Supplementary Information

Discovery of exoticoumarins A–L: New anti-inflammatory coumarin derivatives from *Murraya exotica*

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S1. Figures and Schemes

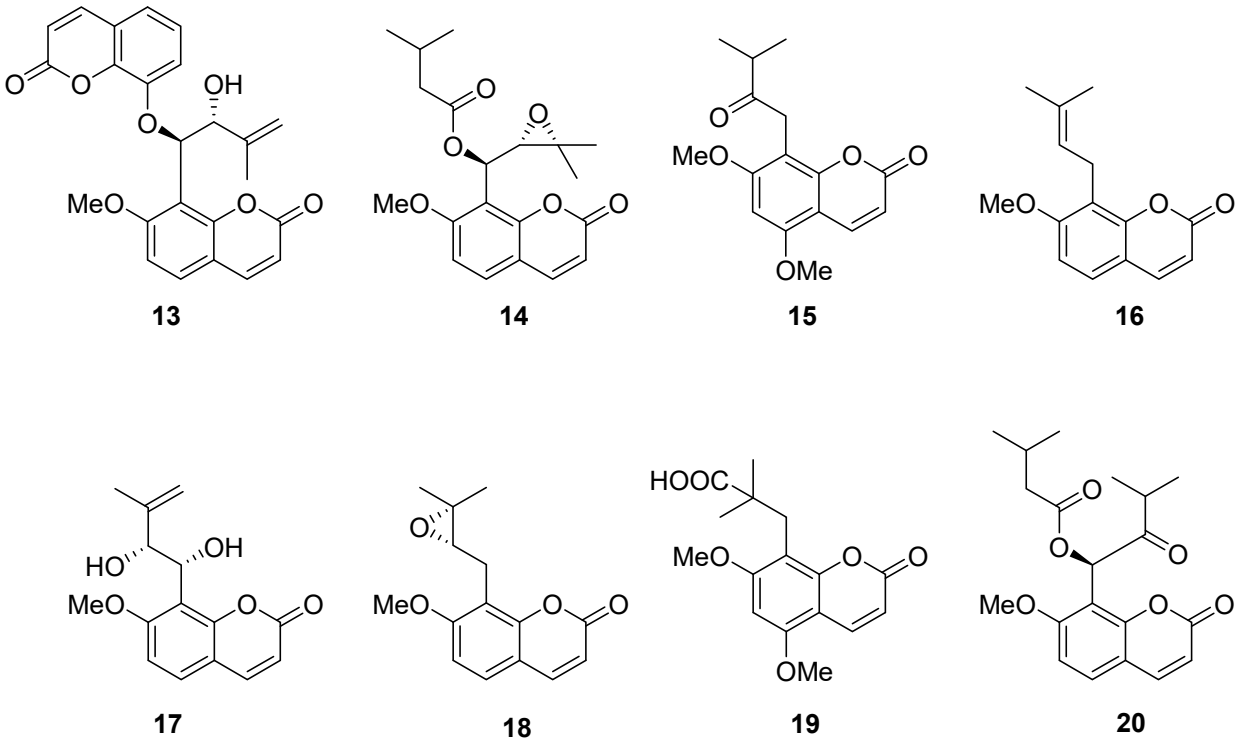


Figure S1. Structures of the known compounds **13**–**20**

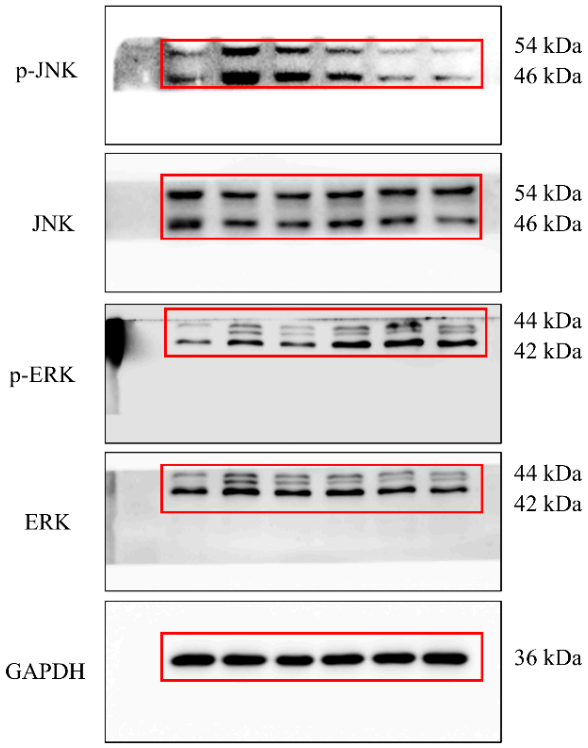


Figure S2. Unprocessed blots for Figure 8

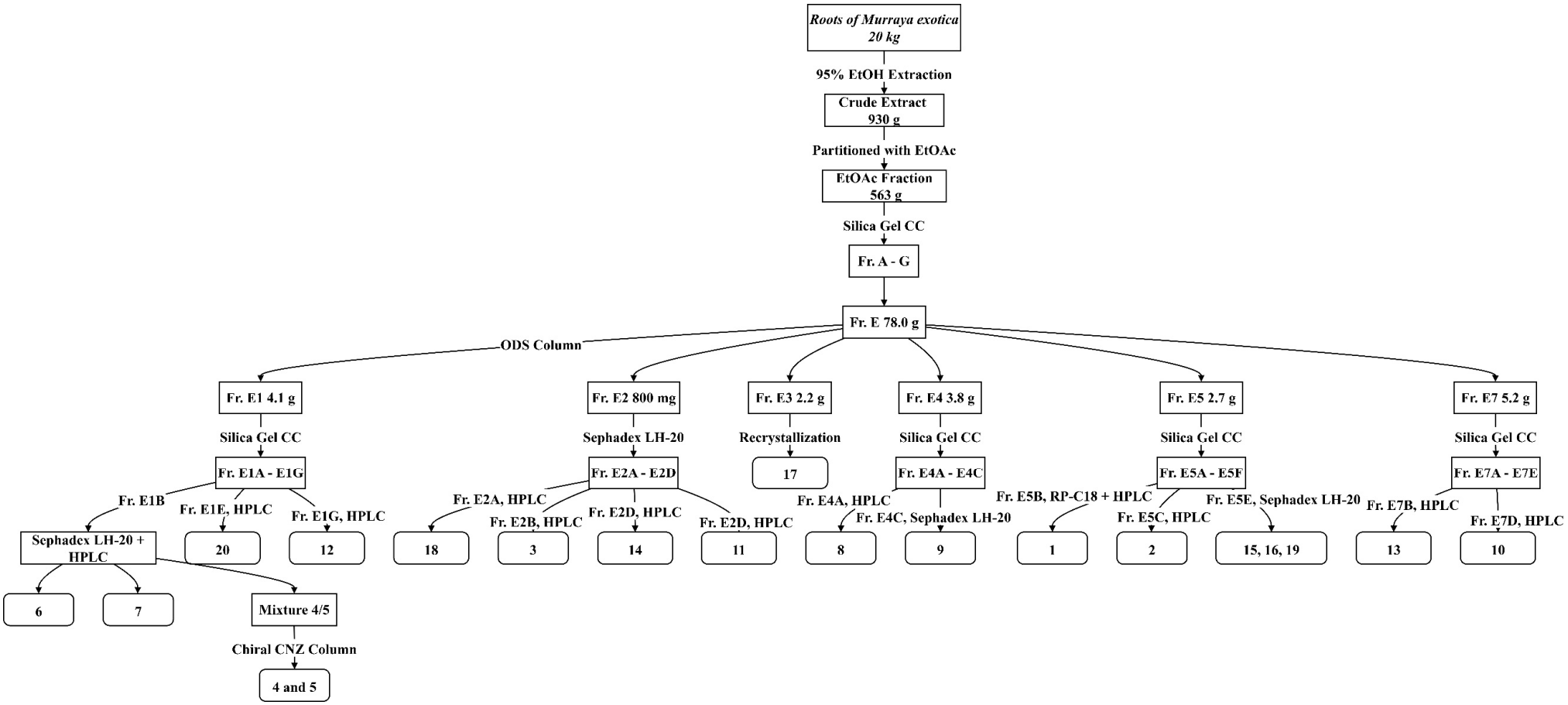
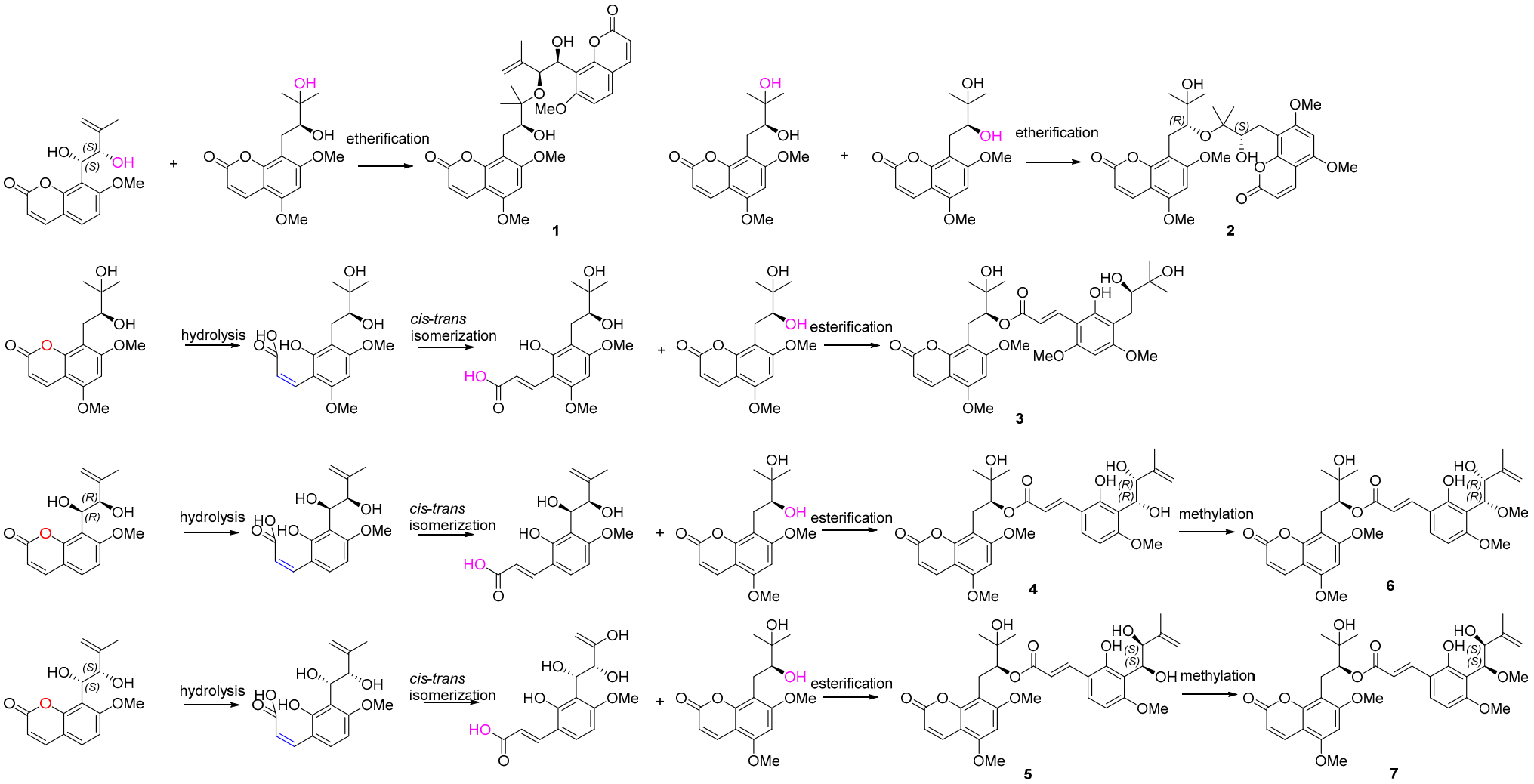


Figure S3. Isolation flow chart of the roots of *Murraya exotica*



Scheme S1. Proposed biosynthetic routes for **1**–**7**

S2. Experimental section

S2.1. ECD calculations of compound **2**

The absolute configuration of **2** was determined by quantum chemical calculations of their theoretical ECD spectra. One of the two enantiomers for each configuration (12*S**,12′*S**)-**2a**, and (12*S*,12′*R**)-**2b**, were arbitrary chosen for theoretical studies. Conformational analyses were first carried out via Monte Carlo searching using molecular mechanism with MMFF force field in the Spartan'14 software (Wavefunction Inc., Irvine, CA, USA). The results showed two lowest energy conformers for **2a** and one for **2b** within an energy window of 5.0 Kcal/mol. These conformers were reoptimized using DFT at the B3LYP/6-31G(d) level[38,39] in gas phase using the Gaussian09[40]. One conformer of **2a** (Figure S4), one conformer of **2b** (Figure S5) were obtained, whose relative Gibbs free energies in the range of 0−1.5 Kcal/mol were refined and considered for next step (Table S1). The energies, oscillator strengths, and rotational strengths of the first 30 electronic excitations were calculated using the TD-DFT methodology at the M062X[41]/TZVP[42] level in PCM (acetonitrile) (Tables S2 and S3). The results were visualized and exported using the SpecDis program[43](sigma = 0.30 for all). The calculated ECD spectra was generated as a sum of Gaussian curve using rotatory strengths computed in the dipole-velocity gauge from ECD data of the individual conformers. Boltzmann distributions of the conformers in equilibrium population were estimated from the relative Gibbs free energies (ΔG) at 298.15K.

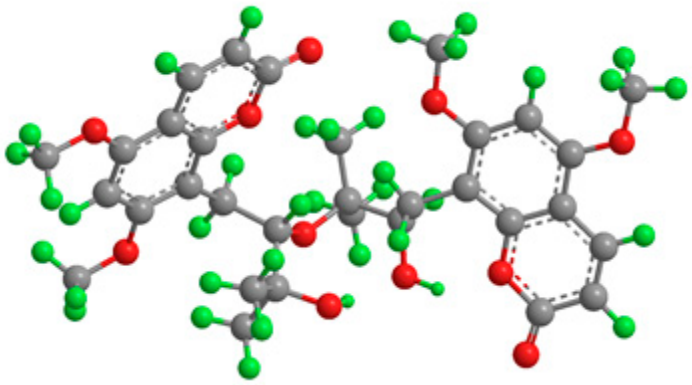


Figure S4. B3LYP/6-31G(d) optimized lowest energy conformers for **2a**

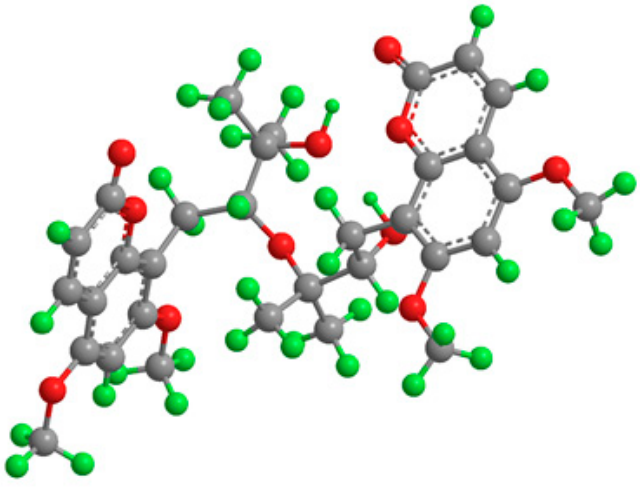


Figure S5. B3LYP/6-31G(d) optimized lowest energy conformers for **2b**

Table S1. Energy (298.15 K) analysis for **2a** and **2b**

Conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
2a1	-2069.128433	0	1
2b1	-2069.131147	0	1

ECD data

ECD spectrum of each conformation is simulated according to the overlapping Gaussian functions expressed as:

$$\Delta\varepsilon(E)=\frac{1}{2.296\times10^{-39}\sqrt{\pi}\sigma}\sum_{i}^{A}\Delta E_i \mathrm{R}_i e^{[-(E-\Delta Ei)^2/\sigma^2]}$$

Where σ is half the bandwidth at 1/e peak height and expressed in energy units. The parameters ΔE_i and R_i are the excitation energies and rotational strengths for the transition *i*, respectively.

The above function is converted to Δε, λ (wavelength) correlations as:

$$\Delta\varepsilon(\lambda)=\frac{1}{2.296\times10^{-39}\sqrt{\pi}\sigma}\sum_{i}^{A}\Delta E_i \mathrm{R}_i e^{[-(1240/\lambda-\Delta Ei)^2/\sigma^2]}$$

and then simulation was accomplished by using the Excel 2016 and the Origin 22 software.

To get the final spectra, all the simulated spectra of conformations of each compound were averaged according to their energy and the Boltzmann distribution theory expressed as:

$$\frac{N_i^*}{N}=\frac{g_i e^{-\varepsilon_i/k_BT}}{\sum g_i e^{-\varepsilon_i/k_BT}}$$

Table S2. Calculated ECD data of **2a** in acetonitrile

State	**2a1**	
	Excitation energies(eV)	Rotatory Strengths*
1	3.9845	50.4349
2	4.0406	-74.285
3	4.488	-75.6403
4	4.4996	92.5635
5	5.21	-3.0955
6	5.27	-0.0408
7	5.2715	-0.6227
8	5.379	204.5318
9	5.3856	-91.4918
10	5.3999	-117.1699
11	5.959	12.4038
12	5.9922	-6.8508
13	6.0249	-0.0477
14	6.0363	0.032
15	6.2532	-13.4819
16	6.3073	-84.7653
17	6.3369	173.2037
18	6.379	-93.3454
19	6.5039	-19.5676
20	6.5226	-0.8077
21	6.6057	134.2311
22	6.6138	-51.6923
23	6.6468	-54.8915
24	6.6875	-2.1874
25	6.6908	3.2075
26	6.7316	5.5712
27	6.8705	0.5163
28	6.8901	1.3606
29	6.9069	-1.05
30	6.9113	-0.4083

* R(velocity) 10**-40 erg-esu-cm

Table S3. Calculated ECD data of **2b** in acetonitrile

State	**2b1**	
	Excitation energies(eV)	Rotatory Strengths*
1	4.0005	-186.3235
2	4.0425	183.0162
3	4.4688	-28.9845
4	4.4874	61.5986
5	5.2206	1.4062
6	5.327	-10.1418
7	5.3285	-3.5561
8	5.3817	-163.2939
9	5.3967	123.5321
10	5.4072	92.3083
11	5.9363	-0.6241
12	5.9747	26.5715
13	5.9853	8.7488
14	5.9992	8.5055
15	6.1389	-2.1851
16	6.1524	-1.3743
17	6.3148	-912.557
18	6.3328	927.5362
19	6.3984	1.1818
20	6.4365	-116.3856
21	6.6039	-9.6399
22	6.6128	0.2651
23	6.6201	-48.9298
24	6.6469	69.8782
25	6.6963	13.202
26	6.7701	-1.7814
27	6.8584	10.9135
28	6.8634	-1.1787
29	6.9036	2.1152
30	6.9581	1.5057

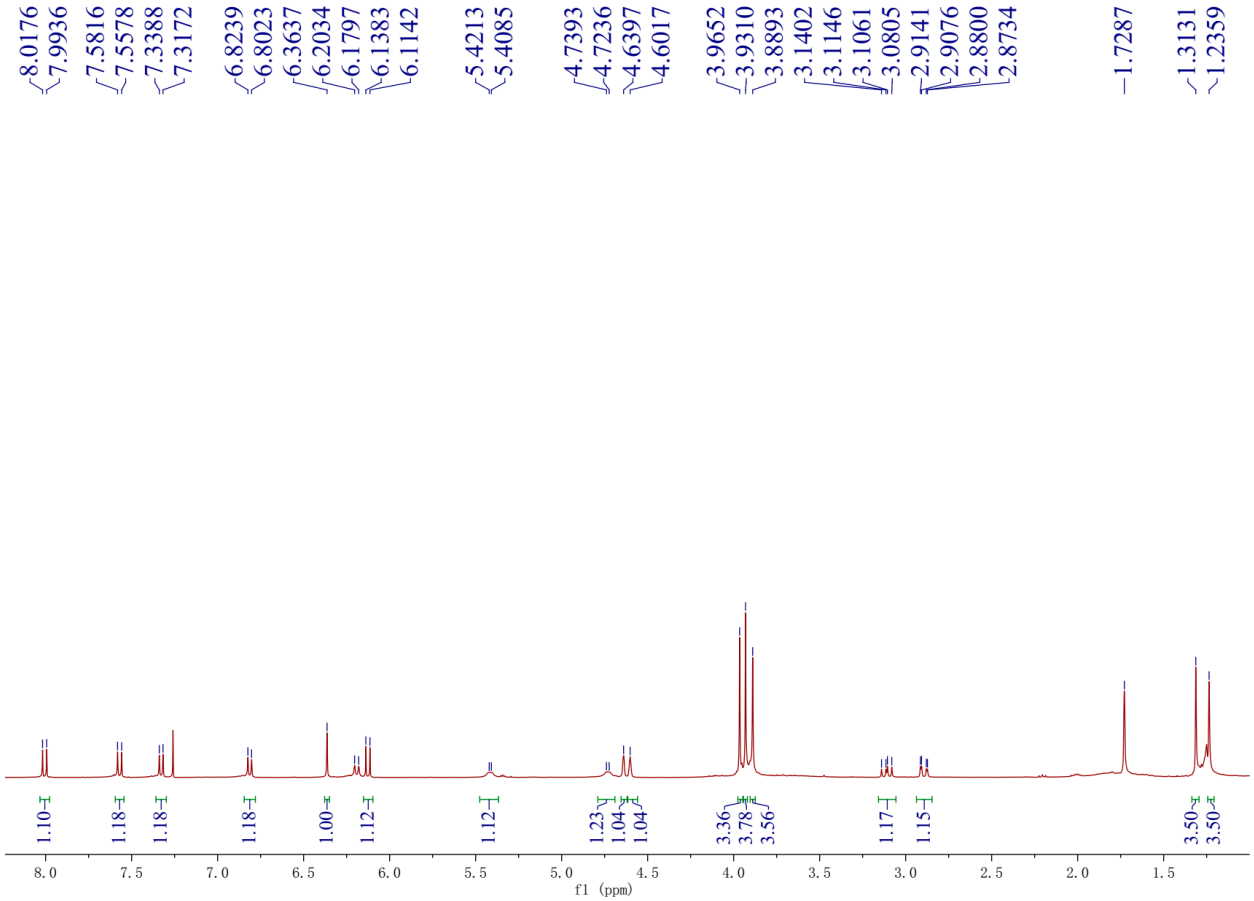
* R(velocity) 10**-40 erg-esu-cm

Reference

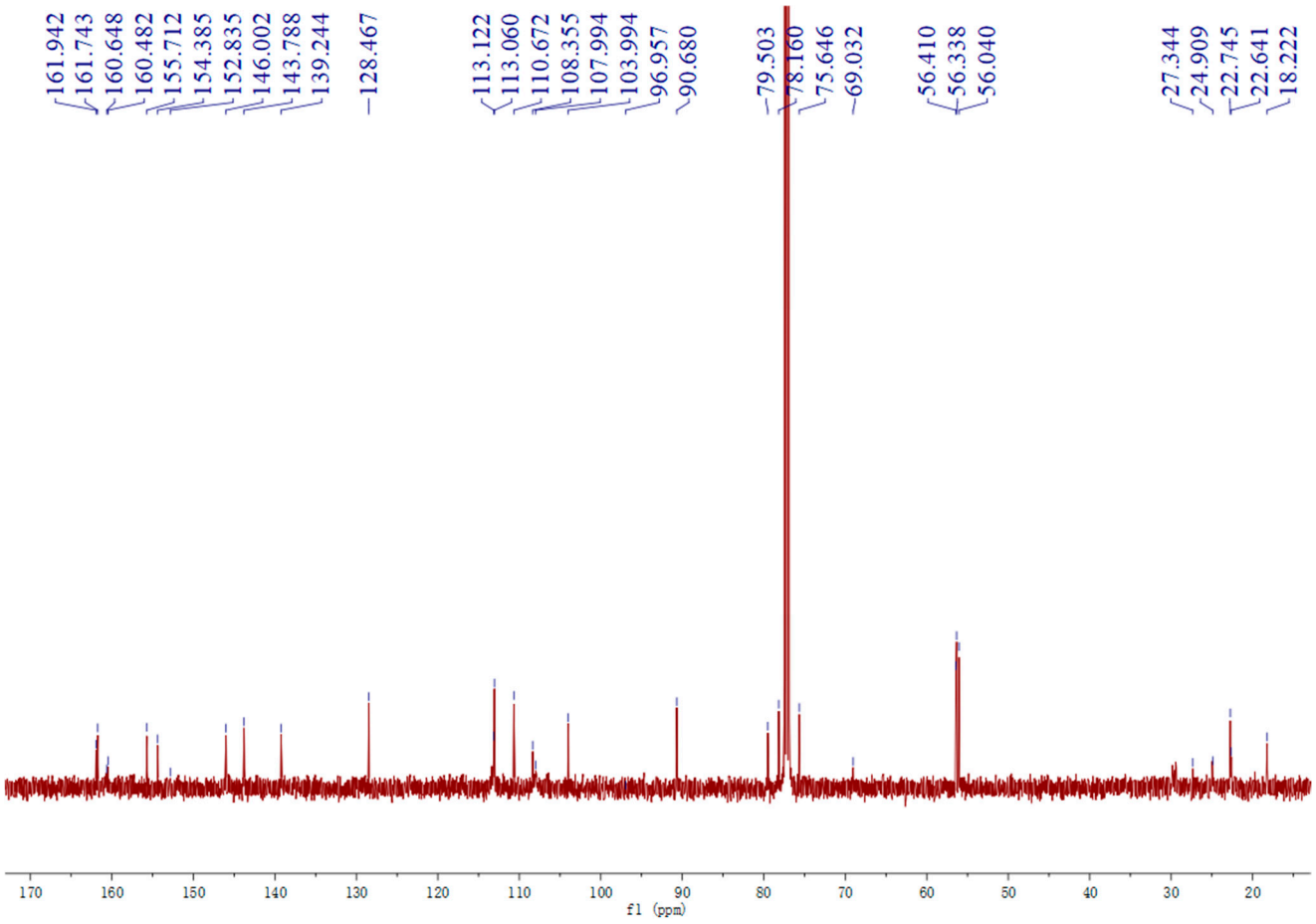
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S3. 1D and 2D NMR spectra of compounds **1**–**12**

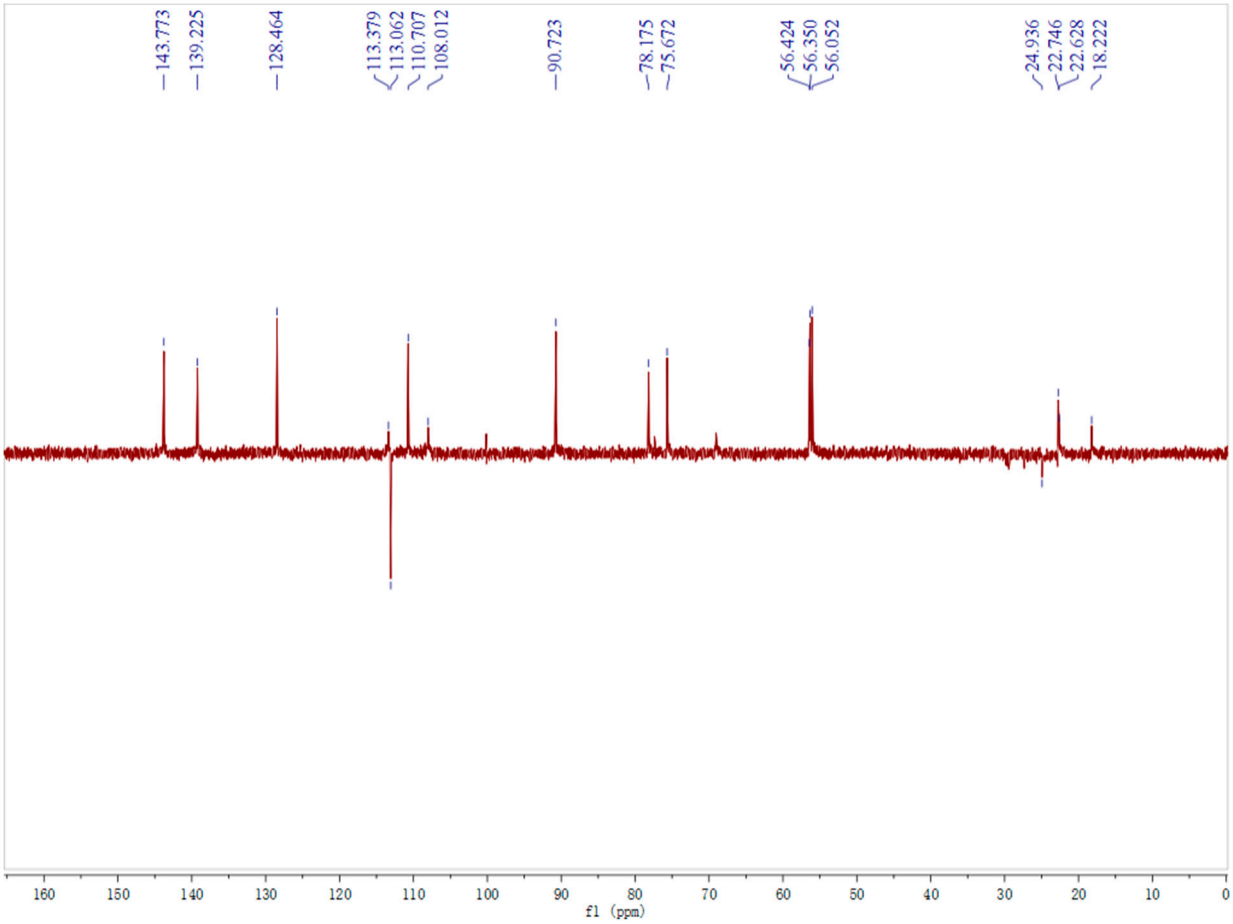
Spectrum S1. ^{1}H NMR spectrum of **1** in $CDCl_3$



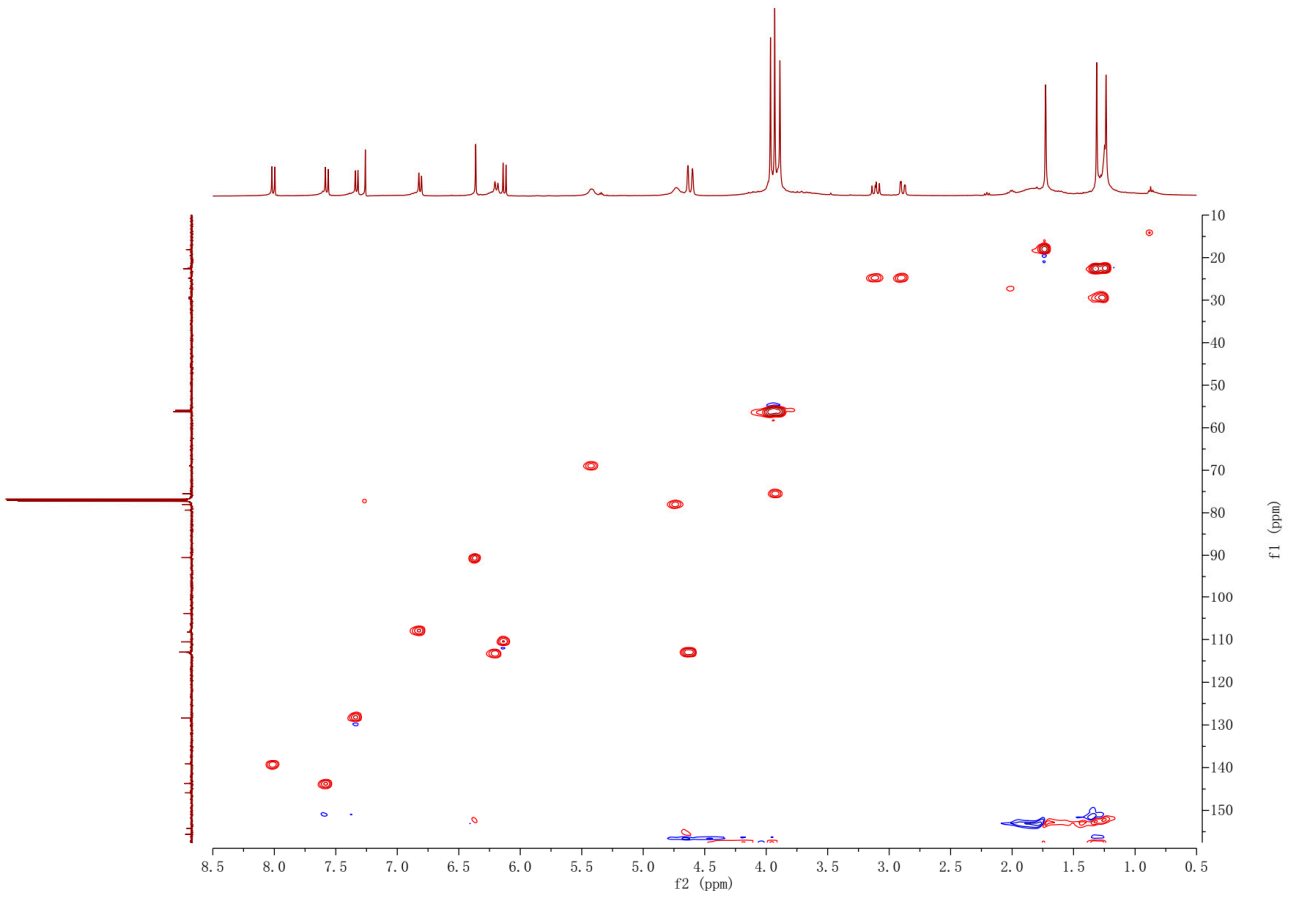
Spectrum S2. ^{13}C NMR spectrum of **1** in $CDCl_3$


161.942
161.743
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160.482
155.712
154.385
152.835
146.002
143.788
139.244
128.467
113.122
113.060
110.672
108.355
107.994
103.994
96.957
90.680
79.503
78.160
75.646
69.032
56.410
56.338
56.040
27.344
24.909
22.745
22.641
18.222
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

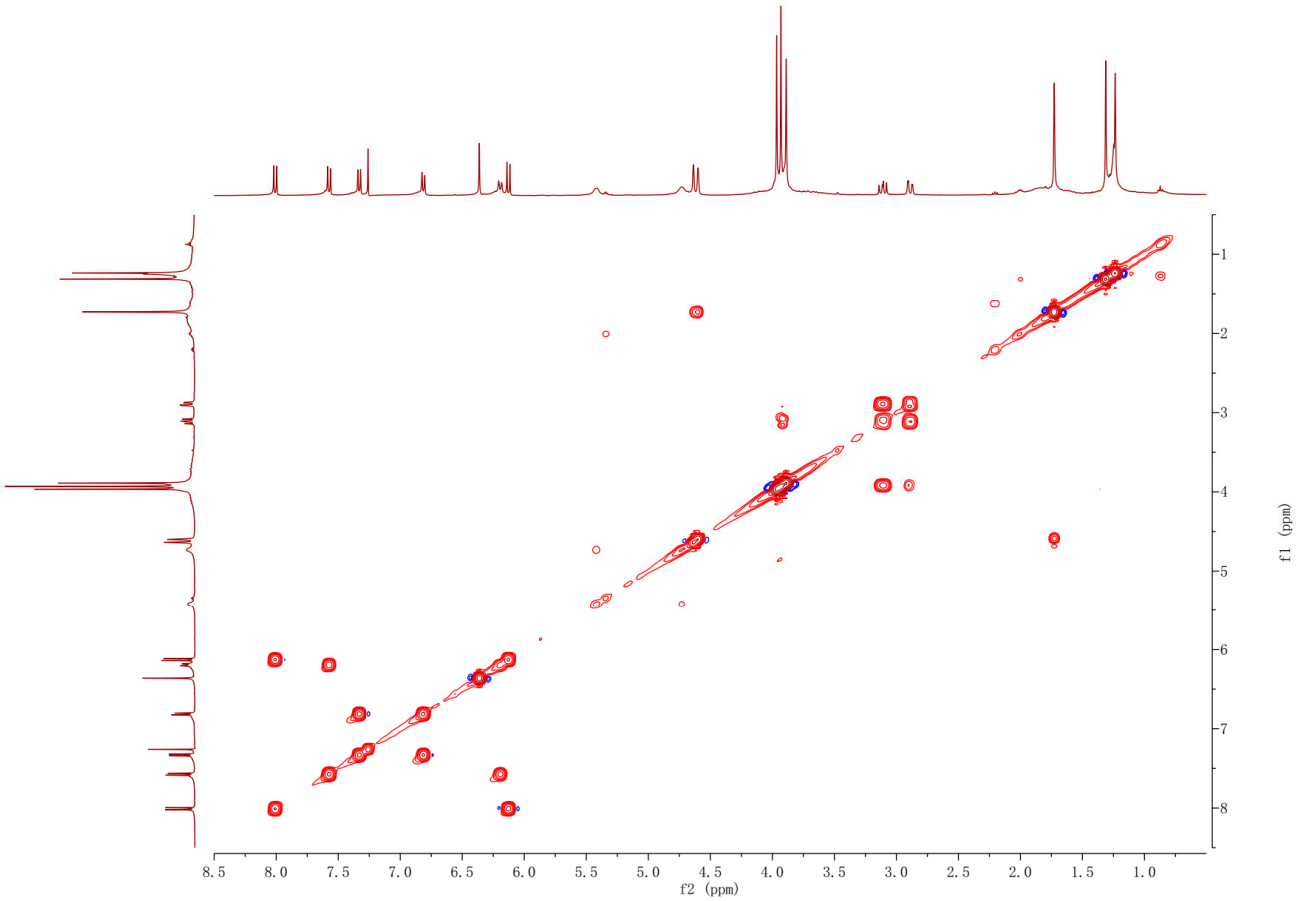
Spectrum S3. DEPT spectrum of **1** in $CDCl_3$



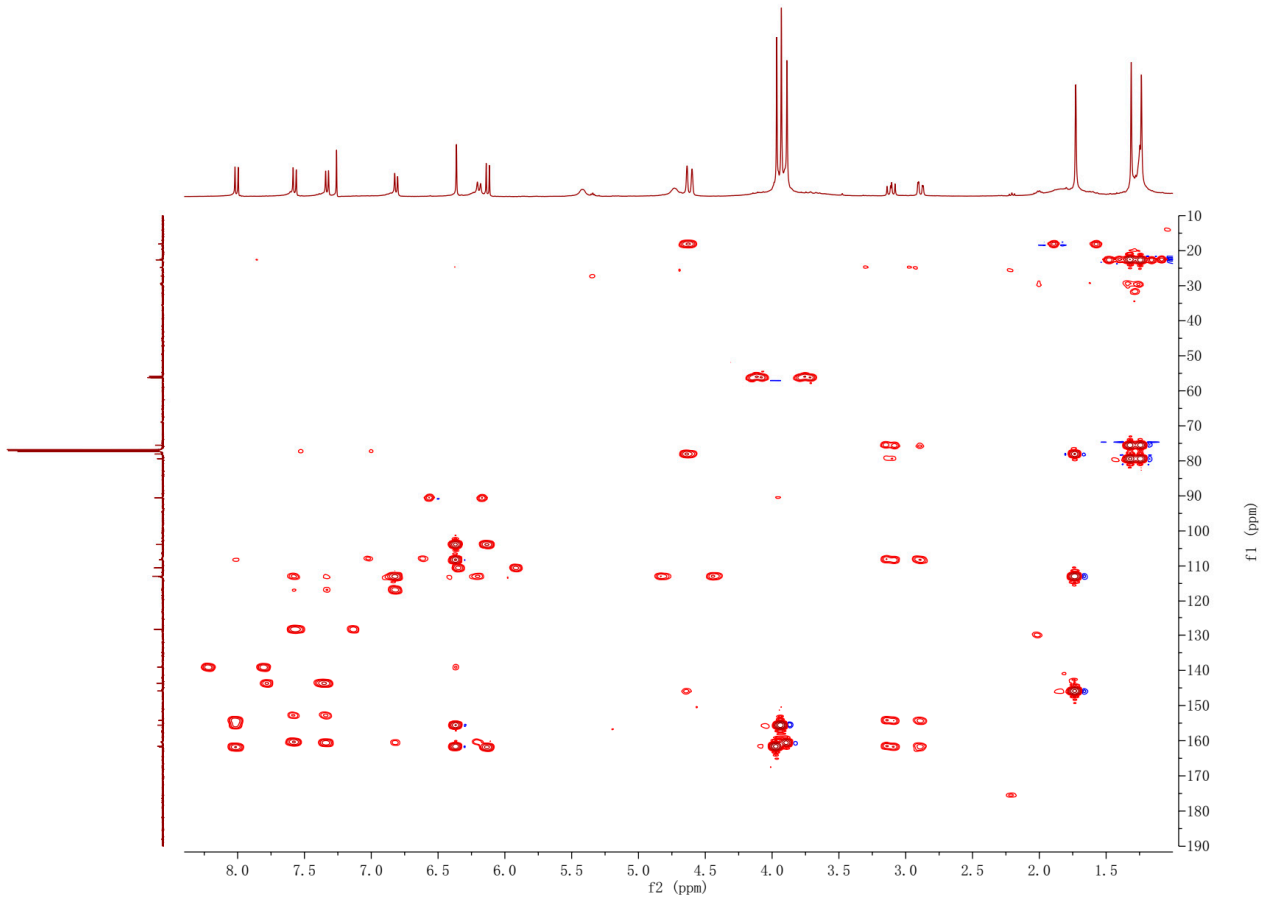
Spectrum S4. HSQC spectrum of **1** in $CDCl_3$



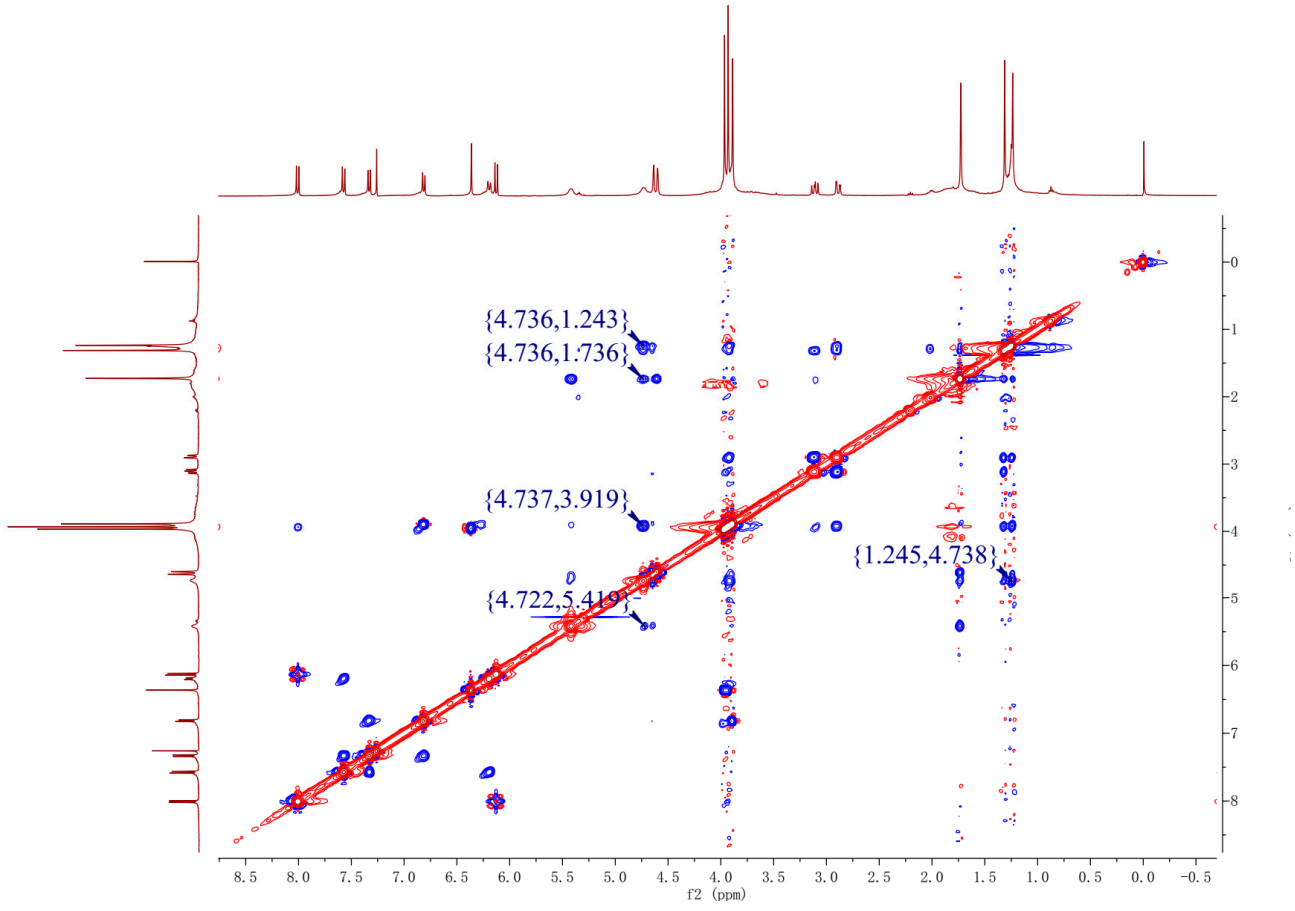
Spectrum S5. $^{1}H–^{1}H$ COSY spectrum of **1** in $CDCl_3$



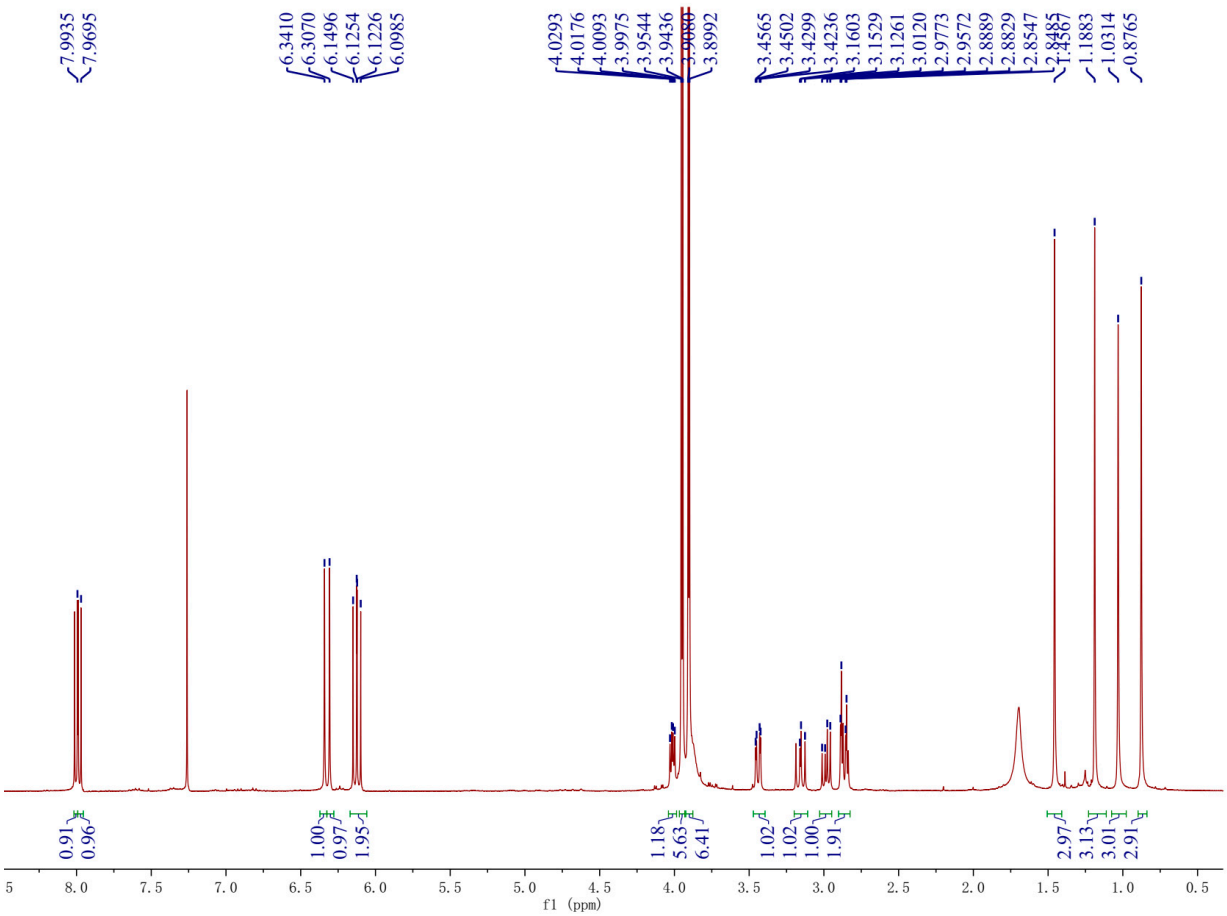
Spectrum S6. HMBC spectrum of **1** in $CDCl_3$



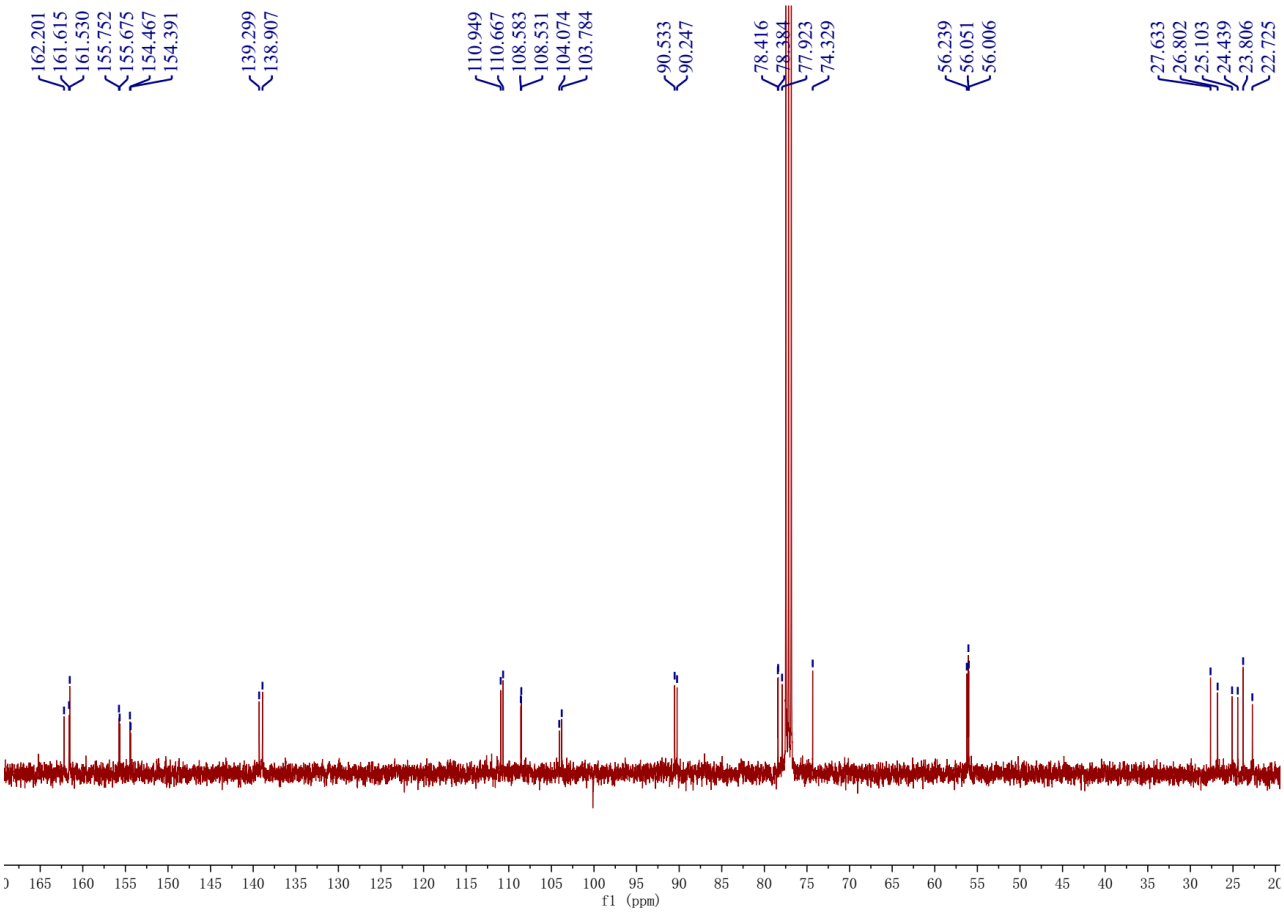
Spectrum S7. NOESY spectrum of **1** in $CDCl_3$



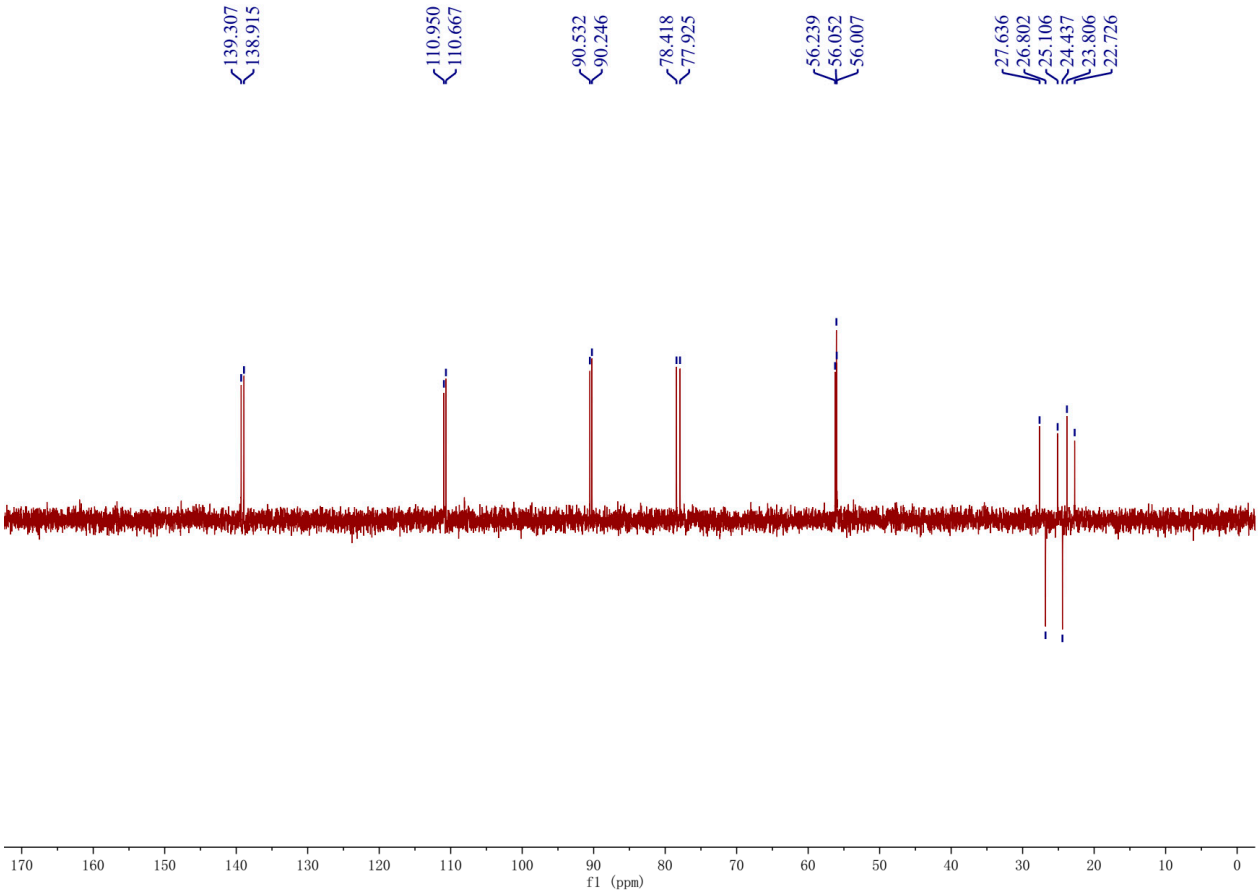
Spectrum S8. ^1H NMR spectrum of **2** in $CDCl_3$



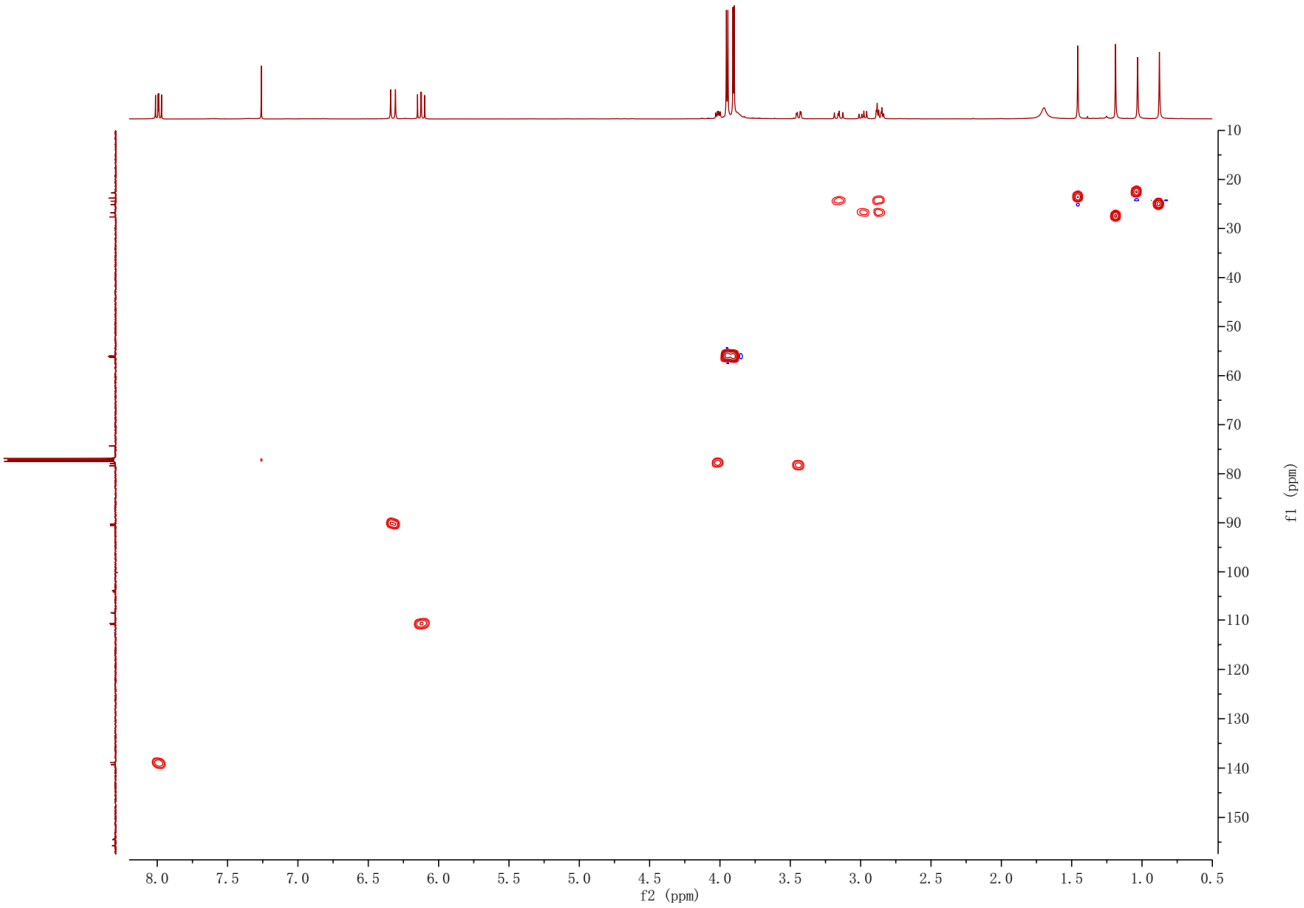
Spectrum S9. ^{13}C NMR spectrum of **2** in $CDCl_3$



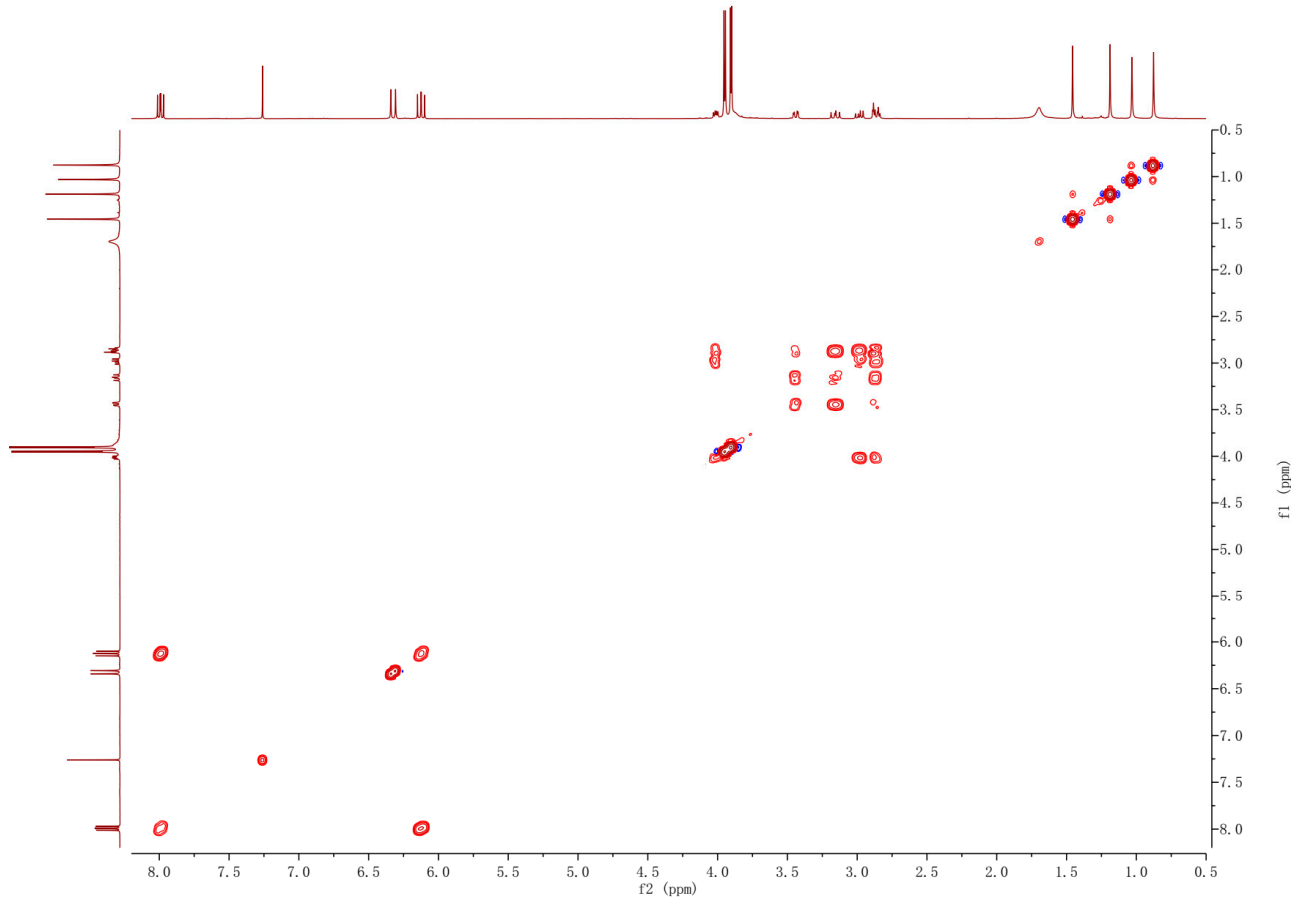
Spectrum S10. DEPT spectrum of **2** in $CDCl_3$



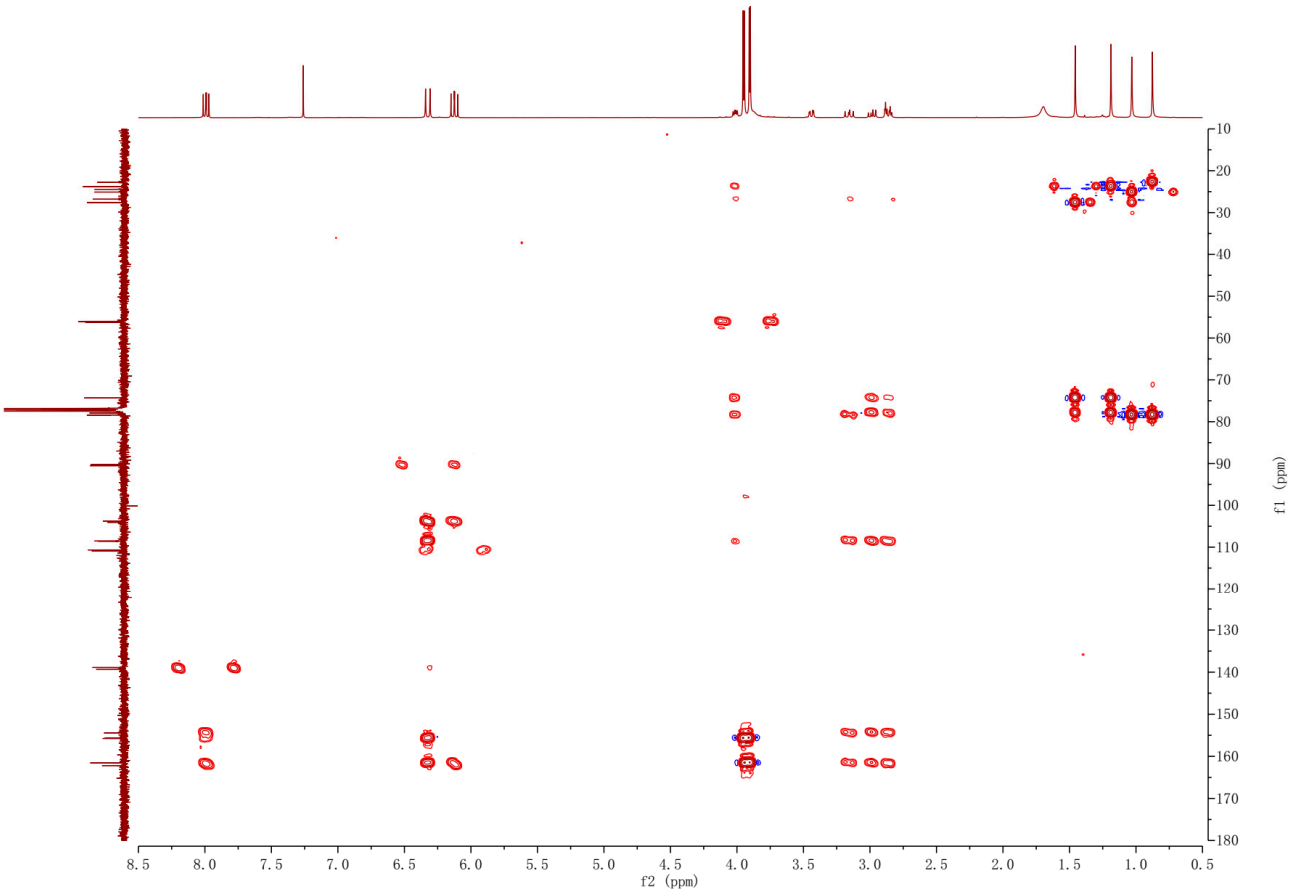
Spectrum S11. HSQC spectrum of **2** in $CDCl_3$



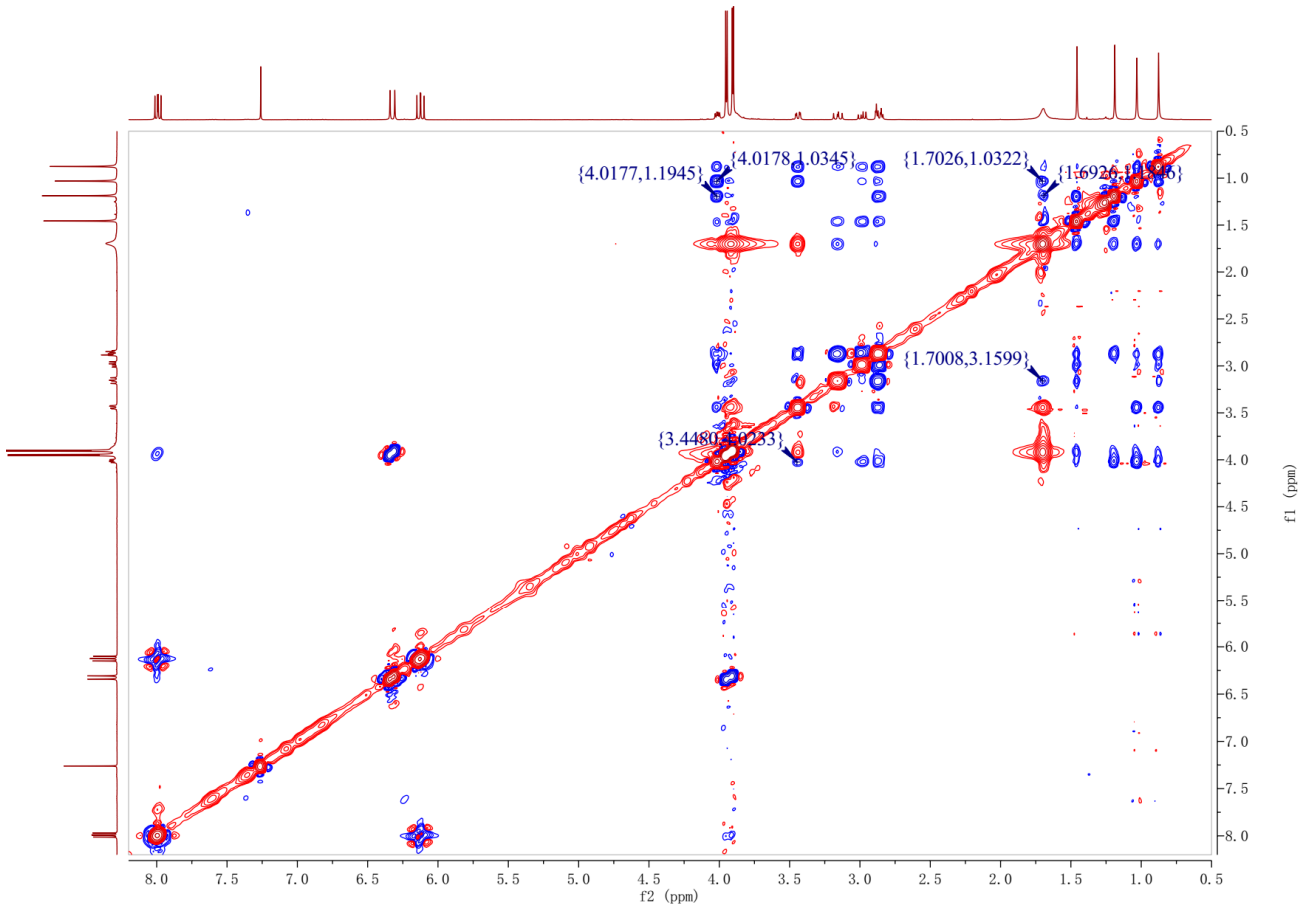
Spectrum S12. $^{1}H-^{1}H$ COSY spectrum of **2** in $CDCl_3$



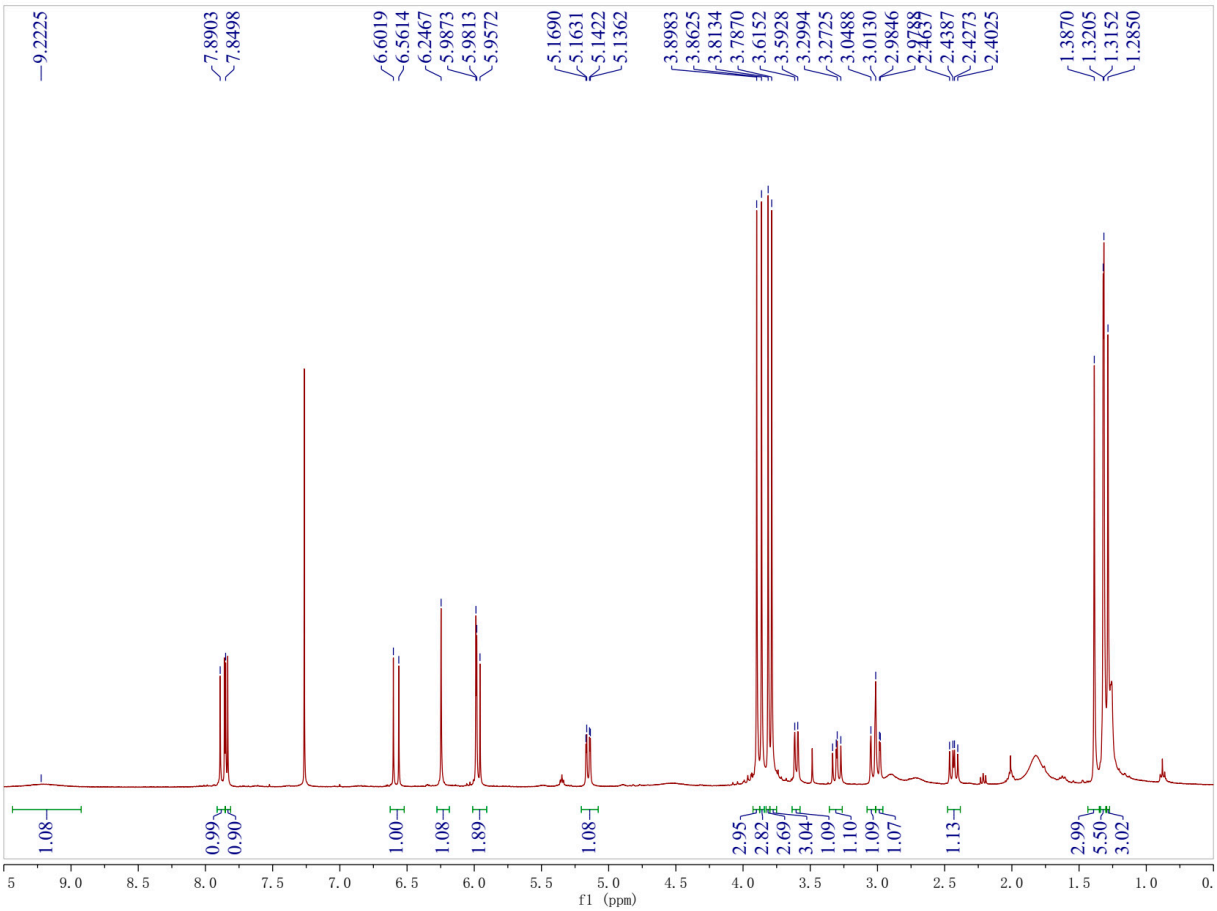
Spectrum S13. HMBC spectrum of **2** in $CDCl_3$



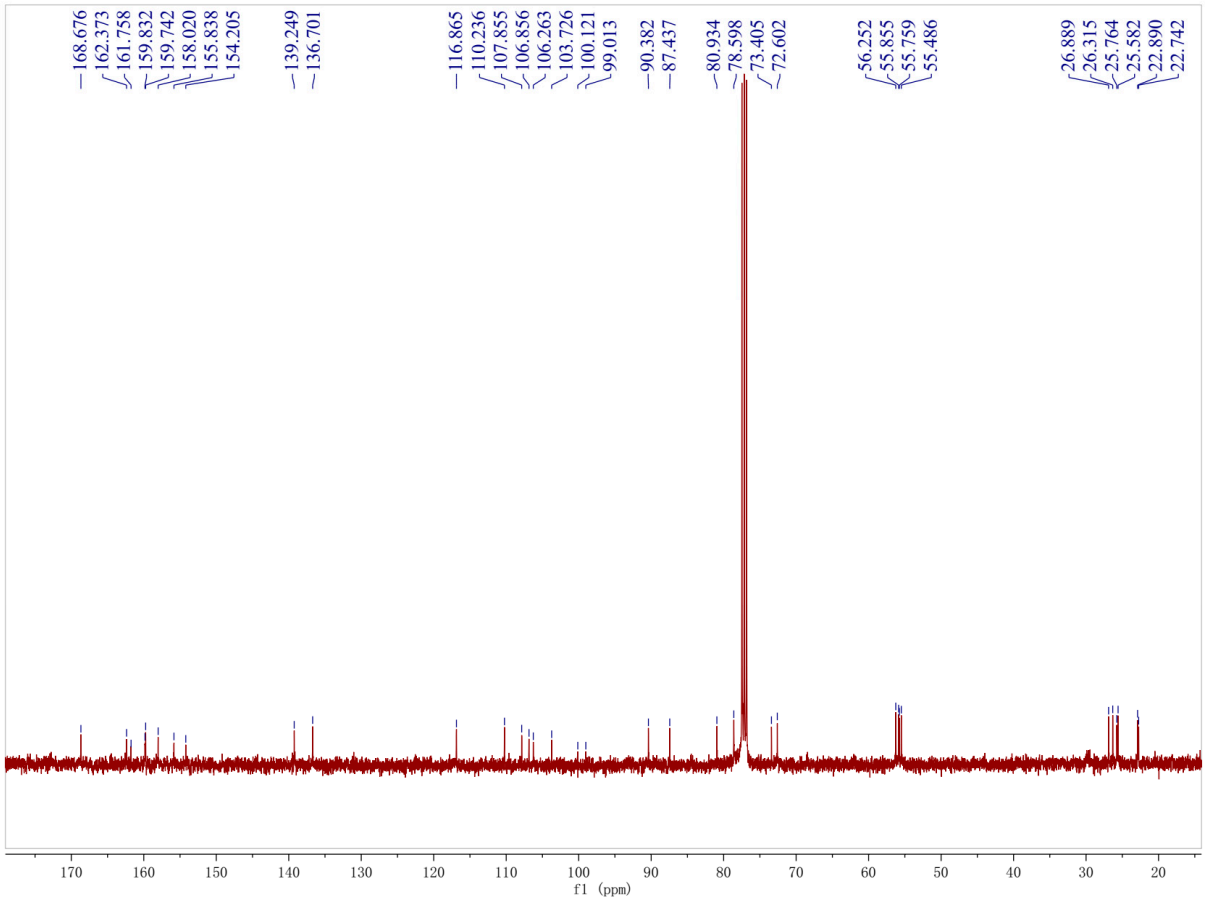
Spectrum S14. NOE spectra of **2** in $CDCl_3$



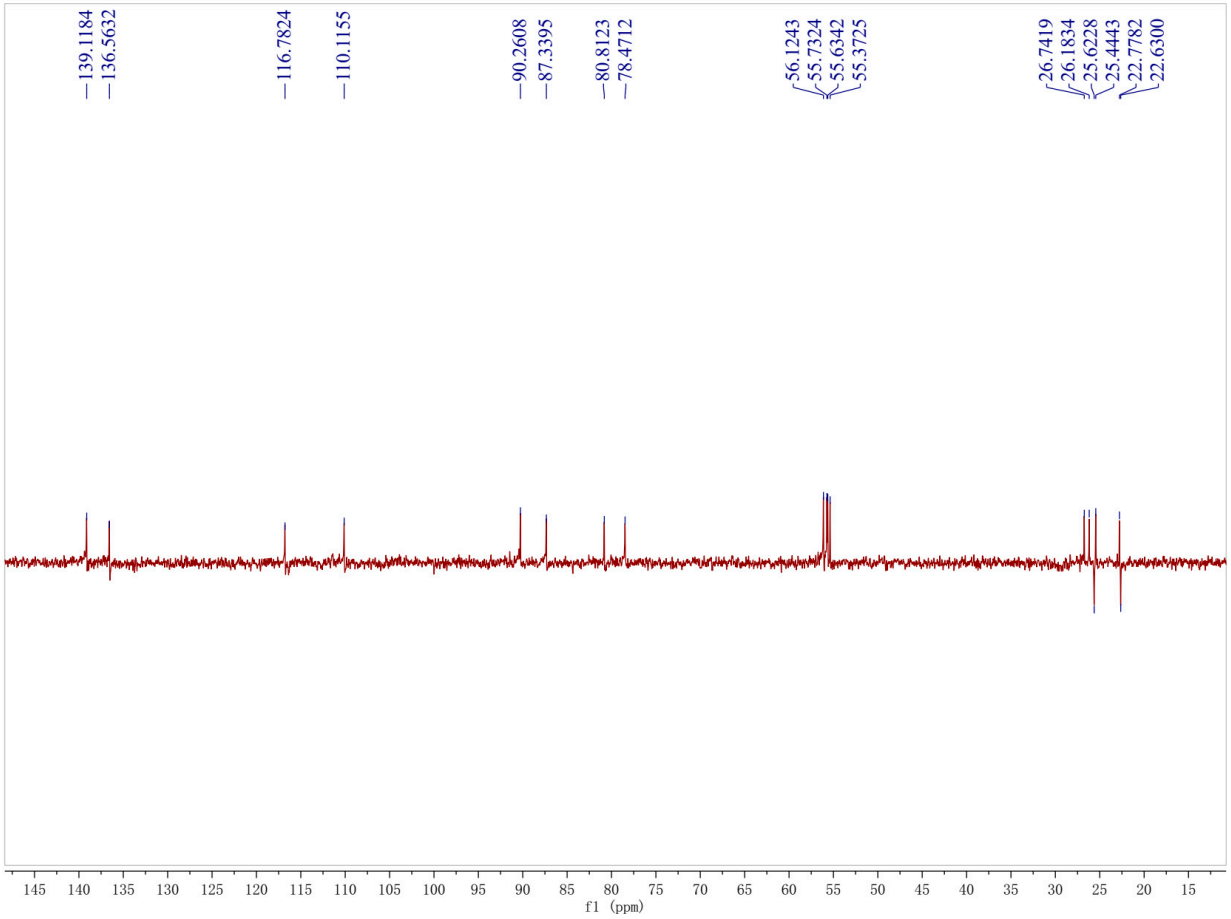
Spectrum S15. ^{1}H NMR spectrum of **3** in $CDCl_3$



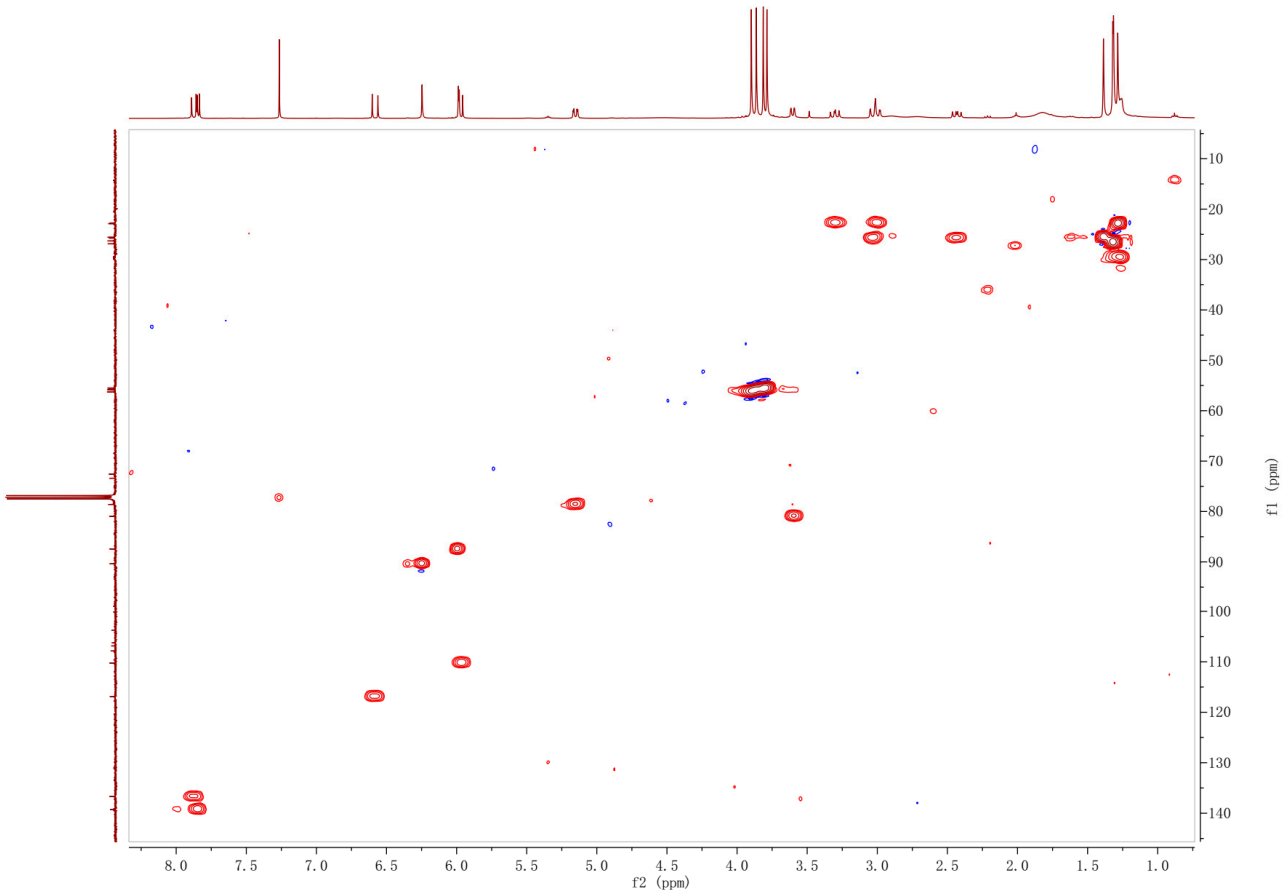
Spectrum S16. ^{13}C NMR spectrum of **3** in $CDCl_3$



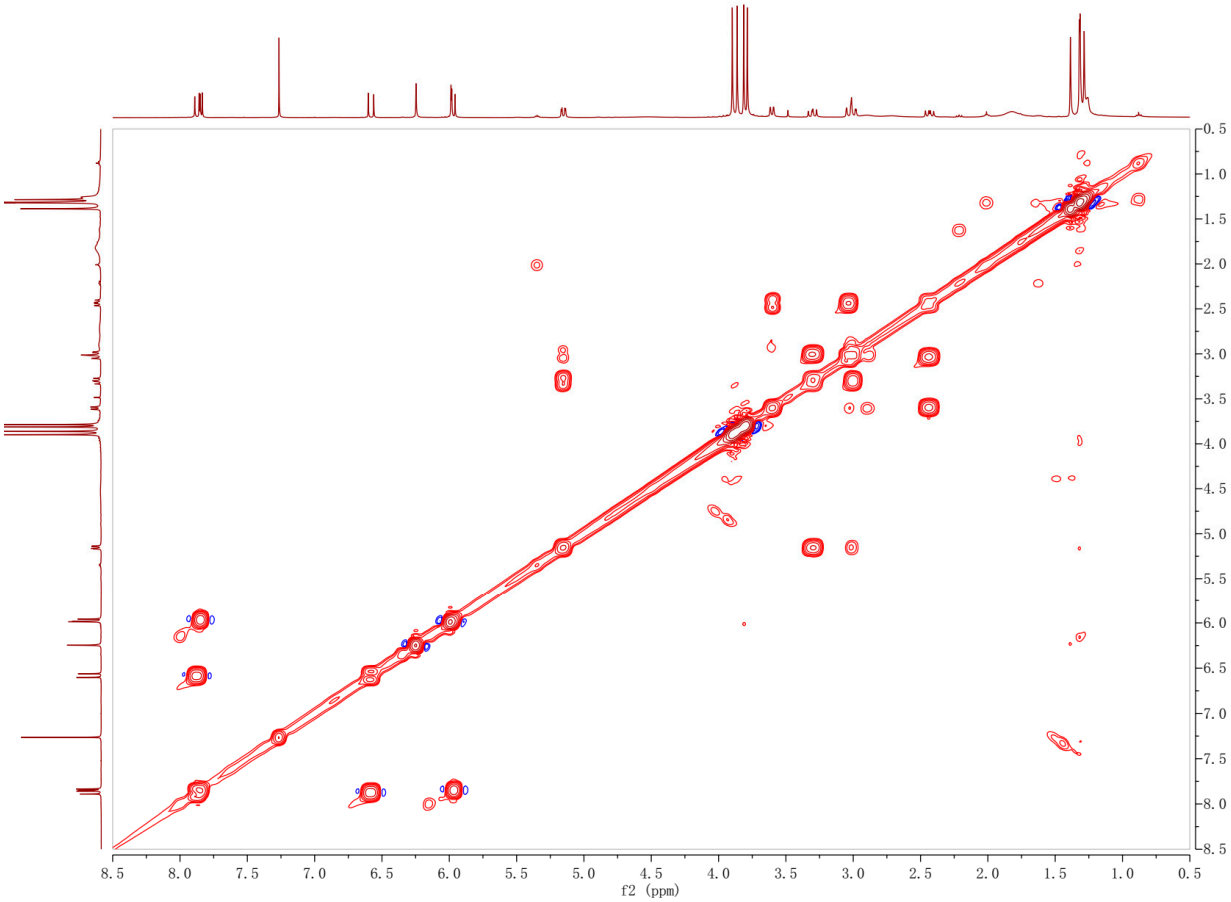
Spectrum S17. DEPT spectrum of **3** in $CDCl_3$



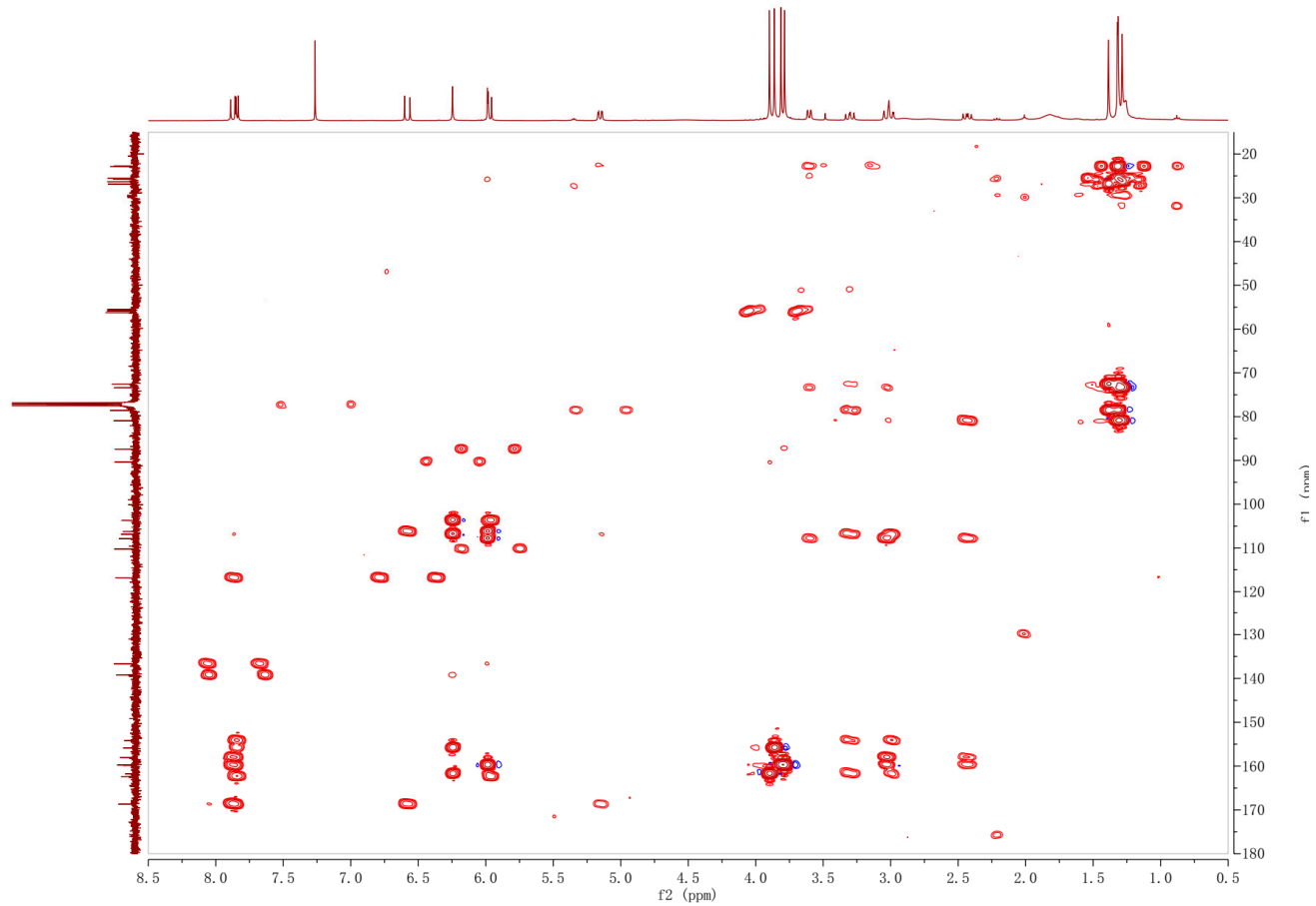
Spectrum S18. HSQC spectrum of **3** in $CDCl_3$



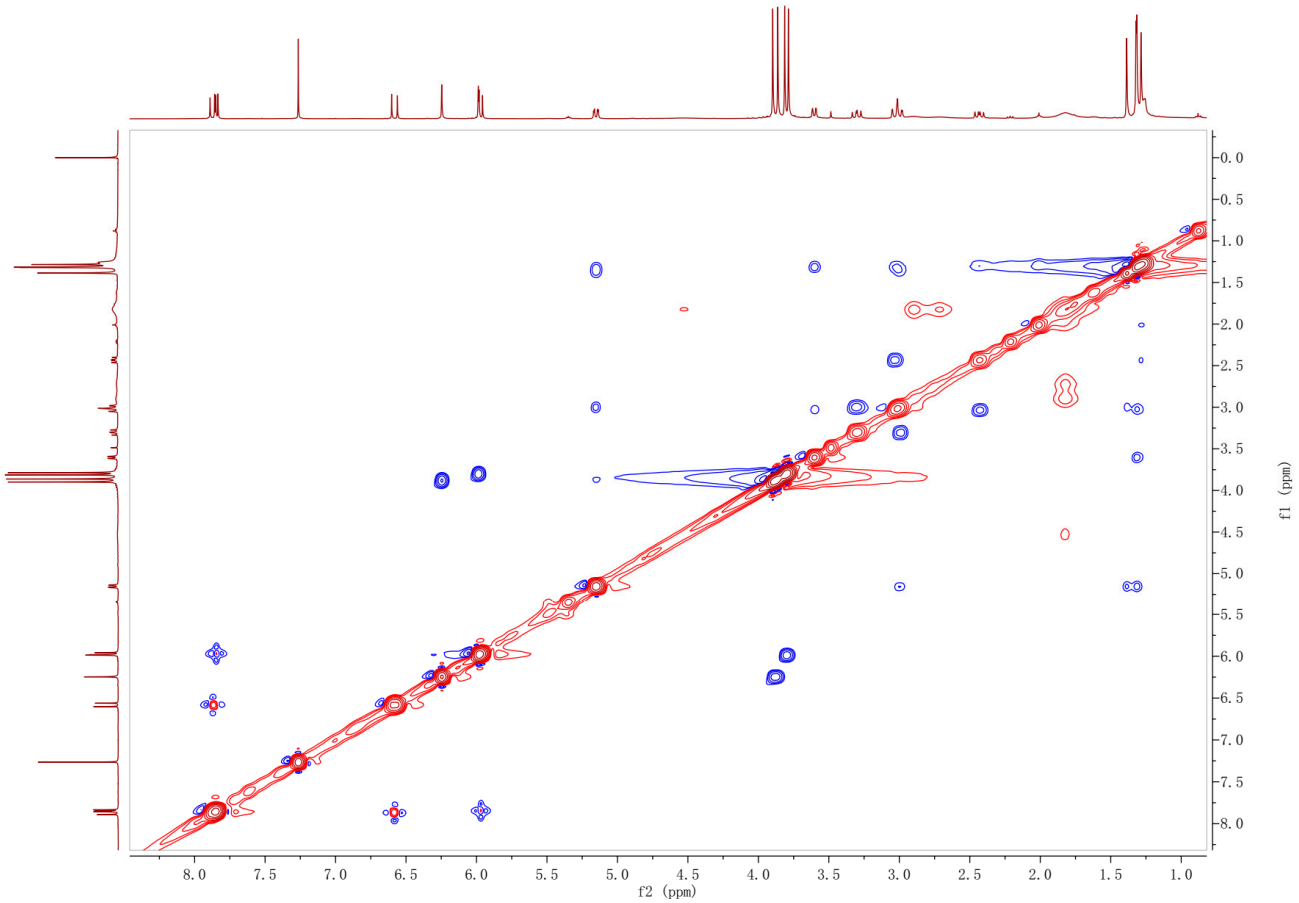
Spectrum S19. $^{1}H-^{1}H$ COSY spectrum of **3** in $CDCl_3$



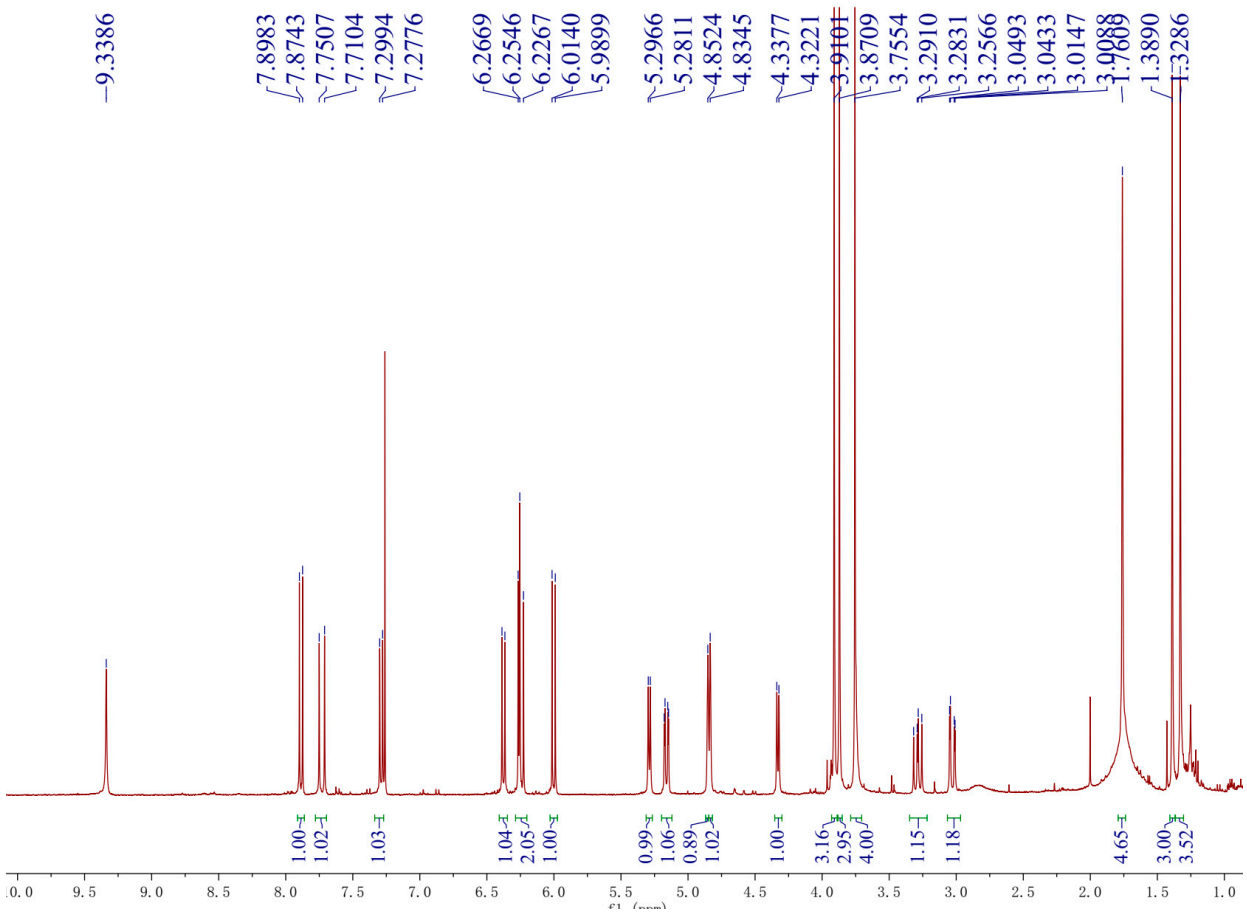
Spectrum S20. HMBC spectra of **3** in $CDCl_3$



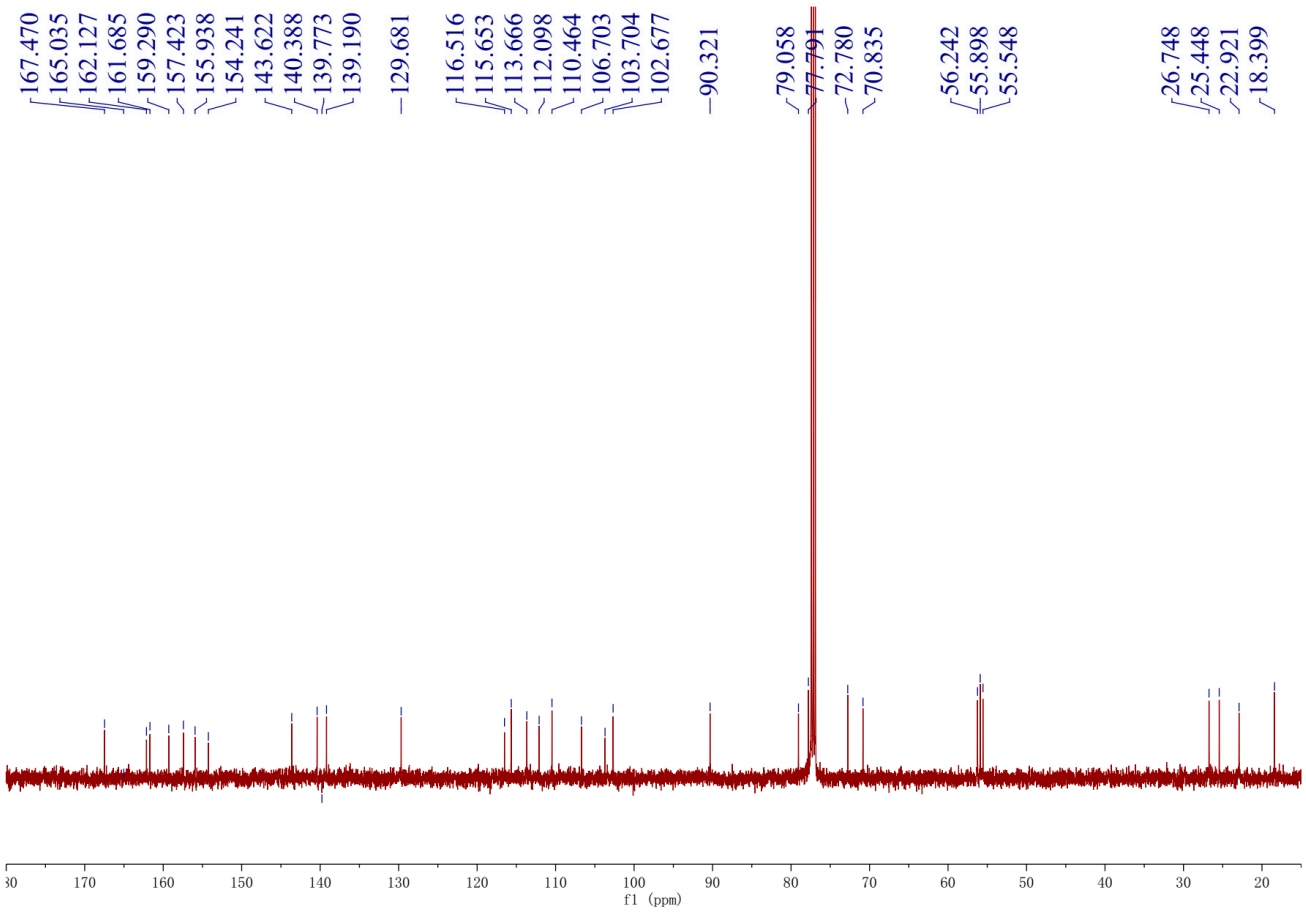
Spectrum S21. NOE spectrum of **3** in $CDCl_3$



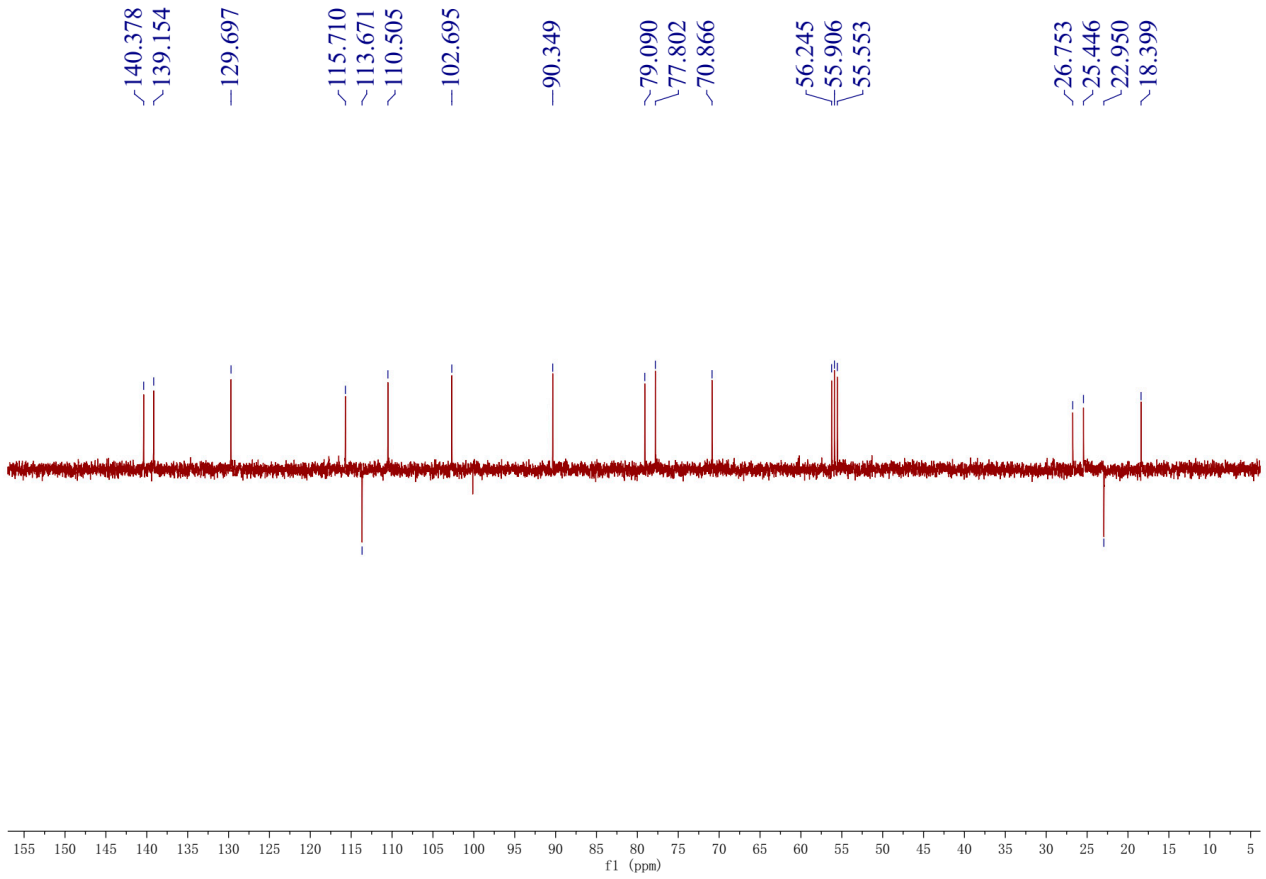
Spectrum S22. ^1H NMR spectrum of **4** in $CDCl_3$



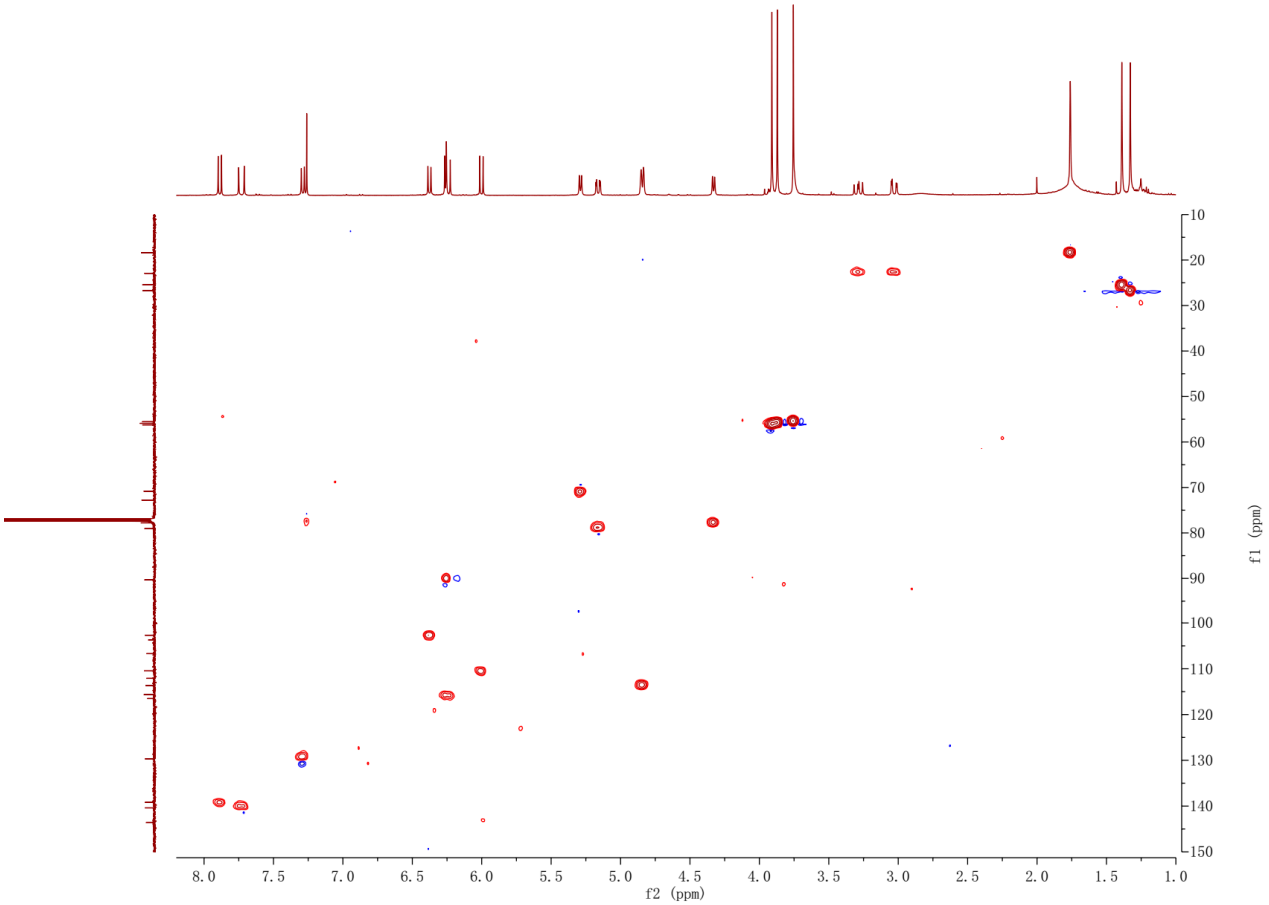
Spectrum S23. ^{13}C NMR spectrum of **4** in $CDCl_3$



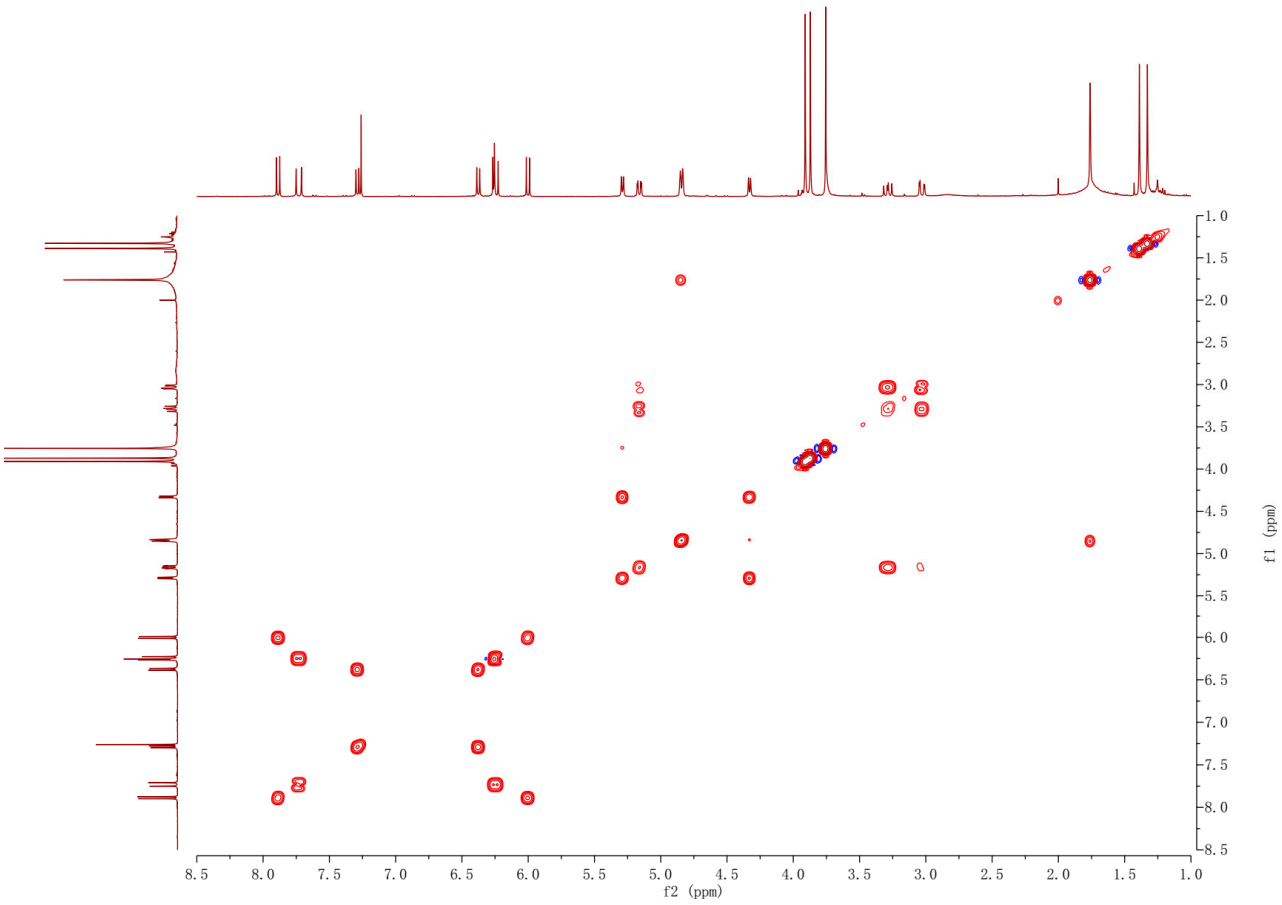
Spectrum S24. DEPT spectrum of **4** in $CDCl_3$



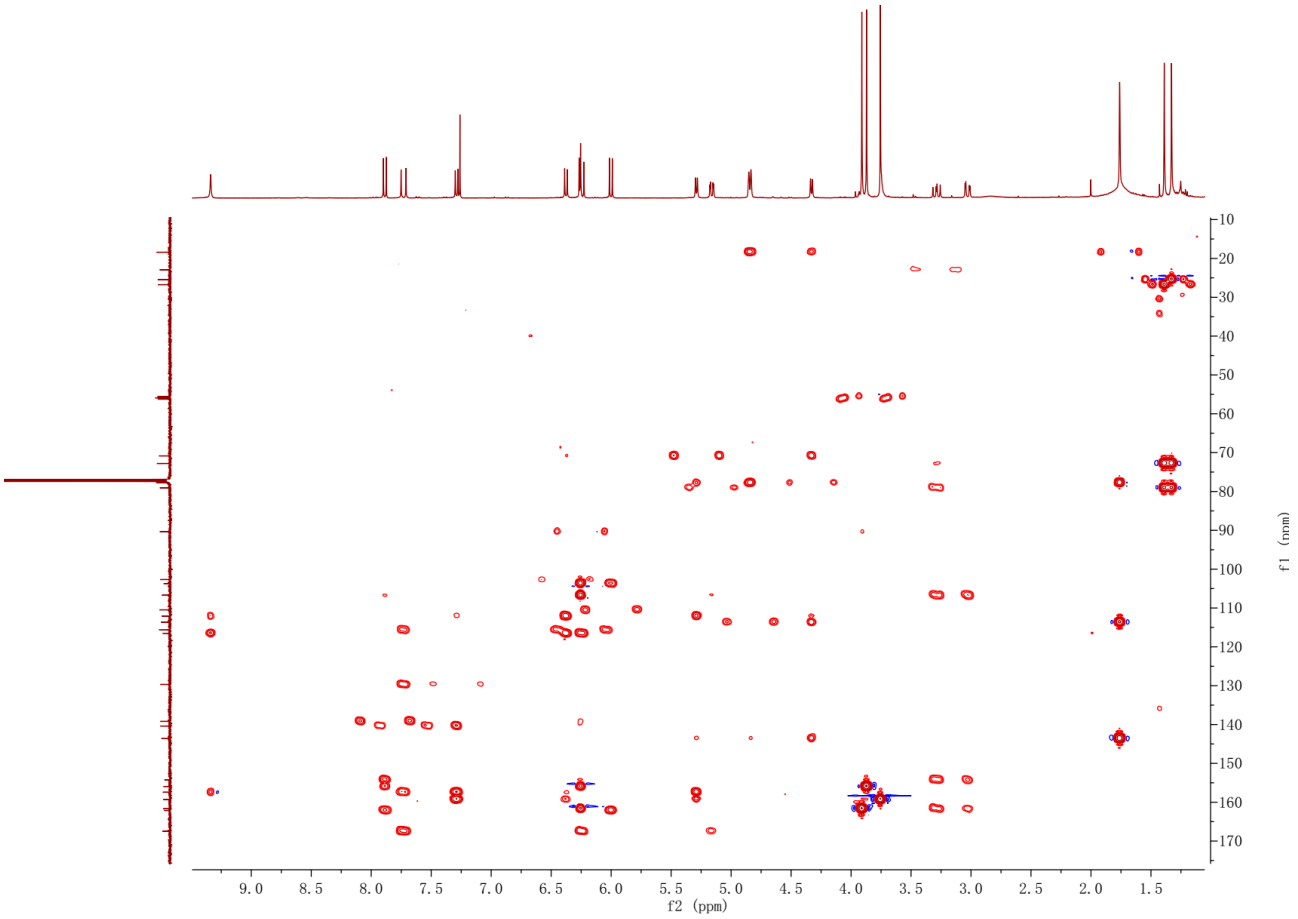
Spectrum S25. HSQC spectrum of **4** in $CDCl_3$



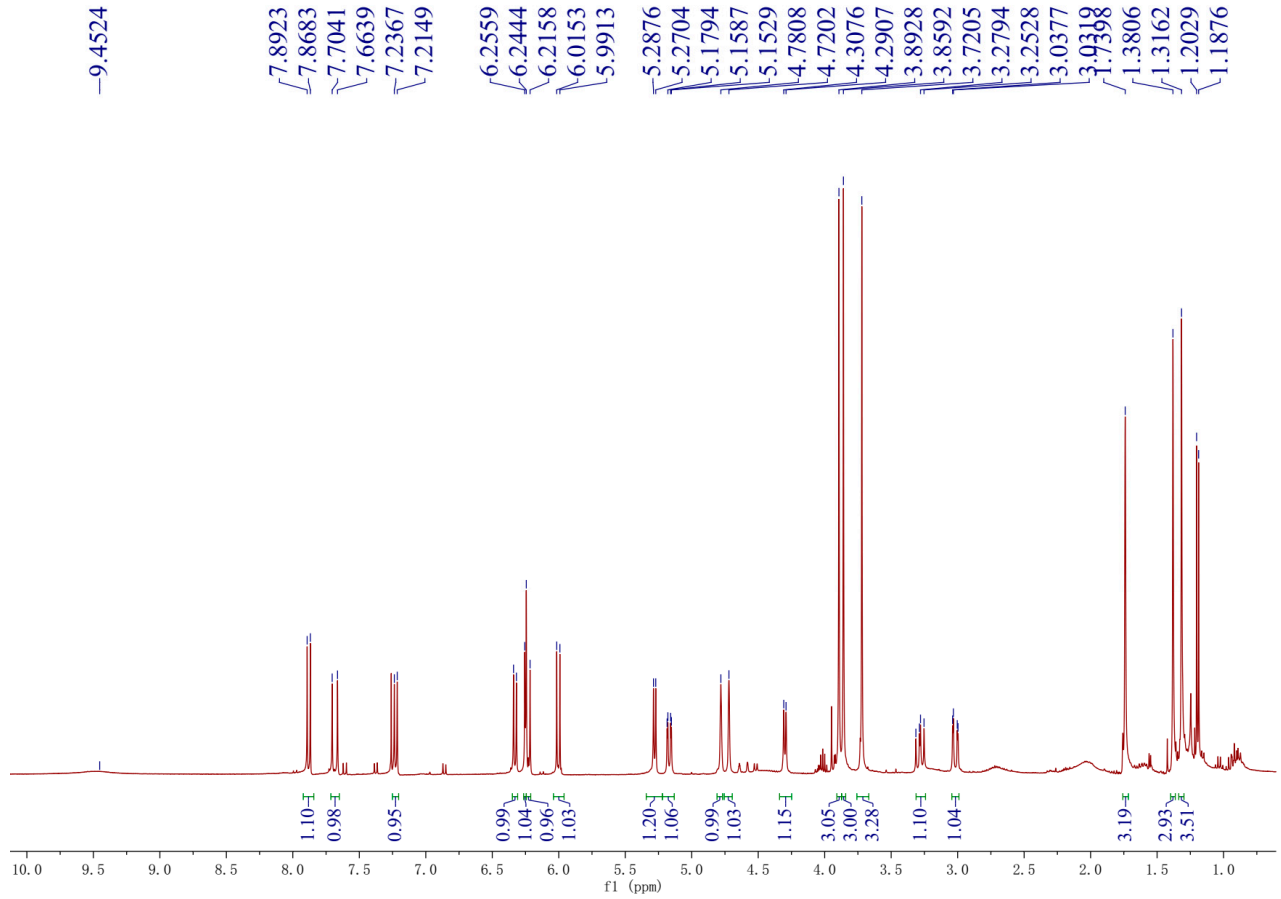
Spectrum S26. $^{1}H–^{1}H$ COSY spectrum of **4** in $CDCl_3$



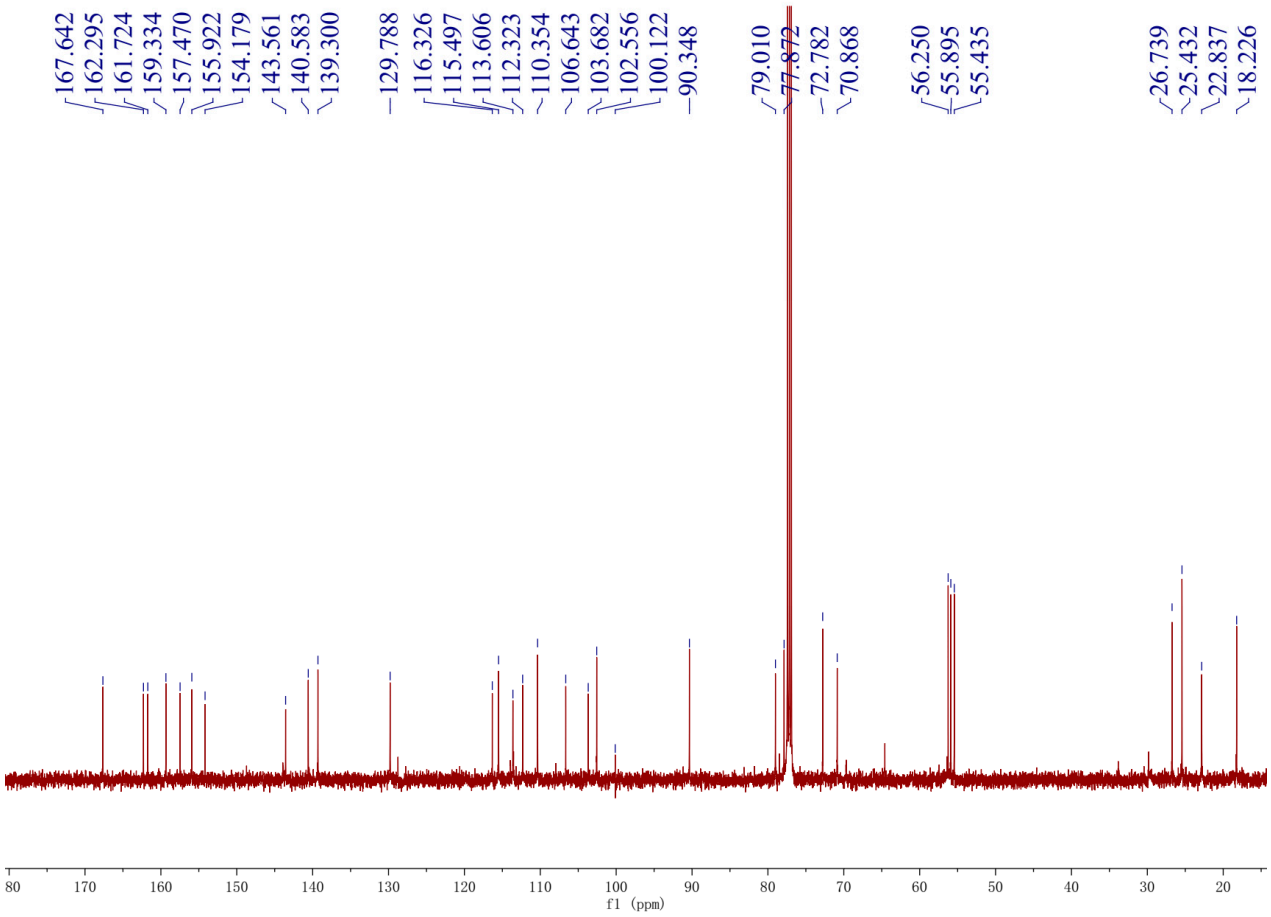
Spectrum S27. HMBC spectrum of **4** in $CDCl_3$



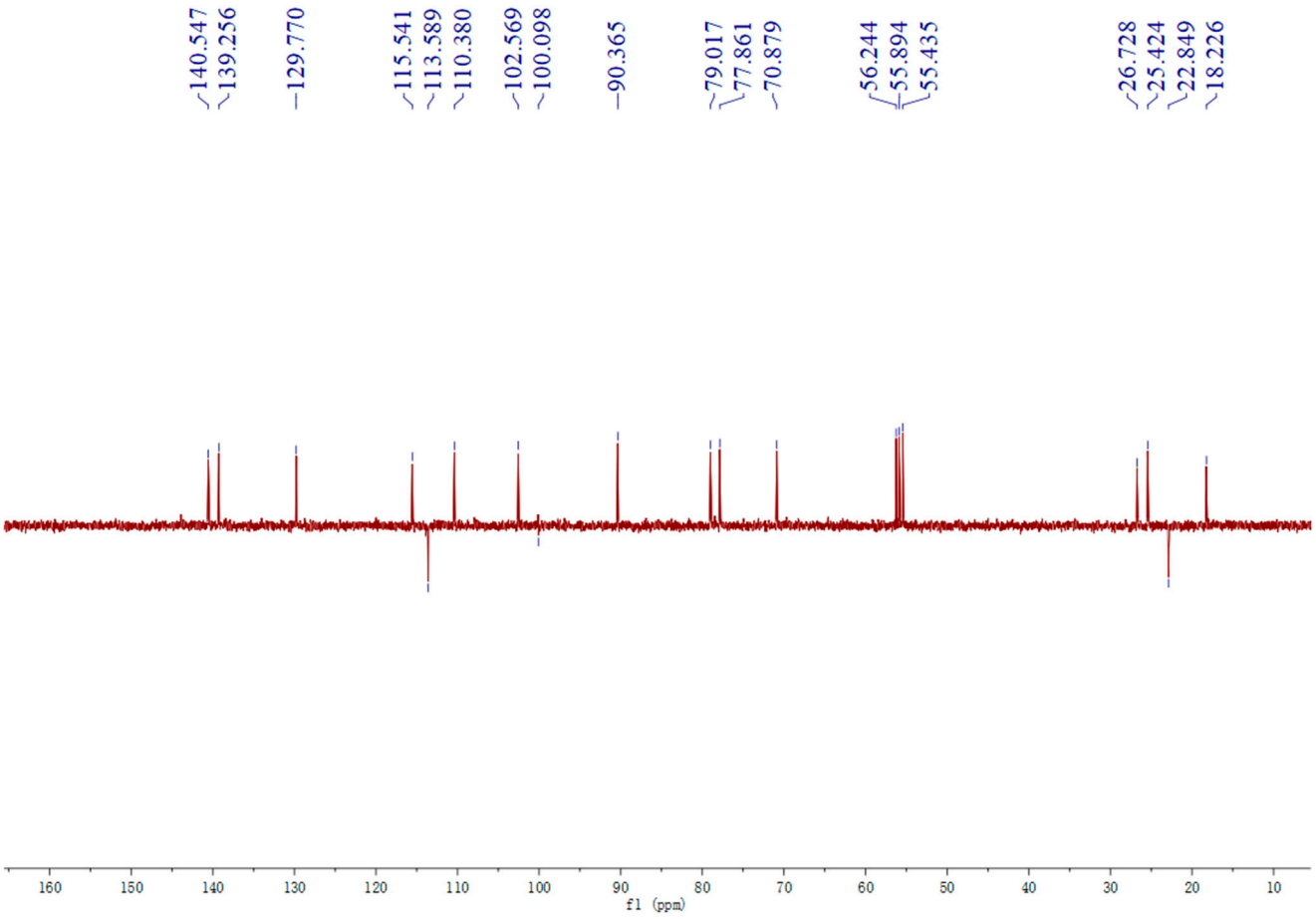
Spectrum S28. ^1H NMR spectrum of **5** in $CDCl_3$



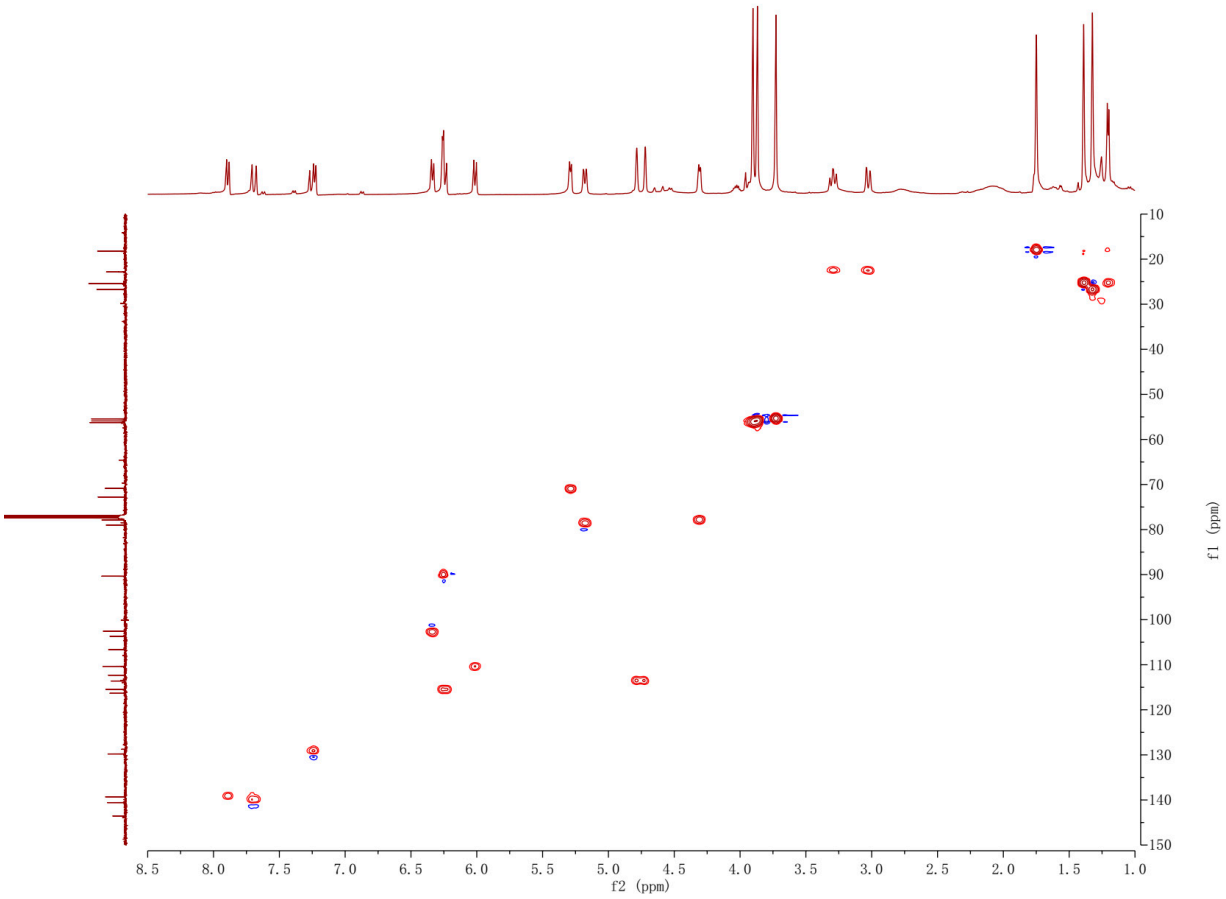
Spectrum S29. ^{13}C NMR spectrum of **5** in $CDCl_3$



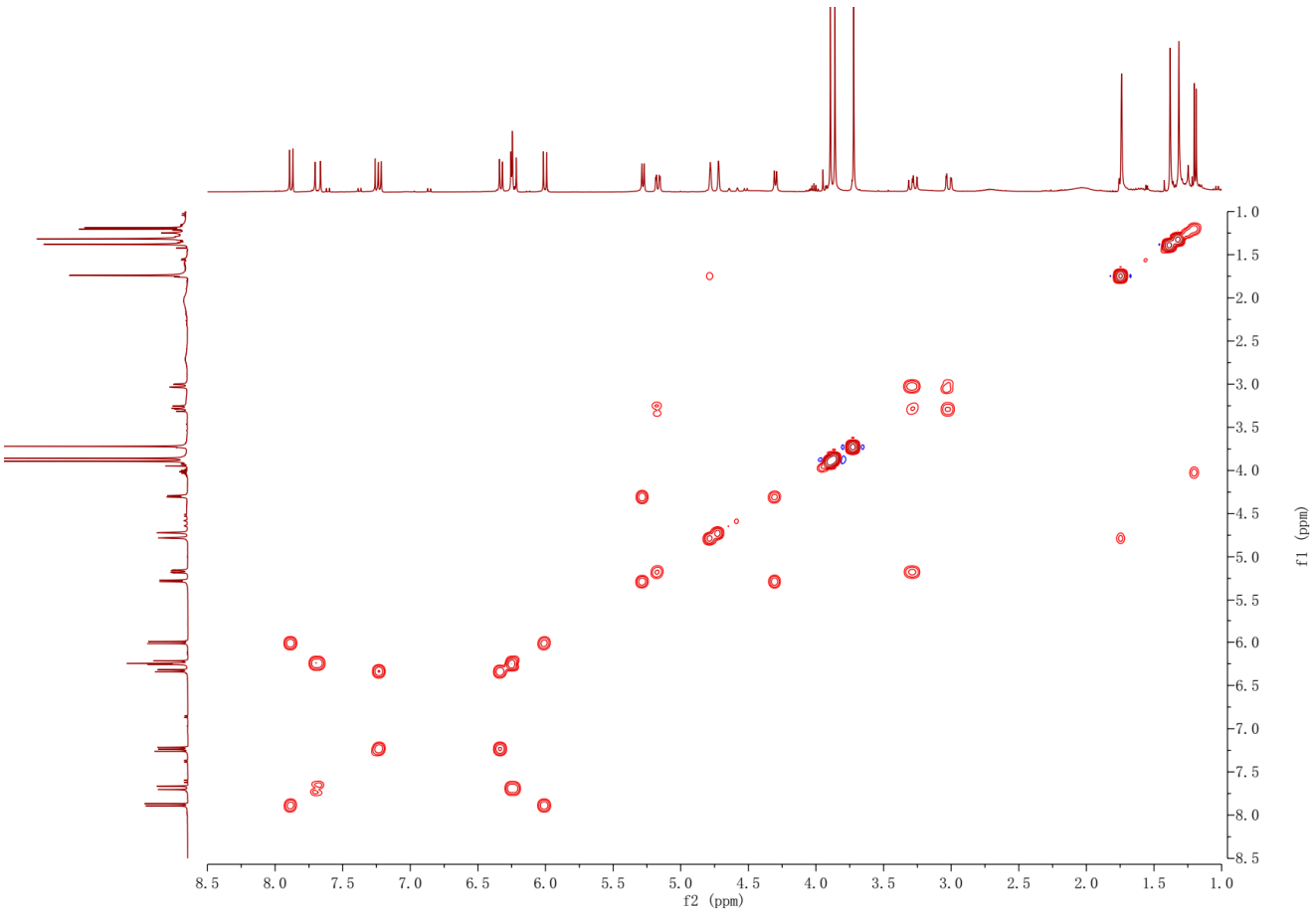
Spectrum S30. DEPT spectrum of **5** in $CDCl_3$



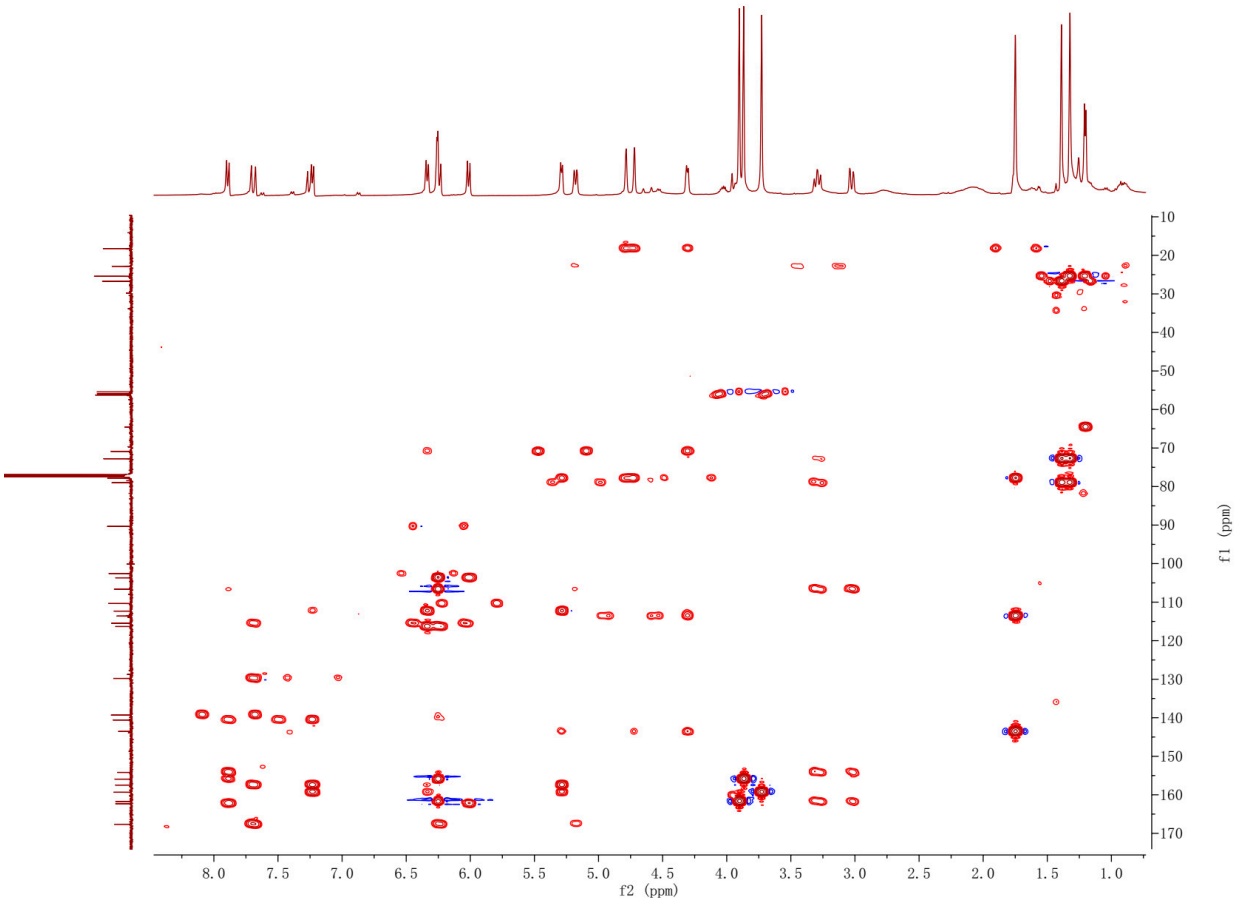
Spectrum S31. HSQC spectrum of **5** in $CDCl_3$



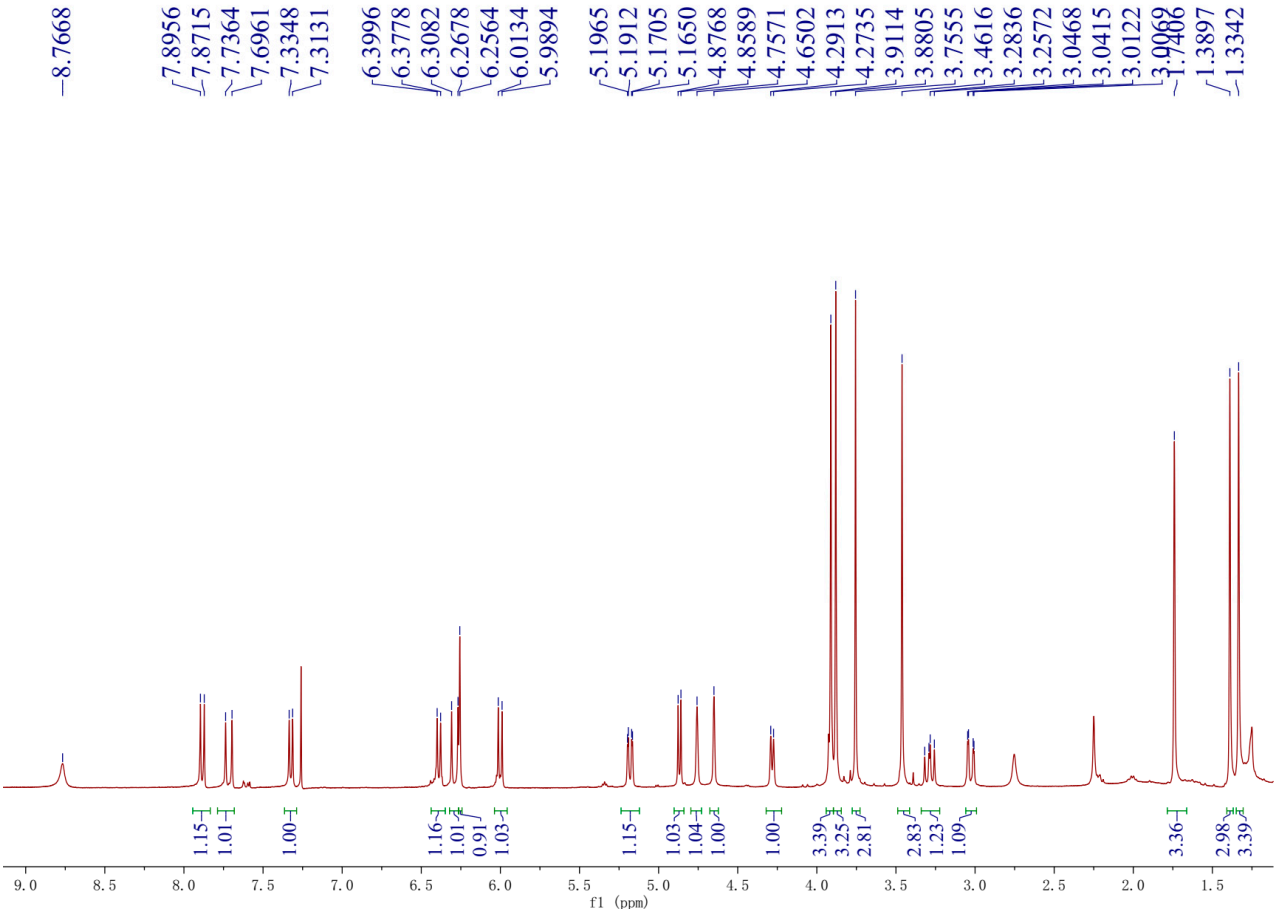
Spectrum S32. $^{1}H–^{1}H$ COSY spectrum of **5** in $CDCl_3$



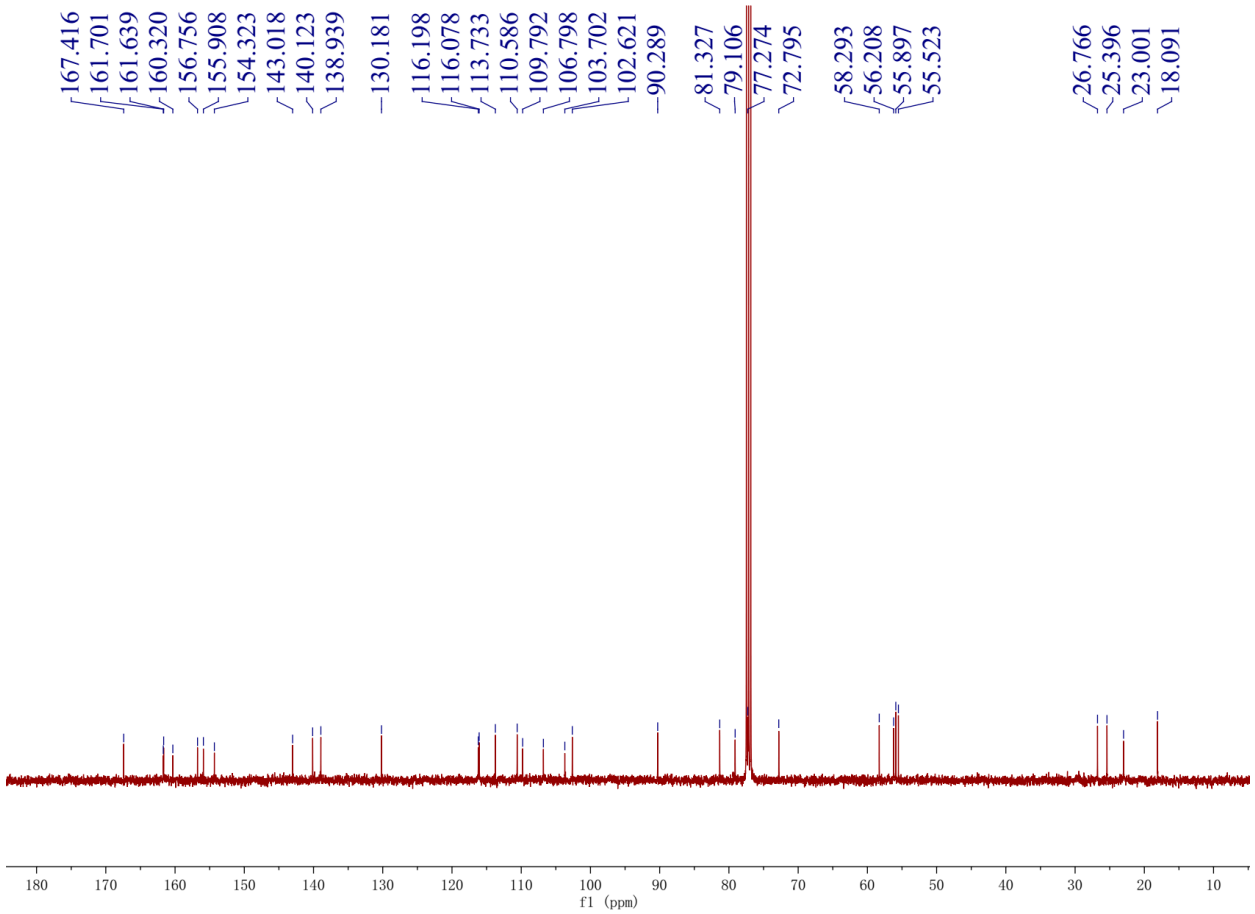
Spectrum S33. HMBC spectrum of **5** in $CDCl_3$



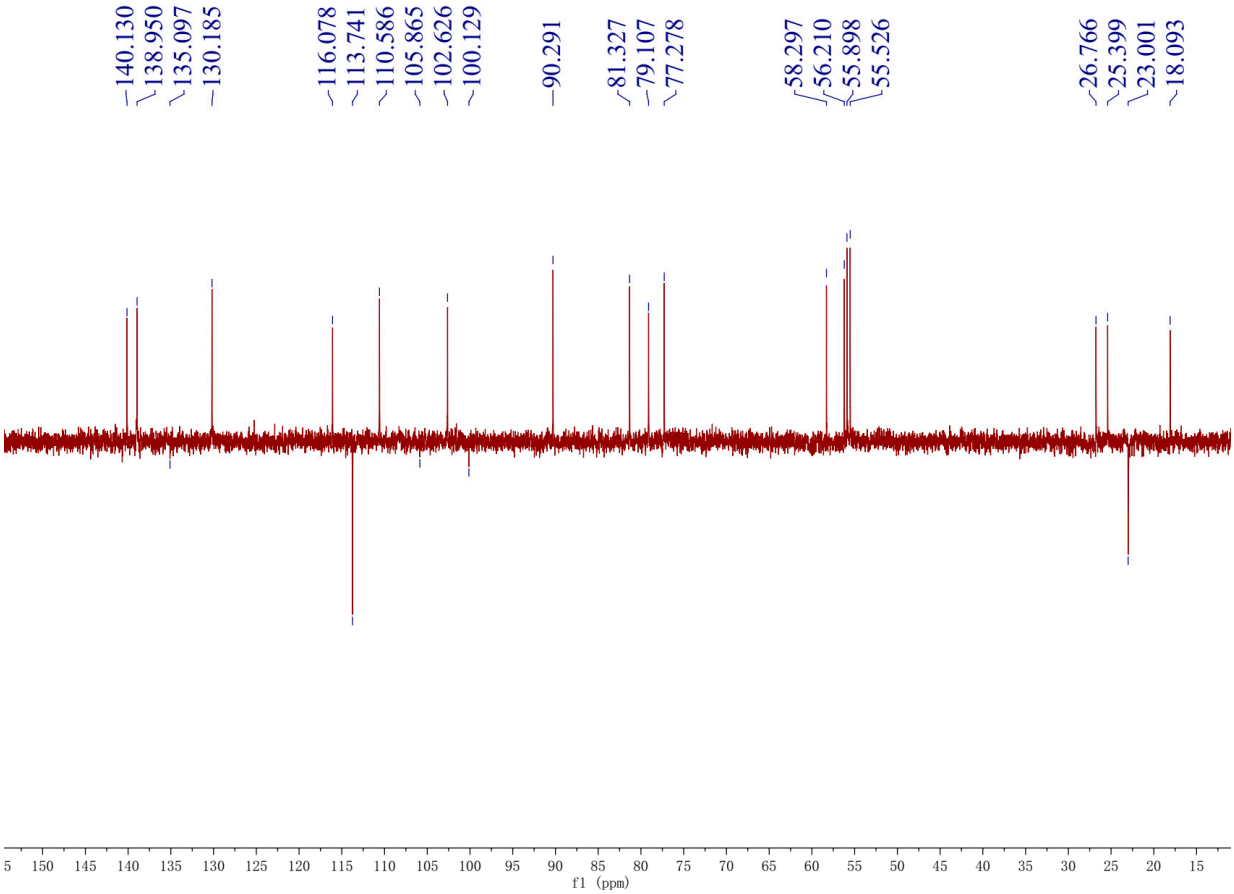
Spectrum S34. ^1H NMR spectrum of **6** in $CDCl_3$



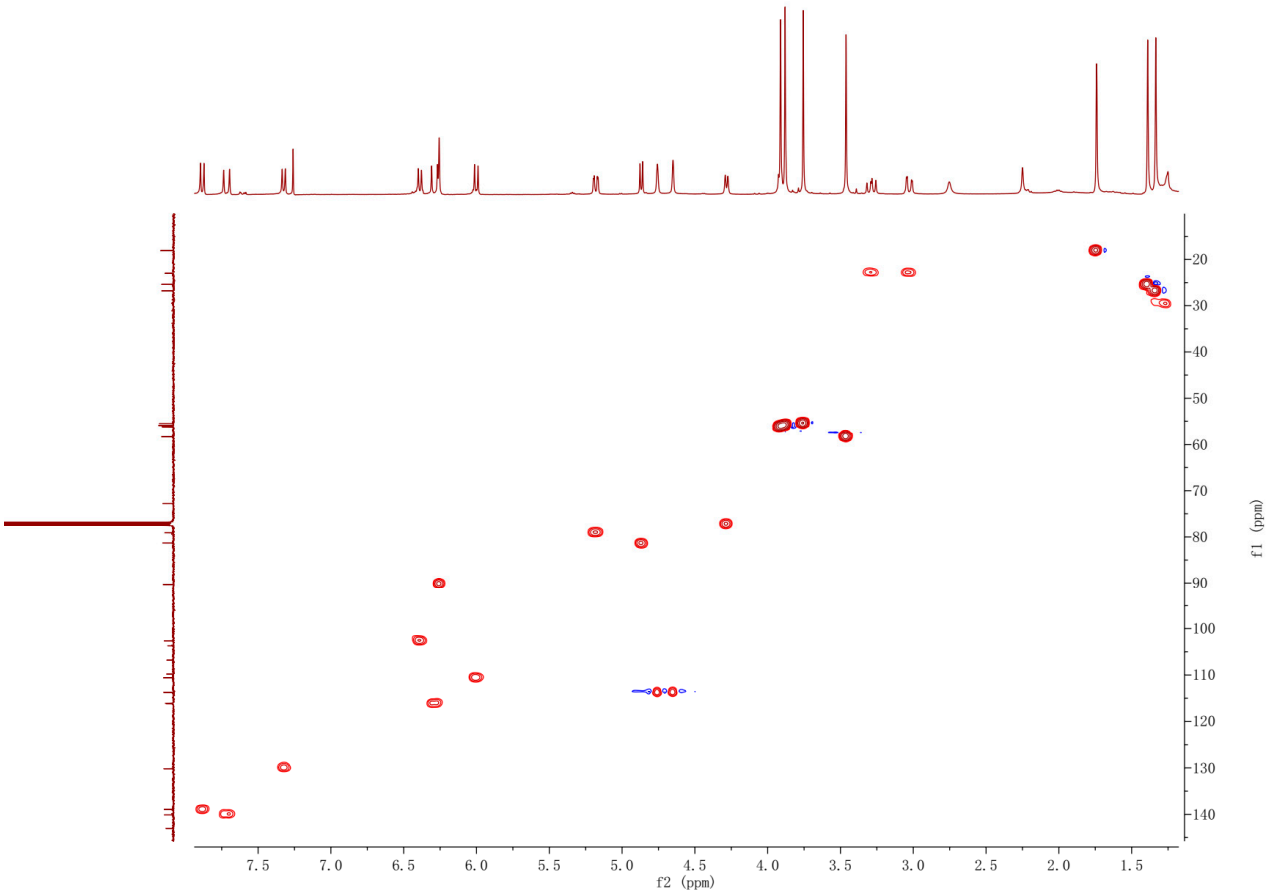
Spectrum S35. ^{13}C NMR spectrum of **6** in $CDCl_3$



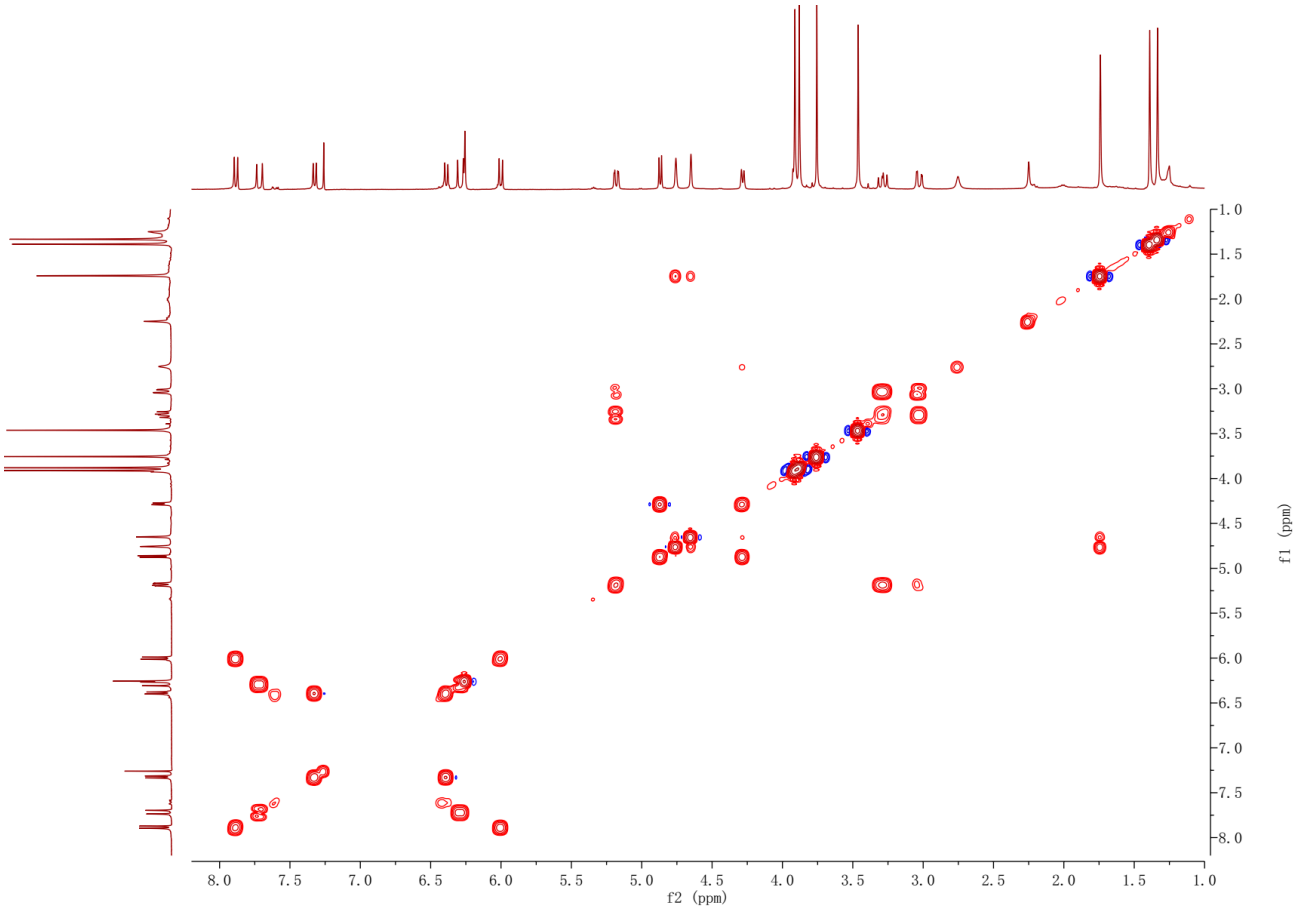
Spectrum S36. DEPT spectrum of **6** in $CDCl_3$



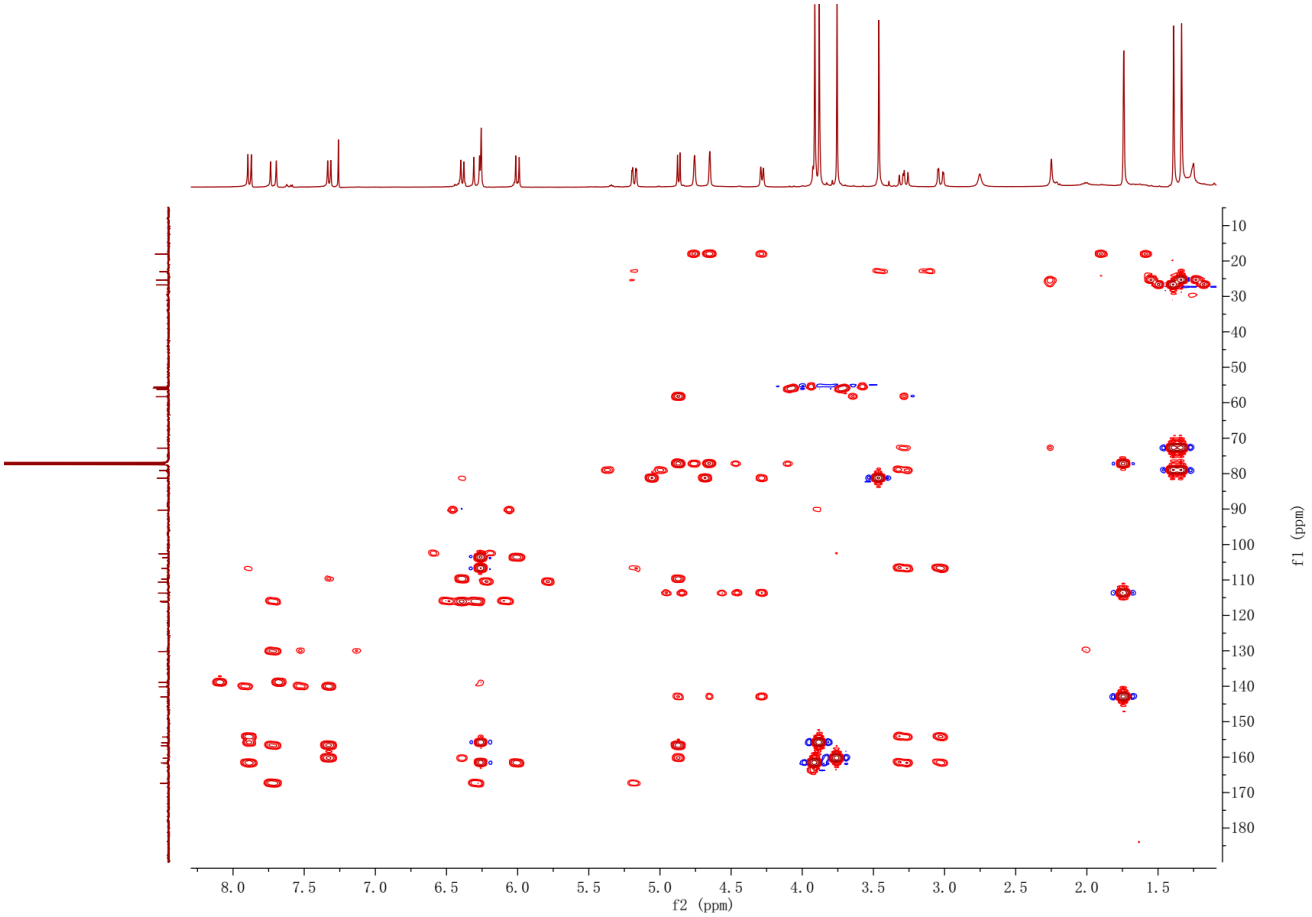
Spectrum S37. HSQC spectrum of **6** in $CDCl_3$



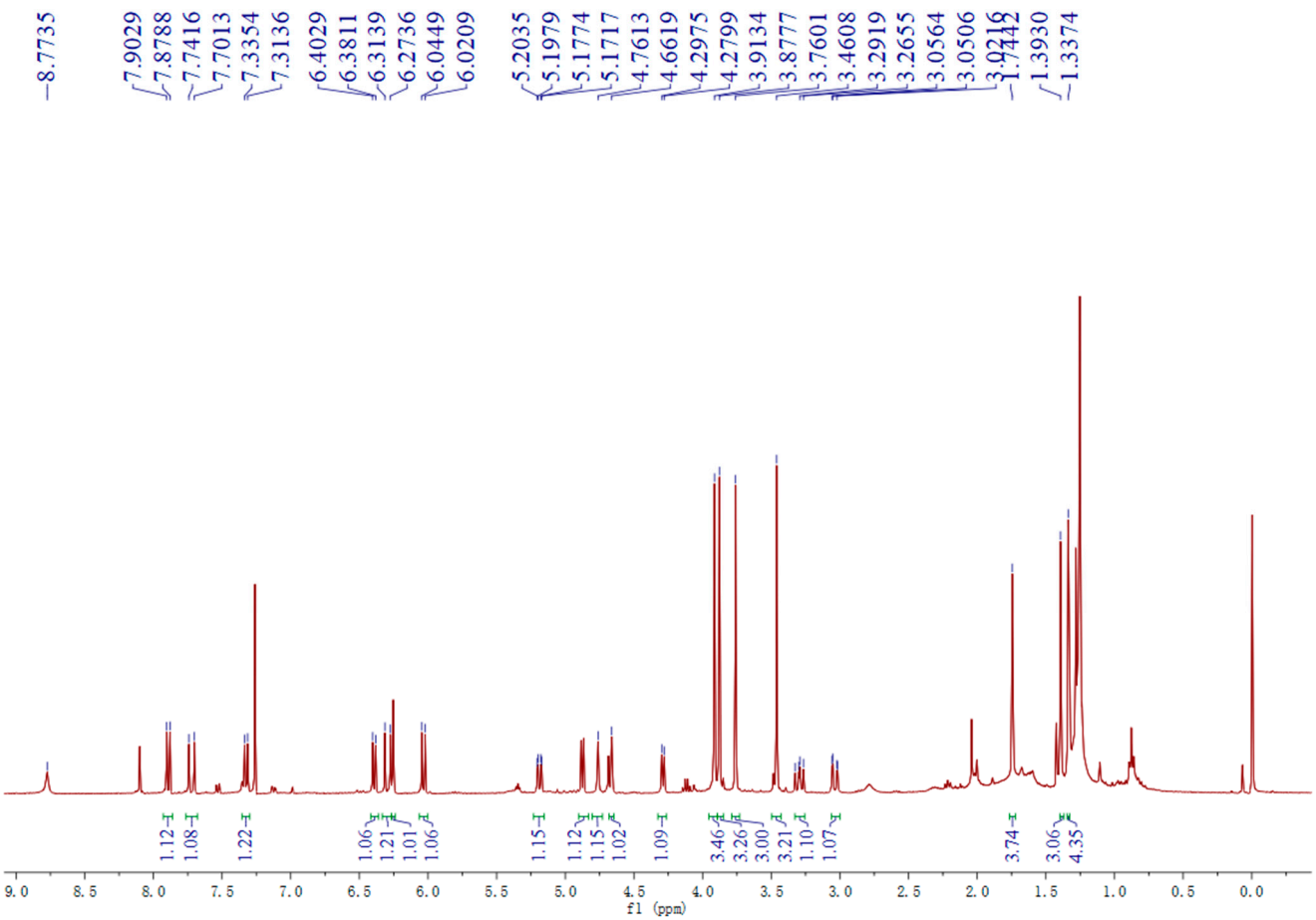
Spectrum S38. $^{1}H–^{1}H$ COSY spectrum of **6** in $CDCl_3$



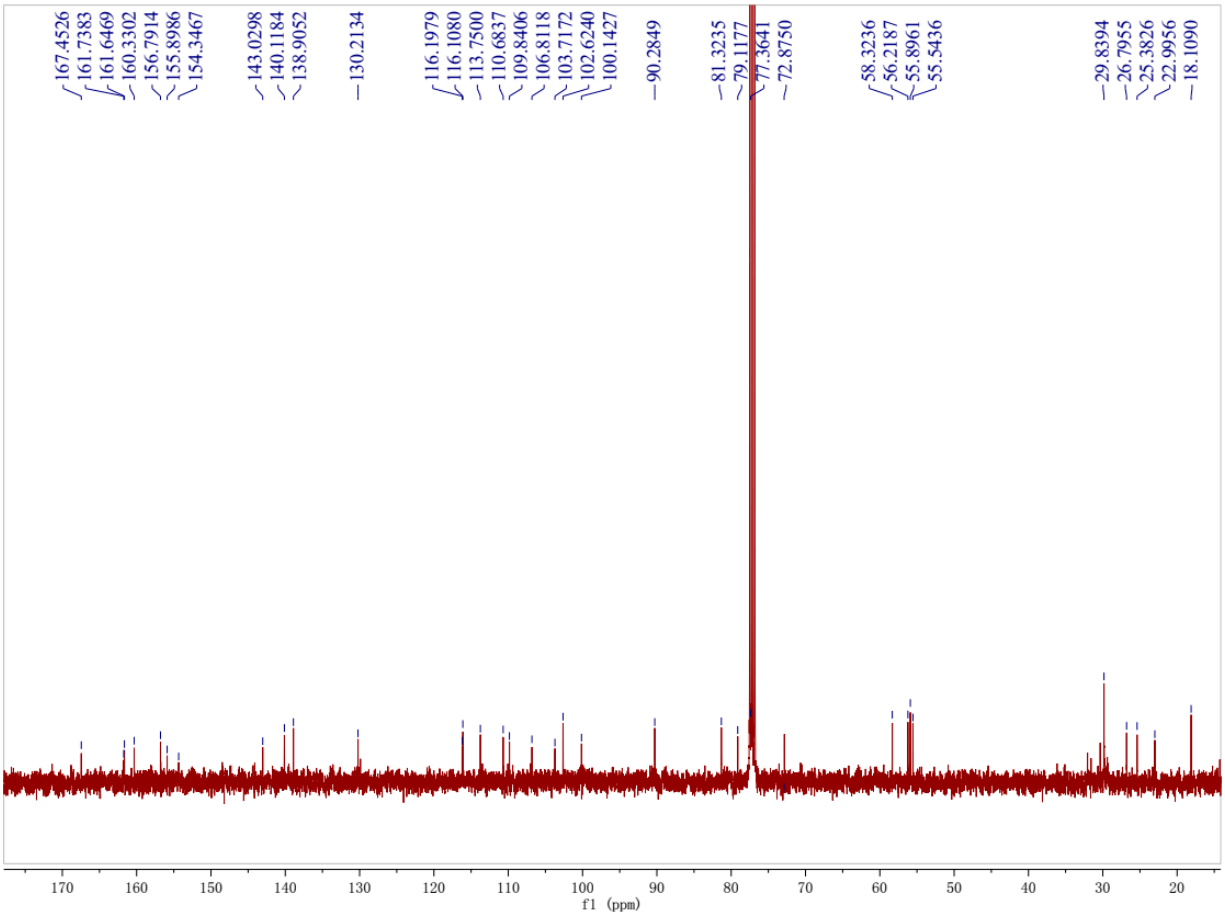
Spectrum S39. HMBC spectrum of **6** in $CDCl_3$



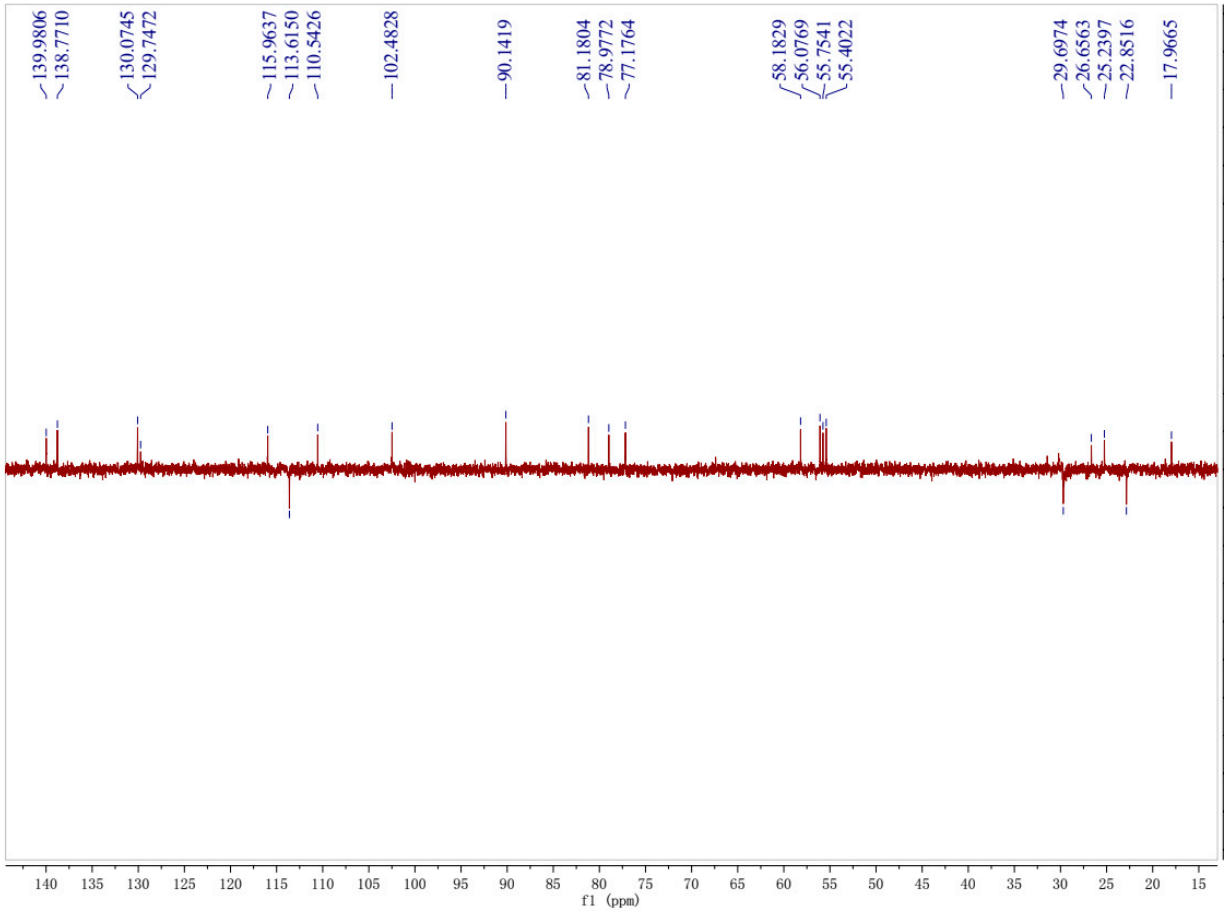
Spectrum S40. ^1H NMR spectrum of **7** in $CDCl_3$



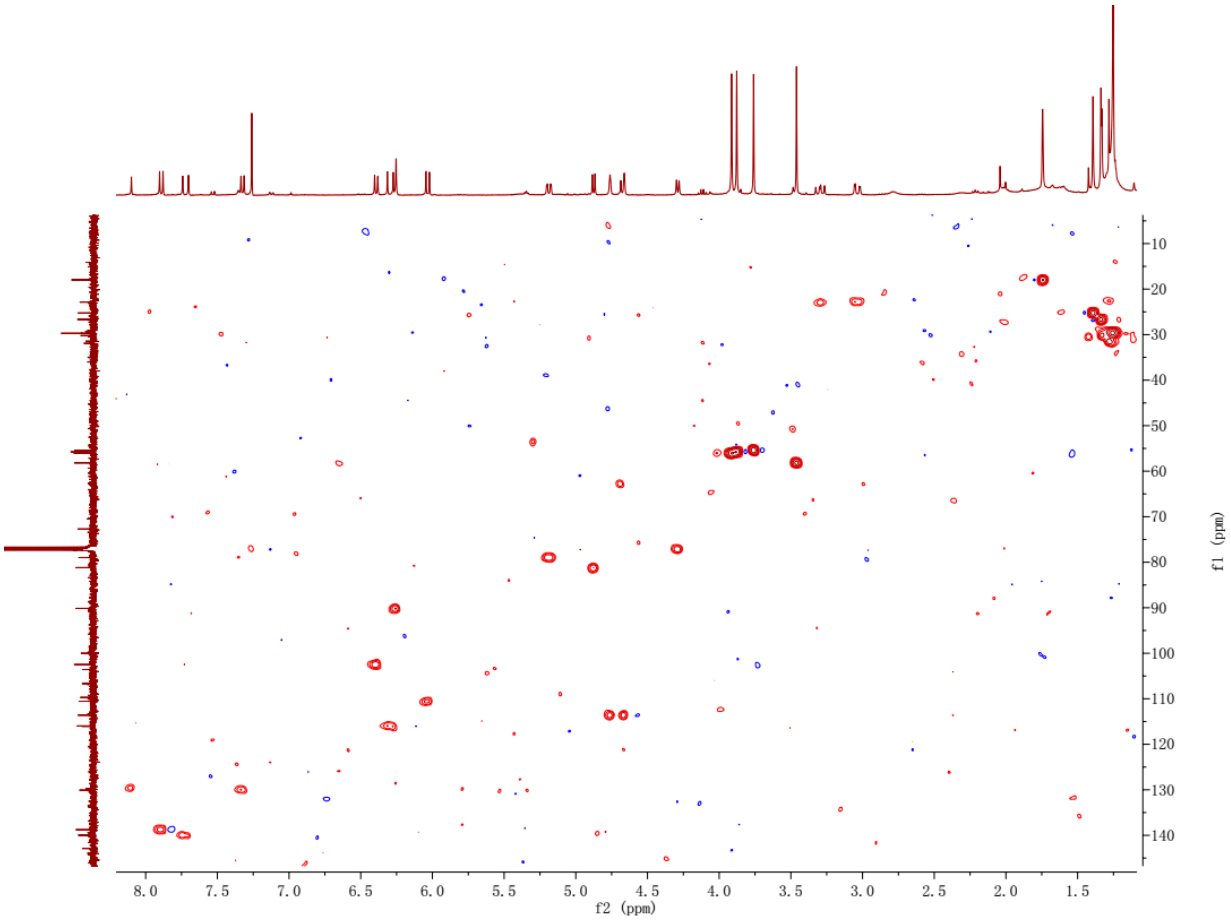
Spectrum S41. ^{13}C NMR spectrum of **7** in $CDCl_3$



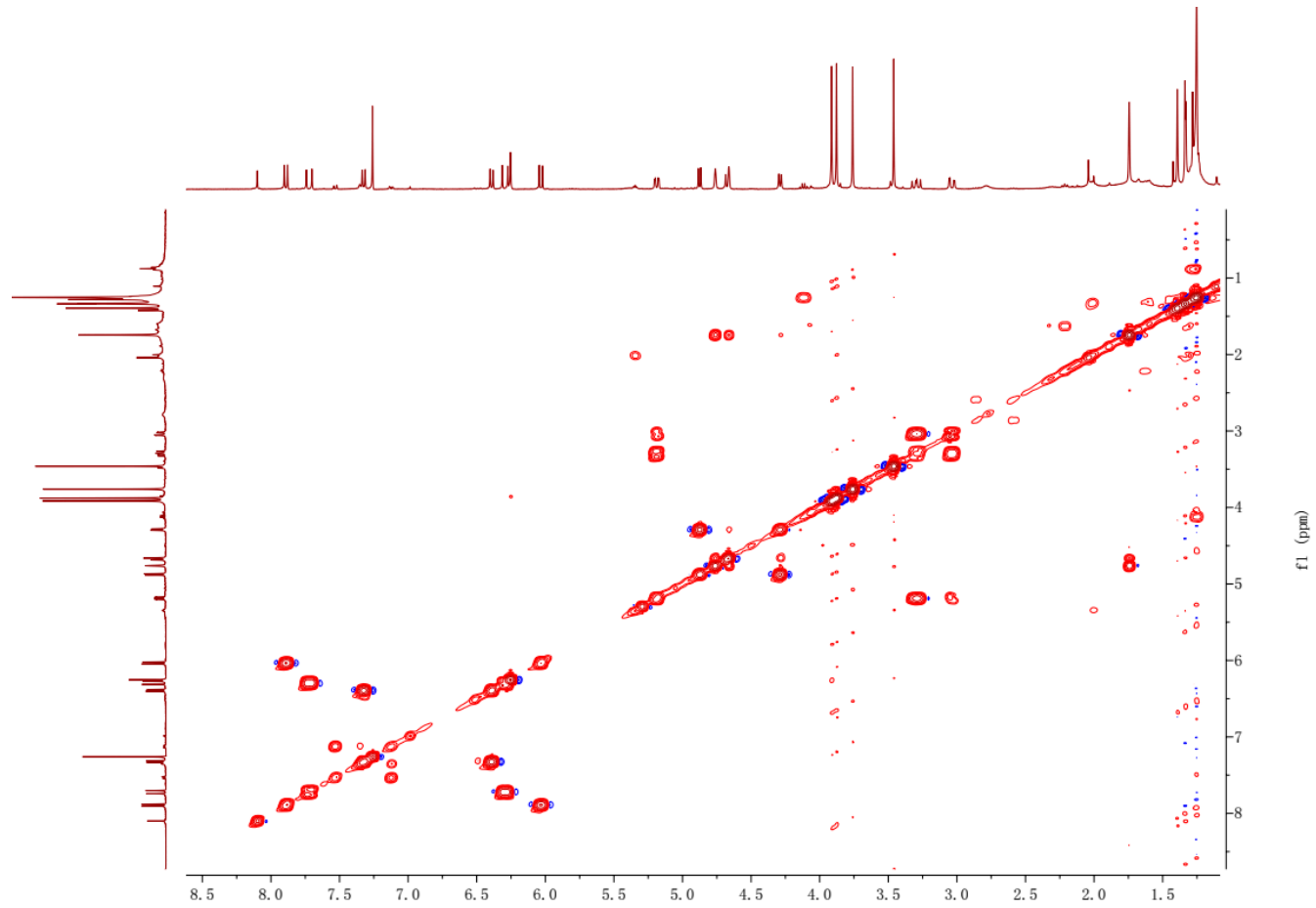
Spectrum S42. DEPT spectrum of **7** in $CDCl_3$



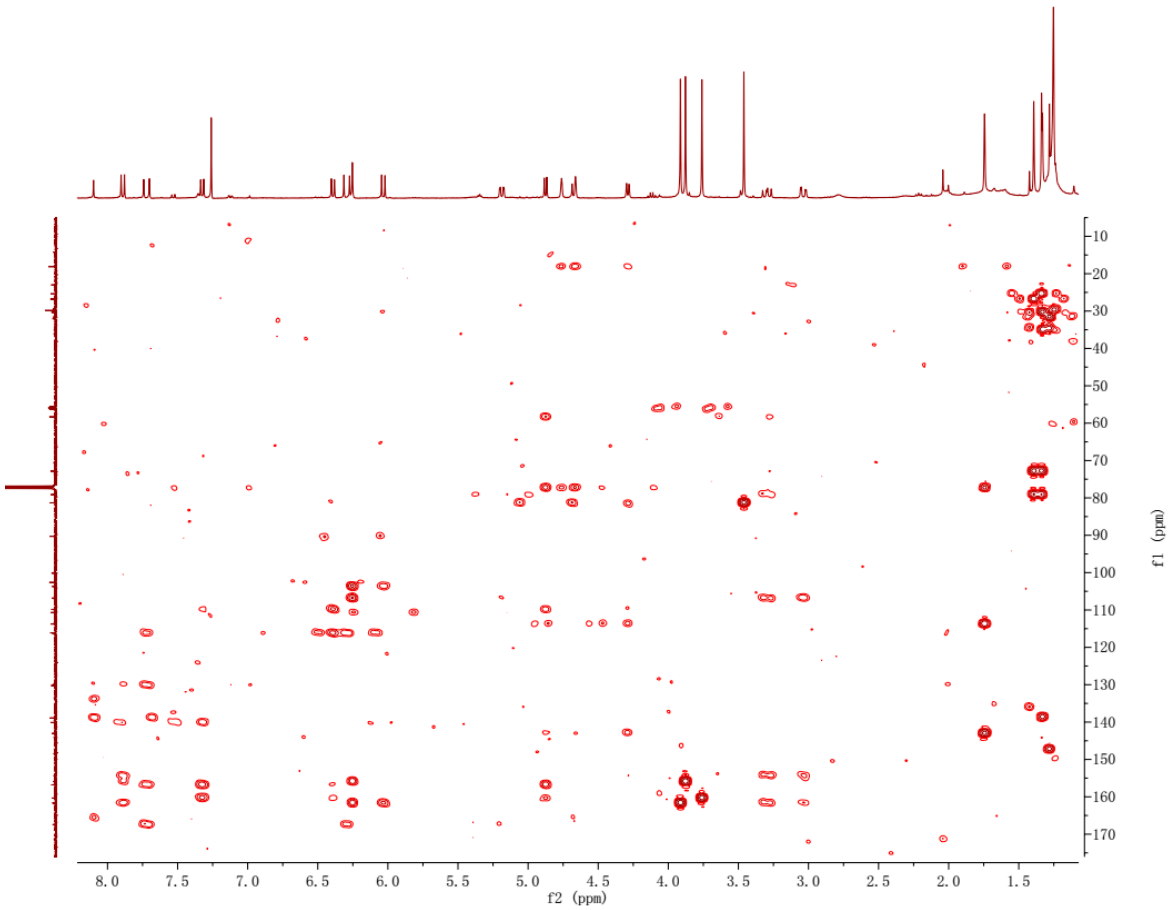
Spectrum S43. HSQC spectrum of **7** in $CDCl_3$



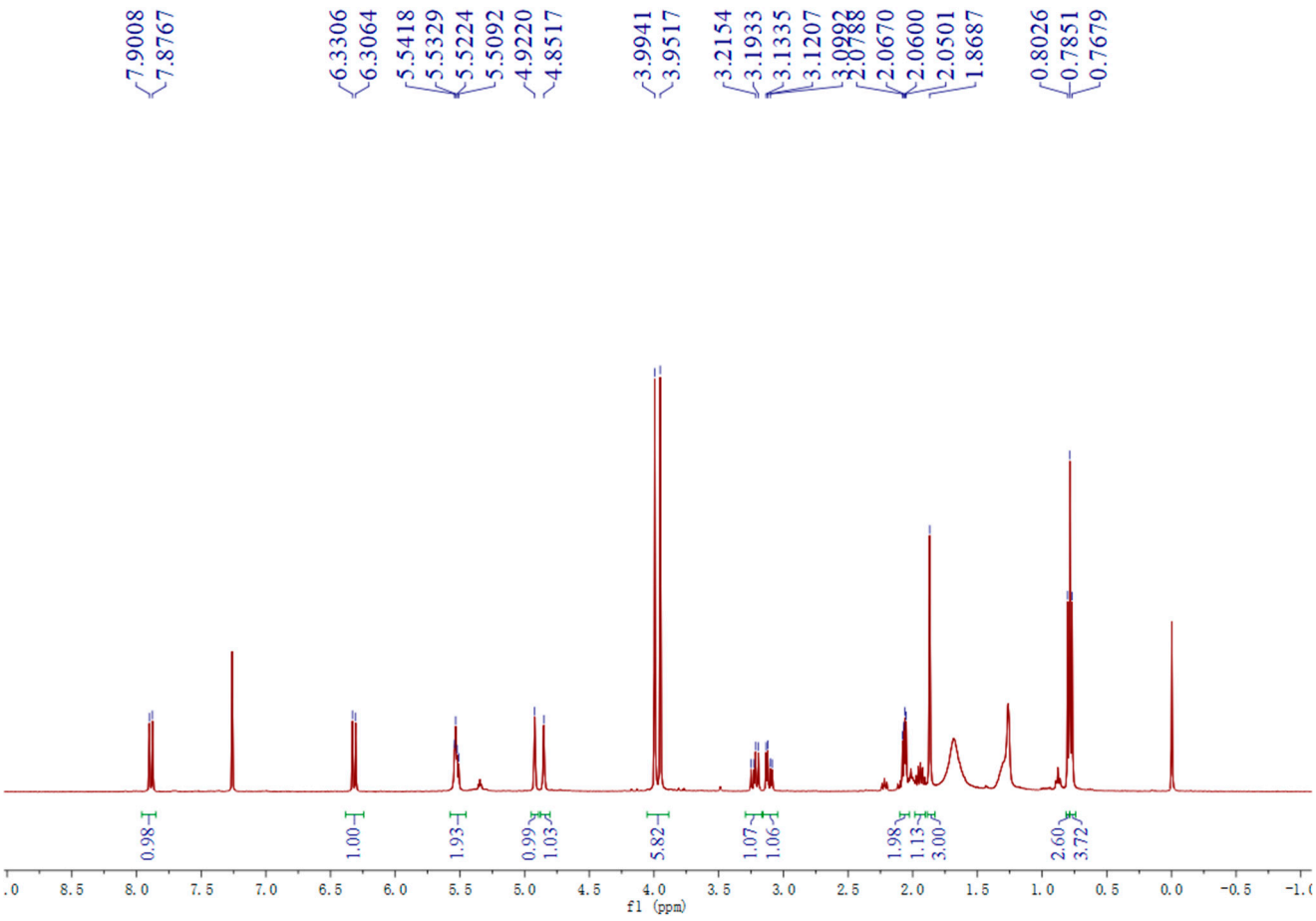
Spectrum S44. $^{1}H–^{1}H$ COSY spectrum of **7** in $CDCl_3$



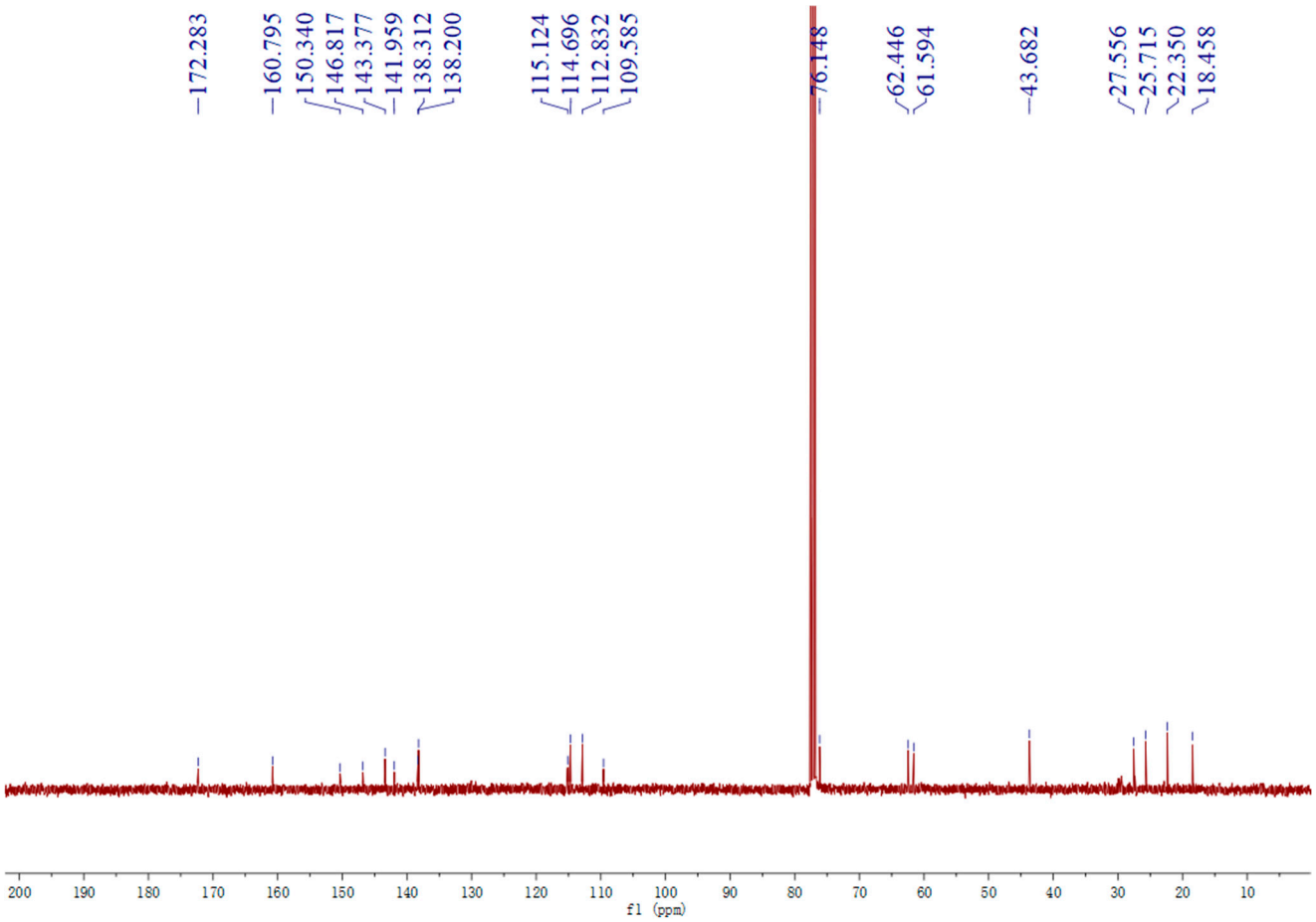
Spectrum S45. HMBC spectrum of **7** in $CDCl_3$



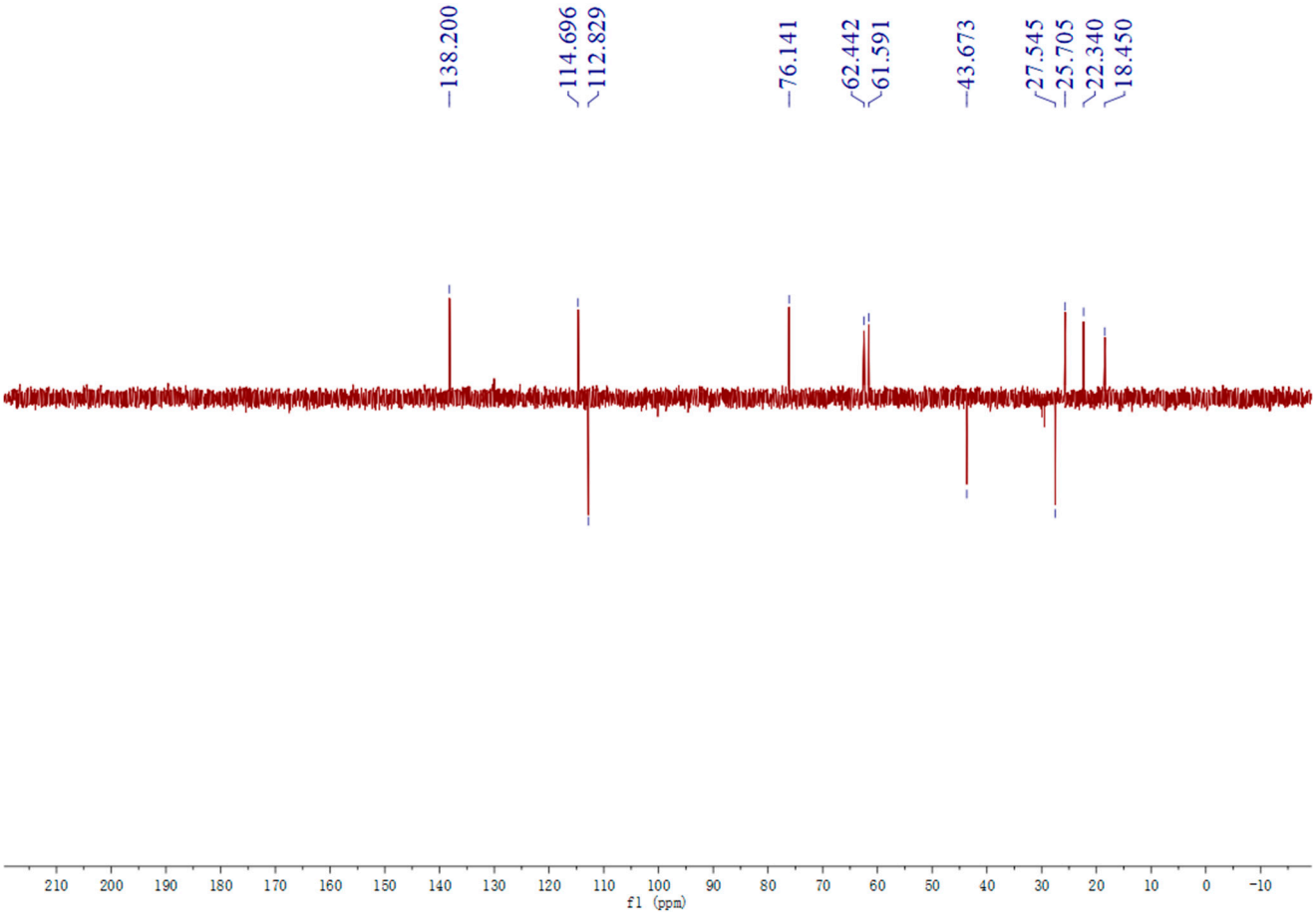
Spectrum S46. ^1H NMR spectrum of **8** in $CDCl_3$



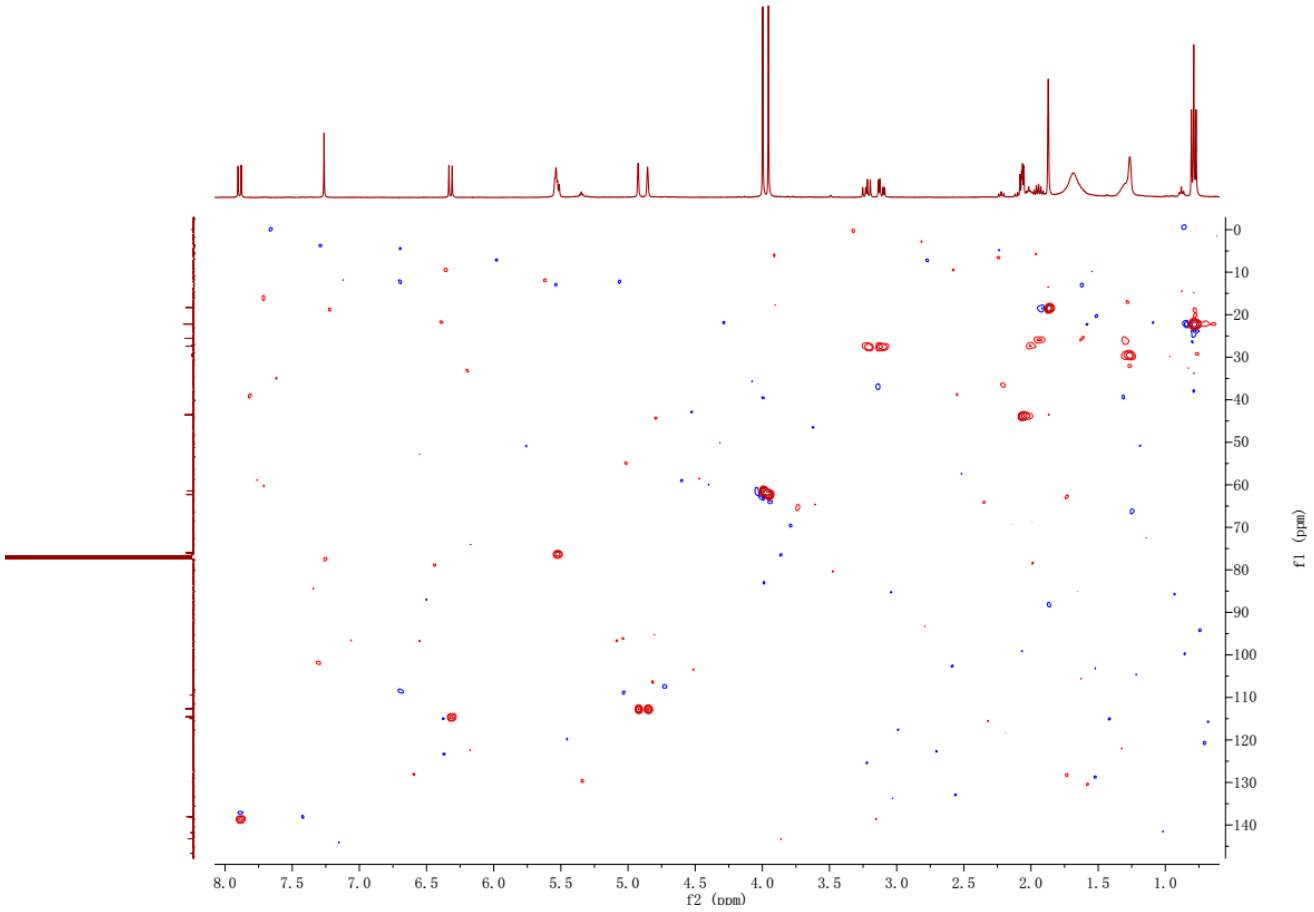
Spectrum S47. ^{13}C NMR spectrum of **8** in $CDCl_3$



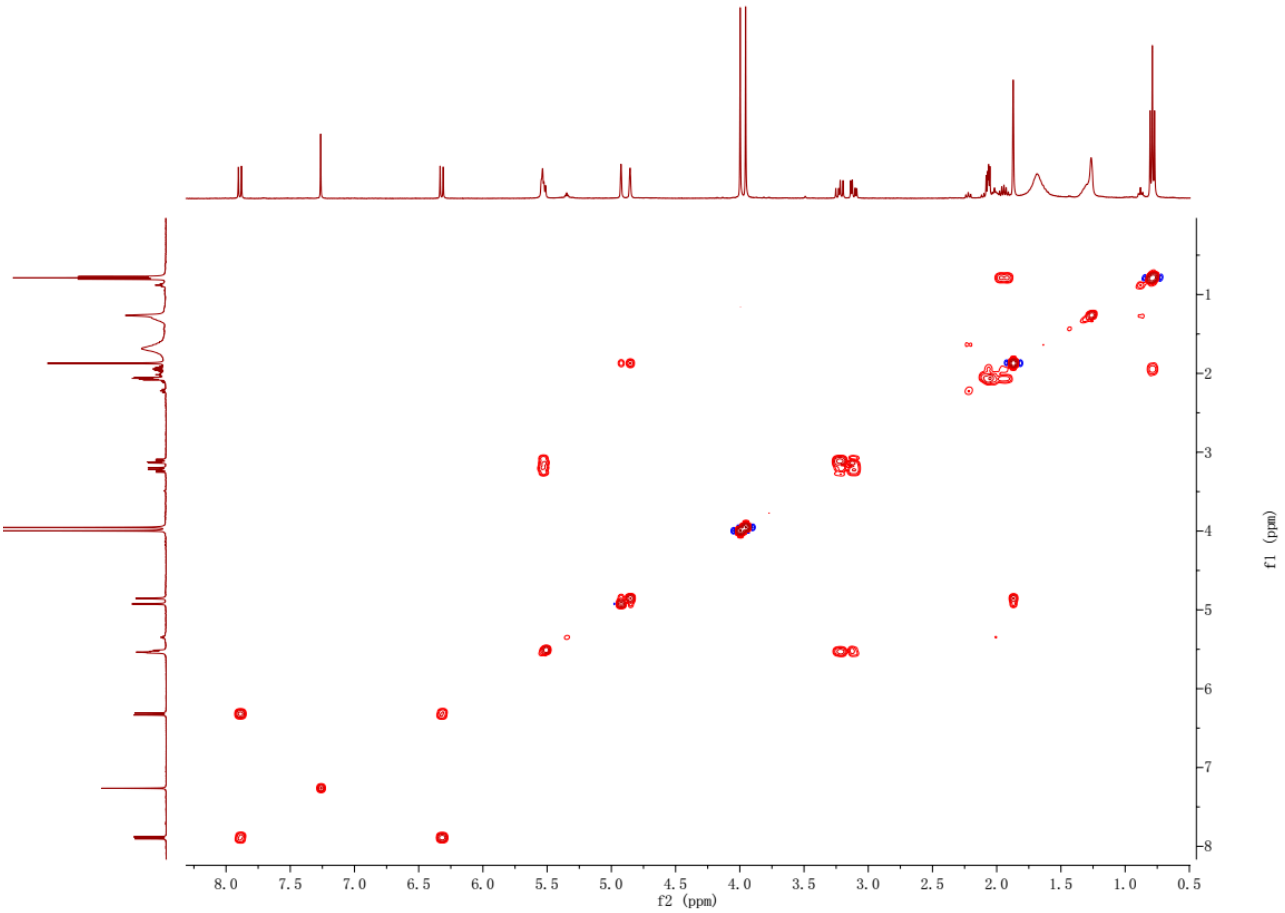
Spectrum S48. DEPT spectrum of **8** in $CDCl_3$



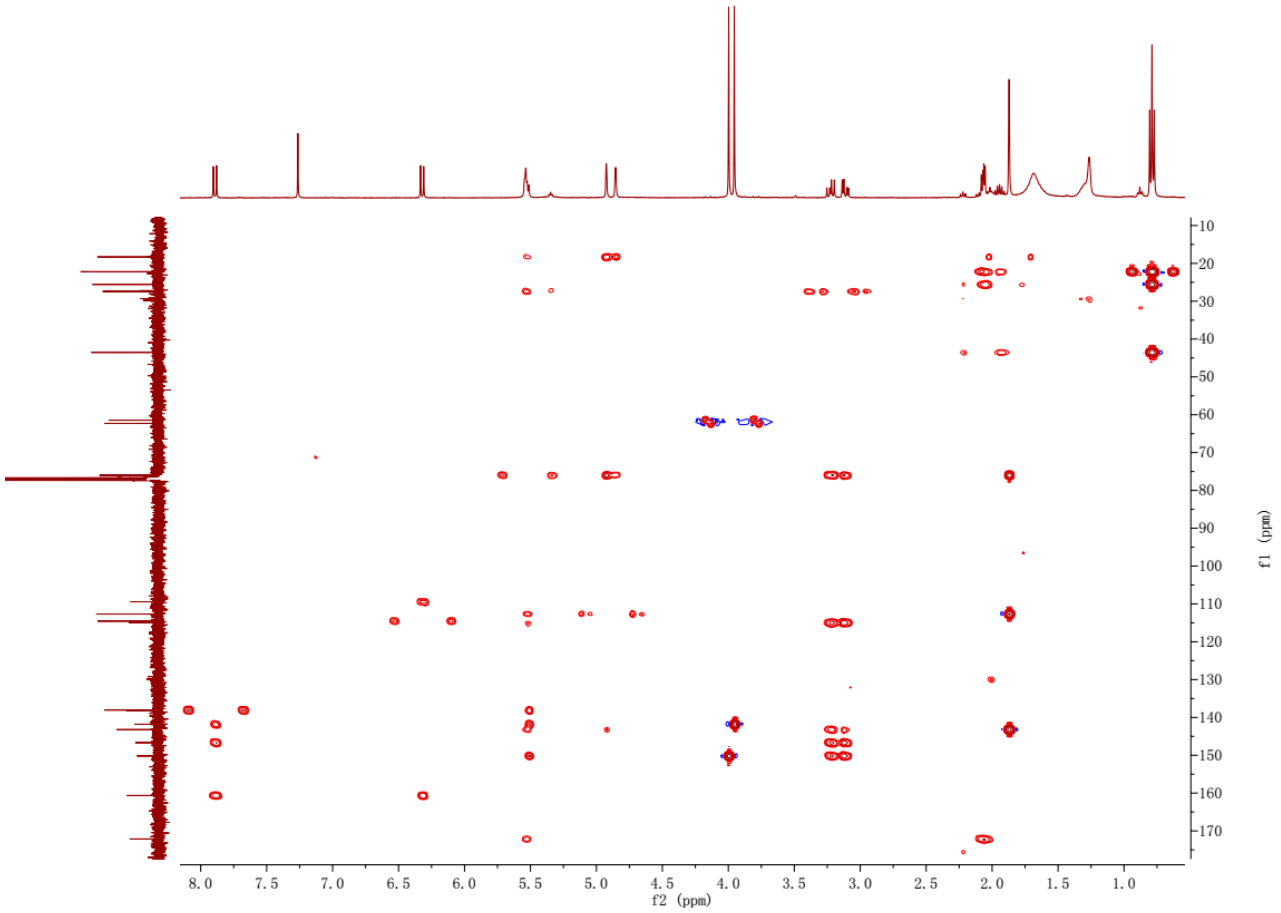
Spectrum S49. HSQC spectrum of **8** in $CDCl_3$



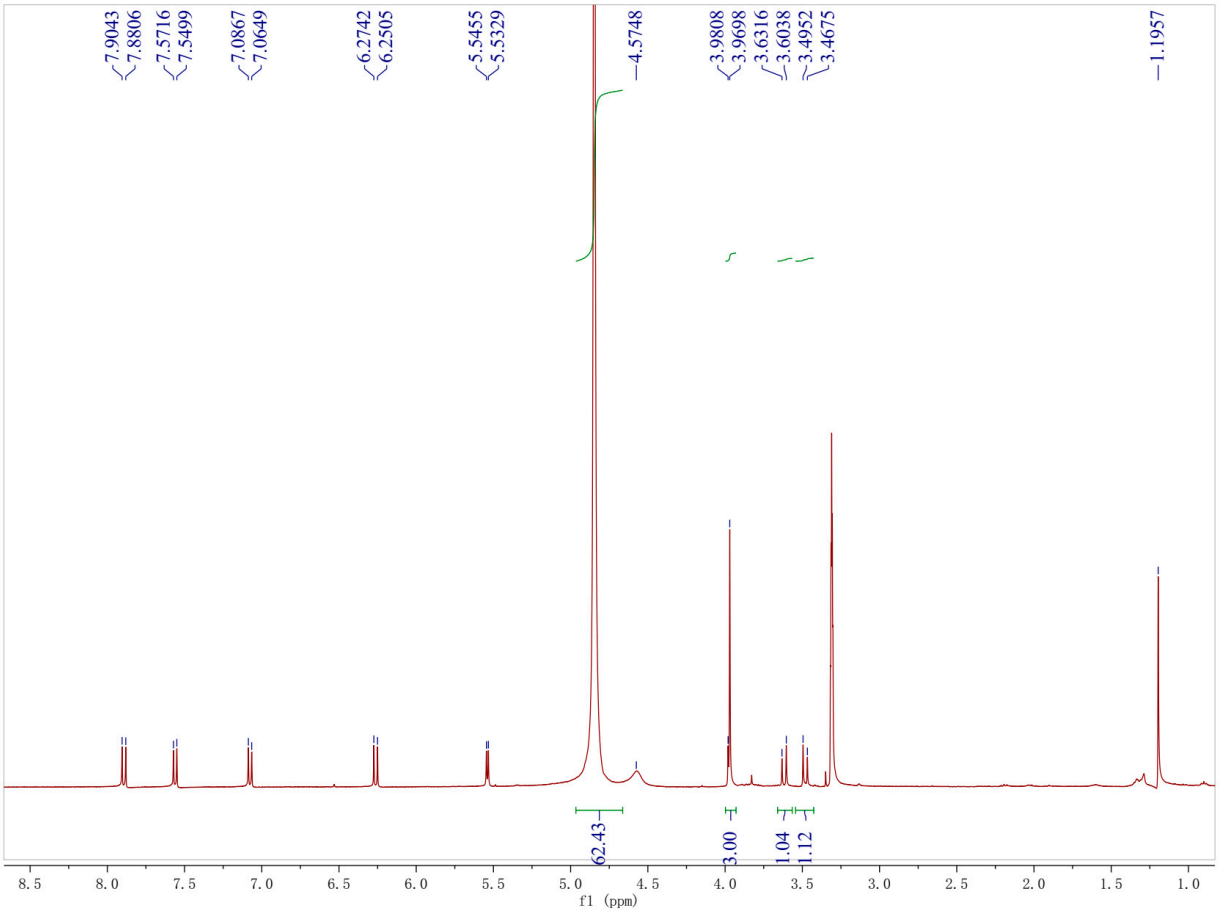
Spectrum S50. $^{1}H–^{1}H$ COSY spectrum of **8** in $CDCl_3$



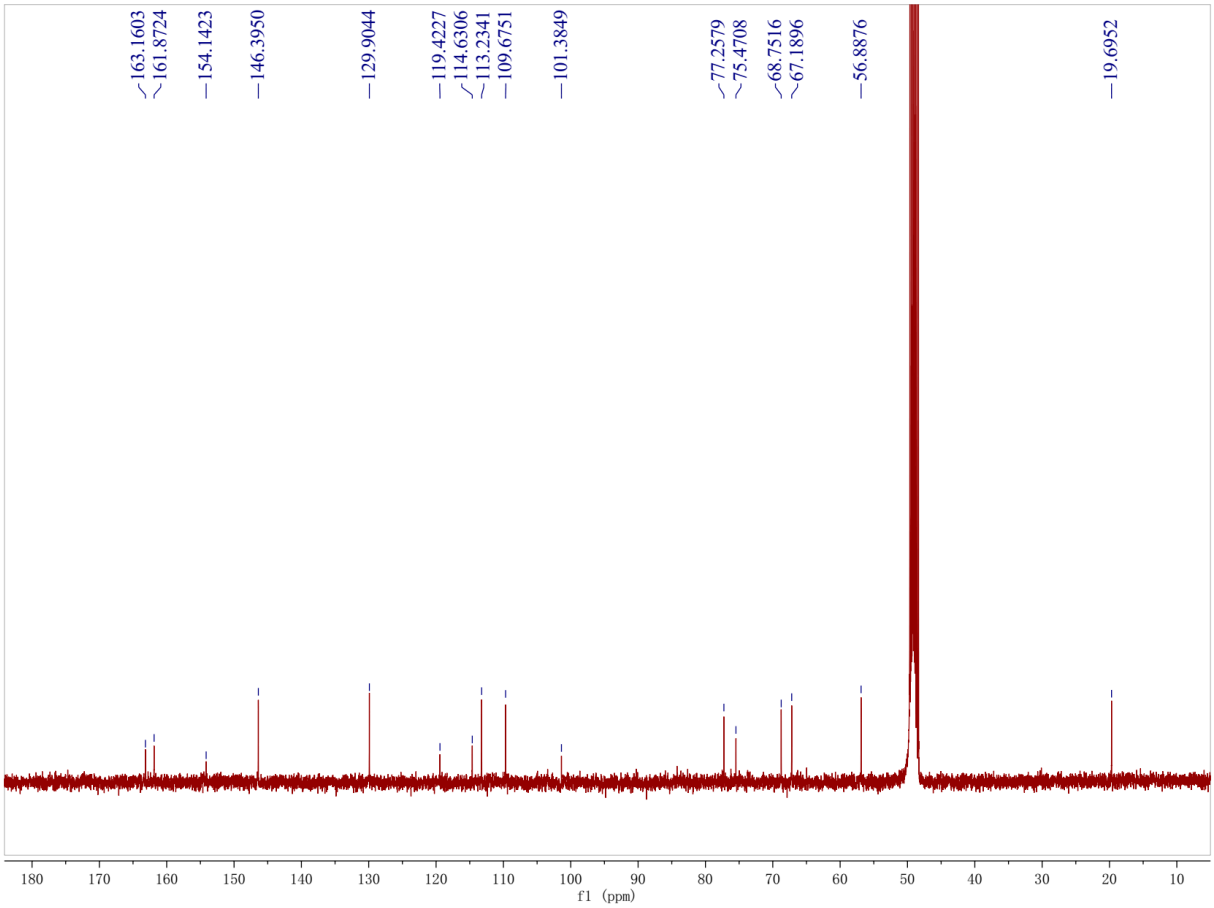
Spectrum S51. HMBC spectrum of **8** in $CDCl_3$



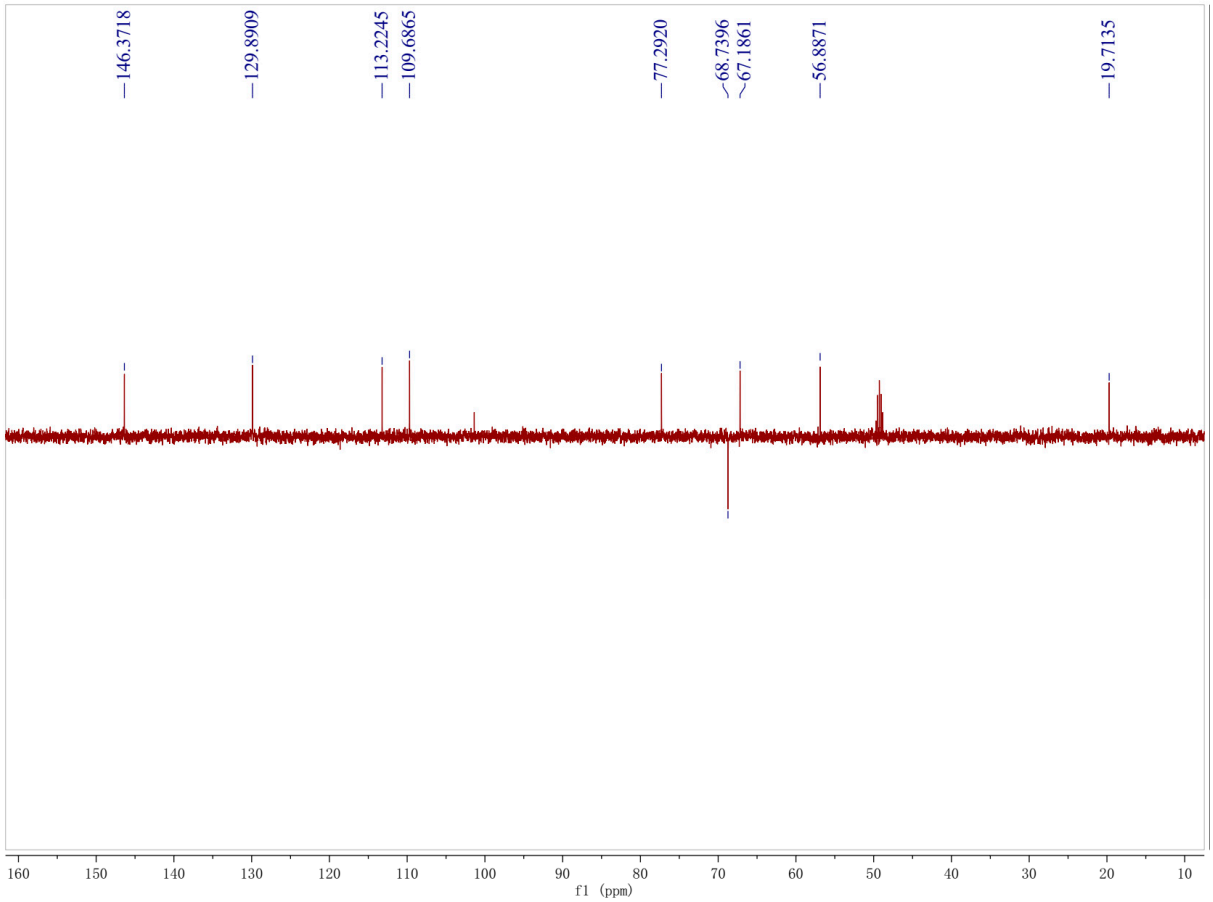
Spectrum S52. ^1H NMR spectrum of **9** in CD_3OD



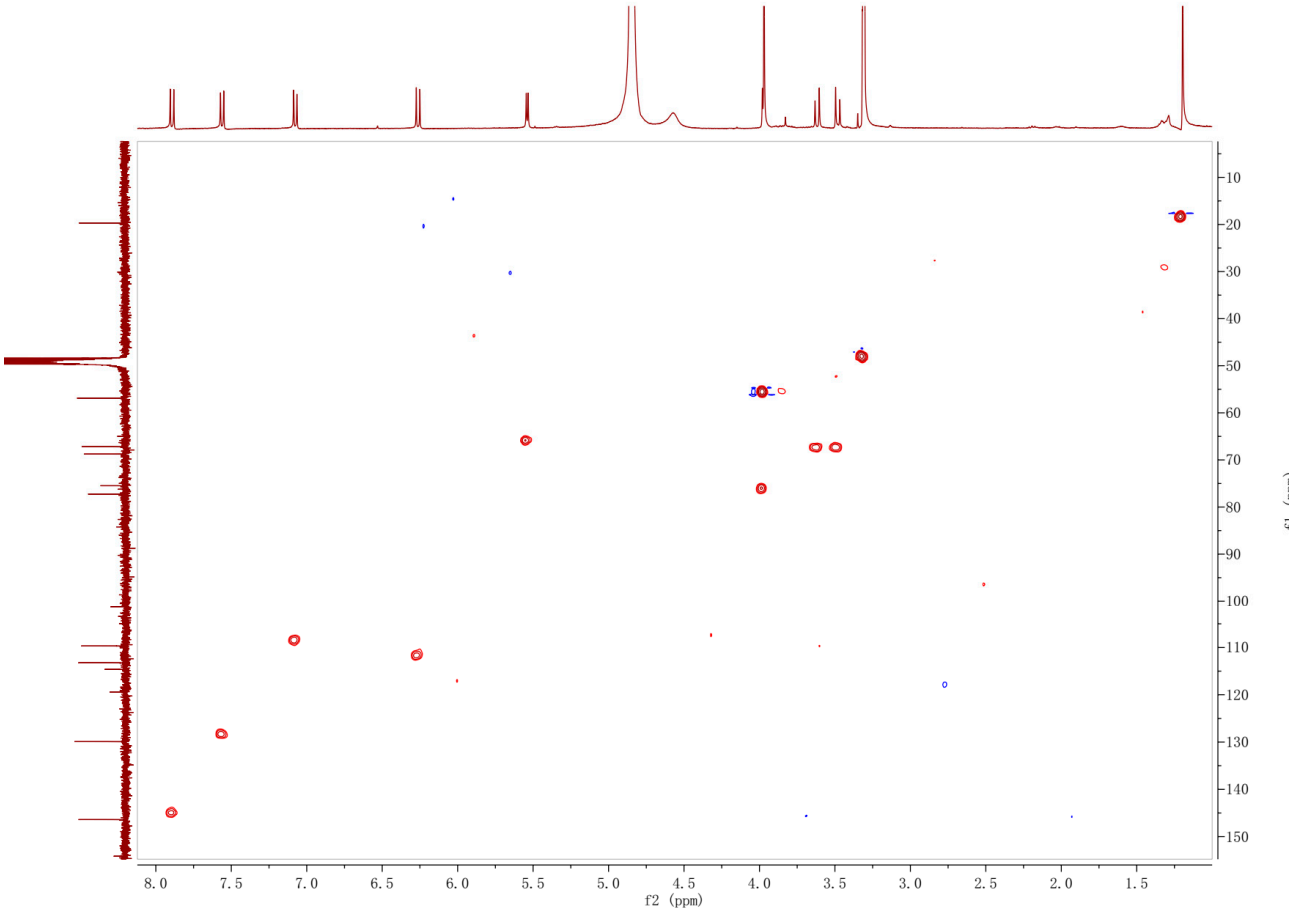
Spectrum S53. ^{13}C NMR spectrum of **9** in CD_3OD



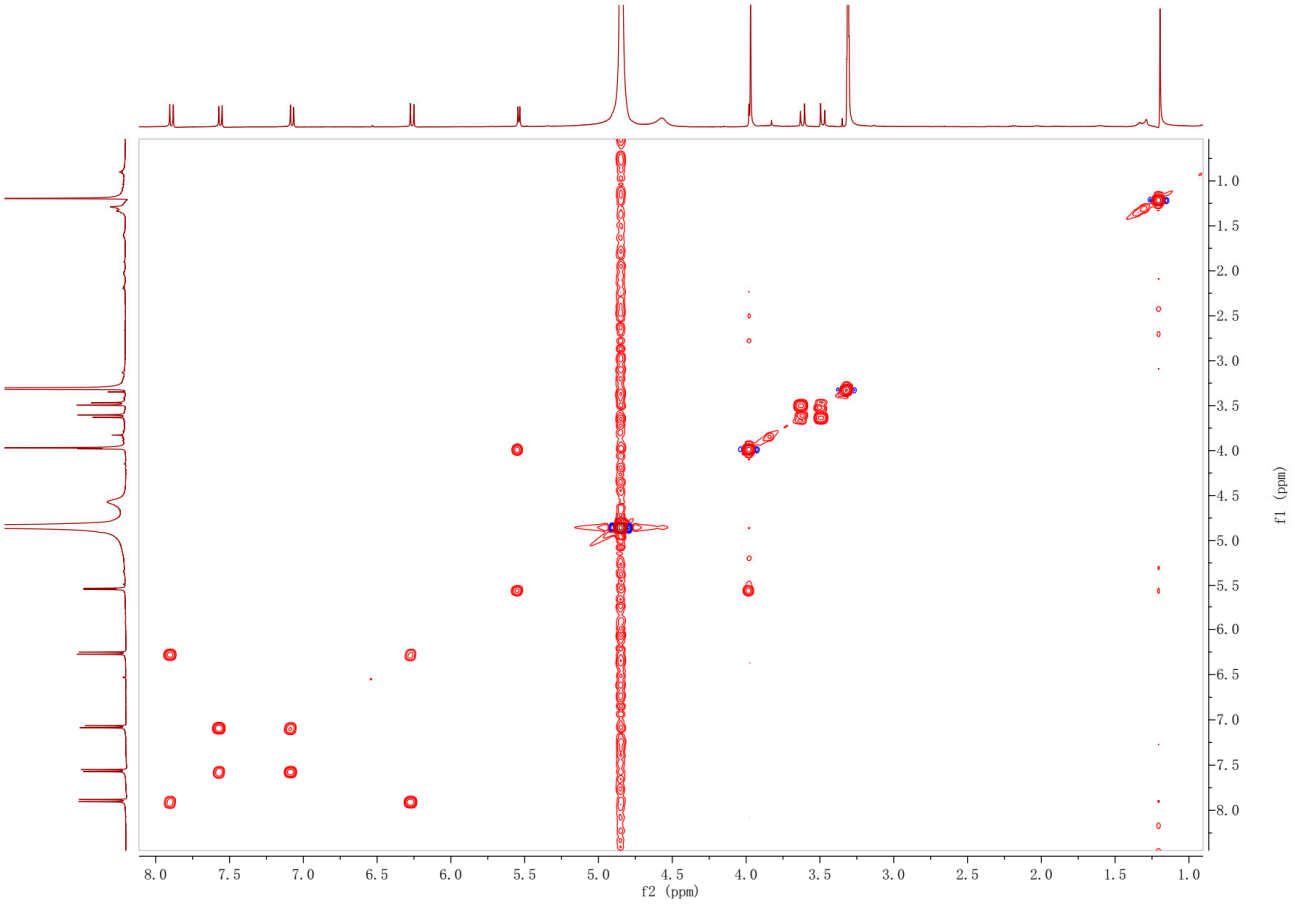
Spectrum S54. DEPT spectrum of **9** in CD_3OD



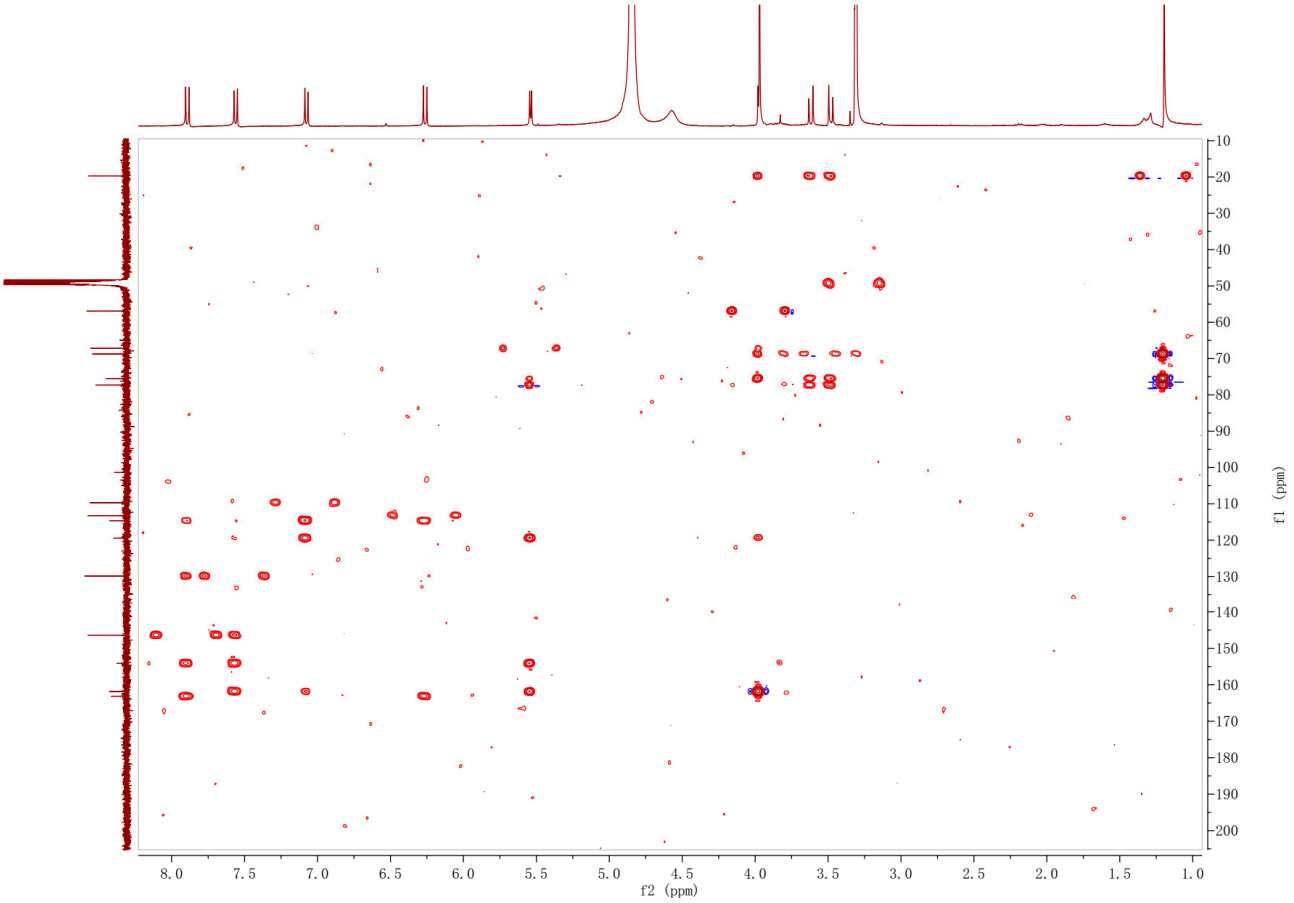
Spectrum S55. HSQC spectrum of **9** in CD_3OD



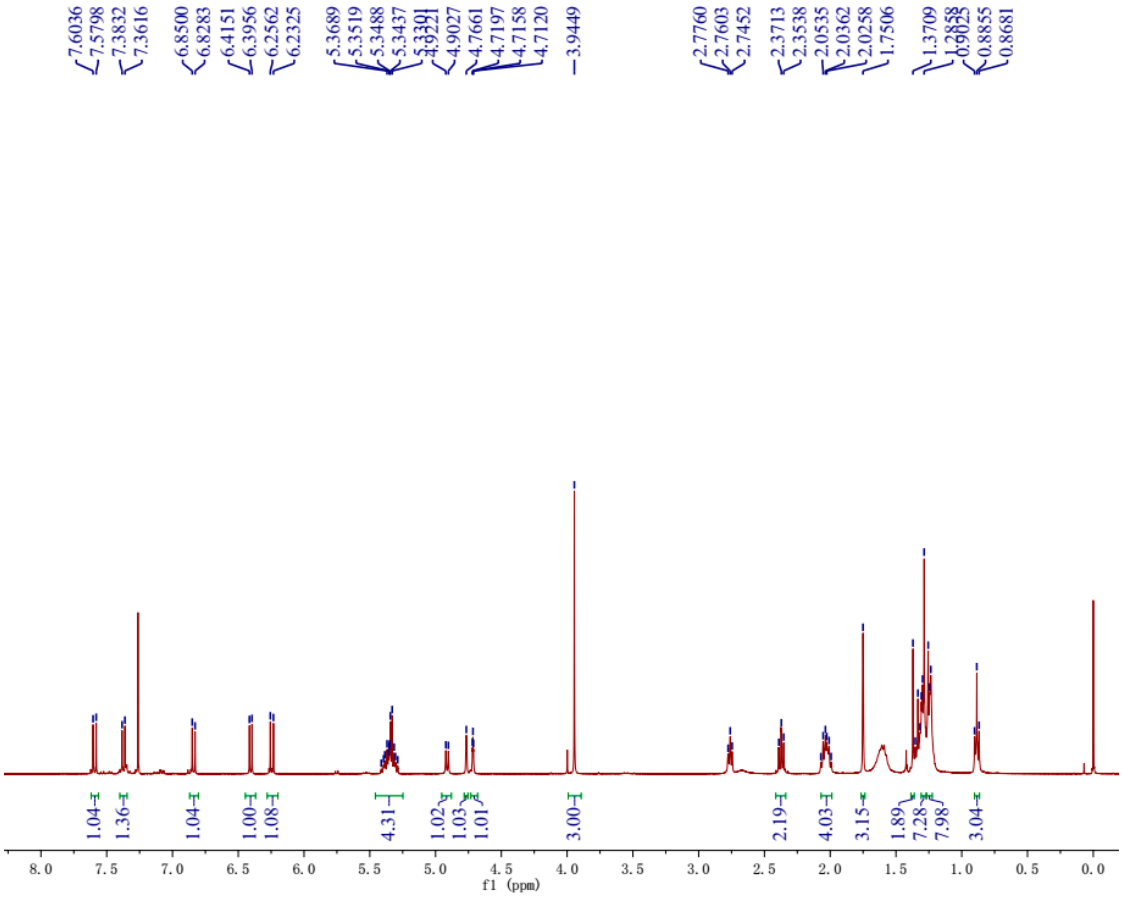
Spectrum S56. ^1H–^1H COSY spectrum of **9** in CD_3OD



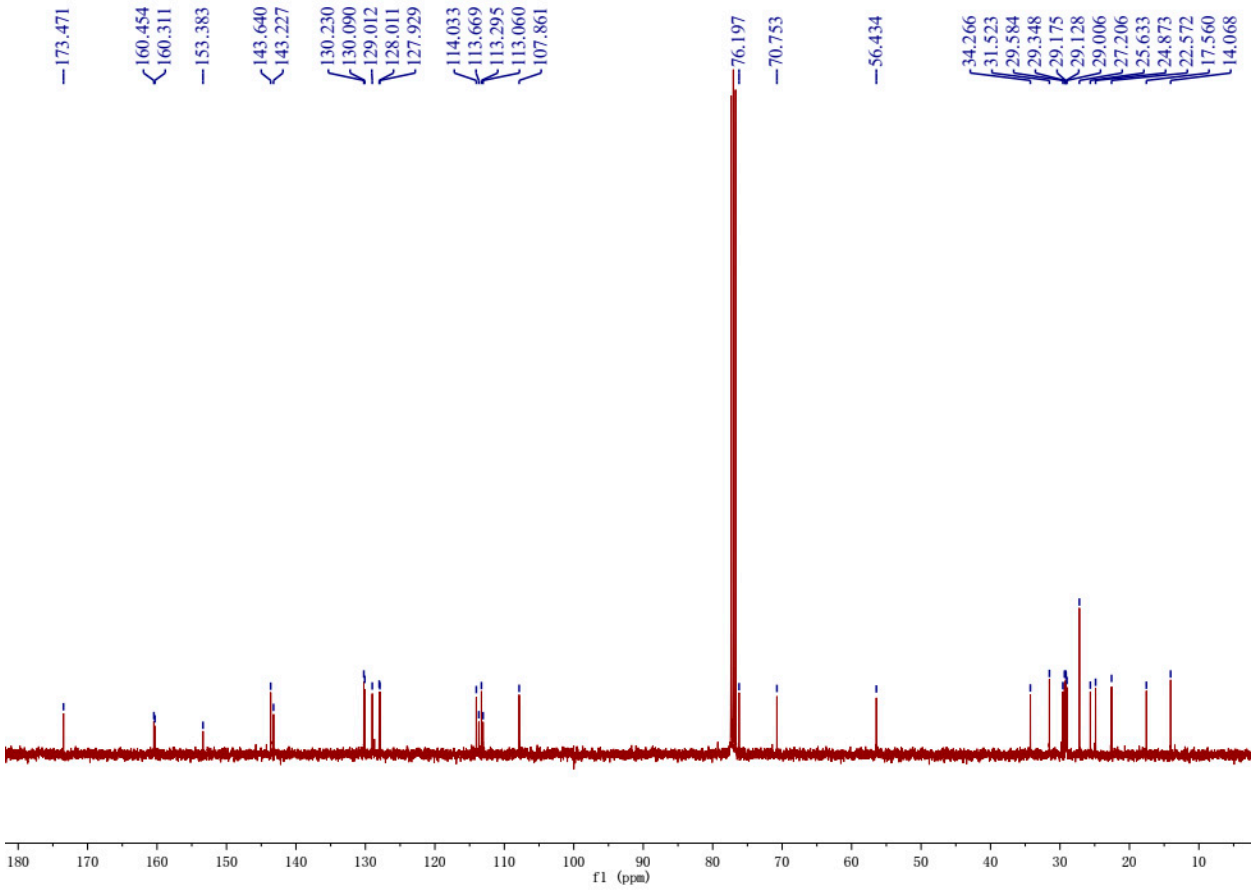
Spectrum S57. HMBC spectrum of **9** in CD_3OD



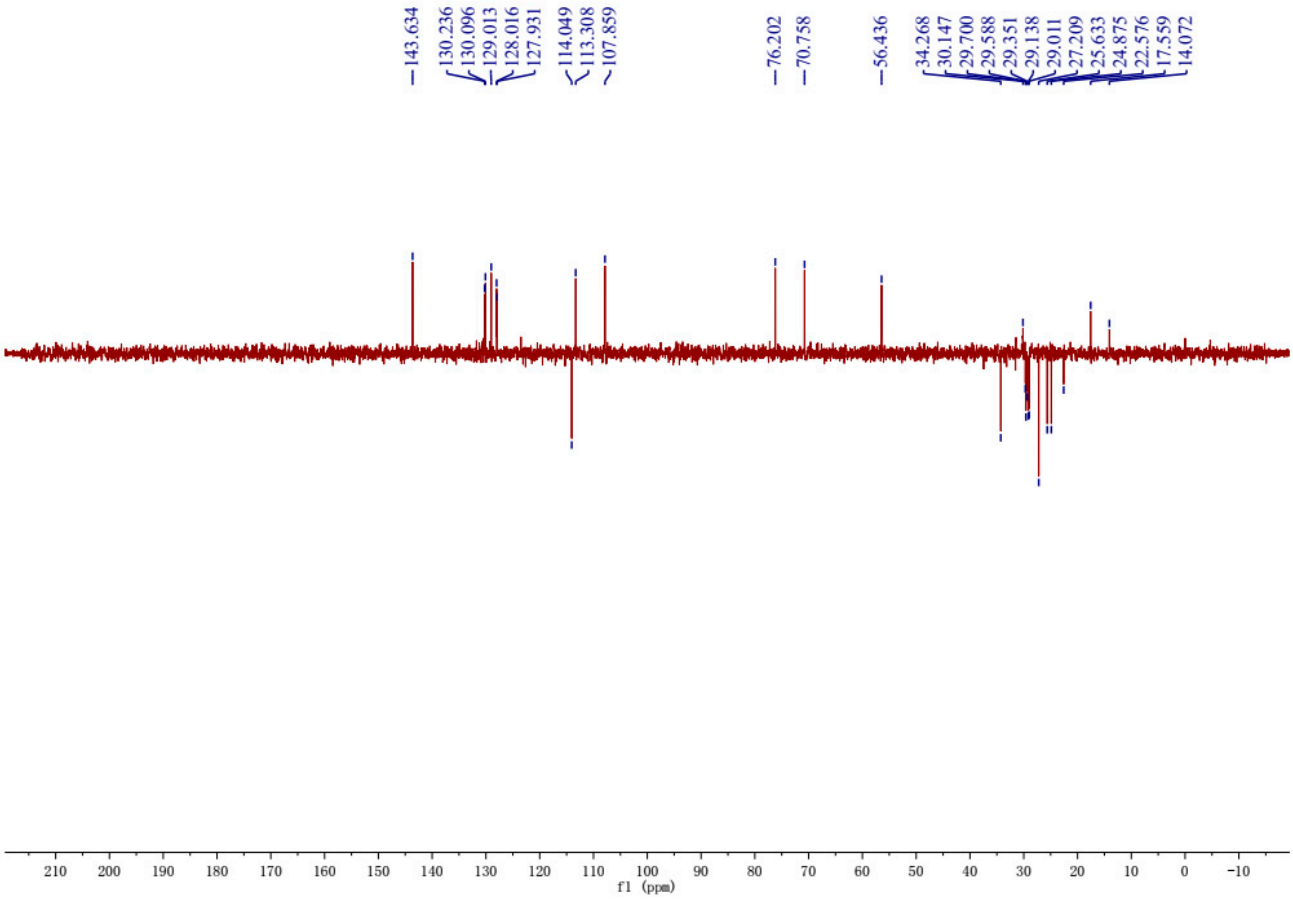
Spectrum S58. ^1H NMR spectrum of **10** in $CDCl_3$



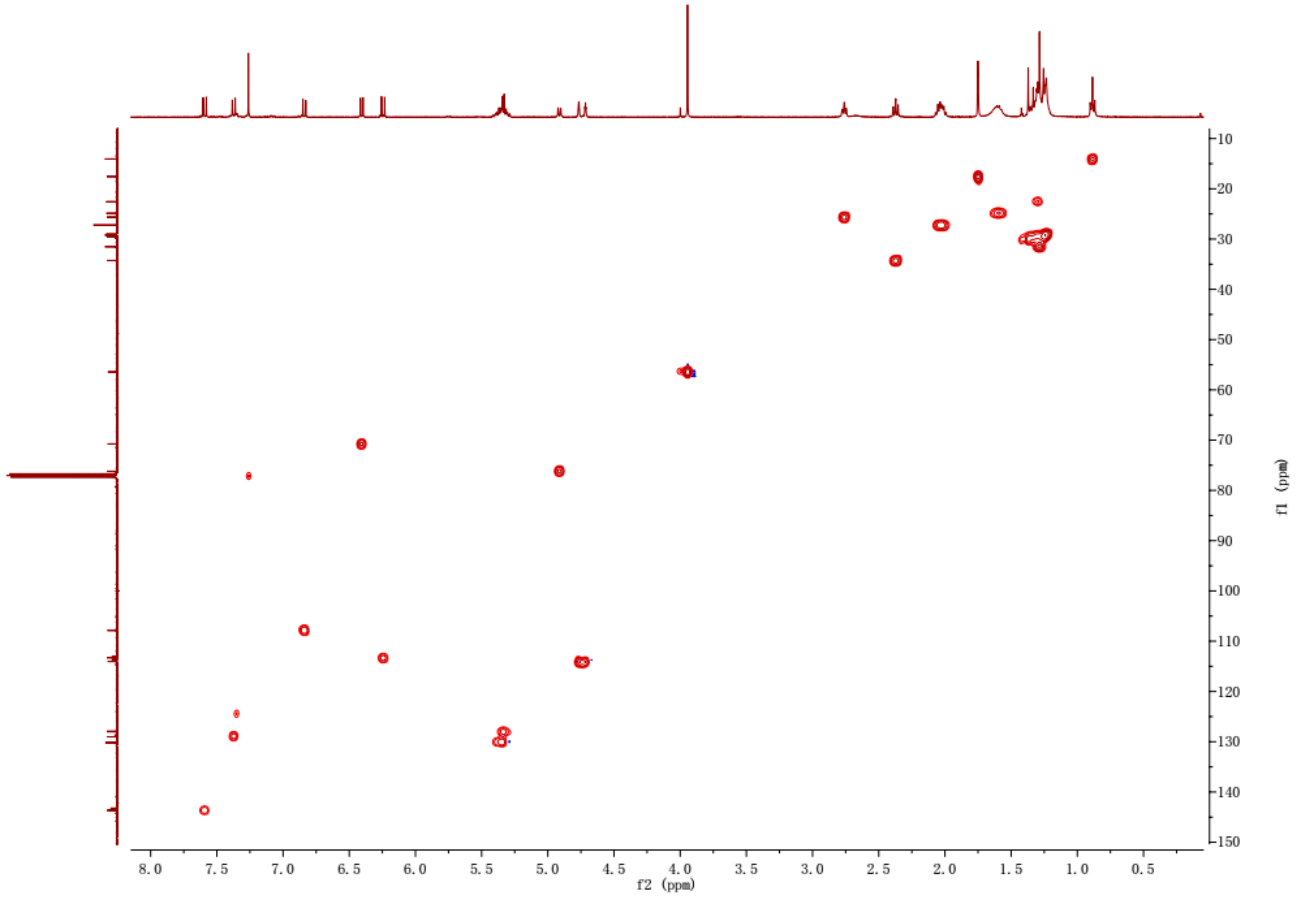
Spectrum S59. ^{13}C NMR spectrum of **10** in $CDCl_3$



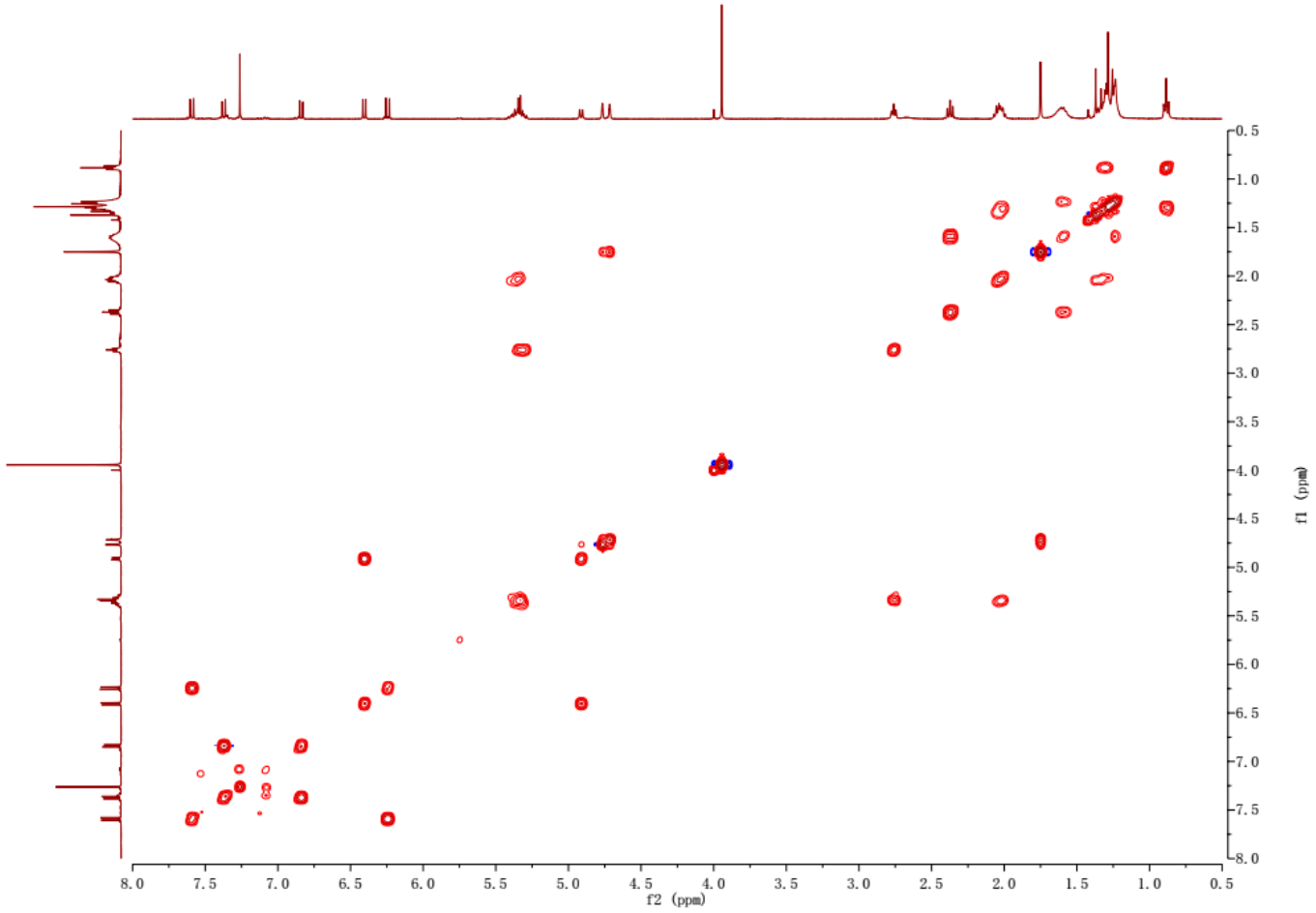
Spectrum S60. DEPT spectrum of **10** in $CDCl_3$



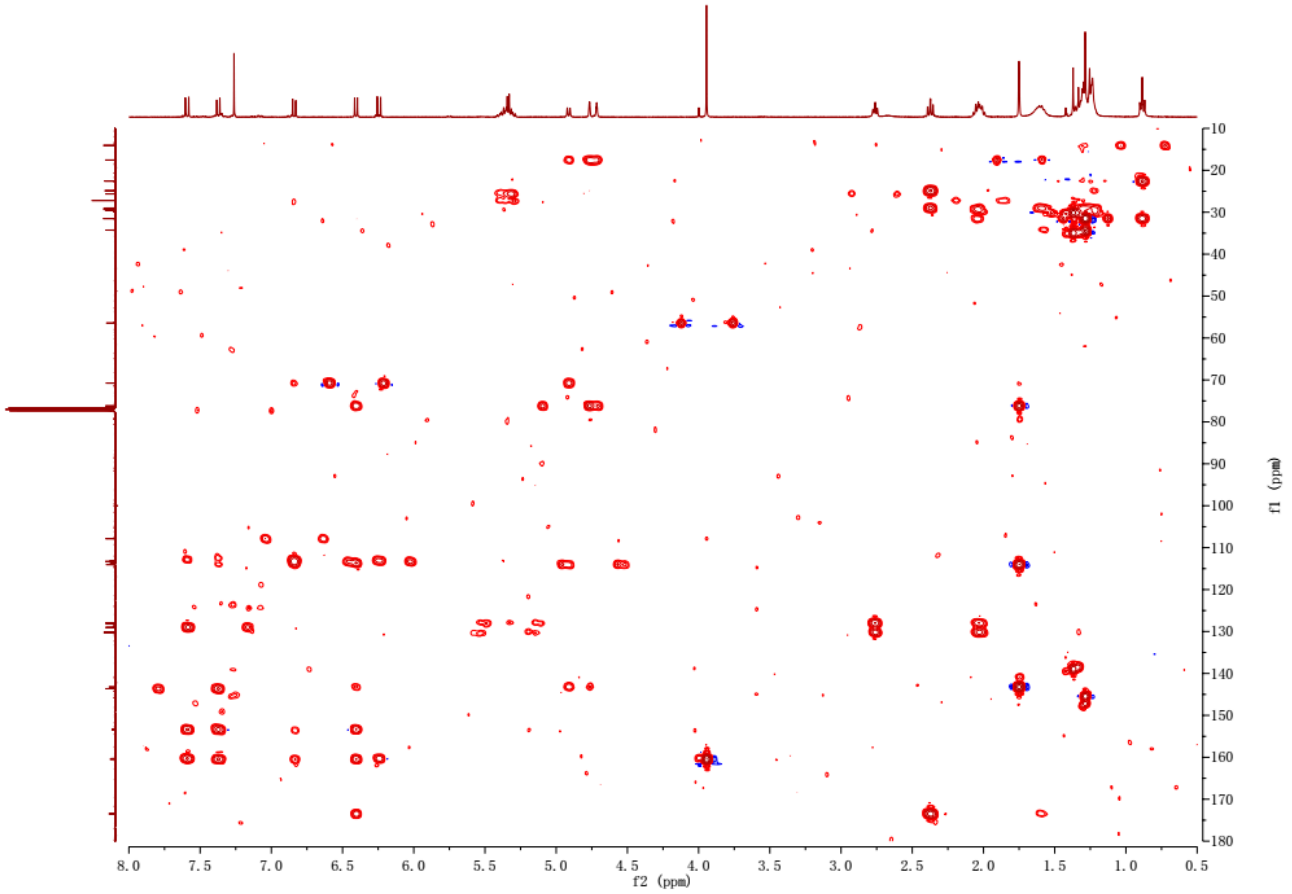
Spectrum S61. HSQC spectrum of **10** in $CDCl_3$



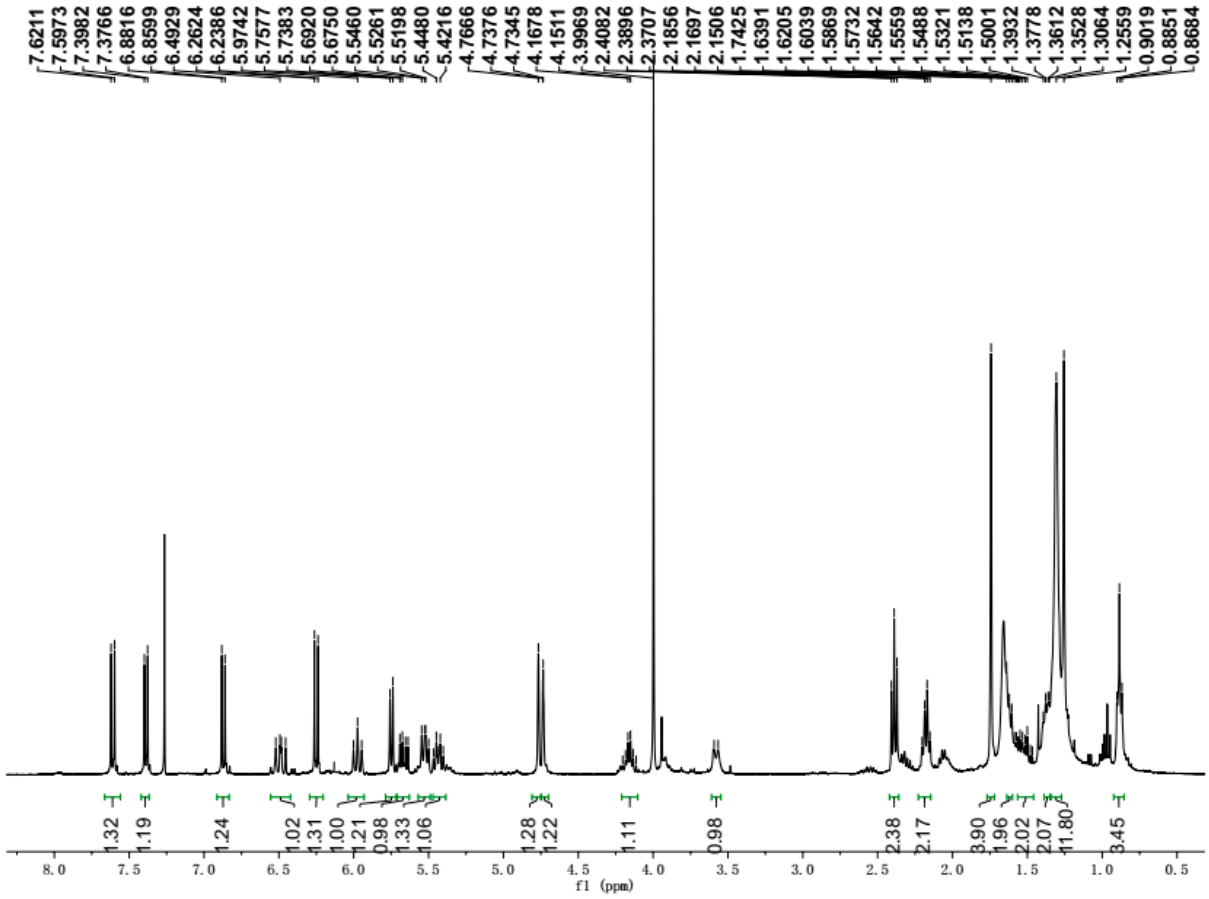
Spectrum S62. $^{1}H–^{1}H$ COSY spectrum of **10** in $CDCl_3$



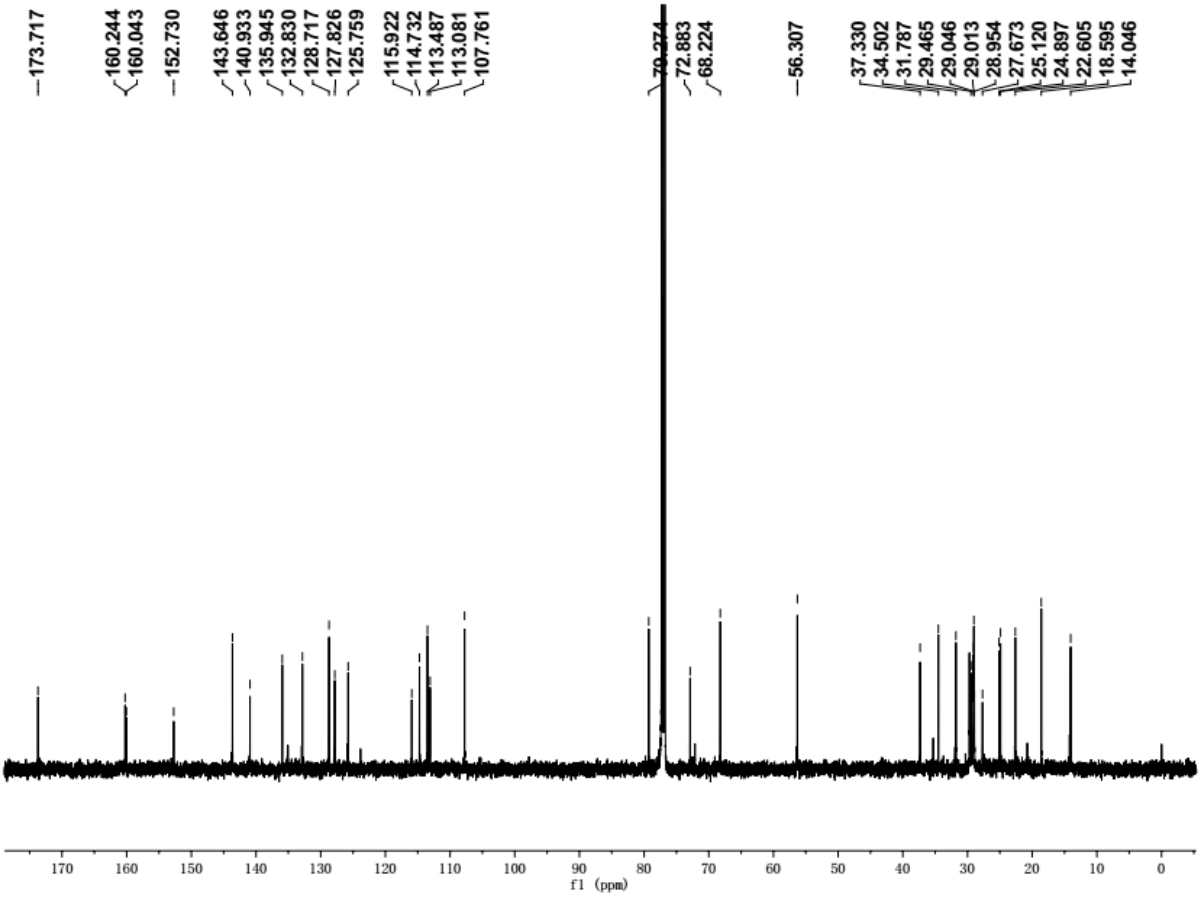
Spectrum S63. HMBC spectrum of **10** in $CDCl_3$



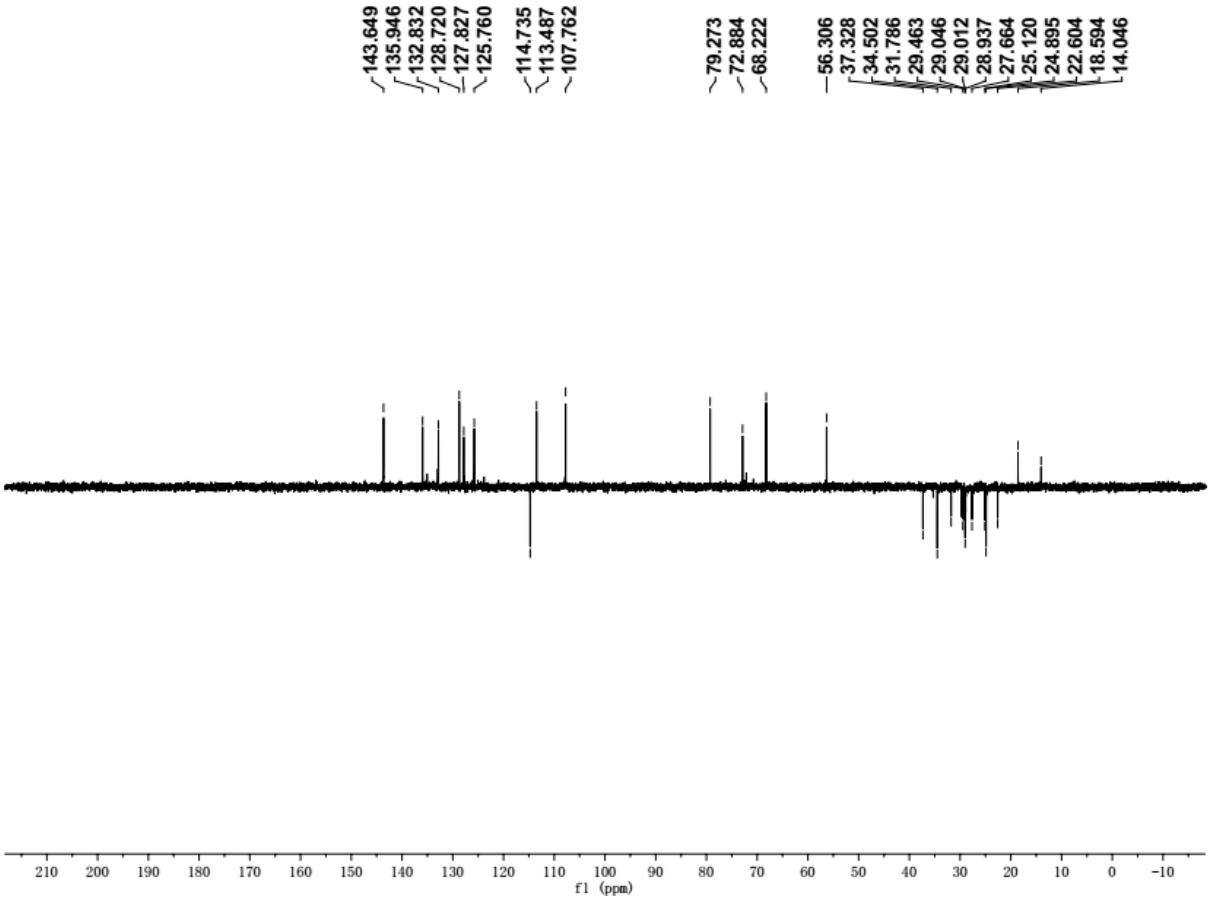
Spectrum S64. ^1H NMR spectrum of **11** in $CDCl_3$



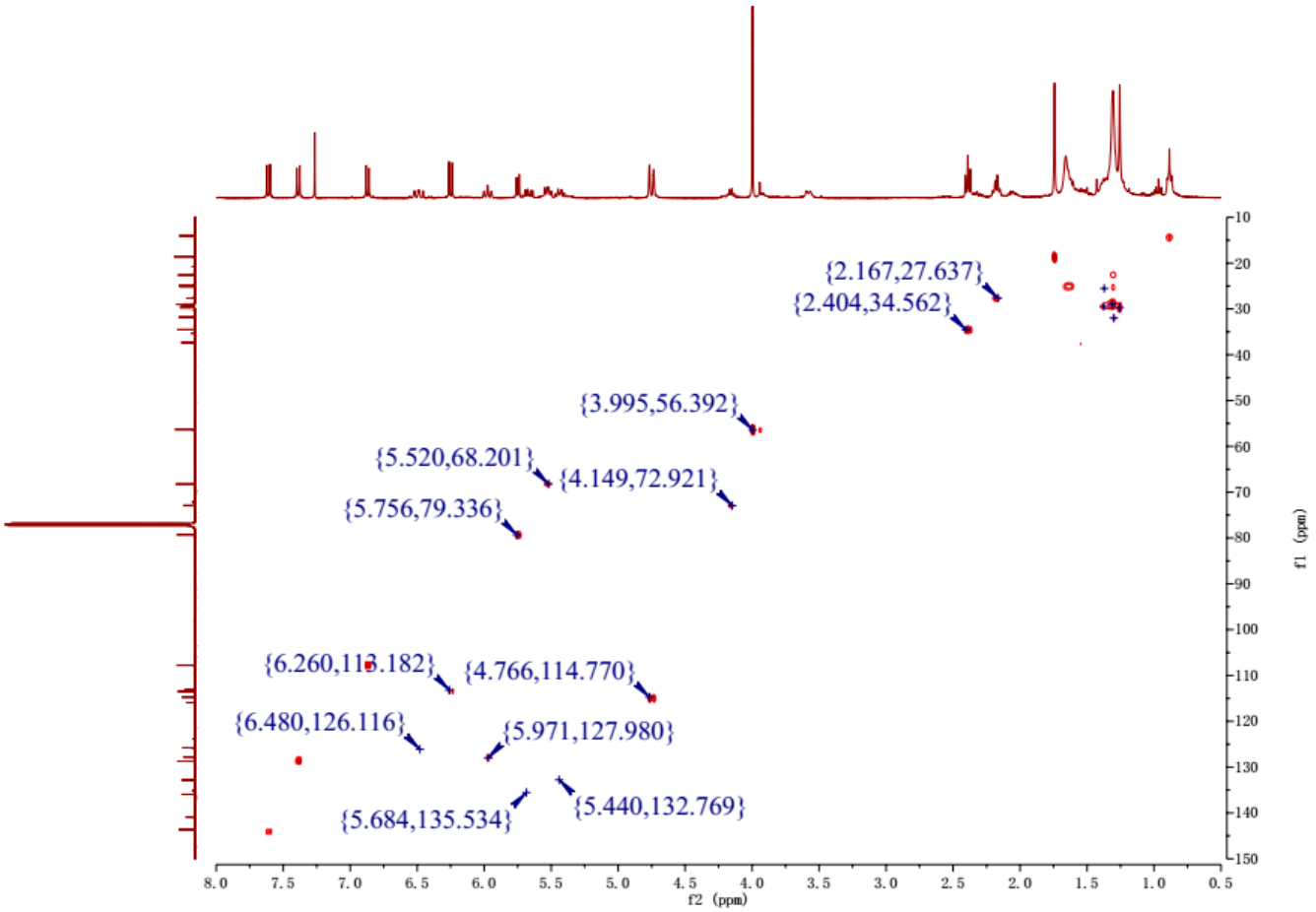
Spectrum S65. ^{13}C NMR spectrum of **11** in $CDCl_3$



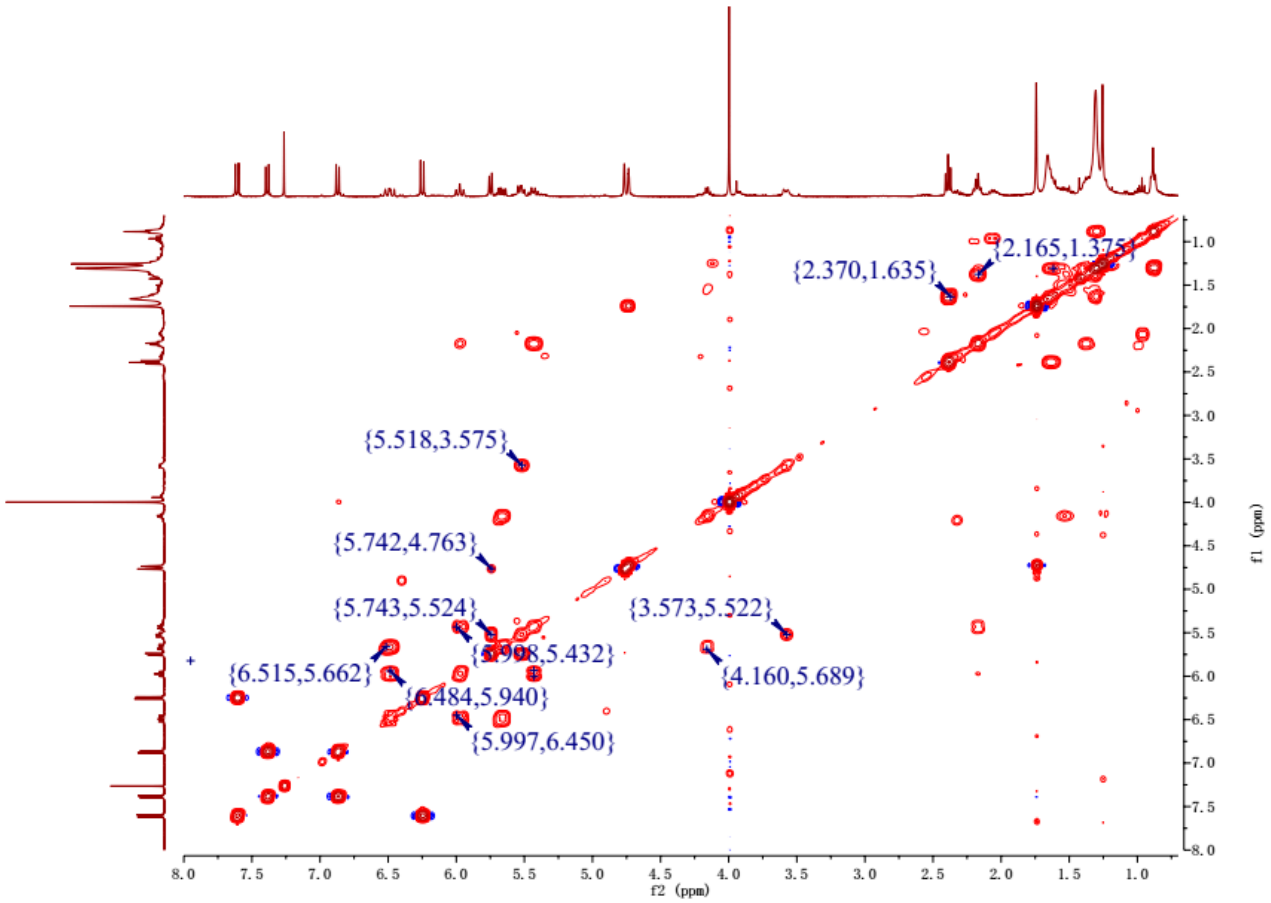
Spectrum S66. DEPT spectrum of **11** in $CDCl_3$



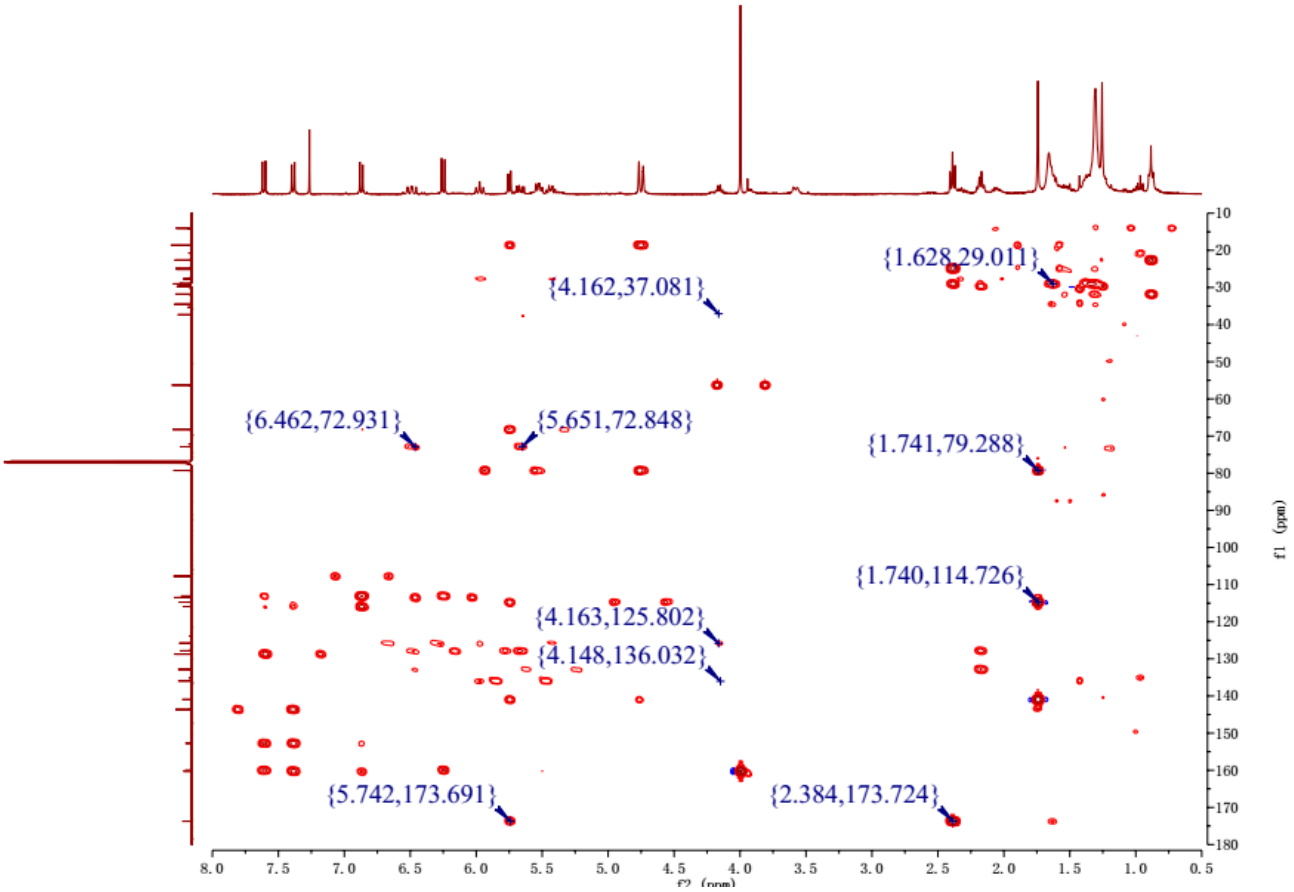
Spectrum S67. HSQC spectrum of **11** in $CDCl_3$



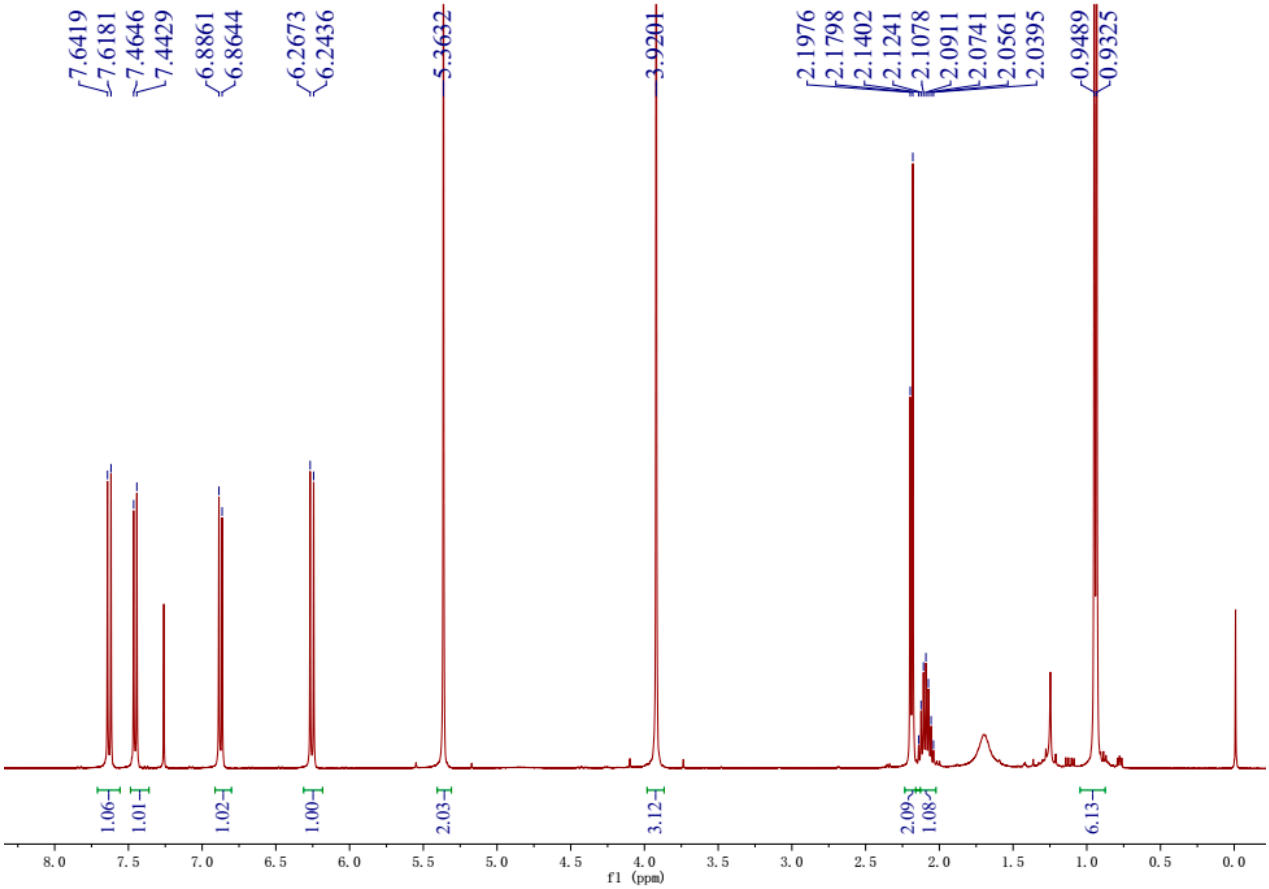
Spectrum S68. $^{1}H–^{1}H$ COSY spectrum of **11** in $CDCl_3$



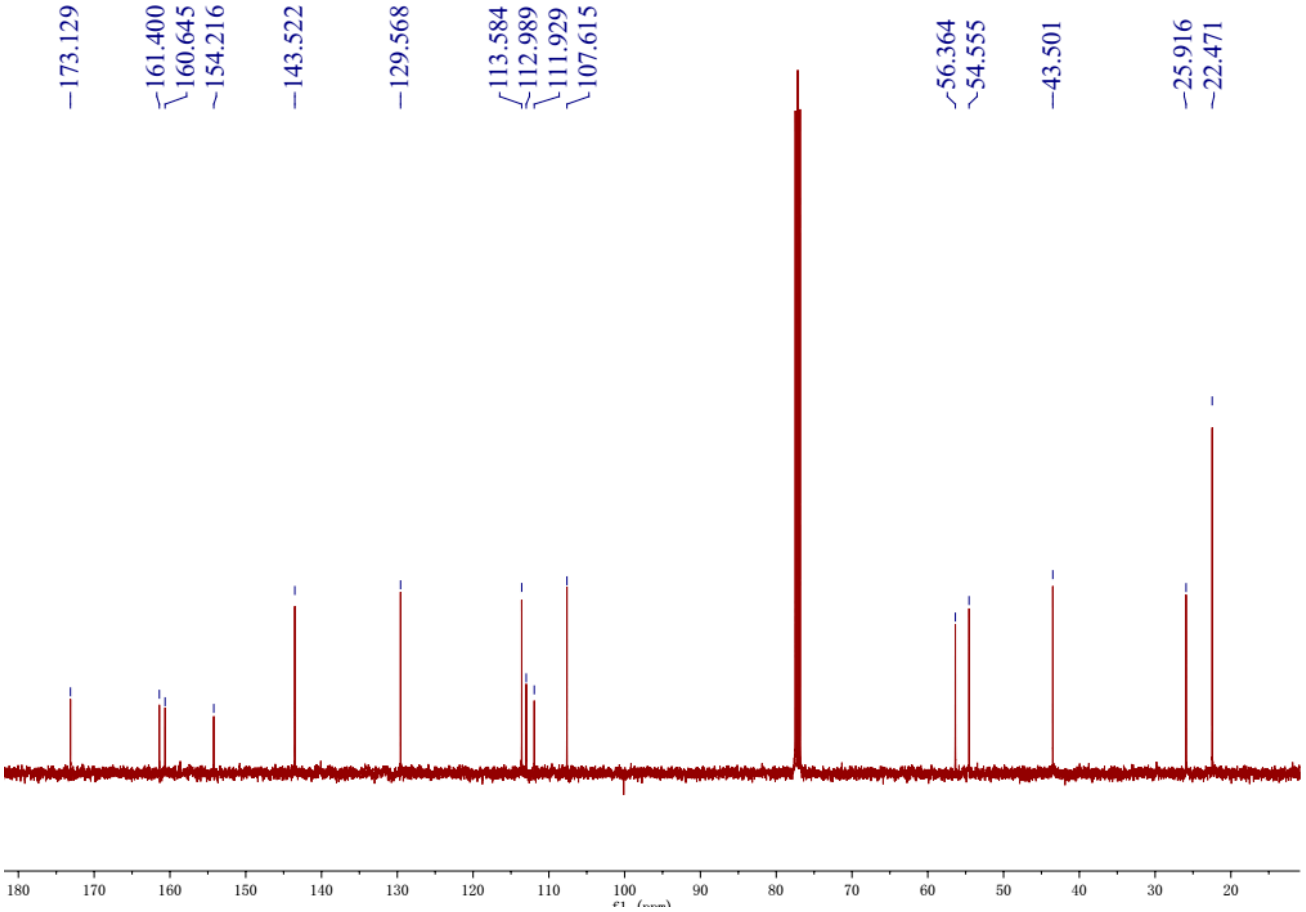
Spectrum S69. HMBC spectrum of **11** in $CDCl_3$



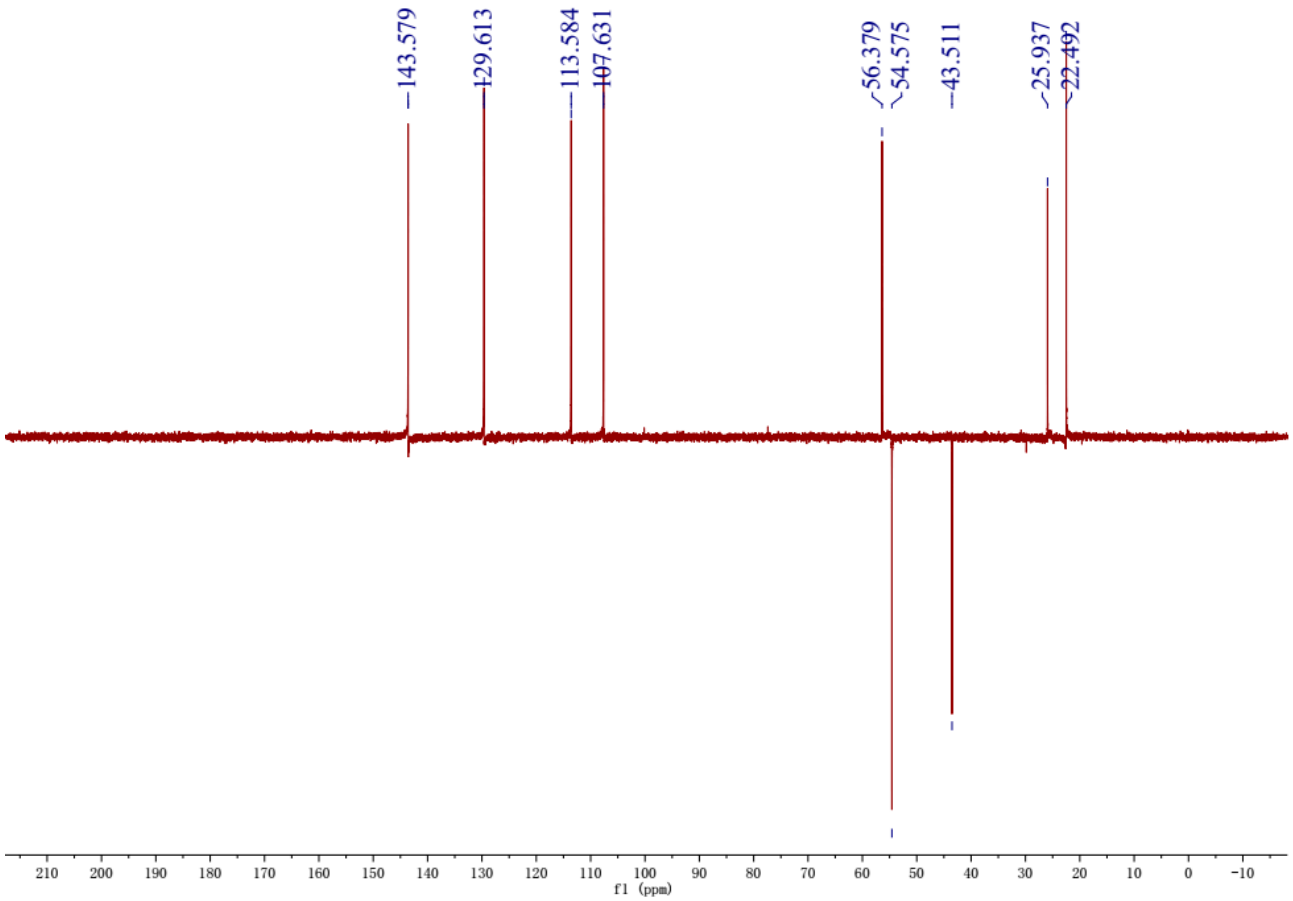
Spectrum S70. ^1H NMR spectrum of **12** in $CDCl_3$



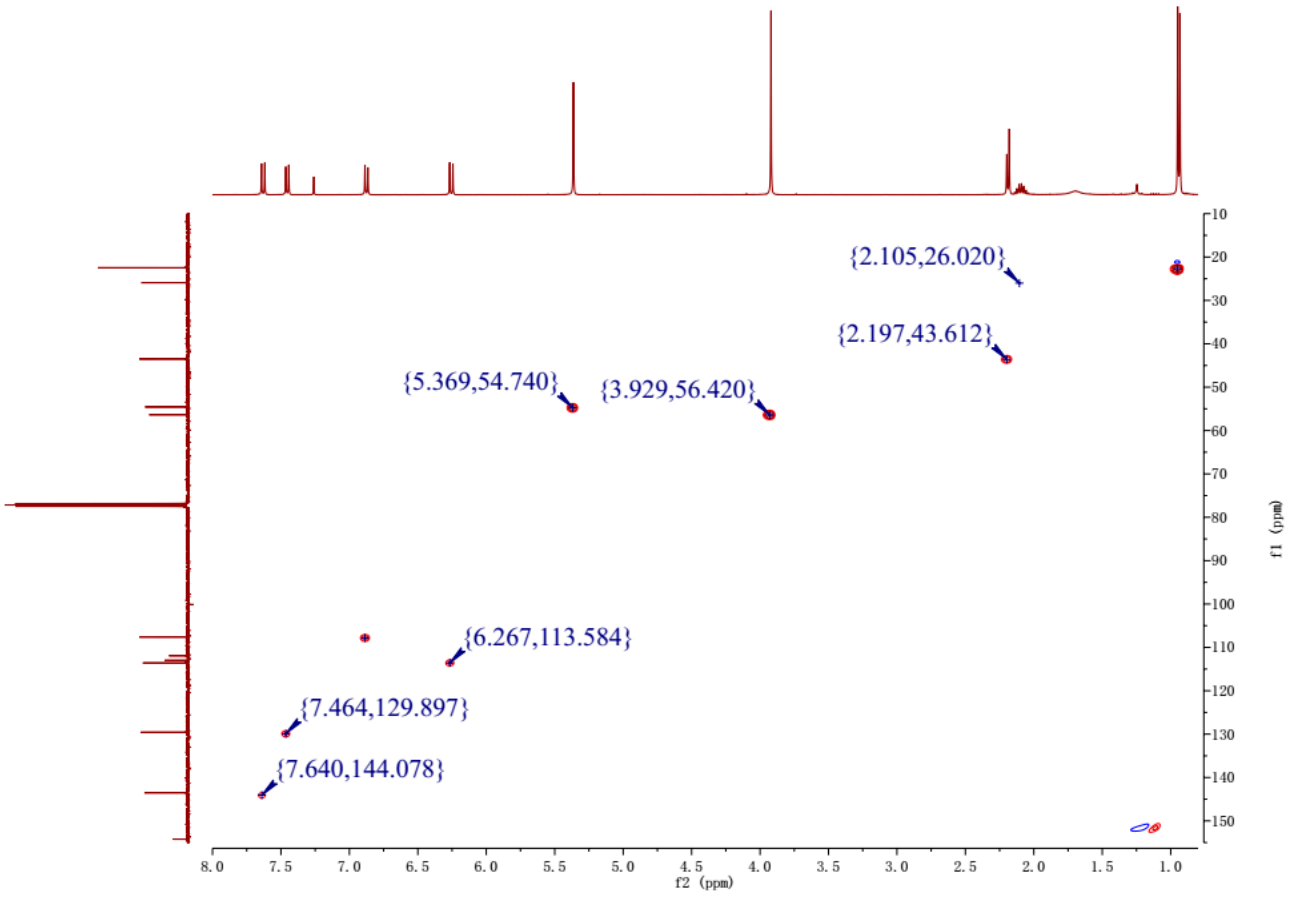
Spectrum S71. ^{13}C NMR spectrum of **12** in $CDCl_3$



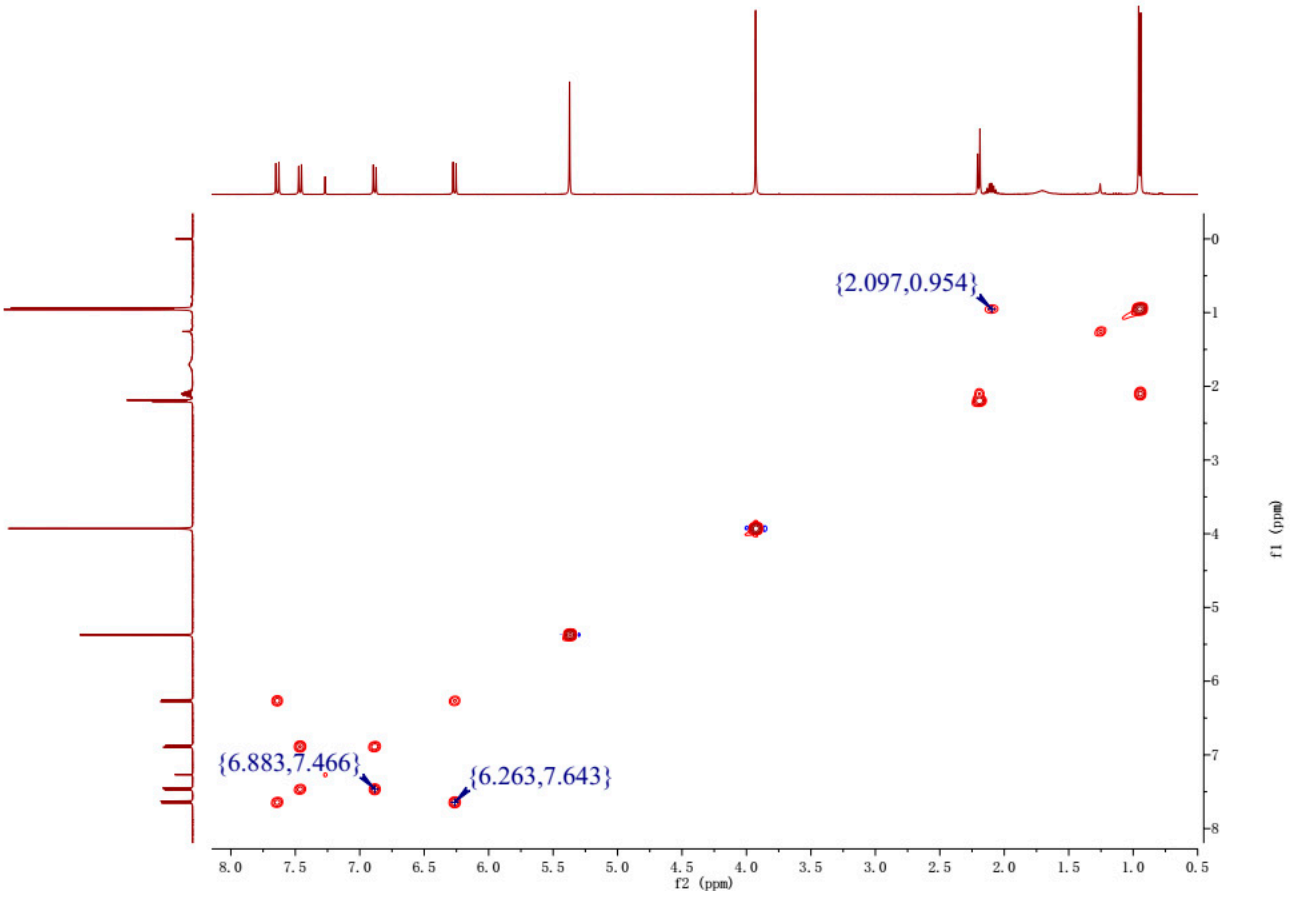
Spectrum S72. DEPT spectrum of **12** in $CDCl_3$



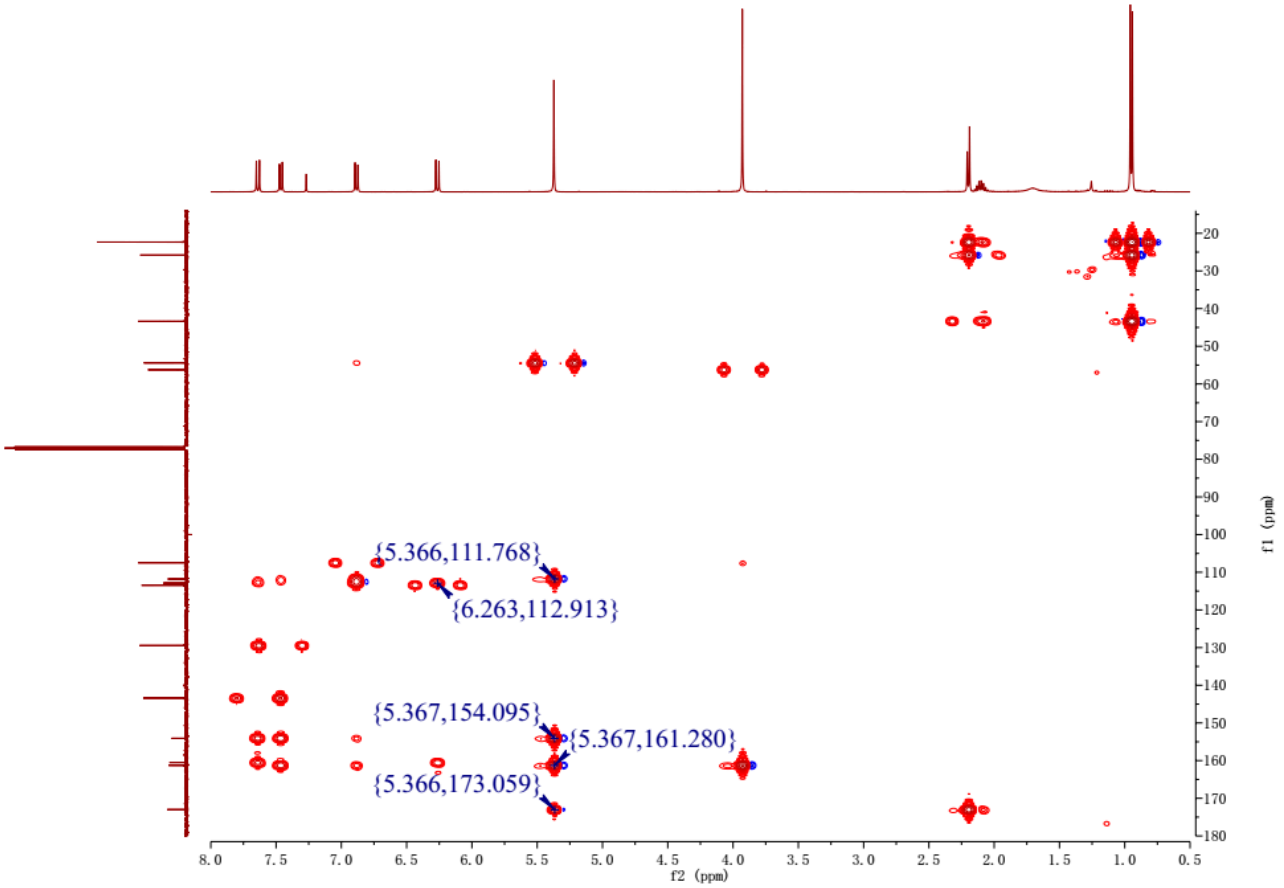
Spectrum S73. HSQC spectrum of **12** in $CDCl_3$



Spectrum S74. $^{1}H–^{1}H$ COSY spectrum of **12** in $CDCl_3$

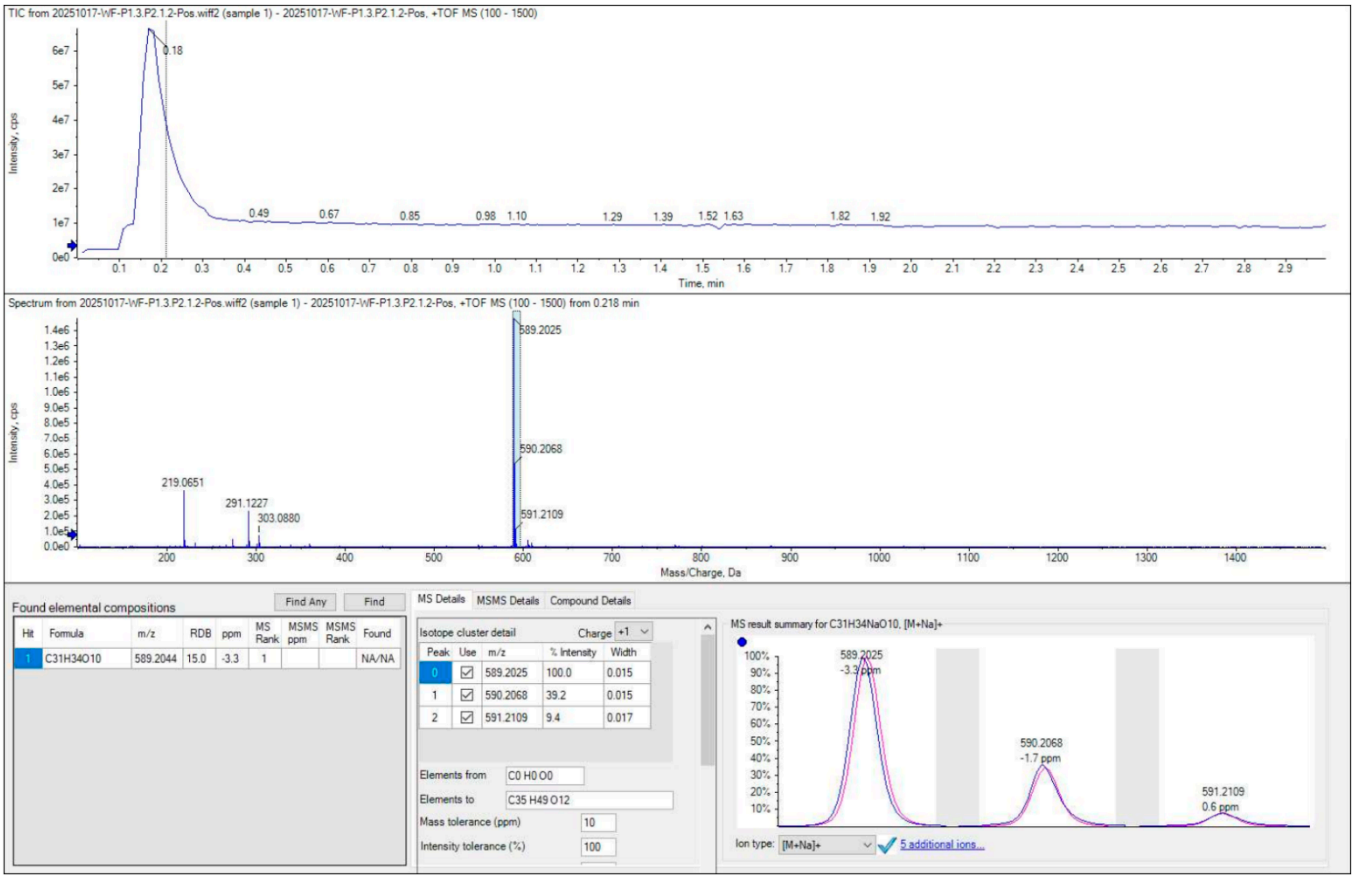


Spectrum S75. HMBC spectrum of **12** in $CDCl_3$

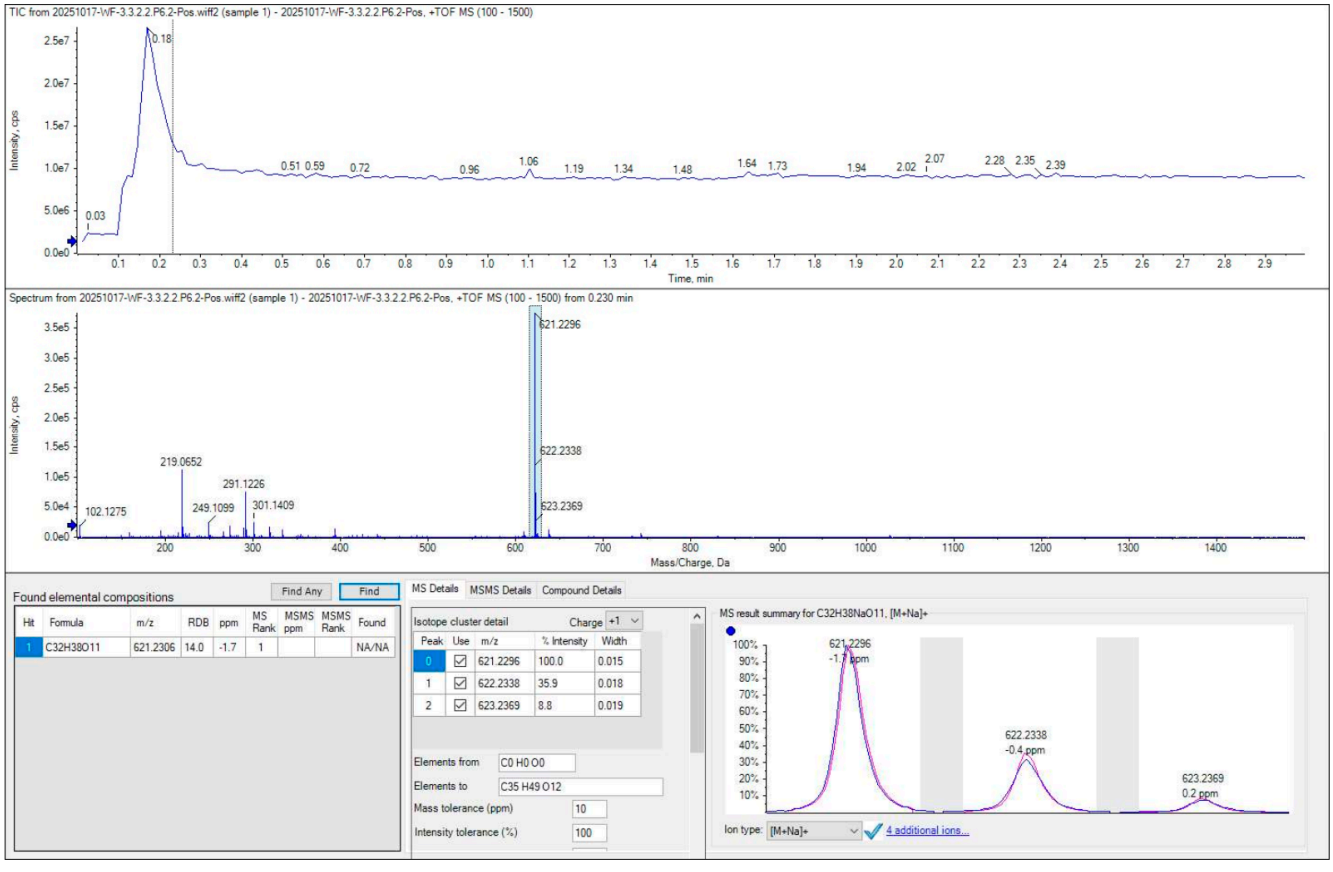


S4. HRESIMS spectra of compounds **1–12**

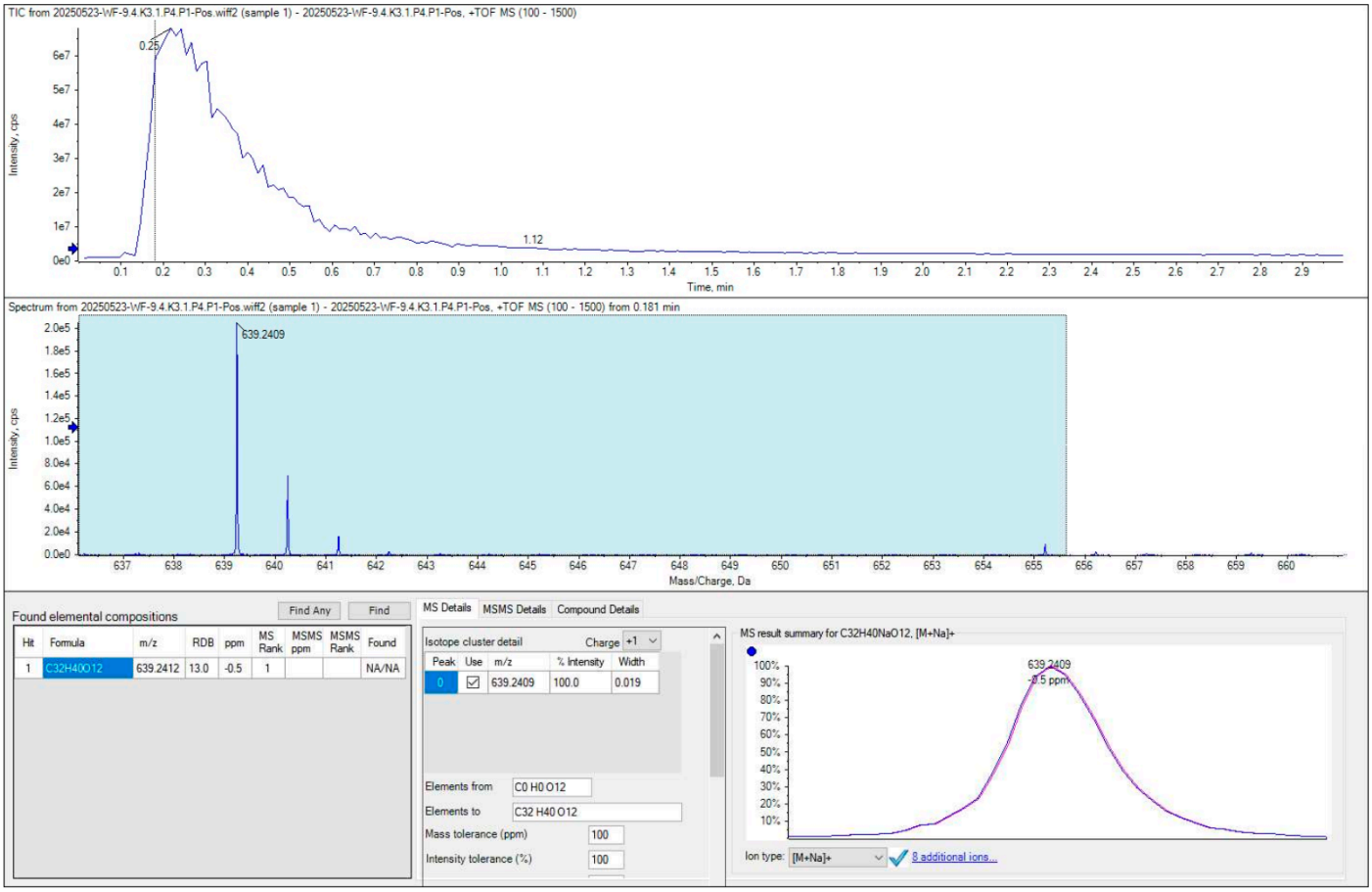
Spectrum S76. HRESIMS spectrum of **1**



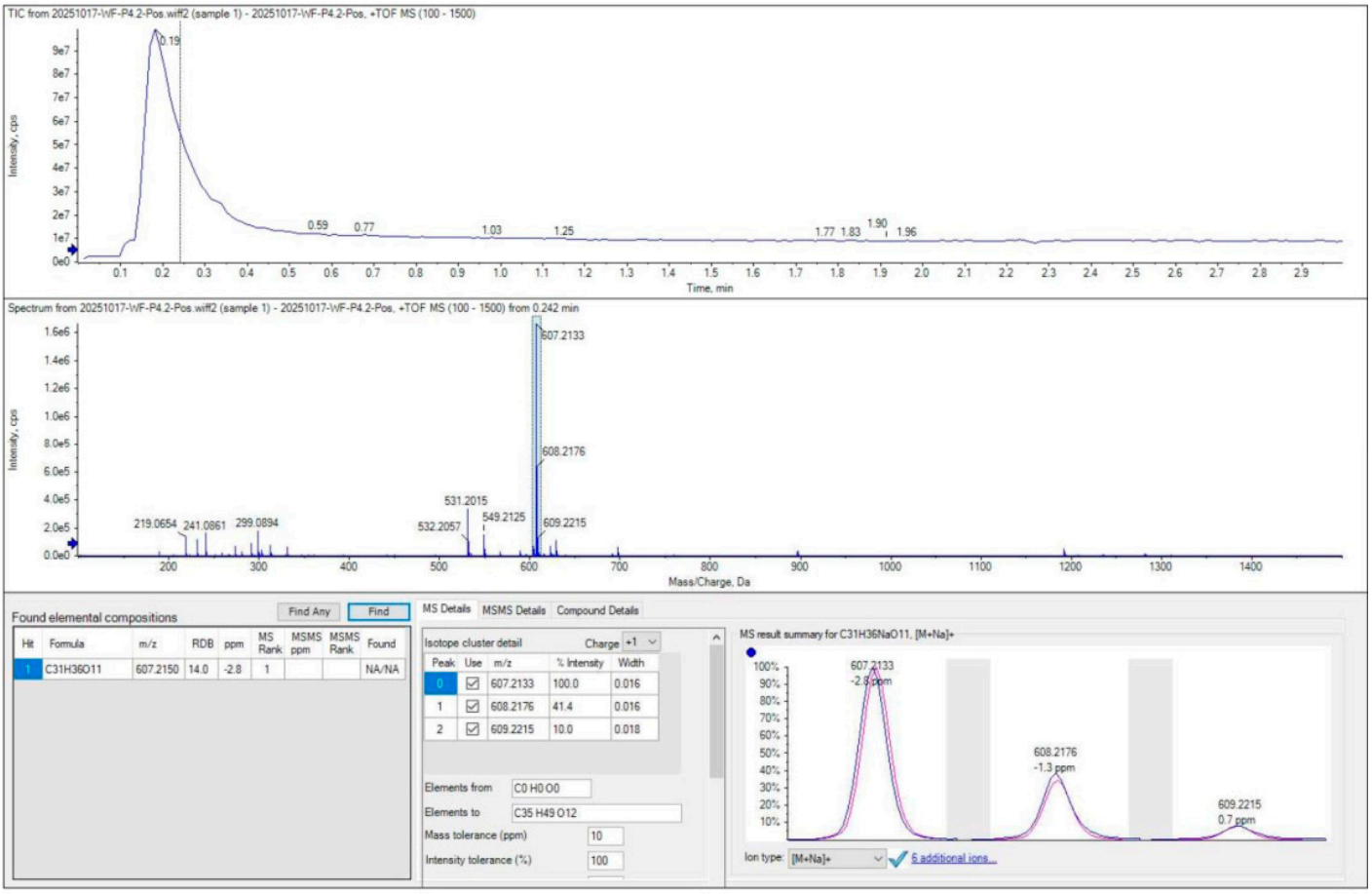
Spectrum S77. HRESIMS spectrum of **2**



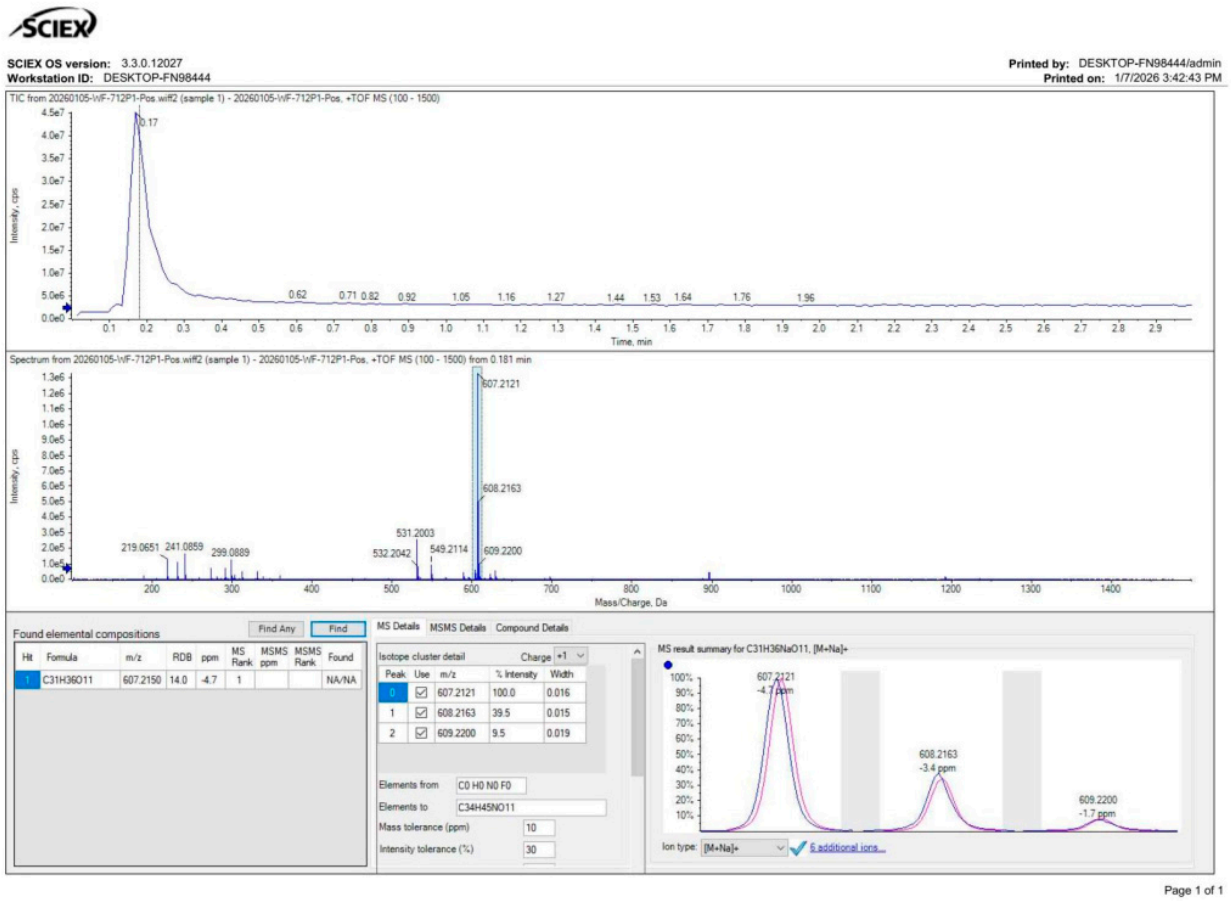
Spectrum S78. HRESIMS spectrum of **3**



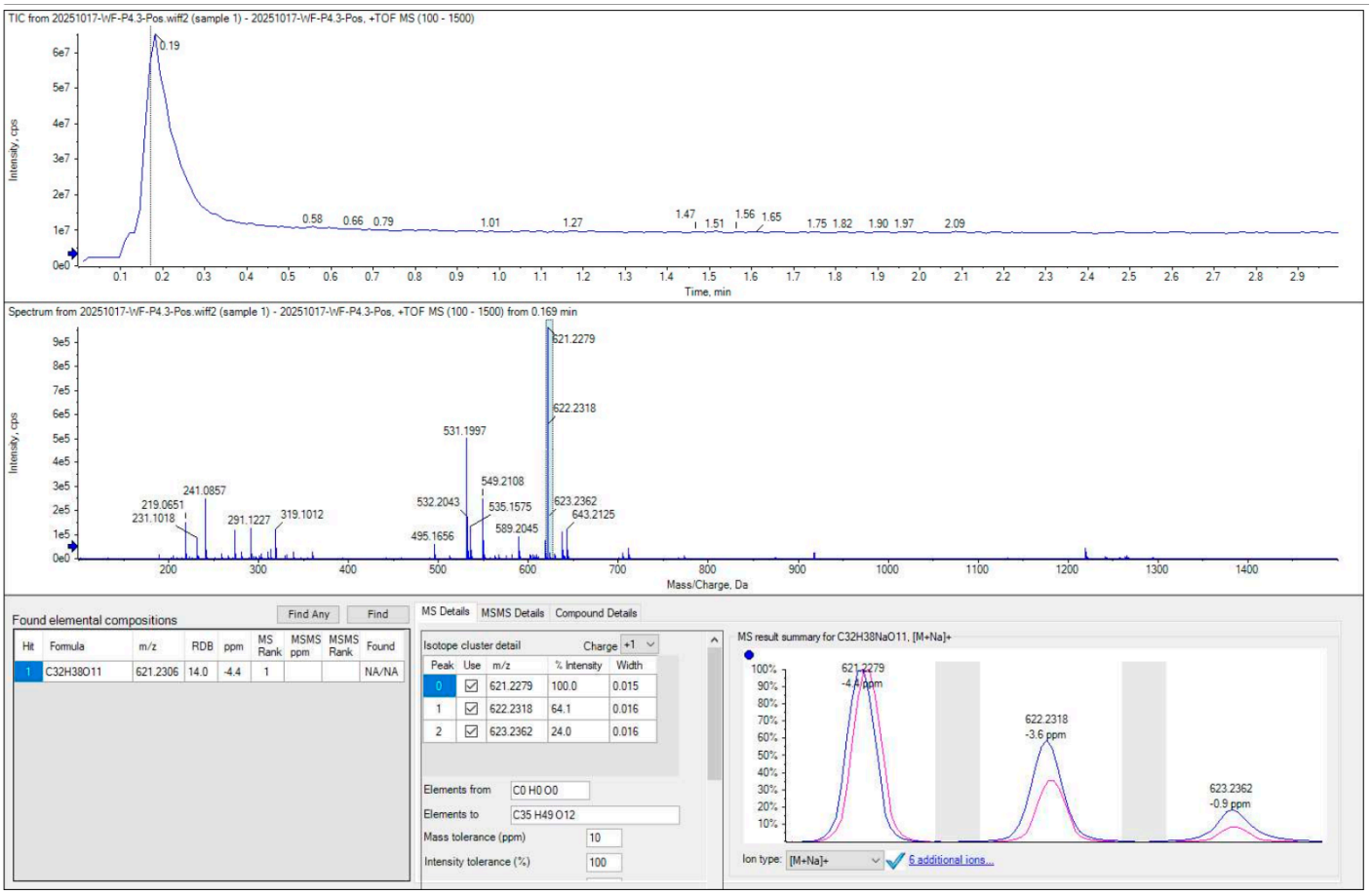
Spectrum S79. HRESIMS spectrum of **4**



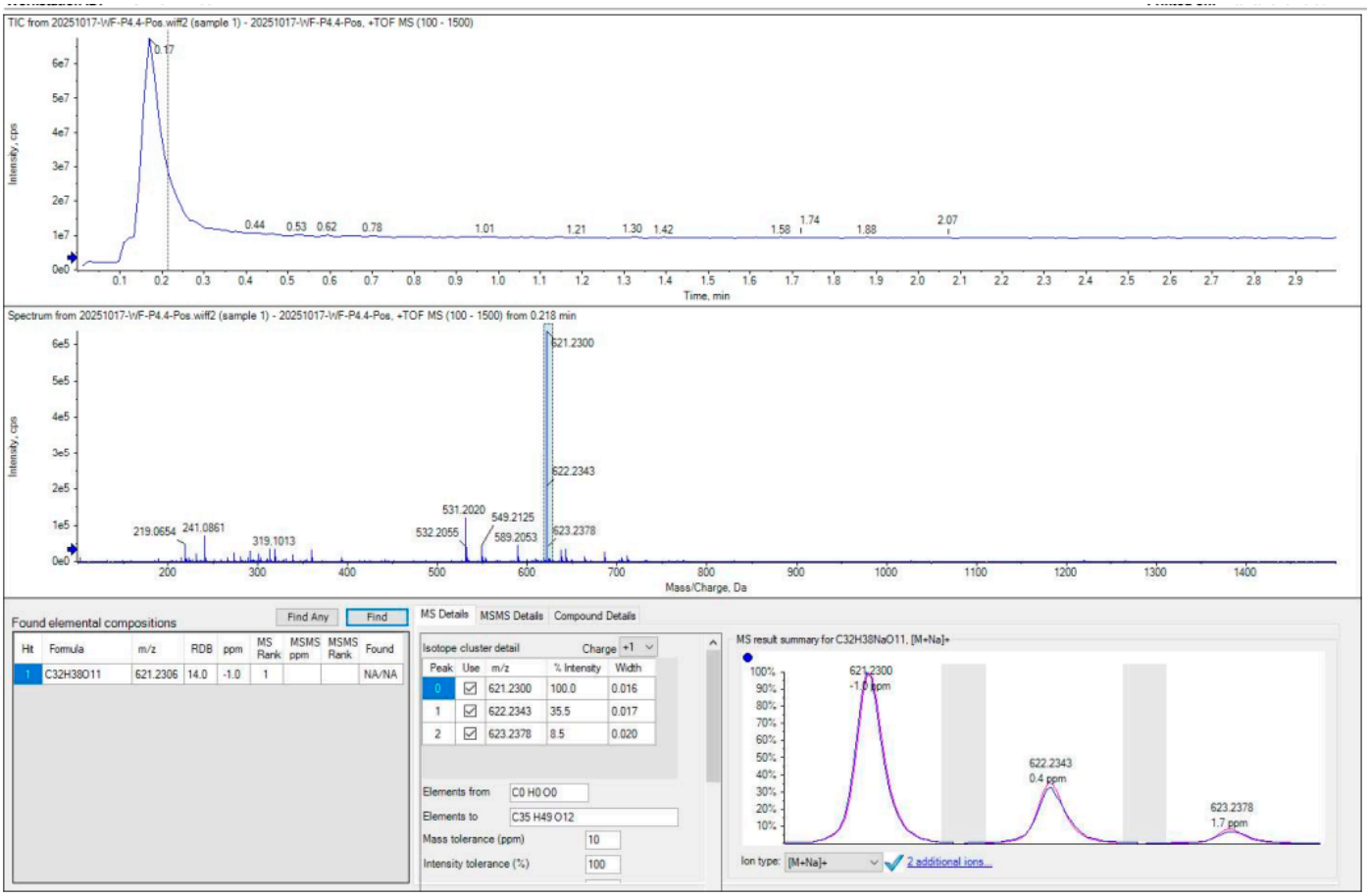
Spectrum S80. HRESIMS spectrum of **5**



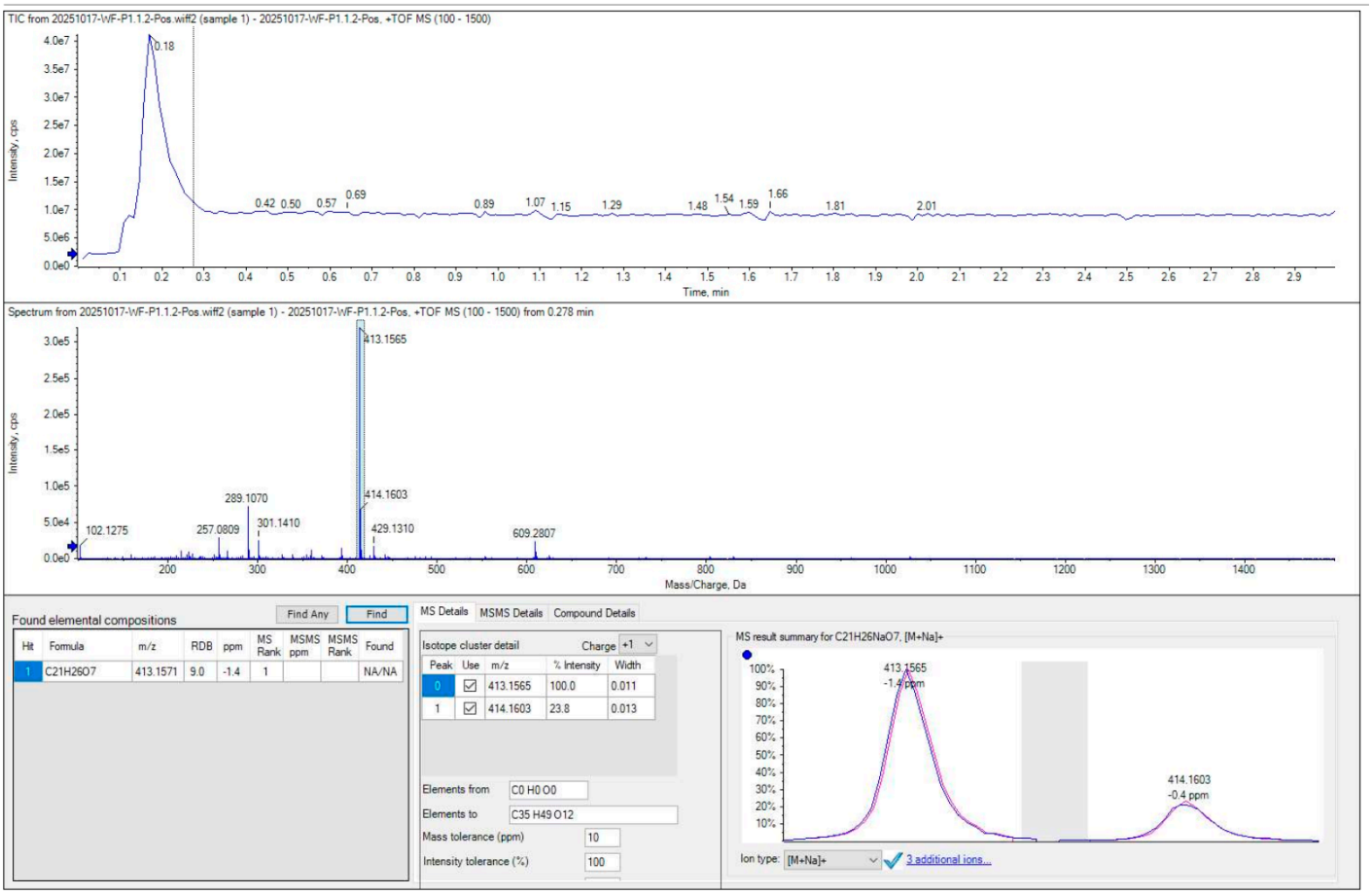
Spectrum S81. HRESIMS spectrum of **6**



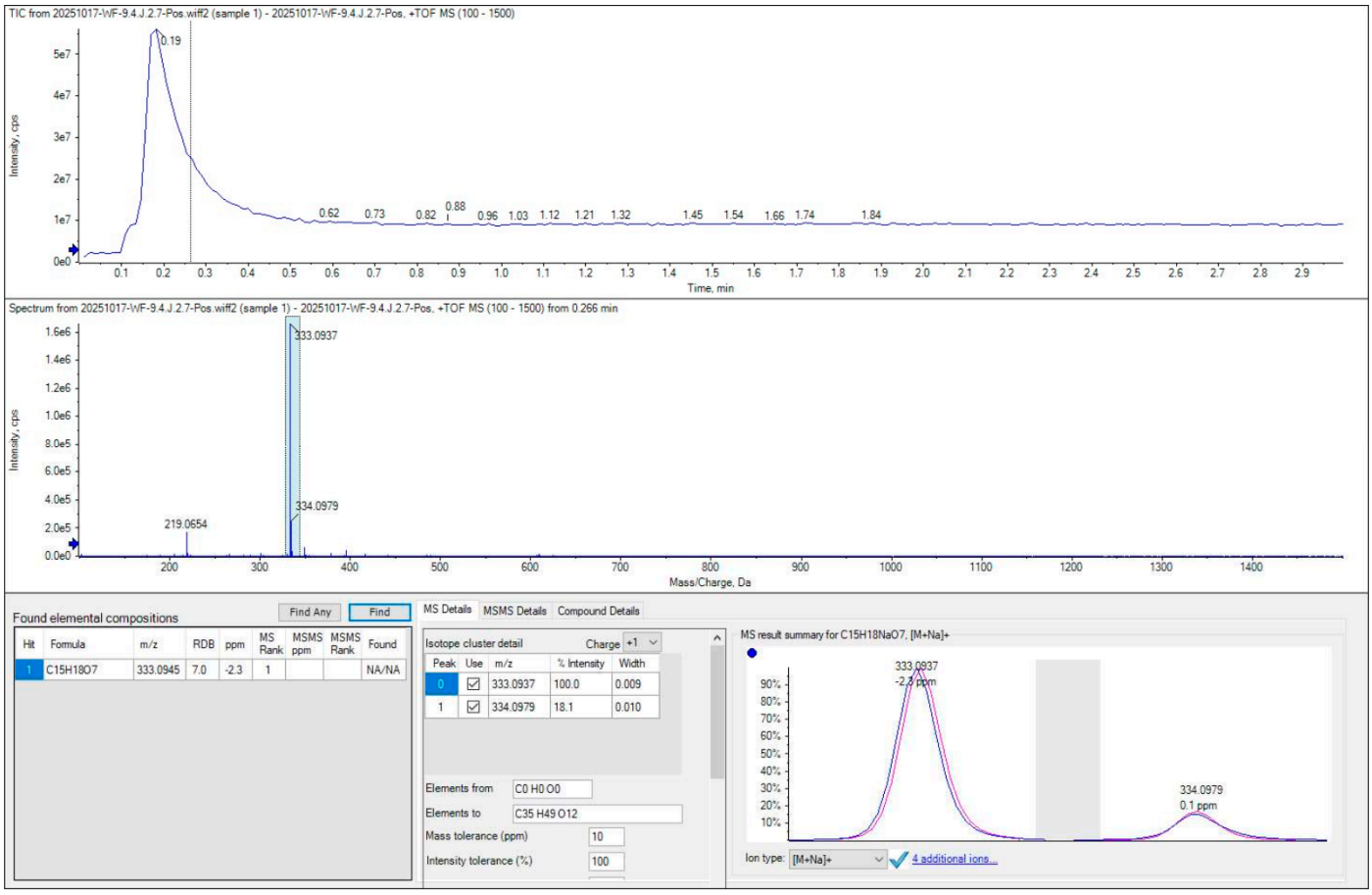
Spectrum S82. HRESIMS spectrum of **7**



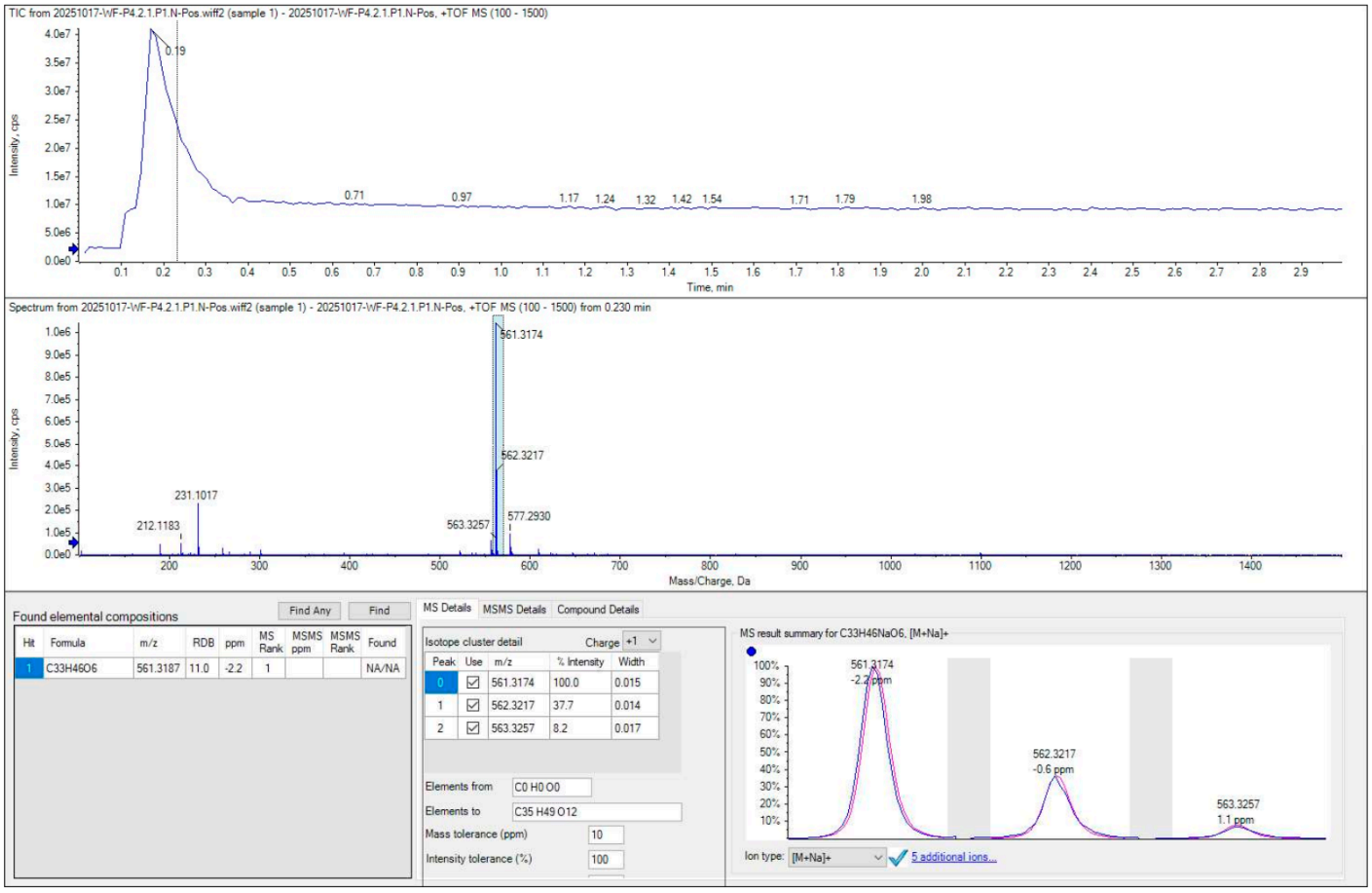
Spectrum S83. HRESIMS spectrum of **8**



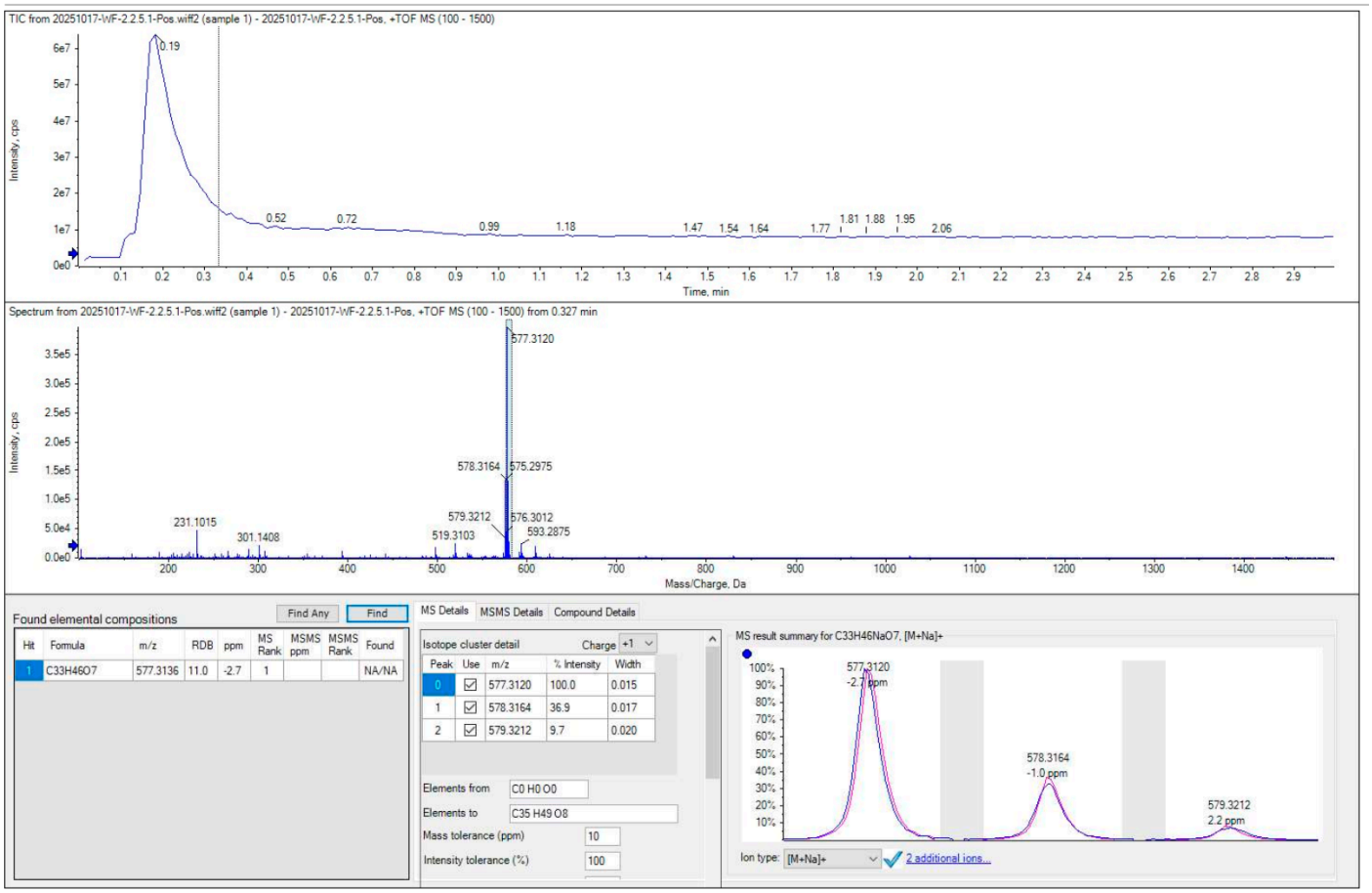
Spectrum S84. HRESIMS spectrum of **9**



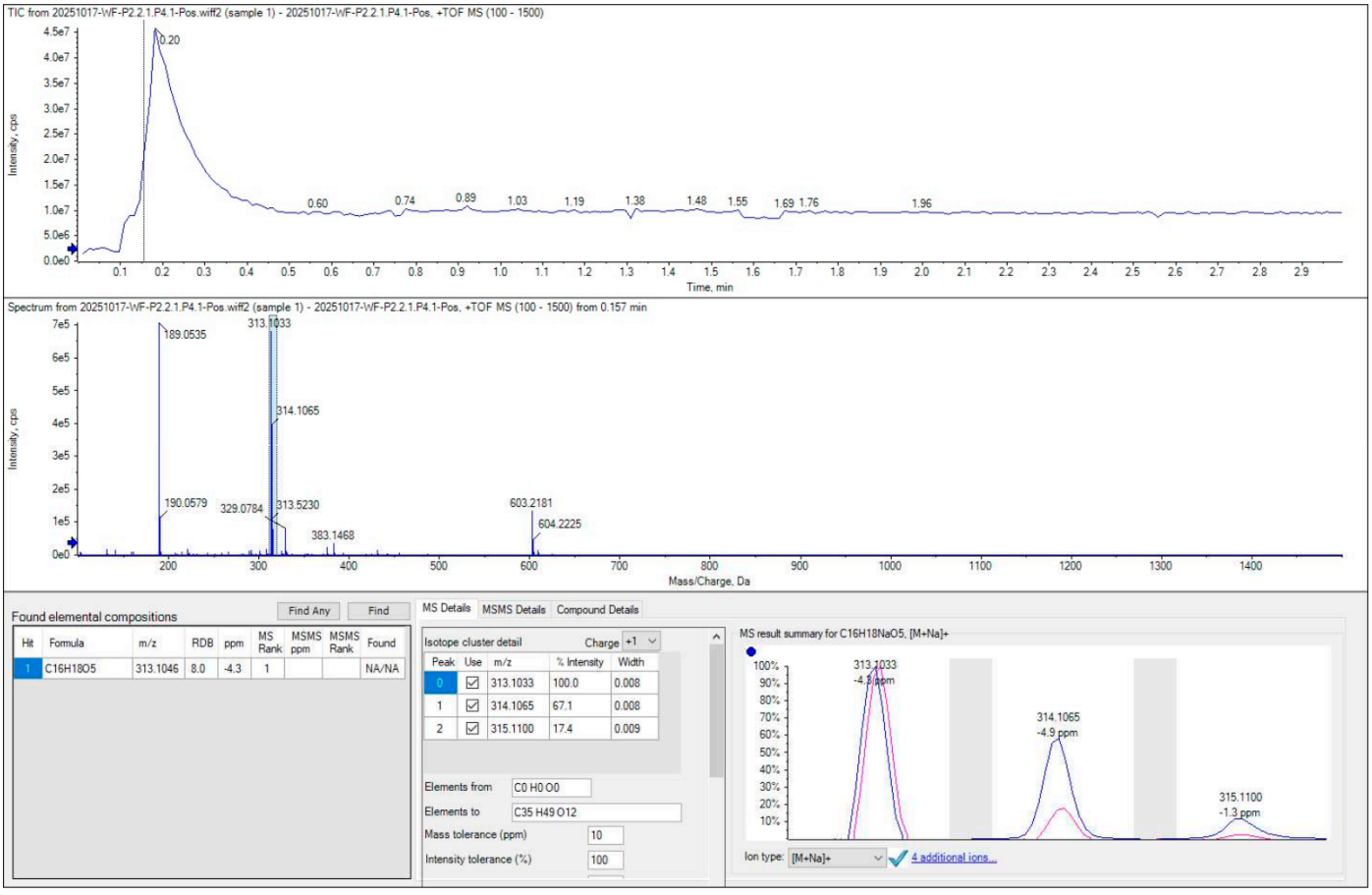
Spectrum S85. HRESIMS spectrum of **10**



Spectrum S86. HRESIMS spectrum of **11**

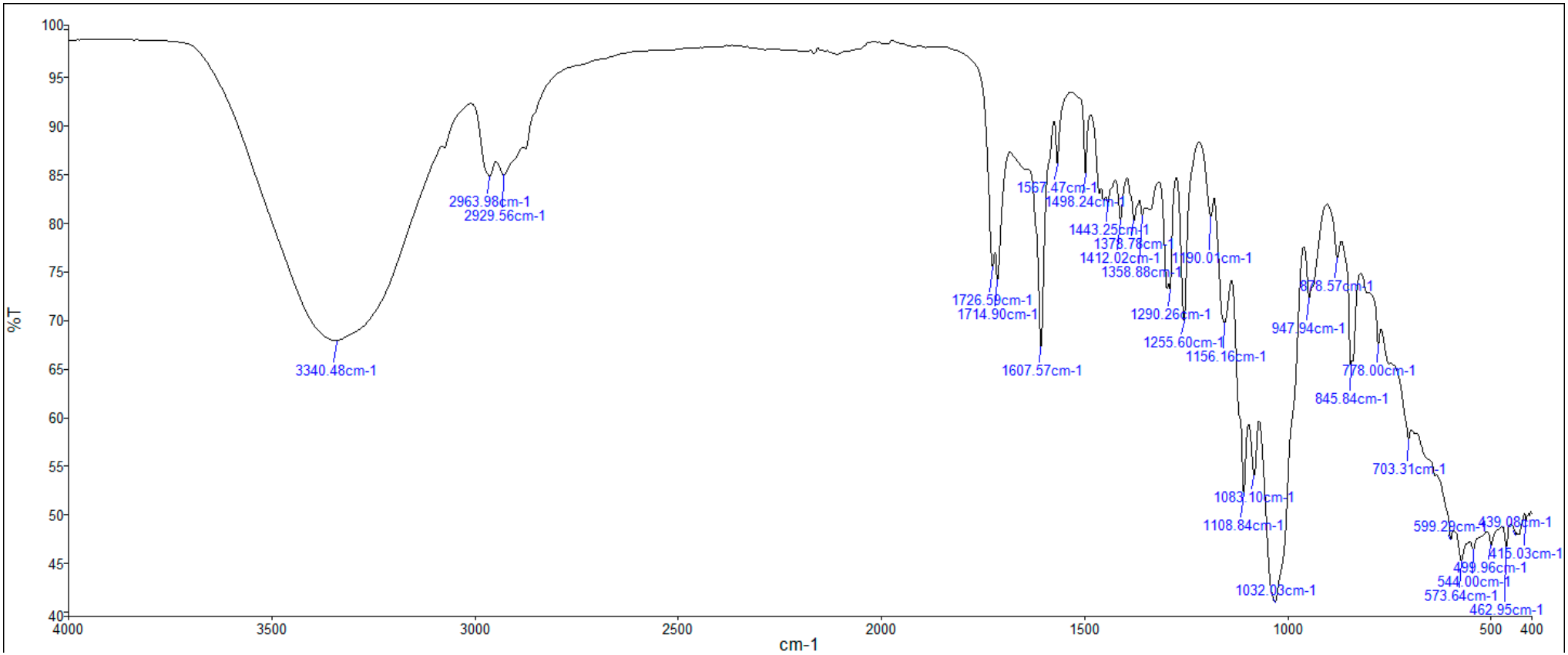


Spectrum S87. HRESIMS spectrum of **12**

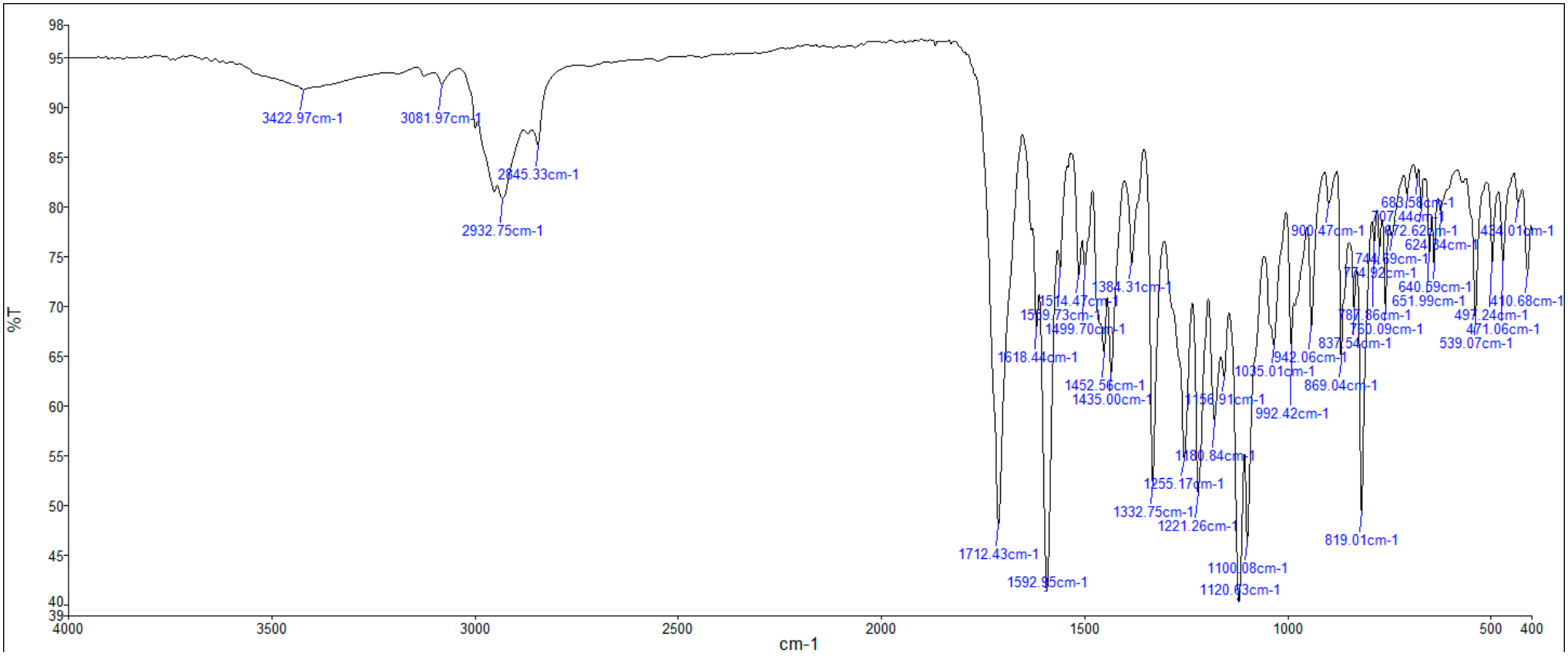


S5. IR spectra of compounds **1–12**

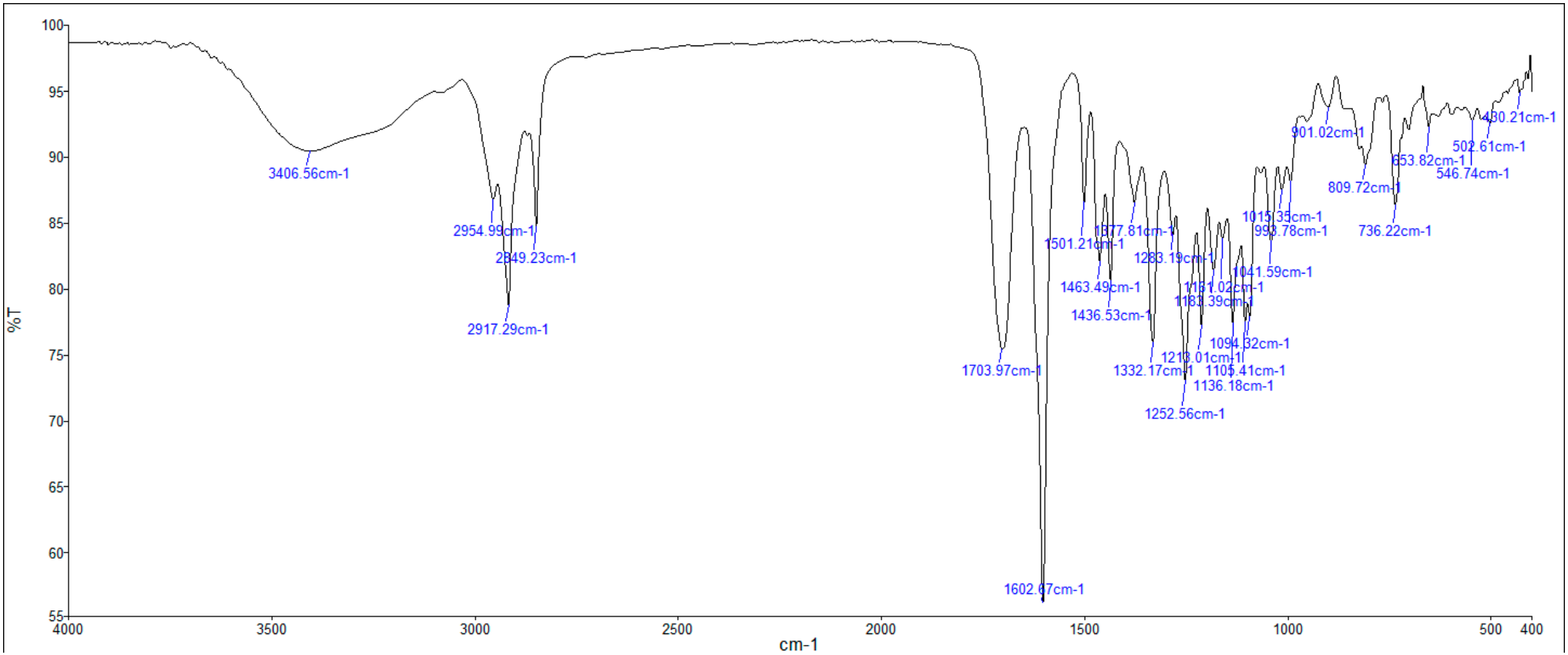
Spectrum S88. The IR spectrum of **1**



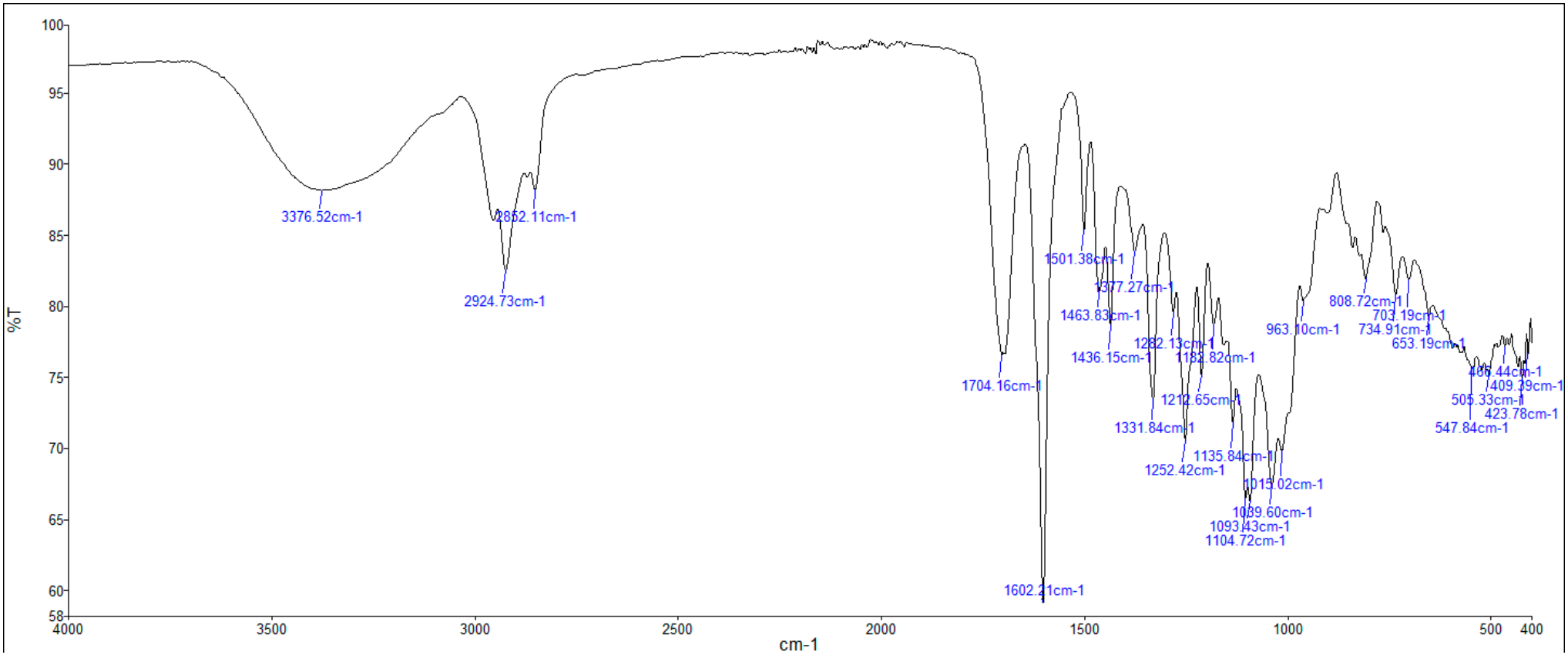
Spectrum S89. The IR spectrum of **2**



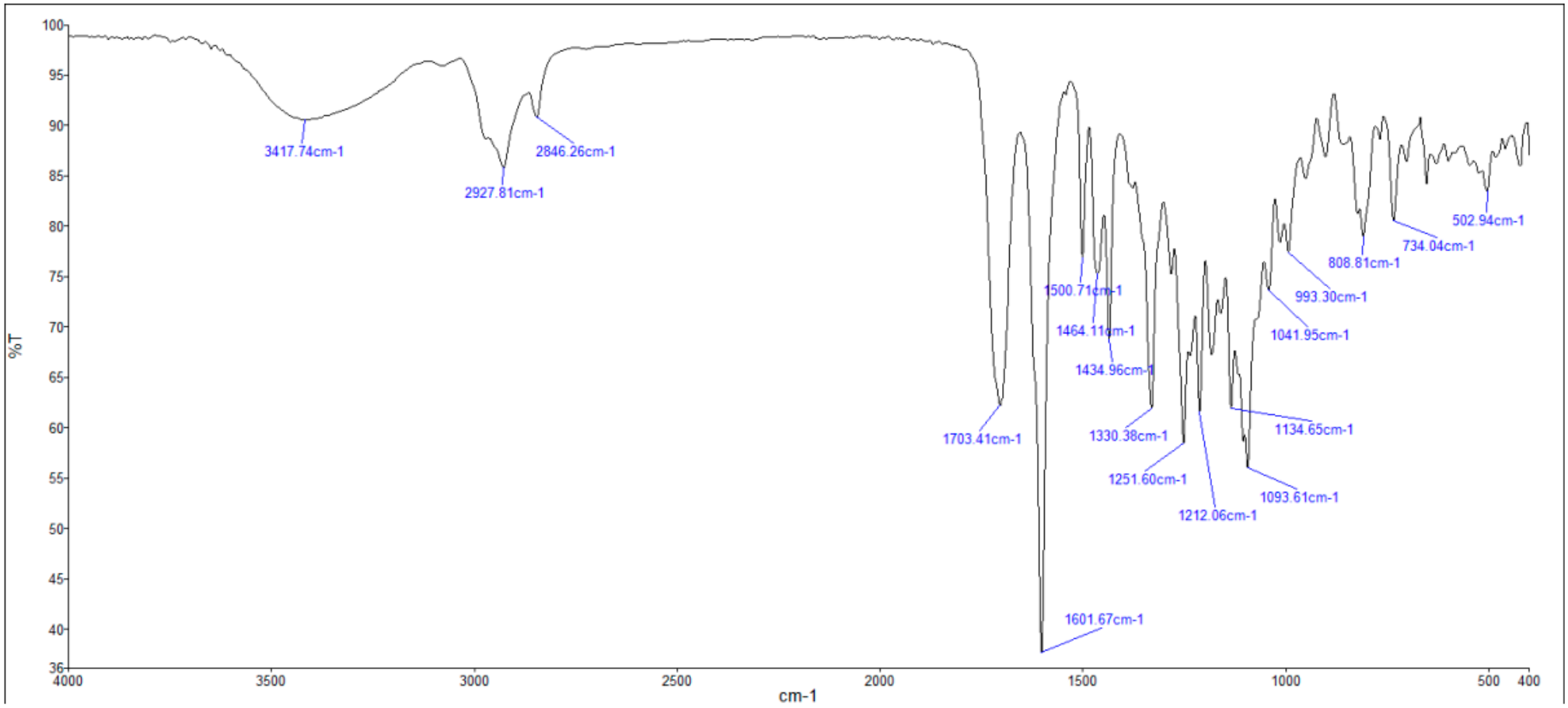
Spectrum S90 The IR spectrum of **3**



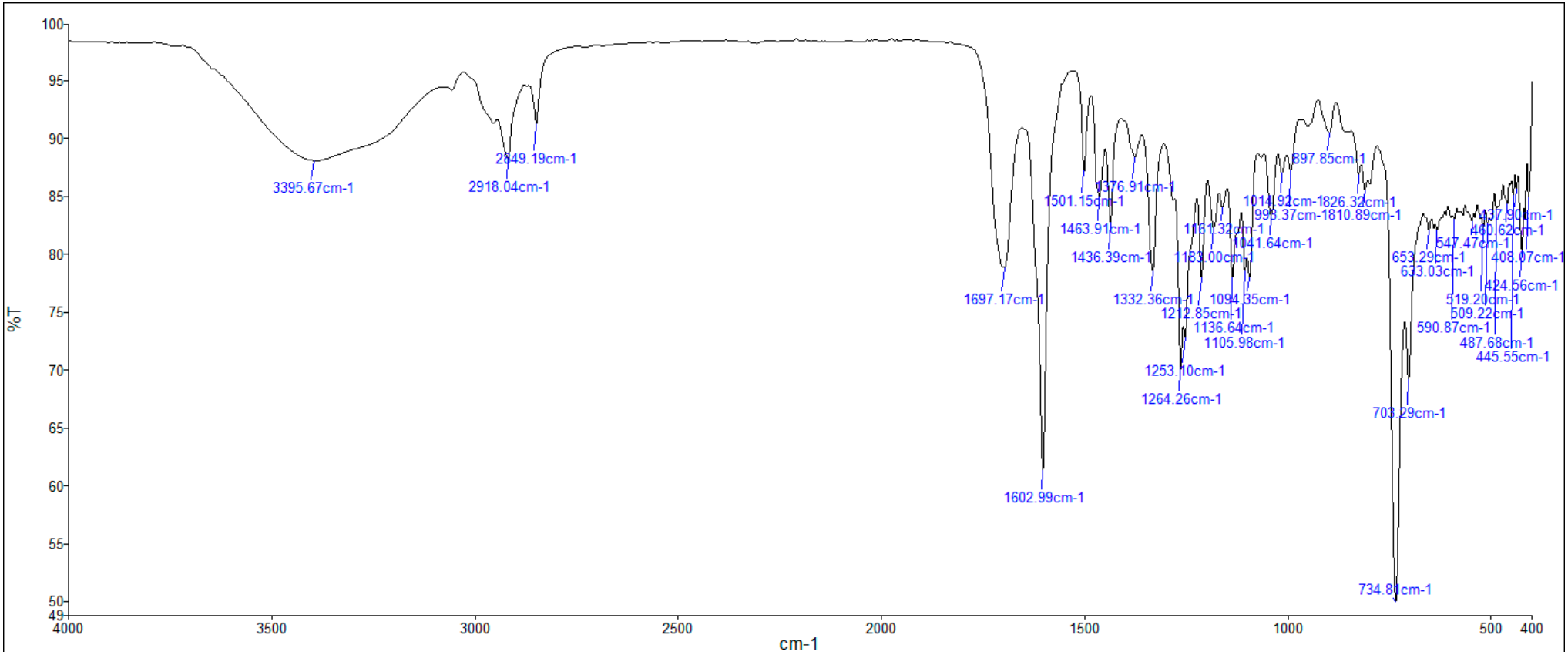
Spectrum S91. The IR spectrum of **4**



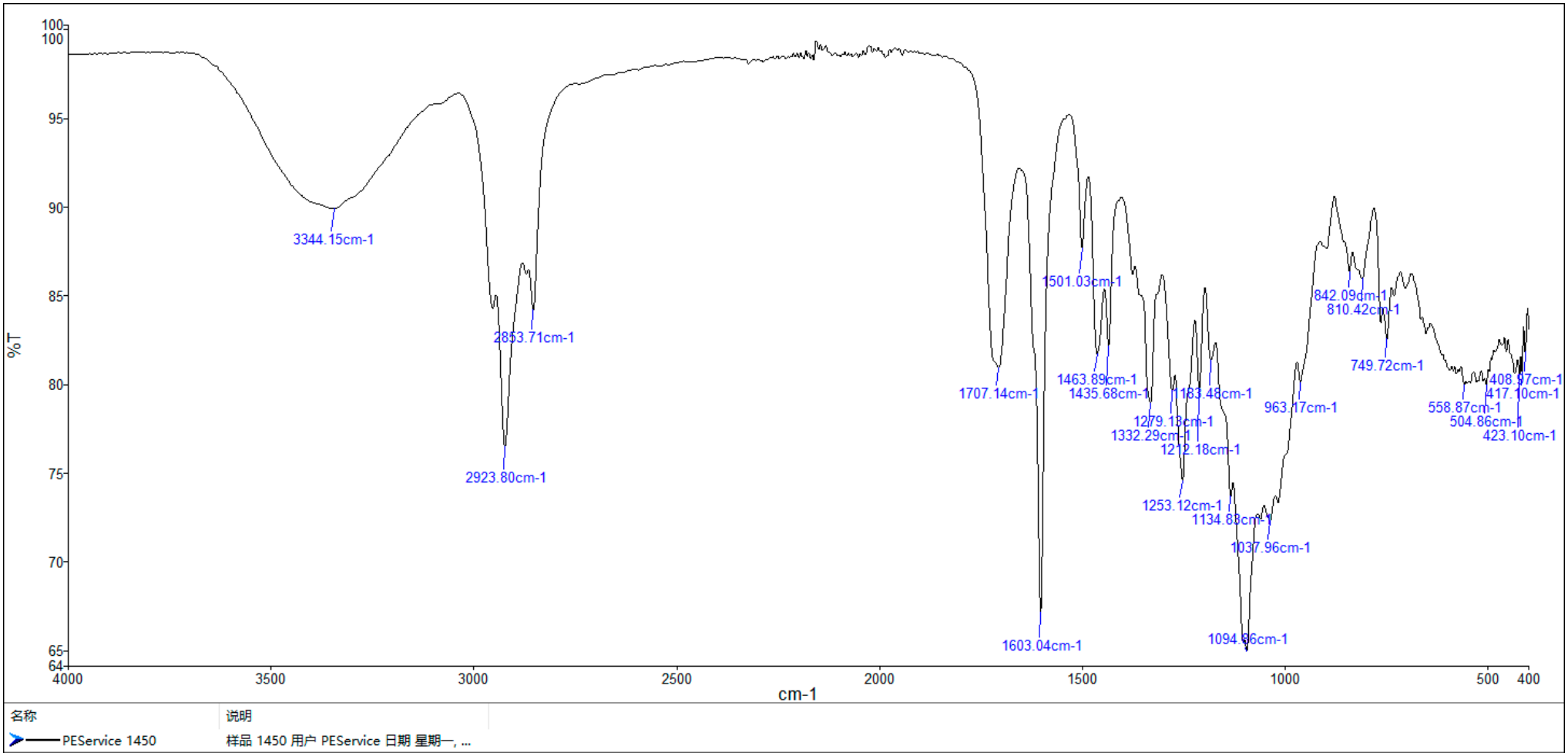
Spectrum S92. The IR spectrum of **5**



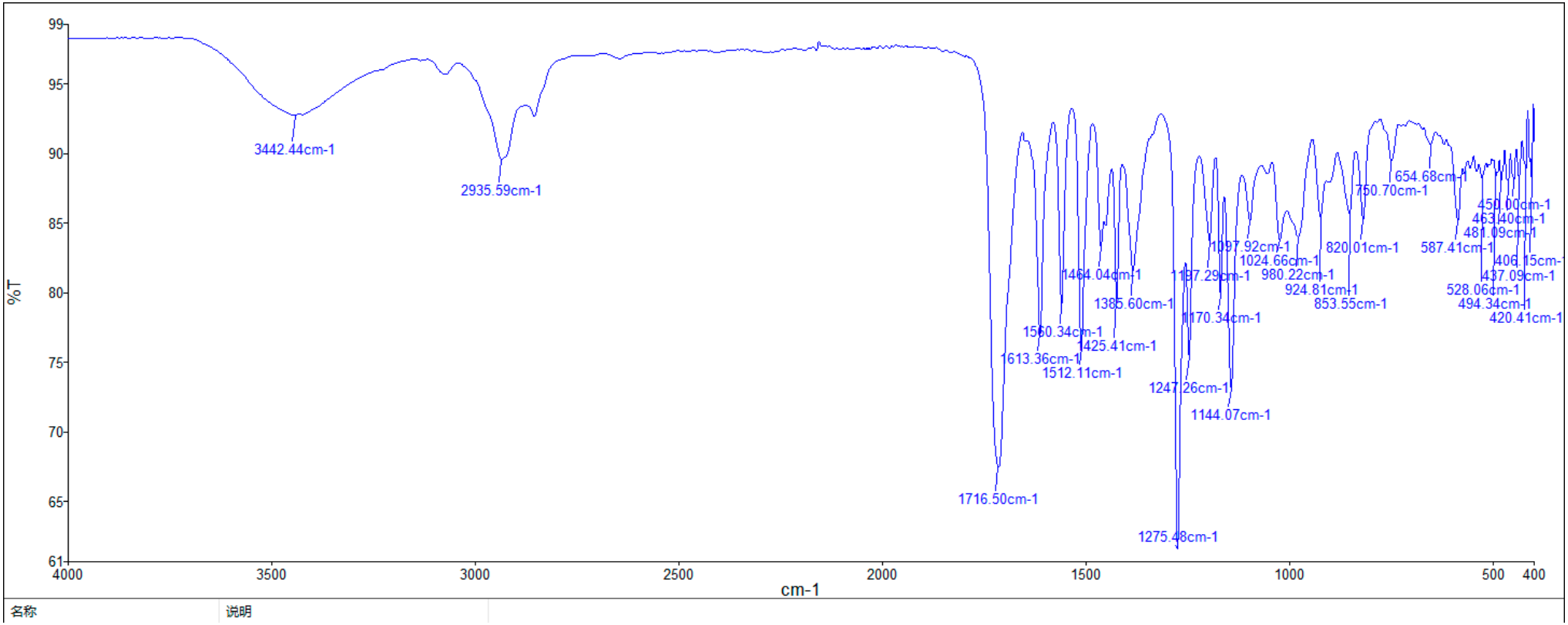
Spectrum S93. The IR spectrum of **6**



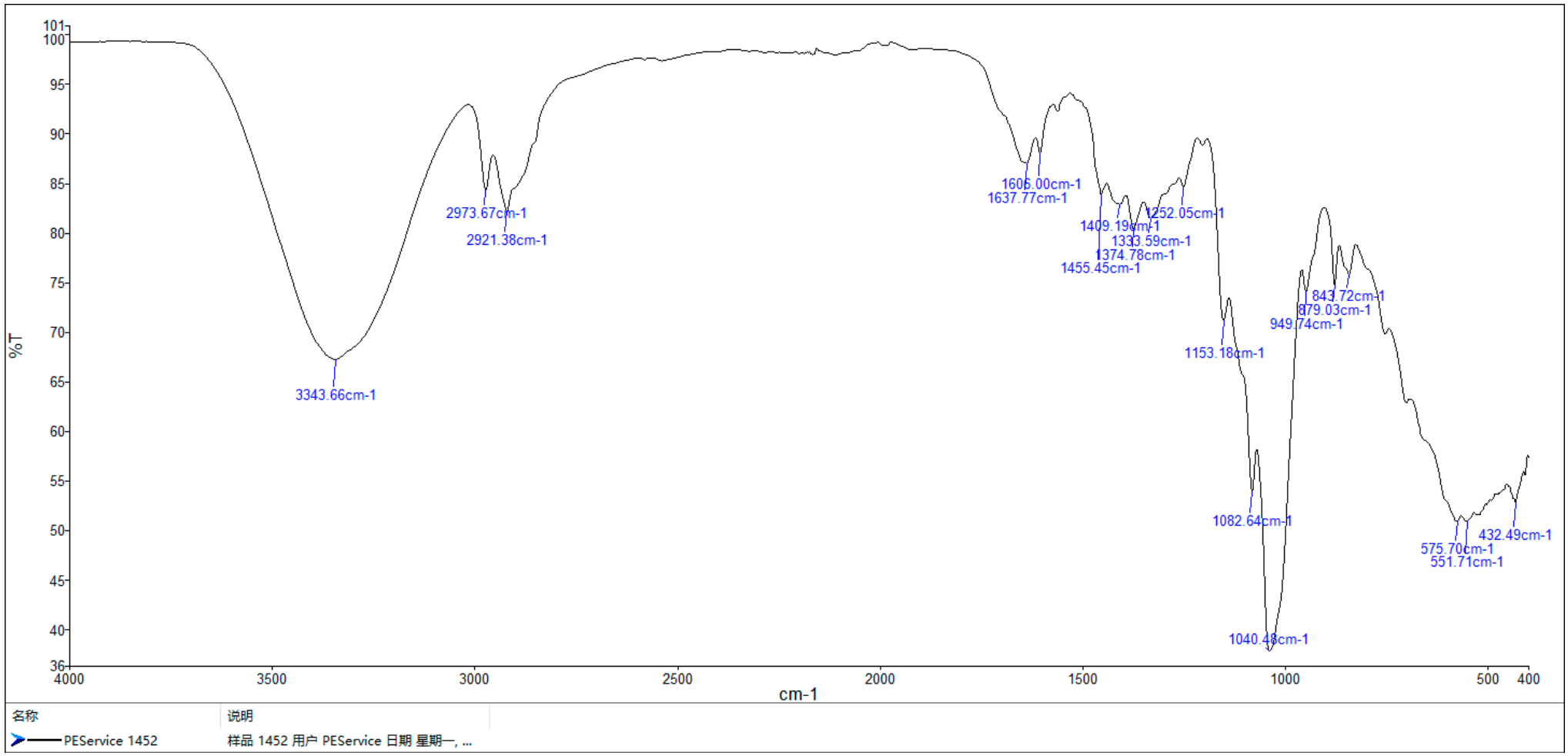
Spectrum S94. The IR spectrum of **7**



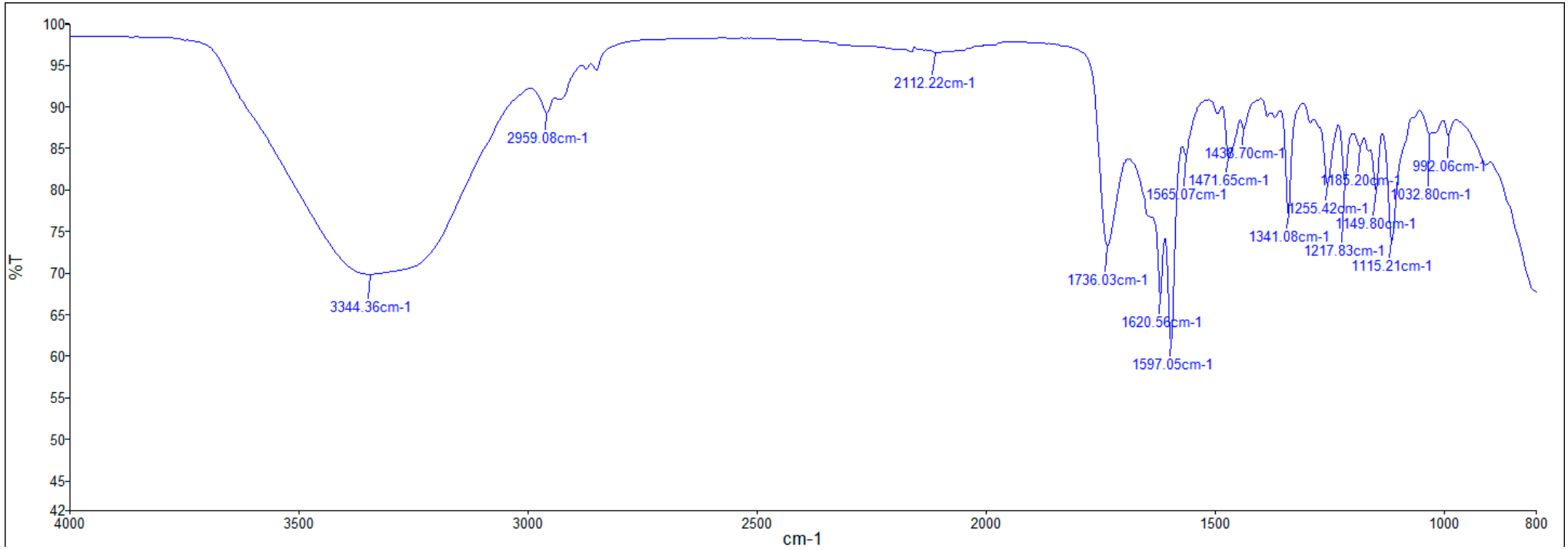
Spectrum S95. The IR spectrum of **8**



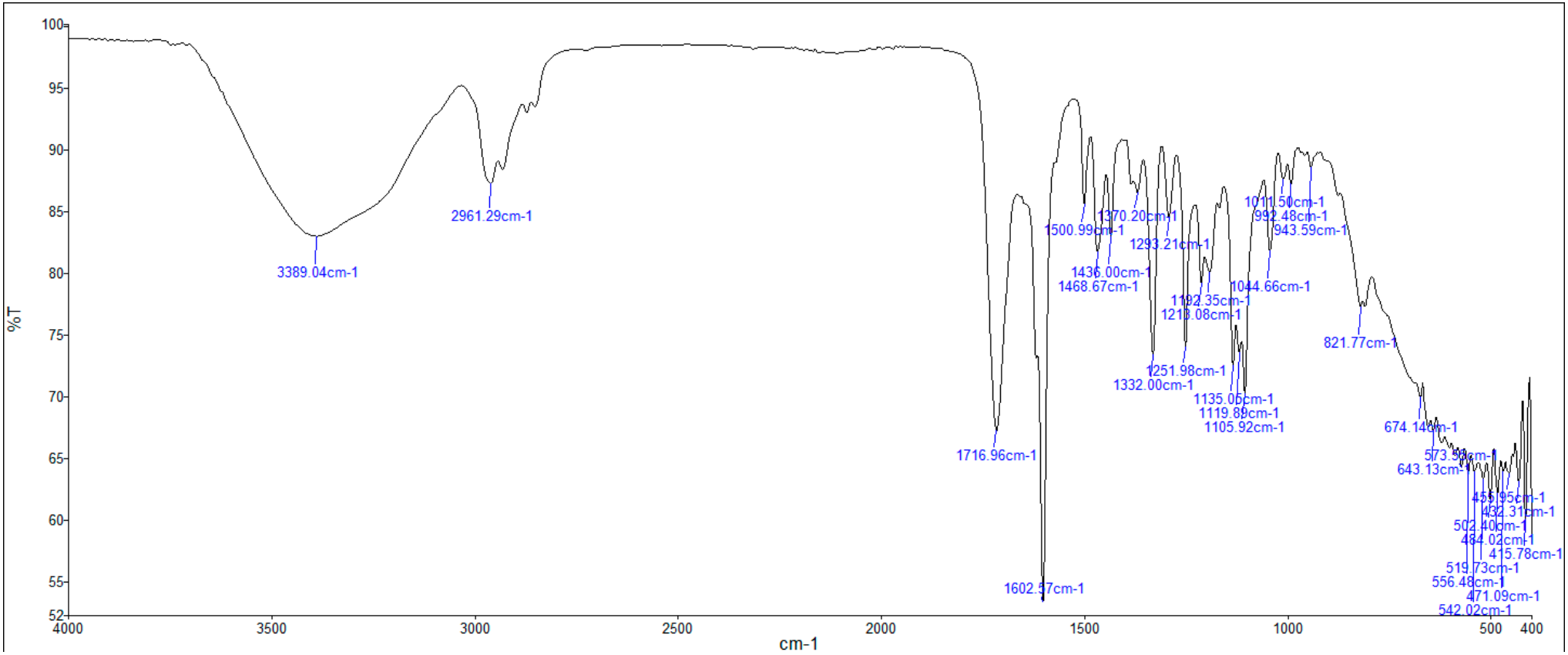
Spectrum S96. The IR spectrum of **9**



Spectrum S97. The IR spectrum of **10**



Spectrum S98. The IR spectrum of **11**



Spectrum S99. The IR spectrum of **12**

