Supporting Information

Pogocablanols A–G, a new class of sesquiterpenoids with an unprecedented bicyclic sesquiterpenoid skeleton from *Pogostemon cablin* (patchouli) and their activities

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ECD calculation of compound 7

Conformation searches based on molecular mechanics with MMFF94s force field were performed for (1*S*,5*R*,7*S*,8*S*,10*S*)-**7** and gave eight conformers with populations higher than 1% [1]. The selected conformers were optimized using DFT at the B3LYP/6-31G (d) level in vacuum with the Gaussian 16 program (Table S1) [2]. The B3LYP/6-31G (d)-optimized conformers were then reoptimized at the *ω*B97XD/DGDZVP level in acetonitrile. ECD computations for the *ω*B97XD/DGDZVP-optimized conformers (Figure S1) were carried out at the CAM-B3LYP/DGDZVP level in acetonitrile [3]. Then, the ECD spectrum for (1*S*,5*R*,7*S*,8*S*,10*S*)-**7** was generated using SpecDis 1.71 with σ = 0.2 eV and a UV shift of +15 nm [4] according to the Boltzmann distribution theory and their relative Gibbs free energy (ΔG). The corresponding theoretical ECD spectrum of (1*R*,5*S*,7*R*,8*R*,10*R*)-**7** was depicted by inverting that of (1*S*,5*R*,7*S*,8*S*,10*S*)-**7**.

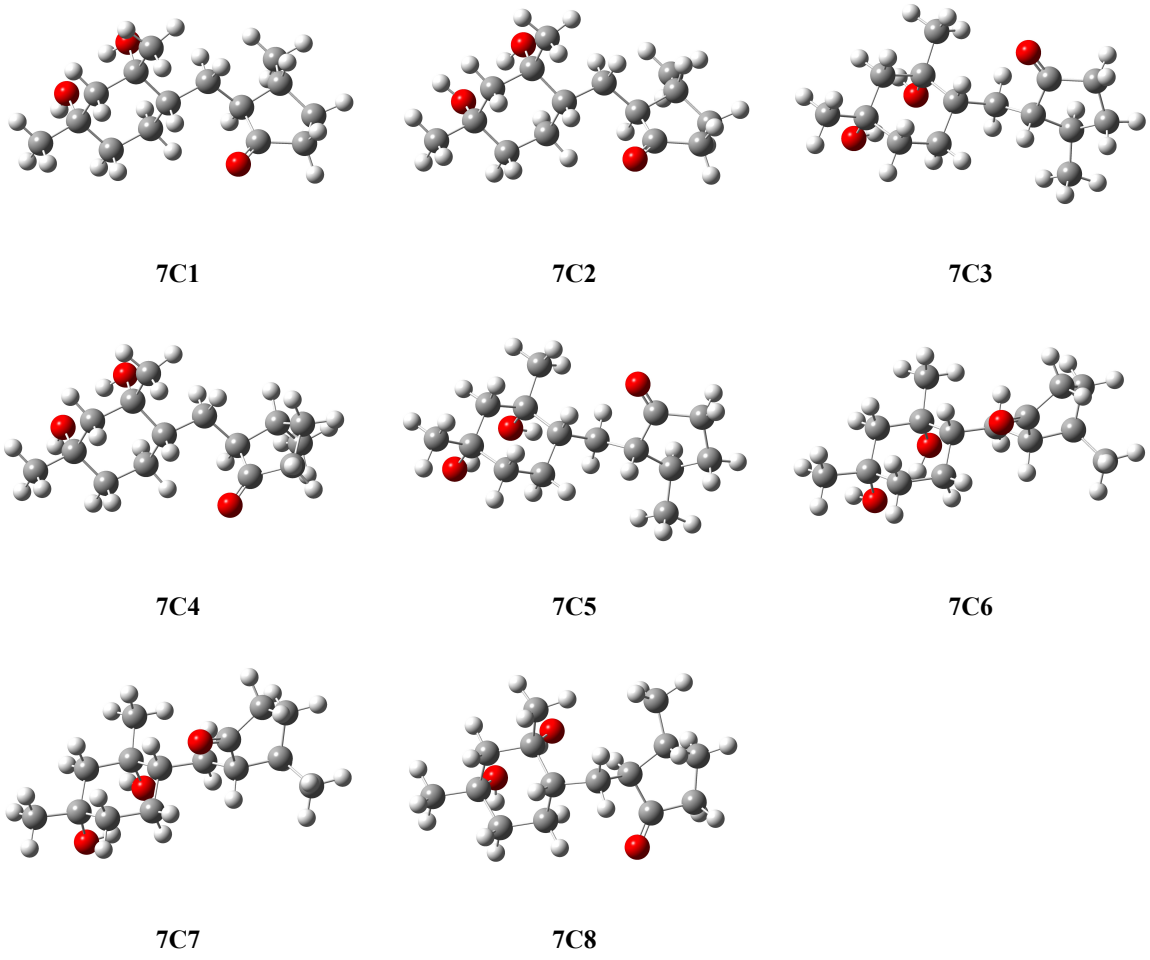

Figure S1. *ω*B97XD/DGDZVP optimized eight conformers of (1*S*,5*R*,7*S*,8*S*,10*S*)-**7**.

Table S1. Energy analysis for the conformers of (1*S*,5*R*,7*S*,8*S*,10*S*)-**7**.

Conf.	MMFF energy	B3LYP/6-31G(d) Gibbs free energy (298.15 K)			*ω*B97XD/DGDZVP Gibbs free energy (298.15 K)		
	ΔE (Kcal/ mol)	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
7C1	0.00000	-812.589599	0.0000	0.311	-812.462169	0.0000	0.444
7C2	0.48818	-812.589472	0.0800	0.271	-812.461155	0.6360	0.152
7C3	0.57338	-812.589481	0.0740	0.274	-812.461417	0.4720	0.200
7C4	0.66893	-812.586036	2.2360	0.007	-812.458776	2.1290	0.012
7C5	0.78336	-812.588665	0.5860	0.115	-812.461295	0.5480	0.176
7C6	1.29817	-812.585750	2.4150	0.005	-812.458501	2.3020	0.009
7C7	1.70531	-812.584991	2.8920	0.002	-812.457139	3.1560	0.002
7C8	1.90831	-812.586652	1.8490	0.014	-812.458002	2.6150	0.005

References

[1] (a) Goto, H., Osawa, E., 1989. Corner flapping: a simple and fast algorithm for exhaustive generation of ring conformations. J. Am. Chem. Soc. 111, 8950−8951. (b) Goto, H., Osawa, E., 1993. An efficient algorithm for searching low-energy conformers of cyclic and acyclic molecules. J. Chem. Soc., Perkin Trans. 2, 187−198.

[2] Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Petersson, G.A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A.V., Bloino, J., Janesko, B.G., Gomperts, R., Mennucci, B., Hratchian, H.P., Ortiz, J.V., Izmaylov, A.F., Sonnenberg, J.L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V.G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J.A.Jr., Peralta, J.E., Ogliaro, F., Bearpark, M.J., Heyd, J.J., Brothers, E.N., Kudin, K.N., Staroverov, V.N., Keith, T.A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A.P., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Millam, J.M., Klene, M., Adamo, C., Cammi, R., Ochterski, J.W., Martin, R.L., Morokuma, K., Farkas, O., Foresman, J.B., Fox, D.J., 2016. Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT.

[3] Liu, Y., Liu, F., Qiao M. M., Guo, L., Chen, M. H., Peng, C., Xiong, L., 2019. Curcumanes A and B, Two bicyclic sesquiterpenoids with significant vasorelaxant activity from *Curcuma longa*. Org. Lett. 21, 1197−1201.

[4] Bruhn, T., Schaumlöffel, A., Hemberger, Y., Bringmann, G., 2017. Spec Dis, version 1.71, University of Würzburg, Germany

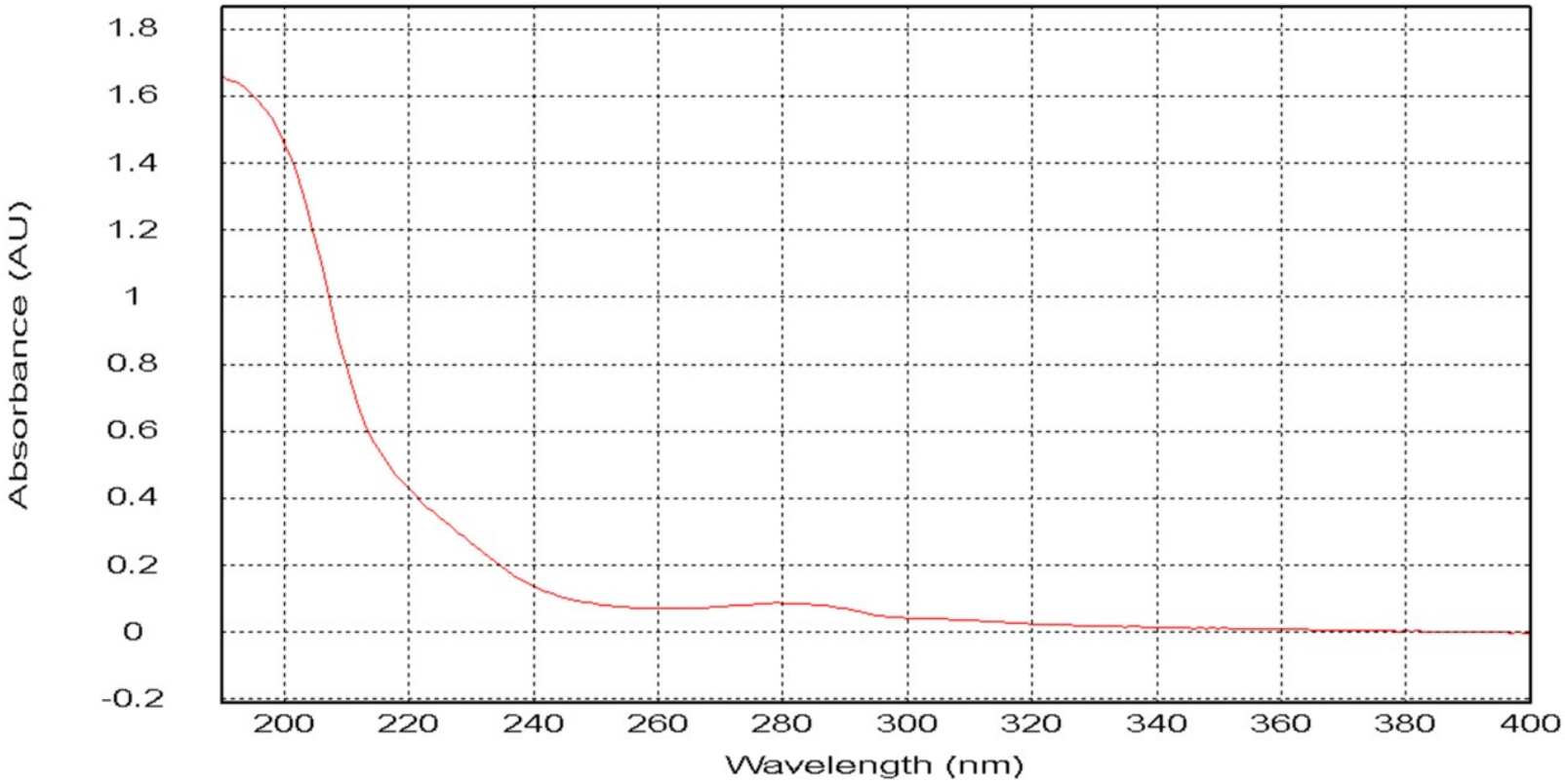

Figure S2. The UV spectrum of compound **1** in acetonitrile.

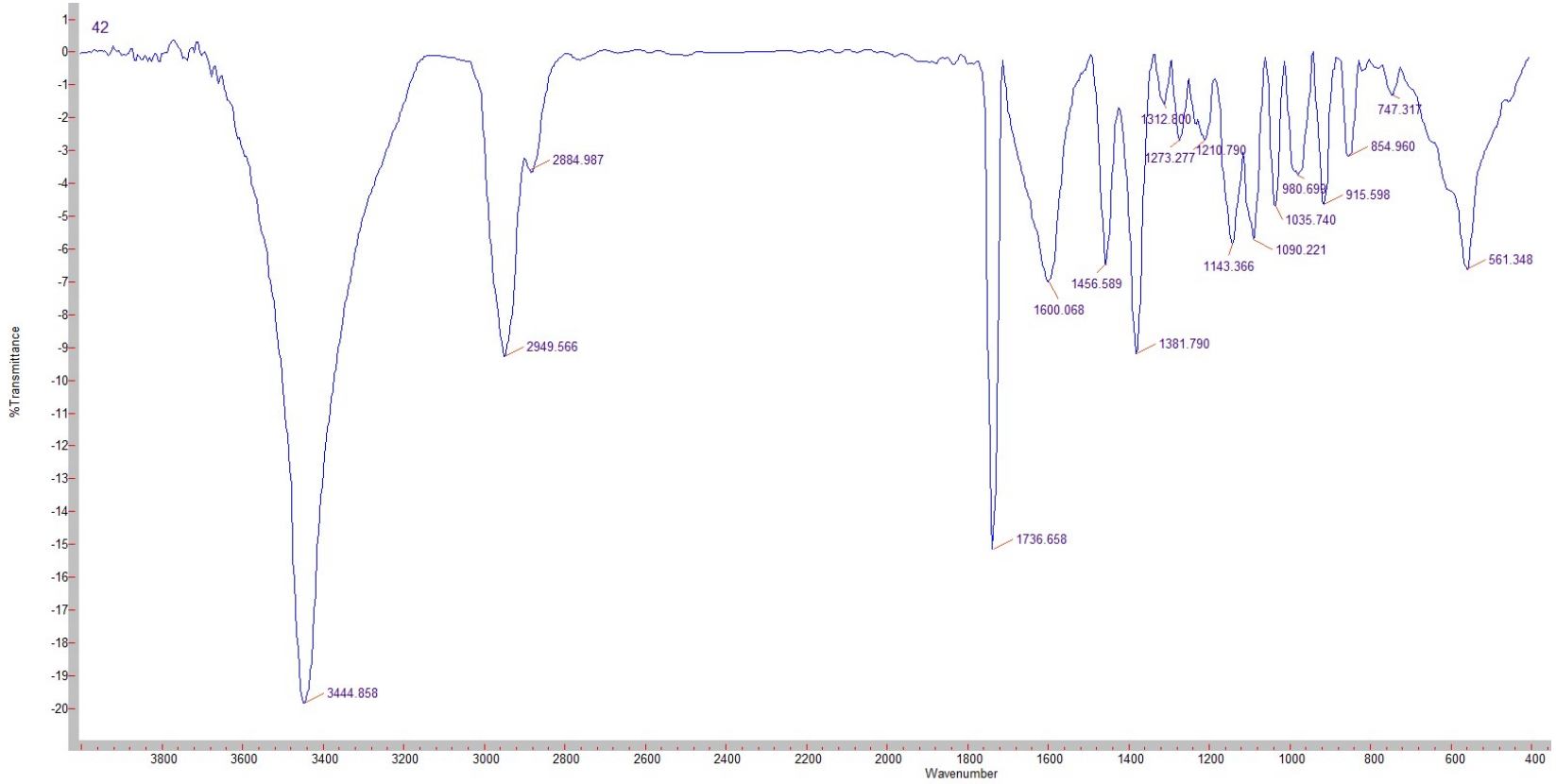

Figure S3. The IR spectrum of compound **1**.

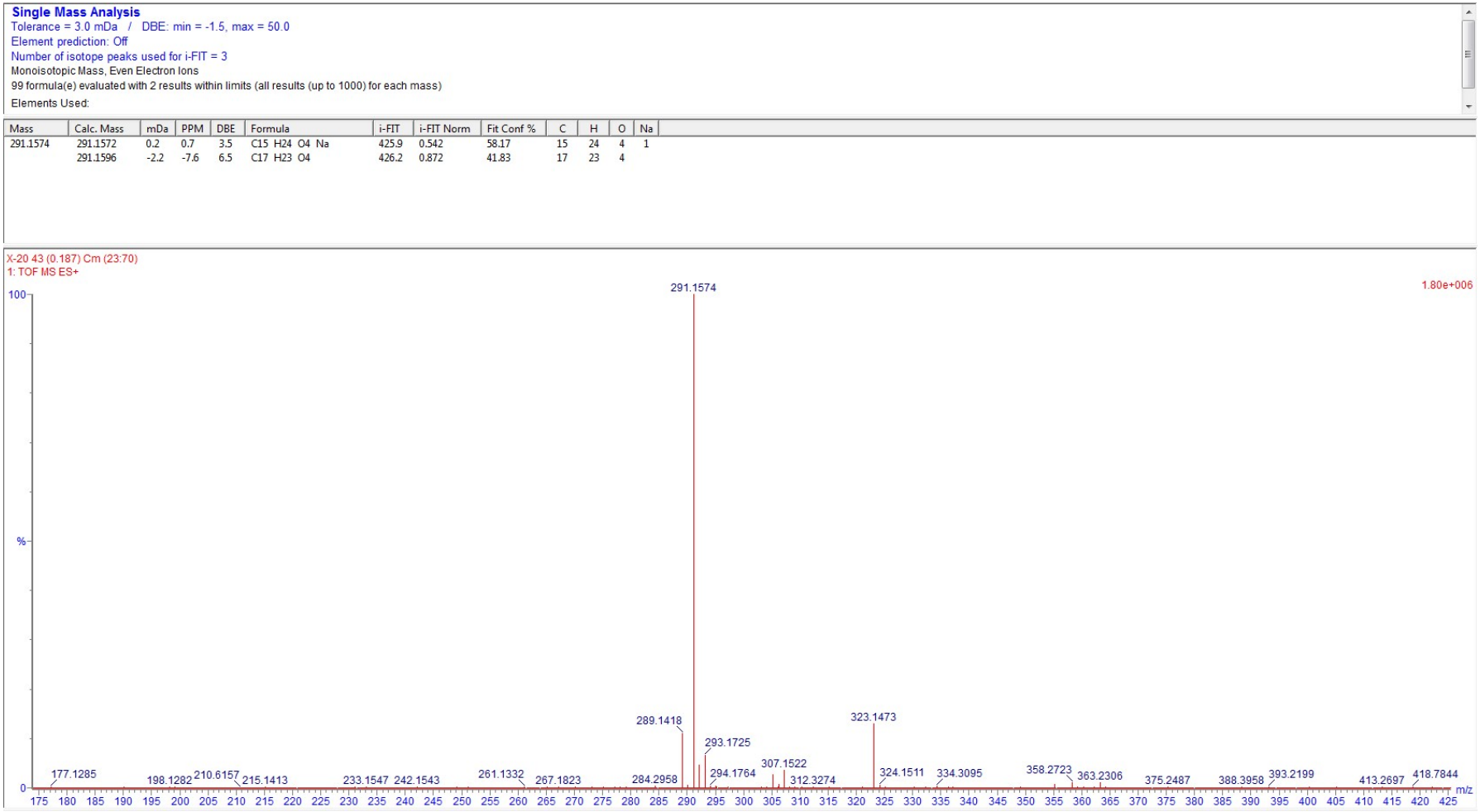

Figure S4. The (+)-HRESIMS spectroscopic data of compound **1**.

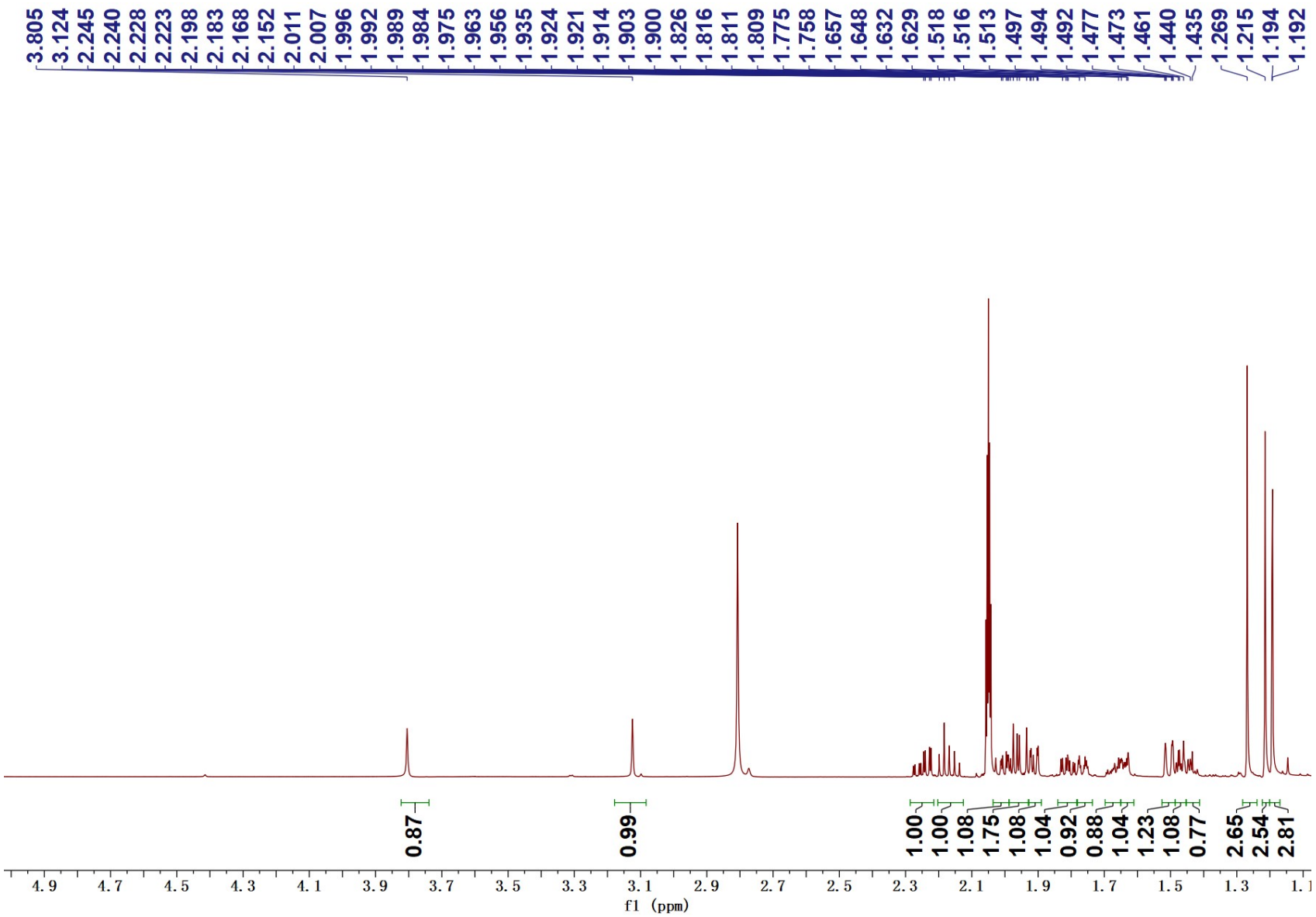

Figure S5. The ^{1}H NMR spectrum of compound **1** in acetone-d_6.

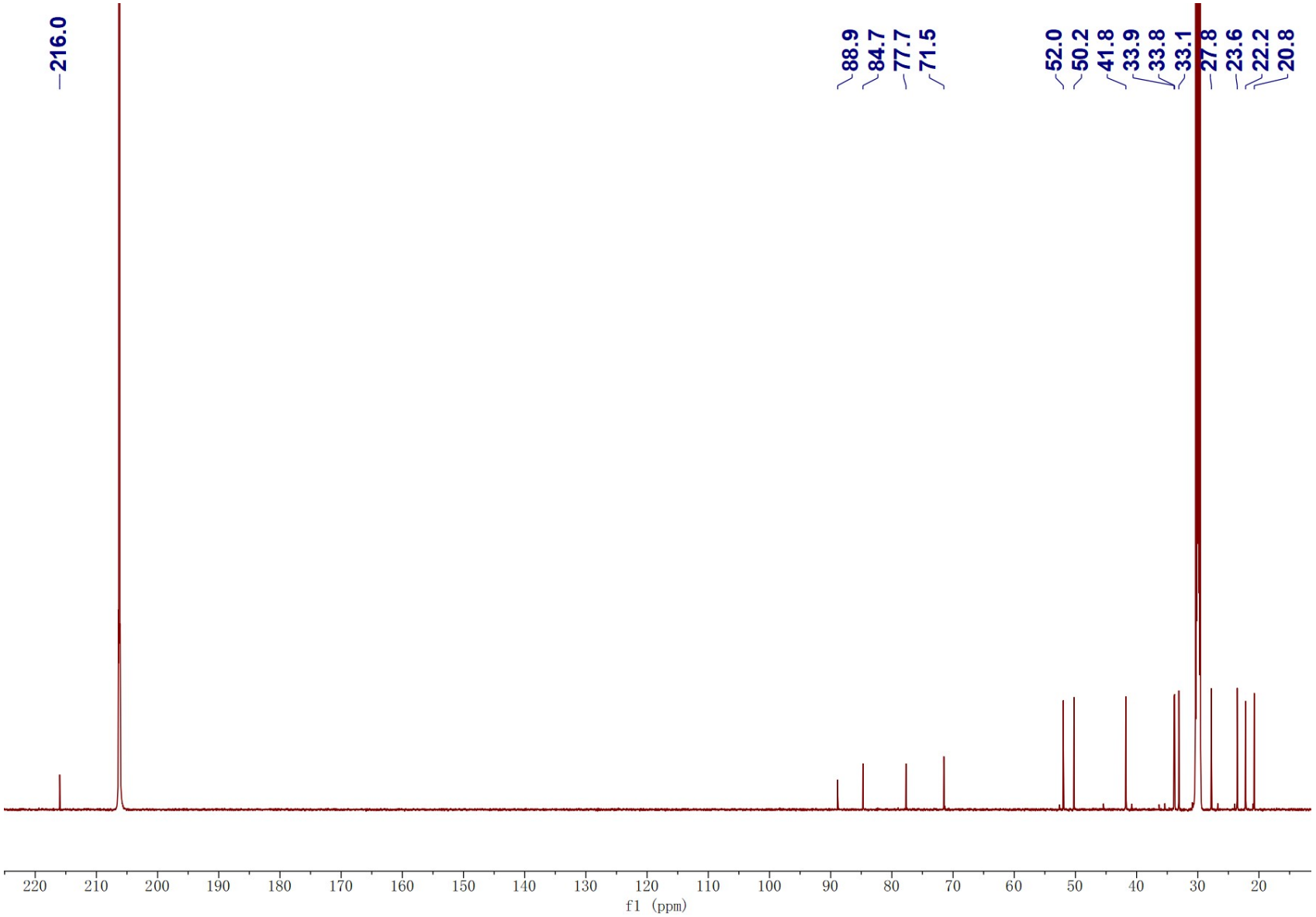

Figure S6. The ^{13}C NMR spectrum of compound **1** in acetone-d_6.

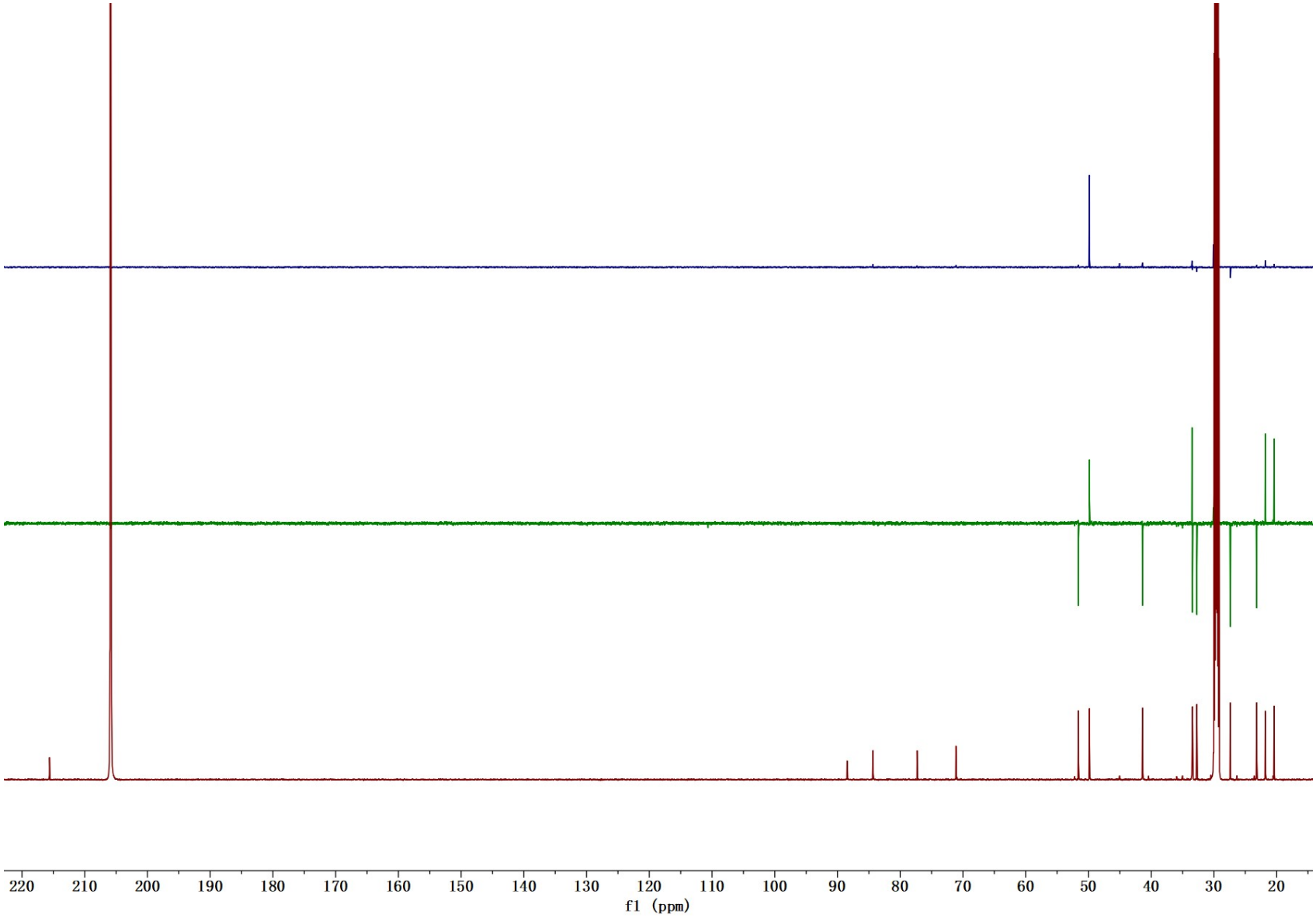

Figure S7. The DEPT spectrum of compound **1** in acetone-d_6.

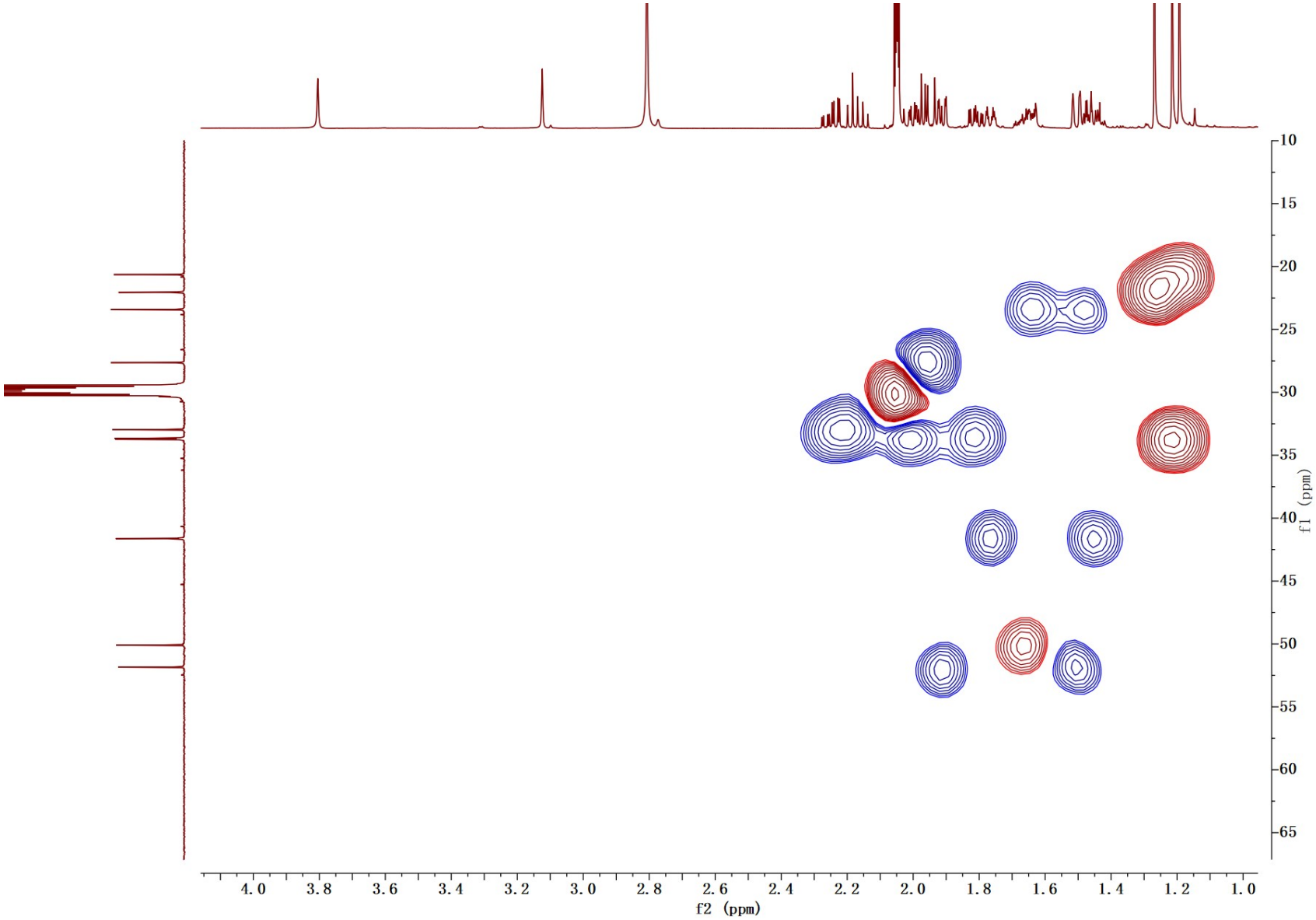

Figure S8. The HSQC spectrum of compound **1** in acetone-d_6.

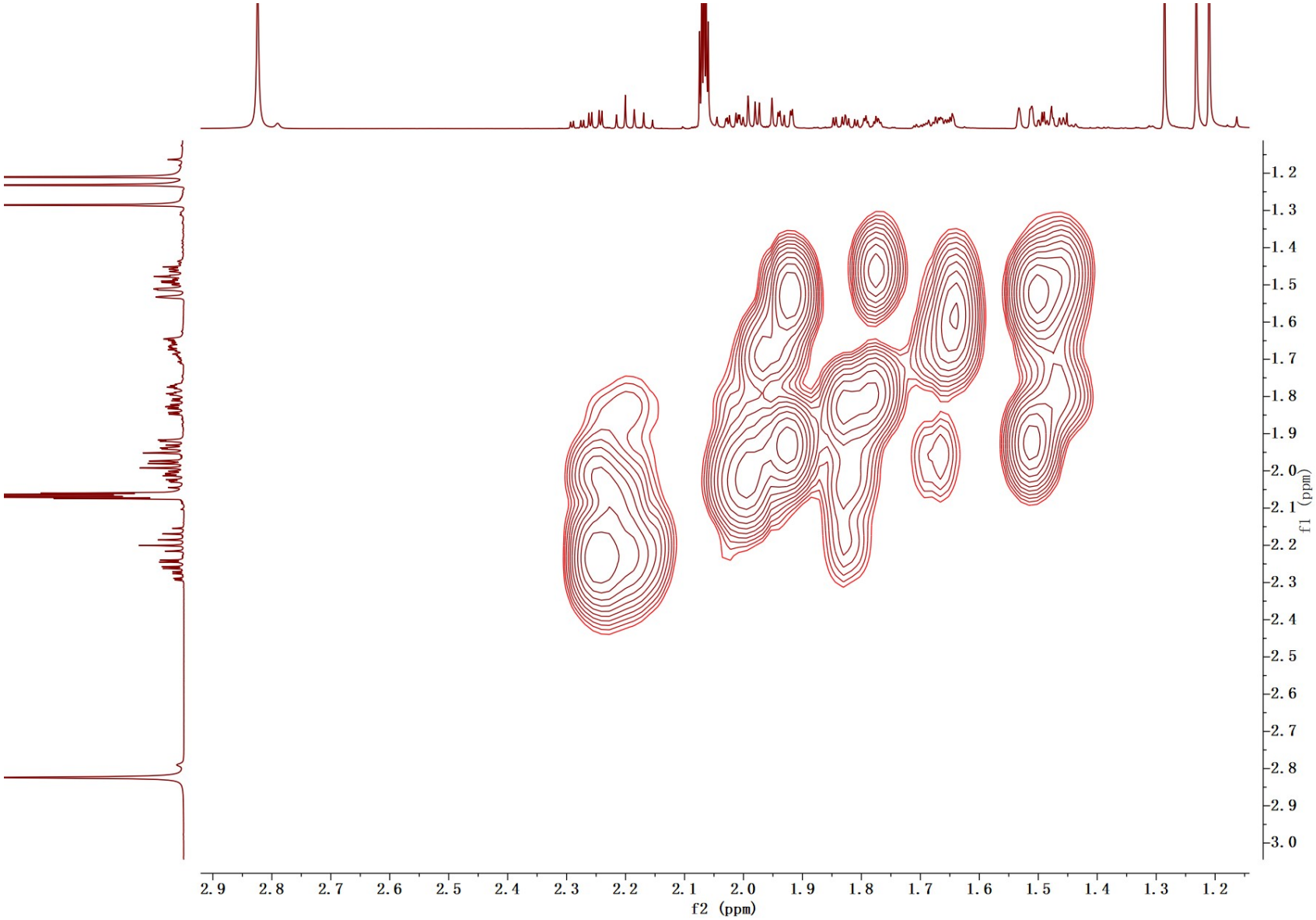

Figure S9. The ^{1}H-^{1}H COSY spectrum of compound **1** in acetone-d_6.

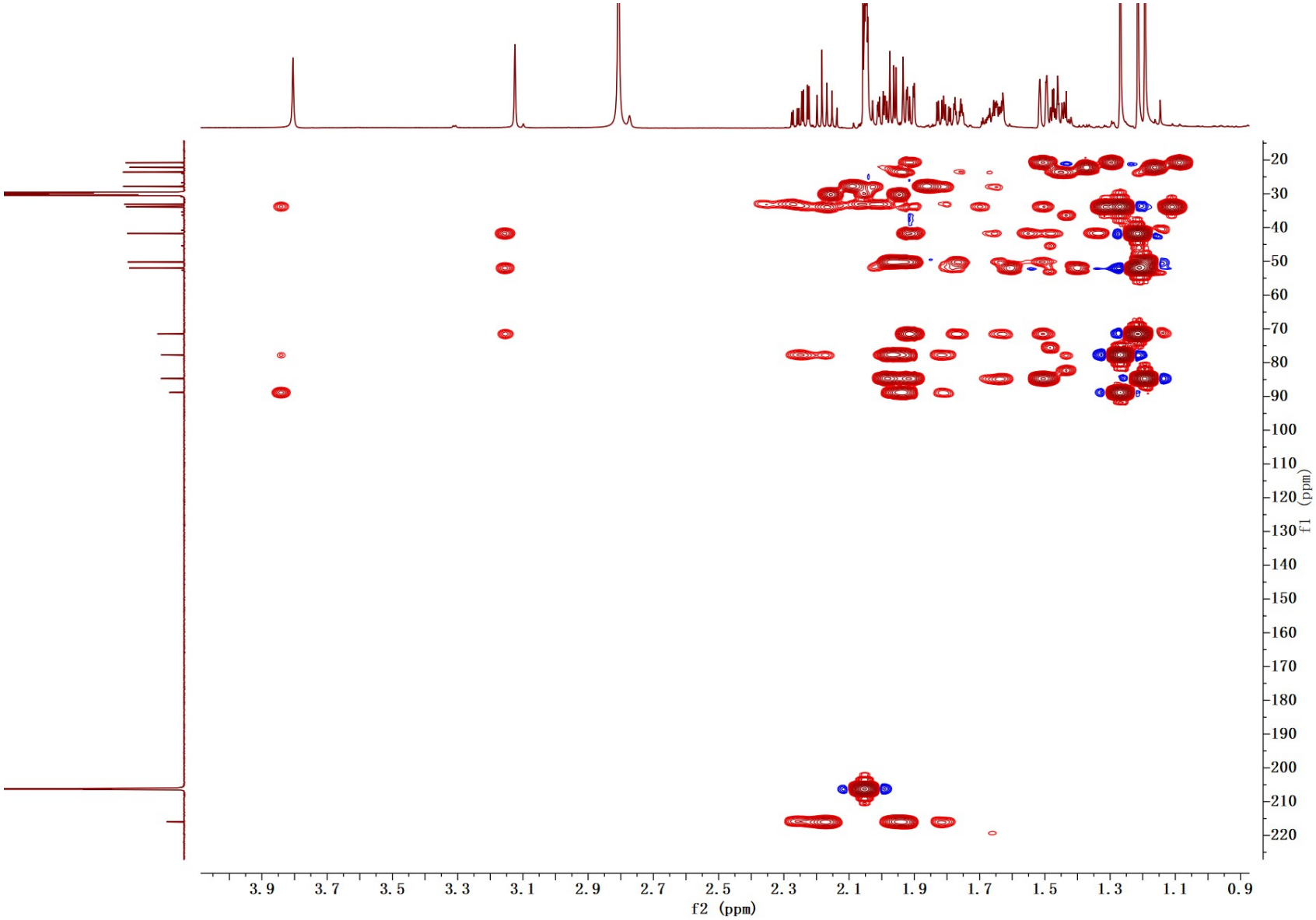

Figure S10. The HMBC spectrum of compound **1** in acetone-d_6.

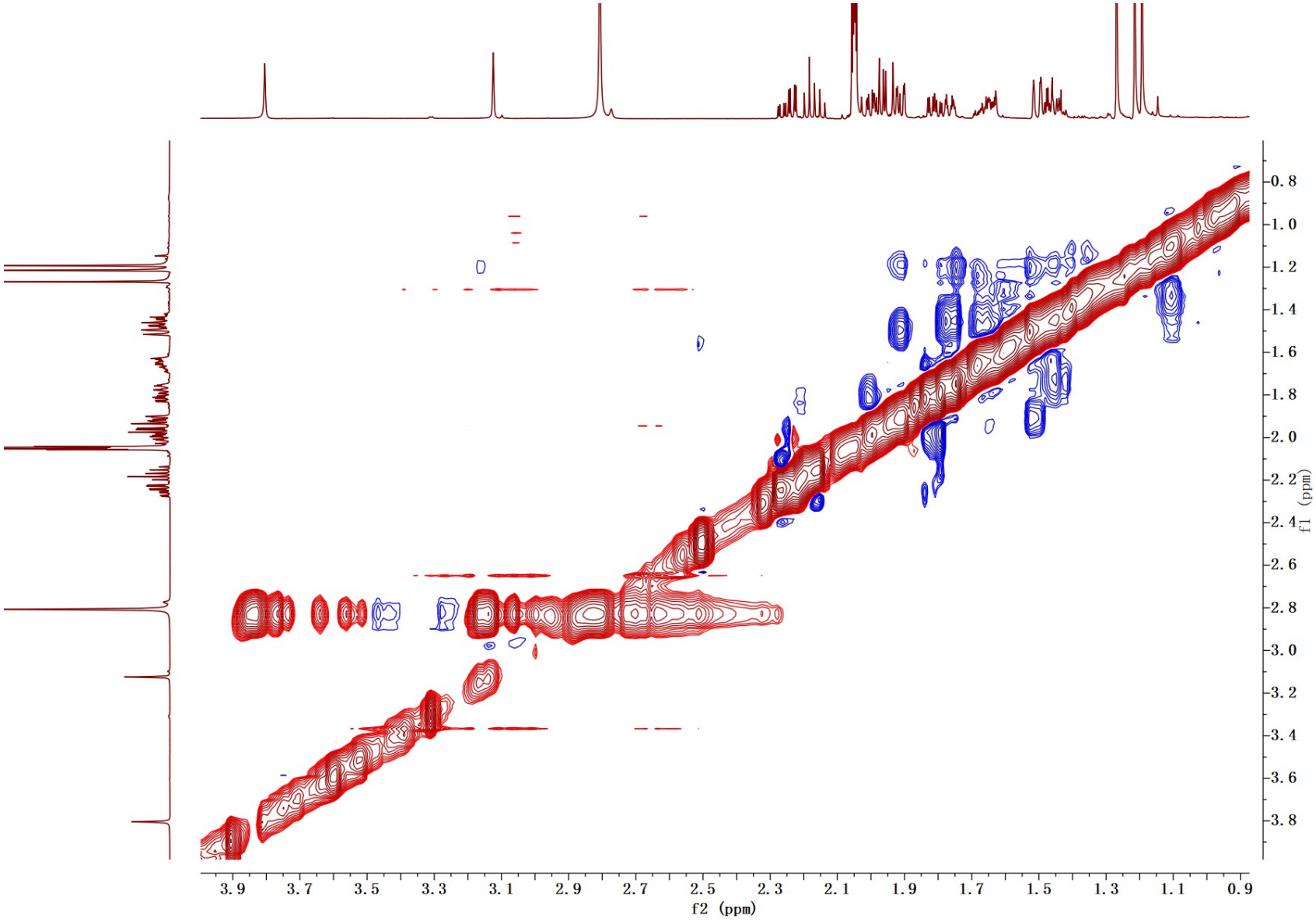

Figure S11. The NOESY spectrum of compound **1** in acetone-d_6.

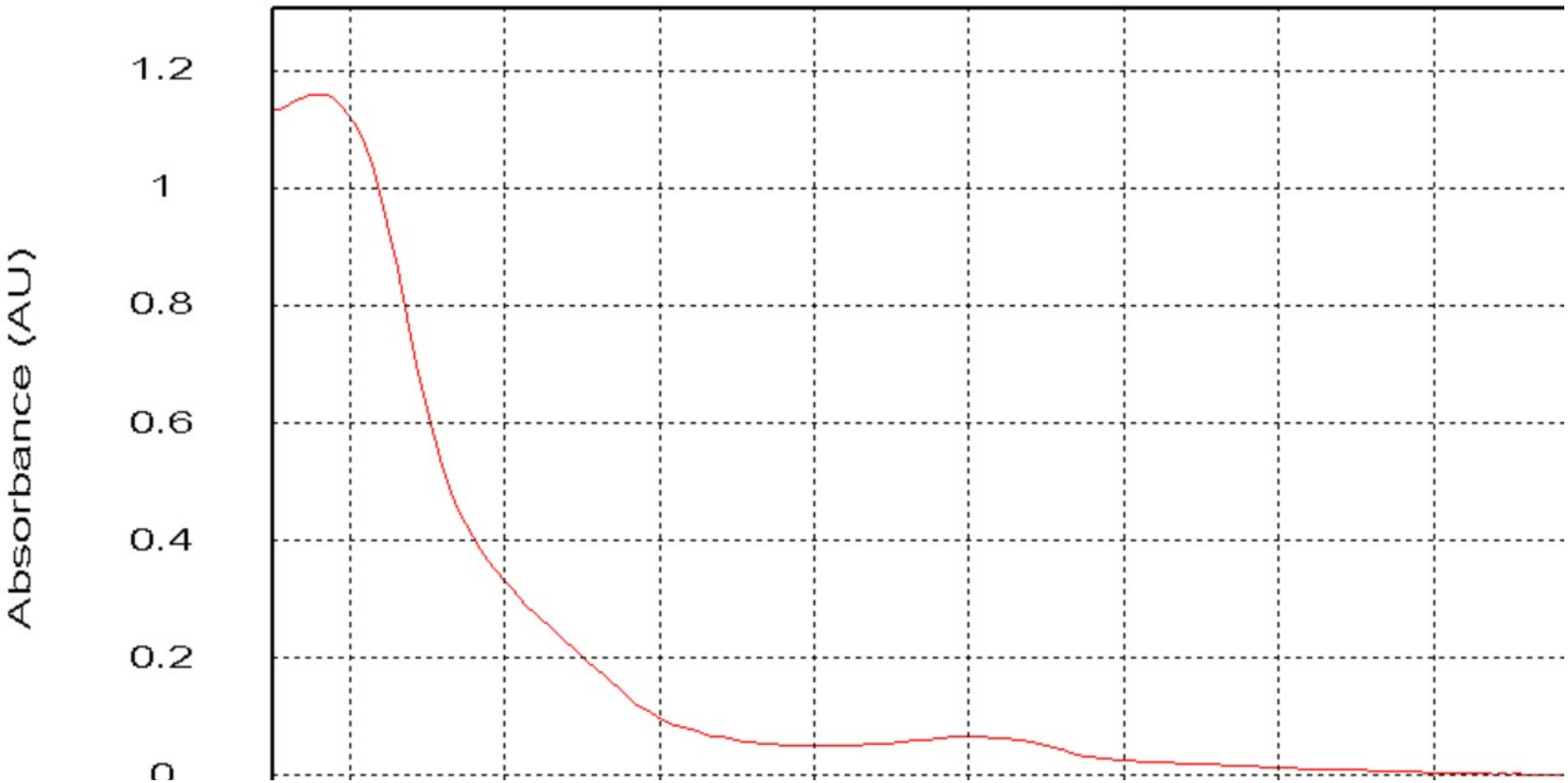

Figure S12. The UV spectrum of compound **2** in acetonitrile.

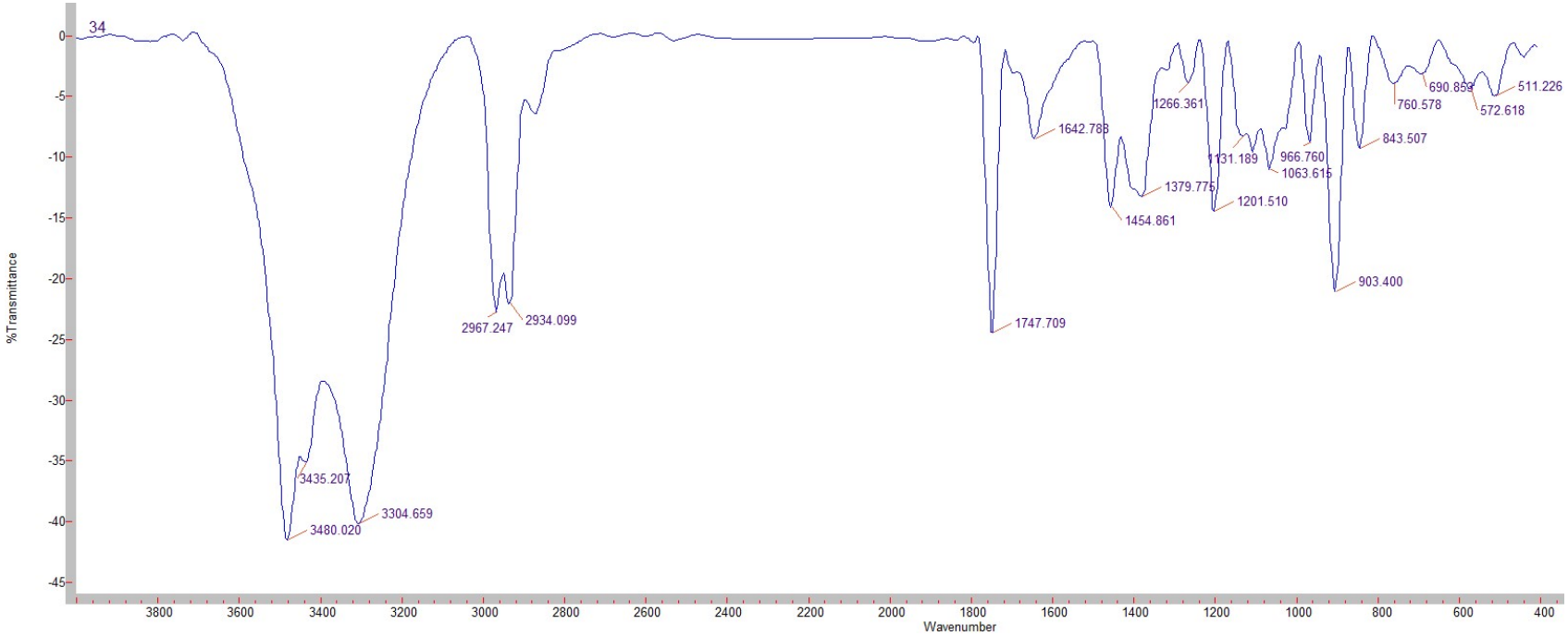

Figure S13. The IR spectrum of compound **2**.

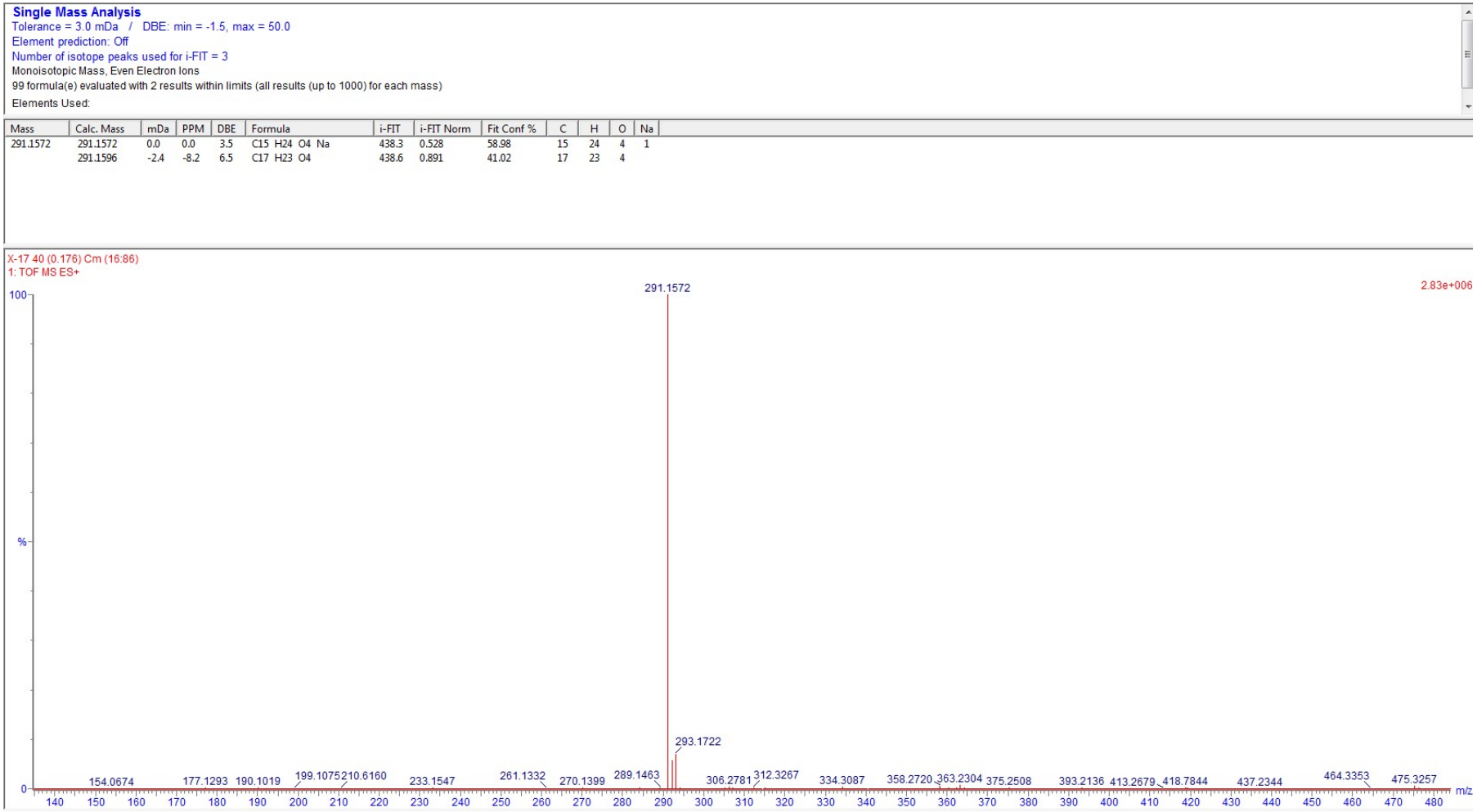

Figure S14. The (+)-HRESIMS spectroscopic data of compound **2**.

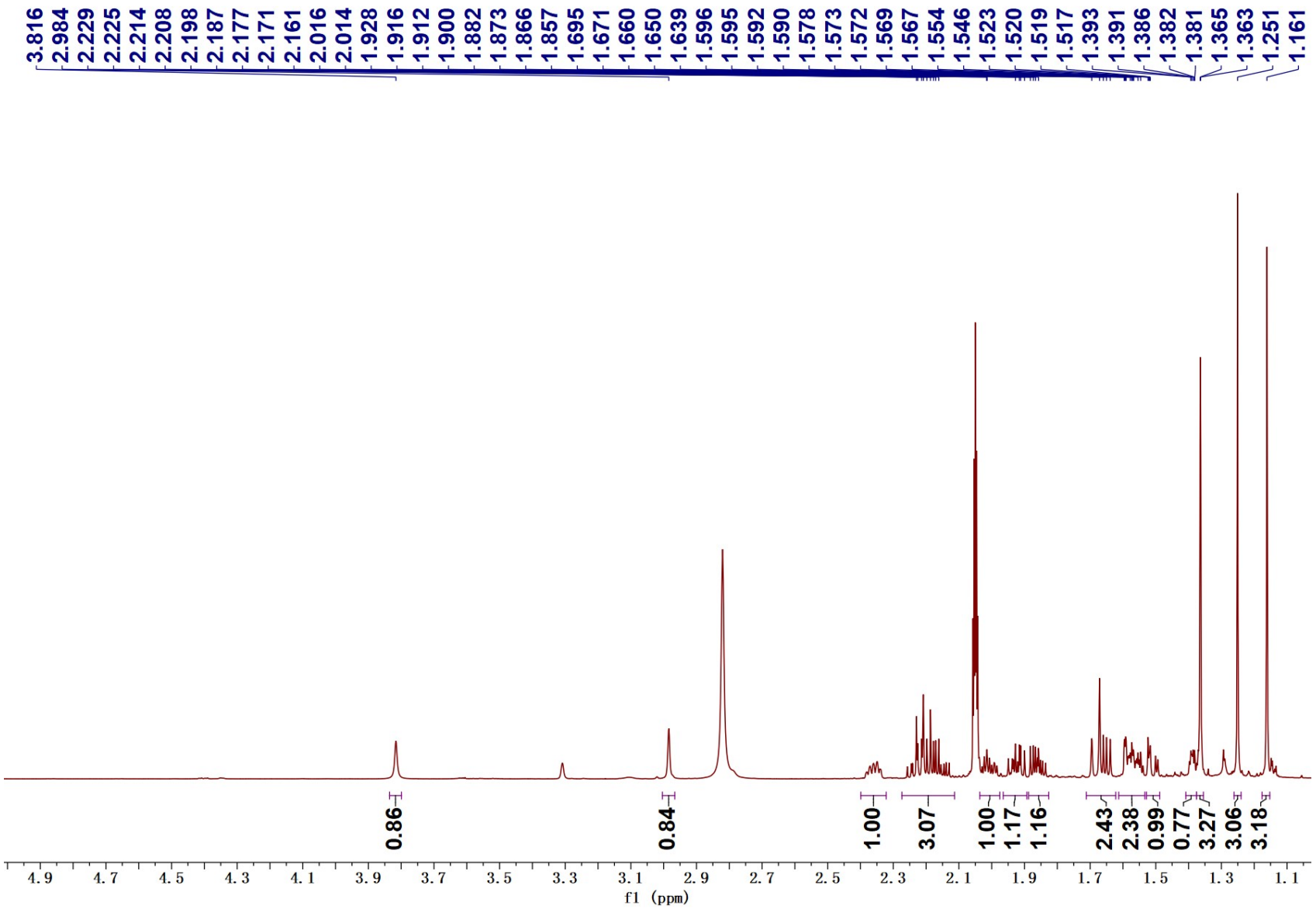

Figure S15. The ^{1}H NMR spectrum of compound **2** in acetone-d_6.

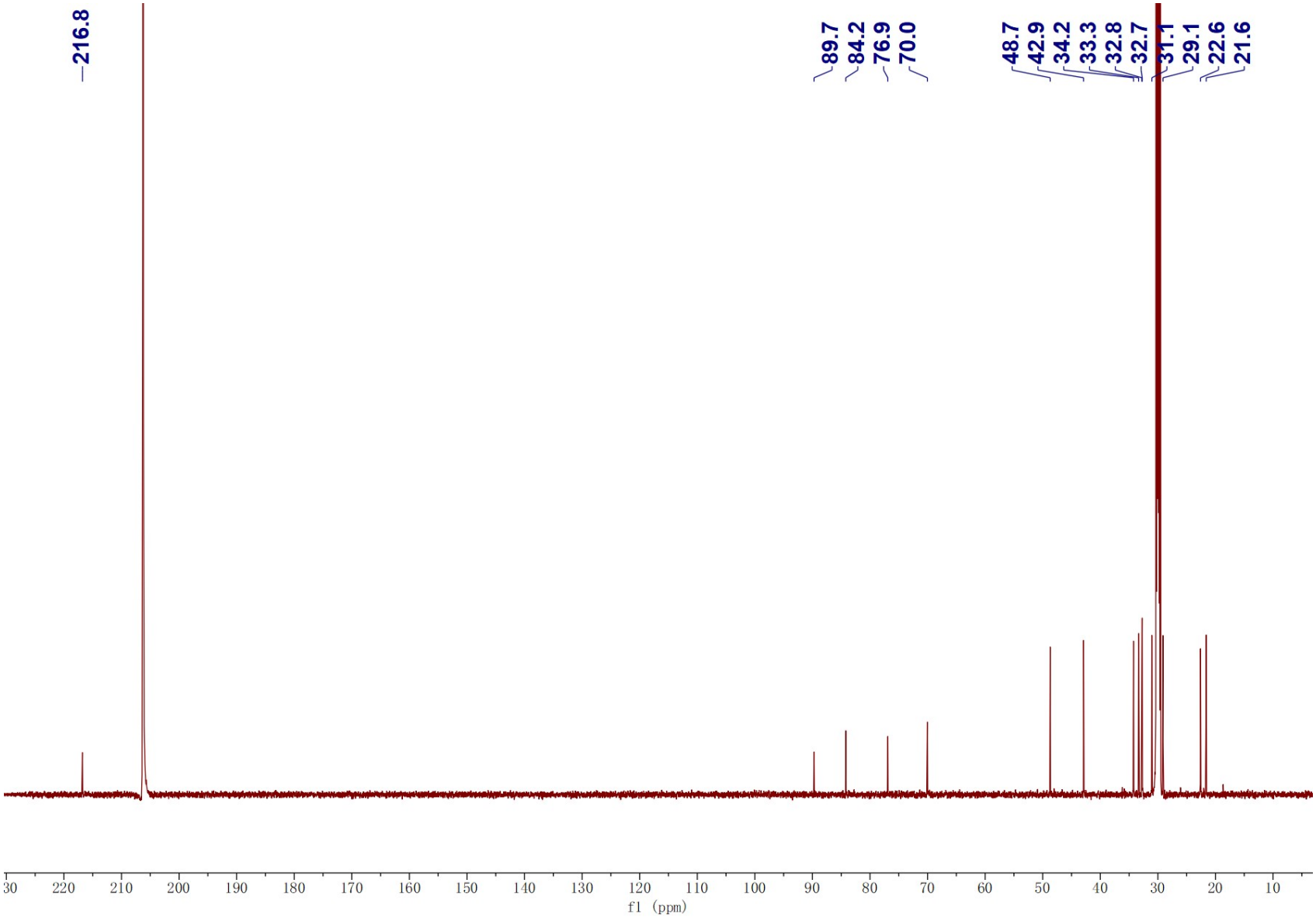

Figure S16. The ^{13}C NMR spectrum of compound **2** in acetone-d_6.

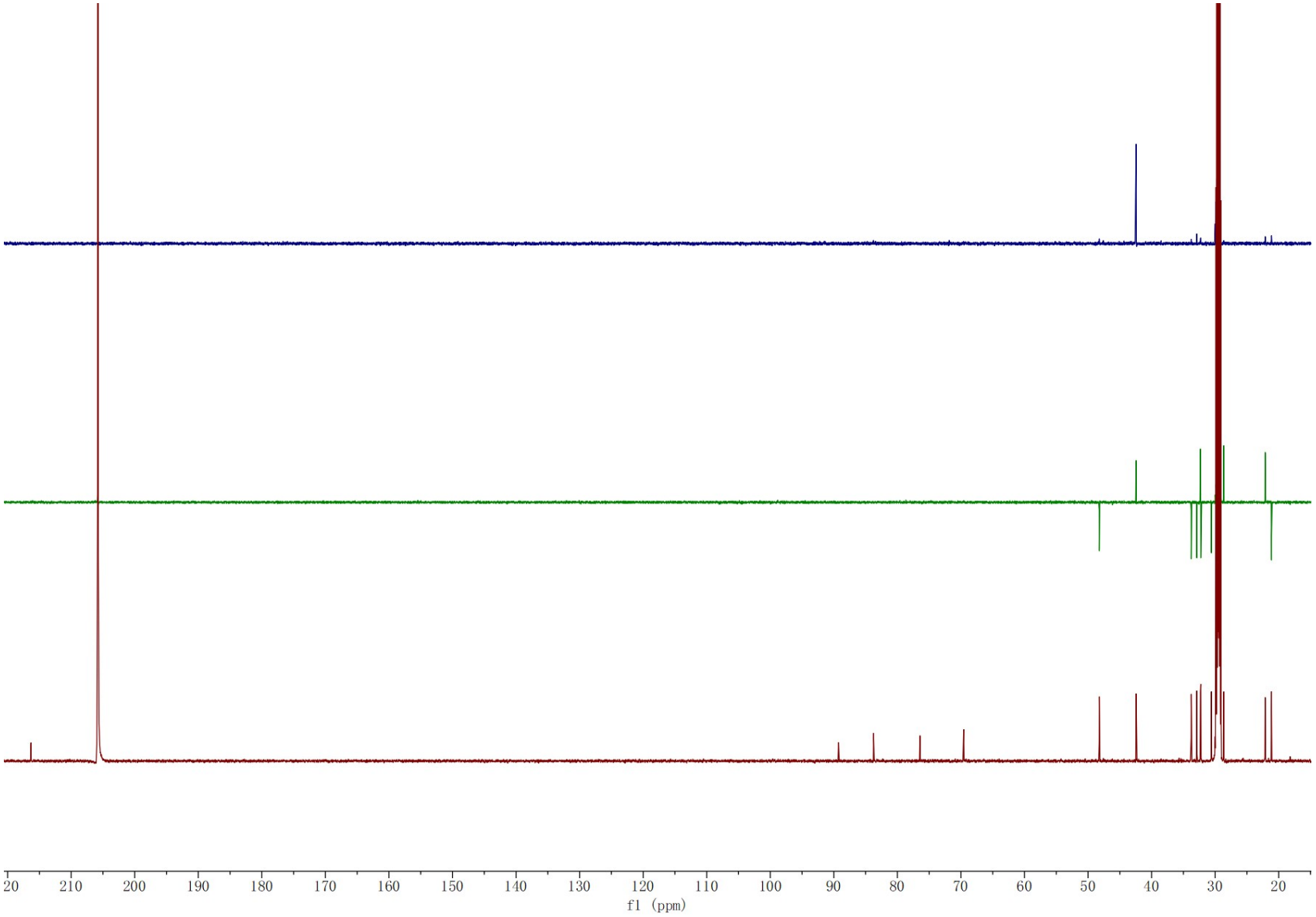

Figure S17. The DEPT spectrum of compound **2** in acetone-d_6.

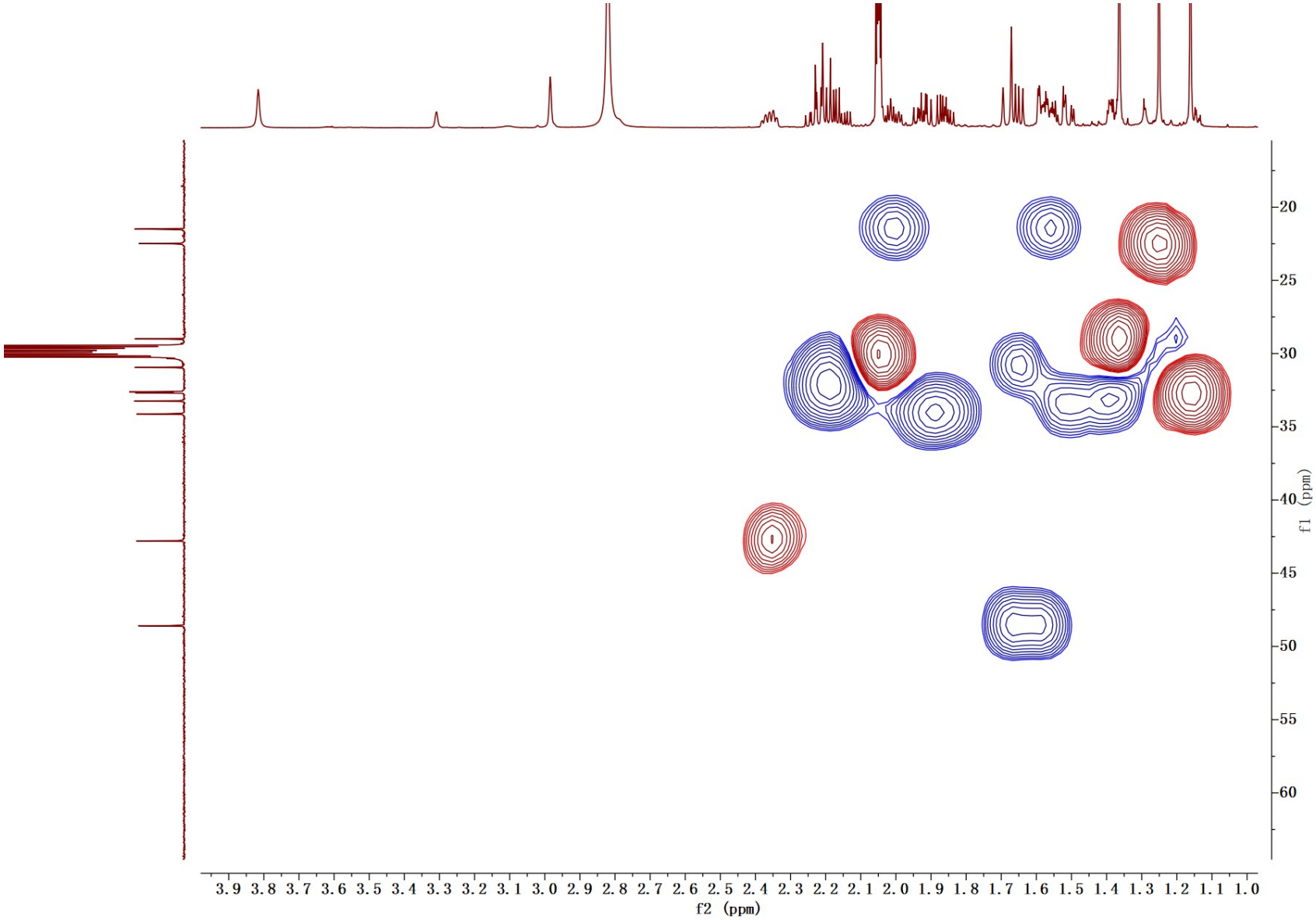

Figure S18. The HSQC spectrum of compound **2** in acetone-d_6.

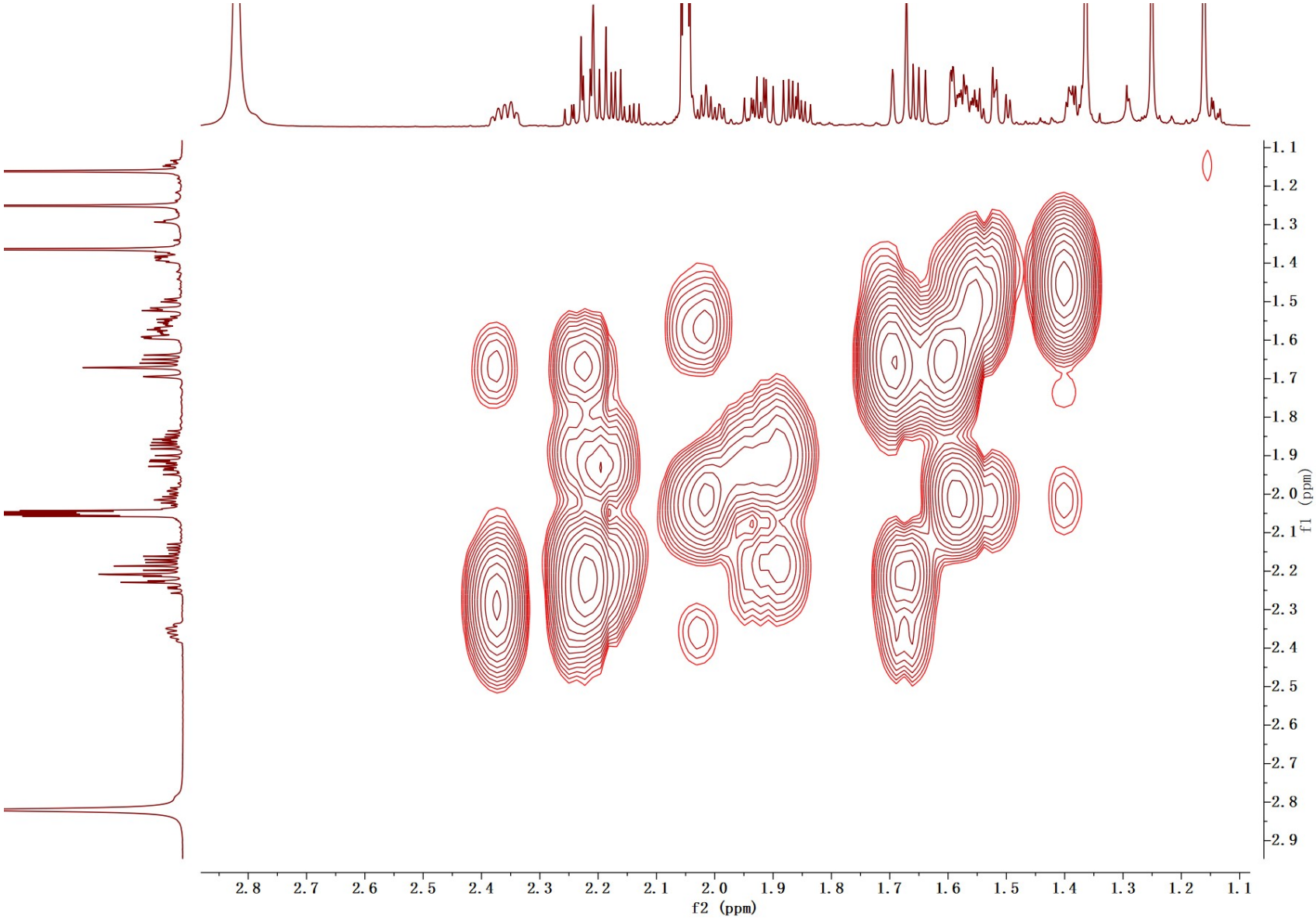

Figure S19. The ^{1}H-^{1}H COSY spectrum of compound **2** in acetone-d_6.

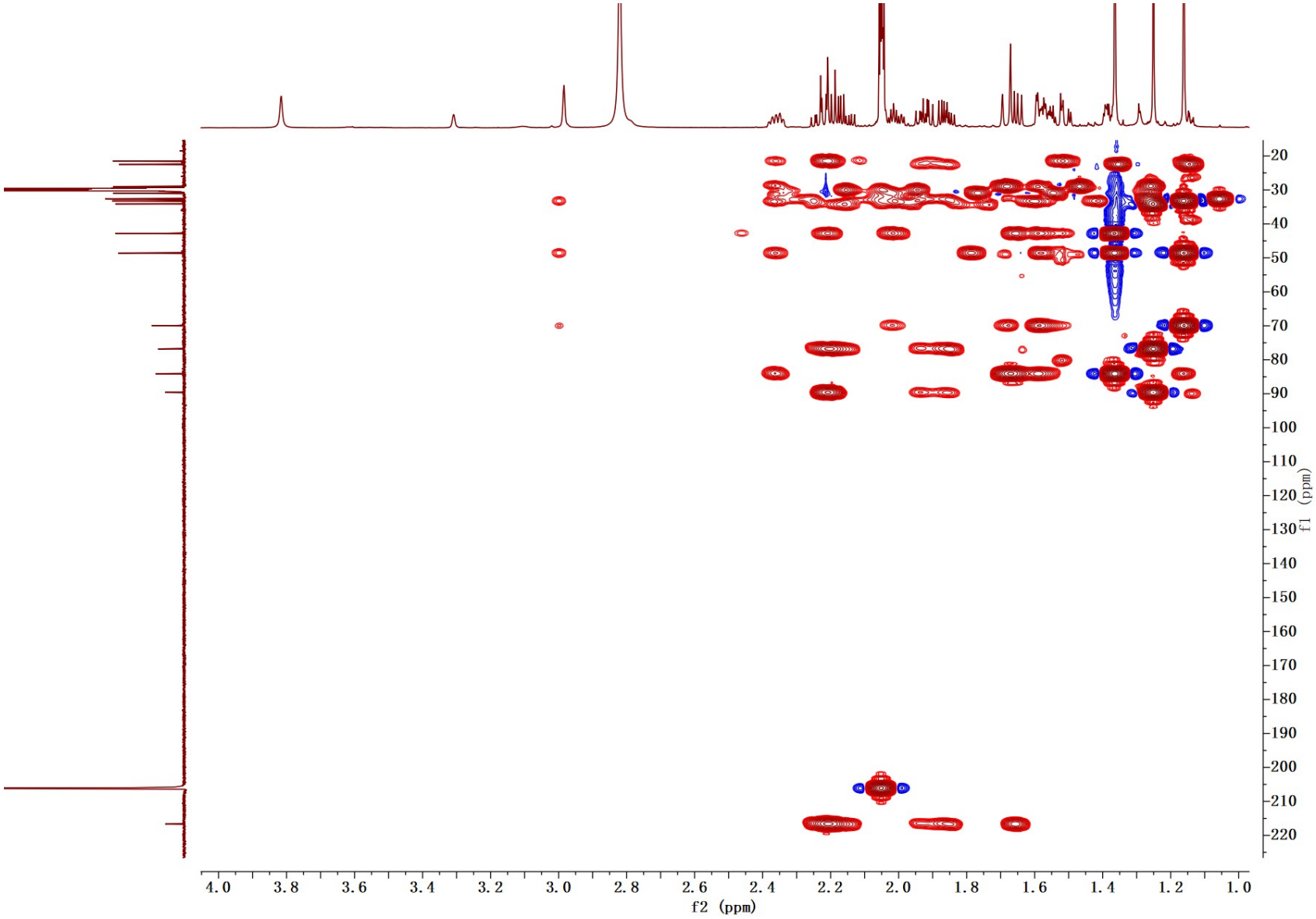

Figure S20. The HMBC spectrum of compound **2** in acetone-d_6.

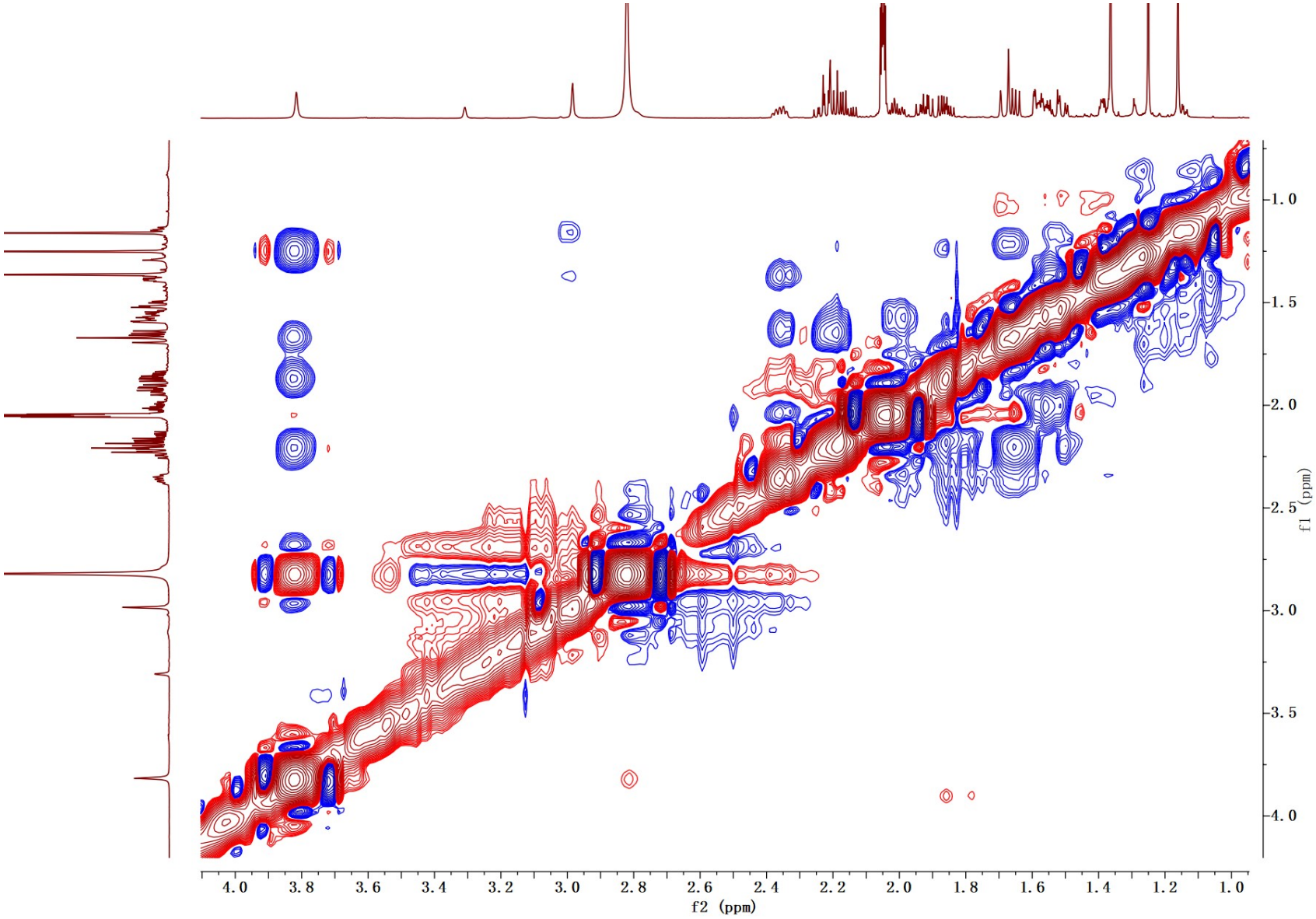

Figure S21. The NOESY spectrum of compound **2** in acetone-d_6.

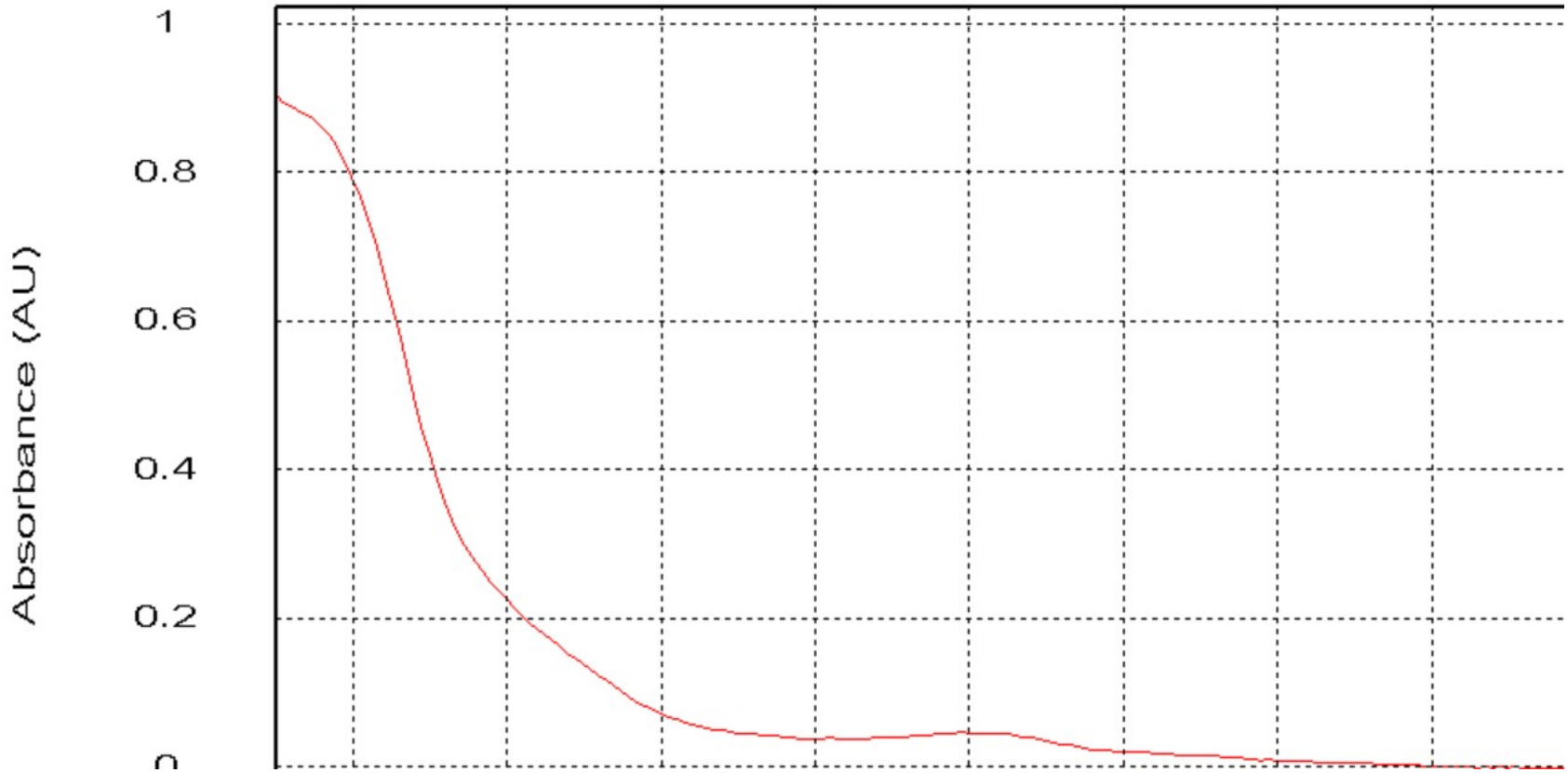

Figure S22. The UV spectrum of compound **3** in acetonitrile.

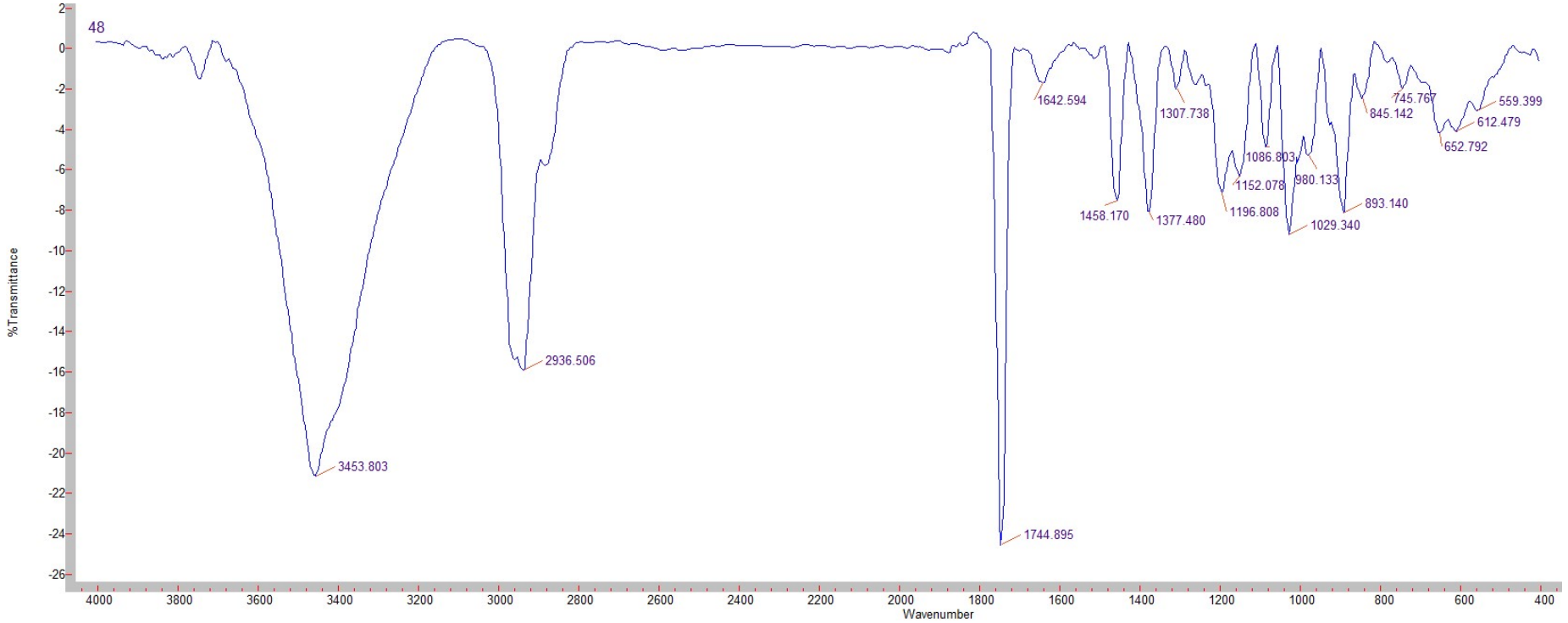

Figure S23. The IR spectrum of compound **3**.

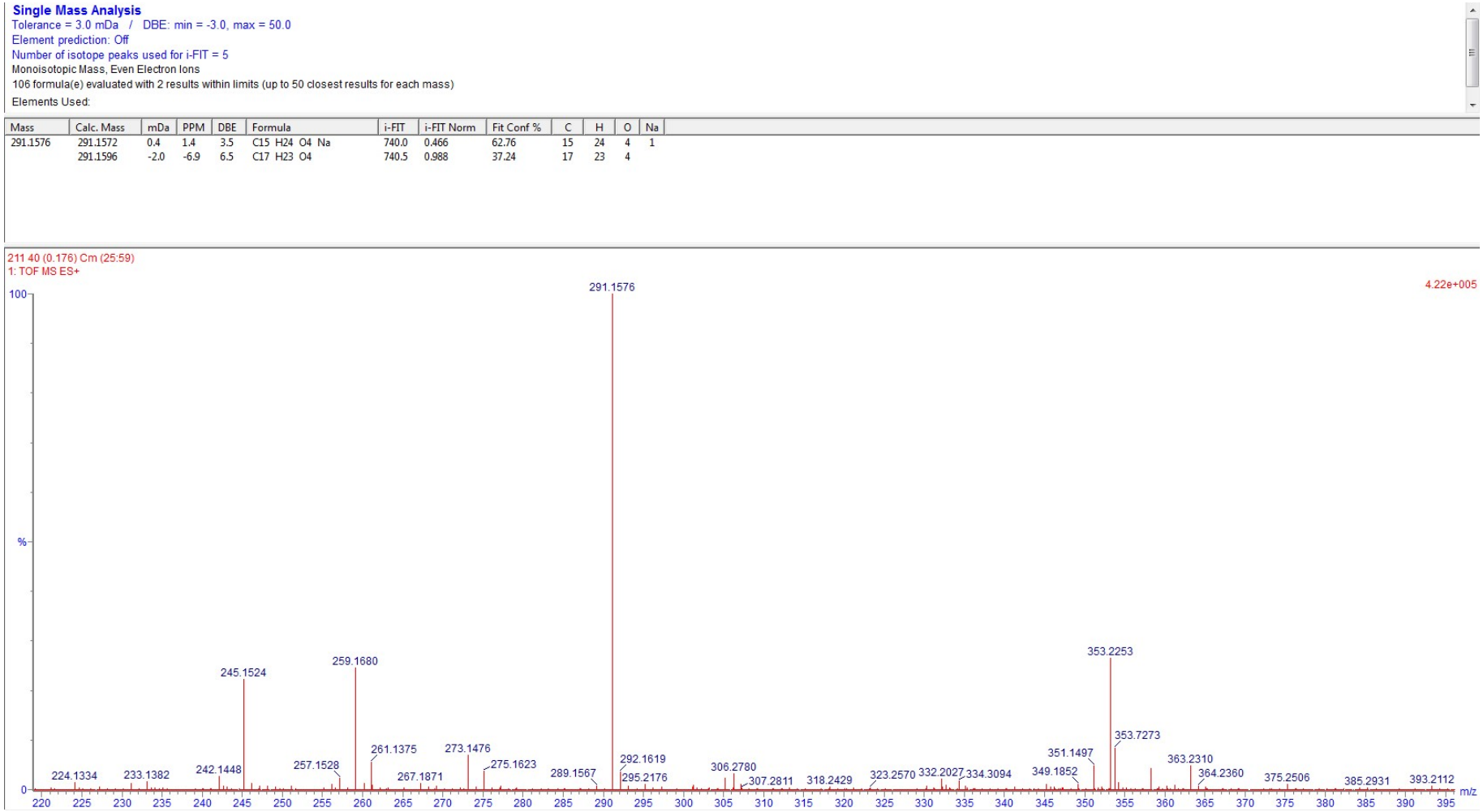

Figure S24. The (+)-HRESIMS spectroscopic data of compound **3**.

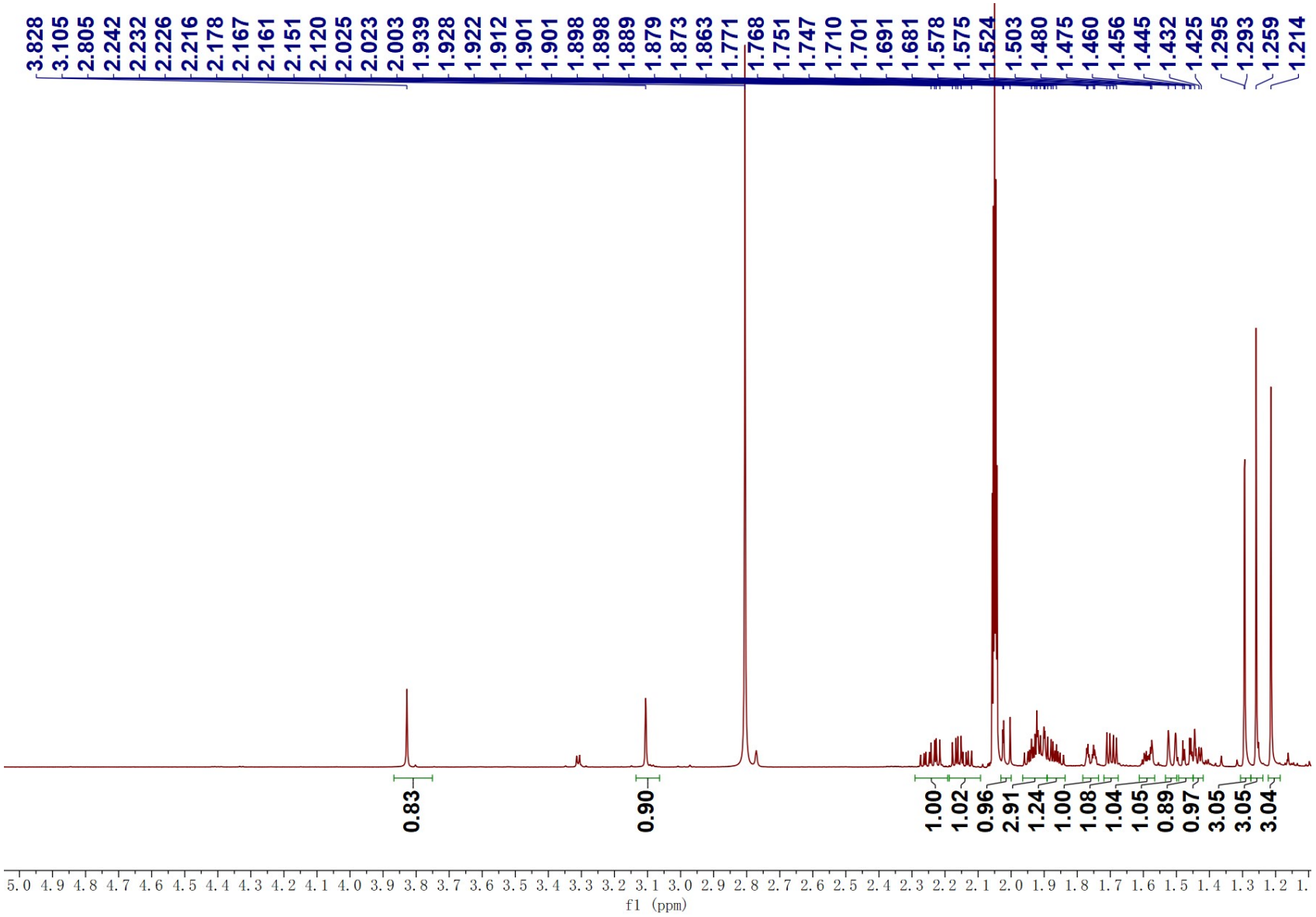

Figure S25. The ^{1}H NMR spectrum of compound **3** in acetone-d_6.

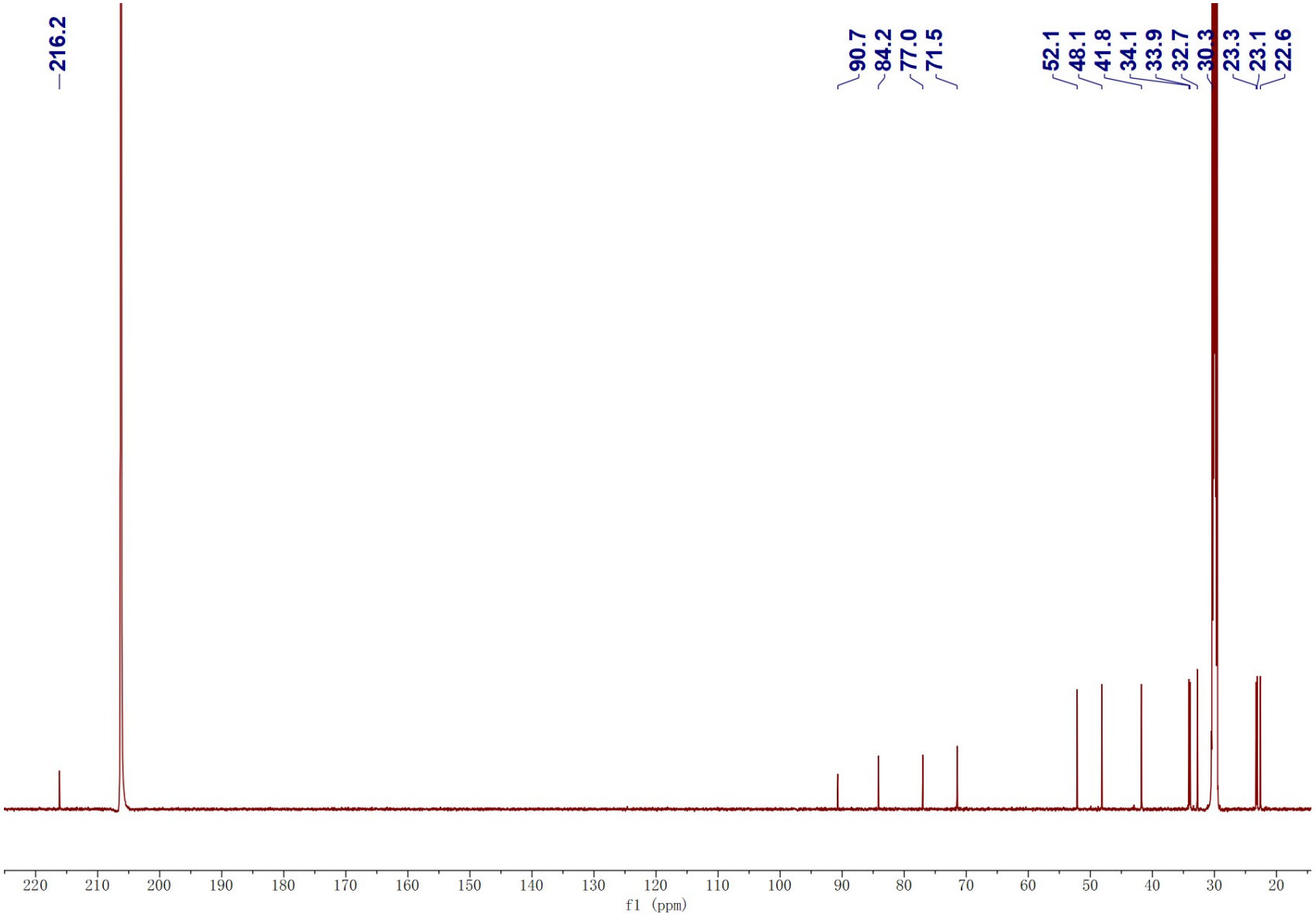

Figure S26. The ^{13}C NMR spectrum of compound **3** in acetone-d_6.

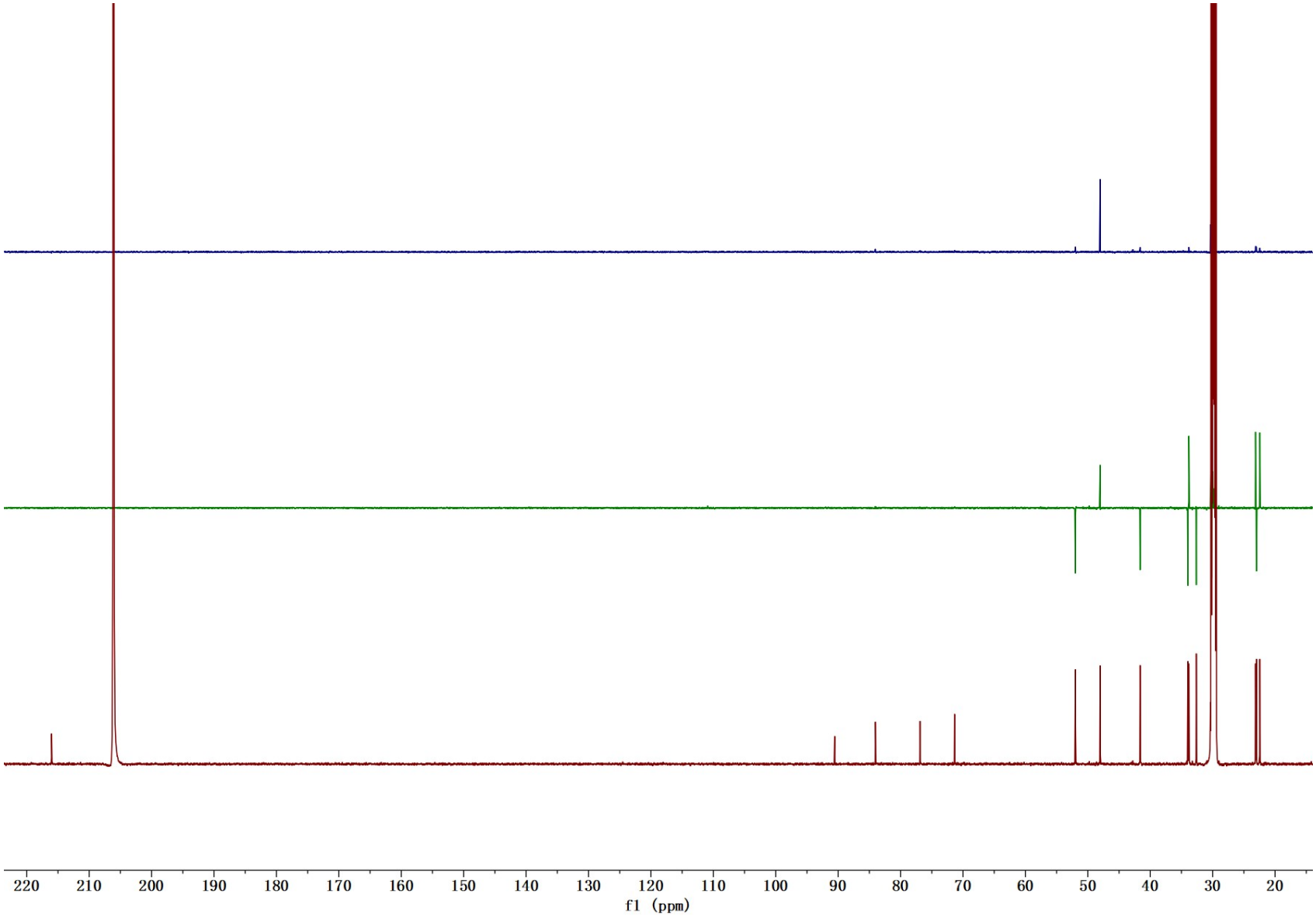

Figure S27. The DEPT spectrum of compound **3** in acetone-d_6.

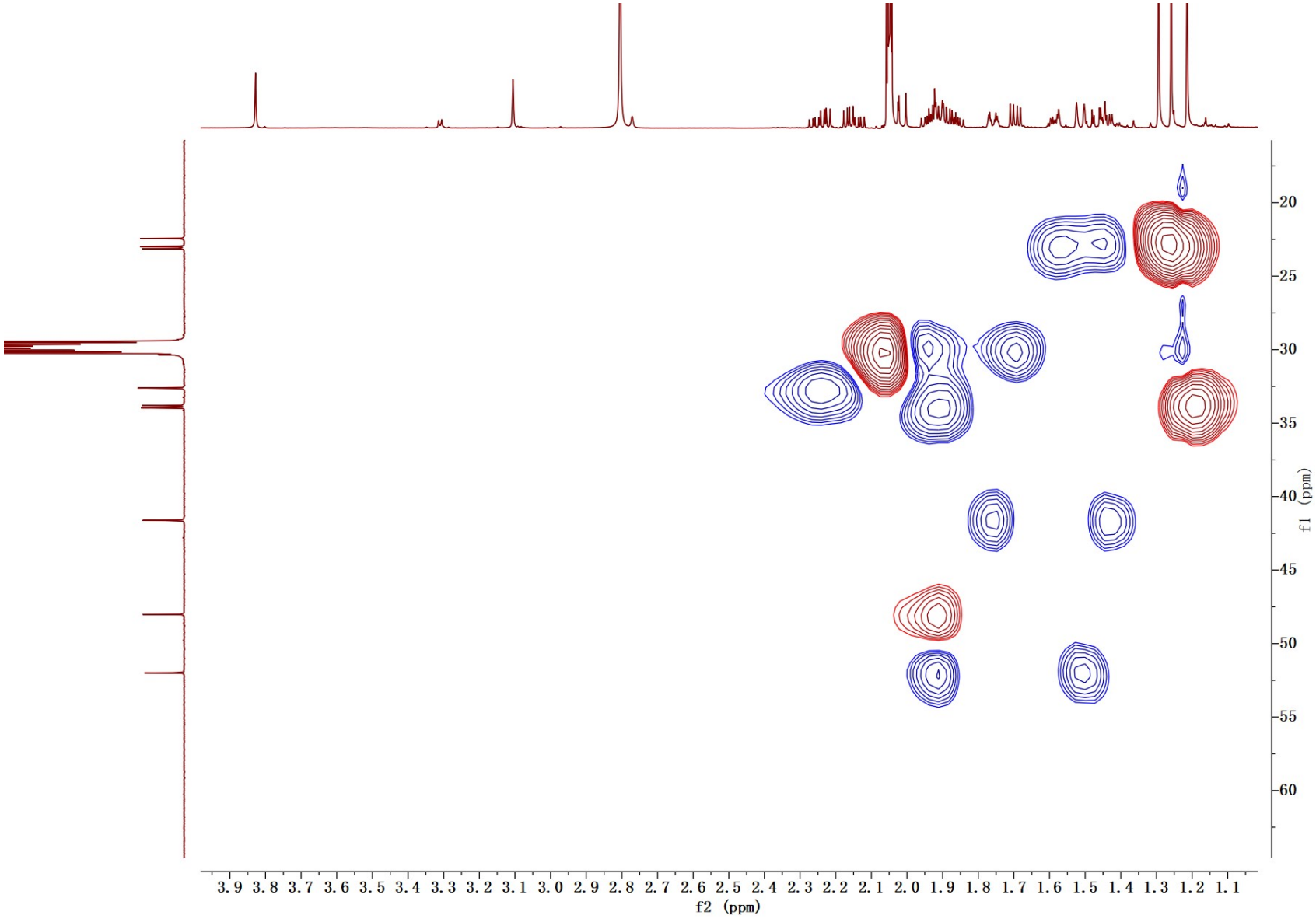

Figure S28. The HSQC spectrum of compound **3** in acetone-d_6.

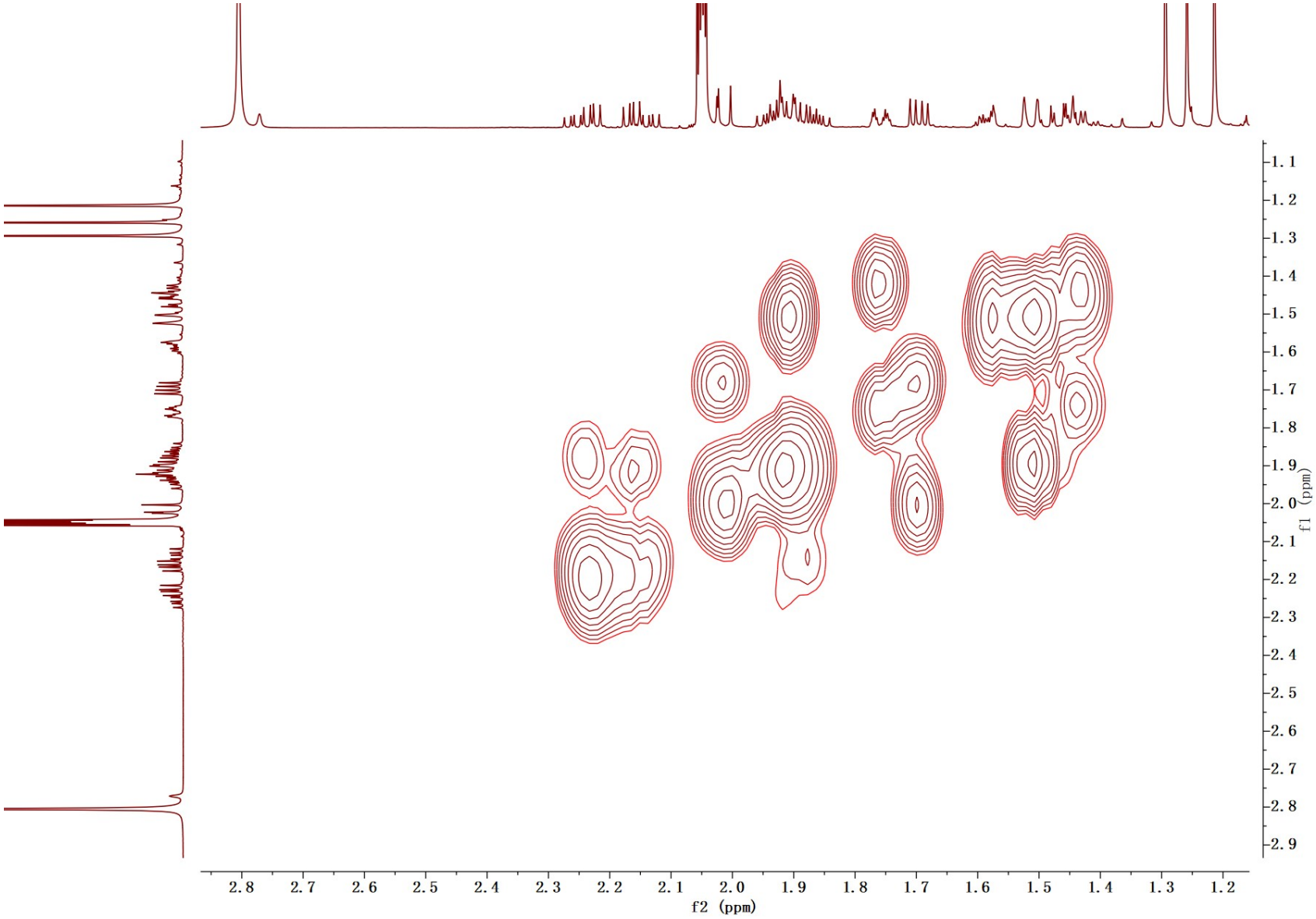

Figure S29. The ^{1}H-^{1}H COSY spectrum of compound **3** in acetone-d_6.

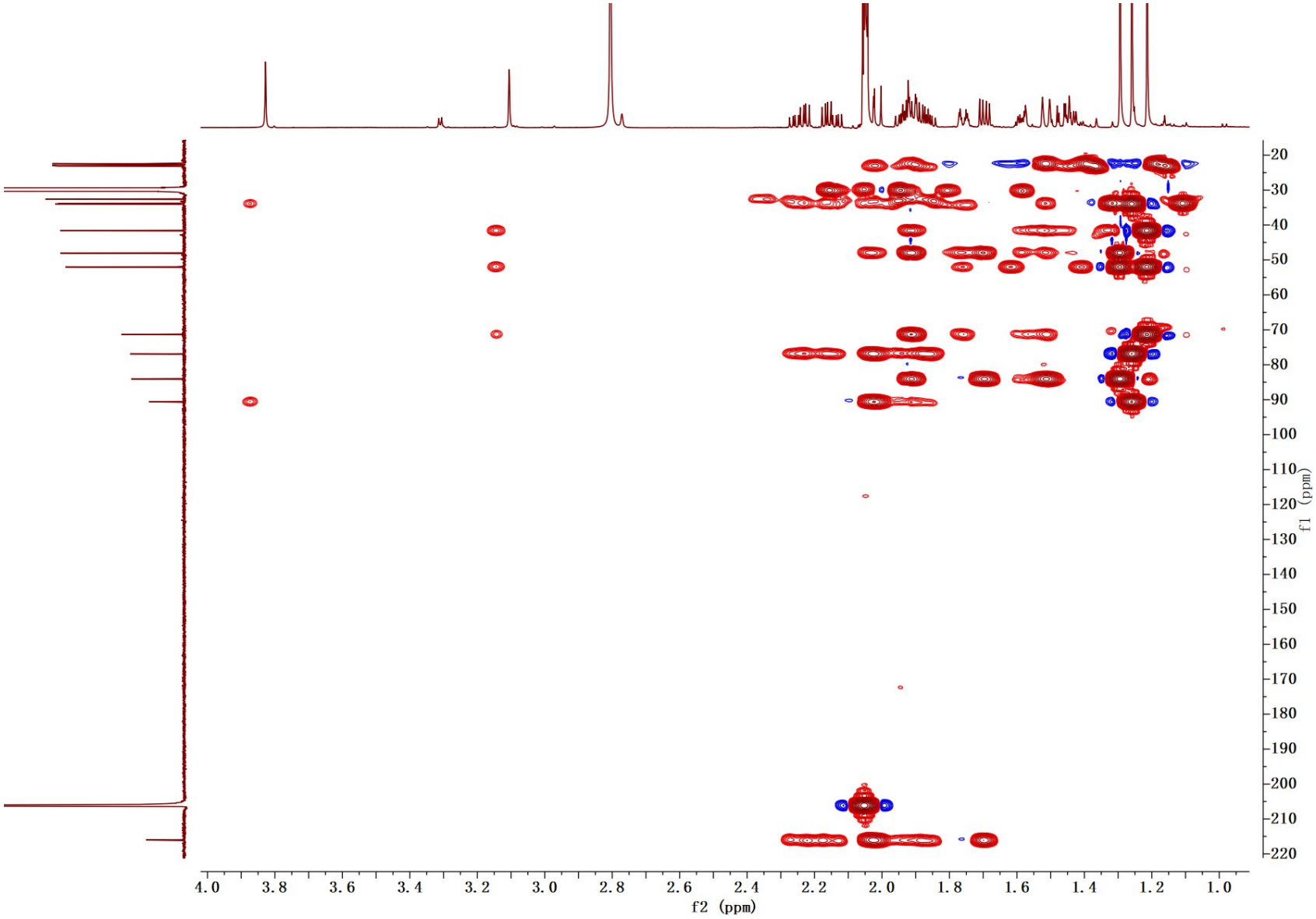

Figure S30. The HMBC spectrum of compound **3** in acetone-d_6.

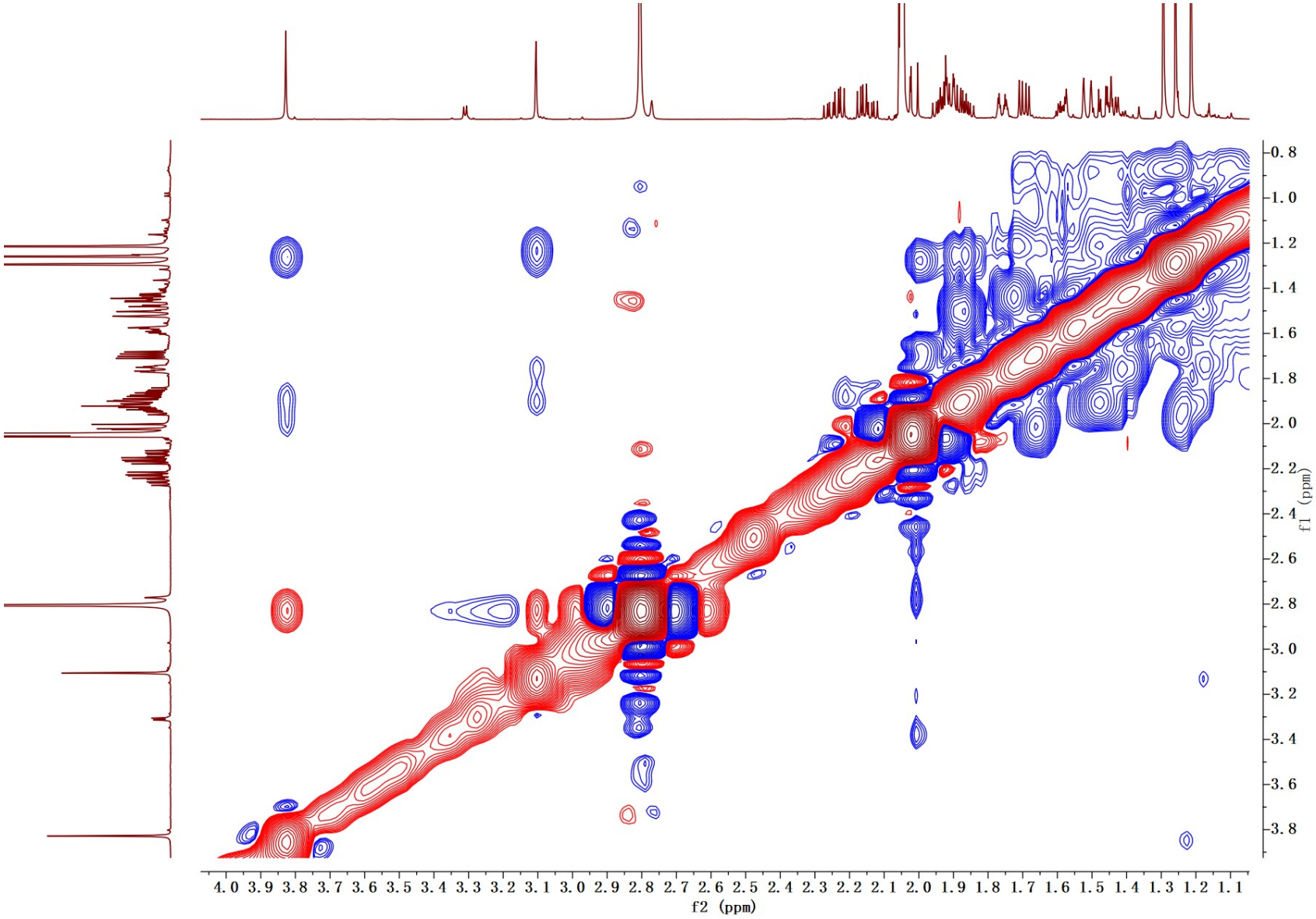

Figure S31. The NOESY spectrum of compound **3** in acetone-d_6.

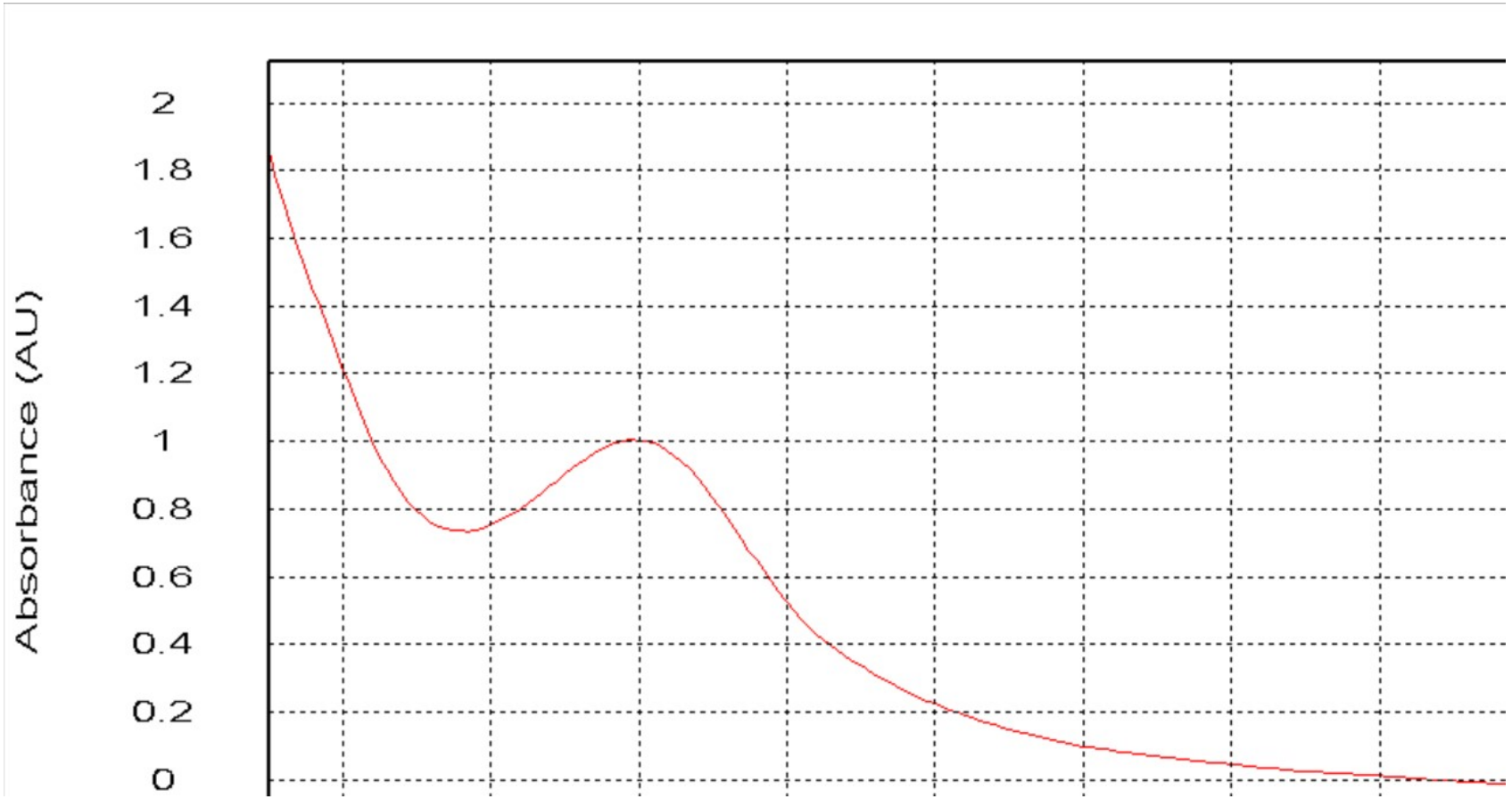

Figure S32. The UV spectrum of compound **4** in acetonitrile.

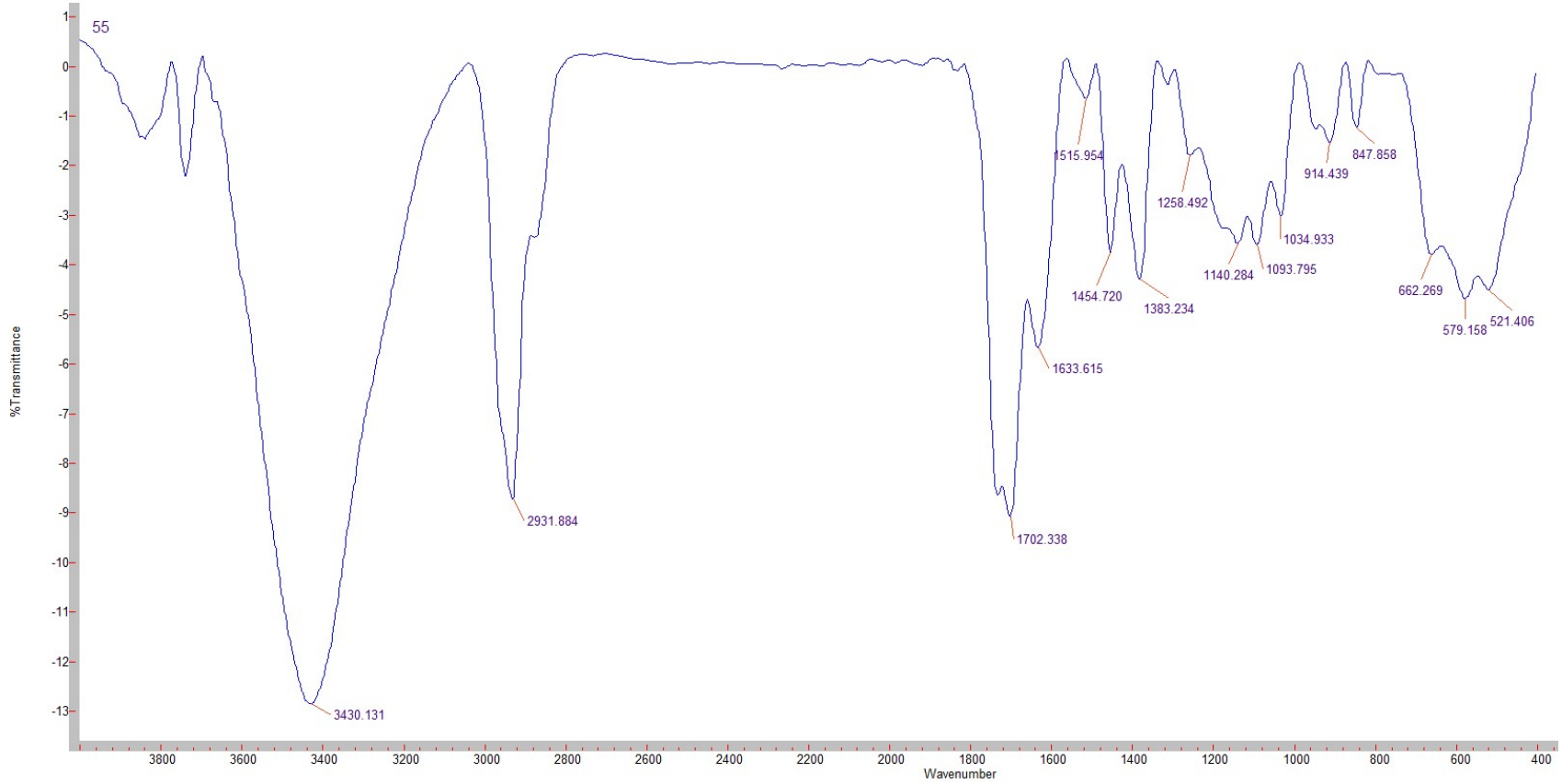

Figure S33. The IR spectrum of compound **4**.

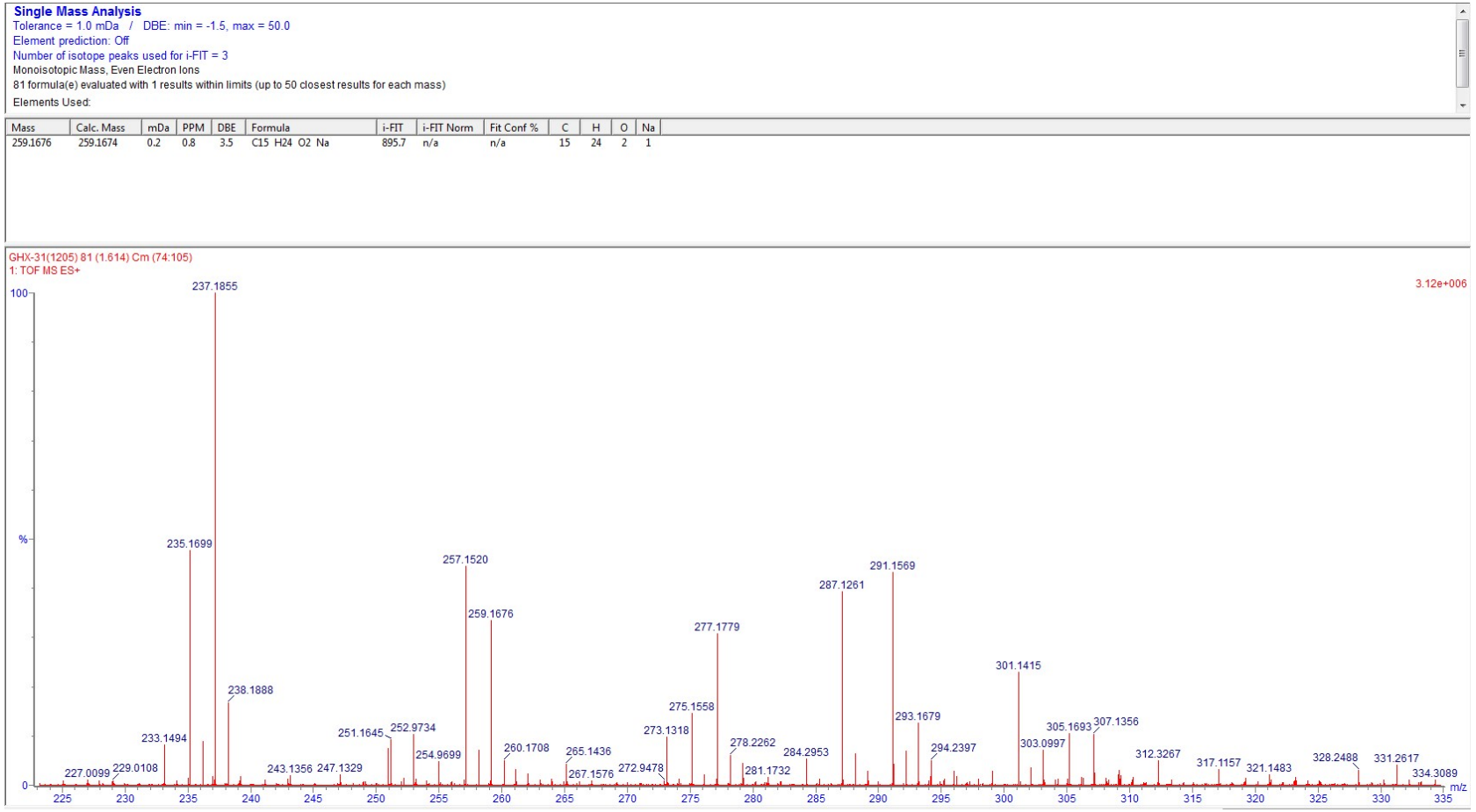

Figure S34. The (+)-HRESIMS spectroscopic data of compound **4**.

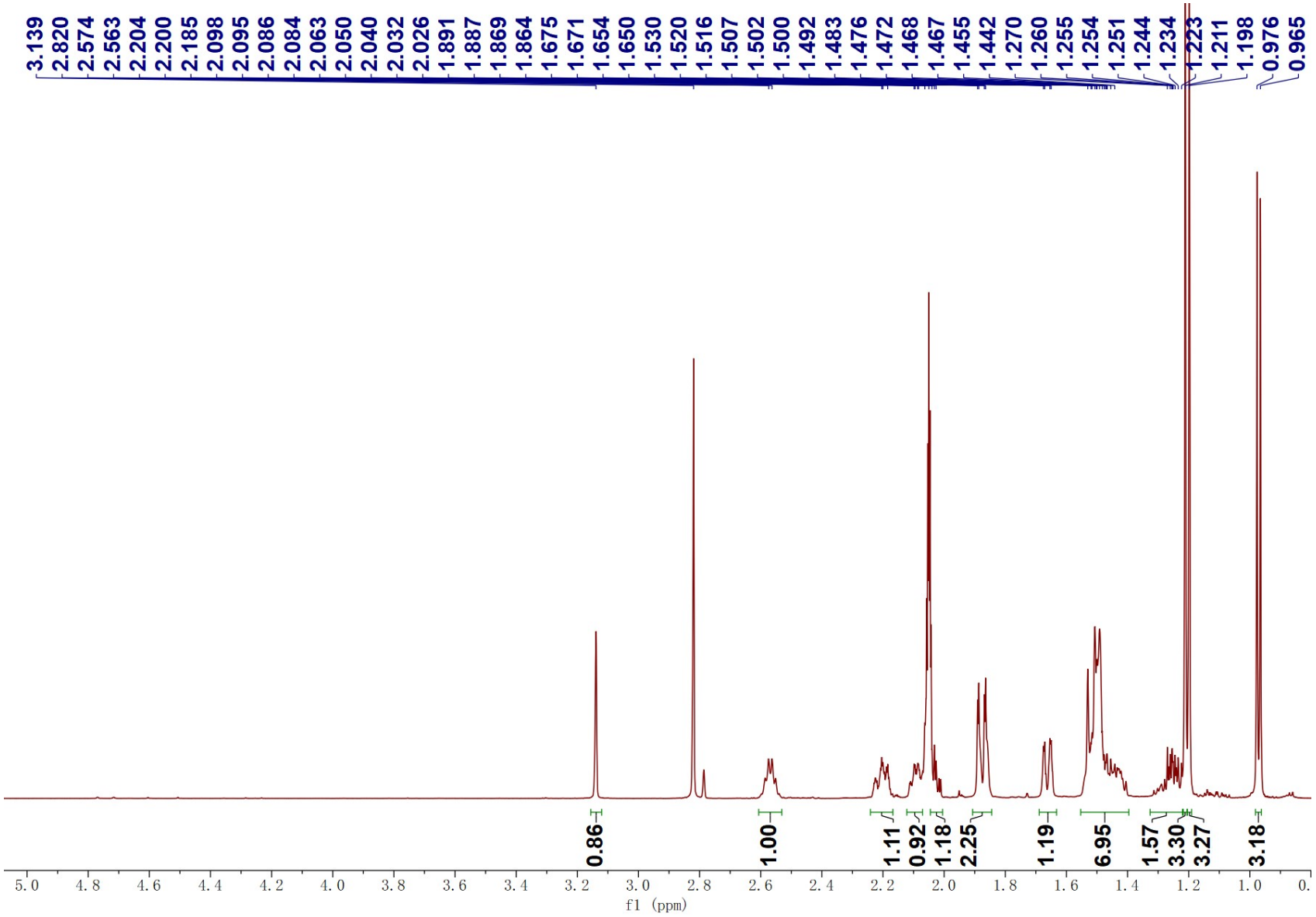

Figure S35. The ^{1}H NMR spectrum of compound **4** in acetone-d_6.

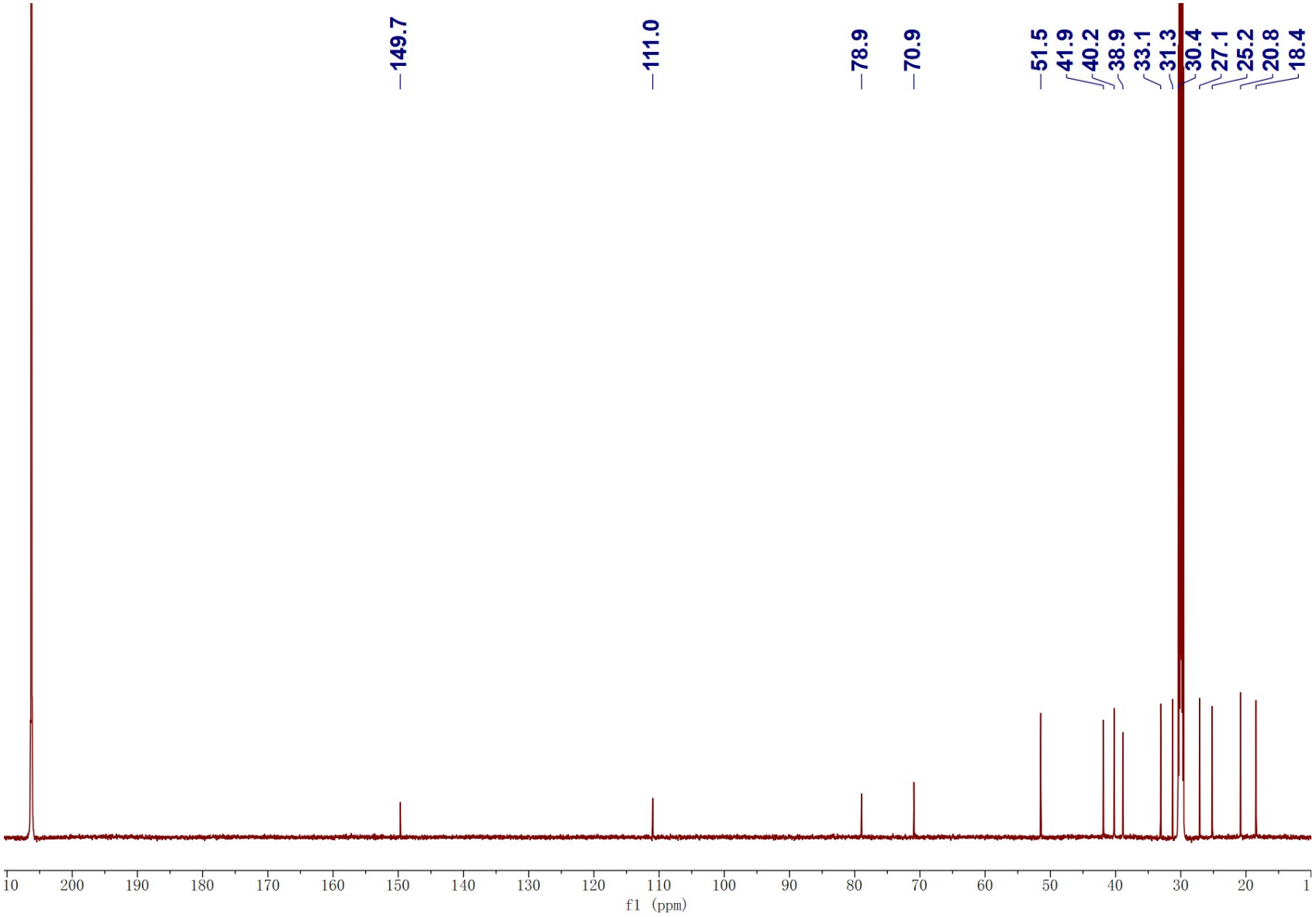

Figure S36. The ^{13}C NMR spectrum of compound **4** in acetone-d_6.

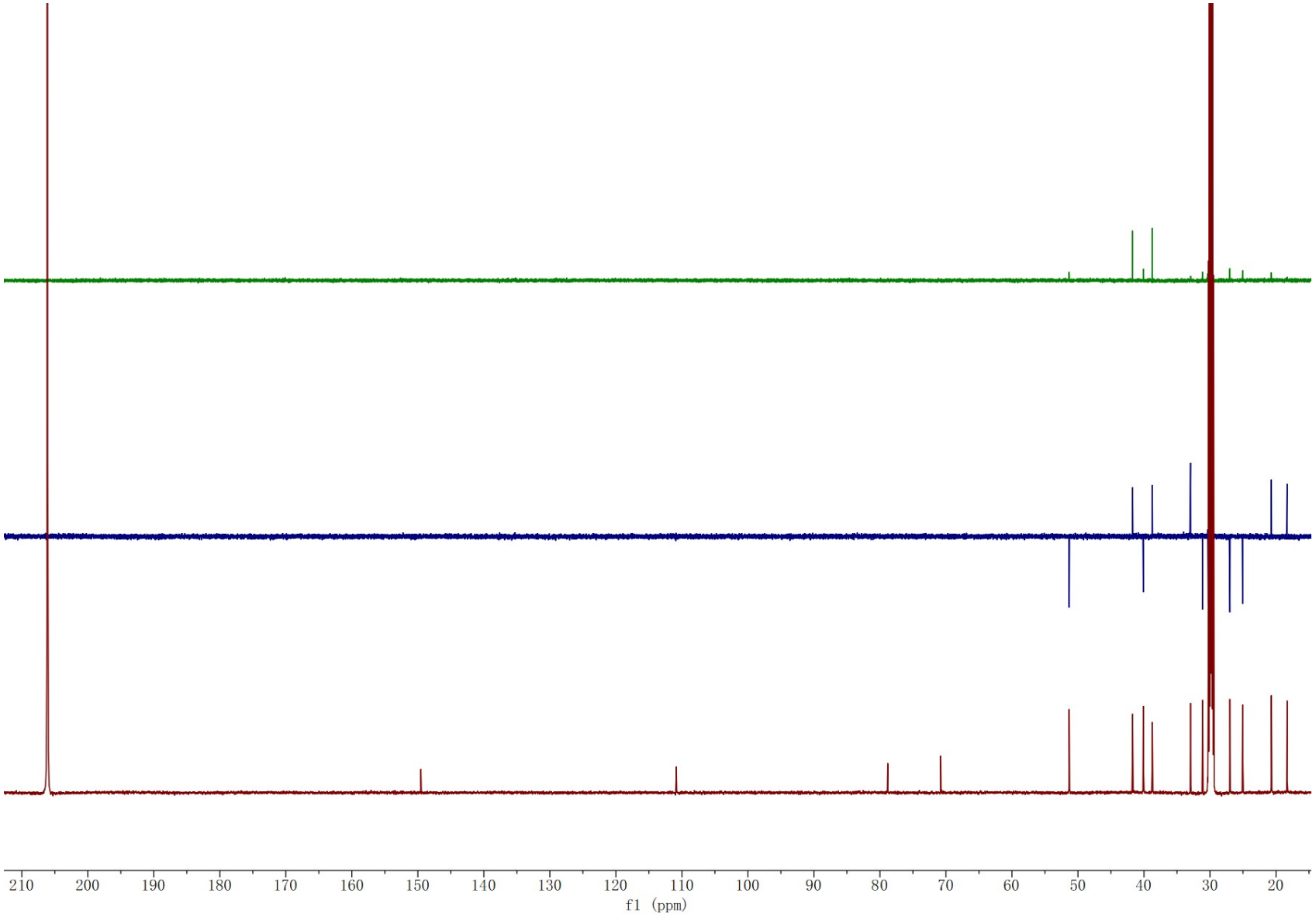

Figure S37. The DEPT spectrum of compound **4** in acetone-d_6.

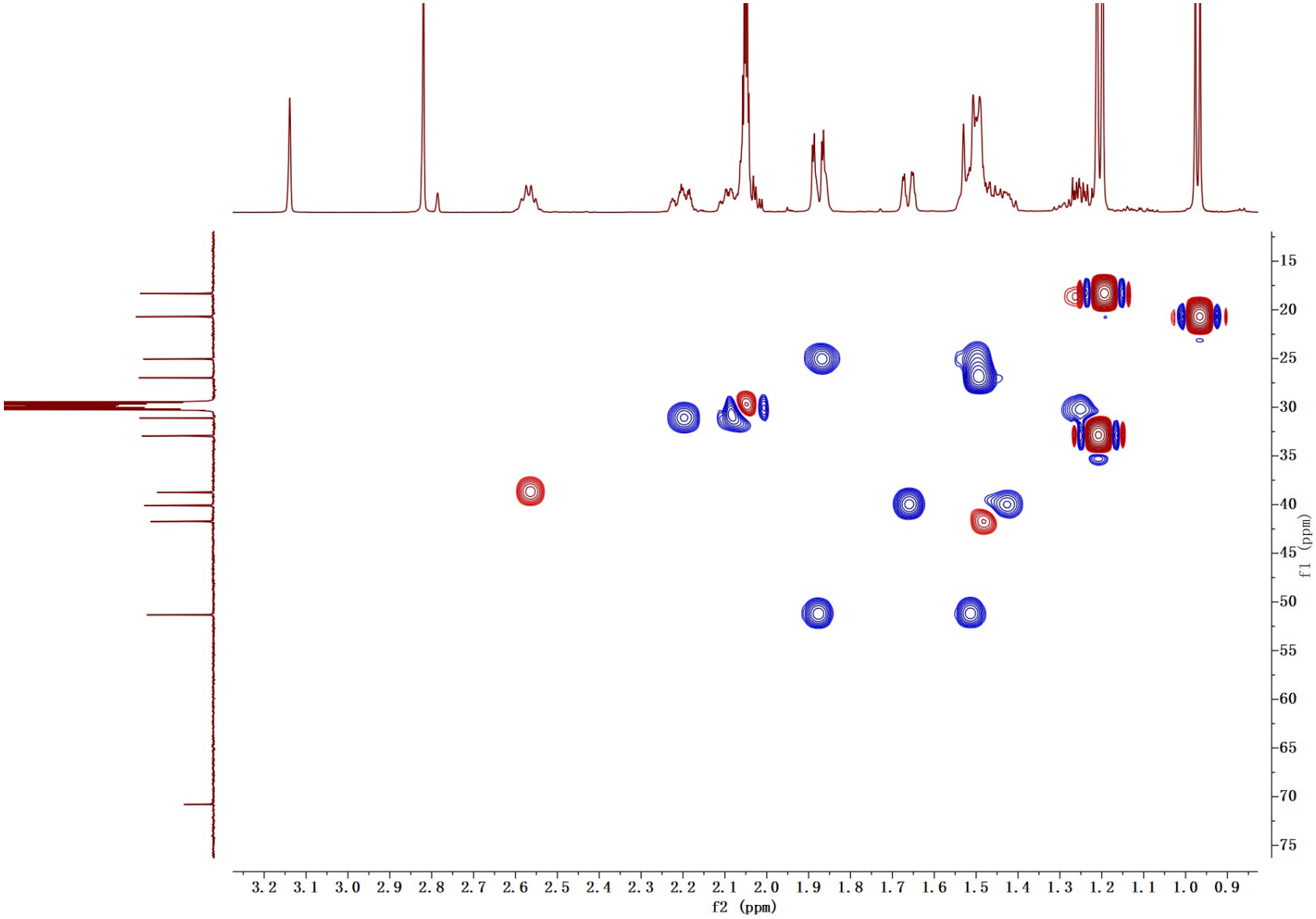

Figure S38. The HSQC spectrum of compound **4** in acetone-d_6.

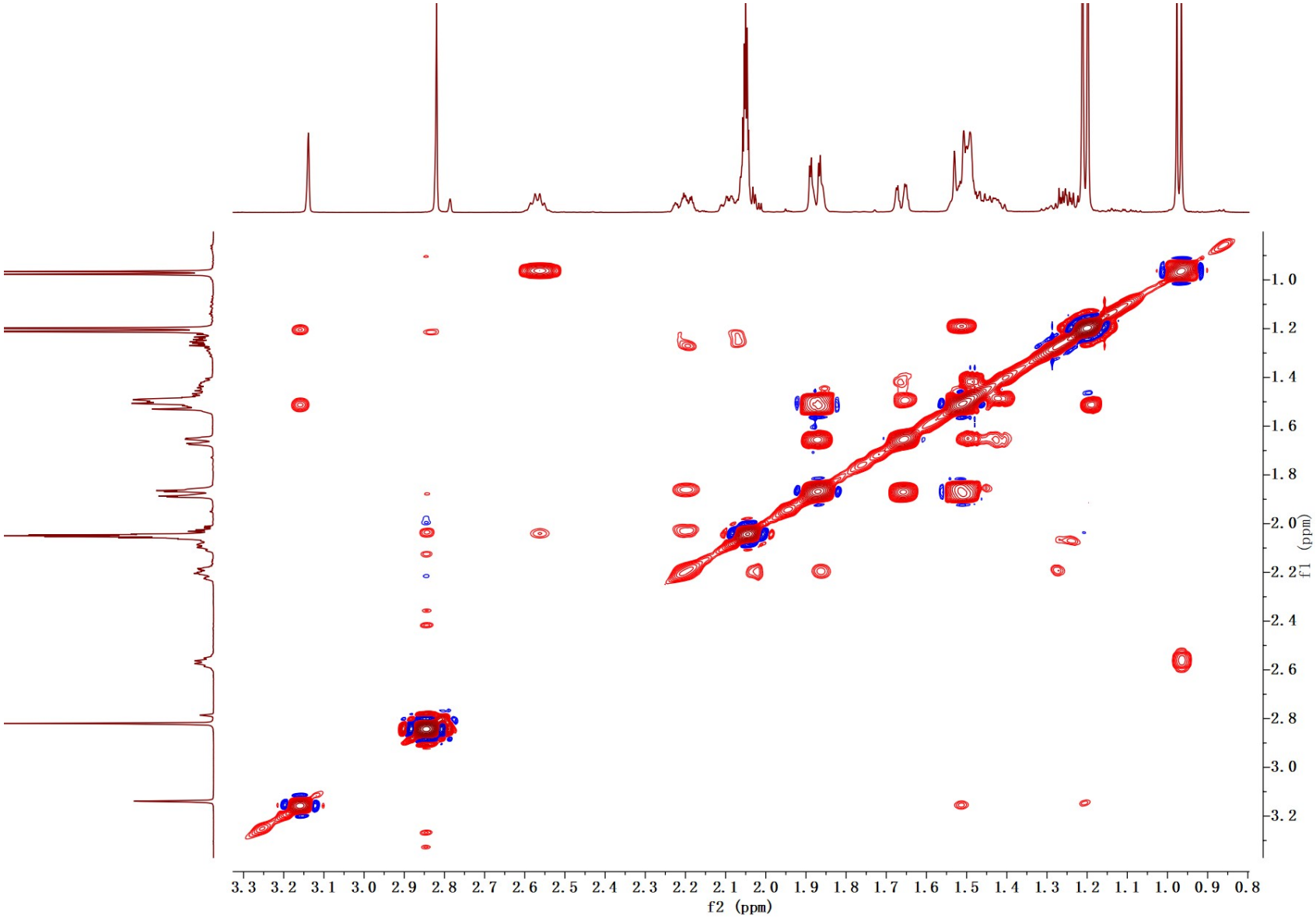

Figure S39. The ^{1}H-^{1}H COSY spectrum of compound **4** in acetone-d_6.

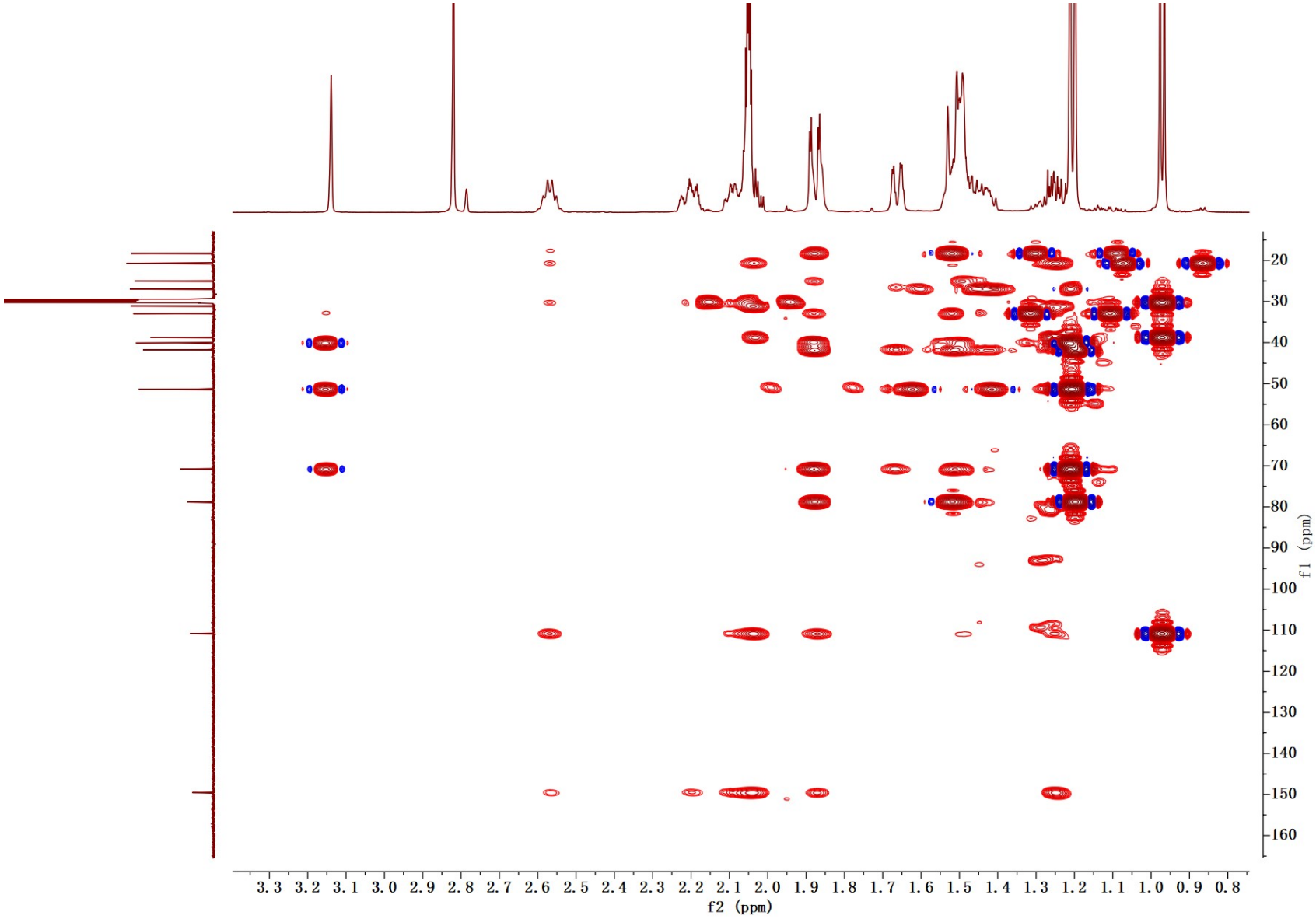

Figure S40. The HMBC spectrum of compound **4** in acetone-d_6.

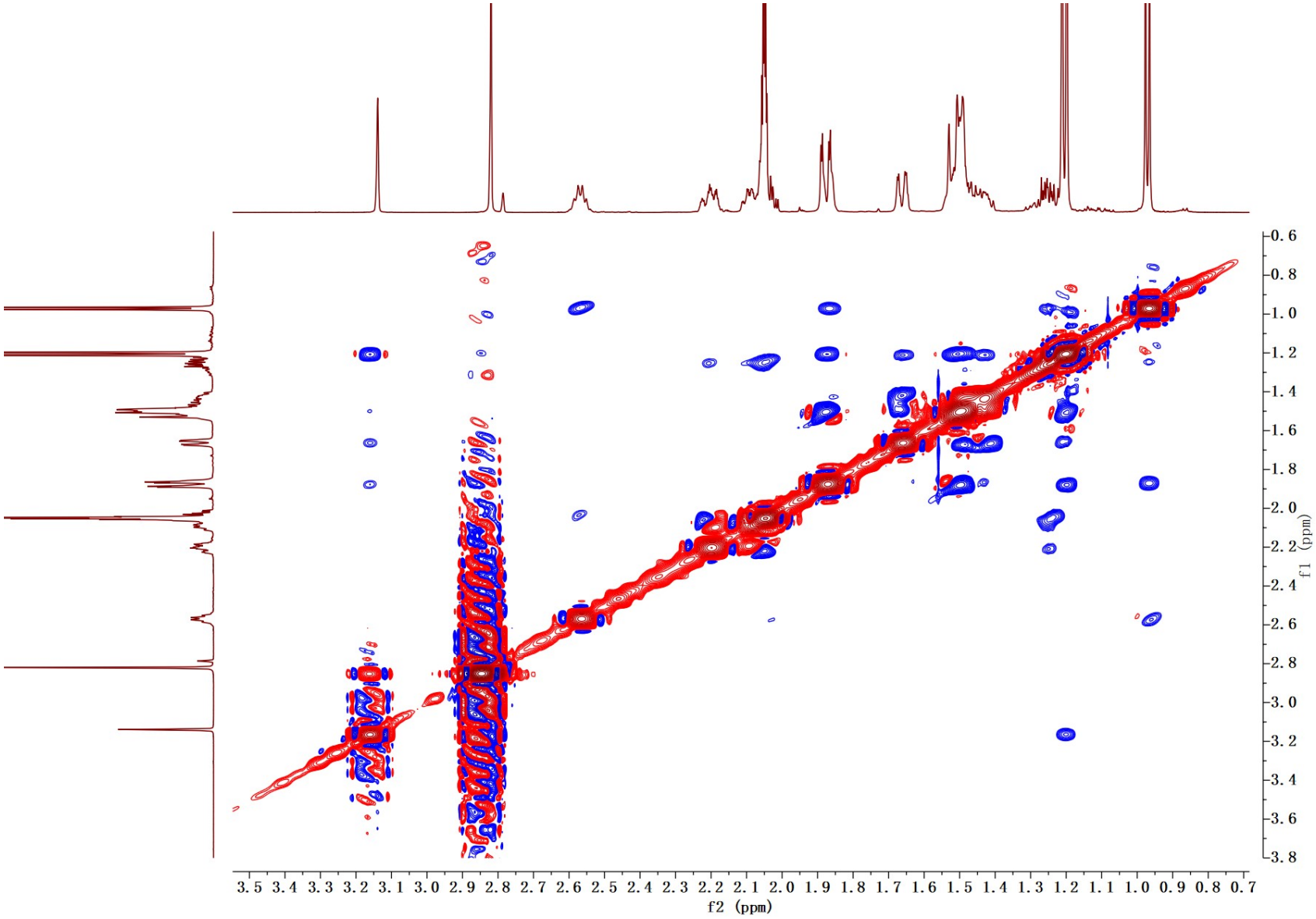

Figure S41. The NOESY spectrum of compound **4** in acetone-d_6.

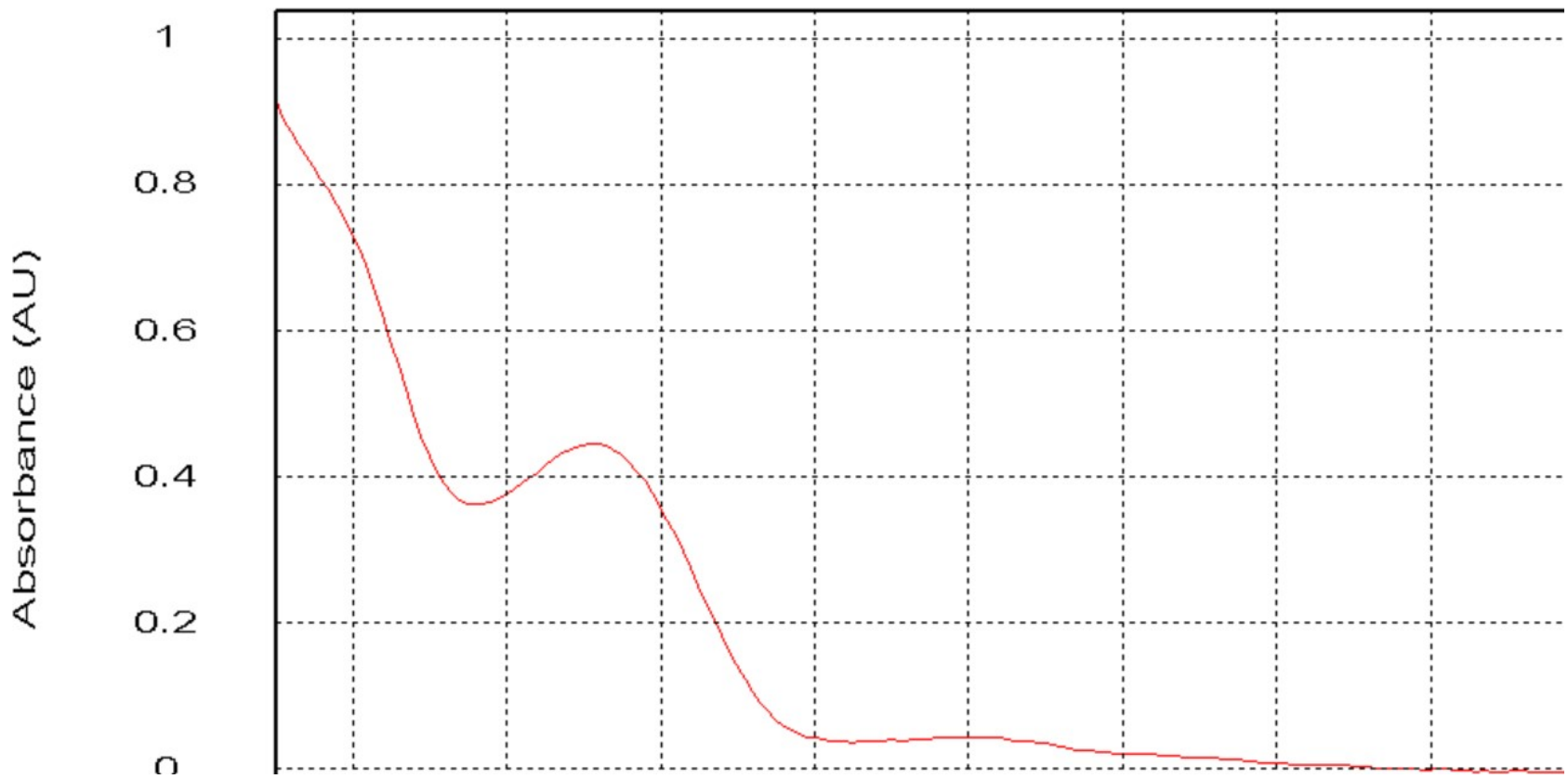

Figure S42. The UV spectrum of compound **5** in acetonitrile.

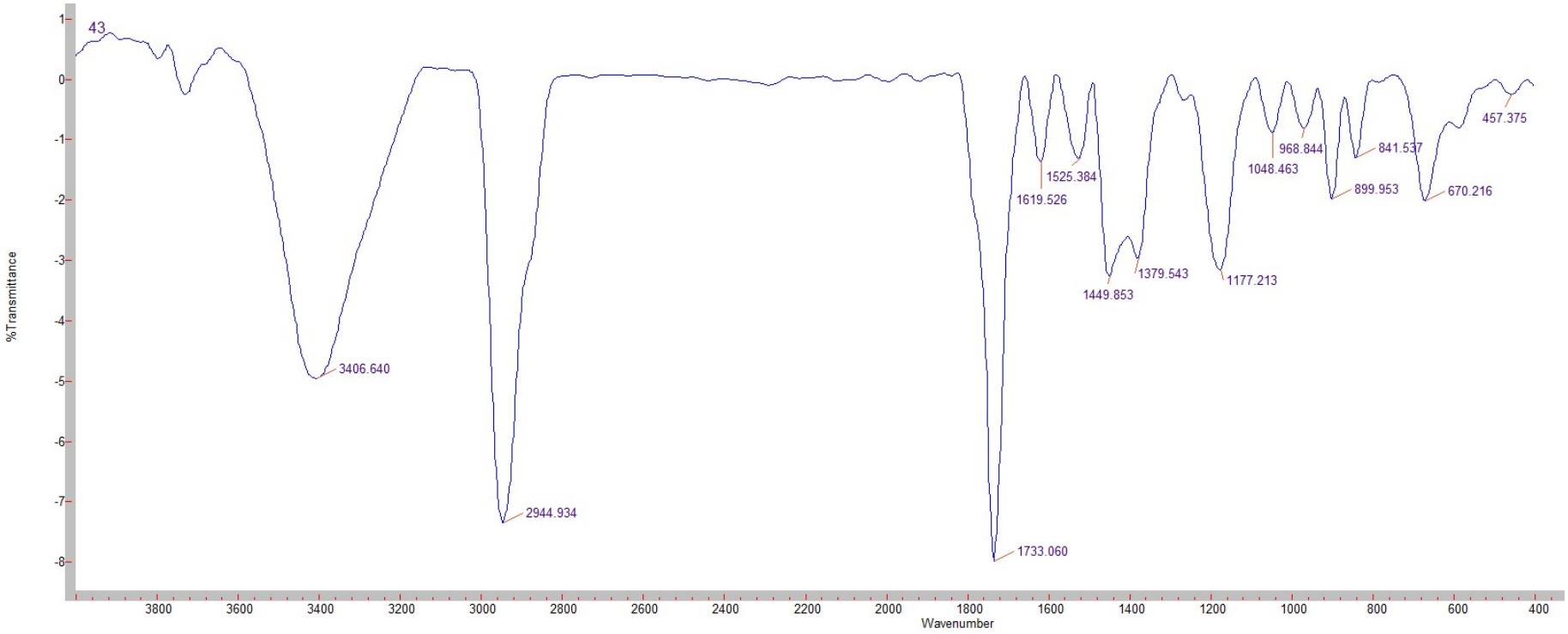

Figure S43. The IR spectrum of compound **5**.

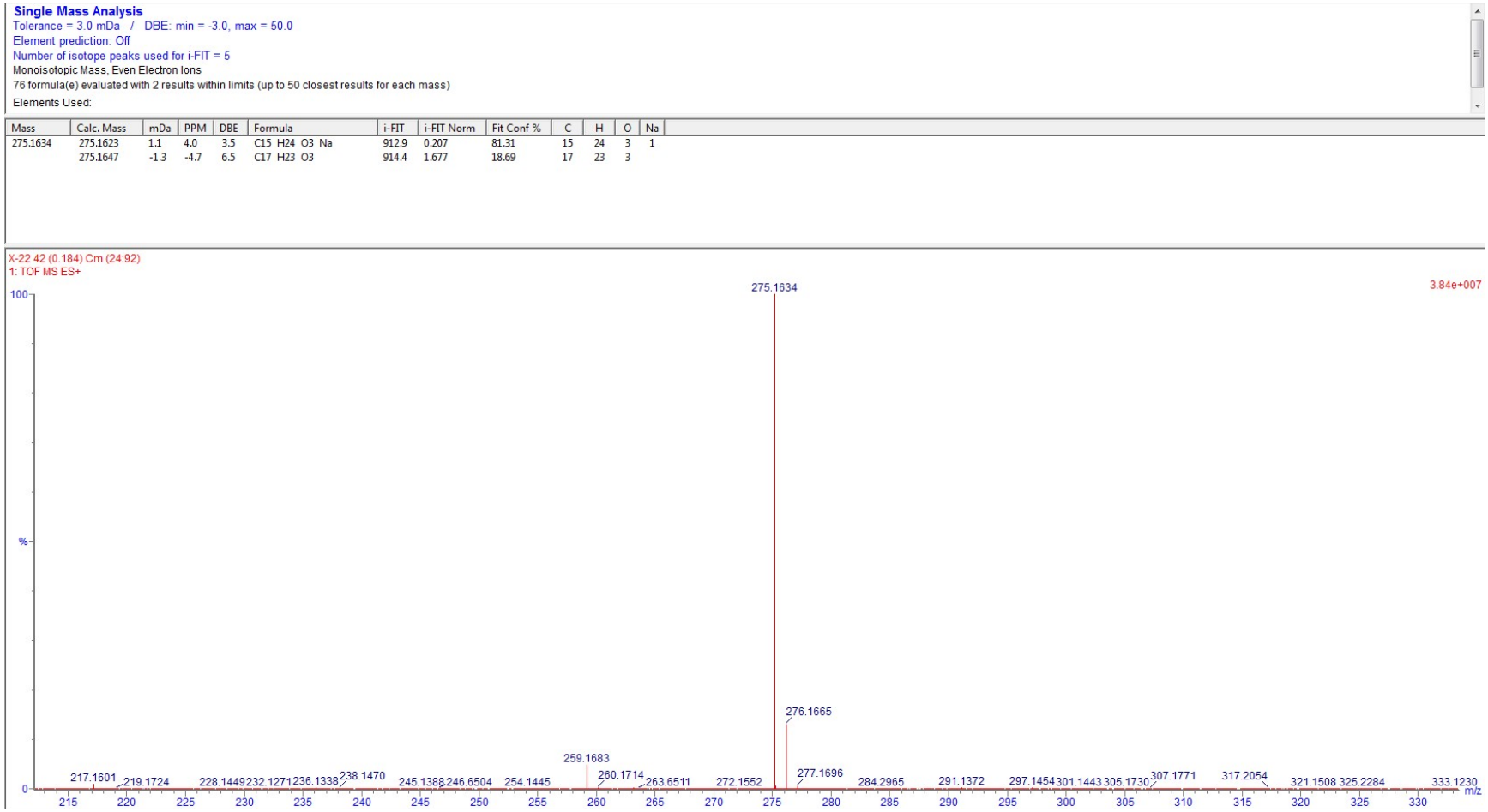

Figure S44. The (+)-HRESIMS spectroscopic data of compound **5**.

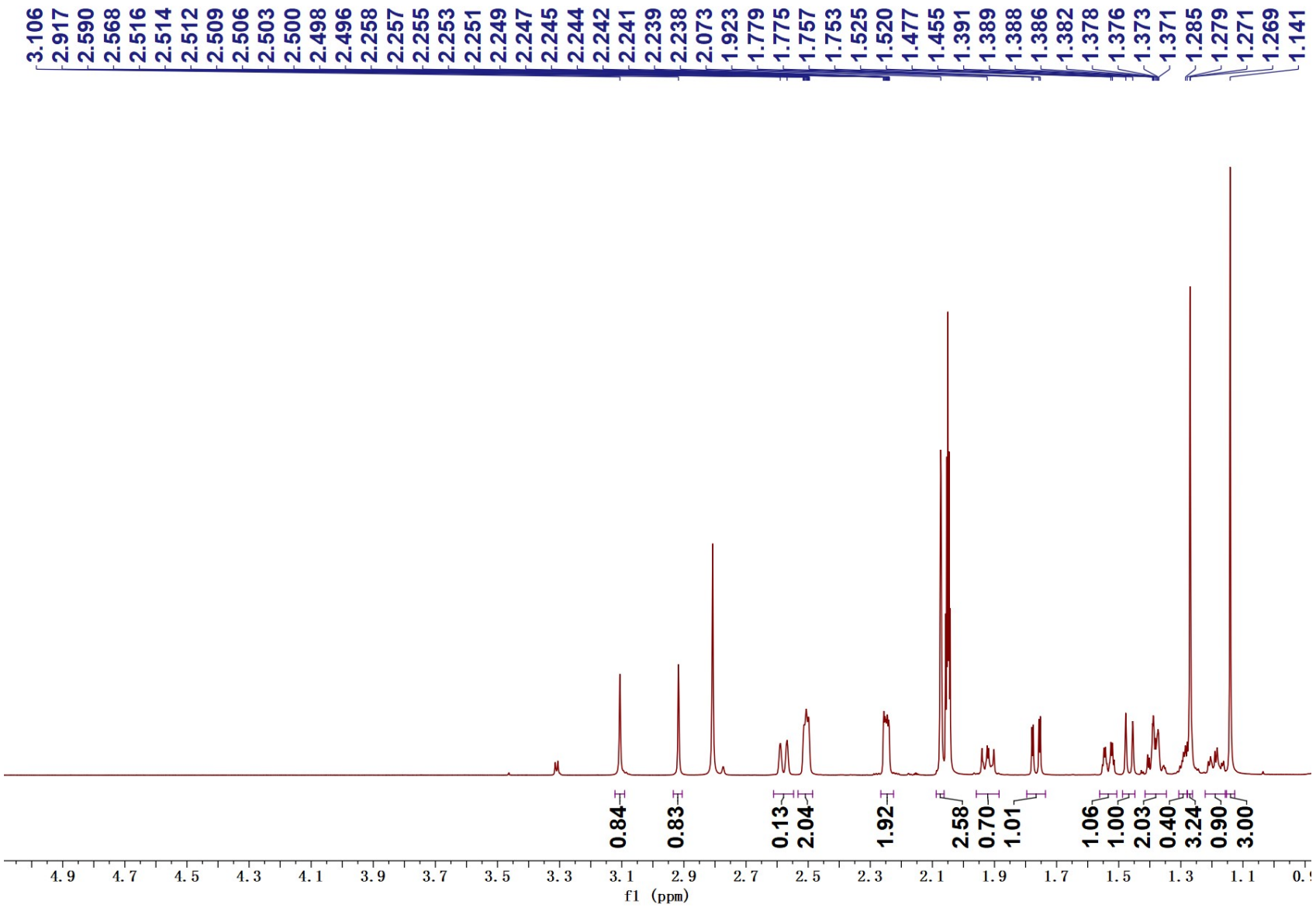

Figure S45. The ^{1}H NMR spectrum of compound **5** in acetone-d_6.

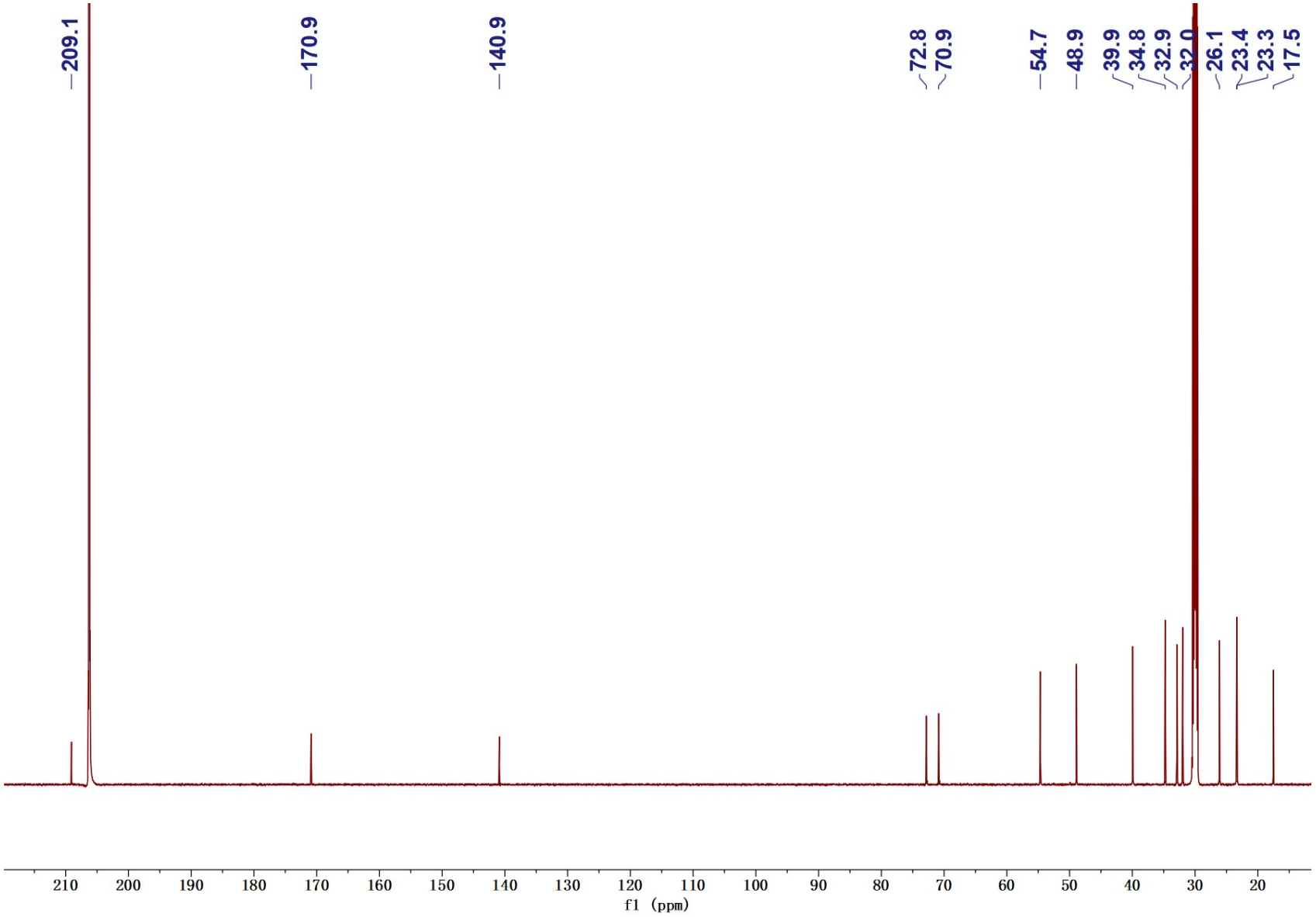

Figure S46. The ^{13}C NMR spectrum of compound **5** in acetone-d_6.

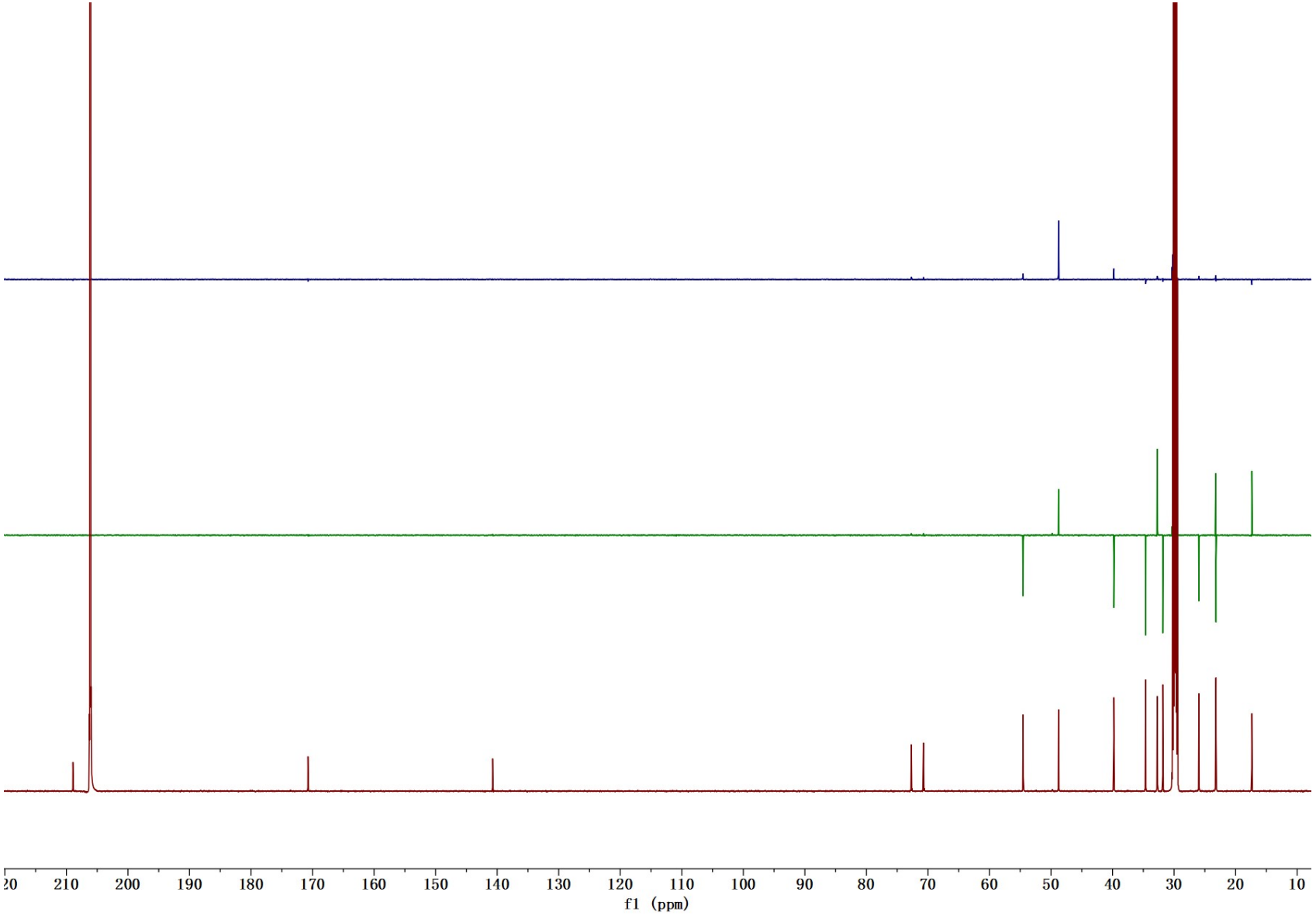

Figure S47. The DEPT spectrum of compound **5** in acetone-d_6.

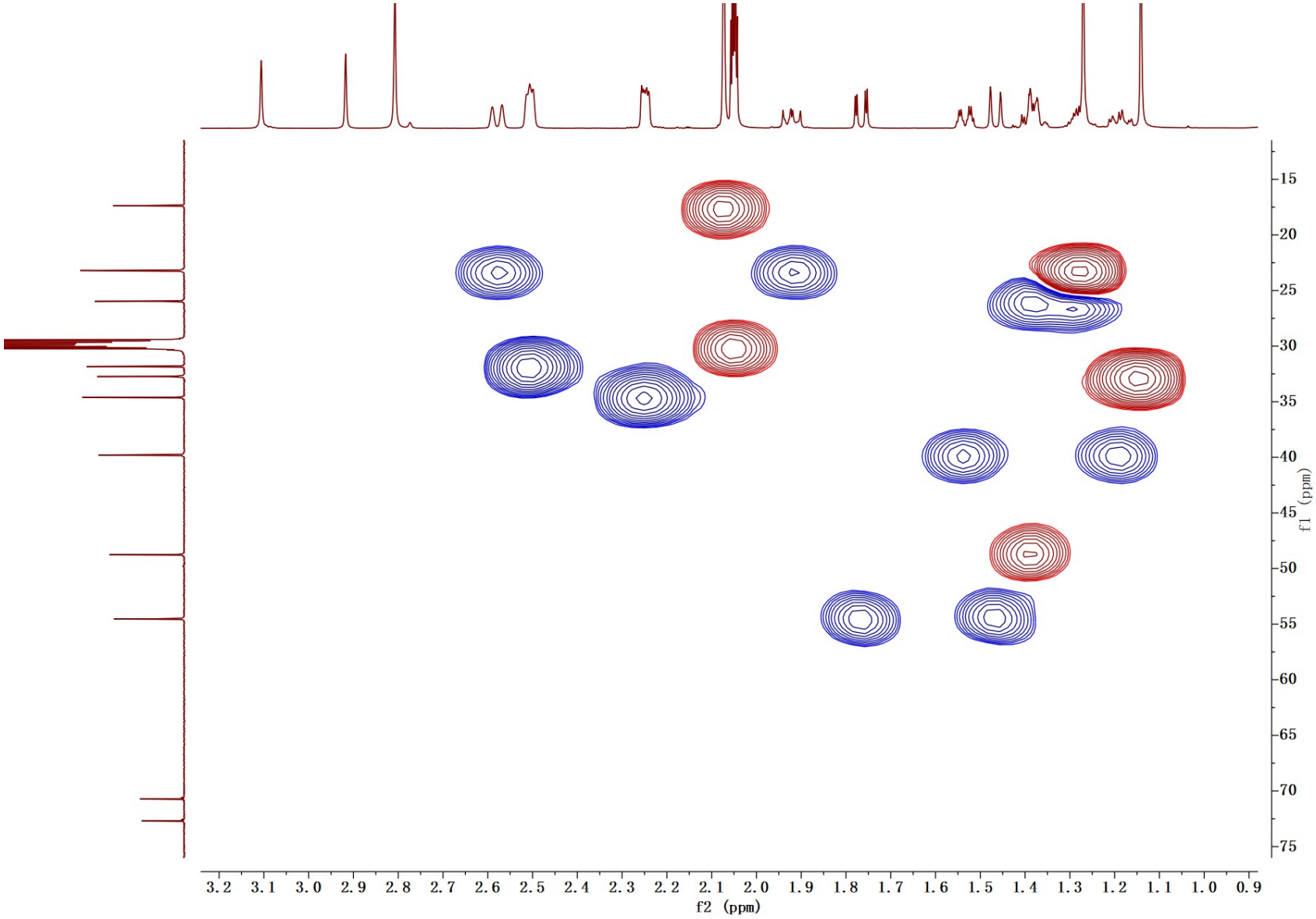

Figure S48. The HSQC spectrum of compound **5** in acetone-d_6.

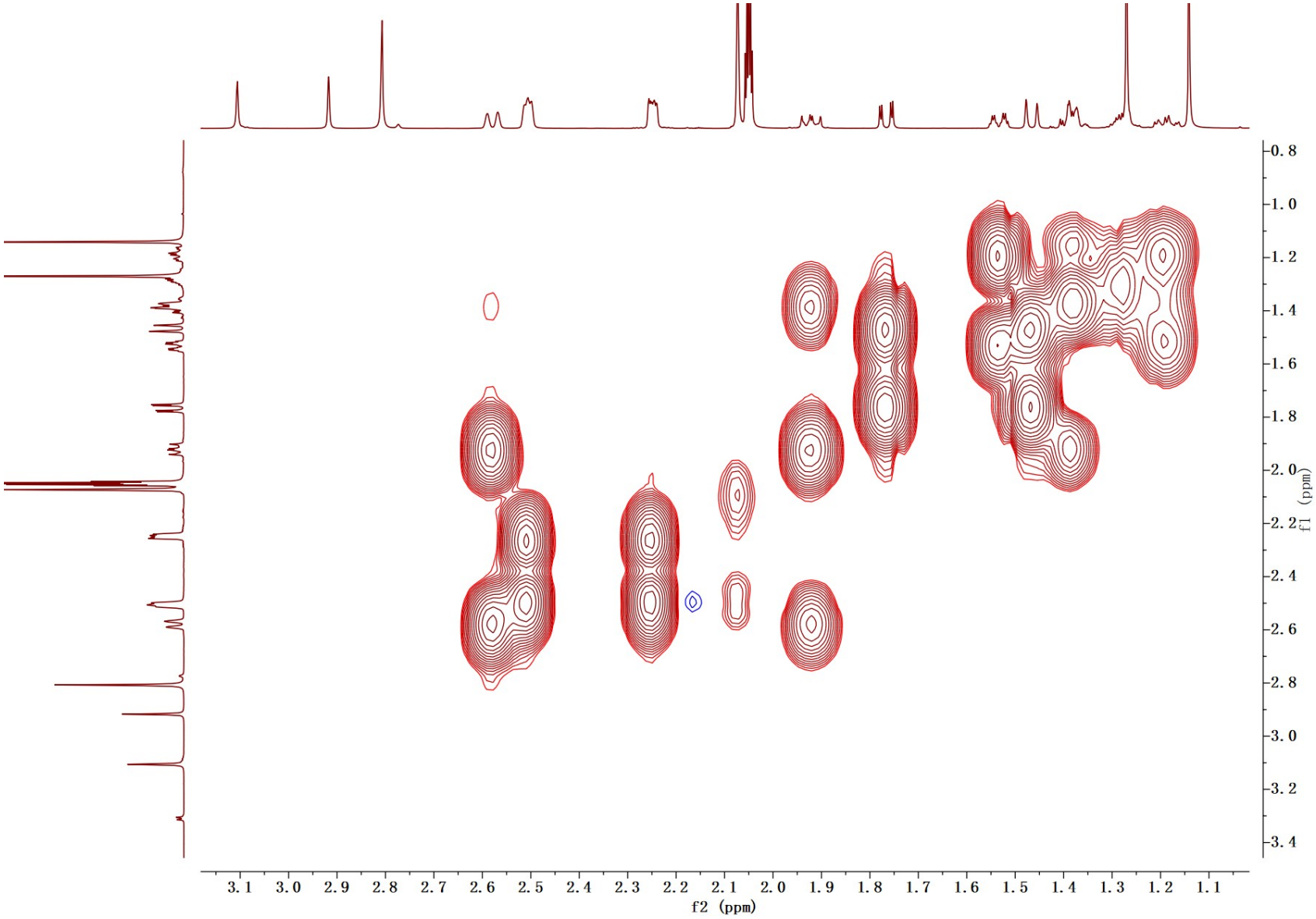

Figure S49. The ^{1}H-^{1}H COSY spectrum of compound **5** in acetone-d_6.

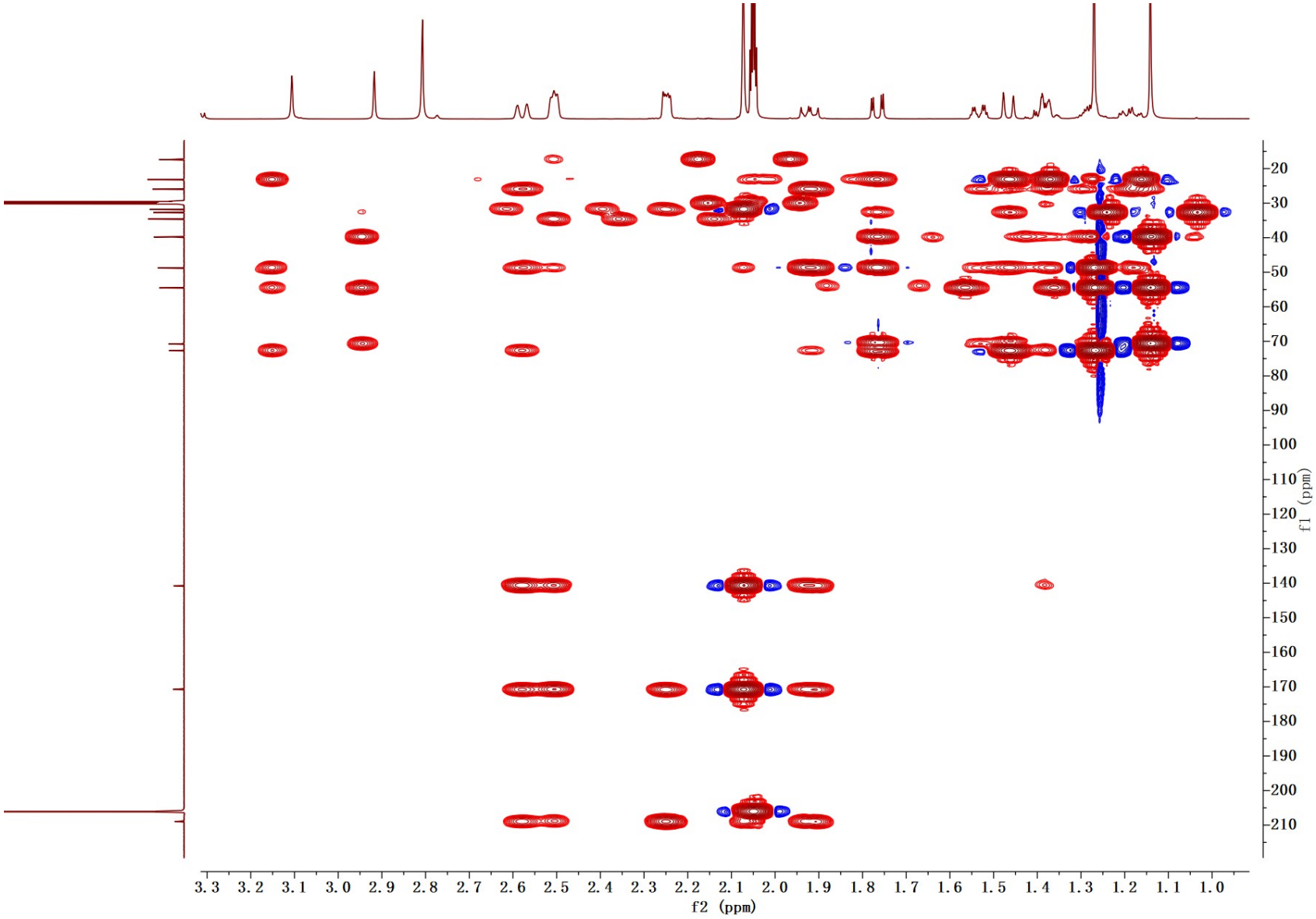

Figure S50. The HMBC spectrum of compound **5** in acetone-d_6.

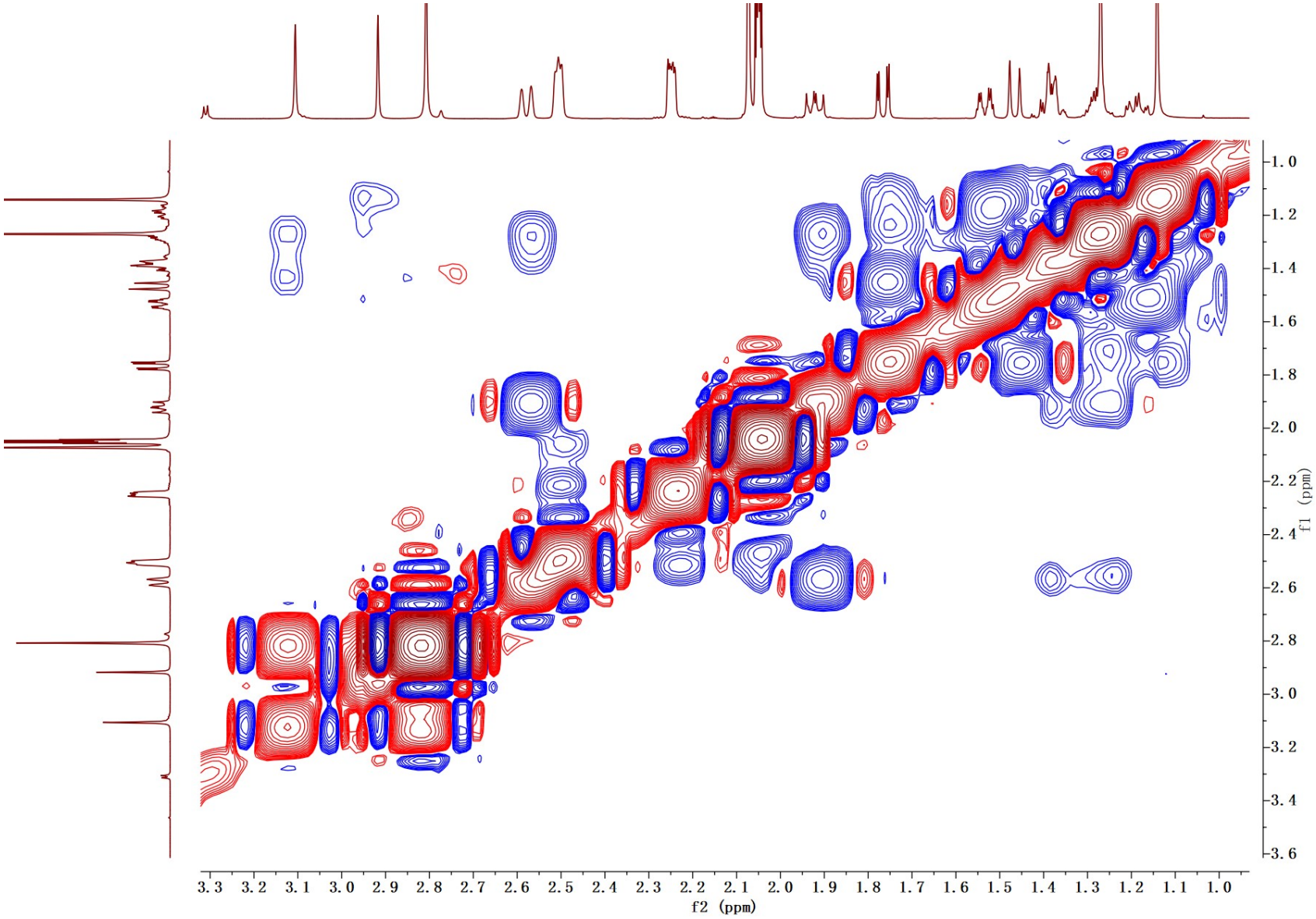

Figure S51. The NOESY spectrum of compound **5** in acetone-d_6.

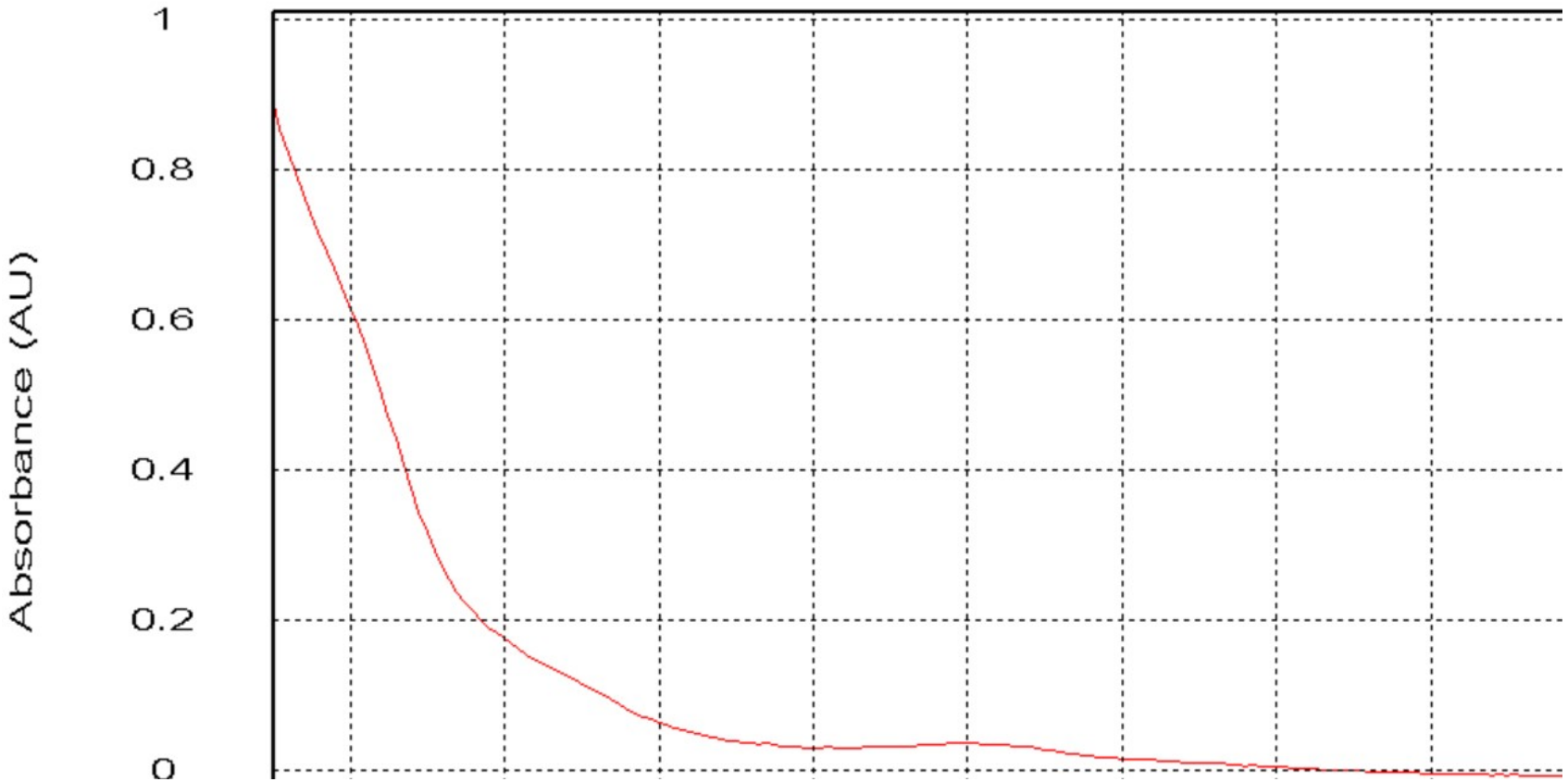

Figure S52. The UV spectrum of compound **6** in acetonitrile.

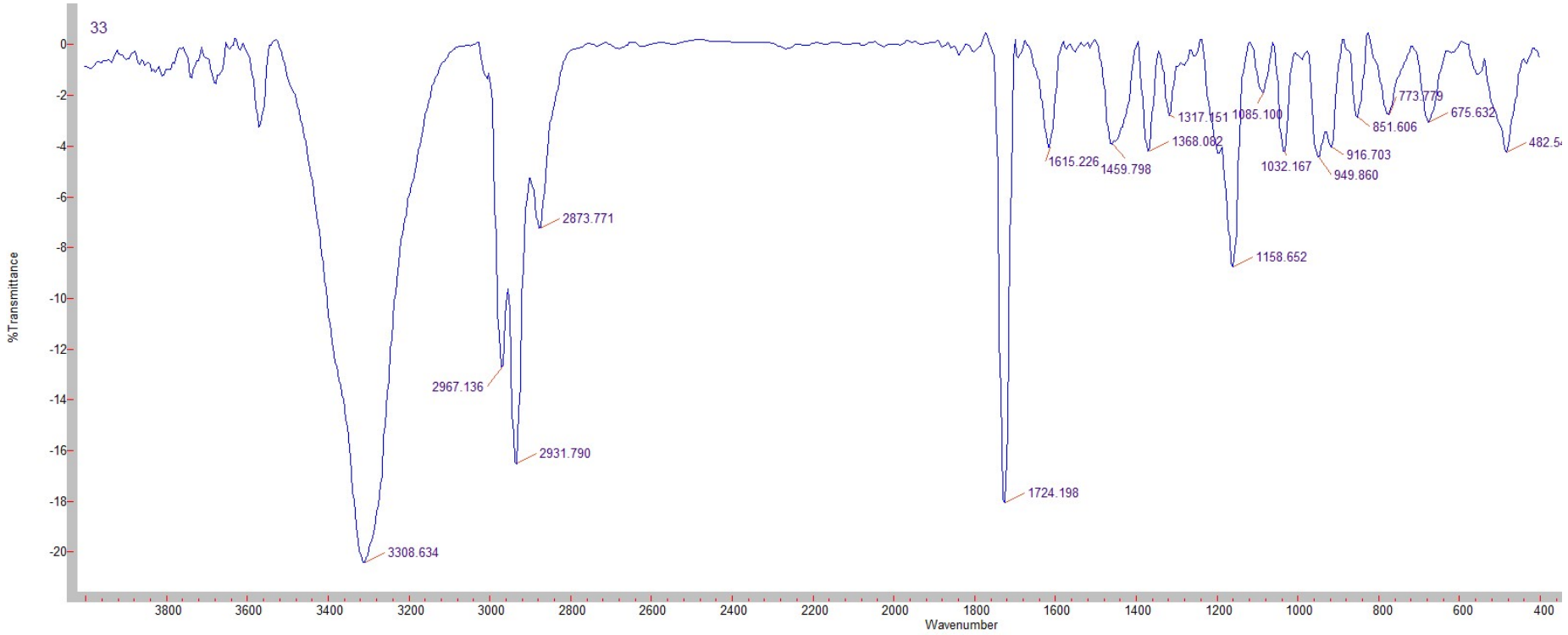

Figure S53. The IR spectrum of compound **6**.

Figure S54. The (+)-HRESIMS spectroscopic data of compound **6**.

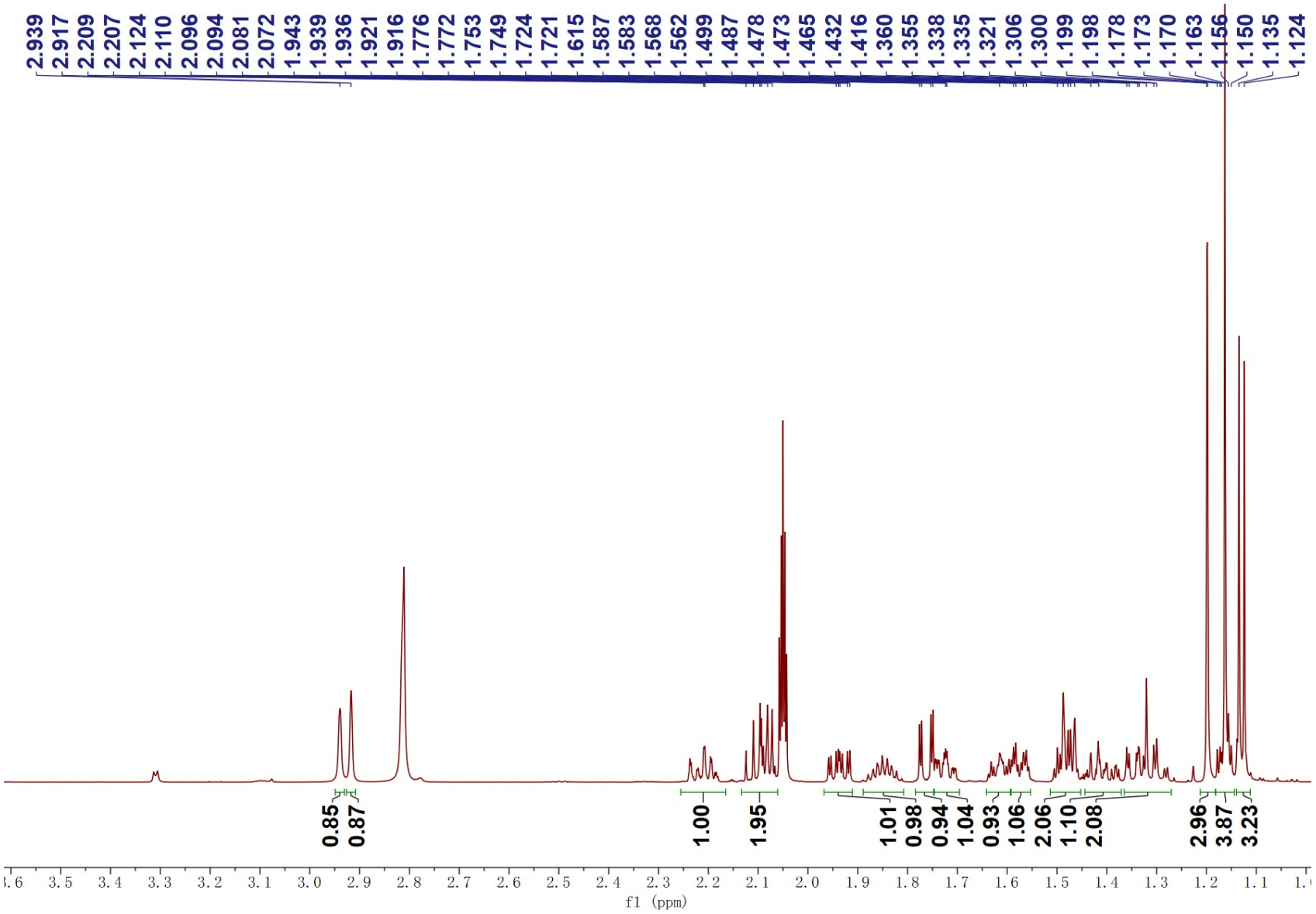

Figure S55. The ^{1}H NMR spectrum of compound **6** in acetone-d_6.

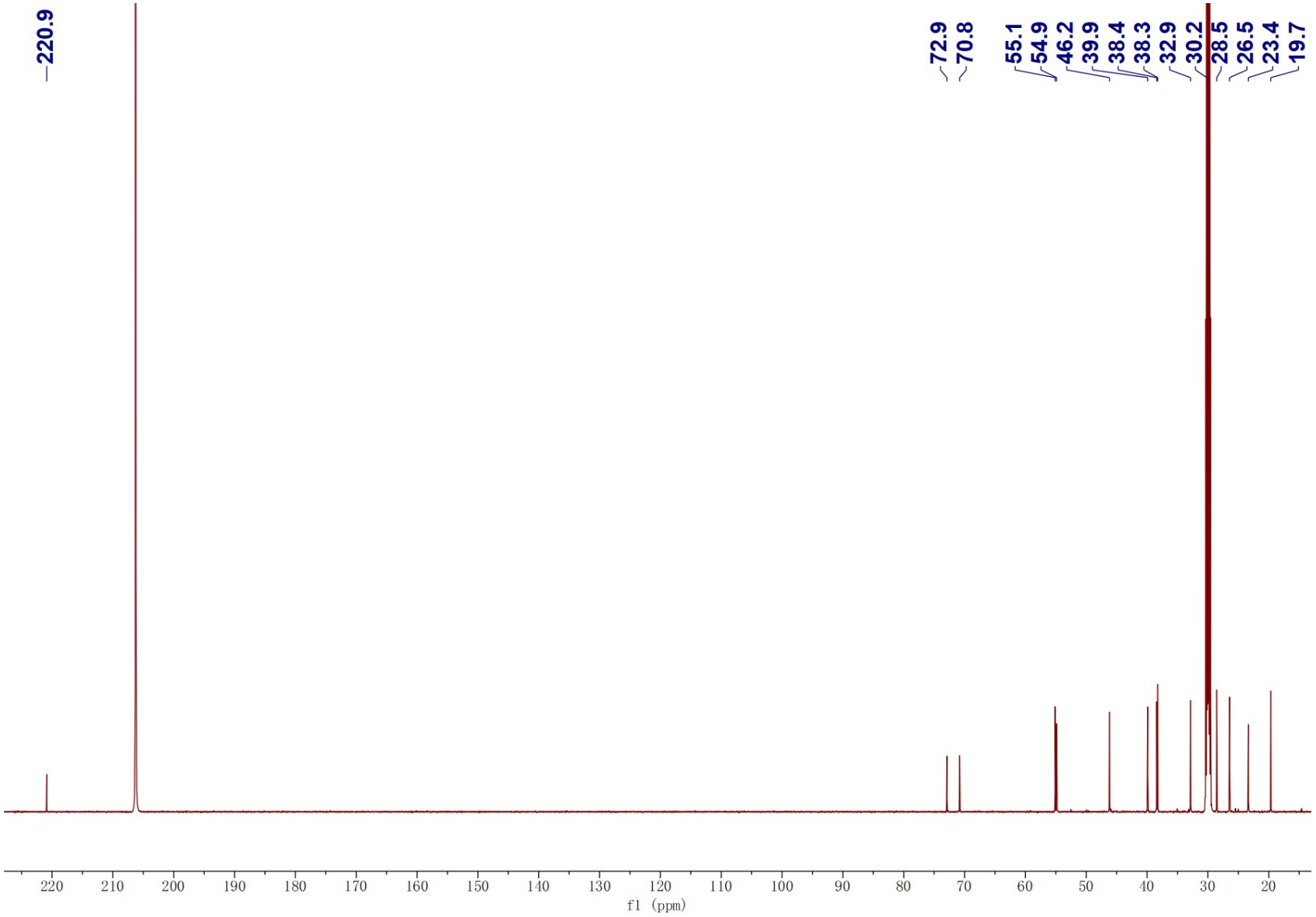

Figure S56. The ^{13}C NMR spectrum of compound **6** in acetone-d_6.

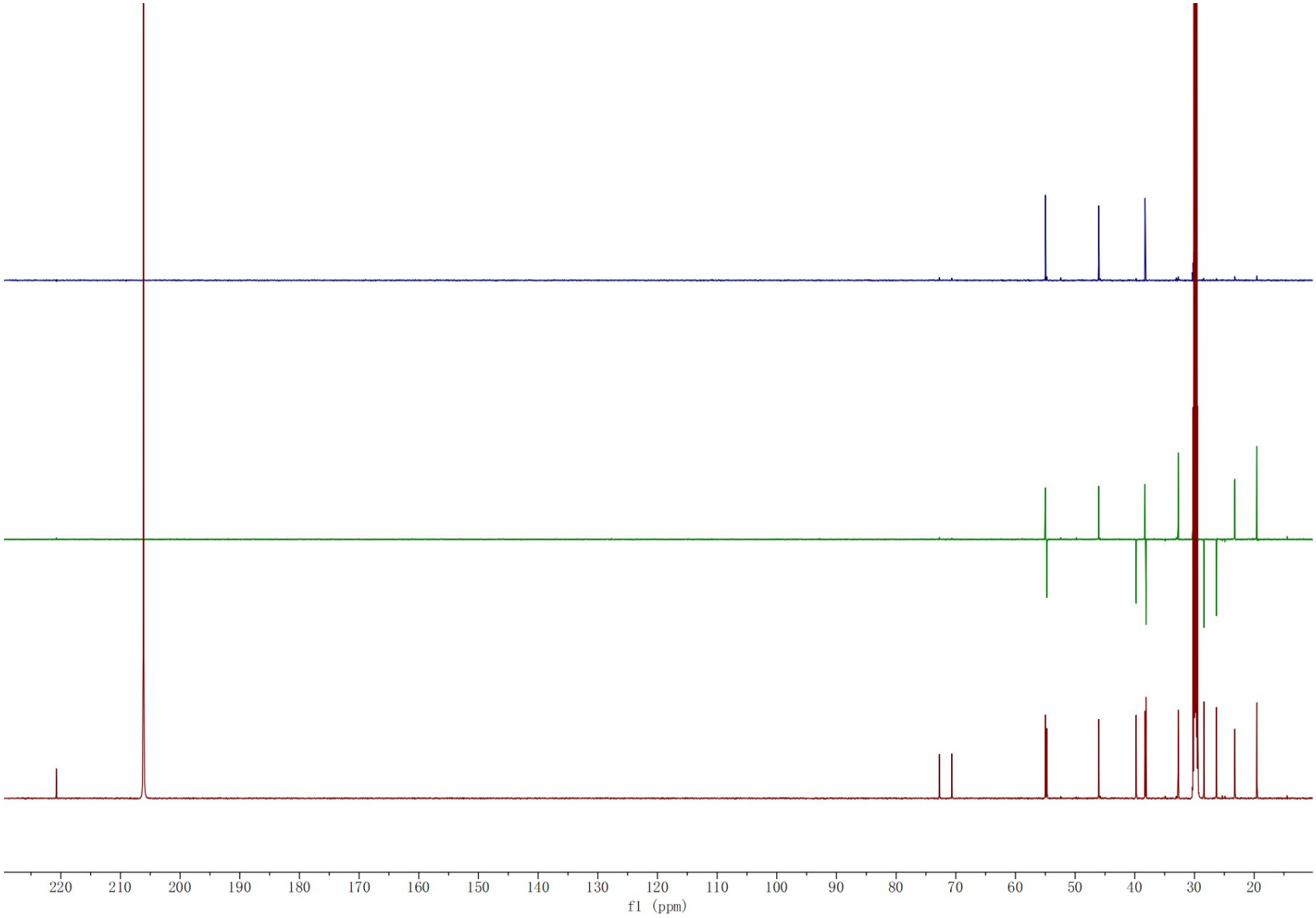

Figure S57. The DEPT spectrum of compound **6** in acetone-d_6.

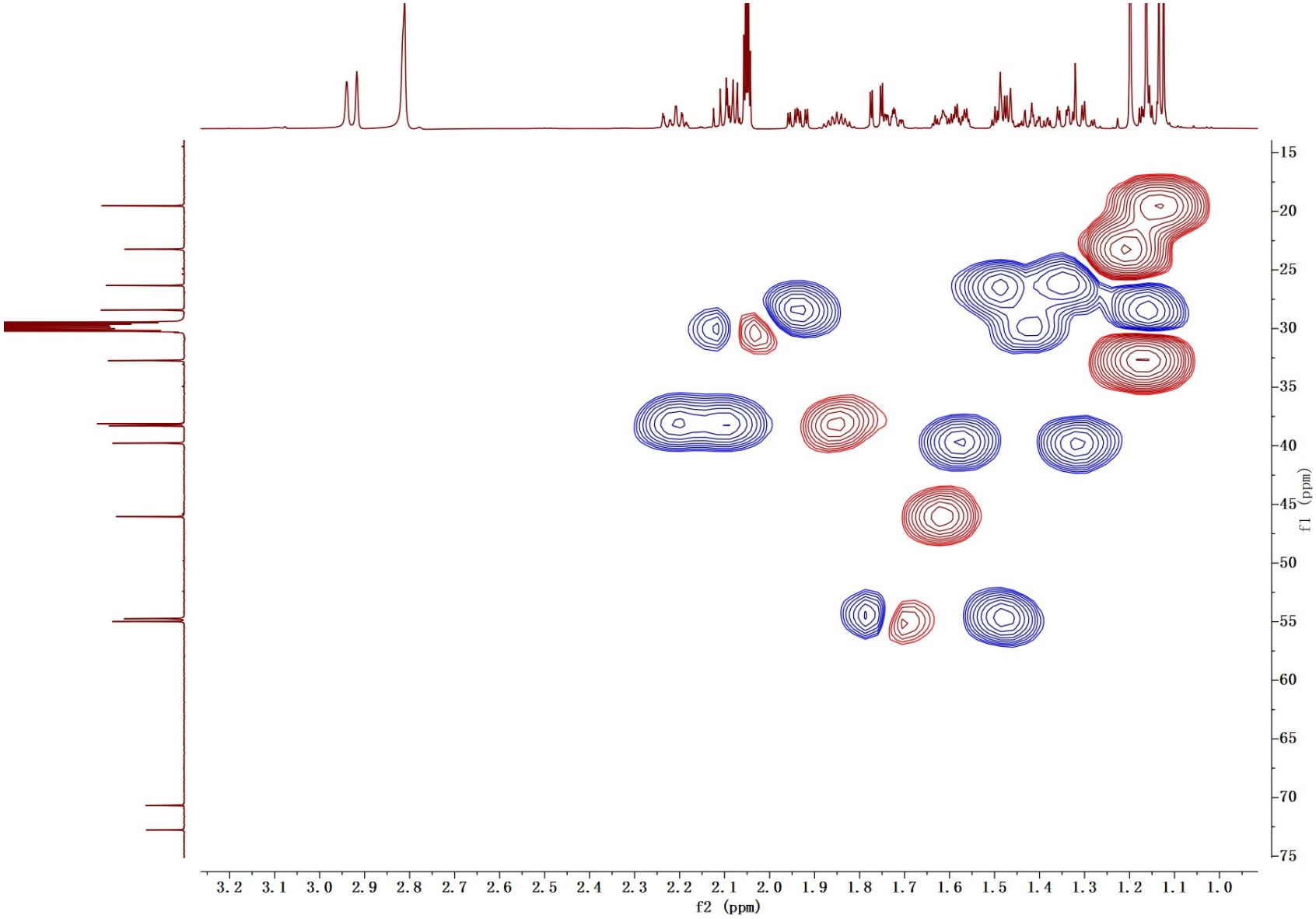

Figure S58. The HSQC spectrum of compound **6** in acetone-d_6.

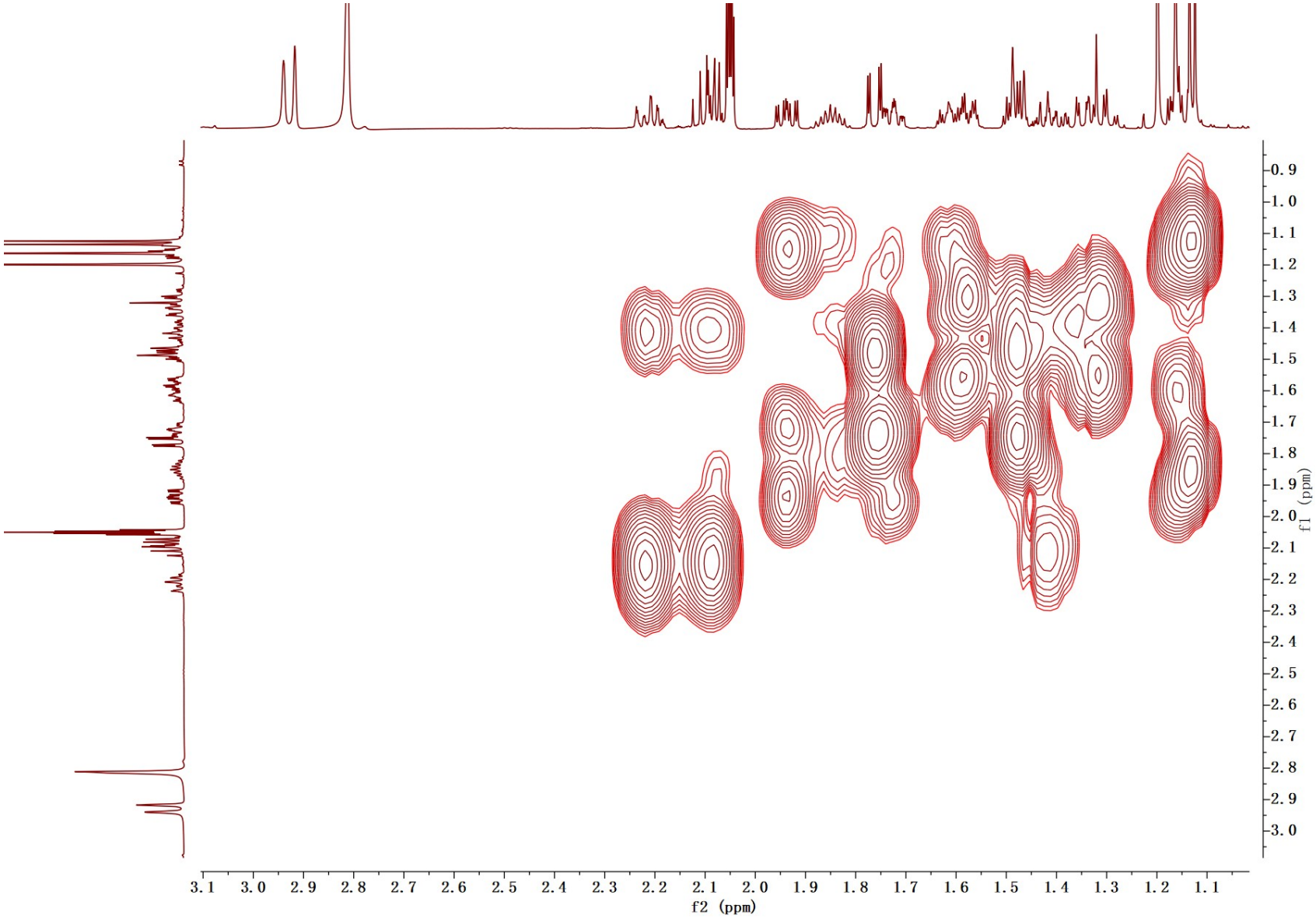

Figure S59. The ^{1}H-^{1}H COSY spectrum of compound **6** in acetone-d_6.

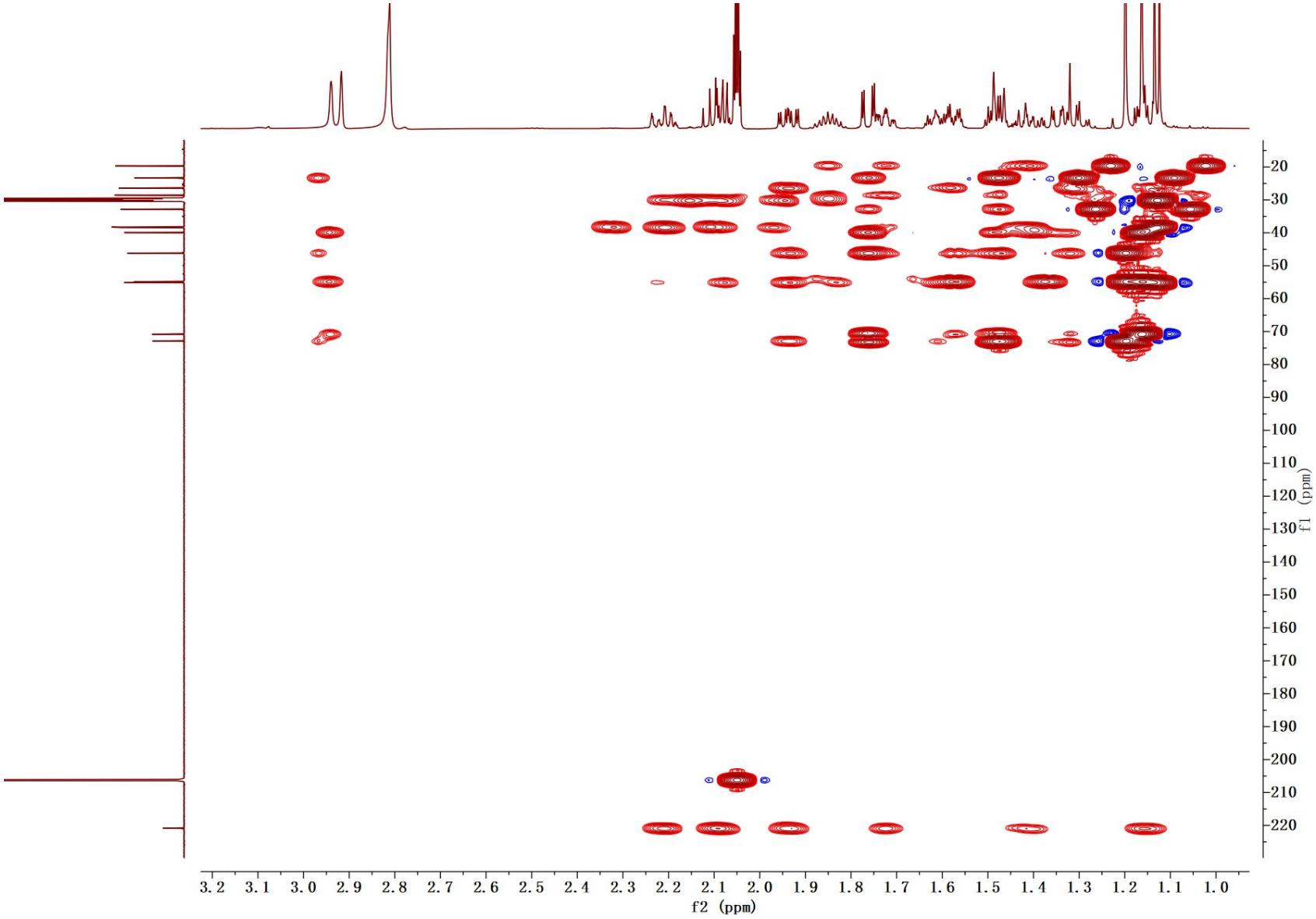

Figure S60. The HMBC spectrum of compound **6** in acetone-d_6.

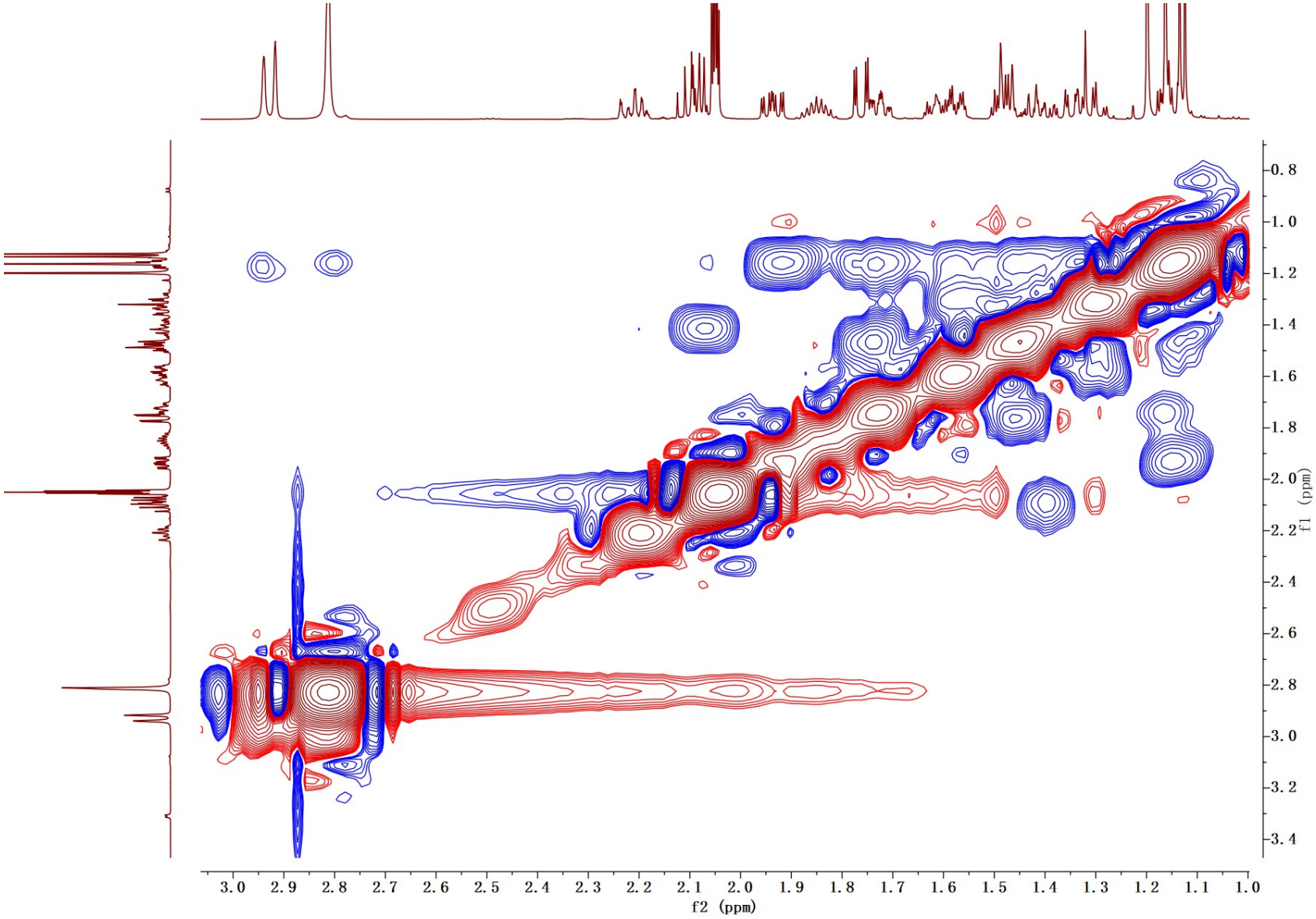

Figure 61. The NOESY spectrum of compound **6** in acetone-d_6.

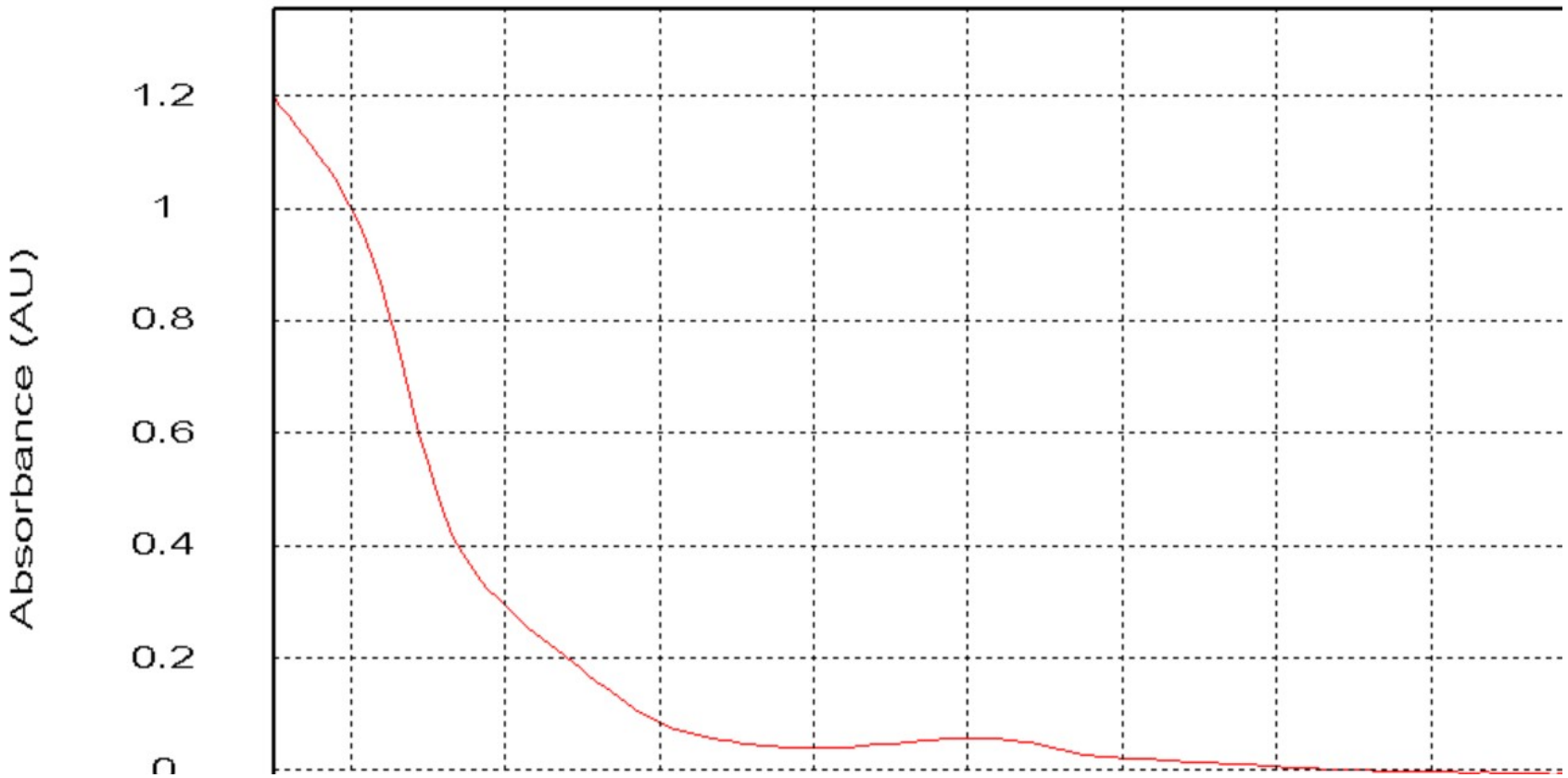

Figure S62. The UV spectrum of compound **7** in acetonitrile.

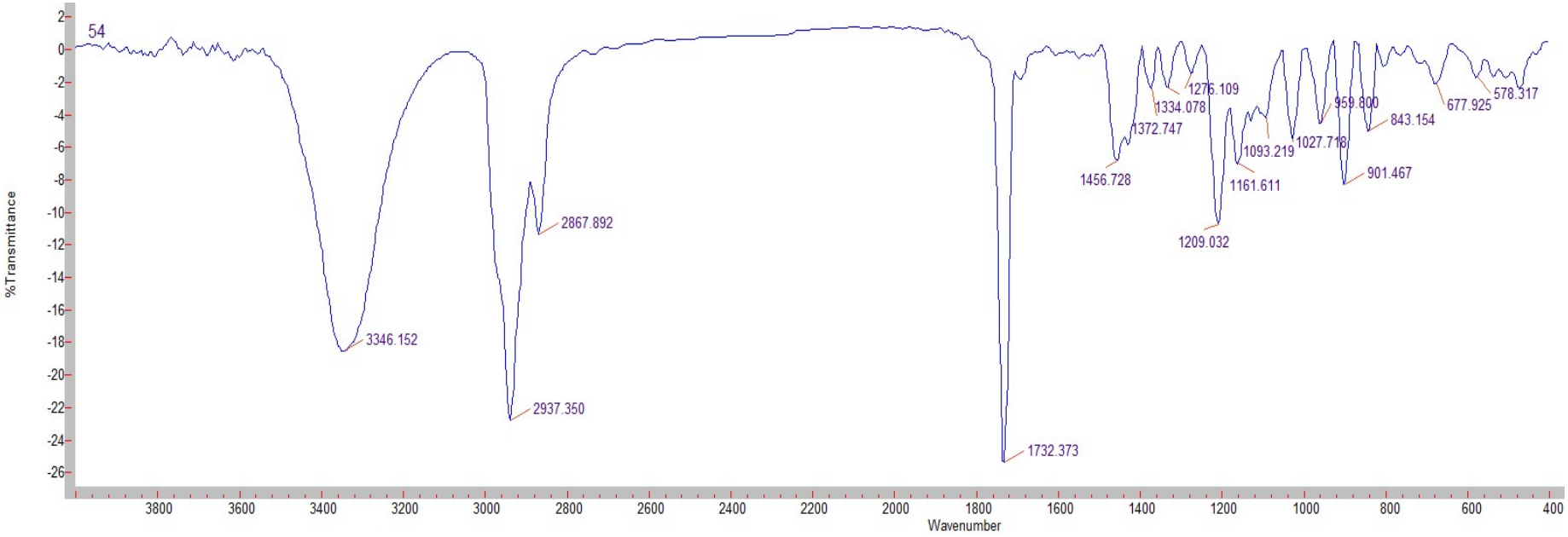

Figure S63. The IR spectrum of compound **7**.

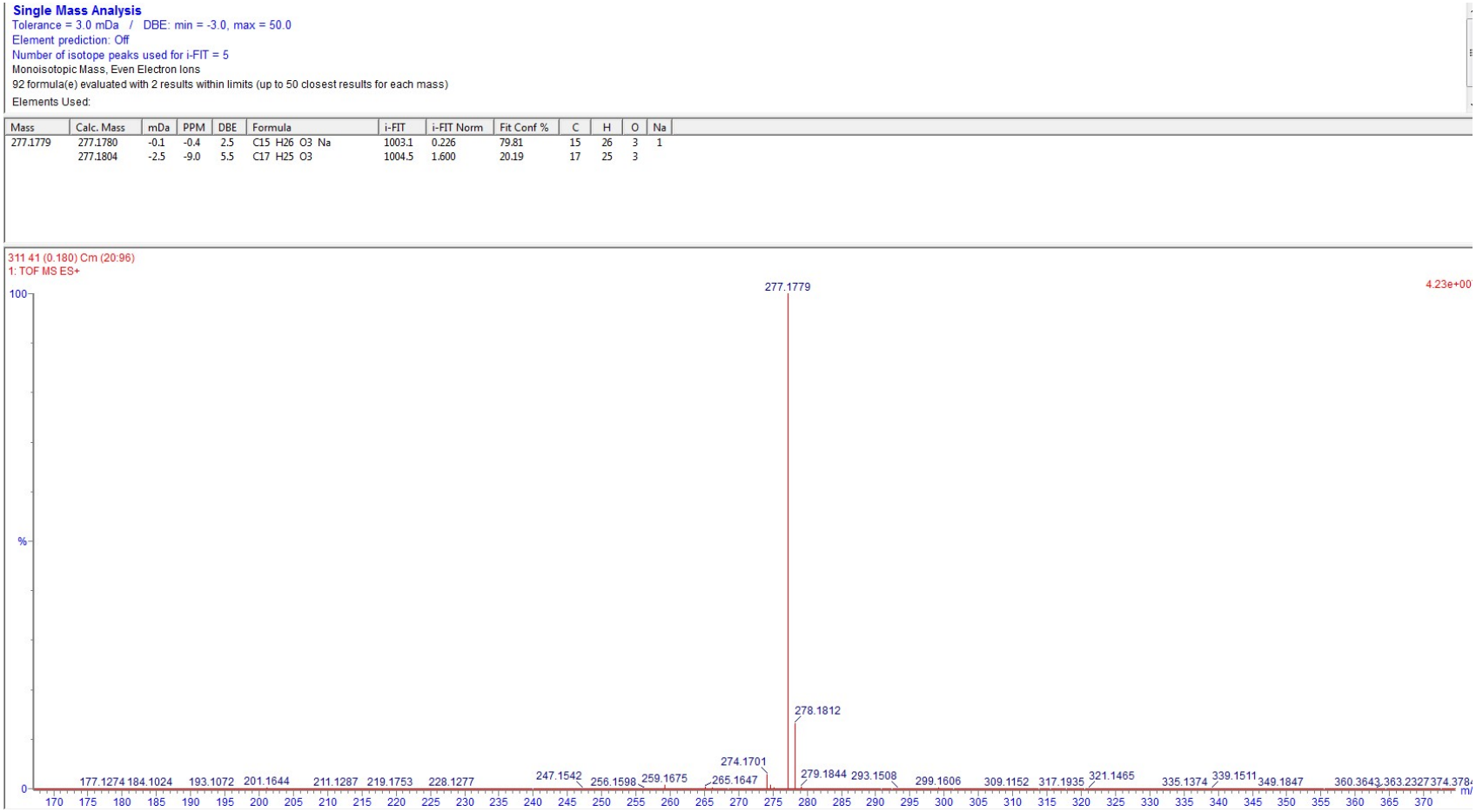

Figure S64. The (+)-HRESIMS spectroscopic data of compound **7**.

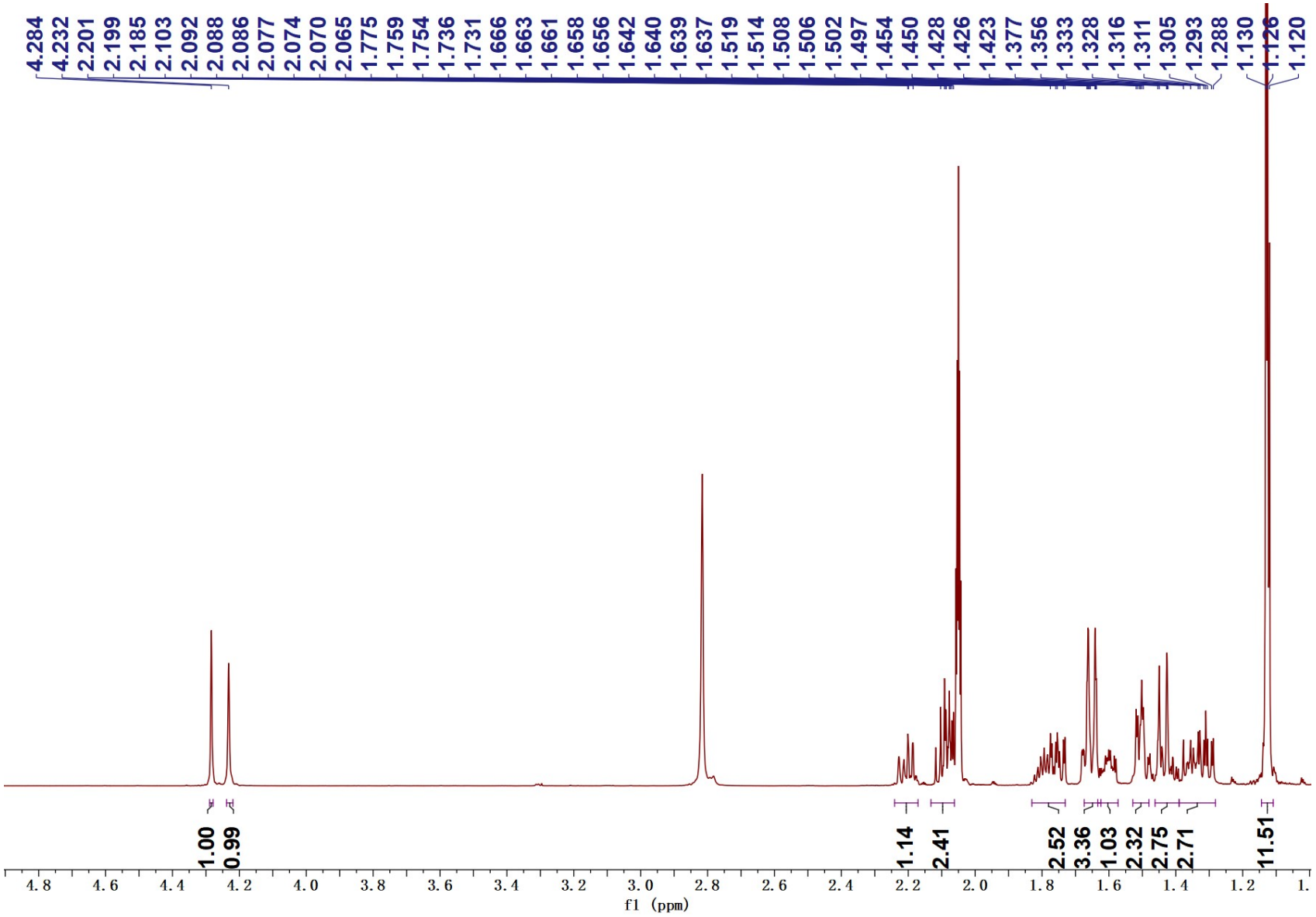

Figure S65. The ^{1}H NMR spectrum of compound **7** in acetone-d_6.

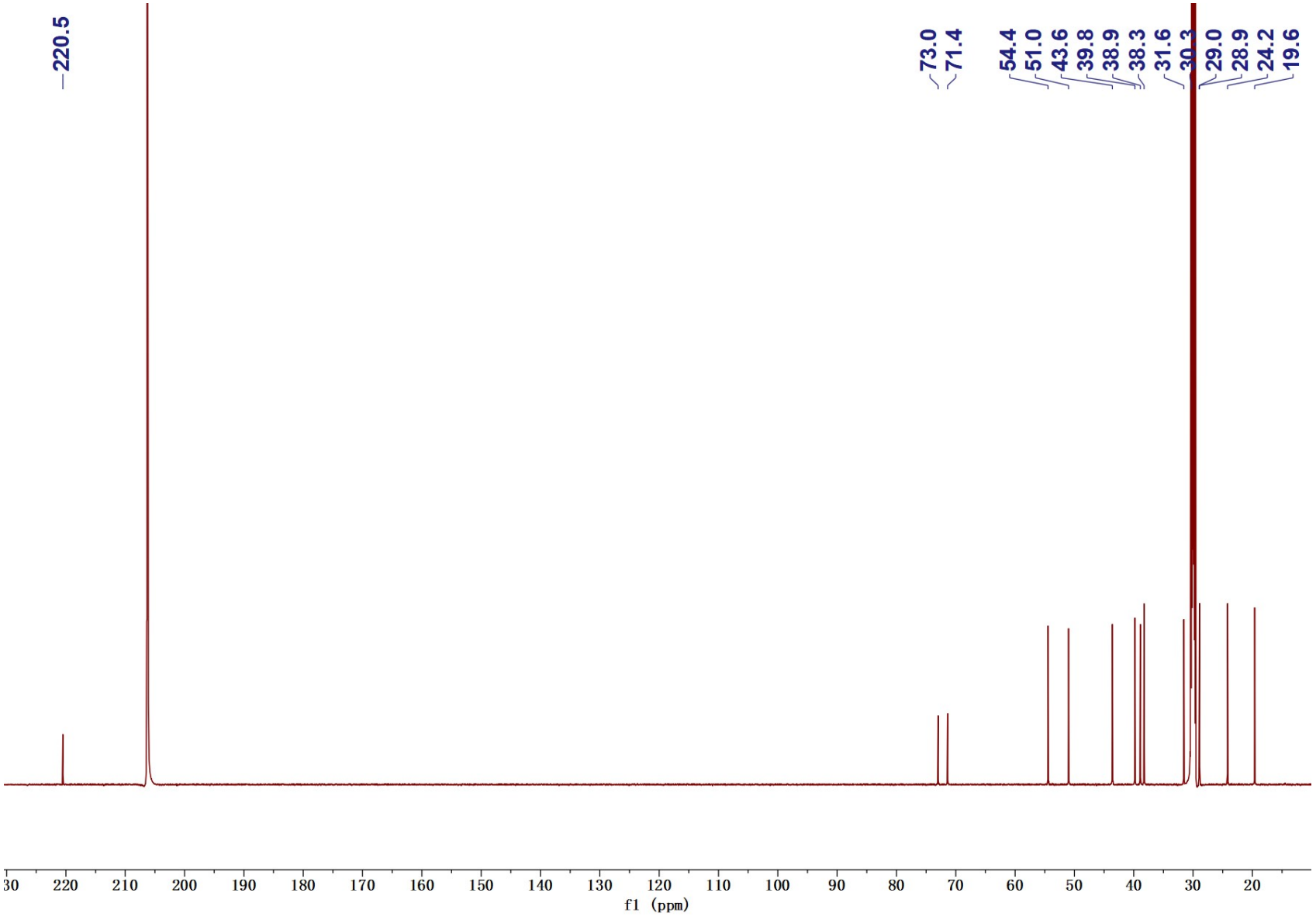

Figure S66. The ^{13}C NMR spectrum of compound **7** in acetone-d_6.

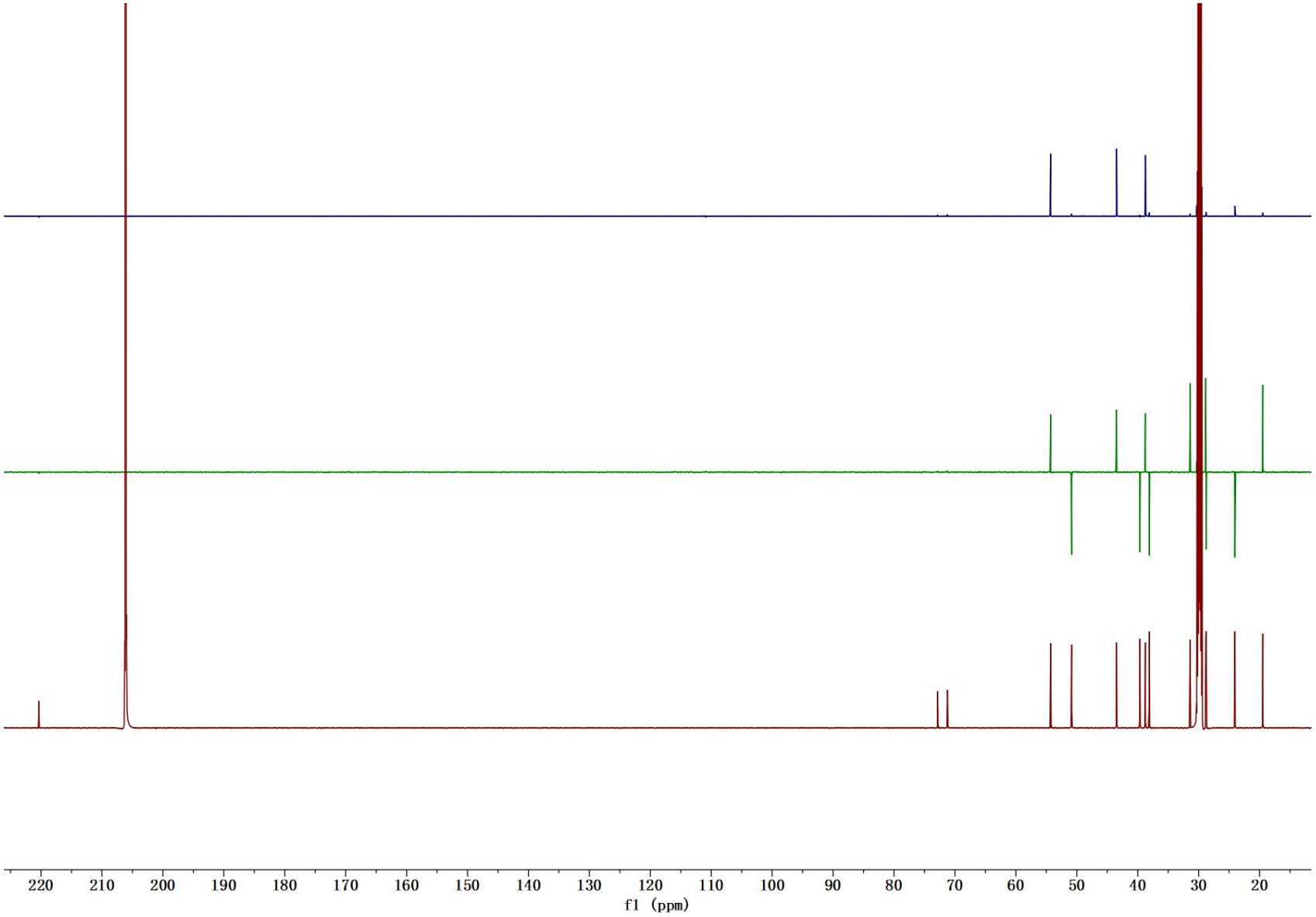

Figure S67. The DEPT spectrum of compound **7** in acetone-d_6.

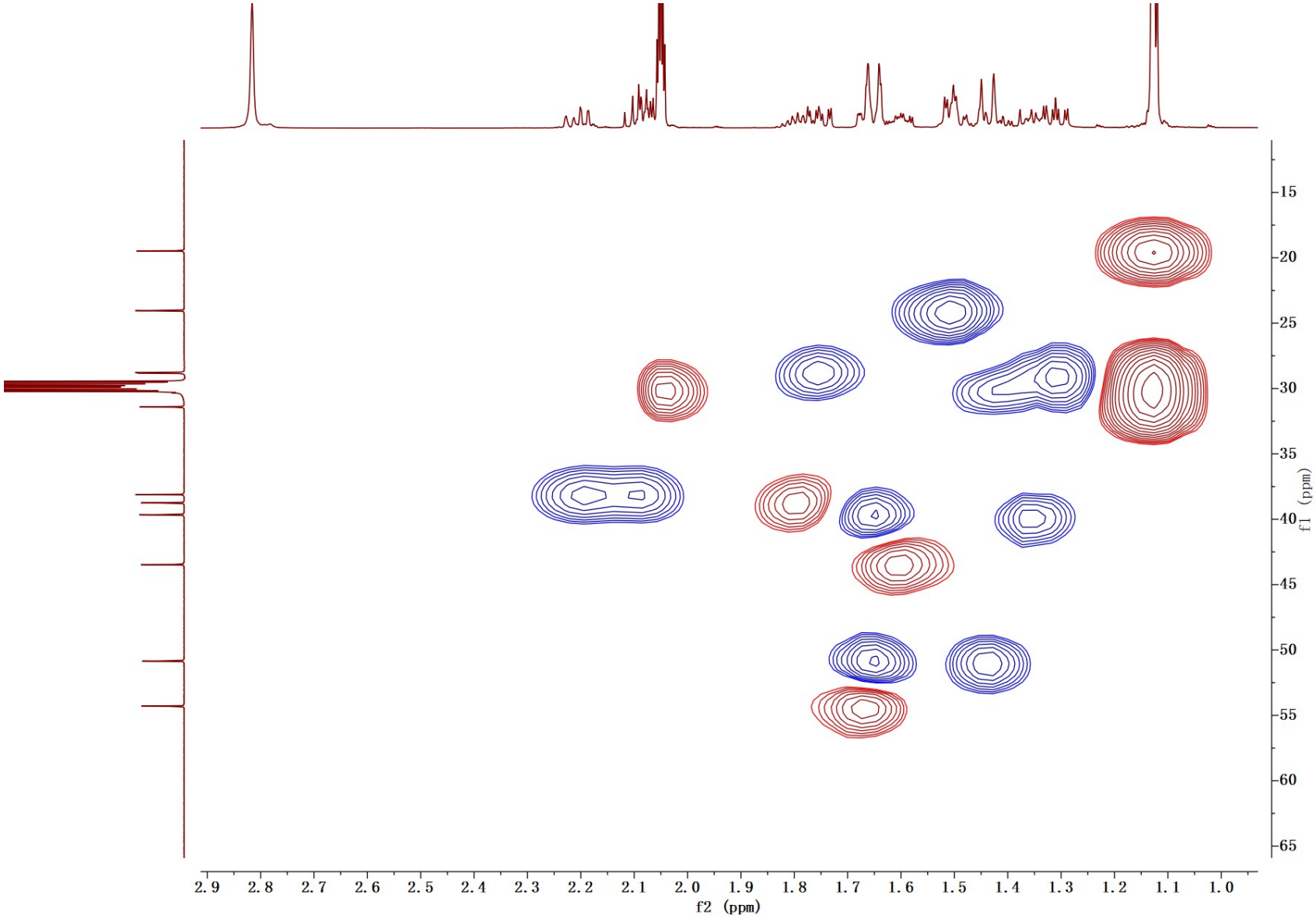

Figure S68. The HSQC spectrum of compound **7** in acetone-d_6.

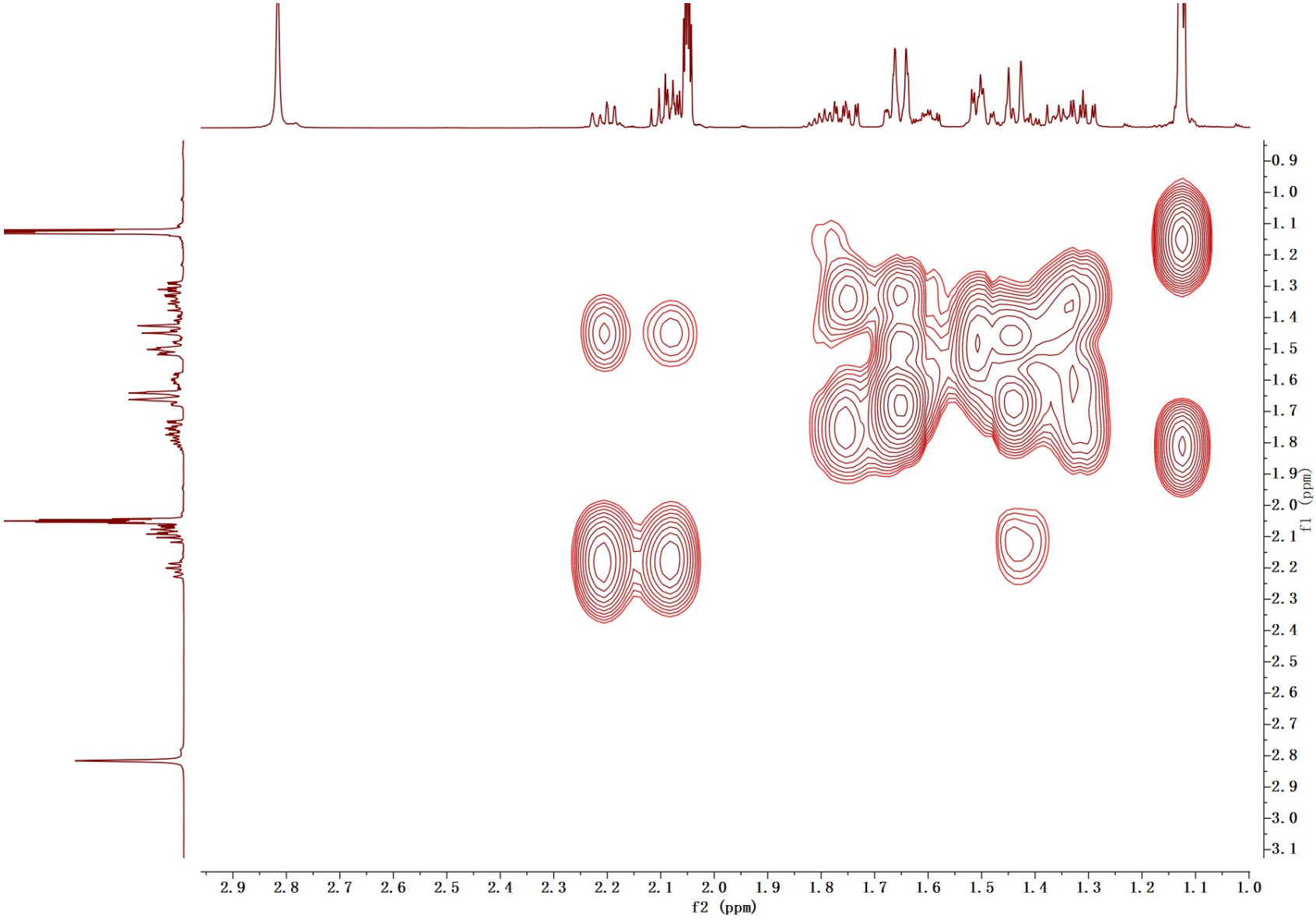

Figure S69. The ^{1}H-^{1}H COSY spectrum of compound **7** in acetone-d_6.

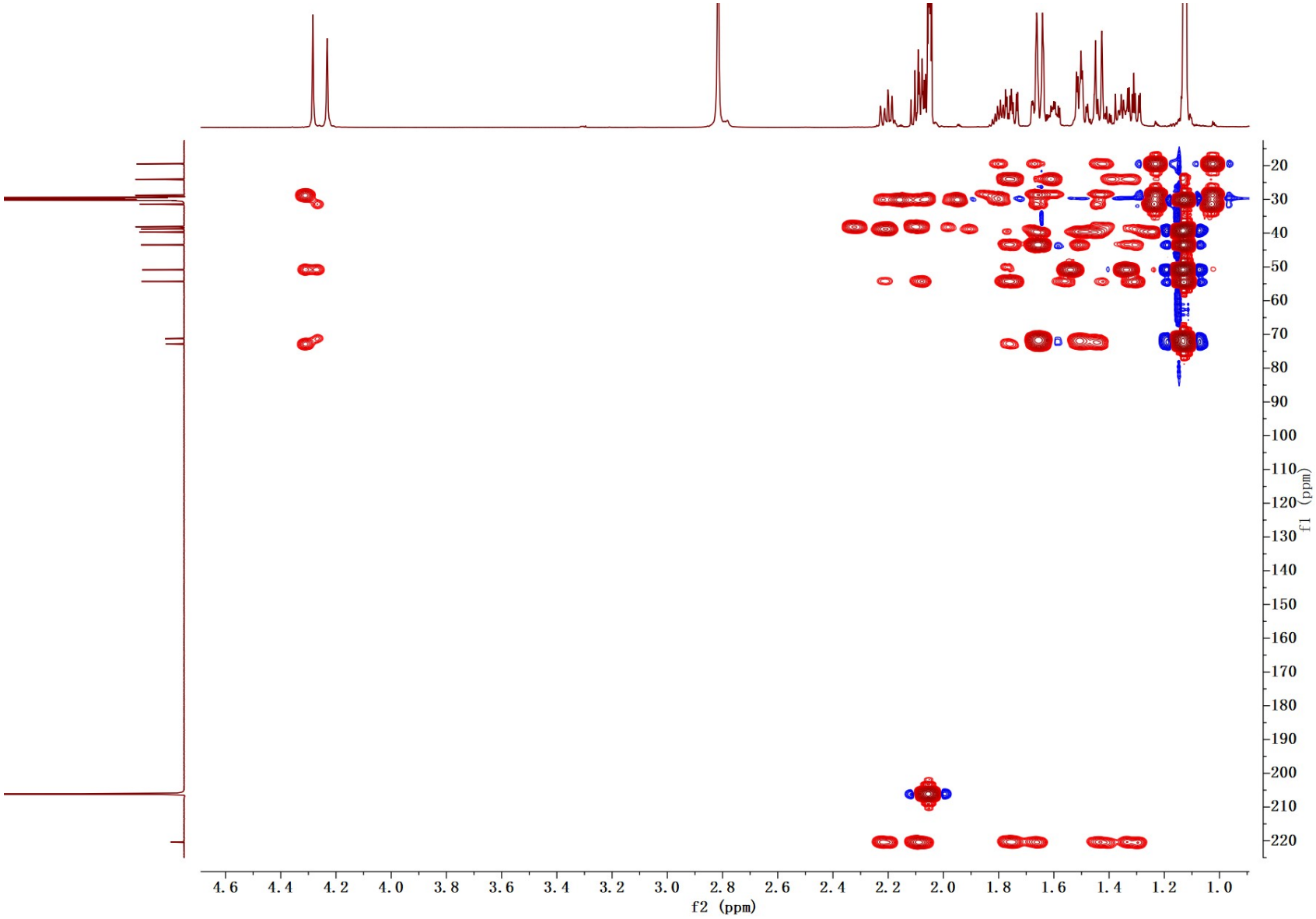

Figure S70. The HMBC spectrum of compound **7** in acetone-d_6.