SUPPLEMENTARY MATERIAL

Surfactin Isoforms Isolated from a Mushroom derived *Bacillus halotolerans* DMG-7-2

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A new iso-C_{14} [Val^2, Val^7] surfactin isoform (**1**) together with eight known ones (**2**–**9**), was isolated from the culture of a mushroom derived bacterium, *Bacillus halotolerans* DMG-7-2. The structures of them were mainly elucidated by NMR and MS data, and the NMR data of **5** also was reported for the first time. The absolute configuration of **1** was determined by Marfey's analysis (for amino acid residues) and the ^{13}C NMR calculation of the two plausible epimers of **1** (for fatty acid). Compounds **1**–**9** showed moderate cytotoxicity against two human cancer cell lines (A549, MCF-7) and mice microglial BV2 cells, the IC_{50} values ranged from 8.91 to 33.00 μM, and the IC_{50} values of the positive control 5-FU were 99.94, 71.49 and 0.12 μM, respectively.

Keywords: surfactin isoform; mushroom; *Cortinarius lucorum*; *Bacillus halotolerans*; cytotoxicity

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Experimental

1.General Experimental Procedures.

The HPLC system used Shimadzu LC-20A HPLC (Shimadzu, Japan) and Waters HPLC system (a Waters 600 pump, a Waters 600 controller and a Waters 2996 or 2998 photodiode array detectors were used for HPLC analysis and HPLC preparation respectively; Waters, Milford, MA, USA). The NMR spectra were clarified by Bruker Avance 500 (500 MHz for ^{1}H/125 MHz for ^{13}C) NMR spectrometer (Bruker, Karlsruhe, Germany). The fermentation of DMG-7-2 was performed on ZHWY-2102 rotary shakers (Shanghai ZhiCheng Analyzing Instrument Manufactory Co., Ltd, Shanghai, China). An Anton paar MCP200 (Anton paar, Austria) polarimeter was used to obtain optical rotations. HRESIMS was obtained by Agilent 1260-6230A Q-TOF LC-MS (Agilent Technologies, Santa Clara, CA, USA) system. The IR spectrum was clarified by the Nicolet IS5 FTIR spectrophotometer (Thermo Scientific, USA), and UV spectrum was measured on a Thermo Scientific Genesys 10S spectrophotometer (Thermo Scientific, USA). The ECD spectra were measured on a Bio-logic MDS 450/AE-CD circular dichroic spectrometer (Bio-Logic, Franch). Venusil XBP C4 (Agela Technologies, Tianjin, China; 5 μm，4.6 × 250 mm), Capcell pak C18 AQ (Shiseido Co., Ltd, Tokyo, Japan; 5 μm, 4.6 × 250 mm), Capcell pak C18 MGII (Shiseido Co., Ltd, Tokyo, Japan; 5 μm, 4.6 × 250 mm), Capcell pak C18 UG80 (Shiseido Co., Ltd, Tokyo, Japan; 5 μm，4.6 × 250 mm) were used for analytical HPLC and Venusil XBP C4 (Agela Technologies, Tianjin, China; 5 μm，21.2 × 250 mm), Capcell pak C18 AQ (Shiseido Co., Ltd, Tokyo, Japan; 5 μm, 20 × 250 mm), Capcell pak C18 MGII (Shiseido Co., Ltd, Tokyo, Japan; 5 μm, 20 × 250 mm) and UG80 (Shiseido Co., Ltd, Tokyo, Japan; 5 μm, 20 × 250 mm) were used for preparative HPLC.

2. Cell Lines and Reagents.

Human lung cancer A549, breast cancer MCF-7 and mice microglial BV2 cells were provided by Prof. Zhiyong Xiao and Yuan Luo from Beijing Institute of Pharmacology and Toxicology, Beijing, China, respectively. Fetal bovine serum was obtained from Zhejiang Tianhang Biotechnology Co., Ltd (Zhejiang, China). MTT (lot no. 0793), Roswell Park Memorial Institute (RPMI)-1640 (lot no. RNBJ6706) and dulbecco's modified eagle medium（DMEM) (lot no. RNBJ7482) were purchased from Amresco (Solon, OH, USA) and Sigma-Aldrich (St. Louis, MO, USA), respectively. Penicillin (lot no. 20190905) and streptomycin (lot no. 20190902) were purchased from Sichuan Jishanzhijia Pharmaceutical Co., Ltd (Sichuan, China). 5-Fluorouracil (5-FU, lot no. 5402) was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China).

3. Strains.

The bacterial strain DMG-7-2 was isolated from a mushroom (*Cortinarius lucorum* (Fr.) E. Berger) collected from coniferous forest in the subboreal area of northeast China, and was identified as *Bacillus halotolerans* by Prof. Caihong Dong from the Institute of Microbiology of the Chinese Academy of Sciences, Beijing, China. The 16S sequence of DMG-7-2 had been submitted to genbank

with NCBI Accession No. MW494656. The strain was kept in Institute of Pharmacology and Toxicology, Beijing 100850, People's Republic of China.

4. Fermentation, Extraction and Isolation.

The DMG-7-2 was inoculated into the potato dextrose agar (PDA) plate medium from the PDA slant medium stored at 4 °C and grew at 28 °C for 4 days. Fresh spores formed on the PDA plates were harvested and suspended in 200 ml of sterilized, distilled water with several glass beads in a 250 ml cone-shaped flask and scattered well by shaken enough to prepare a crude spore suspension. Added the spore suspension (1 mL/bottle) to 150 bottles of 500 mL conical flask containing 250 mL of liquid medium (glucose 2%, maltose 1%, mannitol 2%, glutamic acid 1%, peptone 0.5% and yeast extract 0.3% in distilled water), and placed them in shakers for fermentation (28 ℃, 180 rpm, 17 days). The fermented broth was straightly extracted with an equal volume of EtOAc for 5 times to afford an EtOAC extract (20 g). The crude extract was then subjected to Sephadex LH-20 column separation, eluted with 50% EtOH to yield seven fractions (**Fr1**–**Fr7**). **Fr4** (12.3 g) was separated by ODS column chromatography eluted with MeOH/Water (10%, 30%, 50%, 70%, 100%), and 8 fractions (**Fr4-1**–**Fr4-8**) were obtained. **Fr4-6** (2.1 g, eluted by 100% MeOH) was subjected to preparative HPLC (Capcell pak C18 MGII, 20 × 250 mm, 83% CH_3CN–0.1% aq. CF_3COOH, 8 mL/min, detected on 205 nm) to afford **2** (50 mg, t_R = 28.0 min), **6** (70 mg, t_R = 24.0 min) and four other fractions: **Fr4-6-1** (50 mg, t_R = 19.5 min), **Fr4-6-2** (50 mg, t_R = 27.0 min), **Fr4-6-3** (300 mg, t_R = 31.5 min) and **Fr4-6-4** (90 mg, t_R = 36.5 min). **Fr4-6-1** was further separated using preparative HPLC (Capcell pak C18 MGII, 20 × 250 mm, 65% CH_3CN–0.1% aq. CF_3COOH, 8 mL/min, detected on 205 nm) to yield **4** (17 mg, t_R = 118.0 min) and **5** (18 mg, t_R = 123.0 min). **Fr4-6-2** was subjected to preparative HPLC (Venusil XBP C4, 21.2 × 250 mm, 65% CH_3CN–0.1% aq. CF_3COOH, 8 mL/min, detected on 205 nm) to obtain **1** (5 mg, t_R = 82.0 min) and **7** (30 mg, t_R = 89.0 min). **Fr4-6-3** was subjected to preparative HPLC (Capcell pak C18 AQ, 20 × 250 mm, 66% CH_3CN–0.1% aq. CF_3COOH, 8 mL/min, detected on 205 nm) to afford **8** (160 mg, t_R = 119.0 min) and **9** (30 mg, t_R = 123.0 min). **Fr4-6-4** was subjected to preparative HPLC (Capcell pak C18 AQ, 20 × 250 mm, 66% CH_3CN–0.1% aq. CF_3COOH, 8 mL/min, detected on 205 nm) to afford **3** (50 mg, t_R = 95.0 min).

Compound 1 was obtained as colourless solid, $[\alpha]_D^{25}$ = +1.27 (*c* 0.158, acetone); UV (acetone) λ_{max} (log ε): 210 (3.039) nm; ECD (0.655 mM, CH_2Cl_2) λ_{max} ($\Delta\varepsilon$): 224 (+3.53) nm; IR (film) ν_{max}: 3297.2, 2962.3, 2929.4, 2876.0, 2853.4, 2335.6, 1653.4, 1534.2, 1474.6, 1396.5, 1371.9, 1341.1, 1306.1, 1201.3, 1186.9, 1139.7, 1028.7, 1002.0 cm^{-1}; ^1H and ^{13}C NMR data see **Table S2**; negative HR-ESI-MS *m/z*: 992.6294 $[M - H]^-$, calculated: 992.6289 $[M - H]^-$.

Theory and calculation details of the NMR data of 1. The calculations were performed by using the density functional theory (DFT) as carried out in the Gaussian 09. (Frisch et al. 2010) Conformational searches were run by employing the "systematic" procedure implemented in Spartan'14 (Irvine. 2013) using MMFF. During this process, the lowest-energy conformers of **1** and *epi*-**1** both contributed nearly 100%. So, only one conformer for each possible isomer was used for further calculation. The

MMFF minima were reoptimized with DFT calculations at the B3LYP/6-31G(d) level. The stable conformations obtained at the B3LYP/6-31G(d) level were further used in magnetic shielding constants at the B3LYP/6-311++G(2d,p) level (See Table S5–S7 and Figure S1).

Compound 2 was obtained as colourless solid, $[\alpha]_D^{25}$ = –9.34 (*c* 0.107, acetone); positive ESI-MS *m/z*: 1030 $[M + Na]^+$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

Compound 3 was obtained as colourless solid, $[\alpha]_D^{25}$ = –4.76 (*c* 0.105, acetone); negative ESI-MS *m/z*: 1020 $[M - H]^-$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

Compound 4 was obtained as colourless solid, $[\alpha]_D^{25}$ = –27.18 (*c* 0.103, acetone); positive ESI-MS *m/z*: 1008 $[M + H]^+$, 1030 $[M + Na]^+$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

Compound 5 was obtained as colourless solid, $[\alpha]_D^{25}$ = –28.97 (*c* 0.107, acetone); positive ESI-MS *m/z*: 1008 $[M + H]^+$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

Compound 6 was obtained as colourless solid, $[\alpha]_D^{25}$ = –39.79 (*c* 0.098, acetone); positive ESI-MS *m/z*: 1022 $[M + H]^+$, 1044 $[M + Na]^+$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

Compound 7 was obtained as colourless solid, $[\alpha]_D^{25}$ = –30.20 (*c* 0.149, acetone); positive ESI-MS *m/z*: 1044 $[M + Na]^+$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

Compound 8 was obtained as colourless solid, $[\alpha]_D^{25}$ = –39.00 (*c* 0.141, acetone); positive ESI-MS *m/z*: 1036 $[M + H]^+$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

Compound 9 was obtained as colourless solid, $[\alpha]_D^{25}$ = –46.90 (*c* 0.113, acetone); positive ESI-MS *m/z*: 1036 $[M + H]^+$, ^1H and ^{13}C NMR data see **Table S3** and **Table S4**.

5. Acid hydrolysis and Marfey's analysis.

Acid hydrolysis and Marfey's analysis followed the previous method (Wu et al. 2014). Compounds **1**–**9** were taken at 50 μg each in the semi-sealed glass tube, added 100 μL HCl (6 N) and sealed completely, then hydrolyzed in a high temperature oven at 110 °C for 24 hours. After the hydrolysis was completed, removed solvent and placed in a vacuum desiccator for 24 hours to remove residual HCl. Then added 50 μL of distilled water to dissolve the hydrolysate and the amino acid standards (each 50 μg), added 100 μL of L-FDAA (3 mg/mL) acetone solution and 20 μL of $NaHCO_3$ (1 M), and reacted at 45 °C for 1.5 h. After the reaction was completed, 10 μL of HCl (2 M) was added to terminate the reaction. Then, the samples were centrifuged and injected for HPLC analysis (MGII C18 column, 0.8 mL/min, 20% (0 min) → 75% (50 min) CH_3CN-0.1% aq. HCOOH). Marfey's reagent (L-FDAA, lot no. LI90M24) was purchased from J&K Scientific Ltd. (Beijing, China). L-Glu (lot no. BH-00702-110501), D-Glu (lot no. BH-00701-110501), L-Leu (lot no. BH-01302-110501), D-Leu (lot no. BH-01301-110101), L-Asp (lot no. BH-00403-110501) and D-Asp (lot no. BH-00401-110502) were purchased from Shanghai Hanhong Scientific Co., Ltd. (Shanghai, China). L-Val (lot no. 20120816) and D-Val (lot no. LI40O100) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and J&K Scientific Ltd. (Beijing, China), respectively.

6. Antibacterial activity determination.

The antibacterial activity was assayed using the microdilution broth method (CLSI standard,

2017). Inoculated a single bacterial colony in BHI (brain heart infusion) broth and placed it in a shaker at 37 °C to cultivate to the logarithmic growth phase. Adjusted the bacterial turbidity to 0.5 on the McDonald's turbidimeter, and diluted it with Mueller-Hinton Broth (MHB medium) 100 times (about 1.0×10^6 CFUs/mL). Diluted the drug to be tested with the same medium, and added 100 μL to a 96-well plate, and then added 100 μL of the diluted bacterial solution to each well. The 96-well plate was incubated at 37 °C for 18 hours, and the MIC results were read. The lowest drug concentration that could be distinguished by the naked eye that inhibits bacterial growth was the MIC value of the drug. The tested strains were *Staphylococcus aureus* ATCC 29213, *S. aureus* MRSA T144, *Enterococcus faecium* VRE-10, *Escherichia coli* ATCC 25922, *E. coli* B2 (blaNDM-5 + mcr-1) and *Pseudomonas aeruginosa* PAO1 (VRE: vancomycin resistant *Enterococci*; MRSA: methicillin-resistant *Staphylococcus aureus*).

7. MTT assay

The MTT assay was performed according to the previous procedure (Wu et al. 2014). A549, MCF-7 and BV2 cells in exponential growth phase were treated with samples at 37 °C for 48 h. Made three parallel controls for each sample, and measured the OD value was determined at 570 nm by on a VersaMax-AB plus plate reader. The IR% was calculated using the mean value of the OD according to the formula: $IR\% = (OD_{control} - OD_{sample})/OD_{control} \times 100\%$. Compounds **1**–**9** in DMSO/PBS 1:1 at 4, 2, 1, 0.5 mM were used in the MTT assay. 5-FU was dissolved in DMSO/PBS 1:1 at 20 mM as stock solution and diluted by 2 times used in the MTT assay as positive control. DMSO/PBS 1:1 solution was used as blank controls.

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Table S1 The IC_{50} of **1–9** on the tested cell lines (μM, n = 3)

Comp.	A549	MCF-7	BV2
1	14.83 ± 3.05	9.20 ± 1.03	12.19 ± 0.26
2	8.91 ± 3.71	15.25 ± 2.20	12.46 ± 0.20
3	11.08 ± 0.54	9.32 ± 0.33	20.50 ± 14.47
4	20.18 ± 4.75	27.04 ± 1.30	21.96 ± 2.91
5	18.78 ± 4.14	33.00 ± 4.20	27.47 ± 10.08
6	12.20 ± 1.87	20.63 ± 2.30	16.07 ± 5.12
7	16.56 ± 5.59	24.89 ± 0.31	16.82 ± 5.14
8	16.17 ± 9.50	27.59 ±1.75	19.84 ± 11.98
9	15.64 ± 0.31	26.63 ± 6.24	18.68 ± 9.14
5-FU	99.94 ± 37.67	71.49 ± 12.30	0.12 ± 0.02

Table S2 ^{1}H (500 MHz) and ^{13}C NMR (125MHz) Data of **1** in DMSO-d_6[a]

NO.	δ_H (J in Hz)	δ_C	COSY	HMBC (^{1}H–^{13}C)	ROESY
Glu^{1}					
αCH	4.24, m	51.83	Glu^{1}-NH, Glu^{1}-β		Val^{2}-NH
βCH$_2$	1.75, m	27.21	Glu^{1}-α, Glu^{1}-γ		
	1.90, m				
γCH$_2$	2.21, m	30.07	Glu^{1}-β	Glu^{1}-C=O^{2}	
NH	7.82, d (7.2)		Glu^{1}-α	1′-C=O	3′-H, Val^{2}- NH
C=O^{1}		171.22			
C=O^{2}		174.11			
-COO<u>H</u>	12.20, s				
Val^{2}					
αCH	4.04, t (6.6)	59.15	Val^{2}-NH, Val^{2}-β	Glu^{1}-C=O^{1}	Leu^{3}-NH
βCH	1.91, m	29.55	Val^{2}-α, Val^{2}-γ^{1}, Val^{2}-γ^{2}		
γ^{1}CH$_3$	0.88, m	18.66	Val^{2}-β		
γ^{2}CH$_3$	0.83, m	19.06	Val^{2}-β		
NH	7.91, d (6.6)		Val^{2}-α	Glu^{1}-C=O^{1}, Val^{2}-α-C	Leu^{3}-NH, Glu^{1}-α-H, Glu^{1}-NH
C=O		171.18			
Leu^{3}					
αCH	4.25, m	51.41	Leu^{3}-NH, Leu^{3}-β		Val^{4}- NH
βCH$_2$	1.52, m	40.09	Leu^{3}-α, Leu^{3}-γ		
γCH	1.56, m	24.09	Leu^{3}-β, Leu^{3}-δ^{1}, Leu^{3}-δ^{2}		
δ^{1}CH$_3$	0.80, m	21.02	Leu^{3}-γ		
δ^{2}CH$_3$	0.86, m	23.05	Leu^{3}-γ		
NH	8.40, d (7.4)		Leu^{3}-α	Val^{2}-C=O	Val^{2}- NH, Val^{2}-α-H, Val^{4}- NH
C=O		171.81			
Val^{4}					
αCH	4.12, dd (8.8, 7.2)	58.05	Val^{4}-NH, Val^{4}-β		Asp^{5}- NH
βCH	1.94, m	30.72	Val^{4}-α, Val^{4}-γ^{1}, Val^{4}-γ^{2}	Val^{4}-C=O	
γ^{1}CH$_3$	0.73, d (6.3)	17.85	Val^{4}-β		
γ^{2}CH$_3$	0.80, m	19.16	Val^{4}-β		
NH	7.77, d (8.8)		Val^{4}-α	Leu^{3}-C=O	Leu^{3}- NH, Asp^{5}- NH, Leu^{3}-α-H
C=O		170.43			
Asp^{5}					
αCH	4.56, m	49.47	Asp^{5}-NH, Asp^{5}-β	Asp^{5}-C=O^{1}, Asp^{5}-C=O^{2}	Leu^{6}- NH
βCH$_2$	2.57, dd (16.6, 8.6)	36.05	Asp^{5}-α	Asp^{5}-C=O^{1}, Asp^{5}-C=O^{2}	
	2.69, dd (16.6, 5.1)				
NH	8.16, d (7.4)			Val^{4}-C=O	Val^{4}- NH, Val^{4}-α-H, Leu^{6}- NH
C=O^{1}		169.80			
C=O^{2}		171.58			
-COO<u>H</u>	12.20, s				
Leu^{6}					
αCH	4.58, m	50.44	Leu^{6}-NH, Leu^{6}-β		Val^{7}- NH
βCH$_2$	1.40, m	41.90	Leu^{6}-α, Leu^{6}-γ		
γCH	1.53, m	24.12	Leu^{6}-β, Leu^{6}-δ^{1}, Leu^{6}-δ^{2}		
δ^{1}CH$_3$	0.86, m	22.88	Leu^{6}-γ		
δ^{2}CH$_3$	0.82, m	21.90	Leu^{6}-γ		
NH	7.77, d (8.8)		Leu^{6}-α	Asp^{5}-C=O^{1}	Val^{7}- NH, Asp^{5}-α-H, Asp^{5}- NH
C=O		171.79			
Val^{7}					
αCH	4.19, dd (8.4, 5.4)	57.15	Val^{7}-NH, Val^{7}-β		
βCH	2.05, m	29.58	Val^{7}-α, Val^{7}-γ^{1}, Val^{7}-γ^{2}	Val^{7}-C=O	
γ^{1}CH$_3$	0.83, m	17.80	Val^{7}-β		
γ^{2}CH$_3$	0.83, m	18.91	Val^{7}-β		
NH	8.33, d (8.4)		Val^{7}-α	Leu^{6}-C=O, Val^{7}-α-C	Leu^{6}- NH, Leu^{6}-α-H
C=O		170.57			
Fatty acid part					
1′C=O		169.19			
2′CH$_2$	2.36, dd (14.1, 6.5)	40.12	3′	Fatty acid-C=O, 3′-C	
	2.41, dd (14.1, 6.4)				
3′CH	4.99, m	71.63	2′, 4′	Fatty acid-C=O, Val^{7}-C=O	Glu^{1}-NH
4′CH$_2$	1.52, m	33.10	3′, 5′		
5′CH$_2$	1.20, m	24.19	4′, 6′		
6′CH$_2$	1.21, m	28.4–29.2			

7′CH_2	1.21, m	28.4–29.2		
8′CH_2	1.21, m	28.4–29.2		
9′CH_2	1.21, m	28.4–29.2		
10′CH_2	1.21, m	26.67	9′, 11′	
11′CH_2	1.12, m	38.42	10′, 12′	12′-C
12′CH	1.46, m	27.34	11′, 13′, 14′	
13′CH_3	0.83, m	22.48	12′	12′-C
14′CH_3	0.83, m	22.48	12′	12′-C

[a] Signals assignment were based on the results of DEPT, ^{1}H–^{1}H COSY, HSQC, HMBC, TOCSY and ROESY experiments. The δ_H/δ_C values were recorded using the DMSO-d_6 signals (δ_H 2.50/ δ_C 39.52) as the references, respectively.

Table S3 ^{1}H (500 MHz) Data of **2**–**8** in DMSO-d_6[a]

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Glu[1]								
CH	4.20, m	4.20, m	4.14, m	4.15, m	4.16, m	4.16, m	4.16, m	4.17, m
CH_2	1.77, m	1.77, m	1.78, m	1.78, m	1.79, m	1.79, m	1.79, m	1.80, m
	1.92, m	1.92, m	1.92, m	1.92, m	1.92, m	1.92, m	1.92, m	1.93, m
CH_2	2.20, m	2.20, m	2.22, m	2.23, m	2.23, m	2.2, m	2.23, m	2.23, m
NH	7.83, d (6.9)	7.84, d (6.8)	7.81 d (6.1)	7.81, d (6.4)	7.81, d (6.2)	7.81, d (6.1)	7.81, d (6.1)	7.81, d (6.2)
-COO<u>H</u>	12.19, s	12.25, s	12.25, s	12.20, s	12.26, s	12.23, s	12.27, s	12.25, s
Leu[2]								
CH	4.190, m	4.18, m	4.15, m	4.14, m	4.15, m	4.15, m	4.15, m	4.16, m
CH_2	1.42, m	1.43, m	1.49, m	1.48, m	1.47, m	1.48, m	1.49, m	1.48, m
CH	1.51, m	1.51, m	1.45, m	1.47, m	1.52, m	1.52, m	1.48, m	1.49, m
CH_3	0.85, m	0.85, m	0.79, m	0.79, m	0.79, m	0.79, m	0.79, m	0.79, m
CH_3	0.85, m	0.85, m	0.87, m	0.87, m	0.87, m	0.87, m	0.87, m	0.87, m
NH	8.03, d (6.0)	8.03, d (6.1)	7.98, d (6.7)	7.98, d (6.8)	7.92, d (6.4)	7.99, d (6.3)	7.98, d (6.3)	7.98, d (6.3)
Leu[3]								
CH	4.198, m	4.19, m	4.17, m	4.17, m	4.18, m	4.18, m	4.18, m	4.18, m
CH_2	1.53, m	1.52, m	1.53, m	1.55, m	1.55, m	1.51, m	1.55, m	1.55, m
CH	1.56, m	1.56, m	1.60, m	1.61, m	1.58, m	1.58, m	1.56, m	1.61, m
CH_3	0.79, m	0.79, m	0.80, m	0.80, m	0.80, m	0.80, m	0.80, m	0.80, m
CH_3	0.87, m	0.87, m	0.86, m	0.86, m	0.86, m	0.86, m	0.86, m	0.86, m
NH	8.32, d (7.4)	8.32, d (7.4)	8.11, d (overlapped)	8.13, d (overlapped)	8.12, d (overlapped)	8.12, d (overlapped)	8.12, d (overlapped)	8.13, d (overlapped)
Val[4]								
CH	4.10, m	4.08, m	4.03, m	4.03, m	4.03, m	4.03, m	4.03, m	4.03, m
CH	1.95, m	1.95, m	2.00, m	2.00, m	2.00, m	2.00, m	2.01, m	1.99, m
CH_3	0.75, m	0.75, m	0.80, m	0.78, m	0.79, m	0.79, m	0.79, m	0.79, m
CH_3	0.83, m	0.83, m	0.84, m	0.84, m	0.85, m	0.83, m	0.85, m	0.85, m
NH	7.80, d (8.5)	7.80, d (8.5)	8.02, d (8.6)	8.03, d (8.3)	8.03, d (8.4)	8.03, d (8.8)	8.03, d (9.1)	8.03, d (8.8)
Asp[5]								
CH	4.52, m	4.53, m	4.54, m	4.54, m	4.53, m	4.54, m	4.54, m	4.54, m
CH_2	2.59, dd (16.7, 9.0)	2.59, dd (16.7, 9.0)	2.58, dd (16.7, 9.2)	2.58, dd (16.7, 9.3)	2.59, dd (16.7, 9.3)	2.58, dd (16.7, 9.3)	2.58, dd (16.7, 9.3)	2.59, dd (16.7, 9.3)
	2.70, dd (16.7, 4.9)	2.70, dd (16.7, 4.9)	2.73, dd (16.7 4.7)	2.73, dd (16.7, 4.7)	2.73, dd (16.7, 4.8)	2.73, dd (16.7, 4.8)	2.73, dd (16.7, 4.8)	2.73, dd (16.7, 4.7)
NH	8.17, d (7.4)	8.18 d (7.3)	8.13, d (overlapped)	8.12, d (overlapped)	8.11, d (overlapped)	8.11, d (overlapped)	8.11, d (overlapped)	8.11, d (overlapped)
-COO<u>H</u>	12.19, s	12.25, s	12.25, s	12.20, s	12.26, s	12.23, s	12.27, s	12.25, s
Leu[6]								
CH	4.53, m	4.53, m	4.35, m	4.35, m	4.36, m	4.37, m	4.35, m	4.36, m
CH_2	1.40, m	1.43, m	1.38, m	1.40, m	1.40, m	1.38, m	1.40, m	1.40, m
			1.48, m	1.47, m	1.48, m	1.48, m	1.48, m	1.48, m

CH	1.50, m	1.52, m	1.51, m	1.53, m	1.53, m	1.54, m	1.53, m	1.51, m
CH_3	0.81, m	0.81, m	0.81, m	0.81, m	0.81, m	0.81, m	0.81, m	0.81, m
CH_3	0.85, m	0.85, m	0.85, m	0.85, m	0.85, m	0.85, m	0.85, m	0.85, m
NH	7.69, d (8.6)	7.69, d (8.5)	7.62, d (8.5)	7.62, d (8.4)	7.61, d (8.5)	7.62, d (8.5)	7.61, d (8.5)	7.61, d (8.5)
Val[7]								
CH	4.08, m	4.09, m						
CH	2.07, m	2.07, m						
CH_3	0.84, m	0.84, m						
CH_3	0.86, m	0.86, m						
NH	8.29, d (8.2)	8.29, d (8.1)						
Leu[7]								
CH			4.07, m	4.08, m	4.08, m	4.07, m	4.08, m	4.07, m
CH_2			1.53, m 1.64, m	1.53, m 1.63, m	1.54, m 1.64, m	1.54, m 1.65, m	1.54, m 1.65, m	1.55, m 1.64, m
CH			1.56, m	1.55, m	1.55, m	1.55, m	1.59, m	1.55, m
CH_3			0.80, m	0.80, m	0.80, m	0.80, m	0.80, m	0.80, m
CH_3			0.86, m	0.86, m	0.86, m	0.86, m	0.86, m	0.86, m
NH			8.42, d (7.3)	8.42, d (7.3)	8.42, d (7.3)	8.43, d (7.4)	8.42, d (7.3)	8.42, d (7.3)
Fatty acid part								
2′	2.39, dd (14.4, 6.6) 2.45, dd (14.4, 6.1)	2.39, dd (14.4, 6.6) 2.44, dd (14.4, 6.1)	2.32, dd (14.6, 7.3) 2.50, m	2.32, dd (14.6, 7.3) 2.49, m	2.32, dd (14.6, 7.4) 2.49, m	2.32, dd (14.6, 7.4) 2.48, m	2.32, dd (14.6, 7.4) 2.48, m	2.31, dd (14.6, 7.4) 2.48, m
3′	5.01, m	5.01, m	5.06, m	5.06, m	5.06, m	5.06, m	5.06, m	5.06, m
4′	1.55, m	1.53, m	1.53, m	1.52, m	1.52, m	1.51, m	1.53, m	1.51, m
5′	1.21, m	1.20, m	1.22, m	1.22, m	1.21, m	1.21, m	1.23, m	1.22, m
6′	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m
7′	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m
8′	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m	1.21, m
9′	1.21, m	1.21, m	1.04, m 1.23, m	1.20, m	1.21, m	1.21, m	1.21, m	1.21, m
10′	1.22, m	1.21, m	1.27, m	1.11, m	1.21, m	1.21, m	1.22, m	1.21, m
11′	1.12, m	1.04, m 1.24, m	1.09, m 1.28, m	1.48, m	1.11, m	1.21, m	1.05, m 1.25, m	1.22, m
12′	1.48, m	1.26, m	0.81, m	0.81, m	1.49, m	1.21, m	1.27, m	1.12, m
13′	0.83, m	1.09, m 1.30, m	0.86, m	0.81, m	0.83, m	1.22, m	1.09, m 1.30, m	1.47, m
14′	0.83, m	0.81, m			0.83, m	0.83, m	0.82, m	0.83, m
15′		0.83, m					0.81, m	0.83, m

[a] Signals assignment were based on the results of DEPT, ^{1}H–^{1}H COSY, HSQC, HMBC and ROESY experiments. The δ_H values were recorded using the DMSO-d_6 signals (δ_H 2.50) as the references, respectively.

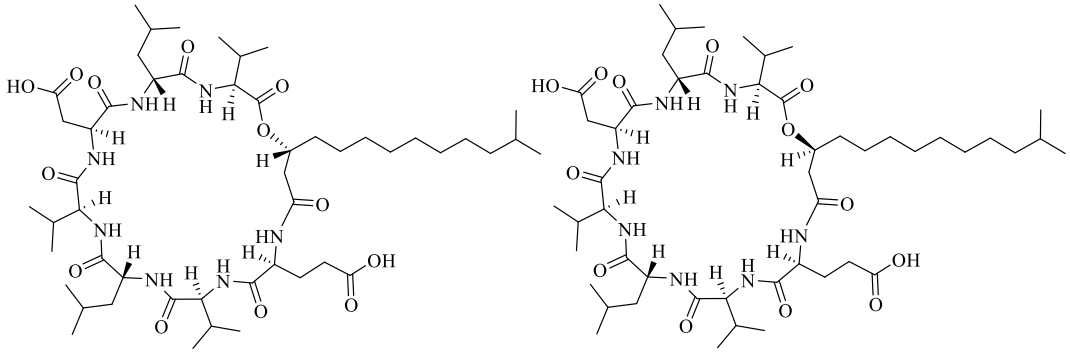
Table S4 ^{13}C NMR (125MHz) Data of **2**–**8** in DMSO-d_6[a]

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Glu[1]								
CH	52.01	52.02	52.46	52.49	52.48	52.49	52.47	52.48
CH_2	27.11	27.11	27.08	27.10	27.08	27.08	27.07	27.09
CH_2	29.87	29.87	29.72	29.74	29.74	29.75	29.74	29.75
C=O[1]	171.01	171.02	171.02	171.03	171.04	171.05	171.04	171.04
C=O[2]	174.04	174.03	173.90	173.92	173.94	173.92	173.93	173.93
Leu[2]								
CH	52.05	52.03	51.87	51.89	51.92	51.88	51.90	51.92
CH_2	39.58	39.62	39.32	39.32	39.30	39.33	39.32	39.31
CH	24.20	24.23	24.22	24.24	24.25	24.25	24.25	24.25
CH_3	22.06	22.05	21.20	21.22	21.24	21.22	21.23	21.23
CH_3	23.02	23.02	22.89	22.91	22.91	22.90	22.90	22.91
C=O	172.22	172.22	172.60	172.64	172.67	172.65	172.66	172.66
Leu[3]								
CH	51.70	51.70	51.79	51.82	51.81	51.80	51.80	51.81
CH_2	39.65	39.68	38.86	38.88	38.86	38.86	38.86	38.86
CH	24.23	24.19	24.22	24.24	24.25	24.25	24.25	24.25
CH_3	21.06	21.09	21.61	21.63	21.63	21.63	21.62	21.63
CH_3	22.89	22.89	22.96	22.98	22.98	22.97	22.98	22.98
C=O	172.17	172.17	172.87	172.91	172.94	172.92	172.94	172.94
Val[4]								
CH	58.22	58.22	58.58	58.60	58.62	58.59	58.62	58.63
CH	30.46	30.46	30.07	30.08	30.09	30.07	30.07	30.07
CH_3	17.93	17.93	17.89	17.89	17.90	17.90	17.90	17.91
CH_3	19.12	19.13	19.02	19.00	19.05	19.05	19.05	19.05
C=O	170.60	170.60	170.71	170.74	170.75	170.75	170.74	170.75
Asp[5]								
CH	49.63	49.63	49.60	49.63	49.64	49.63	49.63	49.64
CH_2	35.96	35.97	35.72	35.73	35.74	35.72	35.72	35.72
C=O[1]	169.92	169.93	169.92	169.94	169.95	169.94	169.95	169.95
C=O[2]	171.65	171.64	171.65	171.68	171.70	171.68	171.69	171.69
Leu[6]								
CH	50.59	50.59	50.78	50.79	50.80	50.79	50.80	50.81
CH_2	41.62	41.62	41.54	41.56	41.59	41.57	41.58	41.57
CH	24.11	24.10	24.00	24.03	24.02	24.02	24.03	24.02
CH_3	21.88	21.87	21.04	21.06	21.07	21.06	21.06	21.07
CH_3	22.54	22.54	22.63	22.64	22.66	22.64	22.65	22.65
C=O	171.81	171.82	171.54	171.56	171.57	171.58	171.56	171.58
Val[7]								
CH	57.39	57.40						
CH	29.36	29.39						
CH_3	18.02	18.03						
CH_3	19.17	19.17						
C=O	170.68	170.67						
Leu[7]								
CH			50.77	50.80	50.80	50.79	50.80	50.81
CH_2			38.76	38.88	38.80	38.79	38.79	38.76
CH			24.18	24.20	24.21	24.20	24.21	24.21
CH_3			21.62	21.65	21.66	21.64	21.65	21.65
CH_3			22.84	22.86	22.87	22.85	22.86	22.86
C=O			171.84	171.88	171.89	171.88	171.88	171.89
Fatty acid part								
1′	169.45	169.45	169.92	169.94	169.95	169.94	169.95	169.95
2′	40.41	40.40	41.19	41.15	41.16	41.14	41.15	41.16
3′	71.52	71.52	71.42	71.41	71.42	71.41	71.41	71.42
4′	33.23	33.23	33.55	33.58	33.58	33.57	33.57	33.59
5′	24.37	24.36	24.27	24.28	24.28	24.28	24.27	24.28
6′	28.5–29.0	28.5–29.0	28.6–29.1	28.5–29.2	28.5–29.2	28.5–29.2	28.5–29.3	28.5–29.2
7′	28.5–29.0	28.5–29.0	28.6–29.1	28.5–29.2	28.5–29.2	28.5–29.2	28.5–29.3	28.5–29.2
8′	28.5–29.0	28.5–29.0	26.29	28.5–29.2	28.5–29.2	28.5–29.2	28.5–29.3	28.5–29.2
9′	29.24	28.5–29.0	35.91	26.72	28.5–29.2	28.5–29.2	28.5–29.3	28.5–29.2
10′	26.74	26.43	33.68	38.42	26.76	28.5–29.2	26.44	28.5–29.2

11′	38.44	35.96	28.87	27.34	38.45	28.5–29.2	35.98.	26.75
12′	27.36	33.68	11.17	22.48	27.36	31.25	33.71	38.46
13′	22.48	28.87	19.02	22.48	22.47	22.05	28.88	27.35
14′	22.48	11.16			22.47	13.89	11.15	22.48
15′		19.05					19.05	22.48

[a] Signals assignment were based on the results of DEPT, ^{1}H–^{1}H COSY, HSQC, HMBC and ROESY experiments. The δ_C values were recorded using the DMSO-d_6 signals (δ_C 39.52) as the references, respectively.

NMR data calculation of 1:



1 *epi*-**1**

Table S5. DFT-optimized structures for the lowest-energy conformers of **1** and *epi*-**1**

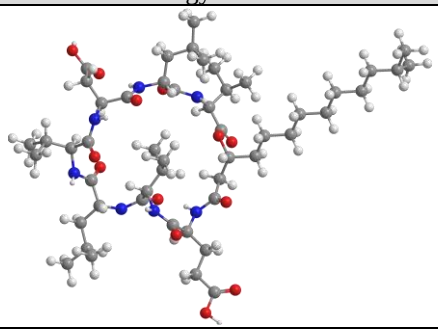
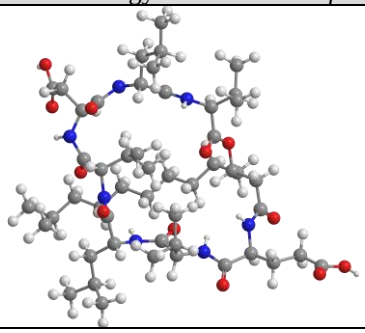
	Lowest-energy conformer for **1**	Lowest-energy conformer for *epi*-**1**
DFT-optimized structure		
Population	100%	100%
Total energy (a.u.)	-3320.12336263	-3320.08760875

Table S6. Optimized Z-matrixes of **1** and *epi*-**1** in the gas phase (Å) at B3LYP/6-31G(d) level

1				*epi*-**1**			
N	-4.05753	-1.10473	-0.61431	N	-4.72541	1.3966	1.17838
N	-2.35421	1.93875	0.32536	N	-1.96251	3.73658	1.65907
O	0.23855	2.03846	0.3662	O	0.88519	3.98512	-0.56641
N	3.56156	0.20305	-2.19173	N	4.93386	2.17389	0.19002
N	2.83222	-2.86117	-2.30463	N	4.58949	-0.49271	0.25962
N	1.36662	-2.15831	-5.12525	N	1.88224	-2.89557	-0.27531
N	-1.33874	-4.64925	-4.89406	N	-0.79962	-2.75456	0.57035
N	-3.19522	-4.47486	-1.73803	N	-4.42251	-2.17542	0.251
O	0.44505	4.03534	-0.74843	O	0.75678	2.78825	1.38839
O	-3.84477	1.50695	-1.36211	O	-3.21967	3.09672	-0.14497
O	-3.02947	-2.89027	0.36979	O	-4.55478	-0.39679	2.60238
O	-1.19183	-5.29958	-2.31851	O	-2.80691	-2.89443	-1.12186
O	-1.32979	-2.36139	-4.95353	O	0.02003	-3.22583	2.65165
O	1.70203	-0.2873	-3.9594	O	2.52734	-0.95608	-1.04599
O	4.84064	-3.04611	-1.44238	O	6.66827	-0.77879	1.15132
O	4.10808	0.43593	0.02371	O	5.22963	3.39528	-1.71662
O	9.24139	-1.73733	-3.30763	O	9.73324	4.70128	0.14804
O	8.73071	0.00767	-2.02129	O	9.4643	3.475	1.98926
O	-7.70229	-2.94787	-2.26791	O	-8.34305	-0.86355	-1.36464
O	-6.05985	-1.46573	-2.56824	O	-6.49202	-1.95156	-1.97547
H	4.40581	-0.96729	-3.6168	H	6.39458	1.26217	-1.02056
H	0.88548	-3.19899	-2.77185	H	4.58969	-2.53317	0.68549
H	-3.14422	-3.74592	-4.35295	H	-2.32001	-2.32945	1.95227
H	-3.82723	-2.70691	-2.70001	H	-4.73252	-0.3339	-0.63899
H	-2.0542	3.13606	-1.35628	H	-1.40284	4.64401	-0.13205

H	1.24165	-4.17425	-4.58082	H	2.20206	-3.94829	1.49281
H	-2.79385	-0.52177	0.93415	H	-3.4347	1.80783	2.77828
C	-3.30594	1.17096	-0.309	C	-3.0243	3.08561	1.07238
C	-3.67846	-0.13736	0.41763	C	-4.00764	2.35937	2.03077
C	-0.24647	3.14687	-0.26831	C	0.30727	3.62303	0.61323
C	-1.78966	3.14739	-0.29129	C	-0.96291	4.46224	0.85704
C	4.03537	-2.29002	-1.99916	C	5.85569	-0.06746	0.5714
C	4.46626	-0.89096	-2.52275	C	6.15572	1.35896	0.04556
C	1.50216	-1.50506	-3.92855	C	2.71952	-1.83454	-0.18731
C	1.50318	-2.31109	-2.6056	C	3.90841	-1.68529	0.81369
C	-0.71987	-3.42395	-5.05573	C	0.16154	-3.22842	1.43234
C	0.80498	-3.49566	-5.3191	C	1.42152	-3.83184	0.7489
C	-2.26834	-4.81507	-2.68211	C	-3.09177	-2.34888	-0.04974
C	-2.62102	-4.69041	-4.18447	C	-1.98593	-1.97668	0.96941
C	-3.65568	-2.41374	-0.57751	C	-4.76262	0.04599	1.47799
C	-4.05772	-3.27832	-1.79677	C	-5.08483	-0.84978	0.26444
C	1.67799	1.85977	0.49005	C	2.06334	3.25919	-1.00709
C	2.3718	1.84858	-0.88106	C	3.30302	3.89735	-0.37223
C	3.43752	0.76866	-0.9457	C	4.57671	3.14845	-0.70798
C	2.29489	2.87026	1.47082	C	2.08608	3.37882	-2.54529
C	5.92574	-0.54536	-2.16878	C	7.34472	1.97359	0.7945
C	6.93224	-1.31462	-3.02823	C	7.8398	3.28033	0.17501
C	8.34883	-0.92642	-2.70398	C	9.06964	3.78448	0.87829
C	0.84491	-1.59279	-1.40743	C	3.64629	-1.39528	2.31241
C	1.0703	-4.01734	-6.73808	C	1.0661	-5.1927	0.13065
C	2.56203	-4.12318	-7.11639	C	2.24799	-5.92173	-0.54123
C	3.33268	-5.07147	-6.19674	C	3.38119	-6.22861	0.43879
C	-3.52937	-5.8501	-4.64479	C	-1.6649	-0.468	0.99424
C	-2.86215	-7.22673	-4.56295	C	-0.65169	-0.02006	-0.05487
C	-4.03608	-5.60451	-6.06933	C	-1.24732	-0.02192	2.39618
C	-5.52687	-3.67479	-1.69847	C	-6.61339	-0.99159	0.24782
C	-6.40944	-2.58037	-2.22048	C	-7.09904	-1.31623	-1.13077
C	-4.84467	0.06429	1.39422	C	-5.00788	3.32366	2.67752
C	-4.5312	0.90594	2.6467	C	-4.44656	4.21788	3.80084
C	-5.80755	1.09439	3.47243	C	-5.54064	5.16939	4.29493
C	-3.44474	0.27683	3.51985	C	-3.89904	3.41002	4.9782
C	-2.33924	4.44071	0.35462	C	-0.58193	5.82192	1.48789
C	-3.84382	4.59683	0.11512	C	-1.74317	6.81573	1.38973
C	-2.03482	4.53816	1.8527	C	-0.11172	5.70991	2.94157
C	2.6941	-4.58975	-8.5686	C	1.75465	-7.22153	-1.18291
H	1.7722	0.86405	0.9412	H	1.98736	2.20593	-0.71385
C	0.72022	-2.52403	-0.19358	C	3.54775	-2.62641	3.20971
C	-0.54299	-1.05298	-1.76038	C	2.47711	-0.4454	2.53573
C	1.68848	2.75757	2.87379	C	0.8938	2.70425	-3.24051
C	2.28006	3.80848	3.81467	C	1.02189	1.18122	-3.24885
C	1.67122	3.71324	5.21436	C	-0.18782	0.50437	-3.89336
C	2.25906	4.77508	6.14529	C	-0.02573	-1.01757	-3.88293
C	1.65238	4.68844	7.5466	C	-1.30421	-1.72516	-4.33059
C	2.24093	5.75614	8.47243	C	-1.15727	-3.2447	-4.21859
C	1.63037	5.67356	9.87458	C	-2.45431	-3.95816	-4.60965
C	2.27447	6.64446	10.88166	C	-2.34497	-5.49347	-4.56544
C	2.0609	8.10996	10.49985	C	-2.09262	-6.02005	-3.15146
C	1.711	6.38888	12.28176	C	-3.62327	-6.12039	-5.12746
H	-4.53337	-0.73055	-1.44012	H	-4.76776	1.67914	0.20091
H	-1.79709	1.51338	1.05871	H	-1.6597	3.40737	2.56965
H	2.86968	0.43718	-2.90564	H	4.39622	2.05741	1.04237
H	2.80329	-3.77778	-1.87133	H	4.03406	0.08409	-0.3722
H	1.22704	-1.49737	-5.882	H	1.2287	-2.73293	-1.03197

H	-0.72101	-5.42158	-4.66329	H	-0.75874	-2.98932	-0.41592
H	-2.81706	-4.63317	-0.8025	H	-4.89345	-2.74016	-0.45392
H	10.1075	3 -1.3849	7 -3.01388	H	10.49399	4.95096	0.71296
H	-8.18022	-2.16206	-2.61049	H	-8.55765	-1.17017	-2.27182
H	2.85718	2.80773	-1.09377	H	3.41484	4.93948	-0.69611
H	1.63358	1.67115	-1.6717	H	3.19038	3.94815	0.71753
H	2.14812	3.89277	1.10578	H	2.06159	4.44324	-2.81315
H	3.37743	2.70611	1.5334	H	3.01179	2.9631	-2.95635
H	6.09387	0.52972	-2.31862	H	7.07335	2.143	1.84515
H	6.12594	-0.74258	-1.10822	H	8.17807	1.25879	0.80918
H	6.83097	-2.39181	-2.86503	H	8.08723	3.11343	-0.87923
H	6.76134	-1.10084	-4.08906	H	7.07847	4.06268	0.2472
H	1.4503	-0.74911	-1.09402	H	4.52865	-0.86742	2.70059
H	0.59879	-5.00185	-6.85725	H	0.6392	-5.83589	0.91197
H	0.56985	-3.35593	-7.45887	H	0.2723	-5.0597	-0.61654
H	3.02172	-3.12965	-7.04627	H	2.64993	-5.28975	-1.34276
H	4.36629	-5.1903	-6.5395	H	4.16392	-6.82219	-0.04597
H	3.37558	-4.68713	-5.17314	H	3.85336	-5.31132	0.80283
H	2.86921	-6.06343	-6.17113	H	3.01638	-6.79286	1.30361
H	-4.40758	-5.87719	-3.98704	H	-2.55574	0.08797	0.73103
H	-3.57136	-8.01198	-4.84731	H	-0.66441	1.06859	-0.15654
H	-2.52415	-7.4464	-3.54573	H	-0.89924	-0.43618	-1.0344
H	-2.00109	-7.30216	-5.23491	H	0.36366	-0.31175	0.21177
H	-4.74074	-6.38725	-6.37002	H	-0.98369	1.03816	2.41376
H	-4.55857	-4.64435	-6.13617	H	-2.05794	-0.17378	3.11439
H	-3.21435	-5.59607	-6.79323	H	-0.39486	-0.58745	2.7689
H	-5.71405	-4.56524	-2.30955	H	-6.95184	-1.77835	0.93126
H	-5.81223	-3.89249	-0.66317	H	-7.08681	-0.05006	0.55303
H	-5.67855	0.53425	0.85437	H	-5.43763	3.96595	1.89649
H	-5.21275	-0.91991	1.71563	H	-5.84686	2.74163	3.08371
H	-4.19511	1.90156	2.33915	H	-3.63608	4.83641	3.40341
H	-5.61526	1.72356	4.34805	H	-5.15143	5.84349	5.06541
H	-6.58718	1.5823	2.87782	H	-5.9189	5.78728	3.47362
H	-6.1995	0.13405	3.82451	H	-6.38494	4.61773	4.72233
H	-3.3027	0.85553	4.43904	H	-3.59528	4.07287	5.79578
H	-2.48007	0.25059	3.00547	H	-3.01641	2.83121	4.69111
H	-3.70805	-0.74763	3.80376	H	-4.65165	2.71652	5.36813
H	-1.84844	5.29583	-0.12962	H	0.25189	6.24401	0.91058
H	-4.19216	5.56932	0.4797	H	-1.44389	7.79855	1.76945
H	-4.07595	4.54104	-0.95355	H	-2.05775	6.94425	0.34867
H	-4.42059	3.82346	0.63224	H	-2.6109	6.48361	1.96767
H	-2.42817	5.47373	2.26494	H	0.21891	6.68671	3.31162
H	-0.9565	4.53122	2.03596	H	0.73394	5.02183	3.03475
H	-2.48269	3.71304	2.41479	H	-0.91181	5.36205	3.60303
H	3.74617	-4.6311	-8.87008	H	2.5725	-7.73637	-1.69821
H	2.18074	-3.90021	-9.24709	H	0.9726	-7.01885	-1.92197
H	2.2625	-5.58695	-8.70702	H	1.34362	-7.90489	-0.432
H	0.2381	-2.00701	0.6435	H	3.84508	-2.36349	4.23215
H	1.70265	-2.85826	0.15433	H	4.21489	-3.42608	2.87402
H	0.12142	-3.40964	-0.43117	H	2.53032	-3.00998	3.28614
H	-1.00599	-0.59761	-0.88101	H	2.3455	-0.2249	3.60011
H	-0.4952	-0.27958	-2.53218	H	2.62829	0.50509	2.01442
H	-1.19867	-1.85196	-2.11803	H	1.5576	-0.8911	2.16487
H	1.87968	1.75484	3.2748	H	-0.04741	3.00501	-2.7664
H	0.60126	2.88228	2.82725	H	0.85155	3.05799	-4.27813
H	2.09913	4.80981	3.40497	H	1.93473	0.89177	-3.78345
H	3.36708	3.676	3.8764	H	1.12131	0.8186	-2.22307
H	1.8571	2.71527	5.62946	H	-1.09459	0.78586	-3.34438

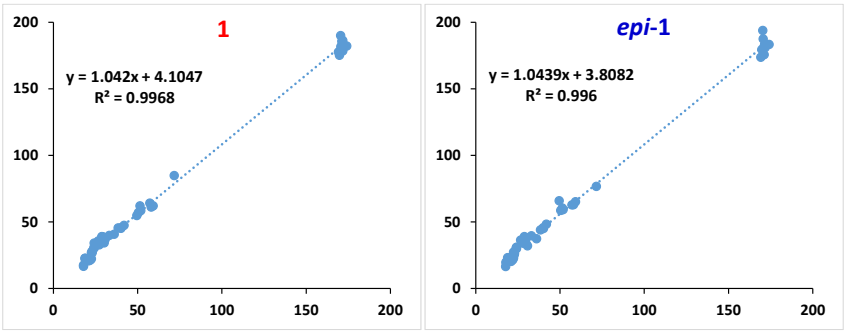
H	0.58363	3.84078	5.15173	H	-0.31095	0.85519	-4.92477
H	2.07465	5.7721	5.72688	H	0.80567	-1.3026	-4.53909
H	3.34663	4.64718	6.20771	H	0.23771	-1.35454	-2.87387
H	1.83964	3.69277	7.96666	H	-2.14408	-1.39425	-3.70744
H	0.56463	4.81493	7.48517	H	-1.53805	-1.44742	-5.36522
H	2.05468	6.74484	8.03871	H	-0.33982	-3.58385	-4.86605
H	3.328	5.62667	8.53654	H	-0.88267	-3.49909	-3.18908
H	1.74754	4.6482	10.24856	H	-3.26753	-3.62681	-3.95136
H	0.55119	5.86378	9.81347	H	-2.72943	-3.64999	-5.62662
H	3.35439	6.45221	10.9145	H	-1.50856	-5.80602	-5.2033
H	2.46852	8.77486	11.26914	H	-2.08531	-7.11539	-3.14068
H	2.56635	8.35534	9.56106	H	-1.12332	-5.68792	-2.76912
H	0.99612	8.33937	10.38528	H	-2.86832	-5.68092	-2.45664
H	2.18654	7.0448	13.01873	H	-3.54915	-7.21303	-5.13819
H	1.89263	5.35436	12.59187	H	-3.79965	-5.78936	-6.15638
H	0.63097	6.56861	12.31466	H	-4.49779	-5.84557	-4.52778

Table S7. The calculated ^{13}C NMR data for isomers of **1**

***δ*exp**	***δ*cal**		***δ*scal**		**corrected error**	
	1	***epi*-1**	**1**	***epi*-1**	**1**	***epi*-1**
51.83	58.44	59.20	52.15	53.07	0.32	1.24
27.21	32.78	34.36	27.52	29.27	0.31	2.06
30.07	34.15	33.35	28.84	28.30	-1.23	-1.77
171.22	182.27	175.59	170.98	164.56	-0.24	-6.66
174.11	182.10	183.36	170.82	172.00	-3.29	-2.11
59.15	62.03	65.18	55.59	58.79	-3.56	-0.36
29.55	36.14	38.09	30.75	32.84	1.20	3.29
18.66	22.74	21.02	17.88	16.49	-0.78	-2.17
19.06	21.17	22.35	16.38	17.76	-2.68	-1.30
171.18	185.67	181.81	174.25	170.51	3.07	-0.67
51.41	62.03	60.42	55.59	54.23	4.18	2.82
40.09	45.20	45.56	39.44	40.00	-0.65	-0.09
24.09	30.85	30.42	25.67	25.49	1.58	1.40
21.02	20.81	20.36	16.03	15.85	-4.99	-5.17
23.05	26.84	26.23	21.82	21.48	-1.23	-1.57
171.81	186.18	180.94	174.74	169.68	2.93	-2.13
58.05	61.14	62.92	54.74	56.63	-3.31	-1.42
30.72	36.89	32.00	31.47	27.00	0.75	-3.72
17.85	16.58	19.53	11.98	15.06	-5.87	-2.79
19.16	22.32	22.00	17.48	17.42	-1.68	-1.74
170.43	189.93	193.77	178.34	181.97	7.91	11.54
49.47	54.83	65.82	48.68	59.40	-0.79	9.93
36.05	40.71	37.36	35.13	32.14	-0.92	-3.91
169.80	175.10	179.48	164.10	168.28	-5.70	-1.52
171.58	182.63	183.49	171.33	172.12	-0.25	0.54
50.44	57.02	58.59	50.78	52.48	0.34	2.04
41.90	47.32	48.29	41.47	42.61	-0.43	0.71
24.12	30.25	31.02	25.09	26.07	0.97	1.95
22.88	27.85	25.54	22.79	20.82	-0.09	-2.06
21.90	21.40	21.42	16.60	16.87	-5.30	-5.03
171.79	178.41	182.49	167.28	171.17	-4.51	-0.62
57.15	64.09	62.75	57.57	56.46	0.42	-0.69
29.58	38.38	36.63	32.89	31.44	3.31	1.86

17.80	17.46	16.49	12.81	12.15	-4.99	-5.65
18.91	22.45	23.11	17.61	18.49	-1.30	-0.42
170.57	181.73	187.41	170.47	175.88	-0.10	5.31
169.19	177.70	173.71	166.59	162.75	-2.60	-6.44
40.12	45.58	44.95	39.80	39.41	-0.32	-0.71
71.63	84.80	76.59	77.44	69.72	5.81	-1.91
33.10	39.80	39.53	34.26	34.22	1.16	1.12
24.19	34.09	29.93	28.77	25.02	4.58	0.83
28.47	37.33	33.96	31.89	28.88	3.42	0.41
29.21	38.80	38.22	33.29	32.96	4.08	3.75
28.90	38.62	38.99	33.13	33.71	4.23	4.81
28.74	38.97	37.61	33.46	32.38	4.72	3.64
26.67	35.61	36.28	30.24	31.10	3.57	4.43
38.42	45.41	43.94	39.64	38.44	1.22	0.02
27.34	35.26	35.65	29.90	30.50	2.56	3.16
22.48	22.27	22.86	17.43	18.25	-5.05	-4.23
22.48	26.77	27.22	21.75	22.43	-0.73	-0.05

(a)



(b)

DP4+ probability of ^{13}C NMR of 1		
Plausible isomer	**1**	***epi*-1**
DP4+	99.93%	0.07%

Figure S1. ^{13}C NMR calculation results of two plausible epimers (**1** and *epi*-**1**) at the B3LYP/6-311++G(2d,p) level. (a) Linear correlation plots of calculated and experimental ^{13}C values. (b) DP4+ probability of ^{13}C values of **1**.

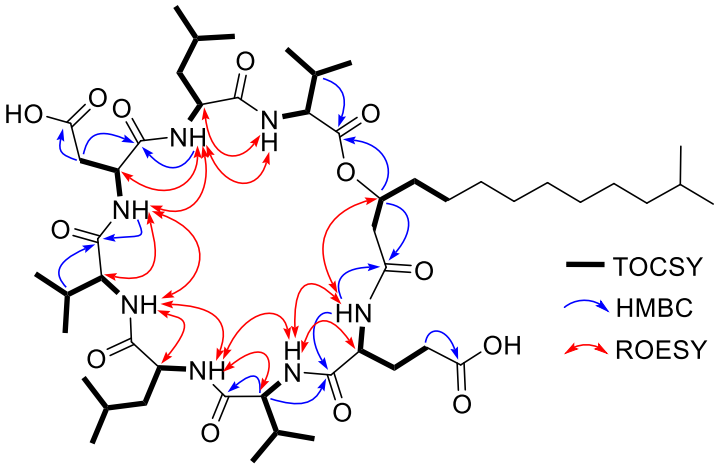


Figure S2. Key HMBC, TOCSY and ROESY correlations of compound **1**

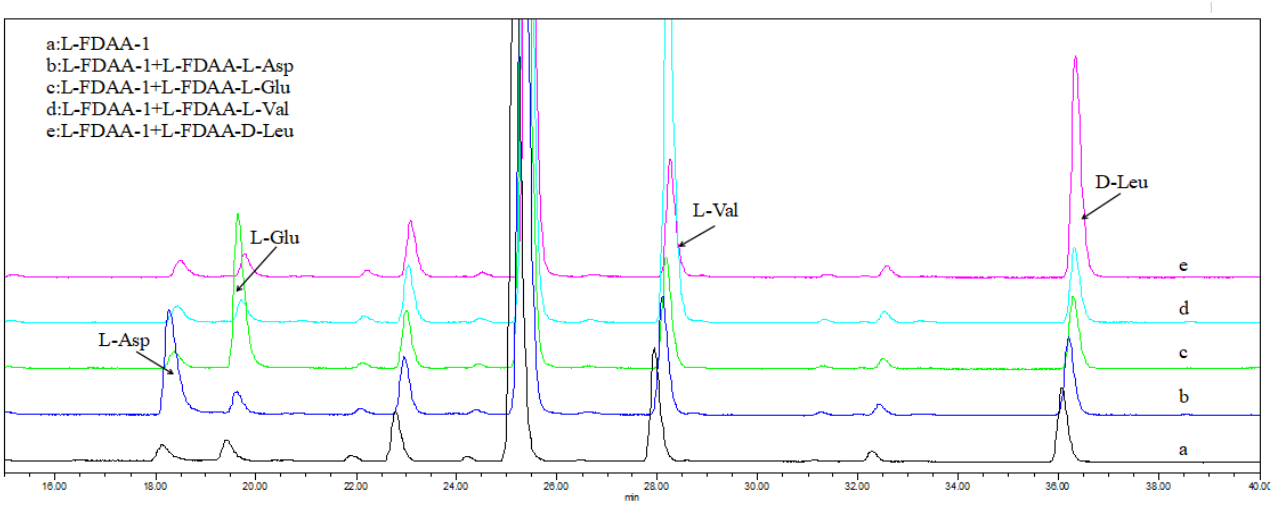


Figure S3. Marfey's analysis result of compound **1**

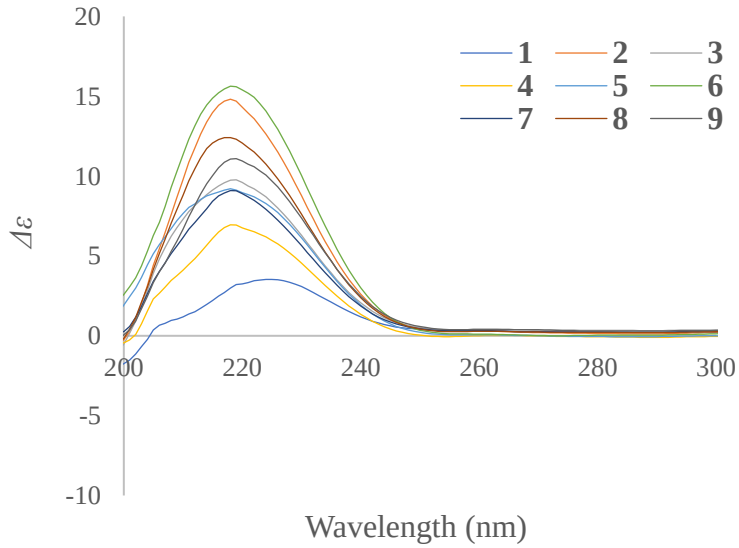


Figure S4. ECD spectra of compounds **1**–**9** in CH_2Cl_2

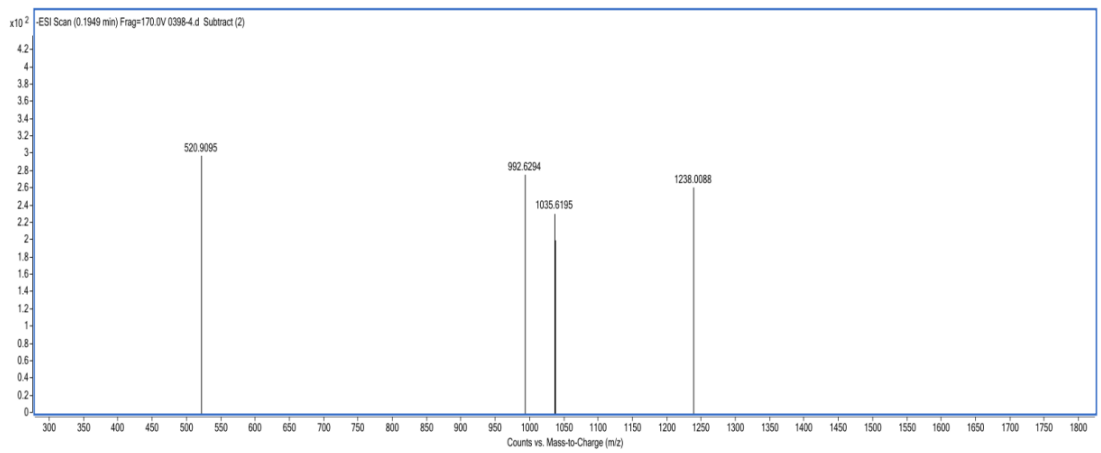


Figure S5 A. Negative HRESIMS spectrum of compound **1**

Figure S5 B. IR spectrum of compound **1**

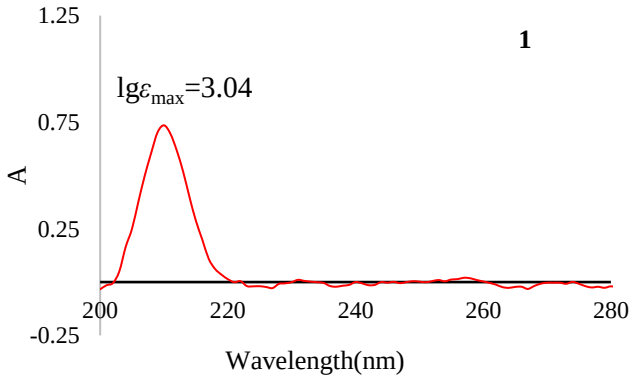


Figure S5 C. UV spectrum of compound **1** in acetone

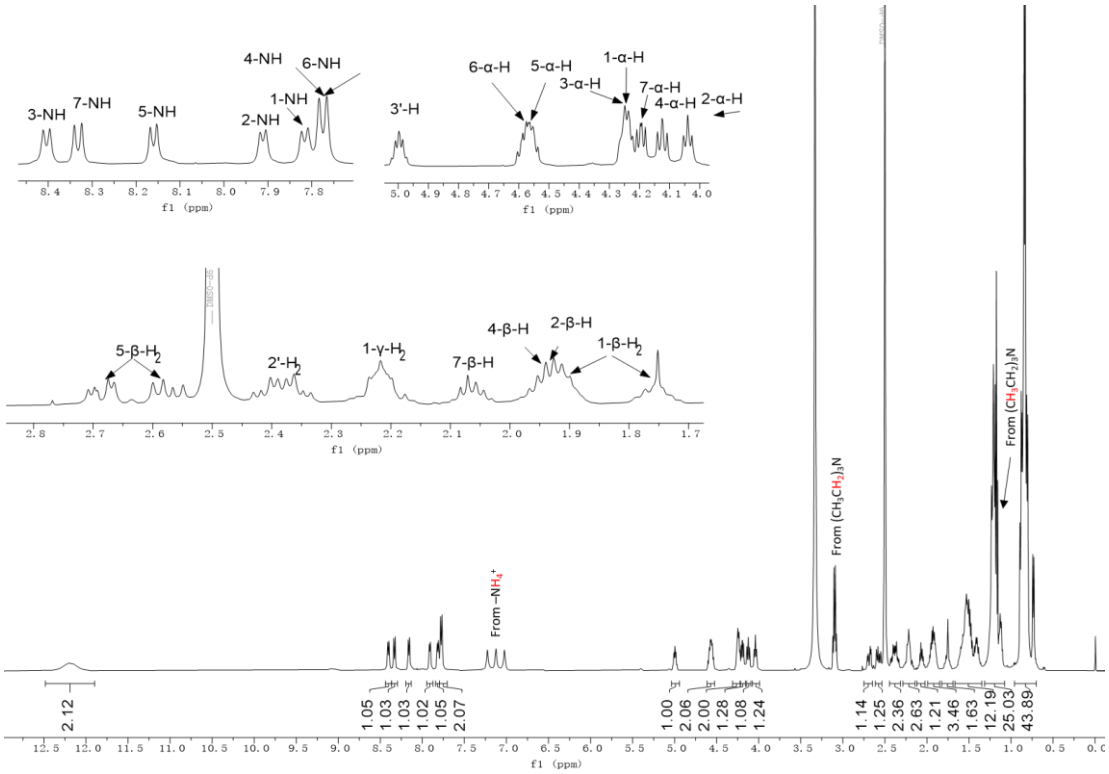


Figure S5 D. The ^{1}H NMR spectrum of compound **1**

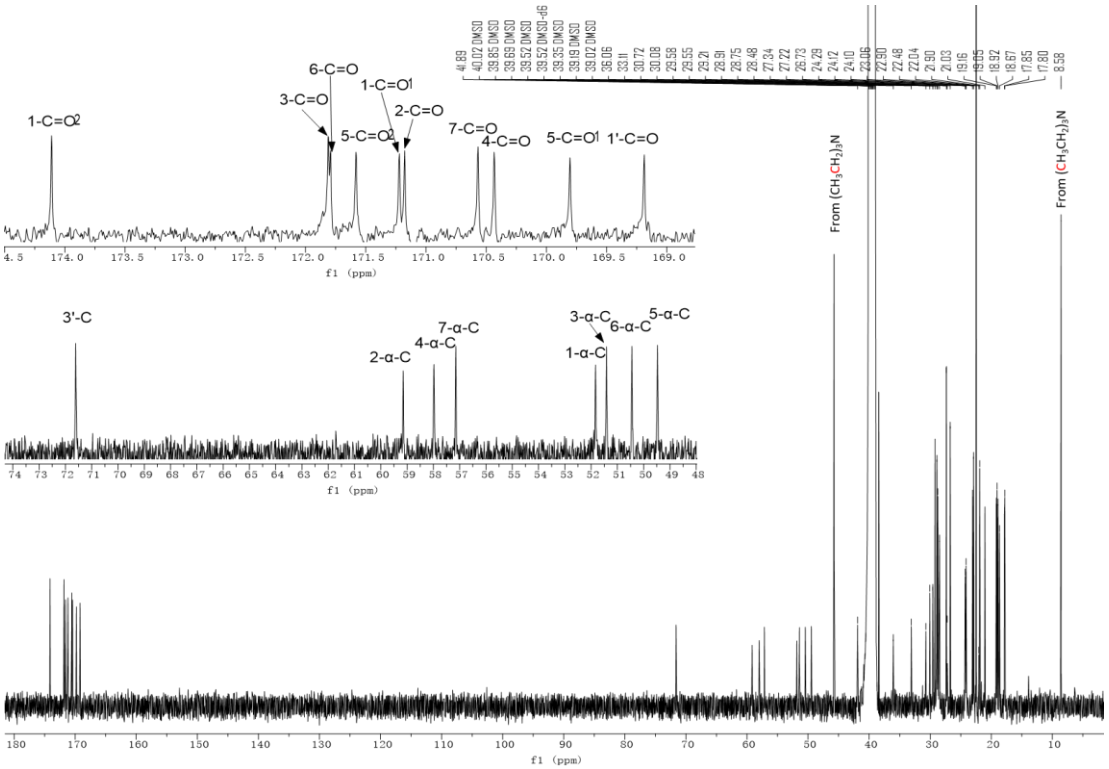


Figure S5 E. The ^{13}C NMR spectrum of compound **1**

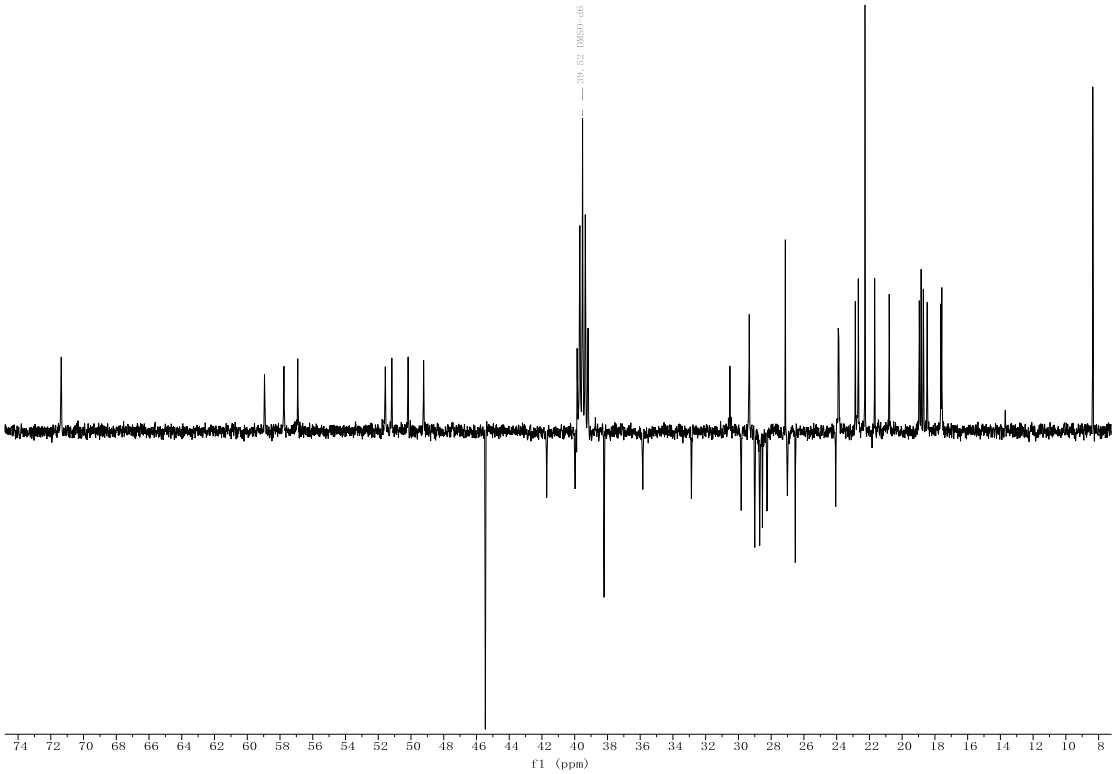


Figure S5 F. The DEPT-135 spectrum of compound **1**

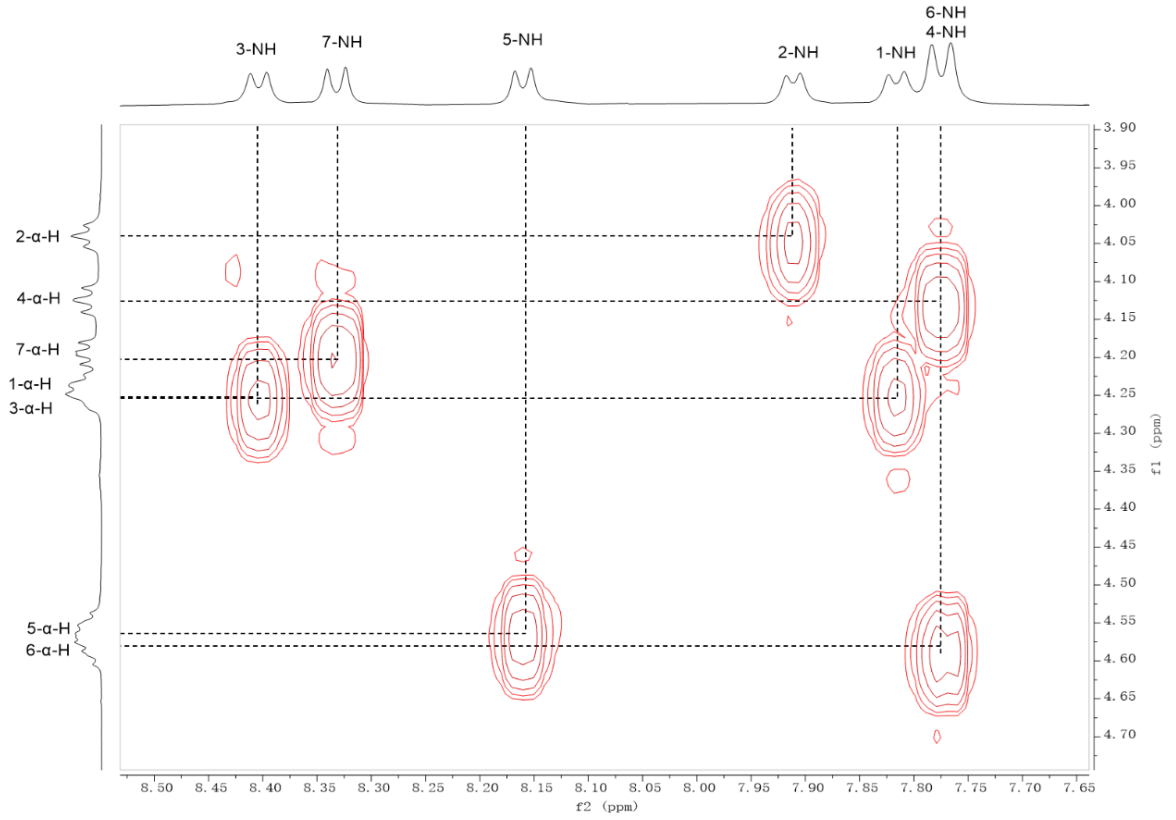


Figure S5 G. The enlarged ^{1}H-^{1}H COSY spectrum of compound **1**

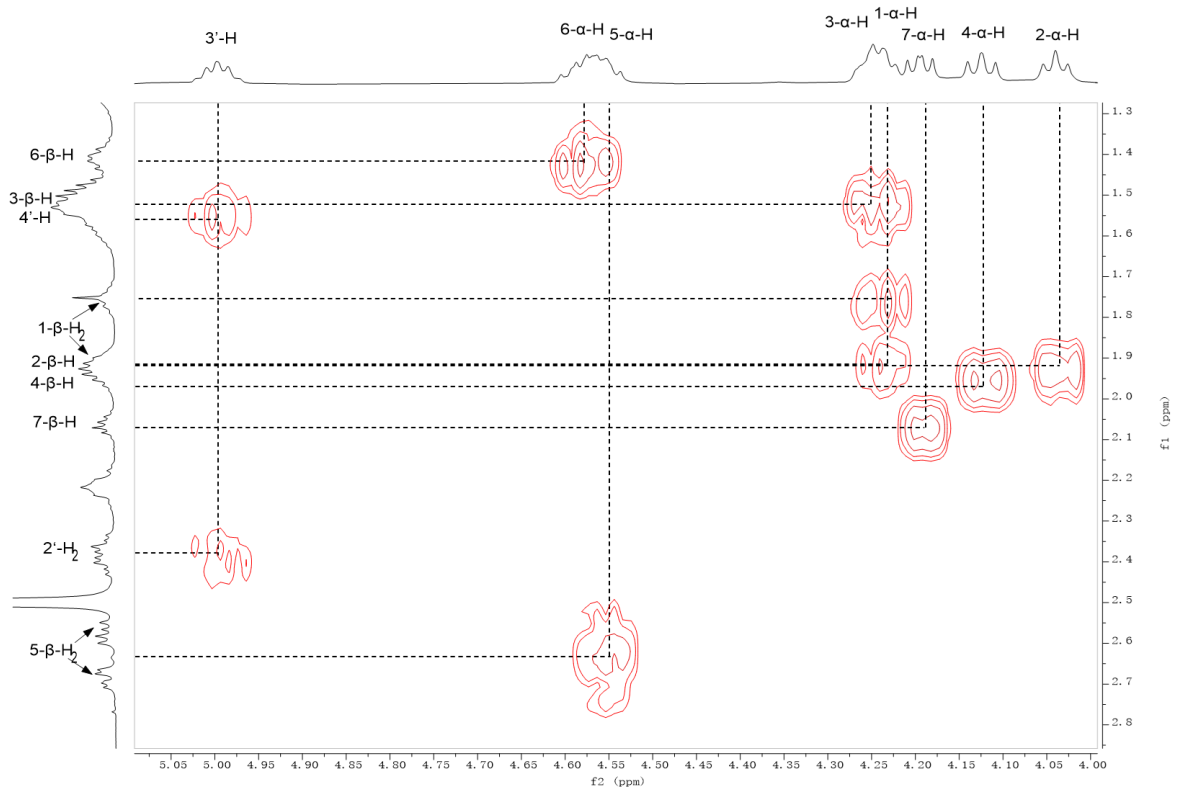


Figure S5 H. The enlarged ^{1}H-^{1}H COSY spectrum of compound **1**

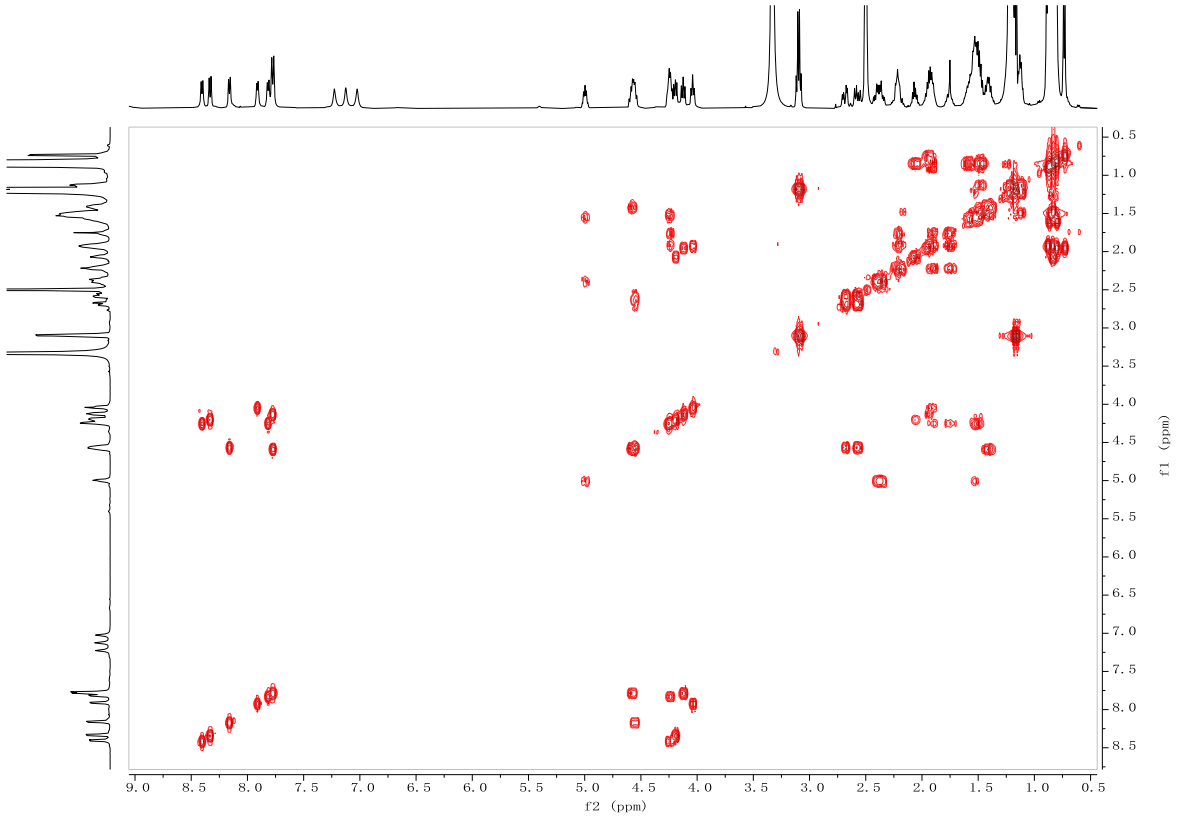


Figure S5 I. The ^{1}H-^{1}H COSY spectrum of compound **1**

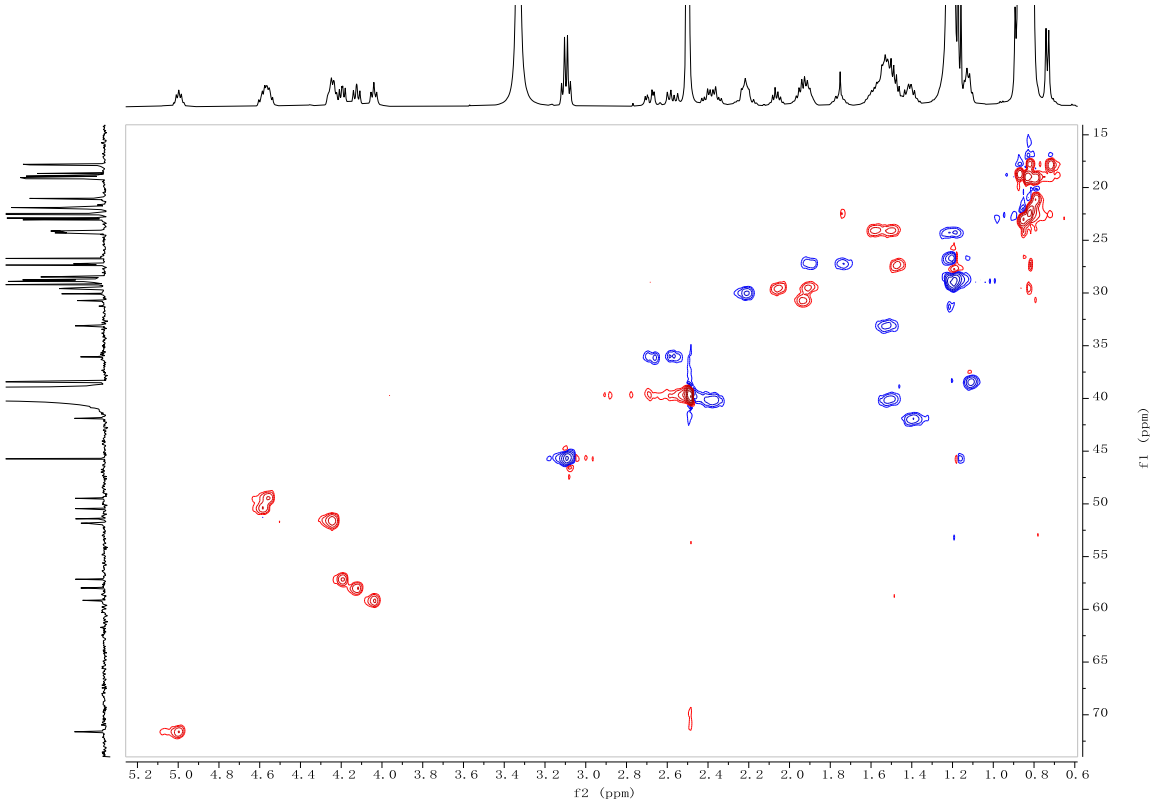


Figure S5 J. The HSQC spectrum of compound **1**

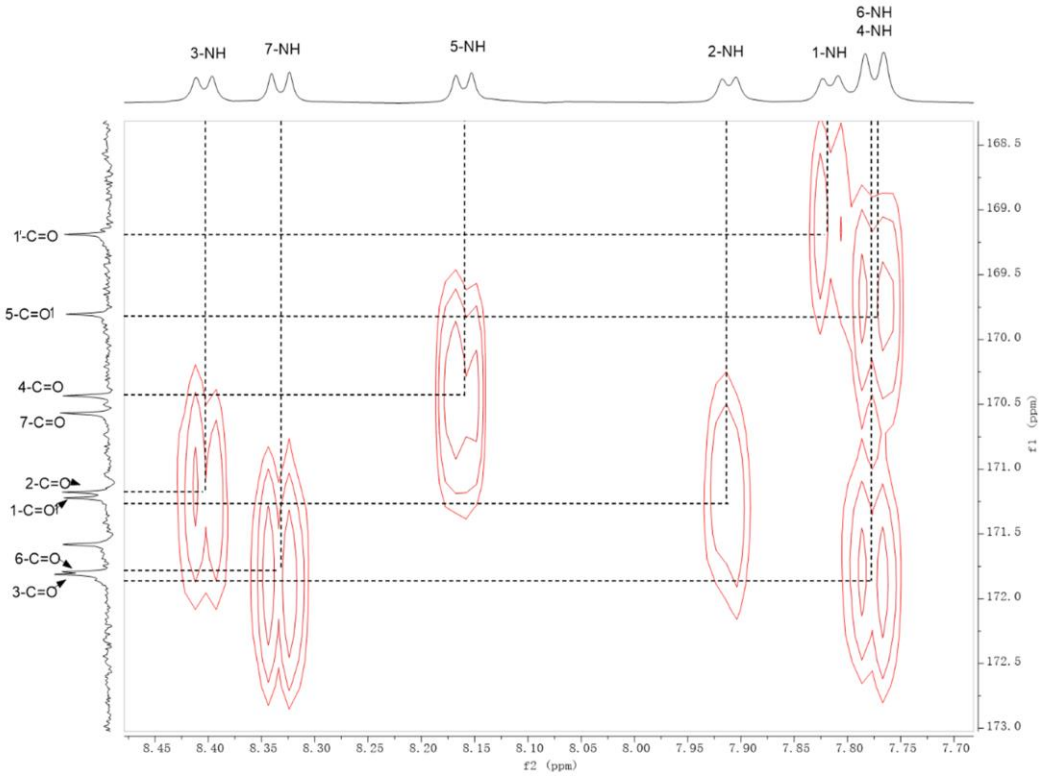


Figure S5 K. The enlarged HMBC spectrum of compound **1**

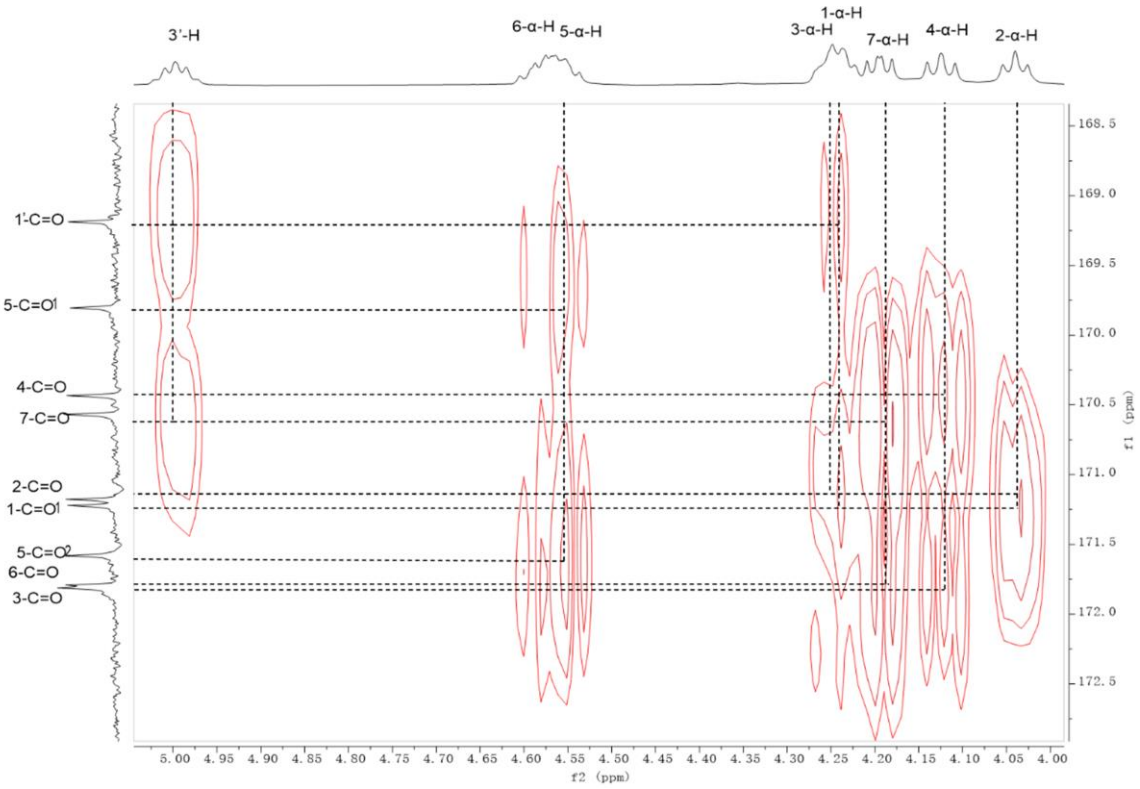


Figure S5 L. The enlarged HMBC spectrum of compound **1**

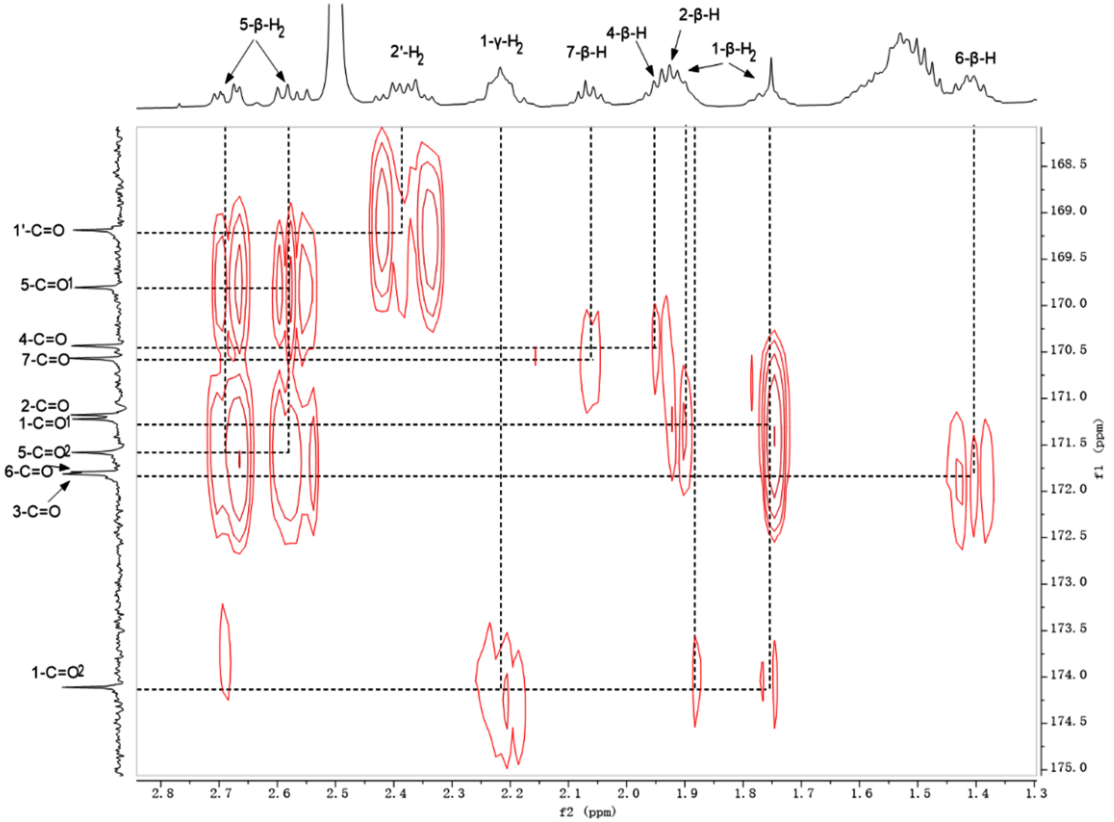


Figure S5 M. The enlarged HMBC spectrum of compound **1**

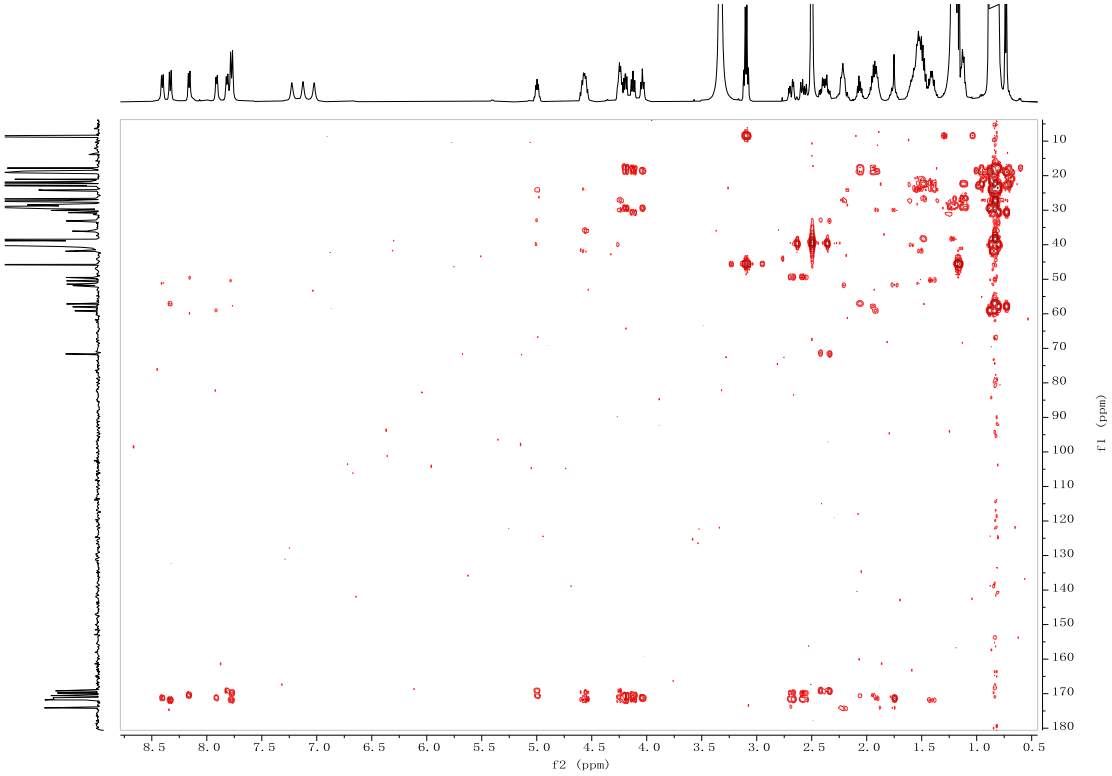


Figure S5 N. The HMBC spectrum of compound **1**

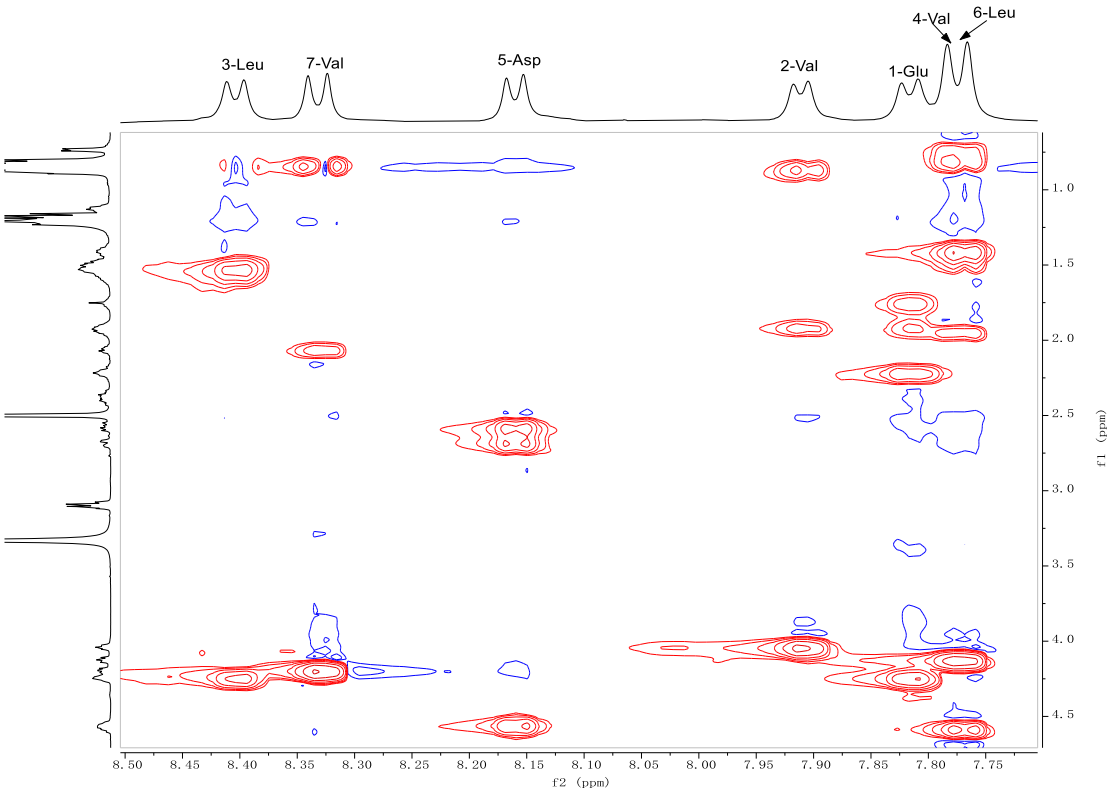


Figure S5 O. The enlarged TOCSY spectrum of compound **1**

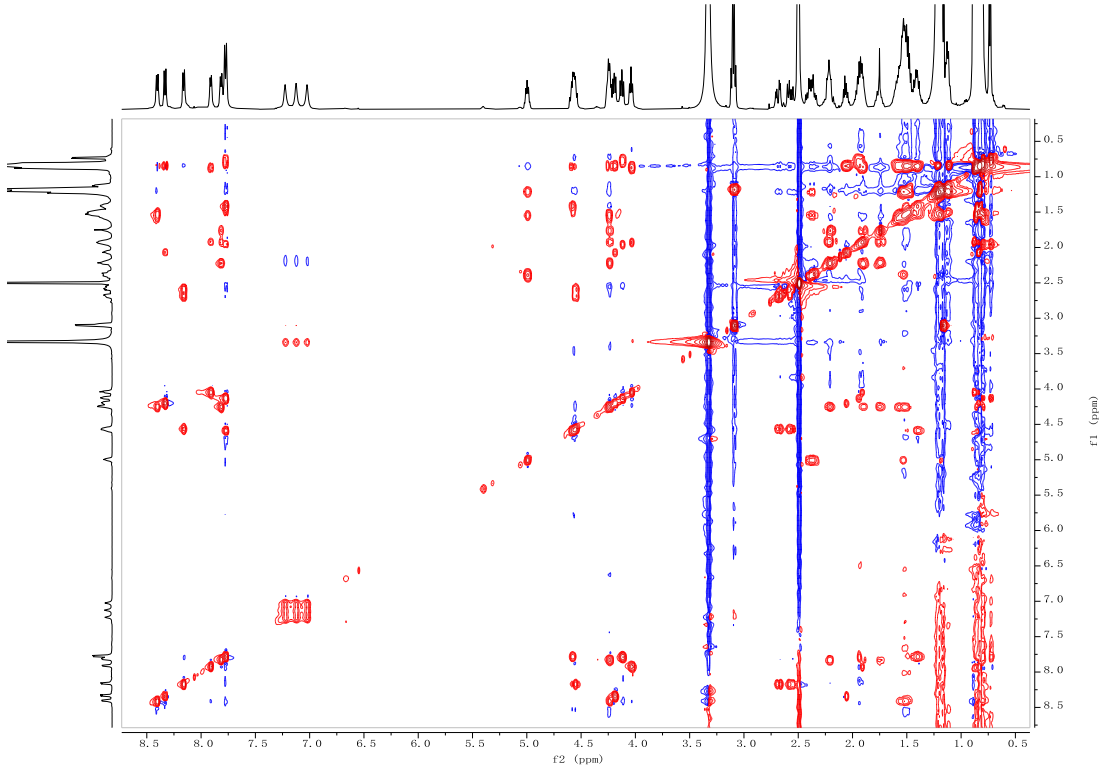


Figure S5 P. The TOCSY spectrum of compound **1**

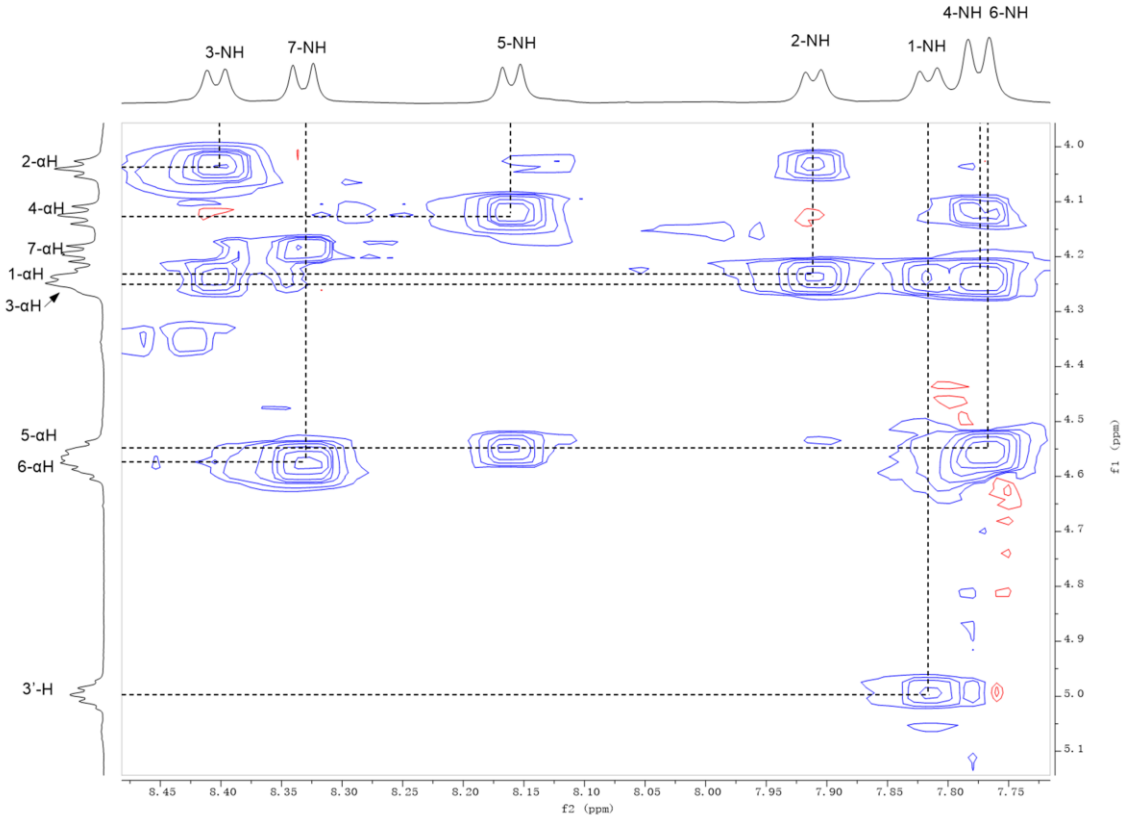


Figure S5 Q. The enlarged ROESY spectrum of compound **1**

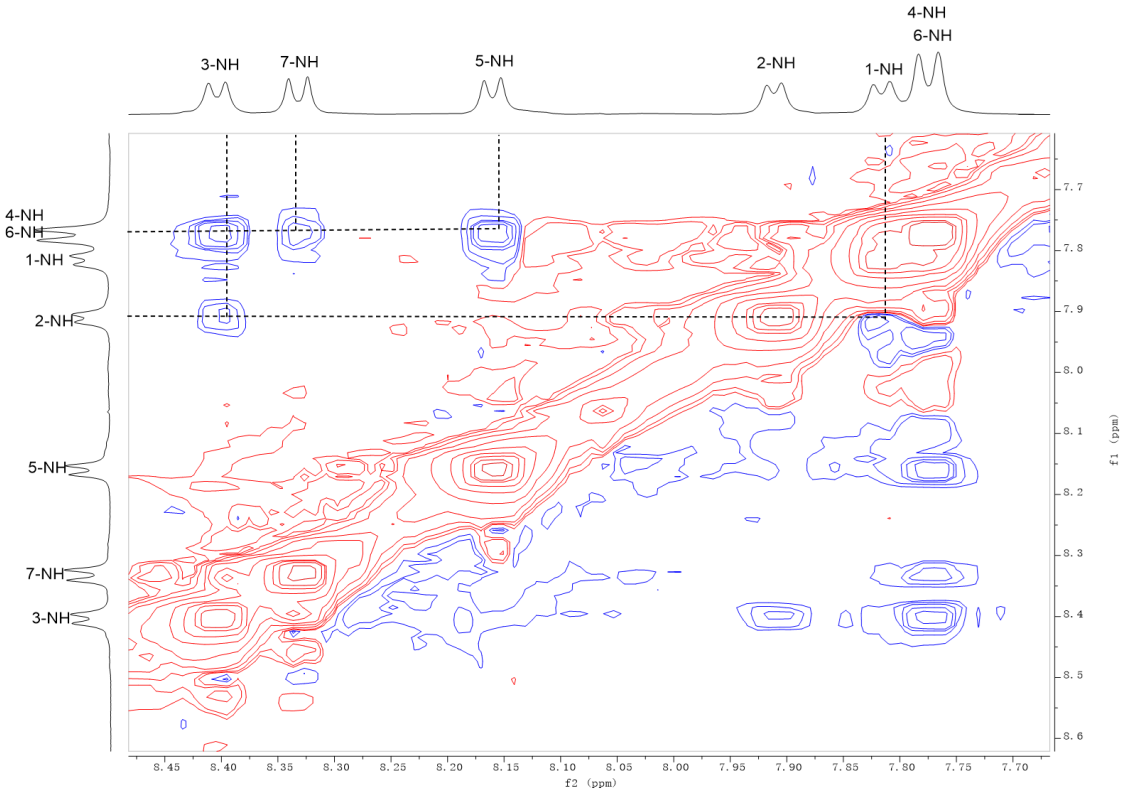


Figure S5 R. The enlarged ROESY spectrum of compound **1**

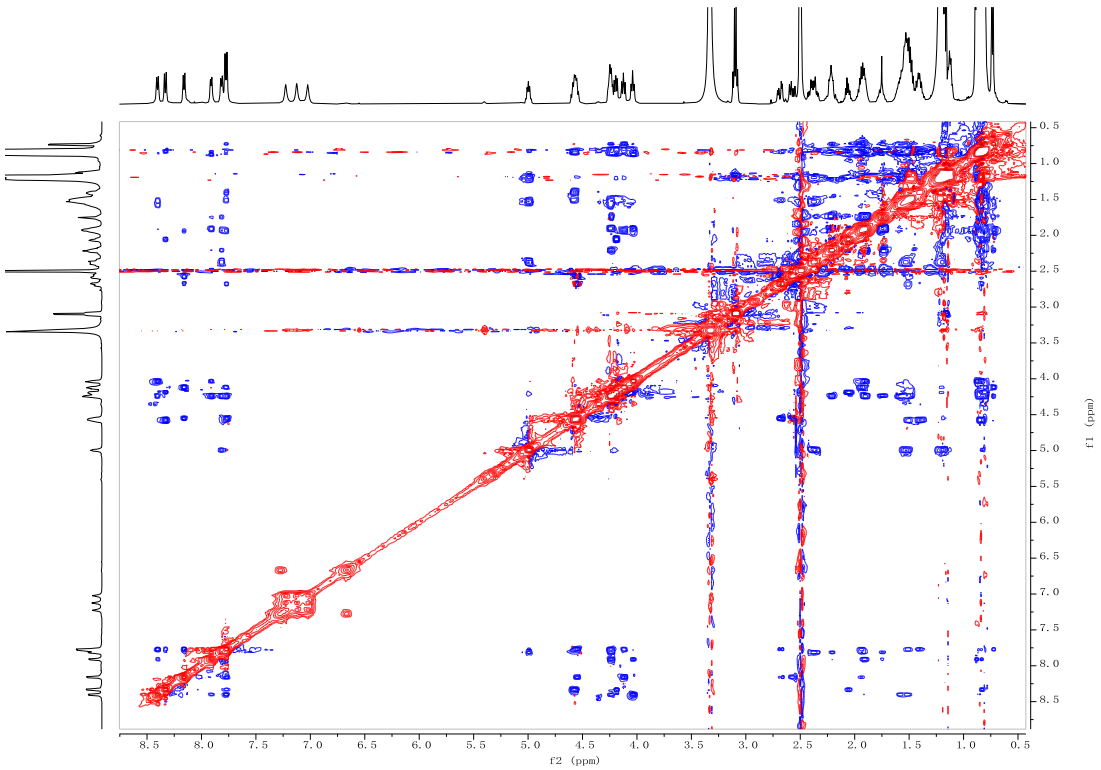


Figure S5 S. The ROESY spectrum of compound **1**

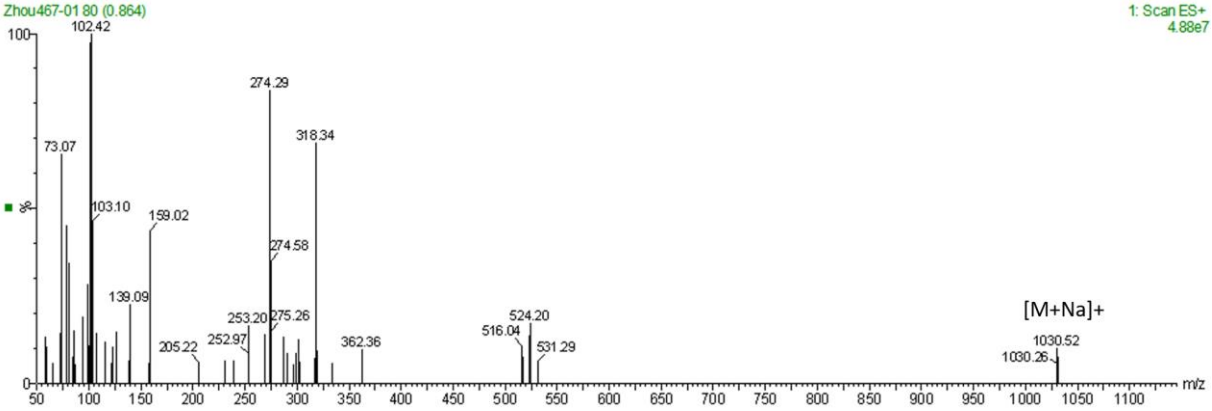


Figure S6 A. The ESI-MS spectrum of compound **2**

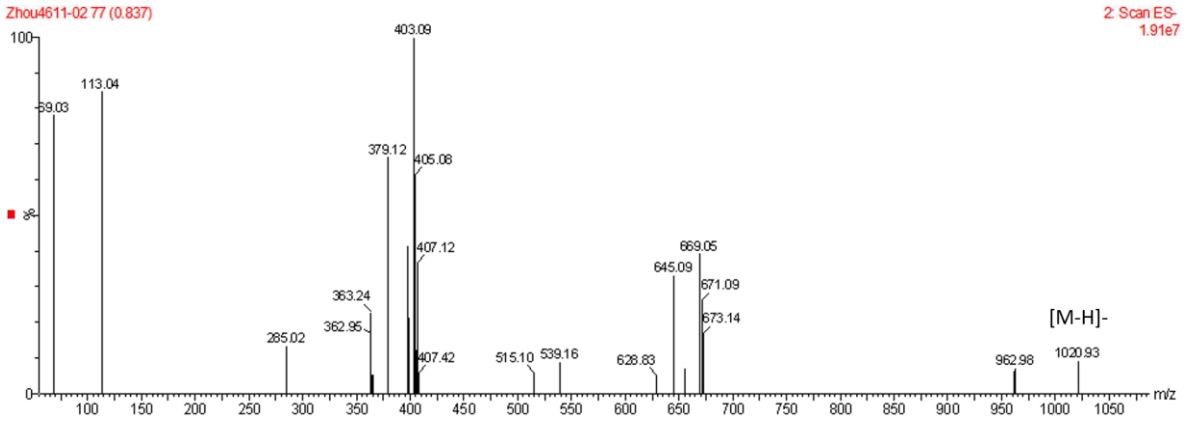


Figure S6 B. The ESI-MS of compound **3**

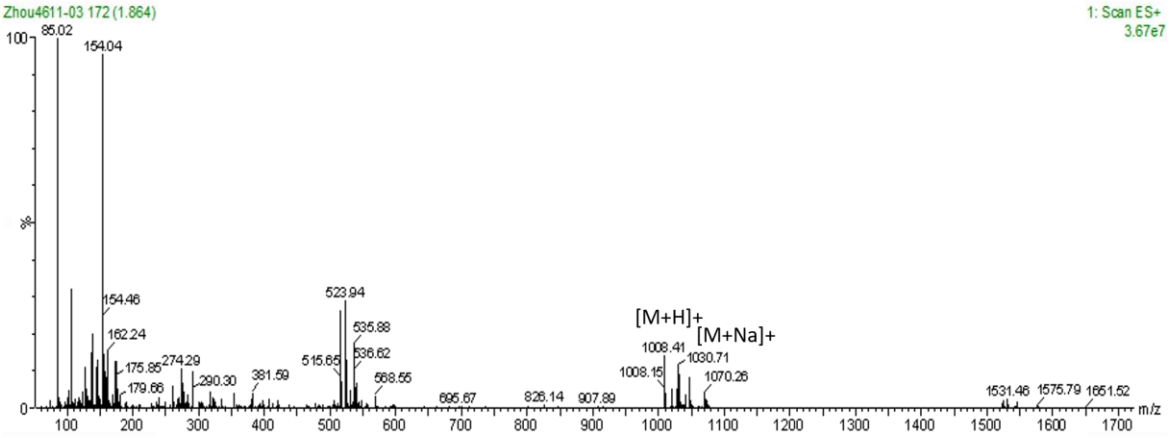


Figure S6 C. The ESI-MS of compound **4**

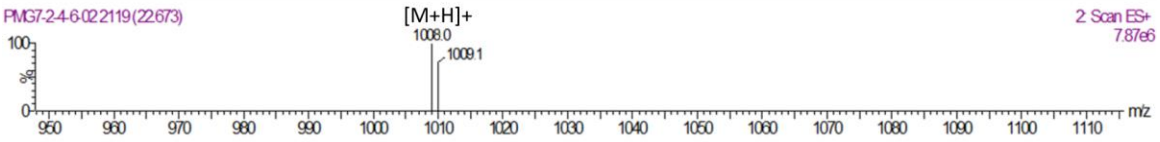


Figure S6 D. The ESI-MS of compound **5**

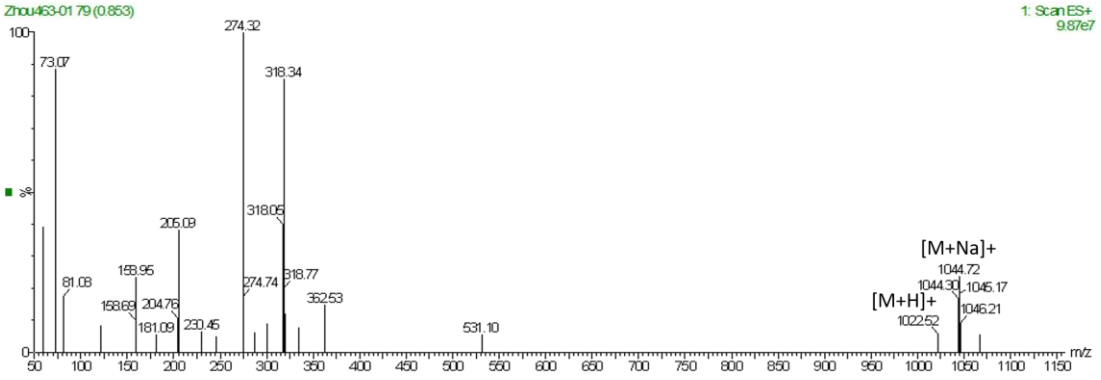


Figure S6 E. The ESI-MS of compound **6**

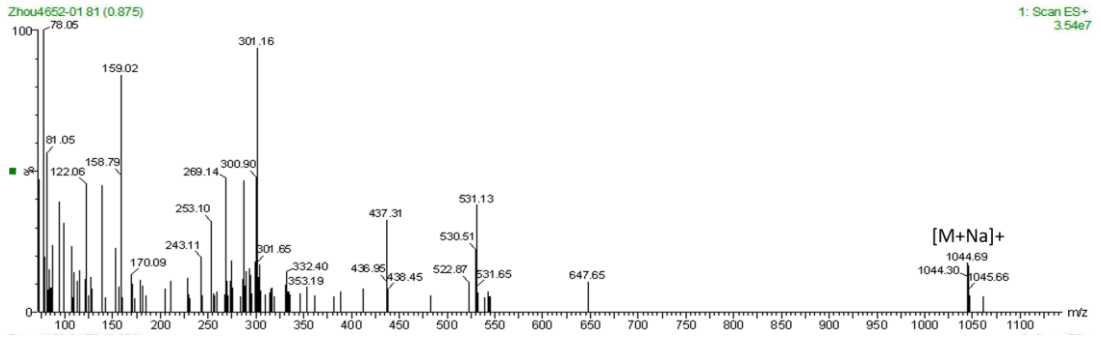


Figure S6 F. The ESI-MS of compound **7**

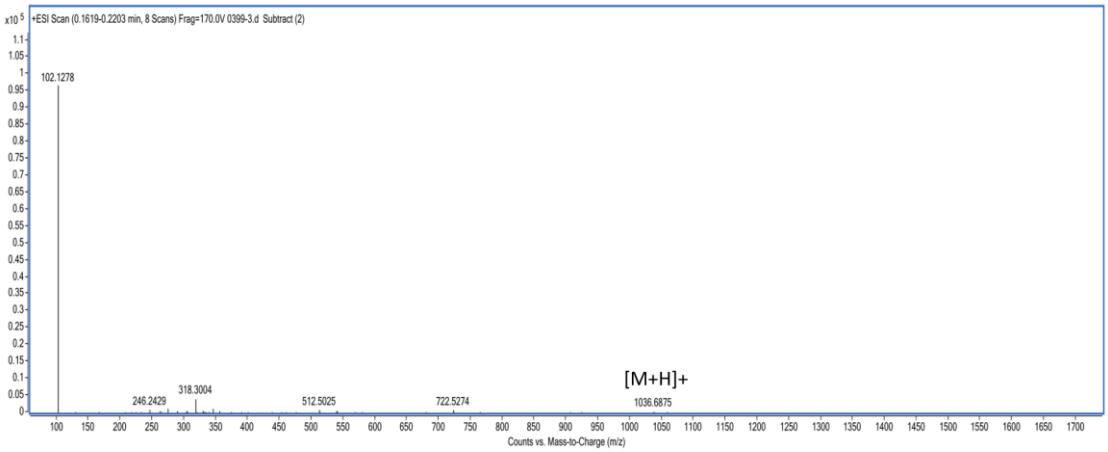


Figure S6 G. The HR-ESI-MS of compound **8**

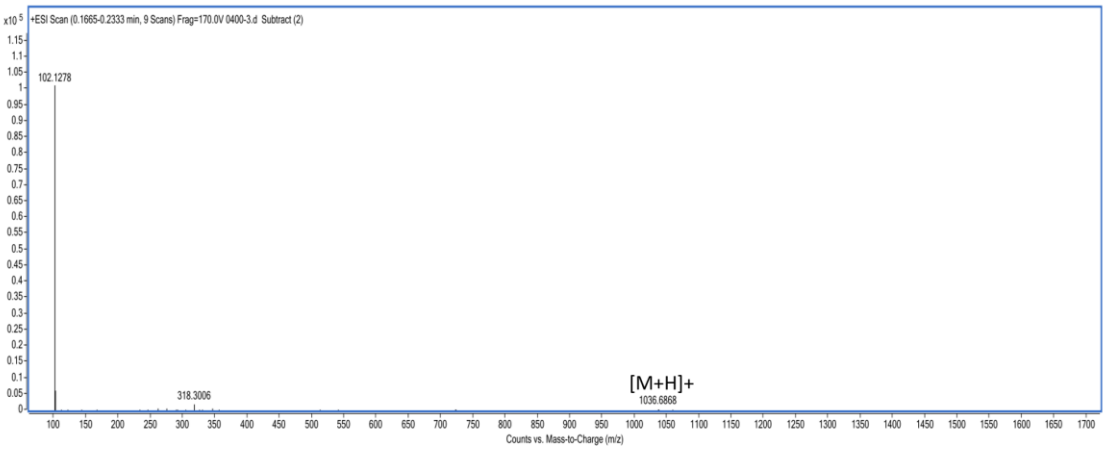


Figure S6 H. The HR-ESI-MS of compound **9**

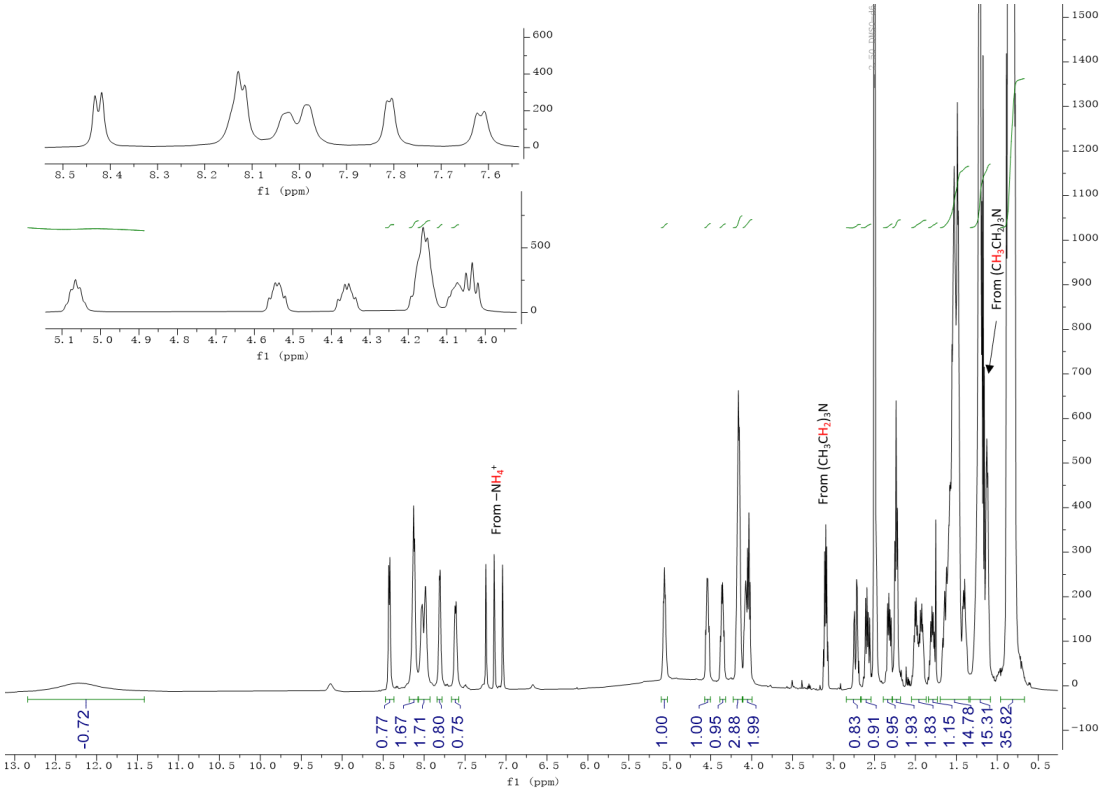


Figure S7 A. The ^{1}H NMR spectrum of compound **5**

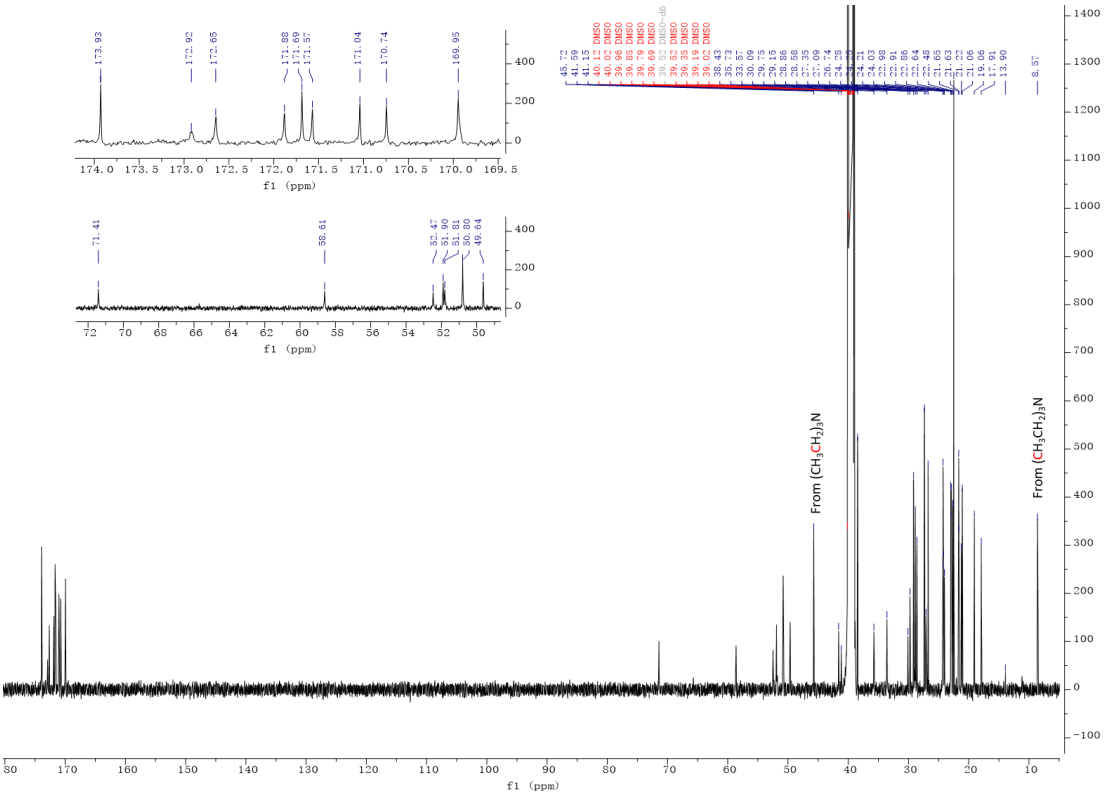


Figure S7 B. The ^{13}C NMR spectrum of compound **5**

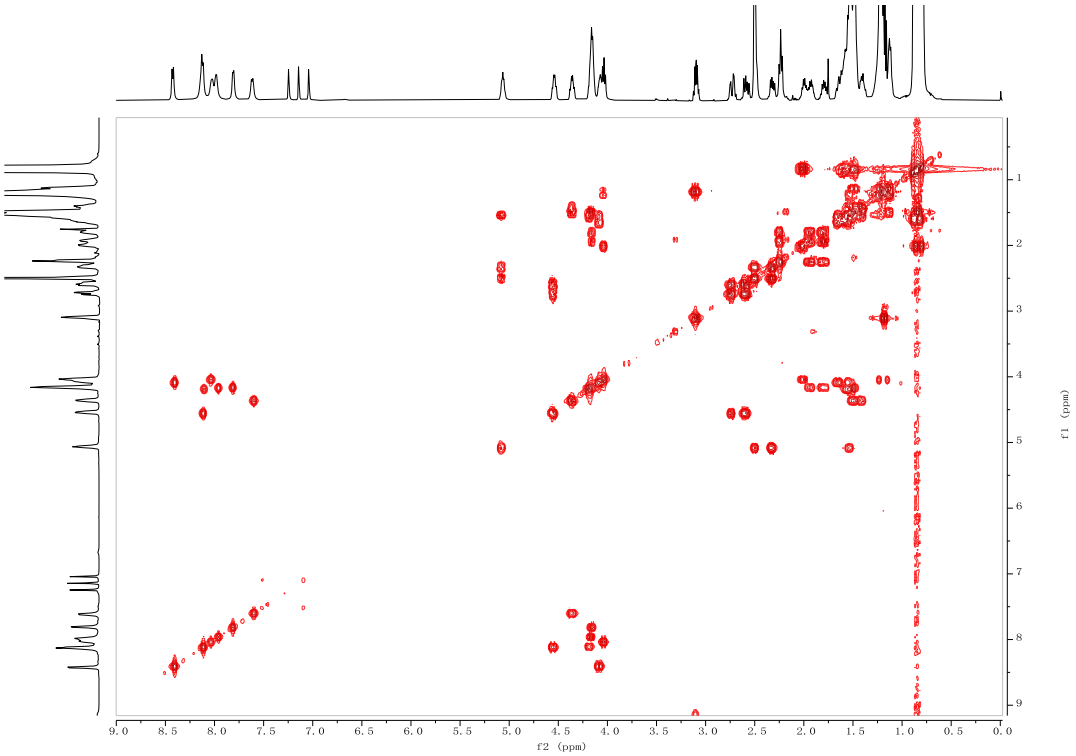


Figure S6 C. The ^{1}H-^{1}H COSY spectrum of compound **5**

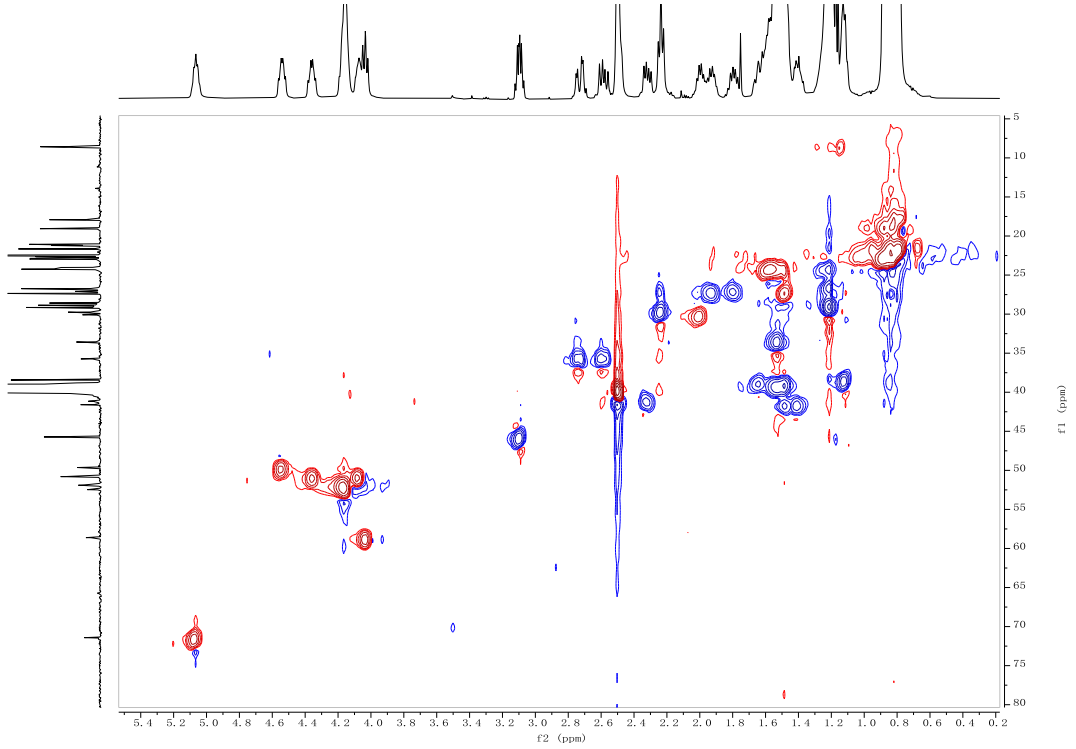


Figure S7 D. The HSQC spectrum of compound **5**

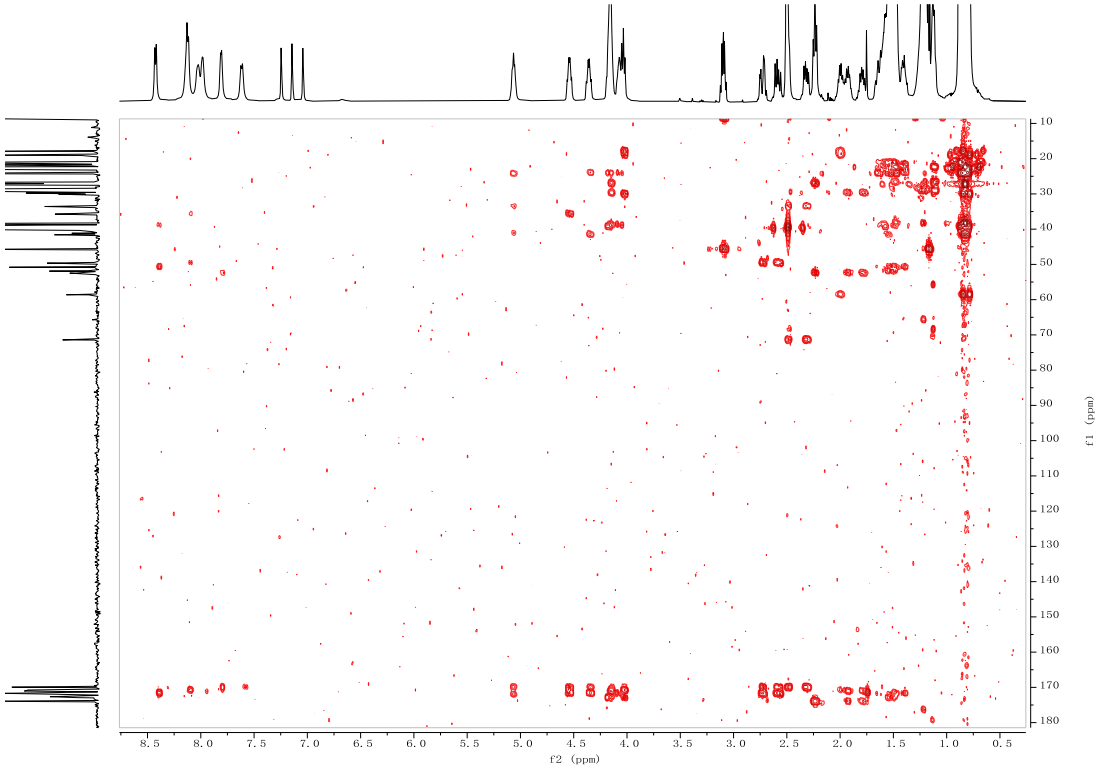


Figure S7 E. The HMBC spectrum of compound **5**

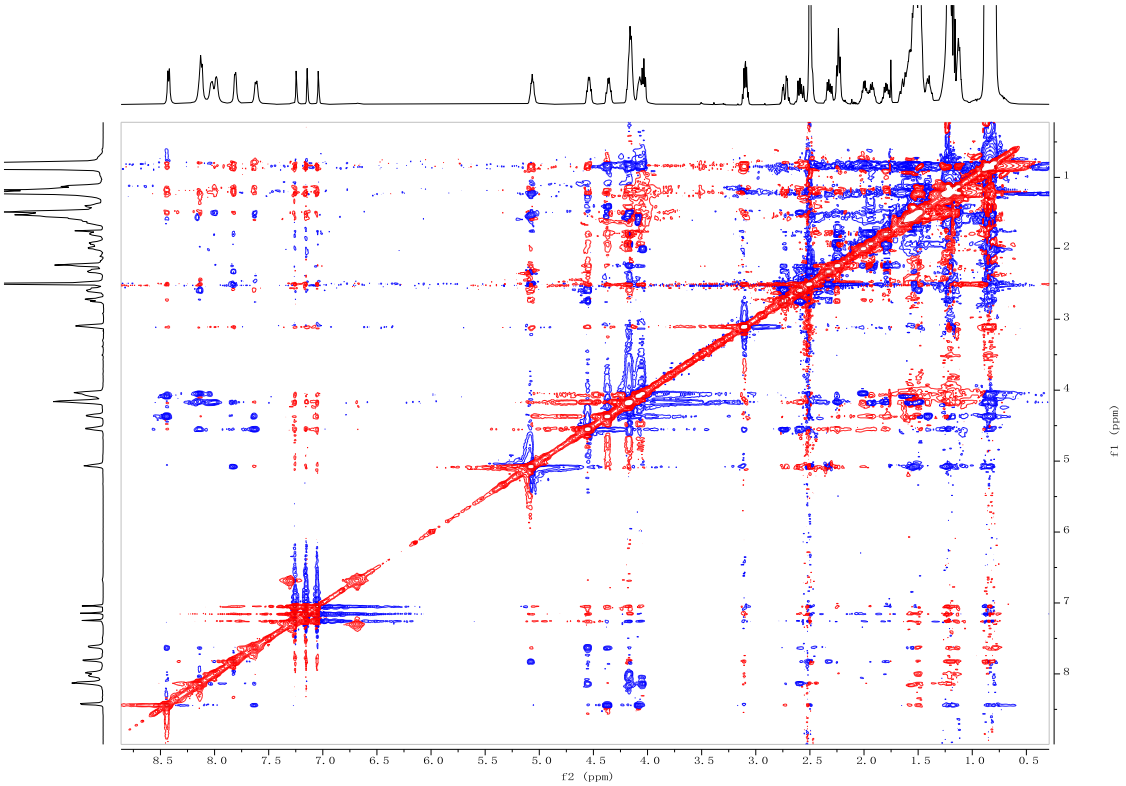


Figure S7 F. The ROESY spectrum of compound **5**

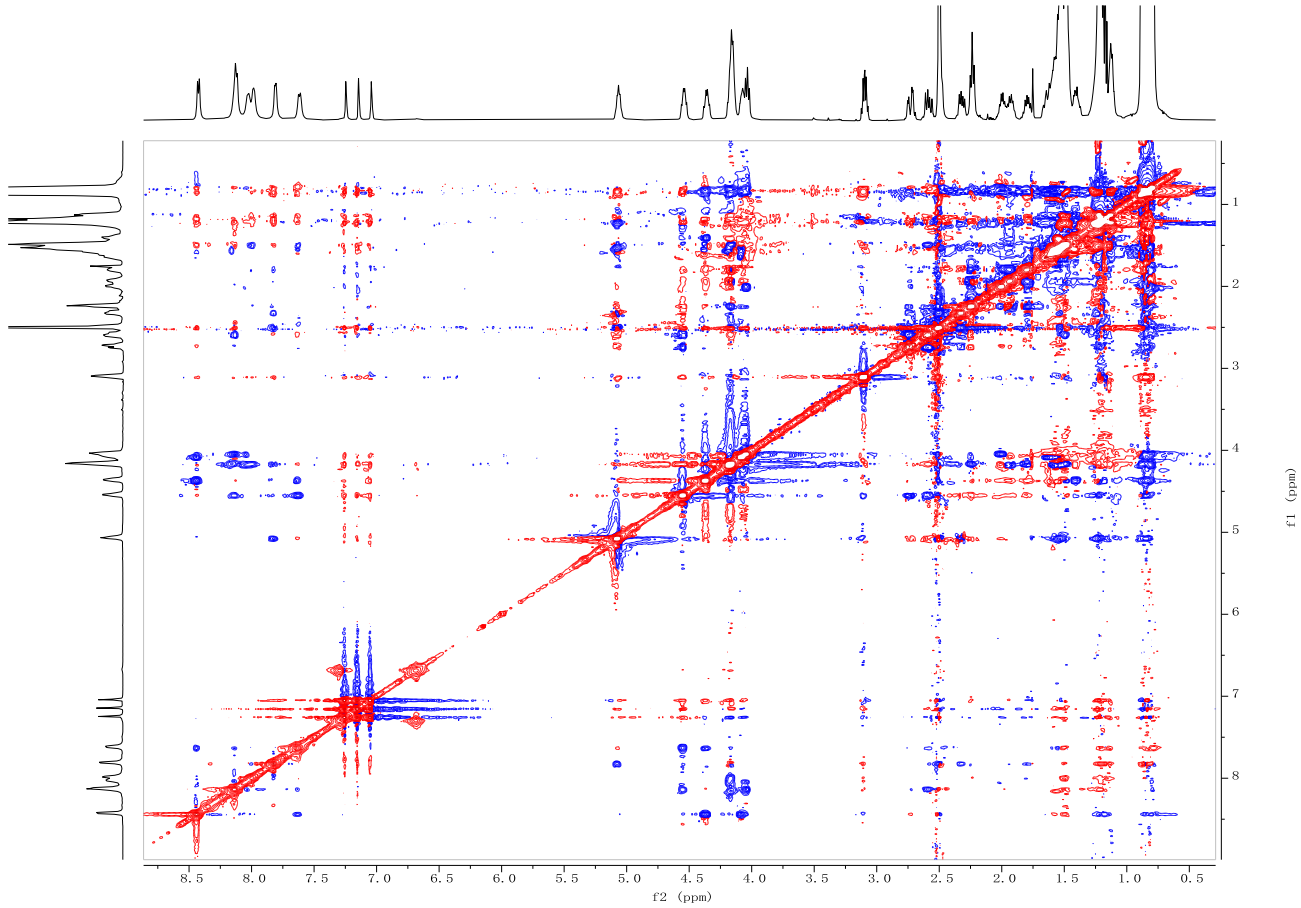


Figure S7 G. The TOCSY spectrum of compound **5**