

## Supplementary Information

Figure S1.  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{OD}$  at 500 MHz.

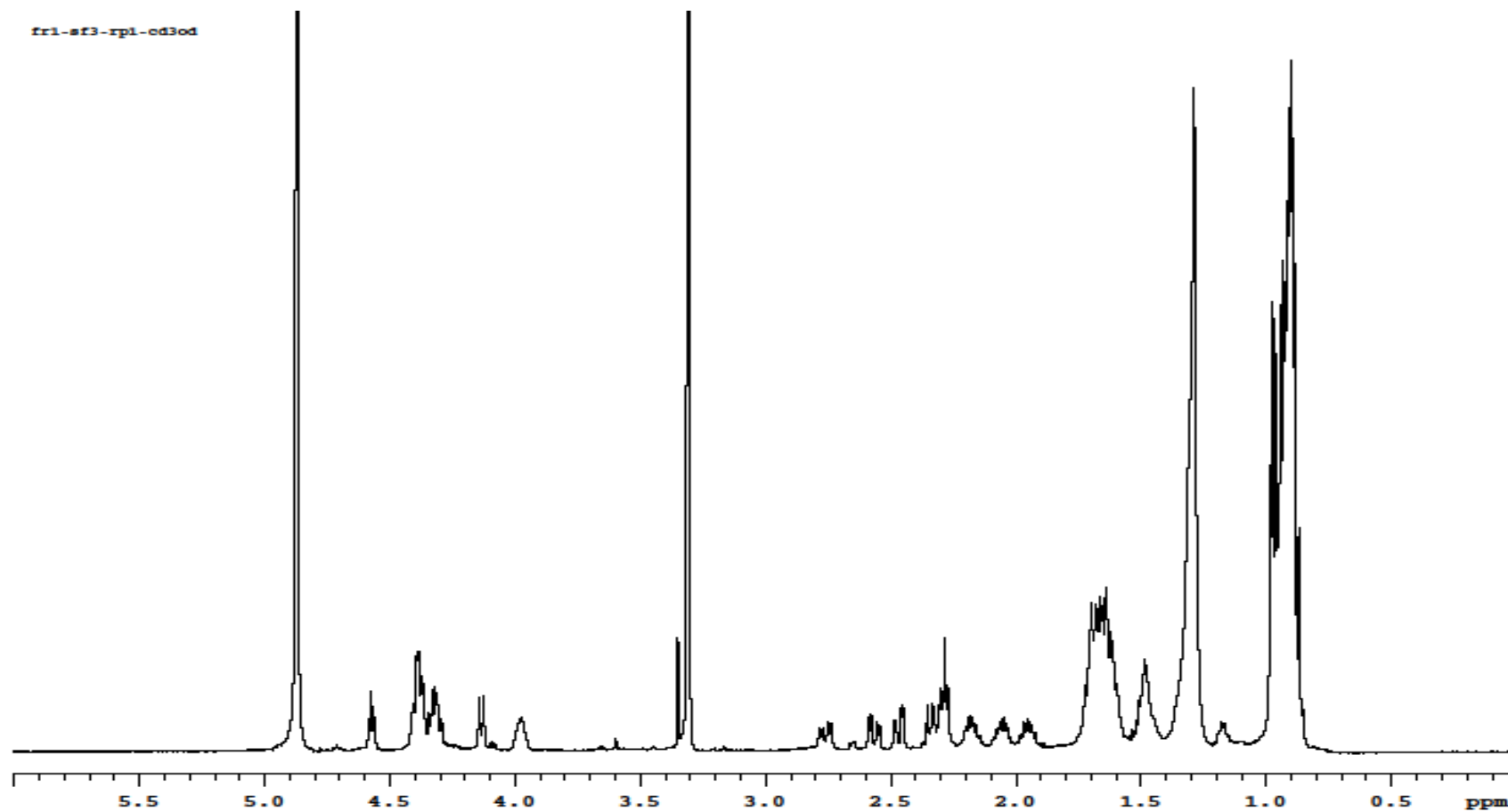


Figure S1. Cont.

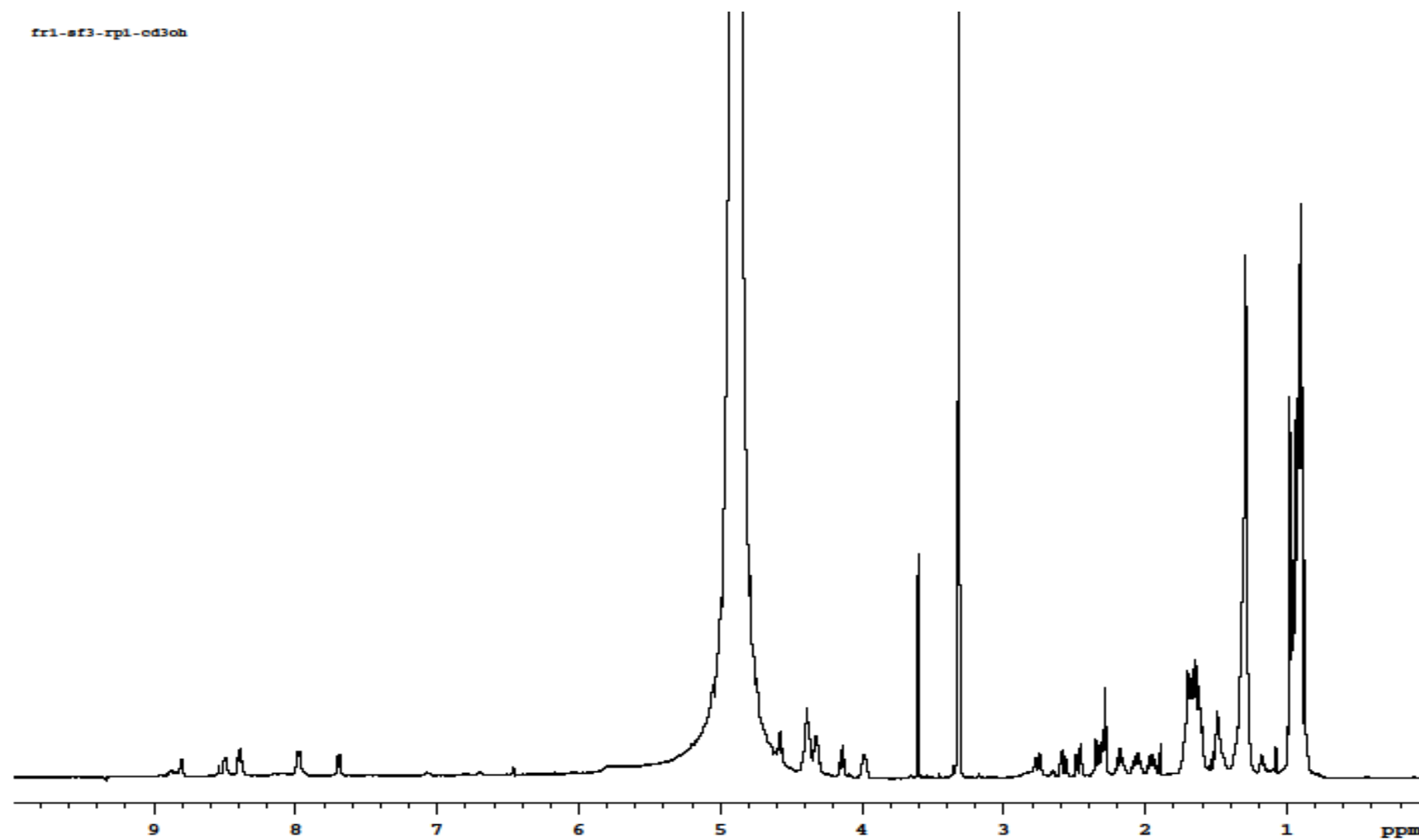


Figure S2.  $^{13}\text{C}$  NMR spectrum of 1 in  $\text{CD}_3\text{OD}$ .

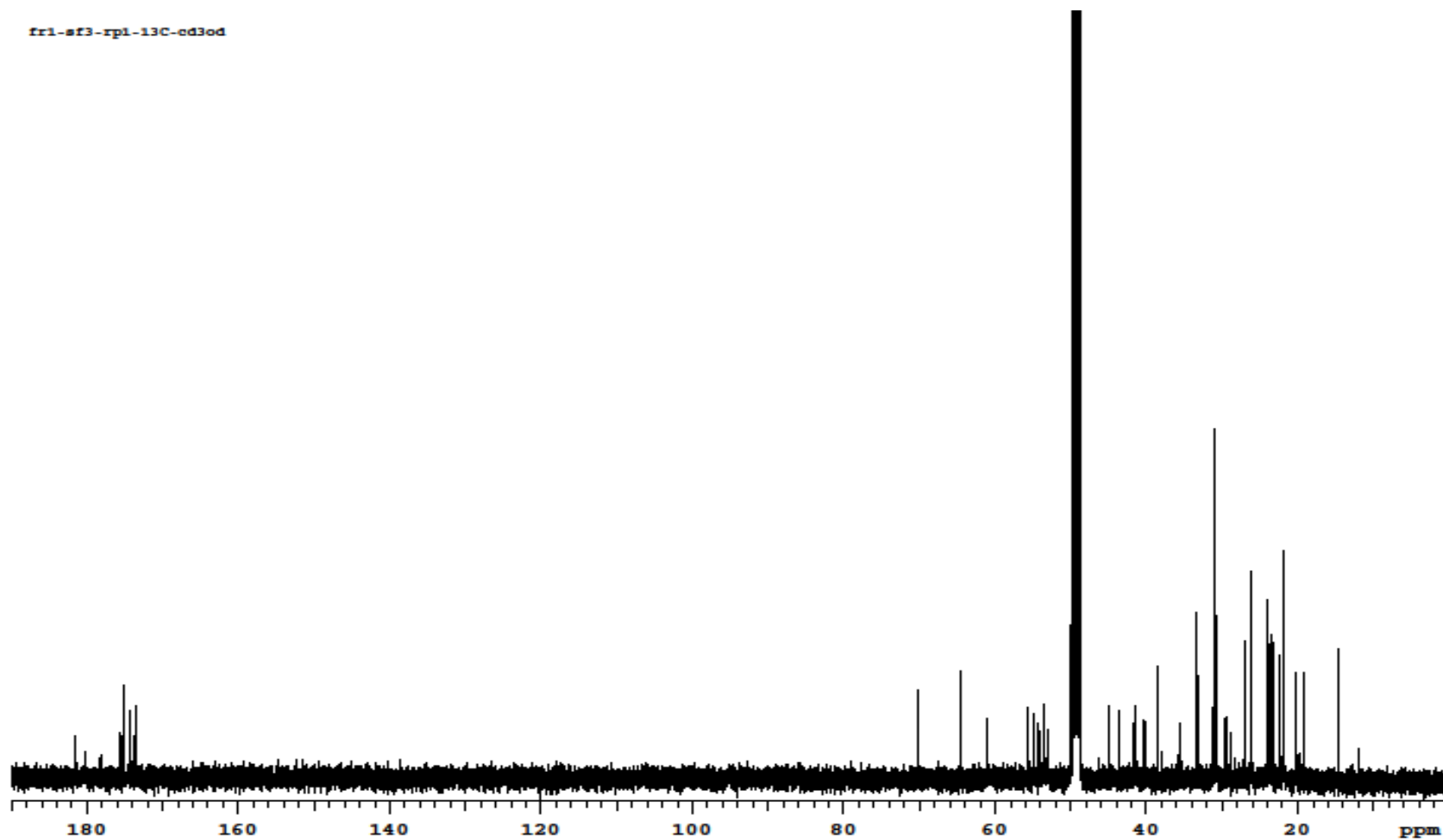


Figure S3. COSY spectrum of 1 in CD<sub>3</sub>OD.

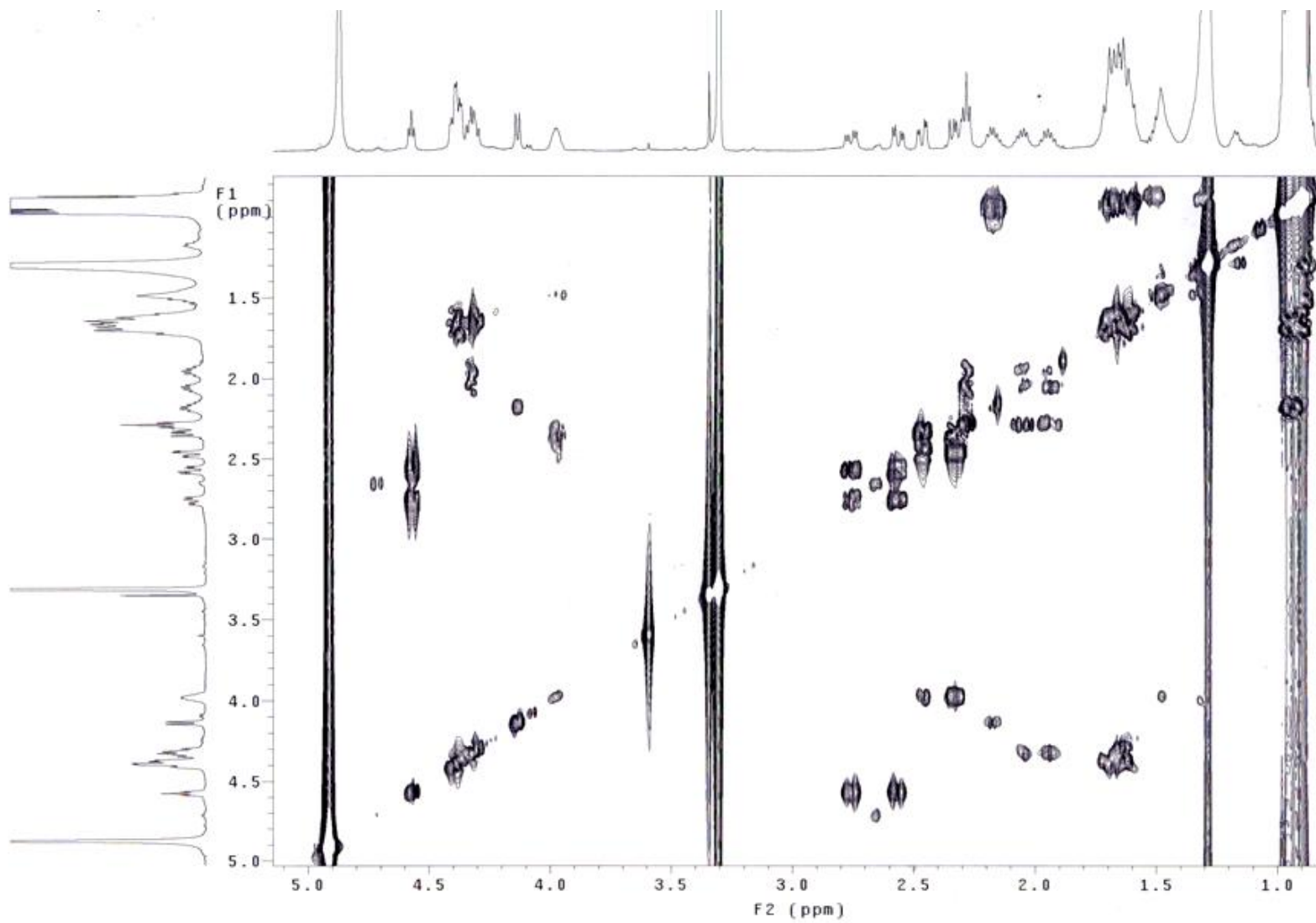


Figure S4. COSY spectrum of 1 in CD<sub>3</sub>OH.

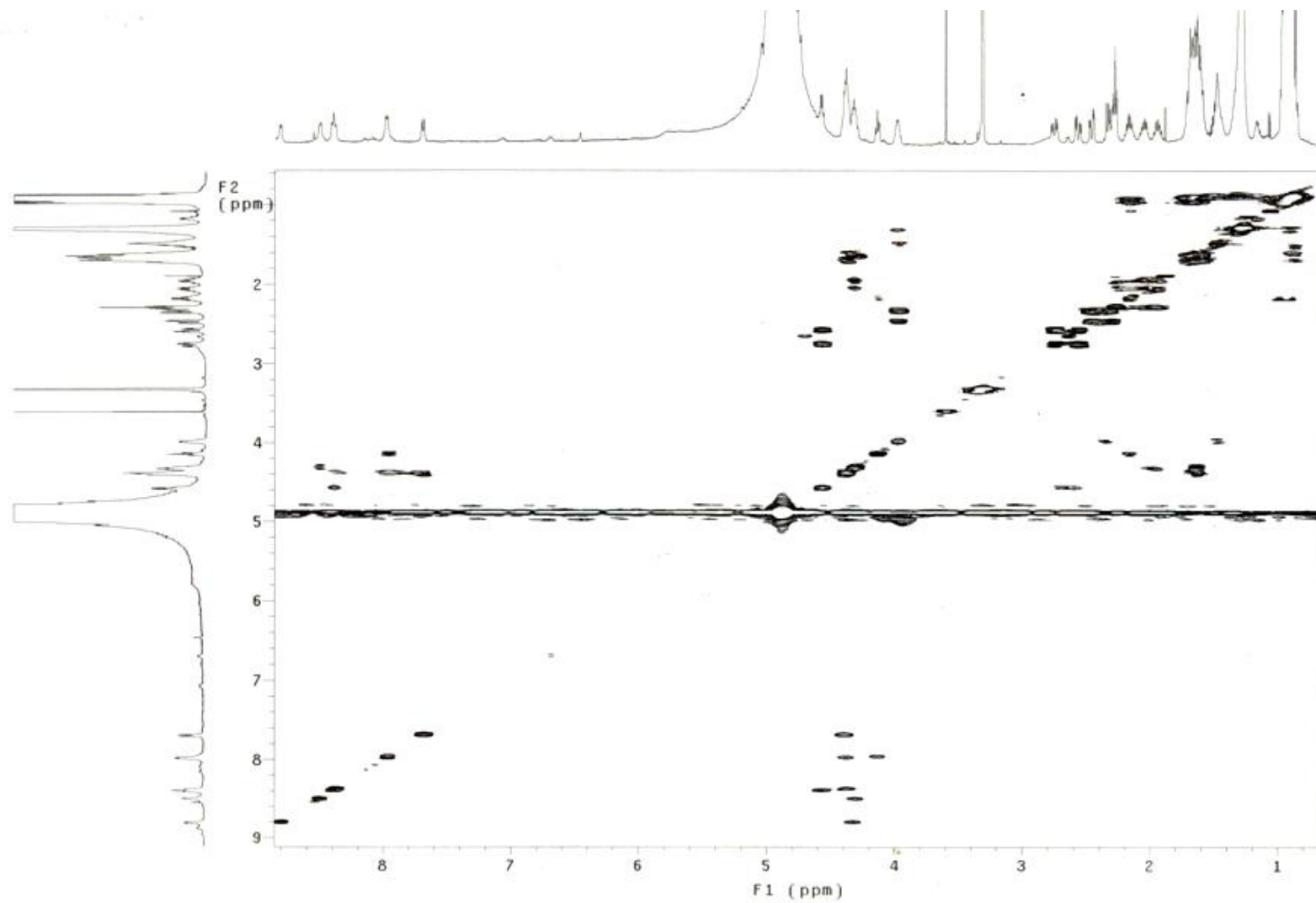


Figure S5. TOCSY spectrum of **1** in CD<sub>3</sub>OH.

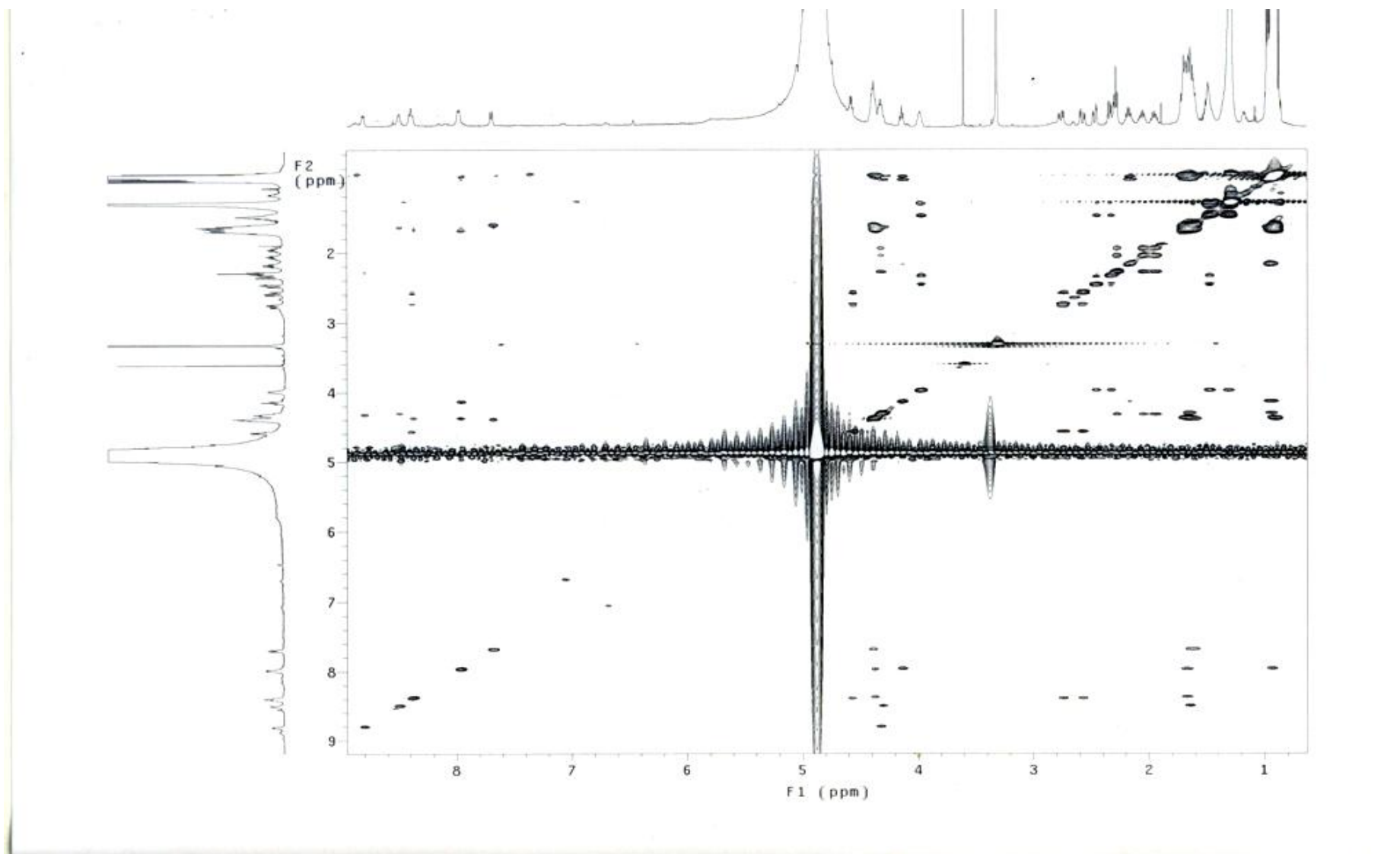


Figure S6. HSQC spectrum of 1 in CD<sub>3</sub>OD.

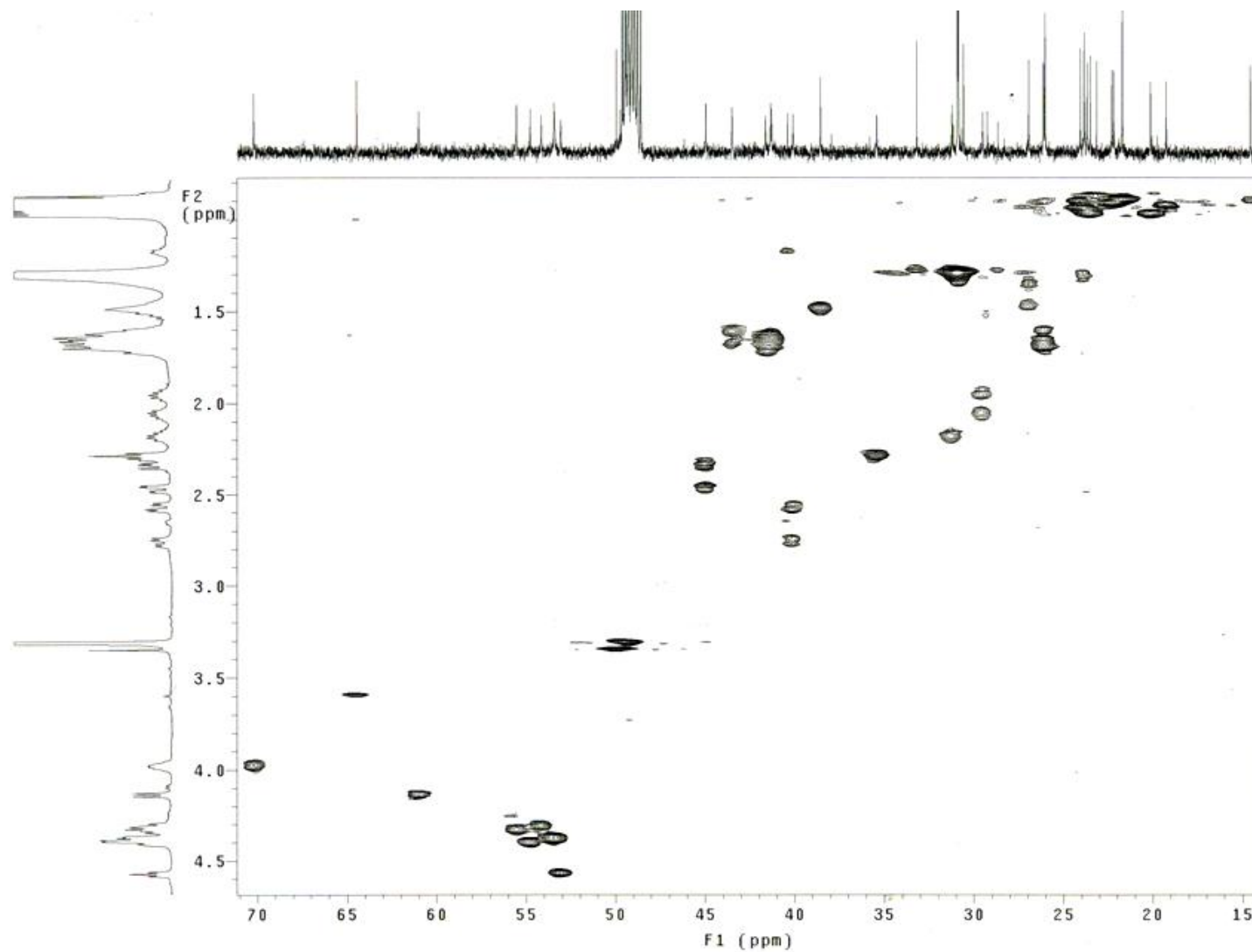


Figure S7. HMBC spectrum of **1** in CD<sub>3</sub>OD.

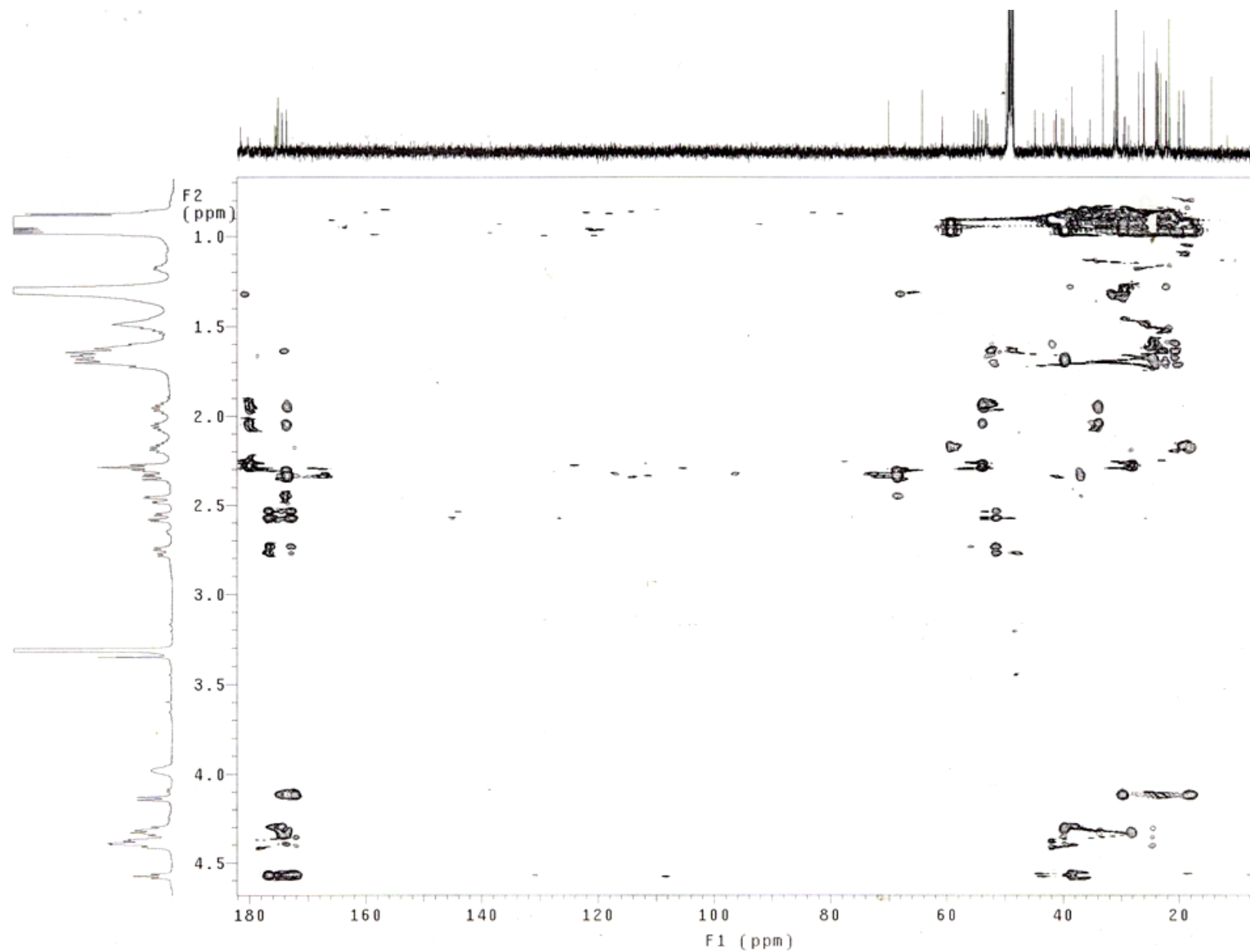




Figure S8. HMBC spectrum of **1** in CD<sub>3</sub>OH.

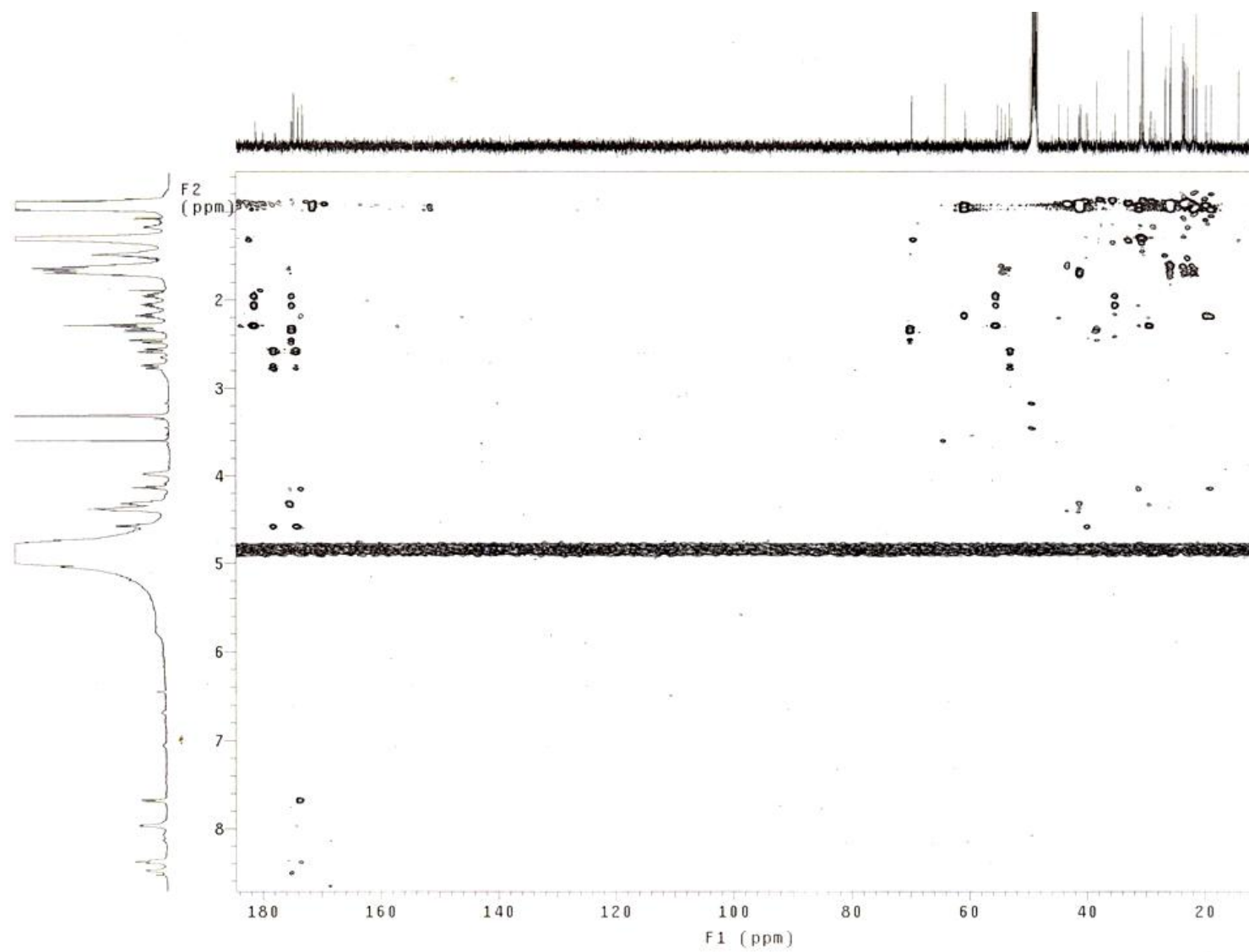


Figure S9.  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{OD}$ .

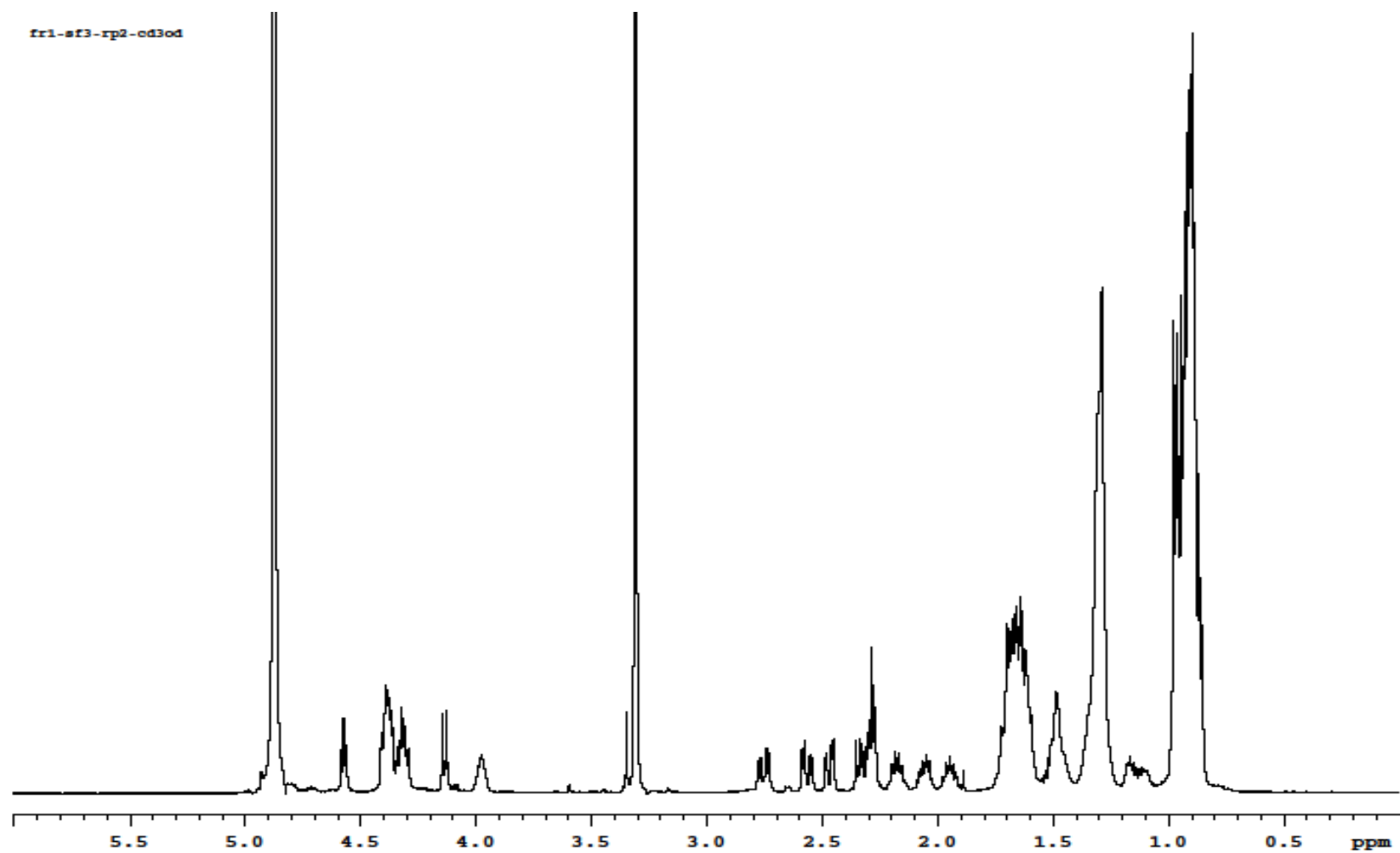


Figure S9. Cont.

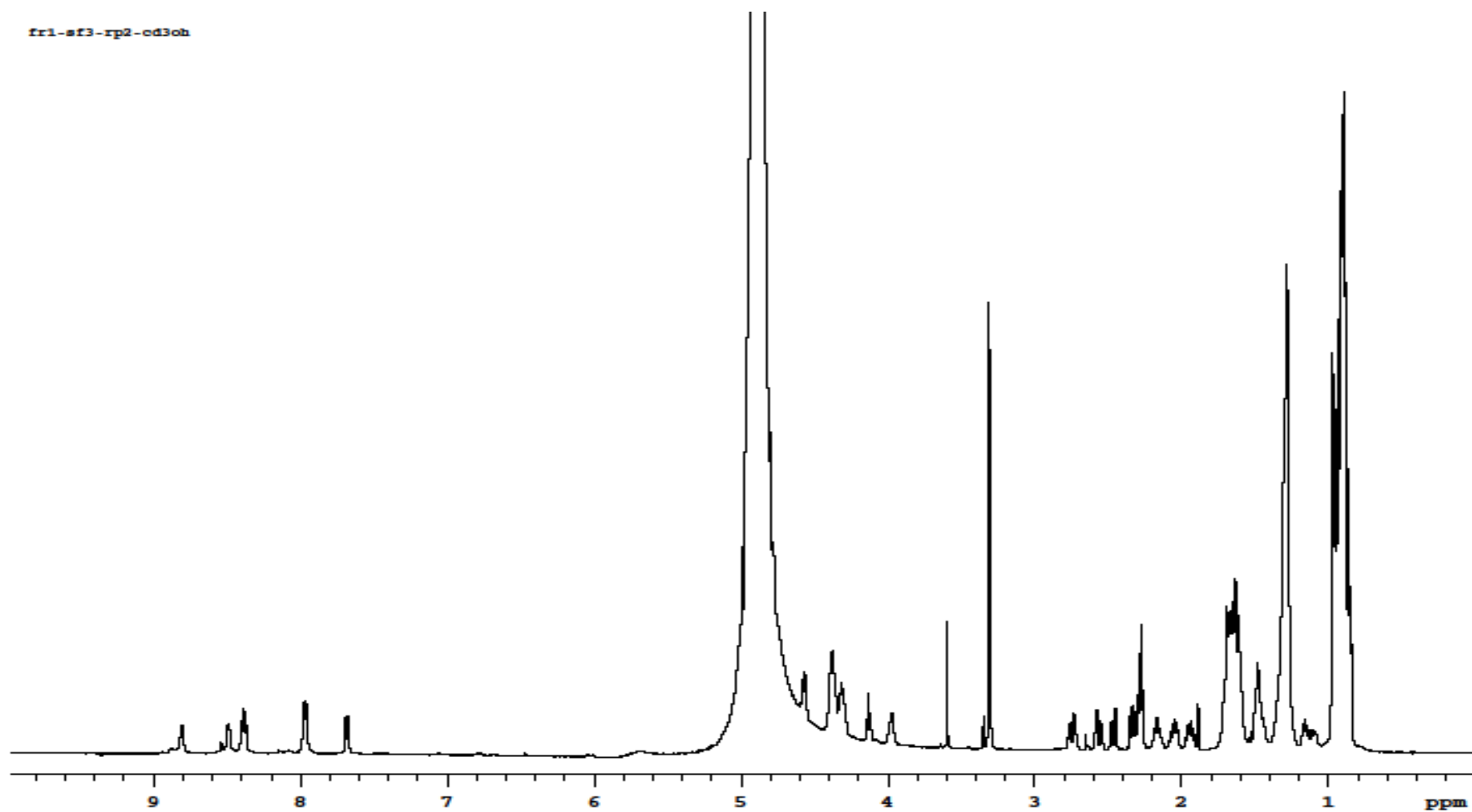


Figure S10.  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CD}_3\text{OD}$ .

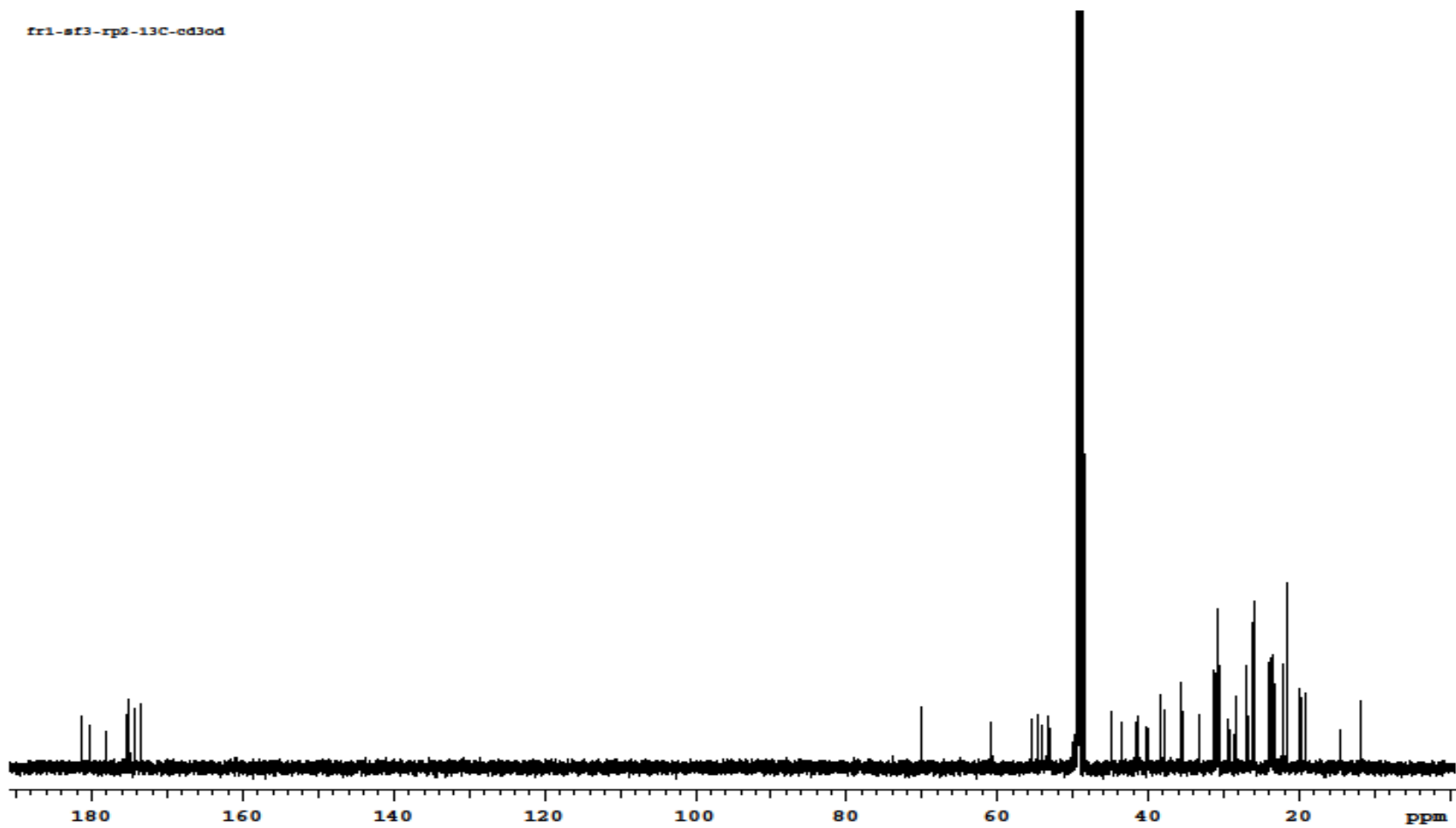


Figure S11. COSY spectrum of **2** in CD<sub>3</sub>OD.

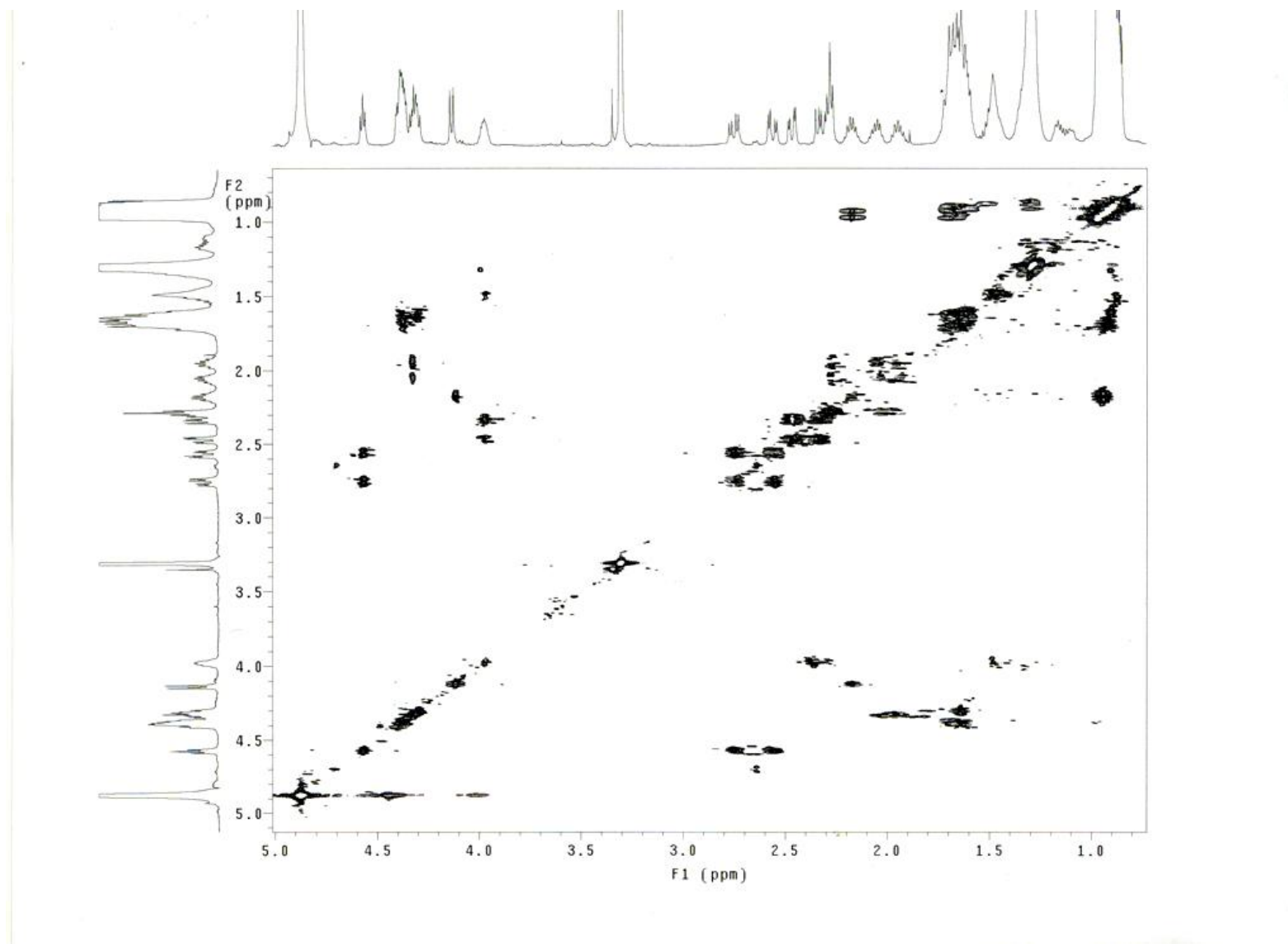


Figure S12. TOCSY spectrum of 2 in CD<sub>3</sub>OH.

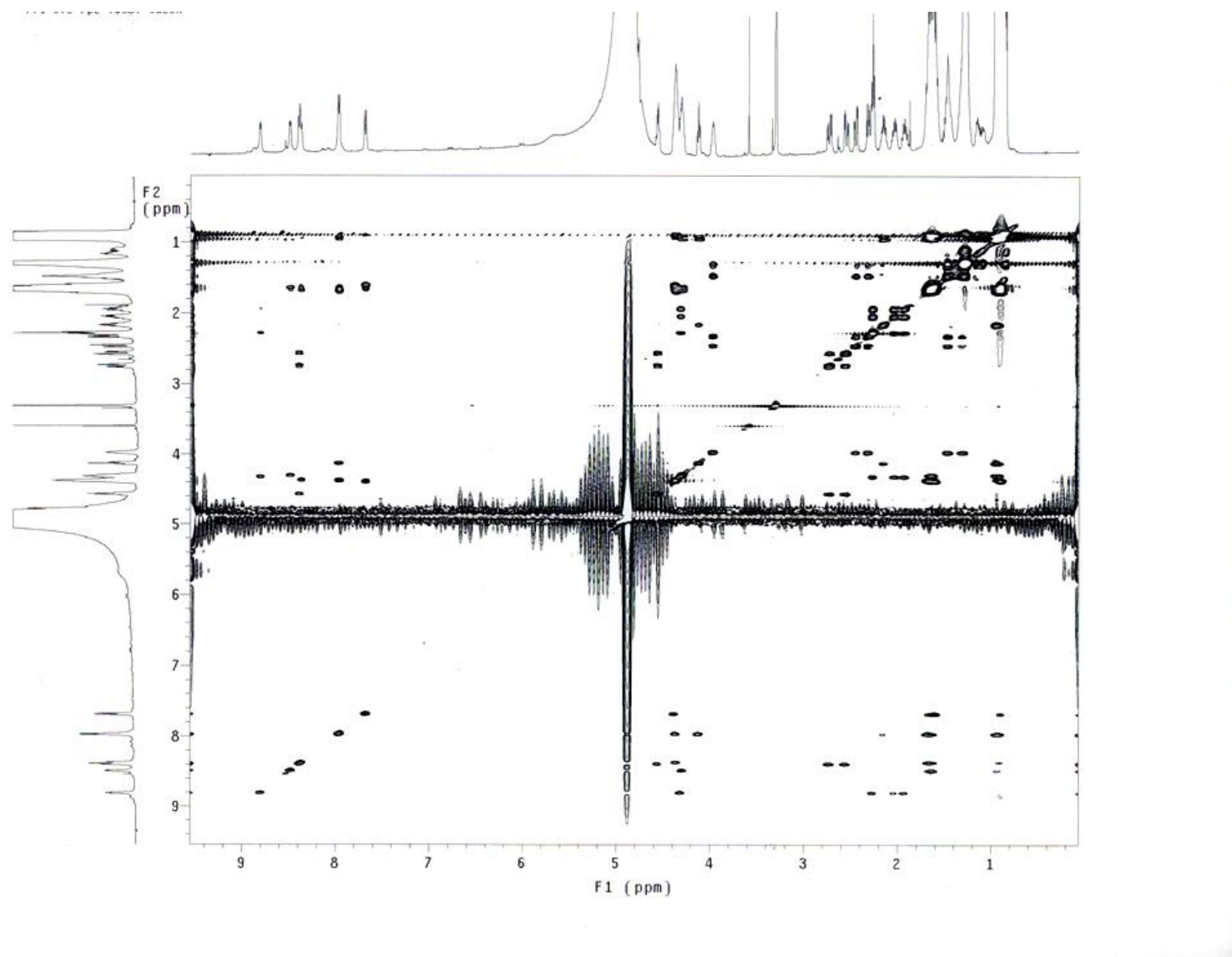


Figure S13. HSQC spectrum of **2** in CD<sub>3</sub>OD.

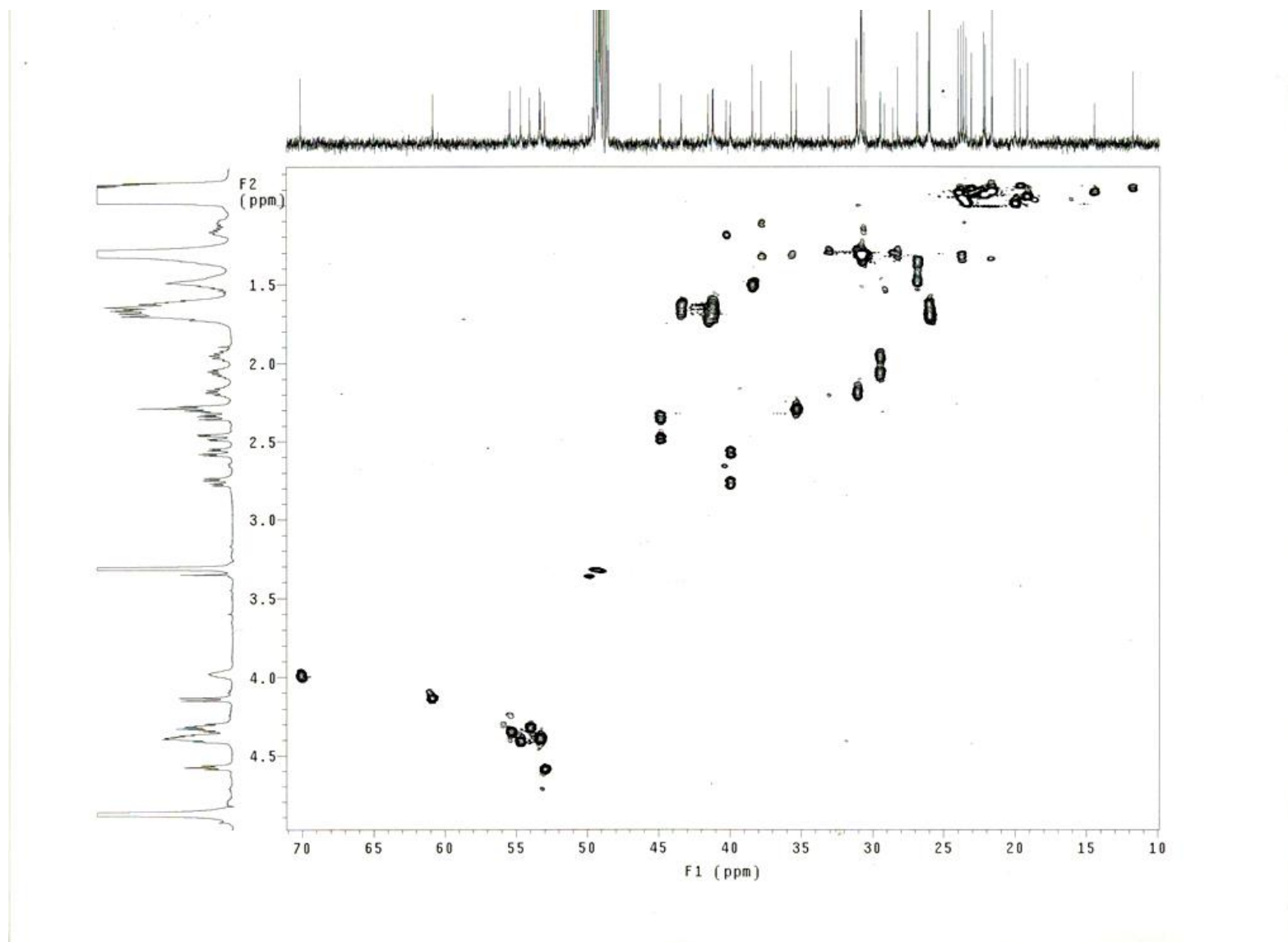


Figure S14. HMBC spectrum of **2** in CD<sub>3</sub>OD.

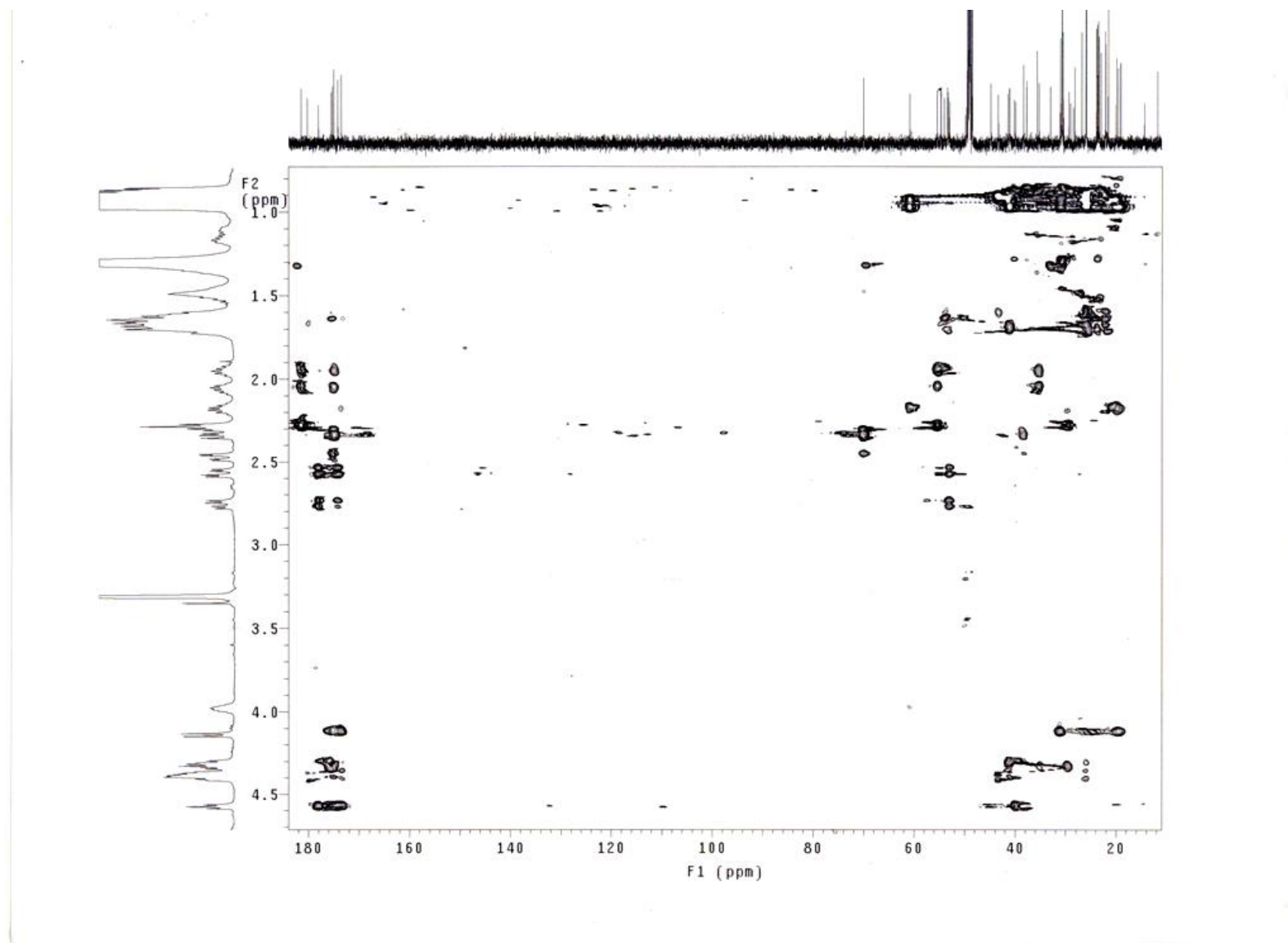




Figure S15. ROESY spectrum of **2** in CD<sub>3</sub>OH.

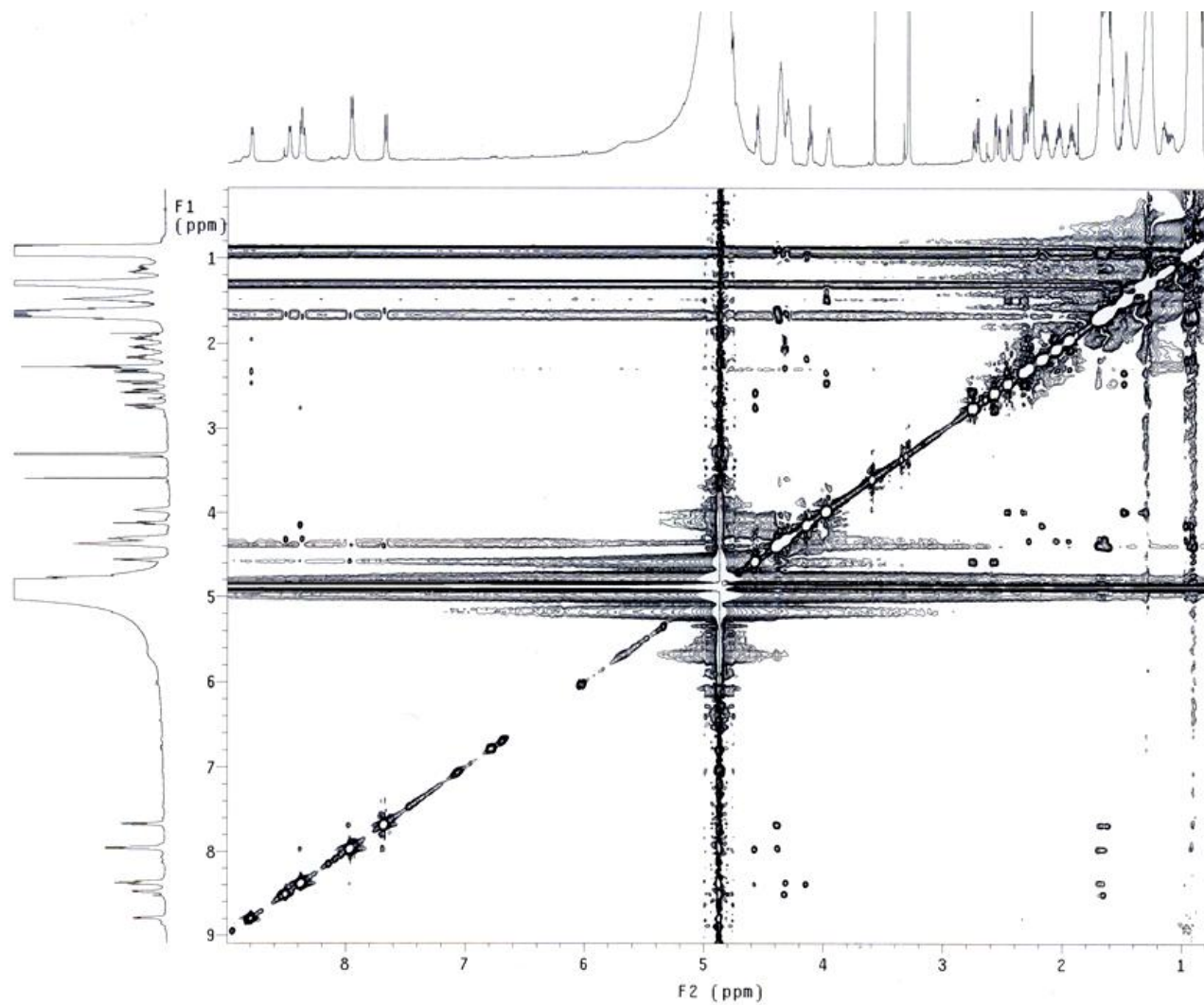


Figure S16.  $^1\text{H}$  NMR spectrum of **3** in  $\text{CD}_3\text{OD}$ .

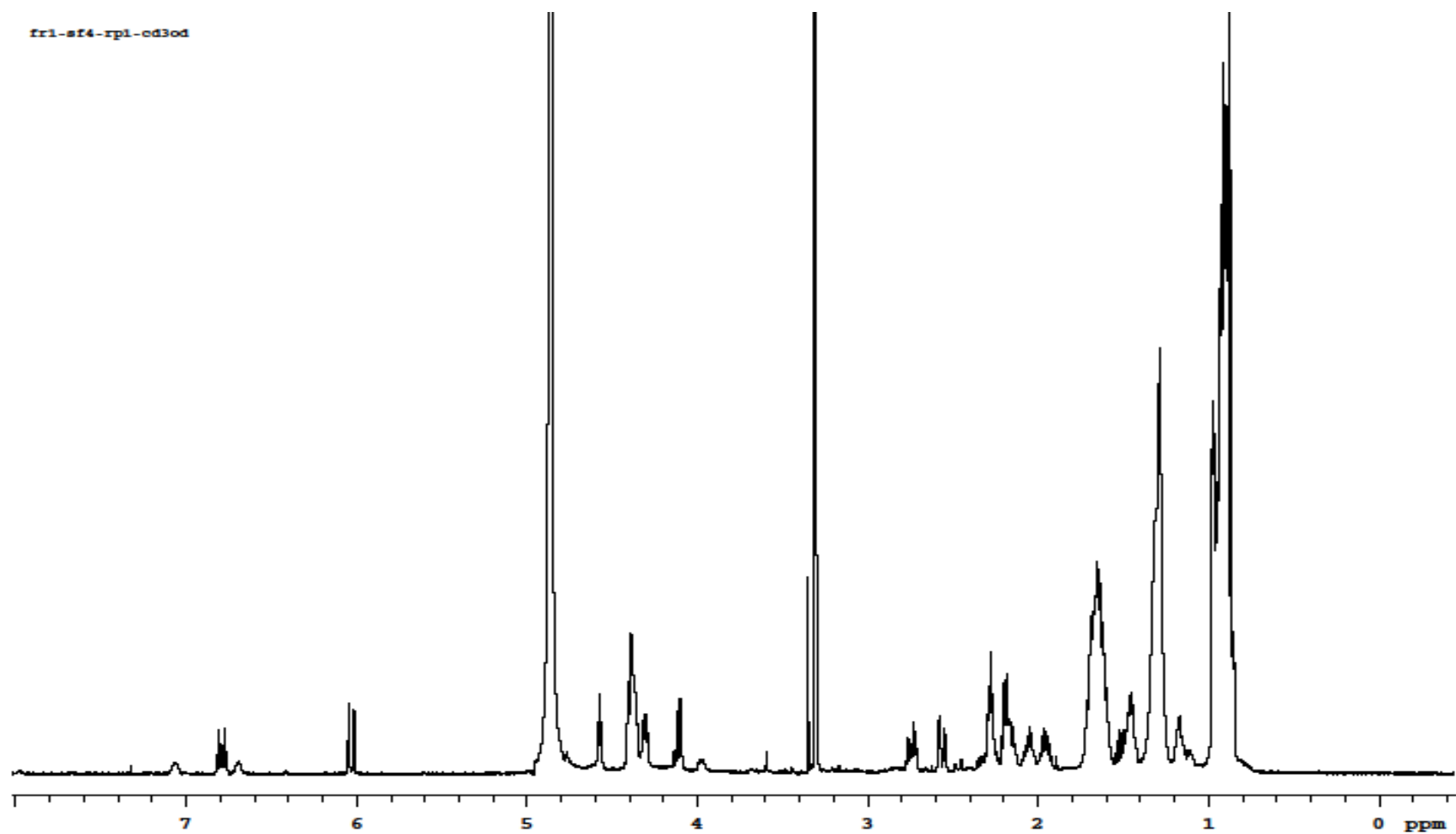


Figure S16. Cont.

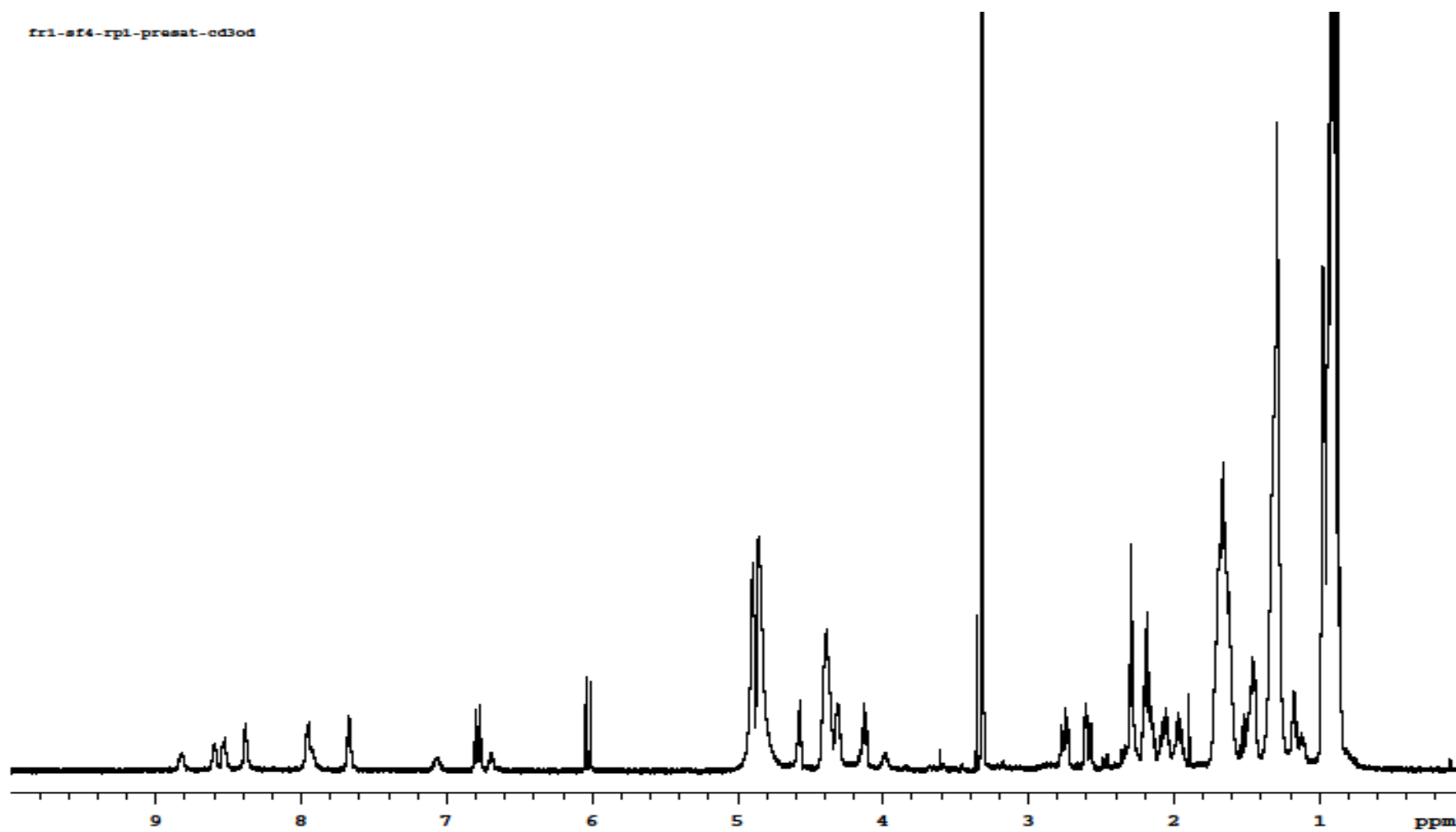


Figure S17.  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CD}_3\text{OD}$ .

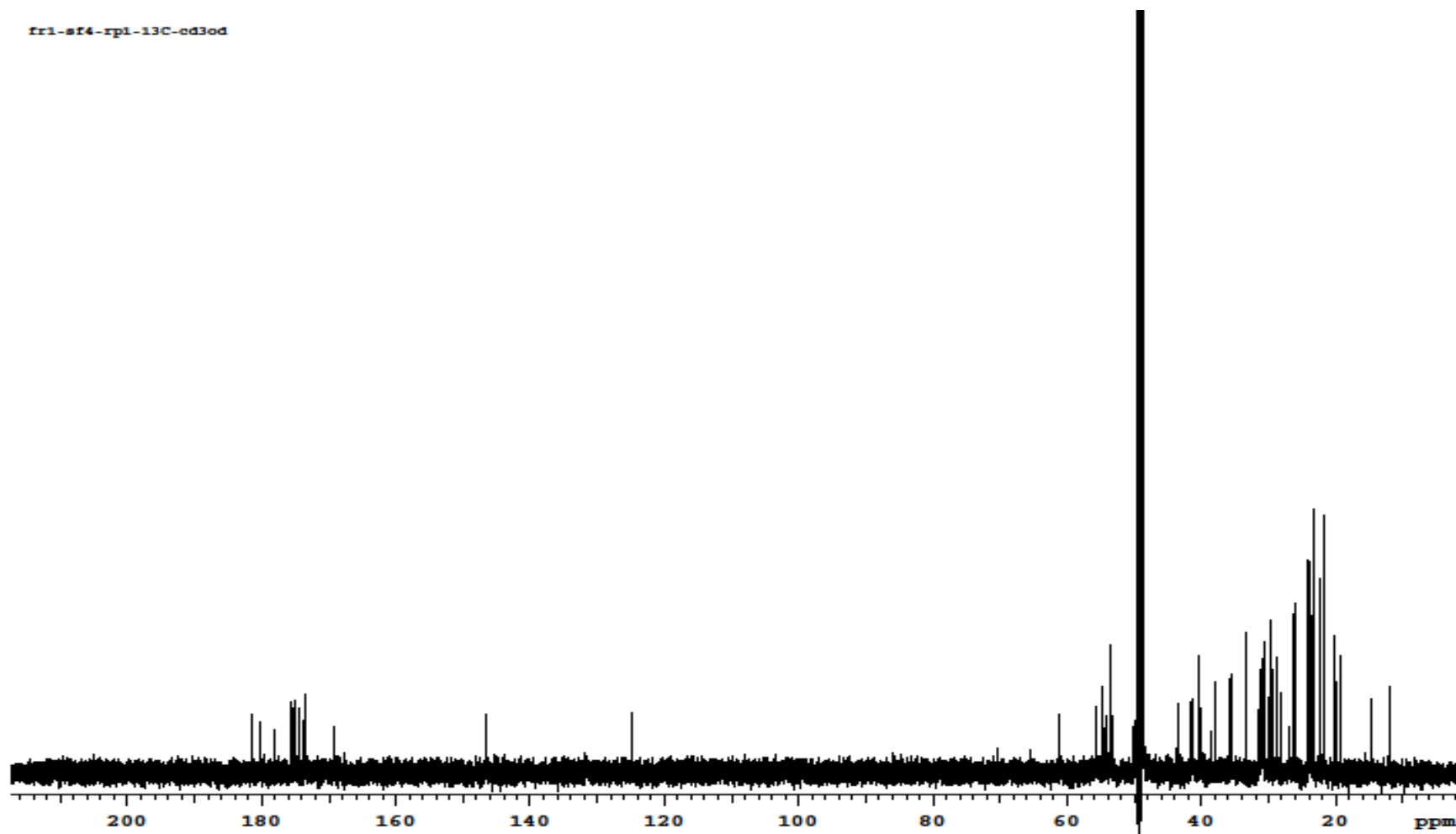


Figure S18. COSY spectrum of **3** in CD<sub>3</sub>OD.

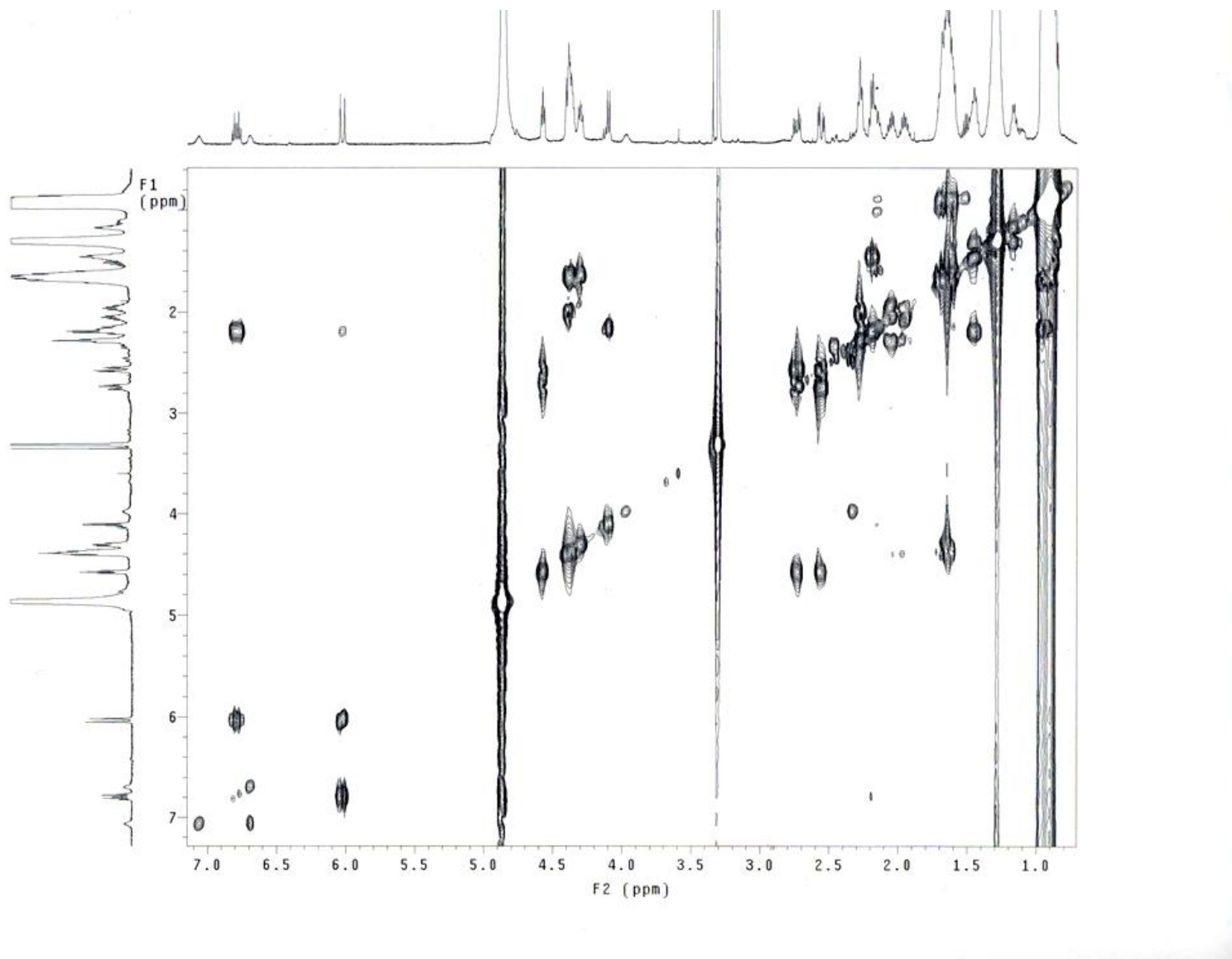


Figure S19. TOCSY spectrum of 3 in CD<sub>3</sub>OH.

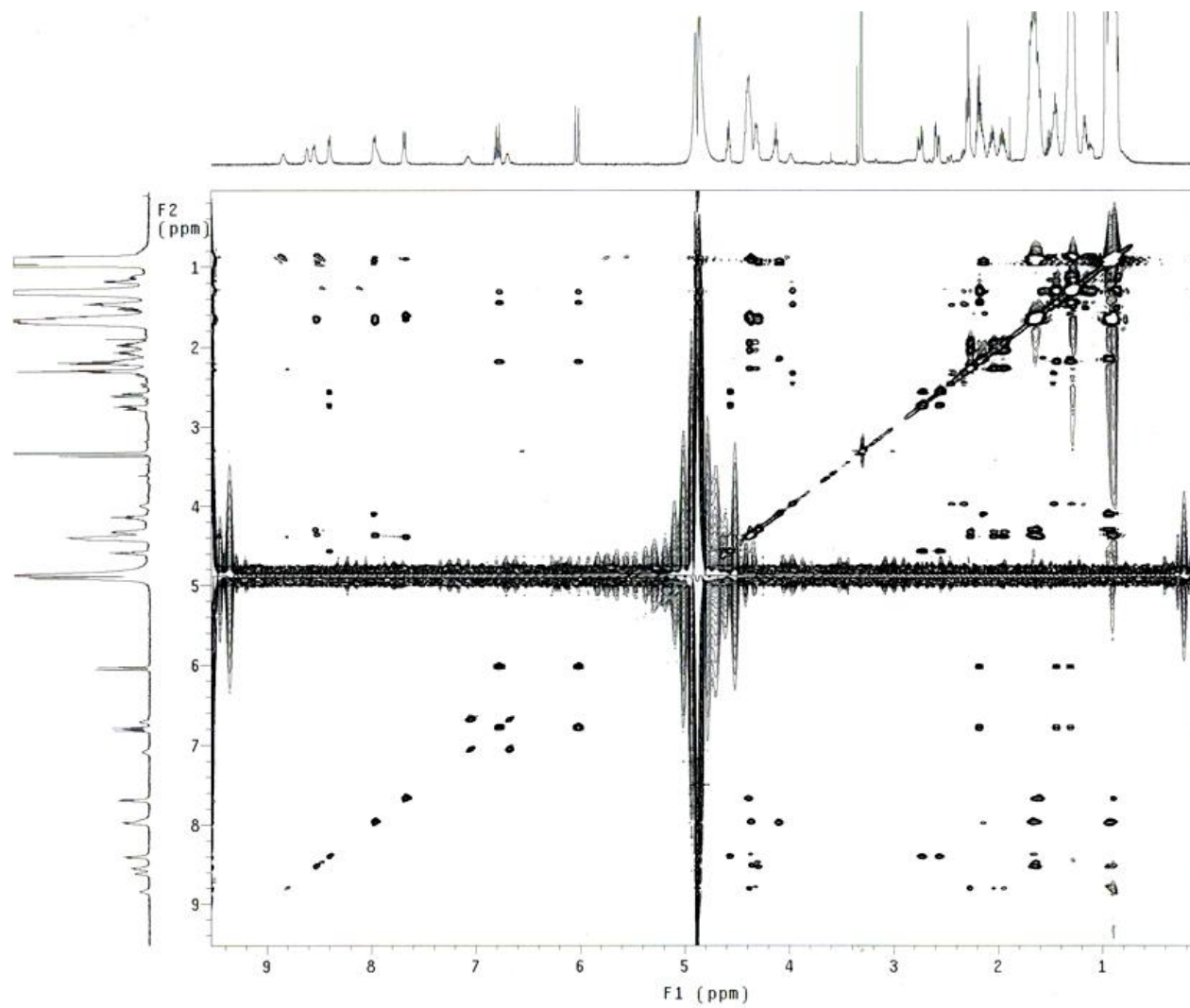


Figure S20. HSQC spectrum of 3 in CD<sub>3</sub>OD.

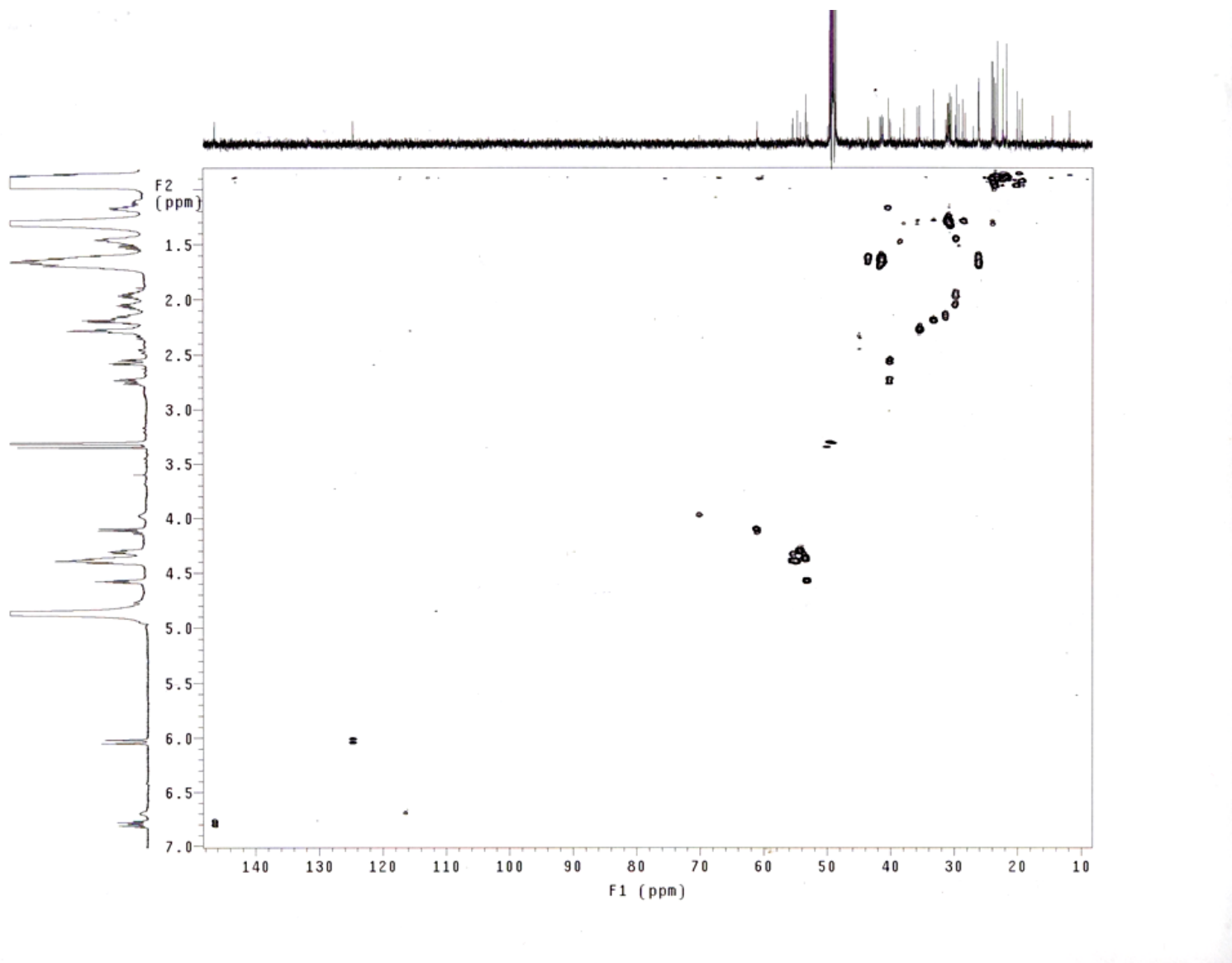


Figure S21. HMBC spectrum of 3 in CD<sub>3</sub>OH.

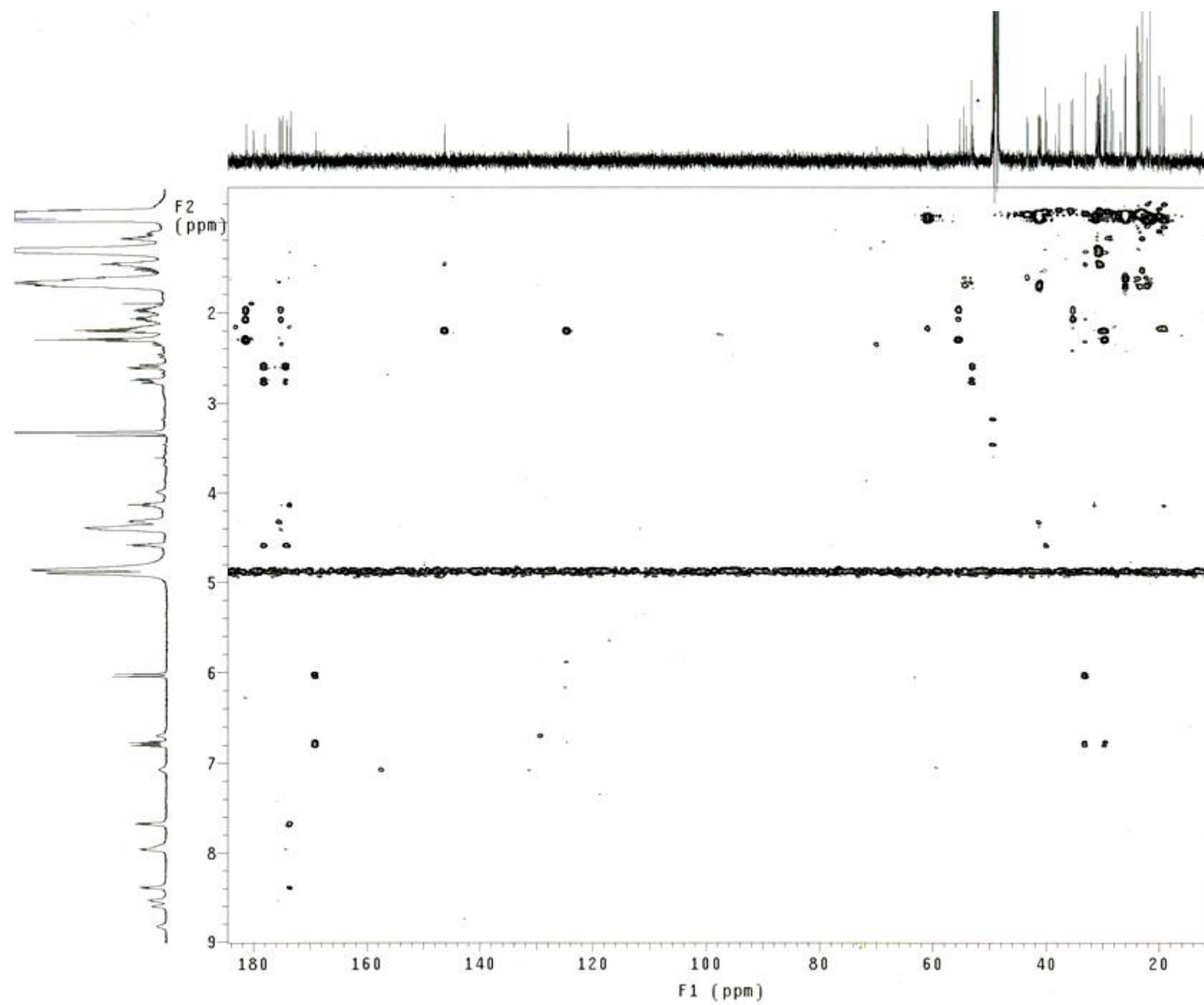




Figure S22. ROESY spectrum of **3** in CD<sub>3</sub>OH.

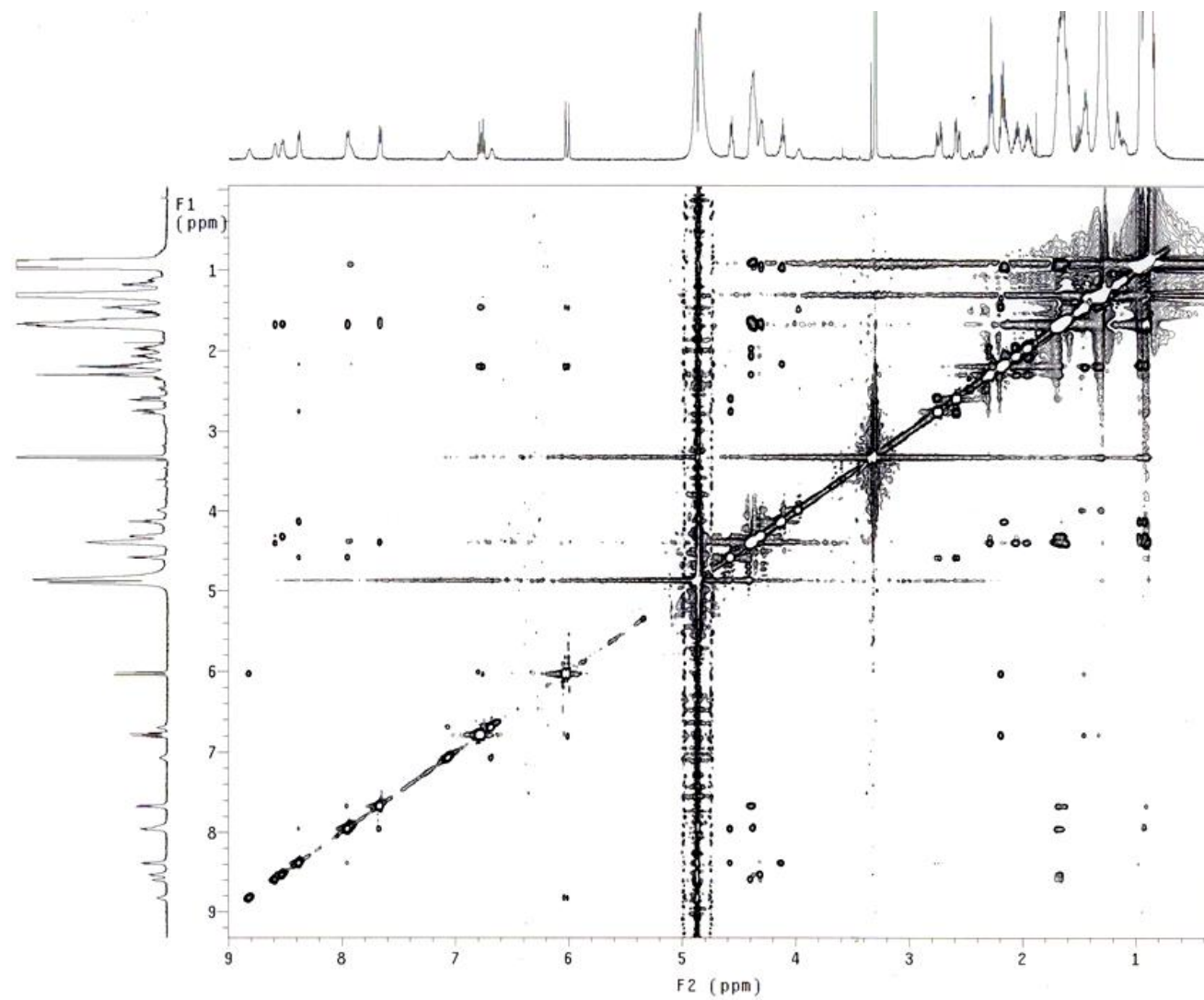


Figure S23. HRESI-MS of 1–3.

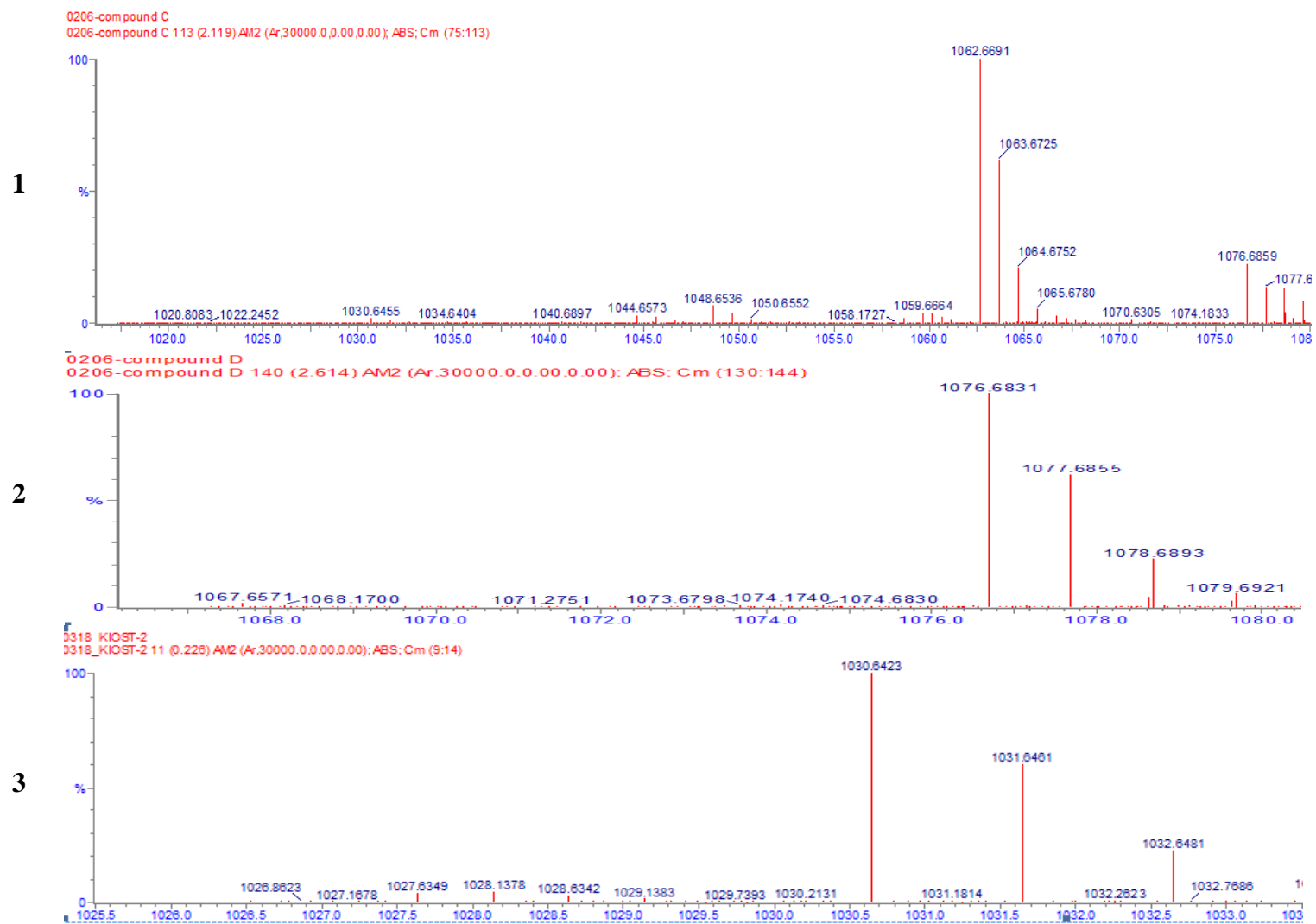


Figure S24. APCI-MS data of fatty acid in 1.

109GGC020-2-myc-100%M-fr1-sf3-rp1-acid-hydr #54 RT: 0.67 AV: 1 NL: 2.33E7

F: {0,5} - c APCI corona sid=70.00 det=1600.00 Full ms

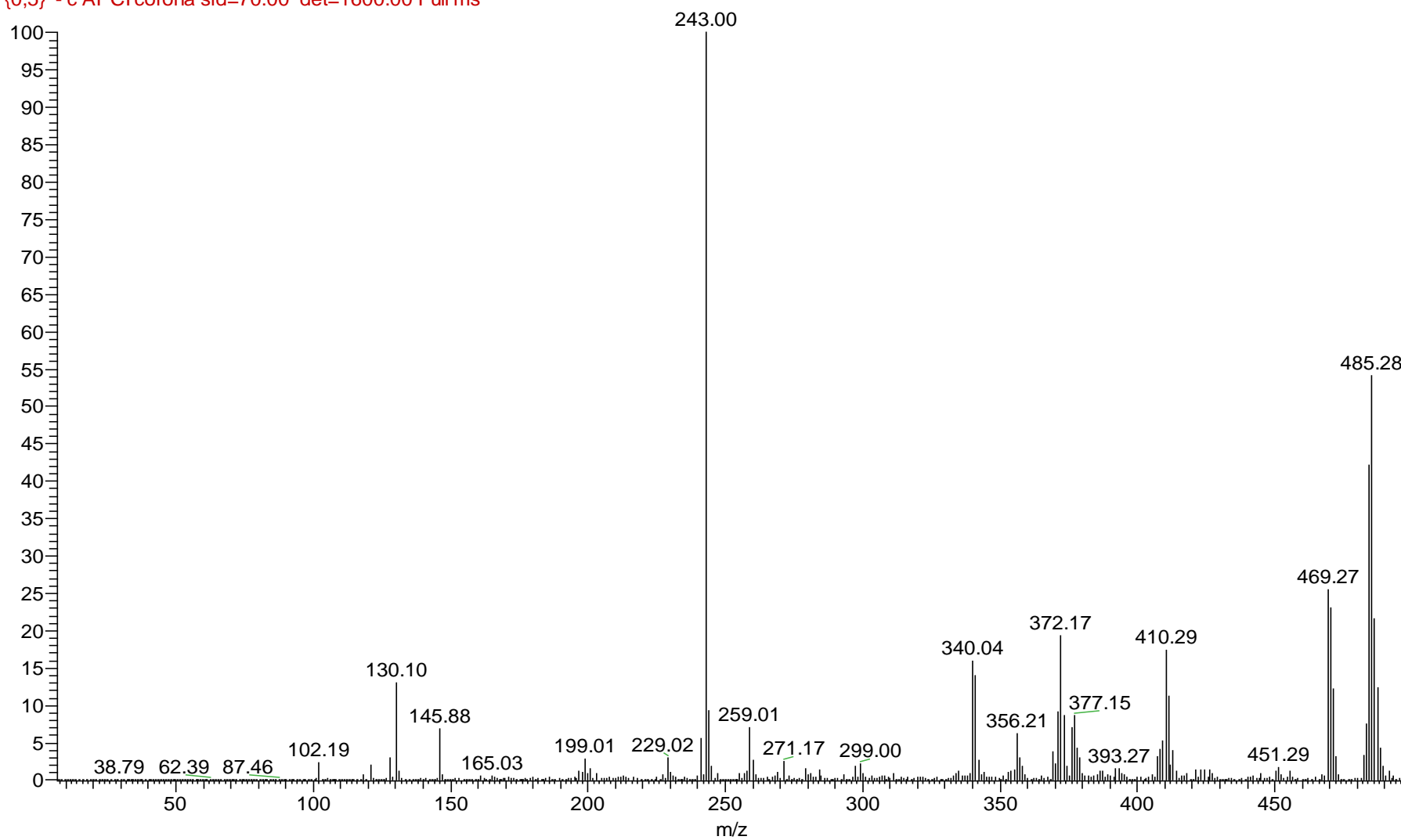


Figure S25.  $^1\text{H}$  NMR spectrum of fatty acid in 1.

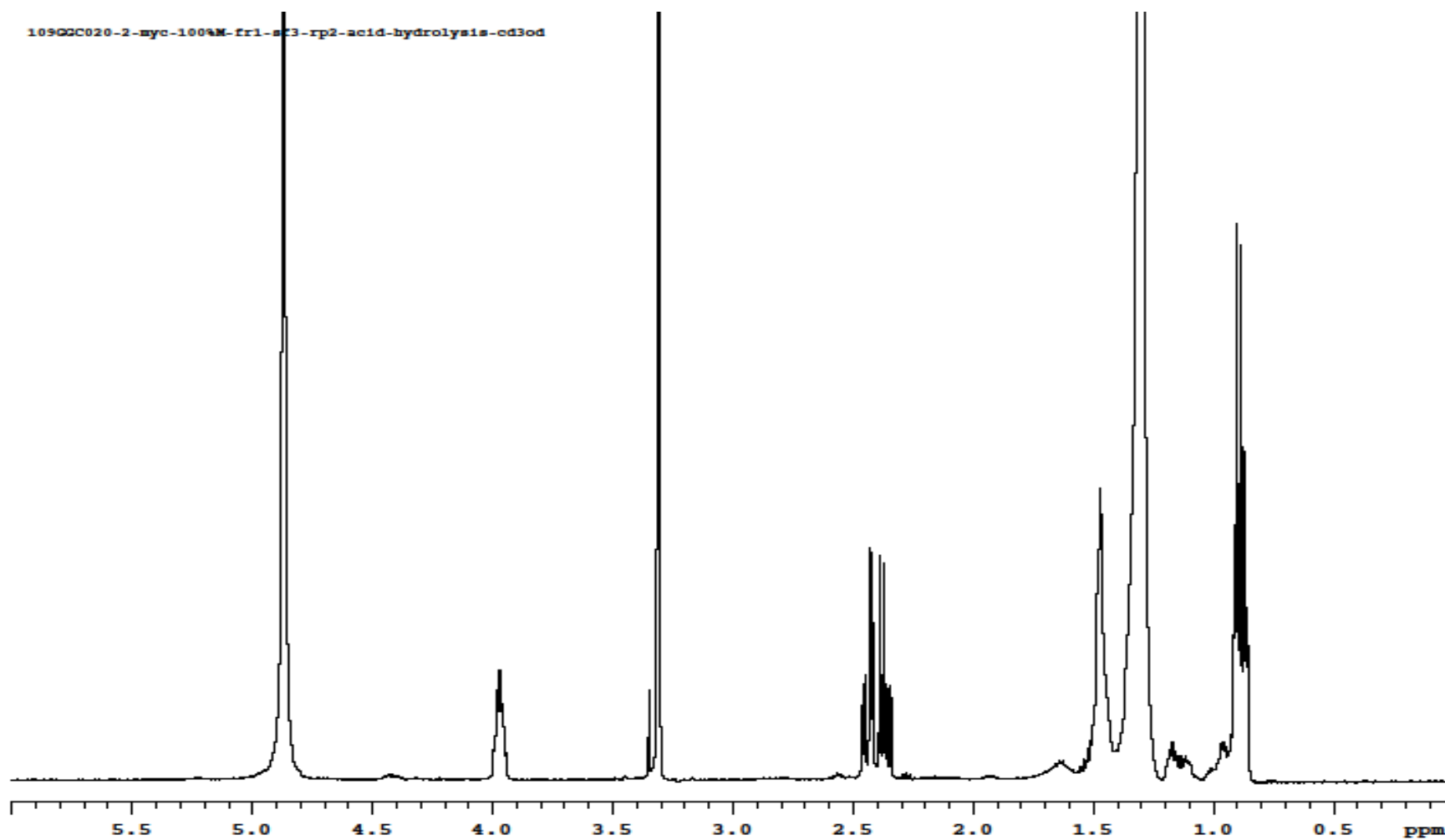


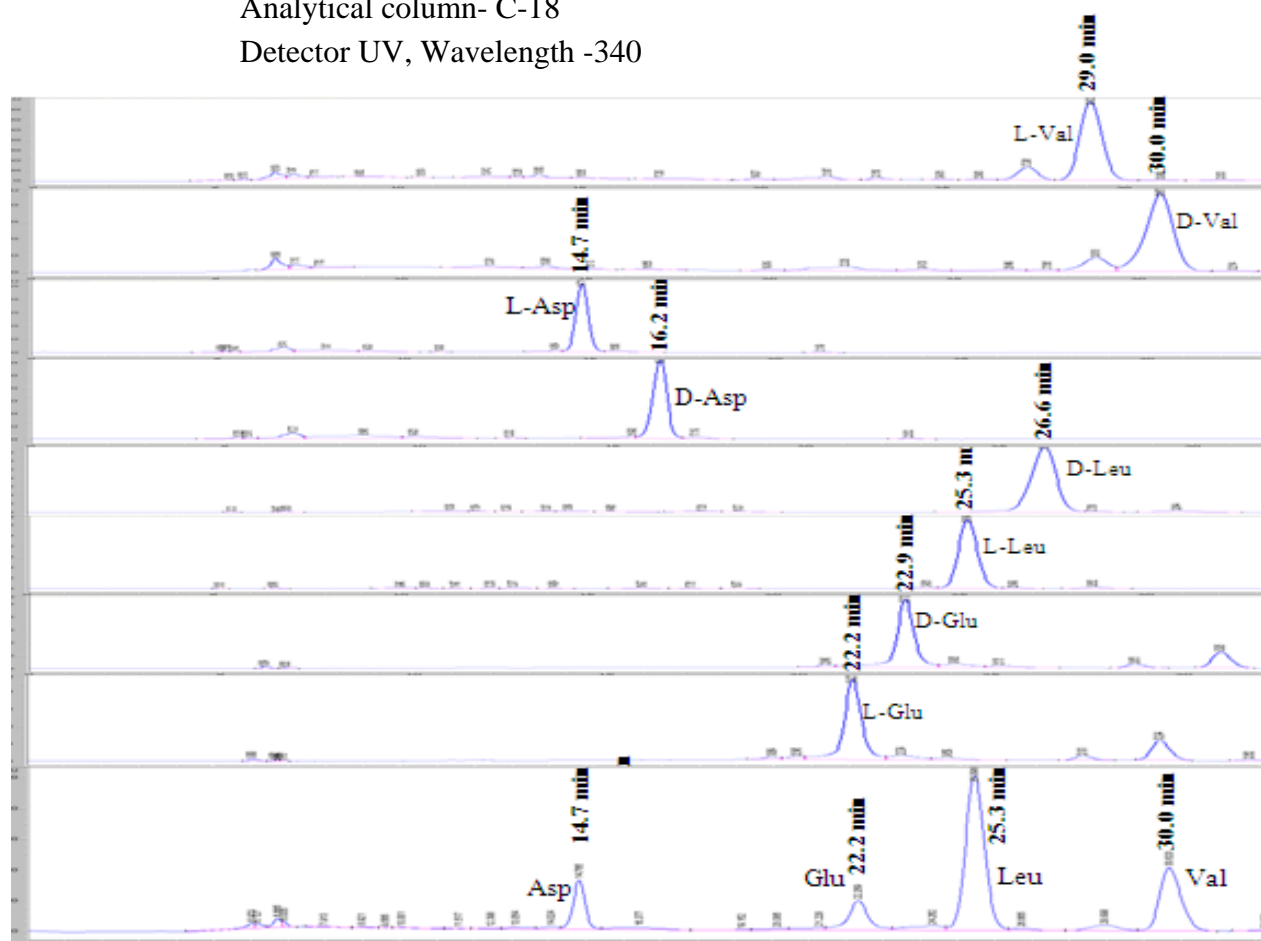
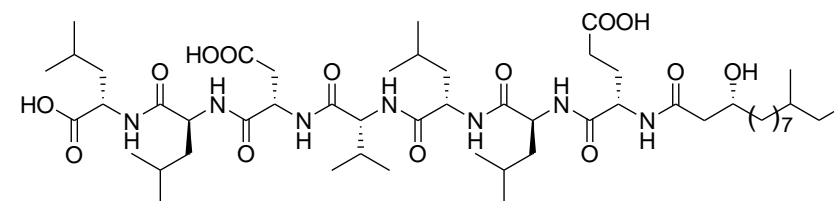
Figure S26. HPLC data for amino acid analysis in **1**.**Gageostatin-A**Solvent system: 40% MeCN in H<sub>2</sub>O + 0.5% TFA

Flow- 0.5 ml/min

Injection - 10

Analytical column- C-18

Detector UV, Wavelength -340



FDAA derivatives of standard L-Val

FDAA derivatives of standard D-Val

FDAA derivatives of standard L-Asp

FDAA derivatives of standard D-Asp

FDAA derivatives of standard D-Leu

FDAA derivatives of standard L-Leu

FDAA derivatives of standard D-Glu

FDAA derivatives of standard L-Glu

FDAA derivatives of amino acids in **1**