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[d] Key Laboratory of Plant Resources Conservation and Sustainable Utilization, South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China

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List of supporting information **Page**

Table S1. ^{1}H and ^{13}C NMR Data for **2** and **3** (500, 125 MHz, CD_3OD, TMS, δ ppm).

No.	**2**		**3**	
	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
2	175.3, C		182.5, C	
3	56.8, C		57.2, C	
4	127.2, CH	7.30, d (7.8)	129.4, CH	7.14, d (7.6)
5	123.5, CH	7.07, t (7.5)	122.1, CH	6.94, t (7.5)
6	130.0, CH	7.32, t (7.5)	130.0, CH	7.01, t (7.5)
7	108.6, CH	7.04, d (7.8)	110.4, CH	6.44, d (7.6)
8	144.7, C		144.5, C	
9	126.4, C		128.4, C	
10	37.6, CH_2	2.74, dd (14.5, 2.0);	34.9, CH_2	2.80, dd (14.9, 1.7);
		2.49, dd (14.5, 9.0)		2.65, dd (14.9, 7.2)
11	54.5, CH	3.52, m	55.1, CH	4.20, dd (7.2, 1.7)
12				
13	161.8, C		160.4, C	
14	124.8, C		128.1, C	
15				
16	166.9, C		168.0, C	
17	107.6, CH	6.57, s	104.6, CH	5.70, s
18	138.0, C		129.8, C	
20	137.3, CH	7.72, s	134.3, CH	8.75, s
22	120.1, CH	7.30, s	121.7, CH	7.64, s
23	43.7, C		43.5, C	
24	143.9, CH	6.02, dd (17.4, 10.9)	144.1, CH	6.00, dd (17.4, 10.9)
25	114.9, CH_2	5.08, d (10.9);	114.6, CH_2	5.06, d (10.9);
		4.99, d (17.4)		4.97, d (17.4)
26	22.6, CH_3	1.08, s	22.3, CH_3	1.06, s
27	22.2, CH_3	0.99, s	21.9, CH_3	0.94, s

Table S2. Relative and free energies[a] and equilibrium populations[b] of low-energy conformers of **1** and **3** in MeOH.

conformer	ΔE	ΔG	P (%)
Compound **1**			
(3*R*,10*S*)-**1a**	0.19	0.00	84.4
(3*R*,10*S*)-**1b**	1.26	1.38	8.2
(3*R*,10*S*)-**1c**	2.22	1.77	4.2
(3*R*,10*S*)-**1d**	0.0	1.97	3.0

(3*R*,10*S*)-**1e** [c]	2.70	3.49	0.2
Compound **3**			
(3*R*,10*S*)-**3a**	0.00	0.00	46.5
(3*R*,10*S*)-**3b**	0.71	0.01	46.0
(3*R*,10*S*)-**3c**	1.04	1.42	4.2
(3*R*,10*S*)-**3d**	2.10	1.97	1.7
(3*R*,10*S*)-**3e** [c]	2.55	2.18	1.2
(3*R*,10*S*)-**3f** [c]	2.88	2.96	0.3

[a] At the B3LYP/def2-TZVP level, in kcal/mol. [b] From ΔG values at 298.15 K. [c] Conformer not used for ECD/TDDFT calculations.

Figure S1. Circular dichroism spectra of **1**–**3**.

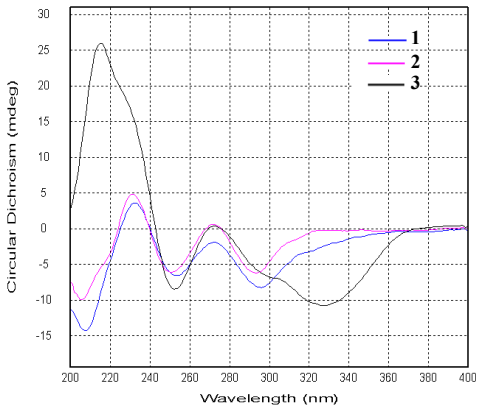
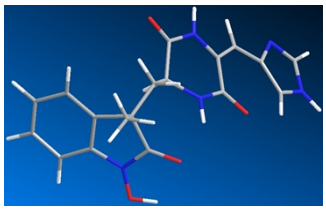
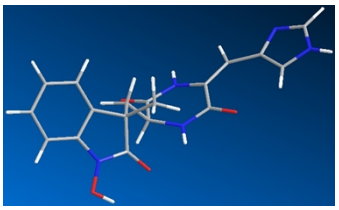


Figure S2. Conformations of low-energy conformers of **1** and **3**.



1a



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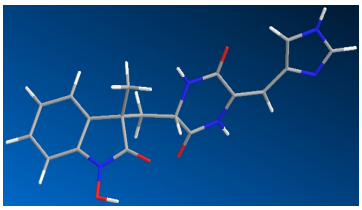

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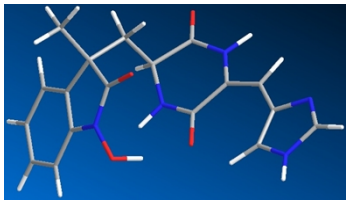

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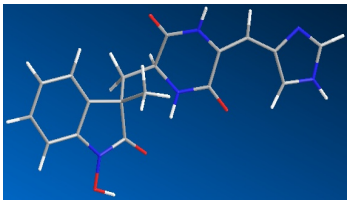

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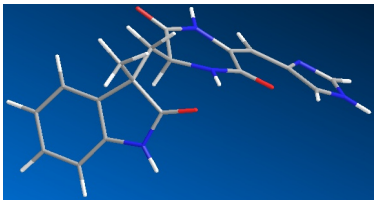

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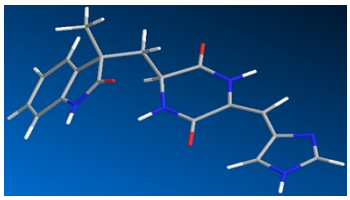

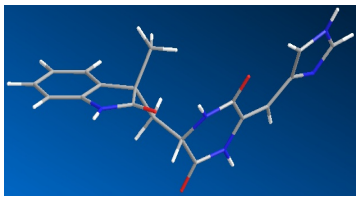

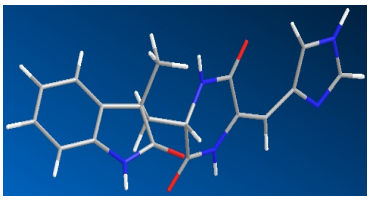

3b **3c** **3d**

Figure S3. The ^{1}H NMR spectrum of penilline A (**1**) in DMSO-d_6

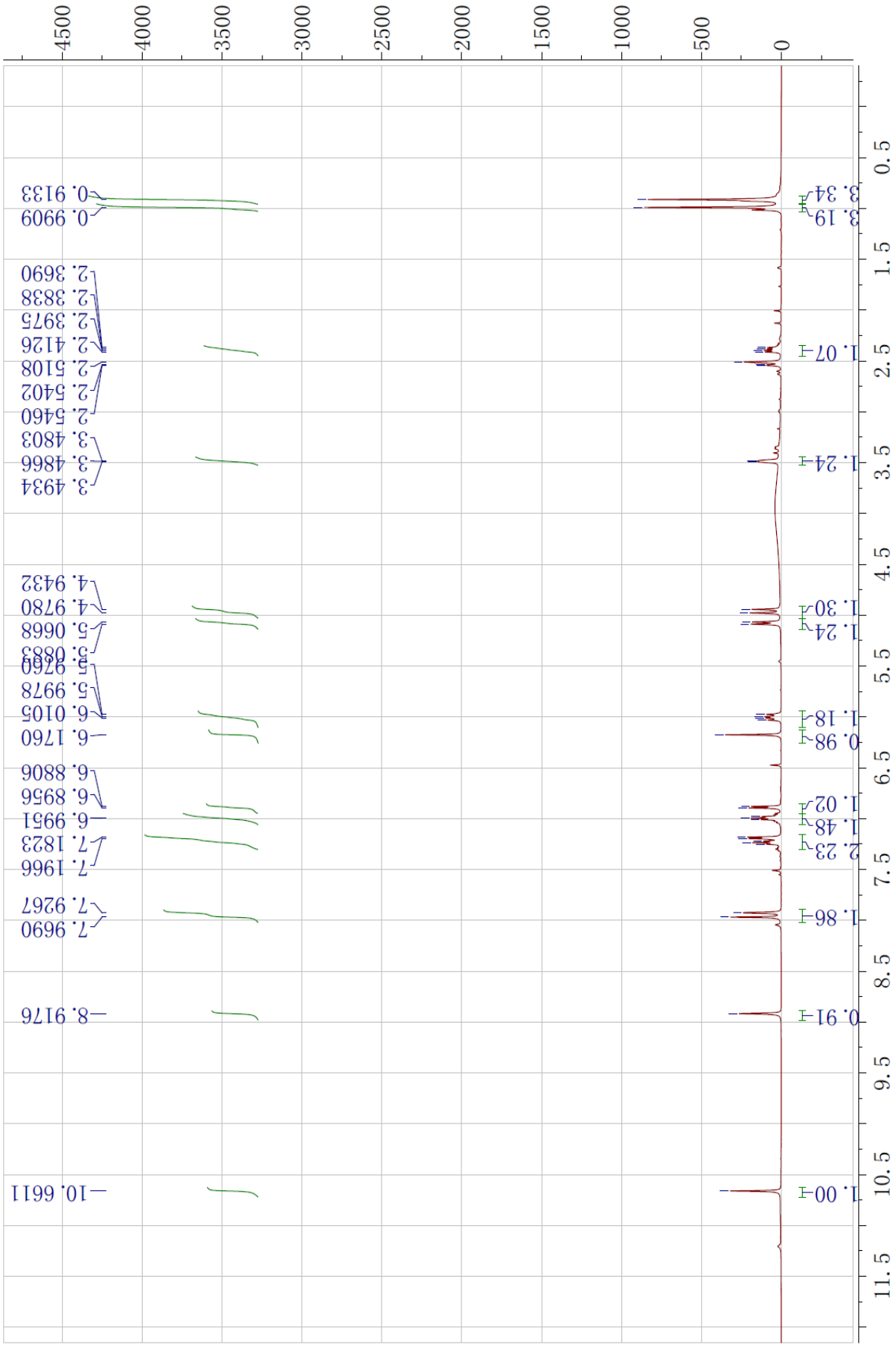

Figure S4. The ^{13}C NMR spectrum of penilline A (**1**) in DMSO-d_6

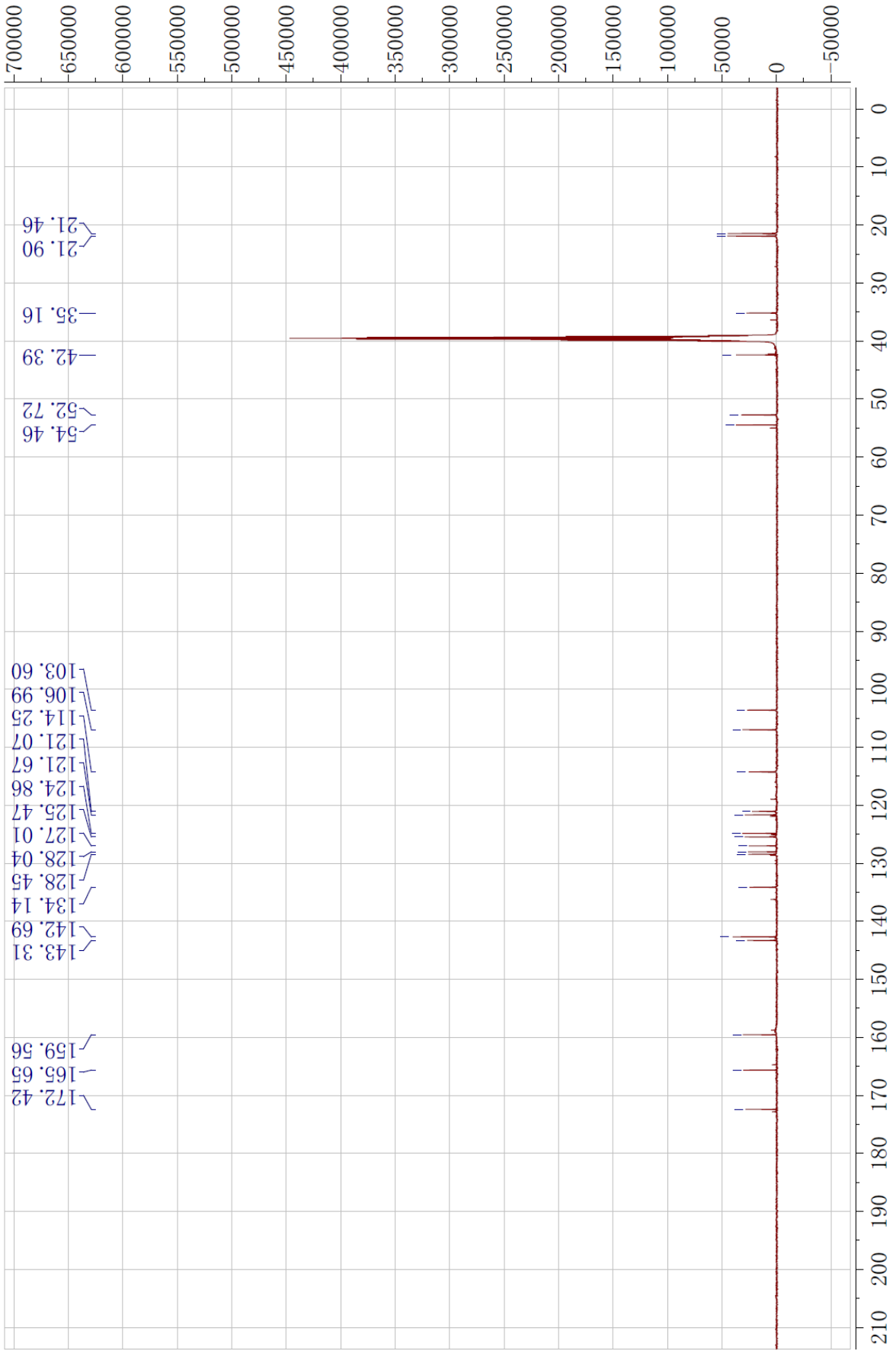

Figure S5. The HMQC spectrum of penilline A (**1**) in DMSO-d_6

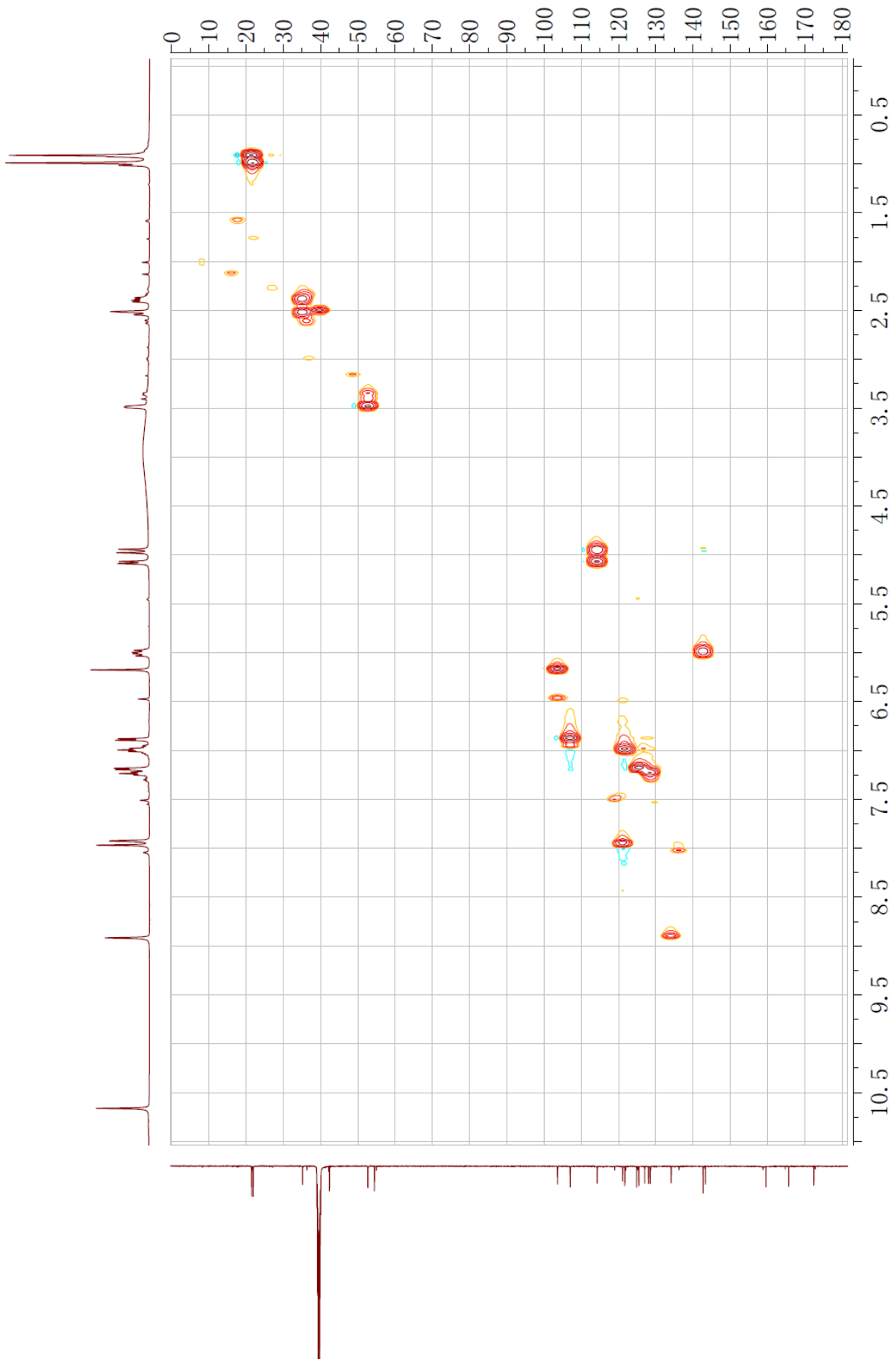

Figure S6. The ^{1}H-^{1}H COSY spectrum of penilline A (**1**) in DMSO-d_6

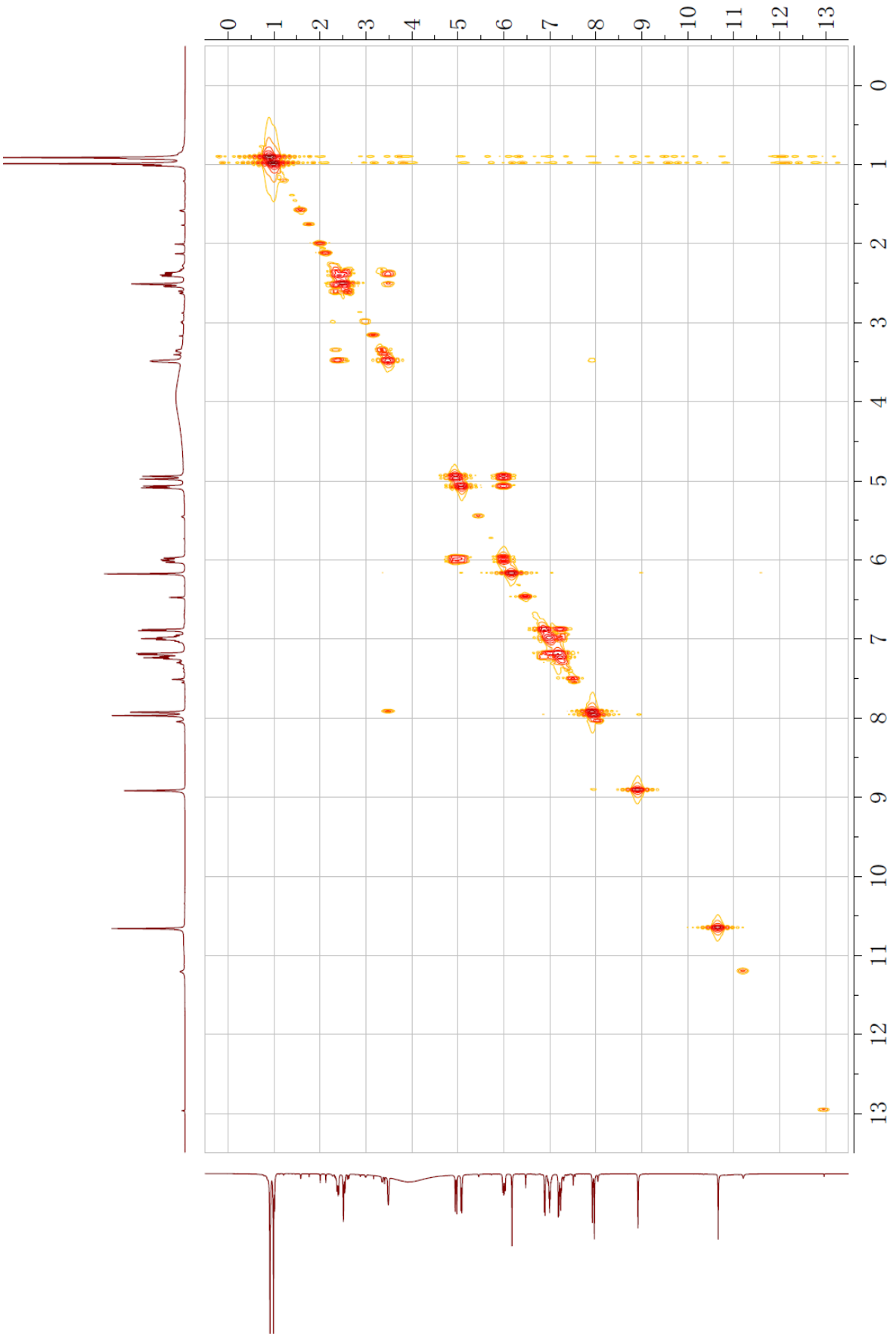

Figure S7. The HMBC spectrum of penilline A (**1**) in DMSO-d_6

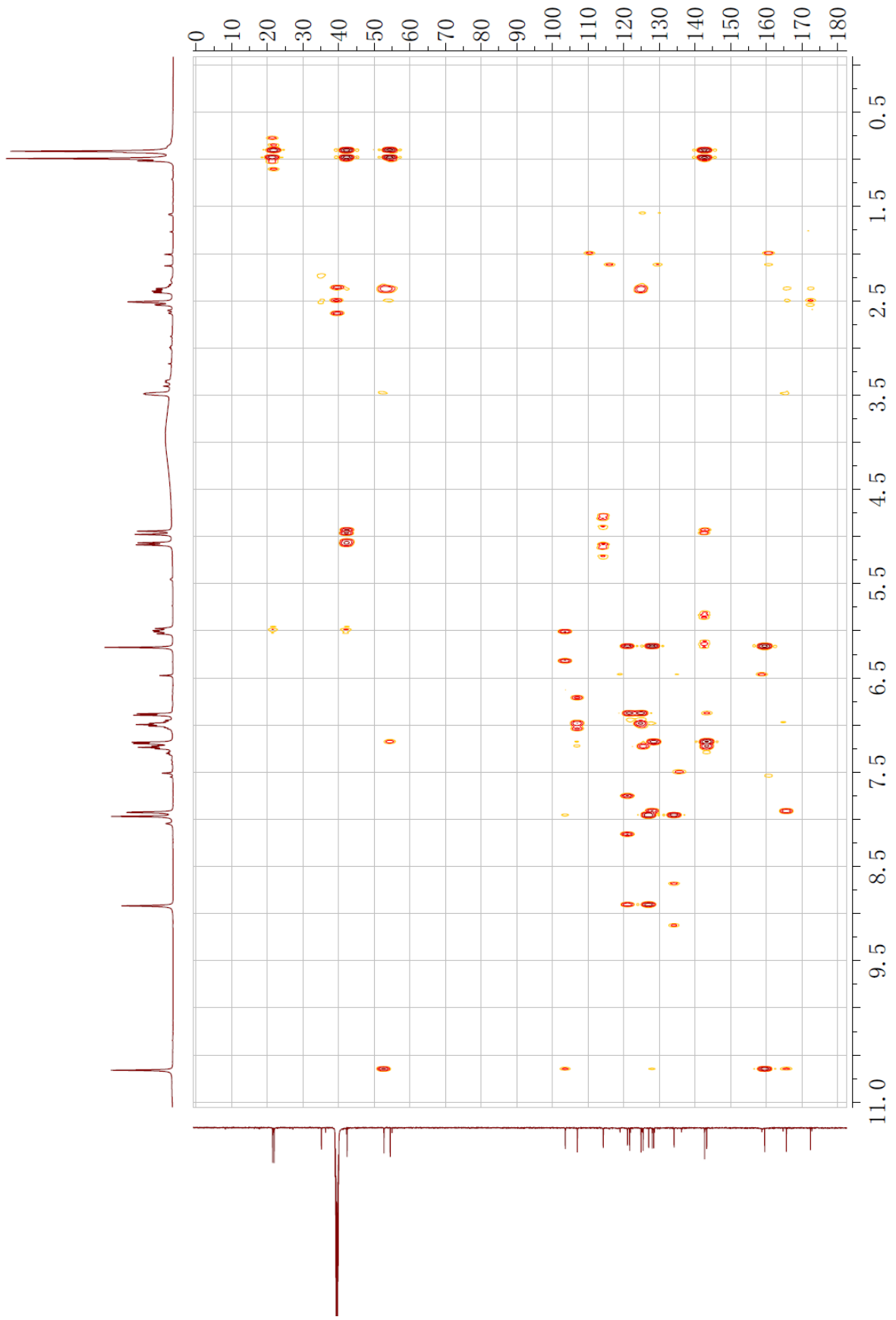

Figure S8. The NOESY spectrum of penilline A (**1**) in DMSO-d_6

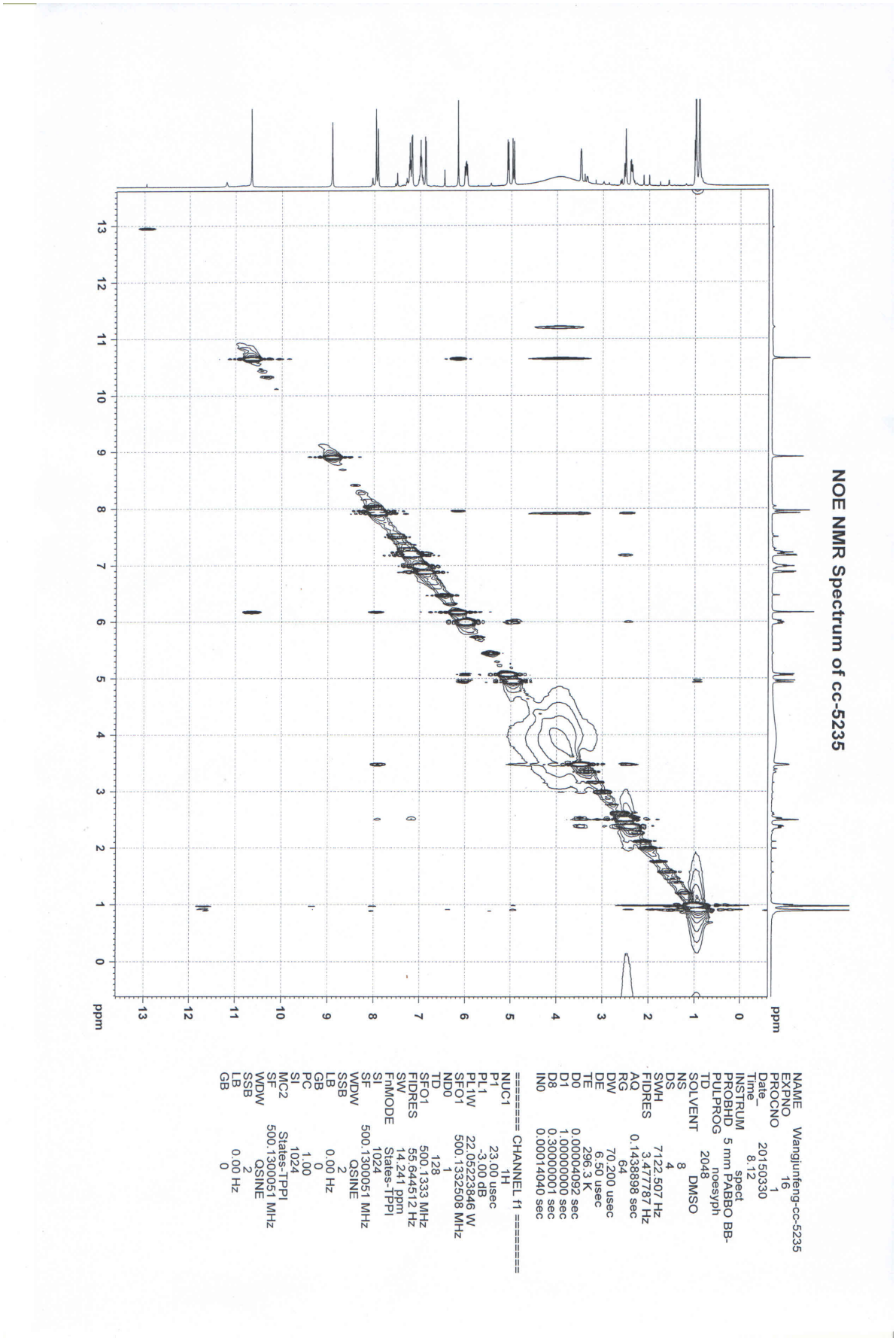

Figure S9. The HRESIMS spectrum of penilline A (**1**)

Mass Spectrum SmartFormula Report

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Comment			

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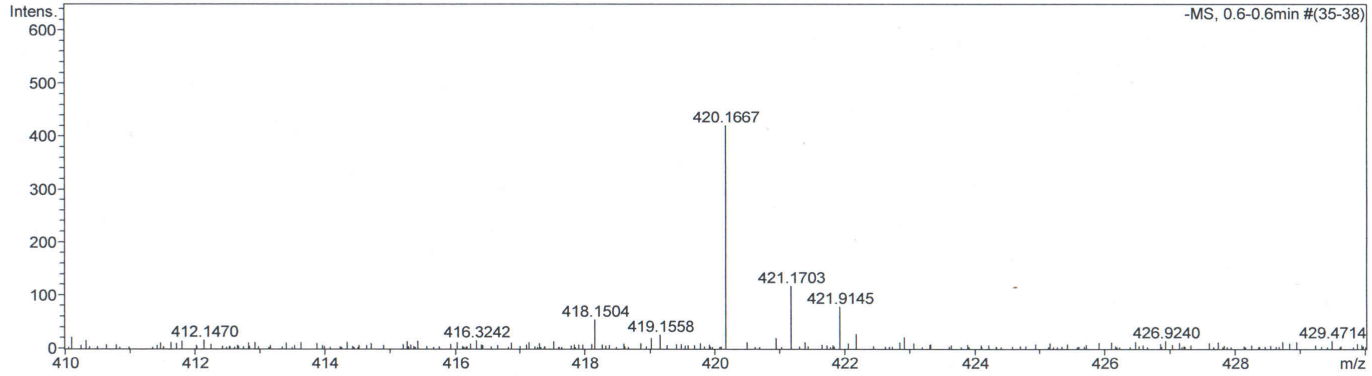

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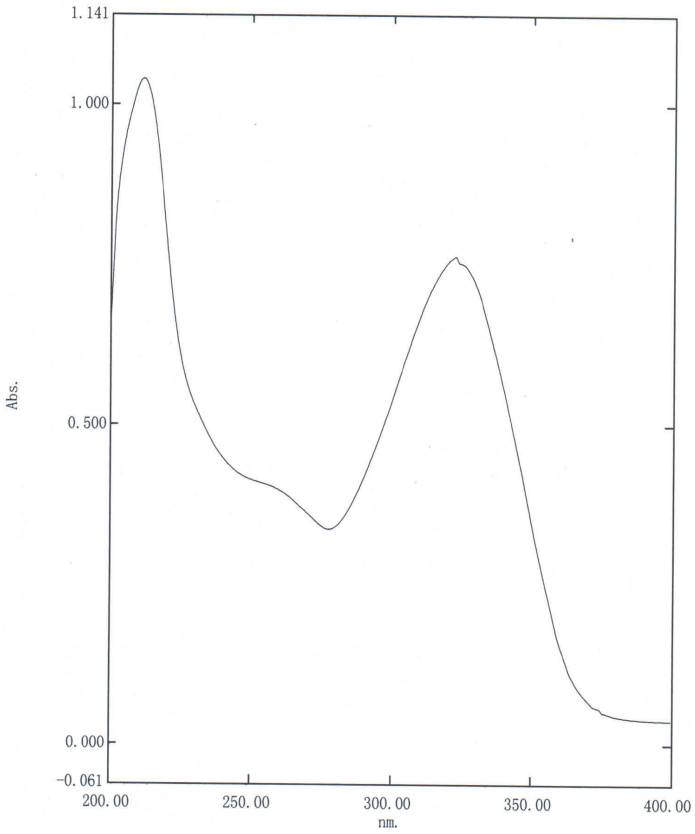
Figure S10. The UV spectrum of penilline A (**1**)

光谱峰值检测报告

2015-04-30 15:35:16

数据集: CC-5235 - RawData



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自动采样间隔: 启用
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阶梯校正: OFF

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平均: 停用

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1	↑	322.60	0.764	
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Figure S11. The ^{1}H NMR spectrum of isopenilline A (**2**) in CD_3OD

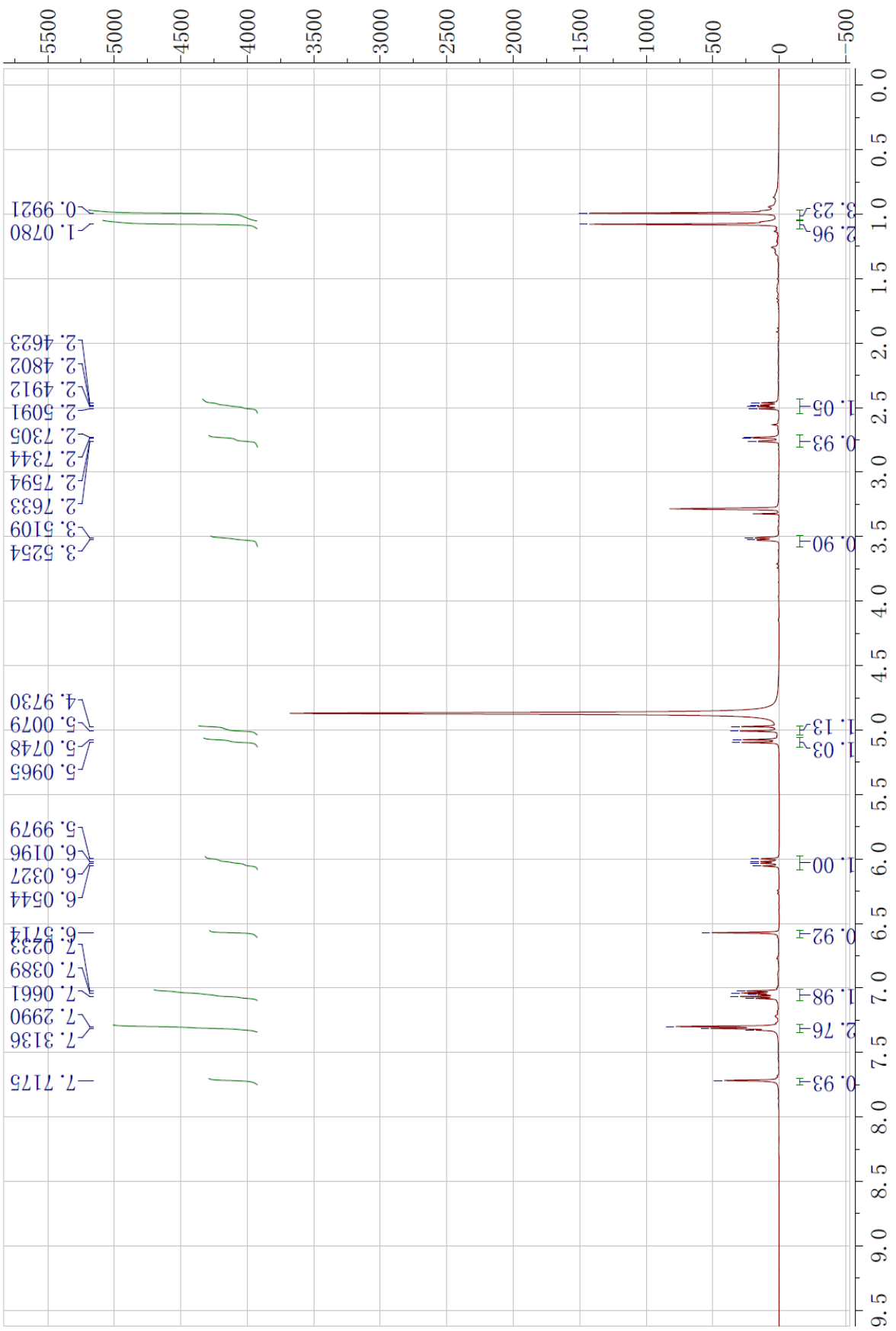

Figure S12. The ^{13}C NMR spectrum of isopenilline A (**2**) in CD_3OD

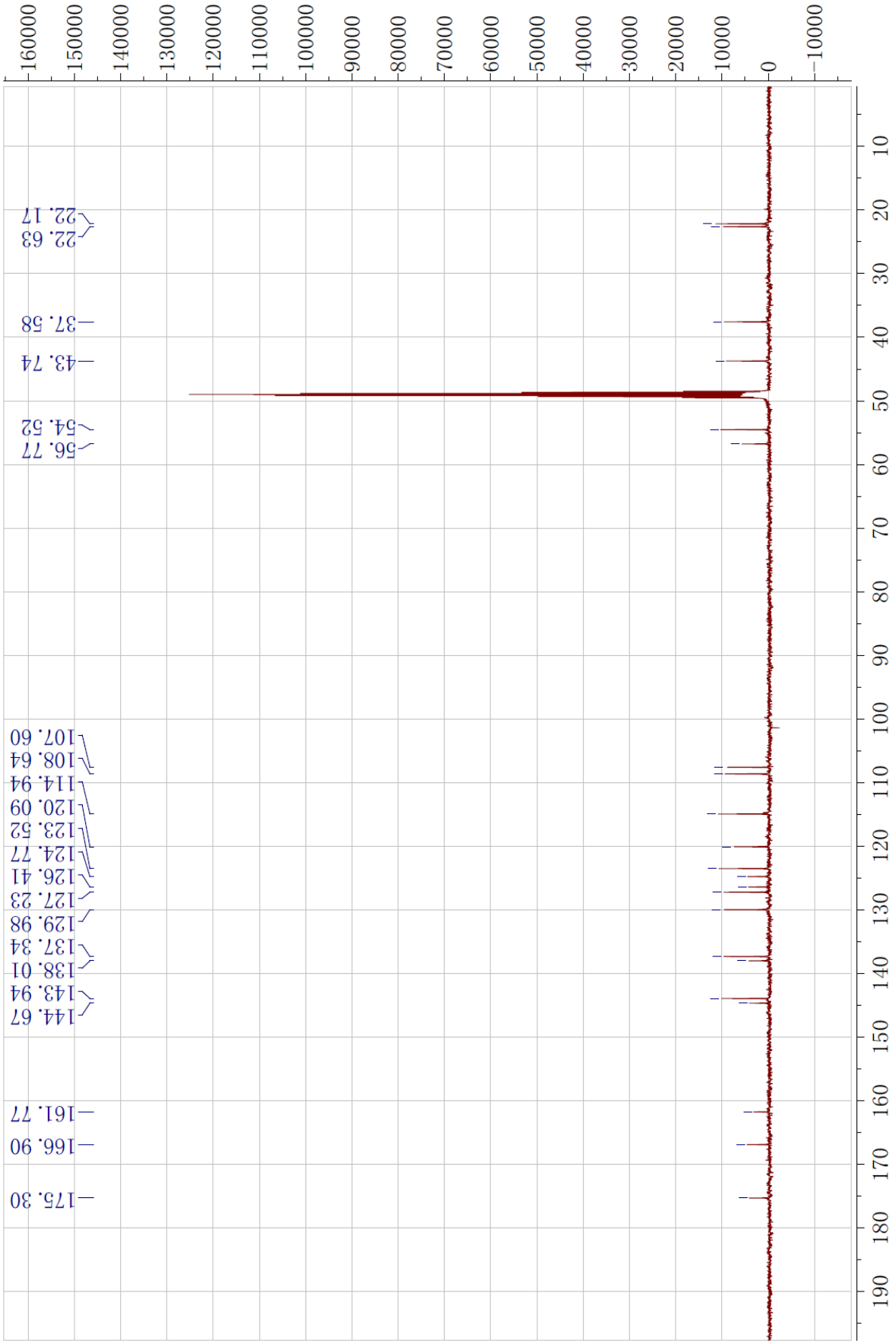

Figure S13. The HMQC spectrum of isopenilline A (**2**) in CD_3OD

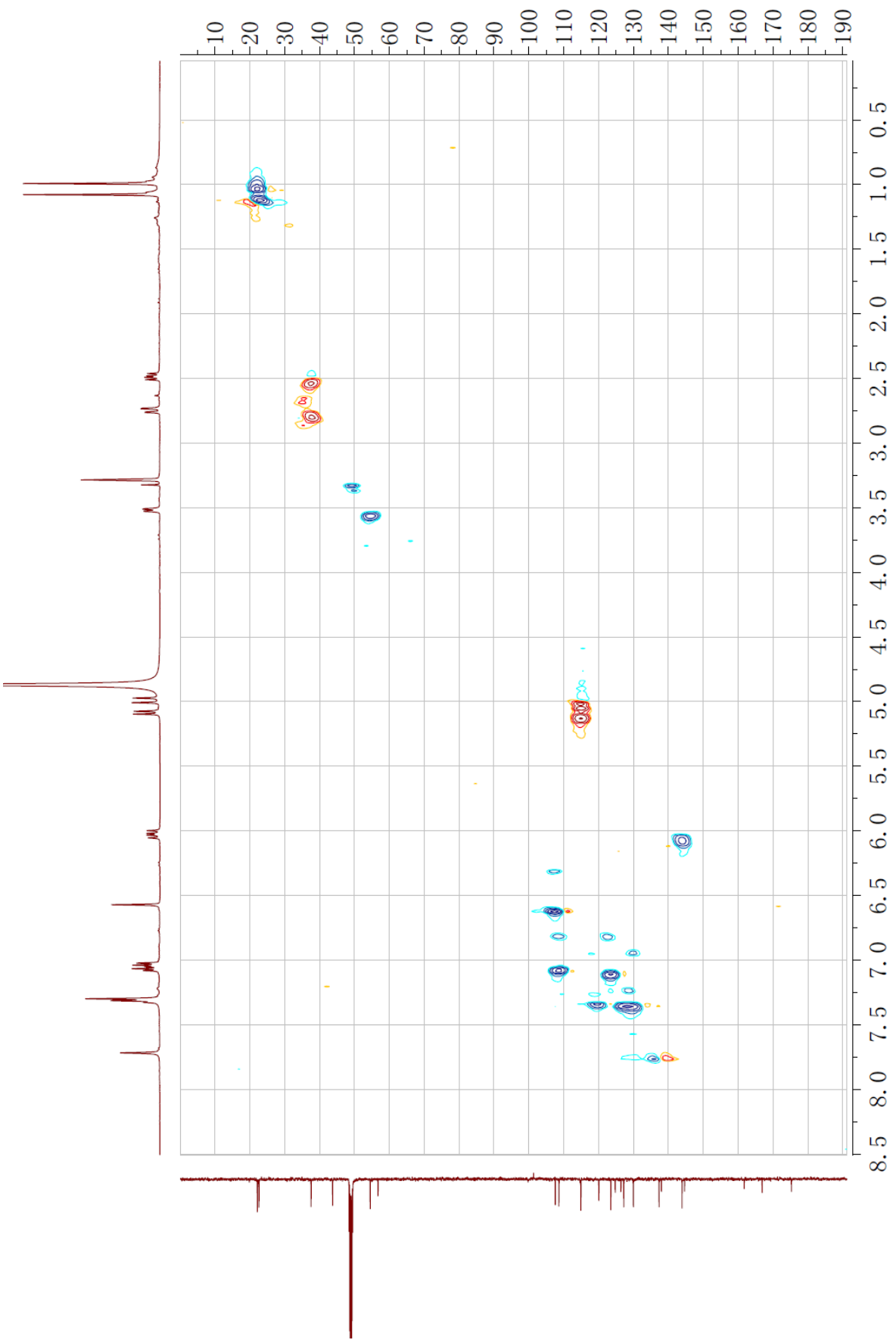

Figure S14. The ^{1}H-^{1}H COSY spectrum of isopenilline A (**2**) in CD_3OD

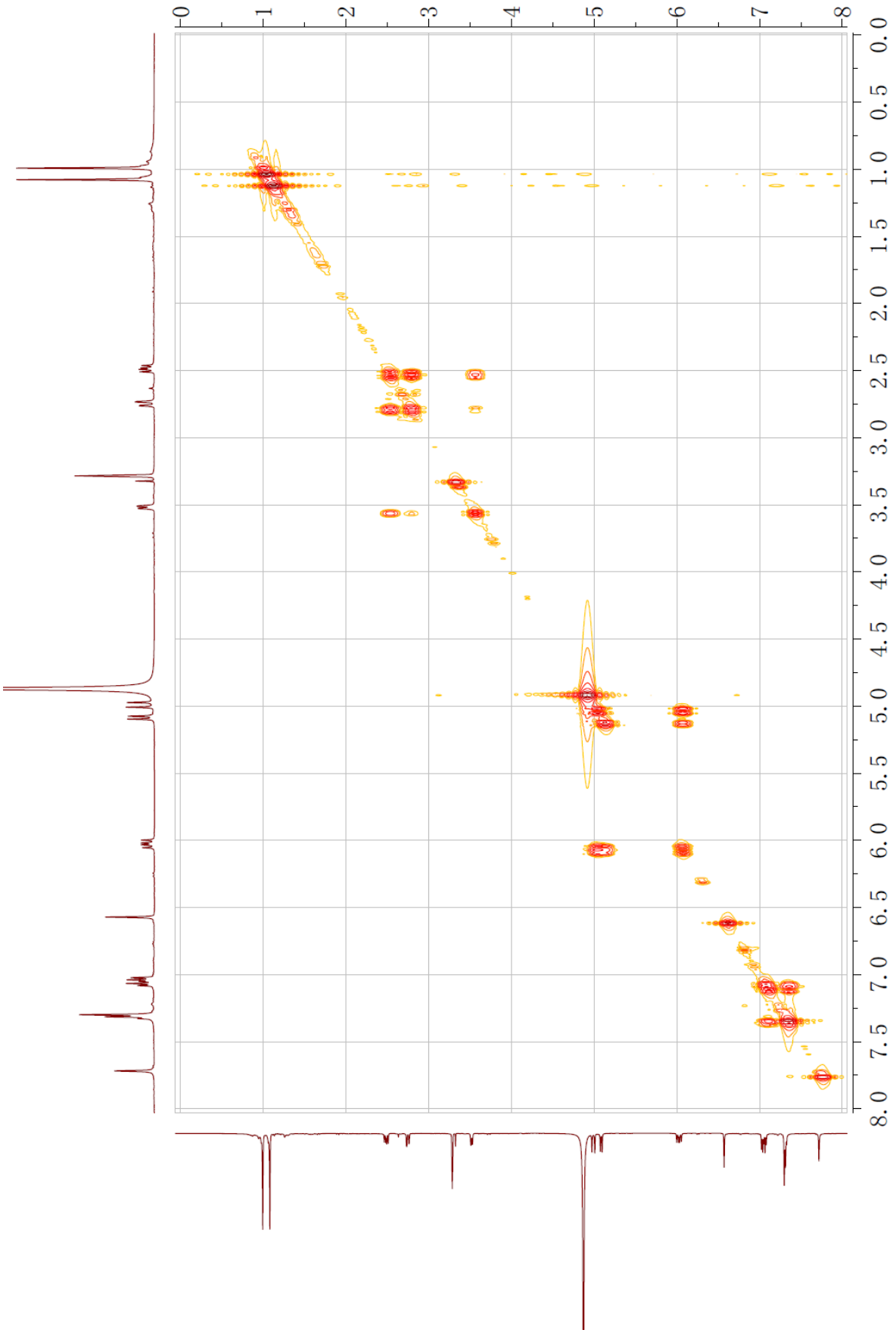

Figure S15. The HMBC spectrum of isopenilline A (**2**) in CD_3OD

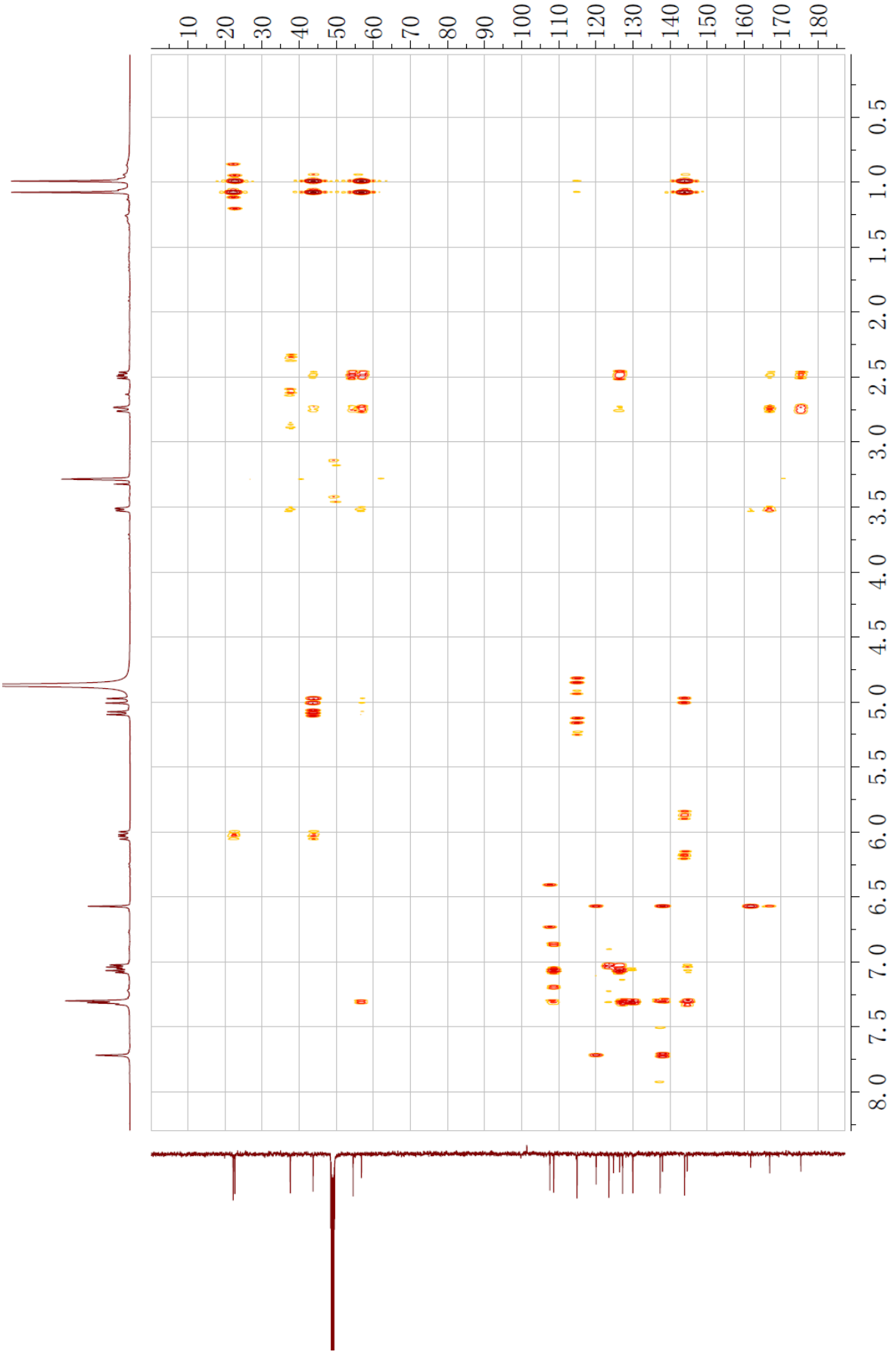

Figure S16. The ^{1}H NMR spectrum of isopenilline A (**2**) in DMSO-d_6

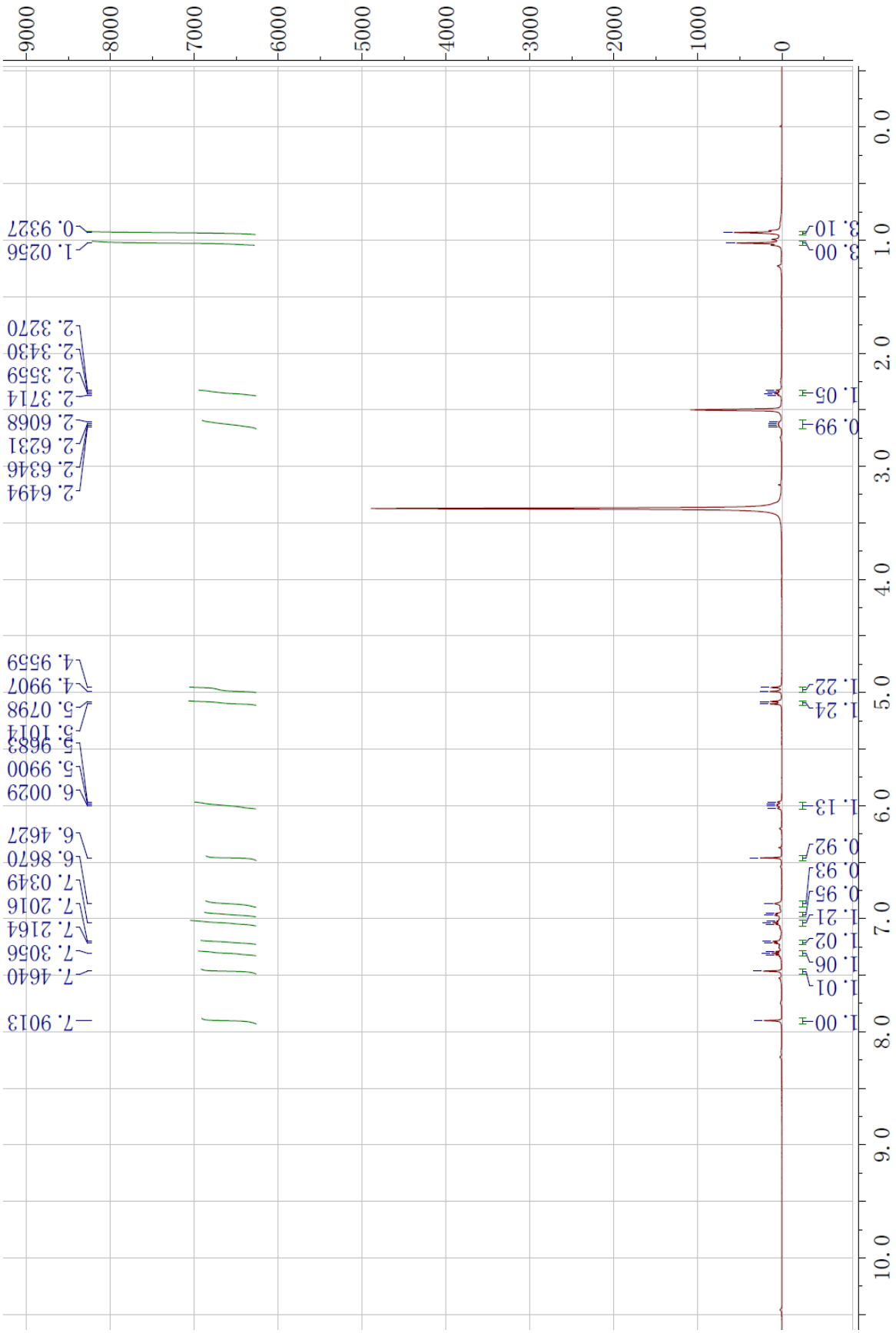

Figure S17. The ^{13}C NMR spectrum of isopenilline A (**2**) in DMSO-d_6

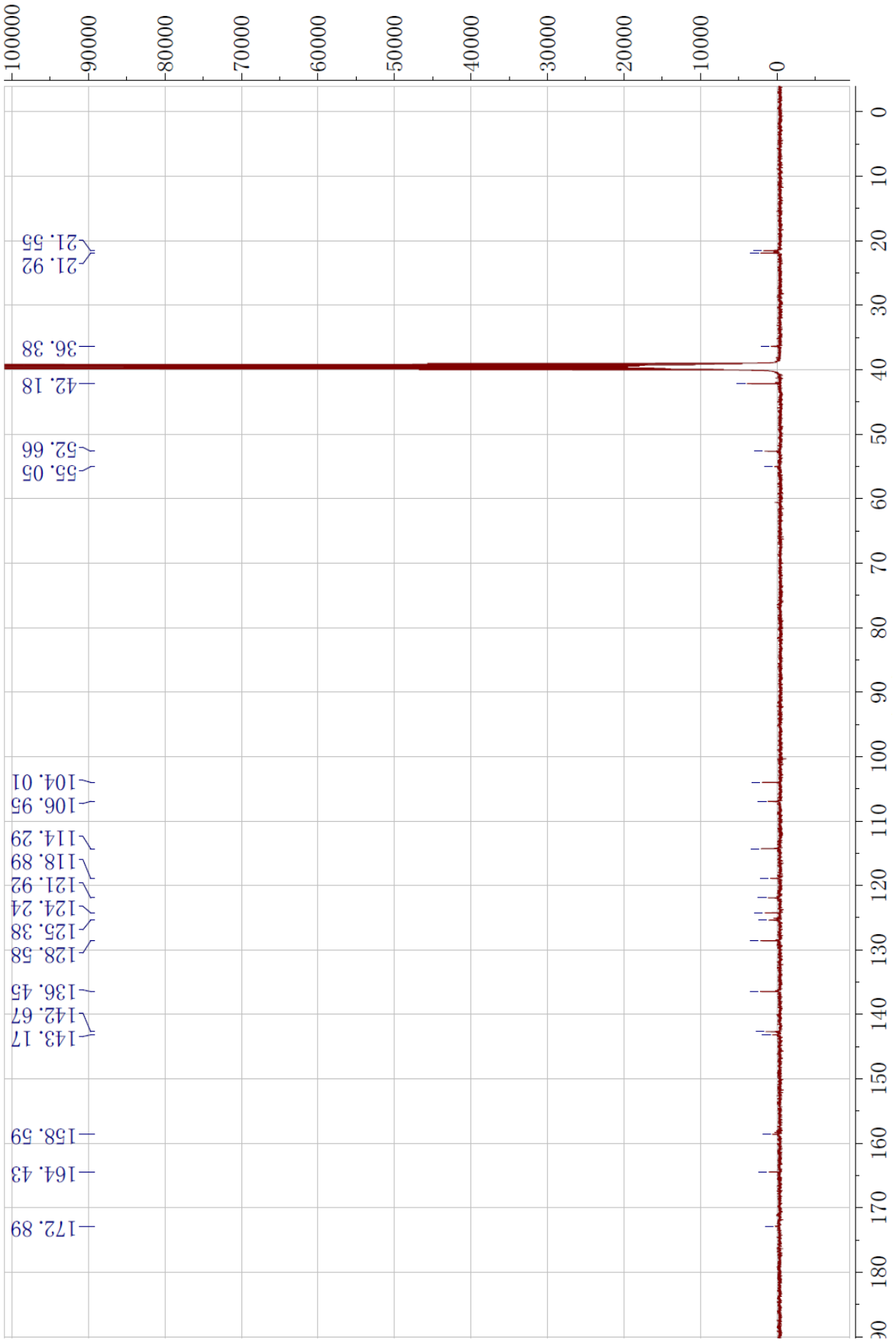

Figure S18. The HMQC spectrum of isopenilline A (**2**) in DMSO-d_6

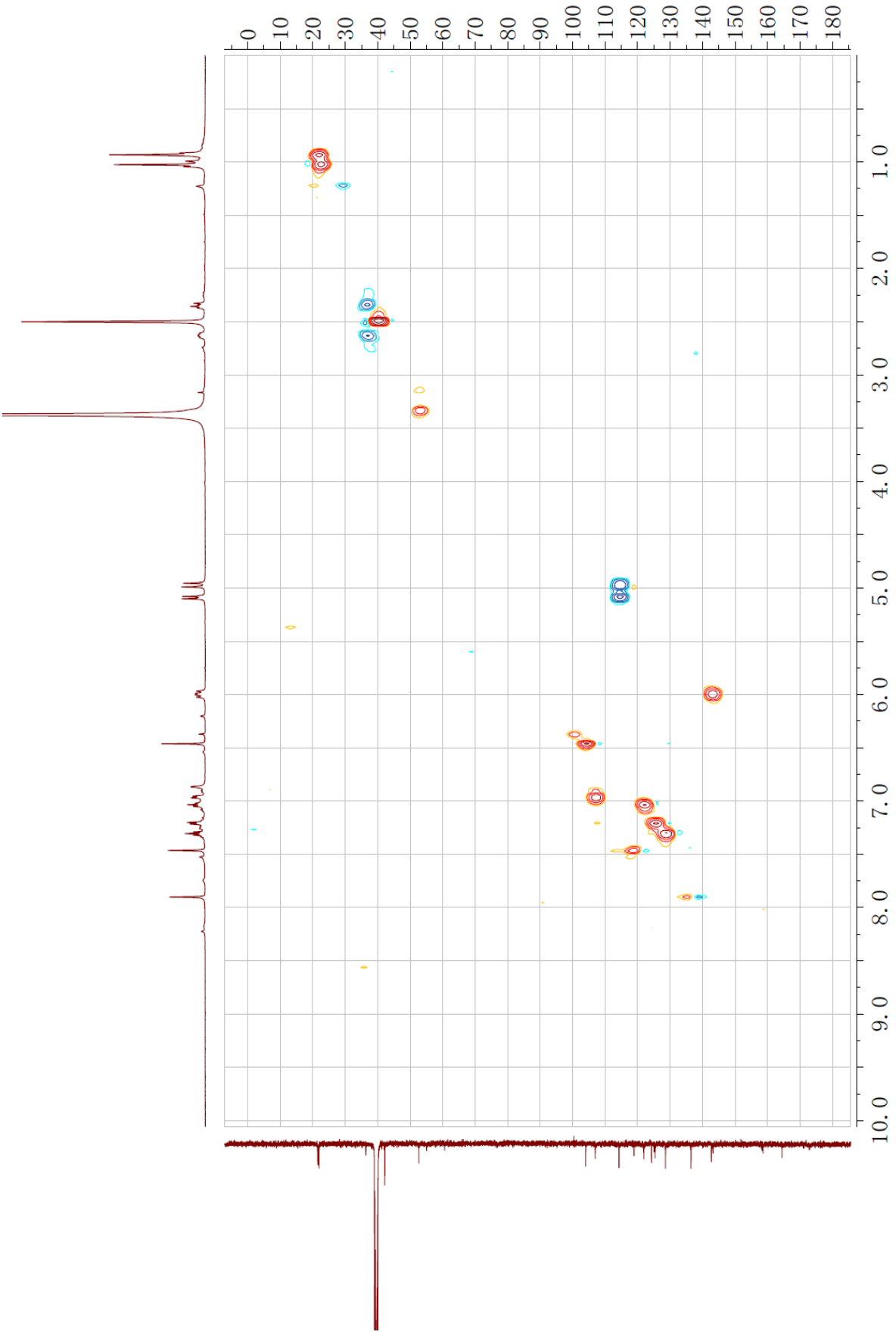

Figure S19. The ^{1}H-^{1}H COSY spectrum of isopenilline A (**2**) in DMSO-d_6

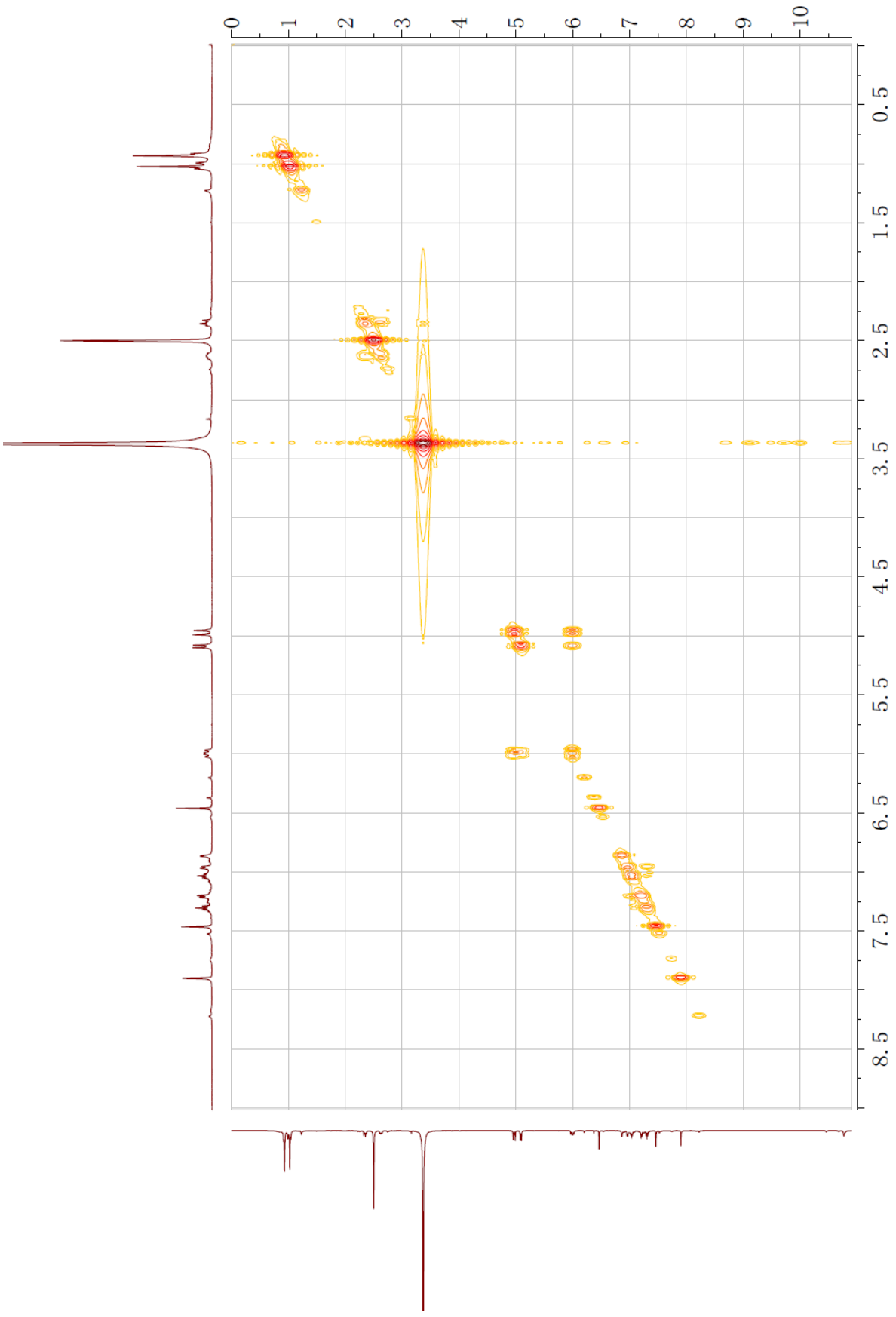

Figure S20. The HMBC spectrum of isopenilline A (**2**) in DMSO-d_6

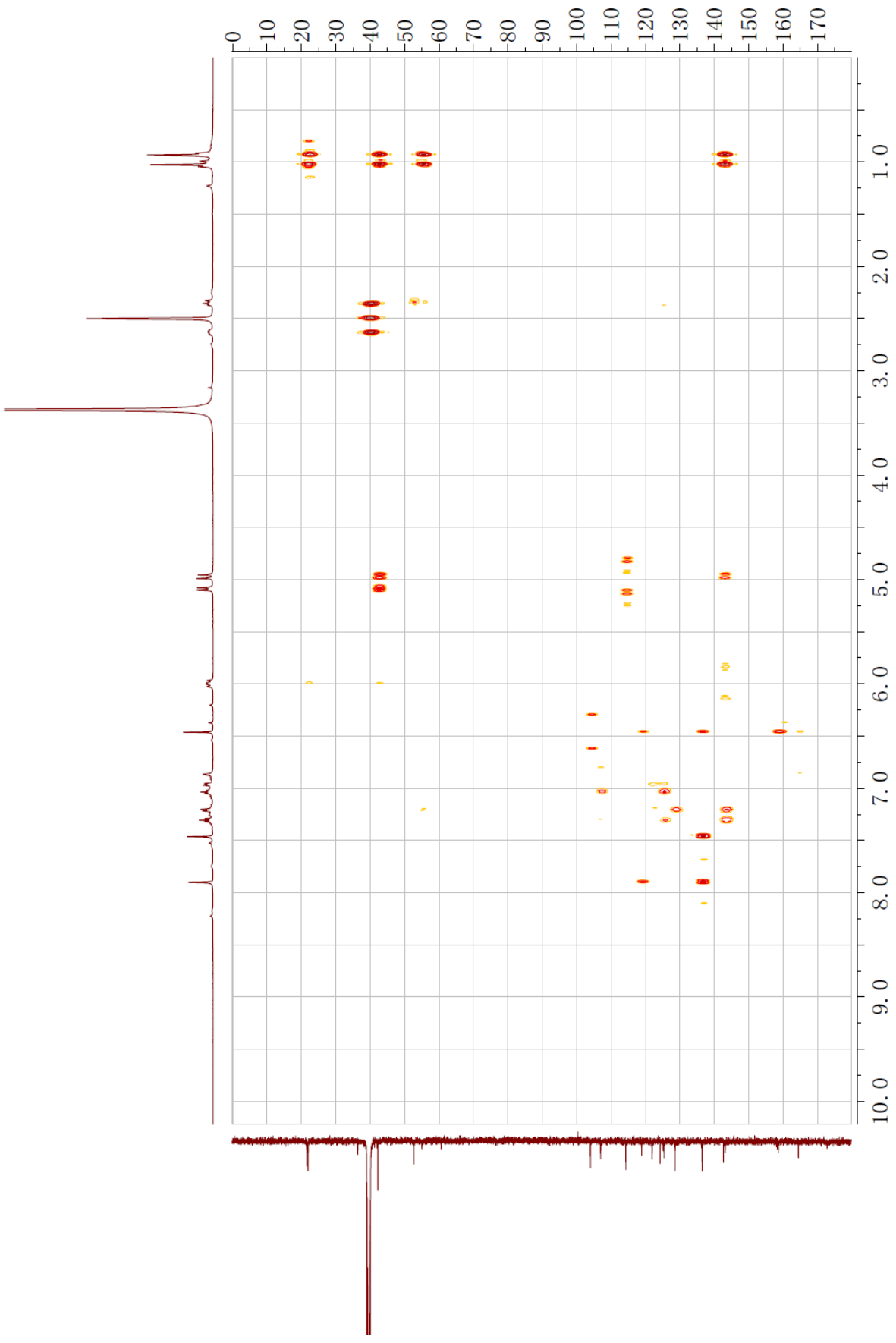

Figure S21. The NOESY spectrum of isopenilline A (**2**) in DMSO-d_6

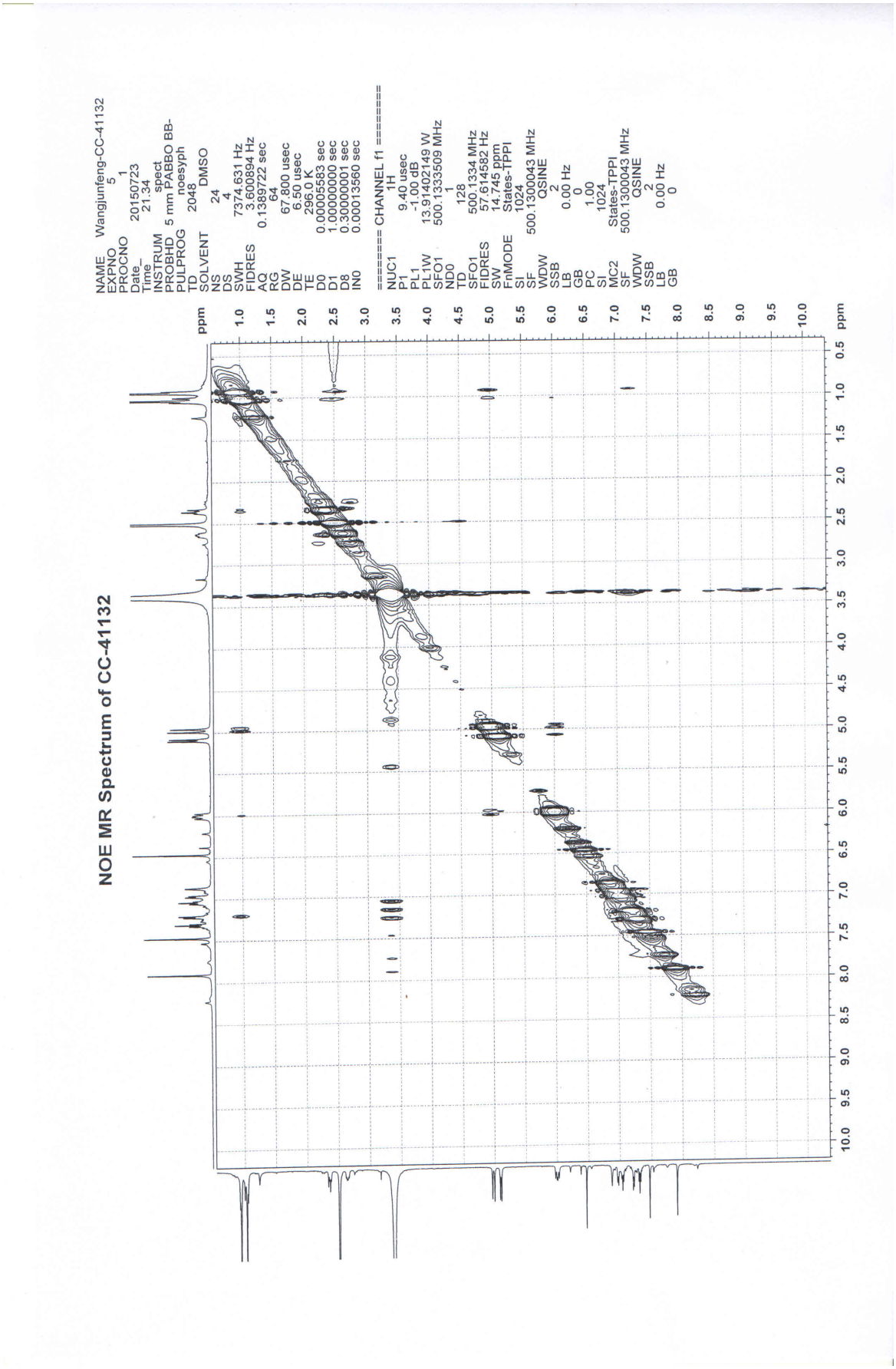

Figure S22. The HRESIMS spectrum of isopenilline A (**2**)

Figure S23. The UV spectrum of isopenilline A (**2**)

Mass Spectrum SmartFormula Report

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Comment			

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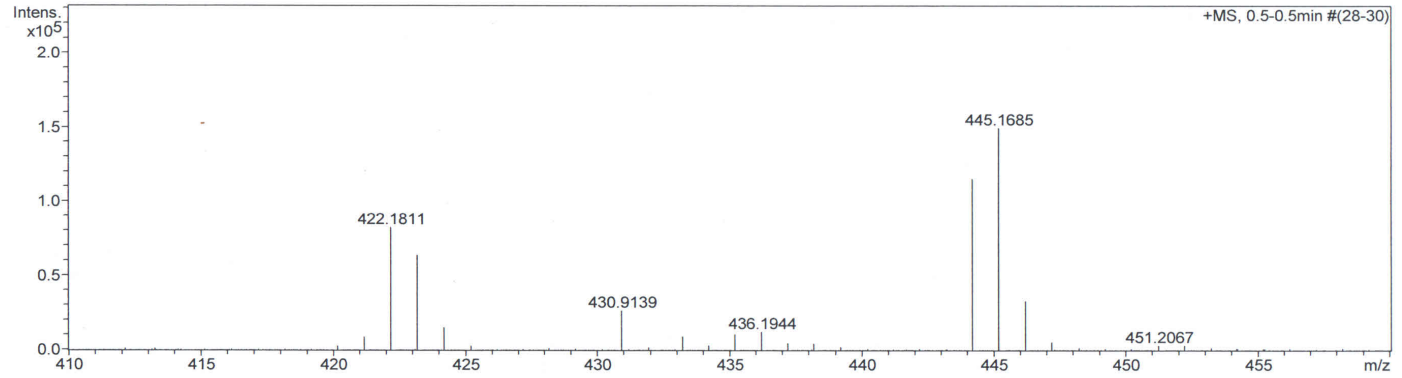

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光谱峰值检测报告

2015-04-30 15:15:04

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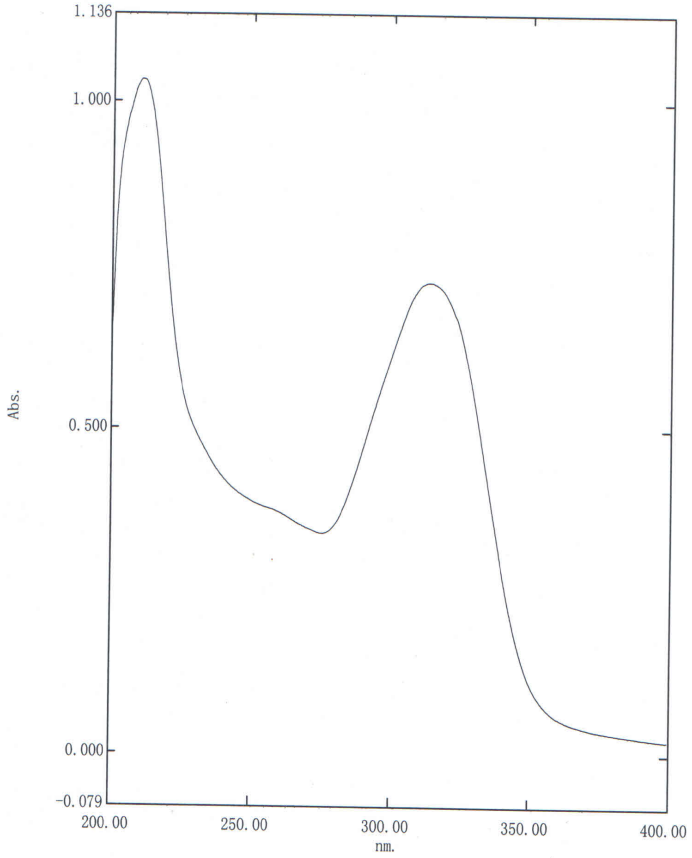

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检测器单元: 直接
S/R 转换: 标准
阶梯校正: OFF

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附件: 无

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平均: 停用

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体积:
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光程长:
附加信息:

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页 1 / 1

Figure S24. The ^{1}H NMR spectrum of penilline B (**3**) in CD_3OD

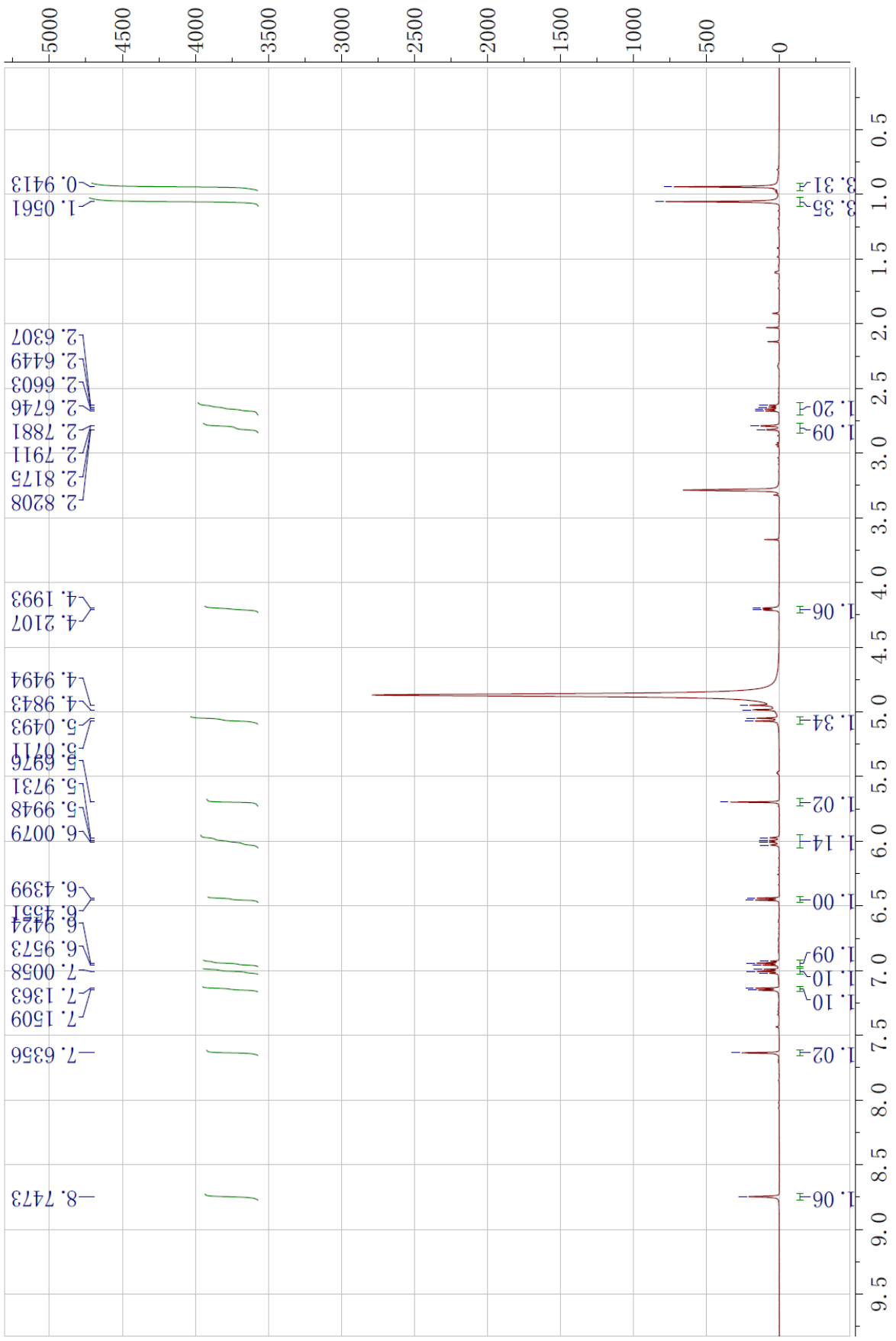


Figure S25. The ^{13}C NMR spectrum of penilline B (**3**) in CD_3OD

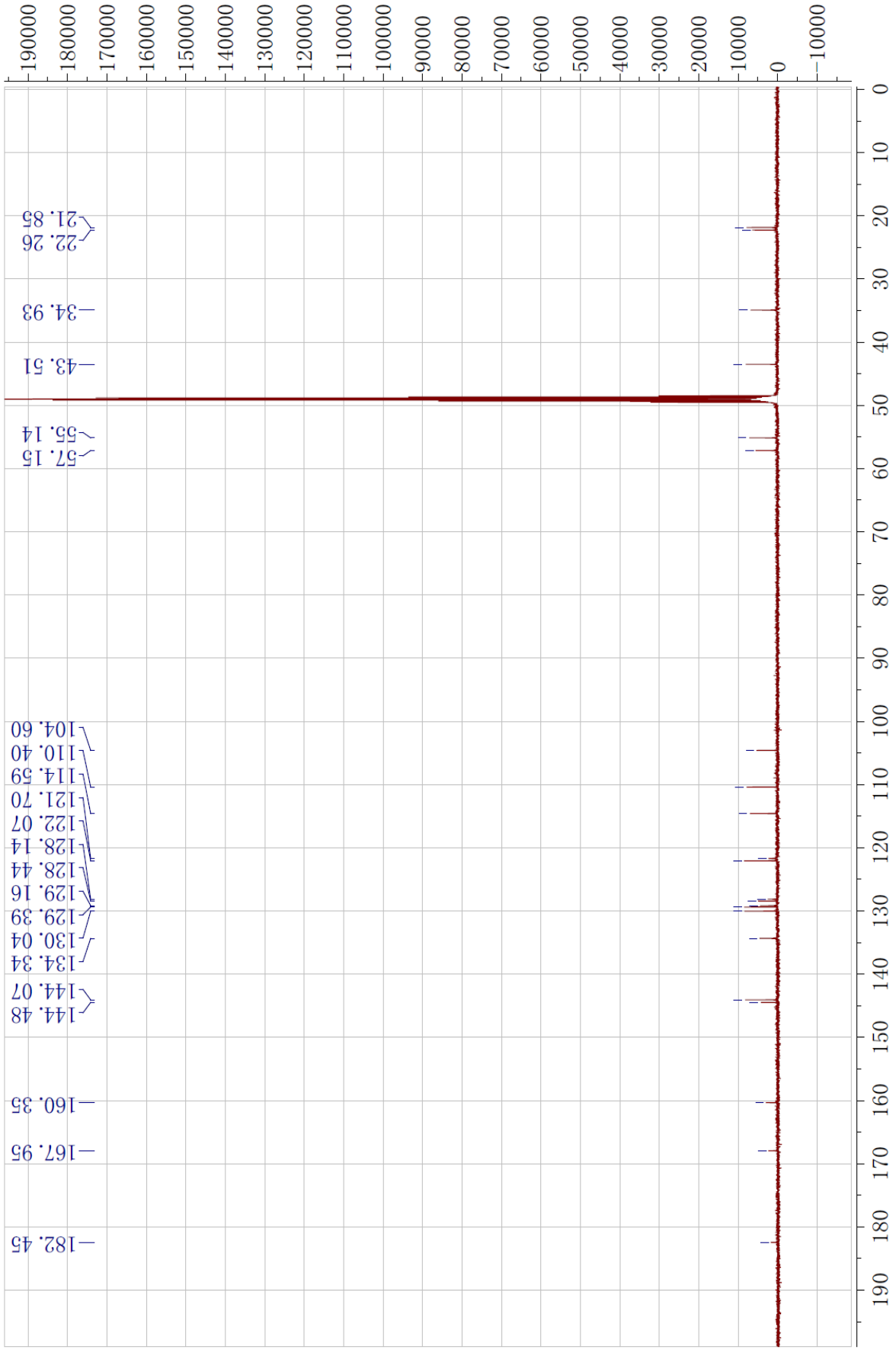


Figure S26. The HMQC spectrum of penilline B (**3**) in CD_3OD

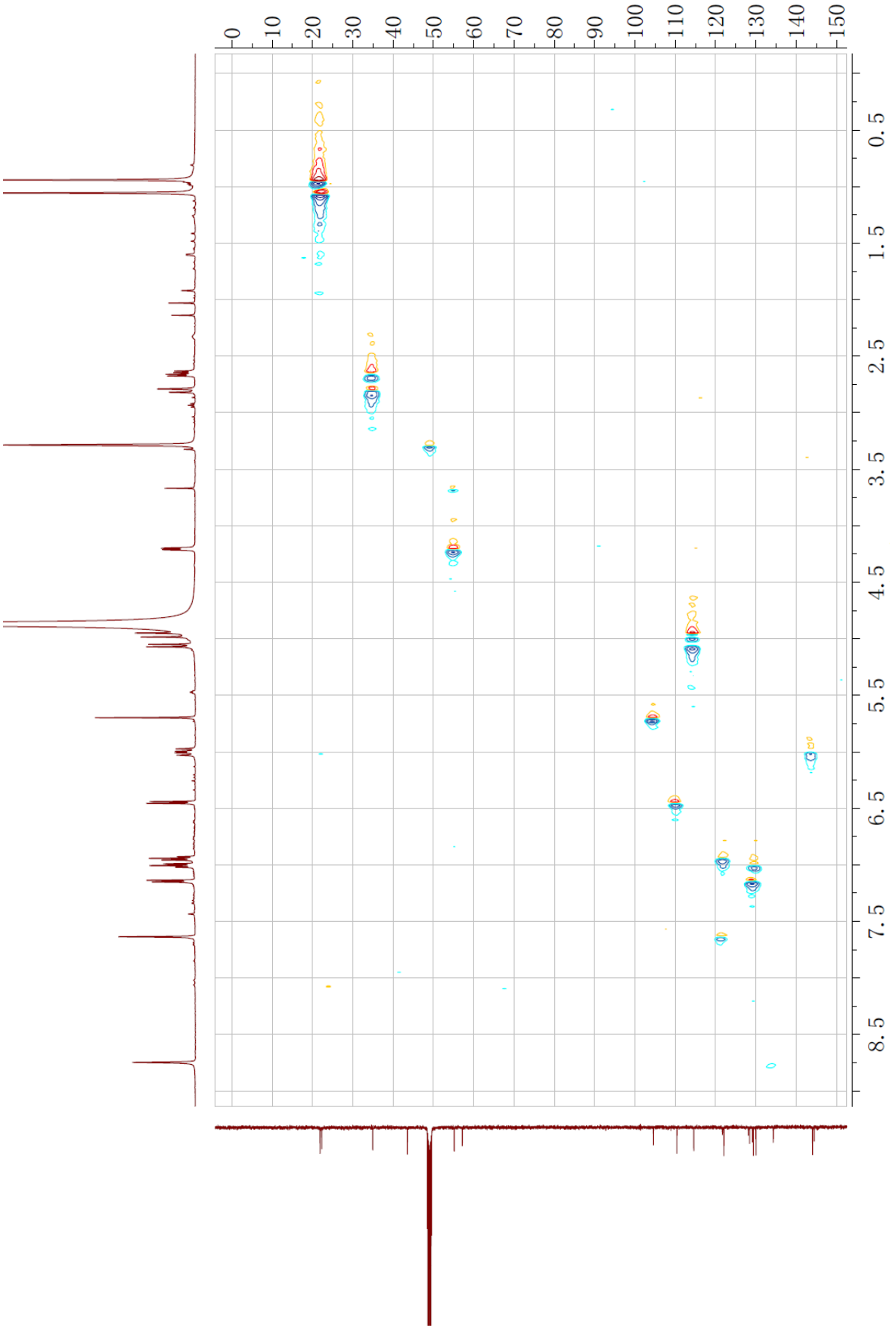


Figure S27. The ^{1}H-^{1}H COSY spectrum of penilline B (**3**) in CD_3OD

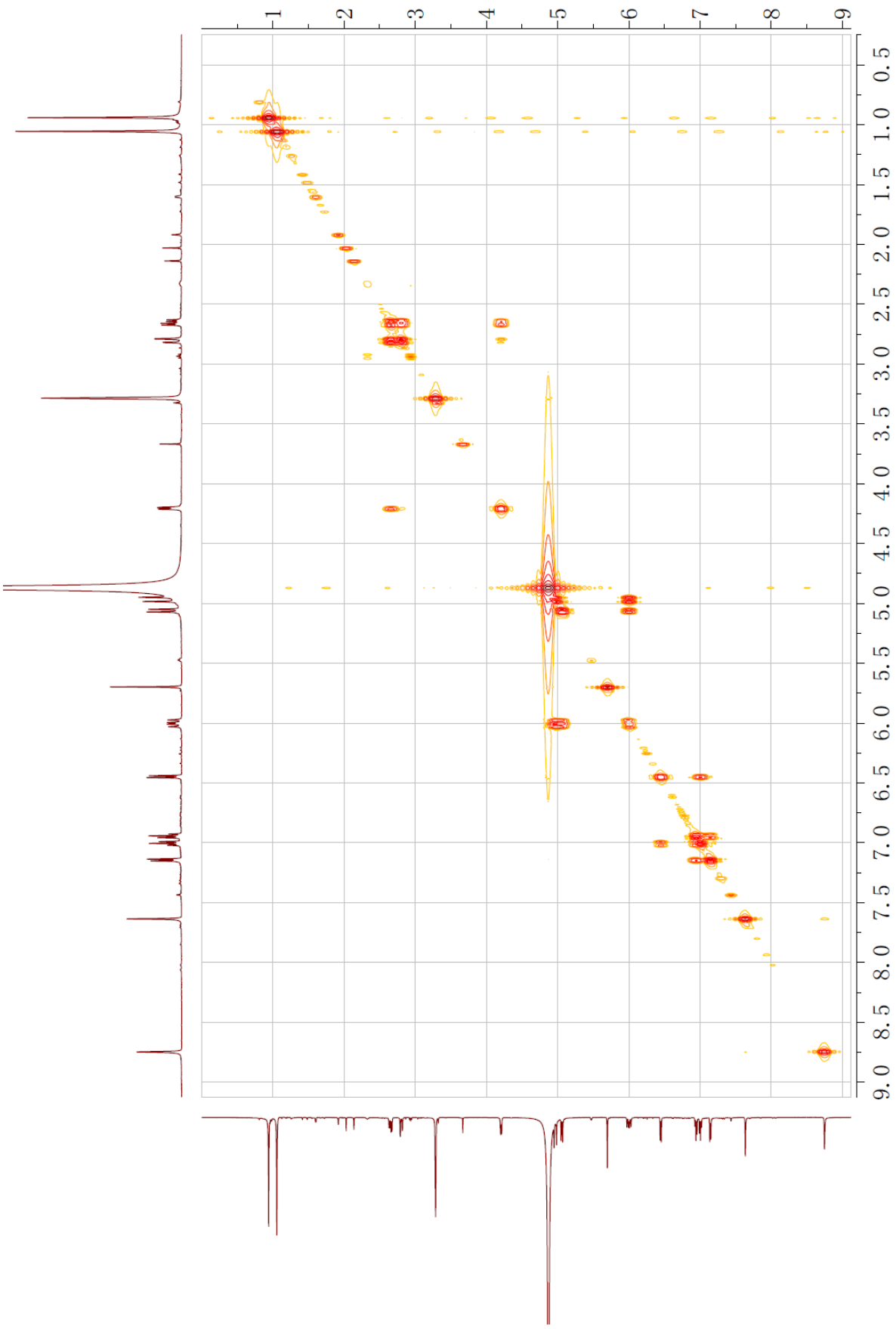


Figure S28. The HMBC spectrum of penilline B (**3**) in CD_3OD

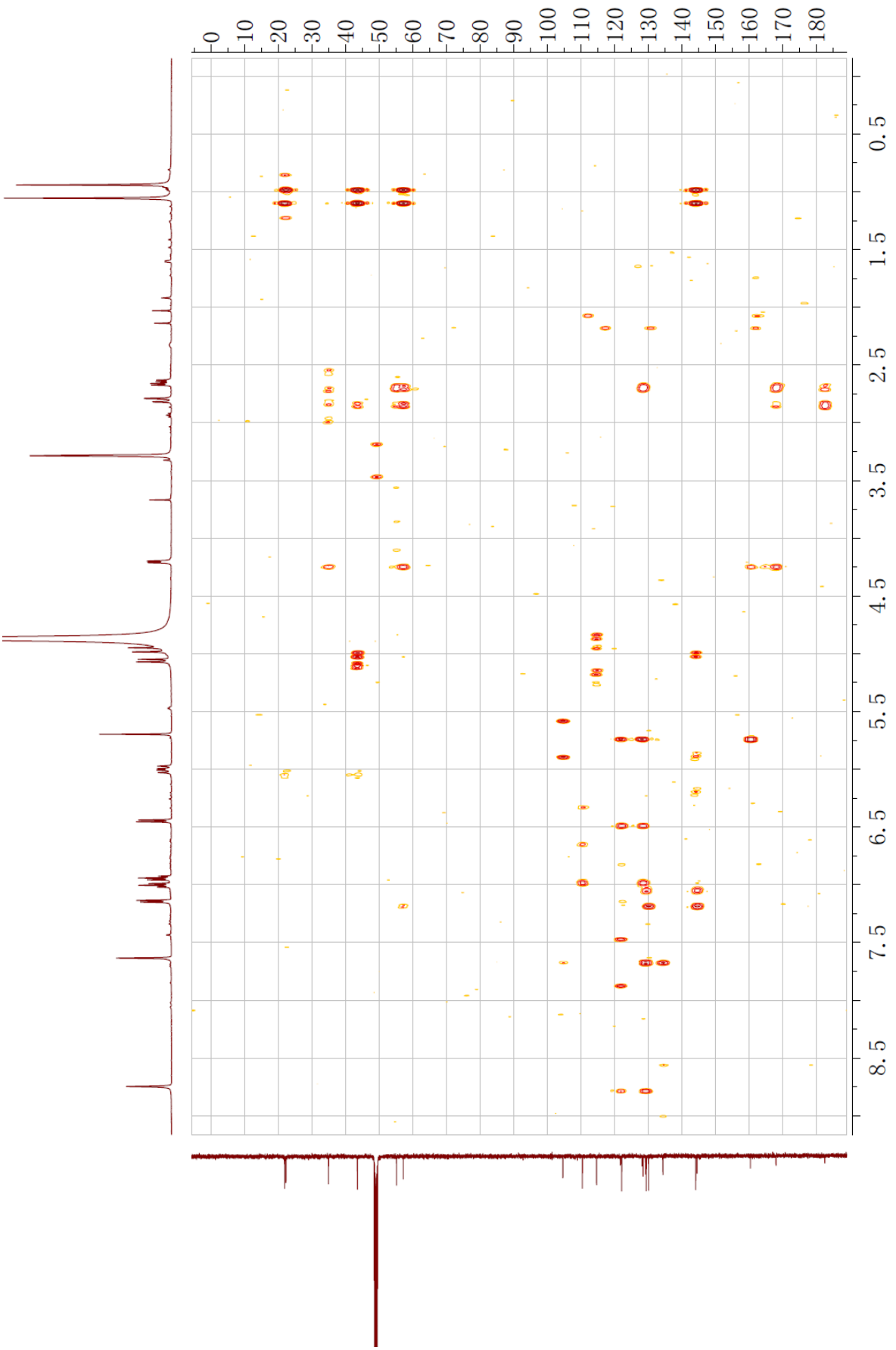


Figure S29. The ^{1}H NMR spectrum of penilline B (**3**) in DMSO-d_6

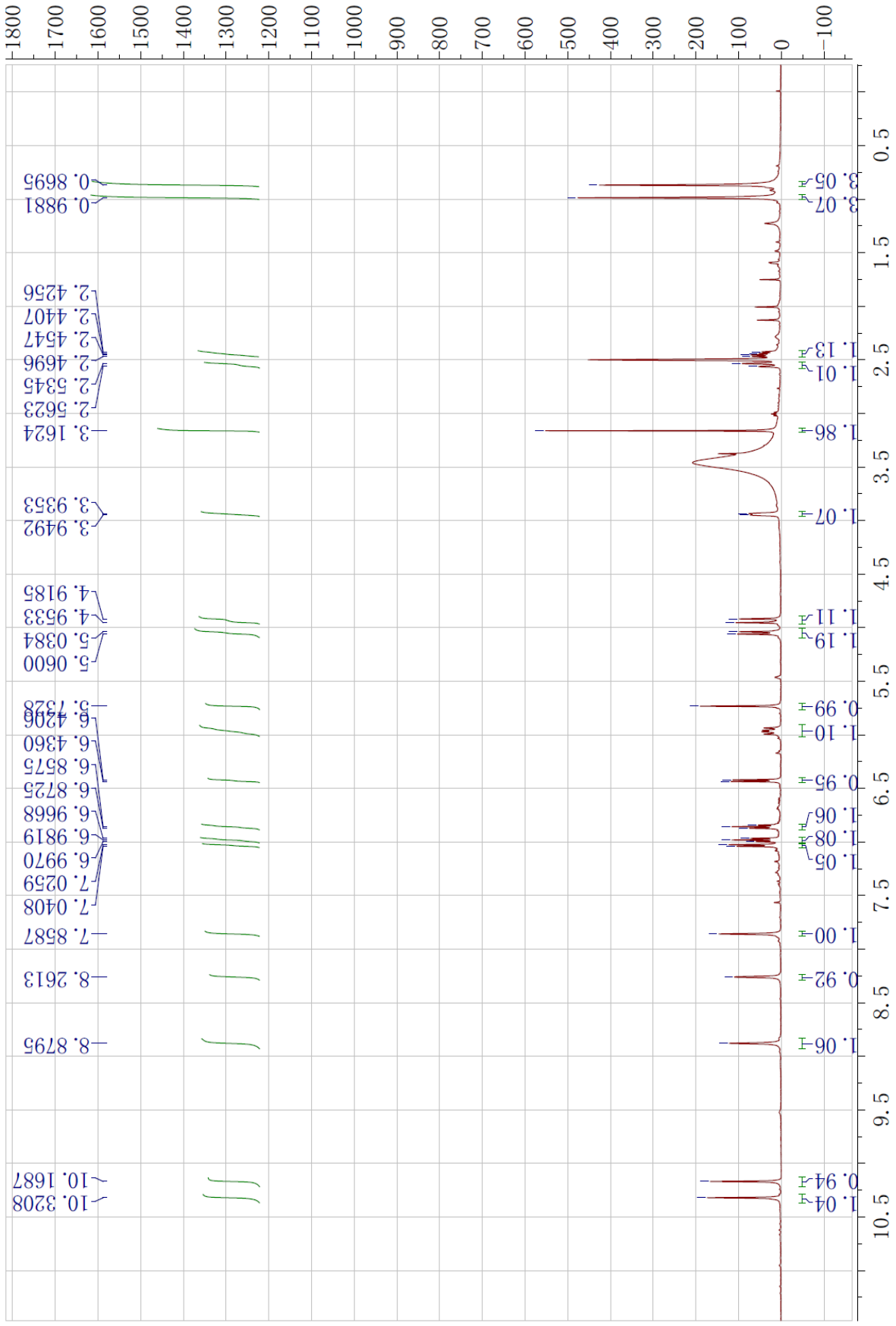


Figure S30. The ^{13}C NMR spectrum of penilline B (**3**) in DMSO-d_6

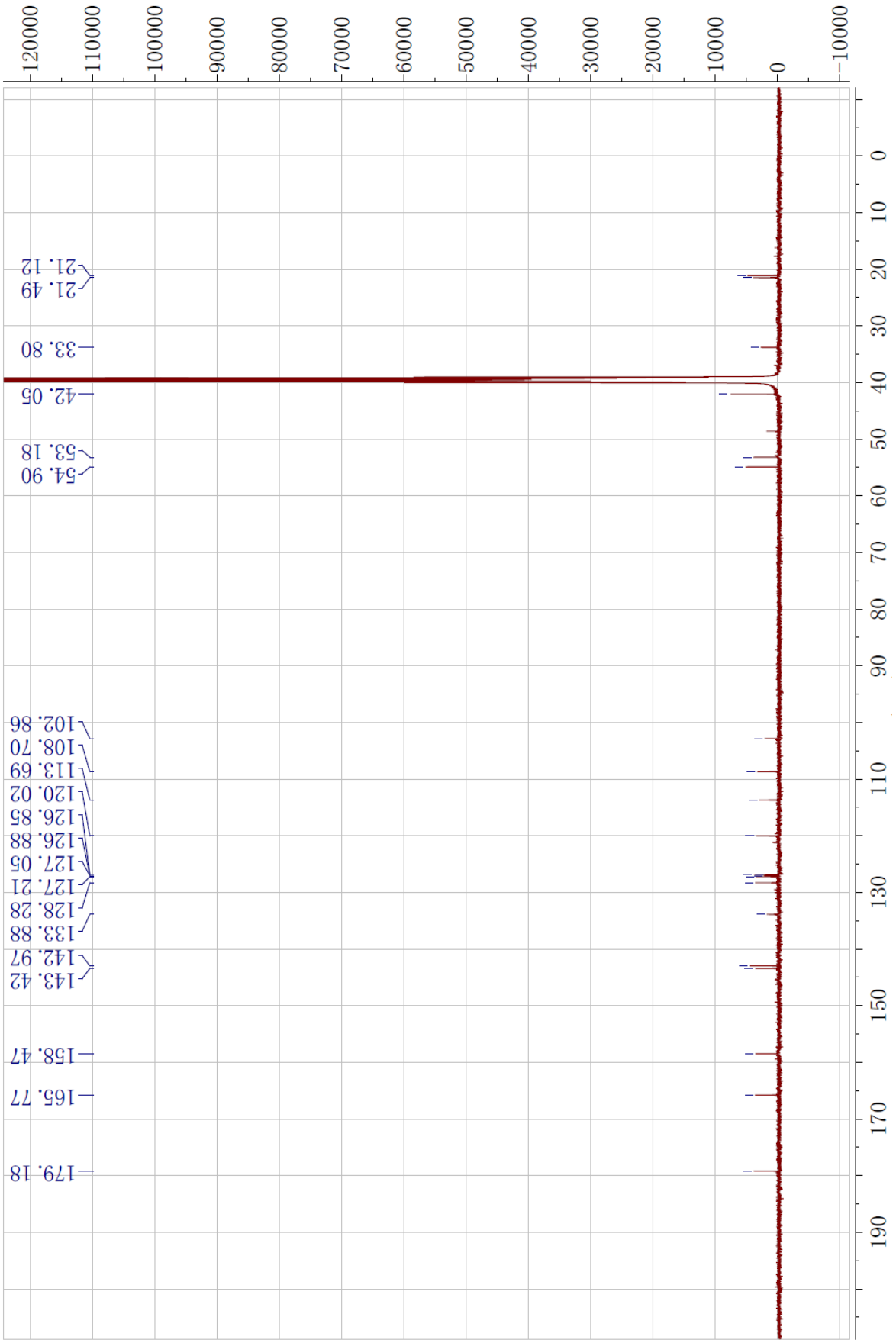


Figure S31. The HMQC spectrum of penilline B (**3**) in DMSO-d_6

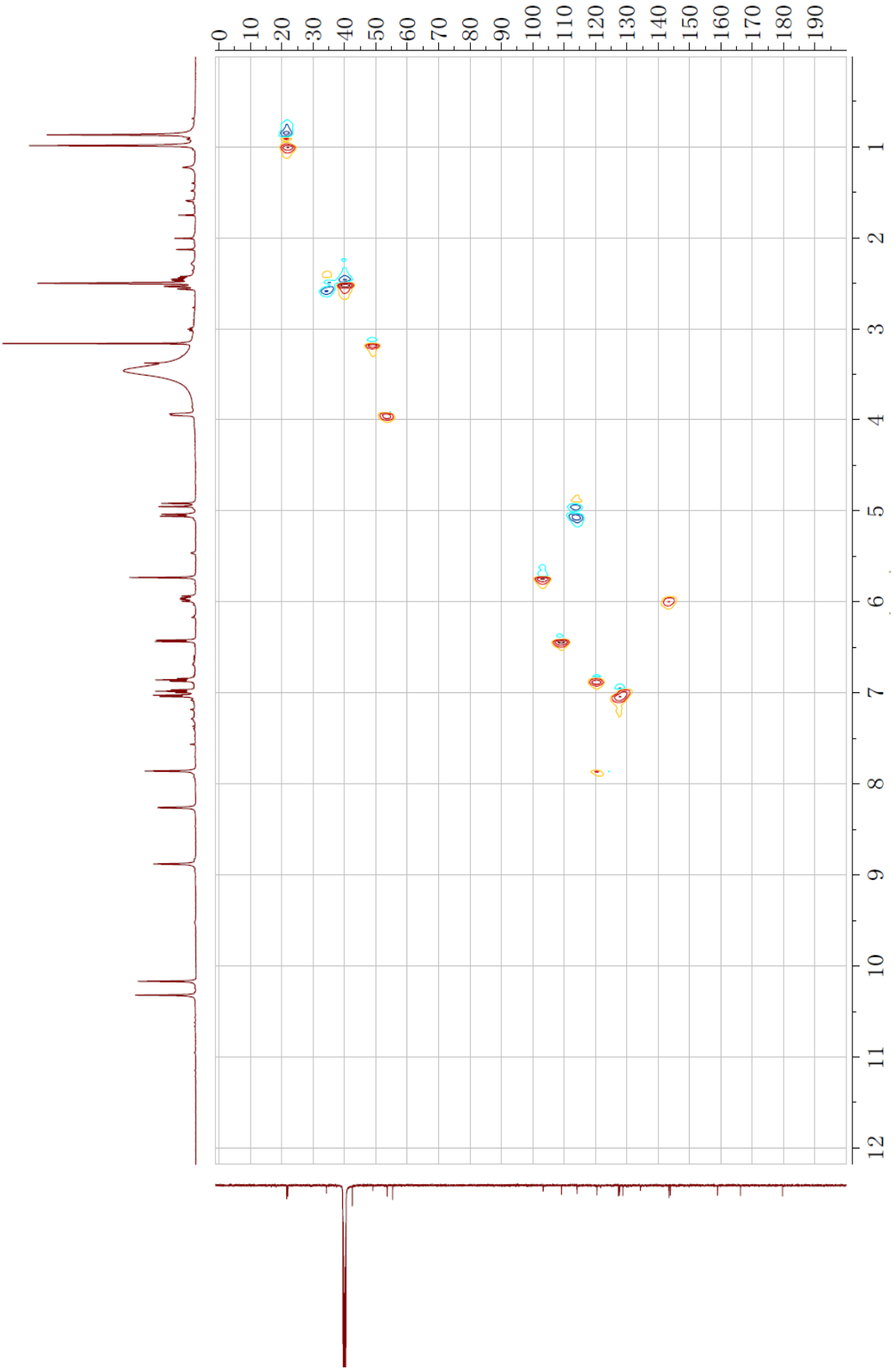


Figure S32. The ^{1}H-^{1}H COSY spectrum of penilline B (**3**) in DMSO-d_6

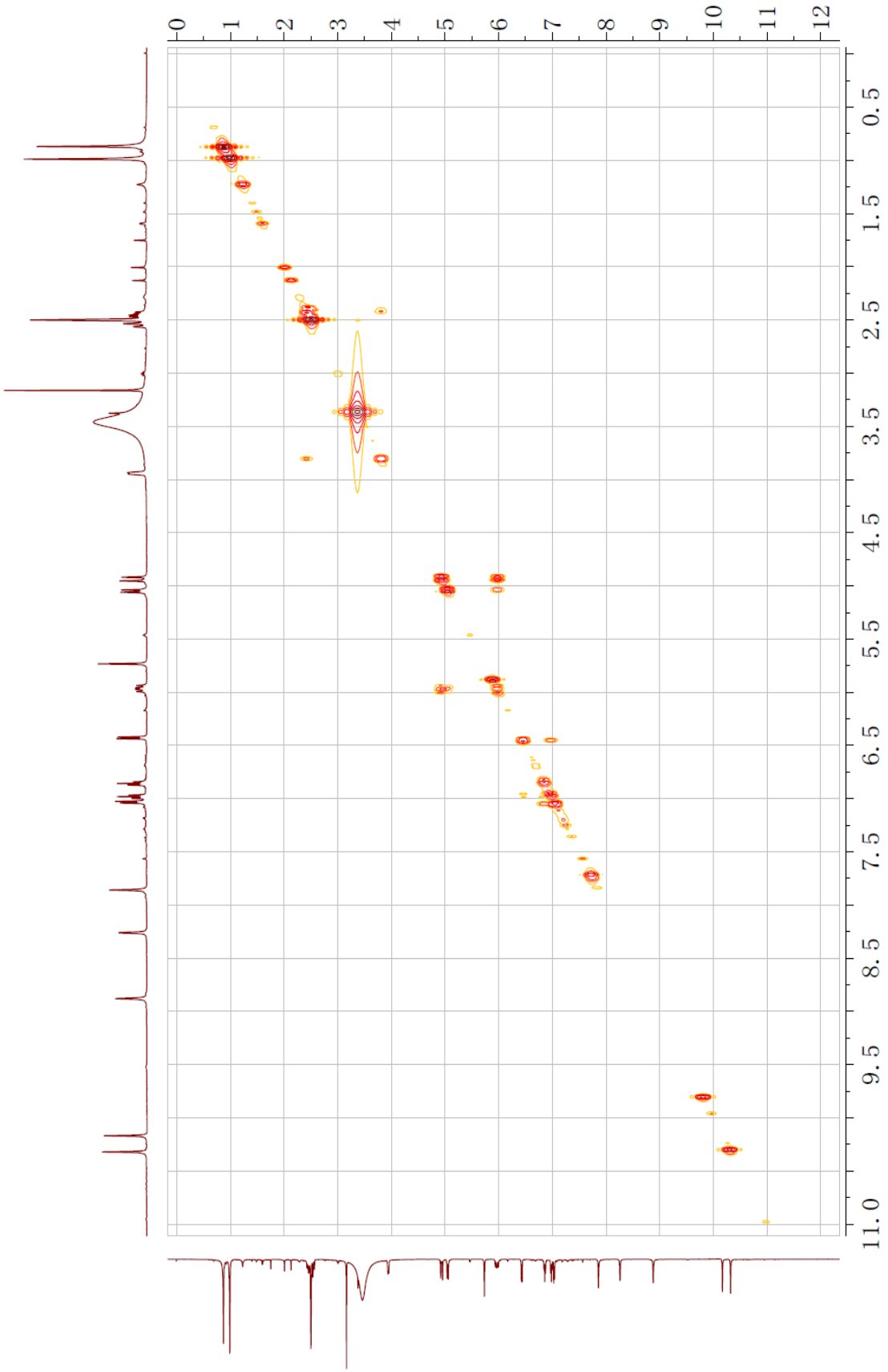


Figure S33. The HMBC spectrum of penilline B (**3**) in DMSO-d_6

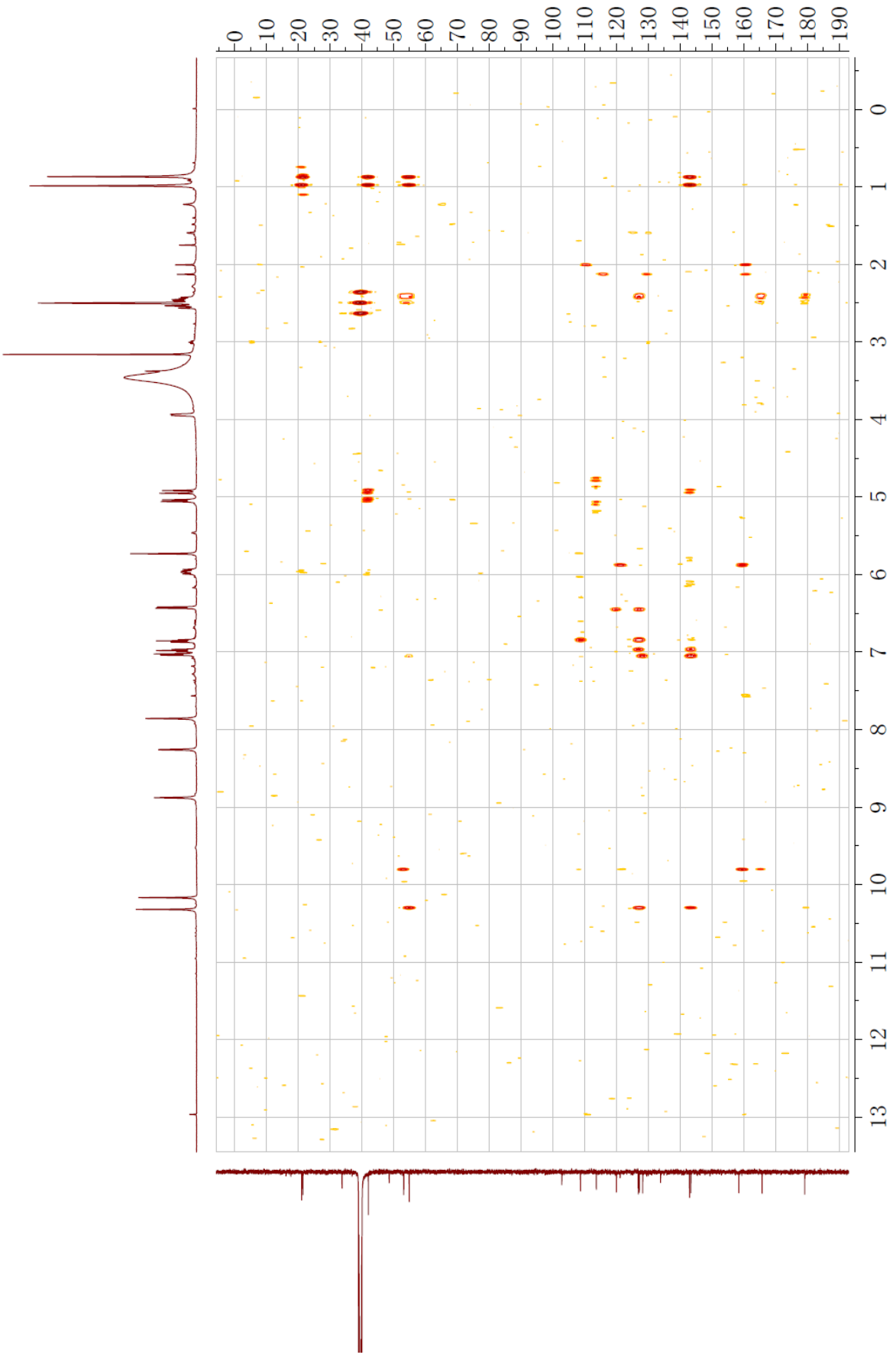


Figure S34. The NOESY spectrum of penilline B (**3**) in DMSO-d_6

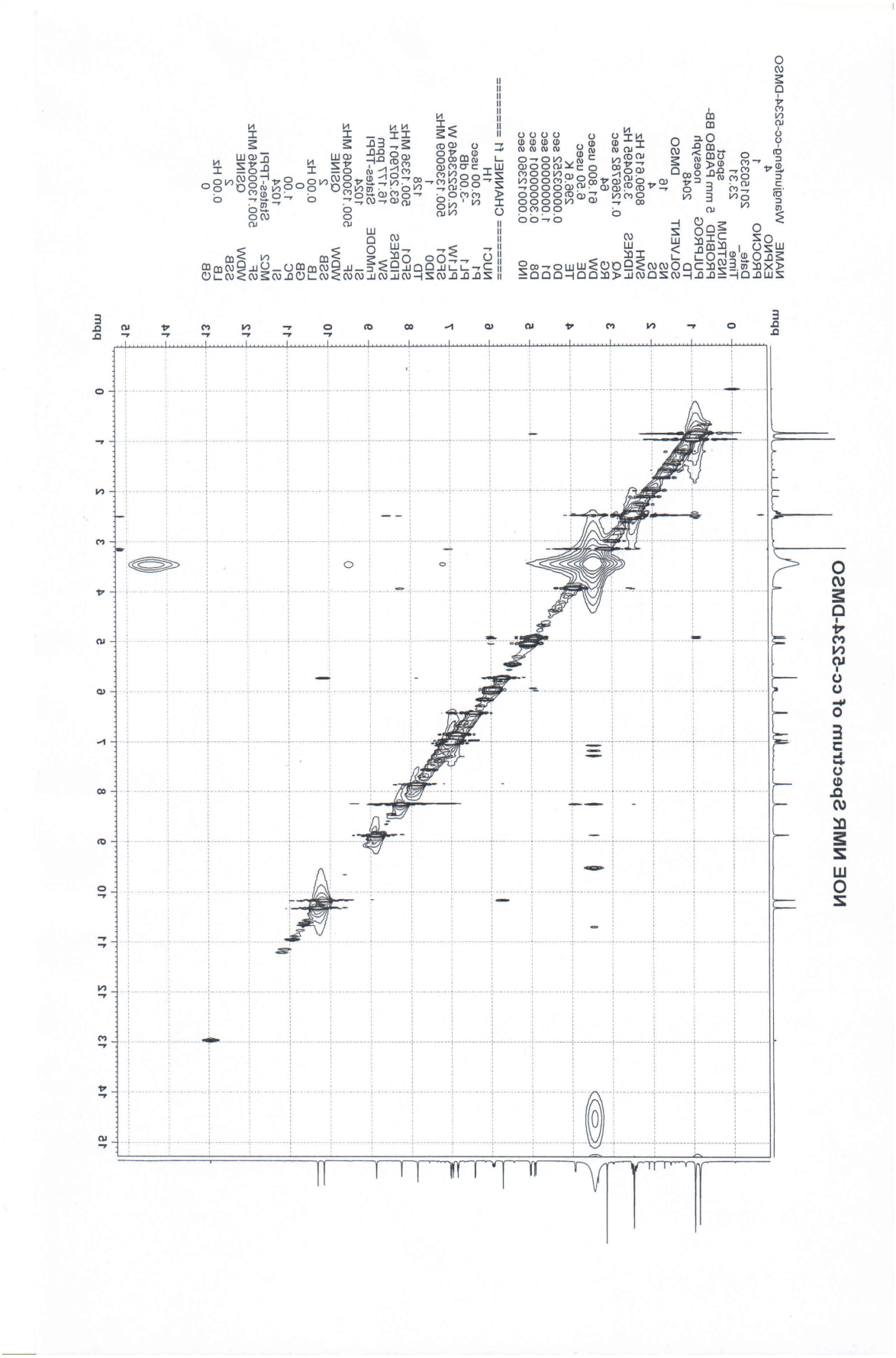


Figure S35. The HRESIMS spectrum of penilline B (**3**)

Figure S36. The UV spectrum of penilline B (**3**)

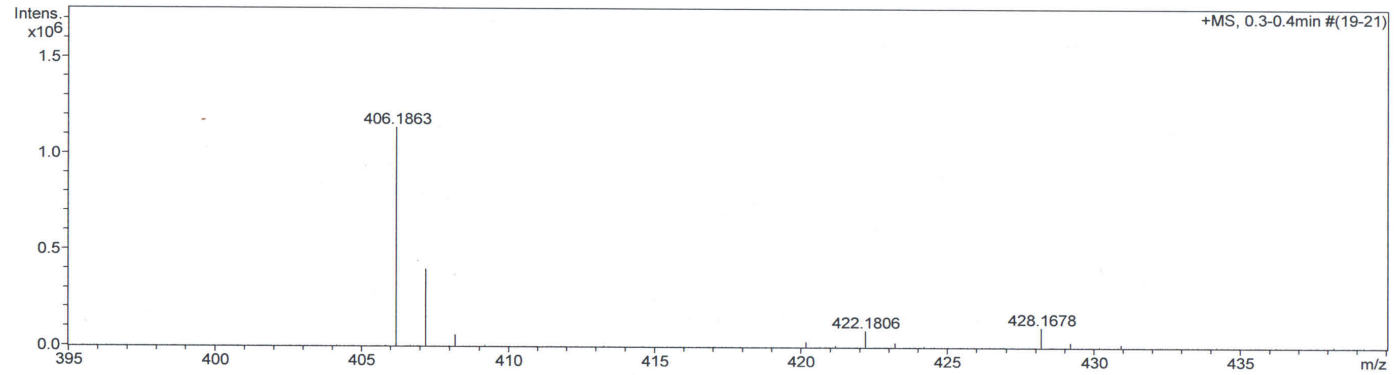
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\MS\data\201503\wangjunfeng_CC-5234_pos.d	Acquisition Date	3/30/2015 9:30:54 AM
Method	POS_100-2000_Direct Infusion.m	Operator	SCSIO
Sample Name	SCSIO	Instrument / Ser#	maXis 29
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Waste

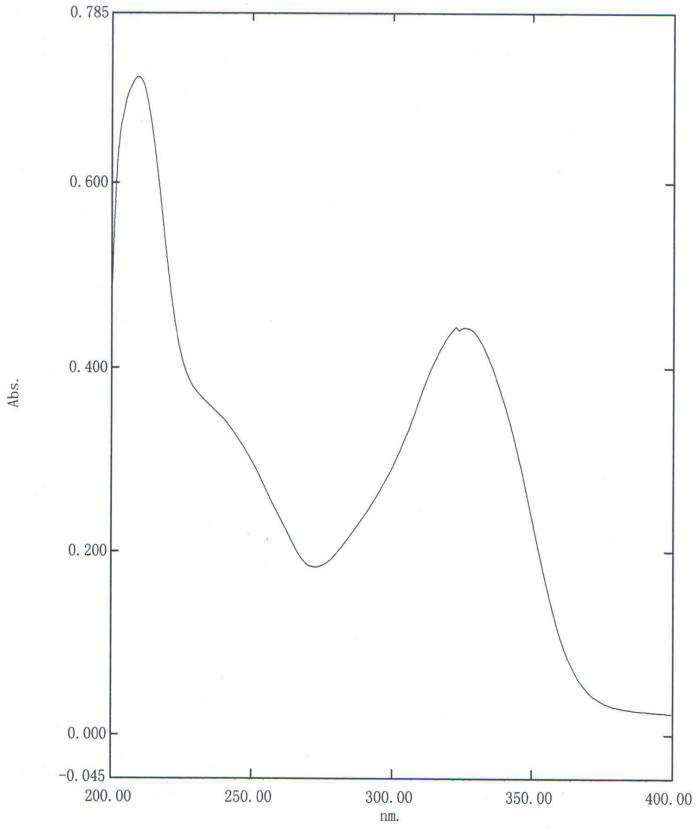


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
406.1863	1	C 22 H 24 N 5 O 3	100.00	406.1874	1.1	2.7	54.8	13.5	even	ok
428.1678	1	C 22 H 23 N 5 Na O 3	100.00	428.1693	1.5	3.4	6.8	13.5	even	ok

光谱峰值检测报告

2015-04-30 15:29:46

数据集: CC-5234 - RawData



[测定属性]
波长范围 (nm.): 200.00 到 400.00
扫描速度: 中速
采样间隔: 0.2
自动采样间隔: 启用
扫描模式: 单个

[仪器属性]
仪器类型: UV-2600 系列
测定方式: 吸收值
狭缝宽: 2.0
积分时间: 0.1 秒.
光源转换波长: 323.0 nm
检测器单元: 直接
S/R 转换: 标准
阶梯校正: OFF

[附件属性]
附件: 无

[数据处理参数]
阈值: 0.0100000
点: 4
内插: 停用
平均: 停用

[样品准备属性]
重量:
体积:
稀释:
光程长:
附加信息:

No.	P/V	波长(nm)	吸收值	描述
1	↑	325.80	0.444	
2	↑	209.20	0.716	
3	↓	272.60	0.183	