Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A Biomimetic Synthesis-Enabled Stereochemical Assignment of Rhodotomentones A and B, Two Unusual Caryophyllene-Derived Meroterpenoids from *Rhodomyrtus tomentosa*

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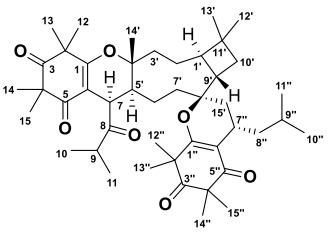


rhodotomentone A (**1**)

Table S1. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectral data of **1** in $CDCl_3$ (δ in ppm, J in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	171.3	8'	–	83.3
2	–	48.0	9'	2.38 m	44.8
3	–	213.1	10'a	1.63 m	35.7
4	–	55.5	10'b	1.48 m	
5	–	197.2	11'	–	34.1
6	–	108.4	12'	0.94 s	22.4
7	4.07 d (7.2)	45.2	13'	0.97 s	30.1
8	–	216.0	14'	1.26 s	21.0
9	2.89 m	42.9	15'a	2.16 m	33.8
10	1.24 d (6.8)	20.4	15'b	1.55 m	
11	1.07 d (6.8)	18.3	1"	–	168.8
12	1.37 s	24.5	2"	–	48.2
13	1.42 s	25.6	3"	–	213.0
14	1.34 s	26.7	4"	–	55.4
15	1.29 s	26.0	5"	–	198.0
1'	1.82 m	48.7	6"	–	112.6
2'a	1.70 m	23.4	7"	2.85 m	25.6
2'b	1.40 m		8"a	1.64 m	43.7
3'a	2.18 m	40.8	8"b	1.03 m	
3'b	1.73 m		9"	1.69 m	25.9
4'	–	84.3	10"	0.92 d (6.0)	24.1
5'	2.15 m	43.2	11"	0.98 d (6.0)	21.3
6'a	1.87 m	21.5	12"	1.36 s	24.9
6'b	1.78 m		13"	1.31 s	21.9
7'a	2.11 m	39.5	14"	1.31 s	22.9
7'b	1.91 m		15"	1.32 s	26.0

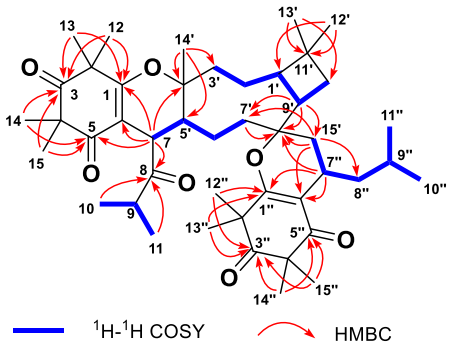


Figure S1. Key ^{1}H–^{1}H COSY and HMBC correlations of **2**.

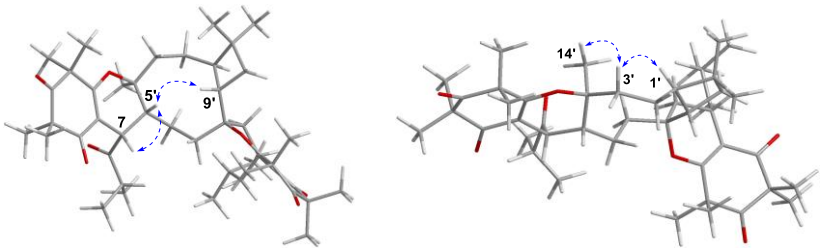


Figure S2. Key NOESY correlations of **2**.

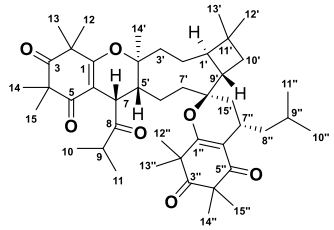
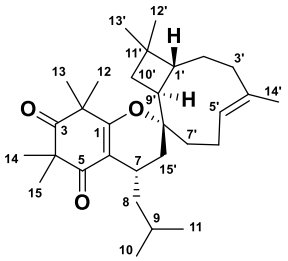


Table S2. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data of **2** in $CDCl_3$ (δ in ppm, J in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	171.7	8'	–	82.8
2	–	48.0	9'	2.58 m	47.5
3	–	212.9	10'a	1.60 m	34.6
4	–	55.5	10'b	1.39 m	
5	–	197.4	11'	–	34.0
6	–	107.9	12'	0.95 s	22.9
7	4.22 d (7.0)	42.6	13'	0.97 s	29.3
8	–	216.3	14'	1.14 s	21.0
9	2.71 m	42.7	15'a	1.98 m	23.6
10	1.32 d (6.5)	21.3	15'b	1.89 m	
11	1.03 d (6.5)	17.4	1"	–	169.8
12	1.37 s	25.2	2"	–	48.1
13	1.44 s	25.5	3"	–	213.3
14	1.36 s	27.3	4"	–	55.5
15	1.31 s	20.8	5"	–	197.9
1'	1.74 m	48.6	6"	–	110.7
2'a	1.53 m	23.0	7"	2.95 m	25.3
2'b	1.25 m		8"a	1.49 m	42.5
3'a	2.11 m	40.7	8"b	1.10 m	
3'b	1.73 m		9"	1.70 m	26.1
4'	–	83.4	10"	0.91 d (6.2)	24.1
5'	2.21 m	40.6	11"	1.03 d (6.2)	21.3
6'a	1.28 m	29.9	12"	1.39 s	24.9
6'b	1.25 m		13"	1.30 s	25.5
7'a	2.27 m	36.7	14"	1.33 s	22.7
7'b	1.72 m		15"	1.36 s	26.5

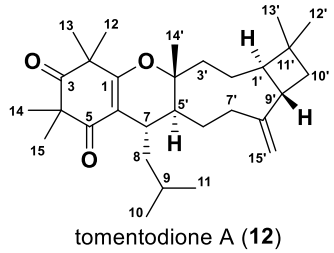


rhodomentone A (**7**)

Table S3. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **7** in $CDCl_3$ (δ in ppm, J in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	169.2	3'a	c	b
2	–	48.1	3'b	c	
3	–	213.8	4'	–	b
4	–	55.5	5'	5.20 brs	b
5	–	197.9	6'a	c	b
6	–	109.9	6'b	c	
7	2.91 m	24.6	7'a	c	b
8a	1.40[a] m	42.3	7'b	c	
8b	1.24[a] m		8'	–	b
9	1.83[a] m	25.7	9'	c	b
10	1.08 d (6.4)	21.0	10'a	1.67[a] m	37.4
11	0.97[a] d (6.4)	24.2	10'b	1.35[a] m	
12	1.26 s	25.4	11'	–	32.7
13	1.32[a] s	25.3	12'	0.90 brs	29.9
14	1.32[a] s	26.8	13'	0.96[a] s	22.8
15	1.31[a] s	22.4	14'	1.71 s	b
1'	c	b	15'a	c	b
2'	c	b	15'b	c	

[a)] Overlapped signals, [b)] Signals invisible, [c)] Signals unassigned



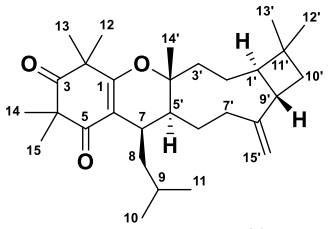
tomentodione A (**12**)

Table S4. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **12** in $CDCl_3$ (δ in ppm, J in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	170.5	3'a	2.08[a] m	37.5
2	–	47.7	3'b	1.90 m	
3	–	214.1	4'	–	83.1
4	–	55.3	5'	2.08[a] m	40.4
5	–	197.6	6'a	1.74 m	33.1
6	–	113.7	6'b	1.43[a] m	
7	2.26 m	34.6	7'a	2.47 m	35.4
8	1.82 m	38.9	7'b	2.12[a] m	

	1.31[a] m		8'	–	152.3
9	1.47[a] m	25.6	9'	2.39 m	42.5
10	0.75 d (6.6)	24.2	10'a	1.68 m	36.4
11	0.83 d (6.6)	24.1	10'b	1.61 m	
12	1.37 s	24.1	11'	–	33.6
13	1.32 s	25.6	12'	0.98[a] s	30.5
14	1.31 s	23.4	13'	0.98[a] s	22.3
15	1.33 s	26.2	14'	1.06 s	21.0
1'	2.03 m	52.2	15'a	4.91 s	110.8
2'a	1.78[a] m	22.4	15'b	4.88 s	
2'b	1.40[a] m				

[a)] Overlapped signals

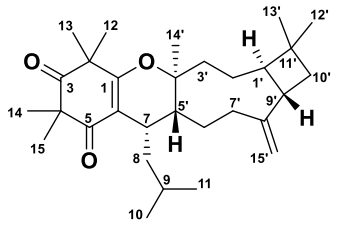


tomentodione B (**13**)

Table S5. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **13** in $CDCl_3$ (δ in ppm, J in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	170.4	3'a	2.03 m	46.3
2	–	47.7	3'b	1.39[a] m	
3	–	213.8	4'	–	86.4
4	–	55.5	5'	1.74[a] m	39.8
5	–	197.2	6'	1.66 m	25.3
6	–	116.4			
7	2.88 m	28.4	7'a	2.33 m	35.4
8a	1.40[a] m	41.0	7'b	2.13 m	
8b	1.10 m		8'	–	150.8
9	1.47[a] m	26.7	9'	2.40 m	42.4
10	0.82 d (6.0)	24.7	10'a	1.72[a] m	36.2
11	0.97[a] d (6.0)	21.7	10'b	1.59[a] m	
12	1.32[a] s	25.0	11'	–	34.5
13	1.35 s	25.5	12'	0.94 s	29.8
14	1.32[a] s	23.8	13'	0.97[a] s	21.9
15	1.32 s	25.5	14'	1.35 s	23.4
1'	1.49[a] m	58.2	15'a	4.91 s	111.1
2'	1.55–1.61[a] m	24.2	15'b	4.90 s	

[a)] Overlapped signals

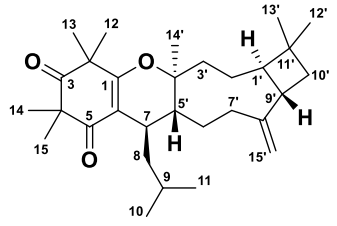


tomentodione C (**14**)

Table S6. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectral data of **14** in $CDCl_3$ (δ in ppm, J in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	169.8	3'a	2.03 m	41.6
2	–	47.9	3'b	1.76 m	
3	–	213.7	4'	–	85.5
4	–	55.5	5'	2.10[a] m	38.5
5	–	198.0	6'a	1.70[a] m	29.2
6	–	114.8	6'b	1.51[a] m	
7	2.98 m	29.3	7'a	2.35 m	36.4
8a	1.49[a] m	42.1	7'b	2.12[a] m	
8b	1.08 m		8'	–	154.9
9	1.67[a] m	27.6	9'	2.57 q (9.2)	42.9
10	0.95 d (6.2)	24.3	10'a	1.73 m	38.6
11	0.87[a] d (6.2)	21.9	10'b	1.65 m	
12	1.35[a] s	25.5	11'	–	33.5
13	1.37 s	26.2	12'	0.96 s	29.6
14	1.35[a] s	22.9	13'	0.88 s	22.3
15	1.34 s	25.2	14'	1.25 s	23.7
1'	1.54[a] m	56.9	15'a	4.83 brs	110.2
2'a	1.44[a] m	23.4	15'b	4.73 brs	
2'b	1.19 m				

[a] Overlapped signals



tomentodione D (**15**)

Table S7. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **15** in $CDCl_3$ (δ in ppm, J in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	170.4	3'a	2.13[a] m	39.4
2	–	47.7	3'b	1.77 m	
3	–	214.1	4'	–	83.5
4	–	55.3	5'	2.09[a] m	40.0
5	–	197.6	6'a	1.65[a] m	34.5
6	–	113.4	6'b	1.47[a] m	
7	2.28 m	35.1	7'a	2.40 m	36.4
8a	1.88[a] m	39.4	7'b	2.19 m	

8b	1.40[a] m		8'	–	155.0
9	1.56[a] m	25.7	9'	2.71 q (9.6)	42.8
10	0.89 d (6.6)	24.1	10'a	1.92 m	40.4
11	0.79 d (6.6)	24.0	10'b	1.56[a] m	
12	1.38 s	24.0	11'	–	33.5
13	1.31[a] s	25.5	12'	1.00 s	29.8
14	1.34 s	25.9	13'	0.97 s	22.4
15	1.31[a] s	23.7	14'	1.03 s	19.9
1'	1.61[a] m	54.6	15'a	4.83 s	110.3
2'	1.52[a] m	22.1	15'b	4.68 s	

[a)] Overlapped signals

Experimental section and results

1. UPLC-UV-MS-guided isolation of Fr.B

Fr.B was speculated to contain caryophyllene-derived meroterpenoids (CDMTs) on the basis of its UPLC-QTOF/MS analysis result, which showed a unique UV profile (λ_{max} 265 nm) as well as the typical ion peak at *m/z* 719.4926 $[M+H]^+$ (Figure S3).

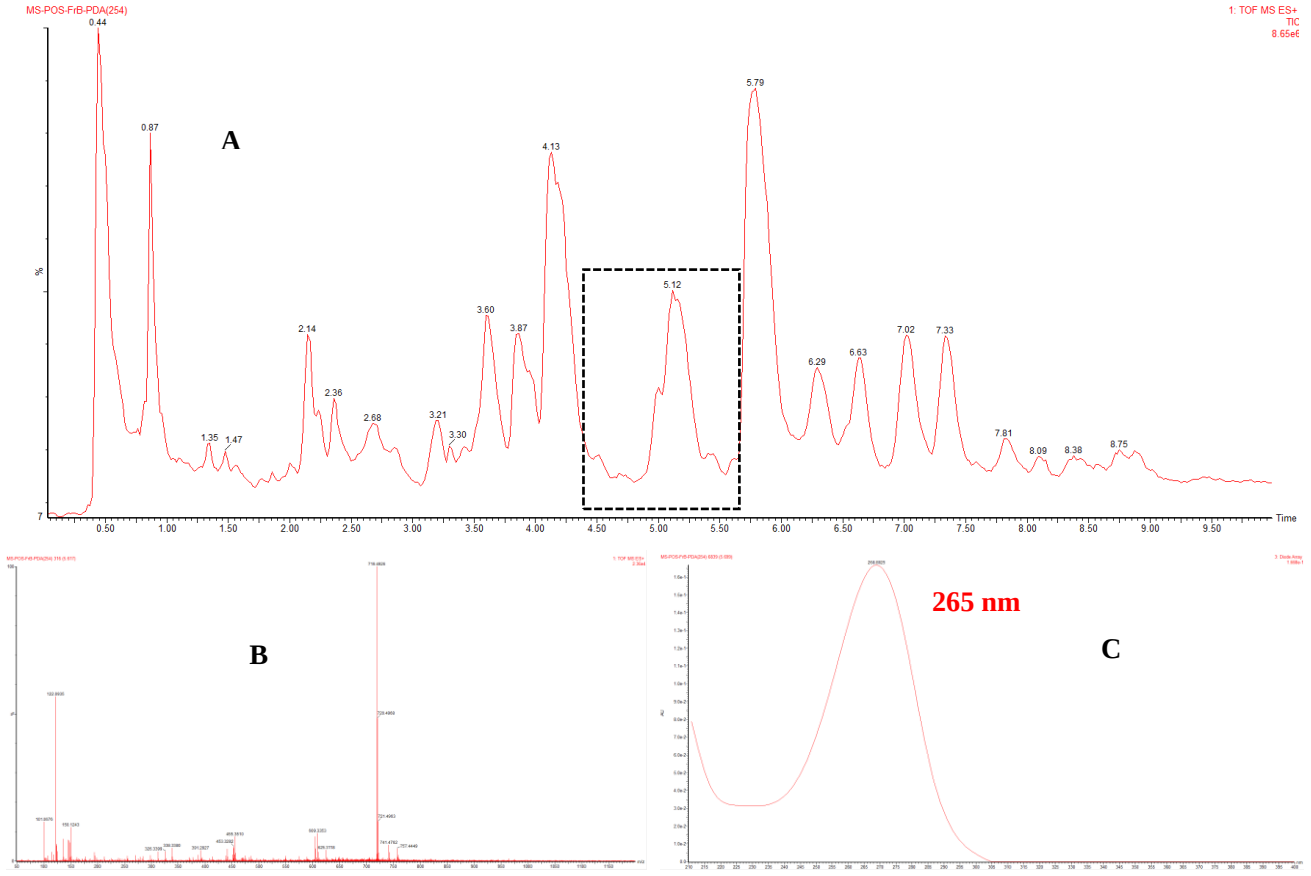


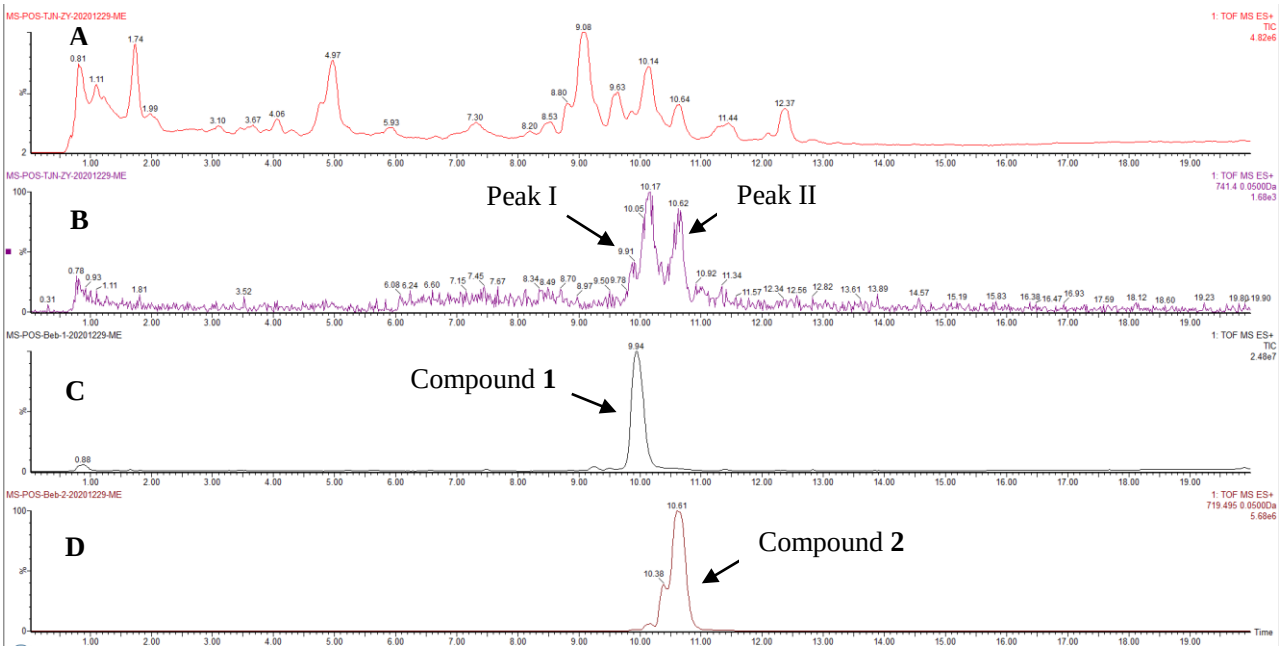
Figure S3. A: UPLC-QTOF/MS analysis for Fr.B; **B** and **C**: Fr.B showed a typical ion peak at *m/z* 719.4926 $[M+H]^+$ as well as a unique UV profile.

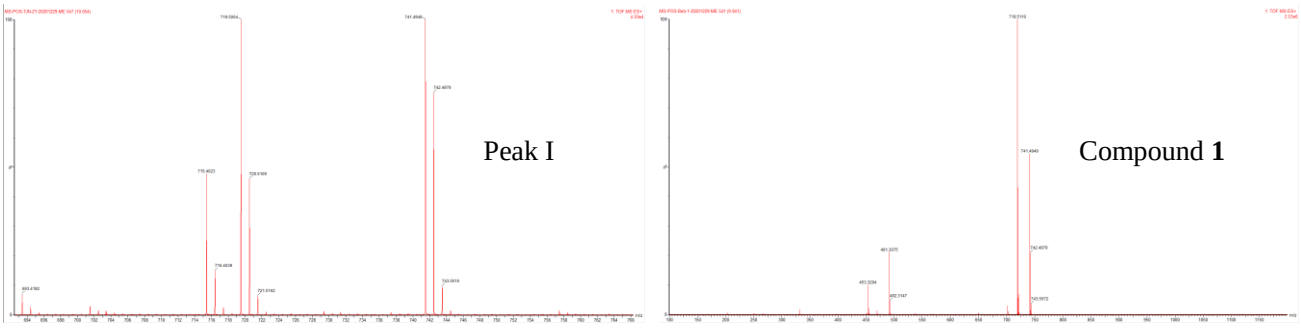
2. UPLC-QTOF/MS analysis of the methanol extract of *Rhodomyrtus tomentosa*

Preparation of the sample solution: The fresh leaves and twigs of *Rhodomyrtus tomentosa* (100 g) were cut into pieces and extracted using methanol by ultrasonic extraction at room temperature for 1 h. The extract was then concentrated *in vacuo* and filtered through a 0.22 μm membrane prior for further UPLC-QTOF/MS analysis.

UPLC condition: UPLC analysis was performed on a Waters Acquity UPLC system equipped with a binary solvent system, an automatic sample manger and a photodiode array detector (PDA). Chromatographic separation was achieved on a SB-C18 column (100 mm × 2.1 mm, 1.8 μm). The mobile phases consisted of (A) 0.1% formic acid-water and (B) MeOH. The UPLC elution program was optimized as linear gradient from 80 to 100% B (0–20 min). The flow rate was set at 0.3 mL/min.

MS condition: HRESIMS analysis was performed on a Waters Xevo-G2 QTOF mass spectrometer equipped with ESI source. Mass spectra were recorded across the range from 100 to 1000 Da. Samples were analyzed in positive mode and the operating parameters were set as follow: capillary voltage of 3.0 kV; sample cone voltage of 30 V; extraction cone voltage of 4 V, source temperature of 100 ℃, desolvation temperature 350 ℃, cone gas flow of 30 L/h and desolvation gas flow of 600 L/h.





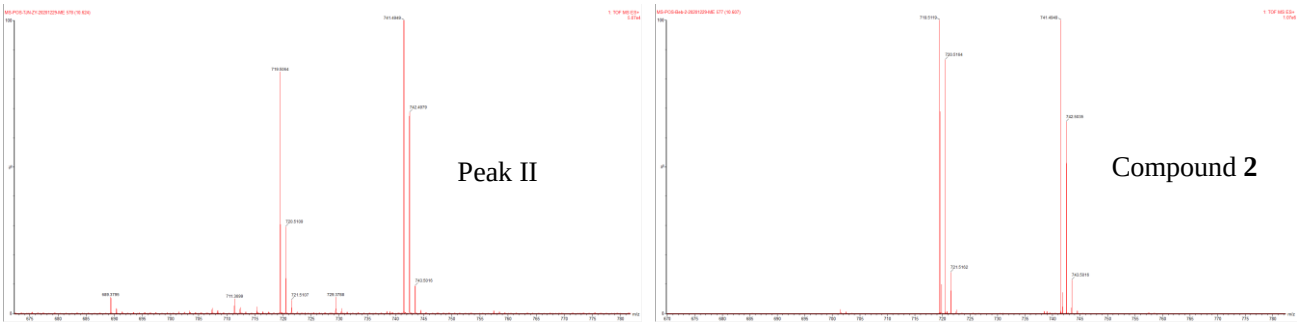


Figure S4. UPLC-QTOF/MS analysis of the methanol extract the fresh leaves and twigs of *Rhodomyrtus tomentosa* (**A**: Total ion chromatogram; **B**: Extracted ion chromatogram, Peak I: retention time: 10.054 min, *m/z* 741.4949 $[M+Na]^+$; Peak II retention time: 10.624 min, *m/z* 741.4949 $[M+Na]^+$; **C**: Ion chromatogram of compound **1** (retention time: 9.941 min), *m/z* 741.4949 $[M+Na]^+$; **D**: Ion chromatogram of compound **2** (retention time: 10.607 min), *m/z* 741.4949 $[M+Na]^+$.

3. Quantum chemical ECD calculation

On the account of the ECD spectra of two enantiomers are mirror images by definition, one of the two plaussible steroisomers of **1** and **2** (7*R*,1'*R*,4'*R*,5'*S*,8'*R*,9'*S*,7"*S*-**1**, 7*S*,1'*R*,4'*S*,5'*R*,8'*R*,9'*S*,7"*S*-**2**) were arbitorarily selected for the following calculation. The systematic random conformational analysis of the selected steroisomers of **1** and **2** were performed in the SYBYL-X 2.1.1 program by using MMFF94s molecular force field with an energy cutoff of 10 kcal/mol to the global minima, which afforded 25 and 18 conformers, respectively. All of the obtained conformers were further optimized using DFT at the B3LYP/6-31+G(d) level in gas phase using Gaussian09 software,[1] which afforded 12 and 12 stable conformers for **1** and **2**, respectively. The optimized stable conformers of the selected steroisomers of **1** and **2** were further subjected to ECD calculations at the B3LYP/6-31+G(d) level with the PCM solvation model of methanol (**1** and **2**). The first 50 excitations for **1** and **2** were considered. The overall ECD curves of **1** and **2** were all weighted by Boltzmann distribution. The calculated ECD spectra were subsequently compared with the experimental ones. The ECD spectra were produced by SpecDis 1.70 software.[2]

Table S8. Cartesian coordinate of dominant conformer of (7*R*,1'*R*,4'*R*,5'*S*,8'*R*,9'*S*,7"*S*)-**1**.

Cartesian coordinate of **1a**						Cartesian coordinate of **1b**				
Standard orientation						Standard orientation				
Center Number	Atomic Number	Coordinates (Angstroms)				Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z				X	Y	Z
1	6	6.474854	-0.002606	-1.398835		1	6	6.742389	-1.20209	0.289961
2	6	6.693882	0.102814	0.116672		2	6	6.829298	0.305778	0.107805
3	6	5.420044	0.35479	0.948622		3	6	5.599023	0.847594	-0.59812
4	6	4.1301	0.046077	0.324974		4	6	4.2658	0.325906	-0.19257
5	6	3.987988	0.08826	-1.024716		5	6	4.199861	-0.90032	0.357961
6	6	5.112322	0.438743	-1.983195		6	6	5.377459	-1.83438	0.60191
7	6	2.958522	-0.177195	1.235425		7	6	3.055162	1.174364	-0.51211
8	6	1.620362	-0.032726	0.474631		8	6	1.741866	0.367391	-0.28107
9	6	1.641088	-0.620695	-0.952195		9	6	1.851275	-0.6284	0.913766

10	8	2.823427	-0.059908	-1.681776		10	8	3.001351	-1.47776	0.738812
11	8	7.365496	-0.36593	-2.134129		11	8	7.76175	-1.90016	0.265474
12	8	5.512165	0.772869	2.089123		12	8	5.663277	1.731812	-1.44978
13	6	4.904457	-0.260867	-3.326655		13	6	5.410807	-2.27557	2.07725
14	6	5.155116	1.962352	-2.156198		14	6	5.224986	-3.07276	-0.30327
15	6	3.153418	-1.494262	2.004169		15	6	3.150291	2.530834	0.218509
16	6	7.270313	-1.235049	0.606662		16	6	6.949466	0.977458	1.481562
17	6	7.677021	1.258689	0.350638		17	6	8.079796	0.641915	-0.72526
18	6	3.604515	-1.333199	3.461623		18	6	3.502944	3.767455	-0.61712
19	6	2.356884	-1.242331	4.346845		19	6	2.264723	4.625	-0.84967
20	6	4.503054	-2.509194	3.8554		20	6	4.593733	4.572099	0.087288
21	6	0.412039	-0.516808	1.286137		21	6	0.457709	1.22936	-0.29422
22	6	-0.579537	0.586505	1.671823		22	6	-0.55423	0.937589	-1.43328
23	6	0.401941	1.375177	-2.059718		23	6	0.412881	-2.6531	-0.0531
24	6	0.496434	-0.13396	-1.840018		24	6	0.631604	-1.59168	1.03096
25	6	-1.801492	0.74898	0.757555		25	6	-1.82771	0.094803	-1.097
26	6	-1.620979	1.684492	-0.430846		26	6	-1.61008	-1.42615	-1.32298
27	6	-0.18952	2.097463	-0.867903		27	6	-0.19082	-2.11	-1.33763
28	6	-1.981	3.180914	-0.259636		28	6	-1.76808	-2.00694	-2.77008
29	6	-0.669914	3.584428	-1.003595		29	6	-0.7782	-3.14225	-2.37523
30	8	-1.958991	-0.614321	0.17245		30	8	-2.15574	0.336982	0.288031
31	6	-3.184236	-0.991225	-0.273646		31	6	-3.43774	0.076798	0.746024
32	6	-4.326103	-0.291727	-0.085101		32	6	-4.47774	-0.11215	-0.08867
33	6	-4.358712	0.962797	0.75509		33	6	-4.35037	0.00982	-1.59126
34	6	-3.056571	1.063836	1.580547		34	6	-2.99107	0.624155	-1.96433
35	6	-3.093765	-2.28335	-1.059369		35	6	-3.50393	-0.06174	2.260159
36	6	-4.446423	-3.036164	-0.991422		36	6	-4.93893	0.179877	2.748007
37	6	-5.743534	-2.21545	-1.024292		37	6	-6.09147	-0.38874	1.935679
38	6	-5.559479	-0.70095	-0.776304		38	6	-5.75422	-0.63795	0.47584
39	6	1.780128	-2.127413	-1.058029		39	6	1.995461	0.042757	2.29826
40	1	-2.180857	1.247639	-1.287763		40	1	-2.28259	-1.96719	-0.63869
41	1	0.53317	2.022684	-0.018172		41	1	0.555071	-1.51627	-1.86794
42	1	1.510055	1.079417	0.324684		42	1	1.732315	-0.25218	-1.17838
43	6	0.20013	4.58417	-0.249411		43	6	0.201288	-3.50882	-3.4913
44	6	-0.923811	4.060615	-2.427549		44	6	-1.46618	-4.39847	-1.83424
45	6	-5.579018	1.016147	1.699644		45	6	-5.50193	0.730326	-2.35104
46	6	-6.31559	2.373843	1.649202		46	6	-5.5878	2.272171	-2.3107
47	6	-7.639464	2.282136	2.429524		47	6	-6.75556	2.738678	-3.18998
48	6	-5.448704	3.518622	2.197905		48	6	-5.76069	2.837745	-0.90512
49	6	-2.820897	-1.954645	-2.532396		49	6	-3.06542	-1.46779	2.69357
50	6	-1.999459	-3.182944	-0.486519		50	6	-2.59211	0.981145	2.944445
51	6	-6.375748	-2.423967	-2.407009		51	6	-6.54036	-1.7092	2.579114
52	6	-6.662707	-2.724903	0.096446		52	6	-7.25662	0.614521	1.979887
53	8	-6.41652	0.08323	-1.131532		53	8	-6.52121	-1.27121	-0.25115
54	8	-4.471228	-4.24586	-0.953257		54	8	-5.16118	0.743224	3.825106

55	8	2.799009	-2.568711	1.571721		55	8	2.953658	2.639342	1.42943
56	1	2.973663	0.647072	2.000223		56	1	3.071711	1.403844	-1.58719
57	1	5.731835	-0.045748	-4.016118		57	1	6.281982	-2.90778	2.285813
58	1	3.966644	0.05556	-3.800263		58	1	4.519191	-2.85171	2.350289
59	1	4.85861	-1.350878	-3.209641		59	1	5.469136	-1.41414	2.751962
60	1	4.233524	2.327973	-2.628569		60	1	4.284307	-3.60332	-0.11564
61	1	5.263164	2.485031	-1.19882		61	1	5.246358	-2.79135	-1.36313
62	1	5.98908	2.263576	-2.803476		62	1	6.037697	-3.79101	-0.14307
63	1	8.195687	-1.486129	0.067526		63	1	7.803267	0.581598	2.043205
64	1	6.56898	-2.063963	0.453681		64	1	6.055796	0.82138	2.095369
65	1	7.516801	-1.194178	1.675929		65	1	7.081488	2.060979	1.381119
66	1	8.624251	1.093325	-0.178664		66	1	8.997083	0.296241	-0.23466
67	1	7.26845	2.220577	0.02426		67	1	8.033788	0.166519	-1.71238
68	1	7.909964	1.357472	1.422216		68	1	8.181421	1.721941	-0.88334
69	1	4.194914	-0.385556	3.564945		69	1	3.888922	3.45218	-1.5909
70	1	2.634353	-1.197531	5.408205		70	1	2.524086	5.556929	-1.36295
71	1	1.767155	-0.346114	4.128777		71	1	1.538733	4.096533	-1.47536
72	1	1.707438	-2.119382	4.225269		72	1	1.768839	4.879799	0.093234
73	1	4.849566	-2.415001	4.890582		73	1	4.920741	5.410862	-0.53605
74	1	5.391657	-2.565953	3.215757		74	1	5.467467	3.947417	0.299816
75	1	3.974134	-3.467273	3.763365		75	1	4.240176	4.978484	1.041429
76	1	-0.116699	-1.332143	0.747106		76	1	-0.03147	1.227029	0.681852
77	1	0.749138	-1.001998	2.219563		77	1	0.744529	2.274334	-0.43471
78	1	-0.935765	0.363913	2.695657		78	1	-0.90729	1.93824	-1.72415
79	1	-0.064855	1.562775	1.747848		79	1	-0.05279	0.564942	-2.33344
80	1	-0.204903	1.557502	-2.966254		80	1	-0.26289	-3.40418	0.373523
81	1	1.40703	1.785524	-2.282534		81	1	1.350307	-3.17621	-0.27265
82	1	0.598389	-0.618168	-2.82937		82	1	0.770221	-2.17531	1.953257
83	1	-0.454579	-0.511003	-1.400586		83	1	-0.28195	-1.01779	1.186675
84	1	-2.908355	3.491576	-0.744146		84	1	-2.77441	-2.33341	-3.04739
85	1	-2.020448	3.522705	0.783547		85	1	-1.39444	-1.34389	-3.56055
86	1	-4.41601	1.825736	0.046614		86	1	-4.36291	-1.02334	-1.96471
87	1	-2.977676	2.071098	2.030817		87	1	-2.79419	0.482441	-3.03324
88	1	-3.114386	0.356067	2.431911		88	1	-3.04824	1.706533	-1.7976
89	1	2.746623	-2.479648	-0.65843		89	1	2.972343	0.513429	2.431965
90	1	1.019037	-2.656704	-0.467653		90	1	1.208166	0.776237	2.490629
91	1	1.721277	-2.477338	-2.09221		91	1	1.952409	-0.70626	3.099123
92	1	1.180564	4.697888	-0.727456		92	1	0.998535	-4.15615	-3.1104
93	1	-0.266585	5.576527	-0.222887		93	1	-0.31013	-4.03952	-4.30165
94	1	0.377179	4.284435	0.78947		94	1	0.674015	-2.62129	-3.92599
95	1	-1.550039	3.356588	-2.985956		95	1	-2.18191	-4.17347	-1.03757
96	1	-1.439142	5.02795	-2.434207		96	1	-2.01613	-4.91166	-2.63093
97	1	0.013315	4.183166	-2.980293		97	1	-0.73017	-5.10208	-1.43044
98	1	-6.29997	0.219741	1.433287		98	1	-5.39958	0.443496	-3.40807
99	1	-5.281236	0.787541	2.737121		99	1	-6.4701	0.320521	-2.04322

100	1	-6.55769	2.593463	0.579547		100	1	-4.67842	2.699191	-2.74801
101	1	-8.196585	3.224484	2.378338		101	1	-7.71291	2.362934	-2.81282
102	1	-8.29104	1.501001	2.020816		102	1	-6.8086	3.832312	-3.21878
103	1	-7.475707	2.056779	3.488699		103	1	-6.63352	2.385344	-4.21941
104	1	-6.001386	4.465164	2.202991		104	1	-5.86863	3.927588	-0.93745
105	1	-4.551583	3.670889	1.589536		105	1	-4.89625	2.622634	-0.27243
106	1	-5.127238	3.325122	3.226885		106	1	-6.6567	2.430253	-0.42896
107	1	-2.816762	-2.864231	-3.14692		107	1	-1.98699	-1.60885	2.575047
108	1	-1.837492	-1.481219	-2.653123		108	1	-3.55738	-2.24933	2.104668
109	1	-3.56803	-1.26915	-2.949093		109	1	-3.3076	-1.65092	3.746953
110	1	-2.17481	-3.402493	0.574315		110	1	-2.87777	2.002159	2.664002
111	1	-1.967777	-4.148178	-1.010915		111	1	-2.65371	0.912017	4.037143
112	1	-1.009394	-2.71554	-0.566124		112	1	-1.538	0.841341	2.680332
113	1	-6.570046	-3.485718	-2.604466		113	1	-6.70021	-1.59689	3.657568
114	1	-5.743645	-2.037362	-3.213064		114	1	-5.7975	-2.50069	2.438091
115	1	-7.33803	-1.893138	-2.475144		115	1	-7.4777	-2.06943	2.139169
116	1	-6.870085	-3.798402	-0.023		116	1	-8.06937	0.325006	1.304146
117	1	-6.213394	-2.588114	1.086784		117	1	-7.67755	0.695849	2.988977
118	1	-7.628009	-2.201981	0.088394		118	1	-6.92464	1.616891	1.689796

Table S9. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **1a**.

HOMO is 196					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R (length)**	**Osc. Strength**	**Major contribs**
1	32621.9	306.5	12.7571	0.0046	H-4->L+4 (19%), H-1->LUMO (12%), H-1->L+4 (55%)
2	32676.7	306.0	-8.887	0.0005	H-2->L+1 (86%)
3	32811.4	304.8	8.2387	0.0005	H-3->LUMO (81%)
4	33873.7	295.2	0.5905	0.0008	H-5->L+3 (42%), H-2->L+3 (48%)
5	33892.2	295.1	-0.5648	0.0003	H-6->L+2 (35%), H-3->L+2 (54%)
6	36369.2	275.0	-0.2714	0.0878	H-1->LUMO (59%), H-1->L+2 (23%)
7	36448.2	274.4	8.13	0.0128	HOMO->L+1 (11%), HOMO->L+3 (83%)
8	37017.6	270.1	-12.0153	0.0308	H-1->LUMO (11%), H-1->L+2 (66%), H-1->L+4 (11%)
9	37769.3	264.8	1.6895	0.0016	HOMO->LUMO (98%)
10	38679.9	258.5	88.6734	0.3665	HOMO->L+1 (77%), HOMO->L+3 (10%)
11	38817.9	257.6	-0.3026	0.0026	H-1->L+1 (97%)
12	39436.5	253.6	-1.719	0.0062	H-6->LUMO (79%), H-3->LUMO (12%)
13	39968.0	250.2	18.8989	0.0487	H-4->LUMO (21%), H-4->L+4 (33%), H-1->L+4 (17%)
14	40005.1	250.0	-20.8487	0.0147	H-5->L+1 (74%), H-2->L+3 (12%)
15	40214.0	248.7	-15.1277	0.0073	H-5->L+3 (51%), H-2->L+3 (35%)
16	40460.8	247.2	0.1242	0.0004	HOMO->L+2 (96%)
17	40674.5	245.9	-0.0855	0.0001	H-1->L+3 (99%)
18	40802.0	245.1	12.2543	0.005	H-6->L+2 (54%), H-3->L+2 (36%)
19	41114.9	243.2	0.5381	0.0104	H-2->LUMO (93%)
20	41329.5	242.0	-5.4462	0.1385	H-4->LUMO (41%), H-3->L+4 (36%)
21	41761.8	239.5	-0.4109	0.001	HOMO->L+4 (96%)

22	42198.9	237.0	-9.0456	0.0726	H-4->LUMO (13%), H-4->L+2 (10%), H-4->L+4 (19%), H-3->L+4 (40%)
23	42799.0	233.7	-0.0177	0.0004	H-3->L+1 (97%)
24	43082.9	232.1	-4.9854	0.0164	H-4->L+2 (77%), H-4->L+4 (13%)
25	43671.7	229.0	-0.0475	0.0001	H-2->L+2 (98%)
26	43859.6	228.0	0.1724	0.0011	H-4->L+1 (97%)
27	44363.7	225.4	-0.128	0.0001	H-5->LUMO (99%)
28	44612.9	224.2	0.013	0	H-3->L+3 (99%)
29	45250.1	221.0	-0.0352	0	H-2->L+4 (99%)
30	45729.2	218.7	-0.1353	0.0002	H-4->L+3 (99%)
31	46111.5	216.9	1.6517	0.003	H-7->LUMO (75%), H-6->L+1 (19%)
32	46129.3	216.8	-2.4227	0.0016	H-7->LUMO (19%), H-6->L+1 (76%)
33	46571.3	214.7	5.7792	0.0078	H-9->L+1 (30%), H-8->L+1 (61%)
34	46762.4	213.8	0.4056	0.0011	H-6->L+4 (36%), H-1->L+5 (46%)
35	46799.5	213.7	-1.3052	0.0027	H-6->L+4 (52%), H-1->L+5 (32%)
36	46932.6	213.1	0.0194	0	H-5->L+2 (99%)
37	47025.3	212.7	4.3606	0.0102	H-7->L+1 (93%)
38	47126.2	212.2	-7.5128	0.0059	HOMO->L+5 (58%), HOMO->L+6 (37%)
39	47256.8	211.6	2.1053	0.0007	H-11->LUMO (11%), H-10->LUMO (17%), H-8->LUMO (65%)
40	47874.7	208.9	-26.025	0.0115	H-9->L+1 (52%), H-8->L+1 (31%)
41	47961.0	208.5	0.2794	0	H-6->L+3 (95%)
42	47965.8	208.5	2.122	0.0012	H-11->LUMO (23%), H-10->LUMO (31%), H-8->LUMO (31%)
43	48435.2	206.5	-0.0259	0	H-5->L+4 (99%)
44	49039.3	203.9	-0.9273	0.0012	HOMO->L+5 (20%), HOMO->L+6 (35%), HOMO->L+7 (17%), HOMO->L+8 (17%)
45	49178.8	203.3	2.761	0.0044	H-7->L+2 (24%), H-1->L+7 (11%), HOMO->L+7 (33%)
46	49182.9	203.3	-5.3813	0.0012	H-7->L+2 (12%), H-1->L+6 (14%), H-1->L+7 (19%), HOMO->L+7 (25%)
47	49200.6	203.2	3.283	0.0025	H-7->L+2 (61%), H-1->L+6 (11%), H-1->L+7 (16%)
48	49399.8	202.4	-0.1318	0.0012	H-8->L+3 (16%), H-7->L+3 (79%)
49	49412.8	202.4	0.1273	0.0036	H-10->LUMO (10%), H-9->LUMO (69%)
50	49538.6	201.9	3.5442	0.0056	H-1->L+6 (12%), H-1->L+7 (26%), H-1->L+8 (42%)

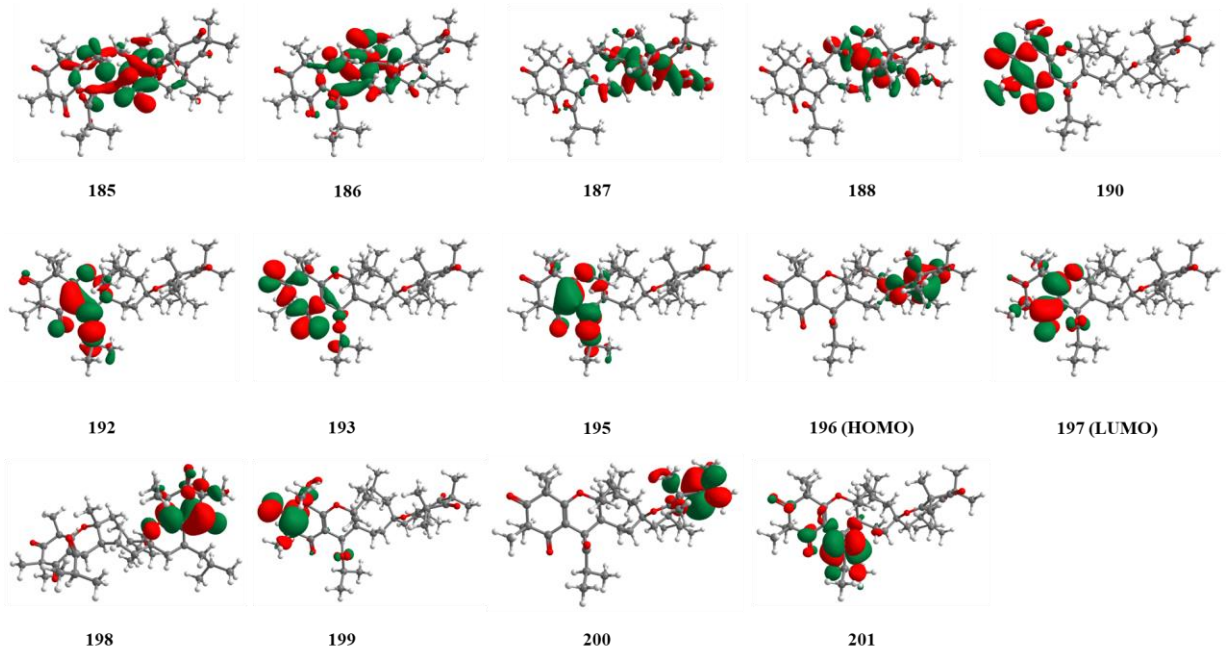


Figure S5. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **1a**.

Table S10. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **1b**.

HOMO is 196					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R (length)**	**Osc. Strength**	**Major contribs**
1	32300.1	309.6	-13.0488	0.0007	H-2->L+1 (86%)
2	32657.4	306.2	22.7729	0.0014	H-4->L+4 (11%), H-3->LUMO (38%), H-1->L+4 (32%)
3	32685.6	305.9	-3.8957	0.0023	H-4->L+4 (11%), H-3->LUMO (46%), H-1->L+4 (29%)
4	33887.4	295.1	16.8454	0.0042	H-5->L+1 (10%), H-5->L+2 (11%), H-5->L+3 (27%), H-2->L+2 (14%), H-2->L+3 (35%)
5	34211.6	292.3	16.2518	0.0073	H-6->LUMO (22%), H-6->L+2 (12%), H-3->L+2 (35%), H-3->L+3 (14%)
6	35719.1	280.0	-7.9618	0.0784	H-1->LUMO (76%)
7	35920.7	278.4	-5.8011	0.0206	HOMO->L+1 (24%), HOMO->L+2 (21%), HOMO->L+3 (54%)
8	37166.0	269.1	0.0097	0.0005	HOMO->LUMO (99%)
9	37485.4	266.8	12.1043	0.0214	H-4->LUMO (13%), H-1->L+2 (51%), H-1->L+3 (20%)
10	38158.9	262.1	83.5298	0.3084	HOMO->L+1 (63%), HOMO->L+3 (16%)
11	38542.8	259.5	-0.1021	0.0001	H-1->L+1 (100%)
12	39564.7	252.8	-0.7173	0.0184	H-6->LUMO (53%), H-4->LUMO (15%), H-3->L+2 (10%)
13	39749.4	251.6	-3.8847	0.0032	H-5->L+1 (68%), H-2->L+3 (20%)
14	40100.3	249.4	16.7337	0.0239	H-6->LUMO (10%), H-4->L+4 (45%), H-1->L+4 (18%)
15	40492.3	247.0	-0.833	0.0015	HOMO->L+2 (62%), HOMO->L+3 (25%)
16	40558.4	246.6	-2.5974	0.0094	H-2->LUMO (87%)
17	40627.8	246.1	23.2781	0.084	H-5->L+1 (15%), H-5->L+2 (12%), H-5->L+3 (29%), H-2->L+3 (12%)
18	40706.0	245.7	-41.3269	0.0619	H-4->LUMO (32%), H-2->LUMO (11%)

19	40764.1	245.3	-2.7713	0.0009	H-1->L+2 (26%), H-1->L+3 (71%)
20	41110.1	243.2	-0.6655	0.0005	HOMO->L+4 (90%)
21	41832.8	239.0	-0.0811	0.0169	H-3->L+4 (80%)
22	42484.4	235.4	-28.1082	0.0867	H-6->L+2 (31%), H-6->L+3 (12%), H-4->LUMO (18%)
23	42714.3	234.1	-0.1764	0.0005	H-3->L+1 (97%)
24	43628.9	229.2	-3.3212	0.0015	H-4->L+1 (95%)
25	43665.2	229.0	-7.155	0.0357	H-4->L+2 (49%), H-4->L+3 (19%)
26	43845.9	228.1	-1.3755	0.0036	H-2->L+2 (61%), H-2->L+3 (24%)
27	44208.1	226.2	-0.4674	0.0007	H-5->LUMO (99%)
28	44645.2	224.0	0.0102	0	H-2->L+4 (97%)
29	44886.4	222.8	0.0002	0	H-3->L+2 (28%), H-3->L+3 (72%)
30	45860.7	218.1	-0.1228	0.0002	H-4->L+2 (28%), H-4->L+3 (71%)
31	46010.7	217.3	0.2098	0.0039	H-7->LUMO (94%)
32	46262.3	216.2	-1.0115	0.0005	H-6->L+1 (96%)
33	46518.0	215.0	-11.569	0.0067	HOMO->L+5 (62%), HOMO->L+6 (32%)
34	46648.7	214.4	4.3574	0.0011	H-9->L+1 (17%), H-8->L+1 (19%), H-7->L+1 (57%)
35	46673.7	214.3	-3.0735	0.0014	H-1->L+5 (73%), H-1->L+6 (20%)
36	46825.3	213.6	26.4496	0.0189	H-8->L+1 (62%), H-7->L+1 (29%)
37	46885.8	213.3	-7.604	0.006	H-6->L+4 (84%)
38	47231.0	211.7	4.3142	0.0021	H-11->LUMO (13%), H-8->LUMO (73%)
39	47478.6	210.6	0.0164	0.0001	H-5->L+2 (68%), H-5->L+3 (27%)
40	47769.0	209.3	-27.4031	0.0102	H-9->L+1 (66%), H-8->L+1 (14%)
41	47915.0	208.7	5.7215	0.0012	H-11->LUMO (46%), H-10->LUMO (17%), H-8->LUMO (25%)
42	48226.3	207.4	-0.0855	0	H-5->L+4 (96%)
43	48412.6	206.6	-3.9896	0.0009	HOMO->L+5 (10%), HOMO->L+6 (16%), HOMO->L+7 (43%), HOMO->L+8 (17%)
44	48459.4	206.4	0.0463	0.0001	H-6->L+2 (28%), H-6->L+3 (71%)
45	48693.3	205.4	0.5409	0.0024	HOMO->L+6 (26%), HOMO->L+7 (42%), HOMO->L+8 (18%)
46	49066.7	203.8	3.2949	0.0064	H-1->L+6 (26%), H-1->L+7 (37%), H-1->L+8 (20%)
47	49174.8	203.4	3.8444	0.0019	HOMO->L+5 (14%), HOMO->L+6 (15%), HOMO->L+8 (43%)
48	49307.9	202.8	-4.2227	0.004	H-2->L+5 (39%), H-2->L+6 (35%)
49	49408.7	202.4	3.8163	0.005	H-1->L+7 (31%), H-1->L+8 (46%)
50	49524.1	201.9	-2.2151	0.0032	H-7->L+2 (41%), H-7->L+3 (47%)

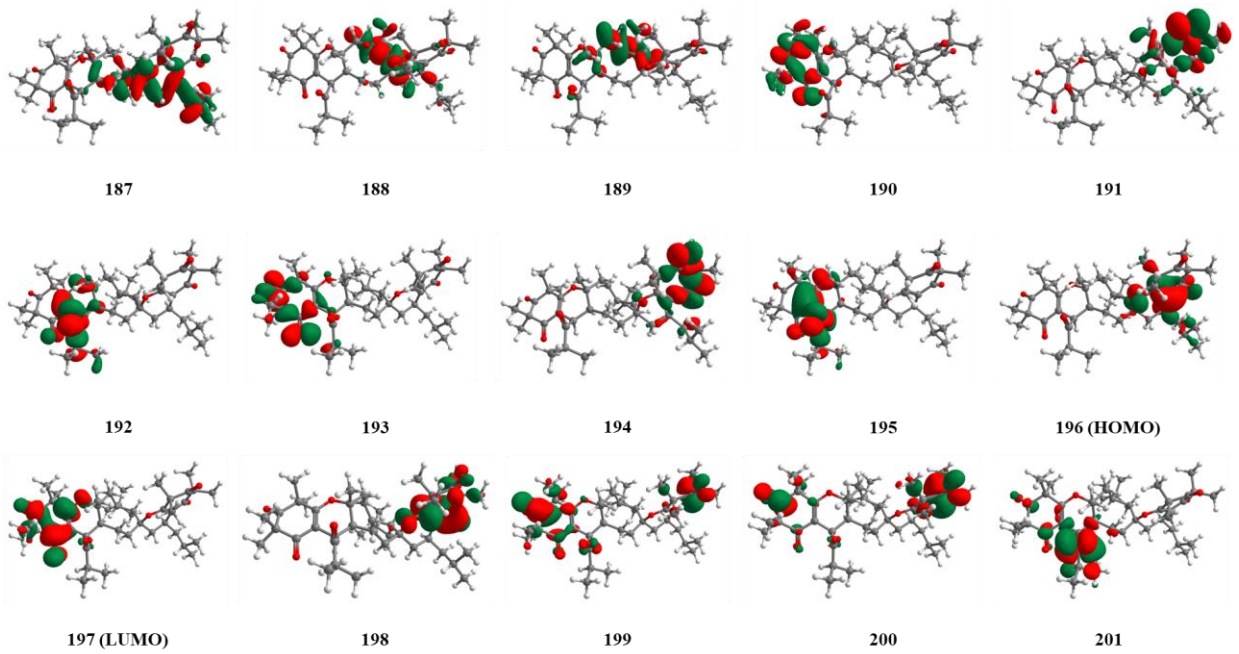


Figure S6. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **1b**.

Table S11. Cartesian coordinate of dominant conformer of (7*S*,1'*R*,4'*S*,5'*R*,8'*R*,9'*S*,7"*S*)-**2**.

Cartesian coordinate of **2a**						Cartesian coordinate of **2b**				
Standard orientation						Standard orientation				
Center Number	Atomic Number	Coordinates (Angstroms)				Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z				X	Y	Z
1	6	6.576121	0.120396	-1.52448		1	6	6.521907	-0.24593	-1.46092
2	6	6.133709	-1.33535	-1.52179		2	6	6.006851	-1.67004	-1.31389
3	6	4.623549	-1.46508	-1.44442		3	6	4.491106	-1.71701	-1.25265
4	6	3.874266	-0.52743	-0.56578		4	6	3.778179	-0.65727	-0.49022
5	6	4.434907	0.640081	-0.22036		5	6	4.39205	0.511514	-0.25836
6	6	5.799139	1.137987	-0.67531		6	6	5.785125	0.8923	-0.73843
7	6	2.499403	-0.95279	-0.12247		7	6	2.378148	-0.9669	-0.03032
8	6	1.686282	0.261789	0.399473		8	6	1.621063	0.332459	0.353097
9	6	2.525436	1.285491	1.217527		9	6	2.501396	1.393654	1.074577
10	8	3.801007	1.553918	0.586464		10	8	3.79424	1.534611	0.437182
11	8	7.593621	0.467455	-2.13453		11	8	7.563907	-0.01513	-2.08448
12	8	4.00884	-2.35237	-2.03395		12	8	3.840349	-2.62963	-1.75896
13	6	5.604328	2.402006	-1.5374		13	6	5.664396	2.065163	-1.73272
14	6	6.676769	1.478667	0.54334		14	6	6.662549	1.318421	0.453195
15	6	2.675489	-2.12724	0.861021		15	6	2.481619	-2.04328	1.068755
16	6	6.629587	-2.01249	-2.81317		16	6	6.48624	-2.50354	-2.51698
17	6	6.750456	-2.05063	-0.31354		17	6	6.569621	-2.2823	-0.02535
18	6	0.345816	-0.14928	1.054768		18	6	0.255149	0.056337	1.026474
19	6	-0.79132	-0.23751	0.030228		19	6	-0.87468	-0.07371	-0.00124
20	6	0.642383	2.996227	2.05499		20	6	0.69926	3.271792	1.709009
21	6	1.870581	2.711488	1.193862		21	6	1.917275	2.839572	0.895981

22	6	-1.8596	0.882269	0.139447		22	6	-1.88888	1.100325	-0.00391
23	6	-1.14108	2.26276	0.047292		23	6	-1.10711	2.428749	-0.23298
24	6	-0.70227	3.089774	1.323138		24	6	-0.63333	3.36065	0.955022
25	6	-2.02913	3.493927	-0.32597		25	6	-1.93232	3.656951	-0.73701
26	6	-1.07735	4.395007	0.515643		26	6	-0.93576	4.591623	0.011933
27	8	-2.64713	0.78668	-1.05994		27	8	-2.69609	0.925901	-1.18282
28	6	-3.85139	0.114054	-1.0844		28	6	-3.85366	0.173892	-1.13059
29	6	-4.42891	-0.39179	0.018567		29	6	-4.39526	-0.2461	0.025937
30	6	-3.80059	-0.30283	1.393075		30	6	-3.83201	0.089822	1.38827
31	6	-2.73914	0.805882	1.40102		31	6	-2.77164	1.193185	1.255214
32	6	-4.41399	0.041517	-2.49332		32	6	-4.43429	-0.05892	-2.51809
33	6	-5.68861	-0.80416	-2.58764		33	6	-5.69556	-0.93569	-2.52302
34	6	-6.56361	-0.97551	-1.35744		34	6	-6.03132	-1.75494	-1.28593
35	6	-5.79565	-0.98999	-0.04972		35	6	-5.67017	-1.01964	-0.0076
36	6	2.840853	0.852356	2.65445		36	6	2.782212	1.095016	2.55231
37	1	-0.33316	2.185678	-0.6954		37	1	-0.30099	2.237077	-0.95675
38	1	-1.43639	2.960722	2.1364		38	1	-1.37894	3.356628	1.768164
39	1	1.444058	0.812287	-0.52262		39	1	1.415944	0.796944	-0.6238
40	6	-1.81627	5.428927	1.36802		40	6	-1.62103	5.747279	0.744354
41	6	-0.00011	5.074188	-0.33038		41	6	0.178824	5.120138	-0.89128
42	6	-3.3326	-1.69571	1.884854		42	6	-3.37727	-1.187	2.141591
43	6	-2.56964	-1.7376	3.22409		43	6	-2.70989	-0.98246	3.517185
44	6	-3.37531	-1.13366	4.37465		44	6	-3.58566	-0.18215	4.481432
45	6	-2.20052	-3.18606	3.559628		45	6	-2.37902	-2.34511	4.134647
46	6	-4.73449	1.452371	-3.01401		46	6	-4.81983	1.30268	-3.13156
47	6	-3.3646	-0.61423	-3.42034		47	6	-3.39483	-0.75195	-3.41861
48	6	-7.57685	0.174934	-1.30326		48	6	-7.54083	-2.06072	-1.28199
49	6	-7.32015	-2.31337	-1.48118		49	6	-5.25354	-3.0764	-1.32794
50	8	-6.31611	-1.42296	0.980567		50	8	-6.36093	-1.09481	1.008014
51	8	-6.05517	-1.25567	-3.6791		51	8	-6.37824	-1.03666	-3.54851
52	6	1.704545	-3.30781	0.738777		52	6	1.451871	-3.17933	1.048967
53	6	2.259404	-4.3587	-0.2137		53	6	1.961305	-4.34844	0.216587
54	6	1.442309	-3.91795	2.115089		54	6	1.141546	-3.63207	2.475042
55	8	3.581913	-2.14421	1.697225		55	8	3.375597	-2.02112	1.918081
56	1	1.960987	-1.34691	-0.99507		56	1	1.83126	-1.42005	-0.86835
57	1	6.564302	2.816951	-1.86659		57	1	6.647976	2.396357	-2.08624
58	1	5.082439	3.195042	-0.98939		58	1	5.175139	2.936027	-1.28126
59	1	5.022192	2.177854	-2.43954		59	1	5.083855	1.774277	-2.61665
60	1	6.791121	0.616607	1.209727		60	1	6.725536	0.527614	1.208808
61	1	7.683961	1.785079	0.237074		61	1	7.687526	1.54219	0.134659
62	1	6.252538	2.29949	1.133108		62	1	6.2717	2.216595	0.945193
63	1	7.721894	-1.97367	-2.89647		63	1	7.580193	-2.52706	-2.58253
64	1	6.212571	-1.51964	-3.69958		64	1	6.107396	-2.08765	-3.45828
65	1	6.337465	-3.06827	-2.85452		65	1	6.141728	-3.54224	-2.45282
66	1	7.841984	-1.95264	-0.30858		66	1	7.664561	-2.2383	-0.00998

67	1	6.382505	-1.64441	0.63459		67	1	6.210024	-1.75984	0.867449
68	1	6.504594	-3.11896	-0.3188		68	1	6.269597	-3.33169	0.077501
69	1	0.440387	-1.10817	1.566925		69	1	0.292701	-0.84987	1.633143
70	1	0.062736	0.525346	1.857279		70	1	0.001235	0.821735	1.75378
71	1	-0.38657	-0.24278	-0.99148		71	1	-0.46261	-0.18698	-1.01372
72	1	-1.26615	-1.21711	0.106569		72	1	-1.39565	-1.02109	0.152664
73	1	0.567643	2.276597	2.875475		73	1	0.580705	2.642617	2.59596
74	1	0.800221	3.958973	2.560533		74	1	0.903578	4.270962	2.117997
75	1	2.647697	3.415549	1.531002		75	1	2.725961	3.536523	1.167249
76	1	1.704027	2.997062	0.150996		76	1	1.771592	3.022985	-0.17268
77	1	-3.05712	3.450029	0.052268		77	1	-2.96093	3.703322	-0.36071
78	1	-2.08099	3.717128	-1.39675		78	1	-1.973	3.770258	-1.82535
79	1	-4.57819	0.033147	2.093777		79	1	-4.64693	0.529365	1.980594
80	1	-3.30633	1.744421	1.476843		80	1	-3.33639	2.134856	1.203187
81	1	-2.13389	0.775184	2.310434		81	1	-2.16868	1.279305	2.161862
82	1	3.27207	1.687454	3.219828		82	1	3.250293	1.961318	3.035404
83	1	1.96173	0.497794	3.197968		83	1	1.881689	0.841819	3.11705
84	1	3.602115	0.06934	2.680353		84	1	3.502501	0.281899	2.668196
85	1	-1.13097	5.91188	2.072826		85	1	-0.91301	6.265245	1.400128
86	1	-2.62501	4.973045	1.949649		86	1	-2.45459	5.3987	1.363907
87	1	-2.2623	6.20763	0.739805		87	1	-2.02313	6.477619	0.033792
88	1	0.469561	4.384578	-1.03776		88	1	0.613983	4.336091	-1.51773
89	1	-0.43012	5.889706	-0.92296		89	1	-0.20537	5.889763	-1.57037
90	1	0.784351	5.500861	0.303259		90	1	0.982537	5.569804	-0.29901
91	1	-4.21493	-2.34168	1.988926		91	1	-4.25528	-1.82969	2.293696
92	1	-2.72851	-2.18689	1.115481		92	1	-2.70759	-1.7823	1.513115
93	1	-1.63074	-1.18266	3.126842		93	1	-1.76029	-0.45249	3.38584
94	1	-2.83463	-1.23562	5.321844		94	1	-3.11515	-0.11541	5.468393
95	1	-3.55733	-0.06618	4.219169		95	1	-3.7394	0.841368	4.126934
96	1	-4.34454	-1.63186	4.484282		96	1	-4.56765	-0.6507	4.606885
97	1	-1.60089	-3.23247	4.474877		97	1	-1.84292	-2.22289	5.081779
98	1	-1.6125	-3.6341	2.75227		98	1	-1.743	-2.93184	3.464402
99	1	-3.0946	-3.80109	3.70859		99	1	-3.28752	-2.92439	4.331952
100	1	-3.82645	2.055622	-3.13001		100	1	-3.96032	1.979509	-3.2
101	1	-5.40072	1.993716	-2.33431		101	1	-5.5923	1.800071	-2.53254
102	1	-5.23049	1.413117	-3.9909		102	1	-5.22034	1.188661	-4.14579
103	1	-3.13834	-1.63778	-3.09745		103	1	-3.05891	-1.70125	-2.9868
104	1	-3.7207	-0.67089	-4.45587		104	1	-3.81012	-0.97701	-4.40806
105	1	-2.42335	-0.05276	-3.44006		105	1	-2.50842	-0.12584	-3.57299
106	1	-8.33107	0.004329	-0.52608		106	1	-7.8311	-2.65549	-0.40811
107	1	-8.09888	0.294846	-2.25929		107	1	-7.84181	-2.6237	-2.1731
108	1	-7.09219	1.128445	-1.06844		108	1	-8.12854	-1.13514	-1.26144
109	1	-7.94485	-2.34425	-2.3814		109	1	-5.45	-3.62361	-2.25694
110	1	-6.61876	-3.15466	-1.53503		110	1	-4.17159	-2.91727	-1.2656
111	1	-7.98007	-2.49036	-0.62406		111	1	-5.52877	-3.72372	-0.48712

112	1	0.750706	-2.94397	0.343461		112	1	0.523307	-2.80888	0.602876
113	1	1.643662	-5.26425	-0.20304		113	1	1.298624	-5.21544	0.308378
114	1	2.267041	-3.98359	-1.24089		114	1	2.0003	-4.08039	-0.84291
115	1	3.285693	-4.6374	0.048878		115	1	2.968462	-4.65122	0.522885
116	1	2.35094	-4.36088	2.537927		116	1	2.016796	-4.08835	2.950819
117	1	0.682617	-4.70401	2.05257		117	1	0.332331	-4.36975	2.480257
118	1	1.087056	-3.15812	2.819365		118	1	0.832668	-2.78504	3.096778

Table S12. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **2a**.

HOMO is 196					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R (length)**	**Osc. Strength**	**Major contribs**
1	32767.1	305.2	-5.5149	0.0005	H-2->L+1 (88%)
2	33072.0	302.4	-9.356	0.0007	H-3->LUMO (83%)
3	33387.3	299.5	-27.5631	0.0036	H-4->L+4 (46%), H-1->L+4 (40%)
4	33827.7	295.6	-4.5696	0.0004	H-5->L+2 (41%), H-2->L+2 (48%)
5	34201.9	292.4	-11.866	0.0017	H-6->LUMO (16%), H-6->L+3 (21%), H-3->L+3 (54%)
6	36502.2	274.0	3.2147	0.0164	HOMO->L+2 (87%)
7	36941.8	270.7	20.7058	0.0458	H-1->LUMO (46%), H-1->L+3 (49%)
8	38025.0	263.0	1.3608	0.0007	HOMO->LUMO (98%)
9	38200.8	261.8	-8.1891	0.0452	H-4->LUMO (31%), H-1->LUMO (16%), H-1->L+3 (22%), H-1->L+4 (25%)
10	38504.1	259.7	-14.2185	0.0211	H-4->L+4 (38%), H-1->LUMO (11%), H-1->L+3 (14%), H-1->L+4 (29%)
11	38908.2	257.0	56.9744	0.343	HOMO->L+1 (79%)
12	39601.8	252.5	0.5128	0.0005	H-1->L+1 (96%)
13	40002.7	250.0	-3.4375	0.0037	H-6->LUMO (74%), H-3->L+3 (17%)
14	40148.7	249.1	15.6259	0.0594	H-5->L+1 (72%)
15	40251.9	248.4	-16.7462	0.0081	H-5->L+2 (49%), H-2->L+2 (35%)
16	40356.8	247.8	-31.6455	0.1424	H-6->L+3 (14%), H-4->LUMO (48%), H-1->LUMO (12%)
17	40531.0	246.7	-25.2566	0.0126	HOMO->L+3 (34%), HOMO->L+4 (61%)
18	40906.8	244.5	-0.3952	0.0005	HOMO->L+3 (64%), HOMO->L+4 (35%)
19	41279.5	242.3	7.9179	0.0154	H-3->L+4 (76%)
20	41419.0	241.4	-0.011	0	H-2->LUMO (99%)
21	41434.3	241.3	0.0235	0	H-1->L+2 (99%)
22	42083.6	237.6	38.8127	0.1125	H-6->L+3 (44%), H-4->LUMO (12%), H-3->L+3 (19%)
23	42661.1	234.4	0.6174	0.0006	H-3->L+1 (95%)
24	43371.7	230.6	3.6499	0.0026	H-4->L+3 (89%)
25	43663.6	229.0	0.0299	0.0001	H-4->L+1 (98%)
26	43948.3	227.5	0.0811	0	H-2->L+3 (72%), H-2->L+4 (28%)
27	44248.4	226.0	0.0108	0	H-2->L+3 (28%), H-2->L+4 (72%)
28	44341.1	225.5	-0.0046	0	H-3->L+2 (99%)
29	44738.0	223.5	0.0652	0.0001	H-5->LUMO (99%)
30	45561.5	219.5	-0.0129	0	H-4->L+2 (99%)
31	45987.3	217.5	-2.1296	0.0027	H-6->L+1 (27%), H-6->L+4 (63%)

32	46384.1	215.6	4.889	0.0009	H-7->L+1 (12%), H-6->L+1 (60%), H-6->L+4 (23%)
33	46602.7	214.6	8.1884	0.0075	H-7->L+1 (78%), H-6->L+1 (12%)
34	46707.6	214.1	7.682	0.008	HOMO->L+5 (72%), HOMO->L+7 (22%)
35	46944.7	213.0	1.0927	0.0013	H-7->LUMO (98%)
36	47311.7	211.4	-0.0094	0	H-5->L+3 (84%), H-5->L+4 (15%)
37	47369.7	211.1	2.6212	0.0016	H-1->L+5 (74%), H-1->L+6 (18%)
38	47456.0	210.7	-13.3396	0.0069	H-9->L+1 (30%), H-8->L+1 (52%)
39	47629.5	210.0	-0.1739	0.0003	H-5->L+3 (15%), H-5->L+4 (84%)
40	48014.2	208.3	-0.0346	0	H-6->L+2 (99%)
41	48409.4	206.6	-2.7667	0.0032	HOMO->L+6 (83%)
42	48561.8	205.9	-2.5738	0.0007	H-10->LUMO (14%), H-8->LUMO (75%)
43	48623.1	205.7	-7.1649	0.0022	H-13->LUMO (10%), H-10->LUMO (37%), H-9->LUMO (17%), H-8->LUMO (24%)
44	48851.4	204.7	0.3487	0.0005	H-9->L+1 (44%), H-8->L+1 (43%)
45	49035.3	203.9	0.4173	0.0015	H-7->L+2 (76%), HOMO->L+7 (11%)
46	49067.5	203.8	2.8282	0.0011	H-7->L+2 (20%), HOMO->L+5 (10%), HOMO->L+7 (41%), HOMO->L+8 (17%)
47	49337.7	202.7	2.4634	0.0016	H-1->L+5 (11%), H-1->L+6 (66%), H-1->L+7 (11%)
48	49439.4	202.3	2.1844	0.0008	HOMO->L+7 (13%), HOMO->L+8 (59%)
49	49608.7	201.6	0.8514	0.0009	H-7->L+3 (50%), H-7->L+4 (49%)
50	49693.4	201.2	-0.8909	0.0038	H-2->L+5 (51%), H-2->L+7 (31%)

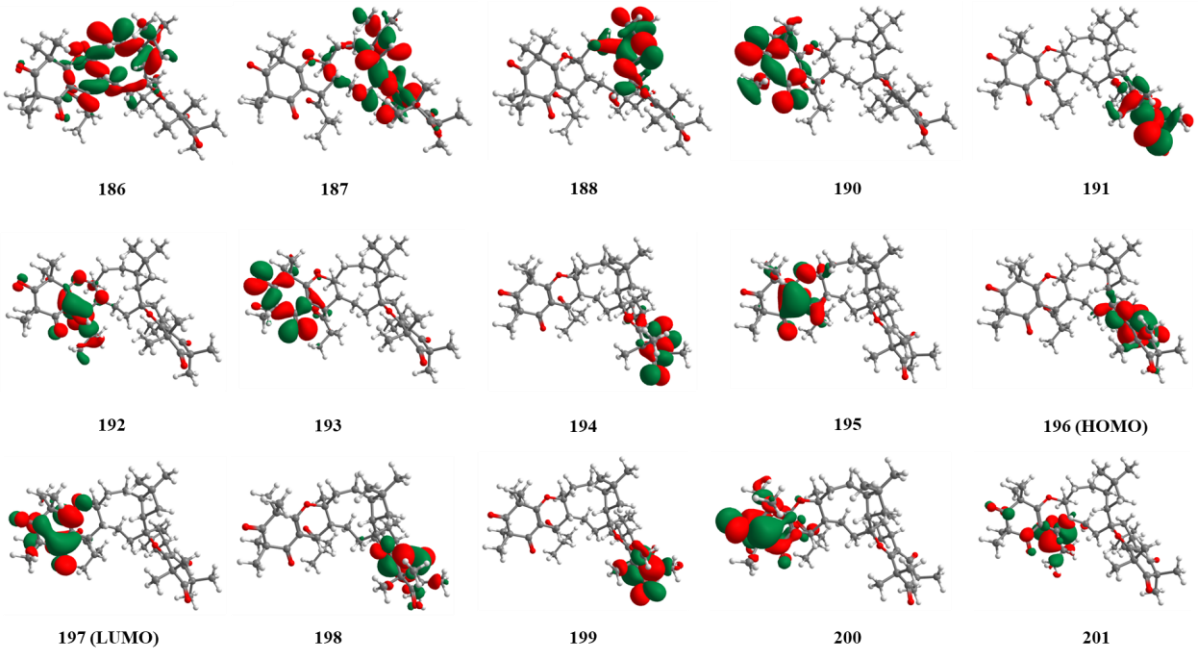


Figure S7. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **2a**.

Table S13. Key transitions and their related rotatory and oscillator strengths of dominant conformer of **2b**.

HOMO is 196					
No.	**Energy (cm^{-1})**	**Wavelength (nm)**	**R (length)**	**Osc. Strength**	**Major contribs**

1	32633.2	306.4	-10.2165	0.0007	H-2->L+1 (86%)
2	33061.5	302.5	-9.681	0.0007	H-3->LUMO (83%)
3	33401.8	299.4	-27.3125	0.0036	H-4->L+4 (39%), H-1->L+4 (32%)
4	34173.7	292.6	-22.6141	0.0065	H-5->L+1 (24%), H-5->L+3 (16%), H-2->L+3 (40%)
5	34214.8	292.3	-11.0246	0.0018	H-6->LUMO (17%), H-6->L+2 (20%), H-3->L+2 (54%)
6	36218.3	276.1	27.8038	0.0511	HOMO->L+1 (51%), HOMO->L+3 (34%)
7	36940.2	270.7	16.2467	0.0467	H-1->LUMO (48%), H-1->L+2 (47%)
8	37898.4	263.9	0.3643	0.0002	HOMO->LUMO (99%)
9	38204.9	261.7	-7.6733	0.042	H-4->LUMO (31%), H-1->LUMO (15%), H-1->L+2 (23%), H-1->L+4 (21%)
10	38496.0	259.8	-14.2291	0.021	H-4->L+4 (30%), H-1->LUMO (11%), H-1->L+2 (15%), H-1->L+4 (22%)
11	38790.4	257.8	-6.983	0.254	HOMO->L+1 (36%), HOMO->L+3 (46%)
12	39292.1	254.5	0.0962	0.0002	H-1->L+1 (96%)
13	39969.6	250.2	-2.6361	0.0072	H-5->L+1 (60%), H-2->L+3 (31%)
14	39993.0	250.0	-2.0772	0.003	H-6->LUMO (74%), H-3->L+2 (17%)
15	40332.6	247.9	-7.2771	0.1303	H-6->L+2 (12%), H-4->LUMO (44%), H-1->LUMO (11%)
16	40386.6	247.6	-25.6266	0.022	HOMO->L+2 (26%), HOMO->L+4 (56%)
17	40818.9	245.0	0.1588	0.0001	HOMO->L+2 (70%), HOMO->L+4 (24%)
18	41279.5	242.3	7.9359	0.0156	H-3->L+3 (15%), H-3->L+4 (62%)
19	41410.9	241.5	-0.0338	0	H-2->LUMO (99%)
20	41998.1	238.1	45.892	0.0815	H-5->L+3 (44%), H-5->L+4 (10%)
21	42090.0	237.6	-27.2301	0.0148	H-1->L+3 (72%), H-1->L+4 (15%)
22	42124.7	237.4	59.3056	0.1019	H-6->L+2 (43%), H-4->LUMO (11%), H-3->L+2 (18%)
23	42326.4	236.3	4.4767	0.0036	H-3->L+1 (91%)
24	43337.0	230.7	0.0773	0.0002	H-4->L+1 (98%)
25	43395.0	230.4	3.7683	0.0027	H-4->L+2 (89%)
26	43965.3	227.5	0.1284	0	H-2->L+2 (65%), H-2->L+4 (29%)
27	44264.5	225.9	0.012	0	H-2->L+2 (34%), H-2->L+3 (12%), H-2->L+4 (53%)
28	44974.3	222.3	0.0946	0.0001	H-5->LUMO (99%)
29	45012.2	222.2	-0.017	0	H-3->L+3 (81%), H-3->L+4 (19%)
30	45854.2	218.1	-1.0811	0.0014	H-6->L+1 (68%), H-6->L+4 (20%)
31	46178.5	216.6	1.6847	0.0011	H-6->L+1 (16%), H-6->L+4 (32%), H-4->L+3 (32%)
32	46197.0	216.5	1.3638	0.0004	H-6->L+4 (16%), H-4->L+3 (50%), H-4->L+4 (14%)
33	46355.1	215.7	5.9956	0.0048	H-7->L+1 (80%)
34	46488.2	215.1	8.3964	0.01	HOMO->L+5 (75%), HOMO->L+7 (15%)
35	46922.9	213.1	1.4345	0.0012	H-7->LUMO (98%)
36	47325.4	211.3	1.9446	0.0027	H-1->L+5 (66%), H-1->L+6 (13%)
37	47327.8	211.3	-12.193	0.0063	H-9->L+1 (25%), H-8->L+1 (48%)
38	47578.6	210.2	-0.1398	0.0001	H-5->L+2 (78%), H-5->L+4 (18%)
39	47876.3	208.9	0.0225	0.0002	H-5->L+2 (21%), H-5->L+3 (14%), H-5->L+4 (64%)
40	48219.9	207.4	-3.5072	0.0049	HOMO->L+6 (83%)
41	48534.4	206.0	-0.7644	0.0002	H-8->LUMO (94%)
42	48615.1	205.7	-10.2508	0.0028	H-13->LUMO (11%), H-10->LUMO (48%), H-9->LUMO (19%)

43	48665.9	205.5	-1.9611	0.001	H-9->L+1 (40%), H-8->L+1 (36%)
44	48693.3	205.4	-0.0513	0.0002	H-6->L+3 (72%), H-6->L+4 (18%)
45	48964.3	204.2	0.8815	0.0007	HOMO->L+8 (75%)
46	49214.3	203.2	0.2124	0.0005	HOMO->L+5 (13%), HOMO->L+7 (70%)
47	49330.5	202.7	3.2656	0.0017	H-1->L+5 (10%), H-1->L+6 (68%), H-1->L+8 (14%)
48	49524.9	201.9	0.8388	0.0033	H-2->L+5 (57%), H-2->L+7 (25%)
49	49561.2	201.8	-0.9003	0.0006	H-7->L+2 (19%), H-7->L+3 (72%)
50	49653.1	201.4	2.4169	0.0009	H-7->L+2 (29%), H-7->L+3 (19%), H-7->L+4 (48%)

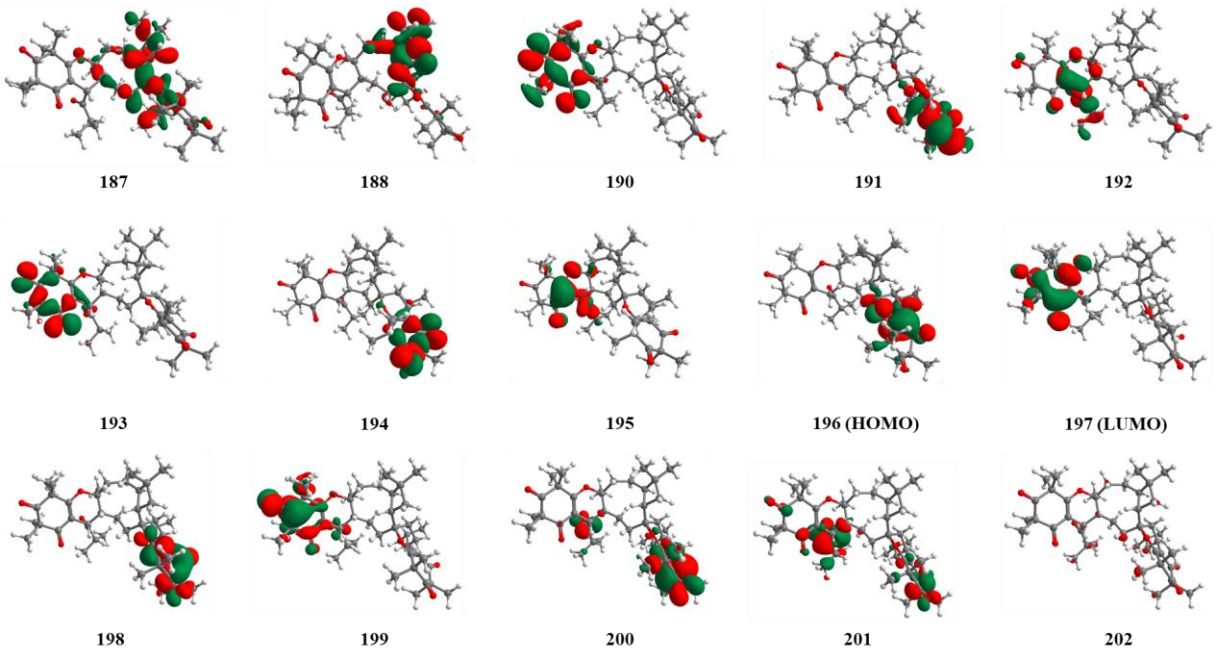


Figure S8. Key molecular orbitals involved in important transitions regarding the ECD spectrum of dominant conformer of **2b**.

4. HRMS, UV, IR, and NMR spectra of the natural 1–2, 7, and 12–15

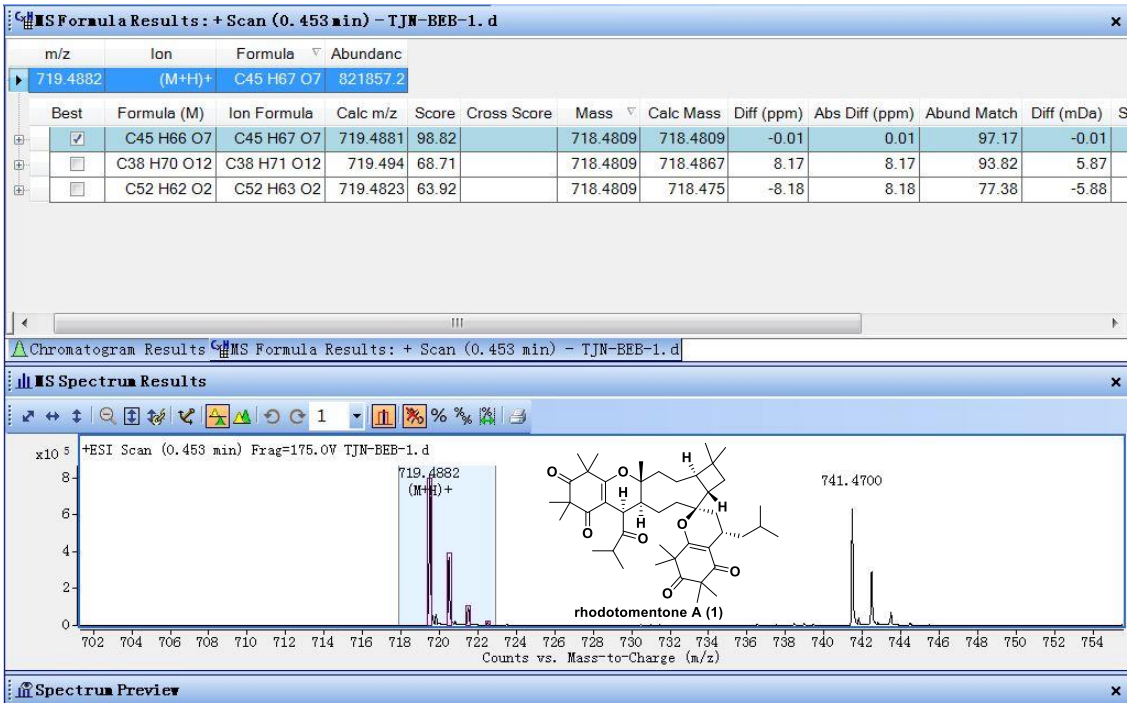


Figure S9. HR-ESI-MS spectrum of rhodotomentone A (**1**).

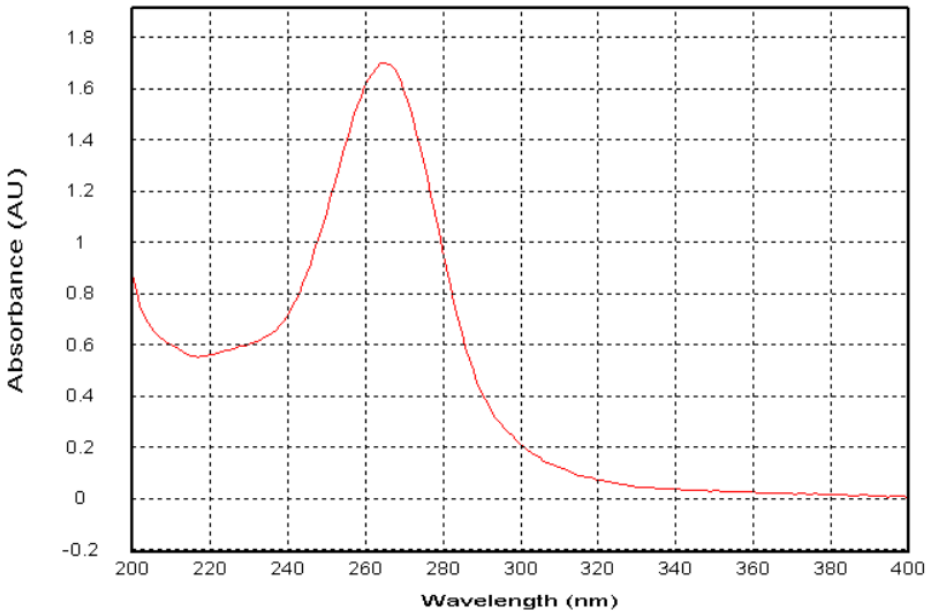


Figure S10. UV spectrum of rhodotomentone A (**1**) in MeOH.

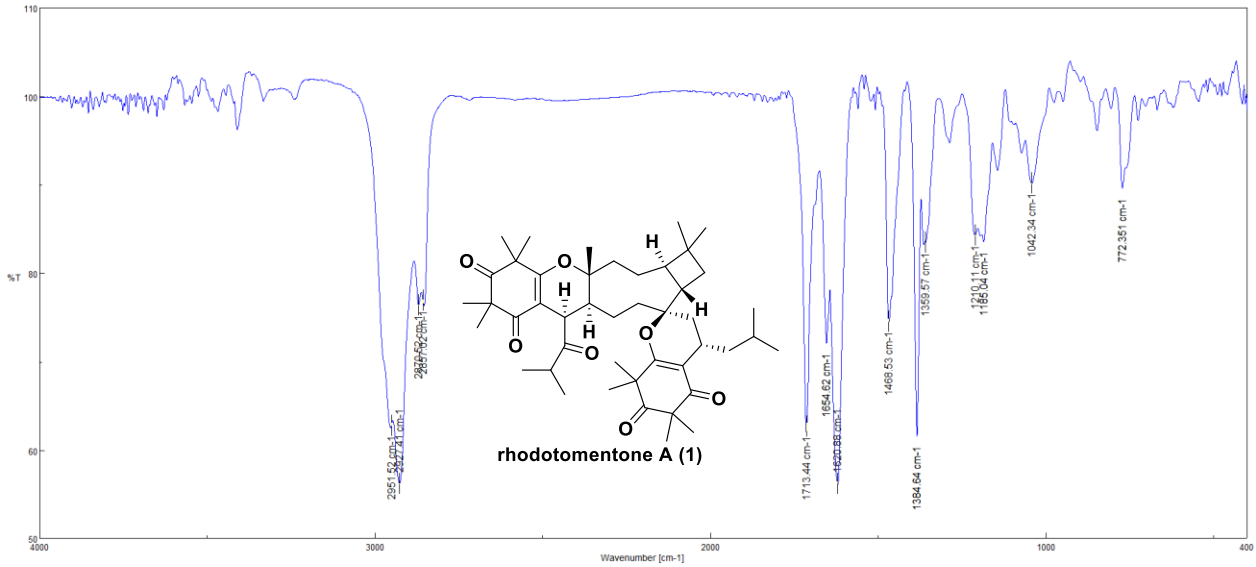


Figure S11. IR spectrum of rhodotomentone A (**1**) (KBr disc).

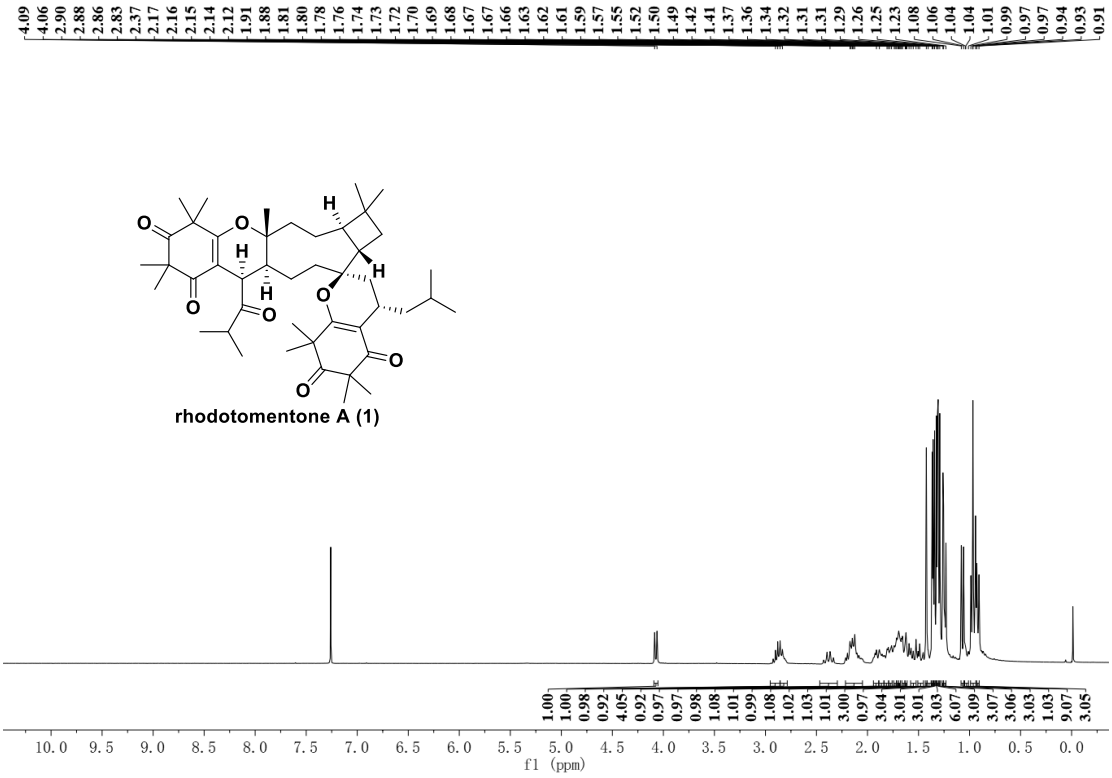


Figure S12. ^{1}H NMR spectrum (300 MHz) of rhodotomentone A (**1**) in $CDCl_3$.

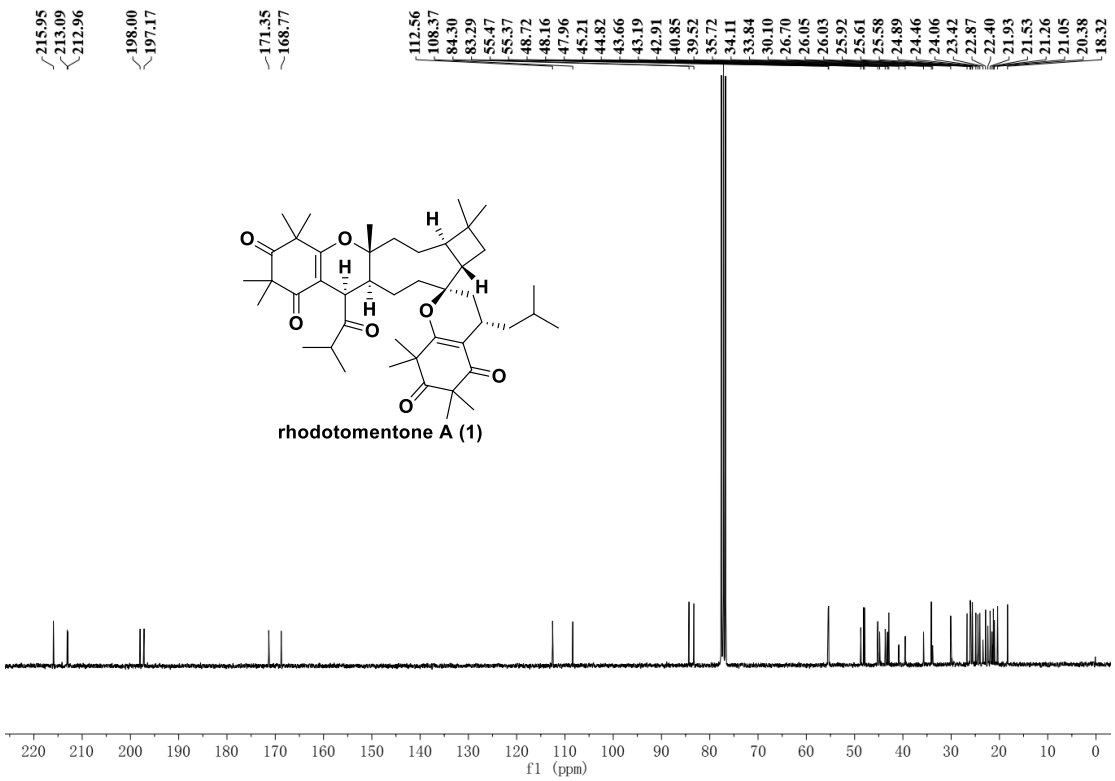


Figure S13. ^{13}C NMR spectrum (75 MHz) of rhodotomentone A (**1**) in $CDCl_3$.

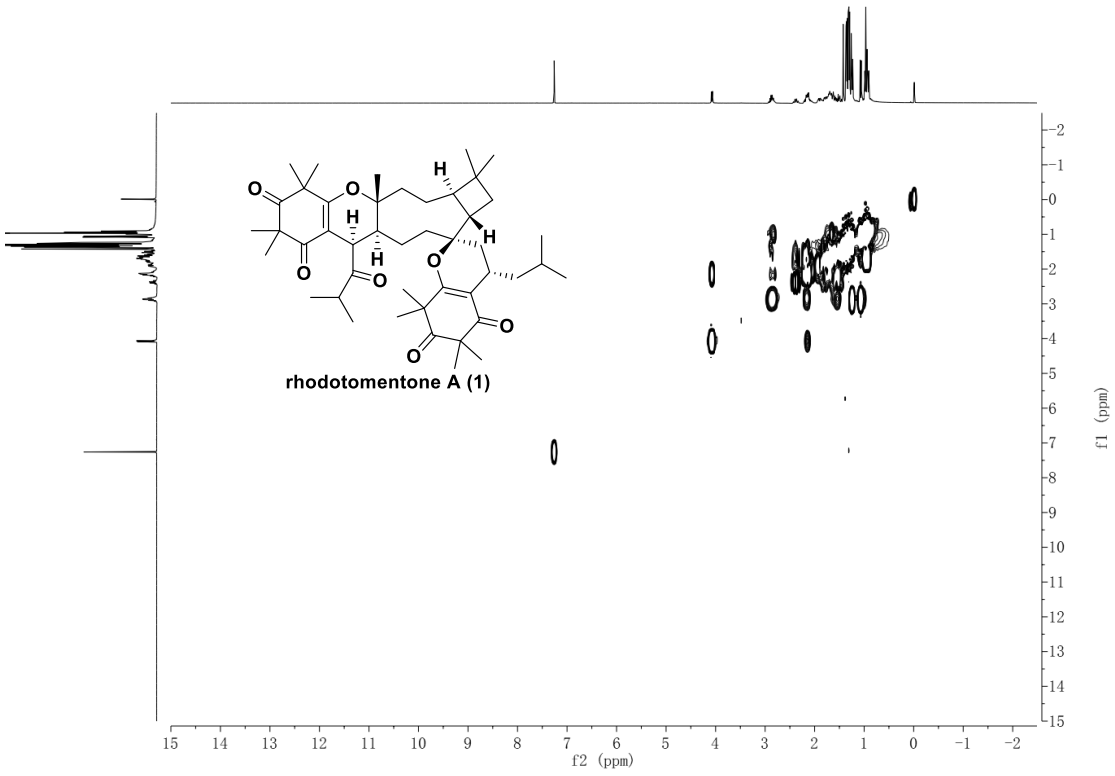


Figure S14. $^{1}H–^{1}H$ COSY spectrum of rhodotomentone A (**1**) in $CDCl_3$.

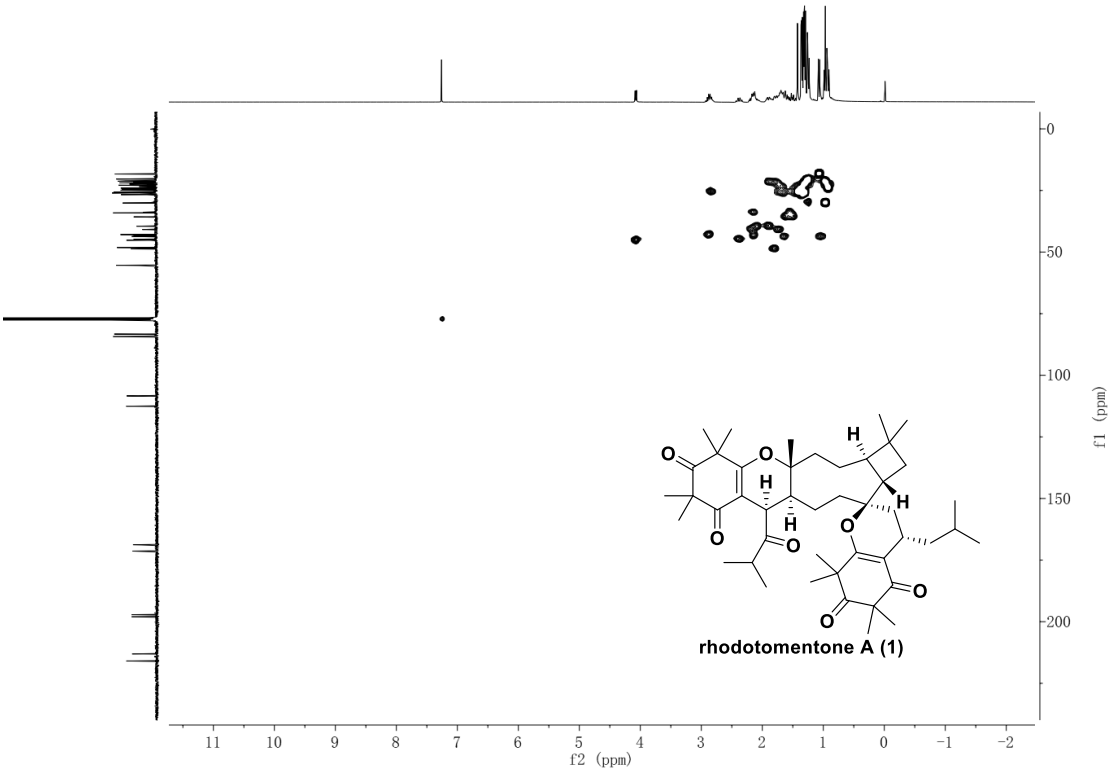


Figure S15. HSQC spectrum of rhodotomentone A (**1**) in $CDCl_3$.

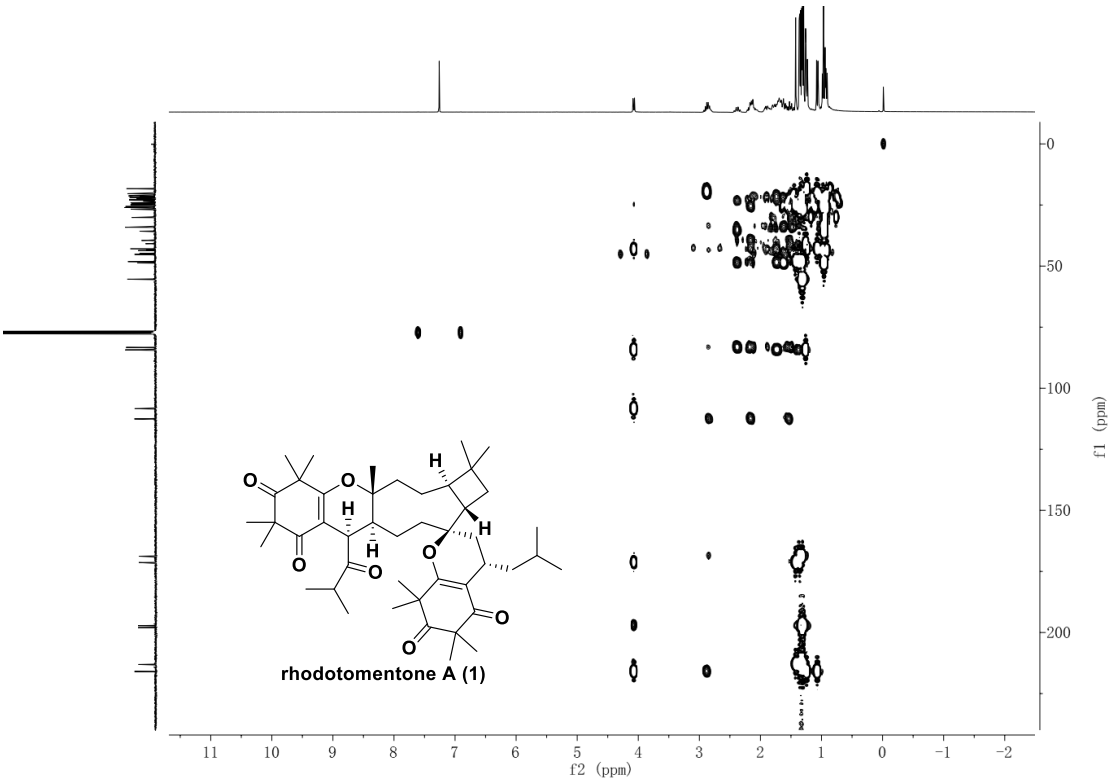


Figure S16. HMBC spectrum of rhodotomentone A (**1**) in $CDCl_3$.

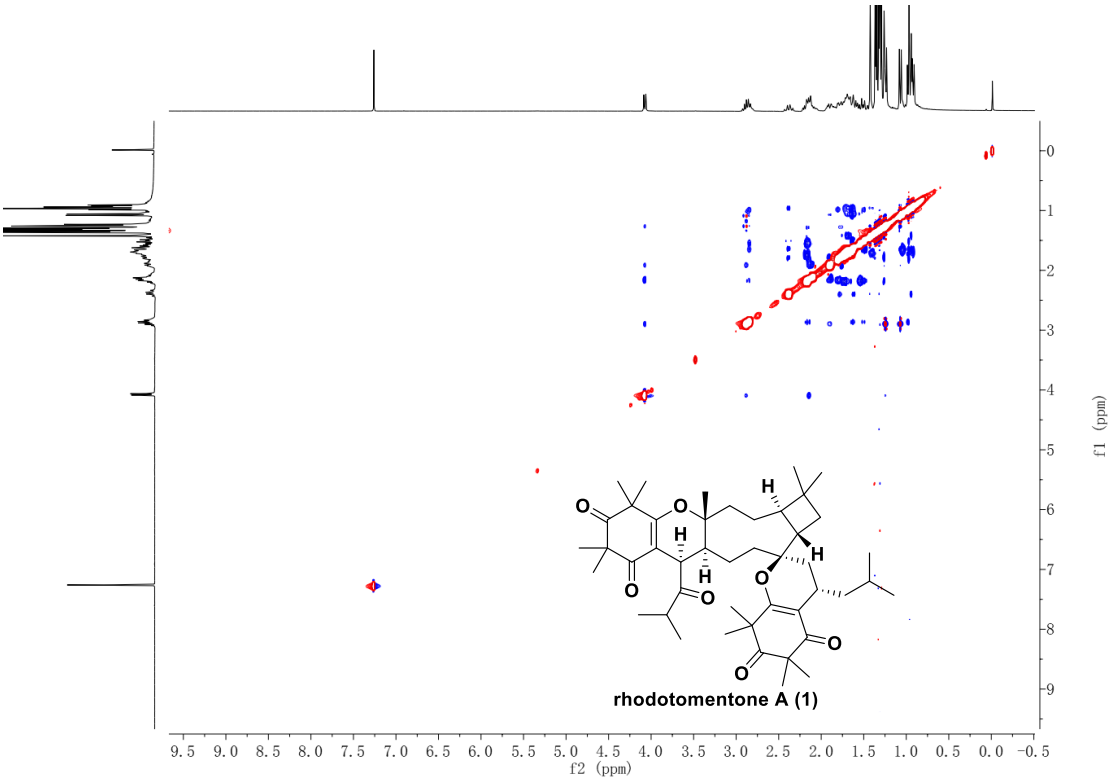


Figure S17. NOESY spectrum of rhodotomentone A (**1**) in $CDCl_3$.

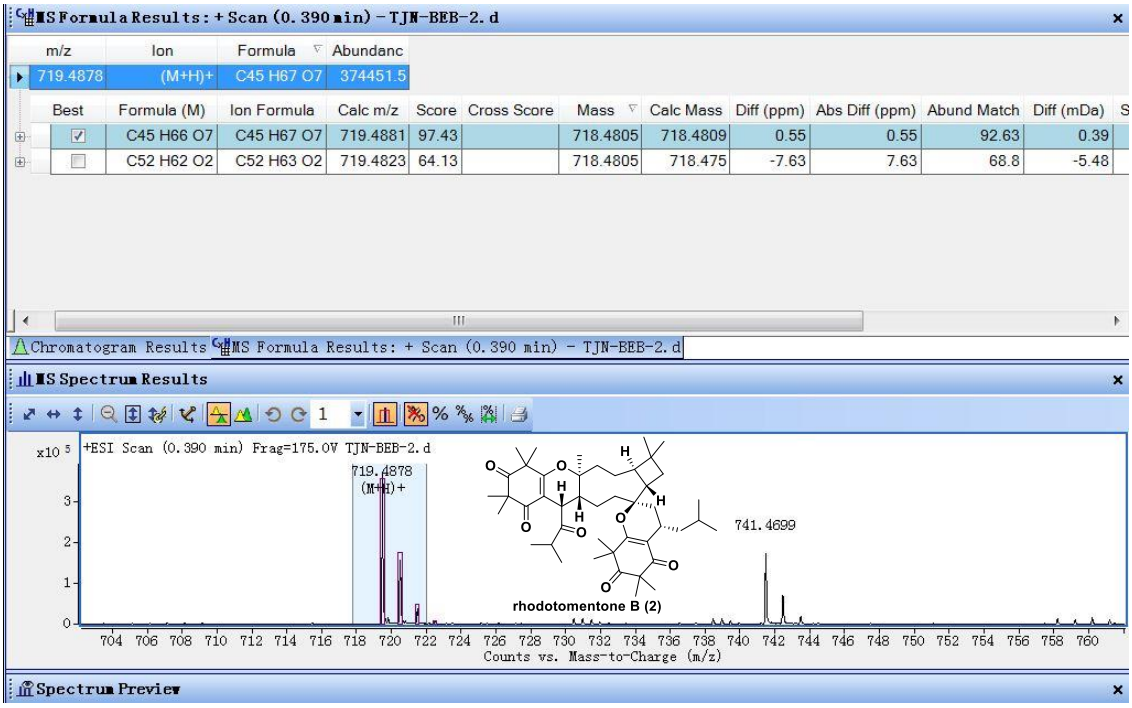


Figure S18. HR-ESI-MS spectrum of rhodotomentone B (**2**).

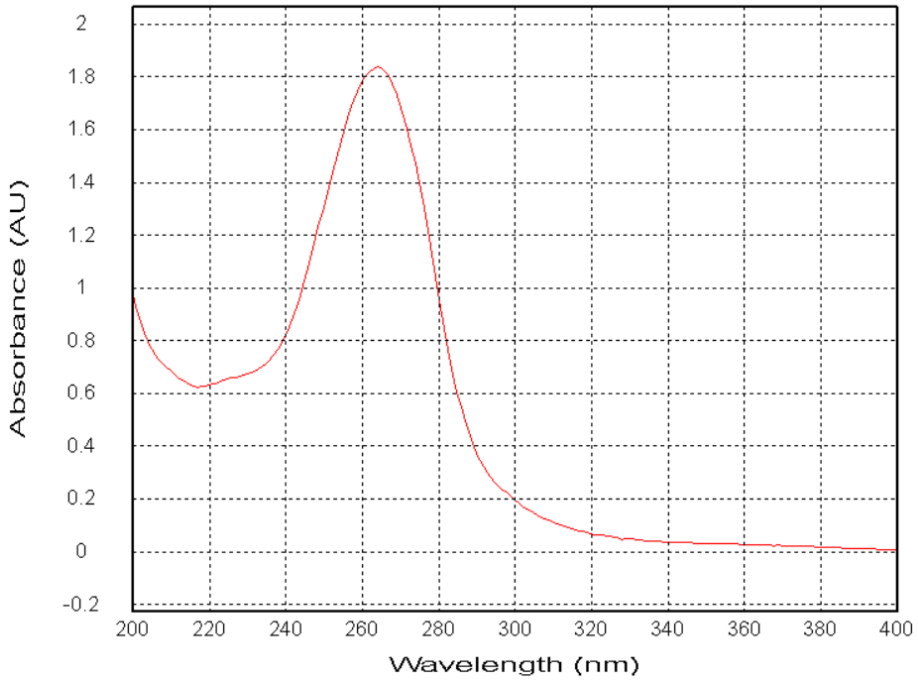


Figure S19. UV spectrum of rhodotomentone B (**2**) in MeOH.

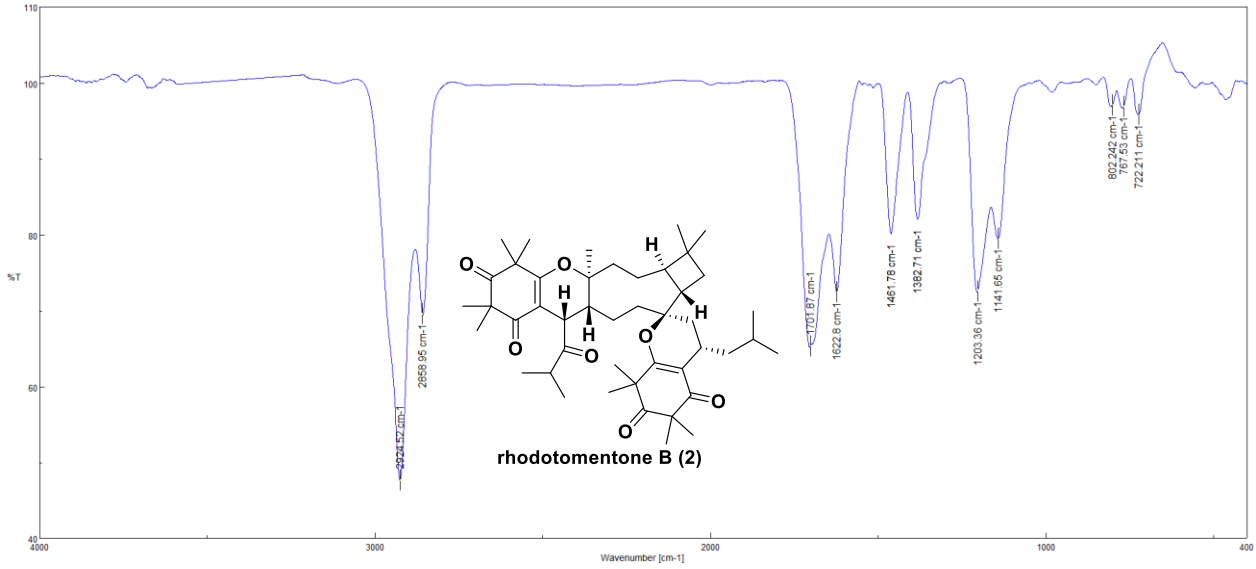


Figure S20. IR spectrum of rhodotomentone B (**2**) (KBr disc).

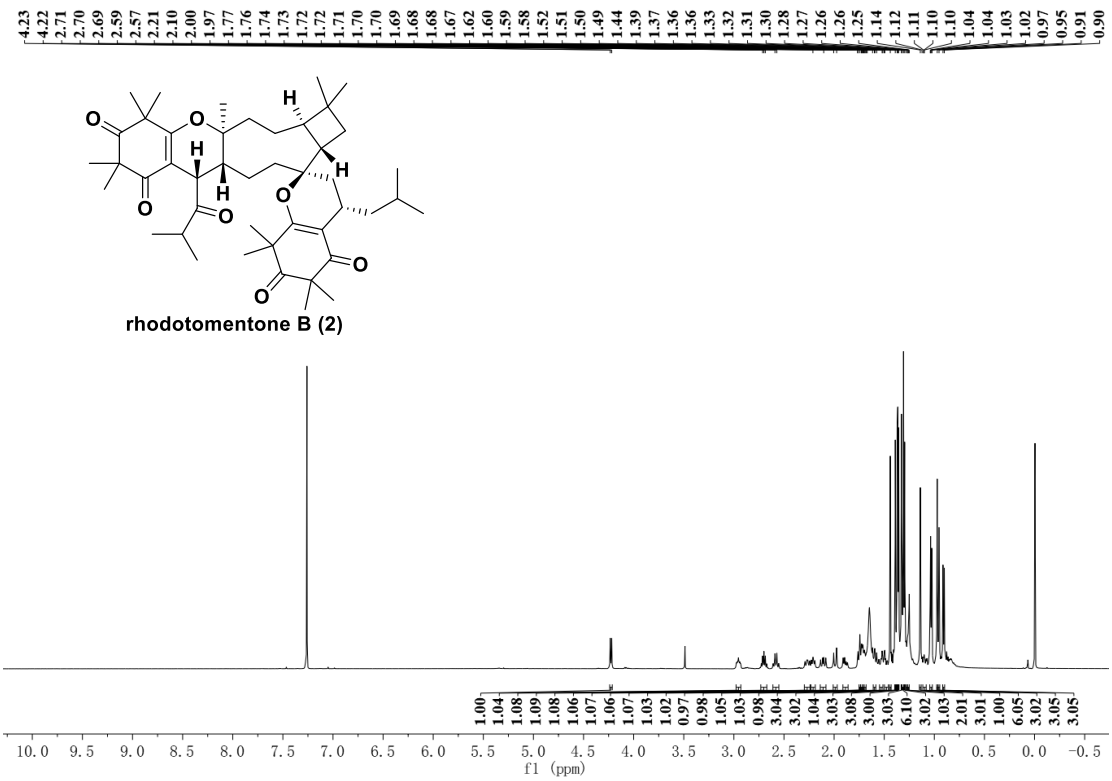


Figure S21. ^{1}H NMR spectrum (500 MHz) of rhodotomentone B (**2**) in $CDCl_3$.

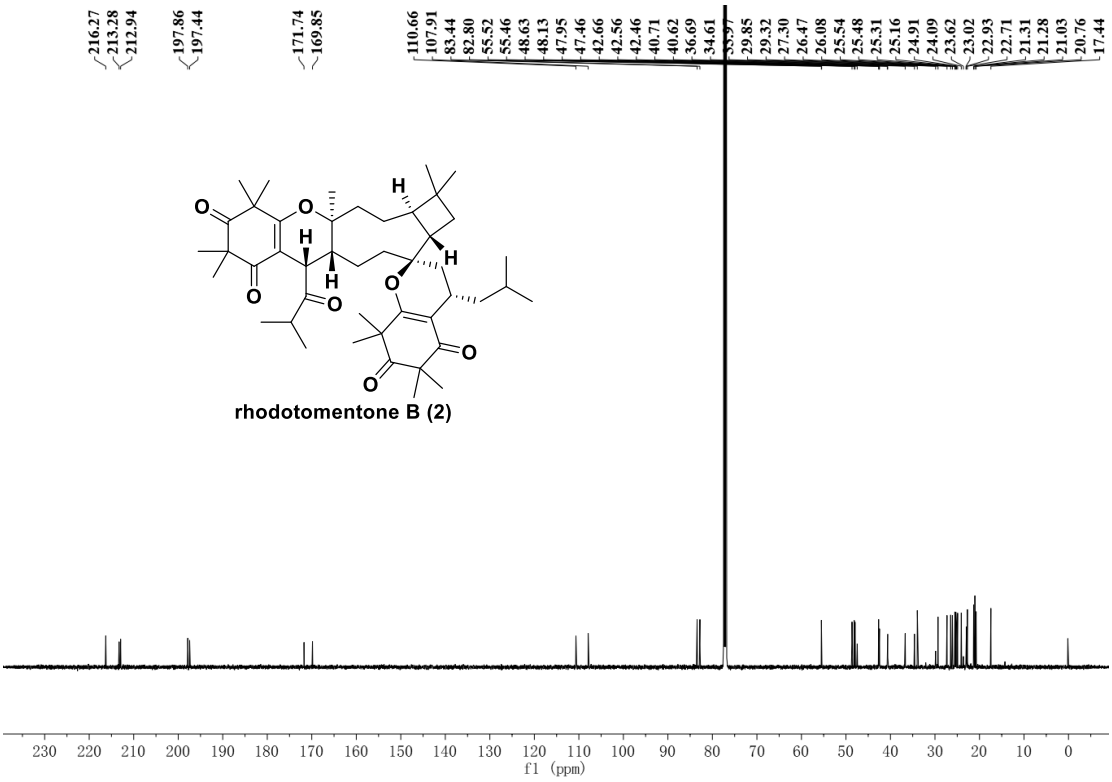


Figure S22. ^{13}C NMR spectrum (125 MHz) of rhodotomentone B (**2**) in $CDCl_3$.

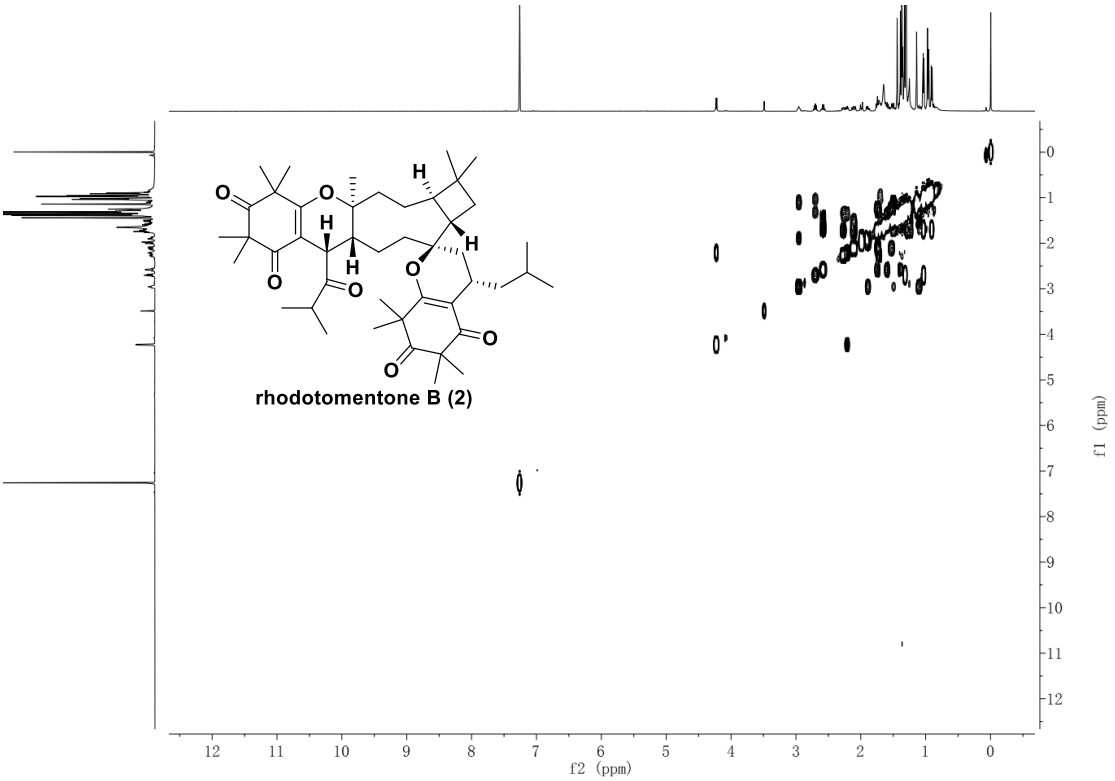


Figure S23. ^{1}H–^{1}H COSY spectrum of rhodotomentone B (**2**) in $CDCl_3$.

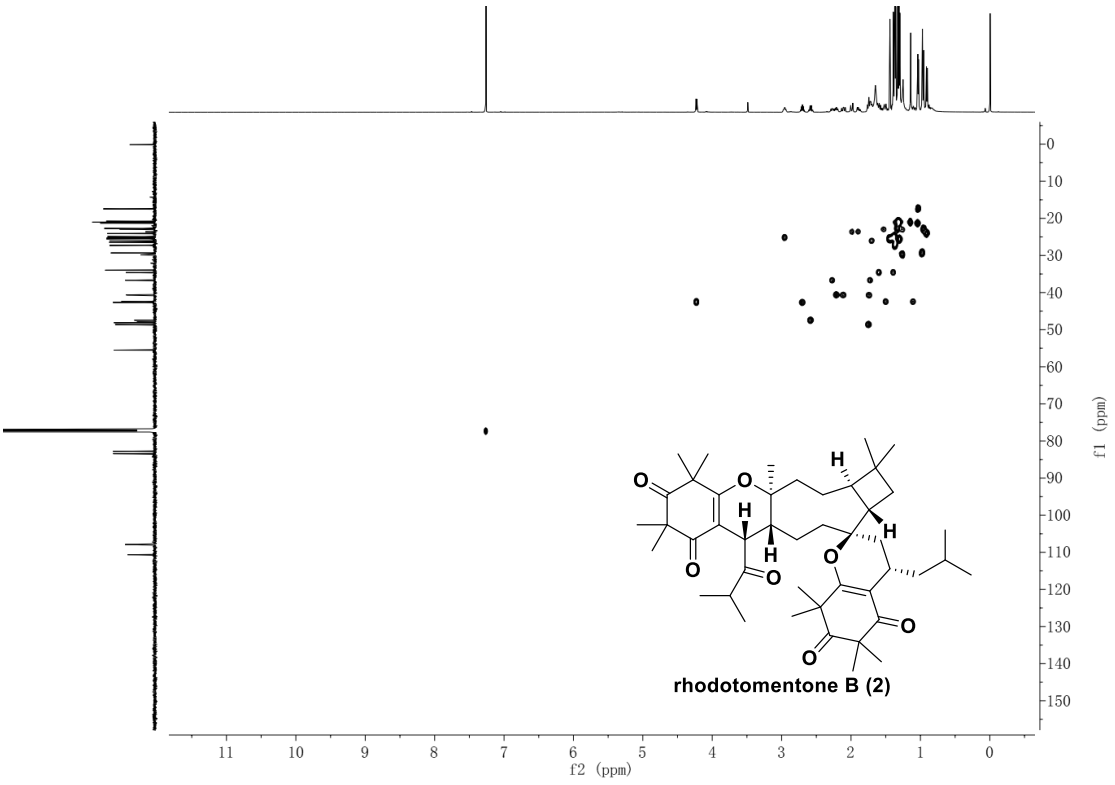


Figure S24. HSQC spectrum of rhodotomentone B (**2**) in $CDCl_3$.

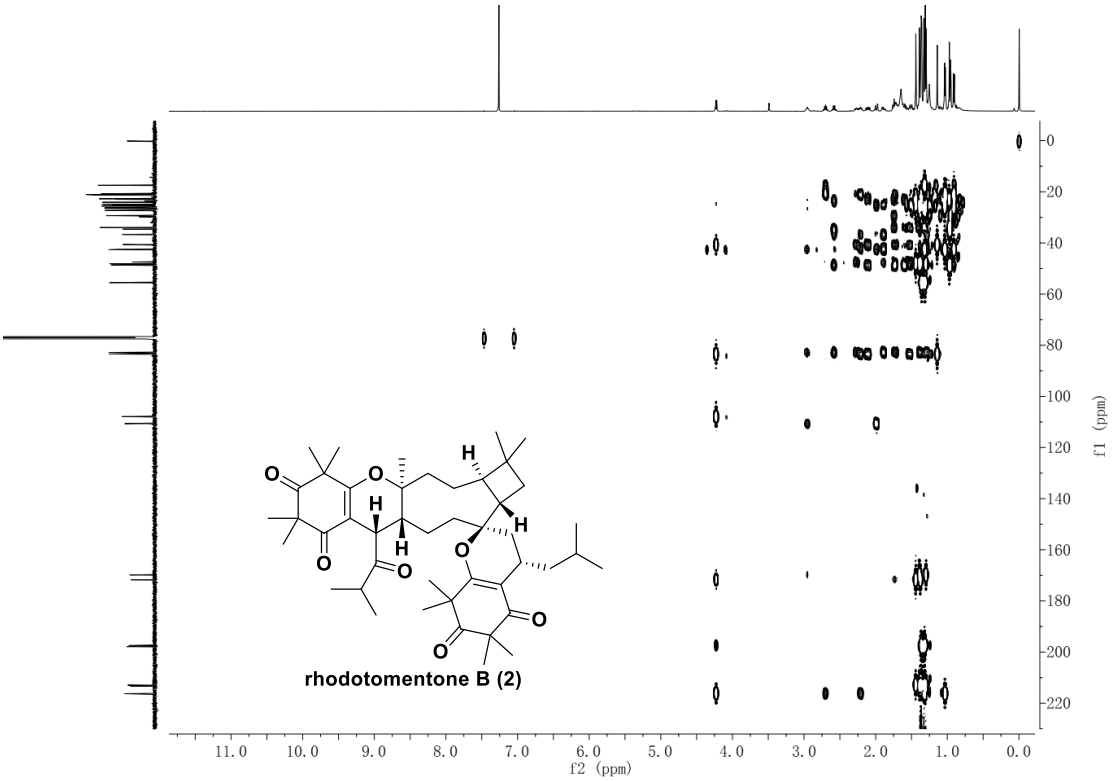


Figure S25. HMBC spectrum of rhodotomentone B (**2**) in $CDCl_3$.

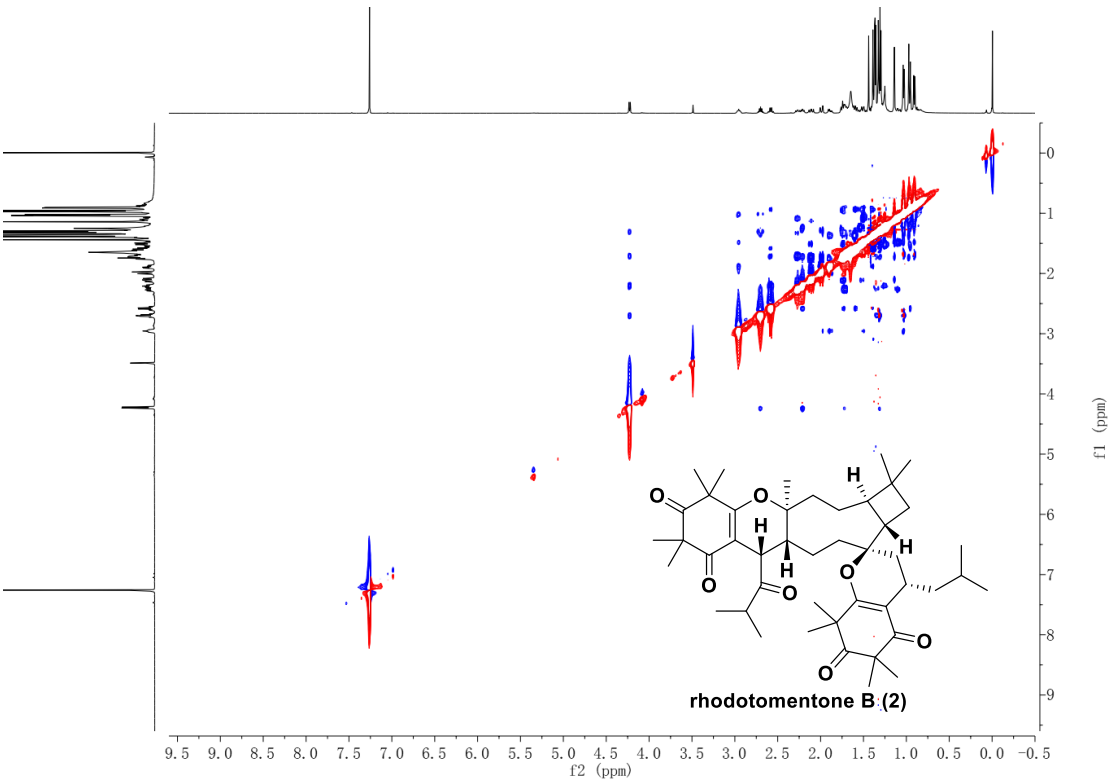


Figure S26. NOESY spectrum of rhodotomentone B (**2**) in $CDCl_3$.

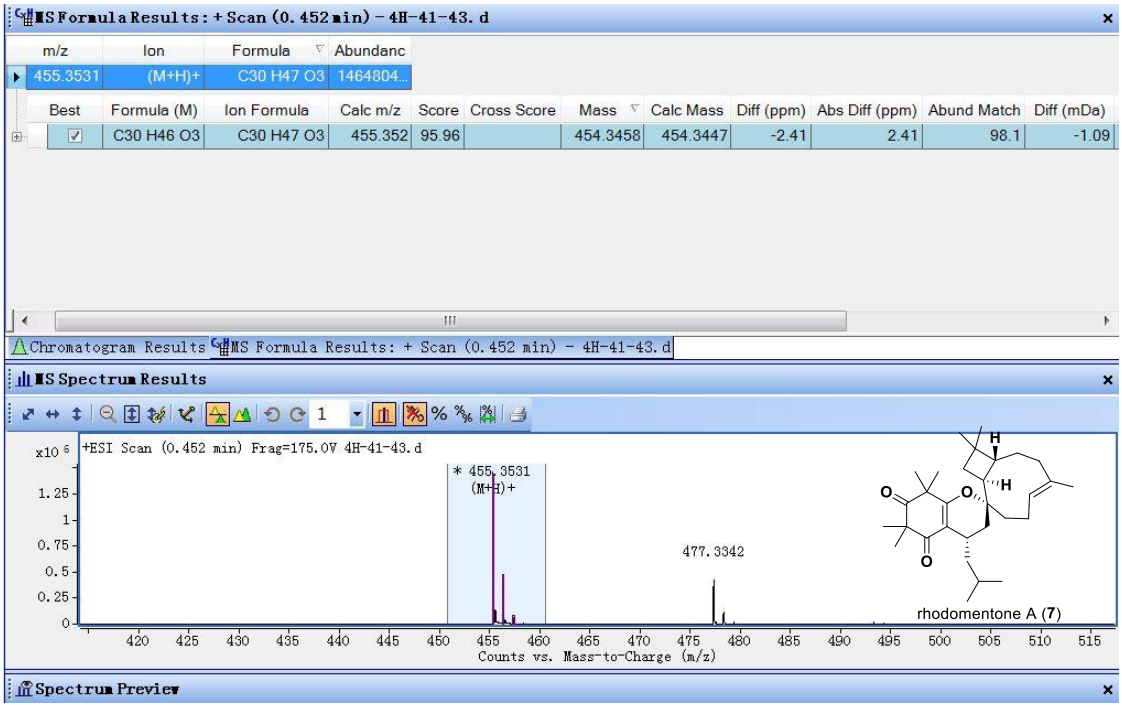


Figure S27. HR-ESI-MS spectrum of rhodomentone A (**7**).

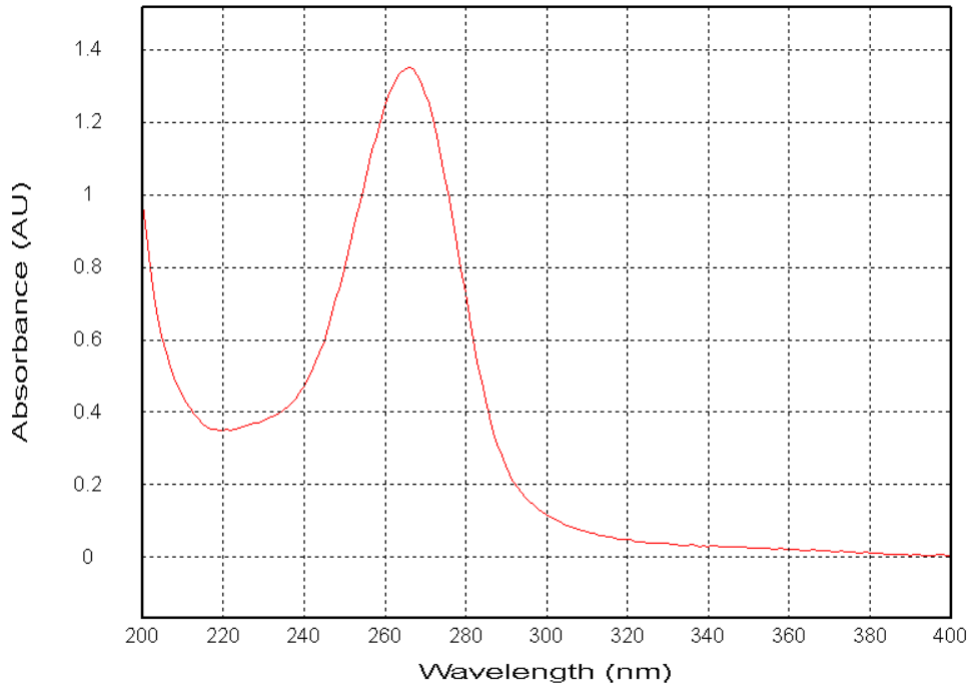


Figure S28. UV spectrum of rhodomentone A (**7**) in MeOH.

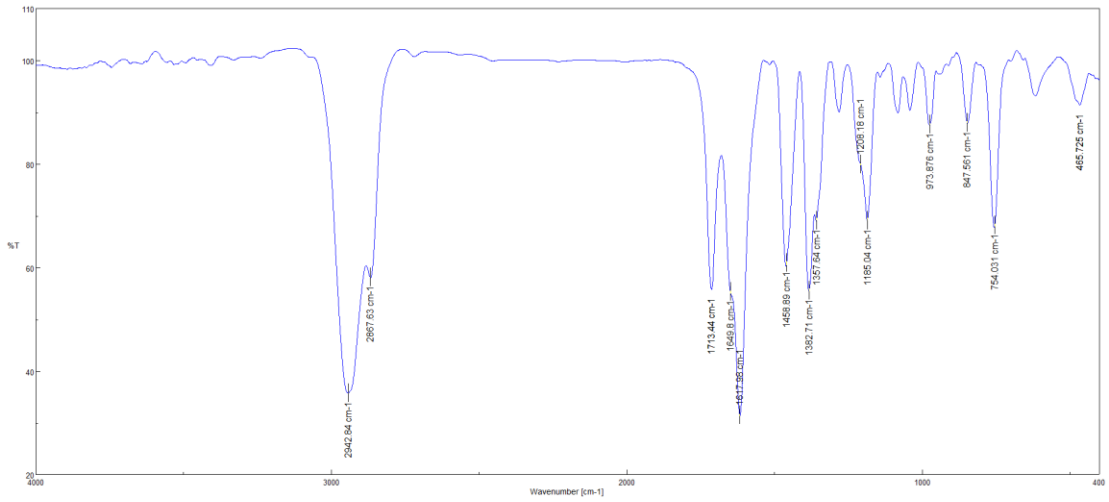


Figure S29. IR spectrum of rhodomentone A (**7**) (KBr disc).

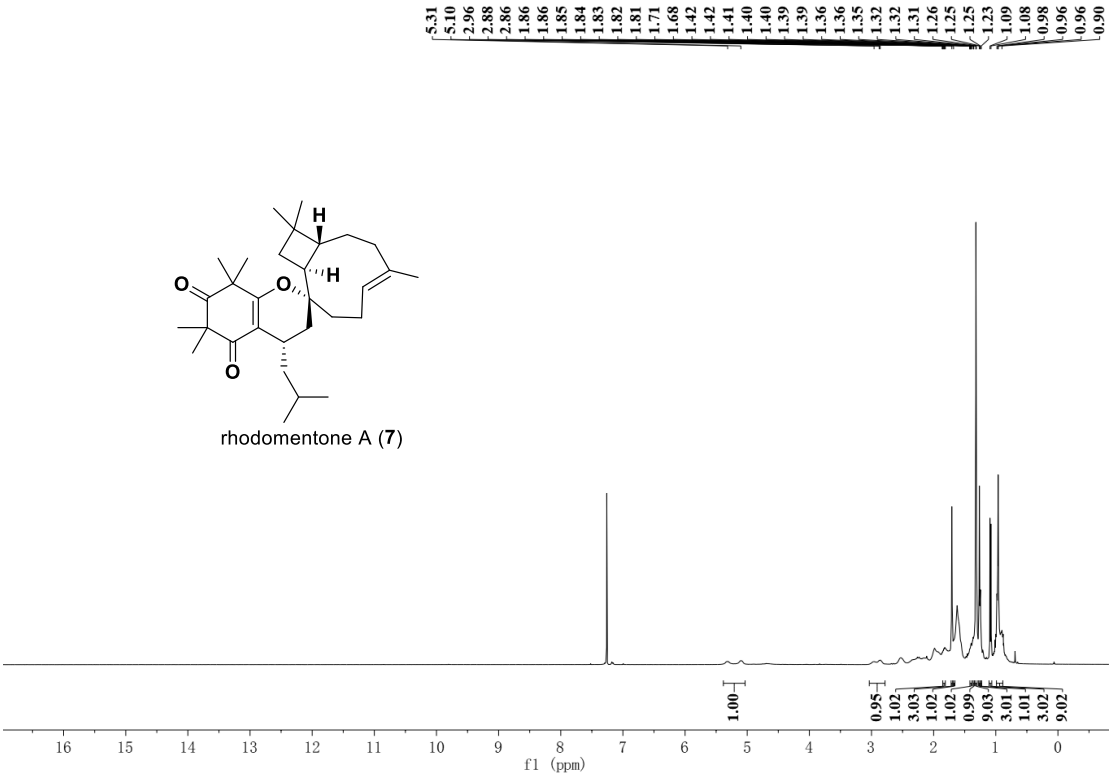


Figure S30. ^{1}H NMR spectrum (400 MHz) of rhodomentone A (**7**) in $CDCl_3$.

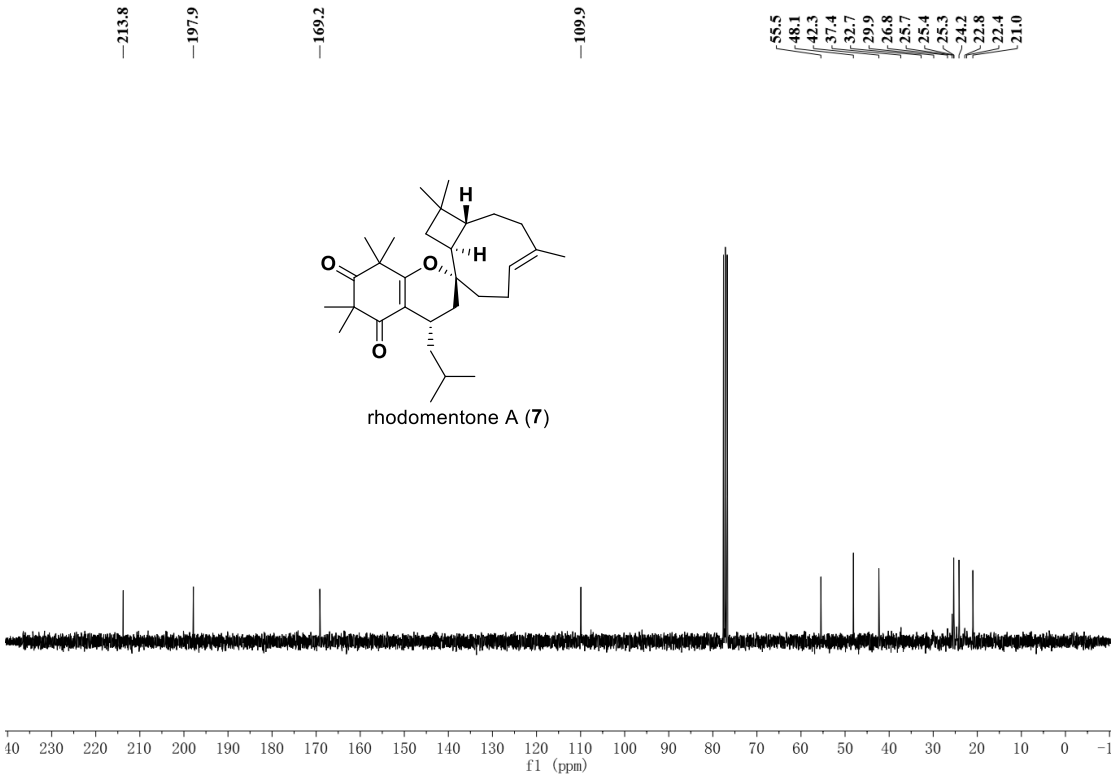


Figure S31. ^{13}C NMR spectrum (100 MHz) of rhodomentone A (**7**) in $CDCl_3$.

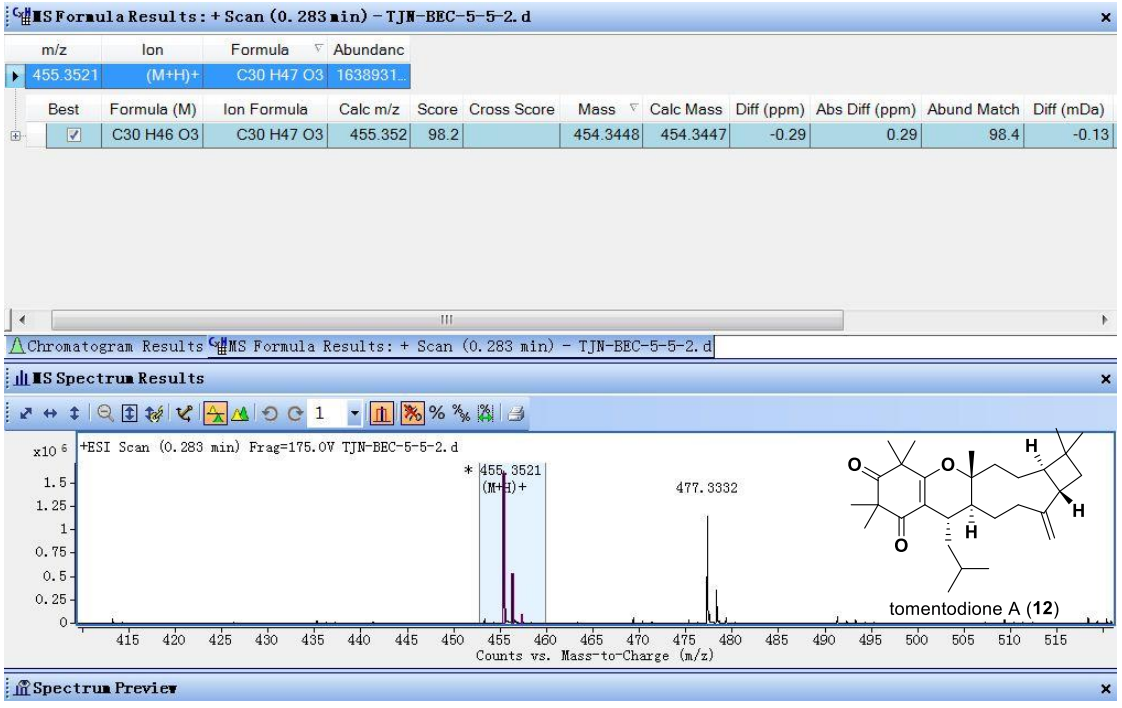


Figure S32. HR-ESI-MS spectrum of tomentodione A (**12**).

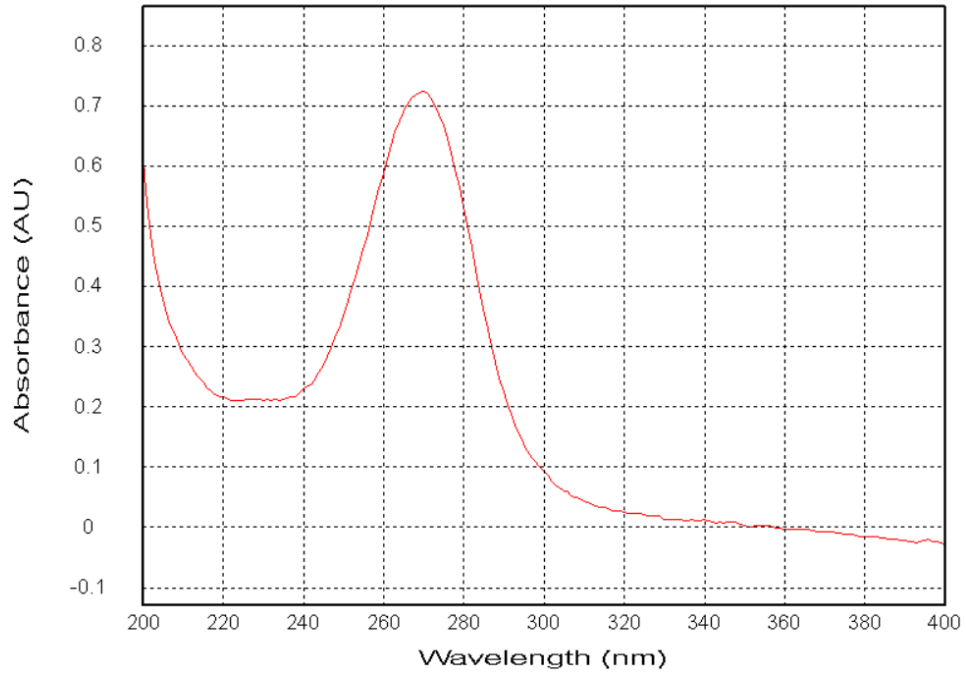


Figure S33. UV spectrum of tomentodione A (**12**) in MeOH.

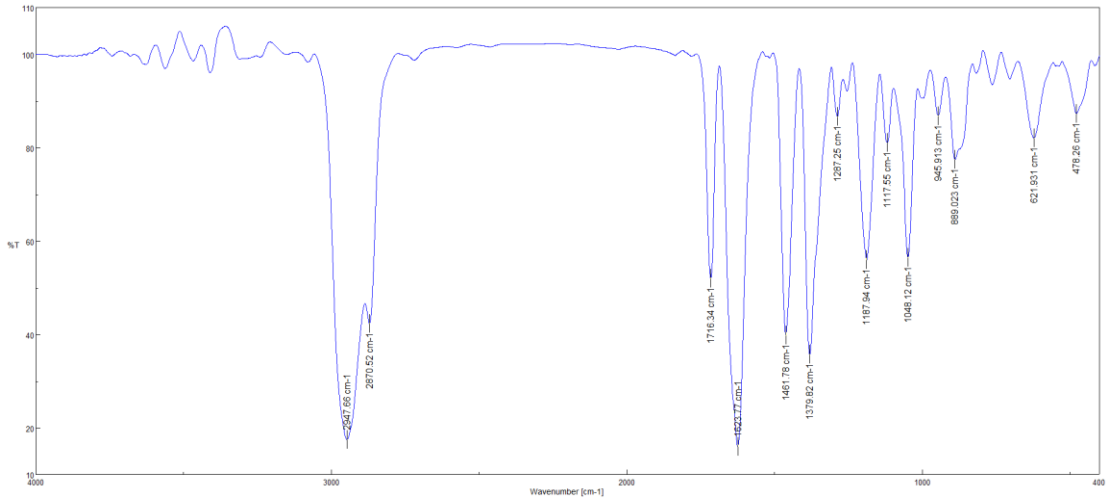


Figure S34. IR spectrum of tomentodione A (**12**) (KBr disc).

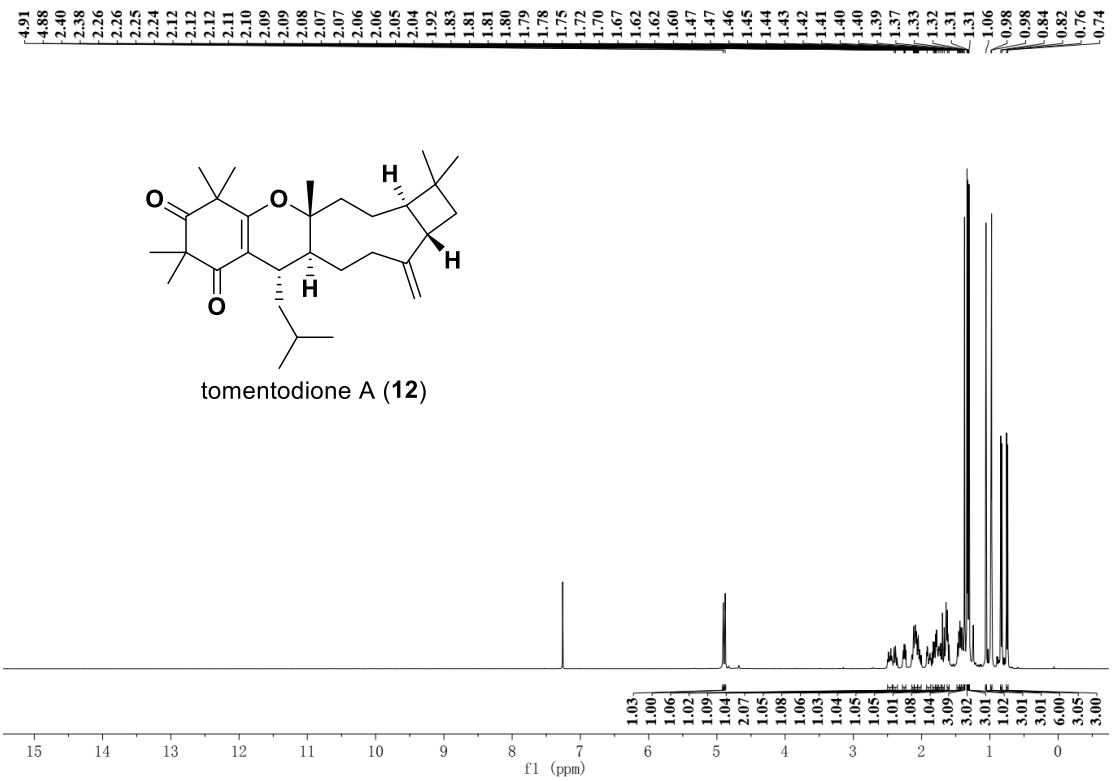


Figure S35. ^{1}H NMR spectrum (400 MHz) of tomentodione A (**12**) in $CDCl_3$.

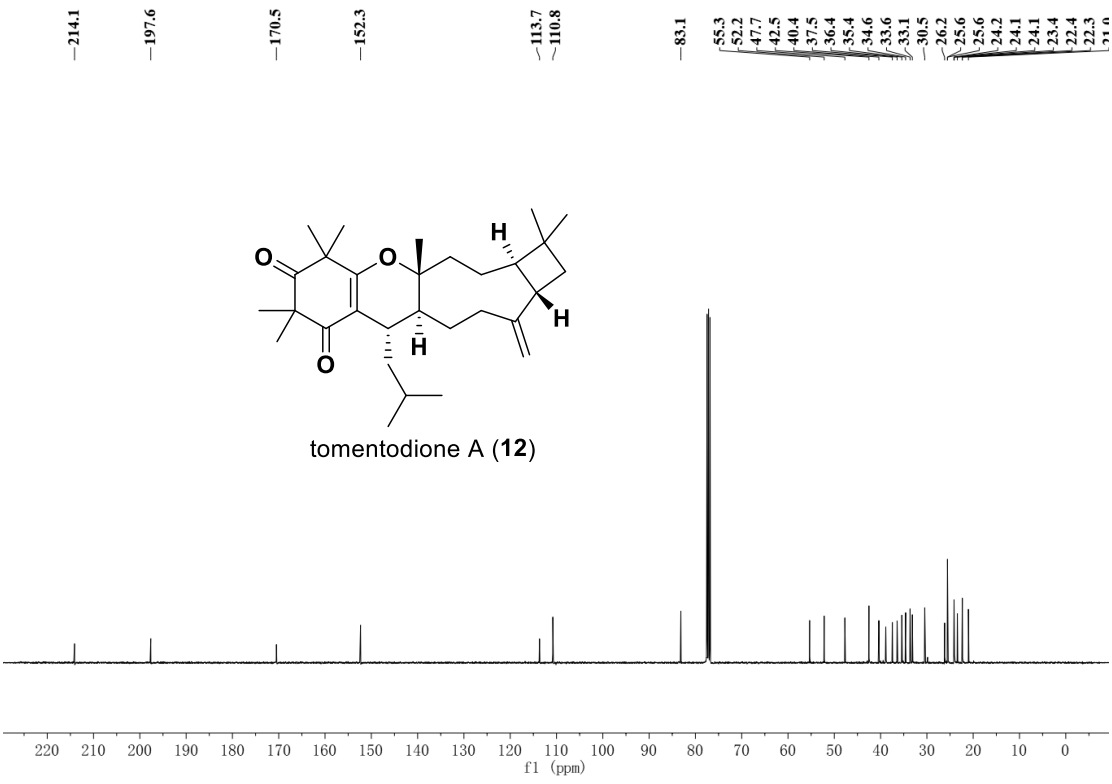


Figure S36. ^{13}C NMR spectrum (100 MHz) of tomentodione A (**12**) in $CDCl_3$.

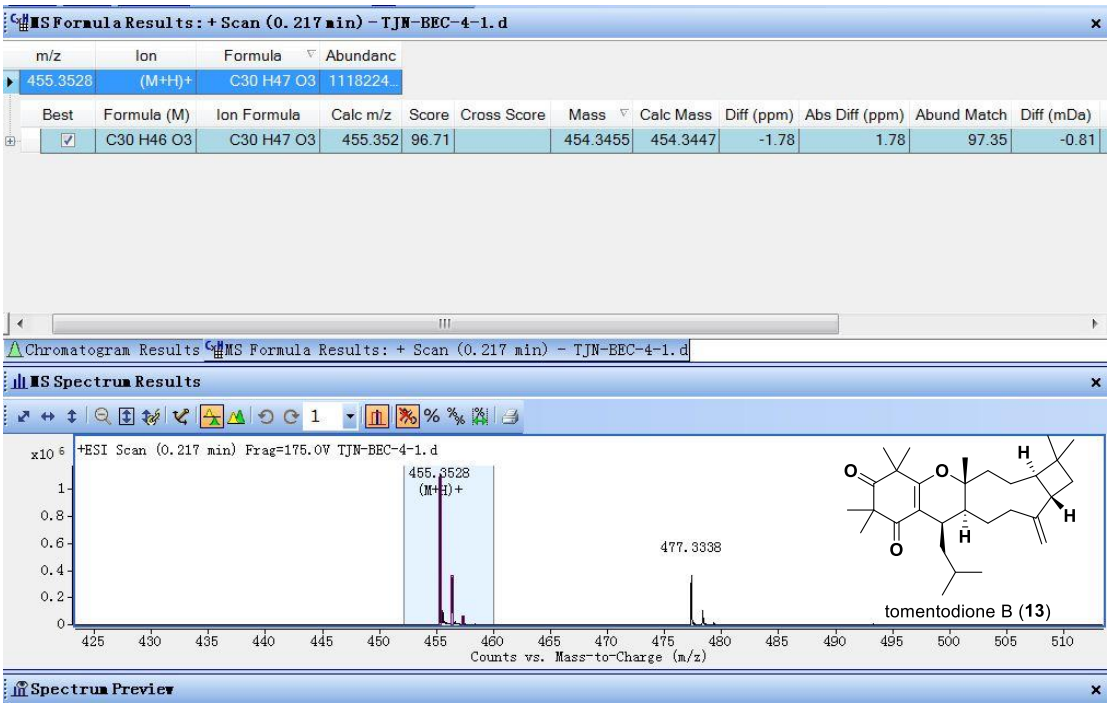


Figure S37. HR-ESI-MS spectrum of tomentodione B (**13**).

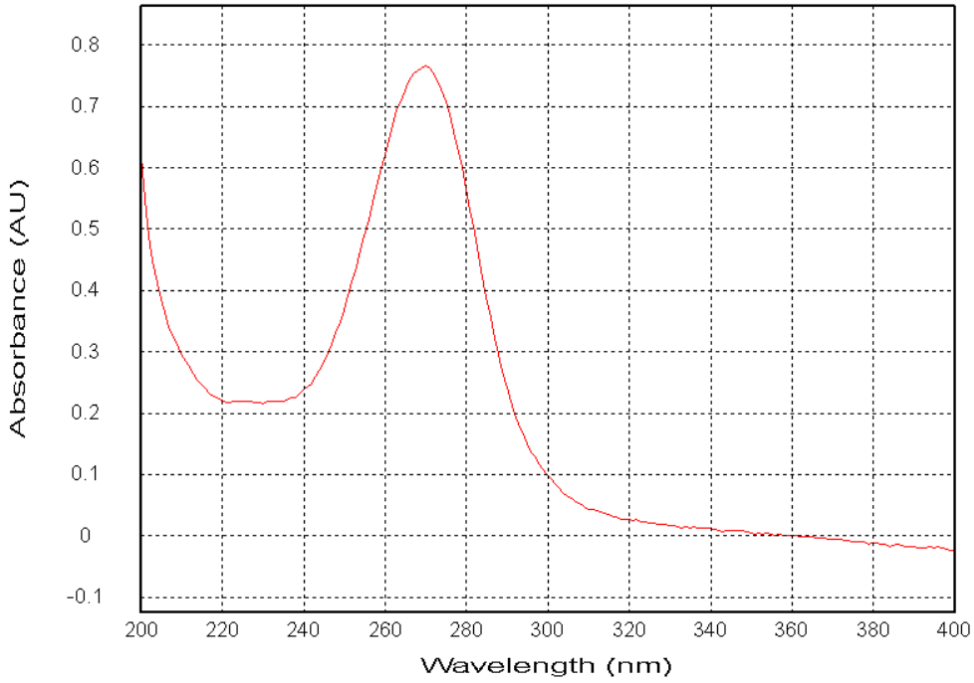


Figure S38. UV spectrum of tomentodione B (**13**) in MeOH.

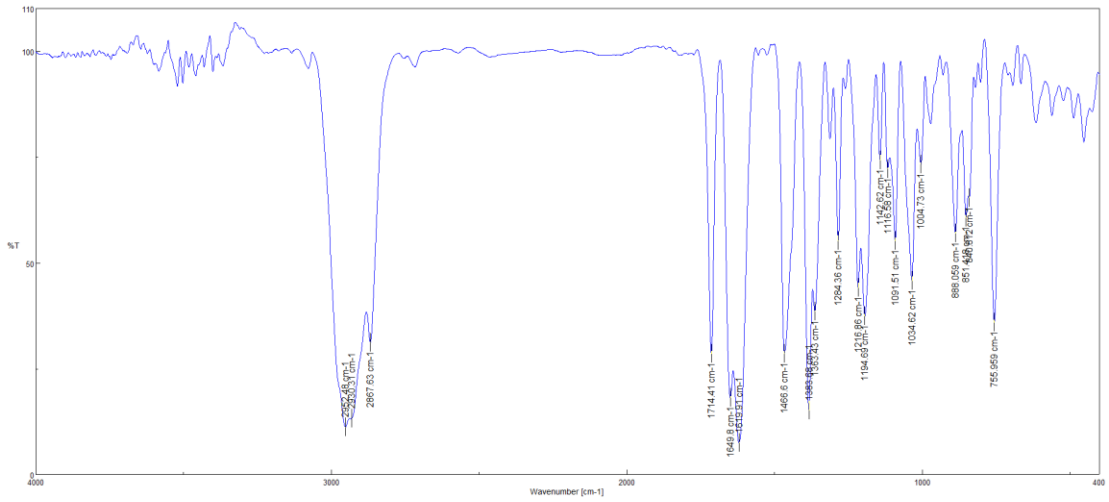


Figure S39. IR spectrum of tomentodione B (**13**) (KBr disc).

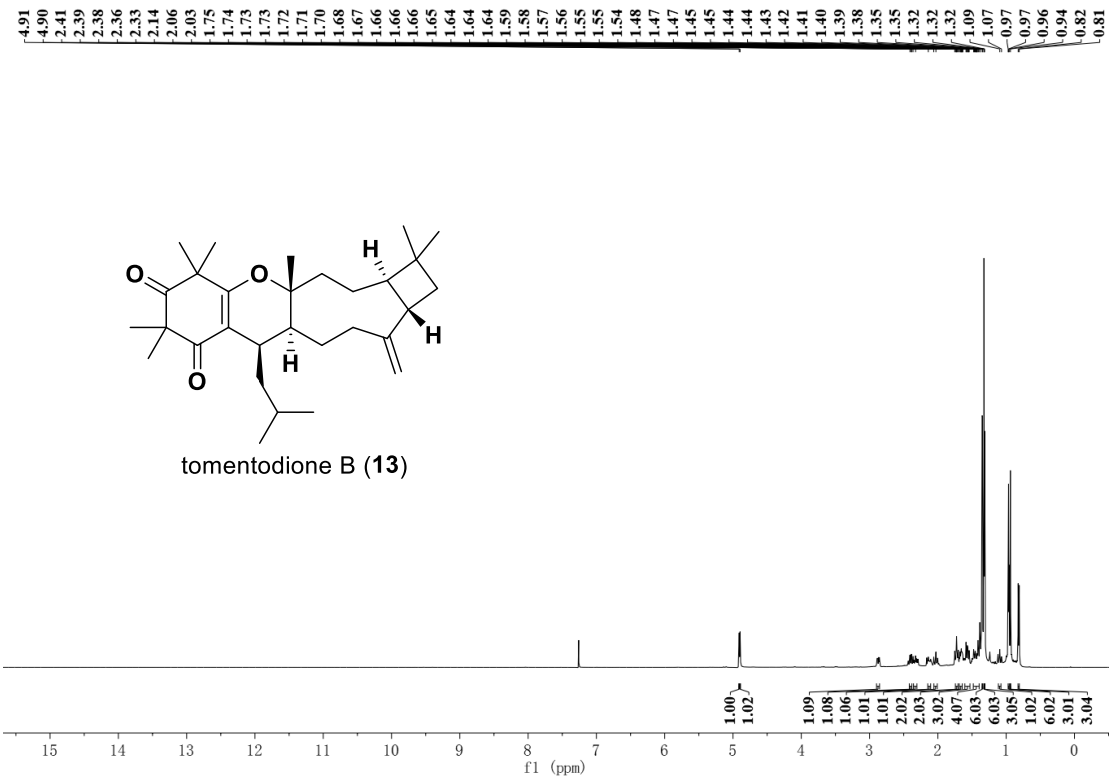


Figure S40. ^{1}H NMR spectrum (400 MHz) of tomentodione B (**13**) in $CDCl_3$.

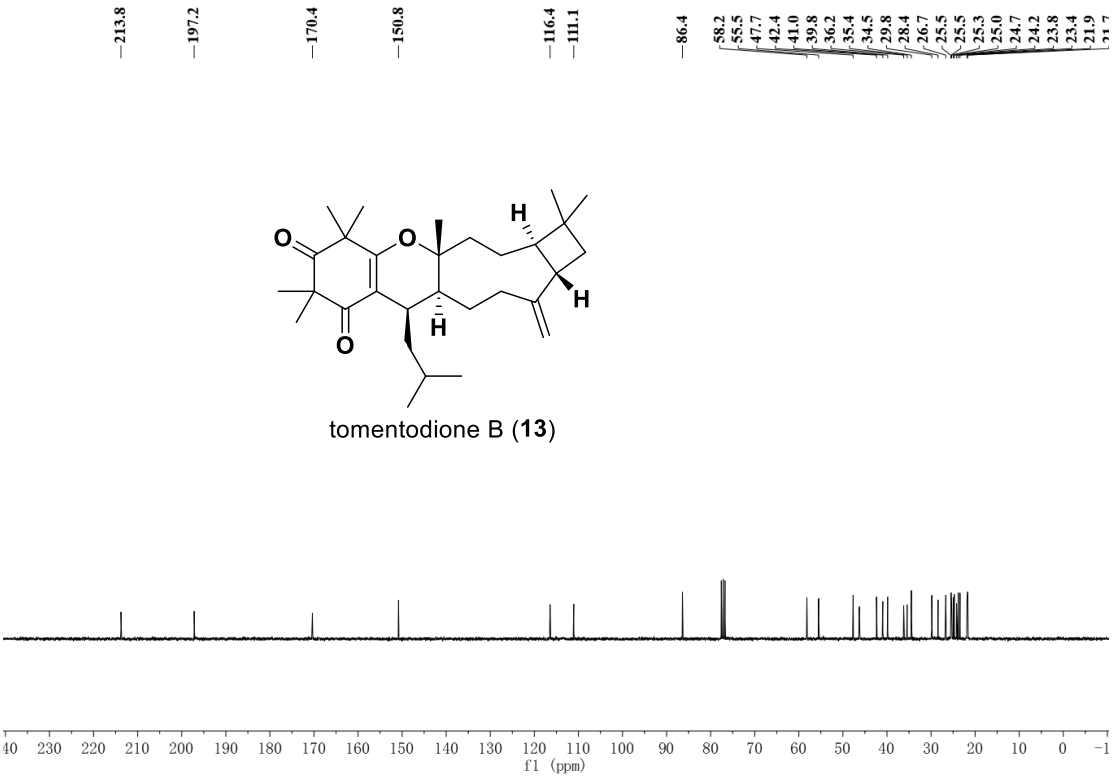


Figure S41. ^{13}C NMR spectrum (100 MHz) of tomentodione B (**13**) in $CDCl_3$.

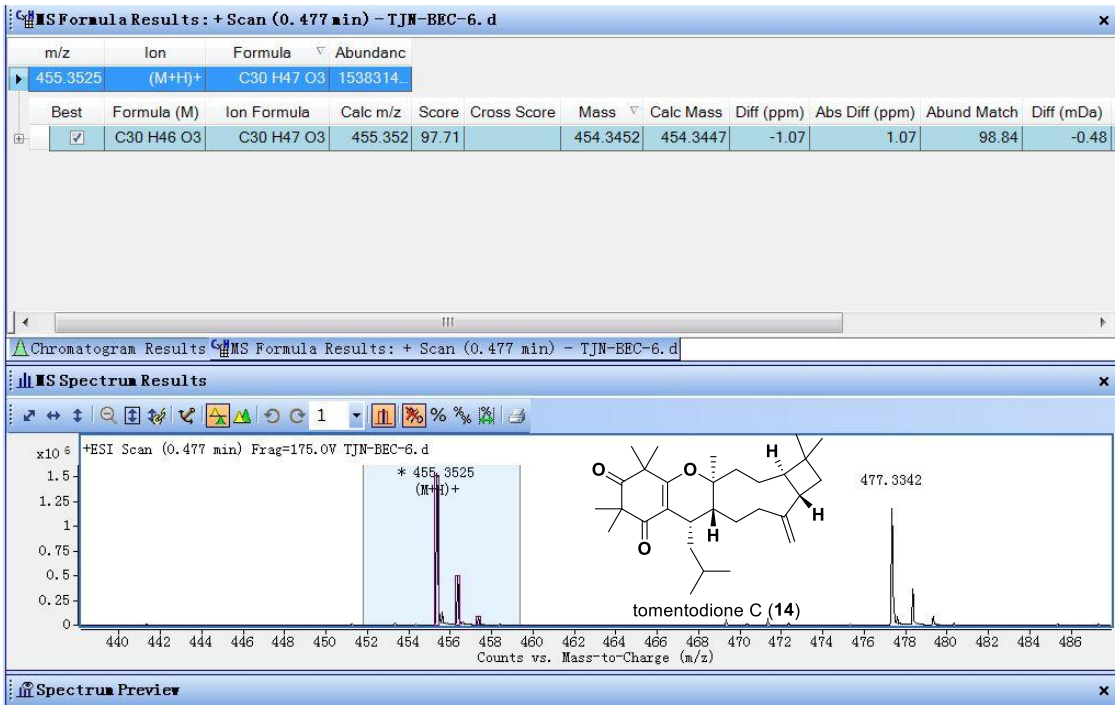


Figure S42. HR-ESI-MS spectrum of tomentodione C (**14**).

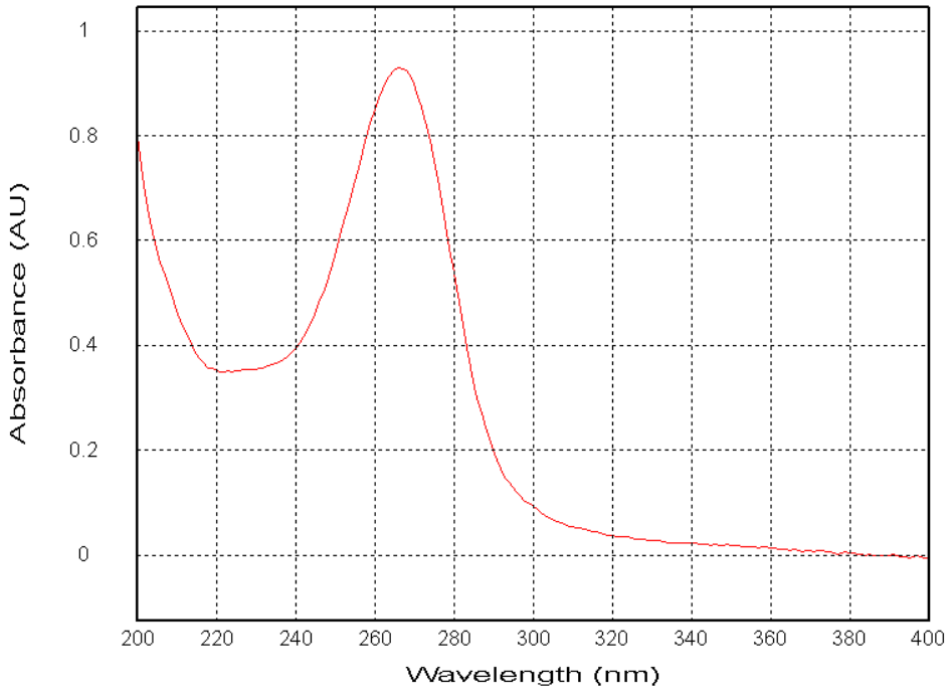


Figure S43. UV spectrum of tomentodione C (**14**) in MeOH.

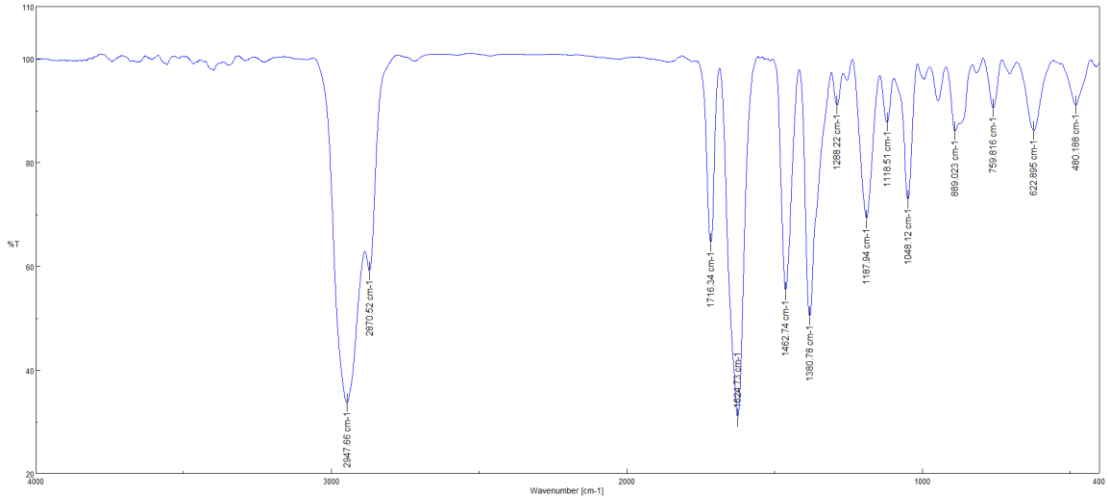


Figure S44. IR spectrum of tomentodione C (**14**) (KBr disc).

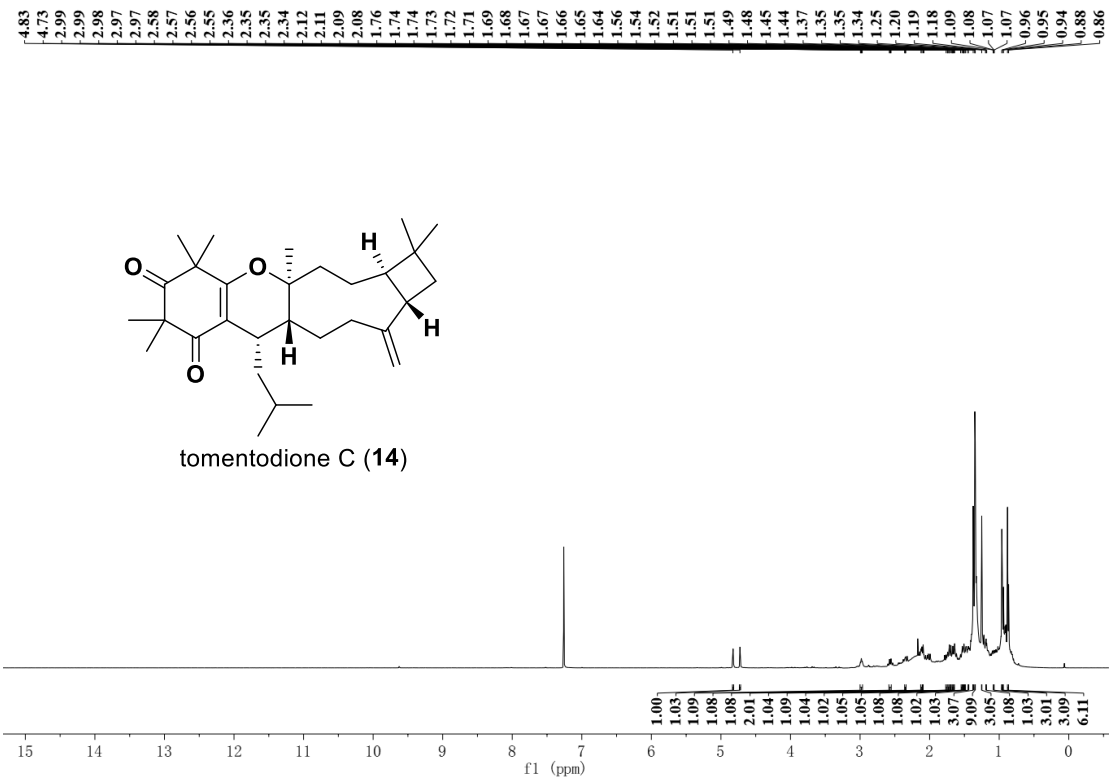


Figure S45. ^{1}H NMR spectrum (300 MHz) of tomentodione C (**14**) in $CDCl_3$.

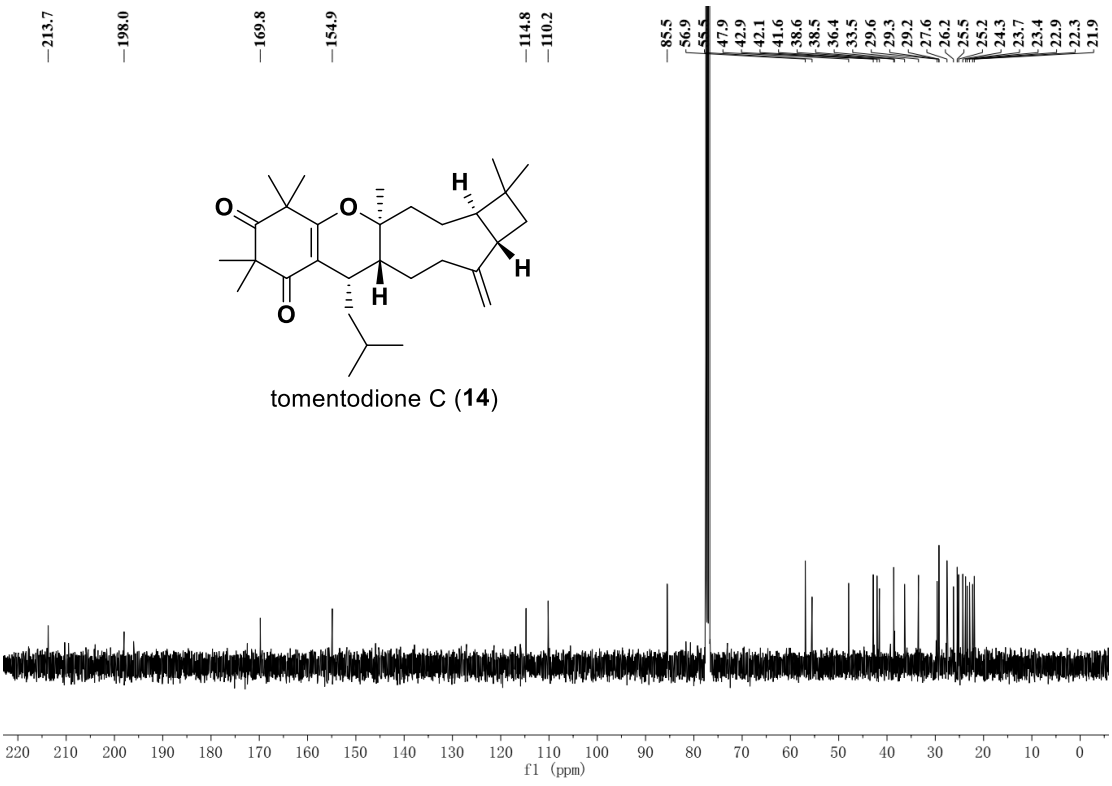


Figure S46. ^{13}C NMR spectrum (75 MHz) of tomentodione C (**14**) in $CDCl_3$.

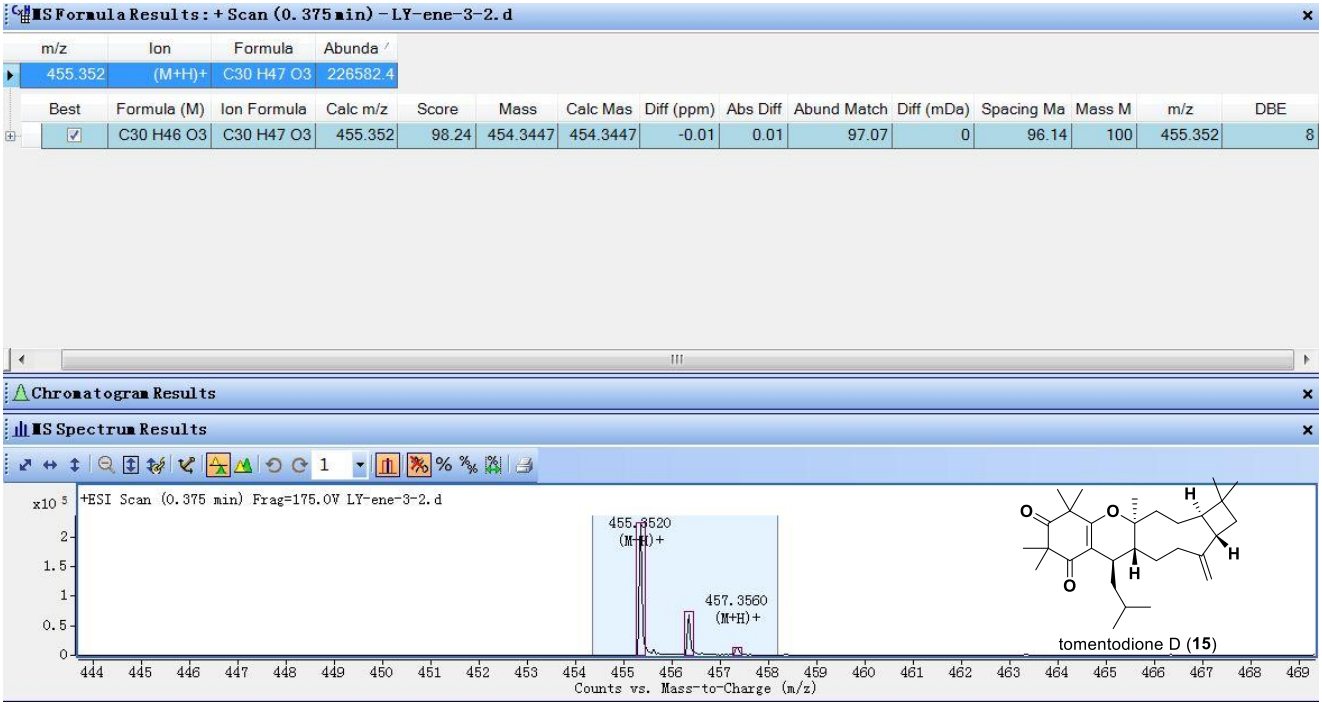


Figure S47. HR-ESI-MS spectrum of tomentodione D (**15**).

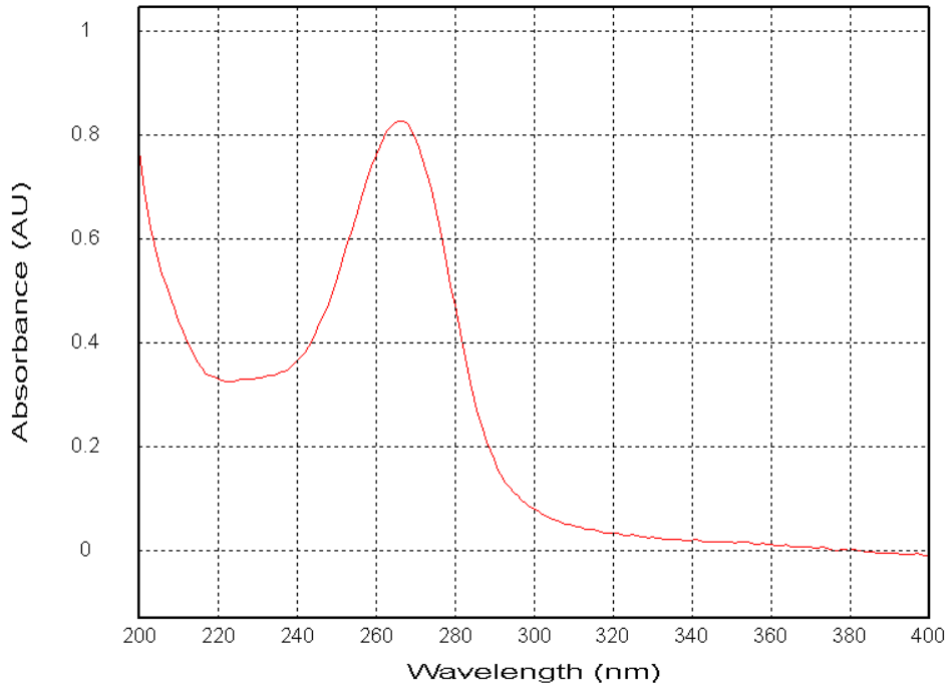


Figure S48. UV spectrum of tomentodione D (**15**) in MeOH.

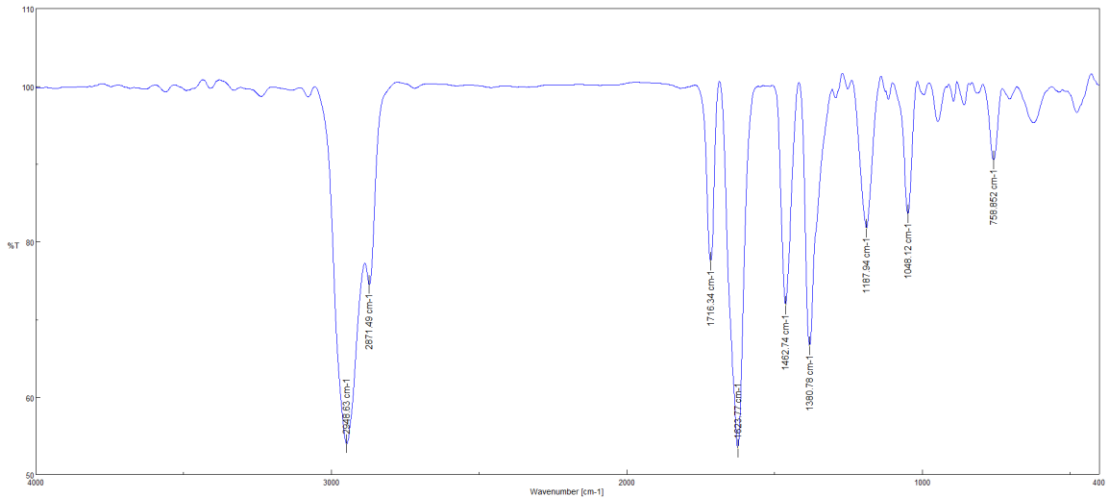


Figure S49. IR spectrum of tomentodione D (**15**) (KBr disc).

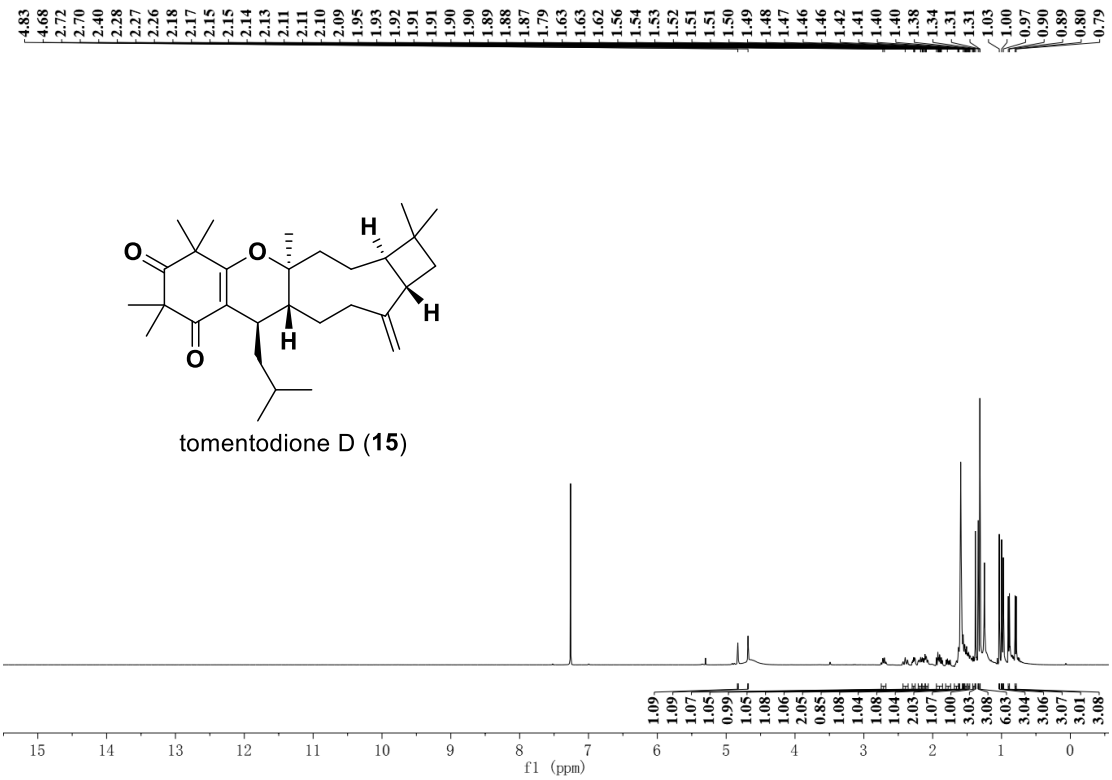


Figure S50. ^{1}H NMR spectrum (400 MHz) of tomentodione D (**15**) in $CDCl_3$.

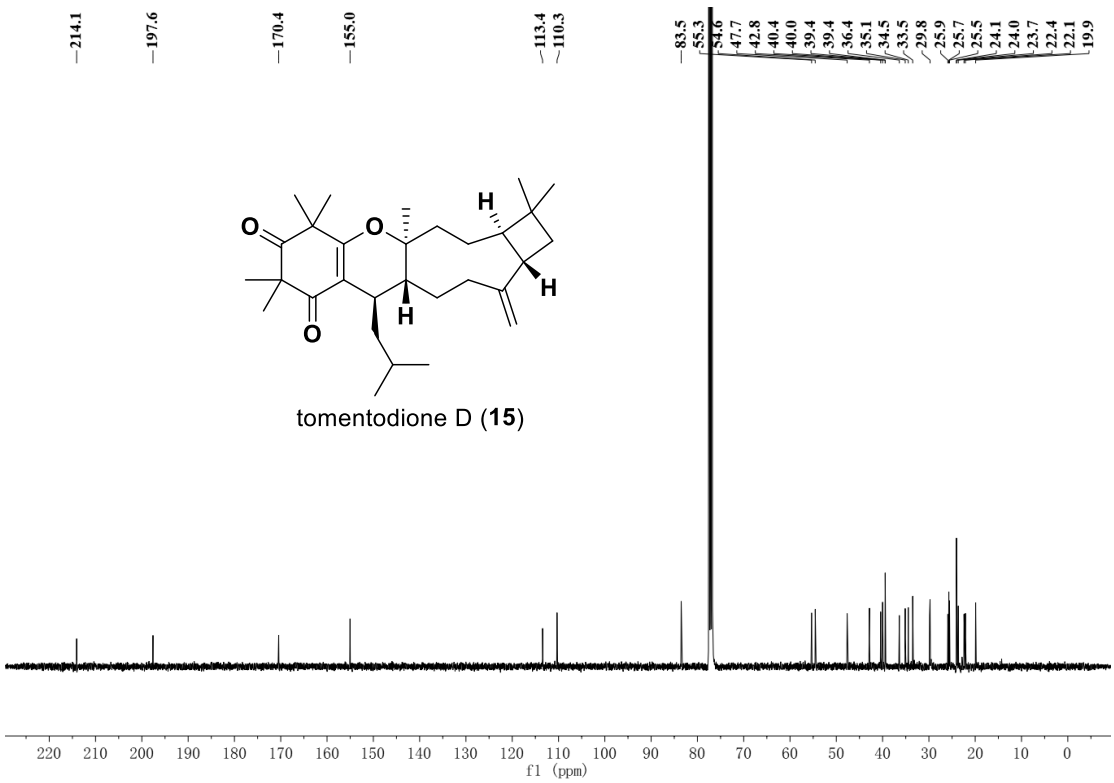


Figure S51. ^{13}C NMR spectrum (100 MHz) of tomentodione D (**15**) in $CDCl_3$.

5. Synthetic experimental procedures

5.1 General information

Unless otherwise mentioned, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions, and all reagents were purchased from commercial suppliers without further purification. Solvent purifications were conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) on plates (GF254) supplied by Yantai Chemicals (P. R. China) using UV light as visualizing agent, an ethanolic solution of *p*-anisaldehyde, and heat as developing agent. If not specially mentioned, flash column chromatography used silica gel (200–300 mesh) supplied by Tsingtao Haiyang Chemicals (P. R. China), Preparative thin layer chromatography (PTLC) separations were carried out 0.50 mm Yantai (P. R. China) silica gel plates. NMR spectra were recorded on Bruker AV400 and Bruker AV300, and calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$, δ 7.26 ppm ^1H NMR, δ 77.00 ^{13}C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, b = broad, and m = multiplet.

The analytic and preparative HPLC were performed on an Agilent 1260 instrument equipped with a multiple wavelength diode array detector (DAD), accompanied by Cosmosil C_{18} (4.6 × 250 mm, 5.0 μm) and Cosmosil $5C_{18}$-MS-II (10 × 250 mm, 5.0 μm) columns, respectively. HR-ESI-MS spectra were acquired on an Agilent 6210 ESI/TOF mass spectrometer (Agilent, Pala Alto, CA, USA). IR spectra were recorded on a JASCO FT/IR-480 plus Fourier Transform infrared spectrometer (JASCO, Tokyo, Japan) using KBr pellets. Optical rotations were measured on a JASCO P-1020 polarimeter (JASCO, Tokyo, Japan) with a 1 cm cell at room temperature.

5.2 Syntheses of 7 and 12–15

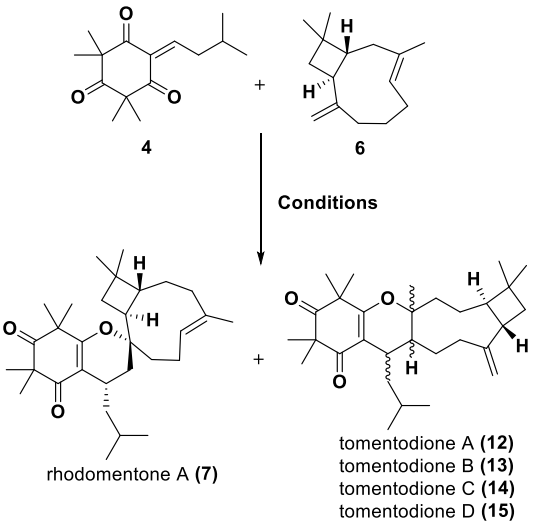
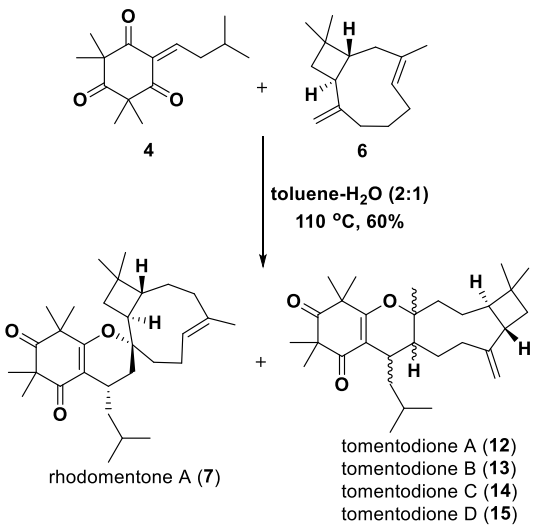


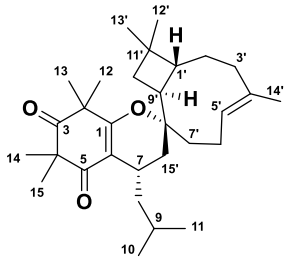
Table S14. Condition screen for the syntheses of compounds **7** and **12**–**15**.

entry[a]	catalyst	mol %	solvent	temp (°C)	time (h)	Yield (%)[b]	7:12:13:14:15
1	–	–	DCM	40	24	25	16:10:15:5:1
2	–	–	H_2O	100	24	trace	–
3	–	–	toluene	rt	48	28	9:19:31:11:1
4	–	–	toluene	60	24	30	14:13:26:9:1
5	–	–	toluene	80	24	36	32:22:14:19:1
6	–	–	toluene	110	24	45	5:6:9:5:1
7	DEAC	60	toluene	110	24	trace	–
8	ZnF_2	60	toluene	110	24	23	9:7:4:10:1
9	$ZnCl_2$	60	toluene	110	24	32	8:6:3:7:1
10	ZnI_2	60	toluene	110	1	53	6:5:2:9:1
11	–	–	neat	rt	24	48	13:11:20:9:1
12	–	–	neat	80	24	55	13:9:16:6:1
13	–	–	toluene/H_2O (1:1)	110	24	49	14:8:14:4:1
14	–	–	toluene/H_2O (2:1)	110	24	60	15:9:14:5:1
15	–	–	toluene/H_2O (1:2)	110	24	50	14:7:13:4:1

[a] Unless otherwise stated, the reactions of entries 1–15 were performed with **4** (0.4 mmol) and **6** (0.4 mmol). [b] Combined isolated yield.



Compound **4** (100 mg, 0.4 mmol) in a toluene-H_2O (2:1) solution (4 mL) was added *β*-caryophyllene (**6**) (91 μL, 0.4 mmol) under reflux at 110 °C (entry 14). The resulting mixture was stirred for 24 h. After the reaction was finished according to TLC, the mixture was concentrated *in vacuum*. The crude residue was further purified by preparative HPLC (CH_3CN-H_2O, 95:5) to afford corresponding products **7** and **12**–**15**.



7

Compound **7**: 36.3 mg, 20% yield, colorless needle crystals, mp 156–158 °C;

R_f = 0.53 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = −23.2° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2948, 2867, 1715, 1647, 1617, 1462, 1385, 1359, 1284, 1185, 1080, 1045, 977, 891, 851, 757, 619, 468 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 5.20 (brs, 1H), 2.89 (m, 1H), 1.83 (m, 1H), 1.70 (s, 3H), 1.67 (m, 1H), 1.39 (m, 1H), 1.35 (m, 1H), 1.31 (s, 3H), 1.31 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.24 (m, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.96 (s, 3H), 0.92 (brs, 3H);

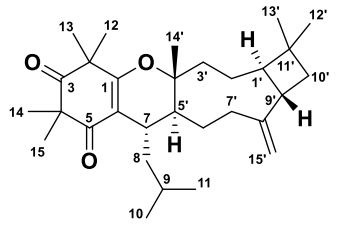
^{13}C NMR (75 MHz, $CDCl_3$) *δ* 213.9, 197.9, 169.2, 109.9, 55.5, 48.1, 42.3, 37.4, 32.7, 29.8, 26.8, 25.7, 25.4, 25.3, 24.6, 24.2, 23.0, 22.5, 21.0;

HRMS (ESI) calcd for $C_{30}H_{47}O_3$ $[M+H]^+$ Exact Mass: 455.3520; found: 455.3523.

Table S15. NMR data ($CDCl_3$) comparison between synthetic **7** and the isolated natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	isolated (400M)	synthesized (300M)	error (iso. - syn.)	isolated (100M)	synthesized (75M)	error (iso. - syn.)
1	-	-	-	169.2	169.2	0
2	-	-	-	48.1	48.1	0
3	-	-	-	213.8	213.9	-0.1
4	-	-	-	55.5	55.5	0
5	-	-	-	197.9	197.9	0
6	-	-	-	109.9	109.9	0
7	2.91 (m, 1H)	2.89 (m, 1H)	0.02	24.6	24.6	0
8a	1.40[a] (m, 1H)	1.39[a] (m, 1H)	0.01	42.3	42.3	0
8b	1.24[a] (m, 1H)	1.24[a] (m, 1H)	0			
9	1.83[a] (m, 1H)	1.83[a] (m, 1H)	0	25.7	25.7	0
10	1.08 (d, *J* = 6.4 Hz, 3H)	1.08 (d, *J* = 6.5 Hz, 3H)	0	21.0	21.0	0
11	0.97[a] (d, *J* = 6.4 Hz, 3H)	0.97[a] (d, *J* = 6.5 Hz, 3H)	0	24.2	24.2	0
12	1.26 (s, 3H)	1.26 (s, 3H)	0	25.4	25.4	0
13	1.32[a] (s, 3H)	1.31[a] (s, 3H)	0.01	25.3	25.3	0
14	1.32[a] (s, 3H)	1.31[a] (s, 3H)	0.01	26.8	26.8	0
15	1.31[a] (s, 3H)	1.31[a] (s, 3H)	0	22.4	22.5	-0.1
1'	c	c		b	b	
2'	c	c		b	b	
3'a	c	c		b	b	
3'b	c	c				
4'	-	-		b	b	
5'	5.20 (brs, 1H)	5.20 (brs, 1H)	0	b	b	
6'a	c	c		b	b	
6'b	c	c				
7'a	c	c		b	b	
7'b	c	c				
8'	-	-		b	b	
9'	c	c		b	b	
10'a	1.67[a] (m, 1H)	1.67[a] (m, 1H)	0	37.4	37.4	0
10'b	1.35[a] (m, 1H)	1.35[a] (m, 1H)	0			
11'	-	-		32.7	32.7	0
12'	0.90 (brs, 3H)	0.92 (brs, 3H)	-0.02	29.9	29.8	0.1
13'	0.96[a] (s, 3H)	0.96[a] (s, 3H)	0	22.8	23.0	-0.2
14'	1.71 (s, 3H)	1.70 (s, 3H)	0.01	b	b	
15'a	c	c		b	b	
15'b	c	c				

[a] Overlapped signals, [b] Signals invisible, [c] Signals unassigned



12

Compound **12**: 21.8 mg, 12% yield, yellow oil;

$\mathbf{R}_f$ = 0.38 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = +78.5° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2949, 2871, 1716, 1624, 1463, 1381, 1188, 1048, 759 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (s, 1H), 4.88 (s, 1H), 2.47 (dt, *J* = 13.8, 5.1 Hz, 1H), 2.39 (m, 1H), 2.26 (m, 1H), 2.11 (m, 1H), 2.08 (m, 1H), 2.08 (m, 1H), 2.03 (m, 1H), 1.90 (m, 1H), 1.81 (m, 1H), 1.78 (m, 1H), 1.74 (m, 1H), 1.68 (m, 1H), 1.62 (m, 1H), 1.46 (m, 1H), 1.43 (m, 1H), 1.40 (m, 1H), 1.37 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.32 (m, 1H), 1.31 (s, 3H), 1.06 (s, 3H), 0.98 (s, 3H), 0.98 (s, 3H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H);

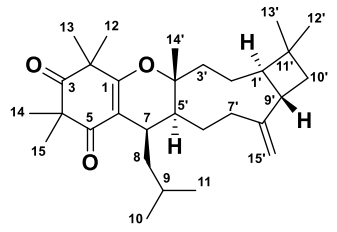
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 197.7, 170.6, 152.3, 113.7, 110.8, 83.2, 55.3, 52.2, 47.7, 42.5, 40.4, 38.9, 37.5, 36.4, 35.4, 34.6, 33.6, 33.1, 30.5, 26.2, 25.6, 25.6, 24.2, 24.1, 24.1, 23.4, 22.4, 22.3, 21.0;

HRMS (ESI) calcd for $C_{30}H_{47}O_3$ $[M+H]^+$ Exact Mass: 455.3520; found: 455.3521.

Table S16. NMR data ($CDCl_3$) comparison between synthetic **12** and the isolated natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	isolated (400M)	synthesized (400M)	error (iso. - syn.)	isolated (100M)	synthesized (100M)	error (iso. - syn.)
1	-	-	-	170.5	170.6	-0.1
2	-	-	-	47.7	47.7	0
3	-	-	-	214.1	214.1	0
4	-	-	-	55.3	55.3	0
5	-	-	-	197.6	197.7	-0.1
6	-	-	-	113.7	113.7	0
7	2.26 (m, 1H)	2.26 (m, 1H)	0	34.6	34.6	0
8a	1.82 (m, 1H)	1.81 (m, 1H)	0.01	38.9	38.9	0
8b	1.31[a] (m, 1H)	1.32[a] (m, 1H)	-0.01			
9	1.47[a] (m, 1H)	1.46[a] (m, 1H)	0.01	25.6	25.6	0
10	0.75 (d, *J* = 6.6 Hz, 3H)	0.75 (d, *J* = 6.5 Hz, 3H)	0	24.2	24.2	0
11	0.83 (d, *J* = 6.6 Hz, 3H)	0.83 (d, *J* = 6.5 Hz, 3H)	0	24.1	24.1	0
12	1.37 (s, 3H)	1.37 (s, 3H)	0	24.1	24.1	0
13	1.32 (s, 3H)	1.32 (s, 3H)	0	25.6	25.6	0
14	1.31 (s, 3H)	1.31 (s, 3H)	0	23.4	23.4	0
15	1.33 (s, 3H)	1.33 (s, 3H)	0	26.2	26.2	0
1'	2.03 (m, 1H)	2.03 (m, 1H)	0	52.2	52.2	0
2'a	1.78[a] (m, 1H)	1.78[a] (m, 1H)	0	22.4	22.4	0
2'b	1.40[a] (m, 1H)	1.40[a] (m, 1H)	0			
3'a	2.08[a] (m, 1H)	2.08[a] (m, 1H)	0	37.5	37.5	0
3'b	1.90 (m, 1H)	1.90 (m, 1H)	0			
4'	-	-	-	83.1	83.2	-0.1
5'	2.08[a] (m, 1H)	2.08[a] (m, 1H)	0	40.4	40.4	0
6'a	1.74 (m, 1H)	1.74 (m, 1H)	0	33.1	33.1	0
6'b	1.43[a] (m, 1H)	1.43[a] (m, 1H)	0			
7'a	2.47 (m, 1H)	2.47 (dt, *J* = 13.8, 5.1 Hz, 1H)	0	35.4	35.4	0
7'b	2.12[a] (m, 1H)	2.11[a] (m, 1H)	0.01			
8'	-	-	-	152.3	152.3	0
9'	2.39 (m, 1H)	2.39 (m, 1H)	0	42.5	42.5	0
10'a	1.68 (m, 1H)	1.68 (m, 1H)	0	36.4	36.4	0
10'b	1.61 (m, 1H)	1.62 (m, 1H)	-0.01			
11'	-	-	-	33.6	33.6	0
12'	0.98[a] (s, 3H)	0.98[a] (s, 3H)	0	30.5	30.5	0
13'	0.98[a] (s, 3H)	0.98[a] (s, 3H)	0	22.3	22.3	0
14'	1.06 (s, 3H)	1.06 (s, 3H)	0	21.0	21.0	0
15'a	4.91 (s, 1H)	4.91 (s, 1H)	0	110.8	110.8	0
15'b	4.88 (s, 1H)	4.88 (s, 1H)	0			

[a] Overlapped signals



13

Compound **13**: 36.3 mg, 20% yield, yellow oil;

$\mathbf{R_f}$ = 0.35 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = +40.6° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2938, 2868, 1713, 1648, 1621, 1459, 1383, 1282, 1190, 890, 843, 759 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (s, 1H), 4.90 (s, 1H), 2.88 (m, 1H), 2.40 (m, 1H), 2.33 (m, 1H), 2.13 (m, 1H), 2.04 (m, 1H), 1.75 (m, 1H), 1.73 (m, 1H), 1.67 (m, 2H), 1.55-1.61 (m, 2H), 1.59 (m, 1H), 1.50 (m, 1H), 1.48 (m, 1H), 1.41 (m, 1H), 1.39 (m, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.10 (m, 1H), 0.97 (s, 3H), 0.97 (d, *J* = 6.0 Hz, 3H), 0.94 (s, 3H), 0.82 (d, *J* = 6.0 Hz, 3H);

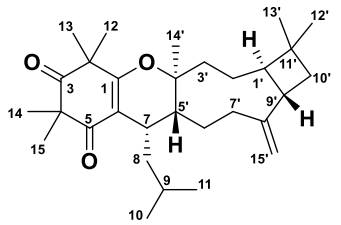
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 197.3, 170.4, 150.9, 116.5, 111.1, 86.5, 58.2, 55.6, 47.7, 46.4, 42.4, 41.0, 39.9, 36.2, 35.4, 34.5, 29.9, 28.4, 26.7, 25.6, 25.5, 25.3, 25.0, 24.8, 24.3, 23.8, 23.5, 21.9, 21.7;

HRMS (ESI) calcd for $C_{30}H_{47}O_3$ $[M+H]^+$ Exact Mass: 455.3520; found: 455.3528.

Table S17. NMR data ($CDCl_3$) comparison between synthetic **13** and the isolated natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	isolated (400M)	synthesized (400M)	error (iso. - syn.)	isolated (100M)	synthesized (100M)	error (iso. - syn.)
1	-	-	-	170.4	170.4	0
2	-	-	-	47.7	47.7	0
3	-	-	-	213.8	214.0	-0.2
4	-	-	-	55.5	55.6	-0.1
5	-	-	-	197.2	197.3	-0.1
6	-	-	-	116.4	116.5	-0.1
7	2.88 (m, 1H)	2.88 (m, 1H)	0	28.4	28.4	0
8a	1.40[a] (m, 1H)	1.41[a] (m, 1H)	-0.01	41.0	41.0	0
8b	1.10 (m, 1H)	1.10 (m, 1H)	0			
9	1.47[a] (m, 1H)	1.48[a] (m, 1H)	-0.01	26.7	26.7	0
10	0.82 (d, *J* = 6.0 Hz, 3H)	0.82 (d, *J* = 6.0 Hz, 3H)	0	24.7	24.8	-0.1
11	0.97[a] (d, *J* = 6.0 Hz, 3H)	0.97[a] (d, *J* = 6.0 Hz, 3H)	0	21.7	21.7	0
12	1.32[a] (s, 3H)	1.33[a] (s, 3H)	-0.01	25.0	25.0	0
13	1.35 (s, 3H)	1.35 (s, 3H)	0	25.5	25.5	0
14	1.32[a] (s, 3H)	1.33[a] (s, 3H)	-0.01	23.8	23.8	0
15	1.32 (s, 3H)	1.32 (s, 3H)	0	25.5	25.6	-0.1
1'	1.49[a] (m, 1H)	1.50[a] (m, 1H)	-0.01	58.2	58.2	0
2'	1.55-1.61[a] (m, 2H)	1.55-1.61[a] (m, 2H)	0	24.2	24.3	-0.1
3'a	2.03 (m, 1H)	2.04 (m, 1H)	-0.01	46.3	46.4	-0.1
3'b	1.39[a] (m, 1H)	1.39[a] (m, 1H)	0			
4'	-	-	-	86.4	86.5	-0.1
5'	1.74[a] (m, 1H)	1.75[a] (m, 1H)	-0.01	39.8	39.9	-0.1
6'	1.66 (m, 2H)	1.67 (m, 2H)	-0.01	25.3	25.3	0
7'a	2.33 (m, 1H)	2.33 (m, 1H)	0	35.4	35.4	0
7'b	2.13 (m, 1H)	2.13 (m, 1H)	0			
8'	-	-	-	150.8	150.9	-0.1
9'	2.40 (m, 1H)	2.40 (m, 1H)	0	42.4	42.4	0
10'a	1.72[a] (m, 1H)	1.73[a] (m, 1H)	-0.01	36.2	36.2	0
10'b	1.59[a] (m, 1H)	1.59[a] (m, 1H)	0			
11'	-	-	-	34.5	34.5	0
12'	0.94 (s, 3H)	0.94 (s, 3H)	0	29.8	29.9	-0.1
13'	0.97[a] (s, 3H)	0.97[a] (s, 3H)	0	21.9	21.9	0
14'	1.35 (s, 3H)	1.36 (s, 3H)	-0.01	23.4	23.5	-0.1
15'a	4.91 (s, 1H)	4.92 (s, 1H)	-0.01	111.1	111.1	0
15'b	4.90 (s, 1H)	4.90 (s, 1H)	0			

[a] Overlapped signals



14

Compound **14**: 12.7 mg, 7% yield, yellow oil;

$\mathbf{R_f}$ = 0.53 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = −26.4° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2950, 2871, 1716, 1623, 1463, 1381, 1188, 1048, 885, 761 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (brs, 1H), 4.73 (brs, 1H), 2.98 (m, 1H), 2.57 (q, *J* = 9.2 Hz, 1H), 2.35 (m, 1H), 2.13 (m, 1H), 2.10 (m, 1H), 2.03 (m, 1H), 1.76 (m, 1H), 1.73 (m, 1H), 1.71 (m, 1H), 1.67 (m, 1H), 1.65 (m, 1H), 1.53 (m, 1H), 1.51 (m, 1H), 1.49 (m, 1H), 1.44 (m, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 1.35 (s, 3H), 1.35 (s, 3H), 1.25 (s, 3H), 1.19 (m, 1H), 1.08 (m, 1H), 0.96 (s, 3H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 3H), 0.87 (d, *J* = 6.4 Hz, 3H);

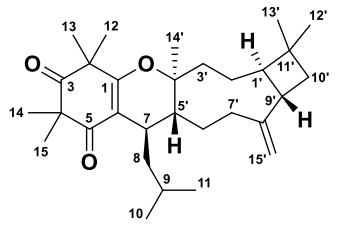
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 198.0, 169.8, 154.9, 114.7, 110.2, 85.5, 56.9, 55.5, 47.9, 42.9, 42.1, 41.6, 38.6, 38.5, 36.4, 33.5, 29.6, 29.3, 29.2, 27.6, 26.2, 25.5, 25.2, 24.3, 23.7, 23.4, 22.9, 22.3, 21.9;

HRMS (ESI) calcd for $C_{30}H_{47}O_3$ $[M+H]^+$ Exact Mass: 455.3520; found: 455.3525.

Table S18. NMR data ($CDCl_3$) comparison between synthetic **14** and the isolated natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	isolated (400M)	synthesized (400M)	error (iso. - syn.)	isolated (100M)	synthesized (100M)	error (iso. - syn.)
1	-	-	-	169.8	169.8	0
2	-	-	-	47.9	47.9	0
3	-	-	-	213.7	213.7	0
4	-	-	-	55.5	55.5	0
5	-	-	-	198.0	198.0	0
6	-	-	-	114.8	114.7	0.1
7	2.98 (m, 1H)	2.98 (m, 1H)	0	29.3	29.3	0
8a	1.49[a] (m, 1H)	1.49[a] (m, 1H)	0	42.1	42.1	0
8b	1.08 (m, 1H)	1.08 (m, 1H)	0			
9	1.67[a] (m, 1H)	1.67[a] (m, 1H)	0	27.6	27.6	0
10	0.95 (d, *J* = 6.2 Hz, 3H)	0.95 (d, *J* = 6.4 Hz, 3H)	0	24.3	24.3	0
11	0.87[a] (d, *J* = 6.2 Hz, 3H)	0.87[a] (d, *J* = 6.4 Hz, 3H)	0	21.9	21.9	0
12	1.35[a] (s, 3H)	1.35[a] (s, 3H)	0	25.5	25.5	0
13	1.37 (s, 3H)	1.37 (s, 3H)	0	26.2	26.2	0
14	1.35[a] (s, 3H)	1.35[a] (s, 3H)	0	22.9	22.9	0
15	1.34 (s, 3H)	1.35 (s, 3H)	-0.01	25.2	25.2	0
1'	1.54[a] (m, 1H)	1.53[a] (m, 1H)	0.01	56.9	56.9	0
2'a	1.44[a] (m, 1H)	1.44[a] (m, 1H)	0	23.4	23.4	0
2'b	1.19 (m, 1H)	1.19 (m, 1H)	0			
3'a	2.03 (m, 1H)	2.03 (m, 1H)	0	41.6	41.6	0
3'b	1.76 (m, 1H)	1.76 (m, 1H)	0			
4'	-	-	-	85.5	85.5	0
5'	2.10[a] (m, 1H)	2.10[a] (m, 1H)	0	38.5	38.6	-0.1
6'a	1.70[a] (m, 1H)	1.71[a] (m, 1H)	-0.01	29.2	29.2	0
6'b	1.51[a] (m, 1H)	1.51[a] (m, 1H)	0			
7'a	2.35 (m, 1H)	2.35 (m, 1H)	-	36.4	36.4	0
7'b	2.12[a] (m, 1H)	2.13[a] (m, 1H)	-0.01			
8'	-	-	-	154.9	154.9	0
9'	2.57 (q, *J* = 9.2 Hz, 1H)	2.57 (q, *J* = 9.2 Hz, 1H)	0	42.9	42.9	0
10'a	1.73 (m, 1H)	1.73 (m, 1H)	0	38.6	38.5	0.1
10'b	1.65 (m, 1H)	1.65 (m, 1H)	0			
11'	-	-	-	33.5	33.5	0
12'	0.96 (s, 3H)	0.96 (s, 3H)	0	29.6	29.6	0
13'	0.88 (s, 3H)	0.88 (s, 3H)	0	22.3	22.3	0
14'	1.25 (s, 3H)	1.25 (s, 3H)	0	23.7	23.7	0
15'a	4.83 (brs, 1H)	4.83 (brs, 1H)	0	110.2	110.2	0
15'b	4.73 (brs, 1H)	4.73 (brs, 1H)	0			

[a] Overlapped signals



15

Compound **15**: 1.8 mg, 1% yield, yellow oil;

$\mathbf{R_f}$ = 0.53 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = −20.4° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2933, 2867, 1713, 1620, 1462, 1383, 1192, 1040 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.68 (s, 1H), 2.71 (q, *J* = 9.3 Hz, 1H), 2.40 (m, 1H), 2.28 (m, 1H), 2.20 (m, 1H), 2.14 (m, 1H), 2.10 (m, 1H), 1.92 (m, 1H), 1.88 (m, 1H), 1.78 (m, 1H), 1.65 (m, 1H), 1.62 (m, 1H), 1.56 (m, 1H), 1.56 (m, 1H), 1.52 (m, 2H), 1.48 (m, 1H), 1.40 (m, 1H), 1.38 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.31 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H), 0.97 (s, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 6.5 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 197.6, 170.4, 155.0, 113.4, 110.3, 83.5, 55.3, 54.6, 47.7, 42.8, 40.4, 40.0, 39.4, 39.4, 36.4, 35.1, 34.5, 33.5, 29.8, 25.9, 25.7, 25.5, 24.1, 24.0, 24.0, 23.7, 22.4, 22.1, 19.9;

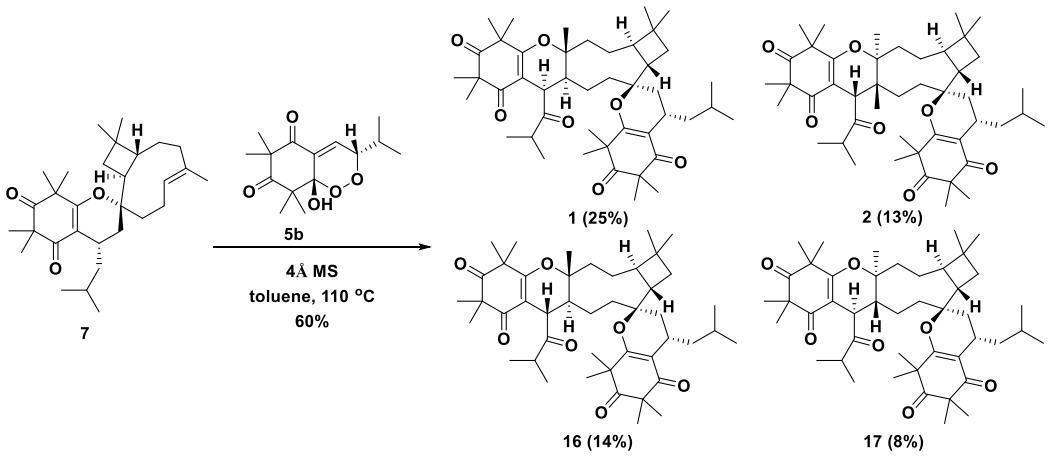
HRMS (ESI) calcd for $C_{30}H_{47}O_3$ $[M+H]^+$ Exact Mass: 455.3520; found: 455.3521.

Table S19. NMR data ($CDCl_3$) comparison between synthetic **15** and the isolated natural product.

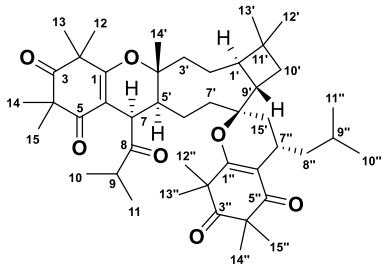
	^1H & ppm (J)			^{13}C & ppm		
position	isolated (400M)	synthesized (400M)	error (iso. - syn.)	isolated (100M)	synthesized (100M)	error (iso. - syn.)
1	-	-	-	170.4	170.4	0
2	-	-	-	47.7	47.7	0
3	-	-	-	214.1	214.1	0
4	-	-	-	55.3	55.3	0
5	-	-	-	197.6	197.6	0
6	-	-	-	113.4	113.4	0
7	2.28 (m, 1H)	2.28 (m, 1H)	0	35.1	35.1	0
8a	1.88[a] (m, 1H)	1.88[a] (m, 1H)	0	39.4	39.4	0
8b	1.40[a] (m, 1H)	1.40[a] (m, 1H)	0			
9	1.56[a] (m, 1H)	1.56[a] (m, 1H)	0	25.7	25.7	0
10	0.89 (d, *J* = 6.6 Hz, 3H)	0.89 (d, *J* = 6.5 Hz, 3H)	0	24.1	24.1	0
11	0.79 (d, *J* = 6.6 Hz, 3H)	0.80 (d, *J* = 6.5 Hz, 3H)	-0.01	24.0	24.0	0
12	1.38 (s, 3H)	1.38 (s, 3H)	0	24.0	24.0	0
13	1.31[a] (s, 3H)	1.31[a] (s, 3H)	0	25.5	25.5	0
14	1.34 (s, 3H)	1.34 (s, 3H)	0	25.9	25.9	0
15	1.31[a] (s, 3H)	1.31[a] (s, 3H)	0	23.7	23.7	0
1'	1.61[a] (m, 1H)	1.62[a] (m, 1H)	-0.01	54.6	54.6	0
2'	1.52[a] (m, 2H)	1.52[a] (m, 2H)	0	22.1	22.1	0
3'a	2.13[a] (m, 1H)	2.14[a] (m, 1H)	-0.01	39.4	39.4	0
3'b	1.77 (m, 1H)	1.78 (m, 1H)	-0.01			
4'	-	-	-	83.5	83.5	0
5'	2.09[a] (m, 1H)	2.10[a] (m, 1H)	-0.01	40.0	40.0	0
6'a	1.65[a] (m, 1H)	1.65[a] (m, 1H)	0	34.5	34.5	0
6'b	1.47[a] (m, 1H)	1.48[a] (m, 1H)	-0.01			
7'a	2.40 (m, 1H)	2.40 (m, 1H)	0	36.4	36.4	0
7'b	2.19 (m, 1H)	2.20 (m, 1H)	-0.01			
8'	-	-	-	155.0	155.0	0
9'	2.71 (q, *J* = 9.6 Hz, 1H)	2.71 (q, *J* = 9.3 Hz, 1H)	0	42.8	42.8	0
10'a	1.92 (m, 1H)	1.92 (m, 1H)	0	40.4	40.4	0
10'b	1.56[a] (m, 1H)	1.56[a] (m, 1H)	0			
11'	-	-	-	33.5	33.5	0
12'	1.00 (s, 3H)	1.00 (s, 3H)	0	29.8	29.8	0
13'	0.97 (s, 3H)	0.97 (s, 3H)	0	22.4	22.4	0
14'	1.03 (s, 3H)	1.03 (s, 3H)	0	19.9	19.9	0
15'a	4.83 (s, 1H)	4.83 (s, 1H)	0	110.3	110.3	0
15'b	4.68 (s, 1H)	4.68 (s, 1H)	0			

[a] Overlapped signals

5.3 Syntheses of 1–2 and 16–17 through path A



Compound **7** (50 mg, 0.11 mmol) in a toluene solution (4 mL) was added **5b** (47 mg, 0.16 mmol) and 4Å molecular sieves under reflux at 110 °C. The resulting mixture was stirred for 24 h. After the reaction was finished according to TLC, the reaction was filtered through a plug of celite (CH_2Cl_2 was used as the eluent) and was concentrated *in vacuum*. The crude residue was further purified by preparative HPLC (CH_3OH-H_2O, 92:8) to afford corresponding products **1**–**2** and **16**–**17**.



1

Compound **1**: 19.7 mg, 25% yield, yellow oil;

R_f = 0.69 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = +117.1° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2954, 2925, 2868, 2850, 1713, 1652, 1618, 1466, 1383, 1362, 1212, 1182, 770 cm^{-1};

ECD (CH_3OH): λ_{max} ($\Delta\varepsilon$) 207 (−14.9), 273 (+60.0) nm;

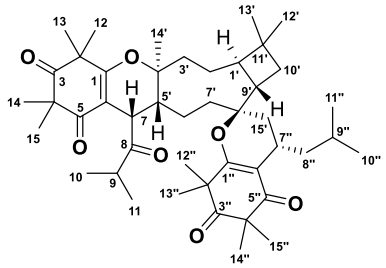
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (d, *J* = 7.2 Hz, 1H), 2.90 (m, 1H), 2.84 (m, 1H), 2.38 (m, 1H), 2.18 (m, 1H), 2.16 (m, 1H), 2.15 (m, 1H), 2.11 (m, 1H), 1.92 (m, 1H), 1.88 (m, 1H), 1.82 (m, 1H), 1.78 (m, 1H), 1.73 (m, 1H), 1.71 (m, 1H), 1.68 (m, 1H), 1.64 (m, 1H), 1.62 (m, 1H), 1.55 (m, 1H), 1.48 (m, 1H), 1.43 (s, 3H), 1.40 (m, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H), 1.03 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.97 (s, 3H), 0.94 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 213.1, 213.0, 198.0, 197.2, 171.4, 168.8, 112.5, 108.3, 84.3, 83.3, 55.5, 55.4, 48.7, 48.2, 48.0, 45.2, 44.8, 43.6, 43.2, 42.9, 40.8, 39.5, 35.7, 34.1, 33.8, 30.1, 26.7, 26.1, 26.0, 25.9, 25.6, 25.5, 24.9, 24.4, 24.1, 23.4, 22.9, 22.4, 21.9, 21.5, 21.2, 21.0, 20.4, 18.3;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4884.

Table S20. NMR data ($CDCl_3$) comparison between synthetic **1** through path A and the isolated natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	isolated (300M)	synthesized (400M)	error (iso. - syn.)	isolated (75M)	synthesized (100M)	error (iso. - syn.)
1	-	-	-	171.3	171.4	-0.1
2	-	-	-	48.0	48.0	0
3	-	-	-	213.1	213.1	0
4	-	-	-	55.5	55.5	0
5	-	-	-	197.2	197.2	0
6	-	-	-	108.4	108.3	0.1
7	4.07 (d, *J* = 7.2 Hz, 1H)	4.08 (d, *J* = 7.2 Hz, 1H)	-0.01	45.2	45.2	0
8	-	-	-	216.0	216.0	0
9	2.89 (m, 1H)	2.90 (m, 1H)	-0.01	42.9	42.9	0
10	1.24 (d, *J* = 6.8 Hz, 3H)	1.25 (d, *J* = 6.6 Hz, 3H)	-0.01	20.4	20.4	0
11	1.07 (d, *J* = 6.8 Hz, 3H)	1.07 (d, *J* = 6.6 Hz, 3H)	0	18.3	18.3	0
12	1.37 (s, 3H)	1.37 (s, 3H)	0	24.5	24.4	0.1
13	1.42 (s, 3H)	1.43 (s, 3H)	-0.01	25.6	25.5	0.1
14	1.34 (s, 3H)	1.35 (s, 3H)	-0.01	26.7	26.7	0
15	1.29 (s, 3H)	1.30 (s, 3H)	-0.01	26.0	26.0	0
1'	1.82 (m, 1H)	1.82 (m, 1H)	0	48.7	48.7	0
2'a	1.70 (m, 1H)	1.71 (m, 1H)	-0.01	23.4	23.4	0
2'b	1.40 (m, 1H)	1.40 (m, 1H)	0			
3'a	2.18 (m, 1H)	2.18 (m, 1H)	0	40.8	40.8	0
3'b	1.73 (m, 1H)	1.73 (m, 1H)	0			
4'	-	-	-	84.3	84.3	0
5'	2.15 (m, 1H)	2.15 (m, 1H)	0	43.2	43.2	0
6'a	1.87 (m, 1H)	1.88 (m, 1H)	-0.01	21.5	21.5	0
6'b	1.78 (m, 1H)	1.78 (m, 1H)	0			
7'a	2.11 (m, 1H)	2.11 (m, 1H)	0	39.5	39.5	0
7'b	1.91 (m, 1H)	1.92 (m, 1H)	-0.01			
8'	-	-	-	83.3	83.3	0
9'	2.38 (m, 1H)	2.38 (m, 1H)	0	44.8	44.8	0
10'a	1.63 (m, 1H)	1.62 (m, 1H)	0.01	35.7	35.7	0
10'b	1.48 (m, 1H)	1.48 (m, 1H)	0			
11'	-	-	-	34.1	34.1	0
12'	0.94 (s, 3H)	0.94 (s, 3H)	0	22.4	22.4	0
13'	0.97 (s, 3H)	0.97 (s, 3H)	0	30.1	30.1	0
14'	1.26 (s, 3H)	1.26 (s, 3H)	0	21.0	21.0	0
15'a	2.16 (m, 1H)	2.16 (m, 1H)	0	33.8	33.8	0
15'b	1.55 (m, 1H)	1.55 (m, 1H)	0			
1''	-	-	-	168.8	168.8	0
2''	-	-	-	48.2	48.2	0
3''	-	-	-	213.0	213.1	-0.1
4''	-	-	-	55.4	55.4	0
5''	-	-	-	198.0	198.0	0
6''	-	-	-	112.6	112.5	0.1
7''	2.85 (m, 1H)	2.84 (m, 1H)	0.01	25.6	25.6	0
8''a	1.64 (m, 1H)	1.64 (m, 1H)	0	43.7	43.6	0.1
8''b	1.03 (m, 1H)	1.03 (m, 1H)	0			
9''	1.69 (m, 1H)	1.68 (m, 1H)	0.01	25.9	25.9	0
10''	0.92 (d, *J* = 6.0 Hz, 3H)	0.92 (d, *J* = 6.6 Hz, 3H)	0	24.1	24.1	0
11''	0.98 (d, *J* = 6.0 Hz, 3H)	0.98 (d, *J* = 6.6 Hz, 3H)	0	21.3	21.2	0.1
12''	1.36 (s, 3H)	1.36 (s, 3H)	0	24.9	24.9	0
13''	1.31 (s, 3H)	1.31 (s, 3H)	0	21.9	21.9	0
14''	1.31 (s, 3H)	1.32 (s, 3H)	-0.01	22.9	22.9	0
15''	1.32 (s, 3H)	1.33 (s, 3H)	-0.01	26.0	26.1	-0.1



2

Compound **2**: 10.3 mg, 13% yield, yellow oil;

$\mathbf{R}_f$ = 0.69 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = −33.2° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2925, 2858, 1699, 1622, 1462, 1383, 1204, 1142, 804, 769, 720 cm^{-1};

ECD (CH_3OH): λ_{max} ($\Delta\varepsilon$) 208 (+30.1), 251 (−30.4), 274 (+10.8), 304 (−15.0) nm;

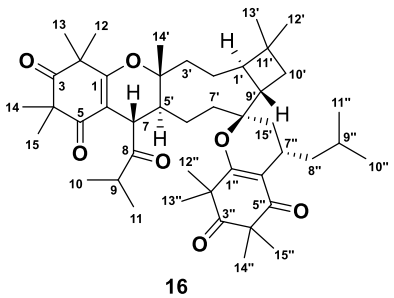
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.23 (d, J = 7.5 Hz, 1H), 2.95 (m, 1H), 2.70 (m, 1H), 2.58 (m, 1H), 2.28 (m, 1H), 2.20 (m, 1H), 2.11 (m, 1H), 1.97 (m, 1H), 1.88 (m, 1H), 1.74 (m, 1H), 1.73 (m, 1H), 1.72 (m, 1H), 1.70 (m, 1H), 1.60 (m, 1H), 1.53 (m, 1H), 1.49 (m, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 1.38 (m, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.32 (d, J = 6.6 Hz, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.28 (m, 1H), 1.26 (m, 2H), 1.14 (m, 3H), 1.10 (m, 1H), 1.03 (d, J = 6.6 Hz, 3H), 1.03 (d, J = 6.6 Hz, 3H), 0.97 (s, 3H), 0.95 (s, 3H), 0.91 (d, J = 6.6 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 216.3, 213.3, 212.9, 197.9, 197.4, 171.7, 169.8, 110.7, 107.9, 83.4, 82.8, 55.5, 55.5, 48.6, 48.1, 48.0, 47.5, 42.7, 42.6, 42.5, 40.7, 40.6, 36.7, 34.6, 34.0, 29.9, 29.3, 27.3, 26.5, 26.1, 25.5, 25.5, 25.3, 25.2, 24.9, 24.1, 23.6, 23.0, 22.9, 22.7, 21.3, 21.3, 21.0, 20.8, 17.4;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4880.

Table S21. NMR data ($CDCl_3$) comparison between synthetic **2** from through A and the isolated natural product.

	^{1}H & ppm (J)			*^{13}C & ppm*		
position	isolated (500M)	synthesized (300M)	error (iso. - syn.)	isolated (125M)	synthesized (75M)	error (iso. - syn.)
1	-	-	-	171.7	171.7	0
2	-	-	-	48.0	48.0	0
3	-	-	-	212.9	212.9	0
4	-	-	-	55.5	55.5	0
5	-	-	-	197.4	197.4	0
6	-	-	-	107.9	107.9	0
7	4.22 (d, *J* = 7.0 Hz, 1H)	4.23 (d, *J* = 7.5 Hz, 1H)	-0.01	42.6	42.6	0
8	-	-	-	216.3	216.3	0
9	2.71 (m, 1H)	2.70 (m, 1H)	0.01	42.7	42.7	0
10	1.32 (d, *J* = 6.5 Hz, 3H)	1.32 (d, *J* = 6.6 Hz, 3H)	0	21.3	21.3	0
11	1.03 (d, *J* = 6.5 Hz, 3H)	1.03 (d, *J* = 6.6 Hz, 3H)	0	17.4	17.4	0
12	1.37 (s, 3H)	1.37 (s, 3H)	0	25.2	25.2	0
13	1.44 (s, 3H)	1.44 (s, 3H)	0	25.5	25.5	0
14	1.36 (s, 3H)	1.36 (s, 3H)	0	27.3	27.3	0
15	1.31 (s, 3H)	1.31 (s, 3H)	0	20.8	20.8	0
1'	1.74 (m, 1H)	1.74 (m, 1H)	0	48.6	48.6	0
2'a	1.53 (m, 1H)	1.53 (m, 1H)	0	23.0	23.0	0
2'b	1.25 (m, 1H)	1.26 (m, 1H)	-0.01			
3'a	2.11 (m, 1H)	2.11 (m, 1H)	0	40.7	40.7	0
3'b	1.73 (m, 1H)	1.73 (m, 1H)	0			
4'	-	-	-	83.4	83.4	0
5'	2.21 (m, 1H)	2.20 (m, 1H)	0.01	40.6	40.6	0
6'a	1.28 (m, 1H)	1.28 (m, 1H)	0	29.9	29.9	0
6'b	1.25 (m, 1H)	1.26 (m, 1H)	-0.01			
7'a	2.27 (m, 1H)	2.28 (m, 1H)	-0.01	36.7	36.7	0
7'b	1.72 (m, 1H)	1.72 (m, 1H)	0			
8'	-	-	-	82.8	82.8	0
9'	2.58 (m, 1H)	2.58 (m, 1H)	0	47.5	47.5	0
10'a	1.60 (m, 1H)	1.60 (m, 1H)	0	34.6	34.6	0
10'b	1.39 (m, 1H)	1.38 (m, 1H)	0.01			
11'	-	-	-	34.0	34.0	0
12'	0.95 (s, 3H)	0.95 (s, 3H)	0	22.9	22.9	0
13'	0.97 (s, 3H)	0.97 (s, 3H)	0	29.3	29.3	0
14'	1.14 (s, 3H)	1.14 (s, 3H)	0	21.0	21.0	0
15'a	1.98 (m, 1H)	1.97 (m, 1H)	0.01	23.6	23.6	0
15'b	1.89 (m, 1H)	1.88 (m, 1H)	0.01			
1''	-	-	-	169.8	169.8	0
2''	-	-	-	48.1	48.1	0
3''	-	-	-	213.3	213.3	0
4''	-	-	-	55.5	55.5	0
5''	-	-	-	197.9	197.9	0
6''	-	-	-	110.7	110.7	0
7''	2.95 (m, 1H)	2.95 (m, 1H)	0	25.3	25.3	0
8''a	1.49 (m, 1H)	1.49 (m, 1H)	0	42.5	42.5	0
8''b	1.10 (m, 1H)	1.10 (m, 1H)	0			
9''	1.70 (m, 1H)	1.70 (m, 1H)	0	26.1	26.1	0
10''	0.91 (d, *J* = 6.2 Hz, 3H)	0.91 (d, *J* = 6.6 Hz, 3H)	0	24.1	24.1	0
11''	1.03 (d, *J* = 6.2 Hz, 3H)	1.03 (d, *J* = 6.6 Hz, 3H)	0	21.3	21.3	0
12''	1.39 (s, 3H)	1.39 (s, 3H)	0	24.9	24.9	0
13''	1.30 (s, 3H)	1.30 (s, 3H)	0	25.5	25.5	0
14''	1.33 (s, 3H)	1.33 (s, 3H)	0	22.7	22.7	0
15''	1.36 (s, 3H)	1.36 (s, 3H)	0	26.5	26.5	0



16

Compound **16**: 11.0 mg, 14% yield, yellow blocks, mp 213–215 °C;

R_f = 0.62 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = +49.4° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2923, 2857, 1707, 1659, 1616, 1459, 1378, 1201 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (d, *J* = 11.2 Hz, 1H), 2.93 (m, 1H), 2.64 (m, 1H), 2.23 (m, 1H), 2.19 (m, 1H), 2.10 (m, 1H), 2.08 (m, 1H), 2.02 (m, 1H), 1.88 (m, 1H), 1.85 (m, 1H), 1.78 (m, 1H), 1.76 (m, 1H), 1.69 (m, 1H), 1.66 (m, 1H), 1.64 (m, 1H), 1.52 (m, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.38 (m, 1H), 1.35 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.28 (s, 3H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.25 (m, 2H), 1.21 (m, 1H), 1.16 (s, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 0.99 (s, 3H), 0.92 (s, 3H), 0.92 (d, *J* = 5.8 Hz, 3H), 0.87 (d, *J* = 5.8 Hz, 3H), 0.80 (m, 1H);

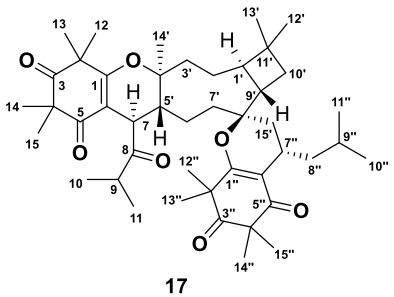
^{13}C NMR (100 MHz, $CDCl_3$) δ 216.5, 212.9, 212.8, 198.5, 197.4, 171.9, 167.4, 114.0, 110.1, 83.3, 83.1, 55.2, 55.1, 49.2, 49.1, 48.5, 48.0, 43.8, 42.8, 42.6, 41.3, 38.8, 38.3, 36.2, 35.7, 33.8, 30.0, 29.9, 26.7, 26.2, 25.9, 25.6, 25.5, 24.9, 24.8, 24.2, 23.9, 23.4, 22.6, 21.7, 21.4, 20.9, 20.7, 20.0, 19.2;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4879.

Table S22. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **16** in $CDCl_3$ (δ in ppm, *J* in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	171.9	8'	–	83.1
2	–	48.0	9'	2.10 m	42.6
3	–	212.9	10'a	1.76 m	36.2
4	–	55.1	10'b	1.38 m	
5	–	197.4	11'	–	33.8
6	–	110.1	12'	0.92 s	21.7
7	3.39 d (11.2)	49.2	13'	0.99 s	30.0
8	–	216.5	14'	1.16 s	20.0
9	2.93 m	41.3	15'a	2.08 m	38.3
10	1.26 d (7.0)	20.7	15'b	1.21 m	
11	1.13 d (7.0)	19.2	1"	–	167.4
12	1.35 s	25.6	2"	–	48.5
13	1.45 s	24.8	3"	–	212.8
14	1.31 s	22.6	4"	–	55.2
15	1.28 s	23.9	5"	–	198.5
1'	2.02 m	49.1	6"	–	114.0
2'	1.25 m	29.9	7"	2.64 m	25.9
			8"a	1.69 m	42.8
3'a	2.19 m	35.7	8"b	0.80 m	
3'b	1.85 m		9"	1.64 m	25.5

4'	–	83.3	10"	0.87 d (5.8)	24.2
5'	2.23 m	43.8	11"	0.92 d (5.8)	20.9
6'a	1.78 m	21.4	12"	1.35 s	26.7
6'b	1.52 m		13"	1.40 s	23.4
7'a	1.88 m	38.8	14"	1.28 s	26.2
7'b	1.66 m		15"	1.34 s	24.9



17

Compound **17**: 6.3 mg, 8% yield, yellow oil;

R_f = 0.62 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = +29.2° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2925, 2857, 1712, 1659, 1621, 1464, 1383, 1354 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (d, *J* = 10.4 Hz, 1H), 2.86 (m, 1H), 2.73 (m, 1H), 2.47 (m, 1H), 2.16 (m, 1H), 2.04 (m, 1H), 2.01 (m, 1H), 1.86 (m, 2H), 1.73 (m, 1H), 1.72 (m, 1H), 1.70 (m, 1H), 1.67 (m, 1H), 1.57 (m, 1H), 1.53 (m, 2H), 1.48 (m, 1H), 1.45 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.37 (m, 1H), 1.32 (s, 3H), 1.32 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.30 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H), 1.18 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.03 (m, 1H), 0.98 (s, 3H), 0.96 (s, 3H), 0.96 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 213.3, 212.8, 197.9, 197.0, 171.2, 169.7, 110.3, 109.7, 82.8, 82.2, 55.7, 55.5, 48.5, 47.9, 47.8, 47.3, 46.9, 43.8, 42.1, 41.6, 38.3, 37.5, 34.6, 33.7, 29.5, 26.9, 26.3, 25.5, 25.5, 25.4, 25.2, 24.9, 24.7, 24.3, 24.0, 22.9, 22.5, 22.1, 21.9, 21.4, 21.4, 20.5, 20.0, 17.8;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4881.

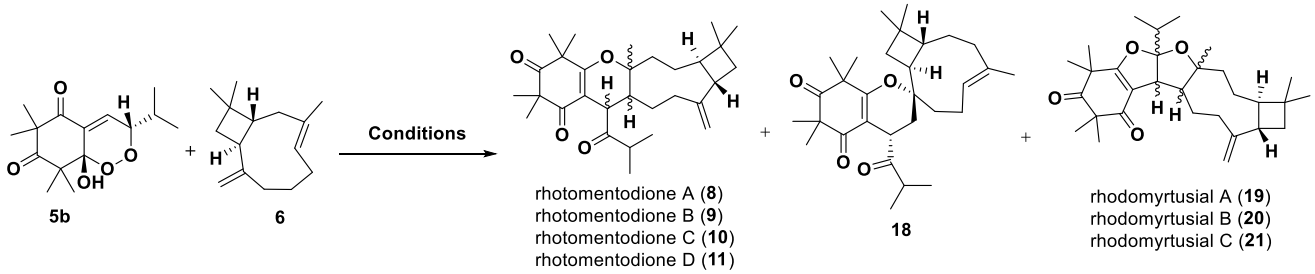
Table S23. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **17** in $CDCl_3$ (δ in ppm, *J* in Hz).

position	δ_H	δ_C	position	δ_H	δ_C
1	–	171.2	8'	–	82.2
2	–	47.8	9'	2.47 m	46.9
3	–	212.8	10'a	1.57 m	34.6
4	–	55.7	10'b	1.30 m	
5	–	197.0	11'	–	33.7
6	–	109.7	12'	0.98 s	22.9
7	3.45 d (10.4)	47.3	13'	0.96 s	29.5
8	–	216.2	14'	1.07 s	21.4
9	2.73 m	43.8	15'	1.86 m	24.0
10	1.43 d (6.8)	20.5			
11	1.09 d (6.8)	17.8	1"	–	169.7
12	1.32 s	21.4	2"	–	47.9
13	1.45 s	24.7	3"	–	213.3

14	1.29 s	22.1	4"	–	55.5
15	1.32 s	22.5	5"	–	197.9
1'	1.72 m	48.5	6"	–	110.3
2'	1.53 m	21.9	7"	2.86 m	25.2
			8"a	1.48 m	42.1
3'a	2.16 m	38.3	8"b	1.03 m	
3'b	1.67 m		9"	1.73 m	26.3
4'	–	82.8	10"	0.96 d (6.8)	24.3
5'	2.01 m	41.6	11"	1.06 d (6.8)	20.0
6'a	1.70 m	25.5	12"	1.24 s	24.9
6'b	1.37 m		13"	1.28 s	25.4
7'a	2.04 m	37.5	14"	1.30 s	25.5
7'b	1.18 m		15"	1.32 s	26.9

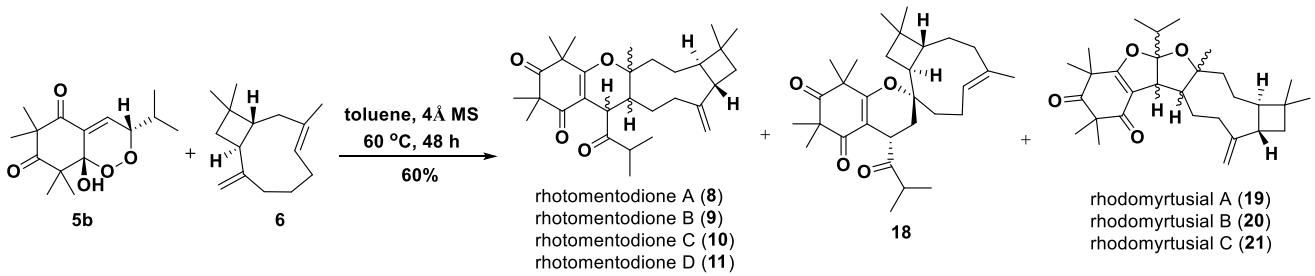
5.4 Syntheses of 8–11 and 18–21

Table S24. Condition screen for the syntheses of compounds **8–11** and **18–21**.

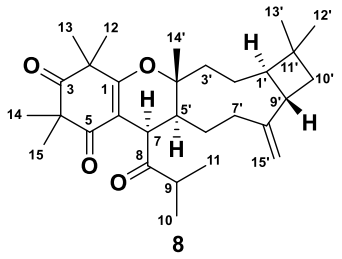


entry[a]	catalyst	mol %	solvent	temp (°C)	time (h)	Yield (%)[b]
1	–	–	DCM	40	48	trace[d]
2	–	–	DCM	40	48	45
3	TFA	20	DCM	40	24	trace
4	–	–	THF	60	48	trace
5	–	–	toluene	60	48	60
6	–	–	toluene	60	48	10[d]
7	TFA	20	toluene	60	24	trace
8	–	–	toluene	110	48	48
9	–	–	toluene	110	48	trace[c]
10	$Sc(CF_3SO_3)_3$	20	toluene	110	24	trace
11	Quinine	50	toluene	rt	48	25
12	Quinine	50	toluene	110	48	30
13	(*S*)-**C1**[e]	20	toluene	110	48	58
14	(*S*)-**C1**	20	toluene	110	48	50[d]

[a] Unless otherwise stated, the reactions of entries 1–14 were performed with **5b** (0.35 mmol), **6** (0.24 mmol) and 4Å MS (30 mg). [b] Combined isolated yield. [c] Without 4Å MS. [d] **5a** was added. [e] (*S*)-**C1** was (11a*S*)-3,7-Bis[3,5-bis(trifluoromethyl)phenyl]-10,11,12,13-tetrahydro-5-hydroxy-5-oxide-diindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin.



Compound **5b** (100 mg, 0.35 mmol) in a toluene solution (4 mL) was added *β*-caryophyllene (**6**) (53.5 μL, 0.24 mmol) and 4Å molecular sieves (30 mg) at 60 °C (entry 5). The resulting mixture was stirred for 48 h. After the reaction was finished according to TLC, the reaction was filtered through a plug of celite (CH_2Cl_2 was used as the eluent) and was concentrated *in vacuum*. The crude residue was further purified by preparative HPLC (CH_3CN-H_2O, 94:6) to afford corresponding products **8**–**11** and **18**–**21**.



Compound **8**: 16.6 mg, 15% yield, yellow oil;

R_f = 0.35 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = +110.4° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2938, 2868, 1709, 1625, 1462, 1380, 1358, 1187, 1105, 1053, 890, 759 cm^{-1};

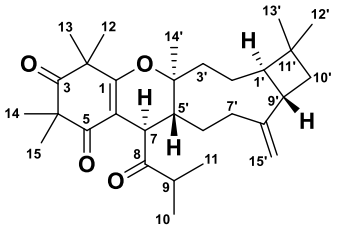
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (s, 2H), 4.05 (d, *J* = 6.6 Hz, 1H), 2.88 (sept, *J* = 6.9 Hz, 1H), 2.50 (m, 1H), 2.42 (m, 1H), 2.24 (m, 1H), 2.12 (m, 1H), 2.08 (m, 1H), 1.78 (m, 1H), 1.75 (m, 1H), 1.68 (m, 1H), 1.63 (m, 1H), 1.61 (m, 1H), 1.59 (m, 1H), 1.57 (m, 1H), 1.43 (s, 3H), 1.40 (m, 1H), 1.36 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.30 (s, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.98 (s, 3H), 0.96 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.9, 213.4, 196.9, 172.0, 150.6, 111.6, 107.6, 84.9, 57.0, 55.3, 48.0, 43.8, 43.4, 42.8, 41.6, 38.1, 36.5, 35.9, 34.4, 30.0, 27.1, 26.2, 25.8, 24.7, 23.4, 22.6, 21.9, 21.7, 20.1, 18.0;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3315.

Table S25. NMR data ($CDCl_3$) comparison between synthetic **8** and the reported natural product.

	^{1}H & ppm (J)			*^{13}C & ppm*		
position	reported (500M)	synthesized (400M)	error (rep. - syn.)	reported (125M)	synthesized (100M)	error (rep. - syn.)
1	-	-	-	171.8	172.0	-0.2
2	-	-	-	47.8	48.0	-0.2
3	-	-	-	213.2	213.4	-0.2
4	-	-	-	55.1	55.3	-0.2
5	-	-	-	196.7	196.9	-0.2
6	-	-	-	107.5	107.6	-0.1
7	4.06 (d, *J* = 6.6 Hz, 1H)	4.05 (d, *J* = 6.6 Hz, 1H)	0.01	43.3	43.4	-0.1
8	-	-	-	216.7	216.9	-0.2
9	2.89 (sept, *J* = 6.9 Hz, 1H)	2.88 (sept, *J* = 6.9 Hz, 1H)	0.01	42.7	42.8	-0.1
10	1.21 (d, *J* = 6.9 Hz, 3H)	1.21 (d, *J* = 6.7 Hz, 3H)	0	19.9	20.1	-0.2
11	1.07 (d, *J* = 6.9 Hz, 3H)	1.07 (d, *J* = 6.7 Hz, 3H)	0	17.9	18.0	-0.1
12	1.36 (s, 3H)	1.36 (s, 3H)	0	24.5	24.7	-0.2
13	1.43 (s, 3H)	1.43 (s, 3H)	0	25.7	25.8	-0.1
14	1.31 (s, 3H)	1.30 (s, 3H)	0.01	22.4	22.6	-0.2
15	1.31 (s, 3H)	1.30 (s, 3H)	0.01	26.1	26.2	-0.1
1'	1.59 (m, 1H)	1.59 (m, 1H)	0	56.8	57.0	-0.2
2'a	1.63 (m, 1H)	1.63 (m, 1H)	0	23.2	23.4	-0.2
2'b	1.40 (m, 1H)	1.40 (m, 1H)	0			
3'a	2.12 (brdd, *J* = 14.0, 10.6 Hz, 1H)	2.12 (m, 1H)	0	43.7	43.8	-0.1
3'b	1.57 (m, 1H)	1.57 (m, 1H)	0			
4'	-	-	-	84.8	84.9	-0.1
5'	2.08 (dt, *J* = 8.5, 6.9 Hz, 1H)	2.08 (m, 1H)	0	38.0	38.1	-0.1
6'a	1.78 (m, 1H)	1.78 (m, 1H)	0	26.9	27.1	-0.2
6'b	1.68 (m, 1H)	1.68 (m, 1H)	0			
7'a	2.51 (ddd, *J* = 14.3, 10.0, 4.4 Hz, 1H)	2.50 (m, 1H)	0.01	35.8	35.9	-0.1
7'b	2.24 (m, 1H)	2.24 (m, 1H)	0			
8'	-	-	-	150.5	150.6	-0.1
9'	2.43 (q, *J* = 8.2 Hz, 1H)	2.42 (m, 1H)	0.01	41.5	41.6	-0.1
10'a	1.75 (t, *J* = 10.6 Hz, 1H)	1.75 (m, 1H)	0	36.3	36.5	-0.2
10'b	1.62 (dd, *J* = 10.6, 7.7 Hz, 1H)	1.61 (m, 1H)	0.01			
11'	-	-	-	34.3	34.4	-0.1
12'	0.98 (s, 3H)	0.98 (s, 3H)	0	21.8	21.9	-0.1
13'	0.97 (s, 3H)	0.96 (s, 3H)	0.01	29.8	30.0	-0.2
14'	1.32 (s, 3H)	1.31 (s, 3H)	0.01	21.5	21.7	-0.2
15'	5.00 (brs, 2H)	4.99 (s, 2H)	0.01	111.5	111.6	-0.1



9

Compound **9**: 10.0 mg, 9% yield, yellow oil;

$\mathbf{R}_f$ = 0.25 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = +13.1° (*c* 2.0, MeOH);

IR (KBr) ν_{max}: 2941, 2872, 1713, 1623, 1462, 1378, 1358, 1187, 1103, 1051, 890 cm^{-1};

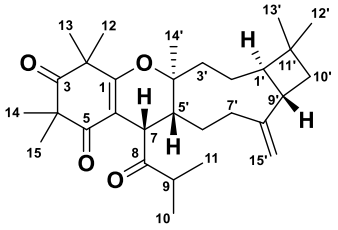
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.74 (s, 1H), 3.40 (d, *J* = 10.5 Hz, 1H), 2.85 (sept, *J* = 6.9 Hz, 1H), 2.50 (m, 1H), 2.32 (m, 1H), 2.22 (dt, *J* = 10.4, 5.2 Hz, 1H), 2.10 (m, 1H), 1.83 (m, 1H), 1.77 (m, 1H), 1.73 (m, 1H), 1.66 (m, 1H), 1.61 (t, *J* = 10.1 Hz, 1H), 1.57 (m, 1H), 1.52 (m, 1H), 1.50 (m, 1H), 1.45 (s, 3H), 1.41 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.6, 213.1, 197.2, 171.5, 154.8, 110.3, 109.4, 83.4, 57.3, 55.3, 47.8, 47.8, 42.6, 42.2, 39.3, 39.0, 38.2, 37.8, 33.3, 33.1, 29.8, 25.4, 24.7, 24.6, 24.0, 22.3, 22.3, 20.2, 20.2, 18.6;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3311.

Table S26. NMR data ($CDCl_3$) comparison between synthetic **9** and the reported natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	reported (500M)	synthesized (400M)	error (rep. - syn.)	reported (125M)	synthesized (100M)	error (rep. - syn.)
1	-	-	-	171.3	171.5	-0.2
2	-	-	-	47.6	47.8	-0.2
3	-	-	-	212.9	213.1	-0.2
4	-	-	-	55.1	55.3	-0.2
5	-	-	-	197.0	197.2	-0.2
6	-	-	-	109.3	109.4	-0.1
7	3.40 (d, *J* = 10.5 Hz, 1H)	3.40 (d, *J* = 10.5 Hz, 1H)	0	47.6	47.8	-0.2
8	-	-	-	216.3	216.6	-0.3
9	2.85 (sept, *J* = 6.9 Hz, 1H)	2.85 (sept, *J* = 6.9 Hz, 1H)	0	42.4	42.6	-0.2
10	1.33 (d, *J* = 6.9 Hz, 3H)	1.33 (d, *J* = 6.9 Hz, 3H)	0	20.1	20.2	-0.1
11	1.14 (d, *J* = 6.9 Hz, 3H)	1.14 (d, *J* = 6.9 Hz, 3H)	0	18.4	18.6	-0.2
12	1.32 (s, 3H)	1.32 (s, 3H)	0	25.2	25.4	-0.2
13	1.44 (s, 3H)	1.45 (s, 3H)	-0.01	24.6	24.7	-0.1
14	1.30 (s, 3H)	1.30 (s, 3H)	0	23.8	24.0	-0.2
15	1.29 (s, 3H)	1.29 (s, 3H)	0	24.5	24.6	-0.1
1'	1.56 (m, 1H)	1.57 (m, 1H)	-0.01	57.1	57.3	-0.2
2'a	1.52 (m, 1H)	1.52 (m, 1H)	0	22.1	22.3	-0.2
2'b	1.42 (m, 1H)	1.41 (m, 1H)	0.01			
3'a	2.10 (brdd, *J* = 15.5, 10.9 Hz, 1H)	2.10 (m, 1H)	0	38.0	38.2	-0.2
3'b	1.77 (brdd, *J* = 15.5, 6.4 Hz, 1H)	1.77 (m, 1H)	0			
4'	-	-	-	83.2	83.4	-0.2
5'	2.22 (dt, *J* = 10.5, 5.2 Hz, 1H)	2.22 (dt, *J* = 10.4, 5.2 Hz, 1H)	-0.01	39.2	39.3	-0.1
6'a	1.67 (m, 1H)	1.66 (m, 1H)	0.01	33.0	33.1	-0.1
6'b	1.50 (m, 1H)	1.50 (m, 1H)	0			
7'a	2.32 (brdd, *J* = 13.3, 9.7 Hz, 1H)	2.32 (m, 1H)	0.01	37.6	37.8	-0.2
7'b	1.84 (brdd, *J* = 13.3, 8.6 Hz, 1H)	1.83 (m, 1H)	0.01			
8'	-	-	-	154.7	154.8	-0.1
9'	2.49 (q, *J* = 9.1 Hz, 1H)	2.50 (q, *J* = 9.2 Hz, 1H)	-0.01	42.1	42.2	-0.1
10'a	1.74 (dd, *J* = 10.5, 8.4 Hz, 1H)	1.73 (m, 1H)	0.01	38.9	39.0	-0.1
10'b	1.61 (t, *J* = 10.1 Hz, 1H)	1.61 (t, *J* = 10.1 Hz, 1H)	0			
11'	-	-	-	33.2	33.3	-0.1
12'	0.97 (s, 3H)	0.97 (s, 3H)	0	22.1	22.3	-0.2
13'	0.99 (s, 3H)	0.99 (s, 3H)	0	29.6	29.8	-0.2
14'	1.07 (s, 3H)	1.07 (s, 3H)	0	20.0	20.2	-0.2
15'a	4.78 (brs, 1H)	4.78 (s, 1H)	0	110.1	110.3	-0.2
15'b	4.74 (brs, 1H)	4.74 (s, 1H)	0			



10

Compound **10**: 8.8 mg, 8% yield, yellow oil;

R_f = 0.4 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = −91.4° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2938, 2868, 1712, 1621, 1464, 1378, 1358, 1289, 1192, 1049, 890, 759 cm^{-1};

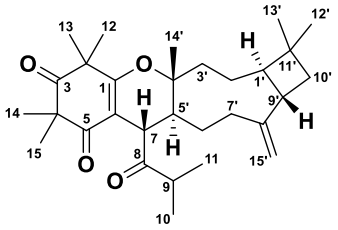
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (s, 1H), 4.81 (s, 1H), 4.20 (d, *J* = 7.2 Hz, 1H), 2.83 (m, 1H), 2.57 (m, 1H), 2.50 (m, 1H), 2.36 (m, 1H), 2.27 (m, 1H), 2.05 (m, 1H), 1.78 (m, 1H), 1.73 (m, 2H), 1.67 (m, 1H), 1.54 (m, 1H), 1.50 (m, 1H), 1.43 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.30 (s, 3H), 1.25 (m, 2H), 1.14 (s, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.99 (s, 3H), 0.94 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 213.3, 197.3, 171.7, 153.8, 110.6, 107.9, 84.0, 57.6, 55.5, 47.9, 43.0, 42.9, 42.7, 40.7, 39.0, 37.5, 36.9, 33.7, 29.7, 28.5, 27.2, 25.5, 24.8, 23.2, 22.4, 21.4, 21.0, 20.7, 17.6;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3309.

Table S27. NMR data ($CDCl_3$) comparison between synthetic **10** and the reported natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	reported (300M)	synthesized (400M)	error (rep. - syn.)	reported (75M)	synthesized (100M)	error (rep. - syn.)
1	-	-	-	171.7	171.7	0
2	-	-	-	47.9	47.9	0
3	-	-	-	213.2	213.3	-0.1
4	-	-	-	55.5	55.5	0
5	-	-	-	197.3	197.3	0
6	-	-	-	107.9	107.9	0
7	4.19 (d, *J* = 7.3 Hz, 1H)	4.20 (d, *J* = 7.2 Hz, 1H)	-0.01	42.9	42.9	0
8	-	-	-	216.9	217.0	-0.1
9	2.83 (m, 1H)	2.83 (m, 1H)	0	43.0	43.0	0
10	1.32 (d, *J* = 6.5 Hz, 3H)	1.32 (d, *J* = 6.8 Hz, 3H)	0	20.7	20.7	0
11	1.06 (d, *J* = 6.5 Hz, 3H)	1.06 (d, *J* = 6.8 Hz, 3H)	0	17.6	17.6	0
12	1.37 (s, 3H)	1.37 (s, 3H)	0	24.9	24.8	0.1
13	1.43 (s, 3H)	1.43 (s, 3H)	0	25.5	25.5	0
14	1.34 (s, 3H)	1.35 (s, 3H)	-0.01	27.1	27.2	-0.1
15	1.30 (s, 3H)	1.30 (s, 3H)	0	21.4	21.4	0
1'	1.53 (m, 1H)	1.54 (m, 1H)	-0.01	57.6	57.6	0
2'	1.25 (m, 2H)	1.25 (m, 2H)	0	23.2	23.2	0
3'a	2.05 (dd, *J* = 15.5, 10.0 Hz, 1H)	2.05 (m, 1H)	0	40.8	40.7	0.1
3'b	1.76 (m, 1H)	1.78 (m, 1H)	-0.02			
4'	-	-	-	84.0	84.0	0
5'	2.36 (m, 1H)	2.36 (m, 1H)	0	39.0	39.0	0
6'a	1.68 (m, 1H)	1.67 (m, 1H)	0.01	28.5	28.5	0
6'b	1.51 (m, 1H)	1.50 (m, 1H)	0.01			
7'a	2.49 (m, 1H)	2.50 (m, 1H)	-0.01	36.9	36.9	0
7'b	2.28 (m, 1H)	2.27 (m, 1H)	0.01			
8'	-	-	-	153.8	153.8	0
9'	2.56 (m, 1H)	2.57 (m, 1H)	-0.01	42.7	42.7	0
10'	1.74 (m, 2H)	1.73 (m, 2H)	0.01	37.6	37.5	0.1
11'	-	-	-	33.7	33.7	0
12'	0.93 (s, 3H)	0.94 (s, 3H)	-0.01	22.4	22.4	0
13'	0.98 (s, 3H)	0.99 (s, 3H)	-0.01	29.7	29.7	0
14'	1.14 (s, 3H)	1.14 (s, 3H)	0	21.0	21.0	0
15'a	4.87 (brs, 1H)	4.87 (brs, 1H)	0	110.6	110.6	0
15'b	4.71 (brs, 1H)	4.71 (brs, 1H)	0			



11

Compound **11**: 12.0 mg, 11% yield, yellow oil;

$\mathbf{R_f}$ = 0.13 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = +25.6° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2936, 2868, 1713, 1623, 1462, 1380, 1355, 1289, 1190, 1051, 892, 759 cm^{-1};

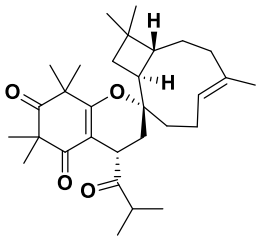
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.75 (s, 1H), 3.24 (d, *J* = 10.7 Hz, 1H), 2.72 (m, 1H), 2.38 (m, 1H), 2.33 (m, 1H), 2.24 (m, 1H), 2.14 (m, 1H), 2.07 (m, 1H), 1.95 (m, 1H), 1.95 (m, 1H), 1.78 (m, 1H), 1.74 (m, 1H), 1.63 (m, 2H), 1.52 (m, 1H), 1.47 (m, 1H), 1.45 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H), 1.27 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.13 (s, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.98 (s, 3H), 0.98 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.2, 213.0, 197.4, 171.7, 151.0, 111.5, 109.1, 83.2, 55.2, 51.9, 49.5, 47.8, 42.1, 39.6, 38.3, 37.0, 36.7, 35.0, 33.8, 31.7, 30.4, 25.3, 25.1, 24.8, 23.6, 22.4, 22.3, 21.2, 20.7, 19.8;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3310.

Table S28. NMR data ($CDCl_3$) comparison between synthetic **11** and the reported natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	reported (300M)	synthesized (400M)	error (rep. - syn.)	reported (75M)	synthesized (100M)	error (rep. - syn.)
1	-	-	-	171.7	171.7	0
2	-	-	-	47.8	47.8	0
3	-	-	-	213.0	213.0	0
4	-	-	-	55.2	55.2	0
5	-	-	-	197.4	197.4	0
6	-	-	-	109.0	109.1	-0.1
7	3.23 (d, *J* = 10.6 Hz, 1H)	3.24 (d, *J* = 10.7 Hz, 1H)	-0.01	49.5	49.5	0
8	-	-	-	215.2	215.2	0
9	2.72 (m, 1H)	2.72 (m, 1H)	0	39.6	39.6	0
10	1.18 (d, *J* = 6.8 Hz, 3H)	1.18 (d, *J* = 6.8 Hz, 3H)	0	20.7	20.7	0
11	1.05 (d, *J* = 6.8 Hz, 3H)	1.05 (d, *J* = 6.8 Hz, 3H)	0	19.8	19.8	0
12	1.35 (s, 3H)	1.35 (s, 3H)	0	25.3	25.3	0
13	1.44 (s, 3H)	1.45 (s, 3H)	-0.01	25.1	25.1	0
14	1.30 (s, 3H)	1.31 (s, 3H)	-0.01	24.8	24.8	0
15	1.27 (s, 3H)	1.27 (s, 3H)	0	23.6	23.6	0
1'	1.95 (m, 1H)	1.95 (m, 1H)	0	51.9	51.9	0
2'a	1.77 (m, 1H)	1.78 (m, 1H)	-0.01	22.4	22.4	0
2'b	1.46 (m, 1H)	1.47 (m, 1H)	-0.01			
3'a	2.14 (m, 1H)	2.14 (m, 1H)	0	37.0	37.0	0
3'b	1.94 (m, 1H)	1.95 (m, 1H)	-0.01			
4'	-	-	-	83.2	83.2	0
5'	2.23 (m, 1H)	2.24 (m, 1H)	-0.01	38.3	38.3	0
6'a	1.74 (m, 1H)	1.74 (m, 1H)	0	31.7	31.7	0
6'b	1.51 (m, 1H)	1.52 (m, 1H)	-0.01			
7'a	2.34 (m, 1H)	2.33 (m, 1H)	0.01	35.0	35.0	0
7'b	2.08 (m, 1H)	2.07 (m, 1H)	0.01			
8'	-	-	-	151.0	151.0	0
9'	2.36 (m, 1H)	2.38 (m, 1H)	-0.02	42.1	42.1	0
10'	1.62 (m, 2H)	1.63 (m, 2H)	-0.01	36.7	36.7	0
11'	-	-	-	33.8	33.8	0
12'	0.98 (s, 3H)	0.98 (s, 3H)	0	22.3	22.3	0
13'	0.98 (s, 3H)	0.98 (s, 3H)	0	30.4	30.4	0
14'	1.13 (s, 3H)	1.13 (s, 3H)	0	21.2	21.2	0
15'a	4.83 (s, 1H)	4.83 (s, 1H)	0	115.5	115.5	0
15'b	4.75 (s, 1H)	4.75 (s, 1H)	0			



18

Compound **18**: 11.0 mg, 10% yield, colorless needle crystals, mp 187–190 °C;

$\mathbf{R_f}$ = 0.38 (petroleum ether/ethyl acetate, 20/1);

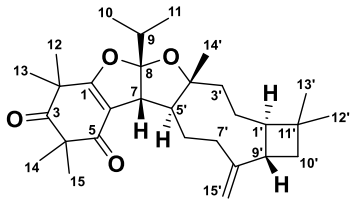
$[\alpha]_D^{25}$ = −43.0° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2968, 2931, 2866, 1709, 1630, 1457, 1387, 1358, 1290, 1185, 1076, 1042, 849, 756, 611 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (brs, 1H), 3.97 (m, 1H), 3.07 (m, 1H), 1.66 (s, 3H), 1.40 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.38 (s, 3H), 1.28 (s, 3H), 1.28 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.97 (s, 3H), 0.93 (brs, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.9, 213.5, 197.4, 55.7, 48.0, 38.8, 37.6, 29.9, 27.5, 25.6, 24.7, 23.3, 21.2, 20.6, 17.7;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3316.



19

Compound **19**: 3.3 mg, 3% yield, yellow oil;

$\mathbf{R}_f$ = 0.4 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = +23.1° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2963, 2934, 2868, 1715, 1628, 1464, 1410, 1378, 1269, 1187, 1123, 1098, 1051, 913, 761 cm^{-1};

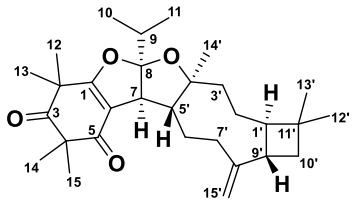
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (s, 1H), 4.78 (s, 1H), 3.16 (d, *J* = 8.2 Hz, 1H), 2.42 (m, 1H), 2.40 (m, 1H), 2.32 (m, 1H), 1.97 (m, 1H), 1.95 (m, 1H), 1.88 (m, 1H), 1.86 (m, 1H), 1.73 (m, 1H), 1.68 (m, 1H), 1.66 (m, 1H), 1.65 (m, 1H), 1.55 (m, 1H), 1.52 (m, 1H), 1.40 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.31 (m, 1H), 1.17 (s, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.94 (s, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8, 193.5, 175.9, 152.7, 127.5, 116.1, 111.0, 89.9, 57.9, 55.5, 52.9, 50.2, 45.5, 42.9, 41.4, 36.2, 35.9, 35.3, 33.8, 30.3, 30.0, 25.2, 25.0, 24.1, 23.7, 22.6, 22.6, 22.4, 16.9, 16.8;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3311.

Table S29. NMR data ($CDCl_3$) comparison between synthetic **19** and the reported natural product.

	^{1}H & ppm (J)			*^{13}C & ppm*		
position	reported (500M)	synthesized (400M)	error (rep. - syn.)	reported (125M)	synthesized (100M)	error (rep. - syn.)
1	-	-	-	175.7	175.9	-0.2
2	-	-	-	45.4	45.5	-0.1
3	-	-	-	213.6	213.8	-0.2
4	-	-	-	55.3	55.5	-0.2
5	-	-	-	193.3	193.5	-0.2
6	-	-	-	115.9	116.1	-0.2
7	3.16 (d, *J* = 8.3 Hz, 1H)	3.16 (d, *J* = 8.2 Hz, 1H)	0	52.7	52.9	-0.2
8	-	-	-	127.3	127.5	-0.2
9	1.94 (sept, *J* = 6.8 Hz, 1H)	1.95 (m, 1H)	-0.01	35.8	35.9	-0.1
10	0.99 (d, *J* = 6.8 Hz, 3H)	0.99 (d, *J* = 6.7 Hz, 3H)	0	16.6	16.8	-0.2
11	0.93 (d, *J* = 6.8 Hz, 3H)	0.93 (d, *J* = 6.7 Hz, 3H)	0	16.7	16.9	-0.2
12	1.40 (s, 3H)	1.40 (s, 3H)	0	24.8	25.0	-0.2
13	1.40 (s, 3H)	1.40 (s, 3H)	0	23.6	23.7	-0.1
14	1.33 (s, 3H)	1.32 (s, 3H)	0.01	23.9	24.1	-0.2
15	1.35 (s, 3H)	1.35 (s, 3H)	0	25.1	25.2	-0.1
1'	1.53 (m, 1H)	1.52 (m, 1H)	0.01	57.7	57.9	-0.2
2'a	1.65 (m, 1H)	1.65 (m, 1H)	0	22.8	22.6	0.2
2'b	1.32 (m, 1H)	1.31 (m, 1H)	0.01			
3'a	2.40 (m, 1H)	2.40 (m, 1H)	0	41.4	41.4	0
3'b	1.67 (m, 1H)	1.66 (m, 1H)	0.01			
4'	-	-	-	89.7	89.9	-0.2
5'	1.97 (m, 1H)	1.97 (m, 1H)	0	50.1	50.2	-0.1
6'a	1.88 (m, 1H)	1.88 (m, 1H)	0	29.8	30.0	-0.2
6'b	1.73 (m, 1H)	1.73 (m, 1H)	0			
7'a	2.43 (m, 1H)	2.42 (m, 1H)	0.01	35.2	35.3	-0.1
7'b	1.87 (m, 1H)	1.86 (m, 1H)	0.01			
8'	-	-	-	152.6	152.7	-0.1
9'	2.33 (q, *J* = 9.0 Hz, 1H)	2.32 (m, 1H)	0.01	42.7	42.9	-0.2
10'a	1.68 (t, *J* = 10.6 Hz, 1H)	1.68 (m, 1H)	0	36.1	36.2	-0.1
10'b	1.55 (dd, *J* = 10.6, 7.8 Hz, 1H)	1.55 (m, 1H)	0			
11'	-	-	-	33.7	33.8	-0.1
12'	0.90 (s, 3H)	0.90 (s, 3H)	0	22.2	22.4	-0.2
13'	0.94 (s, 3H)	0.94 (s, 3H)	0	30.1	30.3	-0.2
14'	1.17 (s, 3H)	1.17 (s, 3H)	0	22.5	22.6	-0.1
15'a	4.89 (s, 1H)	4.89 (s, 1H)	0	110.9	111.0	-0.1
15'b	4.78 (s, 1H)	4.78 (s, 1H)	0			



20

Compound **20**: 1.1 mg, 1% yield, yellow oil;

$\mathbf{R}_f$ = 0.3 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = −59.2° (*c* 0.5, MeOH);

IR (KBr) ν_{max}: 2941, 2872, 1713, 1628, 1571, 1462, 1373, 1264, 1187, 1119, 1051, 913, 768, 615, 464 cm^{-1};

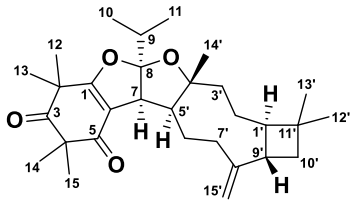
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (s, 1H), 4.47 (s, 1H), 3.18 (d, *J* = 9.8 Hz, 1H), 2.61 (q, *J* = 9.2 Hz, 1H), 2.36 (m, 1H), 2.19 (m, 1H), 2.15 (m, 1H), 2.05 (m, 1H), 2.03 (m, 1H), 1.88 (m, 1H), 1.86 (m, 1H), 1.71 (m, 1H), 1.50 (m, 1H), 1.50 (m, 1H), 1.48 (m, 1H), 1.47 (s, 3H), 1.45 (m, 1H), 1.43 (s, 3H), 1.36 (m, 1H), 1.34 (s, 3H), 1.33 (s, 3H), 1.13 (s, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.89 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4, 193.7, 176.2, 154.4, 126.0, 116.0, 110.8, 88.7, 55.8, 53.6, 52.3, 51.5, 45.6, 43.6, 40.5, 40.1, 37.3, 33.4, 33.3, 29.7, 29.3, 25.3, 25.0, 23.9, 23.8, 23.4, 23.1, 22.8, 17.0, 16.4;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3312.

Table S30. NMR data ($CDCl_3$) comparison between synthetic **20** and the reported natural product.

	^{1}H & ppm (J)			*^{13}C & ppm*		
position	reported (500M)	synthesized (400M)	error (rep. - syn.)	reported (125M)	synthesized (100M)	error (rep. - syn.)
1	-	-	-	176.0	176.2	-0.2
2	-	-	-	45.4	45.6	-0.2
3	-	-	-	213.3	213.4	-0.1
4	-	-	-	55.7	55.8	-0.1
5	-	-	-	193.6	193.7	-0.1
6	-	-	-	115.8	116.0	-0.2
7	3.18 (d, *J* = 9.9 Hz, 1H)	3.18 (d, *J* = 9.8 Hz, 1H)	0	52.2	52.3	-0.1
8	-	-	-	125.8	126.0	-0.2
9	1.89 (sept, *J* = 6.8 Hz, 1H)	1.88 (m, 1H)	0.01	37.1	37.3	-0.2
10	1.07 (d, *J* = 6.8 Hz, 3H)	1.07 (d, *J* = 6.8 Hz, 3H)	0	16.3	16.4	-0.1
11	0.90 (d, *J* = 6.8 Hz, 3H)	0.90 (d, *J* = 6.8 Hz, 3H)	0	16.8	17.0	-0.2
12	1.47 (s, 3H)	1.47 (s, 3H)	0	25.2	25.3	-0.1
13	1.43 (s, 3H)	1.43 (s, 3H)	0	23.6	23.8	-0.2
14	1.33 (s, 3H)	1.33 (s, 3H)	0	23.8	23.9	-0.1
15	1.34 (s, 3H)	1.34 (s, 3H)	0	24.8	25.0	-0.2
1'	1.50 (td, *J* = 9.7, 1.5 Hz, 1H)	1.50 (m, 1H)	0	53.5	53.6	-0.1
2'a	1.50 (m, 1H)	1.50 (m, 1H)	0	22.9	23.1	-0.2
2'b	1.35 (m, 1H)	1.36 (m, 1H)	-0.01			
3'a	2.35 (dd, *J* = 15.5, 9.2 Hz, 1H)	2.36 (m, 1H)	-0.01	39.9	40.1	-0.2
3'b	1.45 (m, 1H)	1.45 (m, 1H)	0			
4'	-	-	-	88.5	88.7	-0.2
5'	2.16 (dt, *J* = 9.9, 3.5 Hz, 1H)	2.15 (m, 1H)	0.01	51.3	51.5	-0.2
6'a	2.05 (m, 1H)	2.05 (m, 1H)	0	29.1	29.3	-0.2
6'b	1.71 (m, 1H)	1.71 (m, 1H)	0			
7'a	2.18 (m, 1H)	2.19 (m, 1H)	-0.01	33.1	33.3	-0.2
7'b	2.04 (m, 1H)	2.03 (m, 1H)	0.01			
8'	-	-	-	154.2	154.4	-0.2
9'	2.61 (q, *J* = 8.6 Hz, 1H)	2.61 (q, *J* = 9.2 Hz, 1H)	0.01	43.4	43.6	-0.2
10'a	1.88 (t, *J* = 7.5 Hz, 1H)	1.86 (m, 1H)	0.02	40.3	40.5	-0.2
10'b	1.49 (m, 1H)	1.48 (m, 1H)	0.01			
11'	-	-	-	33.3	33.4	-0.1
12'	0.89 (s, 3H)	0.89 (s, 3H)	0	22.6	22.8	-0.2
13'	0.94 (s, 3H)	0.94 (s, 3H)	0	29.5	29.7	-0.2
14'	1.13 (s, 3H)	1.13 (s, 3H)	0	23.2	23.4	-0.2
15'a	4.73 (brs, 1H)	4.73 (s, 1H)	0	110.6	110.8	-0.2
15'b	4.47 (brs, 1H)	4.47 (s, 1H)	0			



21

Compound **21**: 3.3 mg, 3% yield, yellow oil;

$\mathbf{R}_f$ = 0.43 (petroleum ether/ethyl acetate, 20/1);

$[\alpha]_D^{25}$ = −20.3° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2968, 2936, 2871, 1713, 1628, 1571, 1464, 1410 , 1190, 1123, 1098, 1051, 913, 761 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (s, 2H), 3.64 (d, *J* = 9.4 Hz, 1H), 2.61 (m, 1H), 2.40 (m, 1H), 2.12 (m, 1H), 2.08 (m, 1H), 2.05 (m, 1H), 1.97 (dd, *J* = 13.9, 9.7 Hz, 1H), 1.79 (t, *J* = 10.5 Hz, 1H), 1.59 (dd, *J* = 10.5, 7.8 Hz, 1H), 1.56 (m, 1H), 1.48 (m, 1H), 1.44 (m, 1H), 1.43 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.34 (m, 1H), 1.33 (s, 3H), 1.25 (m, 2H), 1.11 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H);

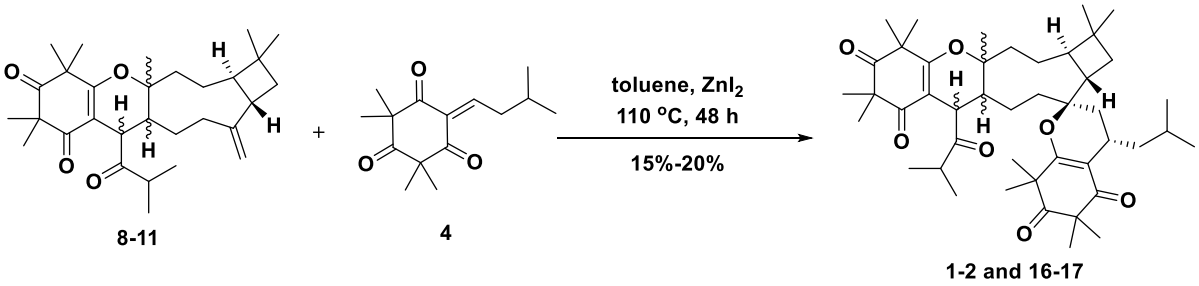
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 194.5, 177.6, 152.4, 127.3, 112.2, 111.1, 88.8, 60.1, 55.8, 48.7, 45.6, 45.2, 44.6, 42.4, 37.0, 36.4, 35.4, 34.5, 29.9, 29.9, 26.3, 24.5, 24.0, 23.4, 23.1, 22.1, 22.1, 16.5, 16.5;

HRMS (ESI) calcd for $C_{30}H_{45}O_4$ $[M+H]^+$ Exact Mass: 469.3312; found: 469.3309.

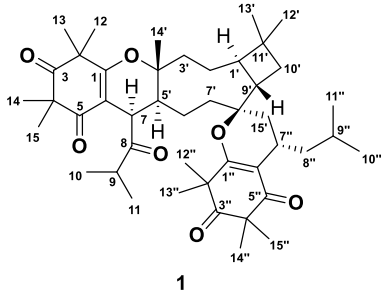
Table S31. NMR data ($CDCl_3$) comparison between synthetic **21** and the reported natural product.

	^{1}H & ppm (J)			*^{13}C & ppm*		
position	reported (500M)	synthesized (400M)	error (rep. - syn.)	reported (125M)	synthesized (100M)	error (rep. - syn.)
1	-	-	-	177.4	177.6	-0.2
2	-	-	-	45.5	45.6	-0.1
3	-	-	-	213.4	213.5	-0.1
4	-	-	-	55.6	55.8	-0.2
5	-	-	-	194.4	194.5	-0.1
6	-	-	-	112.1	112.2	-0.1
7	3.64 (d, *J* = 9.5 Hz, 1H)	3.64 (d, *J* = 9.4 Hz, 1H)	0	48.6	48.7	-0.1
8	-	-	-	127.1	127.3	-0.2
9	2.11 (sept, *J* = 6.8 Hz, 1H)	2.12 (m, 1H)	-0.01	35.2	35.4	-0.2
10	0.96 (d, *J* = 6.8 Hz, 3H)	0.96 (d, *J* = 6.8 Hz, 3H)	0	16.3	16.5	-0.2
11	0.92 (d, *J* = 6.8 Hz, 3H)	0.91 (d, *J* = 6.8 Hz, 3H)	0.01	16.4	16.5	-0.1
12	1.43 (s, 3H)	1.43 (s, 3H)	0	23.9	24.0	-0.1
13	1.39 (s, 3H)	1.39 (s, 3H)	0	24.3	24.5	-0.2
14	1.33 (s, 3H)	1.33 (s, 3H)	0	23.0	23.1	-0.1
15	1.40 (s, 3H)	1.40 (s, 3H)	0	26.2	26.3	-0.1
1'	1.48 (m, 1H)	1.48 (m, 1H)	0	59.9	60.1	-0.2
2'a	1.57 (m, 1H)	1.56 (m, 1H)	0.01	23.4	23.4	0
2'b	1.34 (m, 1H)	1.34 (m, 1H)	0			
3'a	1.97 (dd, *J* = 13.9, 9.5 Hz, 1H)	1.97 (dd, *J* = 13.9, 9.7 Hz, 1H)	0	44.5	44.6	-0.1
3'b	1.44 (m, 1H)	1.44 (m, 1H)	0			
4'	-	-	-	88.6	88.8	-0.2
5'	2.05 (m, 1H)	2.05 (m, 1H)	0	45.0	45.2	-0.2
6'	1.25 (m, 2H)	1.25 (m, 2H)	0	29.6	29.9	-0.3
7'a	2.61 (m, 1H)	2.61 (m, 1H)	0	36.9	37.0	-0.1
7'b	2.09 (m, 1H)	2.08 (m, 1H)	0.01			
8'	-	-	-	152.3	152.4	-0.1
9'	2.40 (q, *J* = 9.0 Hz, 1H)	2.40 (m, 1H)	0	42.3	42.4	-0.1
10'a	1.79 (t, *J* = 10.5 Hz, 1H)	1.79 (t, *J* = 10.5 Hz, 1H)	0	36.2	36.4	-0.2
10'b	1.59 (dd, *J* = 10.5, 7.8 Hz, 1H)	1.59 (dd, *J* = 10.5, 7.8 Hz, 1H)	0			
11'	-	-	-	34.4	34.5	-0.1
12'	0.97 (s, 3H)	0.97 (s, 3H)	0	21.9	22.1	-0.2
13'	0.99 (s, 3H)	0.99 (s, 3H)	0	29.8	29.9	-0.1
14'	1.11 (s, 3H)	1.11 (s, 3H)	0	21.9	22.1	-0.2
15'	5.02 (brs, 2H)	5.02 (s, 2H)	0	110.9	111.1	-0.2

5.5 Syntheses of 1–2 and 16–17 through path B



Compound **4** (53.5 mg, 0.21 mmol) and ZnI_2 (8.3 mg, 0.026 mmol) in a toluene solution (2 ml) was added **8**–**11** (20 mg, 0.043 mmol) under reflux at 110 °C. After 48 h, the reaction was quenced with brine and extracted with ethyl acetate. Then the combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was further purified by preparative HPLC (CH_3CN-H_2O, 95:5) to to afford corresponding products **1**–**2** and **16**–**17**.



1

Compound **1**: 6.2 mg, 20% yield, yellow oil;

R_f = 0.69 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = +106.8° (*c* 0.6, MeOH);

IR (KBr) ν_{max}: 2960, 2865, 1708, 1637, 1468, 1375, 1362, 1208, 1156, 863, 752 cm^{-1};

ECD (CH_3OH): λ_{max} ($\Delta\varepsilon$) 207 (−15.0), 273 (+68.1) nm;

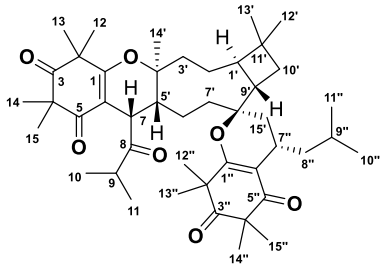
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (d, *J* = 7.2 Hz, 1H), 2.90 (m, 1H), 2.84 (m, 1H), 2.37 (m, 1H), 2.18 (m, 1H), 2.16 (m, 1H), 2.15 (m, 1H), 2.11 (m, 1H), 1.92 (m, 1H), 1.87 (m, 1H), 1.81 (m, 1H), 1.77 (m, 1H), 1.73 (m, 1H), 1.71 (m, 1H), 1.68 (m, 1H), 1.65 (m, 1H), 1.62 (m, 1H), 1.55 (m, 1H), 1.48 (m, 1H), 1.43 (s, 3H), 1.39 (m, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.03 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.97 (s, 3H), 0.94 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.1, 213.1, 213.0, 198.1, 197.2, 171.4, 168.8, 112.5, 108.3, 84.3, 83.3, 55.5, 55.4, 48.7, 48.2, 48.0, 45.2, 44.8, 43.6, 43.1, 42.9, 40.8, 39.5, 35.7, 34.1, 33.8, 30.1, 26.8, 26.1, 26.0, 25.9, 25.6, 25.5, 24.9, 24.4, 24.1, 23.4, 22.9, 22.4, 21.9, 21.5, 21.2, 21.0, 20.4, 18.3;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4880.

Table S32. NMR data ($CDCl_3$) comparison between synthetic **1** thrgouh path B and the isolated natural product.

	^1H & ppm (J)			^{13}C & ppm		
position	isolated (300M)	synthesized (400M)	error (iso. - syn.)	isolated (75M)	synthesized (100M)	error (iso. - syn.)
1	-	-	-	171.3	171.4	-0.1
2	-	-	-	48.0	48.0	0
3	-	-	-	213.1	213.1	0
4	-	-	-	55.5	55.5	0
5	-	-	-	197.2	197.2	0
6	-	-	-	108.4	108.3	0.1
7	4.07 (d, *J* = 7.2 Hz, 1H)	4.07 (d, *J* = 7.2 Hz, 1H)	0	45.2	45.2	0
8	-	-	-	216.0	216.1	-0.1
9	2.89 (m, 1H)	2.90 (m, 1H)	-0.01	42.9	42.9	0
10	1.24 (d, *J* = 6.8 Hz, 3H)	1.25 (d, *J* = 6.8 Hz, 3H)	-0.01	20.4	20.4	0
11	1.07 (d, *J* = 6.8 Hz, 3H)	1.07 (d, *J* = 6.8 Hz, 3H)	0	18.3	18.3	0
12	1.37 (s, 3H)	1.37 (s, 3H)	0	24.5	24.4	0.1
13	1.42 (s, 3H)	1.43 (s, 3H)	-0.01	25.6	25.6	0
14	1.34 (s, 3H)	1.35 (s, 3H)	-0.01	26.7	26.8	-0.1
15	1.29 (s, 3H)	1.30 (s, 3H)	-0.01	26.0	26.1	-0.1
1'	1.82 (m, 1H)	1.81 (m, 1H)	0.01	48.7	48.7	0
2'a	1.70 (m, 1H)	1.71 (m, 1H)	-0.01	23.4	23.4	0
2'b	1.40 (m, 1H)	1.39 (m, 1H)	0.01			
3'a	2.18 (m, 1H)	2.18 (m, 1H)	0	40.8	40.8	0
3'b	1.73 (m, 1H)	1.73 (m, 1H)	0			
4'	-	-	-	84.3	84.3	0
5'	2.15 (m, 1H)	2.15 (m, 1H)	0	43.2	43.1	0.1
6'a	1.87 (m, 1H)	1.87 (m, 1H)	0	21.5	21.5	0
6'b	1.78 (m, 1H)	1.77 (m, 1H)	0.01			
7'a	2.11 (m, 1H)	2.11 (m, 1H)	0	39.5	39.5	0
7'b	1.91 (m, 1H)	1.92 (m, 1H)	-0.01			
8'	-	-	-	83.3	83.3	0
9'	2.38 (m, 1H)	2.37 (m, 1H)	0.01	44.8	44.8	0
10'a	1.63 (m, 1H)	1.62 (m, 1H)	0.01	35.7	35.7	0
10'b	1.48 (m, 1H)	1.48 (m, 1H)	0			
11'	-	-	-	34.1	34.1	0
12'	0.94 (s, 3H)	0.94 (s, 3H)	0	22.4	22.4	0
13'	0.97 (s, 3H)	0.97 (s, 3H)	0	30.1	30.1	0
14'	1.26 (s, 3H)	1.26 (s, 3H)	0	21.0	21.0	0
15'a	2.16 (m, 1H)	2.16 (m, 1H)	0	33.8	33.8	0
15'b	1.55 (m, 1H)	1.55 (m, 1H)	0			
1''	-	-	-	168.8	168.8	0
2''	-	-	-	48.2	48.2	0
3''	-	-	-	213.0	213.0	0
4''	-	-	-	55.4	55.4	0
5''	-	-	-	198.0	198.1	-0.1
6''	-	-	-	112.6	112.5	0.1
7''	2.85 (m, 1H)	2.84 (m, 1H)	0.01	25.6	25.5	0.1
8''a	1.64 (m, 1H)	1.65 (m, 1H)	-0.01	43.7	43.6	0.1
8''b	1.03 (m, 1H)	1.03 (m, 1H)	0			
9''	1.69 (m, 1H)	1.68 (m, 1H)	0.01	25.9	25.9	0
10''	0.92 (d, *J* = 6.0 Hz, 3H)	0.92 (d, *J* = 6.6 Hz, 3H)	0	24.1	24.1	0
11''	0.98 (d, *J* = 6.0 Hz, 3H)	0.98 (d, *J* = 6.6 Hz, 3H)	0	21.3	21.2	0.1
12''	1.36 (s, 3H)	1.36 (s, 3H)	0	24.9	24.9	0
13''	1.31 (s, 3H)	1.32 (s, 3H)	-0.01	21.9	21.9	0
14''	1.31 (s, 3H)	1.31 (s, 3H)	0	22.9	22.9	0
15''	1.32 (s, 3H)	1.33 (s, 3H)	-0.01	26.0	26.1	-0.1



2

Compound **2**: 5.6 mg, 18% yield, yellow oil;

$\mathbf{R}_f$ = 0.69 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = −37.6° (*c* 0.6, MeOH);

IR (KBr) ν_{max}: 2952, 2926, 2868, 1715, 1650, 1625, 1465, 1386, 1360, 1206, 1154, 823, 760 cm^{-1};

ECD (CH_3OH): λ_{max} ($\Delta\varepsilon$) 208 (+19.9), 251 (−21.7), 274 (+8.0), 304 (−11.4) nm;

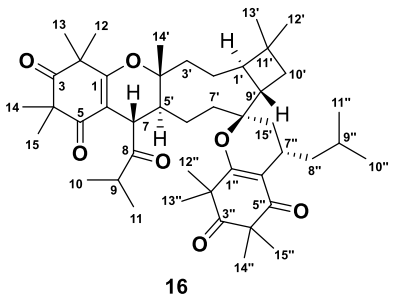
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (d, J = 7.2 Hz, 1H), 2.95 (m, 1H), 2.70 (m, 1H), 2.59 (m, 1H), 2.28 (m, 1H), 2.20 (m, 1H), 2.10 (m, 1H), 1.99 (m, 1H), 1.88 (m, 1H), 1.74 (m, 1H), 1.73 (m, 1H), 1.72 (m, 1H), 1.70 (m, 1H), 1.60 (m, 1H), 1.53 (m, 1H), 1.49 (m, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 1.38 (m, 1H), 1.37 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.32 (d, J = 6.6 Hz, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.28 (m, 1H), 1.26 (m, 2H), 1.14 (m, 3H), 1.10 (m, 1H), 1.03 (d, J = 6.6 Hz, 3H), 1.03 (d, J = 6.4 Hz, 3H), 0.97 (s, 3H), 0.95 (s, 3H), 0.90 (d, J = 6.4 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.4, 213.3, 213.0, 197.9, 197.5, 171.8, 169.9, 110.6, 107.8, 83.4, 82.8, 55.5, 55.5, 48.6, 48.1, 47.9, 47.4, 42.6, 42.5, 42.4, 40.7, 40.6, 36.7, 34.6, 34.0, 29.9, 29.3, 27.3, 26.5, 26.0, 25.5, 25.5, 25.3, 25.1, 24.9, 24.1, 23.5, 23.0, 22.9, 22.7, 21.3, 21.2, 21.0, 20.8, 17.4;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4885.

Table S33. NMR data ($CDCl_3$) comparison between synthetic **2** through path B and the isolated natural product.

	^{1}H & ppm (J)			*^{13}C & ppm*		
position	isolated (500M)	synthesized (400M)	error (iso. - syn.)	isolated (125M)	synthesized (100M)	error (iso. - syn.)
1	-	-	-	171.7	171.8	-0.1
2	-	-	-	48.0	47.9	0.1
3	-	-	-	212.9	213.0	-0.1
4	-	-	-	55.5	55.5	0
5	-	-	-	197.4	197.5	-0.1
6	-	-	-	107.9	107.8	0.1
7	4.22 (d, *J* = 7.0 Hz, 1H)	4.22 (d, *J* = 7.8 Hz, 1H)	0	42.6	42.5	0.1
8	-	-	-	216.3	216.4	-0.1
9	2.71 (m, 1H)	2.70 (m, 1H)	0.01	42.7	42.6	0.1
10	1.32 (d, *J* = 6.5 Hz, 3H)	1.32 (d, *J* = 6.6 Hz, 3H)	0	21.3	21.3	0
11	1.03 (d, *J* = 6.5 Hz, 3H)	1.03 (d, *J* = 6.6 Hz, 3H)	0	17.4	17.4	0
12	1.37 (s, 3H)	1.37 (s, 3H)	0	25.2	25.1	0.1
13	1.44 (s, 3H)	1.44 (s, 3H)	0	25.5	25.5	0
14	1.36 (s, 3H)	1.36 (s, 3H)	0	27.3	27.3	0
15	1.31 (s, 3H)	1.31 (s, 3H)	0	20.8	20.8	0
1'	1.74 (m, 1H)	1.74 (m, 1H)	0	48.6	48.6	0
2'a	1.53 (m, 1H)	1.53 (m, 1H)	0	23.0	23.0	0
2'b	1.25 (m, 1H)	1.26 (m, 1H)	-0.01			
3'a	2.11 (m, 1H)	2.10 (m, 1H)	0.01	40.7	40.7	0
3'b	1.73 (m, 1H)	1.73 (m, 1H)	0			
4'	-	-	-	83.4	83.4	0
5'	2.21 (m, 1H)	2.20 (m, 1H)	0.01	40.6	40.6	0
6'a	1.28 (m, 1H)	1.28 (m, 1H)	0	29.9	29.9	0
6'b	1.25 (m, 1H)	1.26 (m, 1H)	-0.01			
7'a	2.27 (m, 1H)	2.28 (m, 1H)	-0.01	36.7	36.7	0
7'b	1.72 (m, 1H)	1.72 (m, 1H)	0			
8'	-	-	-	82.8	82.8	0
9'	2.58 (m, 1H)	2.59 (m, 1H)	-0.01	47.5	47.4	0.1
10'a	1.60 (m, 1H)	1.60 (m, 1H)	0	34.6	34.6	0
10'b	1.39 (m, 1H)	1.38 (m, 1H)	0.01			
11'	-	-	-	34.0	34.0	0
12'	0.95 (s, 3H)	0.95 (s, 3H)	0	22.9	22.9	0
13'	0.97 (s, 3H)	0.97 (s, 3H)	0	29.3	29.3	0
14'	1.14 (s, 3H)	1.14 (s, 3H)	0	21.0	21.0	0
15'a	1.98 (m, 1H)	1.99 (m, 1H)	-0.01	23.6	23.5	0.1
15'b	1.89 (m, 1H)	1.88 (m, 1H)	0.01			
1''	-	-	-	169.8	169.9	-0.1
2''	-	-	-	48.1	48.1	0
3''	-	-	-	213.3	213.3	0
4''	-	-	-	55.5	55.5	0
5''	-	-	-	197.9	197.9	0
6''	-	-	-	110.7	110.6	0.1
7''	2.95 (m, 1H)	2.95 (m, 1H)	0	25.3	25.3	0
8''a	1.49 (m, 1H)	1.49 (m, 1H)	0	42.5	42.4	0.1
8''b	1.10 (m, 1H)	1.10 (m, 1H)	0			
9''	1.70 (m, 1H)	1.70 (m, 1H)	0	26.1	26.0	0.1
10''	0.91 (d, *J* = 6.2 Hz, 3H)	0.90 (d, *J* = 6.4 Hz, 3H)	0.01	24.1	24.1	0
11''	1.03 (d, *J* = 6.2 Hz, 3H)	1.03 (d, *J* = 6.4 Hz, 3H)	0	21.3	21.2	0.1
12''	1.39 (s, 3H)	1.39 (s, 3H)	0	24.9	24.9	0
13''	1.30 (s, 3H)	1.29 (s, 3H)	0.01	25.5	25.5	0
14''	1.33 (s, 3H)	1.33 (s, 3H)	0	22.7	22.7	0
15''	1.36 (s, 3H)	1.37 (s, 3H)	-0.01	26.5	26.5	0



16

Compound **16**: 5.2 mg, 17% yield, yellow oil;

R_f = 0.62 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = +60.5° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2945, 2868, 1715, 1650, 1465, 1380, 1205, 1183, 872 cm^{-1};

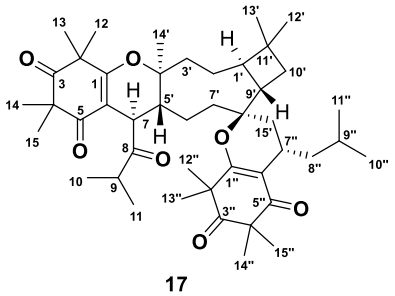
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (d, *J* = 11.6 Hz, 1H), 2.92 (m, 1H), 2.63 (m, 1H), 2.23 (m, 1H), 2.19 (m, 1H), 2.10 (m, 1H), 2.08 (m, 1H), 2.03 (m, 1H), 1.88 (m, 1H), 1.85 (m, 1H), 1.78 (m, 1H), 1.76 (m, 1H), 1.69 (m, 1H), 1.67 (m, 1H), 1.64 (m, 1H), 1.52 (m, 1H), 1.45 (s, 3H), 1.39 (s, 3H), 1.38 (m, 1H), 1.35 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.25 (m, 2H), 1.22 (m, 1H), 1.16 (s, 3H), 1.13 (d, *J* = 6.8 Hz, 3H), 0.99 (s, 3H), 0.92 (s, 3H), 0.92 (d, *J* = 6.0 Hz, 3H), 0.87 (d, *J* = 6.0 Hz, 3H), 0.80 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.5, 212.9, 212.8, 198.5, 197.4, 171.9, 167.4, 114.0, 110.1, 83.3, 83.1, 55.2, 55.1, 49.2, 49.1, 48.5, 48.0, 43.7, 42.8, 42.6, 41.3, 38.8, 38.3, 36.2, 35.8, 33.8, 30.0, 29.9, 26.7, 26.2, 25.9, 25.5, 25.5, 24.9, 24.8, 24.2, 23.9, 23.4, 22.6, 21.7, 21.4, 20.9, 20.7, 19.9, 19.2;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4883.

Table S34. NMR data ($CDCl_3$) comparison between synthetic **16** through path A and path B.

	^1H & ppm (J)			^{13}C & ppm		
position	16 (path A) (400M)	16 (path B) (400M)	error	16 (path A) (100M)	16 (path B) (100M)	error
1	-	-	-	171.9	171.9	0
2	-	-	-	48.0	48.0	0
3	-	-	-	212.9	212.9	0
4	-	-	-	55.1	55.1	0
5	-	-	-	197.4	197.4	0
6	-	-	-	110.1	110.1	0
7	3.39 (d, *J* = 11.2 Hz, 1H)	3.39 (d, *J* = 11.6 Hz, 1H)	0	49.2	49.2	0
8	-	-	-	216.5	216.5	0
9	2.93 (m, 1H)	2.92 (m, 1H)	0.01	41.3	41.3	0
10	1.26 (d, *J* = 7.0 Hz, 3H)	1.26 (d, *J* = 6.8 Hz, 3H)	0	20.7	20.7	0
11	1.13 (d, *J* = 7.0 Hz, 3H)	1.13 (d, *J* = 6.8 Hz, 3H)	0	19.2	19.2	0
12	1.35 (s, 3H)	1.35 (s, 3H)	0	25.6	25.5	0.1
13	1.45 (s, 3H)	1.45 (s, 3H)	0	24.8	24.8	0
14	1.31 (s, 3H)	1.31 (s, 3H)	0	22.6	22.6	0
15	1.28 (s, 3H)	1.27 (s, 3H)	0.01	23.9	23.9	0
1'	2.02 (m, 1H)	2.03 (m, 1H)	-0.01	49.1	49.1	0
2'	1.25 (m, 2H)	1.25 (m, 2H)	0	29.9	29.9	0
3'a	2.19 (m, 1H)	2.19 (m, 1H)	0	35.7	35.8	-0.1
3'b	1.85 (m, 1H)	1.85 (m, 1H)	0			
4'	-	-	-	83.3	83.3	0
5'	2.23 (m, 1H)	2.23 (m, 1H)	0	43.8	43.7	0.1
6'a	1.78 (m, 1H)	1.78 (m, 1H)	0	21.4	21.4	0
6'b	1.52 (m, 1H)	1.52 (m, 1H)	0			
7'a	1.88 (m, 1H)	1.88 (m, 1H)	0	38.8	38.8	0
7'b	1.66 (m, 1H)	1.67 (m, 1H)	-0.01			
8'	-	-	-	83.1	83.1	0
9'	2.10 (m, 1H)	2.10 (m, 1H)	0	42.6	42.6	0
10'a	1.76 (m, 1H)	1.76 (m, 1H)	0	36.2	36.2	0
10'b	1.38 (m, 1H)	1.38 (m, 1H)	0			
11'	-	-	-	33.8	33.8	0
12'	0.92 (s, 3H)	0.92 (s, 3H)	0	21.7	21.7	0
13'	0.99 (s, 3H)	0.99 (s, 3H)	0	30.0	30.0	0
14'	1.16 (s, 3H)	1.16 (s, 3H)	0	20.0	19.9	0.1
15'a	2.08 (m, 1H)	2.08 (m, 1H)	0	38.3	38.3	0
15'b	1.21 (m, 1H)	1.22 (m, 1H)	-0.01			
1''	-	-	-	167.4	167.4	0
2''	-	-	-	48.5	48.5	0
3''	-	-	-	212.8	212.8	0
4''	-	-	-	55.2	55.2	0
5''	-	-	-	198.5	198.5	0
6''	-	-	-	114.0	114.0	0
7''	2.64 (m, 1H)	2.63 (m, 1H)	0.01	25.9	25.9	0
8''a	1.69 (m, 1H)	1.69 (m, 1H)	0	42.8	42.8	0
8''b	0.80 (m, 1H)	0.80 (m, 1H)	0			
9''	1.64 (m, 1H)	1.64 (m, 1H)	0	25.5	25.5	0
10''	0.87 (d, *J* = 5.8 Hz, 3H)	0.87 (d, *J* = 6.0 Hz, 3H)	0	24.2	24.2	0
11''	0.92 (d, *J* = 5.8 Hz, 3H)	0.92 (d, *J* = 6.0 Hz, 3H)	0	20.9	20.9	0
12''	1.35 (s, 3H)	1.34 (s, 3H)	0.01	26.7	26.7	0
13''	1.40 (s, 3H)	1.39 (s, 3H)	0.01	23.4	23.4	0
14''	1.28 (s, 3H)	1.28 (s, 3H)	0	26.2	26.2	0
15''	1.34 (s, 3H)	1.34 (s, 3H)	0	24.9	24.9	0



17

Compound **17**: 4.6 mg, 15% yield, yellow oil;

$\mathbf{R_f}$ = 0.62 (petroleum ether/ethyl acetate, 4/1);

$[\alpha]_D^{25}$ = +36.4° (*c* 1.0, MeOH);

IR (KBr) ν_{max}: 2928, 2865, 1706, 1656, 1623, 1464, 1368, 1280, 1186, 856, 754 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (d, J = 10.4 Hz, 1H), 2.86 (m, 1H), 2.73 (m, 1H), 2.47 (m, 1H), 2.16 (m, 1H), 2.04 (m, 1H), 2.01 (m, 1H), 1.86 (m, 2H), 1.73 (m, 1H), 1.72 (m, 1H), 1.70 (m, 1H), 1.67 (m, 1H), 1.57 (m, 1H), 1.53 (m, 2H), 1.48 (m, 1H), 1.45 (s, 3H), 1.43 (d, J = 7.0 Hz, 3H), 1.37 (m, 1H), 1.32 (s, 3H), 1.32 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.30 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H), 1.17 (m, 1H), 1.09 (d, J = 7.0 Hz, 3H), 1.06 (s, 3H), 1.06 (d, J = 6.6 Hz, 3H), 1.03 (m, 1H), 0.99 (s, 3H), 0.96 (s, 3H), 0.96 (d, J = 6.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.3, 213.3, 212.8, 197.9, 197.1, 171.2, 169.8, 110.2, 109.6, 82.8, 82.2, 55.7, 55.5, 48.4, 48.0, 47.8, 47.3, 46.9, 43.8, 42.0, 41.6, 38.3, 37.5, 34.6, 33.7, 29.5, 26.9, 26.3, 25.5, 25.5, 25.4, 25.2, 24.9, 24.7, 24.3, 24.0, 22.9, 22.5, 22.1, 21.9, 21.4, 21.4, 20.5, 20.0, 17.8;

HRMS (ESI) calcd for $C_{45}H_{67}O_7$ $[M+H]^+$ Exact Mass: 719.4881; found: 719.4884.

Table S35. NMR data ($CDCl_3$) comparison between synthetic **17** through paths A and B.

	^{1}H & ppm (J)			*^{13}C & ppm*		
position	17 (path A) (400M)	17 (path B) (400M)	error	17 (path A) (100M)	17 (path B) (100M)	error
1	-	-	-	171.2	171.2	0
2	-	-	-	47.8	47.8	0
3	-	-	-	212.8	212.8	0
4	-	-	-	55.7	55.7	0
5	-	-	-	197.0	197.1	-0.1
6	-	-	-	109.7	109.6	0.1
7	3.45 (d, J = 10.4 Hz, 1H)	3.45 (d, J = 10.4 Hz, 1H)	0	47.3	47.3	0
8	-	-	-	216.2	216.3	-0.1
9	2.73 (m, 1H)	2.73 (m, 1H)	0	43.8	43.8	0
10	1.43 (d, J = 6.8 Hz, 3H)	1.43 (d, J = 7.0 Hz, 3H)	0	20.5	20.5	0
11	1.09 (d, J = 6.8 Hz, 3H)	1.09 (d, J = 7.0 Hz, 3H)	0	17.8	17.8	0
12	1.32 (s, 3H)	1.32 (s, 3H)	0	21.4	21.4	0
13	1.45 (s, 3H)	1.45 (s, 3H)	0	24.7	24.7	0
14	1.29 (s, 3H)	1.29 (s, 3H)	0	22.1	22.1	0
15	1.32 (s, 3H)	1.32 (s, 3H)	0	22.5	22.5	0
1'	1.72 (m, 1H)	1.72 (m, 1H)	0	48.5	48.4	0.1
2'	1.53 (m, 2H)	1.53 (m, 2H)	0	21.9	21.9	0
3'a	2.16 (m, 1H)	2.16 (m, 1H)	0	38.3	38.3	0
3'b	1.67 (m, 1H)	1.67 (m, 1H)	0			
4'	-	-	-	82.8	82.8	0
5'	2.01 (m, 1H)	2.01 (m, 1H)	0	41.6	41.6	0
6'a	1.70 (m, 1H)	1.70 (m, 1H)	0	25.5	25.5	0
6'b	1.37 (m, 1H)	1.37 (m, 1H)	0			
7'a	2.04 (m, 1H)	2.04 (m, 1H)	0	37.5	37.5	0
7'b	1.18 (m, 1H)	1.17 (m, 1H)	0.01			
8'	-	-	-	82.2	82.2	0
9'	2.47 (m, 1H)	2.47 (m, 1H)	0	46.9	46.9	0
10'a	1.57 (m, 1H)	1.57 (m, 1H)	0	34.6	34.6	0
10'b	1.30 (m, 1H)	1.30 (m, 1H)	0			
11'	-	-	-	33.7	33.7	0
12'	0.98 (s, 3H)	0.99 (s, 3H)	-0.01	22.9	22.9	0
13'	0.96 (s, 3H)	0.96 (s, 3H)	0	29.5	29.5	0
14'	1.07 (s, 3H)	1.06 (s, 3H)	0.01	21.4	21.4	0
15'	1.86 (m, 2H)	1.86 (m, 2H)	0	24.0	24.0	0
1''	-	-	-	169.7	169.8	-0.1
2''	-	-	-	47.9	48.0	-0.1
3''	-	-	-	213.3	213.3	0
4''	-	-	-	55.5	55.5	0
5''	-	-	-	197.9	197.9	0
6''	-	-	-	110.3	110.2	0.1
7''	2.86 (m, 1H)	2.86 (m, 1H)	0	25.2	25.2	0
8''a	1.48 (m, 1H)	1.48 (m, 1H)	0	42.1	42.0	0.1
8''b	1.03 (m, 1H)	1.03 (m, 1H)	0			
9''	1.73 (m, 1H)	1.73 (m, 1H)	0	26.3	26.3	0
10''	0.96 (d, J = 6.8 Hz, 3H)	0.96 (d, J = 6.6 Hz, 3H)	0	24.3	24.3	0
11''	1.06 (d, J = 6.8 Hz, 3H)	1.06 (d, J = 6.6 Hz, 3H)	0	20.0	20.0	0
12''	1.24 (s, 3H)	1.24 (s, 3H)	0	24.9	24.9	0
13''	1.28 (s, 3H)	1.28 (s, 3H)	0	25.4	25.4	0
14''	1.30 (s, 3H)	1.30 (s, 3H)	0	25.5	25.5	0
15''	1.32 (s, 3H)	1.32 (s, 3H)	0	26.9	26.9	0

6. X-ray crystal structures of 7, 16, and 18

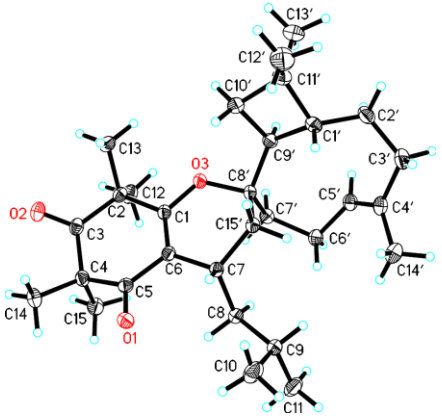


Figure S52. X-ray ORTEP drawing of **7** (thermal ellipsoids at the 50% probability level).

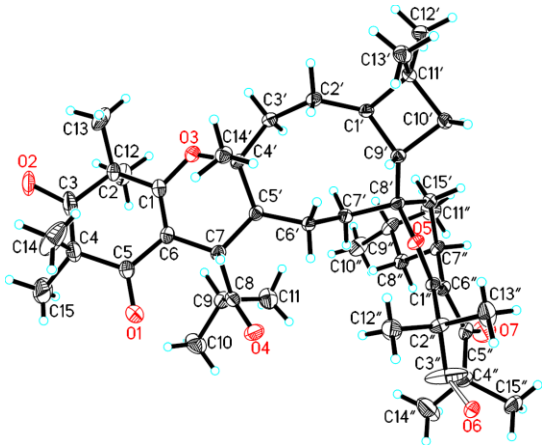


Figure S53. X-ray ORTEP drawing of **16** (thermal ellipsoids at the 50% probability level).

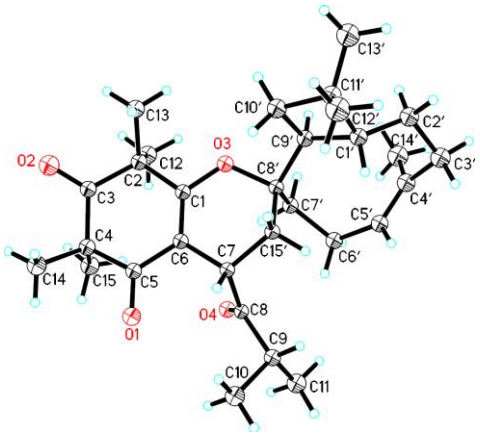


Figure S54. X-ray ORTEP drawing of **18** (thermal ellipsoids at the 50% probability level).

7. ^{1}H and ^{13}C NMR spectra of the synthetic compounds

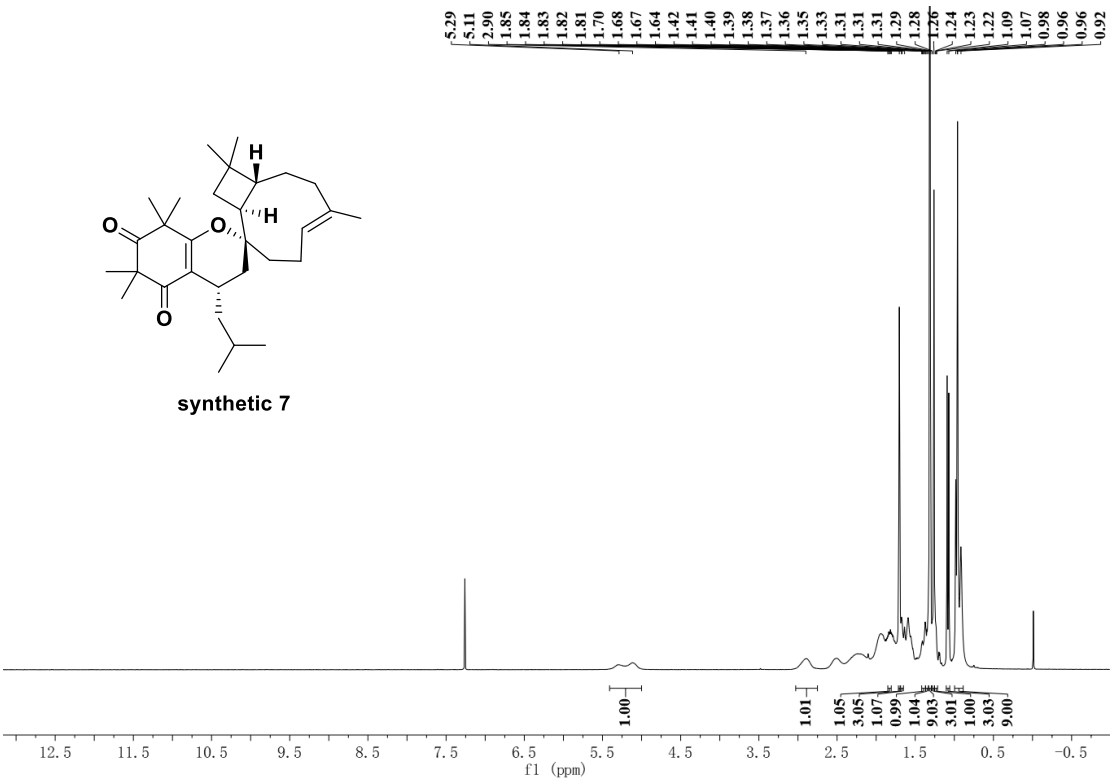


Figure S55. ^{1}H NMR spectrum (300 MHz) of synthetic **7** in $CDCl_3$.

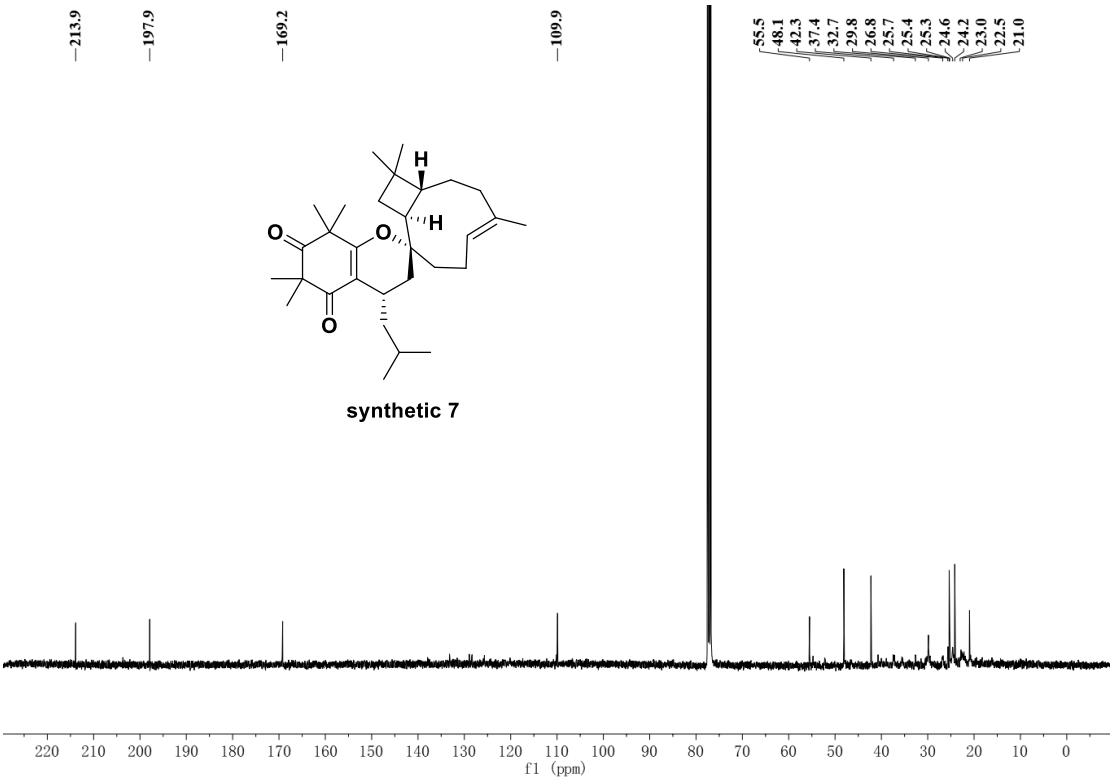


Figure S56. ^{13}C NMR spectrum (75 MHz) of synthetic **7** in $CDCl_3$.

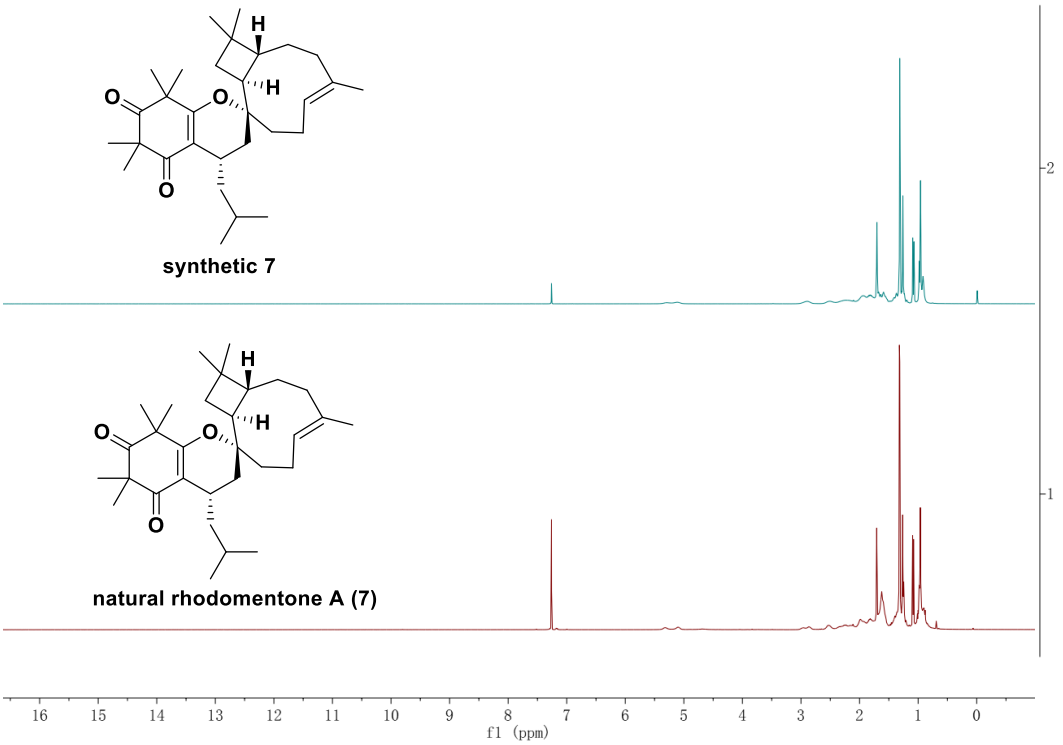


Figure S57. Comparison of ^{1}H NMR spectra between synthetic and natural **7**.

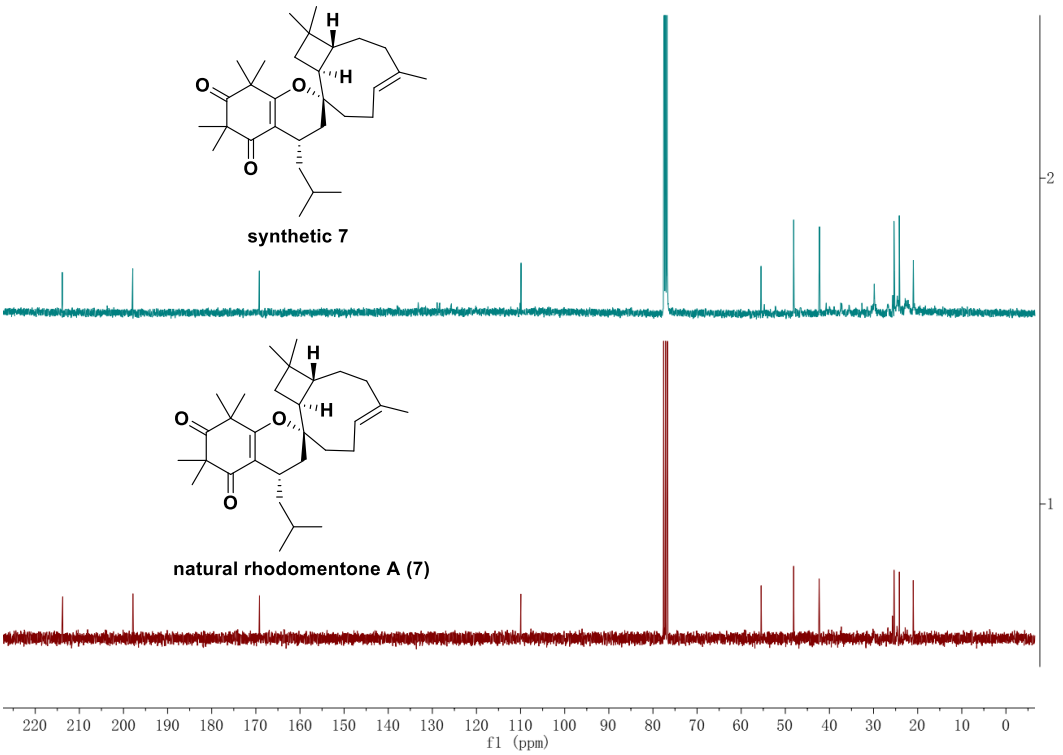


Figure S58. Comparison of ^{13}C NMR spectra between synthetic and natural **7**.

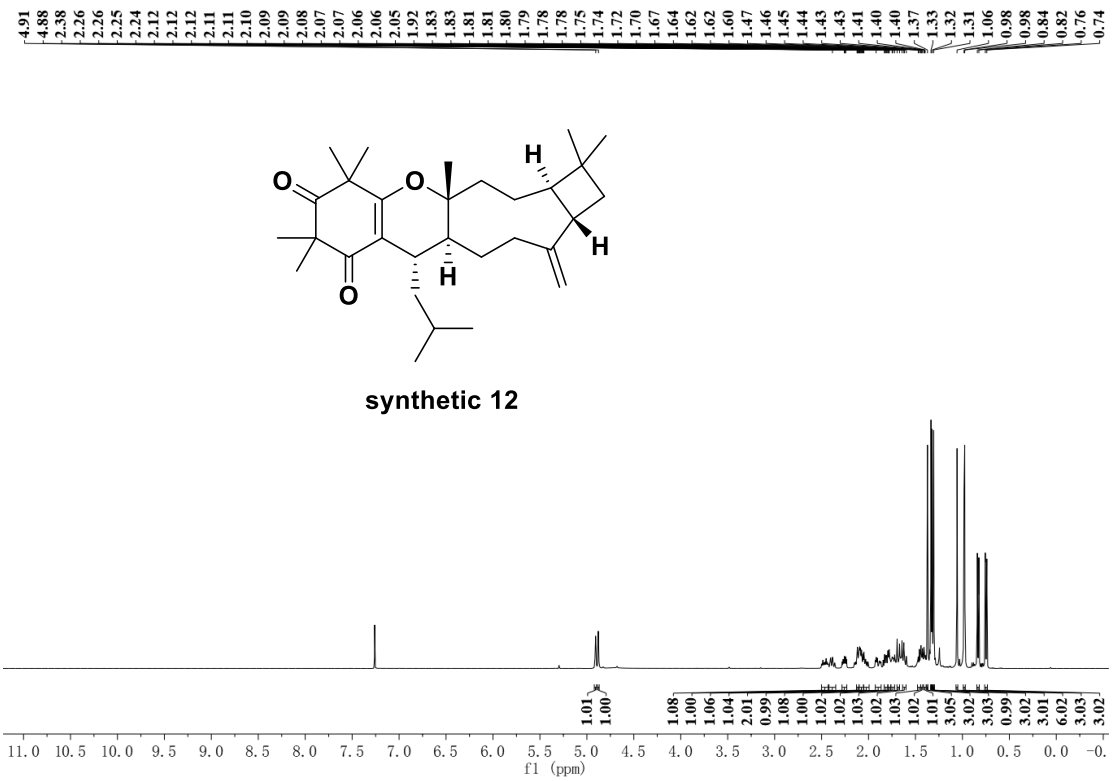


Figure S59. ^{1}H NMR spectrum (400 MHz) of synthetic **12** in $CDCl_3$.

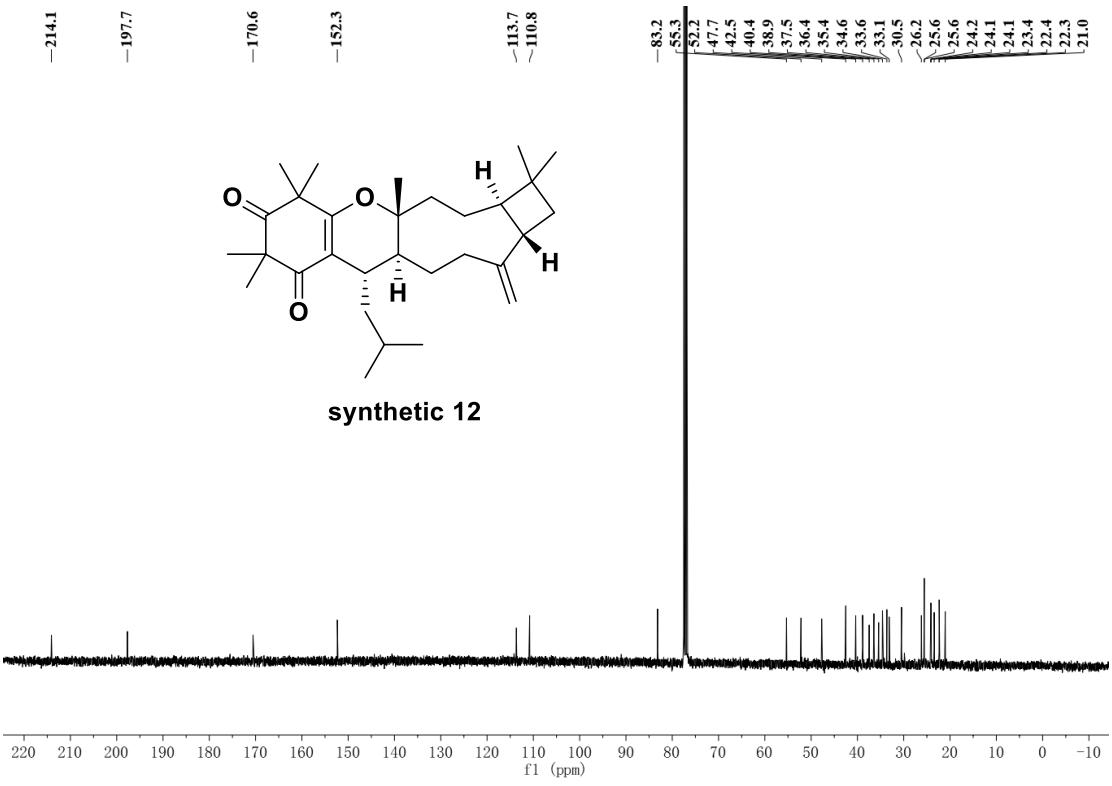


Figure S60. ^{13}C NMR spectrum (100 MHz) of synthetic **12** in $CDCl_3$.

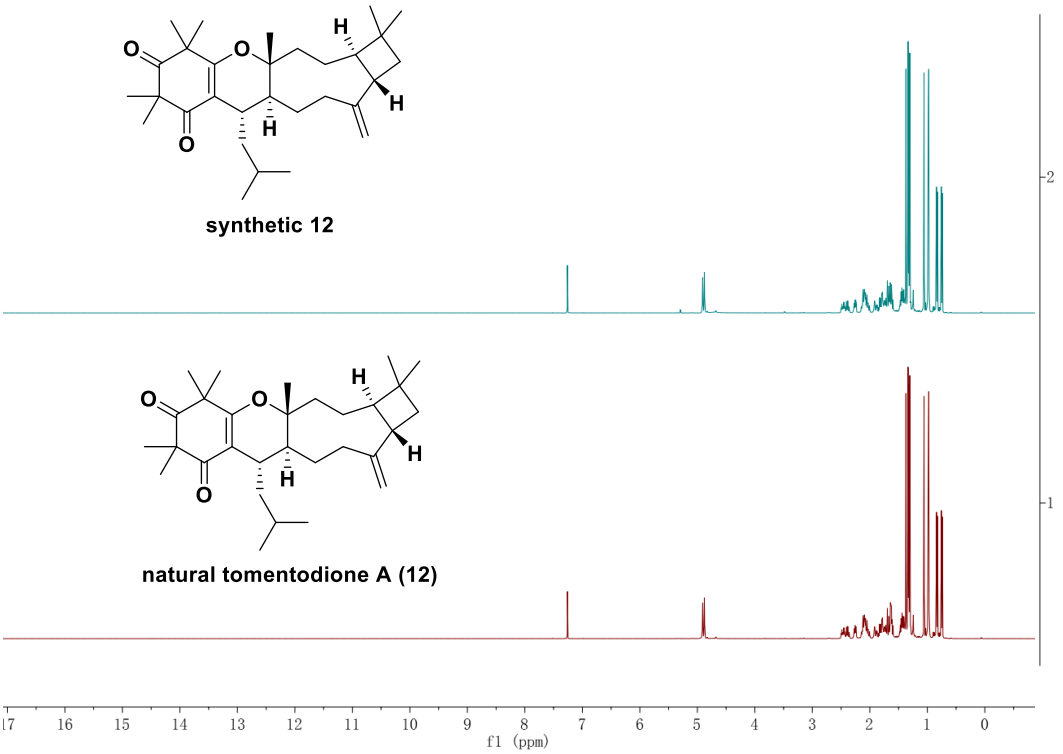


Figure S61. Comparison of ^{1}H NMR spectra between synthetic and natural **12**.

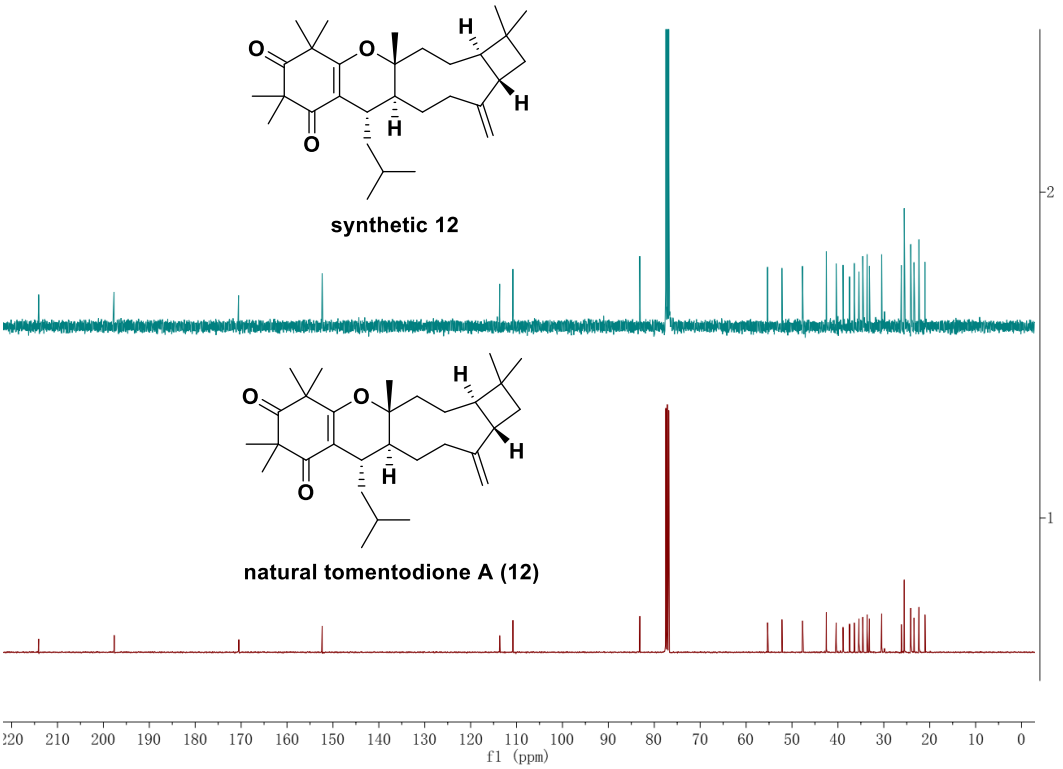


Figure S62. Comparison of ^{13}C NMR spectra between synthetic and natural **12**.

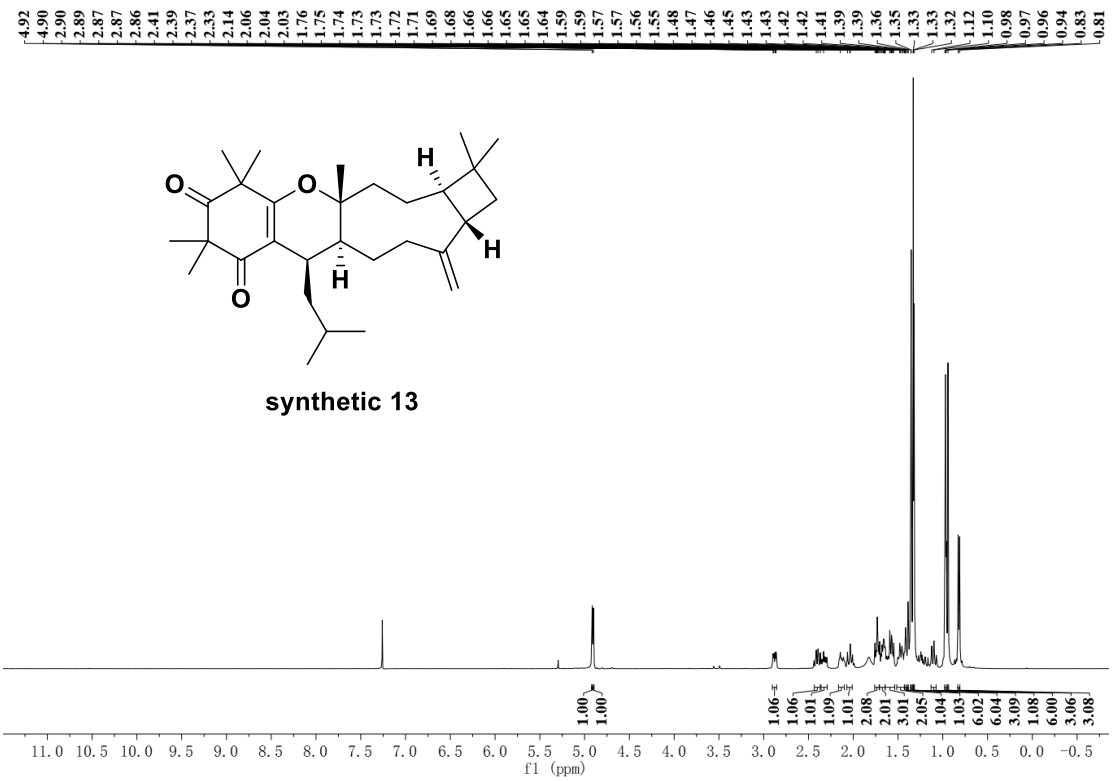


Figure S63. ^{1}H NMR spectrum (400 MHz) of synthetic **13** in $CDCl_3$.

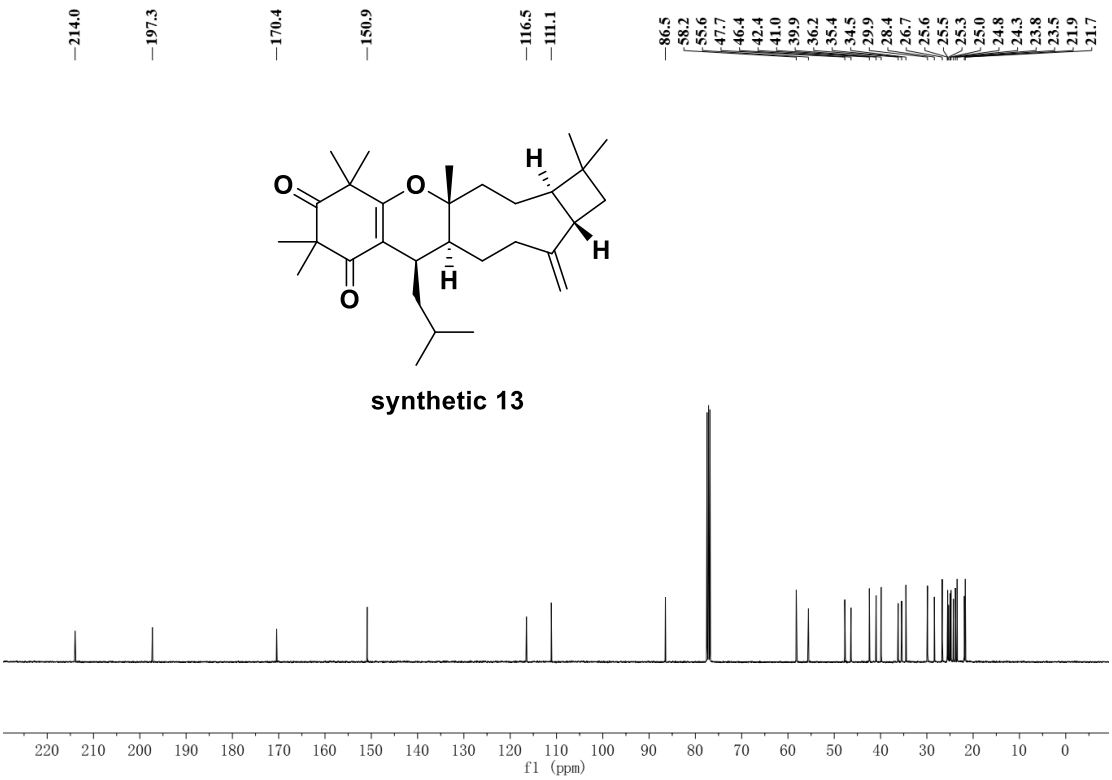


Figure S64. ^{13}C NMR spectrum (100 MHz) of synthetic **13** in $CDCl_3$.

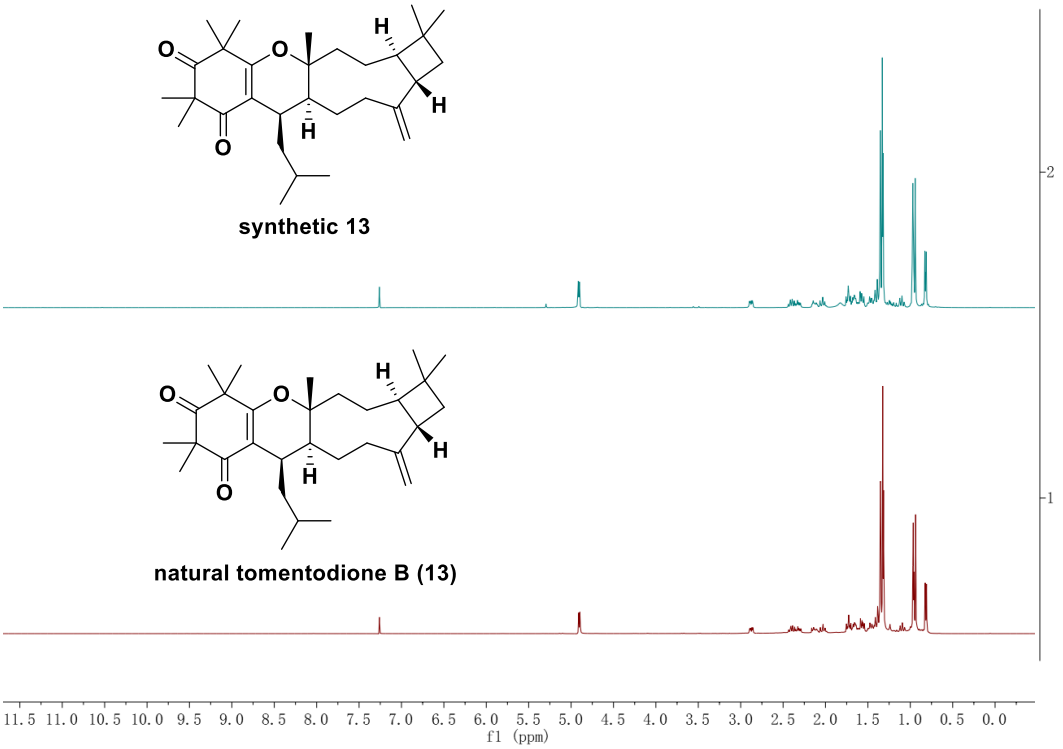


Figure S65. Comparison of ^{1}H NMR spectra between synthetic and natural **13**.

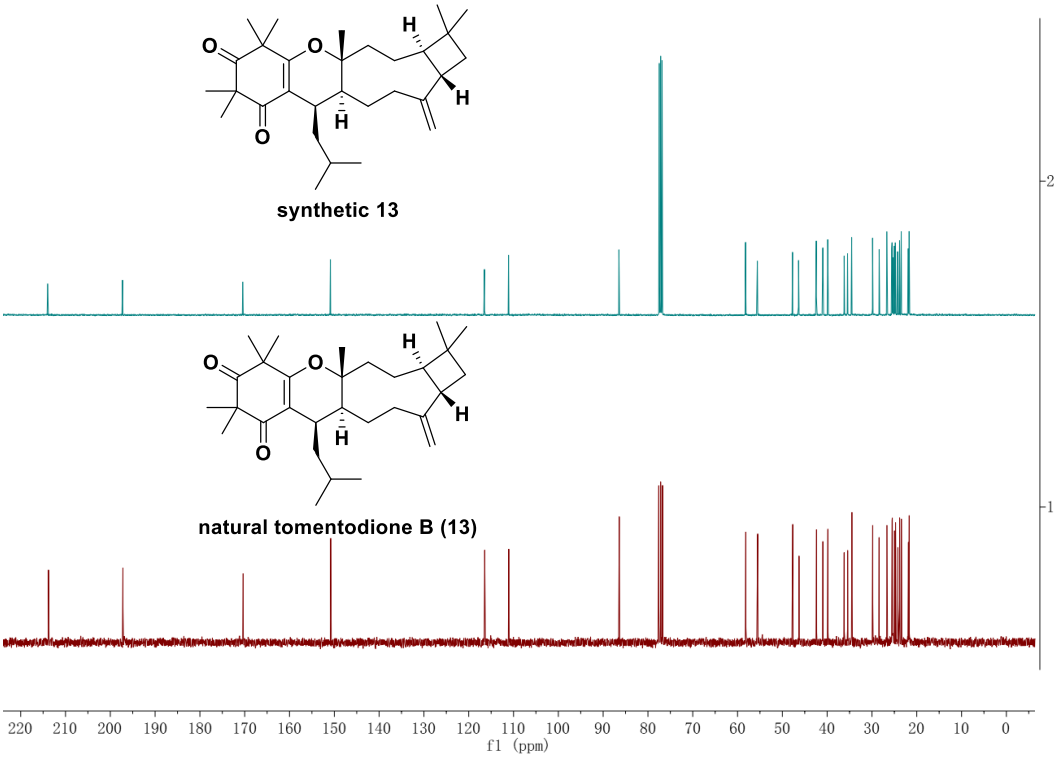


Figure S66. Comparison of ^{1}H NMR spectra between synthetic and natural **13**.

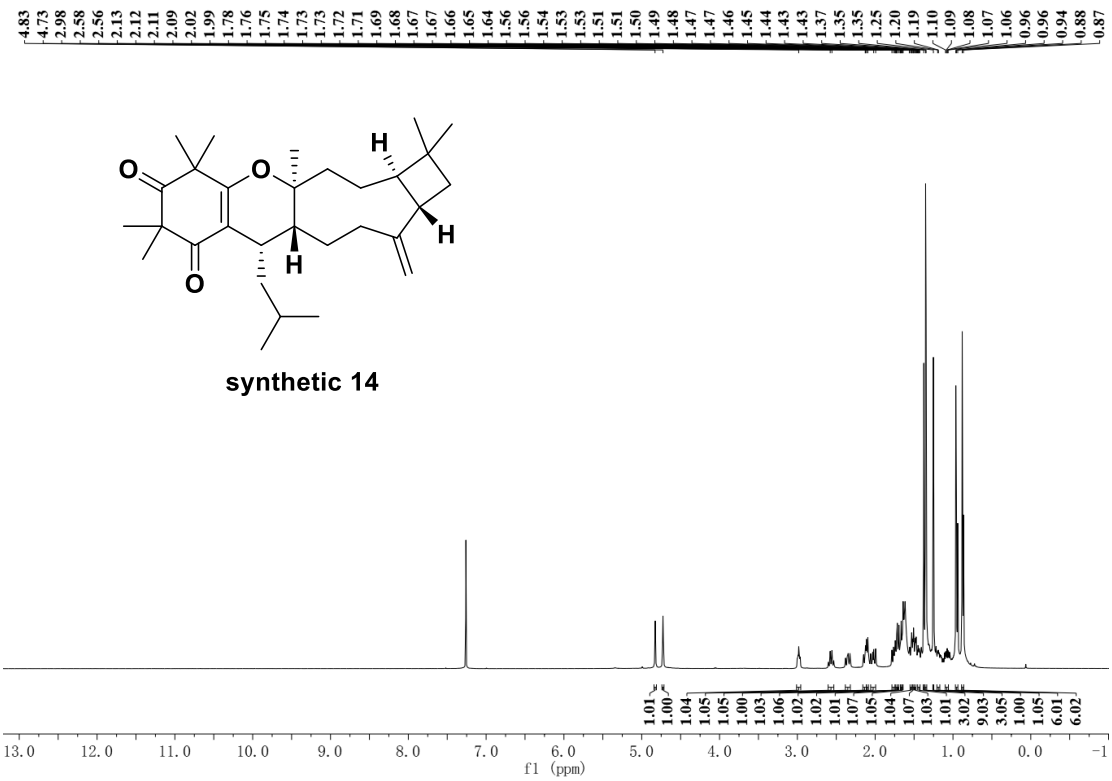


Figure S67. ^{1}H NMR spectrum (400 MHz) of synthetic **14** in $CDCl_3$.

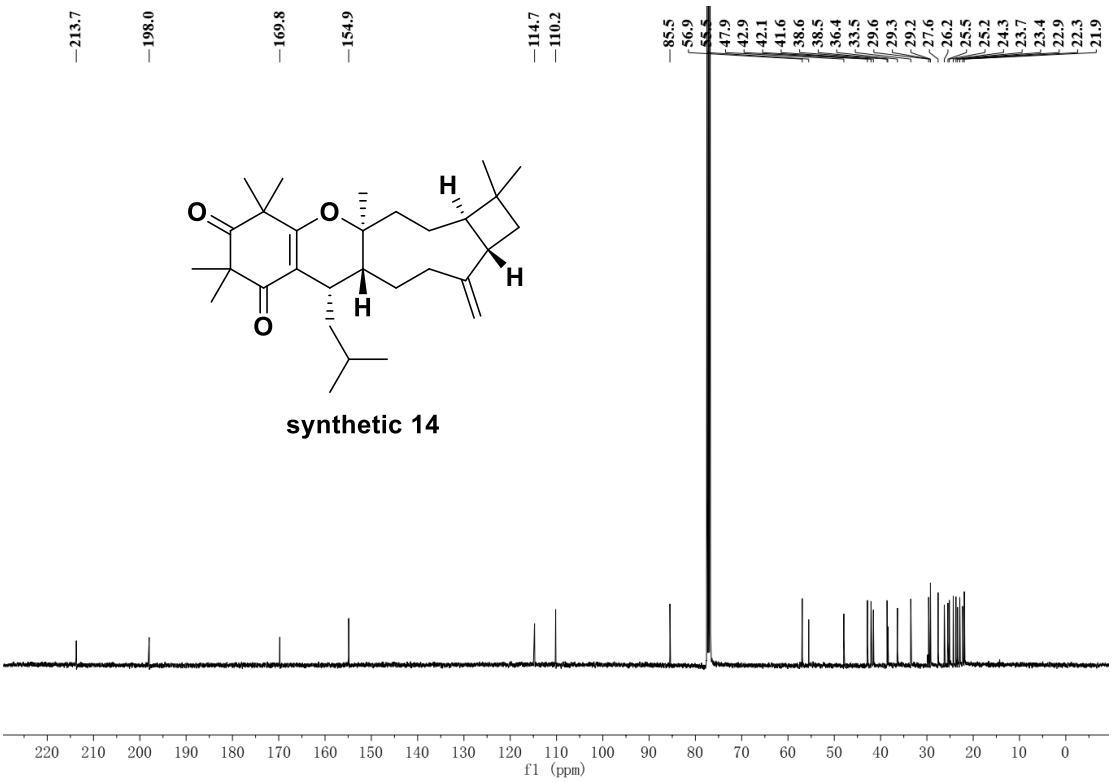


Figure S68. ^{13}C NMR spectrum (100 MHz) of synthetic **14** in $CDCl_3$.

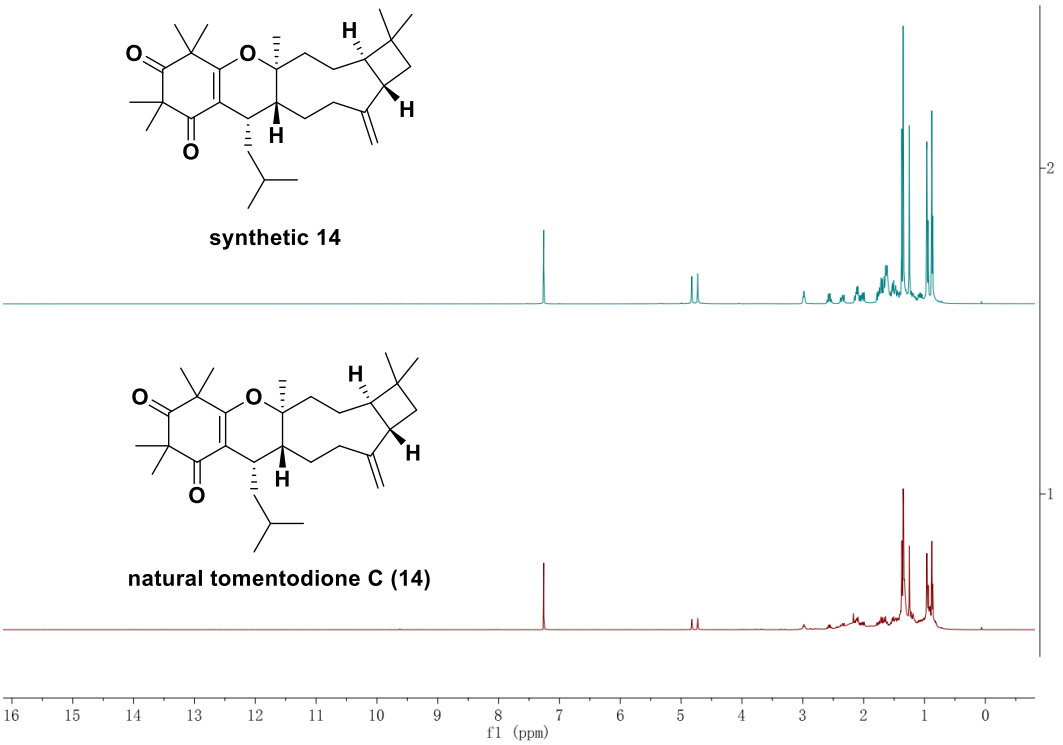


Figure S69. Comparison of ^{1}H NMR spectra between synthetic and natural **14**.

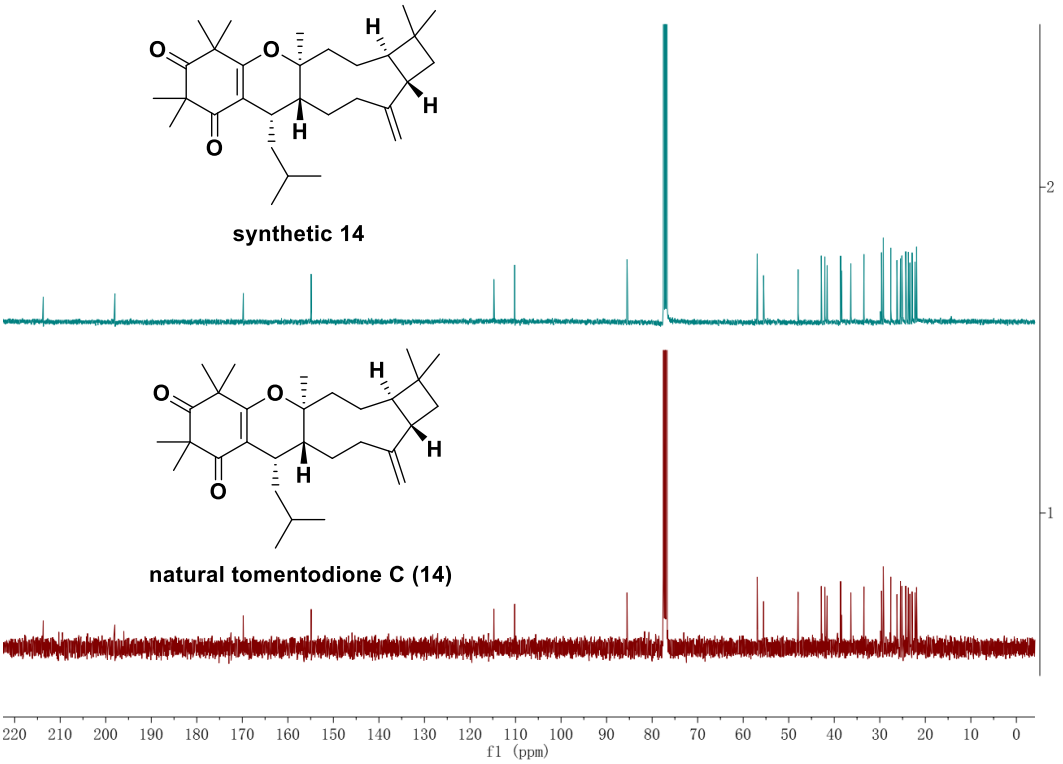


Figure S70. Comparison of ^{13}C NMR spectra between synthetic and natural **14**.

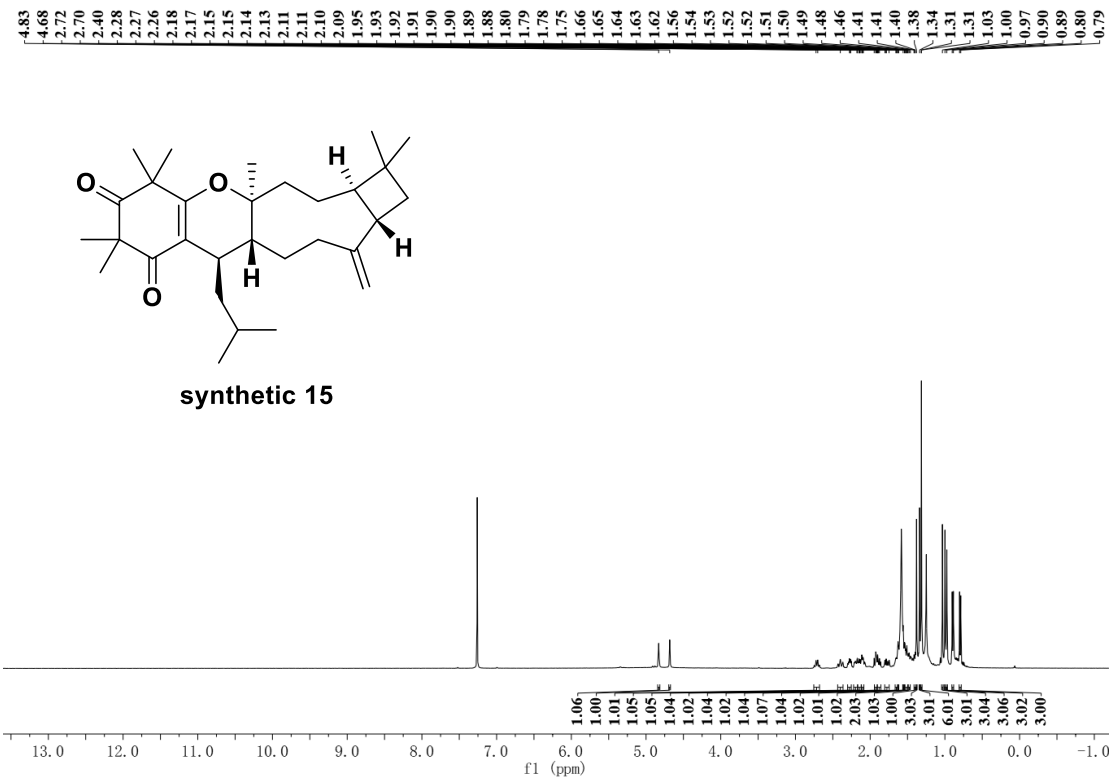


Figure S71. ^{1}H NMR spectrum (400 MHz) of synthetic **15** in $CDCl_3$.

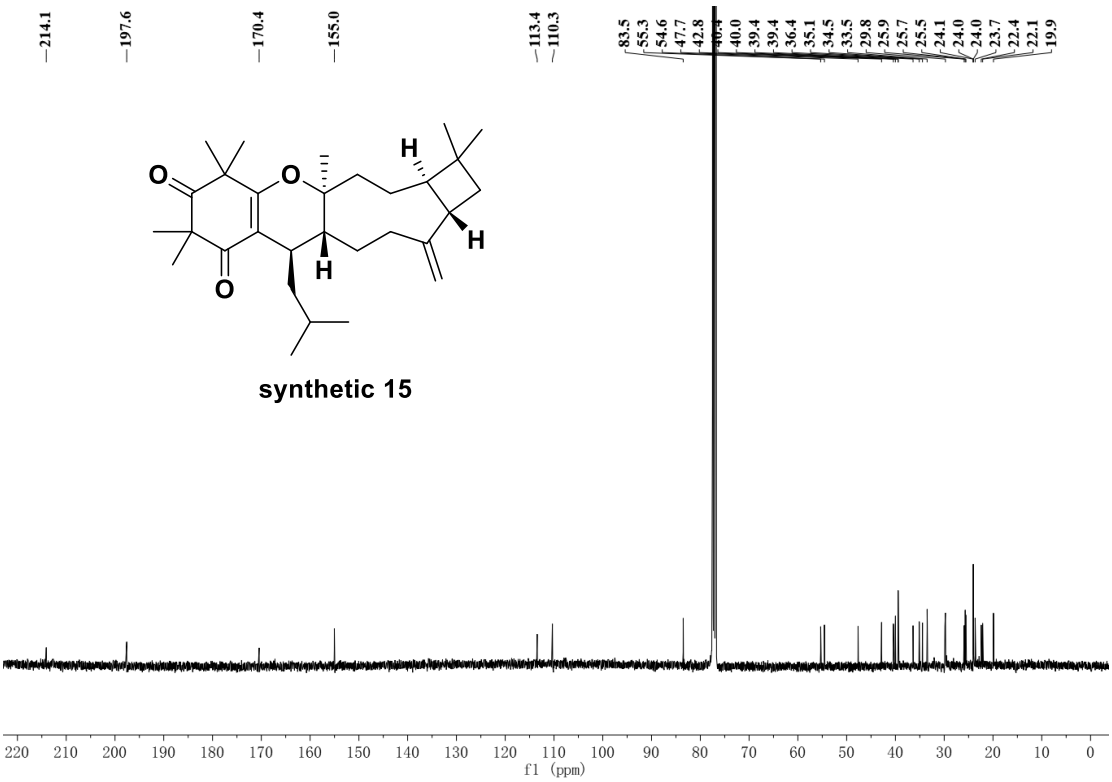


Figure S72. ^{13}C NMR spectrum (100 MHz) of synthetic **15** in $CDCl_3$.

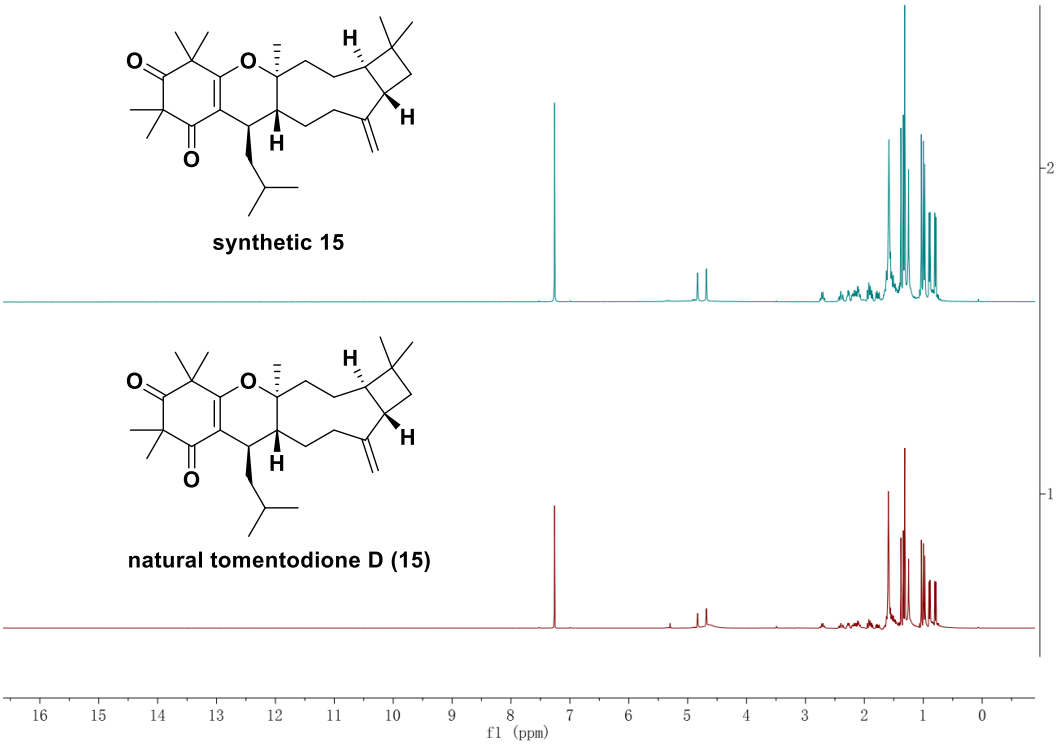


Figure S73. Comparison of ^{1}H NMR spectra between synthetic and natural **15**.

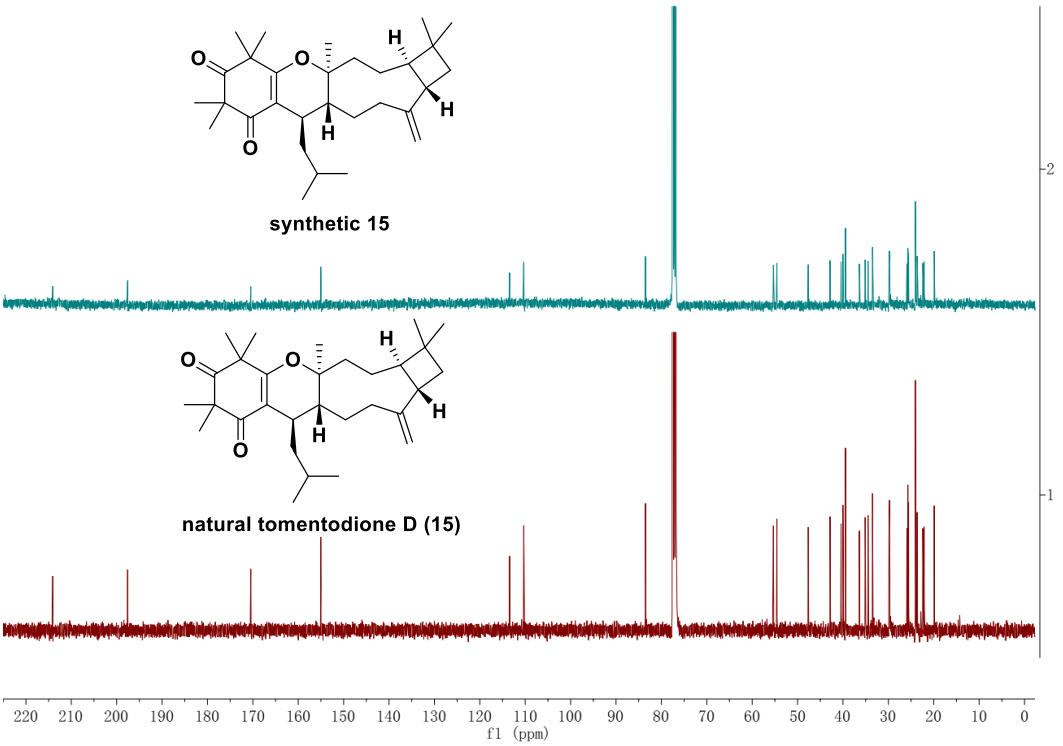


Figure S74. Comparison of ^{13}C NMR spectra between synthetic and natural **15**.

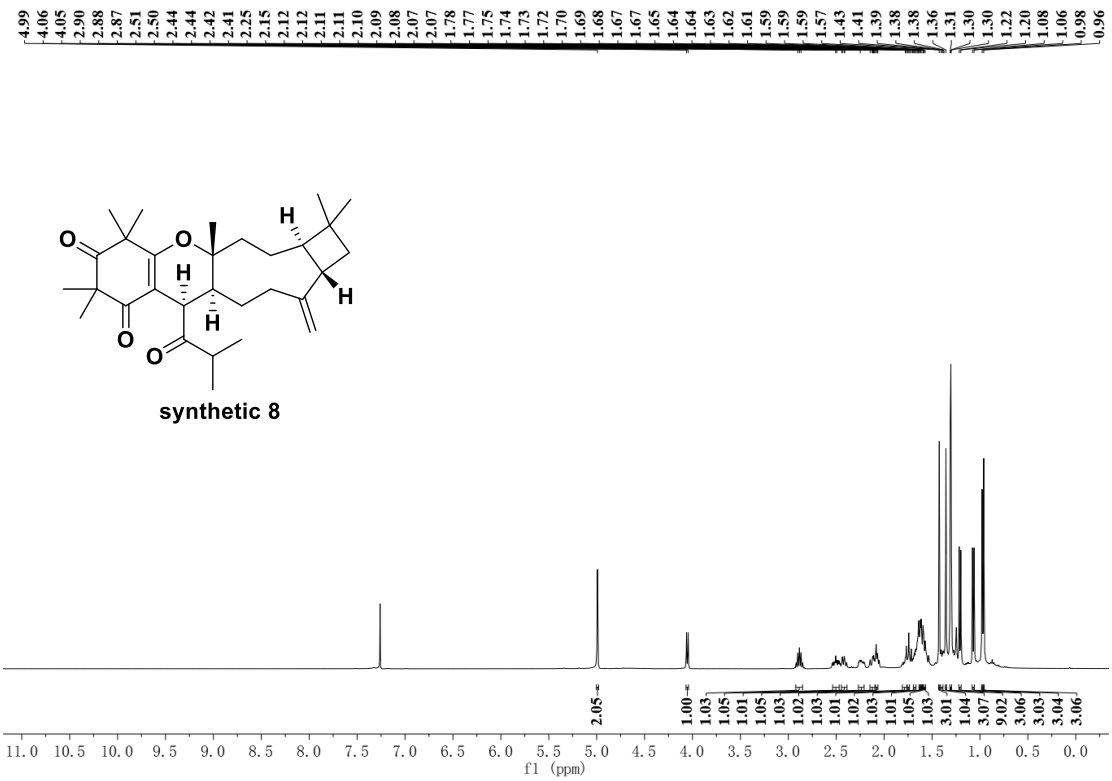


Figure S75. ^{1}H NMR spectrum (400 MHz) of synthetic **8** in $CDCl_3$.

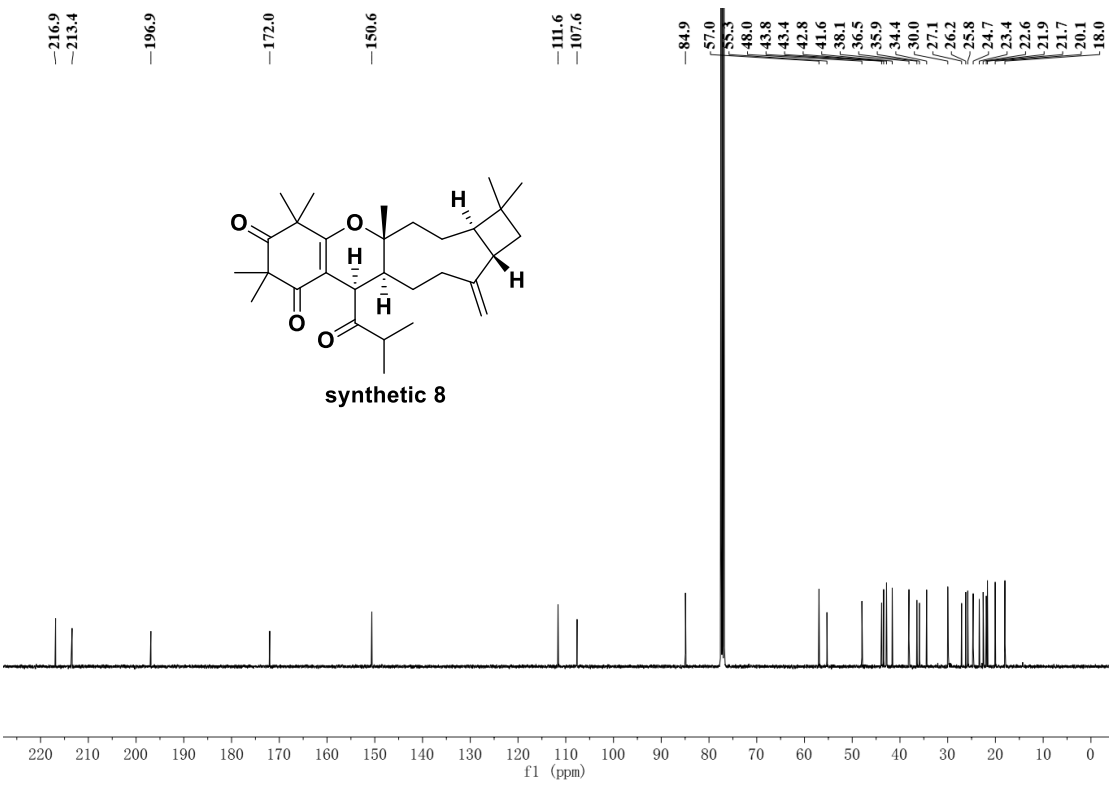


Figure S76. ^{13}C NMR spectrum (100 MHz) of synthetic **8** in $CDCl_3$.

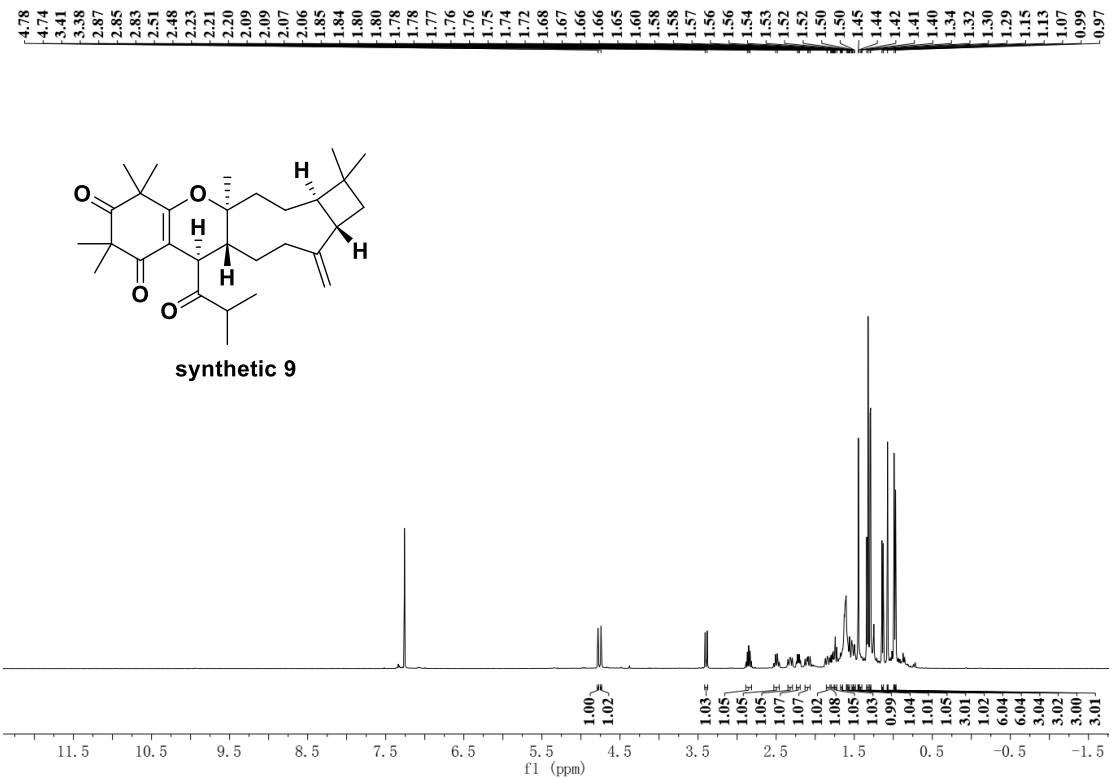


Figure S77. ^{1}H NMR spectrum (400 MHz) of synthetic **9** in $CDCl_3$.

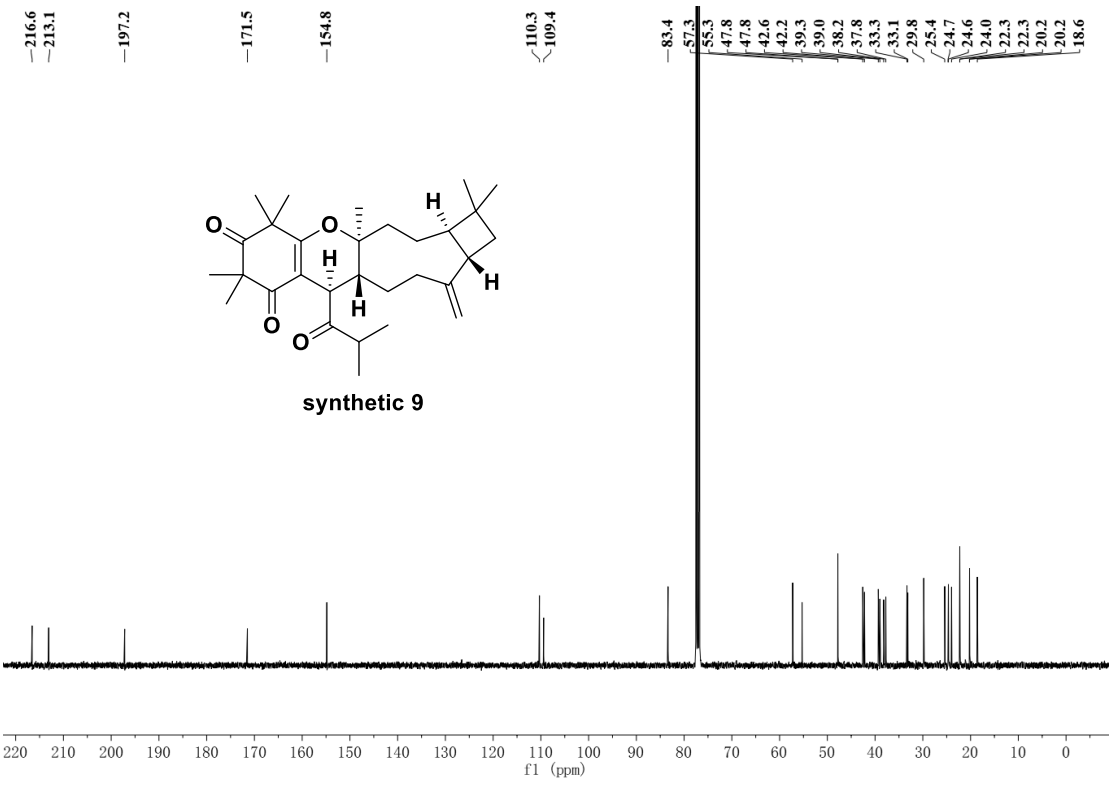


Figure S78. ^{13}C NMR spectrum (100 MHz) of synthetic **9** in $CDCl_3$.

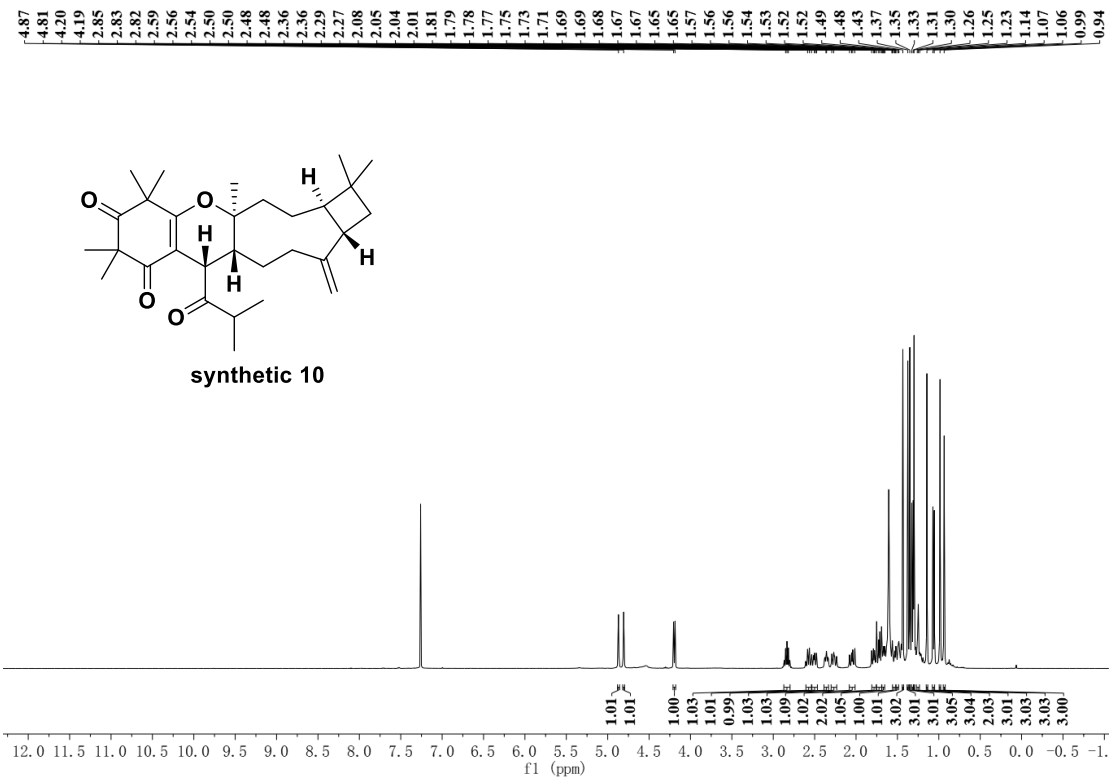


Figure S79. ^{1}H NMR spectrum (400 MHz) of synthetic **10** in $CDCl_3$.

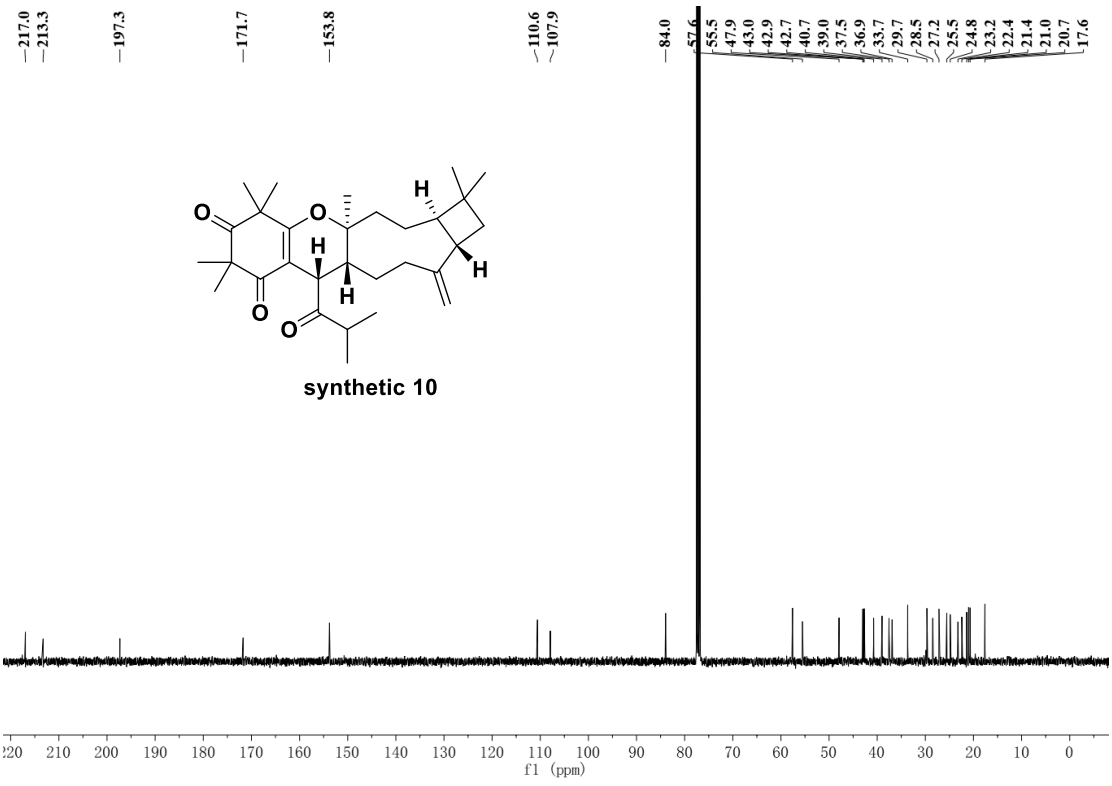


Figure S80. ^{13}C NMR spectrum (100 MHz) of synthetic **10** in $CDCl_3$.

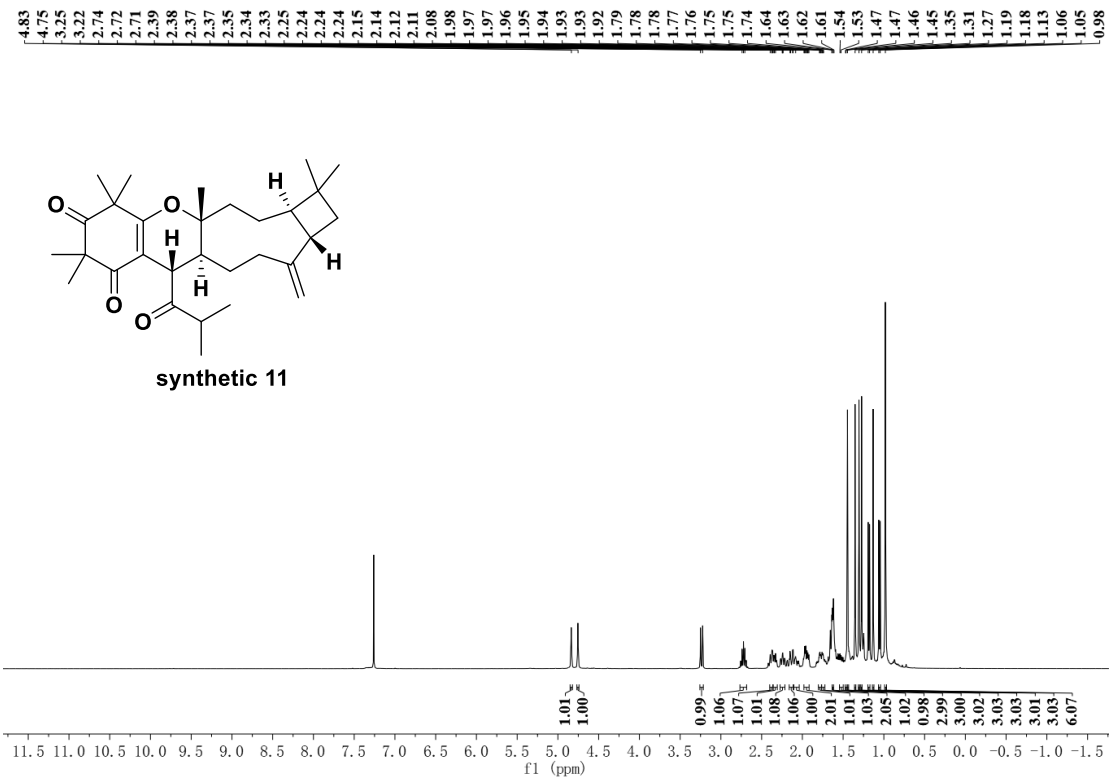


Figure S81. ^{1}H NMR spectrum (400 MHz) of synthetic **11** in $CDCl_3$.

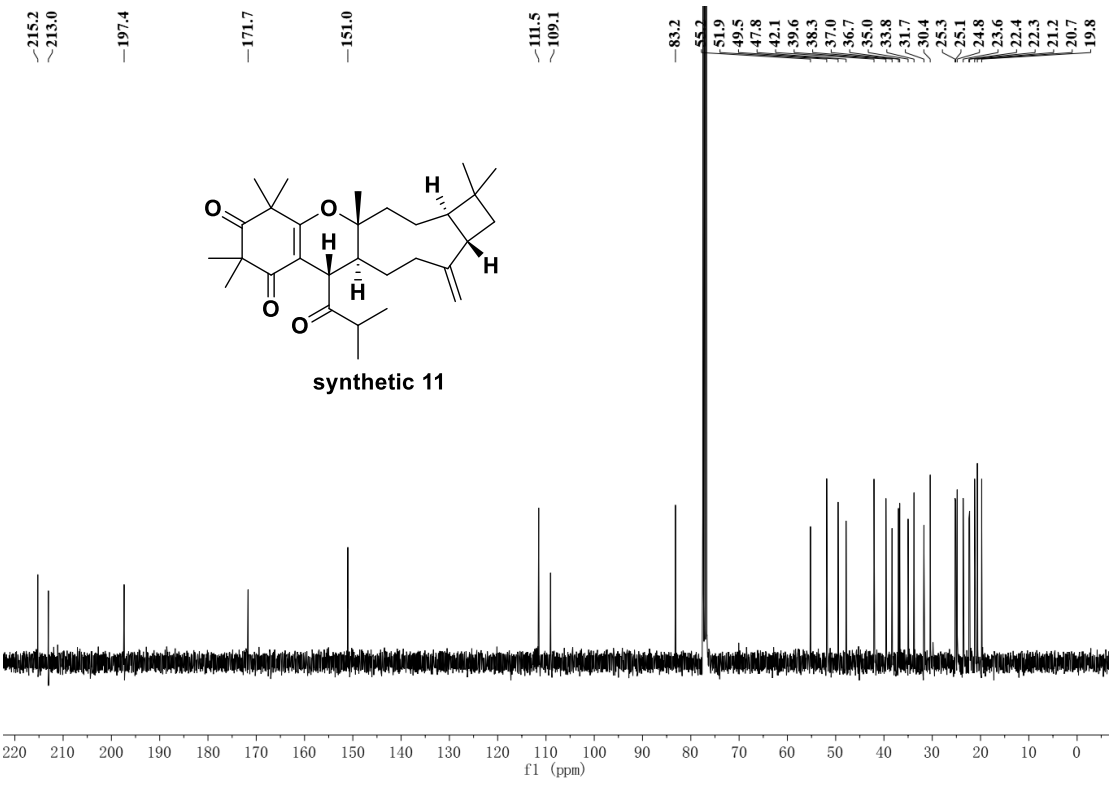


Figure S82. ^{13}C NMR spectrum (100 MHz) of synthetic **11** in $CDCl_3$.

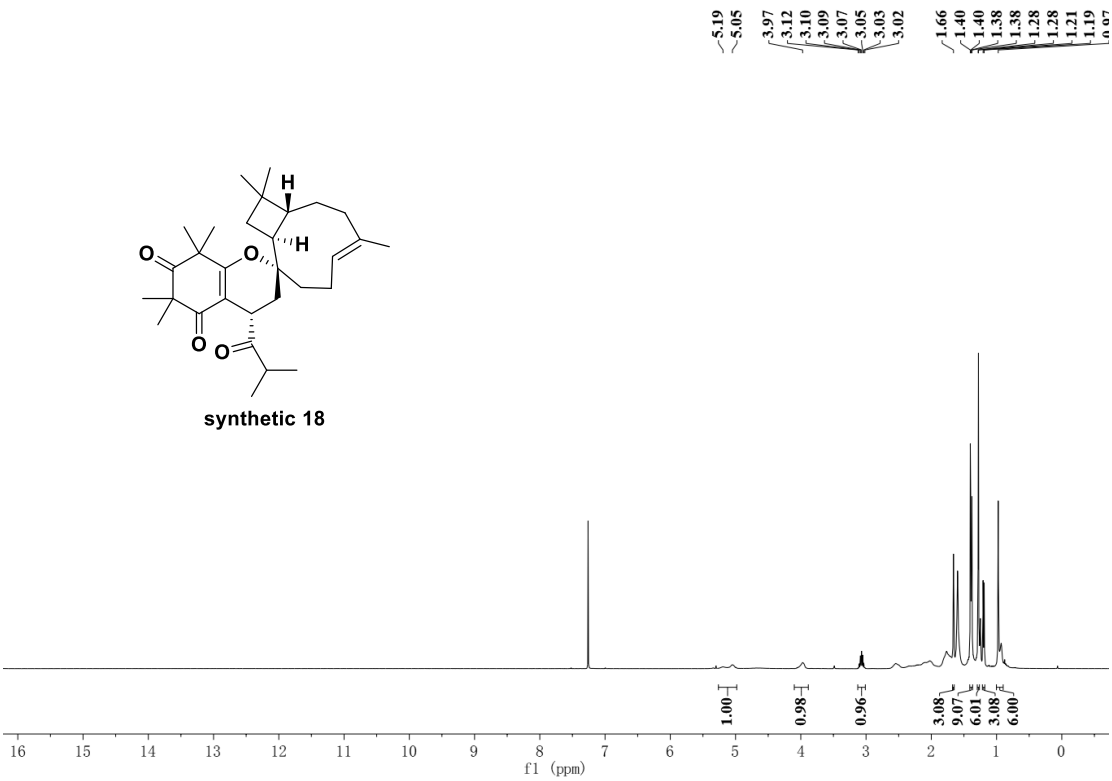


Figure S83. ^{1}H NMR spectrum (400 MHz) of synthetic **18** in $CDCl_3$.

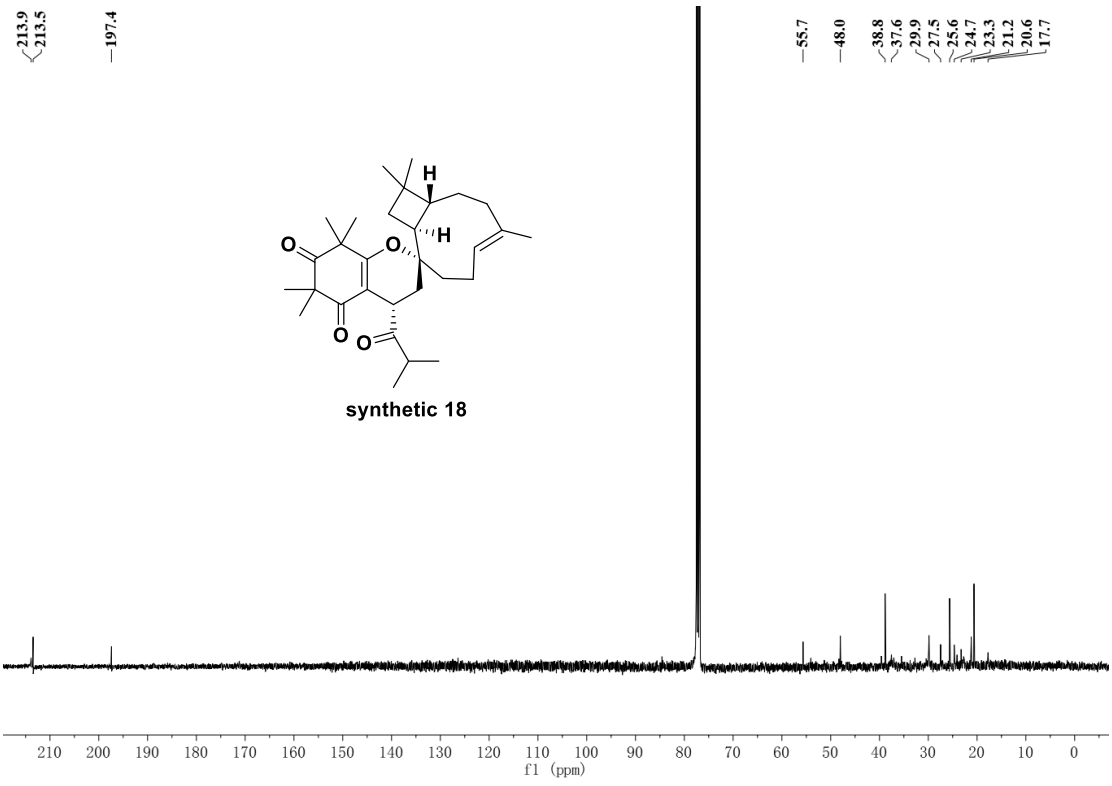


Figure S84. ^{13}C NMR spectrum (100 MHz) of synthetic **18** in $CDCl_3$.

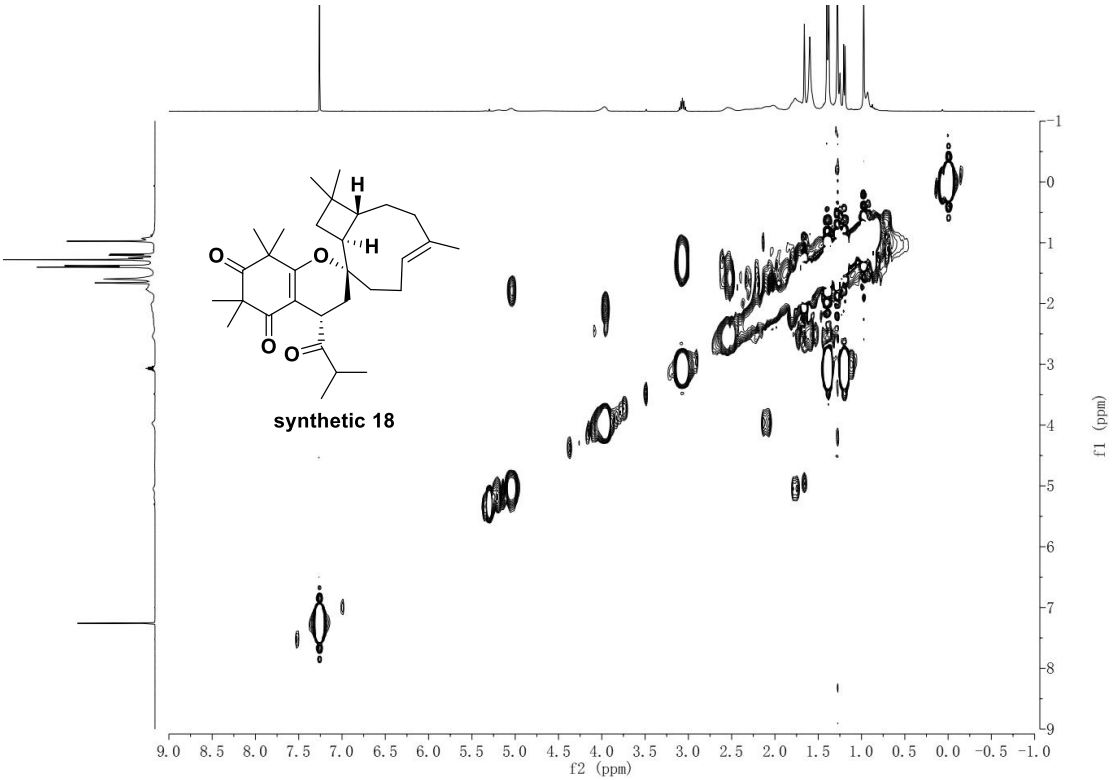


Figure S85. ^{1}H–^{1}H COSY spectrum of synthetic **18** in $CDCl_3$.

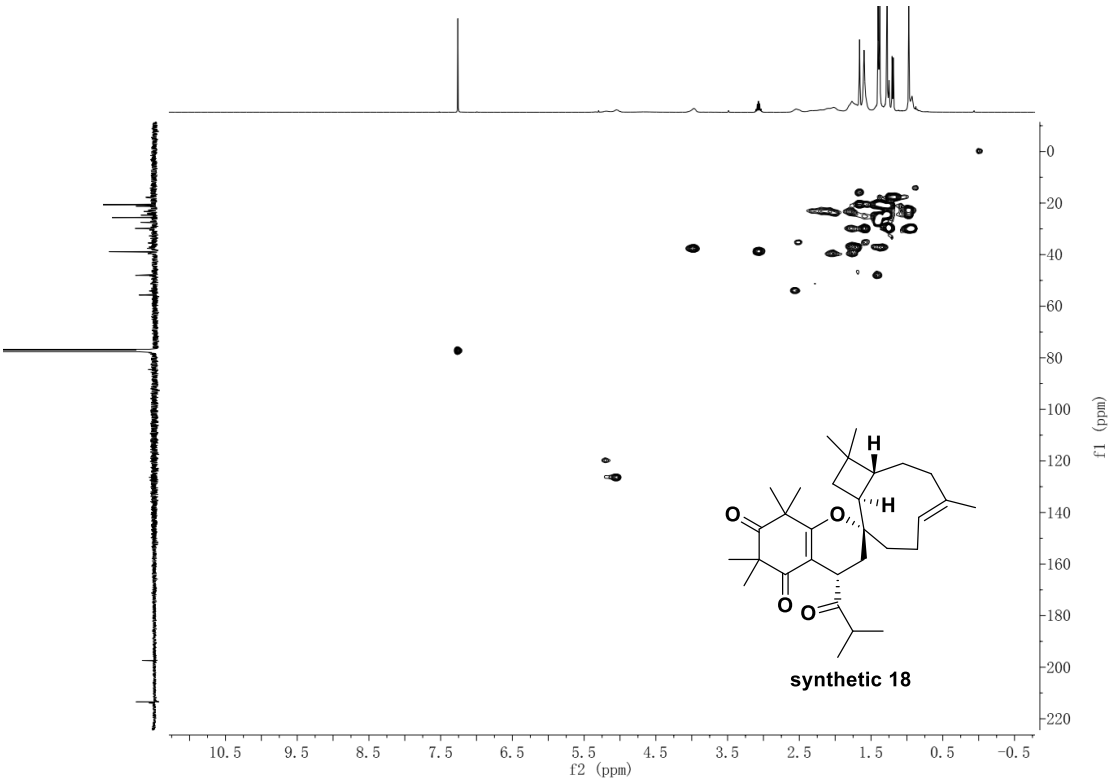


Figure S86. HSQC spectrum of synthetic **18** in $CDCl_3$.

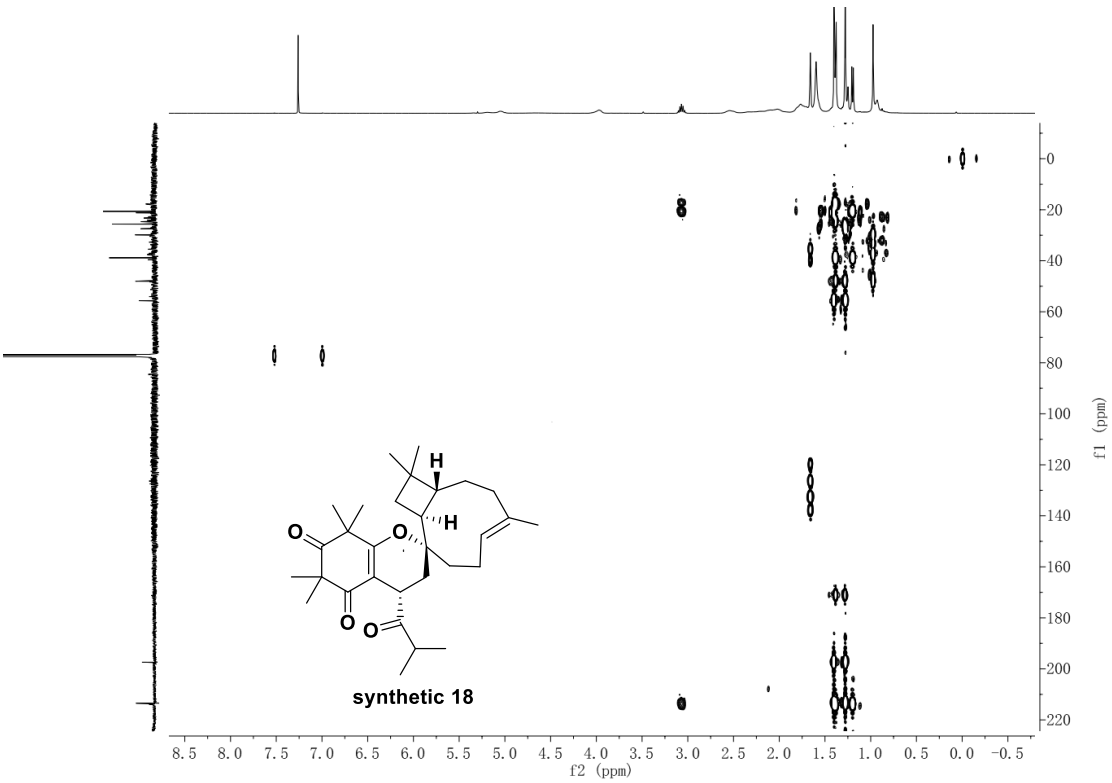


Figure S87. HMBC spectrum of synthetic **18** in $CDCl_3$.

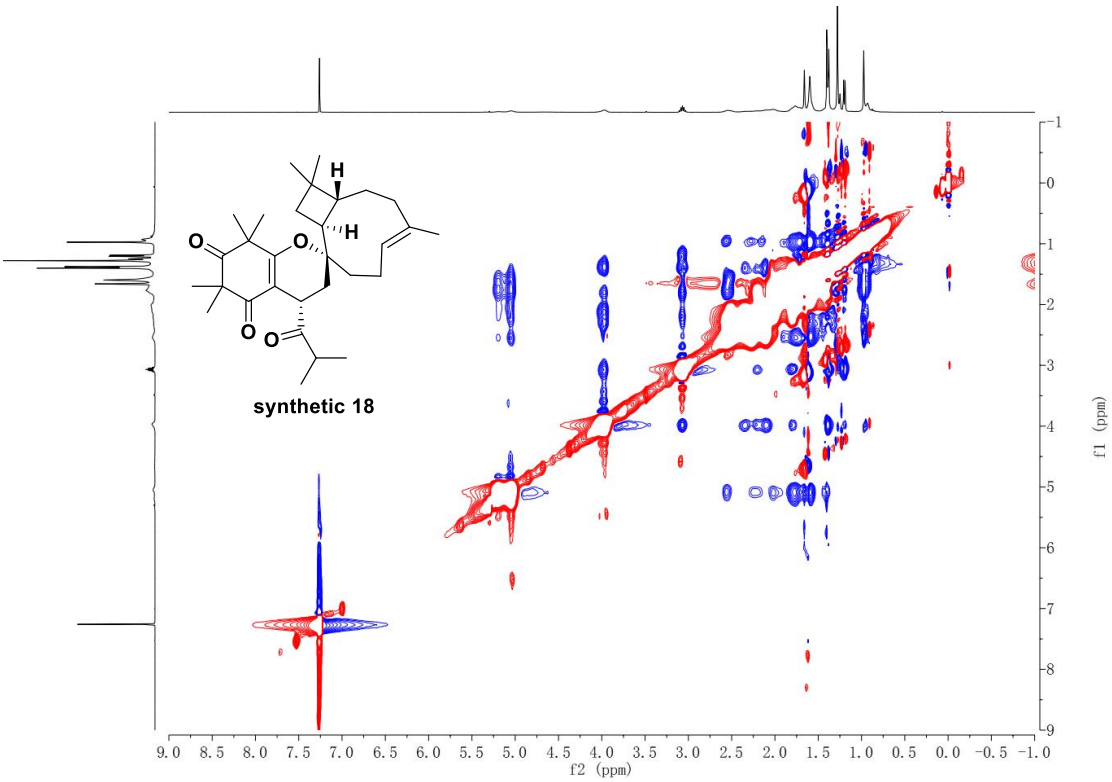


Figure S88. NOESY spectrum of synthetic **18** in $CDCl_3$.

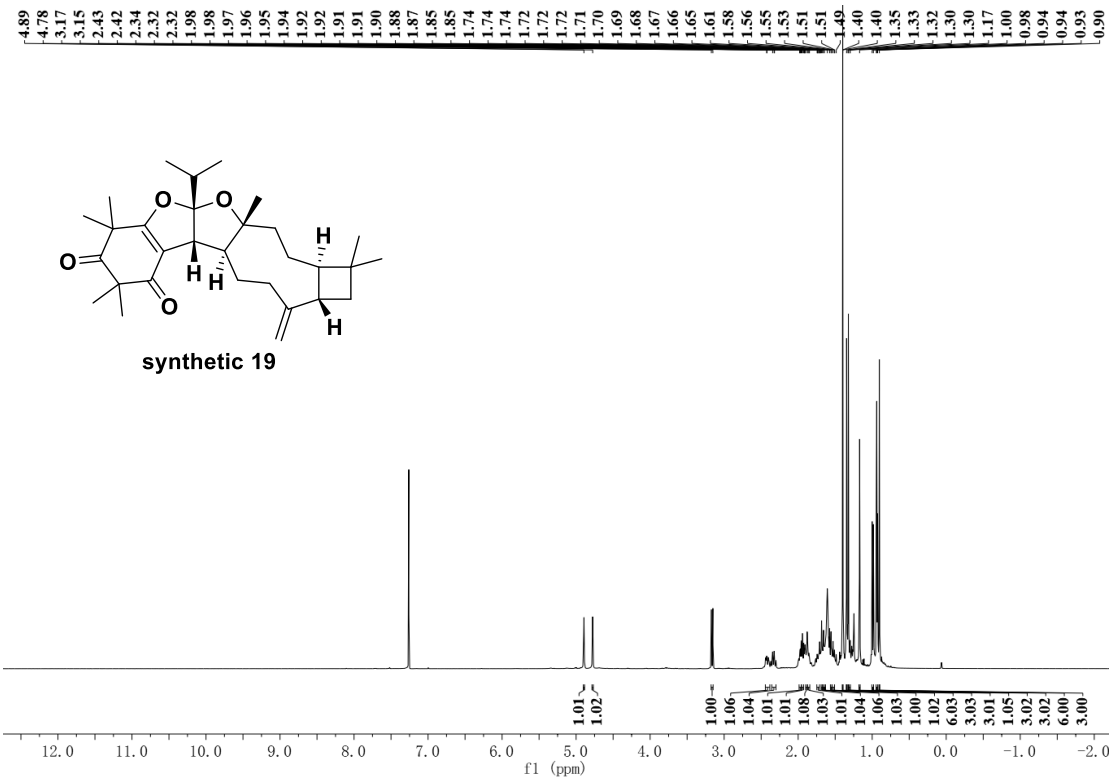


Figure S89. ^{1}H NMR spectrum (400 MHz) of synthetic **19** in $CDCl_3$.

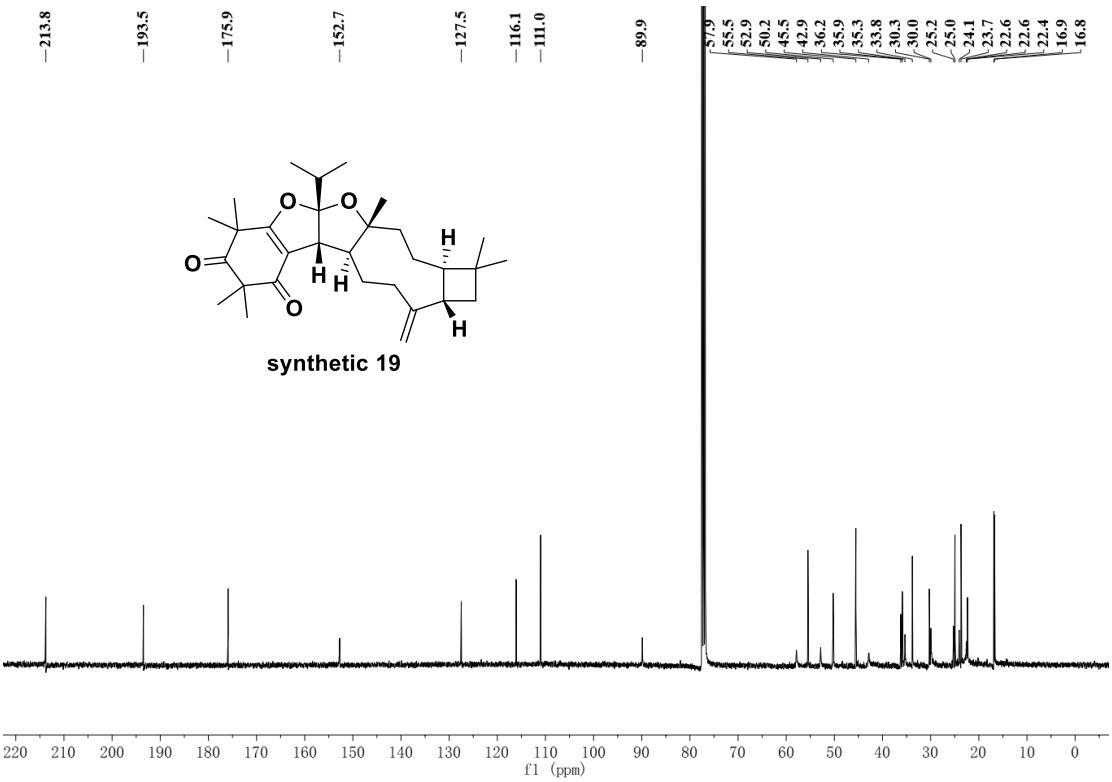


Figure S90. ^{13}C NMR spectrum (100 MHz) of synthetic **19** in $CDCl_3$.

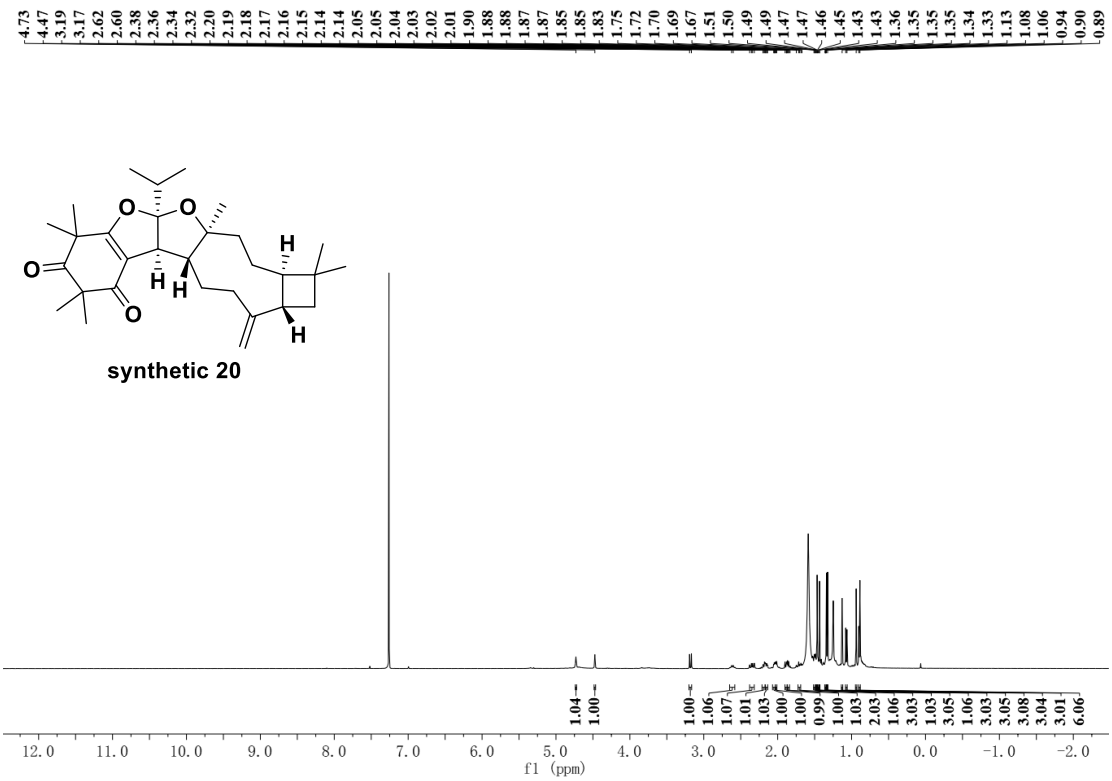


Figure S91. ^{1}H NMR spectrum (400 MHz) of synthetic **20** in $CDCl_3$.

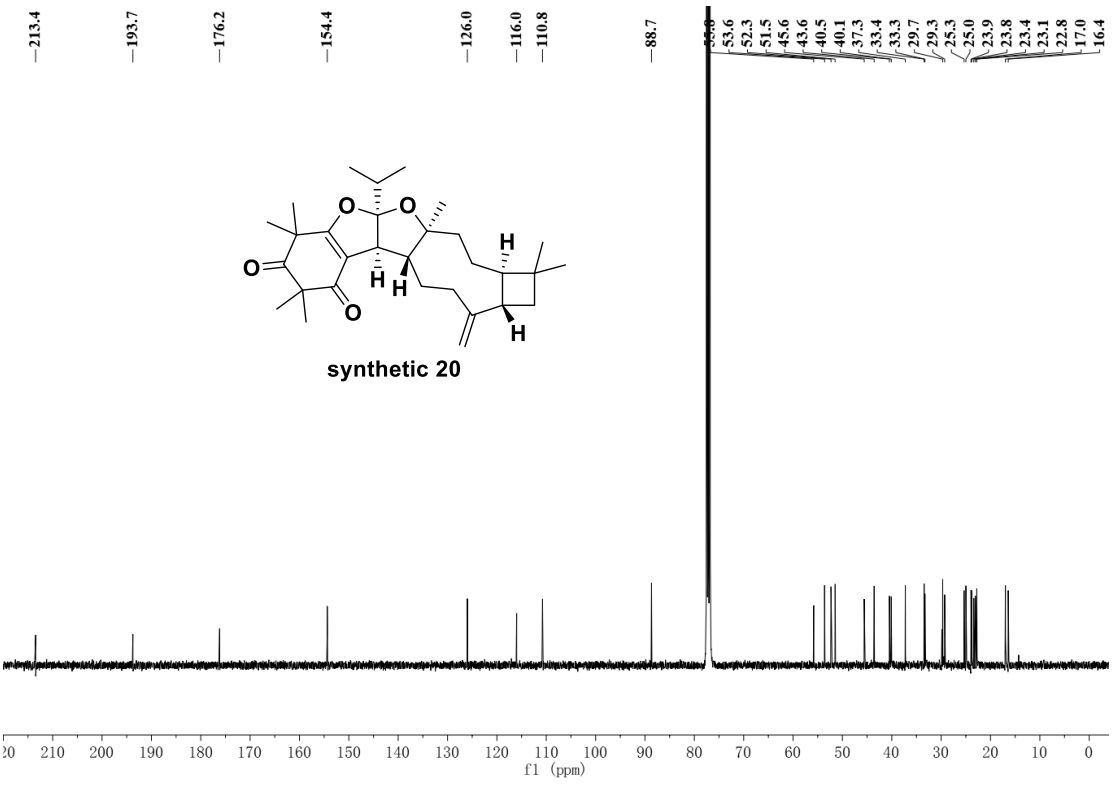


Figure S92. ^{13}C NMR spectrum (100 MHz) of synthetic **20** in $CDCl_3$.

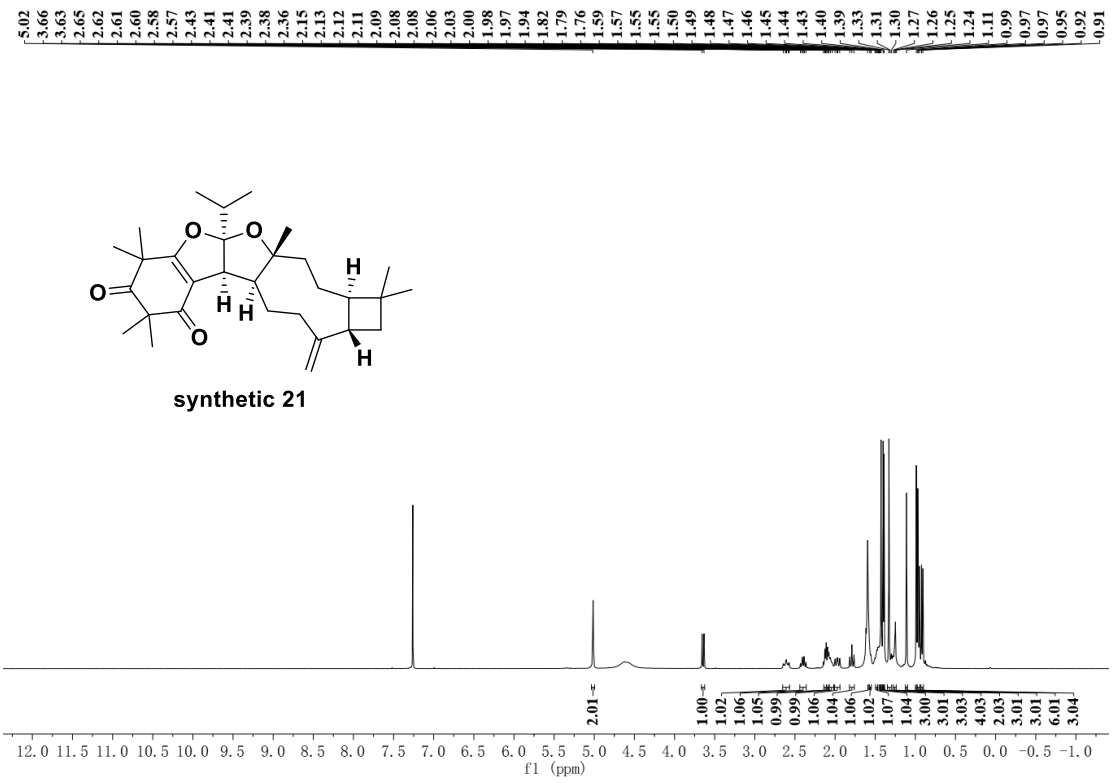


Figure S93. ^{1}H NMR spectrum (400 MHz) of synthetic **21** in $CDCl_3$.

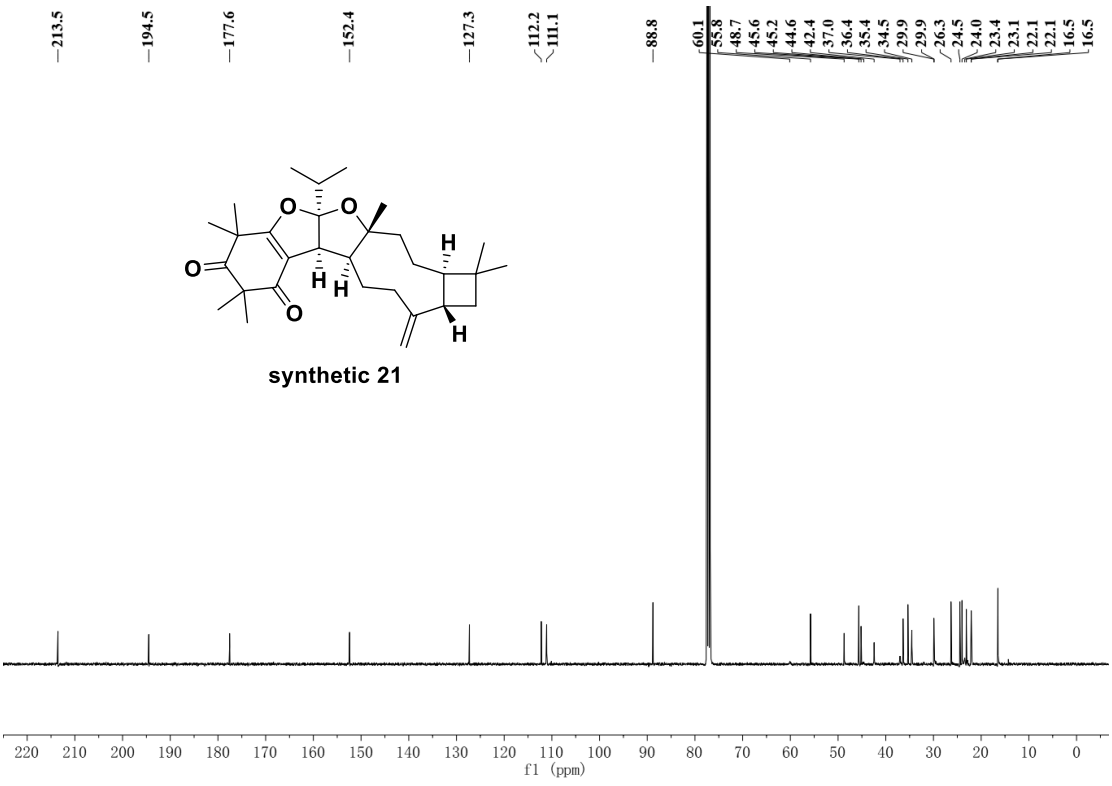


Figure S94. ^{13}C NMR spectrum (100 MHz) of synthetic **21** in $CDCl_3$.

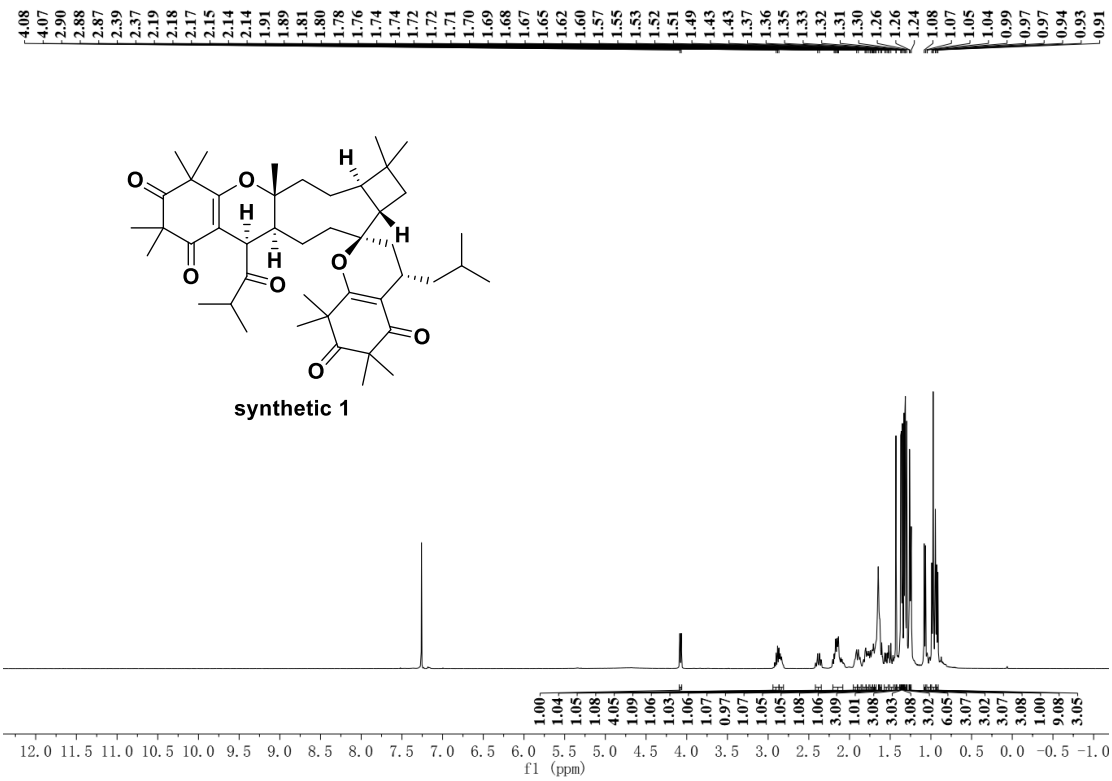


Figure S95. ^{1}H NMR spectrum (400 MHz) of synthetic **1** through path A in $CDCl_3$.

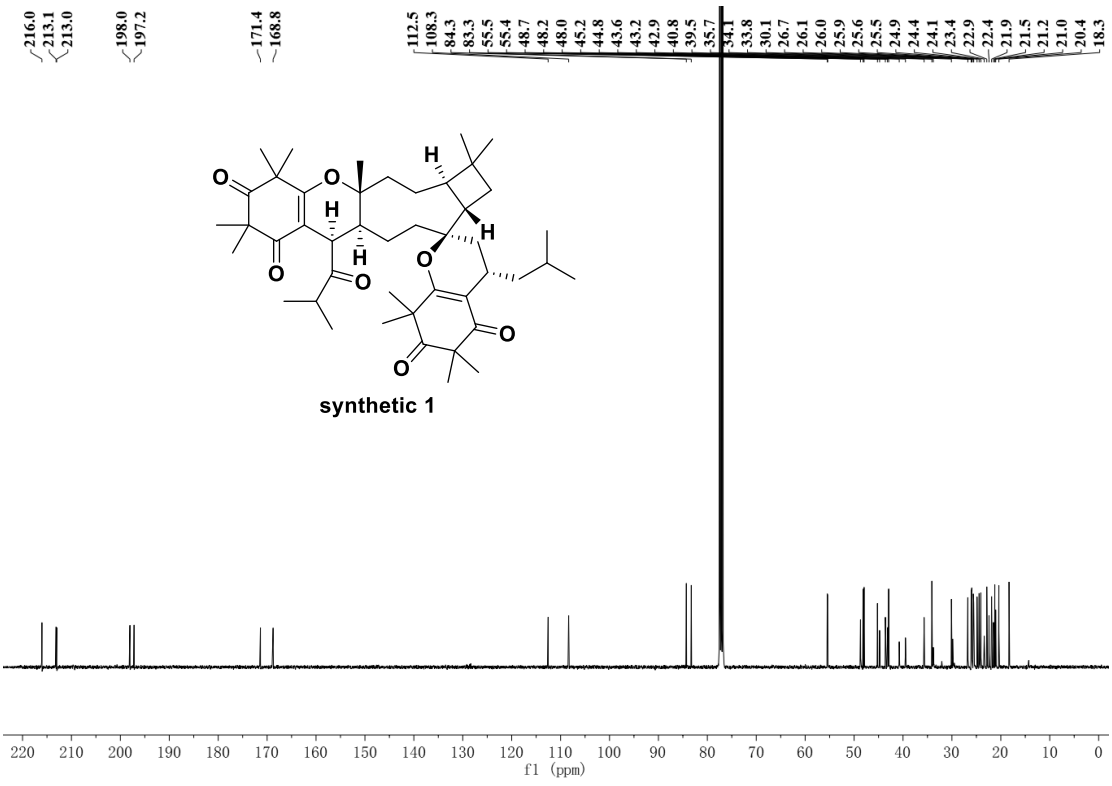


Figure S96. ^{13}C NMR spectrum (100 MHz) of synthetic **1** through path A in $CDCl_3$.

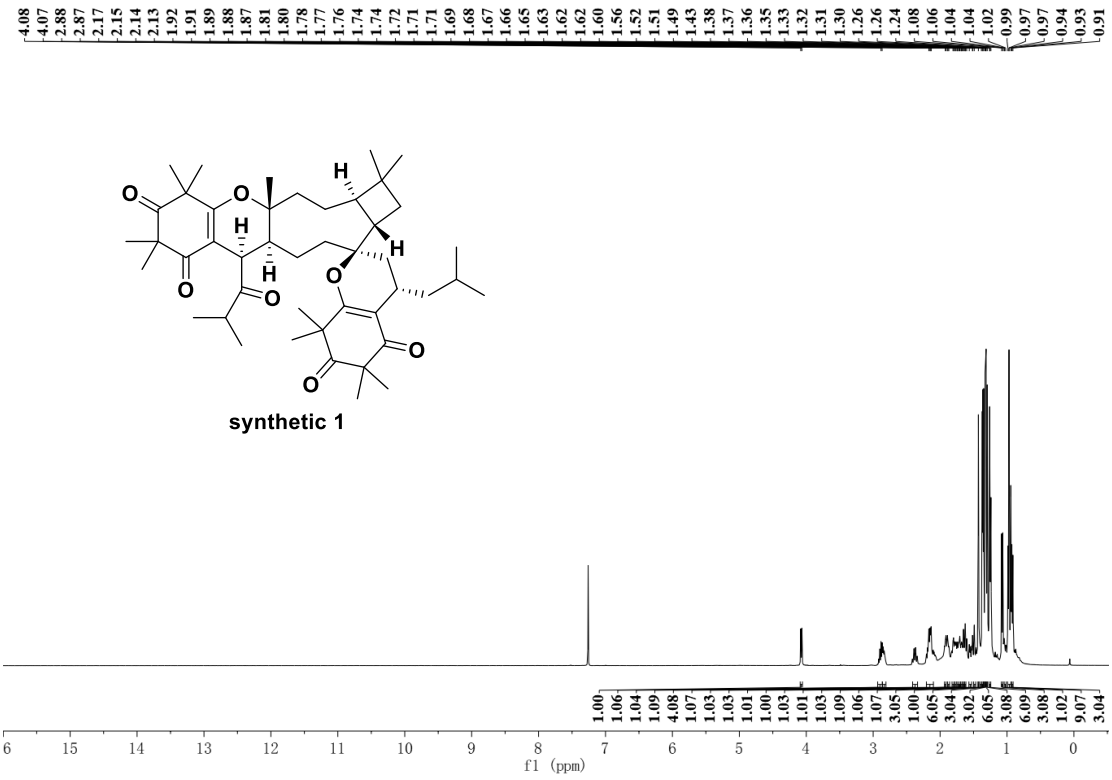


Figure S97. ^{1}H NMR spectrum (400 MHz) of synthetic **1** through path B in $CDCl_3$.

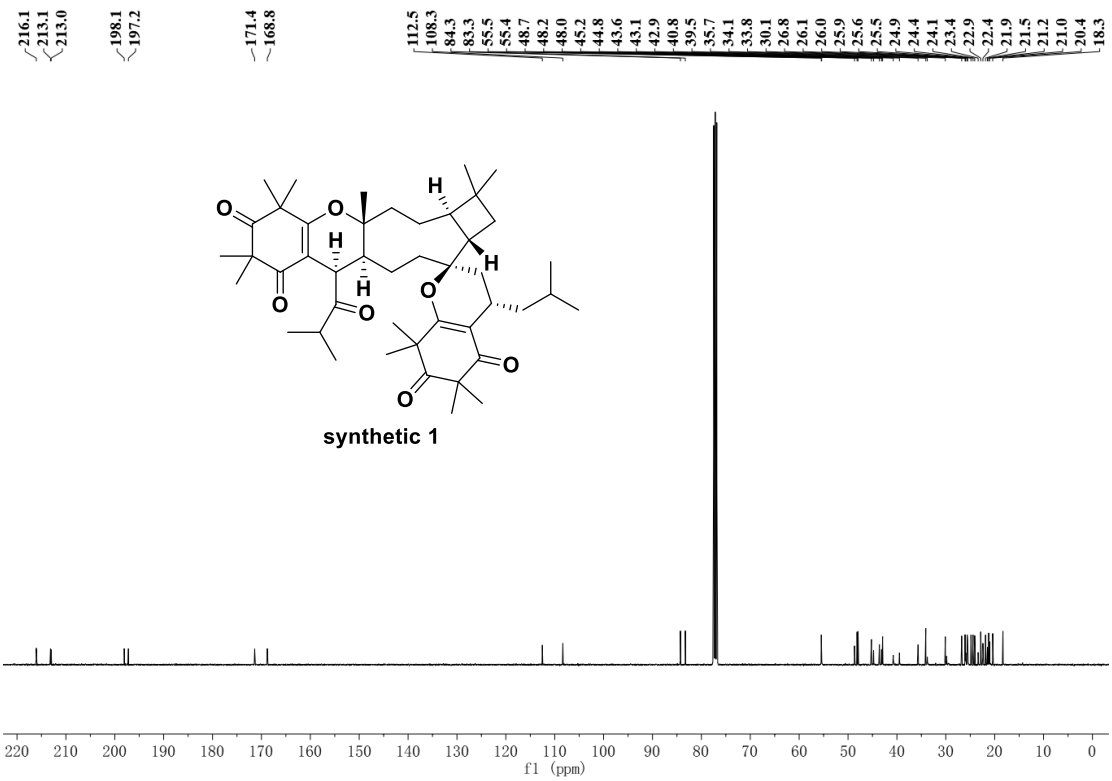


Figure S98. ^{13}C NMR spectrum (100 MHz) of synthetic **1** through path B in $CDCl_3$.

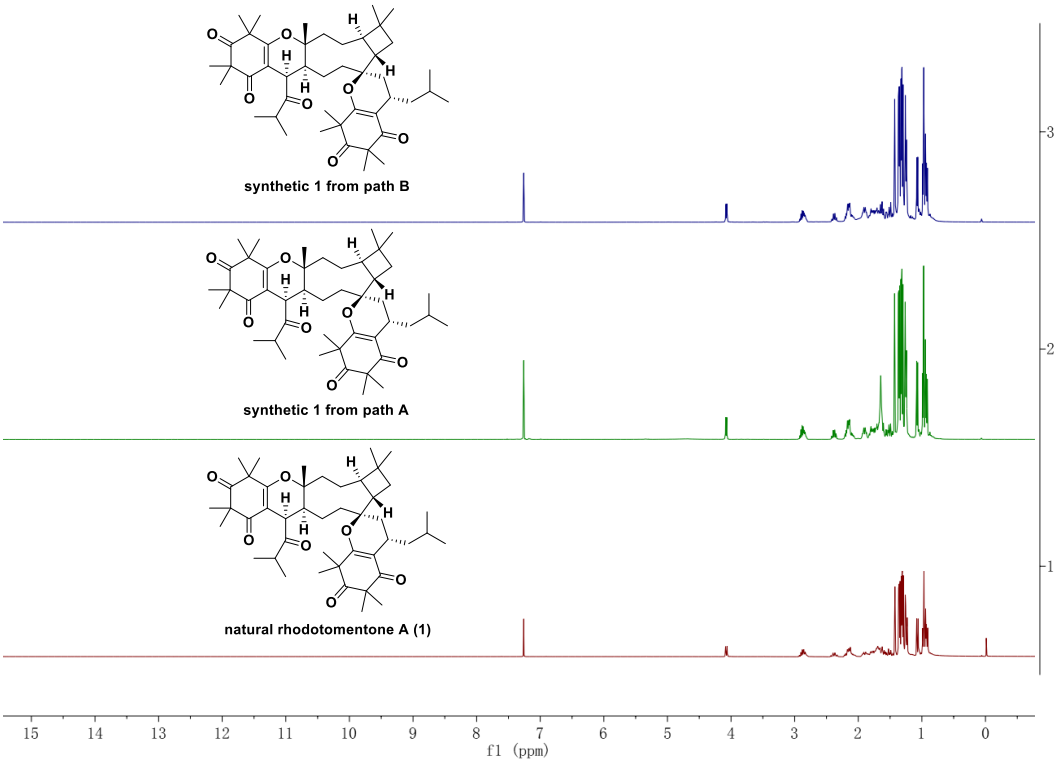


Figure S99. Comparison of ^{1}H NMR spectra between synthetic and natural **1**.

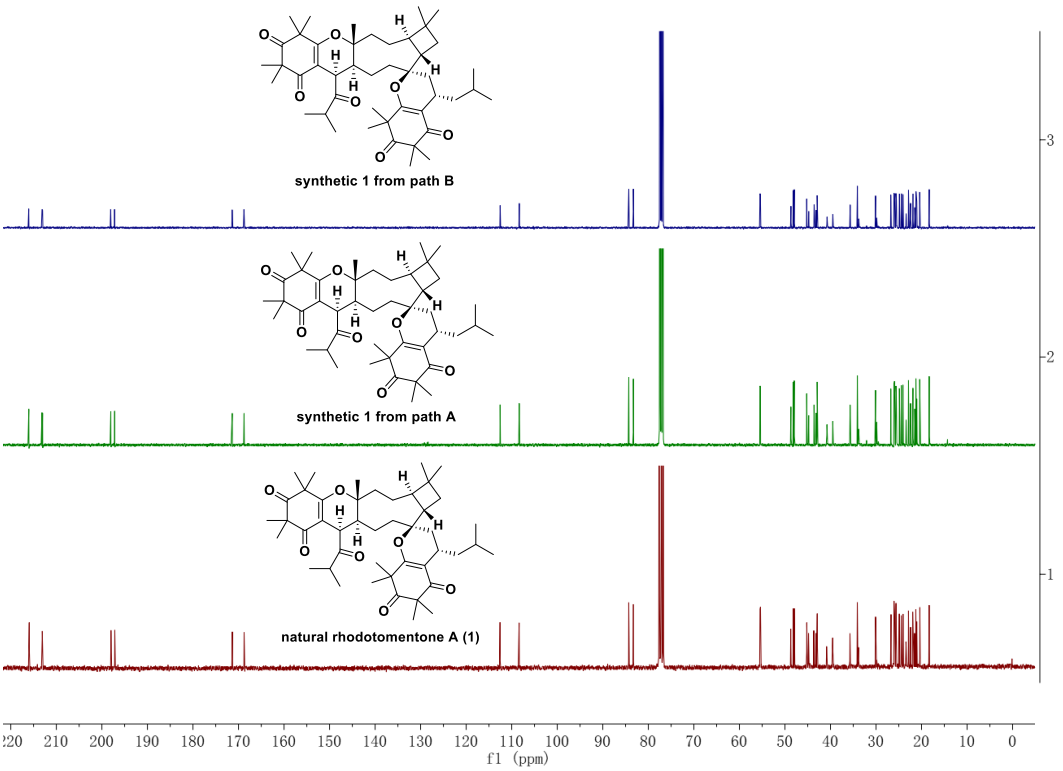


Figure S100. Comparison of ^{1}H NMR spectra between synthetic and natural **1**.

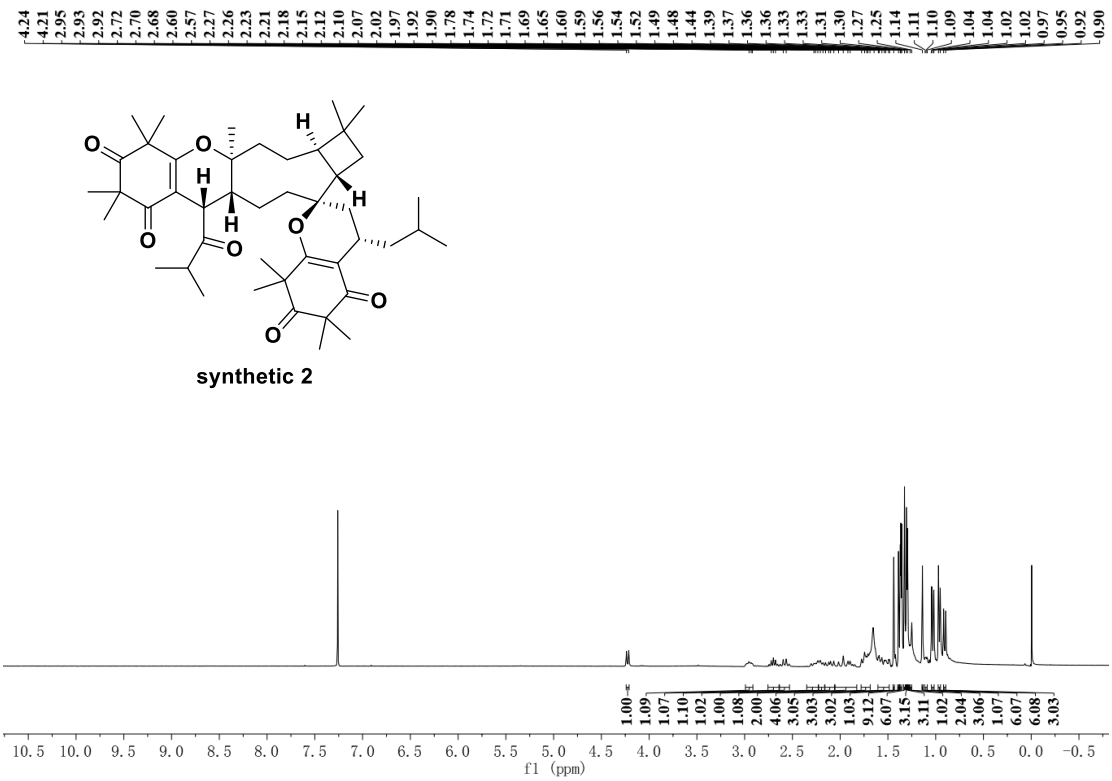


Figure S101. ^{1}H NMR spectrum (400 MHz) of synthetic **2** through path A in $CDCl_3$.

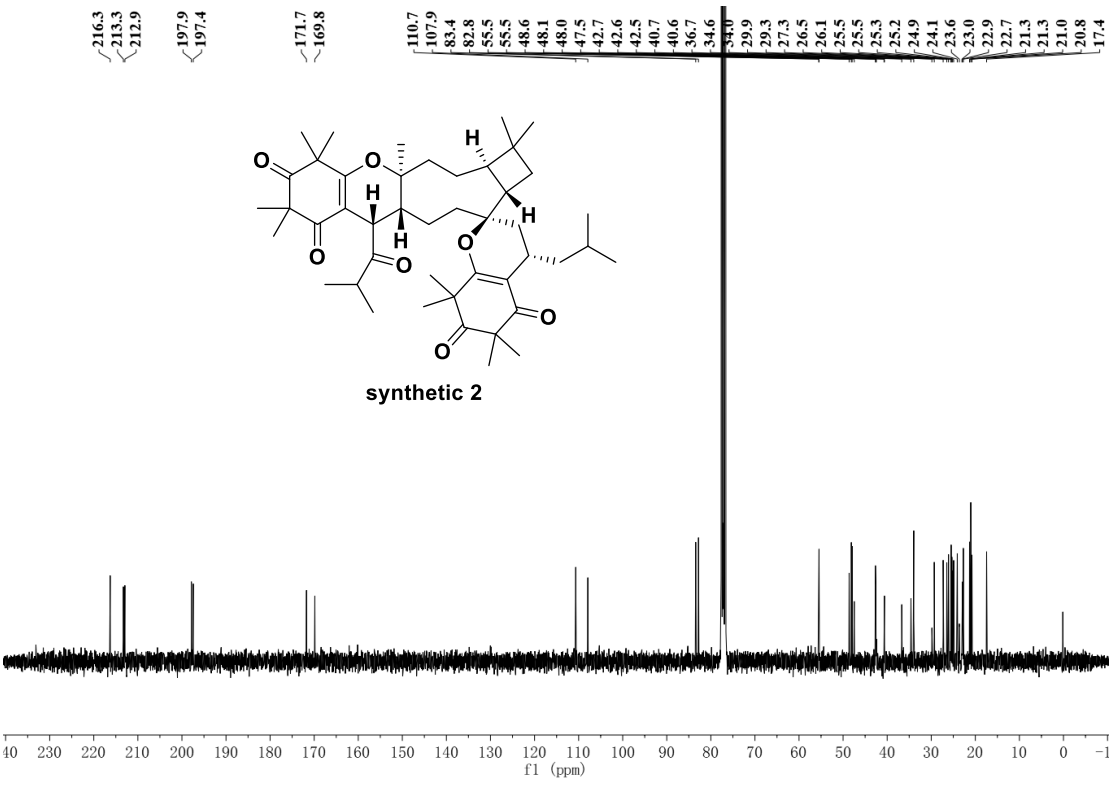


Figure S102. ^{13}C NMR spectrum (100 MHz) of synthetic **2** through path A in $CDCl_3$.

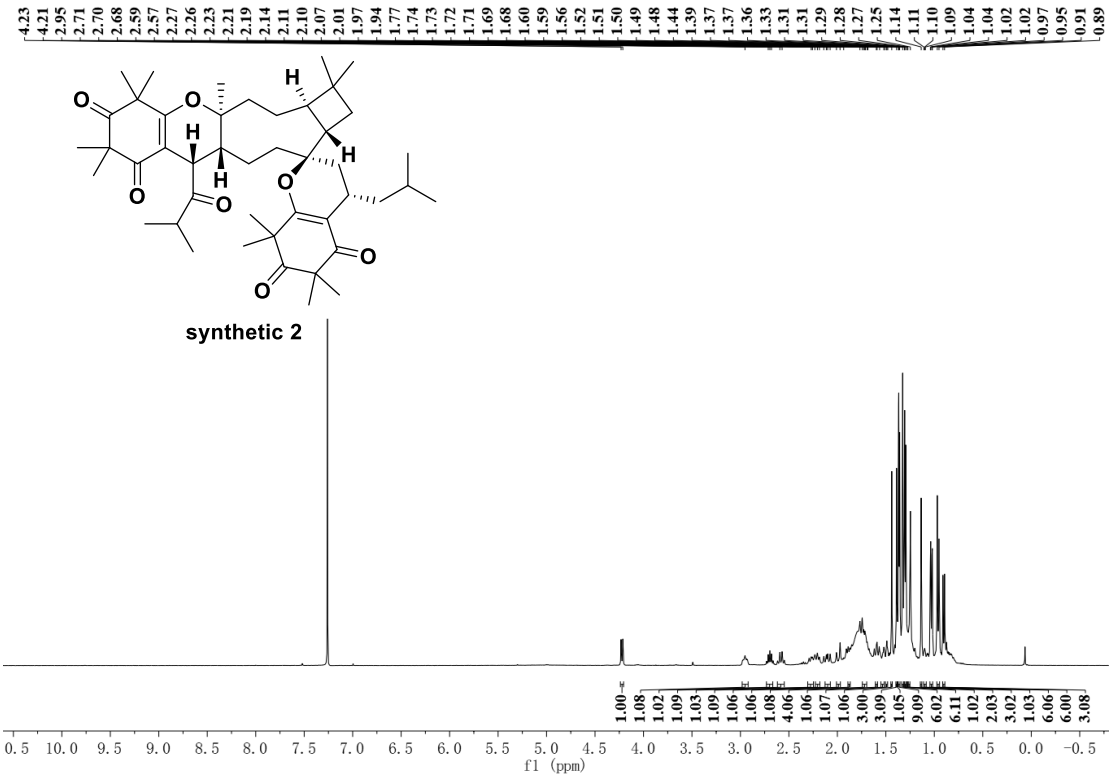


Figure S103. ^{1}H NMR spectrum (400 MHz) of synthetic **2** through path B in $CDCl_3$.

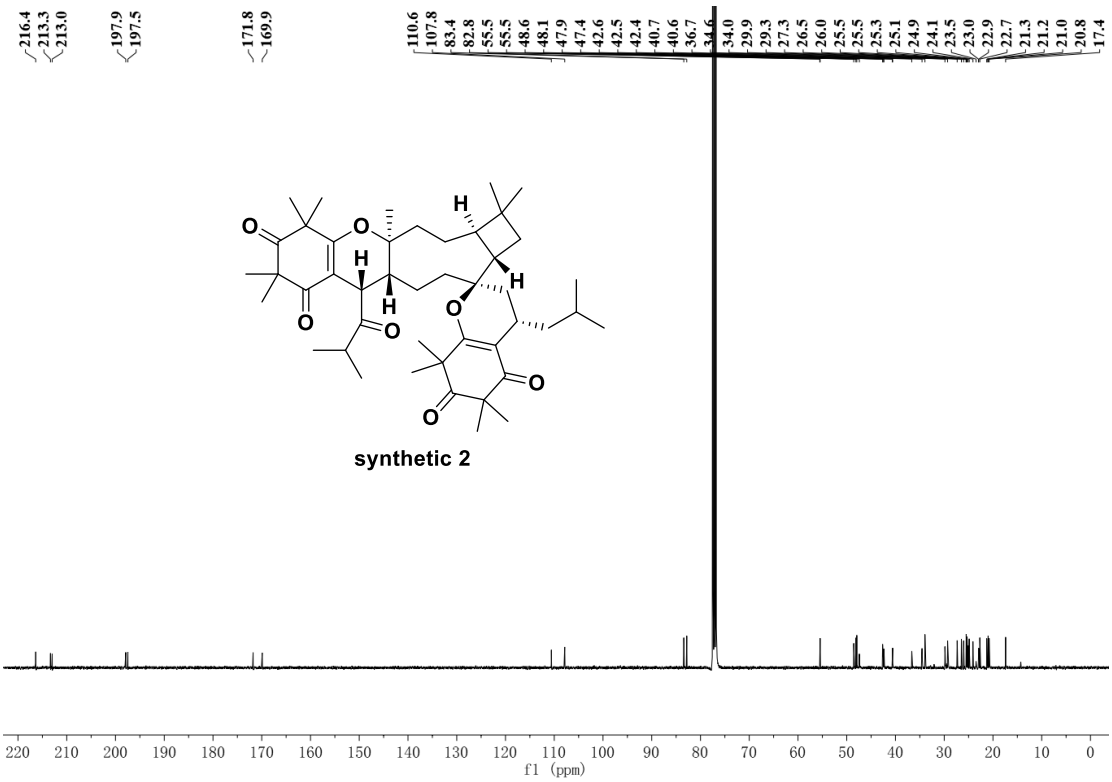


Figure S104. ^{13}C NMR spectrum (100 MHz) of synthetic **2** through path B in $CDCl_3$.

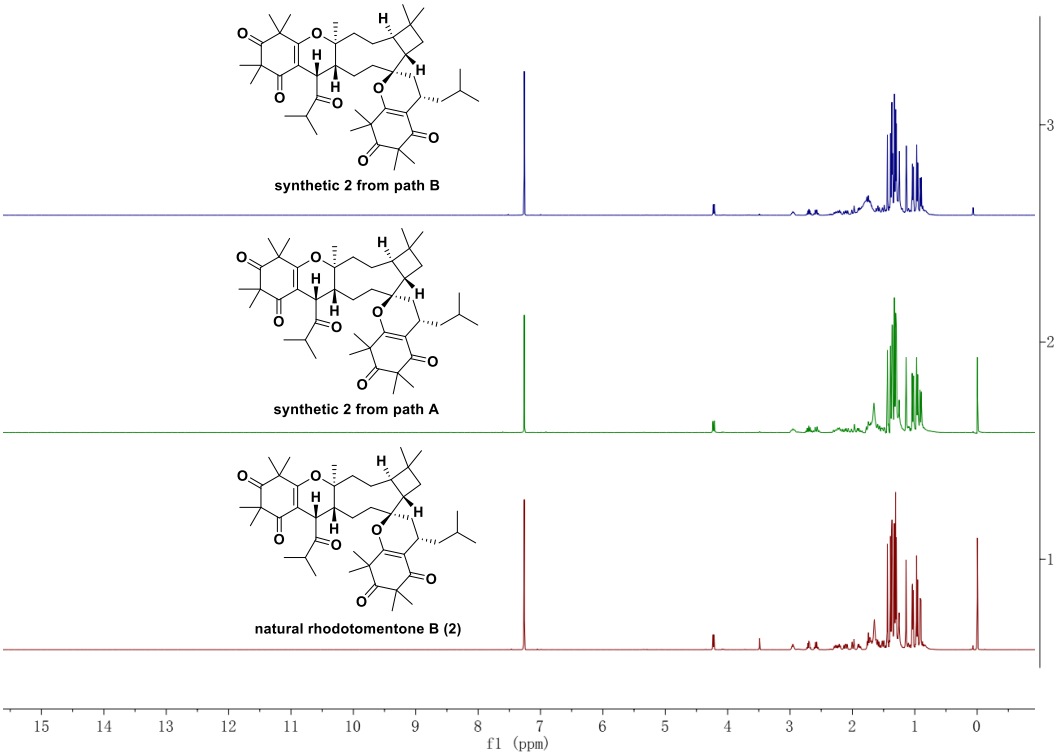


Figure S105. Comparison of ^{1}H NMR spectra between synthetic and natural **2**.

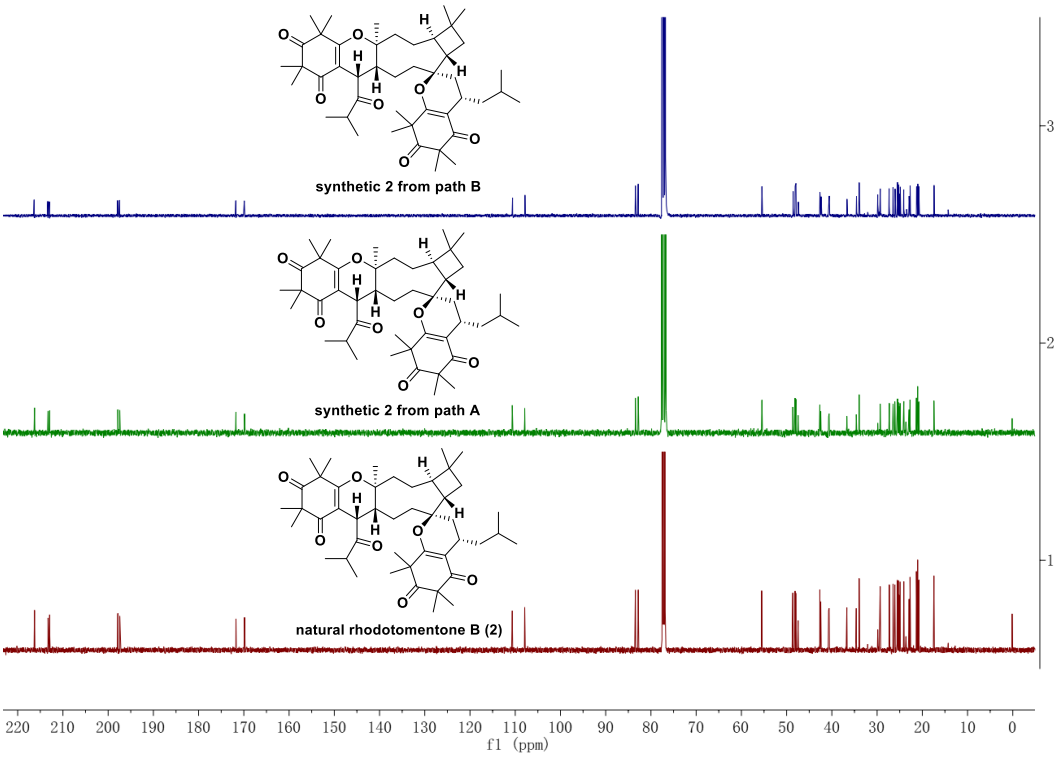


Figure S106. Comparison of ^{1}H NMR spectra between synthetic and natural **2**.

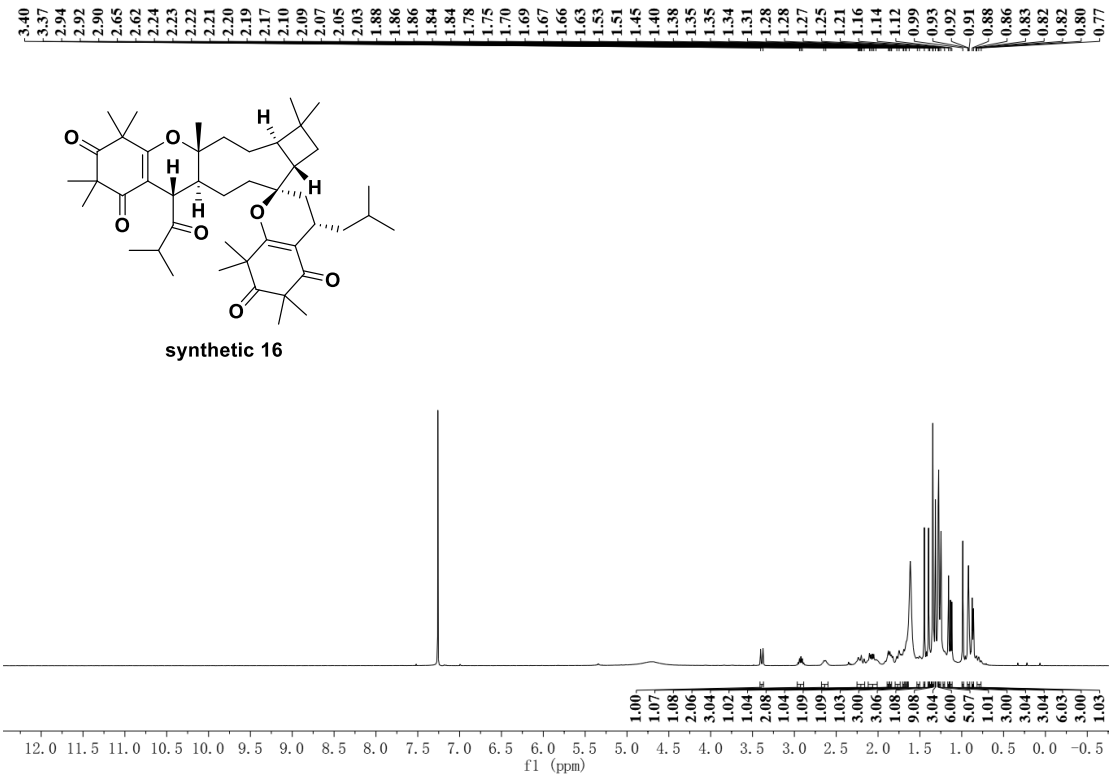


Figure S107. ^{1}H NMR spectrum (400 MHz) of synthetic **16** through path A in $CDCl_3$.

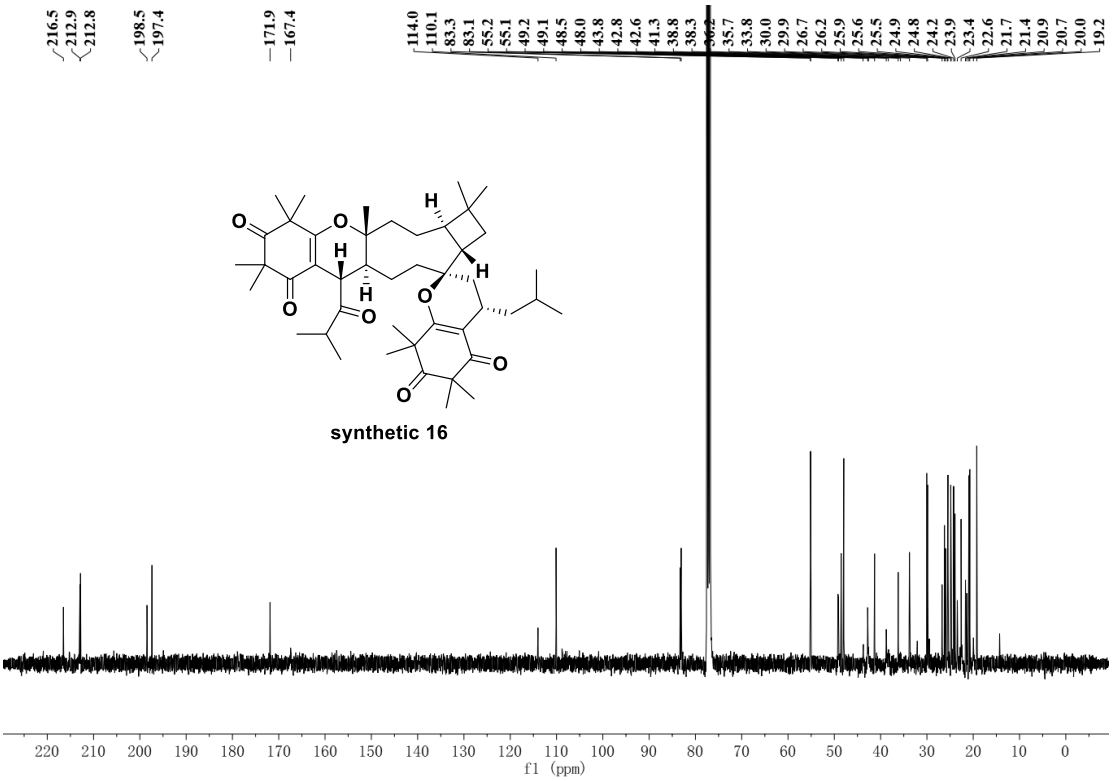


Figure S108. ^{13}C NMR spectrum (100 MHz) of synthetic **16** through path A in $CDCl_3$.

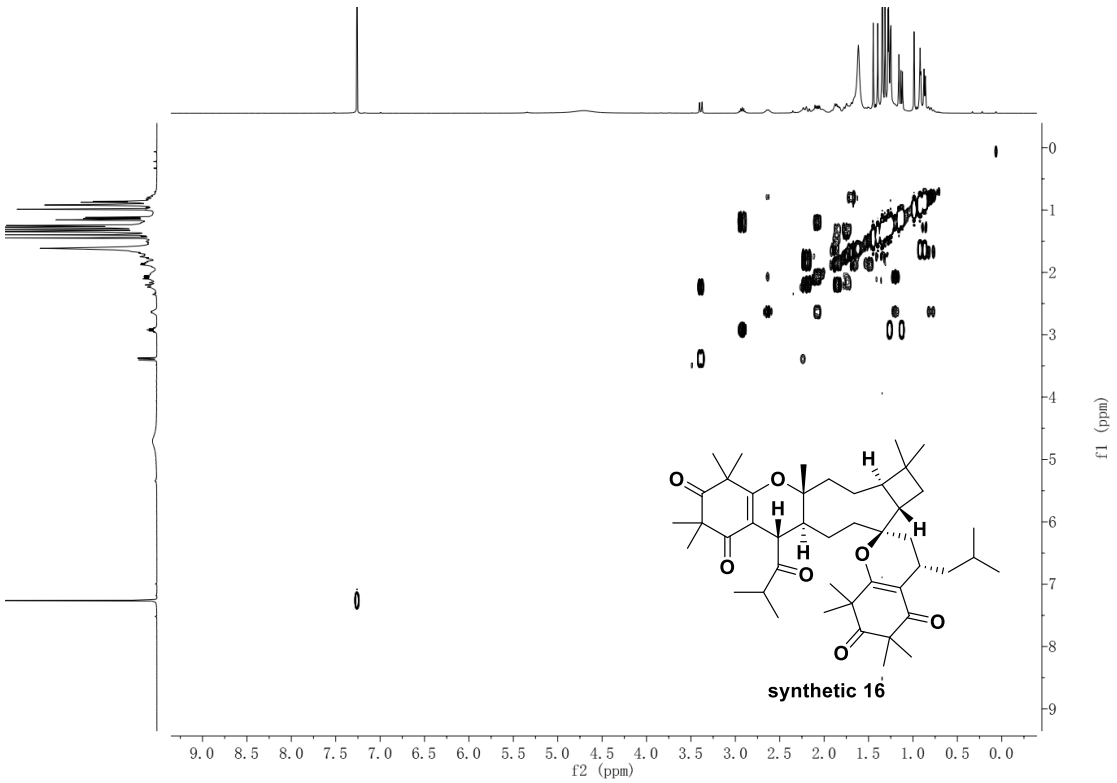


Figure S109. $^{1}H–^{1}H$ COSY spectrum of synthetic **16** through path A in $CDCl_3$.

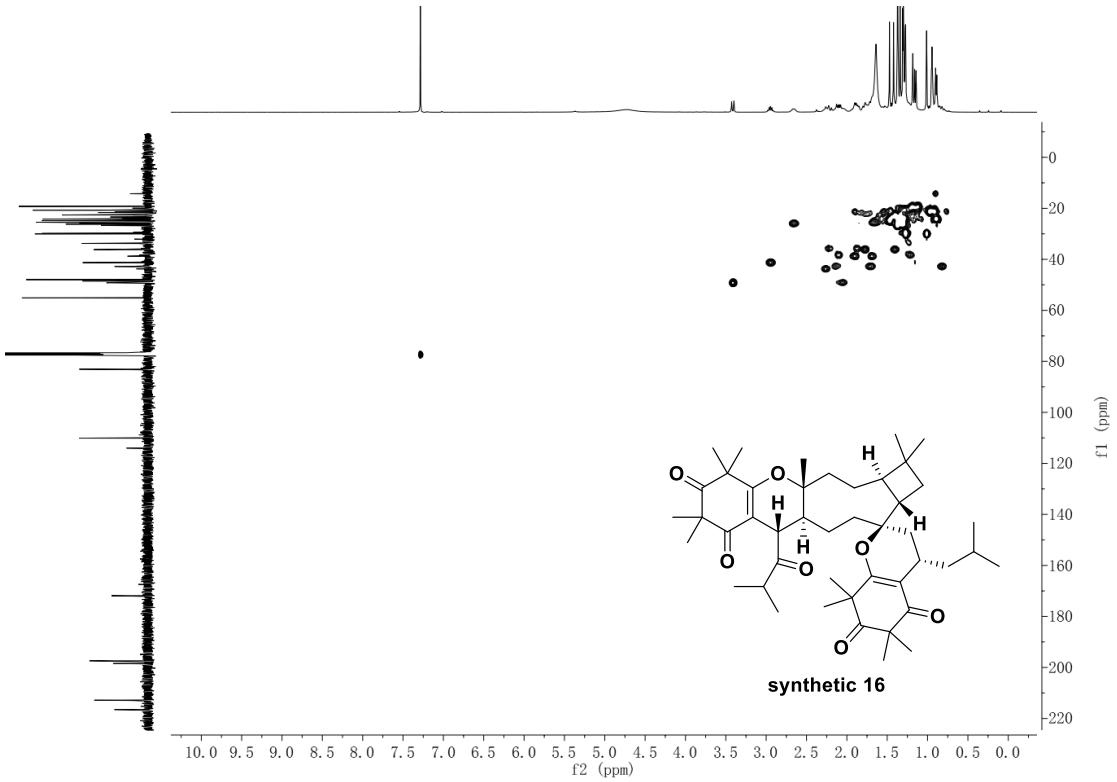


Figure S110. HSQC spectrum of synthetic **16** through path A in $CDCl_3$.

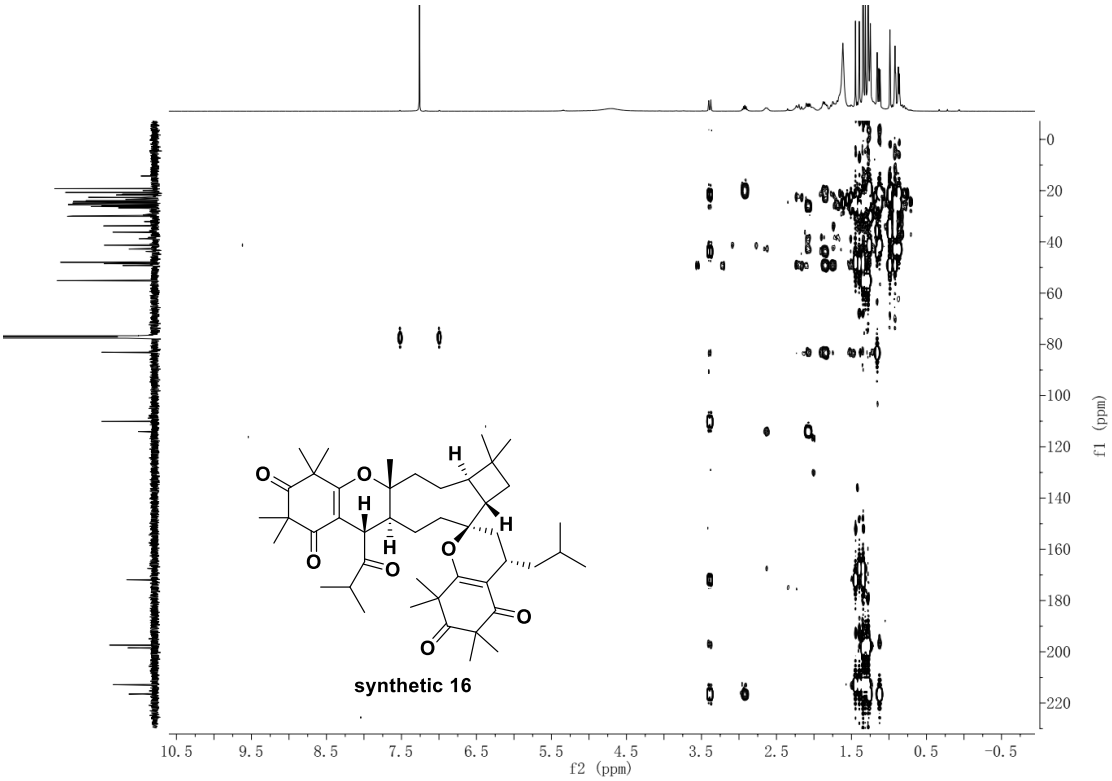


Figure S111. HMBC spectrum of synthetic **16** through path A in $CDCl_3$.

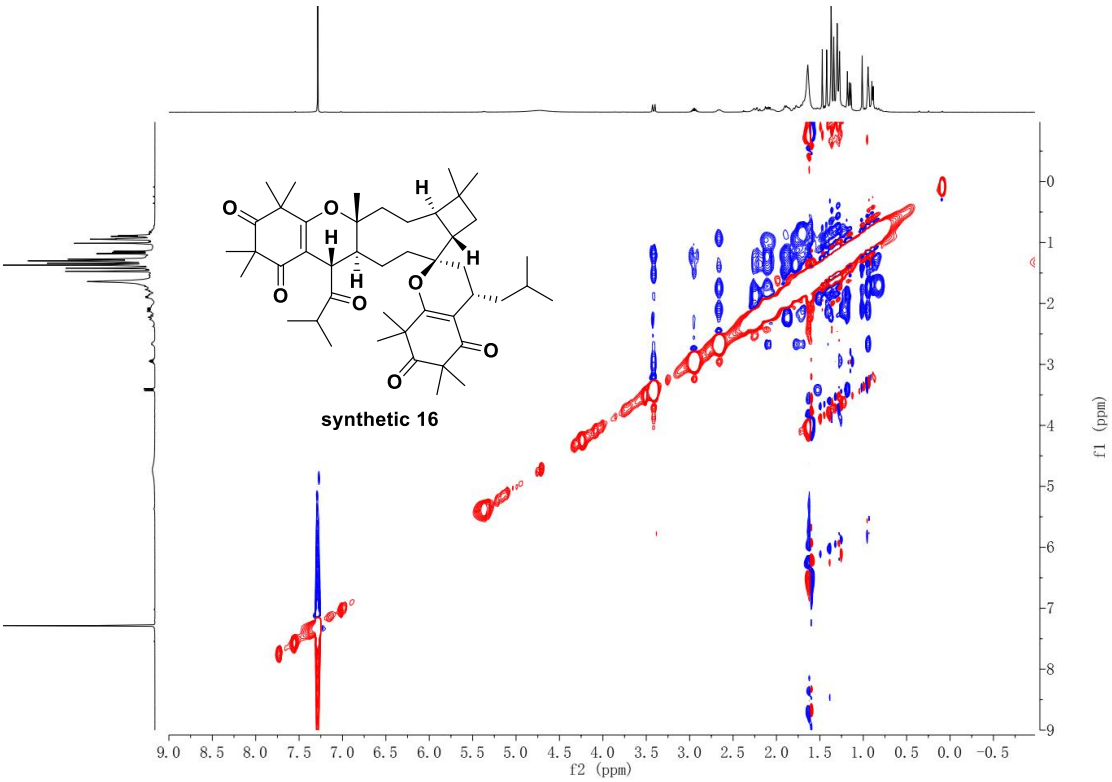


Figure S112. NOESY spectrum of synthetic **16** through path A in $CDCl_3$.

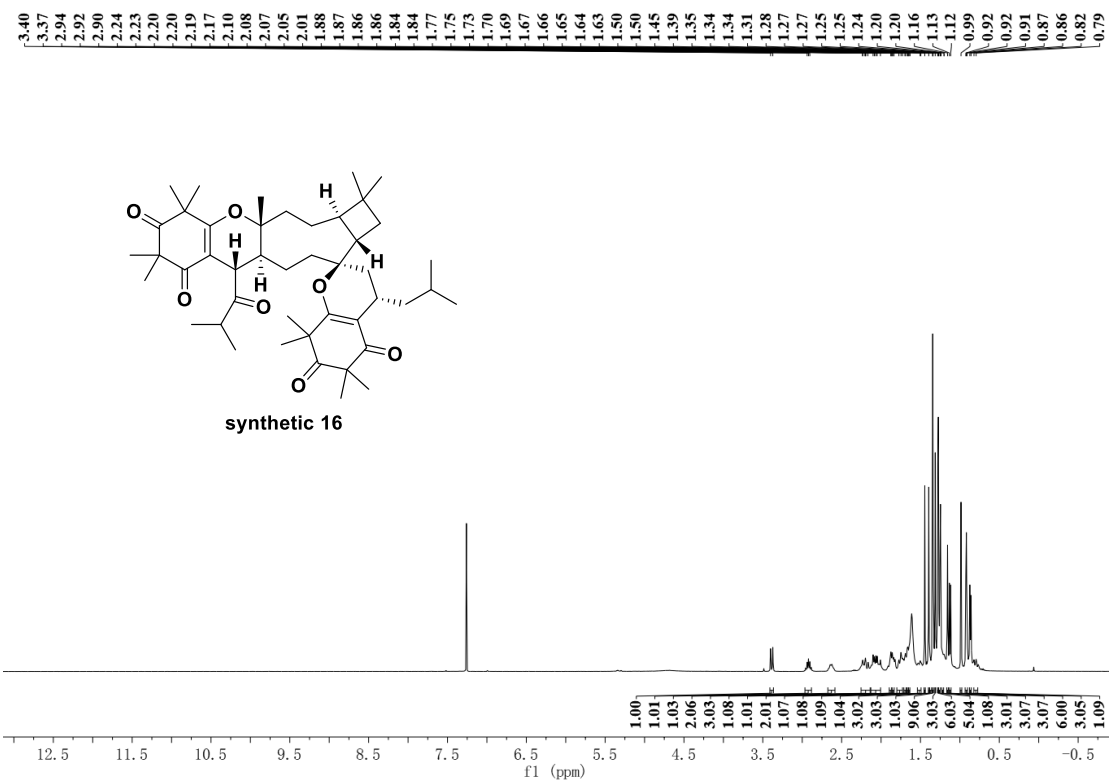


Figure S113. ^{1}H NMR spectrum (400 MHz) of synthetic **16** through path B in $CDCl_3$.

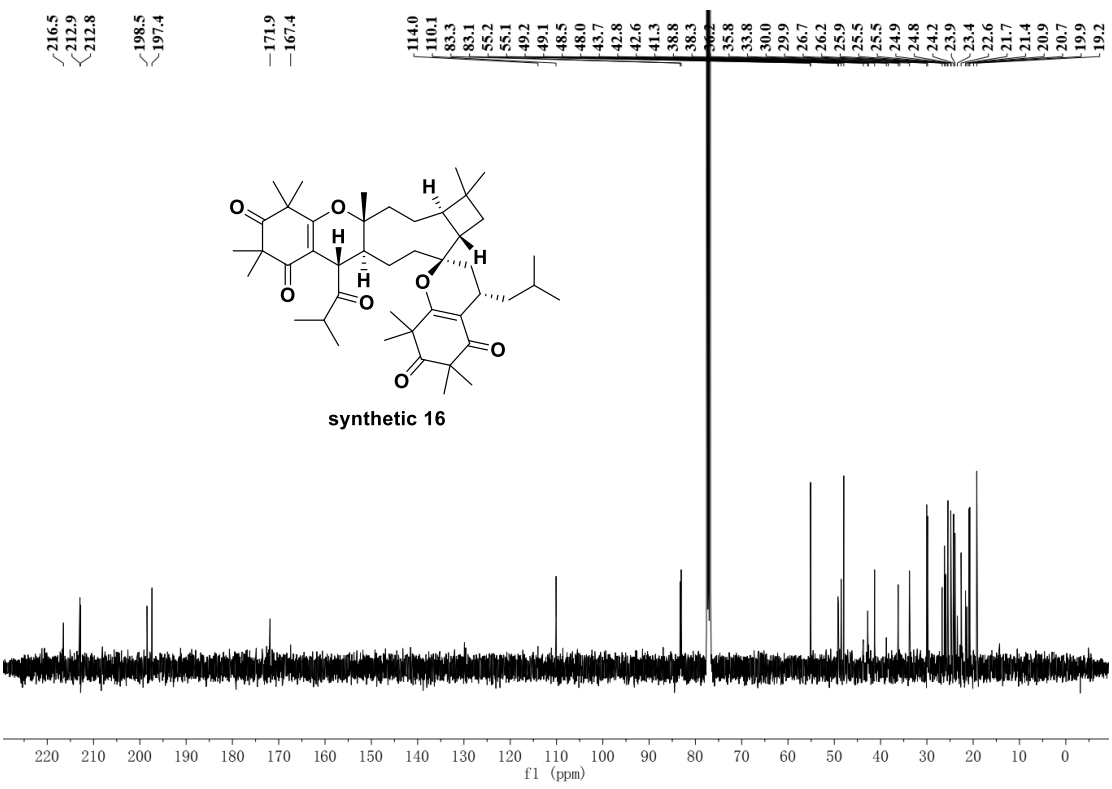


Figure S114. ^{13}C NMR spectrum (100 MHz) of synthetic **16** through path B in $CDCl_3$.

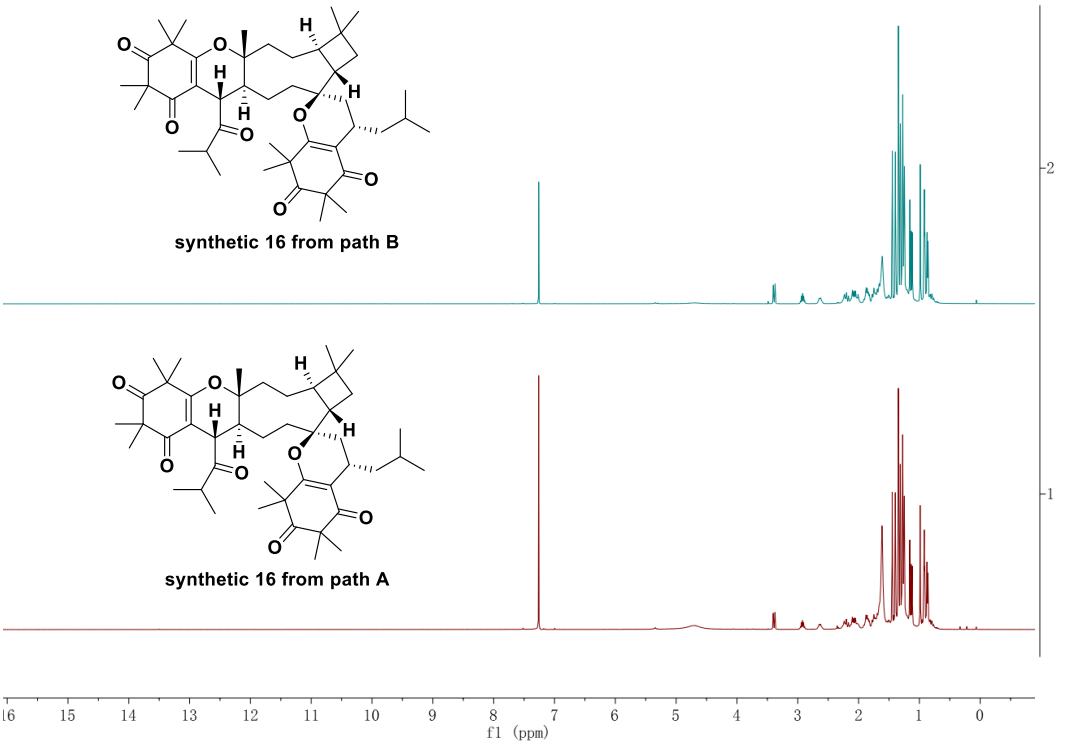


Figure S115. Comparison of ^{1}H NMR spectra between synthetic **16** through paths A and B.

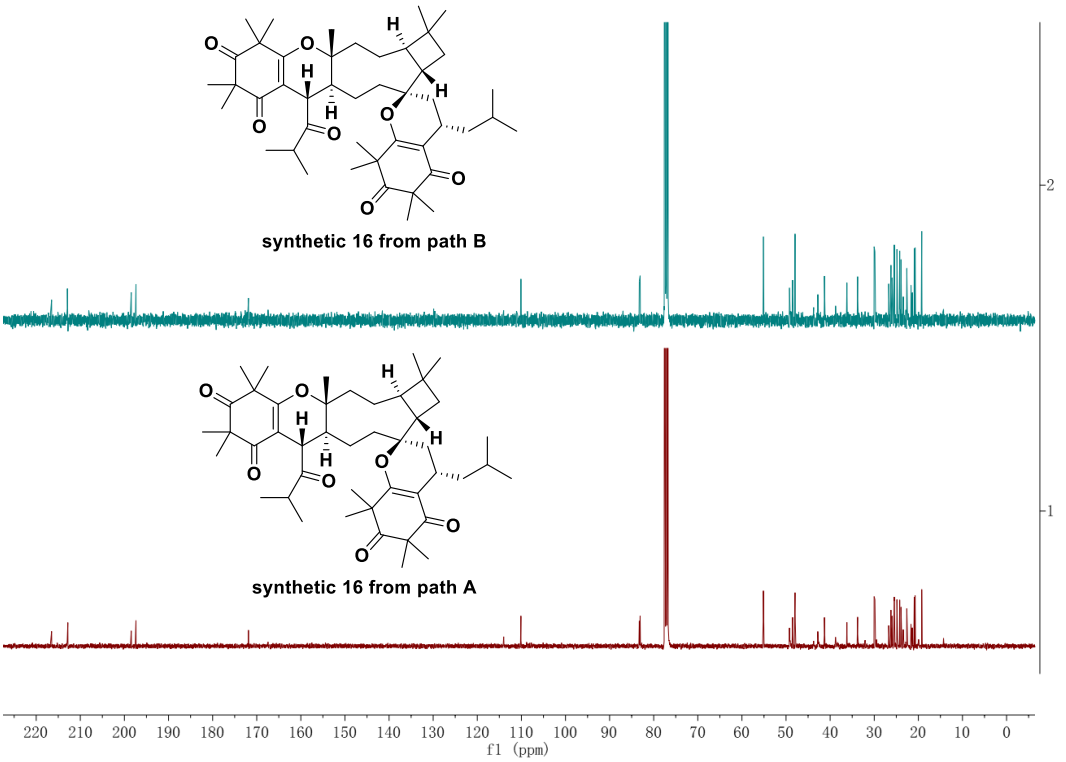


Figure S116. Comparison of ^{13}C NMR spectra between synthetic **16** through paths A and B.

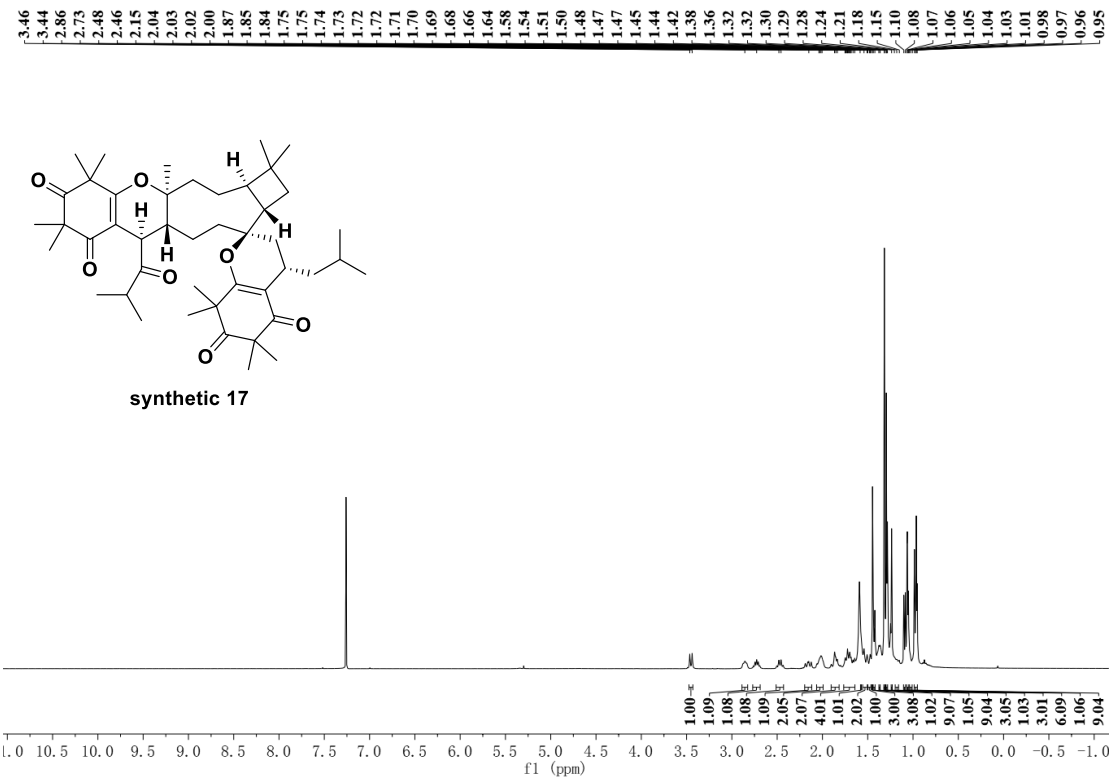


Figure S117. ^{1}H NMR spectrum (400 MHz) of synthetic **17** through path A in $CDCl_3$.

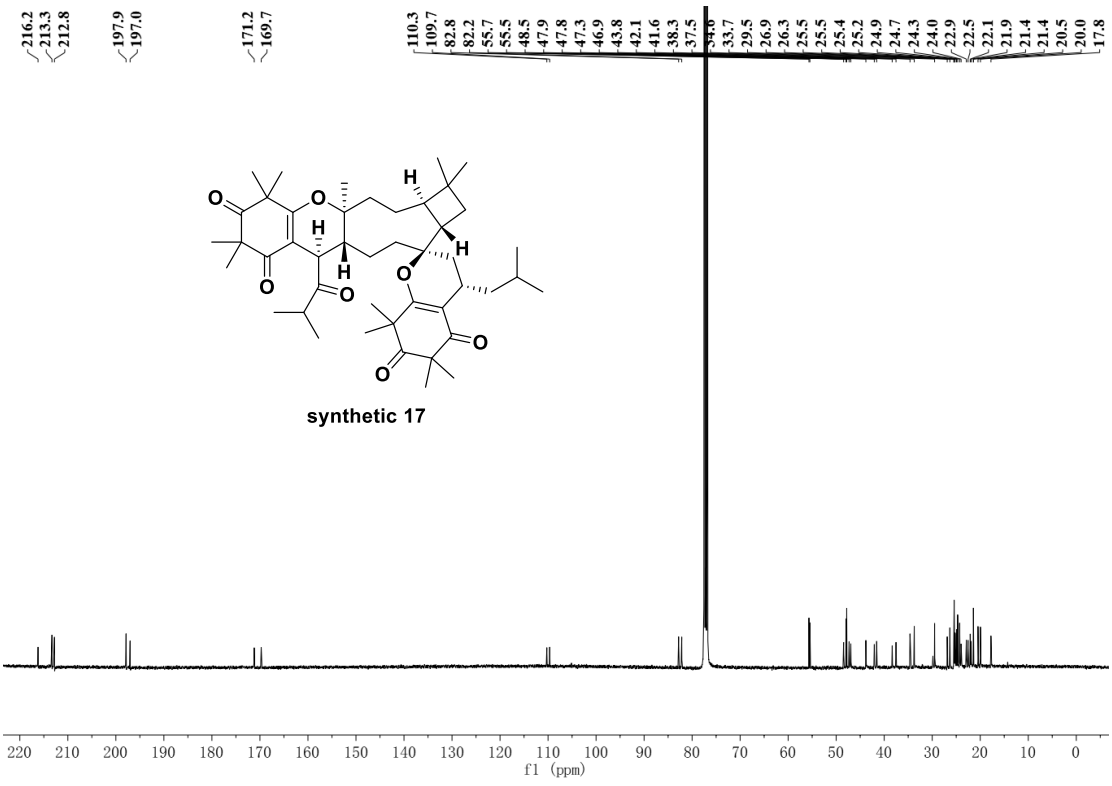


Figure S118. ^{13}C NMR spectrum (100 MHz) of synthetic **17** through path A in $CDCl_3$.

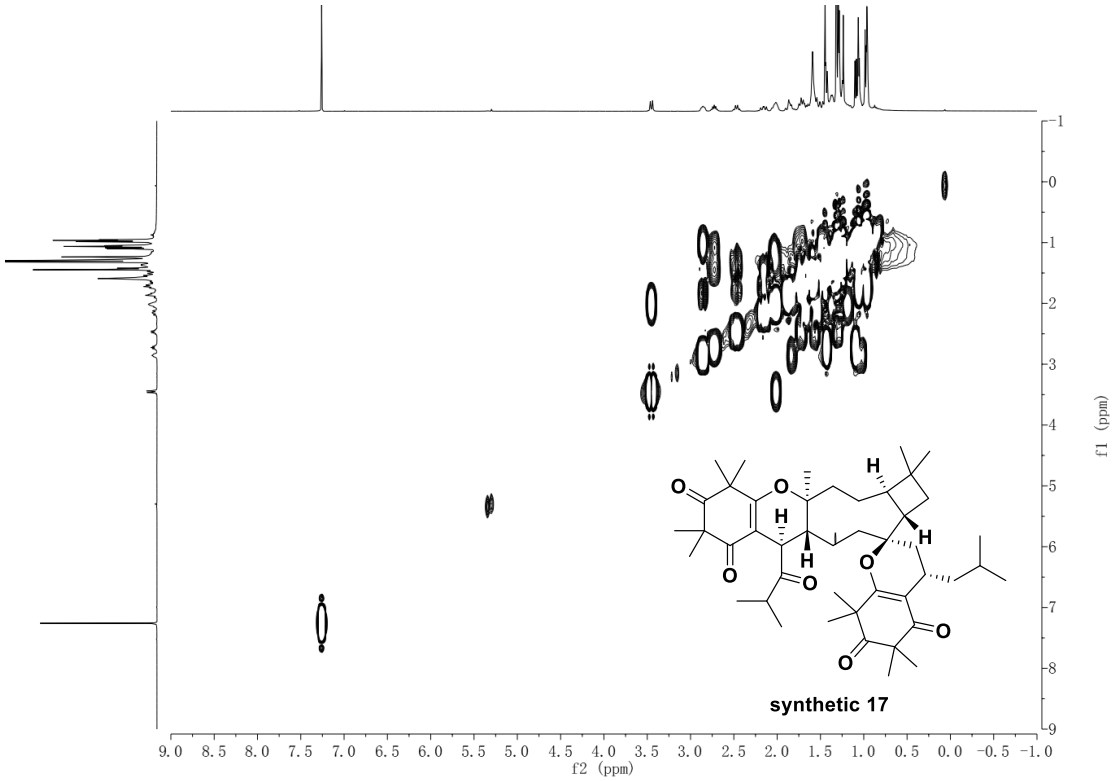


Figure S119. $^{1}H–^{1}H$ COSY spectrum of synthetic **17** through path A in $CDCl_3$.

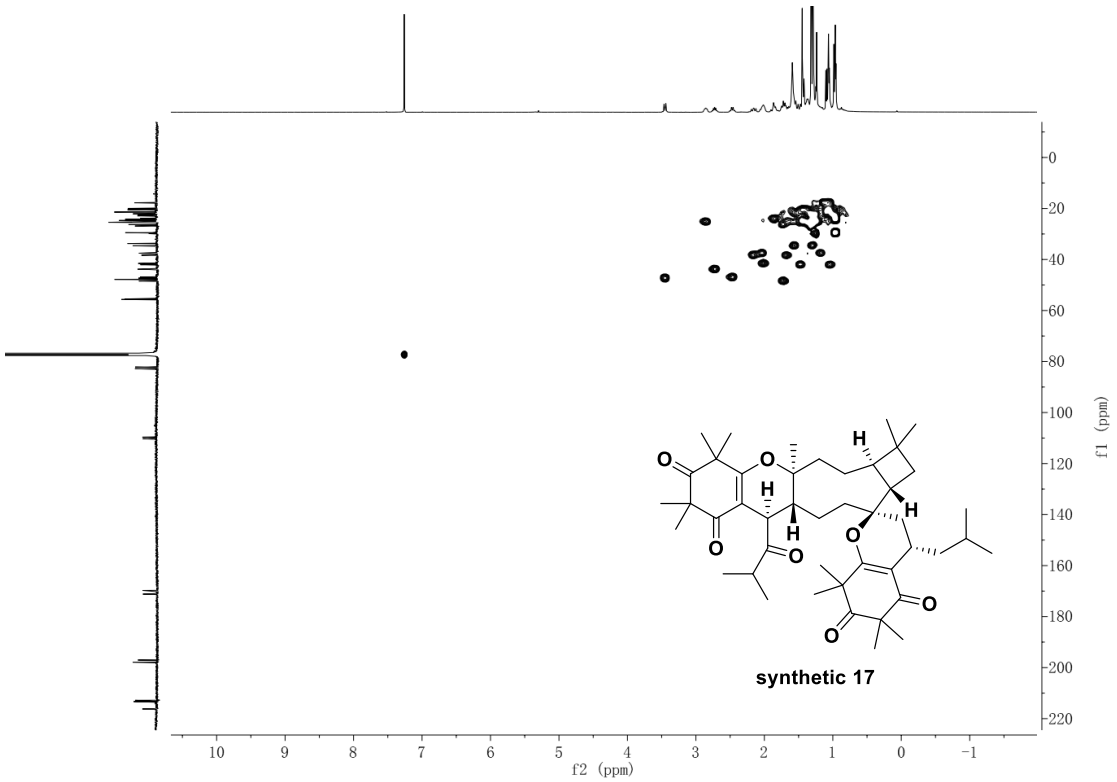


Figure S120. HSQC spectrum of synthetic **17** through path A in $CDCl_3$.

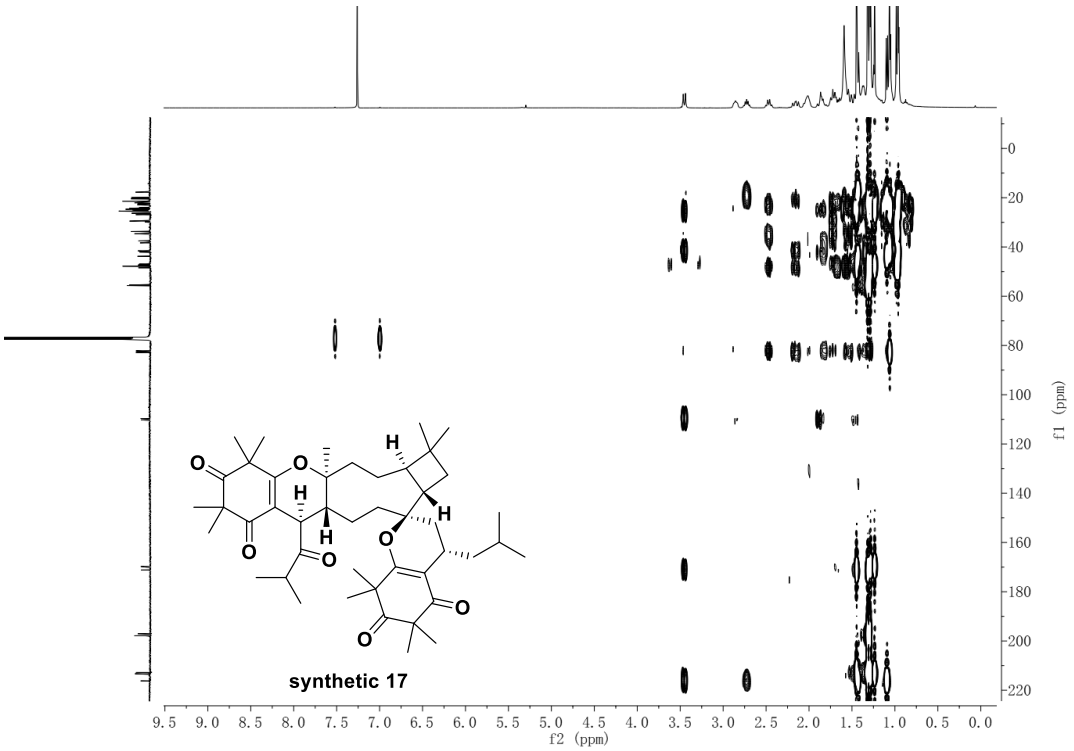


Figure S121. HMBC spectrum of synthetic **17** through path A in $CDCl_3$.

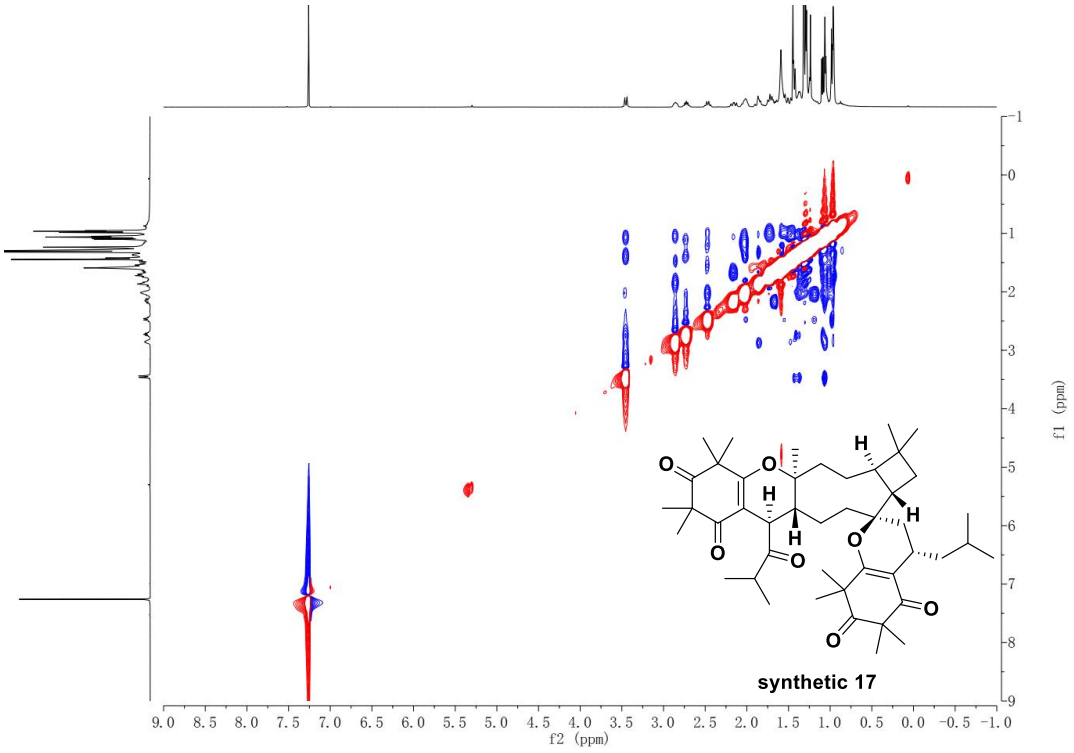


Figure S122. NOESY spectrum of synthetic **17** through path A in $CDCl_3$.

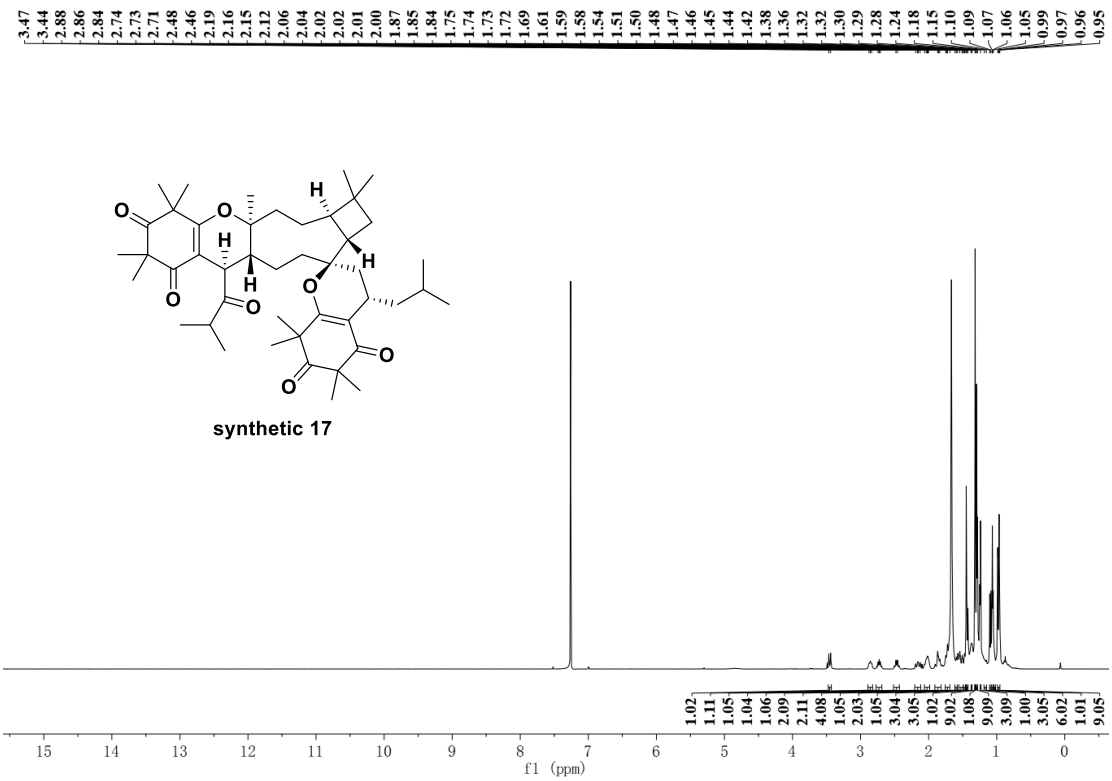


Figure S123. ^{1}H NMR spectrum (400 MHz) of synthetic **17** through path B in $CDCl_3$.

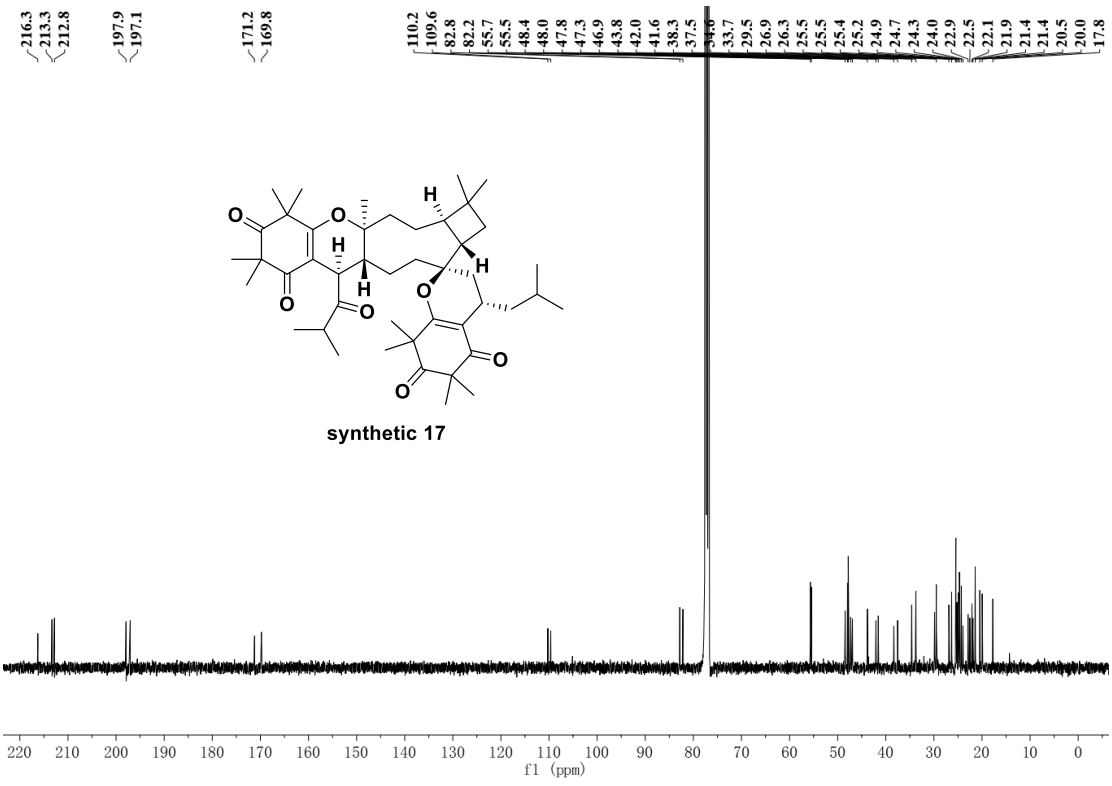


Figure S124. ^{13}C NMR spectrum (100 MHz) of synthetic **17** through path B in $CDCl_3$.

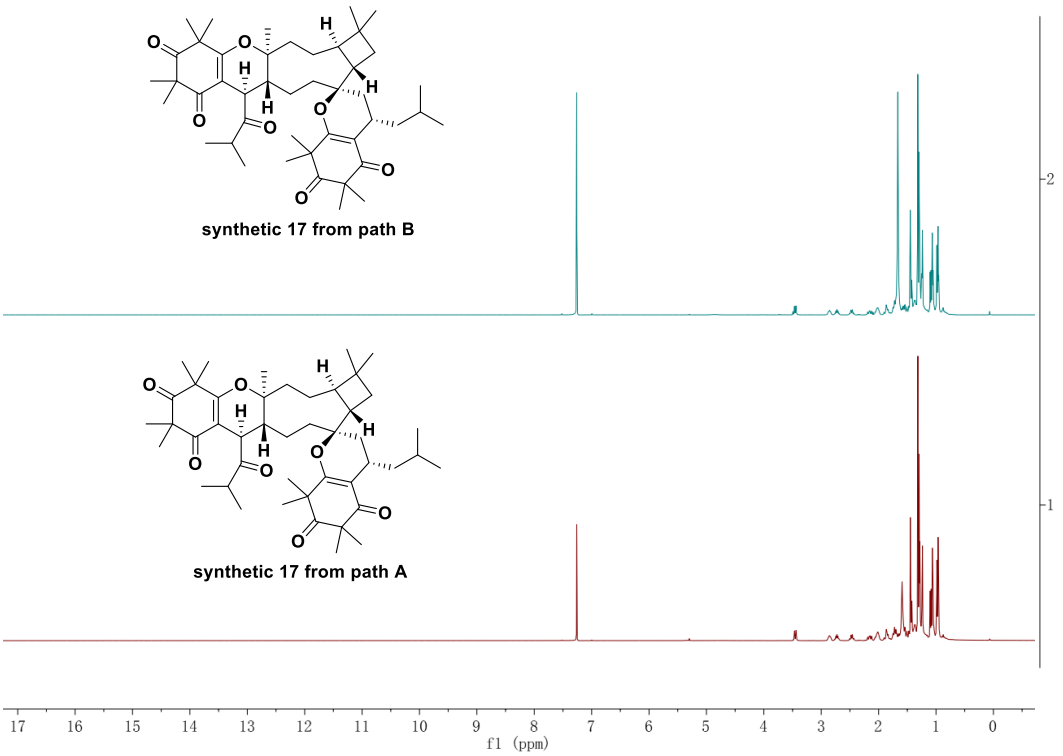


Figure S125. Comparison of ^{1}H NMR spectra between synthetic **17** through paths A and B.

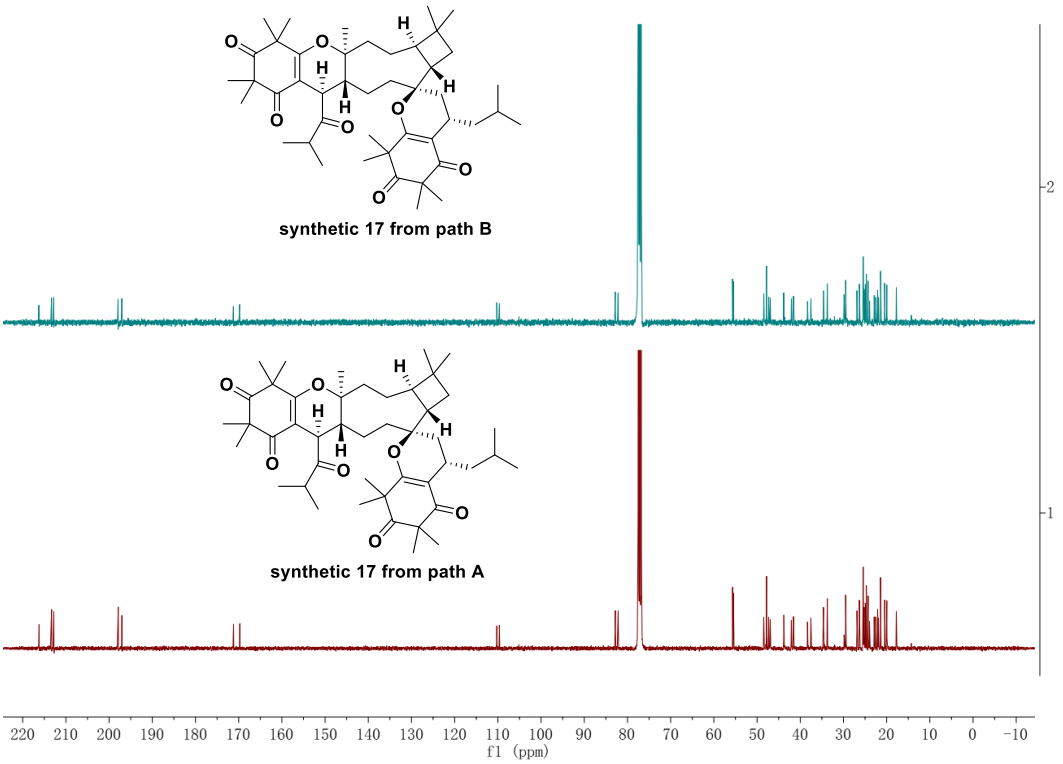


Figure S126. Comparison of ^{13}C NMR spectra between synthetic **17** through paths A and B.

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