

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 $\sigma = 0.2$ 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.

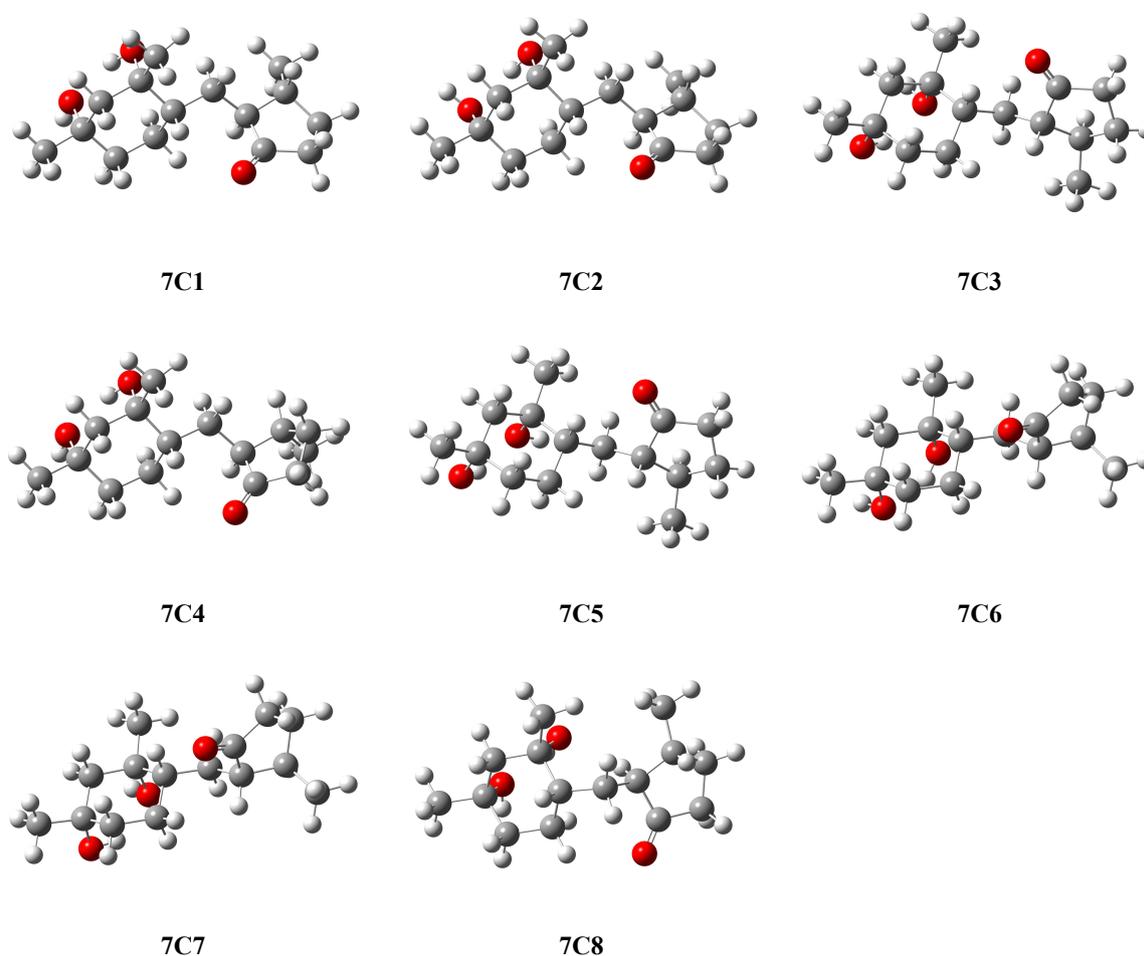


Figure S1. ω B97XD/DGDZVP optimized eight conformers of (1*S*,5*R*,7*S*,8*S*,10*S*)-7.

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

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

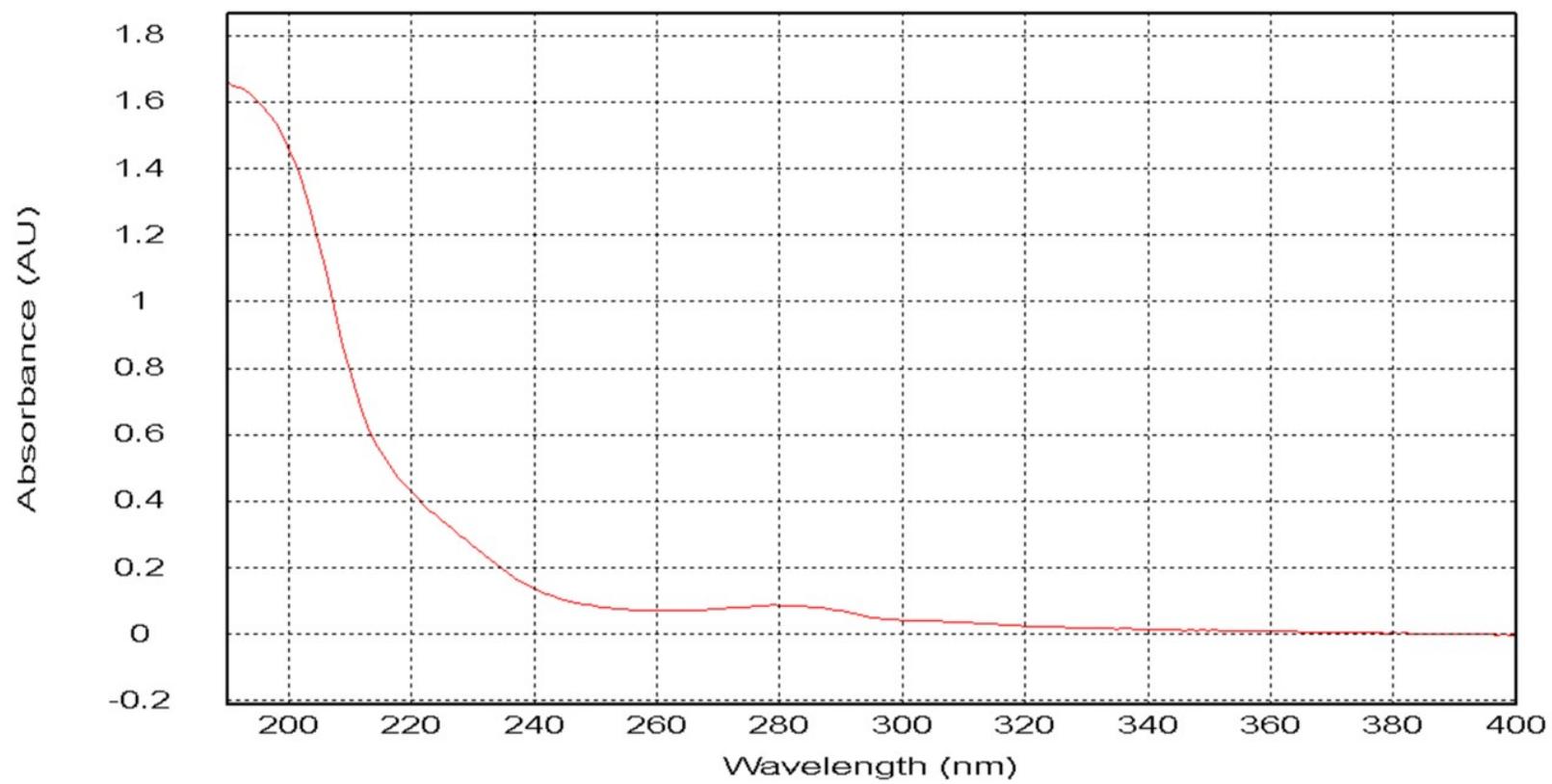


Figure S2. The UV spectrum of compound 1 in acetonitrile.

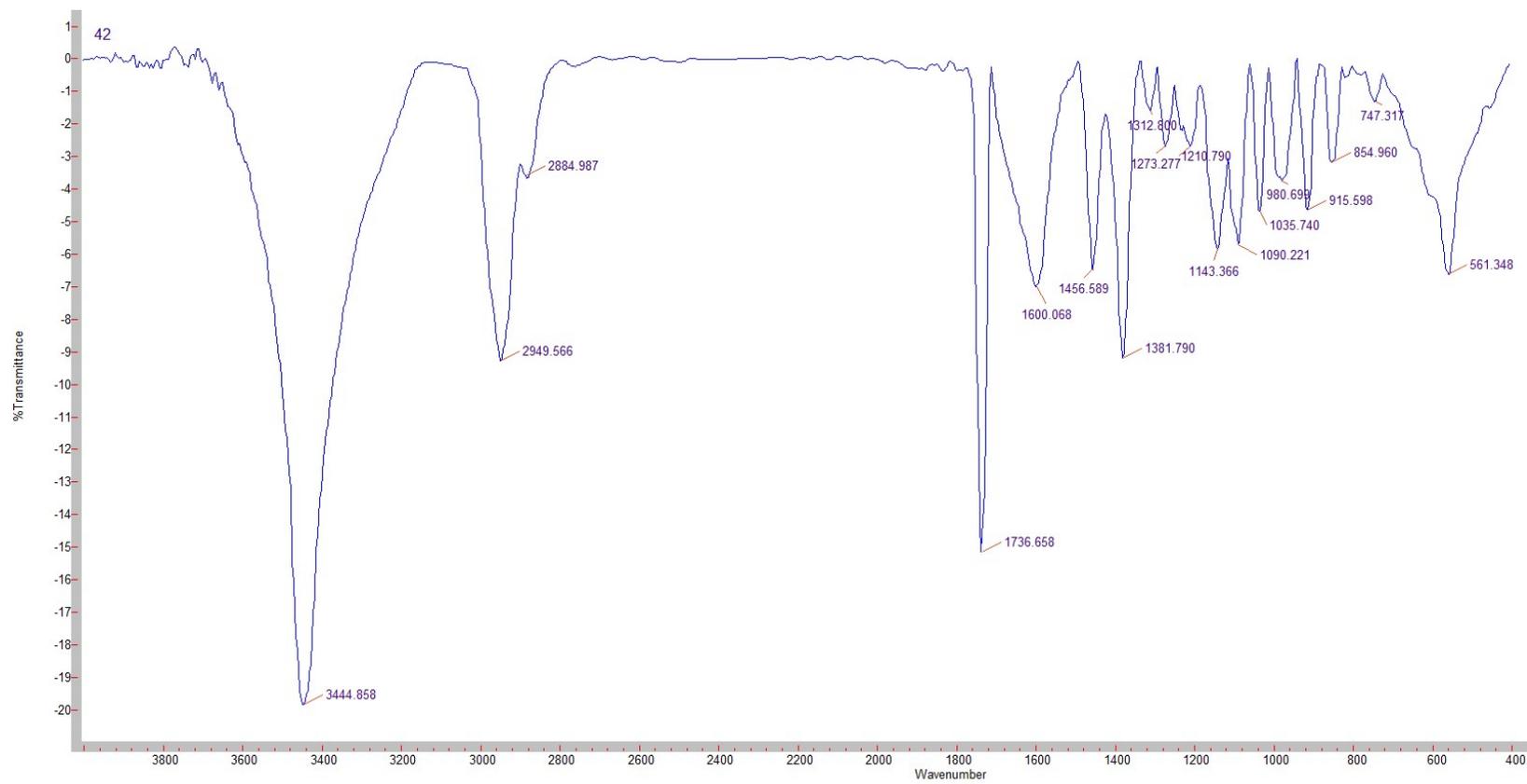


Figure S3. The IR spectrum of compound 1.



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

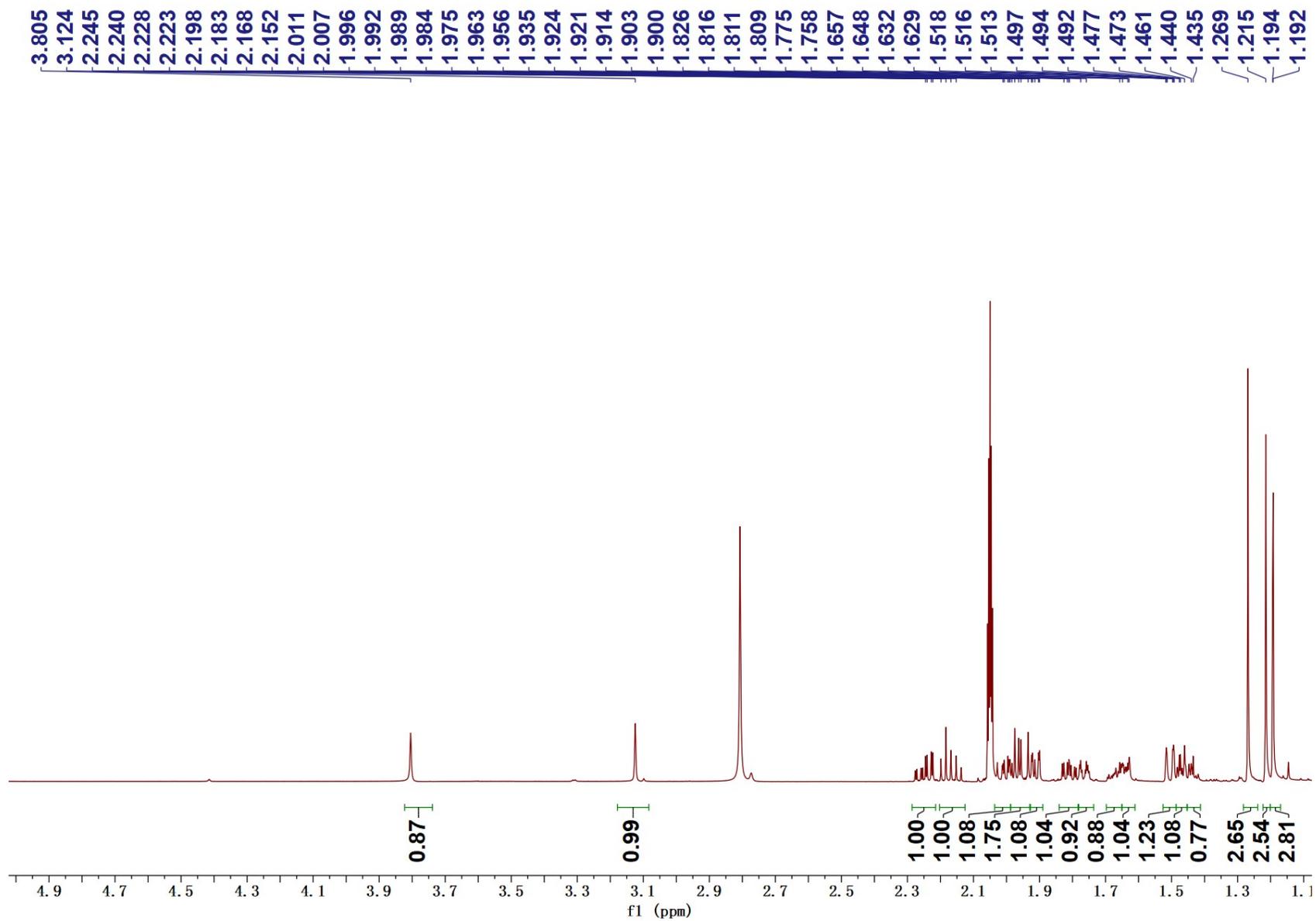


Figure S5. The ^1H NMR spectrum of compound **1** in acetone- d_6 .

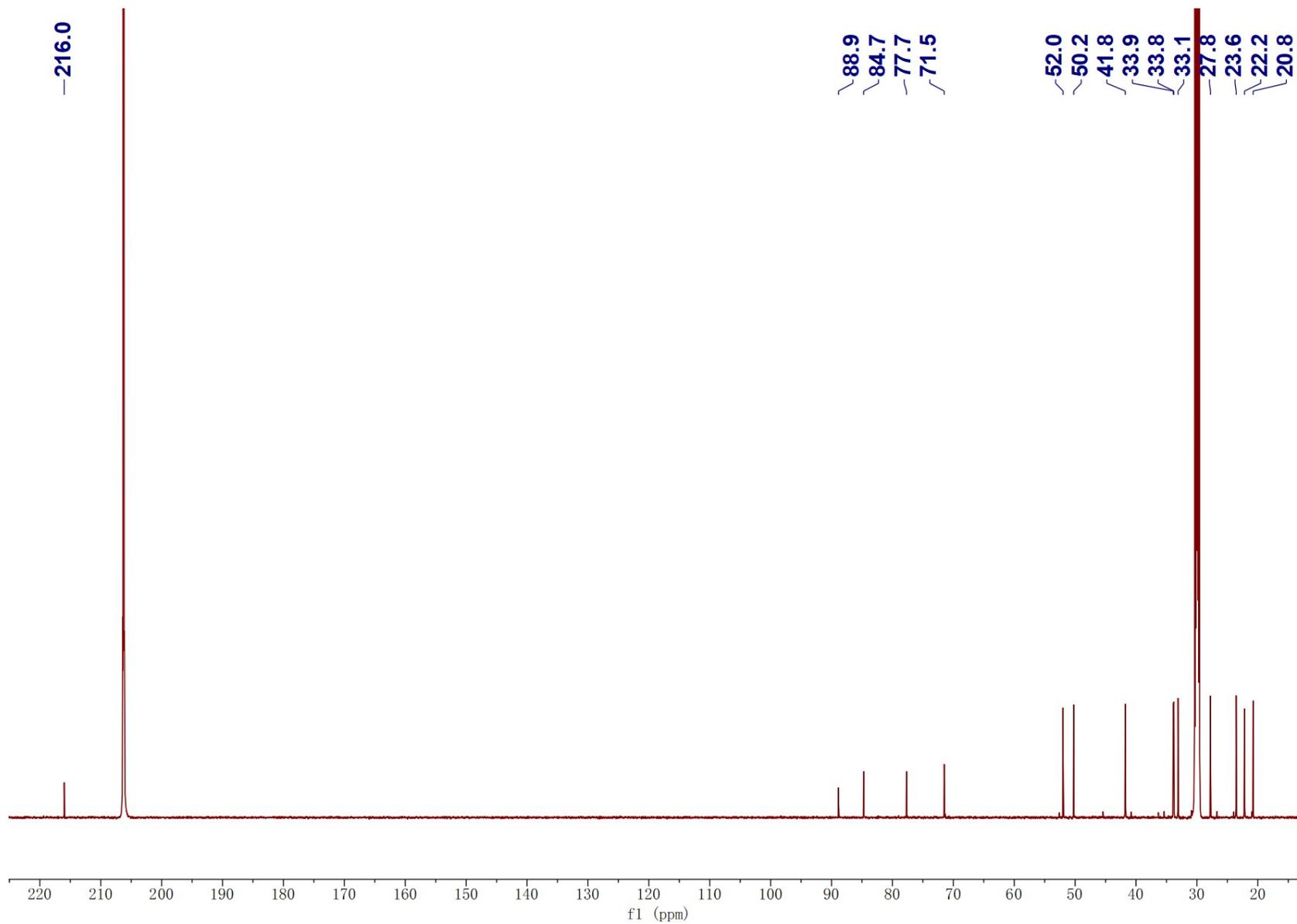


Figure S6. The ^{13}C NMR spectrum of compound **1** in acetone- d_6 .

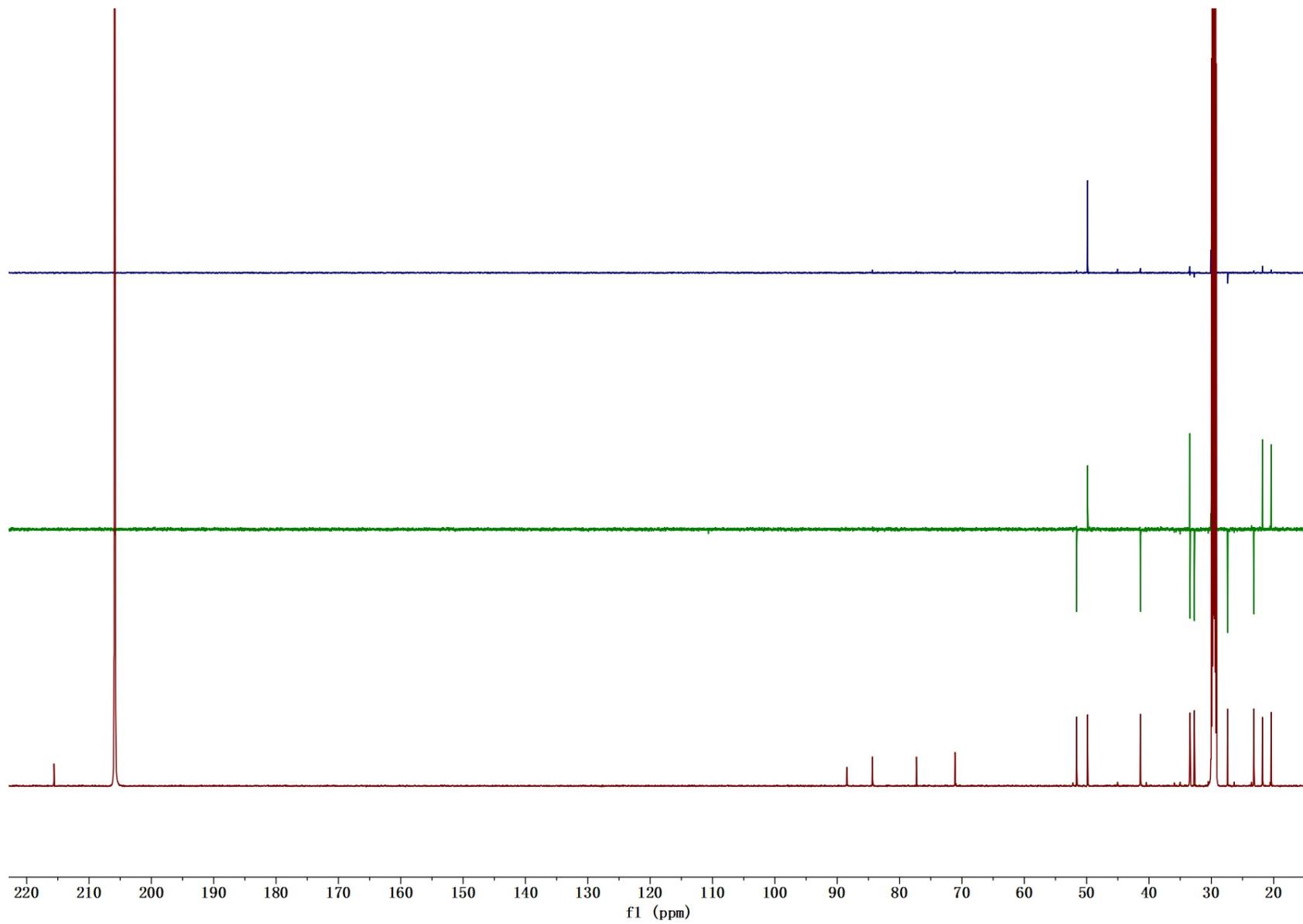


Figure S7. The DEPT spectrum of compound **1** in acetone- d_6 .

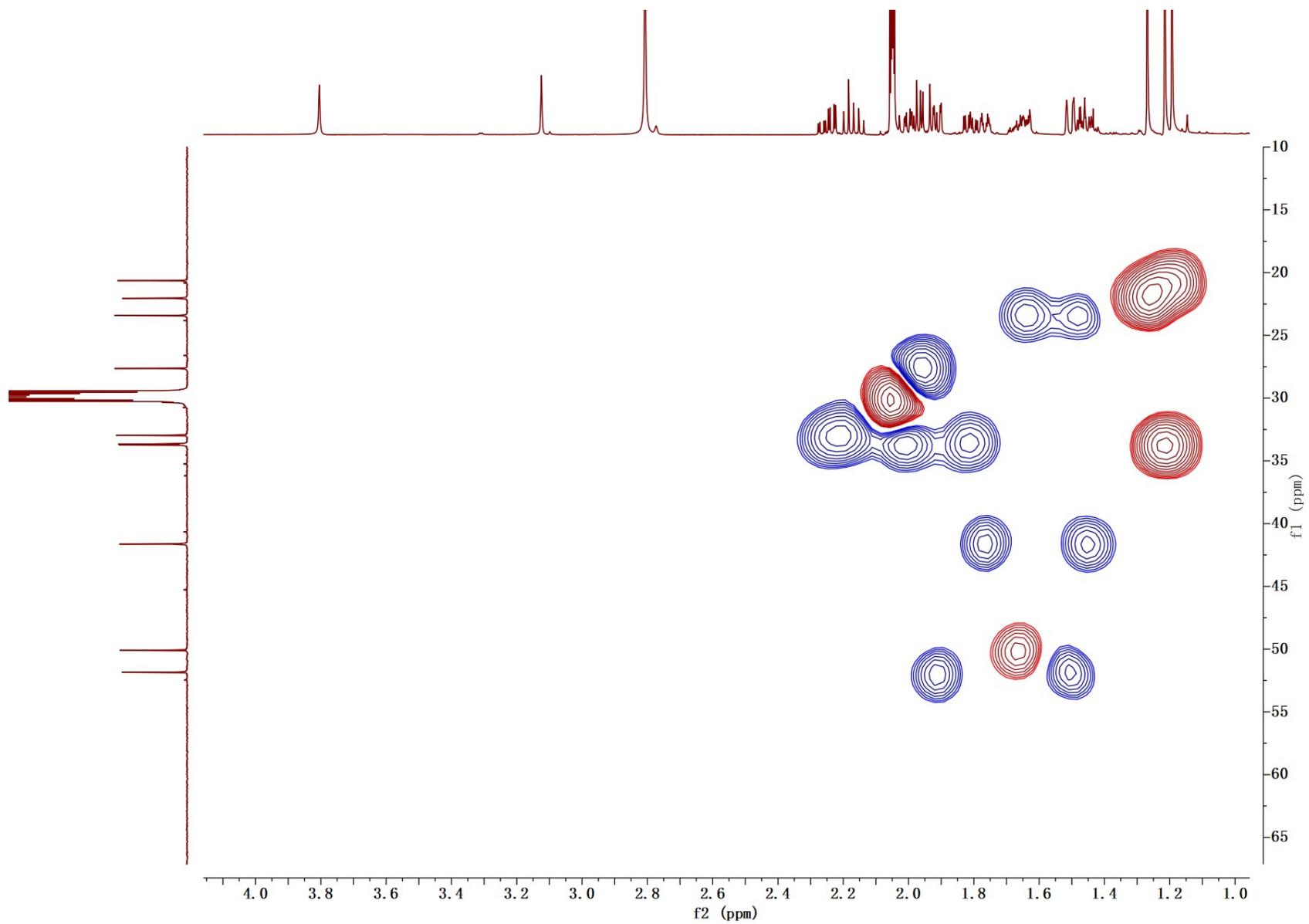


Figure S8. The HSQC spectrum of compound **1** in acetone- d_6 .

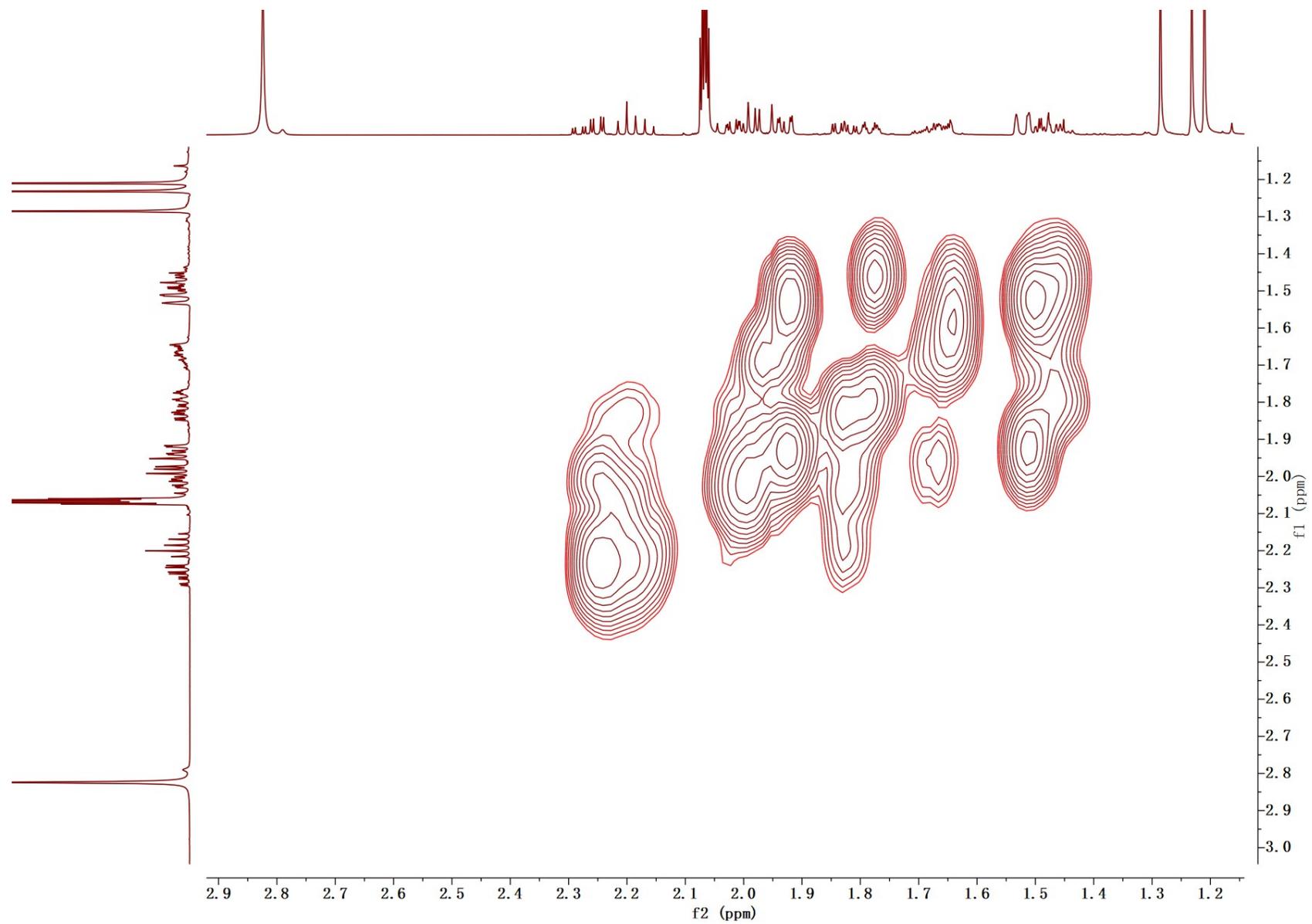


Figure S9. The ^1H - ^1H COSY spectrum of compound **1** in acetone- d_6 .

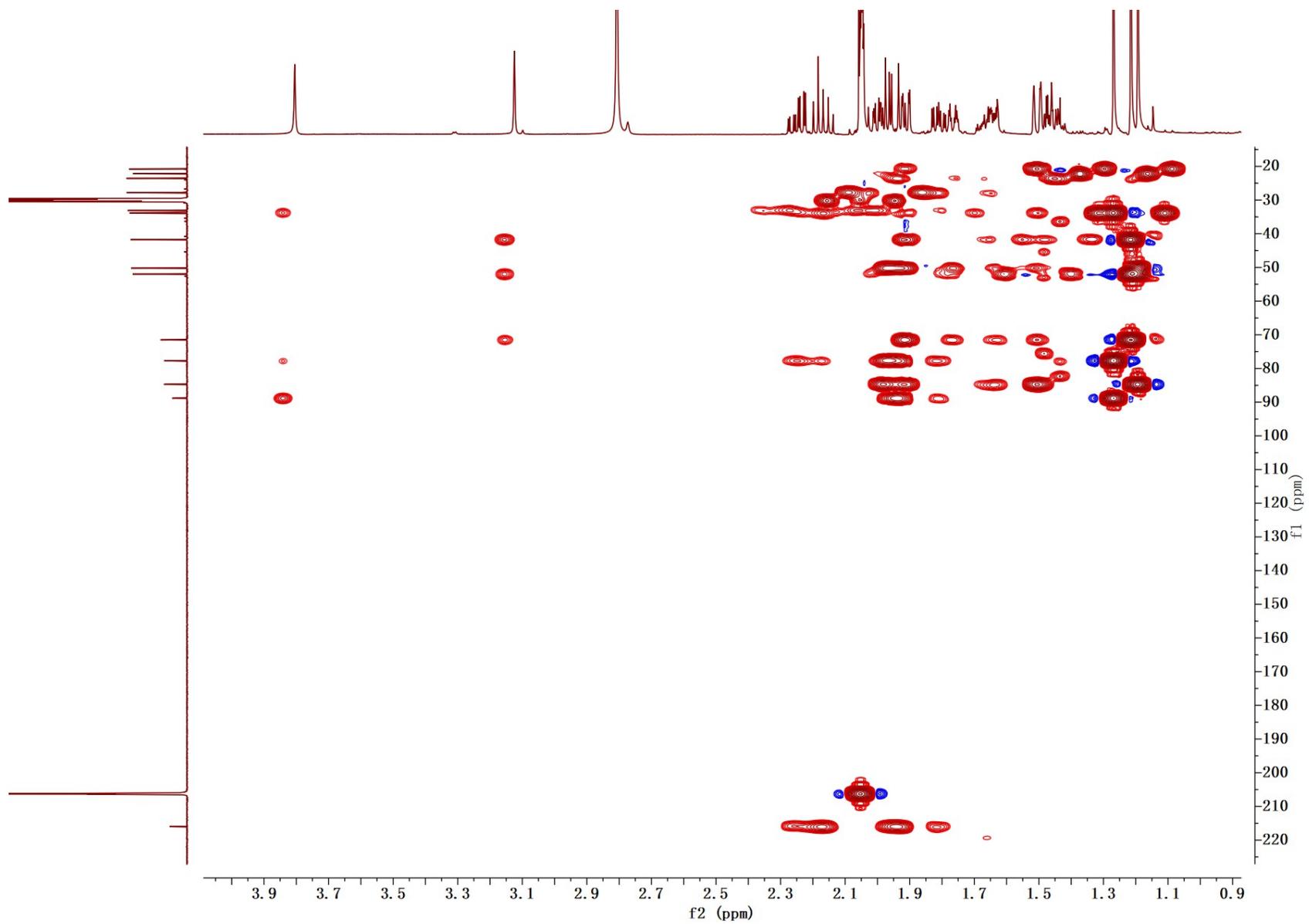


Figure S10. The HMBC spectrum of compound **1** in acetone- d_6 .

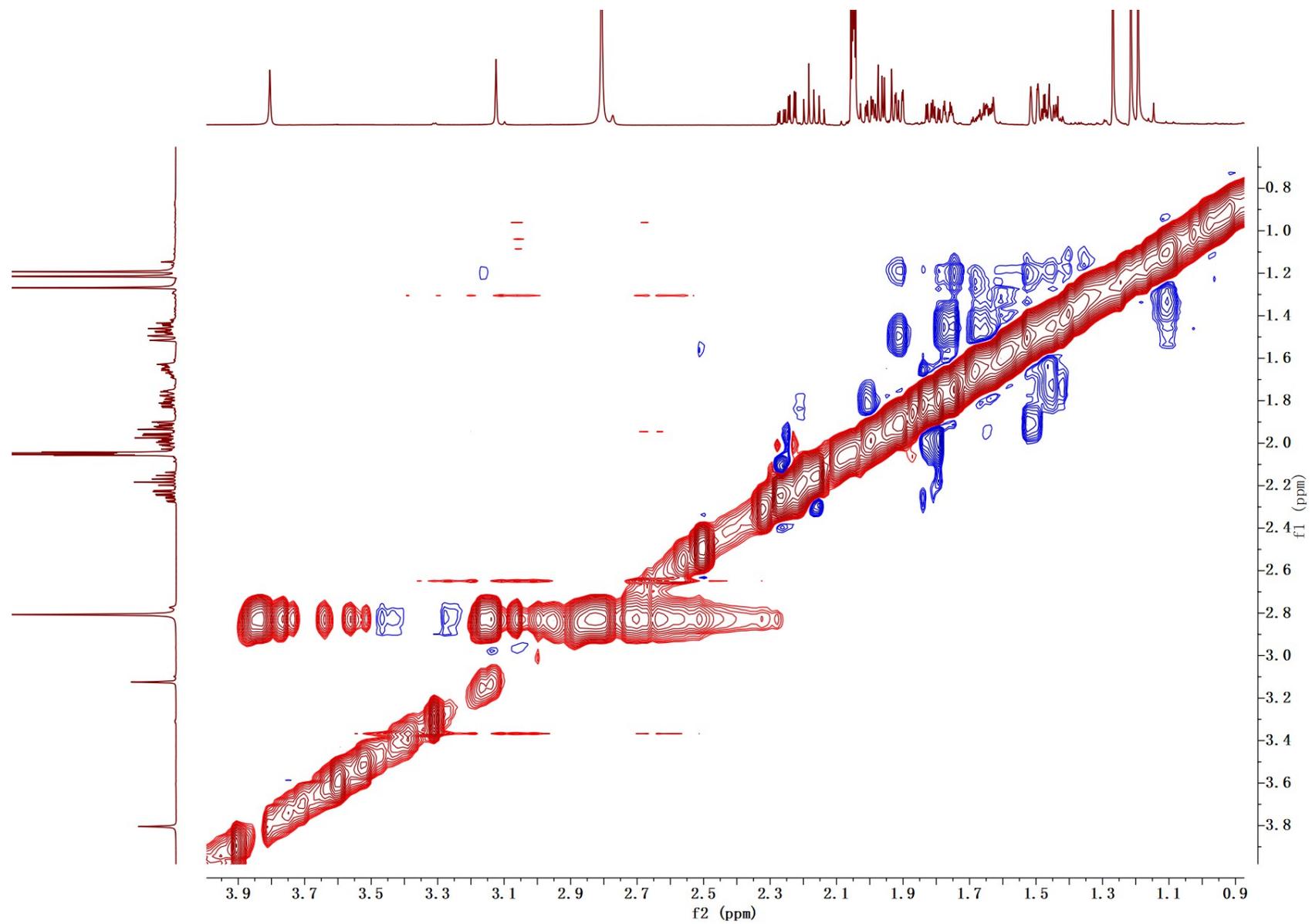


Figure S11. The NOESY spectrum of compound **1** in acetone- d_6 .

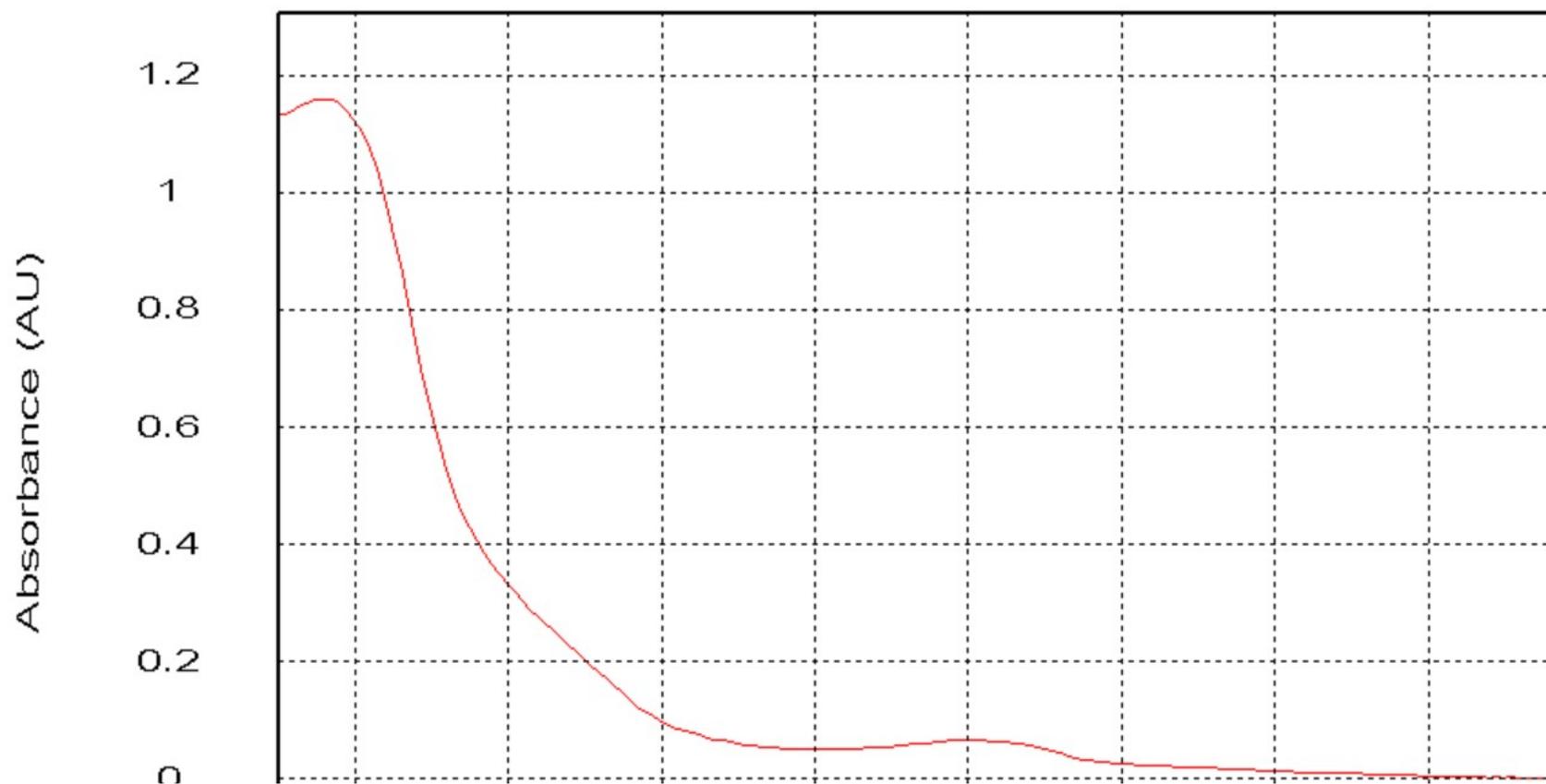


Figure S12. The UV spectrum of compound **2** in acetonitrile.

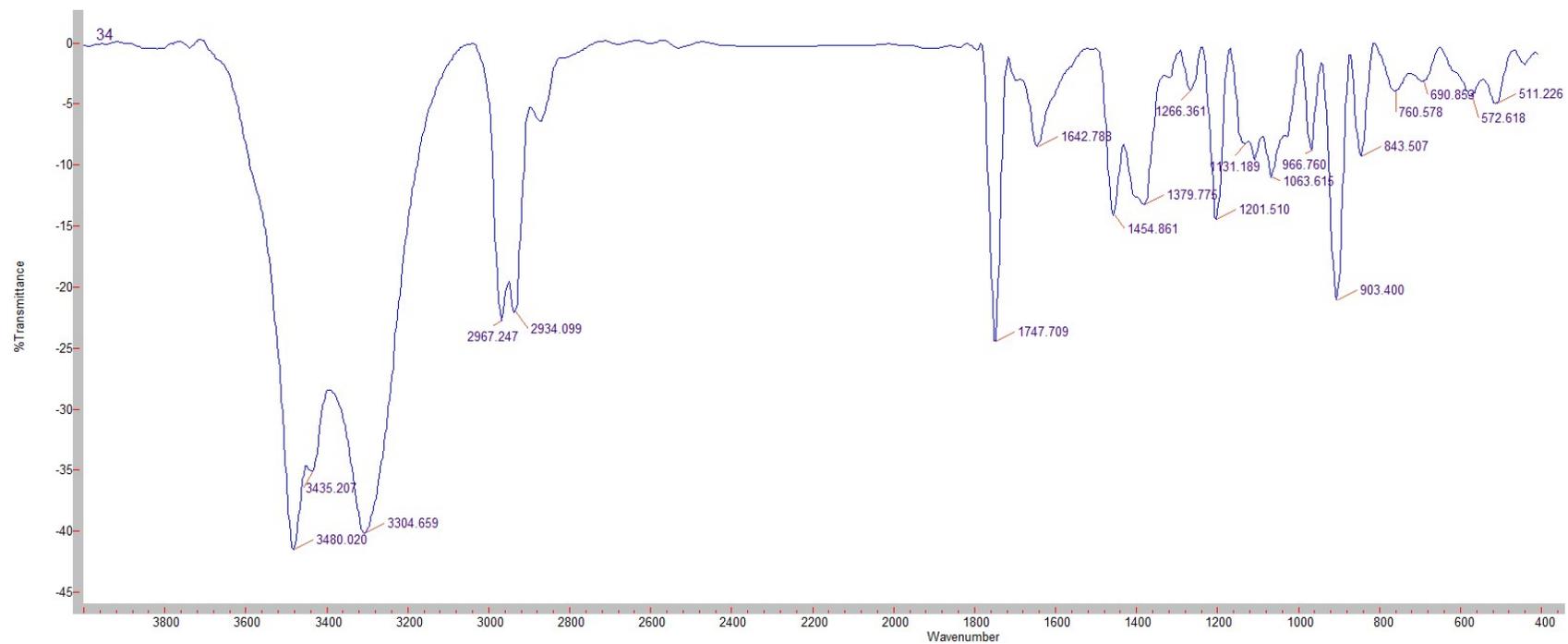


Figure S13. The IR spectrum of compound 2.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

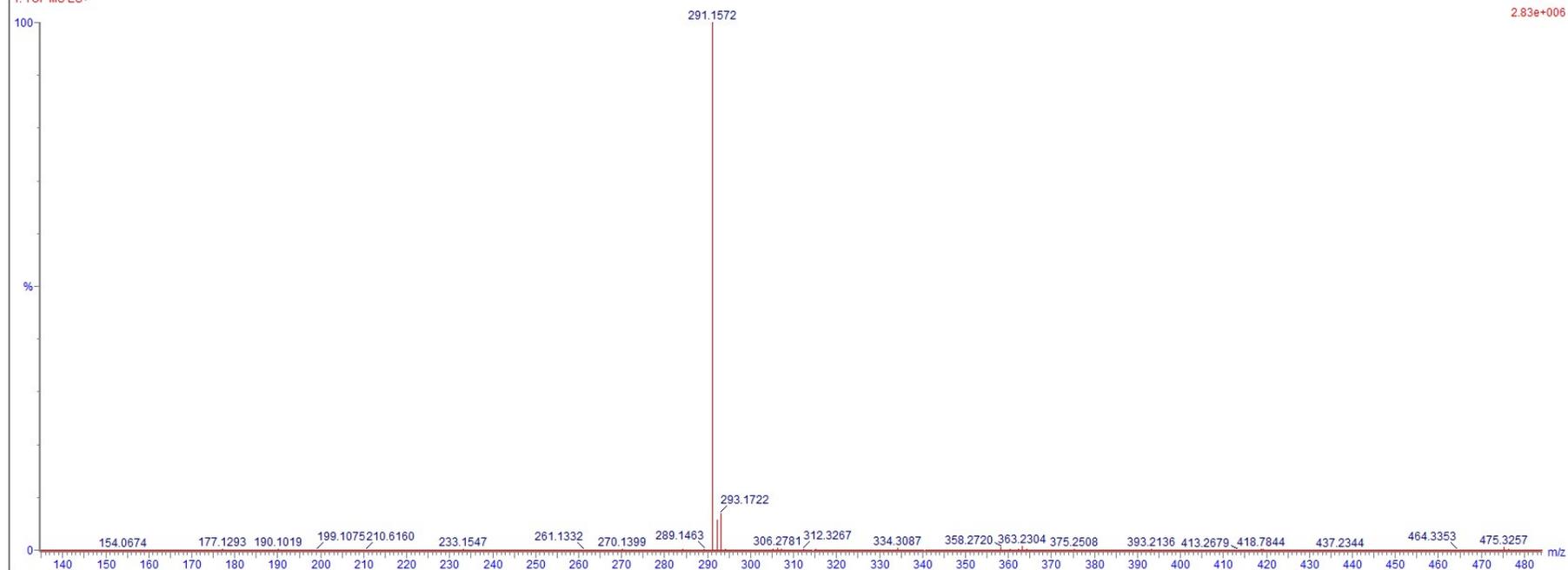
99 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
291.1572	291.1572	0.0	0.0	3.5	C15 H24 O4 Na	438.3	0.528	58.98	15	24	4	1
	291.1596	-2.4	-8.2	6.5	C17 H23 O4	438.6	0.891	41.02	17	23	4	

X-17.40 (0.176) Cm (16:86)

1: TOF MS ES+

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

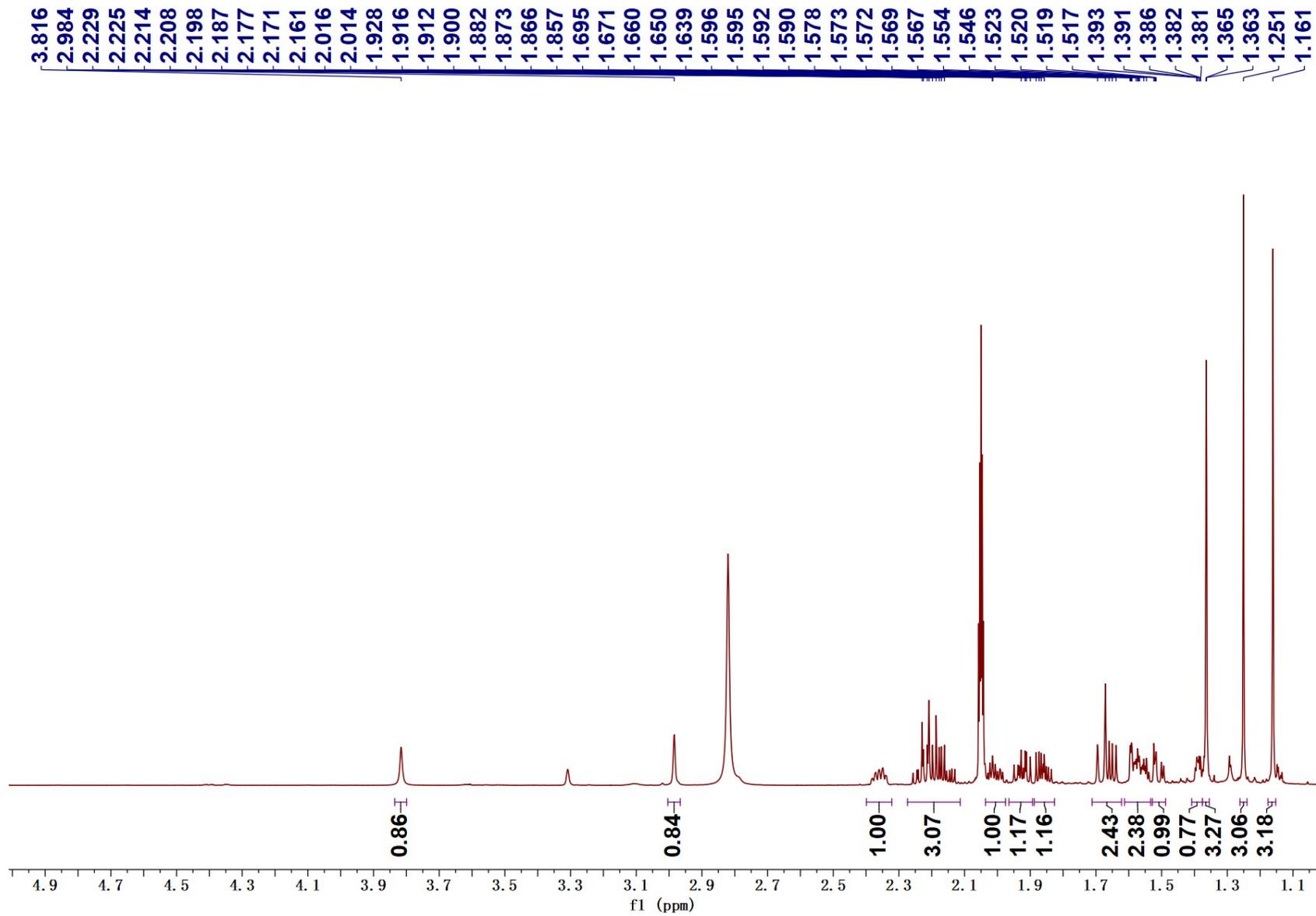


Figure S15. The ^1H NMR spectrum of compound 2 in acetone- d_6 .

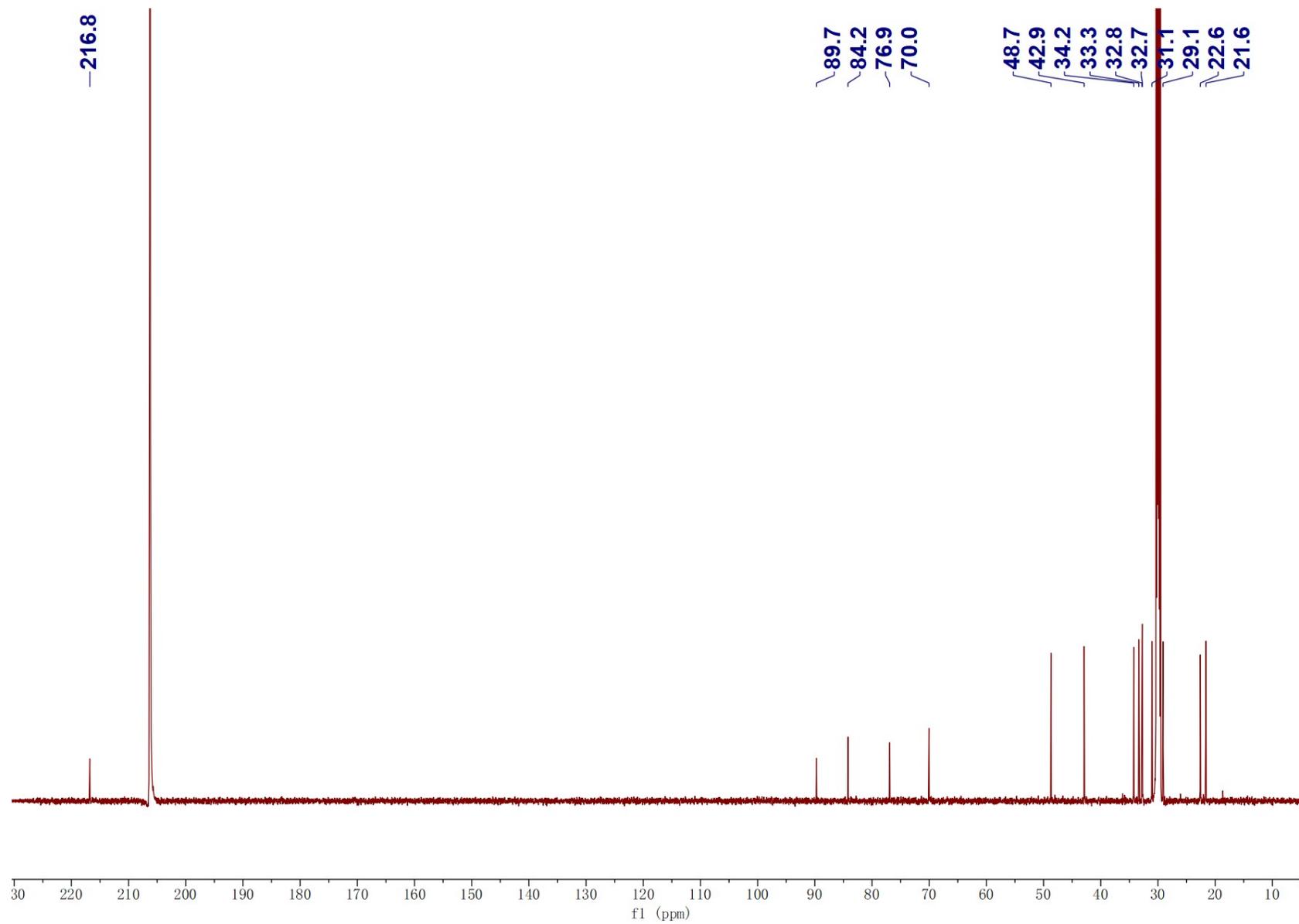


Figure S16. The ^{13}C NMR spectrum of compound **2** in acetone- d_6 .

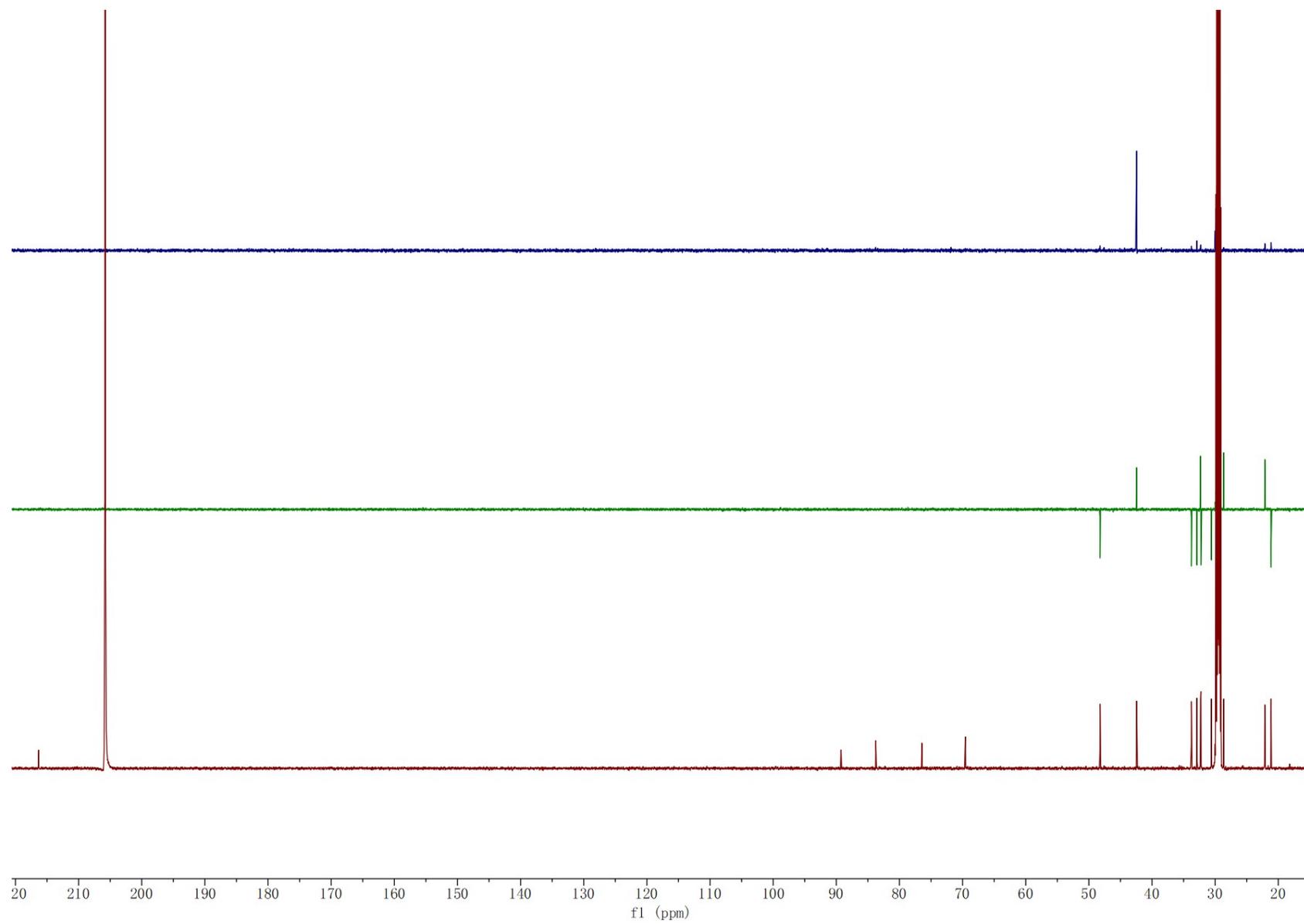


Figure S17. The DEPT spectrum of compound **2** in acetone-*d*₆.

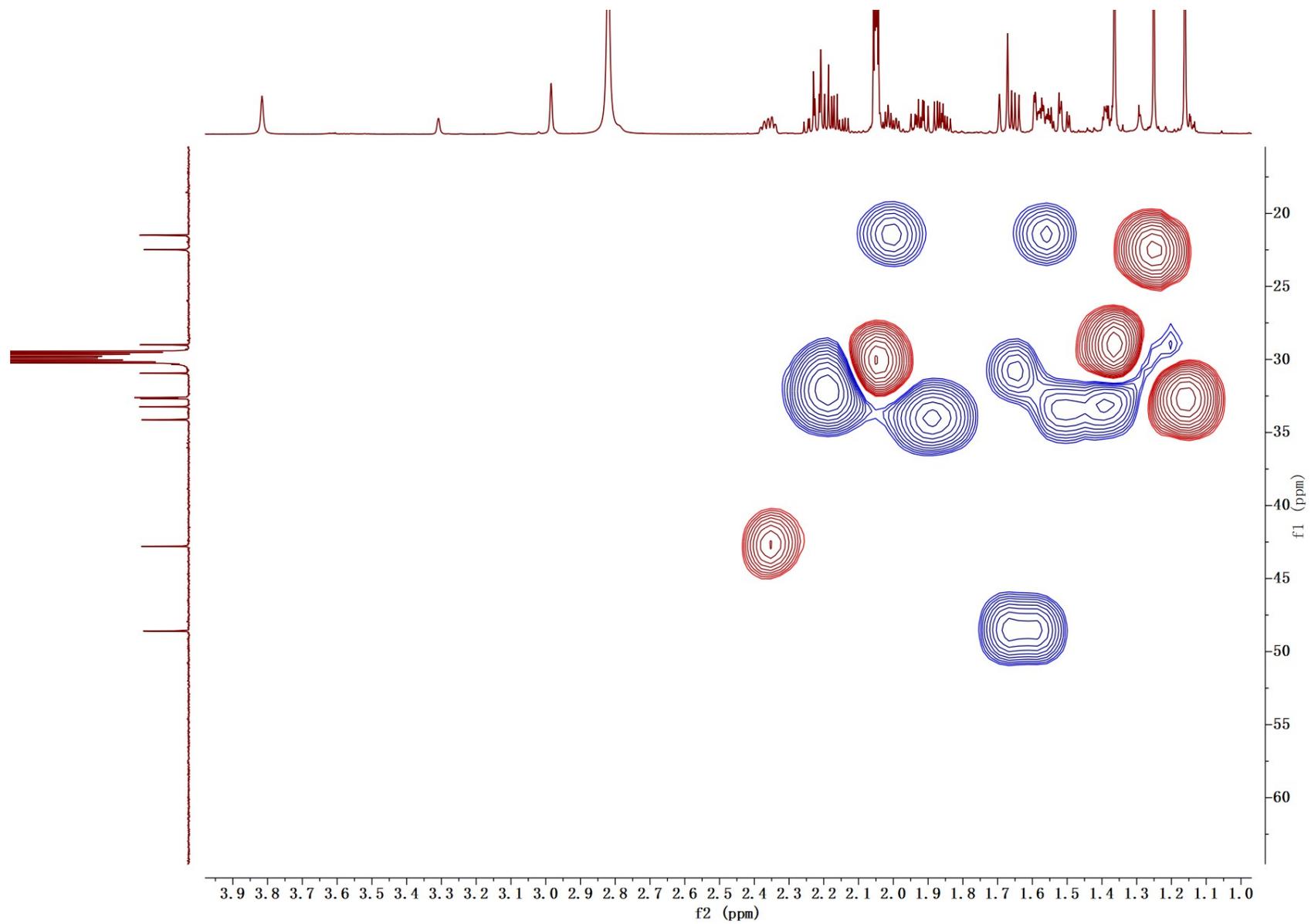


Figure S18. The HSQC spectrum of compound **2** in acetone- d_6 .

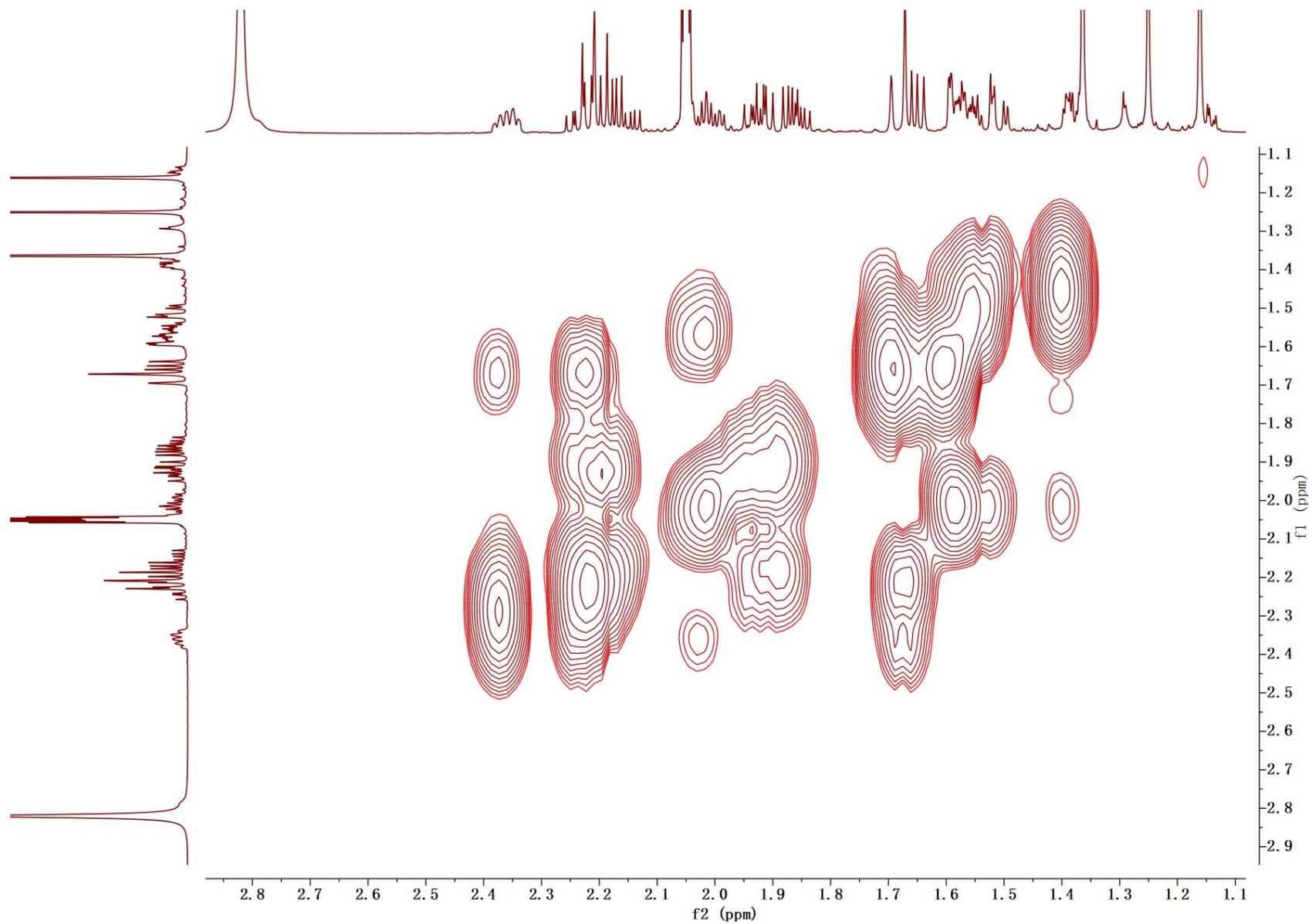


Figure S19. The ^1H - ^1H COSY spectrum of compound **2** in acetone- d_6 .

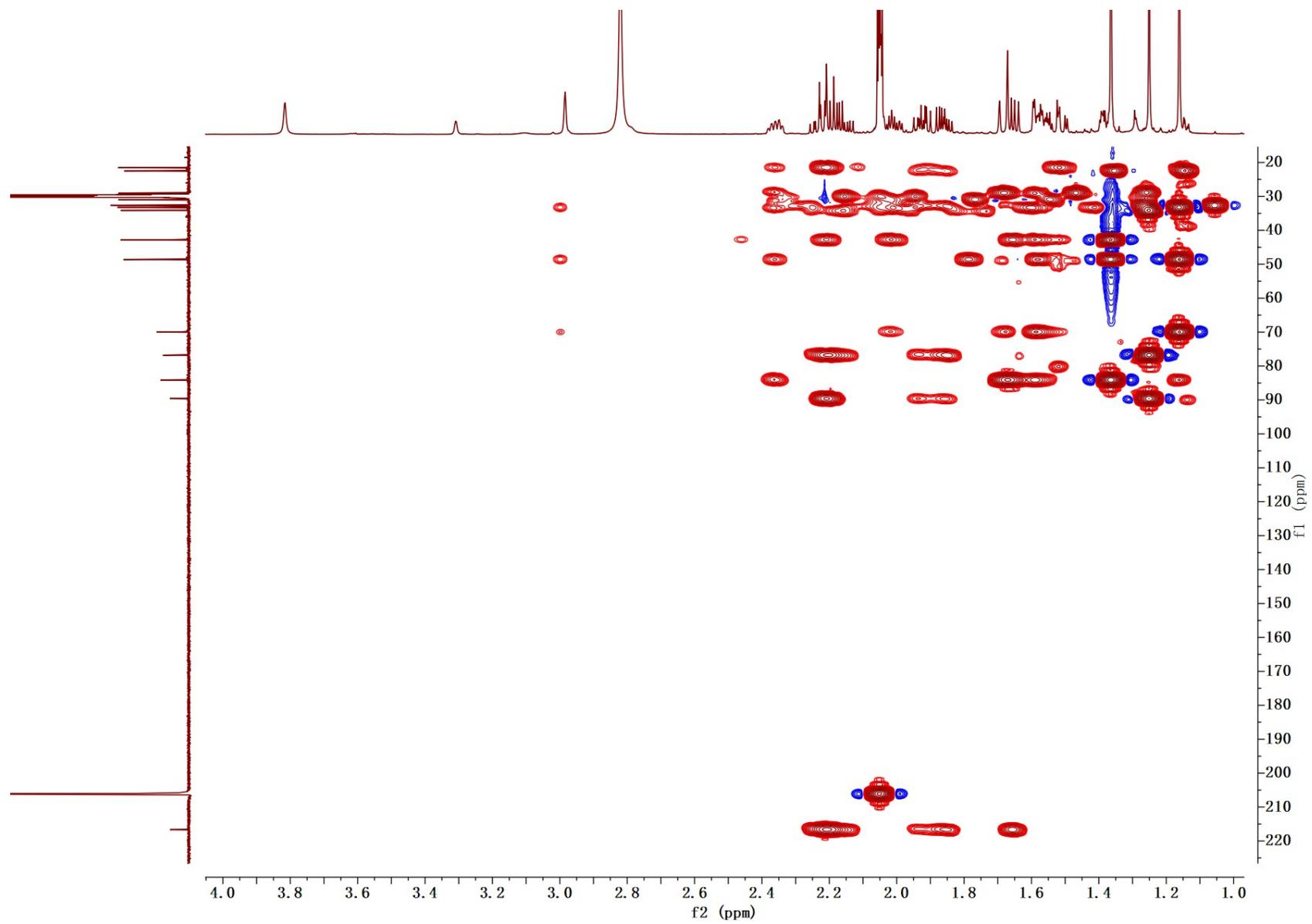


Figure S20. The HMBC spectrum of compound **2** in acetone-*d*₆.

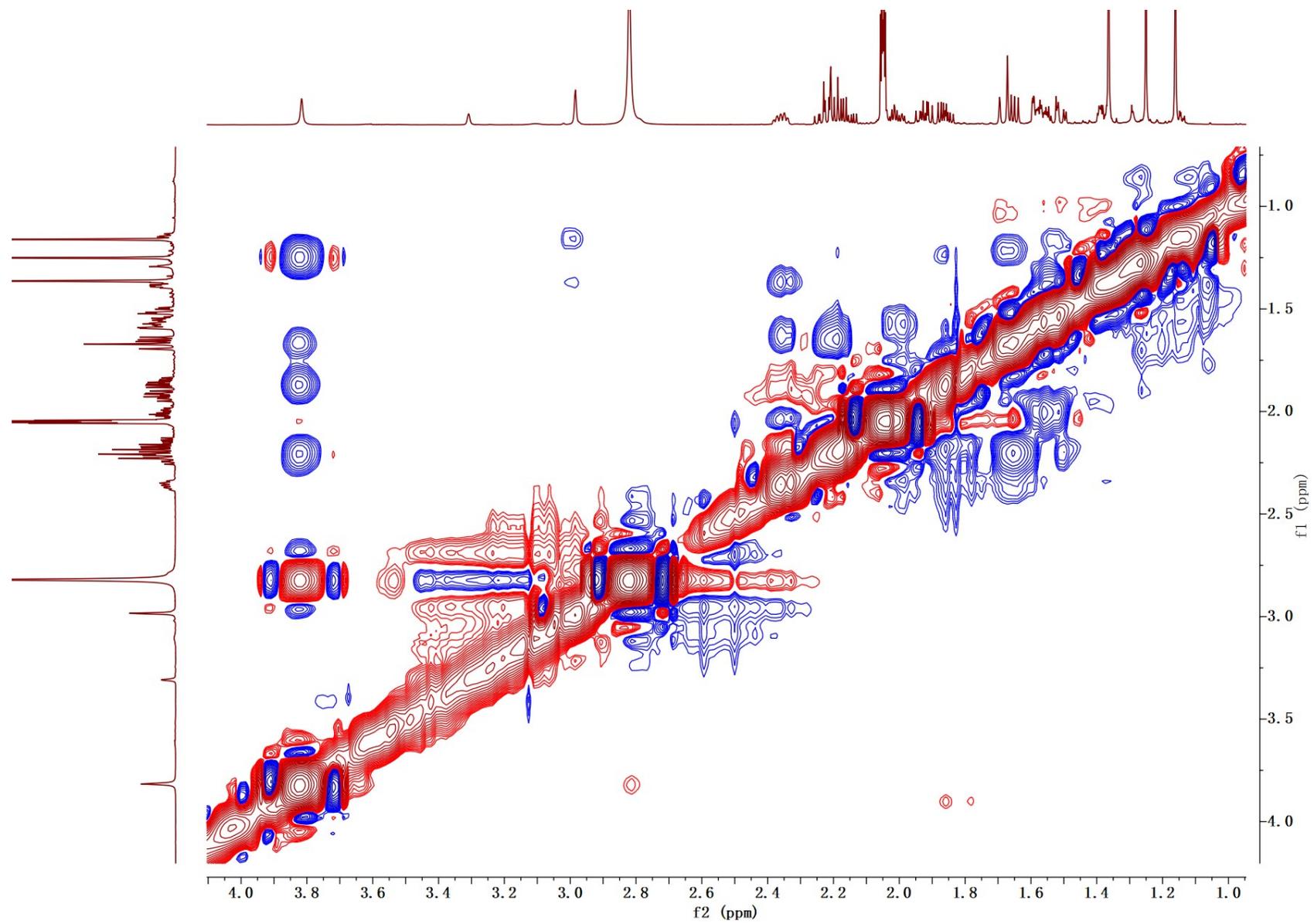


Figure S21. The NOESY spectrum of compound **2** in acetone- d_6 .

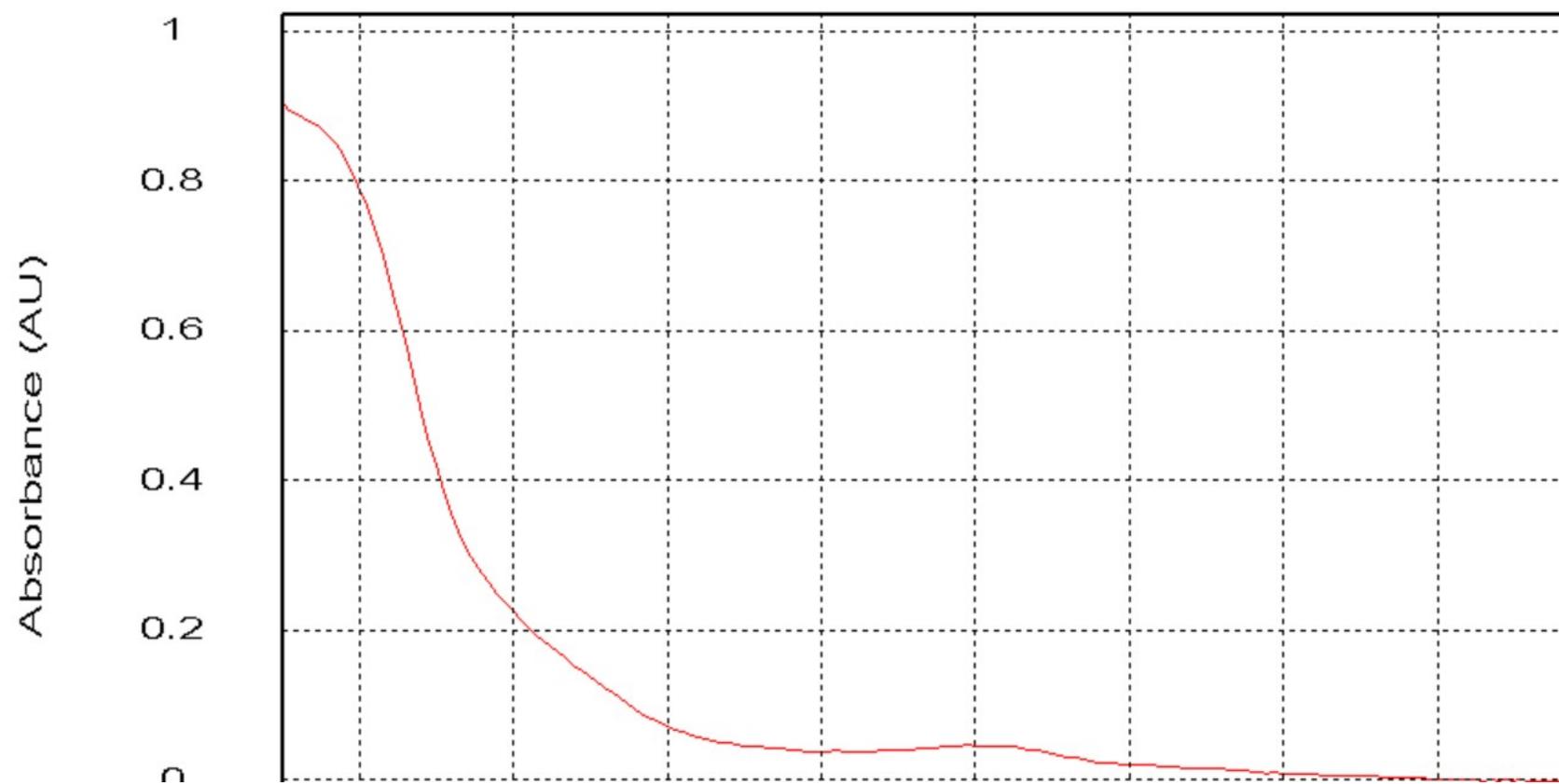


Figure S22. The UV spectrum of compound **3** in acetonitrile.

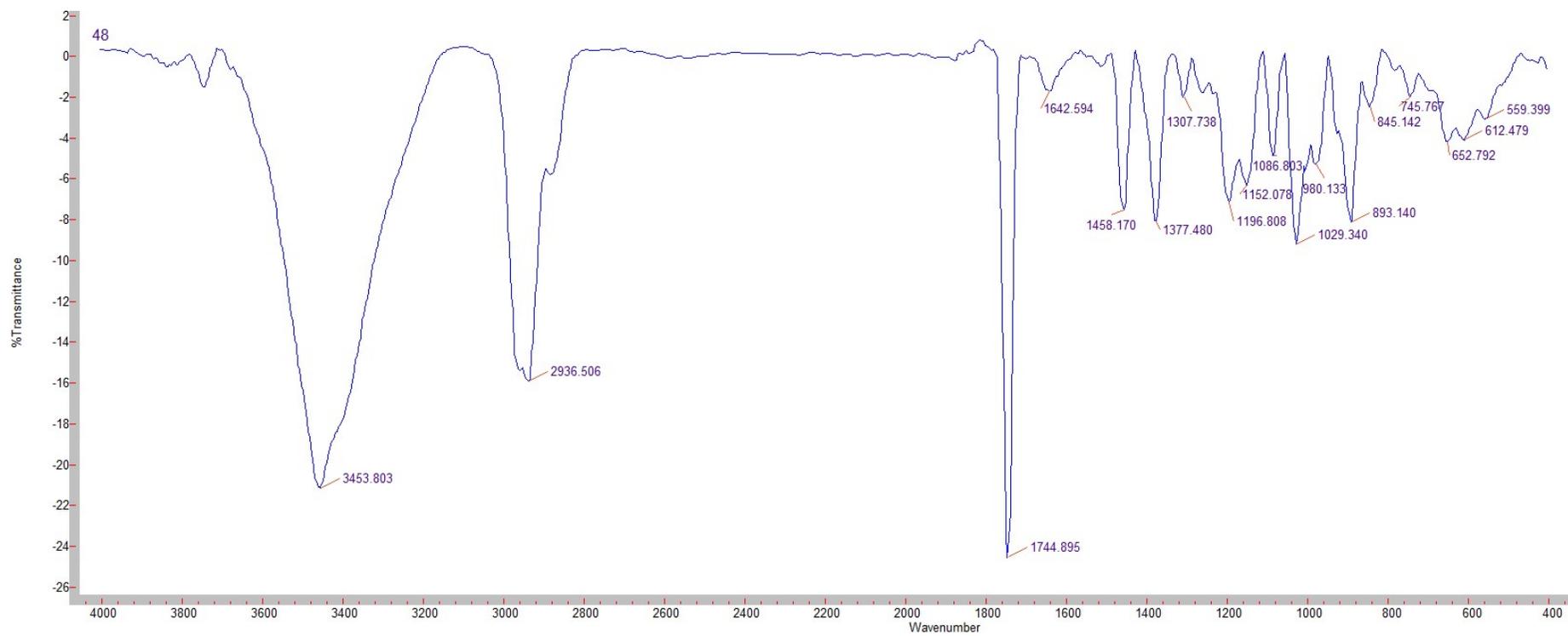


Figure S23. The IR spectrum of compound **3**.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -3.0, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Even Electron Ions

106 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
291.1576	291.1572	0.4	1.4	3.5	C15 H24 O4 Na	740.0	0.466	62.76	15	24	4	1
	291.1596	-2.0	-6.9	6.5	C17 H23 O4	740.5	0.988	37.24	17	23	4	

211.40 (0.176) Cm (25.59)

1: TOF MS ES+

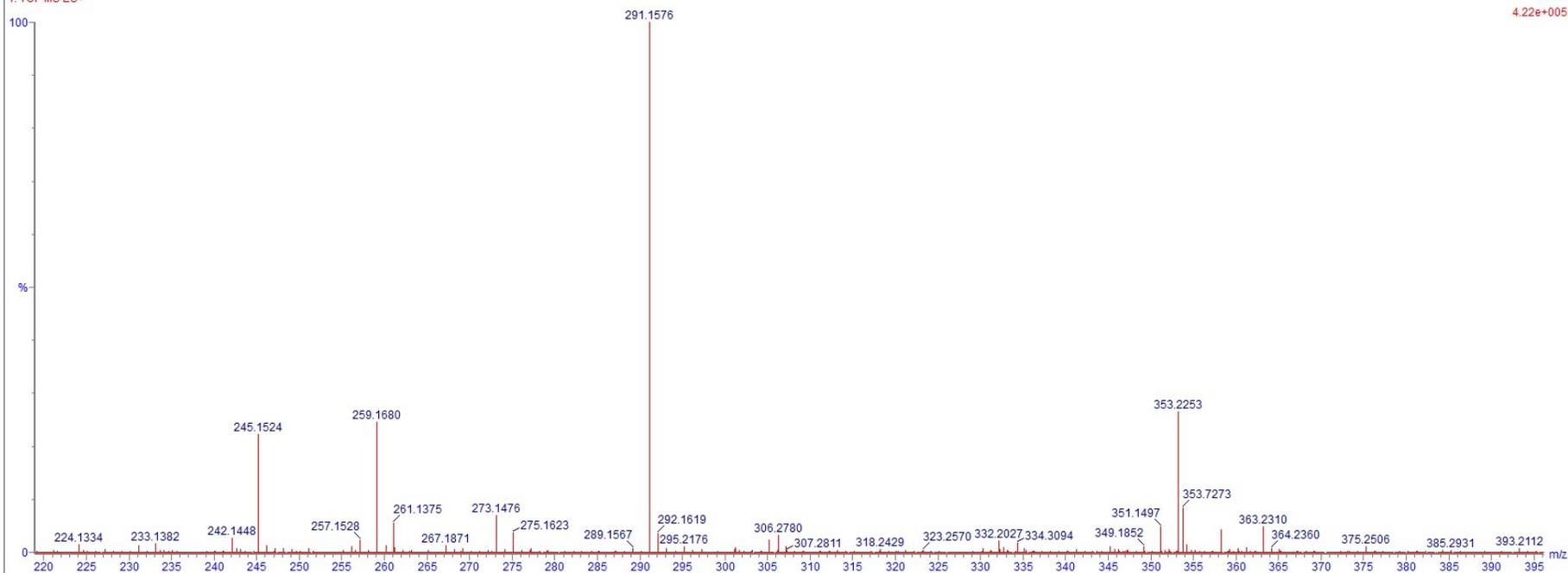


Figure S24. The (+)-HRESIMS spectroscopic data of compound **3**.

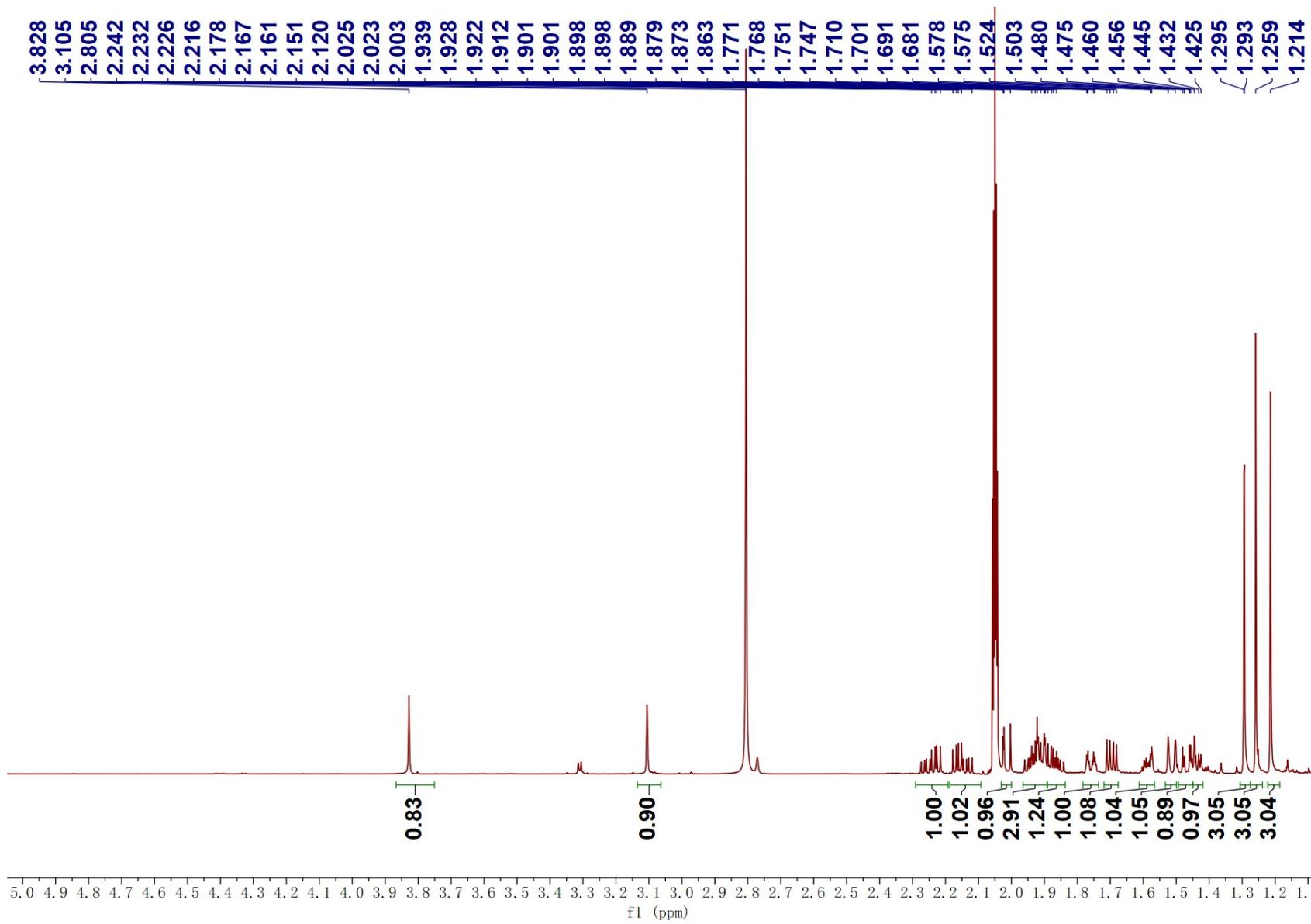


Figure S25. The ^1H NMR spectrum of compound **3** in acetone- d_6 .

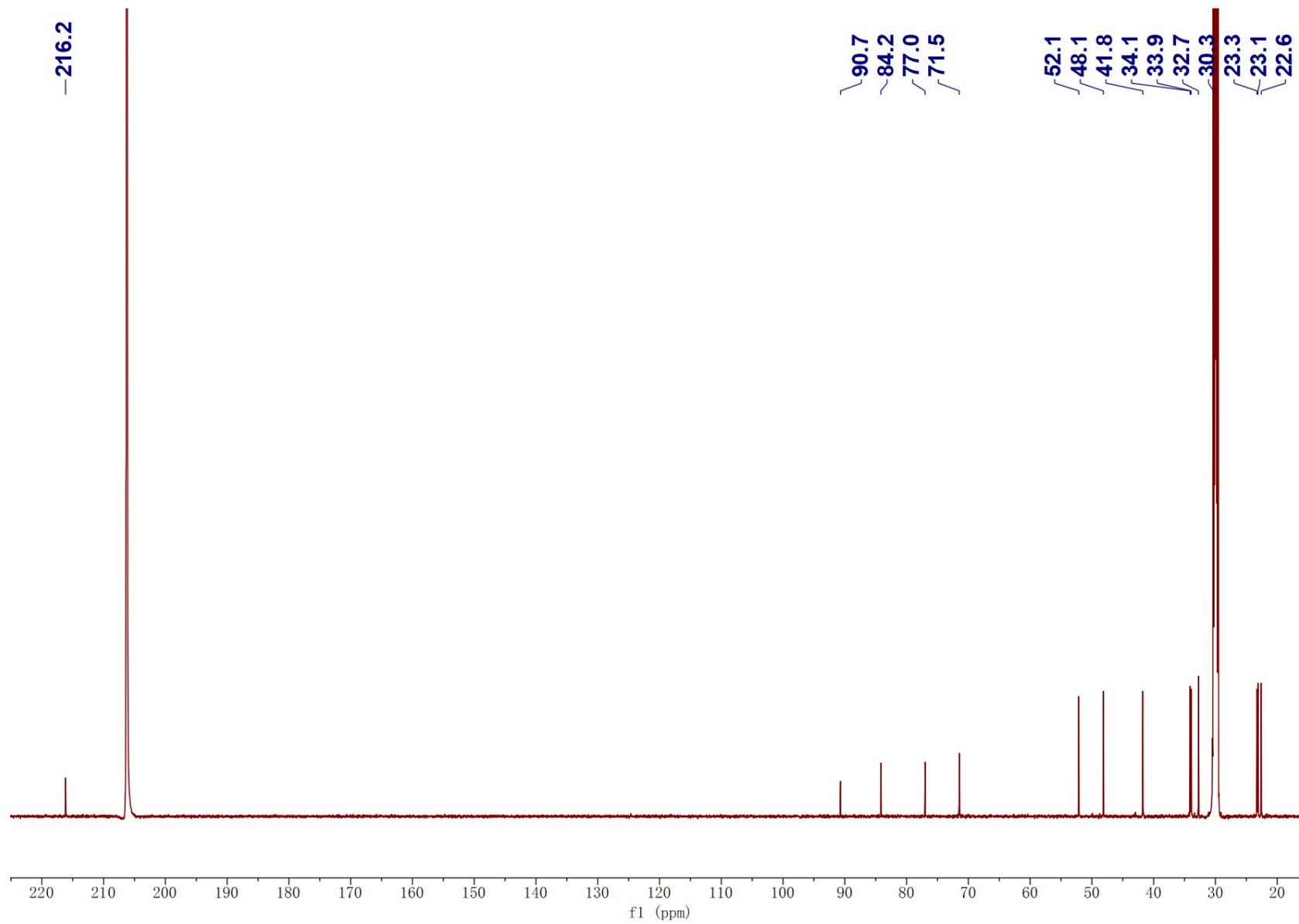


Figure S26. The ^{13}C NMR spectrum of compound **3** in acetone- d_6 .

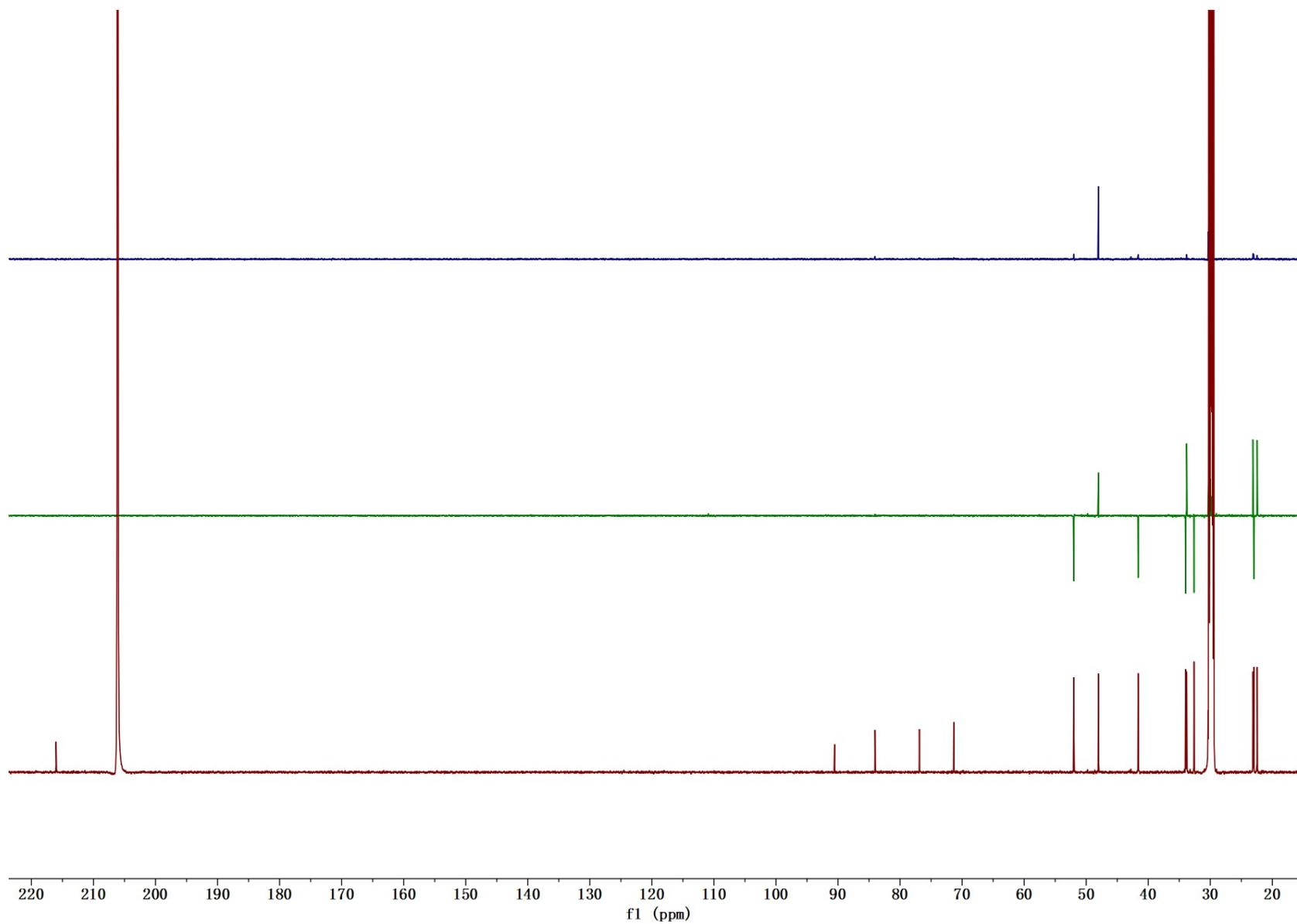


Figure S27. The DEPT spectrum of compound **3** in acetone- d_6 .

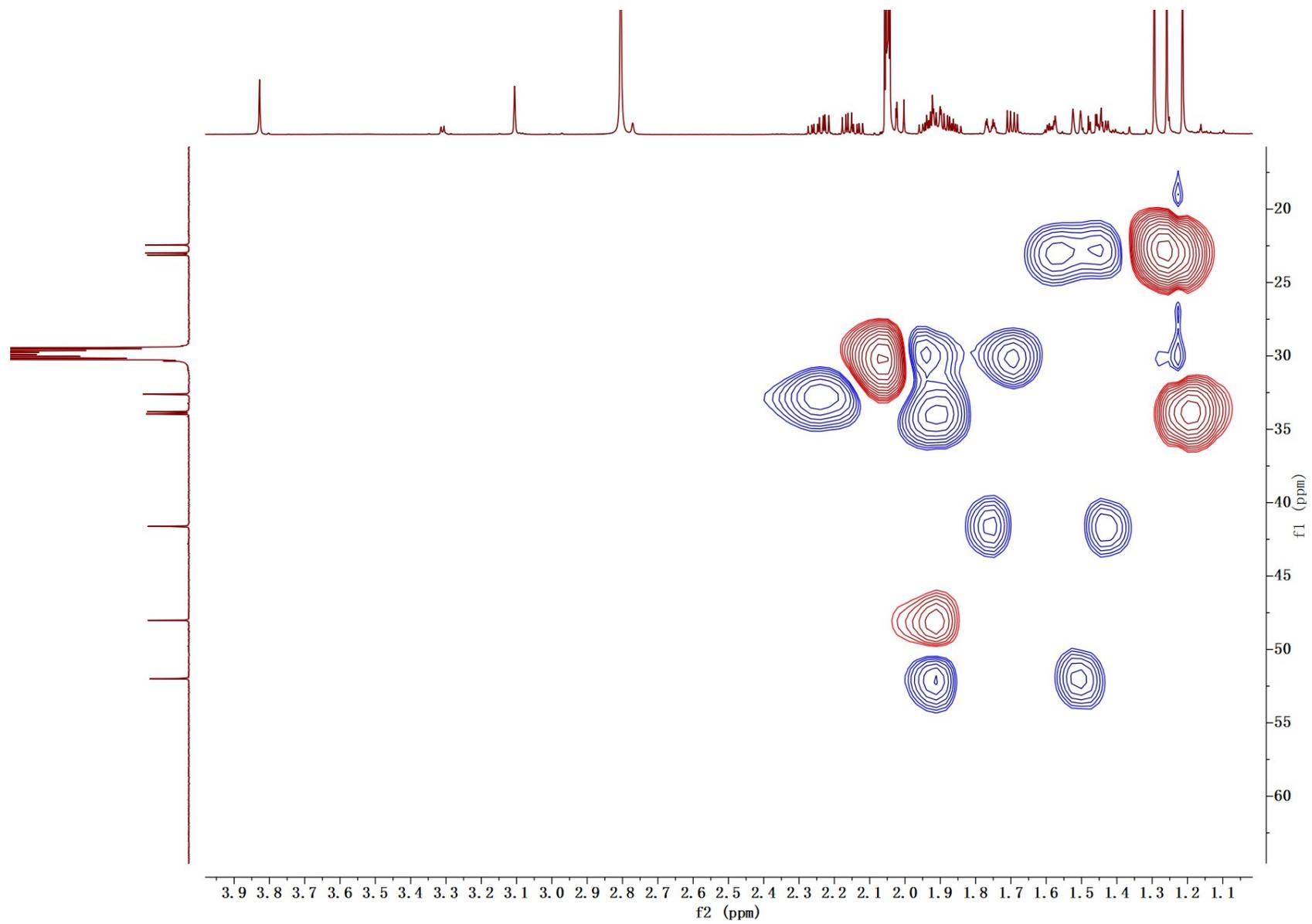


Figure S28. The HSQC spectrum of compound **3** in acetone-*d*₆.

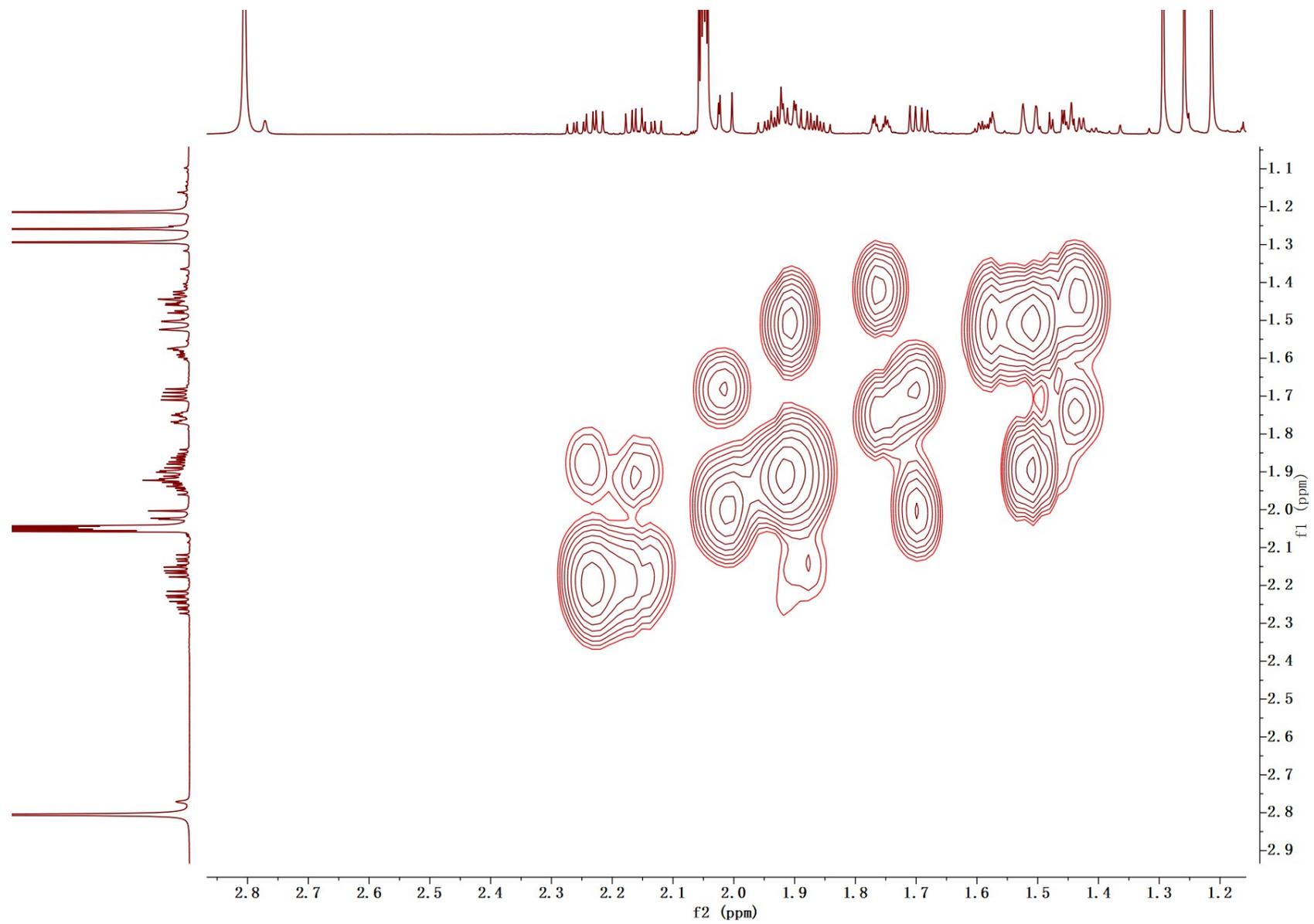


Figure S29. The ^1H - ^1H COSY spectrum of compound **3** in acetone- d_6 .

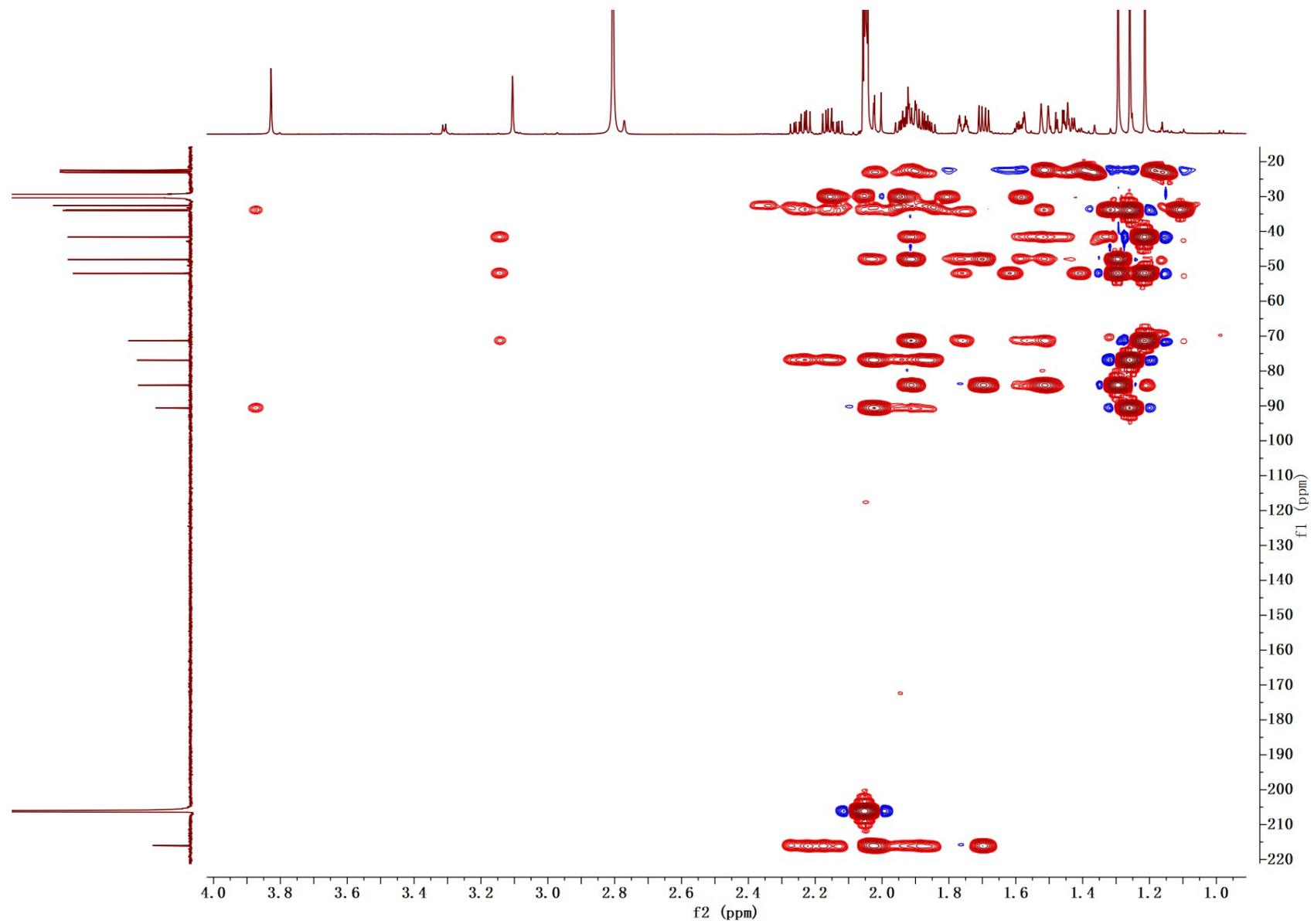


Figure S30. The HMBC spectrum of compound **3** in acetone-*d*₆.

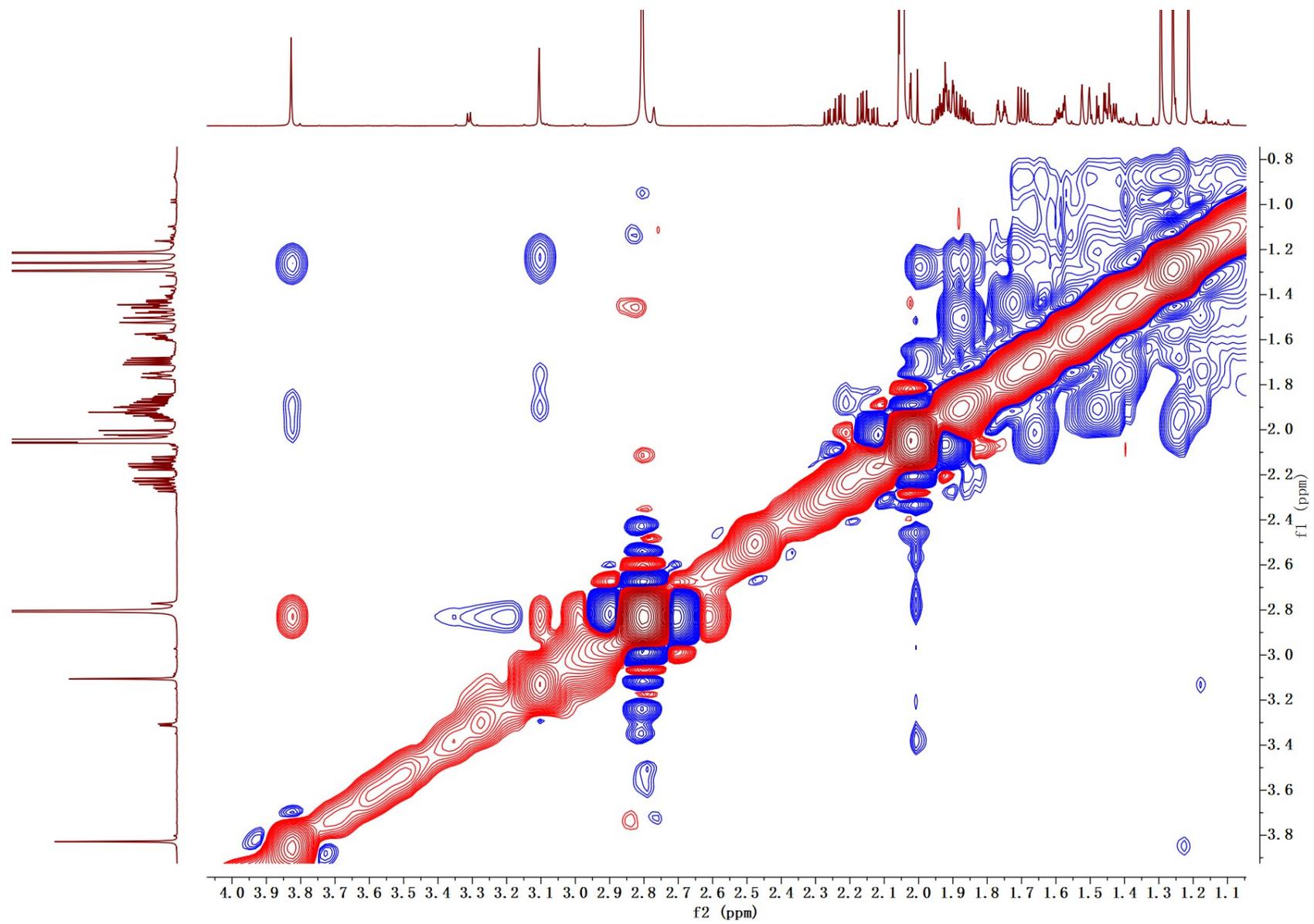


Figure S31. The NOESY spectrum of compound **3** in acetone- d_6 .

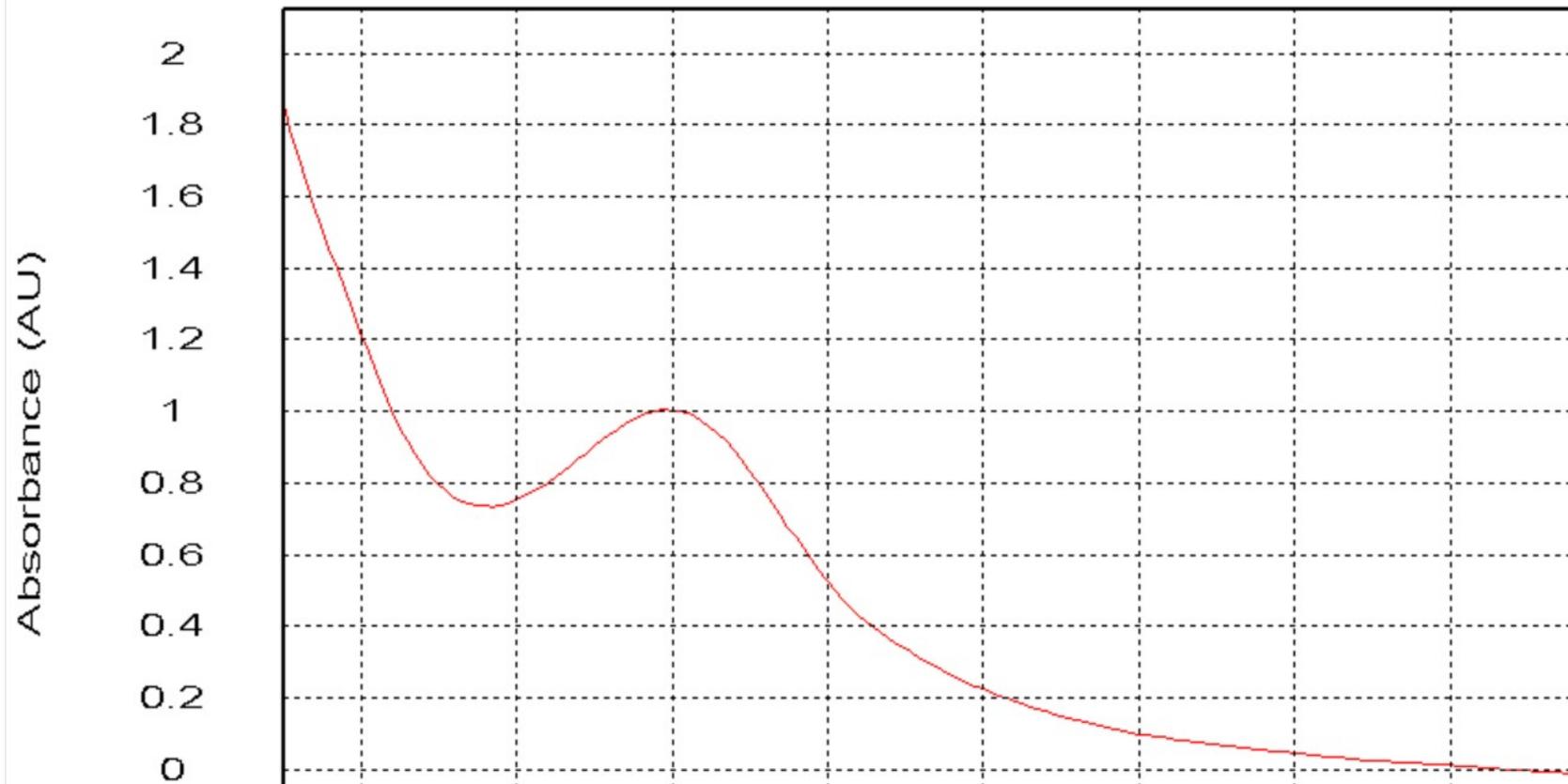


Figure S32. The UV spectrum of compound **4** in acetonitrile.

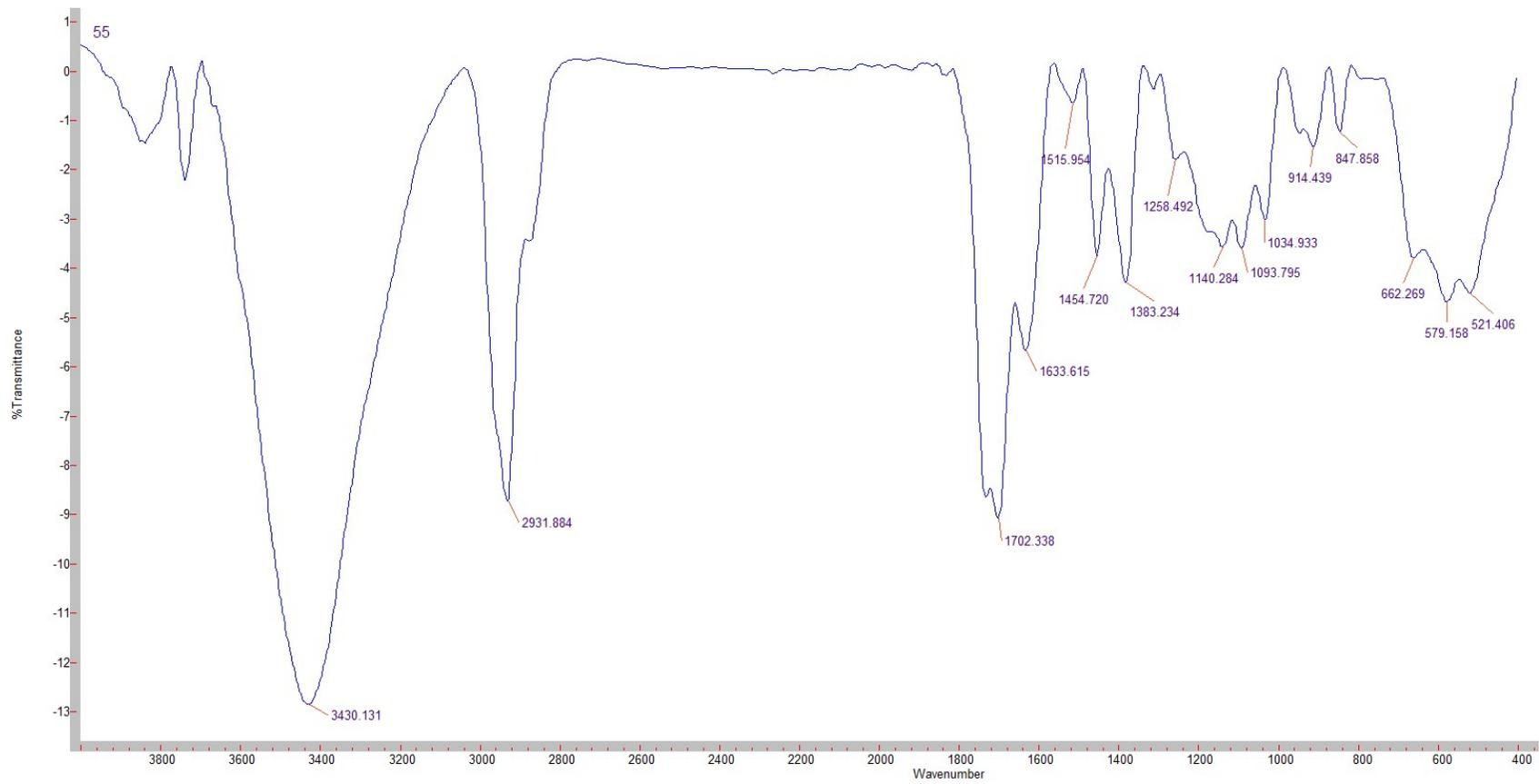


Figure S33. The IR spectrum of compound **4**.

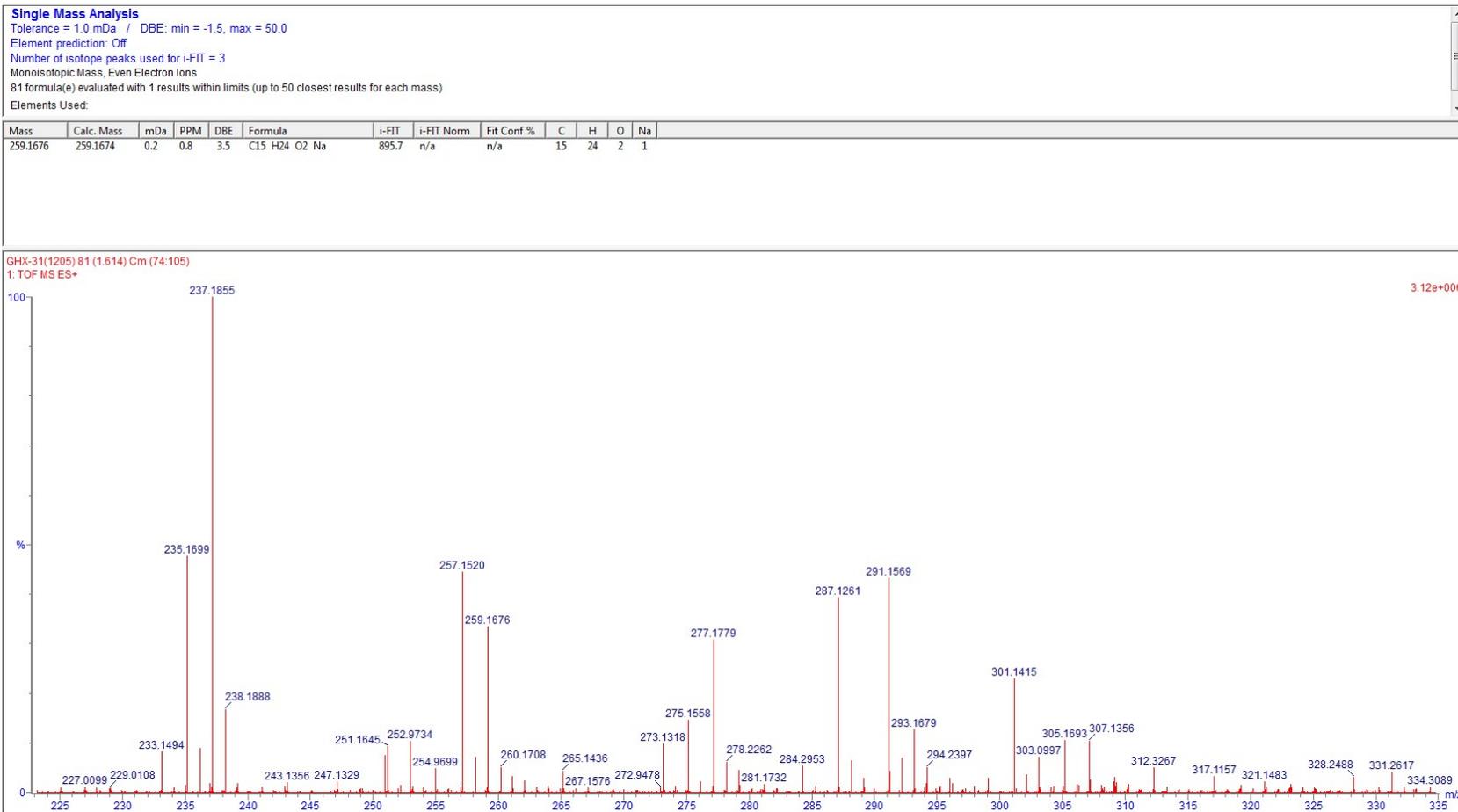


Figure S34. The (+)-HRESIMS spectroscopic data of compound **4**.

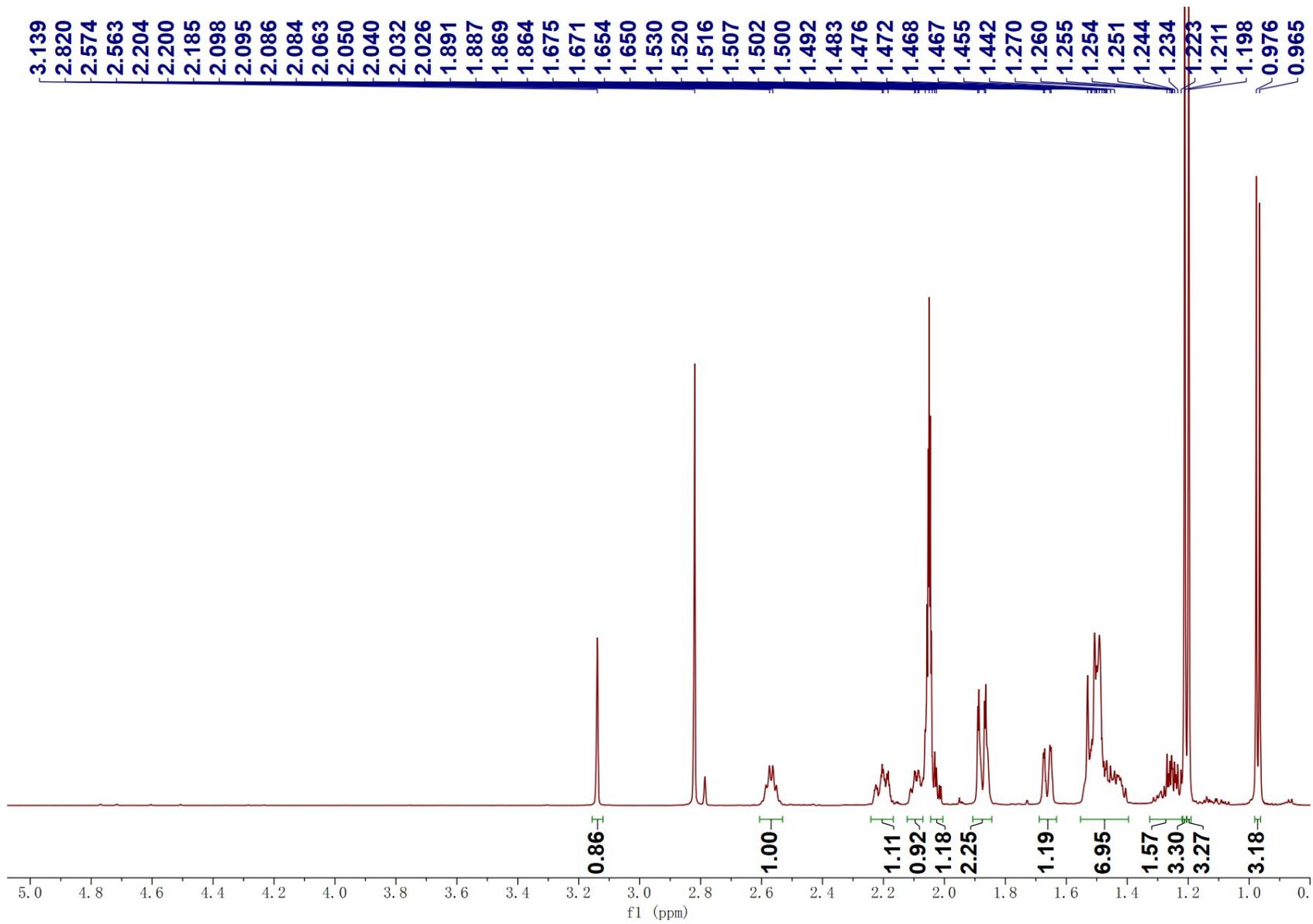


Figure S35. The ^1H NMR spectrum of compound 4 in acetone- d_6 .

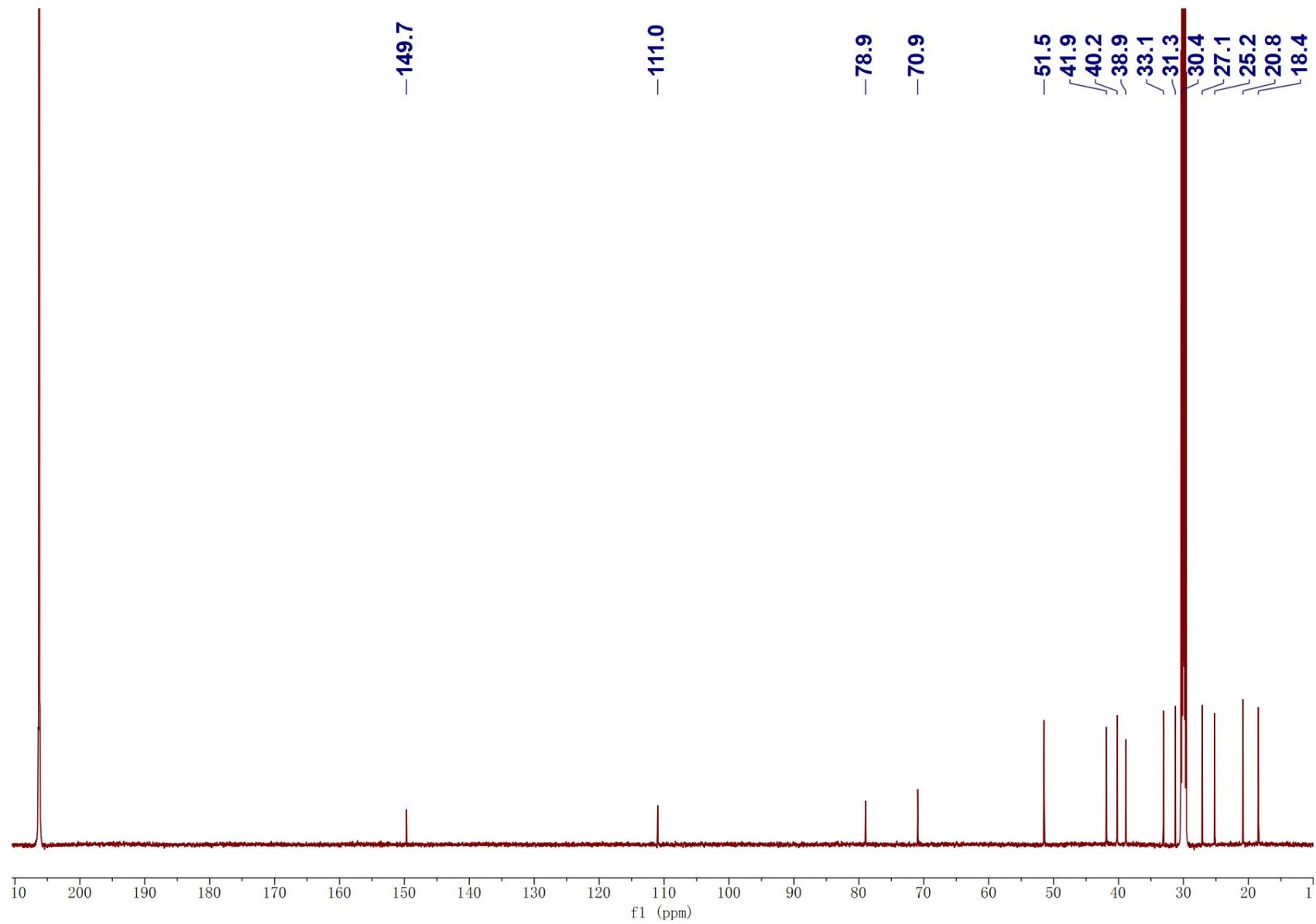


Figure S36. The ^{13}C NMR spectrum of compound **4** in acetone- d_6 .

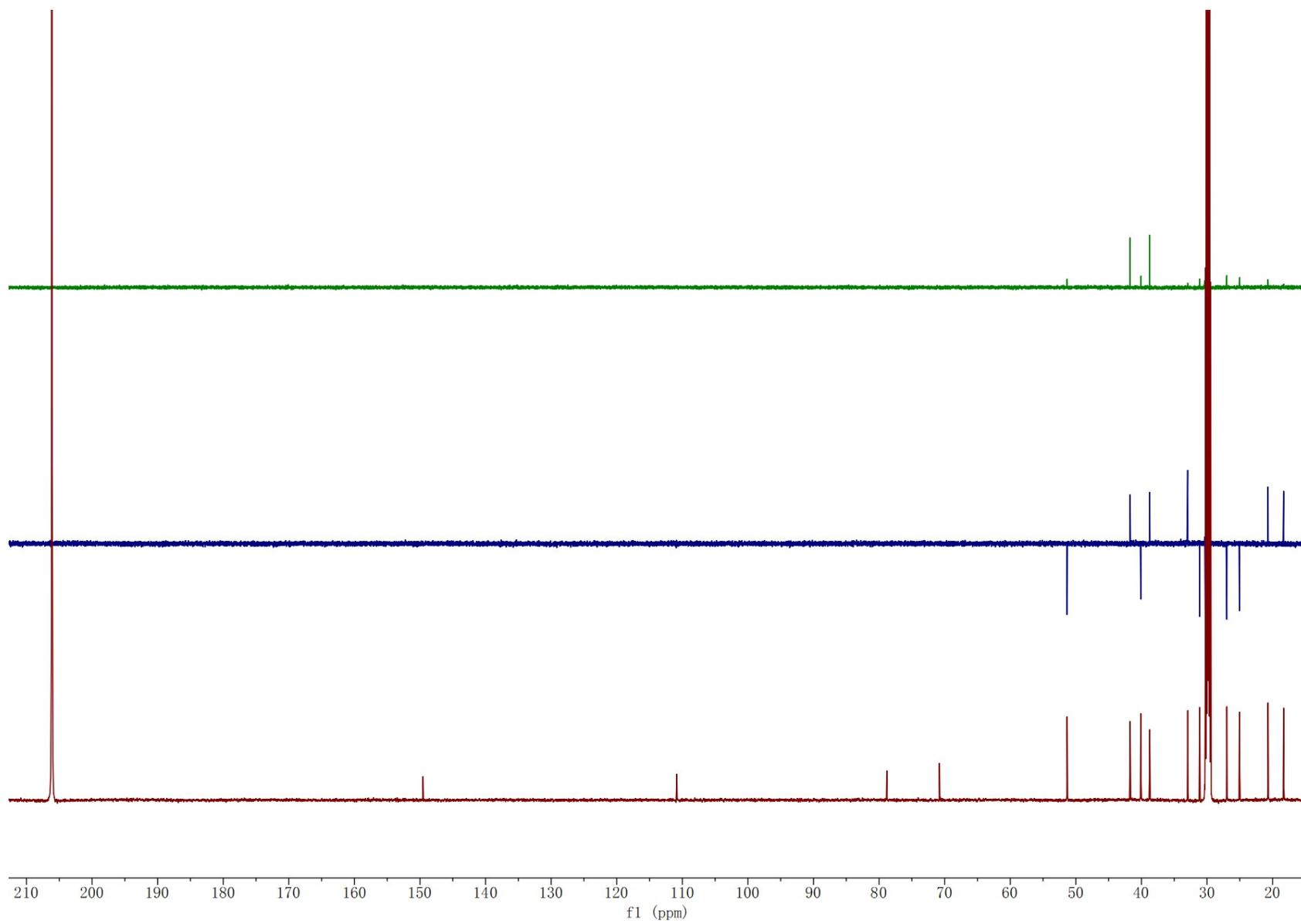


Figure S37. The DEPT spectrum of compound **4** in acetone- d_6 .

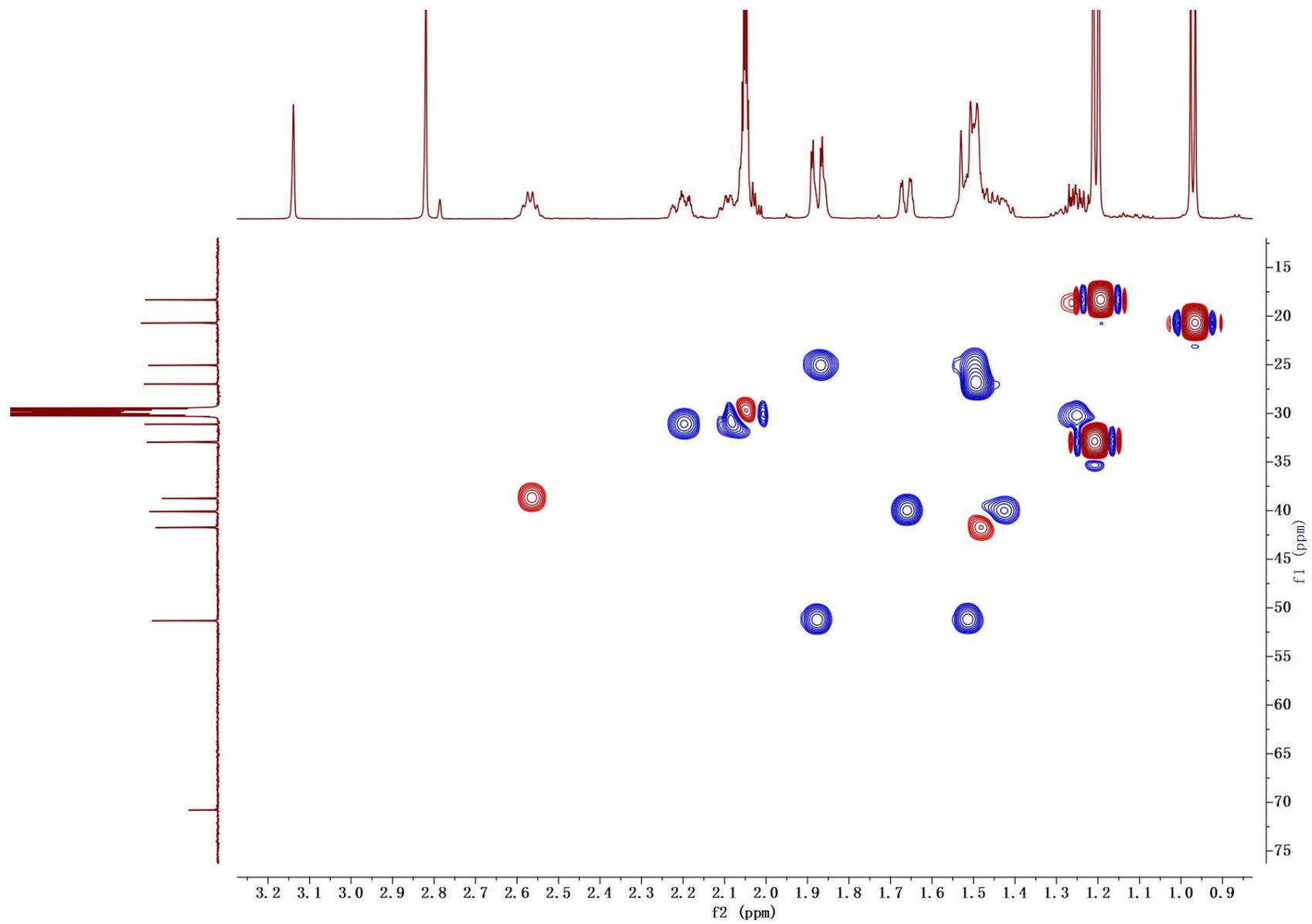


Figure S38. The HSQC spectrum of compound 4 in acetone- d_6 .

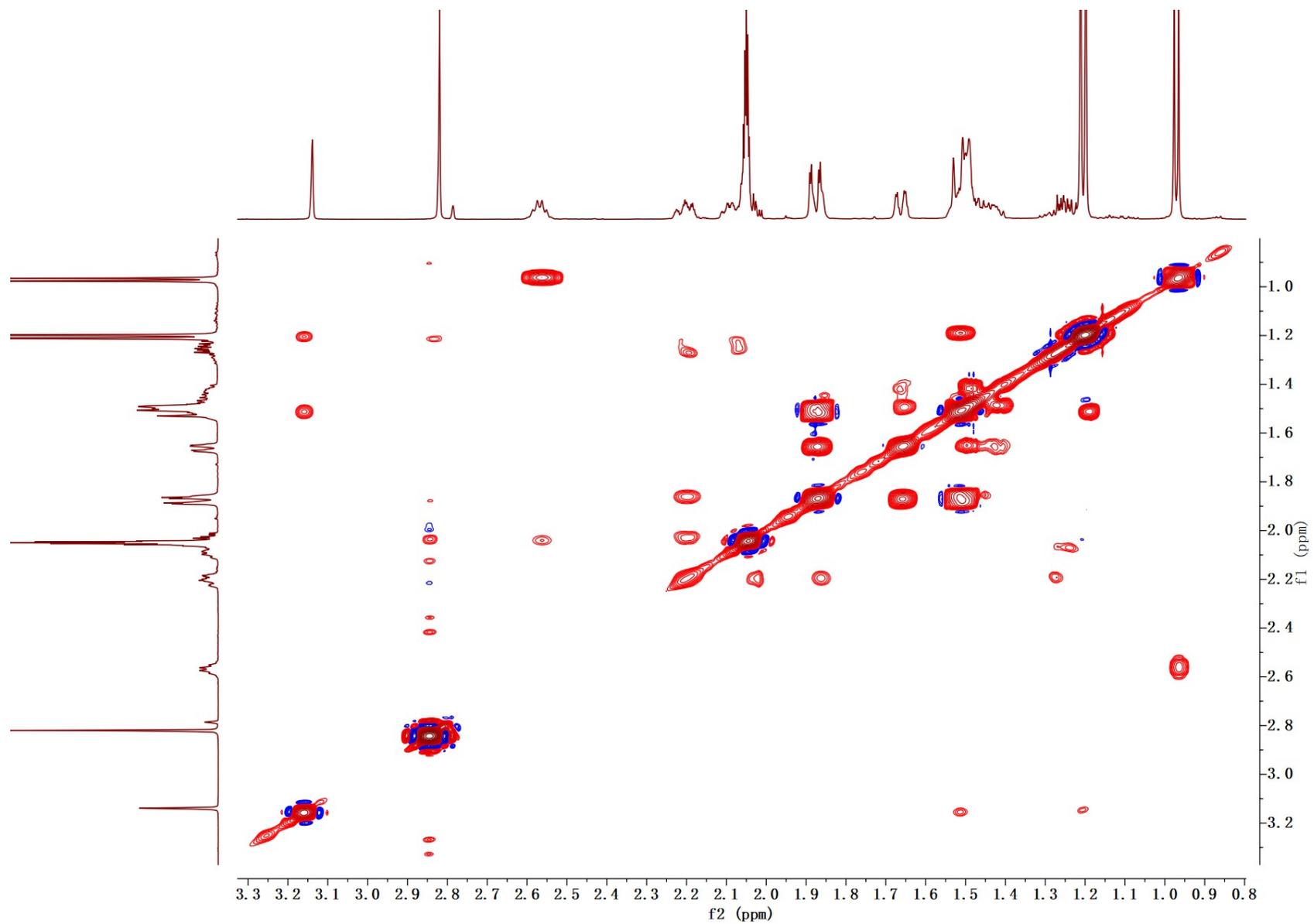


Figure S39. The ^1H - ^1H COSY spectrum of compound **4** in acetone- d_6 .

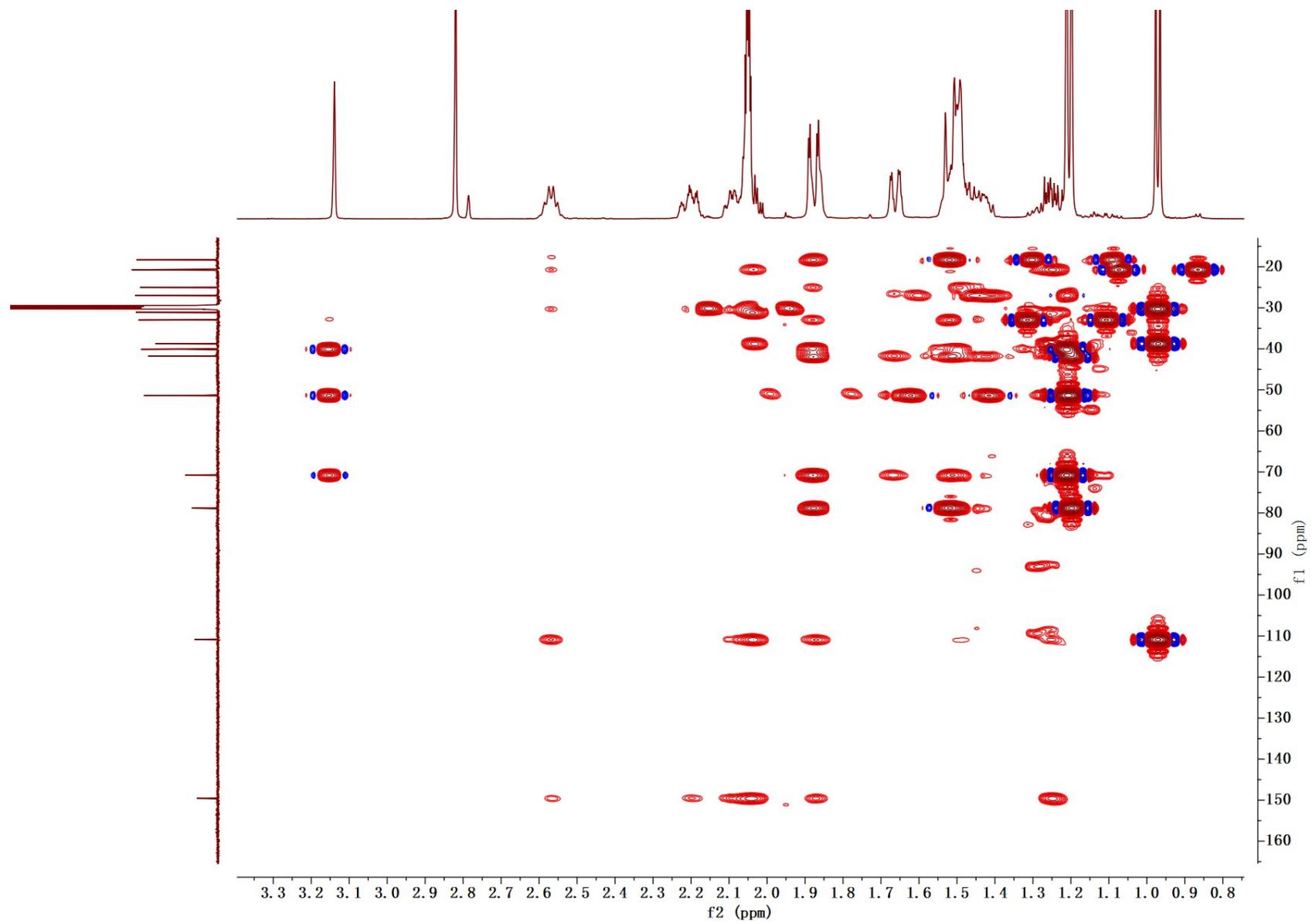


Figure S40. The HMBC spectrum of compound **4** in acetone- d_6 .

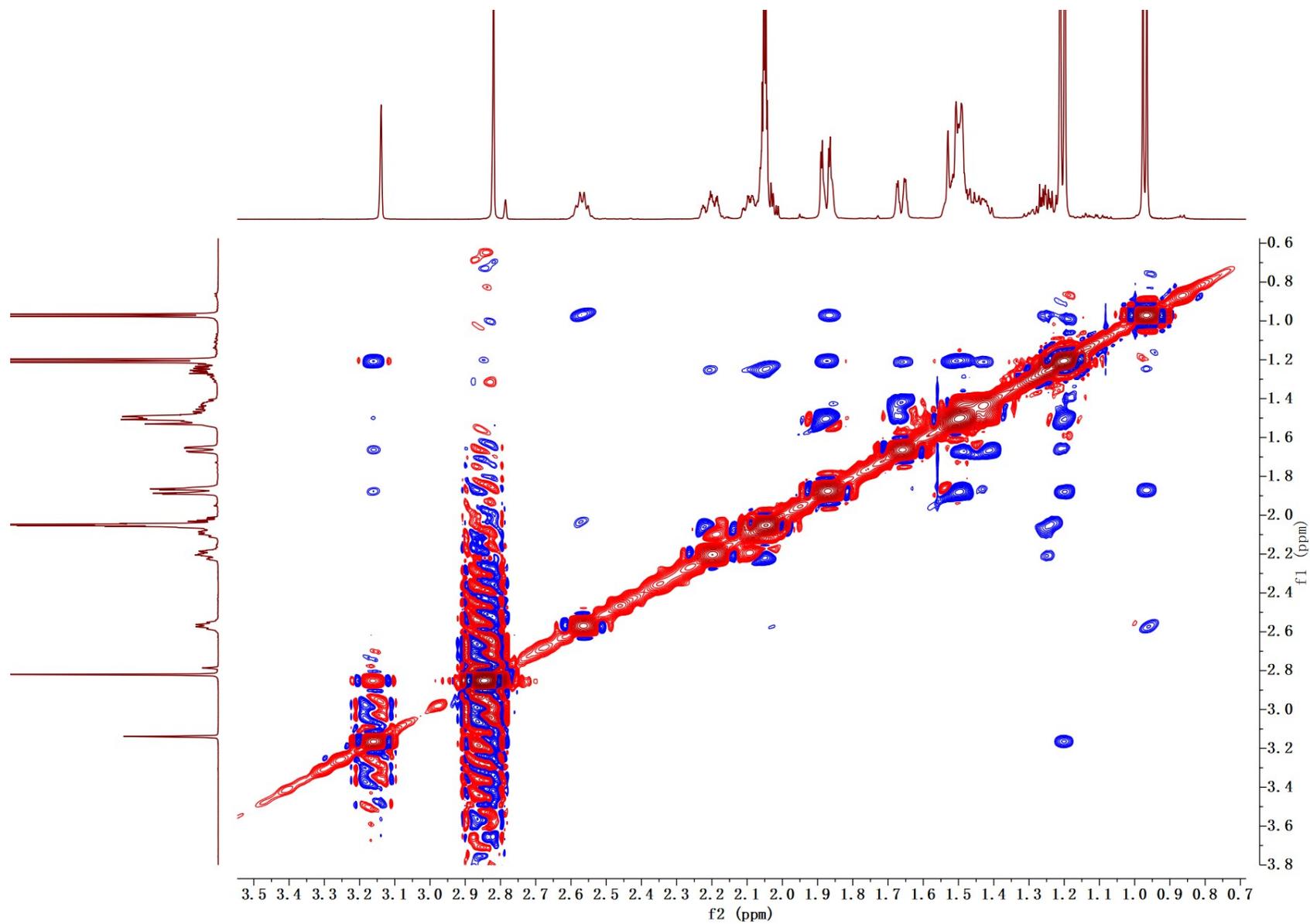


Figure S41. The NOESY spectrum of compound **4** in acetone- d_6 .

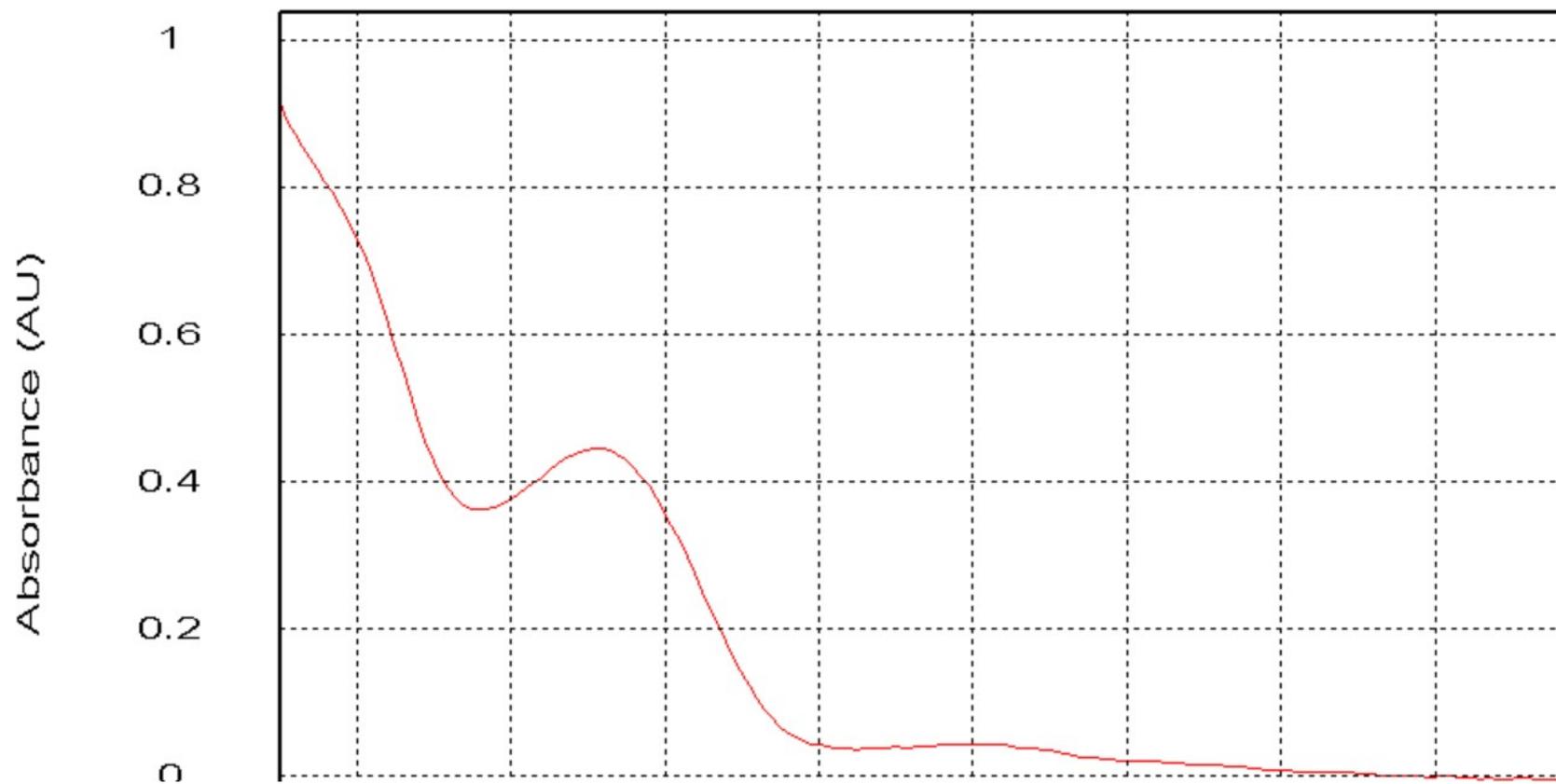


Figure S42. The UV spectrum of compound **5** in acetonitrile.

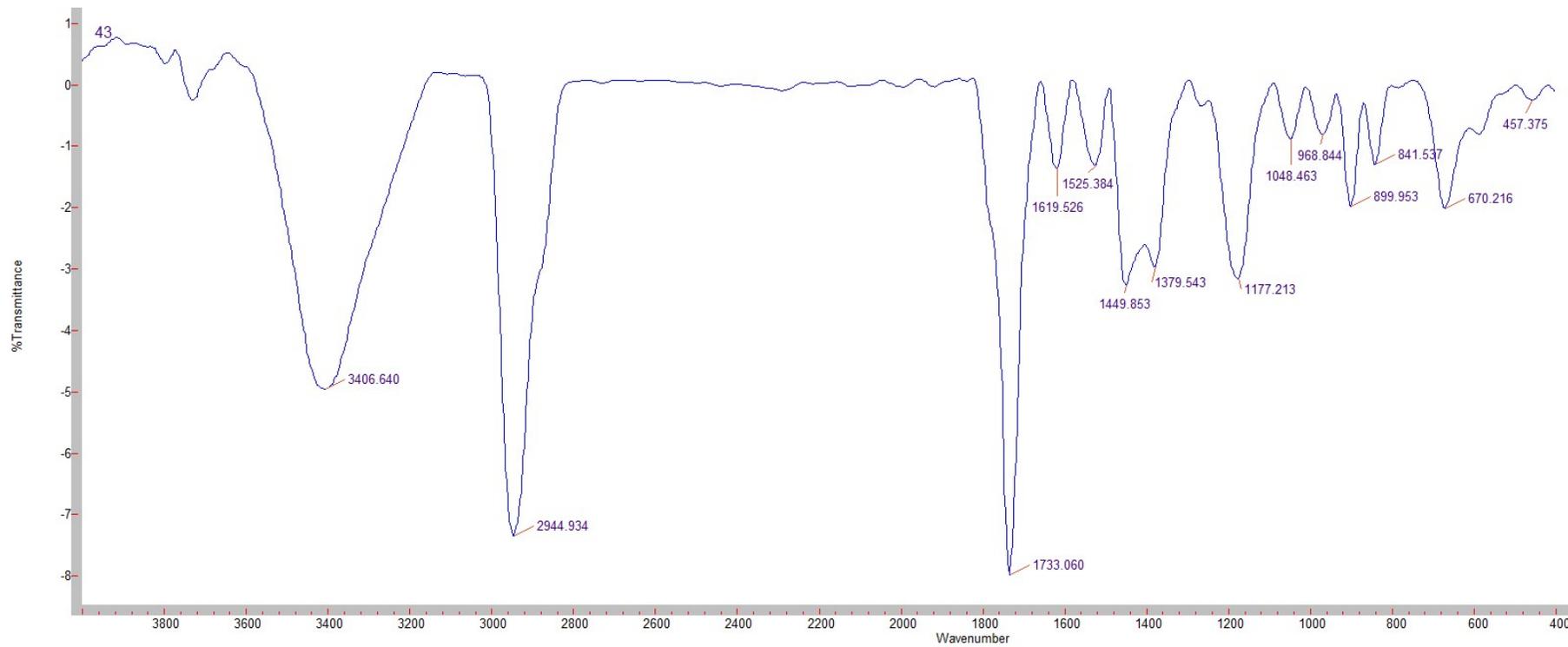


Figure S43. The IR spectrum of compound **5**.

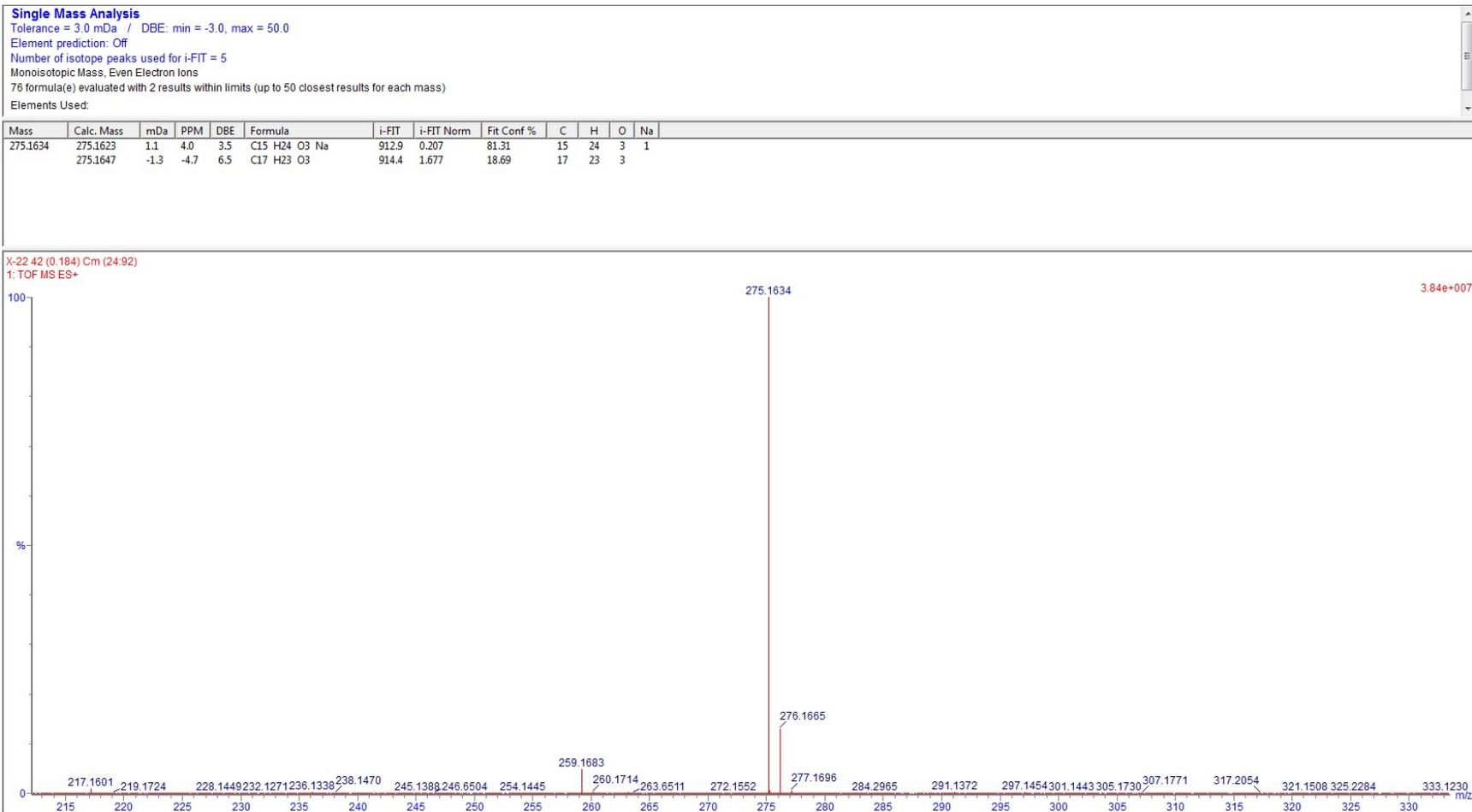


Figure S44. The (+)-HRESIMS spectroscopic data of compound **5**.

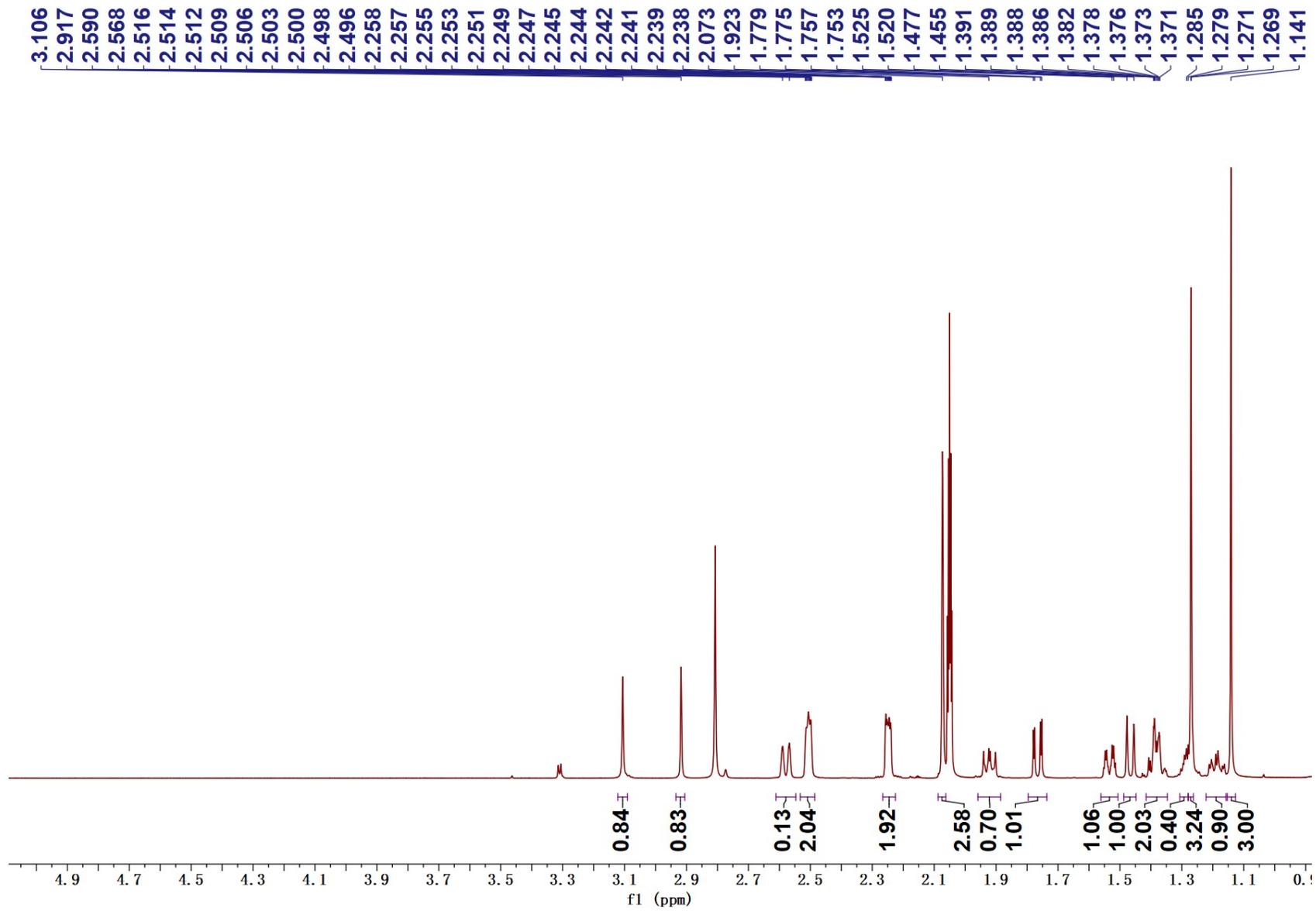


Figure S45. The ^1H NMR spectrum of compound **5** in acetone- d_6 .

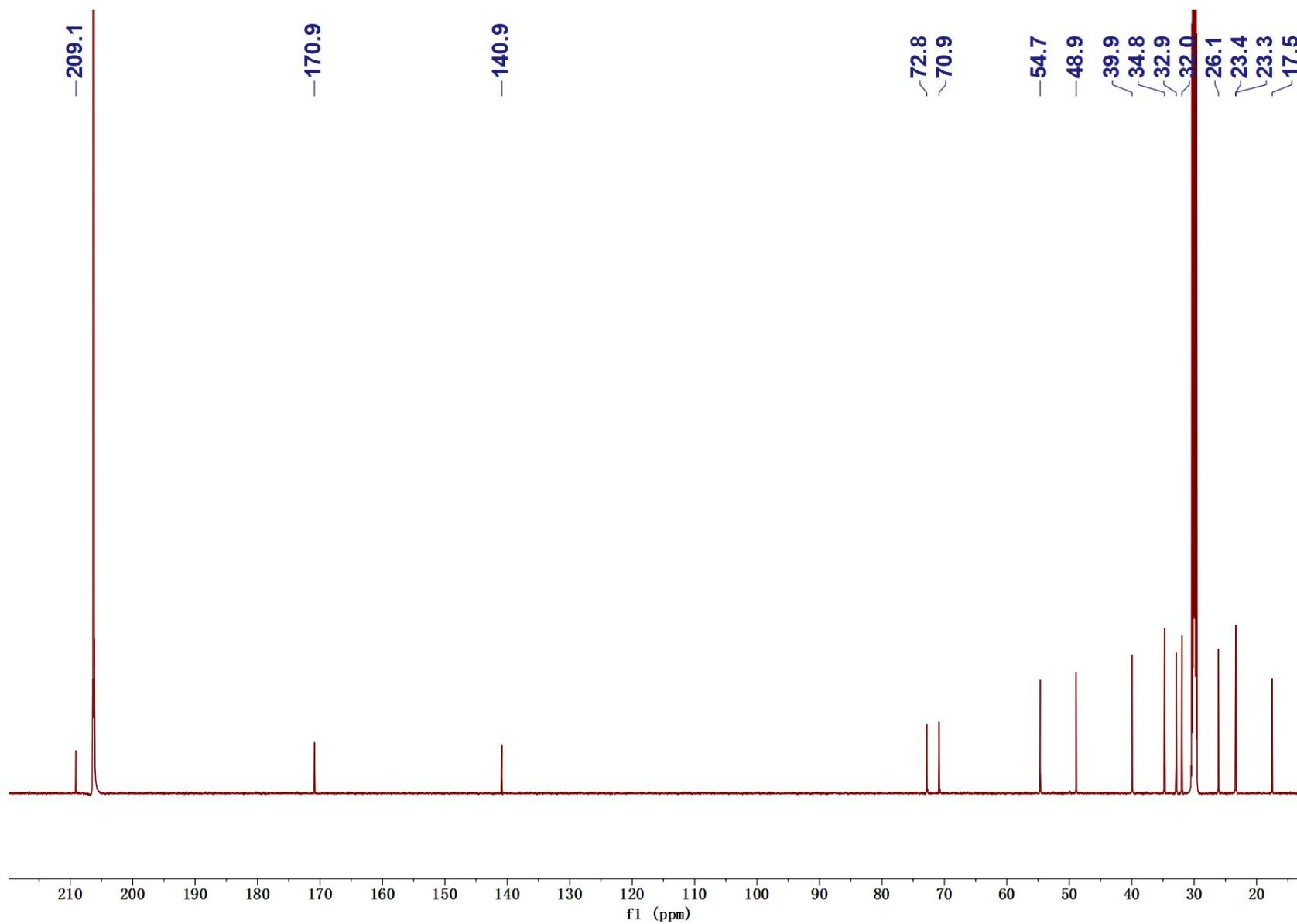


Figure S46. The ^{13}C NMR spectrum of compound 5 in acetone- d_6 .

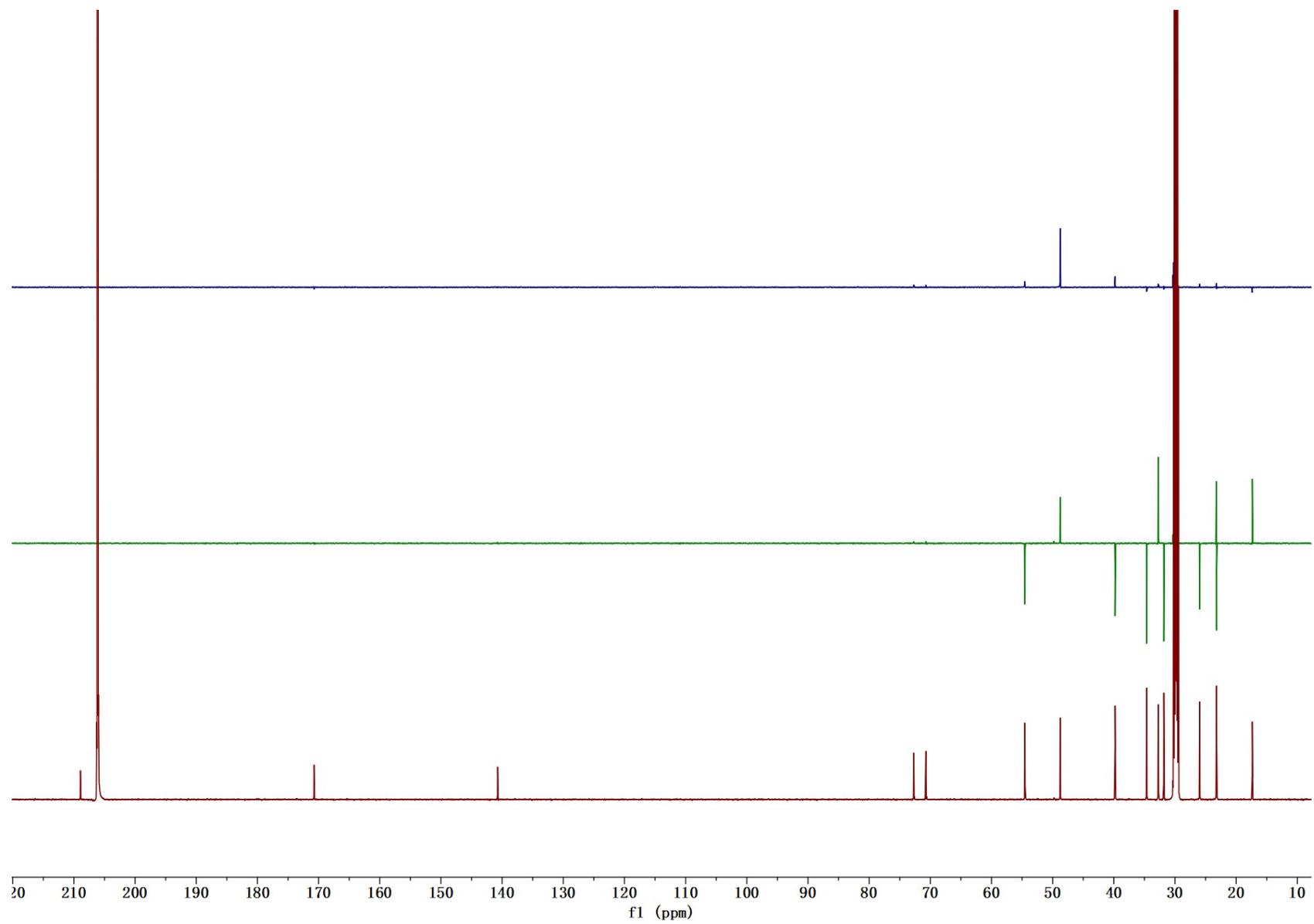


Figure S47. The DEPT spectrum of compound **5** in acetone- d_6 .

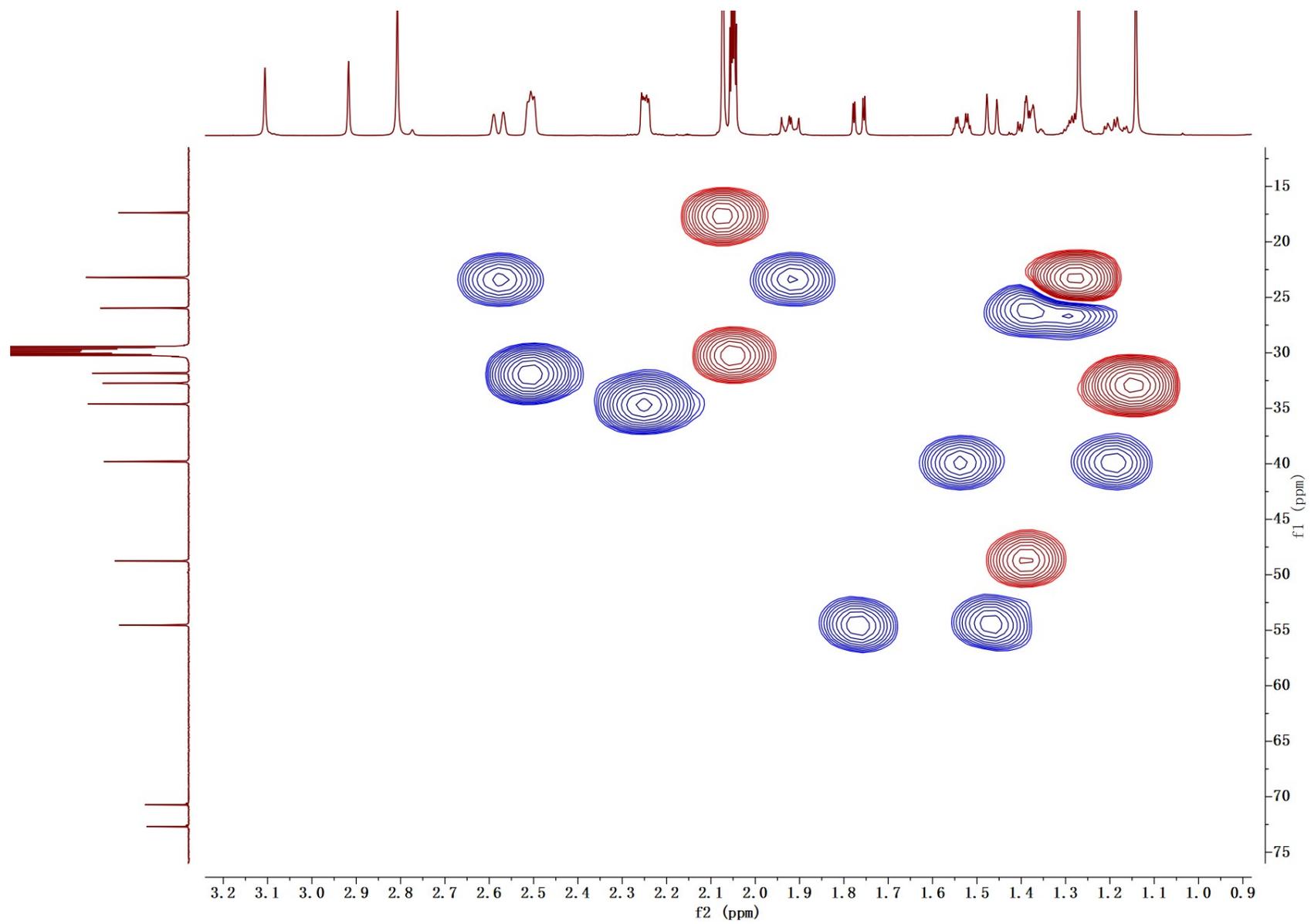


Figure S48. The HSQC spectrum of compound **5** in acetone- d_6 .

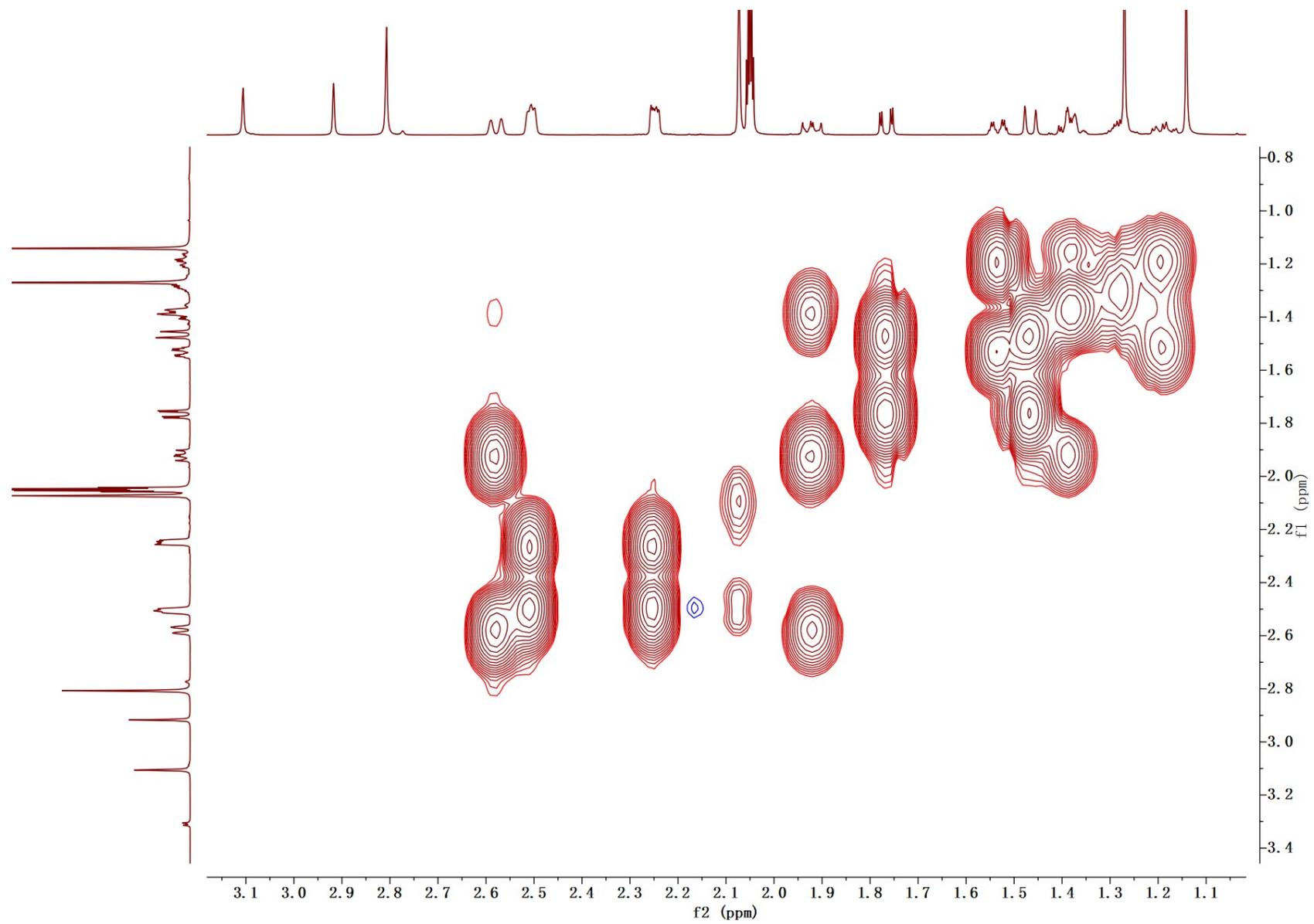


Figure S49. The ^1H - ^1H COSY spectrum of compound **5** in acetone- d_6 .

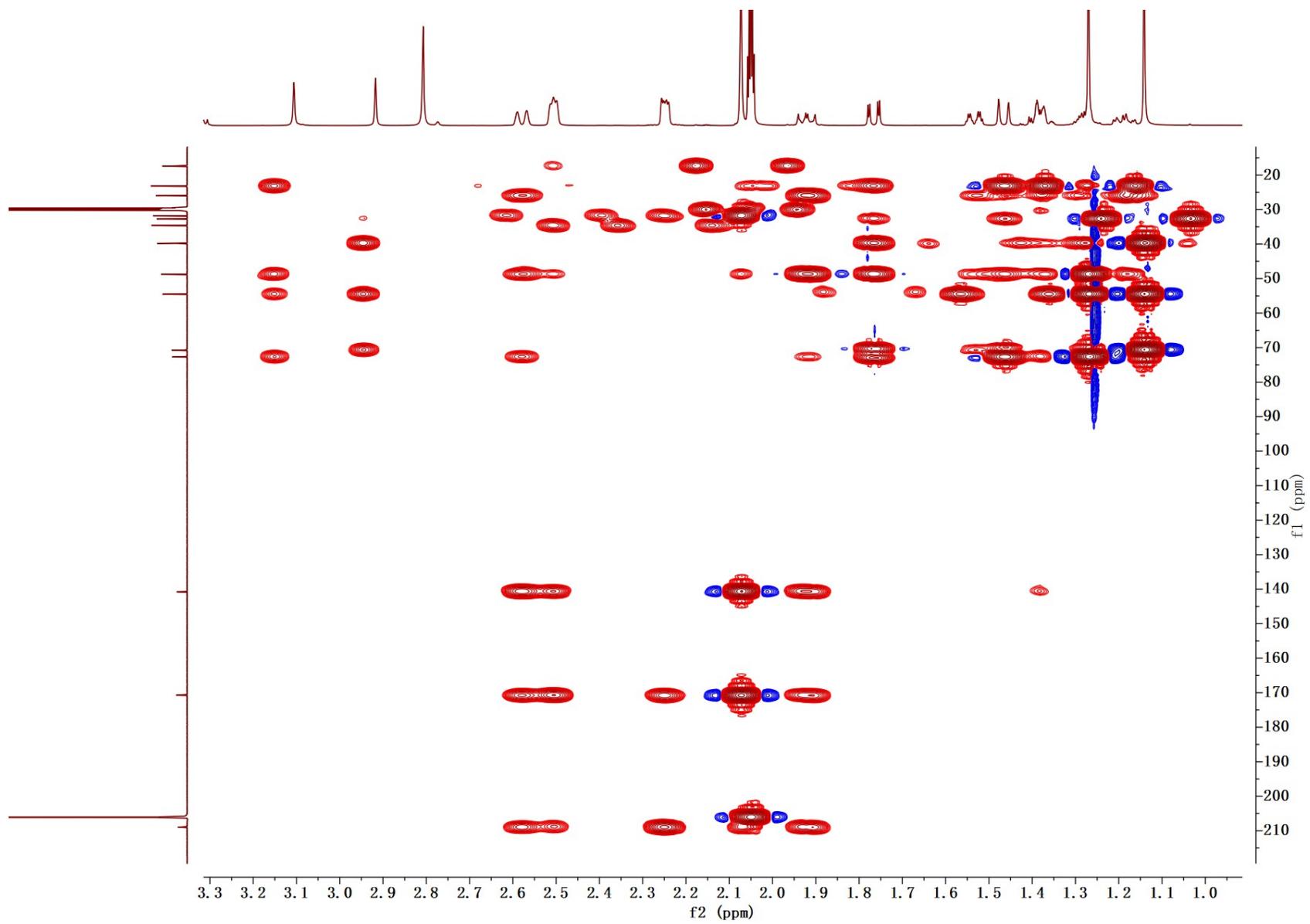


Figure S50. The HMBC spectrum of compound **5** in acetone- d_6 .

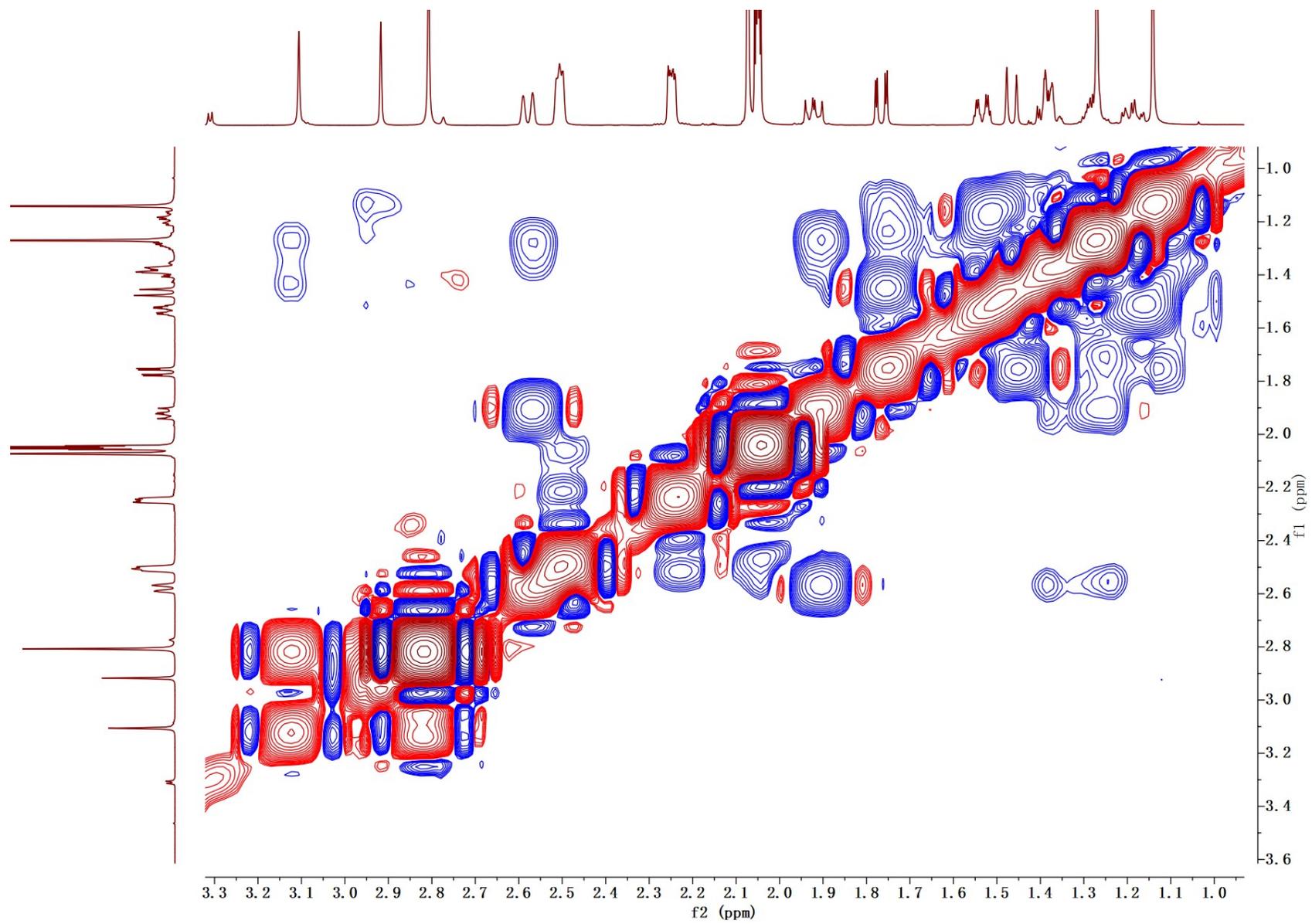


Figure S51. The NOESY spectrum of compound **5** in acetone- d_6 .

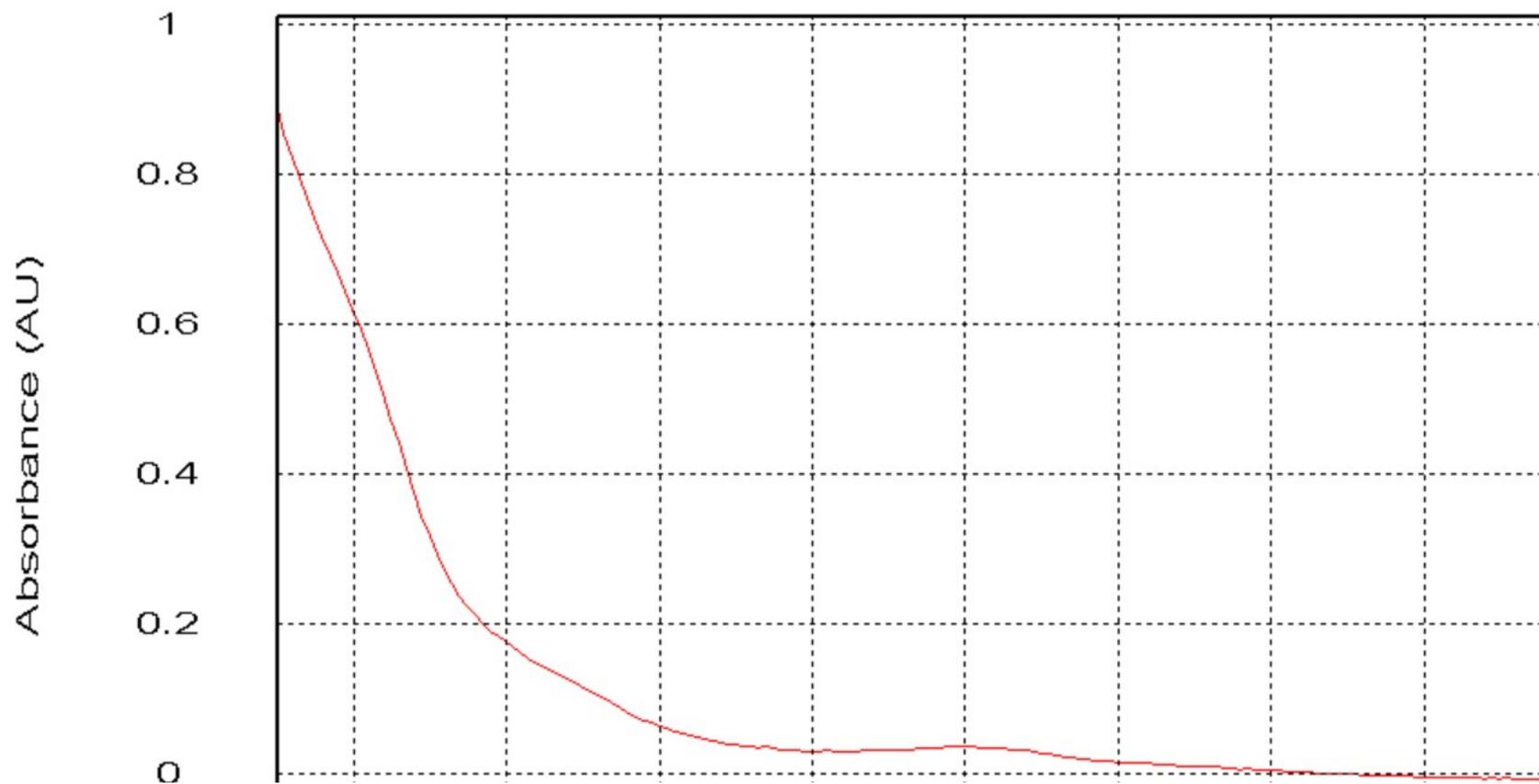


Figure S52. The UV spectrum of compound **6** in acetonitrile.

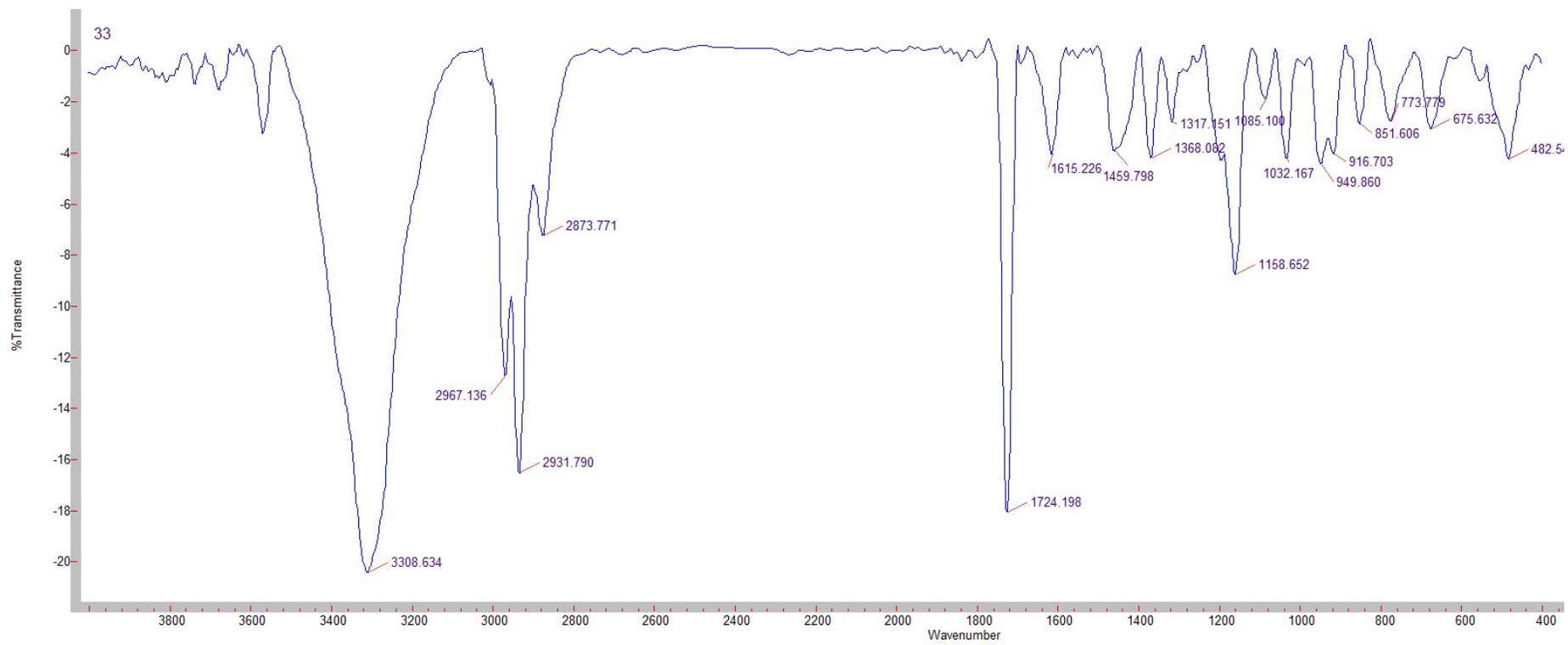


Figure S53. The IR spectrum of compound **6**.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

86 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
277.1784	277.1780	0.4	1.4	2.5	C15 H26 O3 Na	578.3	0.450	63.79	15	26	3	1
	277.1804	-2.0	-7.2	5.5	C17 H25 O3	578.9	1.016	36.21	17	25	3	

X-12 36 (0.161) Cm (14:129)

1: TOF MS ES+

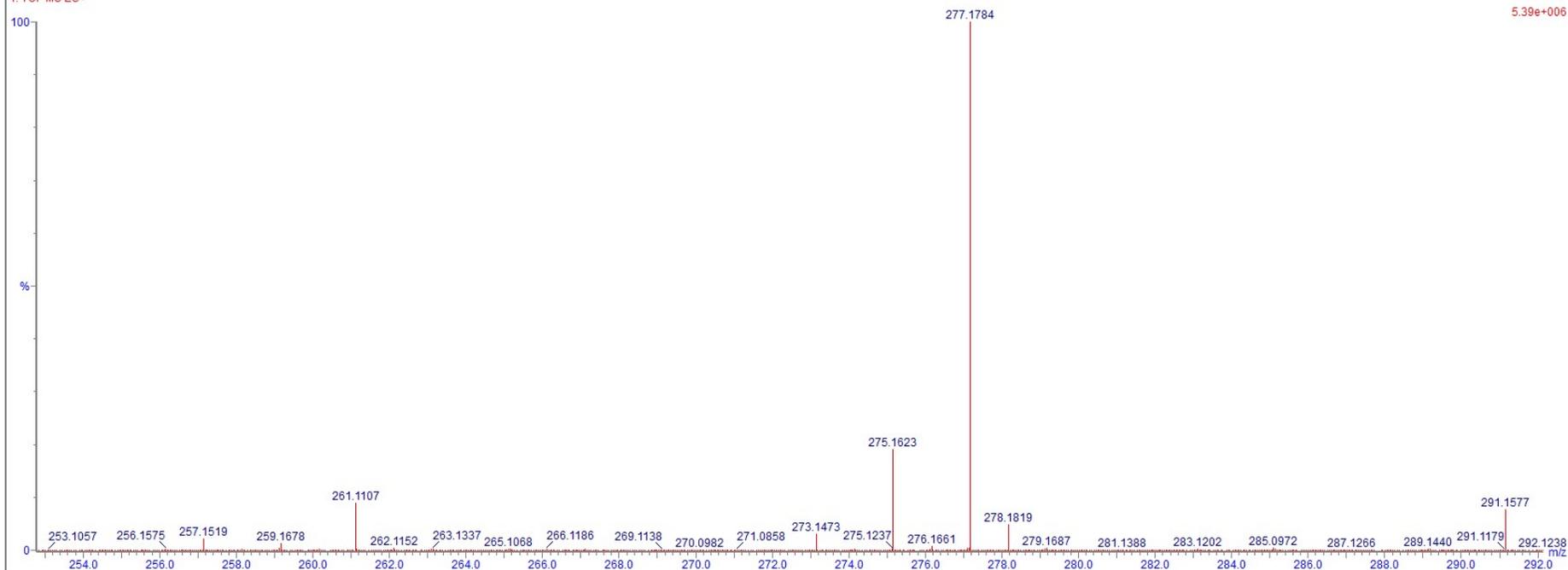


Figure S54. The (+)-HRESIMS spectroscopic data of compound 6.

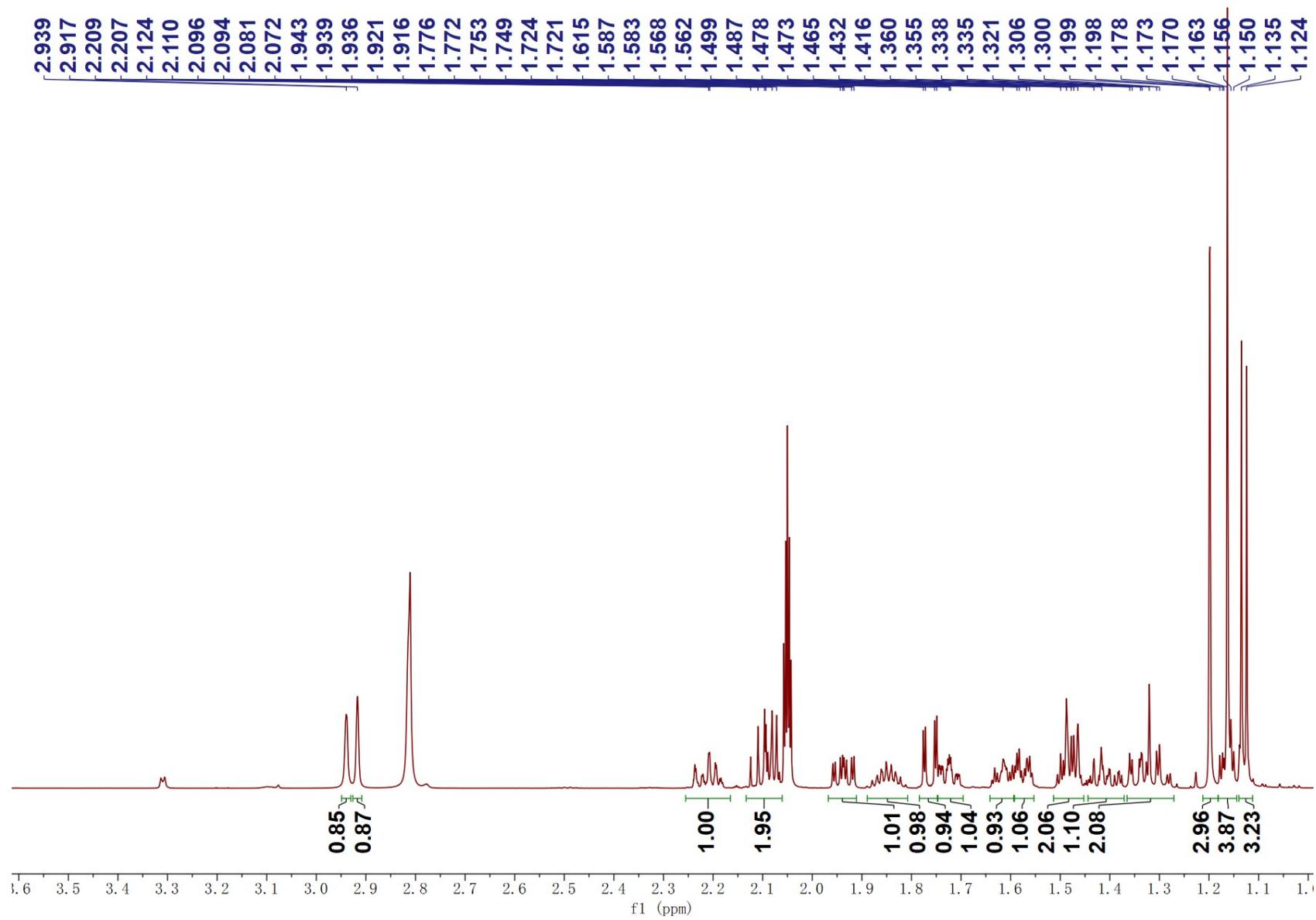


Figure S55. The ^1H NMR spectrum of compound **6** in acetone- d_6 .

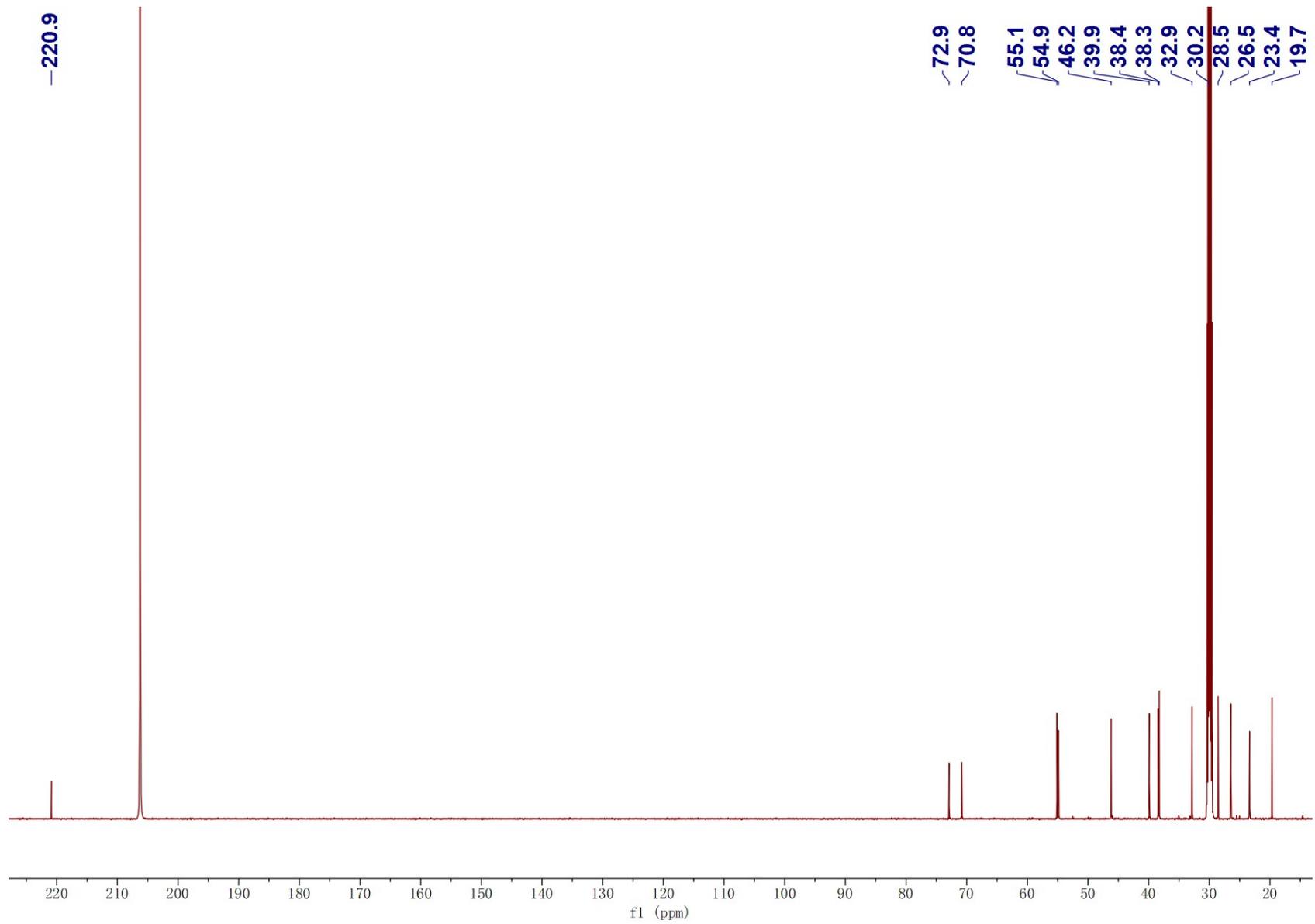


Figure S56. The ^{13}C NMR spectrum of compound **6** in acetone- d_6 .

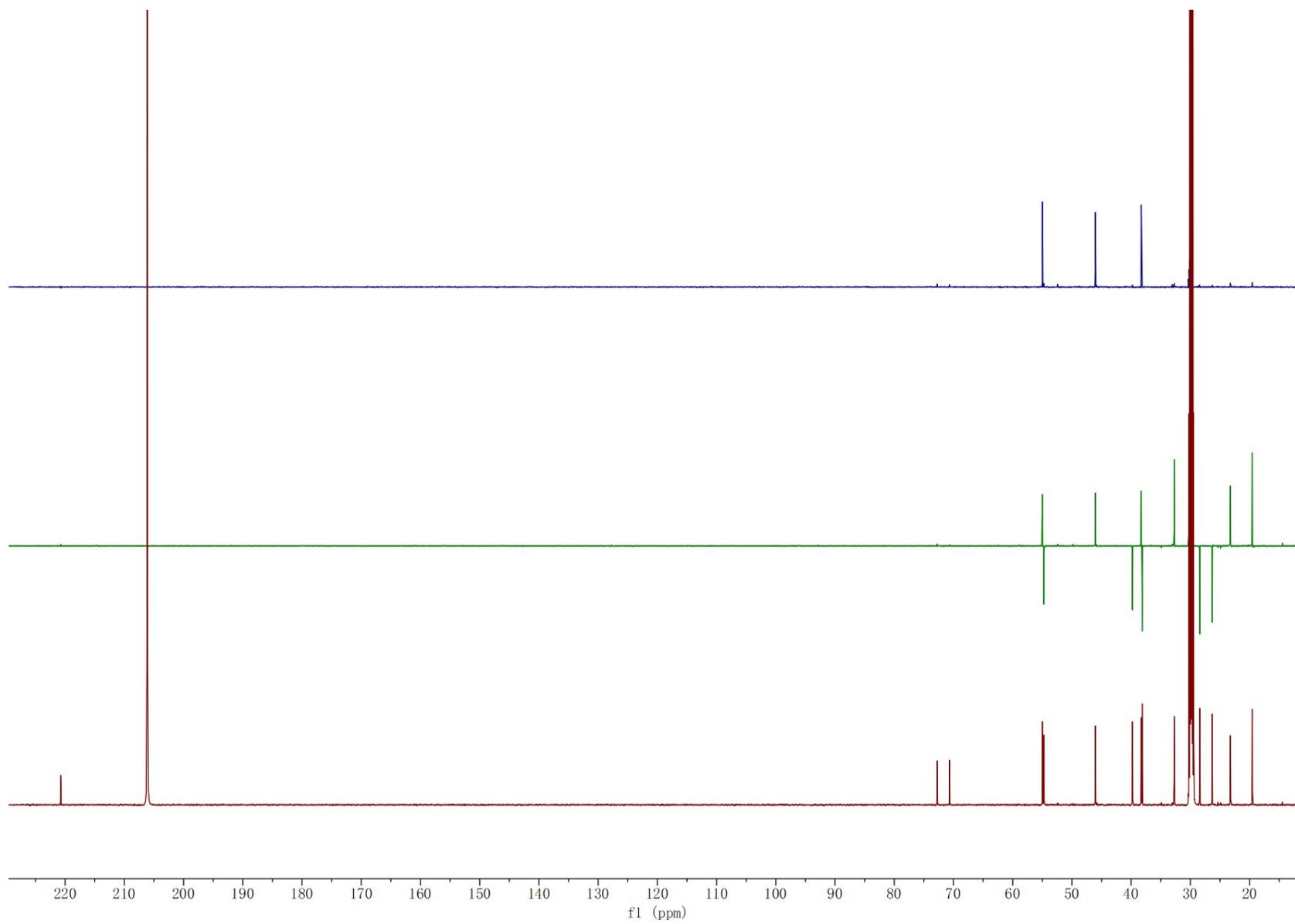


Figure S57. The DEPT spectrum of compound **6** in acetone-*d*₆.

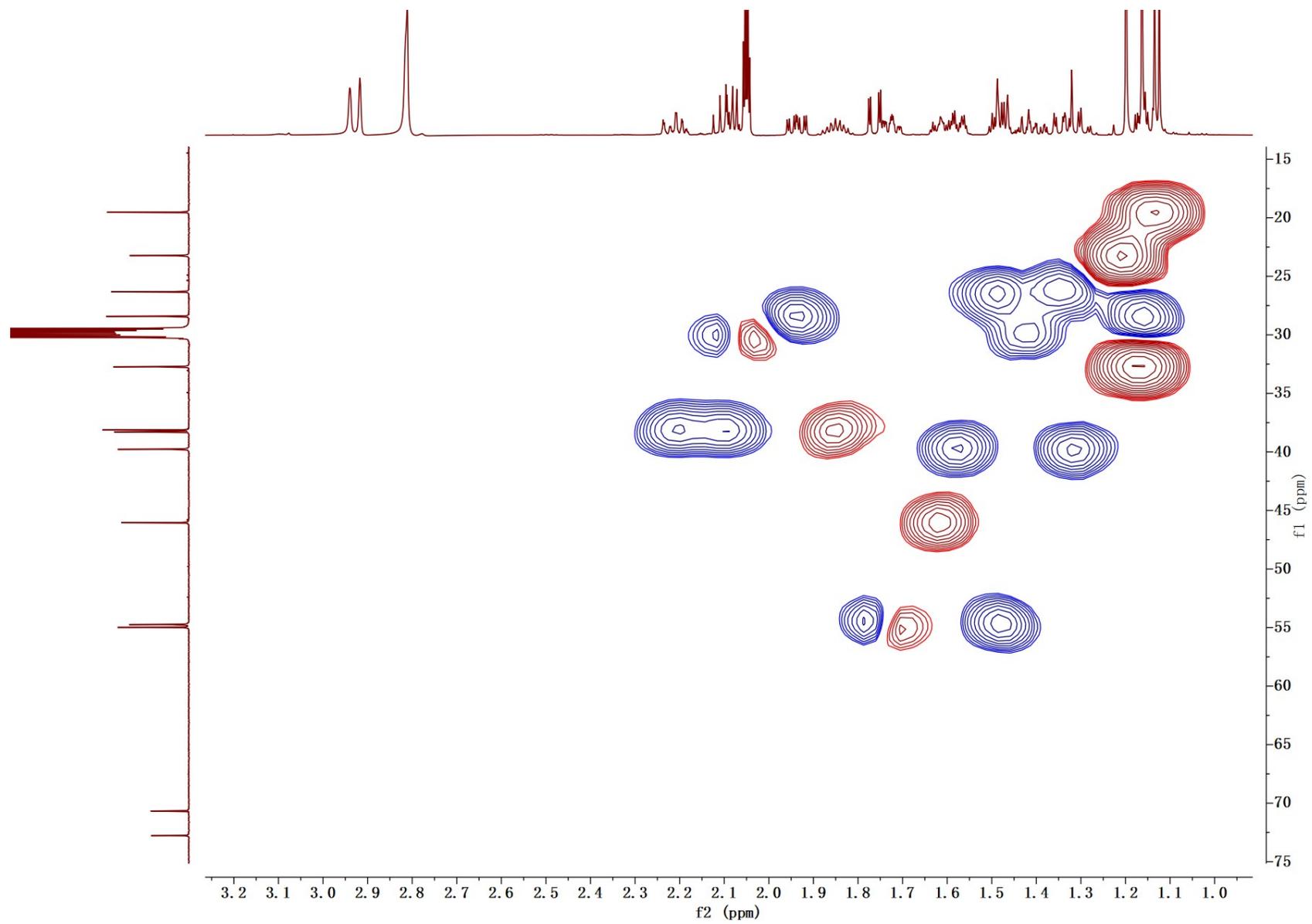


Figure S58. The HSQC spectrum of compound **6** in acetone-*d*₆.

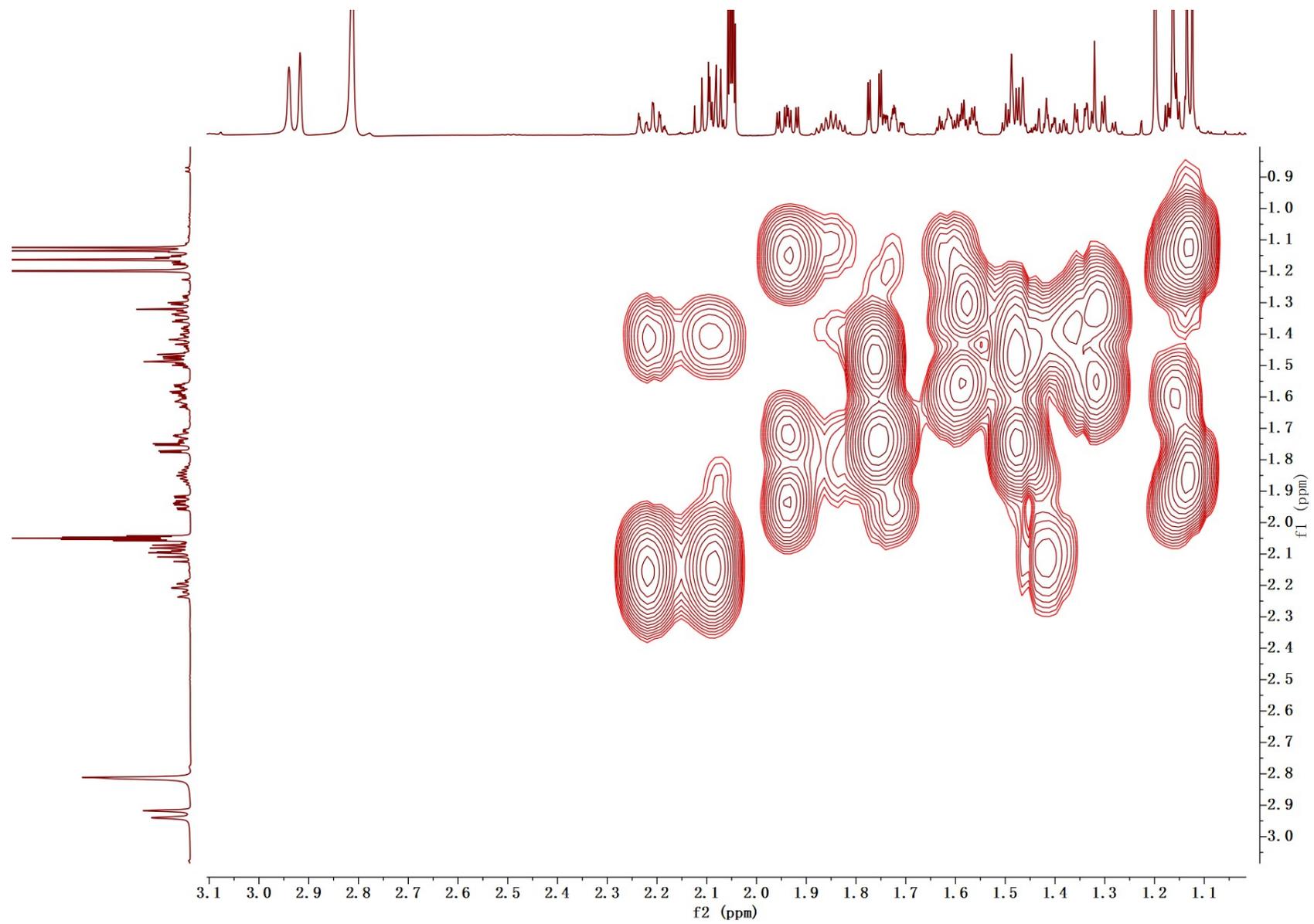


Figure S59. The ^1H - ^1H COSY spectrum of compound **6** in acetone- d_6 .

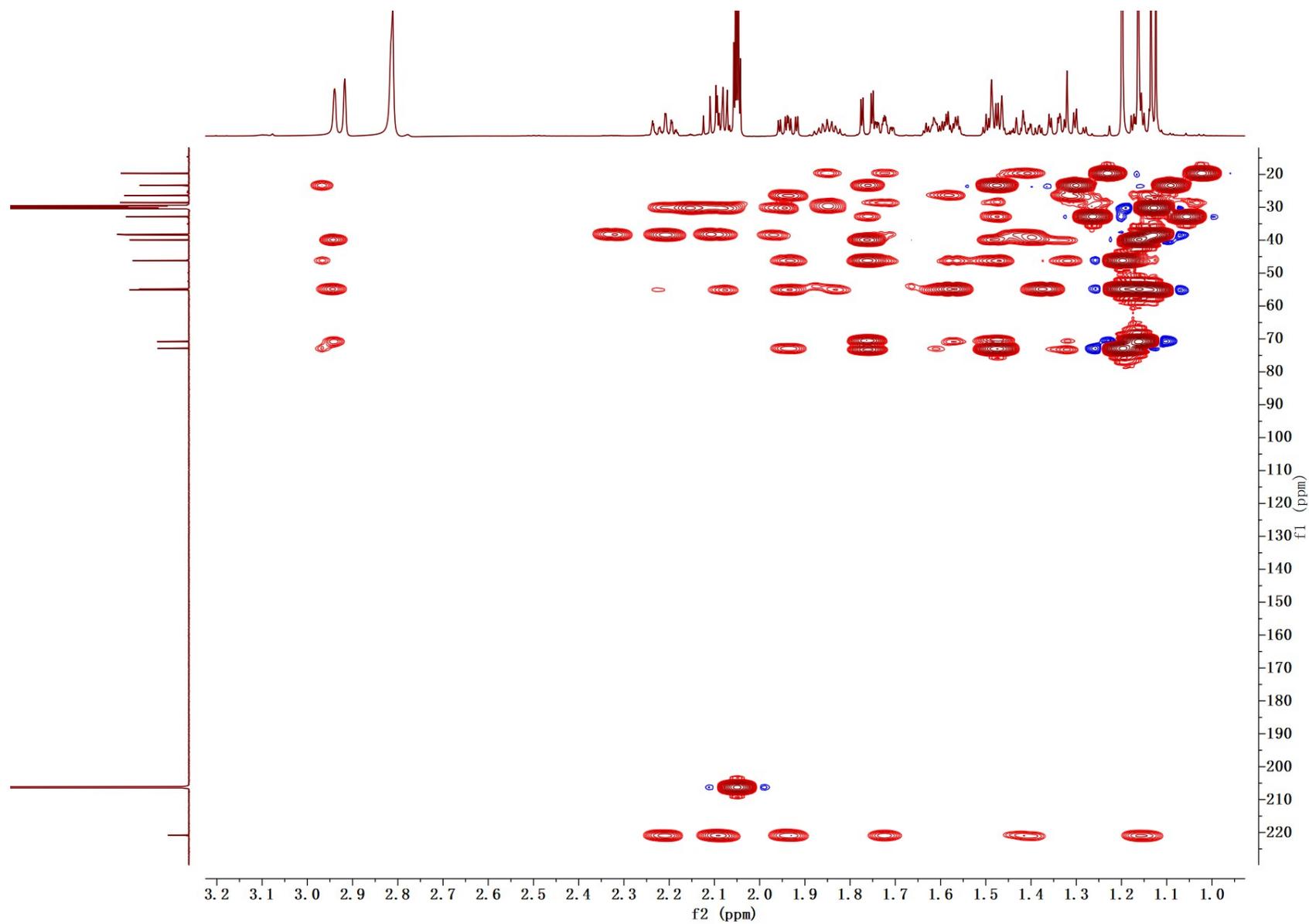


Figure S60. The HMBC spectrum of compound **6** in acetone-*d*₆.

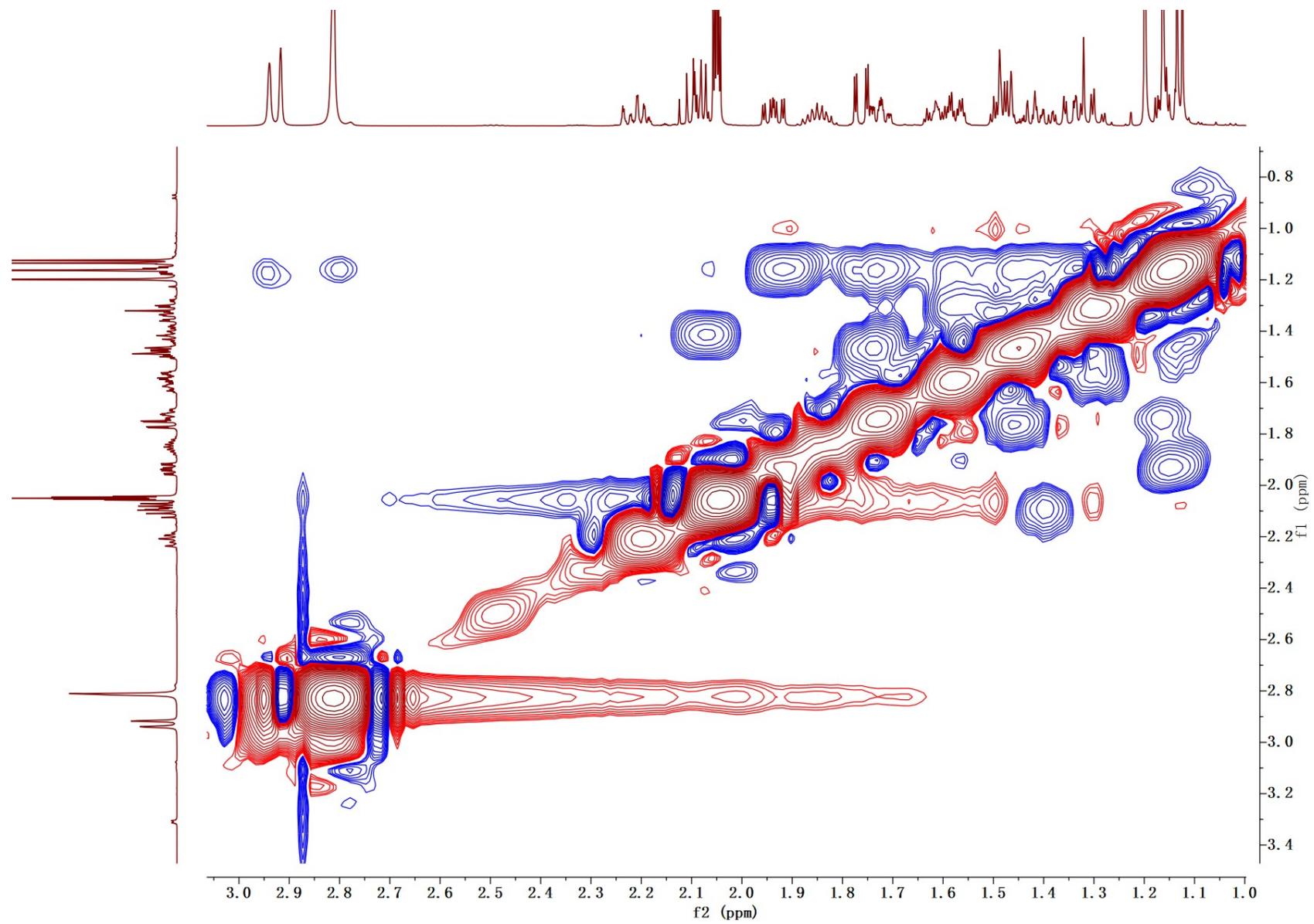


Figure 61. The NOESY spectrum of compound **6** in acetone-*d*₆.

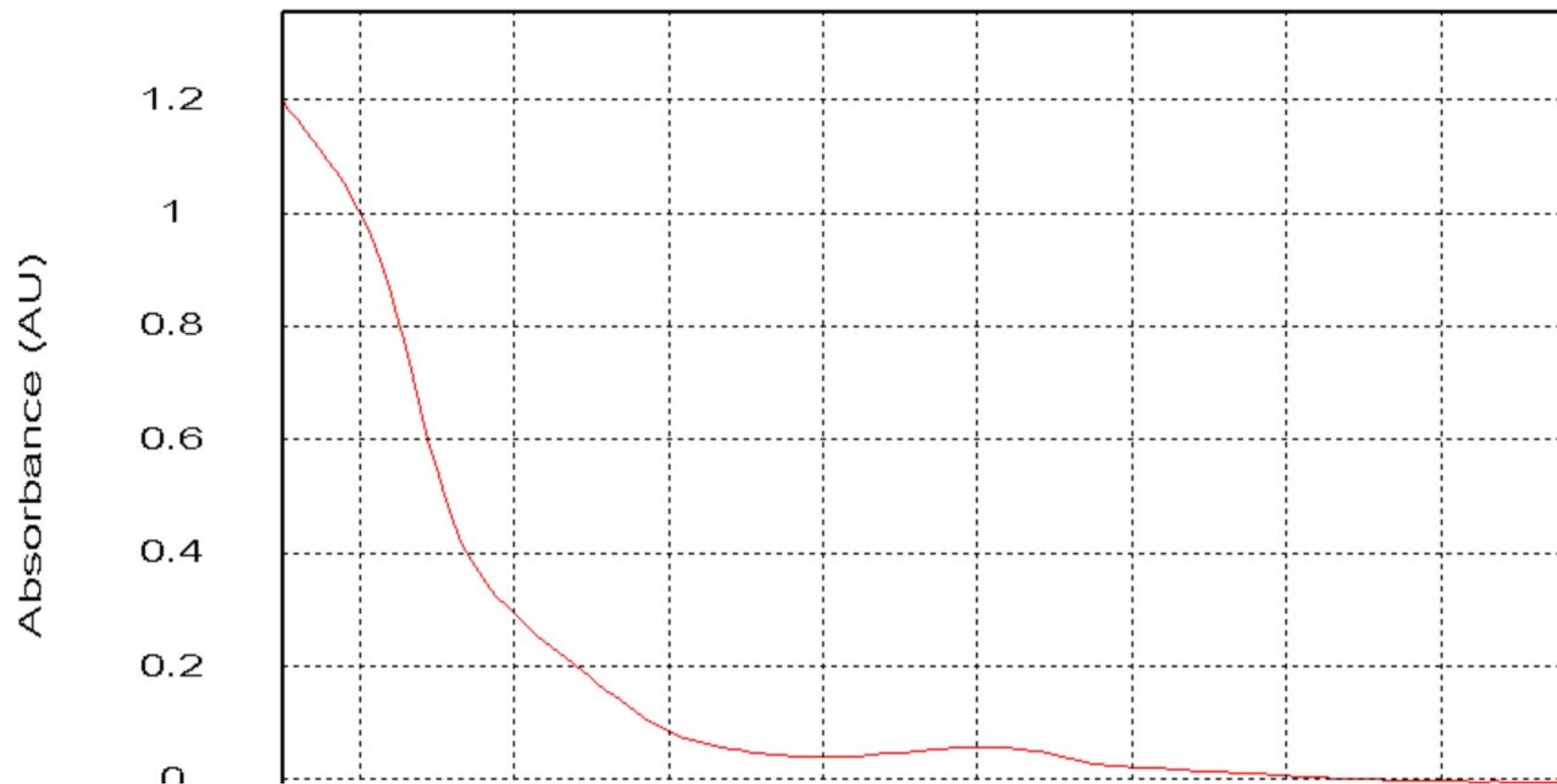


Figure S62. The UV spectrum of compound 7 in acetonitrile.

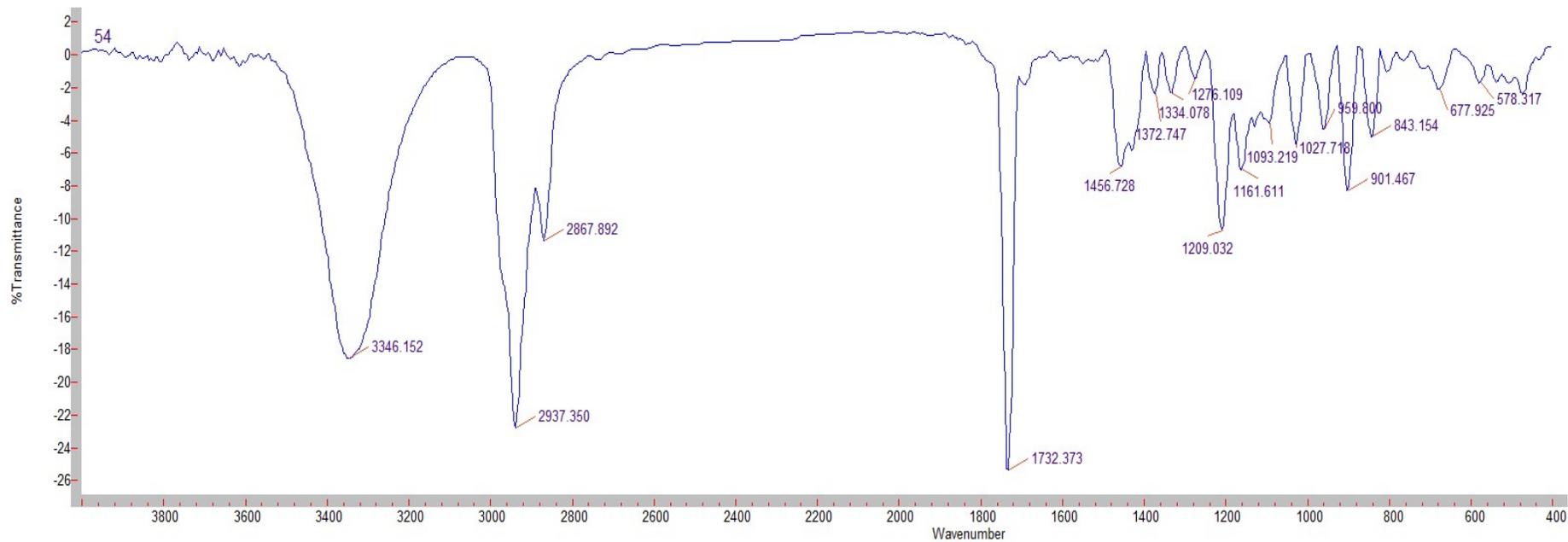


Figure S63. The IR spectrum of compound 7.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -3.0, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Even Electron Ions

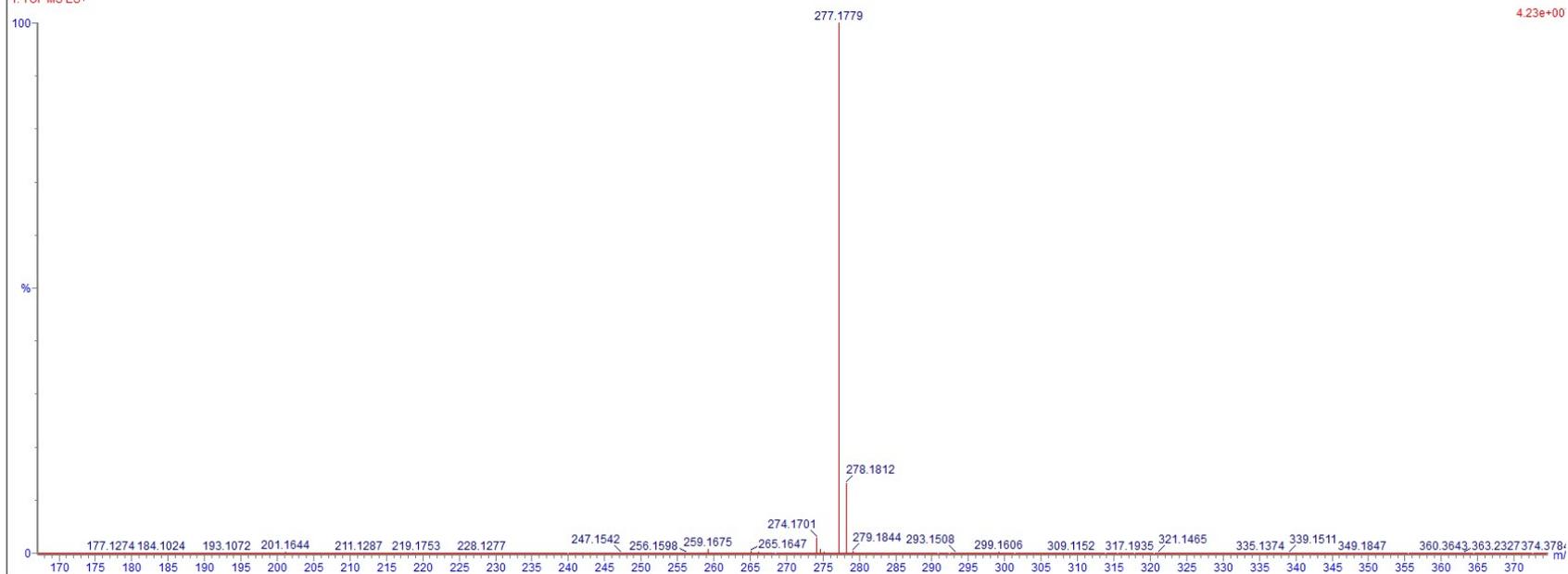
92 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
277.1779	277.1780	-0.1	-0.4	2.5	C15 H26 O3 Na	1003.1	0.226	79.81	15	26	3	1
	277.1804	-2.5	-9.0	5.5	C17 H25 O3	1004.5	1.600	20.19	17	25	3	

311.41 (0.180) Cm (20:96)

1: TOF MS ES+

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

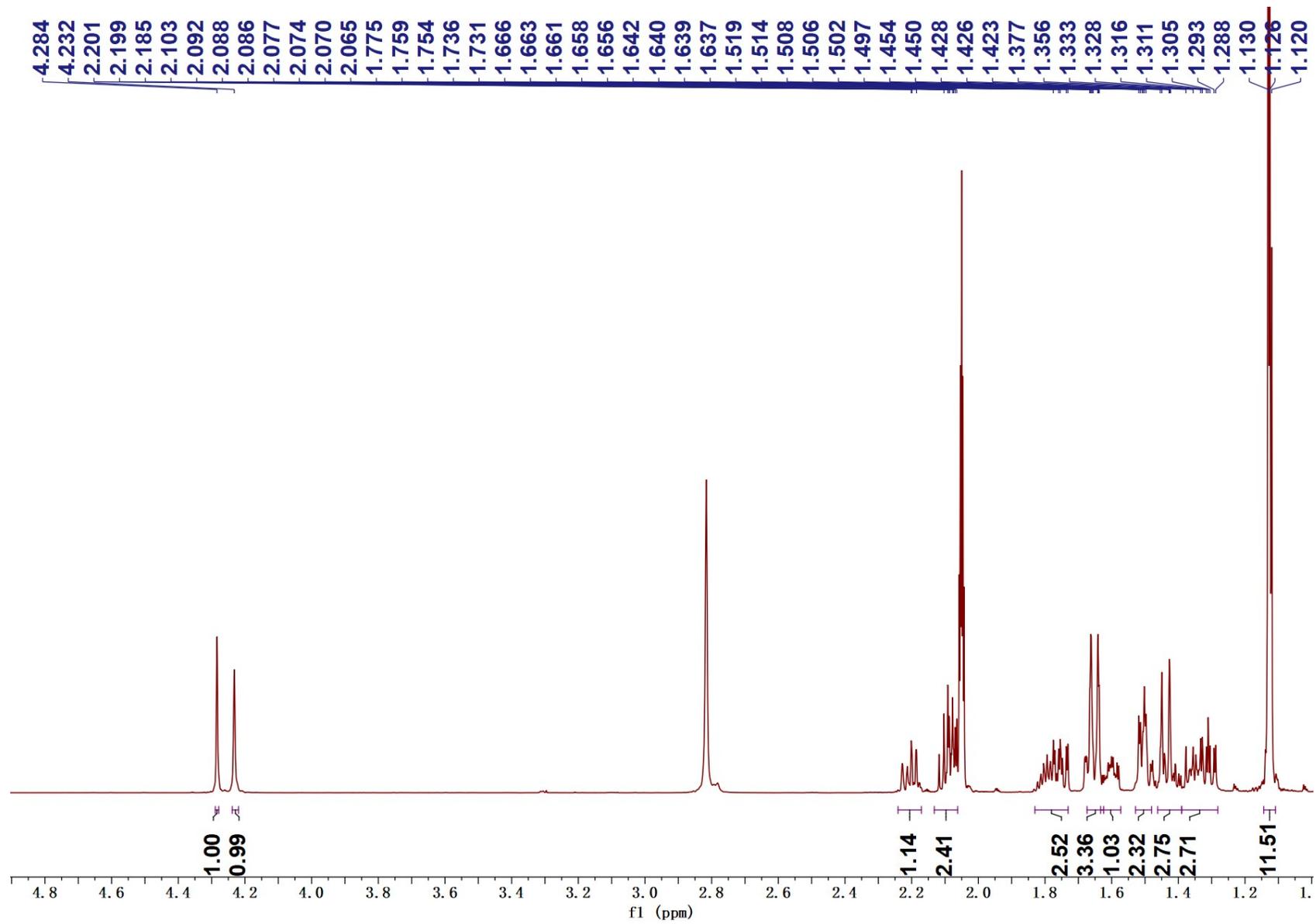


Figure S65. The ^1H NMR spectrum of compound 7 in acetone- d_6 .

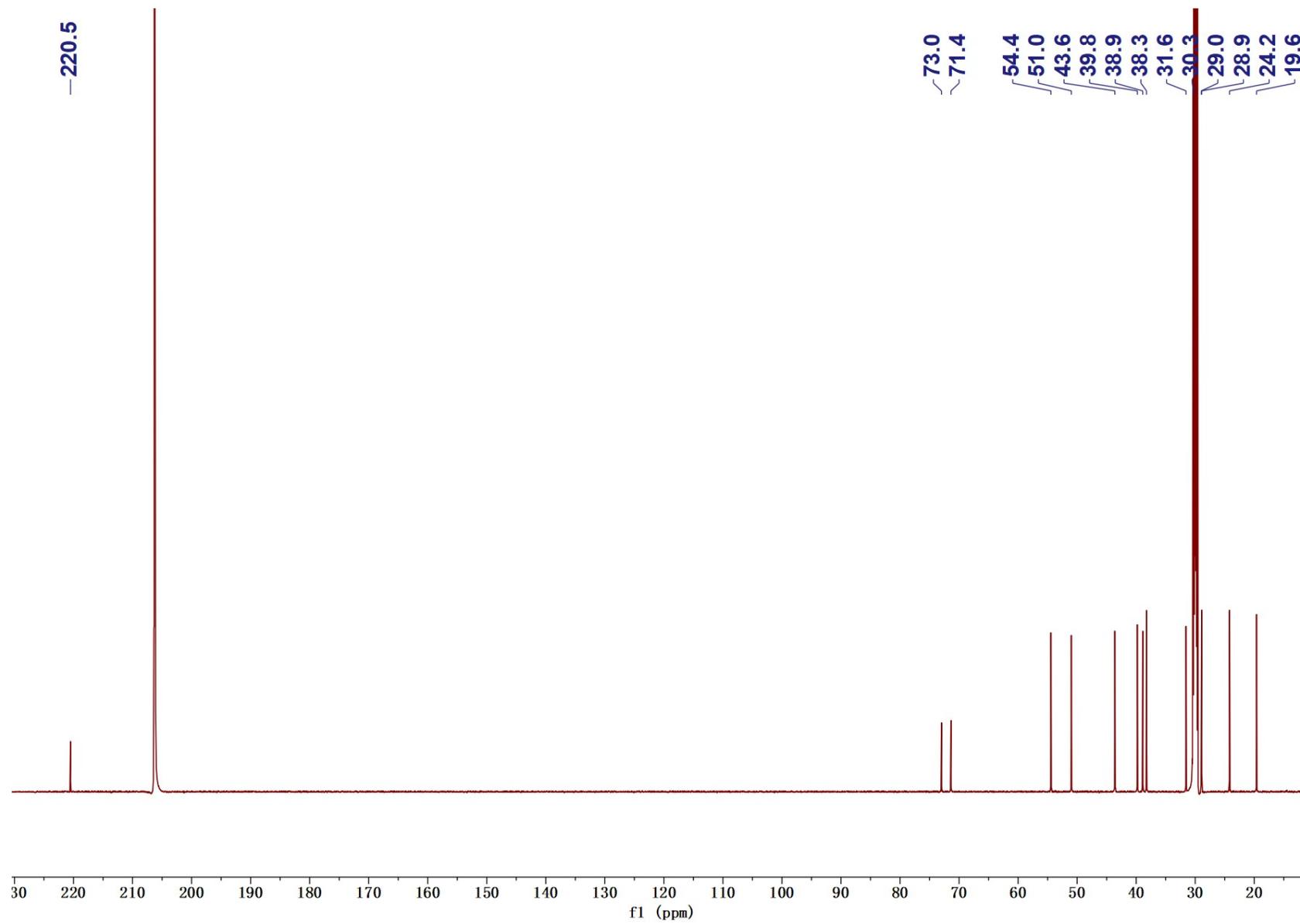


Figure S66. The ^{13}C NMR spectrum of compound **7** in acetone- d_6 .

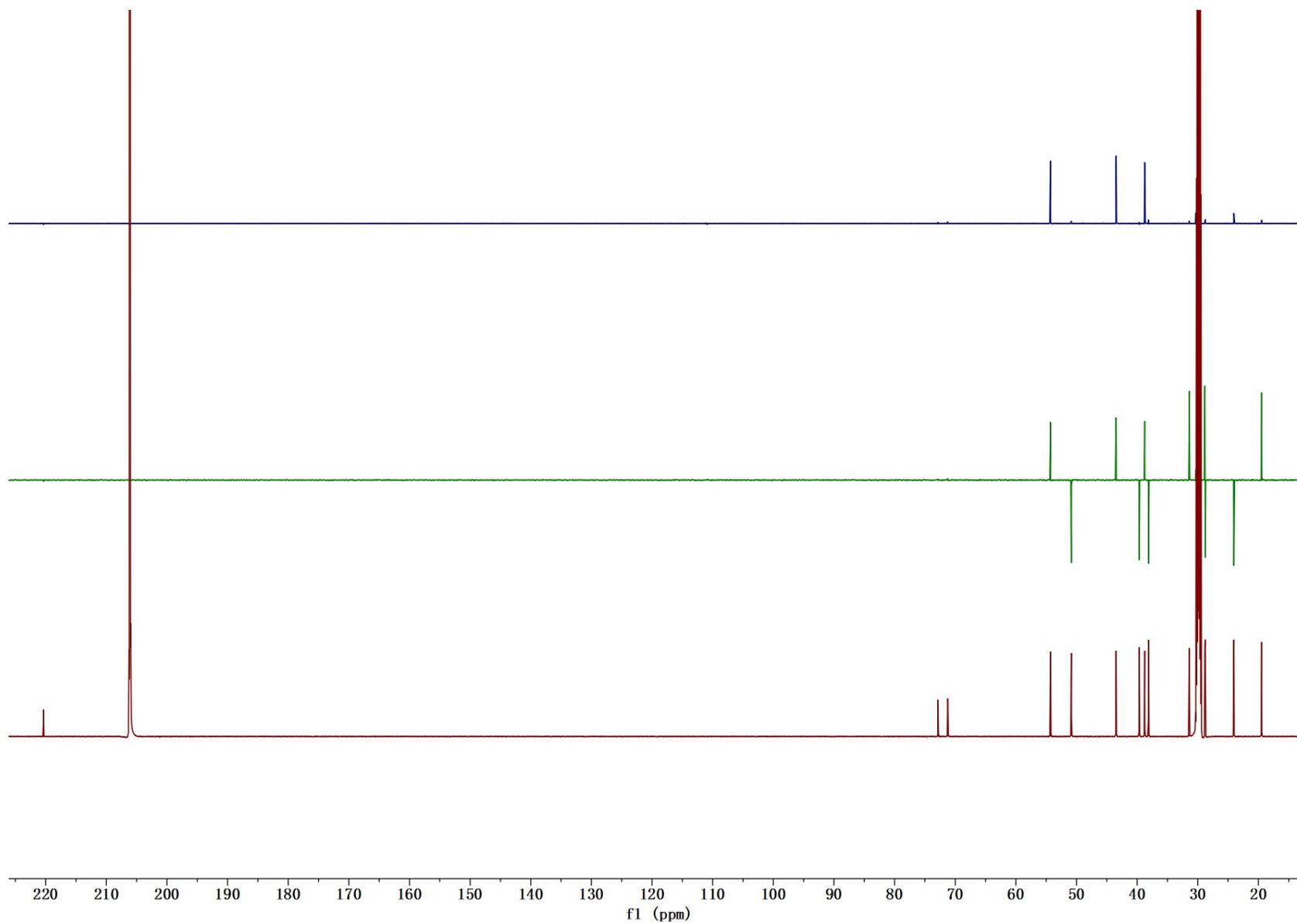


Figure S67. The DEPT spectrum of compound 7 in acetone-*d*₆.

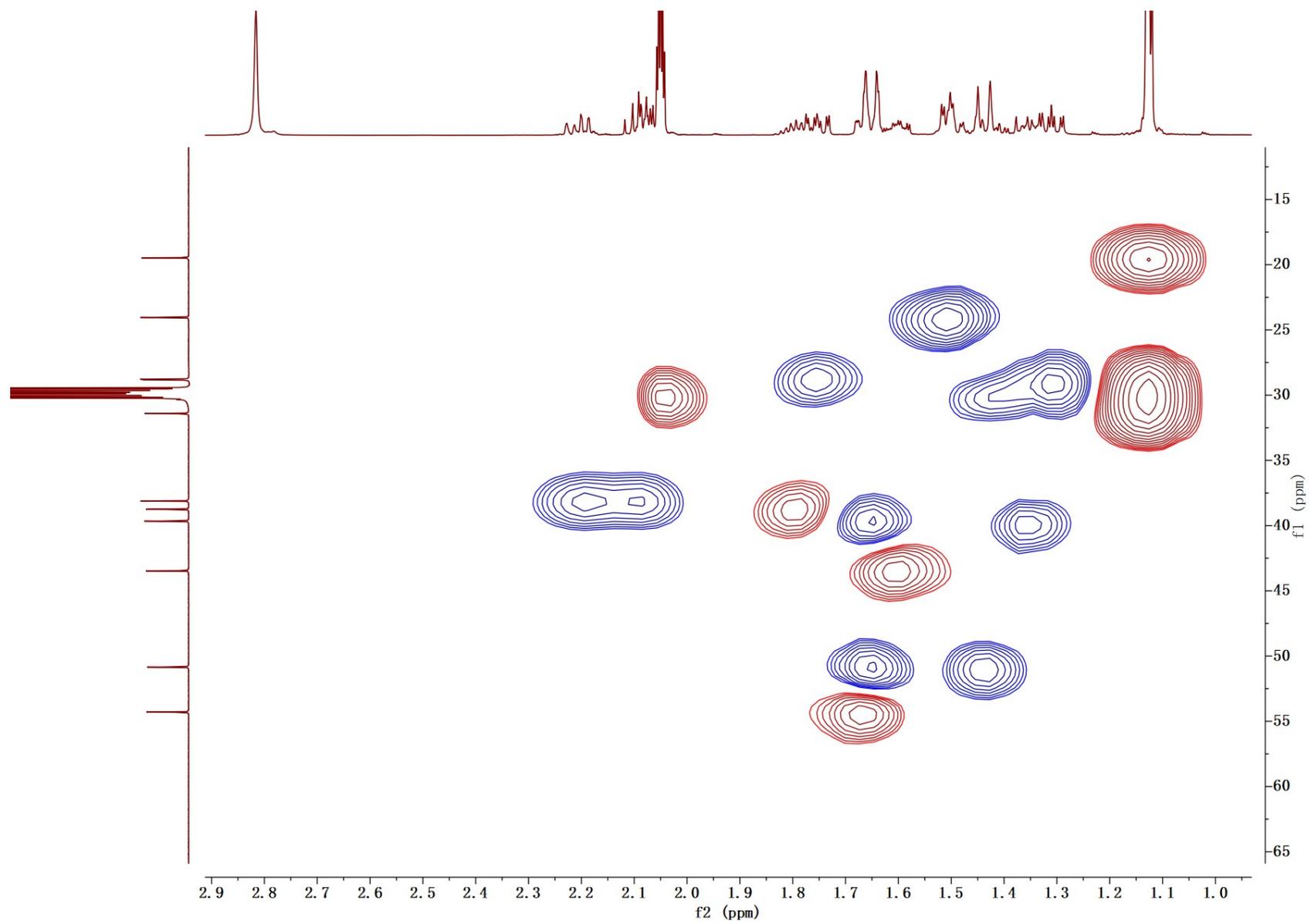


Figure S68. The HSQC spectrum of compound **7** in acetone- d_6 .

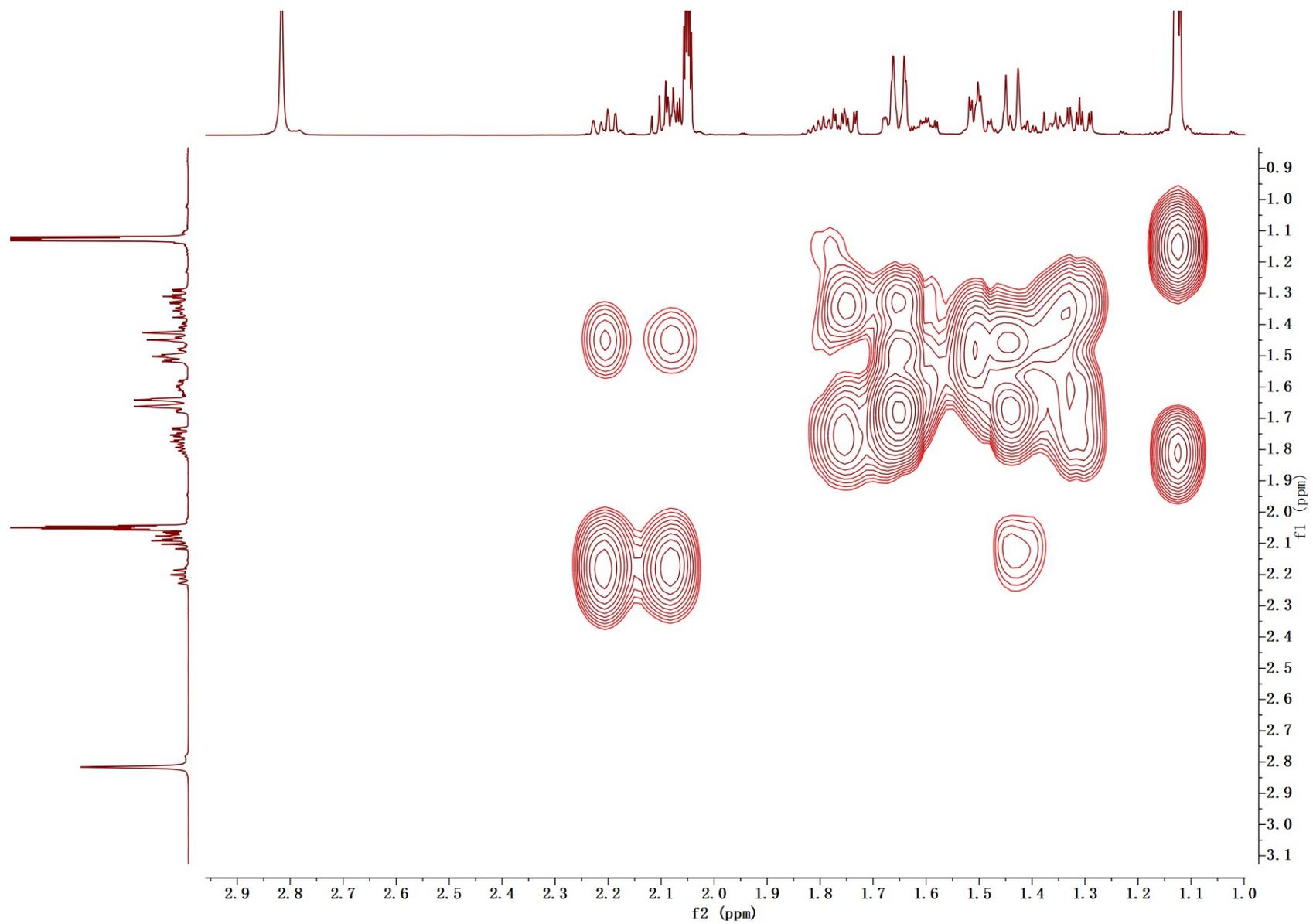


Figure S69. The ^1H - ^1H COSY spectrum of compound 7 in acetone- d_6 .

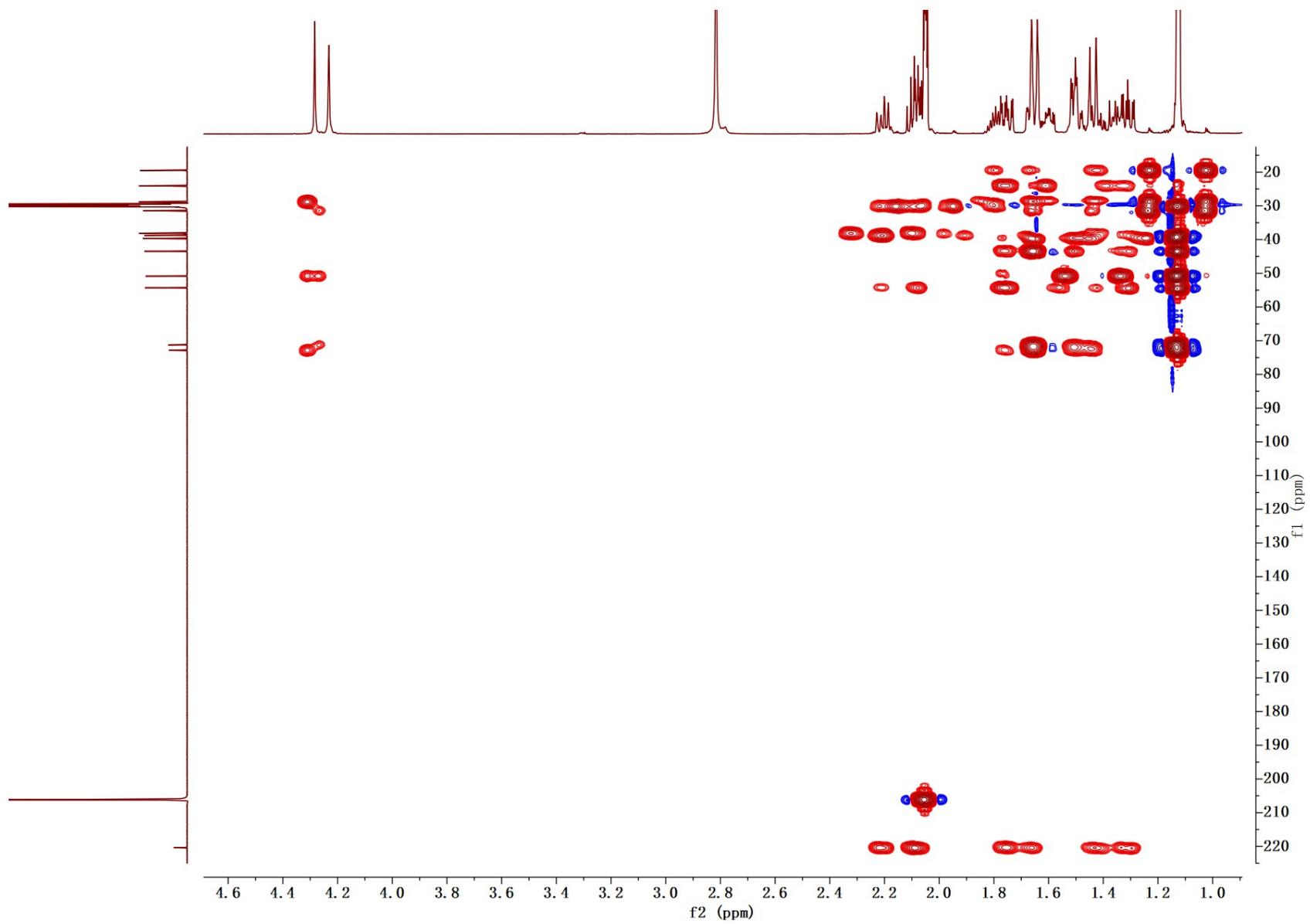


Figure S70. The HMBC spectrum of compound **7** in acetone-*d*₆.