Electronic Supplementary Information (ESI)

Spirodesertols A and B, two highly modified spirocyclic diterpenoids with an unprecedented 6-isopropyl-*3H*-spiro[benzofuran-2,1′-cyclohexane] motif from *Salvia deserta*

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Table S1. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data for spirodesertols A (**1**) and B (**2**) in chloroform-*d*.

	1		**2**	
no.	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1α	1.64, overlap	38.4	1.48, overlap	38.0
1β	1.92, dt (13.1, 3.1)		2.08, dt (13.6, 3.8)	
2α	1.70, m	19.0	1.61, m	18.6
2β	1.70, m		1.93, m	
3α	1.37, m	40.2	1.34, m	40.2
3β	1.47, dt (13.9, 3.4)		1.56, overlap	
4		35.7		34.8
5	2.59, d (3.4)	65.1	2.15, d (4.8)	65.7
6	9.89, d (3.4)	203.6	9.74, d (4.8)	204.5
7	9.83, s	191.8	9.80, s	191.7
8		125.2		124.3
9		126.1		126.0
10		92.5		91.6
11		145.8		146.6
12		143.1		143.0
13		135.3		135.4
14	7.16, s	125.1	7.17, s	125.2
15	3.26, sept (7.0)	27.1	3.28, sept (7.0)	27.2
16	1.24, d (7.0)	22.7	1.25, d (7.0)	22.7
17	1.24, d (7.0)	22.7	1.25, d (7.0)	22.7
18	1.13, s	23.5	1.27, s	24.1
19	1.16, s	31.3	1.03, s	31.5
20a	3.75, d (17.2)	38.7	3.42, d (17.5)	43.3
20b	3.44, d (17.2)		3.36, d (17.5)	

Table S2. DP4+ probability of ^{13}C NMR chemical shift of **2**.

Plausible isomers	DP4+ probability of ^{13}C NMR data of **2**	
	5*S**,10*S**	5*S**,10*R**
Bayer's theorem probability	100.00%	0.00%

Table S3. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectroscopic data for salviadenones A−D (**3**−**6**) in chloroform-*d*.

	3		**4**		**5**		**6**	
no.	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1*α*	5.70, br. s	122.6	3.64, ddd (15.9, 10.9, 5.1)	73.6	6.93, t (3.8)	137.8	6.56, s	128.6
2*α*	1.91, m	23.2	1.84, overlap	29.3	2.26, m	24.3		199.9
2*β*	2.02, m		2.32, td (13.6, 3.6)		2.31, m			
3*α*	1.33, overlap	37.3	1.32, td (13.6, 3.6)	40.6	1.63, dt (12.0, 6.9)	29.2	2.16, d (17.6)	46.6
3*β*	1.33, overlap		1.54, dt (13.6, 3.6)		1.21, overlap		2.62, d (17.6)	
4		32.5		34.2		31.9		36.0
5	2.10, br. d (12.5)	43.0	1.84, overlap	47.6	1.86, dd (13.3, 8.3)	42.7	2.25, dd (9.5, 8.5)	44.4
6*α*	2.82, d (17.5)	43.0	2.24, m	28.3	1.59, m	30.9	1.95, m	27.7
6*β*	2.53, dd (17.5, 12.5)		1.40, m		1.90, m		2.00, m	
7*α*		205.0	2.92, overlap	33.9	2.72, m	32.5	2.76, m	32.4
7*β*			2.92, overlap		2.64, ddd (13.3, 5.8, 2.5)		2.77, m	
8		129.9		138.2		133.7		132.9
9		125.3		118.6		117.7		116.8
10		135.0	3.44, t (5.1)	53.3		141.7		159.9
11		140.2		151.2		148.8		149.6
12		146.9		140.6		140.8		141.2
13		132.7		140.2		140.1		141.9
14	7.40, s	120.1	6.54, s	118.4	6.51, s	117.5	6.56, s	118.4
15	3.11, sept (7.0)	27.5	3.28, sept (6.9)	27.7	3.30, sept (6.8)	27.8	3.33, sept (6.9)	27.9
16	1.22, d (7.0)	22.6	1.19, d (6.9)	22.1	1.23, d (6.8)	22.2	1.23, d (6.9)	22.1
17	1.22, d (7.0)	22.6	1.22, d (6.9)	22.1	1.24, d (6.8)	22.3	1.24, d (6.9)	22.2
18	0.76, s	19.6	0.69, s	19.7	0.81, s	26.5	1.04, s	27.1
19	0.94, s	29.5	0.84, s	30.6	0.90, s	27.9	1.01, s	28.2
20a	3.42, d (15.0)	33.7		210.7		201.0		200.5
20b	3.74, d (15.0)							
11-OH			13.31, s				11.85, s	
12-OH			5.95, s				5.72, s	

Table S4. Cytotoxicity activities of compounds **1**−**7** against five cancer cell lines (IC_{50} in μM) [a]

Comp.	A-549	SMMC-7721	HL-60	MCF-7	SW480	BEAS-2B	Highest index of selectivity [b]
1	6.60 ± 0.35	7.13 ± 0.22	11.32 ± 0.31	11.50 ± 0.49	18.20 ± 1.21	>40	>6.06
2	18.00 ± 0.30	13.64 ± 0.27	18.42 ± 1.10	18.21 ± 0.76	21.65 ± 1.35	>40	>2.93
3	>40	31.98±3.09	17.70±0.83	26.90±1.52	28.79±2.67	30.37±0.45	>1.72
4	>40	>40	>40	>40	>40	>40	N/A
5	>40	>40	>40	>40	>40	>40	N/A
6	>40	>40	>40	>40	>40	>40	N/A
7	>40	32.70±2.91	15.15±0.29	>40	24.79±0.29	>40	>2.64
***cis*-platin** [c]	13.84 ± 0.47	7.82 ± 0.62	2.47 ± 0.12	13.46 ± 0.49	10.06 ± 0.30	>40	>16.19

[a] Values are expressed as the means ± SD, n = 3.

[b] Highest index of selectivity is the ratio of the IC_{50} value for the Beas-2B cell line over the lowest cancer cell IC_{50} value.

[c] *Cis*-platin was used as the positive control.

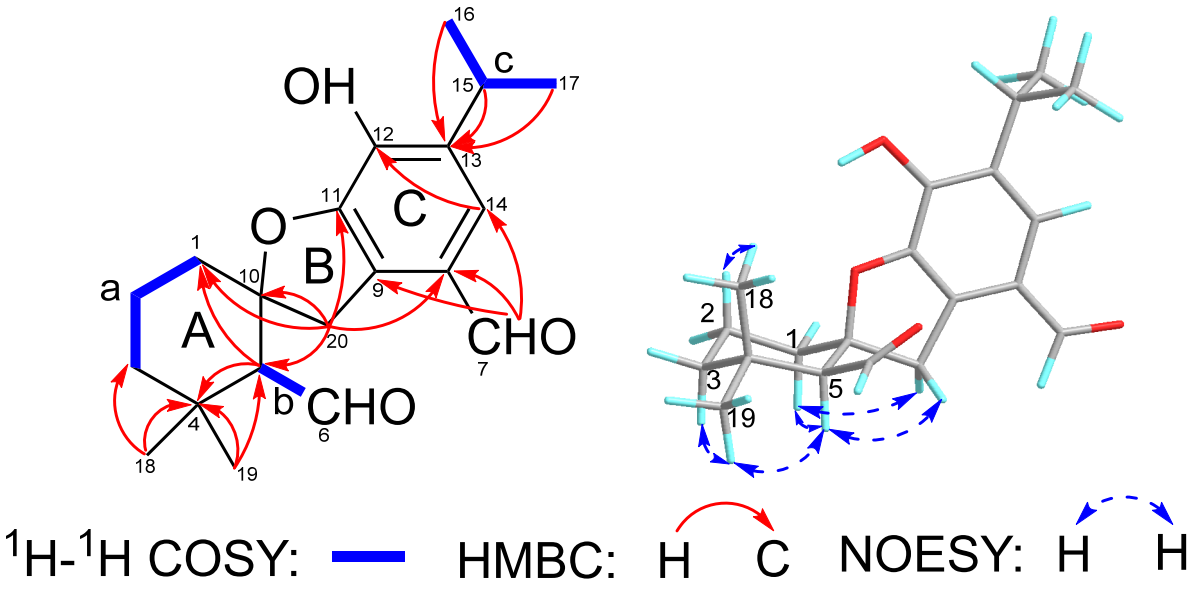


Figure S1. Key ^{1}H–^{1}H COSY, HMBC and NOESY correlations of spirodesertol B (**2**).

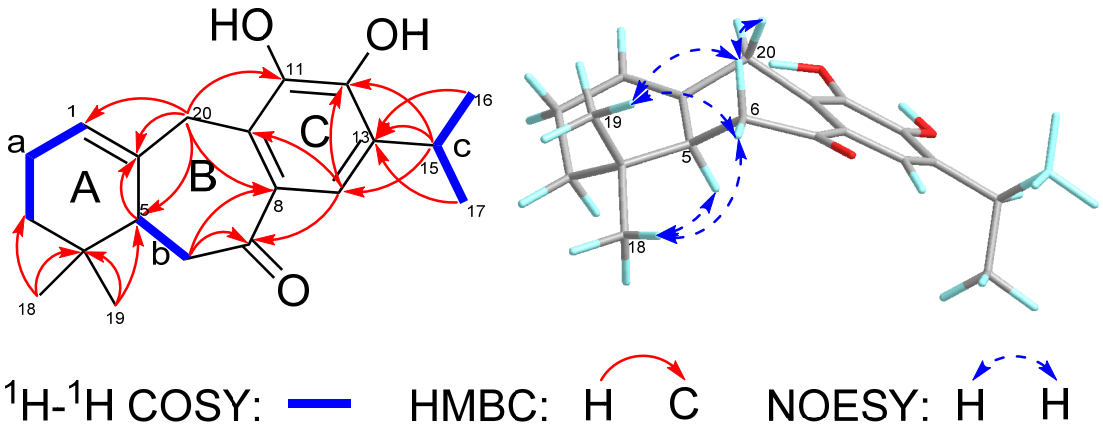


Figure S2. Key ^{1}H–^{1}H COSY, HMBC and NOESY correlations of salviadenone A (**3**).

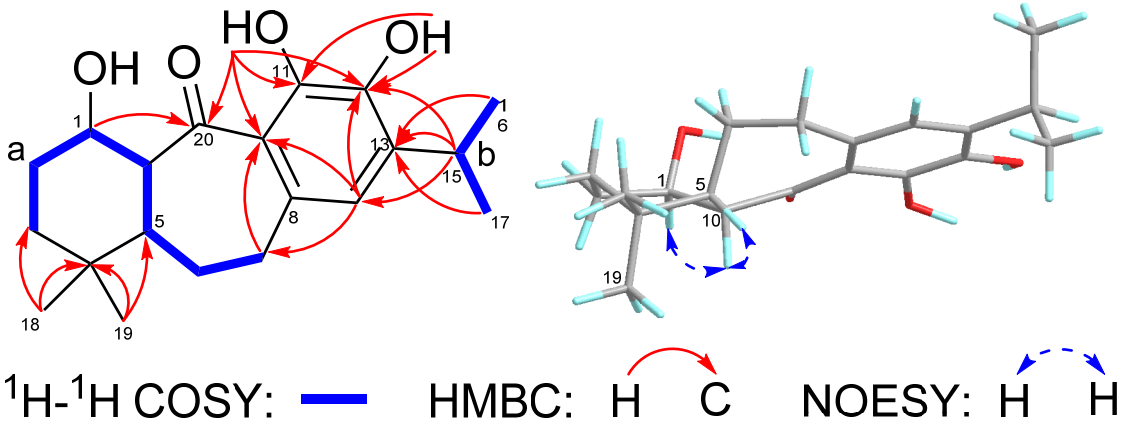


Figure S3. Key ^{1}H–^{1}H COSY, HMBC and NOESY correlations of salviadenone B (**4**).

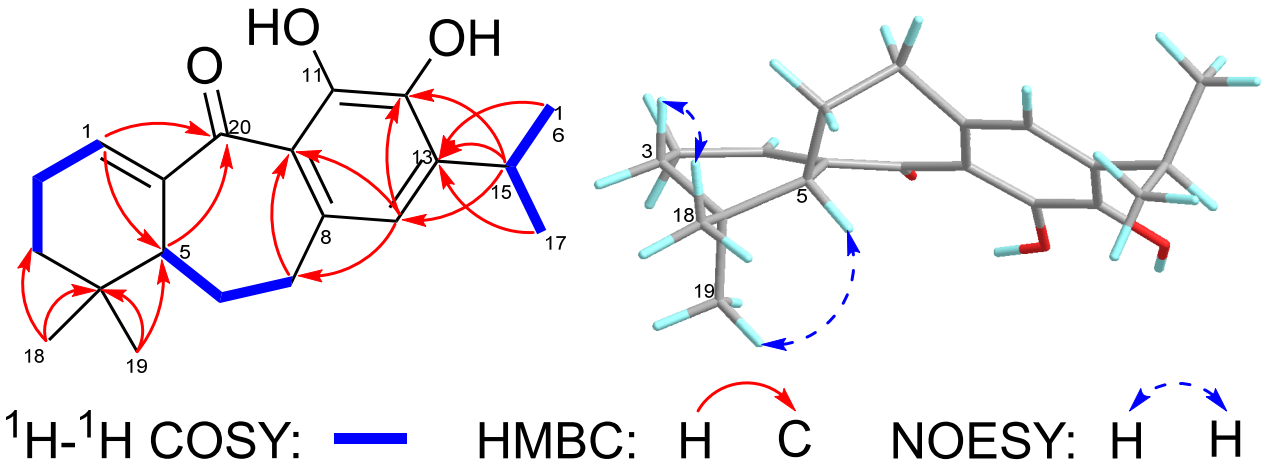


Figure S4. Key ^{1}H–^{1}H COSY, HMBC and NOESY correlations of salviadenone C (**5**).

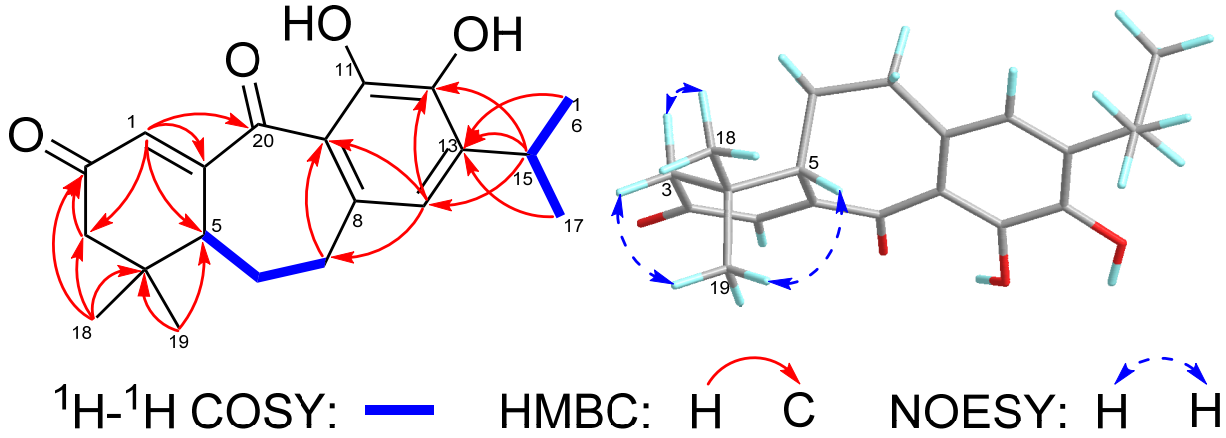


Figure S5. Key ^{1}H–^{1}H COSY, HMBC and NOESY correlations of salviadenone D (**6**).

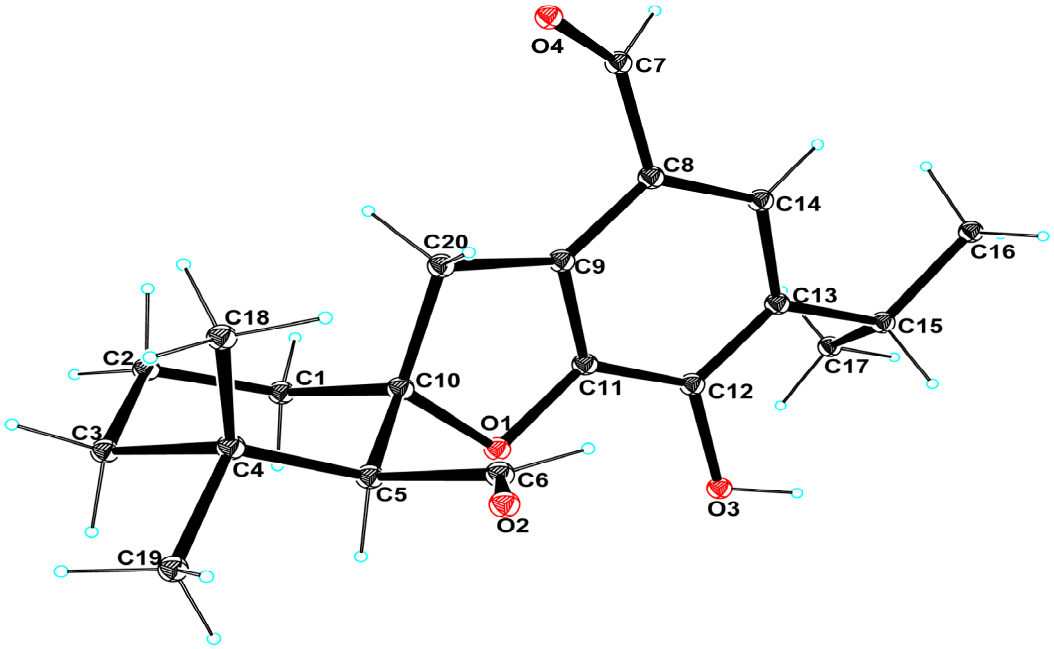


Figure S6. View of the molecule of **1** with the atom-labeling scheme (displacement ellipsoids are drawn at 10% the probability level)

Table S5. Crystal data and structure refinement for **1**

Empirical formula	$C_{20}H_{26}O_4$	
Formula weight	330.41	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Monoclinic, Cc	
Unit cell dimensions	a = 75.889(6) Å	α = 90.00°
	b = 15.6020(13) Å	β= 90.138(3)°
	c = 9.0418(8) Å	γ = 90.00°
Volume	10705.6(16) Å^3	
Z	24	
Calculated density	1.230 Mg/cm^3	
Absorption coefficient	0.679 mm^{-1}	
F(000)	4272	
Crystal size	0.16 × 0.11 × 0.06 mm^3	
Theta range for data collection	2.89 to 63.69°	
Limiting indices	-87<=*h*<=68, -17<=*k*<=6, -9<=*l*<=9	
Reflections collected / unique	29890 / 13612 [$R_{(int)}$ = 0.1856]	
Completeness to theta = 63.69°	94.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13612 / 2 / 1329	
Goodness-of-fit on F^2	2.162	
Final *R* indices [*I* > 2 sigma (*I*)]	R_1 = 0.3272, wR_2 = 0.6367	
R indices (all data)	R_1 = 0.4365, wR_2 = 0.6897	
Absolute structure parameter	1.4(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.102 and -1.640 e.A^{-3}	

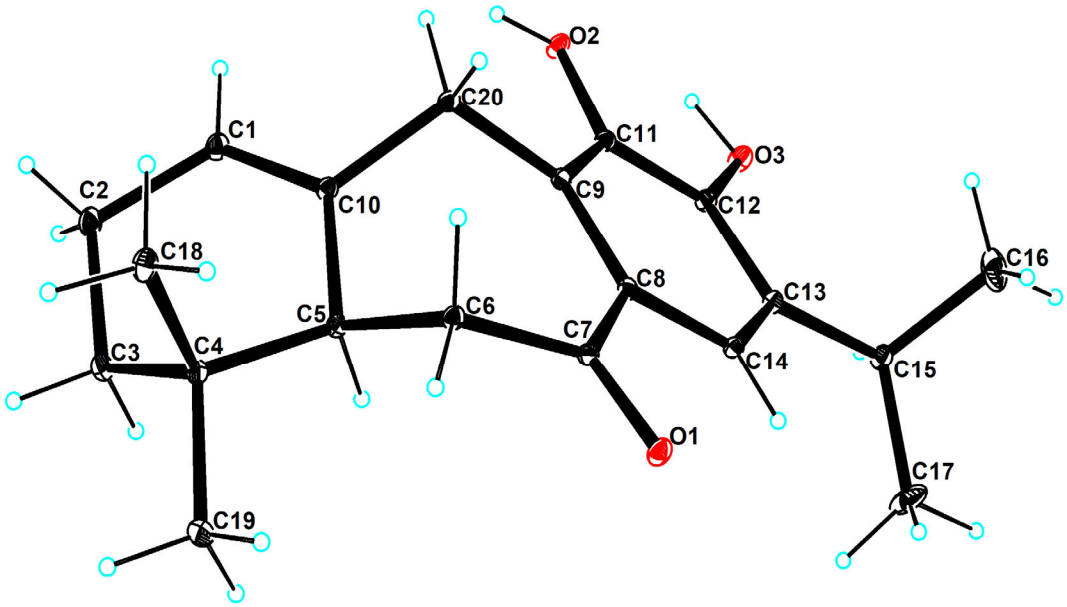


Figure S7. View of the molecule of **3** with the atom-labeling scheme (displacement ellipsoids are drawn at 10% the probability level)

Table S6. Crystal data and structure refinement for **3**

Empirical formula	$C_{20}H_{26}O_3$	
Formula weight	314.41	
Temperature	100(10) K	
Wavelength	1.54184 Å	
Crystal system, space group	monoclinic, $P2_1$	
Unit cell dimensions	a = 7.58780(10) Å	α = 90.00°
	b = 21.5262(3) Å	β= 98.478(2)°
	c = 10.3782(2) Å	γ = 90.00°
Volume	1676.62(5) $Å^3$	
Z	4	
Calculated density	1.246 Mg/cm^3	
Absorption coefficient	0.651 mm^{-1}	
F(000)	680	
Crystal size	0.2 × 0.15 × 0.1 mm^3	
Theta range for data collection	8.614 to 147.384°	
Limiting indices	-9<=*h*<=9, -26<=*k*<=26, -12<=*l*<=12	
Reflections collected / unique	12848 / 6367 [$R_{(int)}$ = 0.0244]	
Completeness to theta = 66.97°	99.81 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6367 / 16 / 457	
Goodness-of-fit on F^2	1.046	
Final *R* indices [$I > 2$ sigma (I)]	R_1 = 0.0349, wR_2 = 0.0895	
R indices (all data)	R_1 = 0.0352, wR_2 = 0.0898	
Absolute structure parameter	0.01(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.23 and -0.28 $e.A^{-3}$	

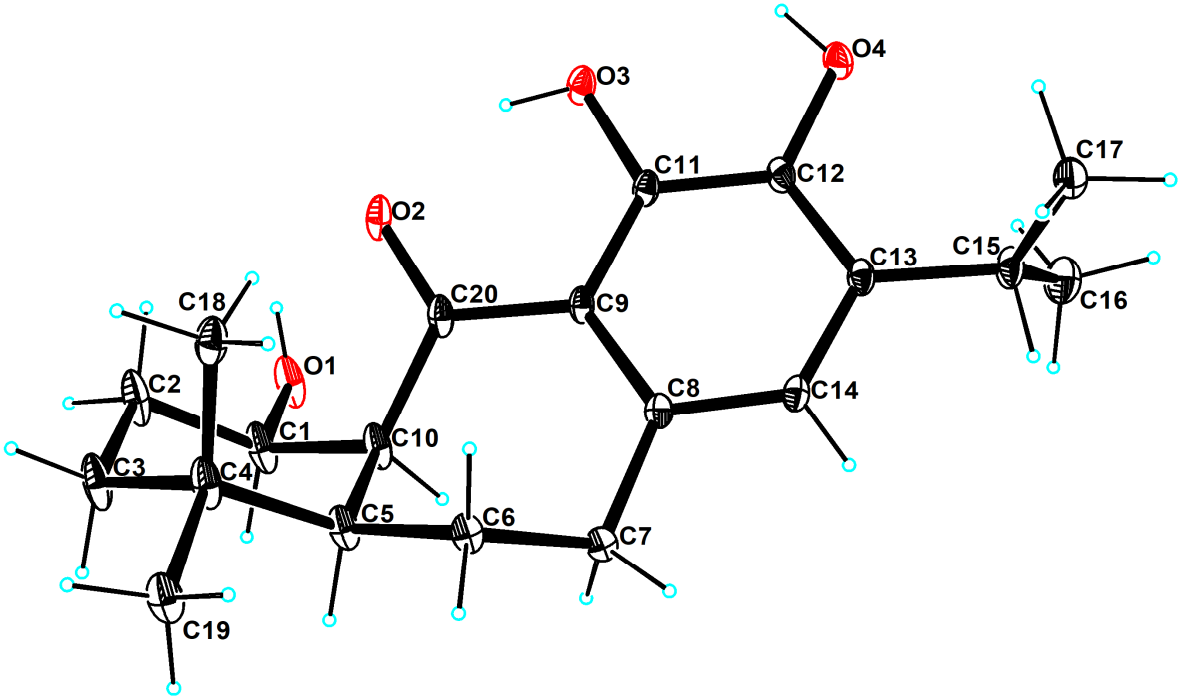


Figure S8. View of the molecule of **4** with the atom-labeling scheme (displacement ellipsoids are drawn at 10% the probability level)

Table S7. Crystal data and structure refinement for **4**

Empirical formula	$C_{40}H_{56}O_8$	
Formula weight	663.84	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Monoclinic, C2	
Unit cell dimensions	a = 20.8185(6) Å	α = 90.00°
	b = 16.8043(5) Å	β= 124.7340(10)°
	c = 12.9355(4) Å	γ = 90.00°
Volume	3719.0(2) $Å^3$	
Z	4	
Calculated density	1.186 Mg/cm^3	
Absorption coefficient	0.652 mm^{-1}	
F(000)	1232	
Crystal size	0.05 × 0.04 × 0.03 mm^3	
Theta range for data collection	3.687 to 66.630°	
Limiting indices	-24<=*h*<=24, -19<=*k*<=19, -15<=*l*<=15	
Reflections collected / unique	20401 / 6495 [$R_{(int)}$ = 0.0250]	
Completeness to theta = 66.63°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6495 / 601 / 447	
Goodness-of-fit on F^2	1.025	
Final *R* indices [$I > 2$ sigma (I)]	R_1 = 0.0777, wR_2 = 0.2040	
R indices (all data)	R_1 = 0.0845, wR_2 = 0.2117	
Absolute structure parameter	0.1(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.545 and -0.310 $e.A^{-3}$	

Table S8. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1** at B3LYP/6-31G (d) level in methanol

Conformations	Gibbs free energies (Hartree)	Boltzmann distribution
1	-1078.542743	80.61%
2	-1078.540751	9.80%
3	-1078.540725	9.59%

Table S9. Optimized coordinate of compound **1** at B3LYP/6-31G (d) level in methanol

Conformation 1							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.121	1.1	-0.241	H	-2.706	3.578	-0.993
C	-1.843	1.682	-0.375	H	1.526	-0.506	-2.19
C	-0.719	0.894	-0.08	H	1.039	2.057	0.439
C	-3.316	-0.222	0.168	H	1.105	1.323	-1.146
C	-0.907	-0.414	0.318	H	2.985	1.909	1.686
C	-2.172	-0.995	0.454	H	3.377	1.023	3.146
C	-1.733	3.075	-0.809	H	1.877	-0.84	2.501
C	2.1	-1.254	-1.607	H	0.97	0.676	2.51
C	0.765	1.158	-0.119	H	5.156	0.72	1.407
C	3.103	0.897	2.092	H	4.405	-0.803	1.869
C	1.775	0.132	2.001	H	2.637	-1.818	0.334
C	4.22	0.15	1.353	H	4.999	1.542	-0.942
C	2.506	-0.866	-0.197	H	3.738	0.958	-2.028
C	1.37	-0.126	0.545	H	3.312	1.928	-0.61
C	3.913	-0.152	-0.136	H	5.983	-0.679	-0.531
C	3.979	1.142	-0.975	H	4.969	-2.075	-0.122
C	4.989	-1.122	-0.664	H	4.86	-1.339	-1.729
C	-5.823	0.139	0.559	H	-5.605	0.776	1.424
C	-5.007	-1.731	-0.943	H	-6.003	0.788	-0.306
C	-4.692	-0.866	0.296	H	-6.756	-0.399	0.761
O	-0.683	3.686	-0.976	H	-5.966	-2.247	-0.816
O	2.38	-2.323	-2.115	H	-4.233	-2.488	-1.107
O	0.246	-1.102	0.571	H	-5.073	-1.109	-1.844
O	-2.304	-2.288	0.858	H	-4.644	-1.543	1.159
H	-3.985	1.719	-0.462	H	-1.416	-2.642	1.045
Conformation 2							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	3.027	0.941	0.053	H	0.655	3.455	0.099
C	1.773	1.584	0.027	H	-2.95	-1.505	2.511
C	0.621	0.79	-0.101	H	-1.116	1.844	-0.897
C	3.173	-0.445	-0.04	H	-1.192	1.489	0.832
C	0.762	-0.581	-0.189	H	-3.527	0.264	-3.259
C	2.004	-1.224	-0.168	H	-3.109	1.463	-2.052
C	1.684	3.043	0.131	H	-2.055	-1.421	-2.204
C	-2.277	-0.864	1.906	H	-1.121	0.03	-2.574
C	-0.858	1.104	-0.133	H	-5.293	0.406	-1.488
C	-3.244	0.385	-2.207	H	-4.567	-1.195	-1.58
C	-1.93	-0.362	-1.946	H	-2.803	-1.839	0.144
C	-4.364	-0.15	-1.306	H	-5.071	-0.774	2.043

C	-2.645	-0.789	0.436	H	-6.131	-0.497	0.661
C	-1.503	-0.284	-0.473	H	-5.115	-1.947	0.711
C	-4.045	-0.094	0.209	H	-3.403	2.024	0.151
C	-5.146	-0.879	0.955	H	-5.085	1.768	0.615
C	-4.07	1.365	0.713	H	-3.791	1.432	1.771
C	5.395	-0.699	-1.231	H	6.356	-1.228	-1.222
C	5.289	-0.826	1.304	H	4.885	-0.939	-2.171
C	4.545	-1.11	-0.014	H	5.605	0.377	-1.227
O	2.641	3.802	0.247	H	6.248	-1.356	1.322
O	-1.341	-0.304	2.443	H	4.702	-1.154	2.17
O	-0.409	-1.272	-0.302	H	5.497	0.244	1.425
O	2.081	-2.58	-0.269	H	4.385	-2.191	-0.074
H	3.908	1.569	0.15	H	1.176	-2.928	-0.364
Conformation 3							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.221	0.807	0.049	H	-1.341	3.708	0.143
C	-2.1	1.663	0.083	H	4.011	1.854	0.3
C	-0.822	1.084	0.093	H	0.81	2.102	-0.889
C	-3.113	-0.584	0.02	H	0.75	2.415	0.845
C	-0.709	-0.293	0.061	H	3.074	-0.94	3.15
C	-1.815	-1.144	0.029	H	2.174	-1.855	1.95
C	-2.28	3.118	0.11	H	0.987	0.276	2.444
C	3.42	1.621	-0.609	H	2.442	1.197	2.085
C	0.579	1.649	0.082	H	4.646	-0.104	1.461
C	2.765	-0.944	2.098	H	4.604	-1.856	1.386
C	1.89	0.285	1.821	H	2.284	0.177	-1.632
C	4.005	-0.956	1.194	H	4.771	-0.61	-2.196
C	2.684	0.288	-0.618	H	5.648	-1.544	-0.972
C	1.468	0.389	0.349	H	5.521	0.209	-0.814
C	3.673	-0.9	-0.319	H	2.812	-2.199	-1.853
C	4.976	-0.691	-1.122	H	2.154	-2.503	-0.243
C	3.062	-2.238	-0.786	H	3.794	-3.043	-0.644
C	-4.545	-2.006	-1.492	H	-4.802	-1.166	-2.149
C	-5.602	-0.907	0.532	H	-5.37	-2.728	-1.526
C	-4.316	-1.516	-0.045	H	-3.651	-2.492	-1.893
O	-3.362	3.693	0.099	H	-5.969	-0.074	-0.079
O	3.378	2.42	-1.525	H	-5.452	-0.539	1.553
O	0.578	-0.759	0.064	H	-6.392	-1.665	0.557
O	-1.66	-2.496	0.007	H	-4.067	-2.398	0.559
H	-4.2	1.273	0.05	H	-0.709	-2.699	0.057

Table S10. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound *ent*-**1** at B3LYP/6-31G (d) level in methanol

Conformations	Gibbs free energies (Hartree)	Boltzmann distribution
1	-1078.54	84.73%
2	-1078.54	9.87%
3	-1078.54	5.40%

Table S11. Optimized coordinate of compound *ent*-**1** at B3LYP/6-31G (d) level in the methanol

Conformation 1							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.12	1.026	0.283	H	-2.737	3.546	0.907
C	-1.854	1.638	0.358	H	1.574	-0.398	2.215
C	-0.722	0.855	0.073	H	1.007	2.019	-0.539
C	-3.3	-0.32	-0.055	H	1.113	1.37	1.08
C	-0.895	-0.472	-0.258	H	3.339	0.891	-3.21
C	-2.152	-1.086	-0.335	H	2.946	1.841	-1.792
C	-1.76	3.052	0.724	H	0.944	0.538	-2.536
C	2.141	-1.172	1.659	H	1.874	-0.961	-2.462
C	0.758	1.146	0.07	H	4.41	-0.853	-1.857
C	3.076	0.812	-2.149	H	5.138	0.703	-1.475
C	1.762	0.032	-2.009	H	2.668	-1.822	-0.257
C	4.212	0.12	-1.386	H	3.744	1.08	1.958
C	2.528	-0.847	0.228	H	3.295	1.975	0.499
C	1.373	-0.161	-0.538	H	4.99	1.63	0.835
C	3.923	-0.116	0.119	H	4.903	-1.211	1.758
C	3.976	1.218	0.895	H	6.005	-0.592	0.518
C	5.019	-1.043	0.682	H	5.008	-2.021	0.186
C	-5.559	-0.28	-1.207	H	-5.746	0.775	-0.974
C	-5.389	-0.93	1.245	H	-6.53	-0.784	-1.277
C	-4.687	-0.949	-0.126	H	-5.078	-0.328	-2.19
O	-0.718	3.687	0.836	H	-5.568	0.095	1.589
O	2.432	-2.215	2.212	H	-4.787	-1.44	2.005
O	0.264	-1.153	-0.505	H	-6.36	-1.436	1.183
O	-2.258	-2.4	-0.674	H	-4.554	-1.997	-0.413
H	-3.995	1.634	0.501	H	-1.363	-2.742	-0.847
Conformation 2							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	3.221	0.807	0.049	H	1.341	3.708	0.143
C	2.1	1.663	0.083	H	-4.011	1.854	0.299
C	0.822	1.084	0.093	H	-0.751	2.415	0.845
C	3.113	-0.583	0.02	H	-0.81	2.102	-0.889
C	0.709	-0.293	0.061	H	-2.174	-1.855	1.95
C	1.815	-1.144	0.029	H	-3.074	-0.94	3.15
C	2.28	3.118	0.11	H	-2.442	1.197	2.085
C	-3.42	1.621	-0.609	H	-0.987	0.276	2.444
C	-0.579	1.649	0.082	H	-4.604	-1.856	1.386
C	-2.765	-0.944	2.098	H	-4.646	-0.104	1.461
C	-1.89	0.285	1.821	H	-2.283	0.177	-1.632
C	-4.005	-0.956	1.194	H	-4.771	-0.61	-2.196
C	-2.684	0.288	-0.618	H	-5.521	0.209	-0.814
C	-1.468	0.389	0.349	H	-5.648	-1.544	-0.972
C	-3.673	-0.9	-0.319	H	-2.812	-2.199	-1.853
C	-4.976	-0.691	-1.122	H	-3.794	-3.043	-0.644
C	-3.062	-2.239	-0.786	H	-2.154	-2.503	-0.242
C	5.602	-0.907	0.532	H	5.969	-0.074	-0.079
C	4.545	-2.007	-1.491	H	6.392	-1.665	0.557
C	4.316	-1.516	-0.045	H	5.452	-0.538	1.553
O	3.361	3.693	0.099	H	4.802	-1.167	-2.149

O	-3.377	2.42	-1.525	H	3.65	-2.493	-1.892
O	-0.578	-0.759	0.064	H	5.37	-2.729	-1.525
O	1.66	-2.496	0.007	H	4.068	-2.398	0.559
H	4.2	1.274	0.05	H	0.709	-2.698	0.058
Conformation 3							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-2.994	1.257	0.075	H	-0.459	3.609	0.105
C	-1.699	1.816	0.043	H	2.828	-1.58	2.507
C	-0.606	0.945	-0.086	H	1.194	1.877	-0.891
C	-3.24	-0.115	-0.014	H	1.255	1.518	0.838
C	-0.843	-0.413	-0.17	H	3.47	0.137	-3.271
C	-2.123	-0.972	-0.144	H	3.14	1.362	-2.064
C	-1.513	3.266	0.143	H	1.058	0.063	-2.568
C	2.187	-0.904	1.904	H	1.898	-1.446	-2.202
C	0.89	1.156	-0.125	H	4.425	-1.384	-1.598
C	3.204	0.277	-2.217	H	5.255	0.166	-1.513
C	1.845	-0.38	-1.945	H	2.635	-1.911	0.138
C	4.293	-0.328	-1.324	H	3.849	1.288	1.757
C	2.549	-0.853	0.431	H	3.486	1.905	0.14
C	1.436	-0.272	-0.469	H	5.151	1.539	0.589
C	3.99	-0.25	0.193	H	4.987	-0.992	2.02
C	4.113	1.204	0.697	H	6.048	-0.792	0.626
C	5.043	-1.105	0.932	H	4.938	-2.17	0.693
C	-4.935	-1.538	1.25	H	-4.341	-2.456	1.207
C	-5.08	-1.339	-1.286	H	-5.994	-1.819	1.288
C	-4.671	-0.639	0.026	H	-4.69	-1.015	2.181
O	-2.417	4.087	0.262	H	-4.492	-2.245	-1.454
O	1.284	-0.294	2.445	H	-4.939	-0.675	-2.146
O	0.278	-1.182	-0.288	H	-6.139	-1.621	-1.247
O	-2.282	-2.322	-0.241	H	-5.312	0.245	0.132
H	-3.833	1.94	0.172	H	-1.4	-2.723	-0.342

Table S12. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **2** at B3LYP/6-31G (d) level in methanol

Conformations	Gibbs free energies (Hartree)	Boltzmann distribution
1	-1078.54	92.92%
2	-1078.54	4.31%
3	-1078.54	1.46%
4	-1078.54	1.31%

Table S13. Optimized coordinate of compound **2** at B3LYP/6-31G (d) level in the methanol

Conformation 1							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.227	1.096	0.038	H	-3.285	3.72	-0.071
C	-2.086	1.908	-0.117	H	1.299	-0.166	2.11
C	-0.836	1.276	-0.224	H	0.677	2.46	-1.24
C	-3.179	-0.301	0.09	H	0.886	2.369	0.497
C	-0.781	-0.102	-0.169	H	2.126	-1.828	-2.067

C	-1.912	-0.913	-0.02	H	3.038	-0.968	-3.298
C	-2.237	3.362	-0.159	H	2.417	1.215	-2.316
C	2.158	0.48	1.843	H	0.952	0.297	-2.661
C	0.57	1.792	-0.38	H	4.573	-1.772	-1.499
C	2.718	-0.925	-2.251	H	4.558	-0.015	-1.603
C	1.851	0.318	-2.031	H	3.206	1.32	0.22
C	3.945	-0.887	-1.334	H	4.739	-0.478	2.032
C	2.619	0.41	0.399	H	5.371	0.41	0.635
C	1.413	0.486	-0.572	H	5.627	-1.339	0.766
C	3.604	-0.805	0.175	H	2.832	-2.137	1.746
C	4.908	-0.533	0.952	H	3.743	-2.95	0.472
C	3.02	-2.149	0.666	H	2.083	-2.408	0.168
C	-4.485	-1.92	1.565	H	-3.712	-2.694	1.564
C	-4.764	-1.993	-0.967	H	-5.458	-2.41	1.686
C	-4.463	-1.105	0.256	H	-4.32	-1.273	2.434
O	-1.32	4.167	-0.279	H	-4.002	-2.769	-1.094
O	2.683	1.179	2.69	H	-4.801	-1.397	-1.886
O	0.479	-0.627	-0.261	H	-5.735	-2.487	-0.844
O	-1.782	-2.268	0.018	H	-5.273	-0.367	0.324
H	-4.197	1.582	0.12	H	-0.84	-2.488	-0.094
Conformation 2							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	3.155	0.917	-0.193	H	0.924	3.54	-0.503
C	1.937	1.624	-0.251	H	-2.916	-2.385	0.584
C	0.743	0.902	-0.088	H	-0.959	2.134	0.52
C	3.225	-0.462	0.017	H	-1.019	1.563	-1.147
C	0.809	-0.461	0.119	H	-3.427	0.849	3.089
C	2.014	-1.168	0.181	H	-2.971	1.936	1.793
C	1.929	3.073	-0.477	H	-1.034	0.483	2.408
C	-2.763	-1.992	-0.442	H	-2.02	-0.957	2.195
C	-0.719	1.287	-0.13	H	-4.541	-0.688	1.531
C	-3.148	0.879	2.03	H	-5.197	0.927	1.314
C	-1.863	0.064	1.826	H	-2.294	-0.324	-1.618
C	-4.292	0.322	1.174	H	-3.653	1.665	-1.994
C	-2.596	-0.485	-0.577	H	-3.163	2.33	-0.429
C	-1.443	-0.014	0.35	H	-4.875	2.177	-0.819
C	-3.966	0.265	-0.339	H	-4.871	-0.594	-2.144
C	-3.898	1.692	-0.926	H	-6.033	0.089	-0.991
C	-5.099	-0.479	-1.077	H	-5.281	-1.476	-0.663
C	5.429	-0.702	1.247	H	5.703	0.353	1.125
C	5.319	-1.093	-1.262	H	6.357	-1.283	1.304
C	4.56	-1.196	0.075	H	4.903	-0.805	2.202
O	2.928	3.766	-0.632	H	5.582	-0.054	-1.493
O	-2.755	-2.753	-1.389	H	4.718	-1.481	-2.091
O	-0.405	-1.073	0.263	H	6.25	-1.671	-1.217
O	2.02	-2.513	0.393	H	4.344	-2.254	0.249
H	4.069	1.488	-0.319	H	1.098	-2.81	0.496
Conformation 3							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.182	0.768	0.013	H	-1.45	3.662	-0.74
C	-2.108	1.636	-0.264	H	1.609	0.243	2.161

C	-0.81	1.105	-0.277	H	0.62	2.312	-1.415
C	-3.005	-0.59	0.278	H	0.824	2.392	0.331
C	-0.623	-0.242	-0.014	H	2.998	-1.255	-3.203
C	-1.687	-1.108	0.263	H	2.238	-1.976	-1.791
C	-2.355	3.058	-0.526	H	0.892	-0.026	-2.578
C	2.417	0.875	1.742	H	2.314	1.012	-2.476
C	0.552	1.723	-0.495	H	4.712	-1.709	-1.441
C	2.756	-1.079	-2.148	H	4.578	0.01	-1.794
C	1.829	0.133	-2.03	H	3.274	1.528	-0.07
C	4.044	-0.843	-1.351	H	5.067	0.11	1.837
C	2.769	0.621	0.287	H	5.91	-0.882	0.638
C	1.489	0.473	-0.573	H	5.527	0.81	0.275
C	3.815	-0.556	0.154	H	2.406	-2.218	0.522
C	5.155	-0.097	0.765	H	4.12	-2.622	0.743
C	3.364	-1.84	0.884	H	3.269	-1.674	1.964
C	-5.433	-0.832	1.073	H	-6.183	-1.58	1.349
C	-4.515	-2.347	-0.736	H	-5.209	-0.229	1.959
C	-4.178	-1.534	0.534	H	-5.885	-0.178	0.318
O	-3.458	3.592	-0.523	H	-5.309	-3.073	-0.527
O	2.973	1.701	2.441	H	-3.645	-2.894	-1.115
O	0.684	-0.642	-0.034	H	-4.862	-1.679	-1.532
O	-1.368	-2.411	0.495	H	-3.874	-2.245	1.319
H	-4.178	1.196	0.018	H	-2.165	-2.909	0.738
Conformation 4							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	3.202	1.048	-0.103	H	2.922	3.654	-0.185
C	1.959	1.709	-0.089	H	-2.604	-2.435	-1.851
C	0.793	0.926	-0.022	H	-0.935	2.007	0.735
C	3.327	-0.345	-0.058	H	-0.977	1.678	-0.99
C	0.912	-0.446	0.019	H	-3.465	0.318	3.011
C	2.146	-1.109	0.008	H	-2.996	1.584	1.895
C	1.923	3.17	-0.147	H	-1.034	0.124	2.384
C	-2.637	-2.015	-0.825	H	-1.968	-1.31	1.932
C	-0.677	1.262	-0.022	H	-4.462	-1.023	1.207
C	-3.146	0.5	1.978	H	-5.172	0.589	1.196
C	-1.828	-0.245	1.722	H	-2.128	-0.188	-1.747
C	-4.243	0.034	1.01	H	-3.501	1.819	-1.91
C	-2.468	-0.497	-0.75	H	-3.123	2.276	-0.242
C	-1.361	-0.117	0.267	H	-4.803	2.134	-0.754
C	-3.862	0.198	-0.481	H	-4.691	-0.389	-2.428
C	-3.806	1.693	-0.864	H	-5.903	0.064	-1.22
C	-4.948	-0.454	-1.364	H	-5.109	-1.509	-1.115
C	5.523	-0.662	1.169	H	5.75	0.411	1.198
C	5.464	-0.722	-1.371	H	6.476	-1.204	1.164
C	4.691	-1.028	-0.074	H	4.991	-0.917	2.092
O	0.907	3.856	-0.158	H	5.689	0.348	-1.461
O	-2.822	-2.755	0.122	H	4.889	-1.02	-2.255
O	-0.274	-1.119	0.075	H	6.416	-1.265	-1.384
O	2.197	-2.468	0.059	H	4.514	-2.108	-0.045
H	4.103	1.654	-0.153	H	1.285	-2.804	0.124

Table S14. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound *ent*-**2** at B3LYP/6-31G (d) level in methanol

Conformations	Gibbs free energies (Hartree)	Boltzmann distribution
1	-1078.54	73.18%
2	-1078.54	26.76%

Table S15. Optimized coordinate of compound *ent*-**2** at B3LYP/6-31G (d) level in the methanol

Conformation 1							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.138	1.379	-0.272	H	-2.663	3.933	-0.651
C	-1.849	1.949	-0.298	H	2.491	-2.579	0.574
C	-0.749	1.099	-0.103	H	1.097	1.605	-1.089
C	-3.375	0.015	-0.068	H	1.035	2.134	0.586
C	-0.975	-0.247	0.096	H	3.047	1.685	1.846
C	-2.252	-0.818	0.126	H	3.373	0.534	3.126
C	-1.704	3.387	-0.523	H	1.773	-1.086	2.201
C	2.399	-2.157	-0.447	H	0.955	0.454	2.436
C	0.741	1.327	-0.091	H	5.145	0.436	1.353
C	3.102	0.612	2.067	H	4.308	-1.095	1.543
C	1.733	-0.048	1.849	H	2.125	-0.43	-1.601
C	4.177	-0.059	1.203	H	4.66	-0.969	-2.132
C	2.404	-0.64	-0.561	H	4.957	-1.927	-0.672
C	1.311	-0.054	0.372	H	5.886	-0.452	-0.961
C	3.85	-0.053	-0.311	H	3.699	1.402	-1.94
C	4.894	-0.905	-1.063	H	4.97	1.753	-0.759
C	3.944	1.383	-0.872	H	3.285	2.092	-0.365
C	-5.2	-1.094	1.321	H	-4.605	-1.978	1.572
C	-5.068	-1.529	-1.186	H	-6.257	-1.386	1.315
C	-4.802	-0.519	-0.052	H	-5.059	-0.351	2.114
O	-0.639	3.993	-0.577	H	-4.473	-2.438	-1.057
O	2.317	-2.901	-1.405	H	-4.825	-1.097	-2.163
O	0.157	-0.99	0.272	H	-6.127	-1.814	-1.195
O	-2.398	-2.156	0.336	H	-5.449	0.348	-0.237
H	-3.993	2.034	-0.42	H	-1.513	-2.543	0.462
Conformation 2							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	-3.155	0.917	-0.193	H	-0.924	3.54	-0.504
C	-1.937	1.624	-0.251	H	2.916	-2.385	0.584
C	-0.743	0.902	-0.088	H	0.959	2.134	0.52
C	-3.225	-0.462	0.017	H	1.019	1.563	-1.147
C	-0.809	-0.462	0.119	H	3.427	0.849	3.089
C	-2.014	-1.168	0.181	H	2.971	1.936	1.793
C	-1.929	3.073	-0.477	H	2.02	-0.957	2.194
C	2.763	-1.992	-0.442	H	1.034	0.483	2.408
C	0.719	1.287	-0.13	H	5.197	0.927	1.314
C	3.147	0.879	2.03	H	4.541	-0.688	1.531
C	1.863	0.064	1.826	H	2.294	-0.324	-1.618
C	4.292	0.322	1.174	H	4.872	-0.594	-2.144
C	2.596	-0.485	-0.577	H	6.033	0.089	-0.991

C	1.443	-0.014	0.35	H	5.281	-1.476	-0.663
C	3.966	0.265	-0.339	H	3.163	2.33	-0.429
C	5.099	-0.478	-1.077	H	4.875	2.178	-0.819
C	3.898	1.692	-0.925	H	3.653	1.665	-1.994
C	-5.429	-0.702	1.247	H	-6.357	-1.283	1.304
C	-5.319	-1.093	-1.262	H	-4.903	-0.805	2.202
C	-4.56	-1.196	0.075	H	-5.703	0.353	1.125
O	-2.928	3.766	-0.632	H	-6.25	-1.671	-1.217
O	2.755	-2.753	-1.389	H	-4.718	-1.481	-2.091
O	0.405	-1.073	0.263	H	-5.582	-0.054	-1.493
O	-2.02	-2.513	0.393	H	-4.344	-2.254	0.25
H	-4.069	1.489	-0.318	H	-1.098	-2.81	0.496

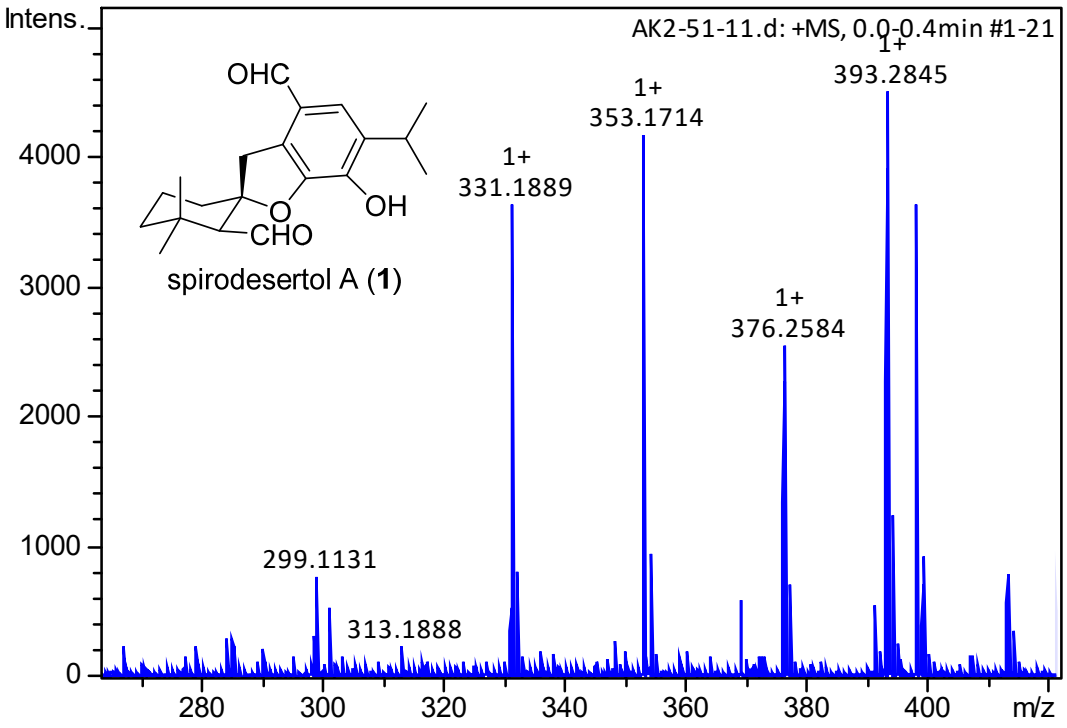


Figure S9. The HRESIMS spectrum of compound **1**

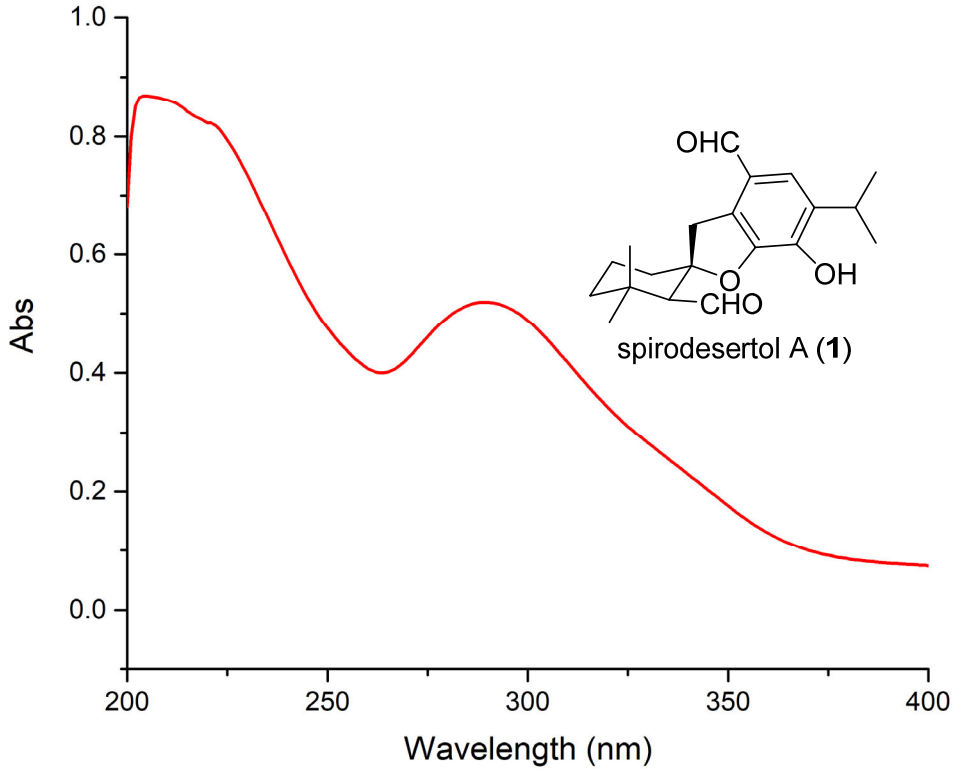


Figure S10. The UV spectrum of compound **1**

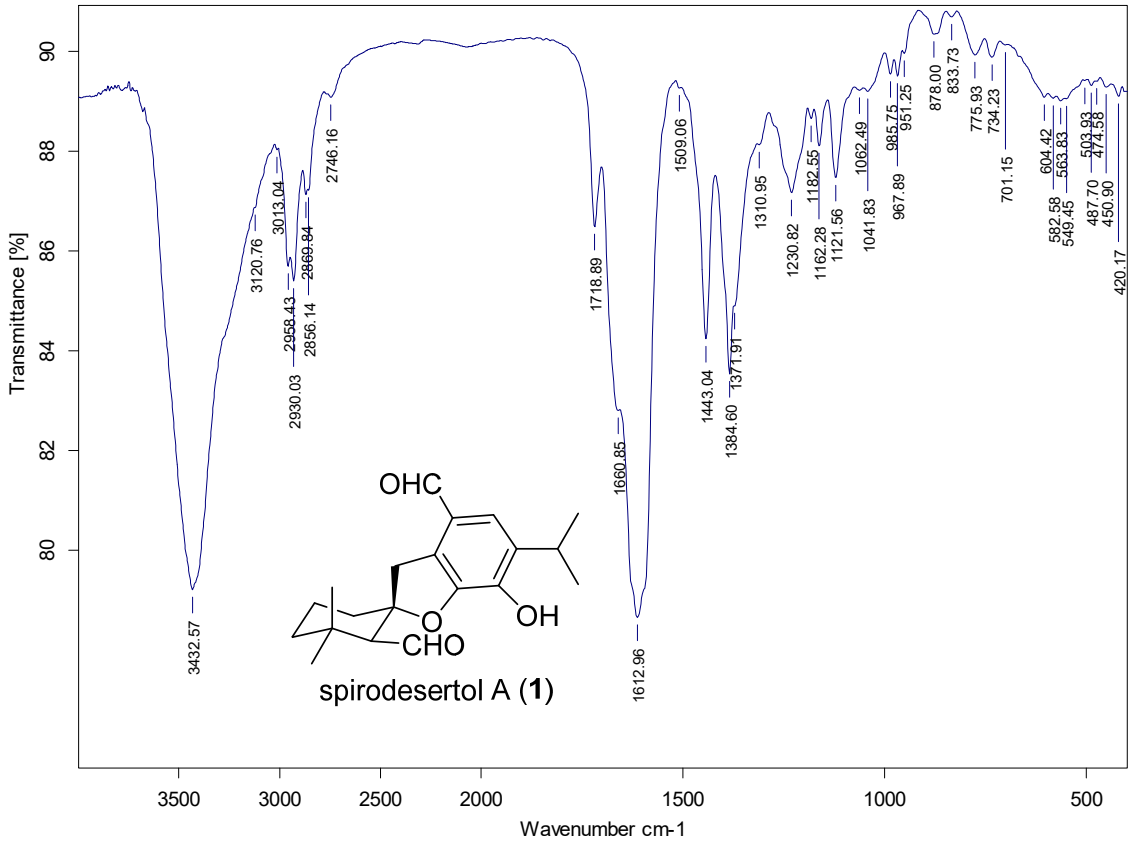


Figure S11. The IR spectrum of compound **1**

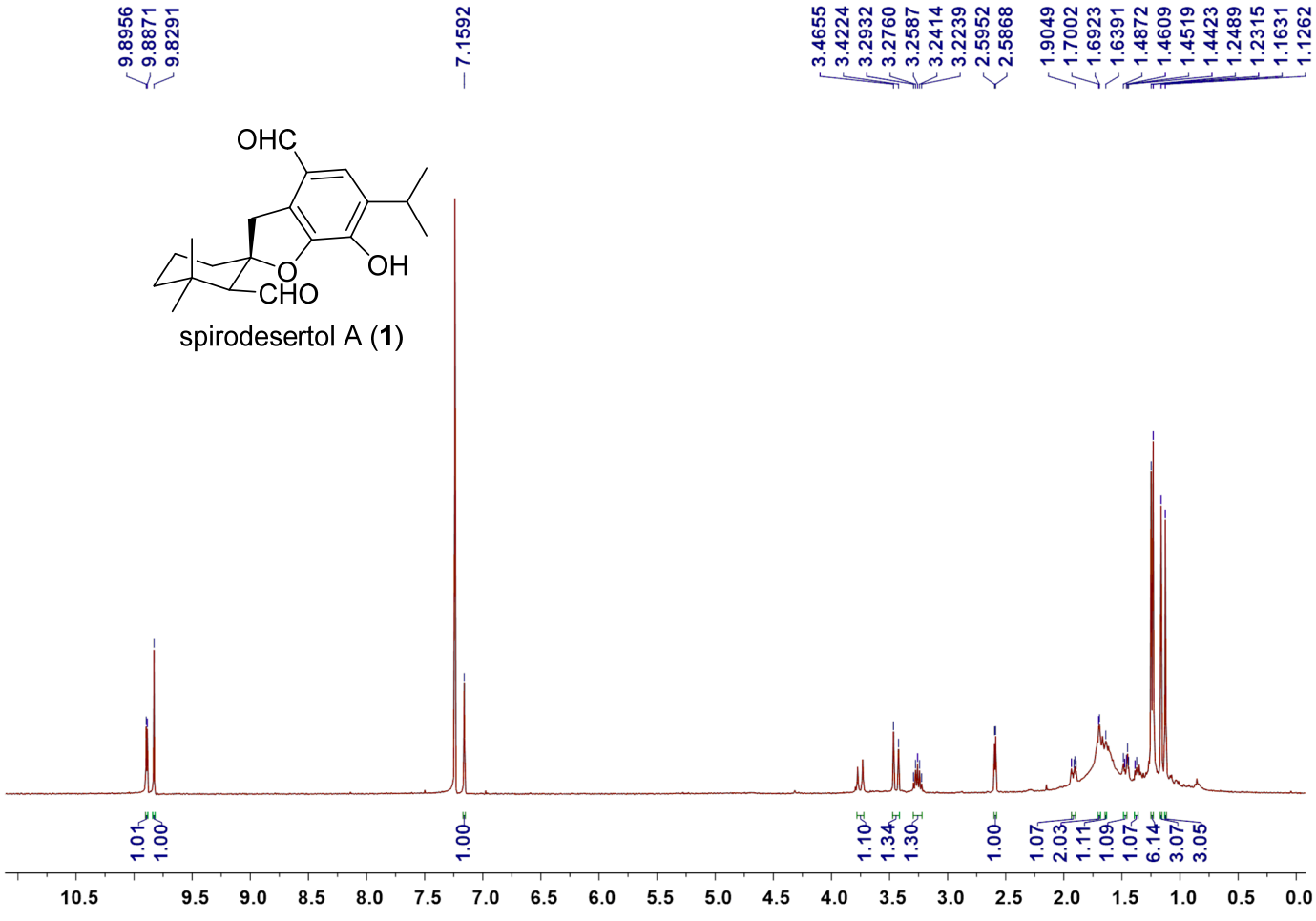


Figure S12. ^{1}H NMR spectrum of compound **1** (400 MHz, chloroform-*d*)

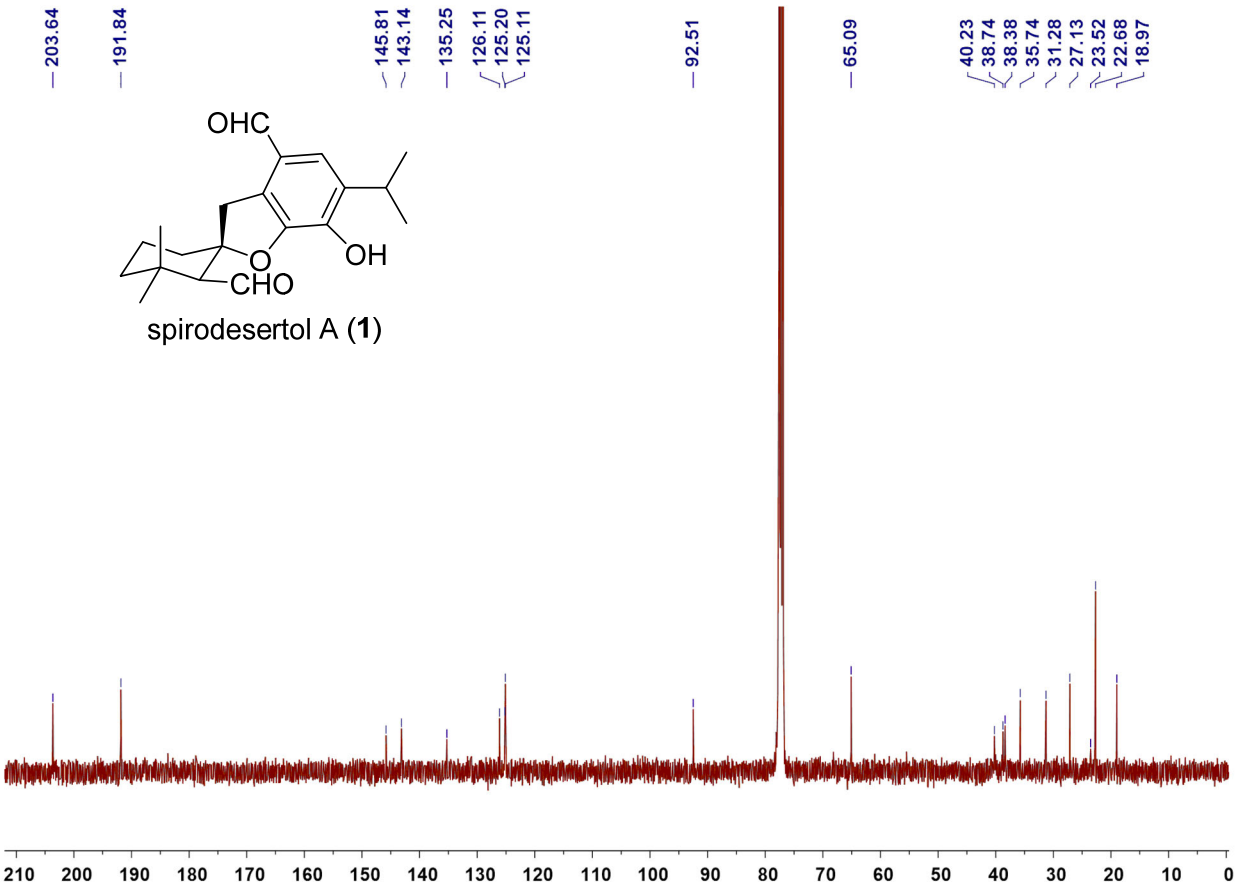


Figure S13. ^{13}C NMR spectrum of compound **1** (100 MHz, chloroform-*d*)

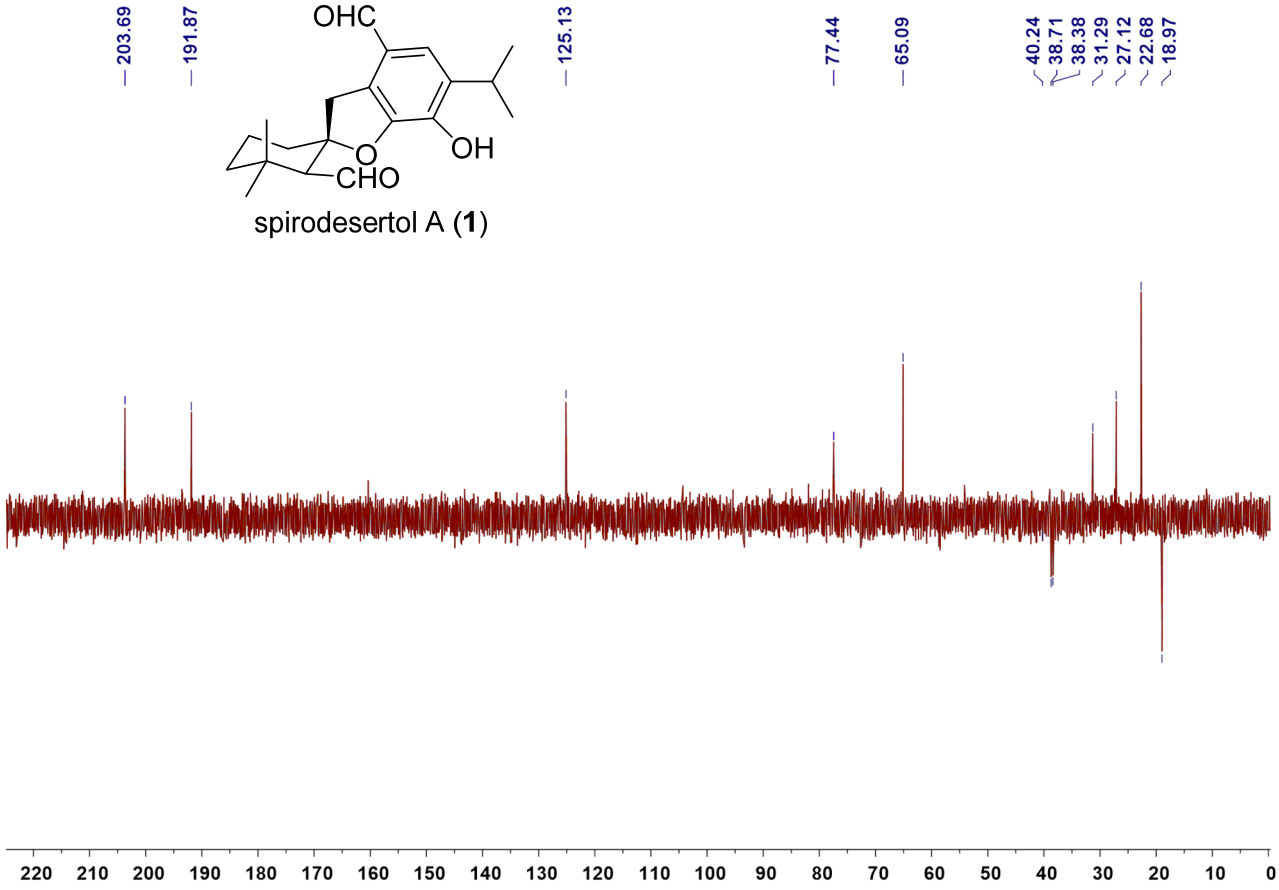


Figure S14. DEPT-135 spectrum of compound **1** (100 MHz, chloroform-*d*)

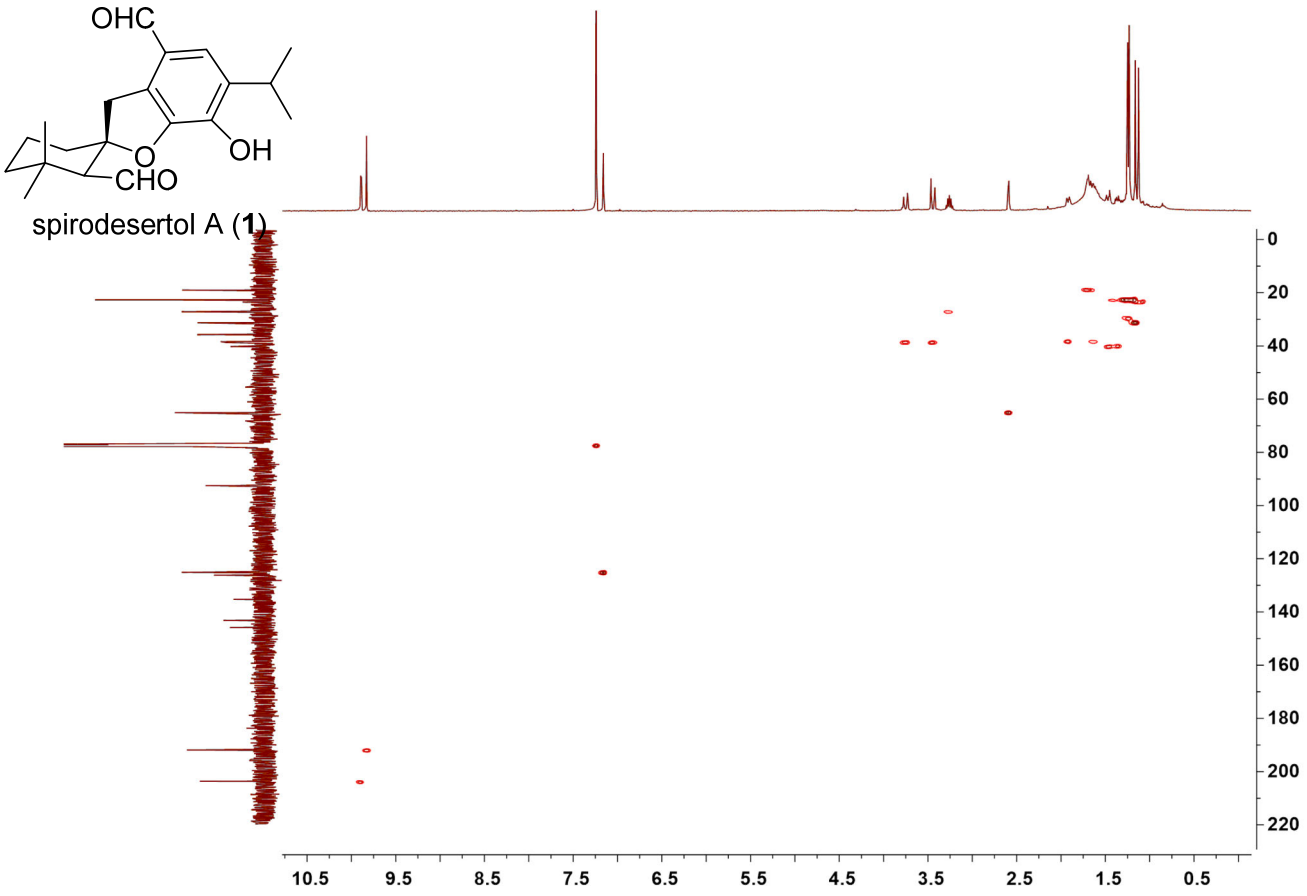


Figure S15. HSQC spectrum of compound **1** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

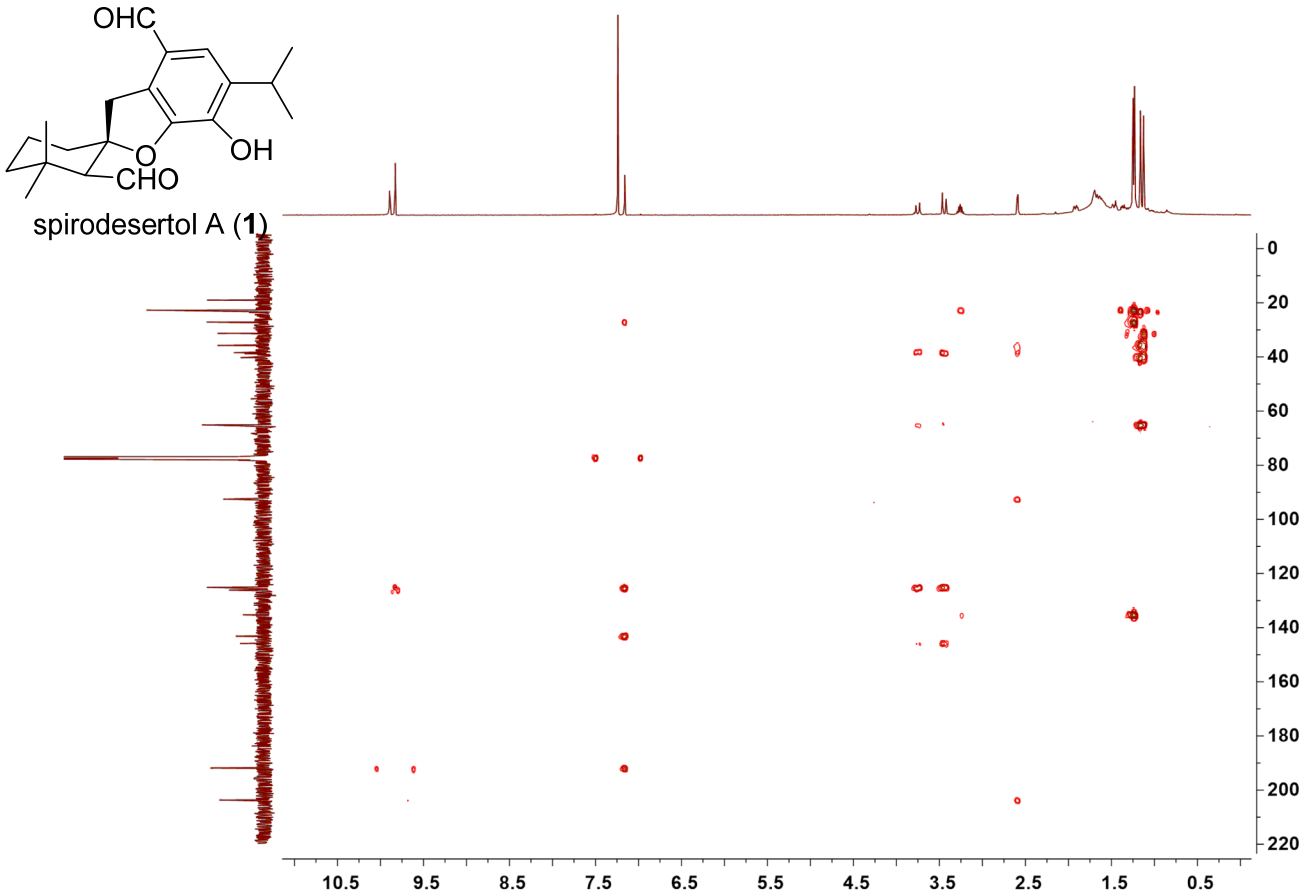


Figure S16. HMBC spectrum of compound **1** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

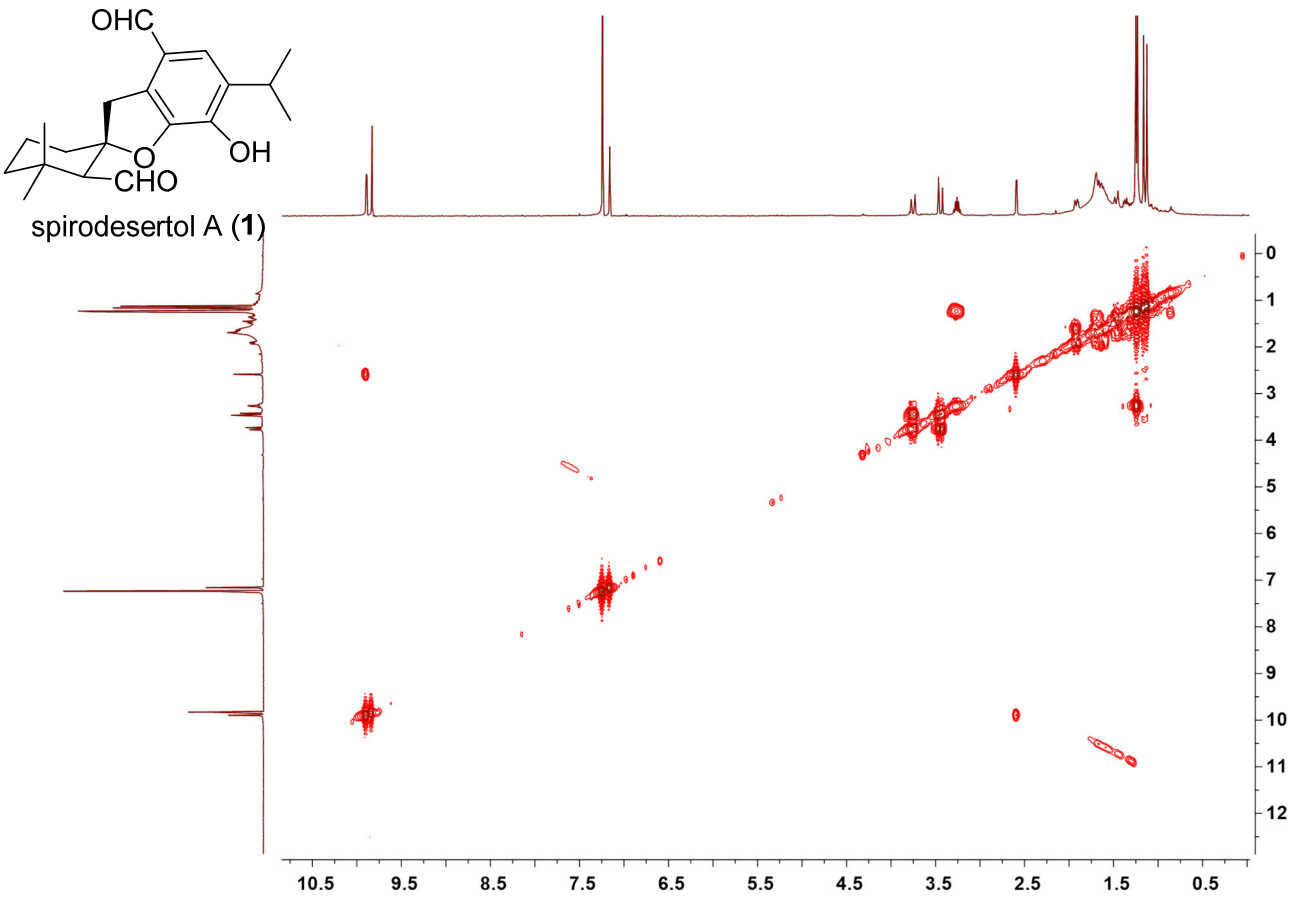


Figure S17. ^{1}H–^{1}H COSY spectrum of compound **1** (400 MHz, chloroform-*d*)

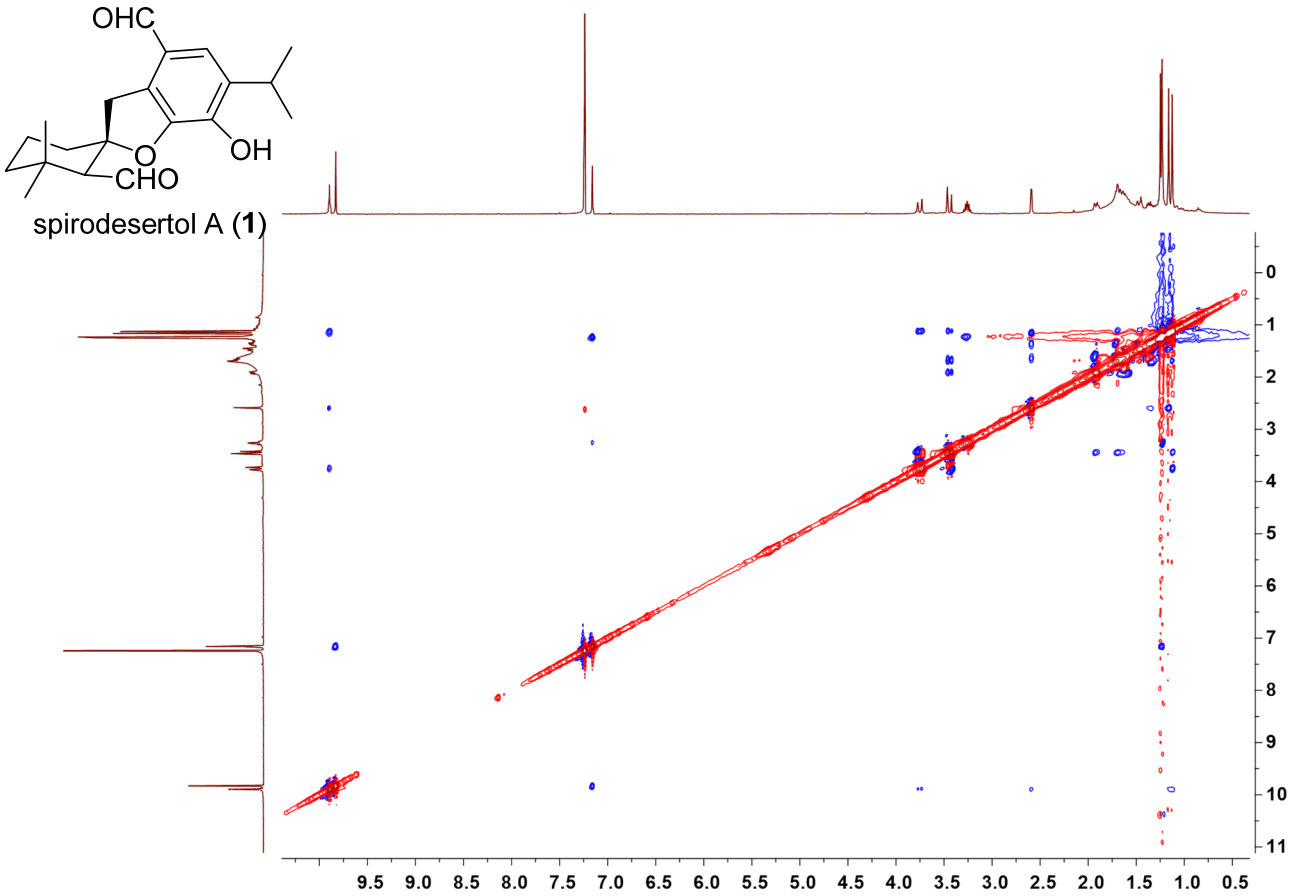


Figure S18. NOESY spectrum of compound **1** (400 MHz, chloroform-*d*)

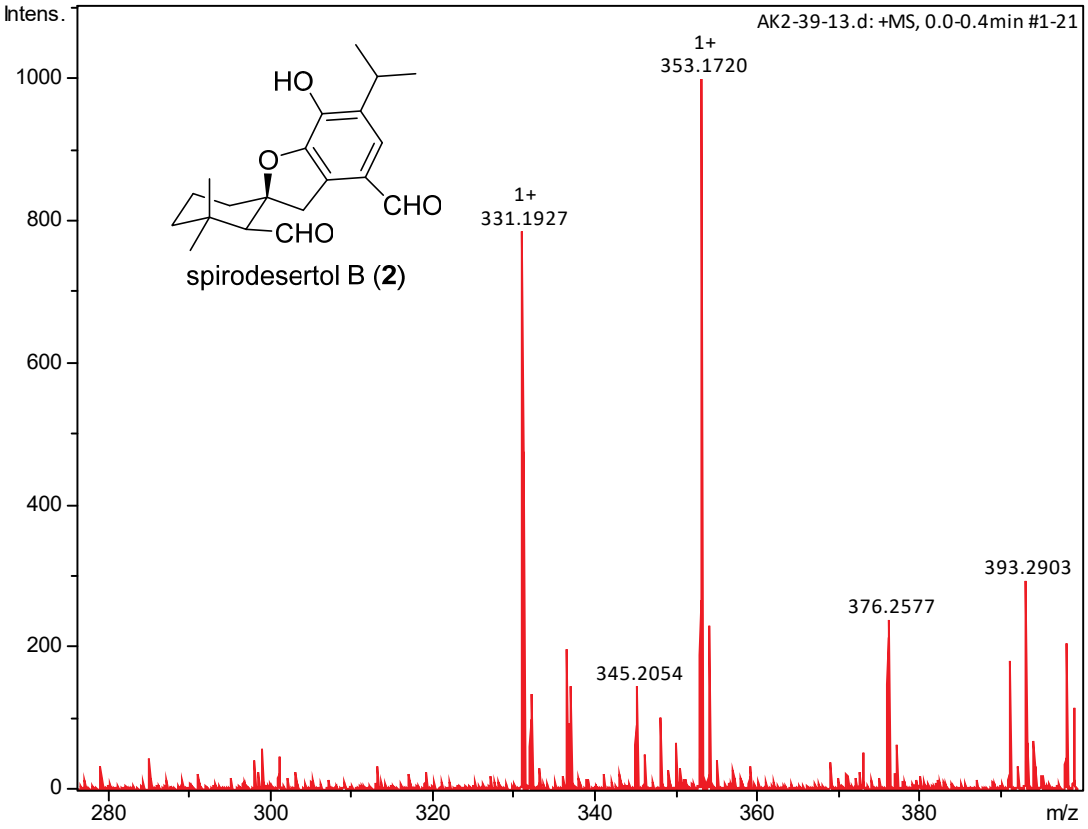


Figure S19. The HRESIMS spectrum of compound **2**

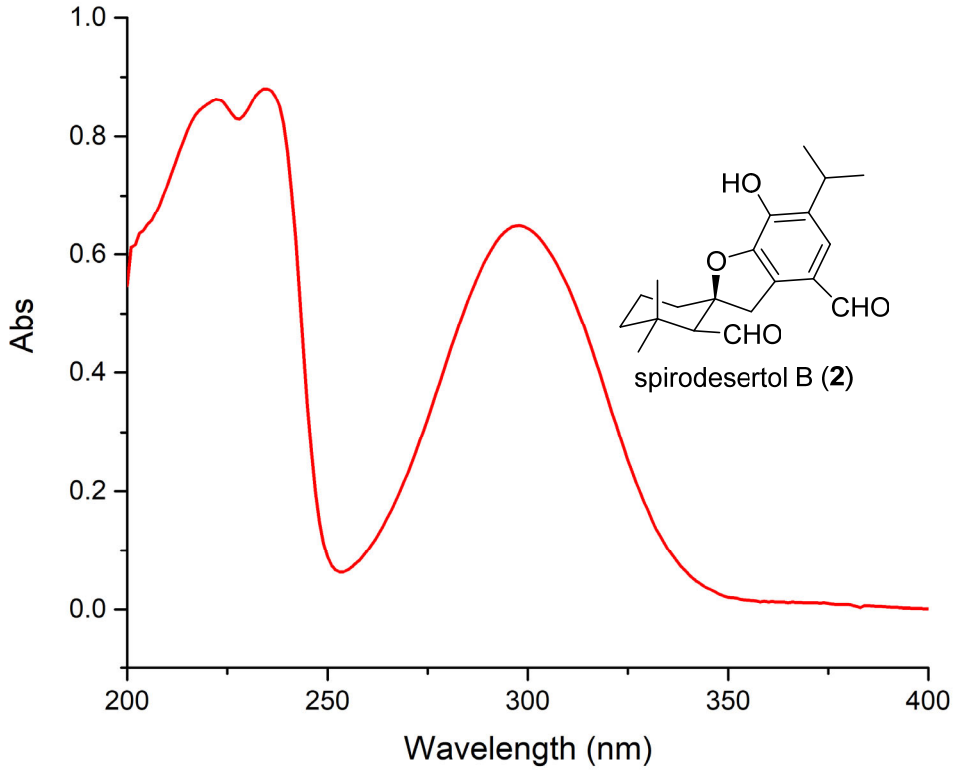


Figure S20. The UV spectrum of compound **2**

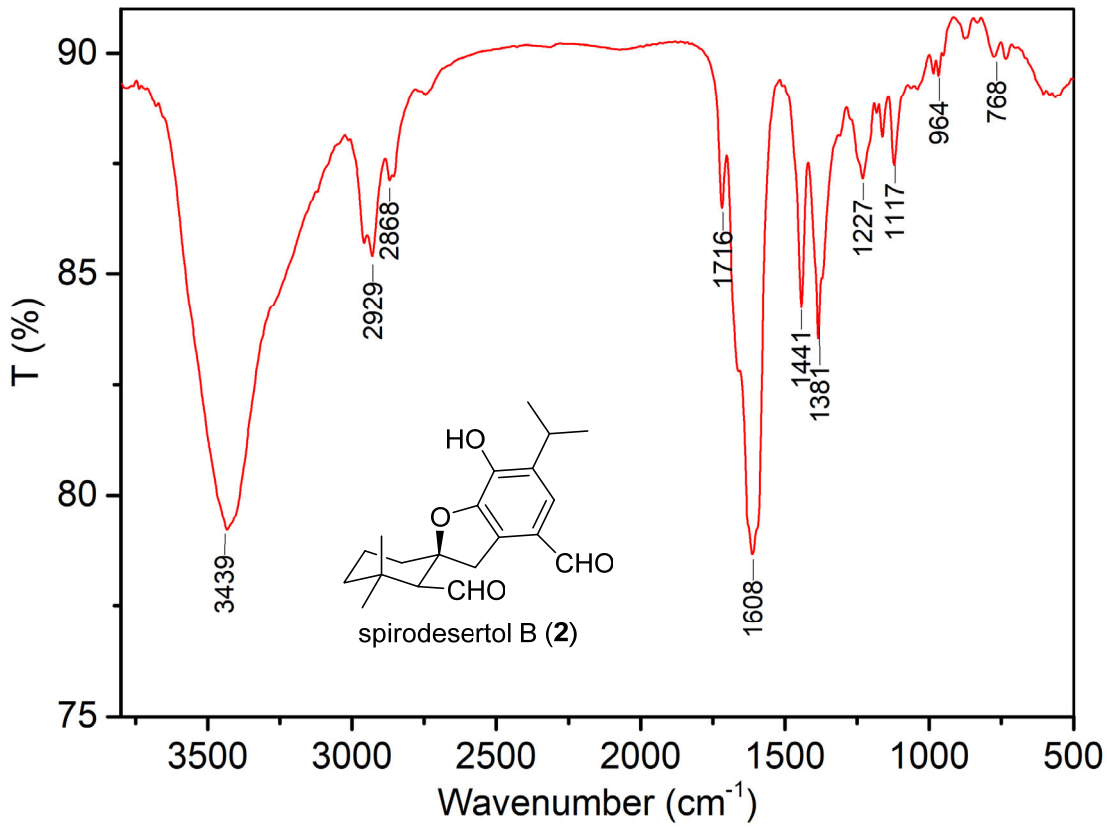


Figure S21. The IR spectrum of compound **2**

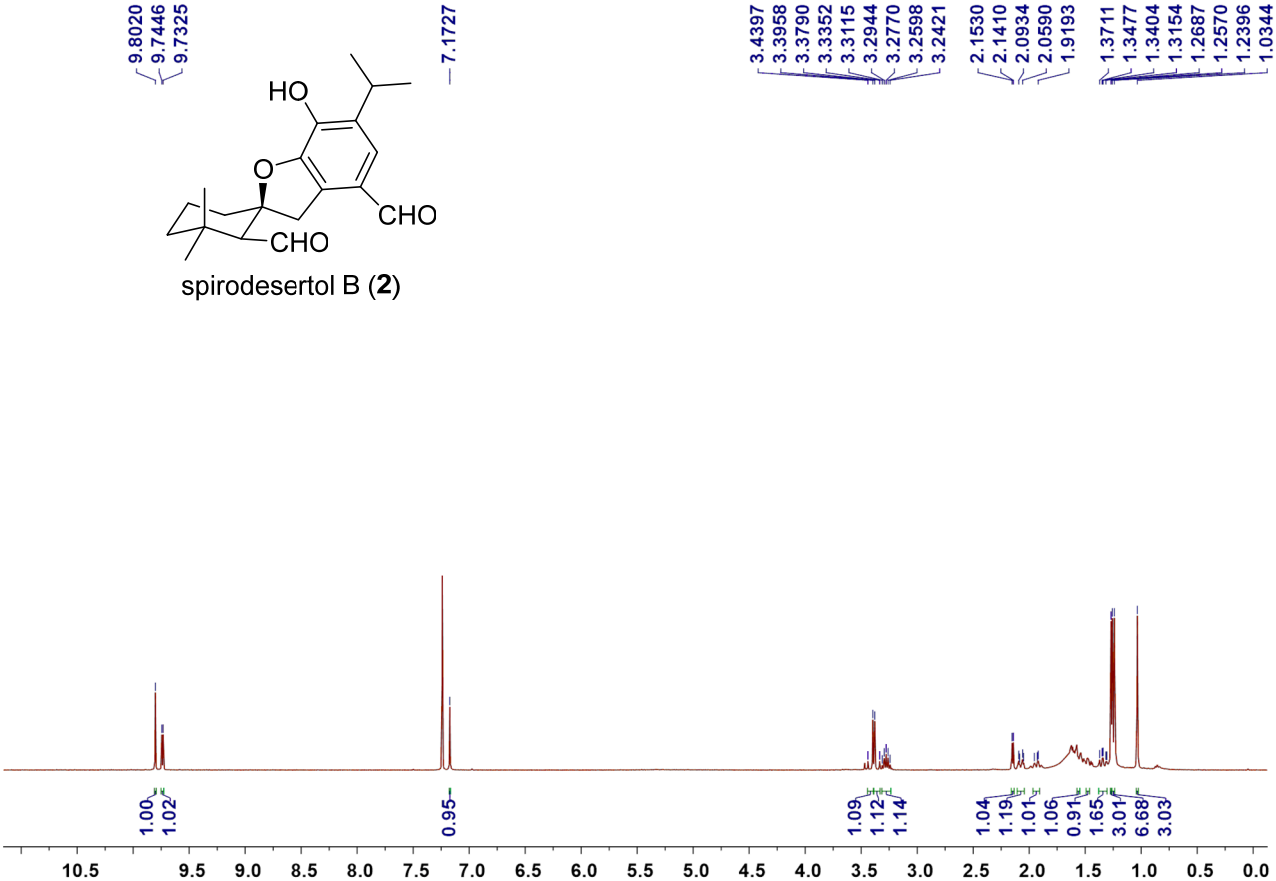


Figure S22. ^{1}H NMR spectrum of compound **2** (400 MHz, chloroform-*d*)

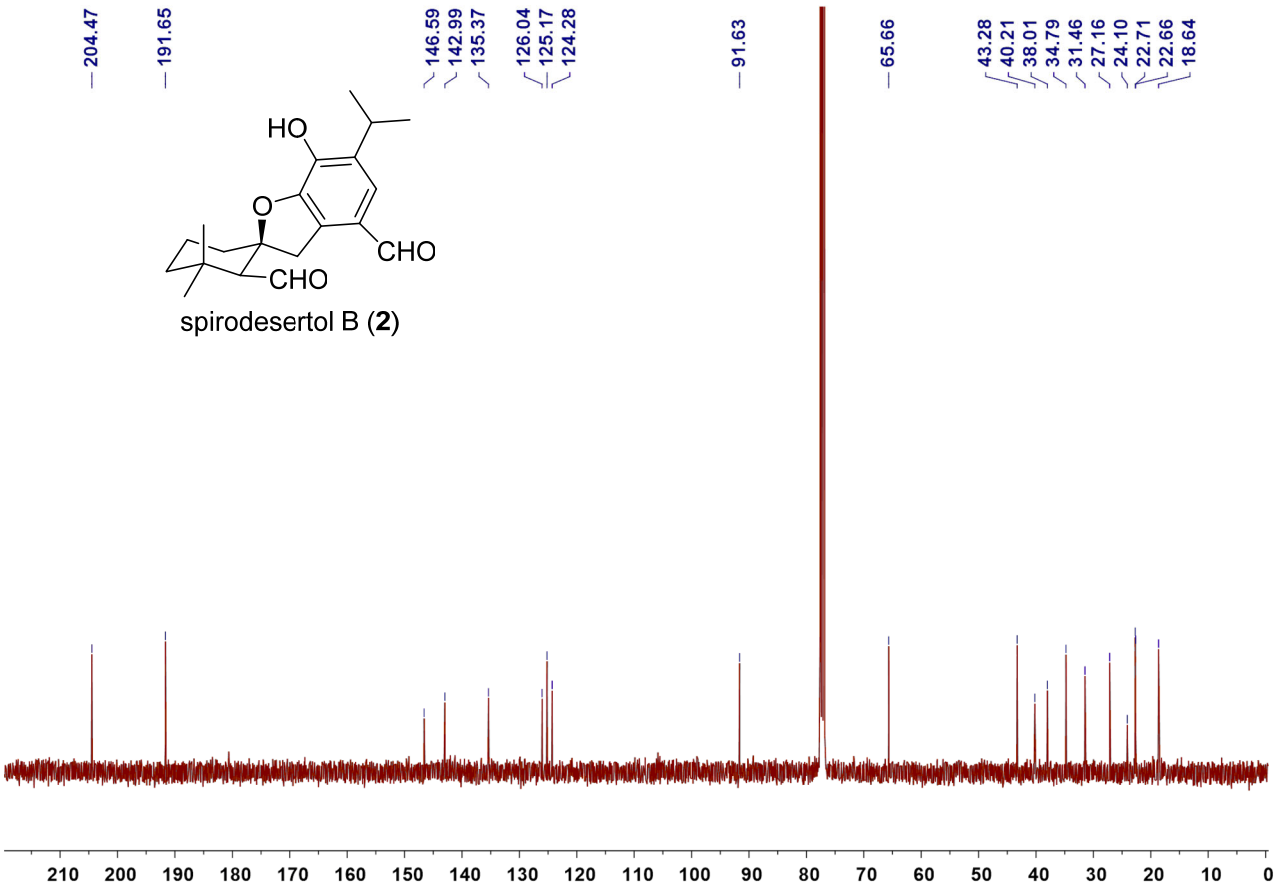


Figure S23. ^{13}C NMR spectrum of compound **2** (100 MHz, chloroform-*d*)

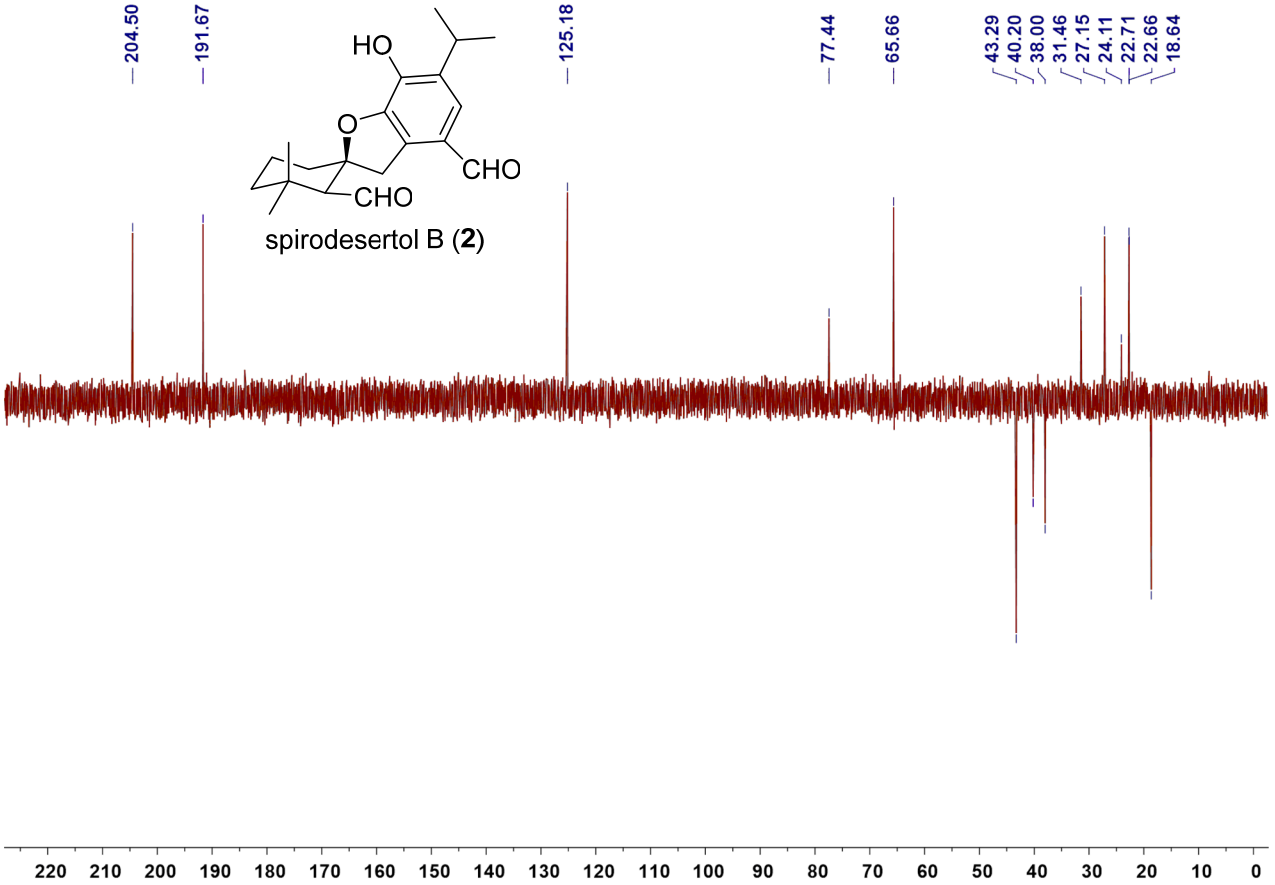


Figure S24. DEPT spectrum of compound **2** (100 MHz, chloroform-*d*)

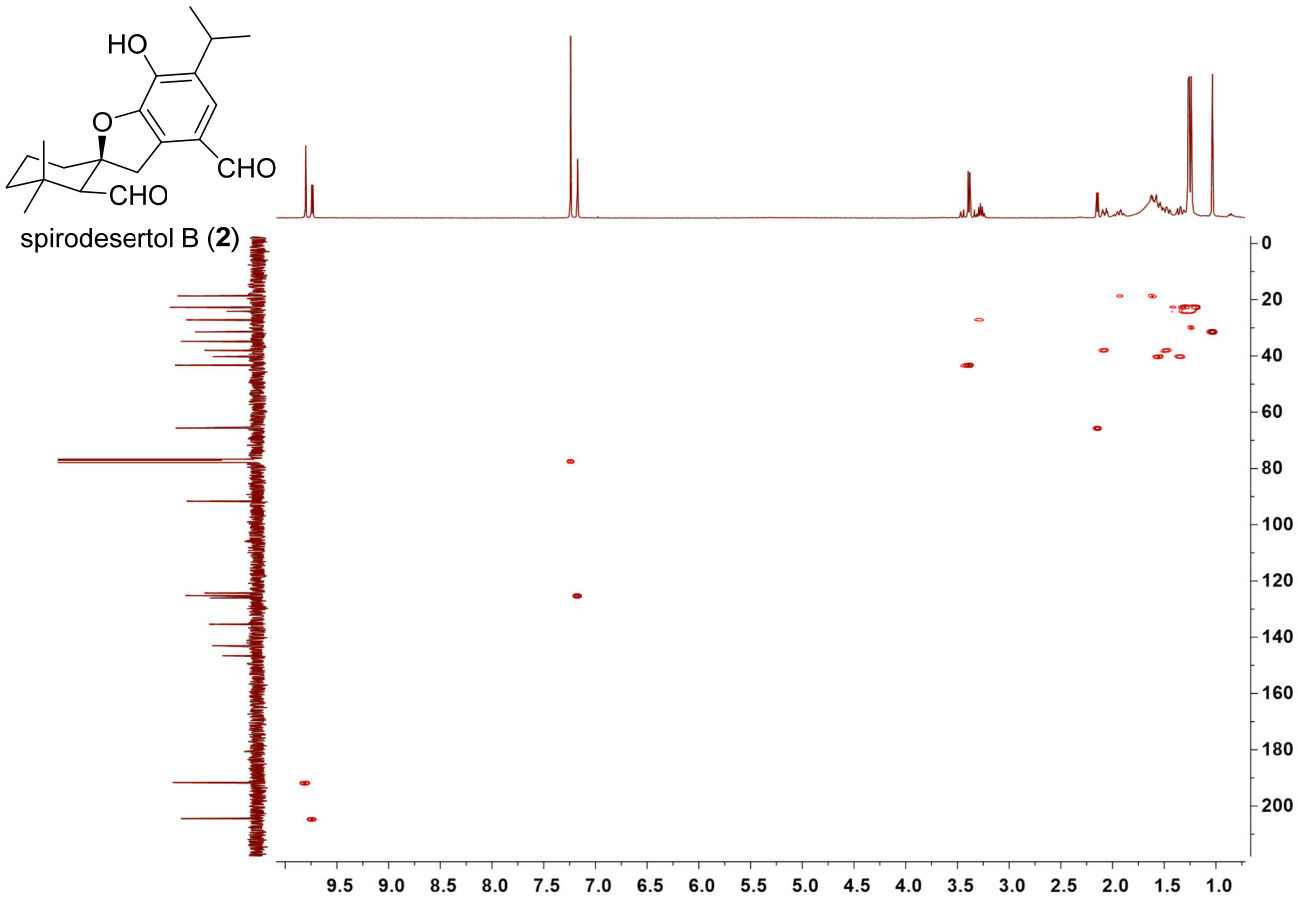


Figure S25. HSQC spectrum of compound **2** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

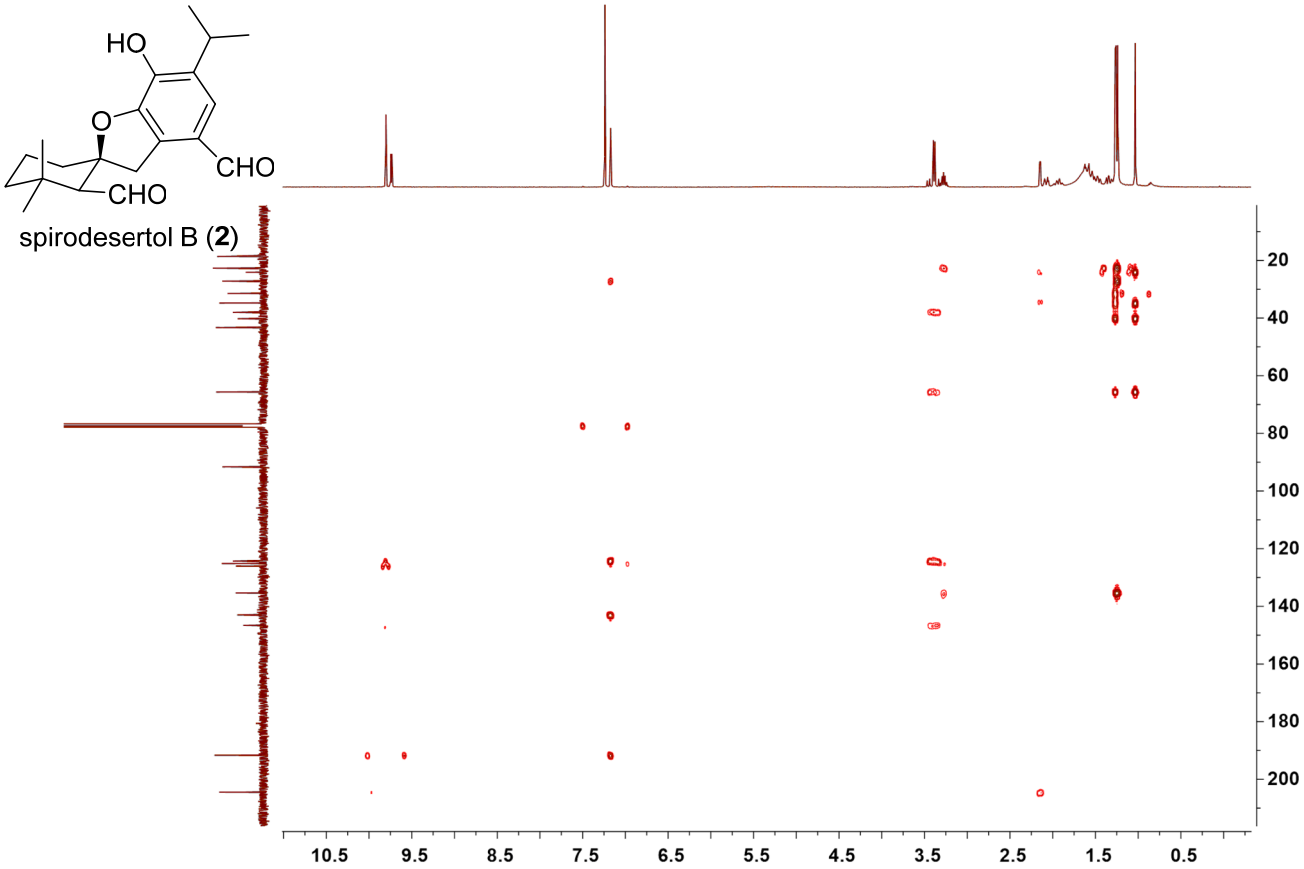


Figure S26. HMBC spectrum of compound **2** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

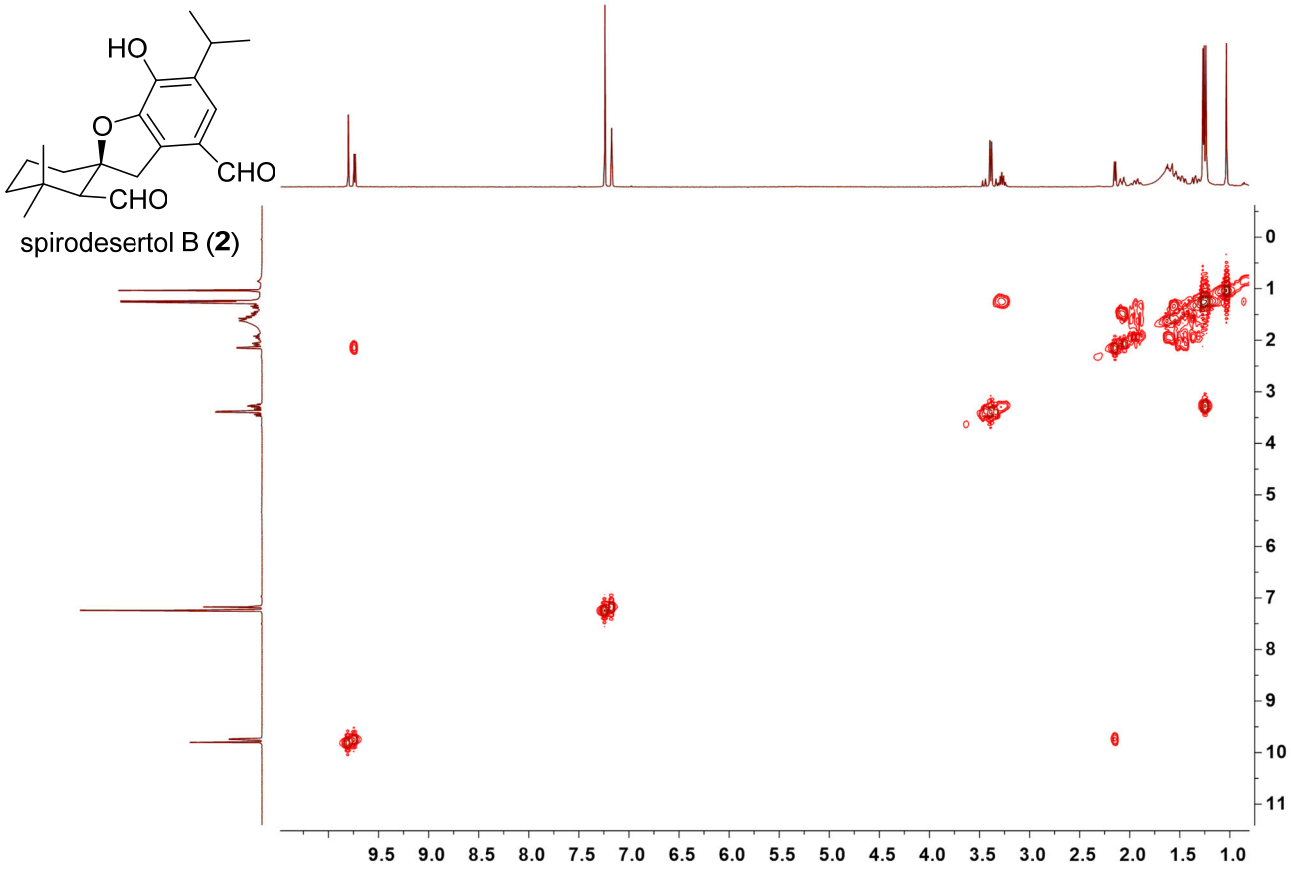


Figure S27. $^{1}H–^{1}H$ COSY spectrum of compound **2** (400 MHz, chloroform-*d*)

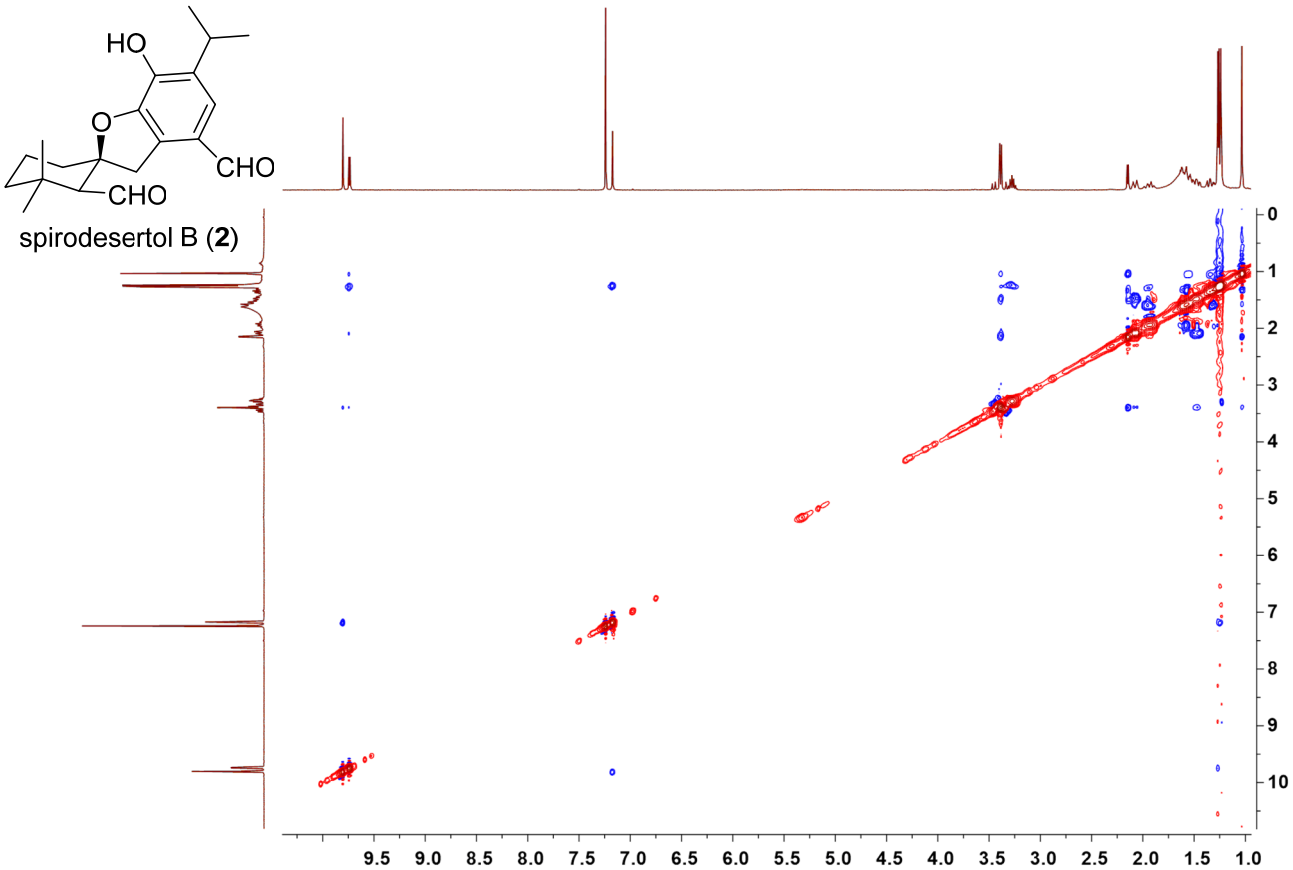


Figure S28. NOESY spectrum of compound **2** (400 MHz, chloroform-*d*)

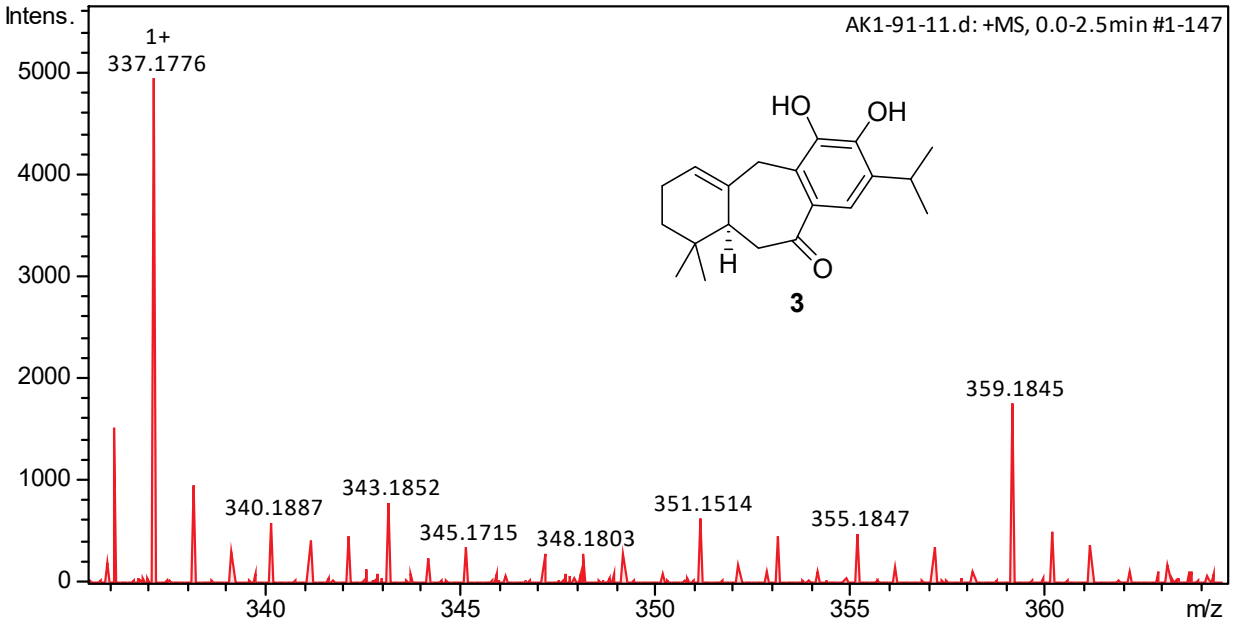


Figure S29. The HRESIMS spectrum of compound **3**

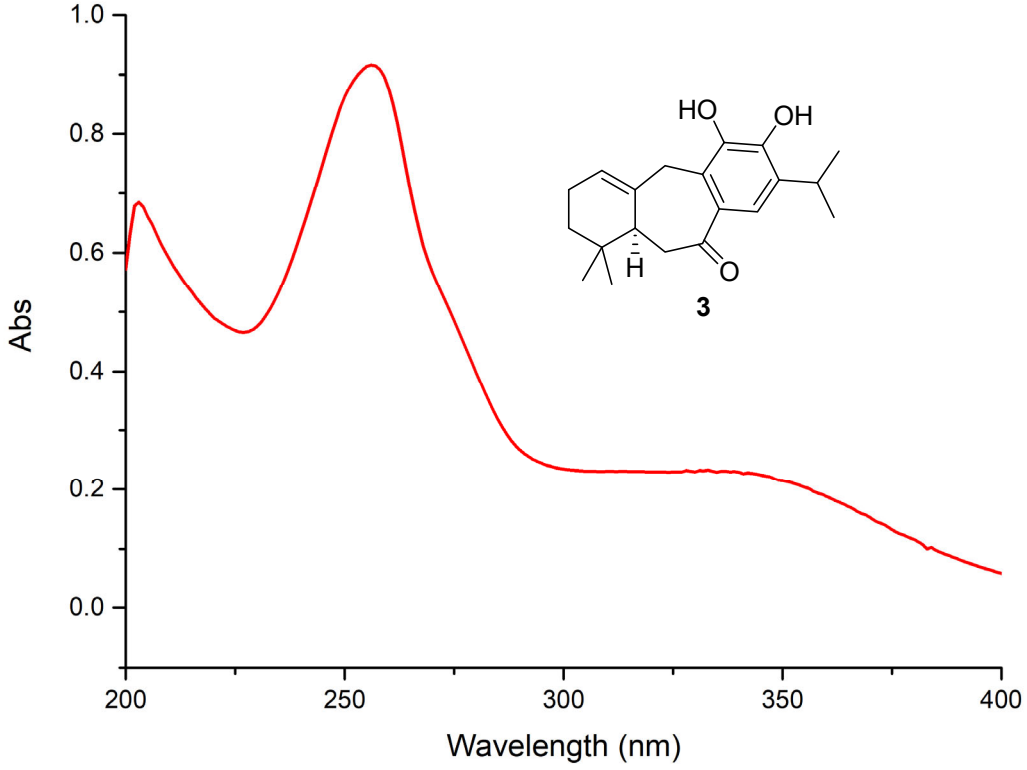


Figure S30. The UV spectrum of compound **3**

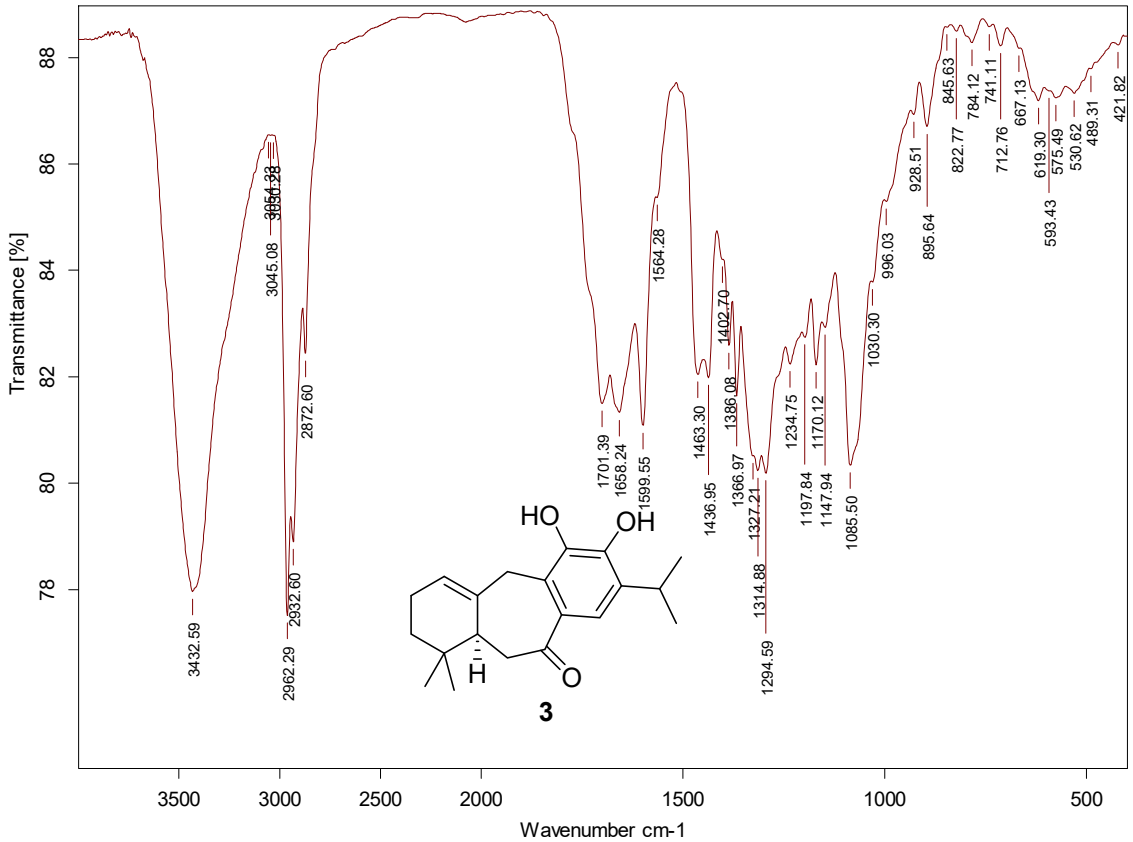


Figure S31. The IR spectrum of compound **3**

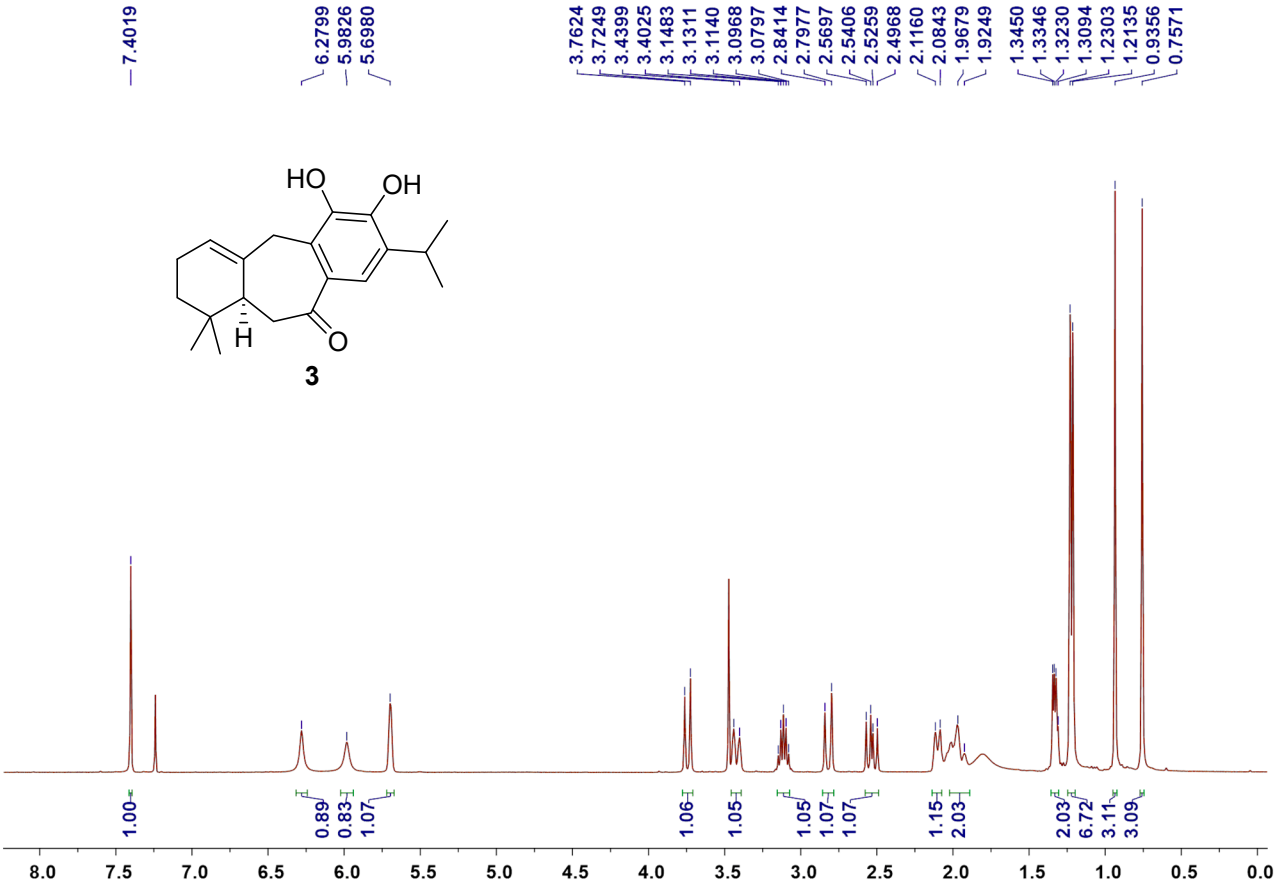


Figure S32. ^{1}H NMR spectrum of compound **3** (400 MHz, chloroform-*d*)

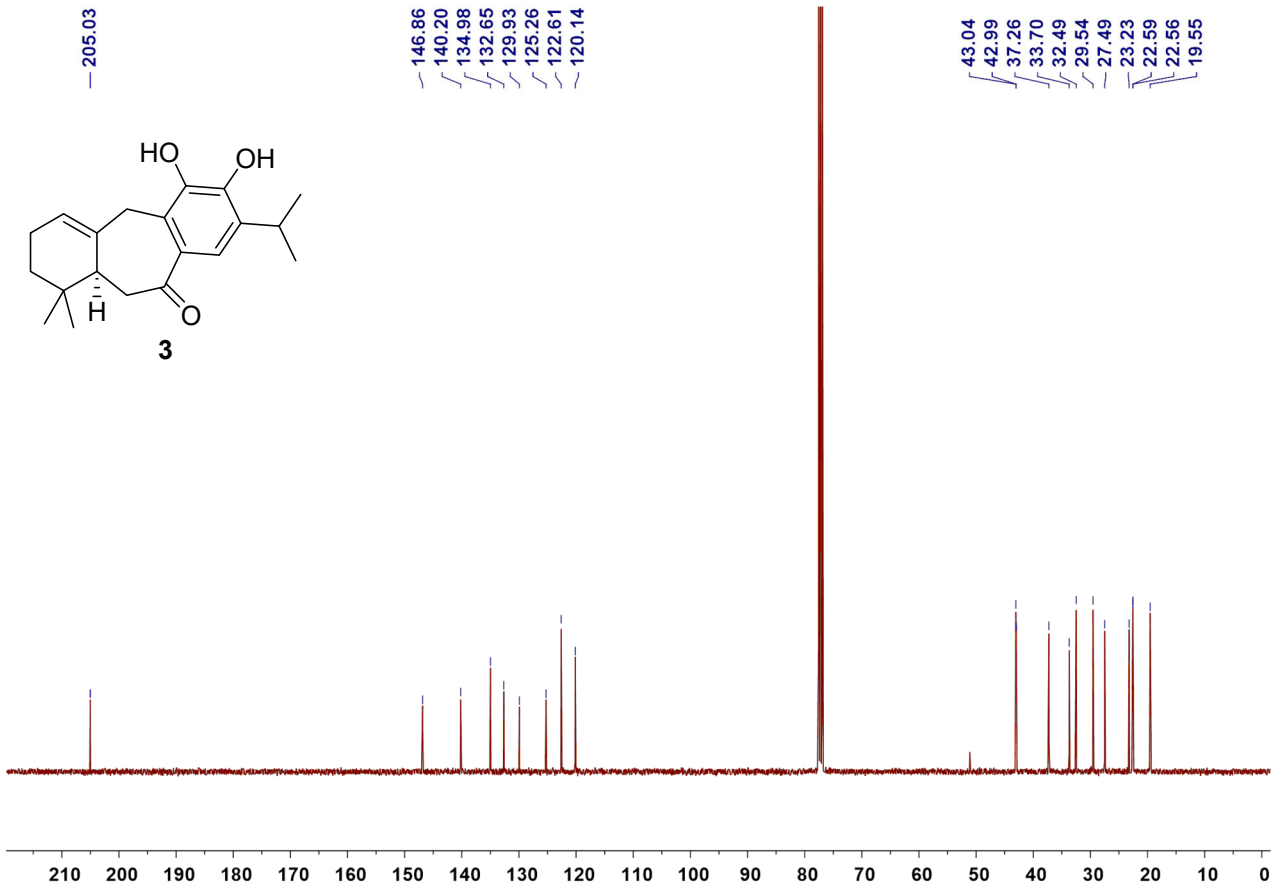


Figure S33. ^{13}C NMR spectrum of compound **3** (100 MHz, chloroform-*d*)

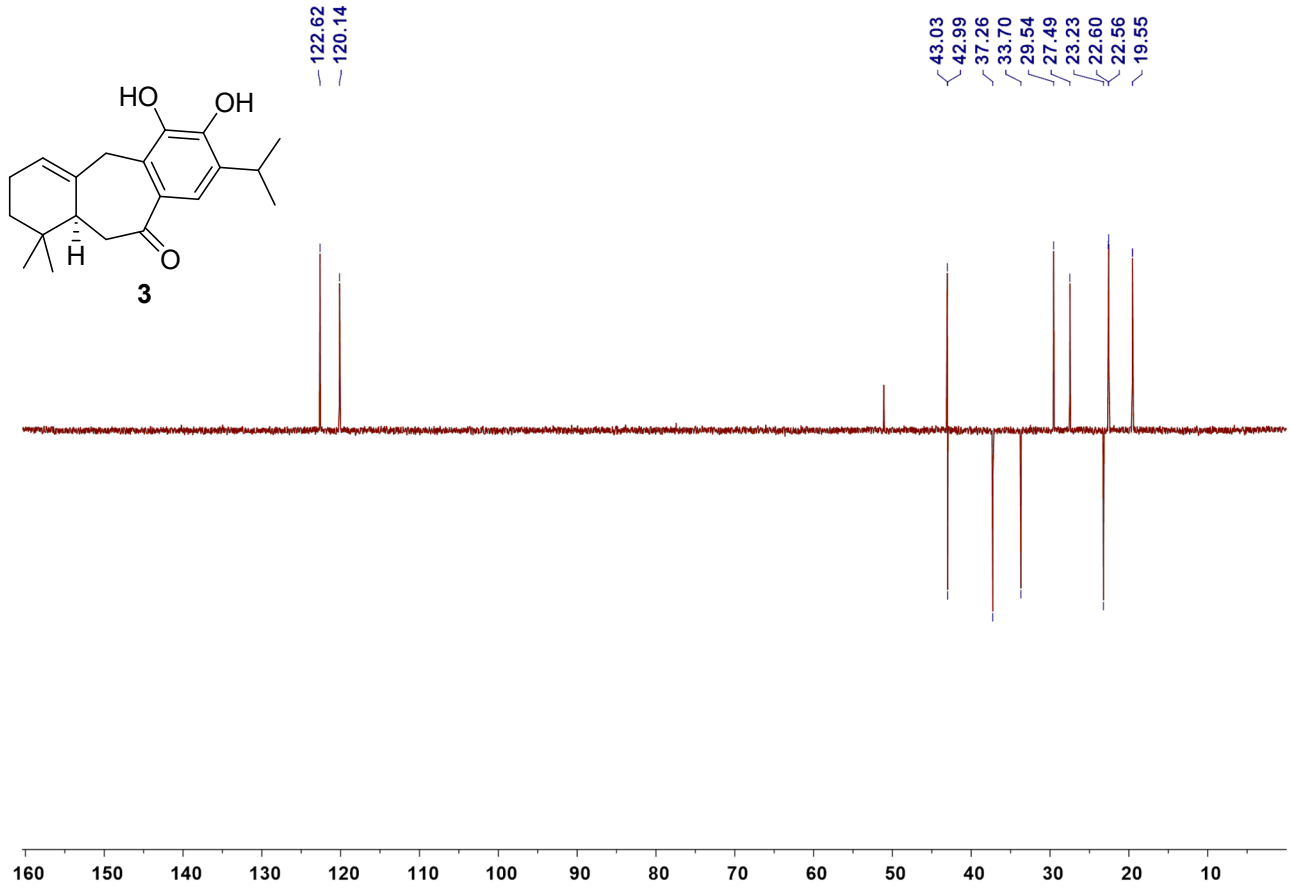


Figure S34. DEPT-135 spectrum of compound **3** (100 MHz, chloroform-*d*)

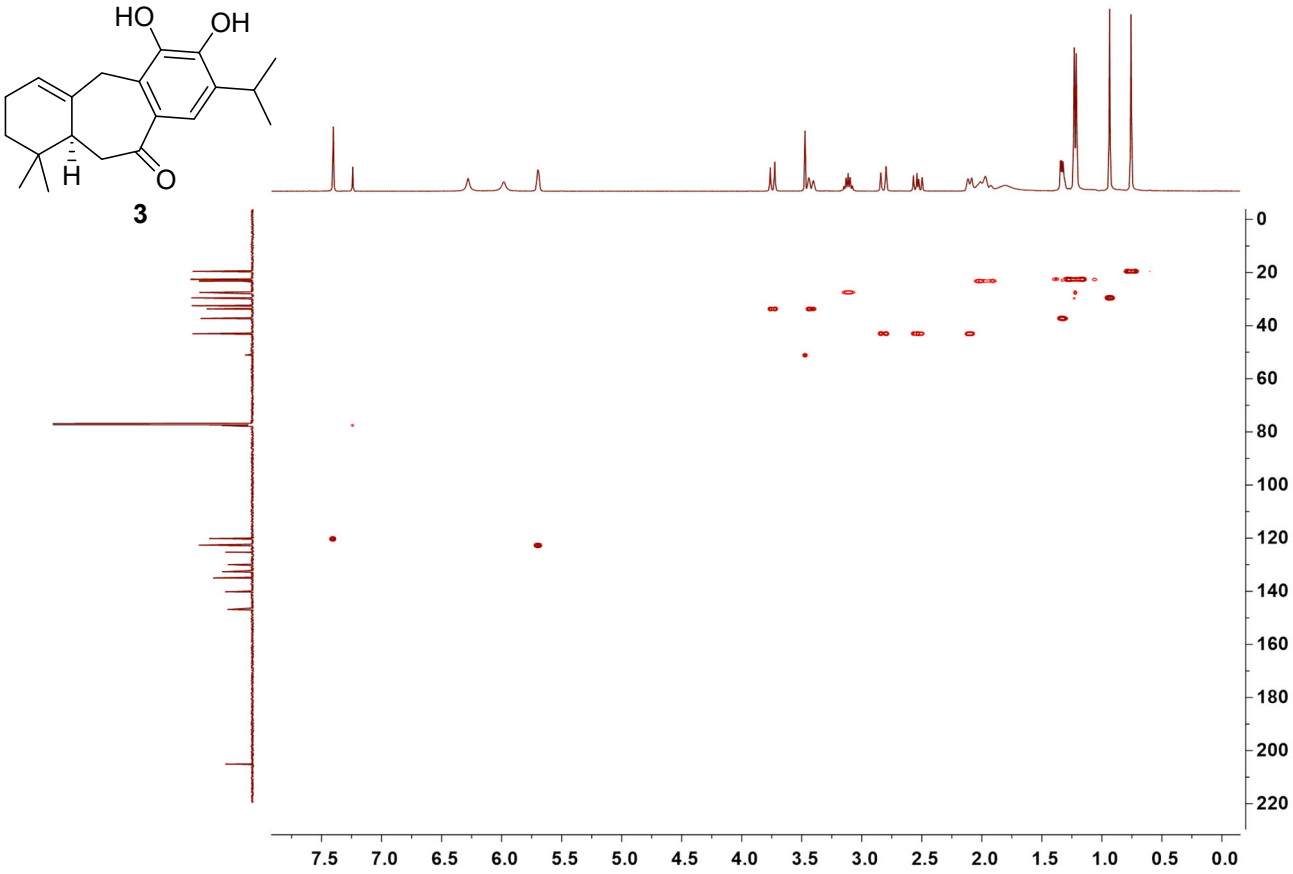


Figure S35. HSQC spectrum of compound **3** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

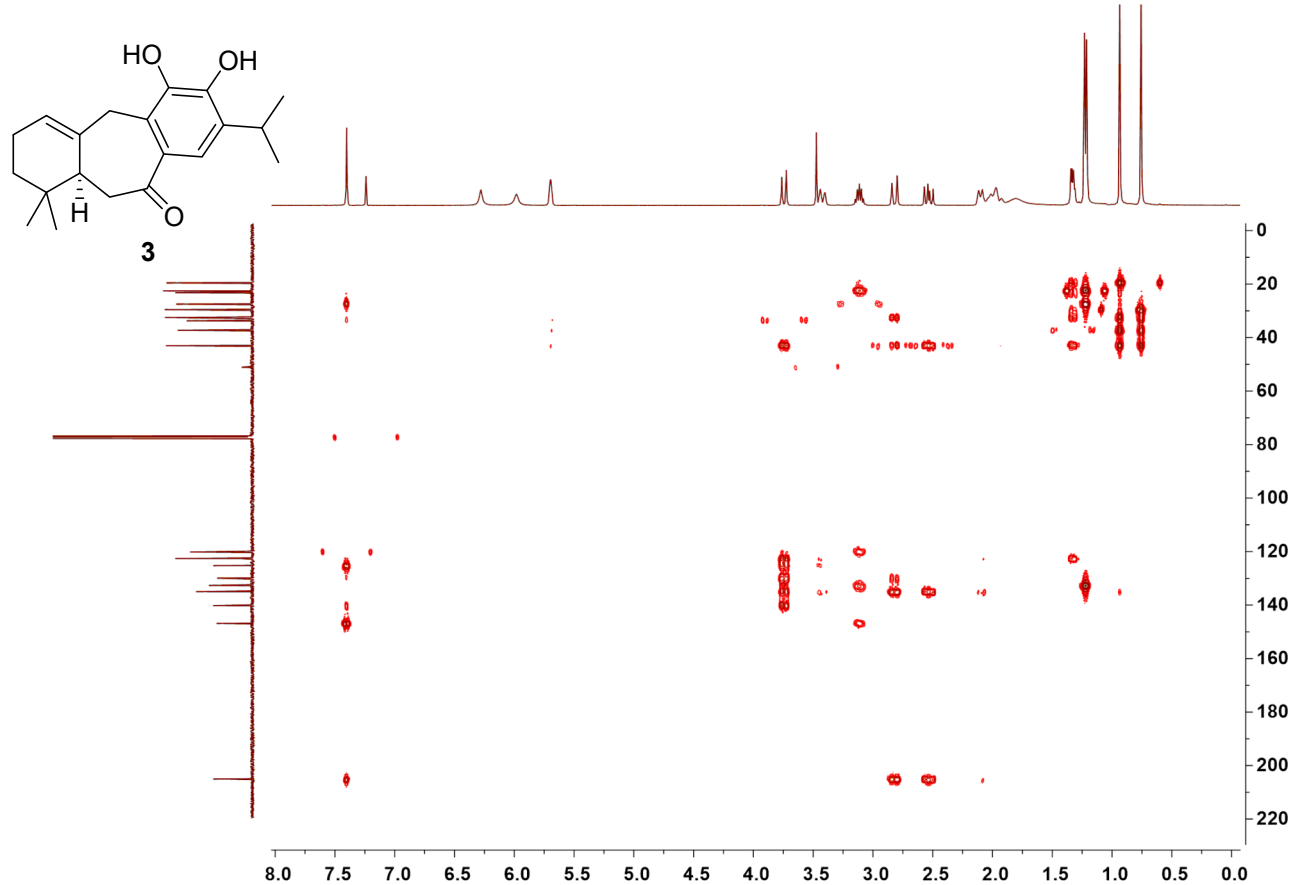


Figure S36. HMBC spectrum of compound **3** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

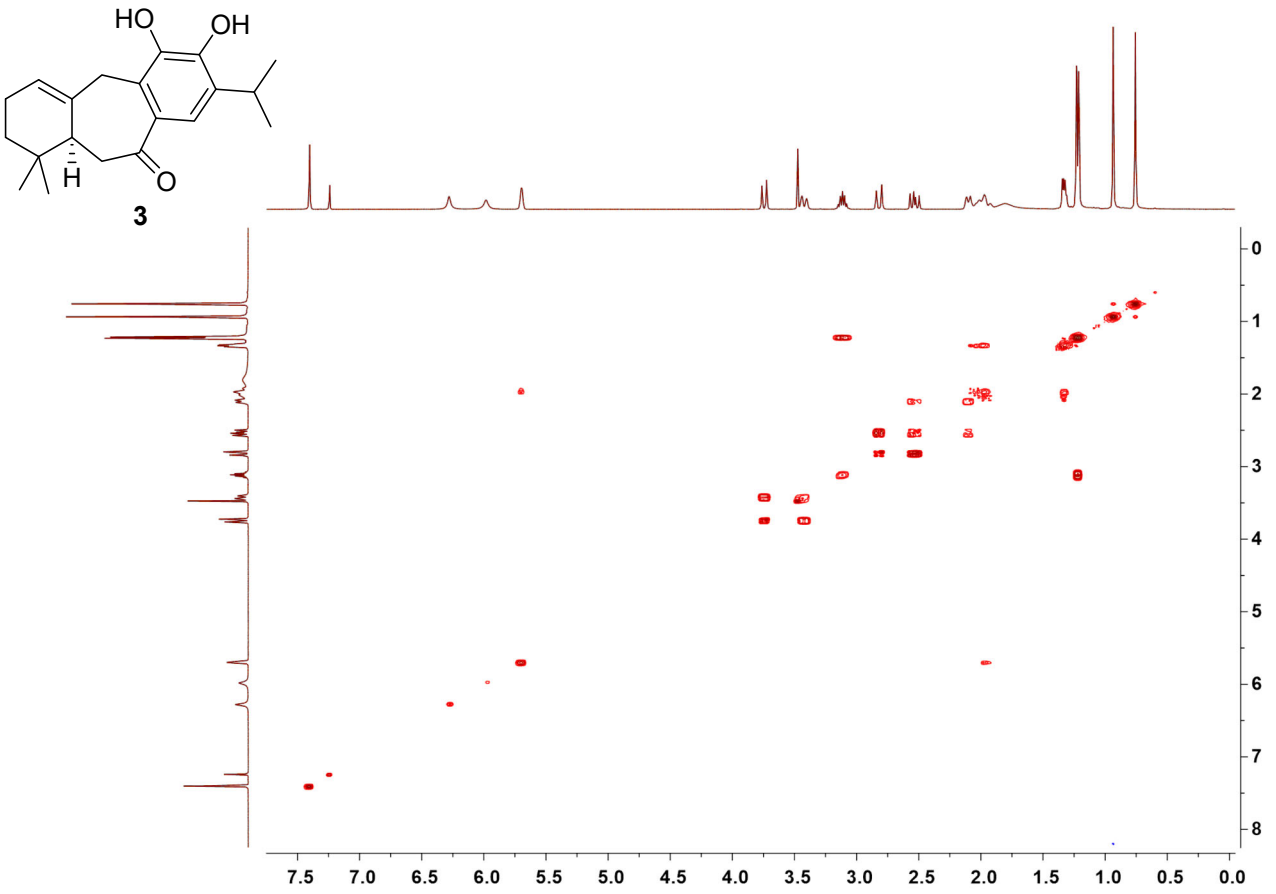


Figure S37. ^{1}H–^{1}H COSY spectrum of compound **3** (400 MHz, chloroform-*d*)

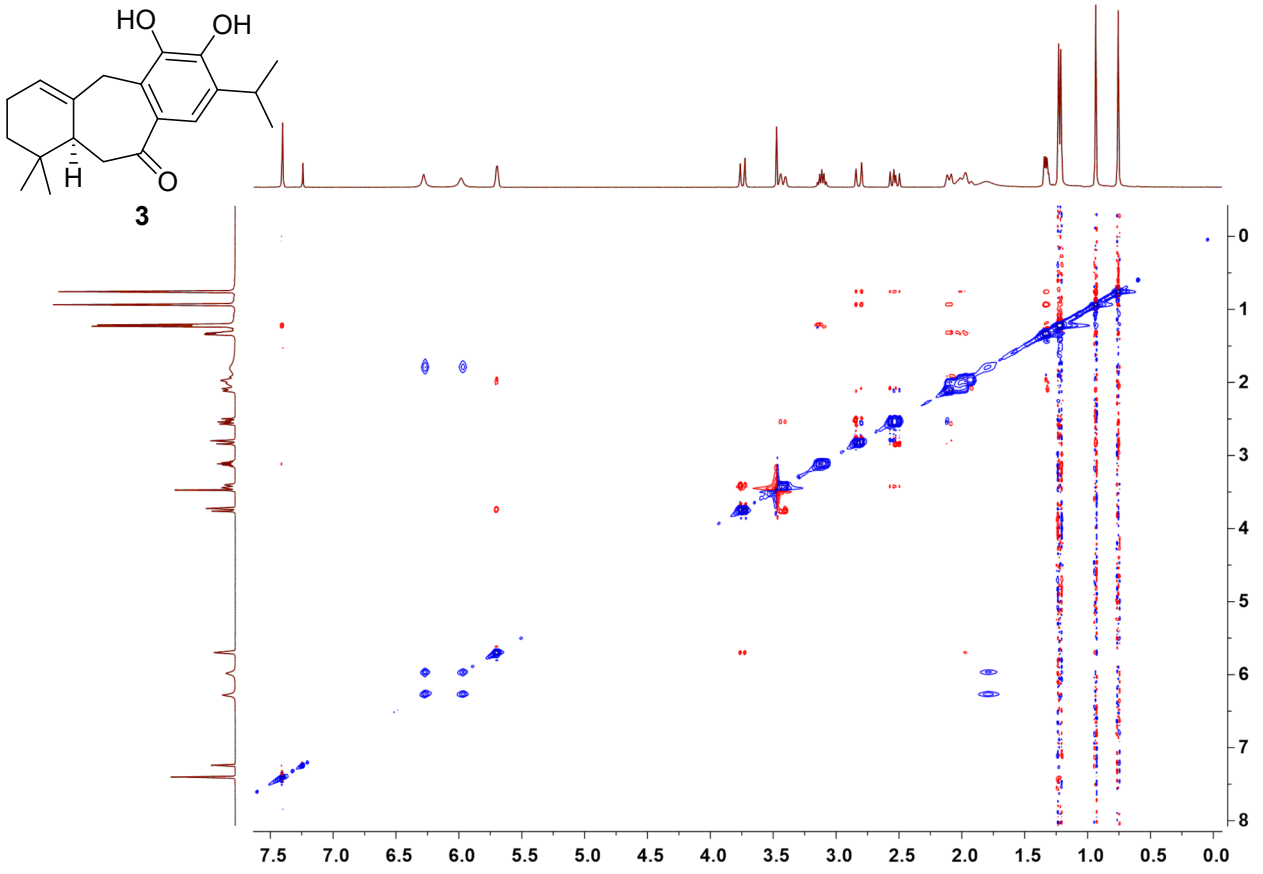


Figure S38. NOESY spectrum of compound **3** (400 MHz, chloroform-*d*)

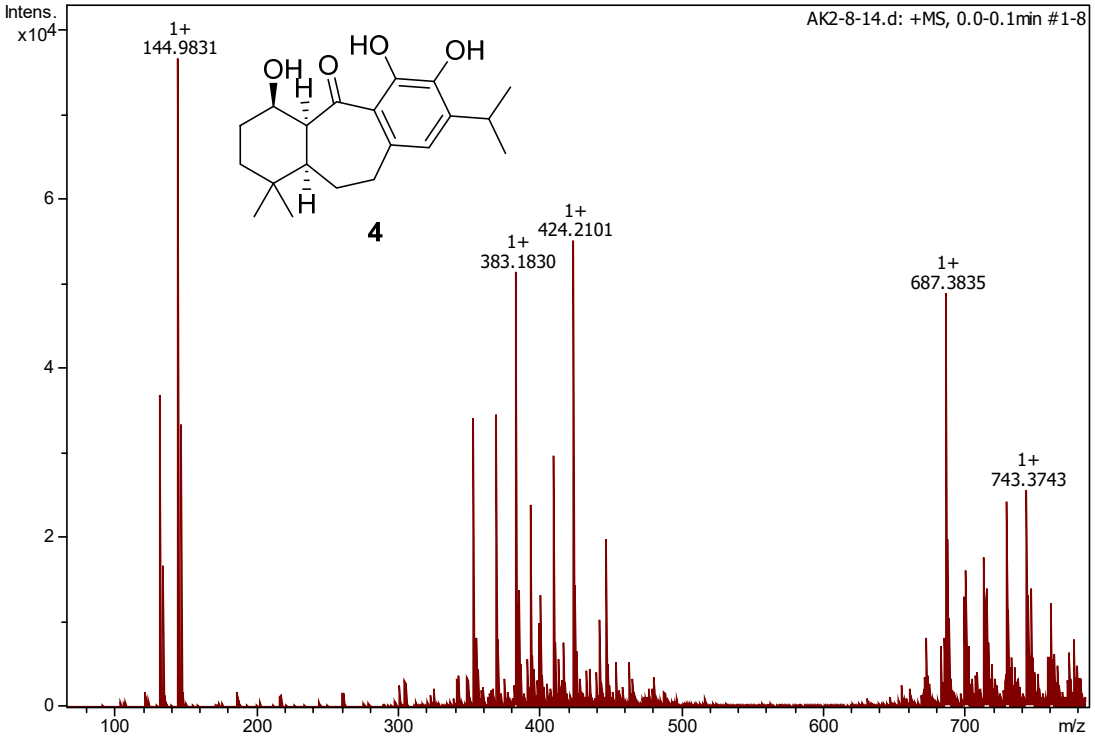


Figure S39. The HRESIMS spectrum of compound **4**

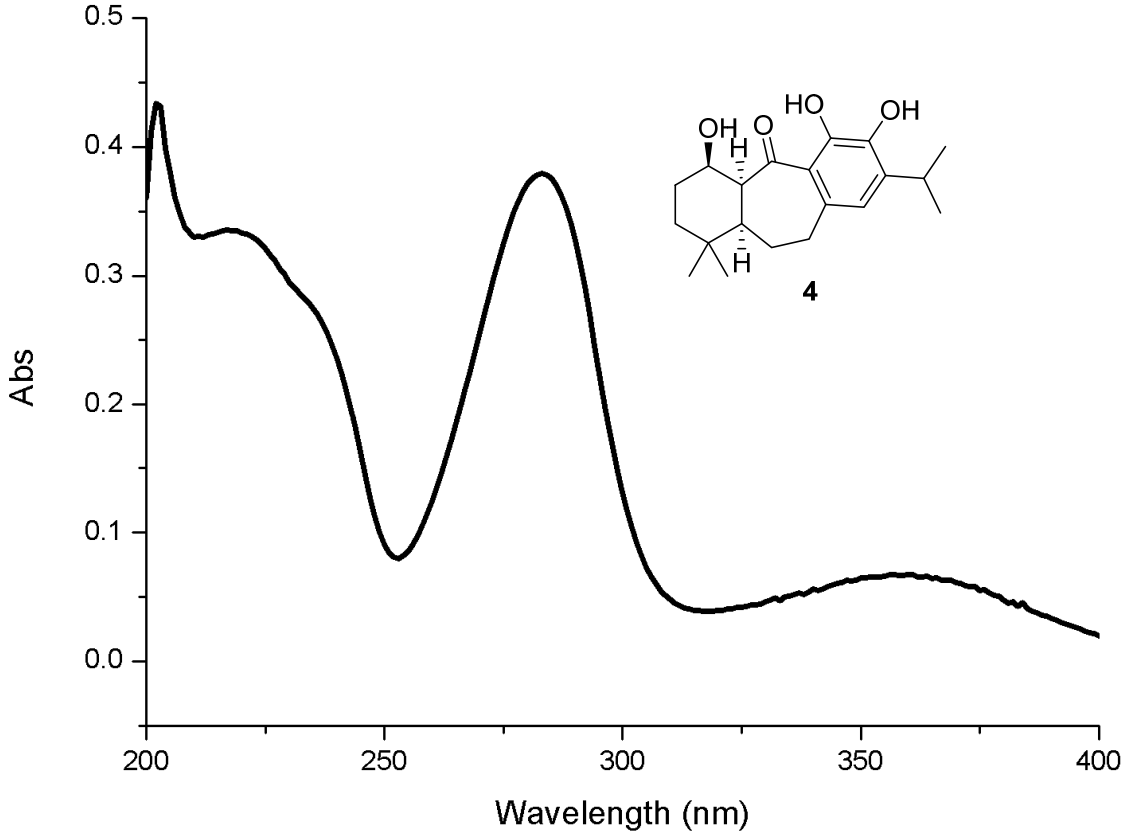


Figure S40. The UV spectrum of compound **4**

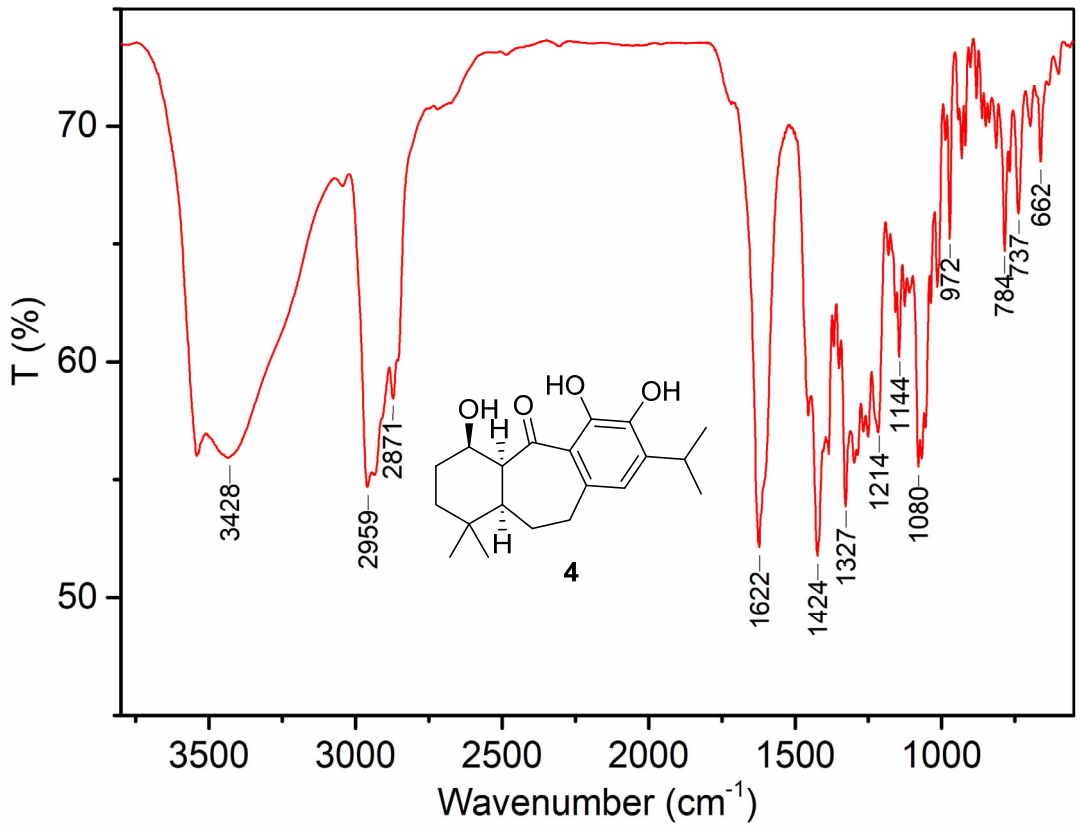


Figure S41. The IR spectrum of compound **4**

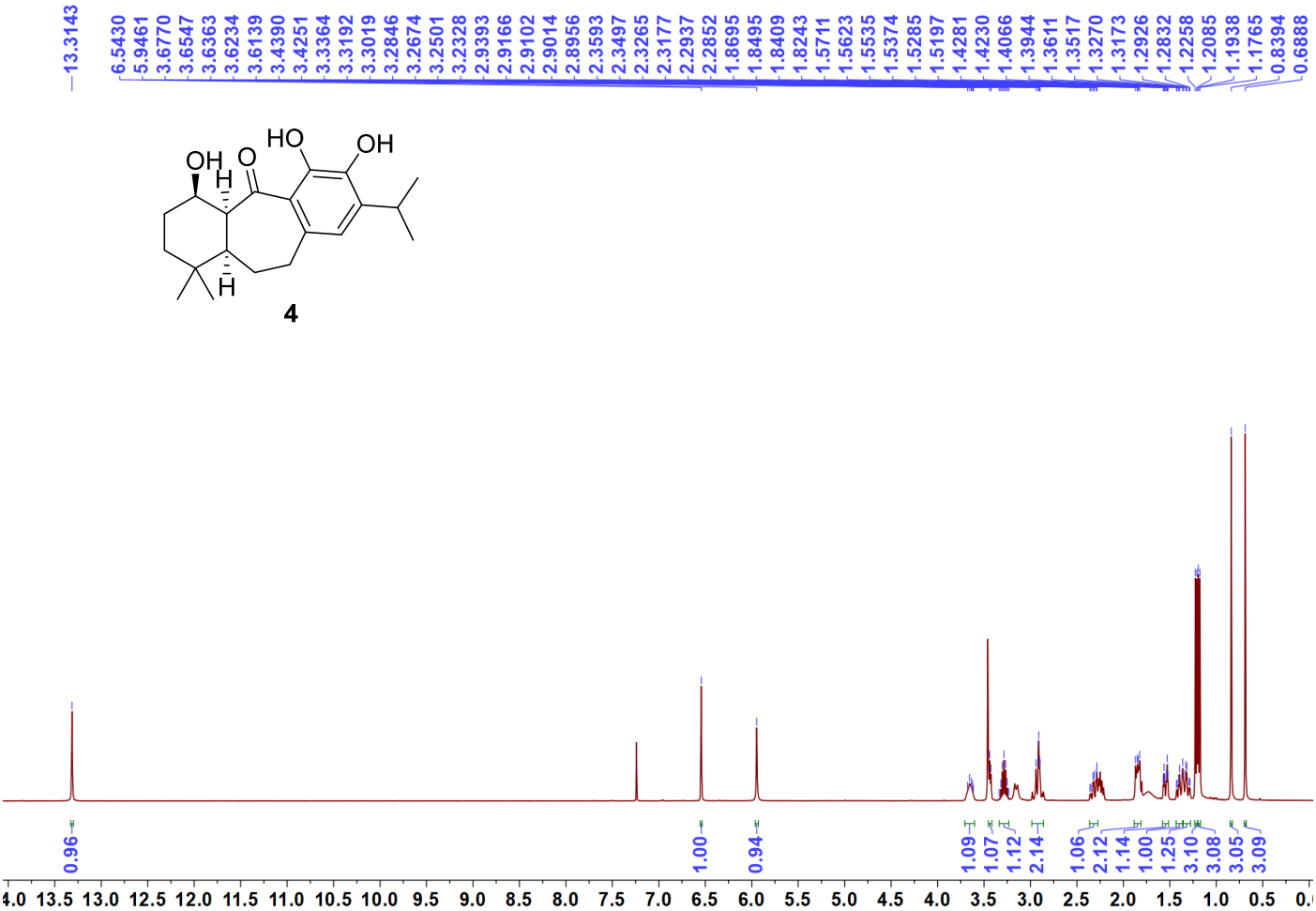


Figure S42. ^{1}H NMR spectrum of compound **4** (400 MHz, chloroform-*d*)

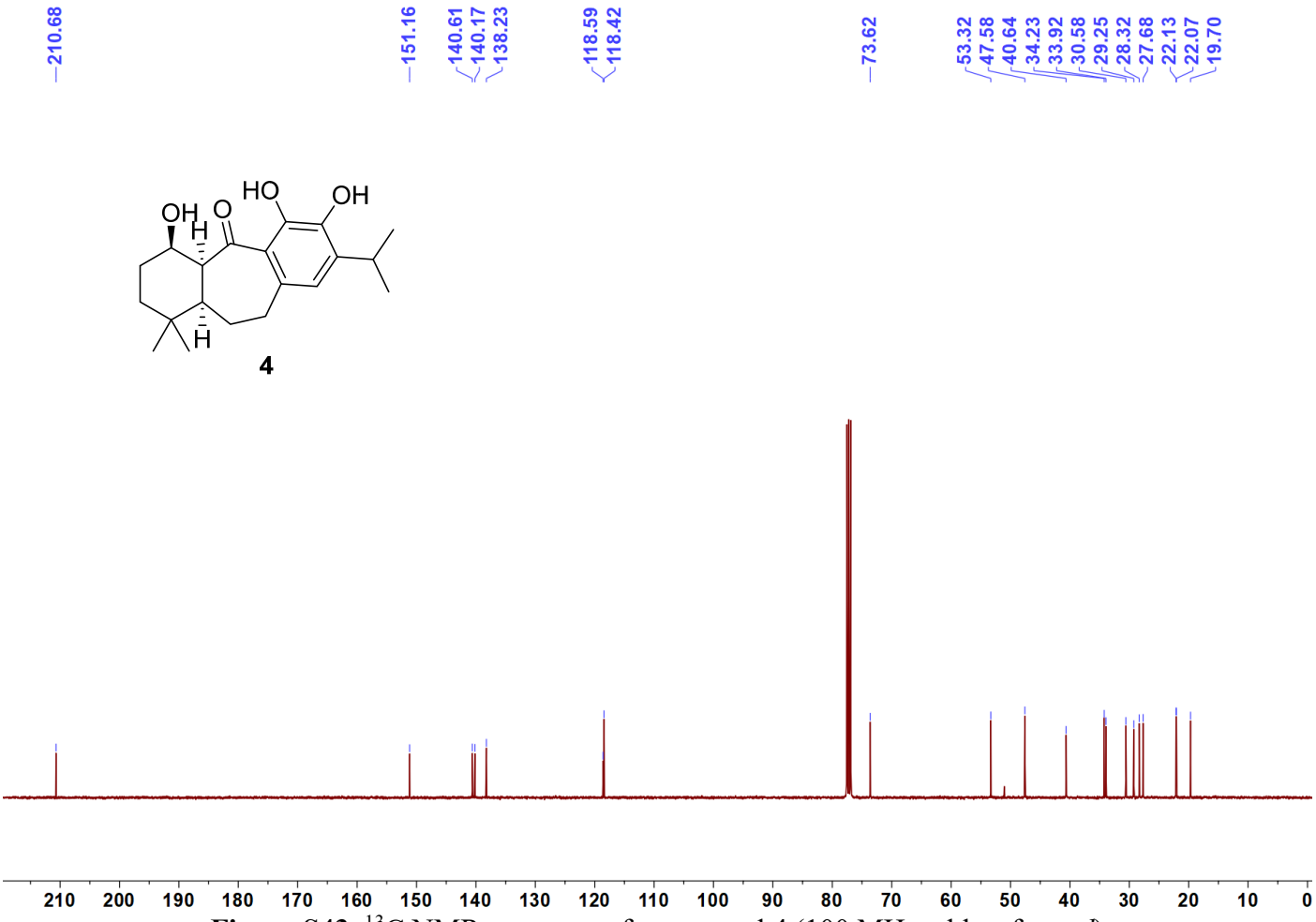


Figure S43. ^{13}C NMR spectrum of compound **4** (100 MHz, chloroform-*d*)

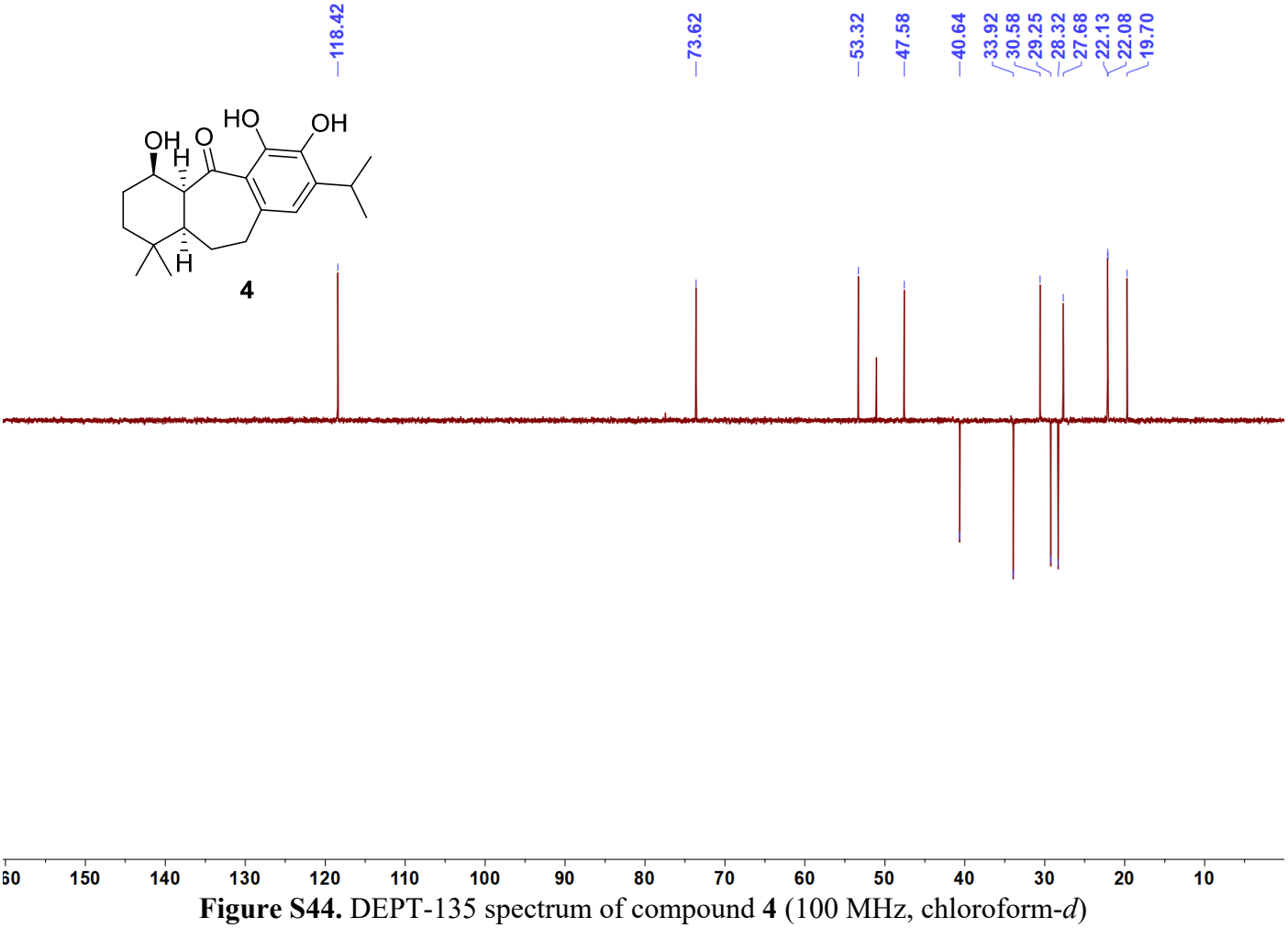


Figure S44. DEPT-135 spectrum of compound **4** (100 MHz, chloroform-*d*)

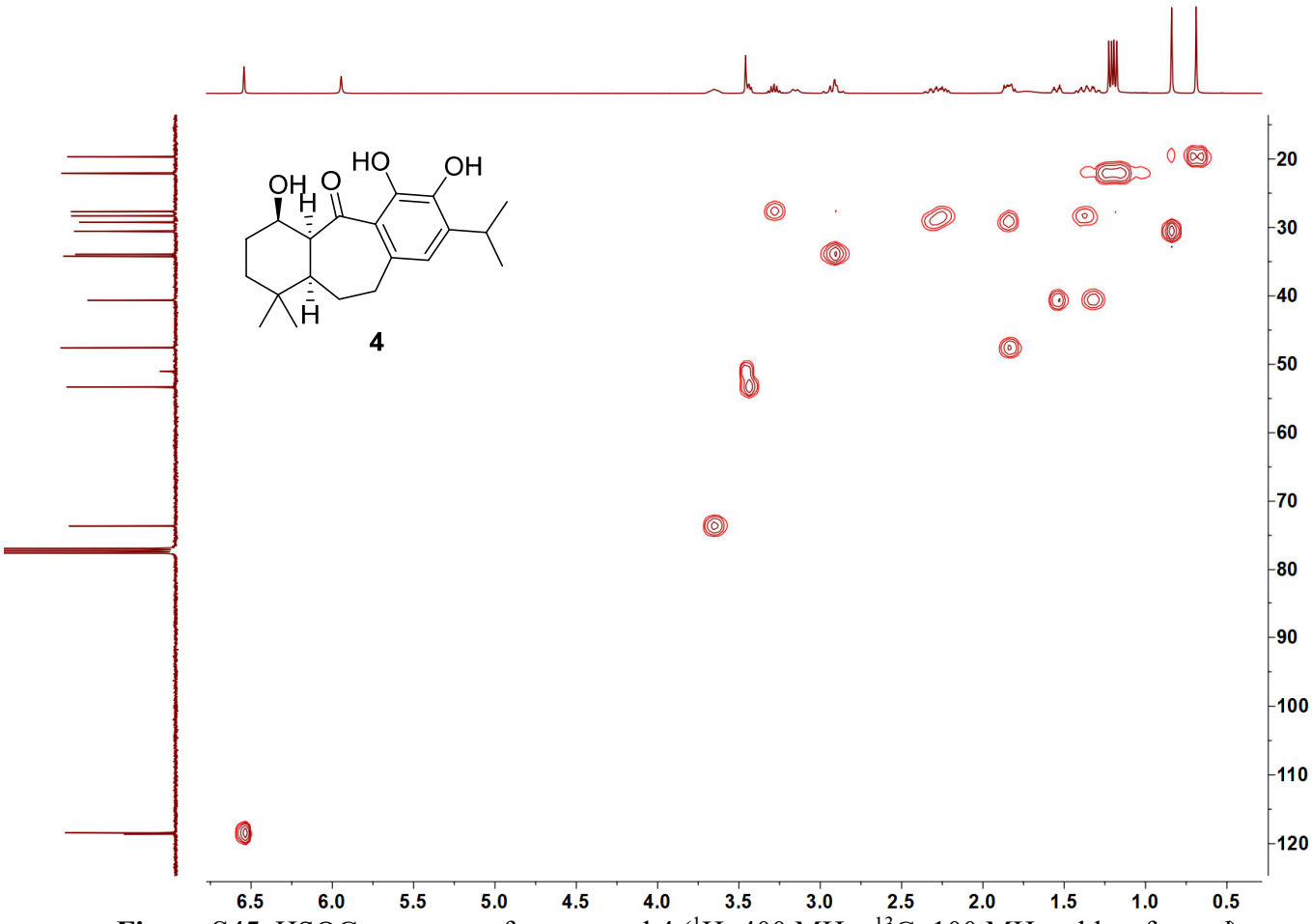


Figure S45. HSQC spectrum of compound **4** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

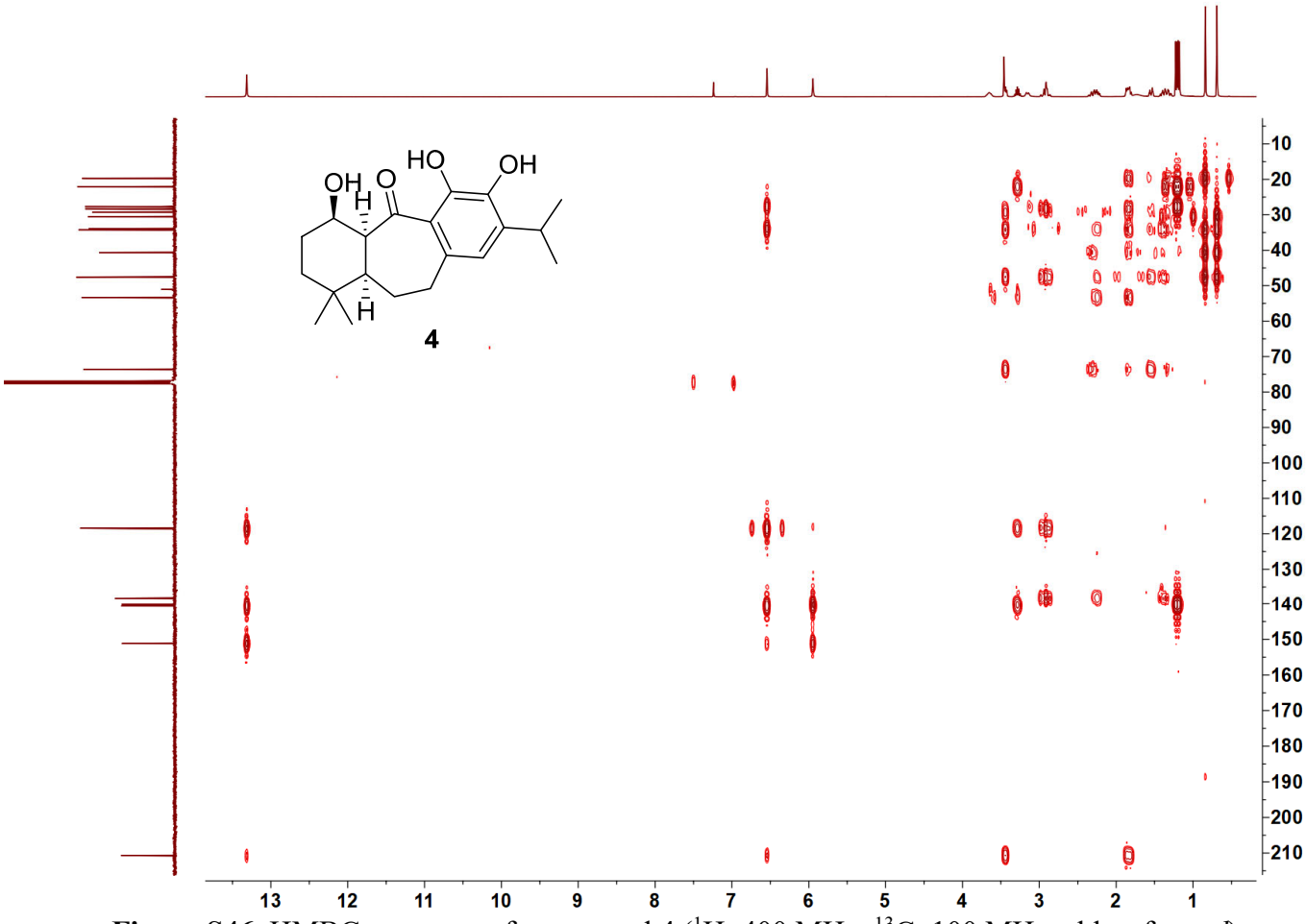


Figure S46. HMBC spectrum of compound **4** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

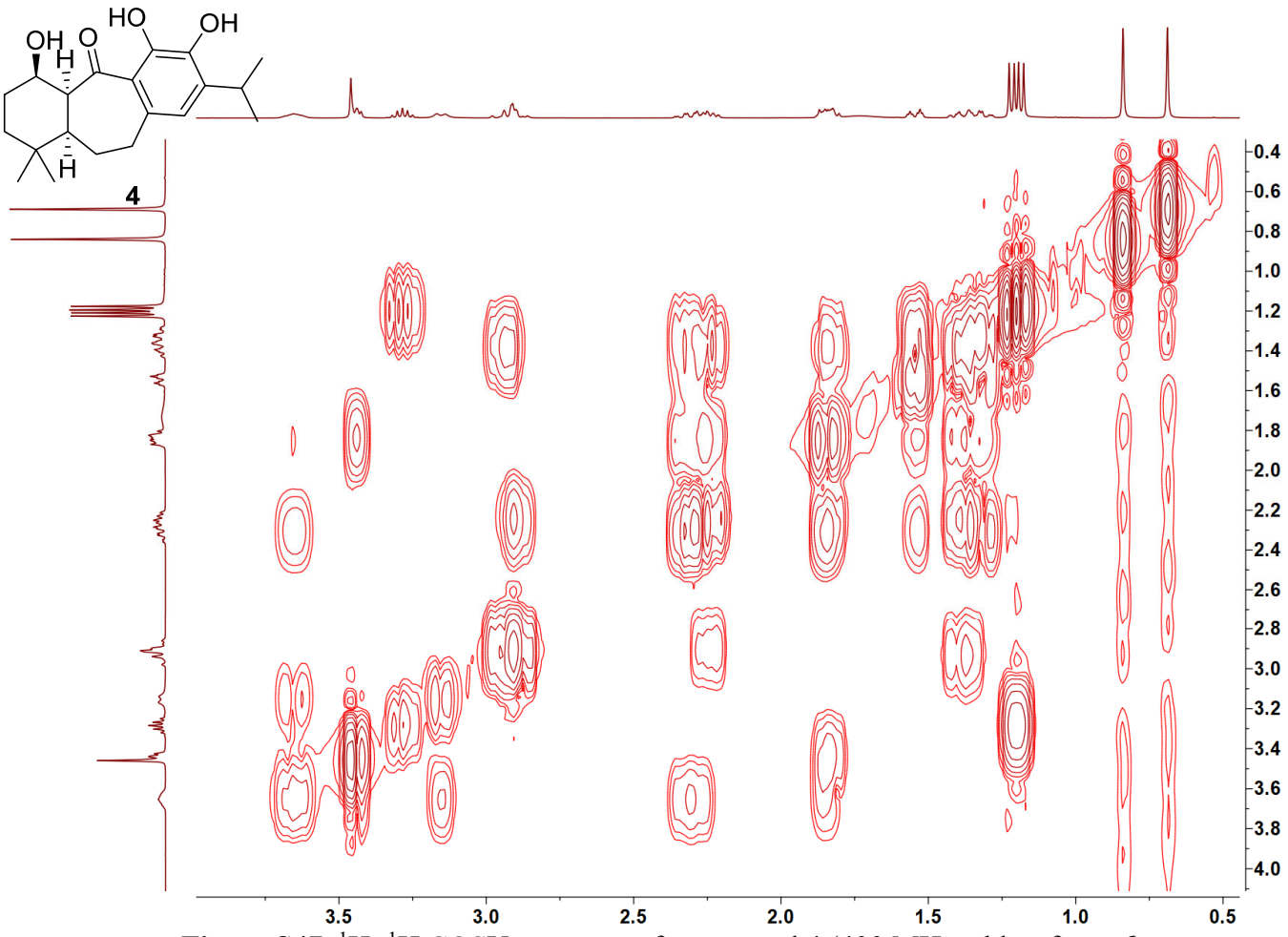


Figure S47. $^{1}H-^{1}H$ COSY spectrum of compound **4** (400 MHz, chloroform-*d*)

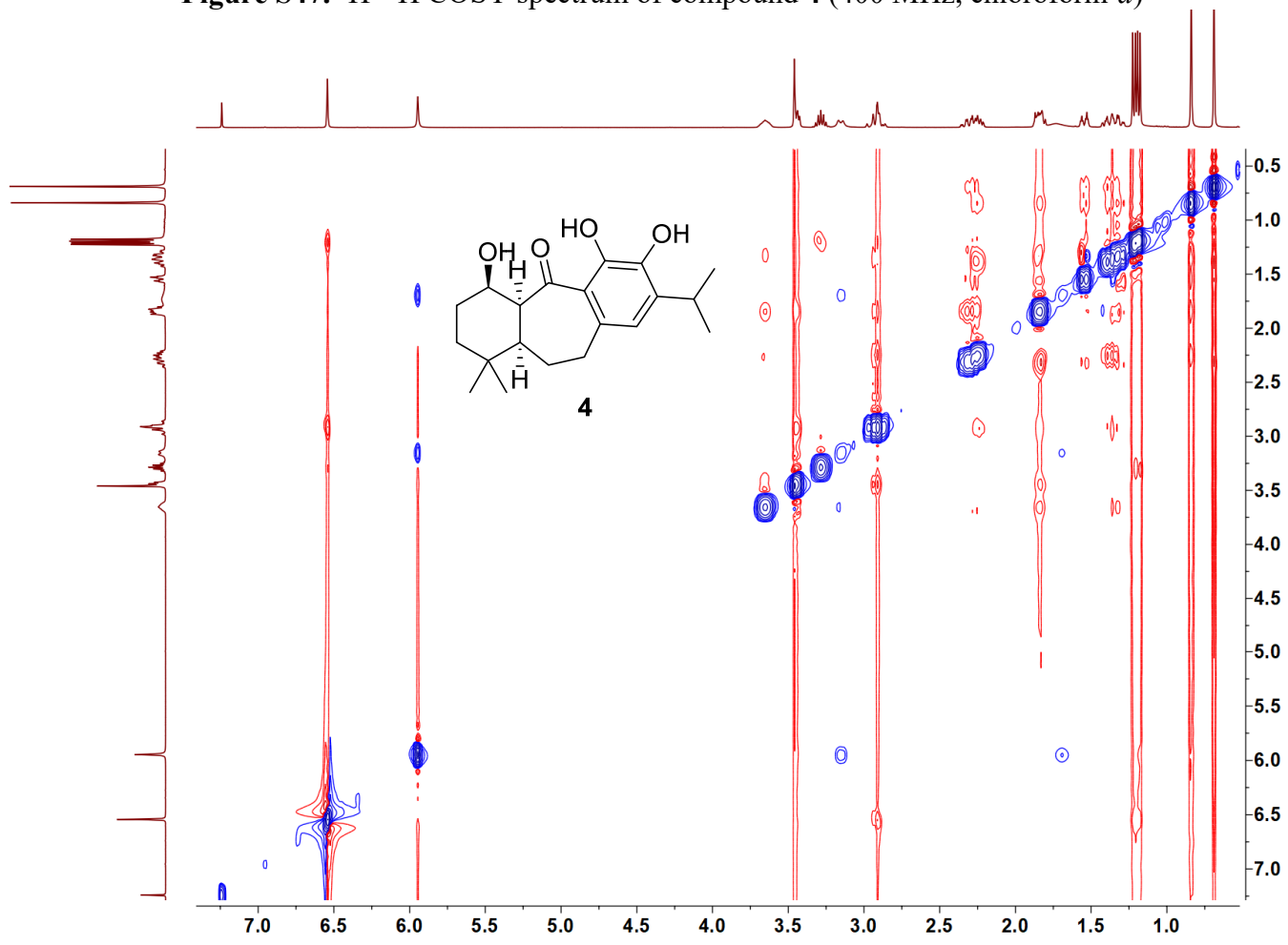


Figure S48. NOESY spectrum of compound **4** (400 MHz, chloroform-*d*)

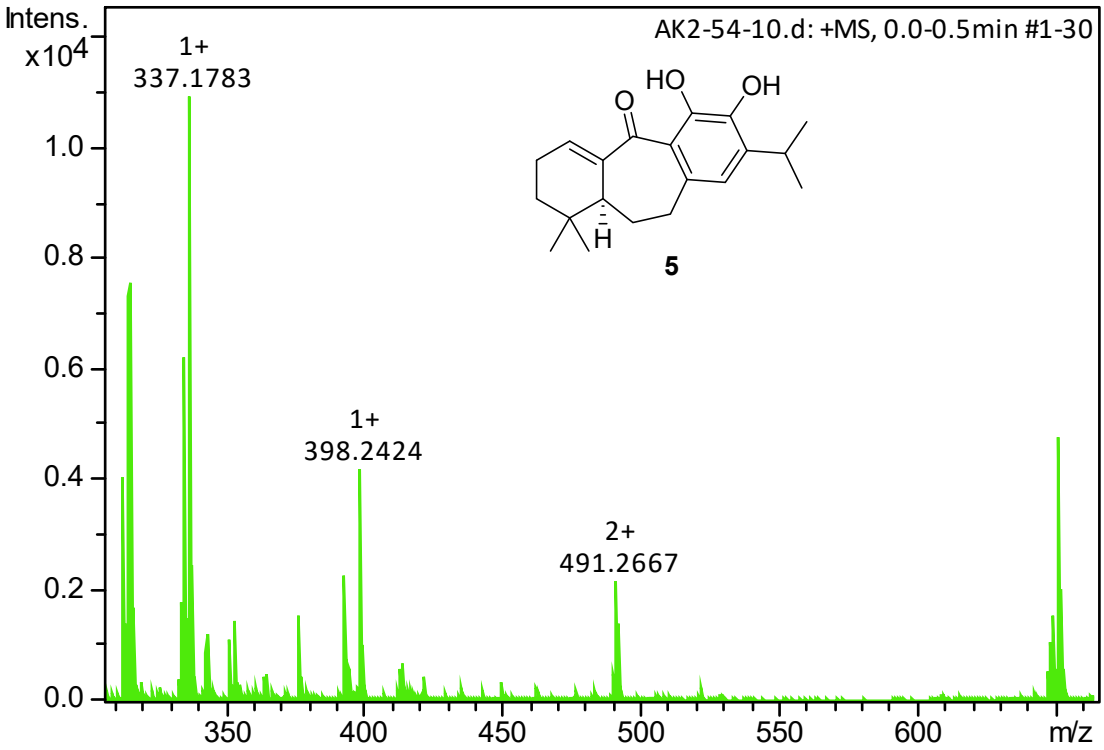


Figure S49. The HRESIMS spectrum of compound **5**

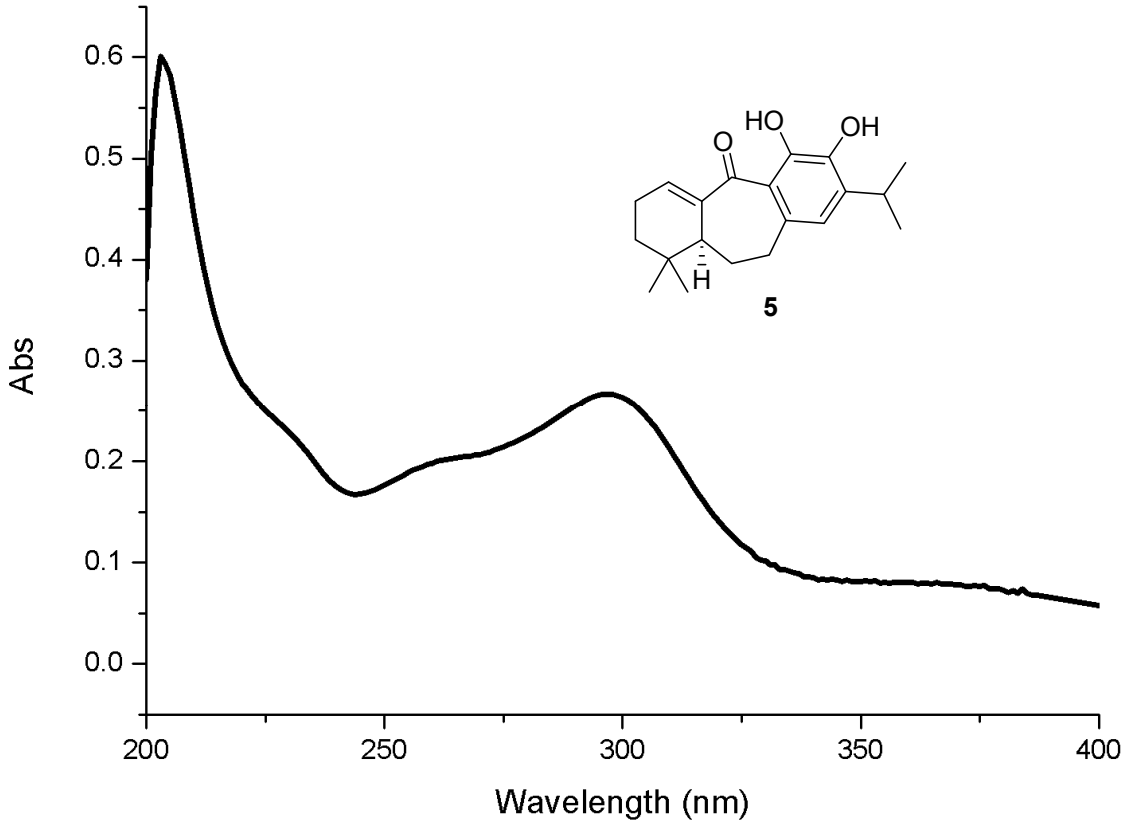


Figure S50. The UV spectrum of compound **5**

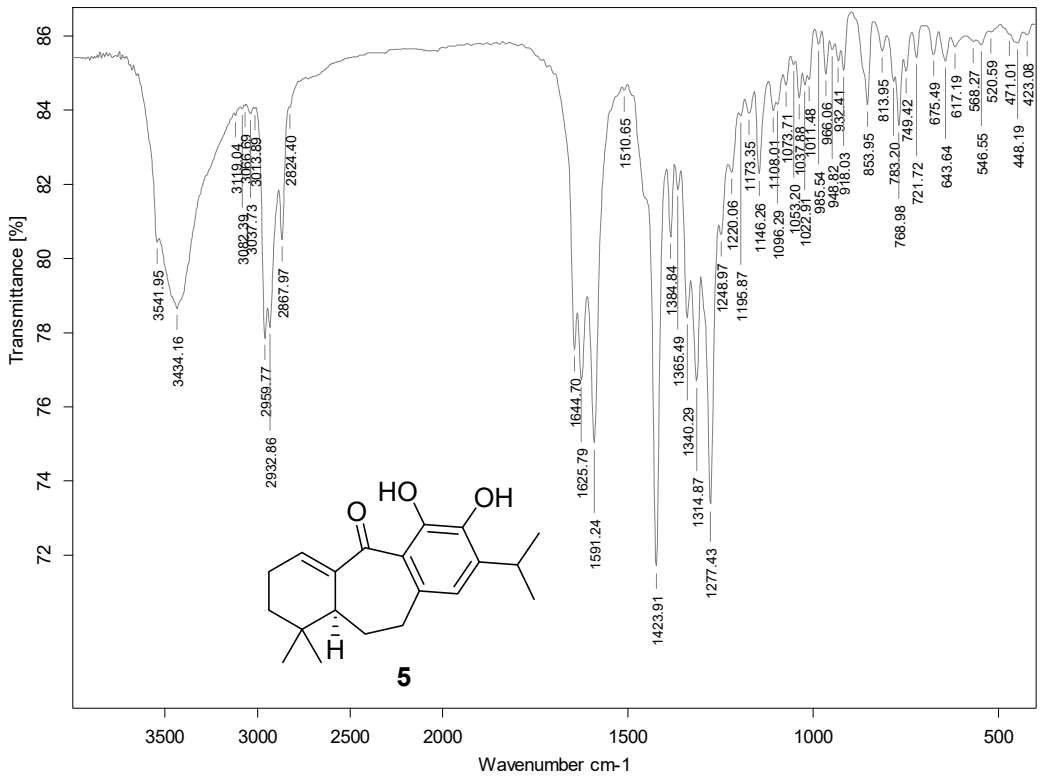
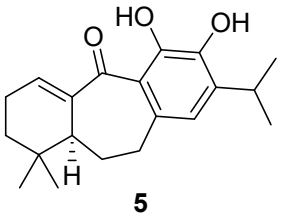


Figure S51. The IR spectrum of compound **5**



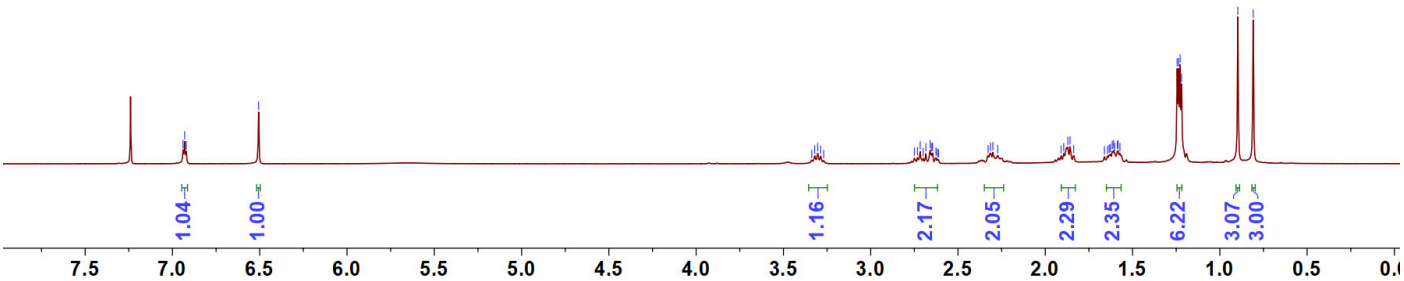


Figure S52. ^{1}H NMR spectrum of compound **5** (400 MHz, chloroform-*d*)

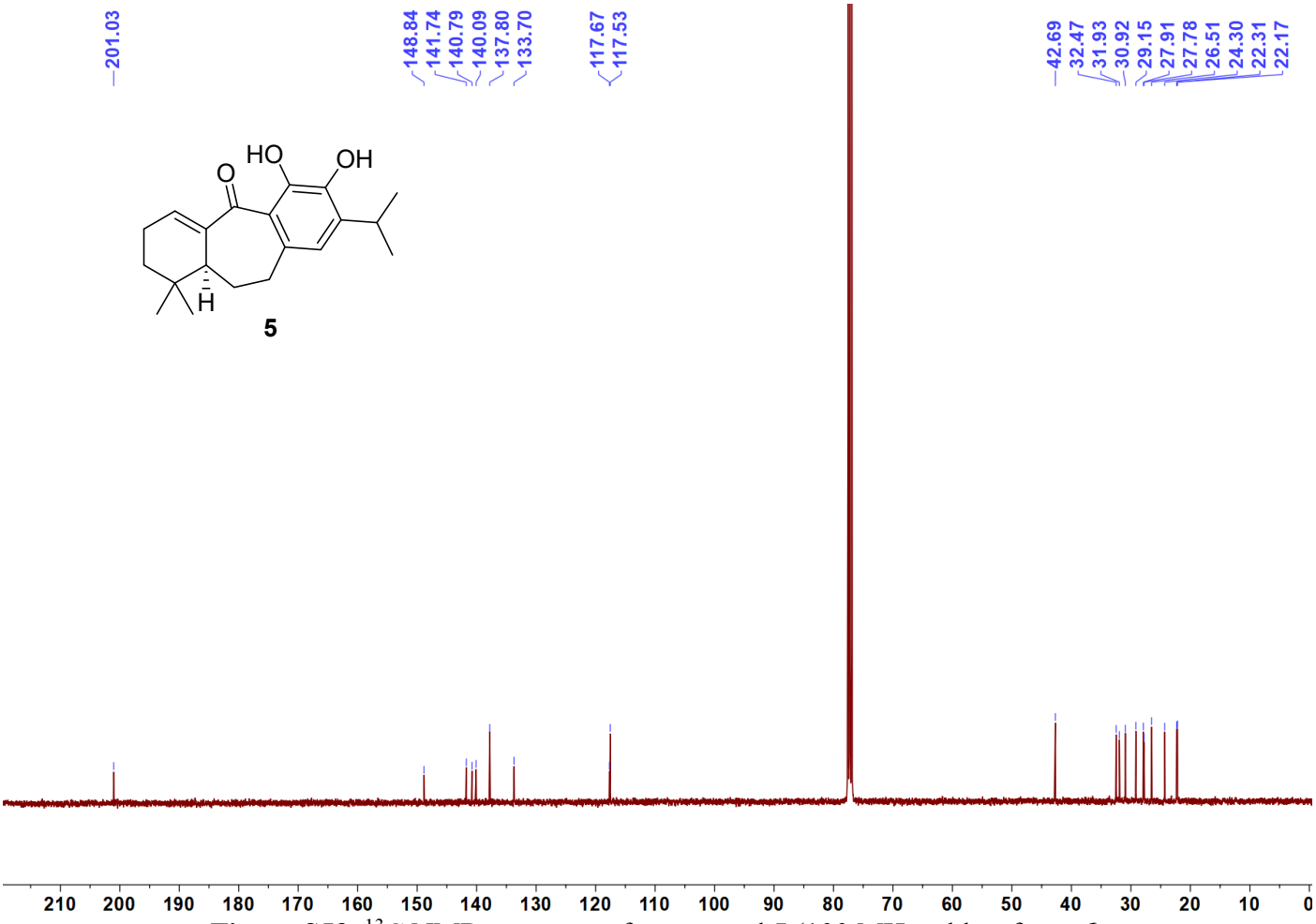


Figure S53. ^{13}C NMR spectrum of compound **5** (100 MHz, chloroform-*d*)

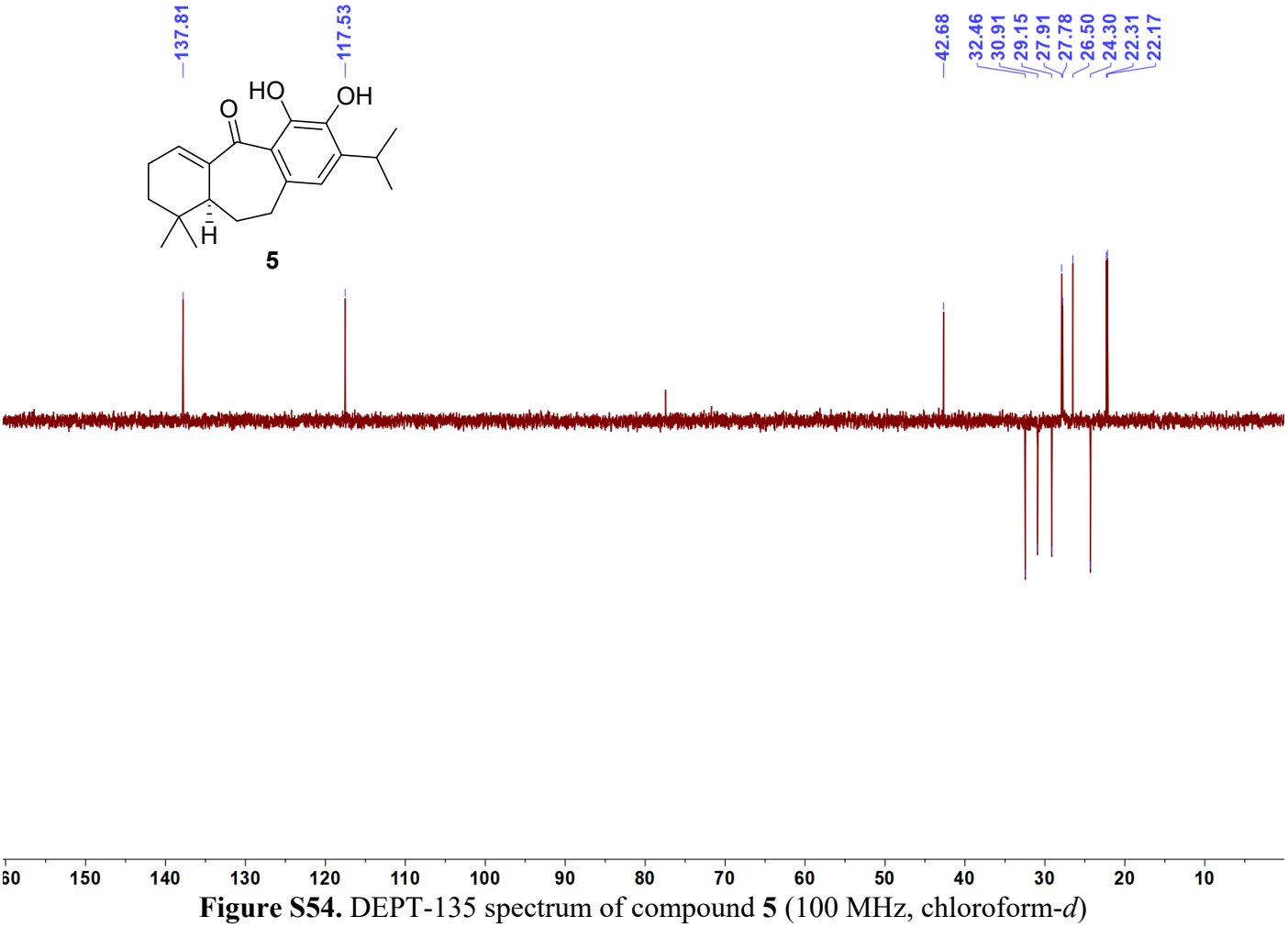


Figure S54. DEPT-135 spectrum of compound **5** (100 MHz, chloroform-*d*)

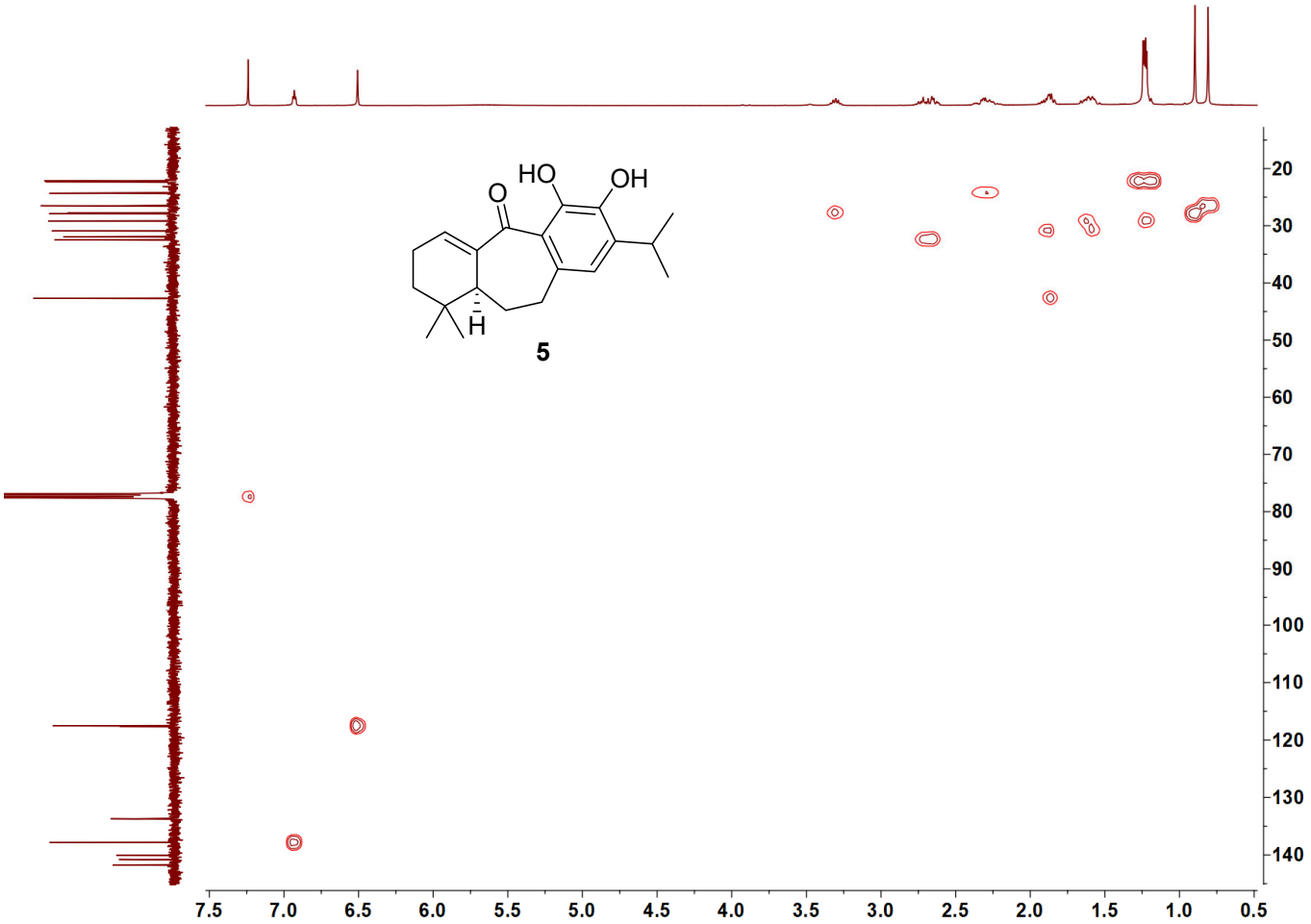


Figure S55. HSQC spectrum of compound **5** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

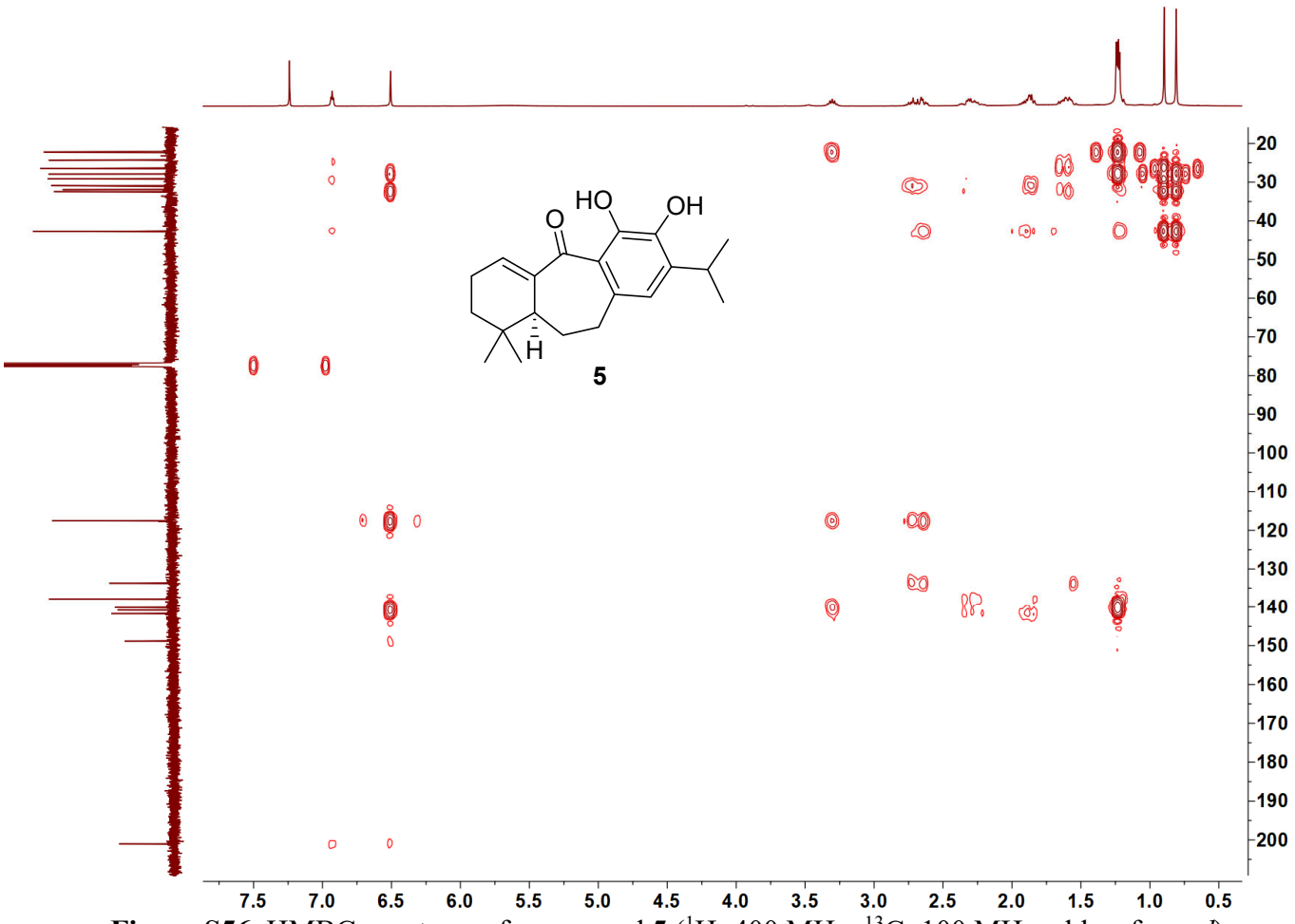


Figure S56. HMBC spectrum of compound **5** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

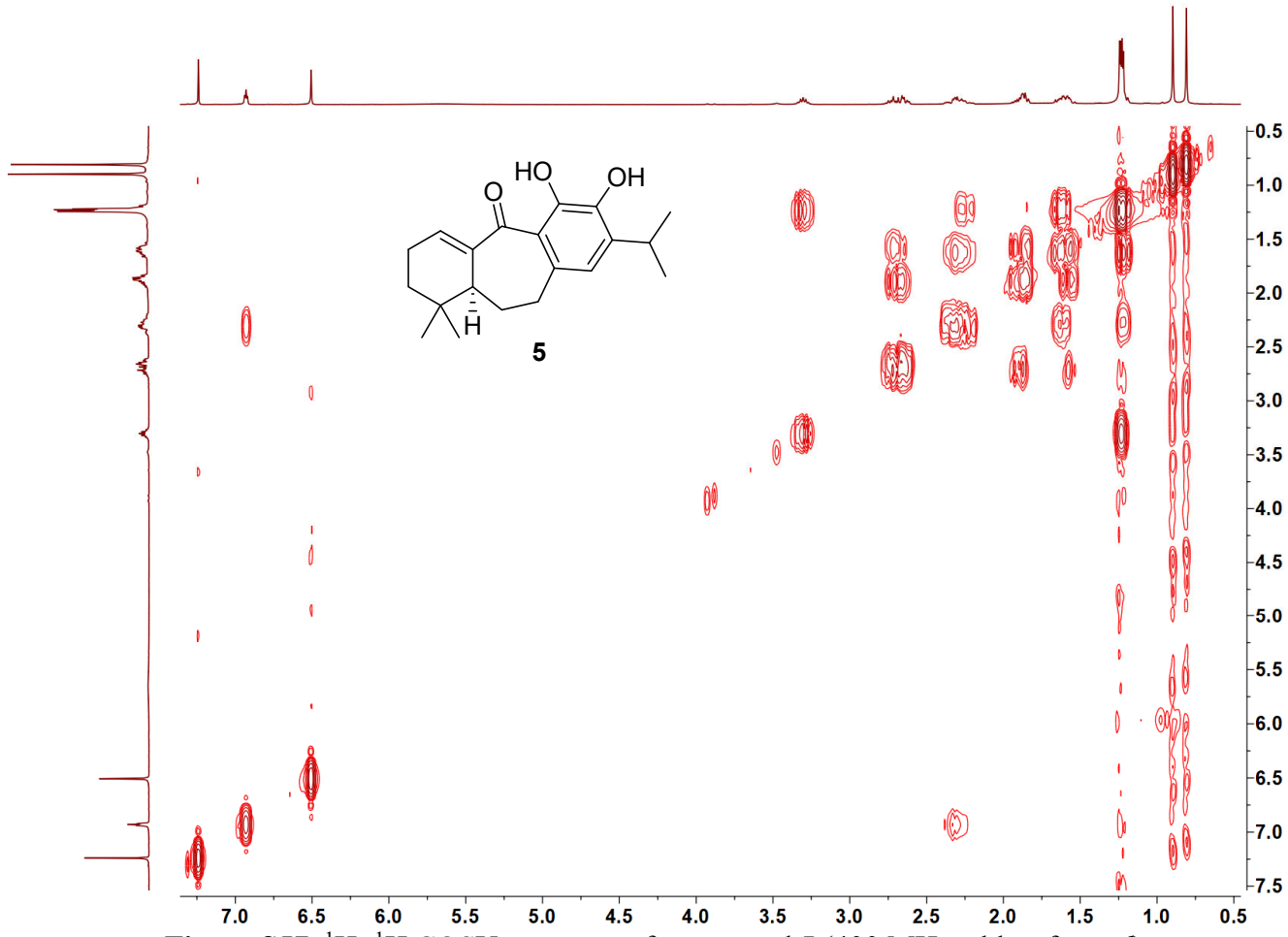


Figure S57. $^{1}H-^{1}H$ COSY spectrum of compound **5** (400 MHz, chloroform-*d*)

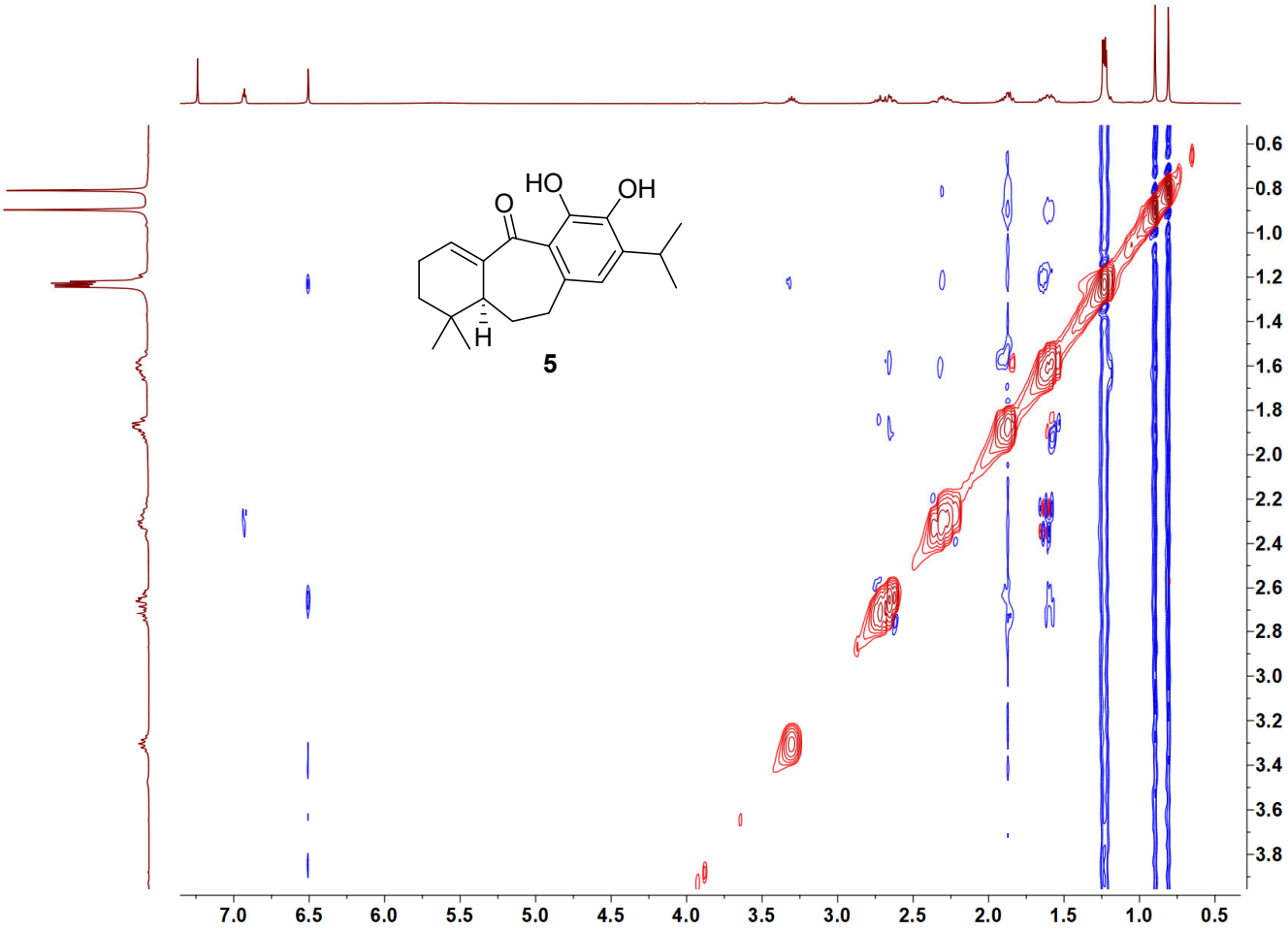


Figure S58. NOESY spectrum of compound **5** (400 MHz, chloroform-*d*)

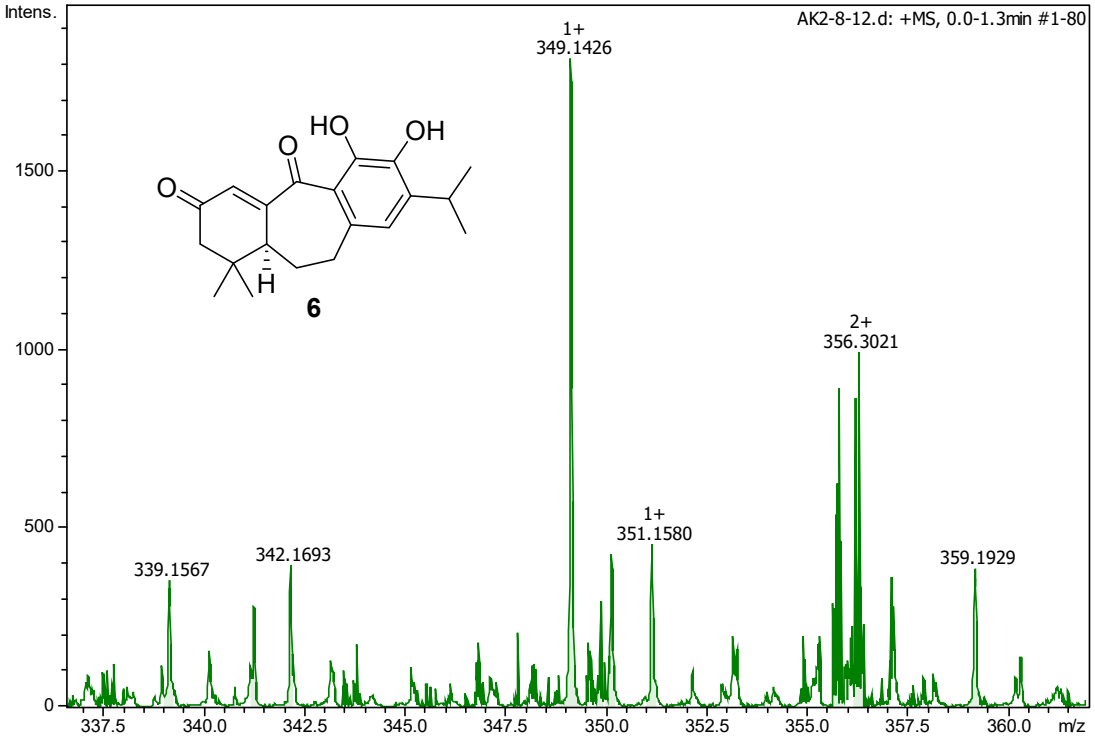


Figure S59. The HRESIMS spectrum of compound **6**

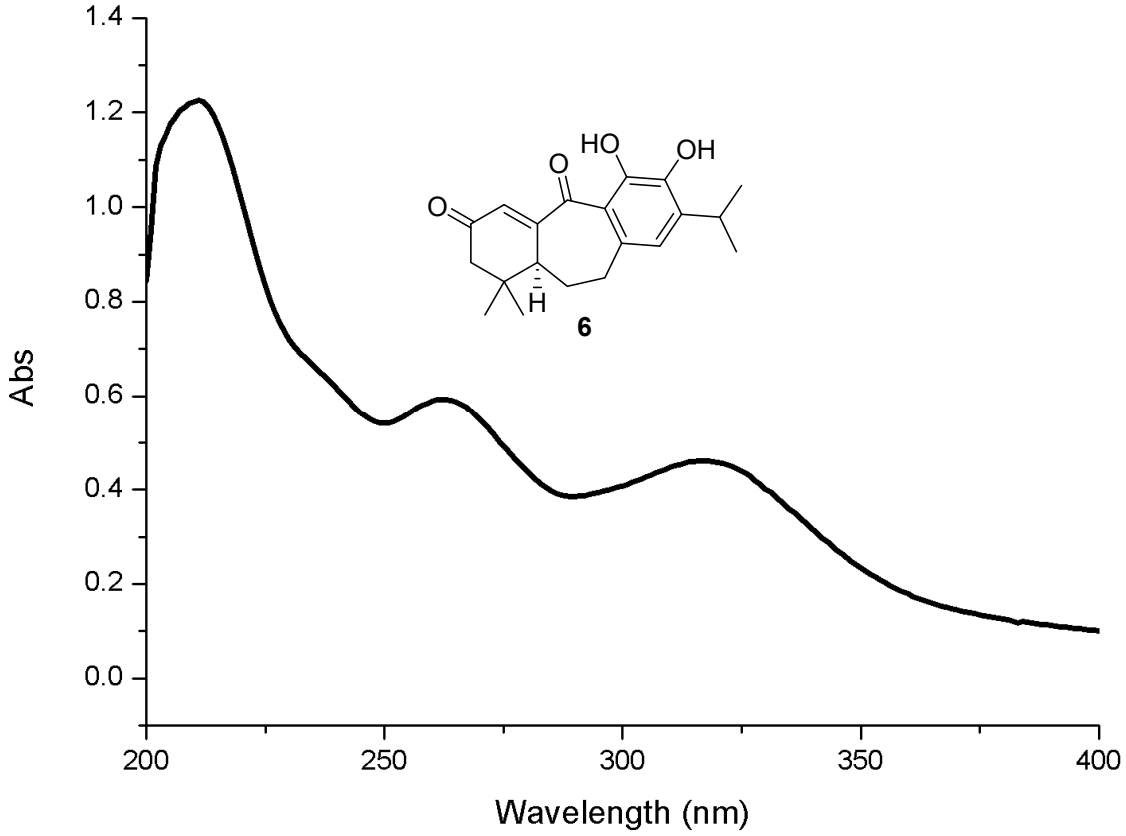


Figure S60. The UV spectrum of compound **6**

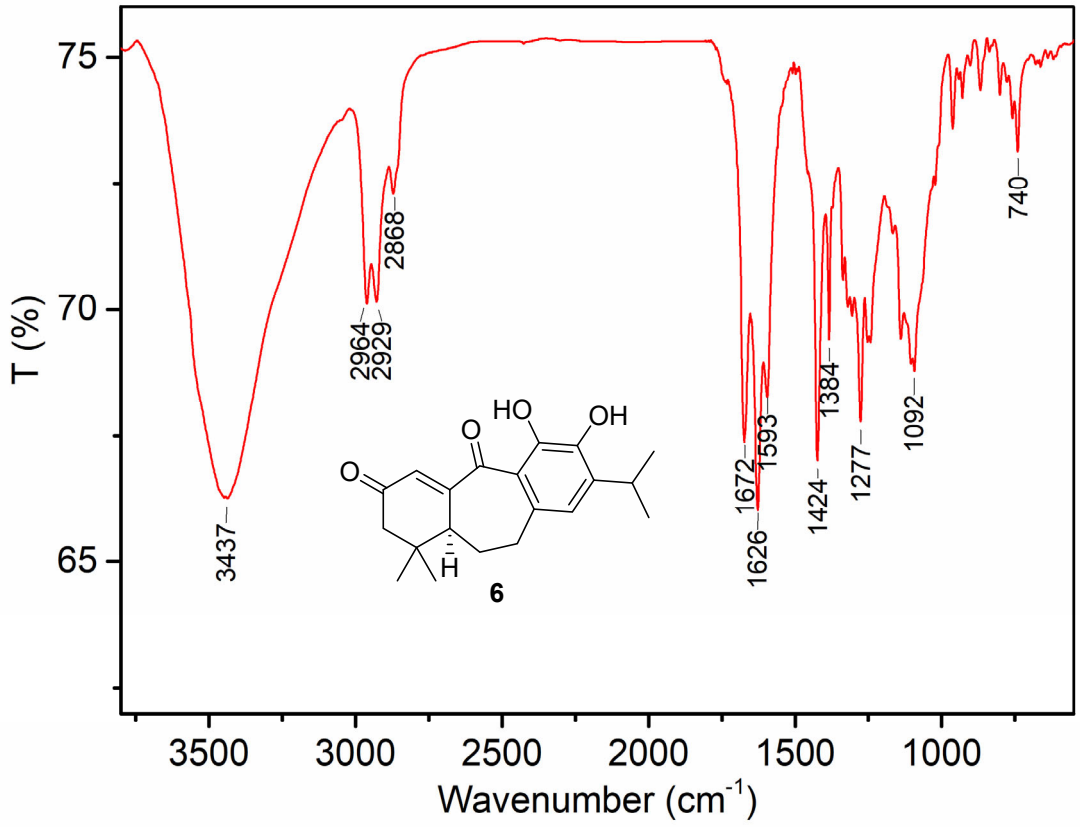
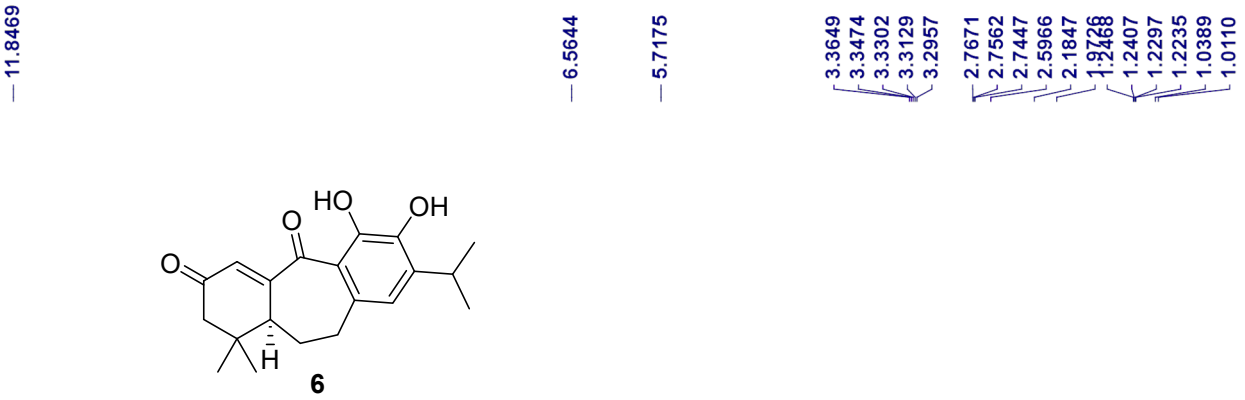


Figure S61. The IR spectrum of compound **6**



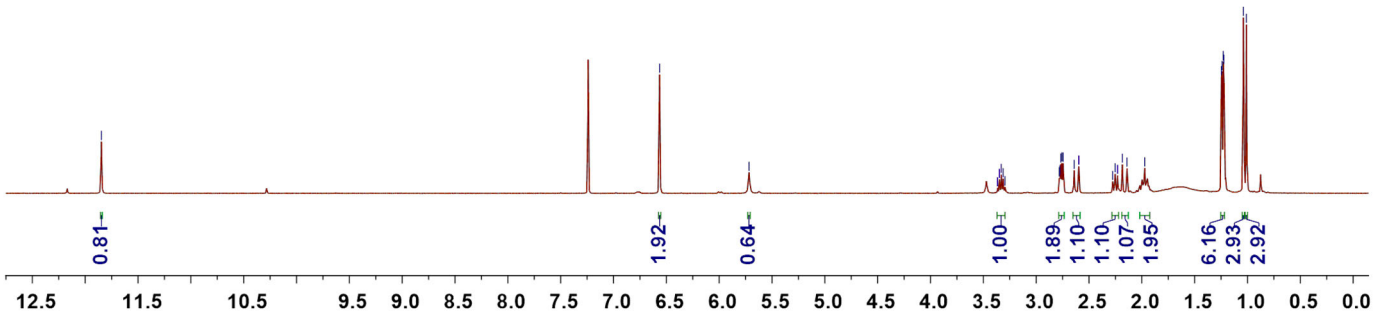


Figure S62. ^{1}H NMR spectrum of compound **6** (400 MHz, chloroform-*d*)

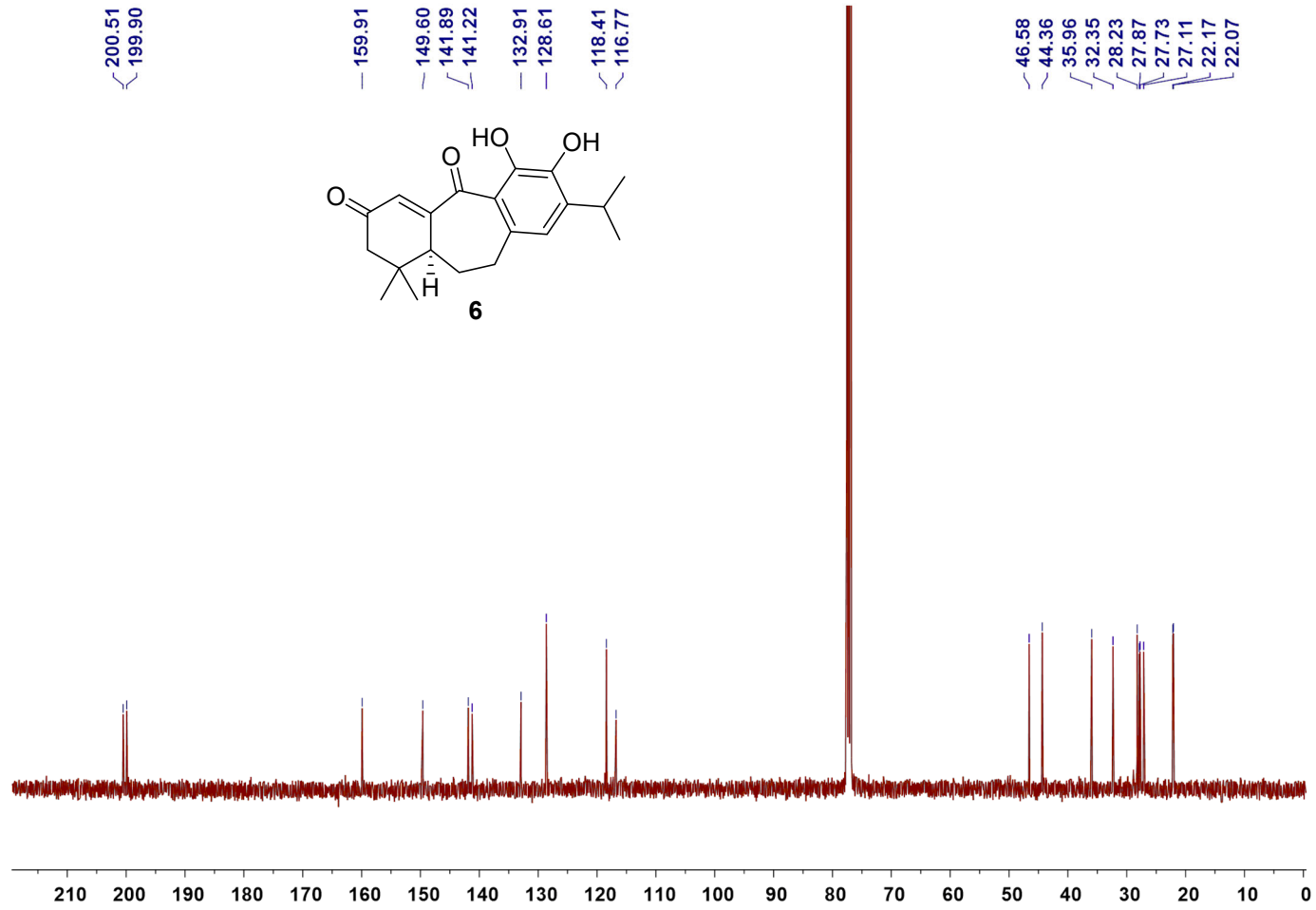


Figure S63. ^{13}C NMR spectrum of compound **6** (100 MHz, chloroform-*d*)

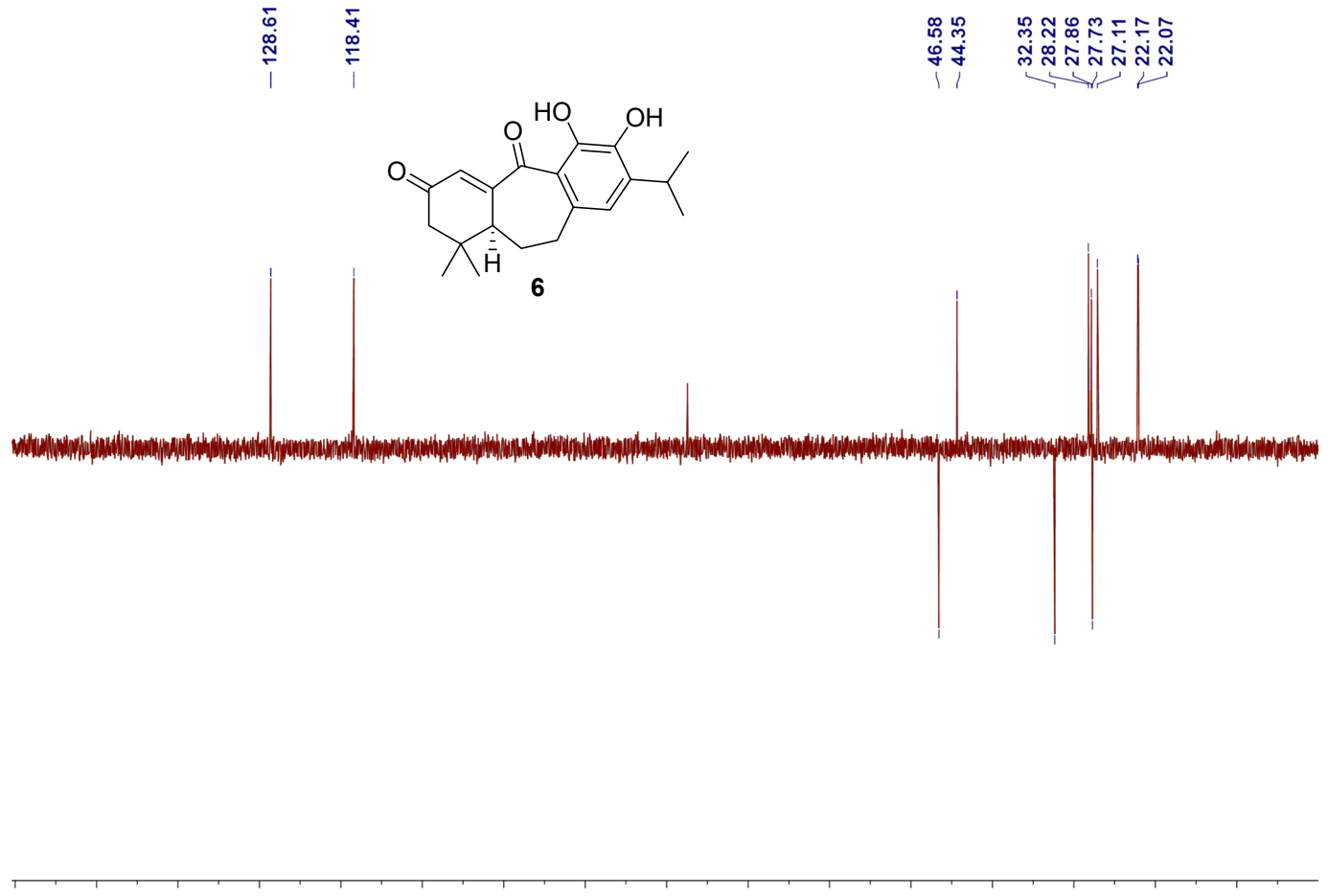


Figure S64. DEPT-135 spectrum of compound **6** (100 MHz, chloroform-*d*)

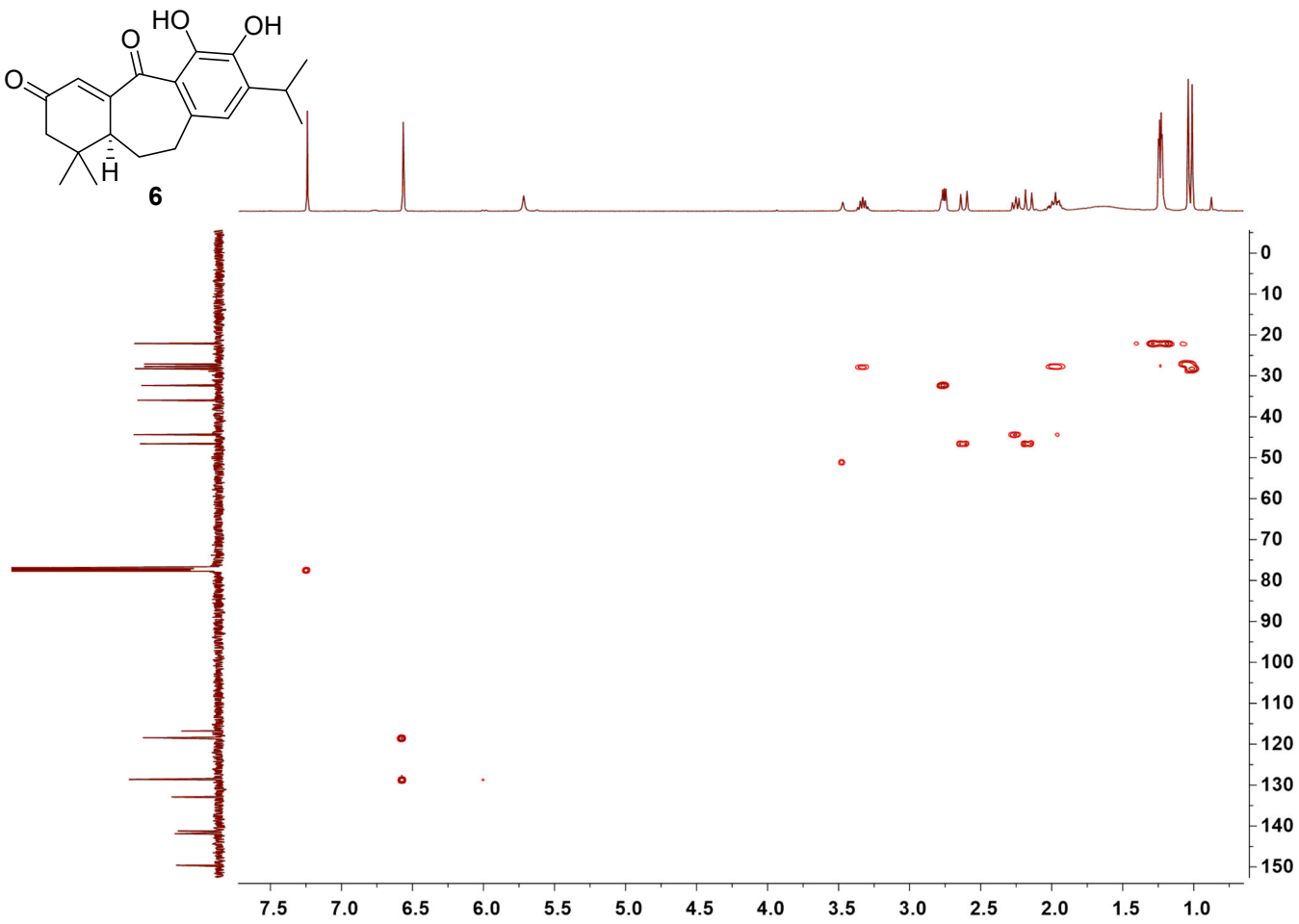


Figure S65. HSQC spectrum of compound **6** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

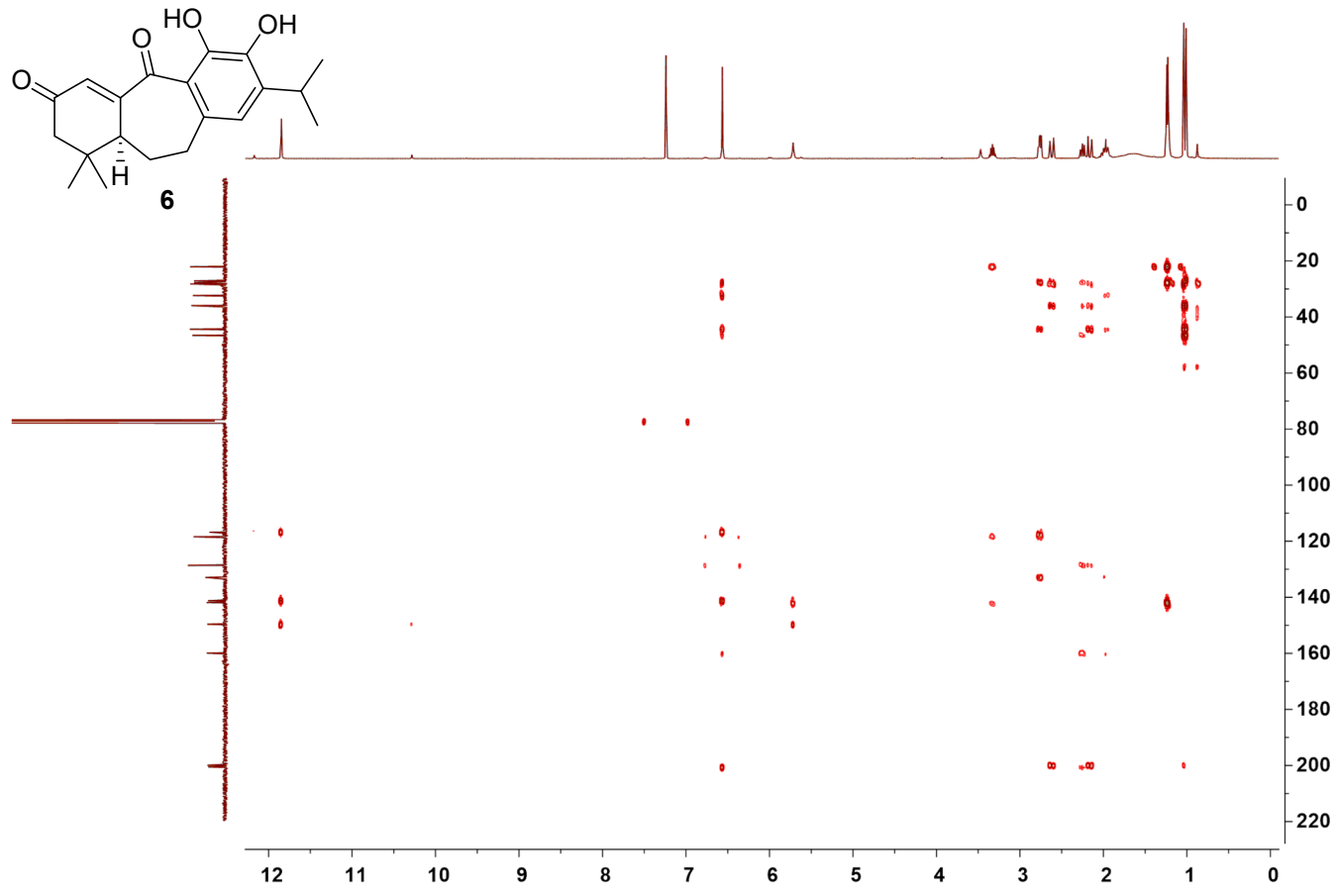


Figure S66. HMBC spectrum of compound **6** (^{1}H: 400 MHz, ^{13}C: 100 MHz, chloroform-*d*)

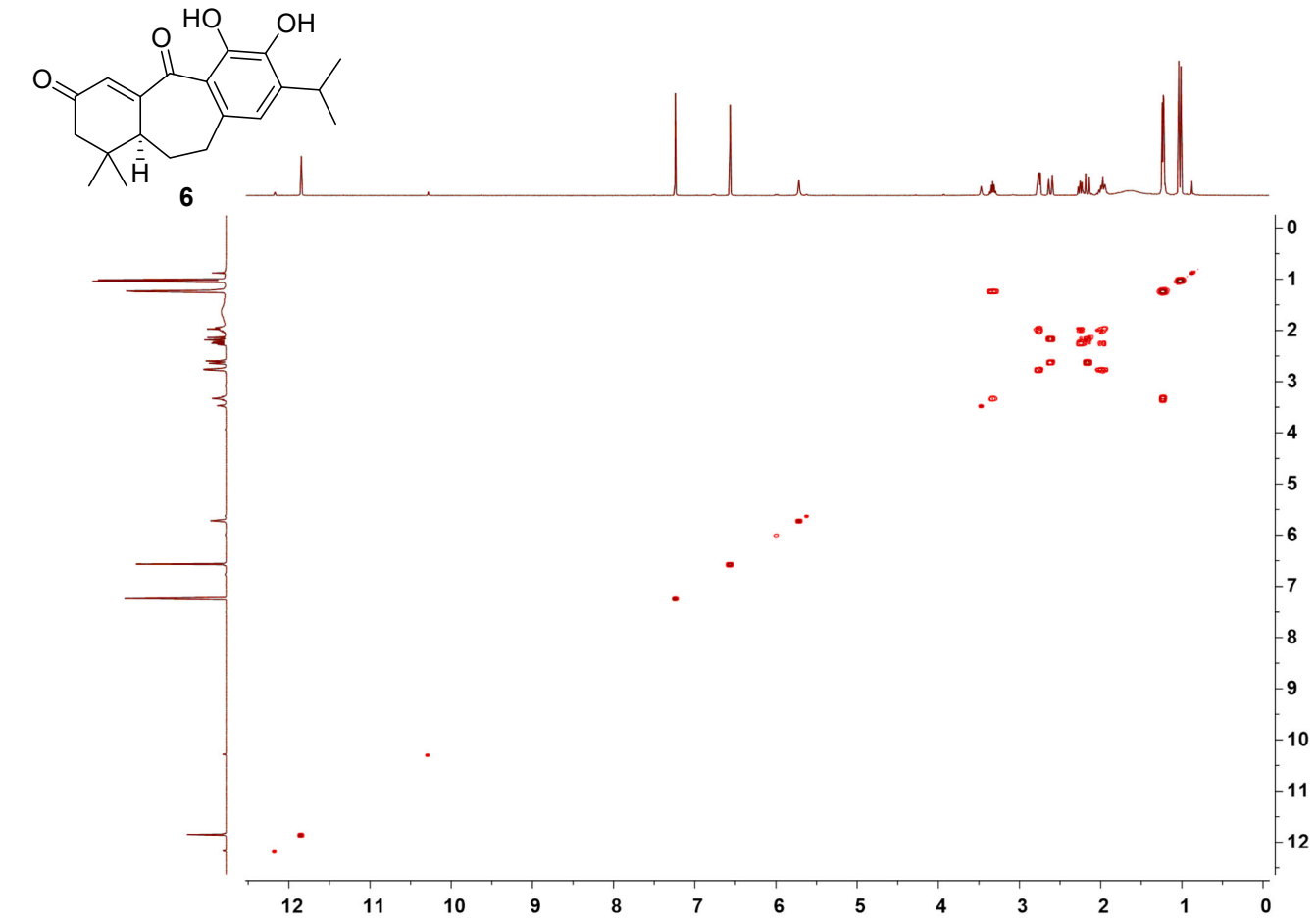


Figure S67. $^{1}H-^{1}H$ COSY spectrum of compound **6** (400 MHz, chloroform-*d*)

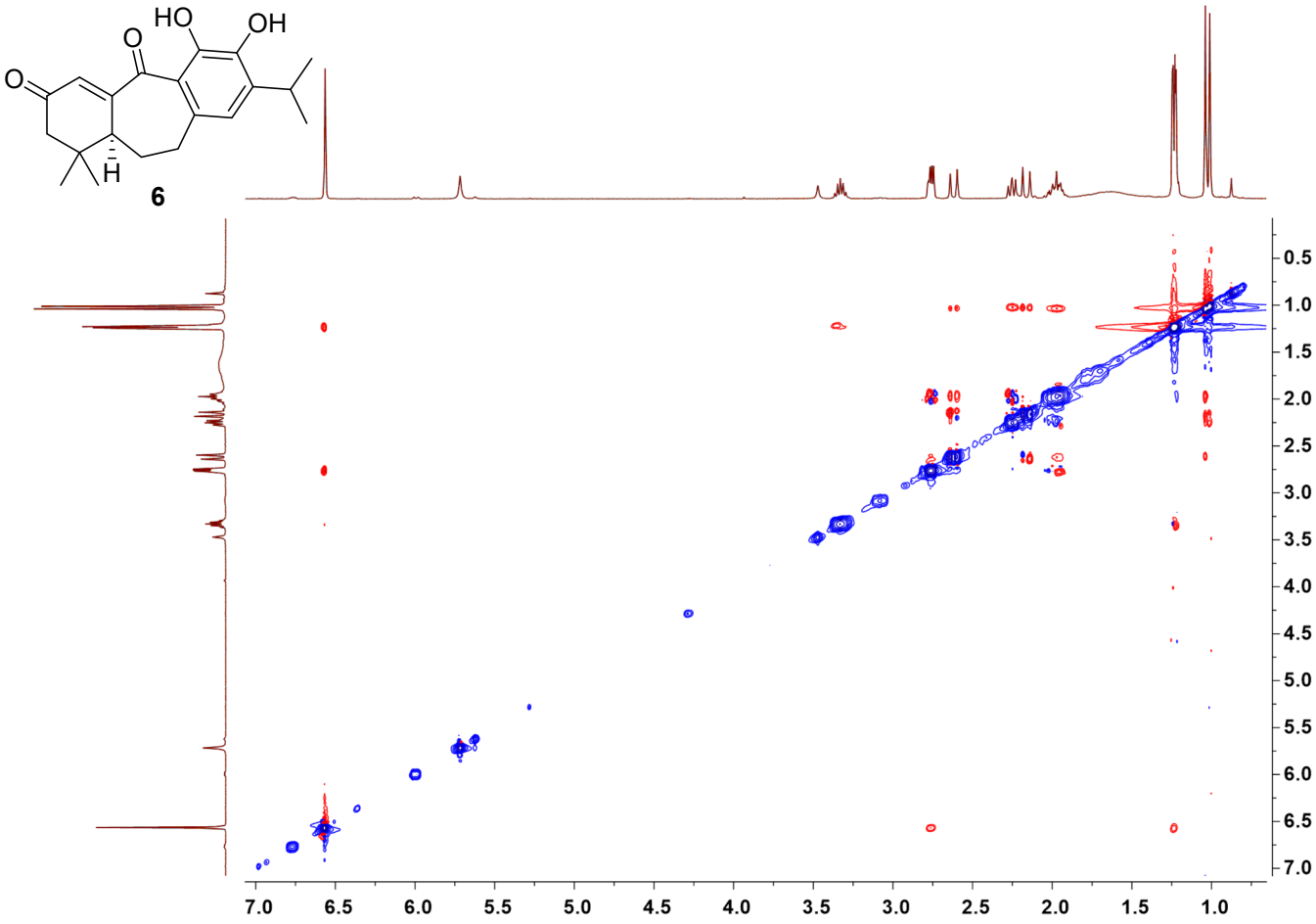


Figure S68. NOESY spectrum of compound **6** (400 MHz, chloroform-*d*)

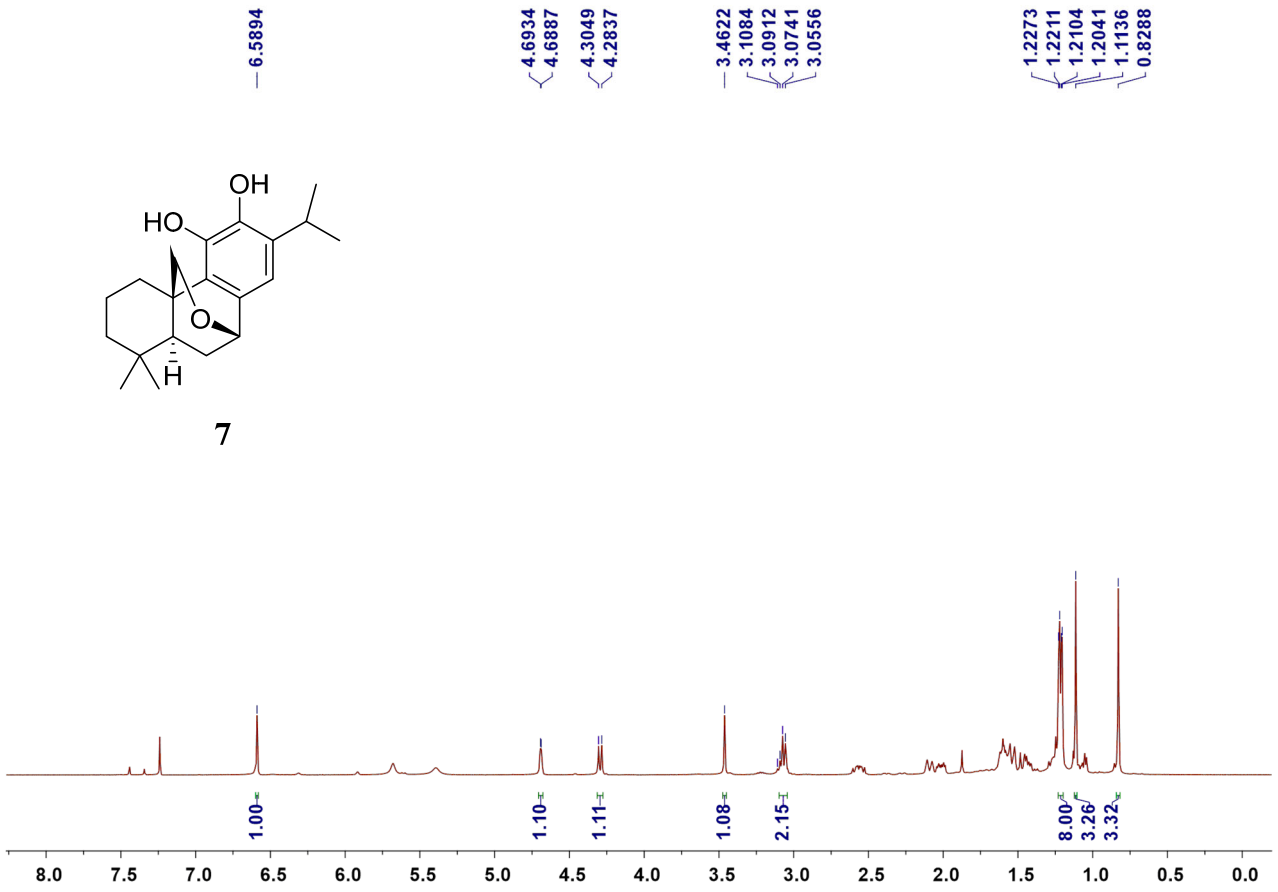


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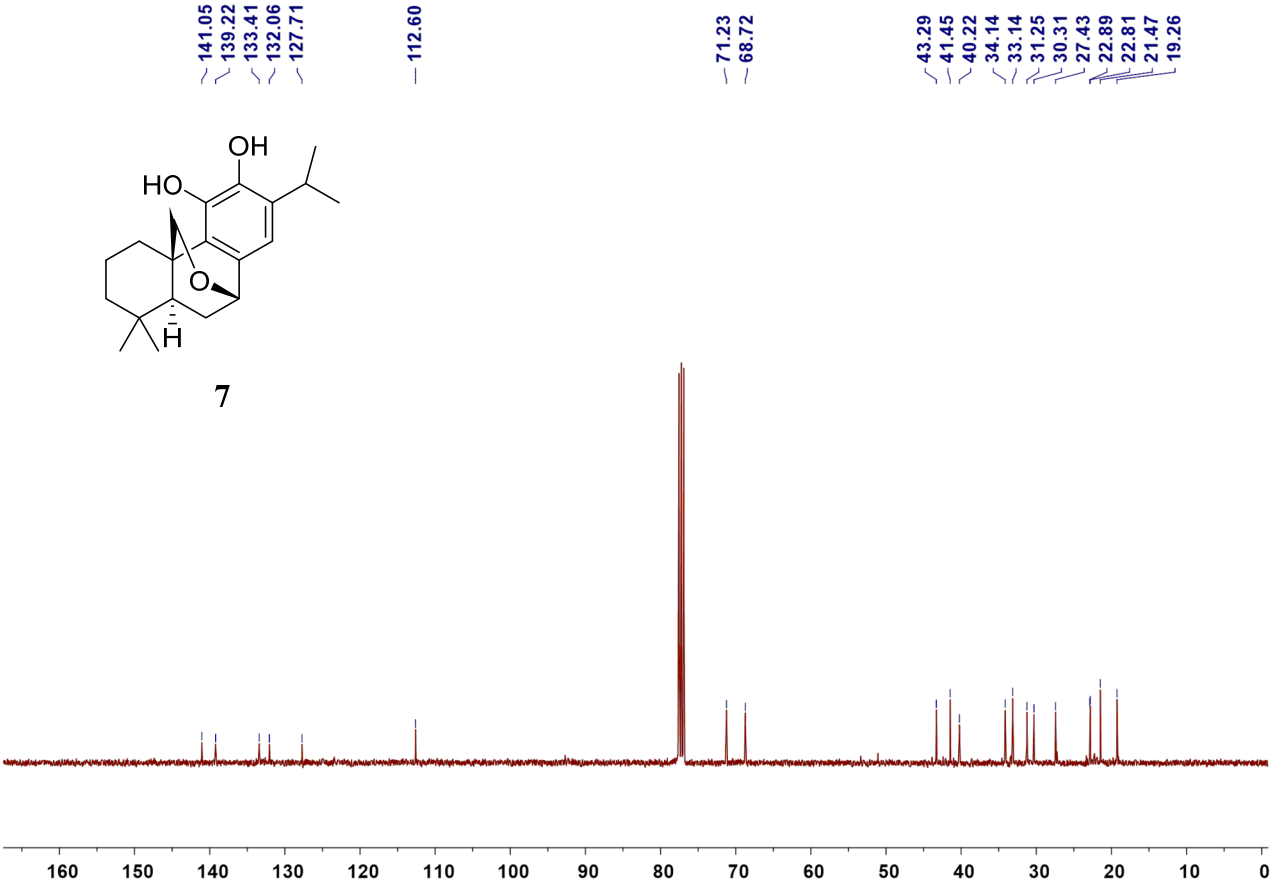
Figure S69. ^{1}H NMR spectrum of compound **7** (400 MHz, chloroform-*d*)



7

Figure S70. ^{13}C NMR spectrum of compound **7** (100 MHz, chloroform-*d*)