Supporting Information

Table S1 ^{1}H and ^{13}C NMR data for (2*R*, 3*S*, 4*S*, *E*)-3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**) in CD_3OD.

position	δ_C	δ_H (mult. *J*)	HMBC
1	178.6		9
2	44.4	2.44 qd (6.8, 6.4)	
3	74.8	4.09 dd (6.4, 6.0)	9, 10
4	43.8	3.45 dq (6.8,6.4)	
5	206.4		10, 11
6	138.4		8
7	139.7	6.90 qq (6.8, 1.2)	11
8	14.9	1.90 dd (6.9 1.0)	
9	12.5	1.14 d (7.1)	
10	13.4	1.12 d (6.9)	
11	11.3	1.77 s	

Table S2 The atomic coordinates of stable conformations for (2*R*,3*S*,4*S*)-**11**.

Conformation I				Conformation II				Conformation III			
Atom	X	Y	Z	Atom	X	Y	Z	Atom	X	Y	Z
O	-3.567	1.168	-0.672	O	-3.925	0.151	-0.129	O	-3.506	-1.533	0.032
C	-3.312	-0.130	-0.926	C	-3.078	-0.892	-0.037	C	-3.379	-0.434	0.801
O	-3.971	-0.760	-1.720	O	-3.464	-2.029	-0.170	O	-4.106	-0.237	1.748
C	-2.173	-0.767	-0.105	C	-1.607	-0.573	0.304	C	-2.296	0.571	0.363
C	-0.974	0.199	-0.003	H	-1.038	-1.358	-0.197	C	-1.006	-0.172	-0.046
H	-0.809	0.586	-1.021	C	-1.128	0.784	-0.260	H	-0.825	-0.925	0.737
C	0.387	-0.399	0.438	C	0.377	1.071	-0.082	C	0.298	0.658	-0.131
H	0.550	-1.294	-0.170	C	1.214	-0.005	-0.791	H	0.385	1.229	0.798
C	1.482	0.637	0.141	O	0.794	-0.475	-1.843	C	1.489	-0.303	-0.244
O	1.222	1.835	0.288	C	2.542	-0.453	-0.266	O	1.345	-1.367	-0.852
C	2.864	0.254	-0.268	C	3.065	0.073	0.859	C	2.816	0.085	0.336
C	3.200	-1.040	-0.449	C	-1.417	-0.733	1.826	C	3.851	-0.729	0.047
H	2.434	-1.795	-0.291	H	-1.962	0.030	2.393	H	3.614	-1.587	-0.578
O	-1.360	1.289	0.843	H	-1.805	-1.705	2.139	O	-1.268	-0.854	-1.280
H	-0.610	1.914	0.790	H	-0.361	-0.687	2.110	H	-0.463	-1.387	-1.438
C	0.490	-0.774	1.933	O	-1.909	1.873	0.288	C	0.386	1.630	-1.331
H	-0.104	-1.658	2.165	H	-1.714	1.938	1.234	H	-0.250	2.503	-1.183
H	0.135	0.052	2.553	H	-1.349	0.807	-1.330	H	0.075	1.121	-2.245
H	1.527	-0.990	2.206	C	0.752	2.446	-0.677	H	1.410	1.989	-1.472
H	-2.908	1.504	-0.023	H	0.590	2.444	-1.759	H	-2.808	-1.523	-0.660
C	4.527	-1.604	-0.851	H	0.134	3.233	-0.241	C	5.278	-0.615	0.474
H	4.883	-2.309	-0.089	H	1.804	2.679	-0.490	H	5.575	-1.513	1.031
H	5.297	-0.847	-1.002	H	0.598	1.083	0.990	H	5.489	0.255	1.097
H	4.426	-2.181	-1.779	H	-3.431	0.984	0.030	H	5.933	-0.575	-0.405

C	3.800	1.424	-0.444	C	4.378	-0.243	1.506	C	2.913	1.326	1.193
H	3.877	1.996	0.484	H	4.955	-1.000	0.973	H	2.307	1.236	2.102
H	3.409	2.116	-1.196	H	4.992	0.662	1.582	H	2.566	2.219	0.663
H	4.801	1.114	-0.745	H	4.221	-0.595	2.533	H	3.940	1.515	1.508
C	-2.769	-1.248	1.235	H	2.490	0.831	1.386	H	-2.081	1.159	1.261
H	-2.991	-0.404	1.891	C	3.207	-1.503	-1.122	C	-2.912	1.492	-0.709
H	-3.696	-1.794	1.043	H	4.175	-1.812	-0.727	H	-3.883	1.854	-0.360
H	-2.092	-1.923	1.762	H	2.566	-2.386	-1.207	H	-2.286	2.364	-0.906
H	-1.862	-1.637	-0.691	H	3.346	-1.130	-2.141	H	-3.059	0.957	-1.650

Table S3 The atomic coordinates of stable conformations for (2*R*,3*S*,4*R*)-**11**.

Conformation I				Conformation II			
Atom	X	Y	Z	Atom	X	Y	Z
C	3.586	-0.010	0.163	C	-3.490	-0.149	0.177
C	2.215	-0.707	0.065	C	-2.205	0.674	0.251
C	1.044	0.290	0.190	C	-1.030	-0.315	0.092
C	-0.345	-0.371	0.331	C	0.359	0.293	0.394
H	1.209	0.904	1.088	H	-1.201	-1.135	0.800
H	-0.469	-1.094	-0.481	H	0.496	1.173	-0.242
C	-1.454	0.688	0.206	C	1.456	-0.726	0.042
C	-2.886	0.309	0.010	C	2.891	-0.320	-0.093
C	-3.227	-0.952	-0.323	C	3.242	0.980	-0.158
C	-4.591	-1.496	-0.615	C	4.610	1.561	-0.346
H	-4.815	-2.335	0.055	H	4.848	2.246	0.477
H	-4.627	-1.900	-1.634	H	4.644	2.162	-1.264
H	-5.387	-0.757	-0.514	H	5.400	0.811	-0.403
C	-0.482	-1.101	1.686	C	0.499	0.707	1.876
H	-0.309	-0.407	2.515	H	0.279	-0.140	2.533
H	0.244	-1.913	1.771	H	-0.191	1.516	2.126
H	-1.478	-1.528	1.812	H	1.510	1.052	2.102
O	1.092	1.139	-0.968	O	-1.100	-0.801	-1.243
H	0.473	1.864	-0.770	H	-0.540	-1.592	-1.253
O	-1.168	1.884	0.291	O	1.166	-1.912	-0.107
O	4.519	-0.509	0.749	O	-3.712	-1.123	0.865
H	-2.432	-1.689	-0.413	H	2.455	1.726	-0.082
O	3.705	1.166	-0.479	O	-4.390	0.319	-0.716
H	2.831	1.402	-0.864	H	-5.147	-0.288	-0.667
C	-3.851	1.460	0.149	C	3.847	-1.481	-0.210
H	-4.889	1.150	0.027	H	4.886	-1.160	-0.278
H	-3.628	2.236	-0.589	H	3.608	-2.084	-1.091
H	-3.743	1.935	1.130	H	3.744	-2.149	0.650
C	2.175	-1.550	-1.225	C	-2.160	1.857	-0.722

H	3.059	-2.192	-1.273	H	-2.112	1.504	-1.753
H	1.293	-2.196	-1.255	H	-3.046	2.485	-0.615
H	2.160	-0.912	-2.112	H	-1.282	2.482	-0.529
H	2.196	-1.379	0.926	H	-2.188	1.047	1.283

Table S4 The atomic coordinates of stable conformations for (2*R*,3*R*,4*S*)-**11**.

Conformation I				Conformation II			
Atom	X	Y	Z	Atom	X	Y	Z
C	3.552	-0.083	-0.334	C	3.423	-0.135	-0.348
C	2.152	0.579	-0.405	C	2.104	0.625	-0.328
C	1.064	-0.306	0.256	C	1.045	-0.302	0.302
H	1.885	0.602	-1.473	H	1.800	0.803	-1.365
C	-0.330	0.372	0.378	C	-0.353	0.366	0.467
H	1.394	-0.597	1.265	H	1.407	-0.612	1.293
H	-0.442	1.074	-0.453	H	-0.467	1.120	-0.318
C	-1.474	-0.651	0.337	C	-1.485	-0.663	0.355
C	-2.858	-0.271	-0.074	C	-2.848	-0.293	-0.136
C	-3.126	0.952	-0.578	C	-3.120	0.950	-0.582
C	-4.438	1.487	-1.060	C	-4.418	1.482	-1.107
H	-4.699	2.399	-0.510	H	-4.743	2.345	-0.512
H	-4.362	1.777	-2.115	H	-4.289	1.849	-2.133
H	-5.262	0.780	-0.960	H	-5.223	0.747	-1.108
C	2.258	2.020	0.102	C	2.341	1.972	0.376
H	1.337	2.582	-0.074	H	1.449	2.602	0.348
H	2.496	2.053	1.169	H	2.639	1.822	1.417
H	3.075	2.521	-0.417	H	3.143	2.521	-0.125
C	-0.477	1.131	1.720	C	-0.511	1.037	1.852
H	-0.431	0.425	2.555	H	-0.466	0.278	2.639
H	0.317	1.865	1.854	H	0.279	1.764	2.041
H	-1.436	1.654	1.774	H	-1.472	1.553	1.935
O	0.994	-1.477	-0.574	O	1.013	-1.416	-0.580
H	0.369	-2.077	-0.126	H	0.437	-2.072	-0.154
O	-1.270	-1.808	0.714	O	-1.293	-1.816	0.742
O	4.558	0.551	-0.113	O	3.964	-0.605	0.629
H	-2.306	1.661	-0.664	H	-2.317	1.683	-0.574
O	3.600	-1.405	-0.561	O	3.975	-0.187	-1.582
H	2.680	-1.733	-0.693	H	4.810	-0.674	-1.480
C	-3.873	-1.373	0.103	C	-3.842	-1.427	-0.083
H	-4.878	-1.063	-0.184	H	-4.830	-1.132	-0.437
H	-3.594	-2.248	-0.491	H	-3.492	-2.269	-0.688
H	-3.896	-1.708	1.144	H	-3.935	-1.806	0.938

Table S5 The atomic coordinates of stable conformations for (2*R*,3*R*,4*R*)-**11**.

Conformation I				Conformation II				Conformation III			
Atom	X	Y	Z	Atom	X	Y	Z	Atom	X	Y	Z
O	-3.719	-1.207	-0.362	C	-3.421	0.047	-0.429	O	-3.632	-1.468	-0.340
C	-3.521	0.118	-0.404	C	-2.182	0.687	0.183	C	-3.567	-0.131	-0.427
O	-4.340	0.860	-0.899	C	-1.007	-0.283	-0.048	O	-4.453	0.506	-0.950
C	-2.217	0.641	0.250	H	-2.351	0.783	1.259	C	-2.324	0.542	0.209
H	-2.399	0.603	1.334	C	0.365	0.238	0.455	H	-2.509	0.528	1.293
C	-1.019	-0.292	-0.032	H	-0.930	-0.438	-1.136	C	-1.038	-0.276	-0.034
H	-0.945	-0.430	-1.123	C	1.472	-0.733	0.024	H	-0.940	-0.445	-1.118
C	0.352	0.231	0.460	C	2.871	-0.275	-0.240	C	0.269	0.395	0.448
H	0.508	1.210	0.001	C	3.213	1.024	-0.127	H	0.349	1.369	-0.041
C	1.462	-0.718	-0.012	C	4.556	1.650	-0.341	C	1.480	-0.452	0.040
O	1.218	-1.921	-0.144	H	4.495	2.422	-1.119	O	1.364	-1.678	-0.043
C	2.850	-0.244	-0.288	H	4.886	2.162	0.571	C	2.798	0.217	-0.212
C	3.175	1.059	-0.165	H	5.330	0.937	-0.629	C	3.854	-0.603	-0.394
H	2.397	1.756	0.136	C	-1.982	2.073	-0.451	H	3.636	-1.668	-0.338
C	-1.976	2.094	-0.171	H	-1.147	2.608	0.010	C	-2.226	1.994	-0.269
H	-1.649	2.154	-1.214	H	-1.792	1.982	-1.525	H	-1.903	2.045	-1.314
H	-2.910	2.652	-0.094	H	-2.877	2.689	-0.320	H	-3.209	2.461	-0.213
H	-1.224	2.579	0.456	O	-1.372	-1.492	0.597	H	-1.526	2.575	0.338
O	-1.313	-1.553	0.587	H	-0.645	-2.108	0.396	O	-1.209	-1.538	0.628
H	-0.557	-2.127	0.348	O	1.224	-1.935	-0.084	H	-0.394	-2.039	0.423
C	0.417	0.374	1.996	O	-3.541	-0.235	-1.601	C	0.304	0.603	1.978
H	-0.303	1.118	2.346	H	2.439	1.733	0.157	H	-0.469	1.310	2.290
H	0.180	-0.578	2.473	O	-4.412	-0.138	0.471	H	0.127	-0.345	2.488
H	1.411	0.690	2.321	H	-5.145	-0.547	-0.018	H	1.269	0.997	2.309
H	-2.932	-1.636	0.046	C	3.817	-1.387	-0.621	H	-2.807	-1.803	0.085
C	4.506	1.705	-0.391	H	4.830	-1.028	-0.804	C	5.279	-0.248	-0.666
H	4.838	2.216	0.521	H	3.852	-2.145	0.166	H	5.601	-0.695	-1.615
H	5.287	1.006	-0.693	H	3.461	-1.900	-1.520	H	5.468	0.825	-0.716
H	4.423	2.481	-1.163	C	0.403	0.409	1.989	H	5.928	-0.676	0.106
C	3.804	-1.339	-0.697	H	-0.287	1.195	2.309	C	2.867	1.725	-0.257
H	3.858	-2.109	0.078	H	0.102	-0.523	2.471	H	2.267	2.131	-1.081
H	3.444	-1.842	-1.599	H	1.404	0.678	2.337	H	2.494	2.182	0.664
H	4.810	-0.965	-0.885	H	0.548	1.205	-0.019	H	3.890	2.076	-0.400

Fig. S1 ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$).

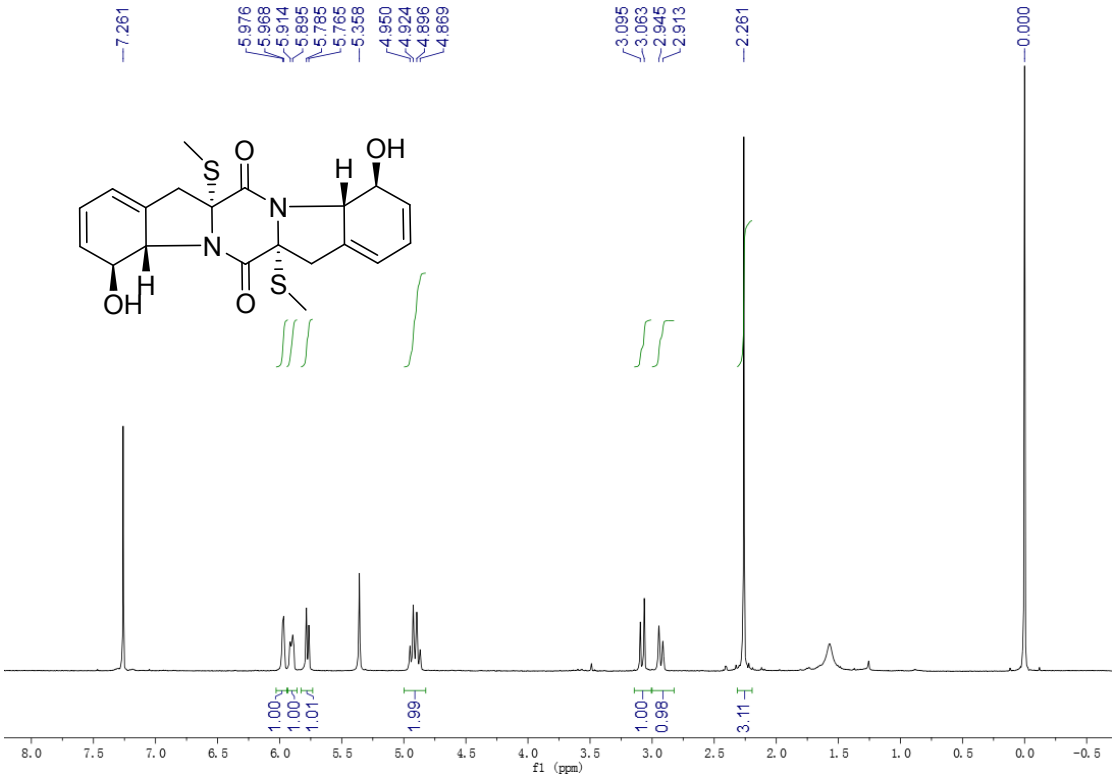


Fig. S2 ^{13}C NMR spectrum of **3** (125 MHz, $CDCl_3$).

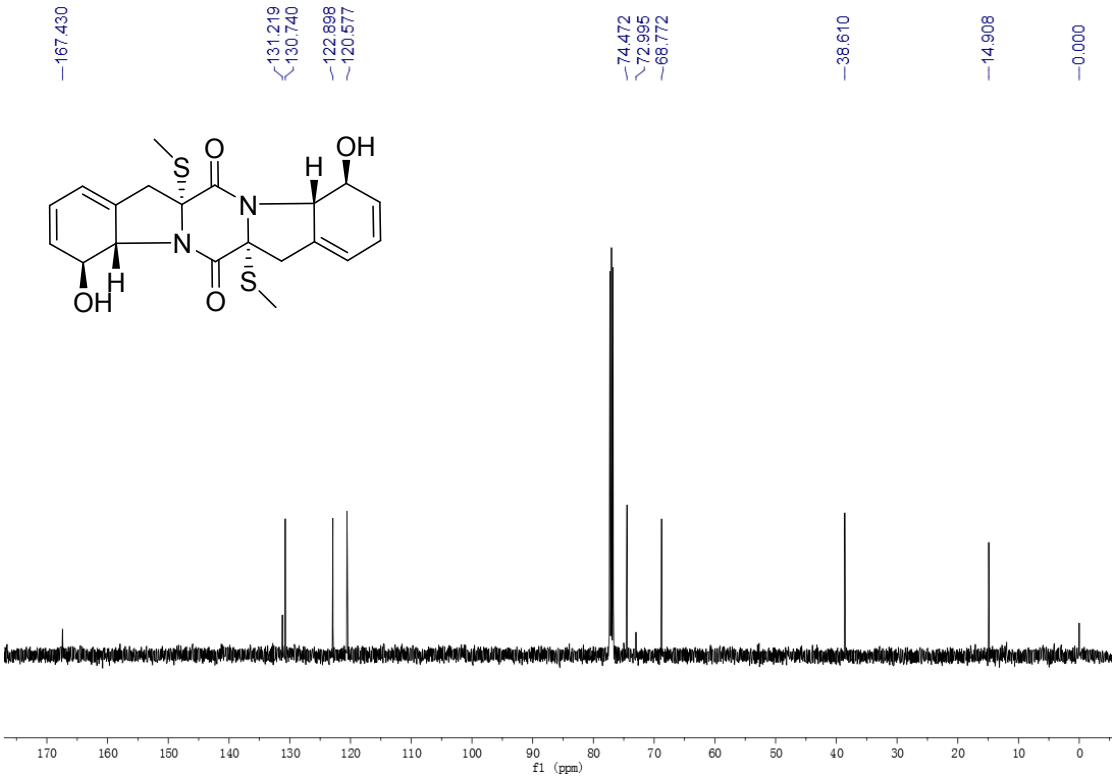


Fig. S3 HSQC spectrum of **3**.

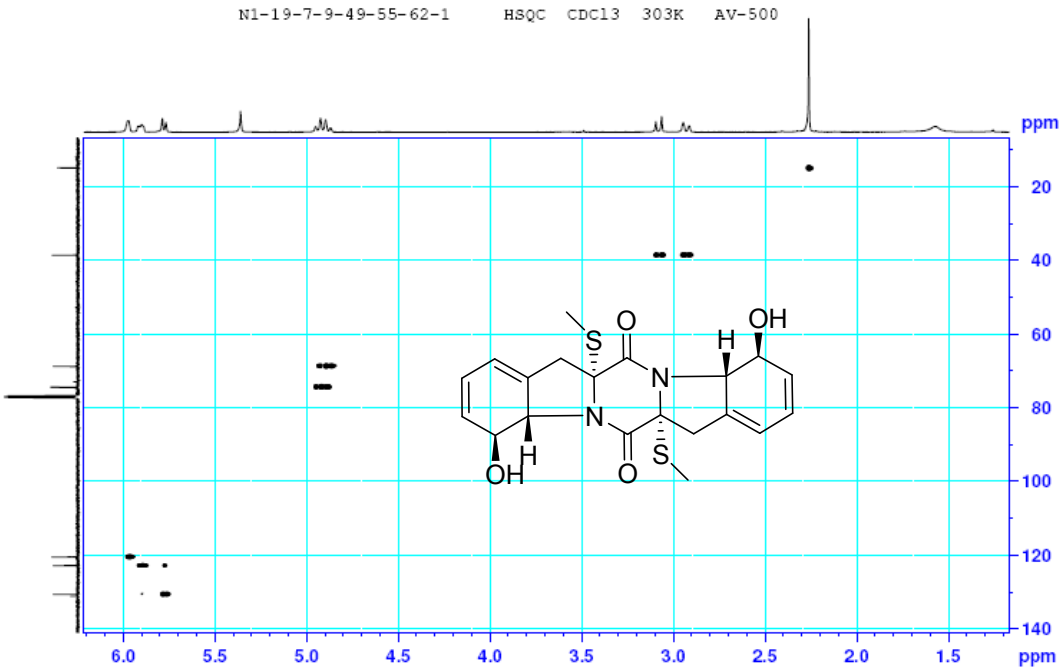


Fig. S4 HMBC spectrum of **3**.

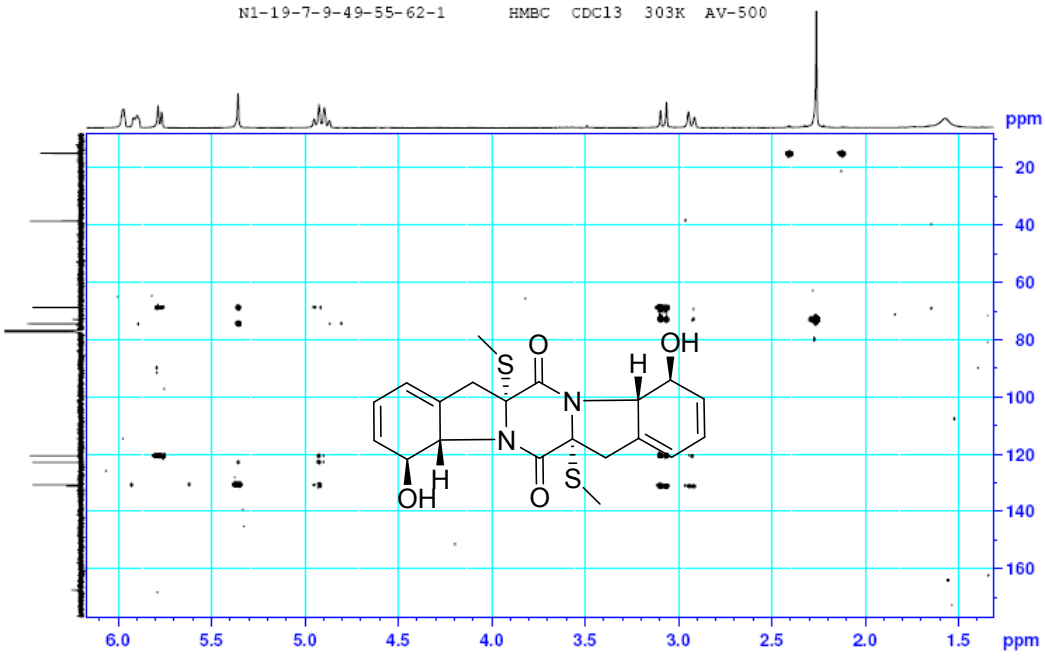


Fig. S5 ^{1}H-^{1}H COSY spectrum of **3**.

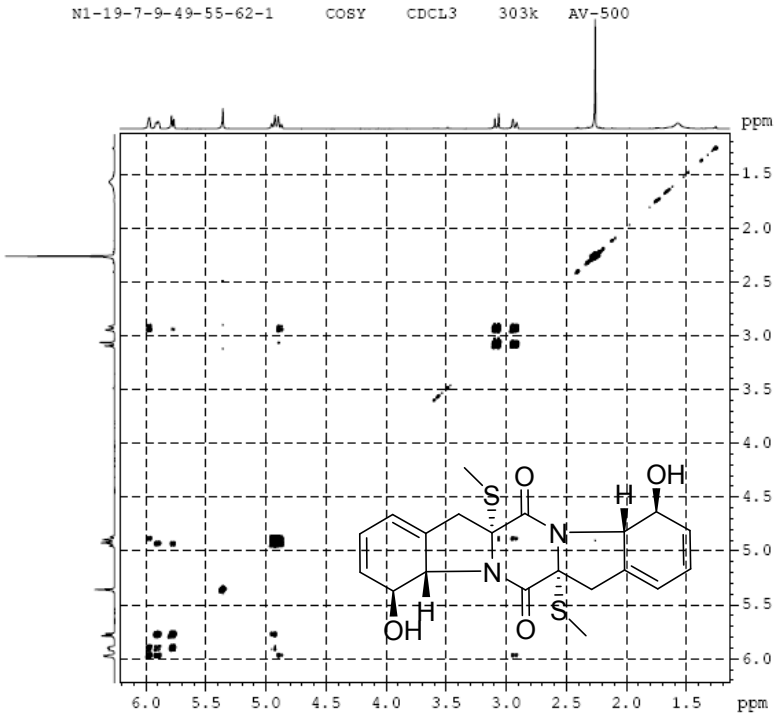


Fig. S6 ROESY spectrum of **3**.

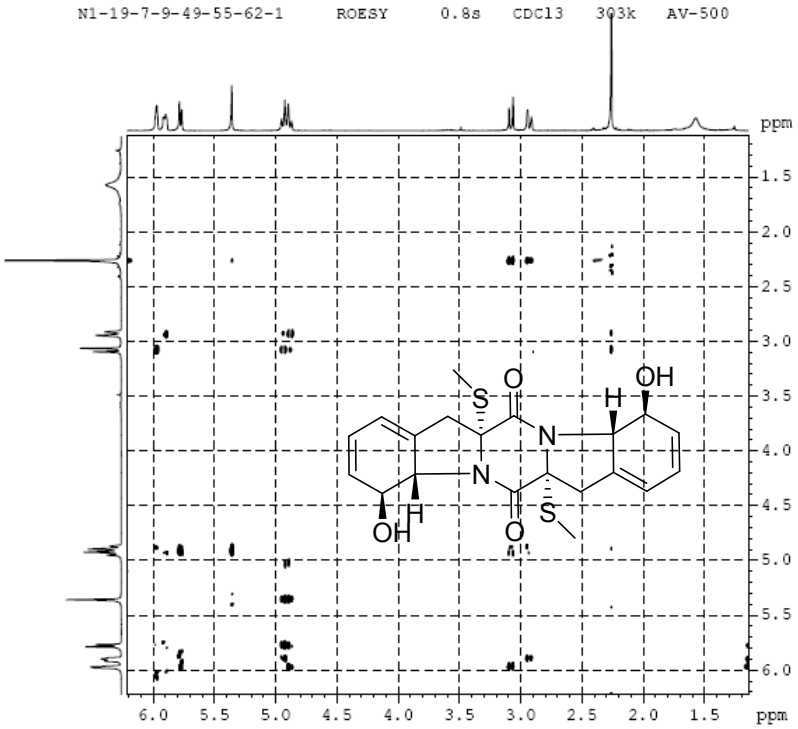


Fig. S7 Key HMBC, COSY and ROESY correlations of **3**.

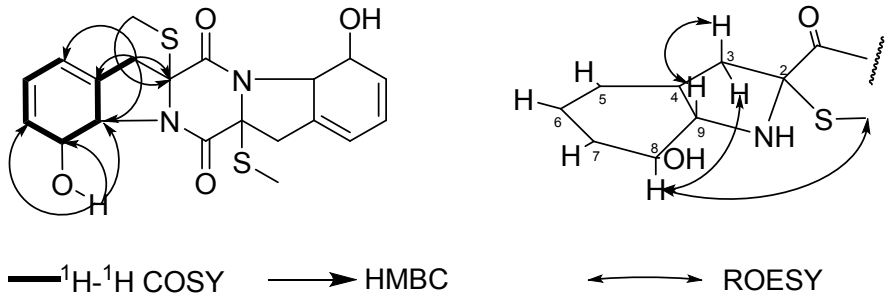


Fig. S8 Assignment of absolute configurations of **3** by comparing between its experimental and calculated CD spectra.

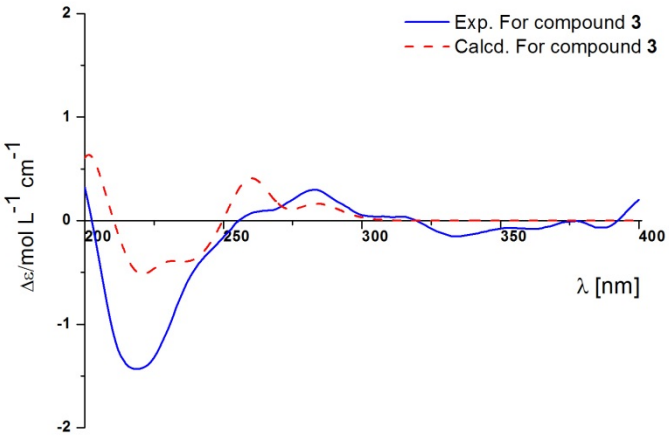
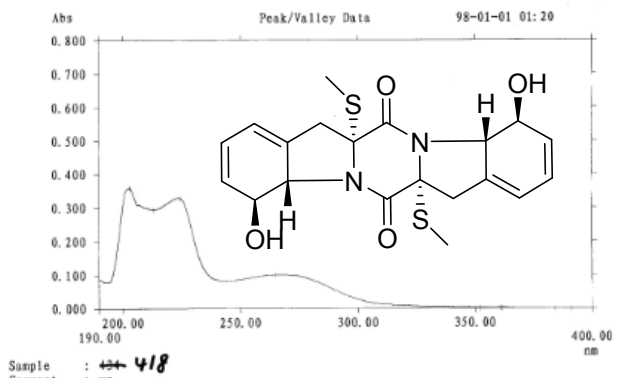


Fig. S9 Ultra-violet spectrum of **3**.



Sample : ~~434~~ 418
Comment : wq
Scan Speed : 600 nm/min Slit : 2.0 nm PMT Voltage : Auto Gain
Baseline : User 1 Sampling Interval: Auto

No.	WL (nm)	Peak (Abs)	No.	WL (nm)	Valley (Abs)
1	391.00	0.000	1	384.00	-0.001
2	361.00	0.002	2	352.00	0.001
3	265.00	0.101	3	244.00	0.083
4	224.00	0.329	4	213.00	0.295
5	203.00	0.360			

Fig. S10 Infrared spectrum of **3**.

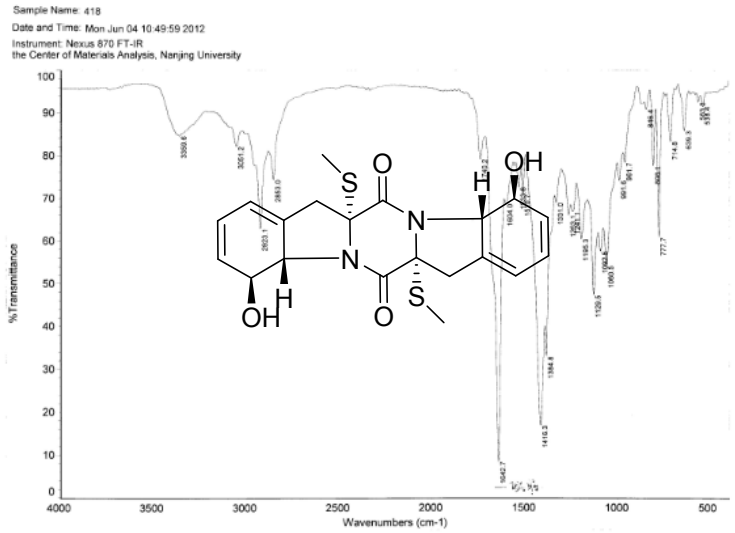


Fig. S11 HR-ESI-MS spectrum of **3** (positive mode).

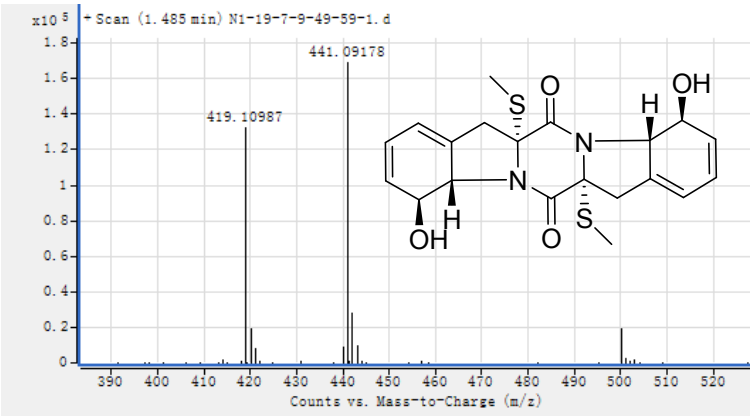


Fig. S12 ^{1}H NMR spectrum of **4** (500 MHz, acetone-d$_6$).

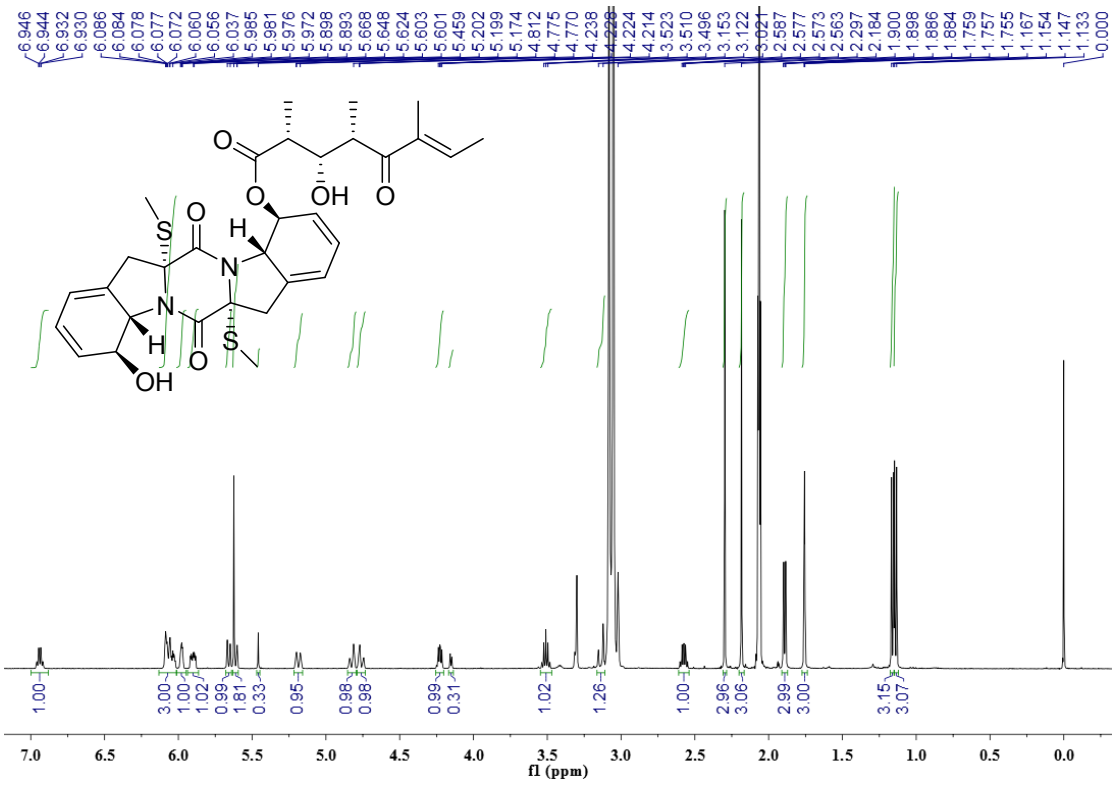


Fig. S13 ^{13}C NMR spectrum of **4** (125 MHz, acetone-d$_6$).

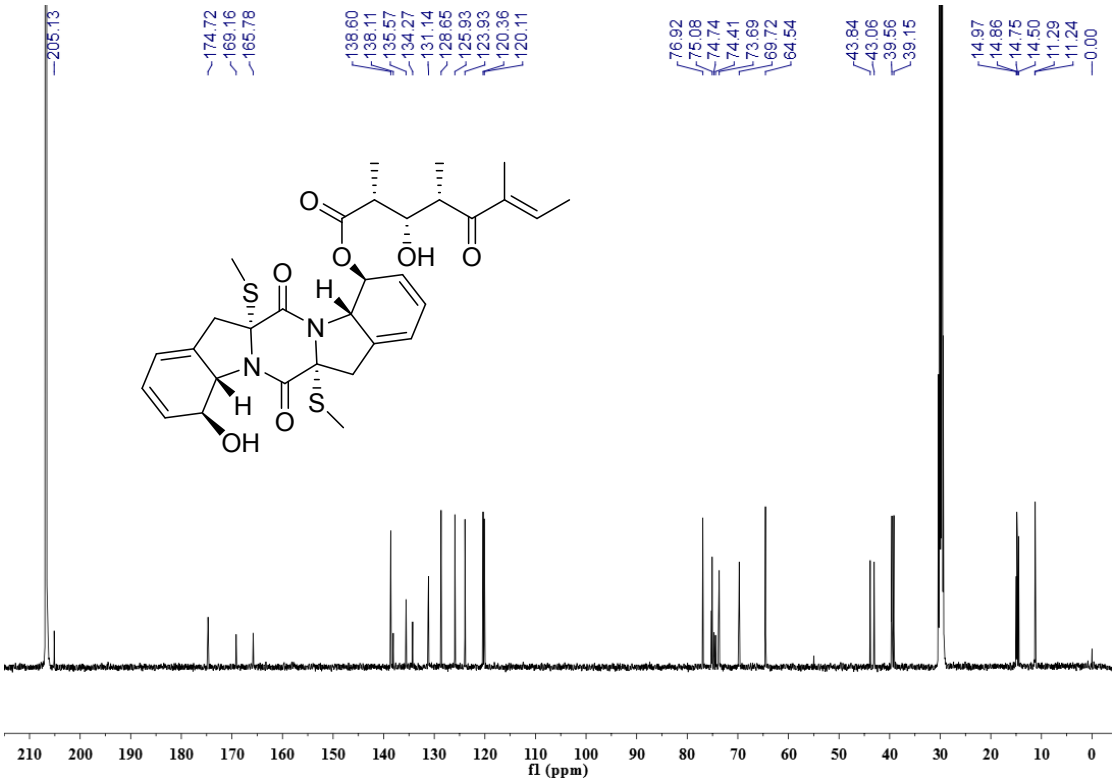


Fig. S14 HSQC spectrum of **4**.

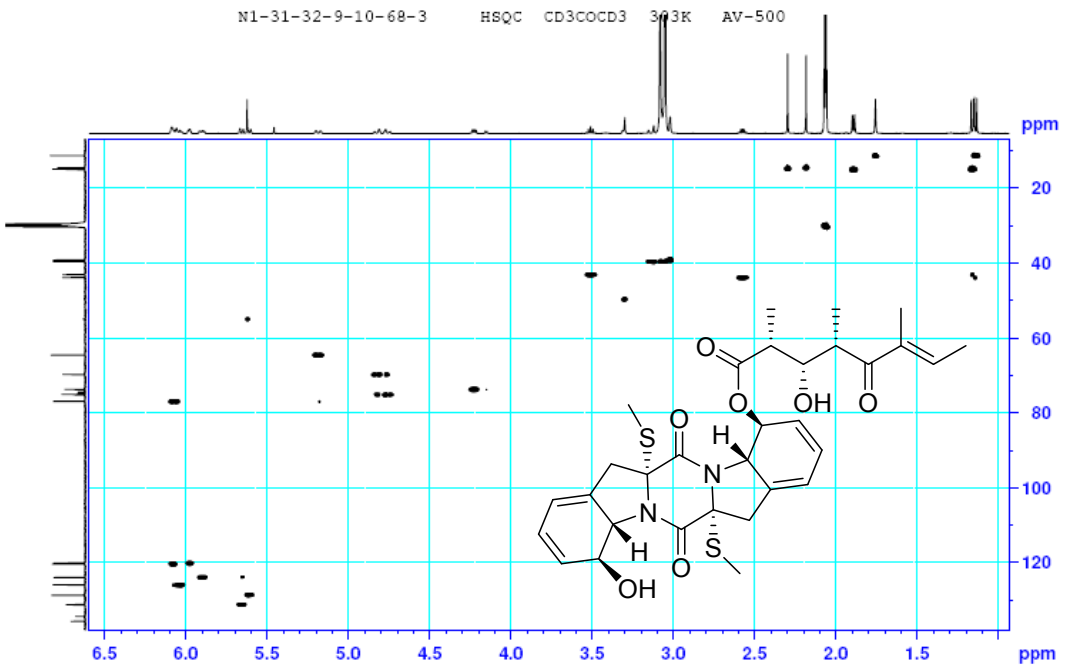


Fig. S15 HMBC spectrum of **4**.

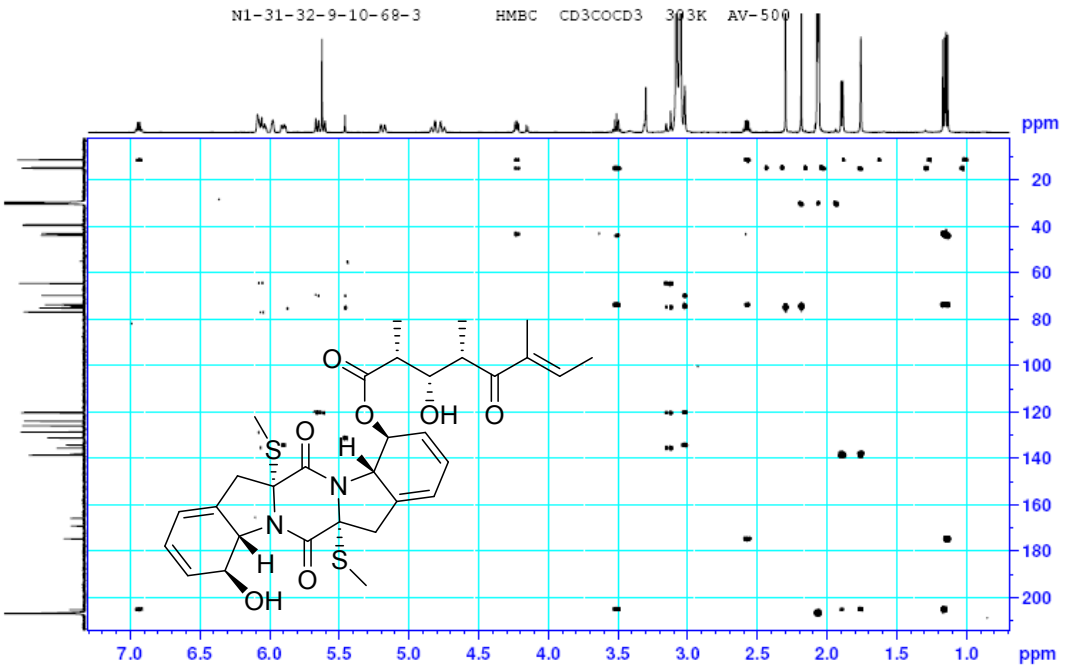


Fig. S16 ^{1}H-^{1}H COSY spectrum of **4**.

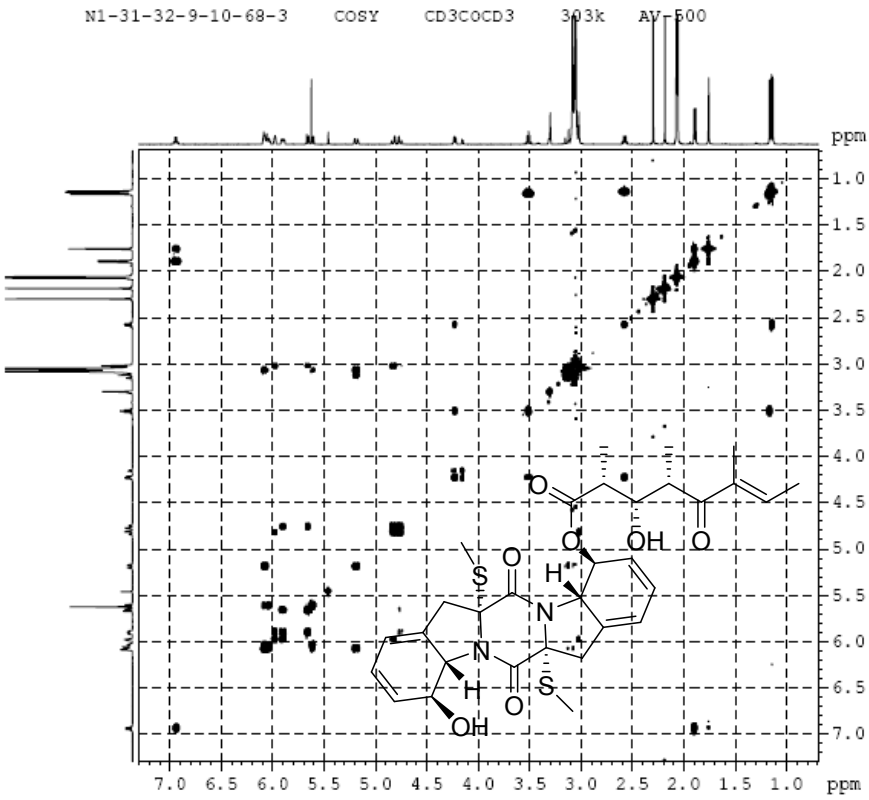


Fig. S17 ROESY spectrum of **4**.

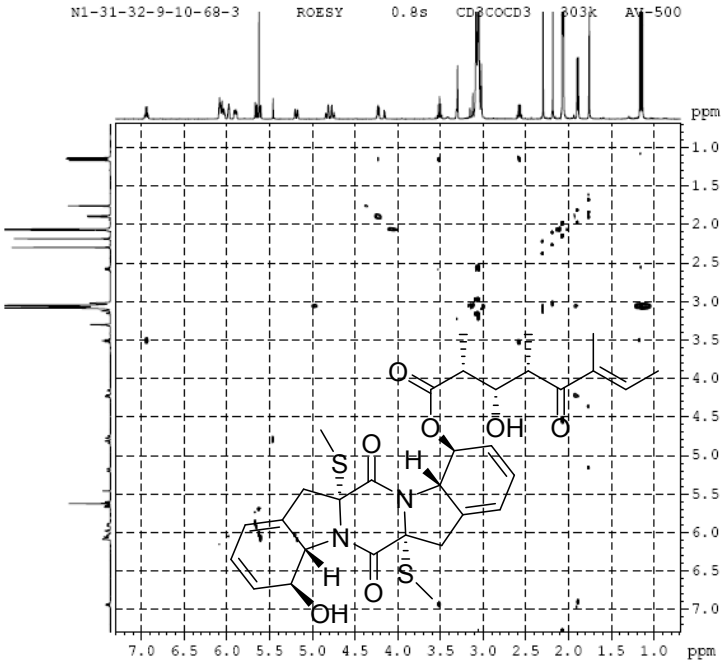
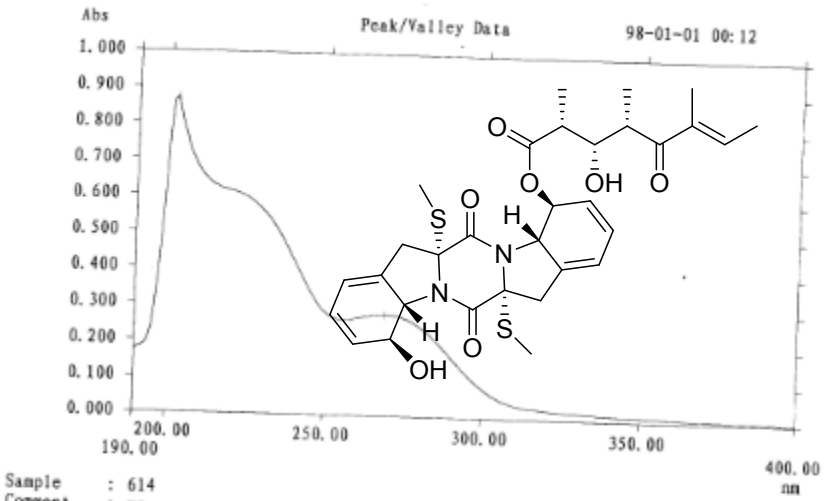


Fig. S18 Ultra-violet spectrum of **4**.



Sample : 614
Comment : wq
Scan Speed : 600 nm/min Slit : 2.0 nm PMT Voltage : Auto Gain
Baseline : User 1 Sampling Interval: Auto

No.	WL (nm)	Peak (Abs)	No.	WL (nm)	Valley (Abs)
1	269.00	0.281	1	256.00	0.264
2	202.00	0.875			

Fig. S19 Infrared spectrum of **4**.

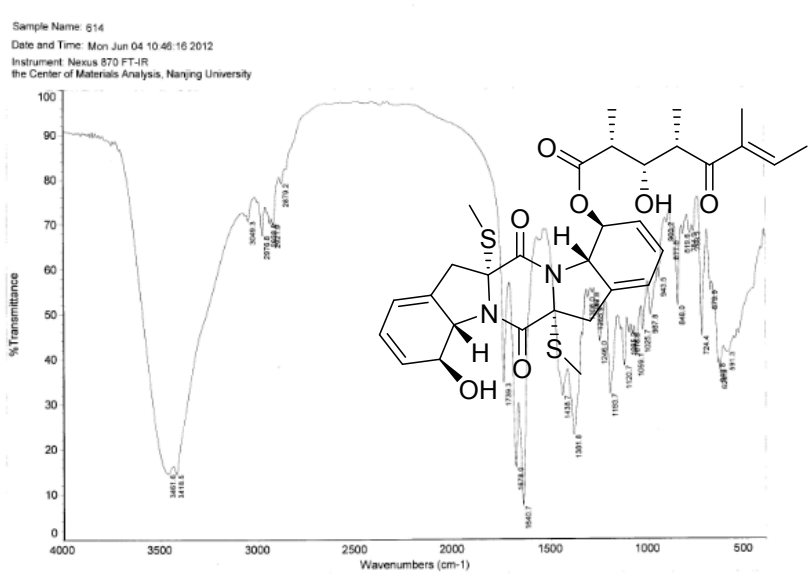


Fig. S20 HR-ESI-MS spectrum of **4** (positive mode).

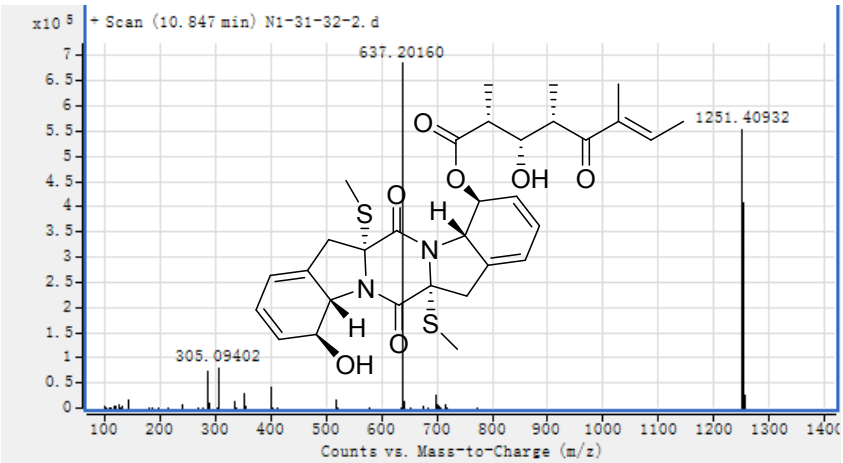


Fig. S21 ^{1}H NMR spectrum of 3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**) (500 MHz, CD_3OD).

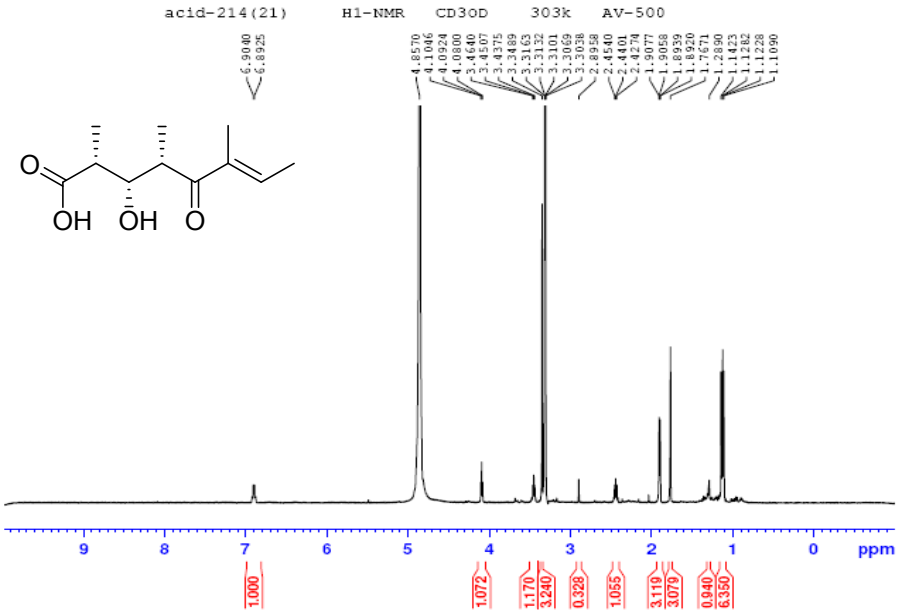


Fig. S22 ^{13}C NMR spectrum of 3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**) (125 MHz, CD_3OD).

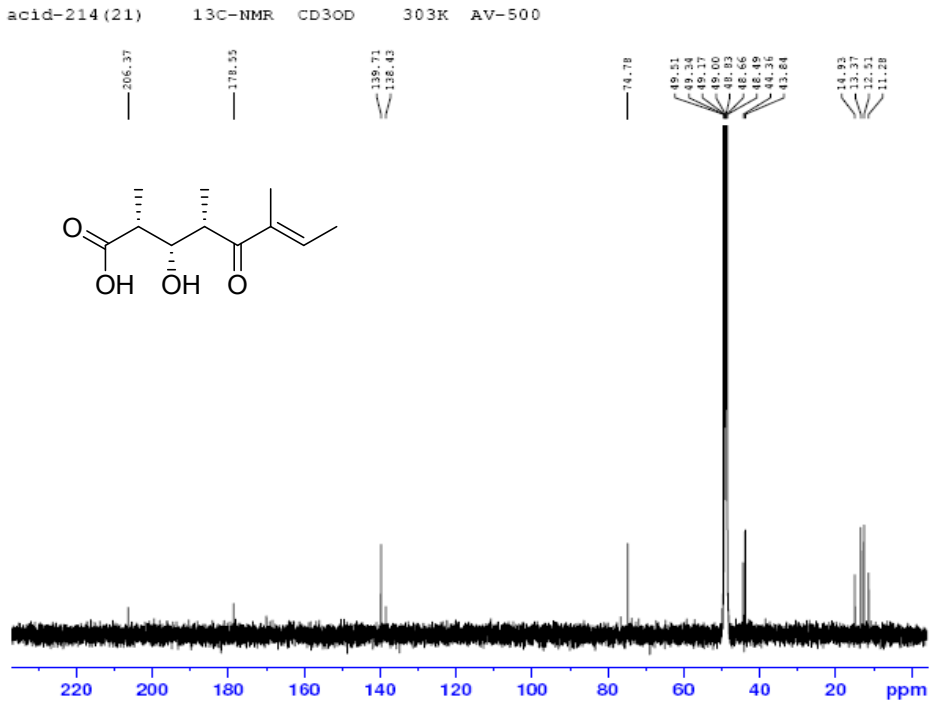


Fig. S23 HSQC spectrum of 3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**).

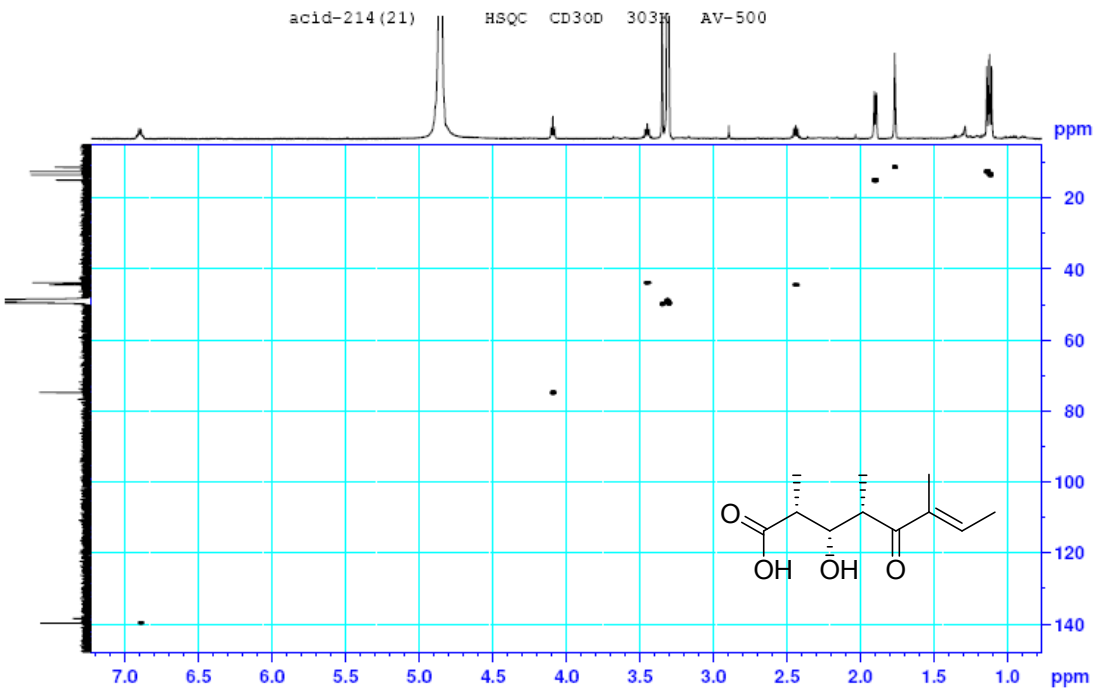


Fig. S24 HMBC spectrum of 3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**).

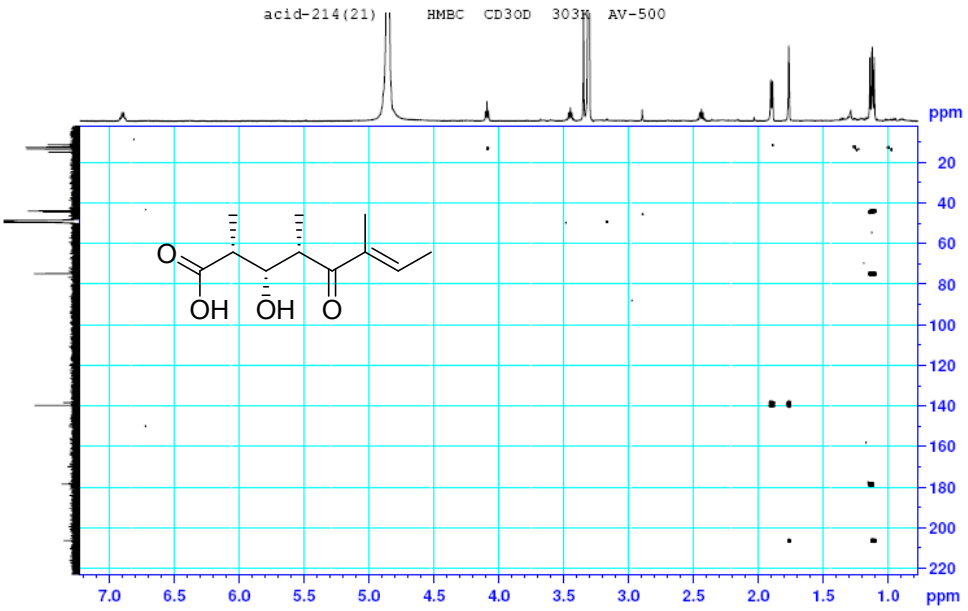


Fig. S25 ^{1}H-^{1}H COSY spectrum of 3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**).

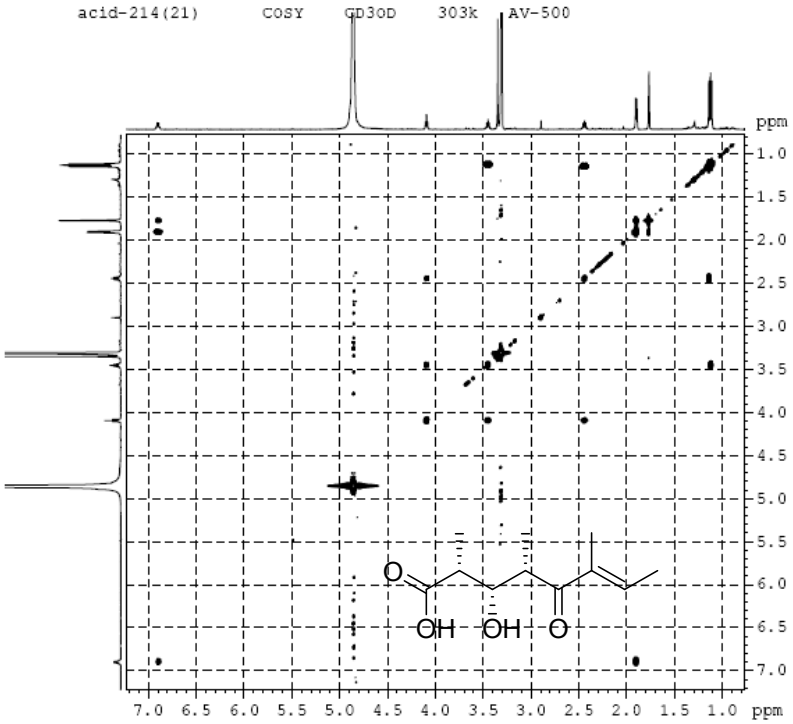


Fig. S26 ROESY spectrum of 3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**).

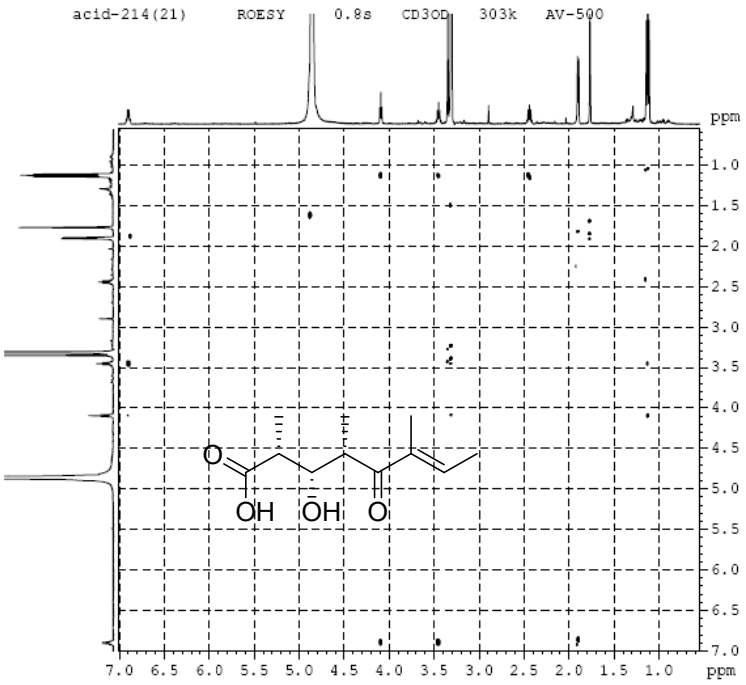


Fig. S27 HR-ESI-MS spectrum of 3-hydroxy-2,4,6-trimethyl-5-oxooct-6-enoic acid (**11**) (positive mode).

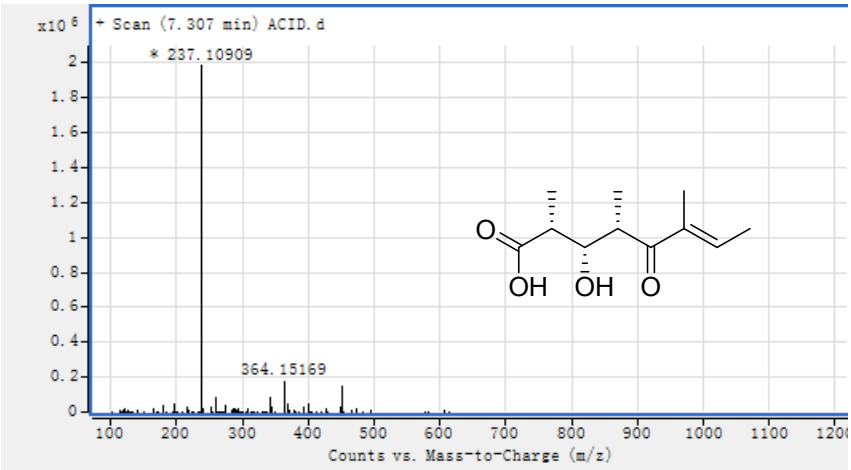
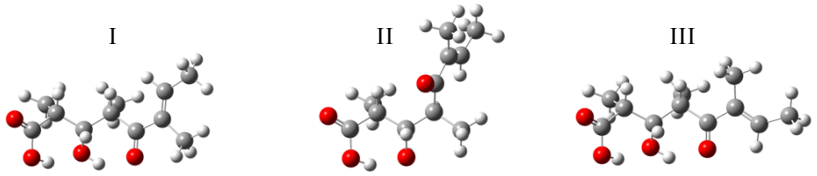


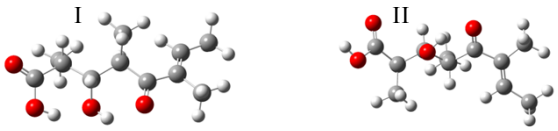
Fig. S28 The stable conformations with their relative energies (kcal/mol), Boltzmann populations (%) and optical rotations $[\alpha]_D$ (deg).

(2*R*,3*S*,4*S*)-11



	I	II	III
Relative energy (kcal/mol)	0.00	1.13	1.36
Boltzmann population (%)	80.58	11.57	7.85
$[\alpha]_D$ (deg)	6.1	53.5	64.8

(2*R*,3*S*,4*R*)-11

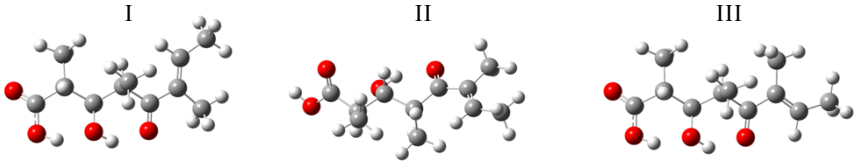


	I	II
Relative energy (kcal/mol)	0.00	1.12
Boltzmann population (%)	87.00	13.00
$[\alpha]_D$ (deg)	−73.3	−19.7

(2*R*,3*R*,4*S*)-11

	I	II
Relative energy (kcal/mol)	0.00	0.90
Boltzmann population (%)	82.04	17.96
$[\alpha]_D$ (deg)	170.9	102.6

(2*R*,3*R*,4*R*)-11



	I	II	III
Relative energy (kcal/mol)	0.00	1.19	1.28
Boltzmann population (%)	79.82	10.74	9.43
$[\alpha]_D$ (deg)	89.1	52.8	10.5

Fig. S29 ^{1}H NMR spectrum of **5** (500 MHz, acetone-d$_6$).

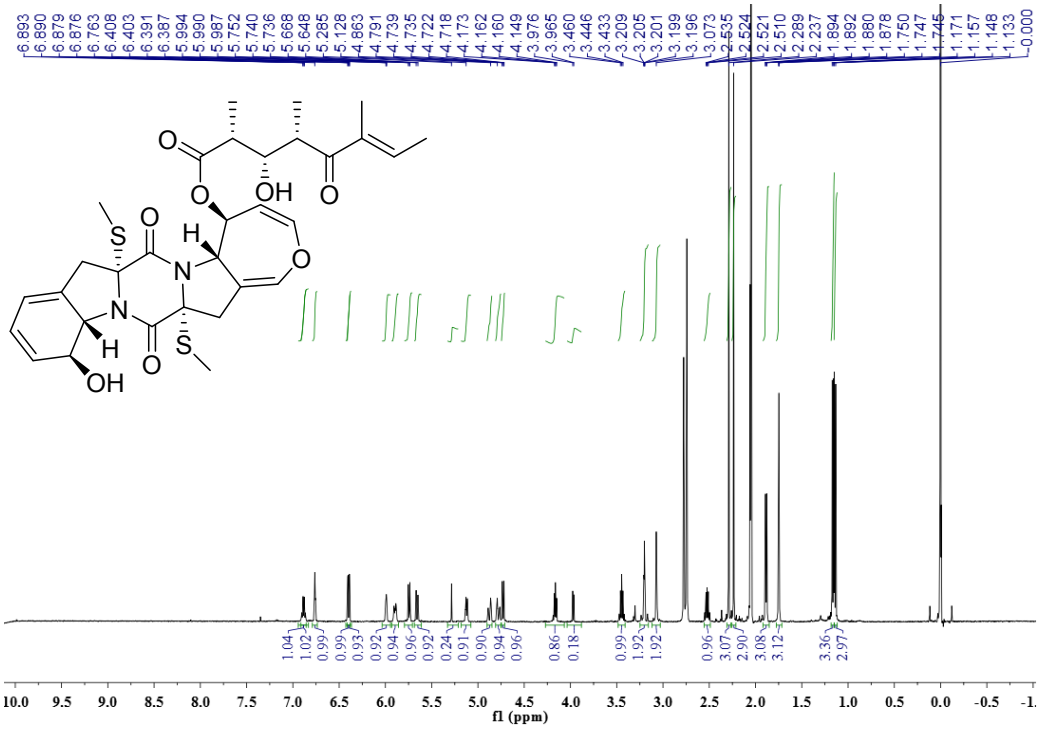


Fig. S30 ^{13}C NMR spectrum of **5** (125 MHz, acetone-d$_6$).

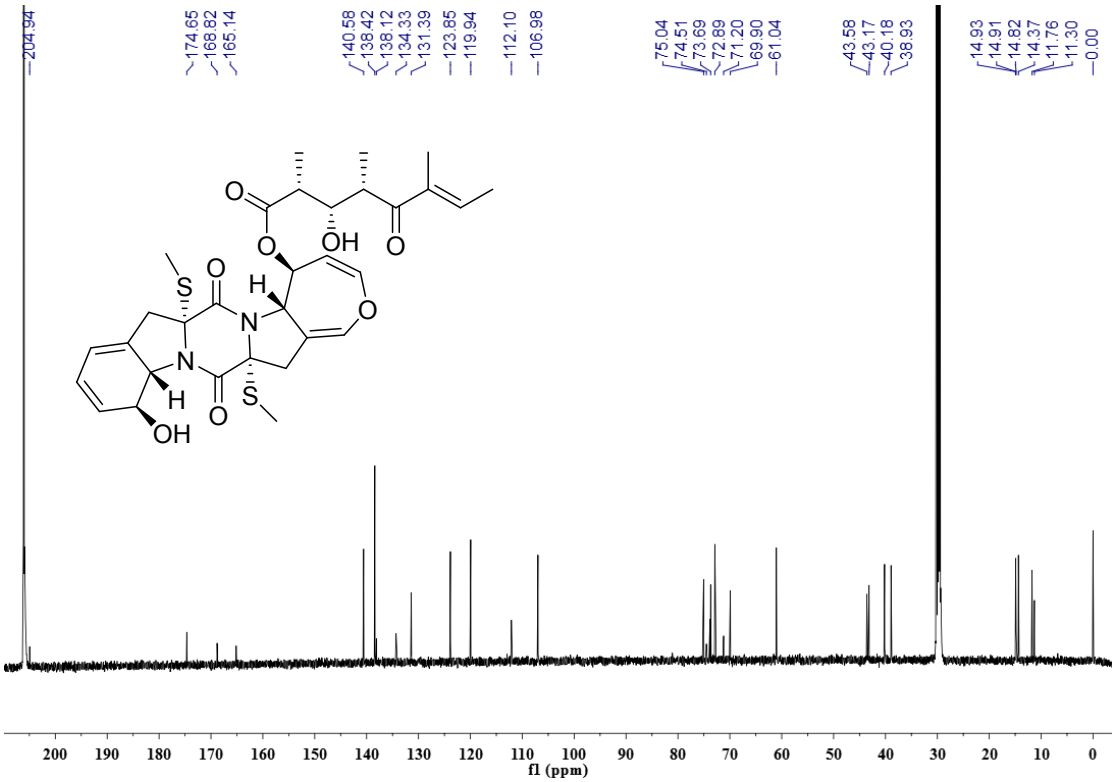


Fig. S31 HSQC spectrum of **5**.

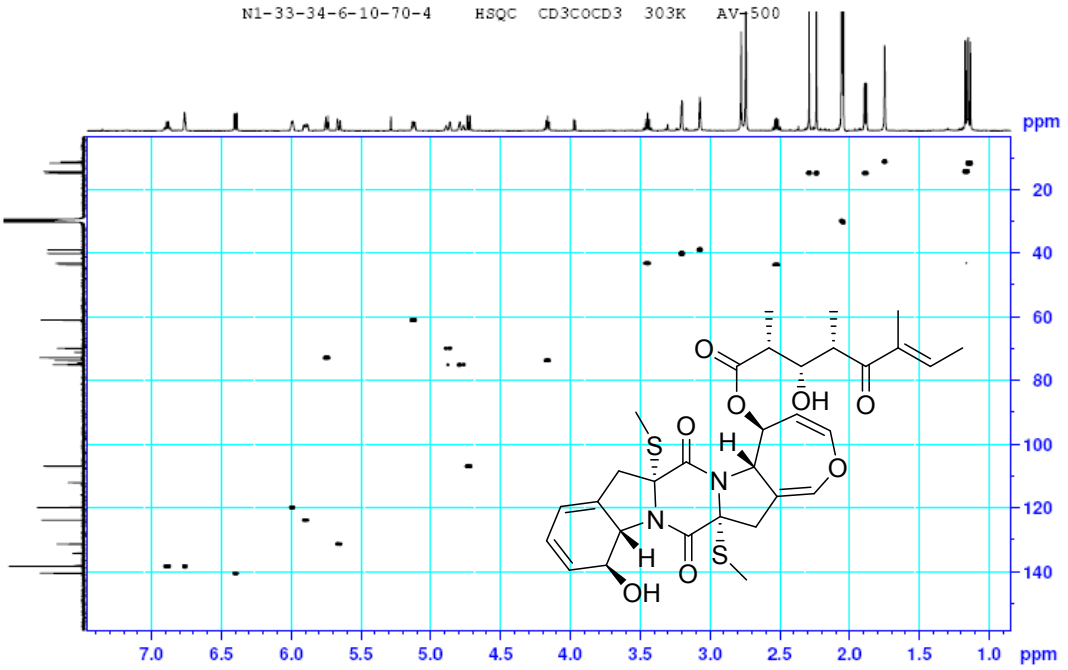


Fig. S32 HMBC spectrum of **5**.

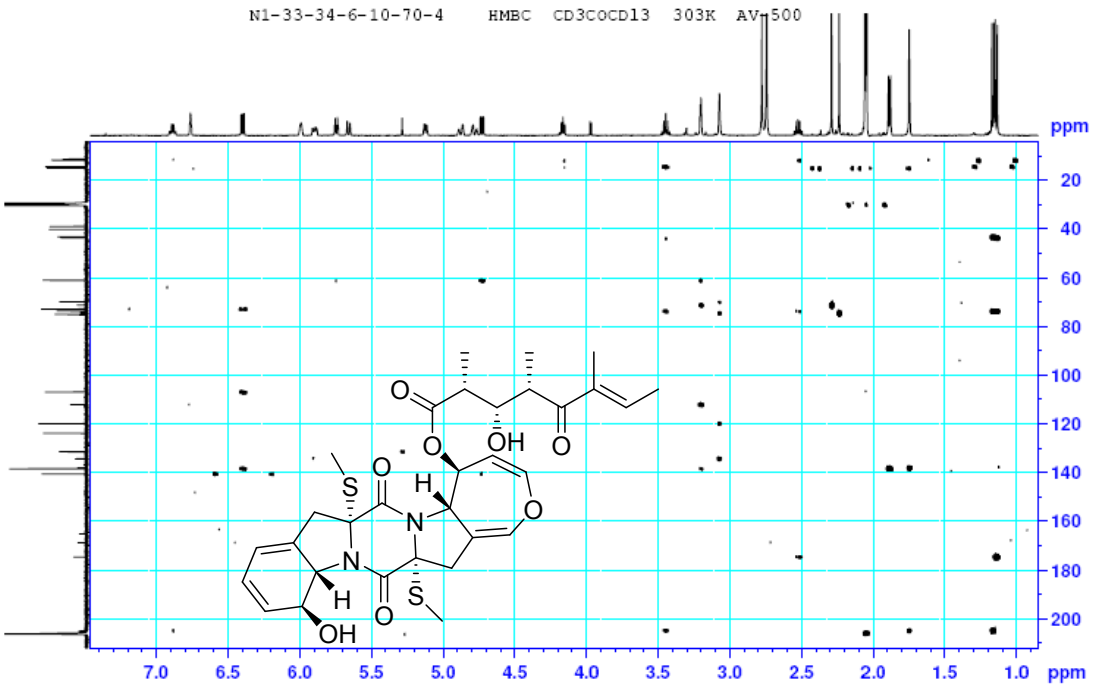


Fig. S33 ^{1}H-^{1}H COSY spectrum of **5**.

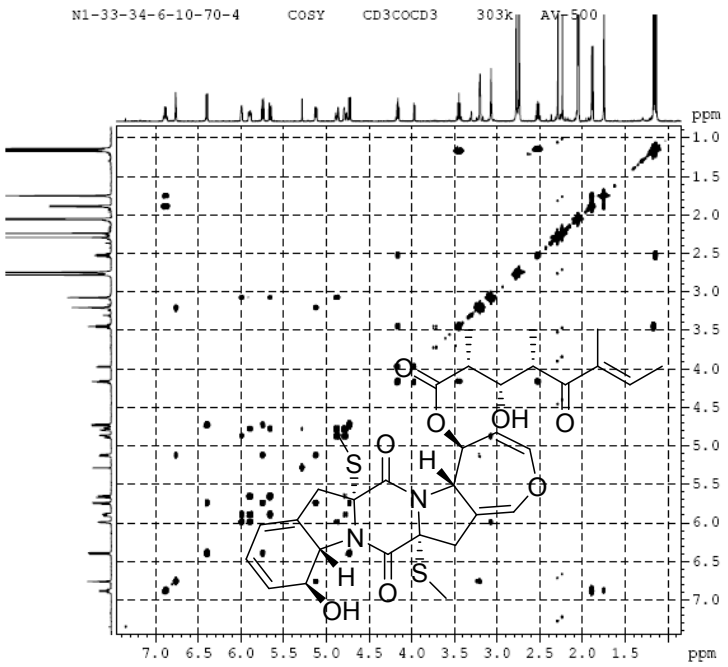


Fig. S34 ROESY spectrum of **5**.

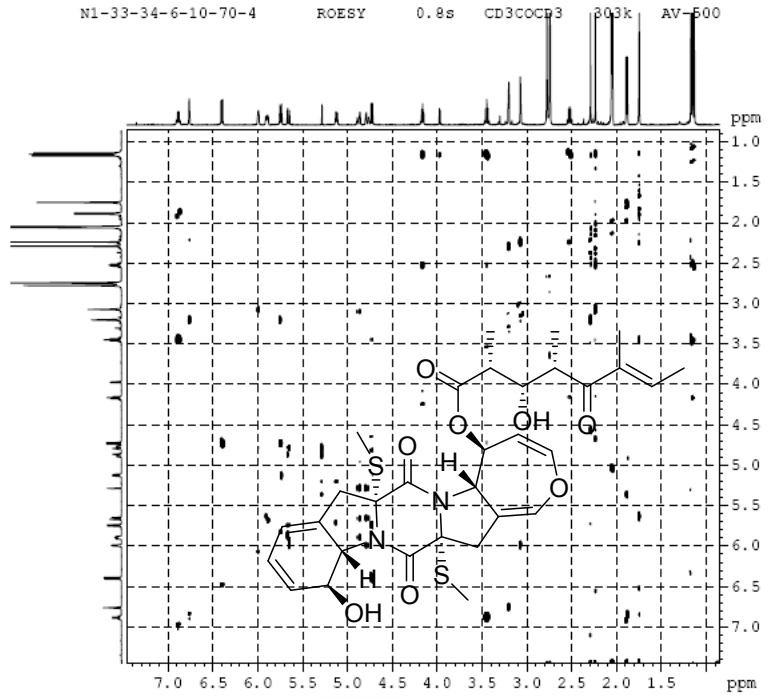
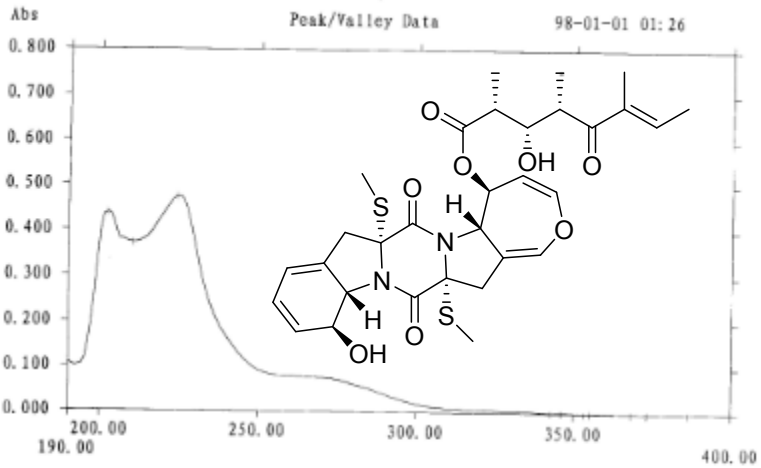


Fig. S35 Ultra-violet spectrum of **5**.



Sample : 630
Comment : wq
Scan Speed : 600 nm/min Slit : 2.0 nm PMT Voltage : Auto Gain
Baseline : User 1 Sampling Interval: Auto

No.	WL (nm)	Peak (Abs)	No.	WL (nm)	Valley (Abs)
1	373.00	0.000	1	386.00	-0.002
2	355.00	0.001	2	368.00	-0.001
3	346.00	0.002	3	353.00	0.001
4	224.00	0.475	4	343.00	0.001
5	202.00	0.438	5	210.00	0.372

Fig. S36 Infrared spectrum of **5**.

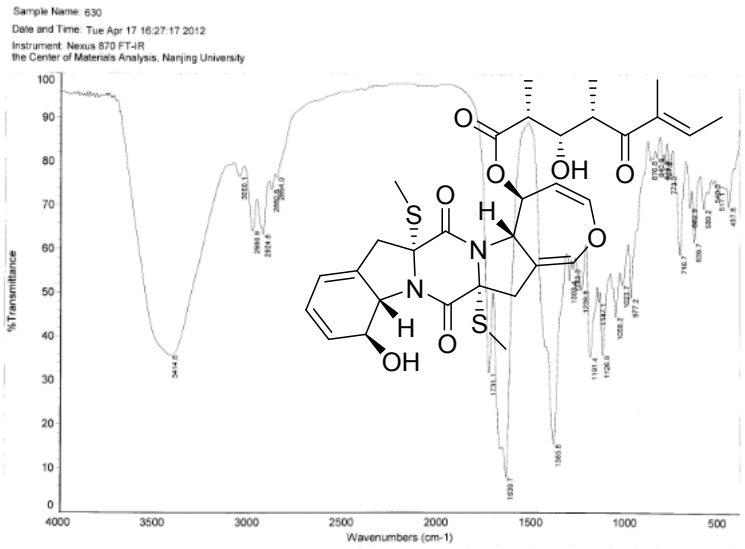


Fig. S37 HR-ESI-MS spectrum of **5** (positive mode).

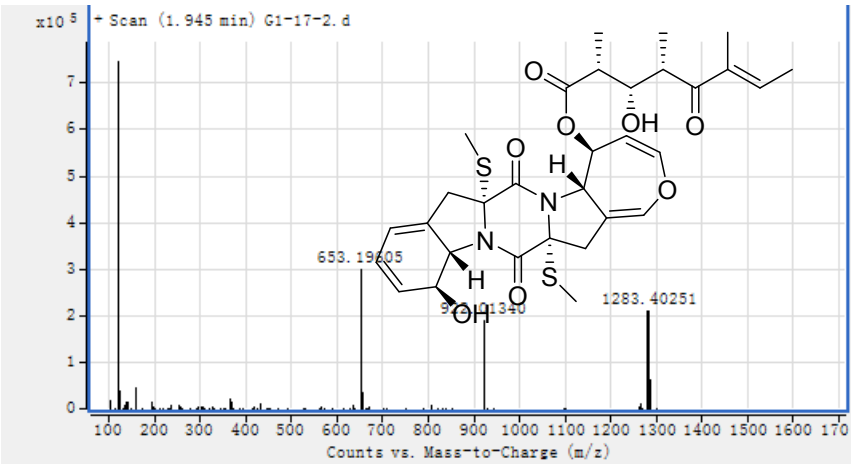


Fig. S38 Comparison between the CD spectra of boydines B (**4**), C (**5**) and D (**6**).

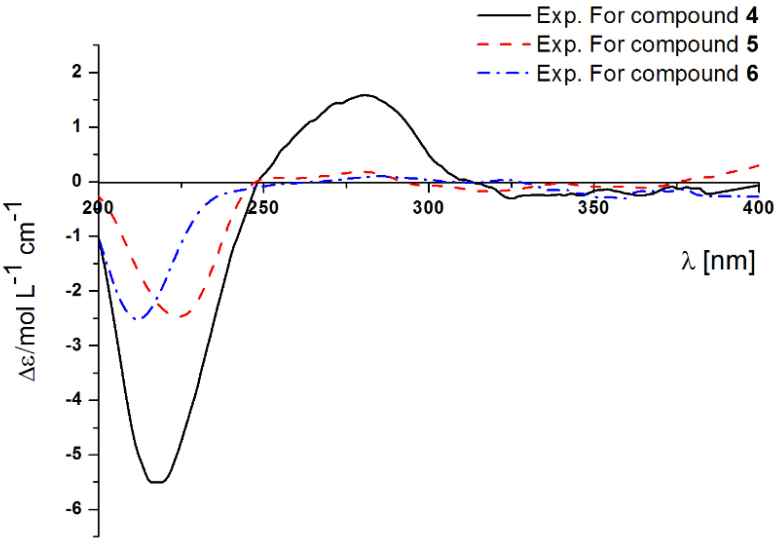


Fig. S39 ^{1}H NMR spectrum of **6** (600 MHz, acetone-d$_6$).

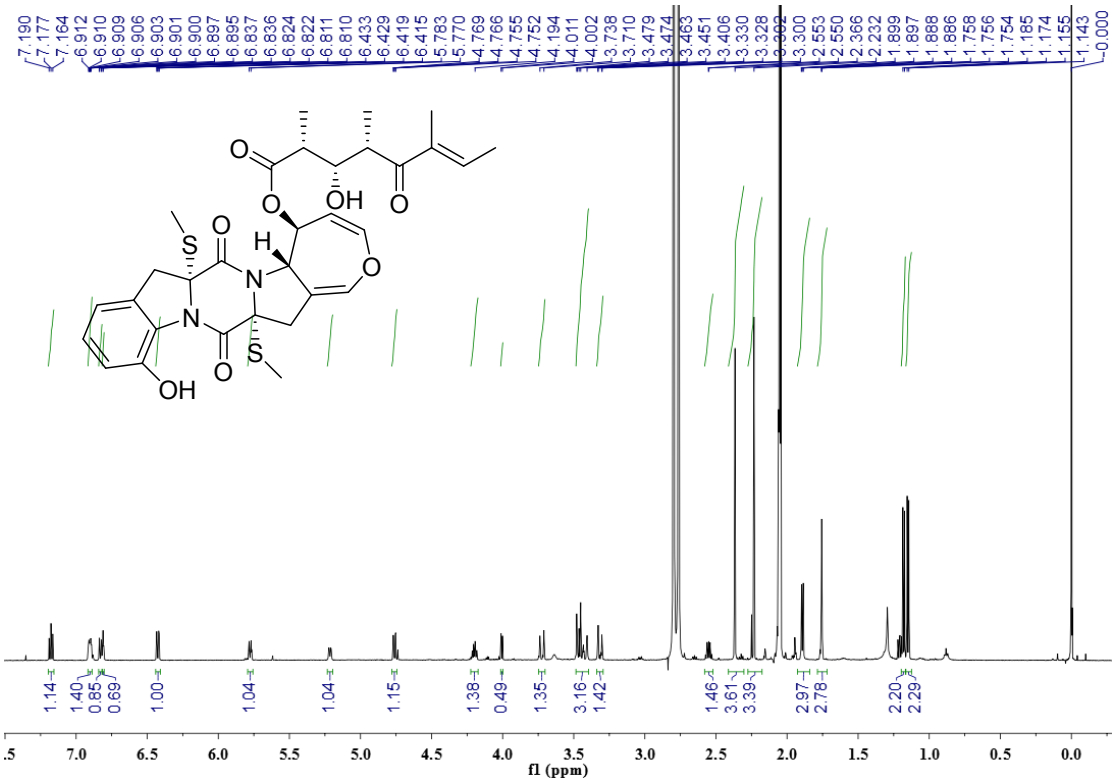


Fig. S40 ^{13}C NMR spectrum of **6** (150 MHz, acetone-d$_6$).

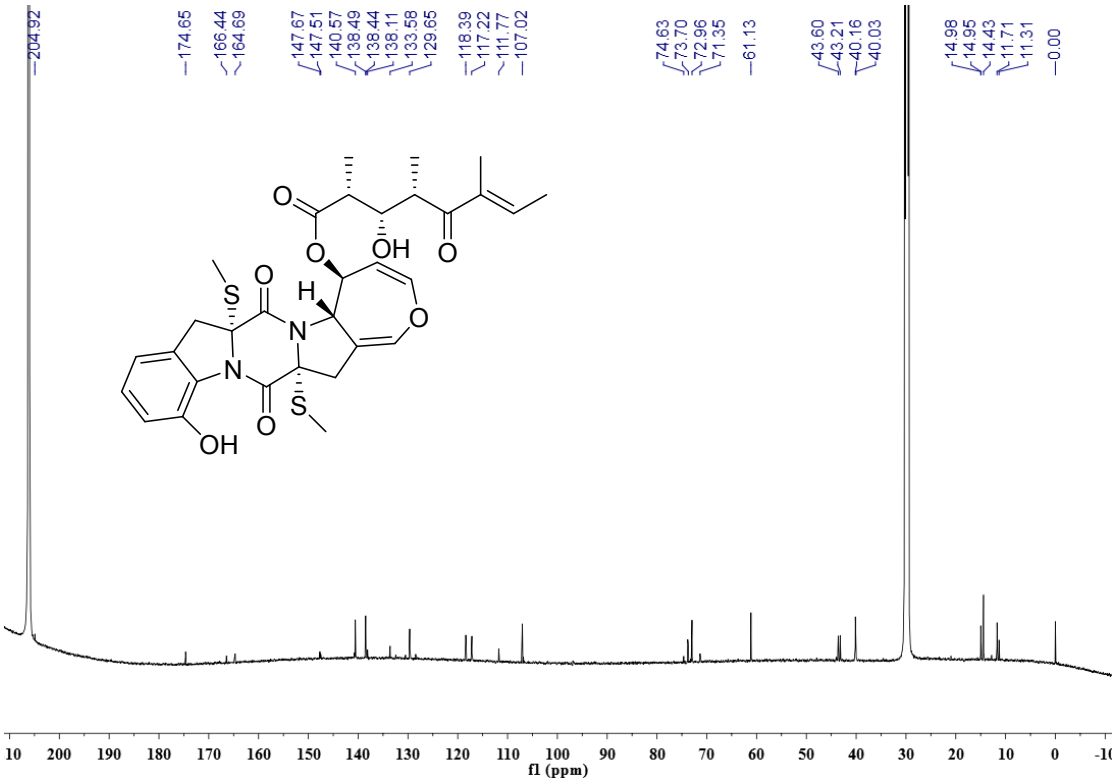


Fig. S41 HSQC spectrum of **6**.

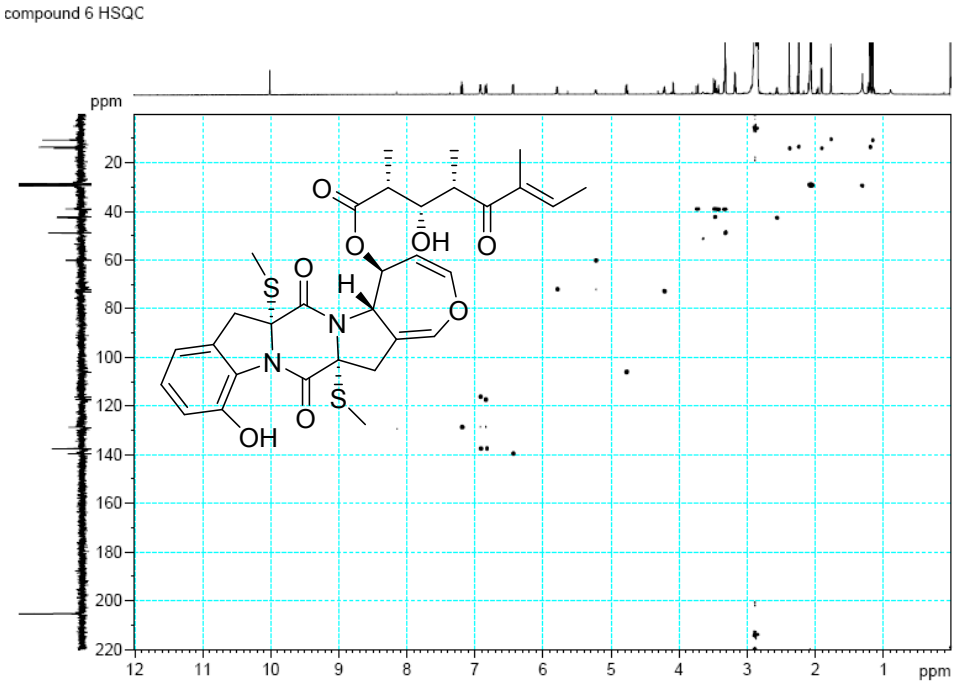


Fig. S42 HMBC spectrum of **6**.

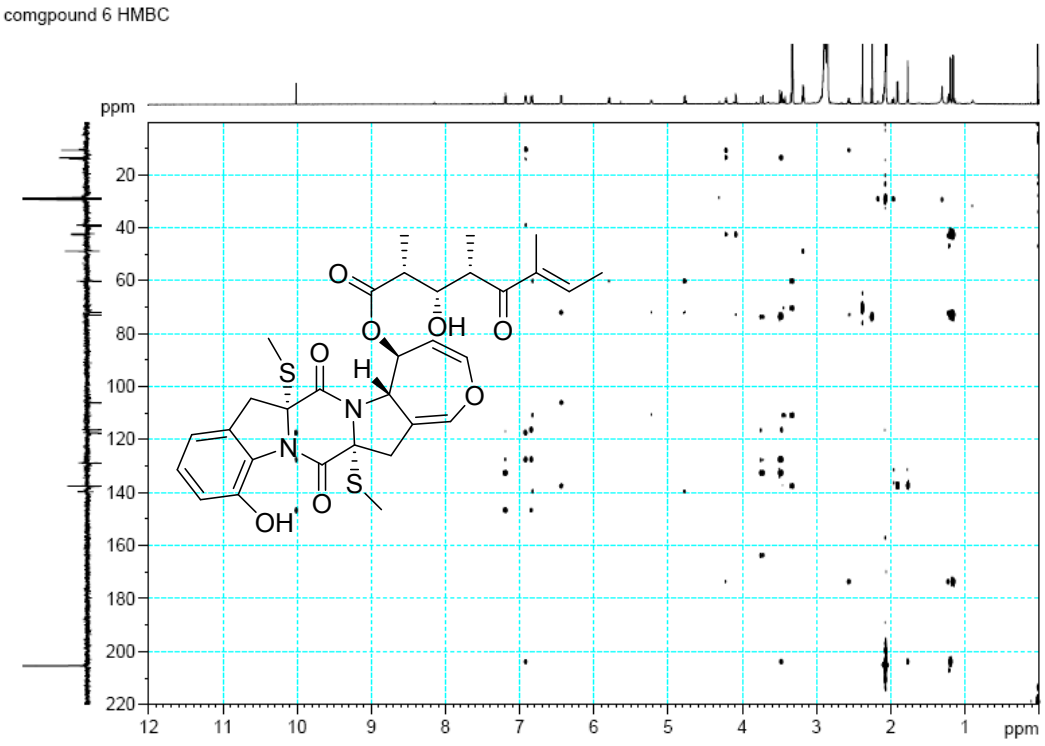


Fig. S43 ^{1}H-^{1}H COSY spectrum of **6**.

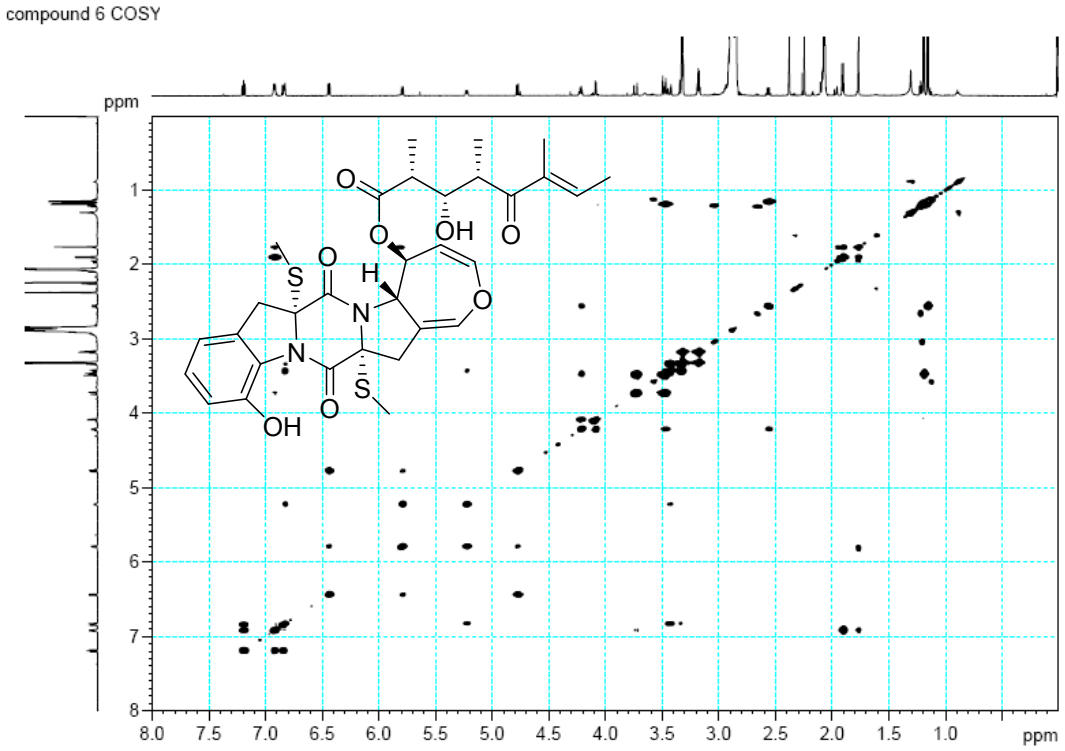


Fig. S44 ROESY spectrum of **6**.

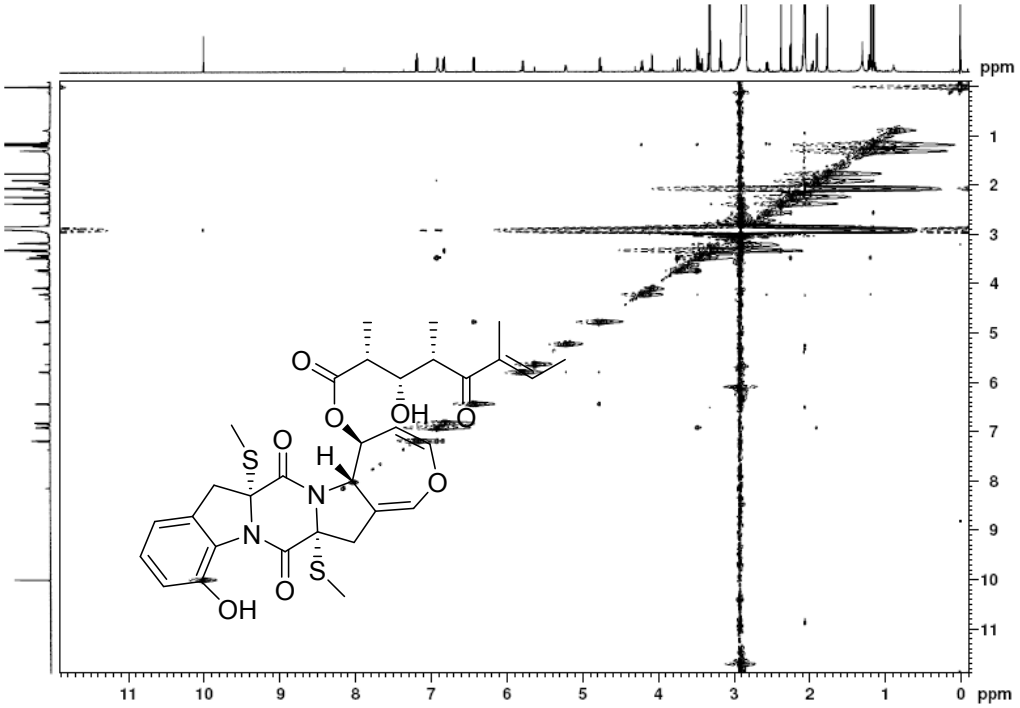


Fig. S45 Ultra-violet spectrum of **6**.

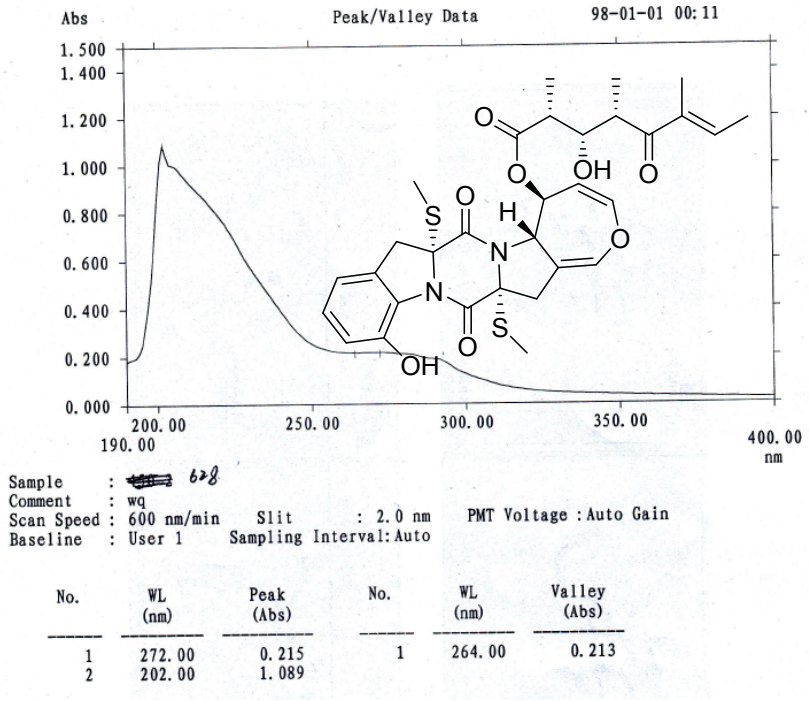


Fig. S46 Infrared spectrum of **6**.

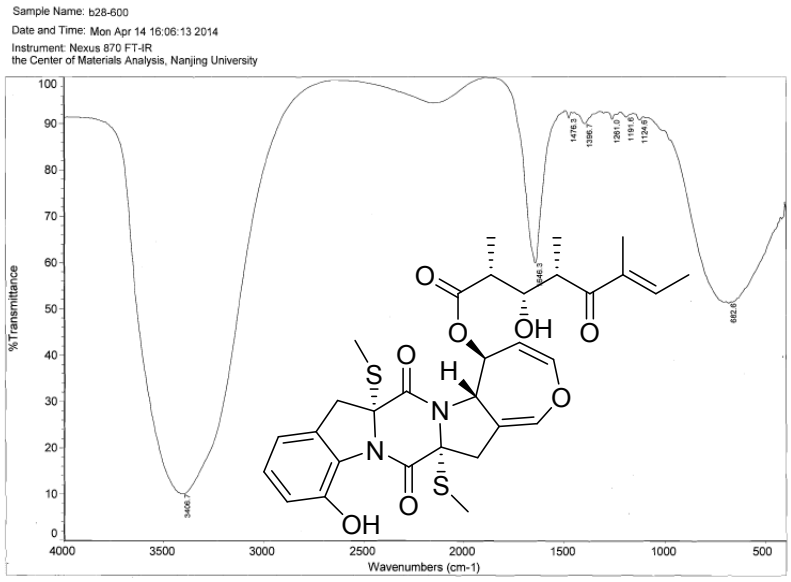


Fig. S47 HR-ESI-MS spectrum of **6** (positive mode).

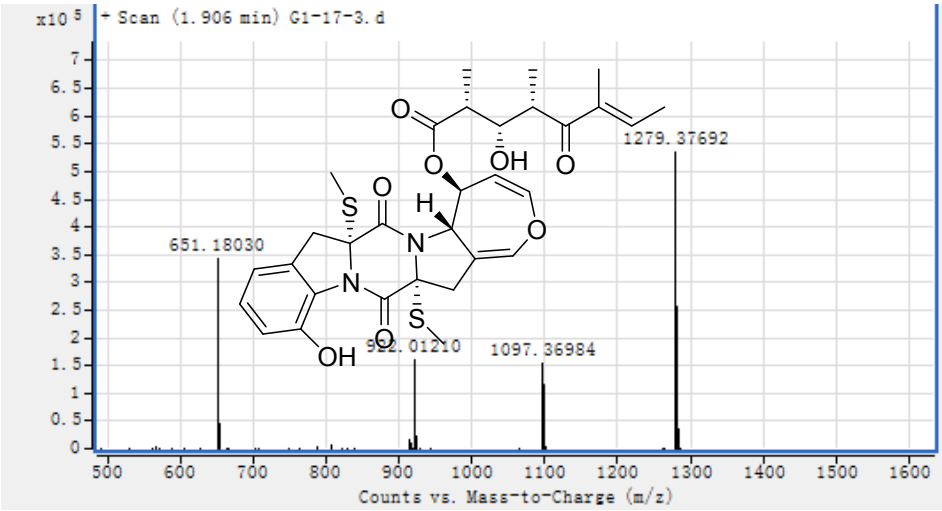


Fig. S48 ^{1}H NMR spectrum of **7** (500 MHz,$CDCl_3$).

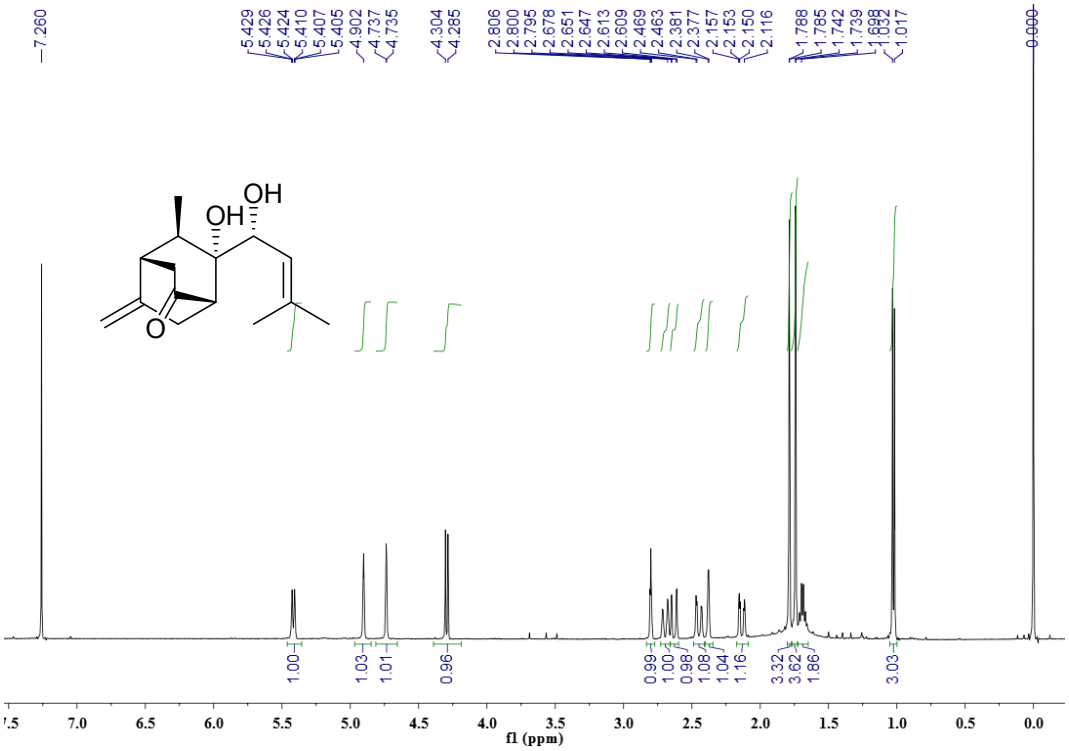


Fig. S49 ^{13}C NMR spectrum of **7** (125 MHz, $CDCl_3$).

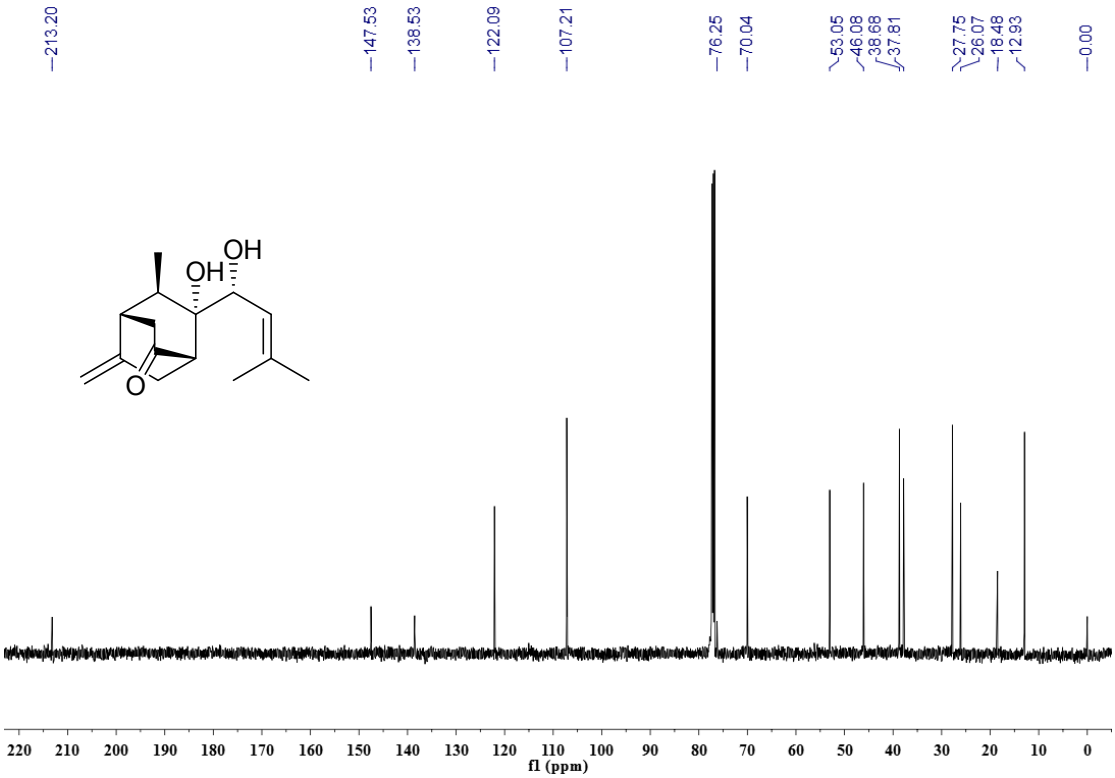


Fig. S50 HSQC spectrum of **7**.

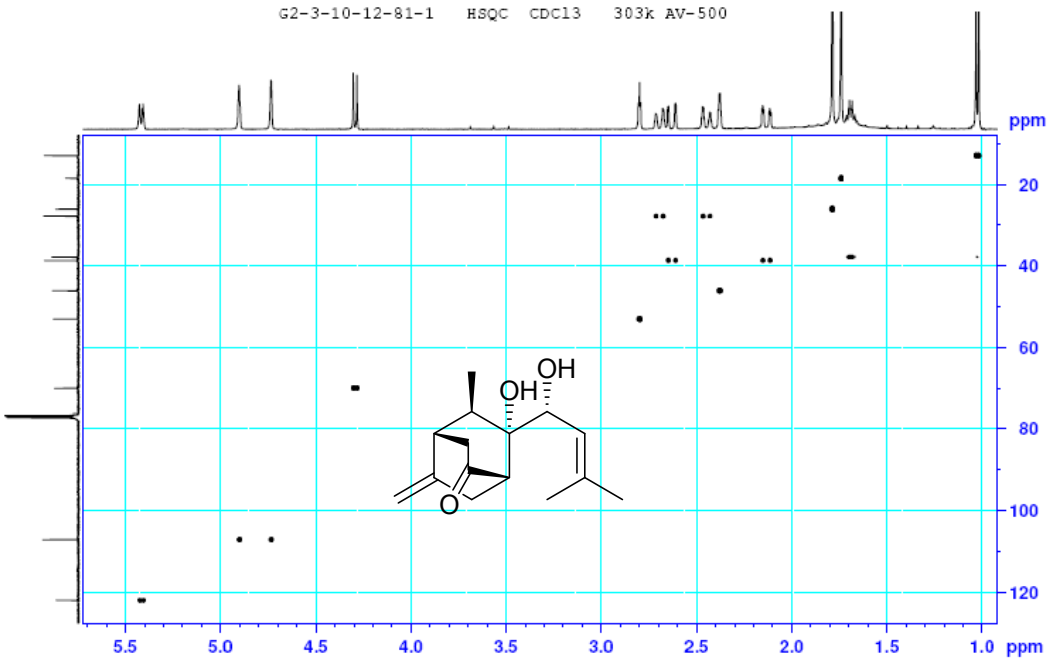


Fig. S51 HMBC spectrum of **7**.

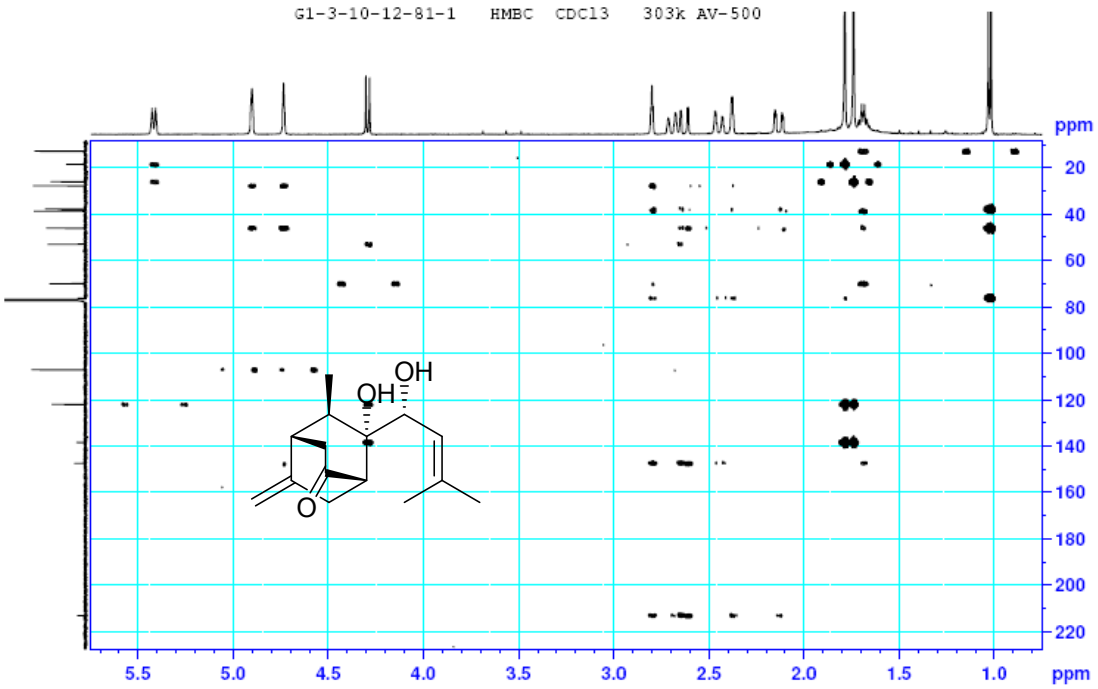


Fig. S52 ^{1}H-^{1}H COSY spectrum of **7**.

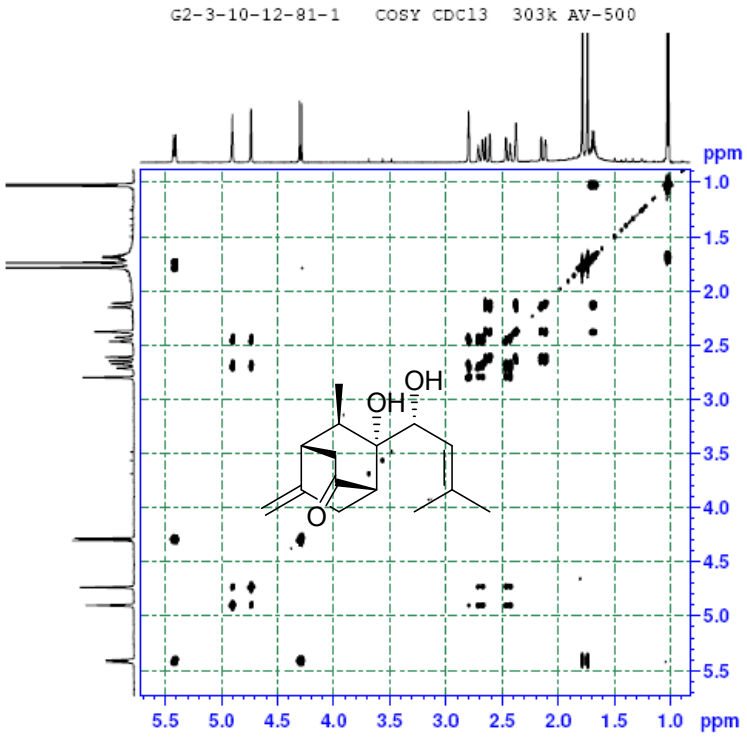


Fig. S53 ROESY spectrum of **7**.

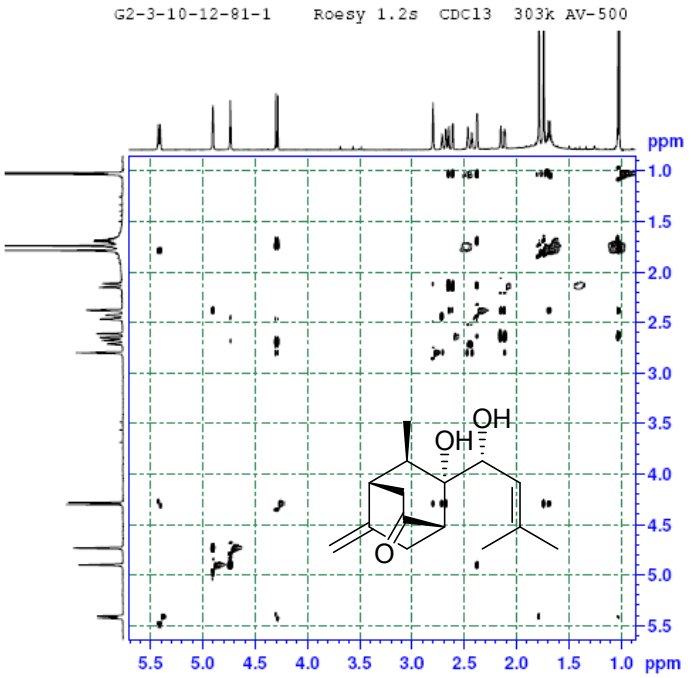


Fig. S54 Ultra-violet spectrum of **7**.

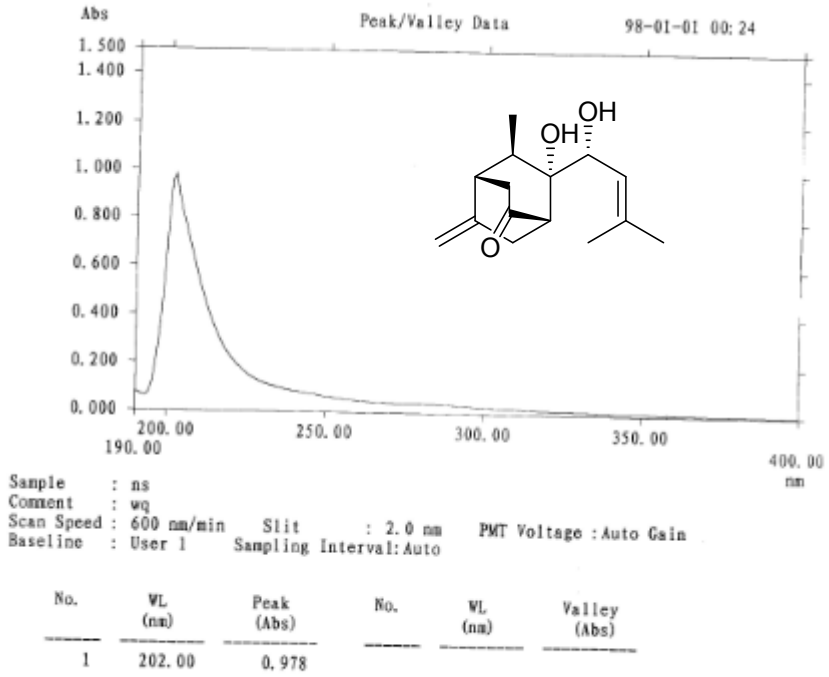


Fig. S55 Infrared spectrum of **7**.

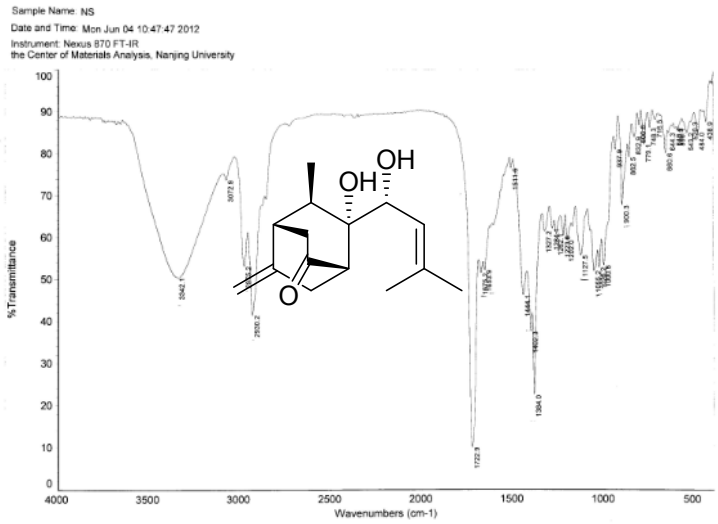


Fig. S56 HR-ESI-MS spectrum of **7** (positive mode).

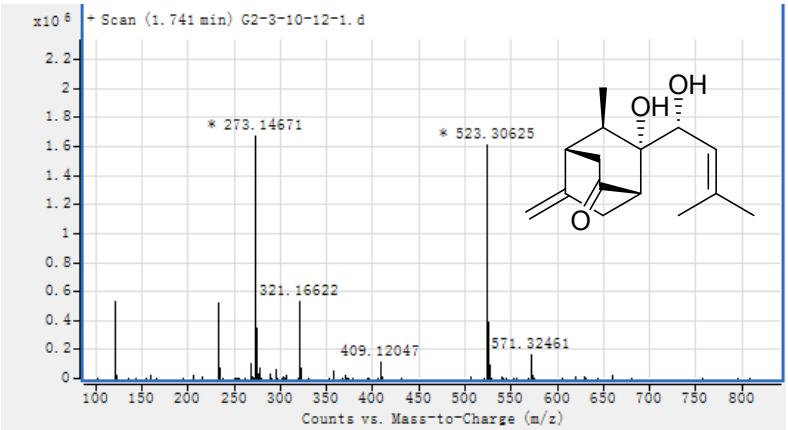


Fig. S57 ^{1}H NMR spectrum of **10** (500 MHz,$CDCl_3$).

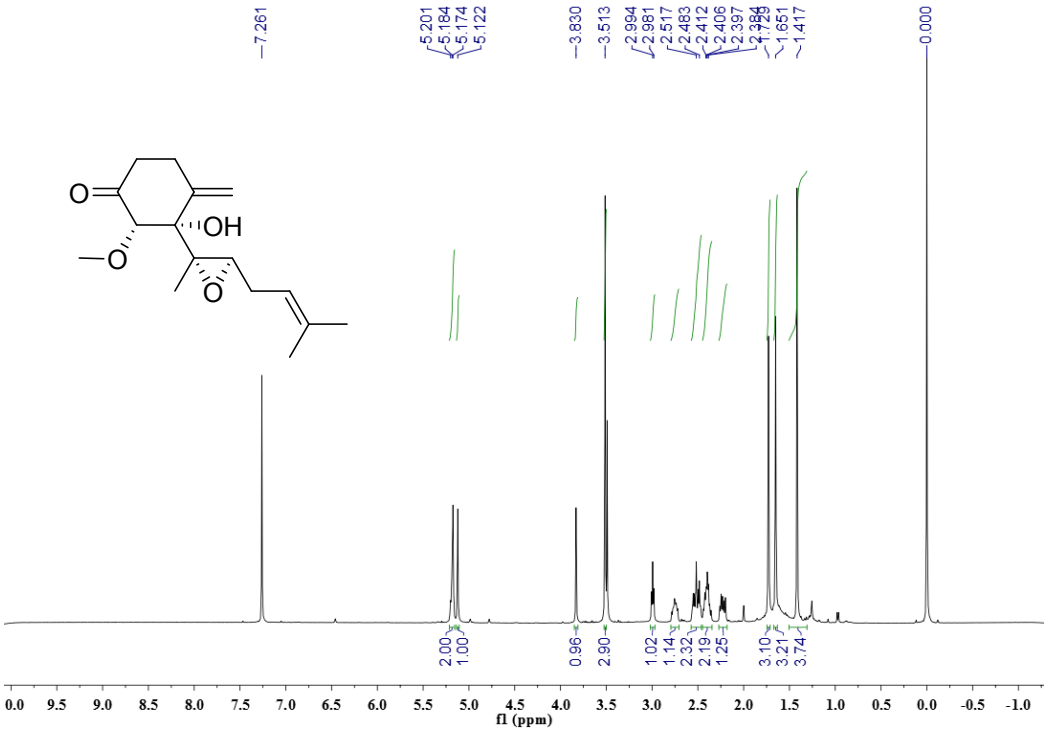


Fig. S58 ^{13}C NMR spectrum of **10** (125 MHz,$CDCl_3$).

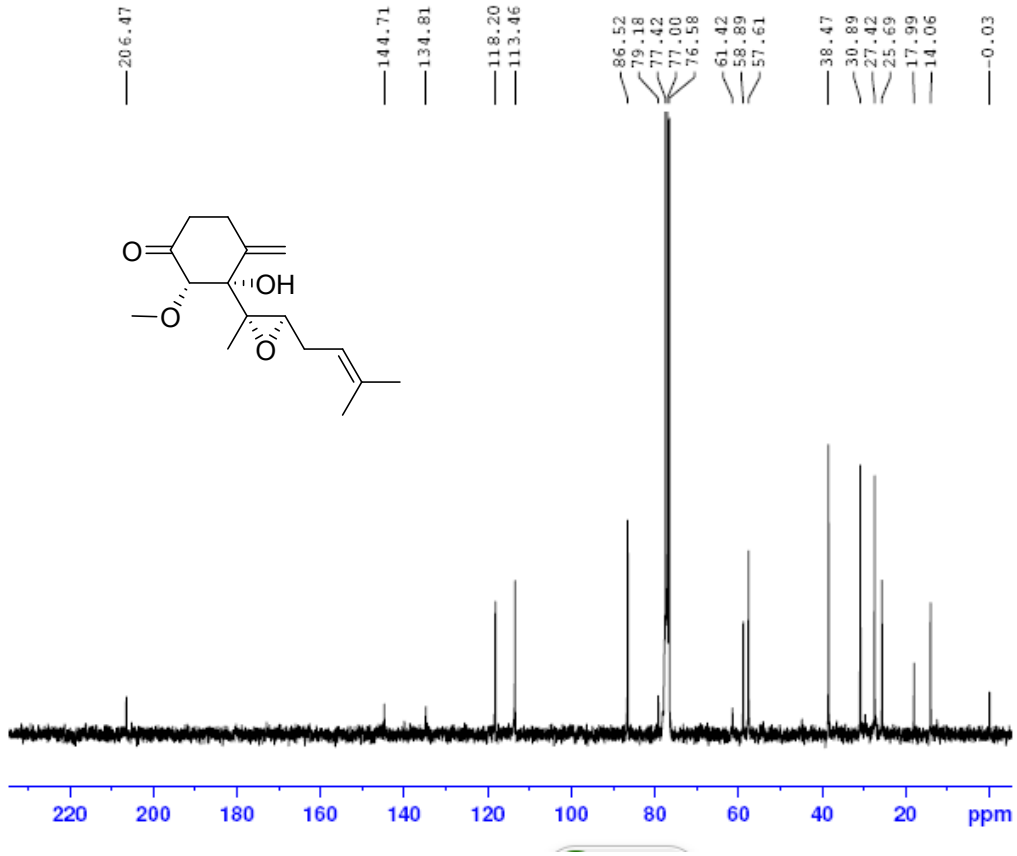


Fig. S59 HSQC spectrum of **10**.

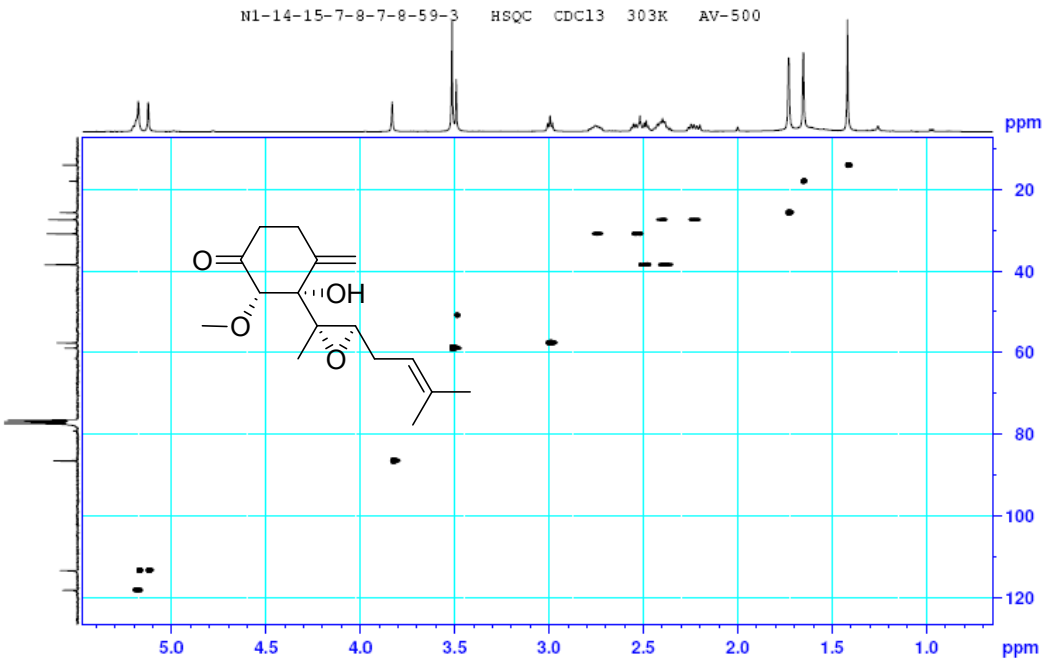


Fig. S60 HMBC spectrum of **10**.

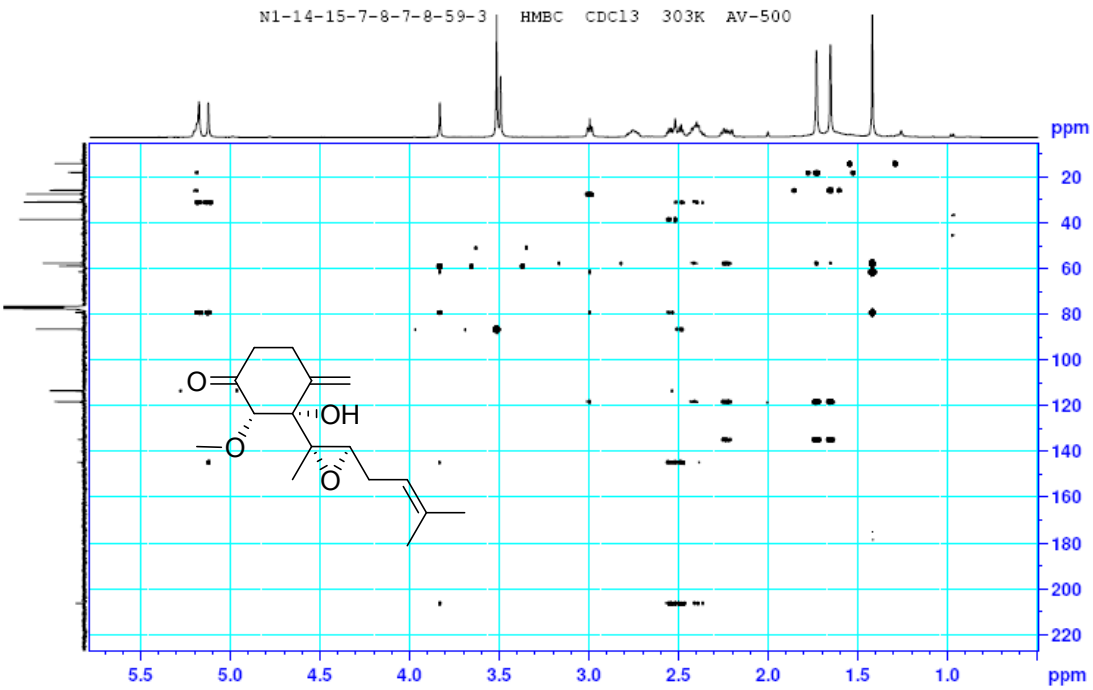


Fig. S61 COSY spectrum of **10**.

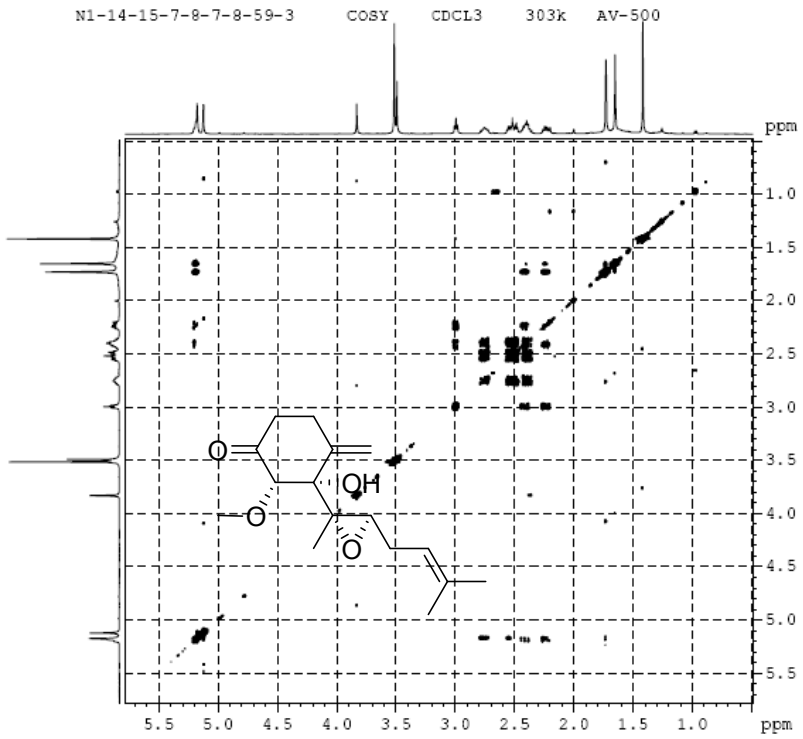


Fig. S62 ROESY spectrum of **10**.

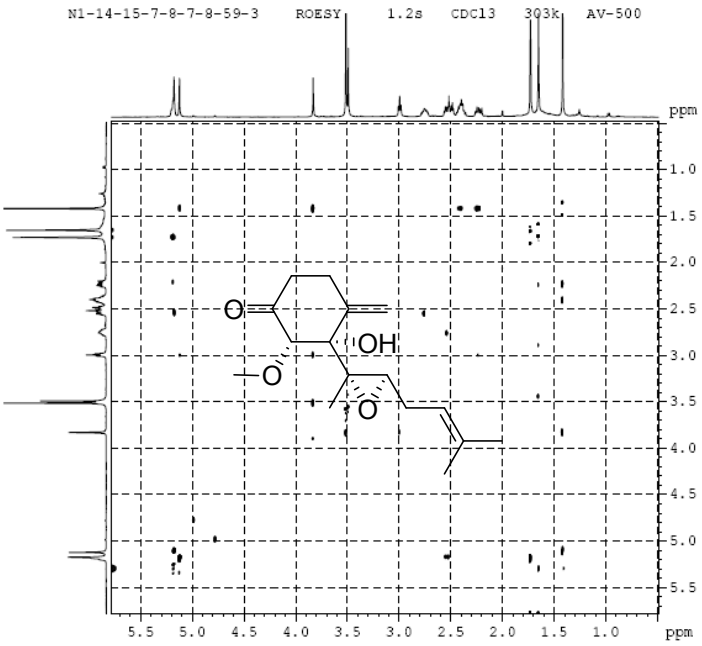


Fig. S63 Key HMBC, COSY and ROESY correlations of **10**.

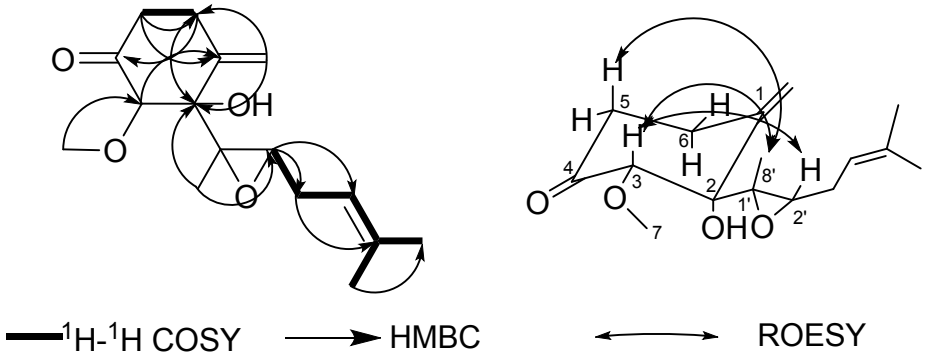
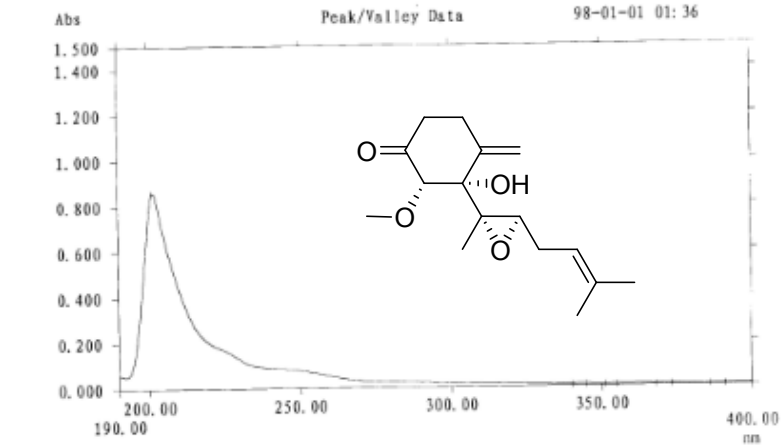


Fig. S64 Ultra-violet spectrum of **10**.



Sample : dhyo
Comment : wq
Scan Speed : 600 nm/min Slit : 2.0 nm PMT Voltage : Auto Gain
Baseline : User 1 Sampling Interval: Auto

No.	WL (nm)	Peak (Abs)	No.	WL (nm)	Valley (Abs)
1	391.00	0.005	1	386.00	0.005
2	373.00	0.006	2	368.00	0.006
3	355.00	0.008	3	351.00	0.008
4	345.00	0.008	4	340.00	0.008
5	201.00	0.861			

Fig. S65 Infrared spectrum of **10**.

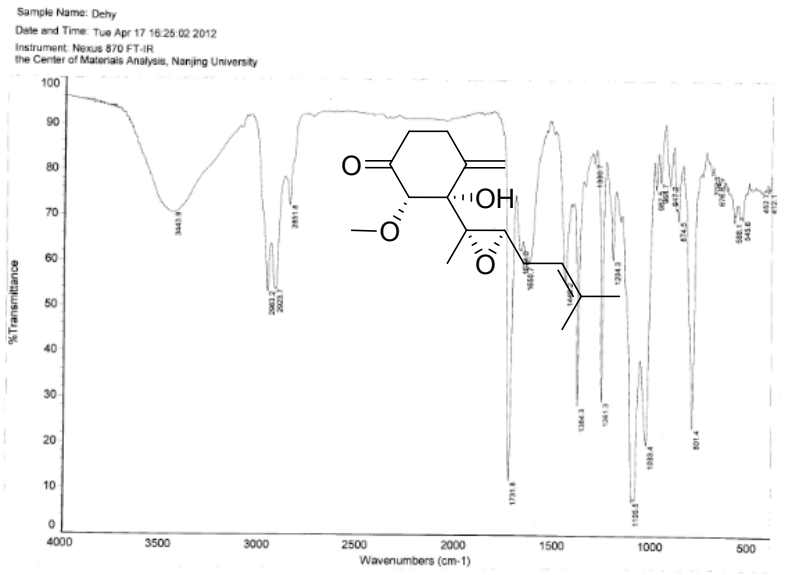


Fig. S66 HR-ESI-MS spectrum of **10** (positive mode).