

Supplementary material for:

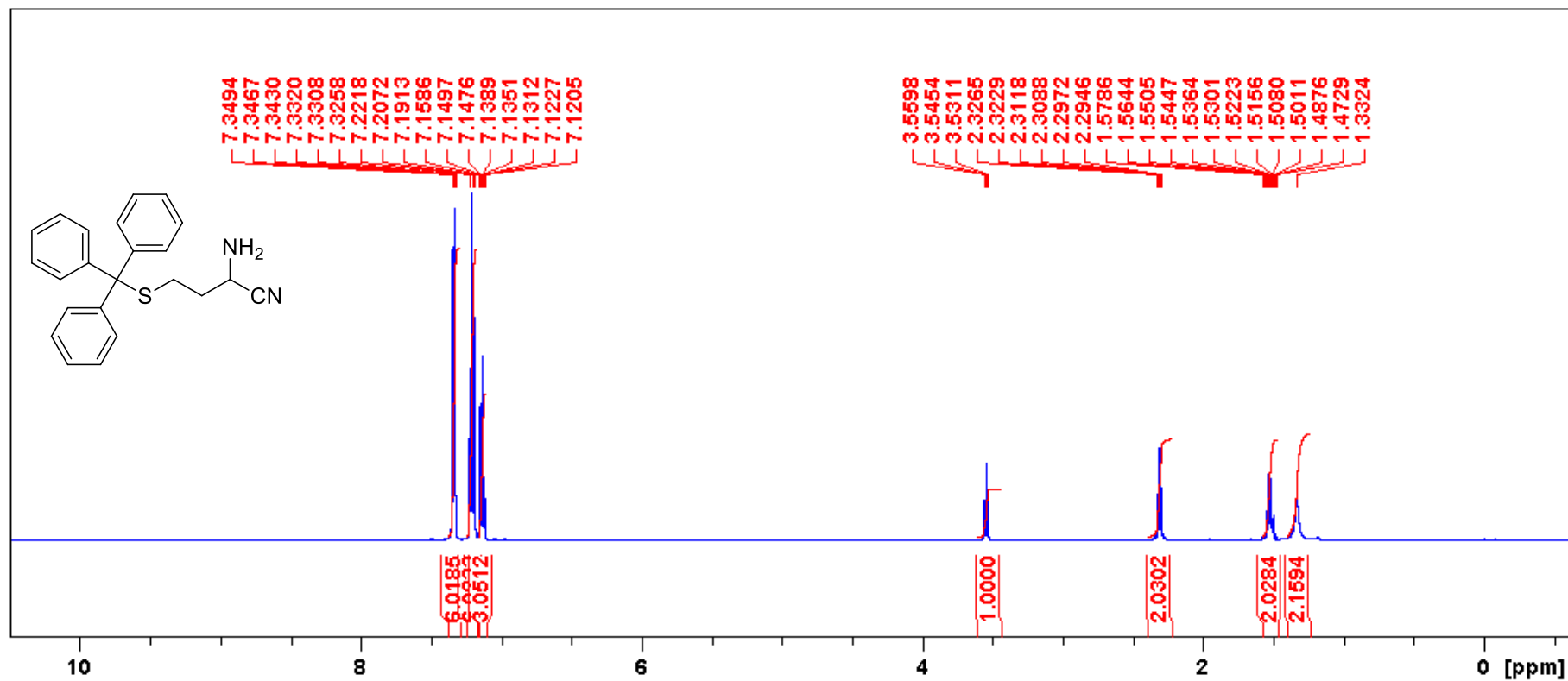
Prebiotic chemistry of homocysteine and its thiolactone

Ibrahim Shalayel and Yannick Vallée*

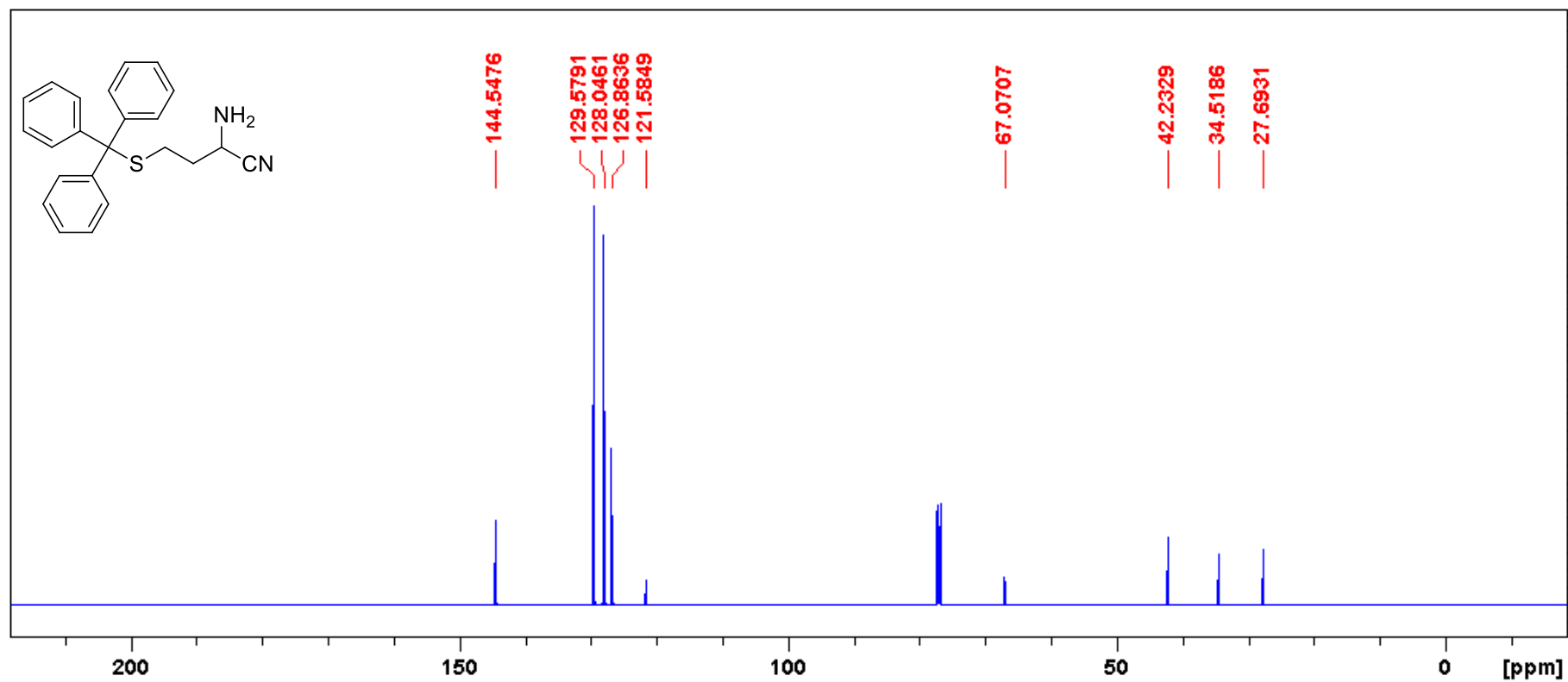
Univ. Grenoble Alpes, CNRS, Département de Chimie Moléculaire, Campus, Grenoble,
France

1- Copies of NMR spectra of 3	2
2- ¹³ C NMR of 1 and 4 mixture	4
3- ¹³ C NMR of 7	6
4- ¹ H-NMR of (CH ₂ -S) protons of 7	7
5- Copies of Mass spectrometry of 7 and 8	8
6- ESI analysis of 4 and 5 reaction mixture	10

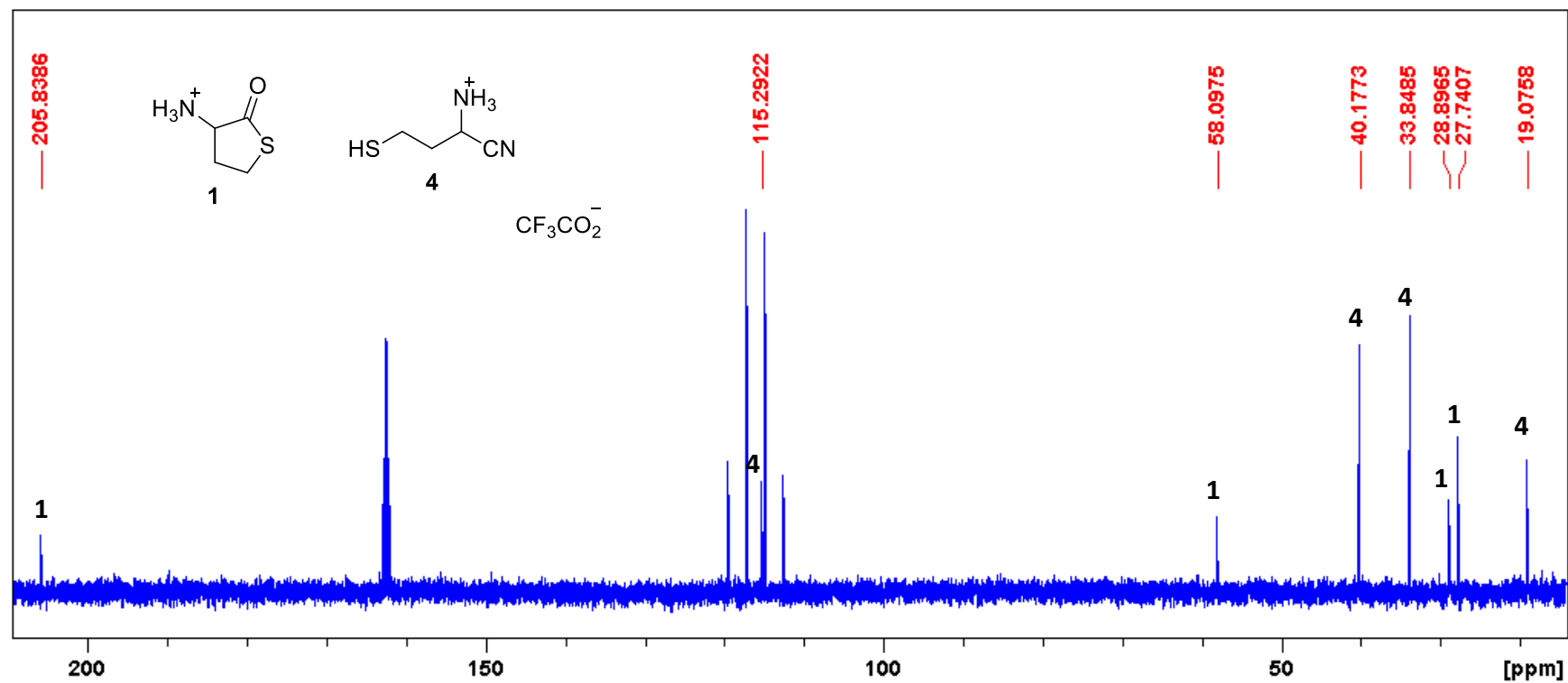
¹H NMR of **3**



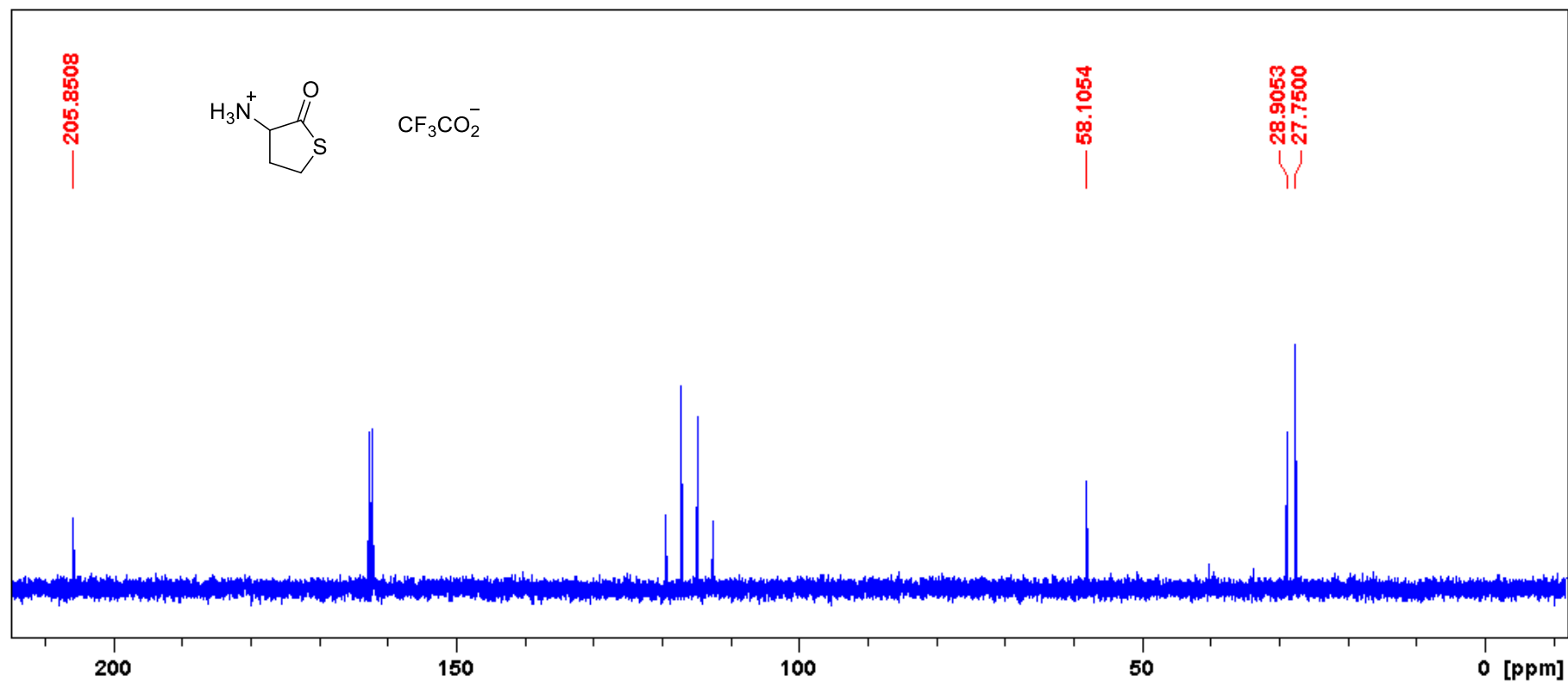
^{13}C NMR of **3**



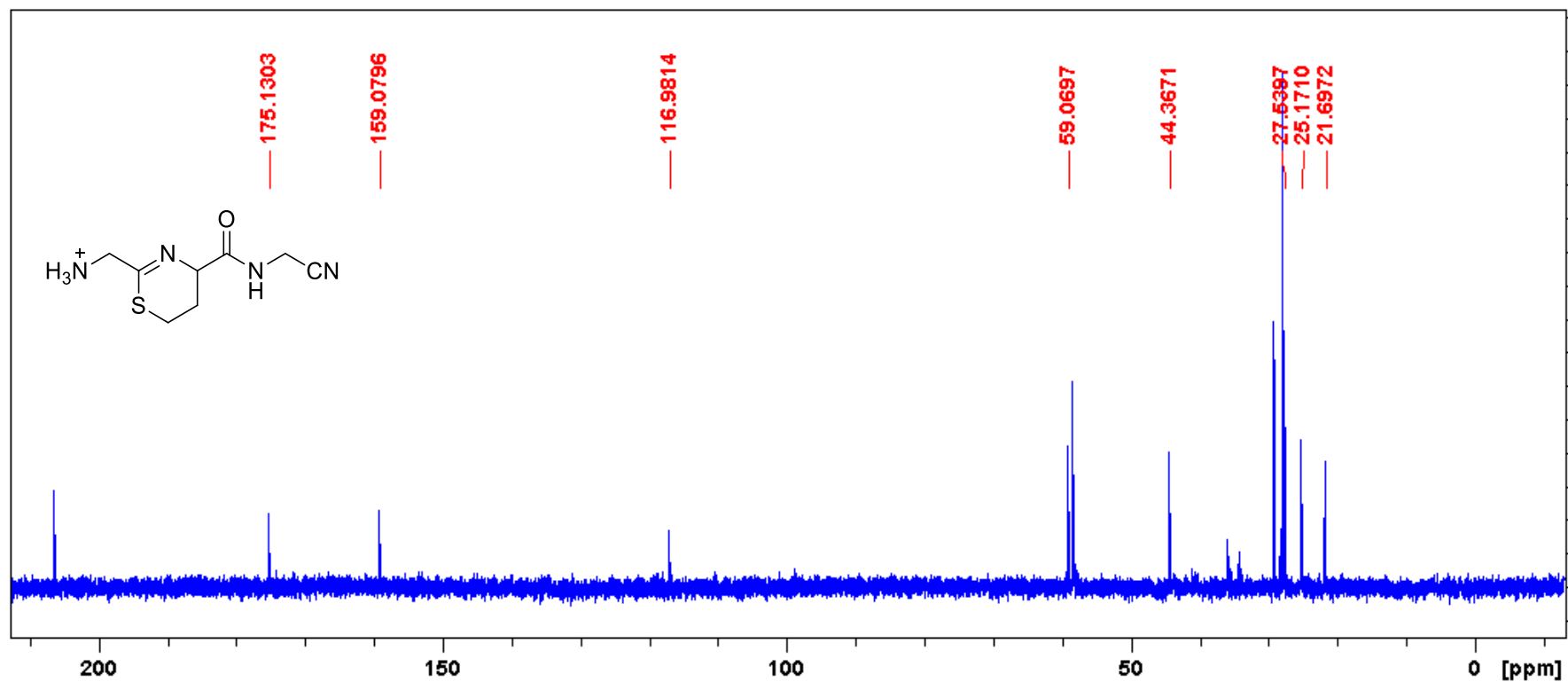
^{13}C NMR of a mixture of **1** and **4**



^{13}C NMR of Hcy-thiolactone **4**

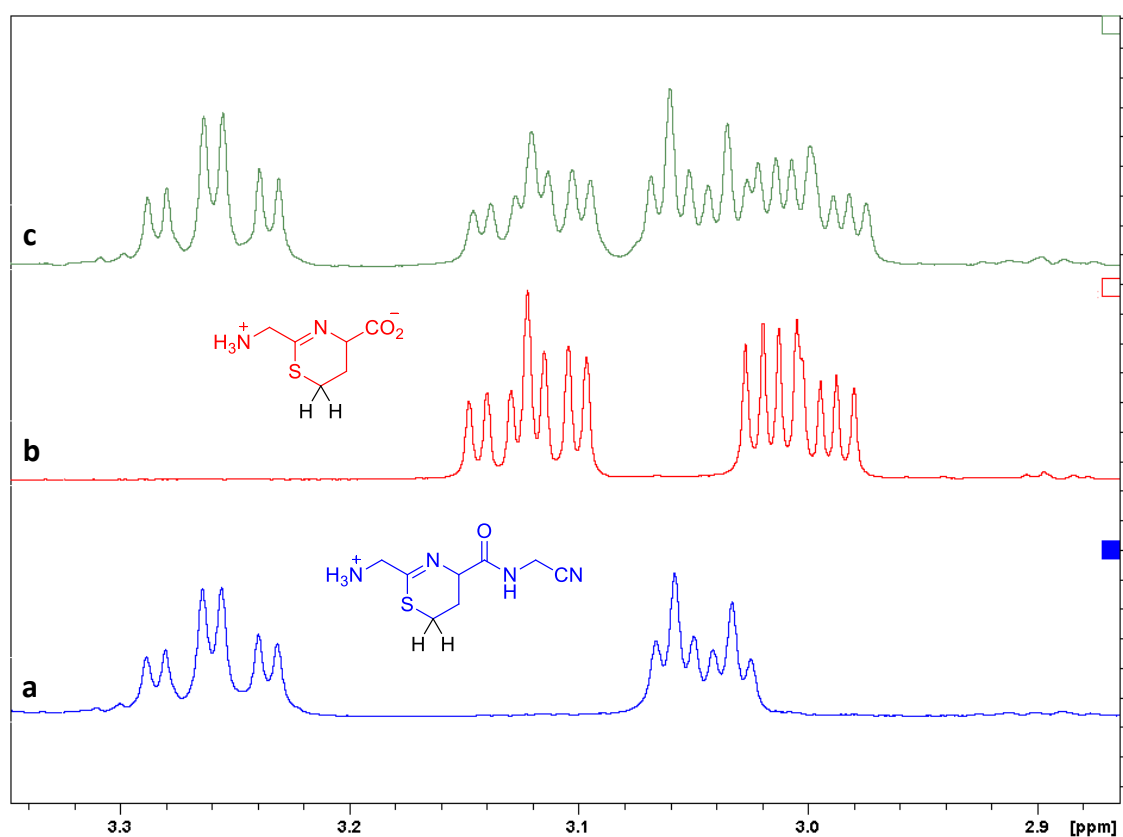


^{13}C NMR of a reaction mixture between Hcy-thiolactone **4** and Gly-CN **5**, peaks corresponding to **7** are identified.



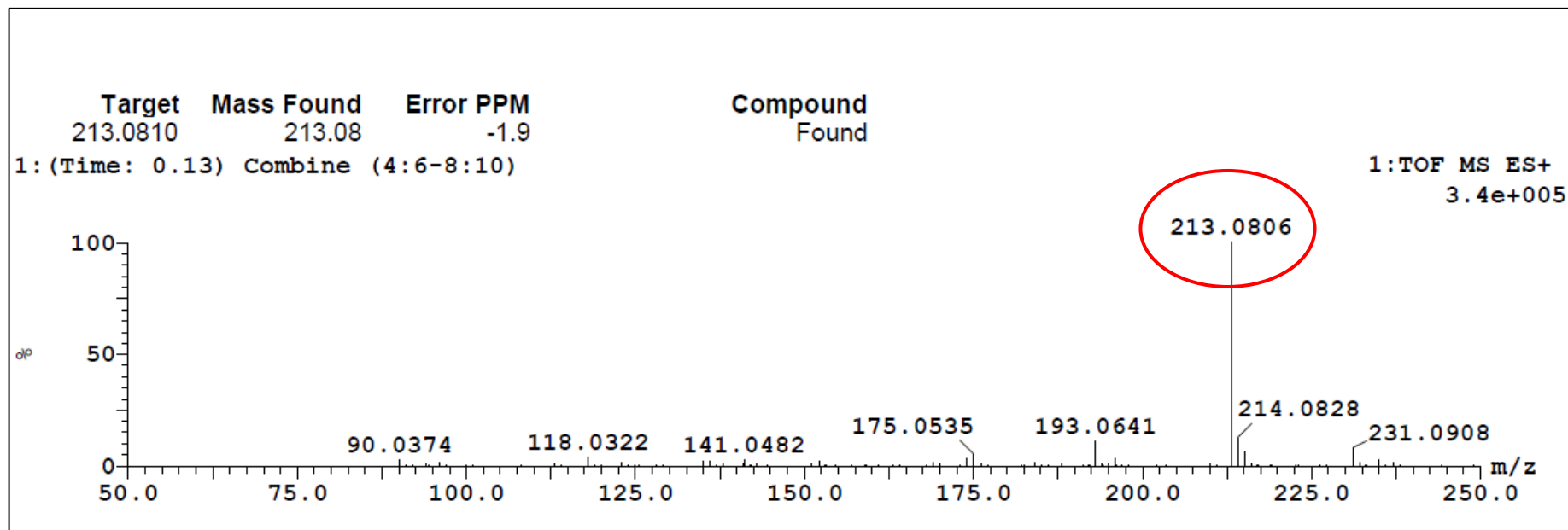
^1H -NMR of ($\text{CH}_2\text{-S}$) protons: **a)** dihydrothiazine **7**, **b)** Gly-Hcy dihydrothiazine 2-(ammoniomethyl)-5,6-dihydro-4H-1,3-thiazine-4-carboxylate, **c)** a mixture of **7** and Gly-Hcy dihydrothiazine.

a) Gly-Hcy dihydrothiazine cycle (obtained by mixing homocysteine and aminoacetonitrile in D_2O at 45°C for 2 hours). **b)** Cycle **7** (obtained by mixing Hcy-thiolactone **4** with aminoacetonitrile in D_2O at 45°C for 3 hours). **c)** Mixture of the two previous solutions together confirming that the observed cycle **7** is not the Gly-Hcy dihydrothiazine cycle.



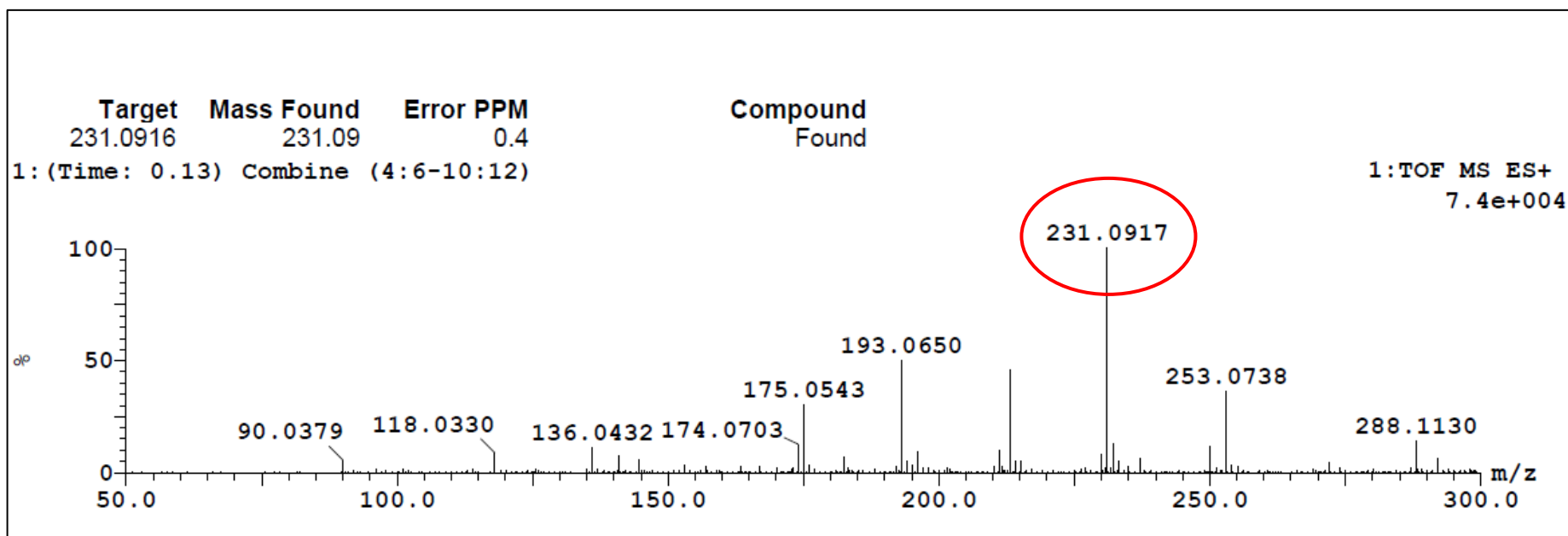
HRMS of **7** in the mixture

calcd for $\text{C}_8\text{H}_{13}\text{N}_4\text{OS}$ $[\text{M} + \text{H}]^+$: 213.0810, found 213.0806



HRMS of **8** in the mixture

calcd for $\text{C}_8\text{H}_{15}\text{N}_4\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$: 231.0916, found 231.0917)



ESI spectrum (law resolution) of **4** and **5** reaction mixture in H₂O.

