

Supporting Information

Citreobenzofuran D–F and Phomenone A–B: Five Novel Sesquiterpenoids from the Mangrove Endophytic Fungus *Penicillium* sp. HDN13-494

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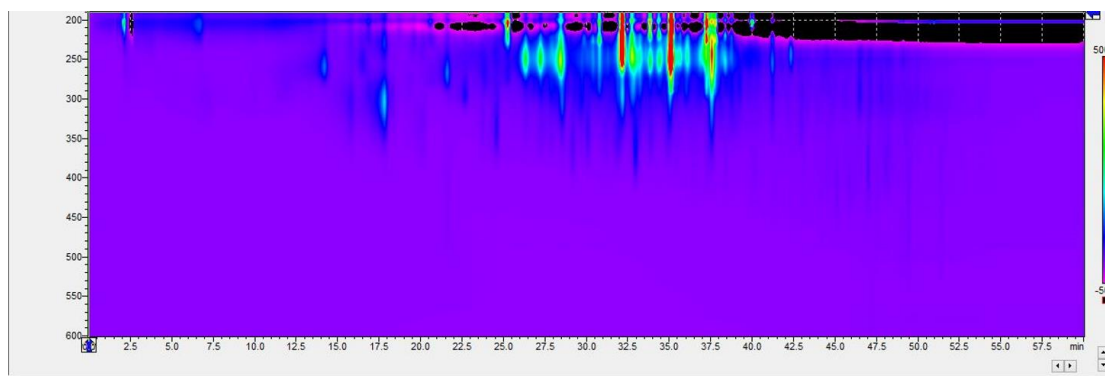


Figure S1. HPLC analysis of the crude extract of *Penicillium* sp. HDN13-494.

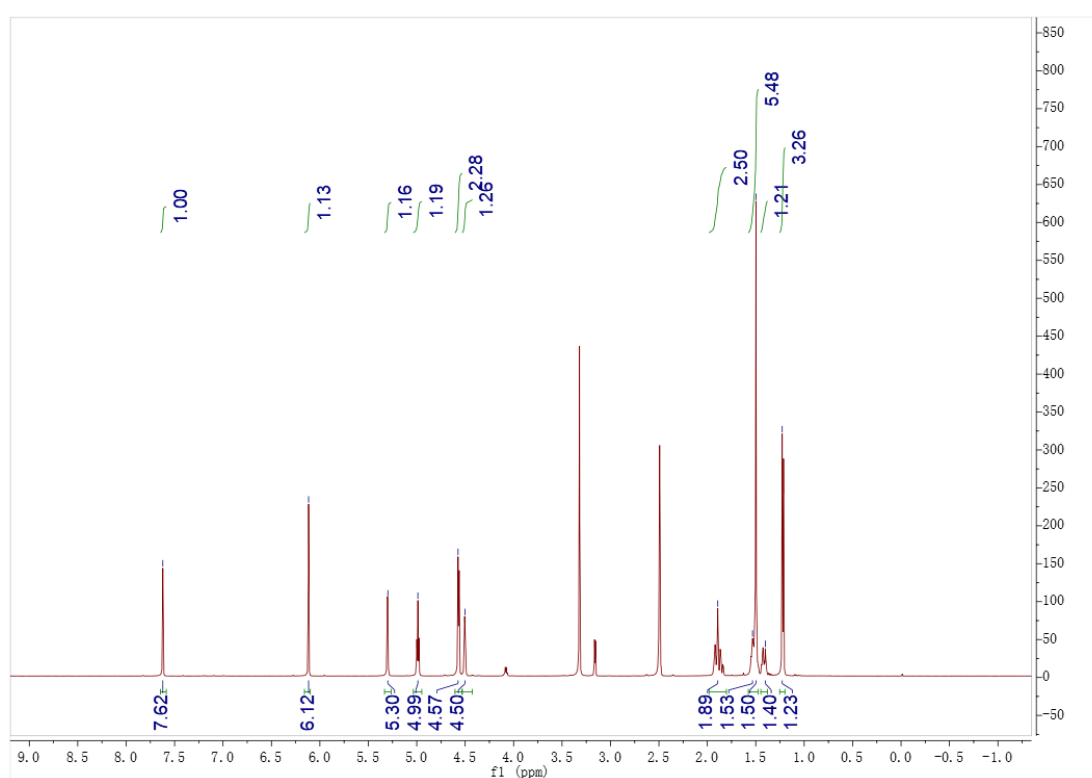


Figure S2. ^1H NMR (500 MHz, DMSO) spectrum of compound **1**.

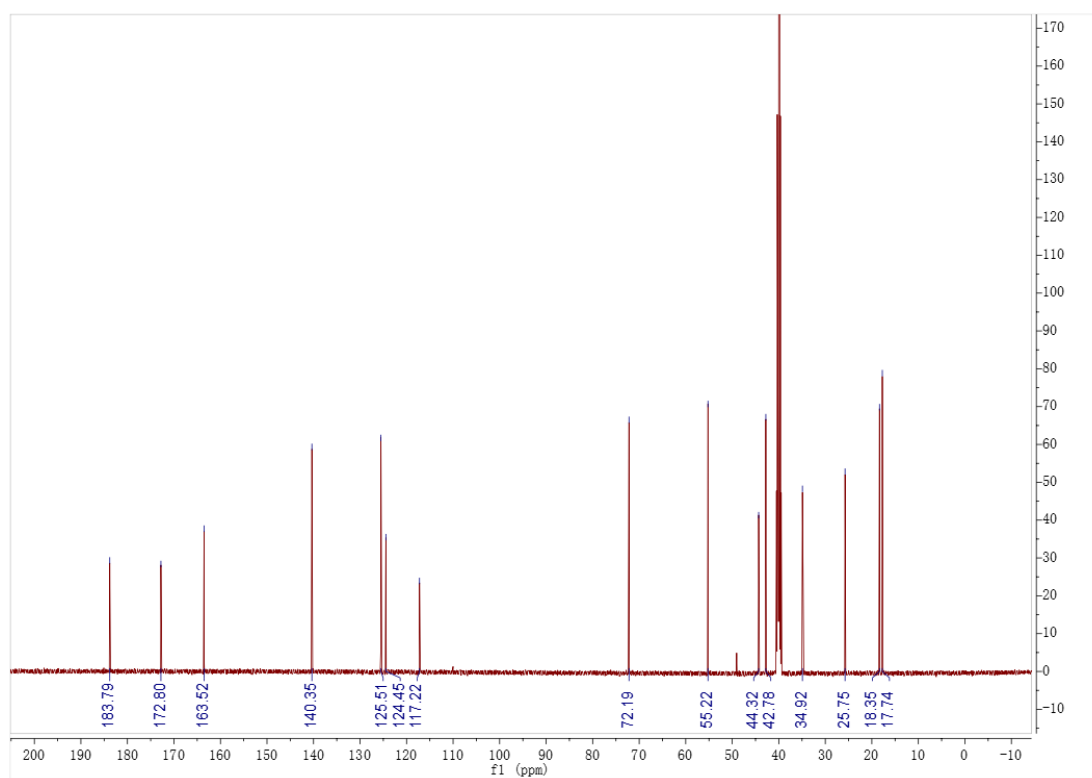


Figure S3. ¹³C NMR (125 MHz, DMSO) spectrum of compound **1**.

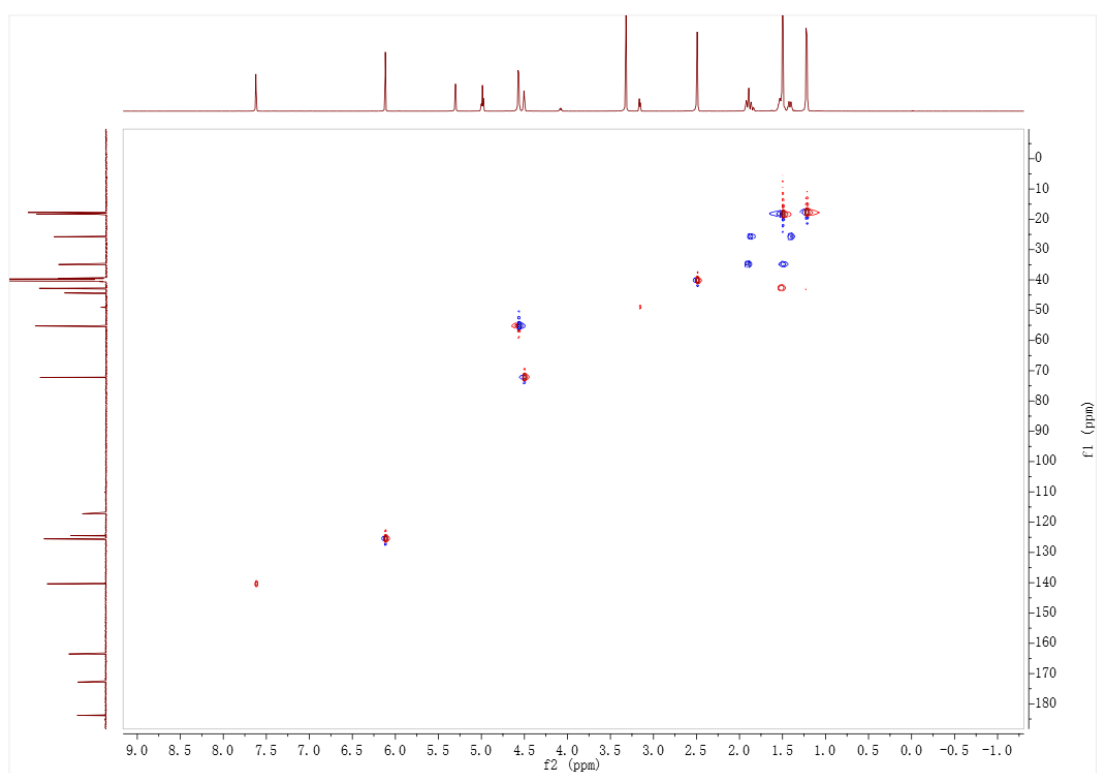


Figure S4. HSQC spectrum of compound **1**.

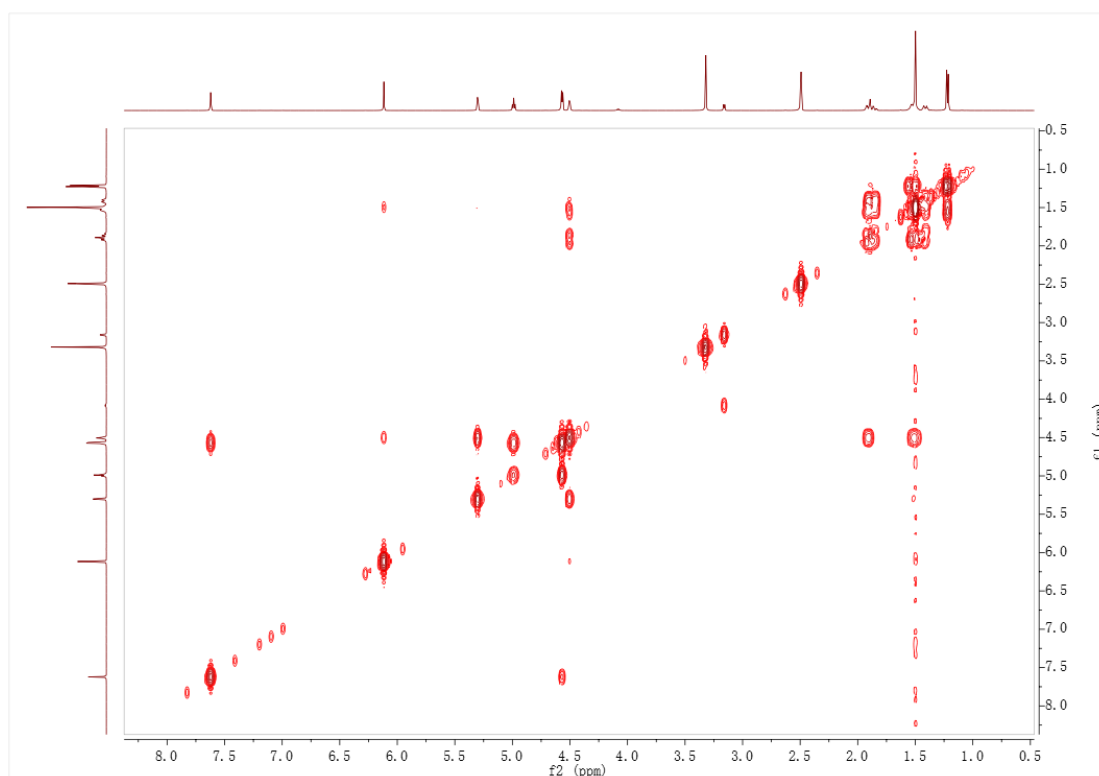


Figure S5. ^1H - ^1H COSY (500 MHz, DMSO) spectrum of compound **1**.

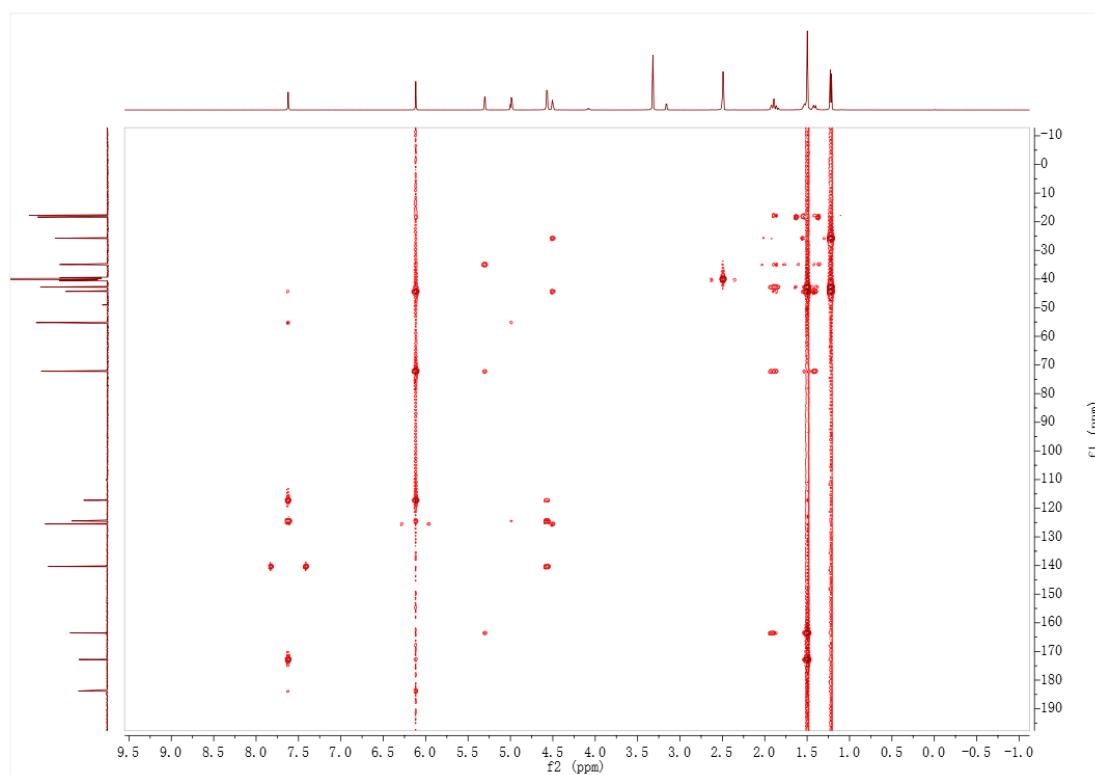


Figure S6. HMBC spectrum of compound **1**.

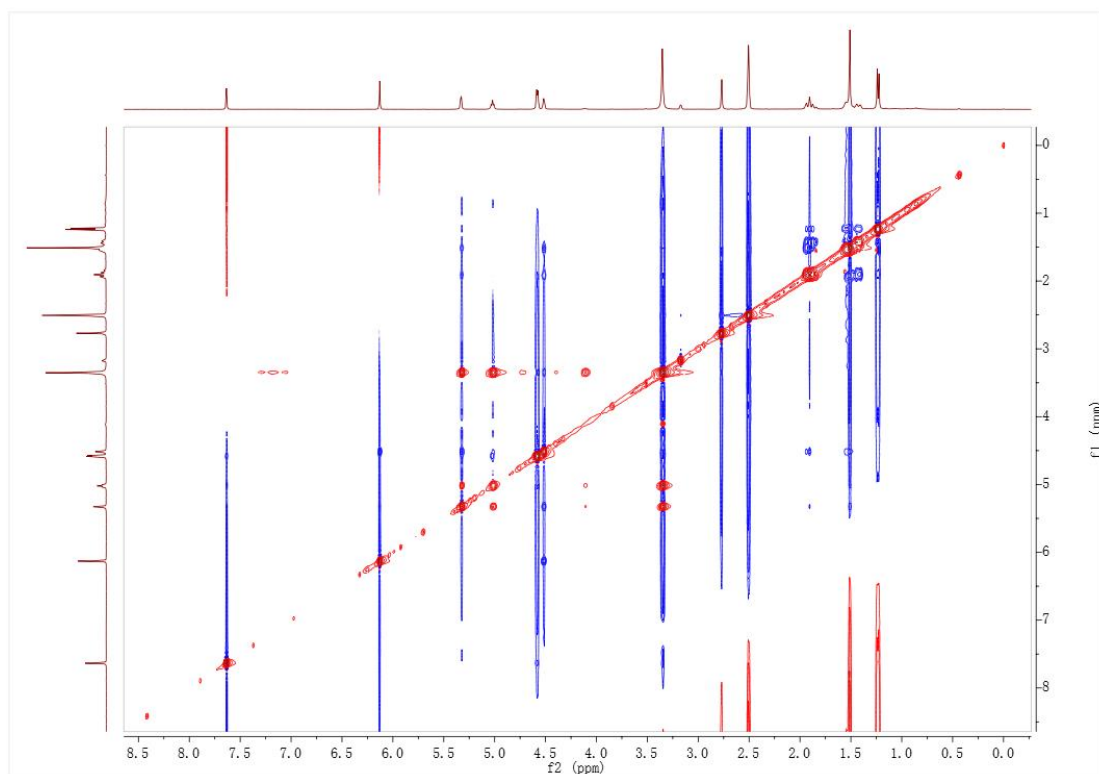


Figure S7. NOESY (400 MHz, DMSO) spectrum of compound **1**.

210707-NUM953 210707112634 #36-37 RT: 0.48-0.49 AV: 2 NL: 1.60E4
FTMS - p ESI Full ms [150.00-1000.00]

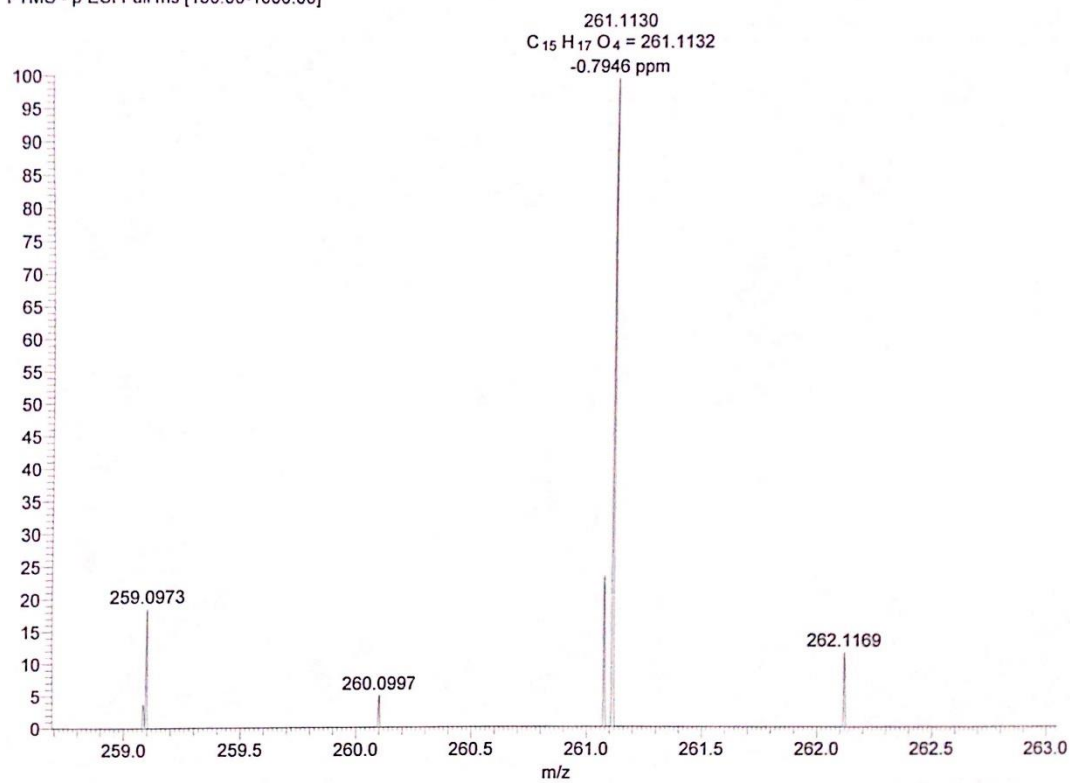


Figure S8. The HRESIMS spectrum of compound **1**.

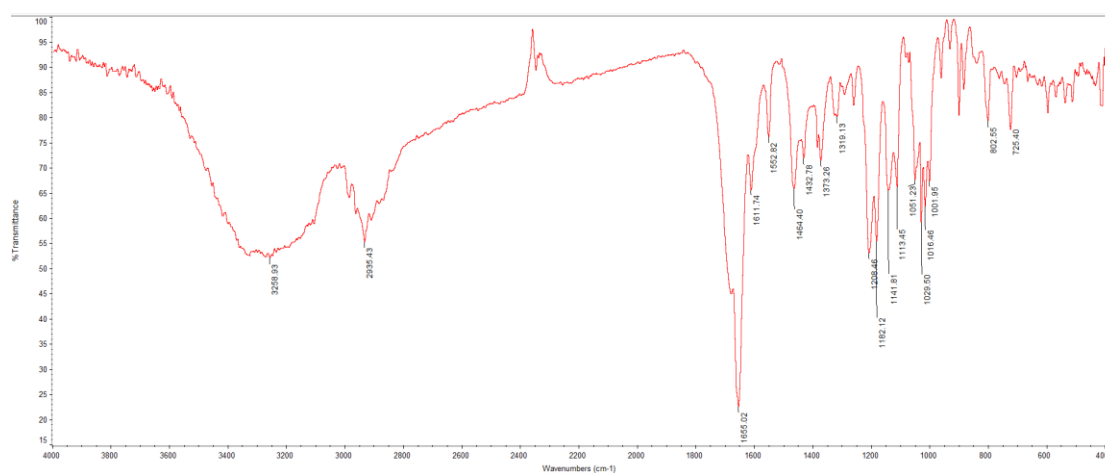


Figure S9. The IR spectrum of compound **1**.

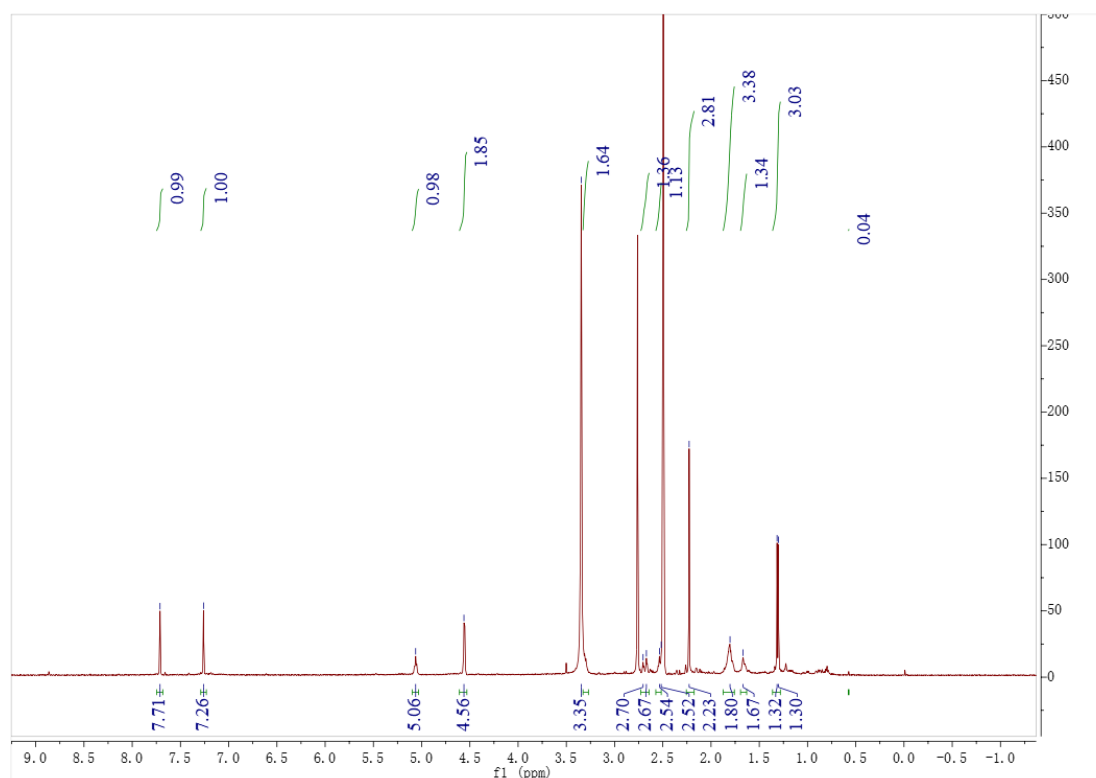


Figure S10. ¹H NMR (500 MHz, DMSO) spectrum of compound **2**.

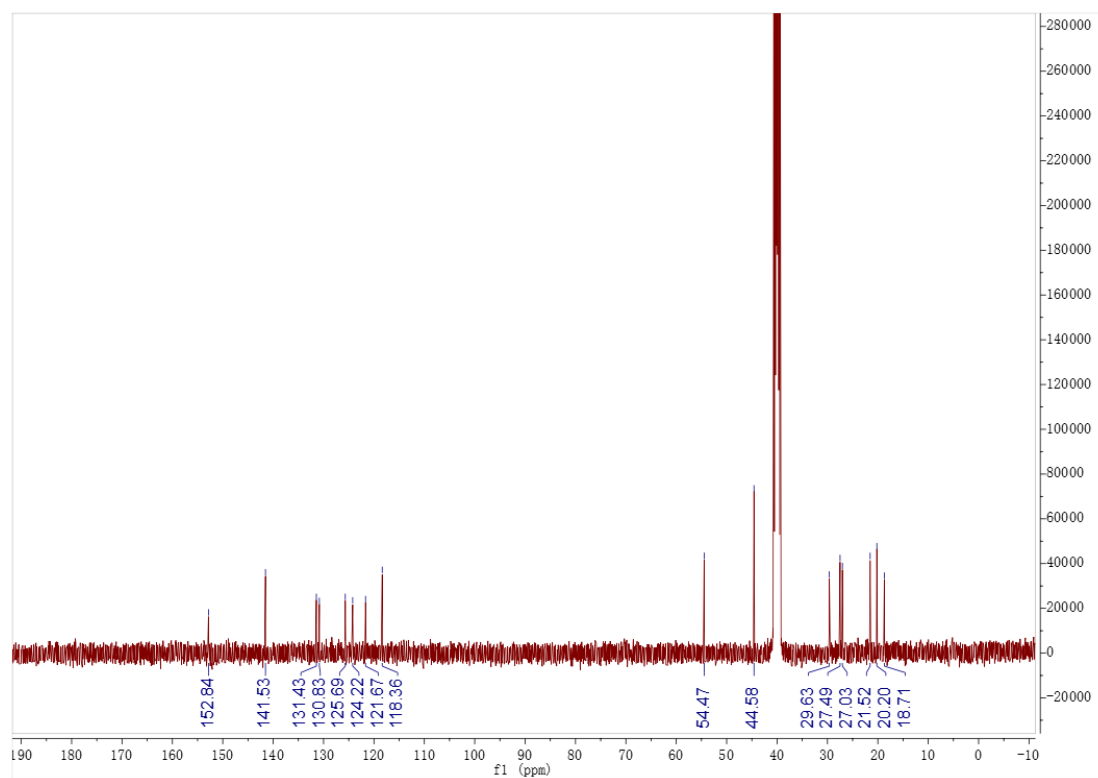


Figure S11. ¹³C NMR (100 MHz, DMSO) spectrum of compound 2.

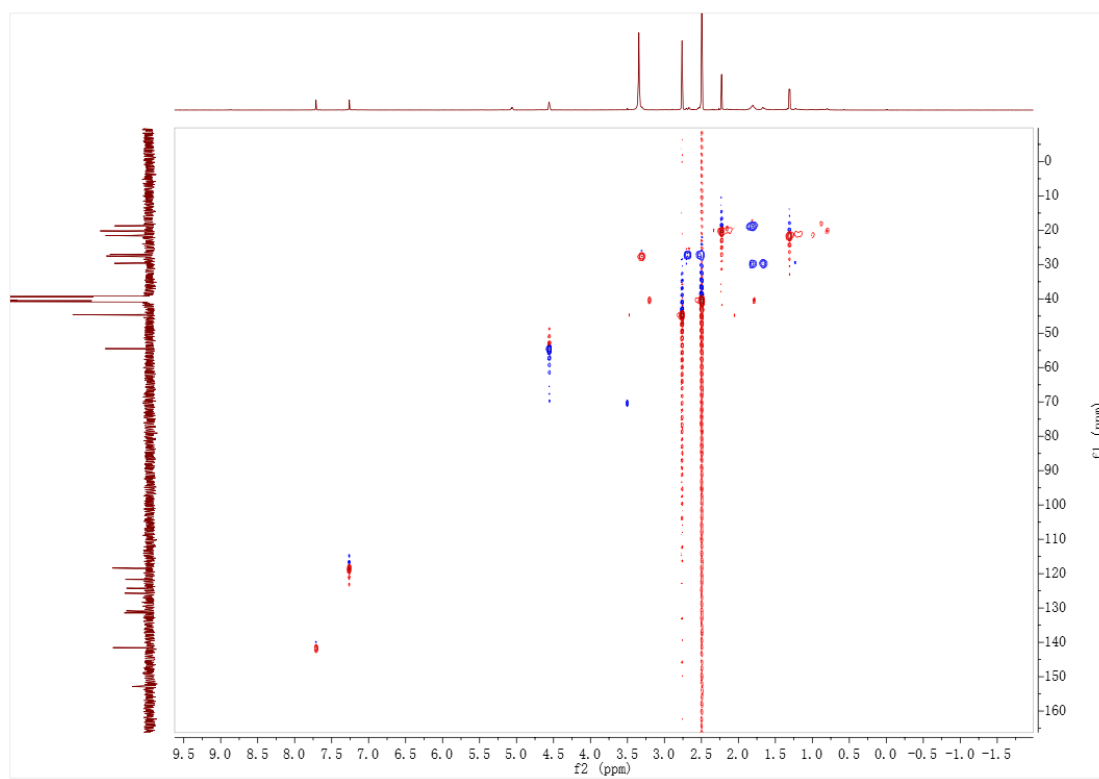


Figure S12. HSQC spectrum of compound 2.

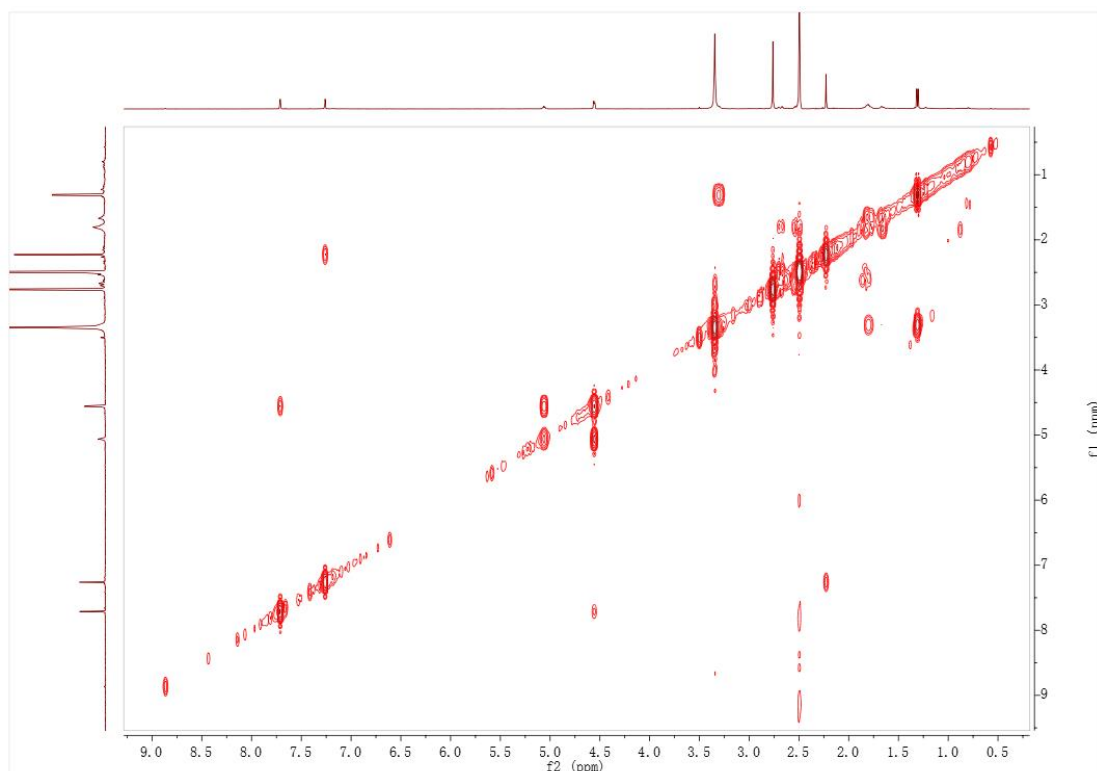


Figure S13. ^1H - ^1H COSY (500 MHz, DMSO) spectrum of compound **2**.

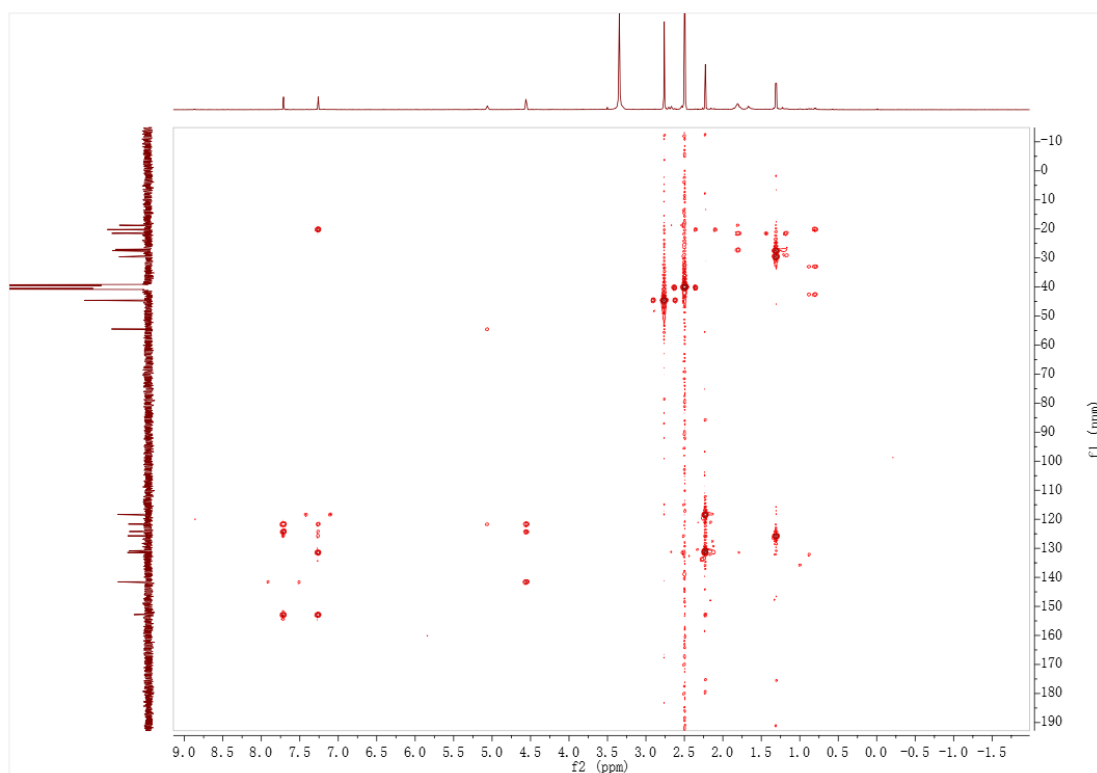


Figure S14. HMBC spectrum of compound **2**.

Mass spectrum of compound 10. The x-axis represents the mass-to-charge ratio (m/z) and the y-axis represents the relative intensity (0 to 100). The base peak is at m/z 231.1017. Other labeled peaks include m/z 224.9979, 226.9650, 229.1227, 230.8806, and 232.9136. The chemical formula $C_{15}H_{17}O_2$ and a value of 229.1234 are also indicated.

m/z	Relative Intensity (%)
224.9979	~90
226.9650	~95
229.1227	~75
230.8806	~55
231.1017	100
232.9136	~70

Wavenumbers (cm⁻¹)

% Transmittance

4000 3000 2000 1800 1600 1400 1200 1000 800 600 400

3053.44
3013.37
3097.37
3049.07
3028.42
3567.07
3545.63
3425.92
2927.60
1716.16
1662.61
1653.80
1646.43
1632.84
1623.72
1616.54
1609.59
1576.40
1569.26
1559.17
1540.10
1506.62
1499.43
1472.61
1465.14
1447.37
1436.92
1436.41
1418.35
1385.72
1299.86
1141.05
446.07

Figure S16. The IR spectrum of compound **2**.

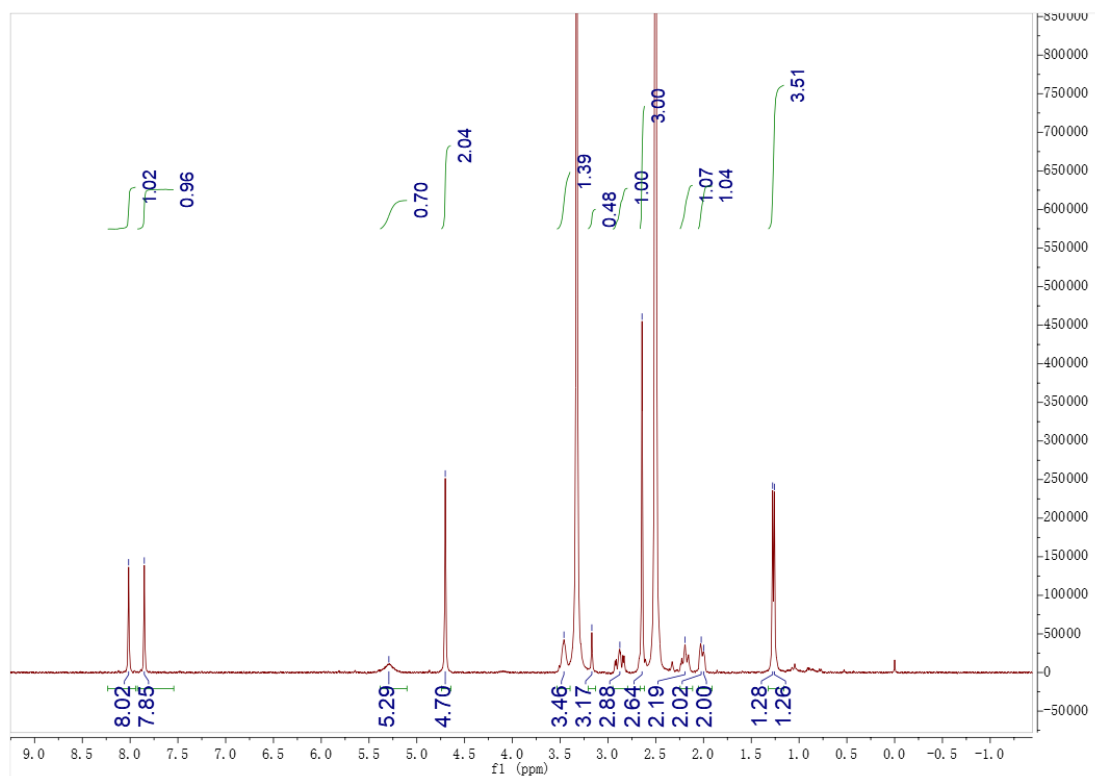


Figure S17. ¹H NMR (400 MHz, DMSO) spectrum of compound **3**.

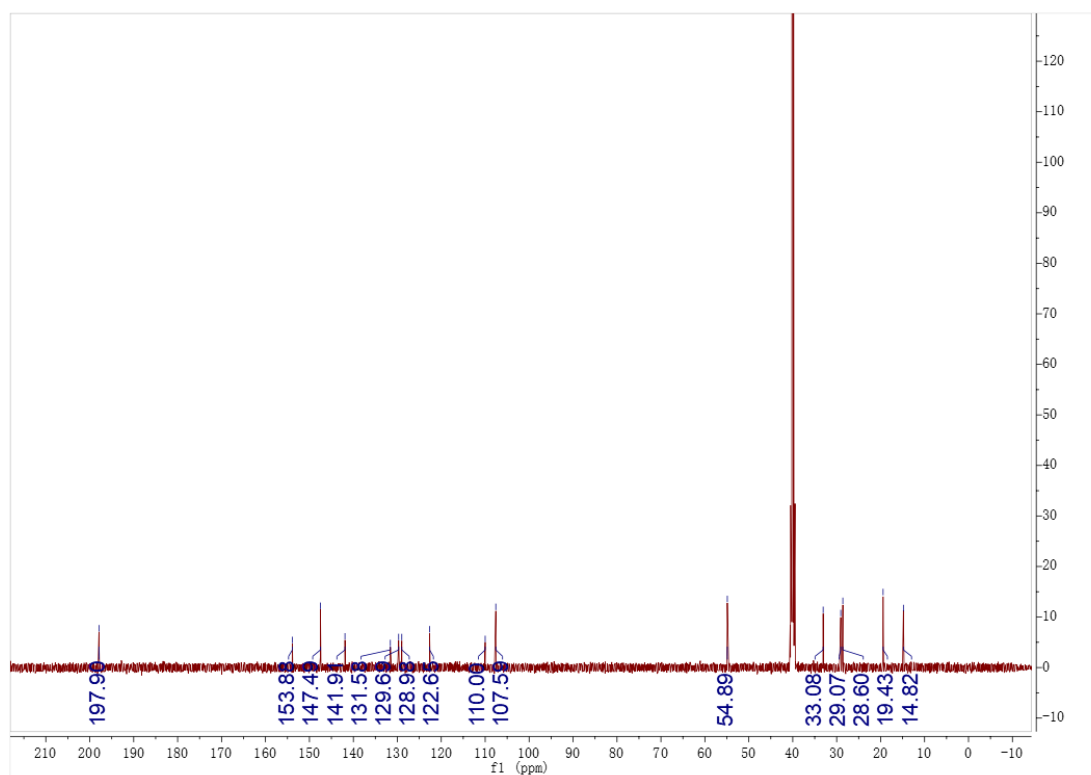


Figure S18. ¹³C NMR (125 MHz, DMSO) spectrum of compound **3**.

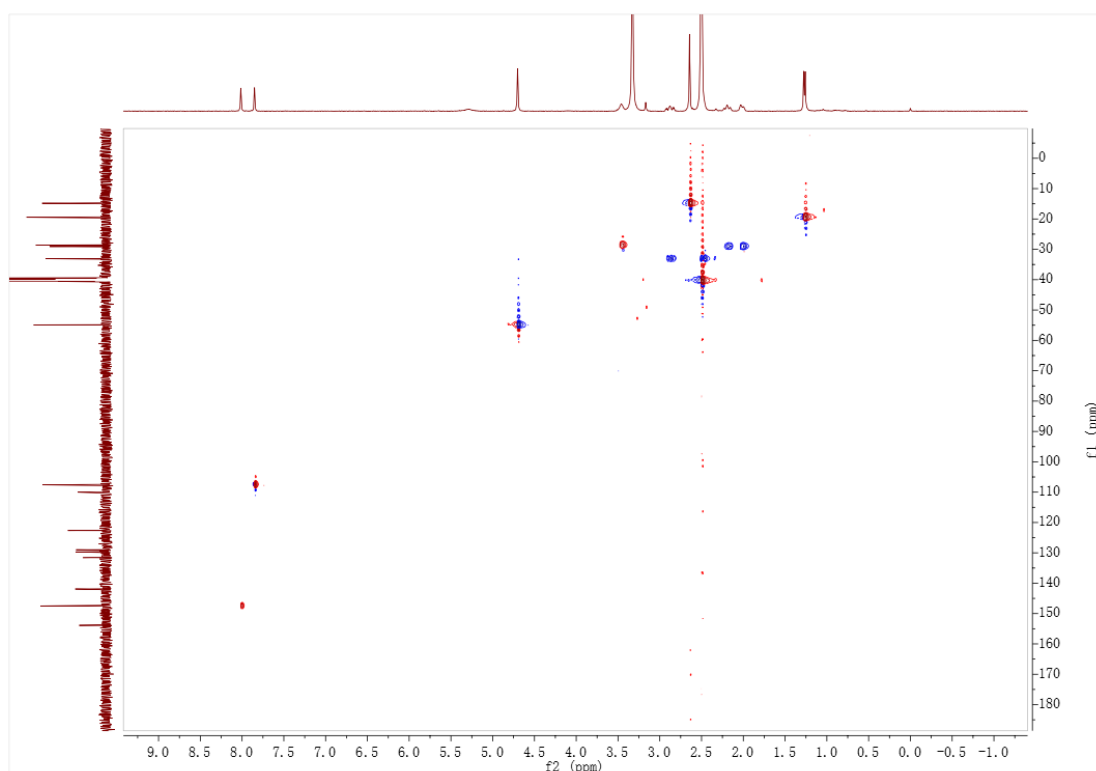


Figure S19. HSQC spectrum of compound **3**.

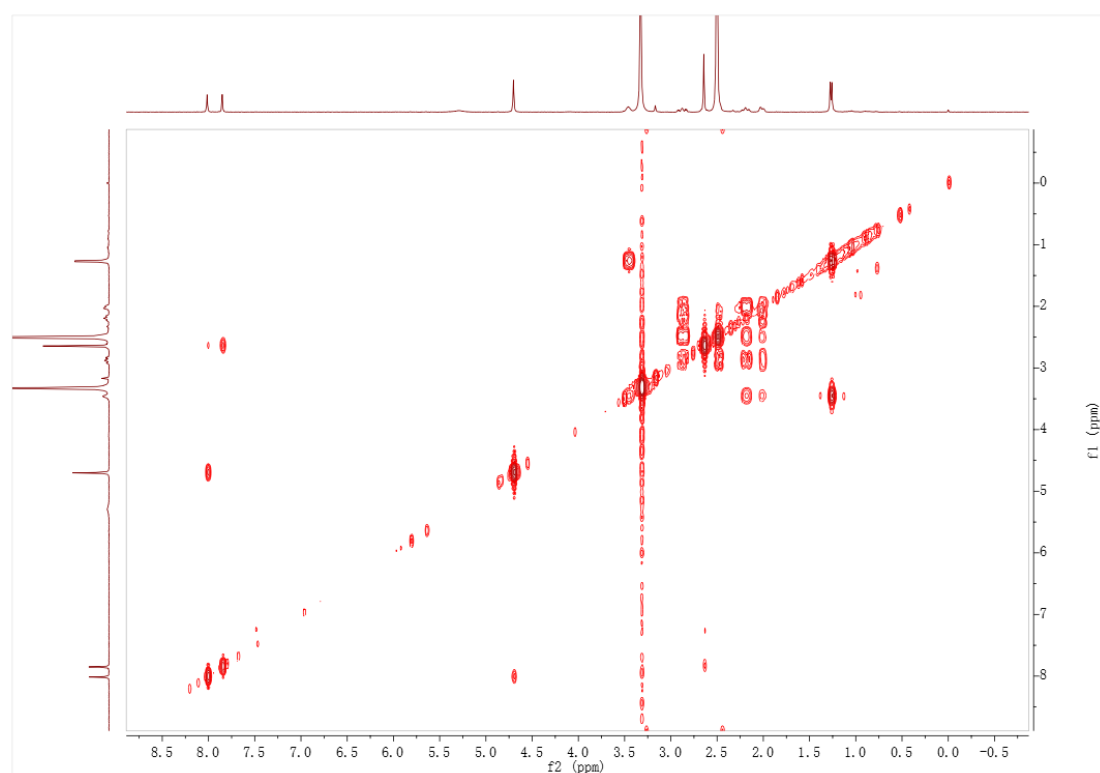


Figure S20. ^1H - ^1H COSY (500 MHz, DMSO) spectrum of compound **3**.

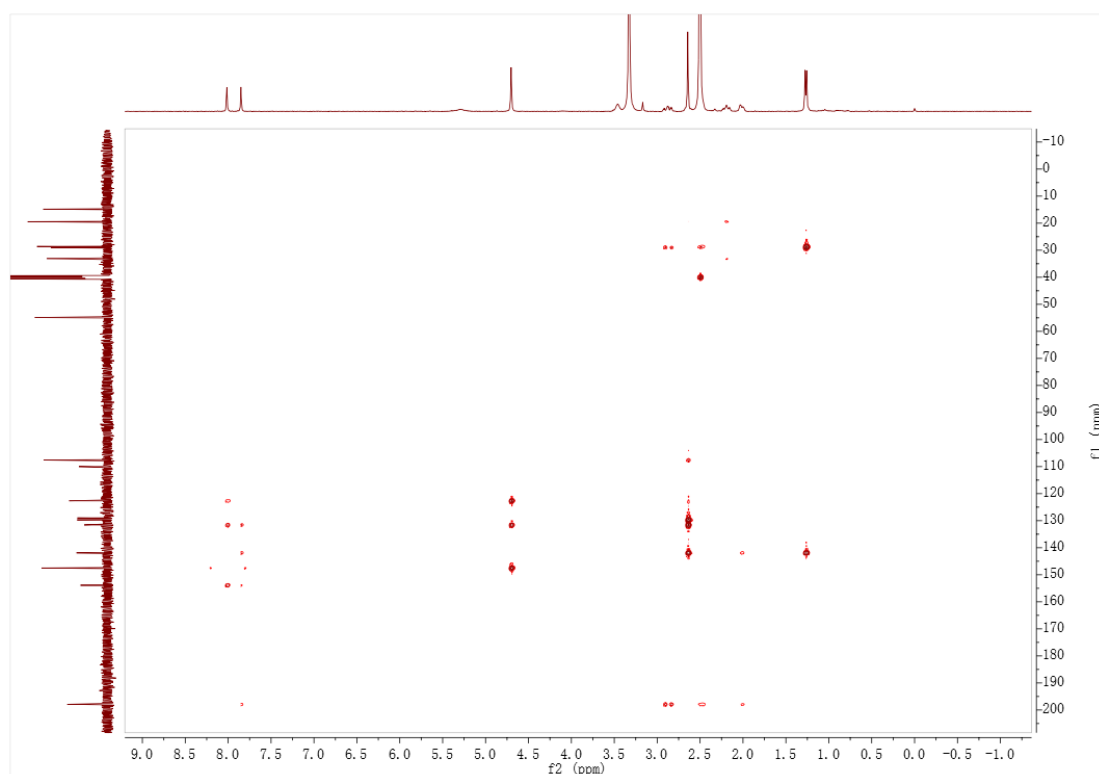


Figure S21. HMBC spectrum of compound **3**.

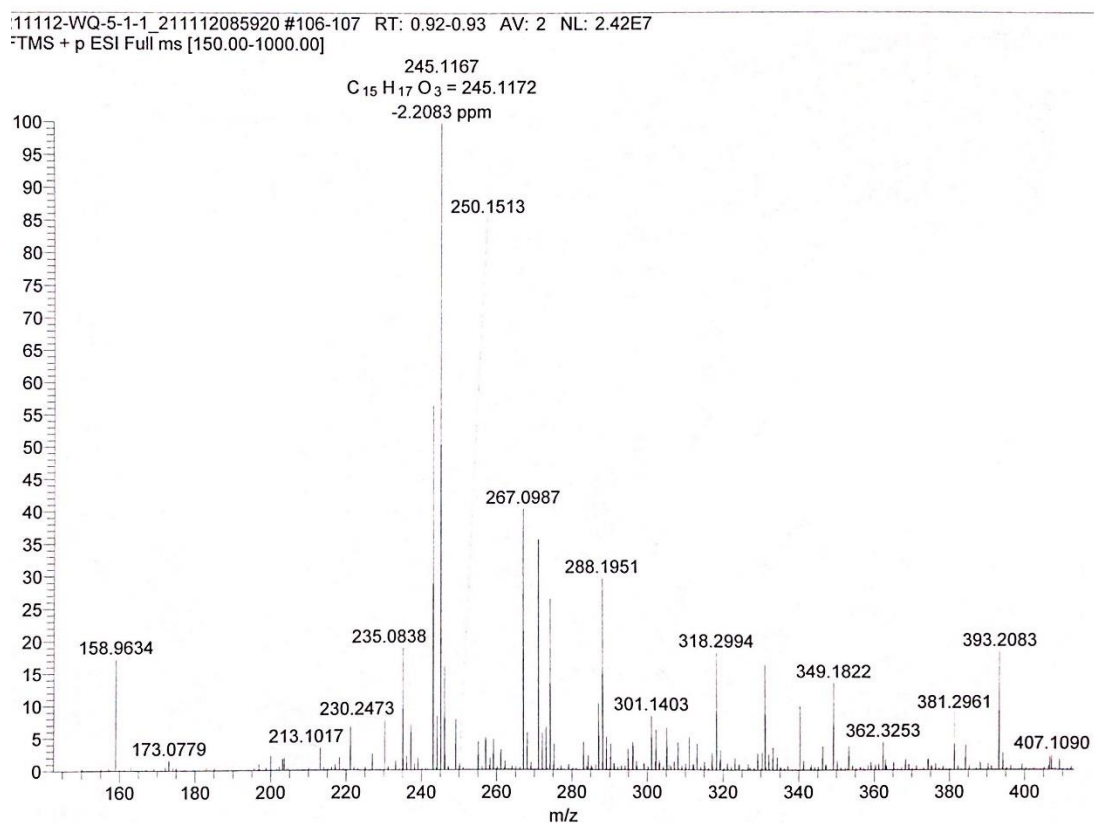


Figure S22. The HRESIMS spectrum of compound **3**.

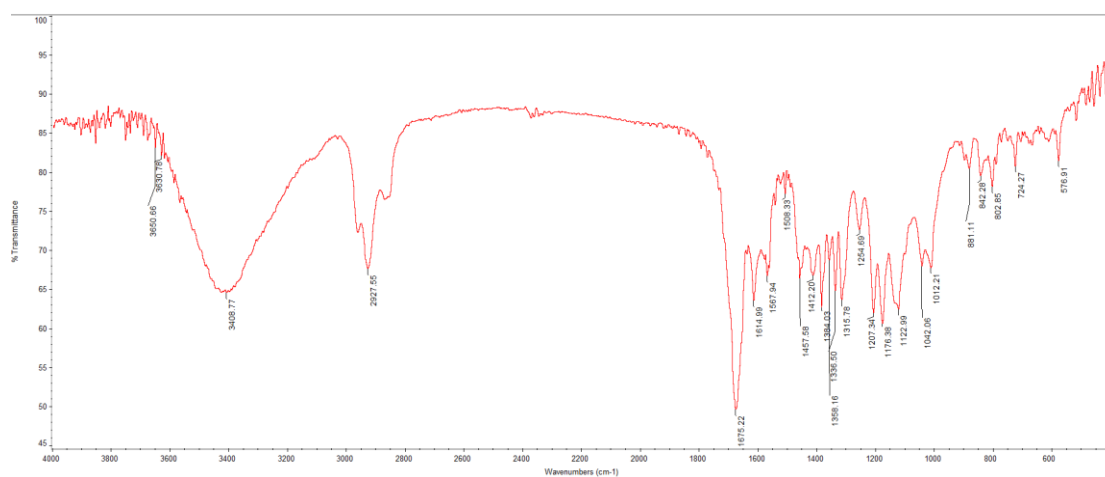


Figure S23. The IR spectrum of compound **3**.

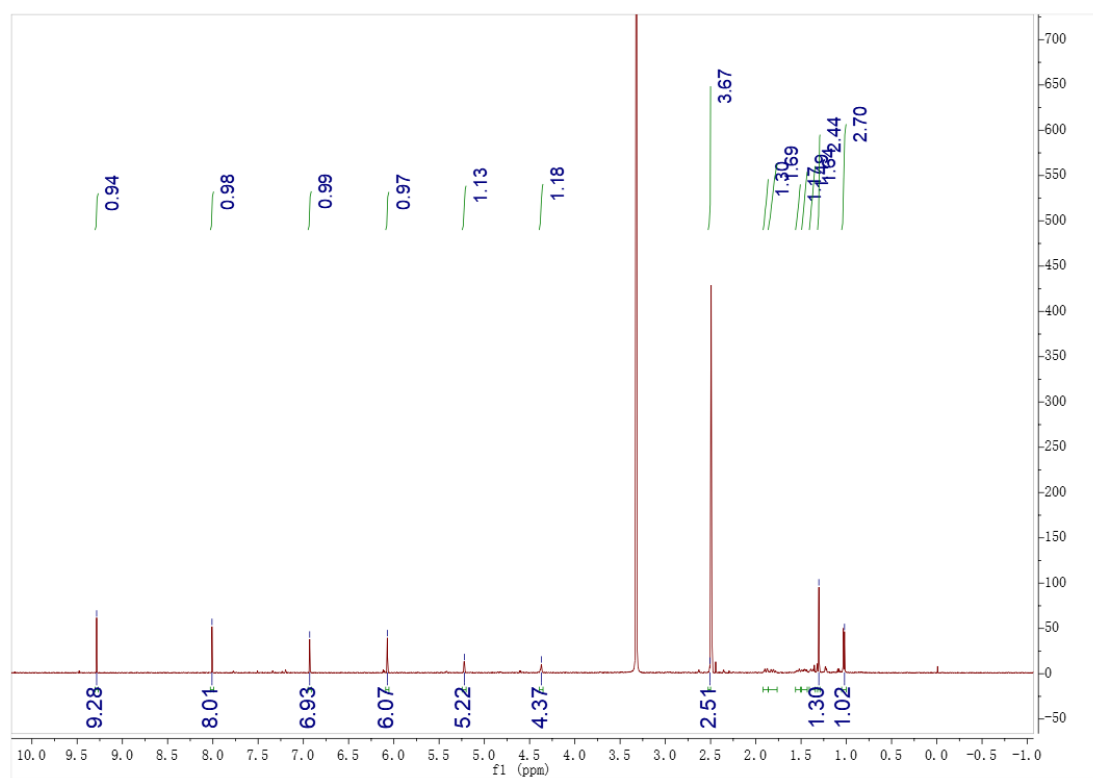


Figure S24. ^1H NMR (500 MHz, DMSO) spectrum of compound **4**.

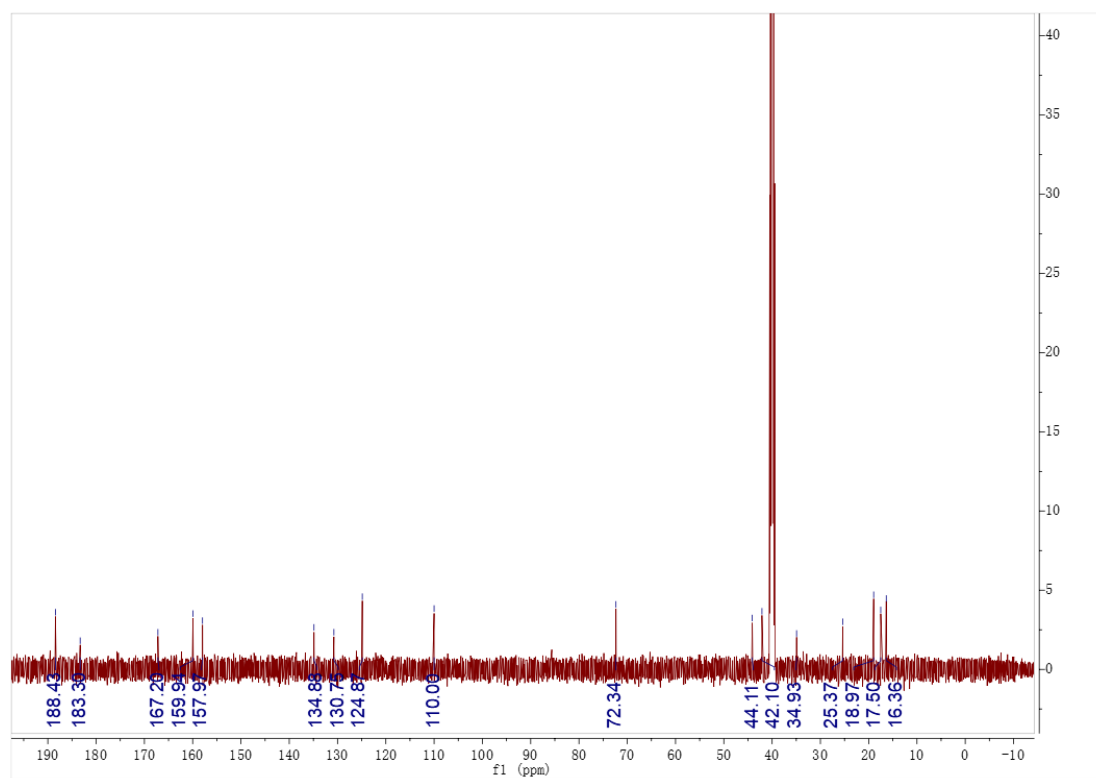


Figure S25. ¹³C NMR (125 MHz, DMSO) spectrum of compound **4**.

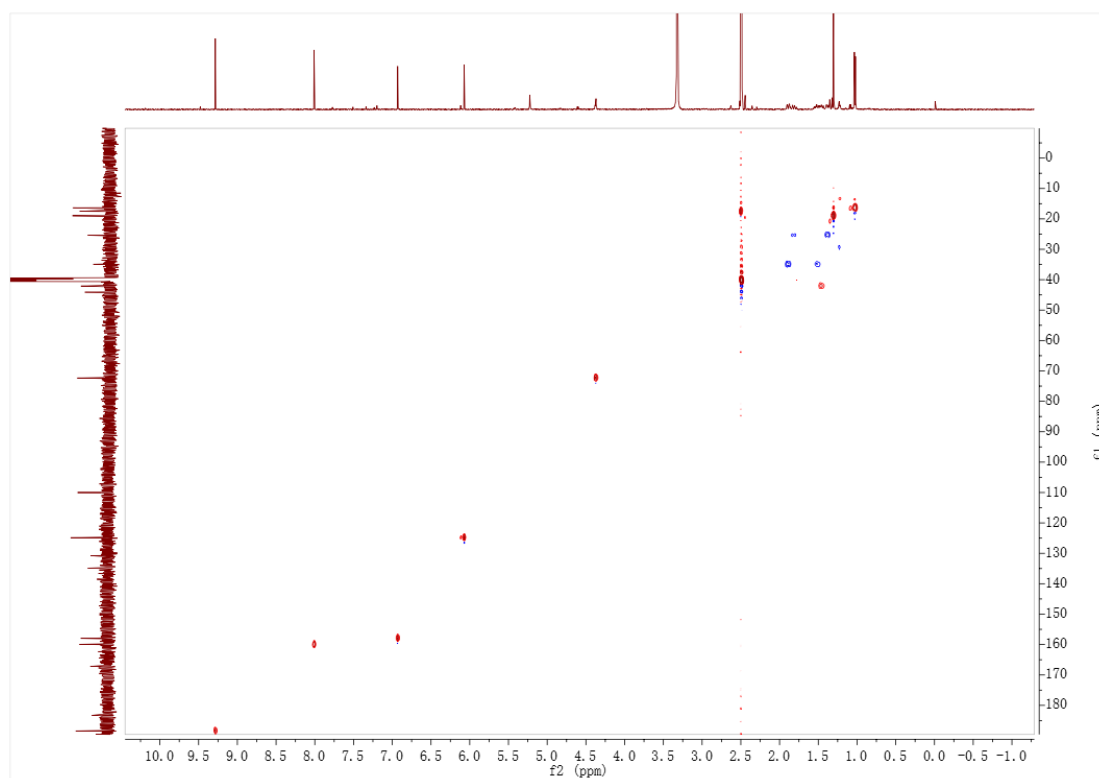


Figure S26. HSQC spectrum of compound **4**.

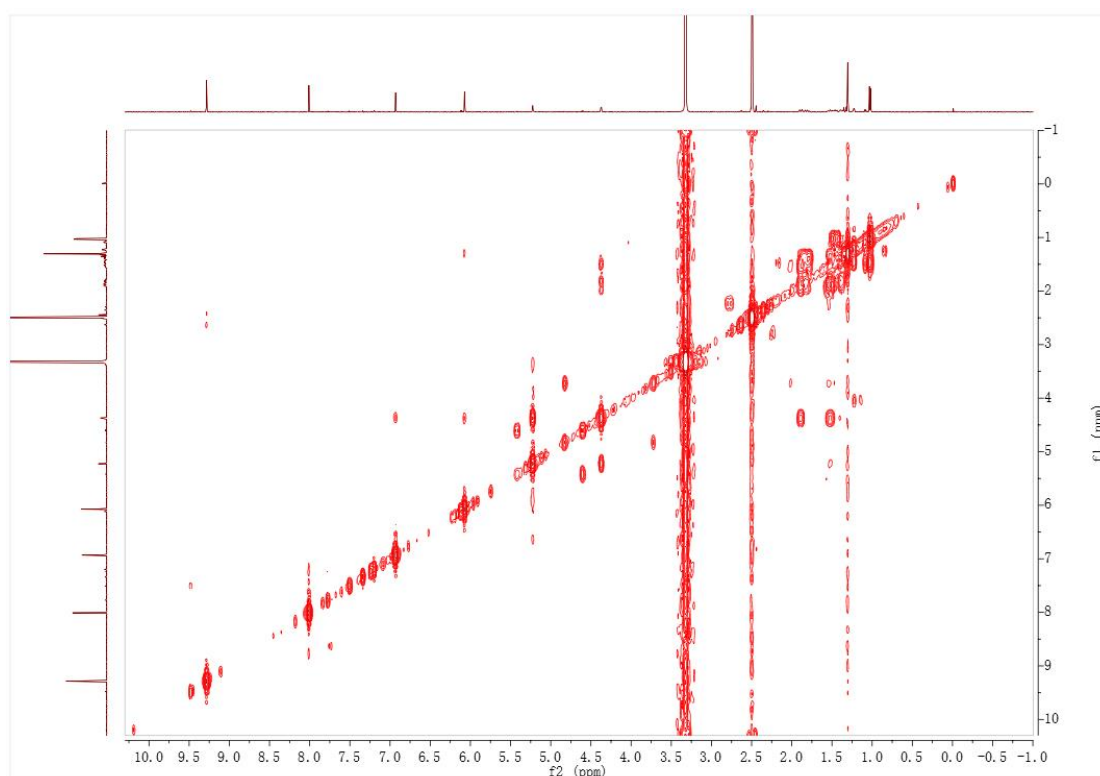


Figure S27. ^1H - ^1H COSY (500 MHz, DMSO) spectrum of compound **4**.

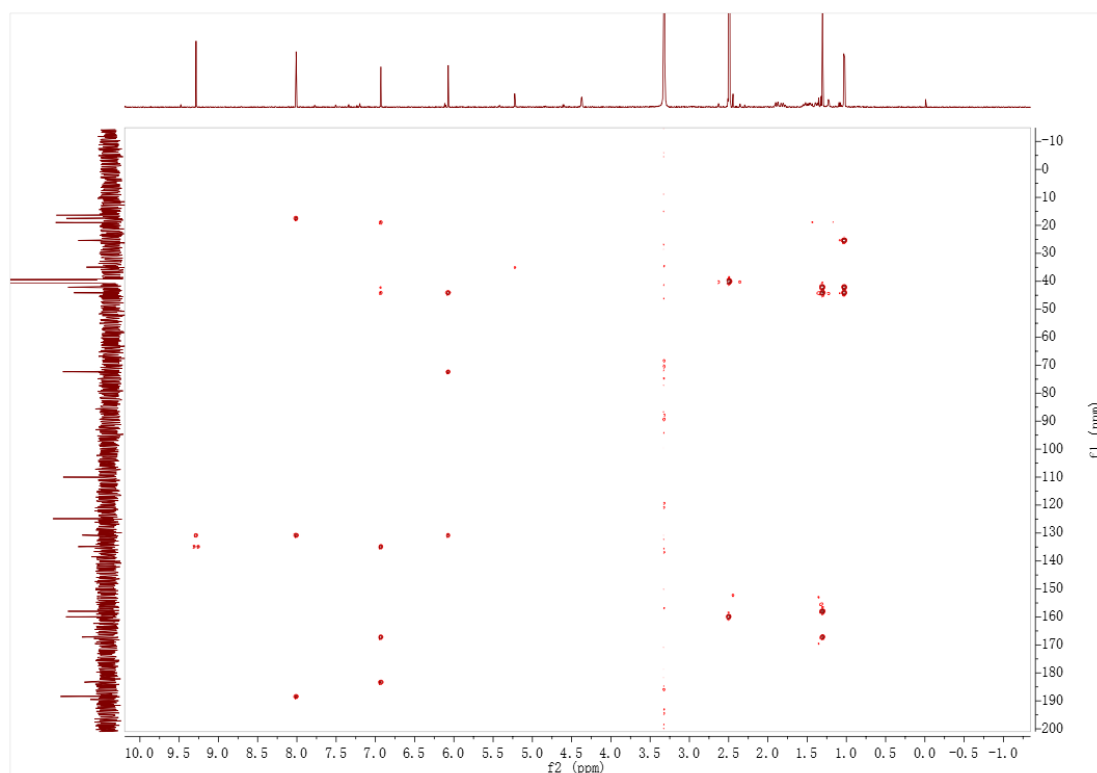


Figure S28. HMBC spectrum of compound **4**.

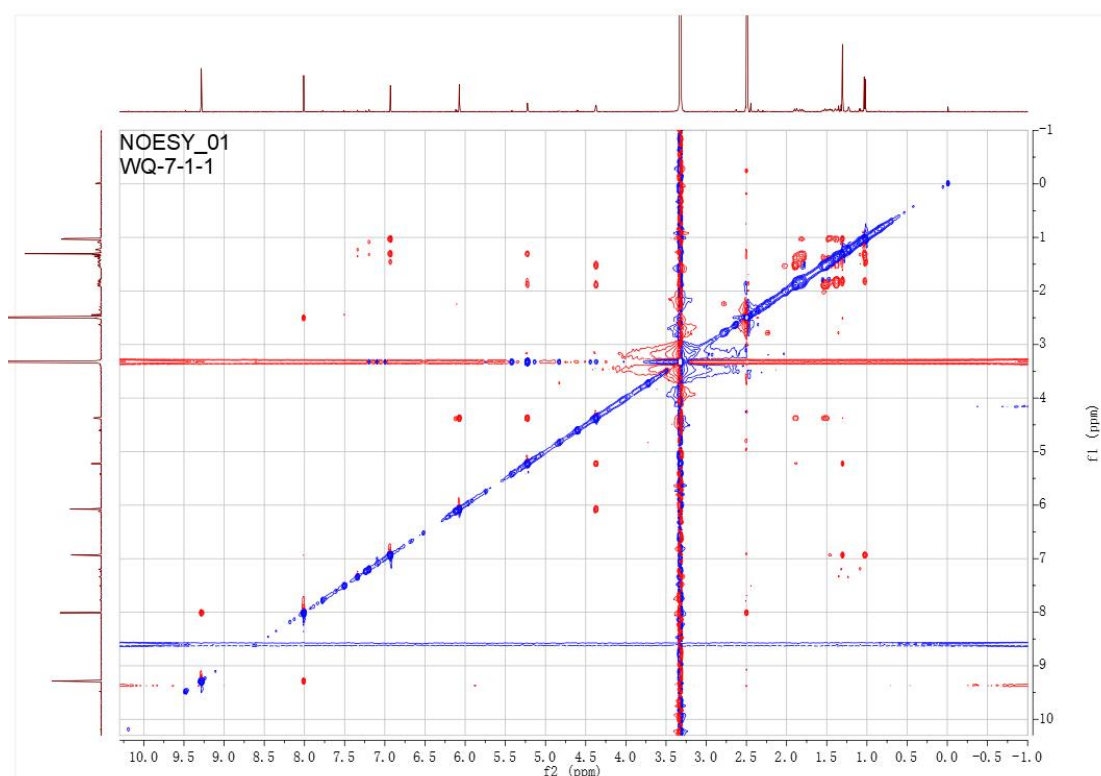


Figure S29. NOESY (500 MHz, DMSO) spectrum of compound **4**.

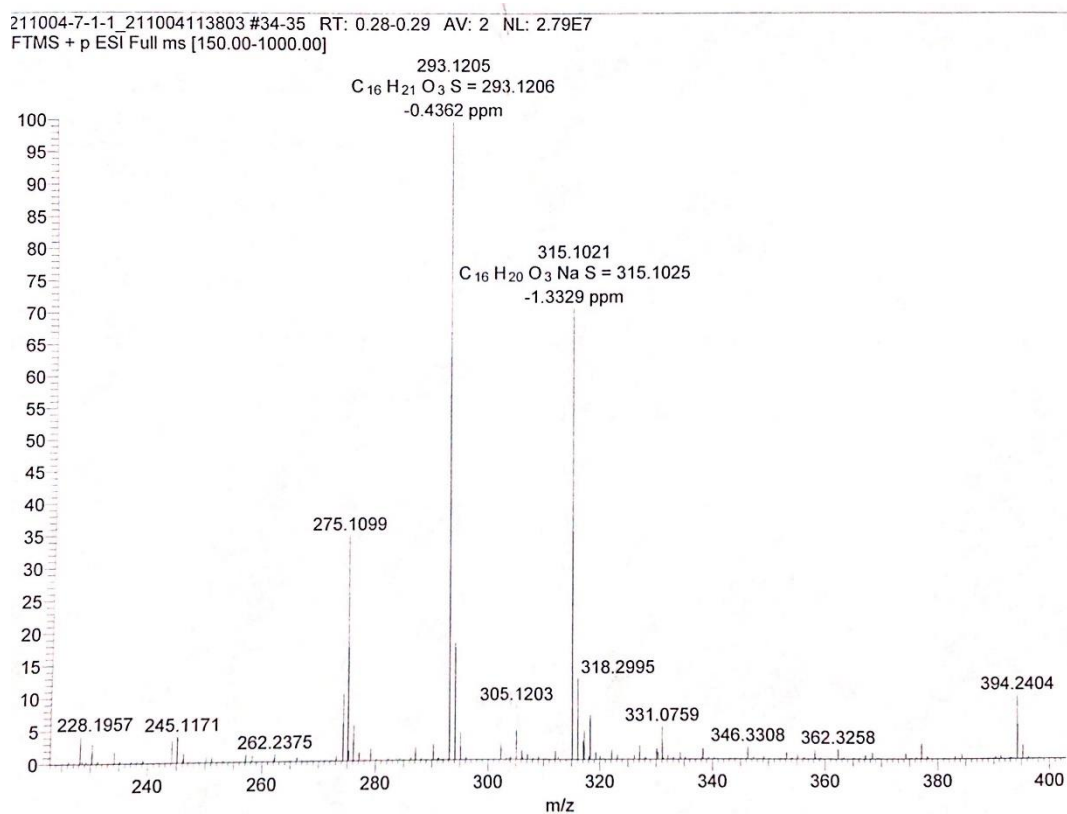


Figure S30. The HRESIMS spectrum of compound **4**.

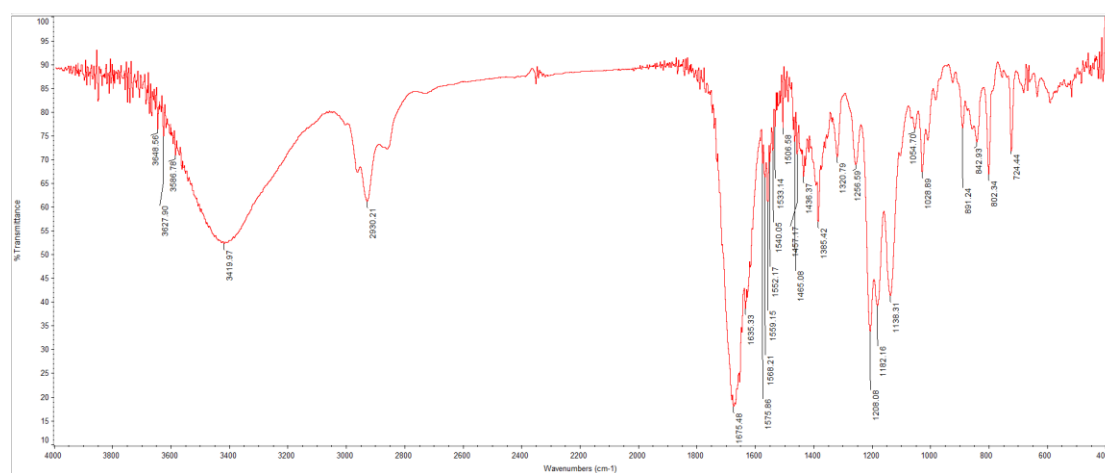


Figure S31. The IR spectrum of compound **4**.

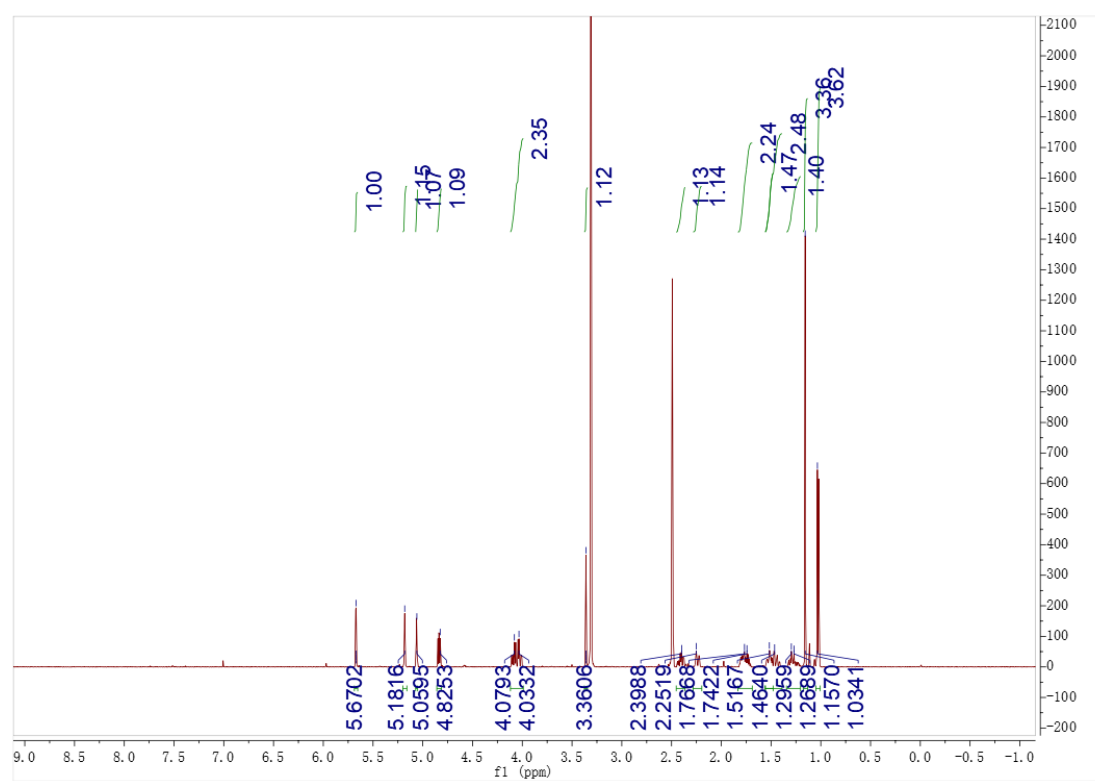


Figure S32. ^1H NMR (500 MHz, DMSO) spectrum of compound **5**.

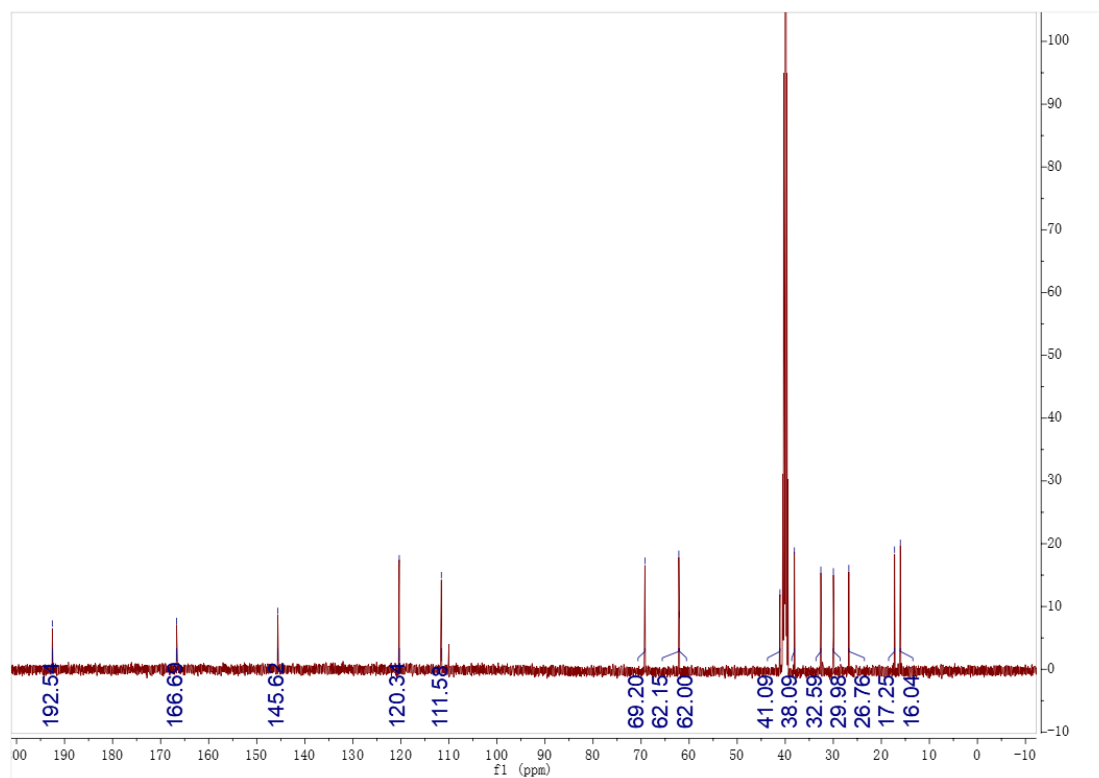


Figure S33. ¹³C NMR (125 MHz, DMSO) spectrum of compound **5**.

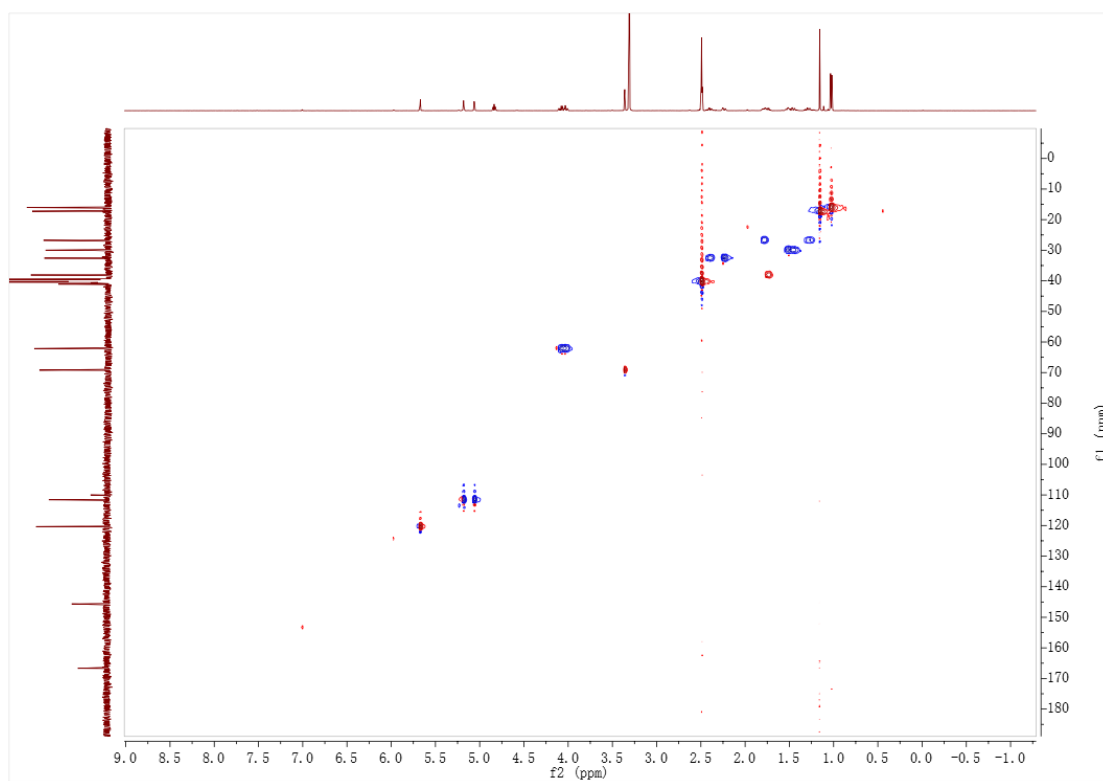


Figure S34. HSQC spectrum of compound **5**.

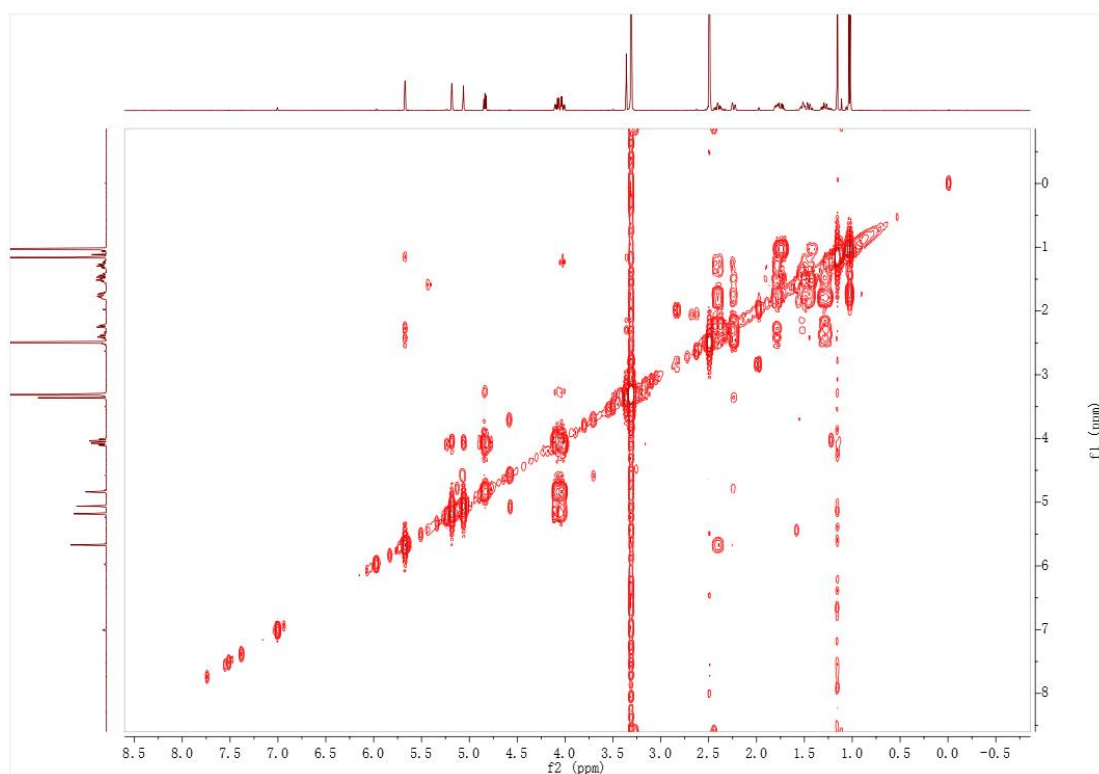


Figure S35. ^1H - ^1H COSY (500 MHz, DMSO) spectrum of compound **5**.

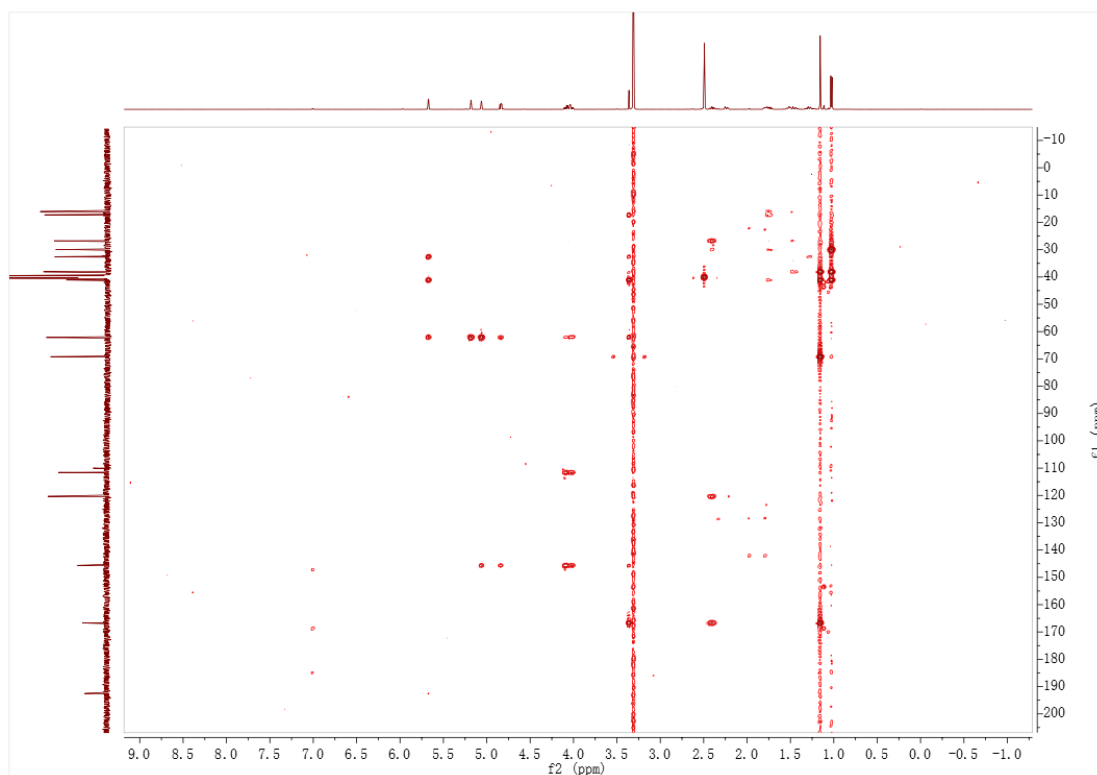


Figure S36. HMBC spectrum of compound **5**.

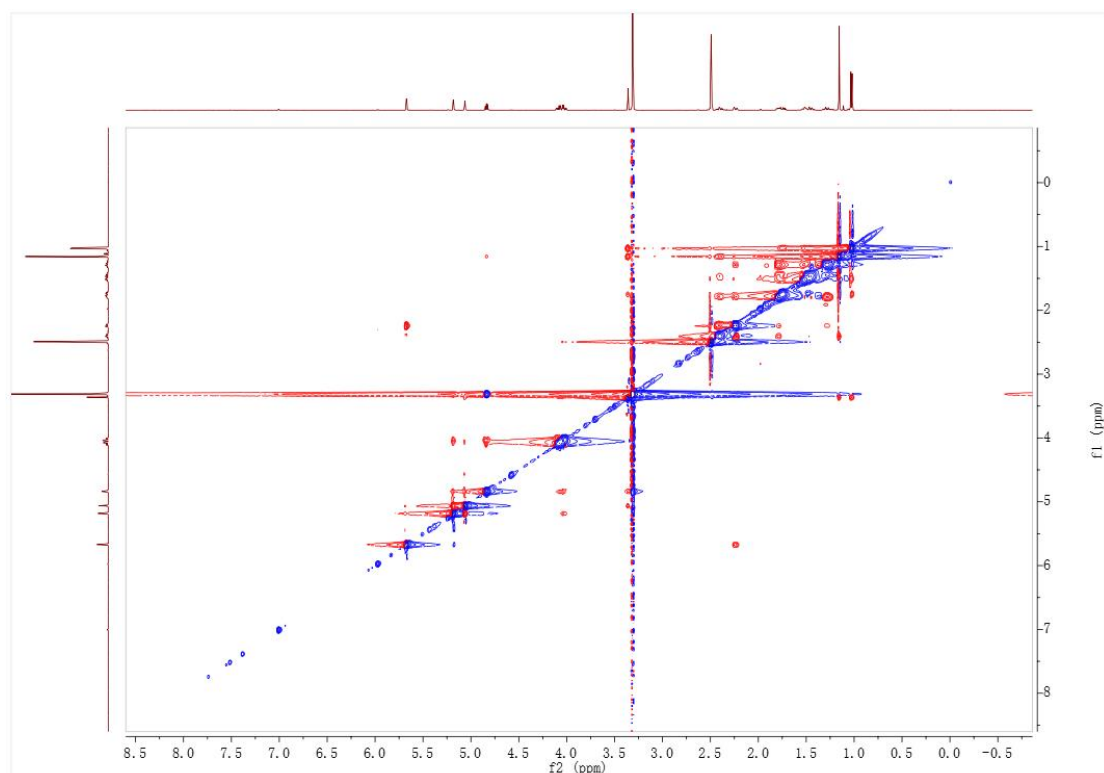


Figure S37. NOESY (500 MHz, DMSO) spectrum of compound **5**.

211112-WQ-5-1-2_211112084204 #21-22 RT: 0.17-0.18 AV: 2 NL: 2.60E8
FTMS + p ESI Full ms [150.00-1000.00]

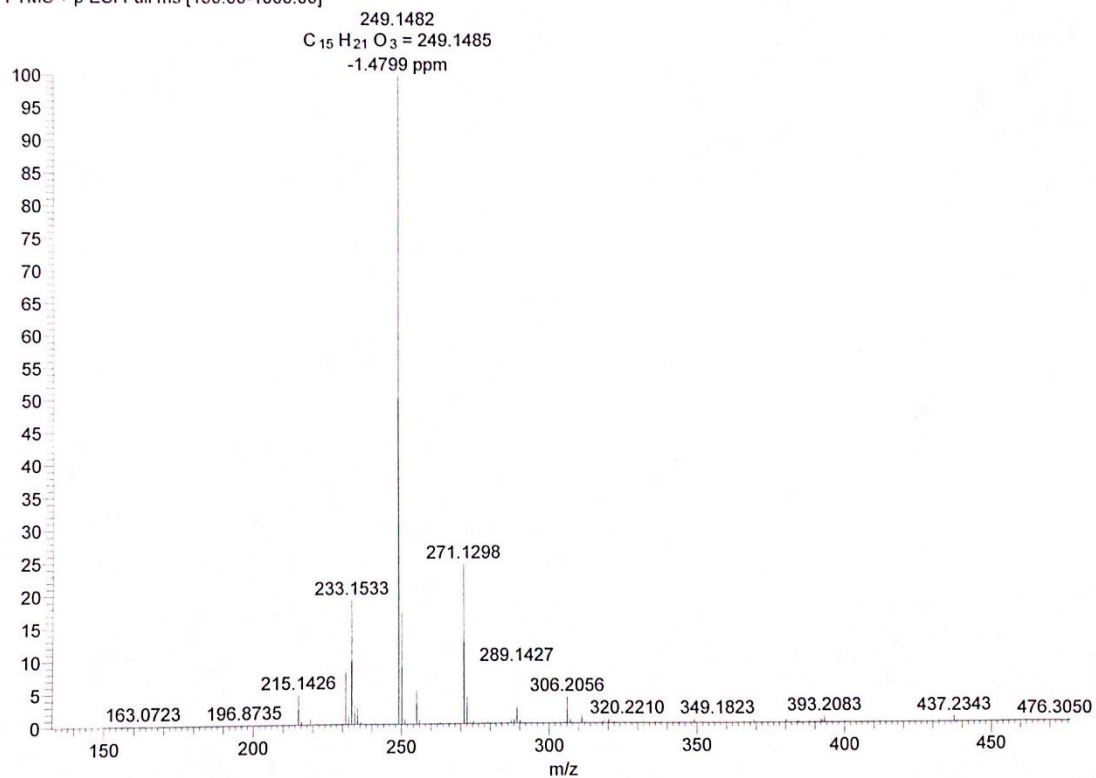


Figure S38. The HRESIMS spectrum of compound **5**.

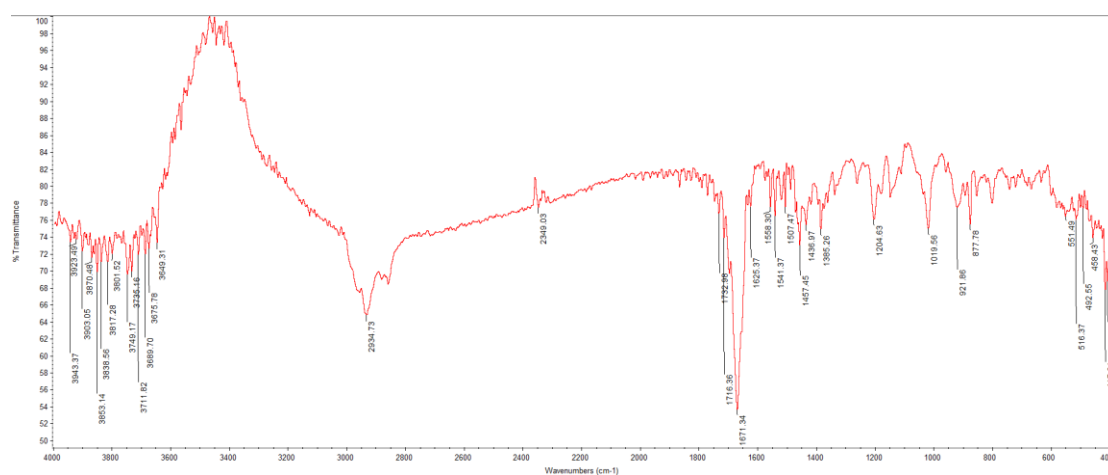


Figure S39. The IR spectrum of compound **5**.

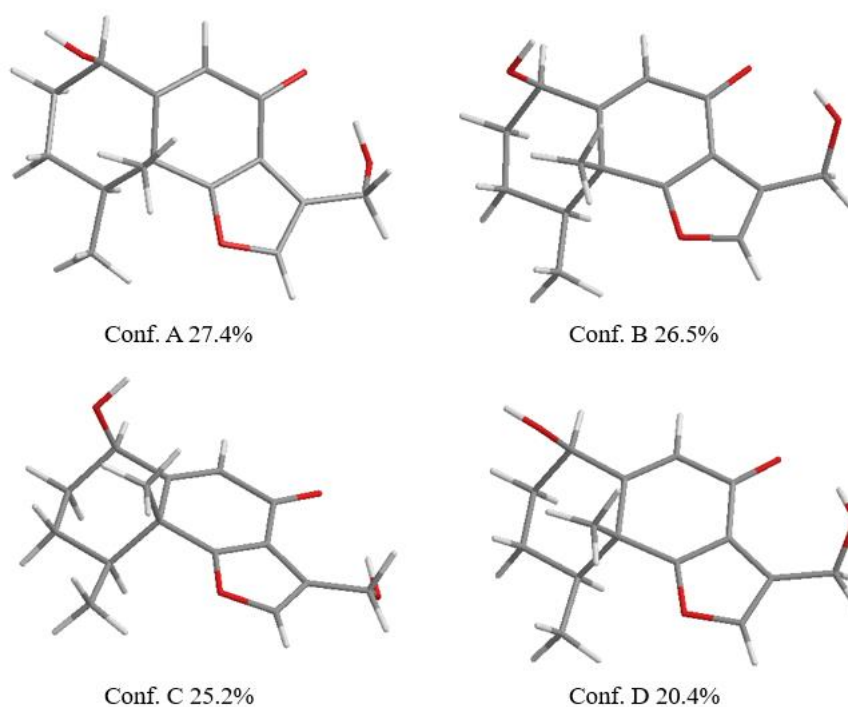


Figure S40. DFT-optimized structures for low-energy conformers of (1*R*, 4*S*, 5*R*)-**1** at B3LYP/TZVP level in DMSO (CPCM) (Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof).

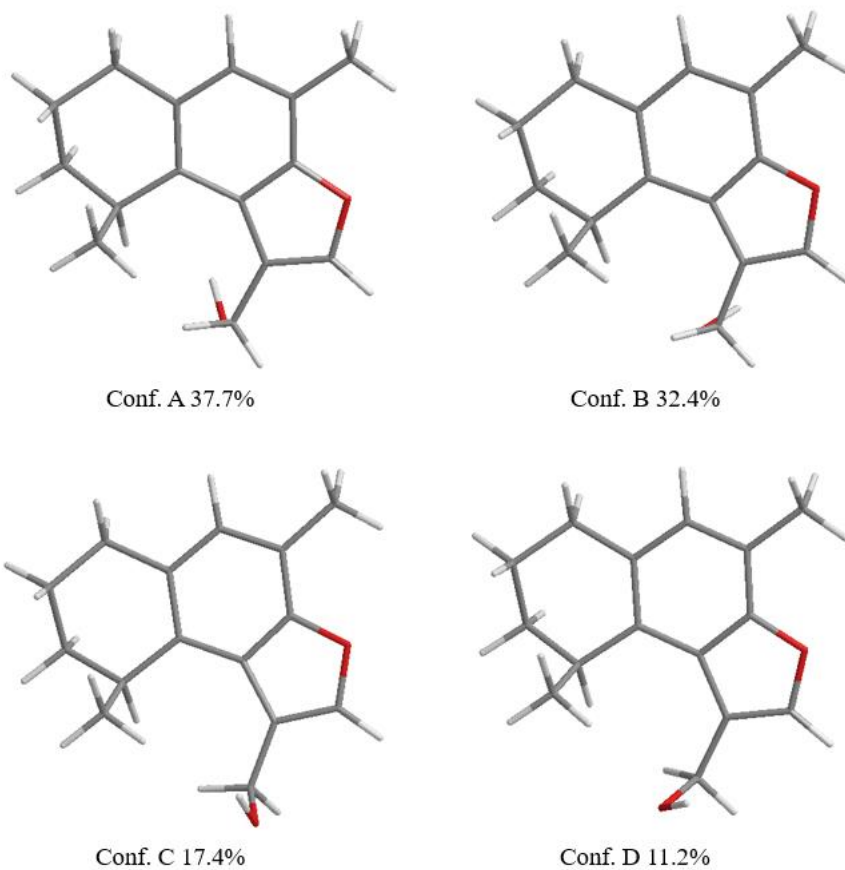


Figure S41. DFT-optimized structures for low-energy conformers of (4*R*)-**2** at B3LYP/TZVP level in DMSO (CPCM) (Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof).

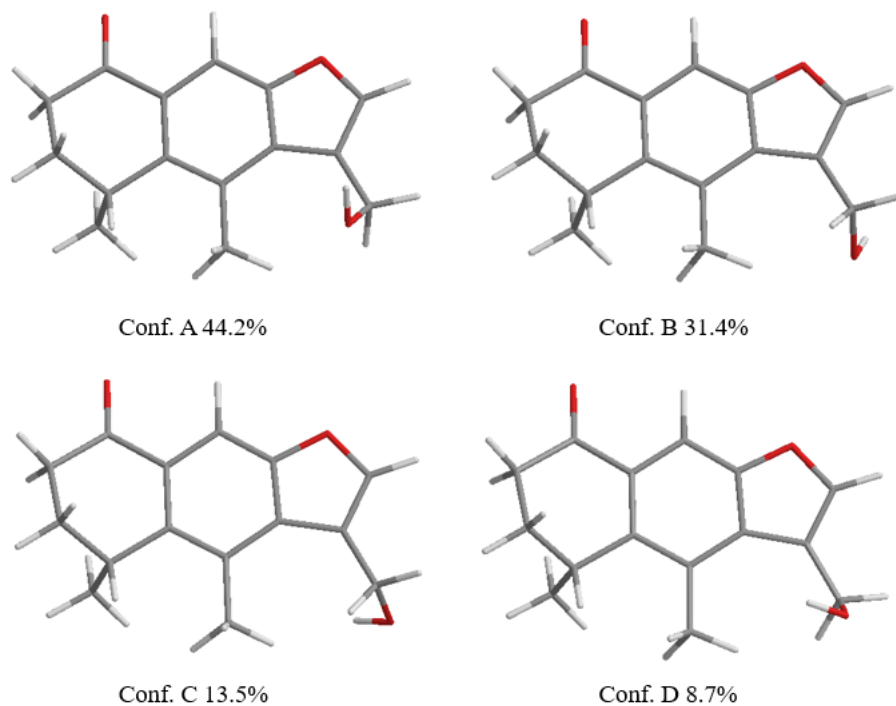


Figure S42. DFT-optimized structures for low-energy conformers of (4R)-3 at B3LYP/TZVP level in DMSO (CPCM) (Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof).

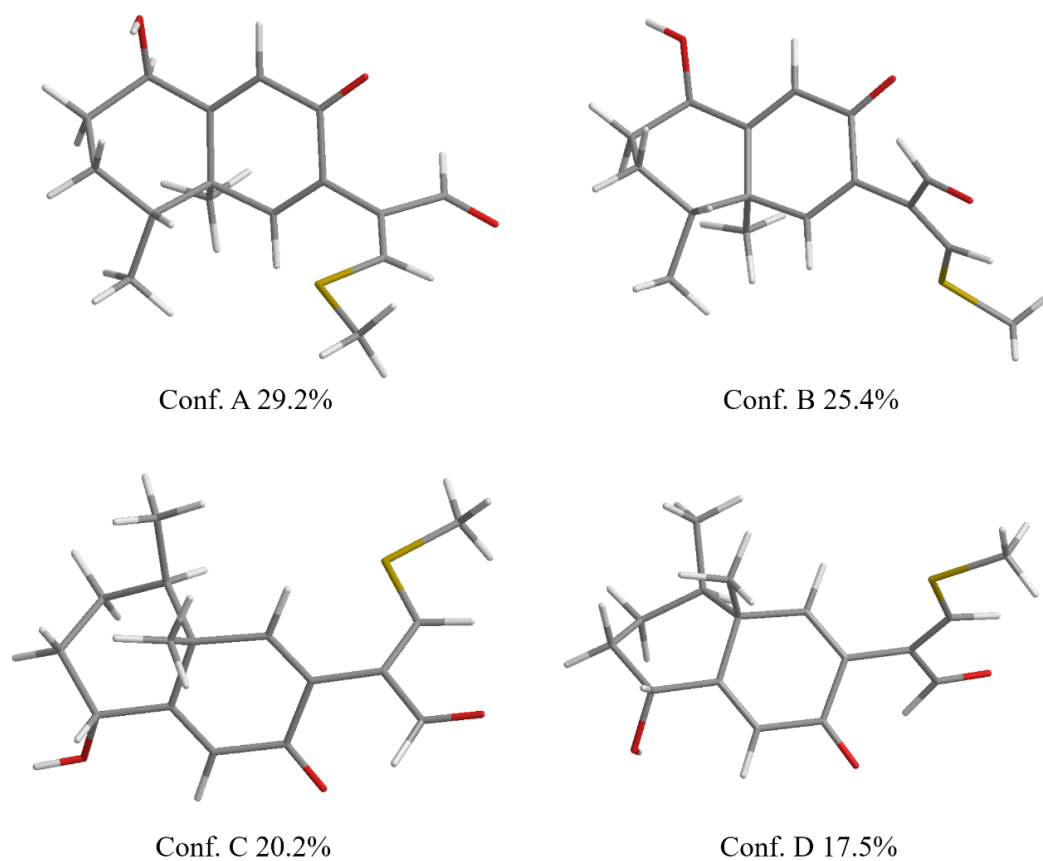


Figure S43. DFT-optimized structures for low-energy conformers of (4*R*)-**4** at B3LYP/TZVP level in DMSO (CPCM) (Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof).

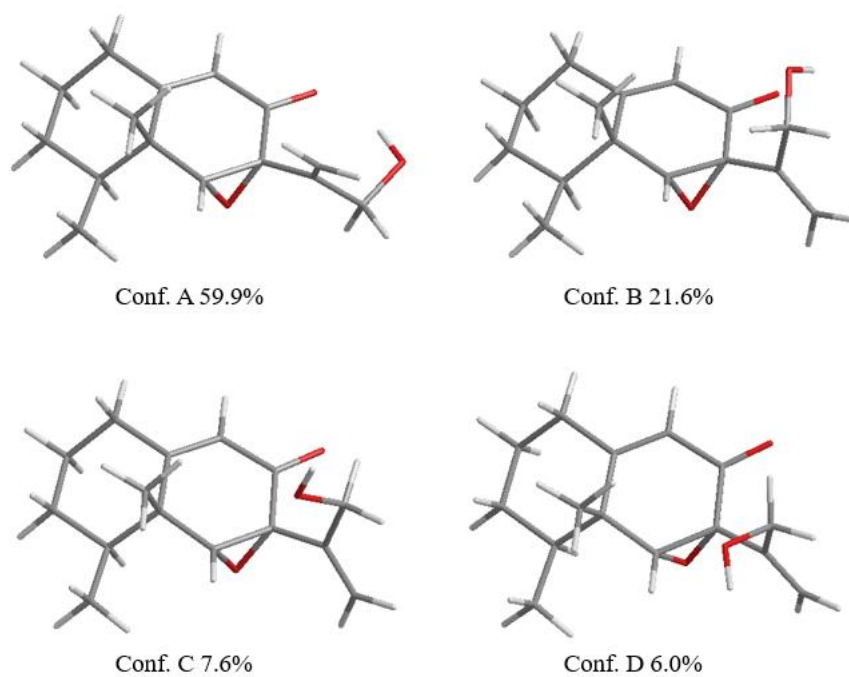


Figure S44. DFT-optimized structures for low-energy conformers of (4*S*,5*R*,6*R*,7*R*)-**5**

at B3LYP/TZVP level in DMSO (CPCM) (Conformer populations were calculated using the Gibbs free energy and Boltzmann population at 298 K estimated thereof).

Conformations	Frequencies		
	1	2	3
A	46.2460	61.6322	93.1044
B	45.9745	61.4710	94.3548
C	49.0526	61.3063	91.5809
D	45.5606	62.5549	94.2921

Table S1. Harmonic frequencies (cm⁻¹) of **1**.

Conformations	Frequencies		
	1	2	3
A	67.1076	77.8603	93.8040
B	63.8522	79.6450	94.4259
C	56.1423	74.2237	87.9819
D	32.3779	71.3376	88.5621

Table S2. Harmonic frequencies (cm⁻¹) of **2**.

Conformations	Frequencies		
	1	2	3
A	50.2389	53.1863	73.1078
B	51.6273	55.2291	82.2034
C	39.4457	53.4979	73.1831
D	48.8863	56.5290	83.2251

Table S3. Harmonic frequencies (cm⁻¹) of **3**.

Conformations	Frequencies		
	1	2	3
A	24.1409	37.0744	54.0982

B	20.6730	40.0519	57.5593
C	25.1176	37.2193	54.8739
D	21.1952	40.7051	57.6114

Table S4. Harmonic frequencies (cm⁻¹) of **4**.

Conformations	Frequencies		
	1	2	3
A	39.6984	54.1896	83.1232
B	40.4606	43.0203	82.7451
C	33.1236	54.1258	60.0852
D	28.4078	52.0435	60.7965

Table S5. Harmonic frequencies (cm⁻¹) of **5**.

Conformations	E+ZPE	G	%
A	-883.034519	-883.077920	27.4
B	-883.035662	-883.078906	26.5
C	-883.035786	-883.079093	25.2
D	-883.034512	-883.077911	20.4

Table S6. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized-1 at B3LYP/TZVP level of theory with PCM solvent model for DMSO. E+ZPE, G: total energy with zero-point energy (ZPE) and Gibbs free energy at B3LYP/TZVP level of theory with PCM solvent model for DMSO. %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Conformations	E+ZPE	G	%
A	-732.614420	-732.656399	37.7
B	-732.616380	-732.658410	32.4
C	-732.612141	-732.654485	17.4
D	-732.613909	-732.656465	11.2

Table S7. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized-2 at B3LYP/TZVP level of theory with PCM solvent model for DMSO.

Conformations	E+ZPE	G	%
A	-806.660788	-806.703905	44.2
B	-806.660883	-806.703900	31.4
C	-806.658457	-806.701935	13.5

D	-806.658376	-806.701177	8.7
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Table S8. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized-3 at B3LYP/TZVP level of theory with PCM solvent model for DMSO.

Conformations	E+ZPE	G	%
A	-1245.272181	-1245.322236	29.2
B	-1245.272372	-1245.322440	25.4
C	-1245.272161	-1245.322083	20.2
D	-1245.272195	-1245.322129	17.5

Table S9. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized-4 at B3LYP/TZVP level of theory with PCM solvent model for DMSO.

Conformations	E+ZPE	G	%
A	-808.959176	-809.002888	59.9
B	-808.957473	-809.001675	21.6
C	-808.957153	-809.001814	7.6
D	-808.957633	-809.002222	6.0

Table S10. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized-5 at B3LYP/TZVP level of theory with PCM solvent model for DMSO.