

Supplementary Information

Spirocitrinols A and B, Citrinin Derivatives with a Spiro[chromane-2,3'-isochromane] Skeleton from *Penicillium citrinum*

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Table S1. NMR Data for **1 in Methanol-*d*₄**

no	1		
	δ_C^a , mult.	δ_H^b (<i>J</i> in Hz)	HMBC
1	137.3, qC		
2	116.0, qC		
3	156.6, qC		
4	100.9, CH	6.01, s	2, 3, 5, 6
5	150.8, qC		
6	111.6, qC		
7	61.1, CH	4.99, dd (4.6, 12.0)	10
8	76.6, CH	4.13, m	7, 9
9	36.2, CH	2.73, m	1, 8
10a	37.0, CH ₂	2.44, dd (4.8, 12.0)	6, 7, 21
10b		1.75, t (12.0)	6, 7, 21
11	18.8, CH ₃	1.41, d (6.6)	8, 9
12	22.8, CH ₃	1.23, d (7.2)	1, 8, 9
13	10.4, CH ₃	2.05, s	1, 2
14	135.0, qC		
15	115.4, qC		
16	153.3, qC		
17	111.9, qC		
18	149.3, qC		
19	113.6, qC		
20a	62.0, CH ₂	4.65, d (14.4)	14, 19
20b		4.82, d (15.0)	14, 19, 21
21	102.4, qC		
22	39.6, CH	2.92, m	10, 14, 19, 21, 23
23	18.7, CH ₃	1.18, d (6.6)	
24	10.8, CH ₃	2.13, s	14, 15, 16
25	9.2, CH ₃	2.15, s	17, 18

^a Recorded at 150 MHz. ^b Recorded at 600 MHz

Figure S1. ^1H NMR Spectrum of Spirocitrinol A (**1**; 600 MHz, $\text{DMSO-}d_6$)

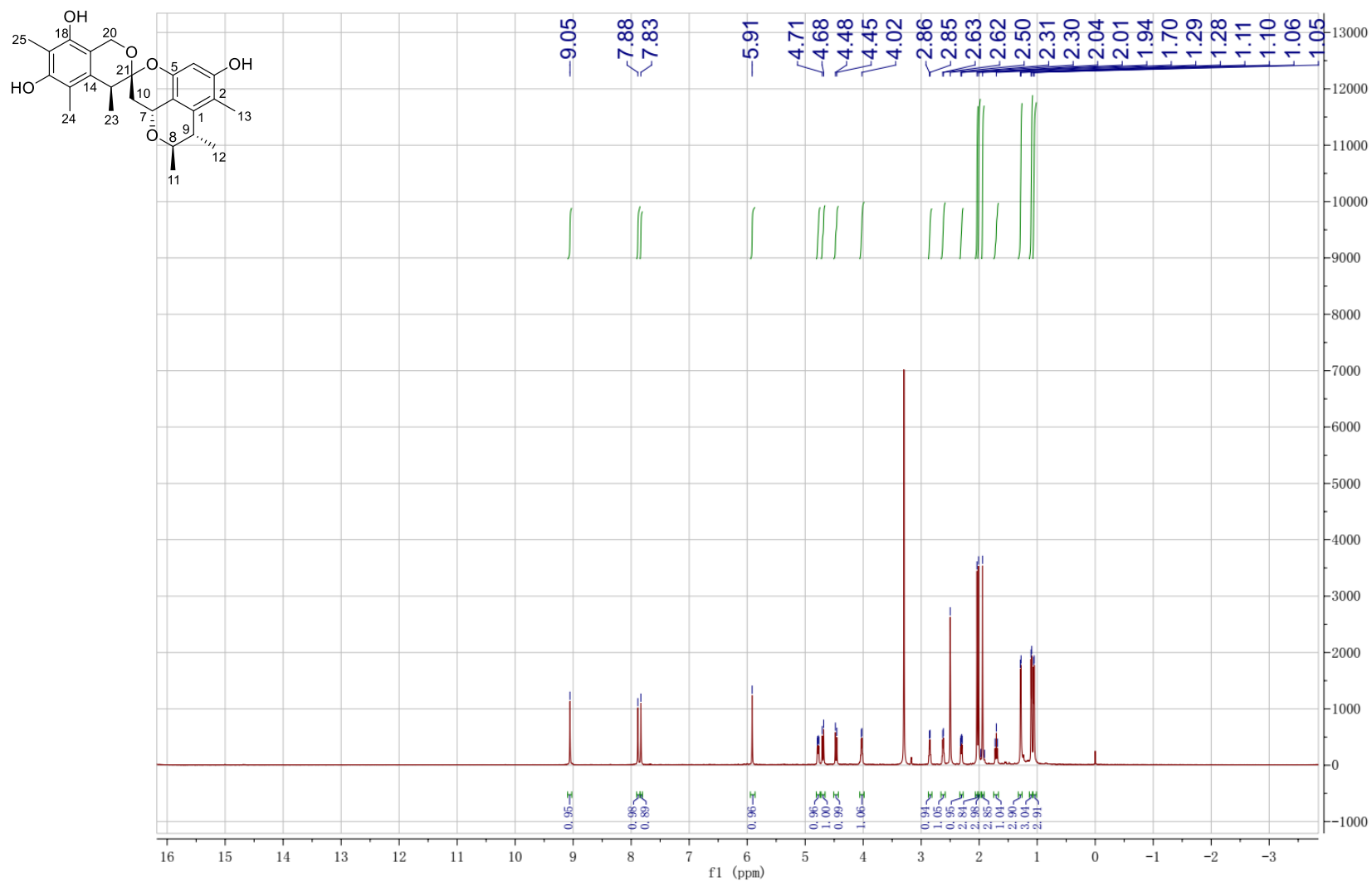


Figure S2. ^{13}C NMR Spectrum of Spirocitrinol A (**1**; 150 MHz, $\text{DMSO-}d_6$)

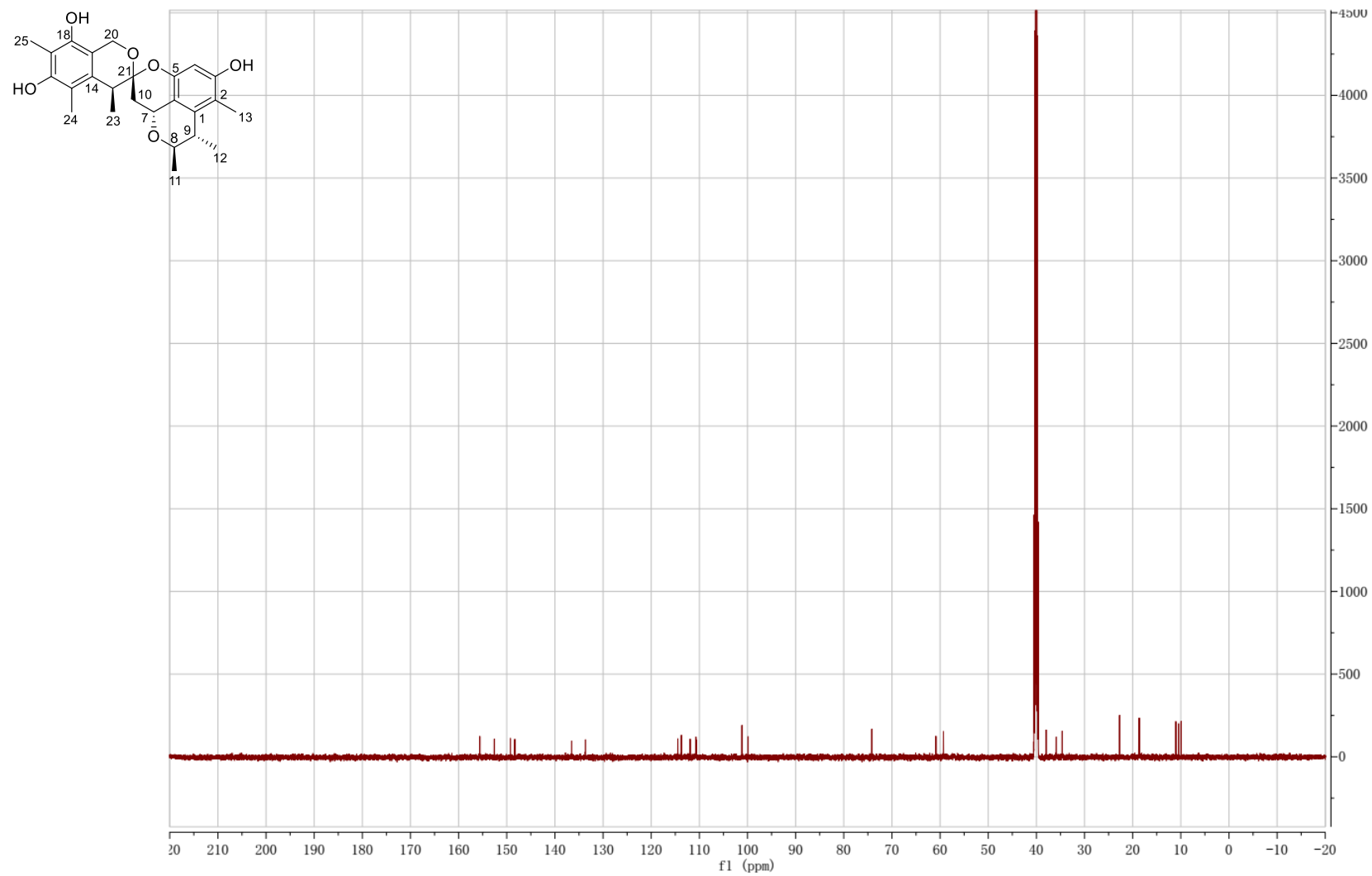


Figure S3. HSQC Spectrum of Spirocitrinol A (**1**; 600 MHz, DMSO-*d*₆)

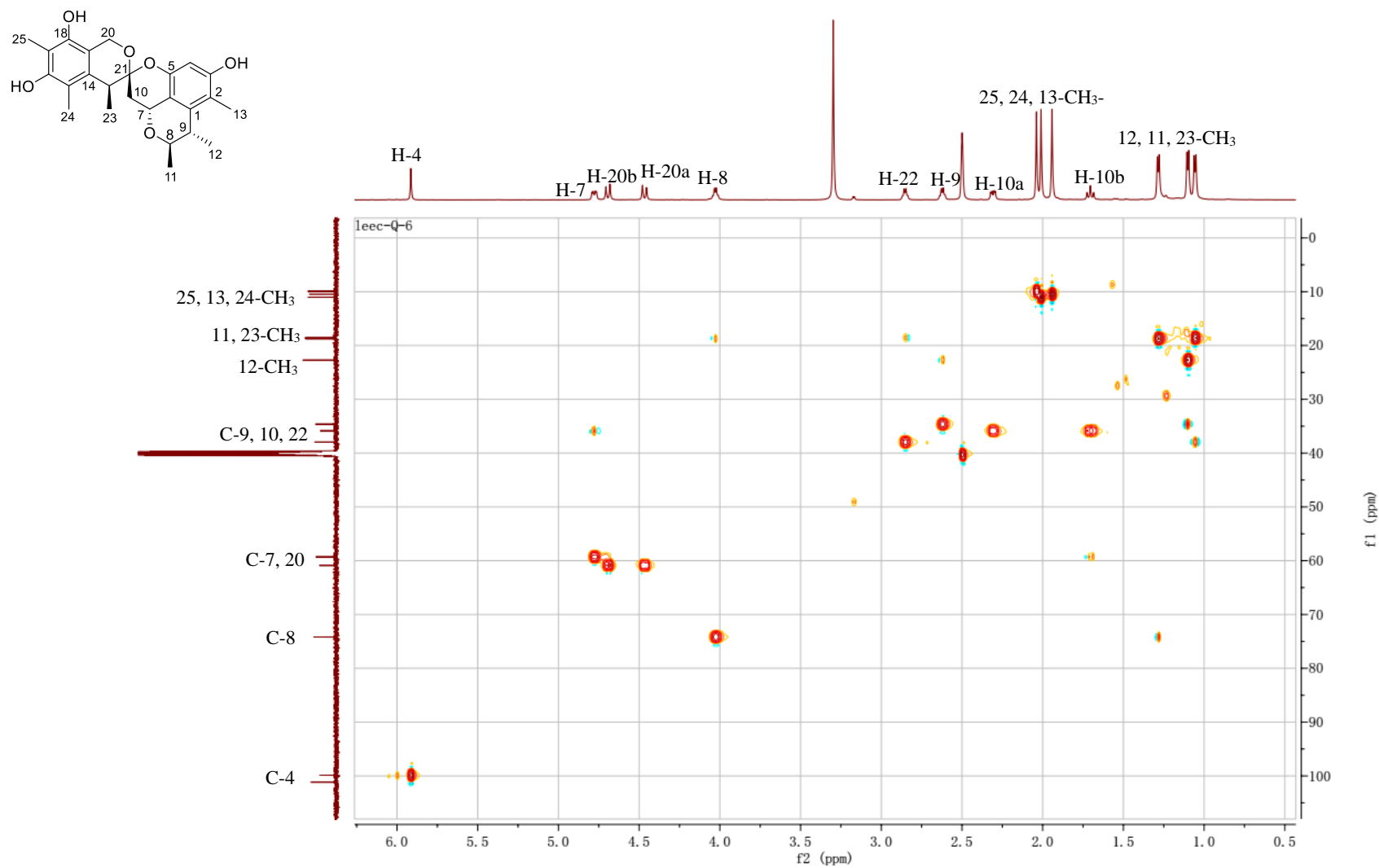


Figure S4. HMBC Spectrum of Spirocitrinol A (1; 600 MHz, DMSO-*d*₆)

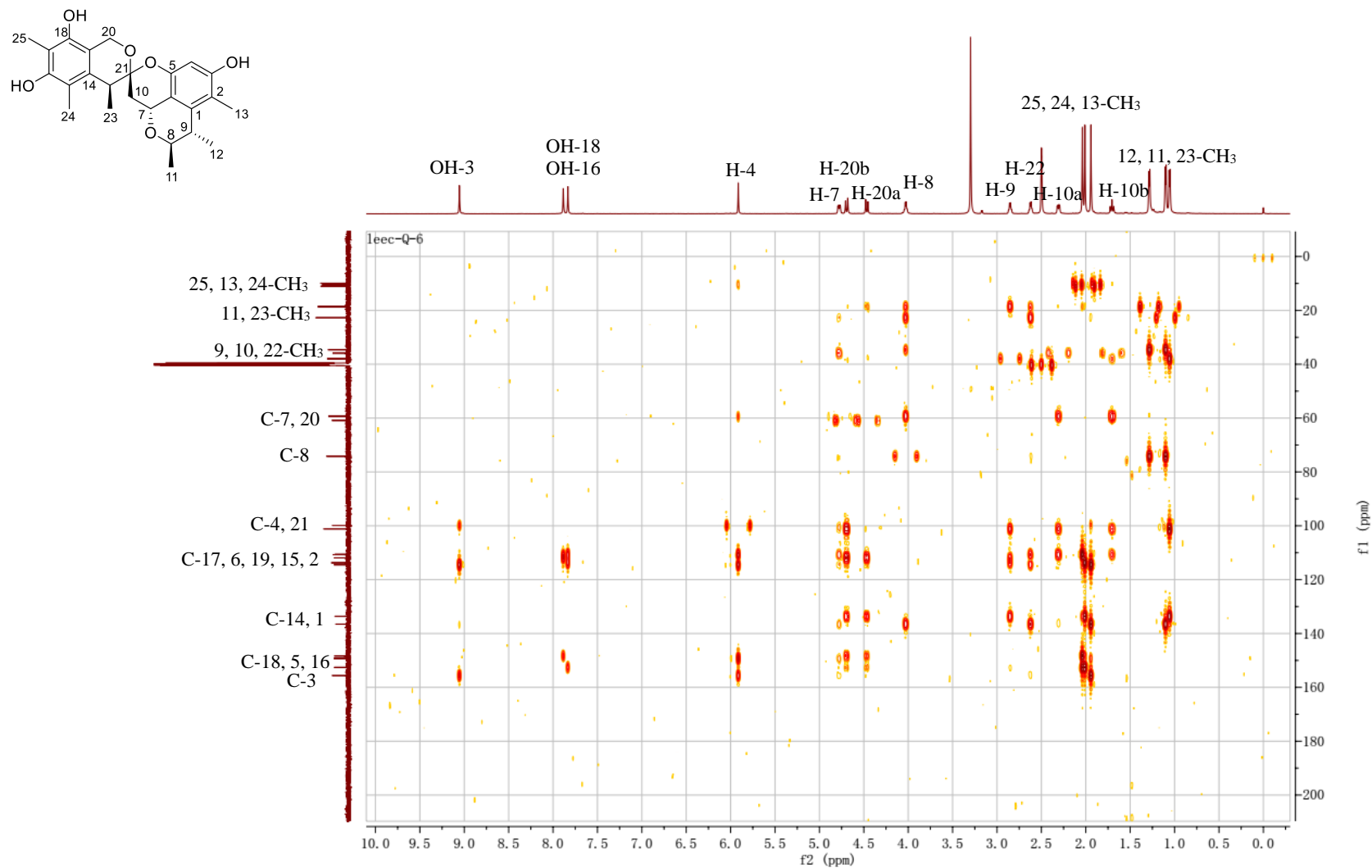


Figure S5. NOESY Spectrum of Spirocitrinol A (**1**; 600 MHz, DMSO-*d*₆)

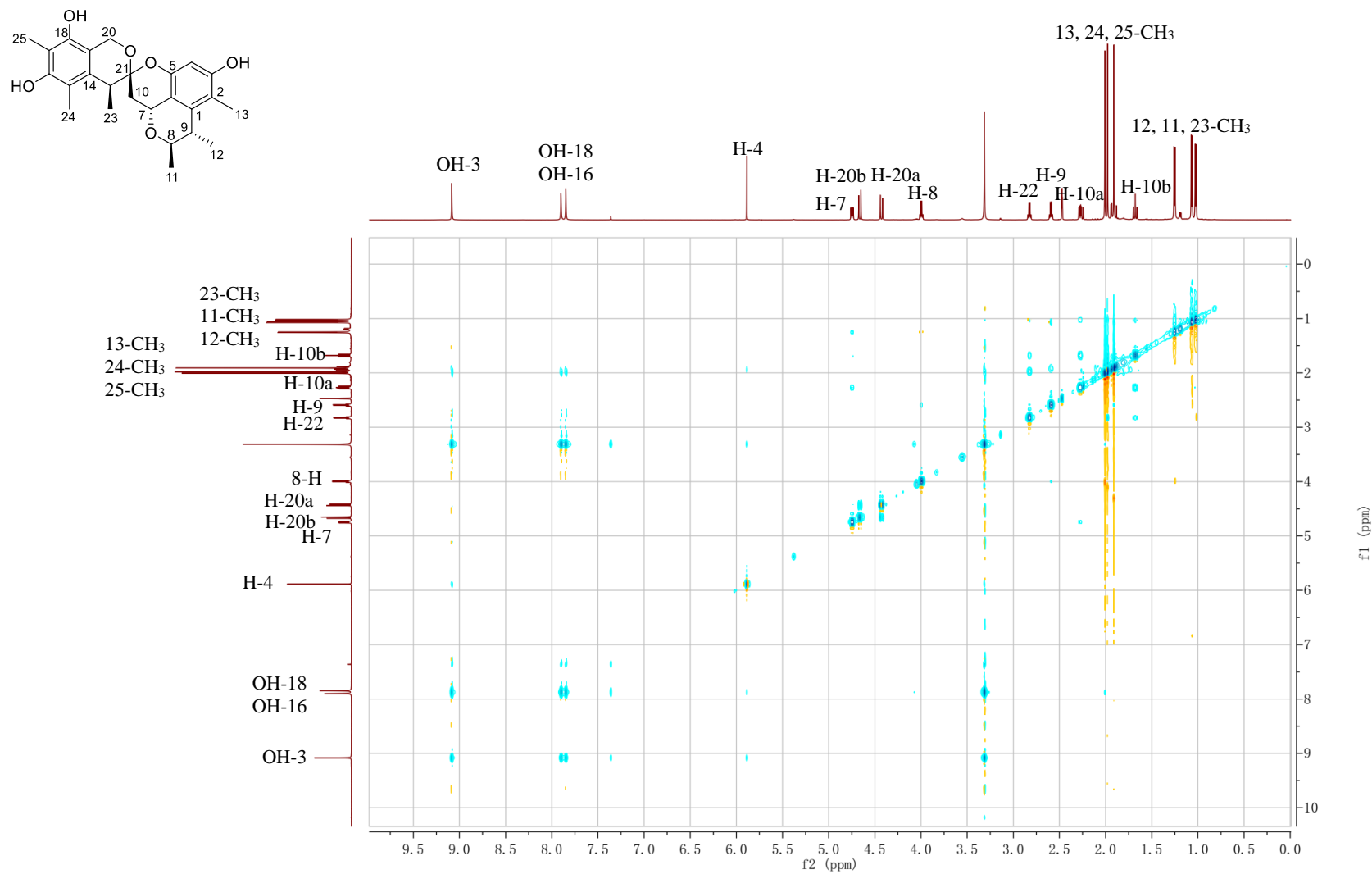
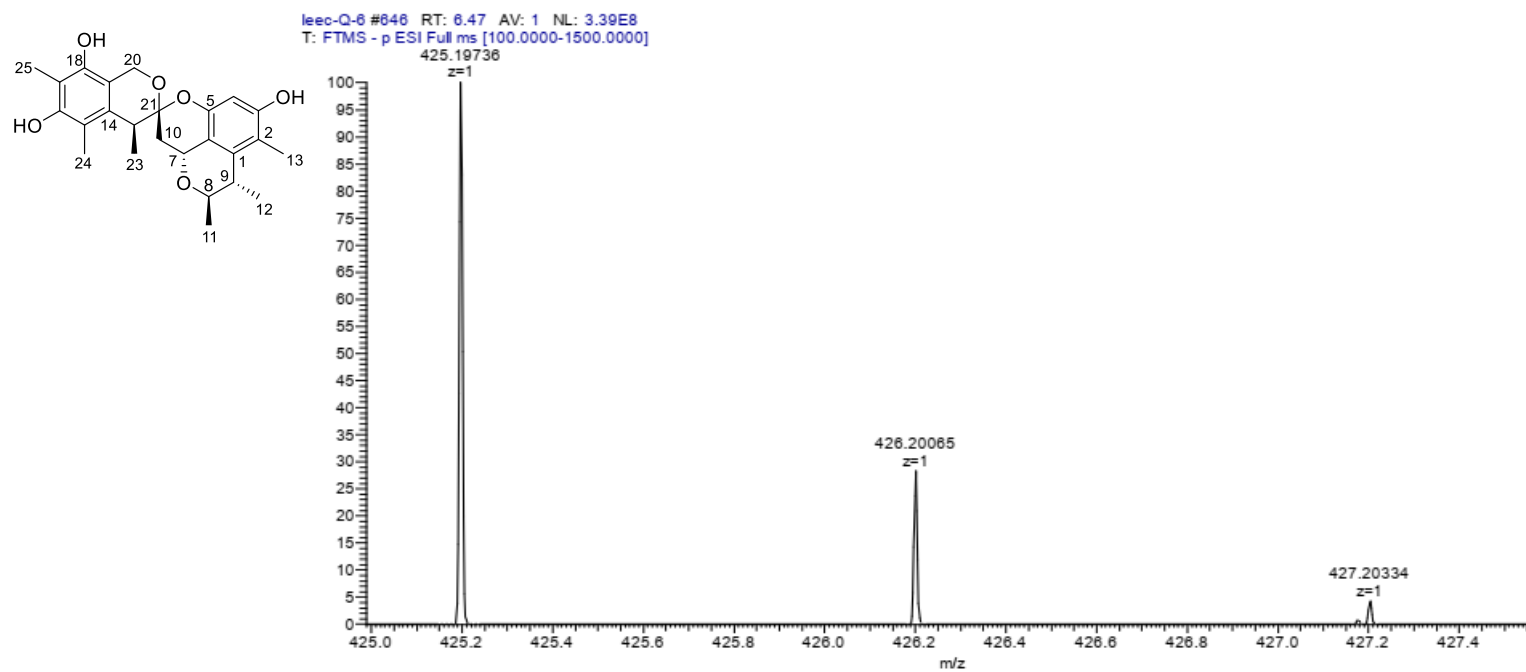


Figure S6. HRESIMS Spectrum of Spirocitrinol A (1)



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
425.19736	425.19696	0.94	11.5	C25 H29 O6	M-H

Figure S7. ^1H NMR Spectrum of Spirocitrinol B (**2**; 600 MHz, $\text{DMSO-}d_6$)

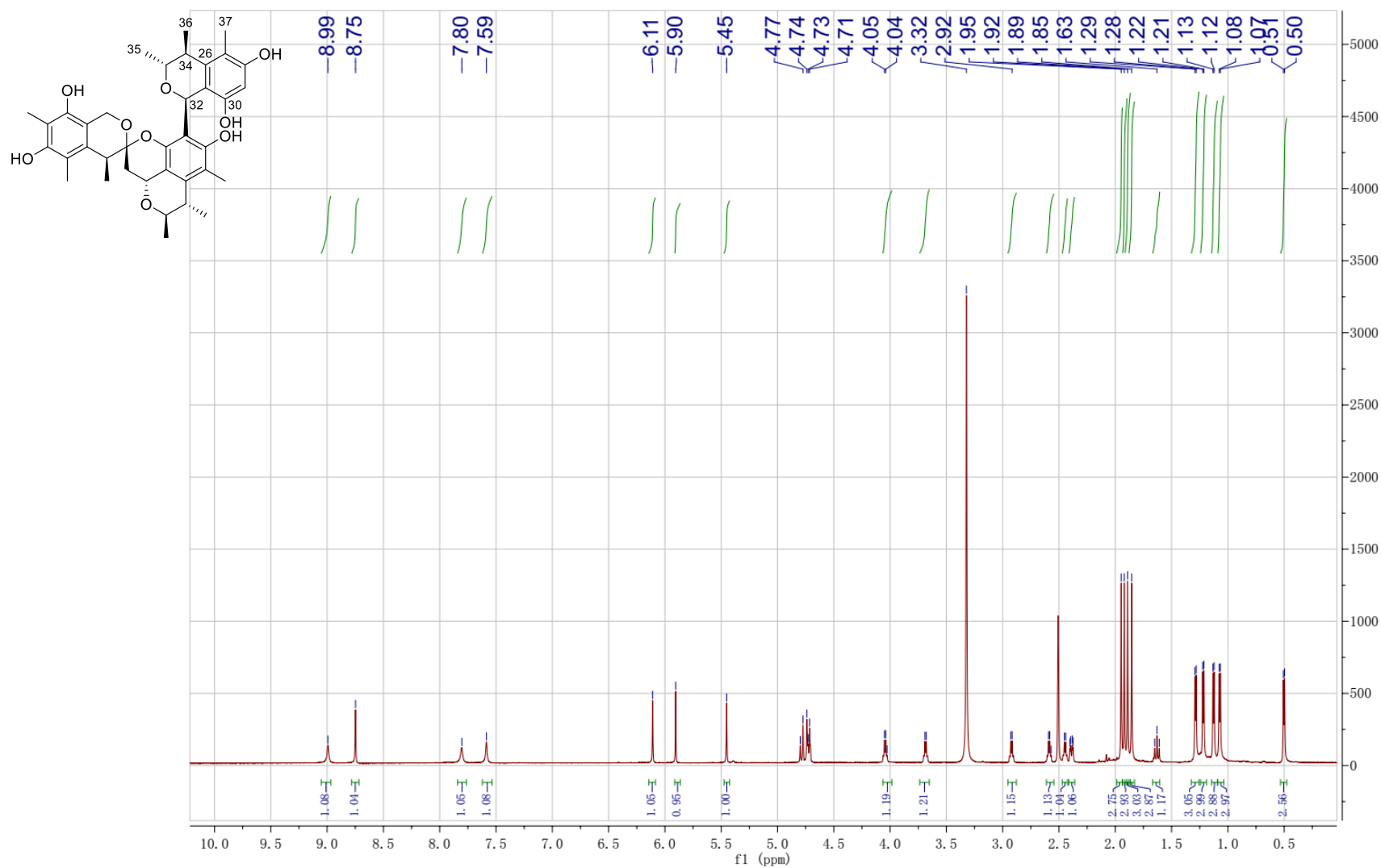


Figure S8. ^{13}C NMR Spectrum of Spirocitrinol B (**2**; 150 MHz, $\text{DMSO-}d_6$)

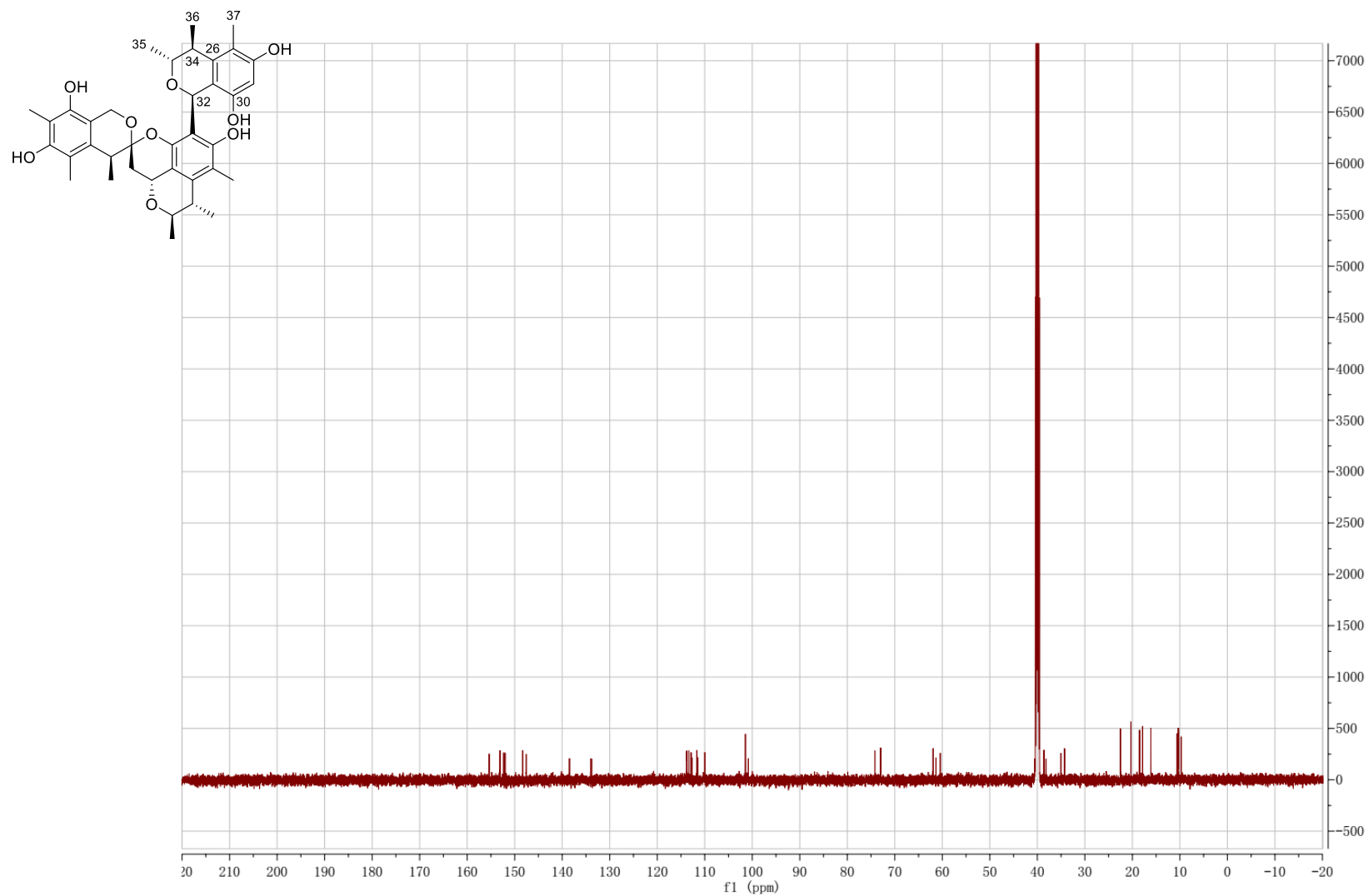


Figure S9. HSQC Spectrum of Spirocitrinol B (**2**; 600 MHz, DMSO-*d*₆)

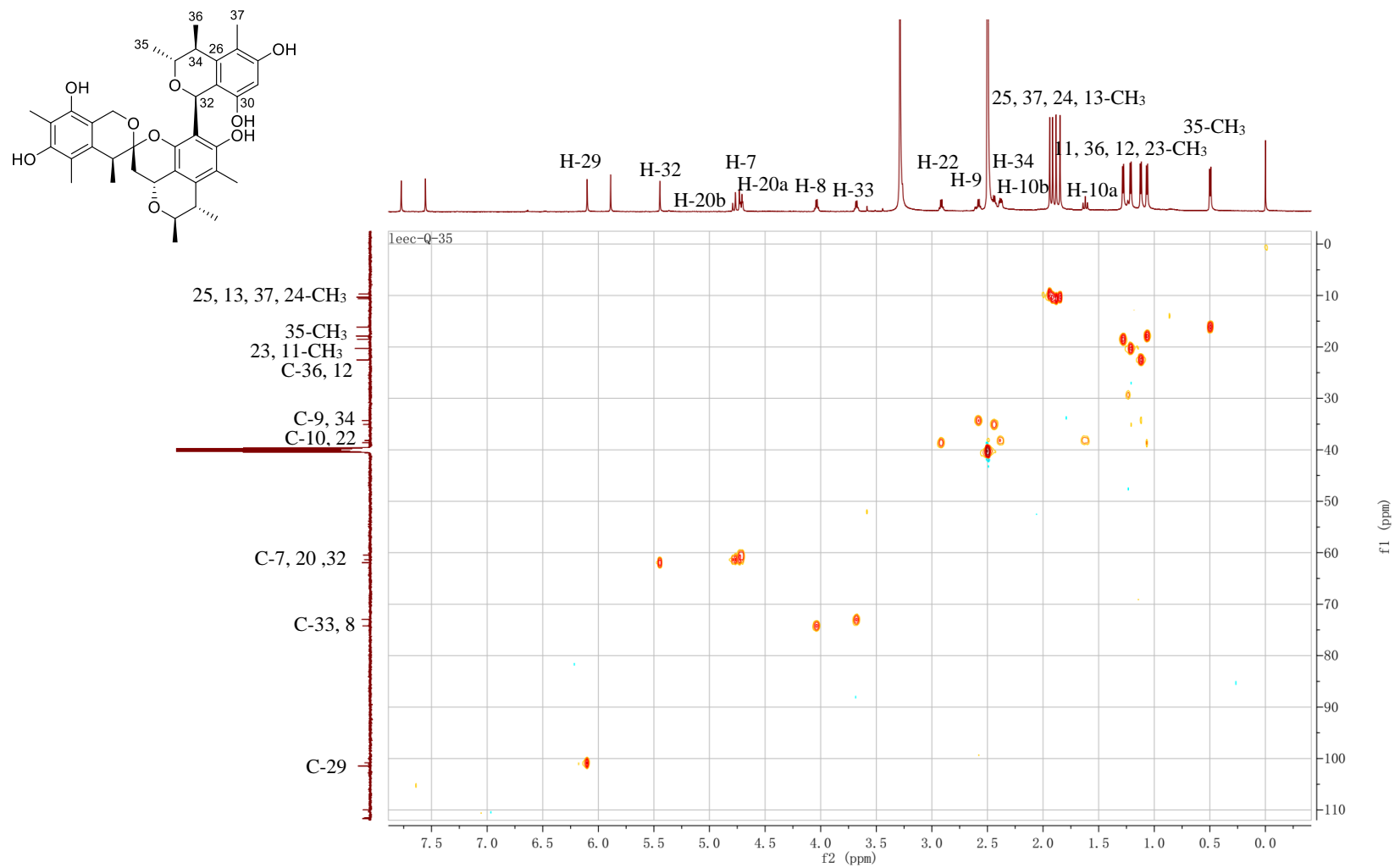


Figure S10. HMBC Spectrum of Spirocitrinol B (**2**; 600 MHz, DMSO-*d*₆)

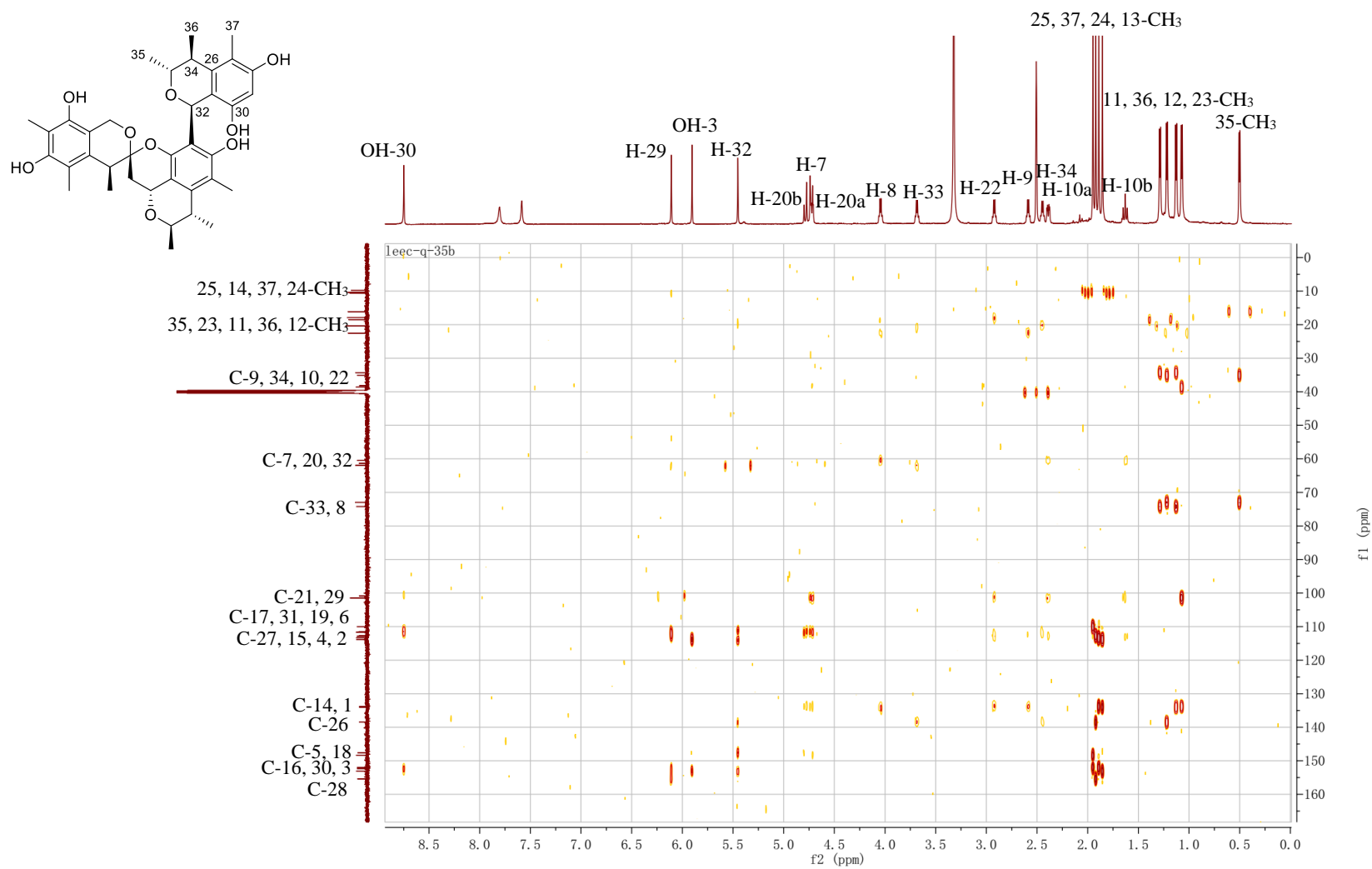


Figure S11. NOESY Spectrum of Spirocitrinol B (**2**; 600 MHz, DMSO-*d*₆)

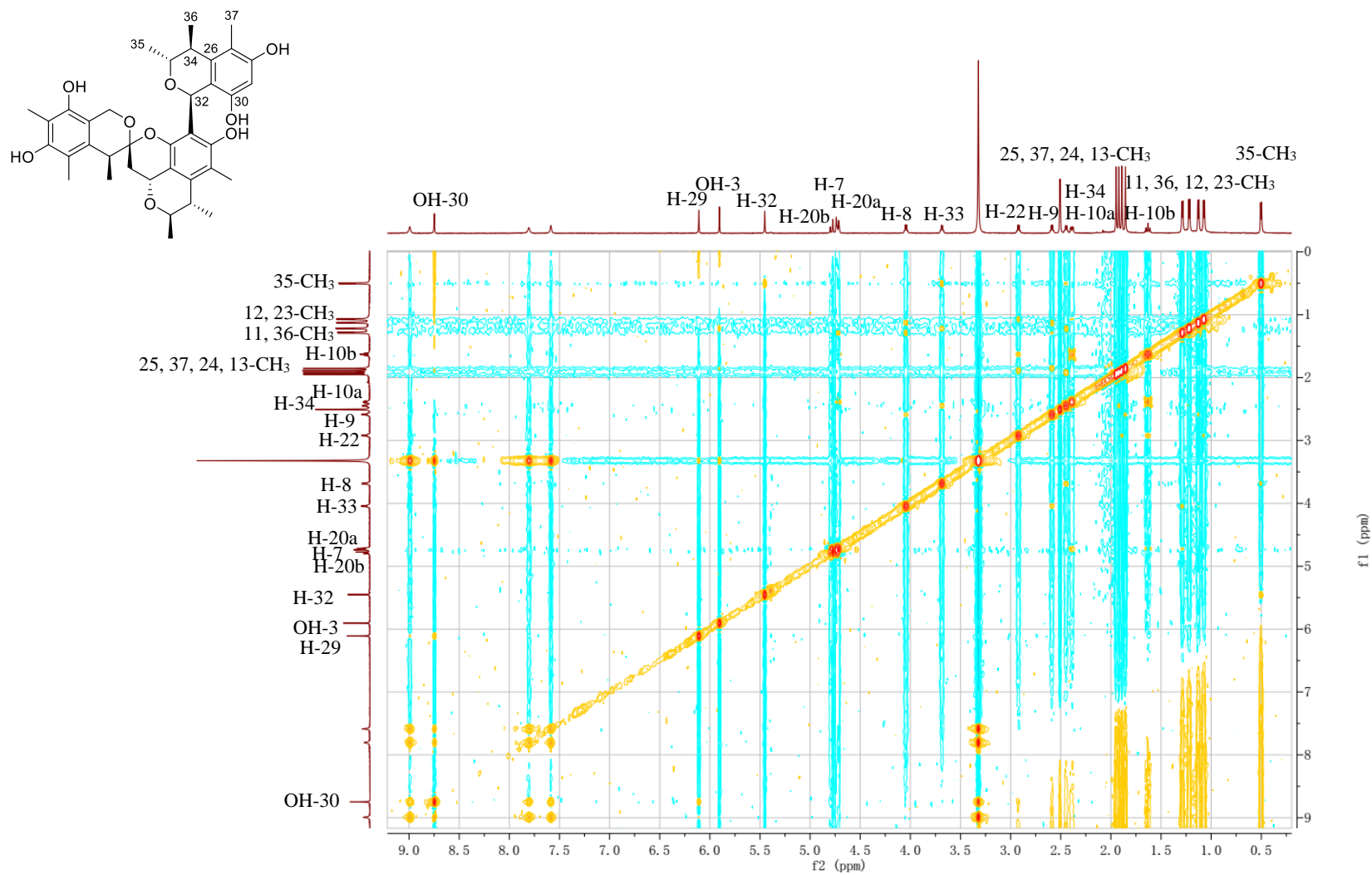


Figure S12. NOE Difference Spectrum of Spirocitrinol B (**2**; 600 MHz, DMSO-*d*₆)

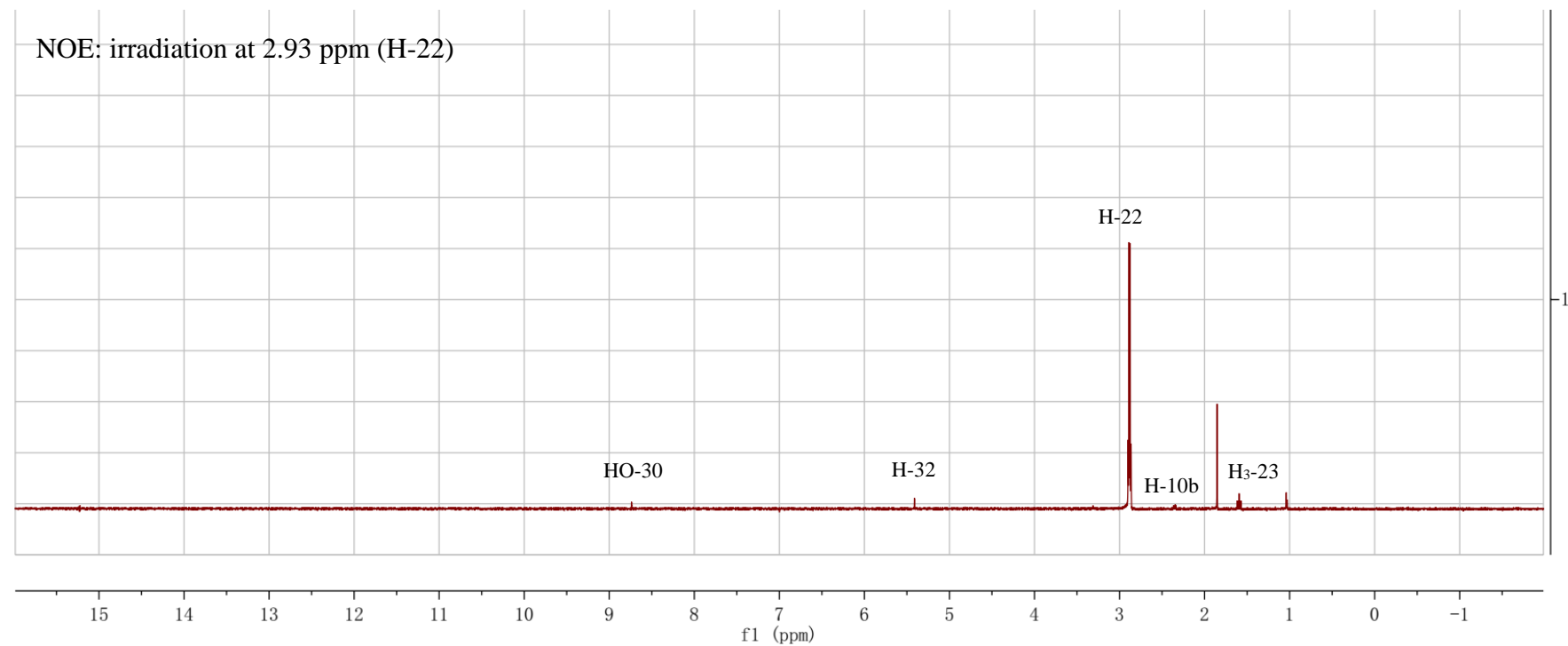
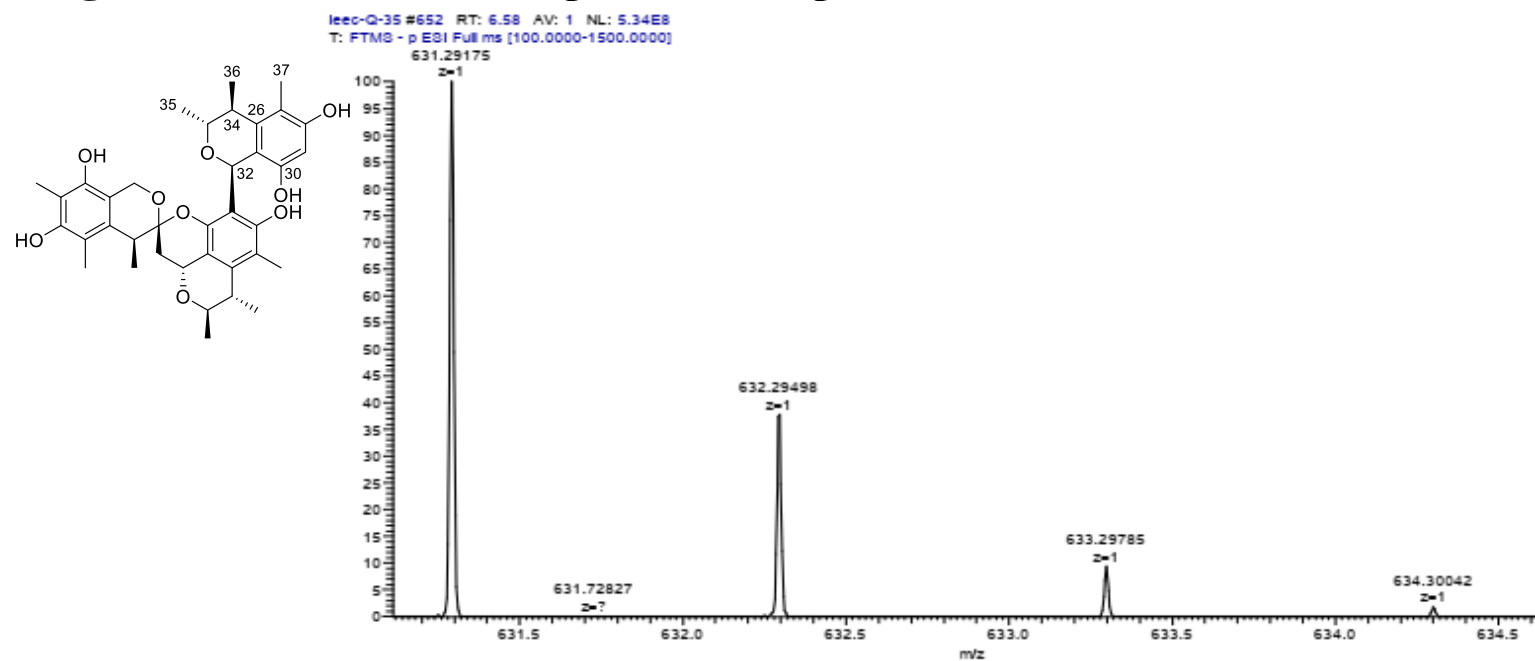
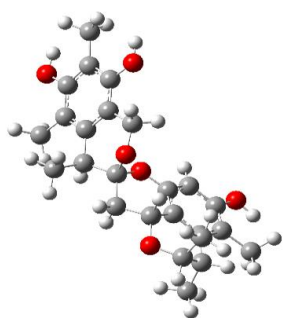


Figure S13. HRESIMS Spectrum of Spirocitrinol B (2)

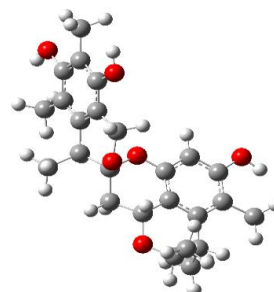


m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
631.29175	631.29126	0.78	16.5	C37 H43 O9	M-H

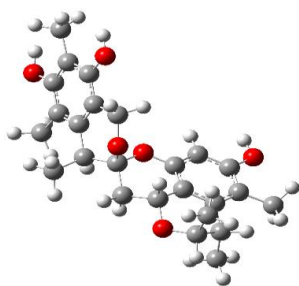
Figure S14. The Optimized Conformers of **1a**



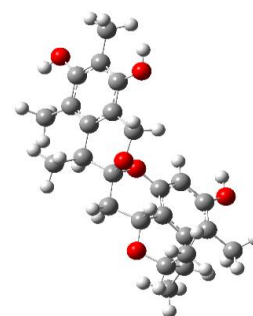
1a C1 (1.72%)



1a C2 (19.82%)

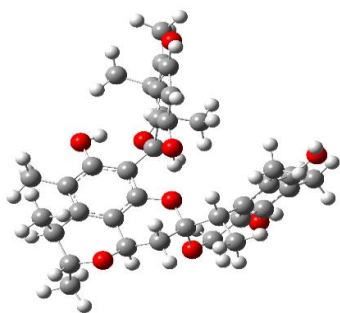


1a C3 (5.84%)

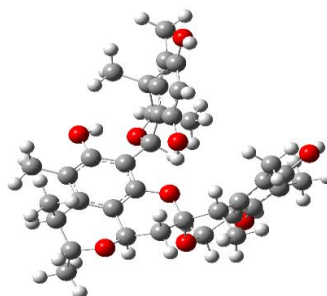


1a C4 (72.62%)

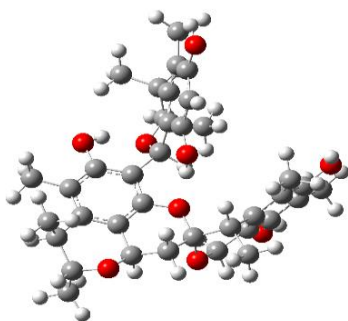
Figure S15. The Optimized Conformers of **2a**



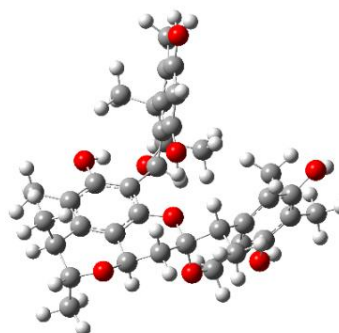
2a C1 (74.29%)



2a C2 (9.47%)



2a C3 (14.92%)



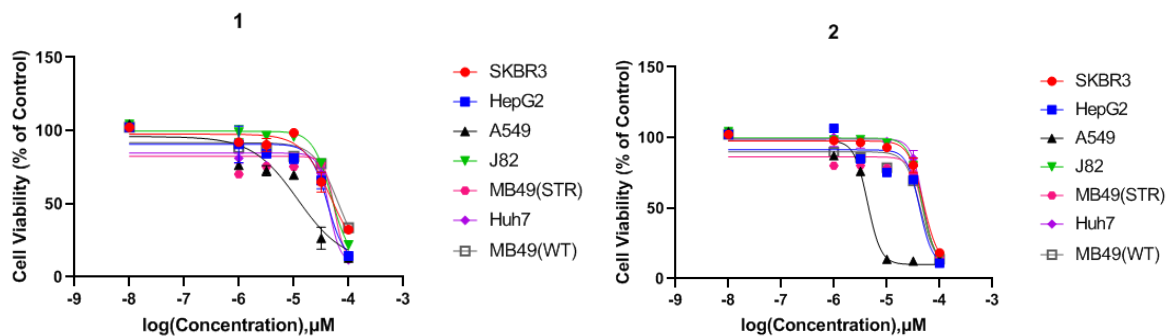
2a C4 (1.31%)

Figure S16. The ITS rDNA Sequence Data of *Penicillium citrinum*

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CCACCTCCCACCCGTGTTGCCCGAACCTATGTTGCCTCGGGCGGGCCCCGCGCCCG
CCGACGGCCCCCTGAACGCTGTCTGAAGTTGCAGTCTGAGACCTATAACGAAAT
TAGTTAAAACCTTTCAACAACGGATCTCTTGGTTCCGGCATCGATGAAGAACGCAG
CGAAATGCGATAACTAATGTGAATTGCAGAATTCAGTGAATCATCGAGTCTTTGA
ACGCACATTGCGCCCTCTGGTATTCCGGAGGGCATGCCTGTCCGAGCGTCATTGC
TGCCCTCAAGCCCGGCTTGTGTGTTGG
    
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Figure S17. Cytotoxic Effects of Compounds 1 and 2 against Seven Tumor Cell Lines



Scheme S1. Plausible Biosynthetic Pathways for Compounds 1 and 2

