

SUPPLEMENTARY MATERIAL

Two new geranylphenylacetate glycosides from the barks of *Cinnamomum cassia*

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Abstract: Two new glycosides, cinnacassides F (**1**) and G (**2**), with a rare geranylphenylacetate carbon skeleton, were isolated from the barks of *Cinnamomum cassia*, along with three known analogues, cinnacassides A (**3**), B (**4**), and C (**5**). The structures of the new compounds were elucidated on the basis of extensive NMR spectroscopic analyses and chemical method. Compounds **1-5** were investigated for their immunomodulatory activities, and compounds **1**, **3**, and **4** showed differential immunosuppressive activities against murine lymphocytes.

Keywords: *Cinnamomum cassia*; geranylphenylacetate glycosides; cinnacasside F-G; immunosuppressive activity

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Table S1. ^1H -(400 MHz) and ^{13}C -NMR (100 MHz) Data for **1** and **2** in CD_3OD .

No.	1		2	
	δ_{C}	δ_{H} (<i>J</i> in Hz)	δ_{C}	δ_{H} (<i>J</i> in Hz)
1	130.4		130.7	
2	148.1		148.0	
3	136.1		136.1	
4	117.4	6.70 (d, 3.0)	117.4	6.72 (d, 2.9)
5	154.9		154.8	
6	116.3	6.53 (d, 3.0)	116.2	6.51 (d, 2.9)
7a	36.6	3.93 (d, 16.3)	37.1	3.94 (d, 16.4)
7b		3.81 (d, 16.3)		3.75 (d, 16.4)
8	175.1		175.3	
9a	33.6	3.03 (dd, 14.2, 2.4)	33.2	3.00 (dd, 14.6, 2.2)
9b		2.87 (dd, 14.2, 10.4)		2.85 (dd, 14.6, 10.1)
10	78.9	3.76 (dd, 10.4, 2.4)	78.5	3.78 (dd, 10.1, 2.2)
11	87.2		87.2	
12 α	34.4	2.18 (m)	35.2	2.16 (m)
12 β		1.67 (m)		1.69 (m)
13	27.5	1.87-1.95 (m)	28.0	1.78-1.90 (m)
14	86.3	3.84 (t, 7.7)	88.3	3.85 (dd, 9.5, 6.0)
15	72.6		72.5	
16	27.2	1.23 (s)	26.5	1.18 (s)
17	25.9	1.15 (s)	24.8	1.17 (s)
18	23.2	1.27 (s)	22.9	1.24 (s)
19	52.4	3.69 (s)	52.4	3.69 (s)
1'	106.9	4.59 (d, 7.6)	106.6	4.80 (d, 7.4)
2'	75.6	3.48 (dd, 9.1, 7.6)	75.7	3.45 (dd, 8.7, 7.4)
3'	77.8	3.41 (t, 8.9)	78.1	3.38 (m)
4'	71.7	3.35 (m)	71.6	3.34 (m)
5'	78.2	3.14 (m)	78.1	3.15 (m)
6'a	62.8	3.75 (dd, 12.0, 2.4)	62.8	3.76 (dd, 11.9, 2.4)
6'b		3.63 (dd, 12.0, 5.8)		3.63 (dd, 11.9, 5.5)

Figure S1. Key ^1H - ^1H COSY, HMBC correlations of compound **1** and **2**.

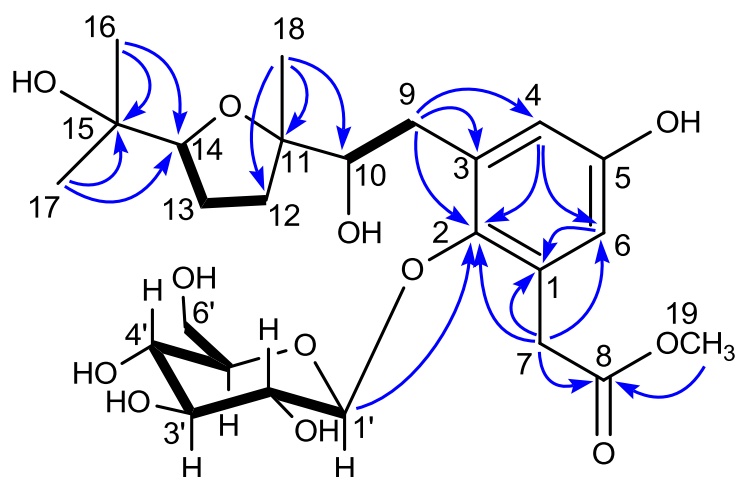


Figure S2. Key NOESY correlations of compounds **1** and **2**.

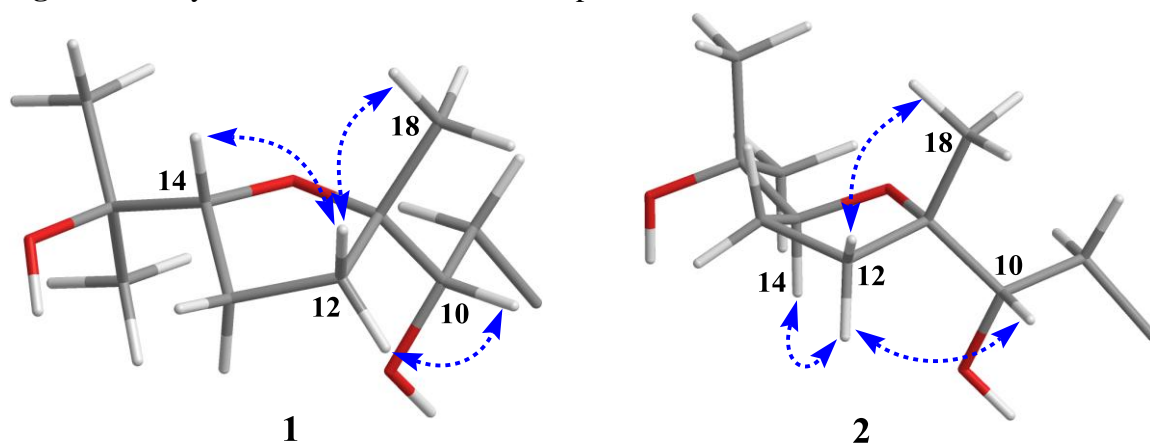


Figure S3. Newman projection of compounds **1** and **2**

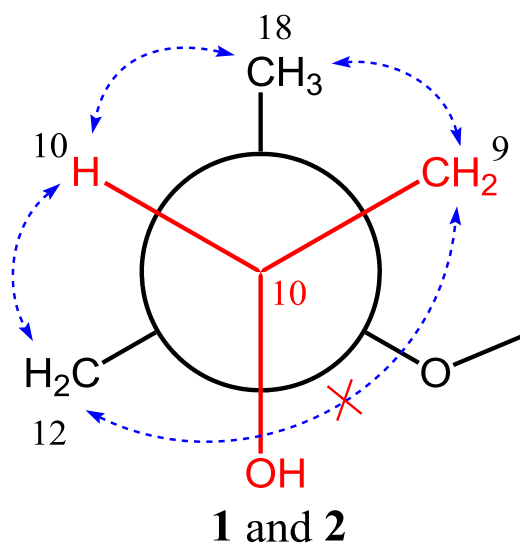


Figure S4. HRESIMS of compound **1**

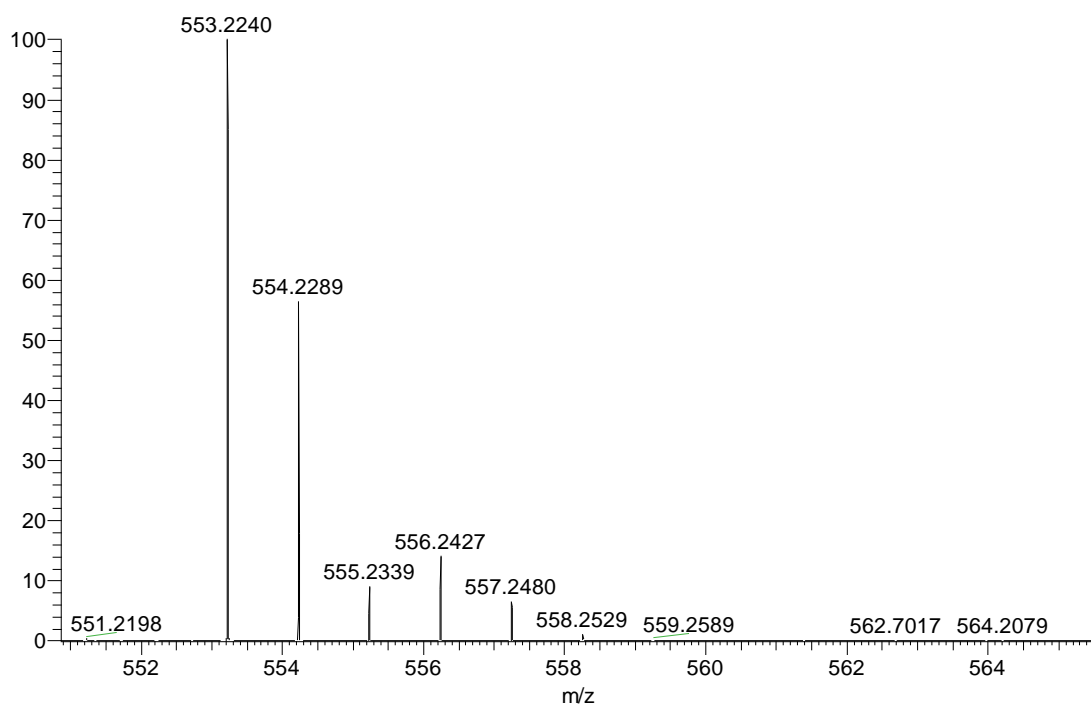


Figure S5. ^1H NMR spectrum of compound **1** in CD_3OD (400 MHz)

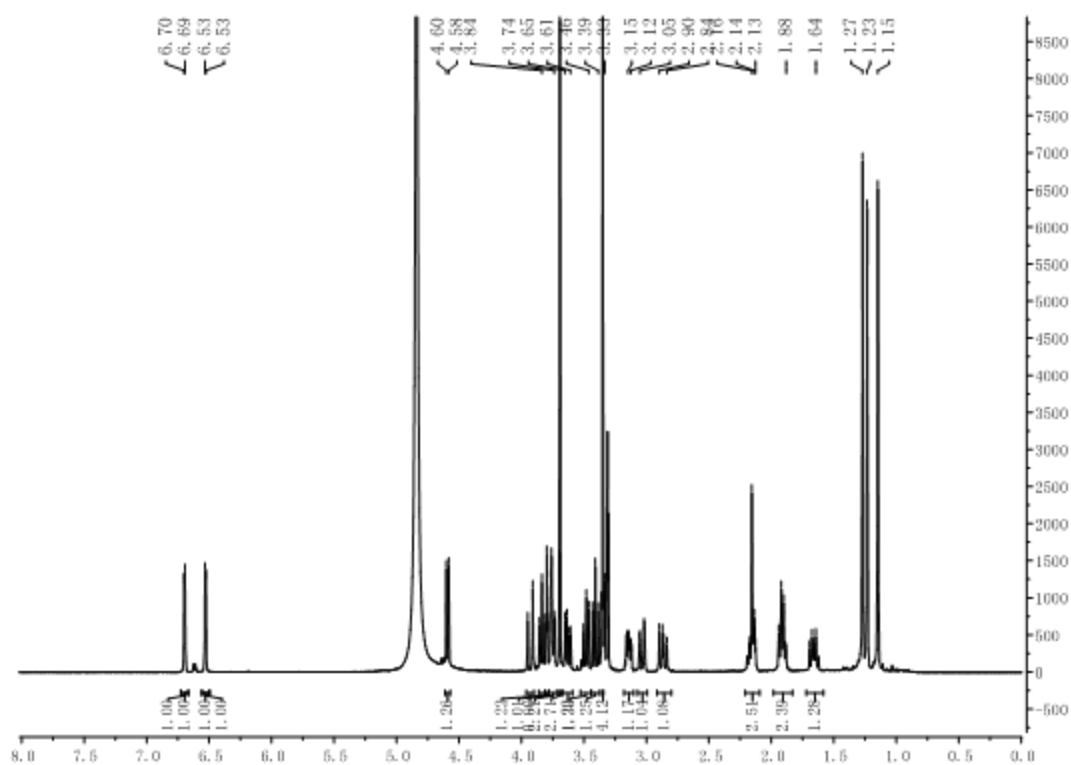


Figure S6. ^{13}C NMR spectrum of compound **1** in CD_3OD (100 MHz)

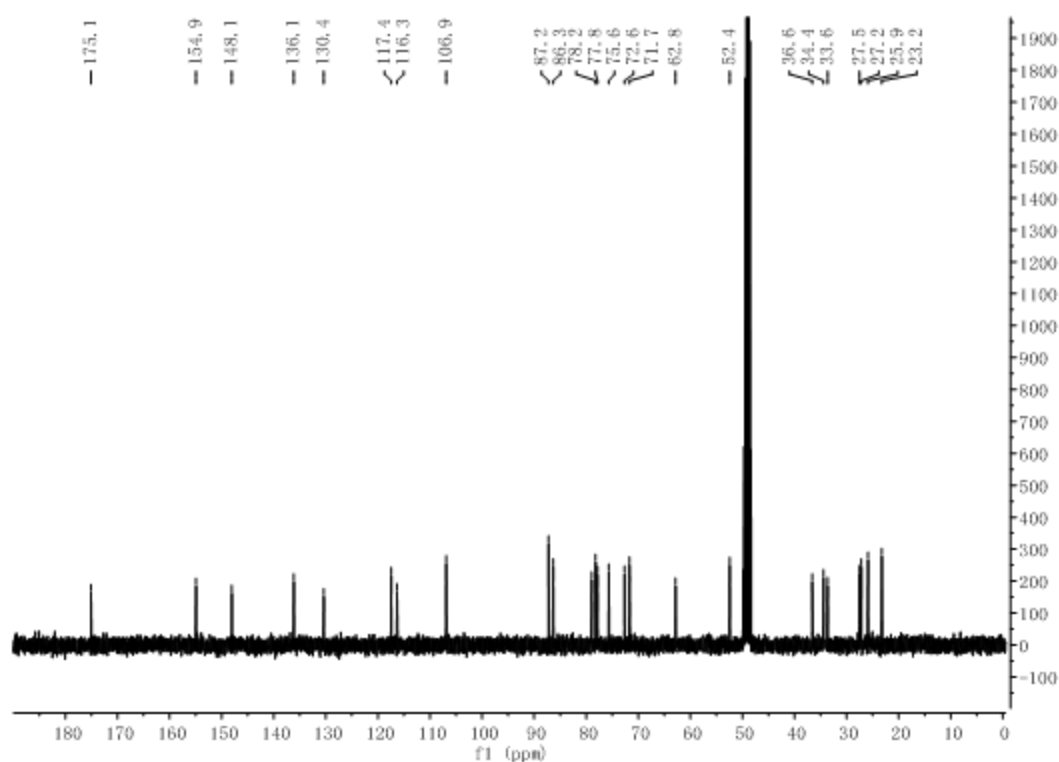


Figure S7. DEPT-135 spectrum of compound **1** in CD_3OD (100 MHz)

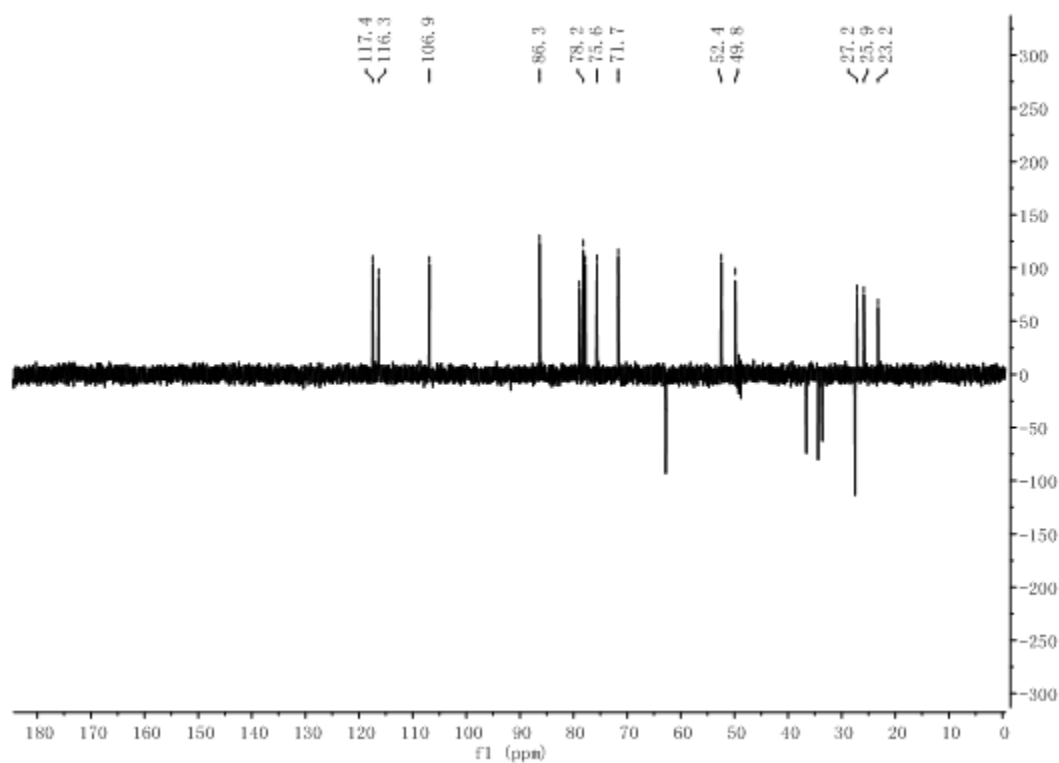


Figure S8. ^1H - ^1H COSY spectrum of compound **1** in CD_3OD

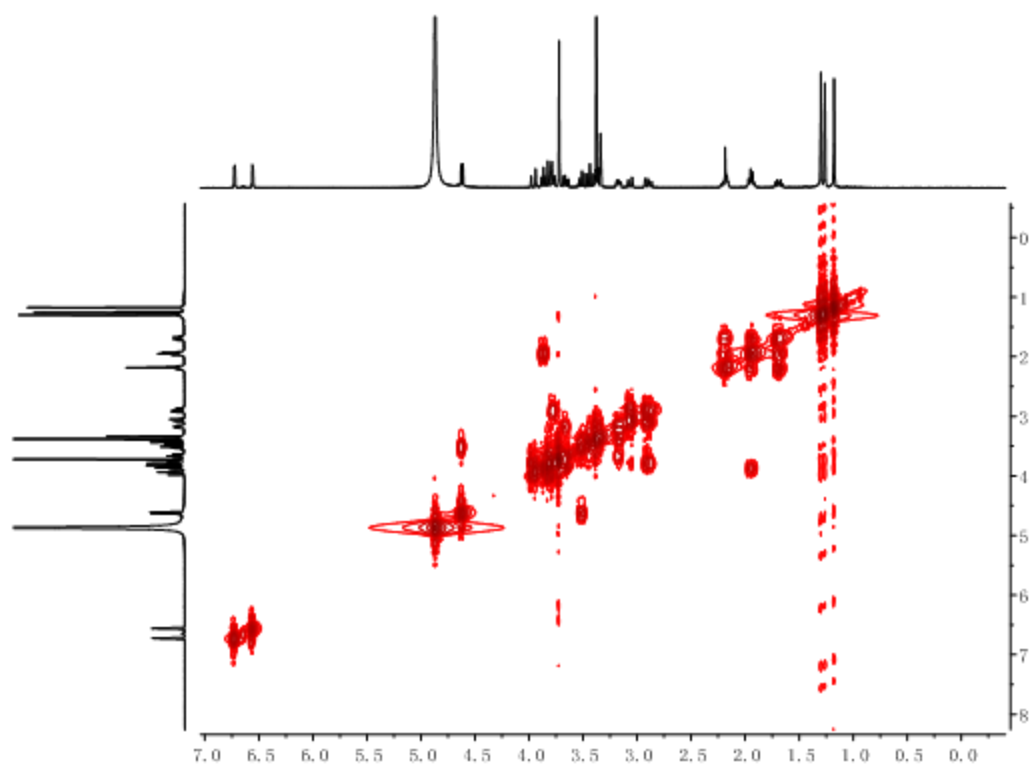


Figure S9. HMQC spectrum of compound **1** in CD_3OD

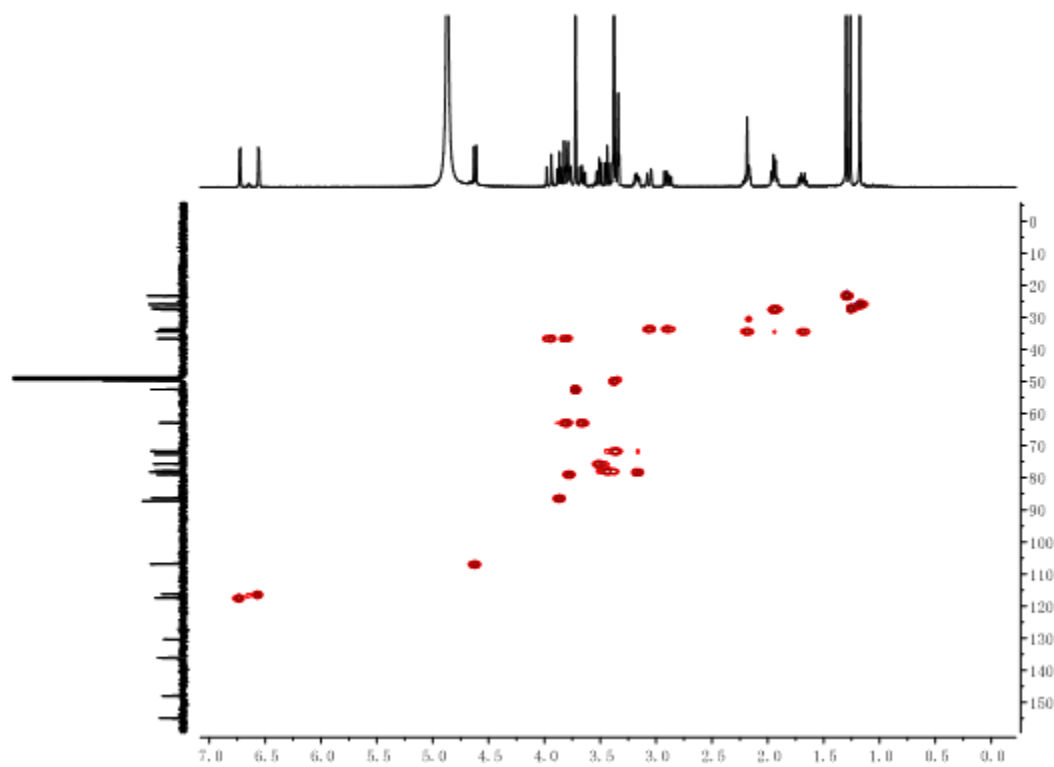


Figure S10. HMBC spectrum of compound **1** in CD₃OD

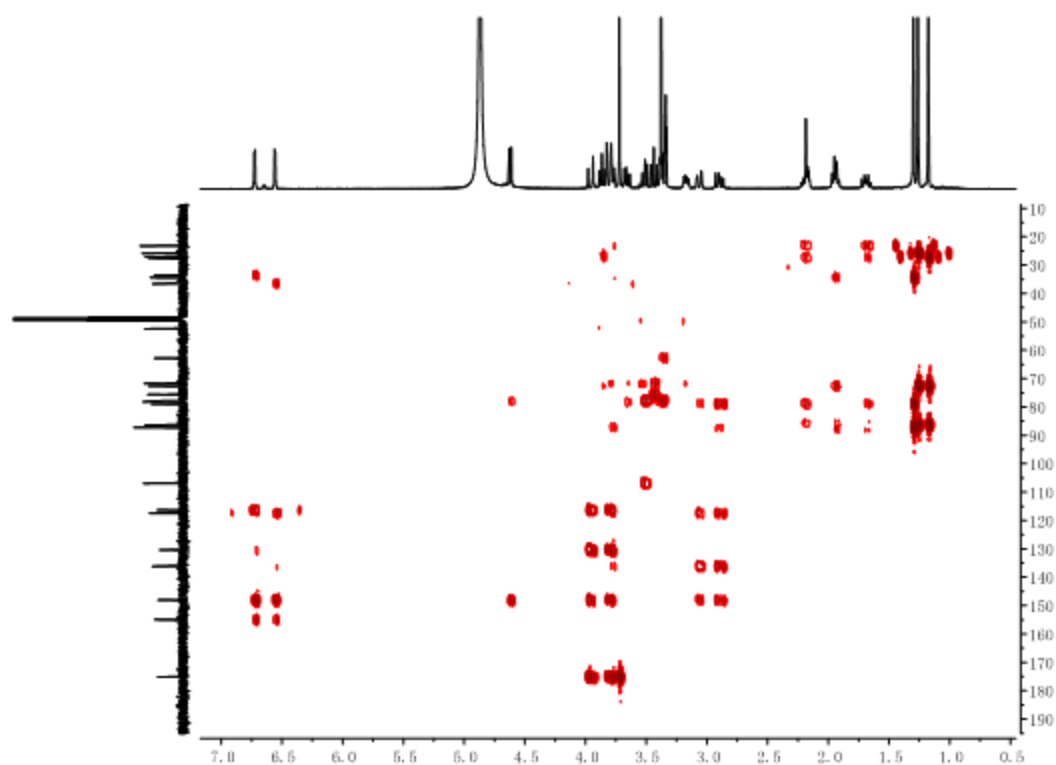


Figure S11. NOESY spectrum of compound **1** in CD₃OD

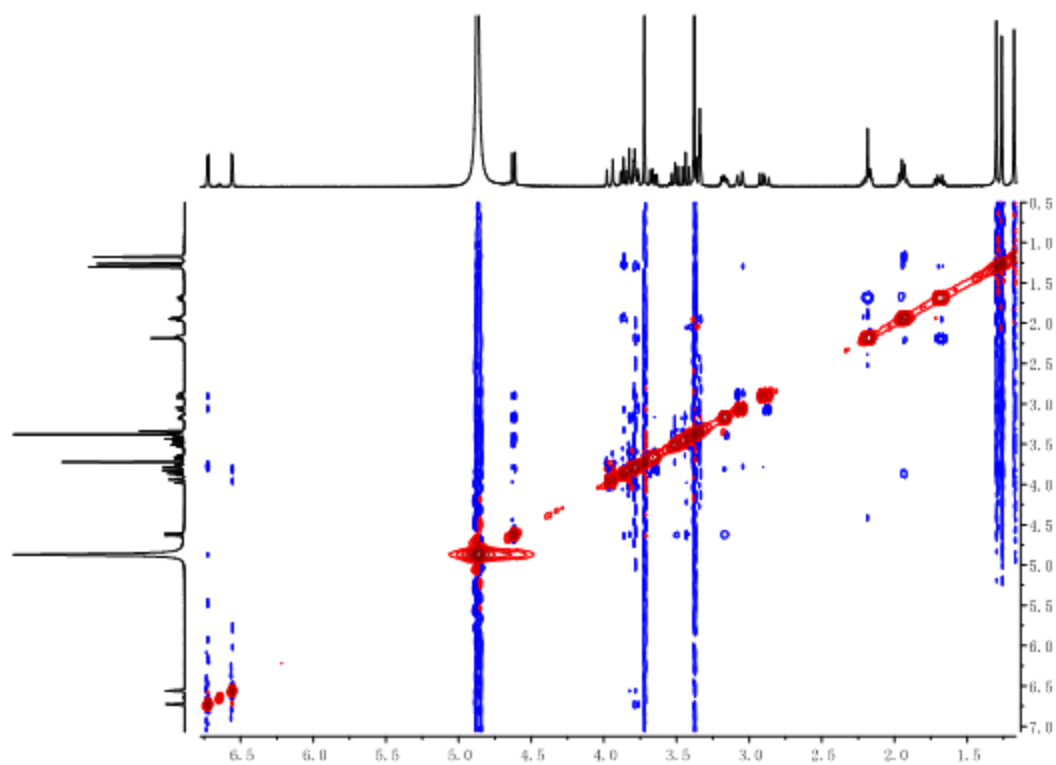


Figure S12. IR spectrum of compound **1**

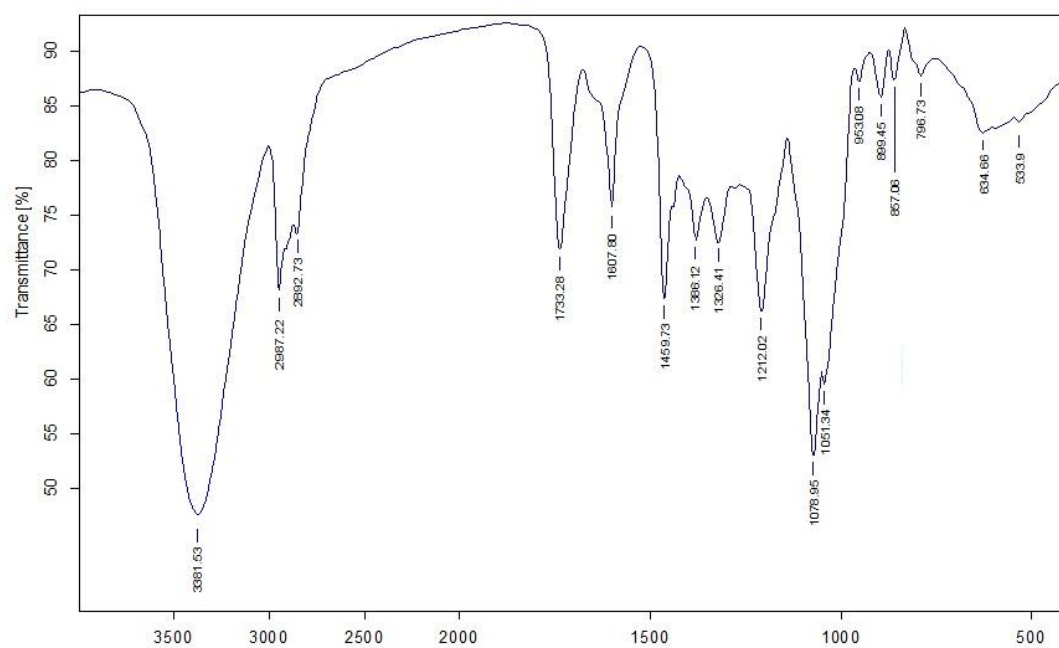


Figure S13. UV spectrum of compound **1**

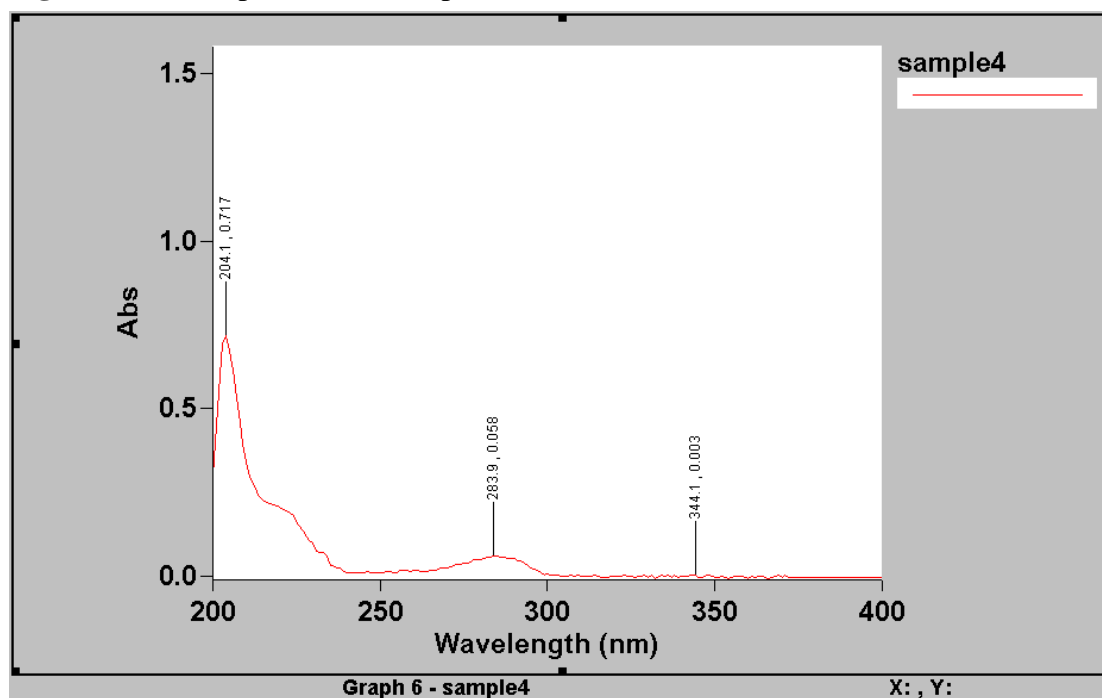


Figure S14. CD spectrum of compound **1**

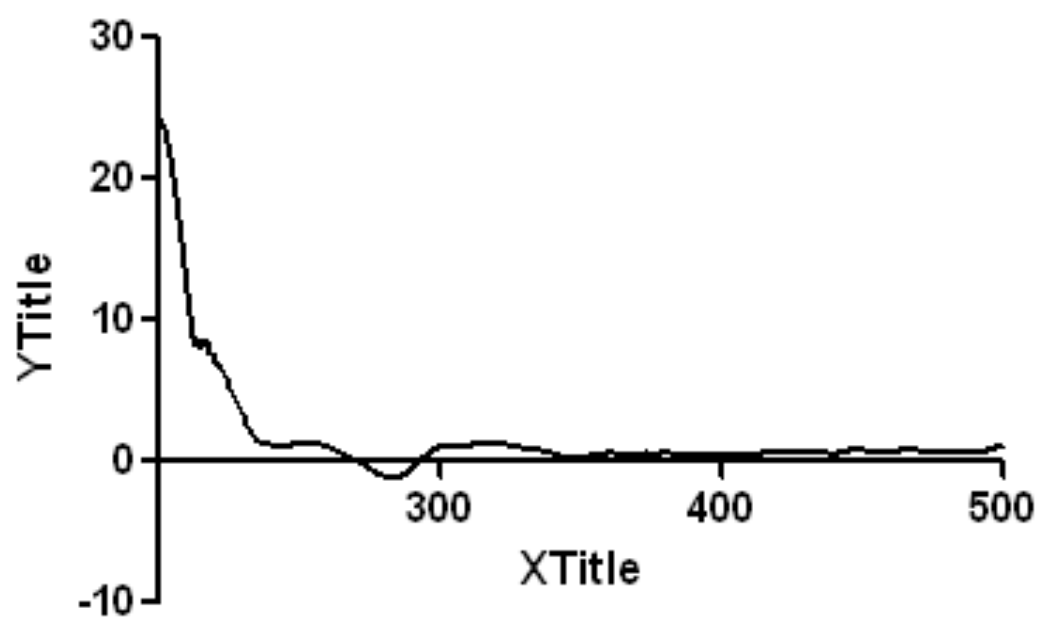


Figure S15. HRESIMS of compound **2**

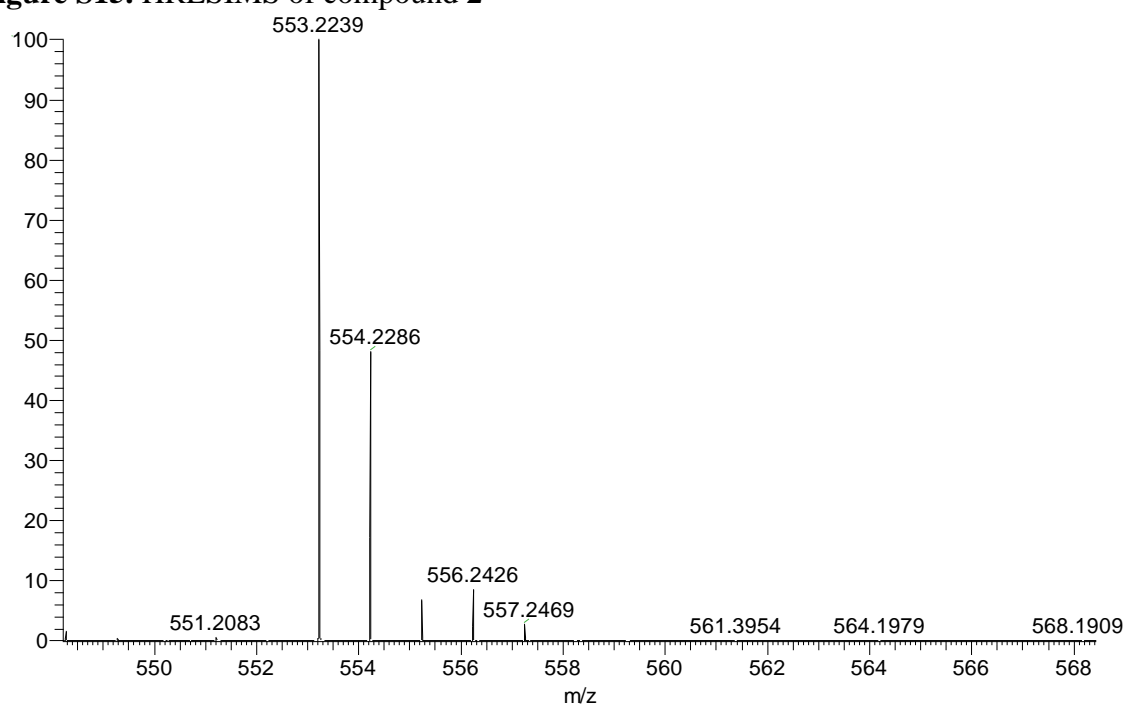


Figure S16. ^1H NMR spectrum of compound **2** in CD_3OD (400 MHz)

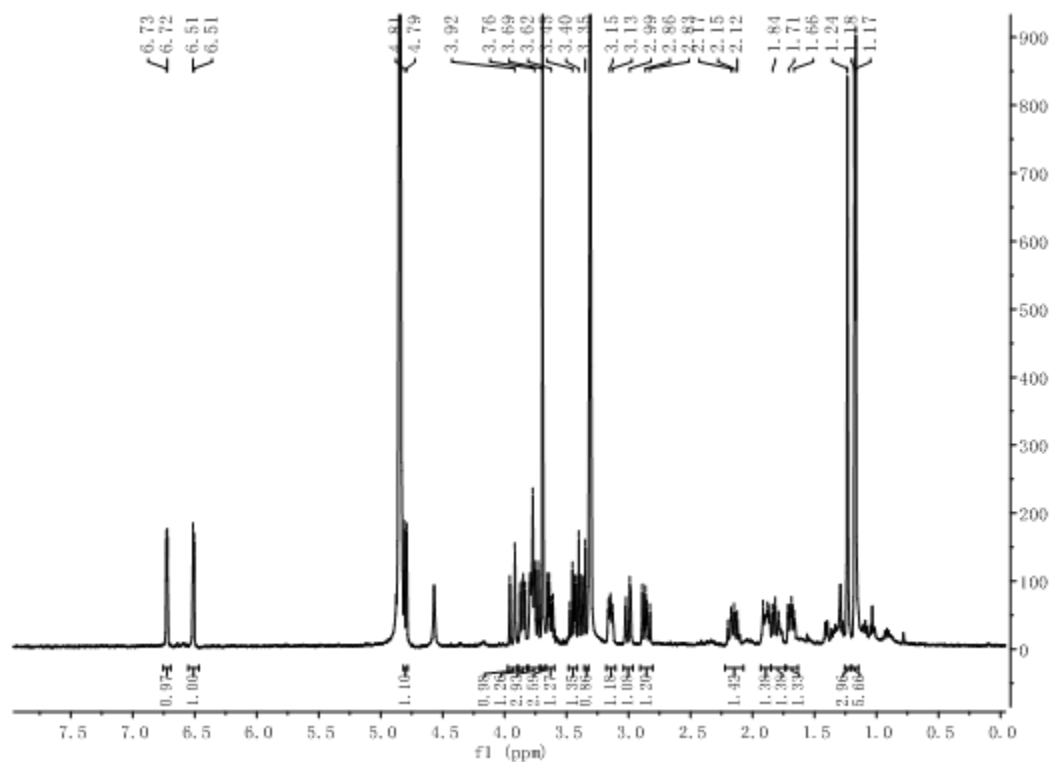


Figure S17. ^{13}C NMR spectrum of compound **2** in CD_3OD (100 MHz)

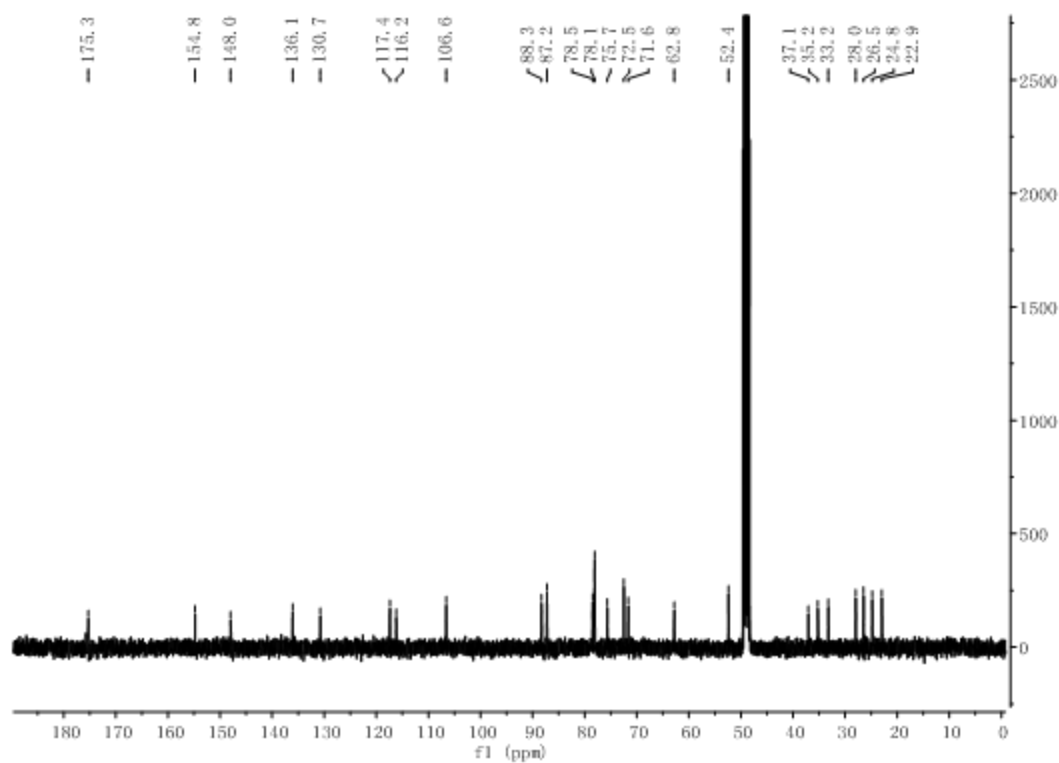


Figure S18. DEPT-135 spectrum of compound **2** in CD₃OD (100 MHz)

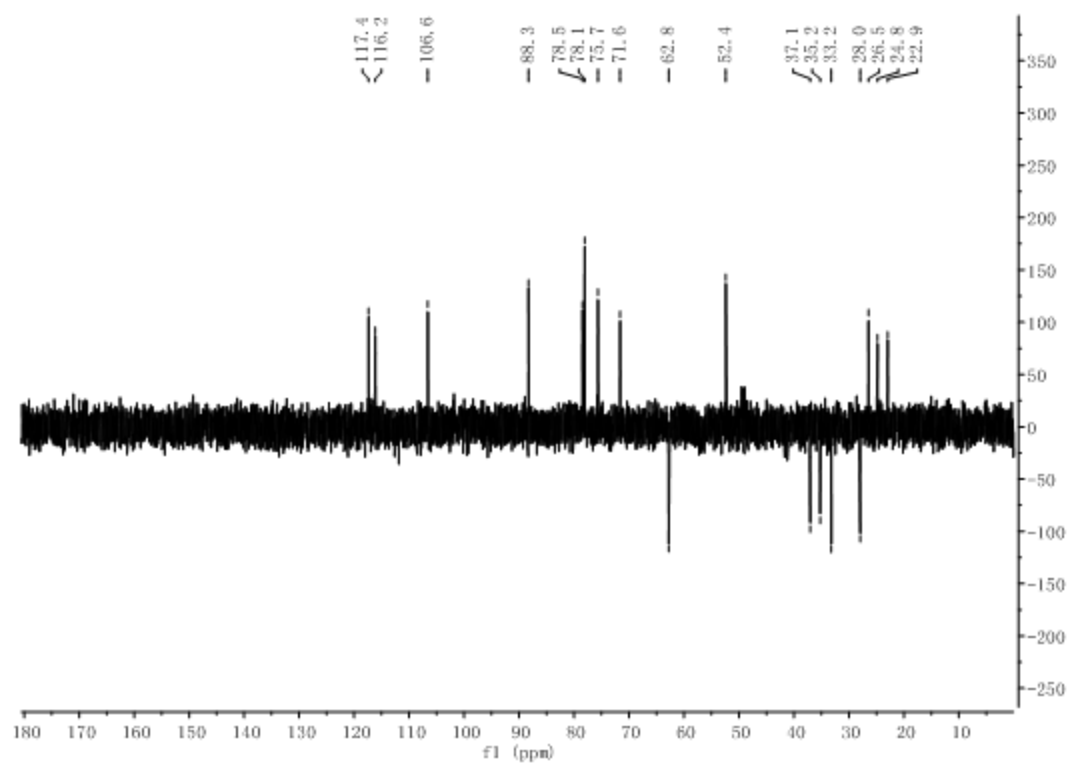


Figure S19. ¹H-¹H COSY spectrum of compound **2** in CD₃OD

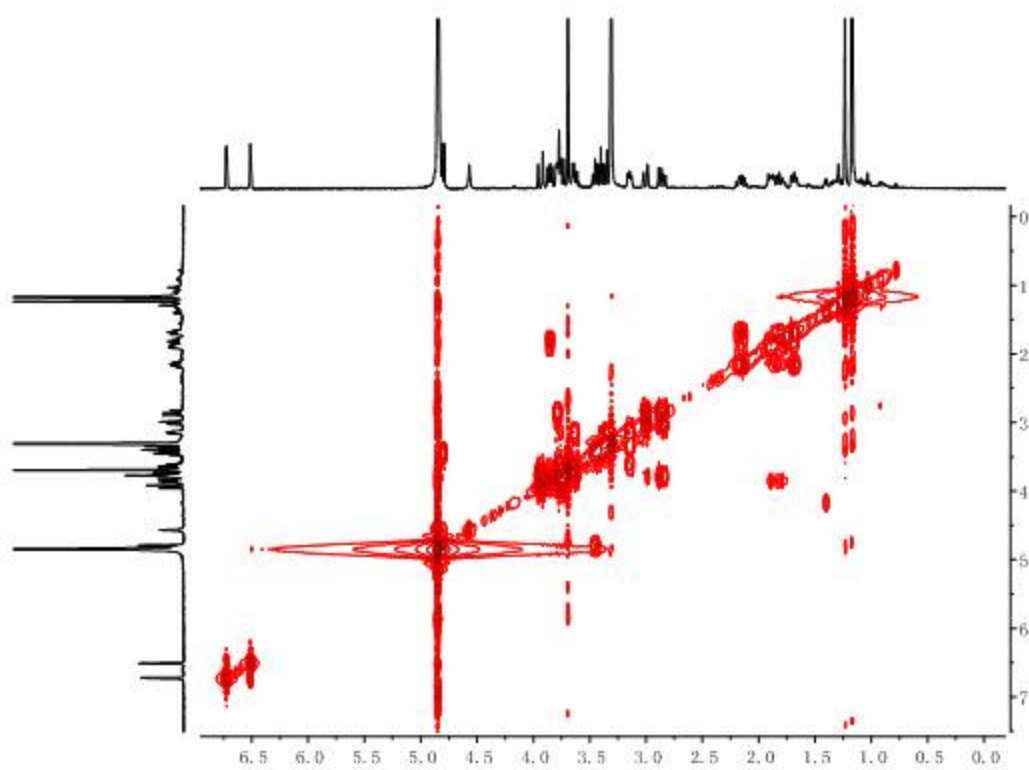


Figure S20. HMQC spectrum of compound **2** in CD₃OD

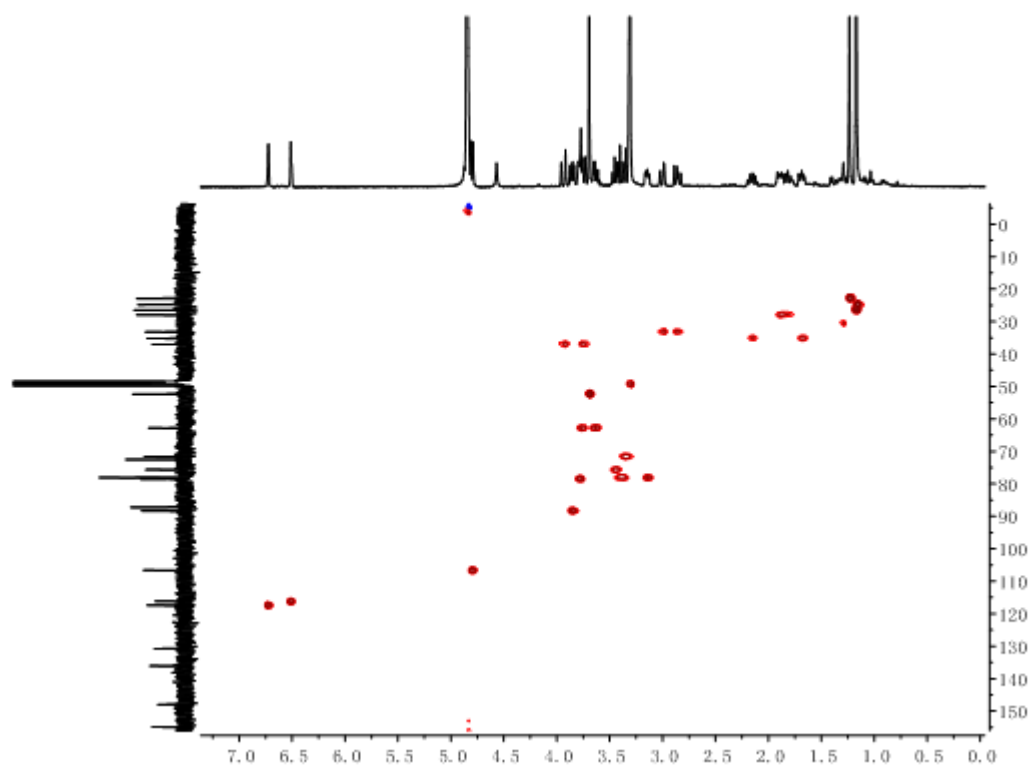


Figure S21. HMBC spectrum of compound **2** in CD₃OD

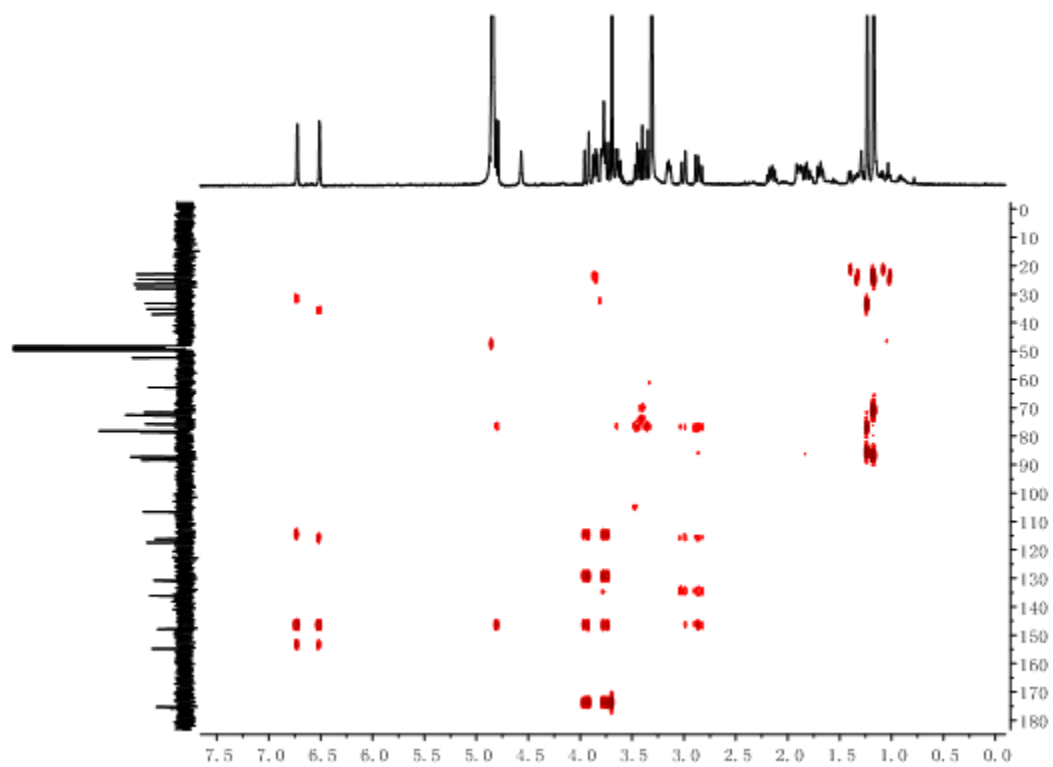


Figure S22. NOESY spectrum of compound **2** in CD₃OD

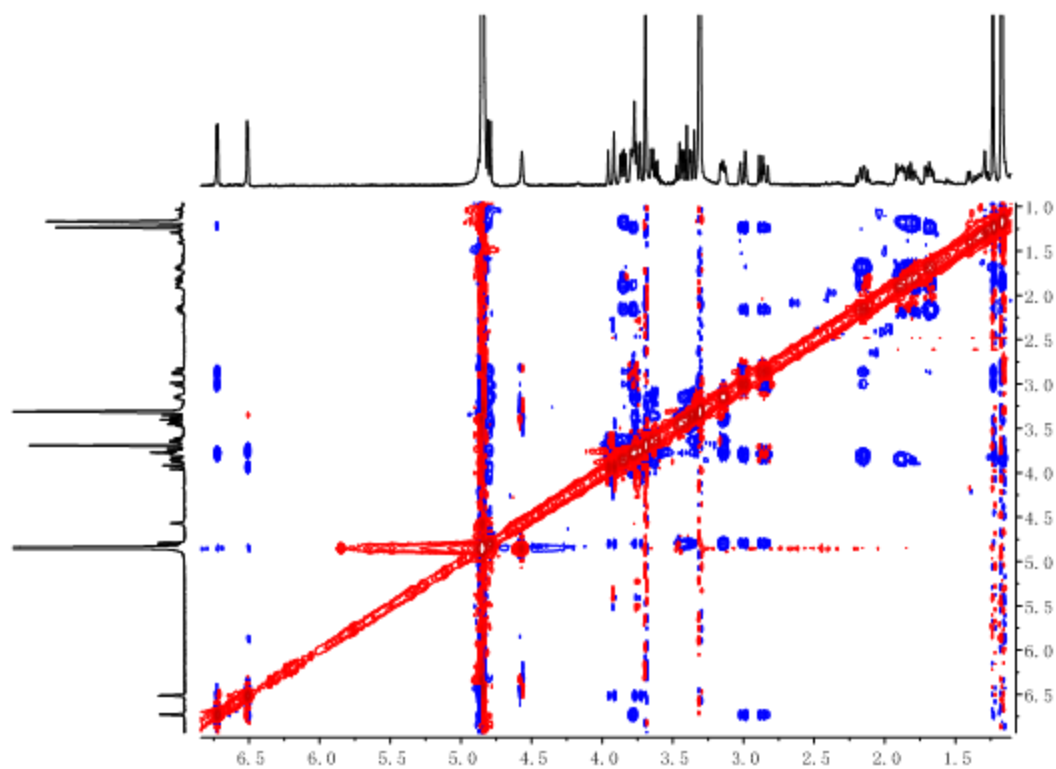


Figure S23. IR spectrum of compound **2**

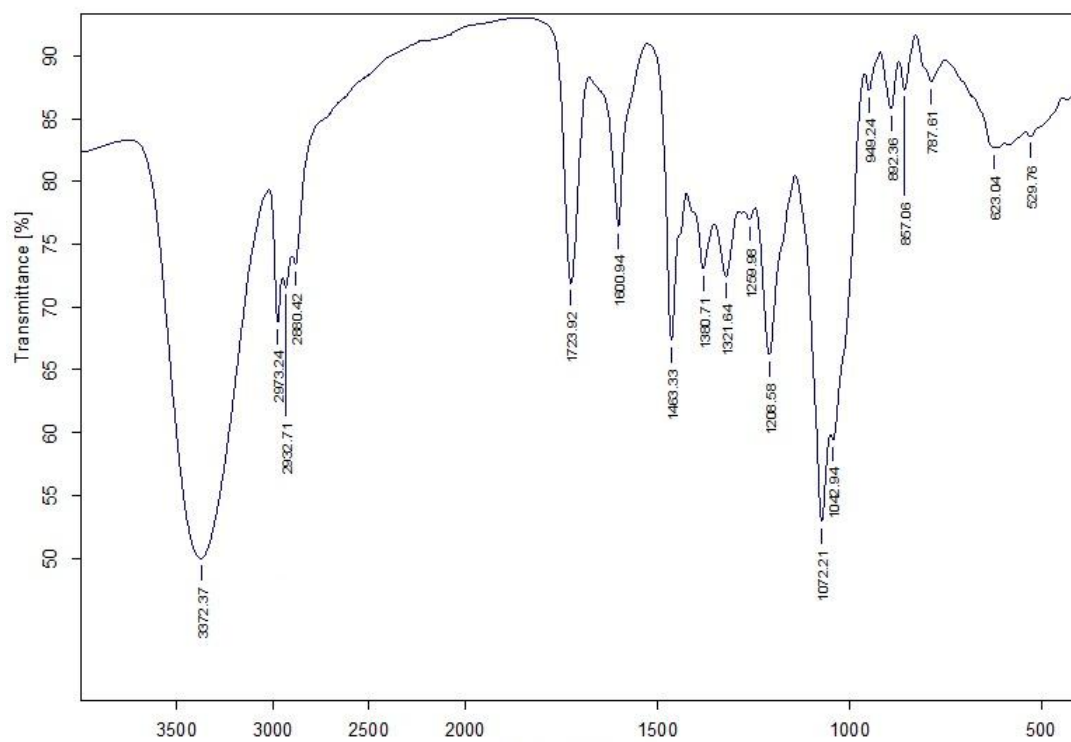


Figure S24. UV spectrum of compound 2

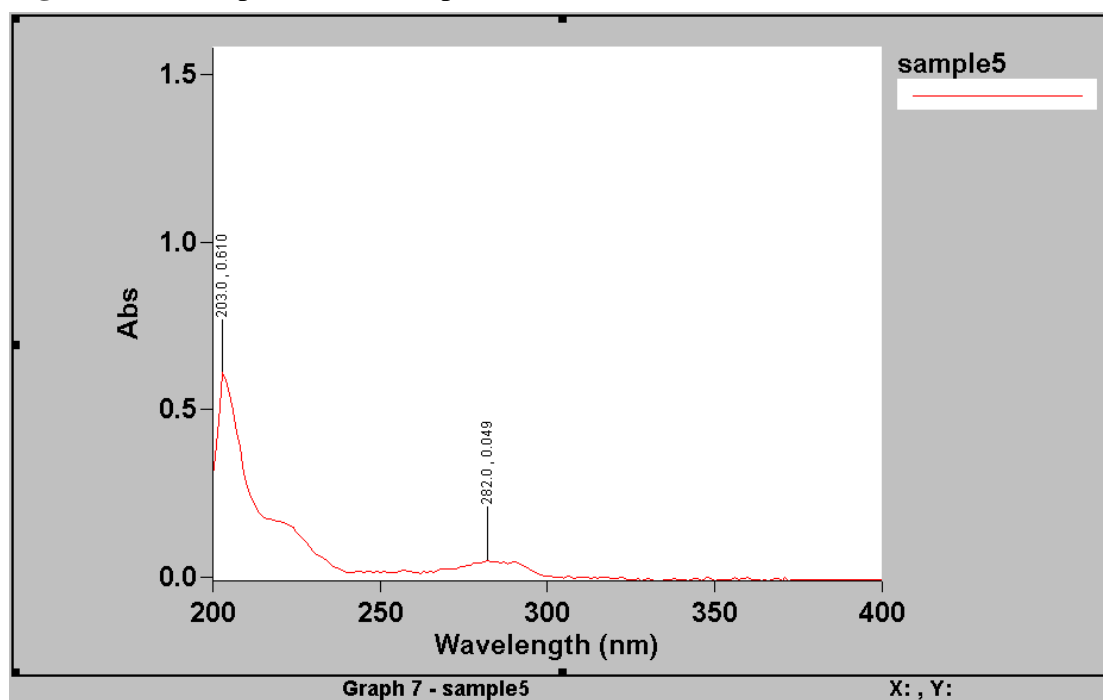


Figure S25. CD spectrum of compound 2

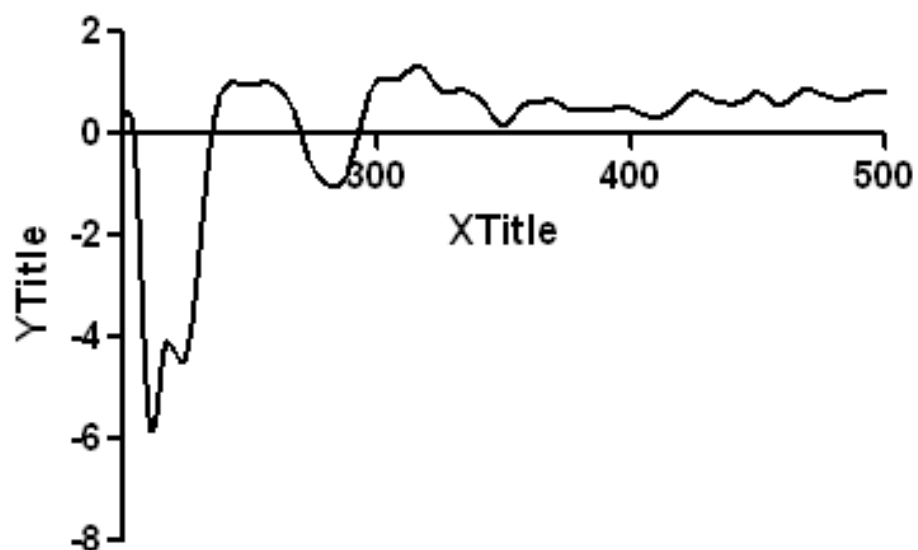
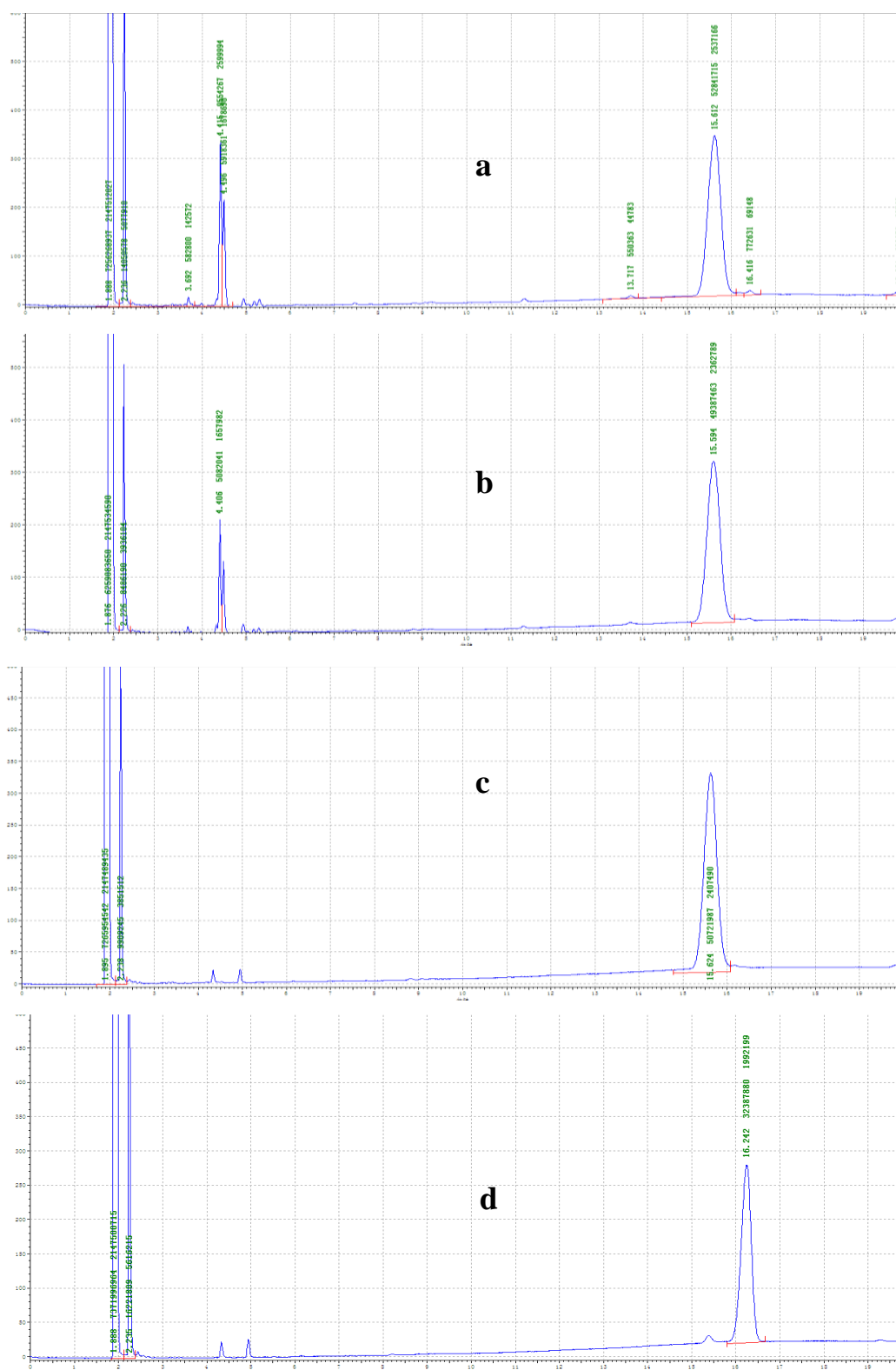


Figure S26. GC analysis of the D-glucose derivatives of compound **1** and **2**



a GC chromatogram of trimethylsilylthiazolidine derivatives of compound **1**

b GC chromatogram of trimethylsilylthiazolidine derivatives of compound **2**

c GC chromatogram of trimethylsilylthiazolidine derivatives of D-glucose

d GC chromatogram of trimethylsilylthiazolidine derivatives of L-glucose