

Supplementary Material

A chiral pool approach towards enantiopure building blocks for naturally occurring hydroporphyrins

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28334 Bremen, Germany

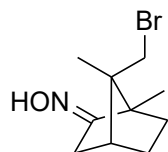
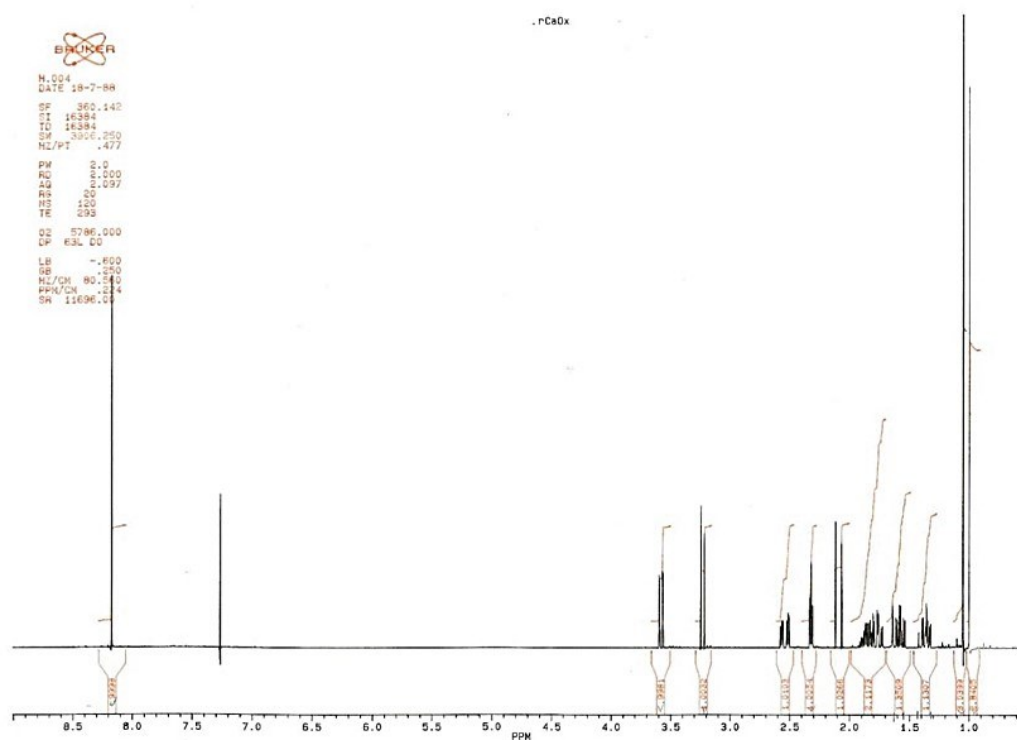
Email: mont@uni-bremen.de

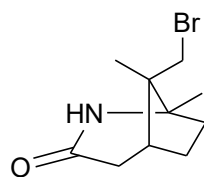
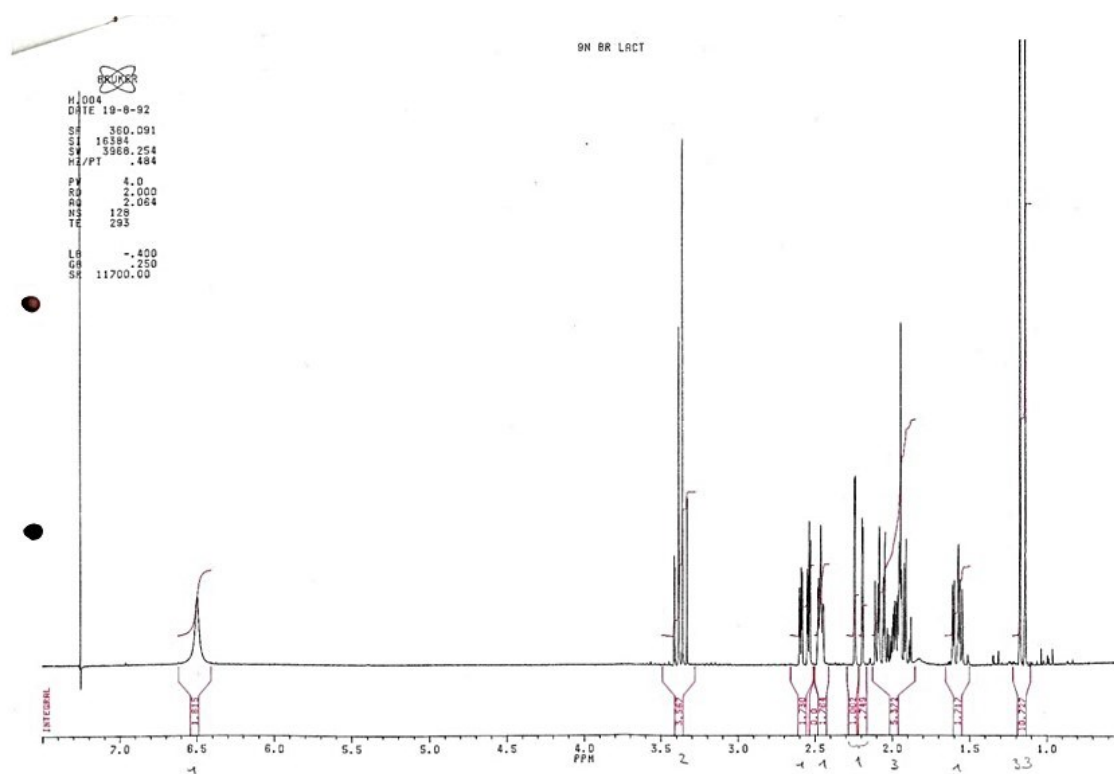
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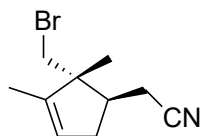
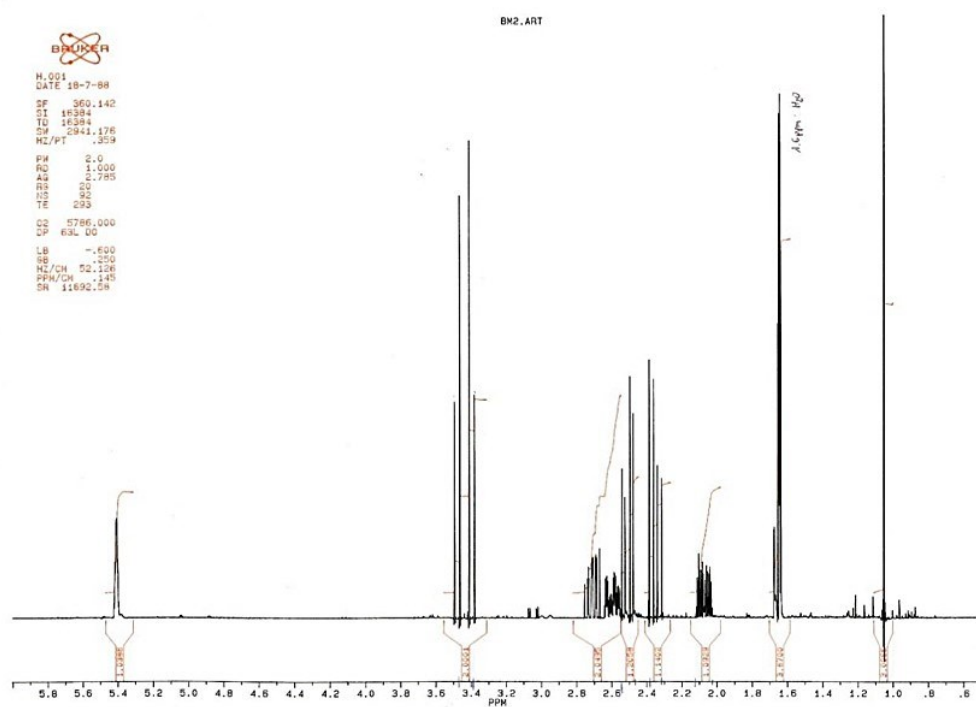
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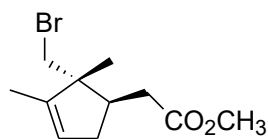
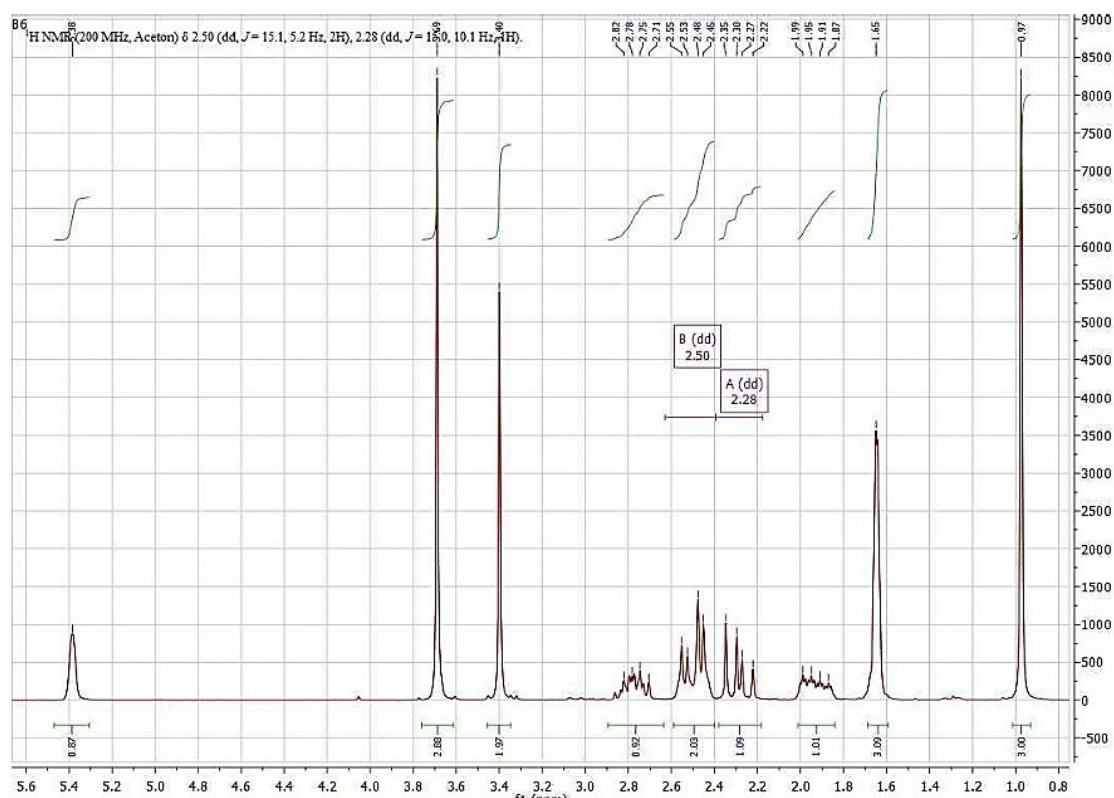
Chemical structure of 1-bromo-2-methyl-2-oxobicyclo[2.2.1]heptane. The structure shows a bicyclic system with a ketone group (=O) and a bromine atom (Br) attached to the bridgehead carbons. Red asterisks (*) are placed on the bridgehead carbons, indicating the sites of interest for the reaction.

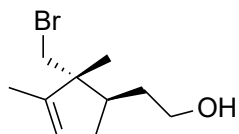
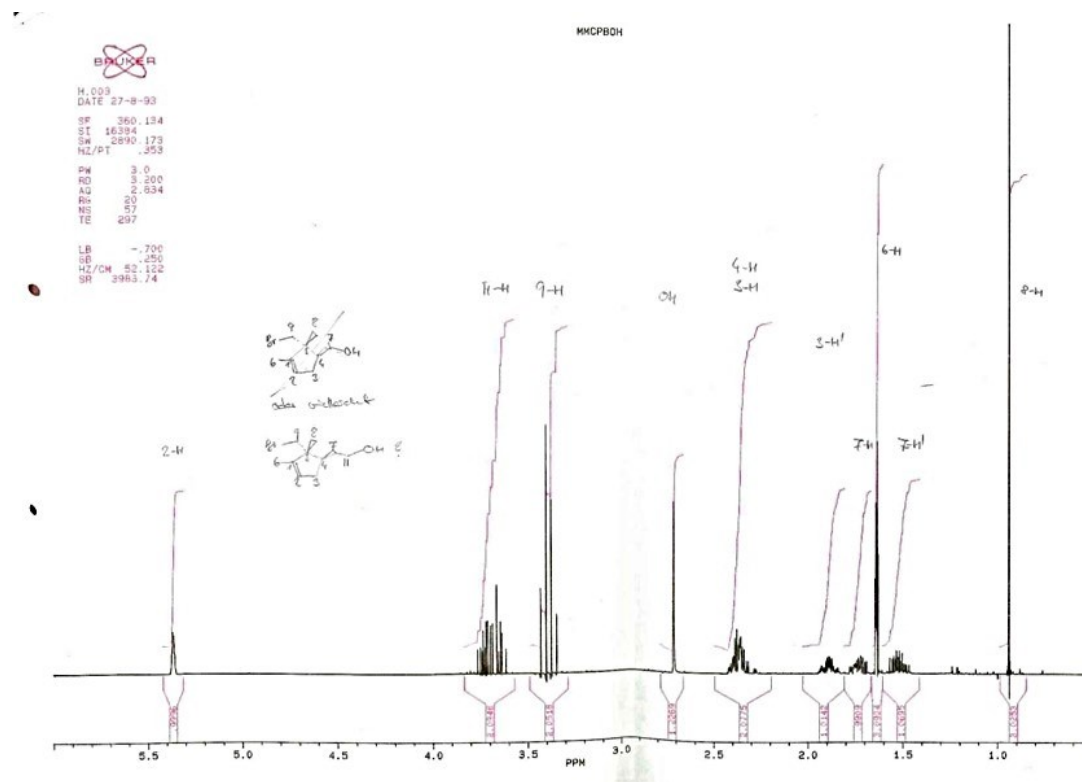
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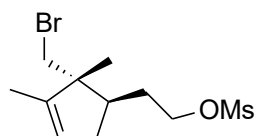
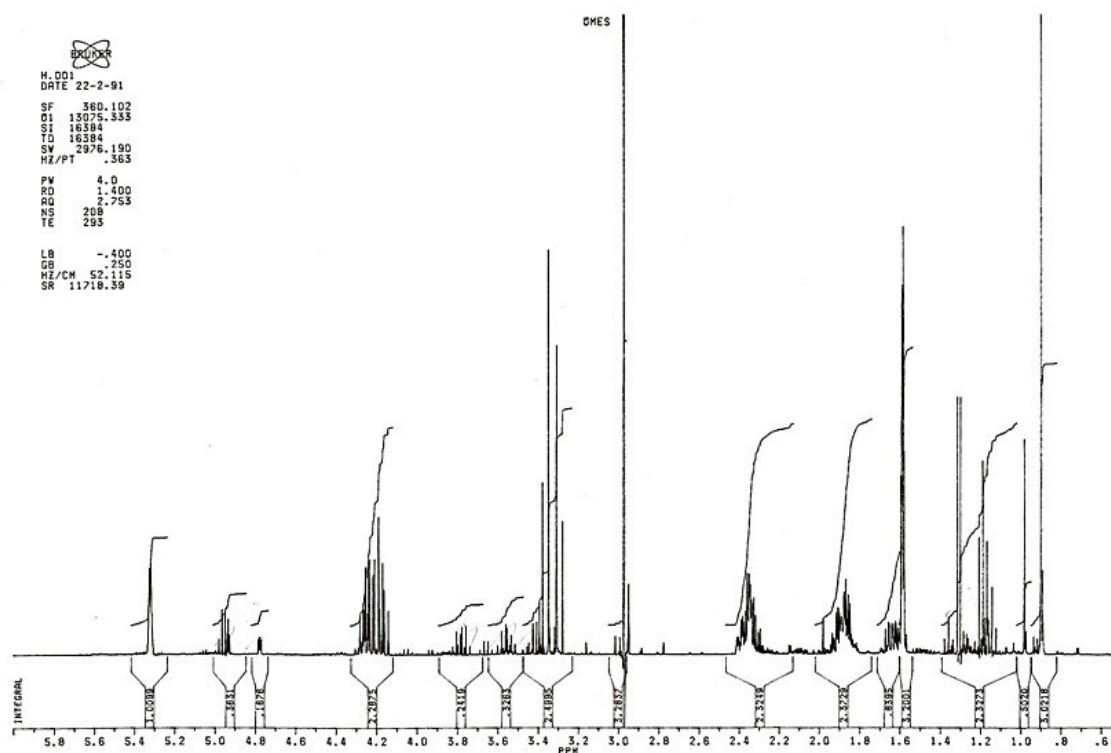
Compound 3**¹H NMR (360 MHz, CDCl₃)**

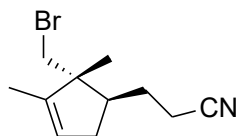
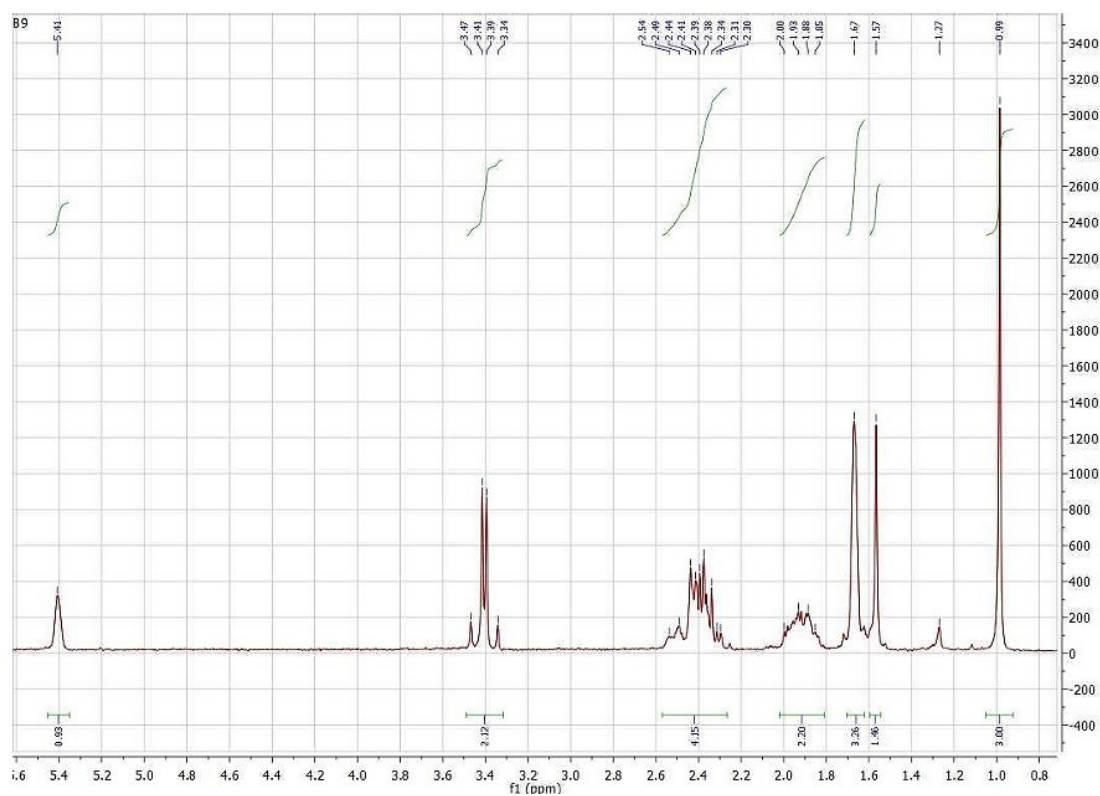
Compound 4 **^1H NMR (360 MHz, CDCl_3)**

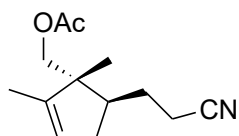
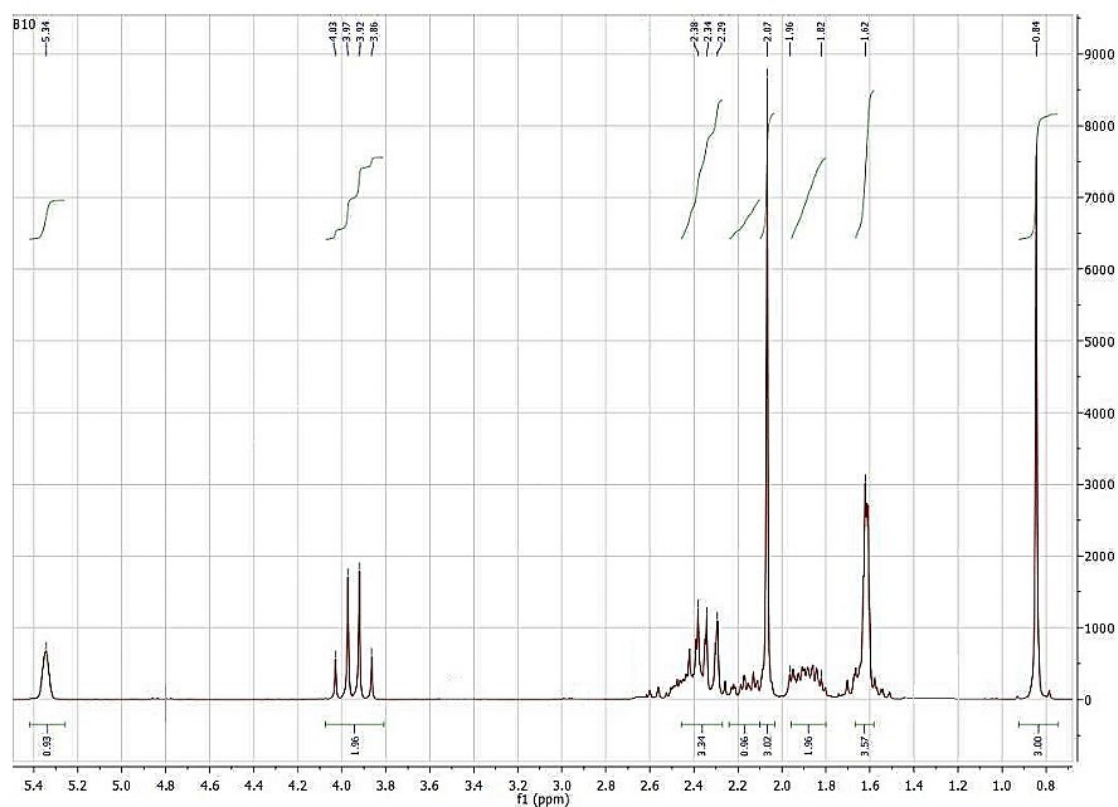
Compound 5**¹H NMR (360 MHz, CDCl₃)**

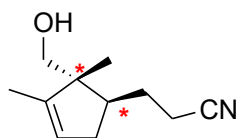
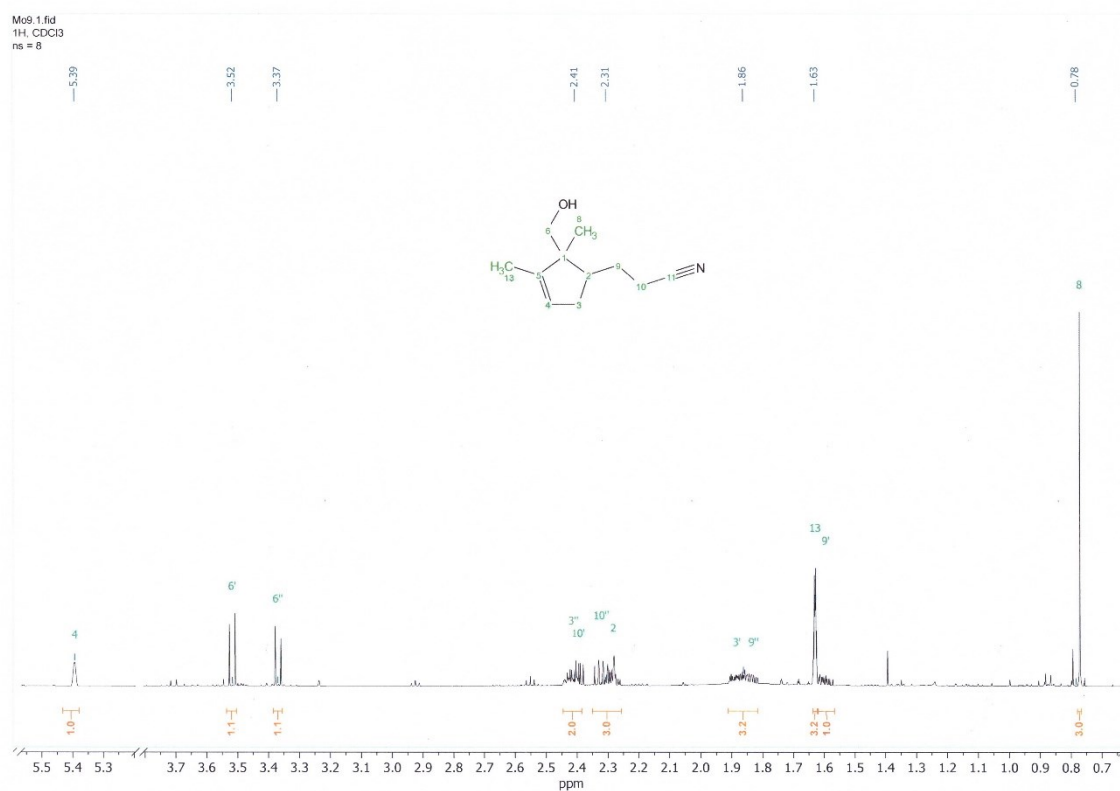
Compound 5a **^1H NMR (200 MHz, D_3COD_3)**

Compound 6**¹H NMR (360 MHz, CDCl₃)**

Compound 6a**¹H NMR (360 MHz, CDCl₃)**

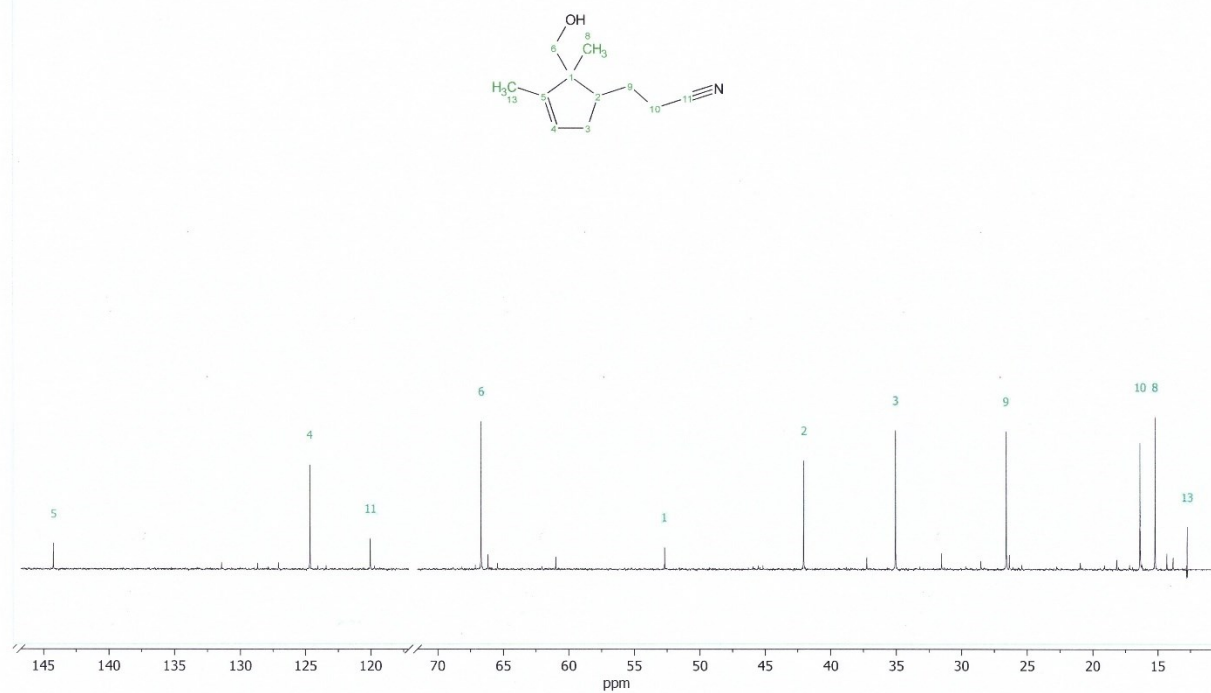
Compound 7 **^1H NMR (360 MHz, CDCl_3)**

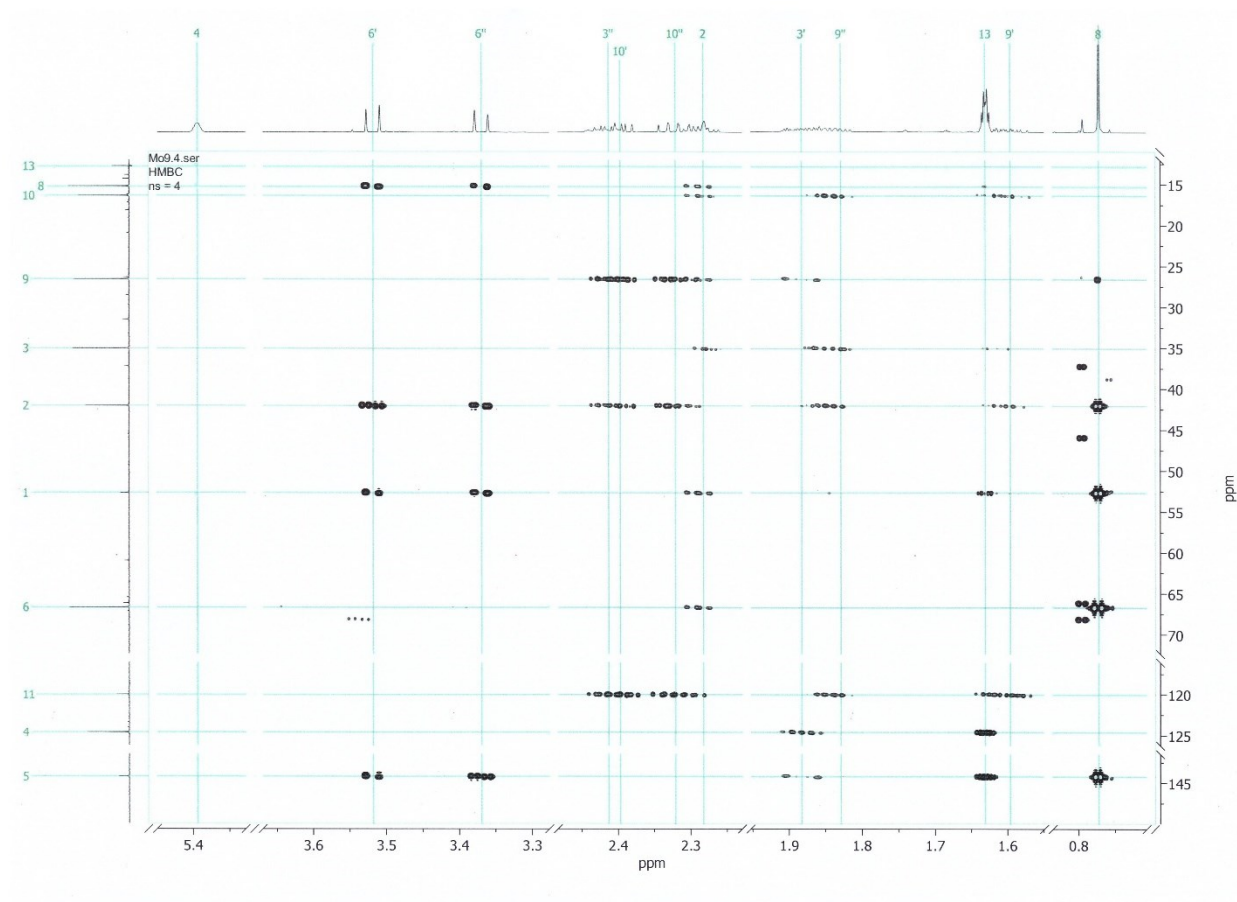
Compound 8**¹H NMR (360 MHz, CDCl₃)**

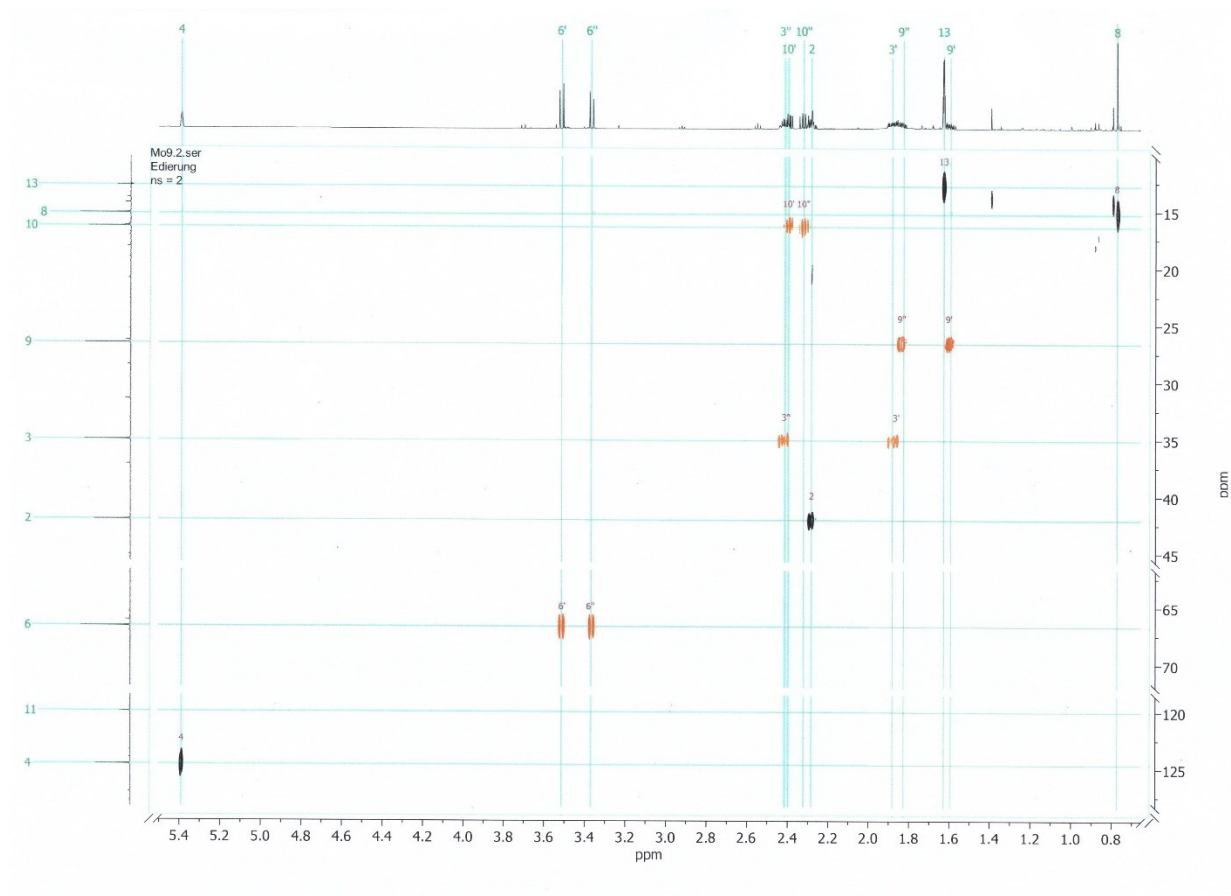
Compound 9 **^1H NMR (600 MHz, CDCl_3)**

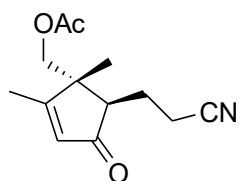
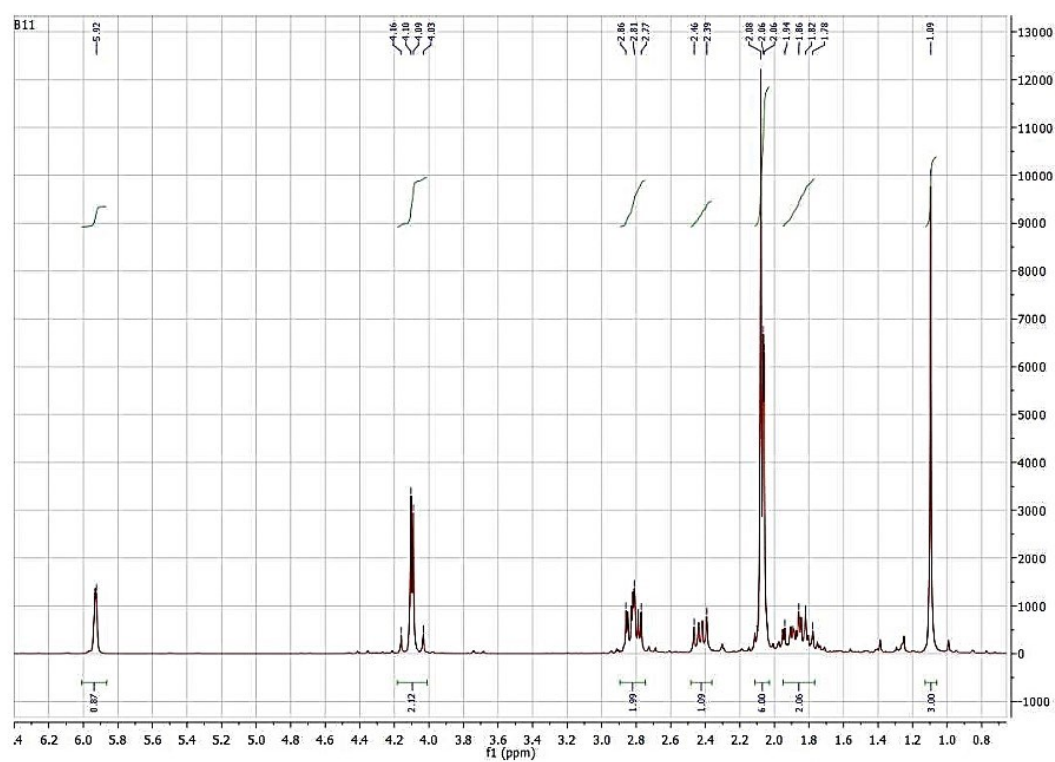
^{13}C NMR (600 MHz, CDCl_3)

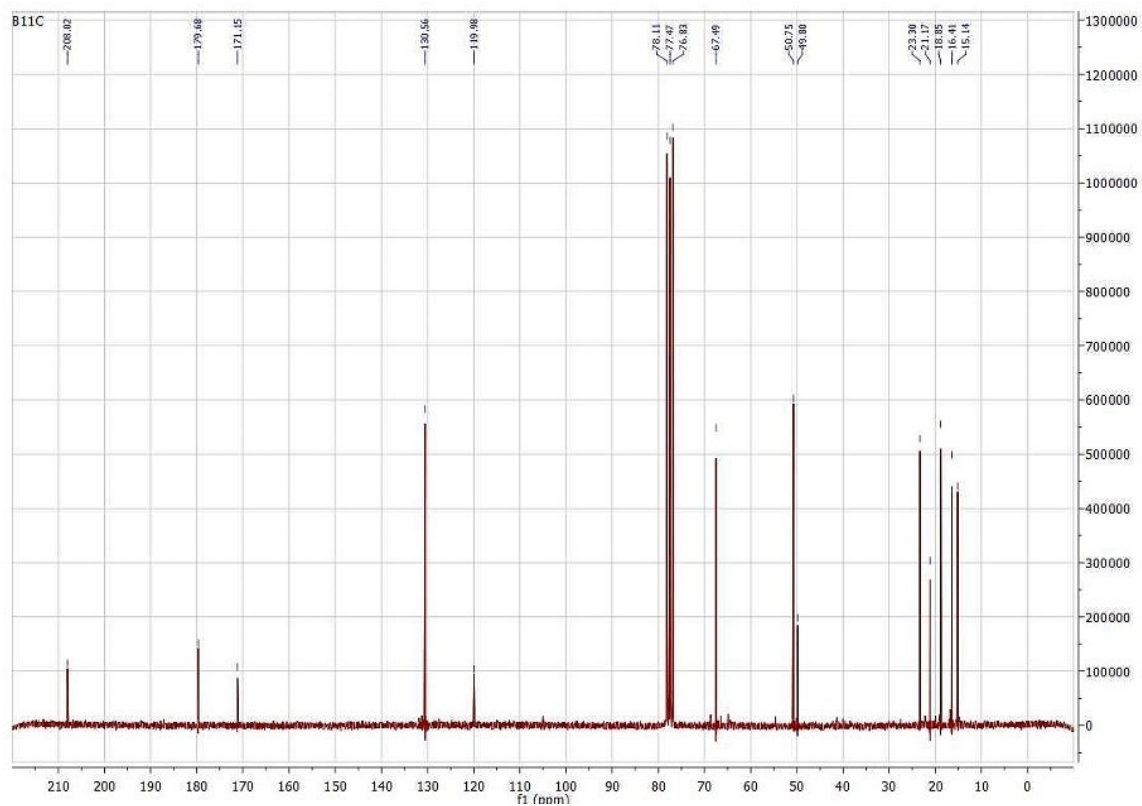
Mo9.3.fid
13C
ns = 128

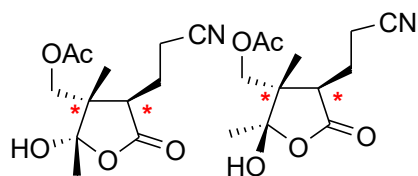
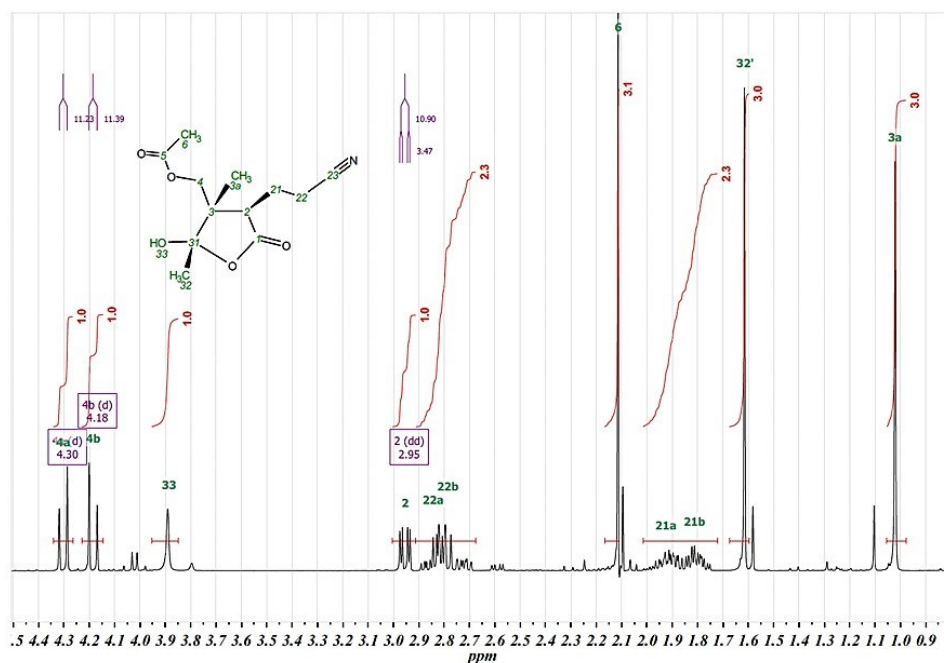


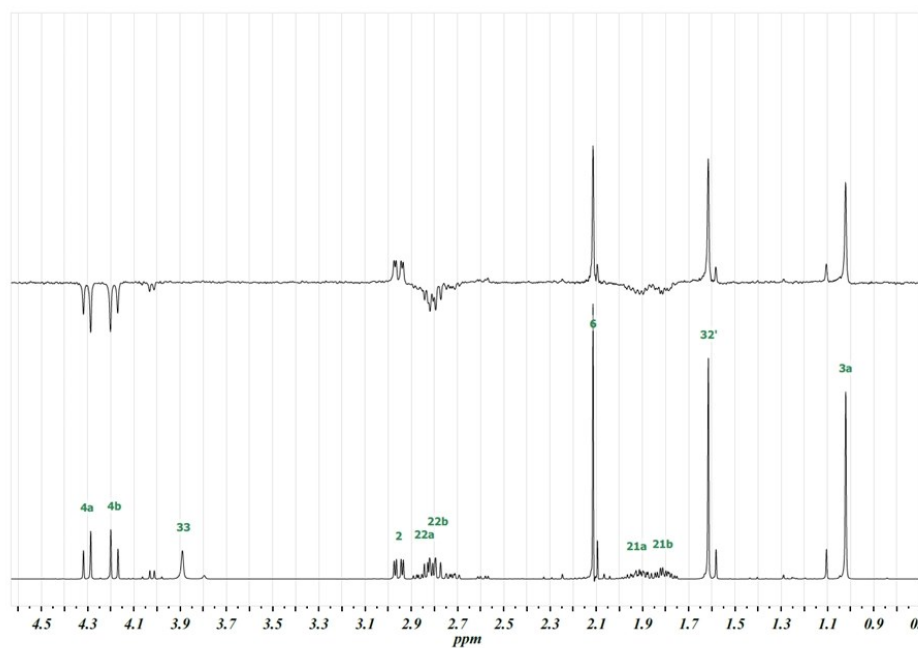
HMBC (600 MHz, CDCl₃)

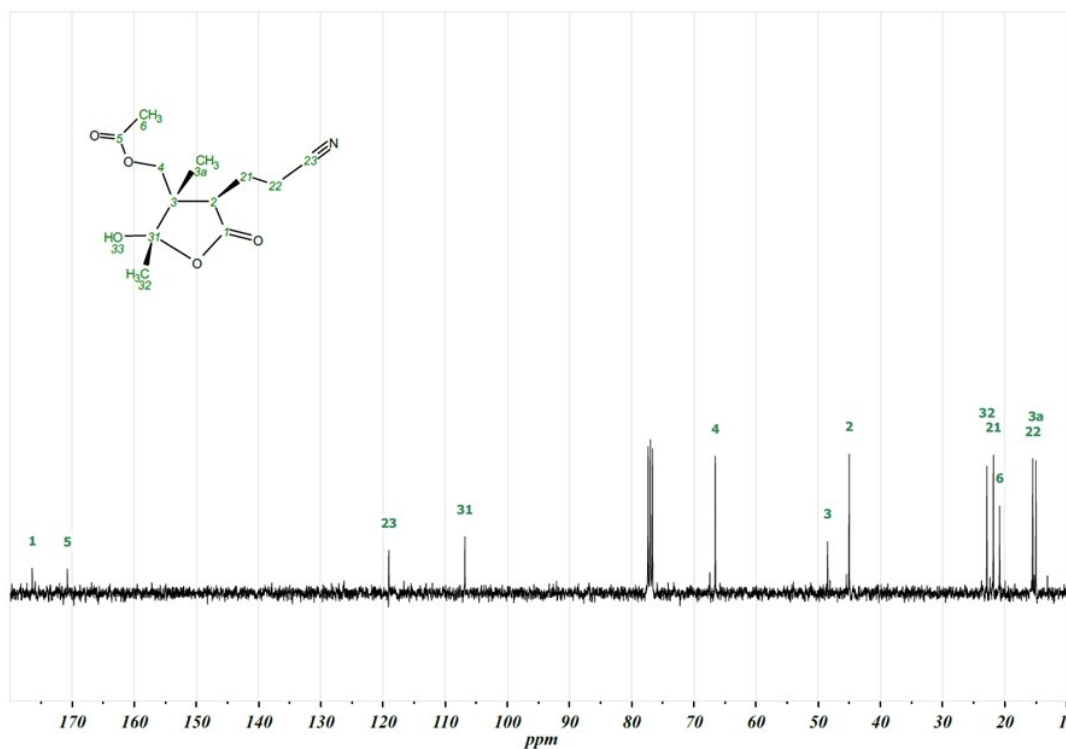
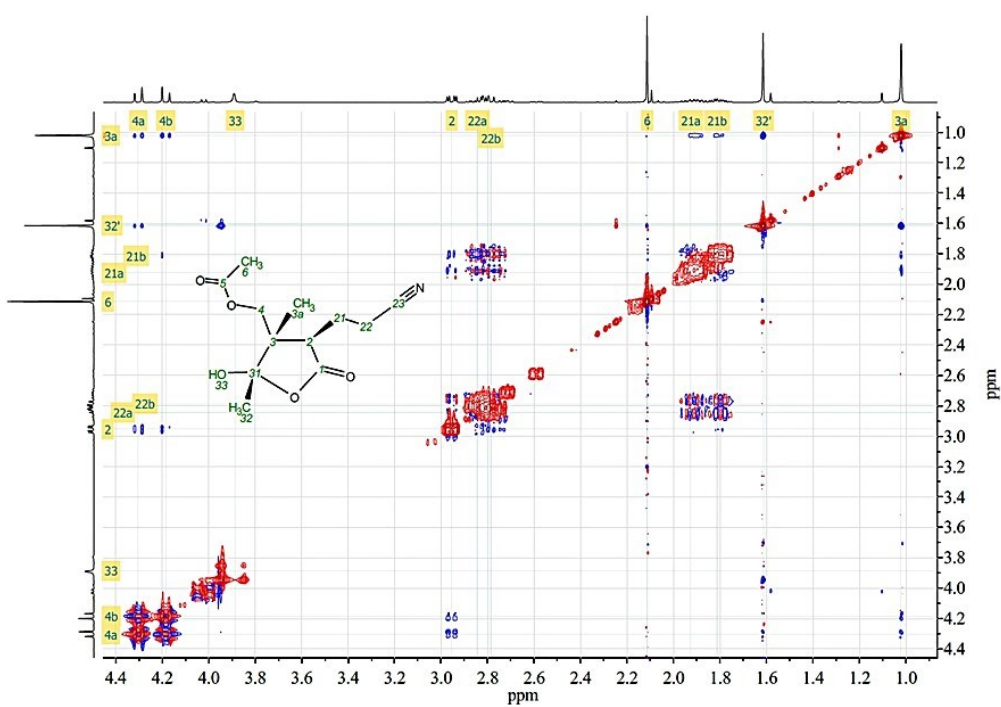
HSQC (600 MHz, CDCl₃, edited)

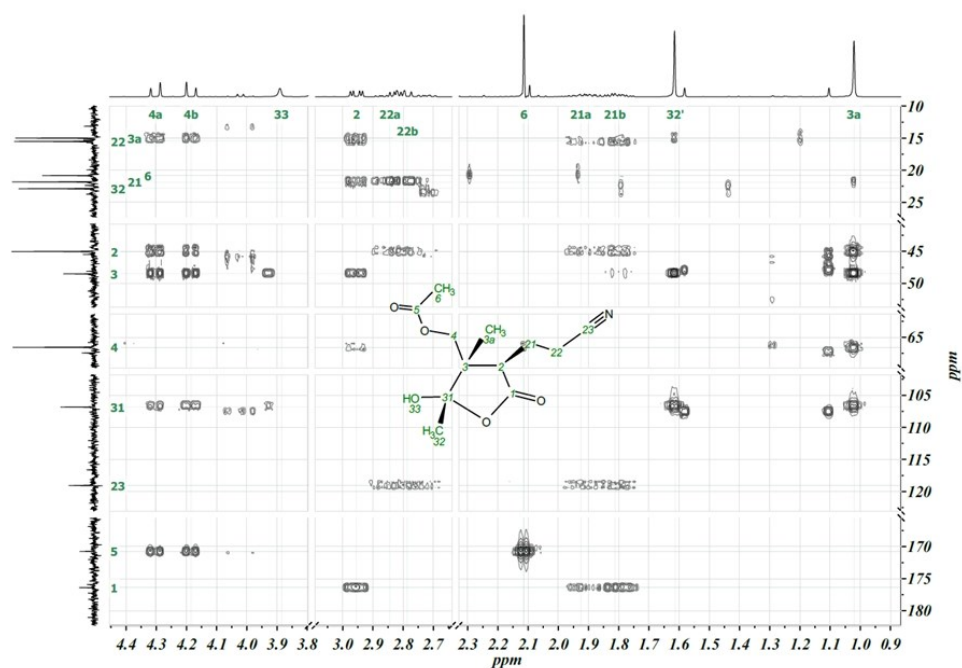
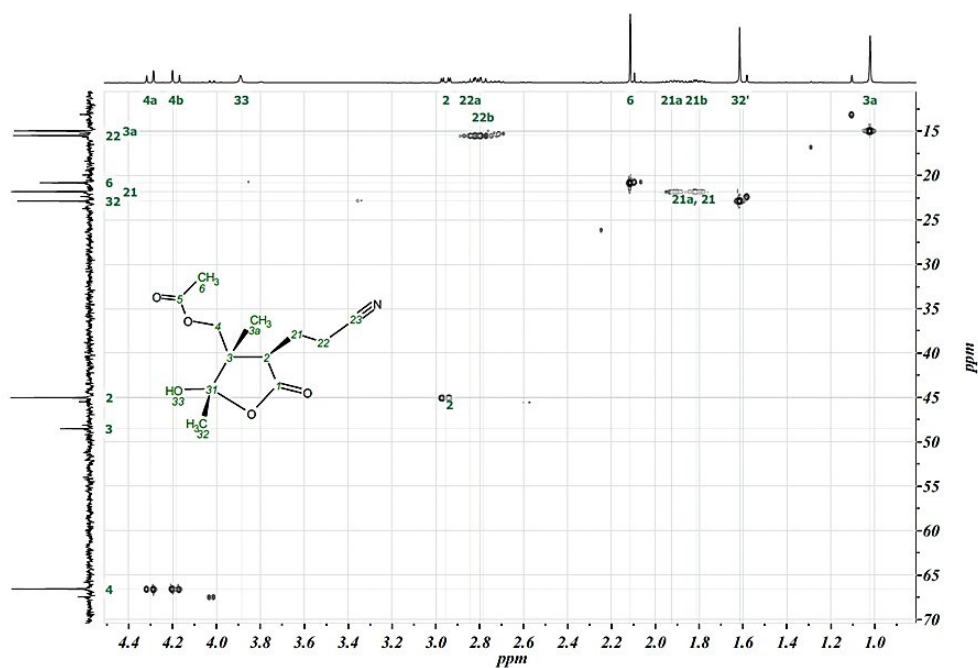
Compound 11**¹H NMR (360 MHz, CDCl₃)**

^{13}C NMR (90 MHz, CDCl_3)

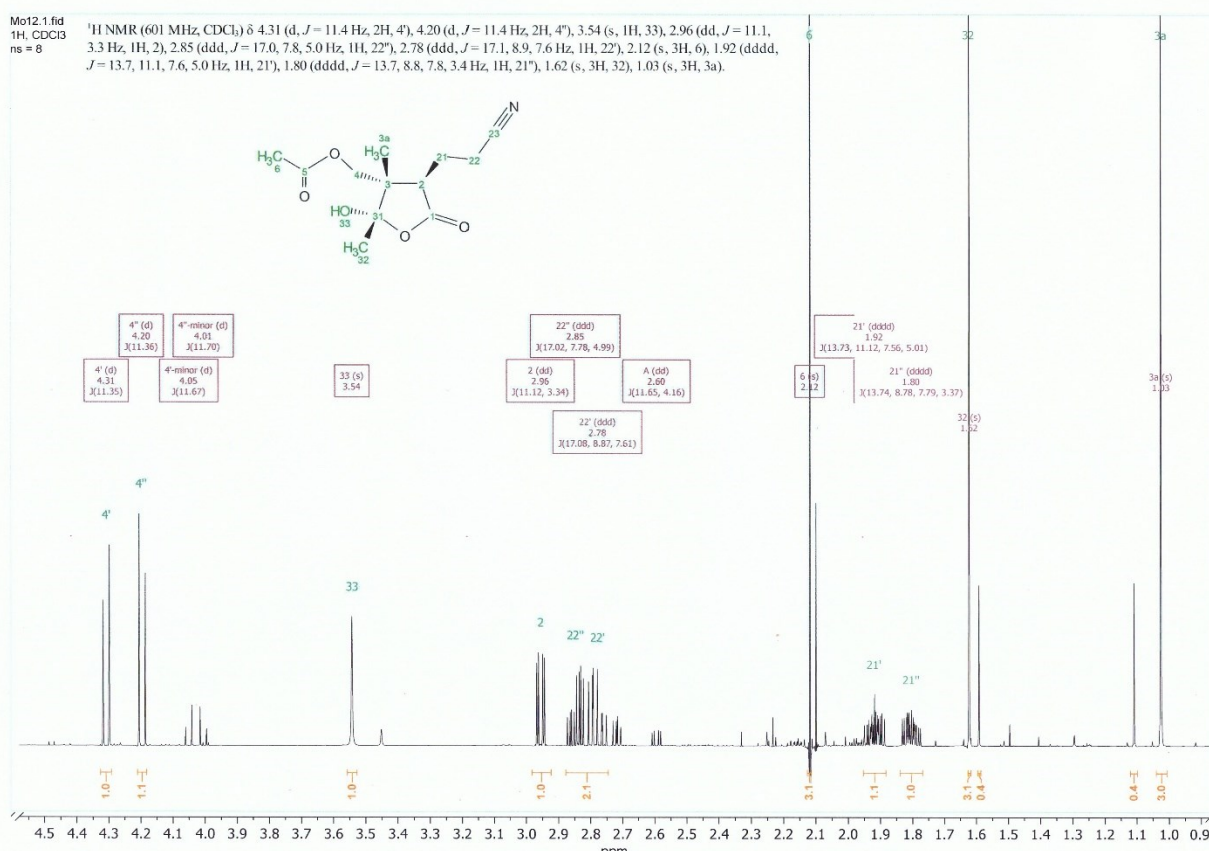
Compound 12a,b**¹H NMR (360 MHz, CDCl₃)**

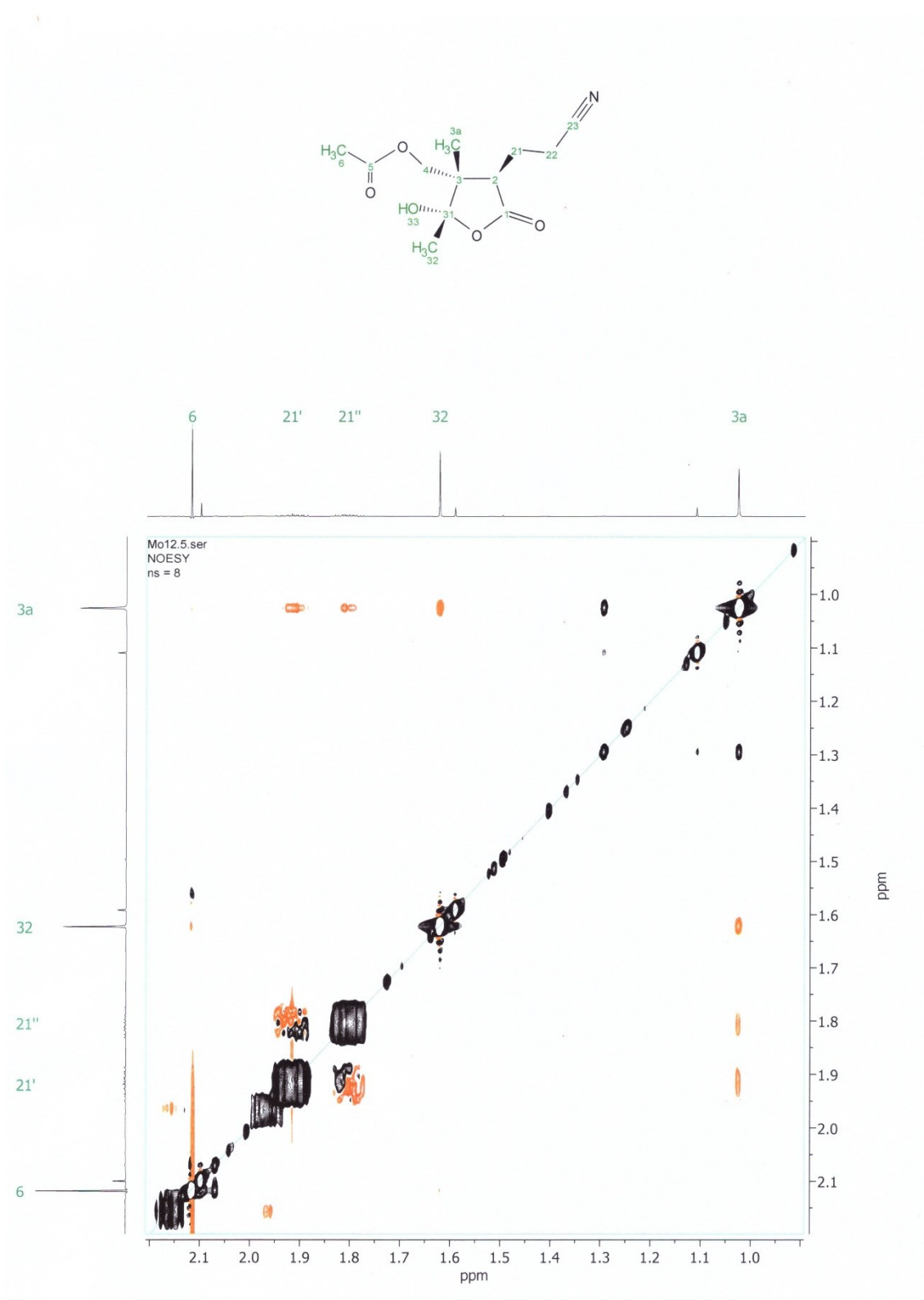
1D INEPT (360 MHz, CDCl₃)

^{13}C NMR (90 MHz, CDCl_3)COSY (360 MHz, CDCl_3)

HMBC (360 MHz, CDCl₃)HSQC (360 MHz, CDCl₃)

¹H NMR (601 MHz, CDCl₃) δ 4.31 (d, *J* = 11.4 Hz, 2H, 4'), 4.20 (d, *J* = 11.4 Hz, 2H, 4'), 3.54 (s, 1H, 3), 2.96 (dd, *J* = 11.1, 3.3 Hz, 1H, 2), 2.85 (ddd, *J* = 17.0, 7.8, 5.0 Hz, 1H, 22'), 2.78 (ddd, *J* = 17.1, 8.9, 7.6 Hz, 1H, 22), 2.12 (s, 3H, 6), 1.92 (dddd, *J* = 13.7, 11.1, 7.6, 5.0 Hz, 1H, 21'), 1.80 (dddd, *J* = 13.7, 8.8, 7.8, 3.4 Hz, 1H, 21'), 1.62 (s, 3H, 32), 1.03 (s, 3H, 3A).



NOESY (600 MHz, CDCl₃)

ClC1(C)C(C#N)C=C2C1C(=N2)C(=O)C3C1C

Mo-MMBIC1.4.fid
1H
ns = 8

Chemical structure of compound 11 is shown in the inset. The structure is a 1,3,4,5-tetrachloro-2-methyl-2H-1,2,4-triazole derivative with a diazomethyl group at position 4. The protons are numbered 1-16.

1H NMR spectrum (CDCl₃) of compound 11. The spectrum shows peaks at 5.97, 5.72, 3.92, 3.85, 2.48, 2.37, 1.97, 1.62, 1.29, and 1.05 ppm. The peaks are assigned to the following protons in the structure:

- 5.97 ppm (s, 1H, 8)
- 5.72 ppm (s, 1H, 7)
- 3.92 ppm (s, 3H, 10)
- 3.85 ppm (s, 3H, 11)
- 2.48 ppm (s, 3H, 14)
- 2.37 ppm (s, 3H, 15)
- 1.97 ppm (s, 3H, 13)
- 1.62 ppm (s, 3H, 12)
- 1.29 ppm (s, 3H, 16)
- 1.05 ppm (s, 3H, 11)

^{13}C NMR (150 MHz, CDCl_3)