Supporting Information

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Multigram-Scale Access to 2-Oxaadamantan-1-amine and 2-Oxaadamantan-1-ol via Optimized Synthesis of Bicyclo[3.3.1]nonane-3,7-dione

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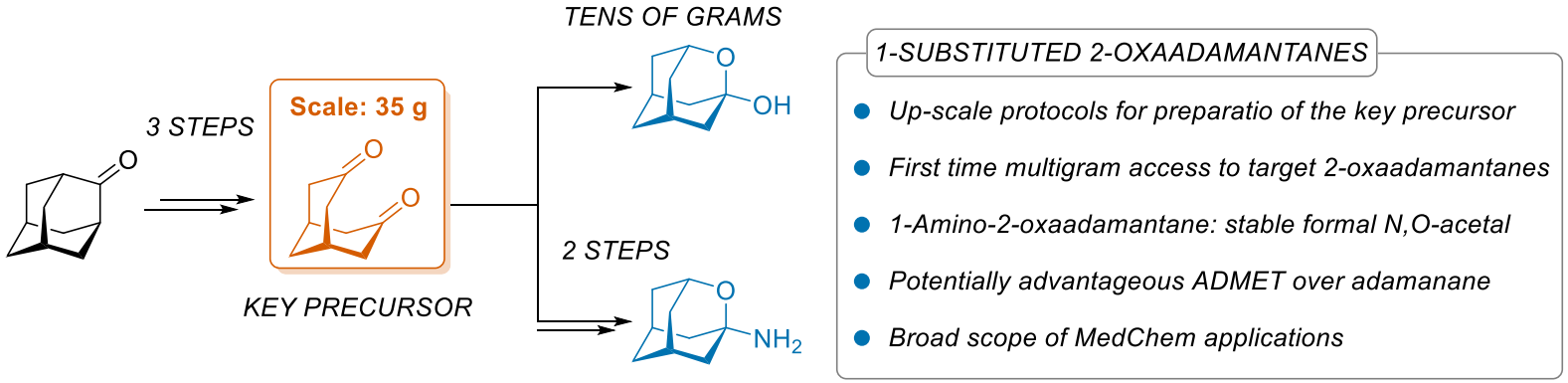

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X-ray experimental part

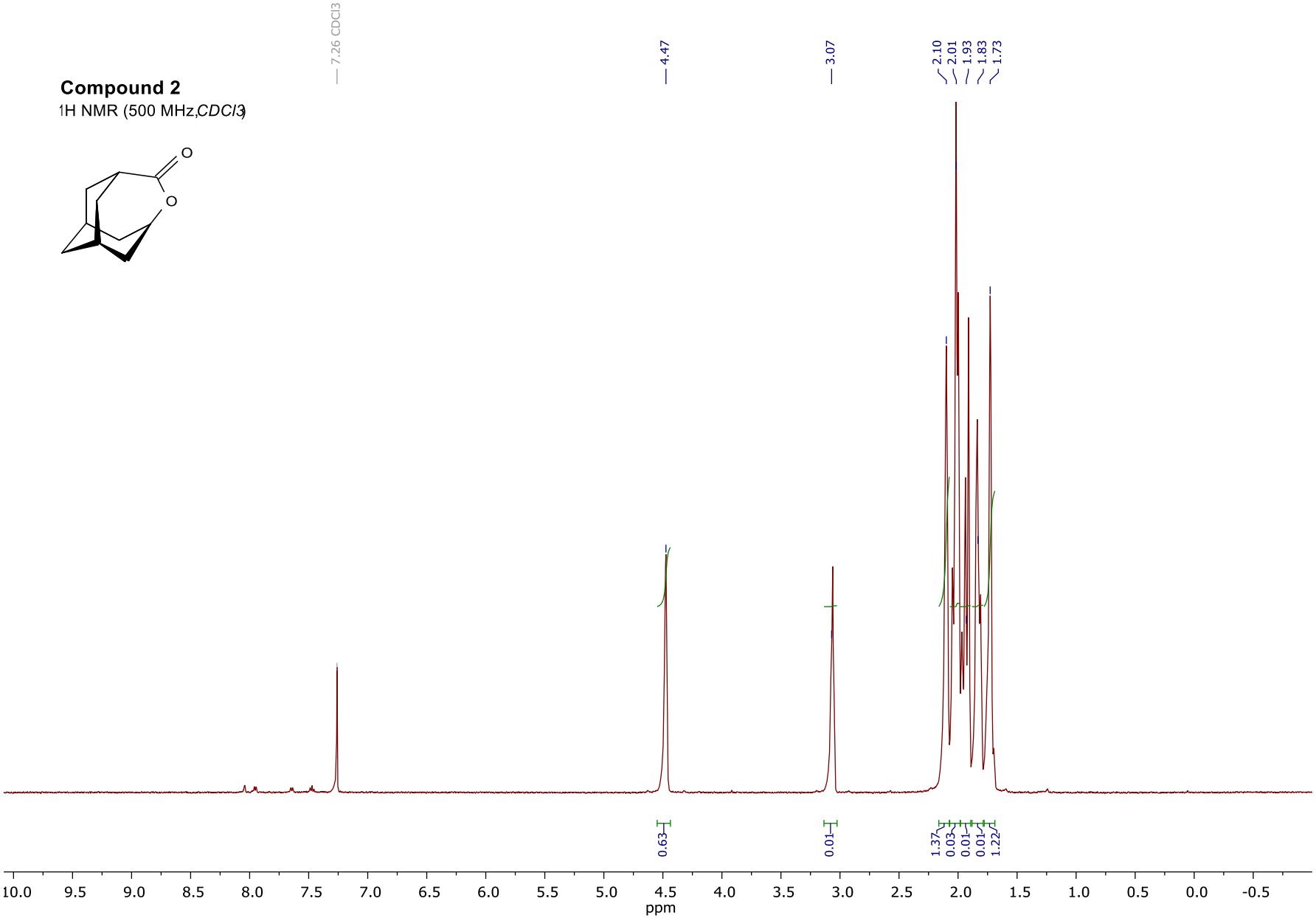
The colourless crystals of compound **3** ($C_{10}H_{18}O_2$) are monoclinic. At 173 K a = 13.081(9), b = 17.450(16), c = 10.354(6) Å, β = 128.81(4)°, V = 1842(3) Å^3, M_r = 170.24, Z = 8, space group $C2/c$, d_{calc}= 1.228 g/cm^3, $\mu(MoK_\alpha)$ = 0.083 mm^{-1}, F(000) = 752. Intensities of 10135 reflections (1619 independent, R_{int}=0.1214) were measured on the Bruker APEX II diffractometer (graphite monochromated MoK_α radiation, CCD detector, φ- and ω-scaning, $2\Theta_{max}$ = 50°). The structure was solved by direct method using OLEX2 [1] package with SHELXT [2] and SHELXL modules [3]. Positions of the hydrogen atoms were located from electron density difference maps and refined using "riding" model with U_{iso} = nU_{eq} of the carrier atom ((n = 1.5 for hydroxyl groups and n = 1.2 for other hydrogen atoms). Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 1619 reflections was converged to wR_2 = 0.2847 (R_1 = 0.0844 for 650 reflections with F>4σ(F), S = 0.919). The final atomic coordinates, and crystallographic data for molecule **3** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 2543739).

The yellow crystals of compound **7** ($C_9H_{16}NOCl$) are monoclinic. At 173 K a = 6.2648(2), b = 15.0005(4), c = 9.8399(3) Å, β = 93.320(2)°, V = 923.15(5) Å^3, M_r = 189.68, Z = 4, space group $P2_1/n$, d_{calc}= 1.365 g/cm^3, $\mu(MoK_\alpha)$ = 0.366 mm^{-1}, F(000) = 408. Intensities of 6367 reflections (1633 independent, R_{int}=0.0261) were measured on the Bruker APEX II diffractometer (graphite monochromated MoK_α radiation, CCD detector, φ- and ω-scaning, $2\Theta_{max}$ = 50°). The structure was solved by direct method using OLEX2 [1] package with SHELXT [2] and SHELXL modules [3]. Positions of the hydrogen atoms were located from electron density difference maps and refined using "riding" model with U_{iso} = nU_{eq} of the carrier atom ((n = 1.5 for protonated amino group and n = 1.2 for other hydrogen atoms). Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 1633 reflections was converged to wR_2 = 0.086 (R_1 = 0.0329 for 1444 reflections with F>4σ(F), S = 1.088). The final atomic coordinates, and crystallographic data for molecule **7** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2

1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 2543738).

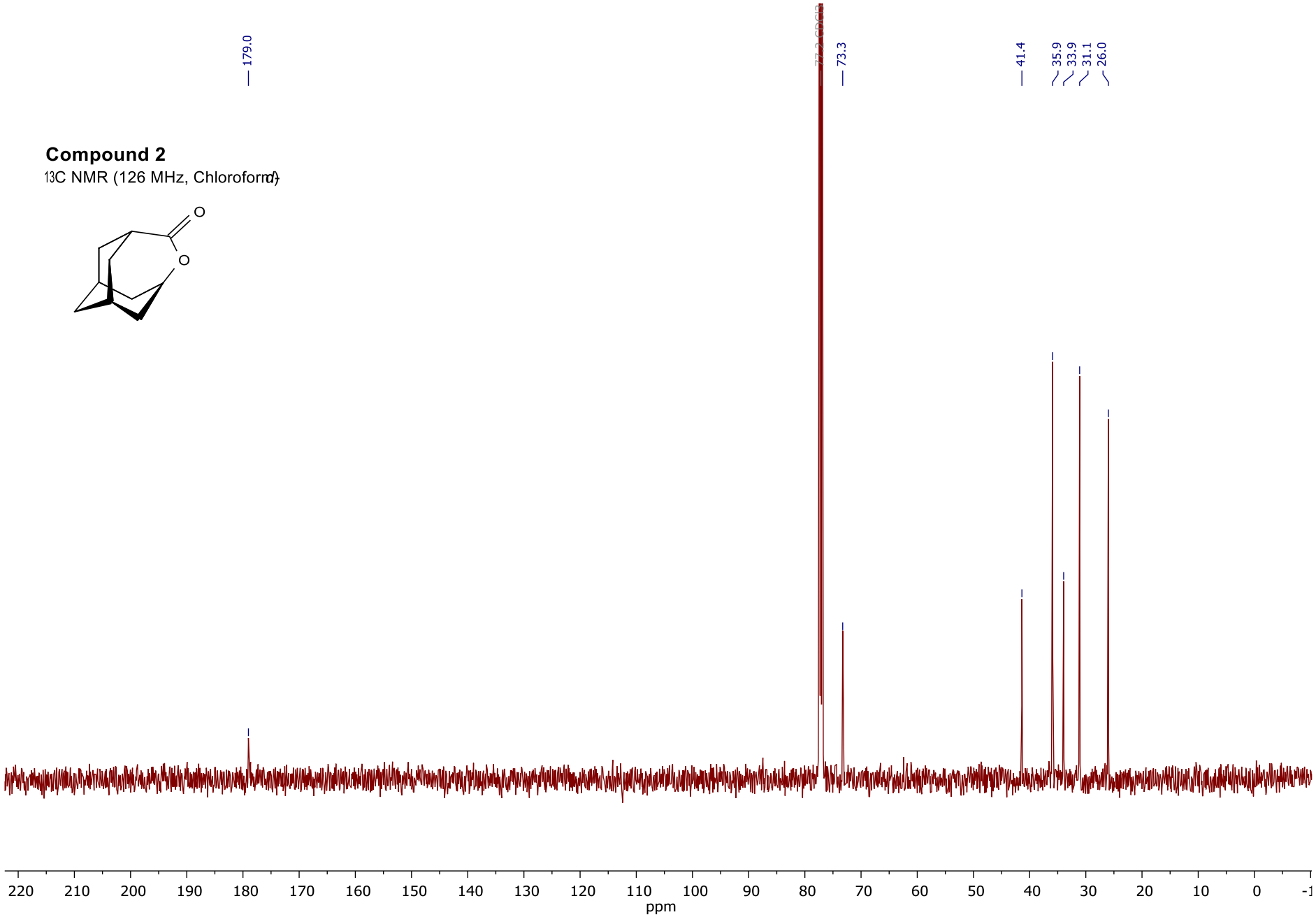
1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2* : A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339–341. https://doi.org/10.1107/S0021889808042726.
2. Sheldrick, G. M. *SHELXT* – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A:Found. Adv.* **2015**, *71* (1), 3–8. https://doi.org/10.1107/S2053273314026370.
3. Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr., Sect. C:Struct. Chem.* **2015**, *71* (1), 3–8. https://doi.org/10.1107/S2053229614024218.

Copies of NMR spectra of the prepared compounds



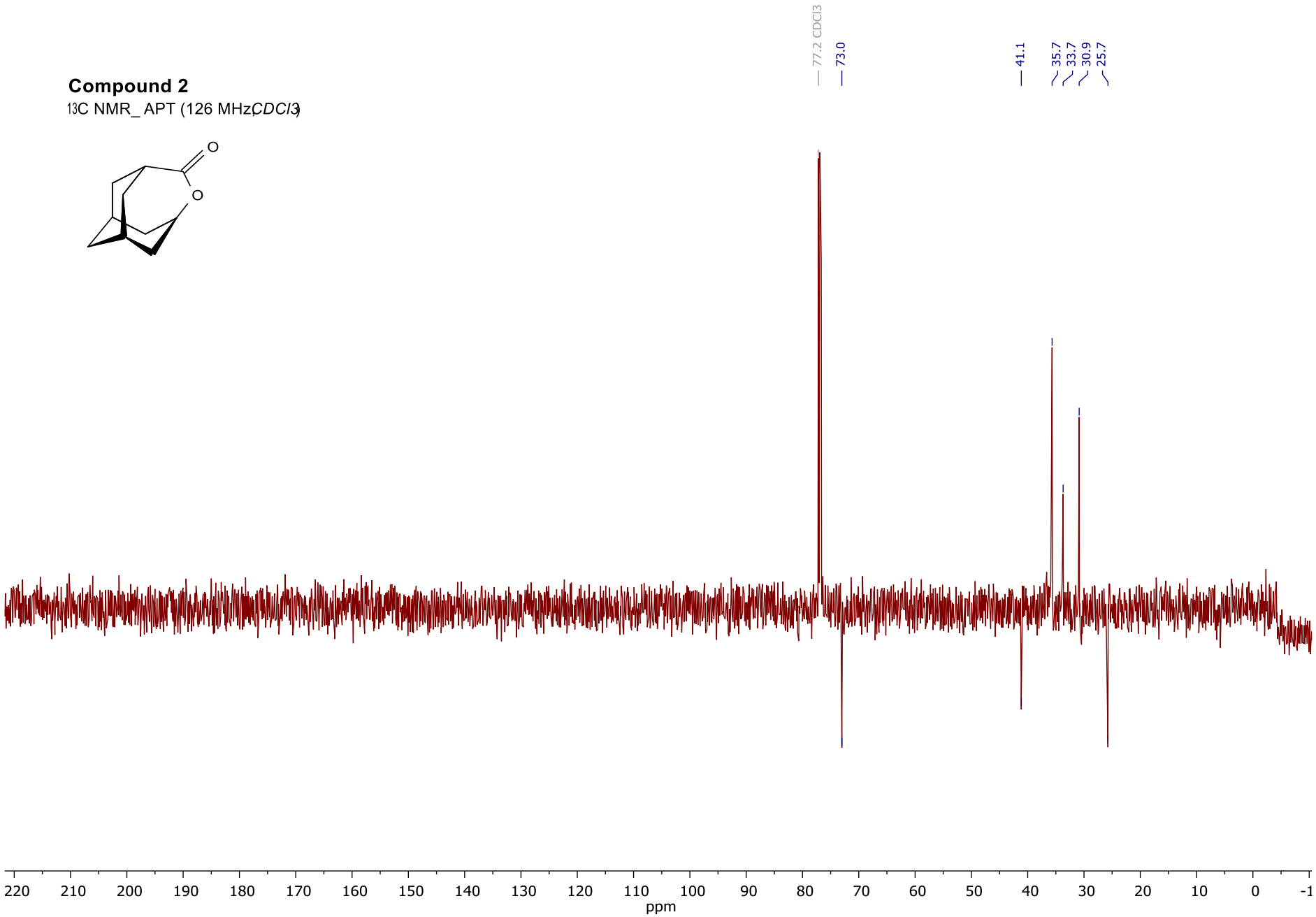
Compound 2

^{13}C NMR (126 MHz, Chloroform-d)



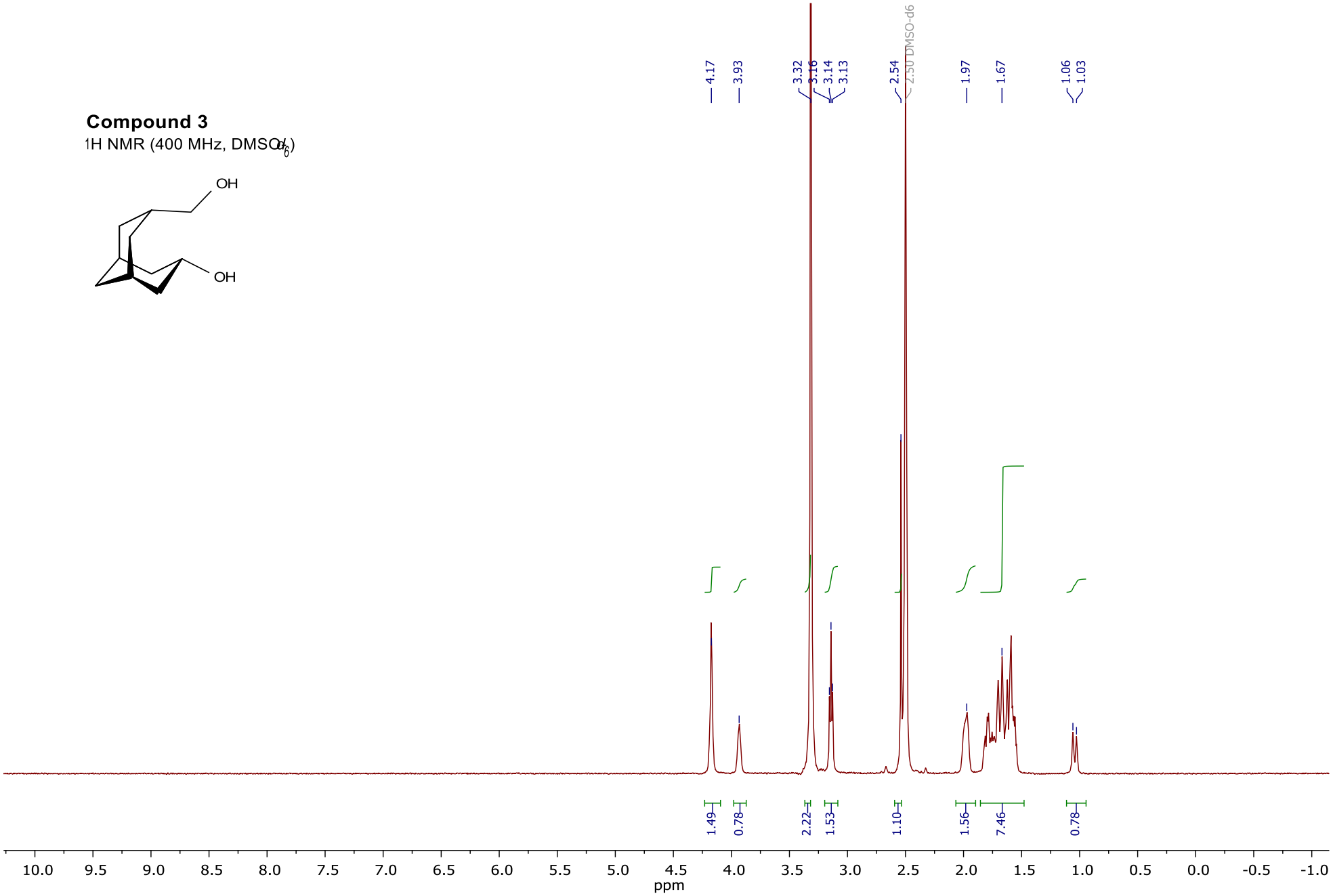
Compound 2

^{13}C NMR_ APT (126 MHz*CDCl3*)



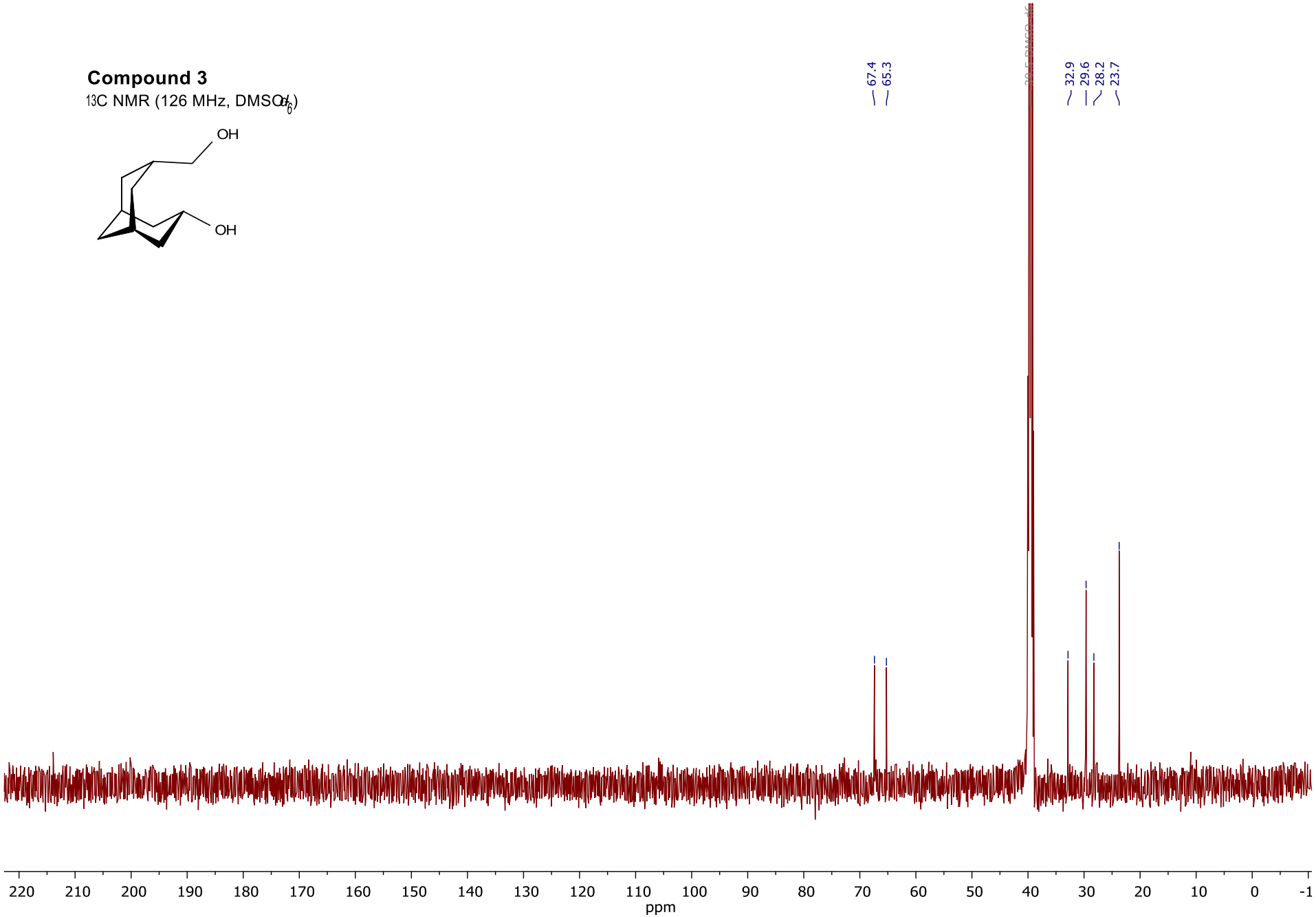
Compound 3

^{1}H NMR (400 MHz, DMSO-d_6)



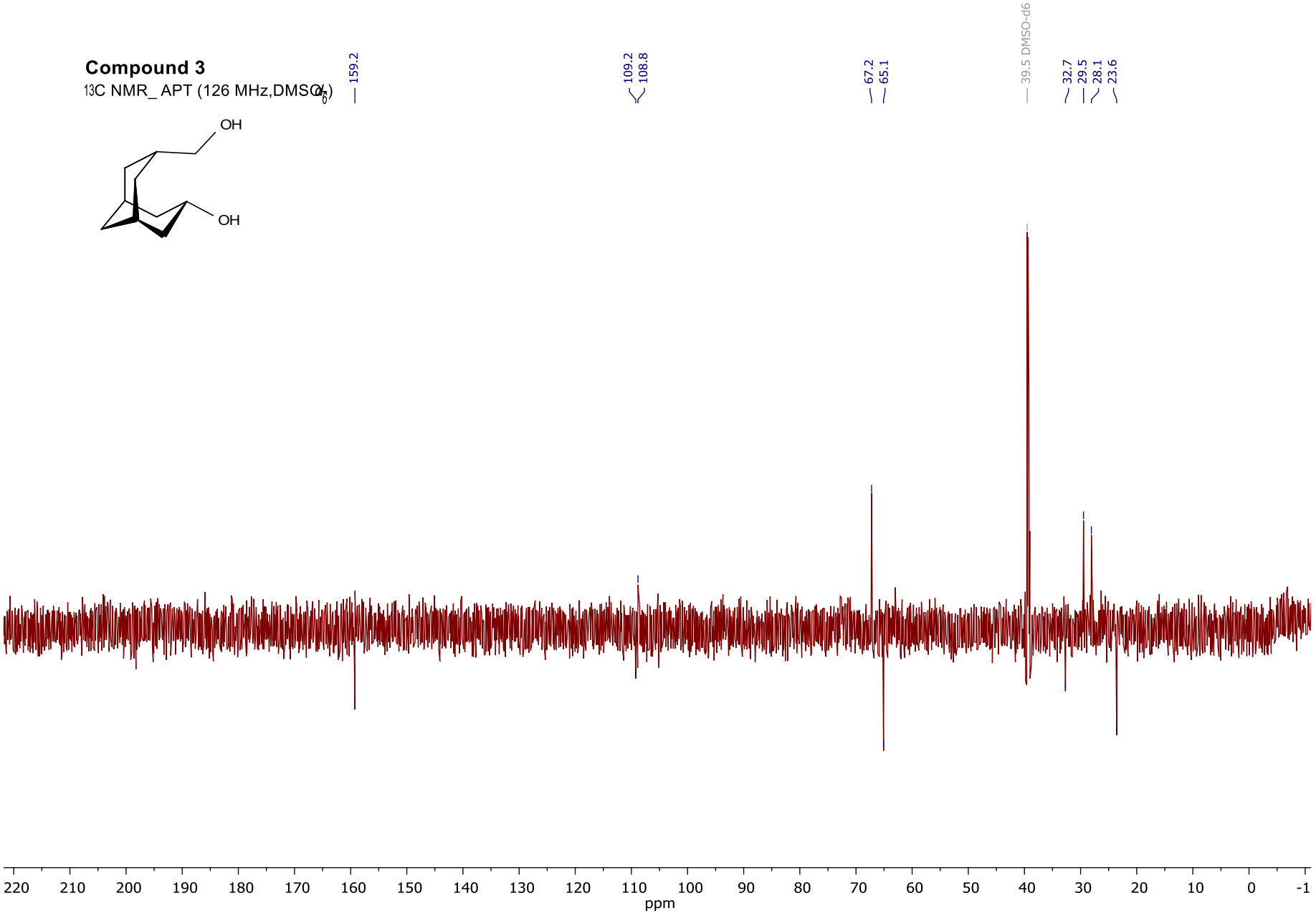
Compound 3

^{13}C NMR (126 MHz, $DMSO-d_6$)



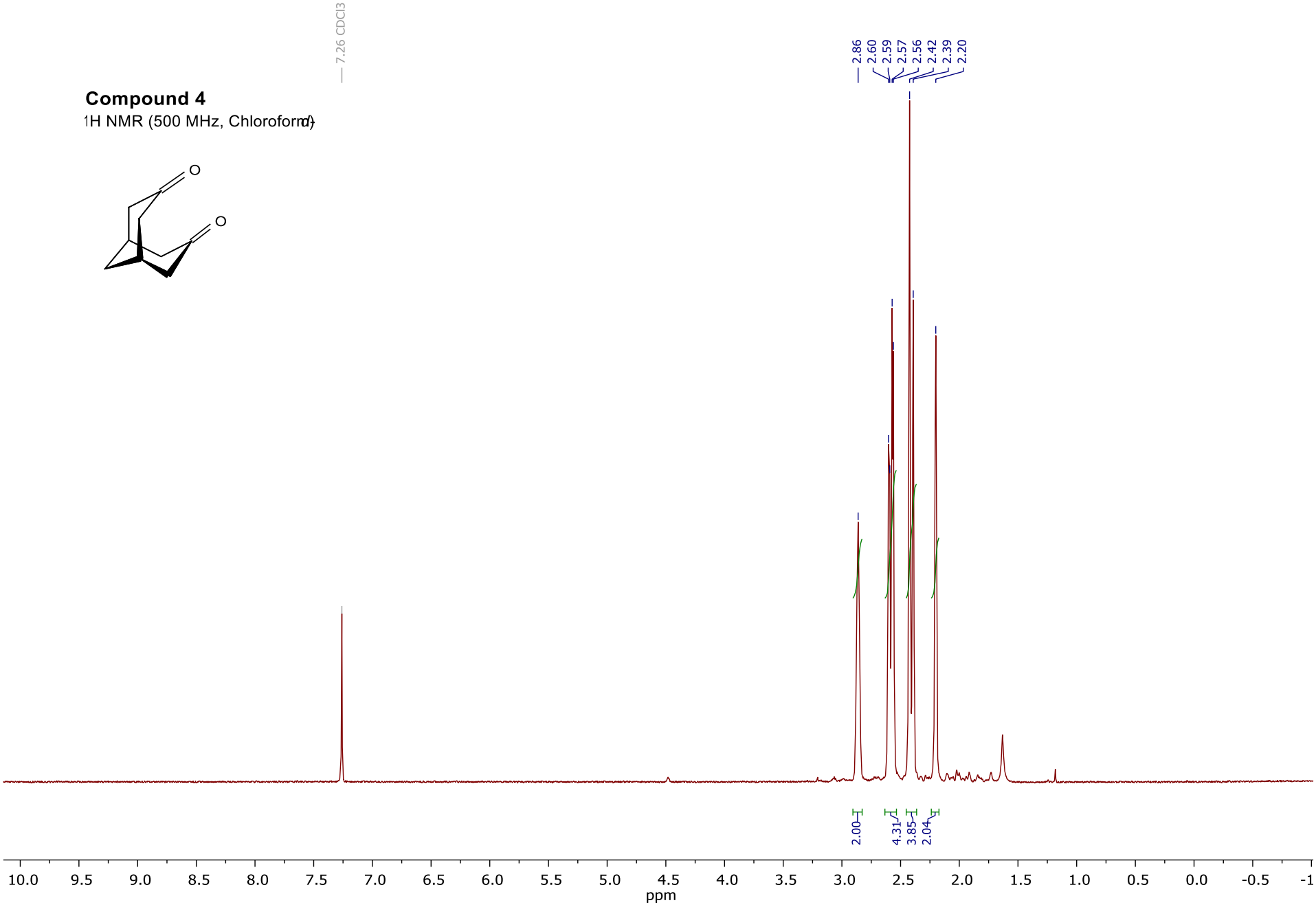
Compound 3

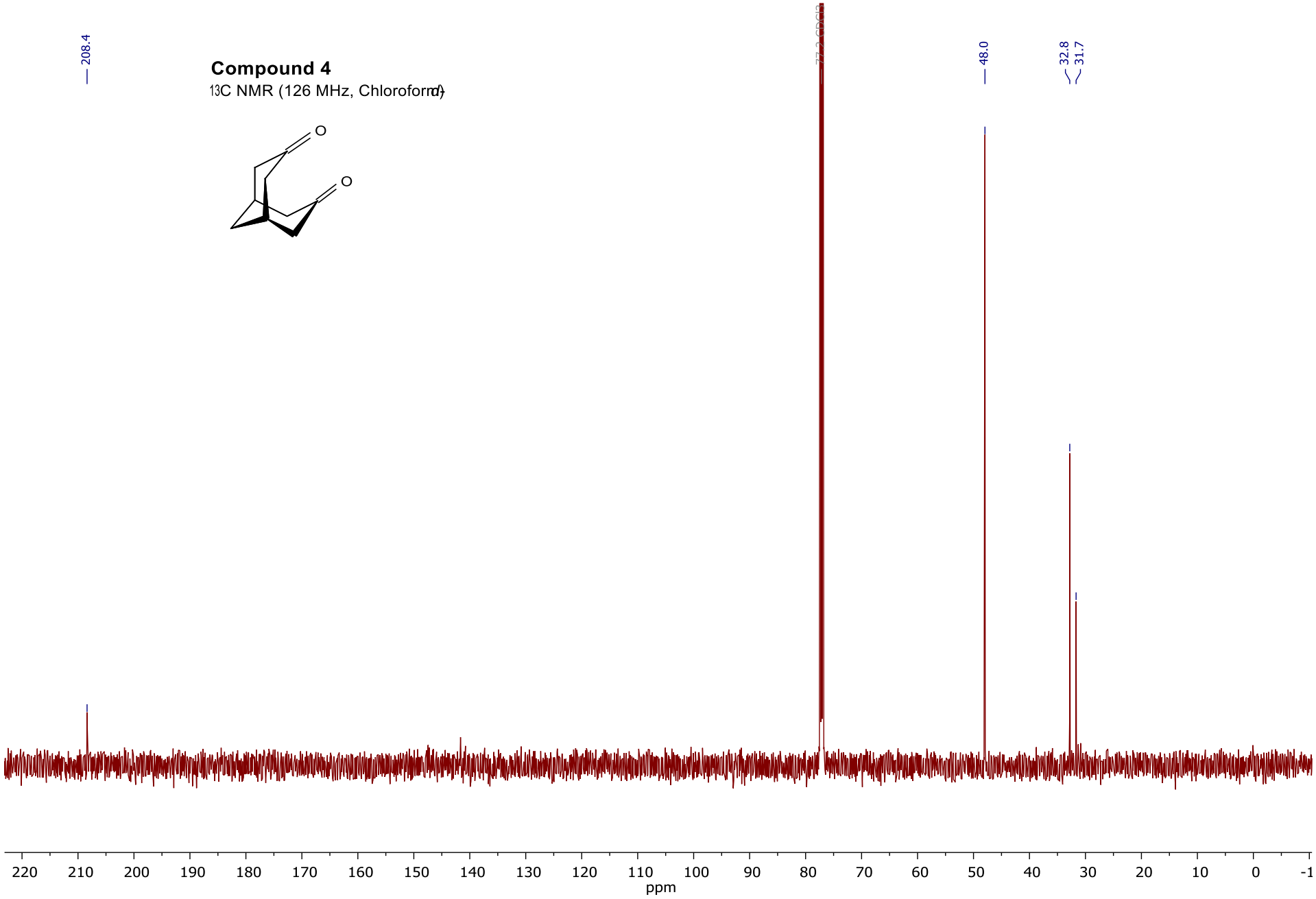
^{13}C NMR_ APT (126 MHz,DMSO-d_6)



Compound 4

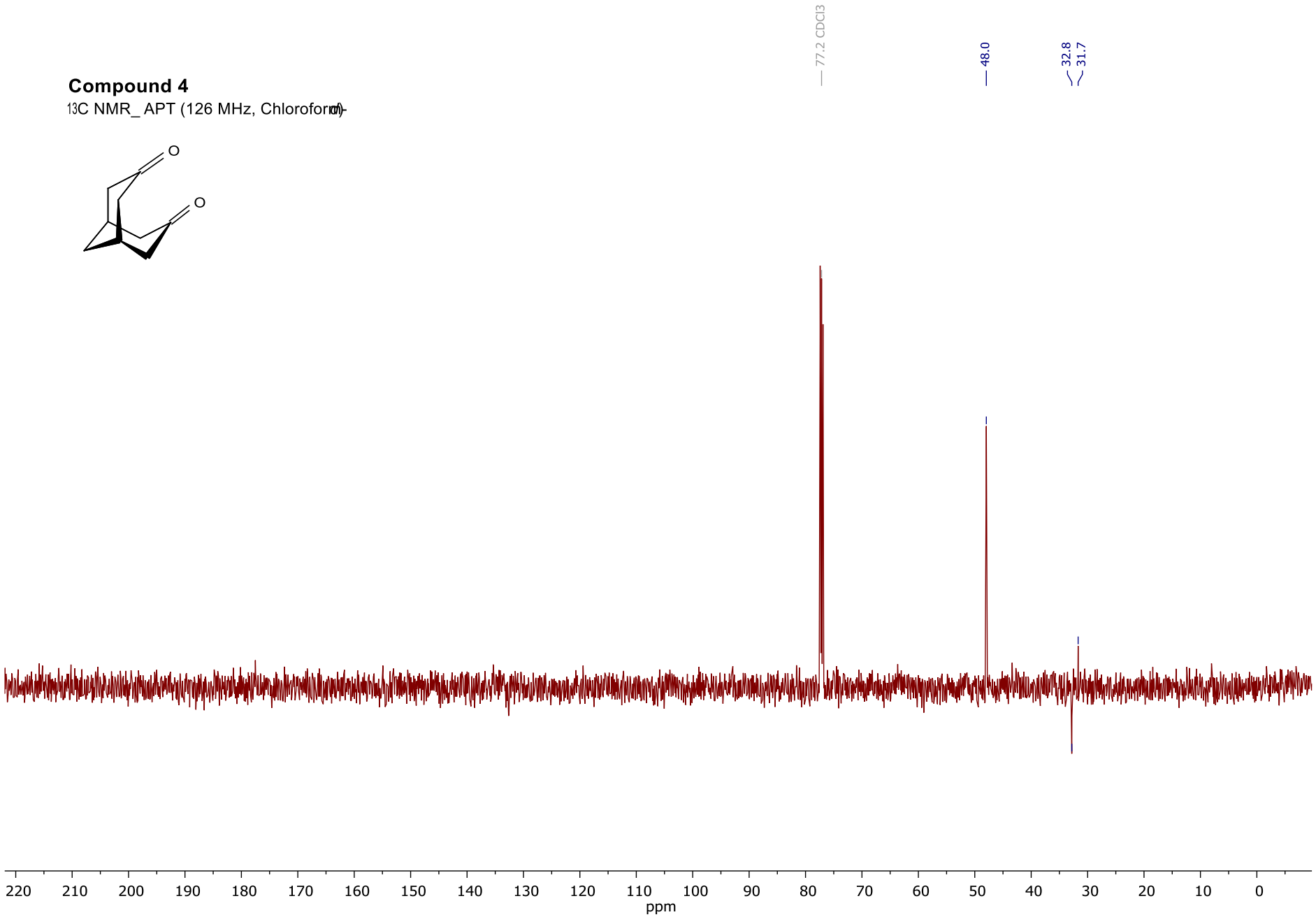
^{1}H NMR (500 MHz, Chloroform-*d*)




208.4
77.2
48.0
32.8
31.7
Compound 4
13C NMR (126 MHz, Chloroform-d)
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
ppm

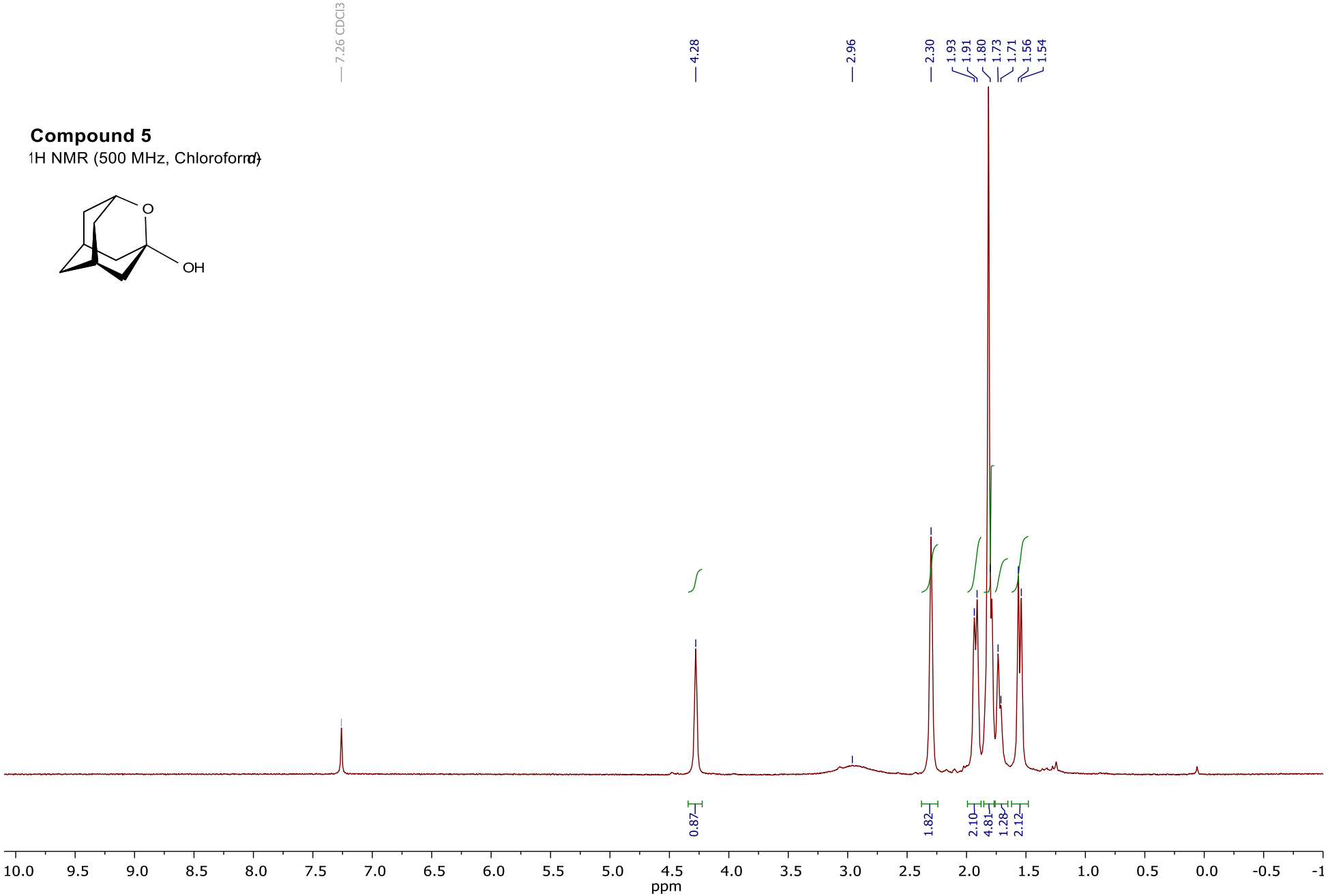
Compound 4

^{13}C NMR_ APT (126 MHz, Chloroform-*d*)



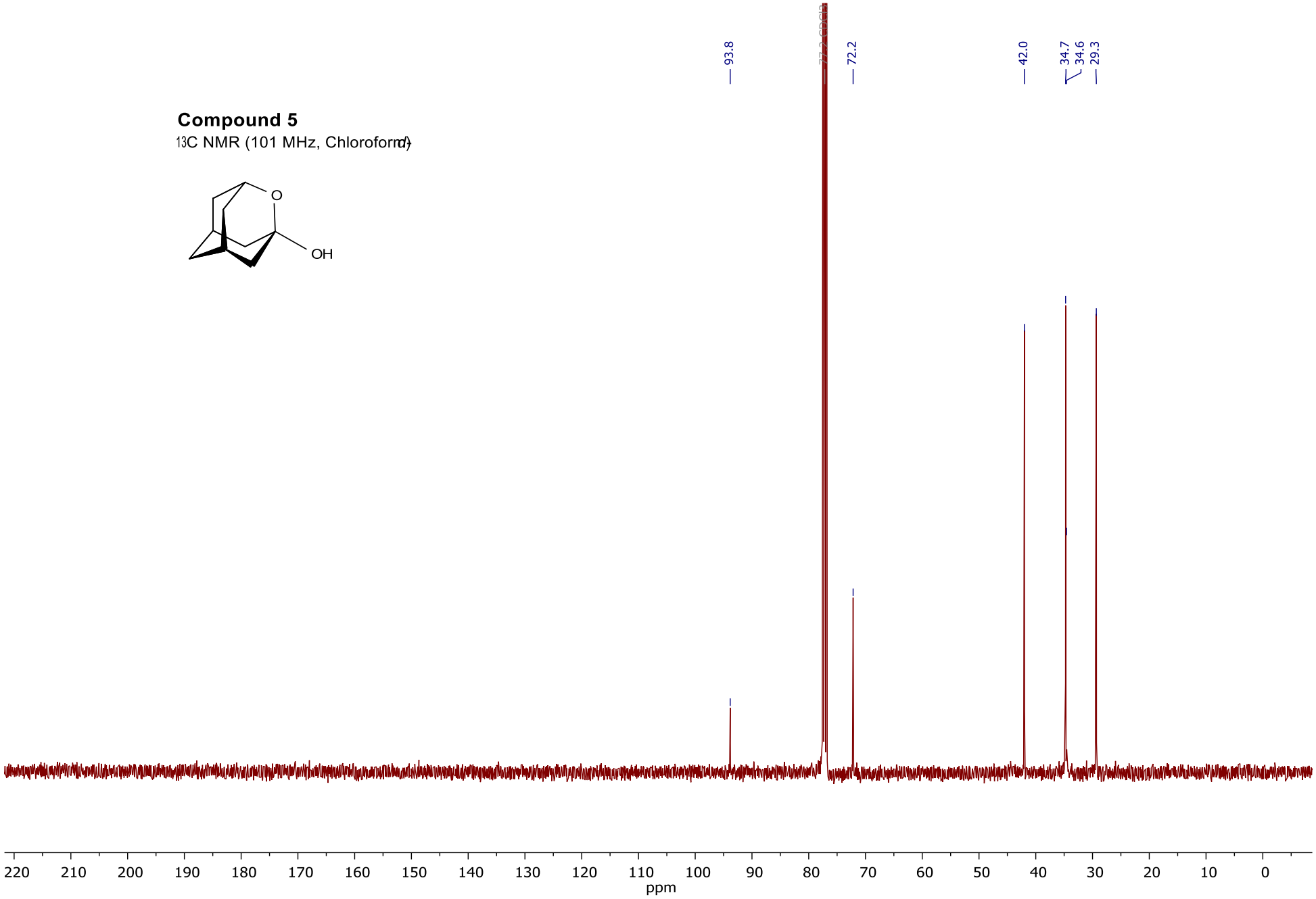
Compound 5

^{1}H NMR (500 MHz, Chloroform-*d*)



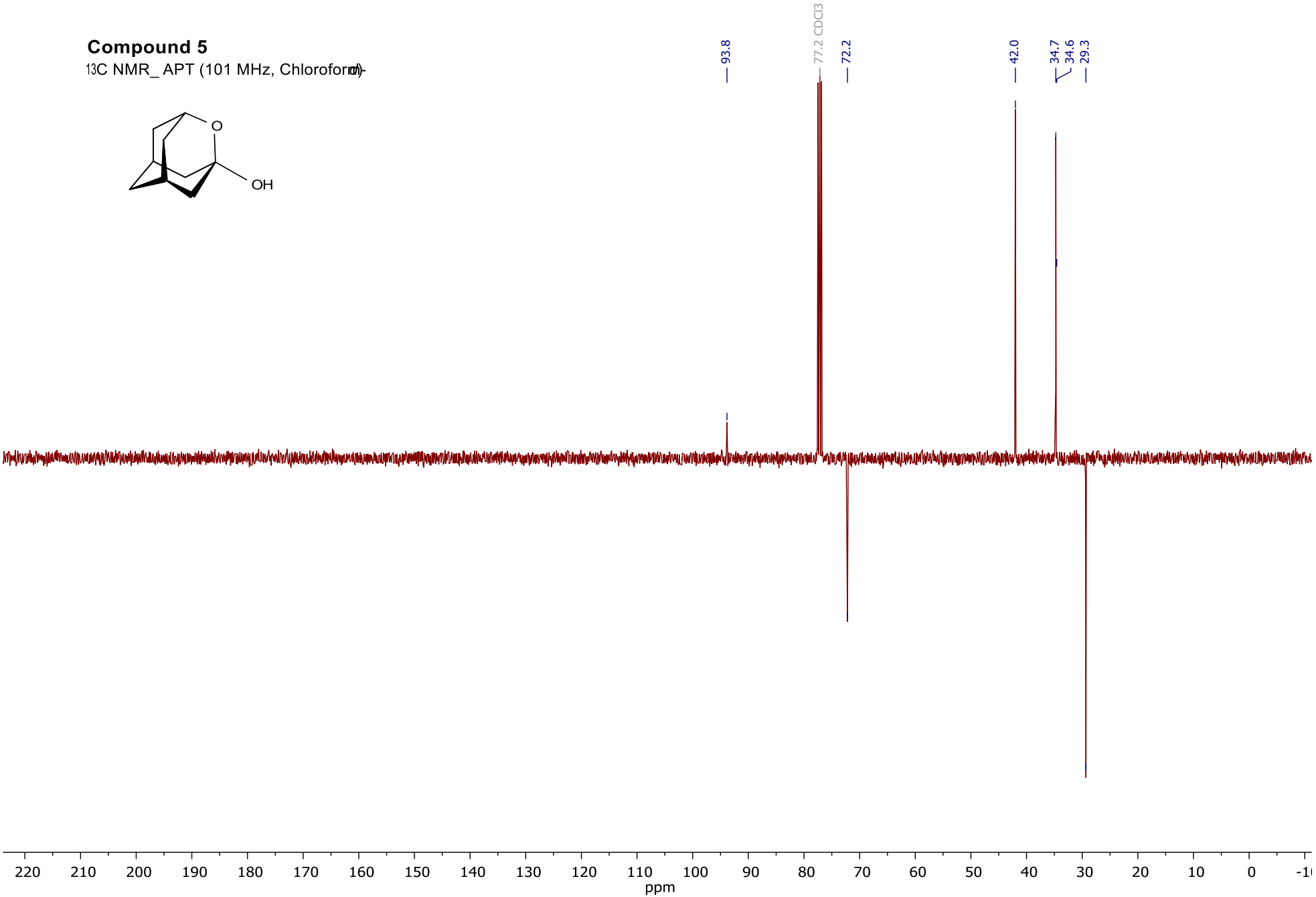
Compound 5

^{13}C NMR (101 MHz, Chloroform-*d*)



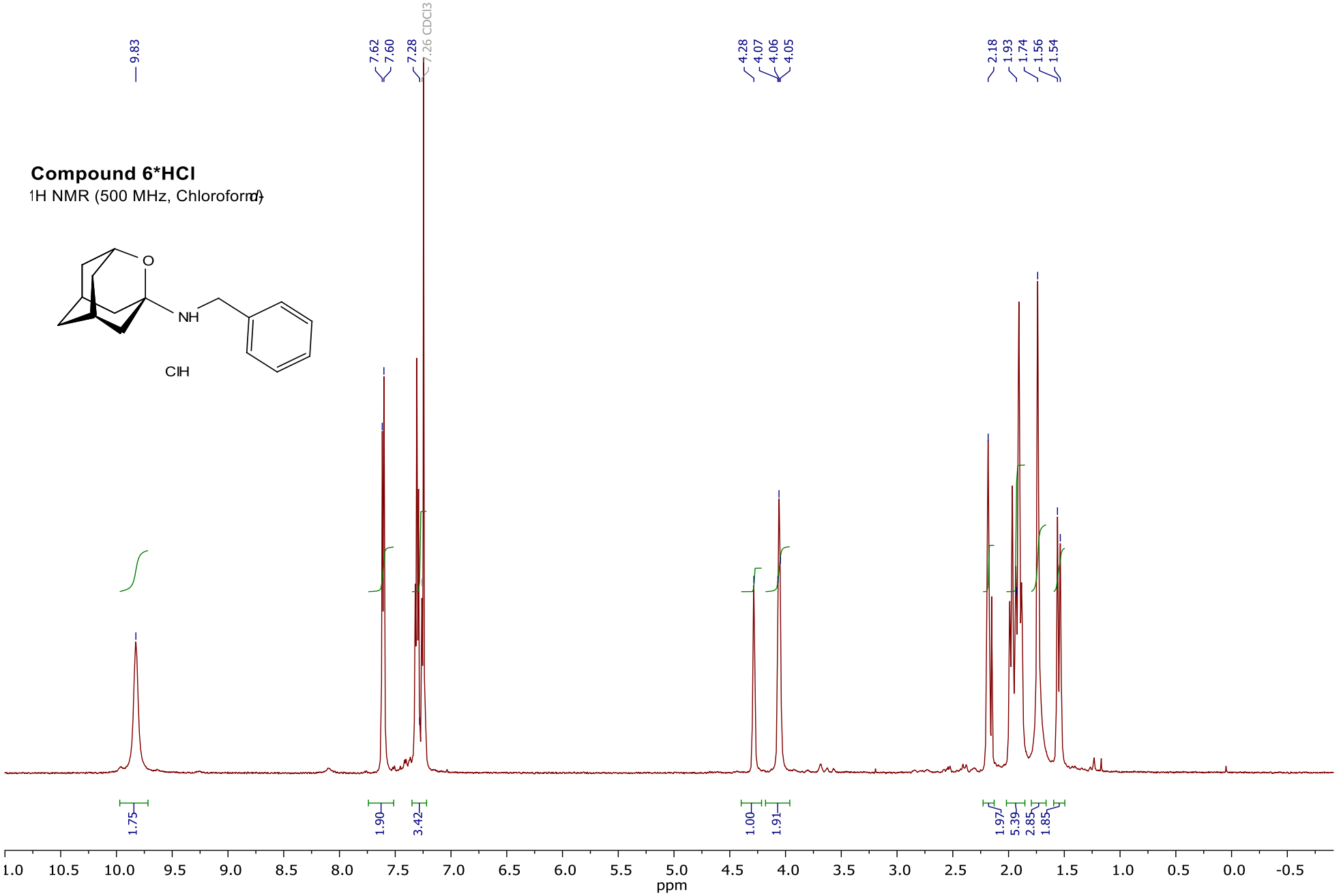
Compound 5

^{13}C NMR_ APT (101 MHz, Chloroform-*d*)



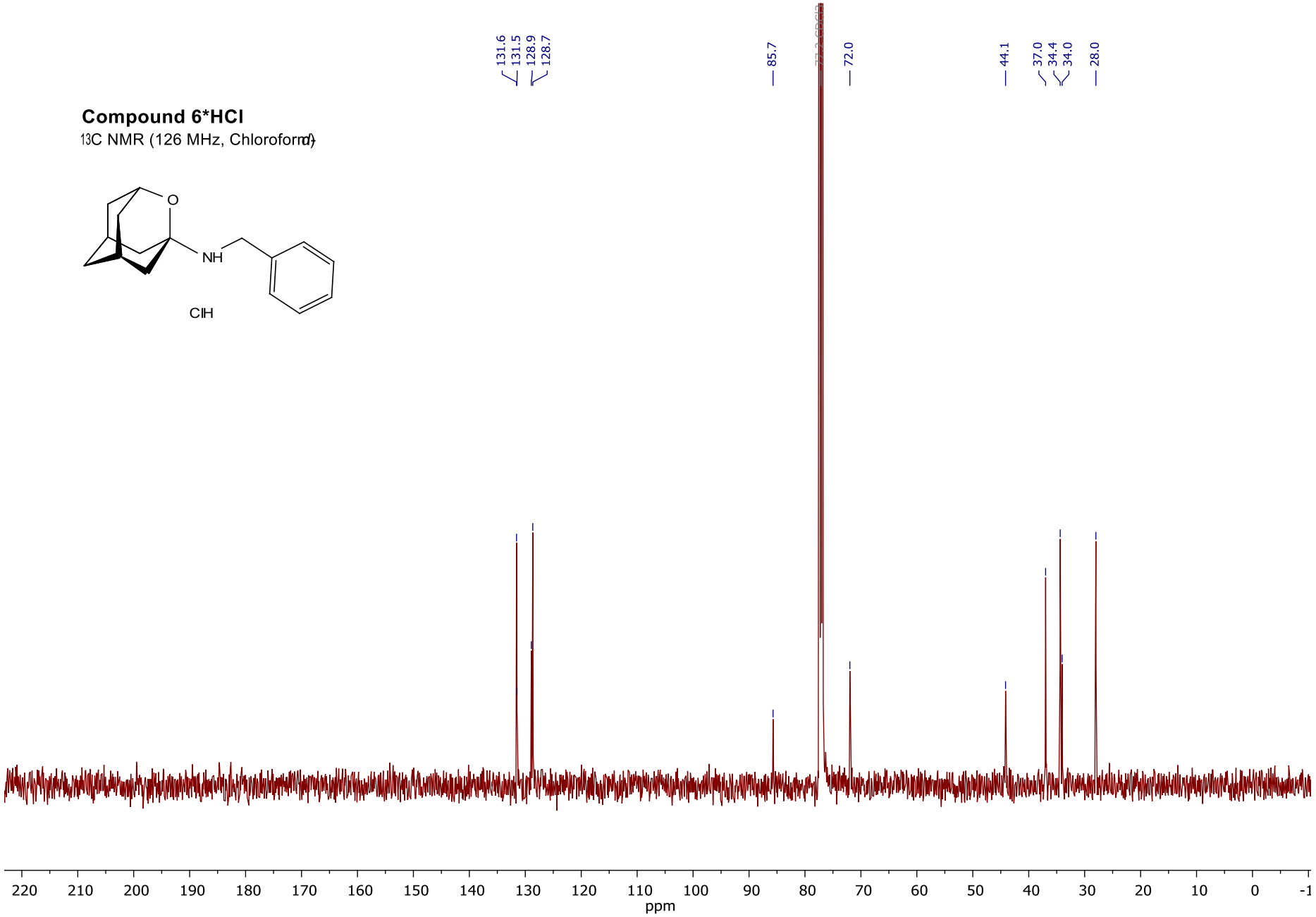
Compound 6*HCl

1H NMR (500 MHz, Chloroform-*d*)



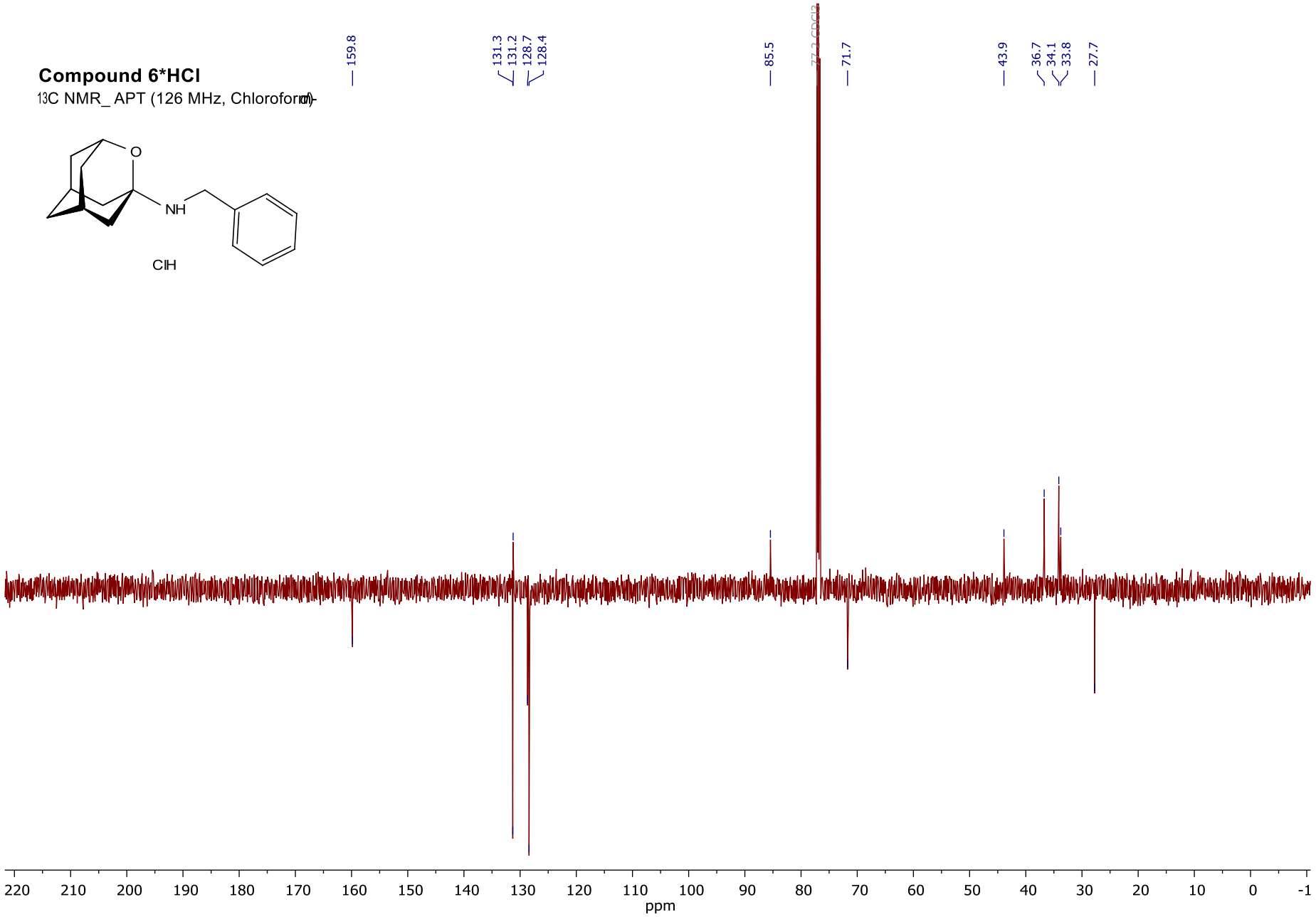
Compound 6*HCl

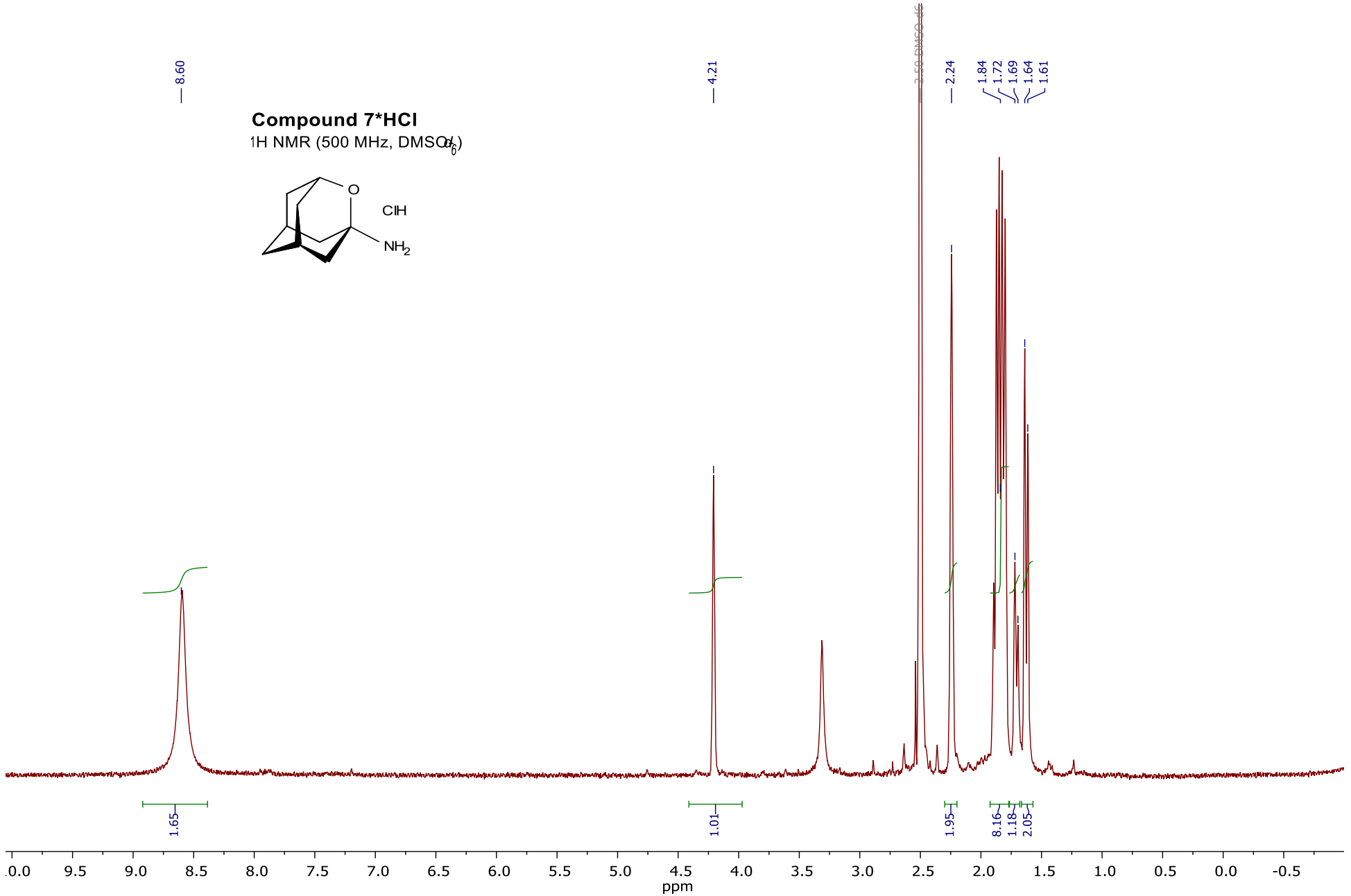
^{13}C NMR (126 MHz, Chloroform-*d*)



Compound 6*HCl

13C NMR_ APT (126 MHz, Chloroform-d)




Compound 7*HCl
1H NMR (500 MHz, DMSO-d6)
ClH
NH2
8.60
4.21
3.50 DMSO-d6
2.24
1.84
1.72
1.69
1.64
1.61
1.65
1.01
1.95
8.16
1.18
2.05
ppm

Compound 7*HCl

^{13}C NMR_ APT (126 MHz, $DMSO_{d6}$)