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Figure S36. The UV spectrum of p	enilline B (3)	

No.		2		3
	$\delta_{ m C}$	$\delta_{\rm H} (J {\rm in} {\rm Hz})$	$\delta_{ m C}$	$\delta_{\rm H} \ (J {\rm in} {\rm Hz})$
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 S1. ¹H and ¹³C NMR Data for **2** and **3** (500, 125 MHz, CD₃OD, TMS, δ ppm).

Table S2. Relative and free energies^{*a*} and equilibrium populations^{*b*} of low-energy conformers of 1 and 3

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

in MeOH.

(3 <i>R</i> ,10 <i>S</i>)-1e ^{<i>c</i>}	2.70	3.49	0.2
Compound 3			
(3 <i>R</i> ,10 <i>S</i>)- 3 a	0.00	0.00	46.5
(3 <i>R</i> ,10 <i>S</i>)- 3 b	0.71	0.01	46.0
(3 <i>R</i> ,10 <i>S</i>)- 3 c	1.04	1.42	4.2
(3 <i>R</i> ,10 <i>S</i>)- 3d	2.10	1.97	1.7
(3 <i>R</i> ,10 <i>S</i>)- 3e ^{<i>c</i>}	2.55	2.18	1.2
(3 <i>R</i> ,10 <i>S</i>)- 3f ^{<i>c</i>}	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.



3d

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

-4500	-4000	-3500	-3000	-2500	-2000	-1500	0001	-1000	-500	0-	
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0010:0											0. 2
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-2, 3975 -2, 4126 -2, 5108										₹ <u>-</u> 1	.0.1 .0.
-2.5400 -2.5400											
+2087 2 -3.4934 -3.4934											
											2
4.9432											1. 30 4
8990 9 8880 :g											2. 2 2. 1 2. 1
9200 9 9-10-9 9-12-00-000-00 9-12-00-000-00-000-000-000-000-000-000-00											86 '0- 86 '0-
9088 [.] 9 9268 [.] 9-											0.1 0.5
1966 9- 8781 27 9961 2											ت ت 2.2
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9216.8—											6.0-
											6
											0.2
1199 01-											- 1° 00
											11.5

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

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71 69 18	134 145													_		140
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99	·691-															160
65 42	-165. 27172															170
																180
																190
																200
																210

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



Figure S6. The ¹H-¹H 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)



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

S13

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数据集: CC-5235 - RawData

Abs.

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UV-2600 系列

吸收值 2.0 0.1 秒.

323.0 nm

直接

标准

OFF

无

4 停用 停用

0.0100000





No.	P/V	波长(nm)	吸收值	描述
1	۲	322.60	0.764	
2	•	211.60	1.040	
3	0	277.60	0.337	

nm.

页1/1

Figure S11. The ¹H NMR spectrum of isopenilline A (2) in CD₃OD

S14

-5500	-5000	-4500	-4000	-3500	-3000	-2500	-2000	-1500	-1000	-500	0-	500
												0.5 0.0
-1266 .0- -1- 0780											53 ₹ 96	1.5 1.0
ר <mark>5: ∳623</mark> ר2: ∲602 ר2: ∲615												5 2.0
-5. 5091 -2. 7344 -2. 7305 -2. 7305 -2. 7505	Ī										-20 -20 -20 -20 -20 -20 -20 -20 -20 -20	3.0 0.
~3. 5254 ~3. 5254	>										F-06	.0 3.5
0826 . •												4.5 4
6200 ·9- 972 · 0248 9960 ·9-	<u> </u>										13 ⁷	5.5 5.0
22: 0325 -9: 0325 -9: 0244 -9: 0244										=	≤ F00	6.0
1990 2- 1990 2- 1990 2-	-										F-86	<u></u>
-7. 7175 -7. 3136 -7. 3190	-										¥ 1-92 1-92 1-93	0 7.5
												8.5 8.(
												5 9.0
												<u>о</u> .

Figure S12. The ¹³C NMR spectrum of isopenilline A (2) in CD₃OD

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																			- 10
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																			30
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₽2	.64–										_								0
29	~24 [.]																		- 10
44	99																		60
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																			- 06
																			- 00
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0.00 0.00 8.22																_			0 1
14 .8	212 212															_			- 12
86.6	~15. 715																		130
10 · 8																			140
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																			0
22.1	91-																_		16
00 8	191																		170
08.30	iZI—																		180
																			- 06
																			16

Figure S13. The HMQC spectrum of isopenilline A (2) in CD₃OD



Figure S14. The ¹H-¹H COSY spectrum of isopenilline A (2) in CD₃OD



Figure S15. The HMBC spectrum of isopenilline A (2) in CD₃OD



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

0006-	-8000	-7000	-6000	-5000	-4000	-3000	-2000	-1000		>	
											0.0
0256 7259 7	0~		-							3* 10 <u>-</u> 3* 00	1.0
0228 9848 6998 4128 8909	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2		-						E C	≖90 °I ≖66 °0	2.0
46458 1828 1828 1828	2- 7 7										3.0
											4.0
6996 2066 8620 8191 8896			-							1. 22 . ∎. 22 .	5.0
729£ . 0029	97 97		-						={	<u>∓-81.1</u>	6.0
0298 9107 9107 9107 9208 9208	9 2 2 2 2 2 2 2 2 2 2 2 2 2		<u> </u>							0.93 1.02 1.02 1.02 1.02	7.0
8106	L—									<u>∓-00 .</u> [8.0
											9.0
											10.0
									1		

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

-100000 -90000	-80000	-70000			-10000)
							- 0
							- 10
<u>- 66.15</u>							- 0
21.92							
-36.38						_	с С
42.18							40
-25.66							20 -
							- 09
							20
							- 8
							- 06
							- 8
−10∛ 01 −100 82							0 1
∠114. 29 ∠114. 29							0
124.24							12
-130.43							130
172.67 7142.67 7143.17							140
							150
-128.59							160
-164.43							170
68.271-						-	- 8
							90

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



Figure S19. The ¹H-¹H 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)

			Mass	Spectru	um Sm	artForn	nula	Repo	Ľ			
Analysis Info								Acquisit	ion Date	3/23/2015	9:16:46 AM	
Method Sample Name Comment		0 Dirrect	Infusion.m	eng_cc-4113	p.sod			Operato	r ent / Ser#	SCSIO maXis	29	
Acquisition P. Source Type Focus Scan Begin Scan End	arameter ESI Not active 100 m/z 2500 m/z		ັດ ທີ່ ທີ່ ດີ	n Polarity et Capillary et End Plate Of st Collision Cell	fset I RF	Positive 4500 V -500 V 2000.0 Vpp			Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve		0.3 Bar 180 °C 4.0 <i>l/</i> min Waste	
Intens. x10 ⁵ 2.0-											+MS, 0.5-0.5mir	ר28-30) #
									445.1685			
1.0-1		422.1u	811									
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0.0	415	420	425	43		436.1944 , , , , 435			445	451.206	455	z/m
Meas. m/z # 422.1811 1 444.1629 1	Formula C 22 H 24 N 5 O 4 C 22 H 23 N 5 Na O 4	Score 100.00 100.00	m/z 422.1823 444.1642	err [mDa] 1.2 1.3	err [ppm] 2.8 2.9	mSigma 307.8 461.2	rdb 6 13.5 13.5	e [–] Conf even even	N-Rule ok ok			

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

S26

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0.339

275.20

Figure S24. The ¹H NMR spectrum of penilline B (3) in CD₃OD

3

-5000	-4500	-4000	-3500	-3000	-2500	-2000	-1500	-1000	-500	0	
-0.9413 										3. 31 ⊾ 3. 32 J	1.5 1.0 0.5
2. 6308 2. 6449 2. 6449 2. 7911 2. 7881 2. 7911 2. 7849 2. 7911 2. 6303 2. 6307 2. 6449 2. 7567 2. 7576 2. 7576 2. 7576 2. 7576 2. 7576 2. 7576 2. 7576 2. 7576 2. 7576 2. 75767 2. 7576 2. 75										F-00.1	3.5 3.0 2.5 2.0
4. 2107 4. 2107 4. 2193										5 ≖-90 .I	0 4.5 4.0
E6+0 · S J / 69 · S I E26 · S 8+66 · S 6200 · 9-										<u>I-141.1</u> 1.02-± 5	6.0 5.5 5.
6687 9 1267 9 1267 9 1267 9 1267 9 1267 9 127										1. 10 1. 09 1. 09 1. 00 1. 10 1. 00 1. 10 1. 10 1	.5 7.0 6.5
-7. 6356										1.02-≖ 5	8.5 8.0 7
											9.5 9.0

Figure S25. The ¹³C NMR spectrum of penilline B (3) in CD₃OD

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<u>96</u> :	291-	-															_					170
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Figure S26. The HMQC spectrum of penilline B (3) in CD₃OD



Figure S27. The ¹H-¹H COSY spectrum of penilline B (3) in CD₃OD



Figure S28. The HMBC spectrum of penilline B (3) in CD₃OD



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

1. 13 x 2. 101 ± 3. 1. 05 ± 1. 11 x 1. 11 x 1. 10 ± 1. 00 ±		-1100		-600	-200	-100	. 5 0. 5
						P	20.1 2.1.13
	;					F	-20.1-
						P	.5 1.19
	:9 -9 -9 -9 -9 -9 -9 -9 -9 -9 -9 -9 -9 -9						21 -0.99- -0.99- -1.10- 0.92- -1.007
	9 9 2 2 2 2						-00-1 -05- -05- -1.05- -05- -05- -05- -05- -05- -05- -05-
	<u>8.8–</u> 2.2					- I	21 <u>1.06-</u> 8 <u>1.06-</u>
	-10.1						10.5 0.94

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

-120000	-110000	-100000	-90006	-80000	-70000	-60000	-50000	-40000	-30000	-20000	-10000	- 0-	10000
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81.6	21-												
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Figure S31. The HMQC spectrum of penilline B (3) in DMSO- d_6



Figure S32. The ¹H-¹H 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)

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数据集: CC-5234 - RawData



No.	P/V	波长(nm)	吸收值	描述
1	۲	325.80	0.444	
2	۲	209.20	0.716	
3	0	272.60	0.183	

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