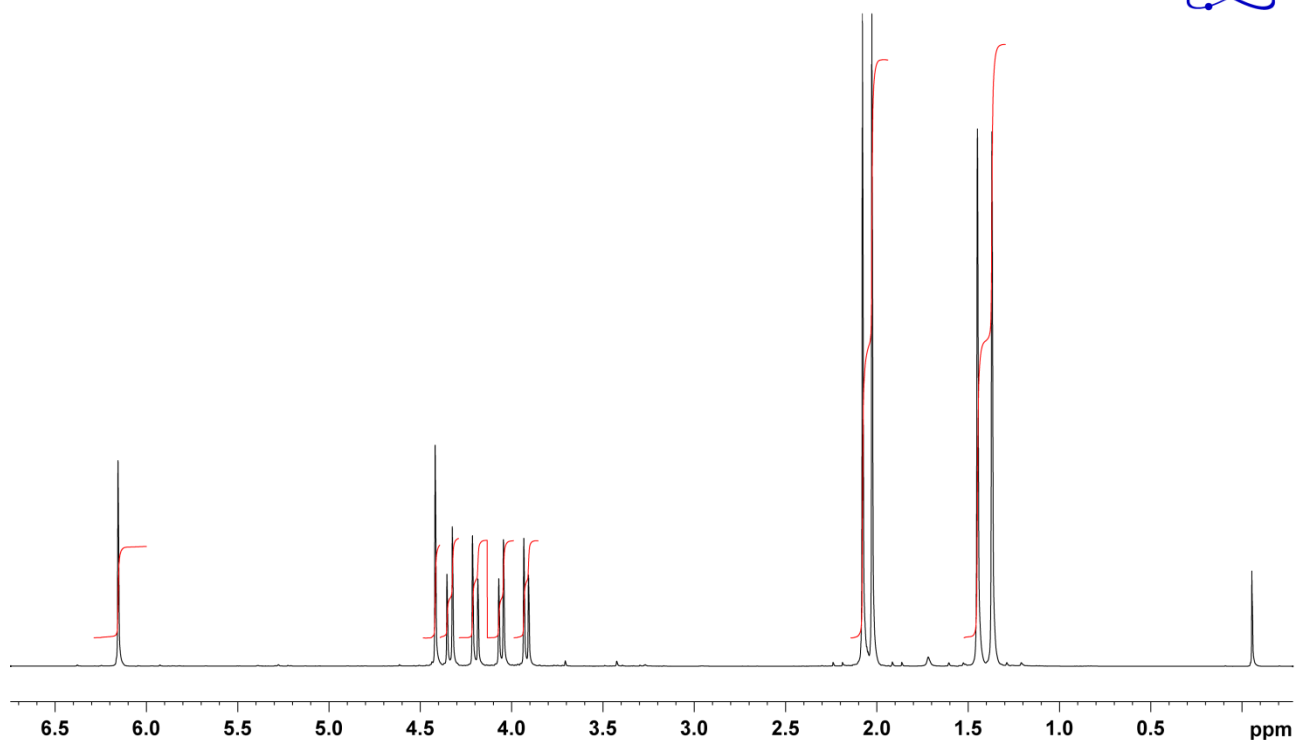
Fig. 1 X-Ray crystal structure of disaccharide derivative **41**.

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

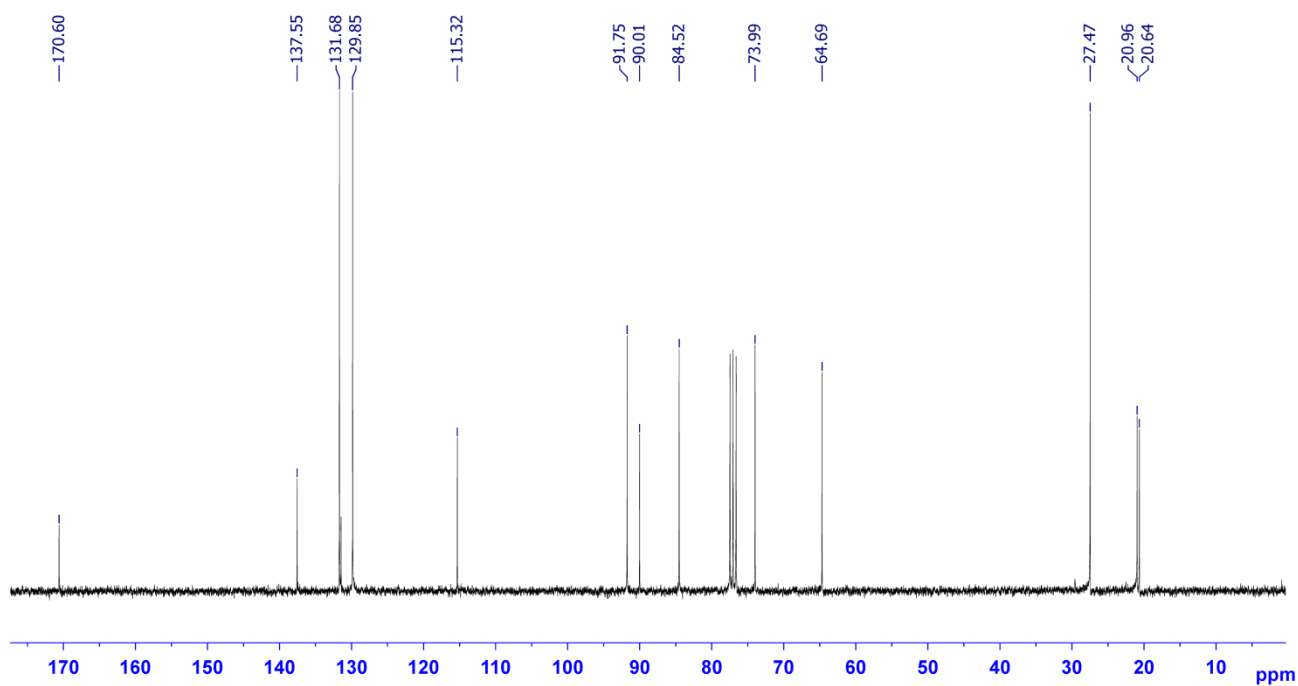
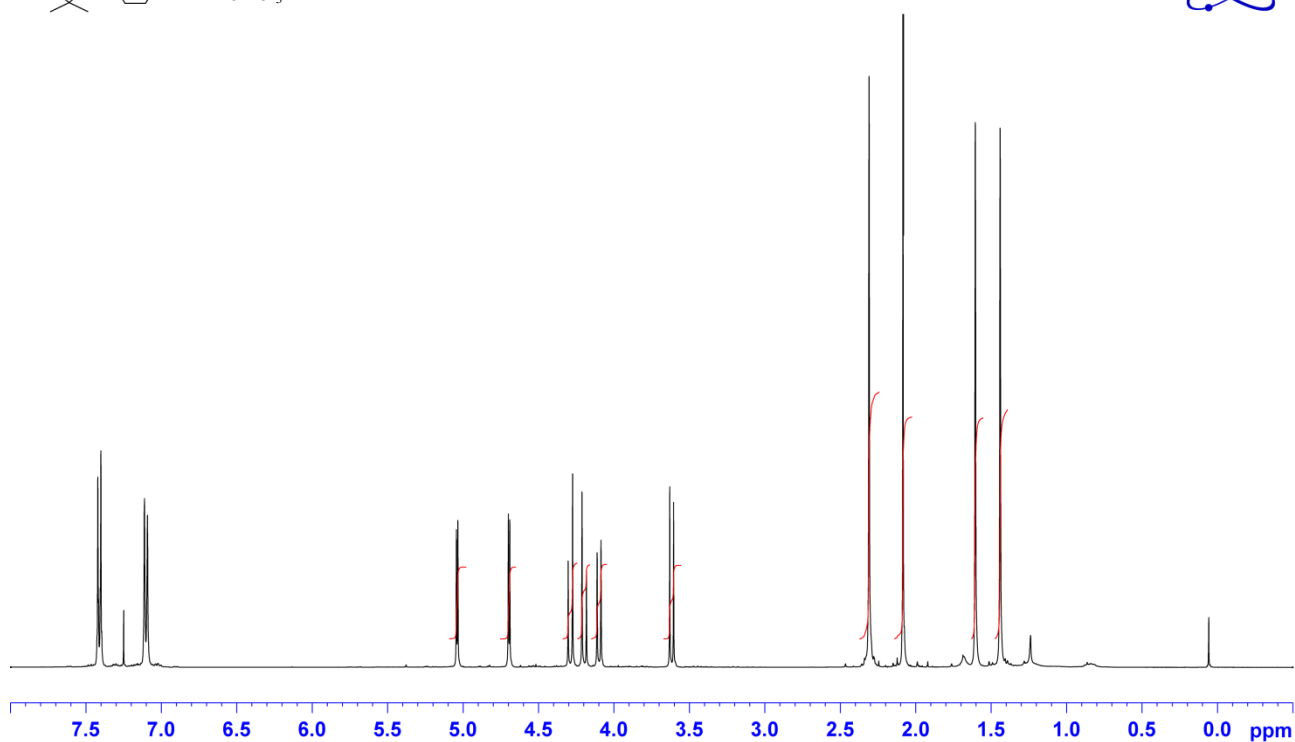
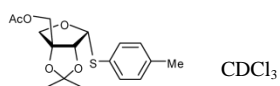
Compound 8



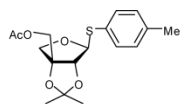
CDCl_3



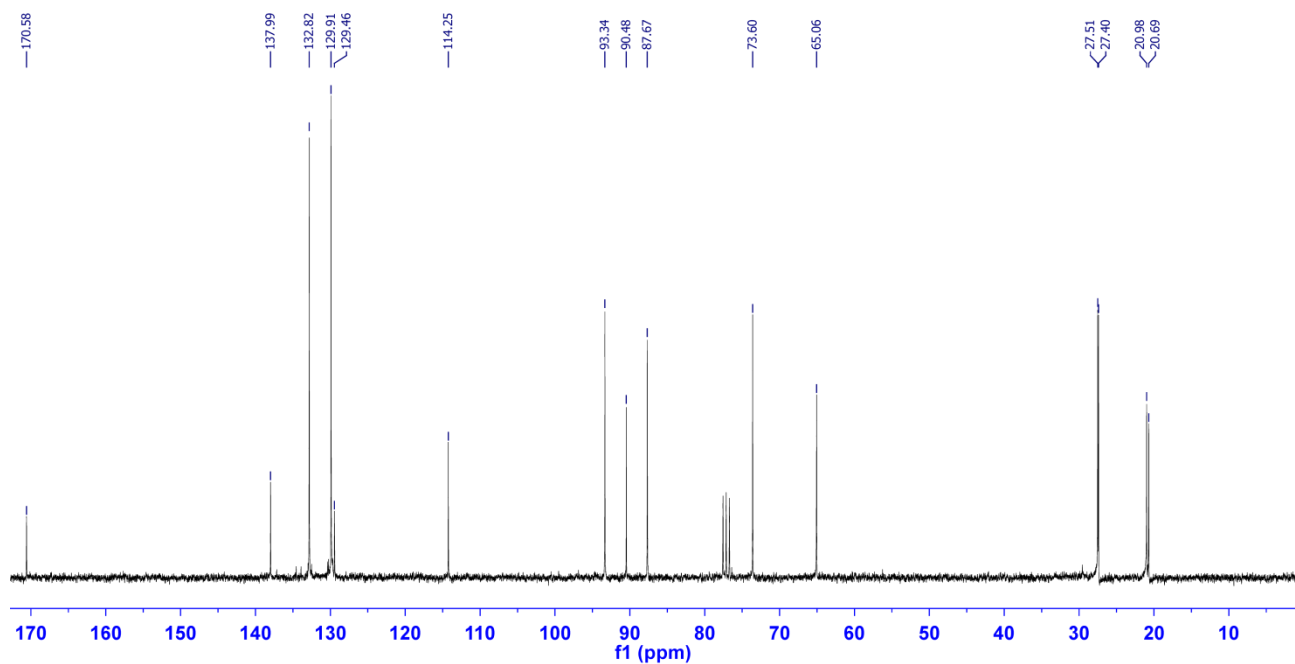
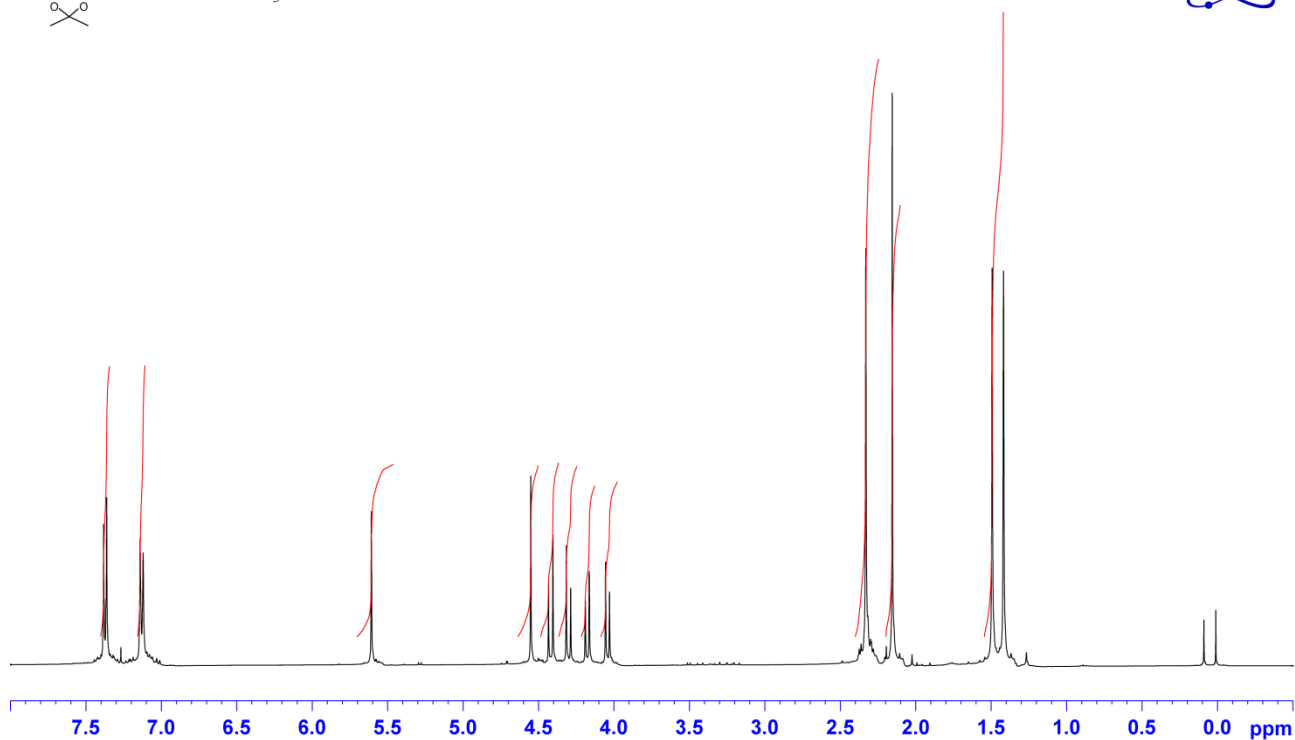
Compound 9a



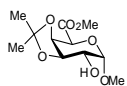
Compound 9b



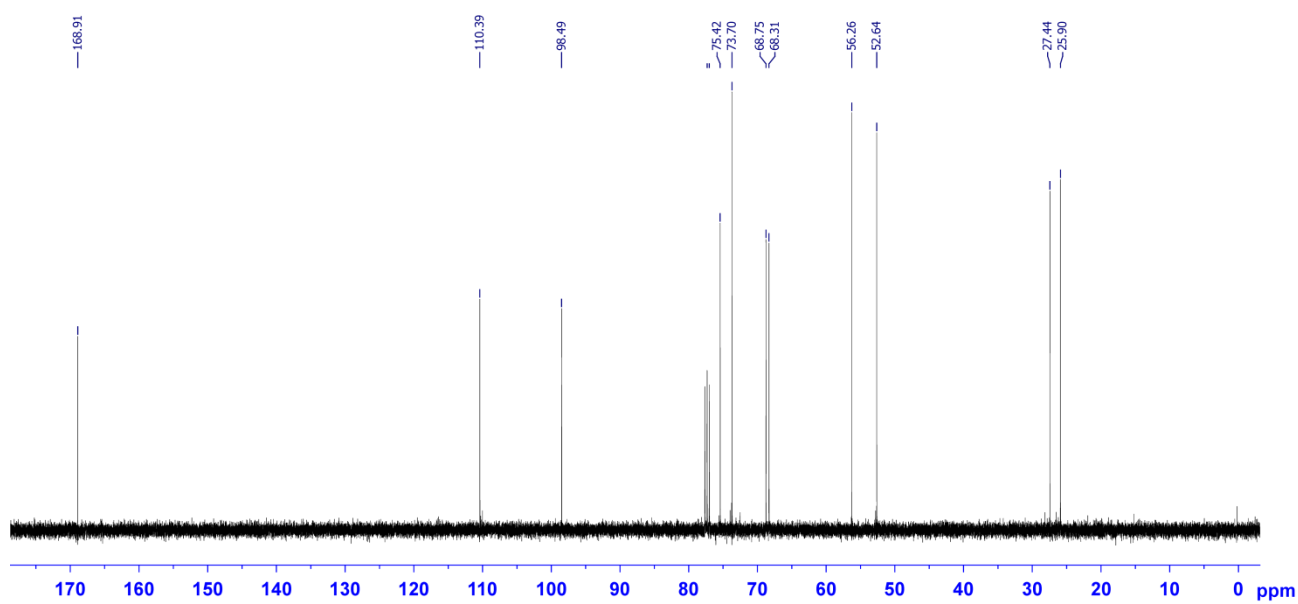
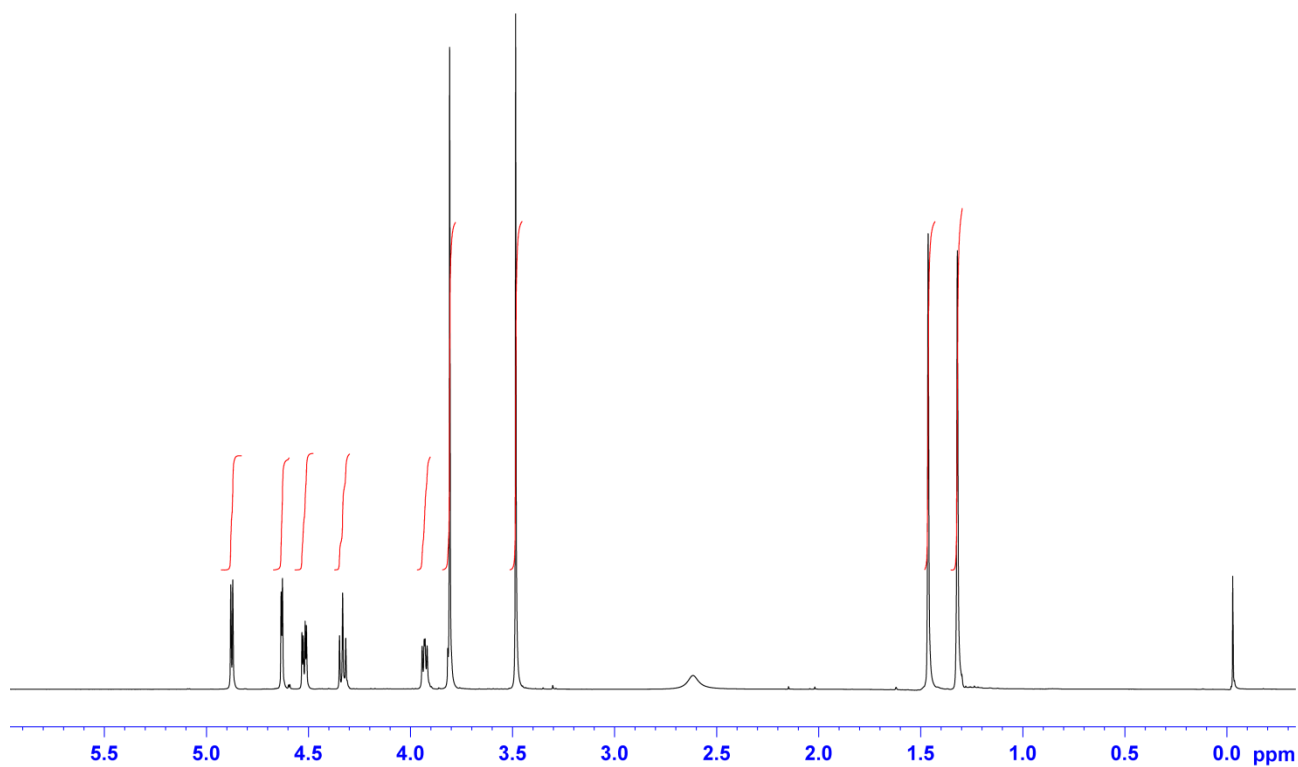
CDCl₃



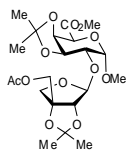
Compound 12



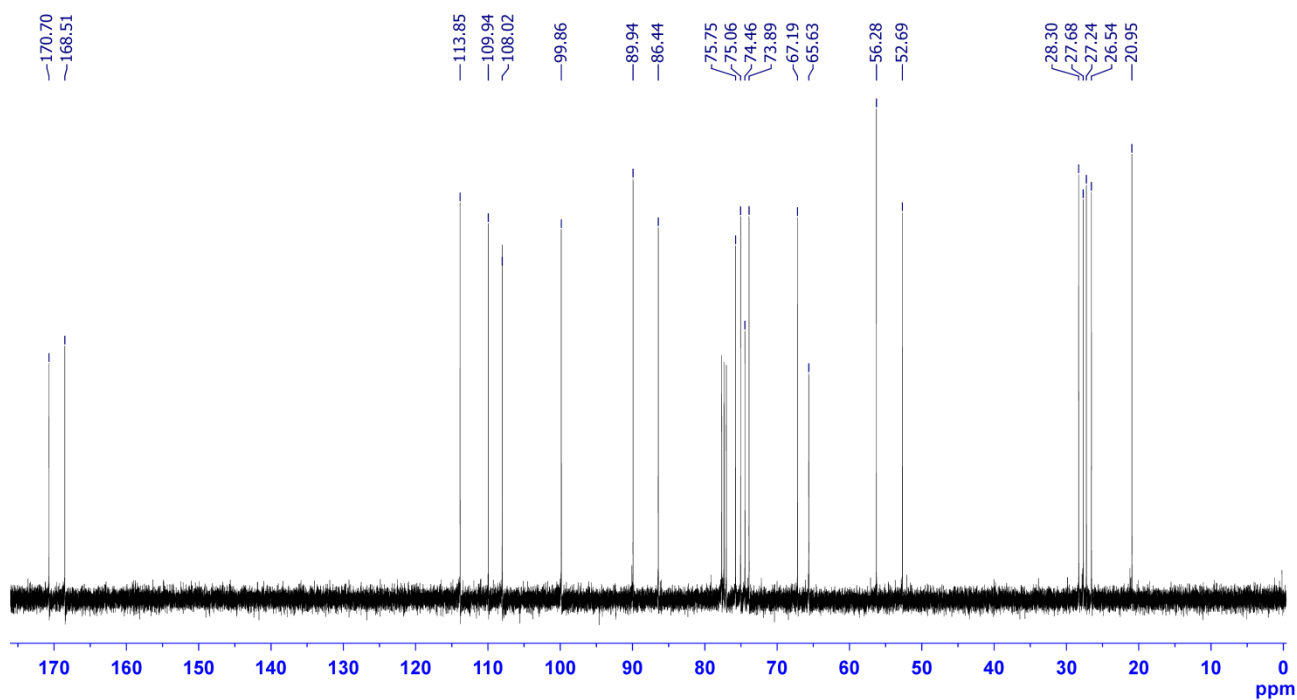
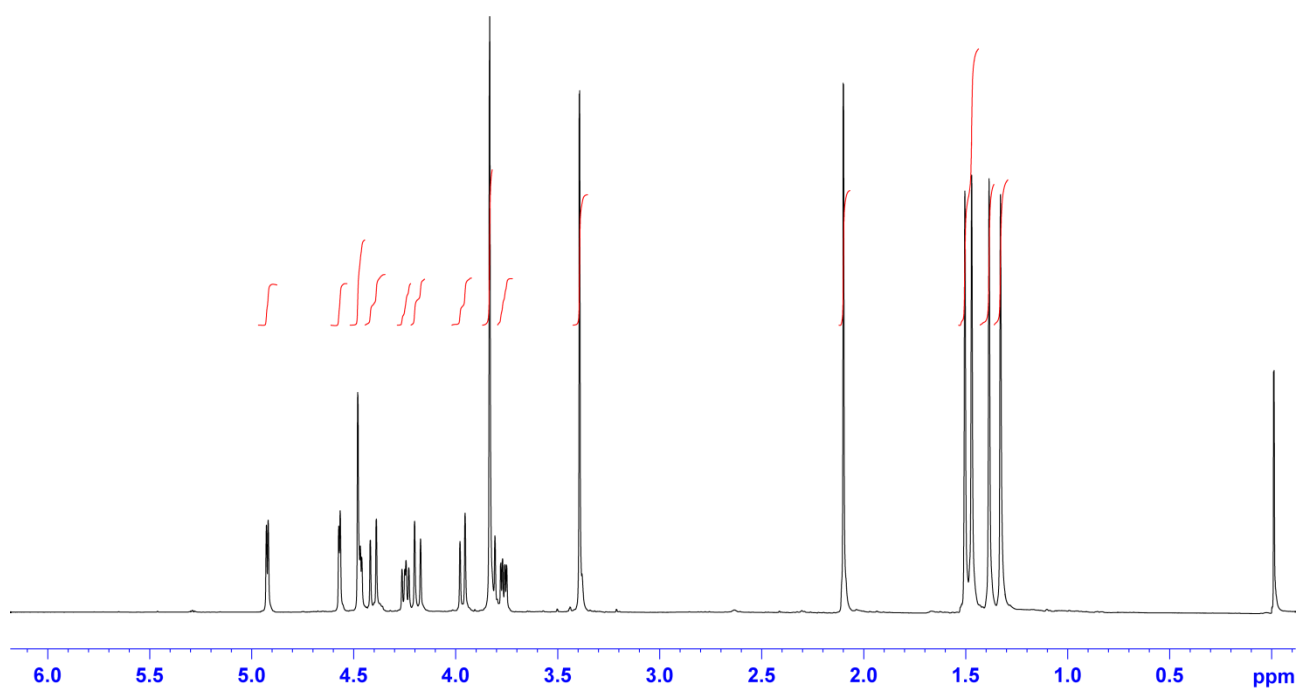
CDCl₃



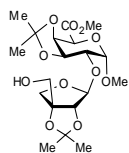
Compound 13



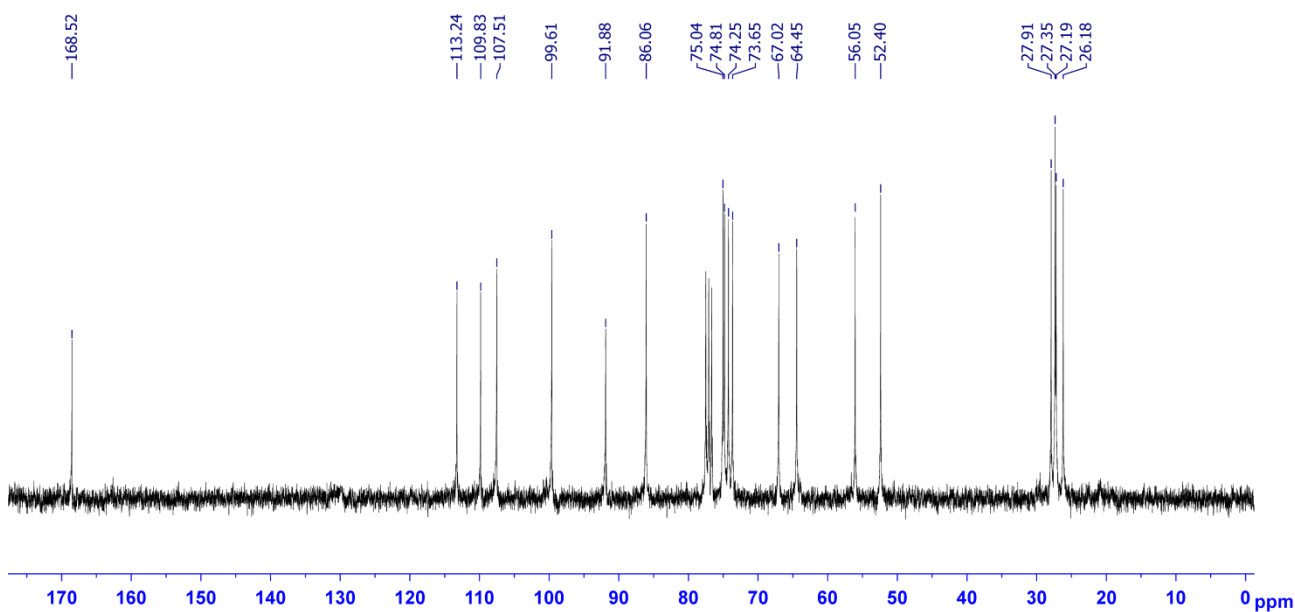
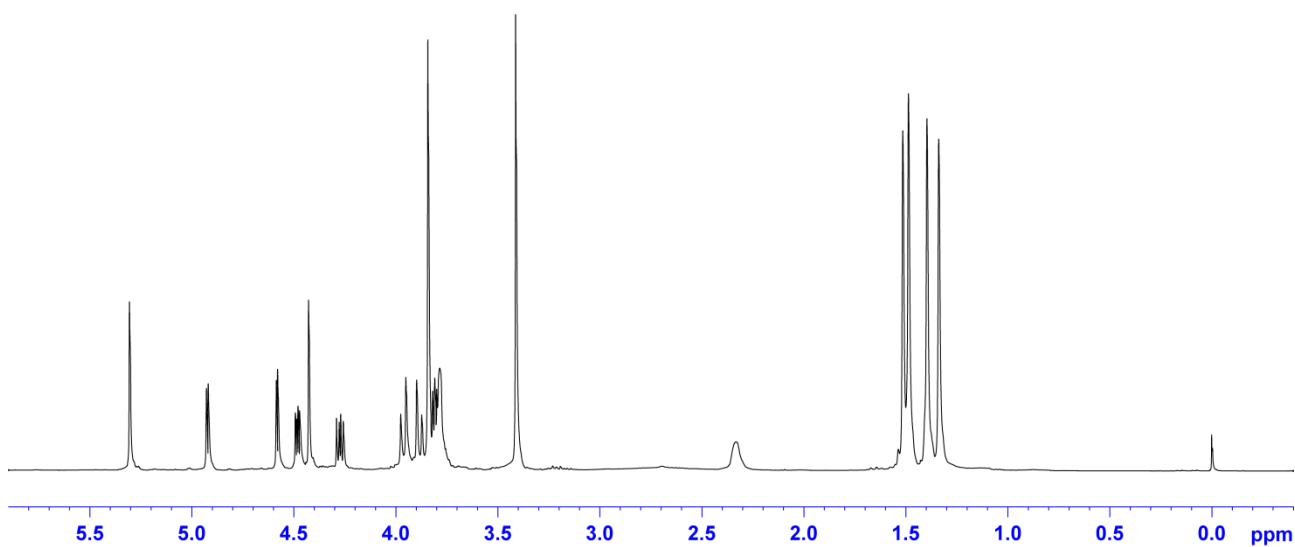
CDCl₃



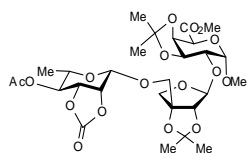
Compound 14



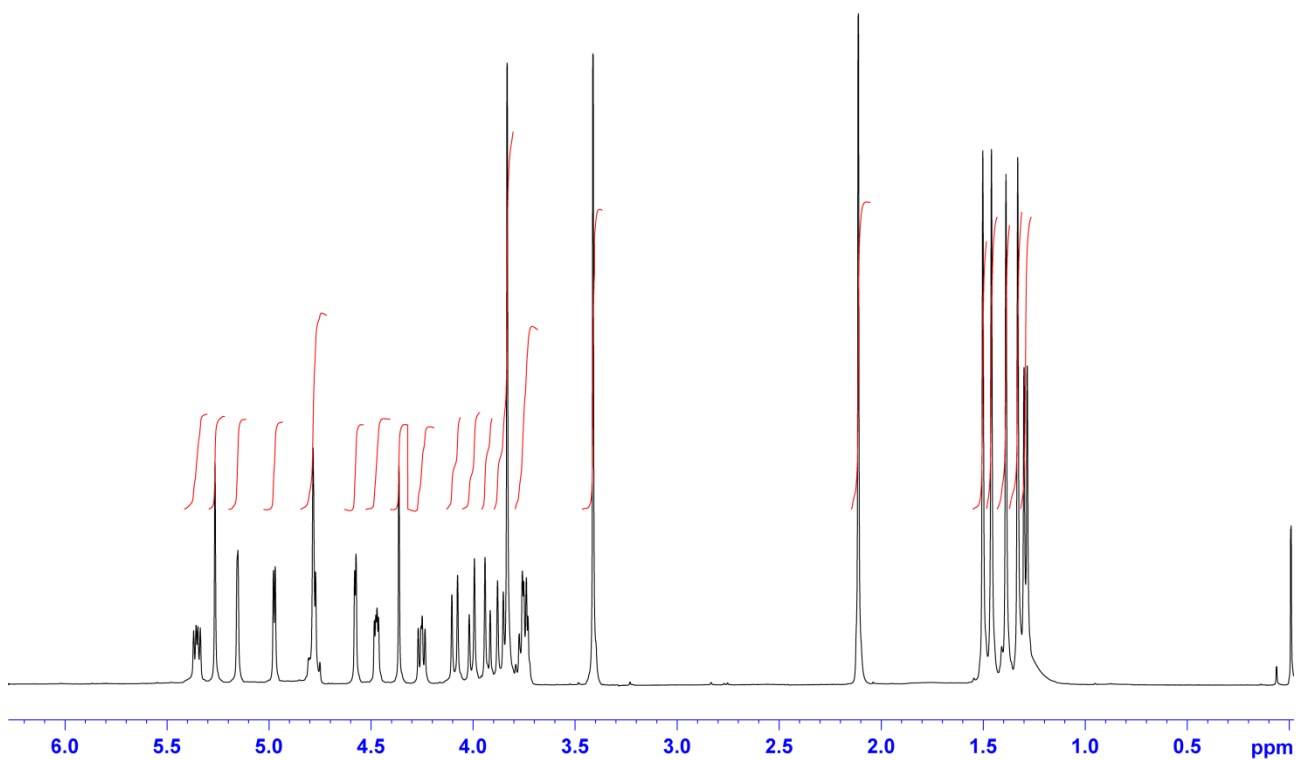
CDCl₃



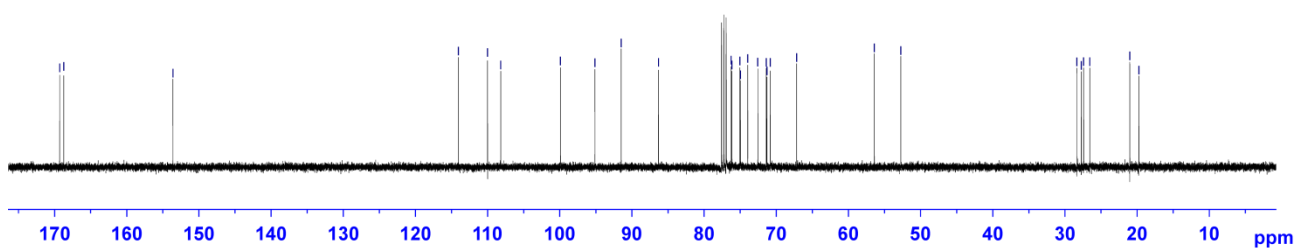
Compound 16



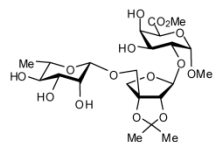
CDCl₃



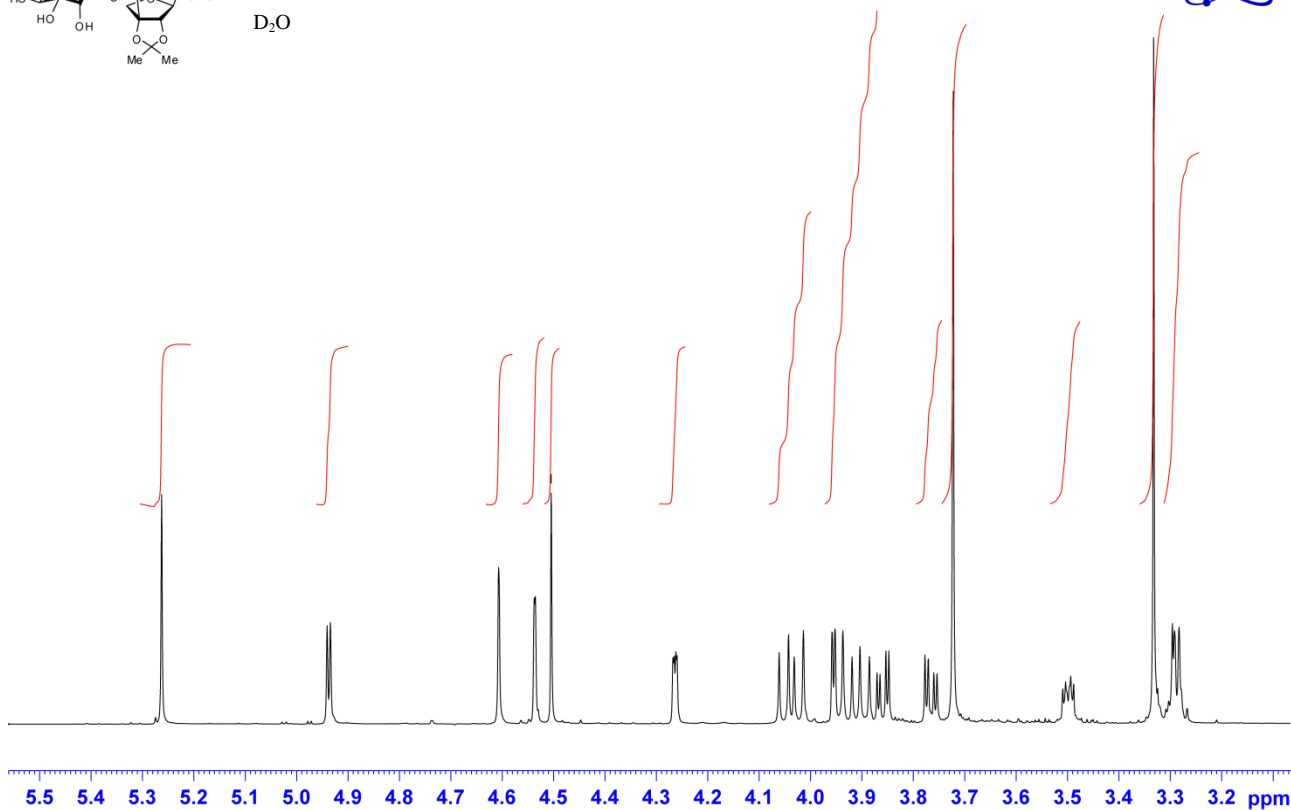
169.29
168.72
153.60
114.05
110.01
108.18
99.91
95.13
91.49
86.33
76.26
73.95
71.38
70.83
67.18
56.42
52.75
28.35
27.74
27.42
26.56
21.02
19.76



Compound 17



D₂O



-171.64

-114.66

-109.13

-100.65

-99.51

-91.53

-86.18

-72.64

-72.48

-71.65

-70.87

-70.75

-70.40

-68.15

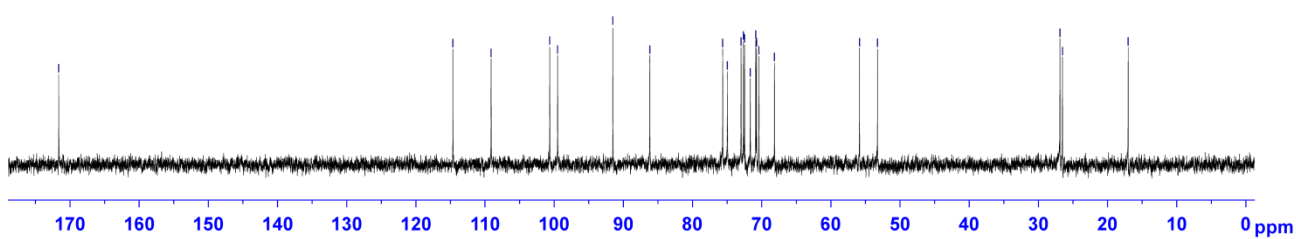
-55.86

-53.27

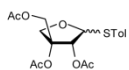
-26.88

-26.52

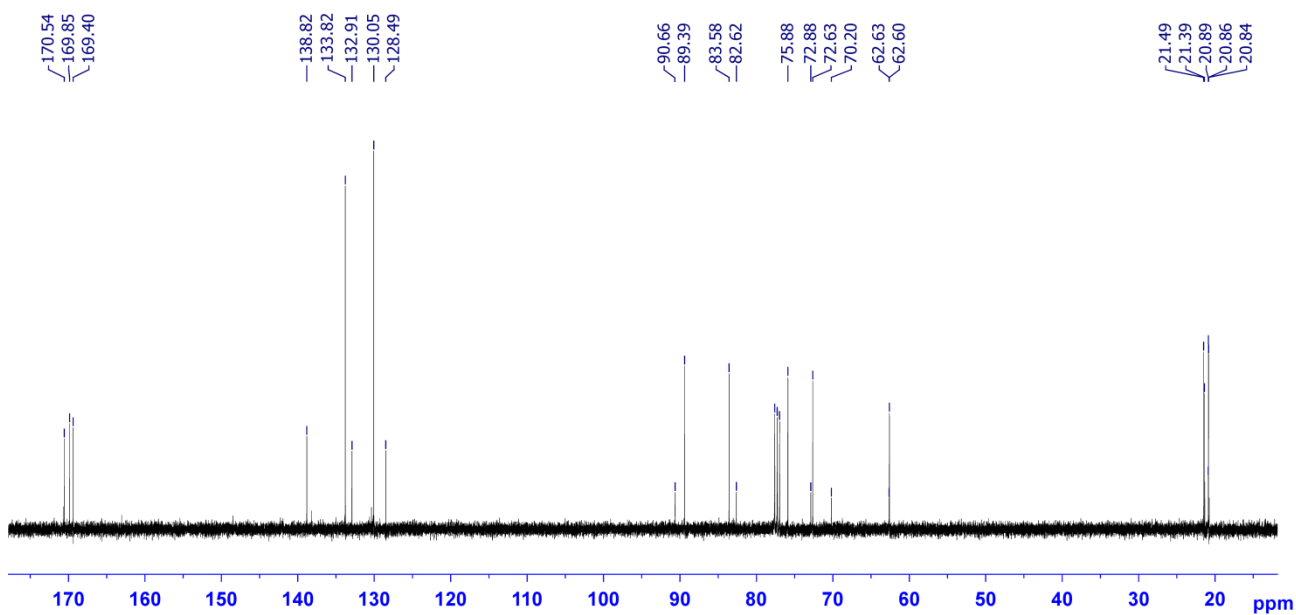
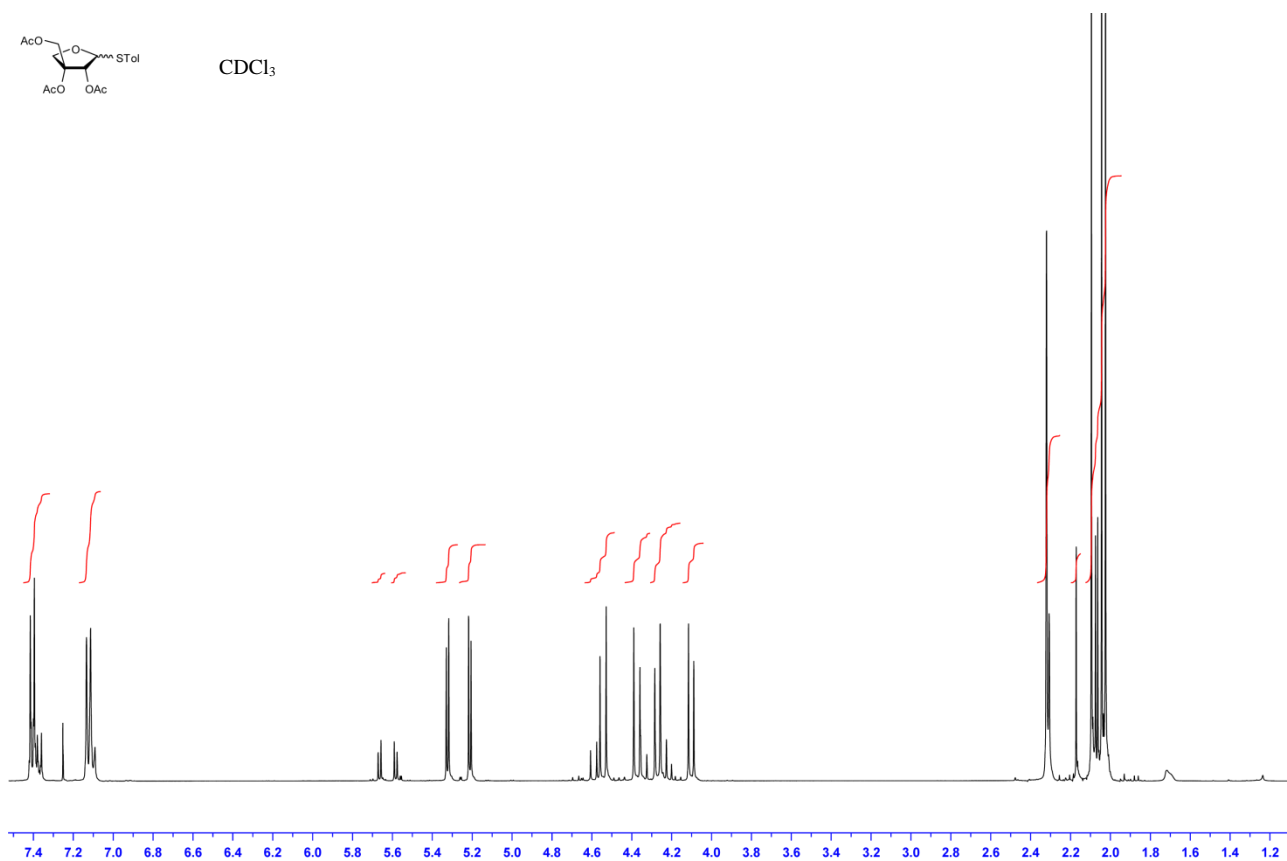
-17.02



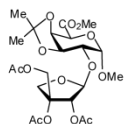
Compound 22a,b



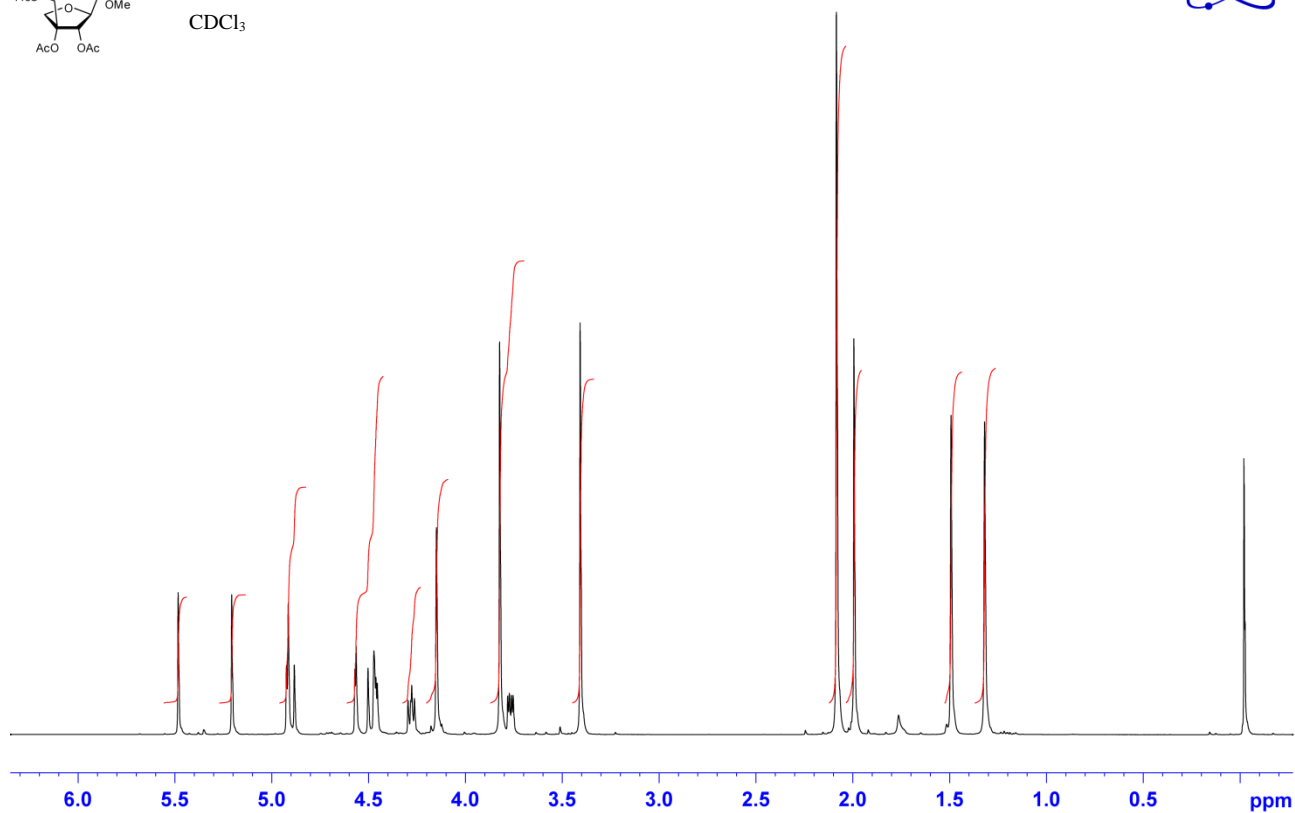
CDCl₃



Compound 23



CDCl₃

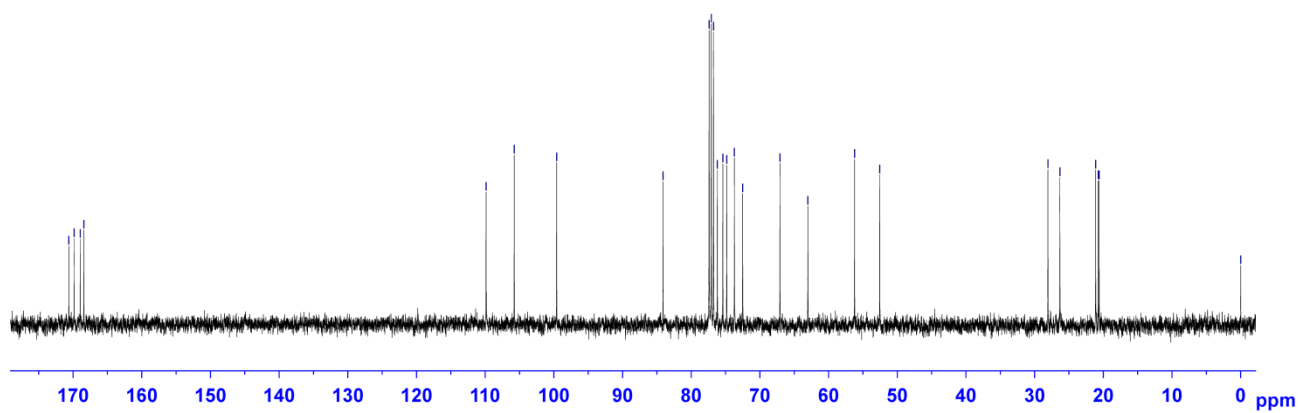


170.61
169.85
168.94
168.42

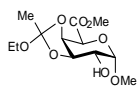
109.86
105.76
99.58

84.10
77.07
74.82
72.50
67.07
63.01
56.21
52.54

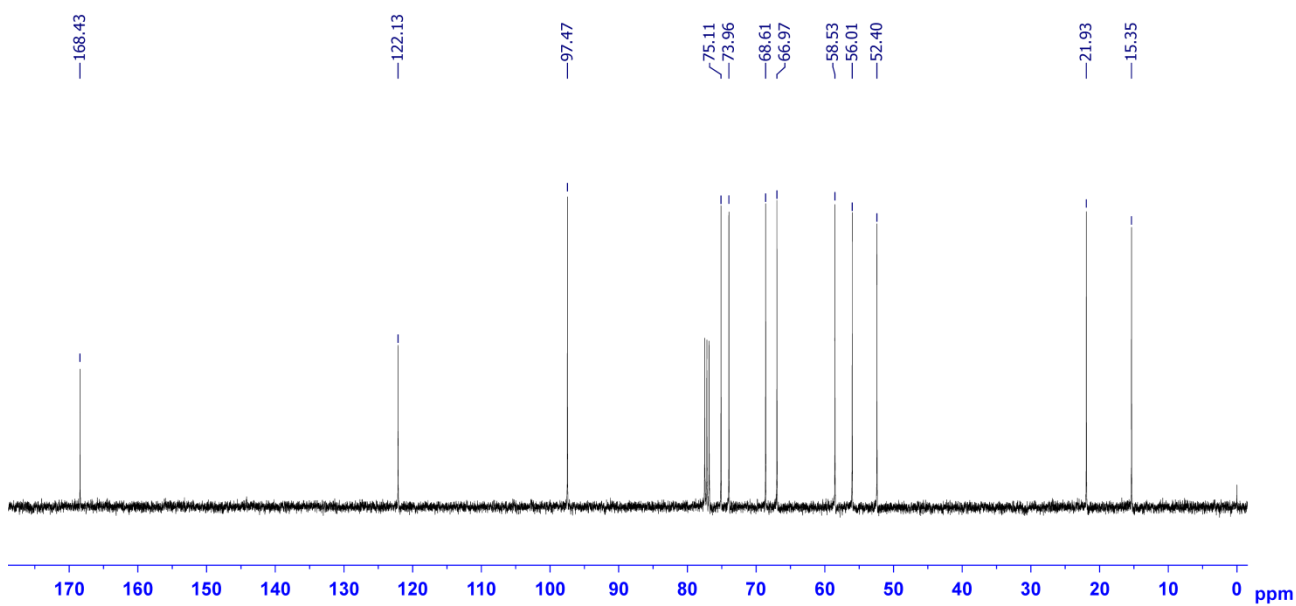
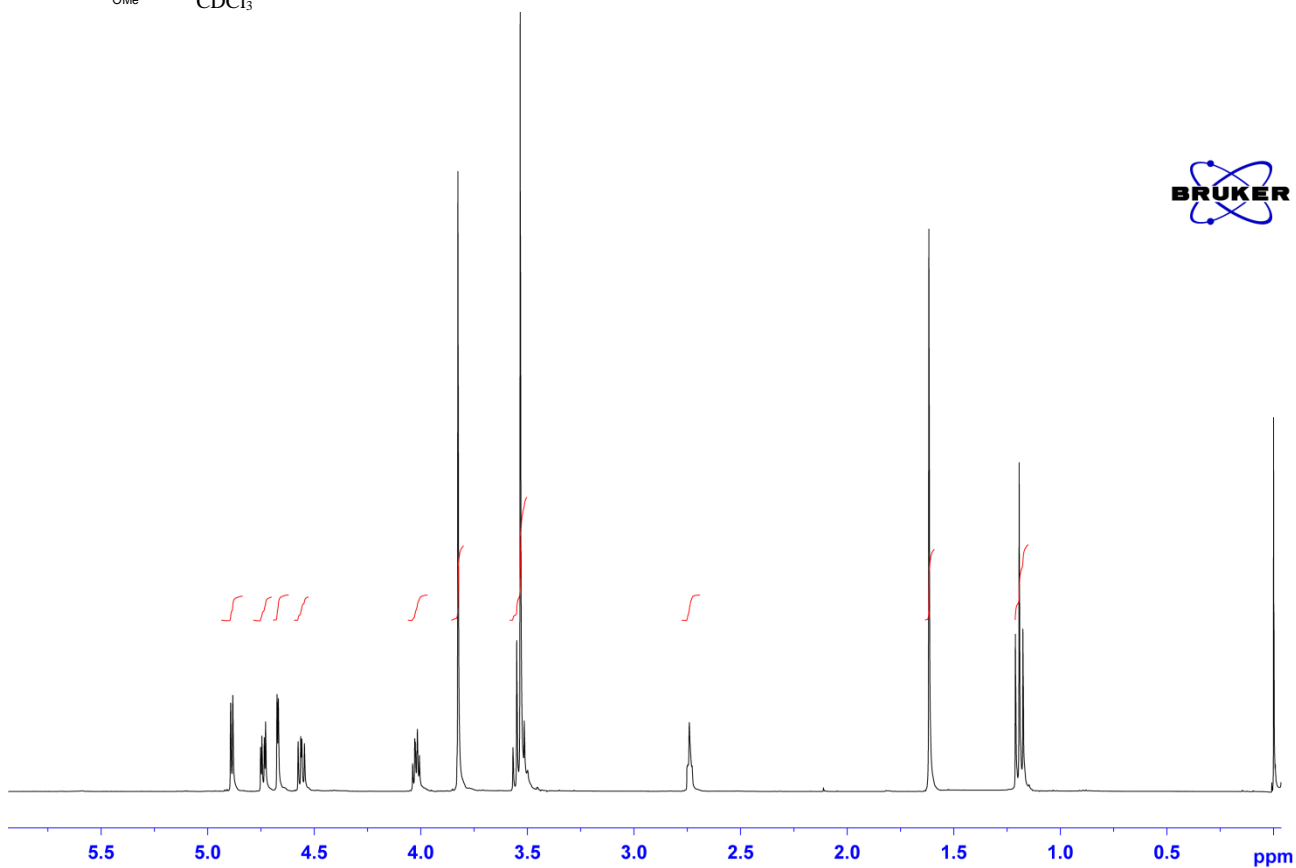
28.06
26.32
21.10
20.73
20.60



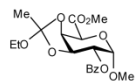
Compound 24



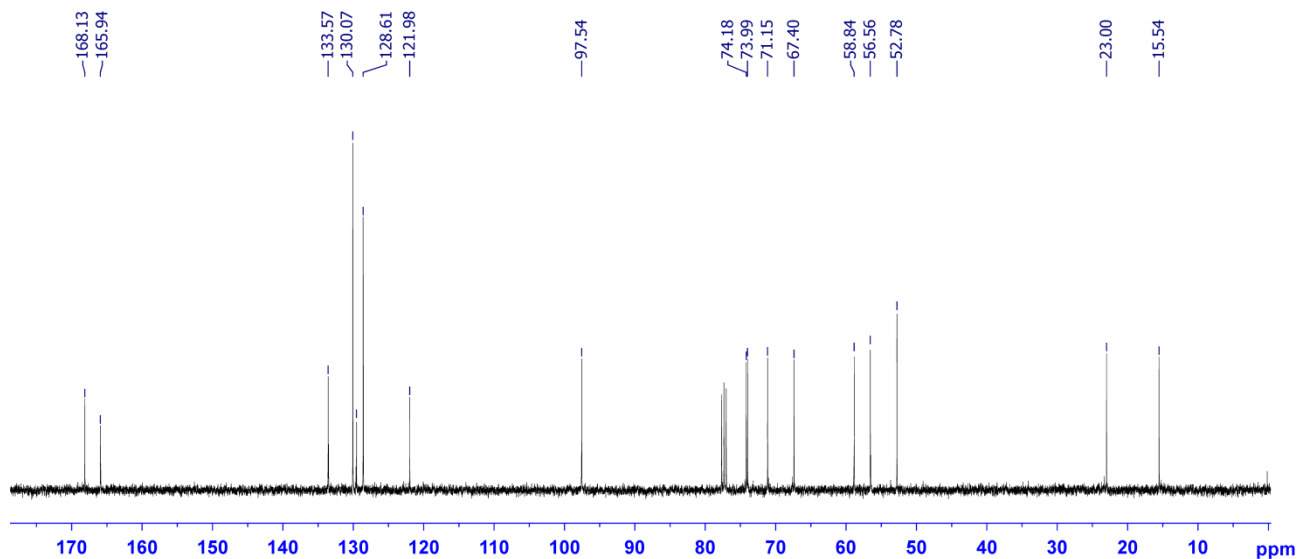
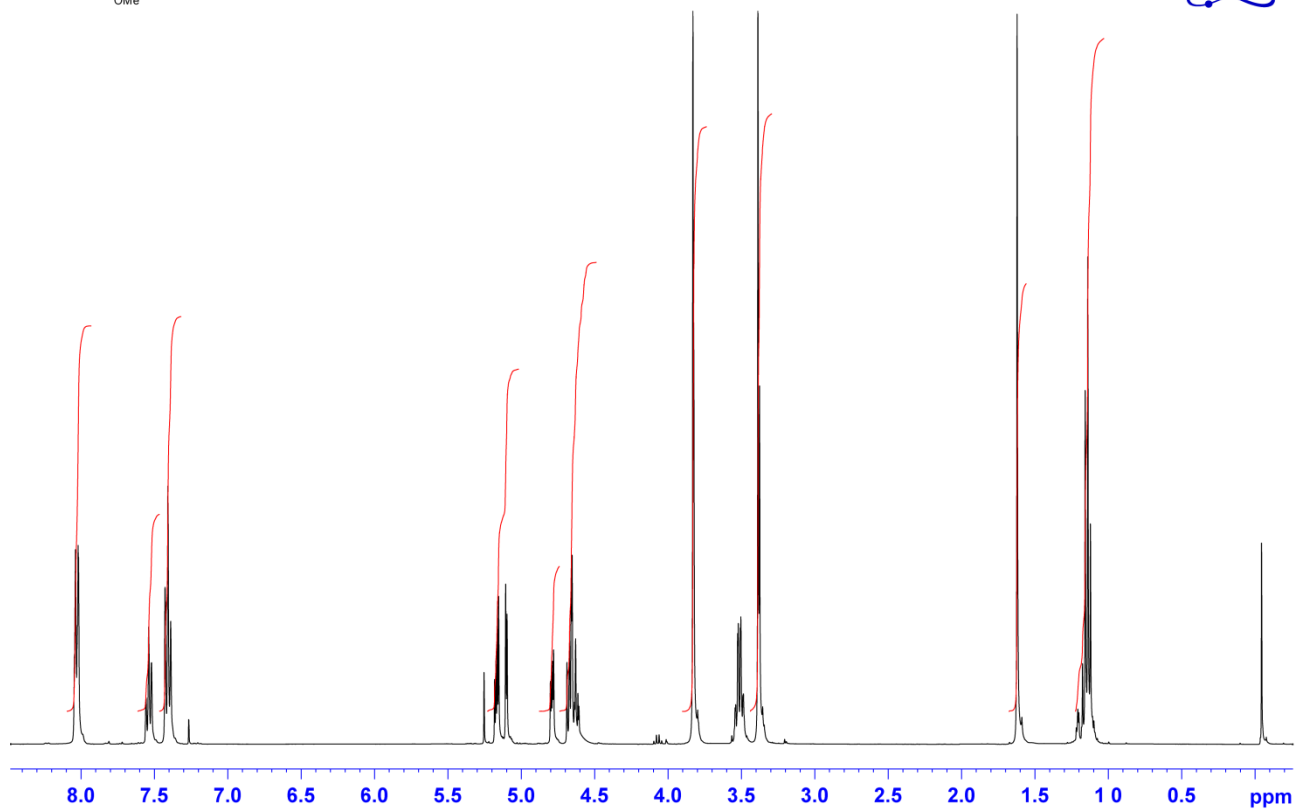
CDCl₃



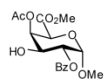
Compound 25



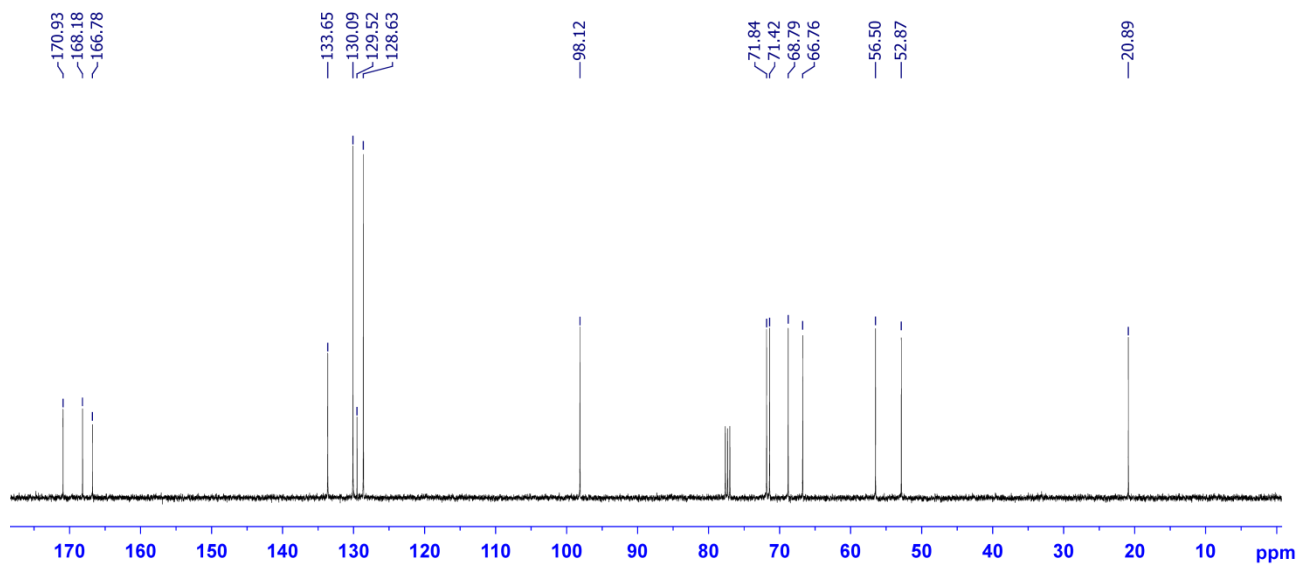
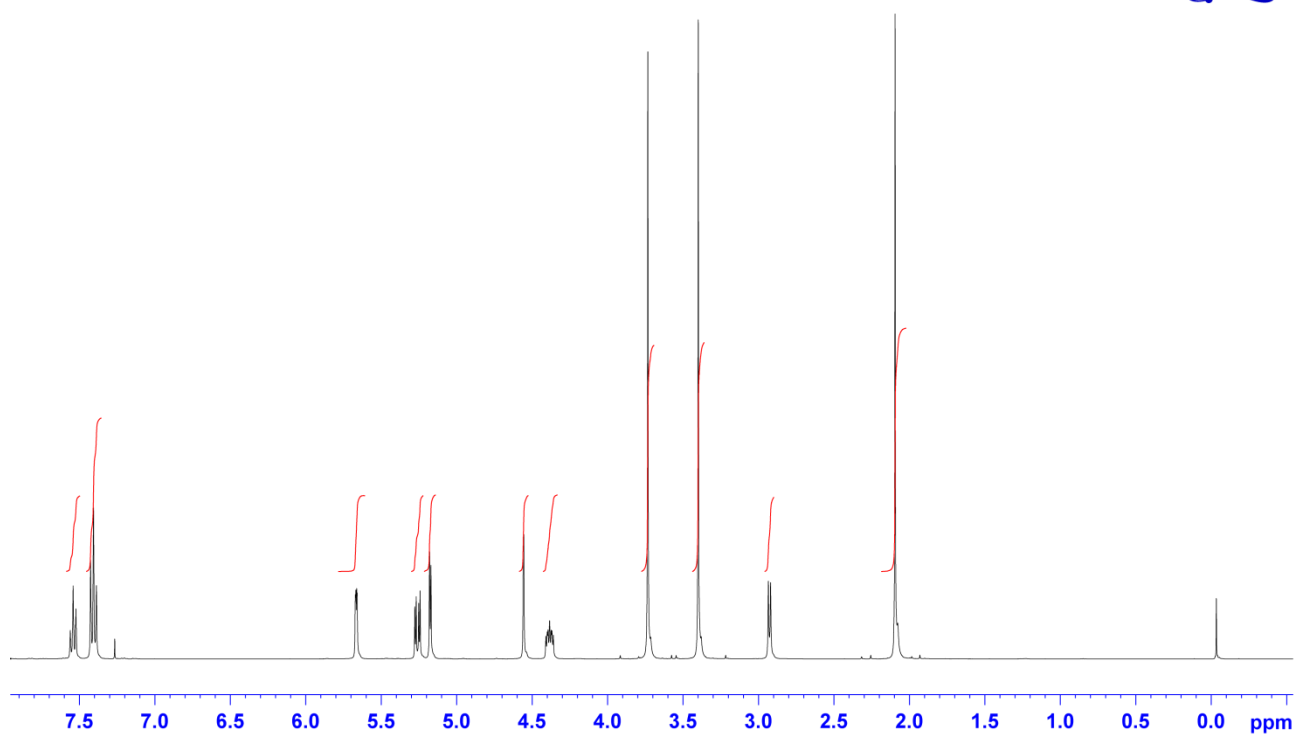
CDCl₃



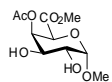
Compound 26



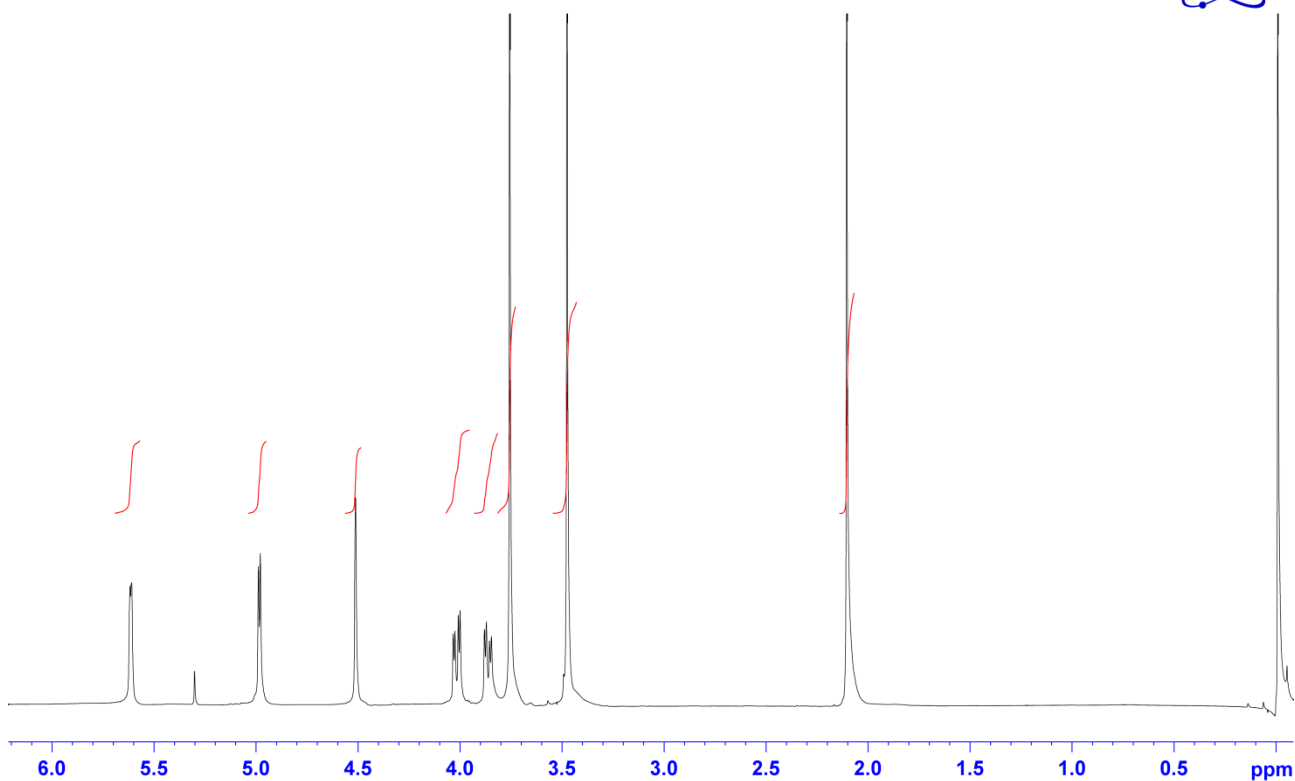
CDCl₃



Compound 27



CDCl₃



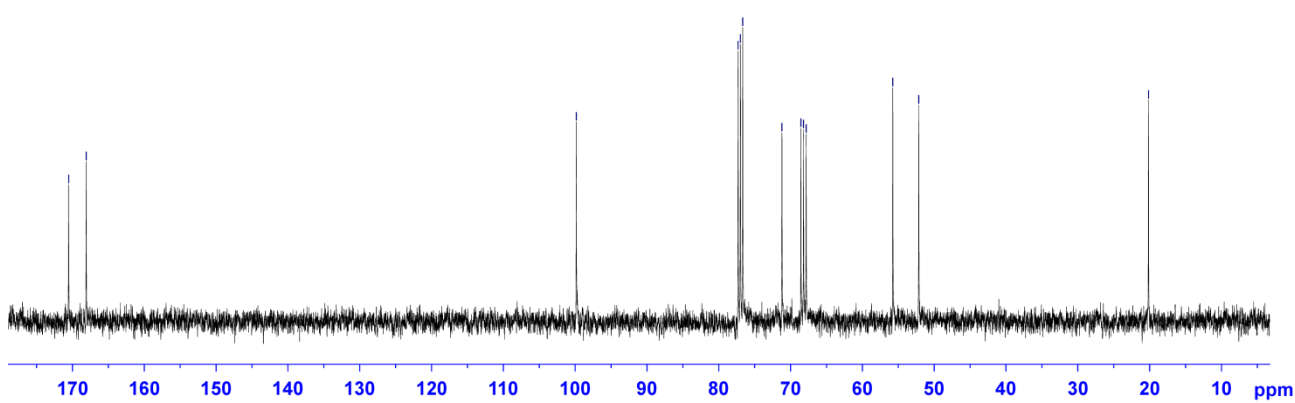
170.44
168.04

99.84

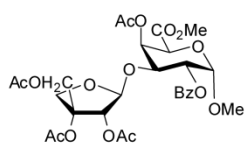
71.20
68.56
68.19
67.85

55.76
52.15

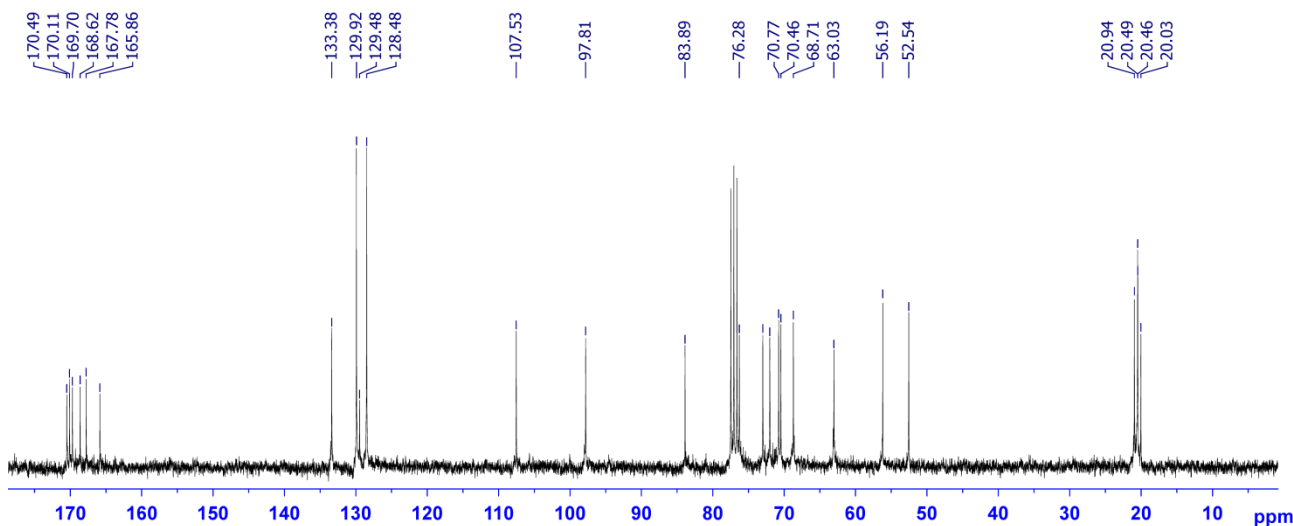
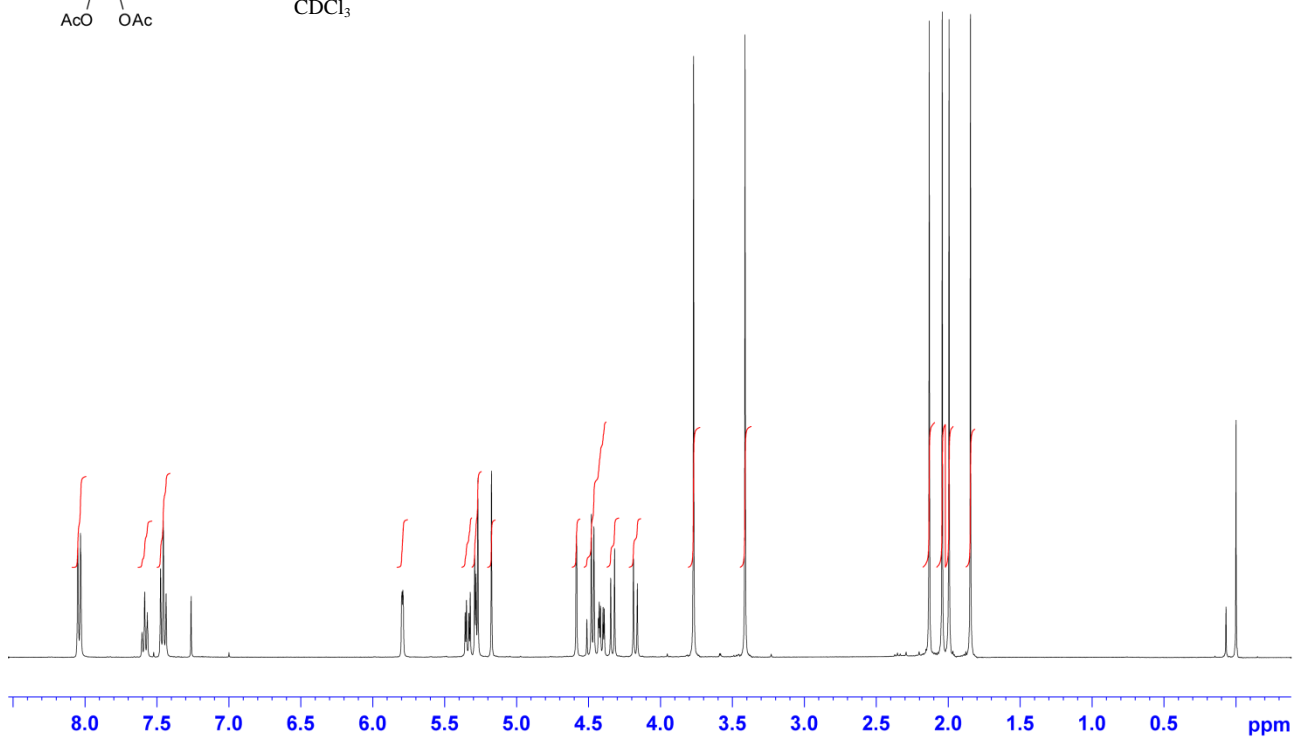
20.16



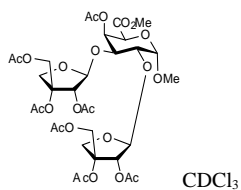
Compound 28



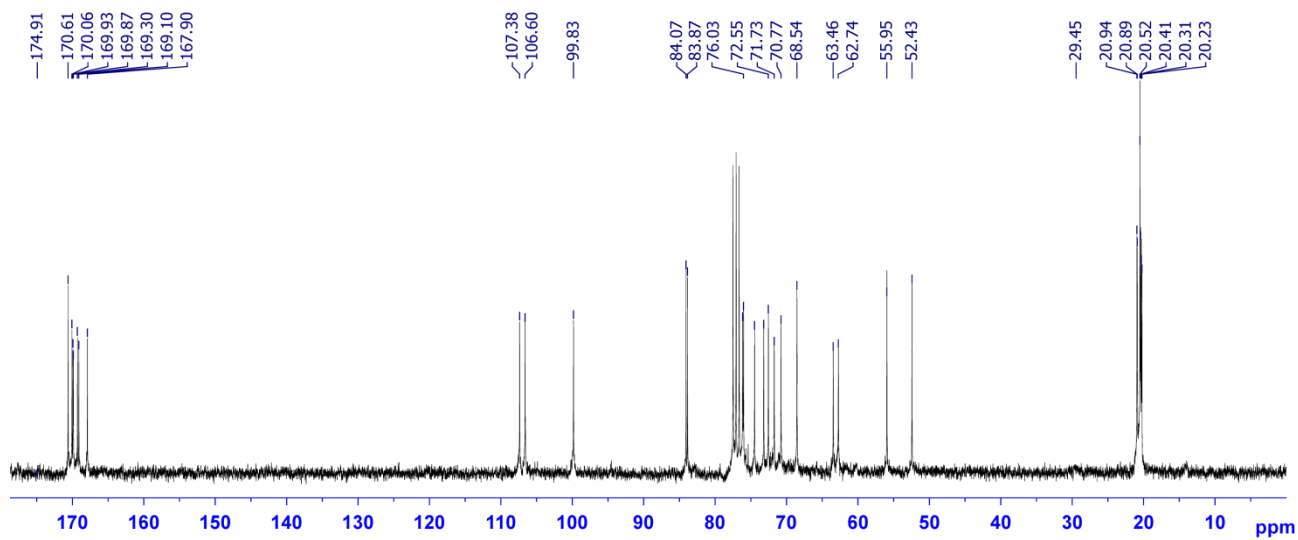
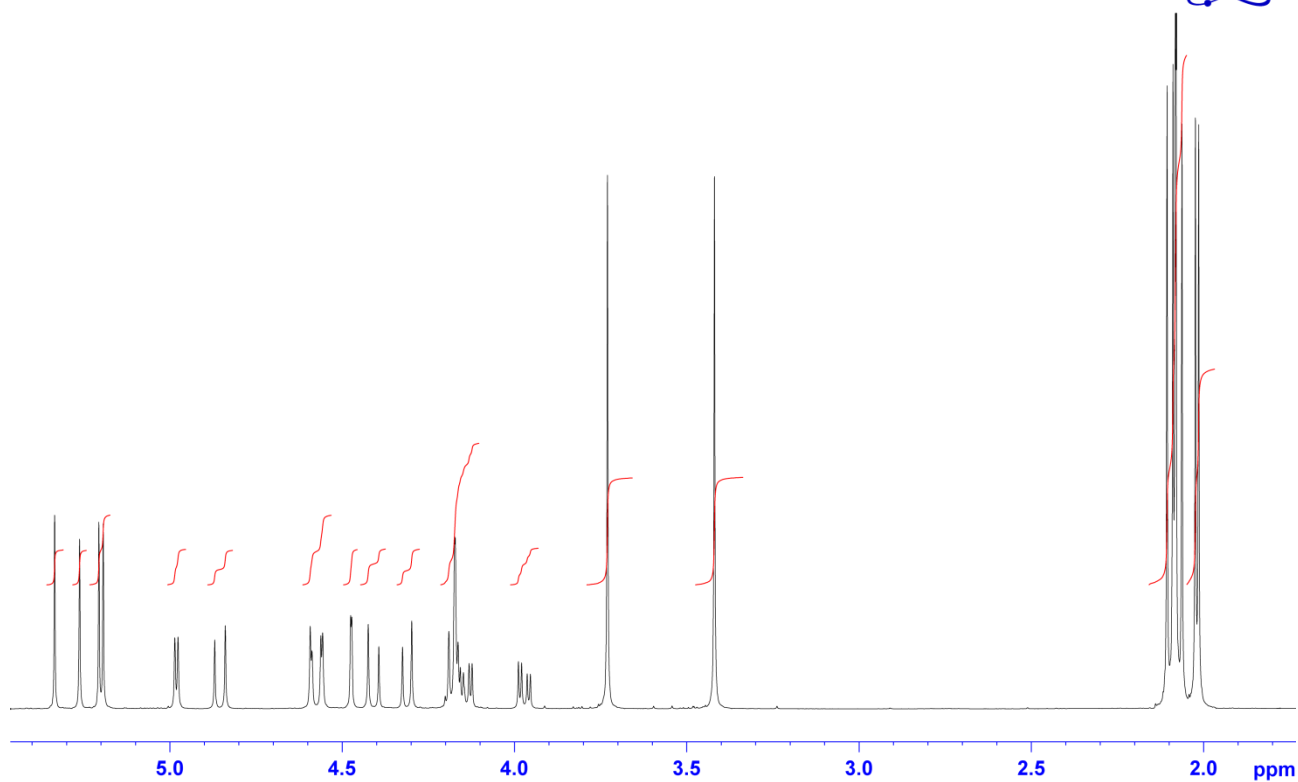
CDCl₃



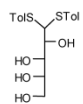
Compound 29



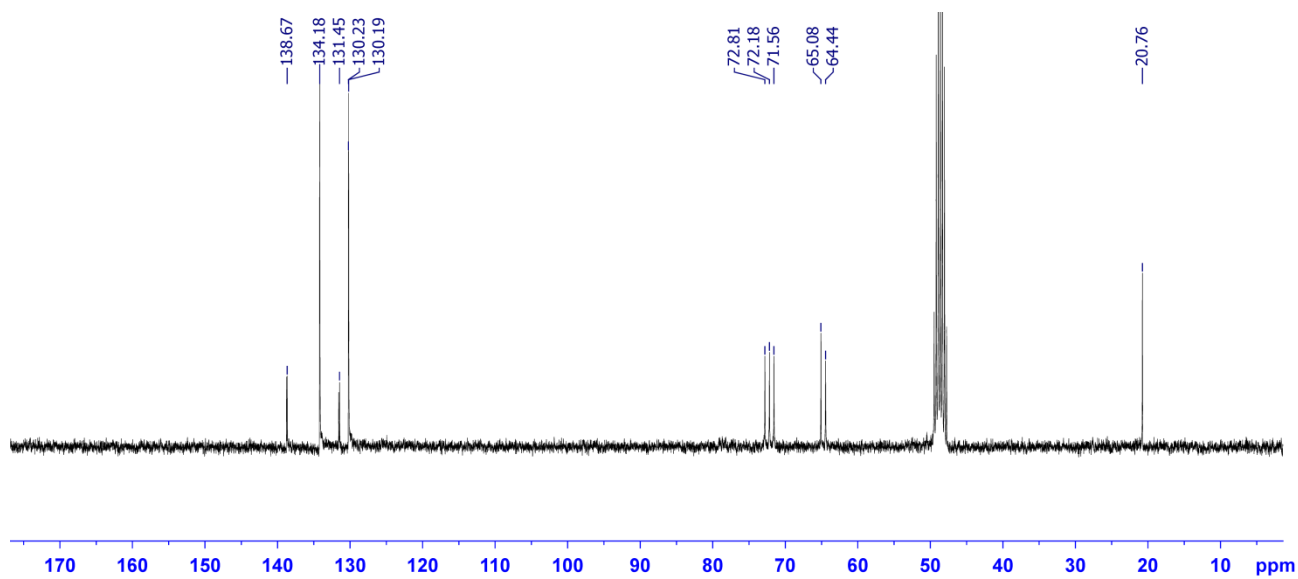
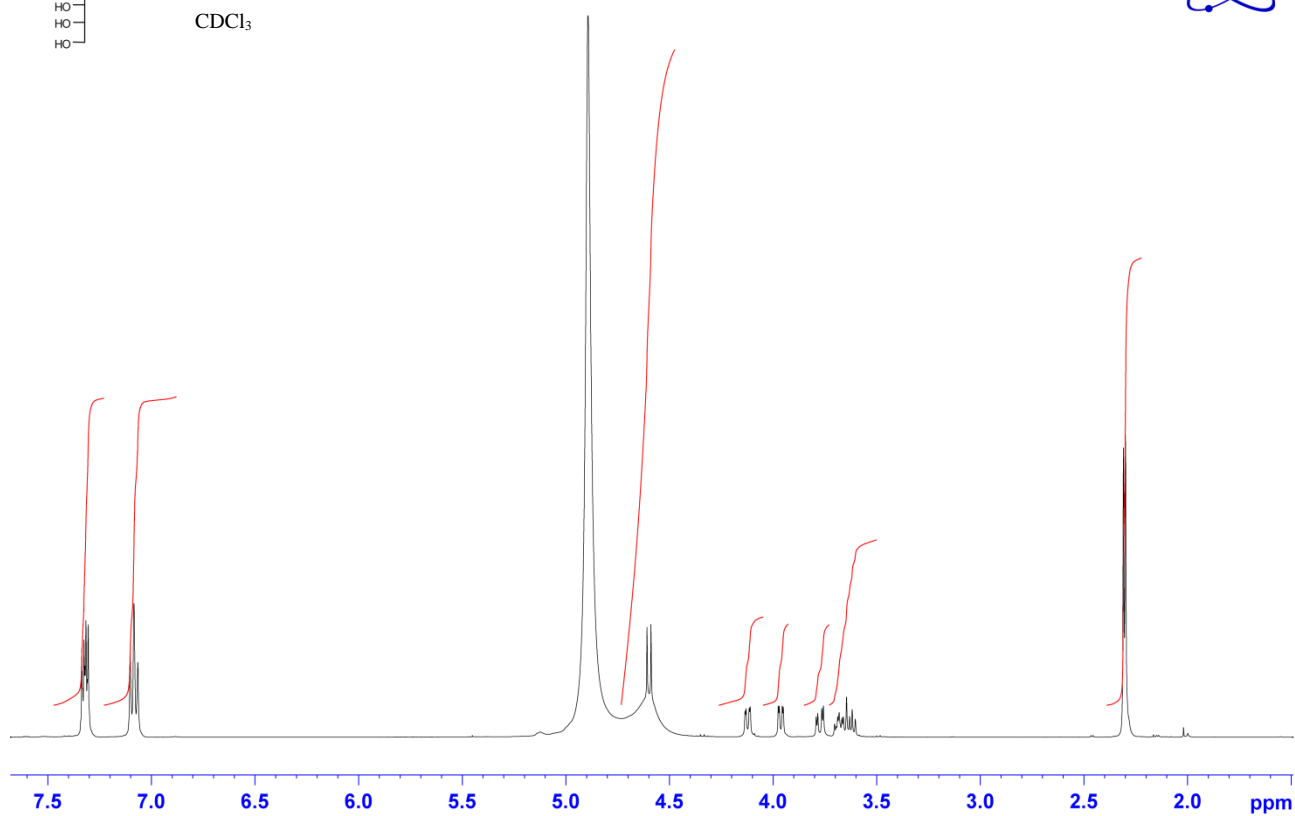
BRUKER



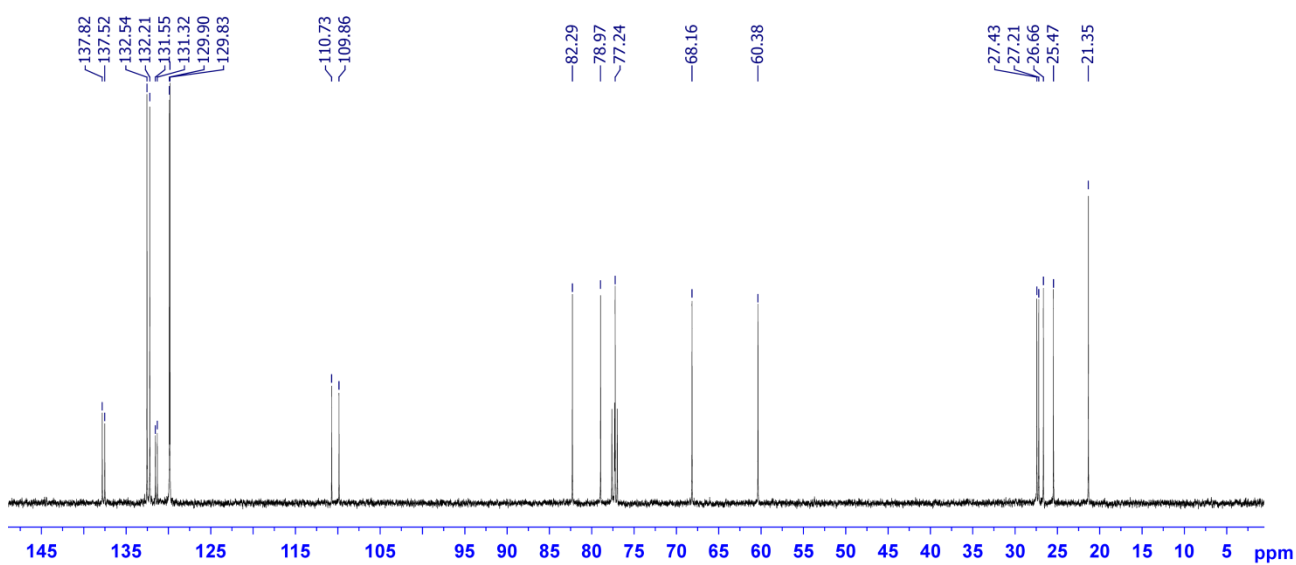
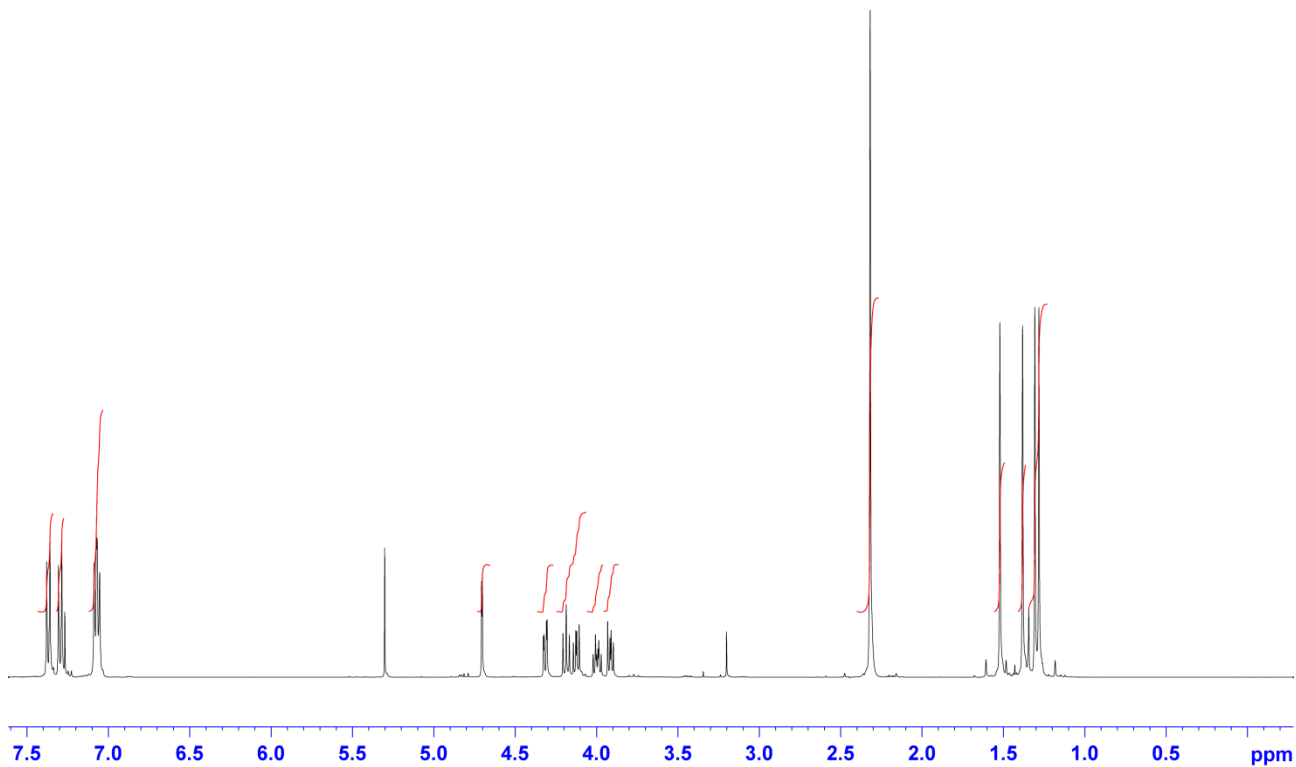
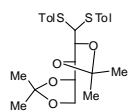
Compound 30



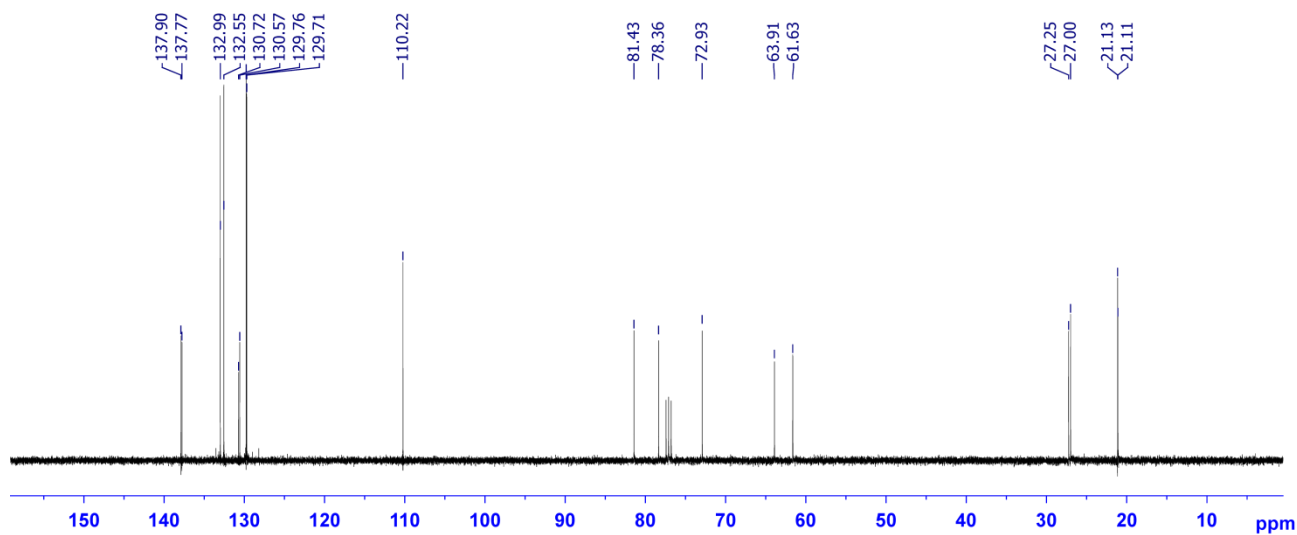
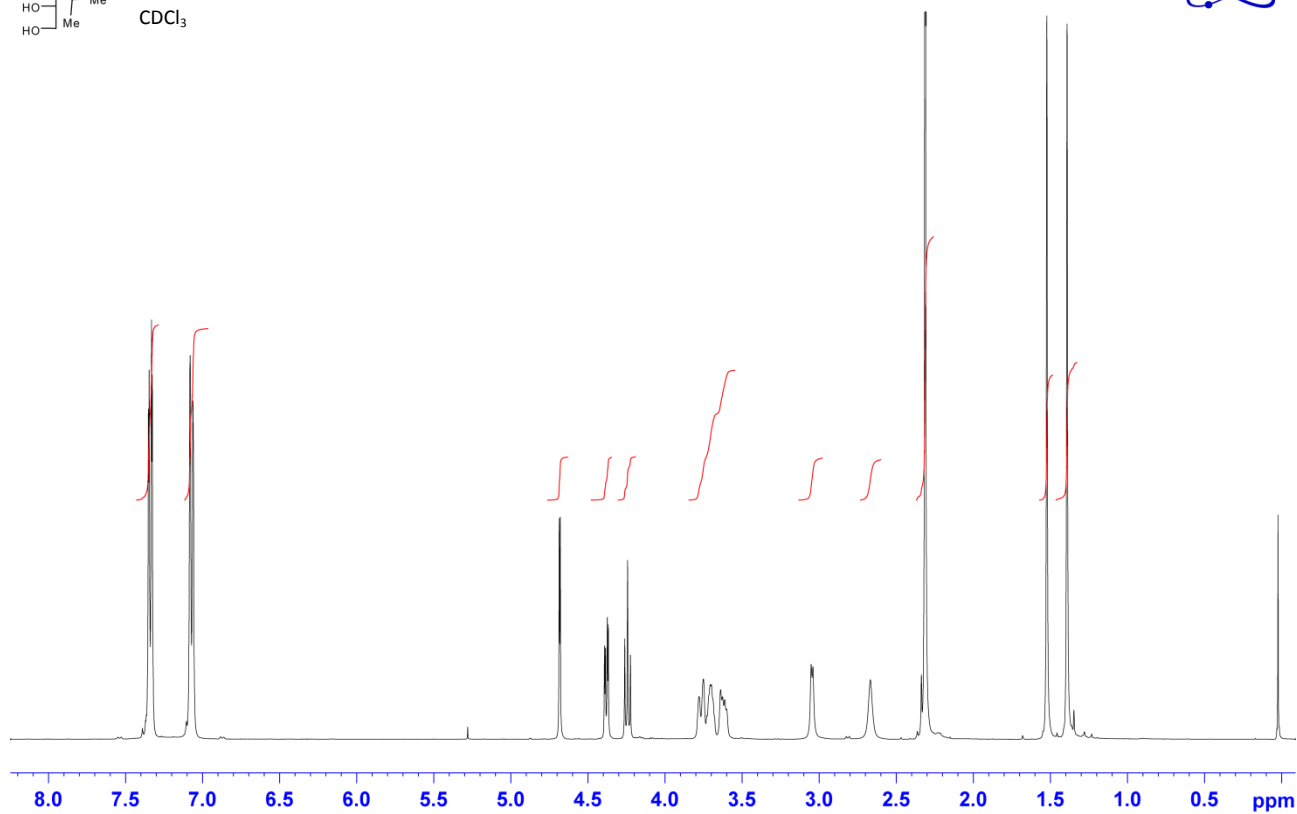
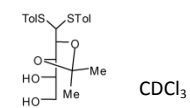
CDCl₃



Compound 31



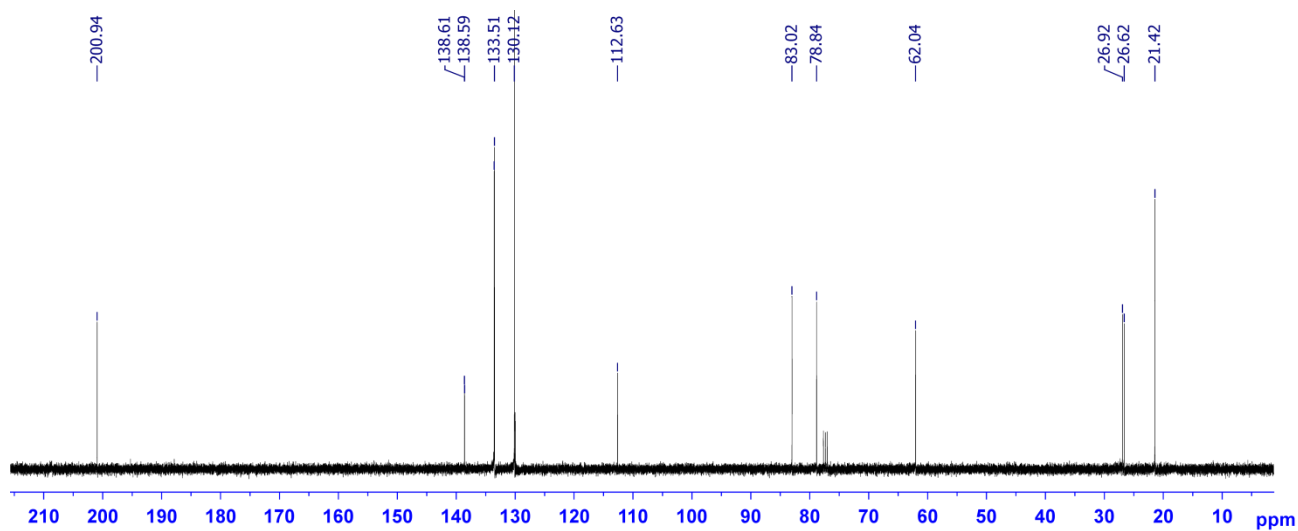
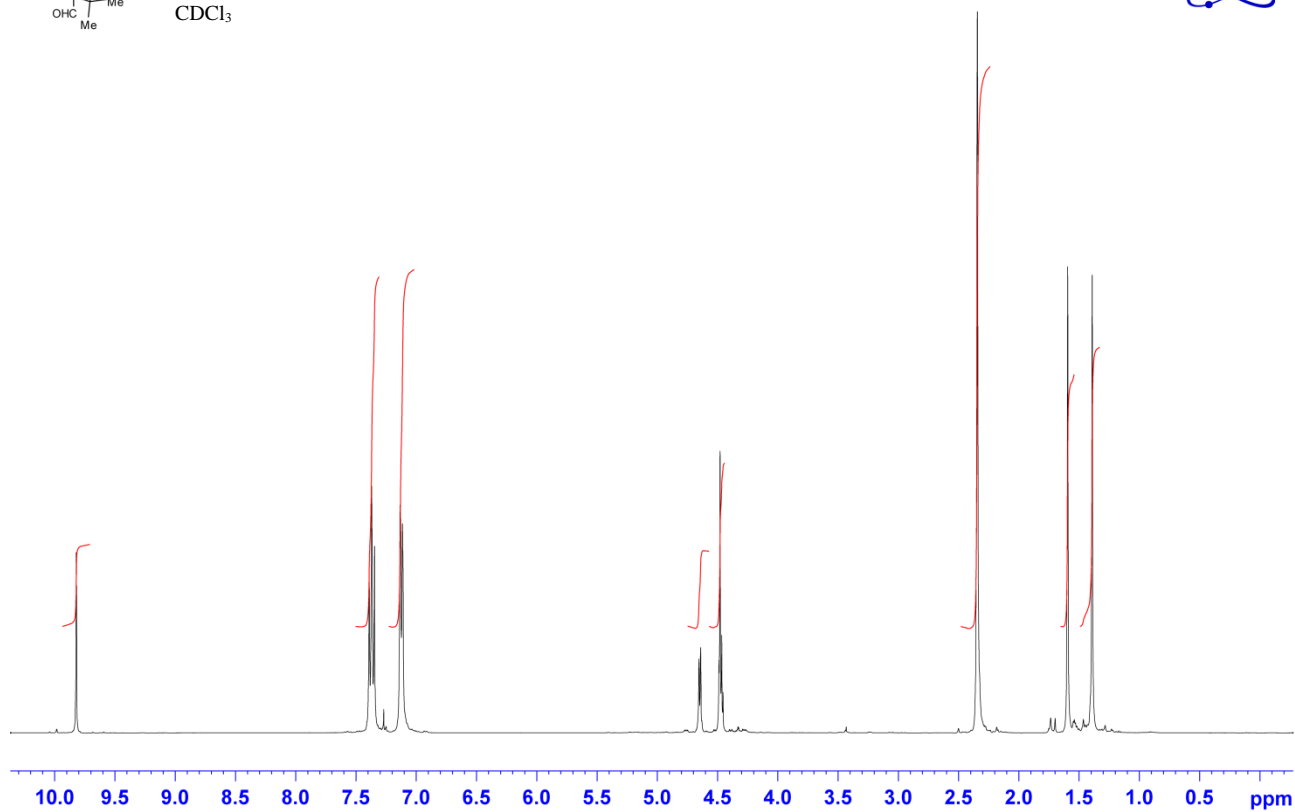
Compound 32



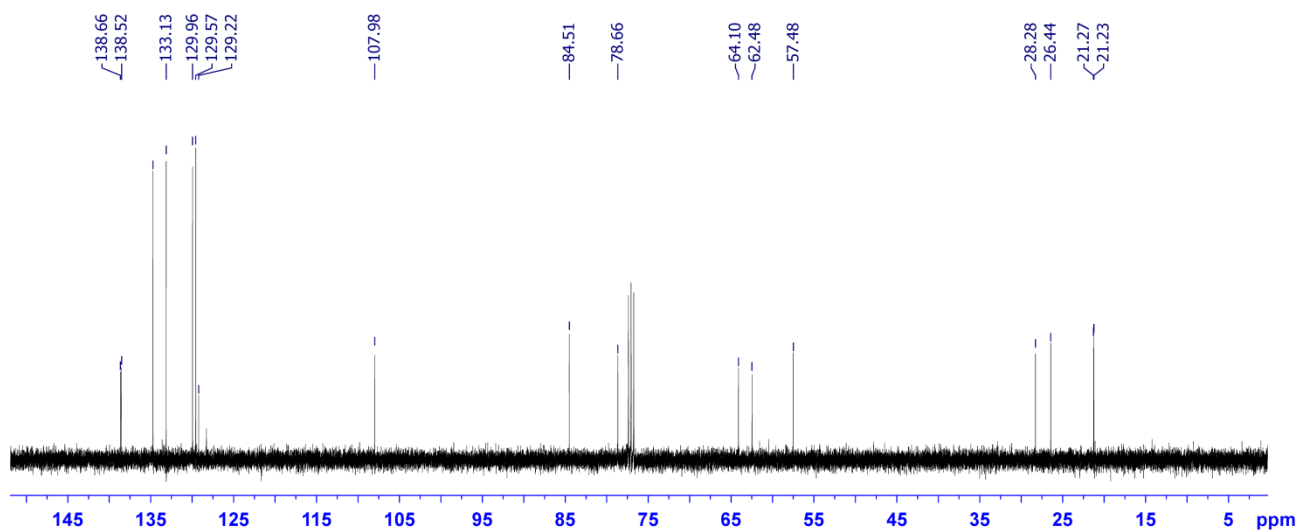
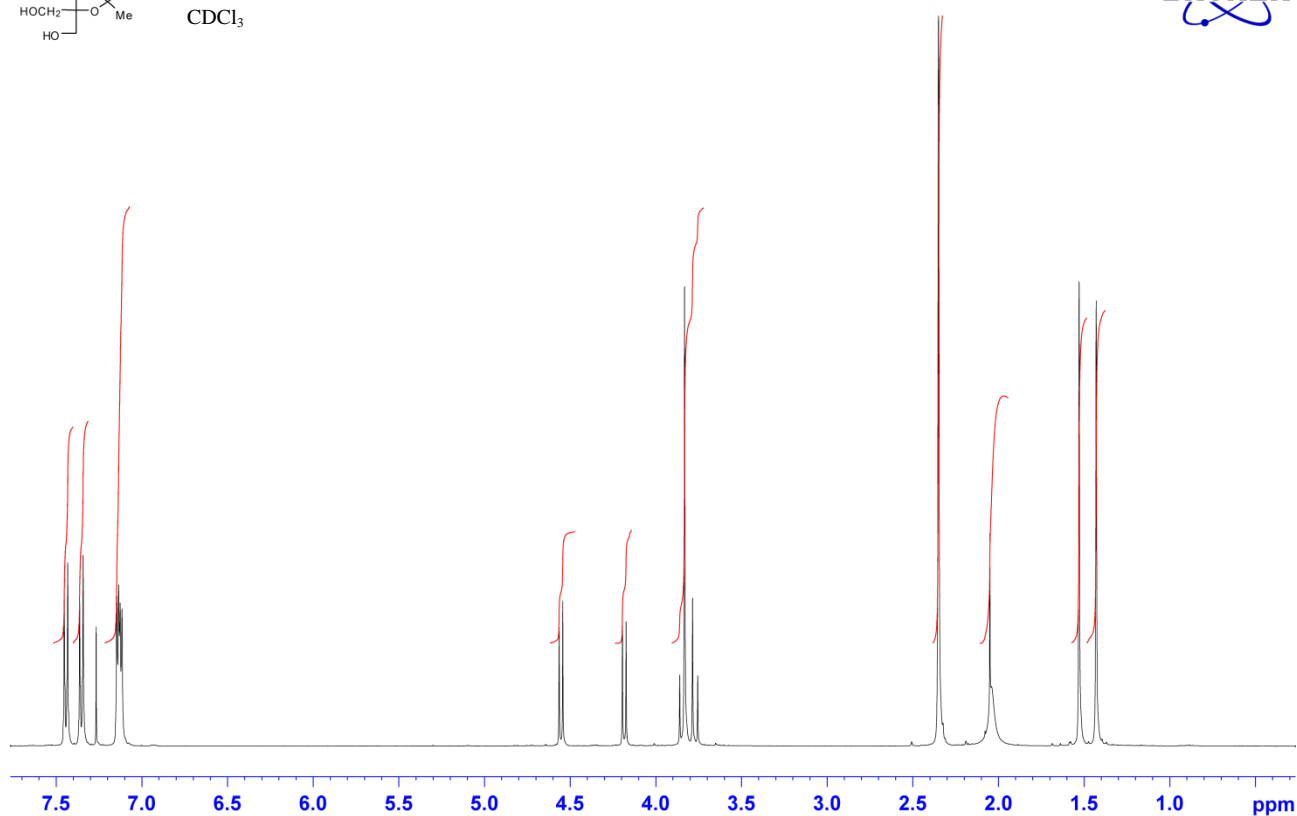
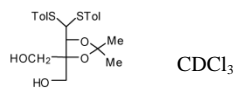
Compound 33



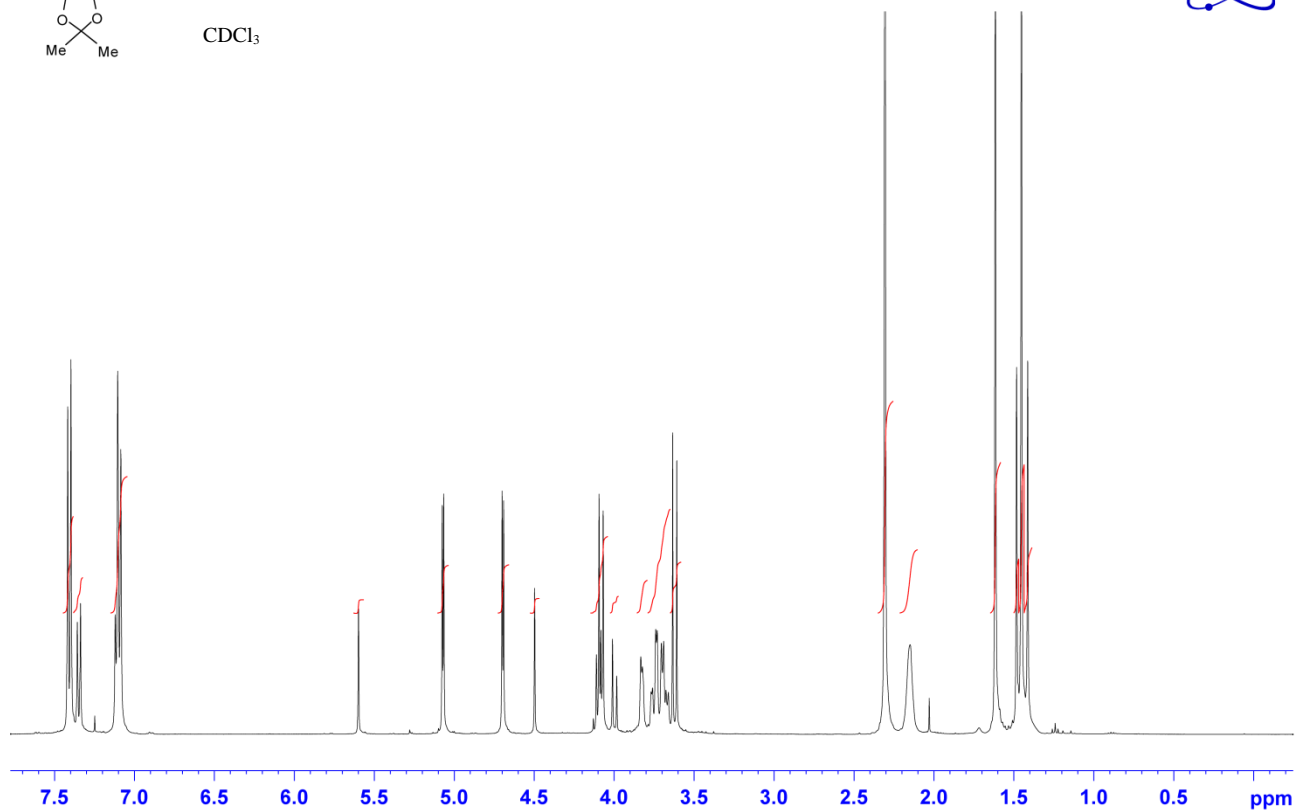
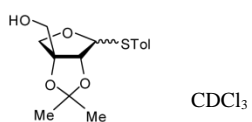
CDCl₃



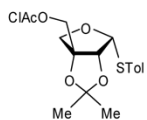
Compound 34



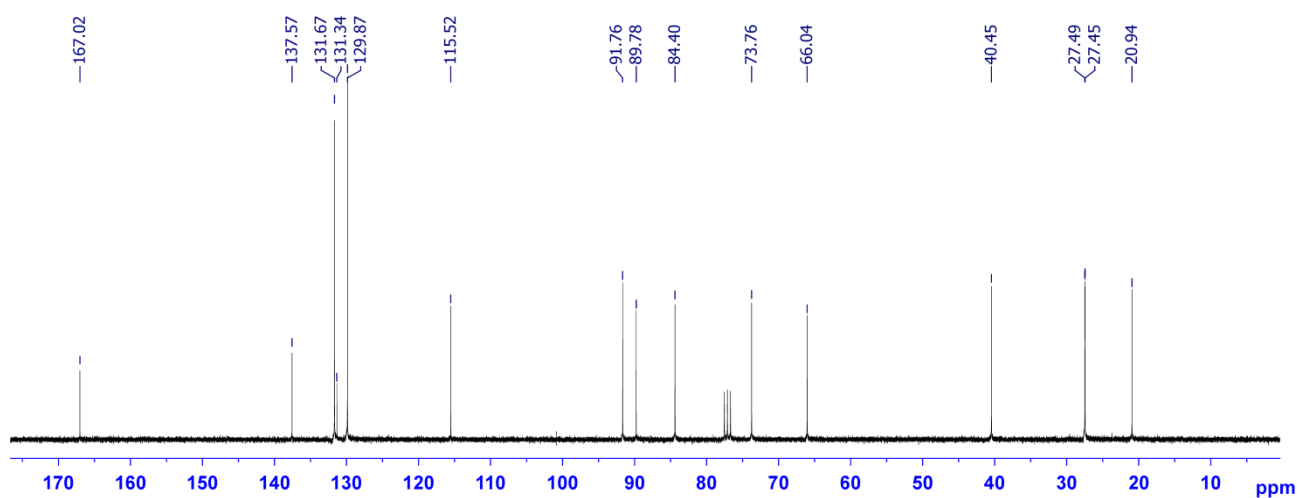
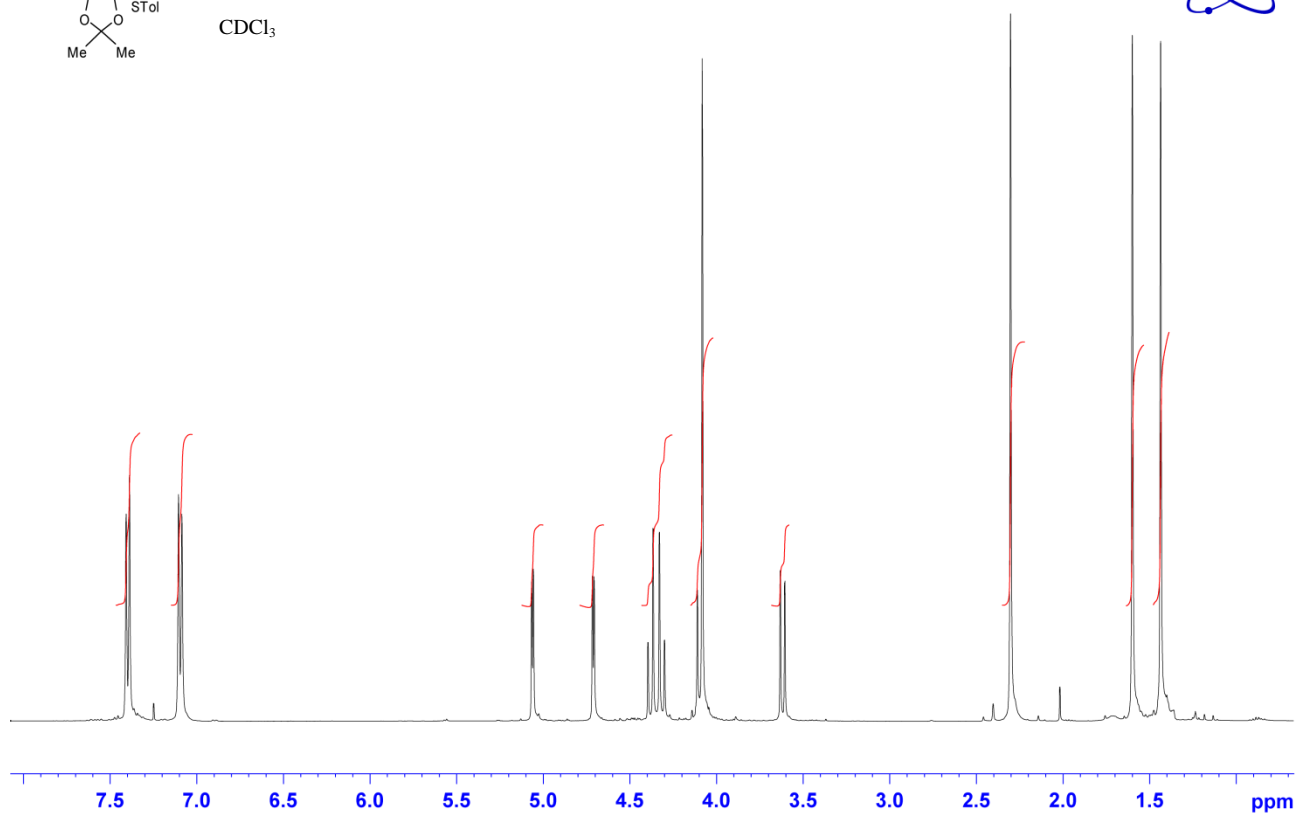
Compound 35



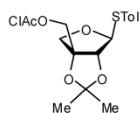
Compound 36a



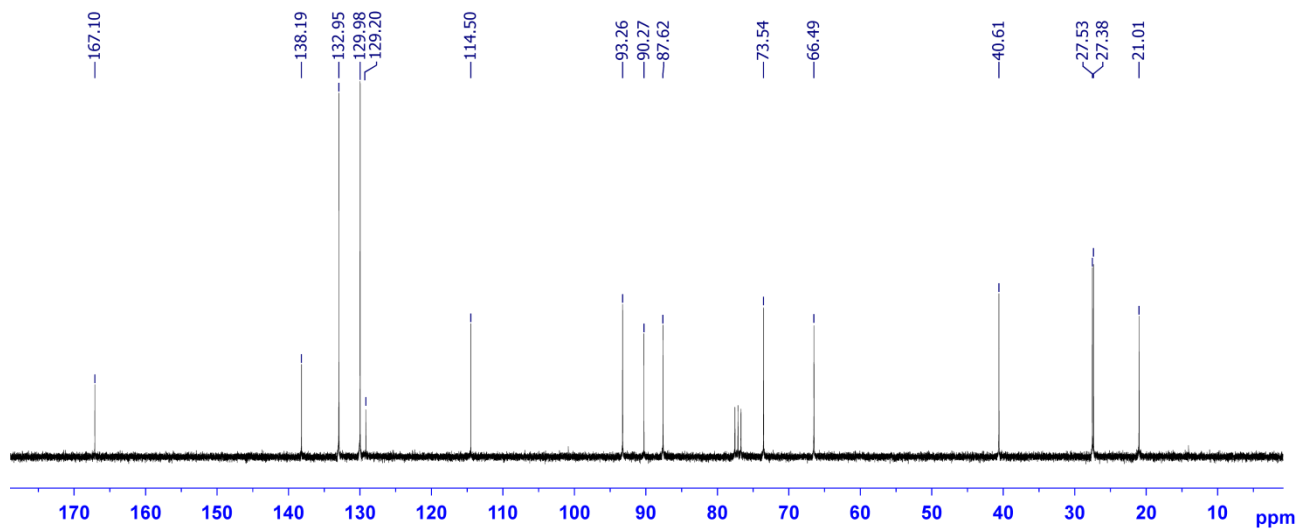
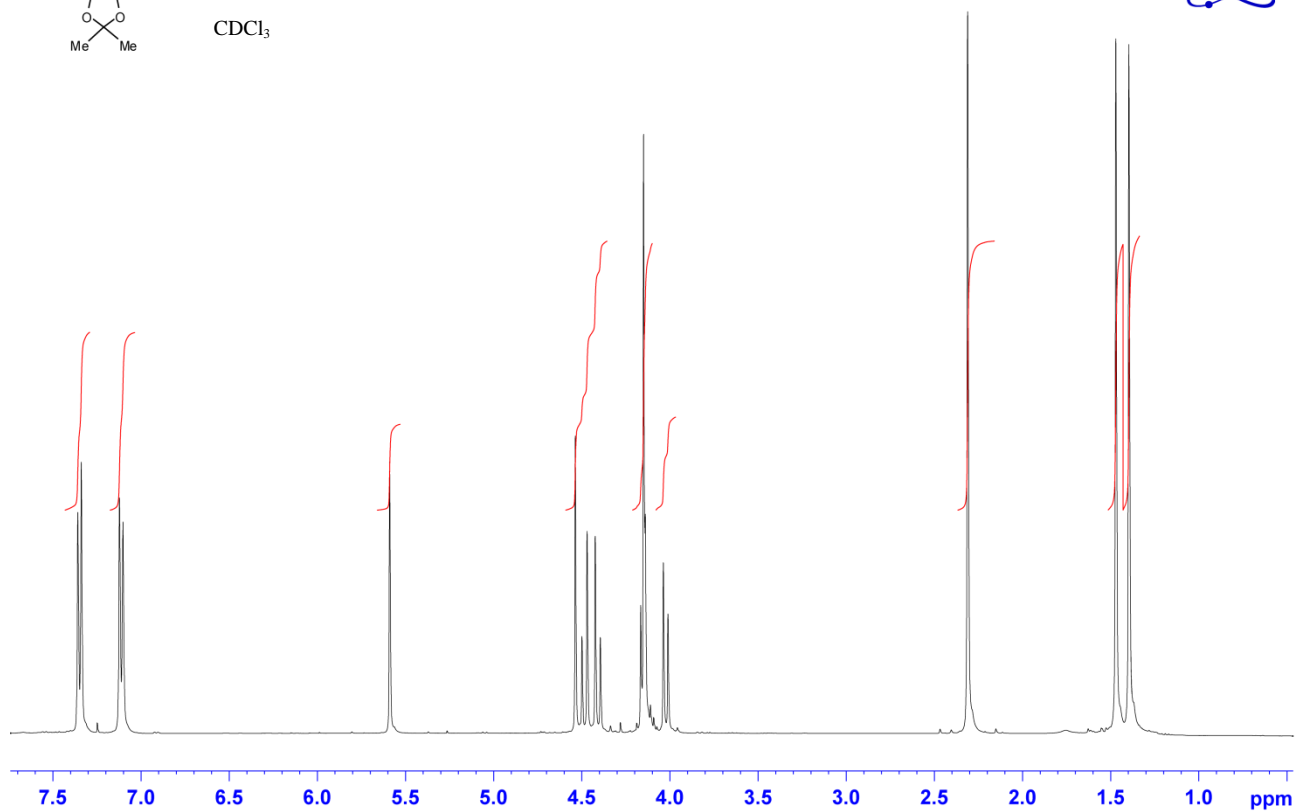
CDCl₃



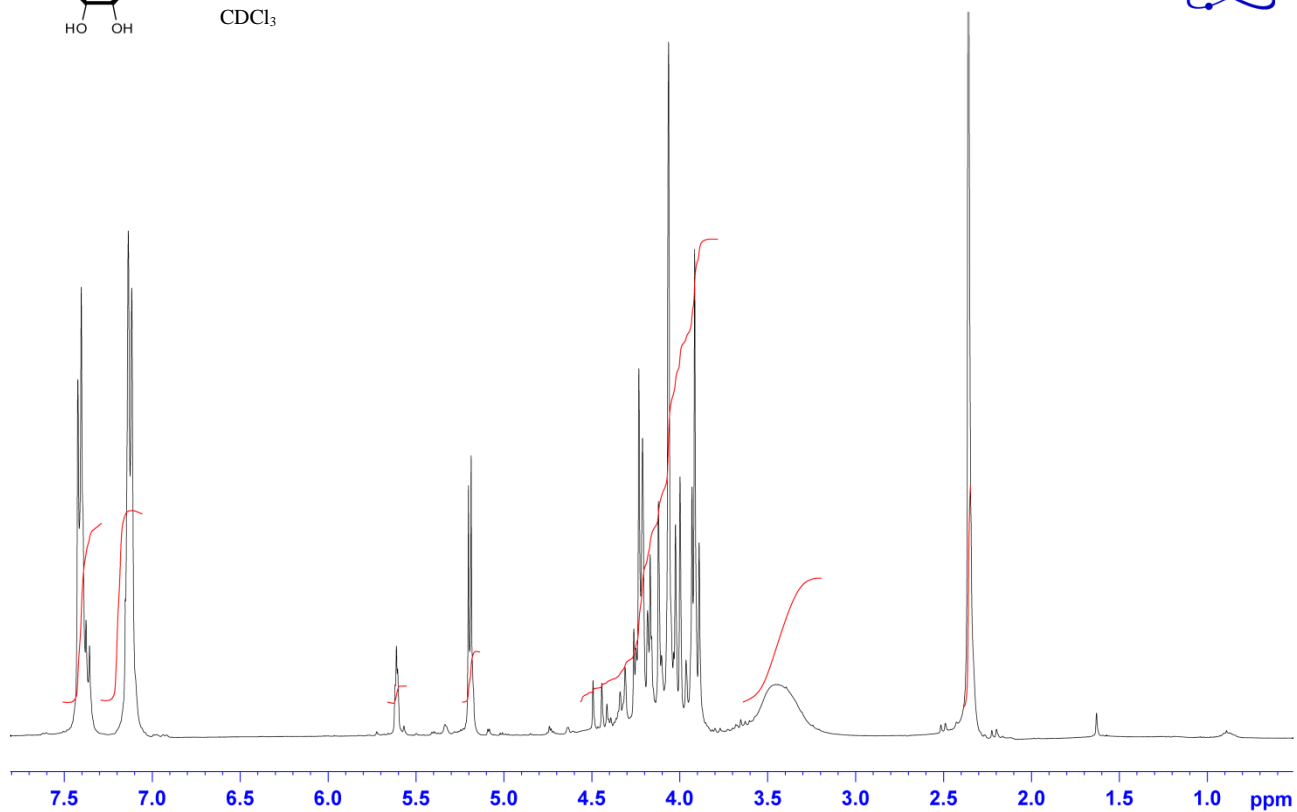
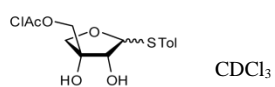
Compound 36b



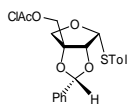
CDCl₃



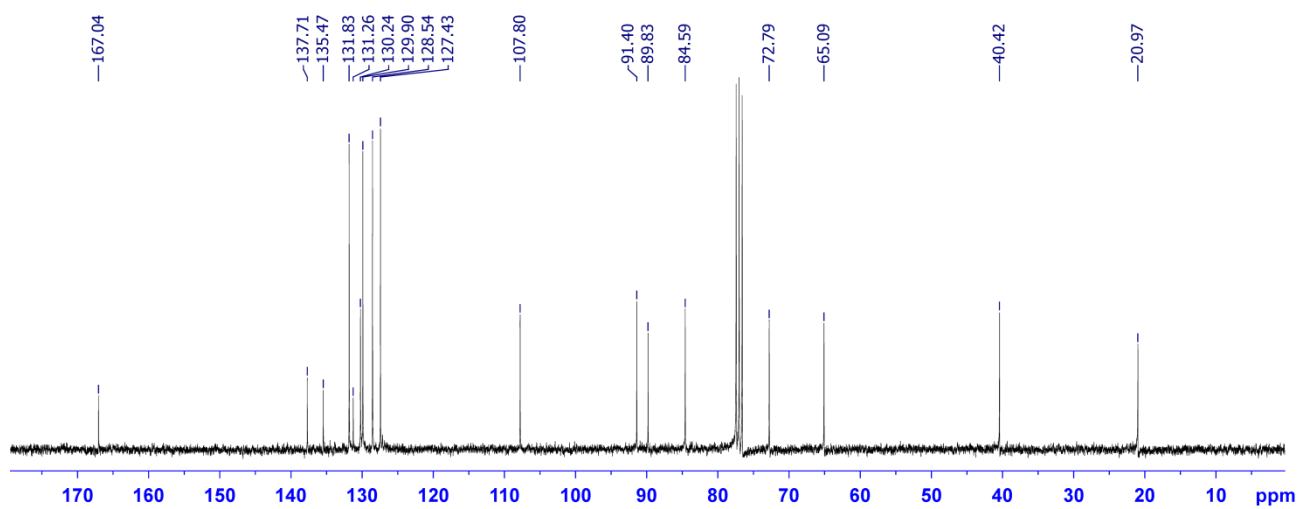
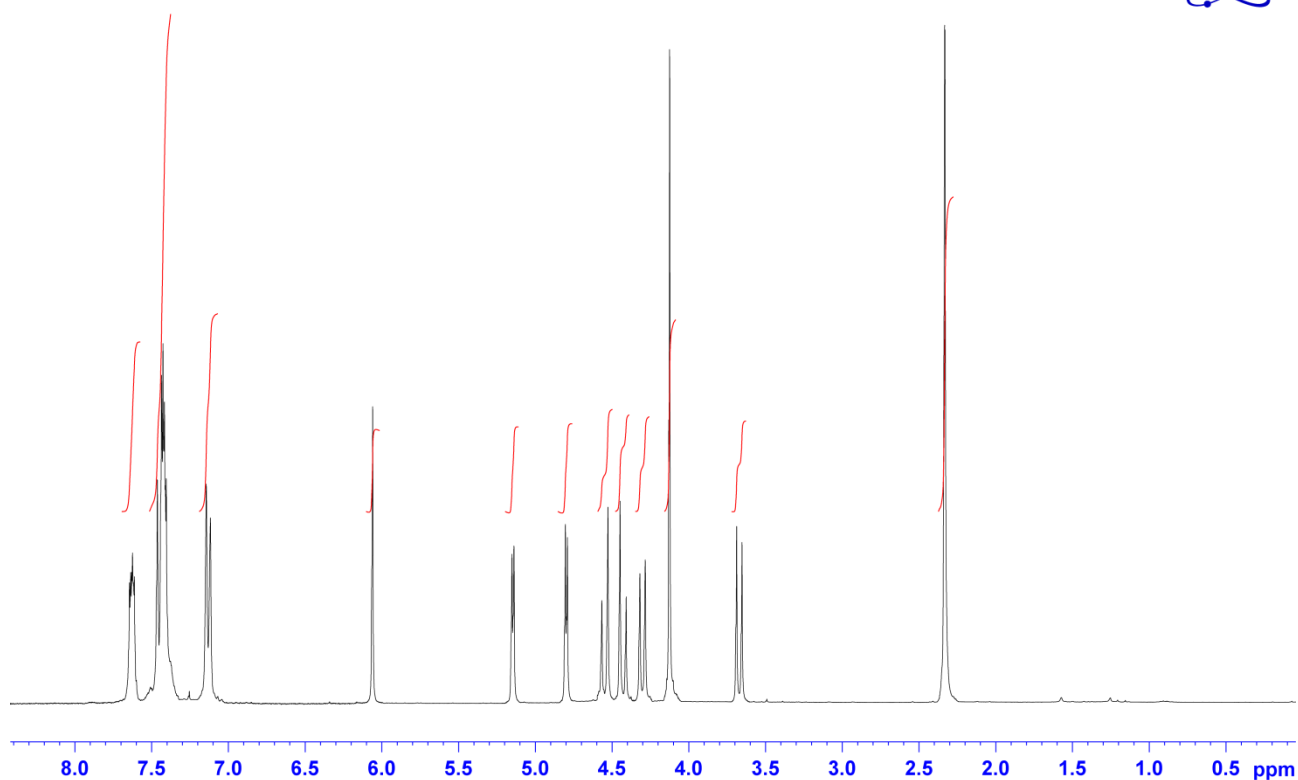
Compound **37a,b**



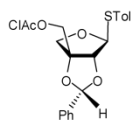
Compound 38a



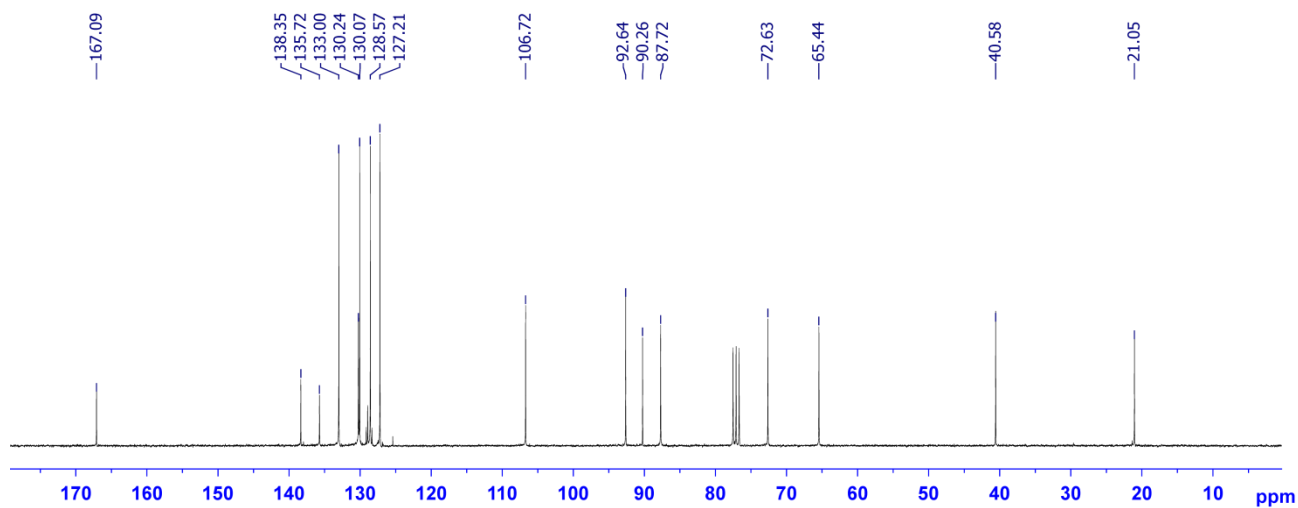
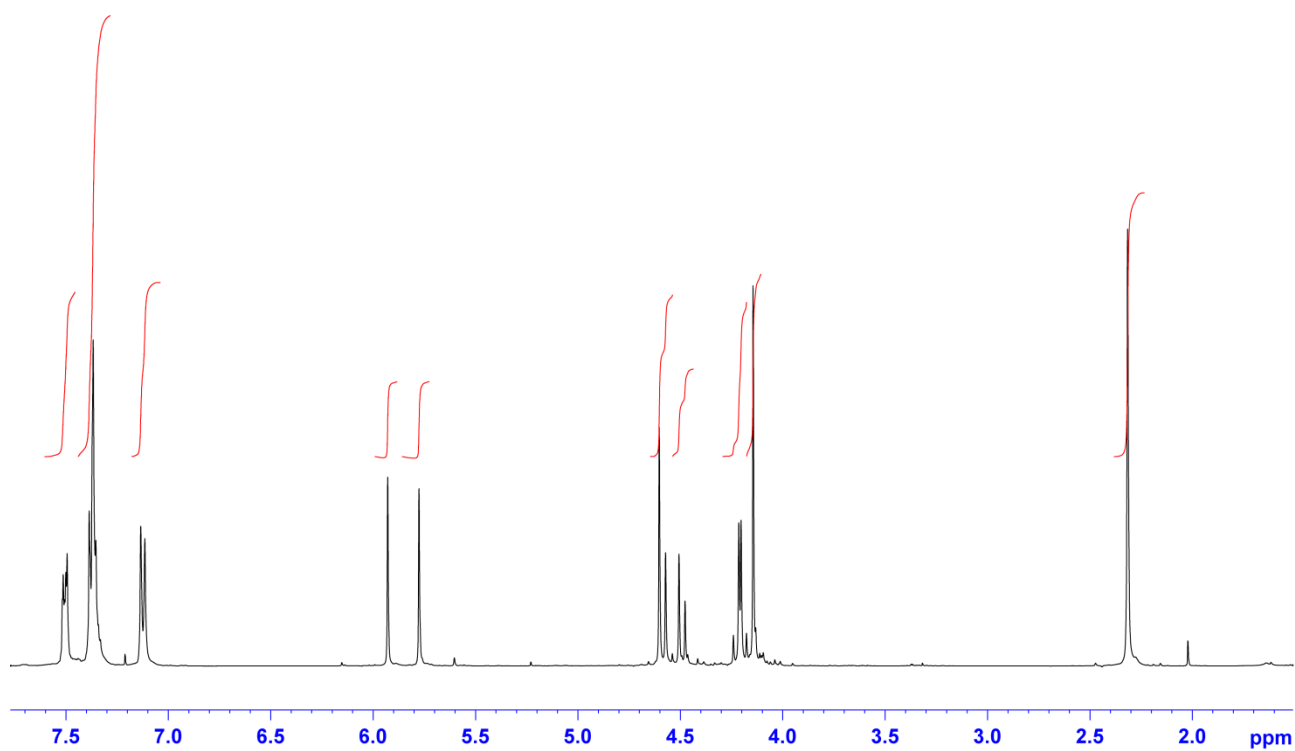
CDCl₃



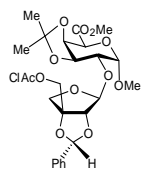
Compound 38b



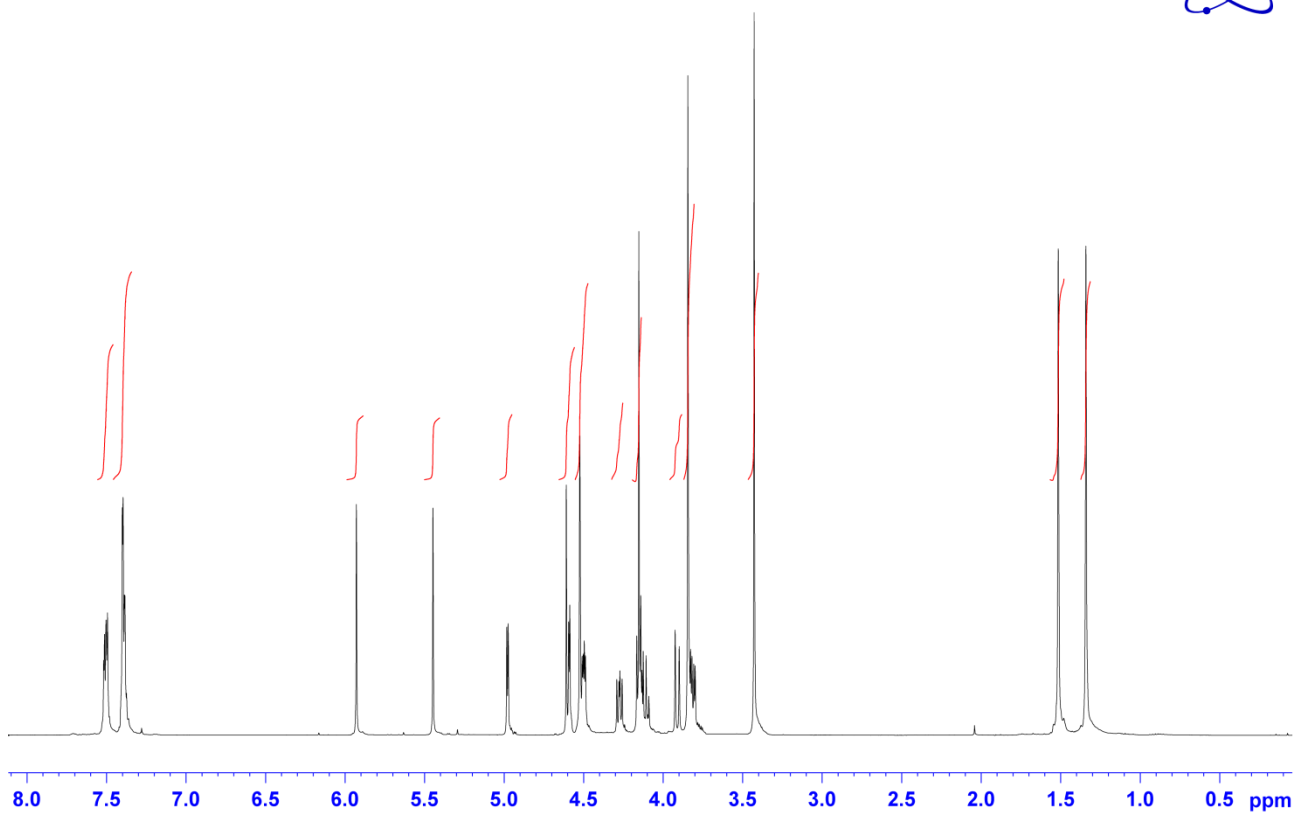
CDCl₃



Compound 39



CDCl₃



~168.47
~167.10

~135.61
~133.87
~130.14
~128.53
~127.14

~109.95
~107.55
~106.40

~99.67

~89.47
~86.90

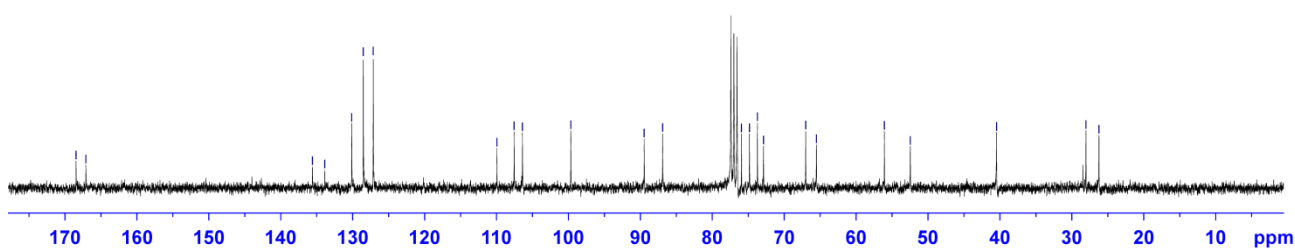
~75.94
~74.83
~73.72
~72.87

~67.01
~65.52

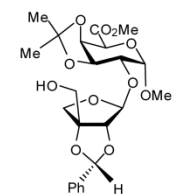
~56.07
~52.46

~40.47

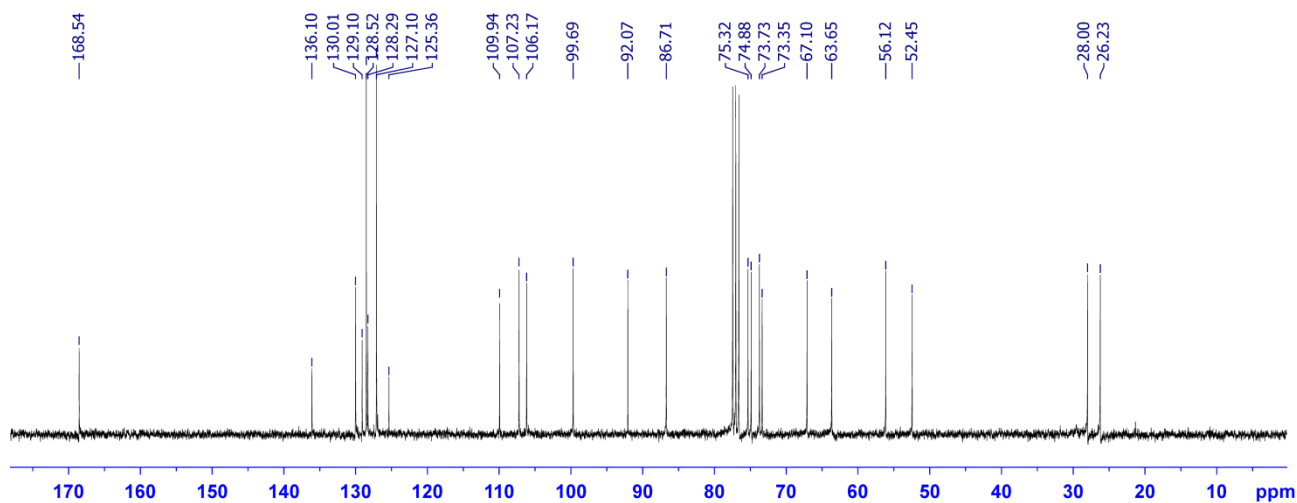
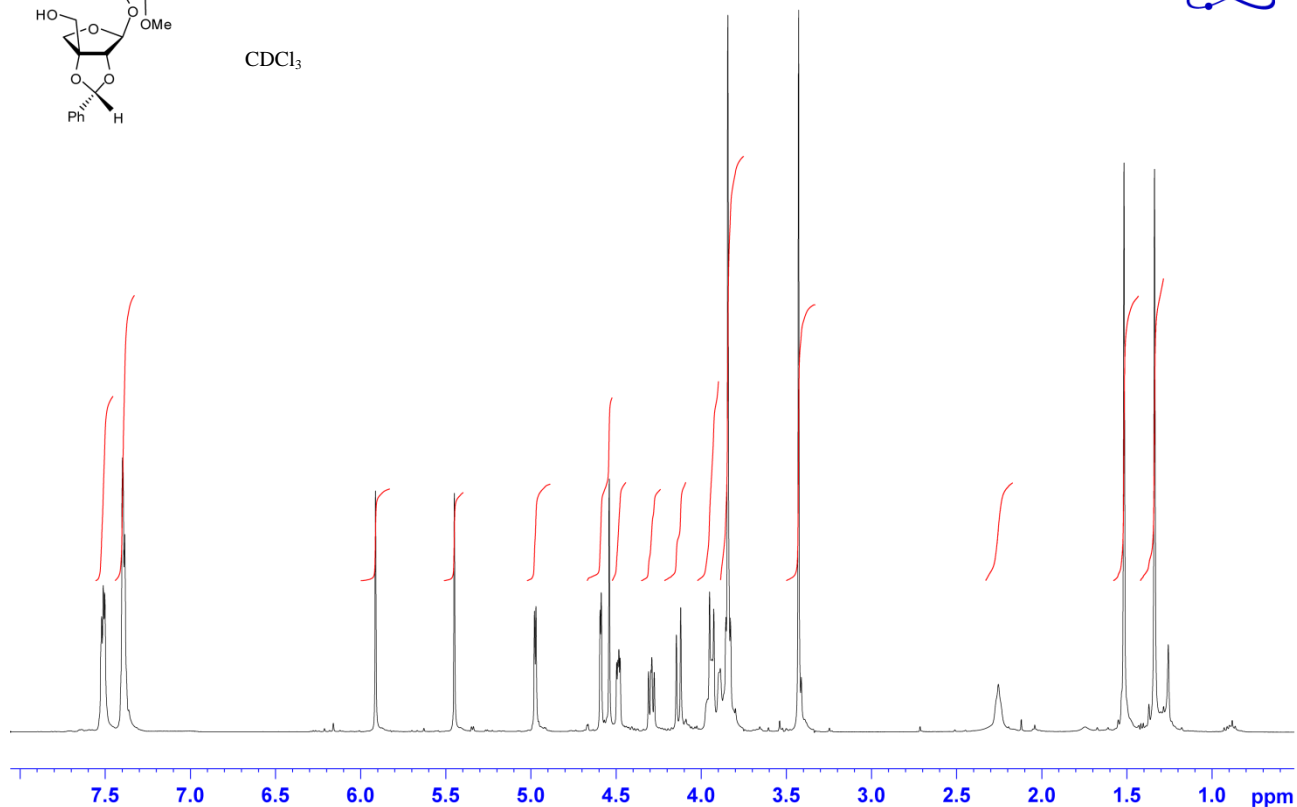
~28.04
~26.22

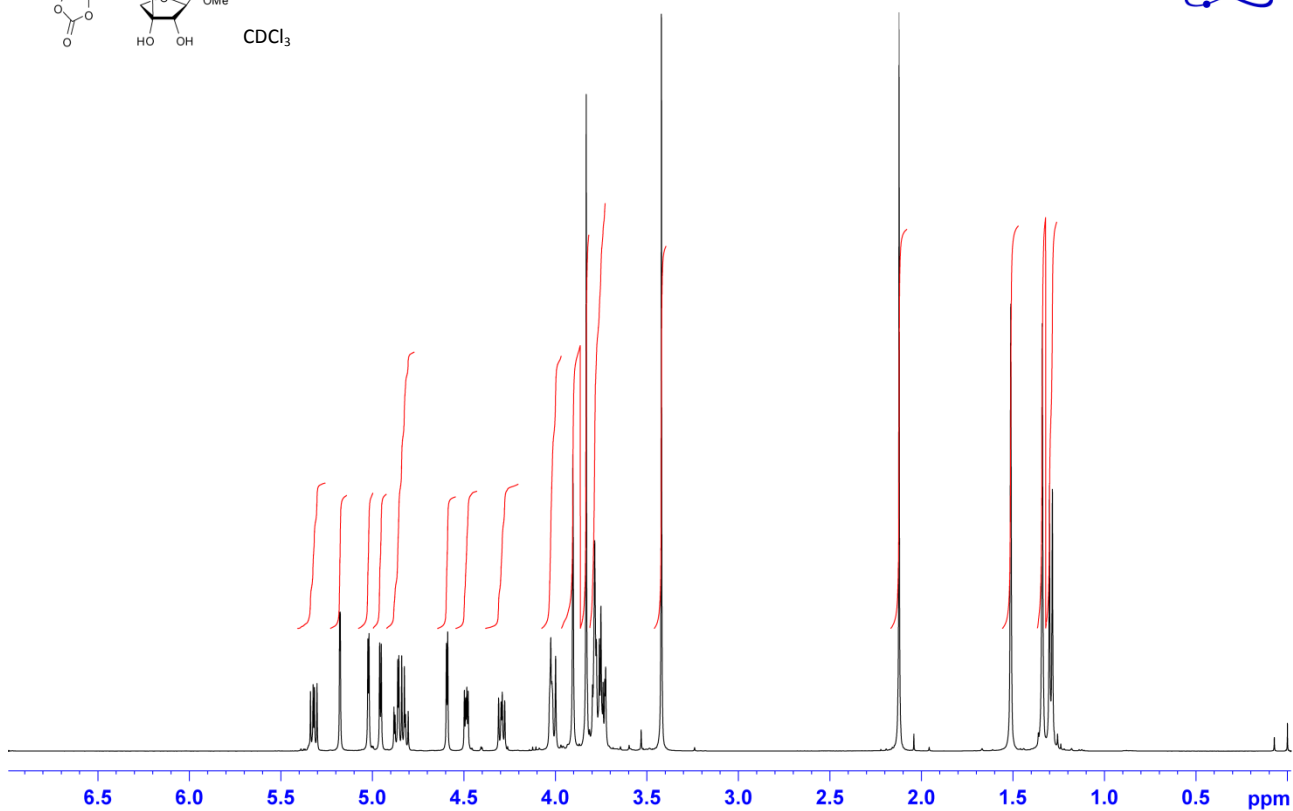
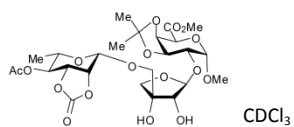


Compound 40

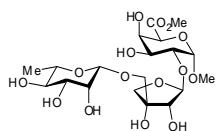


CDCl₃

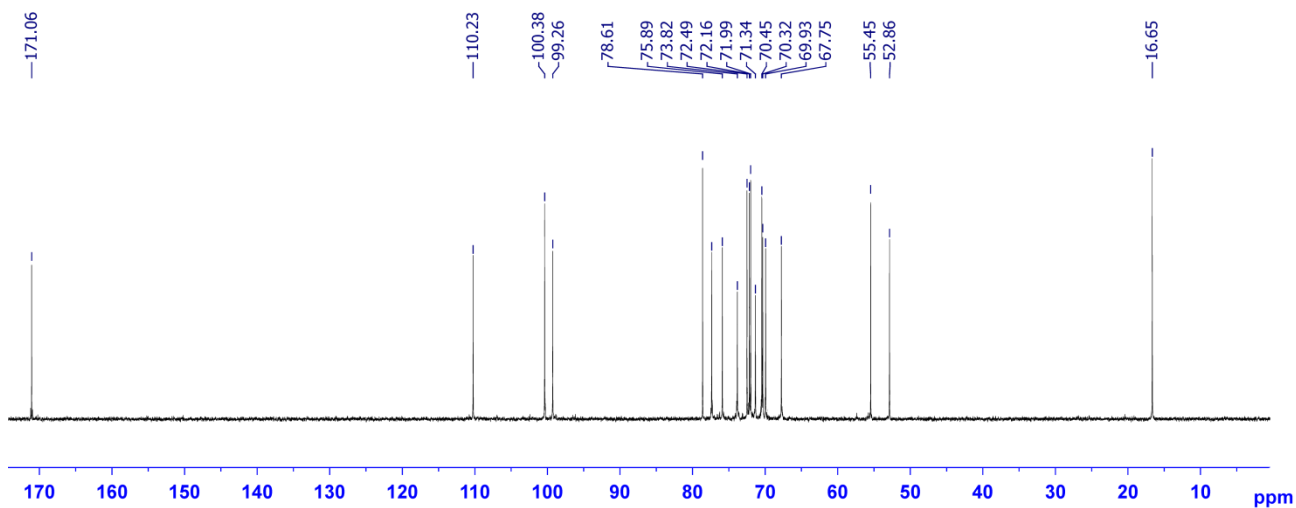
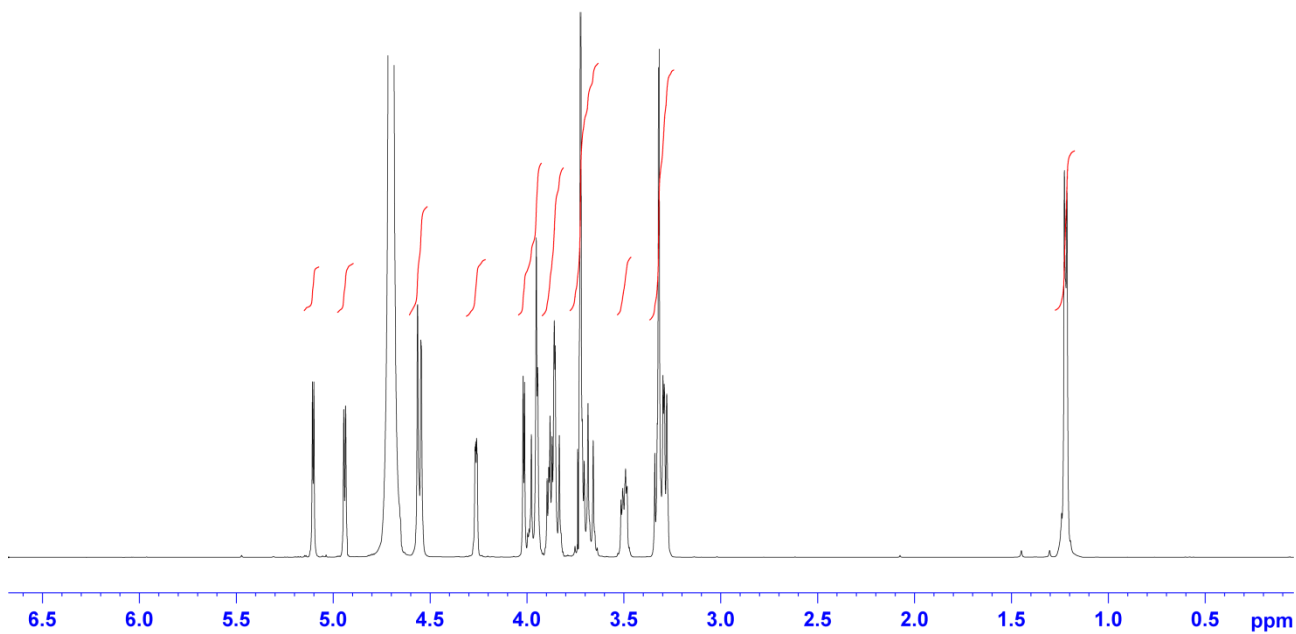




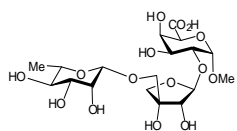
Compound 42



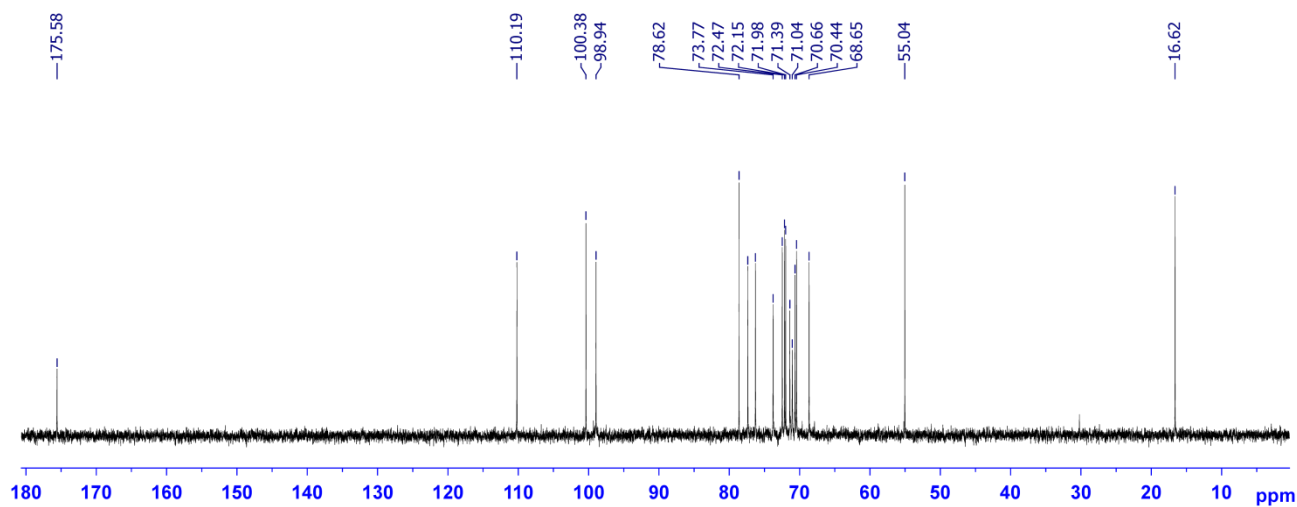
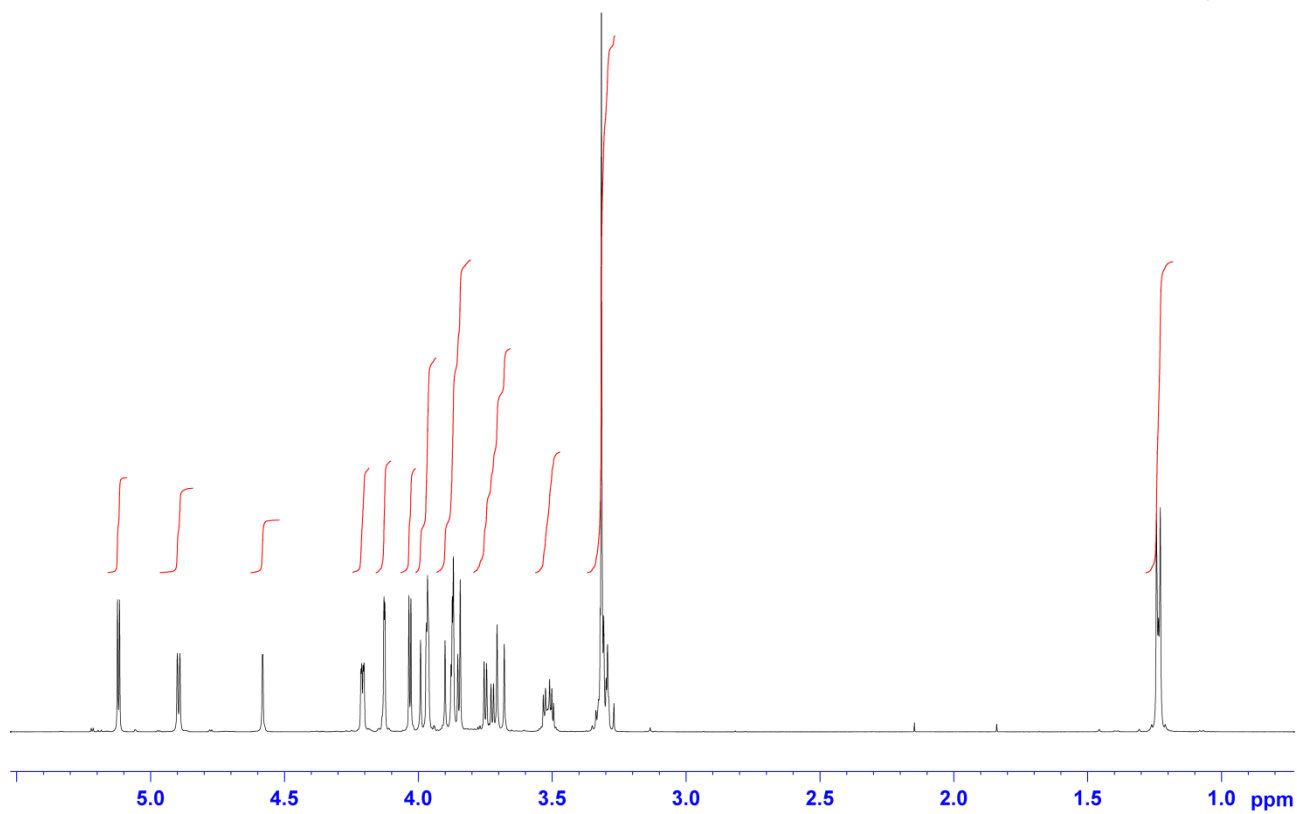
D₂O



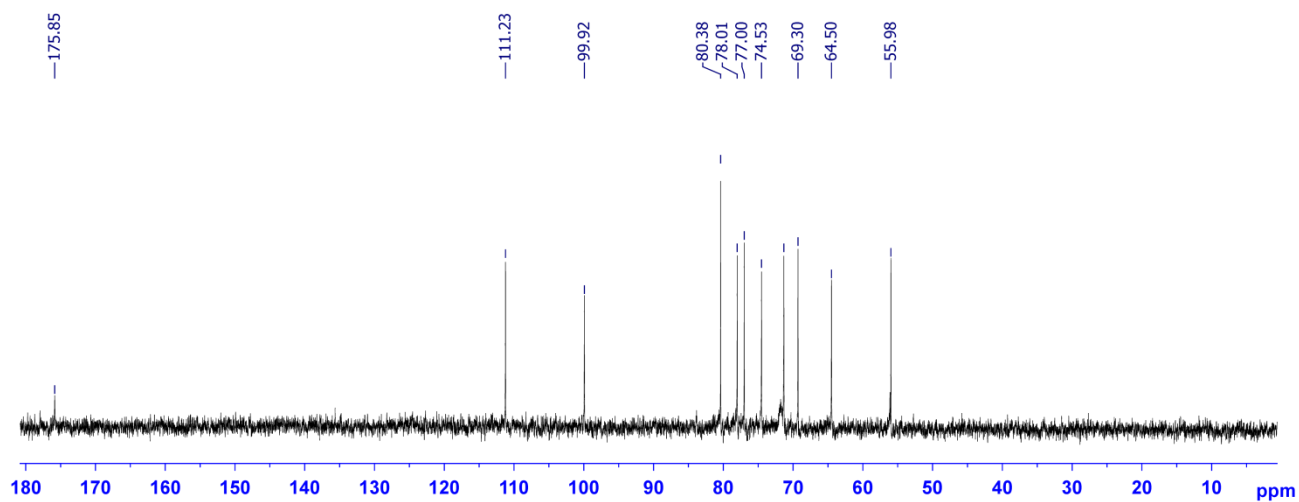
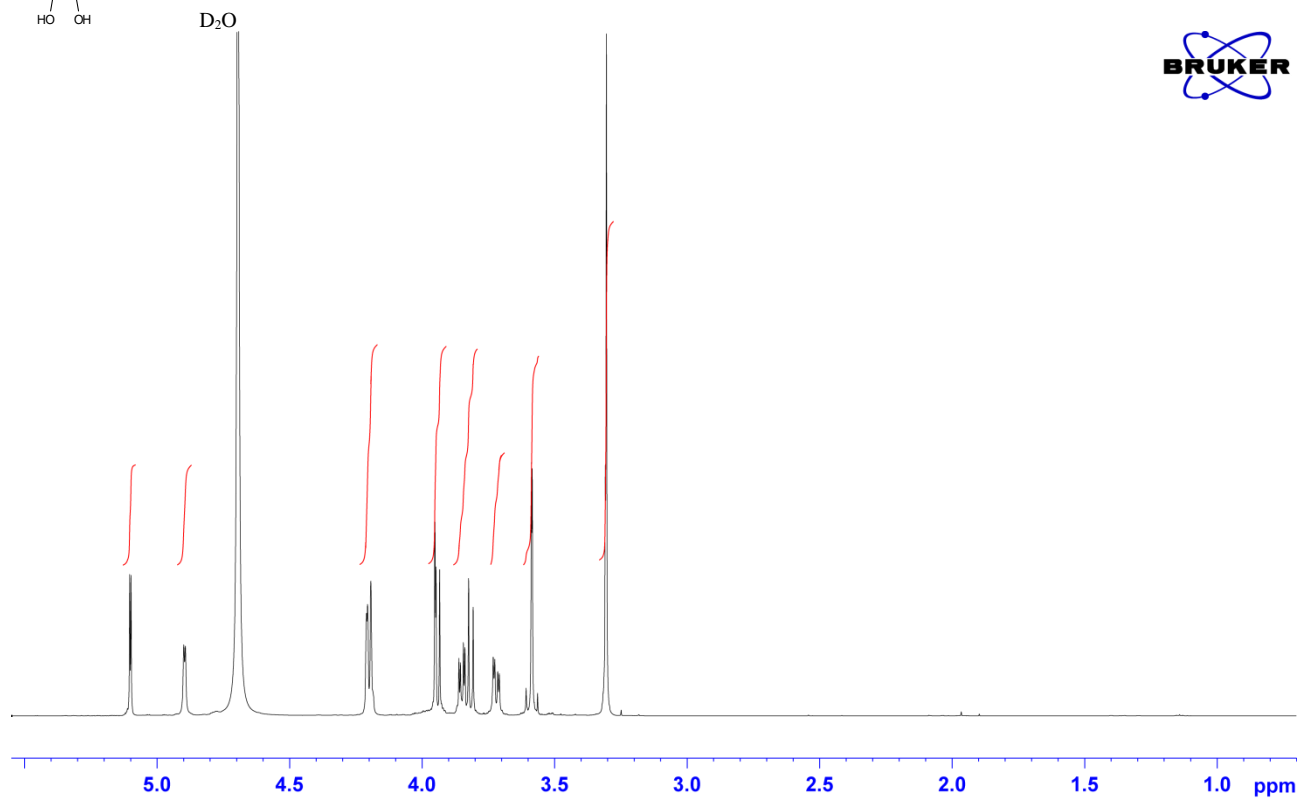
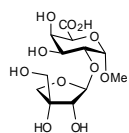
Compound 1



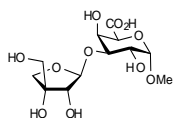
D₂O (1D NOESY presaturation)



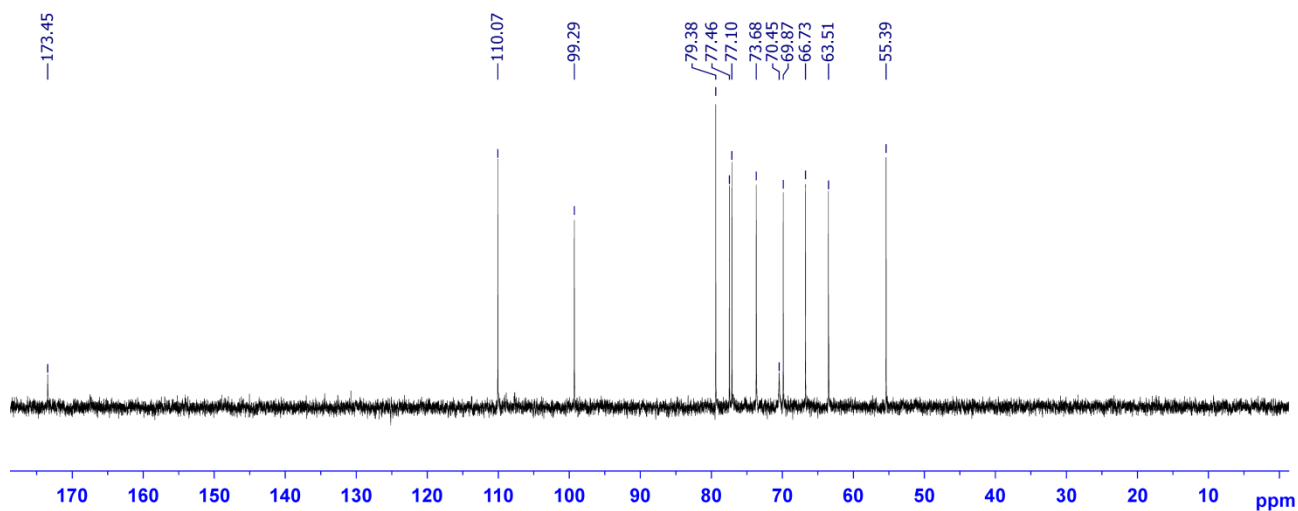
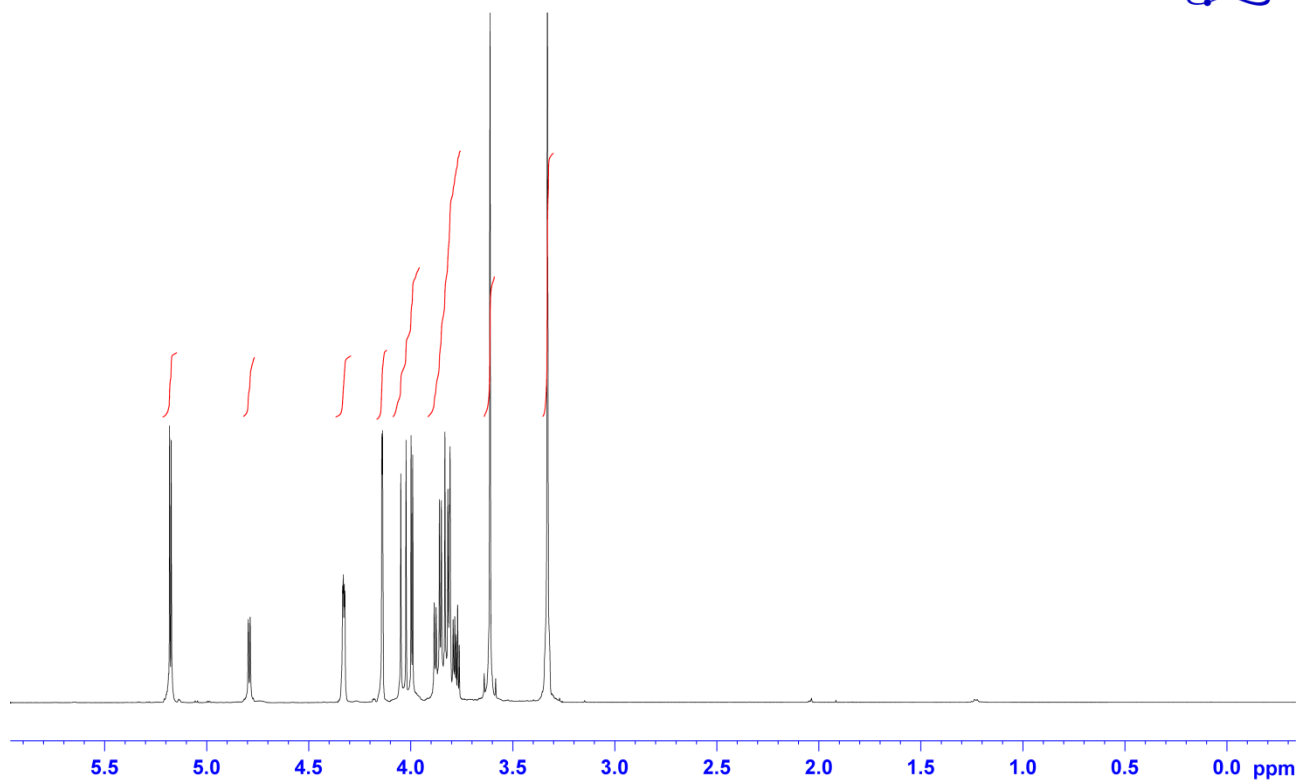
Compound 2



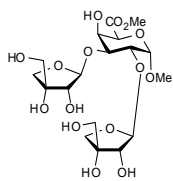
Compound 3



D₂O (1D NOESY presaturation)



Compound 4



D₂O (1D NOESY presaturation)

