Sporormiellin A, the first tetrahydrofuran-fused furochromone with an unprecedented tetracyclic skeleton from *Sporormiella minima*

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List of Supporting Information

1 General Experimental Procedures.

Optical rotations were measured on a JASCO P1020 digital polarimeter, and UV data were recorded on a JASCO V-550 UV/vis spectrometer. ECD data were recorded on a JASCO J-810 spectrophotometer using CH_2Cl_2 as solvent. IR data were recorded using a JASCO FT/IR-480 plus spectrometer. ESI-IT-MS spectra were performed on a Finnigan LCQ Advantage MAX mass spectrometer and HRESIMS spectra were obtained on Waters Synapt G2 mass spectrometer. 1D and 2D NMR data were acquired with Bruker AV 600, AV 400, and AV 300 using solvent signals ($CDCl_3$: δ_H 7.26/δ_C 77.0; DMSO-d_6: δ_H 2.50/δ_C 39.5; CD_3OD: δ_H 3.30/δ_C 49.0) as the internal standard. Column chromatography (CC) was carried out on silica gel (200–300 mesh) (Qingdao Haiyang Chemical Group Corporation, Qingdao, China) and ODS (60–80 μm, YMC), respectively. TLC was performed on precoated silica gel plate (SGF254, 0.2 mm, Yantai Chemical Industry Research Institute, China). The analytical HPLC was performed on a Dionex HPLC system equipped with an Ultimate 3000 pump, an Ultimate 3000 diode array detector (DAD), an Ultimate 3000 Column Compartment, an Ultimate 3000 autosampler (Dionex, USA) and an Alltech (Grace) 2000ES evaporative light scattering detector (ELSD) (Alltech, USA) using a Phenomex Gemini C18 column (4.6 × 250 mm, 5 μm). The semi-preparative HPLC was carried out on a Shimadzu LC-6AD Liquid Chromatography with SPD-20A Detector (Shimadzu, Japan) using a YMC-Pack ODS-A column (10.0 × 250 mm, 5 μm).

2 Fungus Material.

The strain of *Sporormiella minima* was isolated from the lichen *Nephromopsis pallescens* (Schaer.) Y. S. Park collected in Zixin Mountain, Yunnan province, China, in Nov, 2006. The isolate was identified by one of the authors (L.-D. Guo) and assigned the accession number 66-3-4-2 in the culture collection at the Institute of Traditional Chinese Medicine and Natural Products, College of Pharmacy, Jinan University, Guangzhou. The fungal strain was cultured on slants of potato dextrose agar (PDA) at 25 °C for 5 days. Agar plugs were used to inoculate four Erlenmeyer flasks (250 mL), each containing 100 mL of potato dextrose broth (PDB). Four flasks of the inoculated media were incubated at 25 °C on a rotary shaker at 200 rpm for five days to prepare the seed culture. Fermentation was carried out in twenty Erlenmeyer flasks (500 mL), each containing 70 g of rice. Distilled H_2O (105 mL) was added to each flask, and the rice was soaked overnight before autoclaving at 120 °C for 30 min. After cooling to room temperature, each flask was inoculated with 5.0 mL of the spore inoculum and incubated at room temperature for 50 days.

3 Extraction and Isolation.

The fermented material was extracted three times with EtOAc, and the organic solvent was evaporated under vacuum to afford the dry crude extract (30.6 g). Then the crude extract was was fractionated by silica gel column chromatography (CC) using cyclohexane–MeOH (100:0 and 0:100, v/v) to afford cyclohexane fraction (C, 17.6 g) and methanol fraction (W, 12.1 g). Methanol fraction was separated by ODS CC eluting with MeOH–H_2O elution (30:70, 50:50, 70:30 and 100:0, v/v) to afford 4 fractions (W1 to W4). Fraction W2 (3.0 g) was separated by ODS CC eluting with MeOH–H_2O elution (40:60, 50:50, and 60:40, v/v) to afford 8 subfractions (W2-a to W2-h). Subfraction W2-c (20.6 mg) was further separated by semi-preparative reversed-phase HPLC (RPHPLC) eluting with MeOH–H_2O (40:60, v/v) at a flow rate of 3 mL/min to yield **5** (t_R: 21.5 min, 2.5 mg). Subfraction W2-d (35.3 mg) was further separated by semi-preparative reversed-phase HPLC (RPHPLC) using MeOH–H_2O (45:55, v/v) with as eluent at a flow rate of 3 mL/min to yield **4** (t_R: 24.0 min, 5.8 mg). Subfraction W2-e (1.2 g) was further separated by ODS CC eluting with MeOH-H_2O (40:60, 50:50, and 60:40, v/v) to afford 4 sub-subfractions (W2-e-1 to W2-e-4). Sub-subfraction W2-e-4 (730.0 mg) was subjected to semi-preparative RPHPLC using MeCN–H_2O (40:60, v/v) at a flow rate of 3 mL/min to yield **2** (t_R: 16.2 min, 6.4 mg). Subfraction W2-f (223.1 mg) was further separated by silica gel CC eluting with cyclohexane-EtOAc (99:1, 95:5, 90:10, 80:20, 70:30,60:40, and 0:100, v/v) to afford 5 sub-subfractions (W2-f-1 to W2-f-5). Sub-subfraction W2-f-3 (59.2 mg) was subjected to semi-preparative RPHPLC using MeOH–H_2O (50:50, v/v) at a flow rate of 3 mL/min to yield **1** (t_R: 31.8 min, 1.3 mg), **6** (t_R: 22.0 min, 2.0 mg). Fraction W3 (1.5 g) was separated by ODS CC eluting with MeOH–H_2O elution (55:45, 65:35, 75:25, and 100:0, v/v) to afford 15 subfractions (W3-a to W3-o). Subfraction W3-l (35.3 mg) was further separated by semi-preparative reversed-phase HPLC (RPHPLC) using MeCN–H_2O (40:60, v/v) with as eluent at a flow rate of 3 mL/min to yield **3** (t_R: 38.3 min, 1.5 mg).

4 Spectroscopic data of 1–5.

Sporormiellin A (1): colorless crystals (MeOH). M.p. 180-182 °C. [α]27 D +15.9 (*c* 0.21, MeOH); UV (CH_3OH) λ_{max} (logε): 209 (3.74), 226 (3.79), 268 (3.24), 317 (3.22) nm; IR (KBr) ν_{max} 3447 (br), 2955, 2923, 2848, 1732, 1648, 1604, 1472, 1384, 1264, 1157, 1020 cm^{-1}; CD (*c* 3.4 × 10^{-3} M, CH_2Cl_2) λ_{max} ($\Delta\varepsilon$) 385 (-2.5), 282 (-6.9) nm; ESI-MS (positive): *m/z* 319 $[M + Na]^+$, 341 $[M + Na]^+$; HRESI-TOF-MS (positive): *m/z* 319.0813 $[M + H]^+$ (calcd. for $C_{16}H_{15}O_7$, 319.0818).

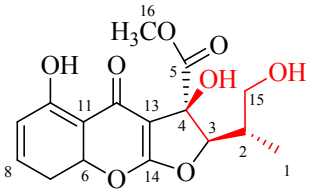
Sporormiellin B (2): pale brown oil; [α]27 D +23.4 (*c* 0.37, MeOH); UV (CH_3OH) λ_{max} (logε): 204 (3.54), 223 (3.56), 232 (3.58), 268 (3.08), 316 (3.07) nm; IR (KBr) ν_{max} 3430 (br), 2955, 2924, 2848, 1739, 1650, 1610, 1482, 1380, 1287, 1180, 1025 cm^{-1}; CD (*c* 4.7 × 10^{-3} M, CH_2Cl_2) λ_{max} ($\Delta\varepsilon$) 379 (-2.5) , 282 (-7.3) nm; ESI-MS (positive): *m/z* 359 $[M + Na]^+$; ESI-MS (negative) *m/z*: 335 $[M - H]^-$; HRESI-TOF-MS (positive): *m/z* 359.0742 $[M + Na]^+$ (calcd. for $C_{16}H_{16}O_8$ Na, 359.0743). ^1H and ^{13}C NMR see Table 1.

Sporormiellin C (3): brown amorphous powder; [α]27 D +24.4 (*c* 0.24, MeOH); UV (CH_3OH) λ_{max} (logε): 204 (3.51), 223 (3.59), 233 (3.62), 268 (3.07), 317 (3.08) nm; IR (KBr) ν_{max} 3447 (br), 2950, 2923, 2853, 1745, 1649, 1610, 1478, 1383, 1228, 1184, 1020 cm^{-1}; CD (*c* 5.2 × 10^{-3} M, CH_2Cl_2) λ_{max} ($\Delta\varepsilon$) 362 (-2.0), 282 (-7.4) nm; ESI-MS (positive): *m/z* 401 $[M + Na]^+$; ESI-MS (negative) *m/z*: 377 $[M - H]^-$; HRESI-TOF-MS (positive): *m/z* 401.0844 $[M + Na]^+$ (calcd. for $C_{18}H_{18}O_9$ Na, 401.0849). ^1H and ^{13}C NMR see Table 2.

Sporormiellinone A (4): yellow amorphous powder; UV (CH_3OH) λ_{max} (logε): 204 (3.64), 216 (3.63), 255 (3.21), 274 (3.17), 350 (2.99) nm; IR (KBr) ν_{max} 3421 (br), 2955, 1680, 1628, 1456, 1348, 1213, 1164, 1030, 804, 701 cm^{-1}; ESI-MS (negative) *m/z*: 317 $[M - H]^-$; HRESI-TOF-MS (positive): *m/z* 317.0675 $[M - H]^-$ (calcd. for $C_{16}H_{13}O_7$ Na, 317.0661). ^1H and ^{13}C NMR see Tables 3.

Sporormiellinone B (5): yellow amorphous powder; UV (CH_3OH) λ_{max} (logε): 206 (3.67), 253 (3.10), 274 (3.18), 350 (2.62) nm; IR (KBr) ν_{max} 3427 (br), 2955, 1716, 1618, 1453, 1333, 1259, 1031, 920 cm^{-1}; ESI-MS (positive): *m/z* 325 $[M + Na]^+$, 627

[2M + Na]$^+$; ESI-MS (negative) *m/z*: 301 [M – H]$^-$; HRESI-TOF-MS (negative): *m/z* 301.0718 [M – H]$^-$ (calcd. for $C_{16}H_{13}O_6$, 301.0712). ^{1}H and ^{13}C NMR see Tables 4.

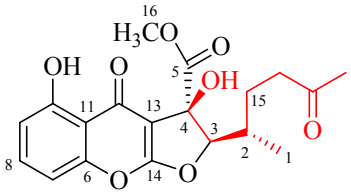


2

Table 1 1D and 2D NMR data of **2**

position	δ_C[a], mult	δ_H[a] (*J* in Hz)	^{1}H-^{1}H COSY[a]	HMBC[a]	δ_C[b], mult	δ_H[b] (*J* in Hz)
1	13.4, CH_3	1.18, d (6.8)	2	2, 3, 15	13.3, CH_3	1.10 ,d (6.7)
2	34.1, CH	2.61, m	1, 3, 15_a, 15_b		34.1, CH	2.27, m
3	94.4, CH	5.09, d (9.4)	2	1,2,4,5,15	94.8, CH	4.98, d (9.0)
4	78.8, qC				77.8, qC	
5	172.6, qC				171.1, qC	
6	153.8, qC				153.1, qC	
7	107.0, CH	6.87, d (8.3)	8	6, 9, 11, 12	107.3, CH	7.09, d (8.3)
8	134.2, CH	7.45, t (8.3)	7, 9	6, 10	134.8, CH	7.62, t (8.3)
9	113.2, CH	6.81, d (8.3)	8	7, 10, 11, 12	112.7, CH	6.86, d (8.3)
10	161.3, qC				160.3, qC	
11	109.5, qC				108.7, qC	
12	179.5, qC				178.4, qC	
13	98.3, qC				99.5, qC	
14	169.8, qC				169.5, qC	
15	64.8, CH_2	3.53, dd (10.2, 7.7), a	2	1, 3, 4	61.8, CH_2	3.43, m, a
		3.78, dd (10.2, 3.5), b	2	1, 3, 4		3.40, m, b
16	54.0, CH_3	3.90, s		5	52.8, CH_3	3.73, s
4-OH						6.30, s
10-OH		12.46, s		9, 10, 11		12.68, s
15-OH						4.78, m

a: The data recorded in $CDCl_3$ (^{1}H NMR for 600 MHz, ^{13}C NMR for 150 MHz); b: The data recorded in DMSO-d_6(^{1}H NMR for 400 MHz, ^{13}C NMR for 100 MHz).

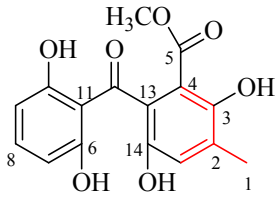


3

Table 2 1D and 2D NMR data of **3**

position	δ_C[a], mult	δ_H[a] (*J* in Hz)	δ_C[b], mult	δ_H[b] (*J* in Hz)	^{1}H-^{1}H COSY[b]	HMBC[b]
1	13.4, CH_3	1.23, d (6.9)	13.6, CH_3	1.15, d (6.8)	2	2, 3, 15
2	32.1, CH	2.66, m	31.5, CH	2.50, m	1, 3, 15_a, 15_b	
3	92.4, CH	5.03, d (8.4)	93.8, CH	4.98, d (9.4)	2	1, 4, 5, 15
4	78.5, qC		77.7, qC			
5	172.3, qC		170.8, qC			
6	153.9, qC		153.0, qC			
7	107.0, CH	6.88, dd (8.3, 0.6)	107.4, CH	7.10, d (8.3)	8	9, 11, 12
8	134.3, CH	7.47, t (8.3)	134.9, CH	7.63, t (8.3)	7, 9	6, 10
9	113.3, CH	6.83, dd (8.3, 0.6)	112.8, CH	6.87, d (8.3)	8	7, 11, 12
10	161.4, qC		160.3, qC			
11	109.6, qC		108.7, qC			
12	179.3, qC		178.4, qC			
13	98.3, qC		99.5, qC			
14	169.9, qC		169.2, qC			
15	65.6, CH_2	4.16, dd (11.5, 4.5), a	64.7, CH_2	4.10, dd (11.2, 4.9), a	2, 15_b	1, 2, 3, 17
		4.07, dd (11.5, 5.6), b		4.03, dd (11.2, 4.1), b	2, 15_a	1, 2, 3, 17
16	54.3, CH_3	3.92, s	52.9, CH_3	3.72, s		5
17	170.5, qC		170.2, qC			
18	20.7, CH_3	2.07, s	20.4, CH_3	2.01, s		17
4-OH				6.52, s		5
10-OH		12.38, s		12.63, s		9, 10, 11

a: The data recorded in $CDCl_3$ (^{1}H NMR for 400 MHz, ^{13}C NMR for 100 MHz); b: The data recorded in DMSO-d_6(^{1}H NMR for 400 MHz, ^{13}C NMR for 100 MHz).

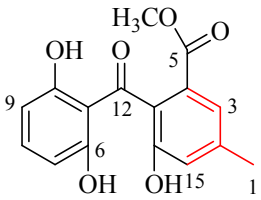


4

Table 3 1D and 2D NMR data of **4**

position	δ_C[a], mult	δ_H[a] (*J* in Hz)	^{1}H-^{1}H COSY[a]	HMBC[a]
1	16.2, CH_3	2.27, br s	15	2, 3, 15
2	132.2, qC			
3	154.5, qC			
4	108.9, qC			
5	169.6, qC			
6, 10	159.8, qC			
7, 9	108.7, CH	6.41, d (8.3)	8	11, 12
8	136.6, CH	7.26, t (8.3)	7, 9	6, 10
11	111.9, qC			
12	198.7, qC			
13	123.8, qC			
14	145.5, qC			
15	126.1, CH	7.00, br s	1	1, 3, 12, 13, 14
16	52.3, CH_3	3.55, s		5
3-OH		10.55, br s		2, 3, 4

a: The data recorded in $CDCl_3$ (^{1}H NMR for 600 MHz, ^{13}C NMR for 150 MHz).



5

Table 4 1D and 2D NMR data of **5**

position	δ_C[a], mult	δ_H[a] (*J* in Hz)	HMBC[a]
1	21.2, CH_3	2.32, s	2, 3, 15
2	140.4, qC		
3	122.1, CH	7.25, br s	5, 13, 15
4	129.5, qC		
5	168.5, qC		
6, 10	163.6, qC		
7, 9	108.1, CH	6.26, d (8.3)	11
8	137.3, CH	7.19, t (8.3)	6, 10
11	113.2, qC		
12	203.4, qC		
13	131.9, qC		
14	155.5, qC		
15	121.8, CH	6.85, br s	3, 13, 14
16	52.4, CH_3	3.66, s	5

a: The data recorded in CD_3OD (^1H NMR for 300 MHz, ^{13}C NMR for 75 MHz).

5 X-ray Crystallographic Analysis of 1.

Upon crystallization from MeOH using the vapor diffusion method, needles of **1** were obtained. Data were collected using a Sapphire CCD with a graphite monochromated Cu Kα radiation, λ = 1.54178 Å at 173.0 (3) K. Crystal data: $C_{16}H_{14}O_7$, M = 318.27, orthorhombic, space group $P212121$; unit cell dimensions were determined to be a = 7.2831(2) Å, b = 12.4744(3)Å, c = 16.0184(4) Å, α = 90.00 °, β = 90.00 °, γ = 90.00 °, V = 1455.31(6) Å^3, Z = 4, Dx = 1.453 g/cm^3, F (000) = 664, μ (Cu K_α) = 0.983 mm^{-1}. 11414 reflections were collected until θ_{max} = 62.70°, in which independent unique 2189 reflections were observed [$F^2 > 4\sigma(F^2)$]. The structure was solved by direct methods using the SHELXS-97 program, and refined by the SHELXL-97 program and full-matrix least-squares calculations[1]. In the structure refinements, nonhydrogen atoms were placed on the geometrically ideal positions by the "ride on" method. Hydrogen atoms bonded to oxygen were located by the structure factors with isotropic temperature factors. The final refinement gave R = 0.0363, R_W = 0.0991, S = 1.064, and Flack = -0.1(2). Crystal data of **1** was deposited in the Cambridge Crystallographic Data Centre (CCDC 990532).

Reference:

(1) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

6 Quantum chemical ECD calculations of 1

The molecules of (2S, 3R, 4R)-**1** and (2R, 3S, 4S)-**1** were converted into SMILES codes before their initial 3D structures were generated with CORINA version 3.4. For each molecule, the initial 3D structure was minimized with MMFF94S force field implemented in SZYBKI version 1.7 with default parameters before it conformation space was sampled. Conformer databases were generated using OMEGA version 2.3, with an energy window for acceptable conformers (ewindow) of 5 kcal mol^{-1} above the ground state using the modified version of the MMFF94 force-field mentioned above, a maximum number of conformations per molecule (maxconfs) of 100 and an RMSD cutoff (rmsd) of 0.5Å. And then each conformer was optimized with HF/6-31G(d) method in Gaussian09[1]. Further optimization at the B3P86/6-31G(d) level led the dihedral angles to be got. The optimized conformers were taken for the ECD calculations, which were performed with Gaussian09 (B3P86/6-311++G(2d,p)). The solvent effects were taken into account by the polarizable-conductor calculation model (CPCM, methanol as the solvent). To gain ECD curves from the output files that were suited for comparison with the experimental data, the length representation of the oscillator and rotatory strengths was always selected and the spectra were overlain with Gaussian profiles that were in turn summed up to give, after Boltzmann weighting of the single spectra and all ECD spectra. These steps were performed with the software SpecDis[2].

Table 5 Conformers distribution of (2S, 3R, 4R)-**1** in solvated models calculations at the B3P86/6-31G (d)

conformers	Contribution %
1	12.37
2	12.67
3	12.67
4	38.73
5	23.56

Coordinates of computations ((2S, 3R, 4R)-**1)**

Conformer 1 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.760443	-1.184930	0.440374
2	6	0	3.565418	-1.812242	0.789381
3	6	0	4.780120	0.043424	-0.210831
4	6	0	2.345449	0.069225	-0.196174
5	6	0	2.383453	-1.170383	0.463063
6	6	0	3.579661	0.679921	-0.532649
7	6	0	1.074953	0.720294	-0.535024
8	6	0	-0.069048	-0.029999	-0.138091
9	6	0	0.080703	-1.214662	0.514692
10	6	0	-2.024641	1.547967	0.252534
11	6	0	-3.182560	-0.634744	-1.645146
12	6	0	-2.992173	-1.736028	-0.599359
13	6	0	-2.141868	-1.017984	0.449508
14	6	0	-1.532397	0.209570	-0.313991
15	6	0	-4.280496	-2.346819	-0.069580
16	6	0	-1.958603	2.958677	2.124210
17	8	0	1.028345	1.831550	-1.107954
18	8	0	-2.769030	2.304247	-0.325224
19	8	0	1.211574	-1.815286	0.829583
20	8	0	-1.020800	-1.840435	0.894028
21	8	0	-1.948986	0.078879	-1.657622
22	8	0	3.602757	1.861516	-1.157667
23	8	0	-1.544665	1.742838	1.482910
24	1	0	5.700402	-1.669787	0.685520
25	1	0	3.542625	-2.768199	1.299296
26	1	0	5.714906	0.524558	-0.477783
27	1	0	-3.354619	-1.019447	-2.652097
28	1	0	-4.010701	0.034847	-1.372067
29	1	0	-2.358040	-2.514329	-1.039739
30	1	0	-2.689846	-0.748033	1.353497
31	1	0	-4.916645	-1.584140	0.393305
32	1	0	-4.072589	-3.117227	0.679061
33	1	0	-4.849218	-2.813140	-0.880109
34	1	0	-1.481577	2.949670	3.102702
35	1	0	-3.045592	2.982342	2.225880
36	1	0	-1.627602	3.821711	1.543298
37	1	0	2.644462	2.126988	-1.282722

Conformer 2 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.898909	-0.996932	-0.239237
2	6	0	-3.754716	-1.749944	-0.498509
3	6	0	-4.825029	0.322757	0.191908
4	6	0	-2.394986	0.189574	0.124608
5	6	0	-2.527218	-1.139001	-0.310729
6	6	0	-3.579434	0.926481	0.375999
7	6	0	-1.078343	0.807219	0.317656
8	6	0	0.005816	-0.070372	0.029425
9	6	0	-0.233823	-1.338461	-0.404395
10	6	0	1.983256	1.274442	-0.725555
11	6	0	3.141339	-0.602512	1.526755
12	6	0	2.865103	-1.846410	0.677781
13	6	0	1.996117	-1.266116	-0.438773
14	6	0	1.487034	0.101361	0.128942
15	6	0	4.106001	-2.587024	0.203538
16	6	0	3.111140	3.317448	-0.771169
17	8	0	-0.948451	1.994321	0.691041
18	8	0	1.782299	1.331027	-1.920088
19	8	0	-1.407886	-1.911086	-0.583780
20	8	0	0.815649	-2.089060	-0.689000
21	8	0	1.939763	0.160819	1.467102
22	8	0	-3.512760	2.195989	0.789752
23	8	0	2.643138	2.186013	-0.021501
24	1	0	-5.873250	-1.454823	-0.379412
25	1	0	-3.804430	-2.777987	-0.837585
26	1	0	-5.720774	0.901443	0.390192
27	1	0	3.341964	-0.827607	2.575732
28	1	0	3.985204	-0.025108	1.119040
29	1	0	2.224388	-2.517833	1.261101
30	1	0	2.503197	-1.171645	-1.399858
31	1	0	4.747185	-1.935643	-0.400852
32	1	0	3.837163	-3.456836	-0.403335
33	1	0	4.694122	-2.942826	1.055299
34	1	0	3.623887	3.951591	-0.050161
35	1	0	2.267562	3.847064	-1.218064
36	1	0	3.796519	2.993929	-1.557225
37	1	0	-2.536853	2.417042	0.847455

Conformer 3 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.898910	-0.996931	-0.239237
2	6	0	-3.754716	-1.749944	-0.498508
3	6	0	-4.825029	0.322758	0.191908
4	6	0	-2.394986	0.189575	0.124607
5	6	0	-2.527219	-1.139000	-0.310729
6	6	0	-3.579434	0.926482	0.375998
7	6	0	-1.078343	0.807219	0.317655
8	6	0	0.005815	-0.070372	0.029423
9	6	0	-0.233824	-1.338461	-0.404395
10	6	0	1.983258	1.274441	-0.725555
11	6	0	3.141337	-0.602512	1.526756
12	6	0	2.865103	-1.846410	0.677781
13	6	0	1.996117	-1.266117	-0.438773
14	6	0	1.487034	0.101360	0.128942
15	6	0	4.106003	-2.587021	0.203537
16	6	0	3.111143	3.317446	-0.771167
17	8	0	-0.948451	1.994322	0.691039
18	8	0	1.782304	1.331026	-1.920089
19	8	0	-1.407887	-1.911087	-0.583780
20	8	0	0.815648	-2.089061	-0.688999
21	8	0	1.939761	0.160818	1.467102
22	8	0	-3.512760	2.195990	0.789751
23	8	0	2.643138	2.186012	-0.021500
24	1	0	-5.873251	-1.454823	-0.379411
25	1	0	-3.804430	-2.777987	-0.837584
26	1	0	-5.720774	0.901444	0.390192
27	1	0	3.341960	-0.827609	2.575734
28	1	0	3.985202	-0.025108	1.119044
29	1	0	2.224390	-2.517835	1.261100
30	1	0	2.503195	-1.171646	-1.399858
31	1	0	4.747185	-1.935638	-0.400853
32	1	0	3.837167	-3.456833	-0.403336
33	1	0	4.694125	-2.942822	1.055298
34	1	0	3.623896	3.951586	-0.050161
35	1	0	2.267566	3.847067	-1.218059
36	1	0	3.796518	2.993925	-1.557226
37	1	0	-2.536853	2.417043	0.847454

Conformer 4 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.914922	-0.812659	-0.267097
2	6	0	-3.806891	-1.607828	-0.555731
3	6	0	-4.779974	0.489978	0.199783
4	6	0	-2.358546	0.251933	0.110210
5	6	0	-2.552366	-1.056974	-0.361045
6	6	0	-3.507677	1.032605	0.391305
7	6	0	-1.014345	0.804858	0.311428
8	6	0	0.027933	-0.108480	-0.018691
9	6	0	-0.272077	-1.351364	-0.478718
10	6	0	2.049890	1.204149	-0.693629
11	6	0	2.255414	-1.370982	1.774474
12	6	0	2.829594	-2.013409	0.509650
13	6	0	1.964157	-1.363368	-0.561775
14	6	0	1.521832	-0.000309	0.083648
15	6	0	4.302696	-1.666498	0.305920
16	6	0	3.346988	3.142843	-0.666155
17	8	0	-0.829422	1.972120	0.722059
18	8	0	1.764193	1.383799	-1.858158
19	8	0	-1.470157	-1.870102	-0.663595
20	8	0	0.744988	-2.139401	-0.784077
21	8	0	2.012486	-0.012561	1.410622
22	8	0	-3.382311	2.285567	0.840531
23	8	0	2.841546	1.989951	0.024539
24	1	0	-5.909434	-1.223082	-0.412513
25	1	0	-3.904266	-2.622794	-0.922728
26	1	0	-5.647886	1.101818	0.420919
27	1	0	1.321677	-1.860082	2.085996
28	1	0	2.948345	-1.363990	2.618496
29	1	0	2.685432	-3.097754	0.500127
30	1	0	2.438560	-1.259848	-1.537862
31	1	0	4.458836	-0.583157	0.341953
32	1	0	4.666959	-2.035071	-0.658094
33	1	0	4.911002	-2.118860	1.094656
34	1	0	3.968899	3.664872	0.058824
35	1	0	2.521144	3.777559	-0.993248
36	1	0	3.937329	2.836993	-1.532181
37	1	0	-2.397423	2.461431	0.898838

Conformer 5 Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.786153	-0.992258	0.464367
2	6	0	3.625934	-1.658223	0.856435
3	6	0	4.740737	0.209533	-0.233311
4	6	0	2.307677	0.127459	-0.179781
5	6	0	2.411544	-1.082730	0.525575
6	6	0	3.508091	0.778575	-0.559980
7	6	0	1.004115	0.707303	-0.523708
8	6	0	-0.098961	-0.073286	-0.071916
9	6	0	0.115676	-1.226176	0.614427
10	6	0	-2.124350	1.445204	0.181136
11	6	0	-2.335968	-1.543092	-1.689064
12	6	0	-2.991450	-1.899092	-0.353241
13	6	0	-2.119997	-1.108763	0.613810
14	6	0	-1.578787	0.084944	-0.256149
15	6	0	-4.443276	-1.431057	-0.282562
16	6	0	-2.075347	3.038883	1.897690
17	8	0	0.899757	1.788662	-1.143950
18	8	0	-2.930965	2.097048	-0.437577
19	8	0	1.275656	-1.765439	0.934563
20	8	0	-0.953866	-1.890553	1.021204
21	8	0	-2.021381	-0.156312	-1.576438
22	8	0	3.468728	1.934094	-1.231049
23	8	0	-1.613053	1.789139	1.365052
24	1	0	5.750560	-1.425025	0.712105
25	1	0	3.653936	-2.593949	1.402356
26	1	0	5.648811	0.721031	-0.533893
27	1	0	-1.425399	-2.134639	-1.862078
28	1	0	-2.998902	-1.658307	-2.549221
29	1	0	-2.919319	-2.968326	-0.133200
30	1	0	-2.618530	-0.808033	1.535819
31	1	0	-4.522535	-0.365489	-0.522076
32	1	0	-4.863035	-1.593115	0.715248
33	1	0	-5.054469	-1.984028	-1.001922
34	1	0	-1.567642	3.153757	2.853809
35	1	0	-3.158146	3.014302	2.037111
36	1	0	-1.812678	3.855604	1.222571
37	1	0	2.497582	2.149762	-1.353427

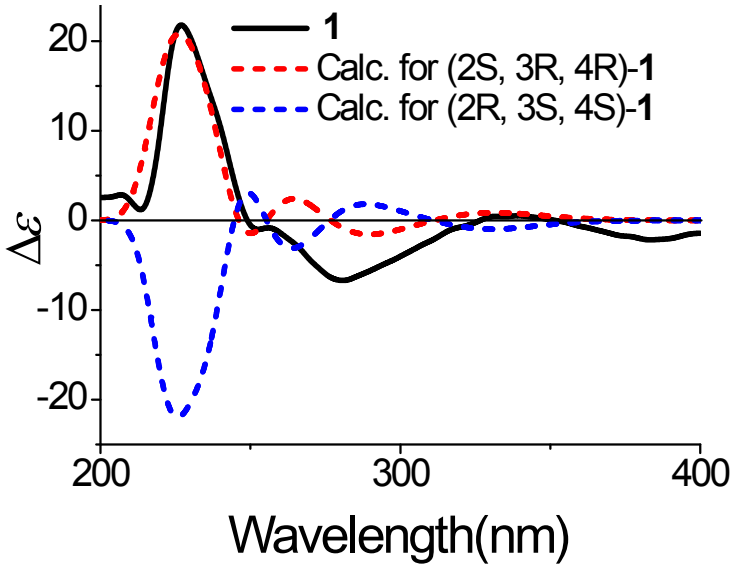


Figure 1 Experimental ECD spectra of **1** and calculated ECD spectra for (2S, 3R, 4R)-**1** and (2R, 3S, 4S)-**1** (UV correction = 17 nm, band width σ = 0.27 eV).

References

(1) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J.A.; Jr.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J. Gaussian, Inc., Wallingford CT, **2010**.

(2) Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G. Quantifying the Comparison of Calculated and Experimental Electronic Circular Dichroism Spectra, *Chirality* **2013**, *25*, 243–249.

7 Derivatization of sporormiellin B (2)

Compound **2** (0.5 mg) was stirred with $SOCl_2$ (10 μL) in $CDCl_3$ (500 μL) at 40 °C for 4 h. Then, the solvent was evaporated under N_2 to yield the mixture. Then the mixture and compound **1** were compared by HPLC with three eluting systems (Fig 2), which displayed that the peak of the major reaction product prepared from compound **2** was identical to the compound **1** isolated from fungal broth.

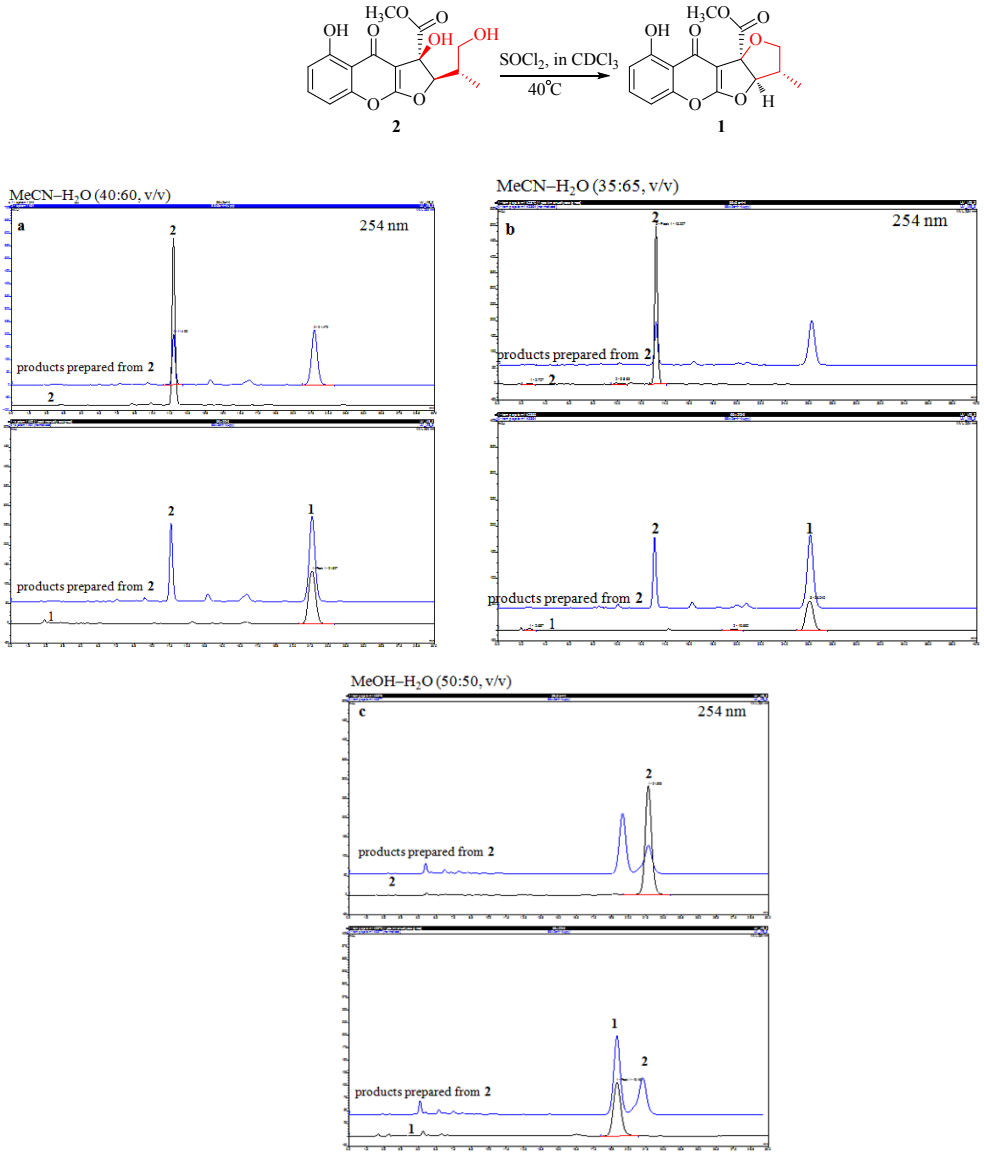


Figure 2 The products prepared from **2**, **2** and **1** were compared by HPLC with three eluting systems (**a**: MeCN–H_2O (40:60, v/v), at a flow rate of 1 mL/min; **b**: MeCN–H_2O (35:65, v/v), at a flow rate of 1 mL/min; **c**: MeOH–H_2O (50:50, v/v), at a flow rate of 1 mL/min)

8 Derivatization of sporormiellin C (3)

Compound **3** (0.6 mg) was stirred with 98% H_2SO_4 (2 μL) in MeOH (1 mL) at 40 °C for 4 h. After neutralization with ammonia, the solvent was evaporated under reduced pressure to yield the mixture. Then the mixture and compound **2** were compared by HPLC with three eluting systems (Fig 3), which displayed that the peak of the major product prepared from compound **3** was identical to the compound **2** isolated from fungal broth.

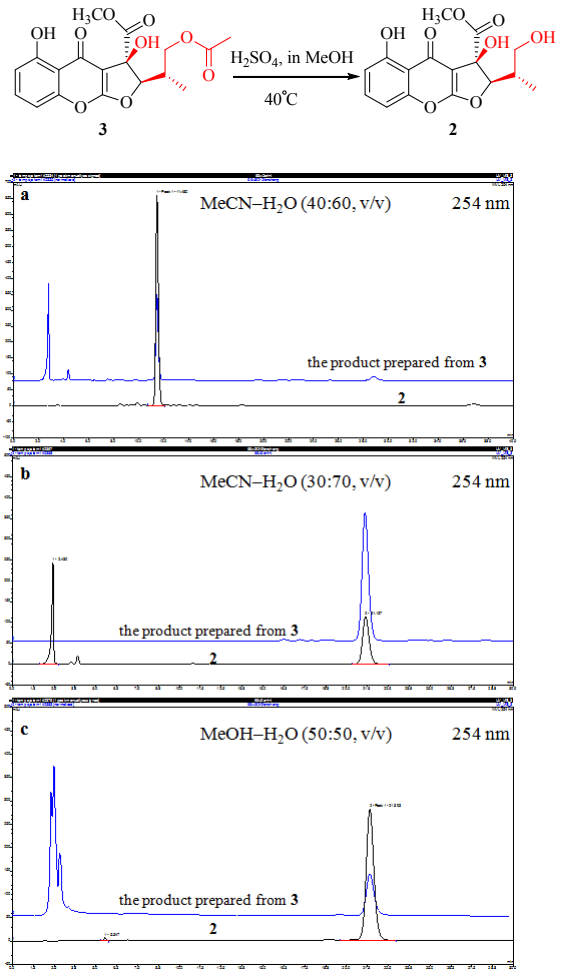
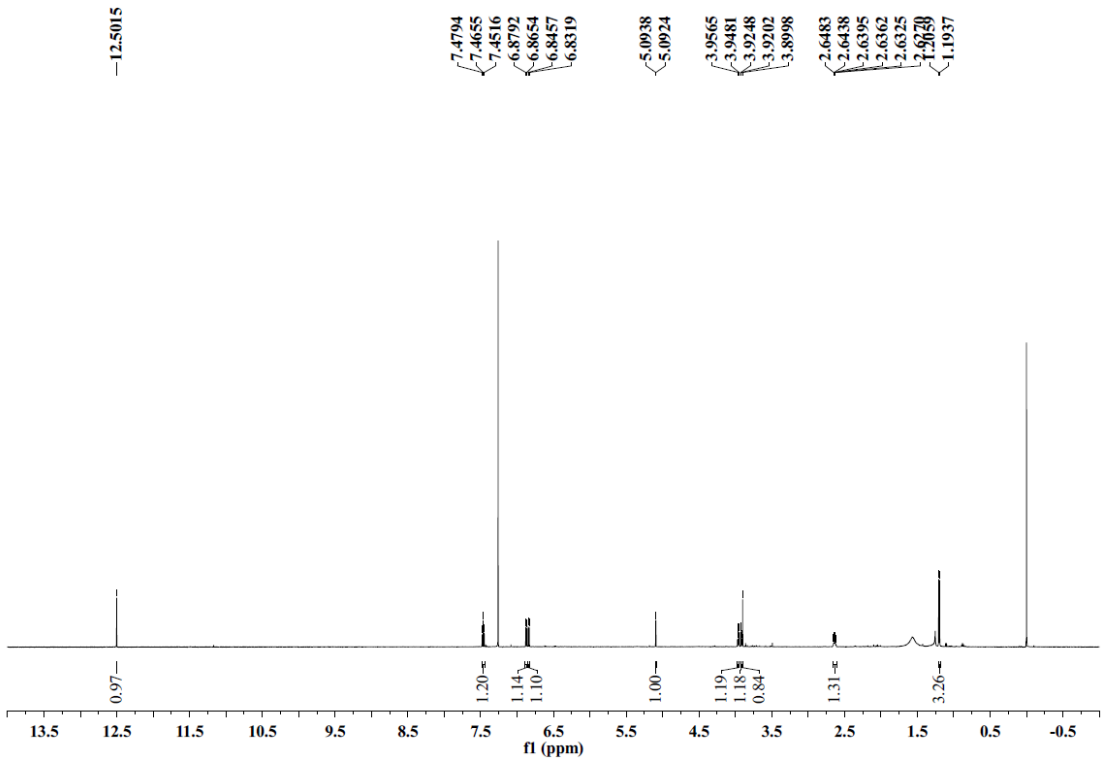
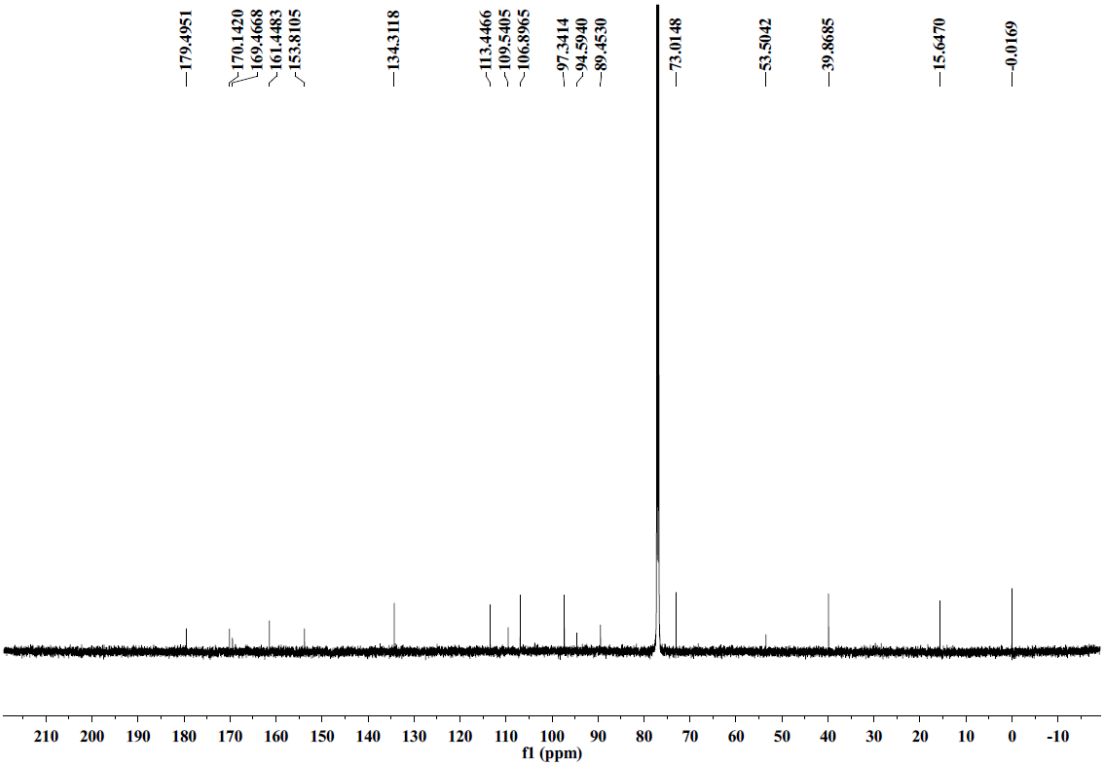


Figure 3 The products prepared from **3** and **2** were compared by HPLC with three eluting systems (**a**: MeCN–H_2O (40:60, v/v), at a flow rate of 1 mL/min; **b**: MeCN–H_2O (30:70, v/v), at a flow rate of 1 mL/min; **c**: MeOH–H_2O (50:50, v/v), at a flow rate of 1 mL/min)

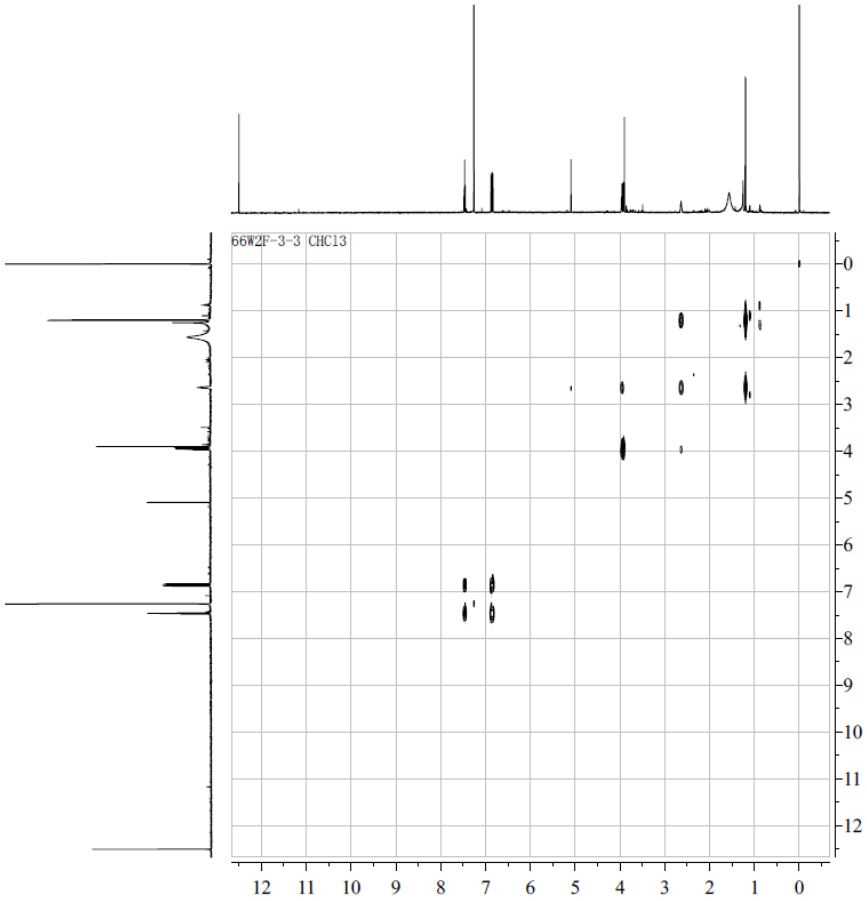
9 The 1D and 2D NMR spectra of sporormiellin A (1)



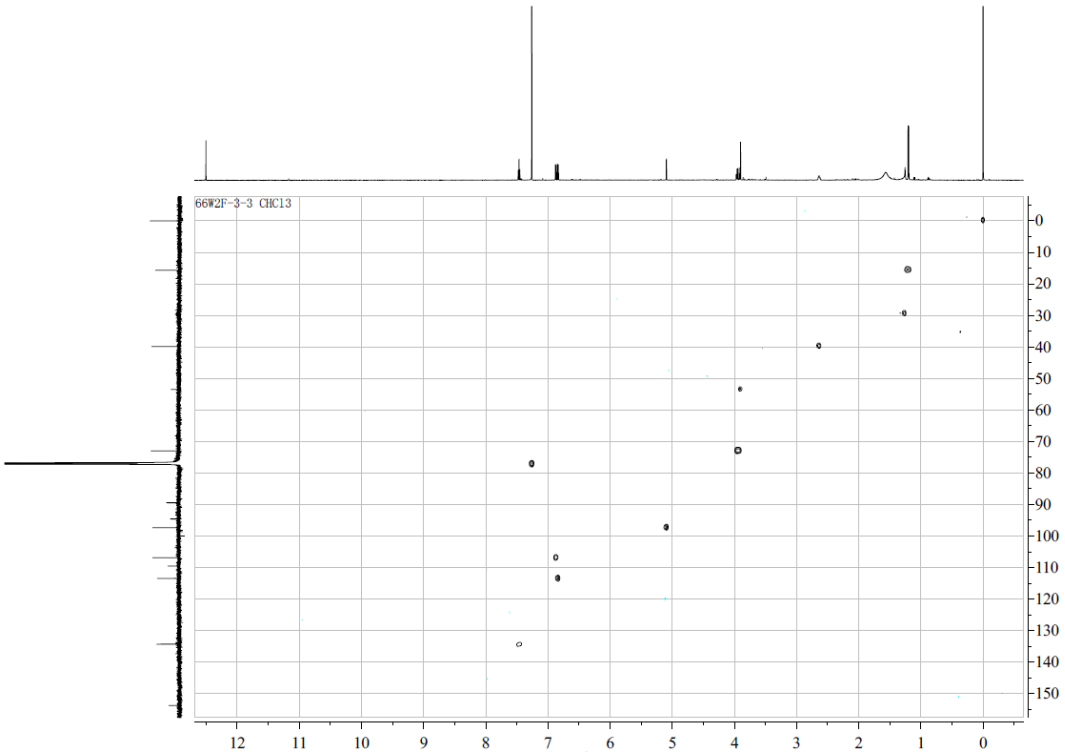
^{1}H NMR spectrum for sporormiellin A (**1**) (600 MHz, in $CDCl_3$)



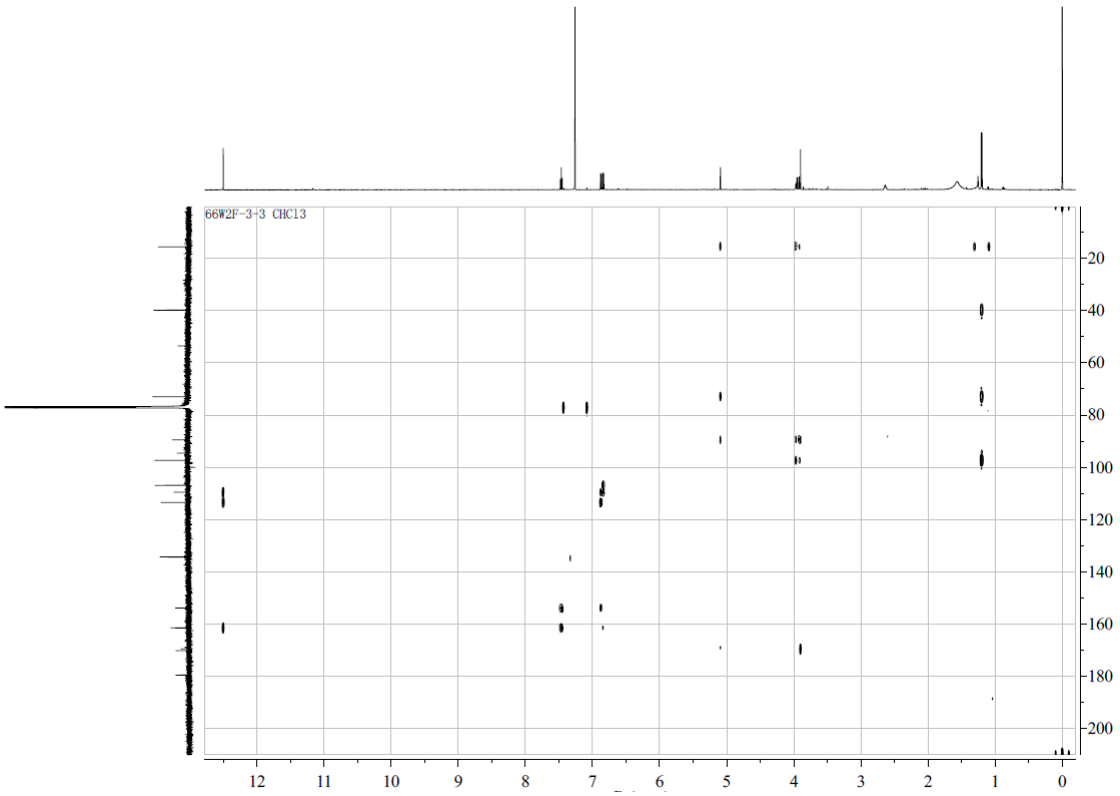
^{13}C NMR spectrum for sporormiellin A (**1**) (150 MHz, in $CDCl_3$)



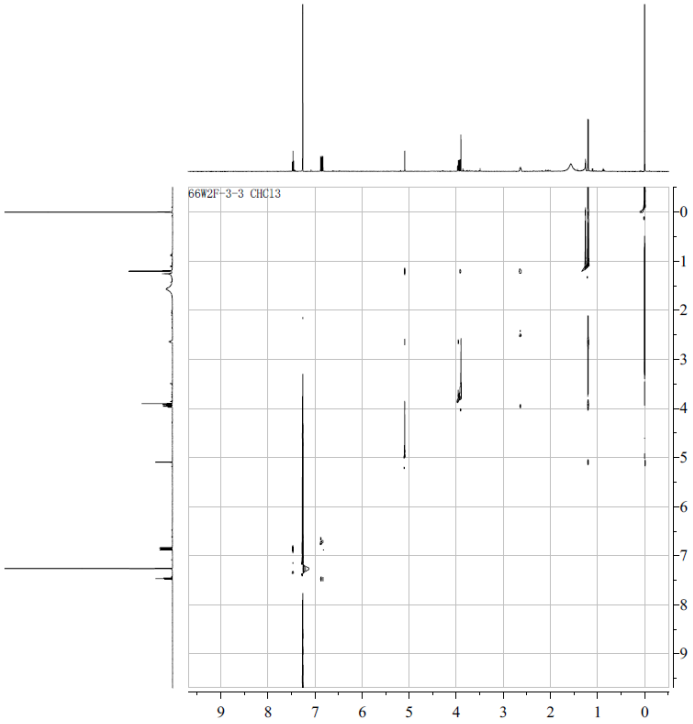
^{1}H-^{1}H COSY spectrum for sporormiellin A (**1**) ($CDCl_3$)



HSQC spectrum for sporormiellin A (**1**) ($CDCl_3$)

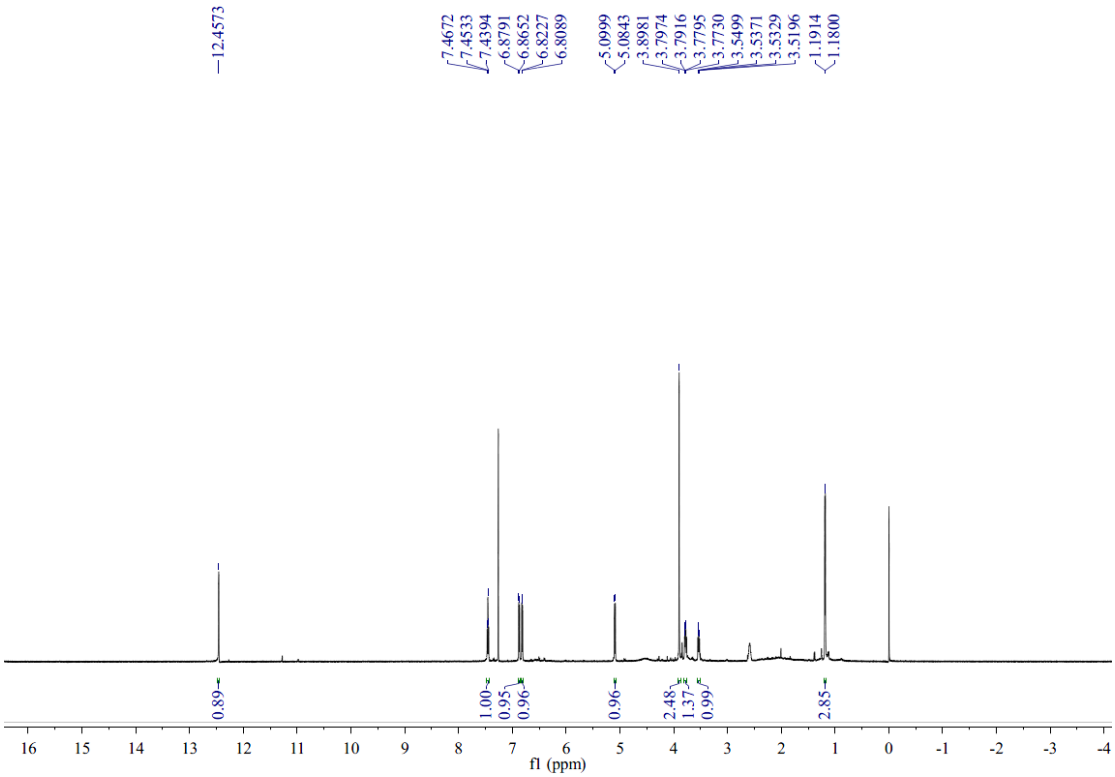


HMBC spectrum for sporormiellin A (**1**) ($CDCl_3$)

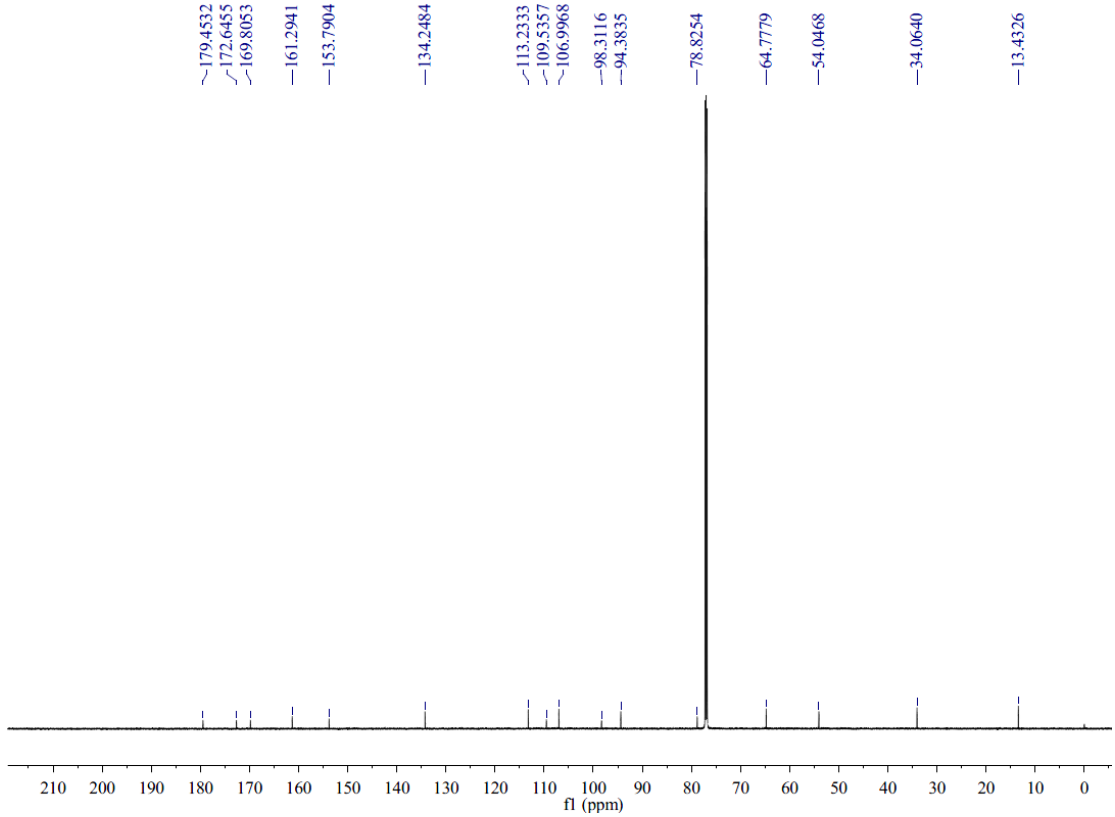


ROESY spectrum for sporormiellin A (**1**) ($CDCl_3$)

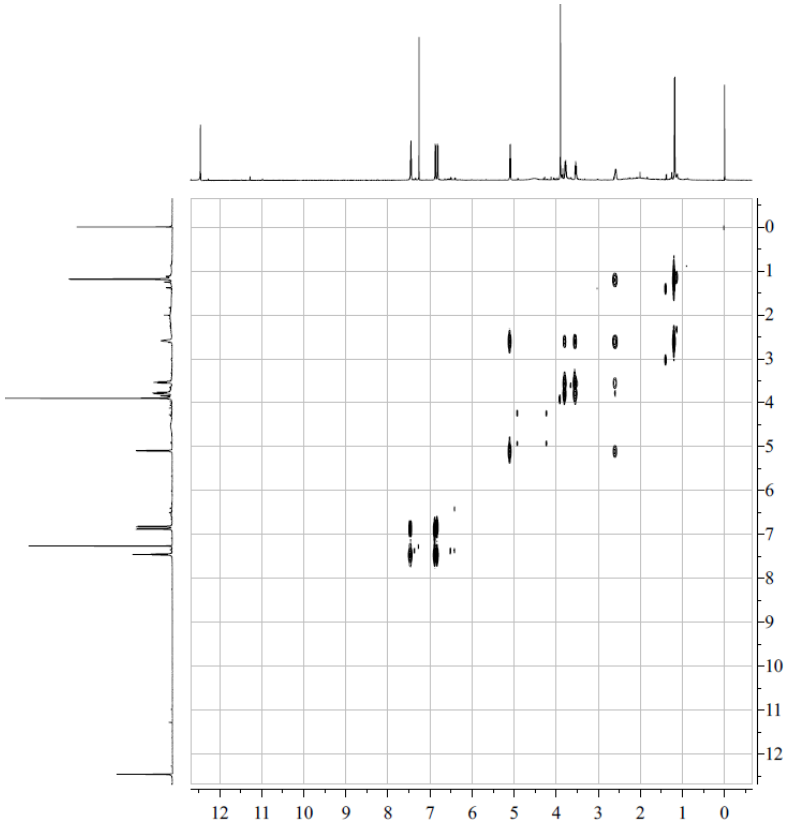
10 The 1D and 2D NMR spectra of sporormiellin B (2)



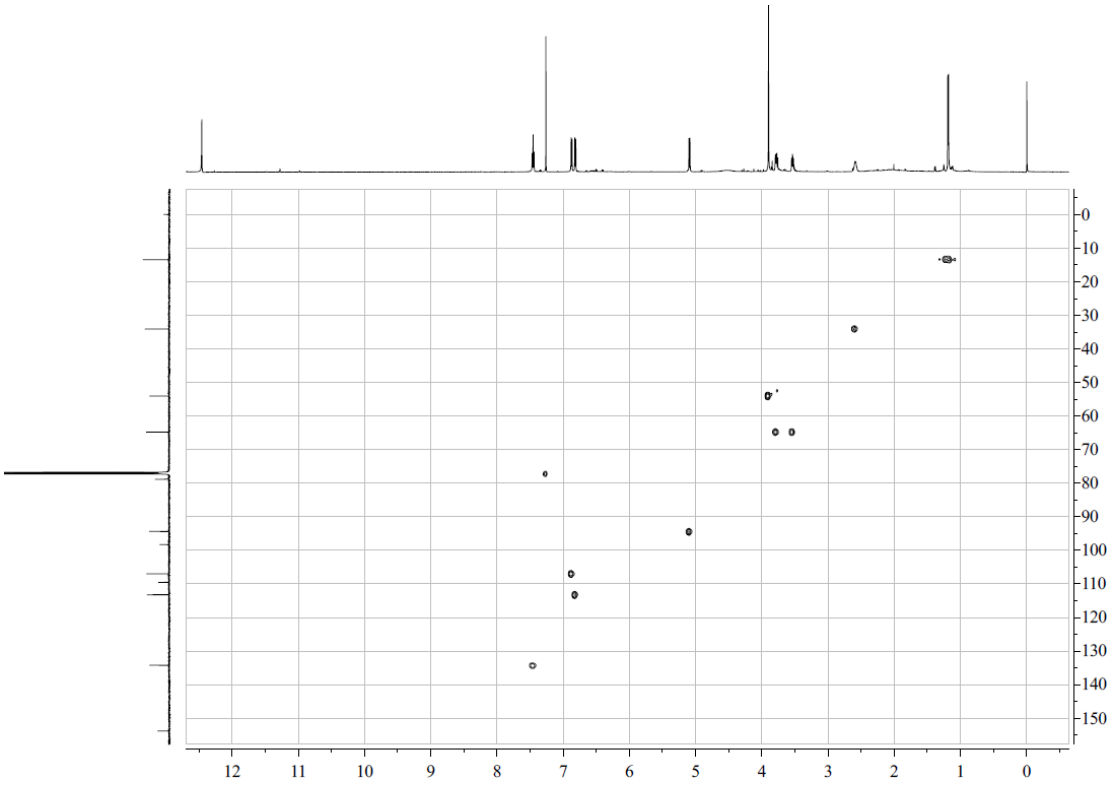
^{1}H NMR spectrum for sporormiellin B (**2**) (400 MHz, in $CDCl_3$)



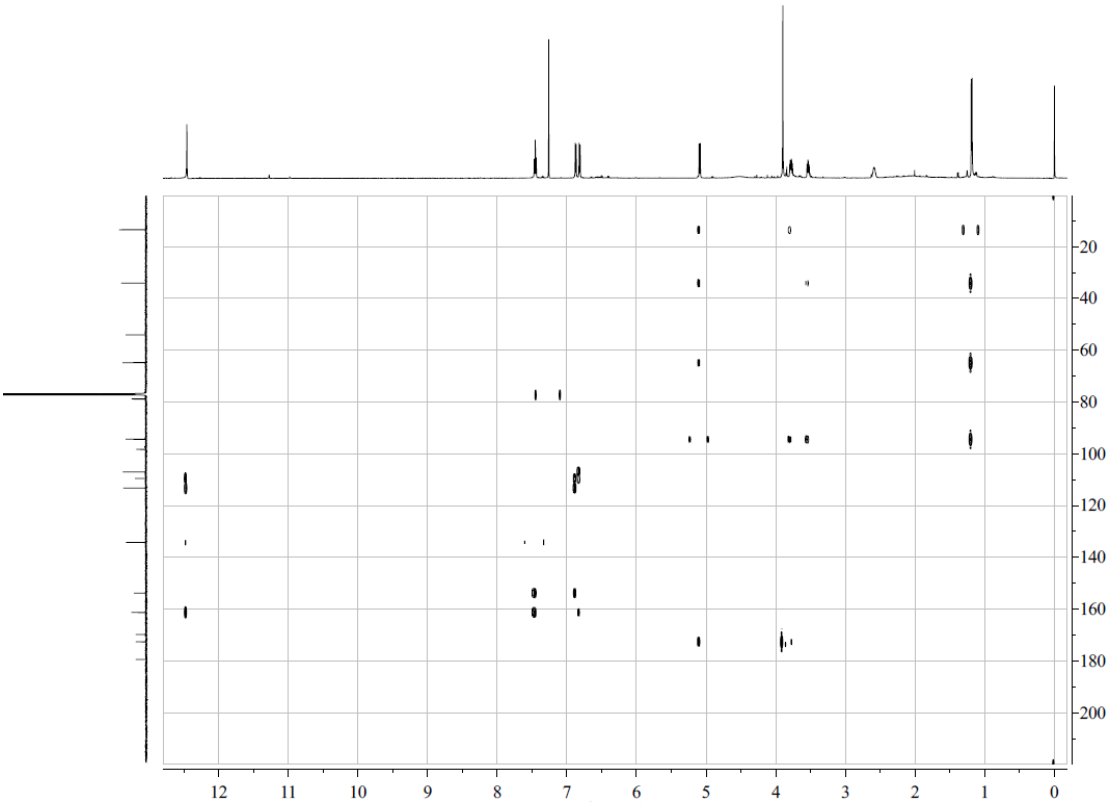
^{13}C NMR spectrum for sporormiellin B (**2**) (100 MHz, in $CDCl_3$)



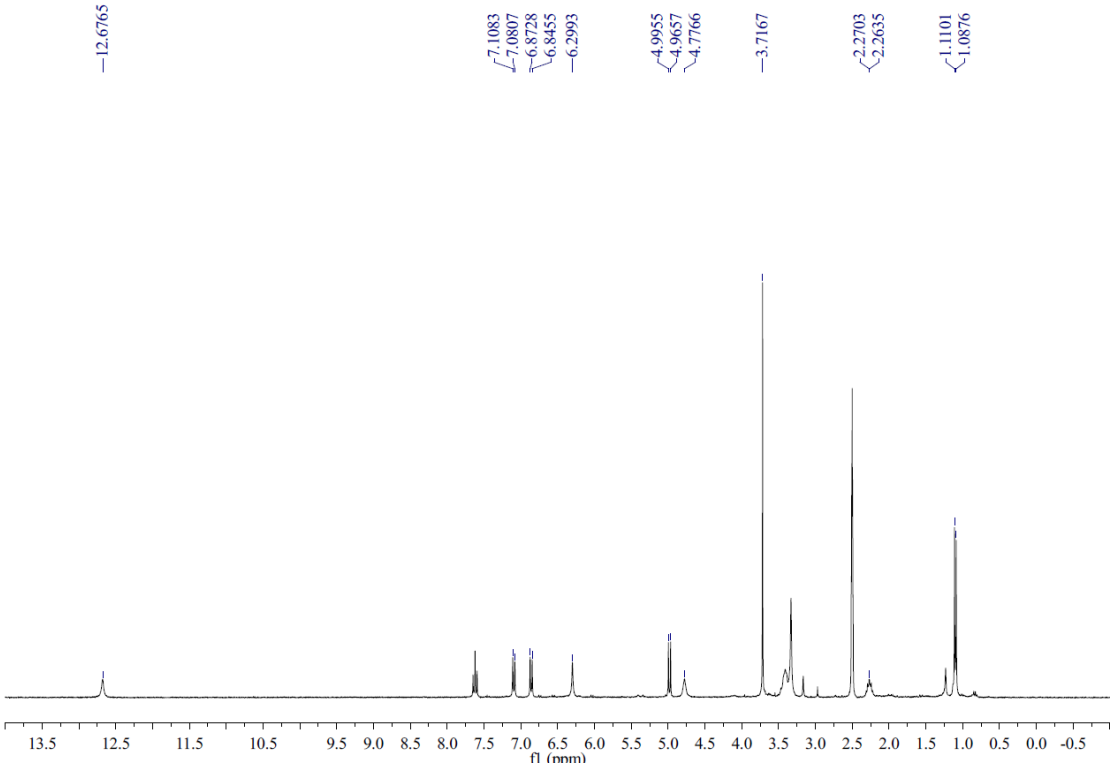
^{1}H-^{1}H COSY spectrum for sporormiellin B (**2**) (in $CDCl_3$)



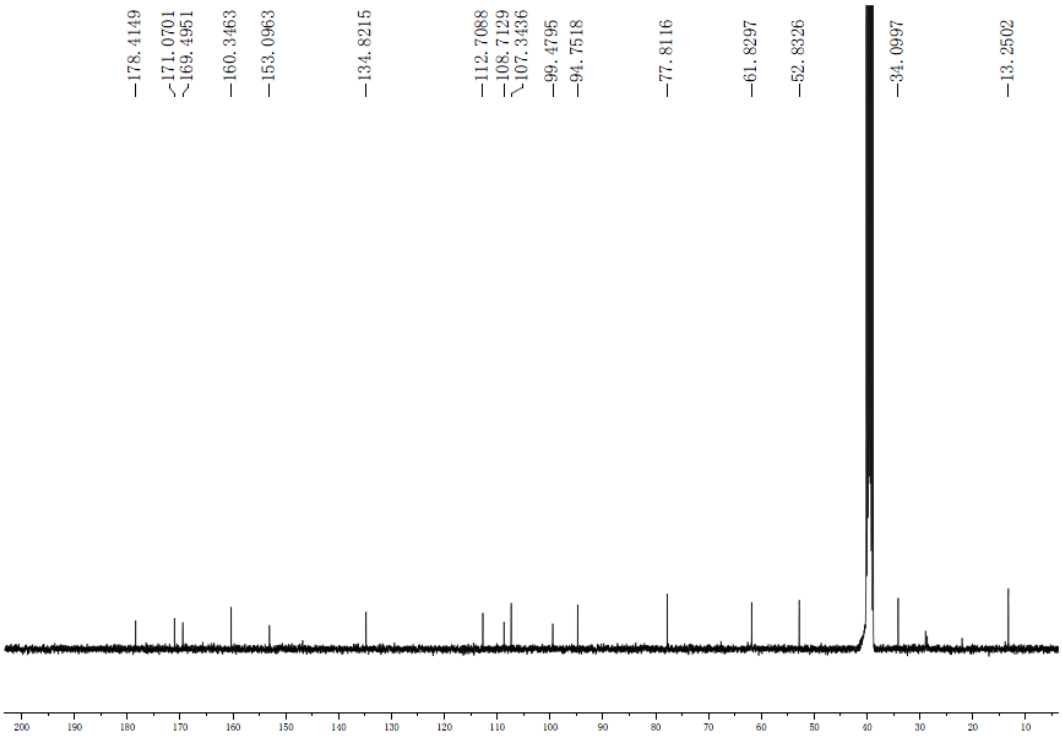
HSQC spectrum for sporormiellin B (**2**) (in $CDCl_3$)



HMBC spectrum for sporormiellin B (**2**) (in $CDCl_3$)

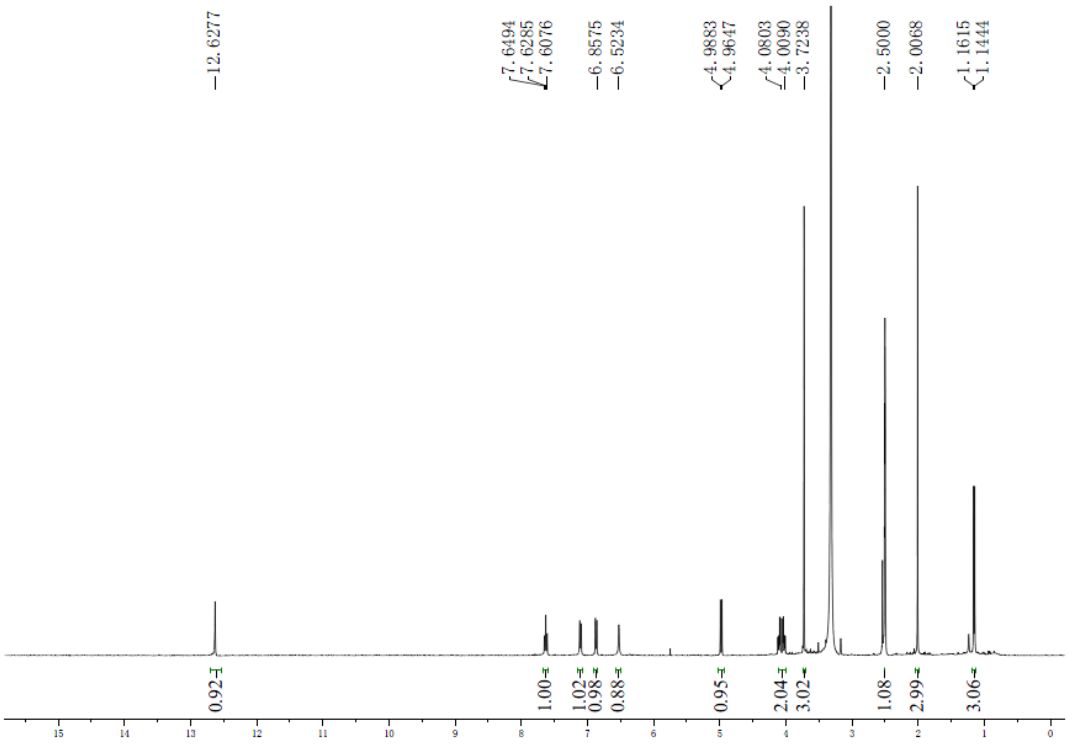


^{1}H NMR spectrum for sporormiellin B (**2**) (400 MHz, in DMSO-d_6)

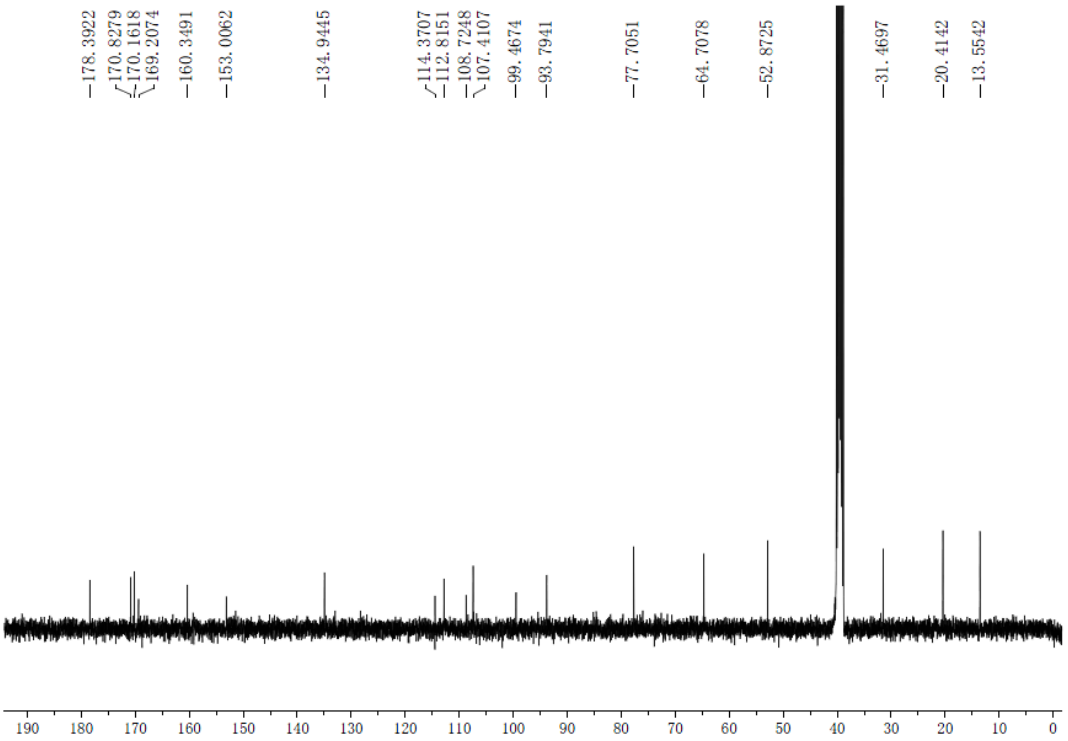


^{13}C NMR spectrum for sporormiellin B (**2**) (100 MHz, in DMSO-d_6)

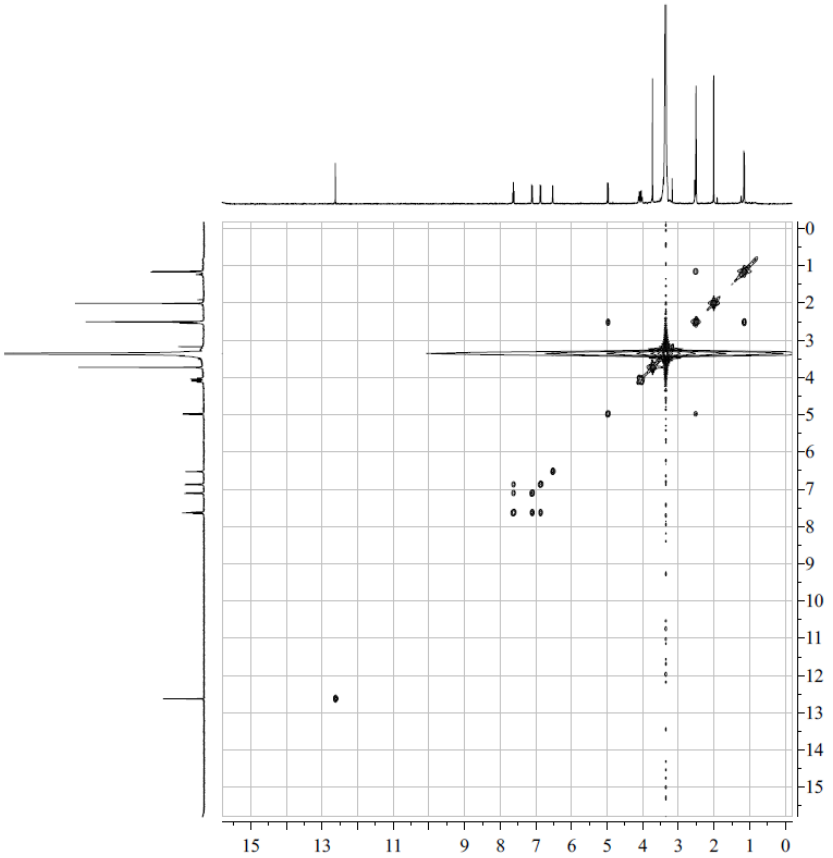
11 The 1D and 2D NMR spectra of sporormiellin C (3)



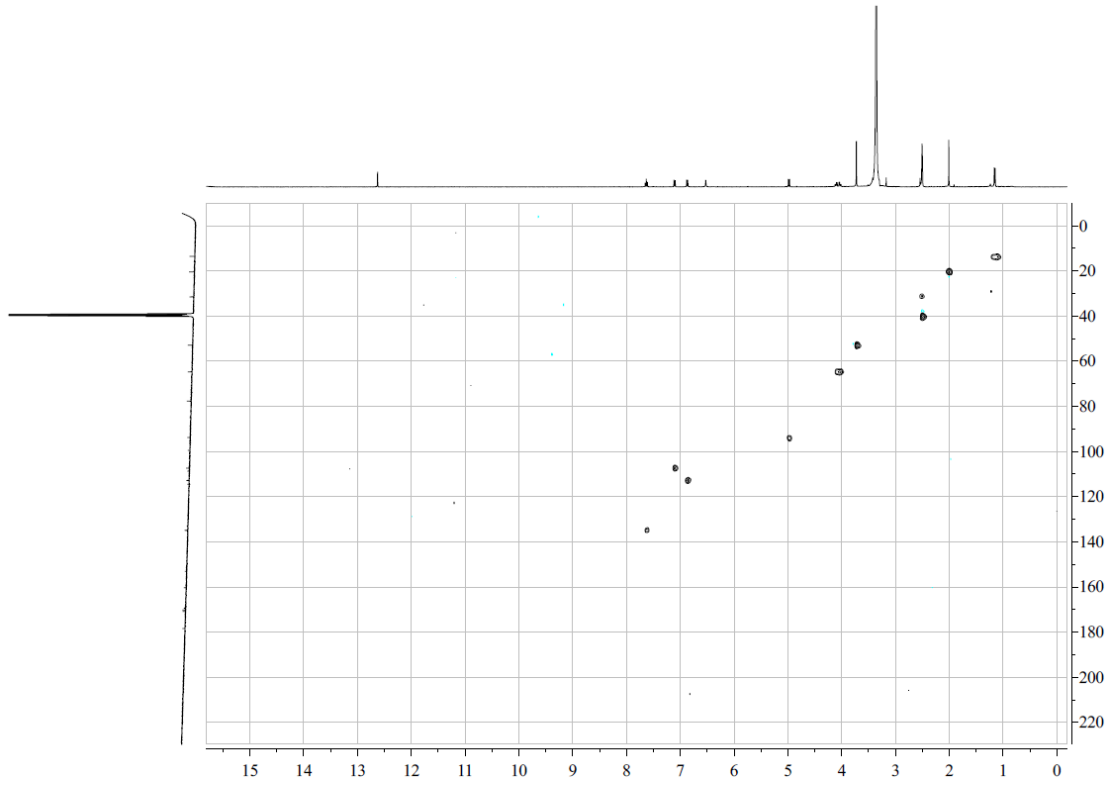
^{1}H NMR spectrum for sporormiellin C (**3**) (400 MHz, in DMSO-d_6)



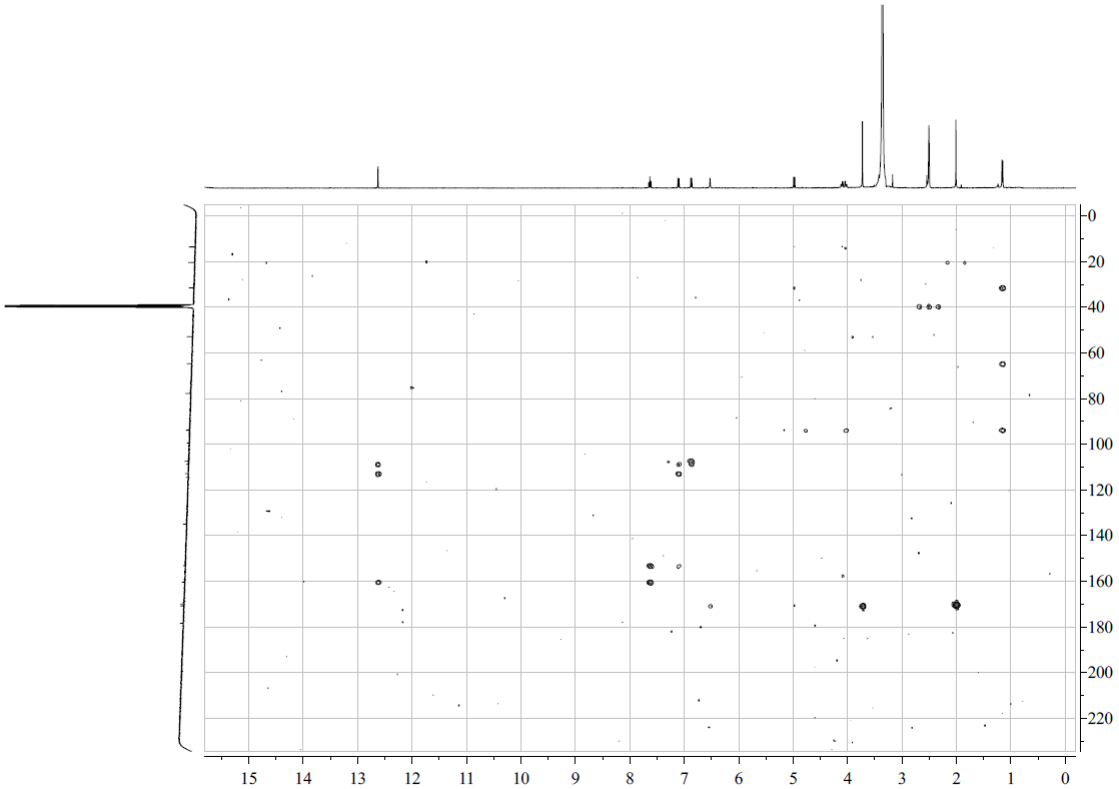
^{13}C NMR spectrum for sporormiellin C (**3**) (100 MHz, in DMSO-d_6)



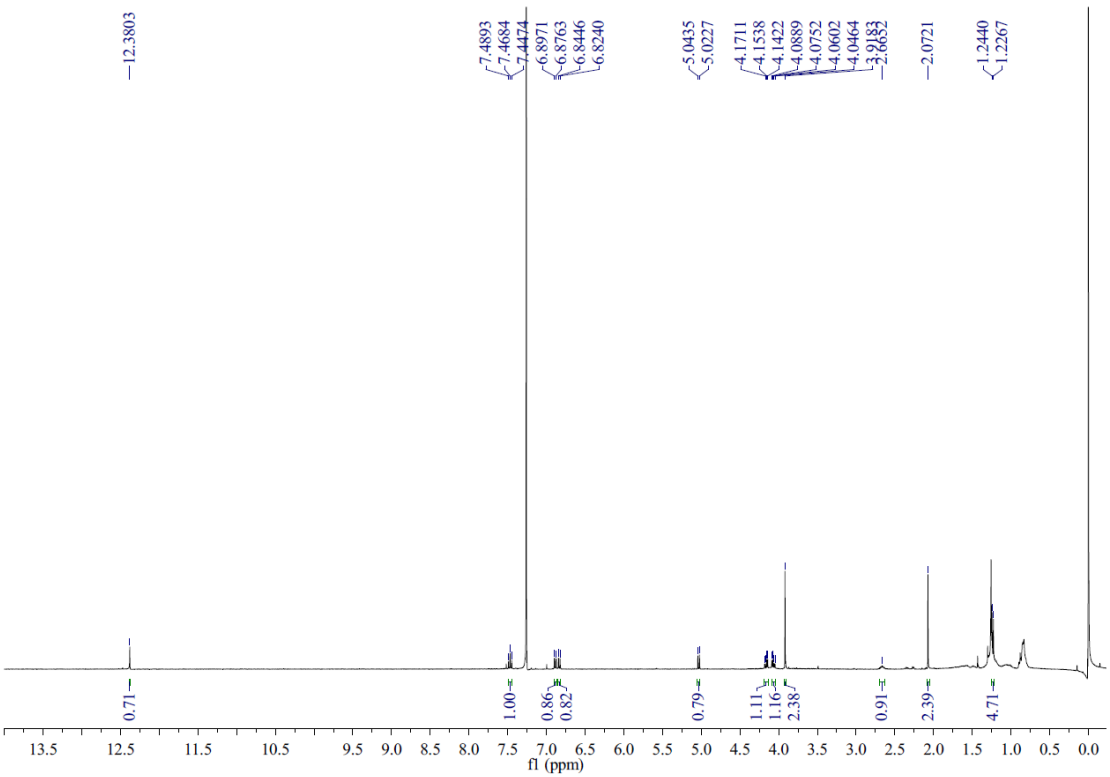
^{1}H-^{1}H COSY spectrum for sporormiellin C (**3**) (in DMSO-d_6)



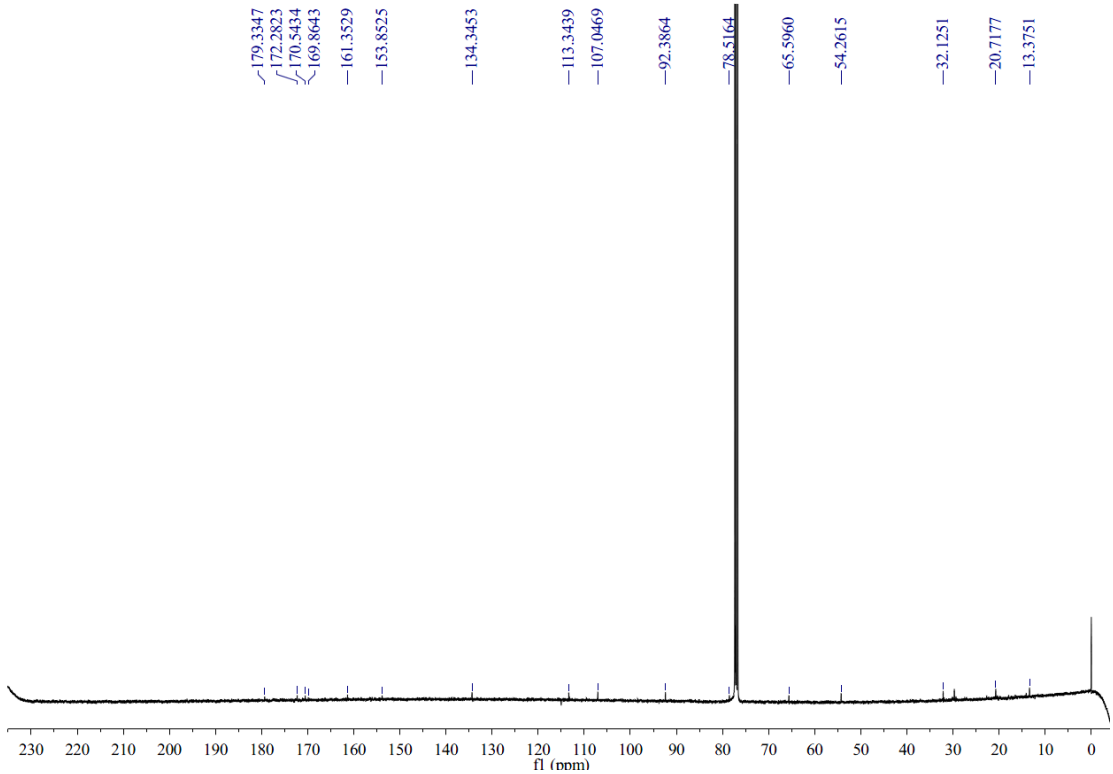
HSQC spectrum for sporormiellin C (**3**) (in DMSO-d_6)



HMBC spectrum for sporormiellin C (**3**) (in DMSO-d_6)

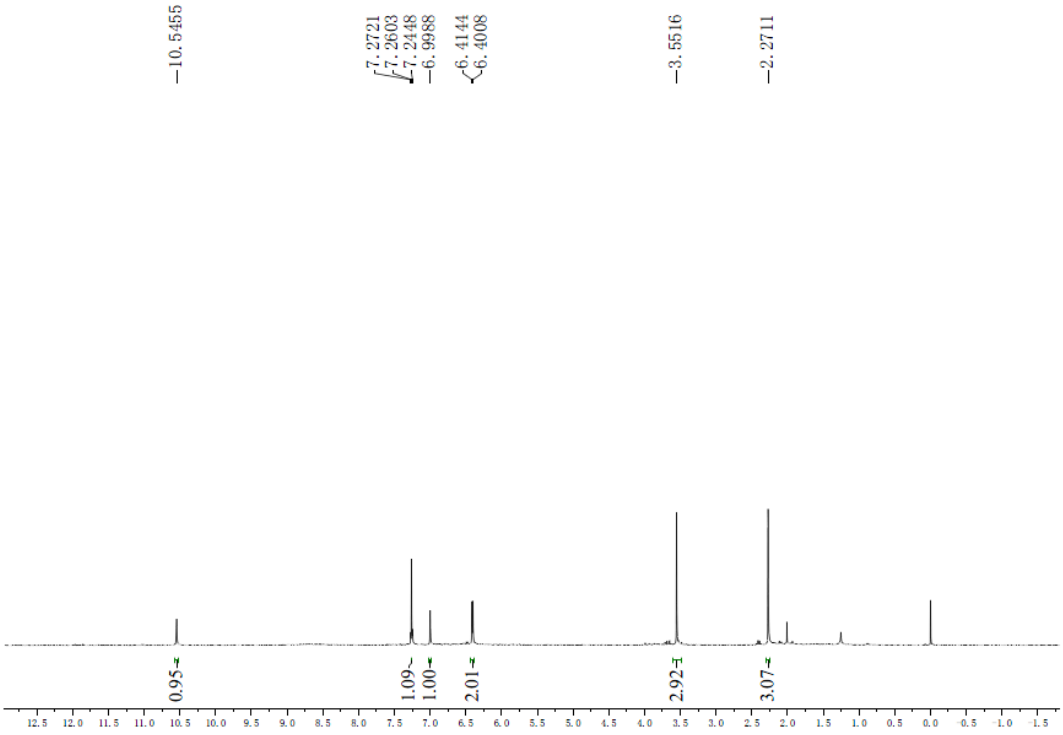


^{1}H NMR spectrum for sporormiellin C (**3**) (400 MHz, in $CDCl_3$)

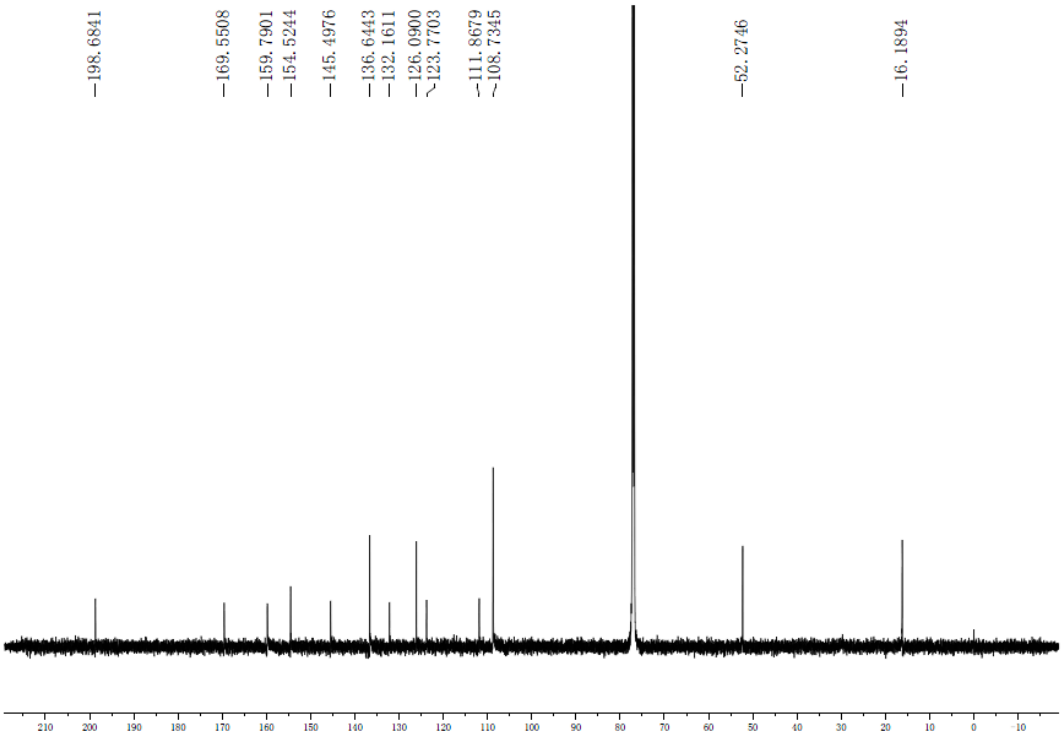


^{13}C NMR spectrum for sporormiellin C (**3**) (100 MHz, in $CDCl_3$)

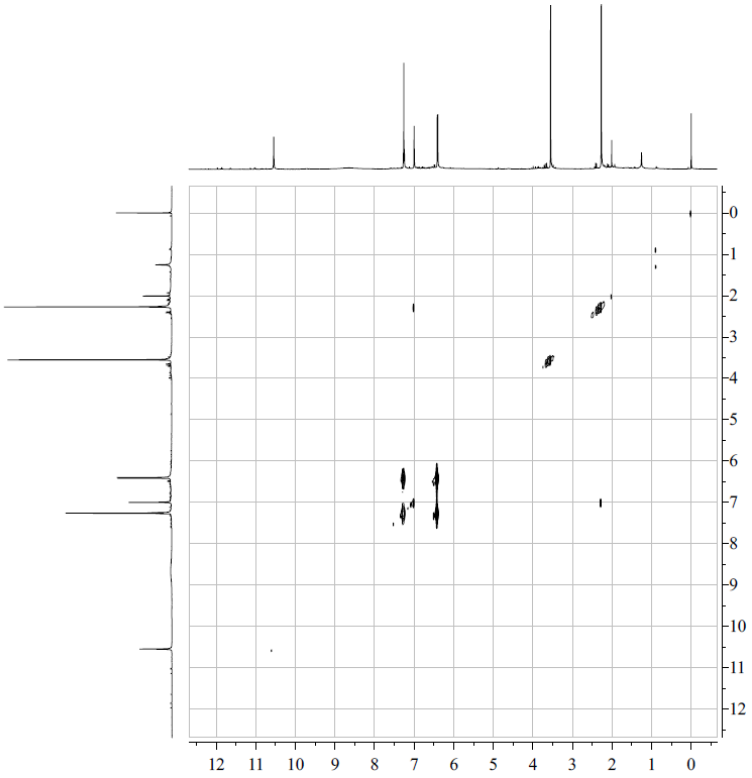
12 The 1D and 2D NMR spectra of sporormiellone A (4)



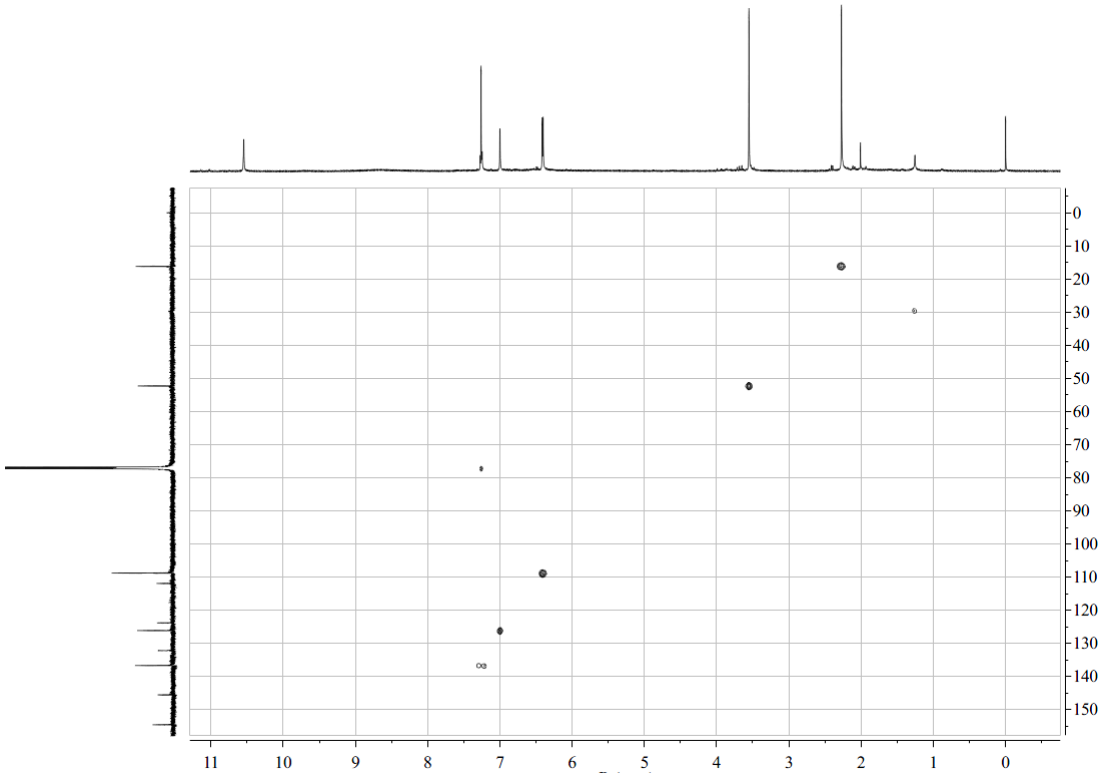
^{1}H NMR spectrum for sporormiellone A (**4**) (600 MHz, in $CDCl_3$)



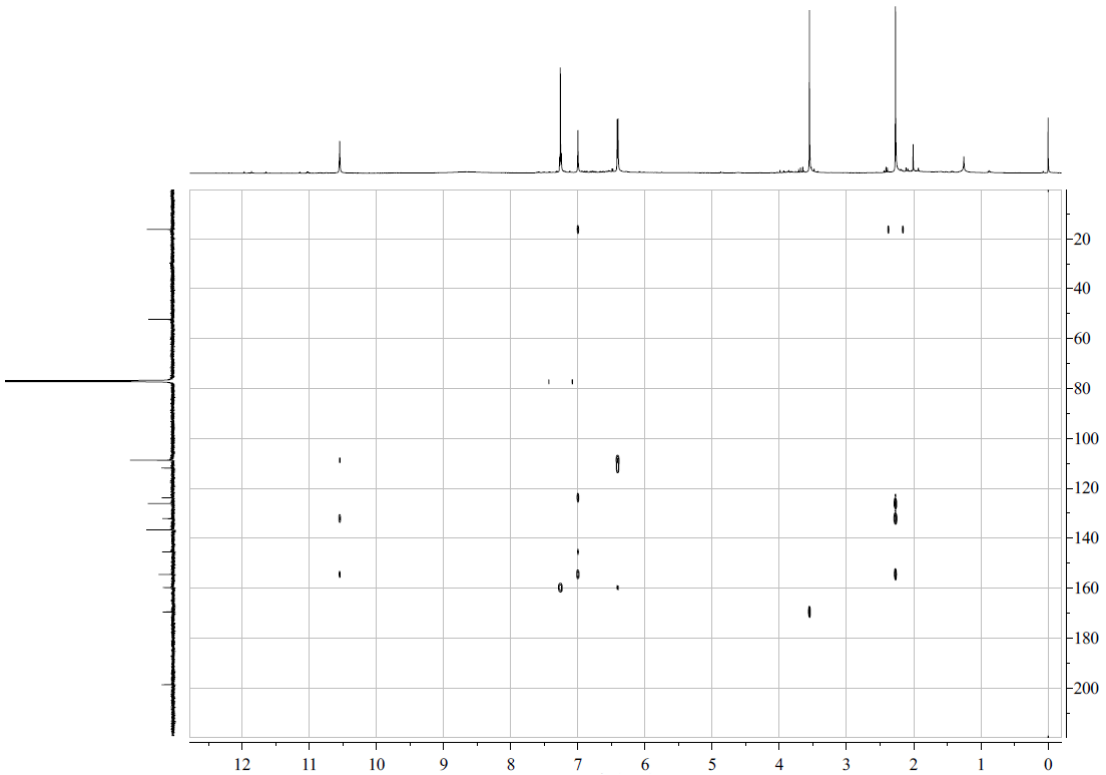
^{13}C NMR spectrum for sporormiellone A (**4**) (150 MHz, in $CDCl_3$)



^{1}H-^{1}H COSY spectrum for sporormiellone A (**4**) (in $CDCl_3$)

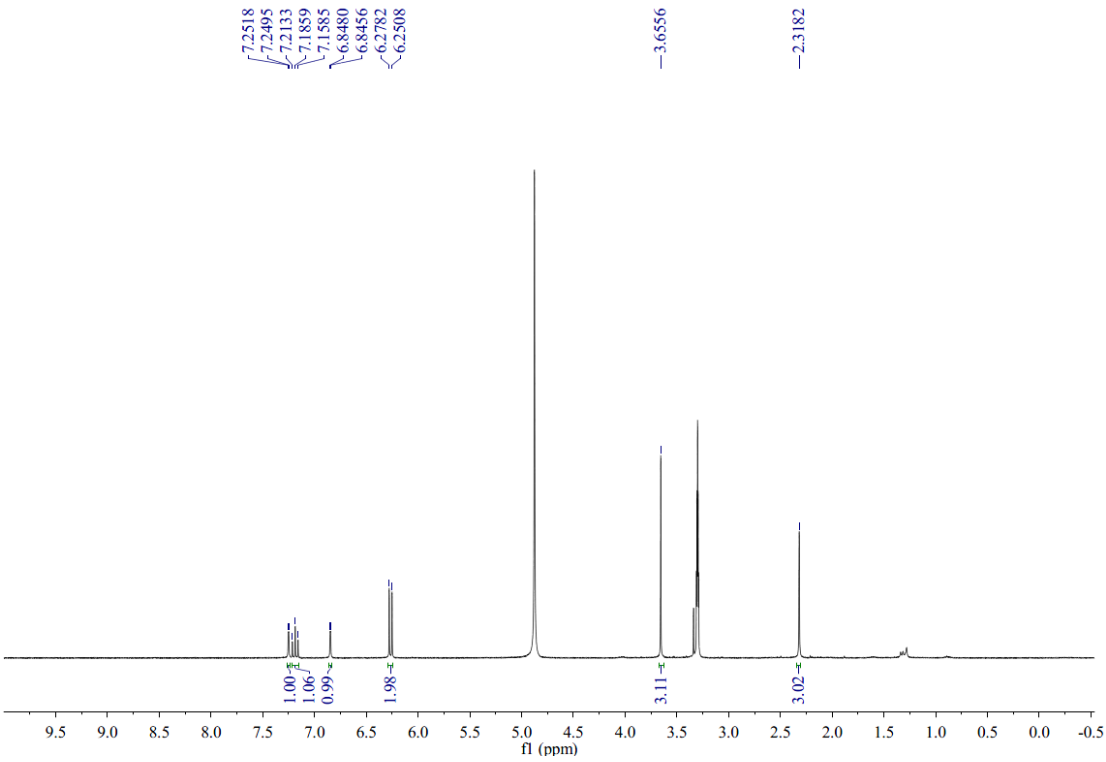


HSQC spectrum for sporormiellone A (**4**) (in $CDCl_3$)

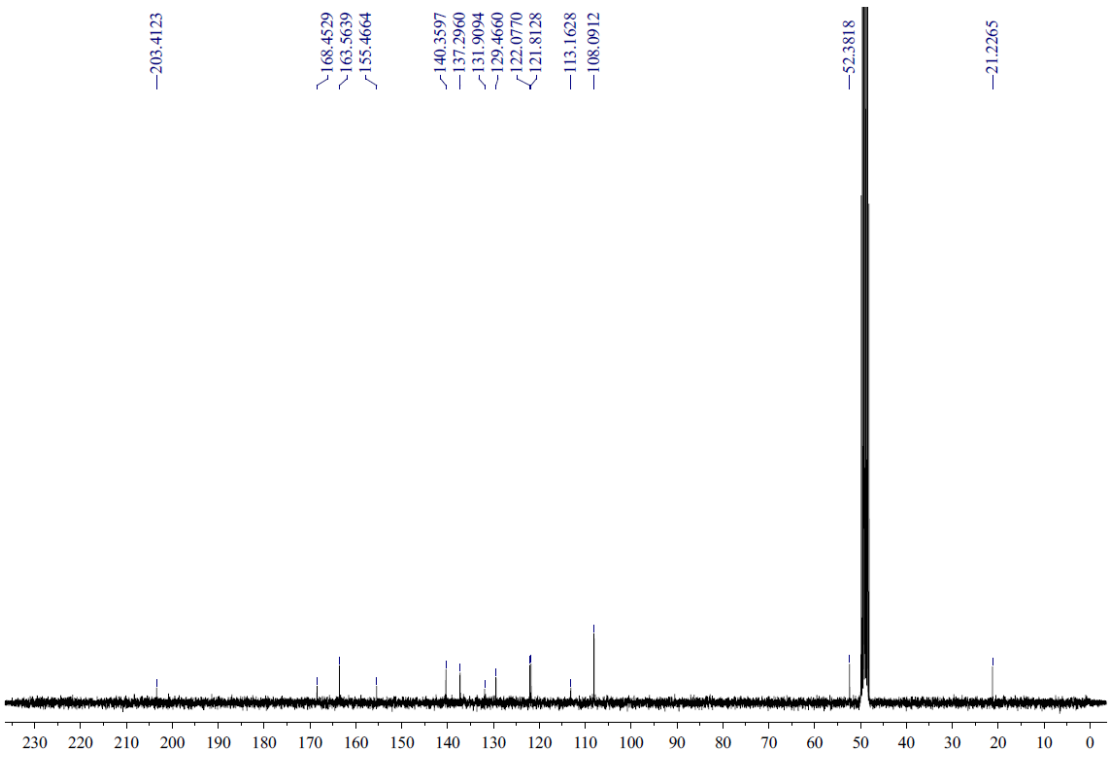


HMBC spectrum for sporormiellone A (**4**) (in $CDCl_3$)

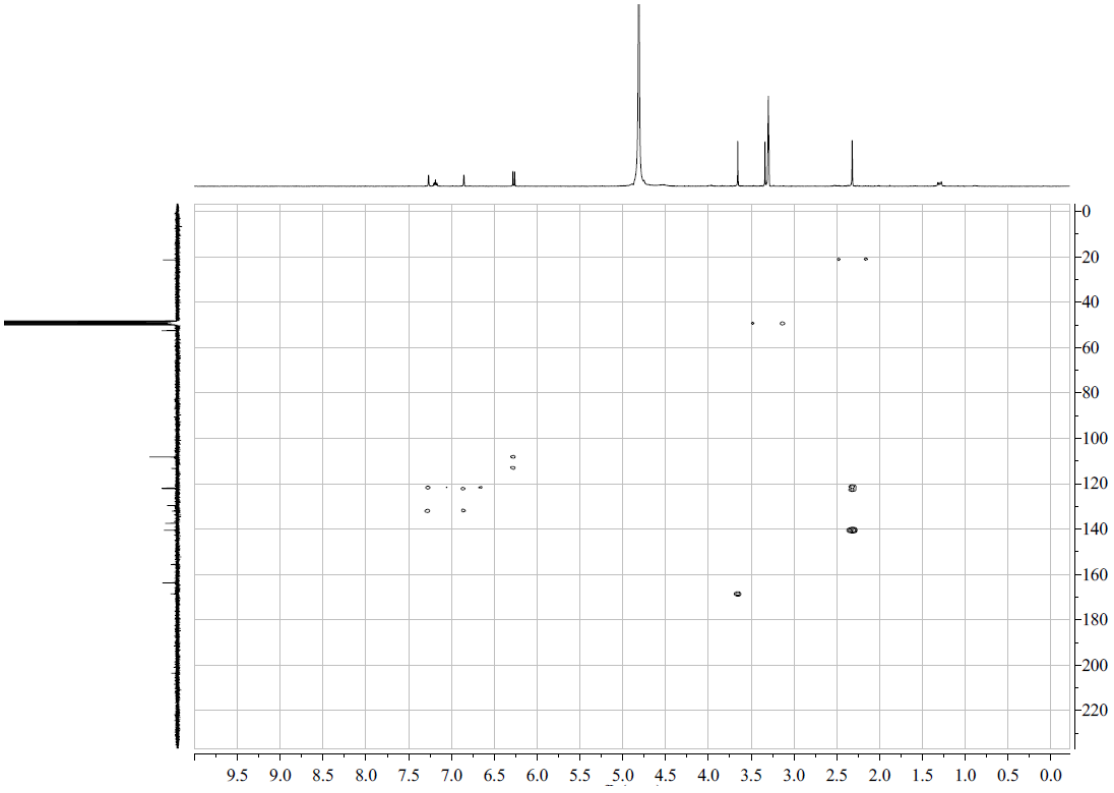
13 The 1D and 2D NMR spectra of sporormiellone B (5)



^{1}H NMR spectrum for sporormiellone B (**5**) (300 MHz, in CD_3OD)



^{13}C NMR spectrum for sporormiellone B (**5**) (75 MHz, in CD_3OD)



HMBC spectrum for sporormiellone B (**5**) (in CD_3OD)