SUPPORTING INFORMATION

Cytotoxic polyketides from the deep-sea-derived fungus *Aspergillus fischeri* FS452

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Six polyketides belong to spinoate family (**1**–**6**) including two new ones fischerins A (**1**) and B (**2**) were isolated from the deep-sea-derived fungus *Aspergillus fischeri* FS452. Their structures were elucidated by comprehensive spectroscopic analysis and the absolute configurations were determined by the e quantum chemical ECD calculations. The *in vitro* cytotoxicity assays indicated that fischerin B (**2**) exhibited potential activities against the four tested human cancer cell lines (SF-268, MCF-7, HepG-2 and A549) with the IC_{50} values in the range of 7 ~ 10 μM.

Keywords: polyketides; deep-sea-derived fungus; quantum chemical calculations; cytotoxicty

Table of contents:

Figure S1. The COSY (red bold lines) and the key HMBC correlations (blue arrows) of **1** and **2.**

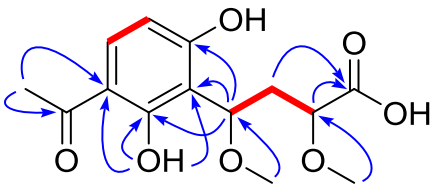


Figure S2. The experimental ECD spectrum of **1**/**2** and the calculated plots of (2*S*,4*R*)-**1**/(2*S*,4*S*)-**2** at b3lyp/6-311+g(d,p) level.

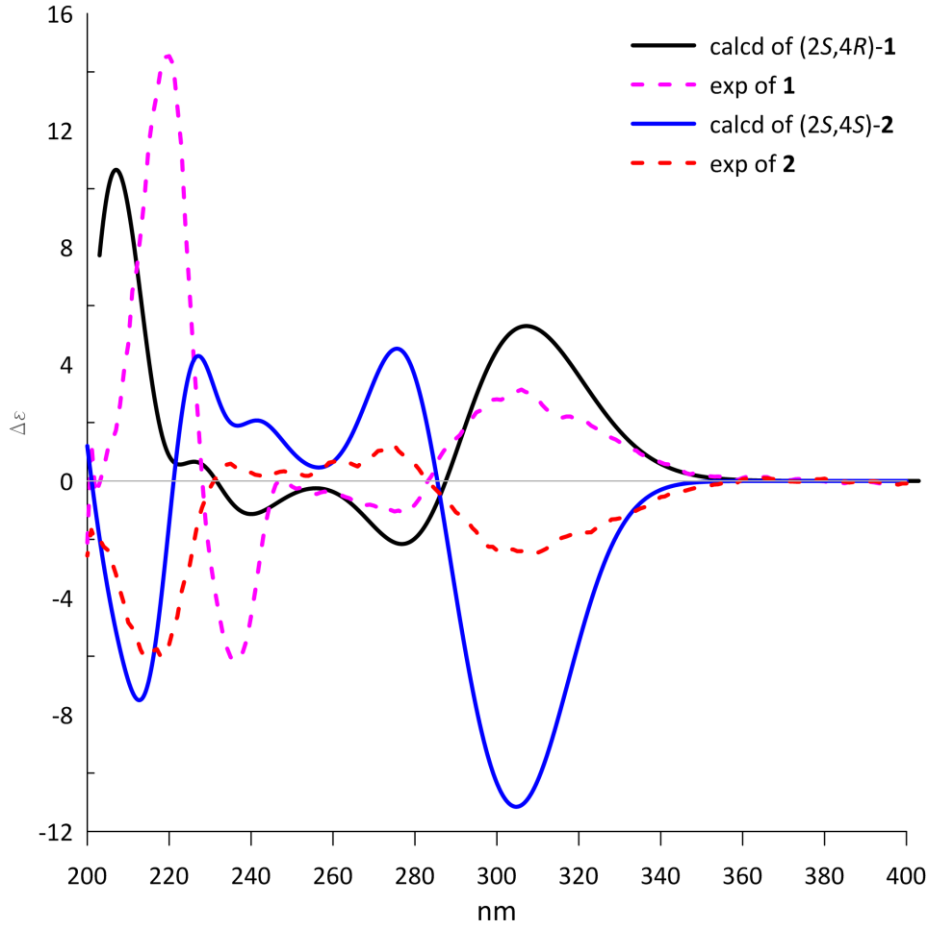


Figure S3. The ortep drawing of the mixture of **5** and **6**.

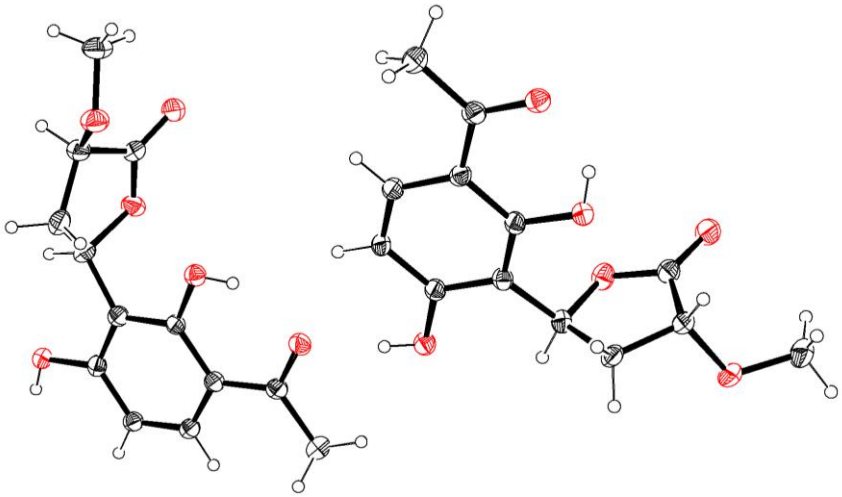


Figure S4. ^{1}H NMR spectrum of **1** in chloroform-*d*.

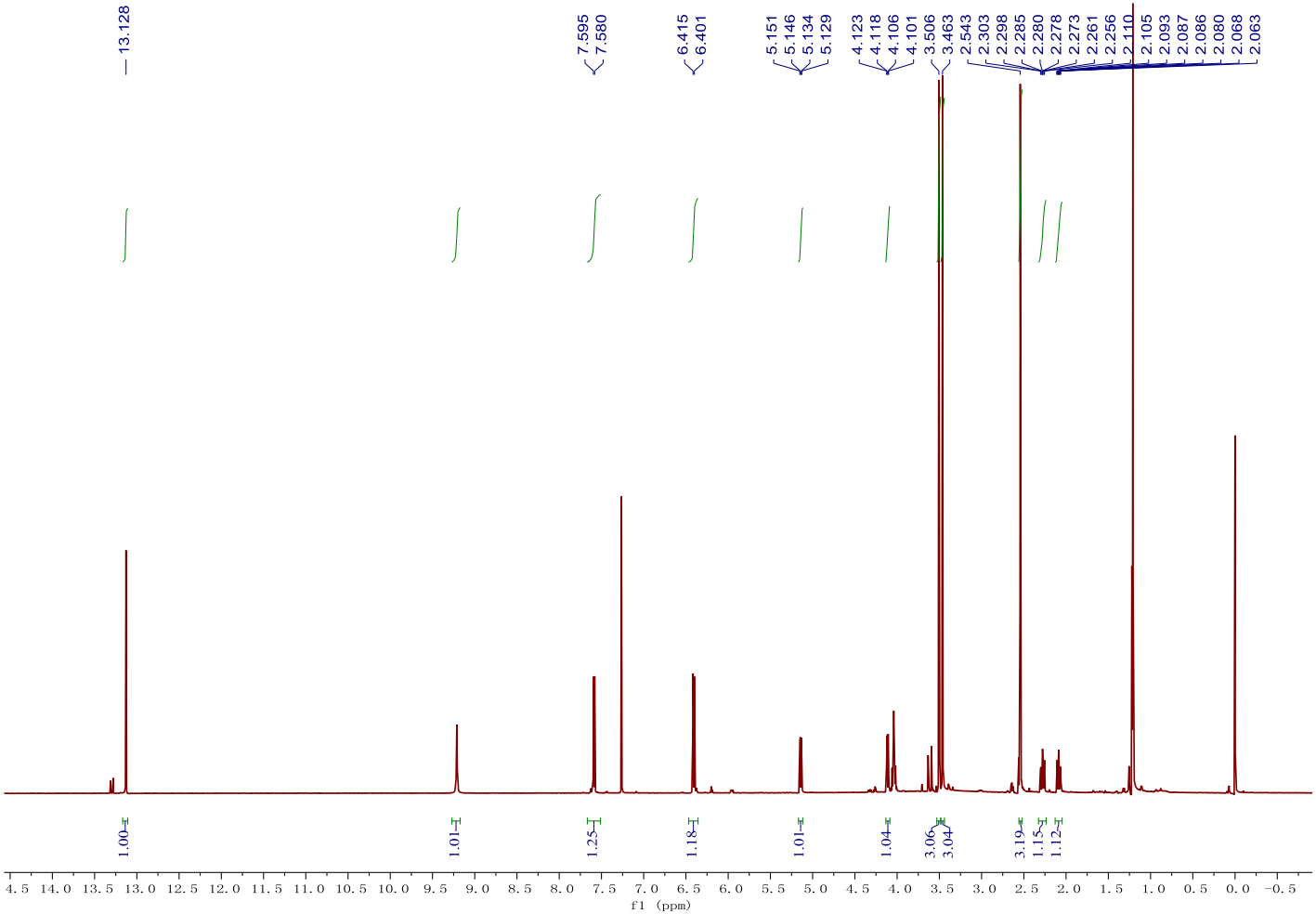


Figure S5. ^{13}C NMR spectrum of **1** in chloroform-*d*.

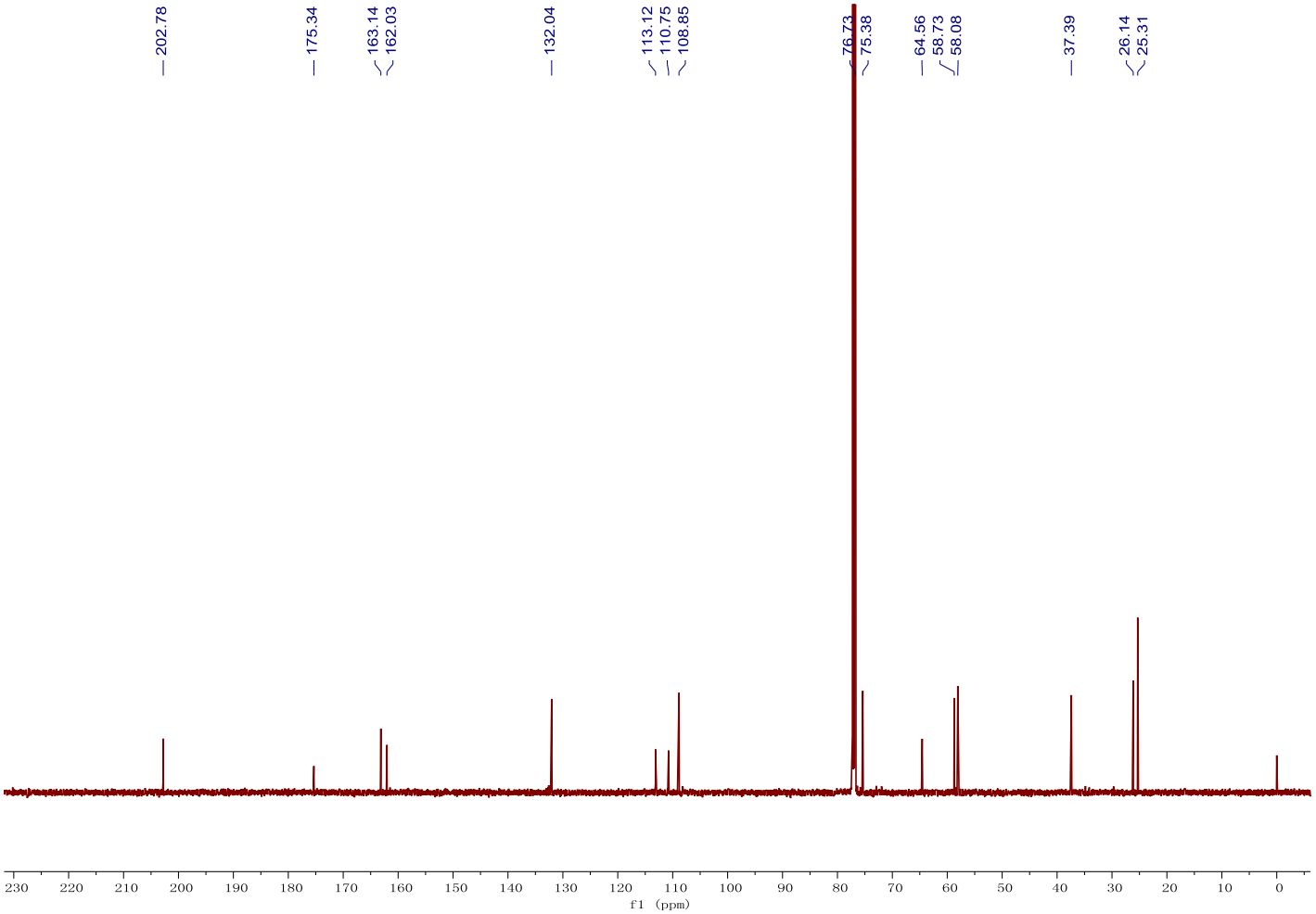


Figure S6. ^{1}H, ^{1}H-COSY spectrum of **1** in chloroform-*d*.

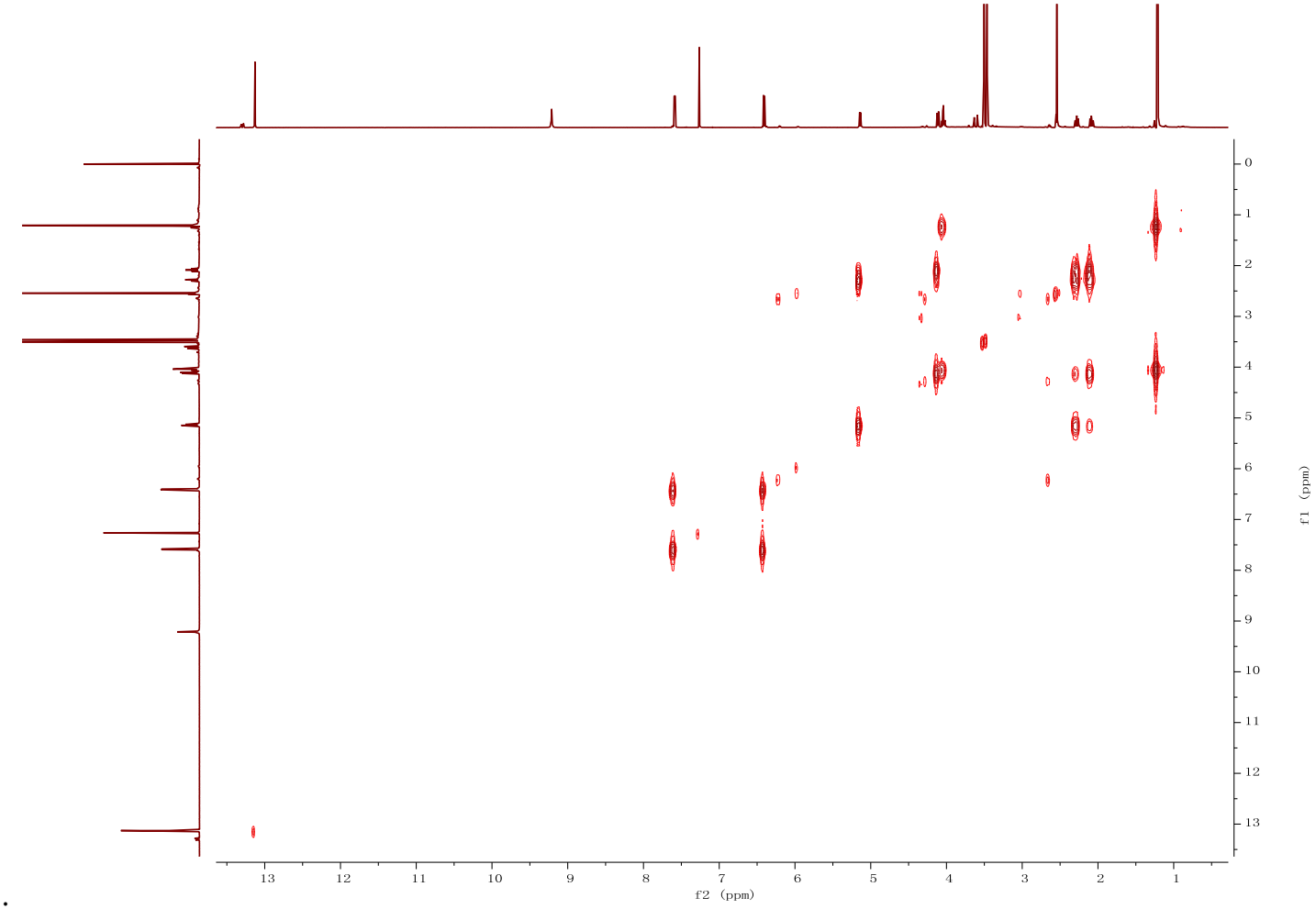


Figure S7. HSQC spectrum of **1** in chloroform-*d*.

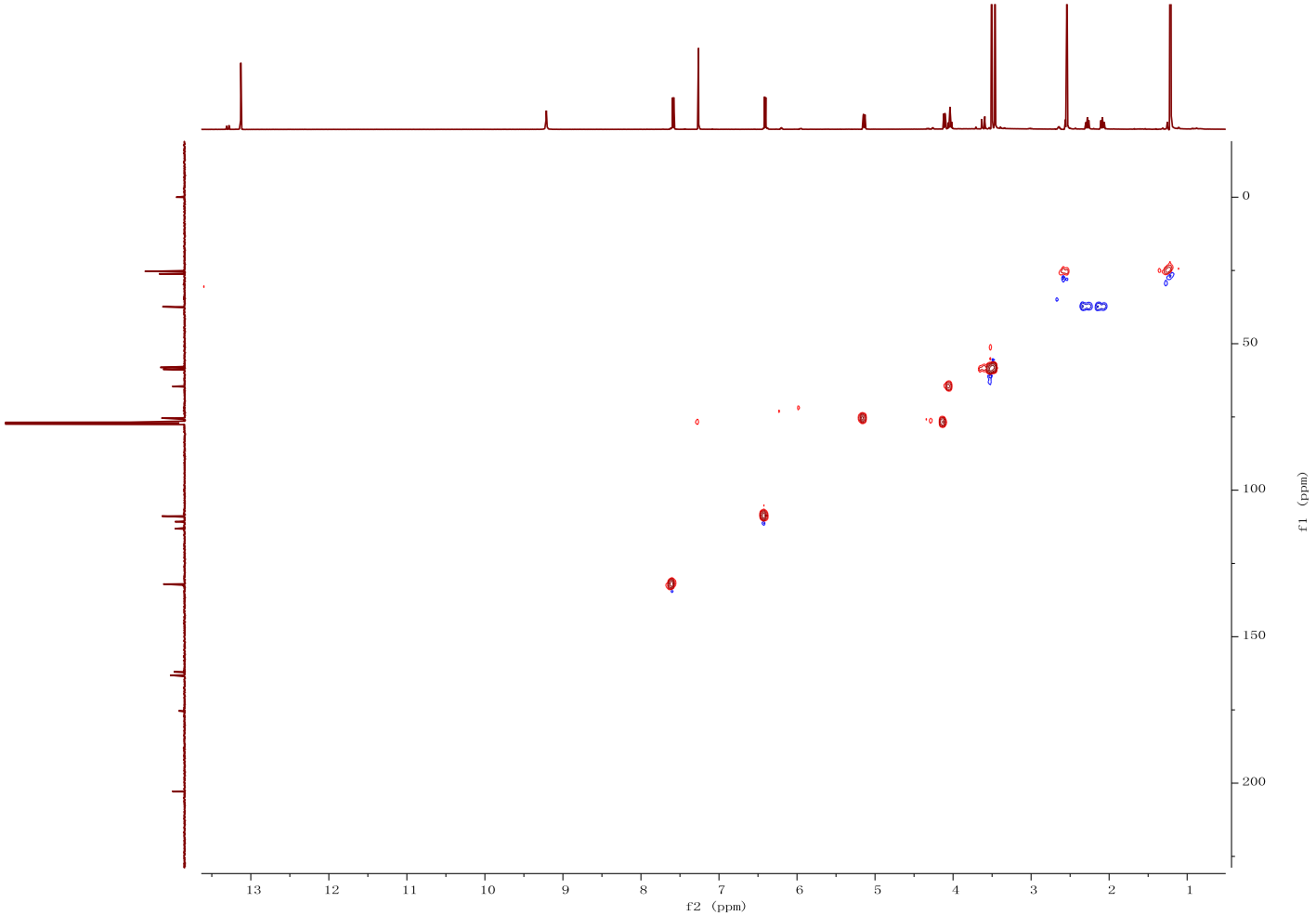


Figure S8. HMBC spectrum of **1** in chloroform-*d*.

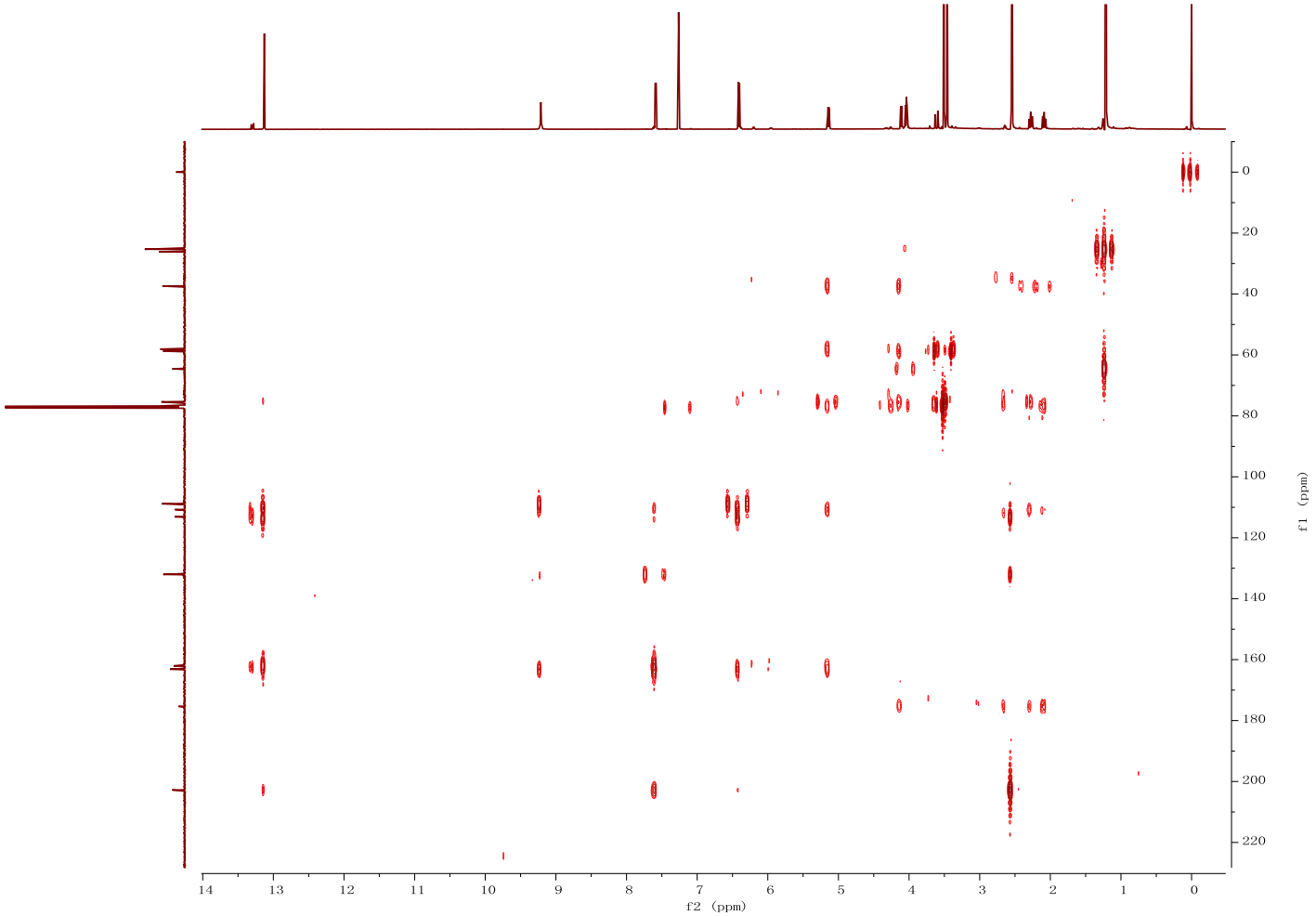


Figure S9. ^{1}H-NMR spectrum of **2** in chloroform-*d*.

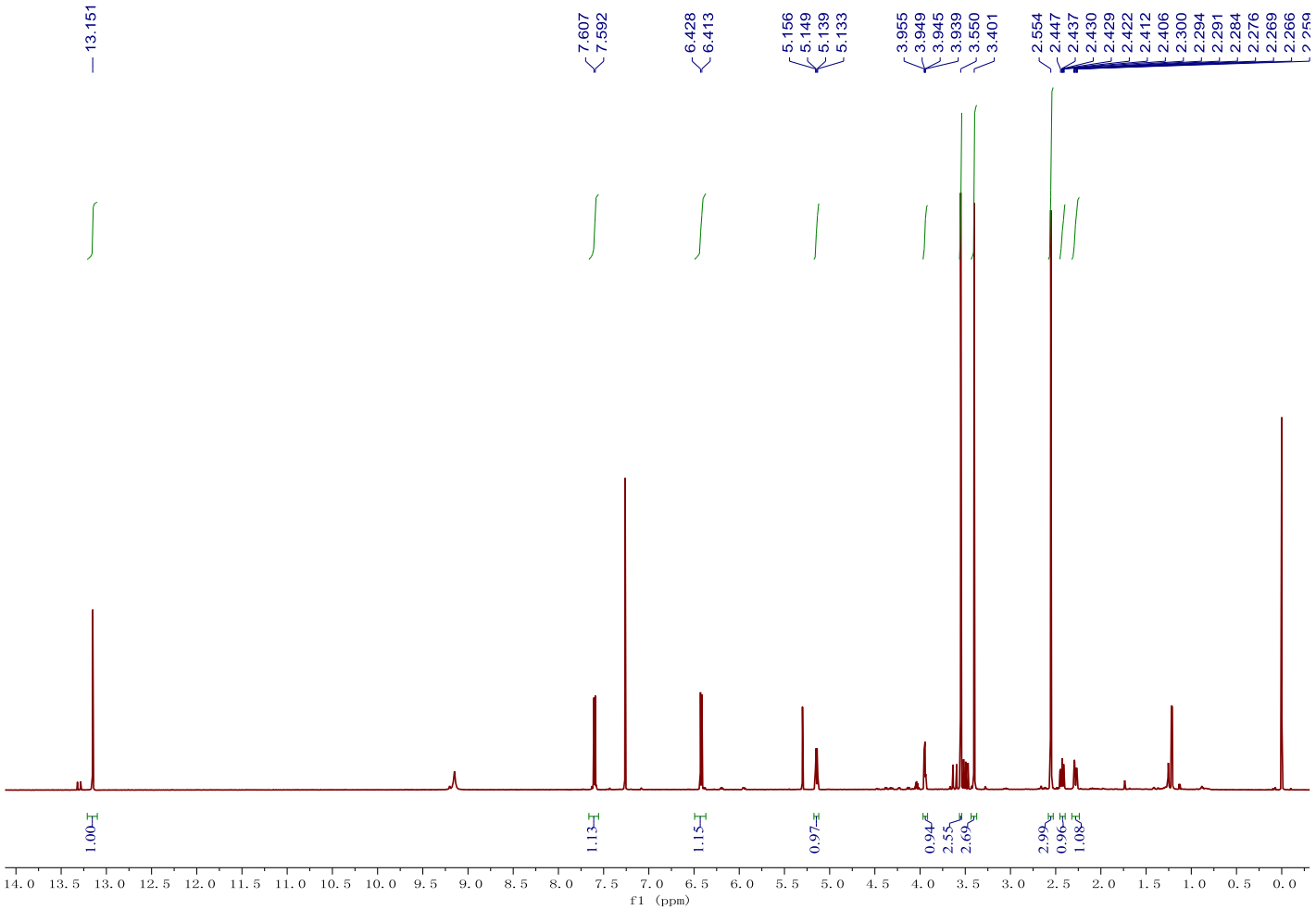


Figure S10. ^{13}C-NMR spectrum of **2** in chloroform-*d*.

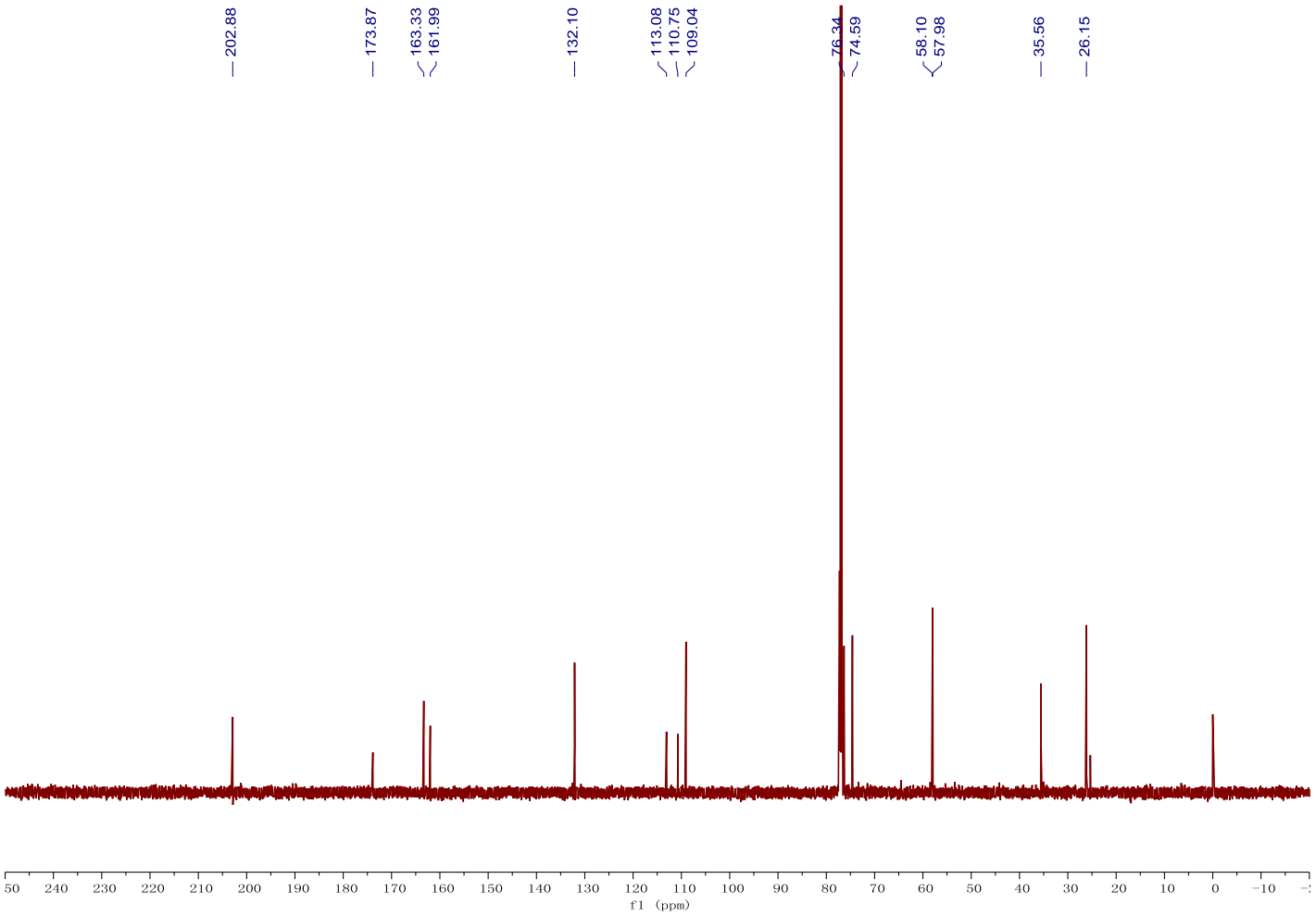


Figure S11. ^{1}H, ^{1}H-COSY spectrum of **2** in chloroform-*d*.

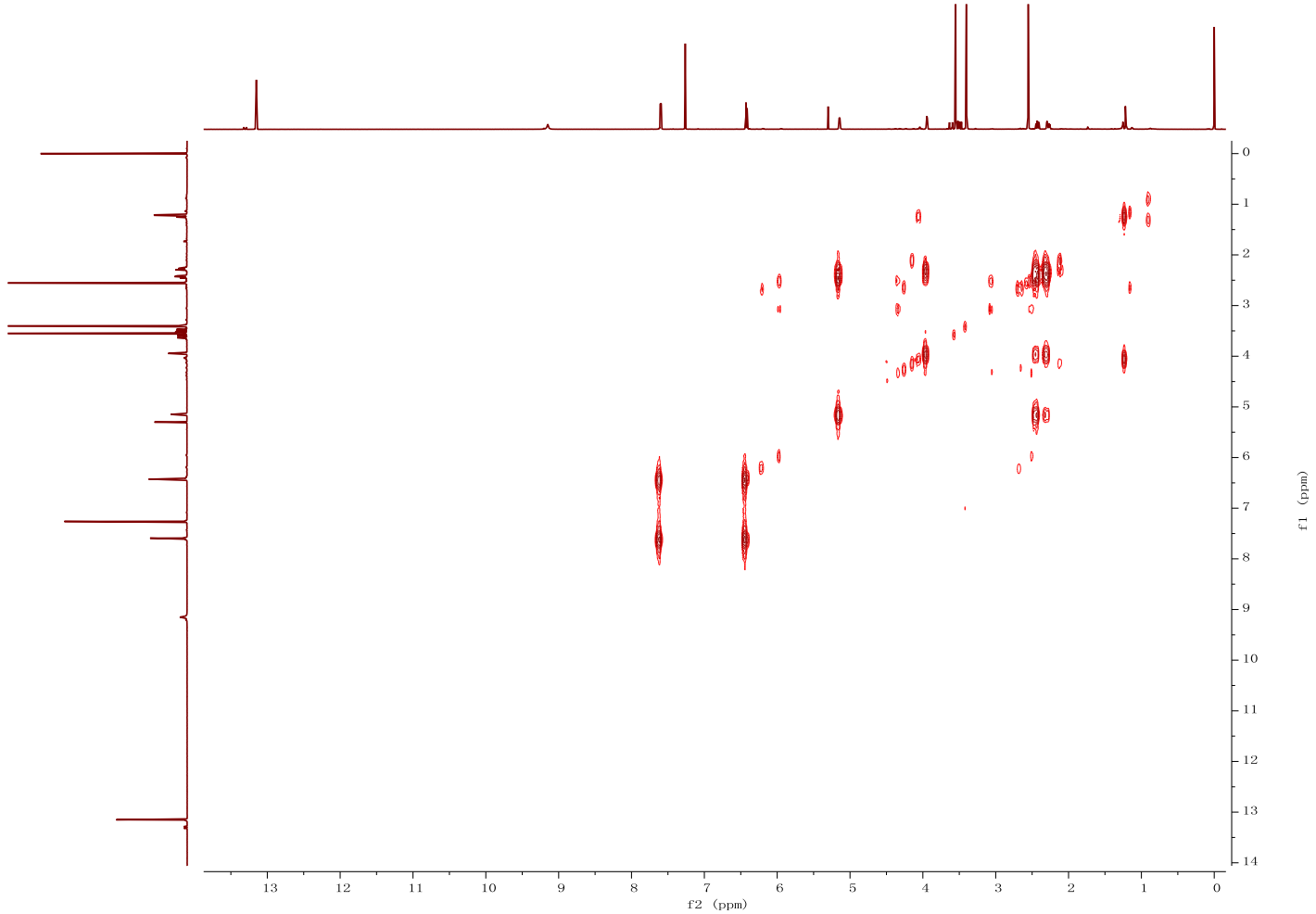


Figure S12. HSQC spectrum of **2** in chloroform-*d*.

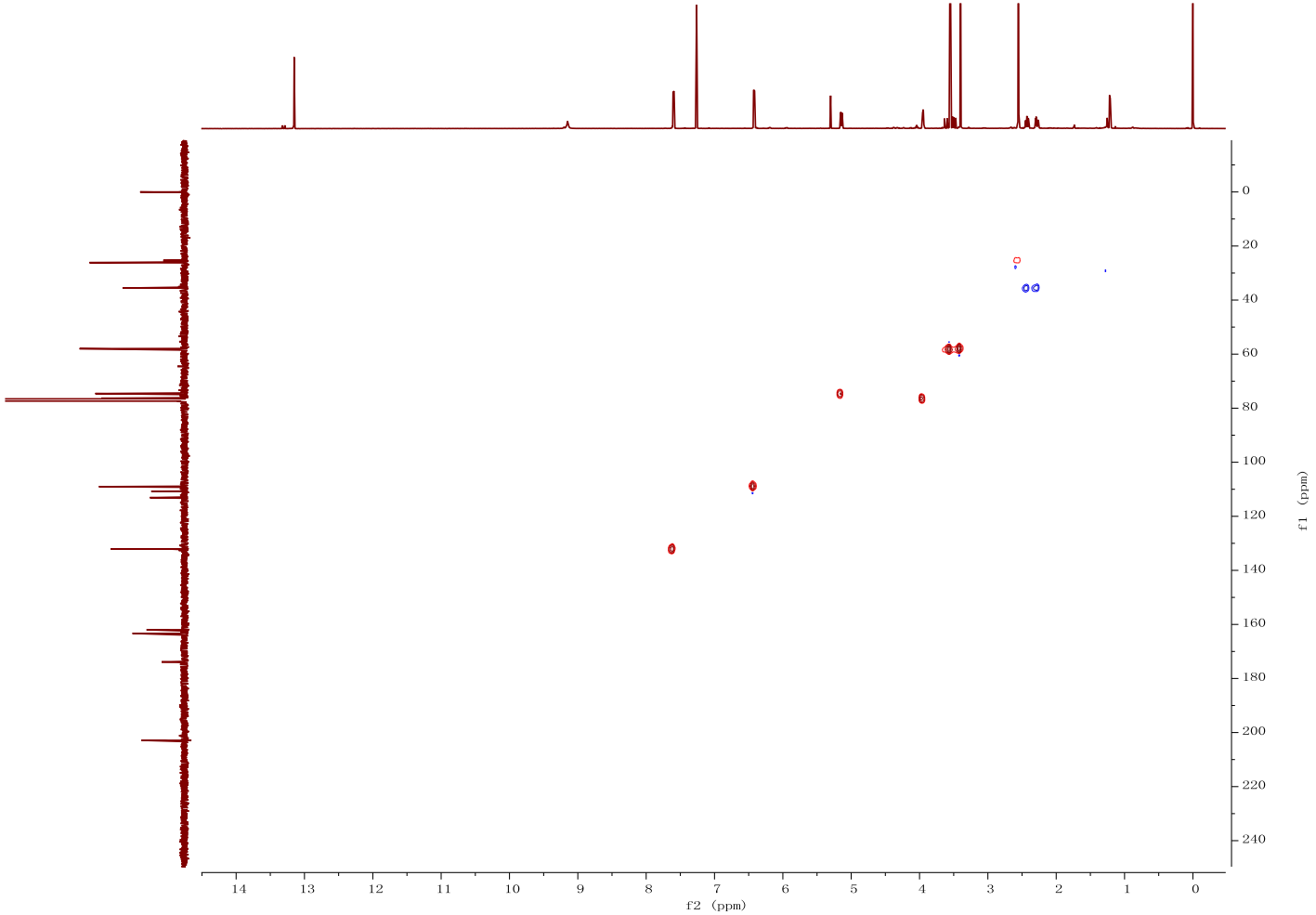


Figure S13. HMBC spectrum of **2** in chloroform-*d*.

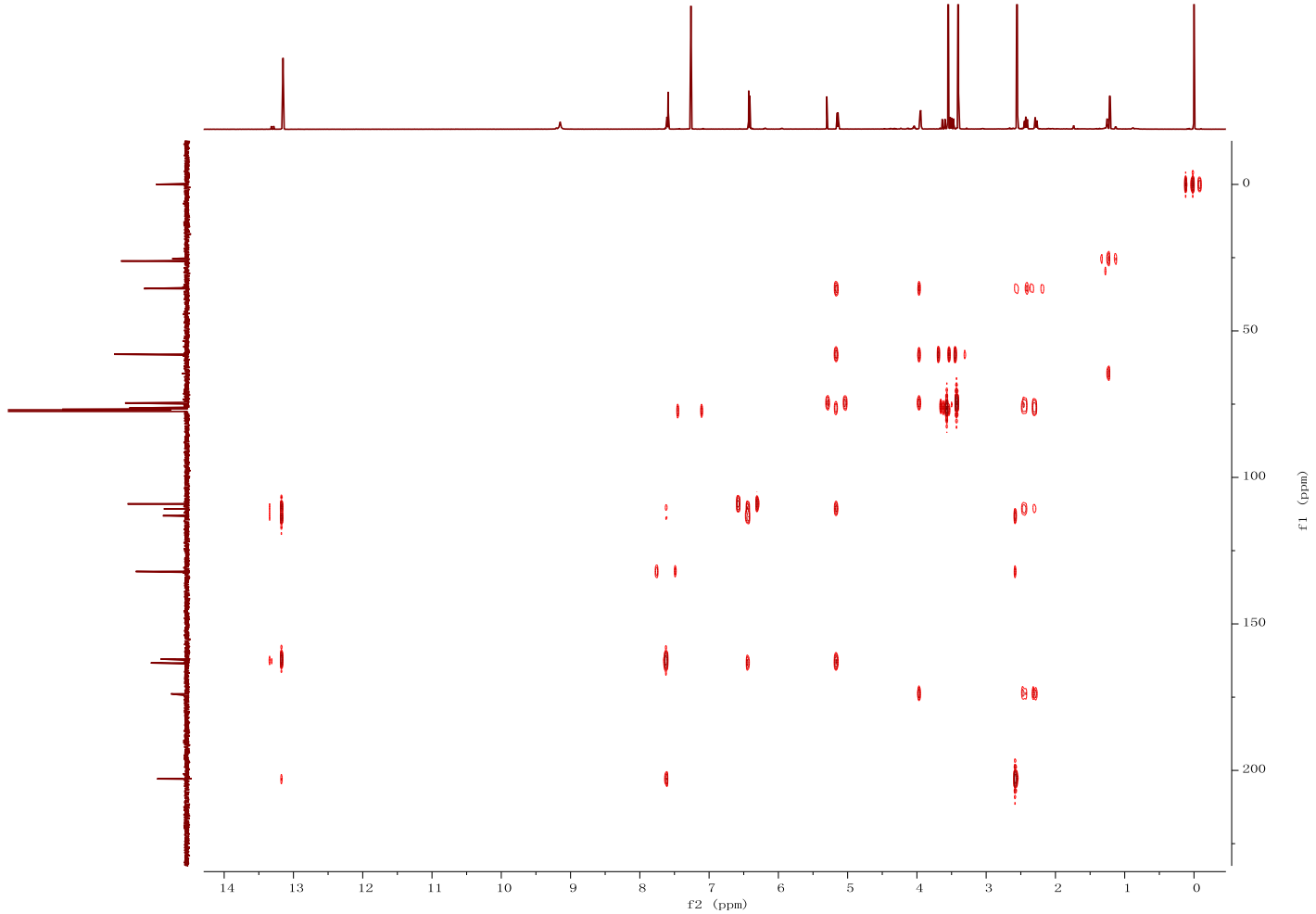
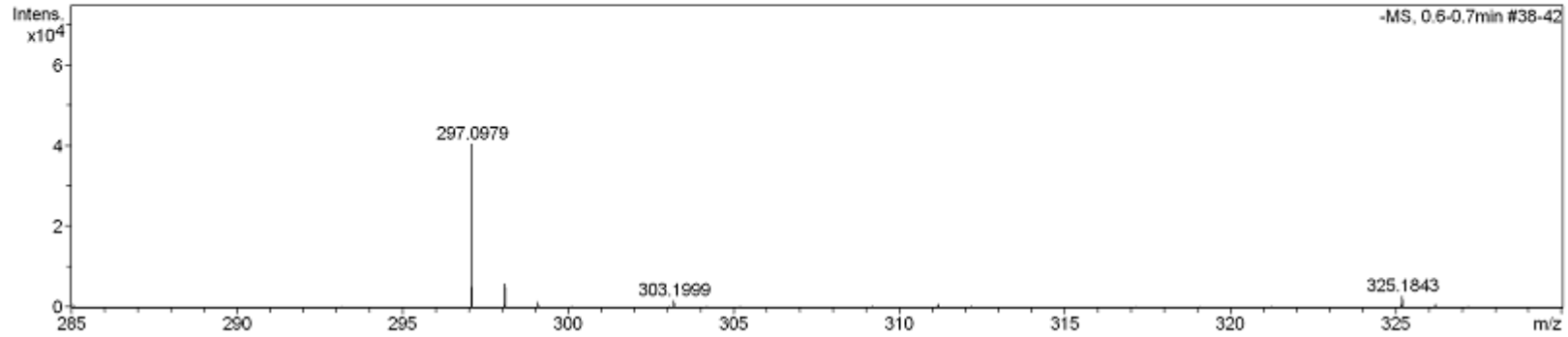


Figure S14. HRESI TOF MS spectrum of **1**.

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	70 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



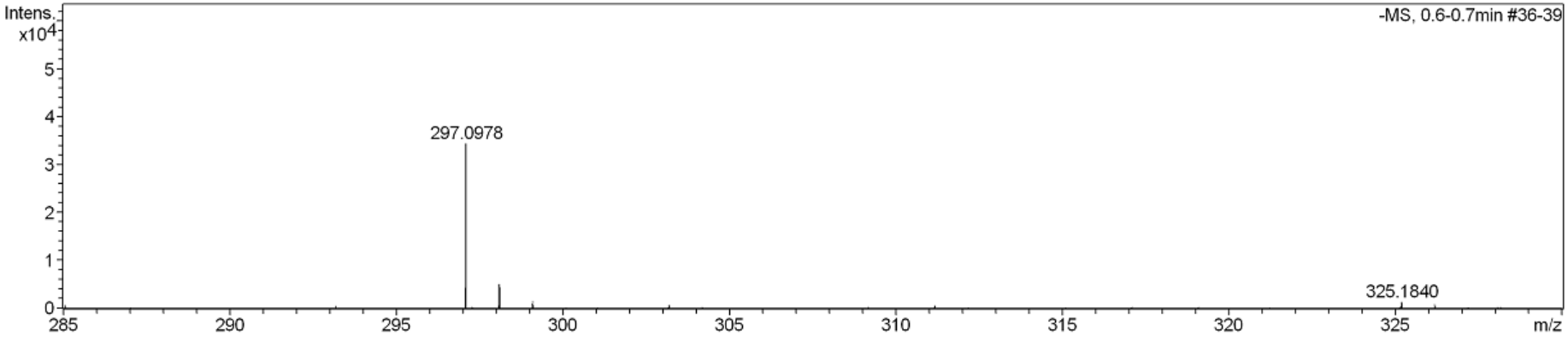
SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
297.0979	297.0980	0.2	6.5	C14 H17 O7

Figure S15. HRESI TOF MS spectrum of **2**.

Acquisition Parameter

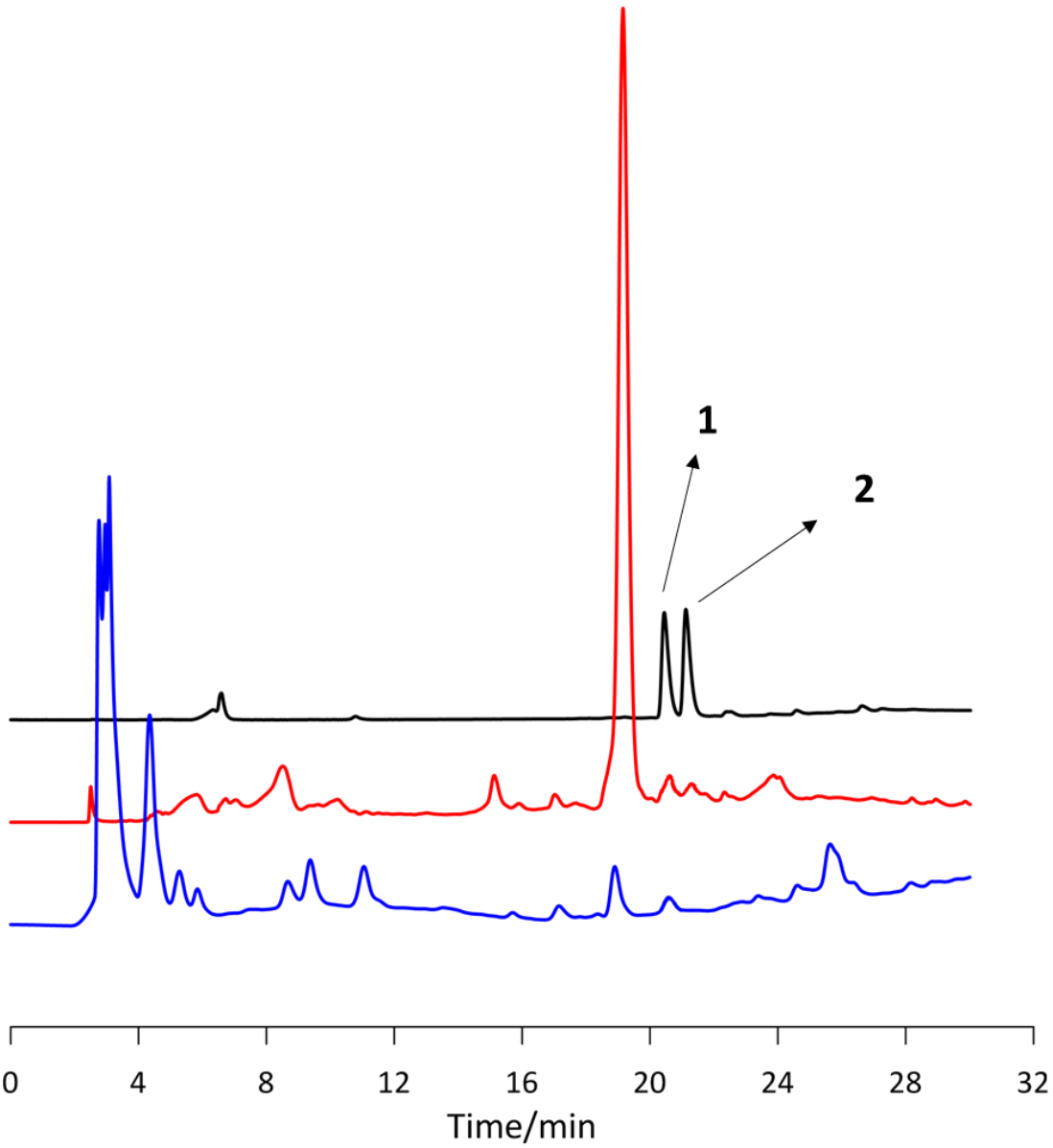
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	70 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



SPECTRUM - simulation :

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
297.0978	297.0980	-0.6	6.5	C14 H17 O7

Figure S16. HPLC analysis of the extract of fermented liquid, mycelia and pure compound **1**/**2**.



Chromatographic condition: Inertsil ODS-3 column; Methanol/H_2O, 35/75 to 100/0; 1 mL/min; 280 nm. (Red: extract of fermented liquid by EtOAc; Blue: extract of mycelia by methanol)

Figure S17. Chiral separation of compounds **5** and **6**.

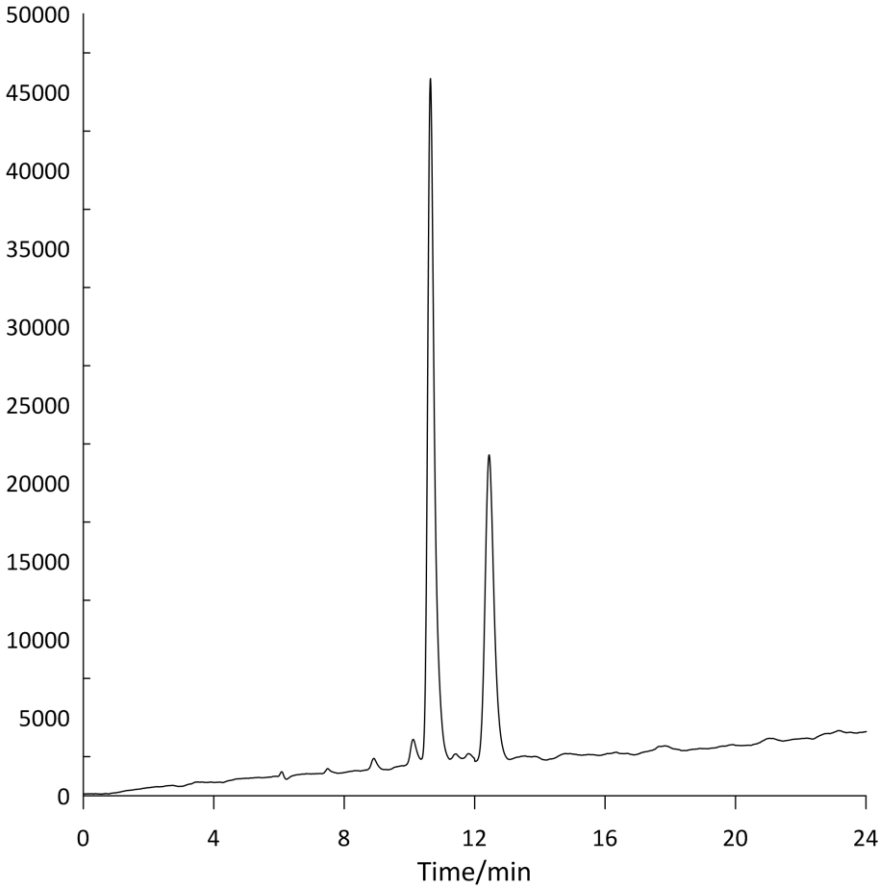


Table S1. The ^{1}H and ^{13}C NMR Data of **1** and **2** recorded at 600 MHz (^{1}H) and 150 MHz (^{13}C).

position	**1**[a]		**2**[a]	
	δ_C, *mult.*	δ_H (*J* in Hz)	δ_C, *mult.*	δ_H (*J* in Hz)
1	175.3, C		173.9, C	
2	76.7, CH	4.11, dd (10.4, 3.1)	76.3, CH	3.95, dd (5.9, 3.8)
3	37.4, CH_2	2.28, ddd (14.6, 10.4, 3.1)	35.6, CH_2	2.43, ddd (14.8, 9.9, 3.8)
		2.09, ddd (14.6, 10.5, 3.1)		2.28, ddd (14.8, 5.9, 4.0)
4	75.4, CH	5.14, dd (10.5, 3.1)	74.6, CH	5.14, dd (9.9, 4.0)
5	110.7, C		110.7, C	
6	163.1, C		163.3, C	
7	113.1, C		113.1, C	
8	132.0, CH	7.59, d (8.8)	132.1, CH	7.60, d (8.9)
9	108.8, C	6.41, d (8.8)	109.0, C	6.42, d (8.9)
10	162.0, C		162.0, C	
11	202.8, C		202.9, C	
12	26.1, CH_3	2.54, s	26.1, CH_3	2.55, s
13	58.7, CH_3	3.51, s	58.1, CH_3	3.55, s
14	58.1, CH_3	3.46, s	58.0, CH_3	3.40, s
OH		13.13, s		13.15

[a]Measured in chloroform-*d*.

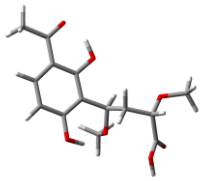
Table S2. Cytotoxicity assays of **1–6**.

Compounds	SF-268	MCF-7	HepG-2	A549
1	> 100	> 100	> 100	> 100
2	7.56 ± 0.20[a]	8.45± 0.27	9.03 ± 0.26	9.98 ± 0.42
3	> 100	> 100	> 100	> 100
4	> 100	> 100	> 100	> 100
5	> 100	> 100	> 100	> 100
6	>100	> 100	> 100	> 100
cis-platinum	3.26 ± 0.29	3.19 ± 0.12	2.42 ± 0.14	1.56 ± 0.08

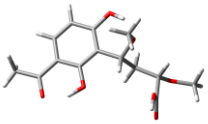
[a]IC_{50} in μM; [b]Not tested.

Table S3. Energy analysis for the conformers of (2*S*,4*R*)-**1**.

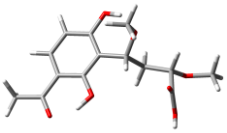
compounds	Conformation	G (Hartree)	G (Kcal/mol)	ΔG (Kcal/mol)	Boltzmann Dist (%)
1	**1-1**	-1071.24307103	-672208.1337	0.00	53.59%
	1-2	-1071.24170473	-672207.2763	0.86	12.59%
	1-3	-1071.24130135	-672207.0232	1.11	8.21%
	1-4	-1071.24188587	-672207.39	0.74	15.26%
	1-5	-1071.24129049	-672207.0164	1.12	8.12%
	1-6	-1071.24006885	-672206.2498	1.88	2.22%



1-1



1-2



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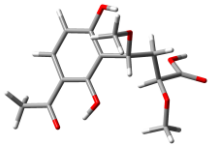

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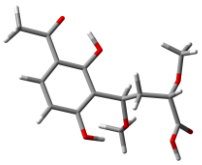
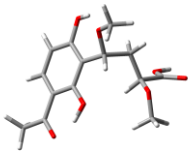


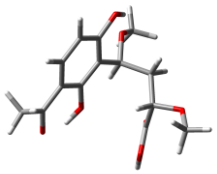
1-5



1-6

Table S4. Energy analysis for the Conformers of (2*S*,4*S*)-**2**.

compounds	Conformation	G (Hartree)	G (Kcal/mol)	ΔG (Kcal/mol)	Boltzmann Dist (%)
2	**2-1**	-1071.23645731	-672203.9835	1.14	4.60%
	2-2	-1071.23826016	-672205.1148	0.00	31.08%
	2-3	-1071.23826731	-672205.1193	0.00	31.32%
	2-4	-1071.23726841	-672204.4925	0.63	10.87%
	2-5	-1071.23778509	-672204.8167	0.30	18.79%
	2-6	-1071.23615786	-672203.7956	1.32	3.35%



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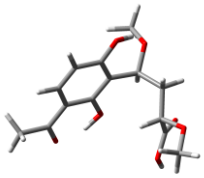

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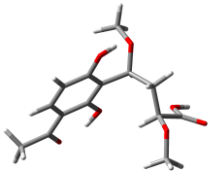

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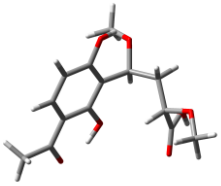

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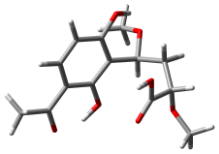

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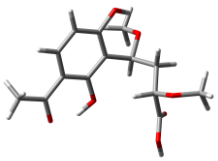

2-6