Chemical Epigenetic Modification Uncovers New Isocoumarins from the Endophyte *Dothideomycetes* sp. BMC-101

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[†] These authors contributed equally to this work.

List of Supplementary Information

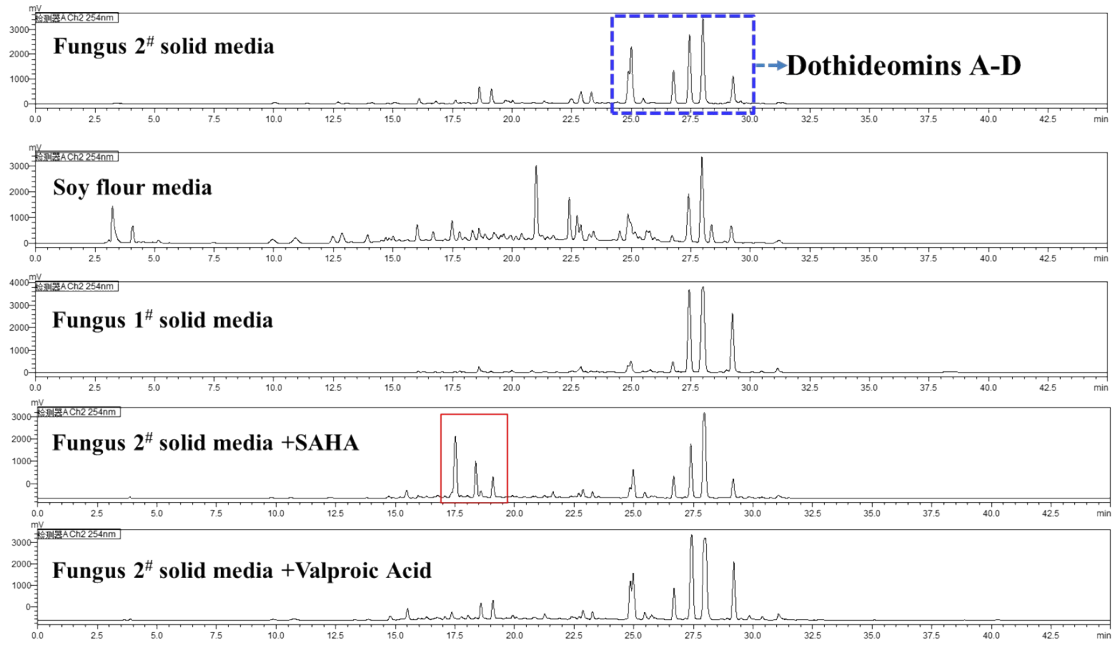


Figure S1. HPLC analysis of the crude extracts of the fungus *Dothideomycetes* sp. BMC-101 using the OSMAC strategy.

Chiral separations of **1a/1b** and **2a/2b**

Chromatographic conditions:

Compounds **1a/1b**:

(1) Column: Daicel Chiralpak OD-H column (4.6 × 250 mm, 5 μm)

(2) Mobile phase: n-hexane -2-propanol (90:10, *v/v*)

(3) Wavelength: 201/254 nm

(4) Flow rate: 1.0 mL/min

Compounds **2a/2b**:

(1) Column: Daicel Chiralpak AD-H column (4.6 × 250 mm, 5 μm)

(2) Mobile phase: n-hexane -2-propanol (96:4, *v/v*)

(3) Wavelength: 201/254 nm

(4) Flow rate: 1.0 mL/min

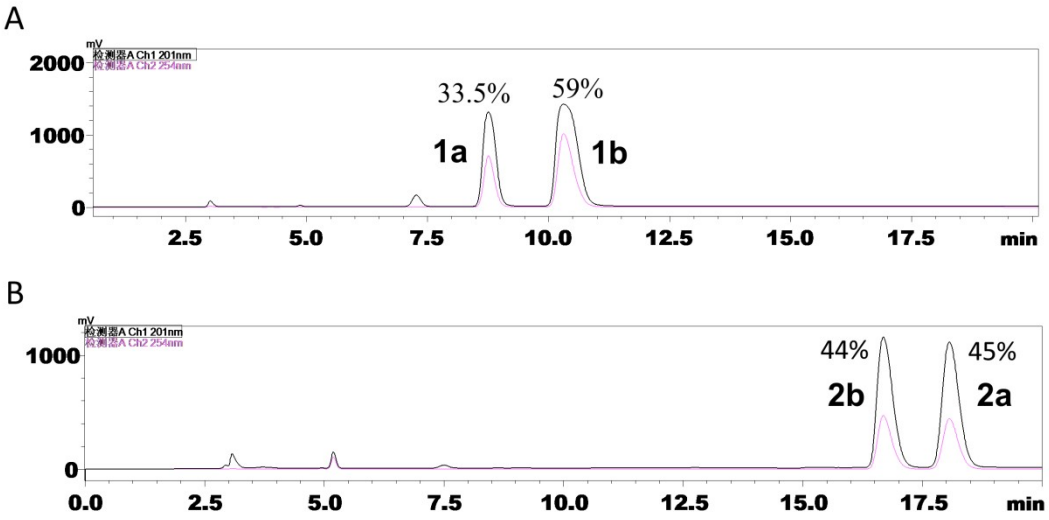


Figure S2. Chiral separations of compounds **1** and **2**.

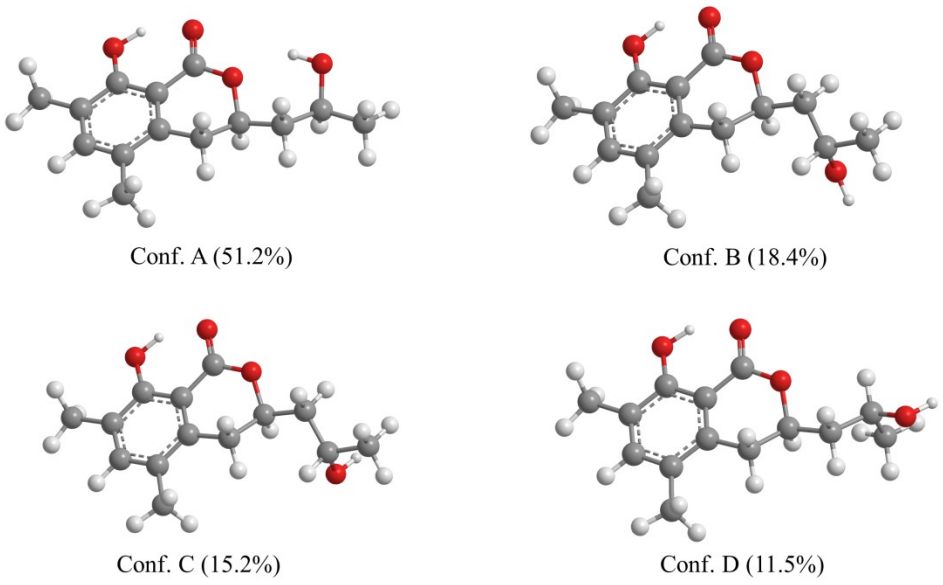


Figure S3. Conformations of lowest-energy conformers (>5% population) of (3R, 2′S)-1 (**1a**).

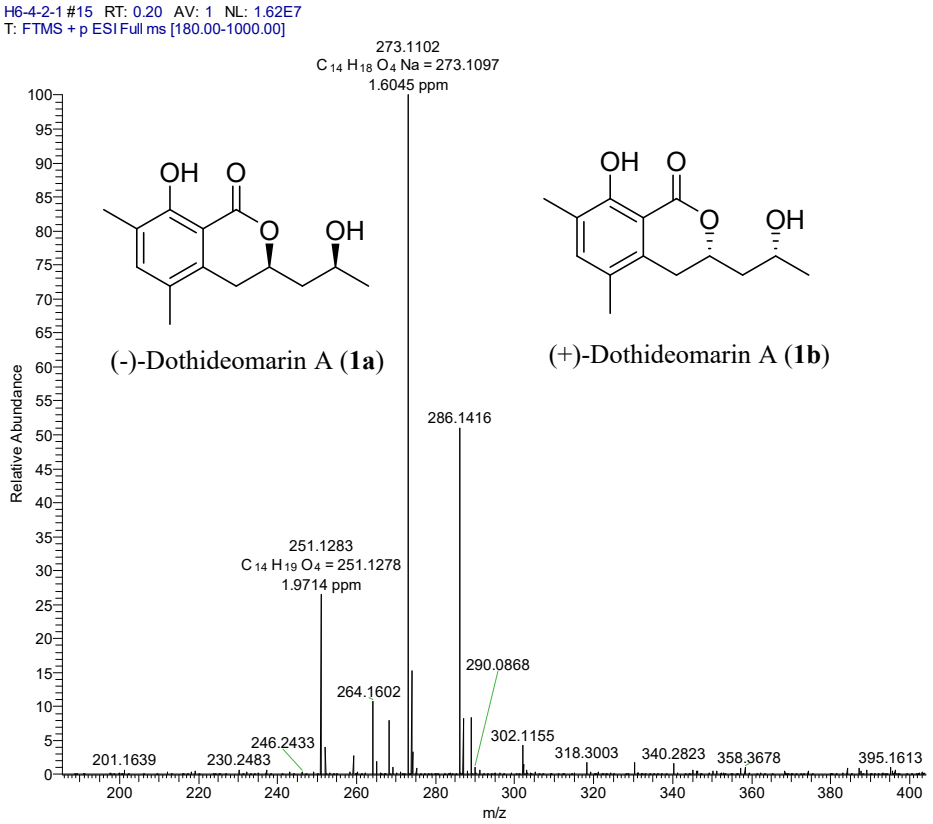


Figure S4. HRESIMS spectrum of (±)-deothideomarin A (**1**)

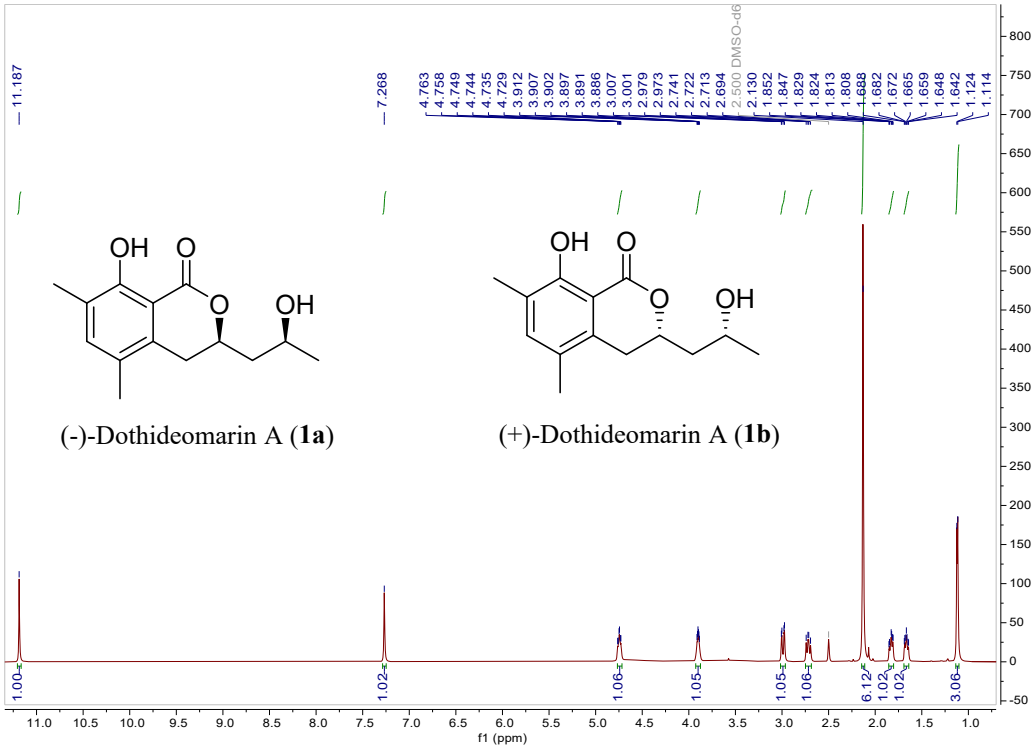
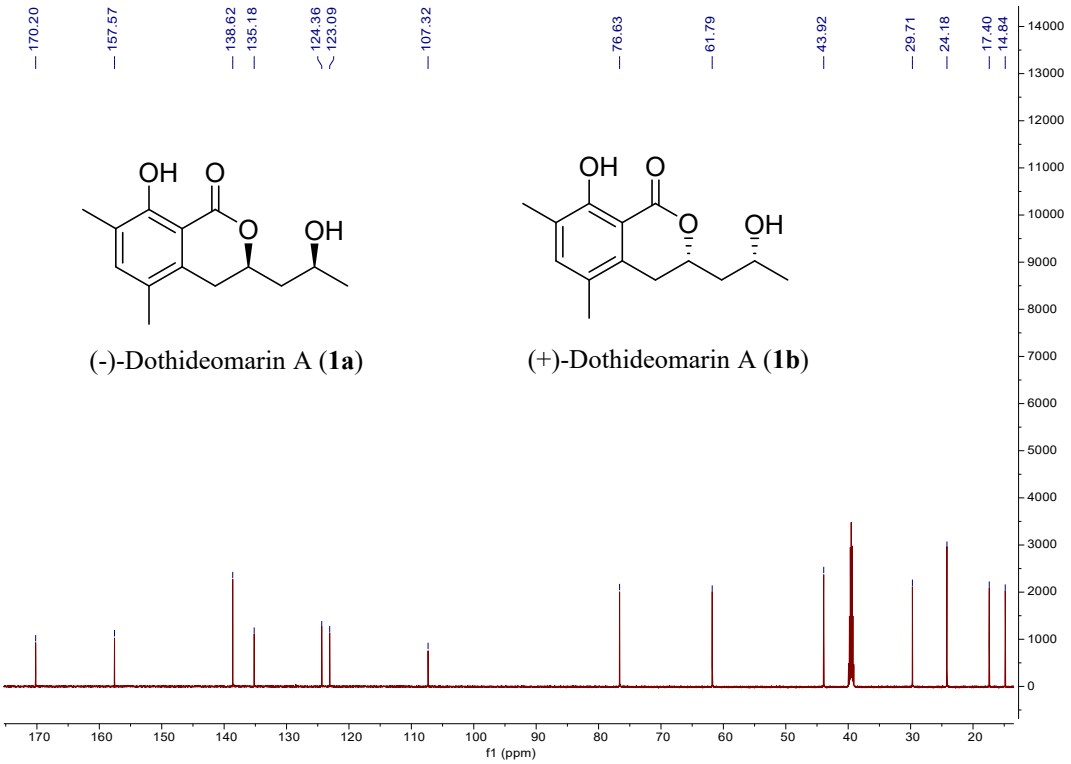


Figure S5. 1H NMR (600 MHz, DMSO-d_6) spectrum of (±)-deothideomarin A **(1)**



(-)-Dothideomarin A (**1a**) (+)-Dothideomarin A (**1b**)

Figure S6. ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of (±)-deothideomarin A (**1**)

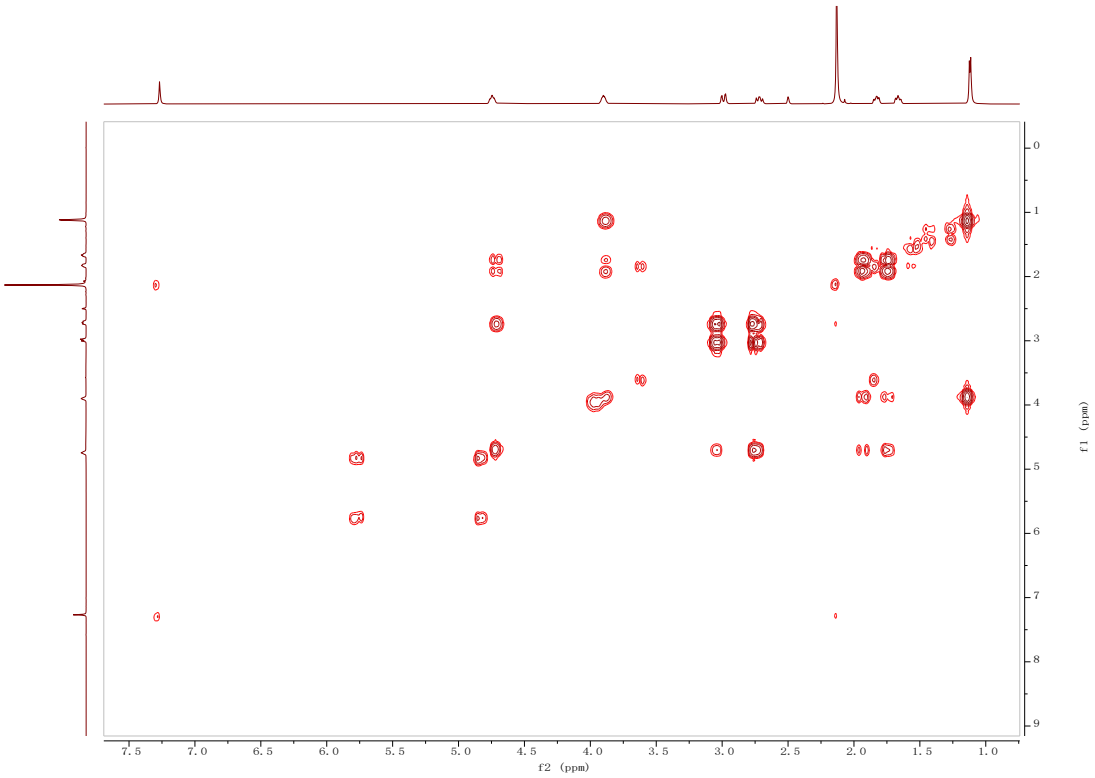


Figure S7. ^{1}H-^{1}H COSY spectrum of (±)-deothideomarin A (**1**)

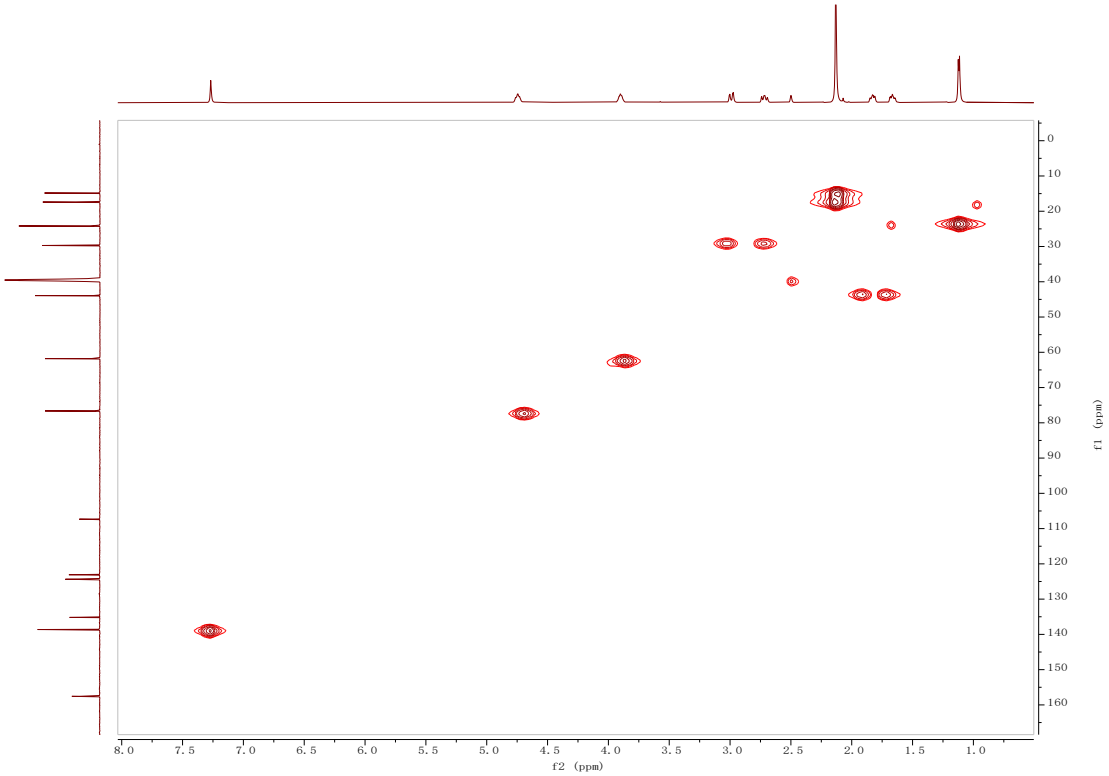


Figure S8. HSQC spectrum of (±)-deothideomarin A (**1**)

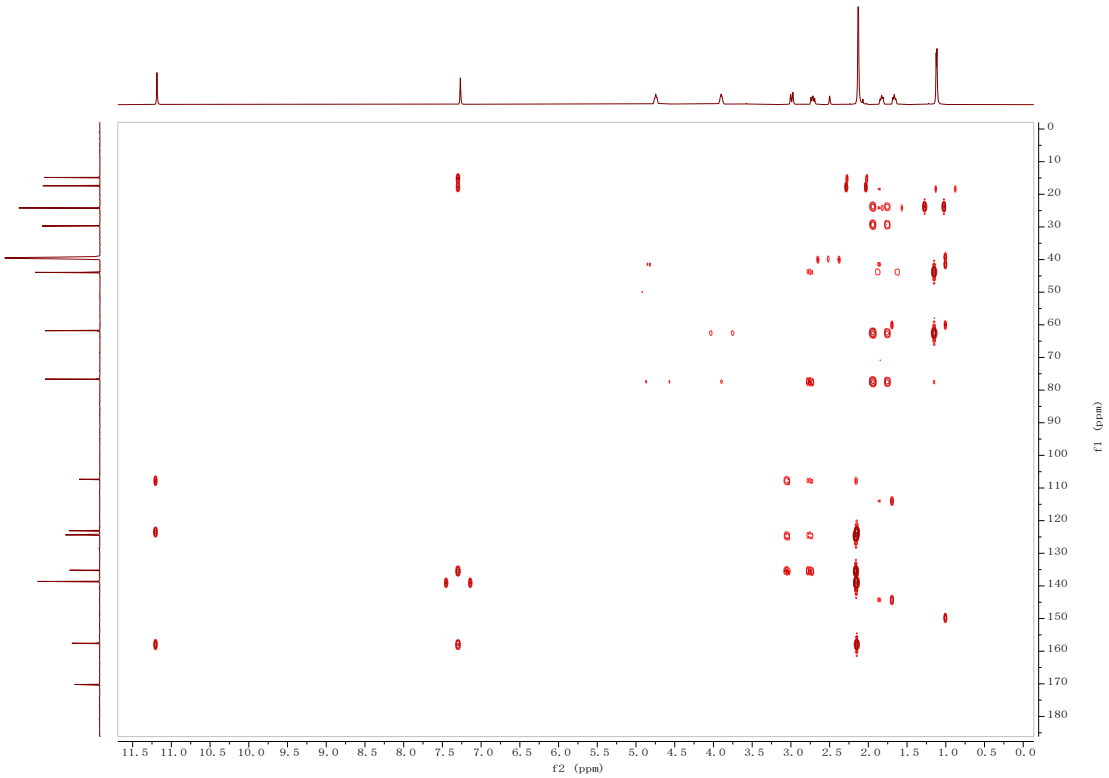


Figure S9. HMBC spectrum of (±)-deothideomarin A (**1**)

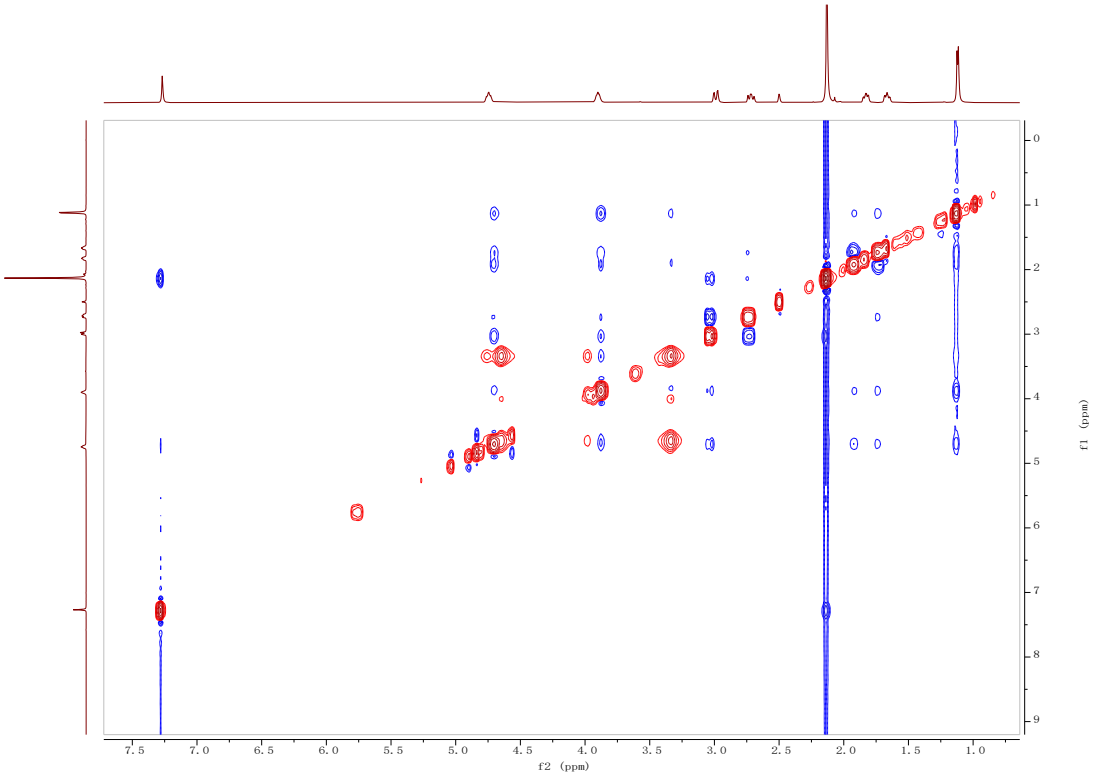


Figure S10. NOESY spectrum of (±)-deothideomarin A (**1**)

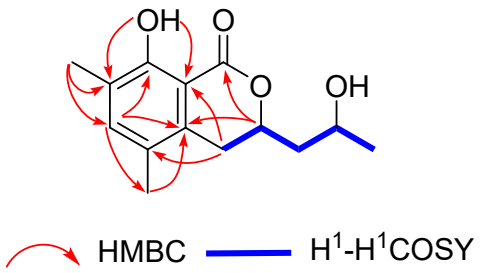


Figure S11. Key HMBC, COSY, correlations of (±)-deothideomarin A (**1**)

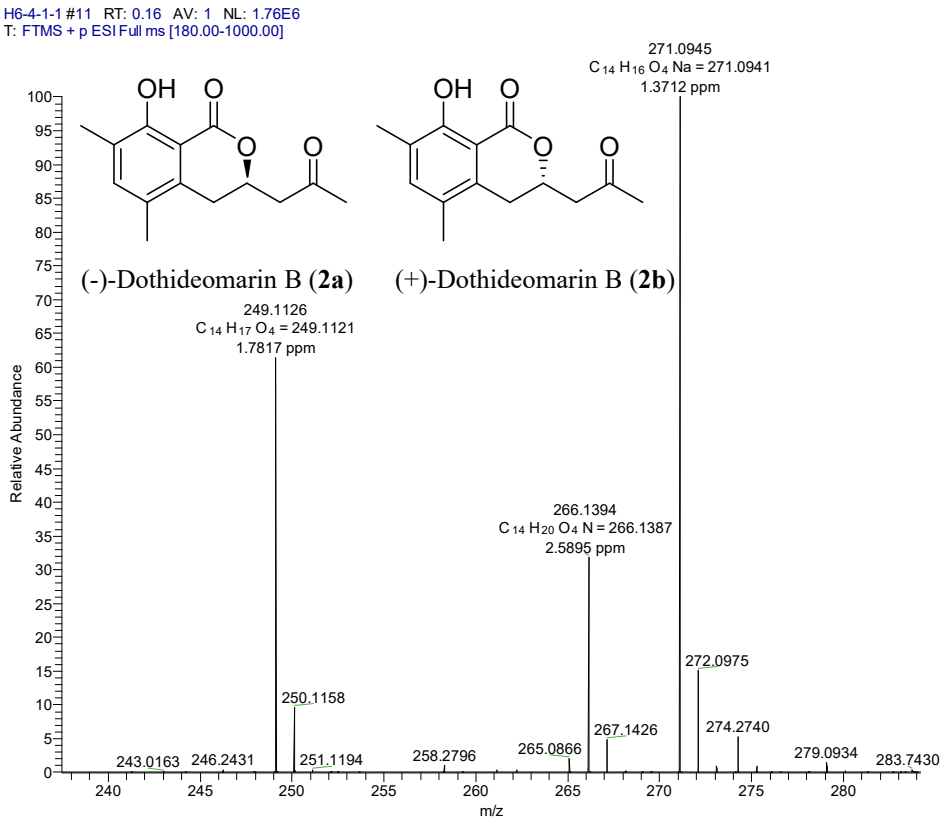


Figure S12. HRESIMS spectrum of (±)-deothideomarin B (**2**)

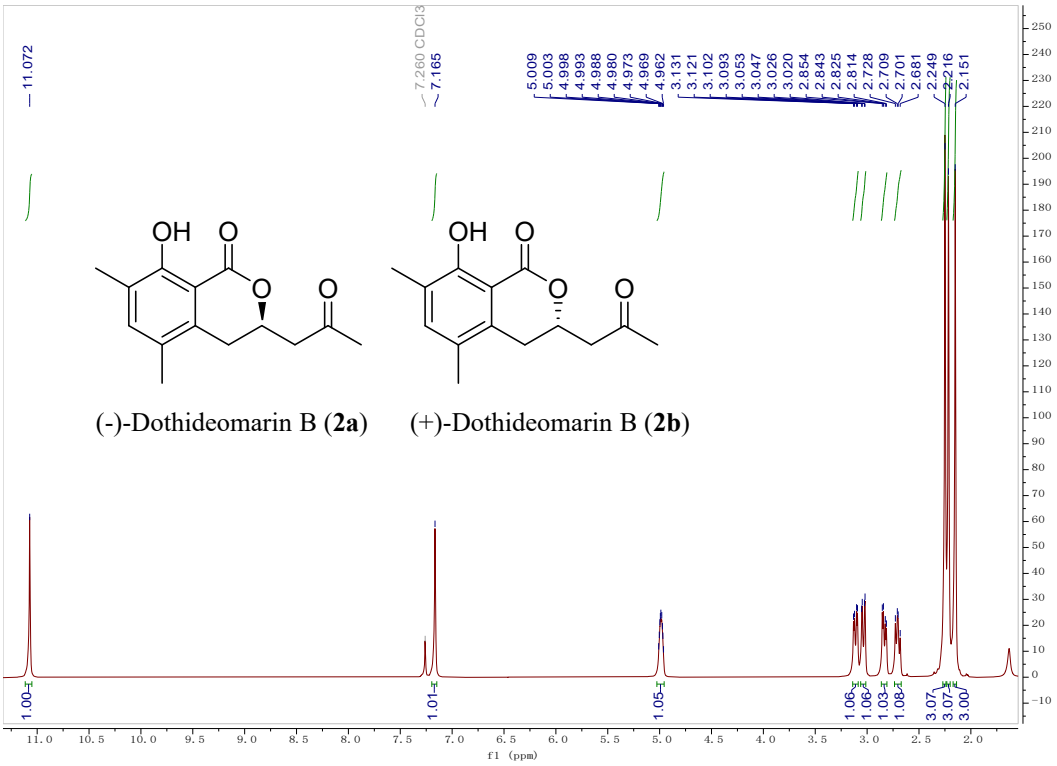


Figure S13. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (±)-deothideomarin B (**2**)

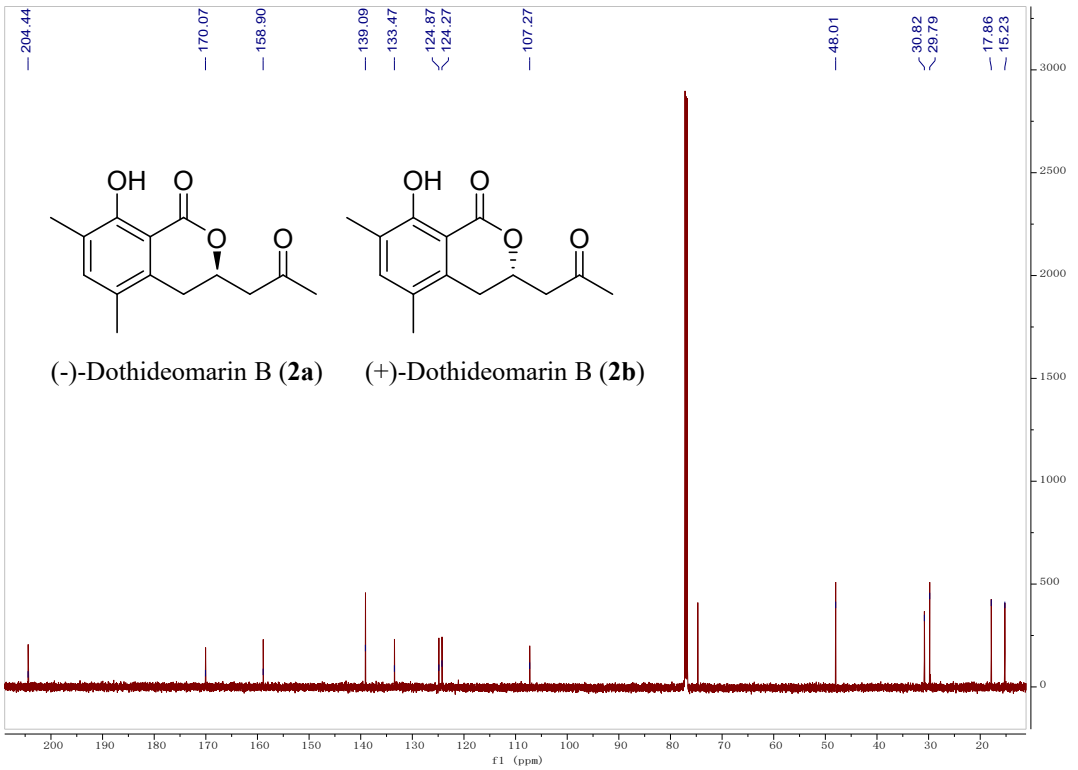


Figure S14. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of (±)-deothideomarin B (**2**)

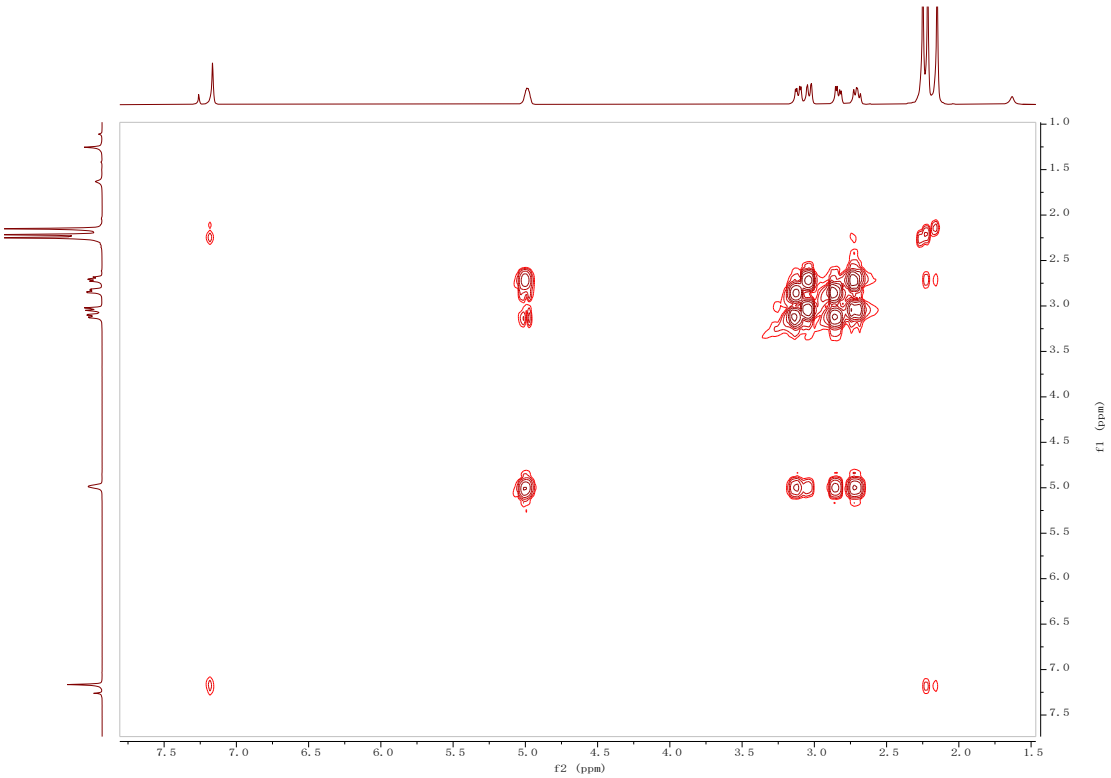


Figure S15. ^{1}H-^{1}H COSY spectrum of (±)-deothideomarin B (**2**)

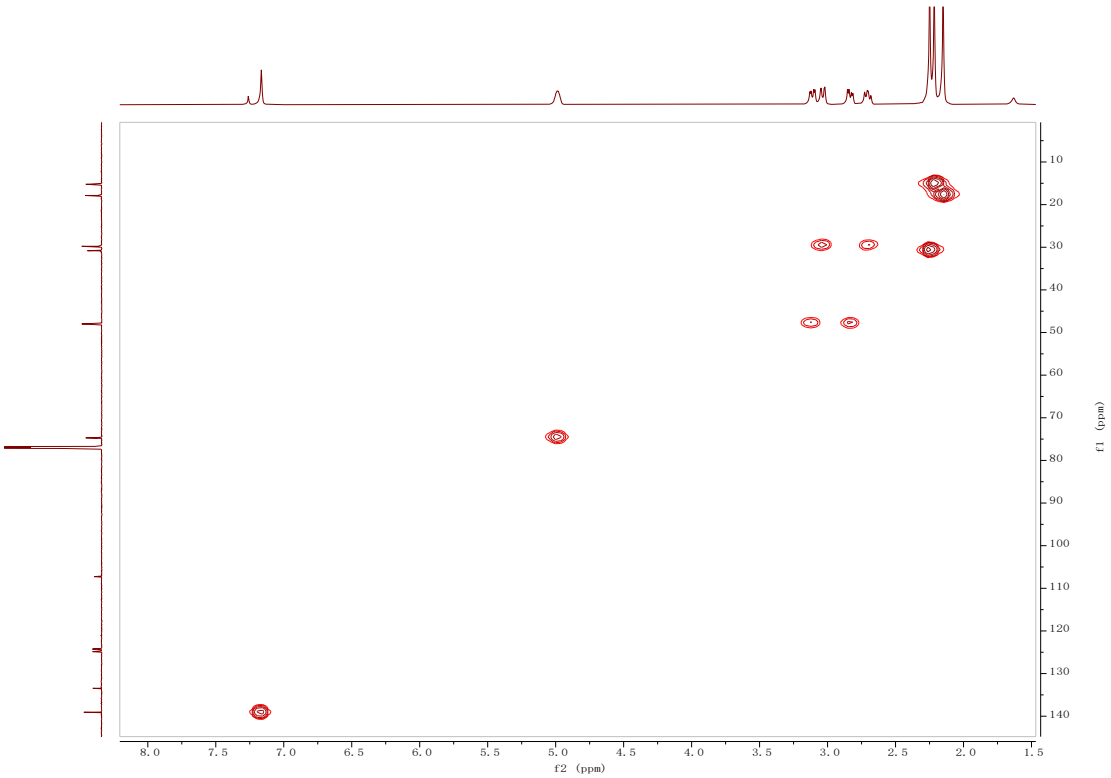


Figure S16. HSQC spectrum of (±)-deothideomarin B (**2**)

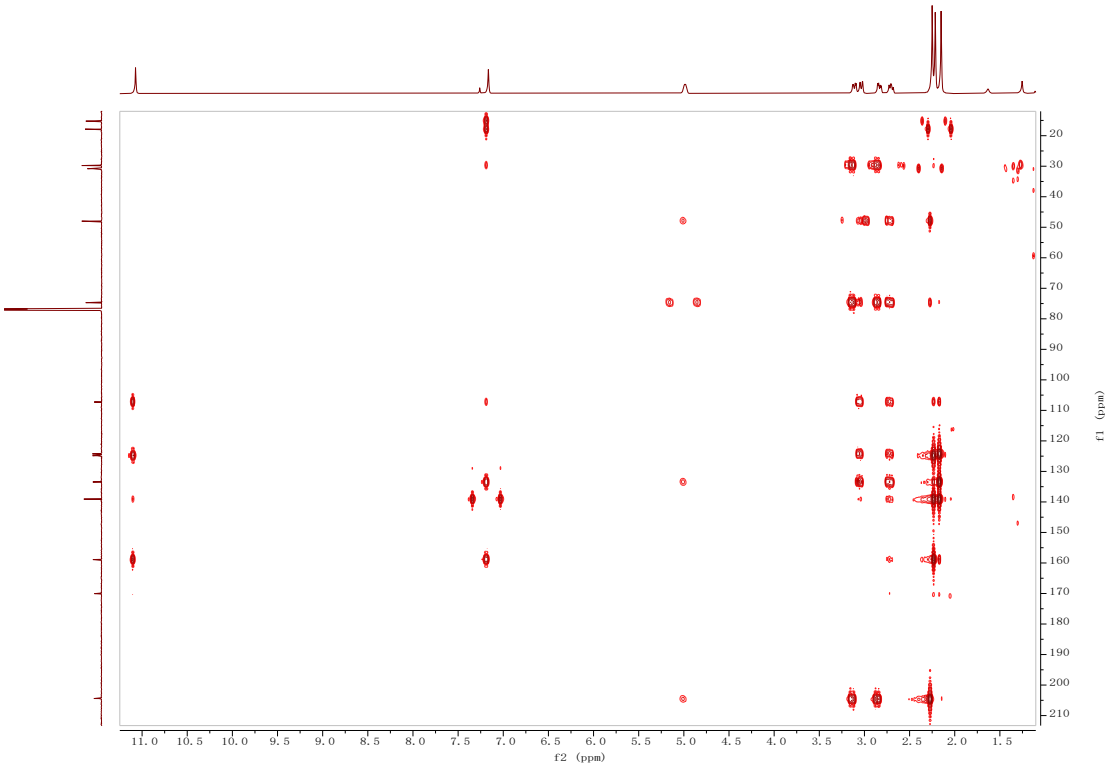


Figure S17. HMBC spectrum of (±)-deothideomarin B (**2**)

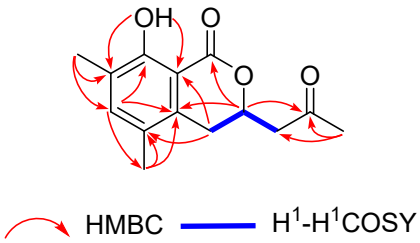


Figure S18. Key HMBC, COSY, correlations of (±)-deothideomarin B (**2**)

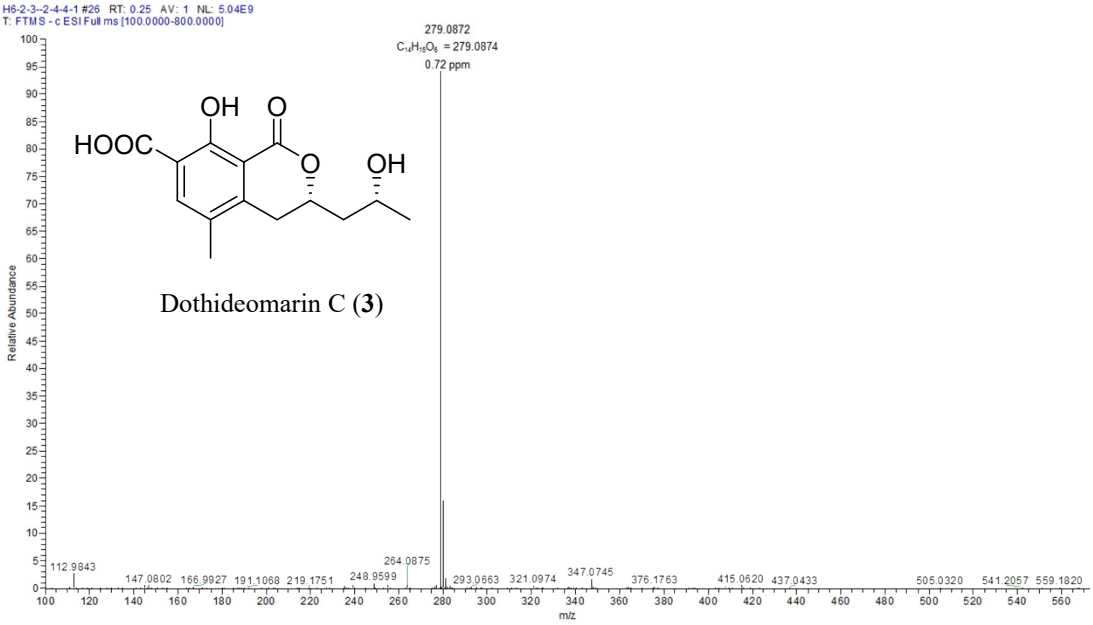


Figure S19. HRESIMS spectrum of deothideomarin C (**3**)

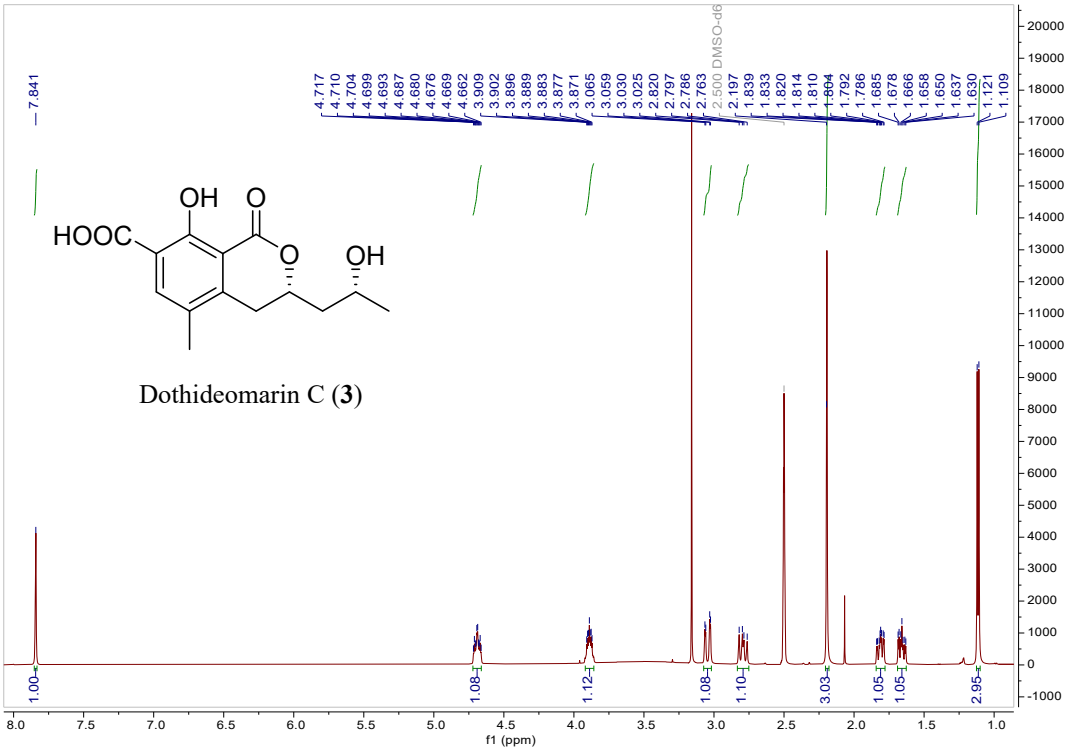


Figure S20. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of deothideomarin C (**3**)

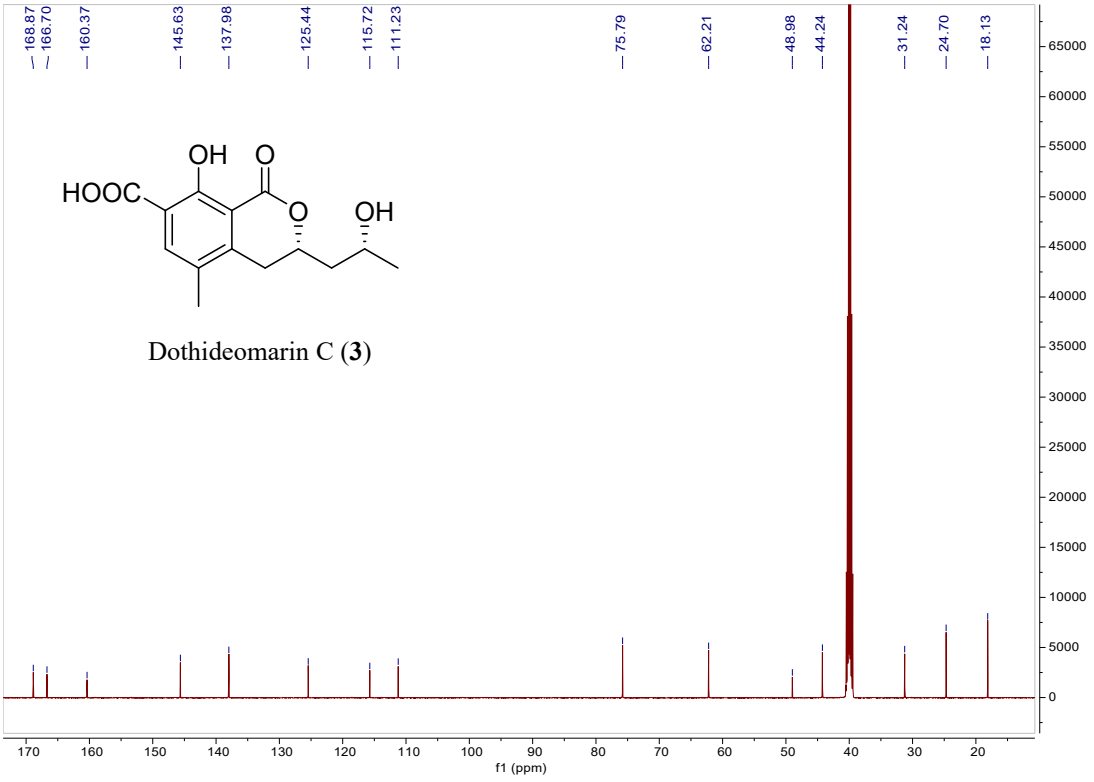


Figure S21. ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of deothideomarin C (**3**)

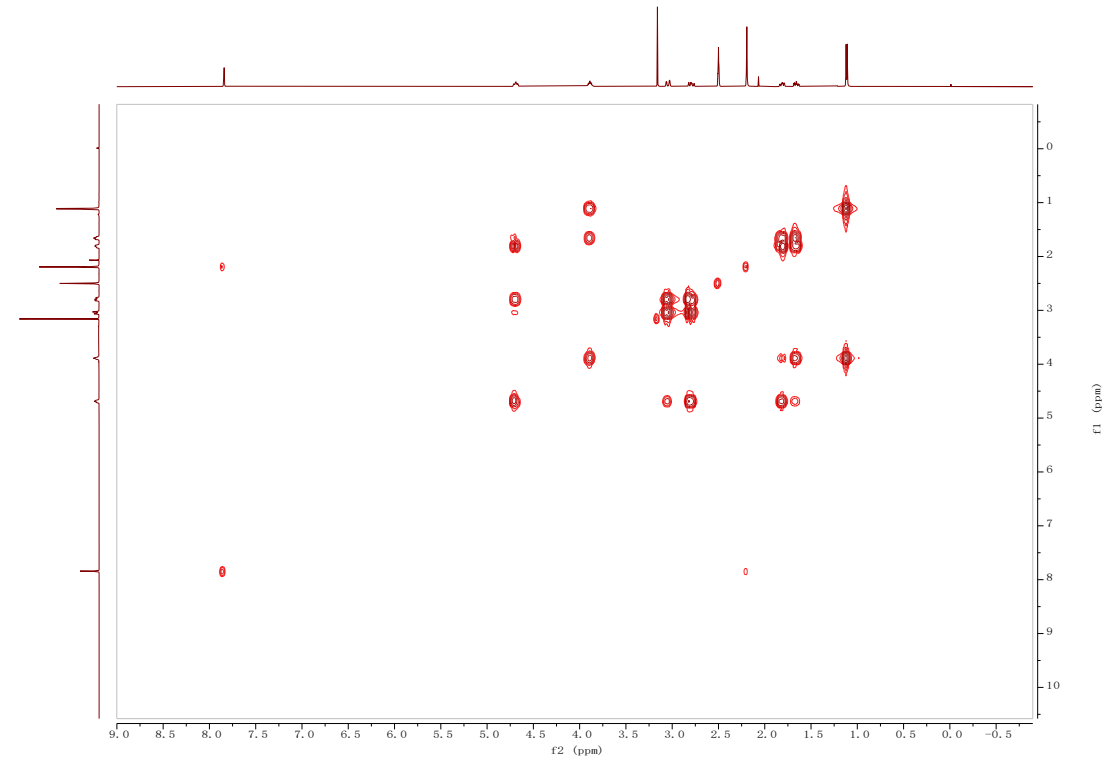


Figure S22. ^{1}H-^{1}H COSY spectrum of deothideomarin C (**3**)

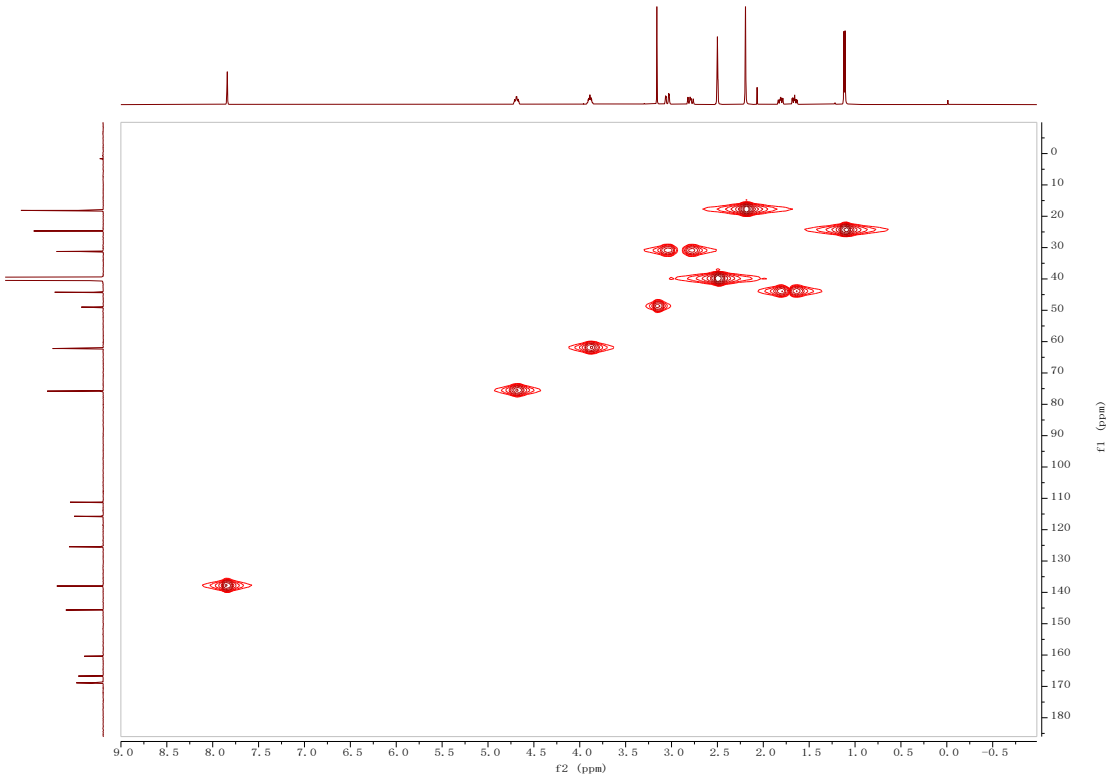


Figure S23. HSQC spectrum of deothideomarin C (**3**)

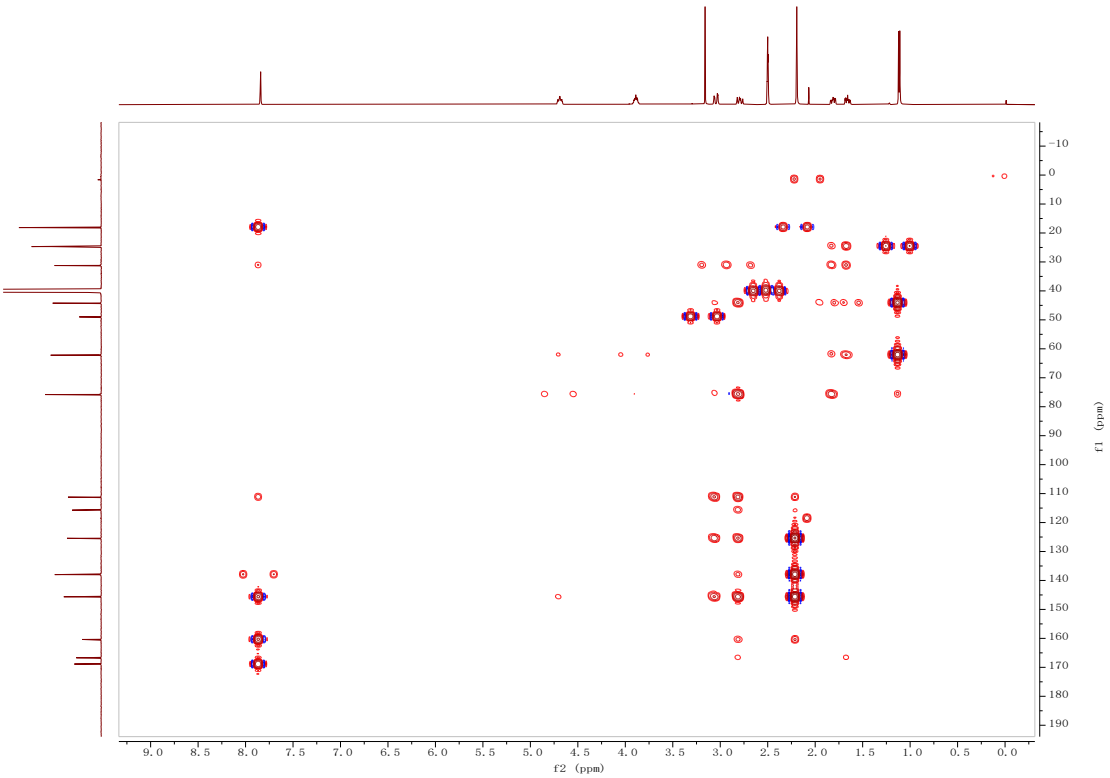


Figure S24. HMBC spectrum of deothideomarin C (**3**)

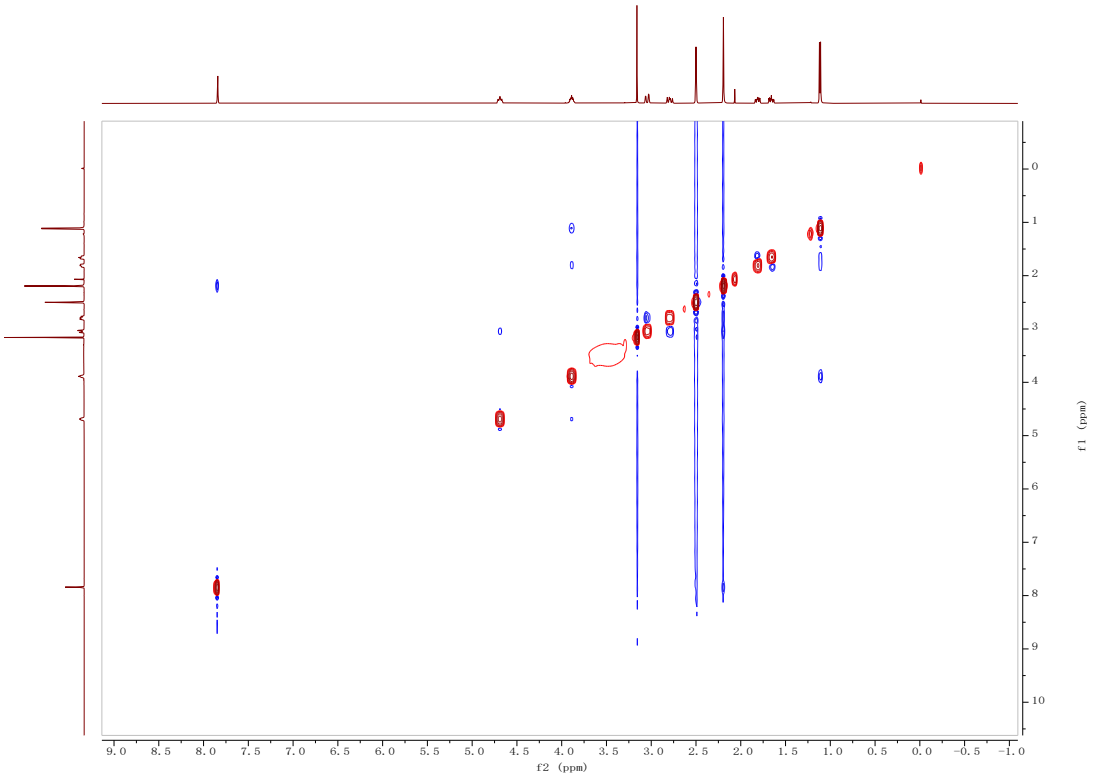


Figure S25. NOESY spectrum of deothideomarin C (**3**)

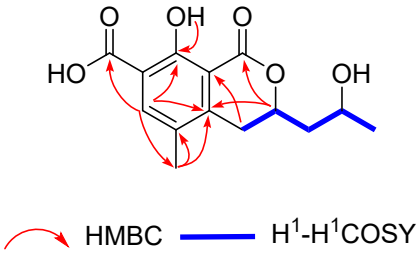


Figure S26. Key HMBC, COSY, correlations of (±)-deothideomarin C (**3**)

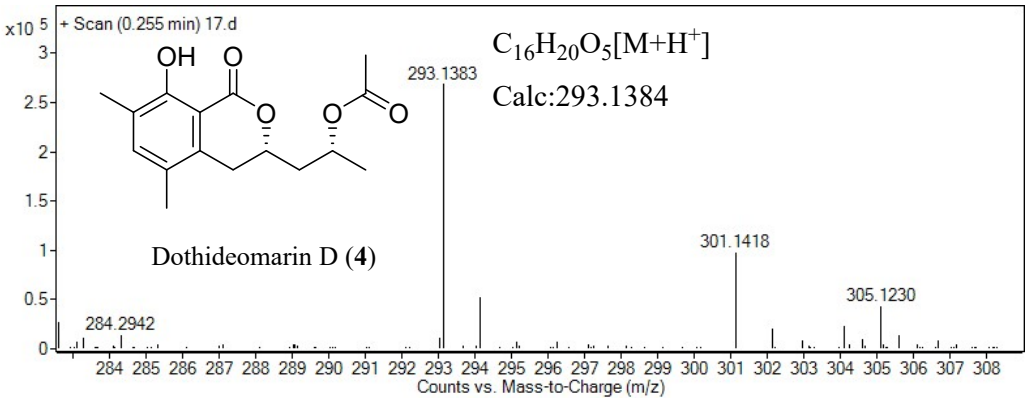


Figure S27. HRESIMS spectrum of deothideomarin D (**4**)

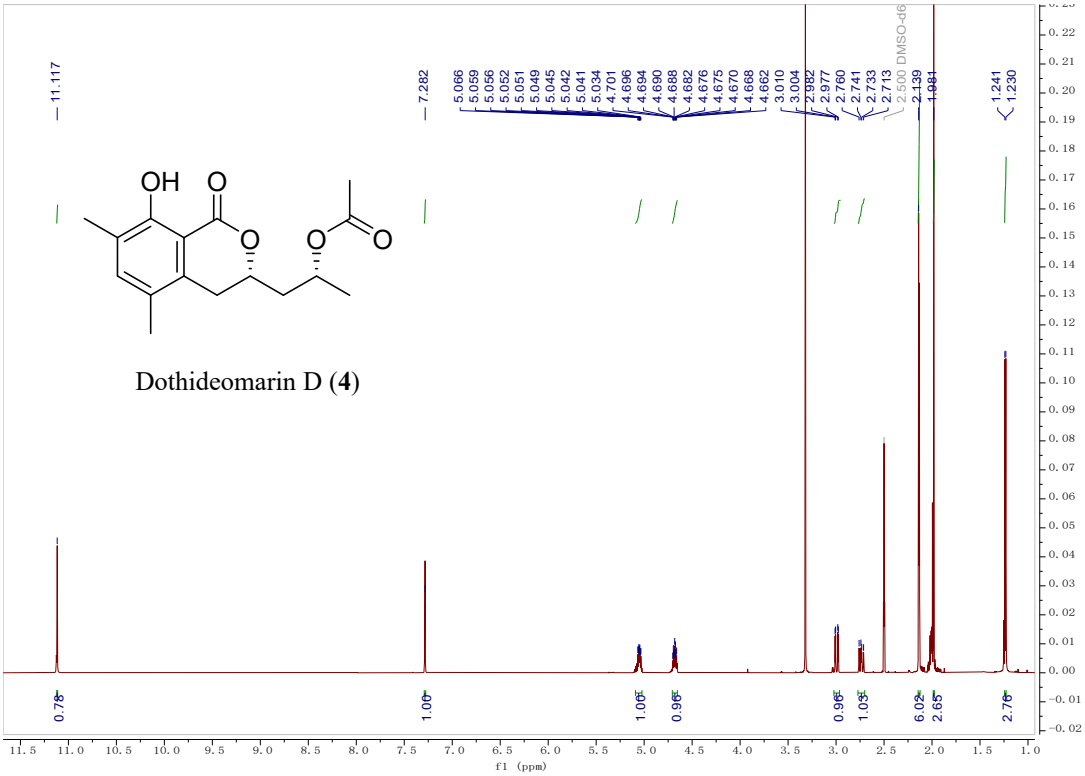


Figure S28. ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of deothideomarin D (**4**)

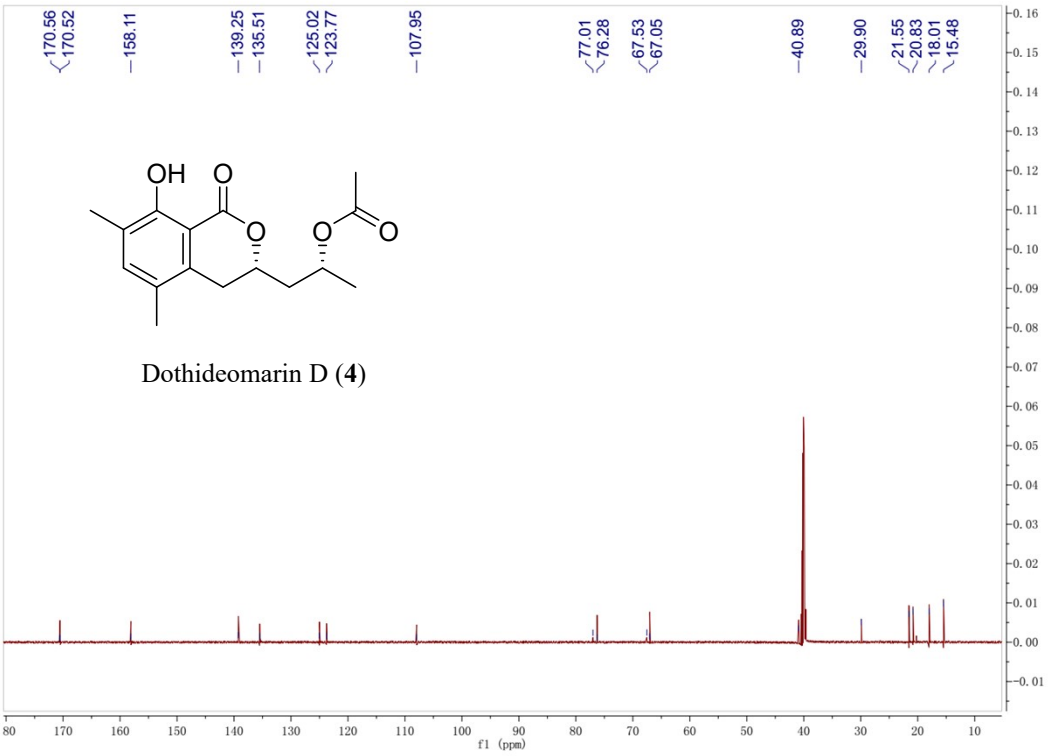


Figure S29. ^{13}C NMR (150 MHz, DMSO-d_6) spectrum of deothideomarin D (**4**)

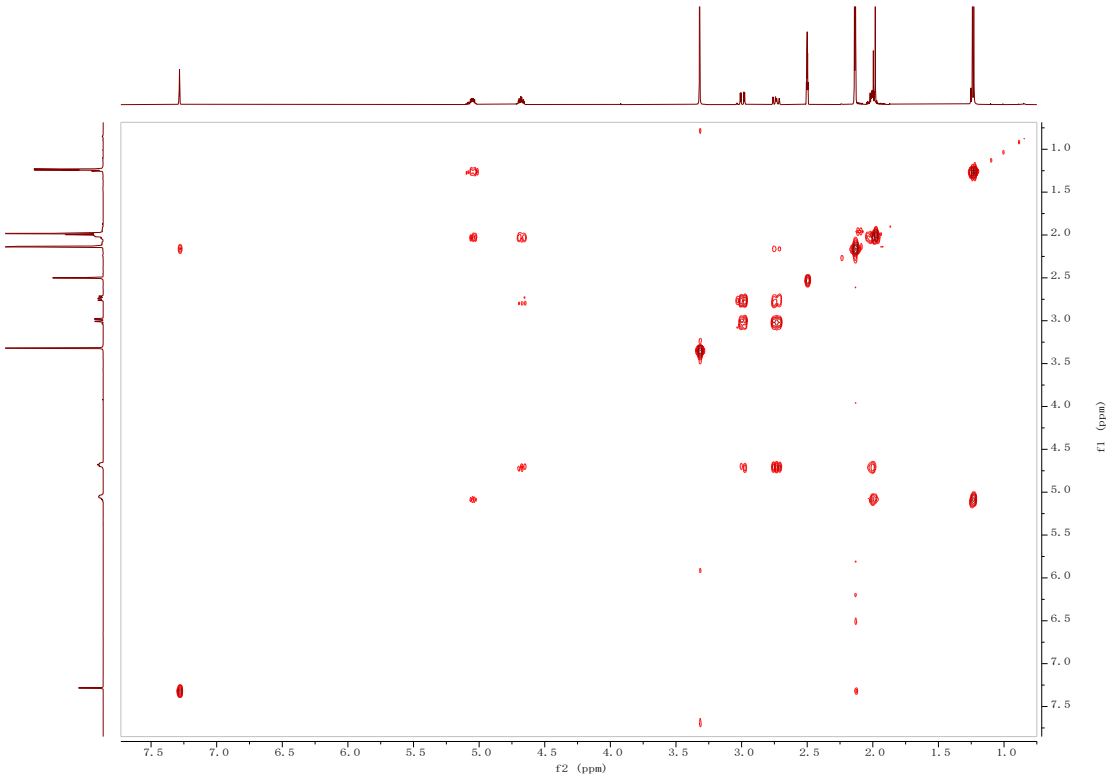


Figure S30. ^{1}H-^{1}H COSY spectrum of deothideomarin D (**4**)

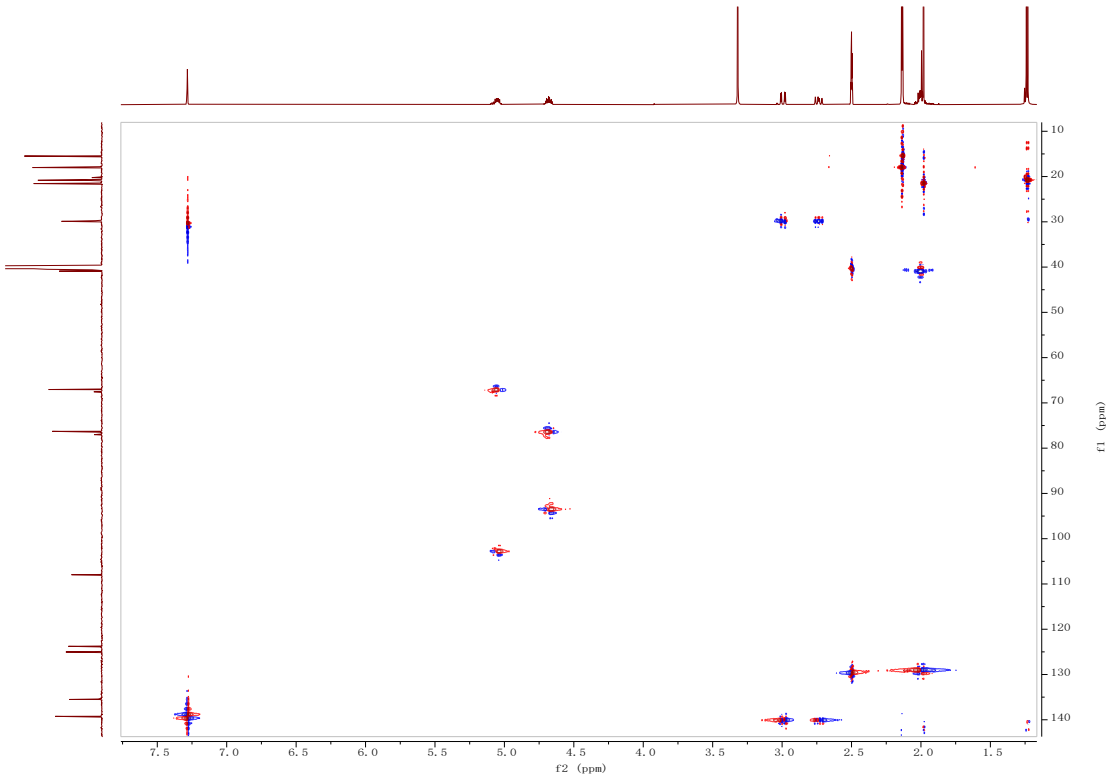


Figure S31. HSQC spectrum of deothideomarin D (**4**)

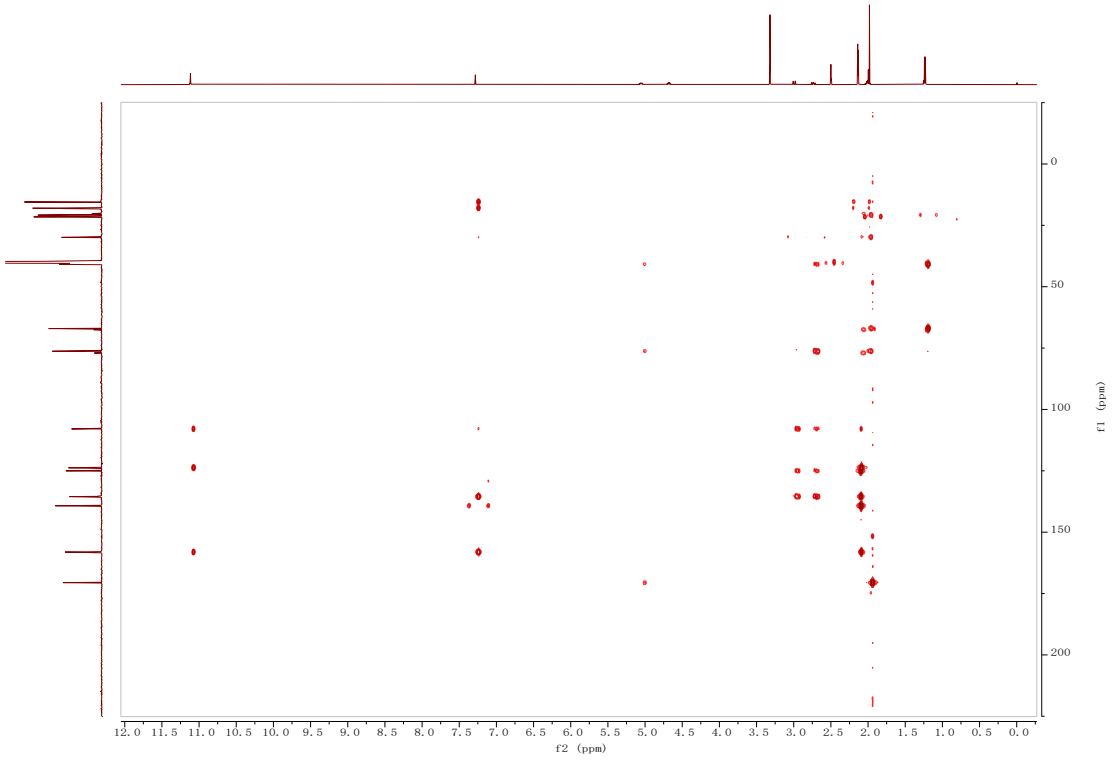


Figure S32. HMBC spectrum of deothideomarin D (**4**)

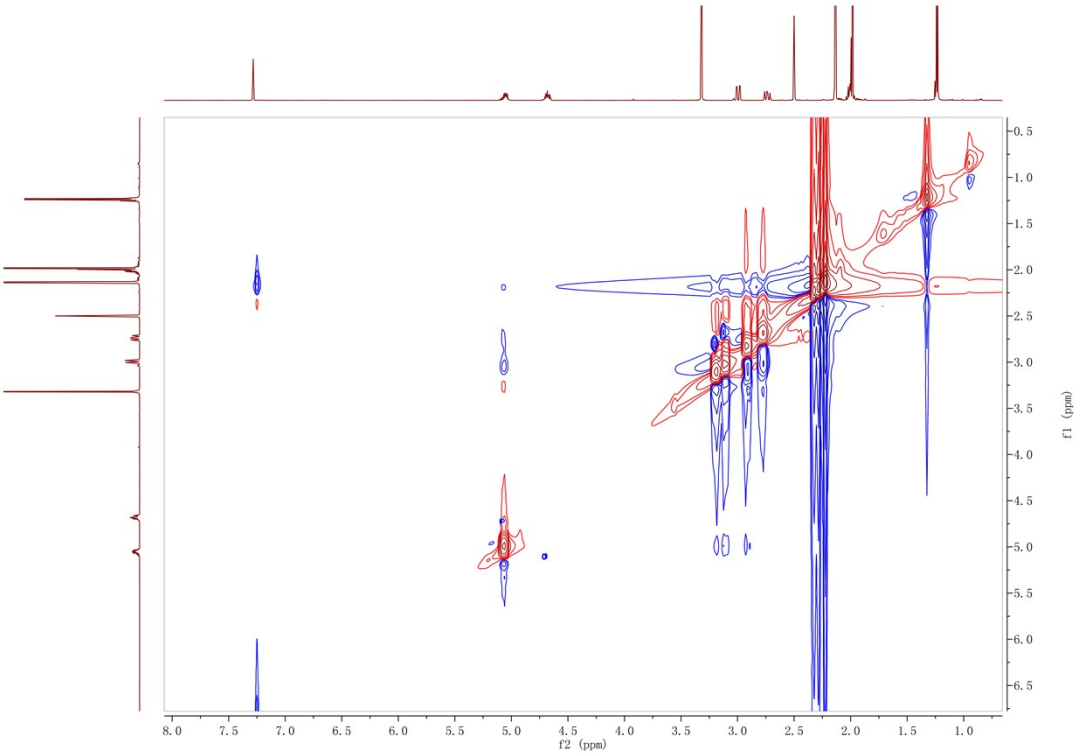


Figure S33. NOESY spectrum of deothideomarin D (**4**)

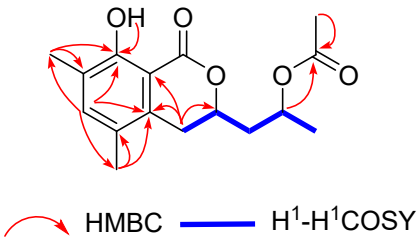
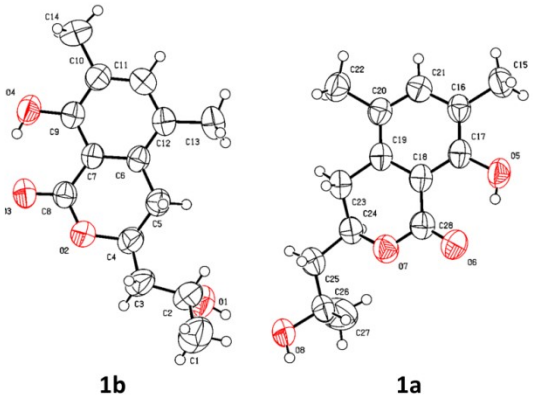


Figure S34. Key HMBC, COSY, correlations of (±)-deothideomarin D (**4**)



CDCC: 2443606

Table S1. Crystal data and structure refinement for **1**

Empirical formula	$C_{14}H_{18}O_4$
Formula weight	250.28
Temperature/K	303.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.5056(3)
b/Å	39.6740(13)
c/Å	7.9424(3)
α/°	90
β/°	94.882(2)
γ/°	90
Volume/Å^3	2670.45(16)
Z	8
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	0.745
F(000)	1072.0
Crystal size/mm^3	0.2 × 0.18 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.454 to 136.784
Index ranges	$-8 \le h \le 9$, $-45 \le k \le 47$, $-9 \le l \le 9$
Reflections collected	19445
Independent reflections	4745 [R_{int} = 0.0389, R_{sigma} = 0.0381]
Data/restraints/parameters	4745/0/335
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0674, wR_2 = 0.1850
Final R indexes [all data]	R_1 = 0.0893, wR_2 = 0.2007
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21

Table S2. Cartesian coordinates of the low-energy reoptimized conformer of(3*R*, 2′*S*)-1 (**1a**) calculated at B3LYP/6 31 + G(d) level of theory with PCM solvent model for MeOH.

Conformer A		Standard Orientation (Ångstroms)		
number	Atom	X	Y	Z
1	C	-3.46624	-0.14901	0.19744
2	C	-3.24131	1.2251	0.12954
3	C	-1.97216	1.80342	-0.0622
4	C	-0.87118	0.94928	-0.16976
5	C	-1.05625	-0.45391	-0.10137
6	C	-2.35446	-1.00002	0.06247
7	C	0.53151	1.46087	-0.4004
8	C	1.56249	0.52426	0.21031
9	O	1.33092	-0.84869	-0.26681
10	C	0.08638	-1.36157	-0.24861
11	O	-2.57934	-2.33558	0.09688
12	C	-4.84544	-0.72763	0.38985
13	C	-1.83099	3.30743	-0.15195
14	O	-0.02202	-2.58678	-0.38009
15	C	3.00679	0.88088	-0.12447
16	C	4.06876	-0.04926	0.48703
17	C	5.47032	0.53985	0.38003
18	O	4.10432	-1.32764	-0.17496
19	H	-4.09994	1.88732	0.22355
20	H	0.72328	1.56877	-1.4786
21	H	0.66315	2.45225	0.04348
22	H	1.43033	0.48542	1.29921
23	H	-1.7152	-2.78435	-0.08084
24	H	-5.12778	-1.37545	-0.44922
25	H	-5.59076	0.06902	0.47334
26	H	-4.89854	-1.3434	1.29617
27	H	-2.81068	3.79093	-0.08913
28	H	-1.21157	3.71062	0.65982
29	H	-1.36682	3.61853	-1.09608
30	H	3.14028	0.91437	-1.21391
31	H	3.1728	1.89724	0.25517
32	H	3.82894	-0.20823	1.55089
33	H	5.72249	0.75219	-0.66606
34	H	6.20831	-0.16601	0.77646
35	H	5.54302	1.47128	0.95218
36	H	3.18837	-1.64914	-0.24408

Conformer B		Standard Orientation (Ångstroms)		
number	Atom	X	Y	Z
1	C	-3.37665	0.53212	0.20594
2	C	-2.71918	1.74909	0.03023
3	C	-1.33997	1.86408	-0.22632
4	C	-0.58341	0.68989	-0.28677
5	C	-1.2124	-0.56592	-0.10893
6	C	-2.60952	-0.64354	0.1168
7	C	0.89881	0.69416	-0.57919
8	C	1.58949	-0.48879	0.08252
9	O	0.9058	-1.73743	-0.28127
10	C	-0.43071	-1.8058	-0.20939
11	O	-3.2553	-1.82713	0.25402
12	C	-4.86011	0.45195	0.46497
13	C	-0.71882	3.22844	-0.43314
14	O	-0.94673	-2.93188	-0.25398
15	C	3.04668	-0.70298	-0.31809
16	C	3.99297	0.41821	0.11621
17	C	5.43363	0.13902	-0.31104
18	O	3.88255	0.52417	1.54999
19	H	-3.31055	2.66113	0.08805
20	H	1.07129	0.665	-1.66612
21	H	1.35871	1.61605	-0.2124
22	H	1.50857	-0.40481	1.17127
23	H	-2.58894	-2.5424	0.09249
24	H	-5.37202	-0.12343	-0.3163
25	H	-5.30148	1.45259	0.49814
26	H	-5.07407	-0.04893	1.41728
27	H	-1.48364	4.01016	-0.39389
28	H	0.0291	3.45997	0.33651
29	H	-0.21498	3.30517	-1.40474
30	H	3.39028	-1.64544	0.12672
31	H	3.10658	-0.81354	-1.40787
32	H	3.6695	1.36904	-0.33208
33	H	5.78801	-0.80619	0.1168
34	H	6.09951	0.94327	0.02461
35	H	5.50735	0.07796	-1.40334
36	H	4.46142	1.24299	1.85181

Conformer C		Standard Orientation (Ångstroms)		
number	Atom	X	Y	Z
1	C	-3.37947	0.5208	0.21653
2	C	-2.72901	1.74199	0.04413
3	C	-1.35182	1.8654	-0.21942
4	C	-0.58984	0.69538	-0.29067
5	C	-1.21155	-0.56455	-0.11629
6	C	-2.60699	-0.65048	0.11656
7	C	0.89073	0.7082	-0.59113
8	C	1.59075	-0.47364	0.06318
9	O	0.91212	-1.72432	-0.30215
10	C	-0.424	-1.79978	-0.22621
11	O	-3.2461	-1.83802	0.25076
12	C	-4.86106	0.43167	0.48319
13	C	-0.73865	3.23407	-0.42144
14	O	-0.93418	-2.92833	-0.27443
15	C	3.04785	-0.67461	-0.34228
16	C	3.99669	0.43369	0.14045
17	C	5.43518	0.18156	-0.31024
18	O	3.91966	0.6028	1.56917
19	H	-3.32454	2.65072	0.11055
20	H	1.05778	0.68276	-1.67895
21	H	1.34749	1.63162	-0.22424
22	H	1.51339	-0.39331	1.15292
23	H	-2.57722	-2.54912	0.08175
24	H	-5.37468	-0.1397	-0.29991
25	H	-5.30683	1.42995	0.52694
26	H	-5.06731	-0.07799	1.43252
27	H	-1.50709	4.0117	-0.3729
28	H	0.01255	3.46454	0.3453
29	H	-0.24086	3.31933	-1.39543
30	H	3.38753	-1.63665	0.06507
31	H	3.11055	-0.74926	-1.4357
32	H	3.66712	1.40068	-0.25423
33	H	5.80805	-0.77234	0.08548
34	H	6.09008	0.98414	0.04508
35	H	5.49905	0.14172	-1.40388
36	H	4.28003	-0.19398	1.99469

Conformer D		Standard Orientation (Ångstroms)		
number	Atom	X	Y	Z
1	C	-3.46064	-0.08183	0.26234
2	C	-3.18112	1.28328	0.21449
3	C	-1.89994	1.8123	-0.03078
4	C	-0.84385	0.91513	-0.21485
5	C	-1.08464	-0.47965	-0.16915
6	C	-2.39487	-0.97476	0.04901
7	C	0.56636	1.37054	-0.50664
8	C	1.58333	0.37071	0.02554
9	O	1.27289	-0.97546	-0.4679
10	C	0.01199	-1.42898	-0.40139
11	O	-2.67433	-2.3007	0.06206
12	C	-4.85178	-0.60738	0.51272
13	C	-1.69802	3.31061	-0.09544
14	O	-0.16412	-2.64452	-0.56371
15	C	3.01357	0.67811	-0.39792
16	C	4.08603	-0.26984	0.15088
17	C	4.23546	-0.22569	1.67154
18	O	5.30898	0.14259	-0.49578
19	H	-4.00461	1.9782	0.36858
20	H	0.70675	1.5006	-1.59039
21	H	0.76636	2.34204	-0.04469
22	H	1.50196	0.31813	1.11773
23	H	-1.83884	-2.77701	-0.17554
24	H	-5.20539	-1.21896	-0.3266
25	H	-5.55674	0.21706	0.65606
26	H	-4.88462	-1.2456	1.40438
27	H	-2.65101	3.83389	0.02945
28	H	-1.01993	3.66795	0.69052
29	H	-1.27028	3.62383	-1.05599
30	H	3.06744	0.66767	-1.49357
31	H	3.24666	1.7002	-0.07133
32	H	3.85285	-1.29618	-0.16237
33	H	4.44346	0.79596	2.01204
34	H	5.06034	-0.87246	1.99453
35	H	3.32859	-0.58338	2.17279
36	H	6.01843	-0.46265	-0.2251