Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Maoeriocalysins A–D, four novel *ent*-kaurane diterpenoids from *Isodon eriocalyx* and their structure determination utilizing quantum chemical calculation in conjunction with quantitative interproton distances analysis

Qian Yang,[a,b,‡] Kun Hu,[a,‡] Bing-Chao Yan,[a] Miao Liu,[a] Xiao-Nian Li,[a] Han-Dong Sun,[a] and Pema-Tenzin Puno[a,*]

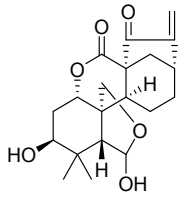
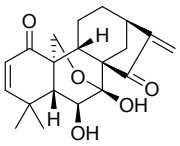
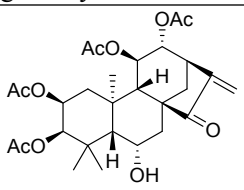
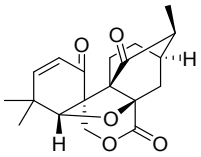
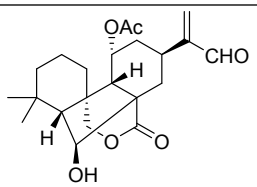
[a] State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, Yunnan, People's Republic of China.
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

[‡] These authors contributed equally to this work.
Corresponding authors. E-mail: punopematenzin@mail.kib.ac.cn

CONTENT

1. The structures of several previously reported *ent*-kaurane diterpenoids from *Isodon* species.

Table S1 Representative *ent*-kaurane diterpenoids previously reported from *Isodon* species that are interesting with aspect to their structures, bioactivities, and organic synthesis.

				
enmein	eriocalyxin B	isoforretin A	maoecrystal V	maoecrystal Z
Enmein type (1,7-lactone) *Acta Crystallogr*, **1966**, *20*, 197.	7,20-epoxy-*ent*-kaurane *Chem. Pharm. Bull.*, **1976**, *24*, 2118.	C-20 non-oxygenated *ent*-kaurane *Cancer Res.*, **2017**, *77*, 926–936.	6,7-Seco-6-nor-15(8→9)-*ent*-kaurane *Org. Lett.*, **2004**, *6*, 4327–4330.	6,7-Seco-8,15-seco-6,8-cyclo-e*nt*-kaurane *Org. Lett.*, **2006**, *21*, 4727–4730.

2. Key 2D NMR correlations of 2–4.

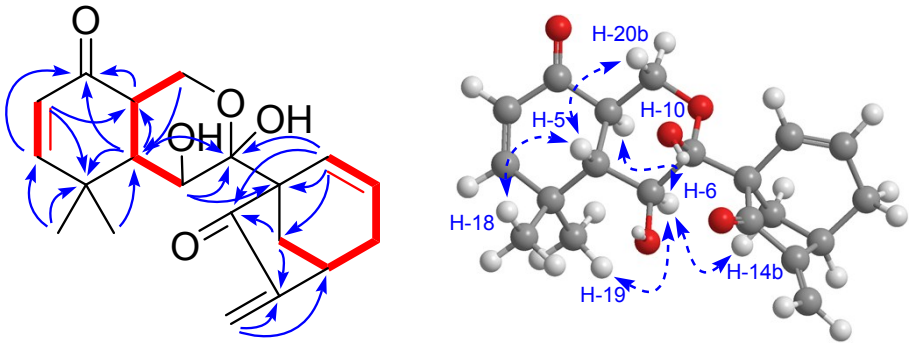


Figure S1 ^{1}H-^{1}H COSY (▬), key HMBC (H→C), and ROESY correlations of **2**.

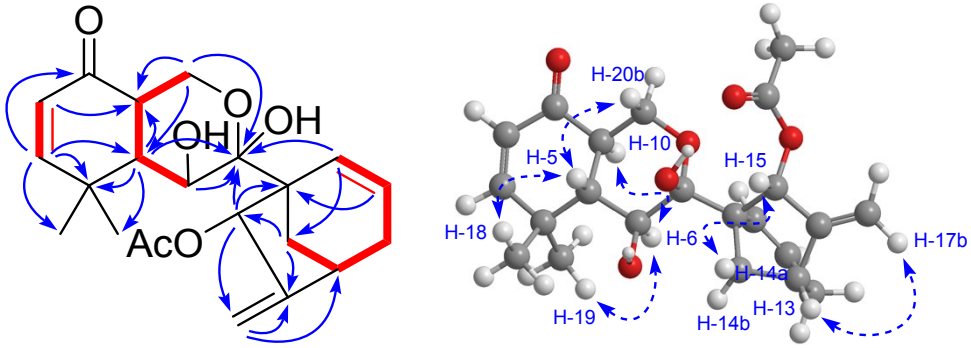


Figure S2 ^{1}H-^{1}H COSY (▬), key HMBC (H→C), and ROESY correlations of **3**.

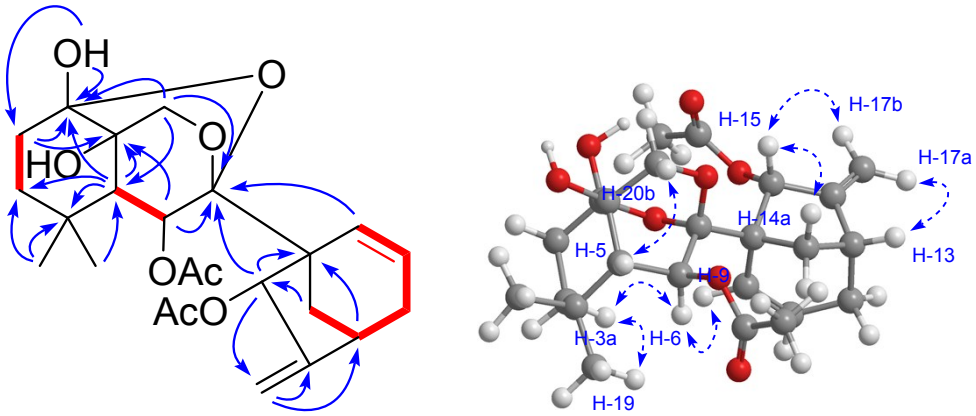
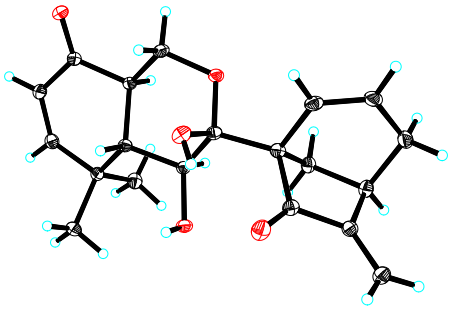


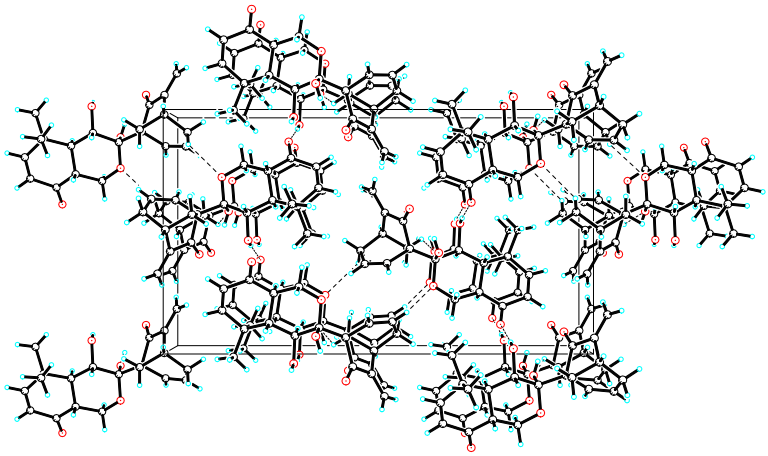
Figure S3 ^{1}H-^{1}H COSY (▬), key HMBC (H→C), and ROESY correlations of **4**.

3. X-ray crystallographic analysis of 2.

Crystal Data for maoeriocalysin B (**2**). Crystal data for **2**_0m: $C_{20}H_{24}O_5$, M = 344.39, a = 6.1036(4) Å, b = 12.5506(7) Å, c = 21.9760(13) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, V = 1683.45(18) Å^3, T = 100(2) K, space group $P212121$, Z = 4, μ(CuKα) = 0.792 mm^{-1}, 18010 reflections measured, 3157 independent reflections (R_{int} = 0.0539). The final R_1 values were 0.0353 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0939 ($I > 2\sigma(I)$). The final R_1 values were 0.0356 (all data). The final $wR(F^2)$ values were 0.0942 (all data). The goodness of fit on F^2 was 1.072. Flack parameter = 0.07(5).



View of a molecule of maoeriocalysin B (**2**) with the atom-labelling scheme.
Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of maoeriocalysin B (**2**).
Hydrogen-bonds are shown as dashed lines.

Note: Crystal data and structure refinement for cu_ maoeriocalysin B (2) _0m.

Identification code	cu_ Maoeriocalysin B (2) _0m	
Empirical formula	$C_{20}H_{24}O_5$	
Formula weight	344.39	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.1036(4) Å	α= 90°.
	b = 12.5506(7) Å	β= 90°.
	c = 21.9760(13) Å	γ = 90°.
Volume	1683.45(18) $Å^3$	
Z	4	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	0.792 mm^{-1}	
F(000)	736	
Crystal size	0.850 x 0.450 x 0.010 mm^3	
Theta range for data collection	4.023 to 70.204°.	
Index ranges	-7<=h<=7, -15<=k<=14, -26<=l<=26	
Reflections collected	18010	
Independent reflections	3157 [R(int) = 0.0539]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3157 / 0 / 234	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0939	
R indices (all data)	R1 = 0.0356, wR2 = 0.0942	
Absolute structure parameter	0.07(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.280 and -0.184 $e.Å^{-3}$	

4. Results of the calculated ^{13}C and ^{1}H chemical shifts of possible candidates.

4.1 Results of DFT calculated ^{13}C and ^{1}H chemical shifts of 1.

Table S1 Results of DFT calculated ^{13}C shifts of **1**.

No.	Experimental (δ_C, ppm)	Calculated (δ_C, ppm)
1	204.8	196.4
2	127.1	123.6
3	179.8	180.8
4	72.1	69.9
5	53.9	53.0
6	73.9	71.9
7	97.6	95.4
8	51.8	52.1
9	38.6	40.1
10	51.0	50.7
11	16.3	18.4
12	32.6	35.0
13	35.0	37.0
14	25.7	26.8
15	74.8	72.1
16	156.3	154.6
17	109.8	108.8
18	29.8	29.6
19	29.8	29.7
20	67.0	66.0
15-$\underline{OCO}CH_3$	170.9	163.9
15-$OCO\underline{CH_3}$	21.7	22.7
R^2		**0.9989**
MAE		**2.0**
CMAE		**1.4**

Table S2 Results of DFT calculated ^{1}H shifts of **1**.

No.	Experimental (δ_H, ppm)	Calculated (δ_H, ppm)
2	5.86	5.91
5	3.48	3.69
6	4.28	4.33
9	2.52	2.46
11a	2.07	2.17
11b	1.73	1.69
12a	2.23	2.09
12b	1.48	1.50
13	2.71	2.61
14a	2.03	1.90
14b	1.60	1.20
15	5.62	5.76
17a	5.11	5.44
17b	4.85	5.23
18	1.56	1.50
19	1.55	1.51
20a	4.12	4.00
20b	3.78	3.72
15-OCO$\underline{CH_3}$	2.13	2.19
R^2		**0.9917**
MAE		**0.13**
CMAE		**0.11**

4.2 Results of DFT calculated ^{13}C and ^{1}H chemical shifts of 3a and 3b.

Table S3 Results of DFT calculated ^{13}C shifts of **3a** and **3b**.

No.	Experimental (δ_C, ppm)	Calculated (δ_C, ppm)	
		3a	**3b**
1	198.2	189.5	191.5

2	124.8	122.0	122.4
3	162.2	158.9	159.9
4	36.0	36.6	37.2
5	48.4	47.2	51.1
6	70.6	70.5	71.9
7	98.0	96.0	95.7
8	52.8	54.2	56.0
9	130.2	129.9	127.9
10	43.4	43.3	39.2
11	128.5	126.6	131.5
12	38.5	40.5	40.5
13	37.6	39.7	38.2
14	33.7	35.4	32.7
15	80.4	80.1	80.7
16	152.2	149.9	150.4
17	108.7	107.6	106.7
18	31.1	31.4	29.5
19	20.1	21.3	22.3
20	58.9	59.0	60.8
15-$\underline{OCO}CH_3$	173.8	168.0	167.7
15-$OCO\underline{CH_3}$	21.3	22.3	22.2
R^2		**0.9995**	**0.9984**
MAE		**1.8**	**2.4**
CMAE		**1.0**	**1.7**

Table S4 Results of DFT calculated ^{1}H shifts of **3a** and **3b**.

No.	Experimental (δ_H, ppm)	Calculated (δ_H, ppm)	
		3a	**3b**
2	5.81	5.85	5.82
3	6.52	6.82	7.06
5	2.15	2.14	1.78

6	3.63	3.70	3.90
9	5.95	6.45	6.42
10	2.41	2.33	3.11
11	5.76	5.98	6.23
12a	2.51	2.48	2.48
12b	2.08	2.05	2.07
13	2.89	2.72	2.72
14a	2.03	2.22	2.49
14b	1.93	1.84	1.71
15	5.83	5.72	6.57
17a	5.13	5.45	5.37
17b	5.04	5.43	5.31
18	1.39	1.41	1.40
19	1.17	1.23	1.19
20a	3.93	3.84	4.06
20b	3.70	3.57	3.73
15-OCO$\underline{CH_3}$	2.09	2.07	2.07
R^2		**0.9927**	**0.9828**
MAE		**0.14**	**0.26**
CMAE		**0.12**	**0.17**

4.3 Results of DFT calculated ^{13}C and ^{1}H chemical shifts of 4a–4e.

Table S5 Results of DFT calculated ^{13}C shifts of **4a**–**4e**.

No.	Experimental (δ_C, ppm)	Calculated (δ_C, ppm)				
		4a	**4b**	**4c**	**4d**	**4e**
1	97.0	95.4	80.2	79.1	78.7	79.0
2	29.3	30.7	27.9	29.7	28.0	28.6
3	33.7	33.0	38.4	38.0	36.7	35.2
4	32.2	32.9	31.8	32.4	32.6	32.1
5	56.0	54.6	44.4	46.3	48.3	51.1
6	69.9	67.9	71.6	70.9	69.2	67.7
7	97.9	95.7	96.4	98.0	94.4	94.9

8	51.4	53.7	56.4	53.7	56.0	53.7
9	128.9	128.6	132.4	131.1	132.0	131.4
10	68.7	66.6	64.0	60.8	57.8	57.2
11	127.4	126.4	120.7	122.8	121.1	121.8
12	38.2	40.6	39.3	37.7	39.4	39.8
13	38.6	40.2	40.0	41.4	40.0	39.3
14	32.3	34.0	33.6	34.1	33.5	32.7
15	80.7	80.5	80.1	77.9	79.9	80.7
16	153.2	150.3	152.5	155.4	152.4	149.9
17	109.9	108.6	109.6	112.5	109.4	108.0
18	28.3	28.3	33.7	31.3	31.1	30.4
19	29.8	30.3	21.4	21.8	23.5	25.1
20	67.3	66.0	62.9	65.8	56.1	60.9
6-$\underline{OCO}CH_3$	168.5	161.3	163.8	163.7	165.5	162.1
6-OCO$\underline{CH_3}$	21.6	22.2	23.3	23.9	23.2	22.9
15-$\underline{OCO}CH_3$	174.0	169.7	167.5	161.8	167.1	168.4
15-OCO$\underline{CH_3}$	21.9	23.4	22.0	21.9	22.1	22.4
R^2		**0.9992**	**0.9881**	**0.9871**	**0.9873**	**0.9908**
MAE		**1.7**	**3.9**	**4.0**	**4.1**	**3.6**
CMAE		**1.1**	**3.8**	**3.9**	**4.1**	**3.1**

Table S6 Results of DFT calculated ^{1}H shifts of **4a**–**4e**.

No.	Experimental (δ_H, ppm)	Calculated (δ_H, ppm)				
		4a	**4b**	**4c**	**4d**	**4e**
2a	2.07	2.06	2.16	2.18	2.02	2.03
2b	1.40	1.36	1.78	1.77	1.70	1.81
3a	1.51	1.65	1.45	1.46	1.46	1.33
3b	1.30	1.20	1.03	1.15	0.90	1.19
5	1.57	1.53	2.28	1.83	1.97	1.47
6	5.23	5.37	5.49	5.33	5.24	5.25
9	5.86	6.45	6.43	6.35	6.43	6.50
11	5.73	5.98	5.75	5.70	5.78	5.81
12a	2.47	2.42	2.47	2.33	2.48	2.38
12b	2.07	2.01	1.97	1.80	2.00	1.97

13	2.82	2.66	2.66	2.70	2.67	2.69
14a	1.97	1.95	2.61	2.29	2.53	1.95
14b	1.30	1.26	1.76	2.12	1.70	1.79
15	6.27	6.54	5.63	5.68	5.69	5.73
17a	5.14	5.47	5.51	5.80	5.29	5.45
17b	4.95	5.36	5.28	5.56	5.51	5.40
18	1.22	1.26	0.89	0.76	0.84	0.90
19	1.02	0.97	1.06	1.14	1.11	1.05
20a	3.94	3.86	4.28	4.21	4.06	4.01
20b	3.76	3.71	3.19	3.75	3.85	3.77
6-OCO$\underline{CH_3}$	2.05	1.97	2.30	2.03	2.23	1.99
15-OCO$\underline{CH_3}$	2.11	2.11	2.09	2.05	2.08	2.09
R^2		**0.9956**	**0.9556**	**0.9632**	**0.9724**	**0.9784**
MAE		**0.13**	**0.31**	**0.27**	**0.24**	**0.19**
CMAE		**0.09**	**0.31**	**0.27**	**0.23**	**0.18**

5. The DFT calculated key spin-spin coupling constants of 4.

Table S7 key spin-spin coupling constants of **4** ($J_{H5/H6}$ and $J_{H20a/H20b}$).

	Experimental	Calculated (J, Hz)				
	(J, Hz)	**4a**	**4b**	**4c**	**4d**	**4e**
H-5/H-6	**1.0**	1.2	10.4	6.8	8.4	0.8
H-20a/H-20b	**8.8**	8.8	11.5	11.9	11.5	11.5

6. The quantitative analysis of key interproton distances of 1 and 4.

Table S8 Key interproton distances of **1** (experimental and calculated).

H-a/H-b	Experimental interproton distances (Å)	Calculated interproton distances (Å)
H-2/H_3-19	3.00	3.14
H-5/H-9	2.18	2.20
H-20a/H-11b	2.25	2.20
H-6/H-20b	2.53	2.51
H-15/H-14b	2.45	2.37
H-15/H-17b	3.22	3.19
H-17a/H-17b	1.86	1.88
H-17a/H-13	2.78	2.69
MAD		**0.06**
STD		**0.43**

Table S9 Key interproton distances of **4** (experimental and calculated).

H-a/H-b	Experimental interproton distances (Å)	Calculated interproton distances (Å)				
		4a	**4b**	**4c**	**4d**	**4e**
H-15/H-17b	3.13	3.07	2.94	2.68	2.93	3.15
H-15/H-14a	2.54	2.70	2.64	3.64	2.58	2.41
H-9/H-3a	2.63	2.86	8.19	6.98	8.02	7.55
H-9/H-6	2.57	2.44	4.39	3.27	4.18	3.97
H-9/H-11	2.43	2.51	2.44	2.35	2.37	2.44
H-6/H-3a	2.27	2.51	4.86	4.61	4.64	4.42
H-6/H-5	2.87	2.78	3.06	2.90	2.94	2.78
H-20b/H-5	2.46	2.36	2.43	2.69	3.14	3.13
H-17a/H-13	2.79	2.70	2.70	2.60	2.68	2.82
H-17a/H-17b	1.87	1.87	1.87	1.87	1.82	1.87
H3-19/H-3a	2.79	2.83	3.32	3.35	3.06	3.58
H3-19/H-6	2.34	2.33	3.01	2.90	2.52	3.11
MAD		**0.12**	**1.06**	**0.95**	**1.06**	**0.94**
STD		**0.30**	**1.62**	**1.27**	**1.44**	**1.32**

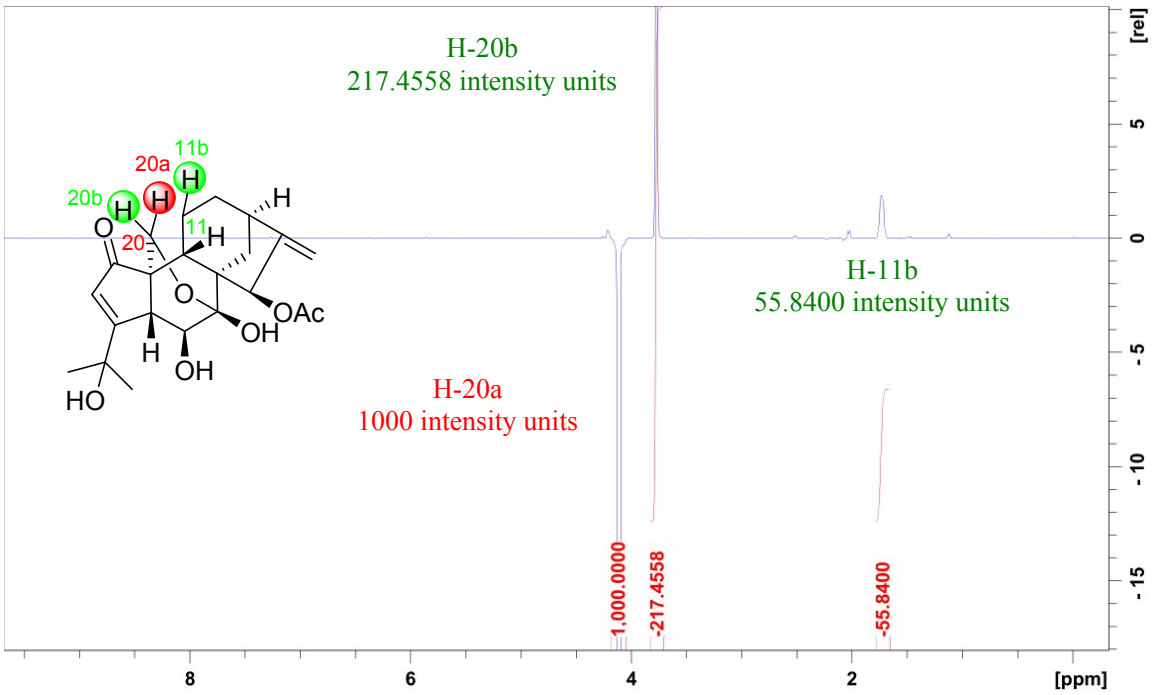


Figure S4 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-20a of **1**, with red intergrals as the intensity of each proton.

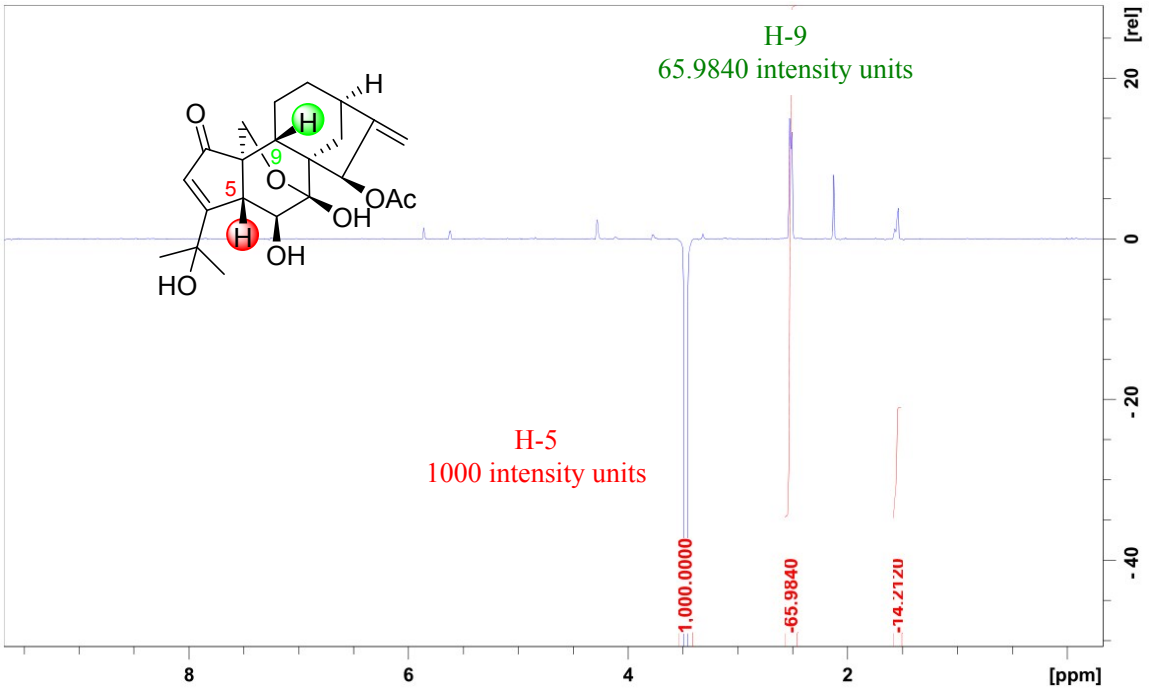


Figure S5 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-5 of **1**, with red intergrals as the intensity of each proton.

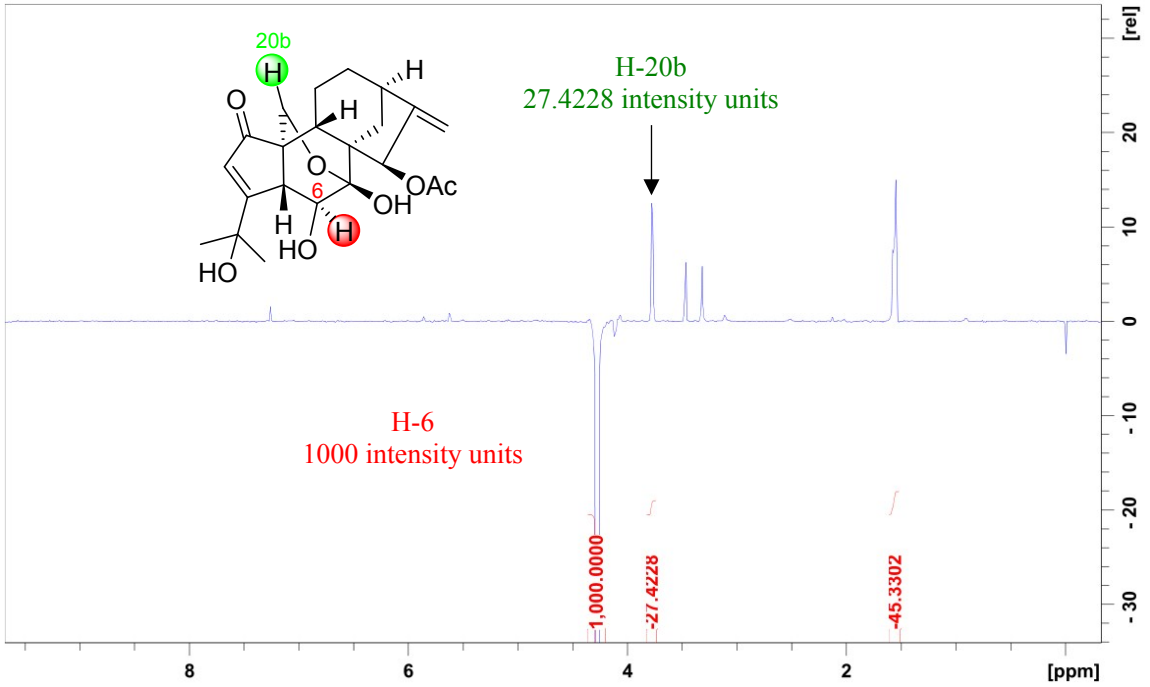


Figure S6 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-6 of **1**, with red intergrals as the intensity of each proton.

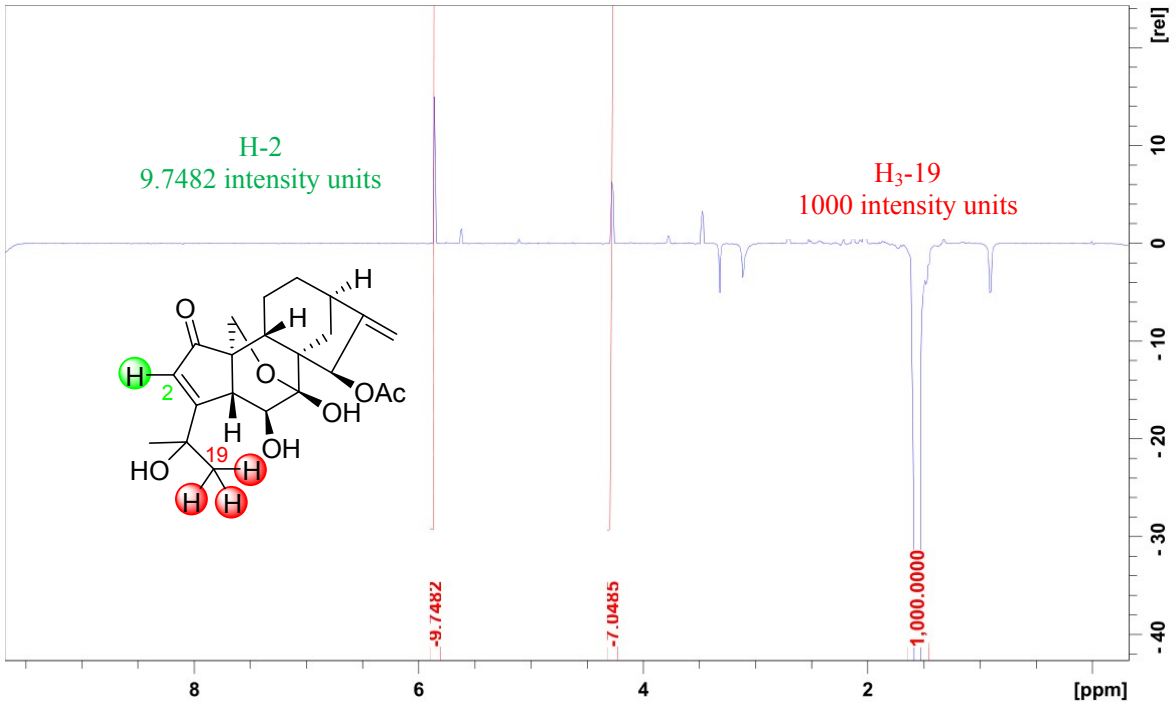


Figure S7 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H_3-19 of **1**, with red intergrals as the intensity of each proton.

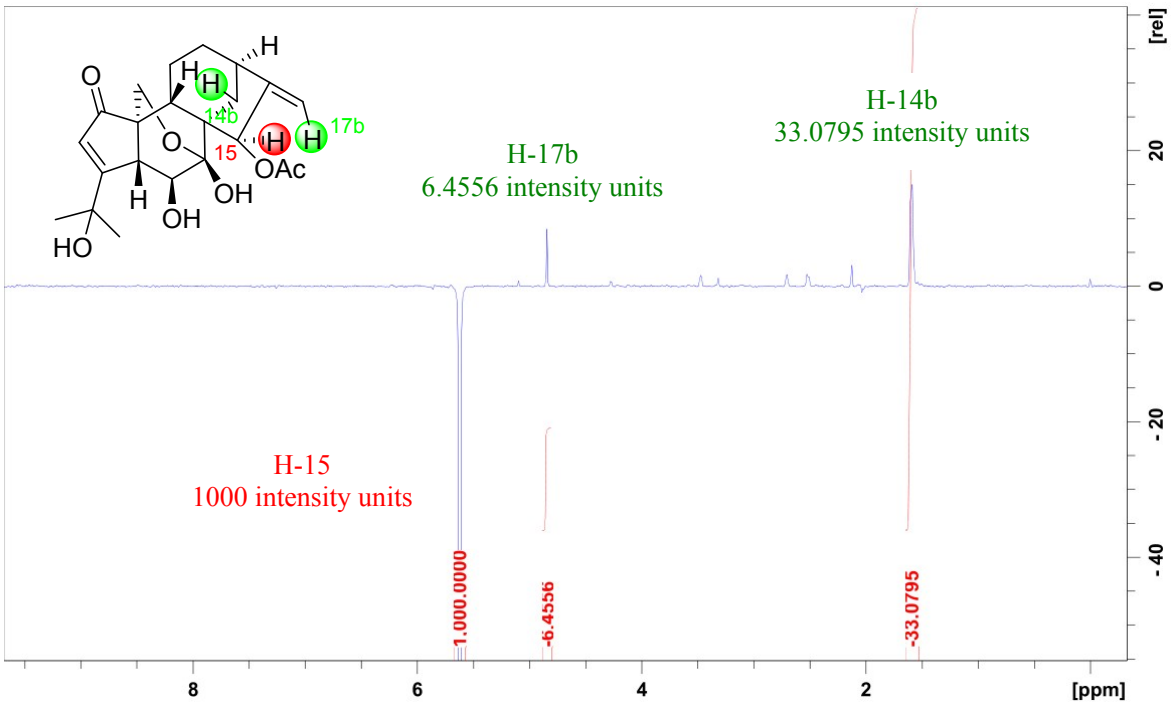


Figure S8 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-15 of **1**, with red intergrals as the intensity of each proton.

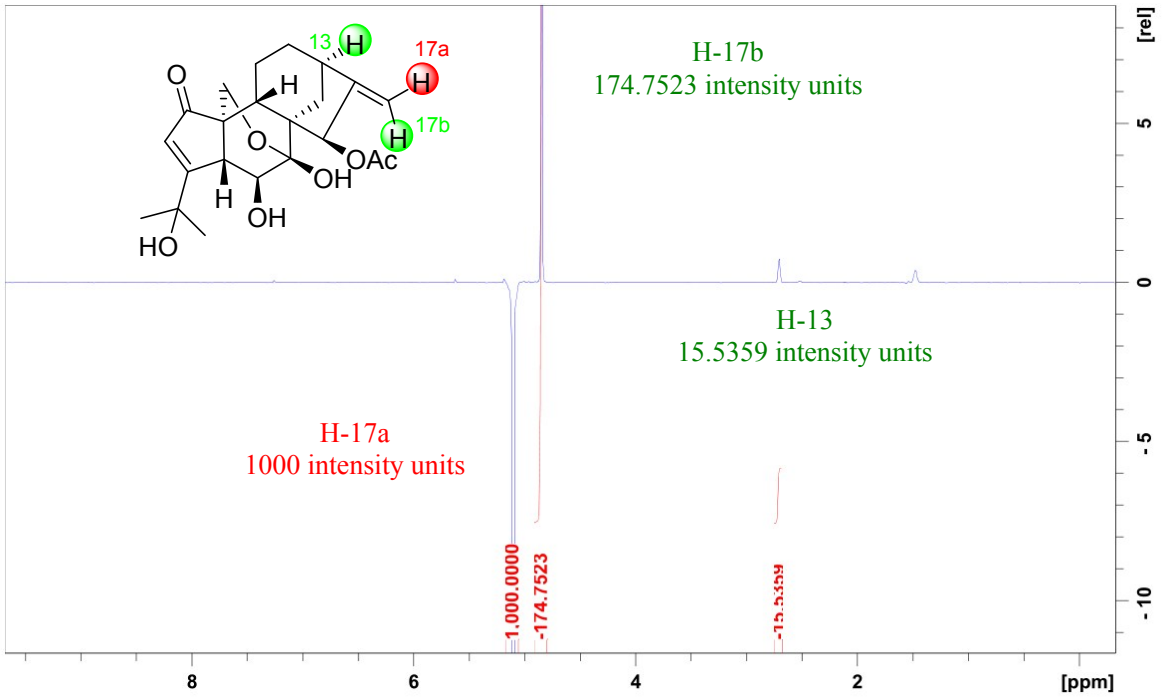


Figure S9 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-17a of **1**, with red intergrals as the intensity of each proton.

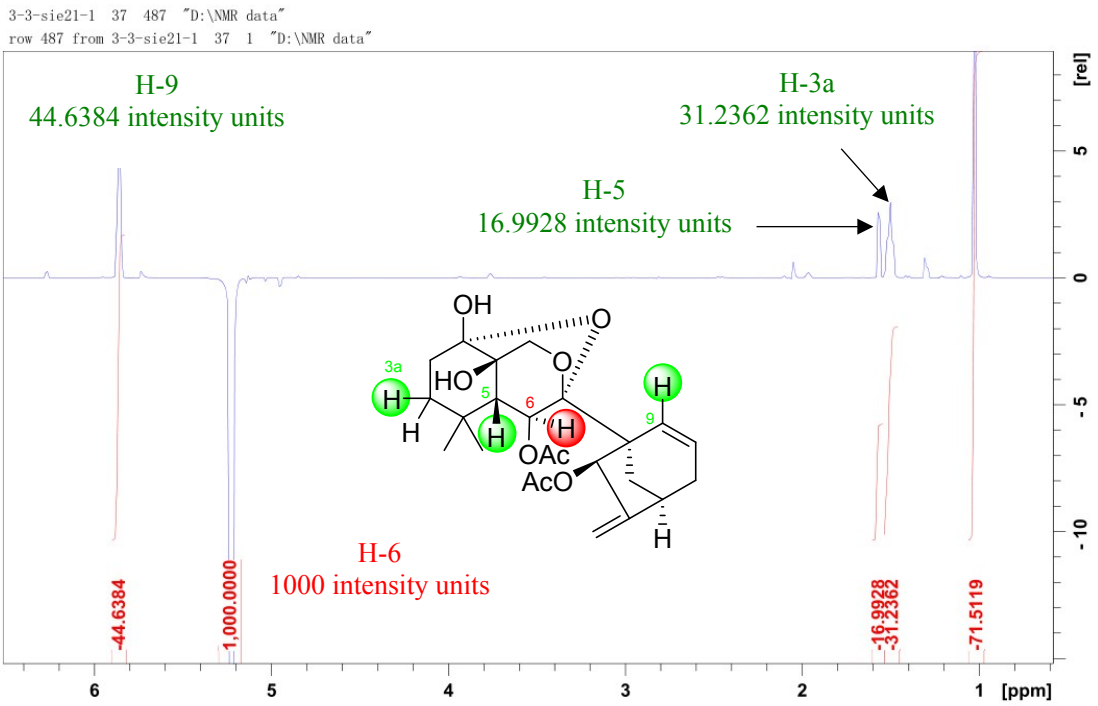


Figure S10 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-6 of **4**, with red intergrals as the intensity of each proton.

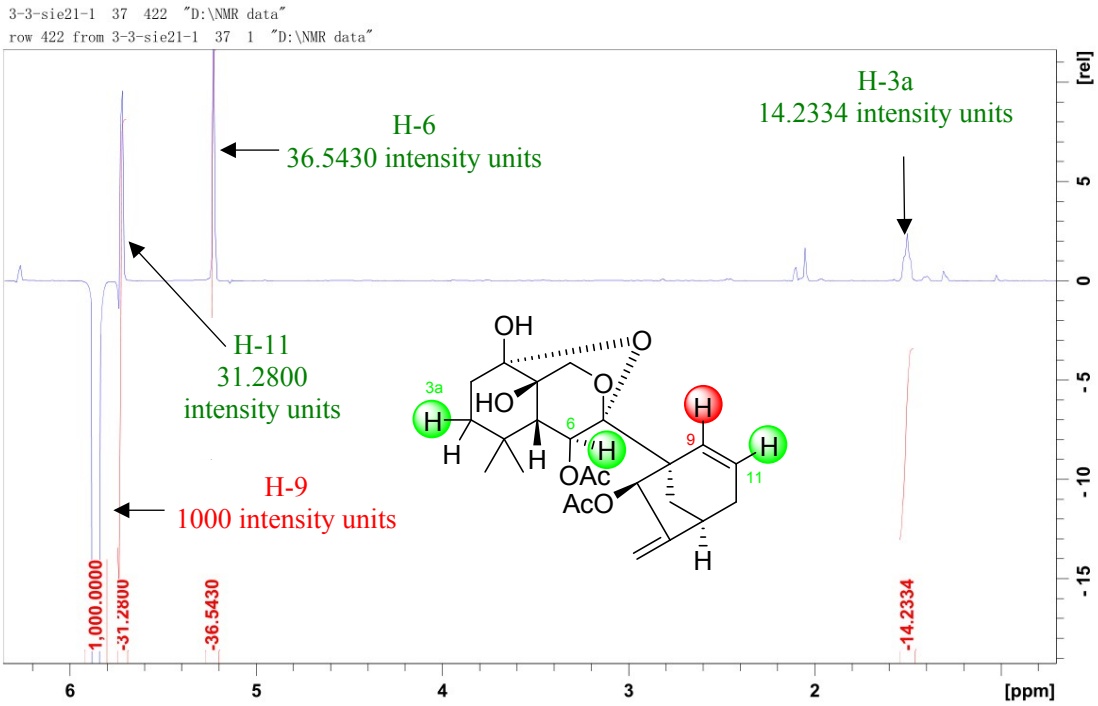


Figure S11 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-9 of **4**, with red intergrals as the intensity of each proton.

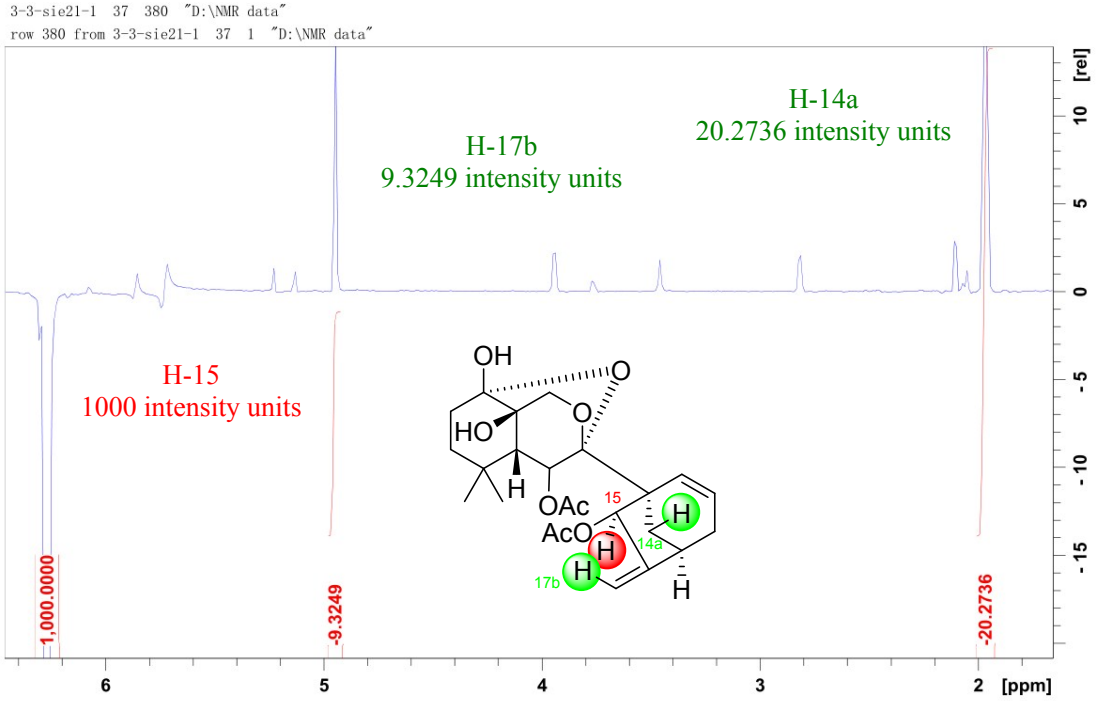


Figure S12 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-15 of **4**, with red intergrals as the intensity of each proton.

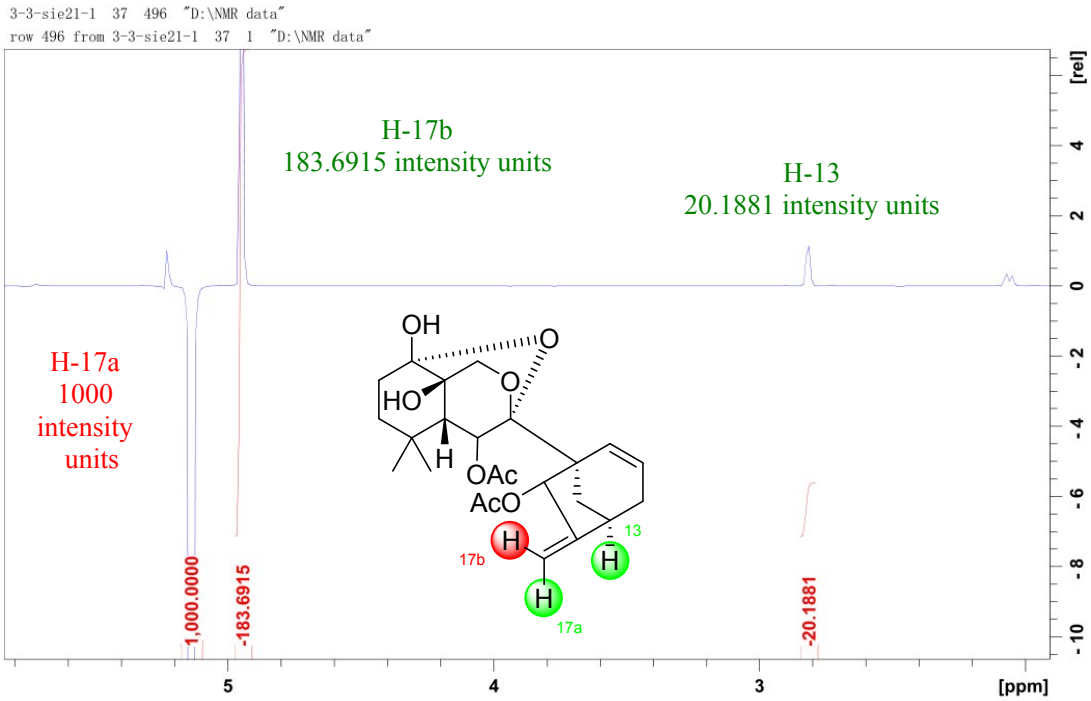


Figure S13 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-17a of **4**, with red intergrals as the intensity of each proton.

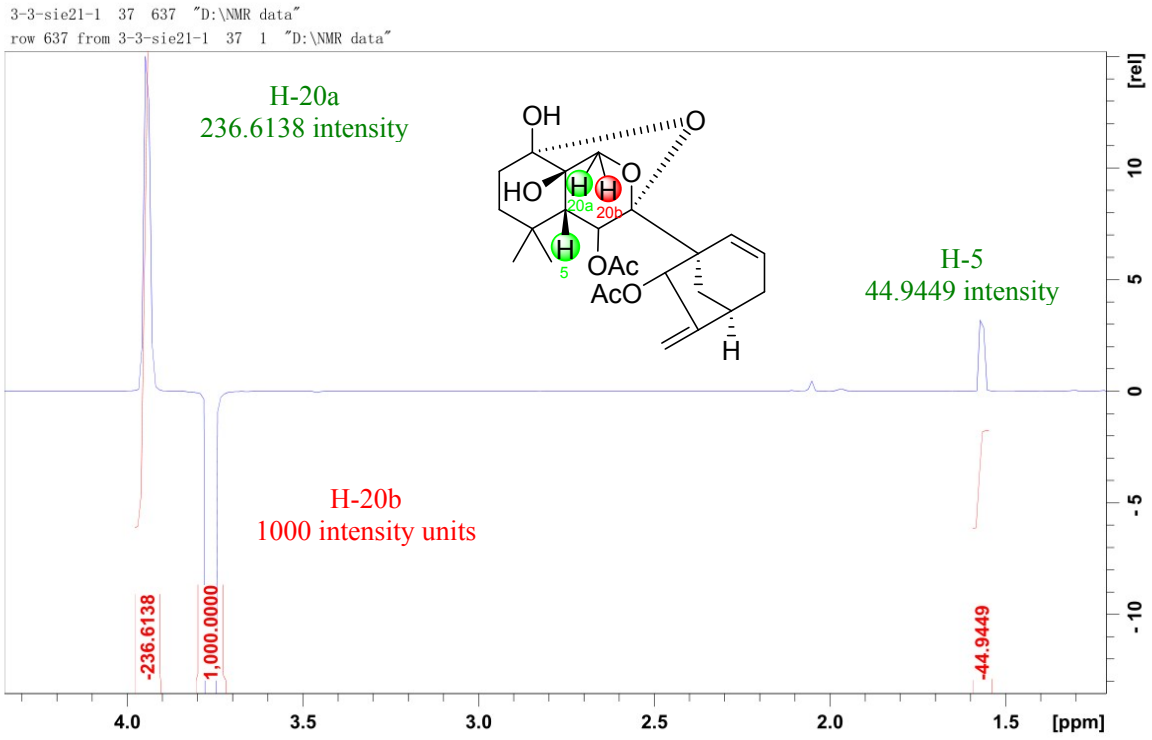
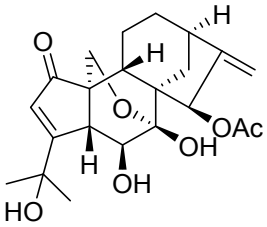


Figure S14 2D ROESY f1 slice at f2 chemical shifts (800 MHz, $CDCl_3$) of H-20b of **4**, with red intergrals as the intensity of each proton.

7. Computational data of 1, 3 and 4.

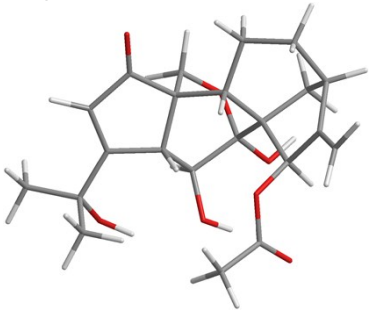
7.1 Computational data — Maoeriocalysin A (1)

Figure S15 One candidate of compound **1**.

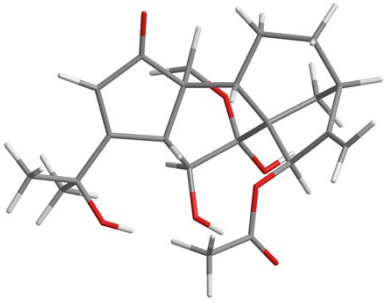


1

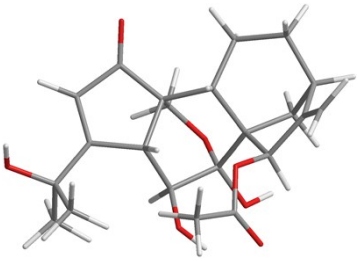
Figure S16 Optimized geometries of 4 dominant conformers of **1** at the M06-2X/def2-SVP level in the gas phase.



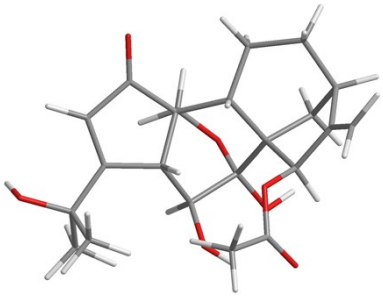
1-1



1-2



1-3



1-4

Table S10 Important thermodynamic parameters (a.u.) of the optimized **1** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
1-1	-1379.708057	-1379.682096	-1379.681152	-1379.761499
1-2	-1379.710340	-1379.684835	-1379.683891	-1379.762255
1-3	-1379.705380	-1379.679292	-1379.678348	-1379.758569
1-4	-1379.705241	-1379.679146	-1379.678202	-1379.758373

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S11 Conformational analysis of the optimized **1** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
1-1	0.00	67.34%
1-2	0.47	30.21%
1-3	2.31	1.35%

1-4	2.44	1.10%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S17 Regression analysis of experimental versus calculated NMR chemical shifts of **1**.

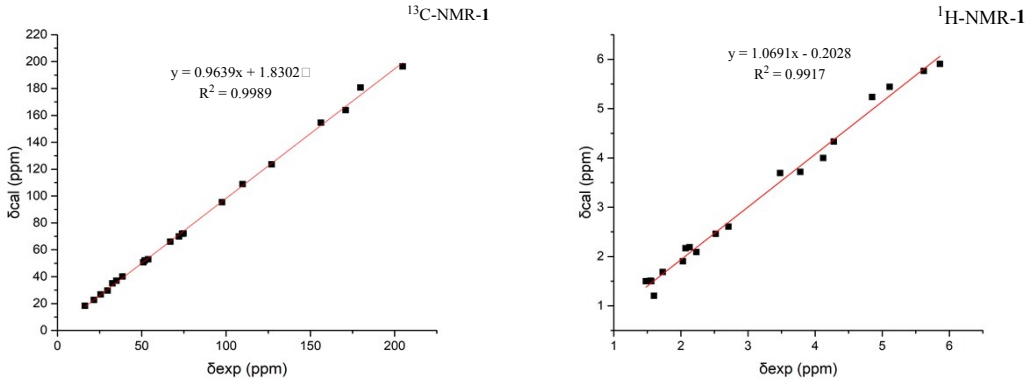


Table S12 Optimized Z-matrixes of **1**-1 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-1.20746	-2.45493	-1.05574	H	3.539143	-1.5086	-2.11132
C	-2.57015	-1.86119	-1.05667	H	4.192961	-2.61045	-0.89305
C	-2.57252	-0.67303	-0.4211	H	4.874	-0.5578	0.032574
C	-3.71757	0.311622	-0.24982	H	2.930443	-1.68267	1.583027
C	-1.17493	-0.30487	0.013709	H	3.33613	0.027284	1.879944
C	-0.86169	0.331442	1.362685	H	2.252604	1.835597	0.791924
C	0.545792	-0.16512	1.749019	H	4.727915	1.031891	-2.27454
C	1.582935	-0.21657	0.604658	H	3.351601	2.293534	-2.15188
C	1.068871	-1.20419	-0.51942	H	-4.34651	0.202663	-2.31487
C	-0.35691	-1.59851	-0.11662	H	-5.2519	-0.8871	-1.22071
C	2.045019	-2.35402	-0.77006	H	-5.56209	0.872374	-1.19361
C	3.453449	-1.81267	-1.05751	H	-4.69813	-0.8549	1.318218
C	3.792657	-0.59544	-0.15526	H	-5.15126	0.878125	1.257562
C	2.957177	-0.6852	1.129228	H	-3.57726	0.392657	1.928582
C	2.029017	1.121292	-0.01599	H	0.172129	-3.27693	1.173768
C	3.298416	0.716237	-0.74994	H	-1.35674	-2.47178	1.611106
C	3.82102	1.381912	-1.77559	H	-0.119	3.137403	-2.61103
C	-4.78723	0.103674	-1.3139	H	-1.33727	2.762296	-1.37209
C	-4.32209	0.164246	1.152555	H	-0.65949	4.422242	-1.46423
C	-0.32559	-2.29976	1.253966	O	0.944307	0.614669	2.818824
C	0.639401	2.96288	-0.61508	O	-0.95999	1.727919	1.266839
C	-0.43559	3.357976	-1.58384	O	0.386998	-1.50263	2.187887
H	-3.40498	-2.33605	-1.57102	O	-3.23188	1.629182	-0.4314
H	-0.80053	0.416747	-0.72953	O	1.089855	1.715407	-0.89201
H	-1.51095	-0.04779	2.172315	O	1.057079	3.630935	0.287489
H	0.989817	-0.62747	-1.45547	H	-2.62777	1.862645	0.292757
H	1.678261	-2.97229	-1.59996	H	1.727832	0.220933	3.222467
H	2.075443	-3.01365	0.110109	O	-0.83723	-3.43984	-1.64416
				H	-0.44953	2.131188	1.985435

Table S13 Optimized Z-matrixes of **1**-2 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-1.29094	-2.43589	-1.02919	H	3.50783	-1.67371	-2.08123
C	-2.64955	-1.83489	-0.99265	H	4.083171	-2.78874	-0.83596
C	-2.62358	-0.63213	-0.38588	H	4.845477	-0.75154	0.067787
C	-3.76512	0.356099	-0.22288	H	2.833607	-1.78577	1.600932
C	-1.20524	-0.26375	-0.00958	H	3.313946	-0.09603	1.898703
C	-0.86495	0.400062	1.318578	H	2.358064	1.736533	0.799158
C	0.519497	-0.13839	1.732177	H	4.761075	0.788465	-2.29126
C	1.566974	-0.26184	0.602508	H	3.446084	2.115665	-2.18869
C	1.019992	-1.23707	-0.51581	H	-2.70054	1.892659	-1.33709
C	-0.41727	-1.5806	-0.11121	H	-3.78859	0.900896	-2.34201
C	1.949636	-2.42821	-0.75611	H	-4.46589	2.13305	-1.22831
C	3.386621	-1.95848	-1.0256	H	-5.29847	-0.85028	-1.18876
C	3.765568	-0.74793	-0.13206	H	-5.90381	0.403457	-0.06914
C	2.912074	-0.79219	1.145039	H	-5.16173	-1.0818	0.580969
C	2.089173	1.046222	-0.01527	H	0.05705	-3.24392	1.221537
C	3.330848	0.573712	-0.75072	H	-1.45378	-2.38967	1.626811
C	3.8753	1.191806	-1.79462	H	0.024252	4.547155	-1.77849
C	-3.67461	1.381448	-1.3607	H	-0.28464	2.889475	-2.42873
C	-5.11632	-0.34435	-0.23153	H	-1.15604	3.48759	-0.979
C	-0.41583	-2.2527	1.277004	O	0.94193	0.652082	2.785314
C	0.845971	2.982832	-0.58661	O	-0.90939	1.799525	1.174773
C	-0.20331	3.50506	-1.52649	O	0.306885	-1.45642	2.203097
H	-3.51013	-2.3263	-1.44546	O	-3.67117	1.011812	1.026262
H	-0.81993	0.423709	-0.78289	O	1.181759	1.707771	-0.87856
H	-1.54813	0.078203	2.122606	O	1.321335	3.606941	0.319159
H	0.963262	-0.66479	-1.45675	H	-2.91076	1.613682	1.021589
H	1.563455	-3.03116	-1.58818	H	1.685053	0.219412	3.224195
H	1.939534	-3.08767	0.124496	O	-0.94271	-3.42535	-1.62347
				H	-0.41819	2.197556	1.910095

Table S14 Optimized Z-matrixes of **1**-3 in the gas phase (Å) at the M06-2X/def2-SVP level.

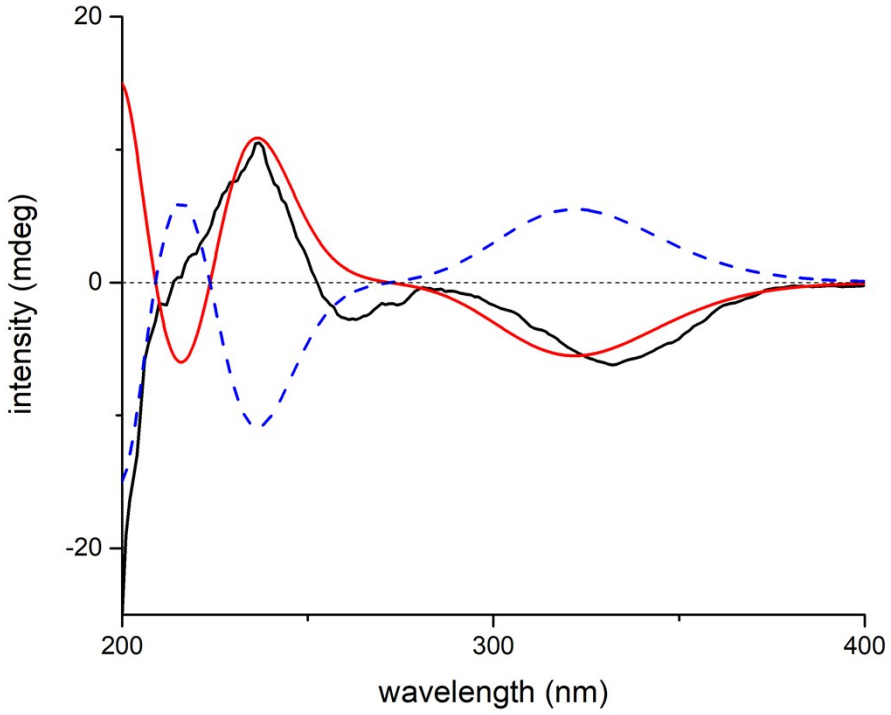
C	-1.32908	-2.38338	-1.06149	H	3.490953	-1.70802	-2.06454
C	-2.67882	-1.76754	-1.02337	H	4.026437	-2.85687	-0.8323
C	-2.63747	-0.56949	-0.40835	H	4.831863	-0.8581	0.115117
C	-3.81774	0.365053	-0.25213	H	2.774445	-1.85354	1.60994
C	-1.21678	-0.21528	-0.02162	H	3.291048	-0.17851	1.932589
C	-0.85771	0.440136	1.310412	H	2.38057	1.697143	0.833969
C	0.504979	-0.15028	1.732743	H	4.841135	0.732836	-2.20067
C	1.559639	-0.28778	0.612894	H	3.555996	2.089228	-2.10394
C	0.998177	-1.23509	-0.52018	H	-4.33693	-0.44058	1.69779
C	-0.45003	-1.5484	-0.13083	H	-3.40547	1.09792	1.755868
C	1.902282	-2.44488	-0.766	H	-5.1249	1.102471	1.274116
C	3.3529	-2.00622	-1.01468	H	-2.65104	2.200466	-0.32365
C	3.75518	-0.82009	-0.09822	H	-4.36493	2.372347	-0.81492
C	2.883737	-0.85724	1.166235	H	-3.19129	1.611829	-1.92797

C	2.118057	1.013366	0.011901	H	-0.02467	-3.23588	1.187546
C	3.366852	0.5223	-0.70106	H	-1.52134	-2.35524	1.586898
C	3.952642	1.147245	-1.71821	H	0.335917	3.294139	-2.63576
C	-4.18388	0.537882	1.221842	H	-0.98942	2.998741	-1.48897
C	-3.47798	1.725772	-0.86958	H	-0.15751	4.58784	-1.47649
C	-0.47676	-2.23534	1.249474	O	0.940616	0.61586	2.799609
C	0.935362	2.978967	-0.6026	O	-0.84229	1.833435	1.177824
C	-0.0276	3.511633	-1.62348	O	0.251448	-1.46449	2.191603
H	-3.55755	-2.23489	-1.46491	O	-4.96076	-0.18614	-0.87221
H	-0.8202	0.468973	-0.79199	O	1.244976	1.691078	-0.87262
H	-1.54212	0.128169	2.11991	O	1.384106	3.59268	0.322863
H	0.962687	-0.65084	-1.4546	H	-4.79399	-0.2301	-1.82142
H	1.51143	-3.02889	-1.60918	H	1.64476	0.139521	3.257138
H	1.86847	-3.11464	0.106296	O	-0.98876	-3.37085	-1.66414
				H	-0.32487	2.203836	1.908581

Table S15 Optimized Z-matrixes of **1**-4 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-1.32017	-2.37273	-1.08189	H	3.493705	-1.69414	-2.06344
C	-2.66543	-1.74691	-1.06545	H	4.031747	-2.84689	-0.83594
C	-2.63432	-0.56736	-0.41464	H	4.833515	-0.85128	0.120295
C	-3.81696	0.362989	-0.25285	H	2.776753	-1.85347	1.611219
C	-1.21678	-0.21867	-0.01461	H	3.292897	-0.17886	1.93769
C	-0.85826	0.433776	1.317029	H	2.372234	1.702559	0.841772
C	0.504122	-0.15637	1.737517	H	4.846175	0.750111	-2.1853
C	1.559889	-0.28698	0.617949	H	3.558416	2.103793	-2.08724
C	1.000745	-1.23126	-0.51885	H	-4.17164	-0.23225	1.821969
C	-0.4481	-1.54892	-0.13401	H	-3.2719	1.306656	1.64407
C	1.906872	-2.43892	-0.76756	H	-5.01874	1.248008	1.288109
C	3.356574	-1.9968	-1.01476	H	-2.69447	2.182187	-0.57856
C	3.756954	-0.81357	-0.09368	H	-4.43831	2.292196	-0.97147
C	2.884889	-0.85597	1.169965	H	-3.33979	1.426911	-2.08136
C	2.115168	1.017012	0.019345	H	-0.02189	-3.24283	1.176268
C	3.367625	0.530741	-0.69126	H	-1.52009	-2.36562	1.57703
C	3.955558	1.161081	-1.70382	H	0.442086	3.402259	-2.6397
C	-4.07536	0.687903	1.22369	H	-0.93699	2.909296	-1.6401
C	-3.54659	1.652621	-1.02568	H	-0.2433	4.555666	-1.43552
C	-0.47492	-2.2429	1.241631	O	0.935853	0.60416	2.80904
C	0.92082	2.975335	-0.60153	O	-0.84831	1.826556	1.179521
C	-0.01608	3.506847	-1.6473	O	0.250838	-1.47498	2.18792
H	-3.52818	-2.18105	-1.56804	O	-4.97049	-0.21573	-0.82693
H	-0.82161	0.469525	-0.7823	O	1.242615	1.689935	-0.86896
H	-1.54164	0.122303	2.127692	O	1.351553	3.590188	0.331747
H	0.965535	-0.64391	-1.45122	H	-5.21674	-0.98307	-0.29643
H	1.517265	-3.02121	-1.61247	H	1.669049	0.148081	3.240659
H	1.874183	-3.11095	0.103077	O	-0.97677	-3.3605	-1.68251
				H	-0.32807	2.203041	1.905142

Figure S18 Calculated ECD of **1**.



Computational Data of (5*R*, 6*S*, 7*S*, 8*S*, 9*S*, 10*S*, 13*R*, 15*R*)-**1**

Experimental ECD spectrum of **1** (black); Calculated ECD spectrum of (5*R*, 6*S*, 7*S*, 8*S*, 9*S*, 10*S*, 13*R*, 15*R*)-**1** (shift = 16 nm, red) and (5*S*, 6*R*, 7*R*, 8*R*, 9*R*, 10*R*, 13*S*, 15*S*)-**1** (shift = 16 nm, blue dash) at the CAM-B3LYP-SCRF/def2-SVP level of theory in MeOH with PCM.

Time-dependent density-functional theory (TDDFT) ECD theoretical calculations were run at the CAM-B3LYP-SCRF/def2-SVP level in MeOH with polarizable continuum model (PCM).

Table S16 Key transitions, oscillator strengths, and rotatory strengths in the ECD spectra of conformer **1**-1 at the CAM-B3LYP-SCRF/def2-SVP level in MeOH with PCM.

Num[a]	*exited state*[b]	*CI Coefficient*	*ΔE (eV)*[c]	*λ (nm)*[d]	*f*[e]	R_{vel}[f]	R_{len}[g]
1	107->109	0.39779	4.0582	305.52	0.0007	-11.7803	-11.7232
□	108->109	0.49356	□	□	□	□	□
2	105->109	0.63949	5.7945	213.97	0.2835	43.4372	44.8415
3	105->109	0.25119	5.8847	210.69	0.0346	-37.6763	-32.1322
□	106->109	0.54848	□	□	□	□	□
4	102->111	0.42	6.1472	201.69	0.0014	-0.6511	-1.337
□	103->111	0.43768	□	□	□	□	□
□	104->111	-0.2411	□	□	□	□	□
5	102->109	0.37695	6.2175	199.41	0.0070	-17.363	-16.9366
□	104->109	0.43508	□	□	□	□	□
□	106->109	-0.27785	□	□	□	□	□

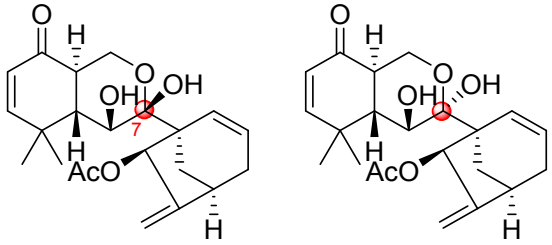
6	103->109	-0.24086	6.6186	187.33	0.0088	1.0015	0.7645
□	107->109	0.44083	□	□	□	□	□
□	108->109	-0.36215	□	□	□	□	□
7	100->109	-0.23858	6.7818	182.82	0.0153	2.8671	2.7657
□	103->109	0.32934	□	□	□	□	□
□	104->109	0.30353	□	□	□	□	□
□	107->109	0.32357	□	□	□	□	□
8	107->110	0.52289	6.9448	178.53	0.3565	61.0097	64.1963
□	108->110	-0.42863	□	□	□	□	□
9	99->109	0.33037	7.0494	175.88	0.0360	-11.8326	-14.1221
□	101->109	0.43243	□	□	□	□	□
10	107->113	0.2637	7.246	171.11	0.0080	-31.0808	-29.7497
□	108->113	0.3238	□	□	□	□	□
11	100->110	0.23502	7.3298	169.15	0.0388	-86.449	-81.2921
□	103->110	0.35631	□	□	□	□	□
□	104->110	0.40879	□	□	□	□	□
12	98->109	-0.29938	7.3547	168.58	0.0027	8.4457	8.0612
□	100->109	0.26964	□	□	□	□	□
□	101->109	0.35256	□	□	□	□	□
13	92->109	-0.26329	7.4814	165.72	0.0073	23.2508	23.0823
□	99->109	0.45216	□	□	□	□	□
14	101->109	-0.23875	7.613	162.86	0.0051	-1.3524	-2.261
□	102->109	0.35183	□	□	□	□	□
□	103->109	0.32616	□	□	□	□	□
15	107->111	0.52865	7.6197	162.71	0.0392	-12.4088	-13.2702
□	108->111	-0.32695	□	□	□	□	□
16	100->109	0.48128	7.7279	160.44	0.0103	-3.9772	-4.0993
□	104->109	0.2478	□	□	□	□	□
17	106->110	0.43365	7.7877	159.21	0.0081	-5.438	-6.1302
□	107->110	-0.2532	□	□	□	□	□
□	108->110	-0.37064	□	□	□	□	□
18	93->109	-0.23072	7.8549	157.84	0.0140	-3.1077	-2.4499
□	97->109	0.32787	□	□	□	□	□
□	98->109	0.27192	□	□	□	□	□
□	103->109	0.27721	□	□	□	□	□
19	106->110	0.35134	7.9263	156.42	0.0186	-4.1536	-4.8105
20	92->109	-0.22464	7.9648	155.67	0.0020	3.4787	7.2029
□	96->109	0.27079	□	□	□	□	□
21	95->109	0.28137	8.0853	153.34	0.0093	-4.8658	-4.0914
22	106->111	0.37906	8.1121	152.84	0.0062	-0.6491	-0.2449
□	108->111	-0.33168	□	□	□	□	□
23	103->111	0.33211	8.1981	151.24	0.0452	28.4493	20.759
□	104->111	0.35589	□	□	□	□	□
24	96->110	-0.30716	8.2258	150.73	0.0124	54.2749	50.0021
□	101->110	0.34001	□	□	□	□	□
25	96->109	0.24658	8.2937	149.49	0.0014	4.4303	6.6671
□	97->109	0.32695	□	□	□	□	□
□	106->112	0.23636	□	□	□	□	□

26	97->109	0.30872	8.322	148.98	0.0010	-4.8784	-6.201
□	106->112	-0.24362	□	□	□	□	□
27	105->112	-0.31056	8.4101	147.42	0.0666	-39.362	-37.86
□	105->113	0.42144	□	□	□	□	□
28	107->112	0.27157	8.4275	147.12	0.0246	-39.4801	-38.931
□	107->116	0.25458	□	□	□	□	□
□	107->117	0.22551	□	□	□	□	□
□	108->116	-0.22476	□	□	□	□	□
29	102->110	0.26975	8.4692	146.39	0.0602	29.0587	24.1438
□	103->110	0.33573	□	□	□	□	□
□	106->111	-0.3146	□	□	□	□	□
30	106->111	0.28992	8.4845	146.13	0.0268	39.5558	33.2678
□	108->111	0.27684	□	□	□	□	□

[a]Number of the excited states. [b]only excited states with contribution over 10% were listed. [c]Excitation energy. [d]Wavelength. [e]Oscillator strength. [f]Rotatory strength in velocity form (10-40 cgs.). [g]Rotatory strength in length form (10^{-40} cgs.).

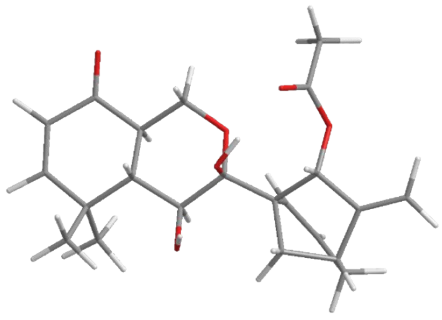
7.2 Computational data — Maoeriocalysin C (3)

Figure S19 Two possible candidates of compound **3**.



3a **3b**

Figure S20 Optimized geometries of 1 dominant conformers of **3a** at the M06-2X/def2-SVP level in the gas phase.



3a-1

Table S17 Important thermodynamic parameters (a.u.) of the optimized **3a** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
3a-1	-1304.561099	-1304.536059	-1304.535115	-1304.613508

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S18 Conformational analysis of the optimized **3a** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
3a-1	0.00	100.00%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S21 Regression analysis of experimental versus calculated NMR chemical shifts of **3a**.

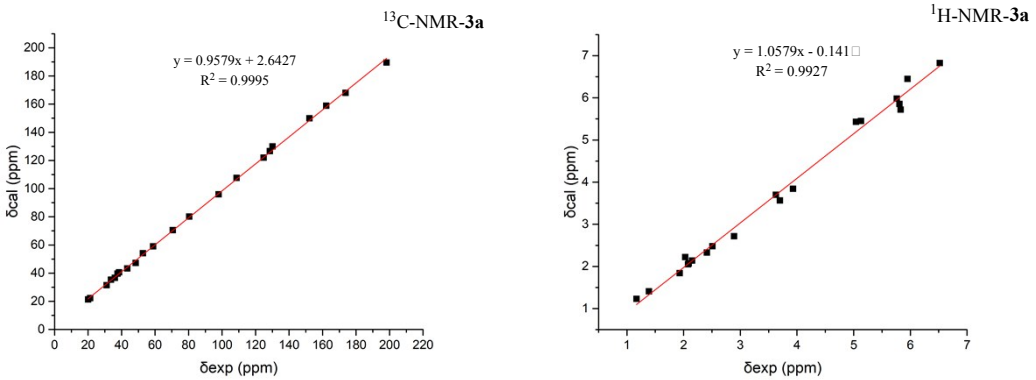
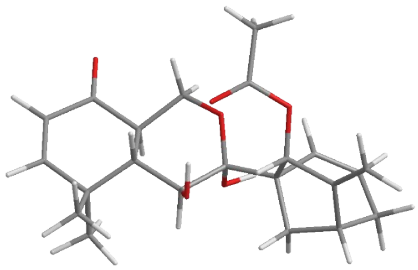


Table S19 Optimized Z-matrixes of **3a**-1 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	2.069	-1.75823	3.2235	H	1.90674	-2.44401	5.29793
C	1.36376	-1.93437	4.51054	H	-0.32214	-1.56217	5.6699
C	0.12922	-1.44772	4.6843	H	-0.32835	-2.09709	1.98167
C	-0.705	-0.74546	3.61873	H	-0.67898	0.85085	1.2783
C	-0.10968	-1.03658	2.18853	H	1.04687	2.09262	-0.53914
C	-0.72506	-0.21266	1.02643	H	1.68385	0.16567	2.40905
C	0.00447	-0.44168	-0.34475	H	-0.0406	4.11355	-1.33357
C	-0.42267	0.6058	-1.44212	H	-1.4857	3.7108	-3.35704
C	0.13117	2.01713	-1.12098	H	-2.51537	3.5261	-1.93418
C	1.41995	-0.874	2.1778	H	-2.99702	1.60265	-3.38066
C	-0.45677	3.13889	-1.57244	H	-2.4163	-0.23767	-1.8644
C	-1.66665	3.08817	-2.47304	H	-2.47935	1.19106	-0.8118
C	-2.01535	1.64484	-2.89809	H	-0.34814	-0.85408	-3.10168
C	-1.9534	0.73648	-1.65891	H	0.02237	0.79402	-5.64683
C	-0.02916	0.17722	-2.8957	H	-1.47326	1.8928	-5.63294
C	-0.92252	1.04772	-3.77013	H	-2.49605	-1.25836	4.78505
C	-0.78582	1.2546	-5.08706	H	-2.86023	-0.70499	3.16525
C	-2.14363	-1.29245	3.74635	H	-2.20671	-2.33539	3.41532
C	-0.72846	0.75463	3.96912	H	0.26194	1.2126	3.87706
C	1.97326	-1.21633	0.80374	H	-1.06411	0.91582	5.00131
C	2.12763	-0.73349	-3.04801	H	-1.41785	1.31005	3.32473
C	3.55426	-0.40736	-3.36289	H	1.79584	-2.26479	0.53499
O	-0.3279	-1.77141	-0.76081	H	3.05894	-1.06908	0.78197
O	1.34816	0.36786	-3.2136	H	3.92069	0.35417	-2.66998
O	1.73074	-1.83523	-2.68589	H	3.63631	-0.06047	-4.39596
O	3.17447	-2.27398	3.07872	H	4.16523	-1.30729	-3.2486
O	-2.10123	-0.59066	0.90061	H	0.36451	-2.00884	-1.41688
O	1.42441	-0.35438	-0.18699	H	-2.09029	-1.43588	0.40418

Figure S22 Optimized geometries of 1 dominant conformers of **3b** at the M06-2X/def2-SVP level in the gas phase.



3b-1

Table S20 Important thermodynamic parameters (a.u.) of the optimized **3b** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
3b-1	-1304.549806	-1304.524639	-1304.523695	-1304.602479

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S21 Conformational analysis of the optimized **3b** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
3b-1	0.00	100.00%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S23 Regression analysis of experimental versus calculated NMR chemical shifts of **3b**.

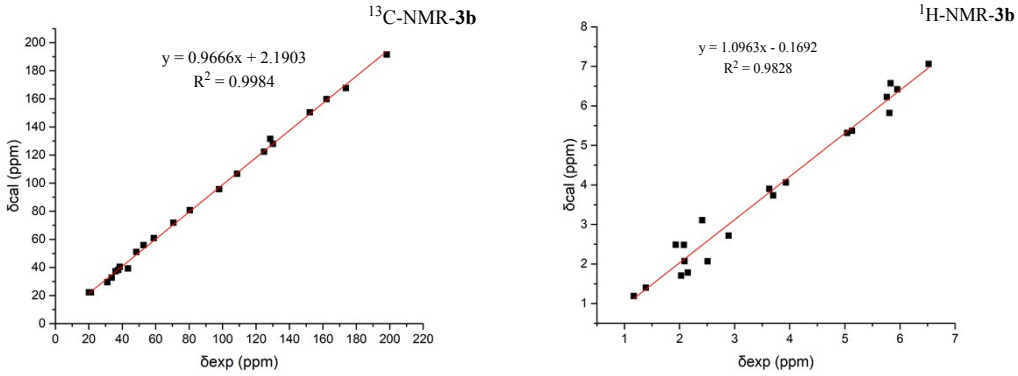


Table S22 Optimized Z-matrixes of **3b**-1 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	3.37498	0.09173	2.5708	H	4.23661	-1.06125	4.22388
C	3.31287	-0.88162	3.68625	H	2.15958	-2.13822	4.88472
C	2.15783	-1.46906	4.02494	H	1.63639	-1.54678	1.34007
C	0.83118	-1.26162	3.30684	H	-1.0109	-0.1823	1.67626
C	1.10565	-0.7286	1.85681	H	0.33351	2.49293	-2.0786
C	-0.17211	-0.42685	1.02003	H	1.6553	1.29566	2.42295
C	0.01381	0.78186	0.03459	H	-1.41527	3.77929	-3.18251

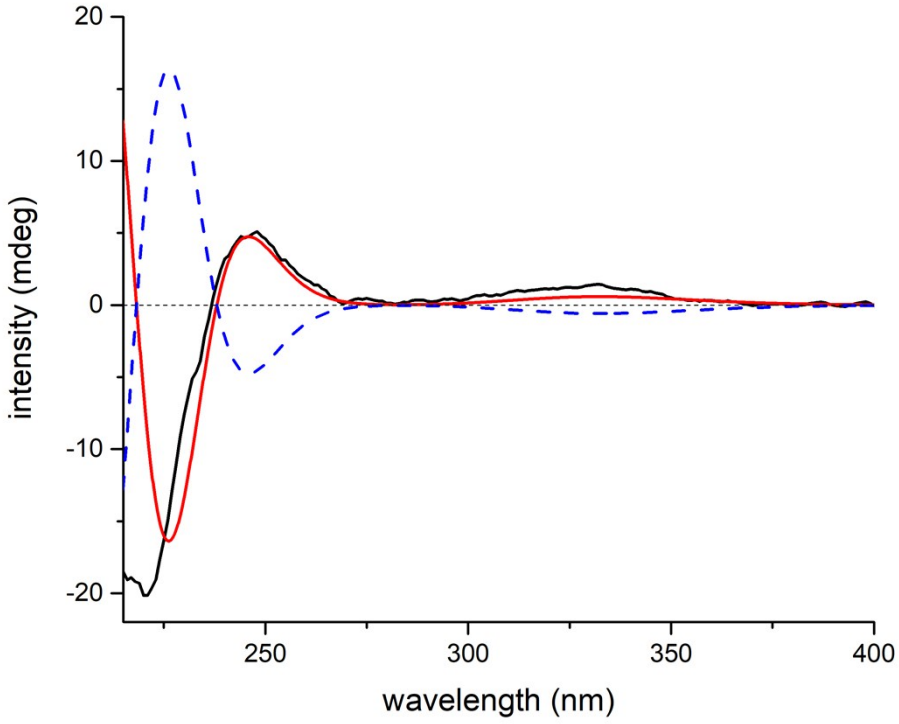
C	-1.01632	0.90056	-1.15107	H	-3.70563	3.14747	-2.05893
C	-0.7074	2.18984	-1.98	H	-3.47012	2.41485	-3.64906
C	2.08158	0.45547	1.86233	H	-4.30546	0.76609	-1.8457
C	-1.66629	2.89204	-2.60786	H	-2.76434	0.11539	-0.06568
C	-3.10001	2.42373	-2.61715	H	-2.6756	1.88459	-0.04499
C	-3.25057	1.02288	-1.98583	H	-1.28634	-1.2634	-1.64972
C	-2.48041	0.99564	-0.65624	H	-2.39483	-1.37299	-4.42977
C	-1.15093	-0.29898	-2.1411	H	-3.95825	-0.3809	-4.30152
C	-2.50667	-0.03052	-2.79805	H	0.64899	-3.34185	2.63394
C	-2.98015	-0.62692	-3.90105	H	-0.0128	-3.05633	4.24738
C	0.10048	-2.61826	3.24812	H	-0.90695	-2.51569	2.83143
C	-0.00442	-0.29665	4.17175	H	-1.0241	-0.17984	3.79297
C	2.38887	0.91554	0.43365	H	-0.09517	-0.66867	5.20028
C	0.92891	-1.17866	-2.81208	H	0.44642	0.69933	4.23122
C	1.97437	-1.09823	-3.8811	H	3.2601	0.39098	0.02471
O	-0.09535	1.96935	0.84866	H	2.64761	1.98135	0.43295
O	-0.11301	-0.36248	-3.12075	H	2.80705	-1.75915	-3.62401
O	1.01641	-1.88233	-1.8126	H	1.55393	-1.42253	-4.83625
O	4.45401	0.61781	2.30588	H	2.35153	-0.07499	-3.9531
O	-0.52666	-1.65232	0.37861	H	-0.21751	2.72256	0.24724
O	1.33395	0.71596	-0.51085	H	0.20165	-1.88491	-0.2437

Table S23 The DP4+ probabilities of **3a** and **3b**.

Functional	Solvent	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d,p)	Unscaled Shifts

□	Isomer 1 (**3a**)	Isomer 2 (**3b**)
sDP4+ (H data)	100.00%	0.00%
sDP4+ (C data)	100.00%	0.00%
sDP4+ (all data)	100.00%	0.00%
uDP4+ (H data)	100.00%	0.00%
uDP4+ (C data)	98.34%	1.66%
uDP4+ (all data)	100.00%	0.00%
DP4+ (H data)	100.00%	0.00%
DP4+ (C data)	100.00%	0.00%
DP4+ (all data)	100.00%	0.00%

Figure S24 Calculated ECD of **3a**.



Computational Data of (5*S*, 6*S*, 7*R*, 8*S*, 10*R*, 13*R*, 15*R*) **-3** (**3a**)

Experimental ECD spectrum of **3a** (black); Calculated ECD spectrum of (5*S*, 6*S*, 7*R*, 8*S*, 10*R*, 13*R*, 15*R*) **-3a** (shift = 23 nm, red) and (5*R*, 6*R*, 7*S*, 8*R*, 10*S*, 13*S*, 15*S*) **-3a** (shift = 23 nm, blue dash) at the CAM-B3LYP-SCRF/def2-SVP level of theory in MeOH with PCM.

Table S24 Key transitions, oscillator strengths, and rotatory strengths in the ECD spectra of conformer **3a**-1 at the CAM-B3LYP-SCRF/def2-SVP level in MeOH with PCM.

Num[a]	*exited state*[b]	*CI Coefficient*	*ΔE (eV)*[c]	*λ (nm)*[d]	*f*[e]	R_{vel}[f]	R_{len}[g]
1	100 ->105	0.28399	4.0245	308.07	0.0001	1.8928	4.6924
□	101 ->105	0.26652	□	□	□	□	□
□	103 ->105	0.41468	□	□	□	□	□
□	104 ->105	0.35995	□	□	□	□	□
2	101 ->105	0.6131	5.8657	211.37	0.2088	50.5148	52.8094
□	104 ->105	-0.22915	□	□	□	□	□
3	100 ->105	0.53699	6.1258	202.4	0.1065	-92.1469	-88.6653
□	104 ->105	-0.34028	□	□	□	□	□
4	95 ->106	0.28041	6.1691	200.98	0.0007	-6.4893	-7.8097
□	98 ->106	0.49115	□	□	□	□	□
5	99 ->105	0.46191	6.6424	186.65	0.0067	-4.1883	-3.8073
□	103 ->105	-0.26212	□	□	□	□	□
6	103 ->107	-0.38049	6.7532	183.59	0.0873	194.0213	192.0839
□	104 ->107	0.49325	□	□	□	□	□
7	99 ->105	0.26631	6.7941	182.49	0.0122	8.1607	8.1901

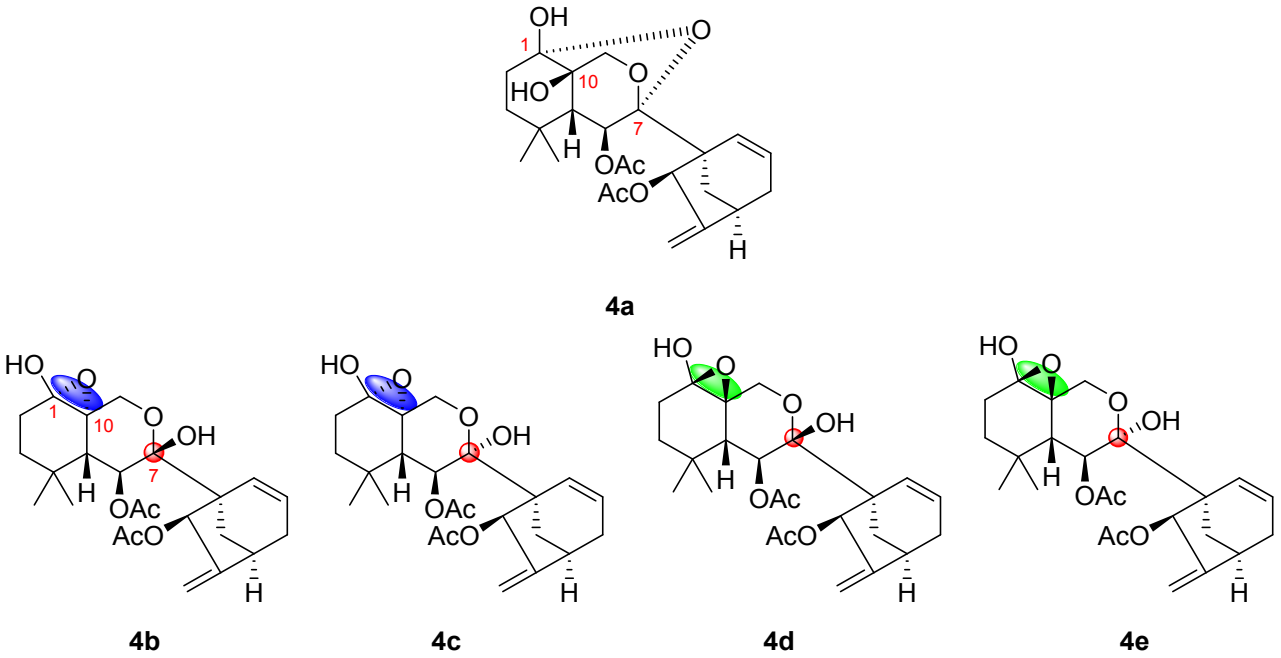
□	103 ->105	0.43852	□	□	□	□	□
□	104 ->105	-0.37925	□	□	□	□	□
8	103 ->108	-0.40377	6.8908	179.93	0.3344	-143.559	-146.871
□	104 ->108	0.55402	□	□	□	□	□
9	93 ->105	0.27929	7.1507	173.39	0.0108	-7.8166	-5.1367
□	96 ->105	0.23549	□	□	□	□	□
□	102 ->105	0.3276	□	□	□	□	□
□	104 ->106	0.26104	□	□	□	□	□
10	102 ->107	0.25206	7.1566	173.25	0.0704	26.0901	26.2446
□	104 ->106	0.52818	□	□	□	□	□
11	102 ->107	0.56603	7.1925	172.38	0.3424	30.5414	37.7019
12	90 ->105	-0.27916	7.2343	171.38	0.0066	31.4497	31.2083
□	94 ->105	0.26479	□	□	□	□	□
□	97 ->105	0.28962	□	□	□	□	□
13	102 ->105	0.45099	7.3345	169.04	0.024	13.0027	12.1632
□	102 ->108	0.33647	□	□	□	□	□
14	102 ->105	-0.32205	7.3494	168.7	0.0883	-7.2798	-6.0363
□	102 ->108	0.47865	□	□	□	□	□
15	103 ->108	0.33092	7.5271	164.72	0.0011	1.7415	2.6173
□	104 ->108	0.25058	□	□	□	□	□
16	103 ->106	0.4475	7.5554	164.1	0.0103	2.0022	6.6172
17	97 ->105	0.30954	7.5894	163.37	0.0125	16.7972	15.787
18	94 ->107	0.23343	7.6057	163.02	0.0051	-15.4487	-19.2192
□	96 ->107	0.2578	□	□	□	□	□
□	103 ->107	0.22746	□	□	□	□	□
19	89 ->105	0.30679	7.6876	161.28	0.0209	-20.0327	-14.826
□	90 ->105	0.27934	□	□	□	□	□
20	102 ->106	0.5769	7.6995	161.03	0.0025	-4.1066	-5.3857
□	103 ->106	0.29664	□	□	□	□	□
21	94 ->108	0.24885	7.7623	159.73	0.0062	-24.9921	-27.8647
□	95 ->108	0.37533	□	□	□	□	□
□	98 ->108	-0.25722	□	□	□	□	□
□	102 ->108	-0.22938	□	□	□	□	□
22	92 ->105	0.3094	7.8971	157	0.0067	0.185	0.8269
□	93 ->105	0.34433	□	□	□	□	□
□	98 ->105	0.38589	□	□	□	□	□
23	97 ->107	0.2237	8.0025	154.93	0.0037	-8.5559	-10.2449
□	103 ->107	0.29849	□	□	□	□	□
□	104 ->107	0.26567	□	□	□	□	□
24	103 ->109	-0.24862	8.0431	154.15	0.0027	-5.7594	-5.2208
□	104 ->109	0.29216	□	□	□	□	□
25	88 ->105	-0.25938	8.1547	152.04	0.0012	2.0559	2.1498
□	89 ->105	-0.30007	□	□	□	□	□
□	96 ->105	0.24341	□	□	□	□	□
□	97 ->105	0.30761	□	□	□	□	□
26	99 ->106	0.22579	8.2036	151.13	0.0165	-33.7699	-32.4979
□	104 ->110	0.3373	□	□	□	□	□
27	87 ->105	-0.32942	8.2447	150.38	0.0136	1.5726	1.7162

□	96 ->105	0.27081	□	□	□	□	□
□	98 ->105	0.42869	□	□	□	□	□
28	96 ->106	-0.24051	8.2575	150.15	0.0169	10.8727	11.6775
□	97 ->108	0.28343	□	□	□	□	□
29	97 ->108	0.29682	8.288	149.59	0.047	3.2532	5.4389
30	88 ->105	-0.23062	8.3359	148.74	0.0089	-7.1594	-3.4771
□	103 ->109	0.26256	□	□	□	□	□
□	104 ->109	0.29552	□	□	□	□	□

[a]Number of the excited states. [b]only excited states with contribution over 10% were listed. [c]Excitation energy. [d]Wavelength. [e]Oscillator strength. [f]Rotatory strength in velocity form (10-40 cgs.). [g]Rotatory strength in length form (10^{-40} cgs.).

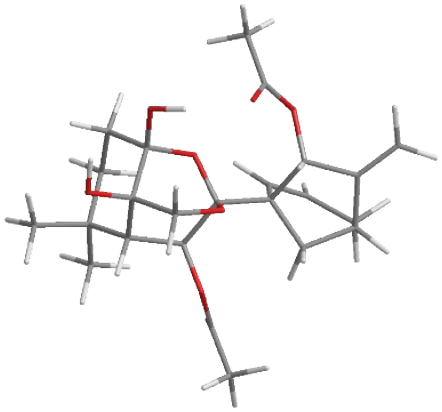
7.3 Computational data — Maoeriocalysin D (4)

Figure S25 Five possible candidates of compound **4**.



Note: (1) When the C-1/O/C-7 bridge is formed and located behind rings A and B, the HO-10 can only be *β*-oriented according to molecular modeling, in this case, only one possible should be considered (**4a**); (2) C-1/O/C-7 bridge can't be in front of rings A and B, for it fails to satisfy the H-5/H-20b, HO-1/H-20a restraints; (3) When the C-1/O/C-10 ether bond is formed and located behind the ring A, the uncertainty of the configurations of C-7 requires 2 diastereoisomers to be considered (**4b** and **4c**); (4) When the C-1/O/C-10 ether bond is formed and is in front of the ring A, the uncertainty of the configurations of C-7 requires 2 diastereoisomers to be considered (**4d** and **4e**).

Figure S26 Optimized geometries of 1 dominant conformers of **4a** at the M06-2X/def2-SVP level in the gas phase.



4a-1

Table S25 Important thermodynamic parameters (a.u.) of the optimized **4a** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
4a-1	-1533.348863	-1533.319747	-1533.318803	-1533.406343

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S26 Conformational analysis of the optimized **4a** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
4a-1	0.00	100.00%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S27 Regression analysis of experimental versus calculated NMR chemical shifts of **4a**.

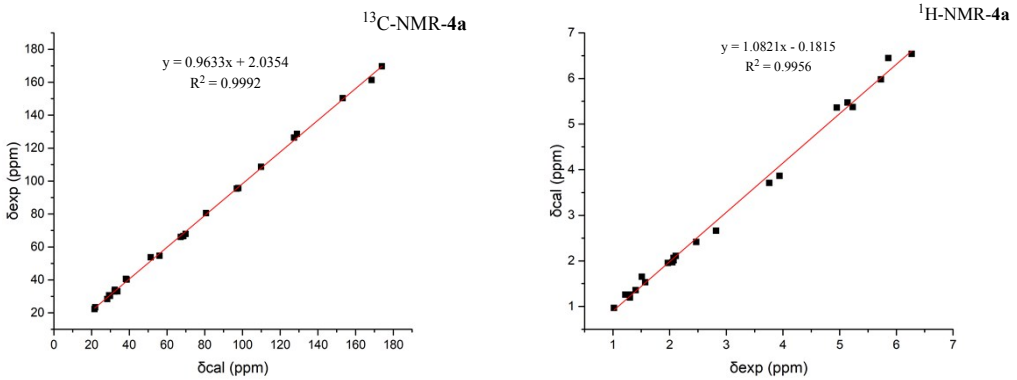
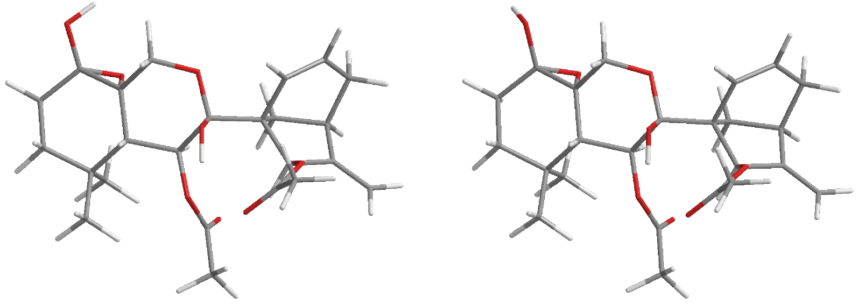


Table S27 Optimized Z-matrixes of **4a**-1 in the gas phase (Å) at the M06-2X/def2-SVP level.

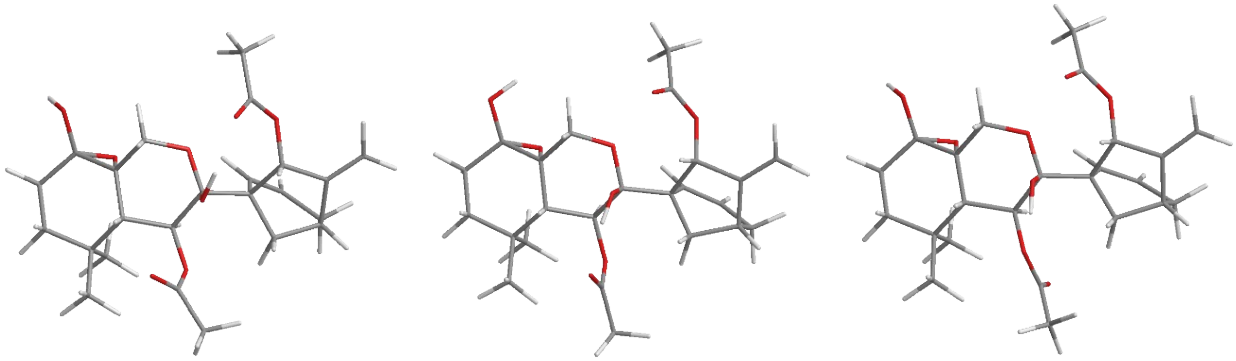
C	0.55124	1.49856	1.74595	H	-1.39049	-4.94167	-1.17439
C	2.05554	1.58962	2.01477	H	-1.12645	-3.97537	-2.62875
C	2.88281	1.37683	0.74628	H	-3.25717	-3.21292	-1.72851
C	2.42483	2.26398	-0.43498	H	-2.77269	-0.85105	-1.26887
C	0.85795	2.18315	-0.61942	H	-1.44002	-1.39243	-2.30452

C	0.34184	0.76773	-1.05604	H	-2.59521	-1.14159	1.341
C	-0.51552	0.13596	0.10619	H	-3.61255	-3.84152	2.03469
C	-0.94418	-1.34858	-0.13242	H	-3.98014	-4.65373	0.40673
C	0.25982	-2.28859	-0.34463	H	2.60082	4.10536	0.79238
C	0.0905	2.52628	0.68672	H	3.97735	3.80429	-0.23654
C	0.13656	-3.45383	-1.00356	H	2.47402	4.39671	-0.95047
C	-1.196	-3.92492	-1.53539	H	4.24193	2.00739	-1.63823
C	-2.3604	-2.98699	-1.14241	H	2.79326	2.3468	-2.5936
C	-1.91434	-1.53246	-1.32872	H	3.0692	0.73762	-1.89723
C	-1.85809	-1.89113	1.02487	H	-2.00381	2.67022	1.30789
C	-2.63079	-3.02069	0.34956	H	-1.76706	2.85217	-0.41537
C	-3.45314	-3.88425	0.96157	H	-1.21766	2.04368	-4.4843
C	2.88448	3.72305	-0.19005	H	-1.83789	0.35907	-4.39373
C	3.16567	1.81075	-1.71384	H	-0.50327	0.76878	-5.4917
C	-1.41199	2.29986	0.46285	H	0.77895	-2.47659	3.94184
C	0.04157	0.67774	-3.43727	H	-0.6912	-3.32845	4.52949
C	-0.95025	0.9845	-4.51707	H	-0.23631	-1.75297	5.20748
C	-1.06613	-1.66254	3.25061	O	0.28386	3.87461	1.09977
C	-0.24809	-2.3571	4.29578	O	1.16023	0.2306	-3.63547
H	2.34479	0.82769	2.75051	O	-0.49621	0.96209	-2.22255
H	2.30174	2.55336	2.47638	H	-0.74891	1.01457	3.07427
H	2.81744	0.31834	0.46322	O	-0.11023	1.75598	2.97774
H	3.94095	1.55951	0.97291	O	-1.70943	0.91744	0.28859
H	0.58999	2.92373	-1.38647	O	0.25535	0.16961	1.32607
H	1.17135	0.09454	-1.27815	H	0.04497	3.90048	2.04946
H	1.21683	-2.01668	0.09421	O	-1.58115	-0.56206	3.40469
H	0.99518	-4.1072	-1.13186	O	-1.12423	-2.42734	2.13202

Figure S28 Optimized geometries of 5 dominant conformers of **4b** at the M06-2X/def2-SVP level in the gas phase.



4b-1 **4b**-2



4b-3 **4b**-4 **4b**-5

Table S28 Important thermodynamic parameters (a.u.) of the optimized **4b** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
4b-1	-1533.307388	-1533.277547	-1533.276603	-1533.365526
4b-2	-1533.307120	-1533.277289	-1533.276345	-1533.365341
4b-3	-1533.305515	-1533.276094	-1533.275150	-1533.362947
4b-4	-1533.304581	-1533.274995	-1533.274051	-1533.362409
4b-5	-1533.303407	-1533.273488	-1533.272544	-1533.362074

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S29 Conformational analysis of the optimized **4b** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
4b-1	0.00	50.46%
4b-2	0.12	41.47%
4b-3	1.62	3.28%
4b-4	1.96	1.85%
4b-5	2.17	1.30%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S29 Regression analysis of experimental versus calculated NMR chemical shifts of **4b**.

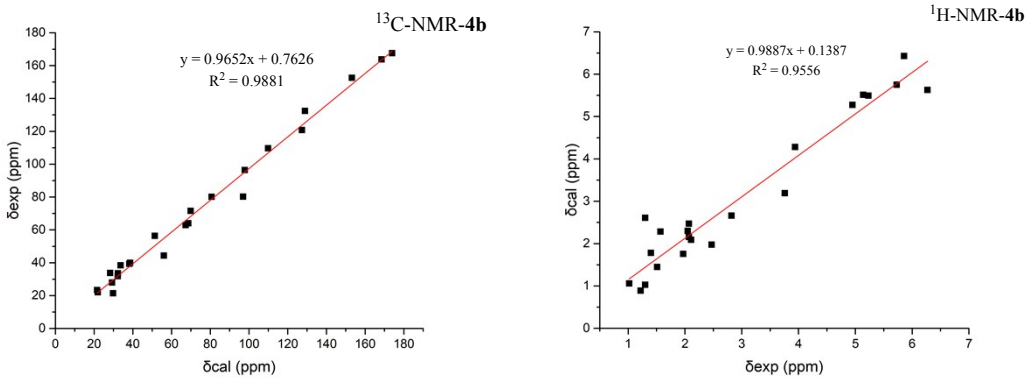


Table S30 Optimized Z-matrixes of **4b-**1 in the gas phase (Å) at the M06-2X/def2-SVP level.

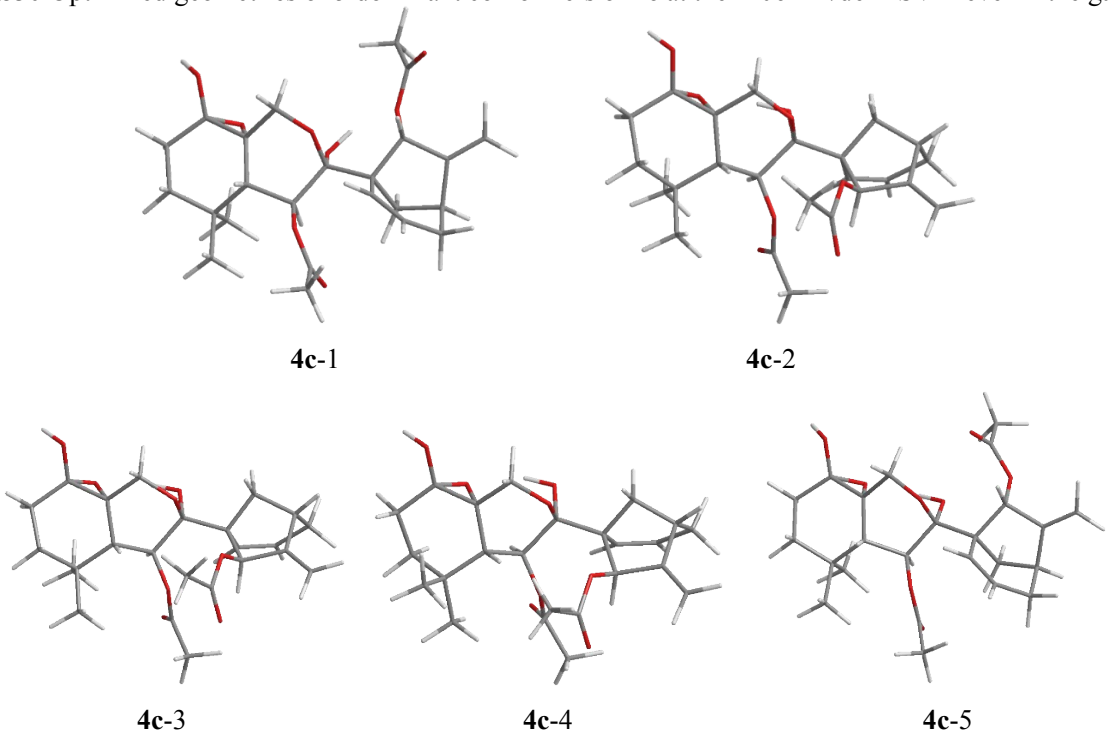
C	0.41555	-0.54145	-4.31681	H	-2.89248	4.40743	1.18672
C	1.73002	-1.13502	-4.68033	H	-3.183	3.82534	2.82859
C	2.25566	-2.03982	-3.57327	H	-0.68433	4.10352	2.16167
C	2.2628	-1.38197	-2.16153	H	-1.13809	2.97527	-0.2039
C	0.78011	-1.03128	-1.7469	H	0.28338	2.42503	0.6922
C	0.55422	-0.12115	-0.4858	H	-0.03235	0.36612	2.45998
C	-1.00416	0.05649	-0.22273	H	-0.60229	1.57443	5.02876
C	-1.4494	1.07065	0.90255	H	-0.77435	3.39548	4.71451
C	-2.99402	1.2692	0.86506	H	3.81396	-2.83201	-1.60774
C	-0.05101	-0.46517	-2.88356	H	3.08551	-2.05151	-0.22411
C	-3.58183	2.40338	1.28358	H	2.19104	-3.30483	-1.09594
C	-2.77459	3.54295	1.85118	H	2.83391	0.67016	-2.74667
C	-1.27457	3.19987	1.97724	H	3.38206	0.2051	-1.14185
C	-0.80997	2.47034	0.71253	H	4.19073	-0.43766	-2.56146
C	-1.04359	0.75581	2.3755	H	-1.9823	-1.25819	-2.37124
C	-1.03008	2.13439	3.03211	H	-2.04293	0.18375	-3.37831
C	-0.78647	2.38163	4.32694	H	2.01092	-0.79277	3.34874
C	2.8644	-2.44887	-1.21454	H	3.6668	-0.58859	2.70528
C	3.20939	-0.16679	-2.15406	H	2.69229	-1.96544	2.182
C	-1.496	-0.29472	-2.55945	H	-2.5178	-3.20529	3.87794
C	2.1162	-0.07952	1.34217	H	-2.79105	-1.77323	4.89012
C	2.6489	-0.91173	2.47031	H	-3.72826	-2.00672	3.37405
C	-1.70315	-1.40425	3.09388	O	-0.55402	-0.49849	-5.36424
C	-2.75863	-2.13856	3.8606	O	-1.6176	0.55912	-1.43006
H	1.63127	-1.7286	-5.59716	O	-1.56726	-1.22814	0.08286
H	2.45262	-0.3424	-4.90672	H	-0.93101	-1.67472	0.68144
H	1.63653	-2.94729	-3.53936	O	1.16731	-0.76747	0.65018
H	3.26649	-2.36864	-3.84756	O	2.45454	1.07354	1.12286
H	0.32374	-2.00506	-1.512	O	0.52137	0.66726	-3.55398
H	0.9938	0.85864	-0.70212	O	-1.96829	-0.07648	3.08829
H	-3.59916	0.44503	0.49379	H	-0.66304	0.42125	-5.66422
H	-4.66142	2.51132	1.23843	O	-0.74694	-1.93863	2.54556

Table S31 Optimized Z-matrixes of **4b-**2 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	0.20151	-0.53547	-4.33908	H	-2.70888	4.51244	1.3436
C	1.48604	-1.16128	-4.75741	H	-2.93867	3.92556	2.99336
C	2.03453	-2.0744	-3.66889	H	-0.46702	4.14201	2.212
C	2.12307	-1.40919	-2.26326	H	-1.06011	3.04386	-0.13623
C	0.67107	-1.01185	-1.78439	H	0.38543	2.44793	0.68928
C	0.53135	-0.0961	-0.51485	H	0.09224	0.38322	2.45906
C	-1.00667	0.12383	-0.18042	H	-0.31697	1.59107	5.05615
C	-1.37261	1.14005	0.97154	H	-0.45202	3.41835	4.76032
C	-2.91122	1.38066	1.00633	H	3.65142	-2.90642	-1.77453
C	-0.19331	-0.42285	-2.88435	H	3.01995	-2.09247	-0.36362
C	-3.44755	2.52706	1.45925	H	2.04137	-3.32121	-1.17869
C	-2.58389	3.63991	1.99616	H	2.72706	0.62221	-2.88653

C	-1.08945	3.25584	2.04992	H	3.33122	0.1503	-1.30414
C	-0.70411	2.52323	0.76081	H	4.05819	-0.52368	-2.7533
C	-0.90941	0.80364	2.42267	H	-2.13475	-1.13129	-2.29831
C	-0.82505	2.17652	3.08571	H	-2.17214	0.32316	-3.28814
C	-0.51191	2.40781	4.36849	H	2.14265	-0.81211	3.25069
C	2.73577	-2.48903	-1.33807	H	3.77212	-0.66151	2.52952
C	3.10387	-0.2221	-2.30533	H	2.73003	-2.00619	2.05517
C	-1.61432	-0.18781	-2.49651	H	-2.43293	-3.12092	3.97198
C	2.17617	-0.10259	1.24016	H	-2.60885	-1.68824	5.00456
C	2.73435	-0.95156	2.34335	H	-3.62916	-1.88156	3.53729
C	-1.603	-1.34074	3.15694	O	-0.82771	-0.50041	-5.33208
C	-2.6406	-2.04709	3.97275	O	-1.65673	0.65511	-1.35384
H	1.33651	-1.75504	-5.66716	O	-1.592	-1.14834	0.13796
H	2.21731	-0.3869	-5.01679	H	-0.9507	-1.60896	0.72042
H	1.39234	-2.96379	-3.6015	O	1.17712	-0.7618	0.59188
H	3.02262	-2.43293	-3.98555	O	2.53869	1.03998	1.00591
H	0.19627	-1.97129	-1.52811	O	0.38406	0.67818	-3.59685
H	0.98852	0.87101	-0.7511	O	-1.82456	-0.00533	3.17396
H	-3.55526	0.57722	0.65596	H	-1.04189	-1.39226	-5.65267
H	-4.52456	2.66562	1.46317	O	-0.69481	-1.90107	2.55535

Figure S30 Optimized geometries of 5 dominant conformers of **4c** at the M06-2X/def2-SVP level in the gas phase.



4c-1 **4c**-2

4c-3 **4c**-4 **4c**-5

Table S32 Important thermodynamic parameters (a.u.) of the optimized **4c** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
4c-1	-1533.303414	-1533.273656	-1533.272711	-1533.361775
4c-2	-1533.301881	-1533.272054	-1533.271110	-1533.360532

4c-3	-1533.301862	-1533.272048	-1533.271104	-1533.360458
4c-4	-1533.301205	-1533.271647	-1533.270703	-1533.359130
4c-5	-1533.300997	-1533.271356	-1533.270411	-1533.358299

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S33 Conformational analysis of the optimized **4c** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
4c-1	0.00	60.37%
4c-2	0.78	16.16%
4c-3	0.83	14.94%
4c-4	1.66	3.66%
4c-5	2.18	1.51%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S31 Regression analysis of experimental versus calculated NMR chemical shifts of **4c**.

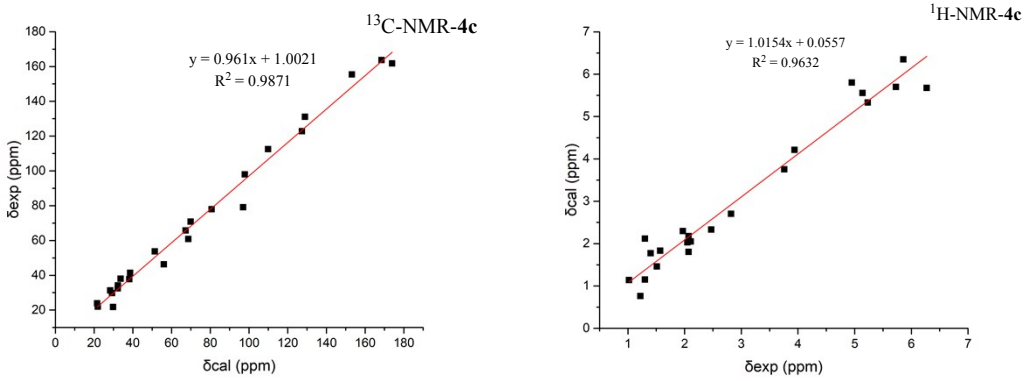


Table S34 Optimized Z-matrixes of **4c**-1 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-0.38657	2.30811	3.33188	H	-0.37756	-3.68261	-4.06027
C	-0.21778	3.7818	3.20885	H	0.57957	-2.23528	-4.39144
C	-0.65464	4.28146	1.83666	H	1.8894	-3.58525	-2.81697
C	-0.02376	3.50218	0.64711	H	2.10376	-2.02338	-0.94831
C	-0.47618	1.993	0.72174	H	1.55767	-1.01939	-2.29247
C	0.21783	0.99374	-0.26493	H	-1.40066	-3.25072	-0.19519
C	0.0293	-0.51182	0.21741	H	-0.30898	-5.86271	-0.65072
C	-0.06919	-1.62199	-0.89877	H	0.67061	-5.88079	-2.22604
C	-1.19069	-1.38183	-1.9303	H	-0.05192	3.82005	-1.53323
C	-0.48515	1.41489	2.11803	H	-0.40984	5.26108	-0.60566
C	-1.12823	-1.88793	-3.17438	H	-1.63703	4.00001	-0.76217
C	0.02076	-2.76533	-3.61083	H	1.99719	3.16409	1.47275
C	0.97271	-3.11652	-2.4447	H	1.95676	3.31955	-0.28244
C	1.27153	-1.8481	-1.64155	H	1.77141	4.7457	0.72858
C	-0.32599	-3.06913	-0.32317	H	-2.15708	0.17631	2.594
C	0.27617	-3.96955	-1.39913	H	-0.60327	-0.56938	2.97258

C	0.21386	-5.30819	-1.42513	H	0.25712	1.44937	-4.72427
C	-0.56302	4.17555	-0.63712	H	-1.25617	1.16493	-3.85991
C	1.50736	3.68462	0.64679	H	-0.56456	2.81307	-3.90803
C	-1.12383	0.06804	2.24818	H	0.82482	-3.20465	3.47721
C	0.45697	1.47048	-2.60753	H	1.64488	-4.63231	2.75544
C	-0.33136	1.74749	-3.85215	H	0.20333	-4.84251	3.76993
C	-0.19296	-4.08309	1.82174	O	-0.92237	1.84437	4.57242
C	0.6833	-4.19294	3.03242	O	-1.17872	-0.61846	0.99222
H	-0.81847	4.29117	3.97196	O	1.15333	-0.78971	1.0714
H	0.82432	4.05953	3.40548	H	1.21005	-1.7561	1.16458
H	-1.7491	4.20747	1.76952	O	-0.37946	1.24572	-1.55919
H	-0.41474	5.35019	1.76449	O	1.6778	1.49644	-2.55471
H	-1.54023	2.0112	0.4344	O	0.73609	1.56063	2.85756
H	1.29447	1.19184	-0.2874	O	0.41104	-3.28936	0.89305
H	-2.0666	-0.81933	-1.61275	H	-0.19278	1.56757	5.15411
H	-1.93444	-1.71402	-3.88171	O	-1.28007	-4.62927	1.71011

Table S35 Optimized Z-matrixes of **4c-**2 in the gas phase (Å) at the M06-2X/def2-SVP level.

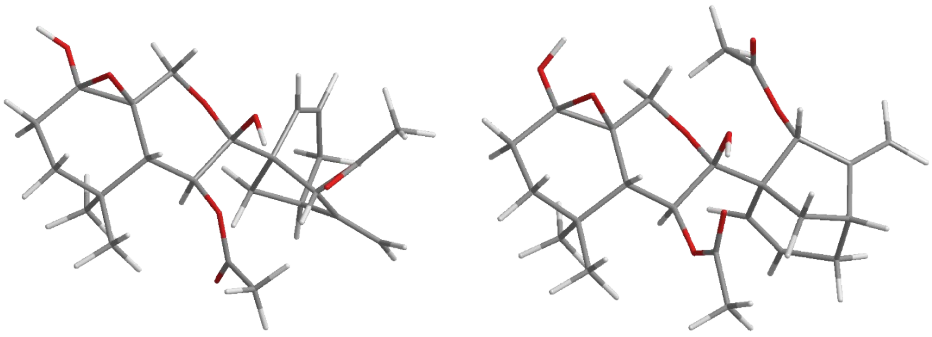
C	-1.31353	3.50773	1.77723	H	-0.34773	-3.16708	-4.87148
C	-1.48281	3.35025	3.24855	H	-1.47511	-1.87386	-5.28821
C	-0.58421	2.24141	3.78736	H	0.71494	-0.81884	-5.26292
C	-0.74793	0.88409	3.04381	H	0.45748	0.83723	-3.48402
C	-0.34173	1.0616	1.52974	H	-1.20281	0.33761	-3.83791
C	-0.75628	-0.08147	0.54048	H	1.10532	-2.19171	-1.32407
C	-0.69346	0.42529	-0.9658	H	3.24258	-2.71923	-3.09663
C	-0.32055	-0.66112	-2.04588	H	2.64677	-2.61201	-4.85168
C	-1.37417	-1.79045	-2.13086	H	0.08012	-1.12972	3.39064
C	-0.74734	2.39215	0.93476	H	0.0227	-0.13002	4.8292
C	-1.58068	-2.48945	-3.26088	H	1.25635	0.1748	3.6021
C	-0.78287	-2.22646	-4.51401	H	-2.92294	0.93297	2.67426
C	0.32138	-1.16864	-4.303	H	-2.27742	-0.68724	2.93022
C	-0.23394	-0.01516	-3.46407	H	-2.47428	0.39976	4.29495
C	1.11038	-1.29615	-1.9523	H	0.75688	3.31036	-0.27159
C	1.41643	-1.69026	-3.39381	H	-0.82687	3.25781	-1.05102
C	2.49338	-2.37531	-3.80376	H	1.50732	-2.9382	1.94415
C	0.20785	-0.10726	3.74852	H	0.27667	-4.20291	1.99776
C	-2.18422	0.35812	3.23836	H	1.0432	-3.80189	0.43941
C	-0.14288	2.70014	-0.40085	H	4.4523	0.72573	-1.25621
C	-0.38992	-2.38025	1.13221	H	3.39575	1.20085	0.11861
C	0.6847	-3.39317	1.38598	H	4.72215	0.04425	0.36024
C	3.03235	-0.75043	-0.65978	O	-1.19737	4.84804	1.29276
C	3.95724	0.38479	-0.34346	O	0.25438	1.50264	-1.06873
H	-1.22421	4.28542	3.75939	O	-1.98673	0.93066	-1.36562
H	-2.5332	3.15184	3.49038	H	-2.41999	1.33379	-0.59268
H	0.46251	2.56729	3.71059	O	0.1521	-1.18028	0.78167
H	-0.79007	2.1175	4.85844	O	-1.5859	-2.61645	1.22236
H	0.75979	1.08471	1.53359	O	-2.15825	2.64955	0.99793
H	-1.79301	-0.37535	0.73377	O	2.10033	-0.34088	-1.5541

H	-1.97812	-2.01508	-1.25643	H	-0.54355	5.35821	1.8001
H	-2.34023	-3.2657	-3.29423	O	3.12096	-1.86456	-0.16348

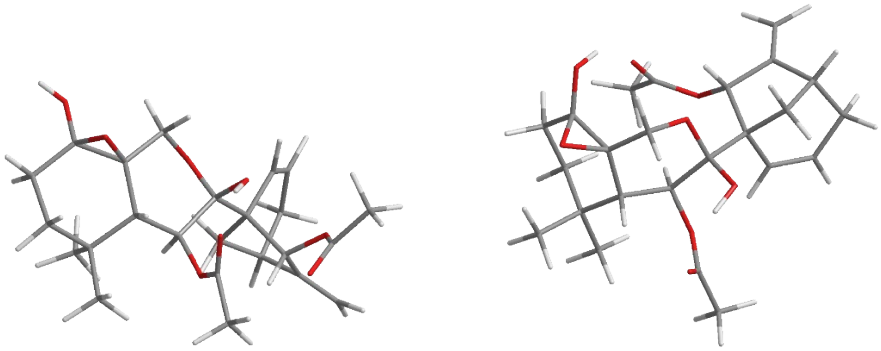
Table S36 Optimized Z-matrixes of **4c**-3 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	1.51833	3.52223	1.56143	H	-2.3909	-2.35249	-4.74199
C	1.27849	3.63199	3.02573	H	-2.27638	-0.67225	-5.27191
C	1.12353	2.25563	3.66488	H	0.02147	-1.45894	-5.16404
C	0.06026	1.35676	2.97005	H	0.98119	0.01719	-3.46892
C	0.49825	1.08675	1.47954	H	-0.54546	0.80331	-3.89642
C	-0.5811	0.48936	0.51318	H	-0.7166	-2.43986	-1.15804
C	-0.15843	0.70232	-1.00583	H	0.4531	-4.43311	-2.78474
C	-0.64411	-0.4029	-2.01961	H	0.12727	-4.05865	-4.57367
C	-2.1862	-0.47091	-2.11945	H	-0.1362	0.22867	4.84041
C	1.15187	2.27244	0.80499	H	-0.78183	-0.62307	3.45125
C	-2.8104	-0.89812	-3.23124	H	0.96922	-0.51451	3.68011
C	-2.04261	-1.35581	-4.44666	H	-1.43905	2.89533	2.46501
C	-0.51647	-1.36599	-4.21499	H	-2.12986	1.31322	2.82126
C	-0.11004	-0.10127	-3.45478	H	-1.52519	2.31685	4.12922
C	-0.07517	-1.85074	-1.82011	H	2.89338	1.76365	-0.32281
C	-0.11714	-2.44257	-3.22542	H	1.76269	2.79366	-1.20641
C	0.17128	-3.71181	-3.54634	H	-1.90228	-3.42506	0.67282
C	0.02612	0.03525	3.77321	H	-2.74942	-3.06363	2.19885
C	-1.33124	2.00884	3.09493	H	-0.98468	-3.02602	2.1643
C	1.83066	1.96379	-0.49355	H	3.40378	-3.26688	0.64583
C	-1.93715	-1.36224	1.21862	H	3.27295	-1.53282	0.2834
C	-1.88341	-2.81576	1.57834	H	3.71539	-2.70281	-1.00794
C	1.65855	-2.72135	-0.4422	O	2.5413	4.36485	1.03126
C	3.10865	-2.5377	-0.11406	O	1.27373	0.79546	-1.09647
H	2.12187	4.14409	3.50435	O	-0.71435	1.94276	-1.49819
H	0.39547	4.25169	3.21919	H	-0.77782	2.57137	-0.75852
H	2.09577	1.74393	3.63934	O	-0.70531	-0.91063	0.85112
H	0.87537	2.39126	4.72551	O	-2.95704	-0.68873	1.2465
H	1.29931	0.33382	1.5529	O	0.32849	3.45056	0.76628
H	-1.53029	1.01605	0.655	O	1.29519	-1.83908	-1.40454
H	-2.78451	-0.1506	-1.2714	H	2.15126	5.19657	0.70925
H	-3.89578	-0.92018	-3.27661	O	0.93225	-3.54317	0.09879

Figure S32 Optimized geometries of 4 dominant conformers of **4d** at the M06-2X/def2-SVP level in the gas phase.



4d-1 **4d**-2



4d-3 **4d**-4

Table S37 Important thermodynamic parameters (a.u.) of the optimized **4d** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
4d-1	-1533.305208	-1533.275567	-1533.274623	-1533.364055
4d-2	-1533.303564	-1533.273909	-1533.272965	-1533.362131
4d-3	-1533.303341	-1533.273929	-1533.272985	-1533.361264
4d-4	-1533.302949	-1533.273674	-1533.272730	-1533.359906

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S38 Conformational analysis of the optimized **4d** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
4d-1	0.00	81.66%
4d-2	1.21	10.62%
4d-3	1.75	4.23%
4d-4	2.60	1.00%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S33 Regression analysis of experimental versus calculated NMR chemical shifts of **4d**.

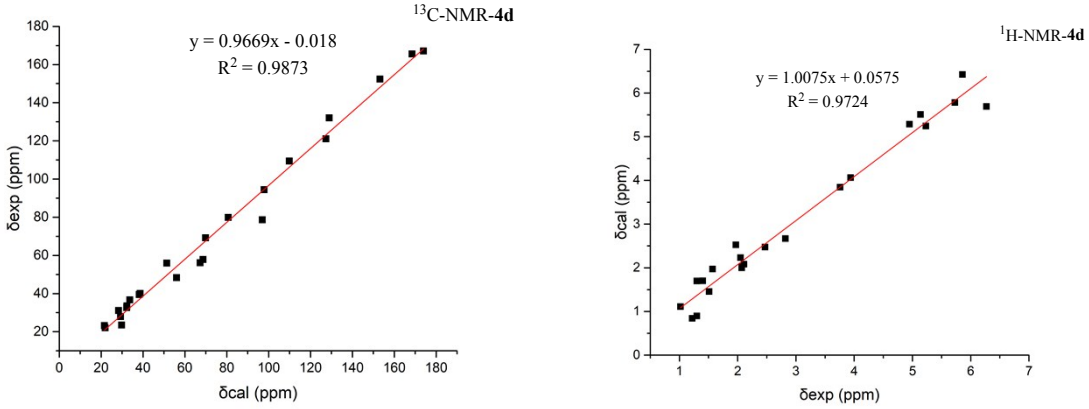


Table S 39 Optimized Z-matrixes of **4d**-1 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	4.072079	-1.366659	0.445874	H	-4.55065	-2.49708	-2.00183

C	5.062416	-0.447341	-0.216135	H	-3.07885	-3.12541	-2.75217
C	4.584221	0.995087	-0.133865	H	-3.20546	-0.73029	-3.27473
C	3.146907	1.176074	-0.659672	H	-1.10072	0.067229	-2.27165
C	2.167244	0.435476	0.304124	H	-0.87941	-1.71673	-2.24952
C	0.710309	0.470517	-0.208766	H	-2.2516	1.22372	-0.16623
C	-0.185161	-0.653606	0.356669	H	-5.21875	1.135389	-0.53238
C	-1.550614	-0.867228	-0.34557	H	-5.50262	0.268077	-2.16486
C	-2.117343	-2.199727	0.129369	H	2.787078	3.103192	0.315388
C	2.674611	-0.959573	0.694163	H	3.679697	3.198884	-1.22322
C	-2.966072	-2.91249	-0.612788	H	1.940829	2.91183	-1.25185
C	-3.450292	-2.449737	-1.961502	H	2.1491	0.980421	-2.60117
C	-2.983497	-1.01107	-2.236313	H	3.013448	-0.48992	-2.09137
C	-1.494263	-0.883078	-1.882825	H	3.917294	0.927269	-2.6816
C	-2.649567	0.20273	-0.107812	H	2.050096	-3.02148	0.677652
C	-3.624532	-0.049964	-1.25065	H	1.377489	-2.02465	2.004249
C	-4.841709	0.480538	-1.321349	H	-1.37266	4.451087	-0.73233
C	2.860854	2.682809	-0.699141	H	0.059343	4.371139	0.351925
C	3.047072	0.610877	-2.085586	H	-1.4438	3.570187	0.854291
C	1.638307	-2.040125	0.936029	H	-4.77268	0.214338	3.189203
C	-0.369429	2.57075	-0.684566	H	-3.25664	-0.48078	3.79671
C	-0.826067	3.832114	-0.01489	H	-3.63395	1.232452	4.161936
C	-2.988746	0.834918	2.167137	O	4.314157	-2.71038	0.296863
C	-3.72364	0.438622	3.414438	O	0.493202	-1.8559	0.141446
H	6.036083	-0.564959	0.289872	O	-0.36647	-0.46063	1.731897
H	5.197683	-0.770326	-1.258516	H	-0.53766	0.484078	1.881841
H	4.630324	1.334809	0.912904	O	-0.4471	2.326626	-1.85892
H	5.25685	1.64101	-0.718556	O	0.16947	1.726812	0.213077
H	2.154631	0.988977	1.257944	O	3.666121	-0.94752	1.72153
H	0.680392	0.407162	-1.300322	O	-2.17227	1.722646	2.102245
H	-1.8089	-2.541521	1.118575	H	5.201751	-2.89856	0.626767
H	-3.340044	-3.867904	-0.234853	O	-3.32415	0.058196	1.140572

Table S40 Optimized Z-matrixes of **4d-**2 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	3.471471	1.872214	-0.111496	H	-4.99946	-1.69779	1.68246
C	4.699903	1.186843	0.410766	H	-3.86926	-3.04315	1.500906
C	4.611628	-0.313622	0.182248	H	-4.46173	-2.27698	-0.75661
C	3.301111	-0.939555	0.700679	H	-2.17944	-1.66806	-1.59682
C	2.126107	-0.392246	-0.166776	H	-1.86699	-2.58349	-0.0821
C	0.736568	-0.854034	0.31305	H	-2.56902	0.848051	-1.48967
C	-0.392857	0.009599	-0.297045	H	-5.47923	1.482689	-0.57713
C	-1.817283	-0.390067	0.128012	H	-6.26985	-0.20491	-0.4021
C	-1.991969	-0.475632	1.630529	H	2.621832	-2.99879	1.042647
C	2.197708	1.139259	-0.334491	H	3.492973	-2.75554	-0.50151
C	-2.972334	-1.202936	2.174635	H	4.384441	-2.78652	1.036274
C	-3.982798	-1.955282	1.344903	H	2.321686	-1.20998	2.640474
C	-3.832029	-1.612942	-0.14888	H	2.816114	0.468229	2.316481
C	-2.340266	-1.689193	-0.508668	H	4.03284	-0.75978	2.741992
C	-2.849237	0.620148	-0.449725	H	1.073931	2.852921	0.34447

C	-4.156048	-0.148048	-0.383162	H	0.661442	2.289016	-1.3096
C	-5.363718	0.403014	-0.460787	H	0.472386	-4.88089	-1.78013
C	3.447182	-2.460925	0.560204	H	-0.24919	-4.68024	-0.13755
C	3.101905	-0.58645	2.180137	H	1.513461	-4.71415	-0.32409
C	0.916753	1.967661	-0.288775	H	-3.17998	4.078116	1.380352
C	0.600998	-2.908609	-0.982845	H	-1.46812	3.660135	1.582549
C	0.576234	-4.398564	-0.803849	H	-1.92566	4.932556	0.39727
C	-2.310597	2.917361	-0.205277	O	3.46868	3.21536	0.18822
C	-2.223872	3.982785	0.851502	O	-0.16522	1.275319	0.284885
H	5.572011	1.620864	-0.101215	O	-0.30746	0.126222	-1.67507
H	4.800747	1.431483	1.478315	H	0.0965	-0.67885	-2.0451
H	4.699546	-0.522601	-0.896294	O	0.649499	-2.35432	-2.05581
H	5.459702	-0.811368	0.676958	O	0.559737	-2.2761	0.186522
H	2.264131	-0.777349	-1.189546	O	3.068862	1.540772	-1.40248
H	0.643819	-0.701797	1.393635	O	-1.88332	3.010991	-1.32085
H	-1.327155	0.122409	2.258436	H	2.951176	3.67224	-0.48689
H	-3.078667	-1.239422	3.26218	O	-2.92607	1.825282	0.286038

Table S41 Optimized Z-matrixes of **4d-**3 in the gas phase (Å) at the M06-2X/def2-SVP level.

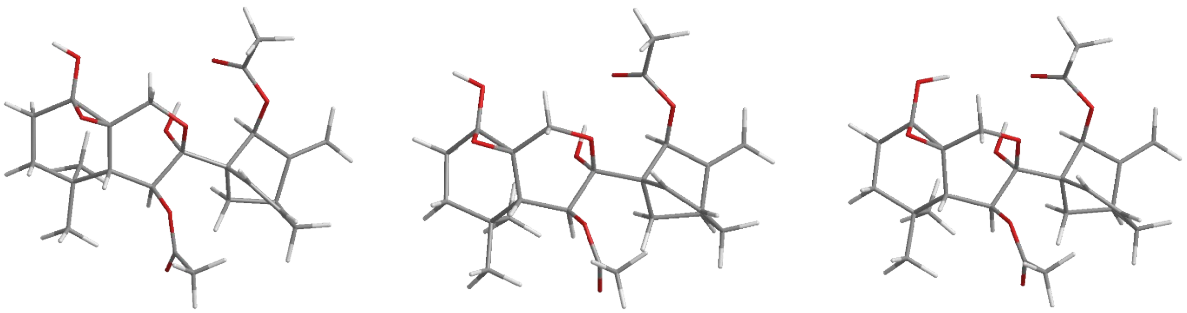
C	-3.991552	-1.119807	-0.861622	H	4.554773	-3.23485	0.900061
C	-4.958004	-0.702278	0.214325	H	3.06423	-4.13847	1.193995
C	-4.492577	0.578791	0.89297	H	3.120083	-2.26991	2.784011
C	-3.026395	0.500621	1.361583	H	1.04711	-1.09883	2.177072
C	-2.117506	0.446739	0.0942	H	0.859408	-2.65464	1.304525
C	-0.619473	0.29833	0.470899	H	2.207741	0.892577	0.977376
C	0.285337	-0.455917	-0.535301	H	5.235174	0.633843	1.285602
C	1.602643	-1.004627	0.059931	H	5.479413	-0.90961	2.315495
C	2.217688	-1.957758	-0.957985	H	-1.71128	1.748692	2.595008
C	-2.615214	-0.588664	-0.924467	H	-2.85412	2.66532	1.576824
C	3.043703	-2.941519	-0.597971	H	-3.43463	1.821803	3.033142
C	3.456695	-3.1715	0.831994	H	-1.92191	-0.6839	2.848045
C	2.95114	-2.02849	1.725685	H	-2.78828	-1.66876	1.648349
C	1.475123	-1.749563	1.398691	H	-3.67836	-0.83816	2.949455
C	2.667267	0.055496	0.431822	H	-1.96712	-2.34685	-1.98582
C	3.616431	-0.71921	1.334029	H	-1.28655	-0.80841	-2.58538
C	4.837013	-0.309639	1.666317	H	0.390463	4.715681	0.261362
C	-2.7315	1.756445	2.188693	H	1.186887	3.677416	1.493963
C	-2.838527	-0.743776	2.243831	H	-0.54281	4.088542	1.66899
C	-1.564222	-1.374764	-1.682467	H	4.616382	1.590278	-2.60246
C	-0.115462	2.658614	0.157456	H	2.943513	1.530903	-3.19661
C	0.258543	3.874077	0.946988	H	3.640208	3.11256	-2.71167
C	3.07962	1.805132	-1.11776	O	-4.20542	-2.3671	-1.39596
C	3.622229	2.040074	-2.496583	O	-0.43878	-1.61751	-0.87927
H	-5.950673	-0.560796	-0.246185	O	0.605162	0.29598	-1.65984
H	-5.049439	-1.528513	0.934055	H	0.081829	1.118695	-1.68379
H	-4.600207	1.422625	0.193227	O	-0.47488	2.666632	-0.99584
H	-5.134075	0.792437	1.761867	O	-0.05466	1.547104	0.905407
H	-2.242006	1.402387	-0.432995	O	-3.65723	-0.10785	-1.77301

H	-0.579749	-0.314596	1.374313	O	2.470605	2.614249	-0.46743
H	1.965739	-1.789548	-2.005793	H	-5.09623	-2.39022	-1.76762
H	3.454385	-3.606884	-1.361965	O	3.346708	0.562037	-0.70507

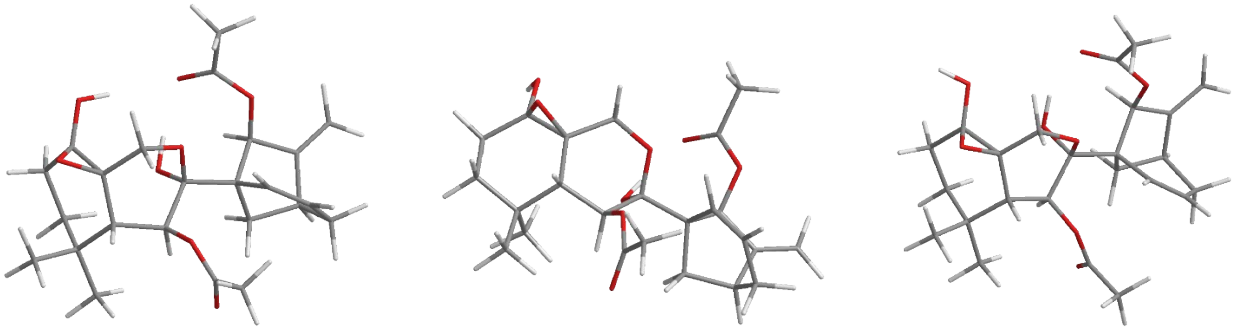
Table S42 Optimized Z-matrixes of **4d-**4 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-2.432668	-1.900384	-0.979547	H	5.546747	0.42828	0.826291
C	-2.990561	-2.216785	0.395	H	5.349085	1.690514	-0.39524
C	-2.734093	-1.10572	1.410018	H	5.021595	-0.48245	-1.51075
C	-2.977433	0.326096	0.903623	H	2.704594	-0.12531	-2.38986
C	-2.036884	0.614131	-0.312497	H	3.184118	1.51054	-1.85739
C	-0.560878	0.892272	0.095993	H	1.638148	-1.70033	-0.80143
C	0.558949	0.7504	-1.001151	H	3.709451	-3.03823	1.140116
C	1.95518	0.403474	-0.419966	H	5.344265	-2.38325	0.515398
C	2.406204	1.286109	0.732813	H	-4.61592	1.571977	0.2055
C	-2.023217	-0.521378	-1.326101	H	-4.708	-0.0995	-0.38948
C	3.70132	1.509579	0.977507	H	-5.10972	0.271009	1.312647
C	4.809423	0.901937	0.158316	H	-1.73558	1.169057	2.522665
C	4.240391	-0.13834	-0.819347	H	-3.47885	1.071169	2.864859
C	3.025325	0.476635	-1.528437	H	-2.86618	2.331233	1.777958
C	2.119089	-1.085587	-0.030774	H	-1.06109	-1.17251	-3.12073
C	3.623129	-1.289818	-0.043298	H	-1.19988	0.608393	-2.97062
C	4.257231	-2.287202	0.565872	H	-1.01144	5.360594	0.874426
C	-4.440719	0.518544	0.473576	H	0.488406	4.532265	1.418824
C	-2.735586	1.280622	2.080842	H	-1.04744	4.164173	2.227361
C	-1.011735	-0.33217	-2.421303	H	0.15216	-1.75275	3.314285
C	-0.827486	3.32303	0.271052	H	-0.63918	-3.28567	2.776472
C	-0.594428	4.426795	1.262506	H	1.110199	-3.23608	3.176109
C	0.604801	-2.355255	1.306756	O	-1.90614	-2.95833	-1.67503
C	0.270644	-2.678367	2.737069	O	0.267655	-0.33507	-1.84077
H	-4.068752	-2.406131	0.276661	O	0.711516	1.923209	-1.72606
H	-2.531886	-3.152523	0.742979	H	-0.13564	2.383789	-1.82335
H	-3.350642	-1.273242	2.307686	O	-1.30921	3.47565	-0.82445
H	-1.687619	-1.171423	1.750954	O	-0.41533	2.154297	0.767083
H	-2.420908	1.501539	-0.837563	O	-3.25397	-1.07443	-1.7586
H	-0.294647	0.170297	0.882136	O	0.085522	-2.86886	0.347195
H	1.65513	1.717768	1.393307	H	-1.11043	-3.22739	-1.18945
H	3.982635	2.145674	1.82128	O	1.563855	-1.43061	1.23898

Figure S34 Optimized geometries of 6 dominant conformers of **4e** at the M06-2X/def2-SVP level in the gas phase.



4e-1 **4e**-2 **4e**-3



4e-4 **4e**-5 **4e**-6

Table S43 Important thermodynamic parameters (a.u.) of the optimized **4e** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*U(0)*[a]	*U(T)*[b]	*H(T)*[c]	*G(T)*[d]
4e-1	-1533.313715	-1533.284318	-1533.283374	-1533.371180
4e-2	-1533.313262	-1533.284276	-1533.283332	-1533.370828
4e-3	-1533.312297	-1533.282638	-1533.281694	-1533.370527
4e-4	-1533.312370	-1533.282894	-1533.281950	-1533.370245
4e-5	-1533.311674	-1533.282057	-1533.281113	-1533.369557
4e-6	-1533.311382	-1533.281931	-1533.280987	-1533.368226

[a]*U(0)* = electronic energy (ε_{ele}) + zero point energy (ZPE); [b]$U(T) = \varepsilon_{ele} + ZPE + \Delta U_{0\rightarrow T}$;
[c]$H(T) = \varepsilon_{ele}$ + ZPE + $\Delta H_{0\rightarrow T}$; [d]$G(T) = \varepsilon_{ele} + ZPE + \Delta G_{0\rightarrow T}$

Table S44 Conformational analysis of the optimized **4e** at the M06-2X/def2-SVP level in the gas phase.

Conformers	*ΔG(kcal/mol)*	*Population*
4e-1	0.00	35.86%
4e-2	0.22	24.69%
4e-3	0.41	17.94%
4e-4	0.59	13.31%
4e-5	1.02	6.42%
4e-6	1.85	1.56%

[a]relative *G(T)* in kcal/mol. [b]Conformational distribution calculated at the M06-2X/def2-SVP level in the gas phase. (T=298.15 K)

Figure S35 Regression analysis of experimental versus calculated NMR chemical shifts of **4e**.

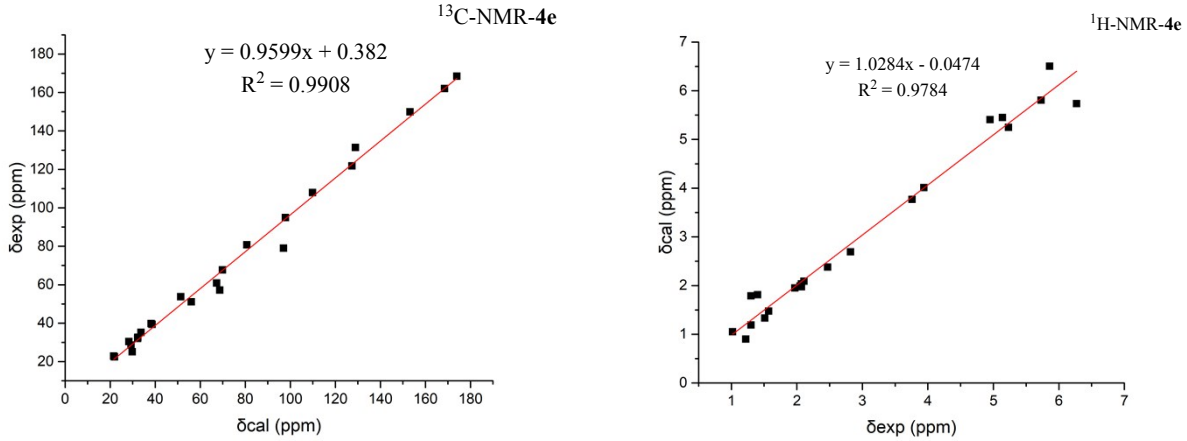


Table S45 Optimized Z-matrixes of **4e-**1 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-3.614049	-1.526459	-0.308407	H	5.180841	1.752939	-0.11635
C	-4.685245	-0.904286	0.547894	H	3.972473	3.012157	0.169778
C	-4.560421	0.613809	0.548126	H	4.080774	1.570719	2.177039
C	-3.139776	1.097138	0.895331	H	1.672899	0.883743	2.267573
C	-2.173713	0.646348	-0.235681	H	1.685984	2.219851	1.083147
C	-0.701279	1.039308	0.018447	H	2.136374	-1.40178	1.636133
C	0.225299	-0.177413	0.147933	H	5.163974	-2.00635	0.981992
C	1.725988	0.18697	0.210967	H	5.980408	-0.39221	1.46324
C	2.279378	0.660869	-1.122908	H	-2.16519	3.057205	1.124008
C	-2.37996	-0.808872	-0.668956	H	-3.82278	2.968064	1.762439
C	3.34854	1.460434	-1.194364	H	-3.54919	3.044388	0.005556
C	4.102037	1.924805	0.026537	H	-3.50349	0.770095	3.006608
C	3.61508	1.163052	1.269742	H	-2.56818	-0.54672	2.234463
C	2.076619	1.216626	1.298987	H	-1.78305	0.985006	2.611084
C	2.596279	-0.990586	0.724162	H	-1.15216	-2.56203	-0.37766
C	3.901325	-0.320175	1.09548	H	-1.31015	-2.01563	-2.0655
C	5.074559	-0.938027	1.189186	H	1.430485	3.225788	-2.55174
C	-3.162958	2.62836	0.949698	H	-0.26006	3.547624	-2.98571
C	-2.72527	0.539716	2.261619	H	0.680482	4.791822	-2.07674
C	-1.177384	-1.675896	-1.030653	H	1.666843	-3.49717	-2.22646
C	0.079537	3.103341	-0.919802	H	3.194381	-4.11598	-1.56266
C	0.507143	3.721316	-2.220438	H	1.630622	-4.93657	-1.15946
C	1.926047	-3.061428	-0.186917	O	-3.51992	-2.89719	-0.24579
C	2.127354	-3.981132	-1.352224	O	0.064313	-1.00084	-0.98155
H	-4.5975	-1.316734	1.563203	O	-0.19651	-0.81895	1.308906
H	-5.668679	-1.213384	0.153468	H	0.173182	-1.7222	1.307907
H	-5.270459	1.046188	1.270117	O	-0.25186	1.814868	-1.09386
H	-4.833543	0.996845	-0.447996	O	0.043538	3.669879	0.139961
H	-2.461331	1.220956	-1.129959	O	-3.4736	-0.96112	-1.58372
H	-0.610565	1.641757	0.929888	O	2.784765	-2.04107	-0.21026
H	1.775321	0.307775	-2.023069	H	-4.38411	-3.27207	-0.45674
H	3.716702	1.77935	-2.173975	O	1.075257	-3.20687	0.659283

Table S46 Optimized Z-matrixes of **4e-**2 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-3.395497	-1.618126	-0.197086	H	5.125388	1.7583	0.235068
C	-4.355606	-1.140188	0.86443	H	3.903546	3.009593	0.501546
C	-4.473947	0.381106	0.836348	H	3.863869	1.472665	2.436134
C	-3.110823	1.081714	0.979338	H	1.451682	0.799166	2.317052
C	-2.221659	0.707518	-0.245221	H	1.561123	2.185184	1.189664
C	-0.737305	1.0827	-0.074406	H	1.953984	-1.46957	1.602582
C	0.164258	-0.158682	0.055855	H	5.024098	-2.05132	1.164085
C	1.657945	0.19365	0.240262	H	5.80455	-0.46613	1.781838
C	2.30306	0.733241	-1.024804	H	-2.35344	3.133733	0.951117
C	-2.372806	-0.72158	-0.752268	H	-3.88876	2.93113	1.830707
C	3.372385	1.534717	-0.979948	H	-3.87407	2.902498	0.048988
C	4.039977	1.930242	0.312761	H	-3.23075	0.938538	3.128736
C	3.464932	1.109959	1.479153	H	-2.2419	-0.36177	2.397769
C	1.929123	1.170936	1.397176	H	-1.58746	1.267152	2.552235
C	2.486263	-1.011913	0.754524	H	-1.29634	-2.38382	-1.57998
C	3.75981	-0.365688	1.257971	H	-1.32774	-0.90013	-2.57875
C	4.921386	-0.993152	1.413191	H	-0.19743	3.408581	-3.20108
C	-3.31787	2.600323	0.949892	H	0.720922	4.699854	-2.33344
C	-2.503934	0.699345	2.336311	H	1.483343	3.115911	-2.70593
C	-1.209569	-1.288681	-1.554317	H	1.786208	-3.39564	-2.37337
C	0.096688	3.07149	-1.105111	H	3.282023	-4.00622	-1.63252
C	0.549233	3.623474	-2.426619	H	1.715082	-4.87752	-1.36971
C	1.897361	-3.039547	-0.303863	O	-3.14503	-2.96496	-0.22437
C	2.200211	-3.904201	-1.49009	O	0.087791	-0.93394	-1.10722
H	-4.014914	-1.508984	1.84213	O	-0.33022	-0.86668	1.148197
H	-5.337849	-1.603645	0.666158	H	0.006146	-1.78163	1.081264
H	-5.13574	0.721545	1.647813	O	-0.30461	1.795539	-1.23377
H	-4.93907	0.681825	-0.115284	O	0.09777	3.671345	-0.06385
H	-2.580123	1.326486	-1.084105	O	-3.59287	-0.99074	-1.44449
H	-0.601011	1.723125	0.803291	O	2.745461	-2.01072	-0.21848
H	1.868612	0.421047	-1.975147	H	-3.98948	-3.43211	-0.24323
H	3.809388	1.902317	-1.913205	O	0.988512	-3.22886	0.467313

Table S47 Optimized Z-matrixes of **4e-**3 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-3.246247	-1.691102	-0.125227	H	5.128091	1.7128	0.344593
C	-4.196499	-1.240905	0.955487	H	3.924197	2.976628	0.632666
C	-4.457141	0.25871	0.847319	H	3.832766	1.384135	2.520969
C	-3.162063	1.088543	0.926431	H	1.409192	0.764302	2.352622
C	-2.248052	0.718435	-0.285154	H	1.558024	2.174189	1.258861
C	-0.765052	1.113407	-0.098795	H	1.88612	-1.49092	1.596305
C	0.145201	-0.122599	0.043189	H	4.946615	-2.12304	1.156602
C	1.635835	0.20871	0.263563	H	5.751924	-0.57041	1.822315
C	2.307846	0.770588	-0.977992	H	-2.57896	3.18747	0.777267
C	-2.347904	-0.723016	-0.769071	H	-4.09256	2.912678	1.672273
C	3.3876	1.554767	-0.896897	H	-4.07724	2.782424	-0.10534
C	4.044911	1.901116	0.414603	H	-3.27739	1.028614	3.07989

C	3.440392	1.057186	1.548685	H	-2.11948	-0.15919	2.414391
C	1.906292	1.149573	1.449158	H	-1.69489	1.556269	2.494771
C	2.431848	-1.027323	0.760113	H	-1.26224	-2.2582	-1.83118
C	3.712926	-0.417502	1.288548	H	-1.31033	-0.66341	-2.60581
C	4.861717	-1.070219	1.433606	H	-0.17276	3.468918	-3.19152
C	-3.498026	2.579047	0.808313	H	0.784749	4.72039	-2.30789
C	-2.518337	0.853239	2.301566	H	1.50386	3.125401	-2.71284
C	-1.186019	-1.176707	-1.636924	H	1.786318	-3.26228	-2.46883
C	0.1275	3.088477	-1.103156	H	3.190645	-4.00417	-1.67513
C	0.584196	3.650676	-2.41865	H	1.560787	-4.78095	-1.54069
C	1.799391	-3.005391	-0.381337	O	-2.96307	-3.03005	-0.07974
C	2.111034	-3.836522	-1.588318	O	0.100664	-0.88863	-1.13292
H	-3.774642	-1.51777	1.932149	O	-0.37018	-0.84715	1.116504
H	-5.128065	-1.81478	0.831686	H	-0.0061	-1.75086	1.056404
H	-5.133453	0.583429	1.65324	O	-0.32422	1.829809	-1.25229
H	-4.965054	0.461081	-0.108314	O	0.163937	3.664649	-0.05005
H	-2.602125	1.319111	-1.139559	O	-3.5612	-1.12855	-1.38686
H	-0.641991	1.754728	0.779834	O	2.677915	-2.0148	-0.23058
H	1.88244	0.49153	-1.942504	H	-2.01342	-3.16929	-0.1798
H	3.841344	1.942788	-1.813608	O	0.855605	-3.19388	0.352418

Table S48 Optimized Z-matrixes of **4e-**4 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	2.864642	-1.78367	0.091835	H	-5.1193	1.716607	-0.28866
C	3.565632	-1.544196	-1.232559	H	-3.92981	2.981789	-0.62589
C	3.279731	-0.168129	-1.843844	H	-3.8714	1.349607	-2.4851
C	3.306459	1.000342	-0.845614	H	-1.44029	0.756642	-2.36416
C	2.297773	0.756673	0.315184	H	-1.57123	2.186313	-1.29787
C	0.810002	1.138491	0.056619	H	-1.88015	-1.45915	-1.58887
C	-0.113327	-0.088759	-0.053018	H	-4.92337	-2.13259	-0.99615
C	-1.609194	0.239596	-0.260106	H	-5.76584	-0.59902	-1.66059
C	-2.262997	0.814611	0.984806	H	4.754192	2.06788	0.38273
C	2.31293	-0.659781	0.86193	H	5.457349	1.264066	-1.04022
C	-3.350637	1.589131	0.916336	H	4.986345	0.305147	0.3924
C	-4.039046	1.909761	-0.385602	H	2.781923	3.127867	-0.89456
C	-3.453316	1.047847	-1.5154	H	3.830483	2.584308	-2.22701
C	-1.916712	1.15577	-1.456007	H	2.10307	2.197445	-2.25101
C	-2.401598	-1.011074	-0.729182	H	1.273824	-1.94757	2.219168
C	-3.70773	-0.42334	-1.215181	H	1.175255	-0.20303	2.629153
C	-4.857146	-1.085473	-1.298597	H	0.20035	3.658394	3.011744
C	4.710919	1.158811	-0.237786	H	-0.75069	4.864751	2.060906
C	2.97806	2.298856	-1.592971	H	-1.47517	3.294049	2.544787
C	1.168746	-0.937733	1.805414	H	-1.50936	-3.24019	2.44431
C	-0.092298	3.171241	0.944637	H	-2.97597	-3.9788	1.765017
C	-0.553138	3.801715	2.22742	H	-1.36155	-4.75945	1.504567
C	-1.684689	-2.981856	0.370786	O	2.357392	-3.04956	0.289067
C	-1.906121	-3.814801	1.593893	O	-0.07286	-0.86698	1.120792
H	3.245996	-2.332169	-1.927898	O	0.383033	-0.79459	-1.15145
H	4.644128	-1.689149	-1.062491	H	0.001967	-1.69103	-1.1193

H	2.288722	-0.190446	-2.316439	O	0.353414	1.919324	1.162326
H	4.014554	0.035571	-2.639474	O	-0.12045	3.689633	-0.13737
H	2.602059	1.422211	1.141156	O	3.537885	-1.26795	1.217345
H	0.703071	1.724577	-0.861316	O	-2.58755	-2.0105	0.263379
H	-1.815292	0.555491	1.944707	H	1.443625	-3.08413	-0.03317
H	-3.786857	1.987042	1.837319	O	-0.7774	-3.15402	-0.41606

Table S49 Optimized Z-matrixes of **4e-**5 in the gas phase (Å) at the M06-2X/def2-SVP level.

C	-3.607714	-1.529191	-0.302874	H	5.186301	1.736294	-0.06445
C	-4.659261	-0.91901	0.588316	H	3.981261	2.998746	0.221699
C	-4.549803	0.600751	0.576554	H	4.062792	1.538171	2.21657
C	-3.131184	1.108384	0.896435	H	1.650331	0.86455	2.277096
C	-2.173703	0.66118	-0.244366	H	1.682492	2.20978	1.102674
C	-0.699869	1.05008	0.004004	H	2.10992	-1.4174	1.632534
C	0.219511	-0.172445	0.132912	H	5.140654	-2.03282	0.996662
C	1.720909	0.184092	0.215208	H	5.960619	-0.42696	1.499002
C	2.290046	0.667128	-1.108802	H	-2.17532	3.080003	1.085189
C	-2.376891	-0.793316	-0.674407	H	-3.81929	2.981758	1.757407
C	3.363213	1.46276	-1.162443	H	-3.58166	3.040898	-0.00549
C	4.107052	1.912181	0.069805	H	-3.46741	0.806864	3.015305
C	3.604203	1.141299	1.300901	H	-2.52191	-0.5086	2.252878
C	2.065671	1.202885	1.315251	H	-1.75448	1.037687	2.599974
C	2.579791	-1.002221	0.727476	H	-1.16095	-2.56553	-0.47711
C	3.884919	-0.341806	1.115624	H	-1.31693	-1.93479	-2.13361
C	5.054442	-0.966055	1.213014	H	-0.23641	3.545115	-3.00639
C	-3.172455	2.639773	0.935196	H	0.711227	4.785705	-2.09966
C	-2.693929	0.575401	2.265679	H	1.451885	3.214201	-2.56997
C	-1.180664	-1.645952	-1.083637	H	1.653214	-3.48607	-2.24779
C	0.098843	3.103948	-0.939037	H	3.179751	-4.10753	-1.58364
C	0.531123	3.715984	-2.240862	H	1.615344	-4.93217	-1.19088
C	1.90602	-3.062944	-0.205323	O	-3.58372	-2.91051	-0.34079
C	2.112053	-3.975075	-1.375426	O	0.067384	-0.98506	-1.00429
H	-4.54275	-1.313679	1.610578	O	-0.21601	-0.8262	1.282984
H	-5.643734	-1.249001	0.220978	H	0.158311	-1.7277	1.274491
H	-5.255537	1.031058	1.303975	O	-0.24758	1.818967	-1.11132
H	-4.844597	0.967605	-0.419441	O	0.070684	3.671491	0.120452
H	-2.468061	1.239568	-1.134345	O	-3.49376	-0.96153	-1.56127
H	-0.604258	1.655406	0.912918	O	2.770061	-2.04759	-0.21273
H	1.793372	0.324336	-2.017029	H	-3.74591	-3.24658	0.547387
H	3.742179	1.789092	-2.13547	O	1.046141	-3.21019	0.632296

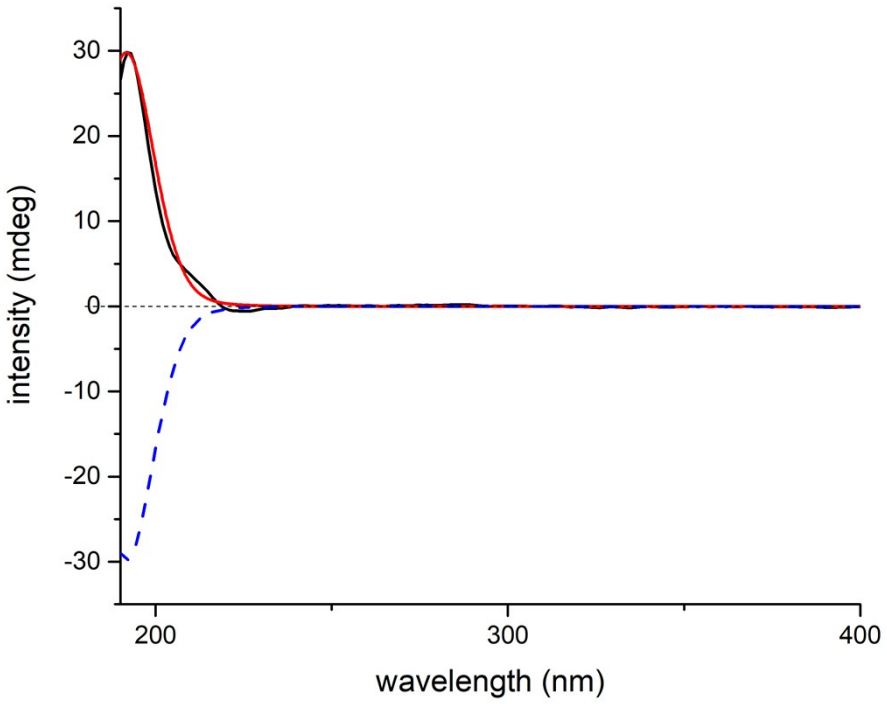
Table S50 The DP4+ probabilities of **4a**, **4b**, **4c**, **4d**, and **4e**.

Functional	Solvent	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d,p)	Unscaled Shifts

□	Isomer 1 (**4a**)	Isomer 2 (**4b**)	Isomer 3 (**4c**)	Isomer 4 (**4d**)	Isomer 5 (**4e**)
sDP4+ (H data)	100.00%	0.00%	0.00%	0.00%	0.00%

sDP4+ (C data)	100.00%	0.00%	0.00%	0.00%	0.00%
sDP4+ (all data)	100.00%	0.00%	0.00%	0.00%	0.00%
uDP4+ (H data)	100.00%	0.00%	0.00%	0.00%	0.00%
uDP4+ (C data)	100.00%	0.00%	0.00%	0.00%	0.00%
uDP4+ (all data)	100.00%	0.00%	0.00%	0.00%	0.00%
DP4+ (H data)	100.00%	0.00%	0.00%	0.00%	0.00%
DP4+ (C data)	100.00%	0.00%	0.00%	0.00%	0.00%
DP4+ (all data)	100.00%	0.00%	0.00%	0.00%	0.00%

Figure S36 Calculated ECD of **4a**.



Computational Data of (1*S*, 5*S*, 6*S*, 7*R*, 8*S*, 10*R*, 13*R*, 15*R*) **-4** (**4a**)

Experimental ECD spectrum of **4a** (black); Calculated ECD spectrum of (1*S*, 5*S*, 6*S*, 7*R*, 8*S*, 10*R*, 13*R*, 15*R*) **-4a** (shift = 5 nm, red) and (1*R*, 5*R*, 6*R*, 7*S*, 8*R*, 10*S*, 13*S*, 15*S*) **-4a** (shift = 5 nm, blue dash) at the CAM-B3LYP-SCRF/def2-SVP level of theory in MeOH with PCM.

Table S51 Key transitions, oscillator strengths, and rotatory strengths in the ECD spectra of conformer **4a**-1 at the CAM-B3LYP-SCRF/def2-SVP level in MeOH with PCM.

Num[a]	*exited state*[b]	*CI Coefficient*	*ΔE (eV)*[c]	*λ (nm)*[d]	*f*[e]	R_{vel}[f]	R_{len}[g]
1	113 ->121	0.27515	6.0015	206.59	0.0021	1.6474	-1.1744
□	114 ->121	0.3955	□	□	□	□	□
□	114 ->122	0.25838	□	□	□	□	□
2	114 ->123	-0.22553	6.0716	204.2	0.0007	-0.9069	-1.9429
□	116 ->123	0.45504	□	□	□	□	□
3	120 ->121	-0.40882	6.7523	183.62	0.1087	213.5377	210.5781
□	120 ->122	0.52534	□	□	□	□	□
4	120 ->123	-0.29618	6.8883	179.99	0.3581	-157.9556	-161.4597
□	120 ->124	0.61381	□	□	□	□	□
5	119 ->121	-0.36995	7.1779	172.73	0.3451	63.469	67.4034
□	119 ->122	0.5216	□	□	□	□	□
6	120 ->121	0.4713	7.2413	171.22	0.029	-17.715	-12.9353

□	120 ->122	0.37412	□	□	□	□	□
7	119 ->123	-0.33752	7.3577	168.51	0.0921	26.5538	27.8792
□	119 ->124	0.56176	□	□	□	□	□
8	118 ->121	0.5786	7.5543	164.12	0.0003	0.5435	1.3738
□	118 ->122	0.331	□	□	□	□	□
9	112 ->122	0.26397	7.6015	163.1	0.018	-43.7525	-46.895
10	119 ->121	0.42599	7.6814	161.41	0.0043	-2.3667	-2.6143
□	119 ->122	0.30522	□	□	□	□	□
□	120 ->123	0.28195	□	□	□	□	□
11	110 ->123	-0.23331	7.7013	160.99	0.0057	-30.9954	-32.8277
□	110 ->124	0.3172	□	□	□	□	□
12	119 ->121	-0.2787	7.7102	160.8	0.0128	-1.6874	-1.7164
□	119 ->122	-0.27156	□	□	□	□	□
□	120 ->123	0.39274	□	□	□	□	□
13	117 ->121	-0.24909	7.9134	156.68	0.0767	9.3847	2.8103
□	117 ->123	0.34454	□	□	□	□	□
□	119 ->123	0.25589	□	□	□	□	□
14	117 ->121	0.50239	7.9976	155.03	0.0038	6.7276	7.489
□	117 ->122	0.22861	□	□	□	□	□
15	120 ->125	0.38394	8.0456	154.1	0.0012	0.2761	0.1127
□	120 ->127	0.3796	□	□	□	□	□
16	117 ->123	-0.30988	8.1386	152.34	0.0163	-16.0349	-17.7508
□	117 ->124	0.33854	□	□	□	□	□
17	117 ->122	0.25622	8.1531	152.07	0.0166	18.2979	15.8805
18	118 ->122	0.23644	8.1713	151.73	0.0421	-19.9092	-4.0189
□	118 ->123	0.29465	□	□	□	□	□
□	118 ->124	0.22675	□	□	□	□	□
19	118 ->123	0.46918	8.2075	151.06	0.0043	-7.7244	-7.1561
□	118 ->124	-0.34598	□	□	□	□	□
20	110 ->122	0.25998	8.2971	149.43	0.0149	-10.1591	-8.6435
□	117 ->122	0.33446	□	□	□	□	□
□	117 ->124	-0.26599	□	□	□	□	□
21	118 ->128	0.28605	8.3607	148.29	0.0115	18.321	28.7991
22	117 ->124	0.26412	8.3972	147.65	0.0108	-28.1608	-21.6317
□	118 ->122	-0.25046	□	□	□	□	□
□	118 ->124	0.32777	□	□	□	□	□
23	112 ->121	0.32254	8.4171	147.3	0.0108	-8.6308	-12.859
24	112 ->124	0.2372	8.4251	147.16	0.0188	-45.083	-49.7241
25	119 ->125	0.26005	8.4359	146.97	0.0028	-12.6652	-12.2367
□	119 ->127	0.28865	□	□	□	□	□
26	117 ->123	0.23319	8.4602	146.55	0.0201	-35.4905	-33.1283
27	112 ->121	0.21757	8.511	145.68	0.0108	33.972	39.546
28	119 ->123	0.43652	8.529	145.37	0.0137	-19.6374	-20.525
29	118 ->122	-0.23066	8.5469	145.06	0.012	-1.4405	-3.1371

□	118 ->124	0.24166	□	□	□	□	□
30	116 ->124	0.23429	8.6319	143.63	0.019	22.4587	24.7793

[a]Number of the excited states. [b]only excited states with contribution over 10% were listed. [c]Excitation energy. [d]Wavelength. [e]Oscillator strength. [f]Rotatory strength in velocity form (10-40 cgs.). [g]Rotatory strength in length form (10^{-40} cgs.).

8. Results of the biological activity evaluation.

Compounds **1**–**4** were evaluated neurotrophic activities, including Acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) inhibitory activity, induction PC-12 cells differentiation activity, the inhibitory effects of samples on platelet aggregation in rabbits induced by ADP, AA, and PAF, only compound **2** showed weak anti-AChE activity (IC_{50} = 37.6 ± 2.3 μM) and weak anti-ADP (inhibited rate = 39.2±10.7%) and anti-AA induced (inhibited rate = 15.9±10.3%) platelet aggregation in rabbits.

8.1 Acetylcholinesterase/butyrylcholinesterase inhibitory activity

Acetylcholinesterase/butyrylcholinesterase (AChE/BuChE) inhibitory activity of the compounds isolated was assayed by the spectrophotometric method developed by Ellman et al[1] with slightly modification. S-Acetylthiocholine iodide, S-butyrylthiocholineiodide, 5,5'-dithio-bis-(2-nitrobenzoic) acid (DTNB, Ellman's reagent), acetylcholinesterase and butyrylcholinesterase derived from human erythrocytes were purchased from Sigma Chemical. Compounds were dissolved in DMSO. The reaction mixture (totally 200 μL) containing phosphate buffer (pH 8.0), test compound (50 μM), and acetyl cholinesterase (0.02 U/mL) or butyrylcholinesterase (0.016 U/mL), was incubated for 20 min (37 °C). Then, the reaction was initiated by the addition of 40μL of solution containing DTNB(0.625mM) and acetylthiocholine iodide (0.625 mM) or butyrylthiocholine iodide (0.625 mM) for AChE or BuChE inhibitory activity assay, respectively. The hydrolysis of acetylthiocholine or butyrylthiocholine was monitored at 405 nm every 30seconds for one hour. Tacrine was used as positive control with final concentration of 0.333μM. All the reactions were performed in triplicate.

The percentage inhibition was calculated as follows:

% inhibition = (E - S)/E × 100 (E is the activity of the enzyme without test compound and S is the activity of enzyme with test compound).

Table S52 AChE inhibitory effects of compounds **1**–**4**.

Sample	Tacrine	1	2	3	4
Inhibited rate (%)	55.41	35.26	51.64	4.43	11.93
SD	2.04	2.96	0.21	2.32	2.44
Inhibited activity		++	++	–	+

% inhibition = (E – S)/E × 100 (E is the activity of the enzyme without test compound and S is the activity of enzyme with test compound).

Table S53 BuChE inhibitory effects of compounds **1**–**4**.

Sample	Tacrine	1	2	3	4
Inhibited rate (%)	90.96	0.66	9.36	1.40	0.04
SD	0.17	0.23	0.35	0.88	0.83
Inhibited activity	□	–□	–□	–□	–□

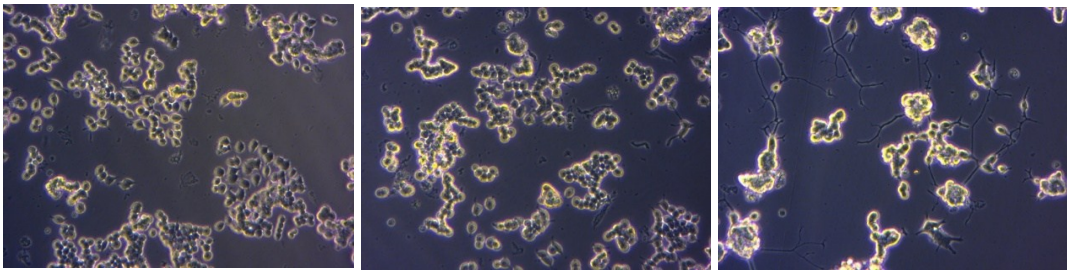
% inhibition = (E – S)/E × 100 (E is the activity of the enzyme without test compound and S is the activity of enzyme with test compound).

8.2 Neurite outgrowth-promoting activity

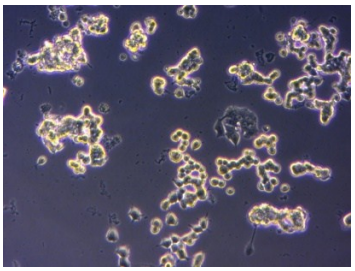
The neurotrophic activities of the test compounds were examined according to an assay using PC12 cells as reported.[2] Briefly, PC12 cells were maintained in 1640 medium supplemented with 10% horse serum (HS), and 5% fetal bovine serum (FBS), and incubated at 5% CO_2 and 37℃. Test compounds were dissolved in DMSO. For the neurite outgrowth-promoting activity bioassay, PC12 cells were seeded at a density of $5*10^4$ cells/ml in 48-well plate coated with poly-L-lysine. After 24 h, the medium was changed to that containing 10 μM of each test compounds plus 5 ng/ml NGF, or various concentrations of NGF (50 ng/ml for the positive control, 5 ng/ml for the negative control). The final concentration of DMSO was 0.05%, and the same concentration of DMSO was added into the negative control. After 72 h incubation, the neurite outgrowth was assessed under a phase contrast microscope. Neurite processes with a length equal to or greater than the diameter of the neuron cell body was scored as neurite bearing cells. The ratio of the neurite-bearing cells to total cells (with at least 100 cells examined/view area; 5 viewing area/well) was determined and expressed as a percentage.

Table S54 Neurite outgrowth-promoting activity (PC-12 cells).

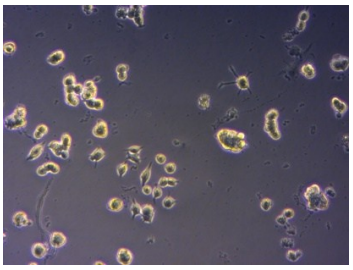
Group	Blank	Negative 5ng/mL NGF	Positive 50ng/mL NGF	1	2	3	4
72 h differentiation rate (%)	0.00%	4.31%	21.03%	6.03%	6.57%	5.45%	5.70%



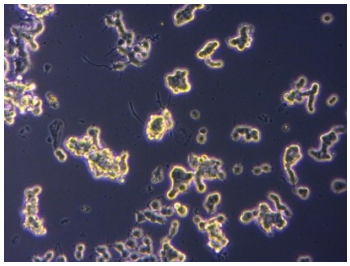
(1) Blank (2) Negative 5ng/mL NGF (3) Positive 50ng/mL NGF



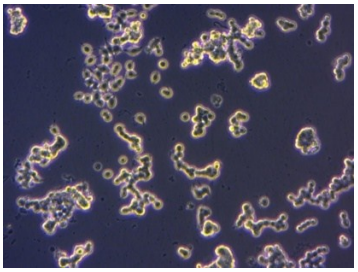
(4) compound **1** 10μM



(5) compound **2** (10μM)



(6) compound **3** (10μM)



(7) compound **4** (10μM)

Figure S37 72 h cellular morphology of **1**–**4**.

8.3 Test of platelet aggregation assays.

Turbid metric measurements of platelet aggregation of the compounds **1**–**4** and Ginkgolide B were performed in a Chronolog Model 700 Aggregometer (Chronolog Corporation, Havertown, PA, USA) according to Born's method.[3-5]

The blood from the central aural artery of rabbits by a butterfly infusion set, were anticoagulated with 3.8% sodium citrate (9:1, v/v). Platelet-rich plasma (PRP) was prepared shortly after blood collection by spinning the sample at 180 g for 10 min at 22 °C. The PRP was carefully removed and the remaining blood were centrifuged at 2400 g for 10 min to obtain PPP. The centrifuge temperature was maintained at 22°C. Platelet counts were adjusted by the addition of PPP to the PRP to achieve a count of 500×10^9 L^{-1}. Platelet aggregation studies were completed within 3h of the preparation of PRP. Immediately after the preparation of PRP, 250 μL was transferred into each of prepared test tubes, with 250 μL PPP set as a control. Before addition of inducers, compounds were incubated with PRP at 37°C for 5 min. The change of optical density as a results of platelet aggregation was recorded, and inhibition percentage of compounds was calculated according to the formula:

Inhibition of aggregation (%) = (A–B)/Ax100%

A: maximum change of turbidity in DMSO added

B: maximum change of turbidity in sample added

Table S55 The inhibitory effects of samples on platelet aggregation in rabbits induced by ADP.

Sample			Inducer			Maximum aggregation rate (%)	Inhibited rate (%)
	sample amounts (C×V)	concentration		sample amounts (C×V)	concentration		
DMSO	2.5μl	1%	---	---	---	1.0±0.0***	---
CON.(DMSO)	2.5μl	1%	**ADP**	1mM×2.5μl	10μM	50.0±4.7	---
Ticagrelor	0.5mg/ml×2.5μl	5 μg/ml				10.0±2.0***	80.1±4.9***
1	10.0mM×2.5μl	100μM				49.0±8.2	3.7±6.3
2	10.0mM×2.5μl	100μM				30.5±6.4**	39.2±10.7**
3	10.0mM×2.5μl	100μM				48.3±2.5	4.2±5.6
4	10.0mM×2.5μl	100μM				51.7±4.7	-2.1±2.1

In comparison with the control: *****P* **< 0.01, ******P* **< 0.001.

Table S56 The inhibitory effects of samples on platelet aggregation in rabbits induced by AA.

Sample			Inducer			Maximum aggregation rate (%)	Inhibited rate (%)
	sample amounts (C×V)	concentration		sample amounts (C×V)	concentration		
DMSO	2.5μl	1%	---	---	---	1.0±0.0***	---
CON.(DMSO)	2.5μl	1%	**AA**	50mM×2.5μl	0.5mM	57.8±5.5	---
Aspirin	4mg/ml×2.5μl	40μg/ml				8.0±6.2***	87.3±9.7***
1	10.0mM×2.5μl	100μM				62.0±0.0	-4.1±11.2
2	10.0mM×2.5μl	100μM				48.4±5.2*	15.9±10.3*
3	10.0mM×2.5μl	100μM				60.0±2.6	-0.5±8.6
4	10.0mM×2.5μl	100μM				56.0±3.6	5.9±13.2

In comparison with the control: ****P* **< 0.05, ******P* **< 0.001.

Table S57 The inhibitory effects of samples on platelet aggregation in rabbits induced by PAF.

Sample			Inducer			Maximum aggregation rate (%)	Inhibited rate (%)
	sample amounts (C×V)	concentration		sample amounts (C×V)	concentration		
DMSO	2.5μl	1%	---	---	---	1.0±0.0***	---
CON.(DMSO)	2.5μl	1%	**PAF**	0.04 mg/ml×2.5μl	0.4μg/ml	65.8±11.5	---
GB	3.7mg/ml×2.5μl	37μg/ml				7.5±5.0***	88.3±9.0***
1	10.0mM×2.5μl	100μM				69.3±11.7	-2.3±4.5

2	10.0mM×2.5μl	100μM				60.3±8.7	8.0±4.1
3	10.0mM×2.5μl	100μM				69.3±9.1	-2.8±7.8
4	10.0mM×2.5μl	100μM				62.3±5.7	6.9±12.3

In comparison with the control: ******P* **< 0.001.

Reference:

1. Ellman, G. L.; Courtney, K. D.; Andres, V.; Featherstone, R. M., A new and rapid colorimetric determination of acetylcholinesterase activity. *Biochem Pharmacol* **1961**, *7*, 88-95.

2. Rede, L. A.; Tischler, A. S., Establishment of a noradrenergic clonal line of rat adrenal pheochromocytoma cells which respond to nerve growth factor. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2424-2428.

3. Born, G. V. R. Aggregation of blood platelets by adenosine diphosphate and its reversal. *Nature* **1962**, *194*, 927–929.

4. Küster, L. J., Filep, J., Frölich, J. C. Mechanism of PAF-induced platelet aggregation in man. *Thromb Res.* **1986**, *43*, 425-33.

5. Ming, Y. W., Wen, D. D., Gao, N., Xiao, C., Yang, L., Li Xu, Wu Lian, Peng, W., L., Jiang, J., M., Zhao, J. H. Anticoagulant and antithrombotic evaluation of native fucosylated chondroitin sulfates and their derivatives as selective inhibitors of intrinsic factor Xase. *Eur J Med Chem* **2015**, *92*, 257–269.

9. HRESIMS, NMR, UV, CD and OR spectra of compounds 1–4

9.1 HRESIMS, NMR, UV, CD and OR spectra of maoeriocalysin A (1)

Qualitative Analysis Report

Data Filename	Sie-57.d	**Sample Name**	Sie-57
Sample Type	Sample	**Position**	P1-A7
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	3/12/2018 4:27:45 PM
IRM Calibration Status	[redacted]	**DA Method**	Default.m
Comment			

Sample Group **Info.**

Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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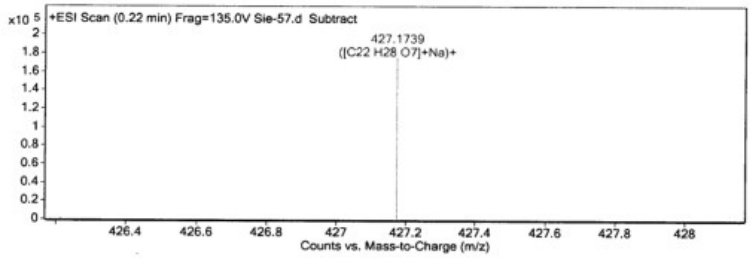

Peak List

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299.1617	1	62307.68		
318.3	1	47407.16		
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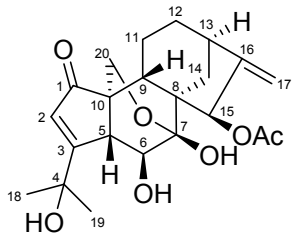
443.1476	1	178656.66		
444.1508	1	39199.72		
453.168	1	59150.43		
831.357	1	84183.29		



Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C22 H28 O7	404.1835	427.1727	427.1739	-1.1	-2.6	9.0000

--- End Of Report ---

Figure S38 HRESIMS spectrum of maoeriocalysin A (**1**).

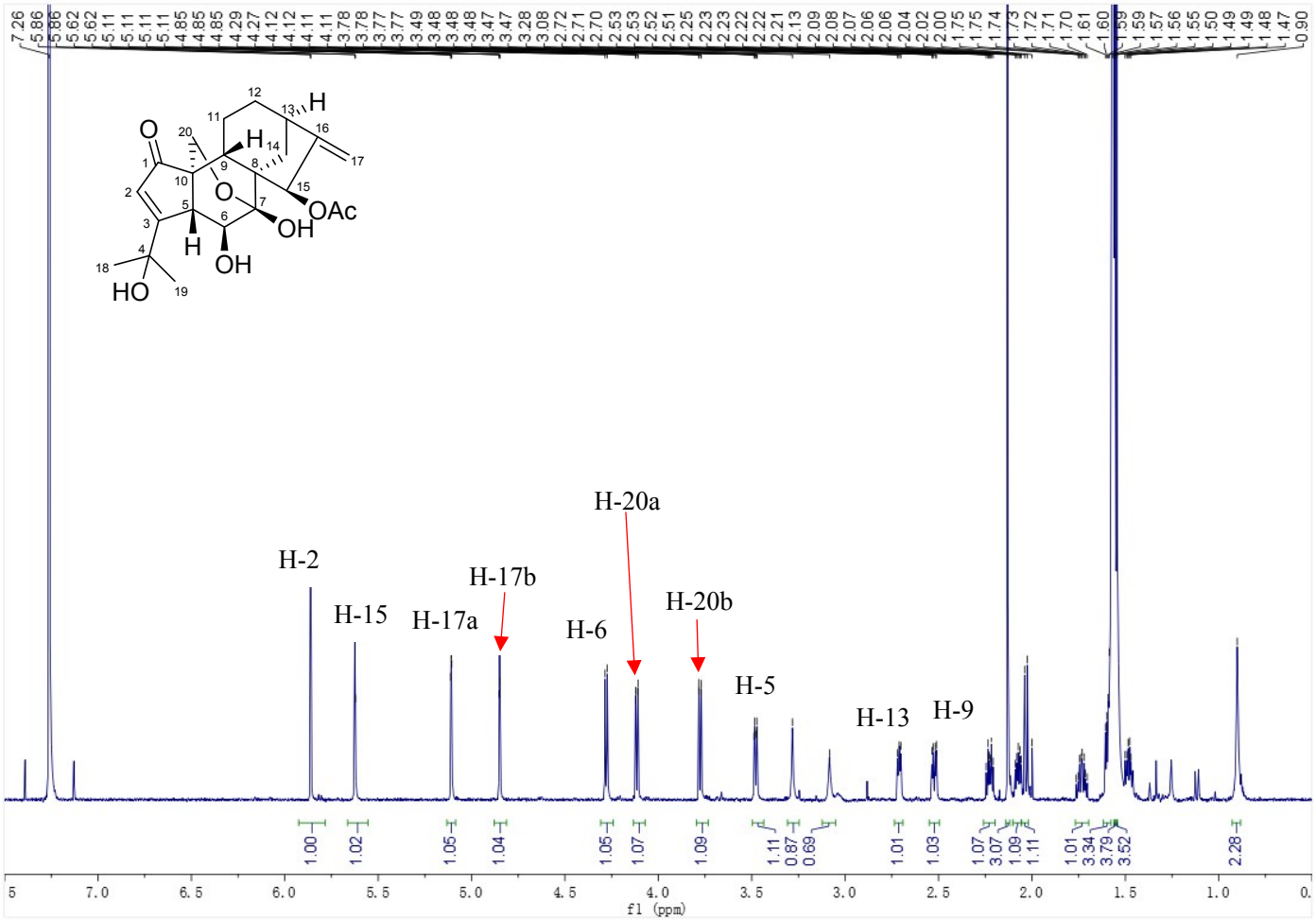
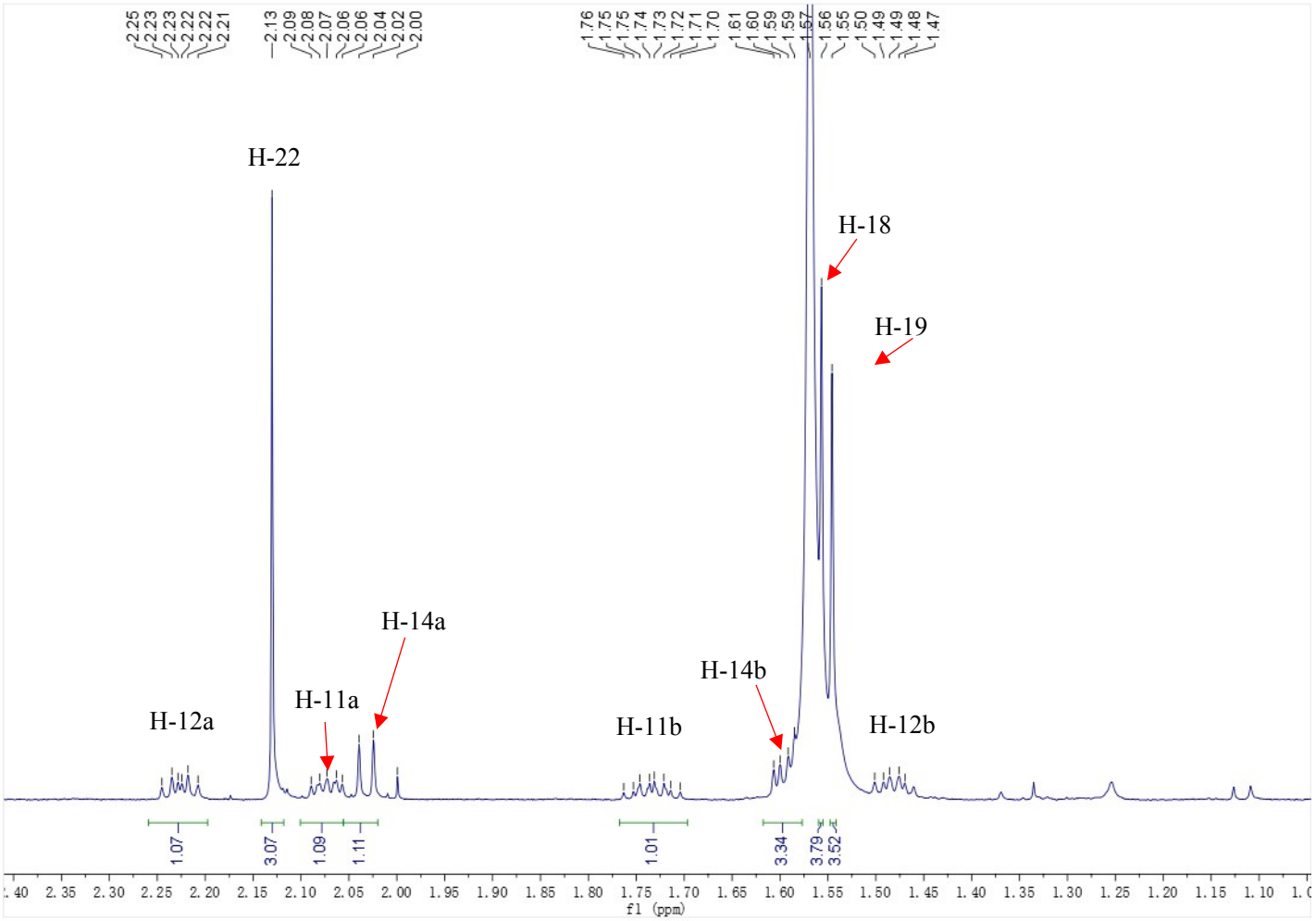


Figure S39 ^{1}H NMR spectrum ($CDCl_3$, 800MHz) of maoeriocalysin A (**1**).


H-22
H-18
H-19
H-14a
H-14b
H-11a
H-11b
H-12a
H-12b
fl (ppm)

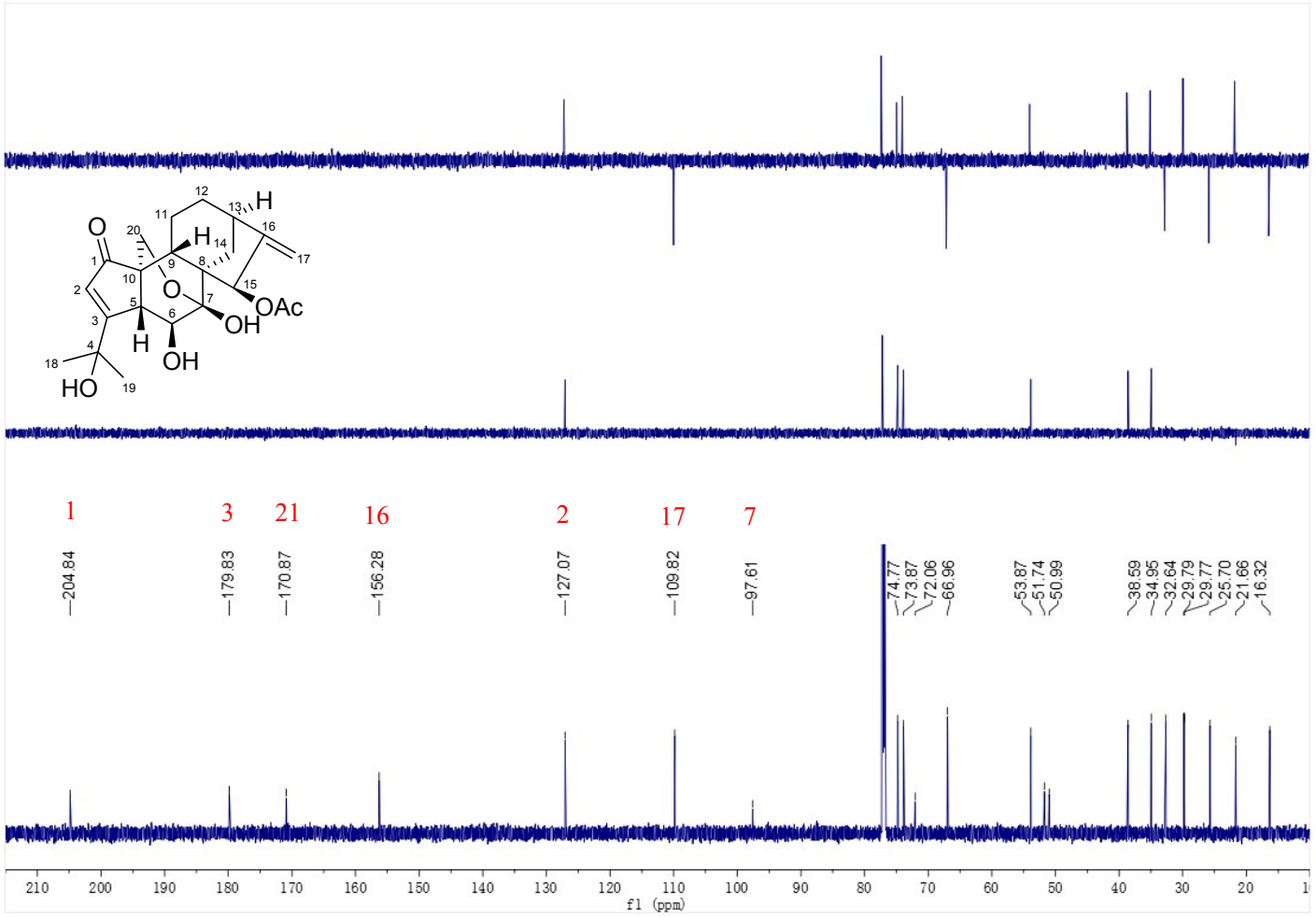
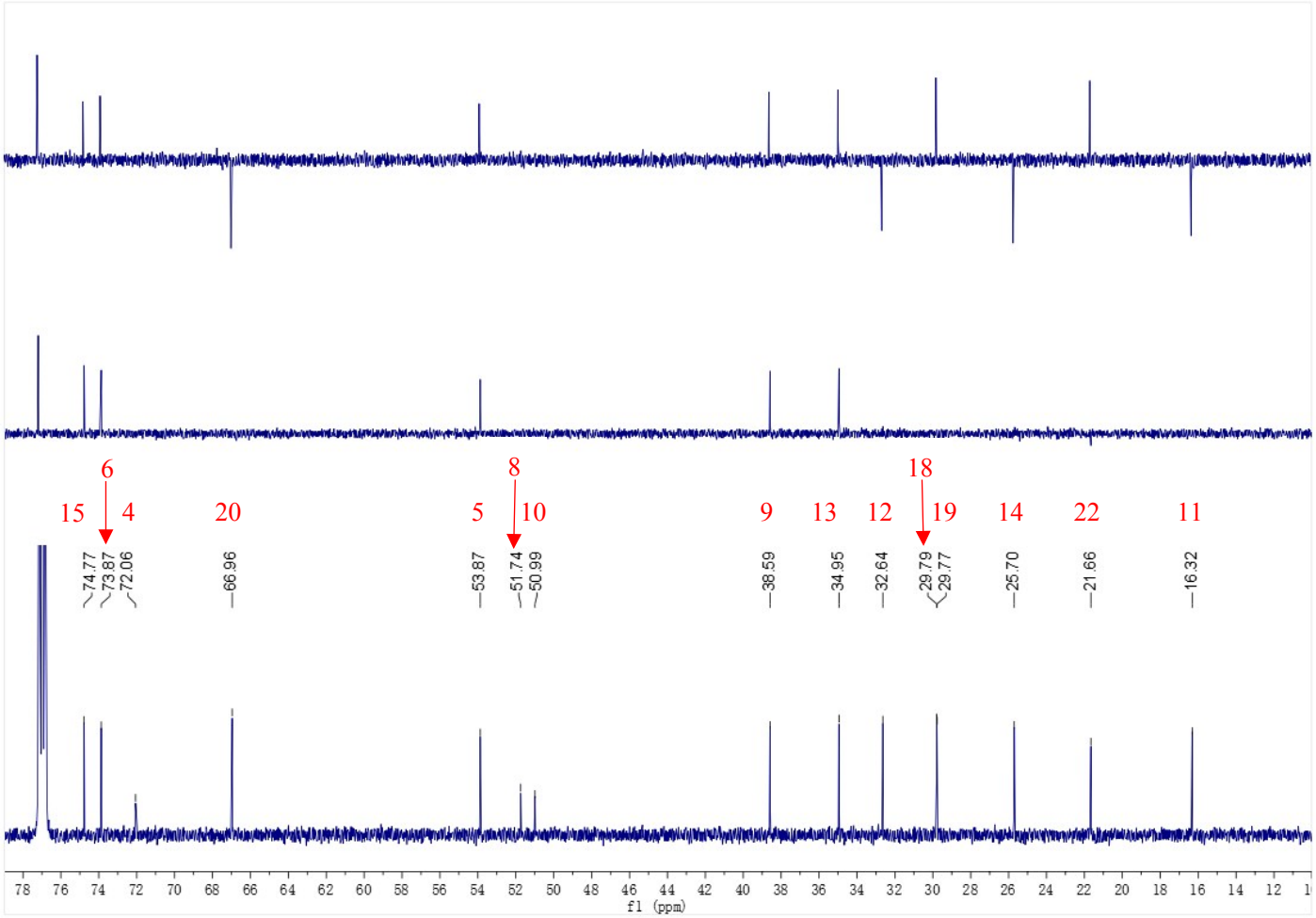


Figure S40 ^{13}C NMR spectrum ($CDCl_3$, 800MHz) of maoeriocalysin A (**1**).


6
15
4
20
8
5
10
18
9
13
12
19
14
22
11
74.77
73.87
72.06
66.96
53.87
51.74
50.99
38.59
34.95
32.64
29.79
29.77
25.70
21.66
16.32
f1 (ppm)

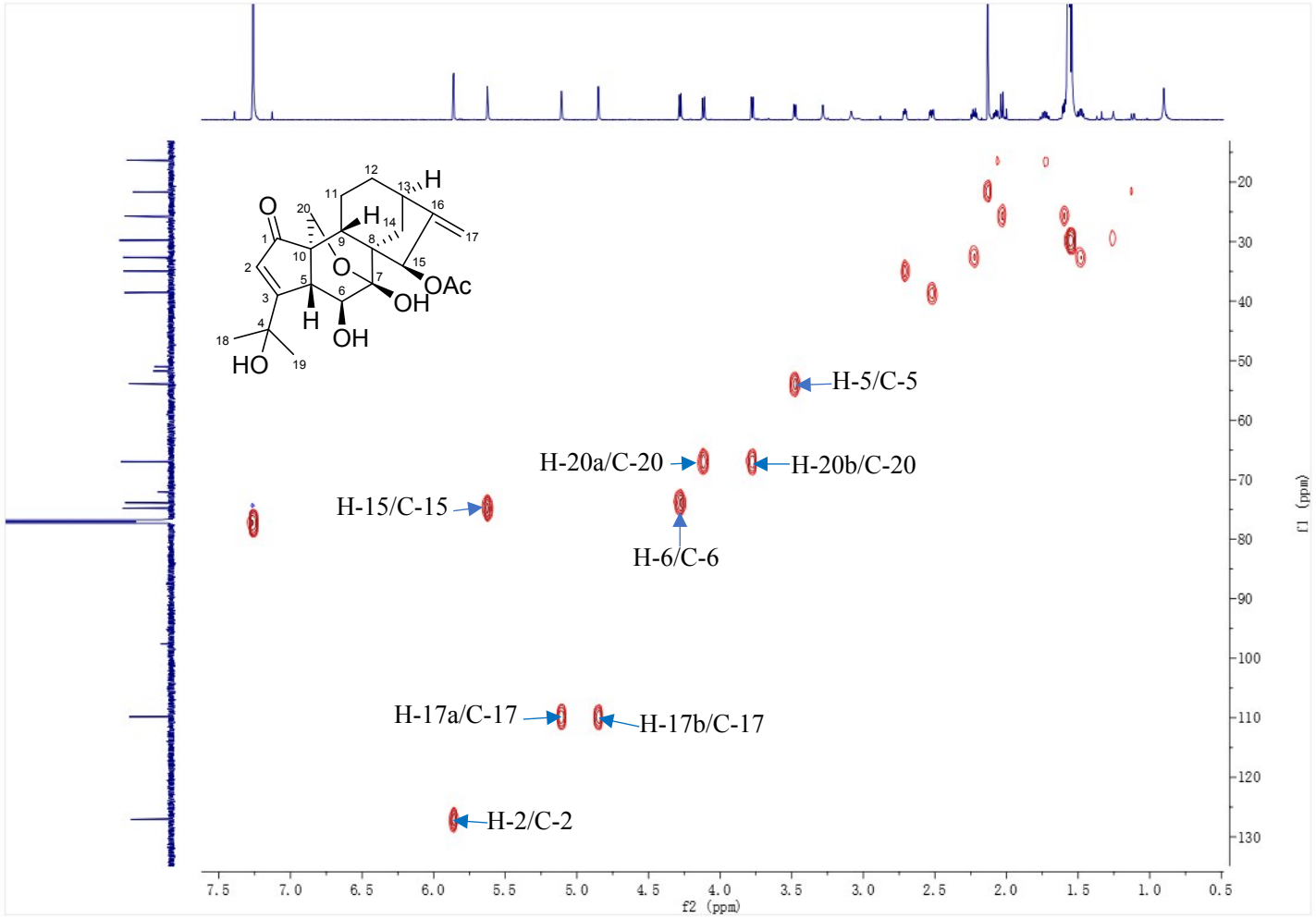
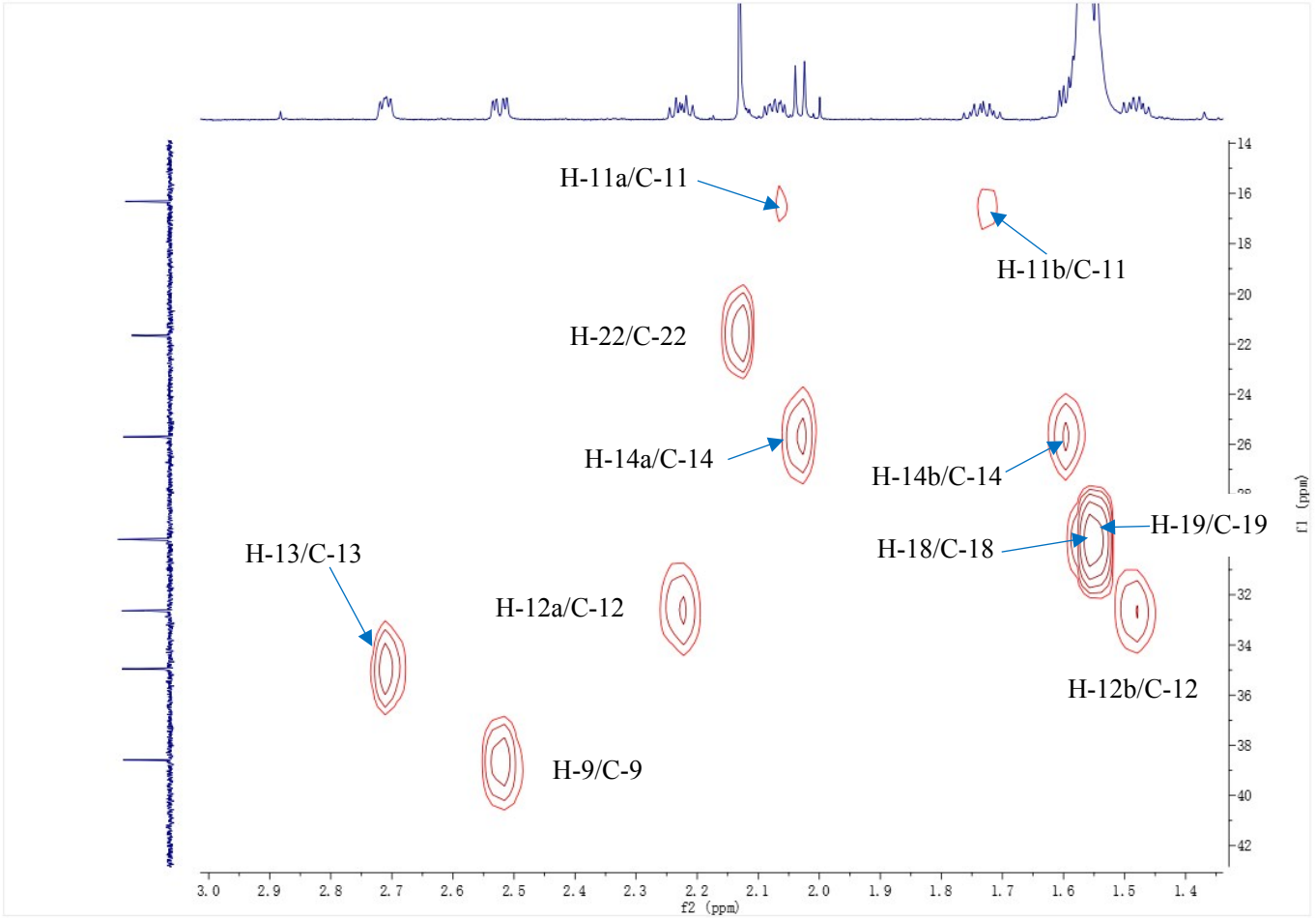


Figure S41 HSQC spectrum ($CDCl_3$, 800MHz) of maoeriocalysin A (**1**).


H-11a/C-11
H-11b/C-11
H-22/C-22
H-14a/C-14
H-14b/C-14
H-19/C-19
H-18/C-18
H-13/C-13
H-12a/C-12
H-12b/C-12
H-9/C-9
f2 (ppm)
f1 (ppm)

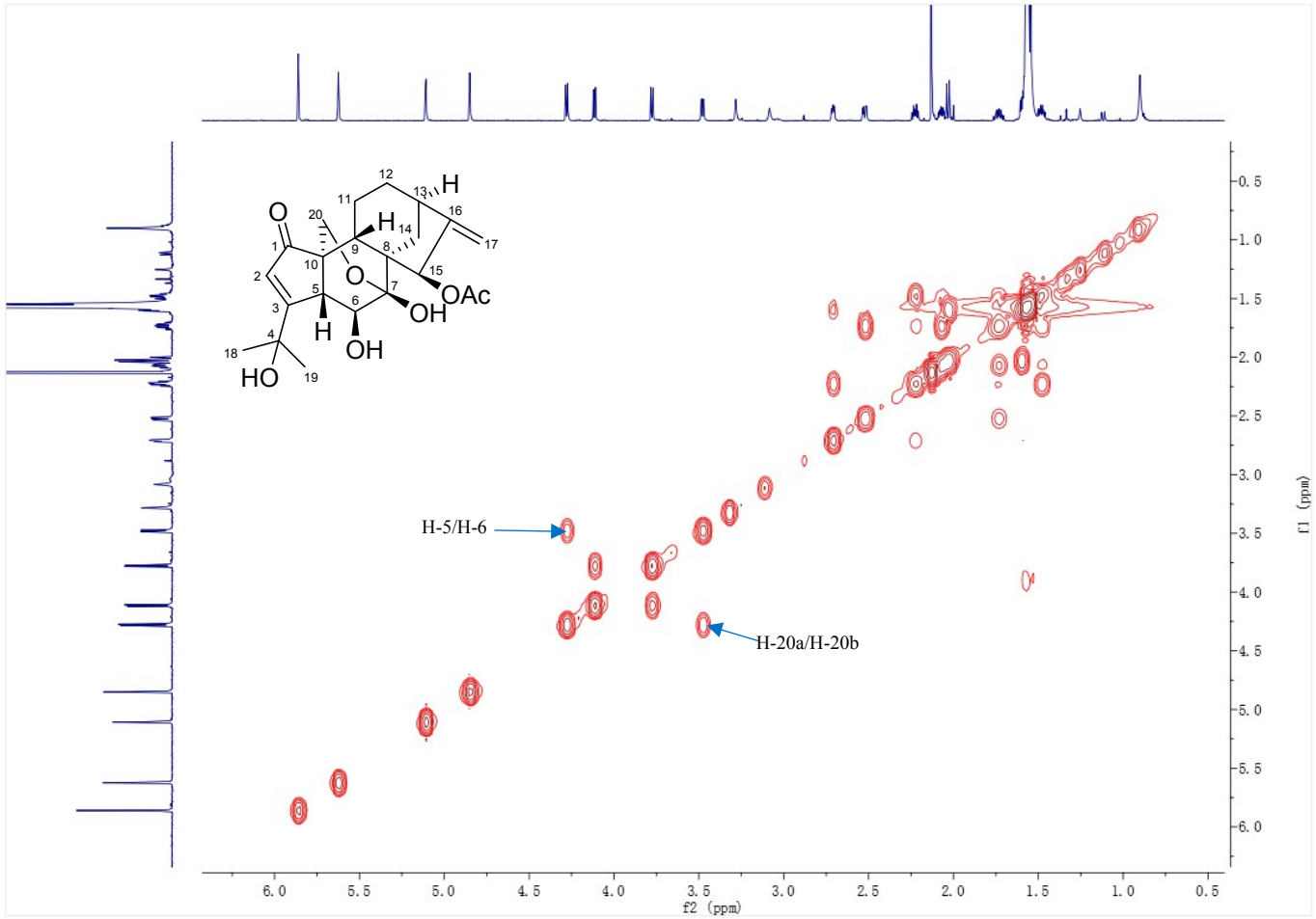
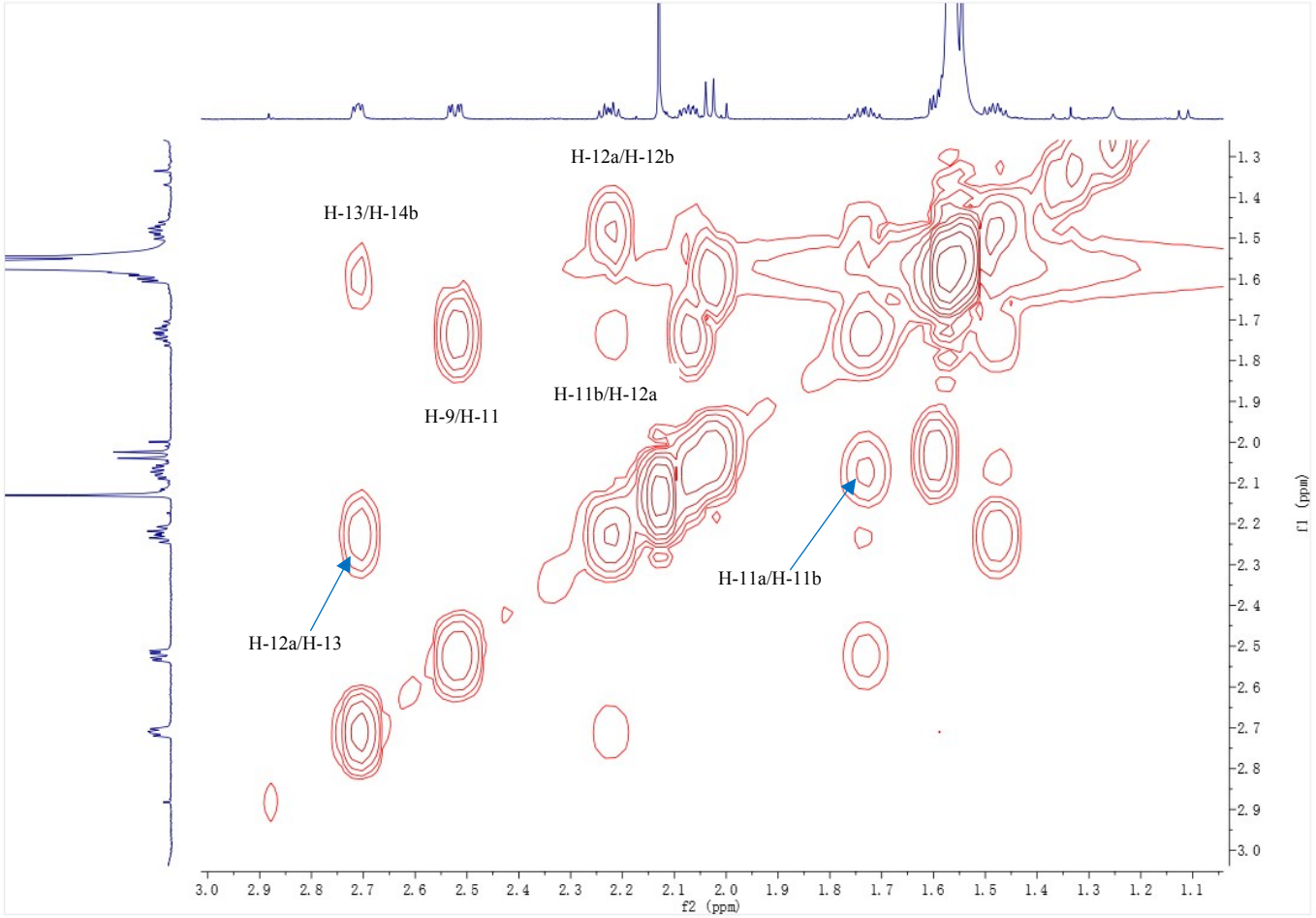


Figure S42 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 800MHz) of maoeriocalysin A (**1**).


H-12a/H-12b
H-13/H-14b
H-9/H-11
H-11b/H-12a
H-11a/H-11b
H-12a/H-13
f2 (ppm)
f1 (ppm)

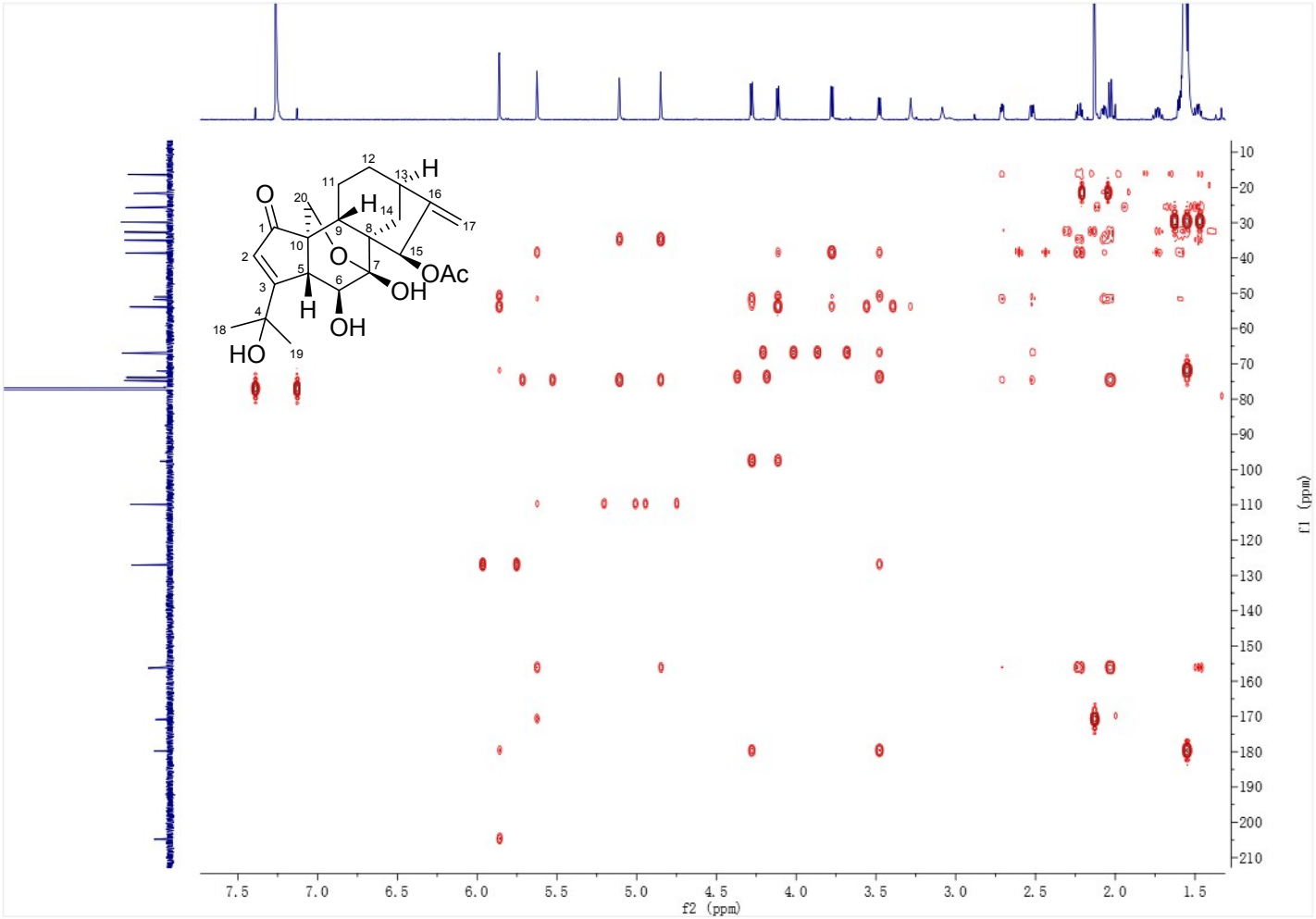
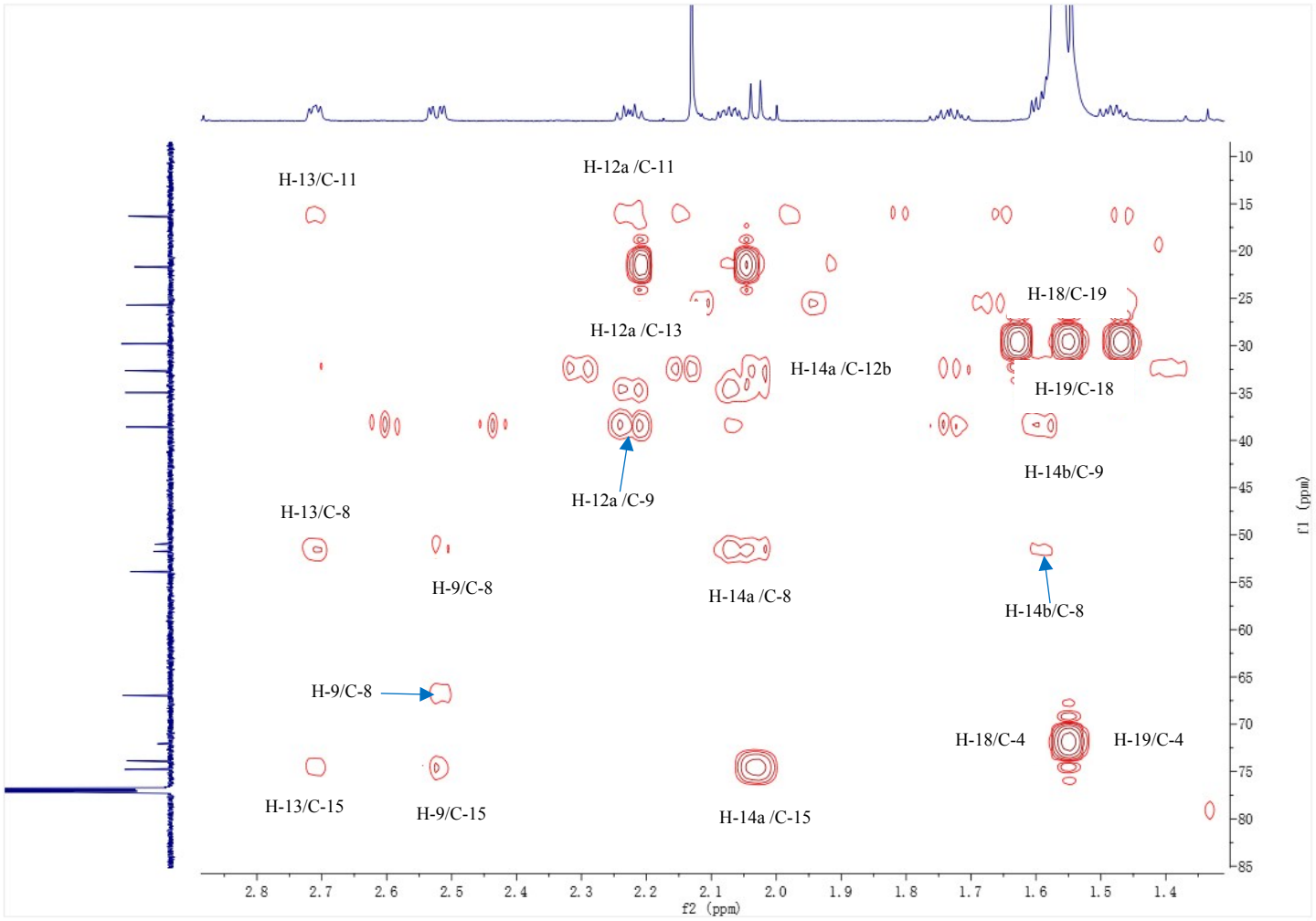
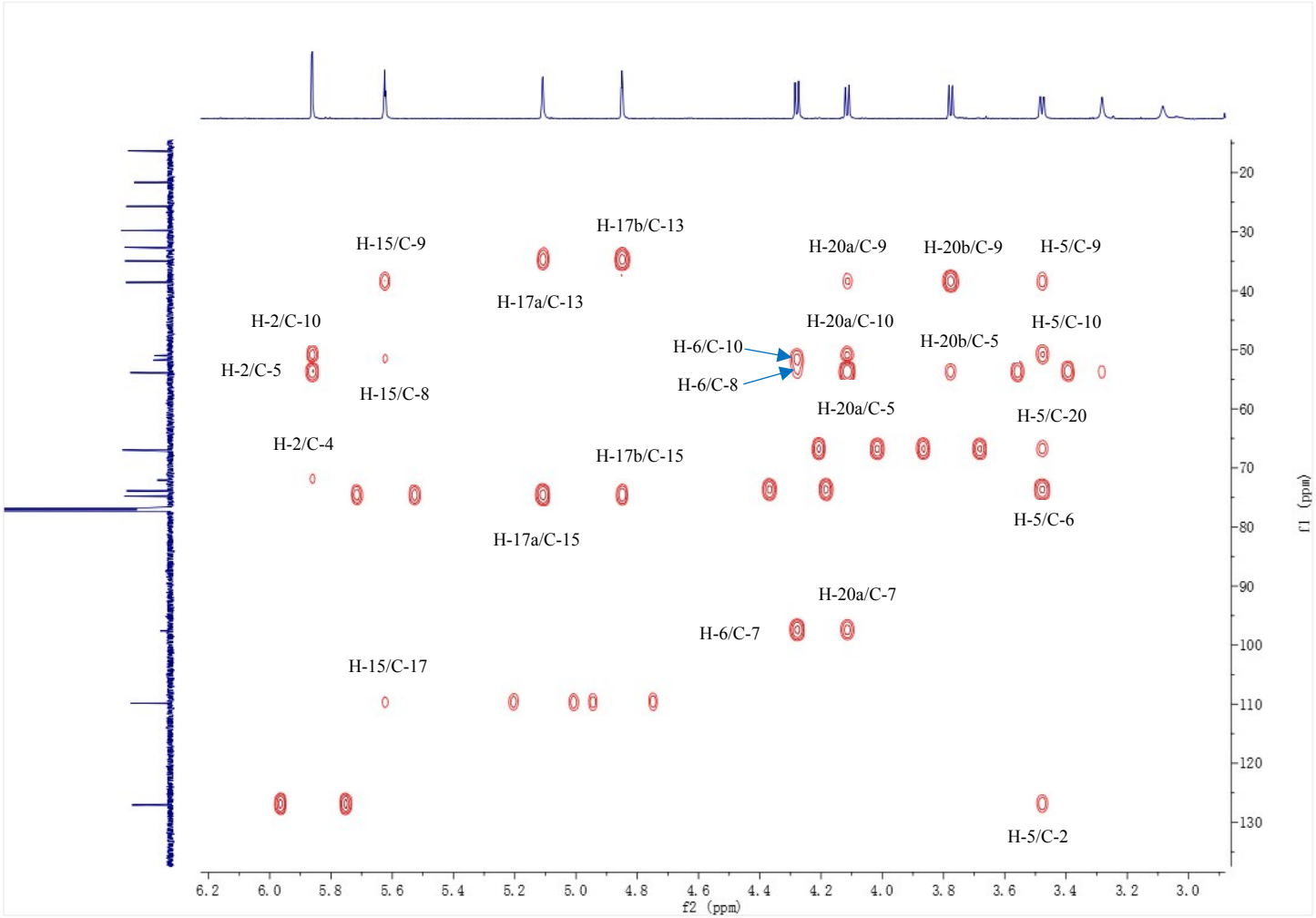
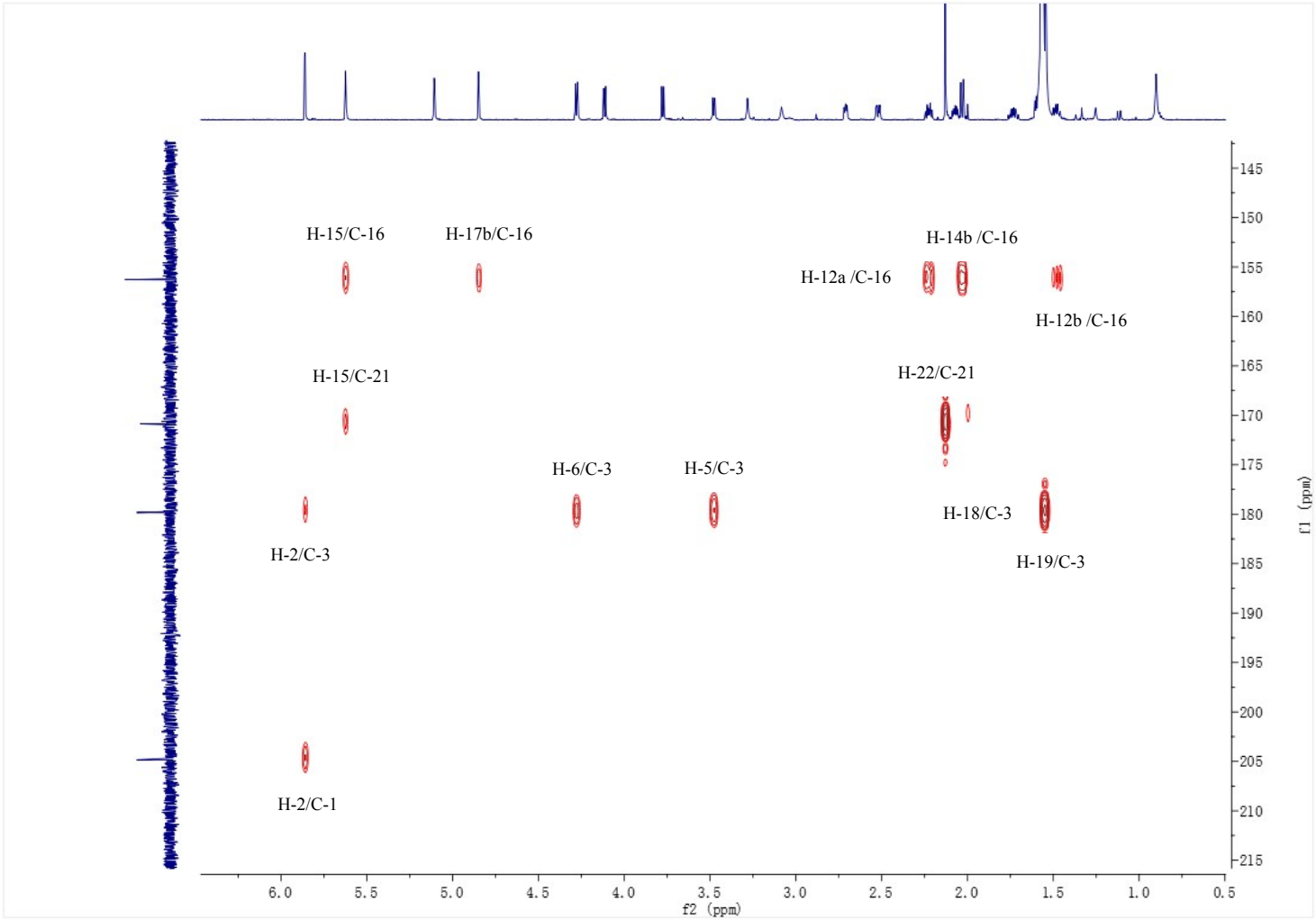


Figure S43 HMBC spectrum ($CDCl_3$, 800MHz) of maoeriocalysin A (**1**).


H-13/C-11
H-12a /C-11
H-18/C-19
H-12a /C-13
H-14a /C-12b
H-19/C-18
H-14b/C-9
H-12a /C-9
H-13/C-8
H-9/C-8
H-14a /C-8
H-14b/C-8
H-9/C-8
H-18/C-4
H-19/C-4
H-13/C-15
H-9/C-15
H-14a /C-15
f2 (ppm)
f1 (ppm)


H-15/C-9
H-17b/C-13
H-17a/C-13
H-20a/C-9
H-20b/C-9
H-5/C-9
H-2/C-10
H-20a/C-10
H-5/C-10
H-6/C-10
H-20b/C-5
H-2/C-5
H-6/C-8
H-15/C-8
H-20a/C-5
H-5/C-20
H-2/C-4
H-17b/C-15
H-5/C-6
H-17a/C-15
H-20a/C-7
H-6/C-7
H-15/C-17
H-5/C-2
f2 (ppm)
f1 (ppm)


H-15/C-16
H-17b/C-16
H-14b /C-16
H-12a /C-16
H-12b /C-16
H-15/C-21
H-22/C-21
H-6/C-3
H-5/C-3
H-18/C-3
H-2/C-3
H-19/C-3
H-2/C-1
f2 (ppm)
f1 (ppm)

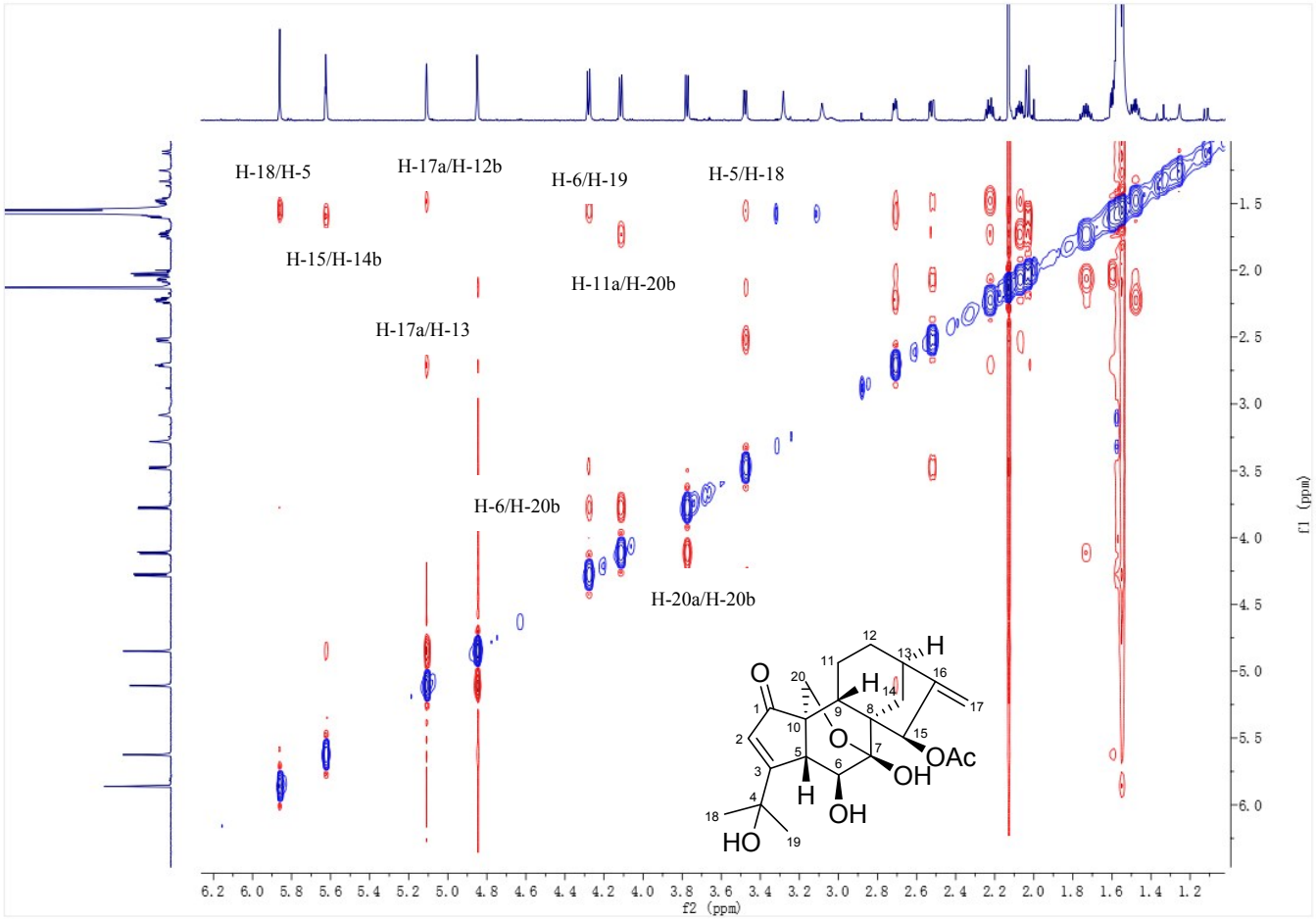
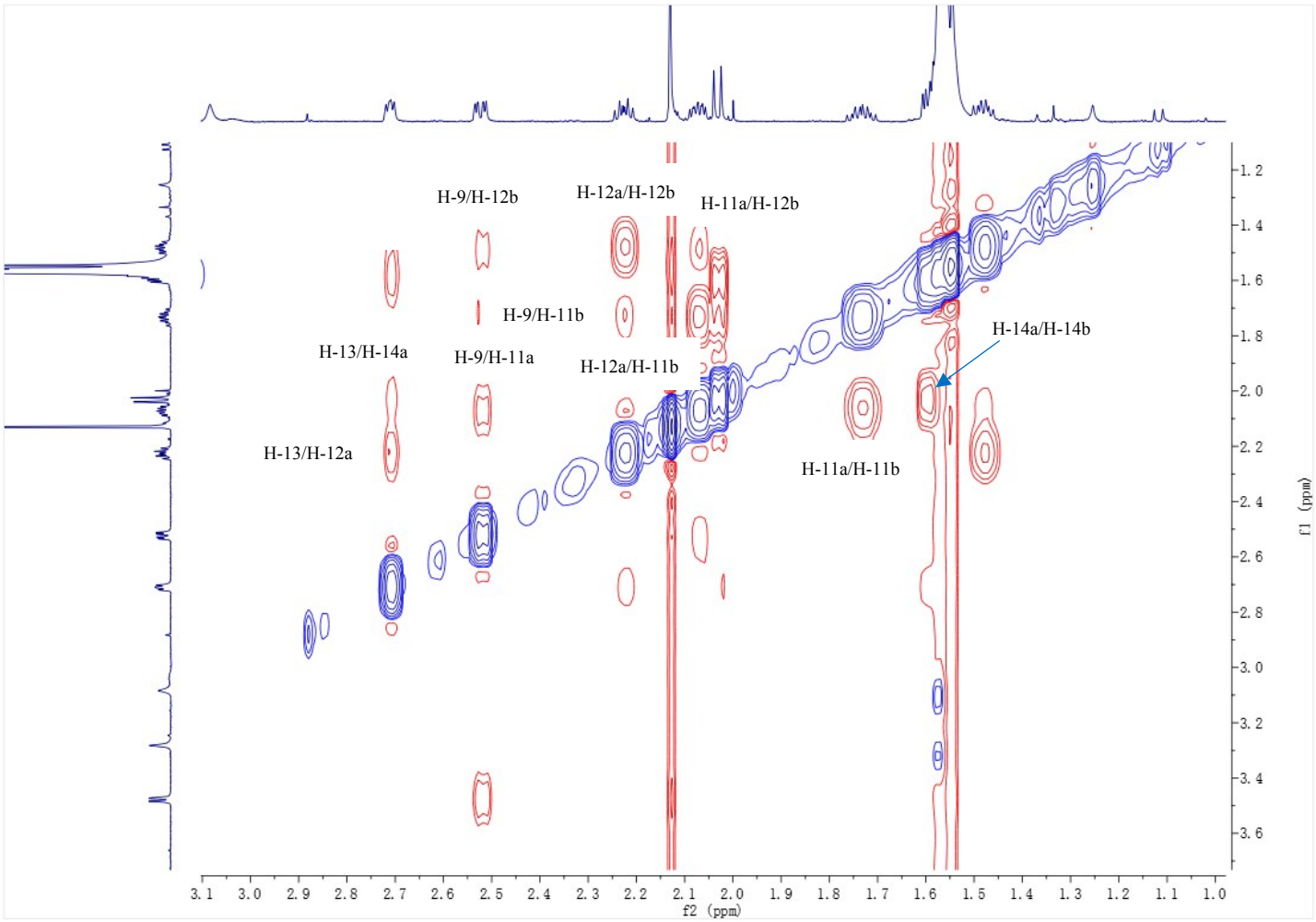


Figure S44 ROESY spectrum ($CDCl_3$, 800MHz) of maoeriocalysin A (**1**).


H-9/H-12b
H-12a/H-12b
H-11a/H-12b
H-9/H-11b
H-14a/H-14b
H-13/H-14a
H-9/H-11a
H-12a/H-11b
H-13/H-12a
H-11a/H-11b
f2 (ppm)
f1 (ppm)

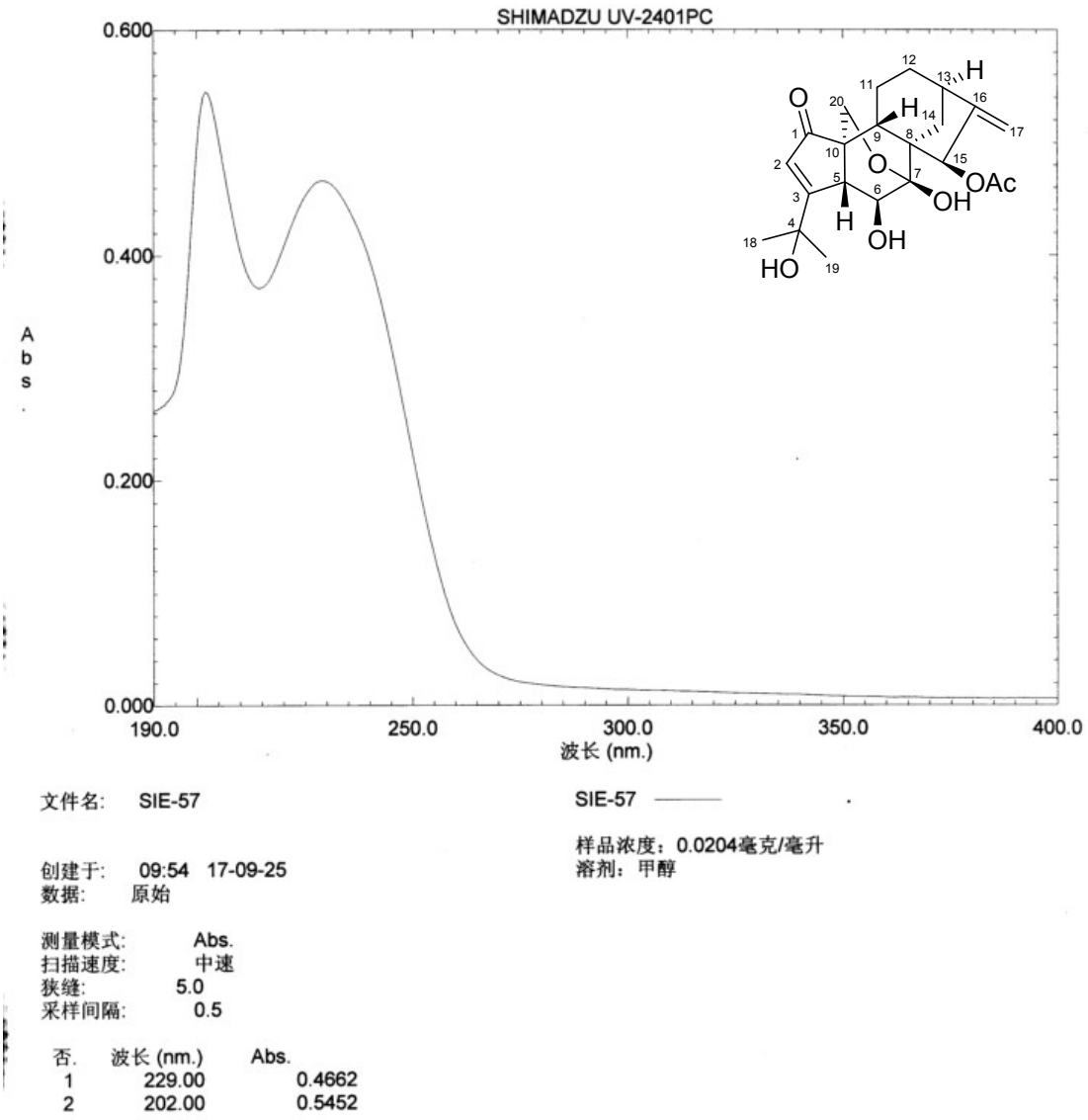


Figure S45 UV spectrum of maoeriocalysin A (**1**).

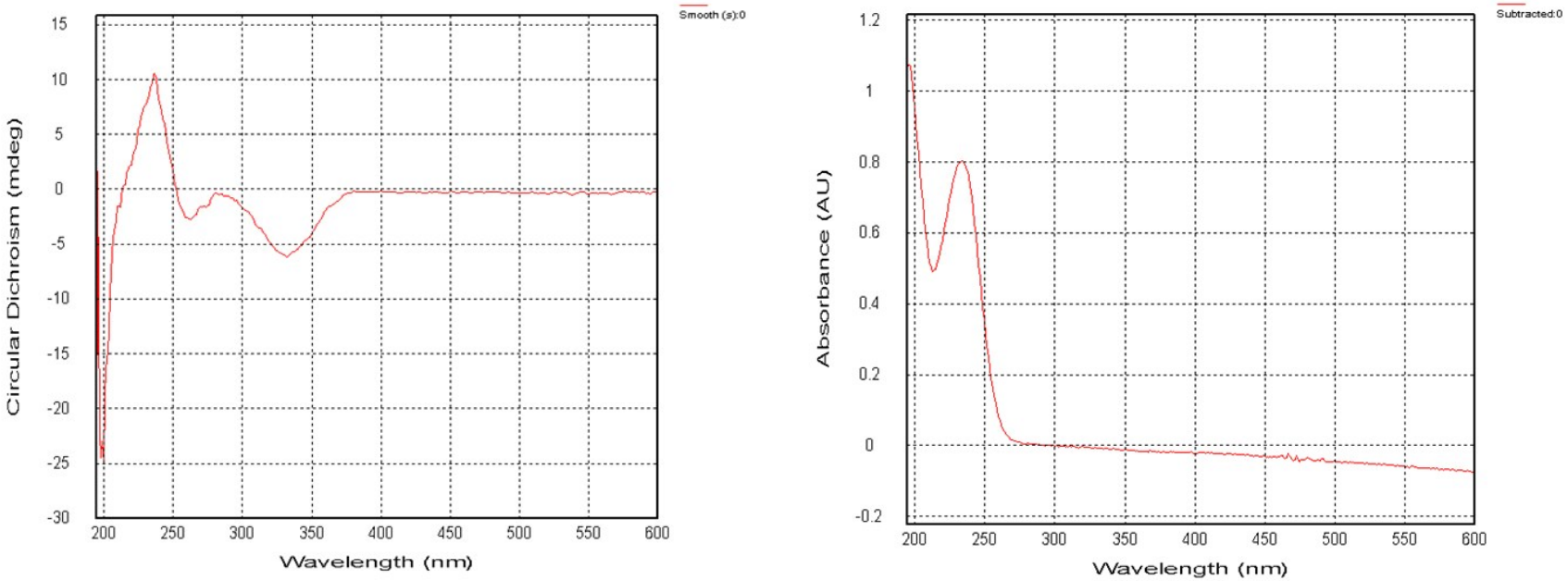


Figure S46 CD spectrum of maoeriocalysin A (**1**).

Optical rotation measurement

Model : P-1020 (A060460638)

No.	Sample	Mode	Data	Monitor Blank	Temp. Cell Temp Point	Date Comment Sample Name	Light Filter Operator	Cycle Time Integ Time
No.1	20 (1/3)	Sp.Rot	-110.0000	-0.0275	24.1	Wed Sep 20 09:25:30 2017	Na	2 sec
				0.0000	50.00	0.00050g/mL MeOH	589nm	2 sec
					Cell	SIE-57		
No.2	20 (2/3)	Sp.Rot	-120.0000	-0.0300	24.1	Wed Sep 20 09:25:36 2017	Na	2 sec
				0.0000	50.00	0.00050g/mL MeOH	589nm	2 sec
					Cell	SIE-57		
No.3	20 (3/3)	Sp.Rot	-118.0000	-0.0295	24.1	Wed Sep 20 09:25:41 2017	Na	2 sec
				0.0000	50.00	0.00050g/mL MeOH	589nm	2 sec
					Cell	SIE-57		
No.4	21 (1/3)	Sp.Rot	-107.2000	-0.0268	24.1	Wed Sep 20 09:25:51 2017	Na	2 sec
				0.0000	50.00	0.00050g/mL MeOH	589nm	2 sec
					Cell	SIE-57		
No.5	21 (2/3)	Sp.Rot	-126.8000	-0.0317	24.1	Wed Sep 20 09:25:56 2017	Na	2 sec
				0.0000	50.00	0.00050g/mL MeOH	589nm	2 sec
					Cell	SIE-57		
No.6	21 (3/3)	Sp.Rot	-111.2000	-0.0278	24.0	Wed Sep 20 09:26:02 2017	Na	2 sec
				0.0000	50.00	0.00050g/mL MeOH	589nm	2 sec
					Cell	SIE-57		

-111.2247°

Figure S47 OR spectrum of maoeriocalysin A (**1**).

9.2 HRESIMS, NMR, UV, CD and OR spectra of maoeriocalysin B (2)

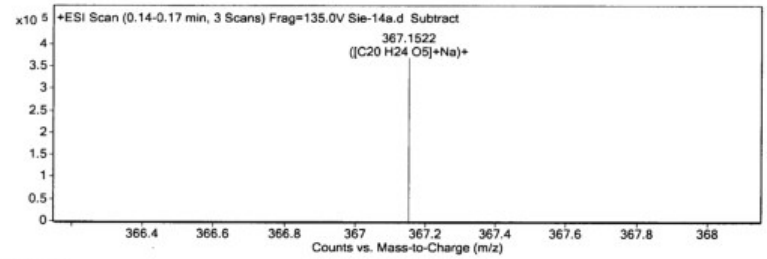
Qualitative Analysis Report

Data Filename	Sie-14a.d	**Sample Name**	Sie-14a
Sample Type	Sample	**Position**	P1-A2
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	3/12/2018 4:21:49 PM
IRM Calibration Status	[redacted]	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

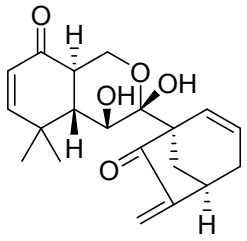
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
274.2743	1	166227.17		
290.2691	1	78980.37		
318.3002	1	95284.89		
327.1594	1	70240.45		
367.1522	1	370167.84	C20 H24 O5	(M+Na)+
368.155	1	73732.25	C20 H24 O5	(M+Na)+
383.1258	1	150378.56		
711.3154	1	153961.94		



Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C20 H24 O5	344.1624	367.1516	367.1522	-0.6	-1.7	9.0000

--- End Of Report ---

Figure S48 HRESIMS spectrum of maoeriocalysin B (**2**).

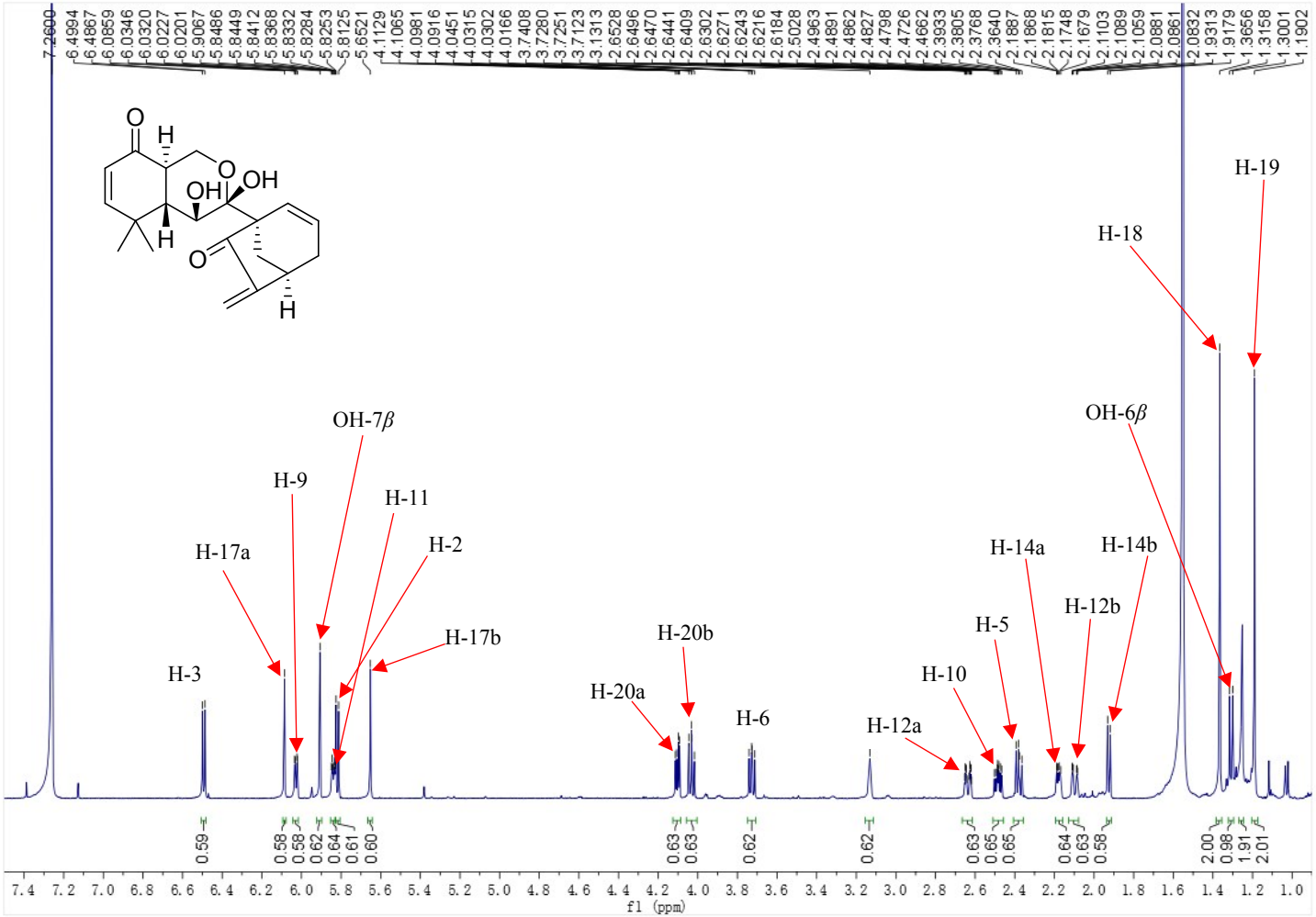


Figure S49 ^{1}H-NMR spectrum of maoeriocalysin B (**2**).

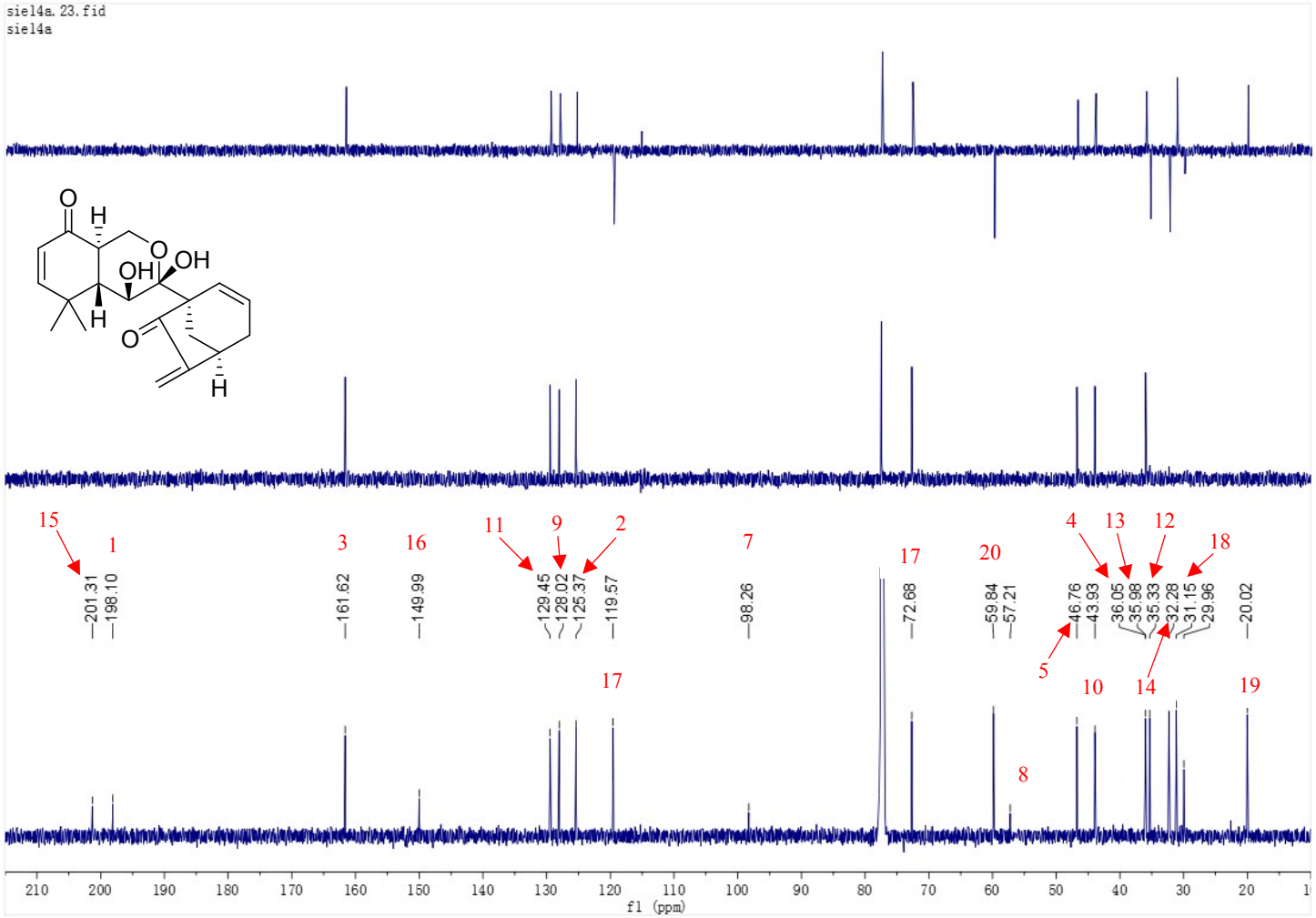


Figure S50 ^{13}C NMR spectrum ($CDCl_3$, 800MHz) of maoeriocalysin B (**2**).

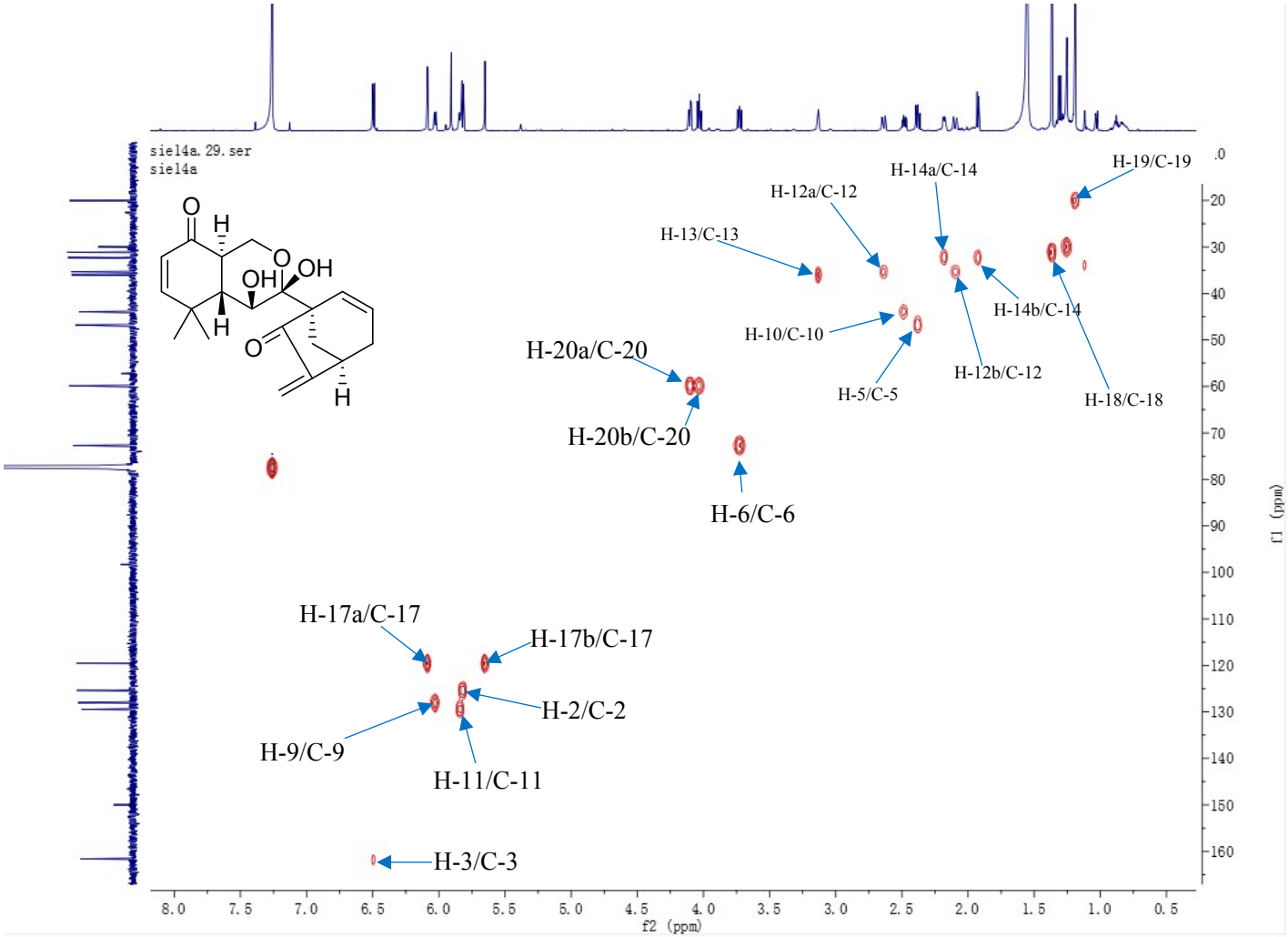


Figure S51 HSQC spectrum ($CDCl_3$, 800MHz) of maoeriocalysin B (**2**).

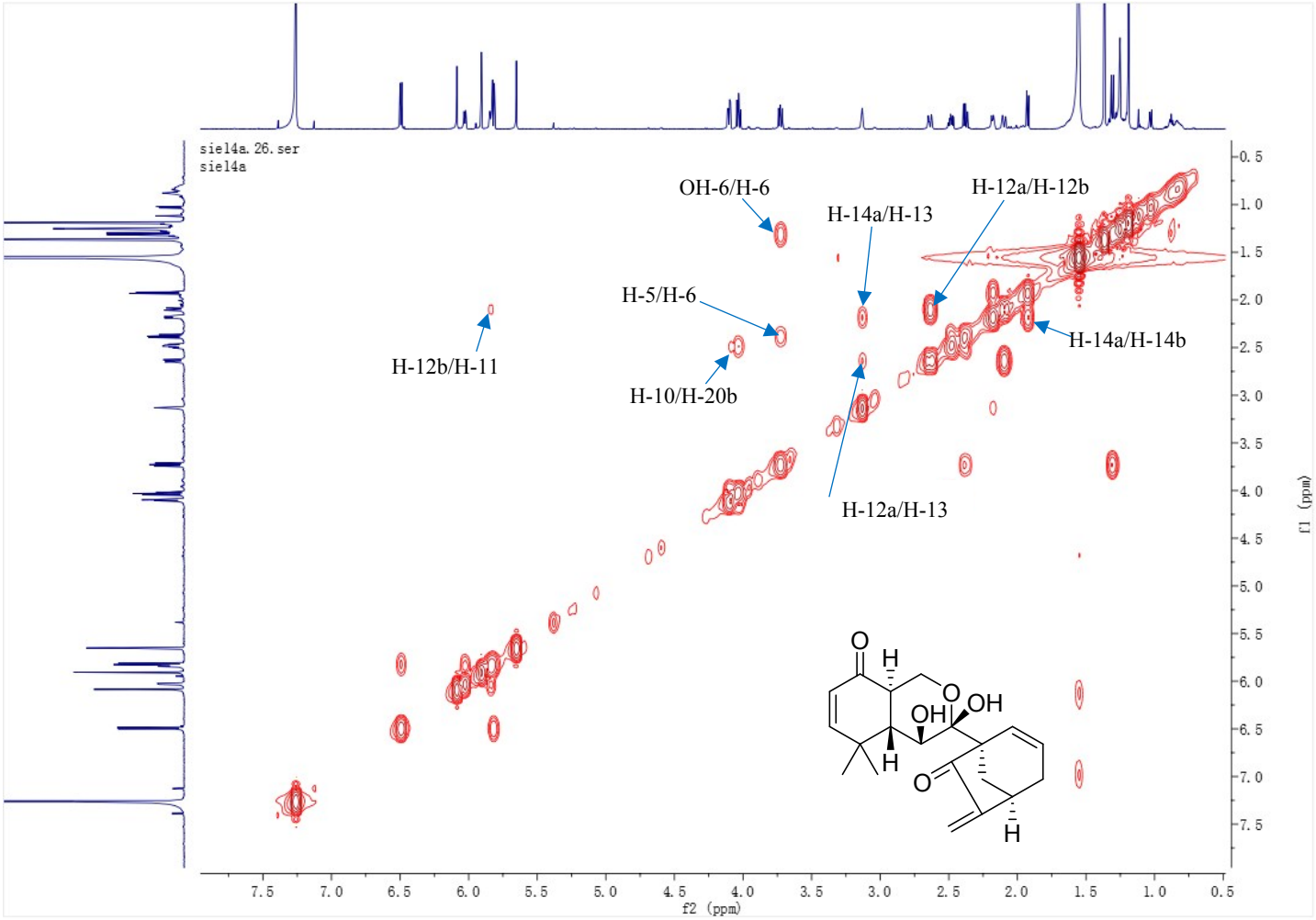


Figure S52 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 800MHz) of maoeriocalysin B (**2**).

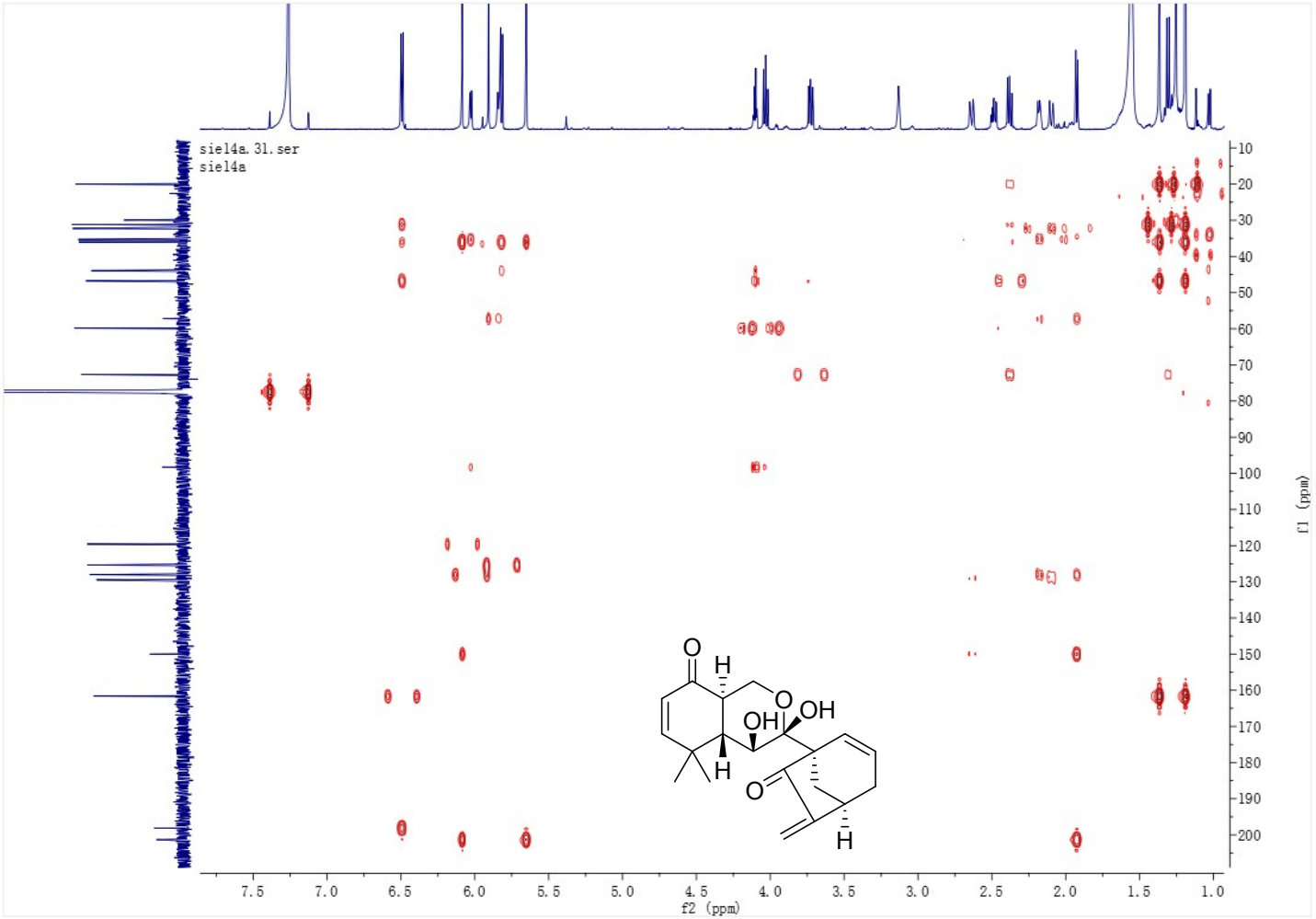
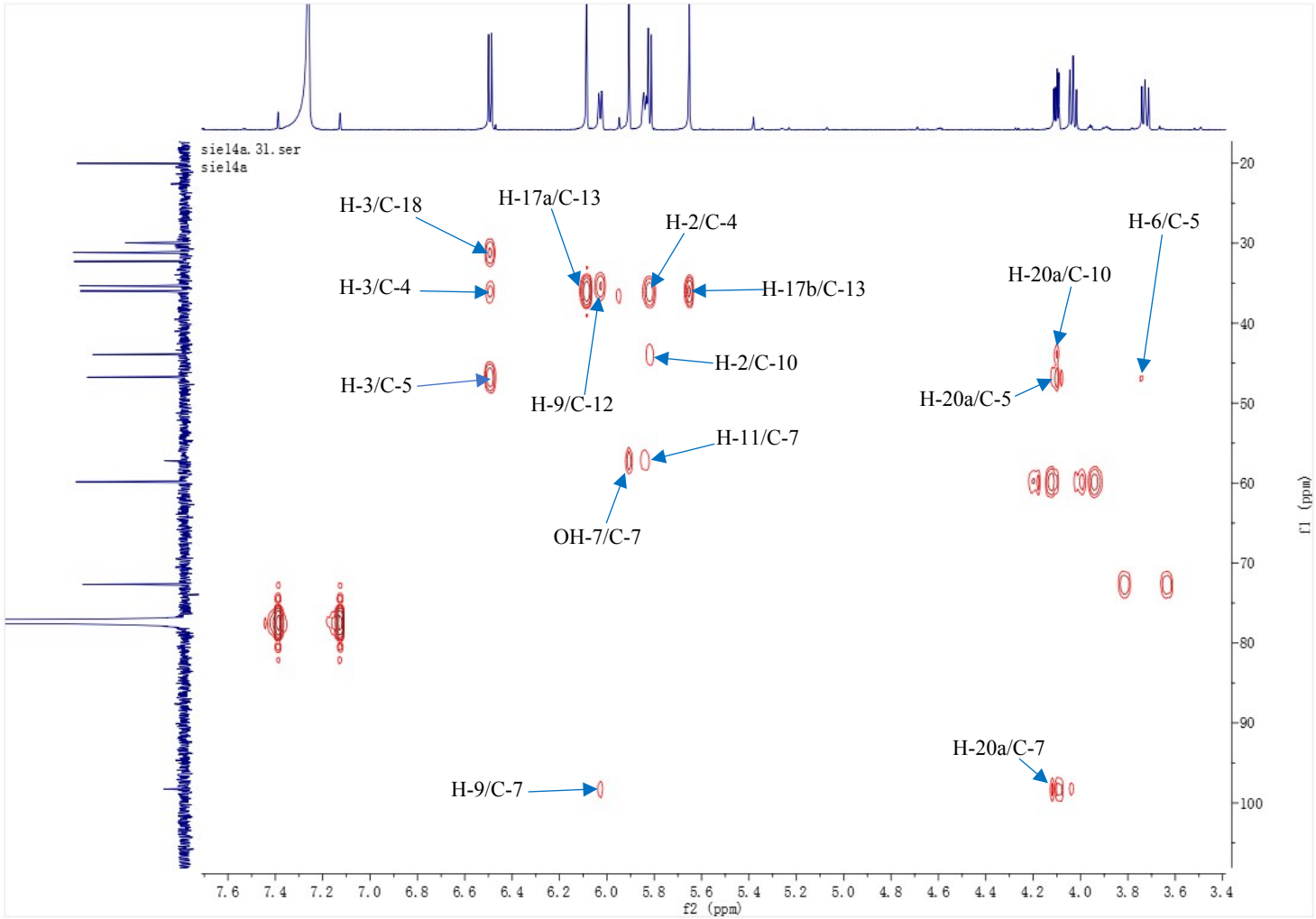
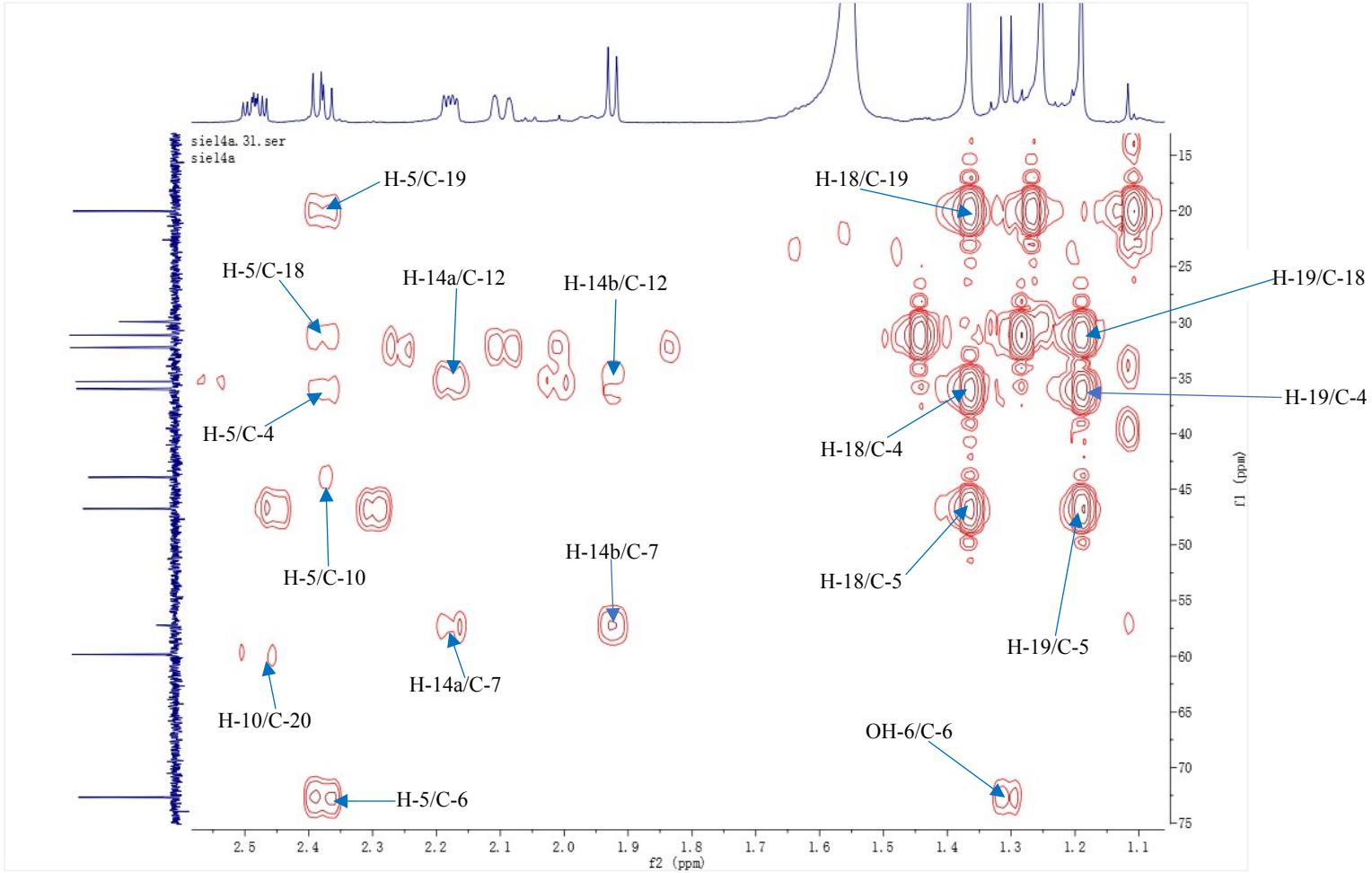
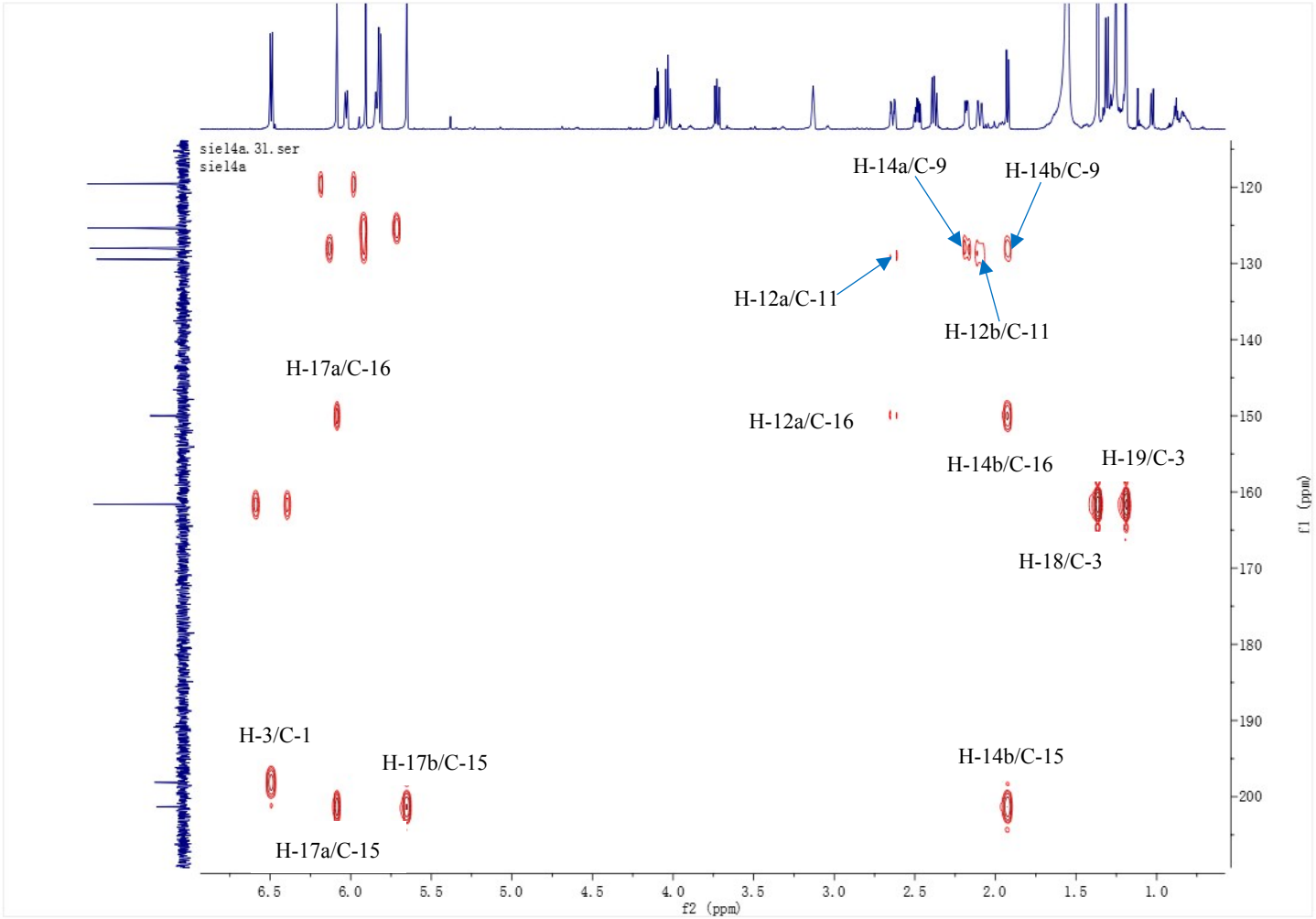


Figure S53 HMBC spectrum ($CDCl_3$, 800MHz) of maoeriocalysin B (**2**).


siel4a. 31. ser
siel4a
H-3/C-18
H-17a/C-13
H-2/C-4
H-6/C-5
H-20a/C-10
H-3/C-4
H-17b/C-13
H-2/C-10
H-3/C-5
H-9/C-12
H-20a/C-5
H-11/C-7
OH-7/C-7
H-20a/C-7
H-9/C-7
f2 (ppm)
f1 (ppm)


siel4a.31.ser
siel4a
H-5/C-19
H-5/C-18
H-14a/C-12
H-14b/C-12
H-5/C-4
H-5/C-10
H-14b/C-7
H-14a/C-7
H-10/C-20
H-5/C-6
H-18/C-19
H-19/C-18
H-19/C-4
H-18/C-4
H-18/C-5
H-19/C-5
OH-6/C-6
f2 (ppm)
f1 (ppm)


siel4a.31.ser
siel4a
H-14a/C-9
H-14b/C-9
H-12a/C-11
H-12b/C-11
H-17a/C-16
H-12a/C-16
H-14b/C-16
H-19/C-3
H-18/C-3
H-3/C-1
H-17b/C-15
H-14b/C-15
H-17a/C-15
f2 (ppm)
f1 (ppm)

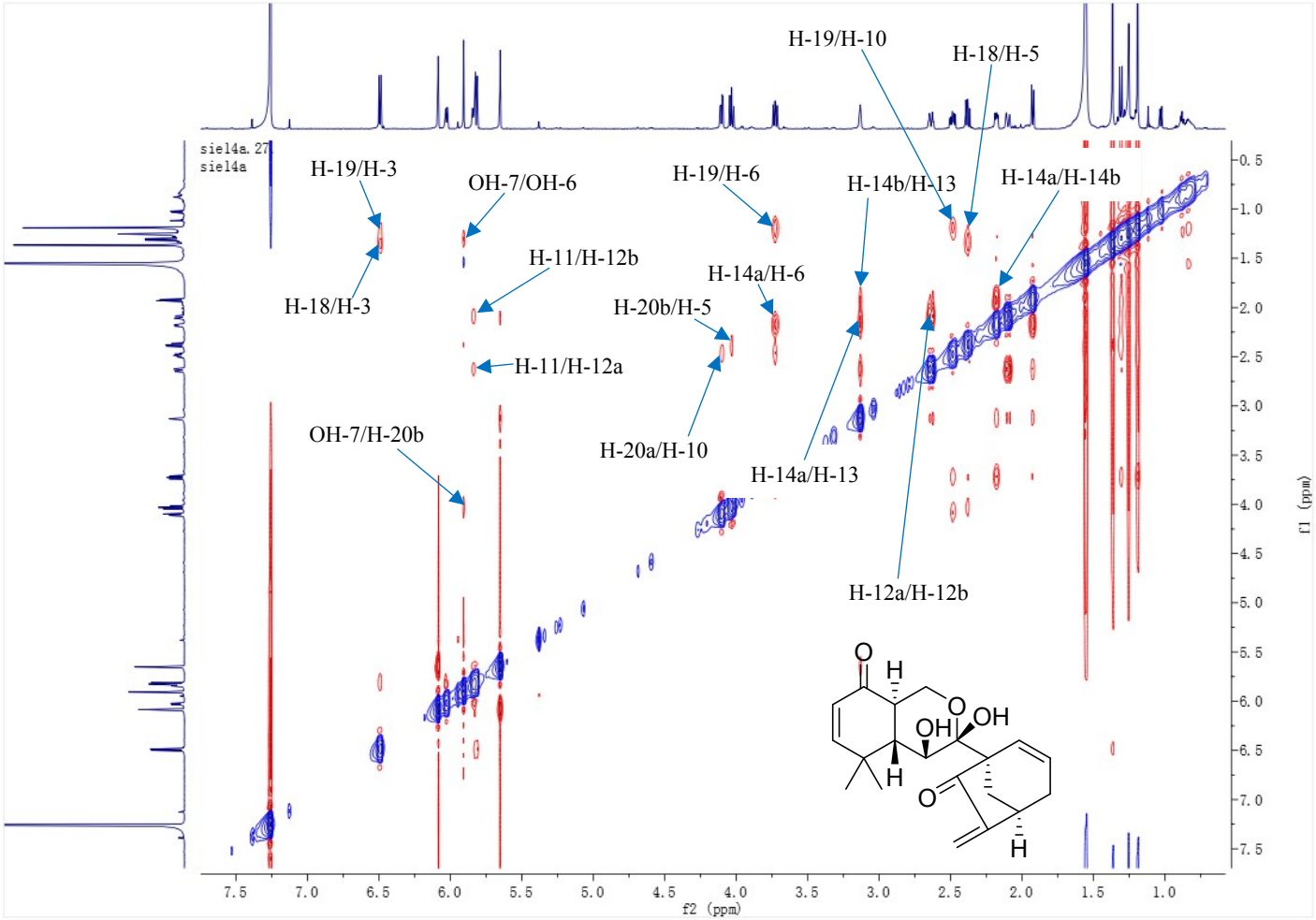
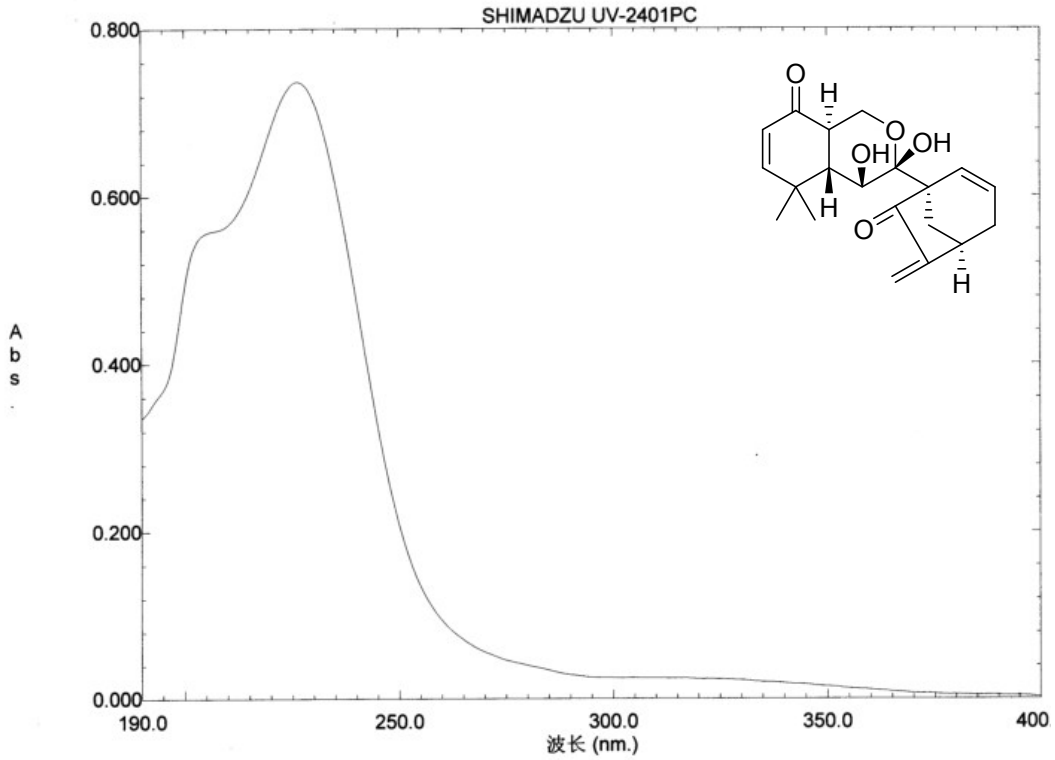


Figure S54 ROESY spectrum ($CDCl_3$, 800MHz) of maoeriocalysin B (**2**).



文件名: SIE-14A

SIE-14A ———

样品浓度：0.0286毫克/毫升
溶剂：甲醇

创建于: 10:03 17-06-05
数据: 原始

测量模式: Abs.
扫描速度: 中速
狭缝: 5.0
采样间隔: 0.5

否.	波长 (nm.)	Abs.
1	207.00	0.5584
2	227.00	0.7362
3	314.00	0.0241

Figure S55 UV spectrum of maoeriocalysin B (**2**).

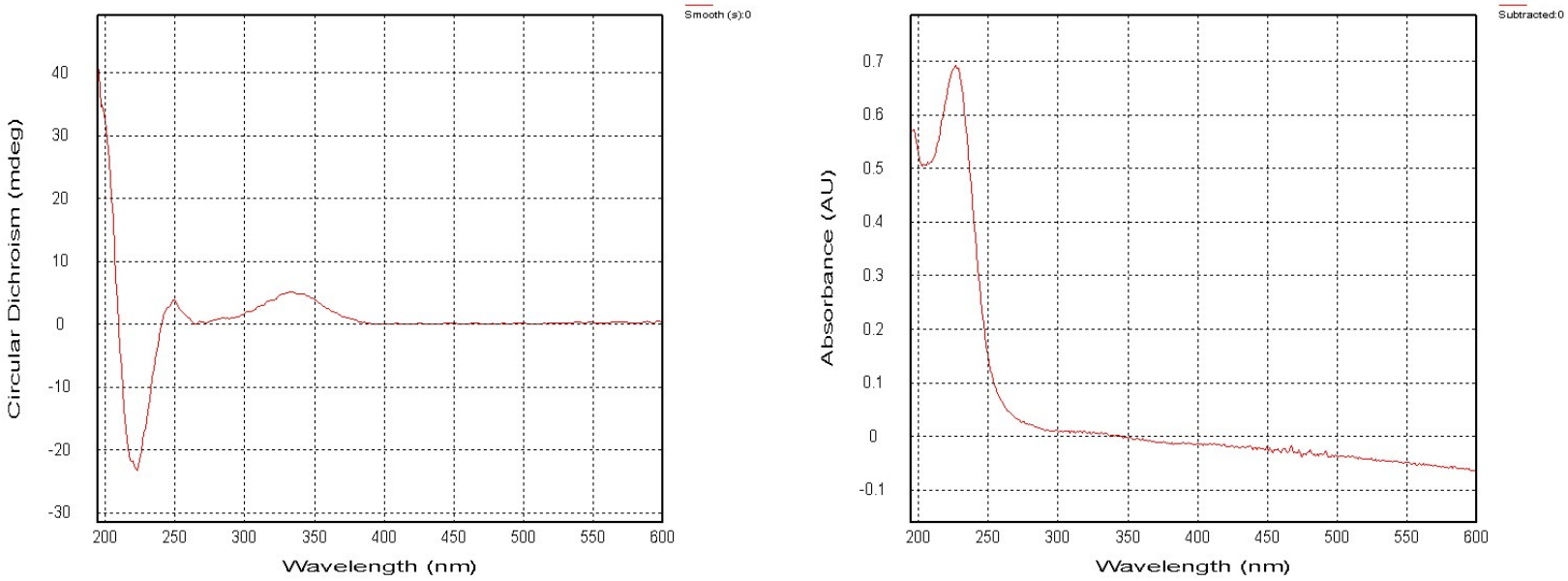


Figure S56 CD spectrum of maoeriocalysin B (**2**).

Optical rotation measurement

Model : P-1020 (A060460638)

No.	Sample	Mode	Data	Monitor Blank	Temp. Cell Temp Point	Date Comment Sample Name	Light Filter Operator	Cycle Time Integ Time
No.1	16 (1/3)	Sp.Rot	38.5450	0.0212 0.0000	23.3 50.00 Cell	Thu May 25 08:51:19 2017 0.00110g/mL MeOH SIE-14A	Na 589nm	2 sec 2 sec
No.2	16 (2/3)	Sp.Rot	39.8180	0.0219 0.0000	23.3 50.00 Cell	Thu May 25 08:51:24 2017 0.00110g/mL MeOH SIE-14A	Na 589nm	2 sec 2 sec
No.3	16 (3/3)	Sp.Rot	41.2730	0.0227 0.0000	23.4 50.00 Cell	Thu May 25 08:51:29 2017 0.00110g/mL MeOH SIE-14A	Na 589nm	2 sec 2 sec

+39.88°

Figure S57 OR spectrum of maoeriocalysin B (**2**).

9.3 HRESIMS, NMR, UV, CD and OR spectra of maoeriocalysin C (3)

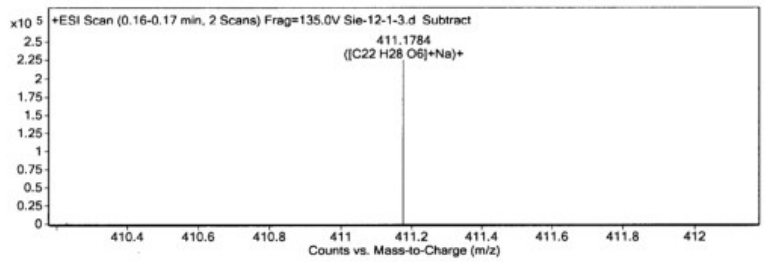
Qualitative Analysis Report

Data Filename	Sie-12-1-3.d	**Sample Name**	Sie-12-1-3
Sample Type	Sample	**Position**	P1-A4
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	3/12/2018 4:24:12 PM
IRM Calibration Status	[redacted]	**DA Method**	Default.m
Comment			

Sample Group **Info.**
Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

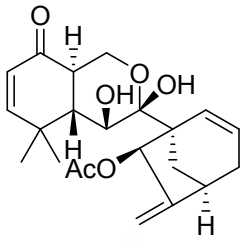
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
112.1873	1	61725.59		
290.2689	1	39637.48		
411.1784	1	226087.08	C22 H28 O6	(M+Na)+
412.1816	1	51856.26	C22 H28 O6	(M+Na)+
413.1928	1	63103.4		
427.1521	1	91125.02		
429.1661	1	46415.21		
799.3671	1	56641.21		



Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C22 H28 O6	388.1886	411.1778	411.1784	-0.5	-1.4	9.0000

--- End Of Report ---

Figure S58 HRESIMS spectrum of maoeriocalysin C (**3**).

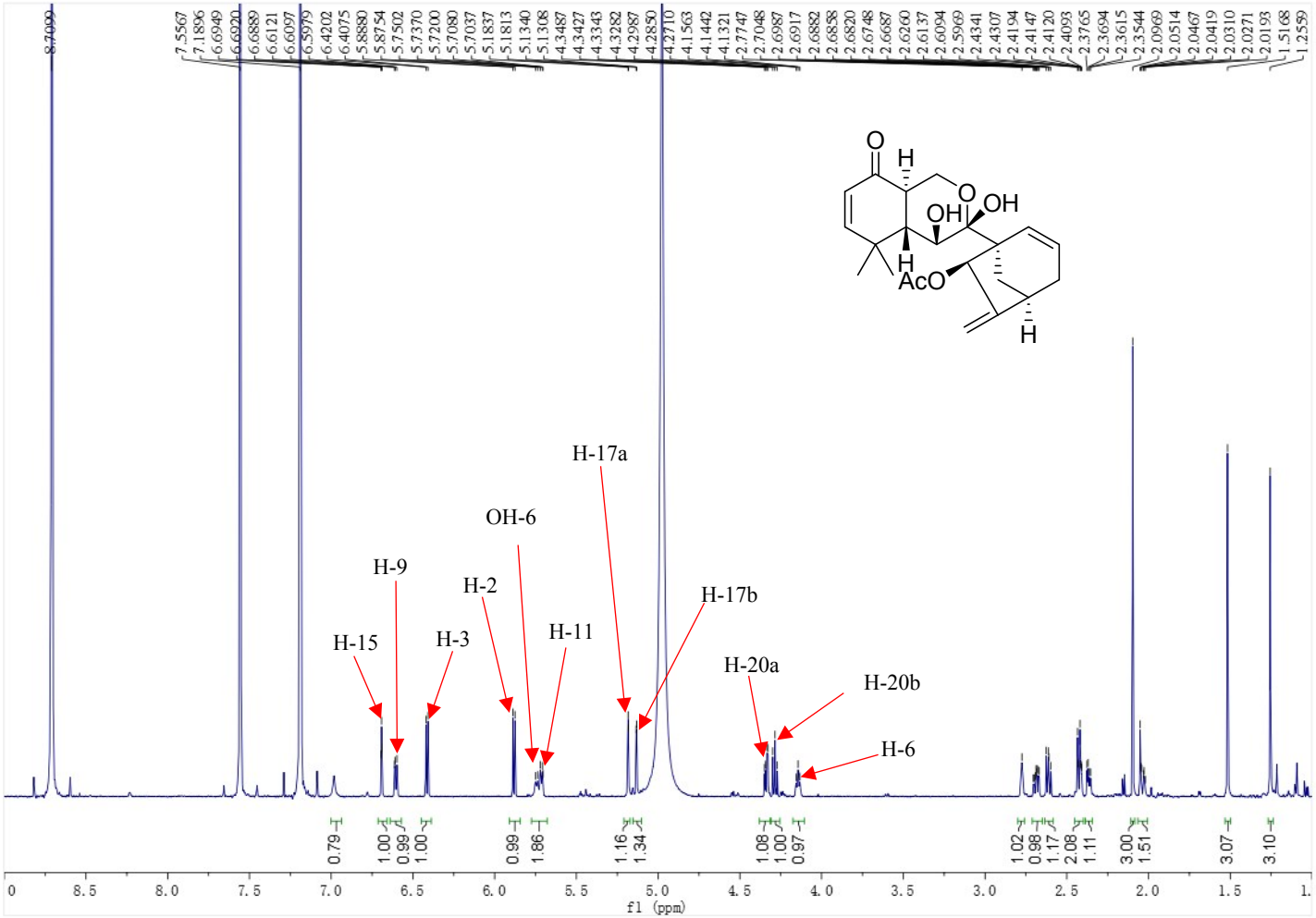
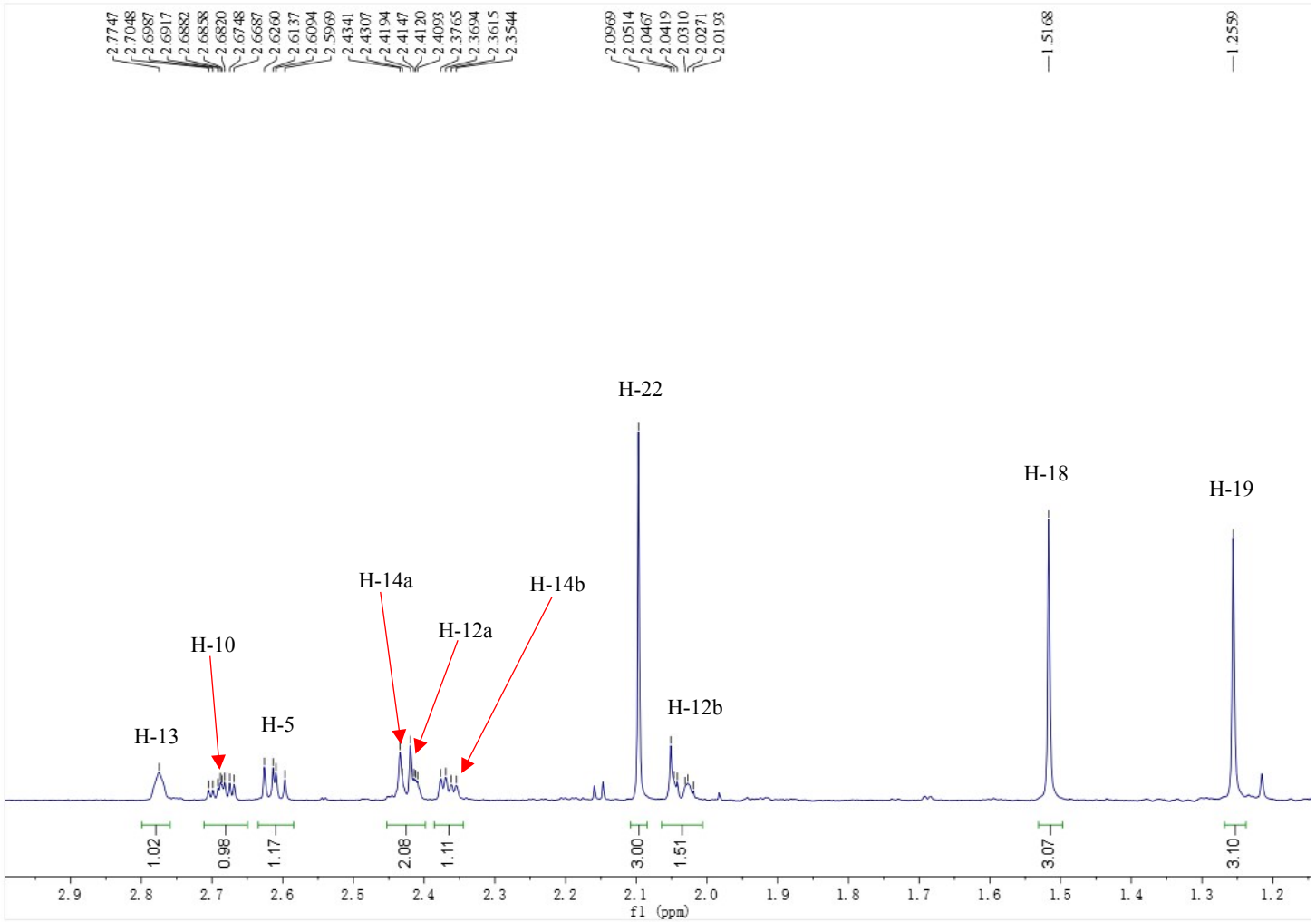


Figure S59 ^{1}H-NMR spectrum (pyridine-d_5, 800MHz) of maoeriocalysin C (**3**).


2.7747
2.7048
2.6987
2.6917
2.6882
2.6858
2.6820
2.6748
2.6687
2.6260
2.6137
2.6094
2.5969
2.4341
2.4307
2.4194
2.4147
2.4120
2.4093
2.3765
2.3694
2.3615
2.3544
2.0969
2.0514
2.0467
2.0419
2.0310
2.0271
2.0193
1.5168
1.2559
H-22
H-18
H-19
H-14a
H-14b
H-12a
H-10
H-12b
H-5
H-13
1.02
0.98
1.17
2.08
1.11
3.00
1.51
3.07
3.10
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
f1 (ppm)

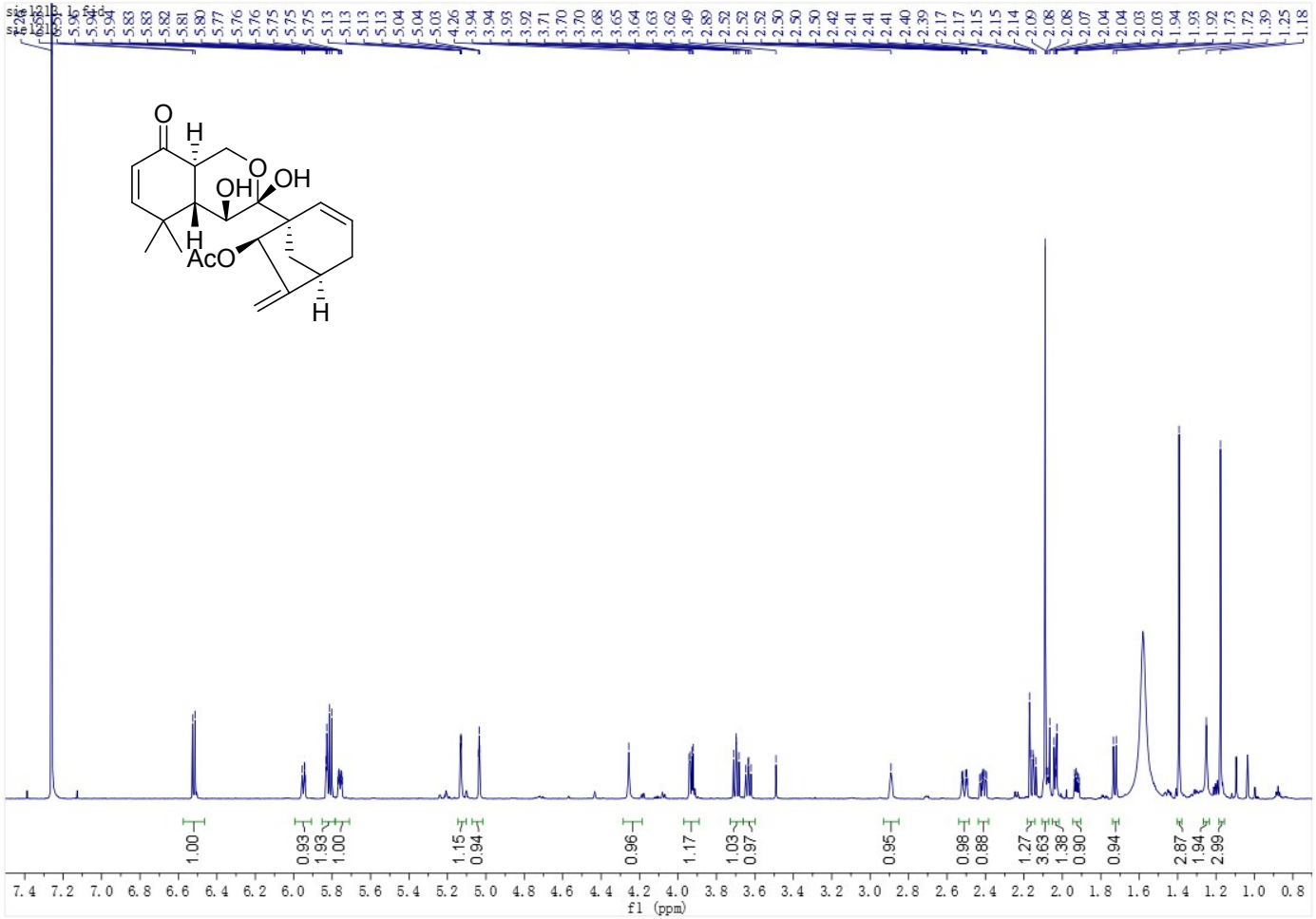


Figure S60 ^{1}H-NMR spectrum ($CDCl_3$, 800MHz) of maoeriocalysin C (**3**).

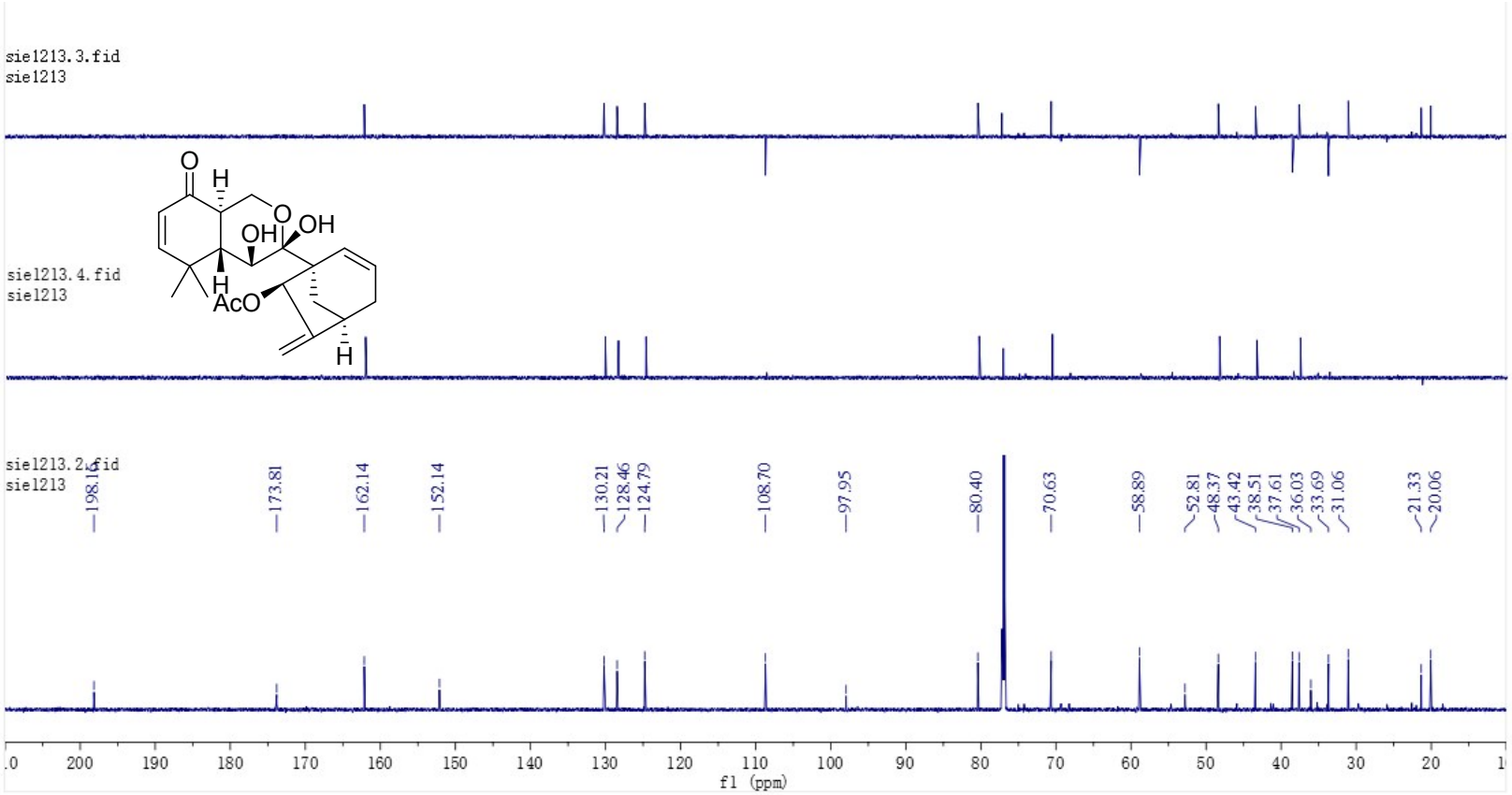


Figure S61 ^{13}C NMR spectrum ($CDCl_3$, 800MHz) of maoeriocalysin C (**3**).

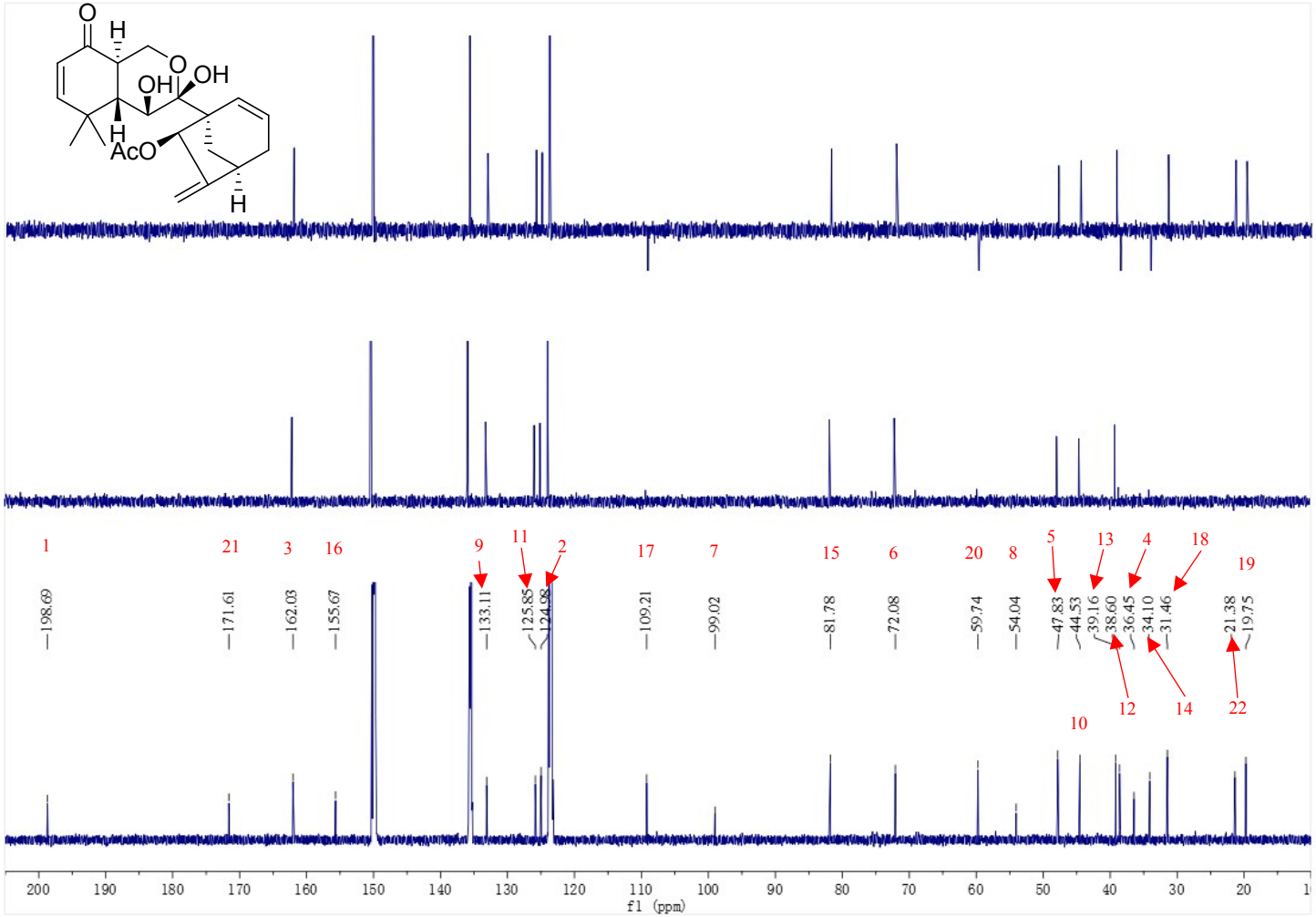


Figure S62 ^{13}C NMR spectrum (pyridine-d_5, 800MHz) of maoeriocalysin C (**3**).

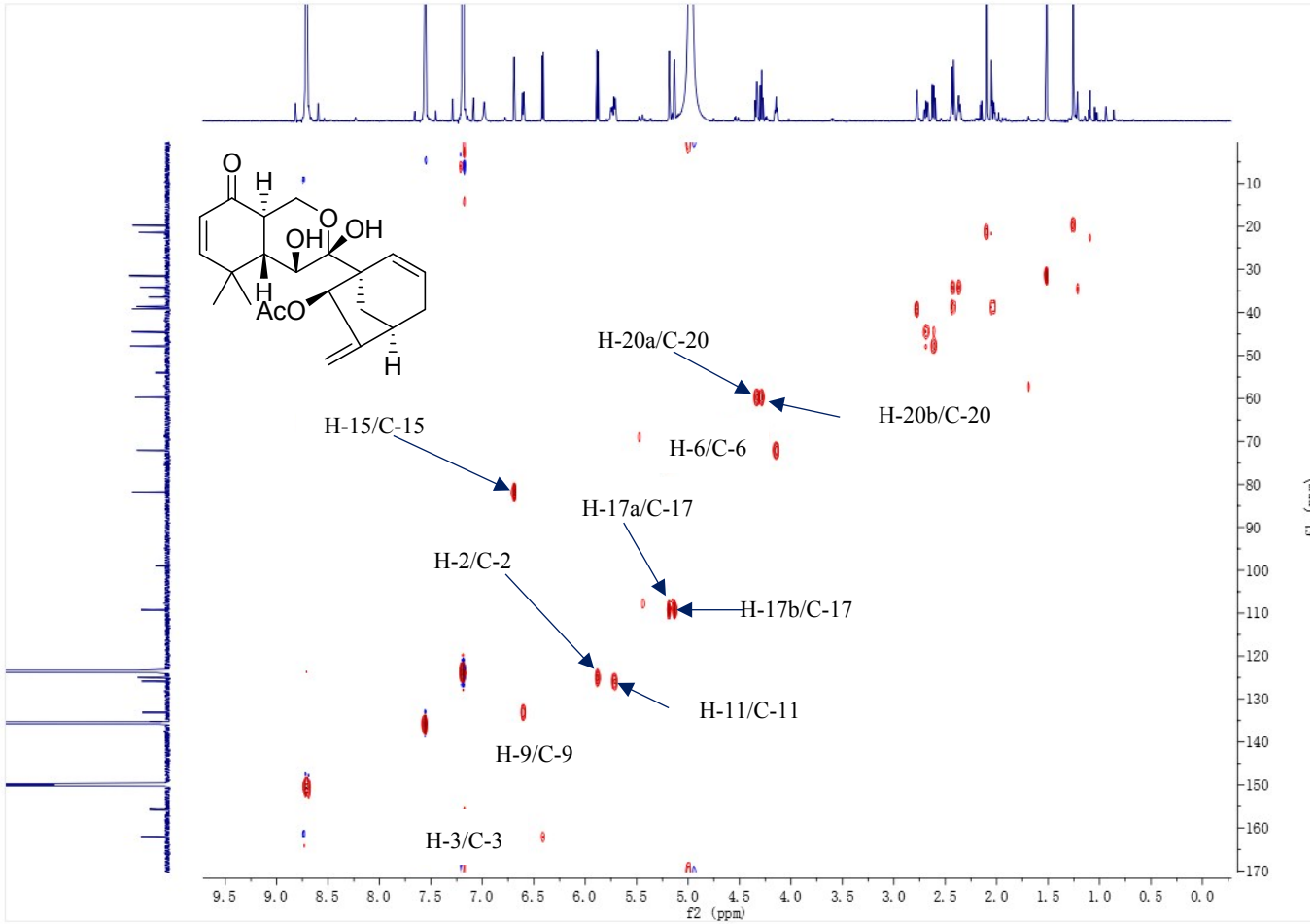
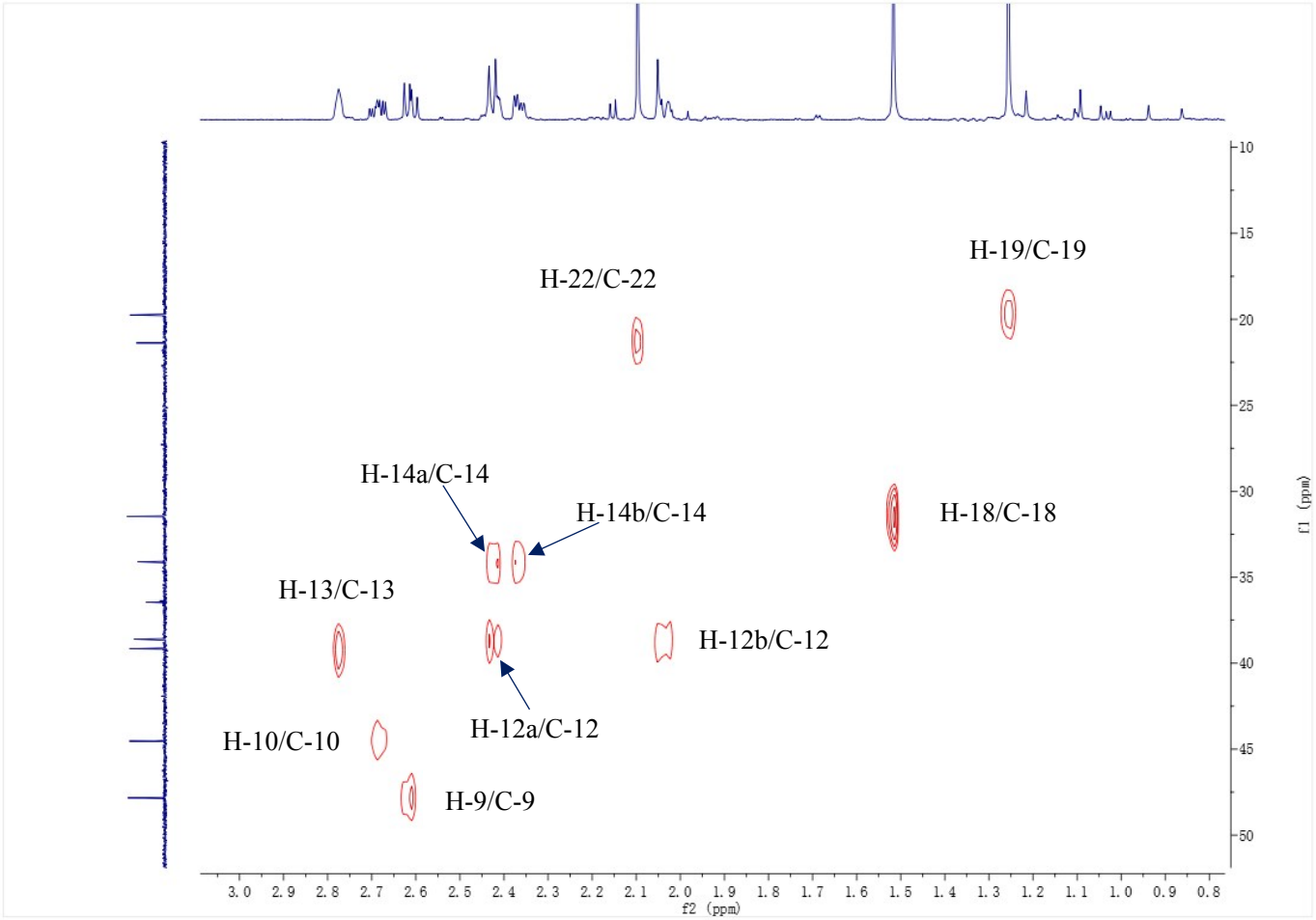


Figure S63 HSQC spectrum (pyridine-d_5, 800MHz) of maoeriocalysin C (**3**).


H-19/C-19
H-22/C-22
H-14a/C-14
H-14b/C-14
H-18/C-18
H-13/C-13
H-12b/C-12
H-12a/C-12
H-10/C-10
H-9/C-9
f2 (ppm)
f1 (ppm)

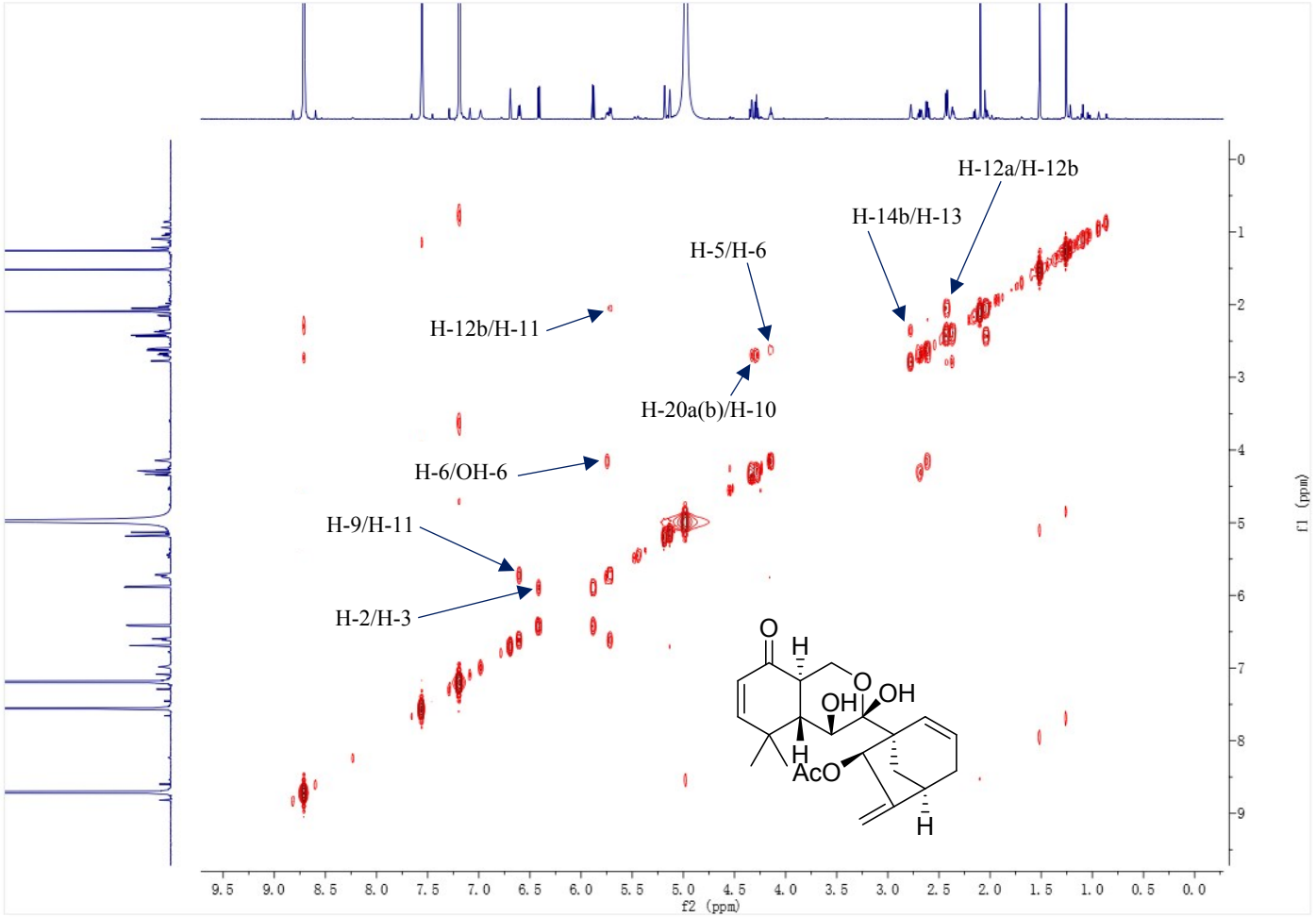


Figure S64 ^{1}H-^{1}H COSY spectrum (pyridine-d_5, 800MHz) of maoeriocalysin C (**3**).

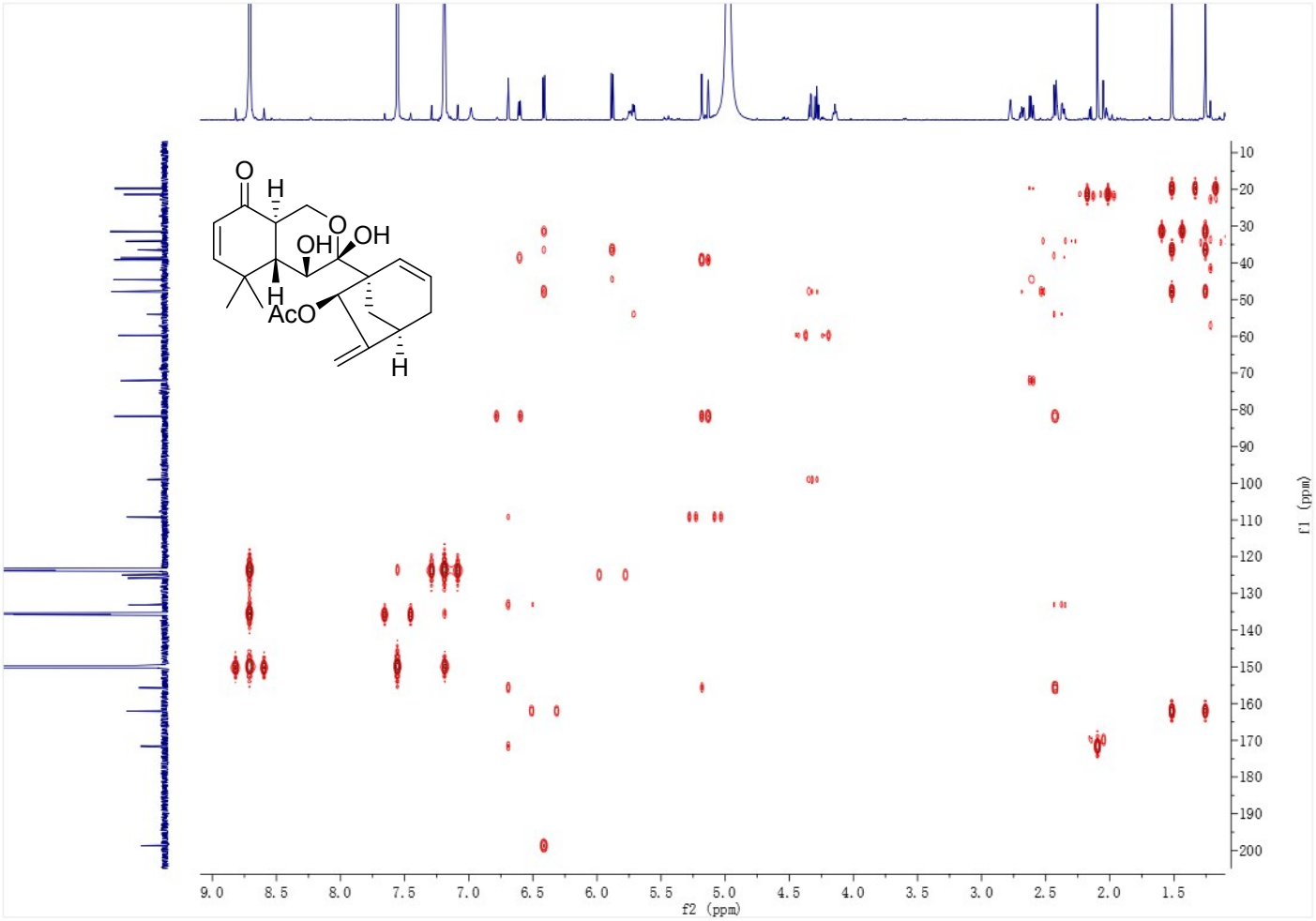
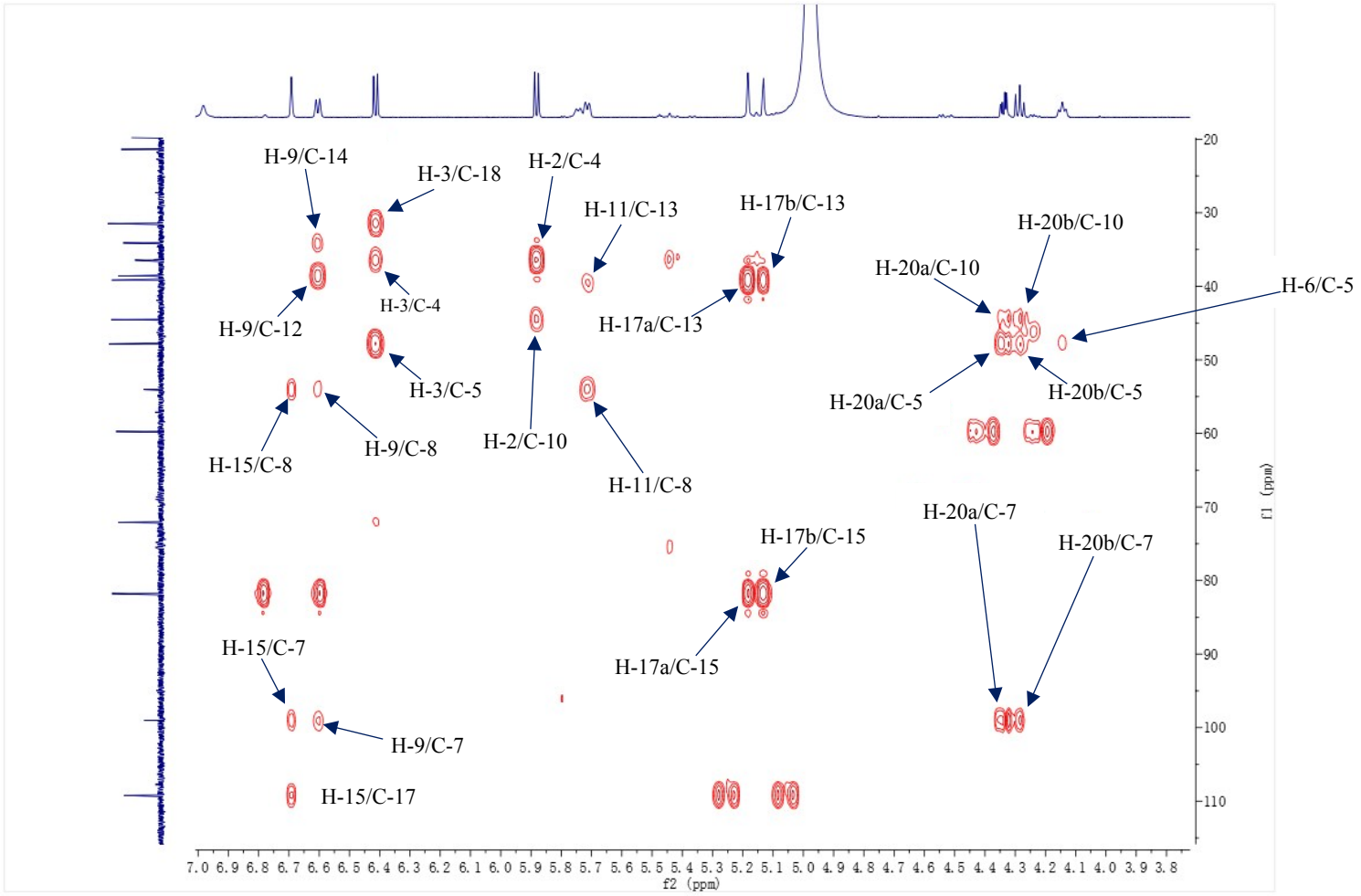
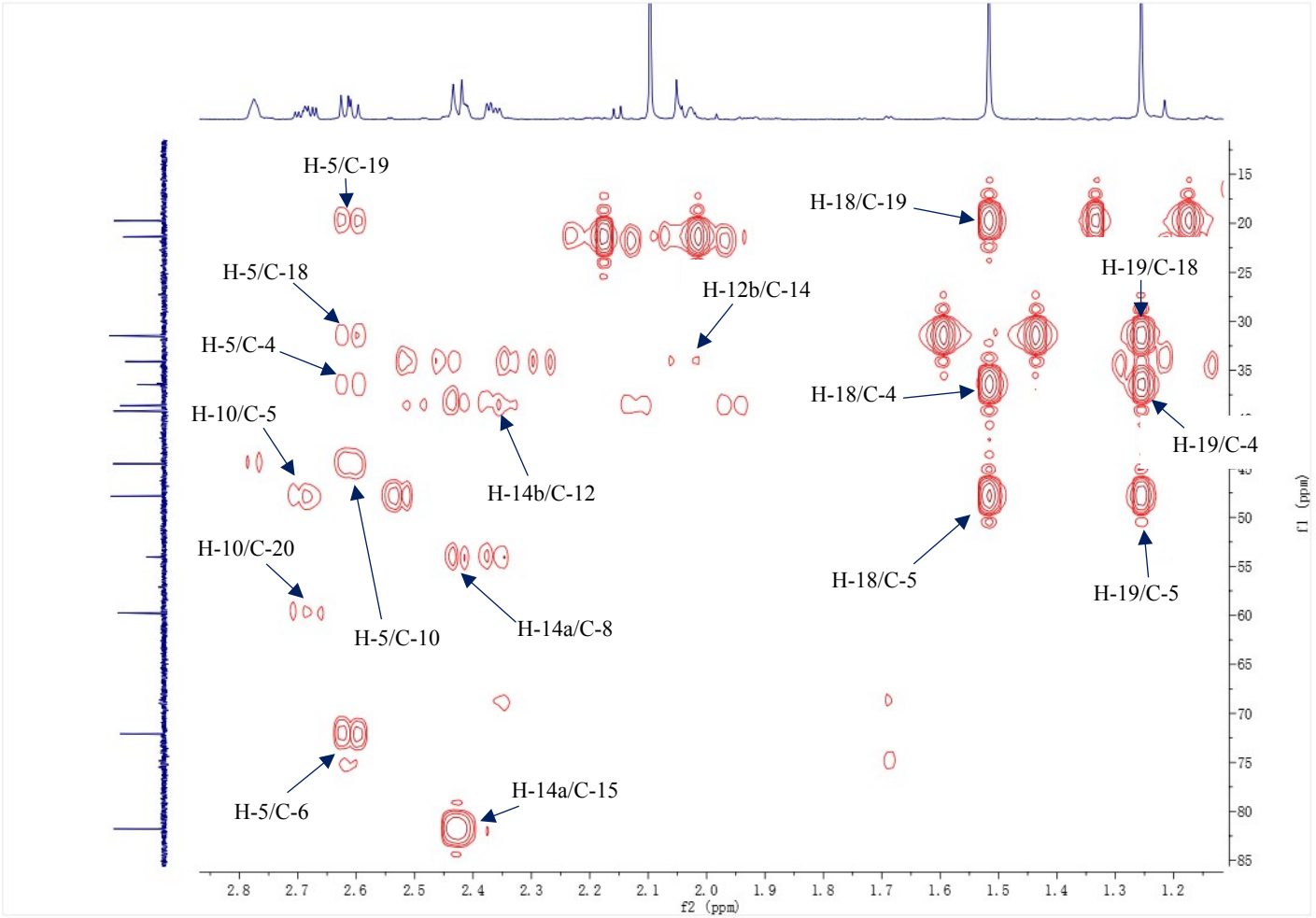
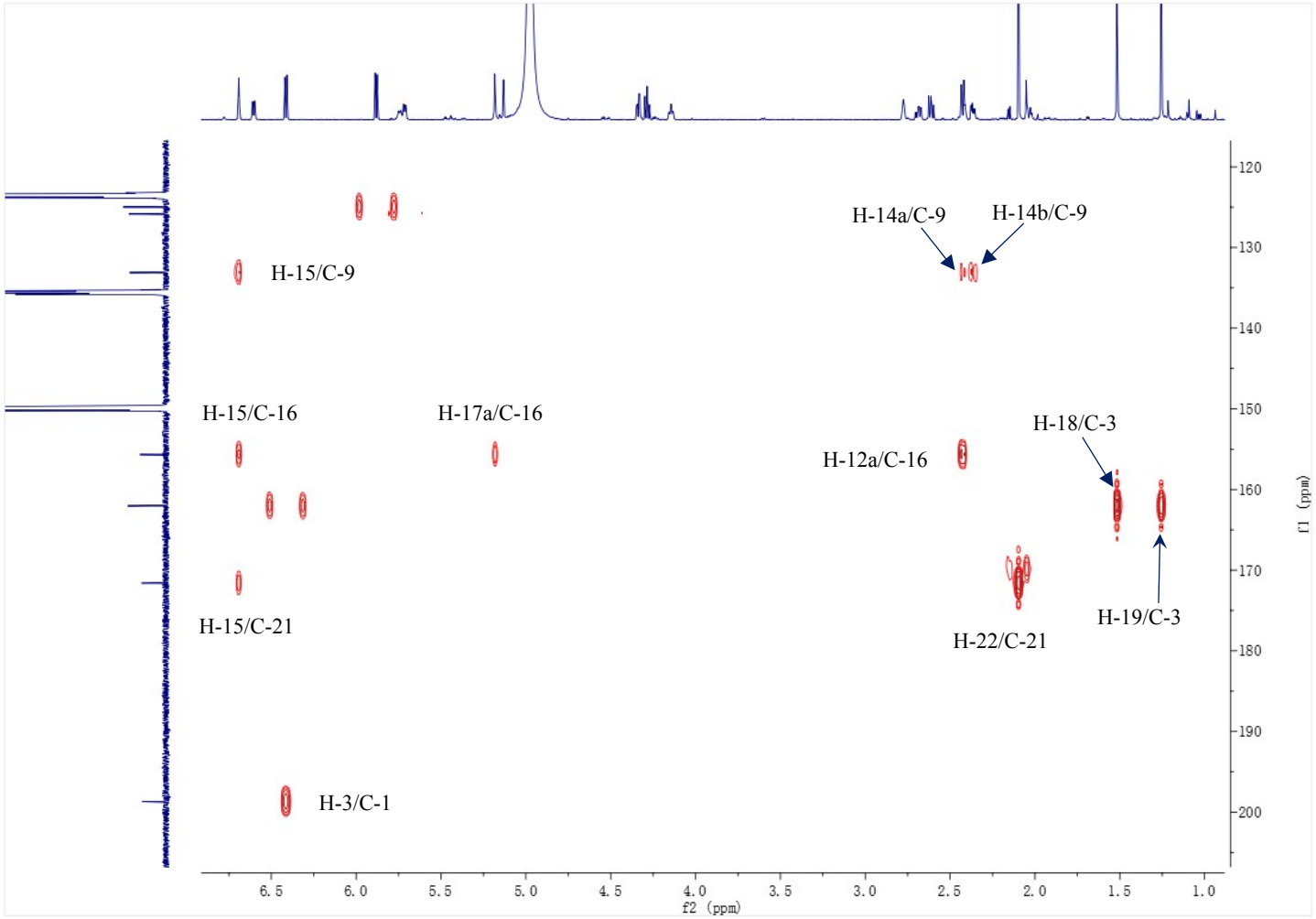


Figure S65 HMBC spectrum (pyridine-d_5, 800MHz) of maoeriocalysin C (**3**).


H-9/C-14
H-3/C-18
H-2/C-4
H-11/C-13
H-17b/C-13
H-20b/C-10
H-20a/C-10
H-6/C-5
H-3/C-4
H-9/C-12
H-17a/C-13
H-3/C-5
H-20a/C-5
H-20b/C-5
H-15/C-8
H-9/C-8
H-2/C-10
H-11/C-8
H-20a/C-7
H-17b/C-15
H-20b/C-7
H-15/C-7
H-17a/C-15
H-9/C-7
H-15/C-17
f2 (ppm)
f1 (ppm)


H-5/C-19
H-5/C-18
H-5/C-4
H-10/C-5
H-10/C-20
H-5/C-10
H-5/C-6
H-14b/C-12
H-14a/C-8
H-14a/C-15
H-12b/C-14
H-18/C-19
H-18/C-4
H-18/C-5
H-19/C-18
H-19/C-4
H-19/C-5
f2 (ppm)
f1 (ppm)


H-14a/C-9
H-14b/C-9
H-15/C-9
H-15/C-16
H-17a/C-16
H-12a/C-16
H-18/C-3
H-15/C-21
H-22/C-21
H-19/C-3
H-3/C-1
f2 (ppm)
f1 (ppm)

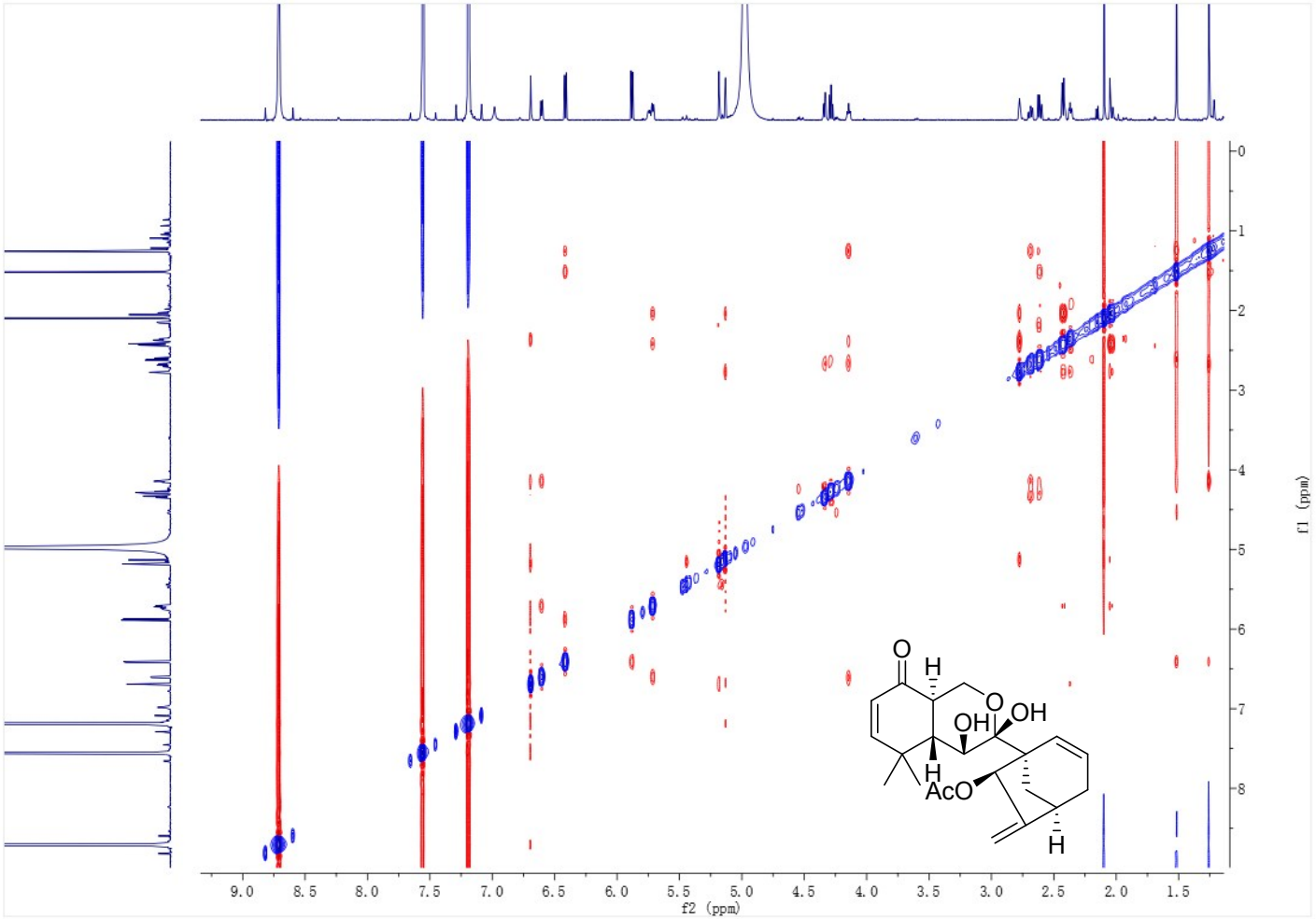
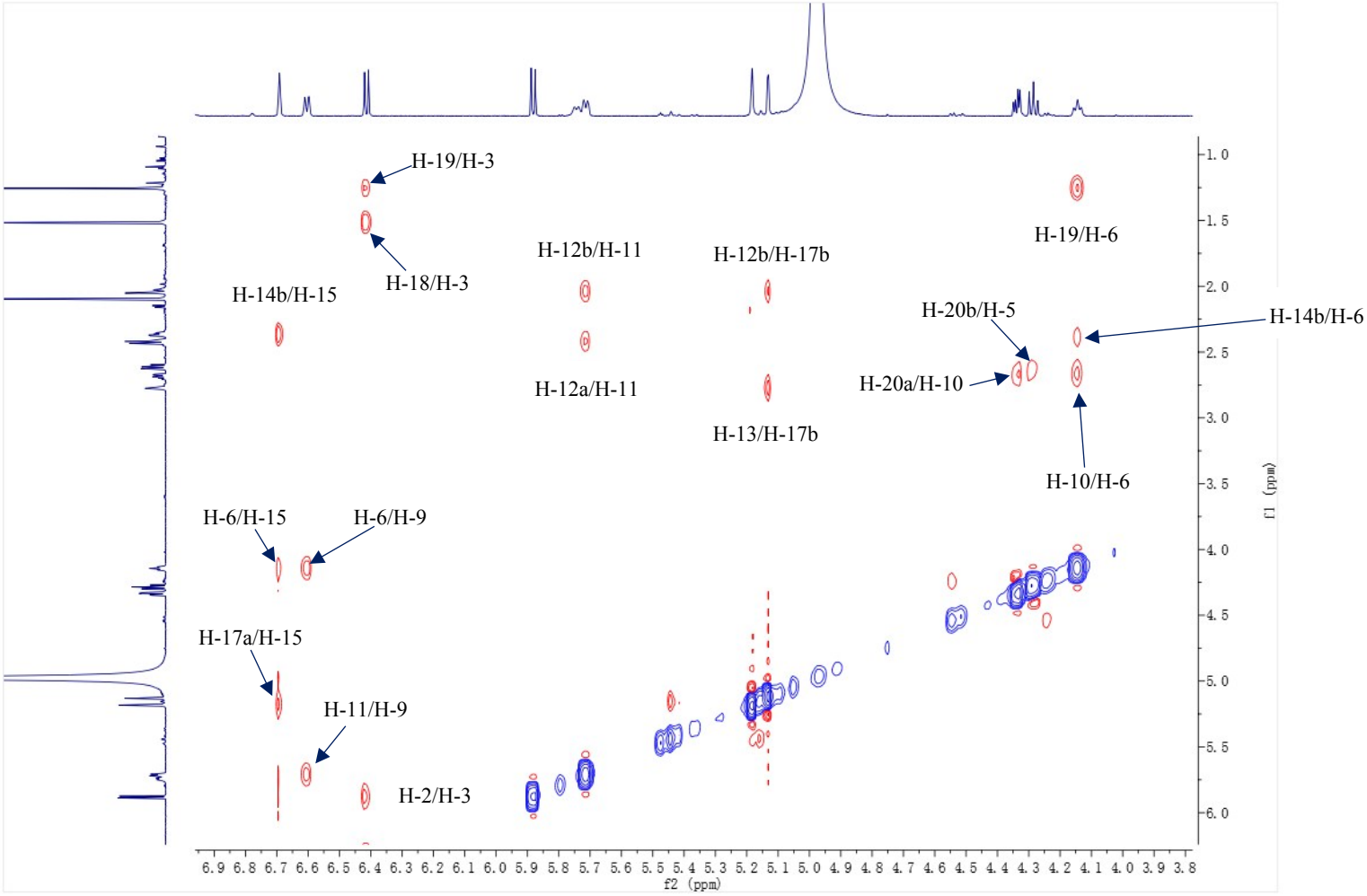
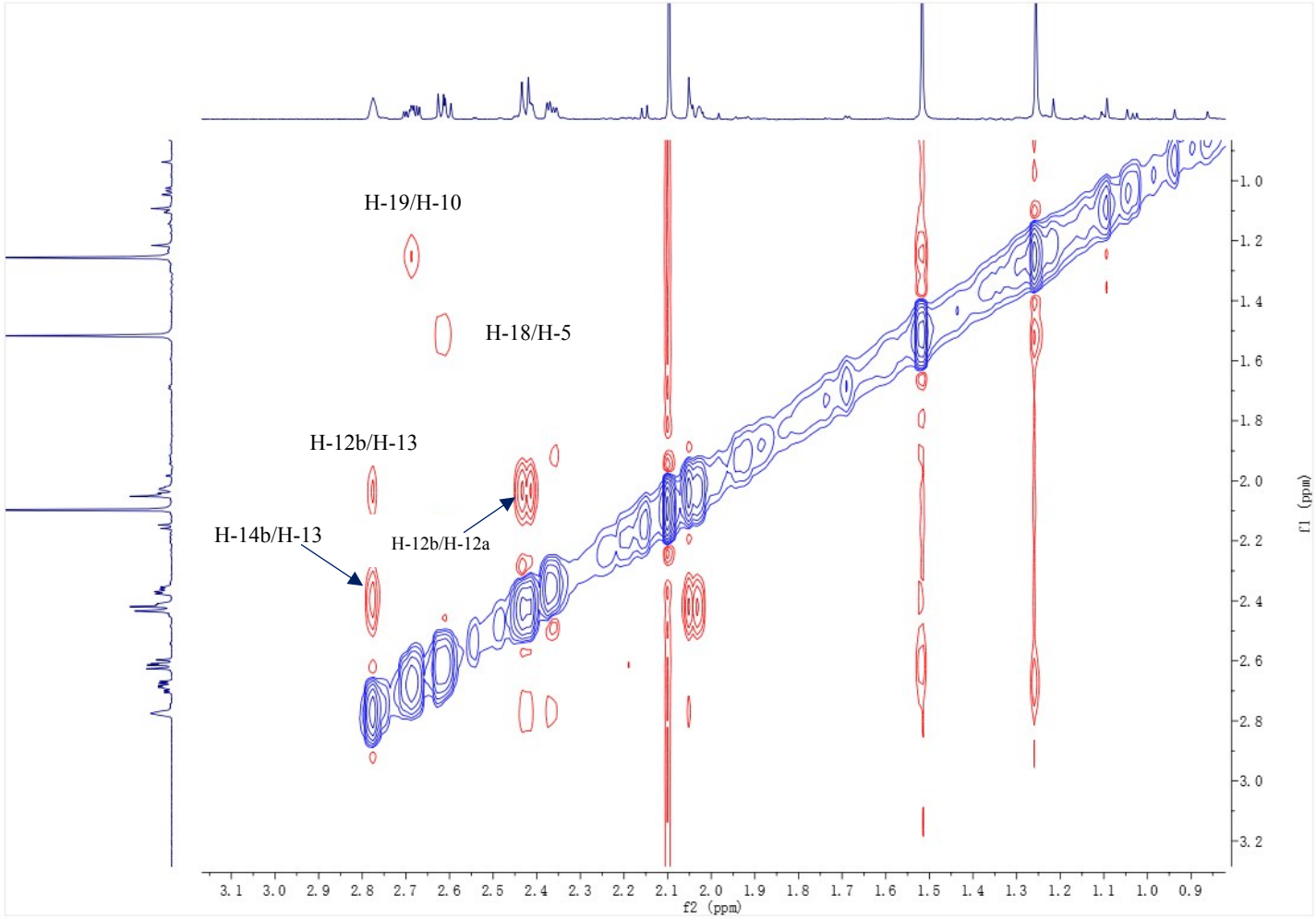
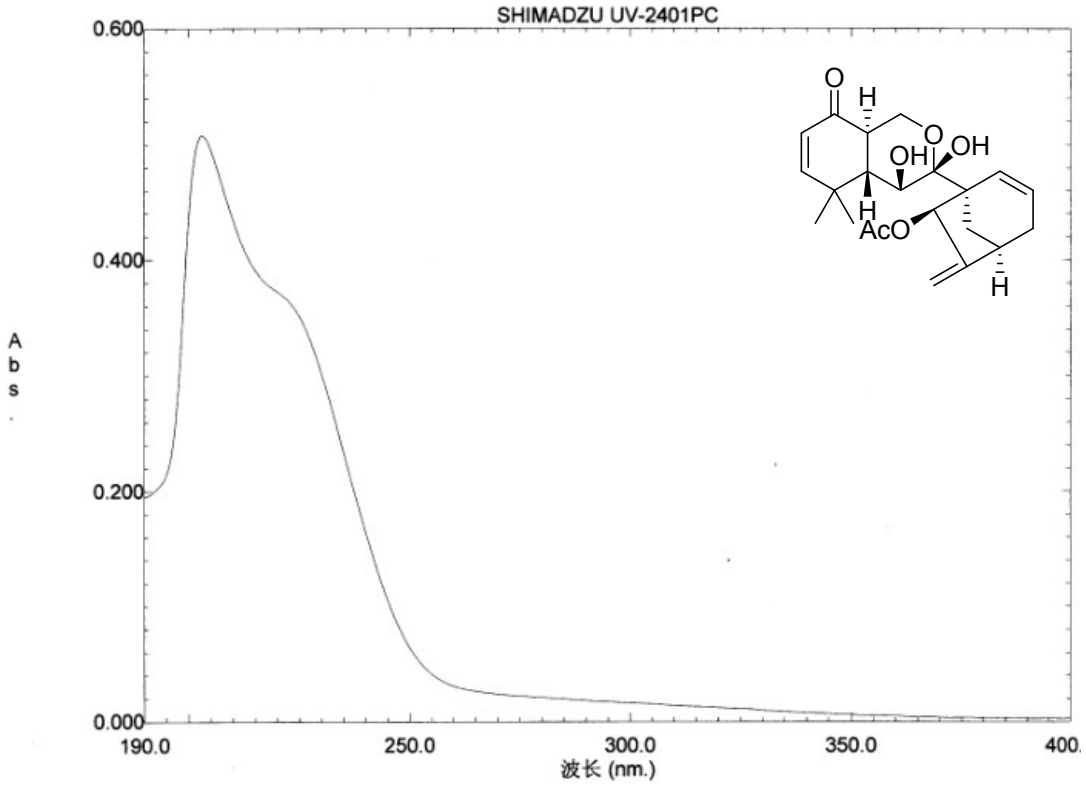


Figure S66 ROESY spectrum (pyridine-d_5, 800MHz) of maoeriocalysin C (**3**).


H-19/H-3
H-18/H-3
H-14b/H-15
H-12b/H-11
H-12a/H-11
H-12b/H-17b
H-13/H-17b
H-19/H-6
H-20b/H-5
H-14b/H-6
H-20a/H-10
H-10/H-6
H-6/H-15
H-6/H-9
H-17a/H-15
H-11/H-9
H-2/H-3
f2 (ppm)
f1 (ppm)


H-19/H-10
H-18/H-5
H-12b/H-13
H-14b/H-13
H-12b/H-12a
f2 (ppm)
f1 (ppm)



文件名: 17081100
样品名称：SIE-12-1-3

创建于: 09:52 17-08-11
数据: 原始

测量模式: Abs.
扫描速度: 中速
狭缝: 5.0
采样间隔: 0.2

否.	波长 (nm.)	Abs.
1	202.80	0.5073
2	217.60	0.3788

17081100

样品浓度：0.0306毫克/毫升
溶剂：甲醇

Figure S67 UV spectrum of maoeriocalysin C (**3**).

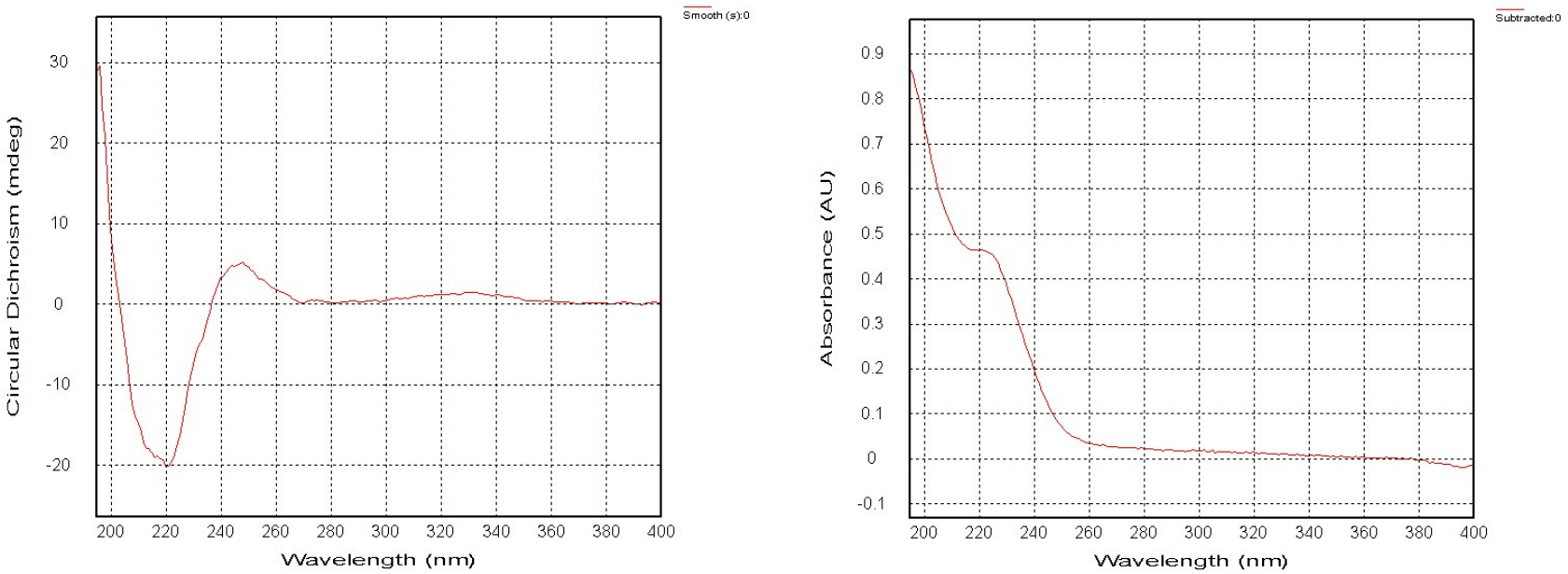


Figure S68 CD spectrum of maoeriocalysin C (**3**).

Optical rotation measurement

Model : P-1020 (A060460638)

No.	Sample	Mode	Data	Monitor Blank	Temp. Cell Temp Point	Date Comment Sample Name	Light Filter Operator	Cycle Time Integ Time
No.1	9 (1/3)	Sp.Rot	-22.3530	-0.0038 0.0000	23.9 10.00 Cell	Fri Jul 21 00:50:46 2017 0.00170g/mL MeOH SIE-12-1-3	Na 589nm	2 sec 2 sec
No.2	9 (2/3)	Sp.Rot	-22.9410	-0.0039 0.0000	23.9 10.00 Cell	Fri Jul 21 00:50:51 2017 0.00170g/mL MeOH SIE-12-1-3	Na 589nm	2 sec 2 sec
No.3	9 (3/3)	Sp.Rot	-24.1180	-0.0041 0.0000	24.0 10.00 Cell	Fri Jul 21 00:50:56 2017 0.00170g/mL MeOH SIE-12-1-3	Na 589nm	2 sec 2 sec

Figure S69 OR spectrum of maoeriocalysin C (**3**).

9.4 HRESIMS, NMR, UV, CD and OR spectra of maoeriocalysin D (4)

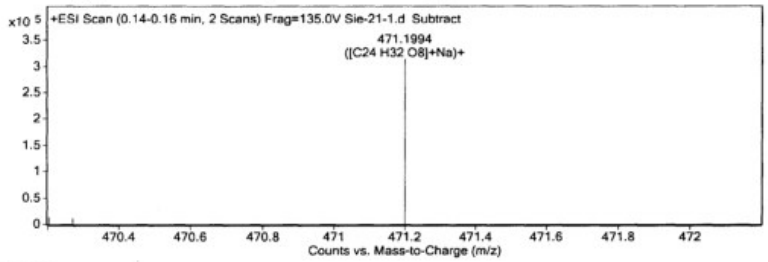
Qualitative Analysis Report

Data Filename	Sie-21-1.d	**Sample Name**	Sie-21-1
Sample Type	Sample	**Position**	P1-A3
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	3/12/2018 4:23:00 PM
IRM Calibration Status	[redacted]	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

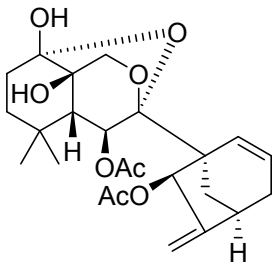
User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
431.2296	1	45297.22		
453.2227	1	52445.54		
459.1815	1	46103.06		
471.1994	1	314629.63	C24 H32 O8	(M+Na)+
472.2025	1	77677.32	C24 H32 O8	(M+Na)+
475.2287	1	52225.03		
487.1736	1	111297.13		
919.4088	1	77509.3		



Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C24 H32 O8	448.2097	471.1989	471.1994	-0.5	-1.2	9.0000

--- End Of Report ---

Figure S70 HRESIMS spectrum of maoeriocalysin D (**4**).

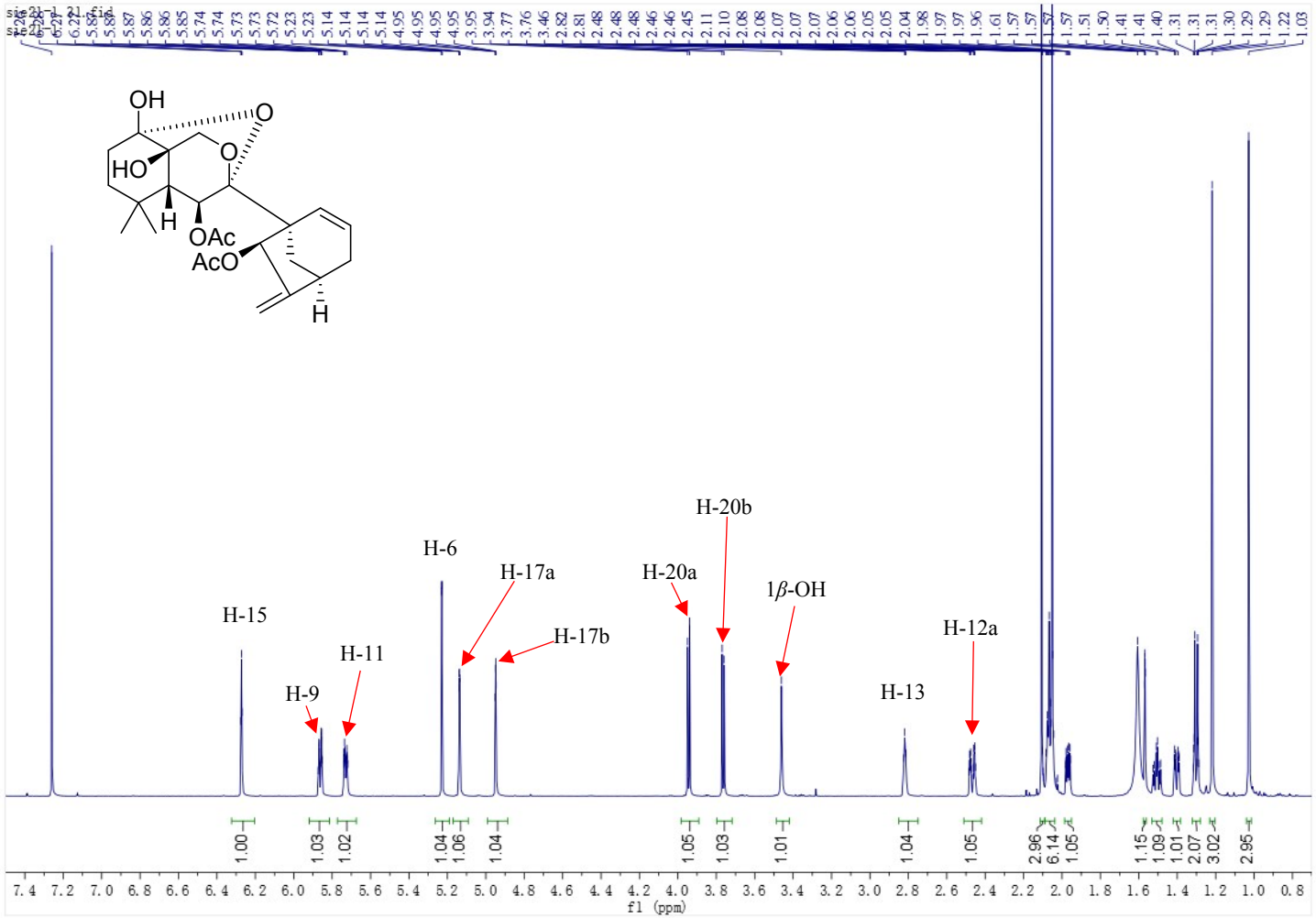
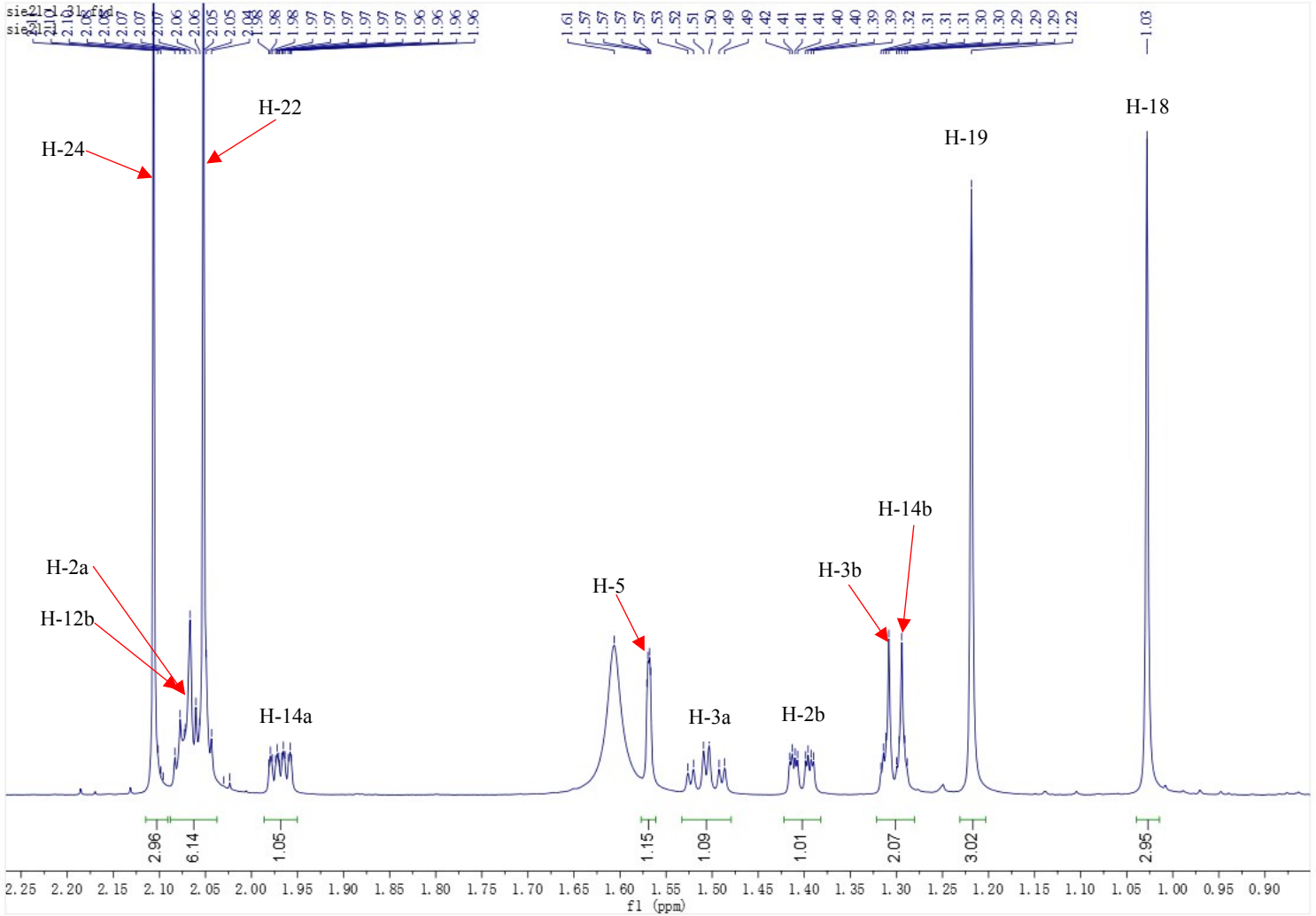


Figure S71 ^{1}H NMR spectrum ($CDCl_3$, 800MHz) of maoeriocalysin D (**4**).


H-24
H-22
H-18
H-19
H-14b
H-2a
H-12b
H-5
H-3b
H-14a
H-3a
H-2b
2.96
6.14
1.05
1.15
1.09
1.01
2.07
3.02
2.95
f1 (ppm)

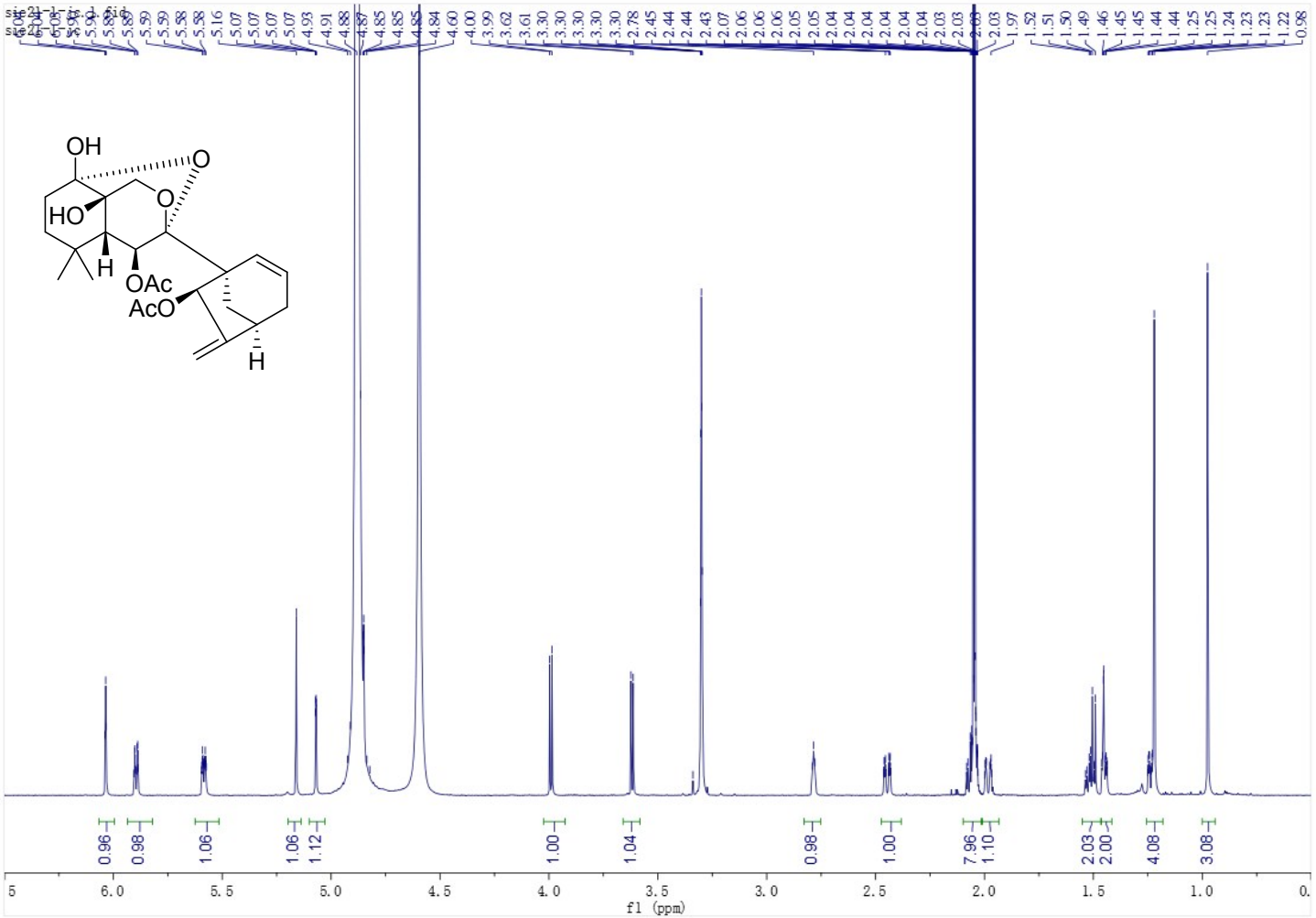


Figure S72 ^{1}H NMR spectrum (CD_3OD, 800MHz) of maoeriocalysin D (**4**).

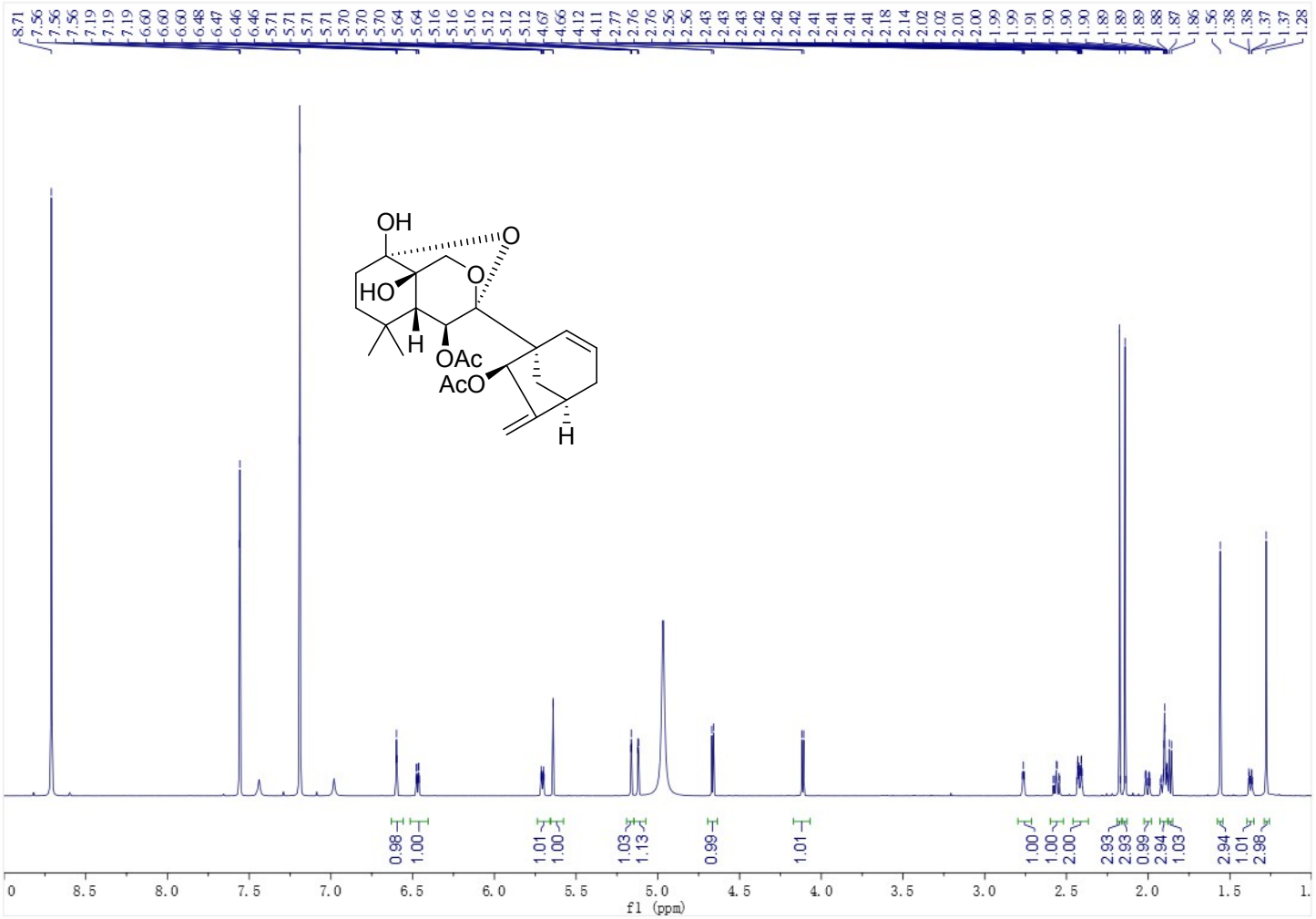


Figure S73 ^{1}H NMR spectrum (pyridine-d_5, 800MHz) of maoeriocalysin D (**4**).

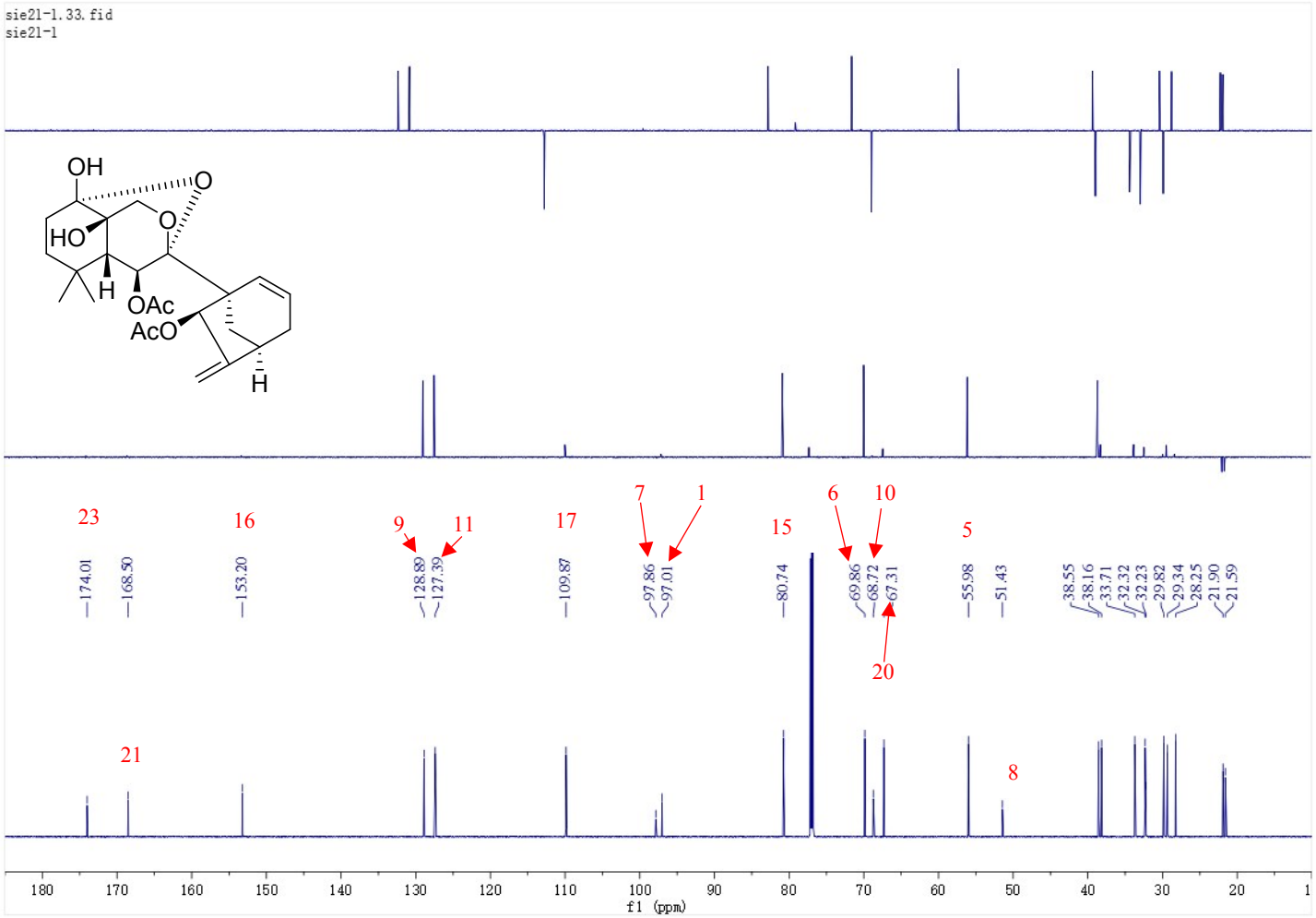
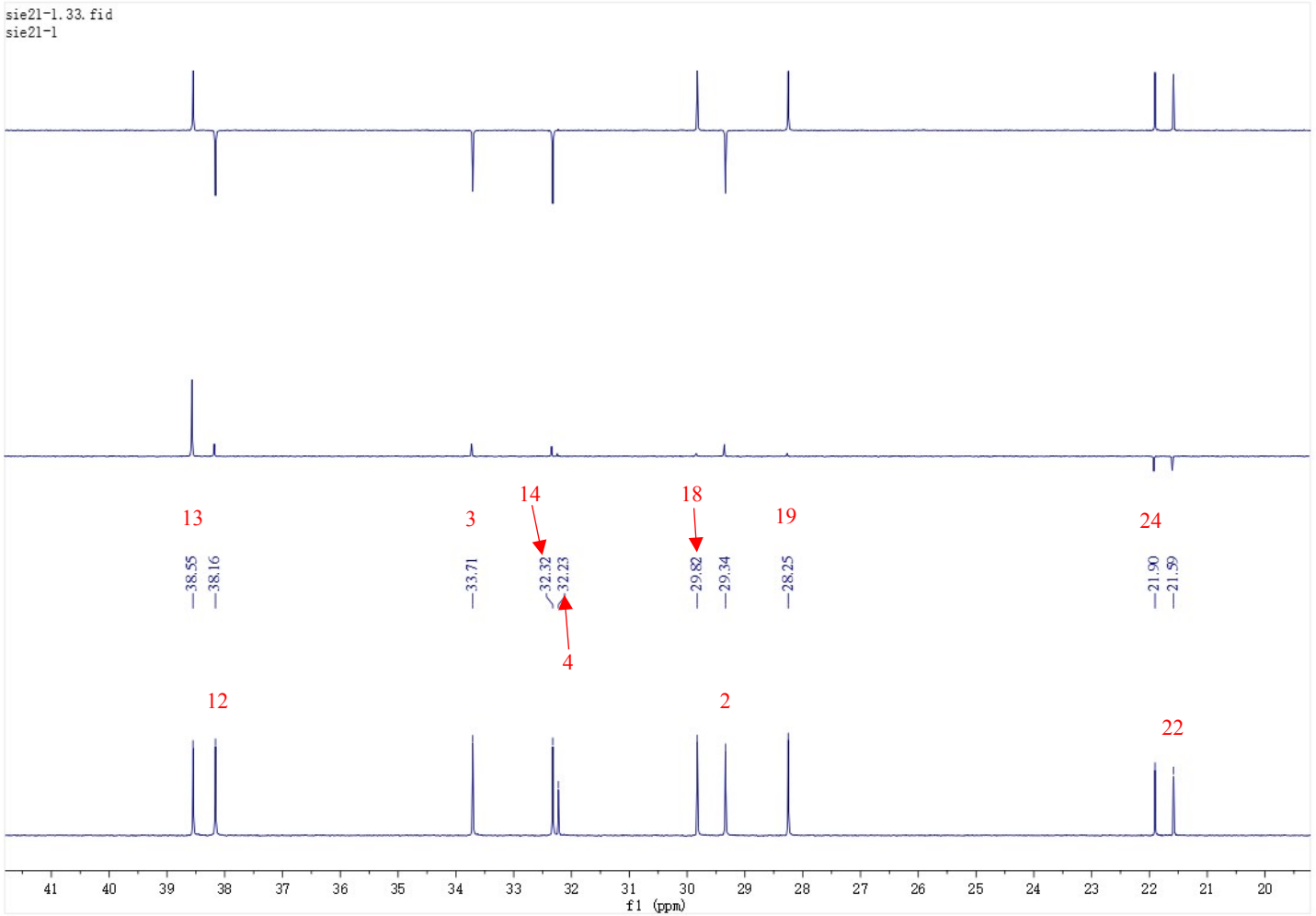


Figure S74 ^{13}C NMR spectrum ($CDCl_3$, 800MHz) of maoeriocalysin D (**4**).


sie21-1.33.fid
sie21-1
13
3
14
18
19
24
38.55
38.16
33.71
32.32
32.23
29.82
29.34
28.25
21.90
21.99
4
12
2
22
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
f1 (ppm)

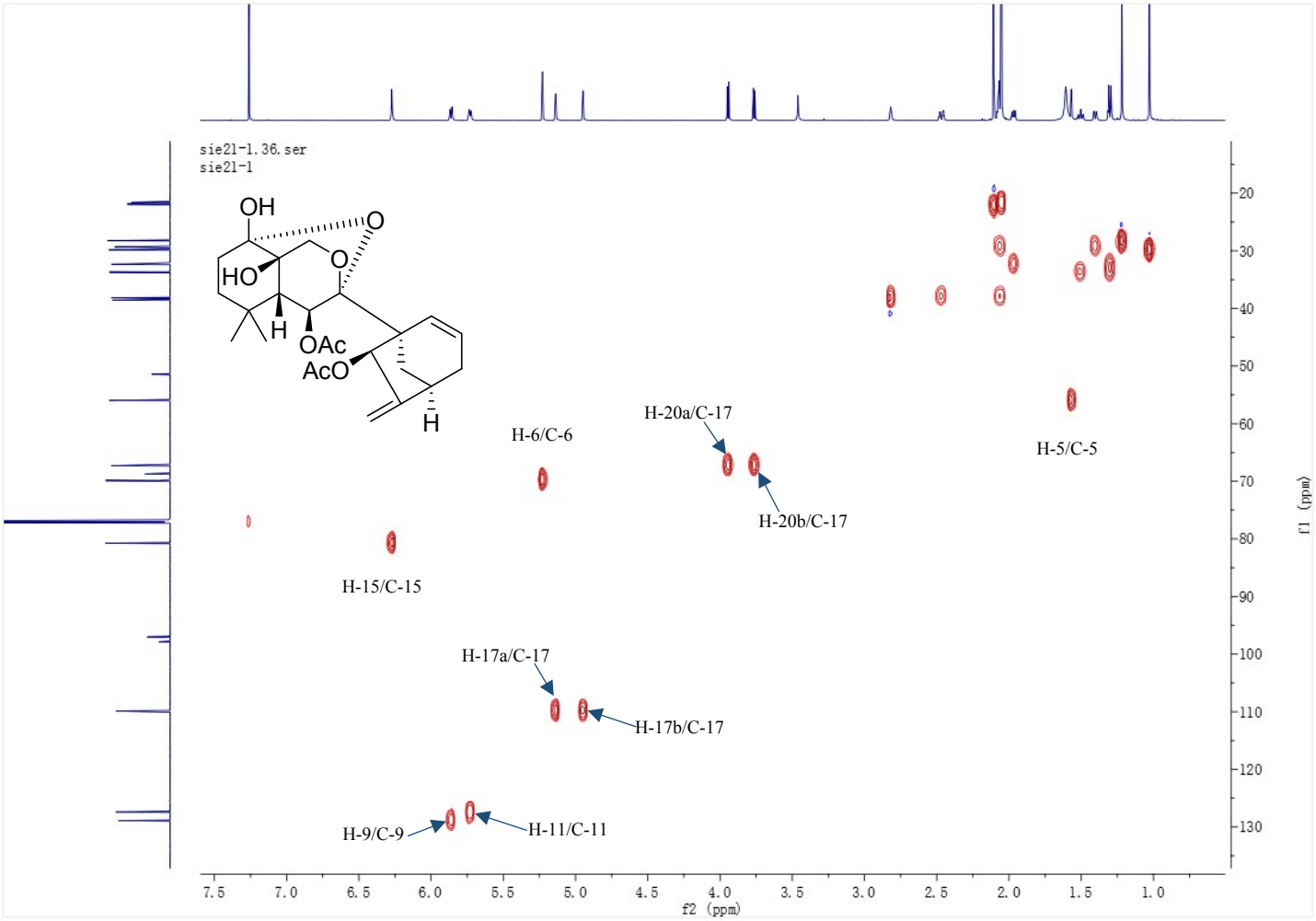
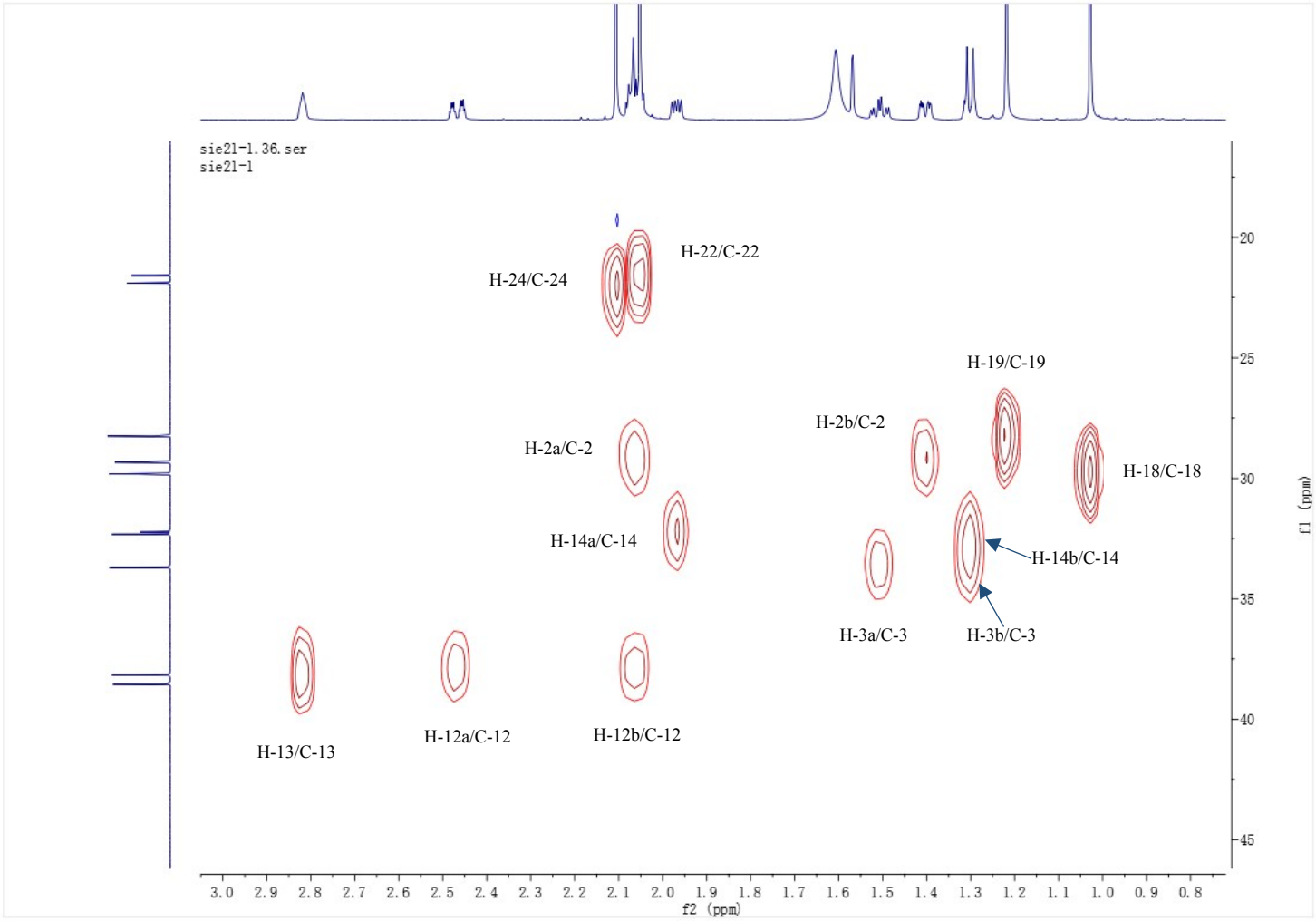


Figure S75 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 800MHz) of maoeriocalysin D (**4**).


sie21-1.36.ser
sie21-1
H-24/C-24
H-22/C-22
H-19/C-19
H-2b/C-2
H-2a/C-2
H-18/C-18
H-14a/C-14
H-14b/C-14
H-3a/C-3
H-3b/C-3
H-13/C-13
H-12a/C-12
H-12b/C-12
f2 (ppm)
f1 (ppm)

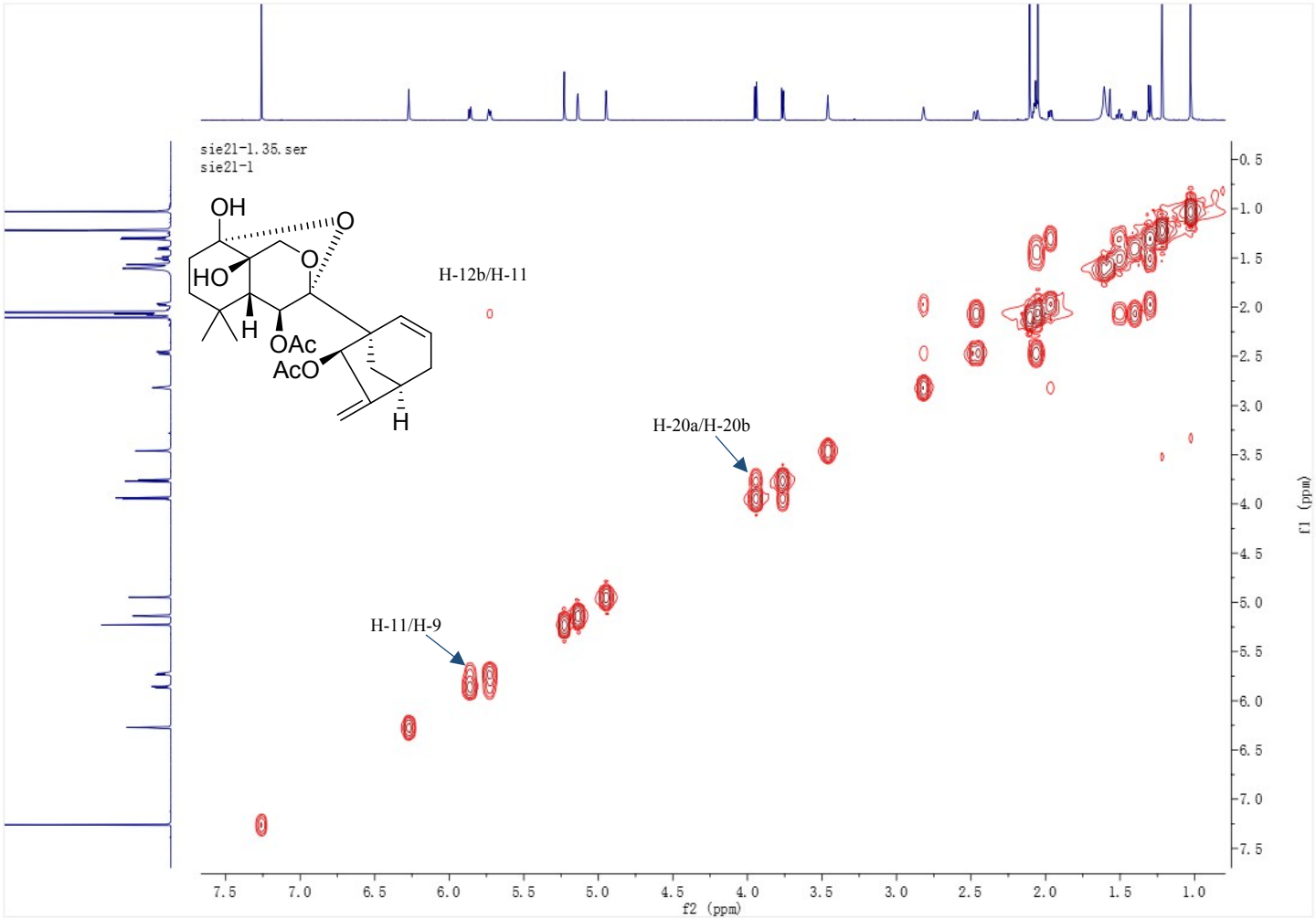
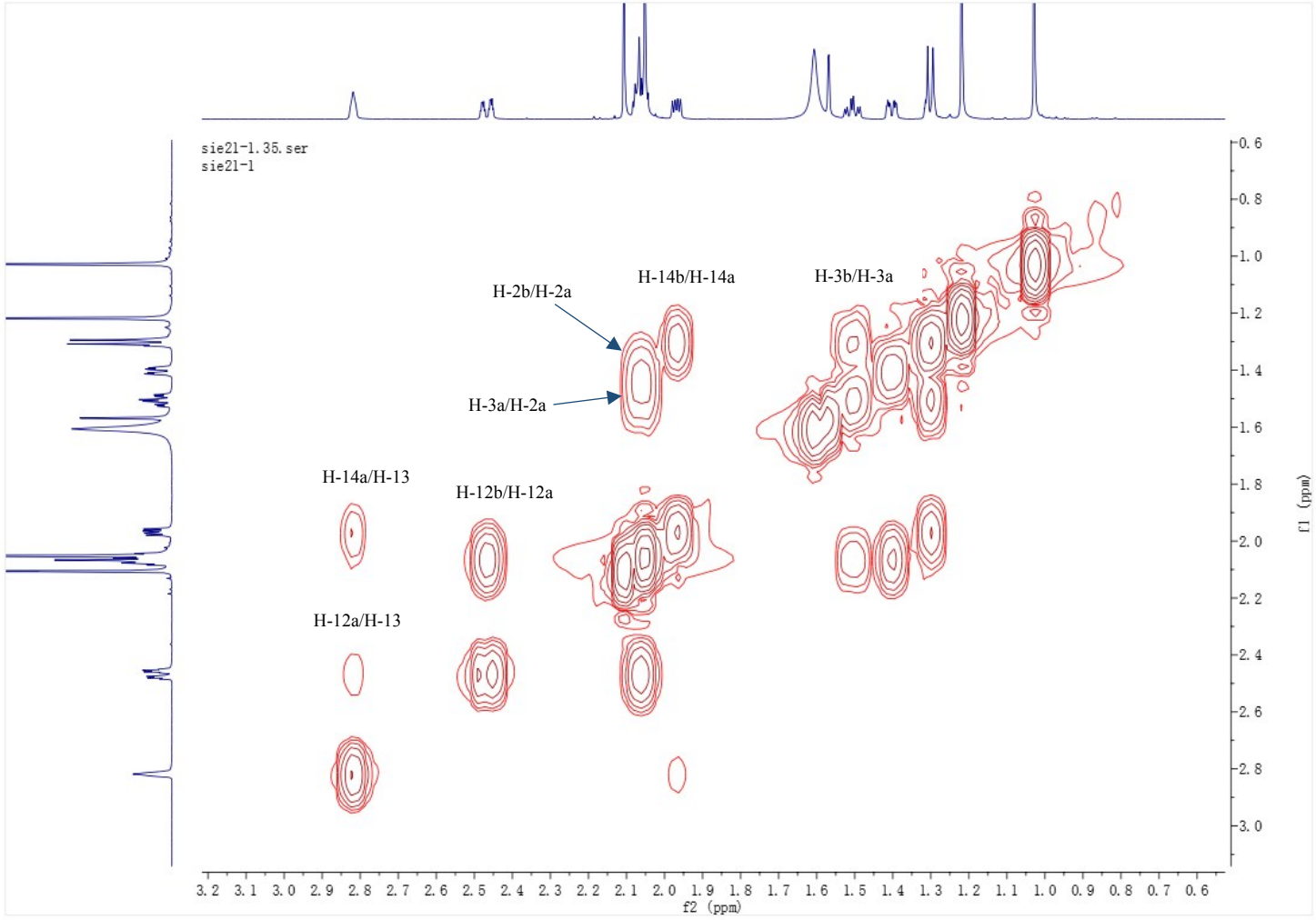


Figure S76 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 800MHz) of maoeriocalysin D (**4**).


sie21-1.35.ser
sie21-1
H-2b/H-2a
H-14b/H-14a
H-3b/H-3a
H-3a/H-2a
H-14a/H-13
H-12b/H-12a
H-12a/H-13
f2 (ppm)
f1 (ppm)

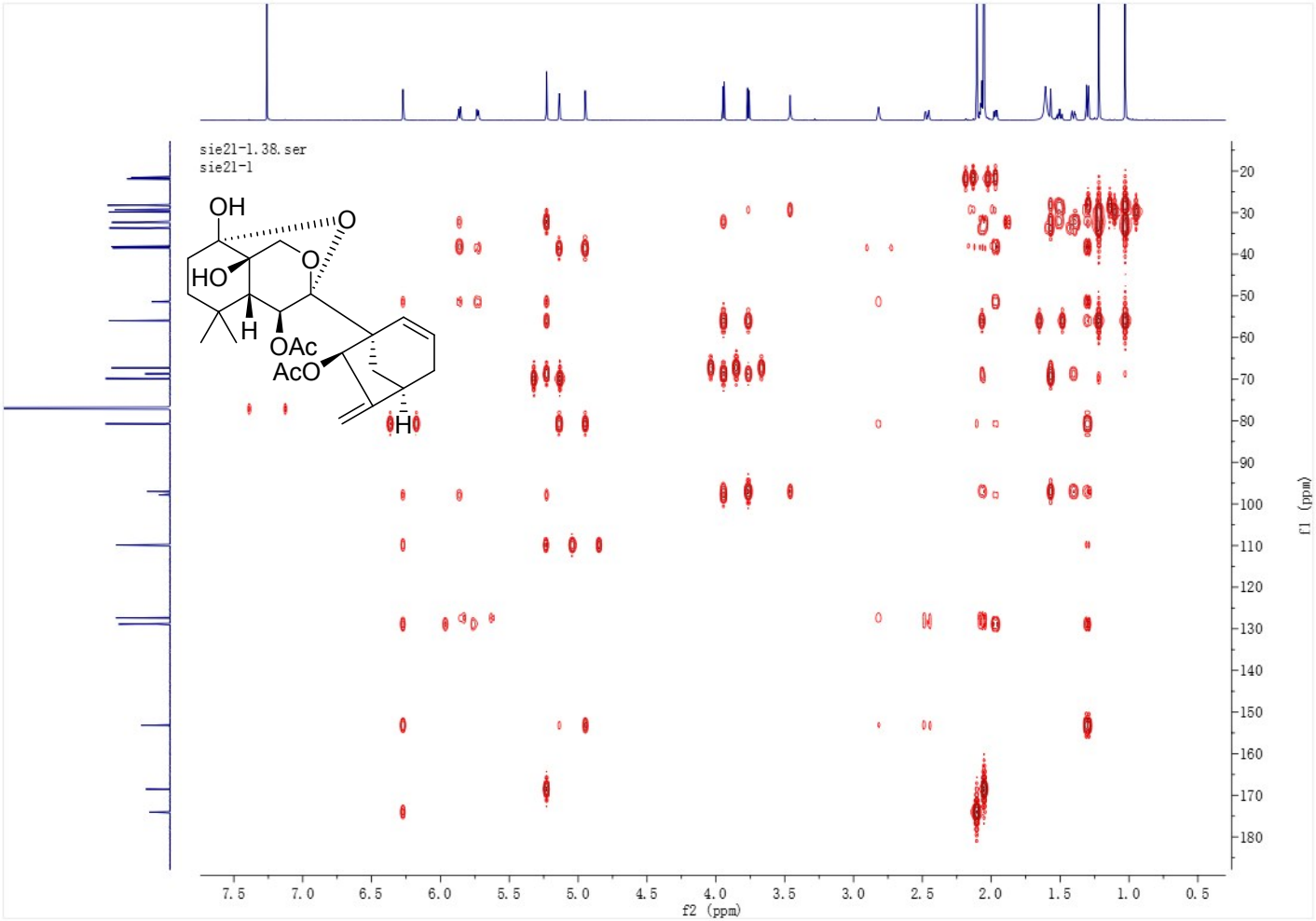
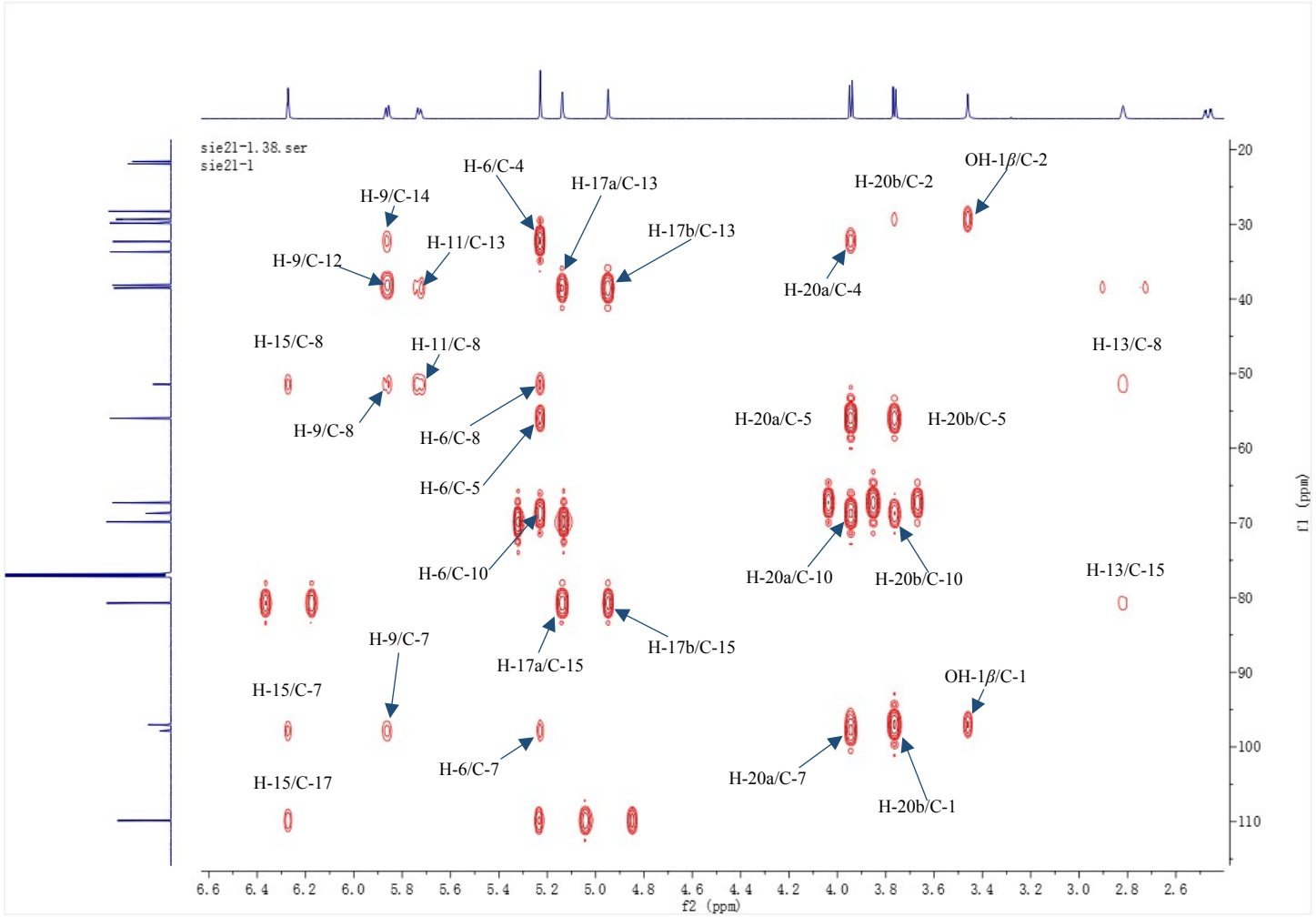
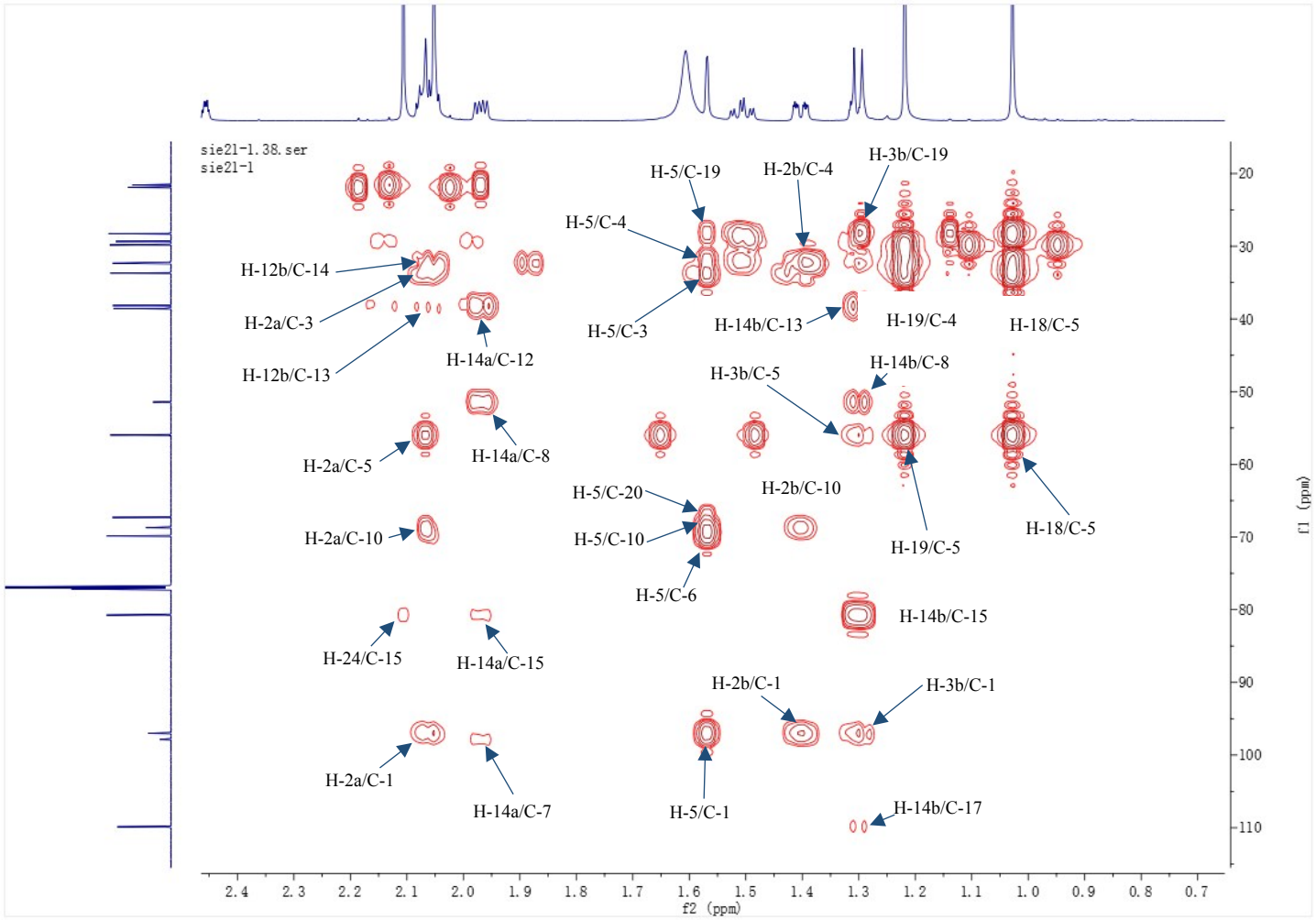
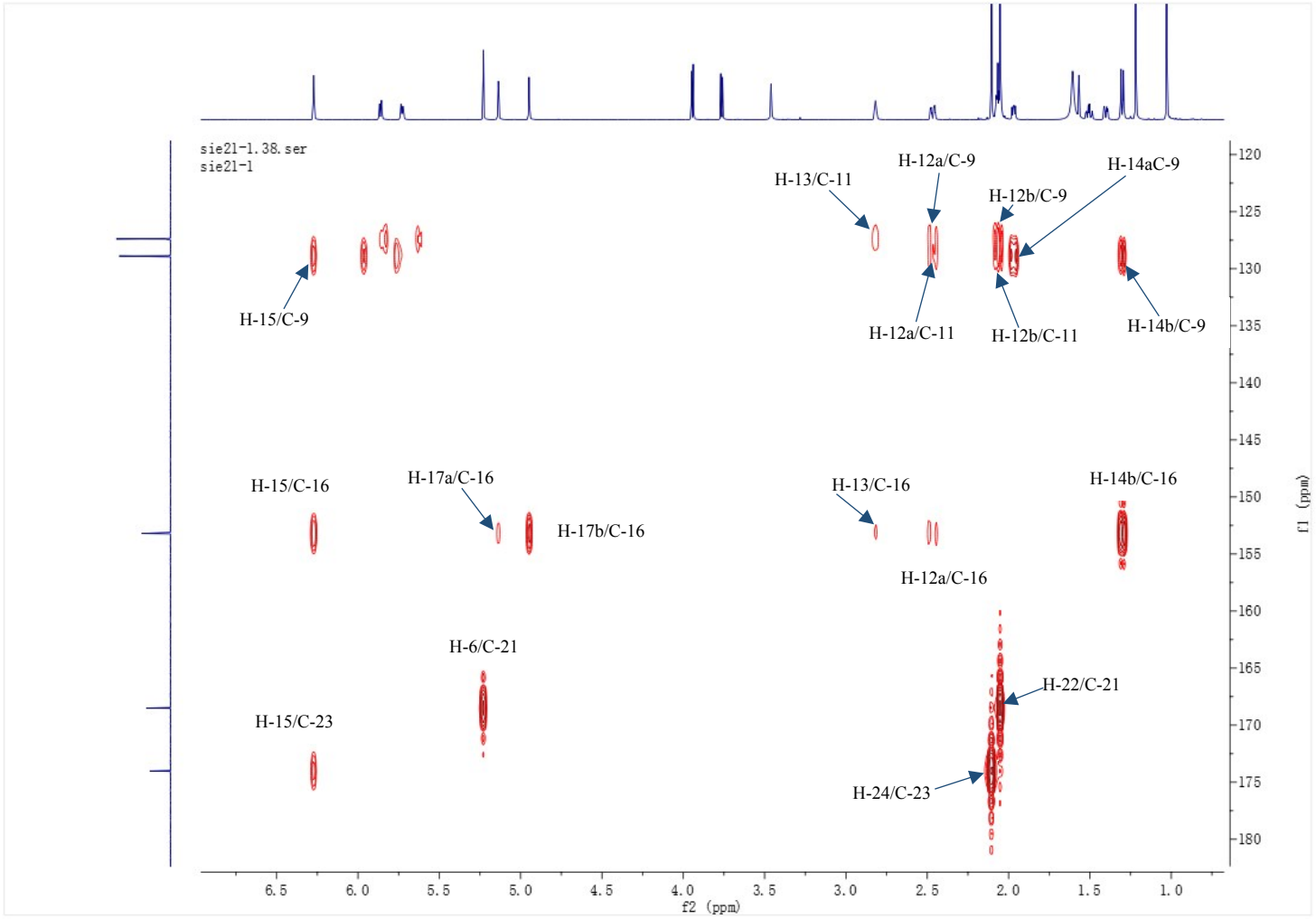


Figure S77 HMBC spectrum ($CDCl_3$, 800MHz) of maoeriocalysin D (**4**).


sie21-1.38.ser
sie21-1
H-6/C-4
H-17a/C-13
H-9/C-14
H-17b/C-13
H-11/C-13
H-9/C-12
H-20b/C-2
OH-1β/C-2
H-20a/C-4
H-15/C-8
H-11/C-8
H-13/C-8
H-9/C-8
H-6/C-8
H-20a/C-5
H-20b/C-5
H-6/C-5
H-6/C-10
H-20a/C-10
H-20b/C-10
H-13/C-15
H-9/C-7
H-17a/C-15
H-17b/C-15
H-15/C-7
OH-1β/C-1
H-6/C-7
H-20a/C-7
H-15/C-17
H-20b/C-1
f2 (ppm)
f1 (ppm)


sie21-1.38.ser
sie21-1
H-12b/C-14
H-2a/C-3
H-12b/C-13
H-14a/C-12
H-2a/C-5
H-14a/C-8
H-2a/C-10
H-24/C-15
H-14a/C-15
H-2a/C-1
H-14a/C-7
H-5/C-19
H-2b/C-4
H-3b/C-19
H-5/C-4
H-5/C-3
H-14b/C-13
H-19/C-4
H-18/C-5
H-3b/C-5
H-14b/C-8
H-5/C-20
H-5/C-10
H-5/C-6
H-2b/C-10
H-19/C-5
H-18/C-5
H-14b/C-15
H-2b/C-1
H-3b/C-1
H-5/C-1
H-14b/C-17
f2 (ppm)
f1 (ppm)


sie21-1.38.ser
sie21-1
H-13/C-11
H-12a/C-9
H-12b/C-9
H-14aC-9
H-15/C-9
H-12a/C-11
H-12b/C-11
H-14b/C-9
H-15/C-16
H-17a/C-16
H-17b/C-16
H-13/C-16
H-14b/C-16
H-12a/C-16
H-6/C-21
H-22/C-21
H-15/C-23
H-24/C-23
f2 (ppm)
f1 (ppm)

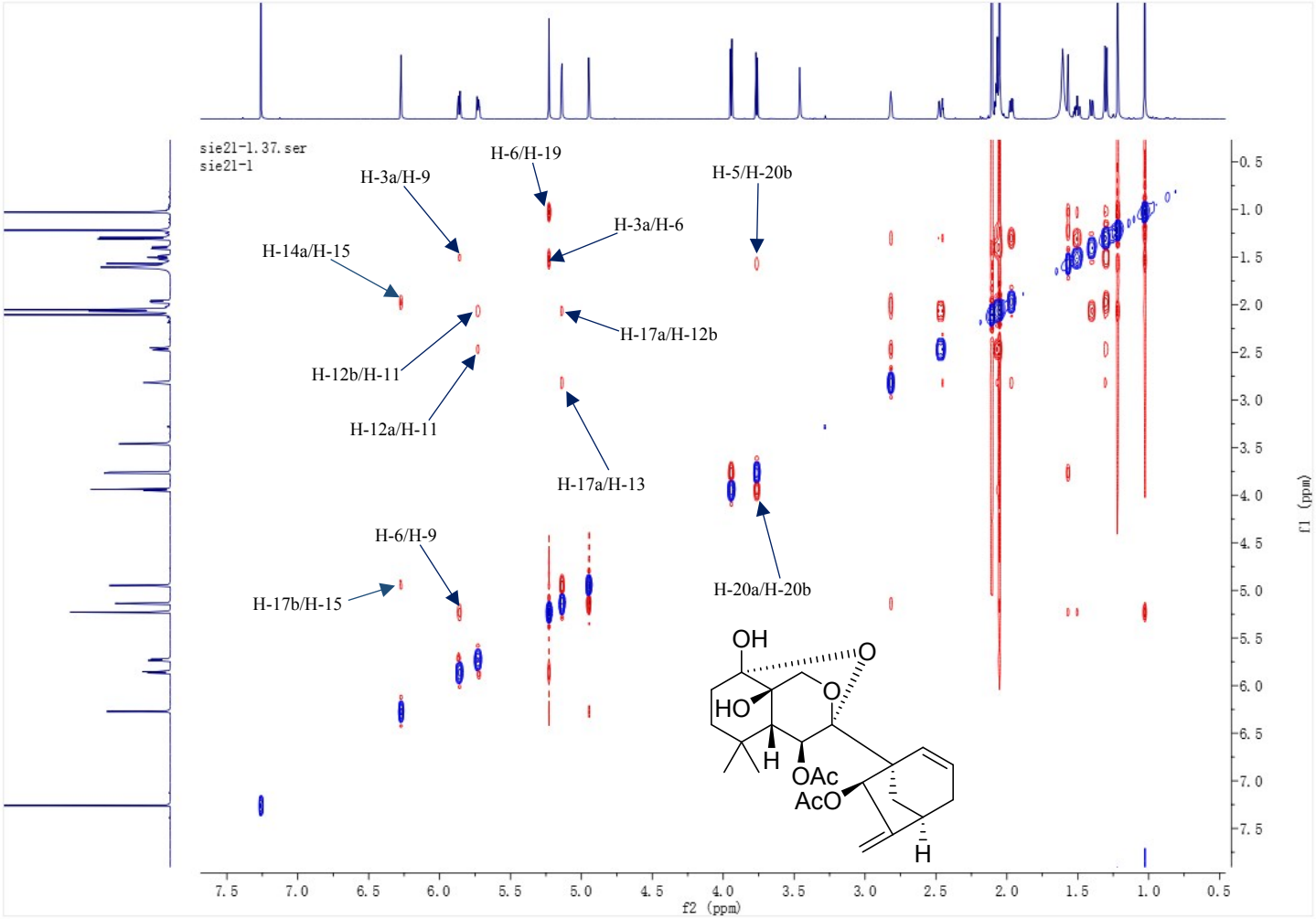
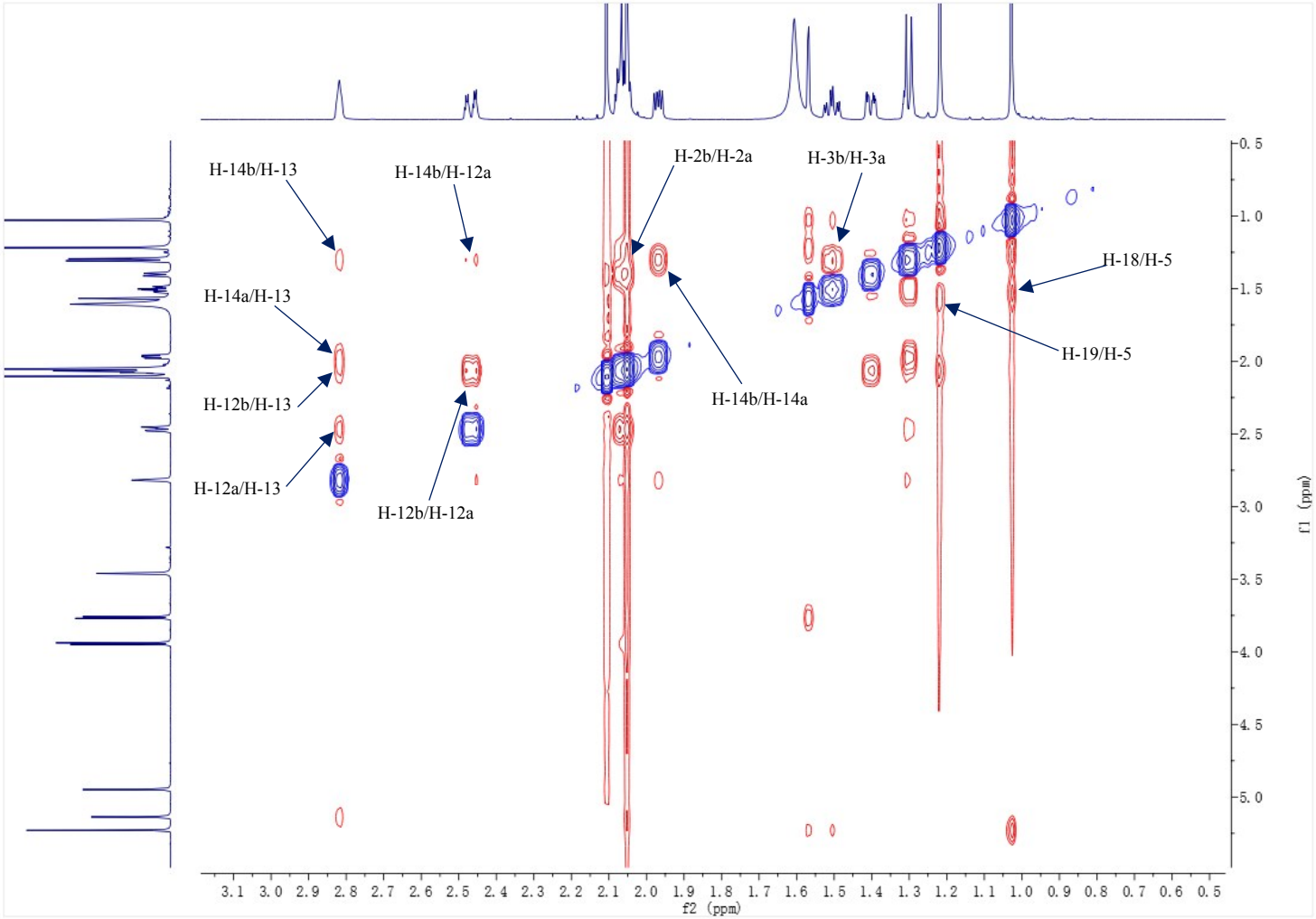


Figure S78 ROESY spectrum ($CDCl_3$, 800MHz) of maoeriocalysin D (**4**).


H-14b/H-13
H-14b/H-12a
H-2b/H-2a
H-3b/H-3a
H-18/H-5
H-14a/H-13
H-19/H-5
H-12b/H-13
H-14b/H-14a
H-12a/H-13
H-12b/H-12a
f2 (ppm)
f1 (ppm)

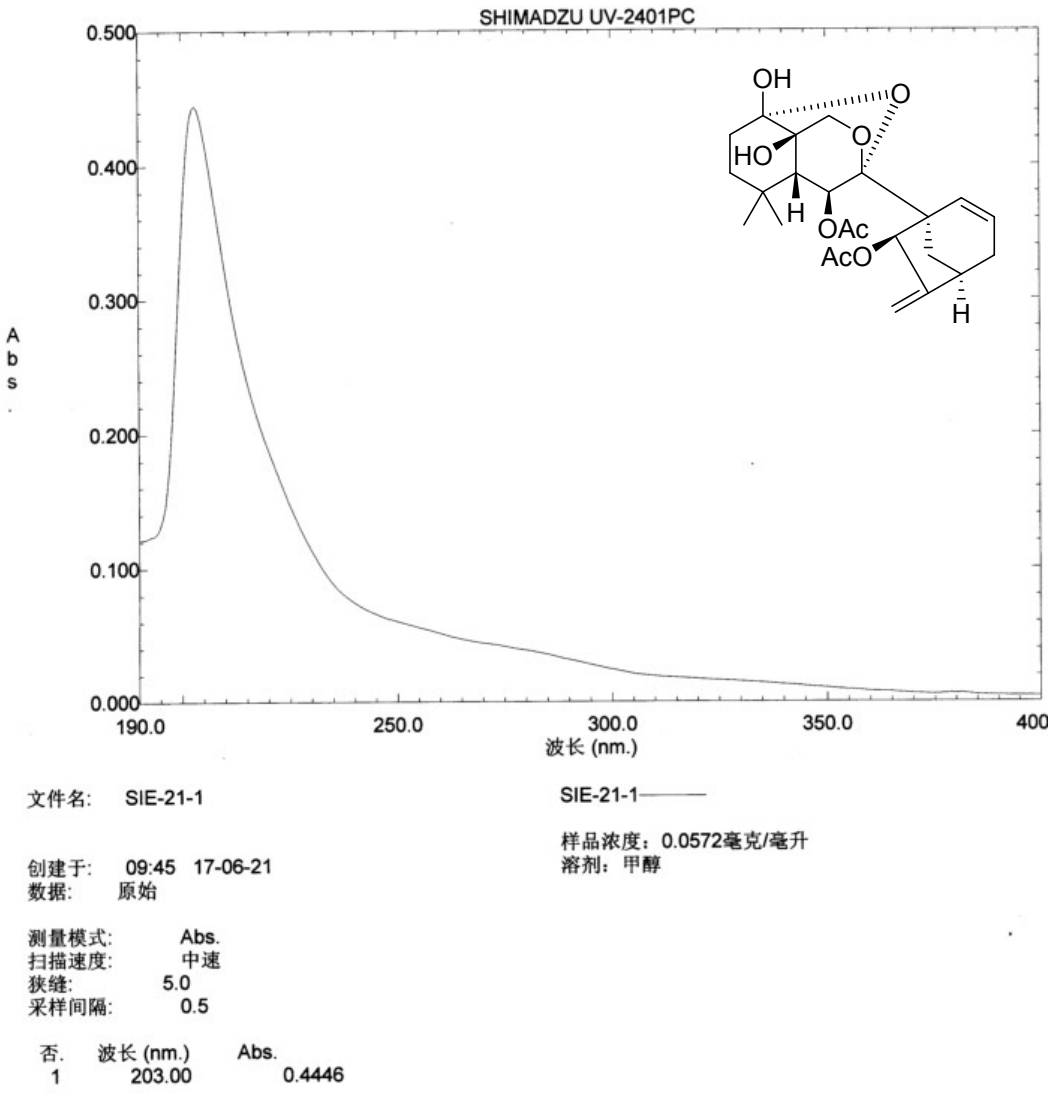


Figure S79 UV spectrum of maoeriocalysin D (**4**).

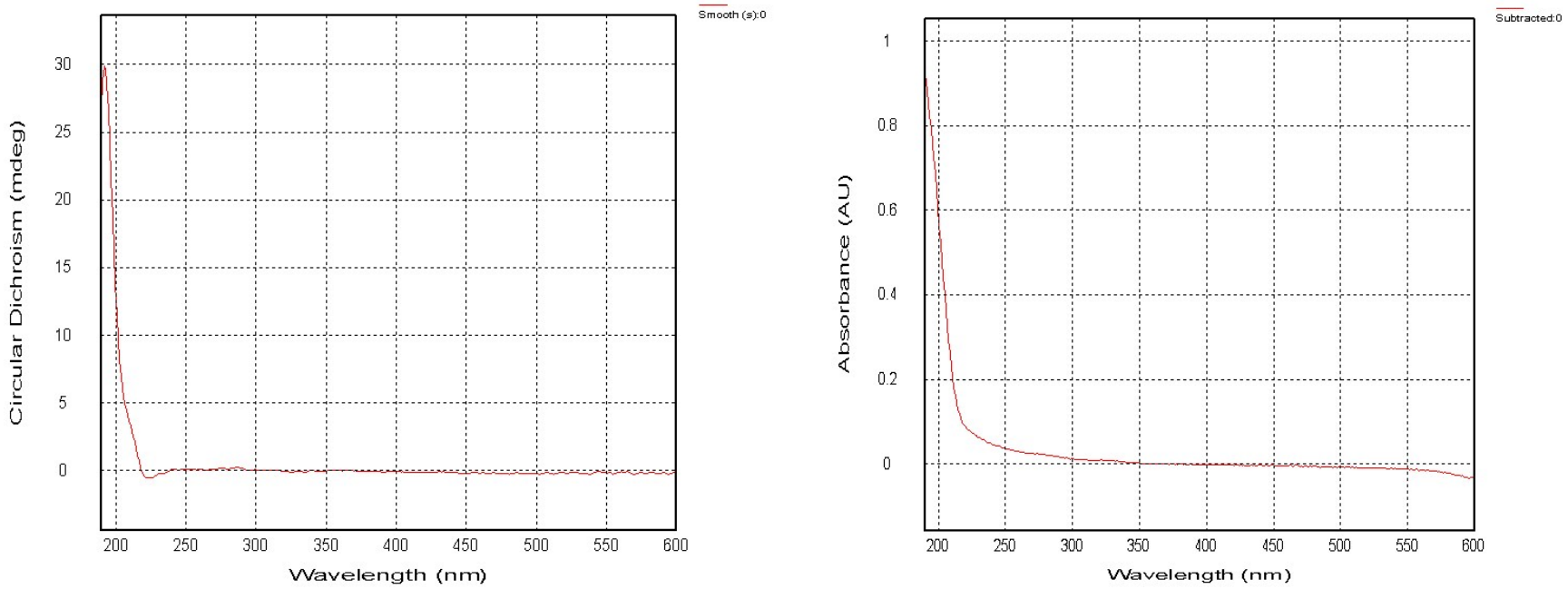


Figure S80 CD spectrum of maoeriocalysin D (**4**).

Optical rotation measurement

Model : P-1020 (A060460638)

No.	Sample	Mode	Data	Monitor Blank	Temp. Cell Temp Point	Date Comment Sample Name	Light Filter Operator	Cycle Time Integ Time
No.1	28 (1/3)	Sp.Rot	66.5600	0.0832 0.0000	27.6 50.00 Cell	Thu Jun 21 14:43:22 2018 0.00250g/mL Acetonitrile SIE-21-1A	Na 589nm	2 sec 2 sec
No.2	28 (2/3)	Sp.Rot	67.0400	0.0838 0.0000	27.6 50.00 Cell	Thu Jun 21 14:43:28 2018 0.00250g/mL Acetonitrile SIE-21-1A	Na 589nm	2 sec 2 sec
No.3	28 (3/3)	Sp.Rot	67.4400	0.0843 0.0000	27.6 50.00 Cell	Thu Jun 21 14:43:33 2018 0.00250g/mL Acetonitrile SIE-21-1A	Na 589nm	2 sec 2 sec

+67.013°

Figure S81 OR spectrum of maoeriocalysin D (**4**).