



Supplementary materials

New Megastigmane and Polyphenolic Components of Henna Leaves and Their Tumor-Specific Cytotoxicity on Human Oral Squamous Carcinoma Cell Lines

Mohamed A. A. Orabi^{1,*}, Esam A Orabi^{2,*}, Ahmed Abdullah Al Awadh³, Mohammed Merae Alshahrani³, Basel A. Abdel-Wahab⁴, Hiroshi Sakagami⁵ and Tsutomu Hatano⁶

¹ Department of Pharmacognosy, College of Pharmacy, Najran University, Najran 66454, Saudi Arabia; mohamedorabi@azhar.edu.eg; maorabi@nu.edu.sa.

² Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke Street West, Montréal, Québec H4B 1R6, Canada; e_orabi@live.concordia.ca.

³ Department of Clinical Laboratory Sciences, Faculty of Applied Medical Sciences, Najran University, Najran 66454, Saudi Arabia; aaalawadh@nu.edu.sa (AAAA), mmalshahrani@nu.edu.sa (MMA)

⁴ Department of Pharmacology, College of Pharmacy, Najran University, Najran 64462, Saudi Arabia; babdelnaem@nu.edu.sa

⁵ Meikai University Research Institute of Odontology (M-RIO), 1-1 Keyakidai, Sakado, Saitama 350-0283, Japan; sakagami@dent.meikai.ac.jp

⁶ Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Okayama University, Tsushima, Okayama 700-8530, Japan; hatano-t@cc.okayama-u.ac.jp

* Correspondence: mohamedorabi@azhar.edu.eg (M.A.A.O.; e_orabi@live.concordia.ca (E.A.O.))

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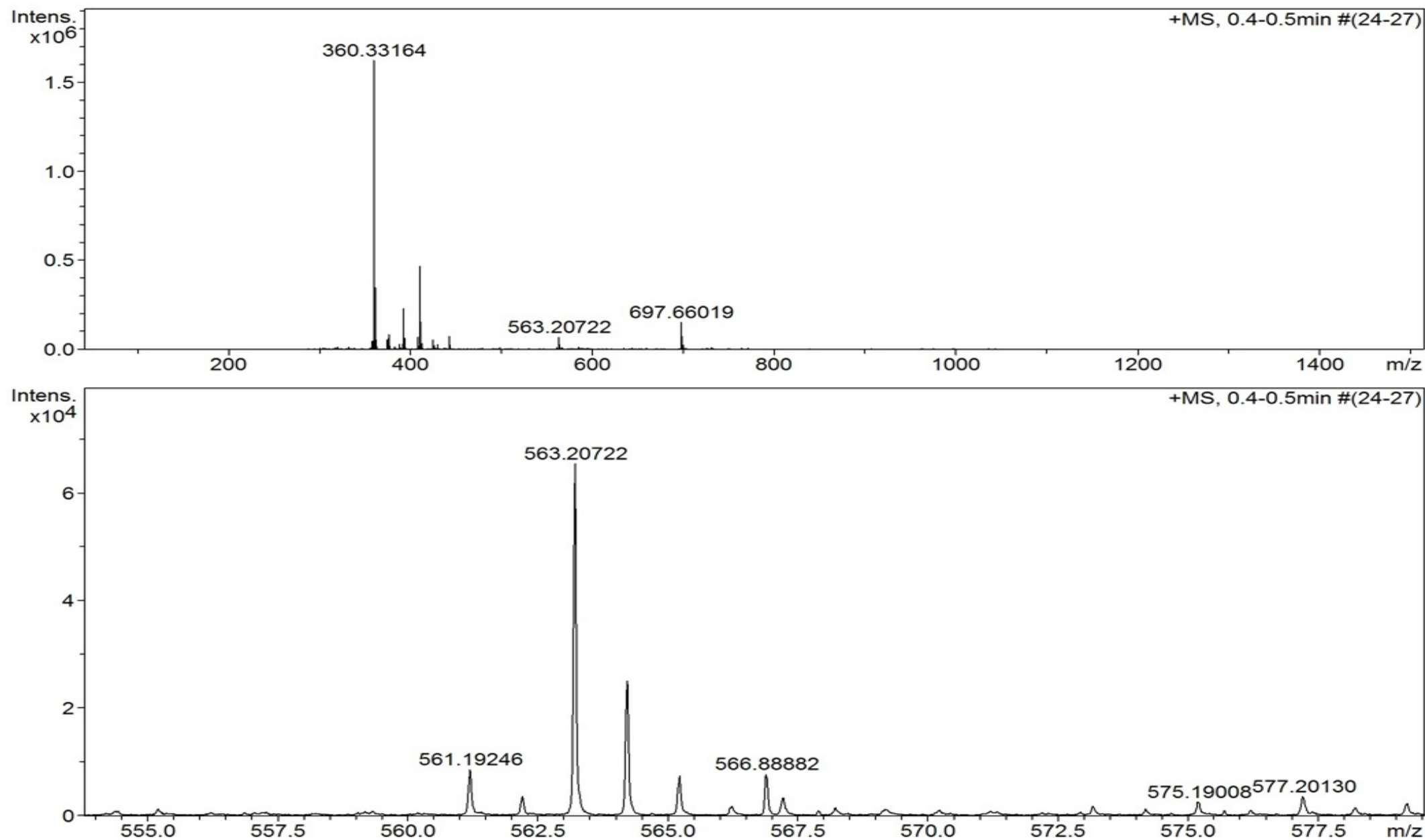


Figure S1. Positive mode HRESIMS spectrum of compound **1**

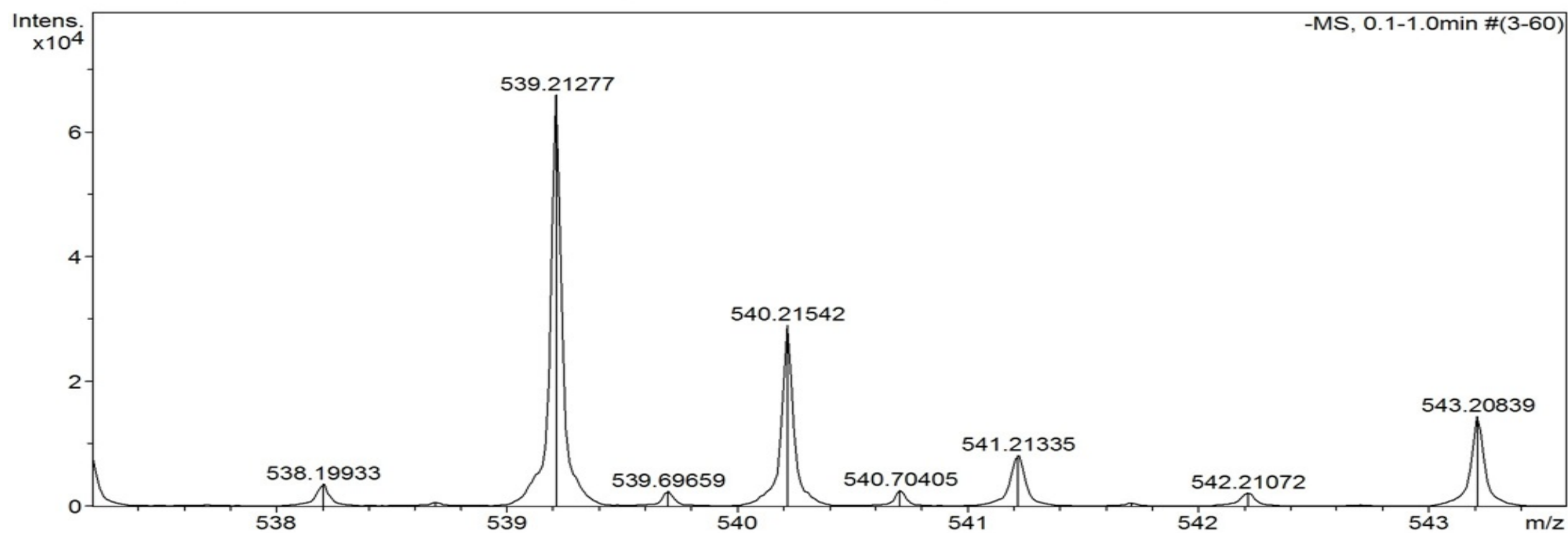
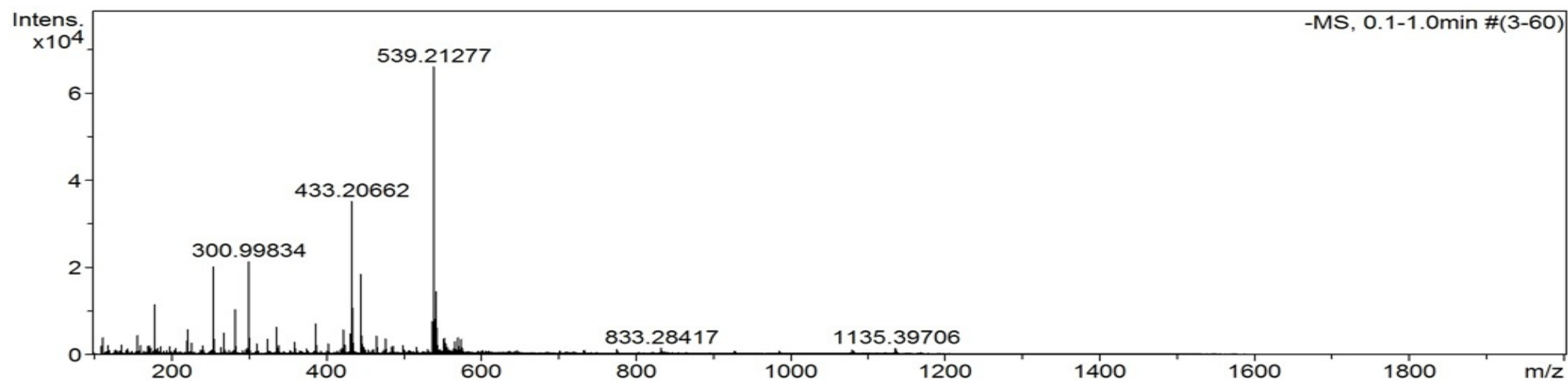


Figure S2. Negative mode HRESIMS spectrum of compound **1**

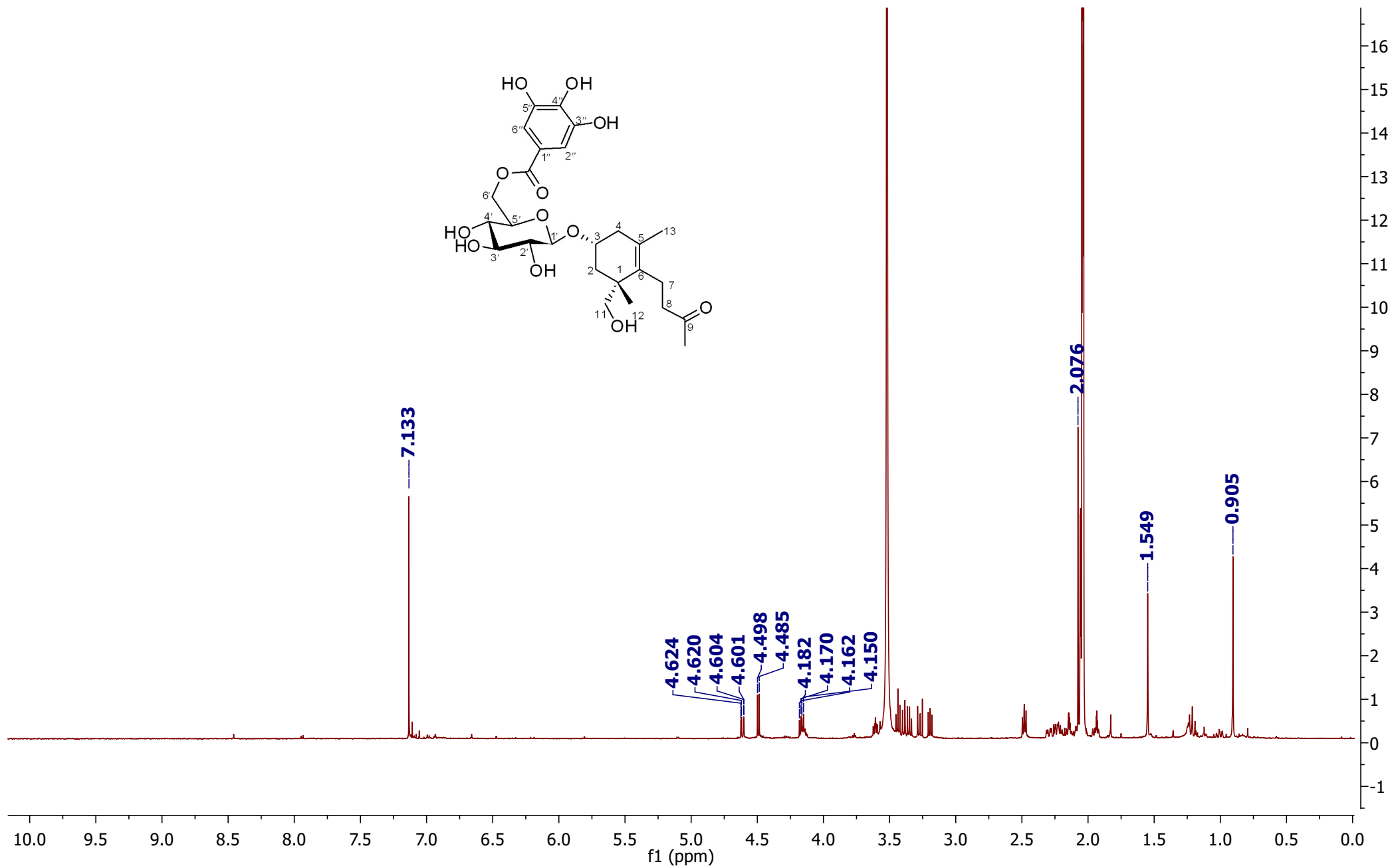


Figure S3. ^1H NMR spectrum of compound **1** [600 MHz, acetone- d_6 + D_2O (9+1)]

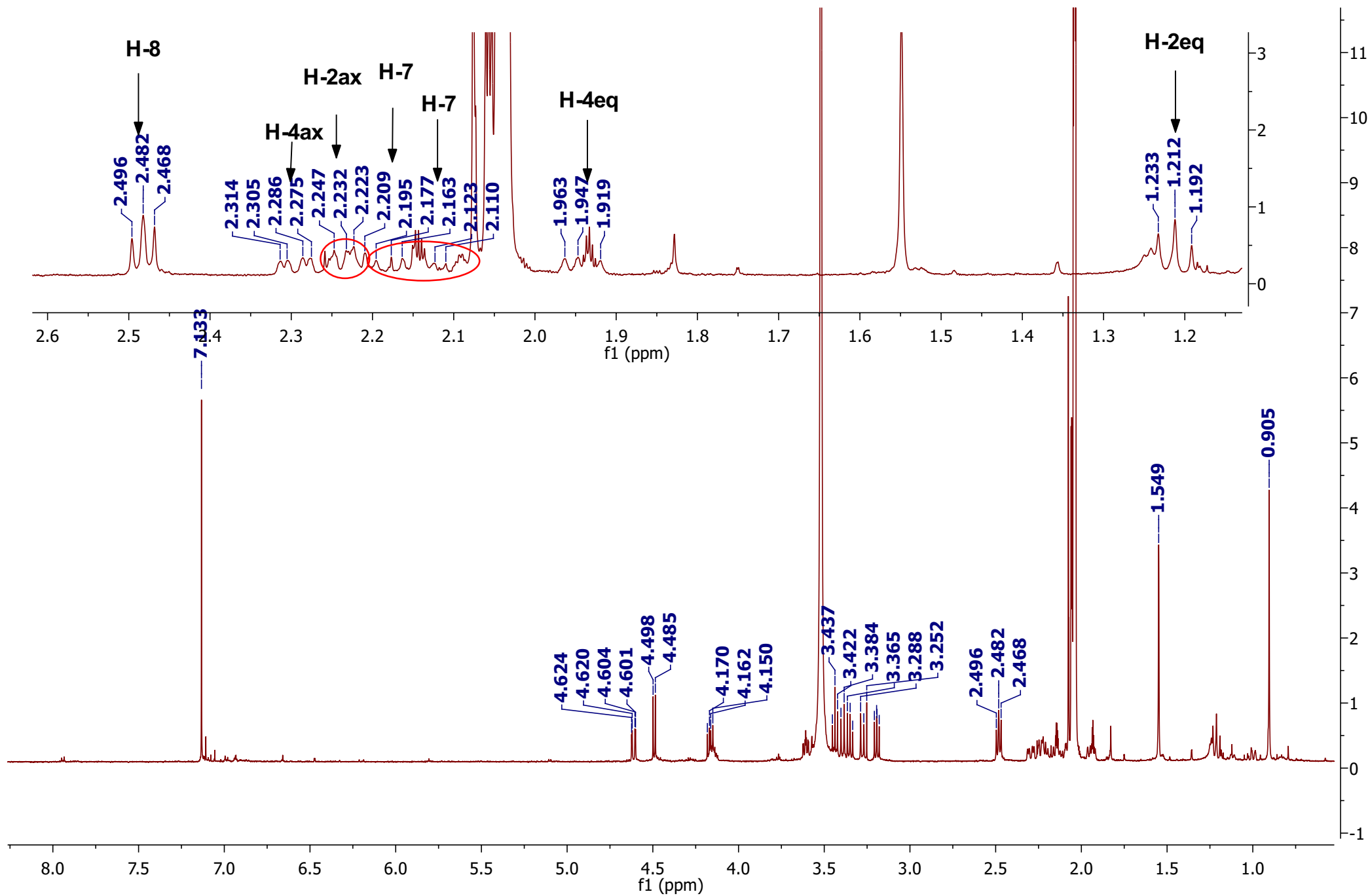


Figure S4. Expanded ^1H NMR spectrum of compound **1** [600 MHz, acetone- d_6 + D_2O (9+1)]

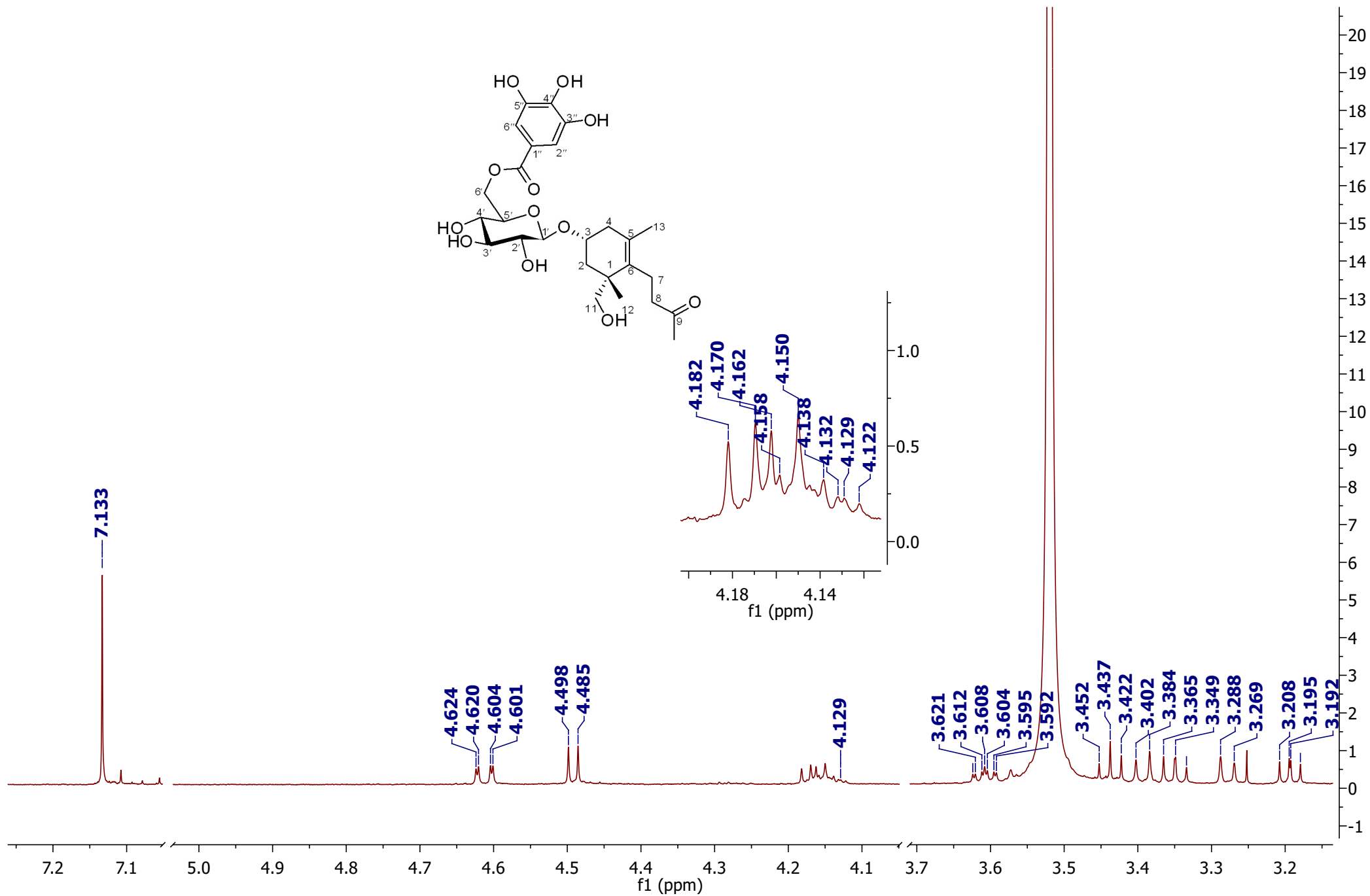


Figure S5. Expanded ¹H NMR spectrum of compound 1 [600 MHz, acetone-d₆ + D₂O (9+1)]

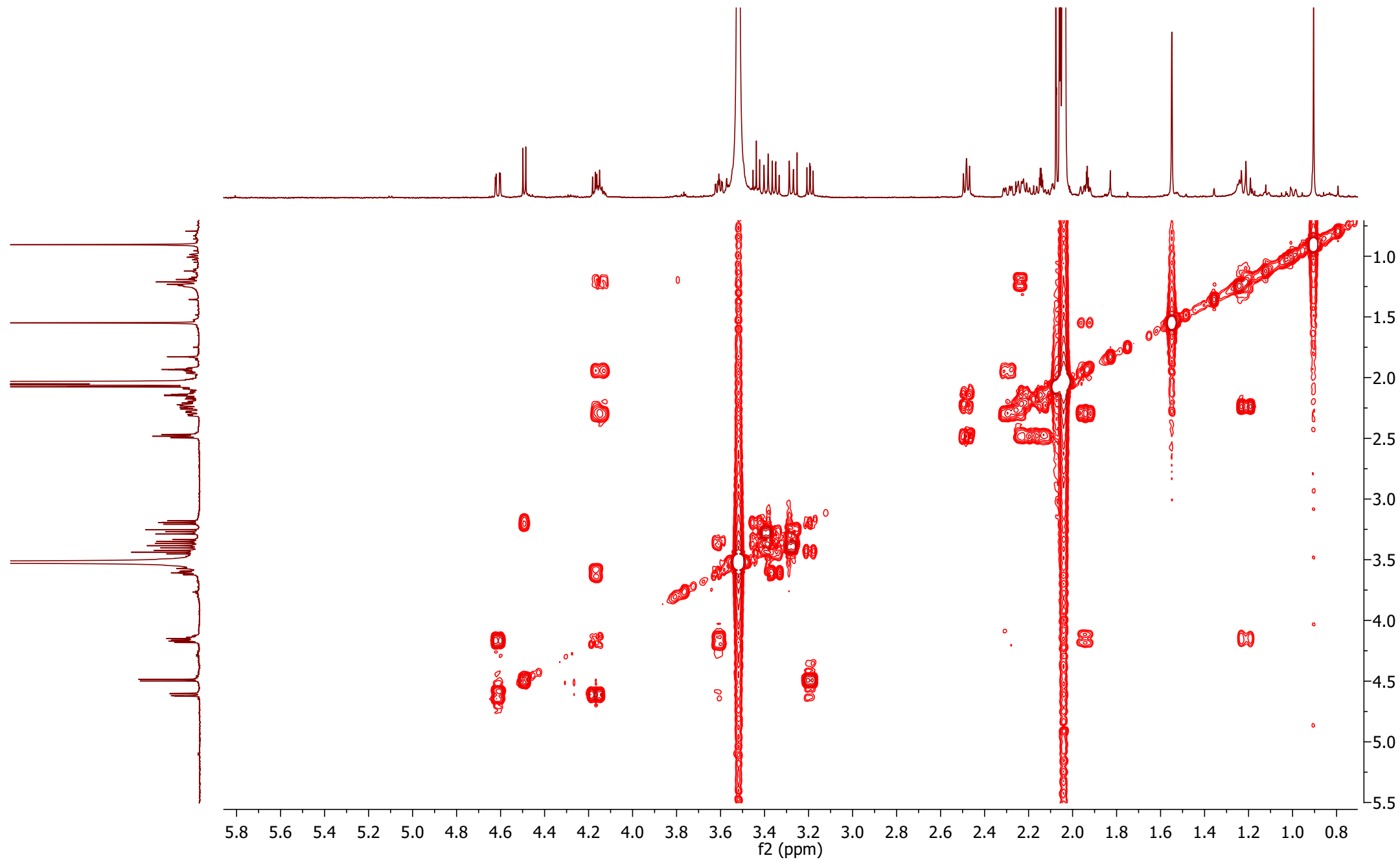


Figure S6. ^1H - ^1H COSY spectrum of compound **1** [600 MHz, acetone- d_6 + D_2O (9+1)]

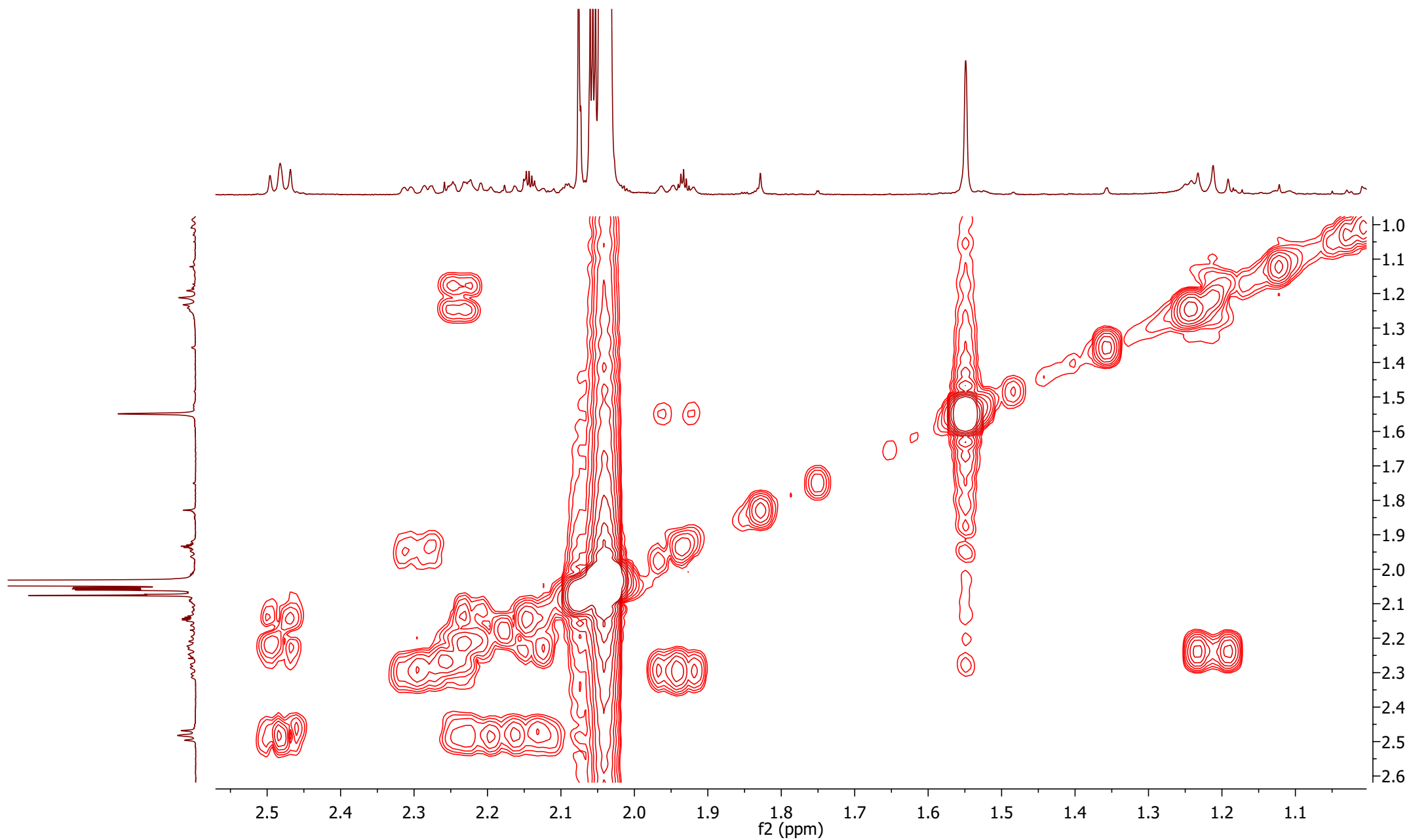


Figure S7. Expanded ^1H - ^1H COSY spectrum of compound **1** [600 MHz, acetone- d_6 + D_2O (9+1)]

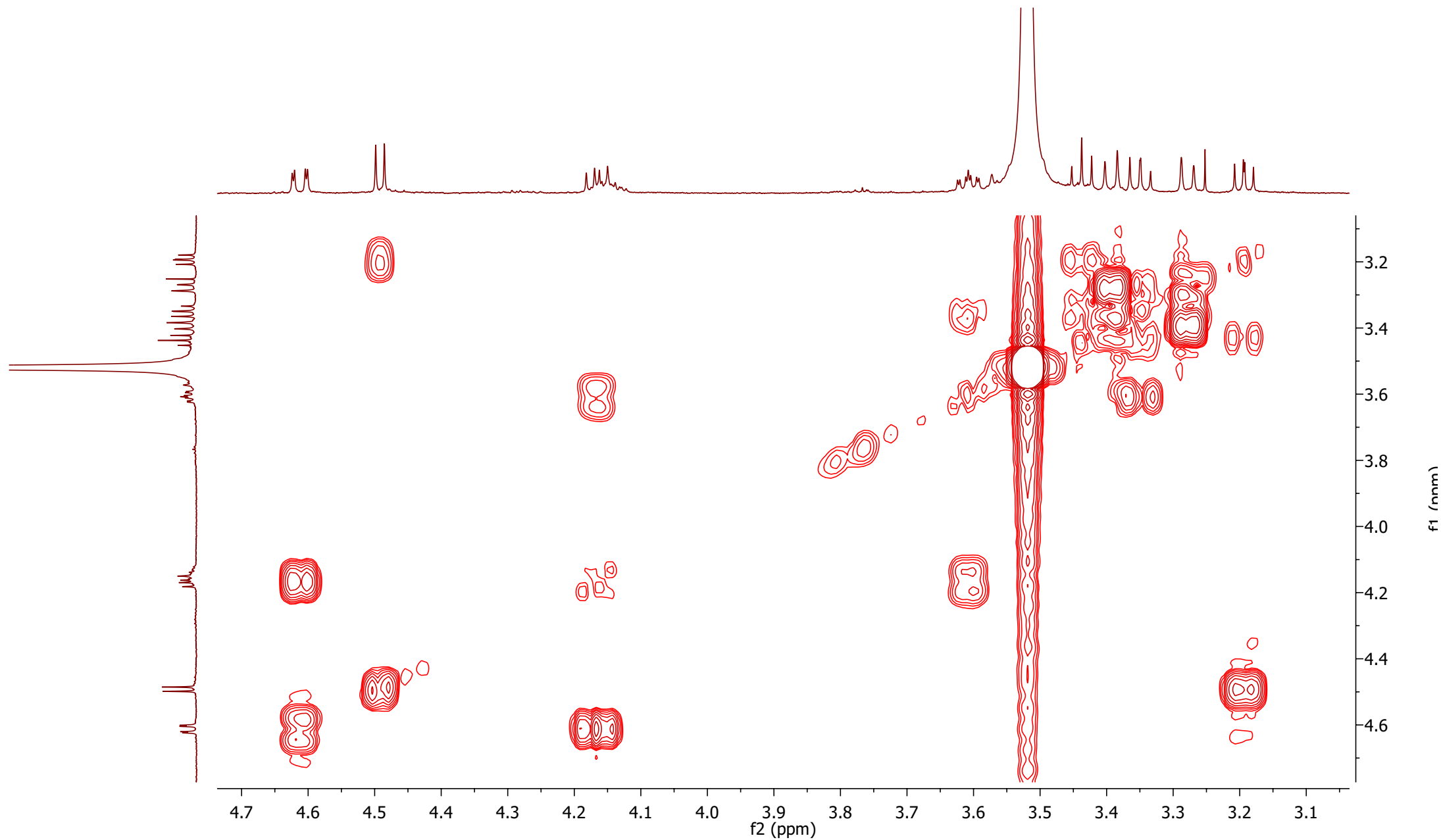


Figure S8. Expanded ^1H - ^1H COSY spectrum of compound **1** [600 MHz, acetone- d_6 + D_2O (9+1)]

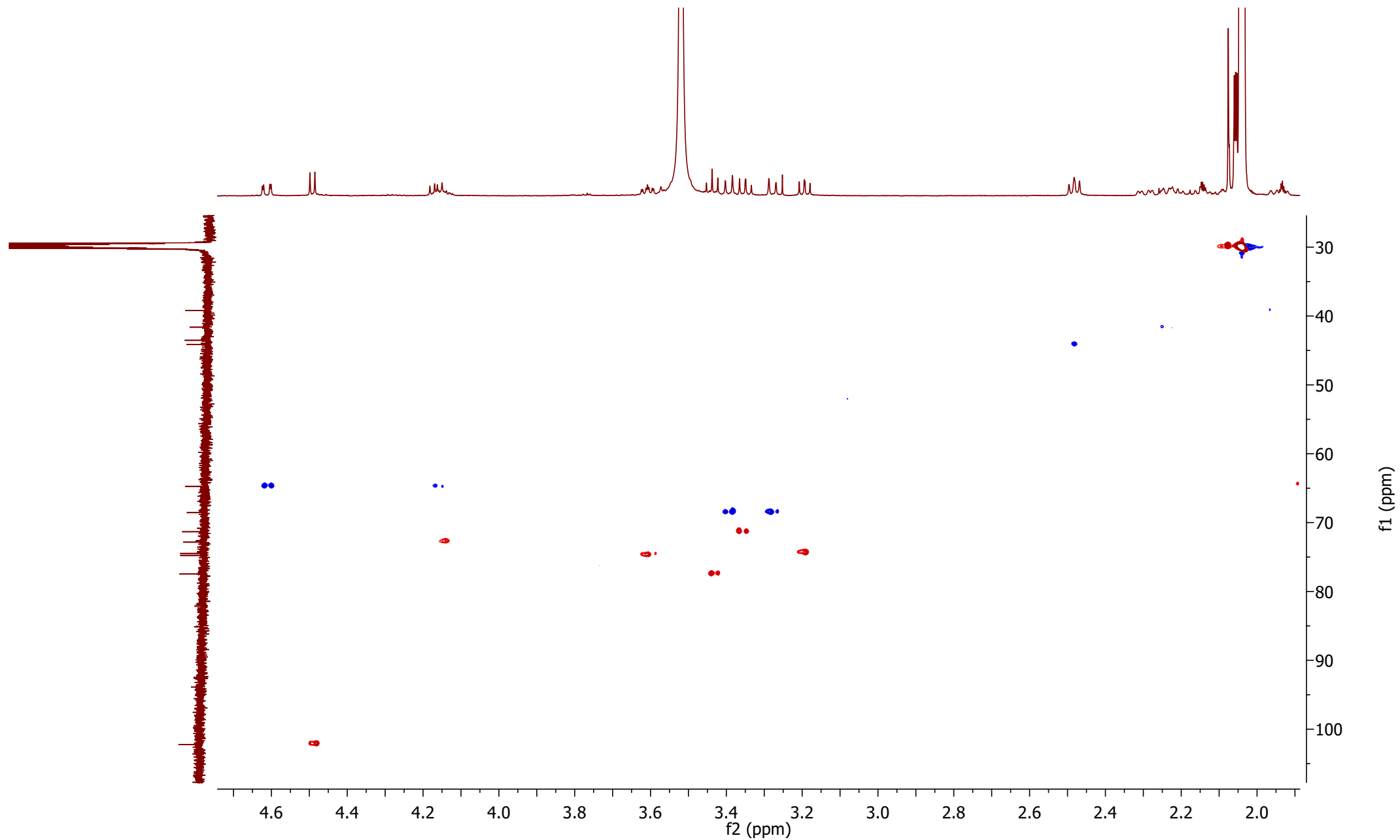


Figure S10. HSQC spectrum of compound **1** [600 MHz, acetone- d_6 + D $_2$ O (9+1)]

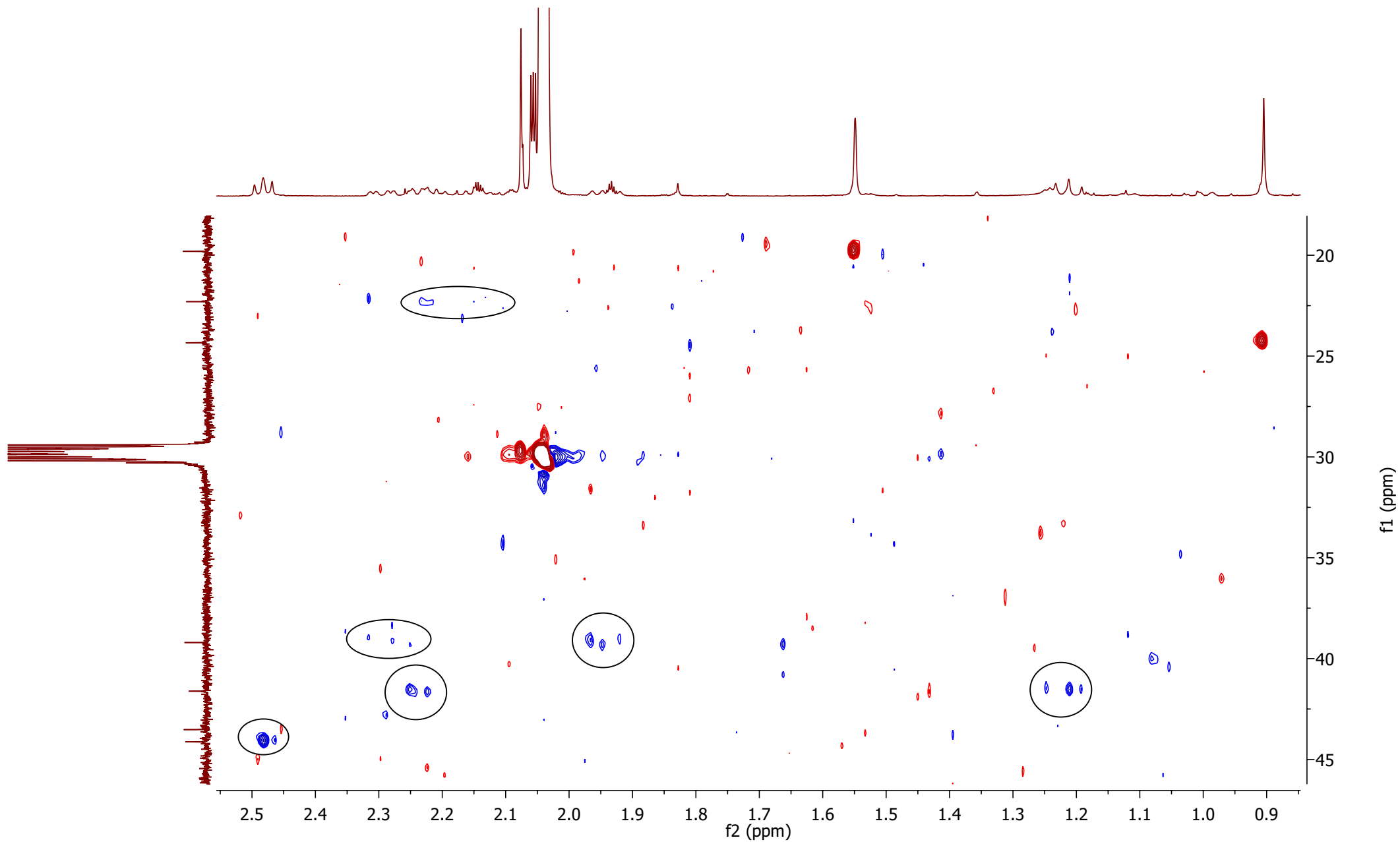


Figure S11. Expanded HSQC spectrum of compound **1** [600 MHz, acetone- d_6 + D₂O (9+1)]

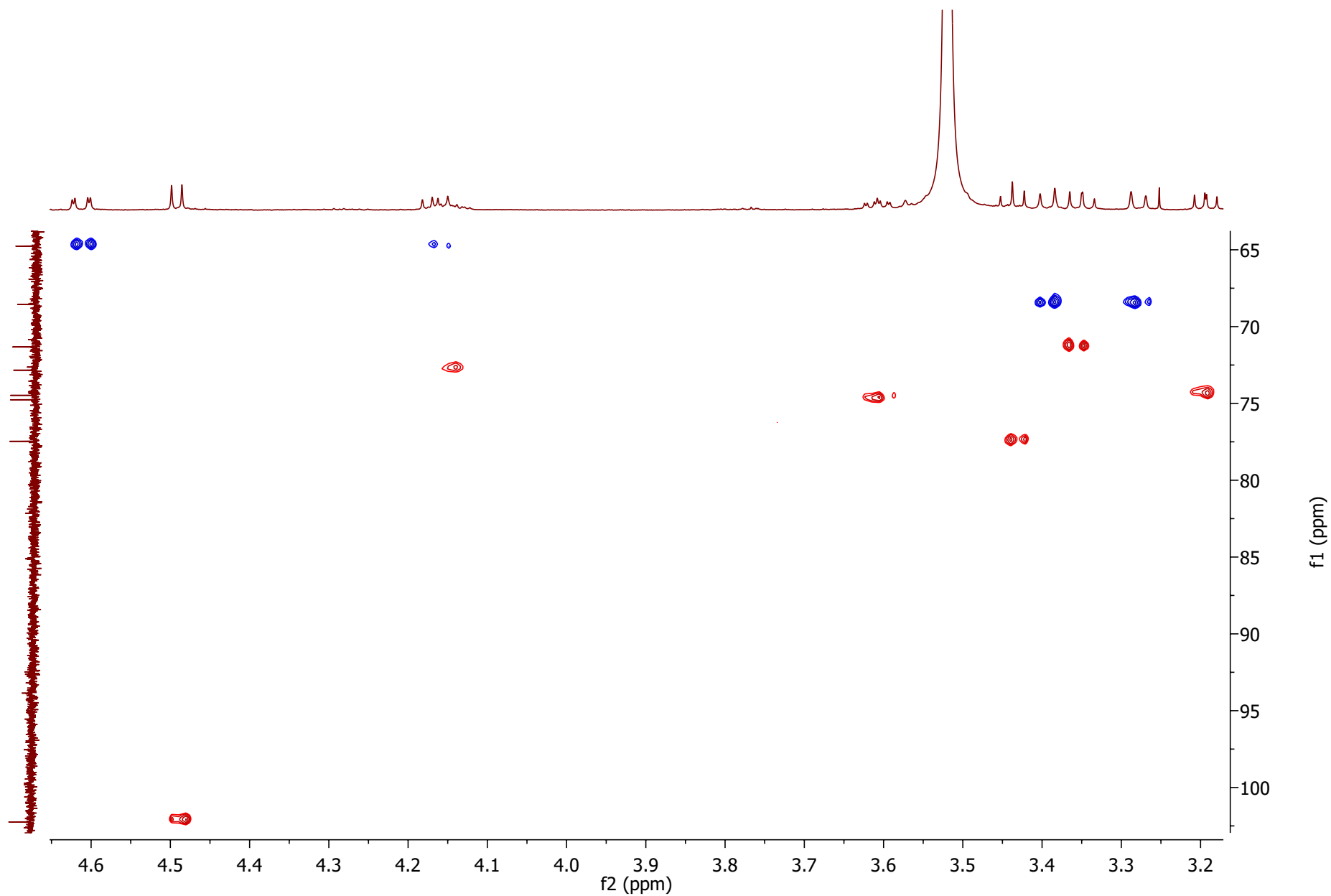


Figure S12. Expanded HSQC spectrum of compound **1** [600 MHz, acetone- d_6 + D_2O (9+1)]

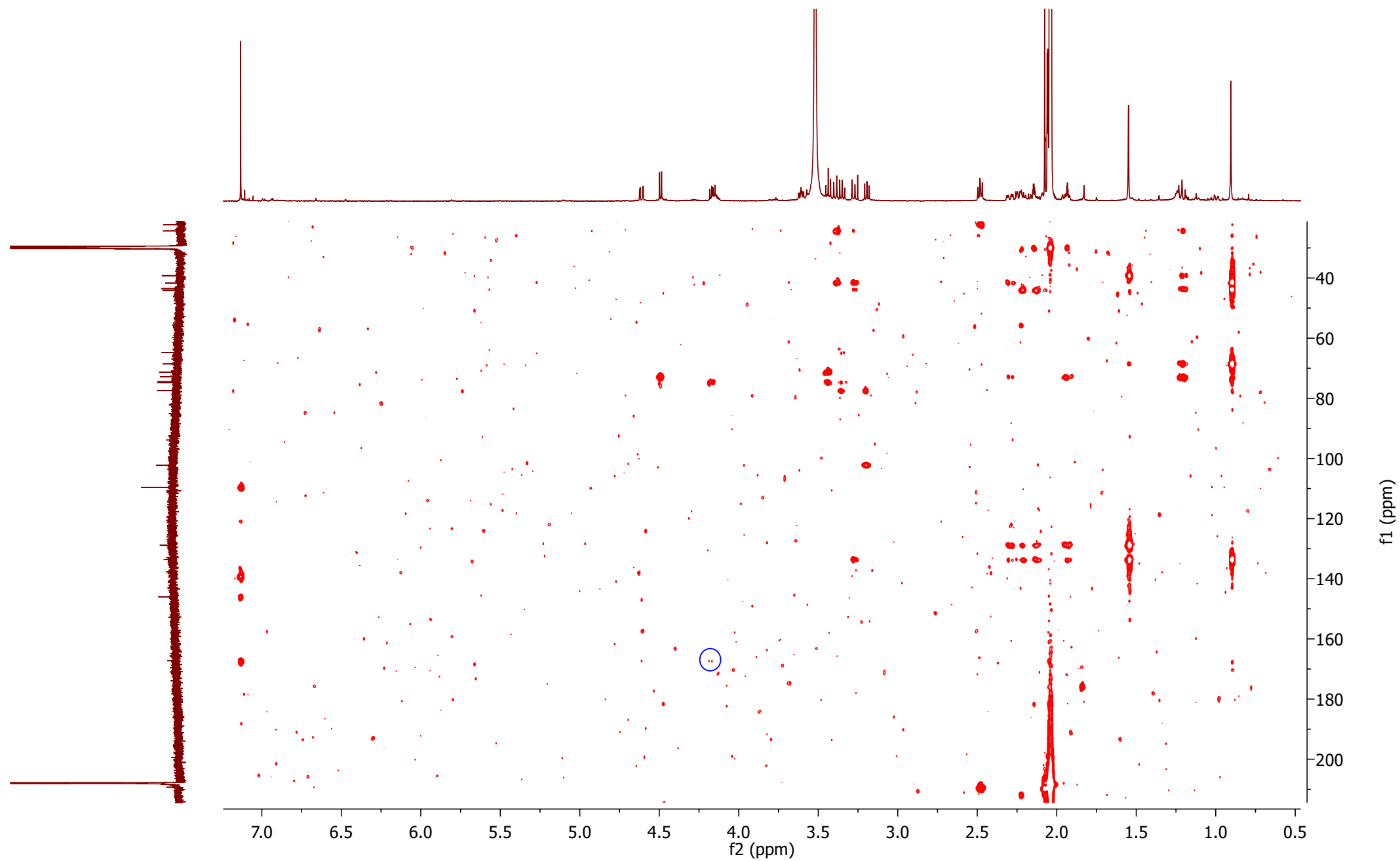


Figure S13. HMBC spectrum of compound **1** [600 MHz, acetone- d_6 + D $_2$ O (9+1)]

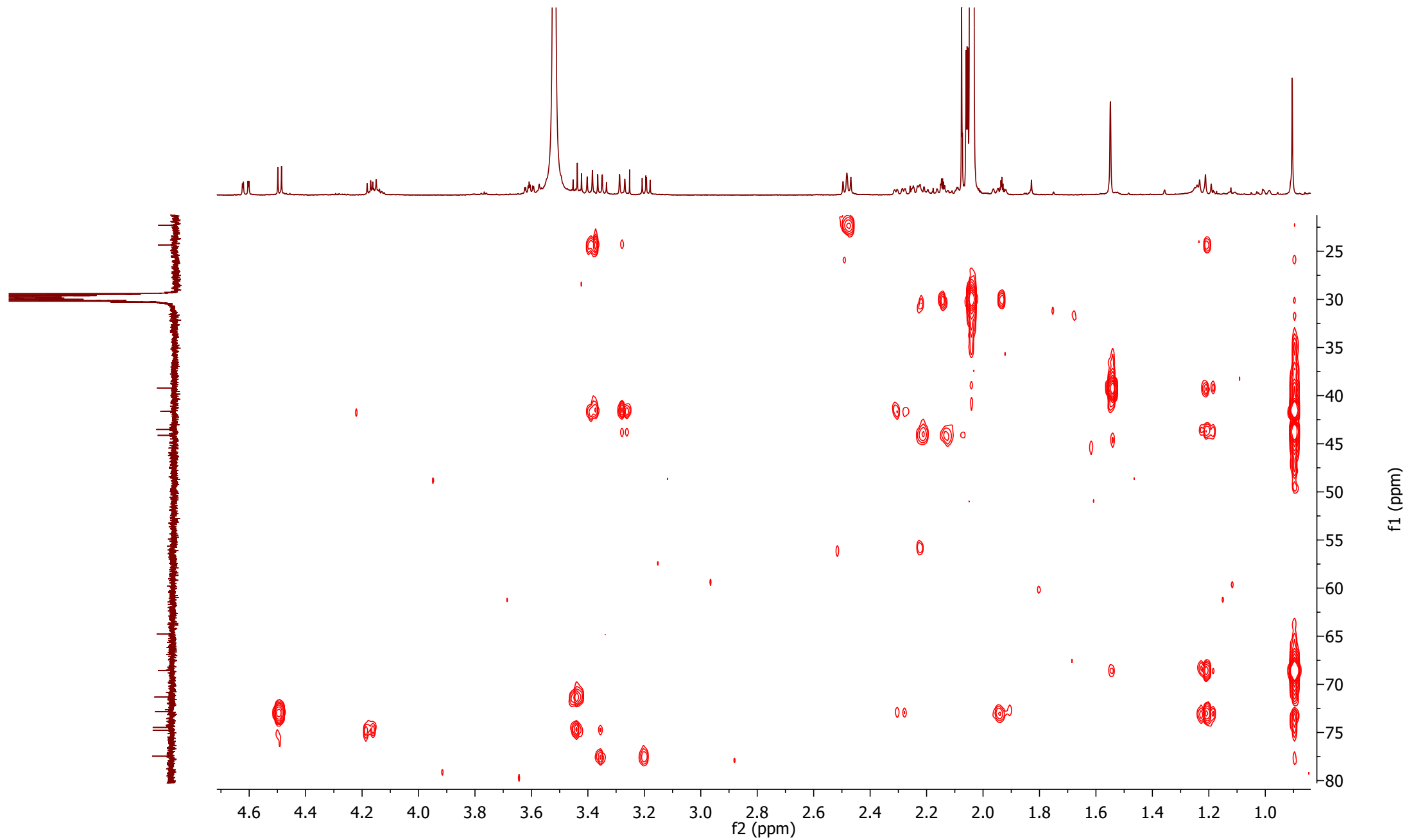


Figure S14. Expanded HMBC spectrum of compound **1** [600 MHz, acetone-*d*₆ + D₂O (9+1)]

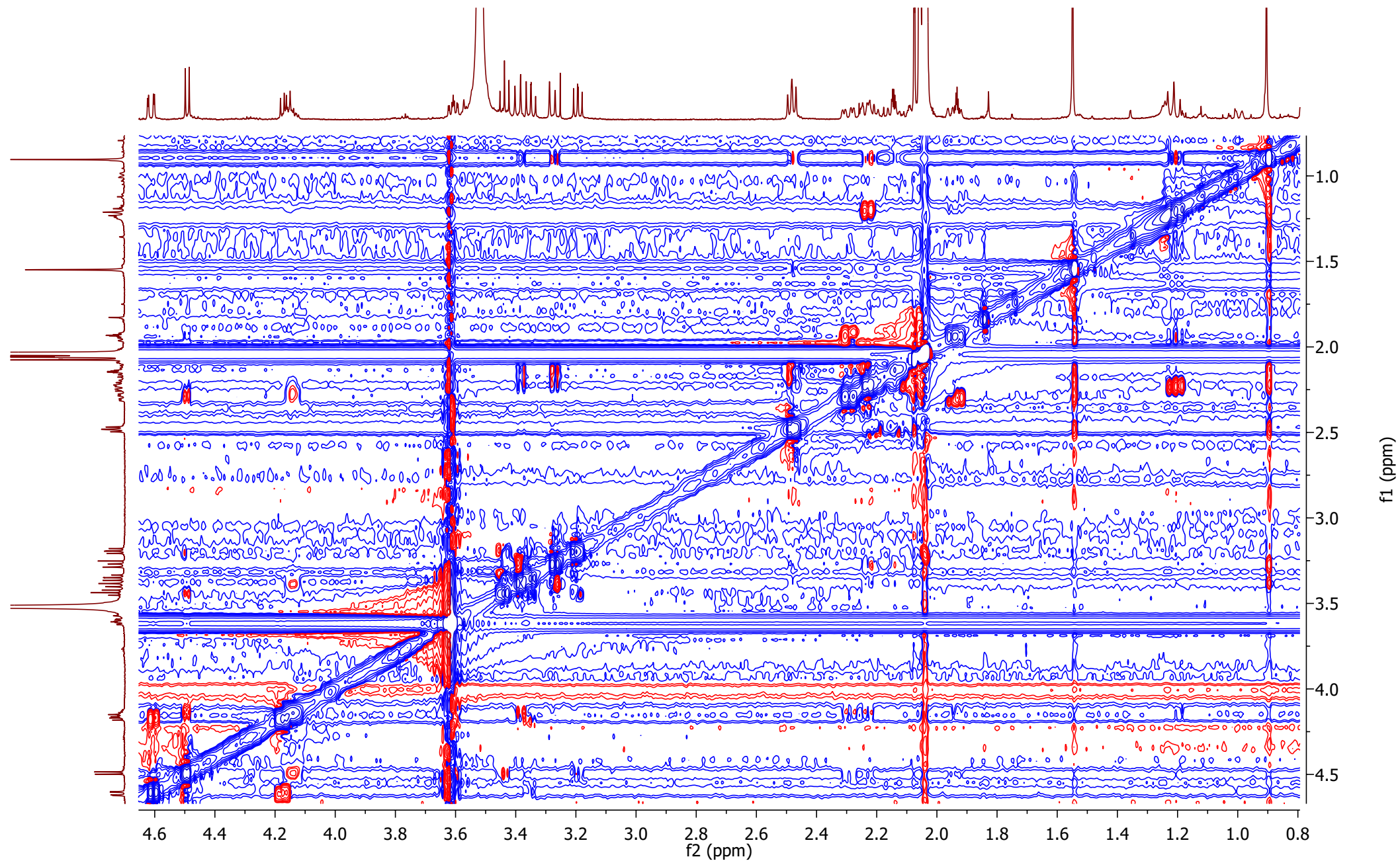


Figure S15. NOESY spectrum of compound **1** [600 MHz, acetone-*d*₆ + D₂O (9+1)]

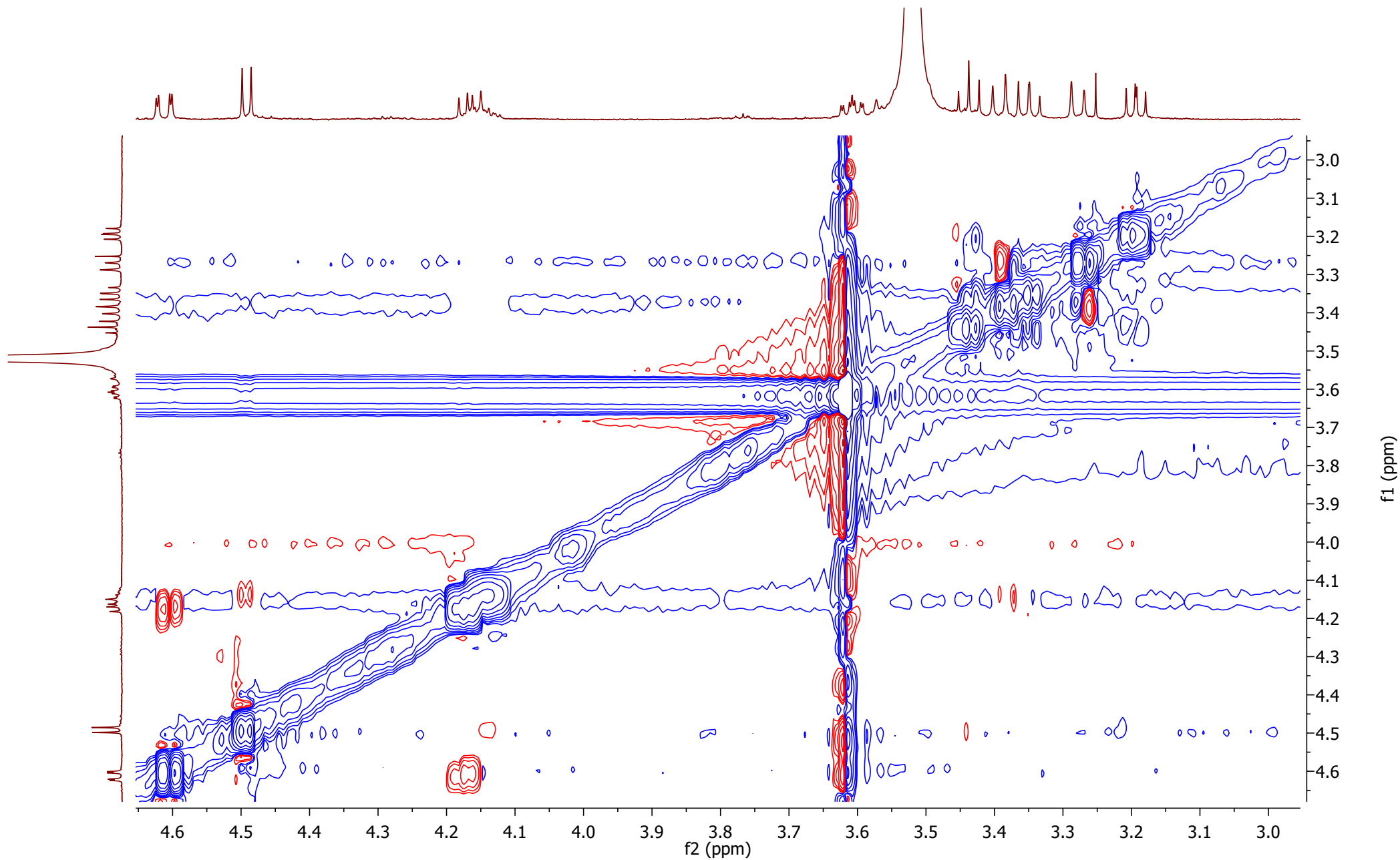


Figure S16. Expanded NOESY spectrum of compound **1** [600 MHz, acetone- d_6 + D_2O (9+1)]

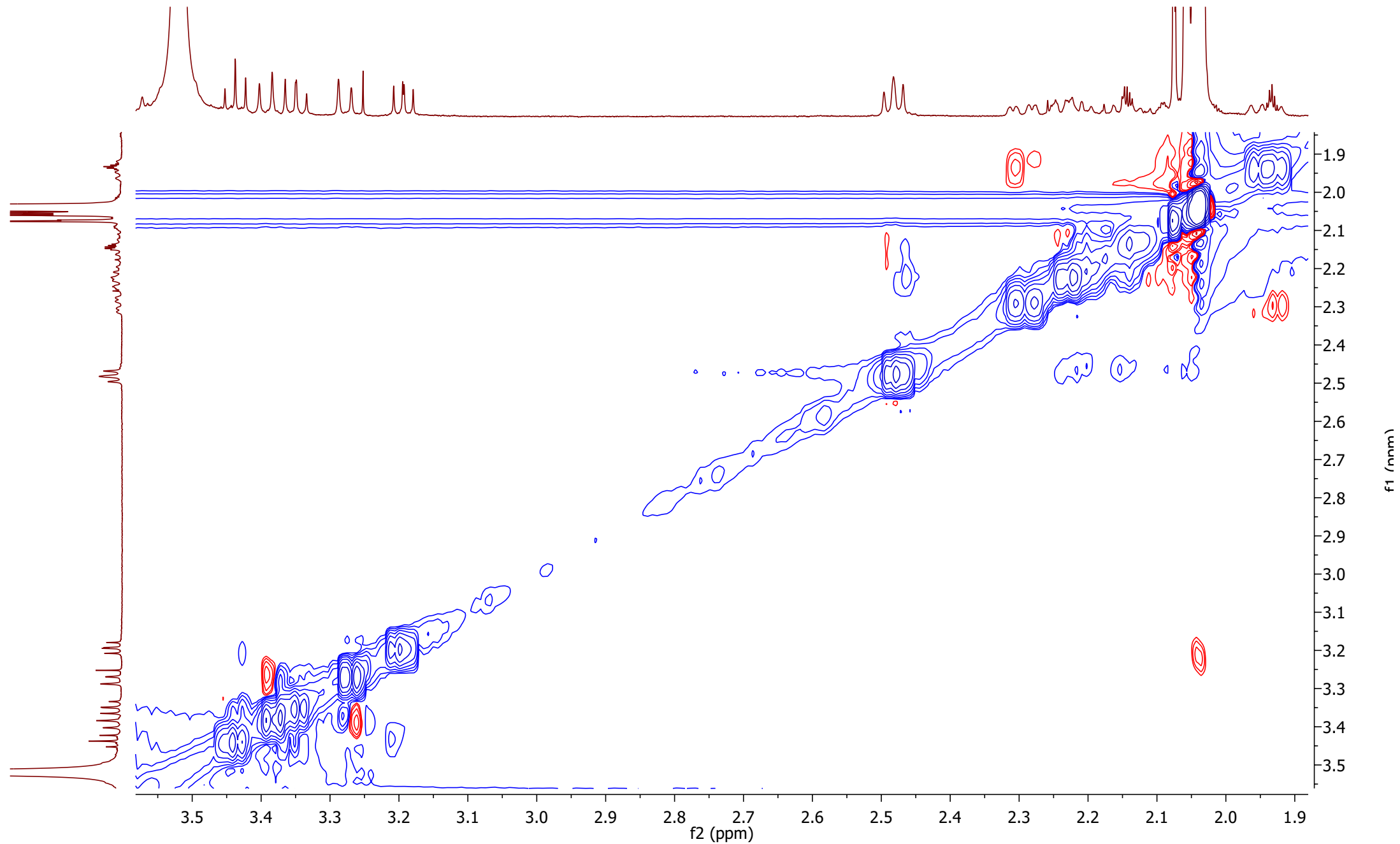


Figure S17. Expanded NOESY spectrum of compound **1** [600 MHz, acetone- d_6 + D $_2$ O (9+1)]

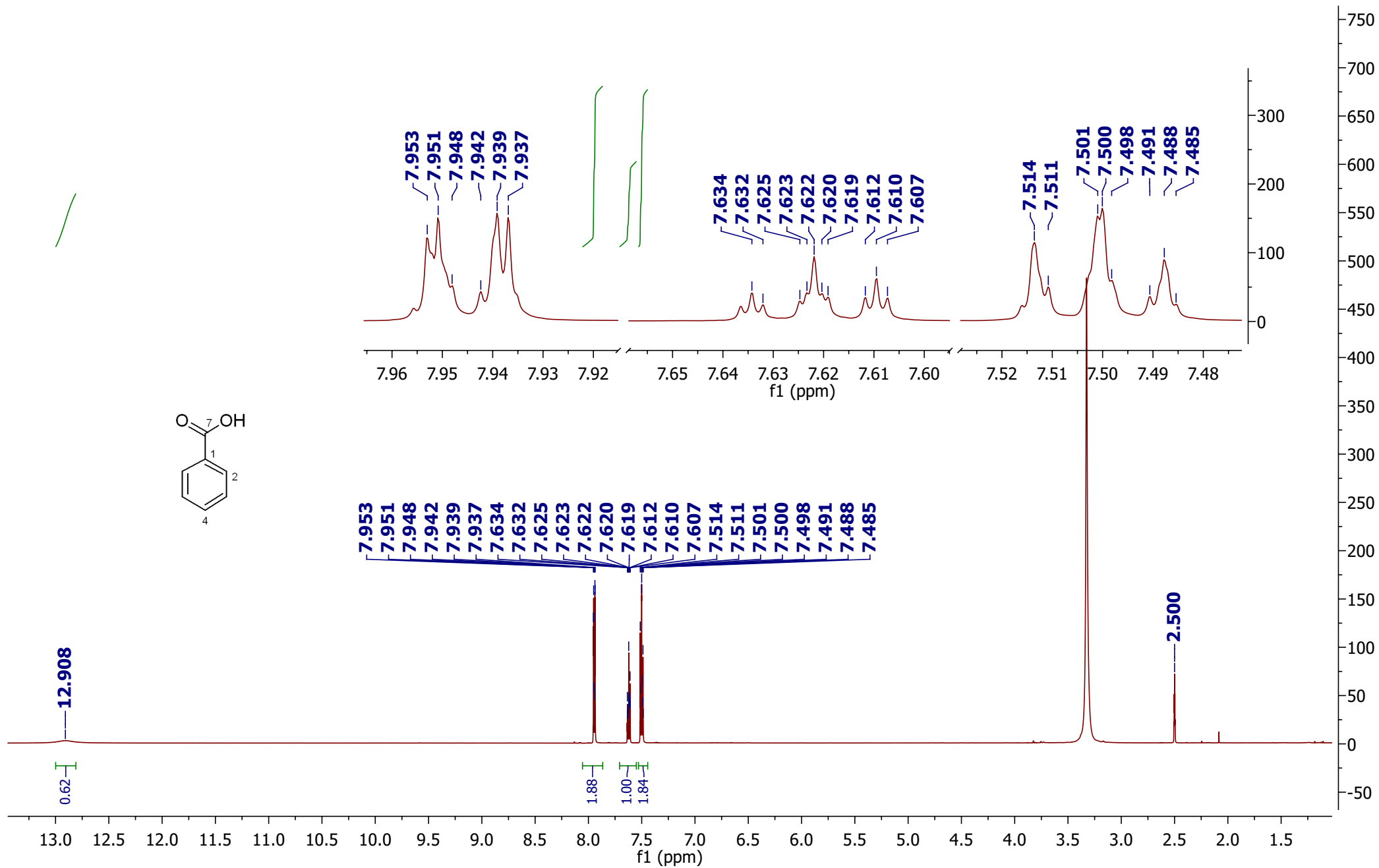


Figure S18. ¹H NMR spectrum of compound **2** (600 MHz, DMSO-*d*₆)

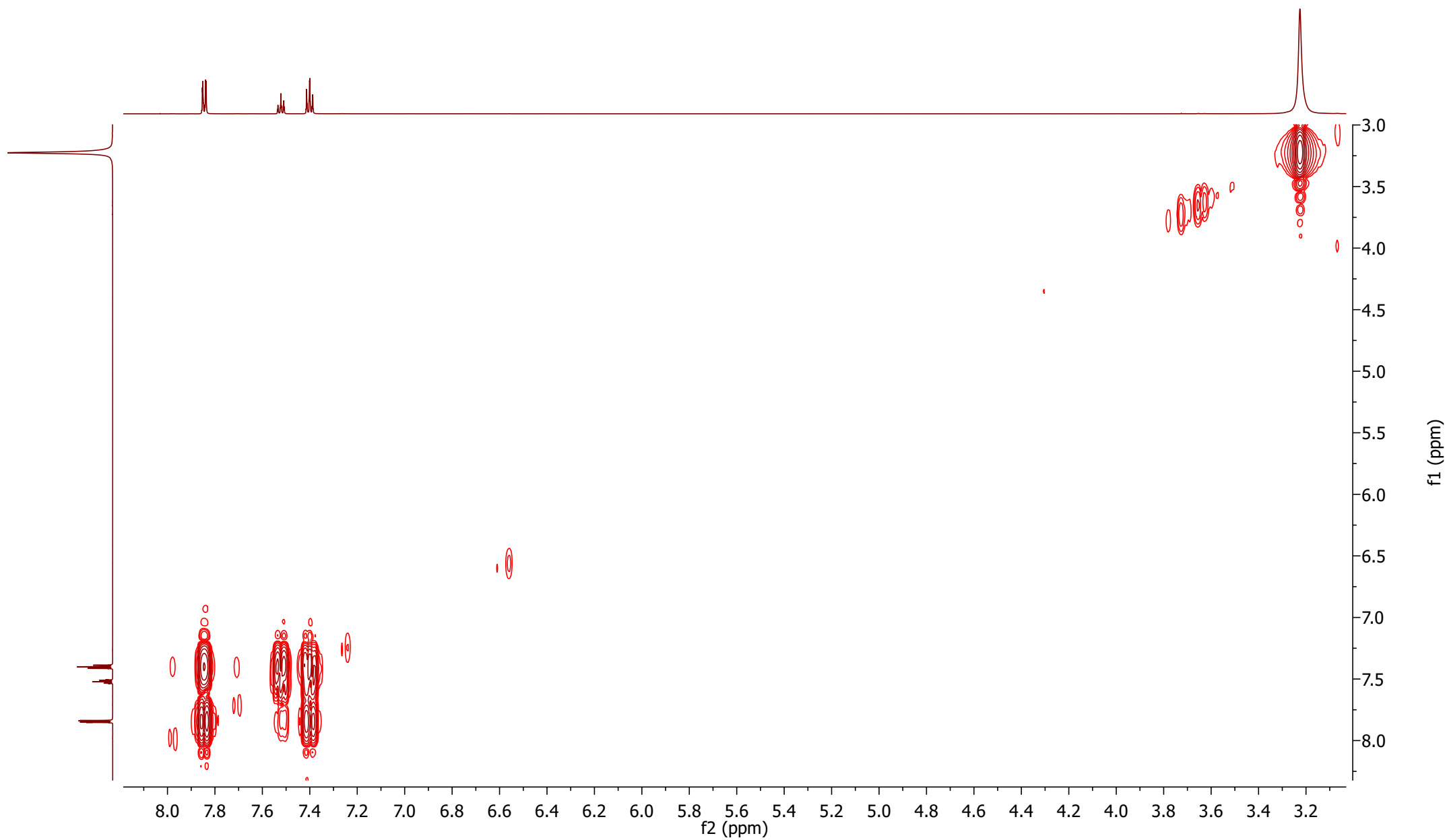


Figure S19. ^1H - ^1H COSY spectrum of compound **2** (600 MHz, DMSO- d_6)

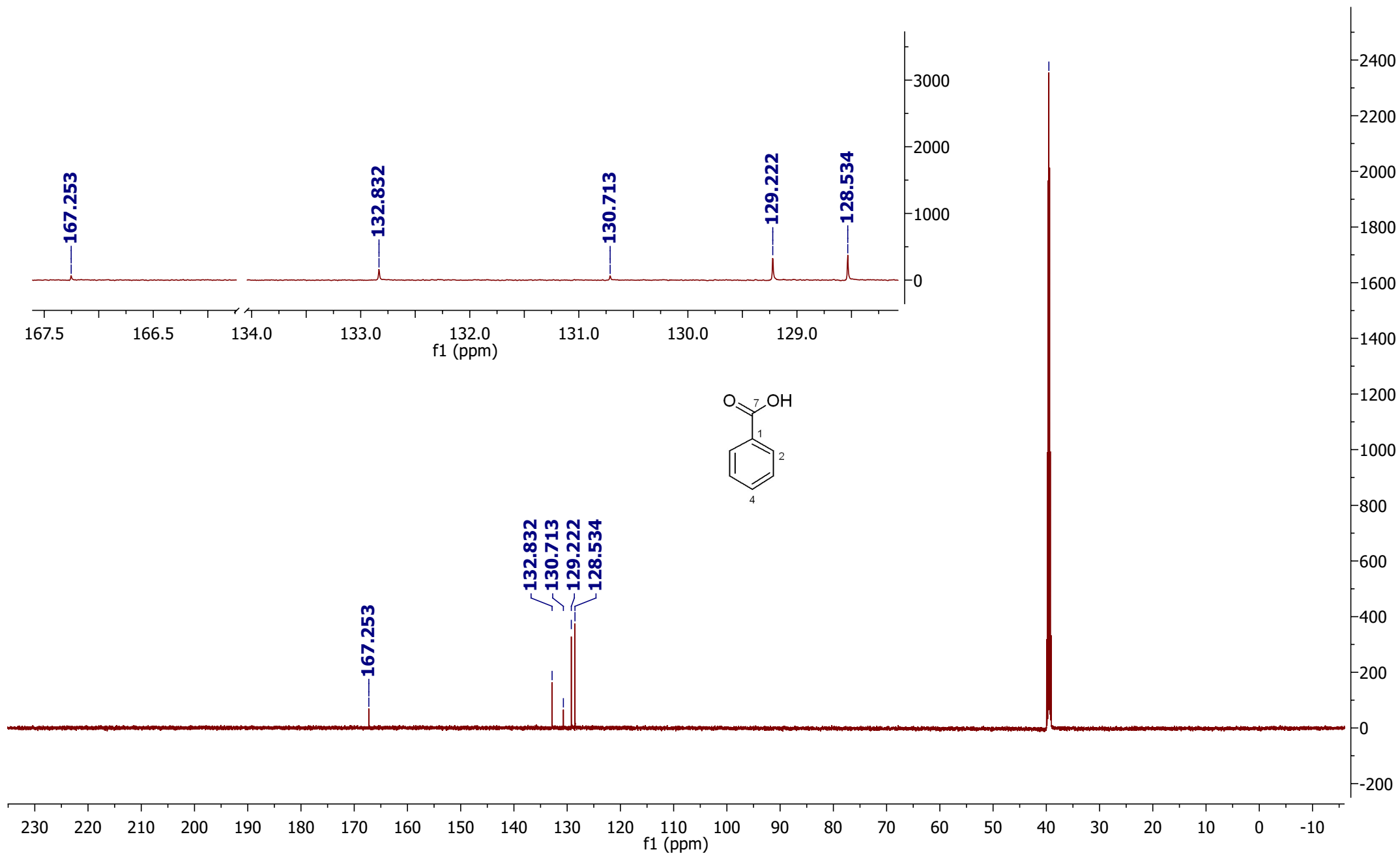


Figure S20. ^{13}C NMR spectrum of compound **2** (151 MHz, $\text{DMSO}-d_6$)

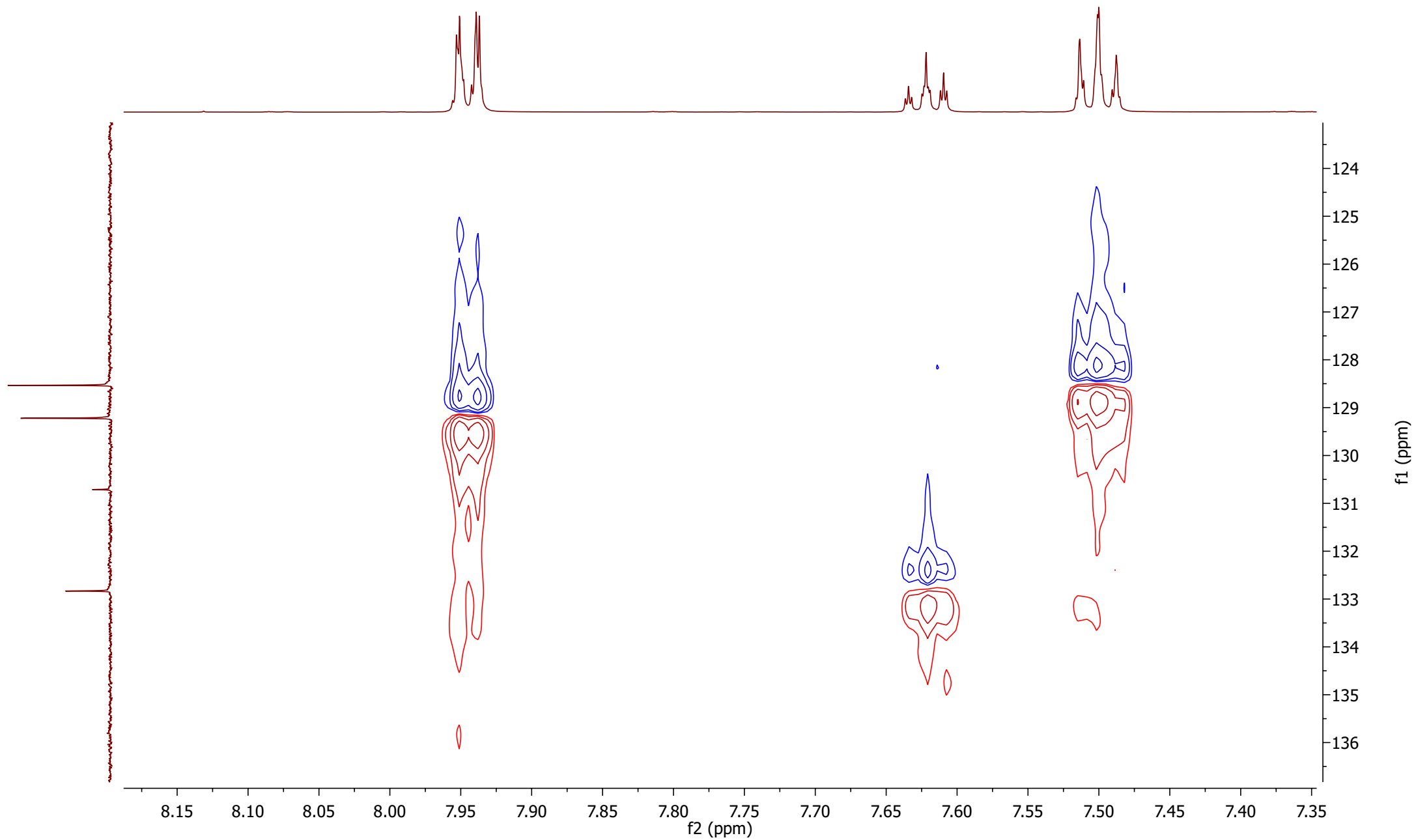


Figure S21. HSQC spectrum of compound **2** (600 MHz, DMSO- d_6)

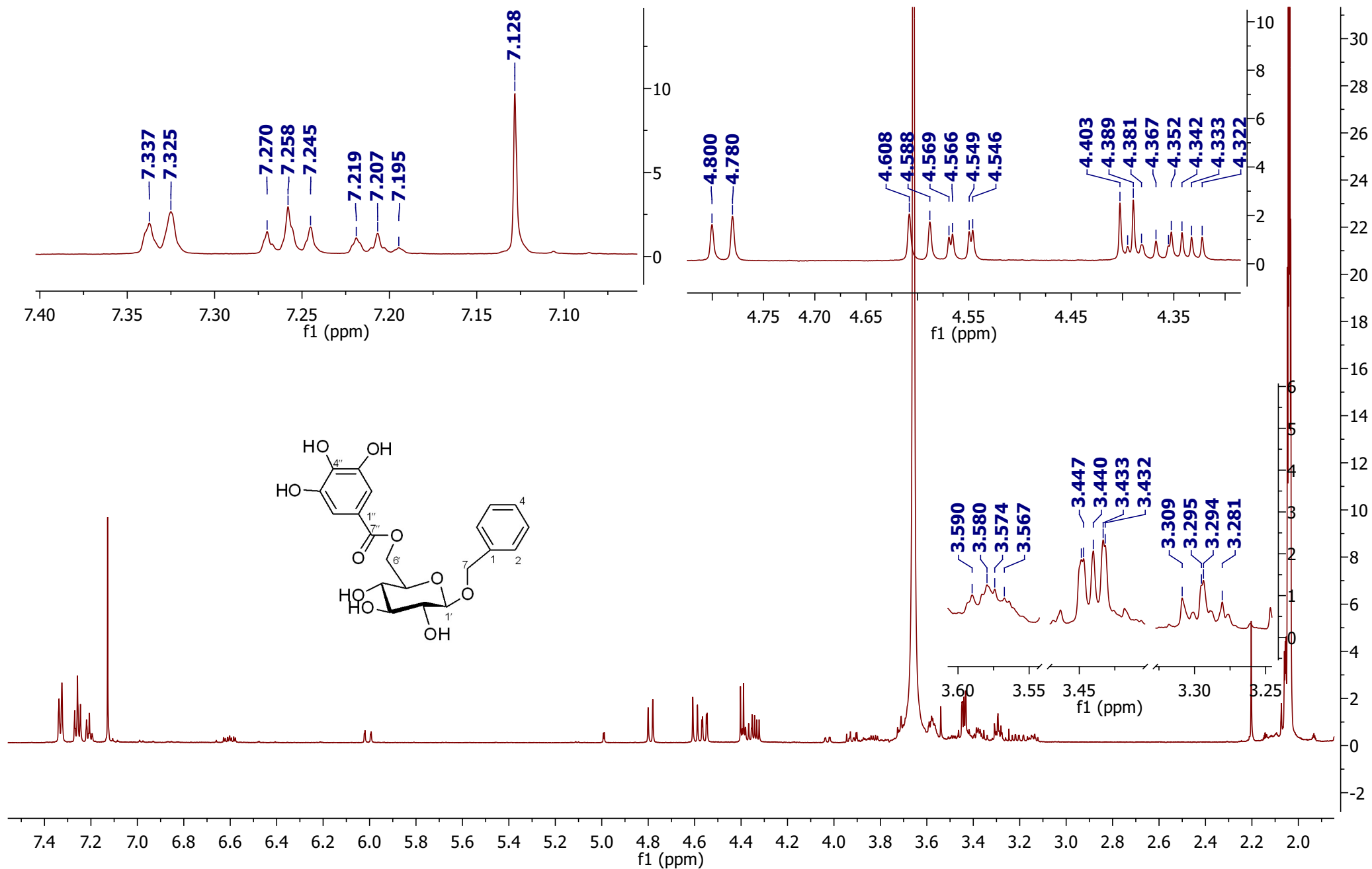


Figure S22. ^1H NMR spectrum of compound **3** [600 MHz, acetone- d_6 + D_2O (9+1)]

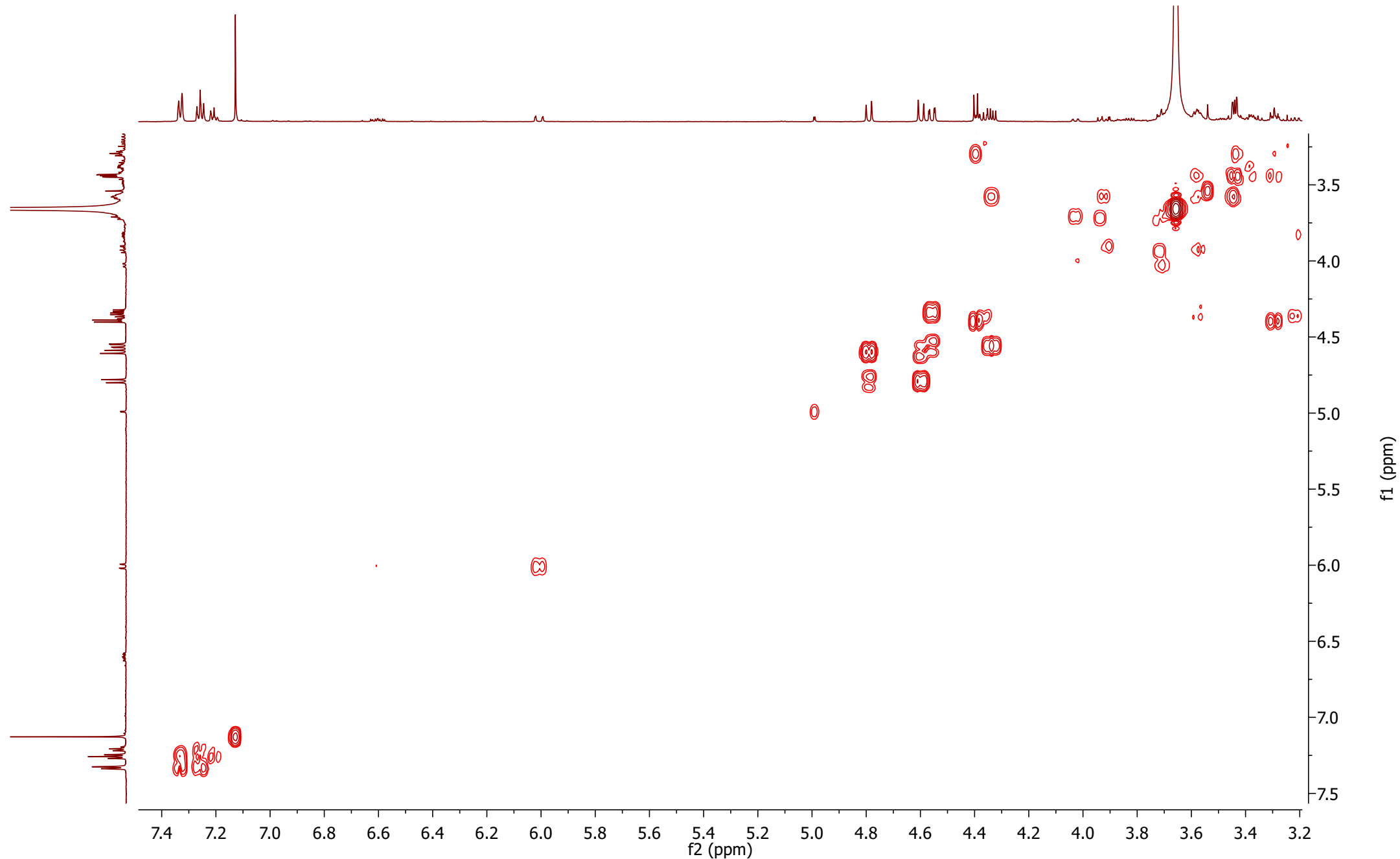


Figure S23. ^1H - ^1H COSY spectrum of compound **3** [600 MHz, acetone- d_6 + D_2O (9+1)]

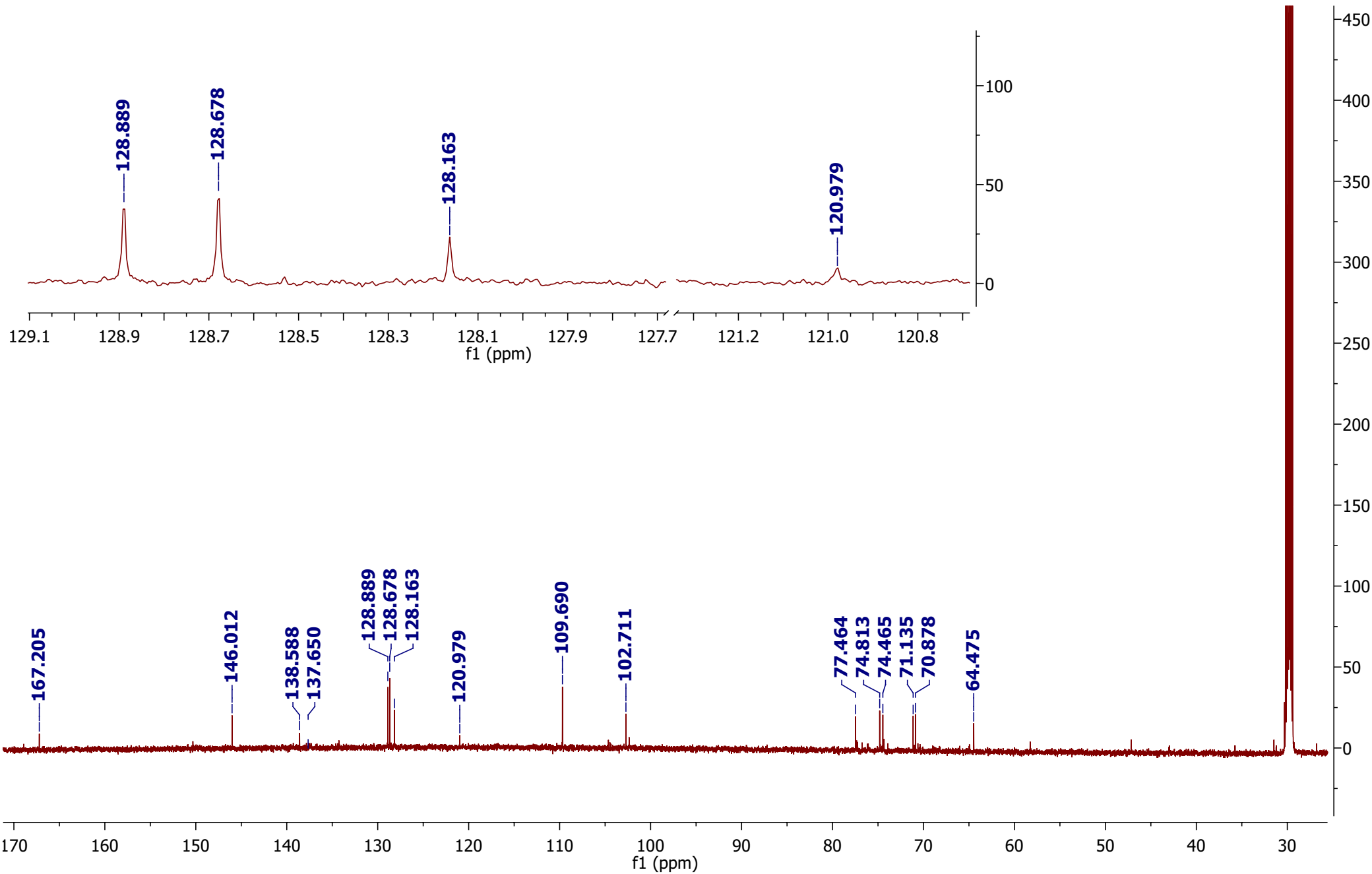


Figure S24. ^{13}C NMR spectrum of compound **31** [151 MHz, acetone- d_6 + D_2O (9+1)]

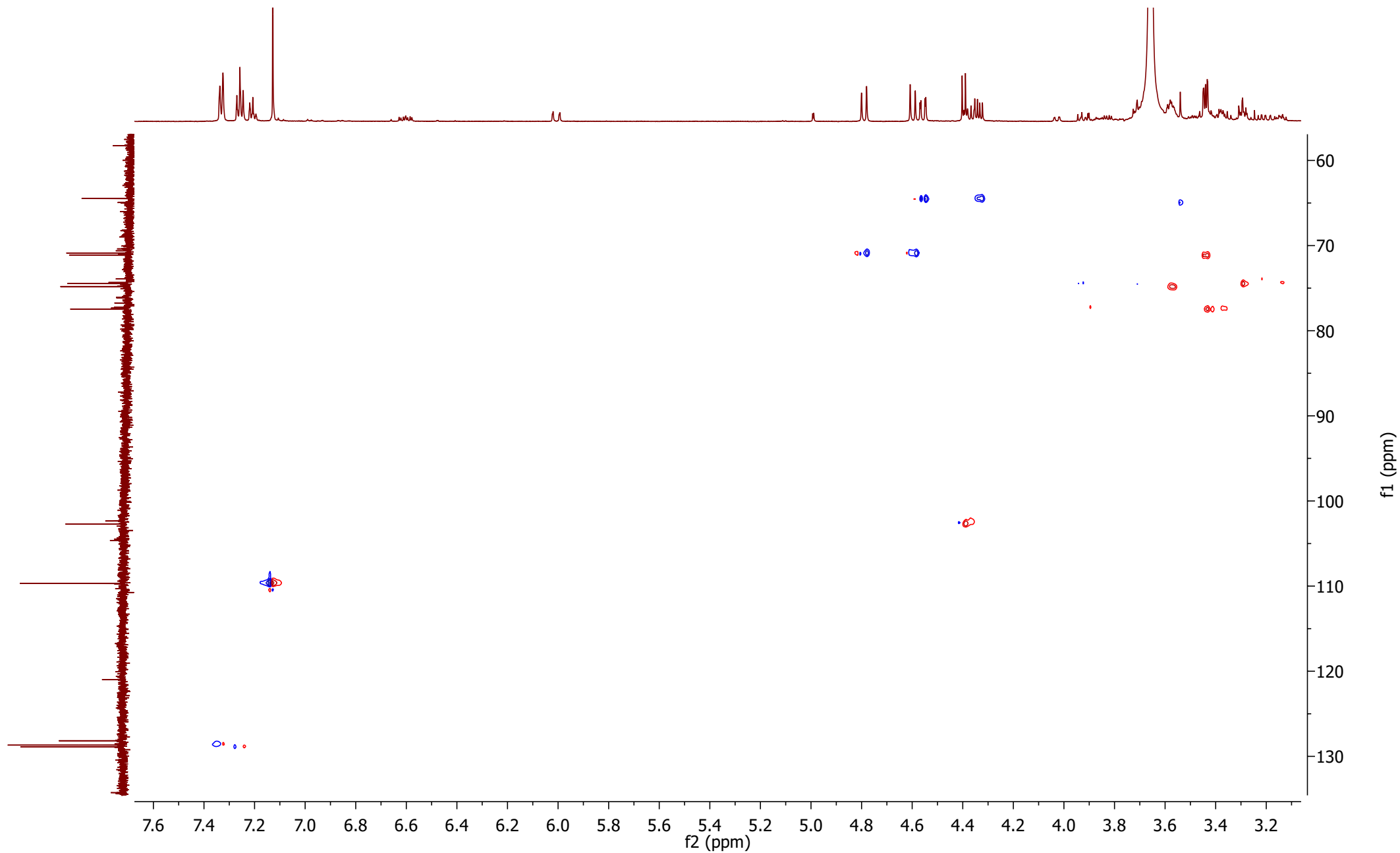


Figure S25. HSQC spectrum of compound **3** [600 MHz, acetone- d_6 + D $_2$ O (9+1)]

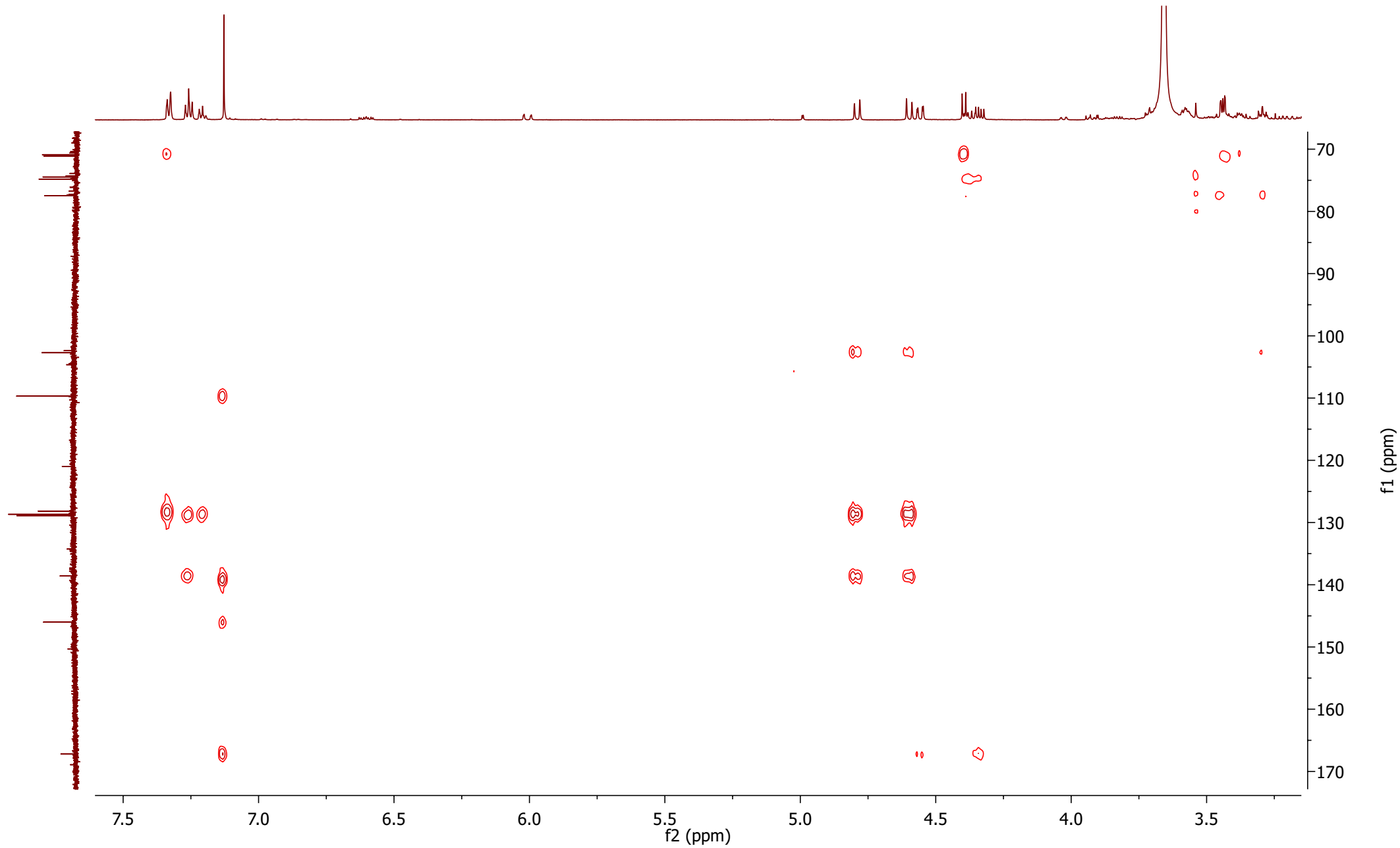


Figure S26. HMBC spectrum of compound **3** [600 MHz, acetone- d_6 + D_2O (9+1)]

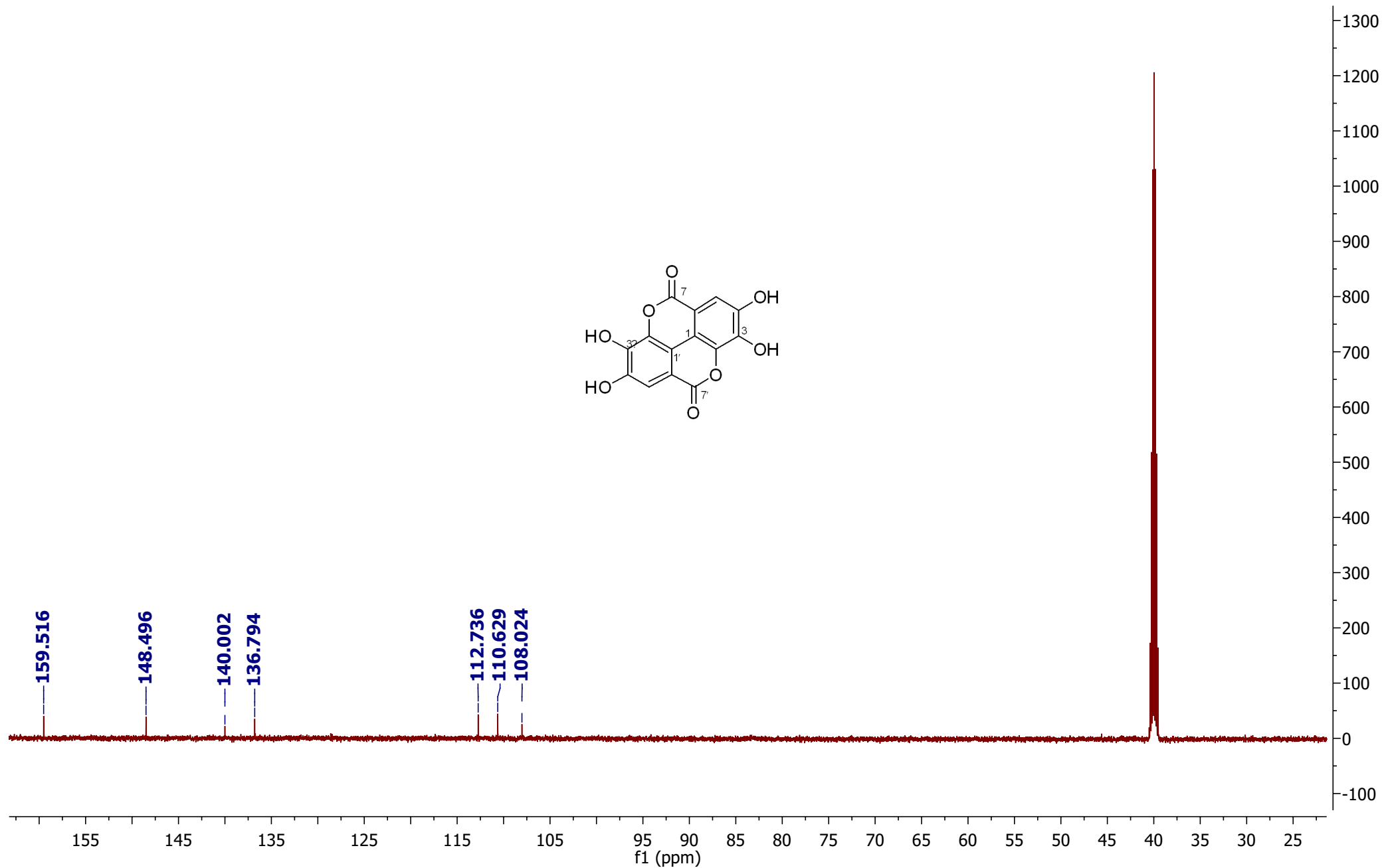


Figure S28. ^{13}C NMR spectrum of compound **4** (151 MHz, $\text{DMSO}-d_6$)

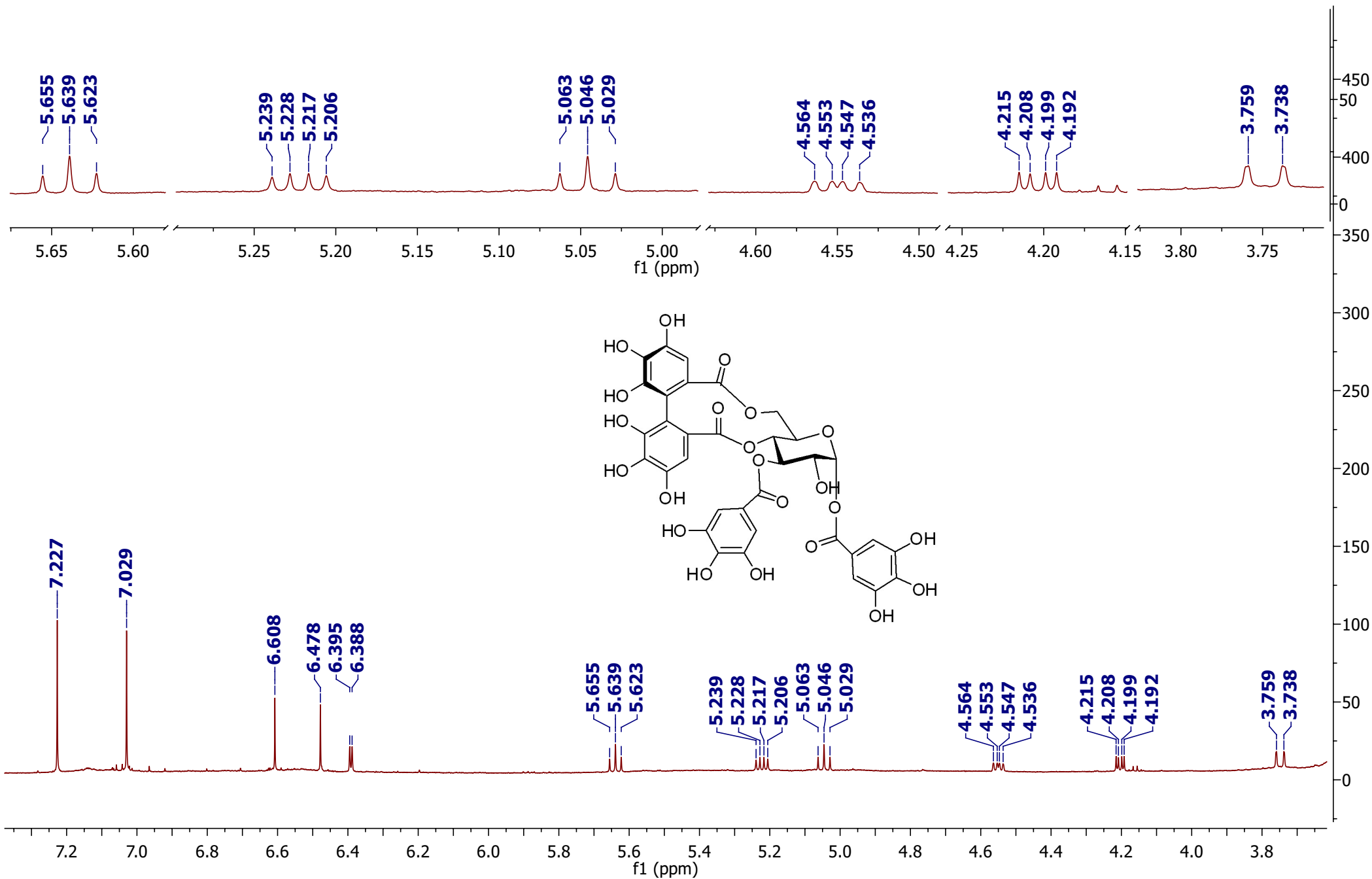


Figure S29. ^1H NMR spectrum of compound **5** [600 MHz, acetone- d_6 + D_2O (9+1)]

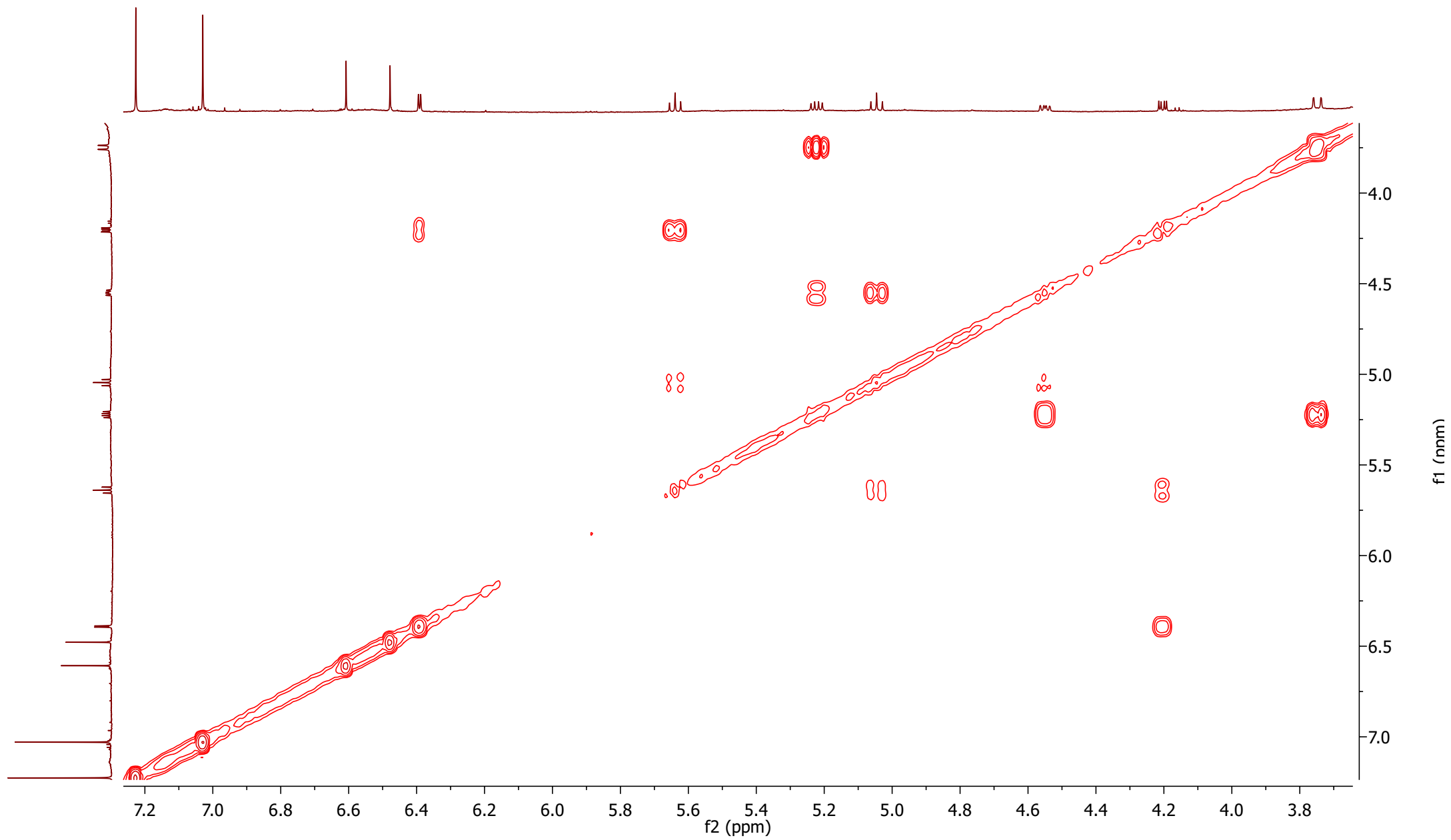


Figure S30. ^1H - ^1H COSY spectrum of compound **5** [600 MHz, acetone- d_6 + D_2O (9+1)]

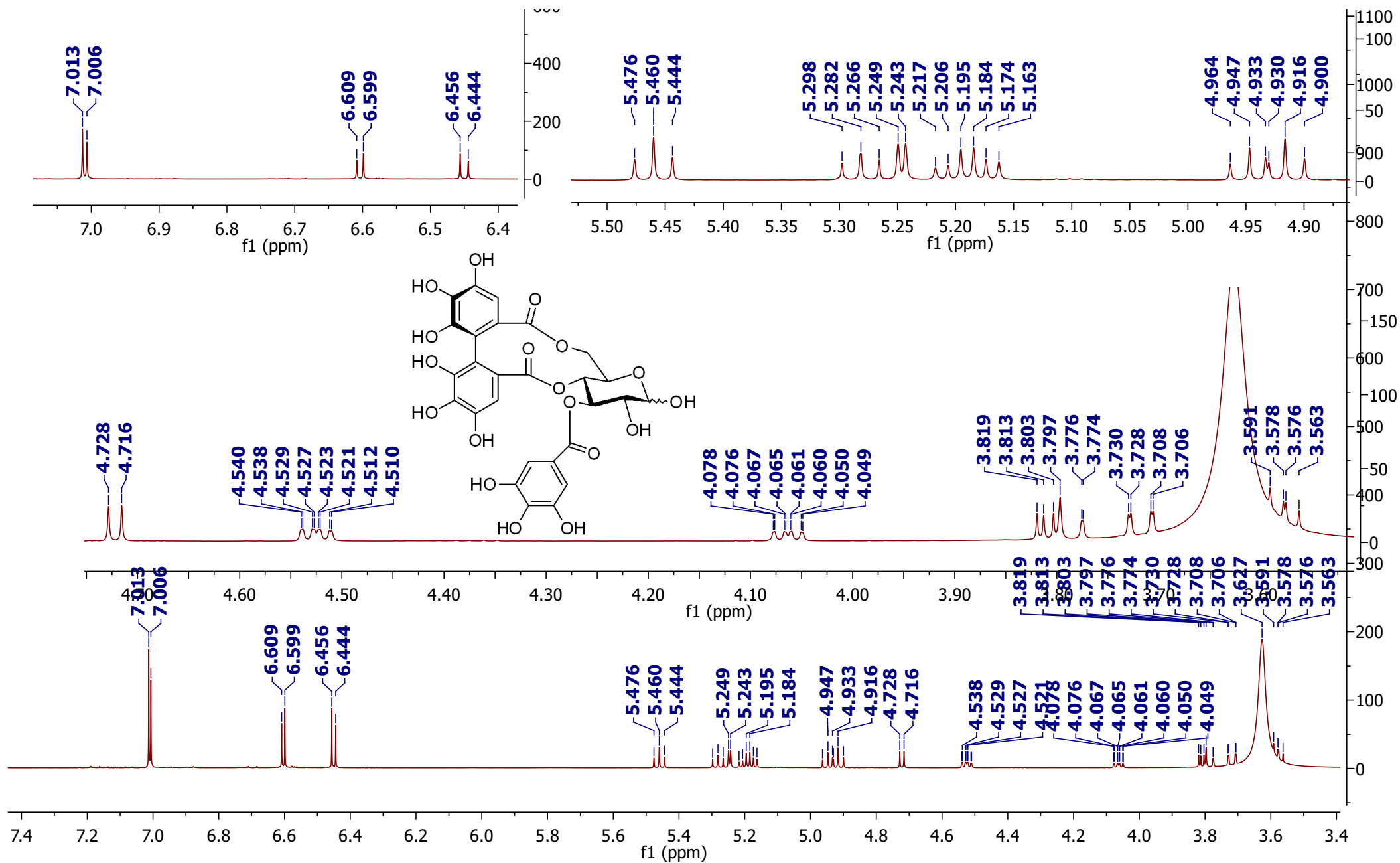


Figure S31. ^1H NMR spectrum of compound **6** [600 MHz, acetone- d_6 + D_2O (9+1)]

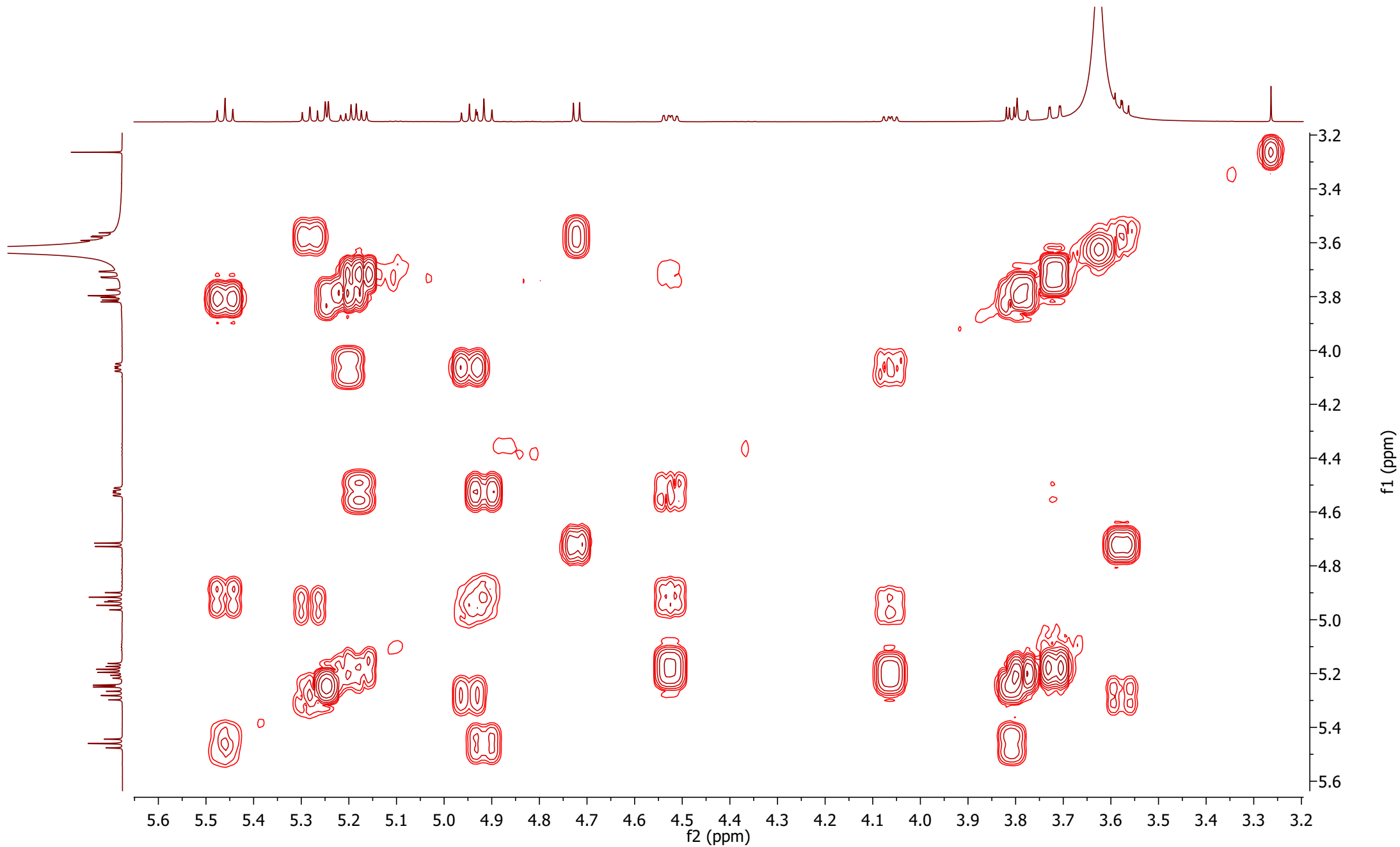


Figure S32. ^1H - ^1H COSY spectrum of compound **6** [600 MHz, acetone- d_6 + D_2O (9+1)]

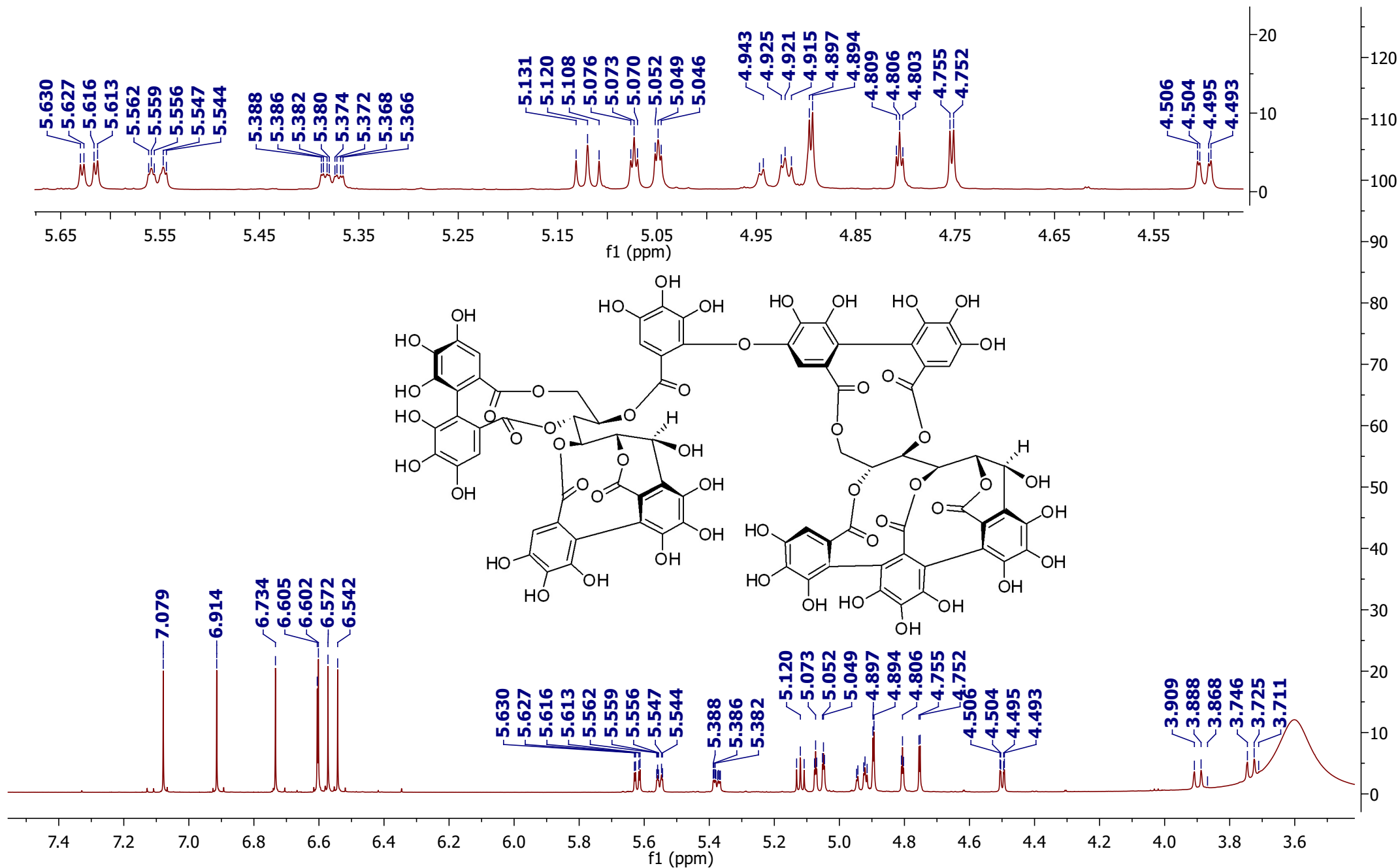


Figure S33. ^1H NMR spectrum of compound **7** [600 MHz, acetone- d_6 + D_2O (9+1)]

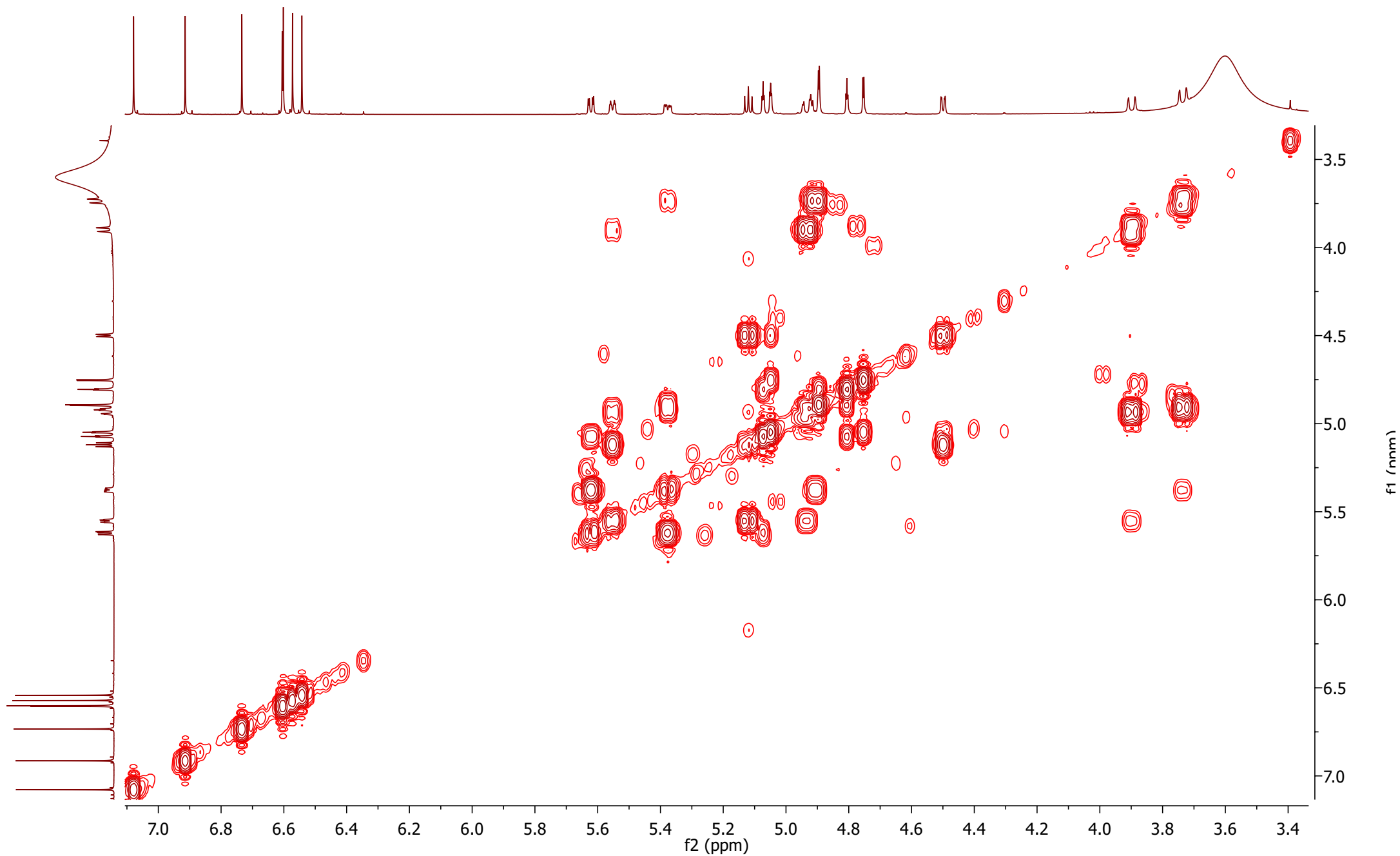


Figure S34. ^1H - ^1H COSY spectrum of compound **7** [600 MHz, acetone- d_6 + D_2O (9+1)]

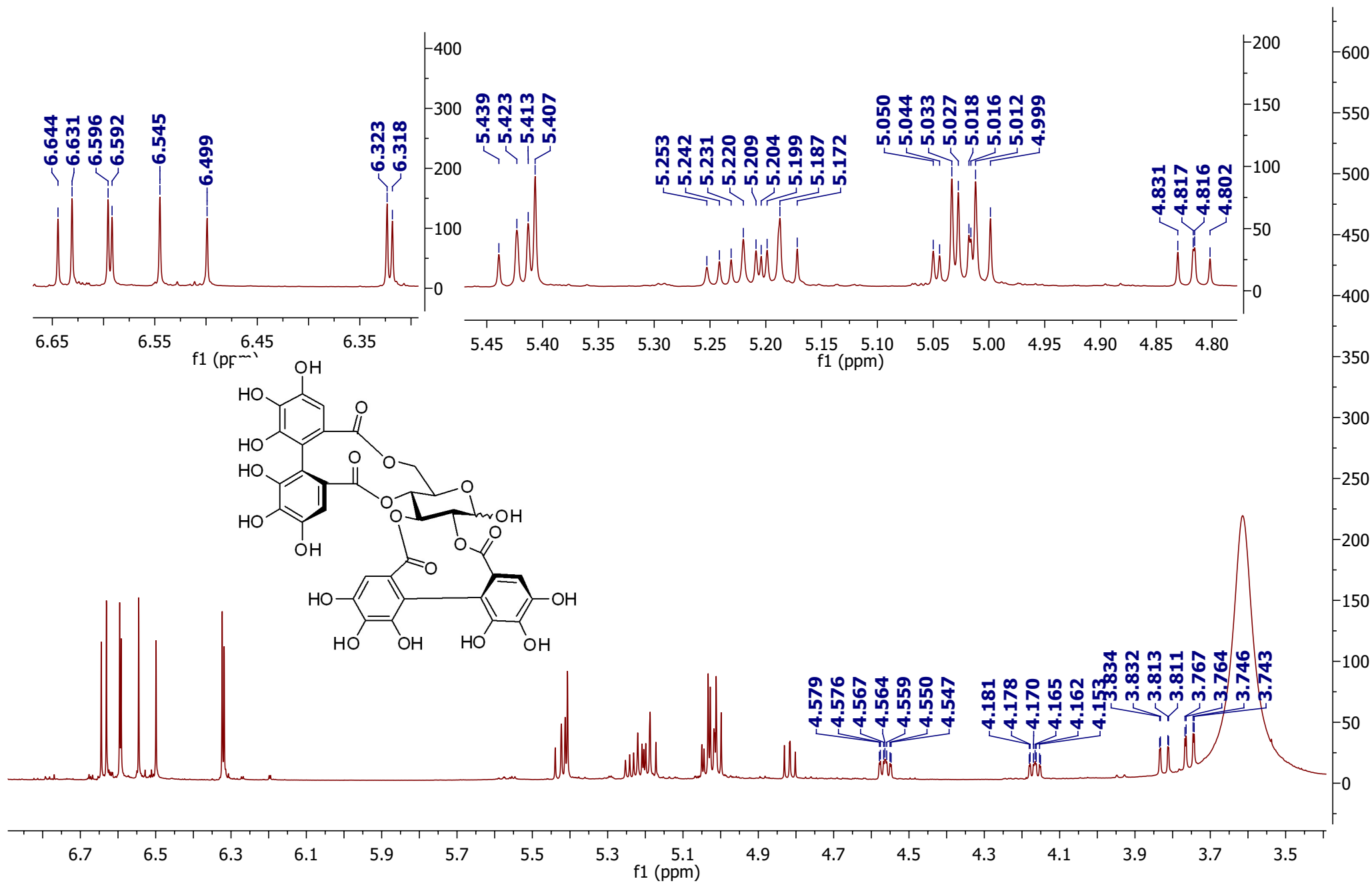


Figure S35. ^1H NMR spectrum of compound **8** [600 MHz, acetone- d_6 + D_2O (9+1)]

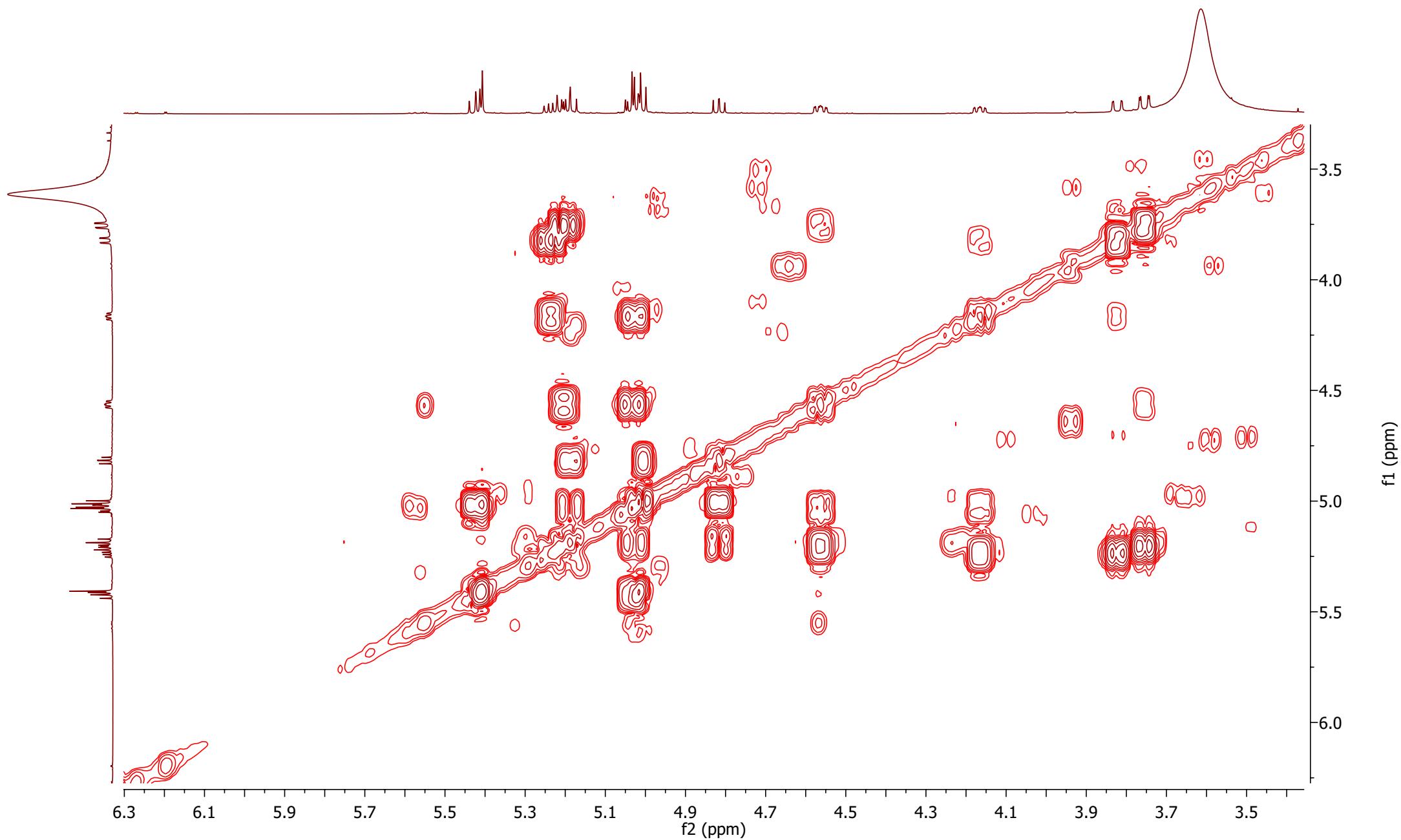


Figure S36. ^1H - ^1H COSY spectrum of compound **8** [600 MHz, acetone- d_6 + D_2O (9+1)]

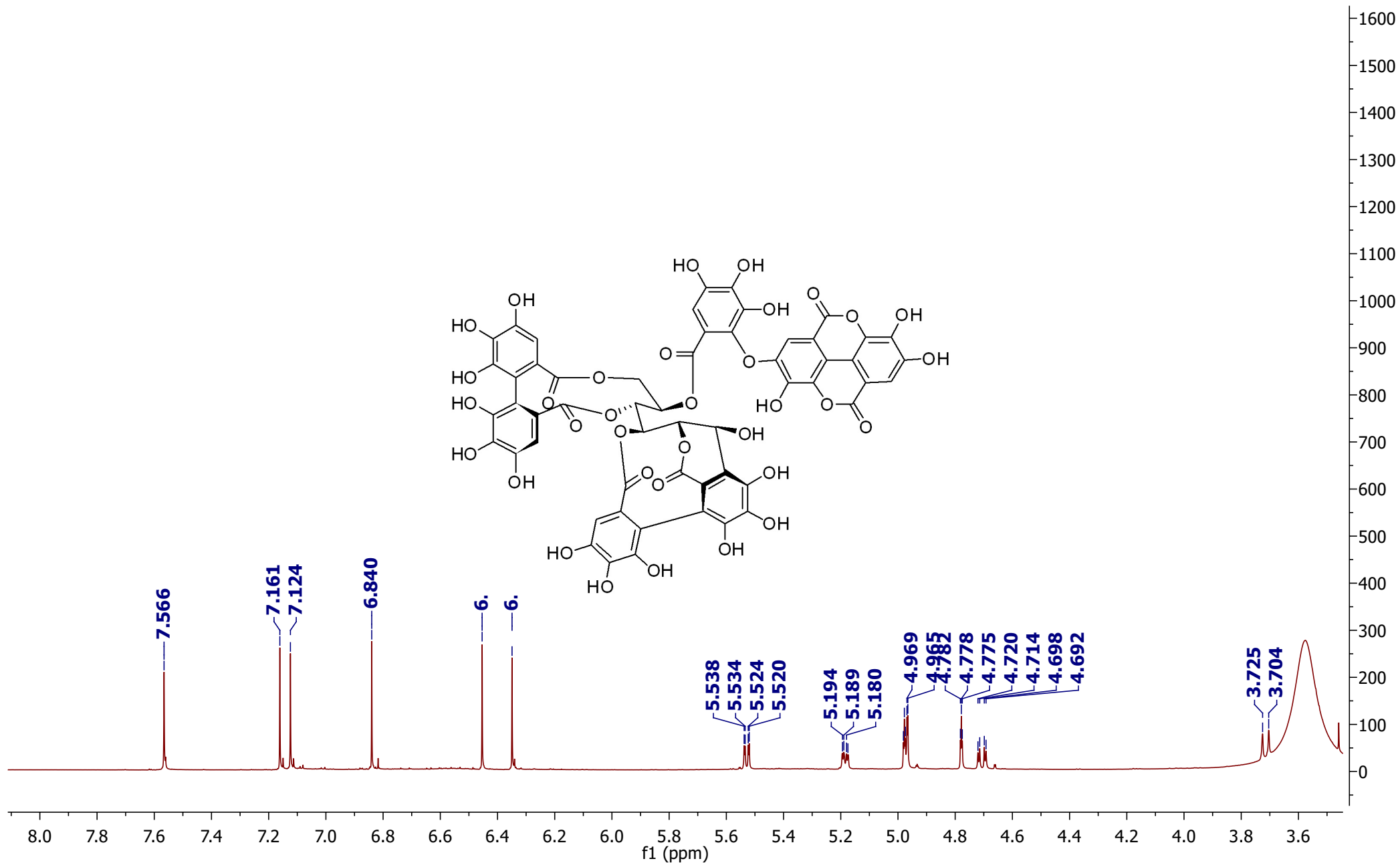


Figure S37. ^1H NMR spectrum of compound **9** [600 MHz, acetone- d_6 + D_2O (9+1)]

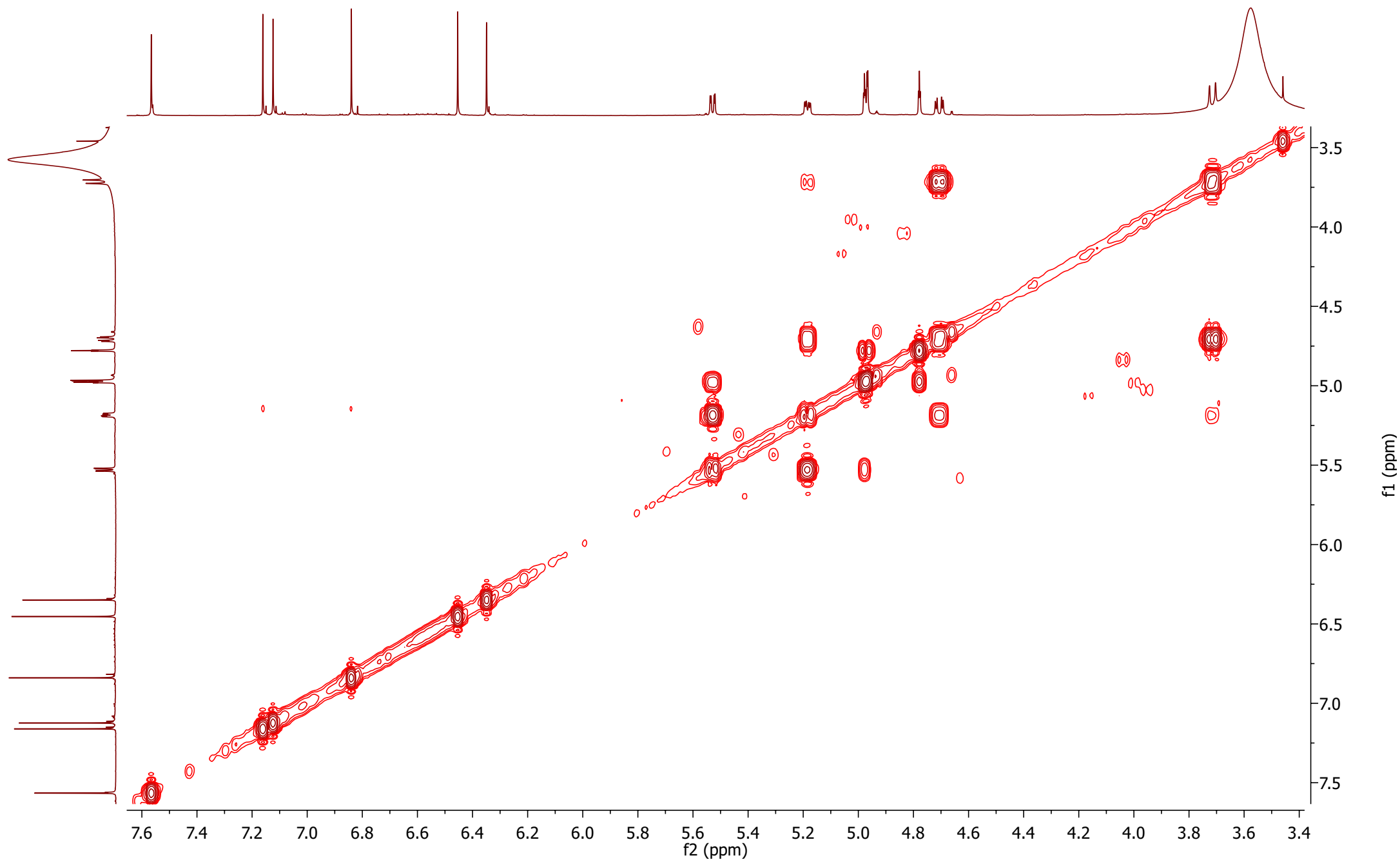


Figure S38. ^1H - ^1H COSY spectrum of compound **9** [600 MHz, acetone- d_6 + D_2O (9+1)]

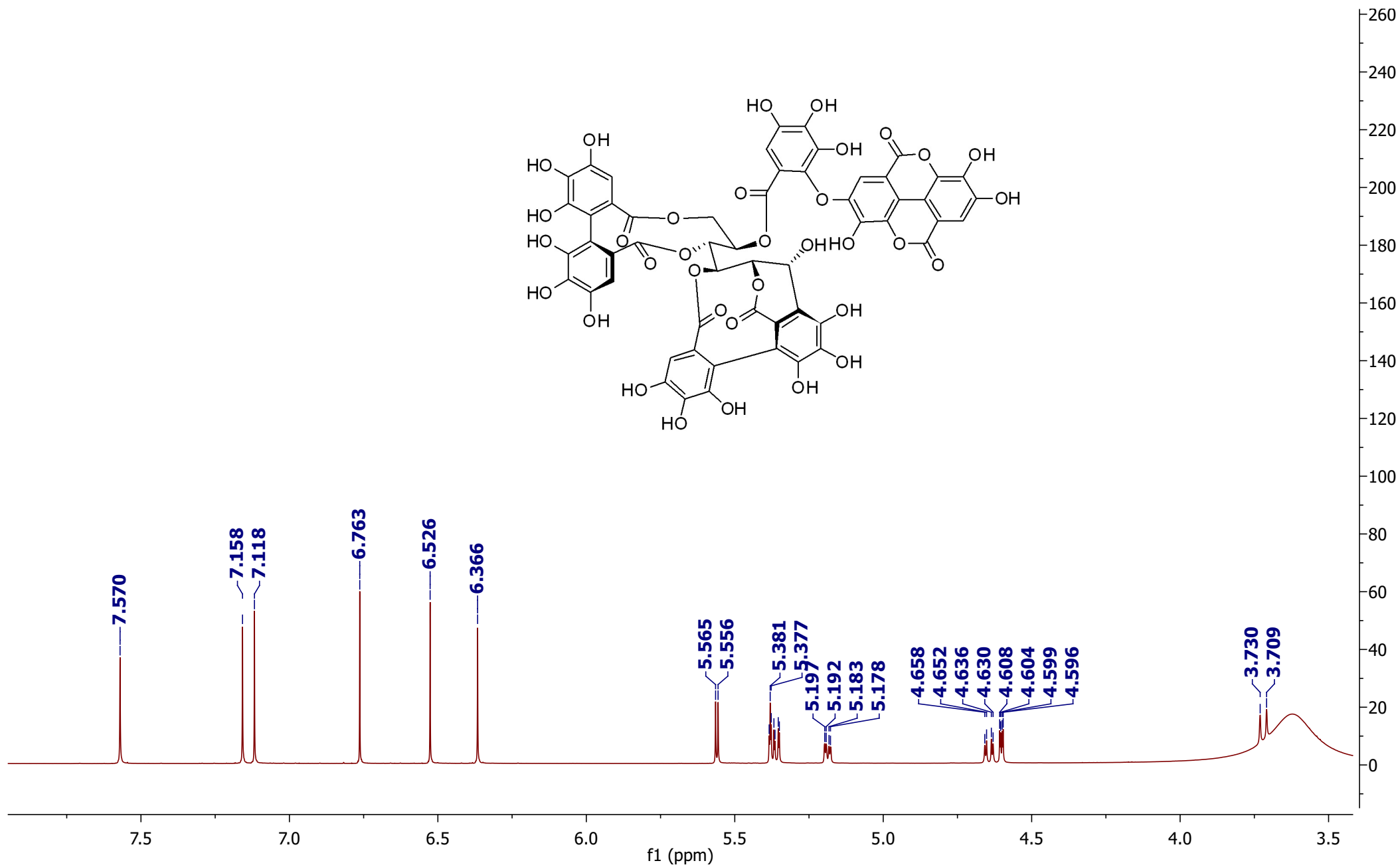


Figure S39. ¹H NMR spectrum of compound **10** [600 MHz, acetone-d₆ + D₂O (9+1)]

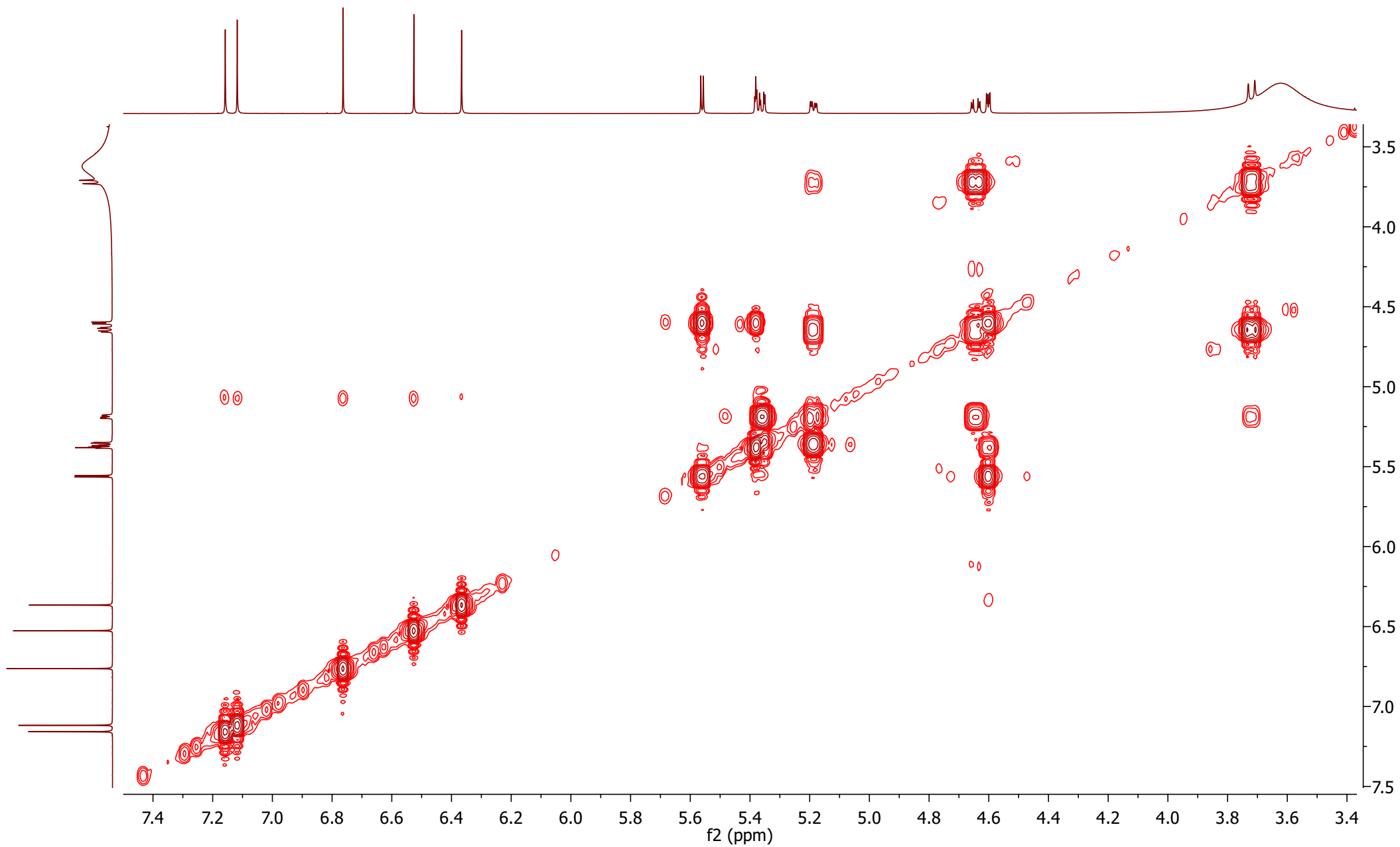


Figure S40. ^1H - ^1H COSY spectrum of compound **10** [600 MHz, acetone- d_6 + D_2O (9+1)]

Experimental procedures of TD-DFT calculation of the ECD spectrum of **1**

Quantum chemical calculations were performed with Gaussian16 [1]. The geometry of the various stereoisomers of compound **1** (1r3r, 1r3s, 1s3r, and 1s3s) were optimized in the gas phase with B3LYP/6-31+G and the resulting were confirmed to be stable structures (no imaginary frequencies). The resulting structures were then optimized with CAM-B3LYP/6-31G(d,p) in methanol using the polarizable continuum model (PCM) [2] and the optimized structures were used to calculate the ECD spectra with TD-DFT [3] at the same level. The CAM-B3LYP functional is chosen as it yields spectral properties in good agreement with experiment [4].

References

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- [4] El-Zohry, A.M., Orabi, E.A., Karlsson, M. and Zietz, B., 2021. Twisted Intramolecular Charge Transfer (TICT) Controlled by Dimerization: An Overlooked Piece of the TICT Puzzle. *The Journal of Physical Chemistry A*, 125(14), pp.2885-2894.

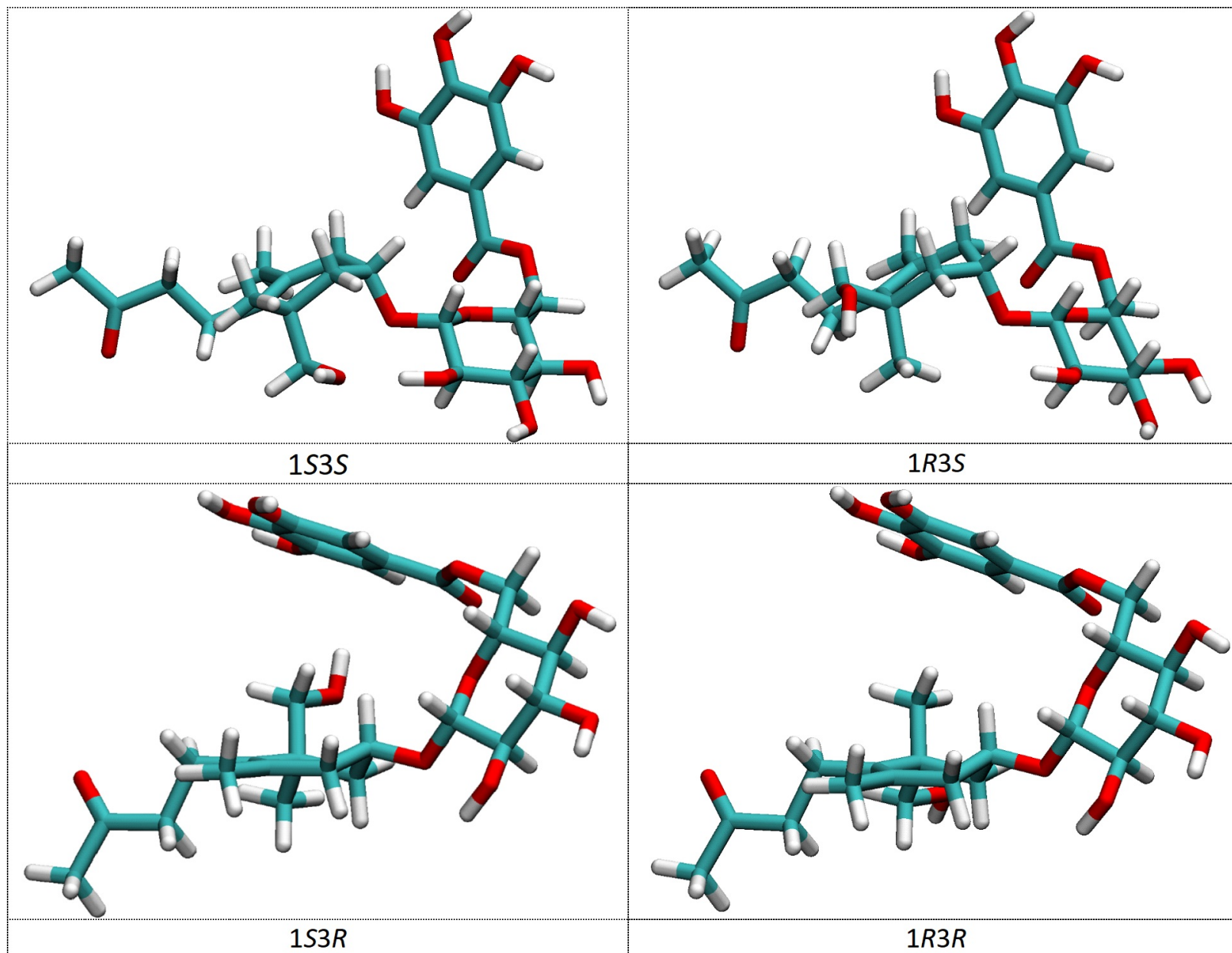


Figure S41. 3D structures of possible stereoisomers of compound **1**

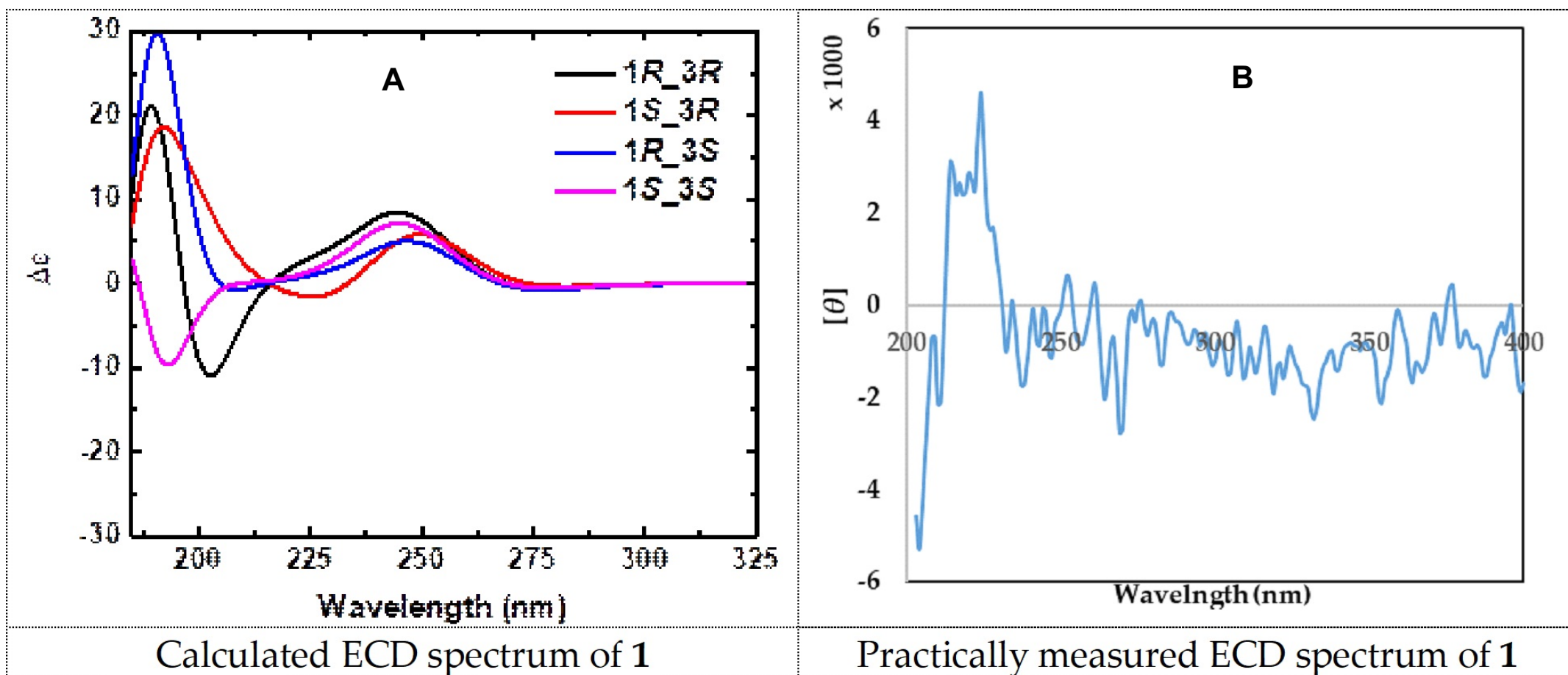


Figure S42. Calculated (**A**) and practically measured (**B**) ECD spectra of compound **1**