Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Chetracins E and F, Cytotoxic Epipolythiodioxopiperazines from the Marine-derived Fungus *Acrostalagmus luteoalbus* HDN13-530

Guihong Yu, [a] Yanjuan Wang, [a] Rilei Yu, [a] Yanyan Feng, [a] Lu Wang, [a] Qian Che, [a] Qianqun Gu,[a] Dehai Li, [a, b] Jing Li, [a, b] and Tianjiao Zhu[a, *]

[a] Key Laboratory of Marine Drugs, Chinese Ministry of Education, School of Medicine and Pharmacy, Ocean University of China, Qingdao 266003, P. R. China

[b] Laboratory for Marine Drugs and Bioproducts of Qingdao National Laboratory for Marine Science and Technology, Qingdao, 266237, P. R. China

[*]To whom correspondence should be addressed. Tel: 0086-532-82031632 and Fax: 0086-532-82033054. E-mail: zhutj@ouc.edu.cn

List of Supporting Information

- M+2 negative ion isotope peaks of many sulfur-containing metabolites in fermentation extract of *A. luteoalbus* HDN13-530 (Figure S1).
- ^{13}C NMR and ^{1}H NMR Spectroscopic data of **1a** (Table S1).
- Key HMBC correlations of **1a** (Figure S2).
- HPLC analysis of conversions of **2** to **3** and standard samples (Figure S3);
- 1D, 2D NMR, NOESY and HRESIMS spectra of chetracin E (**1**) (Figure S4-S10);
- 1D, 2D NMR, NOESY and HRESIMS spectra of chetracin F (**2**) (Figure S11-S17);
- 1D, 2D NMR, NOESY and HRESIMS spectra of **1a** (Figure S18-S23).
- IR spectra of chetracin E (**1**), chetracin F (**2**) and **1a** (Figure S24-S26).

Figure S1. M+2 negative ion isotope peaks of many sulfur-containing metabolites in fermentation extract of *A. luteoalbus* HDN13-530.

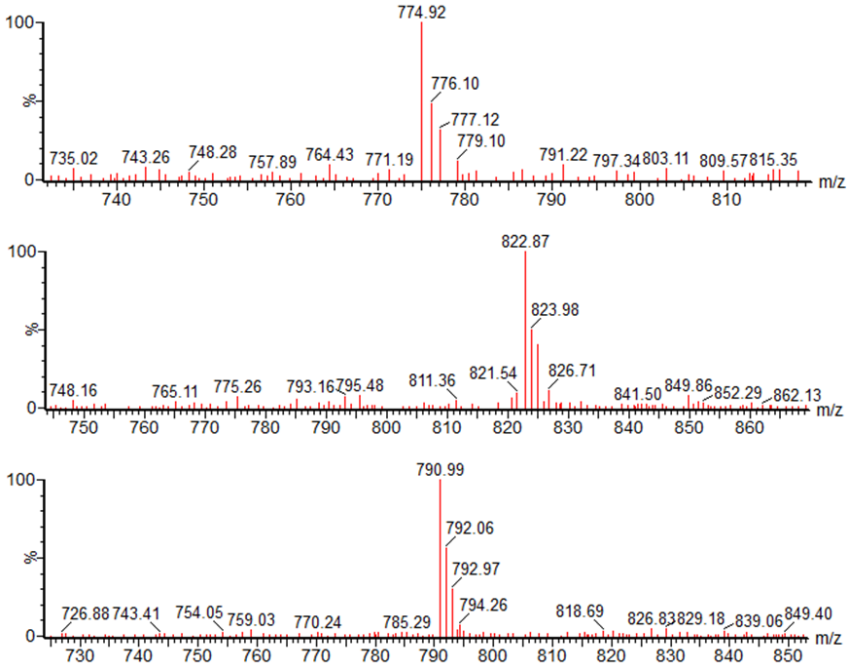


Table S1. ^{13}C NMR (125 MHz) and ^{1}H NMR (500 MHz) Spectroscopic Data of **1a** in DMSO-d_6.

position	**1a** (major conformor)		**1a** (minor symmetric conformor)	
	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	164.3, qC		165.3, qC	
3	72.1, qC		71.4, qC	
4	162.4, qC		162.3, qC	
5a	79.6, CH	6.29 d (1.9)	80.5, CH	5.02 d (2.1)
6a	151.2, qC		151.6, qC	
7	107.8, CH	6.05-6.09 [a]	108.0, CH	6.27 d (7.7)
8	128.6, CH	6.60-6.64 [a]	128.7, CH	6.86-6.90 [a]
9	116.6, CH	6.15-6.18 [a]	117.7, CH	6.37-6.42 [a]
10	121.8, CH	7.20 d (8.2)	126.3, CH	6.65 d (7.7)
10a	130.1, qC		130.1, qC	
10b	63.9, qC		66.8, qC	
11	82.2, CH	4.73 d (9.5)	82.1, CH	5.07 d (7.1)
11a	72.0, qC		73.0, qC	
12	28.2, CH_3	2.88 s	28.4, CH_3	2.95s
13	63.4, CH_2	4.17 dd (11.8, 6.0)	63.2, CH_2	4.17 dd (11.8, 6.0)
		3.61-3.69 [a]		3.98 dd (11.6, 6.2)
3-SCH_3	13.3, CH_3	2.16 s	13.3, CH_3	2.08 s

11a-SCH_3	15.8, CH_3	1.82 s	15.9, CH_3	1.82 s
6-NH		6.85 s		6.67 s
11-OH		7.25 brs		5.99 d (7.2)
13-OH		4.93 t (7.0)		5.10 t (4.5)
1′	163.9, qC		164.6, qC	
3′	67.8, qC		68.3, qC	
4′	163.6, qC		163.6, qC	
5a′	79.9, CH	6.33 d (1.9)	80.3, CH	5.02 d (2.1)
6a′	151.2, qC		151.7, qC	
7′	107.9, CH	6.05-6.09 [a]	108.2, CH	6.31 d (7.8)
8′	128.7, CH	6.60-6.64 [a]	128.7, CH	6.86-6.90 [a]
9′	116.6, CH	6.15-6.18 [a]	117.2, CH	6.37-6.42 [a]
10′	121.8, CH	7.16 d (8.2)	127.3, CH	7.71 d (7.7)
10a′	129.8, qC		130.5, qC	
10b′	63.4, qC		66.5, qC	
11′	81.7, CH	4.83 d (4.8)	81.6, CH	5.13 d (7.0)
11a′	72.1, qC		72.8, qC	
12′	28.2, CH_3	2.93 s	29.0, CH_3	2.95 s
13′	24.7, CH_3	1.74 s	25.1, CH_3	1.65 s
3′-SCH_3	14.5, CH_3	2.16 s	14.3, CH_3	2.06 s
11a′-SCH_3	16.0, CH_3	1.82 s	15.8, CH_3	1.81 s
6′-NH		6.85 s		6.64 s
11′-OH		7.05 brs		5.54 d (6.9)

[a] Signals were overlapped.

Figure S2. Key HMBC correlations of **1a**.

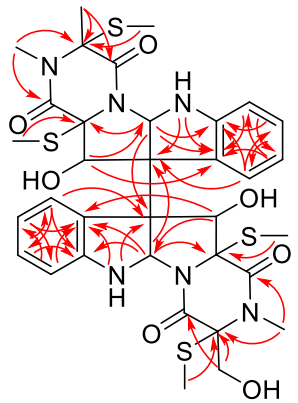
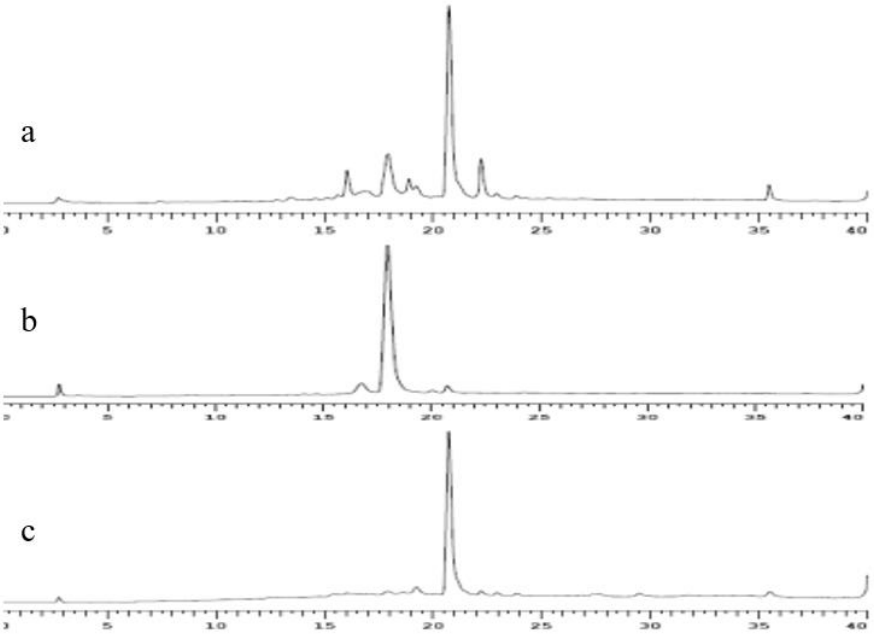


Figure S3. HPLC analysis of conversions of **2** to **3** and standard samples.



Note：a: conversion of **2** to **3** in DMSO after two weeks; b: standard sample of **3**; c: standard sample of **2**. The data were collected by HPLC with MeOH (with 1/1000 formic acid) and water (with 1/1000 formic acid) (0-2 min: 50:50, 2-30 min: from 50:50 to 100:0, 30-35: 100:0, 35-36 min: from 100:0 to 50:50, 36-40 min: 50:50).

Figure S4. ^{1}H NMR spectrum (500 MHz) of chetracin E (**1**) in DMSO

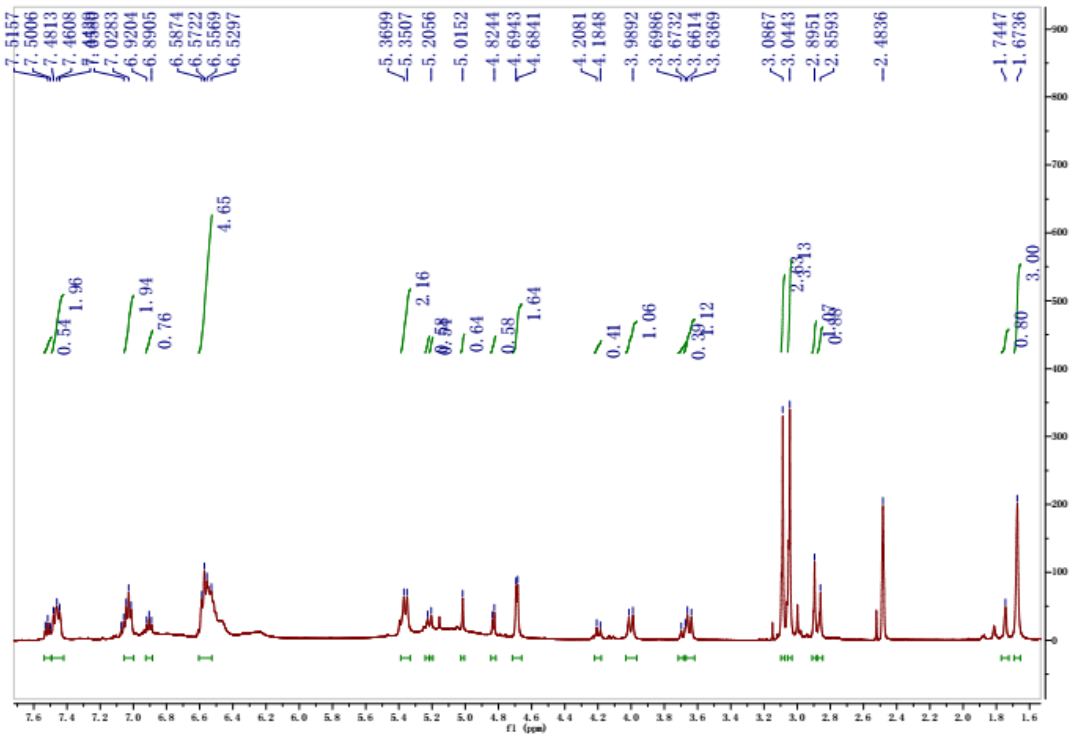


Figure S5. ^{13}C NMR spectrum (125 MHz) of chetracin E (**1**) in DMSO

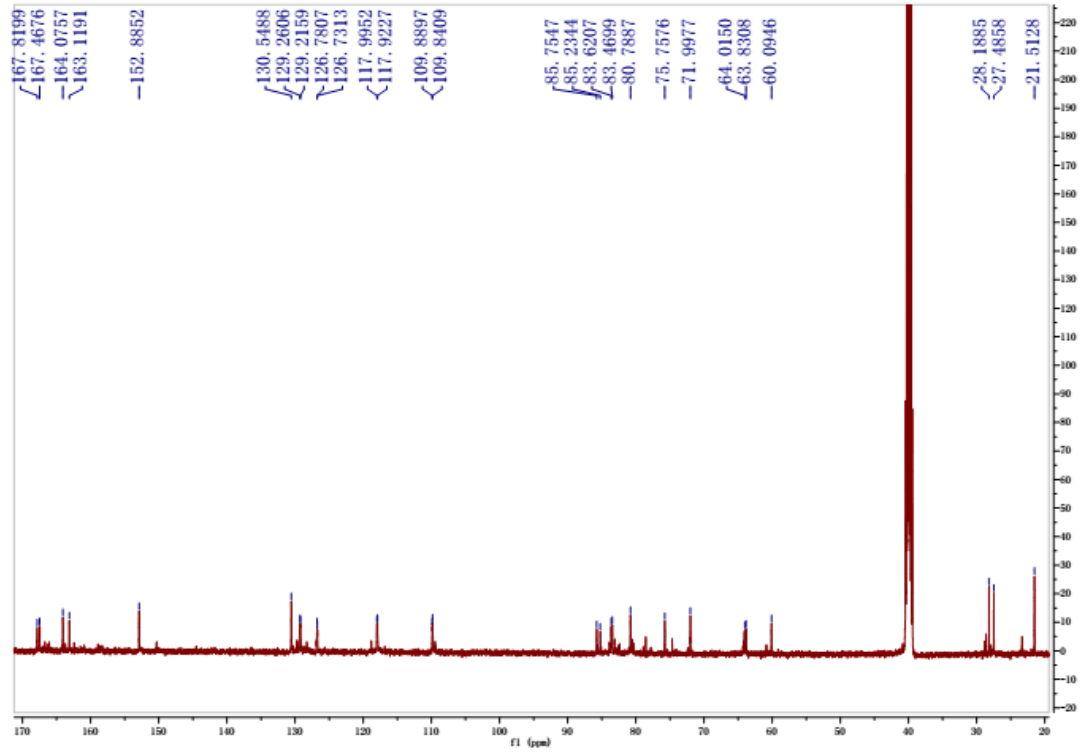


Figure S6. HMQC spectrum of chetracin E (**1**)

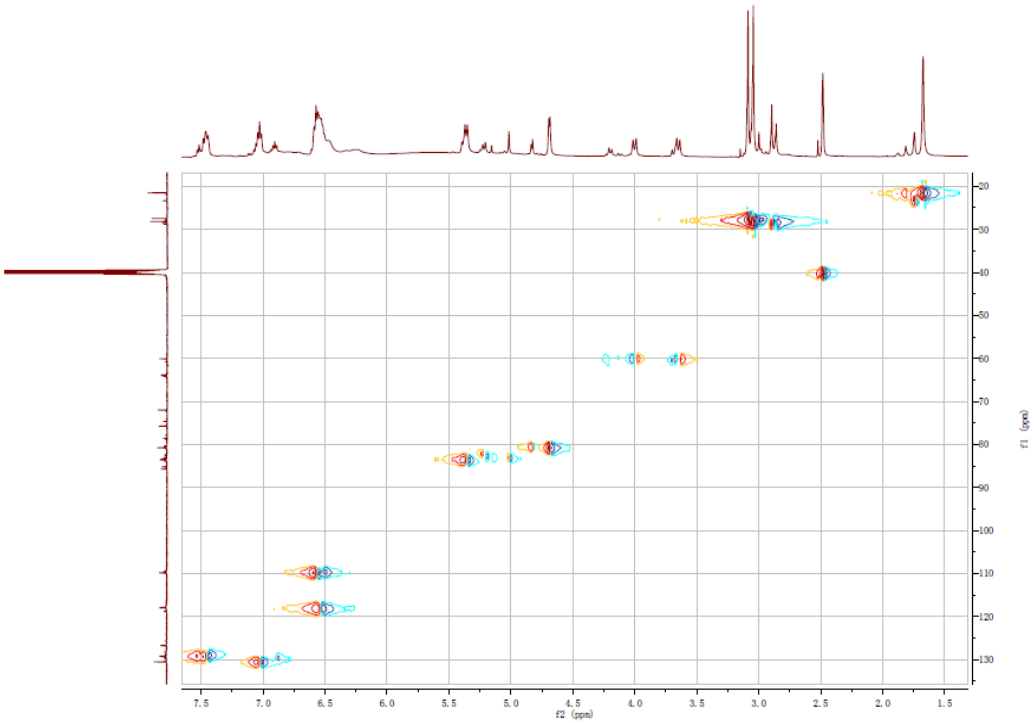


Figure S7. COSY spectrum of chetracin E (**1**)

Figure S8. HMBC spectrum of chetracin E (**1**)

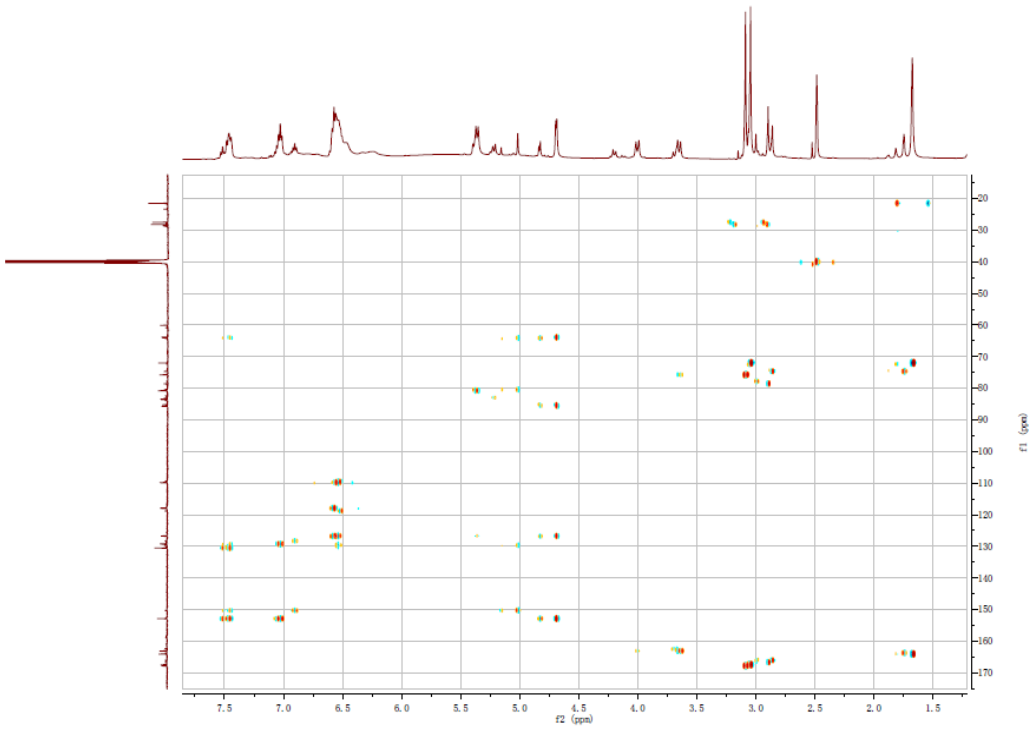


Figure S9. NOESY spectrum of chetracin E (**1**)

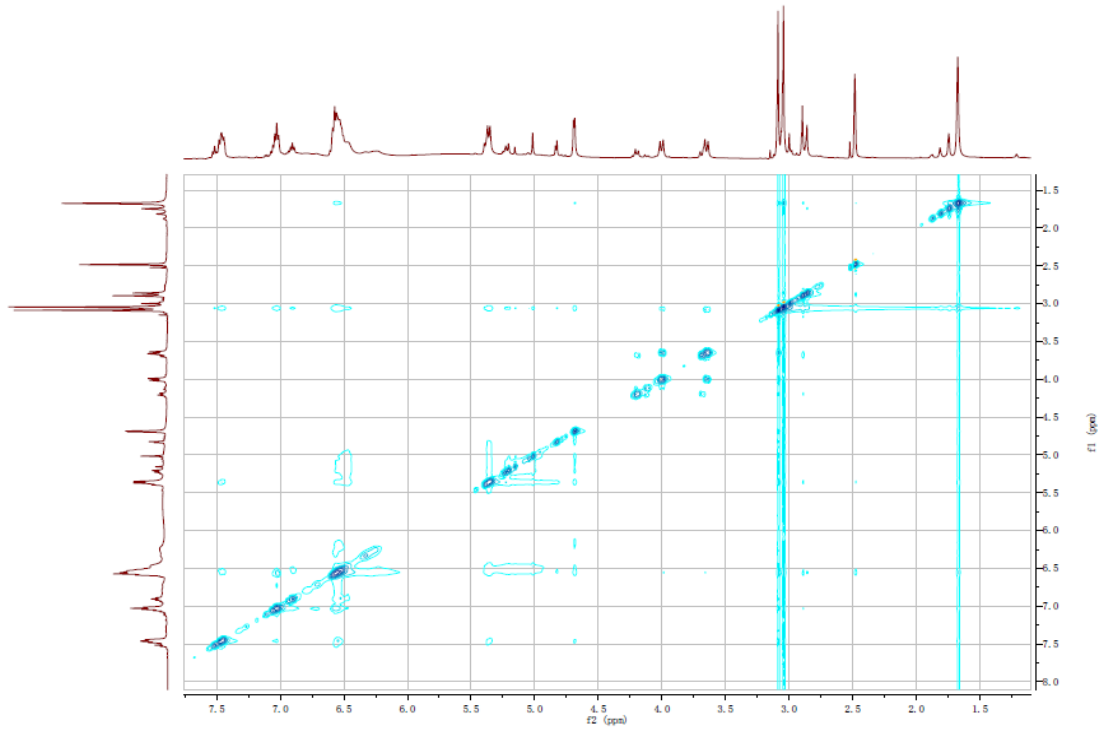


Figure S10. HRESIMS spectrum of chetracin E (**1**)

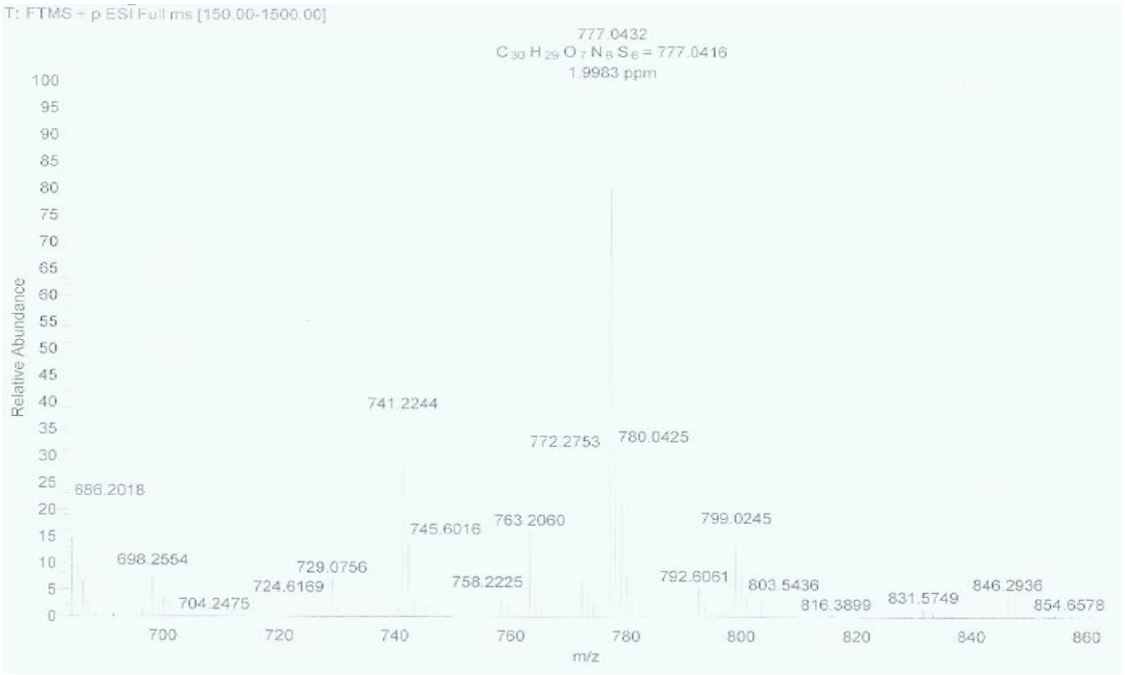


Figure S11. ^{1}H NMR spectrum (500 MHz) of chetracin F (**2**) in DMSO

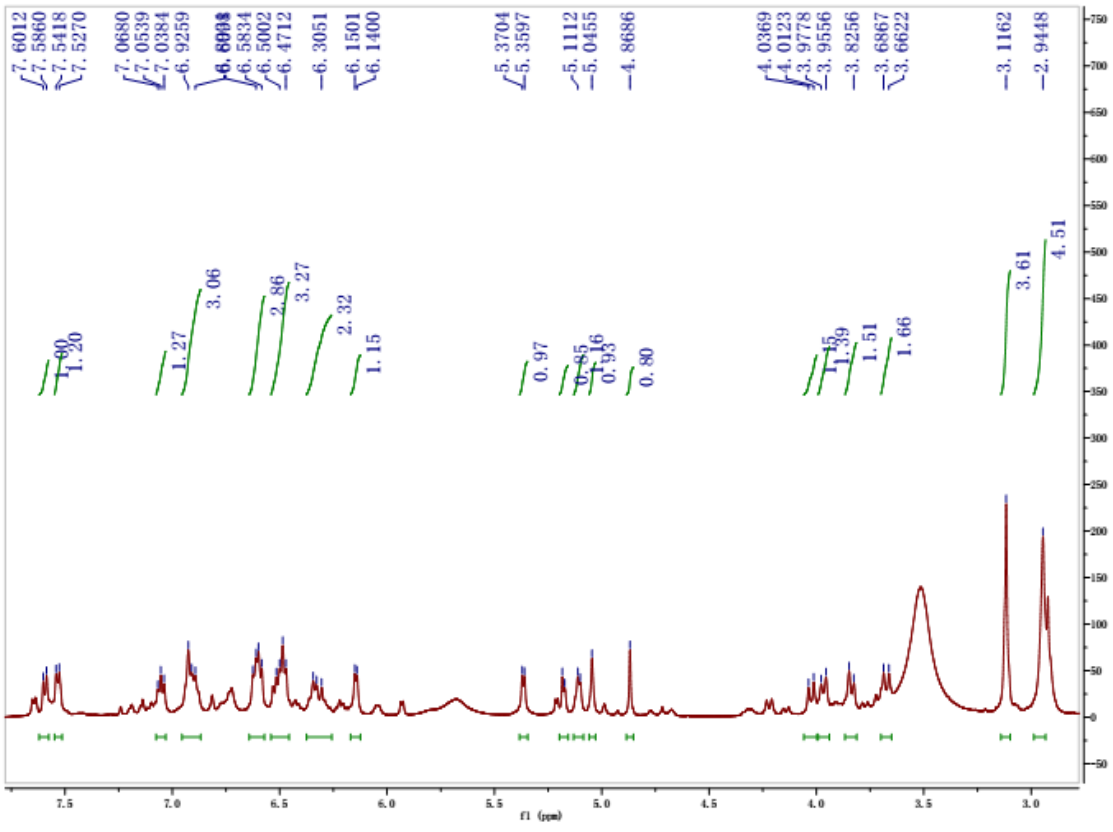


Figure S12. ^{13}C NMR spectrum (125 MHz) of chetracin F (**2**) in DMSO

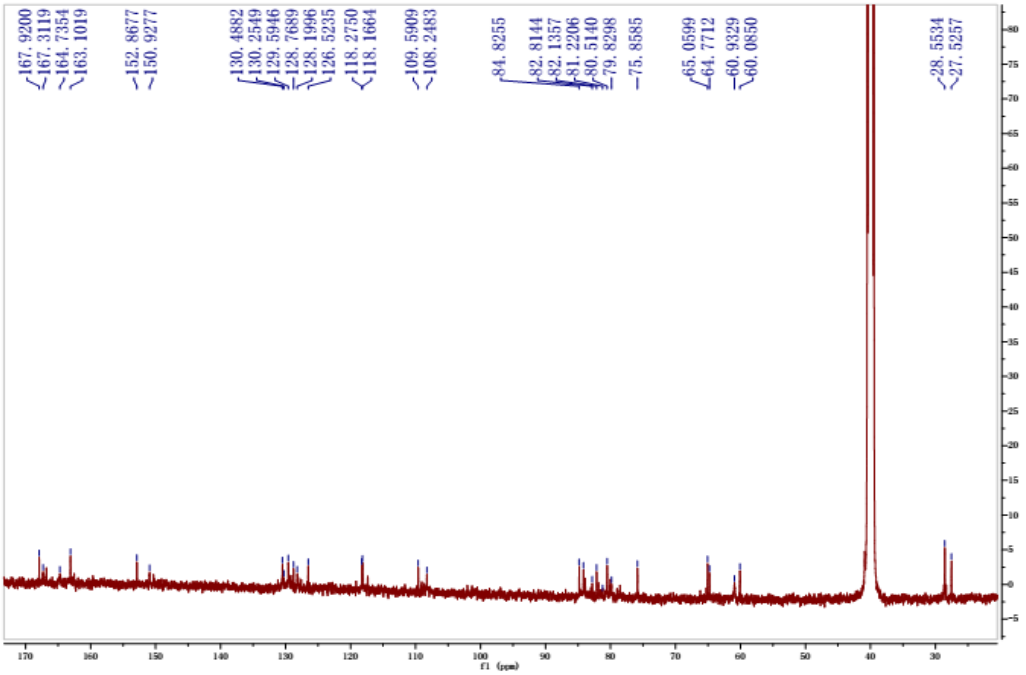


Figure S13. HMQC spectrum of chetracin F (**2**)

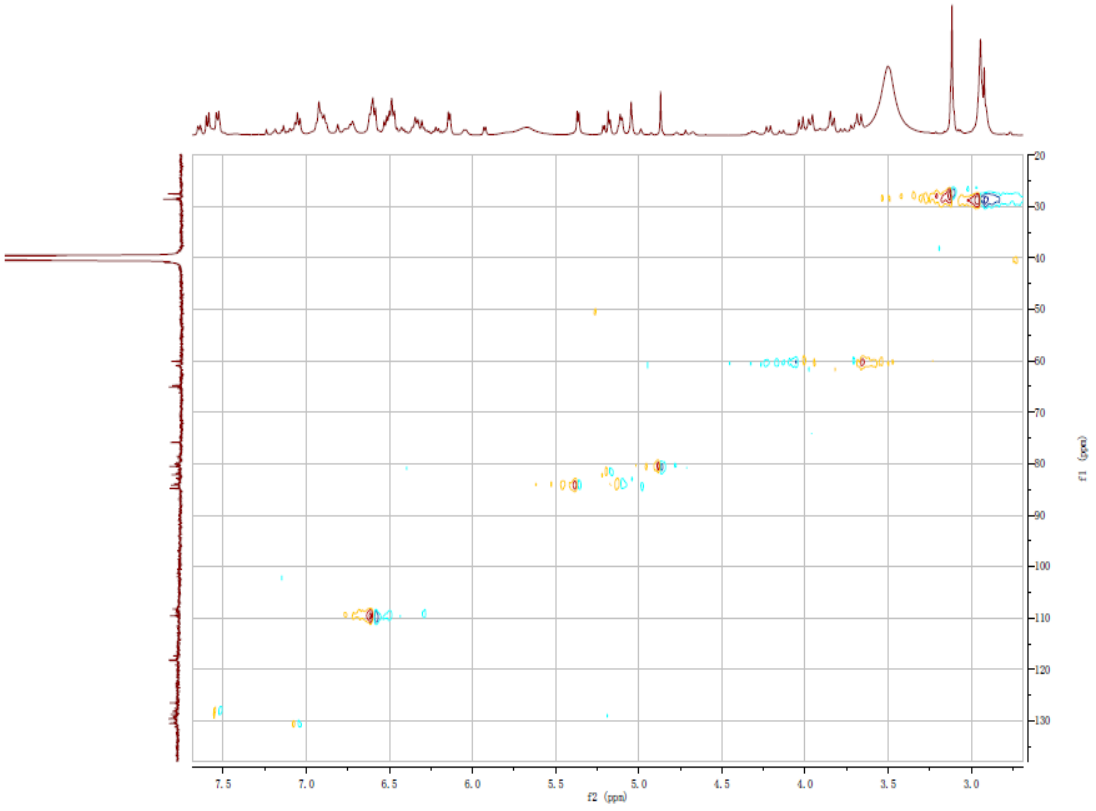


Figure S14. COSY spectrum of chetracin F (**2**)

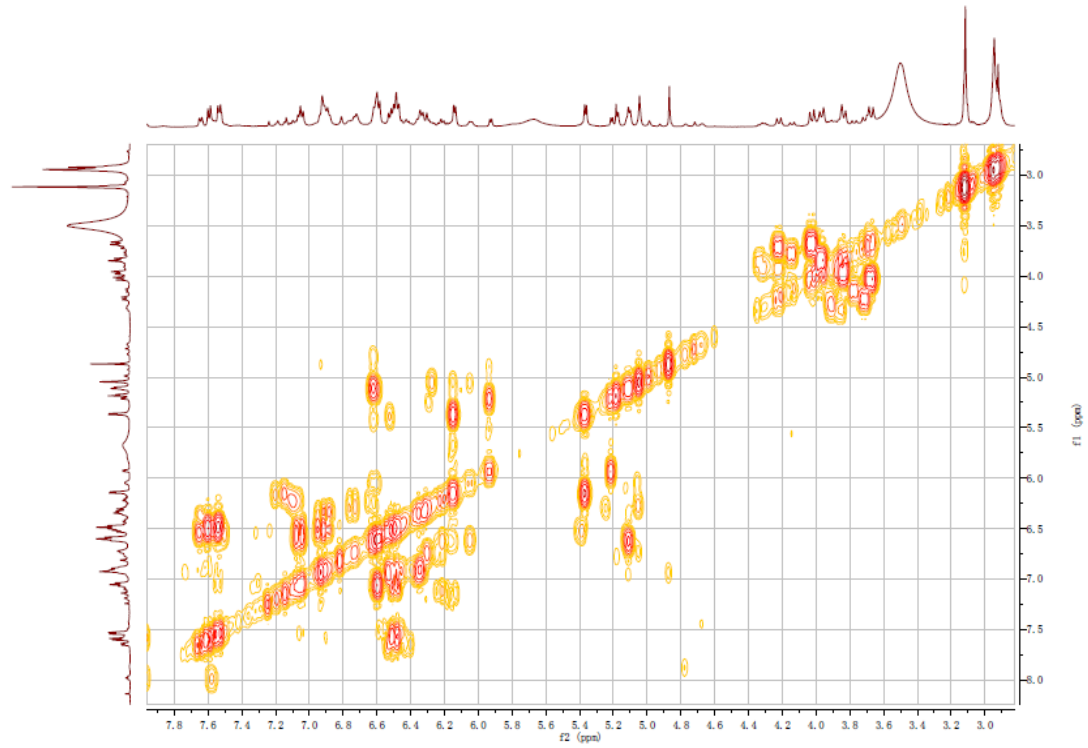


Figure S15. HMBC spectrum of chetracin F (**2**)

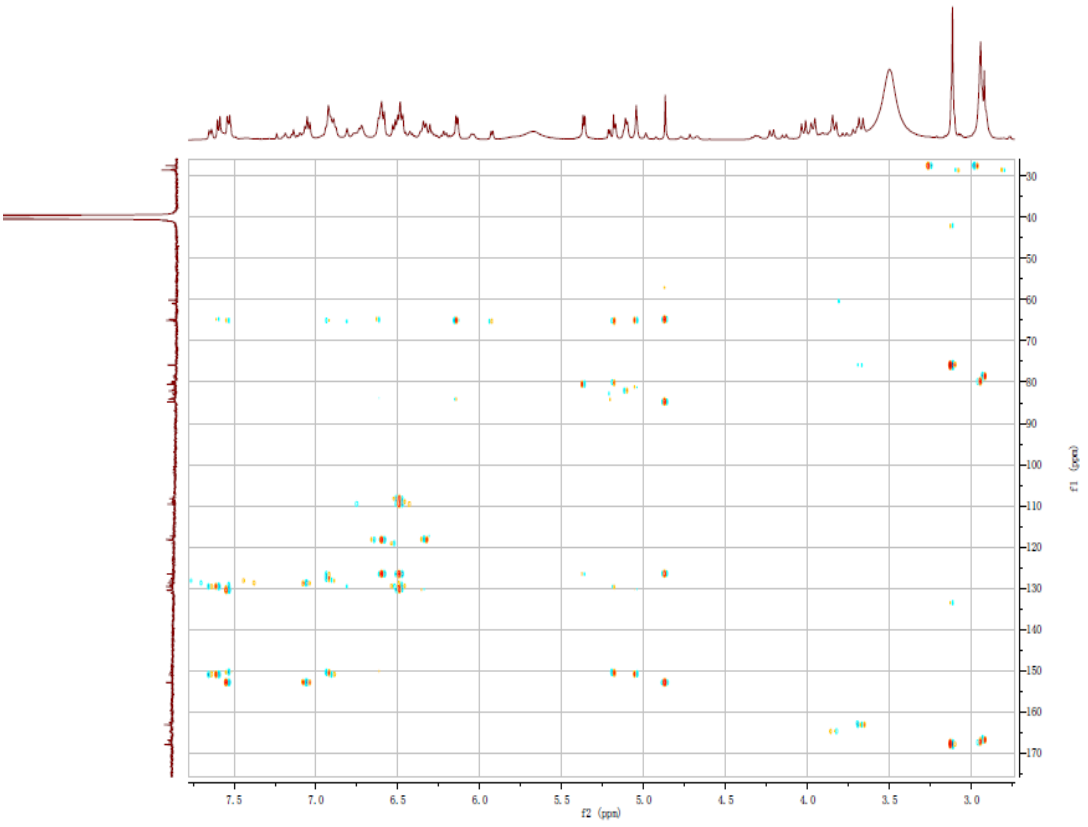


Figure S16. NOESY spectrum of chetracin F (**2**)

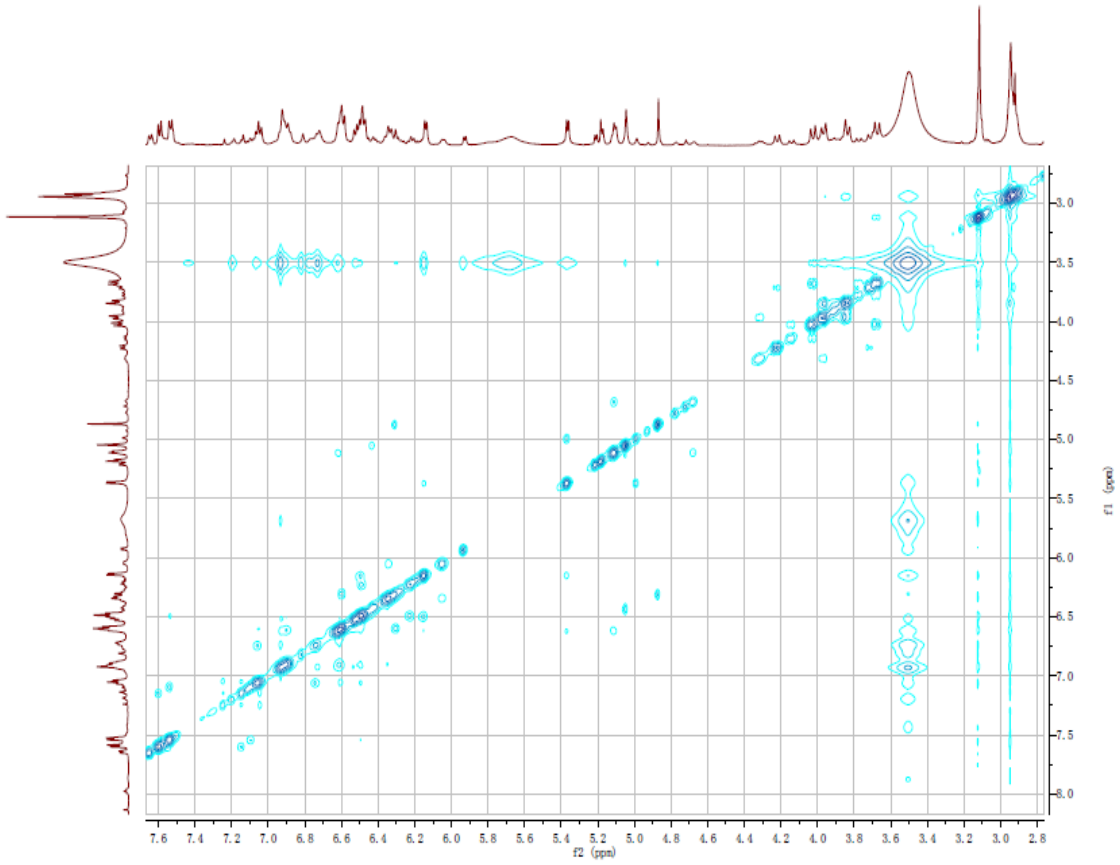


Figure S17. HRESIMS spectrum of chetracin F (**2**)

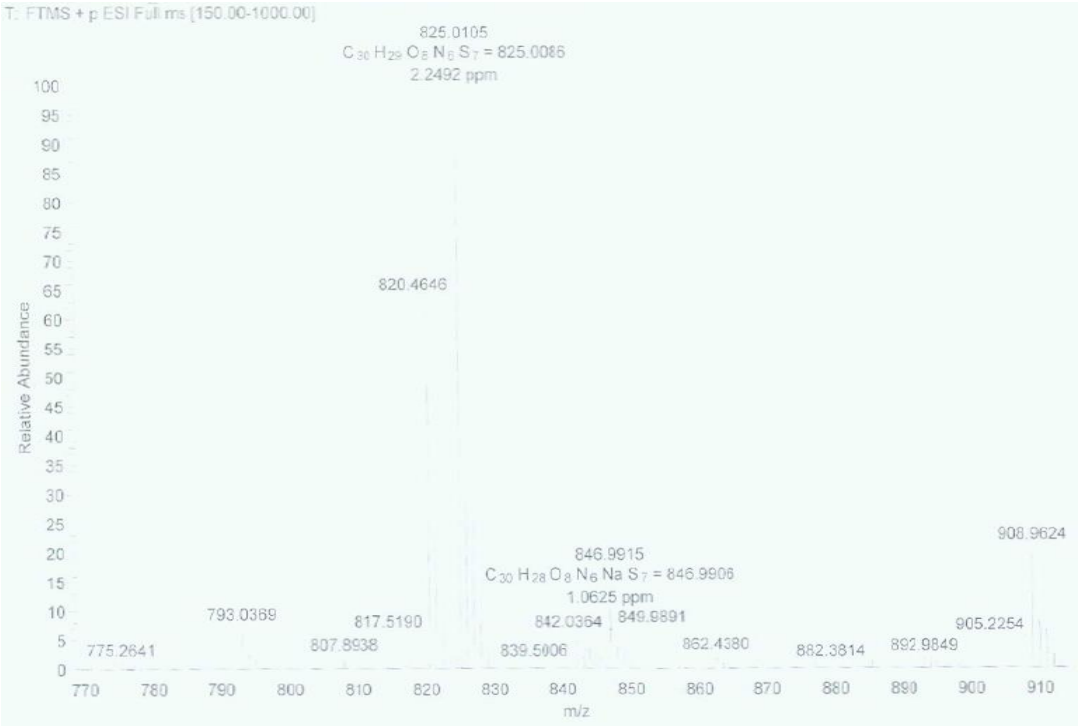


Figure S18. ^{1}H NMR spectrum (500 MHz) of **1a** in DMSO

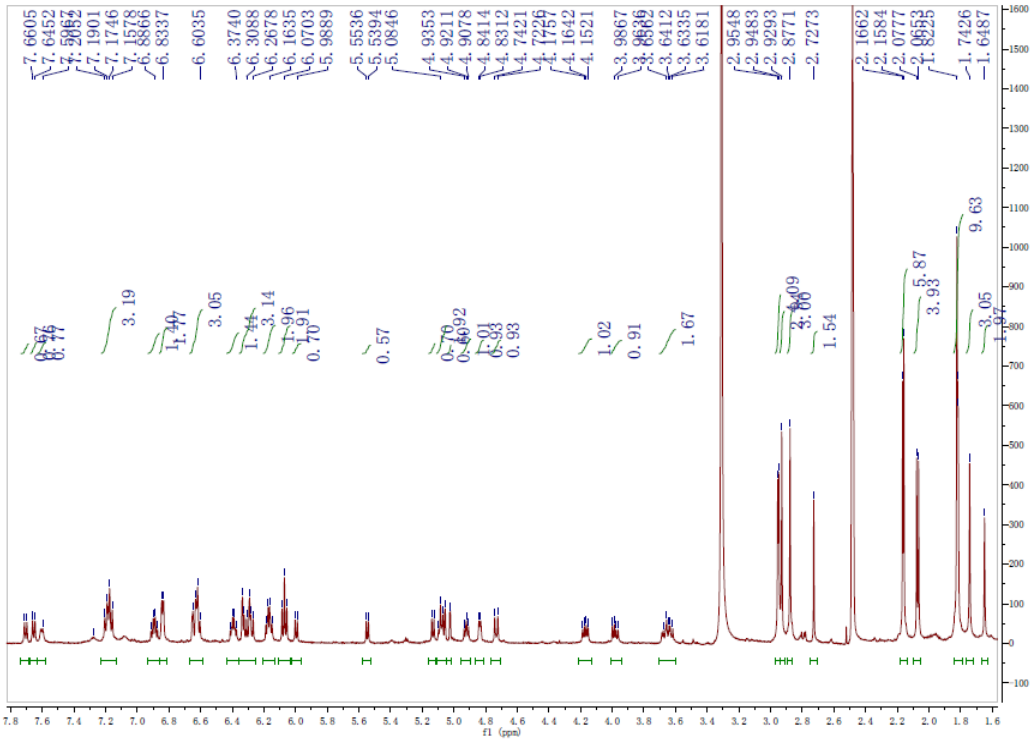


Figure S19. ^{13}C NMR spectrum (125 MHz) of **1a** in DMSO

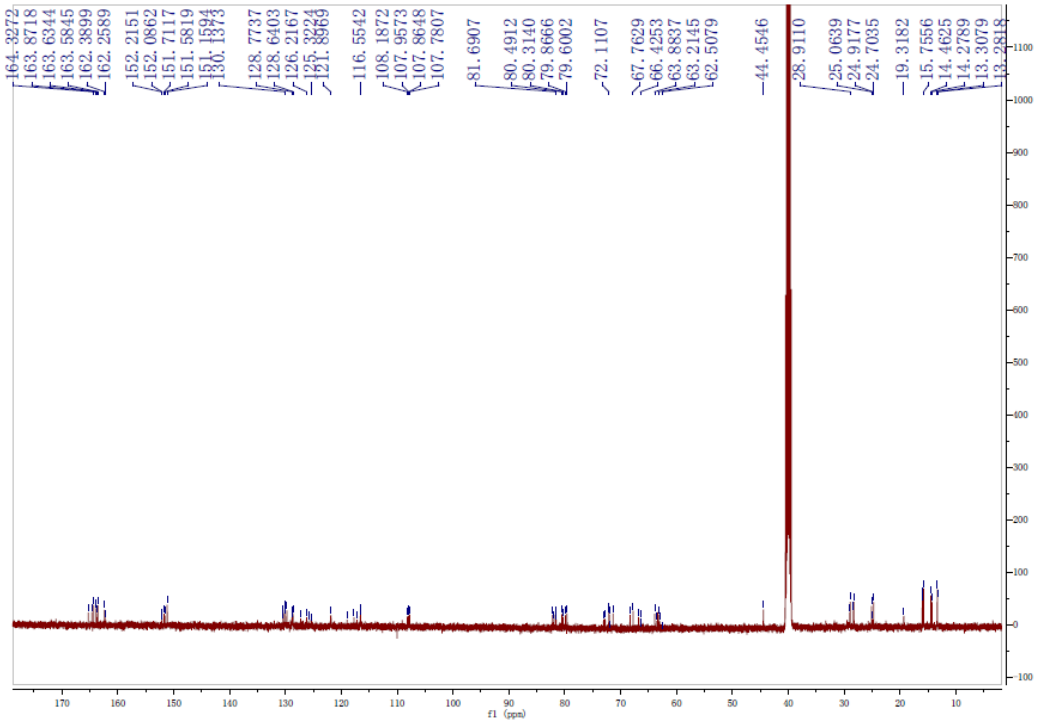


Figure S20. HMQC spectrum of **1a**

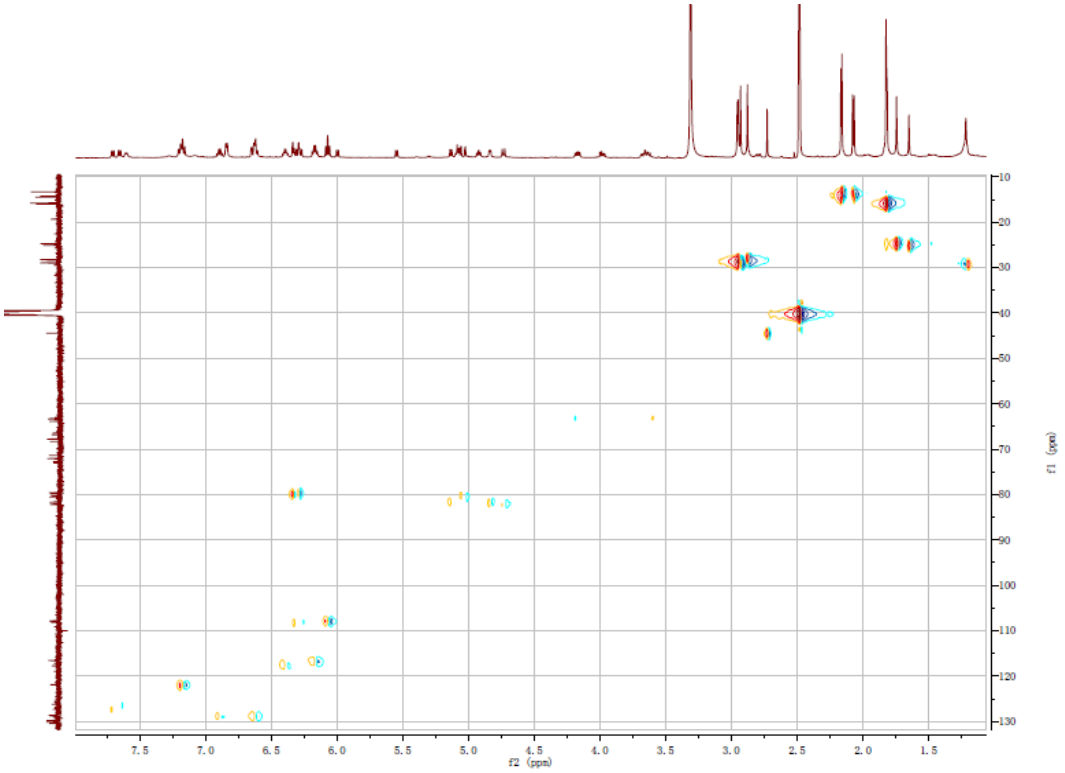


Figure S21. HMBC spectrum of **1a**

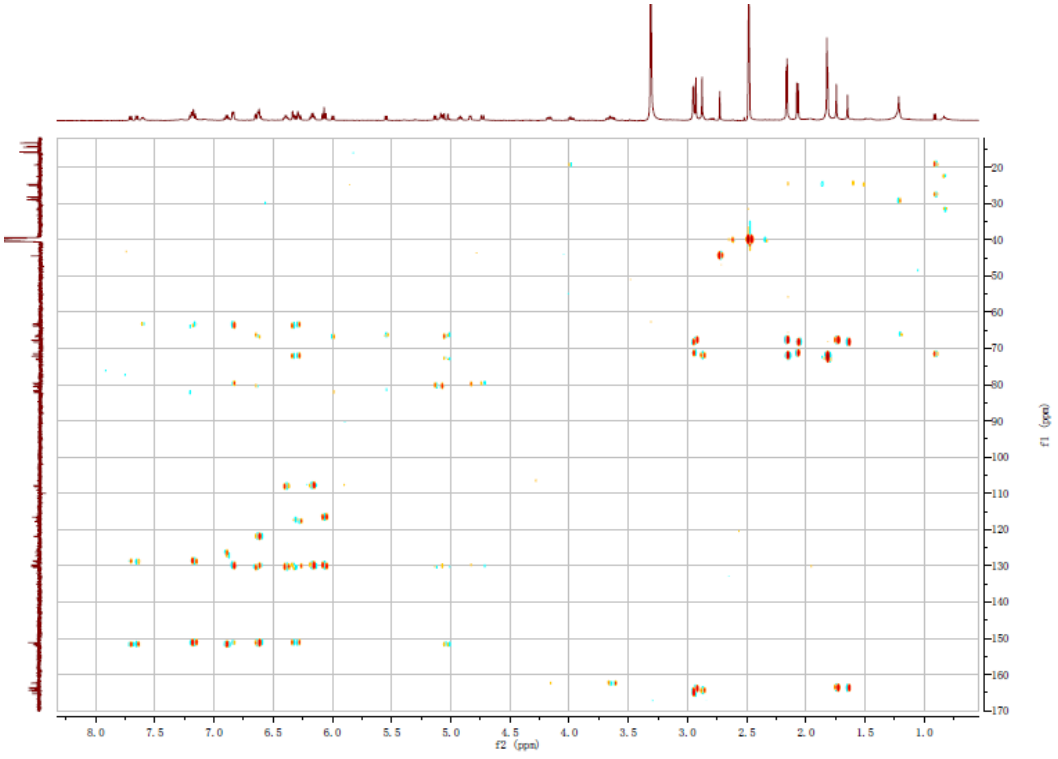


Figure S22. NOESY spectrum of **1a**

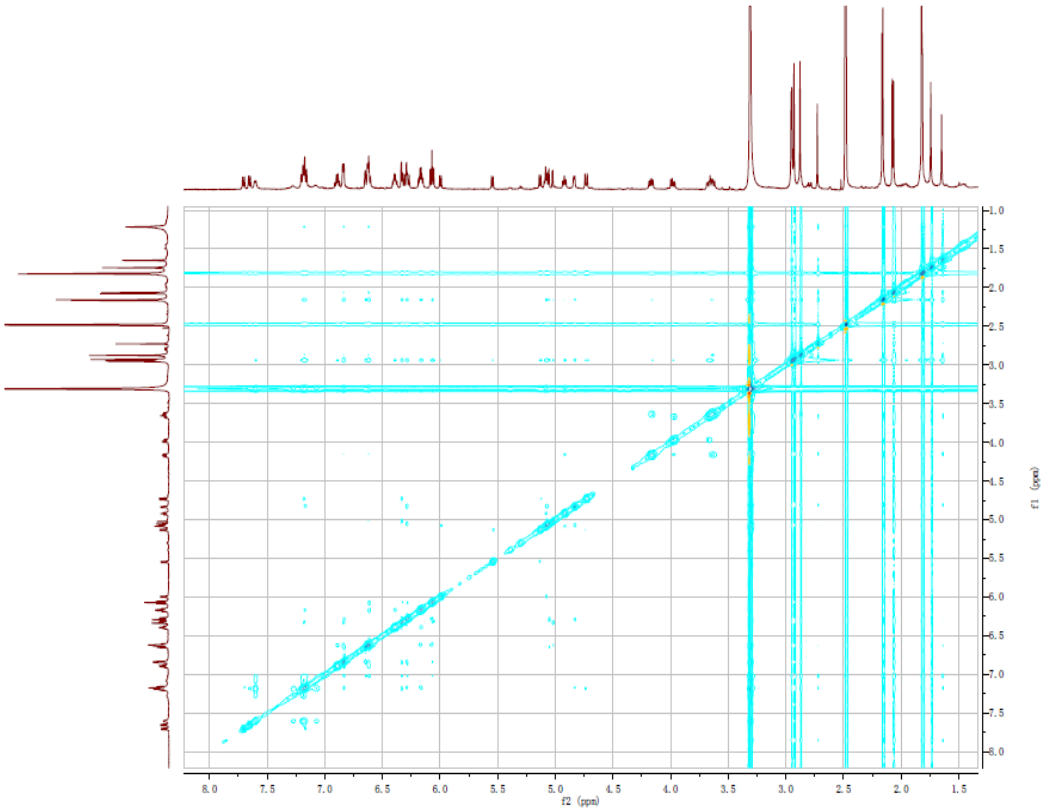


Figure S23. HRESIMS spectrum of **1a**

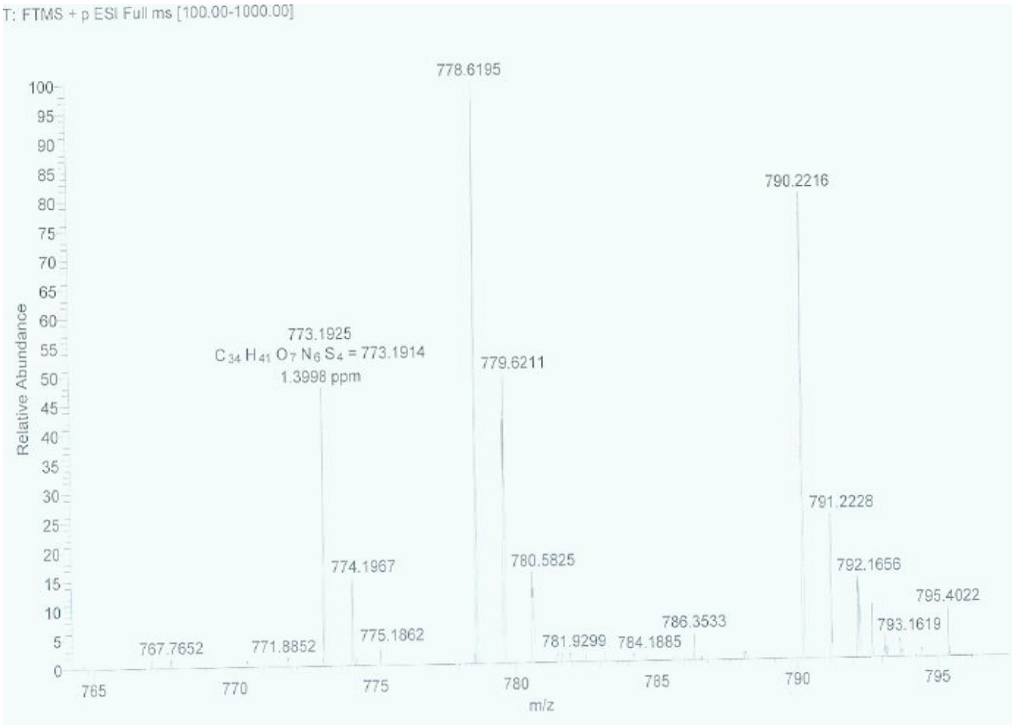


Figure S24. IR spectrum of chetracin E (**1**)

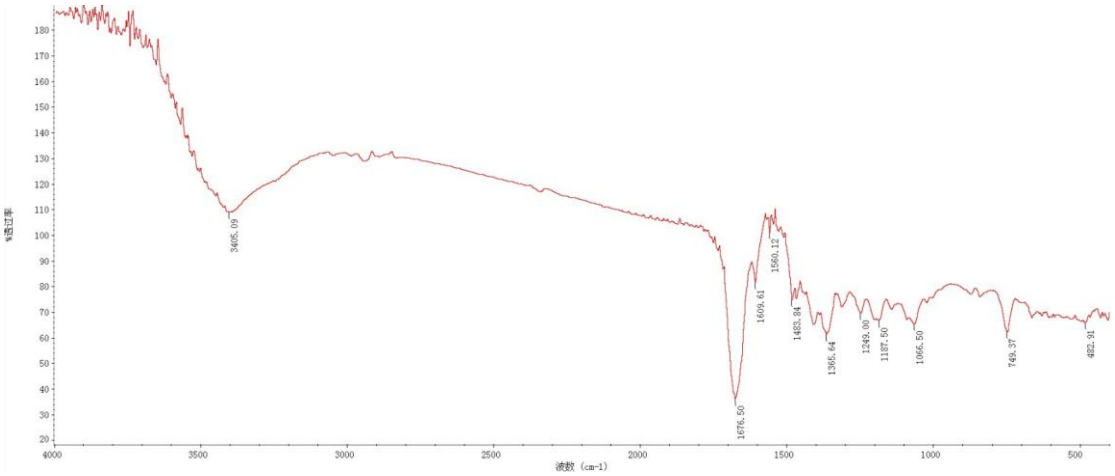


Figure S25. IR spectrum of chetracin F (**2**)

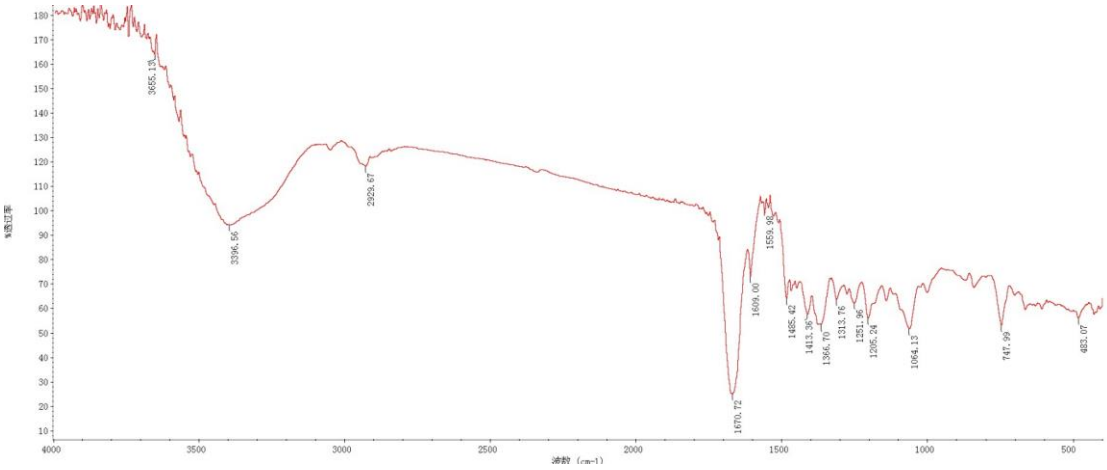


Figure S26. IR spectrum of **1a**