

Supplemental Material

Chrysomycins, anti-tuberculosis C-glycoside polyketides from *Streptomyces* sp. MS751

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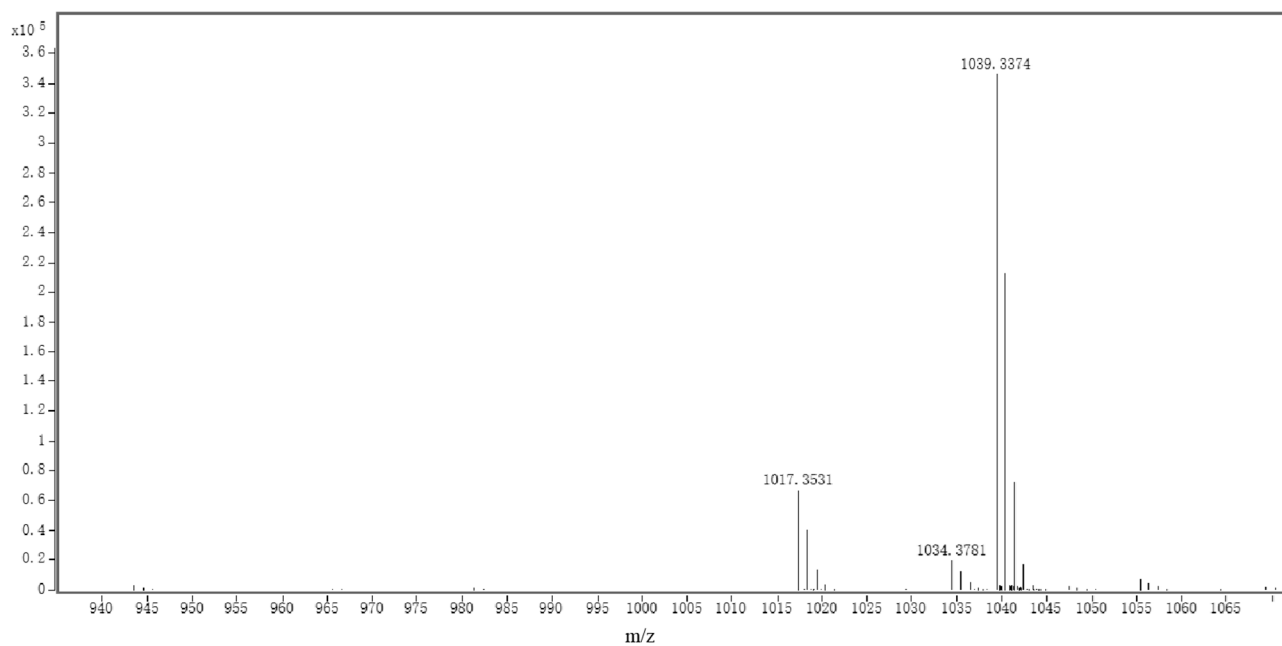


Figure S1a. HRESIMS spectrum of **1**

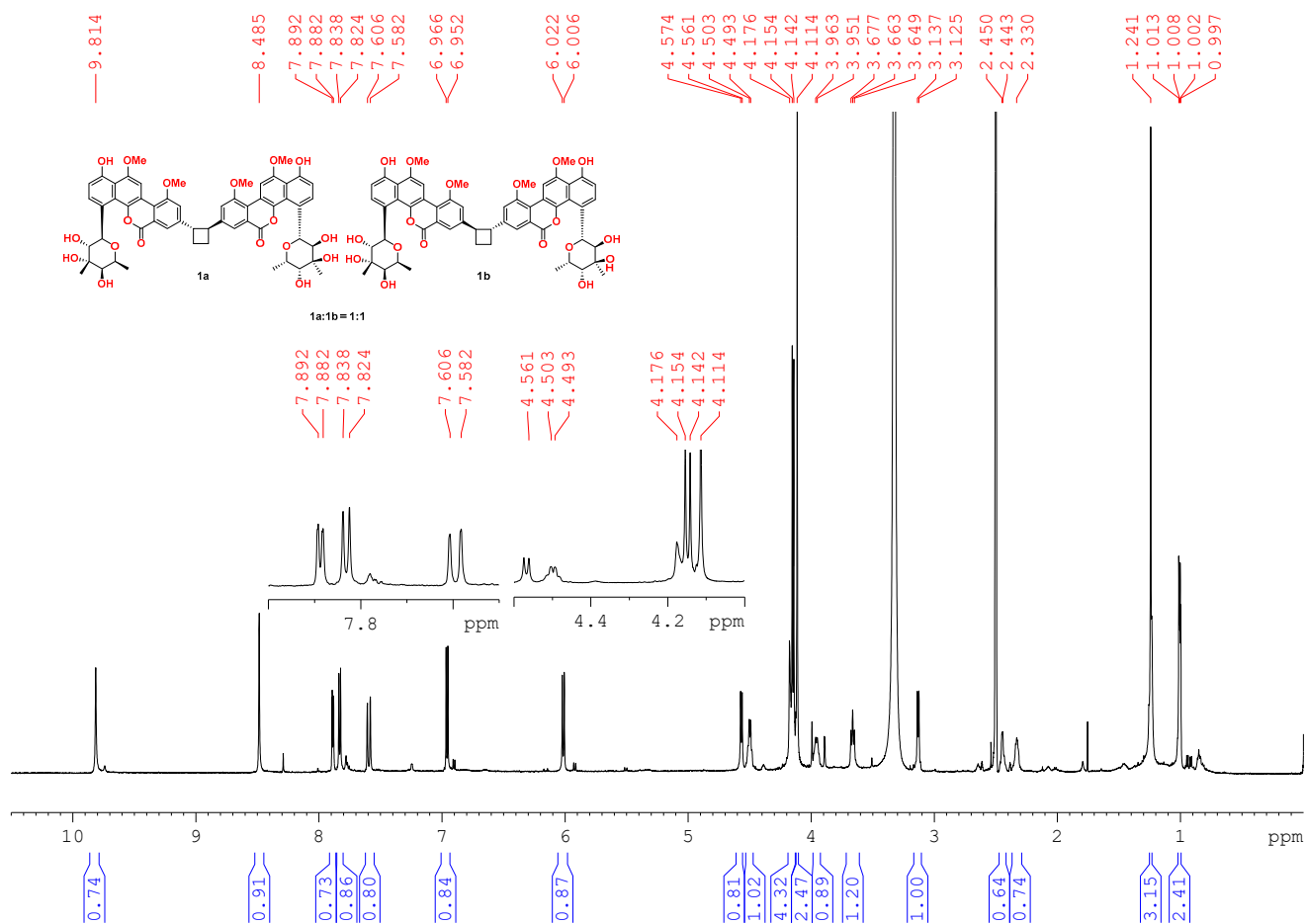


Figure S1b. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of **1**

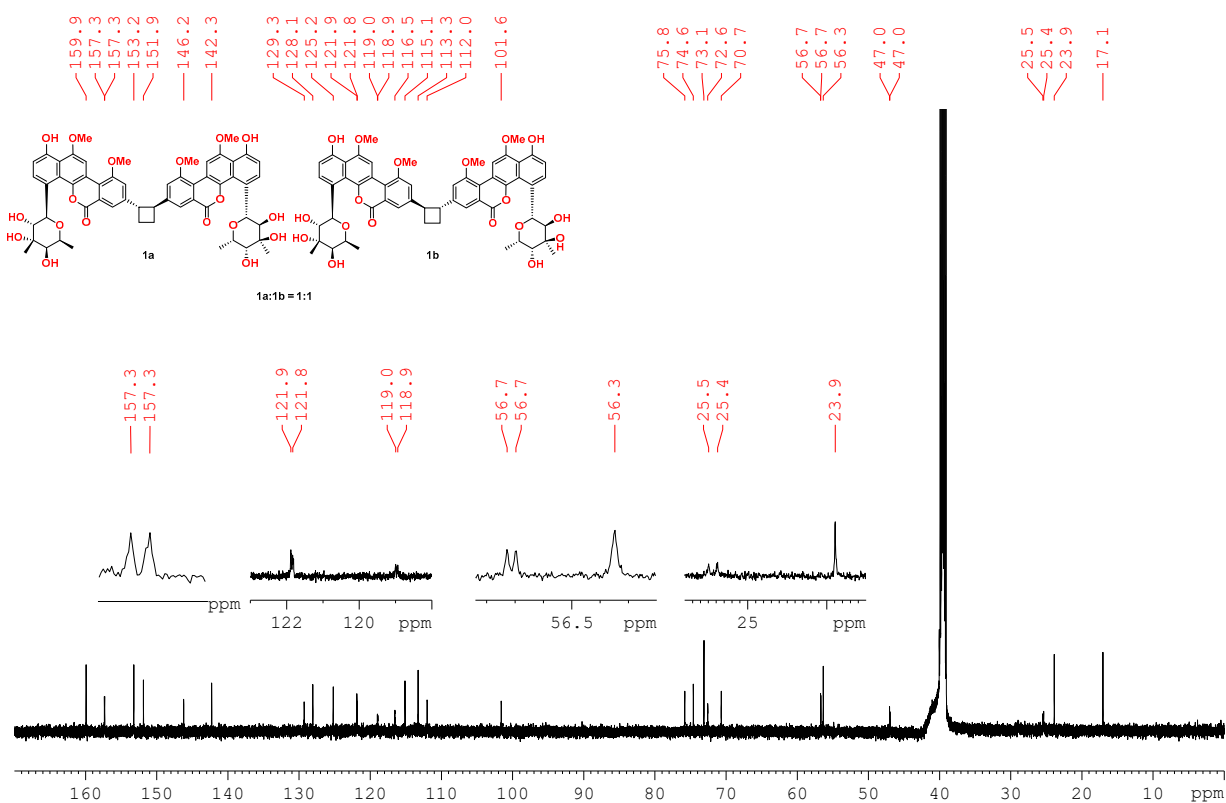


Figure S1c. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of **1**

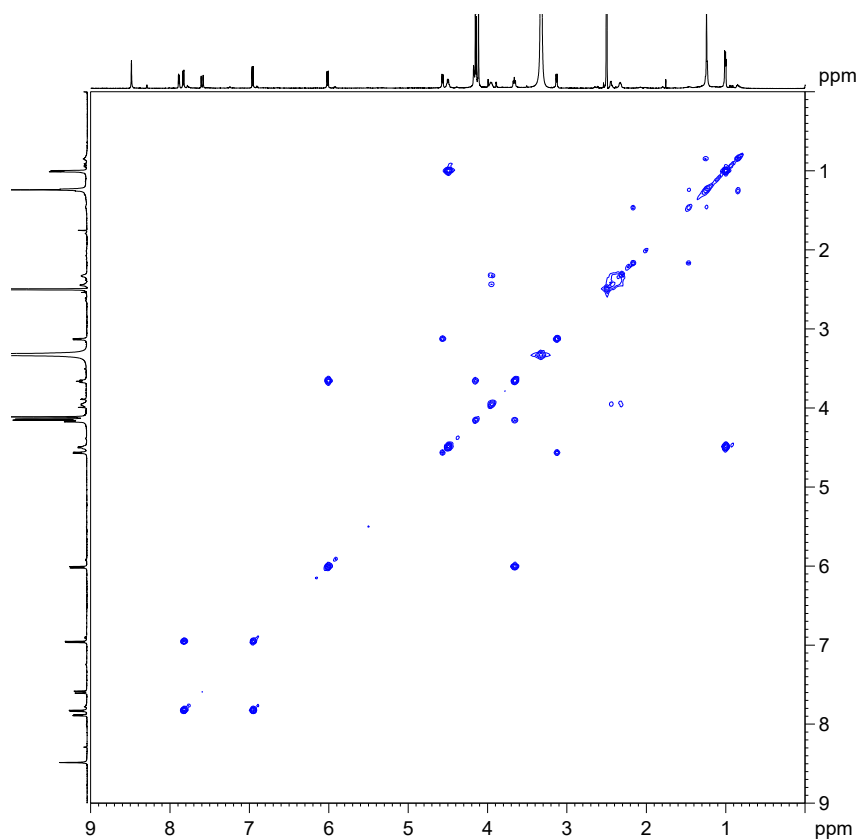


Figure S1d. COSY spectrum (600 MHz, $\text{DMSO}-d_6$) of **1**

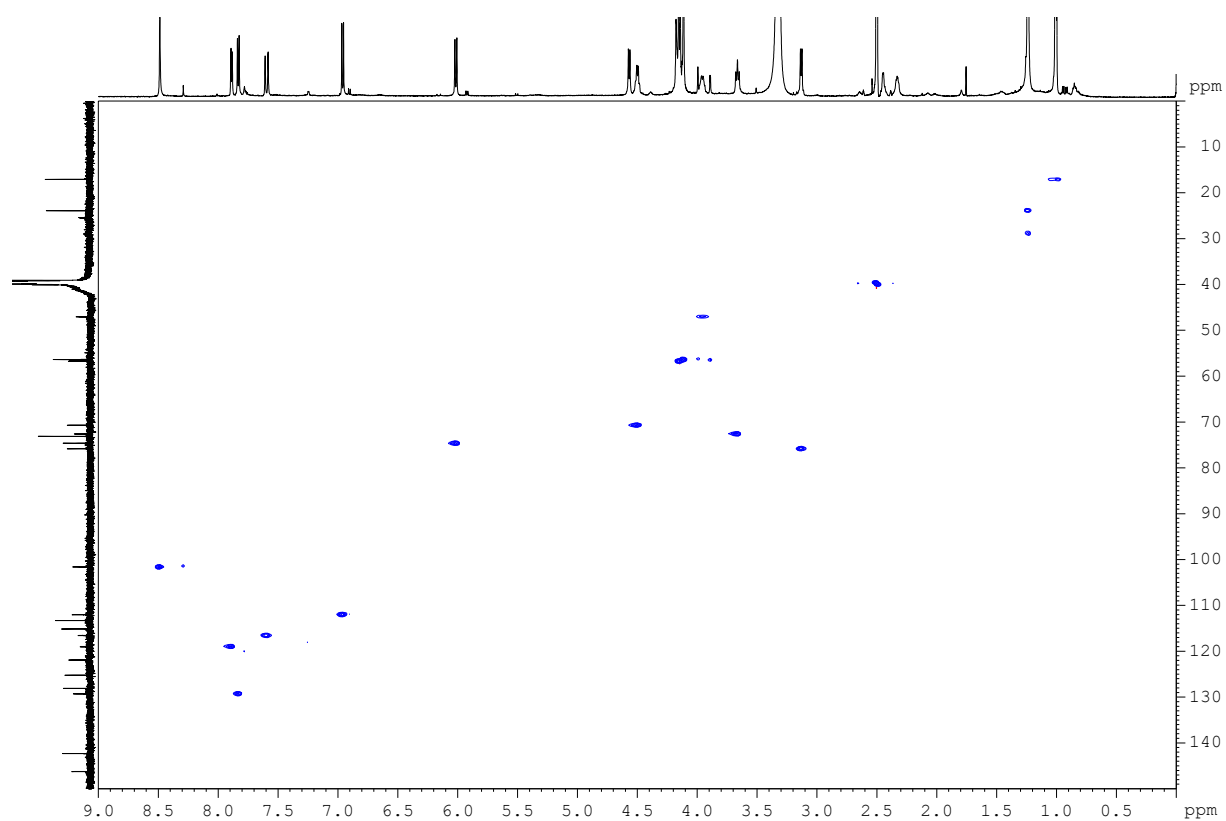


Figure S1e. $^1\text{H} - ^{13}\text{C}$ HSQC spectrum (600 MHz, $\text{DMSO}-d_6$) of **1**

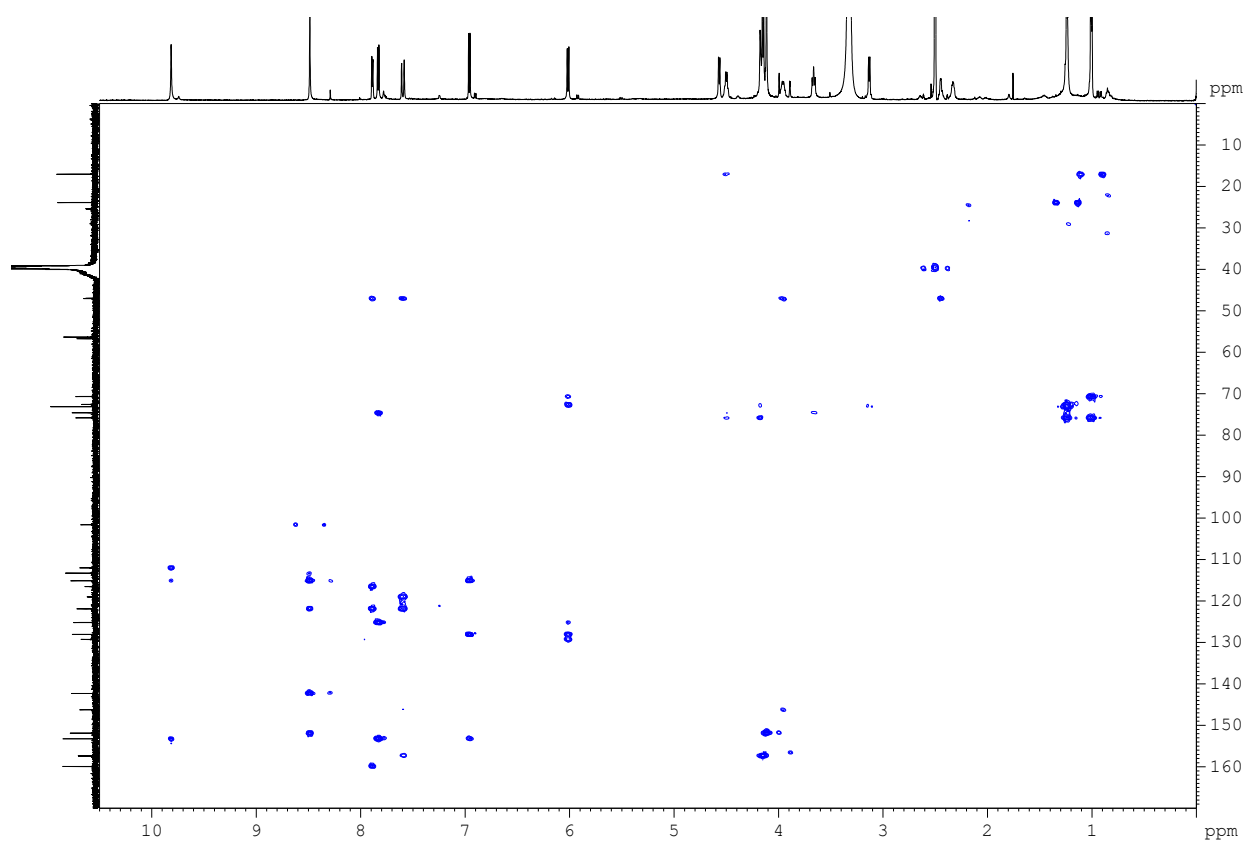


Figure S1f. $^1\text{H} - ^{13}\text{C}$ HMBC spectrum (600 MHz, $\text{DMSO}-d_6$) of **1**

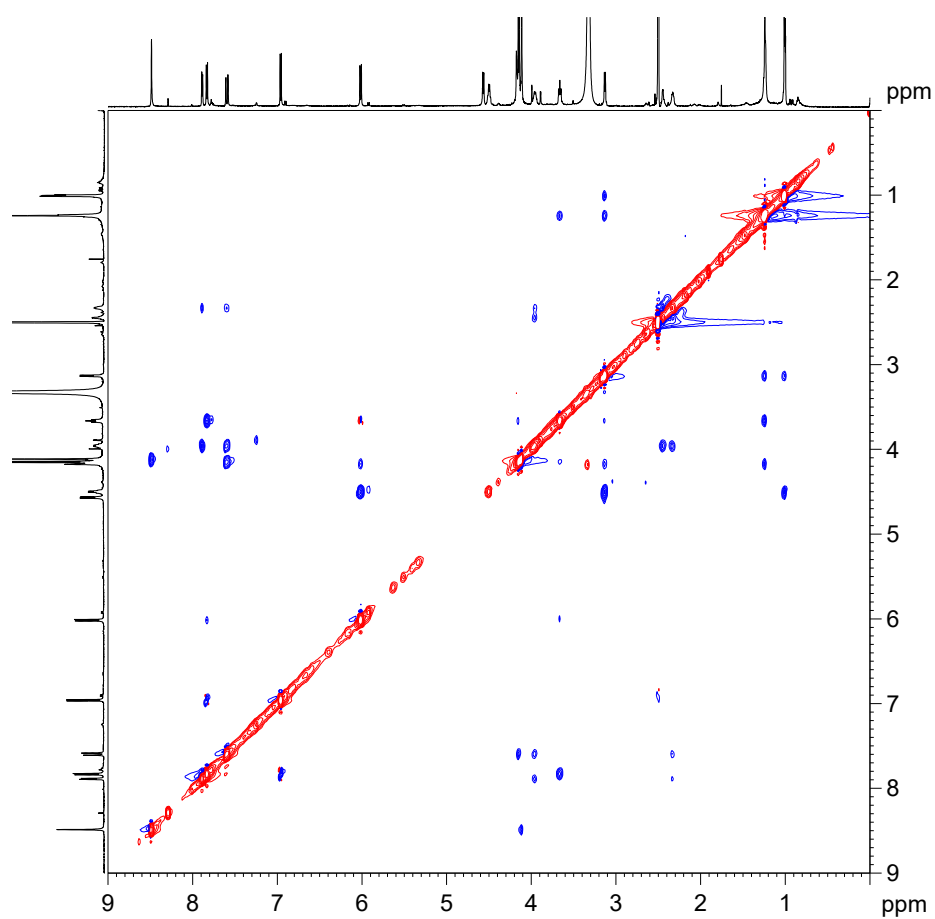


Figure S1g. ROESY spectrum (600 MHz, DMSO-*d*₆) of **1**

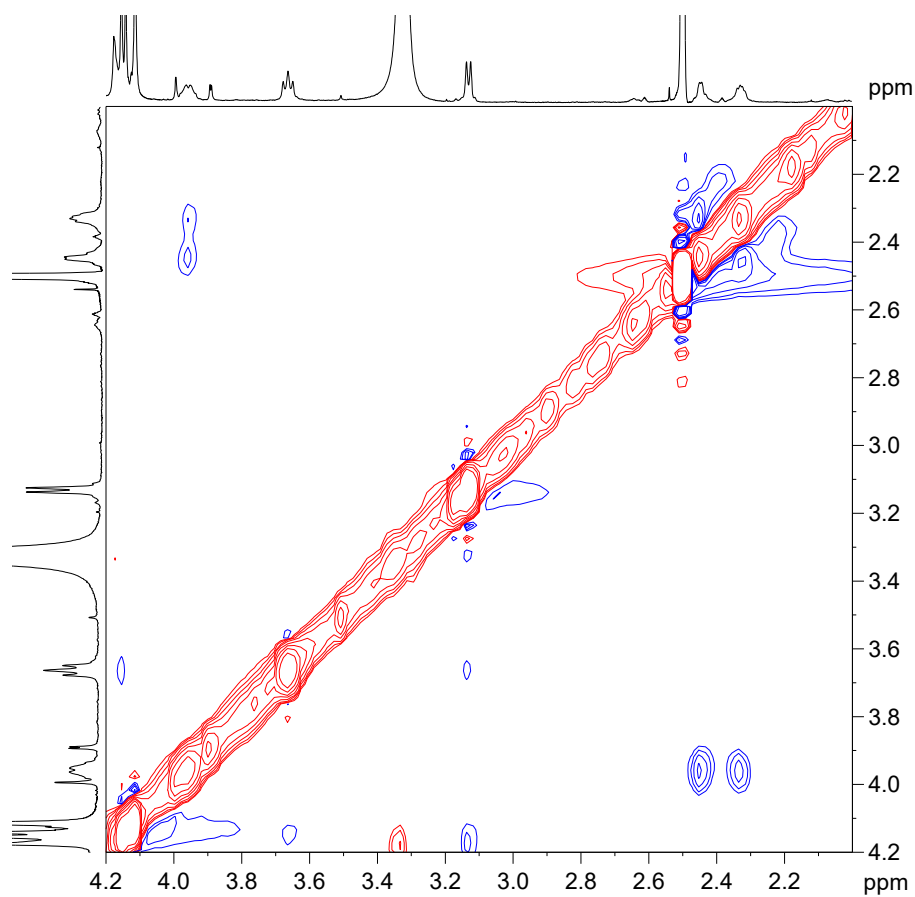


Figure S1h. Expansion of ROESY spectrum (600 MHz, DMSO-*d*₆) of **1**

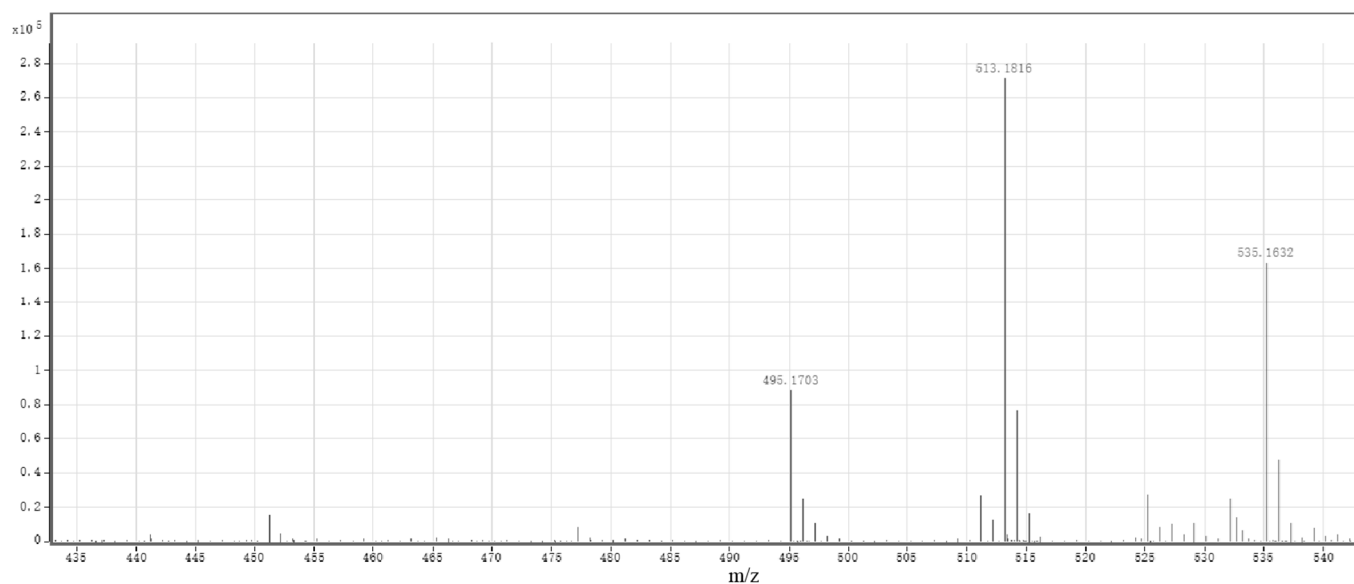


Figure S2a. HRESIMS spectrum of 2

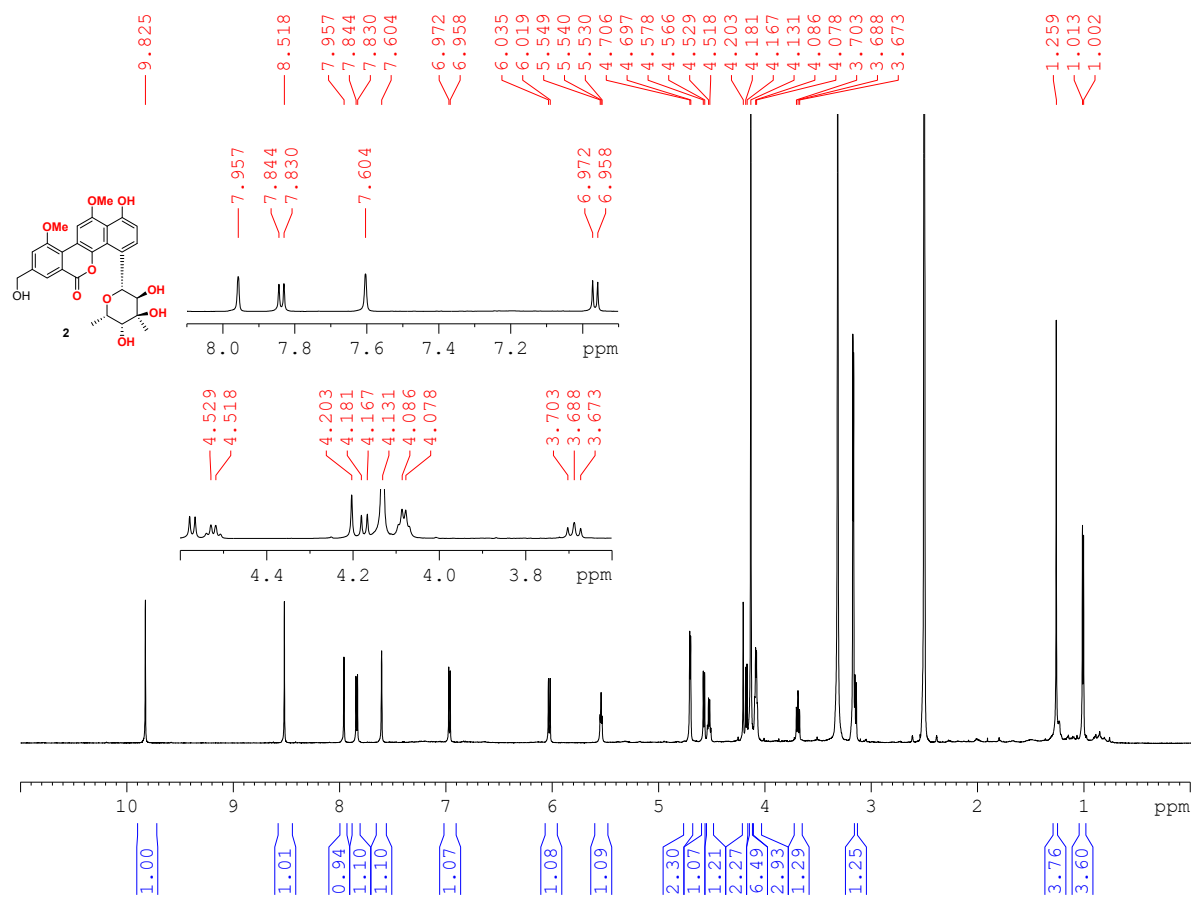


Figure S2b. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 2

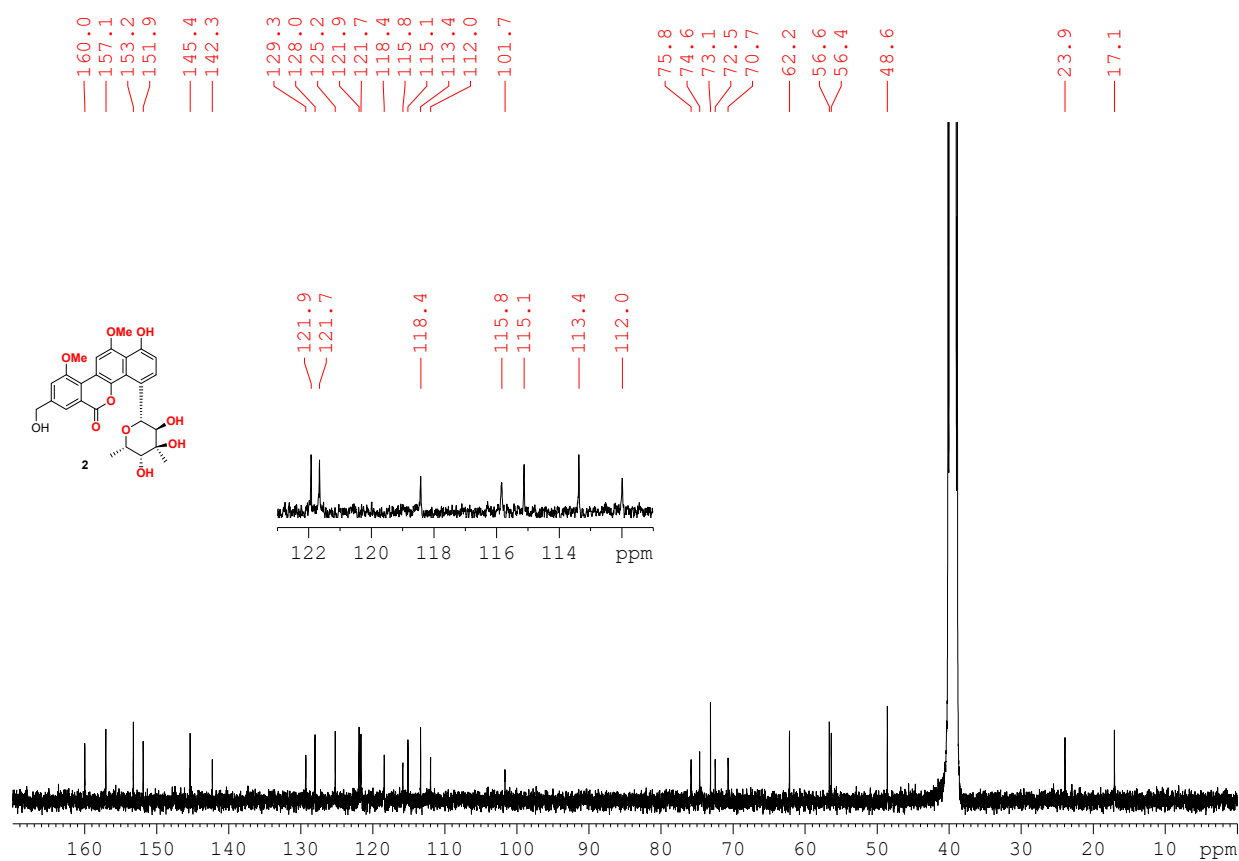


Figure S2c. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of **2**

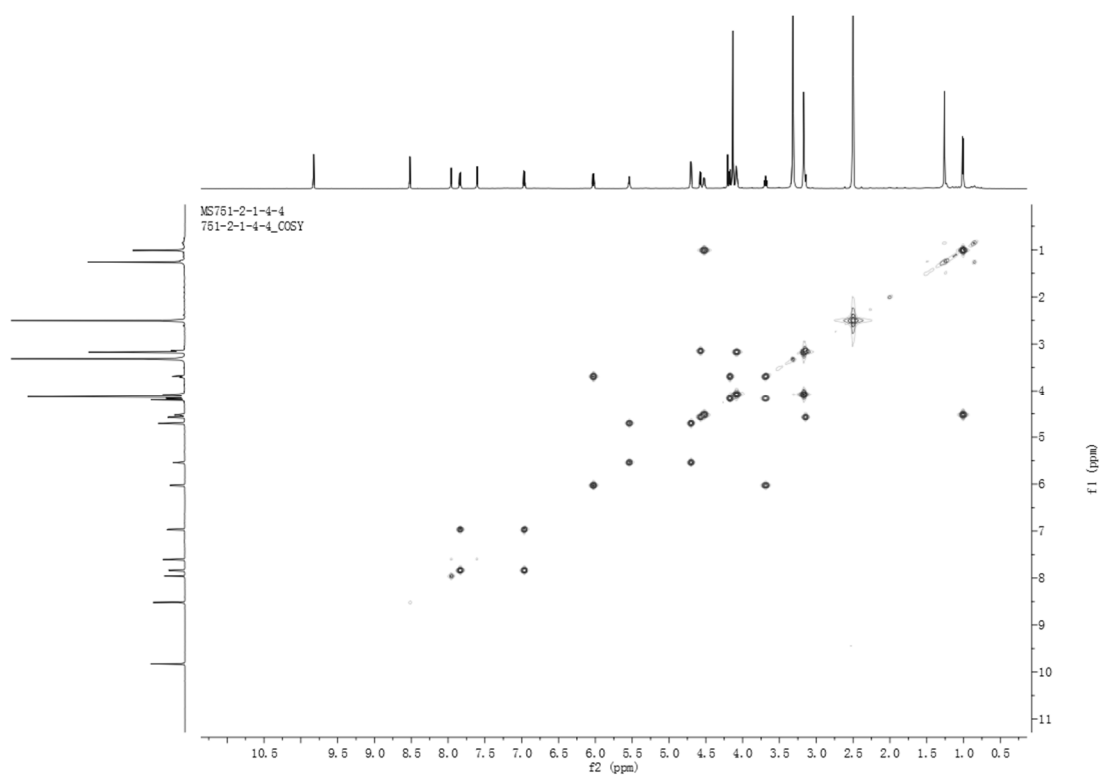


Figure S2d. COSY spectrum (600 MHz, DMSO-*d*₆) of **2**

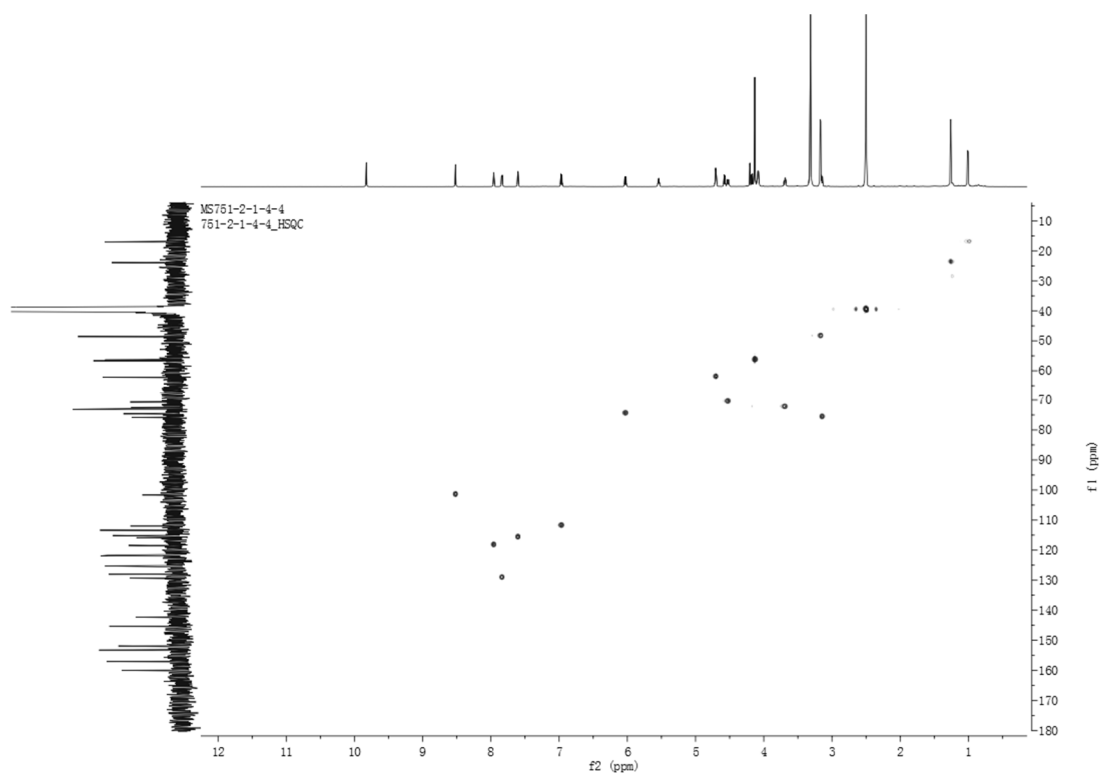


Figure S2e. $^1\text{H} - ^{13}\text{C}$ HSQC spectrum (600 MHz, $\text{DMSO}-d_6$) of **2**

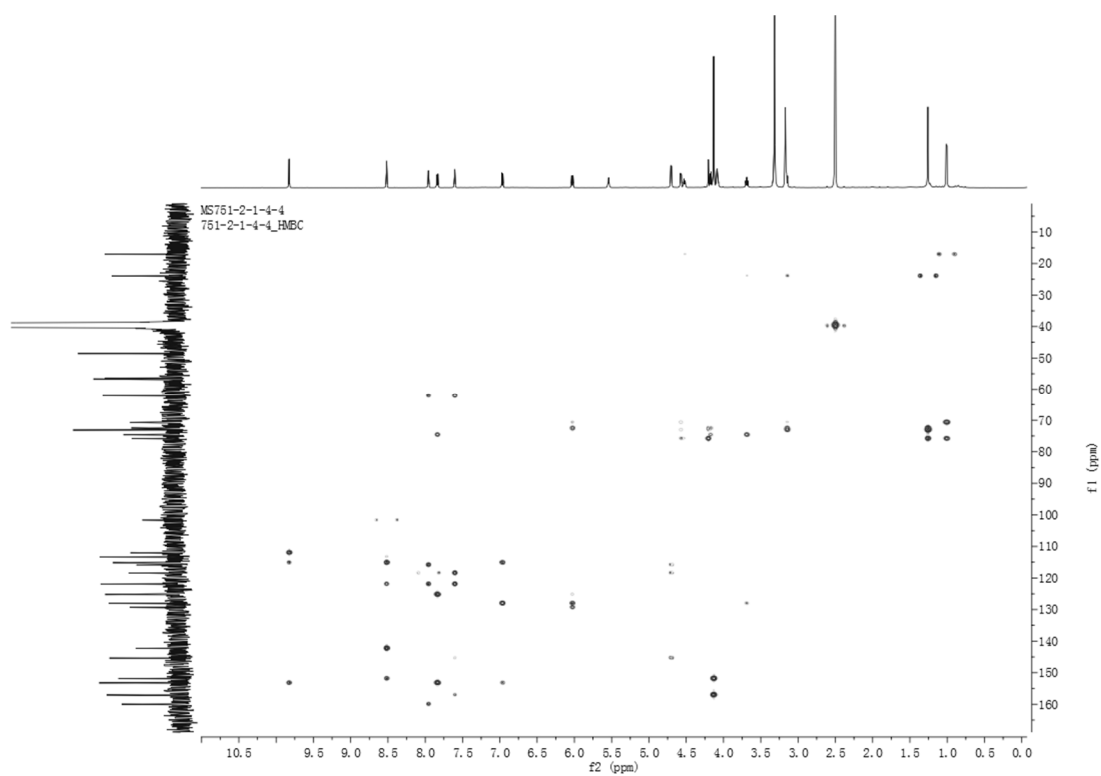


Figure S2f. $^1\text{H} - ^{13}\text{C}$ HMBC spectrum (600 MHz, $\text{DMSO}-d_6$) of **2**

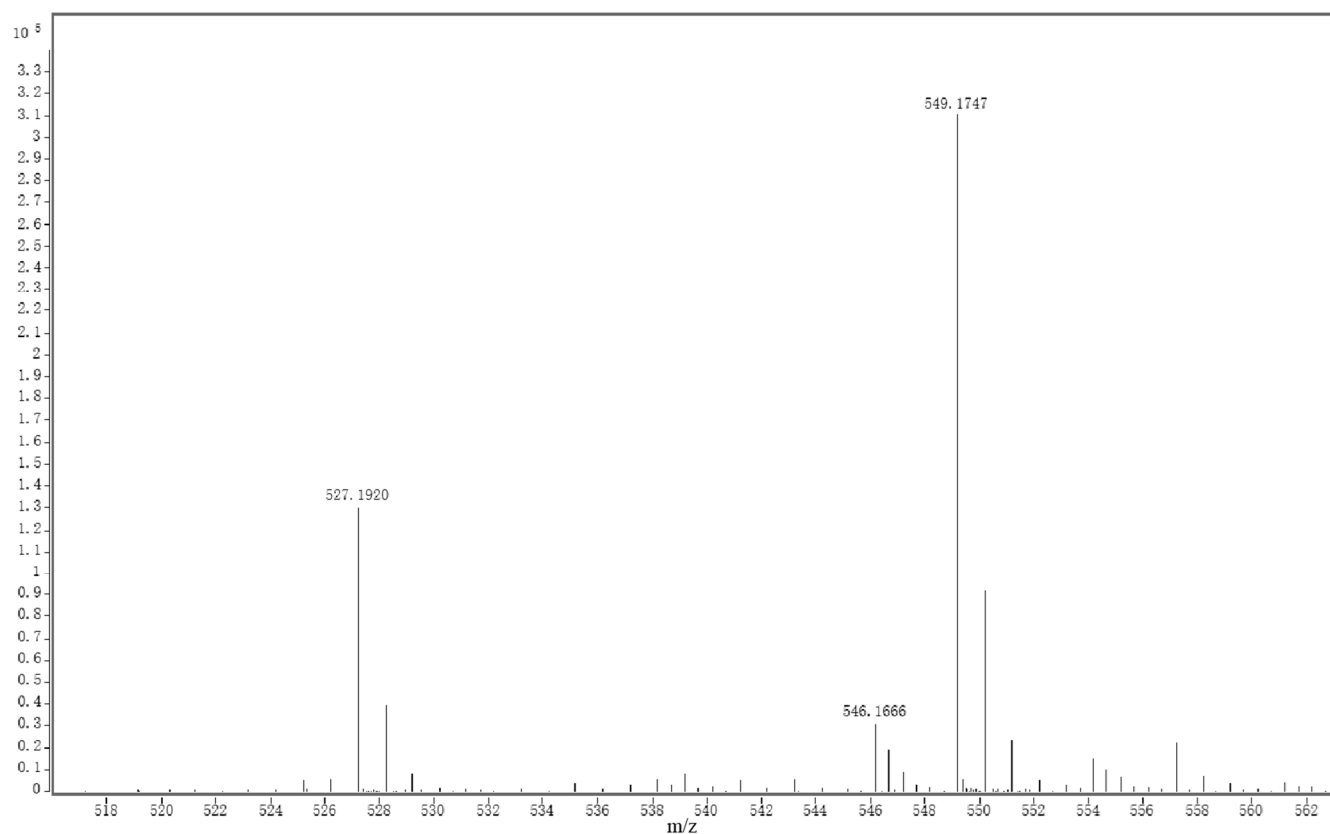


Figure S3a. HRESIMS spectrum of 3

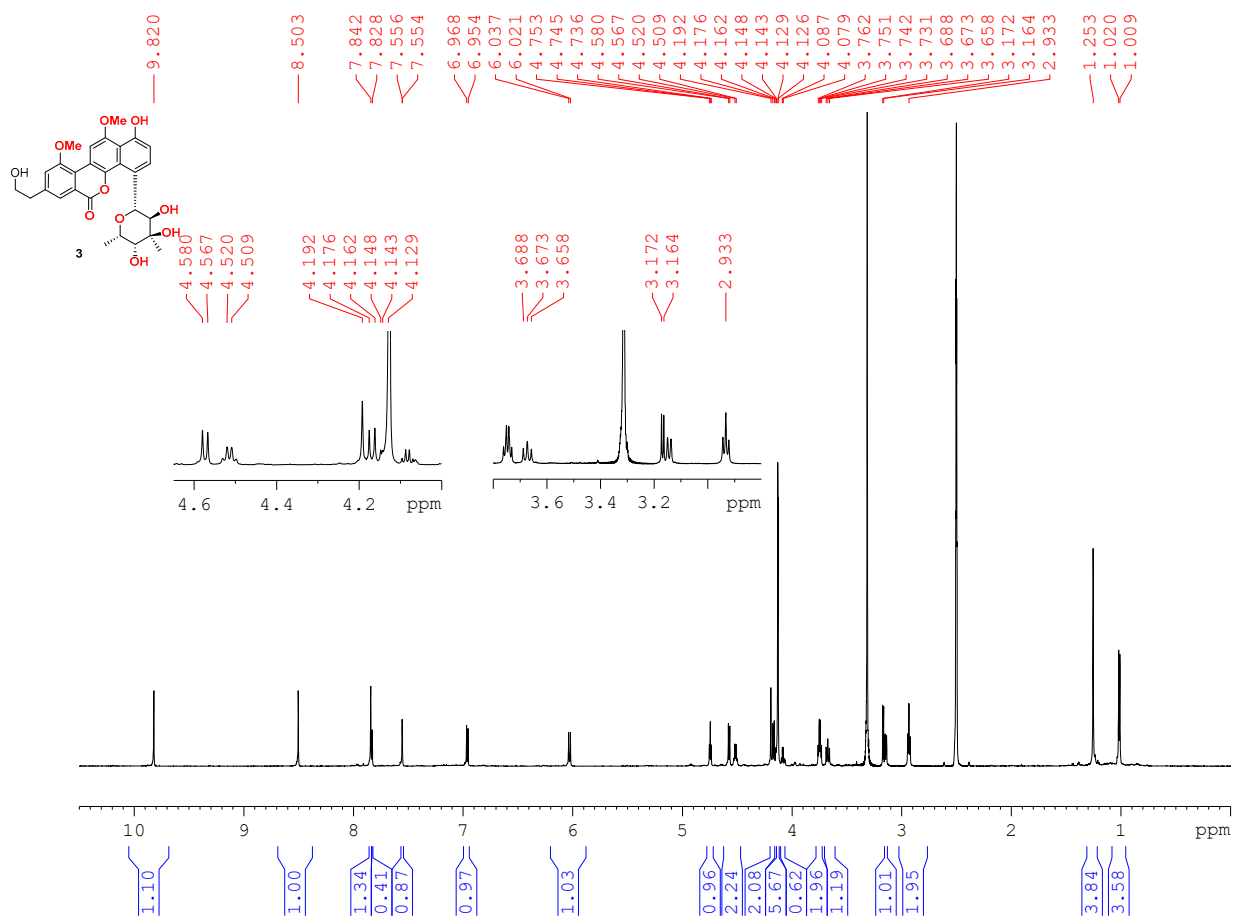


Figure S3b. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 3

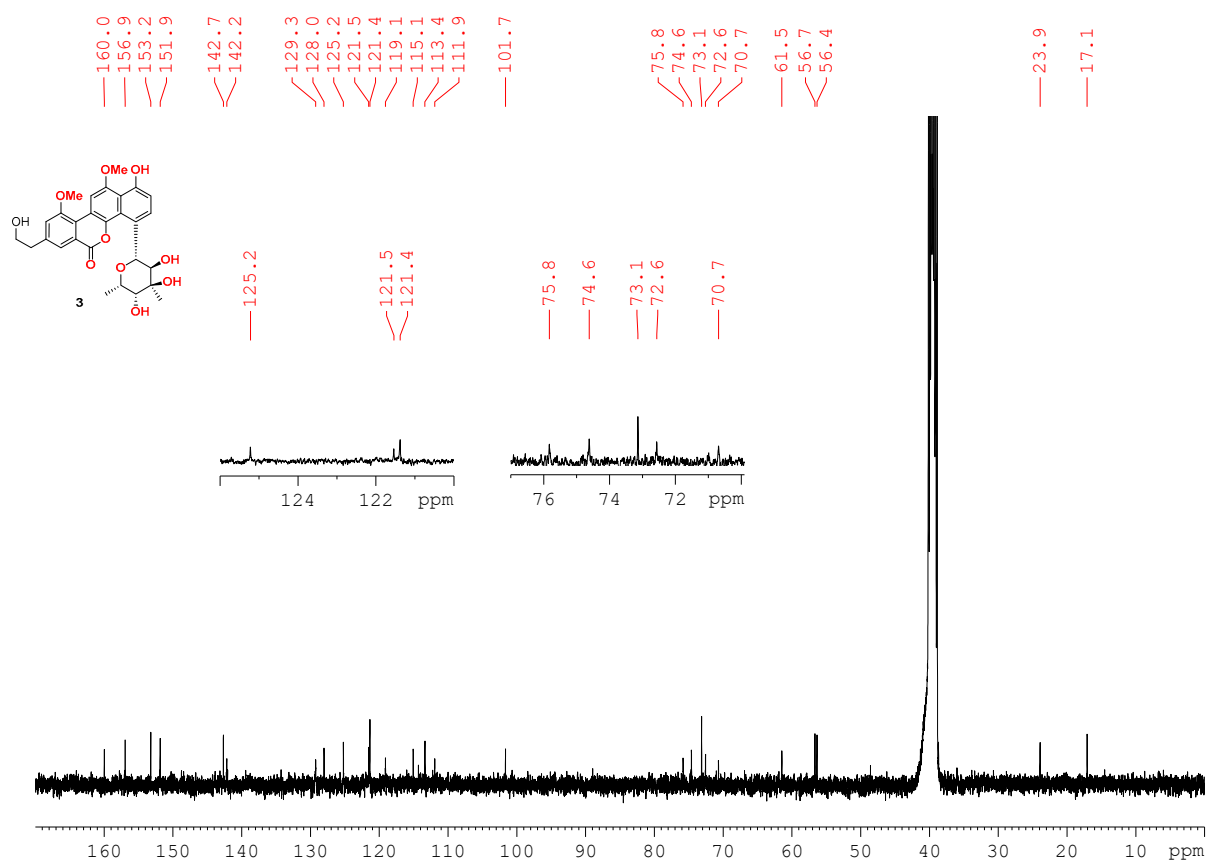


Figure S3c. ¹³C NMR spectrum (150 MHz, DMSO-*d*₆) of 3

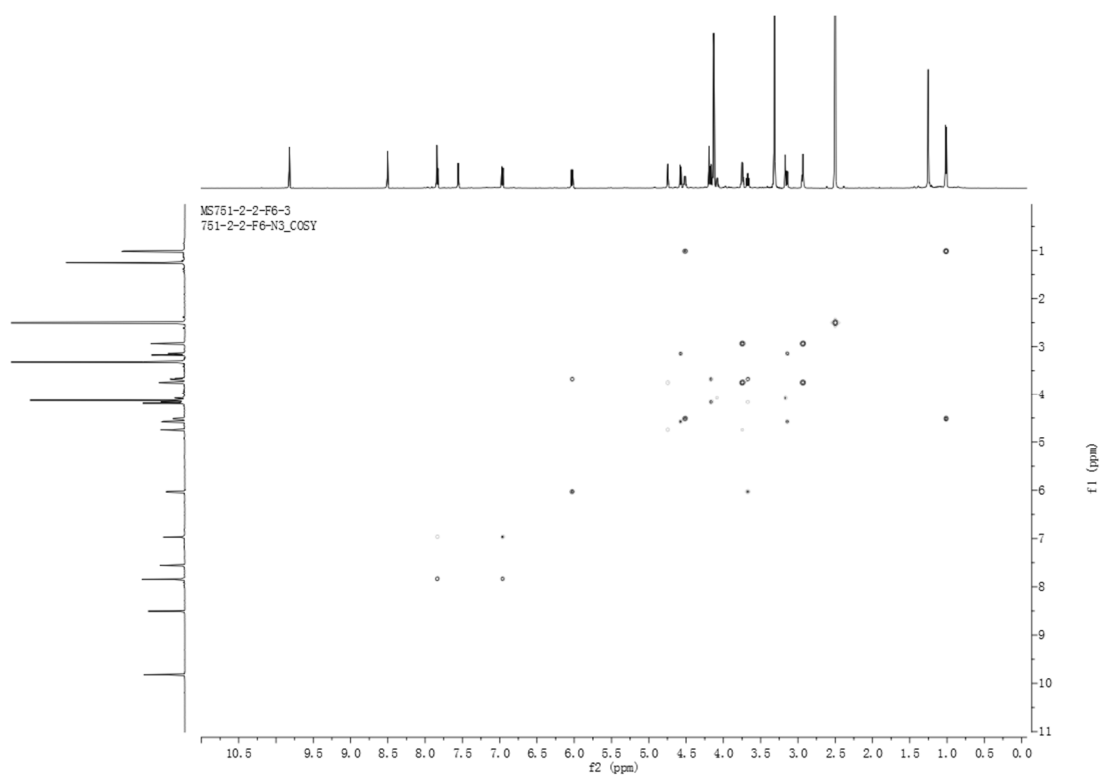


Figure S3d. COSY spectrum (600 MHz, DMSO-*d*₆) of 3

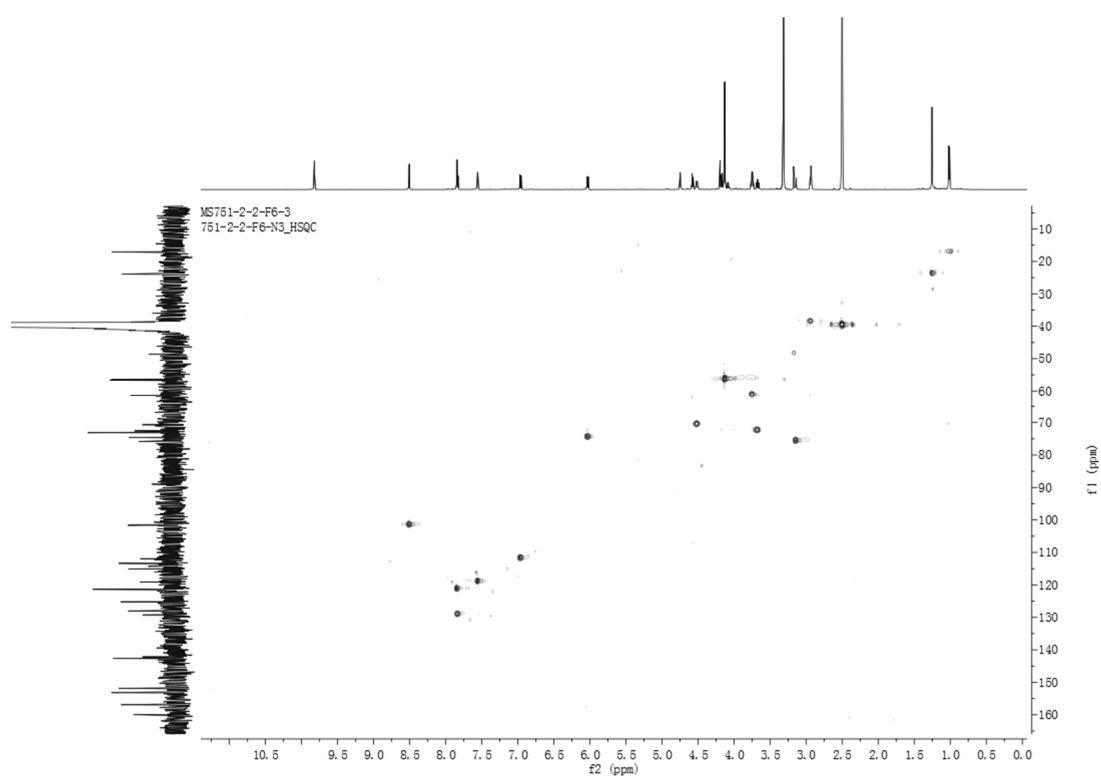


Figure S3e. $^1\text{H} - ^{13}\text{C}$ HSQC spectrum (600 MHz, $\text{DMSO}-d_6$) of **3**

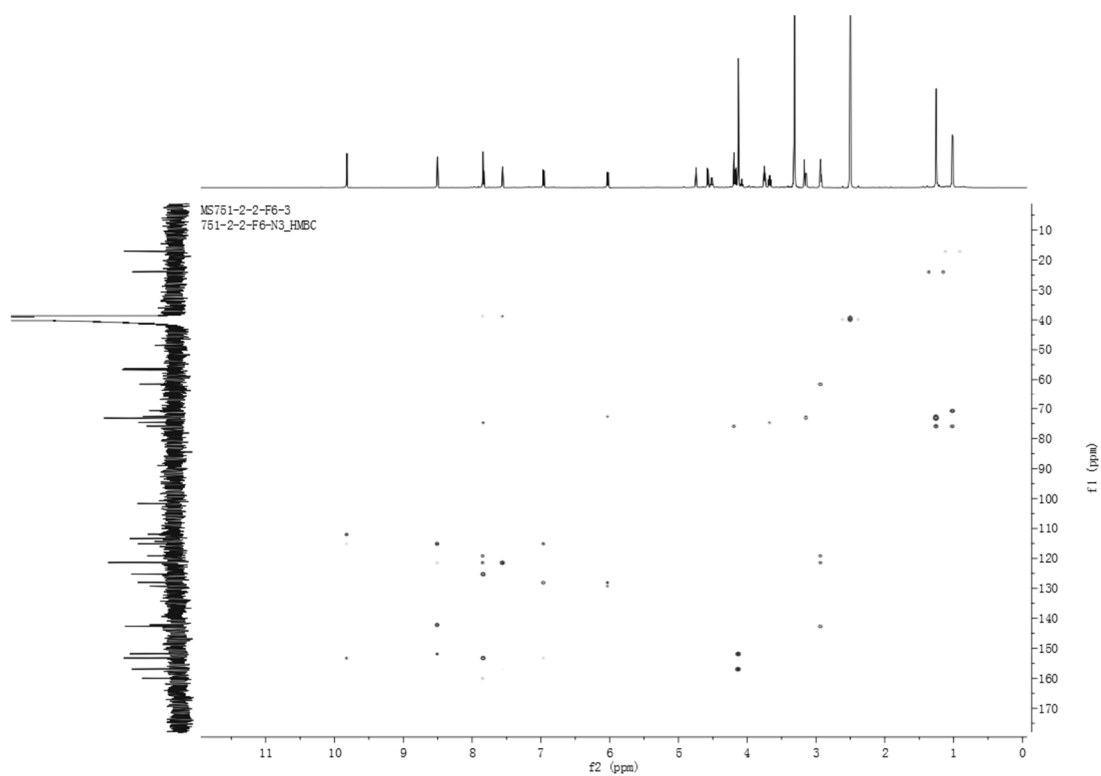


Figure S3f. $^1\text{H} - ^{13}\text{C}$ HMBC spectrum (600 MHz, $\text{DMSO}-d_6$) of **3**

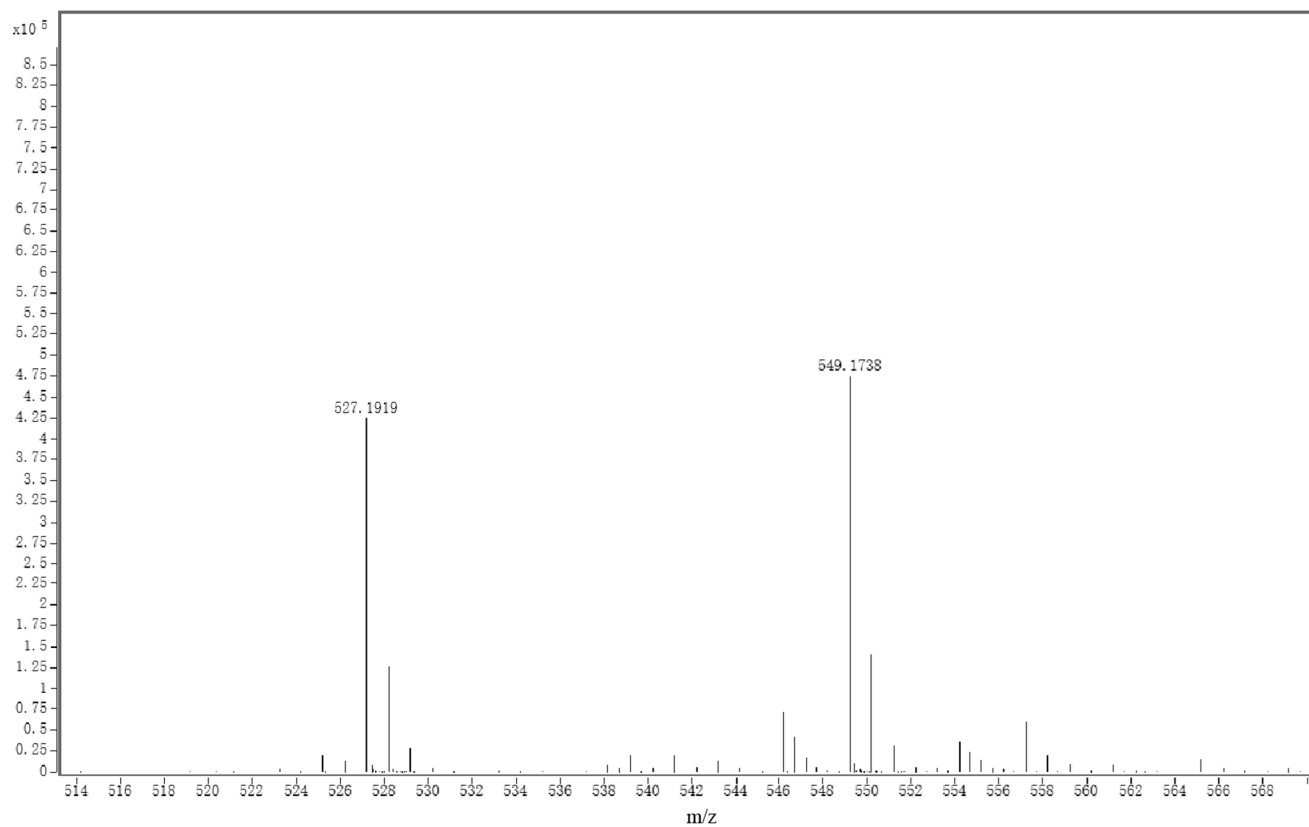


Figure S4a. HRESIMS spectrum of 4

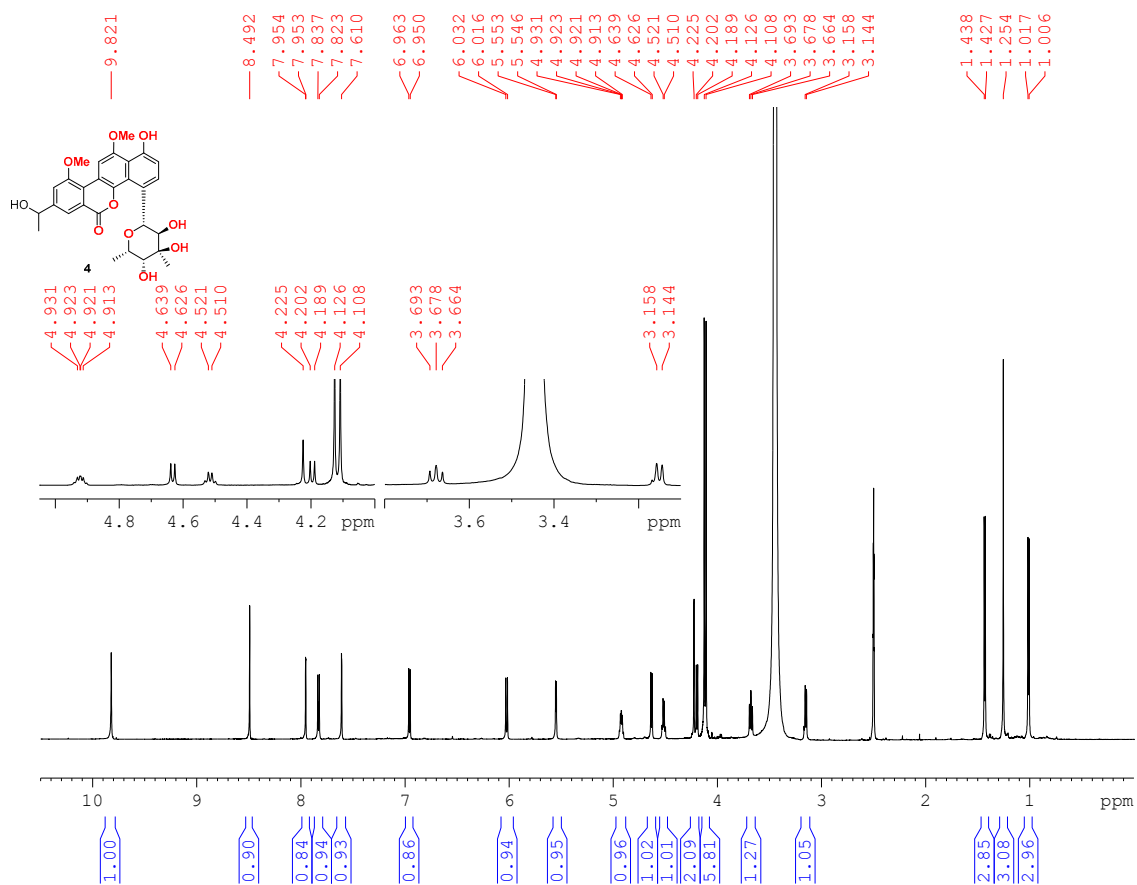


Figure S4b. ¹H NMR spectrum (600 MHz, DMSO-*d*₆) of 4

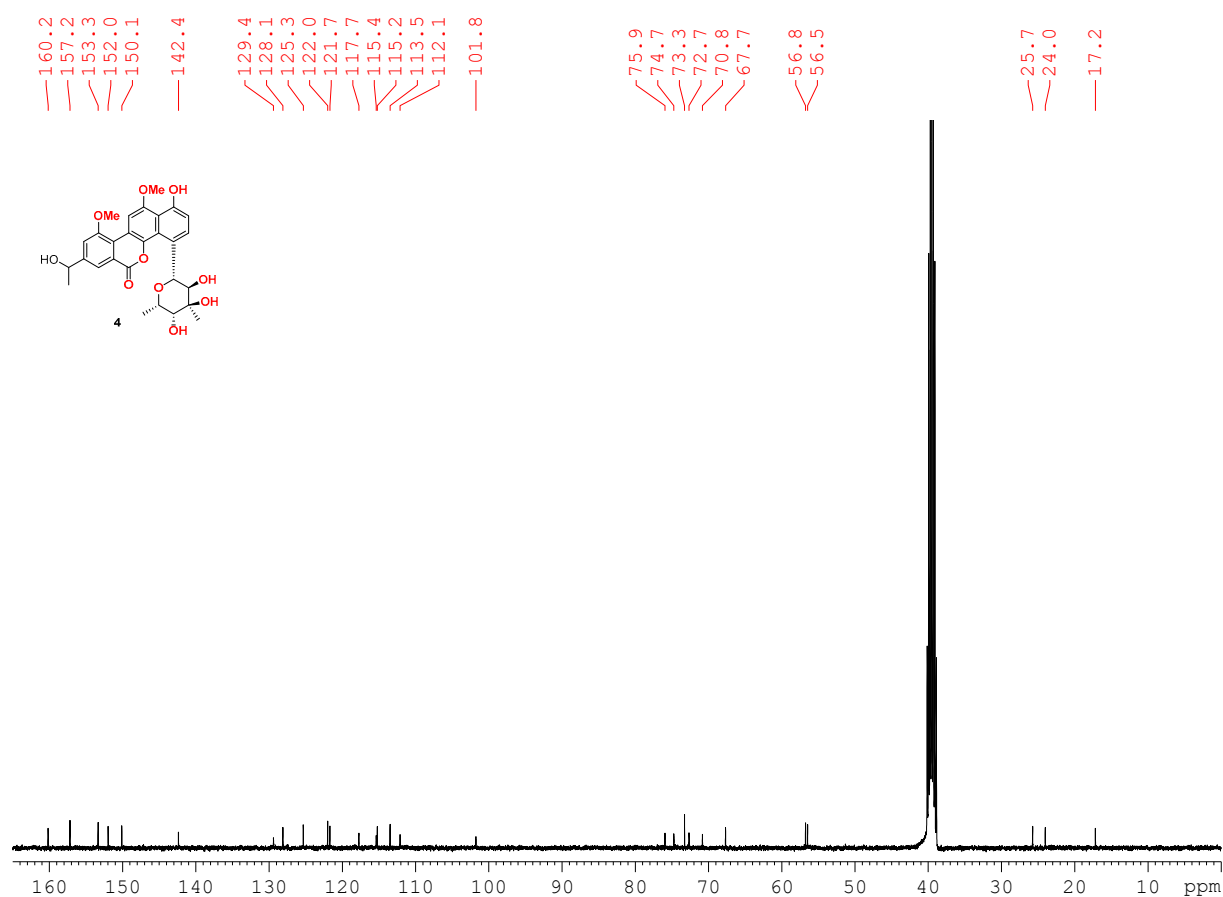


Figure S4c. ^{13}C NMR spectrum (150 MHz, $\text{DMSO}-d_6$) of 4

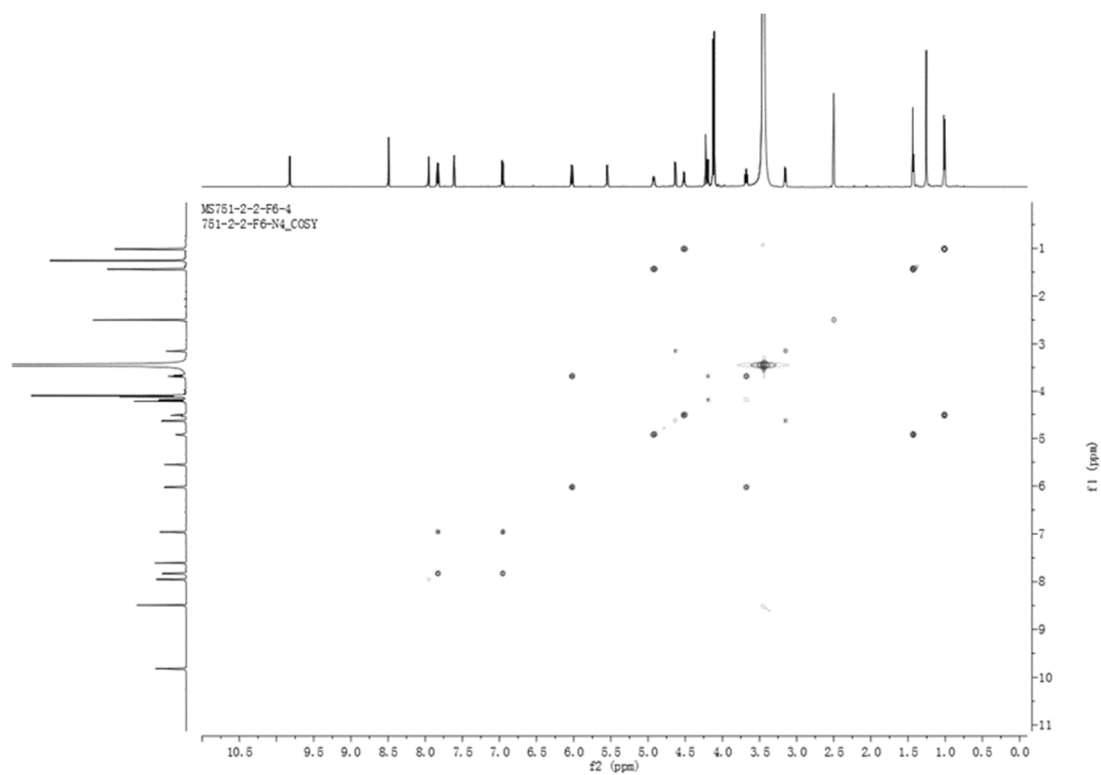


Figure S4d. COSY spectrum (600 MHz, $\text{DMSO}-d_6$) of 4

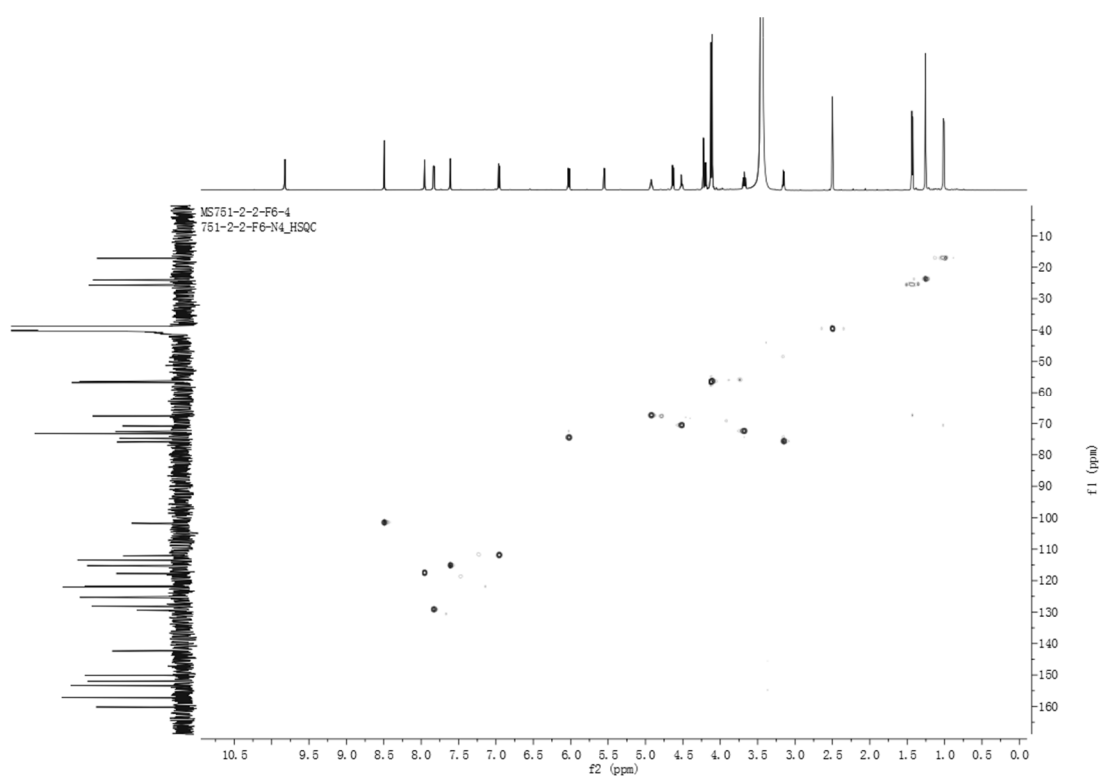


Figure S4e. ^1H – ^{13}C HSQC spectrum (600 MHz, $\text{DMSO-}d_6$) of **4**

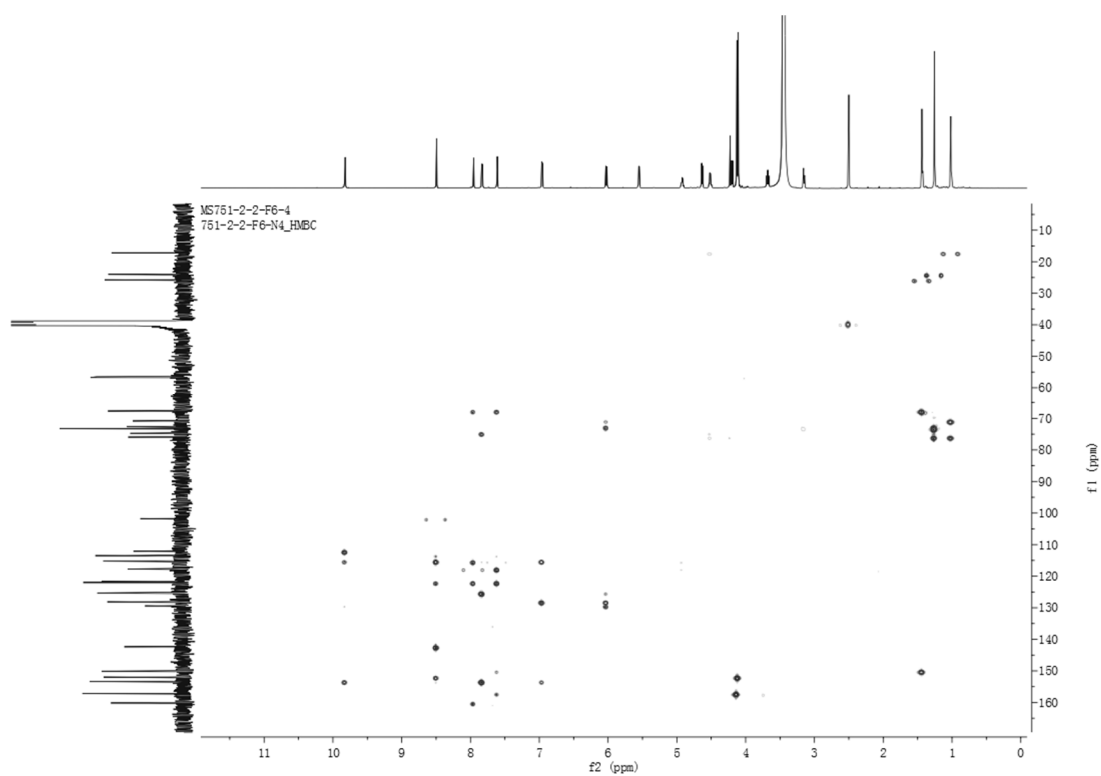


Figure S4f. ^1H – ^{13}C HMBC spectrum (600 MHz, $\text{DMSO-}d_6$) of **4**

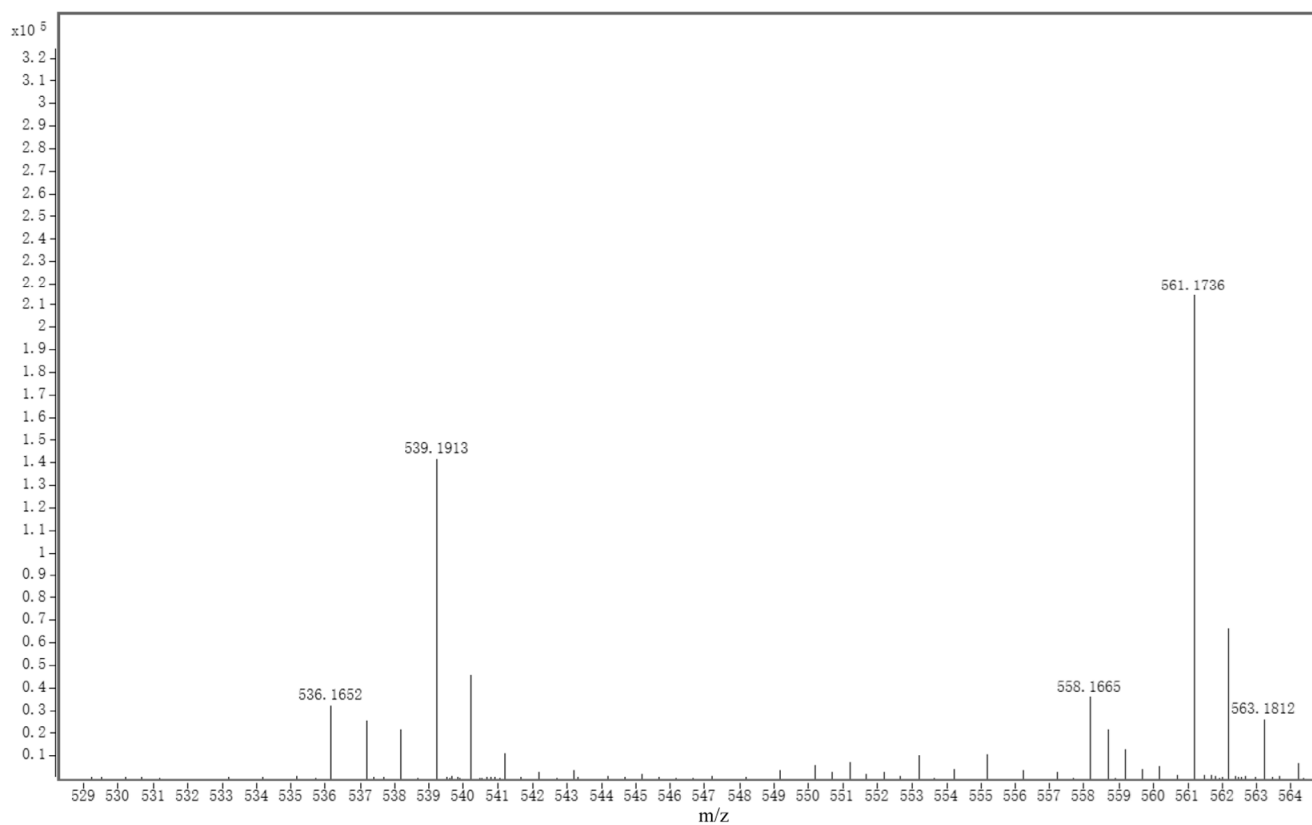


Figure S5a. HRESIMS spectrum of 5

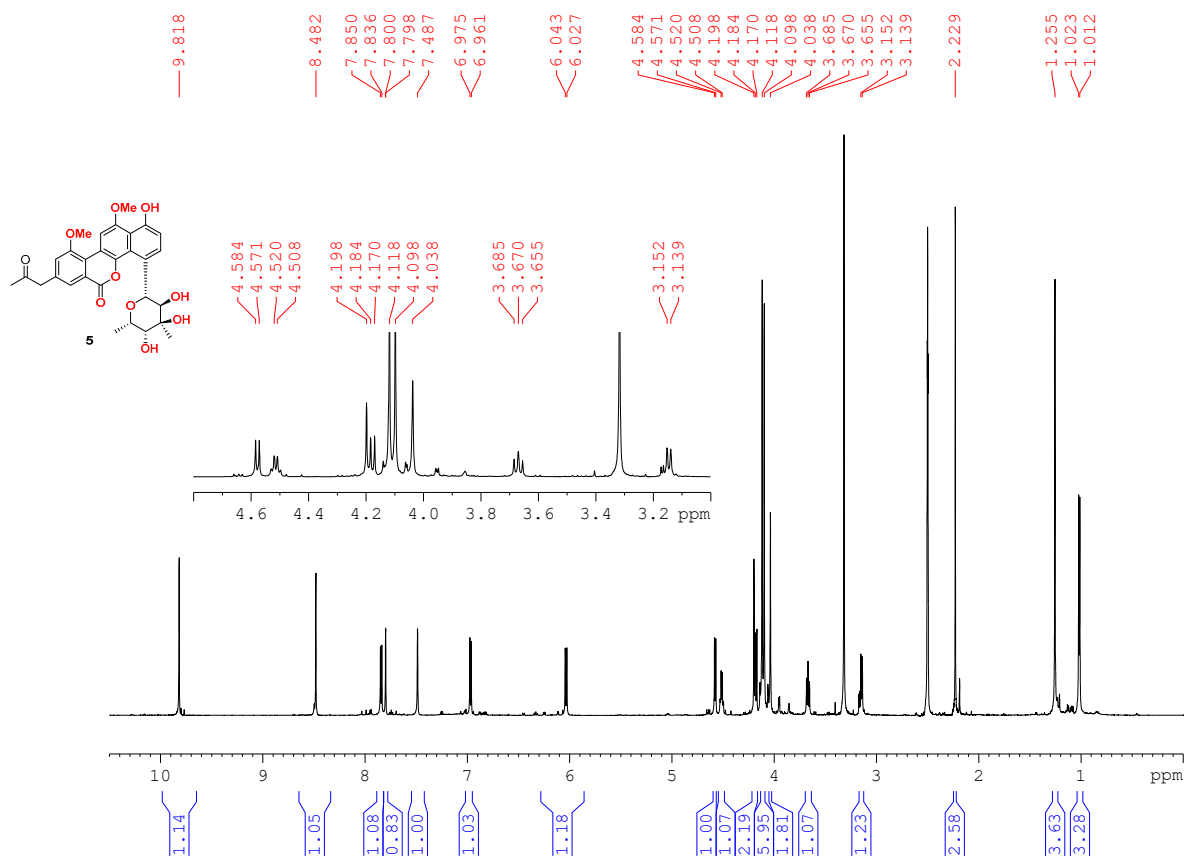


Figure S5b. ^1H NMR spectrum (600 MHz, $\text{DMSO}-d_6$) of 5

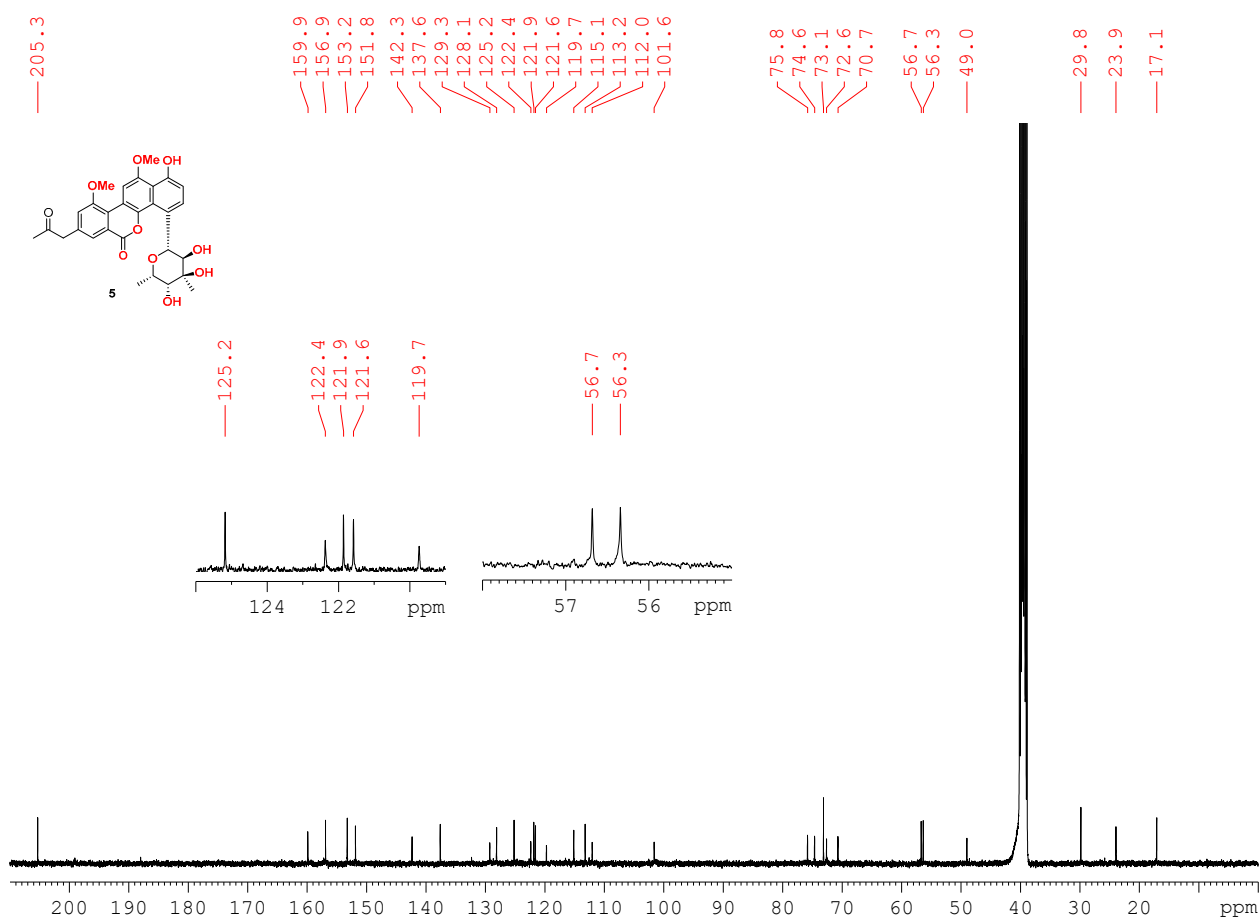


Figure S5c. ^{13}C NMR spectrum (150 MHz, $\text{DMSO-}d_6$) of 5

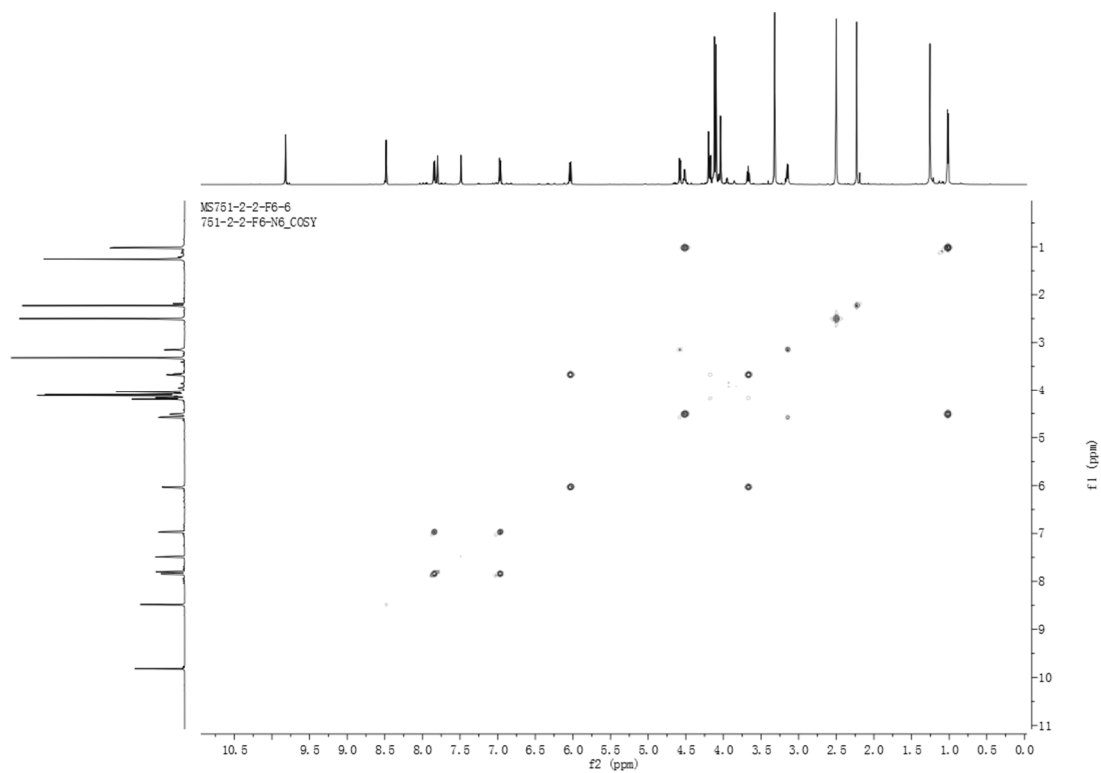


Figure S5d. COSY spectrum (600 MHz, $\text{DMSO-}d_6$) of 5

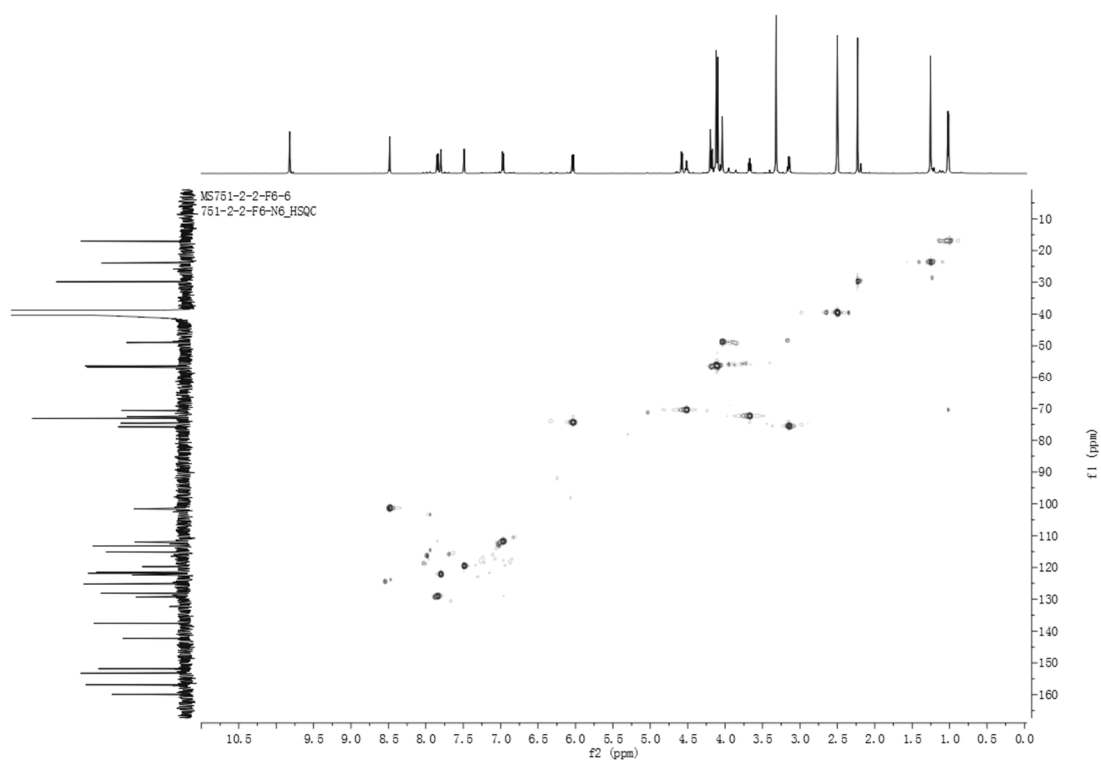


Figure S5e. $^1\text{H} - ^{13}\text{C}$ HSQC spectrum (600 MHz, $\text{DMSO-}d_6$) of **5**

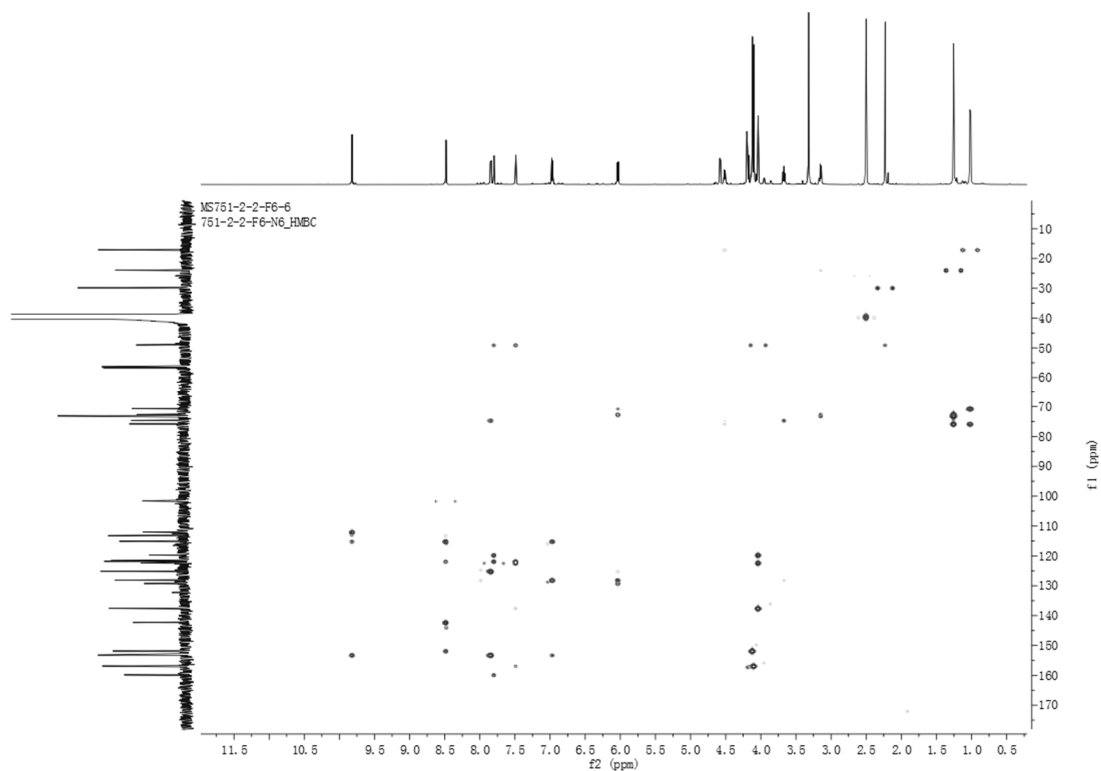
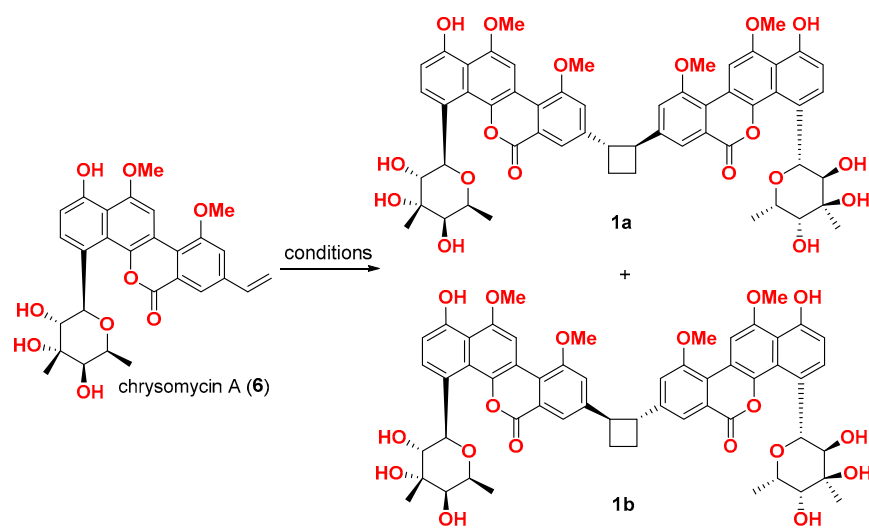


Figure S5f. $^1\text{H} - ^{13}\text{C}$ HMBC spectrum (600 MHz, $\text{DMSO-}d_6$) of **5**

Table S1. Screening of conditions for the [2+2] photodimerization of chrysomycin A



entry	conditions	yield ^{a,b}
1	neat, sunlight, r.t. 2 h	decomp.
2	neat, 500 W high-pressure Hg lamp, 0 °C, 40 min	NR
3	CDCl ₃ , 500 W high-pressure Hg lamp, r.t. 1.5 h	decomp.
4	hexane, 500 W high-pressure Hg lamp, r.t. 1 h	NR
5	9-cyanoanthracene, CH ₃ CN, 500 W high-pressure Hg lamp, 2 h	NR
6	CH ₂ Cl ₂ , 11 W CFL, sealed tube, 75-80 °C, 60 h	40% (1:1)

^aCombined yield of 1a and 1b. ^bRatio of 1a:1b is given in the parenthesis. CFL = compact fluorescent light bulb. NR = no reaction.

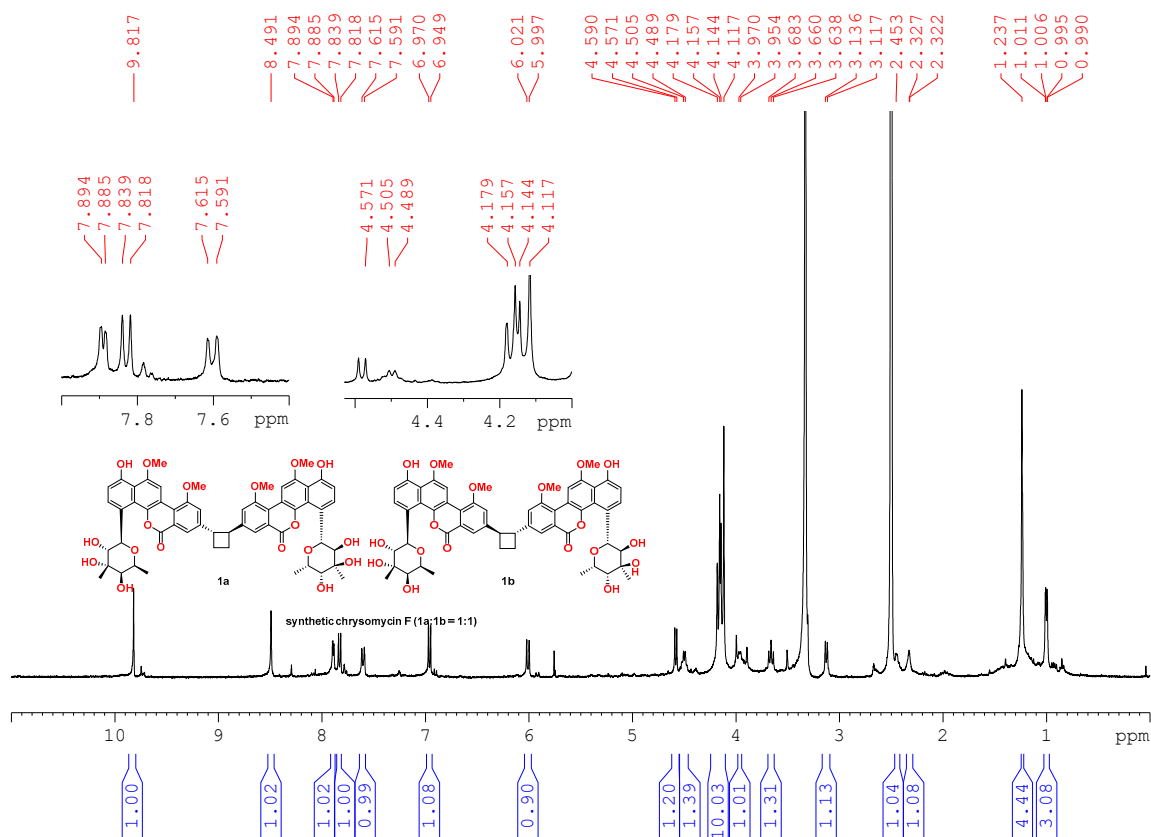


Figure S6a. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of synthetic chrysomycin F (1)

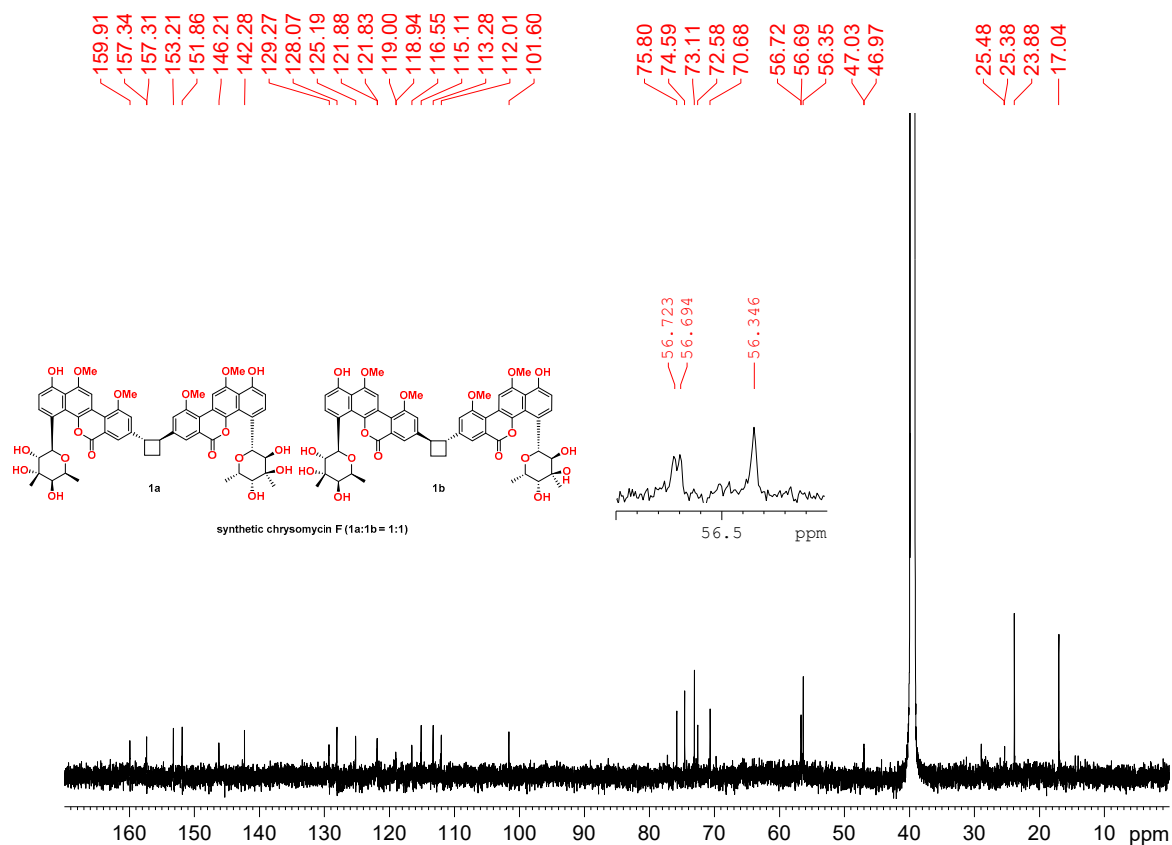


Figure S6b. ^{13}C NMR spectrum (201 MHz, $\text{DMSO}-d_6$) of synthetic chrysomycin F (1)

Table S2. ^1H and ^{13}C NMR data comparison of natural and synthetic chrysomycin F (1) in $\text{DMSO}-d_6$

position	natural chrysomycin F		synthetic chrysomycin F	
	$\delta_{\text{H}},^a$ mult (J in Hz)	δ_{C}^b	$\delta_{\text{H}},^c$ mult (J in Hz)	δ_{C}^d
1/1'		153.2, C		153.2, C
2/2'	6.96, d (8.4)	112.0, CH	6.96, d (8.4)	112.0, CH
3/3'	7.83, d (8.4)	129.3, CH	7.83, d (8.4)	129.3, CH
4/4'		128.1, C		128.1, C
4a/4a'		125.2, C		125.2, C
4b/4b'		142.3, C		142.3, C
6/6'		159.9, C		159.9, C
6a/6a'		121.9, C		121.9, C
7/7'	7.88/7.89, d (1.2)	119.0/118.9, CH	7.88/7.89, d (1.2)	119.0/118.9, CH
8/8'		146.2, C		146.2, C
9/9'	7.58/7.61, d(1.2)	116.5, CH	7.59/7.61, d(1.2)	116.5, CH

10/10'		157.35/157.32, C		157.34/157.31, C
10a/10a'		121.8, C		121.8, C
10b/10b'		113.3, C		113.3, C
11/11'	8.49, s	101.6, CH	8.49, s	101.6, CH
12/12'		151.9, C		151.9, C
12a/12a'		115.1, C		115.1, C
13/13'	6.01, d (9.6)	74.6, CH	6.01, d (9.6)	74.6, CH
14/14'	3.66, dd (9.6, 8.4)	72.6, CH	3.66, t (8.9)	72.6, CH
15/15'		73.1, C		73.1, C
16/16'	3.13, d (7.8)	75.8, CH	3.13, d (7.7)	75.8, CH
17/ 17'	4.50, brq (6.0)	70.7, CH	4.50, brq (6.4)	70.7, CH
18/18'	3.96, m	47.05/46.99, CH	3.96, m	47.03/46.97, CH
19a/19'a	2.33, m	25.4/25.5, CH ₂	2.33, m	25.4/25.5, CH ₂
19b/19'b	2.45, m		2.45, m	
20/20'	4.15/4.14, s	56.74/56.71, CH ₃	4.16/4.14, s	56.72/56.69, CH ₃
21/21'	4.11, s	56.3, CH ₃	4.12, s	56.3, CH ₃
22/22'	1.24, s	23.9, CH ₃	1.24, s	23.9, CH ₃
23/23'	1.00/1.01, d (6.6)	17.1, CH ₃	1.00/1.01, d, (6.5)	17.0, CH ₃
1/1'-OH	9.81, s		9.82, s	
14/14'-OH	4.16, overlap (8.4)		4.17 overlap (8.8)	
15/15'-OH	4.18, s		4.18, s	
16/16'-OH	4.57, d (7.8)		4.58, d (7.7)	

^a ¹H (600 MHz), ^b ¹³C (150 MHz), ^c ¹H (400 MHz), ^d ¹³C (201 MHz)

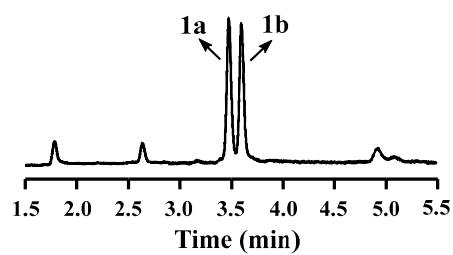


Figure S7. UPLC chromatogram of synthetic chrysomycin F (1).

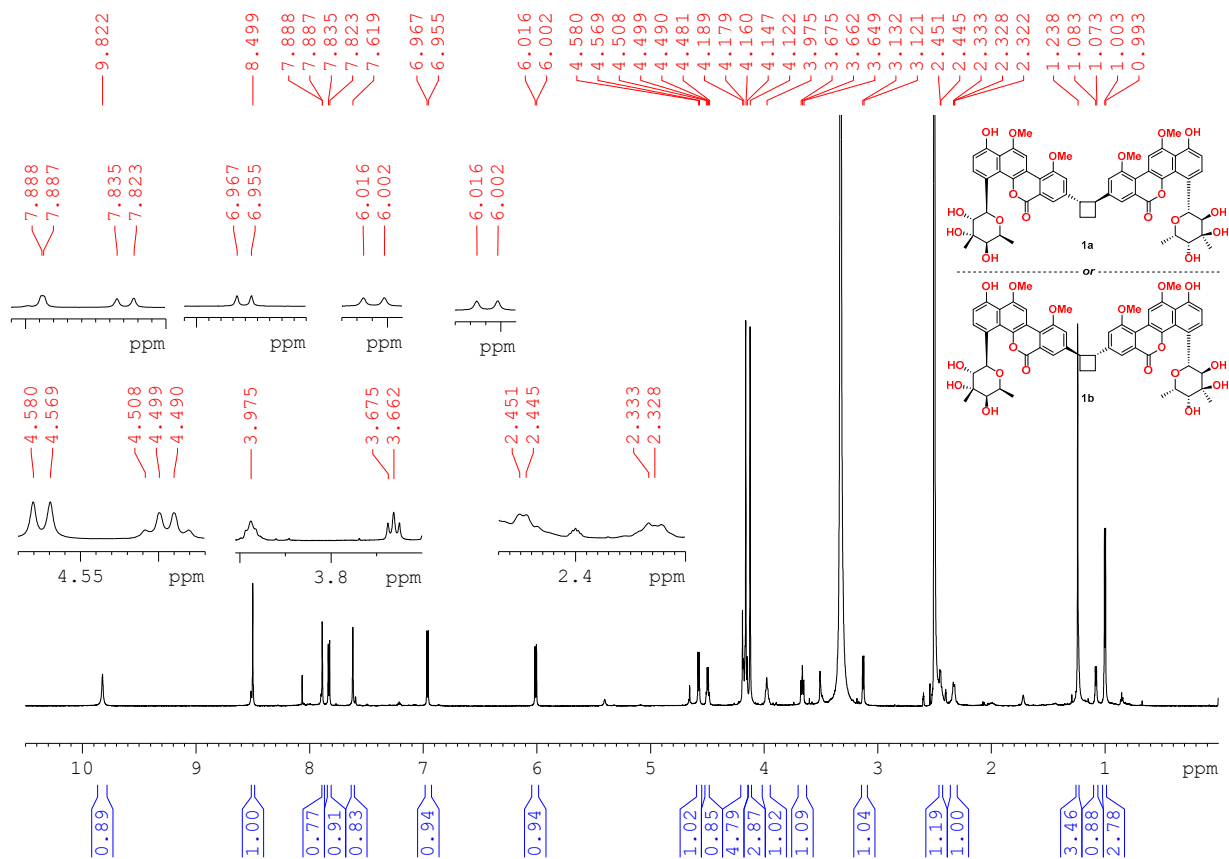


Figure S8a. ¹H NMR spectrum (700 MHz, DMSO-*d*₆) of synthetic *trans*-dimer **1a** (or **1b**)

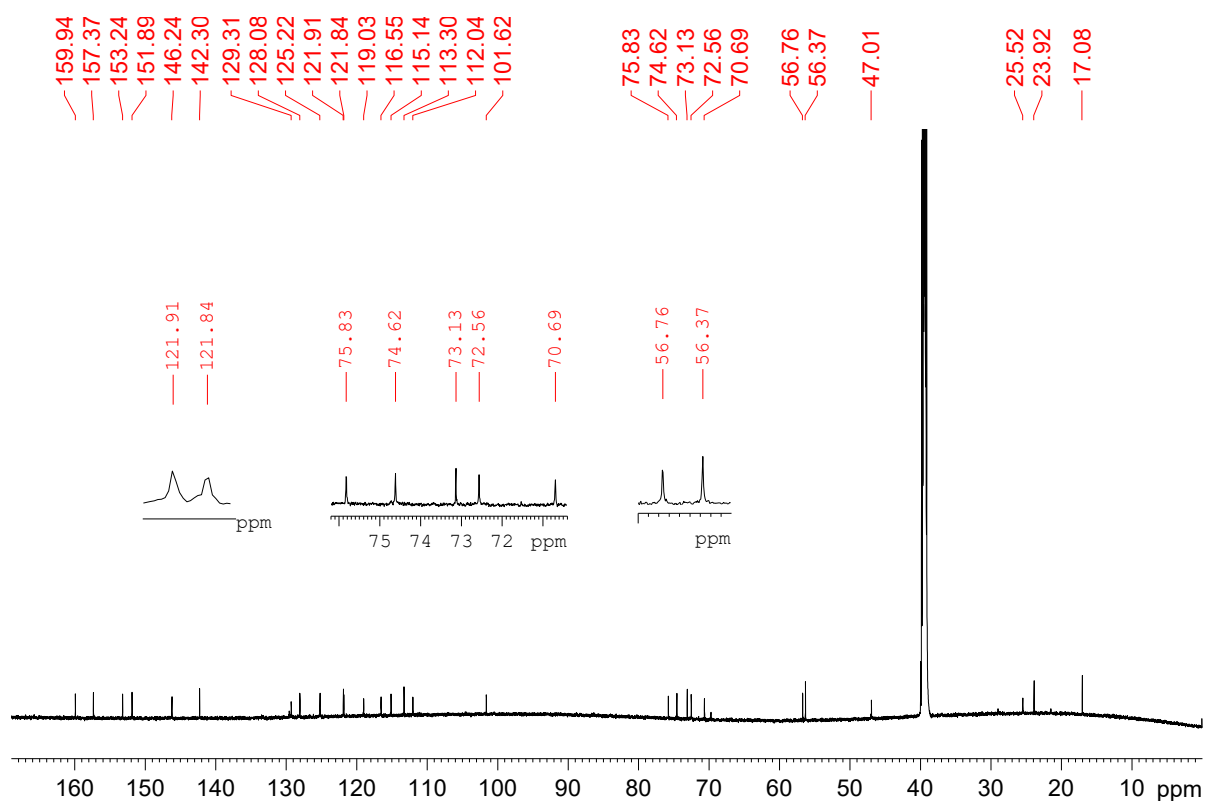


Figure S8b. ^{13}C NMR spectrum (176 MHz, $\text{DMSO}-d_6$) of synthetic *trans*-dimer **1a** (or **1b**)

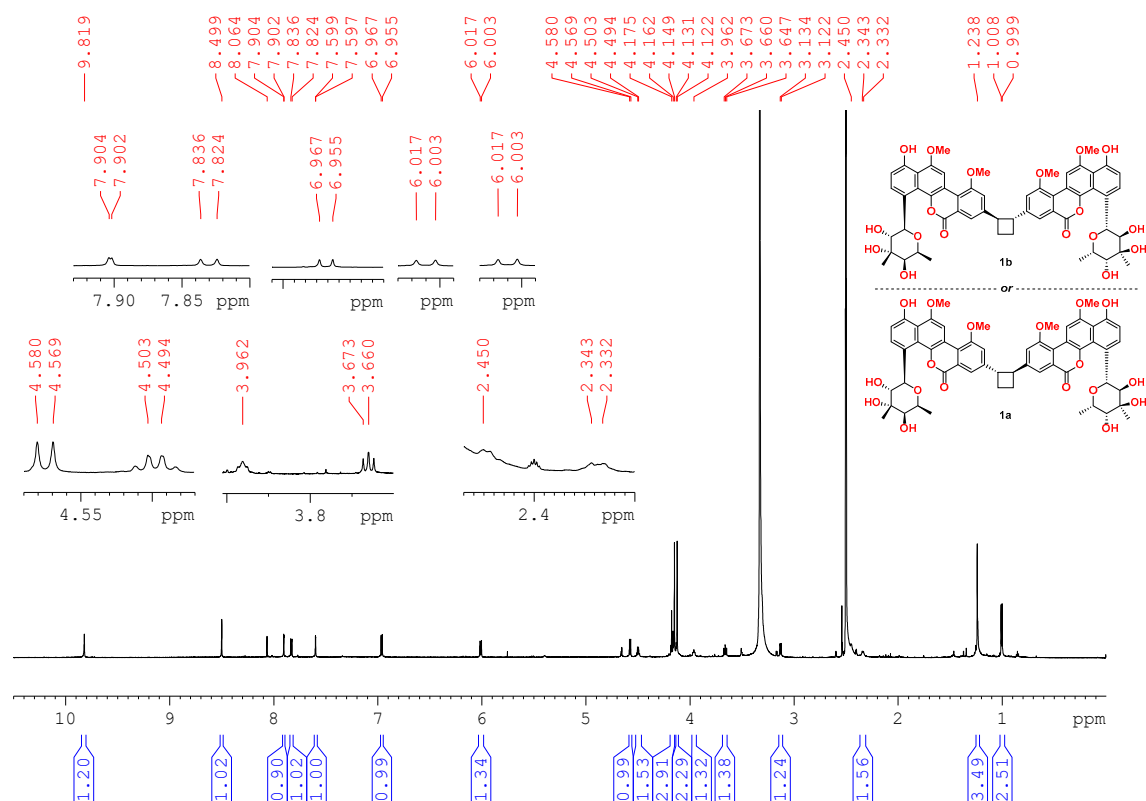


Figure S9a. ^1H NMR spectrum (700 MHz, $\text{DMSO}-d_6$) of synthetic *trans*-dimer **1b** (or **1a**)

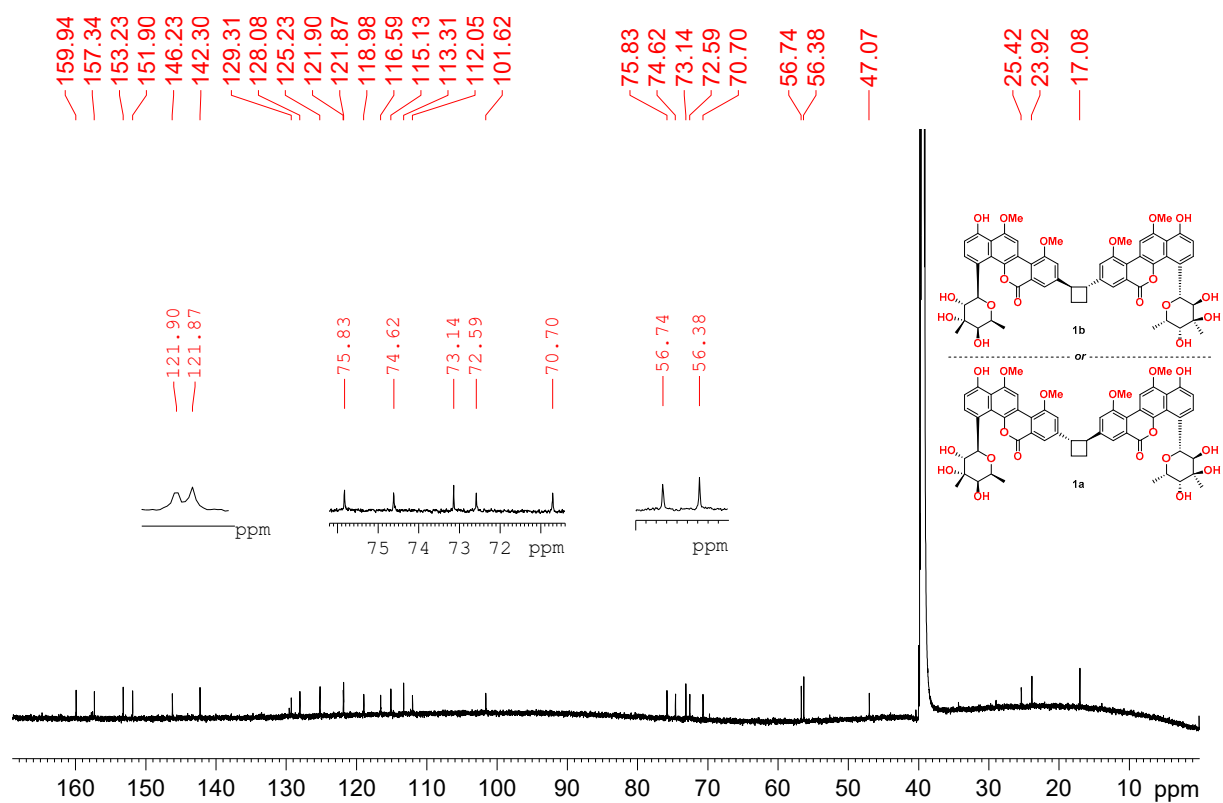


Figure S9b. ^{13}C NMR spectrum (176 MHz, $\text{DMSO}-d_6$) of synthetic *trans*-dimer **1b** (or **1a**)

Table S3. ^1H and ^{13}C NMR data for synthetic *trans*-dimers **1a** and **1b** in $\text{DMSO-}d_6$

position	<i>trans</i> -dimer 1a		<i>trans</i> -dimer 1b	
	$\delta_{\text{H}},^{\text{a}}$ <i>mult</i> (J in Hz)	$\delta_{\text{C}}^{\text{b}}$	$\delta_{\text{H}},^{\text{a}}$ <i>mult</i> (J in Hz)	$\delta_{\text{C}}^{\text{b}}$
1/1'		153.24, C		153.23, C
2/2'	6.96, d (8.4)	112.04, CH	6.96, d (8.4)	112.05, CH
3/3'	7.83, d (8.4)	129.31, CH	7.83, d (8.4)	129.31, CH
4/4'		128.08, C		128.08, C
4a/4a'		125.22, C		125.23, C
4b/4b'		142.30, C		142.30, C
6/6'		159.94, C		159.94, C
6a/6a'		121.91, C		121.90, C
7/7'	7.89, d (0.7)	119.03, CH	7.90, d (1.4)	118.98, CH
8/8'		146.24, CH		146.23, C
9/9'	7.62, d (0.7)	116.55, CH	7.60, d (1.4)	116.59, CH
10/10'		157.37, C		157.34, C
10a/10a'		121.84, C		121.87, C
10b/10b'		113.30, C		113.31, C
11/11'	8.50, s	101.62, CH	8.50, s	101.62, CH
12/12'		151.89, C		151.90, C
12a/12a'		115.14, C		115.13, C
13/13'	6.01, d (9.8)	74.62, CH	6.01, d (9.8)	74.62, CH
14/14'	3.66, dd (9.8, 9.1)	72.56, CH	3.66, dd (9.8, 9.1)	72.59, CH
15/15'		73.13, C		73.14, C
16/16'	3.13, d (7.7)	75.83, CH	3.13, d (8.4)	75.83, CH
17/ 17'	4.49, q (7.0)	70.69, CH	4.50, q (7.0)	70.70, CH
18/18'	3.98, m	47.01, CH	3.96, m	47.07, CH
19a/19'a	2.33, m	25.52, CH_2	2.34, m	25.42, CH_2
19b/19'b	2.45, m		2.45, m	

20/20'	4.16, s	56.76, CH ₃	4.15, s	56.74, CH ₃
21/21'	4.12, s	56.37, CH ₃	4.12, s	56.38, CH ₃
22/22'	1.24, s	23.92, CH ₃	1.24, s	23.92, CH ₃
23/23'	1.00, d, (7.0)	17.08, CH ₃	1.00, d, (7.0)	17.08, CH ₃
1/1'-OH	9.82, s		9.82, s	
14/14'-OH	4.17 overlap (9.1)		4.17 overlap (9.1)	
15/15'-OH	4.19, s		4.17, s	
16/16'-OH	4.57, d (7.7)		4.57, d (7.7)	

^a ¹H (700 MHz), ^b ¹³C (176 MHz)

Table S4. Composition of the culture media.

Media	Component
Gauze–asparagine (GA) agar plate	soluble starch 2.0 %, L-asparagine 0.05 %, KNO ₃ 0.1 %, K ₂ HPO ₄ ·H ₂ O 0.05 %, NaCl 0.05 %, and MgSO ₄ ·7H ₂ O 0.05 % (pH 7.5)
ISP2 liquid medium	yeast extract 0.4%, malt extract 1%, glucose 0.4%, pH 7.2
AM2 liquid medium	starch 0.5%, glucose 2%, soya bean powder 1%, bacto peptone 0.2%, yeast extract 0.2%, NaCl 0.4%, K ₂ HPO ₄ 0.05%, MgSO ₄ ·7H ₂ O 0.05 %, and CaCO ₃ 0.2%, pH 7.8