Supporting Information for

Meroterpenoids with immunosuppressive activity from edible fungus *Craterellus odoratus*

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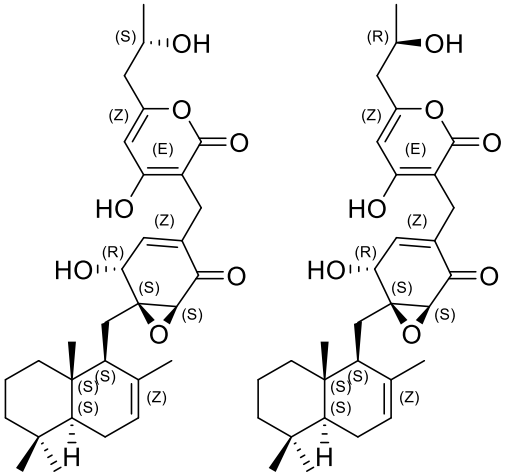
Contents

Section S1. Calculational details for 1

S1.1. Computational details for compound 1 (NMR)



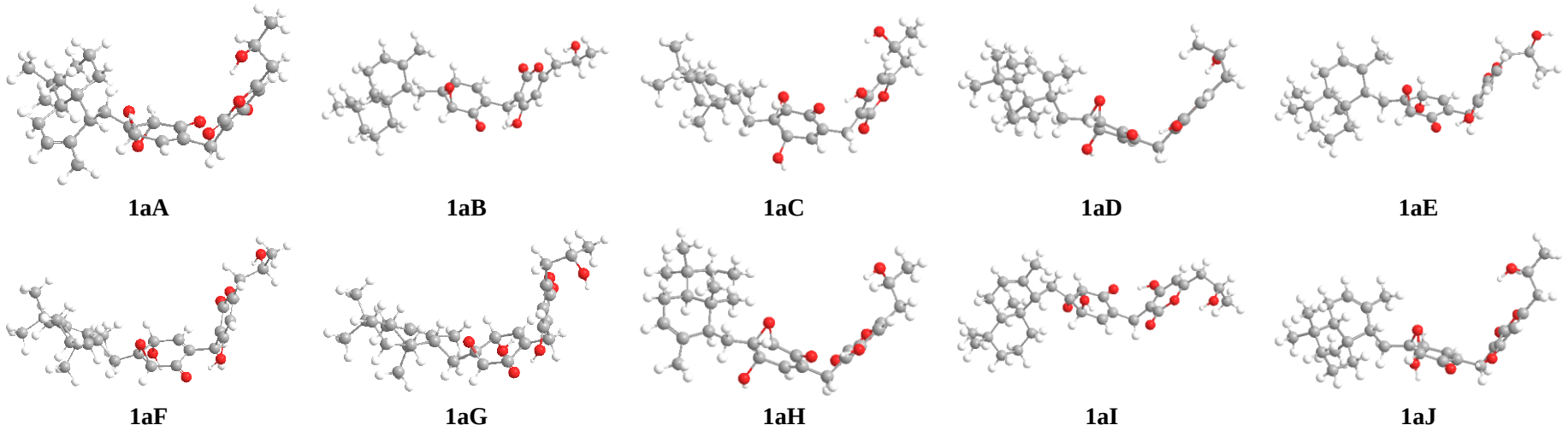
Conformation search based on molecular mechanics with MMFF force fields were performed for **1a** and **1b** gave 16 and 15 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package with g09 default keyword. Gauge Independent Atomic Orbital (GIAO) calculations of their ^{1}H and ^{13}C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The ^{1}H and ^{13}C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by linear correlation coefficients (R^2) and the improved probability DP4+ method.

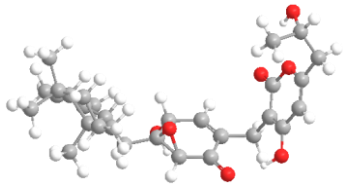
Table S1. Energy analysis for conformers of **1aA-1aP** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
1aA	-1693.121591	-1693.085589	-1693.084645	-1693.189621	0	0	67.13%
1aB	-1693.119144	-1693.083080	-1693.082136	-1693.188044	0.001577	0.989582	12.62%
1aC	-1693.117762	-1693.081574	-1693.080630	-1693.186632	0.002989	1.875626	2.83%
1aD	-1693.117941	-1693.081980	-1693.081036	-1693.186324	0.003297	2.068899	2.04%
1aE	-1693.115998	-1693.079673	-1693.078729	-1693.185513	0.004108	2.577809	0.86%
1aF	-1693.117556	-1693.081614	-1693.080670	-1693.186013	0.003608	2.264054	1.47%
1aG	-1693.113081	-1693.076985	-1693.076041	-1693.181908	0.007713	4.839981	0.02%
1aH	-1693.116180	-1693.080200	-1693.079256	-1693.184354	0.005267	3.305093	0.25%
1aI	-1693.118793	-1693.082959	-1693.082015	-1693.186672	0.002949	1.850526	2.95%
1aJ	-1693.119221	-1693.083200	-1693.082256	-1693.187773	0.001848	1.159638	9.47%
1aK	-1693.115933	-1693.080190	-1693.079246	-1693.183610	0.006011	3.771960	0.11%
1aL	-1693.115019	-1693.078885	-1693.077940	-1693.183357	0.006264	3.930720	0.09%
1aM	-1693.114150	-1693.078176	-1693.077231	-1693.182409	0.007212	4.525599	0.03%
1aN	-1693.112943	-1693.076725	-1693.075780	-1693.181888	0.007733	4.852531	0.02%
1aO	-1693.114303	-1693.078198	-1693.077253	-1693.183313	0.006308	3.958330	0.08%
1aP	-1693.114276	-1693.078232	-1693.077288	-1693.182319	0.007302	4.582074	0.03%

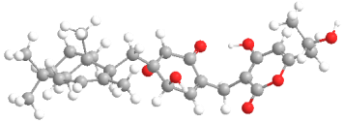
E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy.

Figure S1. Main conformers of **1a** in NMR calculation.

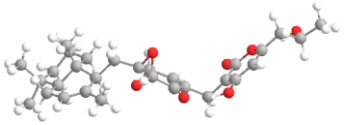




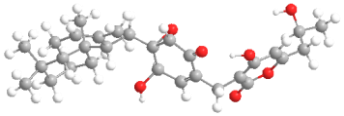
1aK



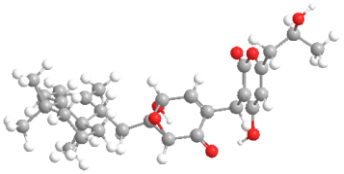
1aL



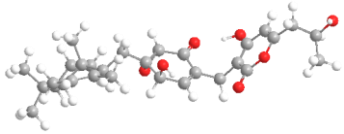
1aM



1aN



1aO



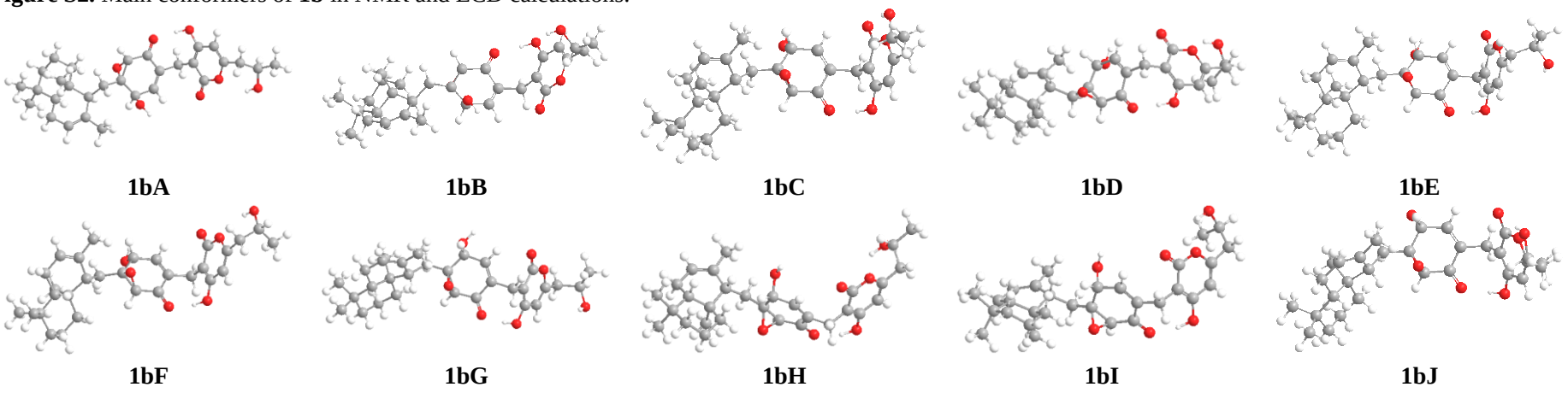
1aP

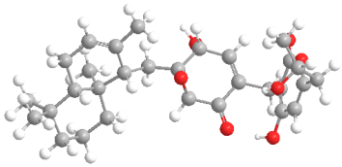
Table S2. Energy analysis for conformers of **1bA-1bO** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
1bA	-1693.118054	-1693.082197	-1693.081252	-1693.185564	0.003066	1.923944	1.28%
1bB	-1693.116921	-1693.080802	-1693.079858	-1693.185526	0.003104	1.947789	1.23%
1bC	-1693.119366	-1693.083239	-1693.082295	-1693.188611	0.000019	0.011923	32.34%
1bD	-1693.117353	-1693.081323	-1693.080379	-1693.186063	0.002567	1.610817	2.17%
1bE	-1693.117753	-1693.081477	-1693.080533	-1693.187555	0.001075	0.674573	10.56%
1bF	-1693.117690	-1693.081779	-1693.080835	-1693.185486	0.003144	1.972890	1.18%
1bG	-1693.118658	-1693.082630	-1693.081686	-1693.186814	0.001816	1.139557	4.82%
1bH	-1693.118315	-1693.082326	-1693.081382	-1693.186605	0.002025	1.270707	3.86%
1bI	-1693.118752	-1693.082986	-1693.082042	-1693.186073	0.002557	1.604542	2.20%
1bJ	-1693.120432	-1693.084627	-1693.083682	-1693.188630	0	0	33.00%
1bK	-1693.11616	-1693.080027	-1693.079083	-1693.184822	0.003808	2.389556	0.58%
1bL	-1693.113694	-1693.077551	-1693.076607	-1693.182597	0.006033	3.785765	0.06%
1bM	-1693.116394	-1693.080591	-1693.079647	-1693.184068	0.004562	2.862698	0.26%
1bN	-1693.119256	-1693.083498	-1693.082553	-1693.187002	0.001628	1.021585	5.88%
1bO	-1693.116048	-1693.079981	-1693.079037	-1693.184846	0.003784	2.374496	0.60%

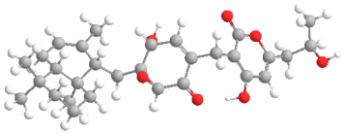
E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy.

Figure S2. Main conformers of **1b** in NMR and ECD calculations.

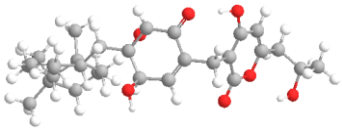




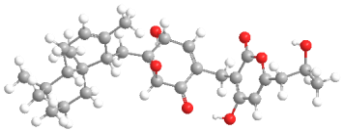
1bK



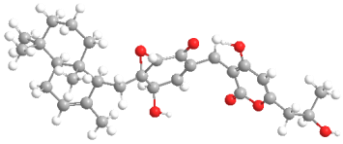
1bL



1bM



1bN



1bO

Table S3. Calculated ^{13}C NMR results for **1a**

No.	**1aA**	**1aB**	**1aC**	**1aD**	**1aE**	**1aF**	**1aG**	**1aH**	**1aI**	**1aJ**	**1aK**	**1aL**	**1aM**	**1aN**	**1aO**	**1aP**	δ_{Calcd}[a]	δ_{Exp}	δ_{Corr}[b]	Relative errors[c]
1	145.95	146.63	147.10	147.44	146.75	149.33	146.64	143.78	144.89	147.41	146.92	147.75	148.52	149.00	149.08	147.55	41.9	40.5	39.3	1.2
2	165.74	165.98	165.45	164.88	165.70	166.08	165.57	165.33	165.53	165.33	165.11	165.87	165.57	165.05	165.77	165.59	22.5	19.6	20.9	-1.3
3	144.42	143.86	144.21	143.77	143.73	144.06	144.89	144.29	143.92	143.92	143.16	144.74	144.66	144.05	144.31	143.88	43.9	43.4	41.2	2.2
4	149.58	149.42	149.91	149.94	149.23	149.41	149.85	149.23	149.29	149.73	149.60	149.53	149.62	148.98	149.02	149.34	38.6	33.9	36.2	-2.3
5	132.14	132.29	132.63	131.98	133.39	129.42	132.49	133.88	133.91	133.02	133.55	132.20	131.60	133.52	133.09	132.07	55.9	51.4	52.5	-1.1
6	160.51	159.62	160.62	160.93	159.74	160.80	160.70	161.08	161.48	160.50	159.99	160.18	160.41	159.87	159.67	160.44	27.7	24.8	25.9	-1.1
7	57.22	57.81	57.43	57.05	58.25	55.43	57.61	56.05	54.91	57.10	55.48	56.74	57.50	57.32	55.71	56.42	131.0	123.2	123.5	-0.3
8	41.60	42.17	41.83	42.26	42.03	42.21	42.38	41.95	41.77	42.17	42.51	41.96	43.01	42.69	42.05	42.10	146.4	136.1	138.0	-1.9
9	135.82	135.50	136.48	137.81	136.09	131.89	132.51	130.95	131.17	136.38	133.35	131.84	135.12	135.09	131.85	132.48	52.5	48.0	49.3	-1.3
10	147.71	146.84	147.14	147.07	146.28	147.40	146.31	147.37	145.54	146.80	146.27	146.00	147.00	144.73	145.83	145.33	40.8	37.3	38.2	-0.9
11	165.31	165.82	164.92	164.56	165.63	164.93	164.61	165.11	164.94	165.06	165.55	164.48	164.42	164.02	164.41	164.41	22.9	33.6	21.3	12.3
12	154.31	154.69	154.48	154.50	154.46	154.94	154.56	153.44	153.61	154.40	154.46	154.45	153.86	154.50	154.79	154.00	33.8	22.2	31.6	-9.4
13	173.33	173.19	173.90	173.30	173.11	175.04	173.78	171.95	172.58	173.87	173.95	173.36	174.32	174.32	173.94	173.85	14.8	14.2	13.7	0.5
14	164.48	164.66	164.83	163.79	164.52	163.09	164.38	162.77	162.74	164.70	163.35	164.13	161.56	161.00	162.56	163.52	23.7	22.1	22.1	0.0
15	158.94	158.85	158.61	159.12	159.13	159.37	160.06	154.01	153.95	158.81	158.95	157.66	150.89	150.74	160.75	158.63	29.4	26.6	27.5	-0.9
1′	118.48	117.39	117.88	117.91	117.52	112.91	115.00	115.12	115.79	116.06	113.45	115.15	116.60	117.16	112.98	114.96	70.3	66.2	66.1	0.1
2′	127.62	128.61	128.47	128.54	128.80	121.24	120.97	123.95	122.17	128.33	121.03	120.40	120.14	120.61	121.16	120.21	60.6	58.0	57.0	1.0
3′	-24.21	-23.82	-23.28	-23.09	-23.82	-23.29	-21.83	-22.87	-23.68	-23.17	-23.06	-23.90	-23.16	-23.79	-23.23	-23.87	212.2	197.1	200.2	-3.1
4′	45.03	48.29	48.22	47.41	48.32	46.70	47.31	47.46	44.81	47.14	47.07	45.40	49.60	49.85	46.77	44.98	142.3	134.5	134.2	0.3
5′	29.52	29.33	28.65	28.44	29.38	30.01	29.47	29.54	29.37	29.24	29.19	29.88	28.80	28.92	30.12	29.67	158.8	140.7	149.7	-9.0
6′	115.79	116.09	116.50	115.99	116.20	117.08	118.89	118.19	118.79	115.76	117.32	119.37	113.48	113.52	117.23	118.86	72.2	67.8	67.9	-0.1
7′	161.91	161.06	160.51	159.85	161.33	159.87	160.27	160.54	161.11	160.40	160.25	161.49	160.64	161.17	160.01	160.66	26.7	23.2	24.9	-1.7
1"	16.78	17.13	17.42	17.42	16.51	17.21	17.04	16.88	17.00	17.55	16.95	16.09	17.36	17.26	16.99	16.07	171.2	171.2	161.5	9.7
2"	85.42	83.59	80.63	82.83	83.39	85.63	81.96	83.70	82.39	80.96	86.40	83.17	81.80	81.72	84.18	81.87	103.7	99.6	97.7	1.9
3"	13.09	14.63	15.86	14.91	15.03	13.79	15.41	14.28	14.09	15.79	13.81	14.83	14.28	16.08	14.71	13.96	174.5	169.2	164.5	4.7
4"	81.14	81.46	79.41	79.10	79.83	80.78	79.26	79.46	78.84	79.44	79.16	79.51	81.49	79.54	79.89	79.77	107.3	104.1	101.1	3.0
5"	12.75	12.54	16.10	13.15	15.76	12.49	16.80	16.02	12.95	16.03	12.90	16.31	12.85	15.98	15.65	15.99	175.0	163.0	165.1	-2.1
6"	141.51	141.58	138.87	143.05	141.74	142.44	142.33	139.14	142.90	138.85	143.23	139.57	141.47	138.86	141.71	138.86	46.9	44.0	44.0	0.0
7"	116.26	116.53	117.54	116.37	116.90	116.63	117.38	118.02	115.90	117.47	116.36	116.29	116.60	117.75	117.10	113.26	71.7	66.2	67.5	-1.3
8"	163.84	163.81	164.95	165.32	163.68	163.61	164.47	164.52	164.46	164.96	165.26	164.25	163.60	164.84	163.86	163.36	24.2	23.3	22.5	0.8
Population	67.13%	12.62%	2.83%	2.04%	0.86%	1.47%	0.02%	0.25%	2.95%	9.47%	0.11%	0.09%	0.03%	0.02%	0.08%	0.03%			RMSD	4.1

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{calcd}$

Table S4. Calculated ^{13}C NMR results for **1b**

No.	**1bA**	**1bB**	**1bC**	**1bD**	**1bE**	**1bF**	**1bG**	**1bH**	**1bI**	**1bJ**	**1bK**	**1bL**	**1bM**	**1bN**	**1bO**	δ_{Calcd}[a]	δ_{Exp}	δ_{Corr}[b]	Relative errors[c]
1	147.48	147.59	147.41	148.14	146.69	147.56	146.78	144.89	144.41	147.35	147.00	147.94	144.56	147.27	147.38	41.1	40.5	38.3	2.2
2	165.55	165.87	165.16	165.56	165.74	164.76	165.22	165.79	164.86	164.82	165.54	165.70	165.31	164.73	165.58	23.1	19.6	21.3	-1.7
3	143.84	144.79	143.86	144.16	143.89	143.47	144.17	143.98	145.36	143.79	144.35	143.94	144.30	143.64	144.12	44.3	43.4	41.4	2.0
4	149.28	149.49	150.07	149.22	149.33	149.87	149.55	149.41	149.30	149.89	149.95	149.45	149.20	149.99	149.53	38.4	33.9	35.8	-1.9
5	132.50	132.31	130.99	133.00	133.58	132.80	133.57	132.67	134.28	132.12	132.39	131.57	134.23	132.28	131.59	56.1	51.4	52.6	-1.2
6	160.39	160.21	161.34	160.40	159.95	160.12	160.66	161.30	161.62	160.86	160.77	160.36	160.77	160.62	160.78	27.3	24.8	25.3	-0.5
7	56.34	56.71	56.36	55.71	58.31	56.86	57.15	54.78	55.66	57.38	57.11	56.68	56.99	56.44	56.16	131.3	123.2	123.9	-0.7
8	42.07	41.94	42.39	42.33	42.02	42.32	41.57	42.17	41.30	42.30	42.08	42.02	42.22	42.47	42.19	145.9	136.1	137.8	-1.7
9	132.50	131.91	138.01	132.13	136.59	137.68	137.78	129.22	130.71	137.82	136.87	132.26	130.08	137.58	132.36	51.3	48.0	48.0	0.0
10	145.46	145.92	147.58	146.26	146.32	146.62	145.34	147.34	145.65	147.00	147.21	145.26	146.55	147.07	145.79	41.2	37.3	38.5	-1.2
11	164.82	164.49	164.76	165.70	165.44	164.40	164.19	164.37	164.33	164.57	165.09	163.66	163.28	164.53	164.47	23.5	33.6	21.7	11.9
12	153.95	154.36	154.35	154.16	154.29	154.44	153.67	153.87	153.82	154.63	154.48	154.06	153.40	154.40	153.98	33.8	22.2	31.5	-9.3
13	173.94	173.33	173.40	174.65	173.13	173.54	173.18	172.07	173.39	173.35	173.83	173.78	172.67	173.38	173.95	14.9	14.2	13.5	0.7
14	163.46	164.09	163.86	163.01	164.42	163.72	164.58	162.69	162.60	163.90	165.01	163.78	162.68	163.79	163.07	24.3	22.1	22.5	-0.4
15	158.45	157.60	158.97	158.70	159.18	159.13	158.82	154.07	154.59	159.31	158.76	158.86	154.03	159.18	159.18	29.4	26.6	27.3	-0.7
1′	114.88	115.19	117.80	114.91	117.48	117.47	117.99	115.80	115.77	115.86	115.34	115.06	114.85	115.78	111.94	71.5	66.2	67.2	-1.0
2′	120.30	120.48	128.67	121.08	128.71	129.06	127.31	122.45	122.50	128.49	128.51	120.08	123.74	128.25	119.91	60.5	58.0	56.7	1.3
3′	-23.95	-23.84	-22.93	-24.37	-23.74	-22.73	-23.69	-23.29	-23.75	-23.26	-22.93	-23.91	-22.54	-23.55	-23.76	211.5	197.1	199.9	-2.8
4′	44.97	45.55	47.33	45.08	48.20	47.44	44.98	45.38	45.27	46.71	47.45	44.69	47.11	47.07	44.42	141.3	134.5	133.4	1.1
5′	29.57	29.88	28.25	29.62	29.30	28.65	29.50	29.43	30.08	29.14	28.94	29.84	29.54	29.89	29.91	159.2	140.7	150.3	-9.6
6′	118.98	119.42	115.99	119.47	116.44	116.00	116.01	118.57	118.56	115.68	116.25	118.64	118.46	115.80	118.04	71.9	67.8	67.6	0.2
7′	160.74	161.72	160.22	161.31	161.11	160.05	160.68	161.14	160.65	159.72	160.55	160.67	160.83	160.26	160.80	27.9	23.2	25.9	-2.7
1"	16.73	16.22	17.40	16.46	16.48	17.53	16.90	16.42	17.22	17.46	17.46	15.95	17.63	17.89	16.15	170.9	171.2	161.5	9.7
2"	82.20	82.97	83.11	83.33	84.15	81.61	80.61	80.93	82.72	83.38	81.14	80.85	83.81	82.27	82.48	105.2	99.6	99.1	0.5
3"	13.52	15.43	14.58	14.65	15.11	14.92	15.27	15.60	14.41	14.56	15.80	14.63	14.28	14.84	13.80	173.5	169.2	163.9	5.3
4"	81.06	78.49	81.07	78.39	79.30	79.42	78.64	78.75	78.15	80.96	79.18	77.68	79.20	79.60	79.58	107.8	104.1	101.6	2.5
5"	12.77	16.06	12.50	13.15	15.60	12.98	16.28	15.85	13.19	12.35	17.07	15.86	13.22	12.62	15.88	175.0	163.0	165.3	-2.3
6"	141.79	139.22	141.47	143.16	139.78	142.70	141.93	139.32	142.97	141.48	142.14	143.83	143.08	142.52	142.21	46.8	44.0	43.8	0.2
7"	116.88	117.64	116.36	116.25	117.92	116.17	117.51	118.35	115.92	116.40	117.75	116.81	115.93	116.58	117.01	71.5	66.2	67.2	-1.0
8"	163.39	164.69	163.65	164.98	164.50	165.10	164.63	164.45	164.99	163.69	164.47	165.03	164.68	165.56	163.82	24.1	23.3	22.3	1.0
Population	1.28%	1.23%	32.34%	2.17%	10.56%	1.18%	4.82%	3.86%	2.20%	33.00%	0.58%	0.06%	0.26%	5.88%	0.60%			RMSD	4.1

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{calcd}$

Figure S3. ^{13}C NMR calculation results of two possible isomers of **1**. (A) Linear correlation plots of predicted versus experimental ^{13}C NMR chemical shifts. (B) Relative errors between the predicted ^{13}C NMR chemical shifts of two potential structures and recorded ^{13}C NMR data.

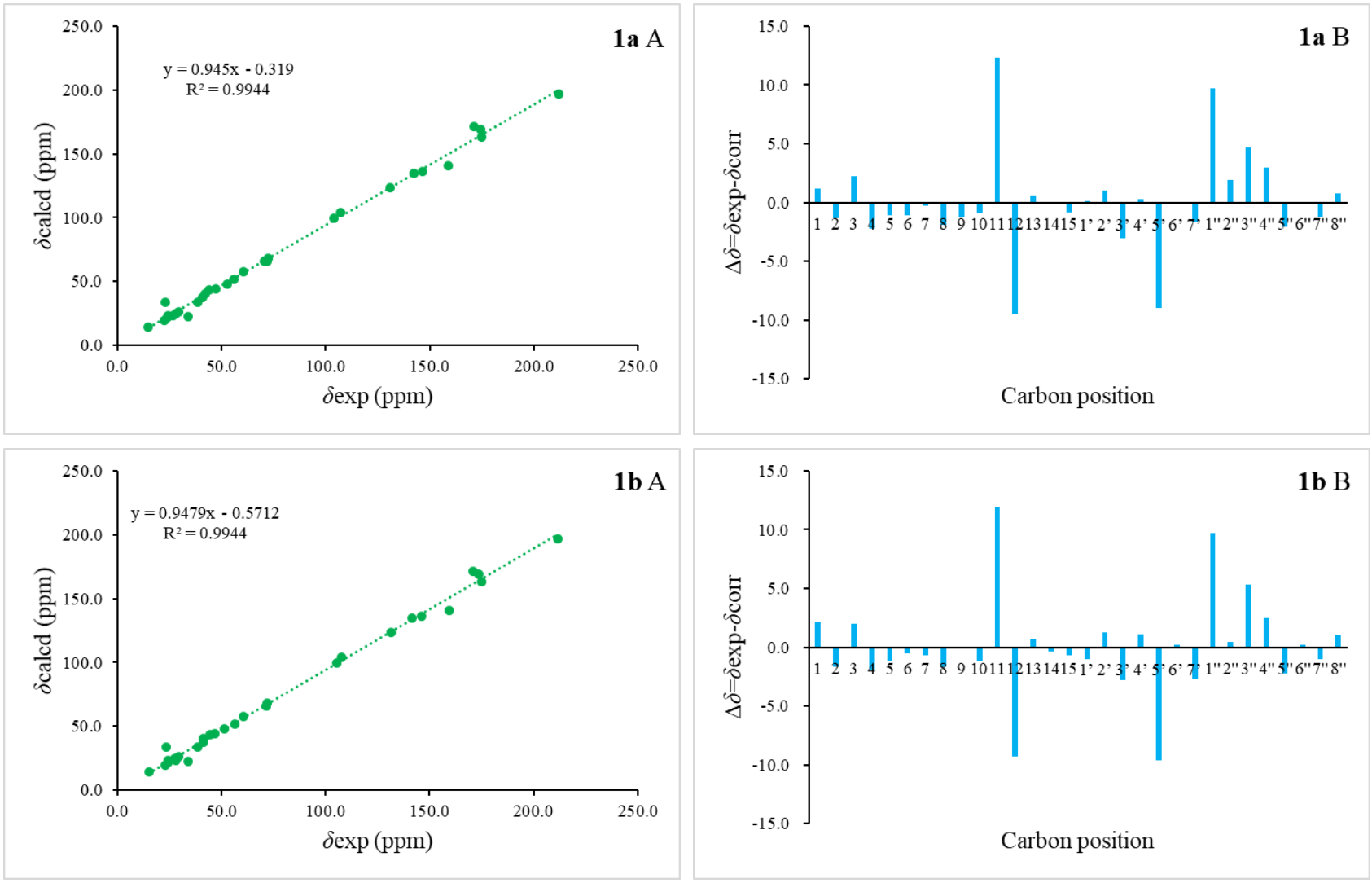


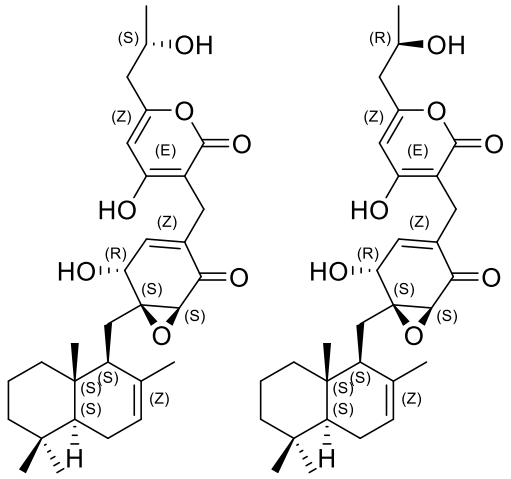
Table S5. DP4+ analysis results of **1a** (Isomer 1) and **1b** (Isomer 2)

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
12			DP4+	0.00%	100.00%	–	–	–
14	Nuclei	sp2?	xperimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
15	C		40.6	146.26	147.13			
16	C		19.8	165.70	165.13			
17	C		43.4	144.25	143.90			
18	C		33.9	149.58	149.82			
19	C		51.4	132.28	132.09			
20	C		24.8	160.43	160.89			
21	C	x	123.3	57.19	56.87			
22	C	x	135.9	41.76	42.24			
23	C		48.1	135.67	136.92			
24	C		37.2	147.40	146.96			
25	C		33.7	165.31	164.71			
26	C		22.3	154.36	154.37			
27	C		14.2	173.38	173.33			
28	C		22.2	164.44	163.87			
29	C		26.6	158.75	158.78			
30	C		66.2	117.89	116.70			
31	C		58.1	127.57	127.71			
32	C	x	197.1	-23.98	-23.29			
33	C	x	134.6	45.84	46.85			
34	C	x	141	29.42	28.99			
35	C		67.7	115.97	116.26			
36	C		23.2	161.51	160.27			
37	C	x	171.2	16.94	17.23			
38	C	x	99.2	84.46	83.01			
39	C	x	168.7	13.72	14.72			
40	C	x	104.2	80.83	80.35			
41	C	x	163	13.18	13.23			
42	C		44.1	141.27	141.37			
43	C		66.2	116.45	116.70			
44	C		23.4	164.02	164.04			
45								
46	H		1.79	30.24	30.11			
47	H		0.9	31.04	30.95			
48	H		1.55	30.00	30.16			
49	H		1.44	30.48	30.35			
50	H		1.4	30.29	30.52			
51	H		1.19	30.49	30.52			
52	H		1.19	30.26	30.32			
53	H		1.96	29.78	30.00			
54	H		1.84	29.88	29.88			
55	H	x	5.38	25.88	25.99			
56	H		1.51	30.36	30.26			
57	H		0.85	30.41	30.40			
58	H		0.85	31.21	31.29			

59	H		0.85	30.75	30.67			
60	H		0.88	31.06	30.89			
61	H		0.88	31.32	31.50			
62	H		0.88	30.43	30.41			
63	H		0.78	30.65	30.49			
64	H		0.78	31.36	30.78			
65	H		0.78	30.35	31.25			
66	H		1.62	30.26	30.14			
67	H		1.62	29.85	29.86			
68	H		1.62	29.98	29.91			
69	H		2.18	29.73	29.76			
70	H		1.99	29.81	29.71			
71	H		3.25	28.41	28.46			
72	H	x	6.2	24.09	24.32			
73	H		4.34	26.99	27.09			
74	H		3.31	28.58	28.47			
75	H		3.15	28.82	28.66			
76	H	x	6.01	25.63	25.68			
77	H		2.53	29.28	29.17			
78	H		2.53	29.24	29.15			
79	H		4.09	27.78	27.72			
80	H		1.2	30.45	30.42			
81	H		1.2	30.68	30.63			
82	H		1.2	30.67	30.67			

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
4			Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
5	sDP4+ (H data)		0.01%	99.99%	-	-	-	-
6	sDP4+ (C data)		74.88%	25.12%	-	-	-	-
7	sDP4+ (all data)		0.02%	99.98%	-	-	-	-
8	uDP4+ (H data)		0.08%	99.92%	-	-	-	-
9	uDP4+ (C data)		38.15%	61.85%	-	-	-	-
10	uDP4+ (all data)		0.05%	99.95%	-	-	-	-
11	DP4+ (H data)		0.00%	100.00%	-	-	-	-
12	DP4+ (C data)		64.77%	35.23%	-	-	-	-
13	DP4+ (all data)		0.00%	100.00%	-	-	-	-

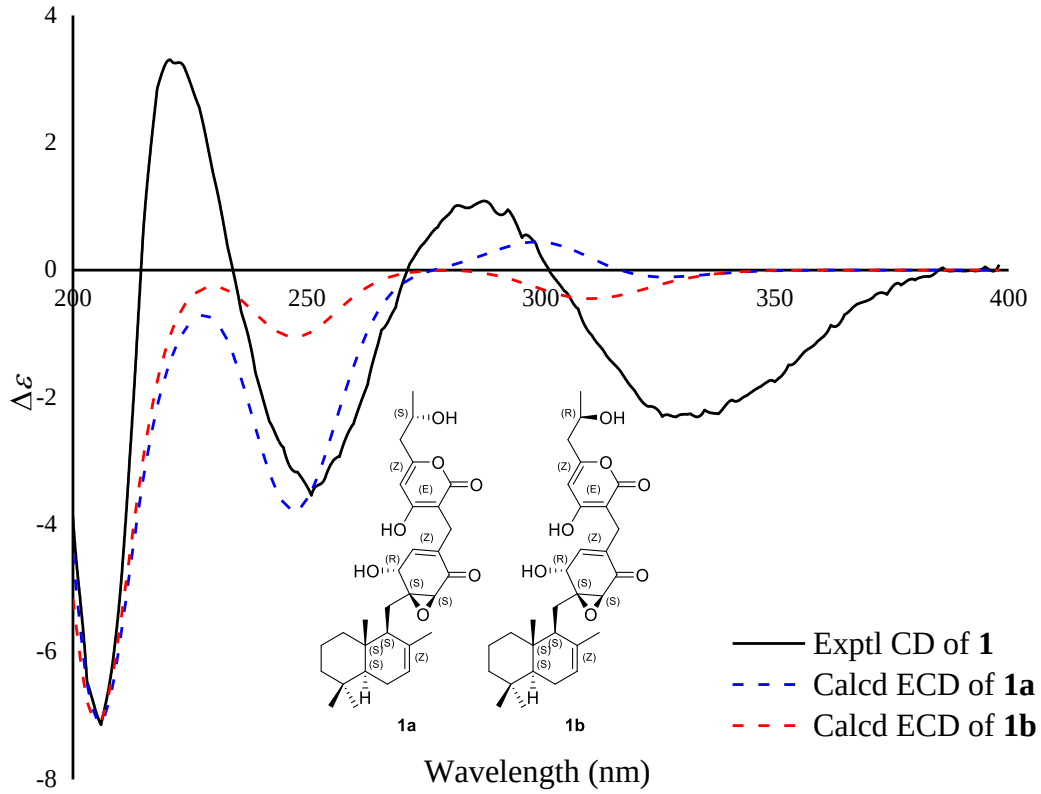
S1.2. Computational details for compound 1 (ECD)



1a **1b**

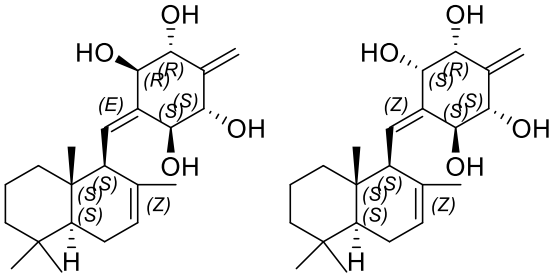
Conformation search based on molecular mechanics with MMFF force fields were performed for **1a** and **1b** gave 16 and 15 stable conformers with populations higher than 1%. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package with g09 default keyword. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-311+G(d,p) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 program package and the calculated ECD data of all conformers were Boltzmann averaged by Gibbs free energy.

Figure S4. Comparison of the calculated ECD spectra for with the experimental spectrum of **1** in methanol with IEFPCM model.



Section S2. Calculational details for 2

S2.1. Computational details for compound 2 (NMR)



2a

2b

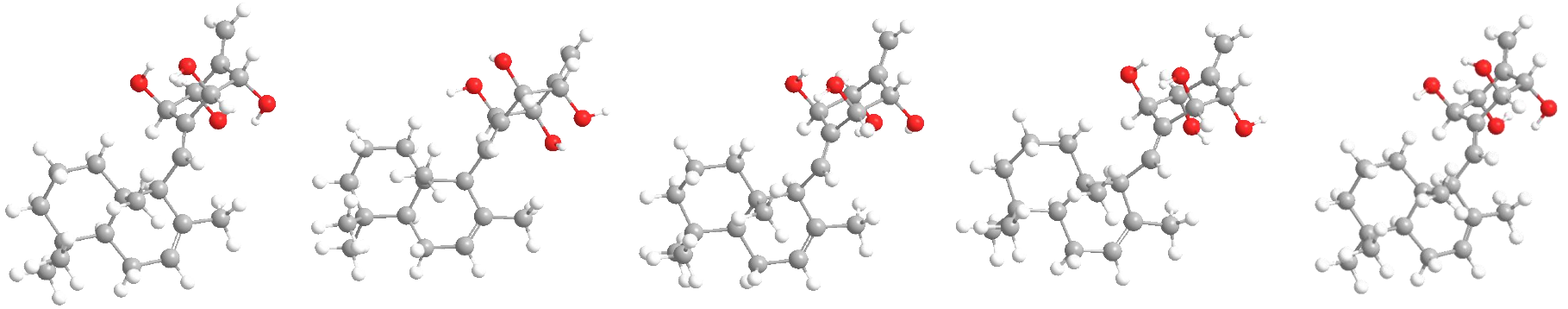
Conformation search based on molecular mechanics with MMFF force fields were performed for **2a** and **2b** gave 14 and 8 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. Gauge Independent Atomic Orbital (GIAO) calculations of their ^{1}H and ^{13}C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The ^{1}H and ^{13}C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by the improved probability DP4+ method.

Table S6. Energy analysis for conformers of **2aA-2aN** at B3LYP/6-31G(d) level in the gas phase

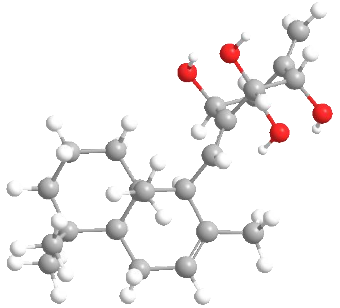
Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
2aA	-1159.111977	-1159.085802	-1159.084858	-1159.165761	0	0	23.98%
2aB	-1159.111569	-1159.085503	-1159.084559	-1159.164837	0.000924	0.579819	9.01%
2aC	-1159.110888	-1159.084671	-1159.083727	-1159.164523	0.001238	0.776857	6.46%
2aD	-1159.111625	-1159.085559	-1159.084615	-1159.164709	0.001052	0.660140	7.86%
2aE	-1159.110705	-1159.084474	-1159.083530	-1159.164350	0.001411	0.885416	5.38%
2aF	-1159.110283	-1159.083989	-1159.083045	-1159.164020	0.001741	1.092494	3.79%
2aG	-1159.111364	-1159.085099	-1159.084155	-1159.165216	0.000545	0.341993	13.46%
2aH	-1159.111165	-1159.085026	-1159.084082	-1159.164441	0.001320	0.828313	5.92%
2aI	-1159.111078	-1159.084871	-1159.083927	-1159.164630	0.001131	0.709713	7.23%
2aJ	-1159.110582	-1159.084349	-1159.083405	-1159.163987	0.001774	1.113202	3.66%
2aK	-1159.109497	-1159.083183	-1159.082239	-1159.163310	0.002451	1.538026	1.79%
2aL	-1159.110156	-1159.083813	-1159.082868	-1159.164123	0.001638	1.027861	4.23%
2aM	-1159.110719	-1159.084545	-1159.083600	-1159.163991	0.001770	1.110692	3.67%
2aN	-1159.110770	-1159.084613	-1159.083669	-1159.163966	0.001795	1.126380	3.58%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy.

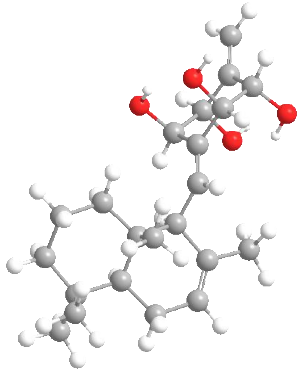
Figure S5. Main conformers of **2a** in NMR calculation.



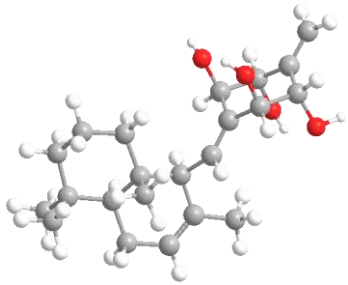
2aA **2aB** **2aC** **2aD** **2aE**



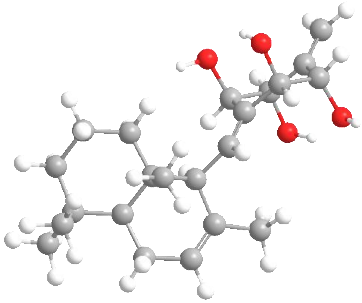
2aF



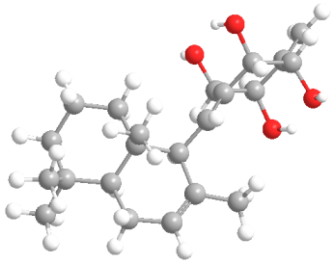
2aG



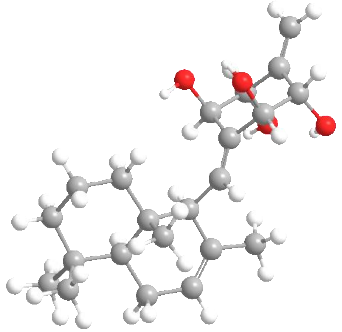
2aH



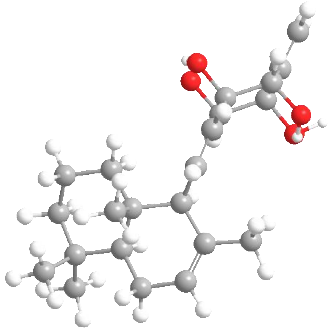
2aI



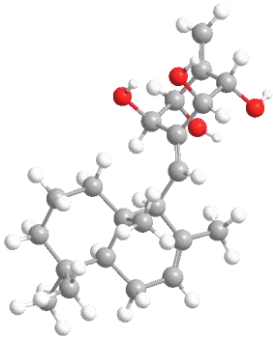
2aJ



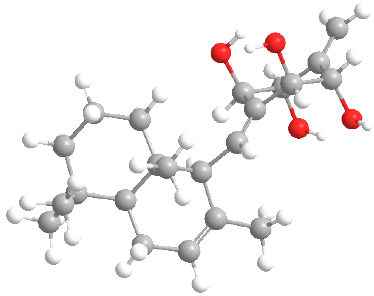
2aK



2aL



2aM



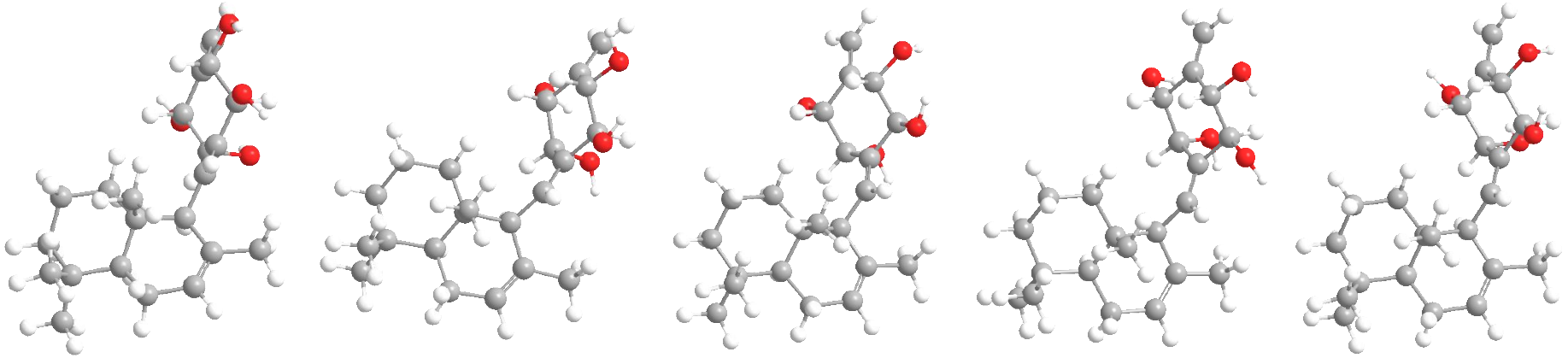
2aN

Table S7. Energy analysis for conformers of **2bA-2bH** at B3LYP/6-31G(d) level in the gas phase

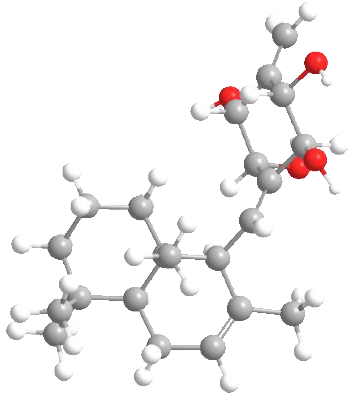
Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
2bA	-1159.108969	-1159.082410	-1159.081465	-1159.163156	0.002061	1.293297	3.57%
2bB	-1159.110681	-1159.084036	-1159.083091	-1159.165217	0	0	31.74%
2bC	-1159.110835	-1159.084465	-1159.083521	-1159.164732	0.000485	0.304342	18.98%
2bD	-1159.110565	-1159.084035	-1159.083091	-1159.164609	0.000608	0.381526	16.66%
2bE	-1159.108984	-1159.082485	-1159.081541	-1159.163312	0.001905	1.195406	4.22%
2bF	-1159.109316	-1159.082842	-1159.081897	-1159.163699	0.001518	0.952559	6.35%
2bG	-1159.110569	-1159.084036	-1159.083092	-1159.164624	0.000593	0.372113	16.93%
2bH	-1159.108756	-1159.082549	-1159.081605	-1159.162362	0.002855	1.791540	1.54%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy.

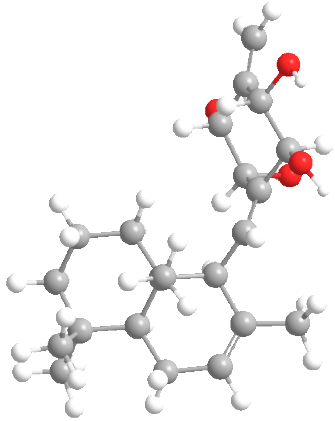
Figure S6. Main conformers of **2b** in NMR and ECD calculations.



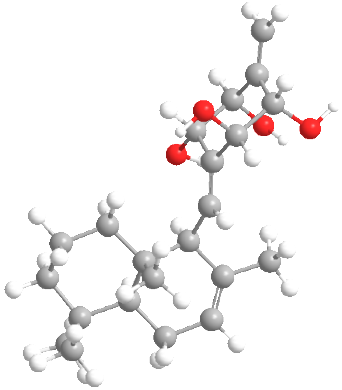
2bA **2bB** **2bC** **2bD** **2bE**



2bF



2bG



2bH

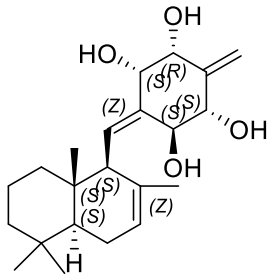
Table S8. DP4+ analysis results of **2a** (Isomer 1) and **2b** (Isomer 2)

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
12			DP4+	0.00%	100.00%	-	-	-
14	Nuclei	sp2?	Experimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
15	C		40.4	144.9	144.8			
16	C		18.3	165.5	165.5			
17	C		42.1	143.7	143.8			
18	C		37.2	149.3	149.4			
19	C		49.9	134.7	134.9			
20	C		23.4	160.6	160.4			
21	C	x	121.2	56.5	56.4			
22	C	x	133.5	44.1	43.8			
23	C		52.9	129.7	130.3			
24	C		36.7	145.3	144.8			
25	C		32.4	164.8	164.9			
26	C		21	153.9	154.0			
27	C		13.5	162.1	162.0			
28	C		21.4	171.6	171.5			
29	C	x	125.6	37.2	48.7			
30	C	x	137.6	44.8	42.9			
31	C		69	101.8	108.7			
32	C		71.6	105.7	107.9			
33	C	x	146.6	34.4	29.2			
34	C		75.3	104.6	111.8			
35	C		73.5	112.5	114.6			
36	C	x	105.8	58.3	75.1			
37								
38	H		1.5	30.08	30.30			
39	H		1	30.58	30.74			
40	H		1.54	30.16	30.15			
41	H		1.4	30.39	30.41			
42	H		1.45	30.35	30.36			
43	H		1.21	30.48	30.48			
44	H		1.29	30.43	30.46			
45	H		2.04	29.73	29.70			
46	H		1.93	29.68	29.68			
47	H	x	5.5	25.72	25.76			
48	H		2.8	28.75	28.79			
49	H		0.89	30.35	30.39			
50	H		0.89	31.33	31.32			
51	H		0.89	30.69	30.71			

52	H		0.93	31.03	31.04			
53	H		0.93	31.19	31.19			
54	H		0.93	30.42	30.41			
55	H		0.9	30.22	30.24			
56	H		0.9	30.16	30.11			
57	H		0.9	30.18	30.23			
58	H		1.52	31.06	30.57			
59	H		1.52	30.75	30.84			
60	H		1.52	30.55	31.11			
61	H	x	5.68	25.61	25.63			
62	H		4.77	27.47	27.47			
63	H		3.99	27.45	27.90			
64	H		3.61	27.36	27.61			
65	H		4.11	26.94	26.88			
66	H	x	5.39	25.93	26.01			
67	H	x	5.28	25.93	26.06			

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
4			Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
5	sDP4+ (H data)		92.04%	7.96%	-	-	-	-
6	sDP4+ (C data)		0.00%	100.00%	-	-	-	-
7	sDP4+ (all data)		0.00%	100.00%	-	-	-	-
8	uDP4+ (H data)		0.06%	99.94%	-	-	-	-
9	uDP4+ (C data)		0.00%	100.00%	-	-	-	-
10	uDP4+ (all data)		0.00%	100.00%	-	-	-	-
11	DP4+ (H data)		0.73%	99.27%	-	-	-	-
12	DP4+ (C data)		0.00%	100.00%	-	-	-	-
13	DP4+ (all data)		0.00%	100.00%	-	-	-	-

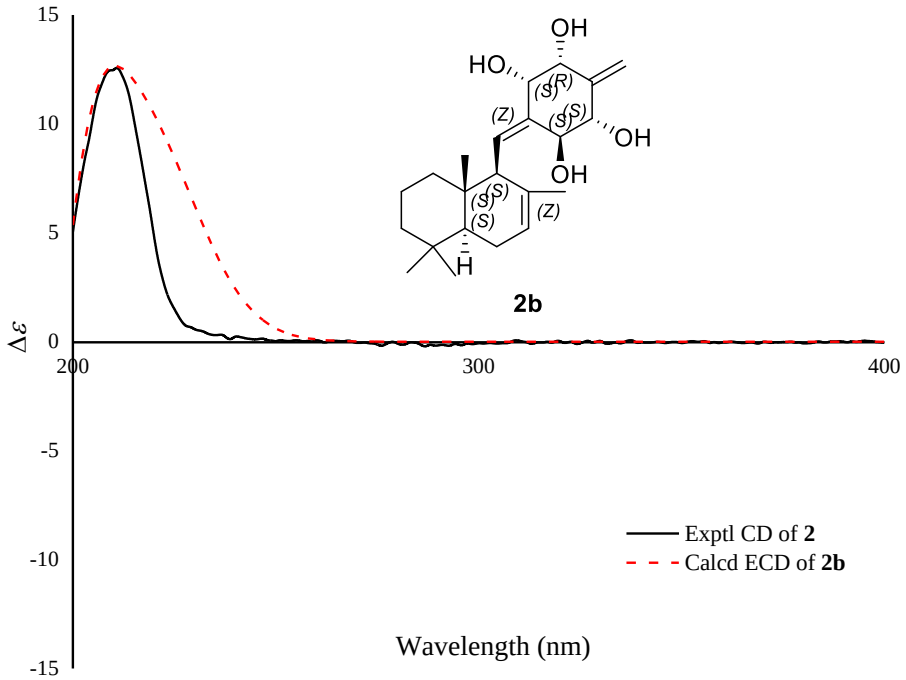
S2.2. Computational details for compound 2 (ECD)



2b

Conformation search based on molecular mechanics with MMFF force fields were performed for **2b** gave 8 stable conformers with populations higher than 1%. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-311+G(d,p) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 program package and the calculated ECD data of all conformers were Boltzmann averaged by Gibbs free energy.

Figure S7. Comparison of the calculated ECD spectra for with the experimental spectrum of **2** in methanol with IEFPCM model.



Section S3. NMR and MS spectra of 1

Figure S8. ^{1}H NMR of **1** in CD_3OD

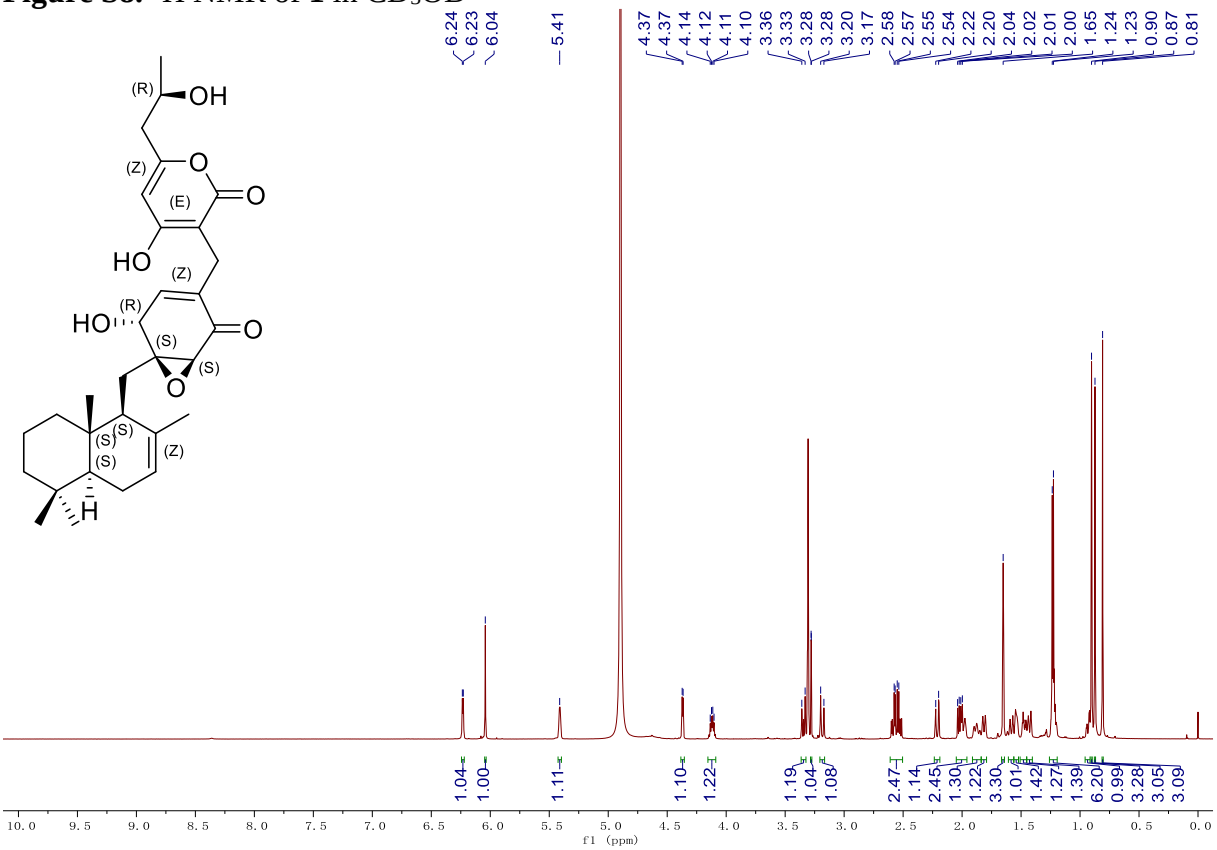


Figure S9. ^{13}C NMR and DEPT of **1** in CD_3OD

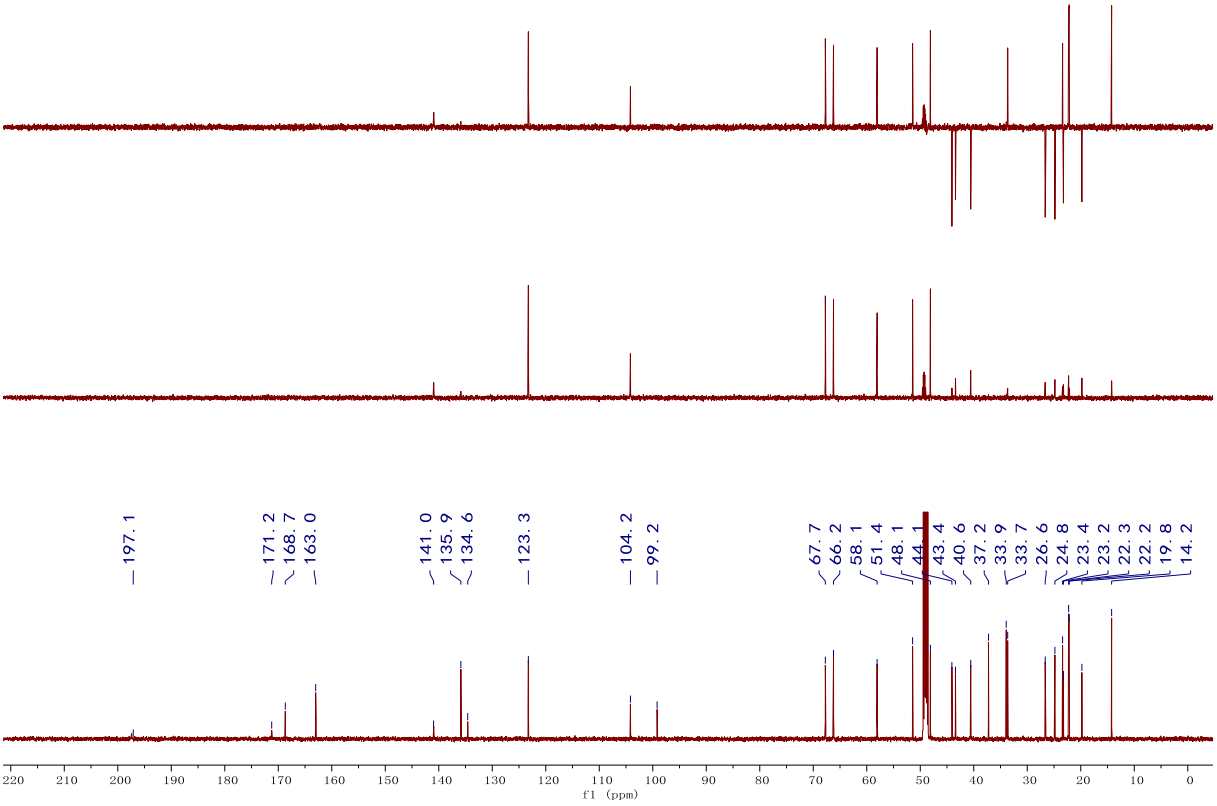


Figure S10. HSQC of **1** in CD_3OD

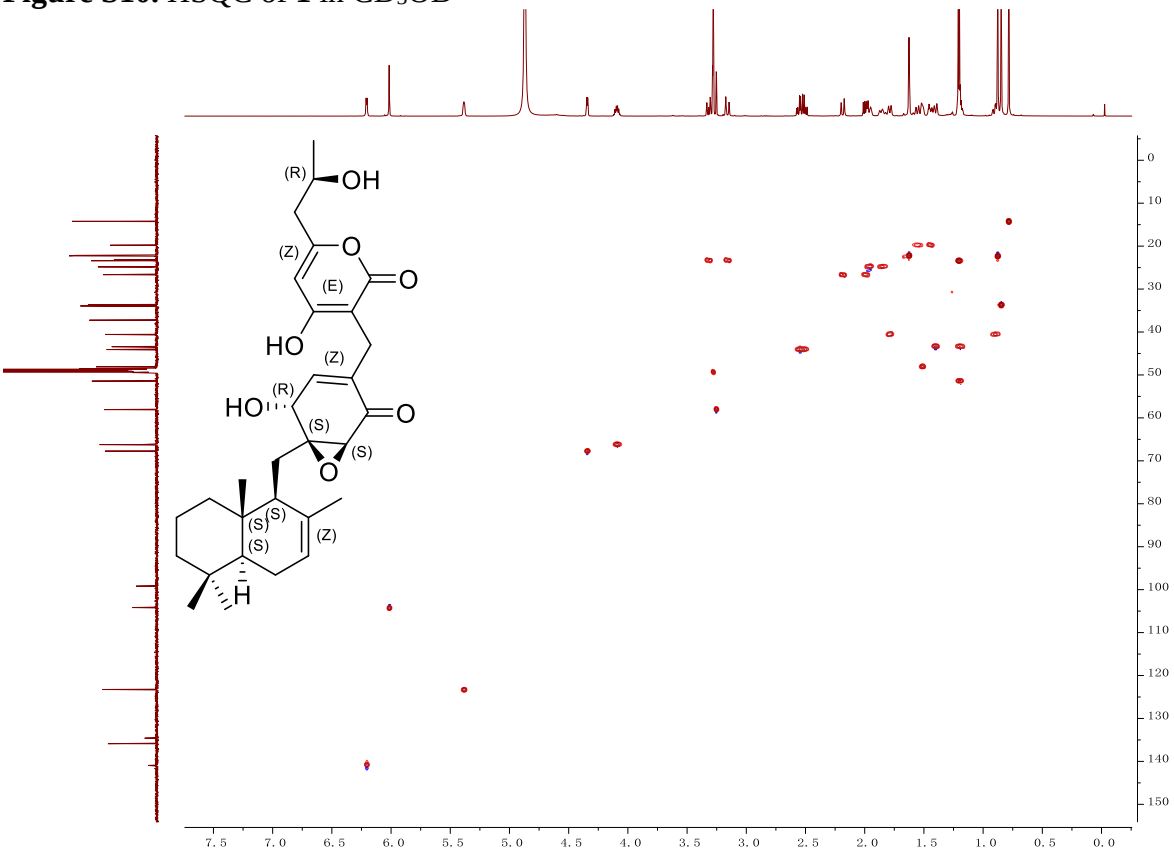


Figure S11. HMBC of **1** in CD_3OD

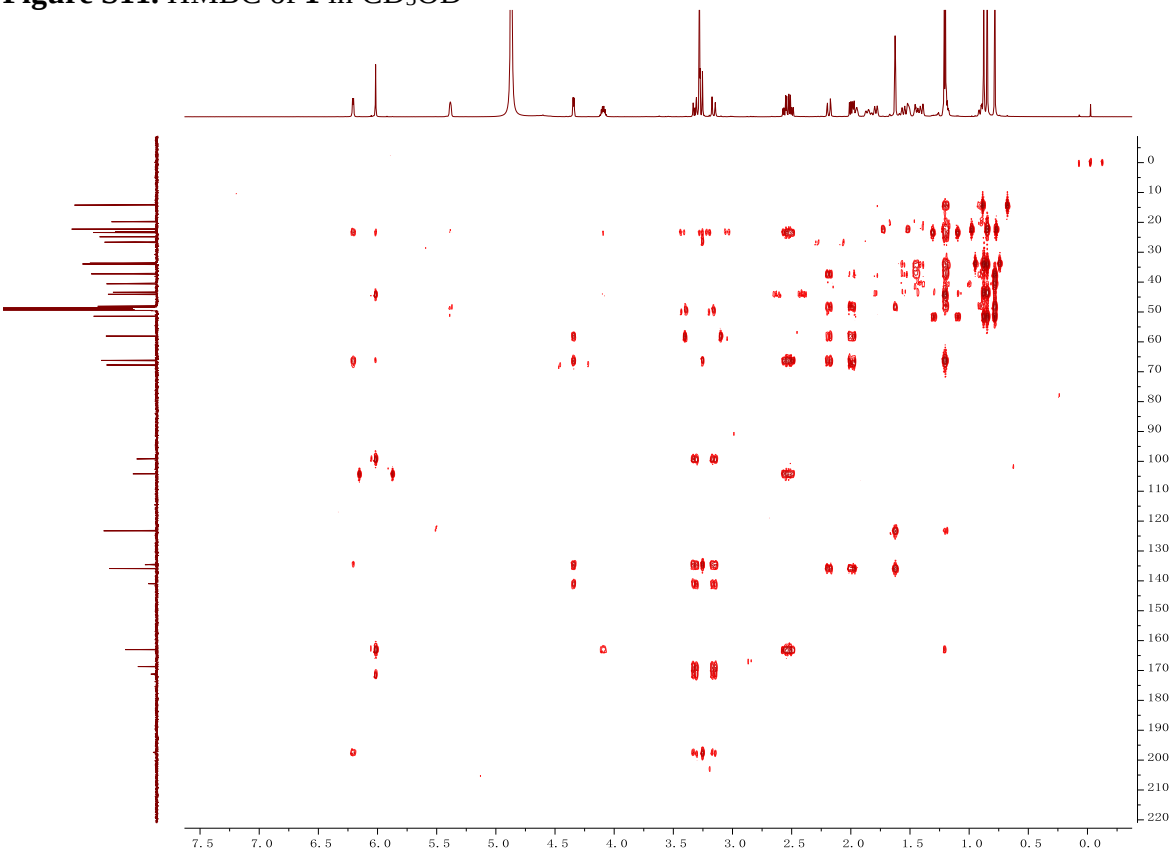


Figure S12. ^{1}H-^{1}H COSY of **1** in CD_3OD

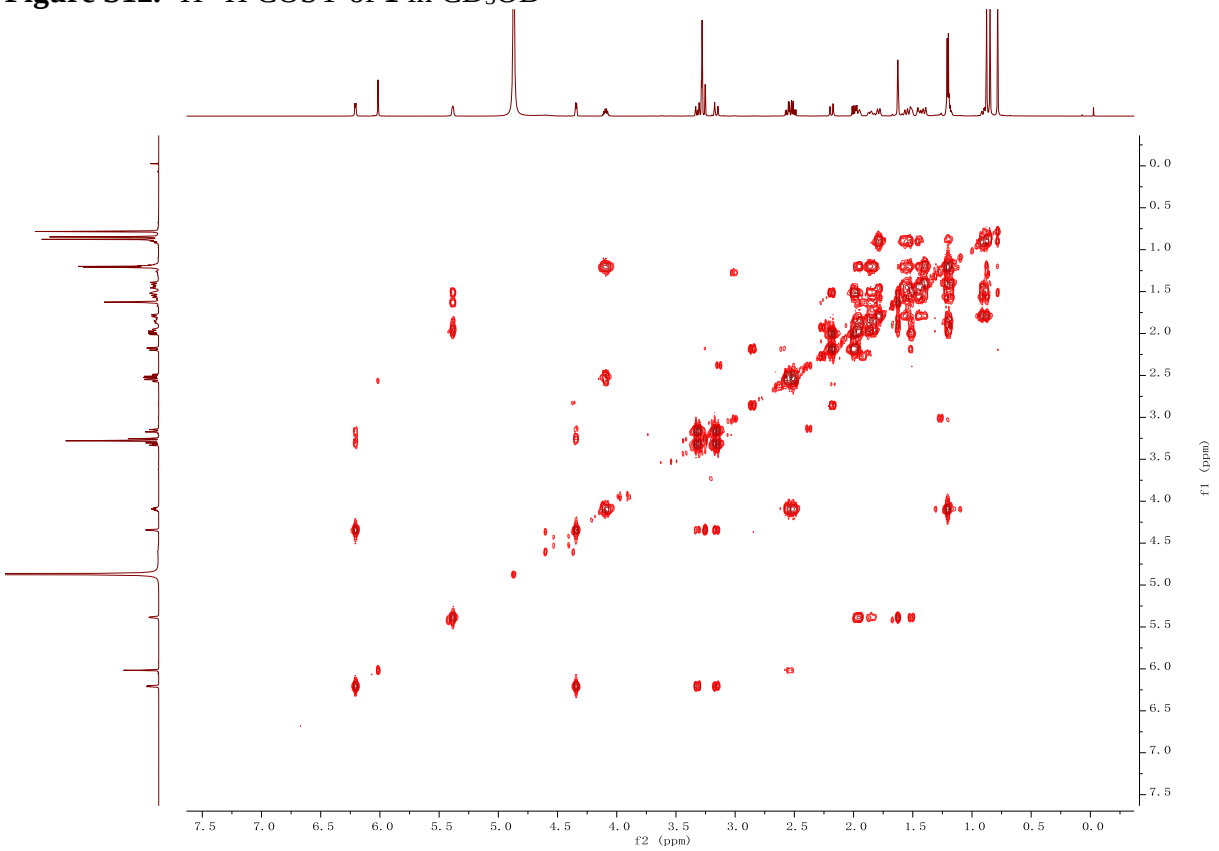


Figure S13. ROESY of **1** in CD_3OD

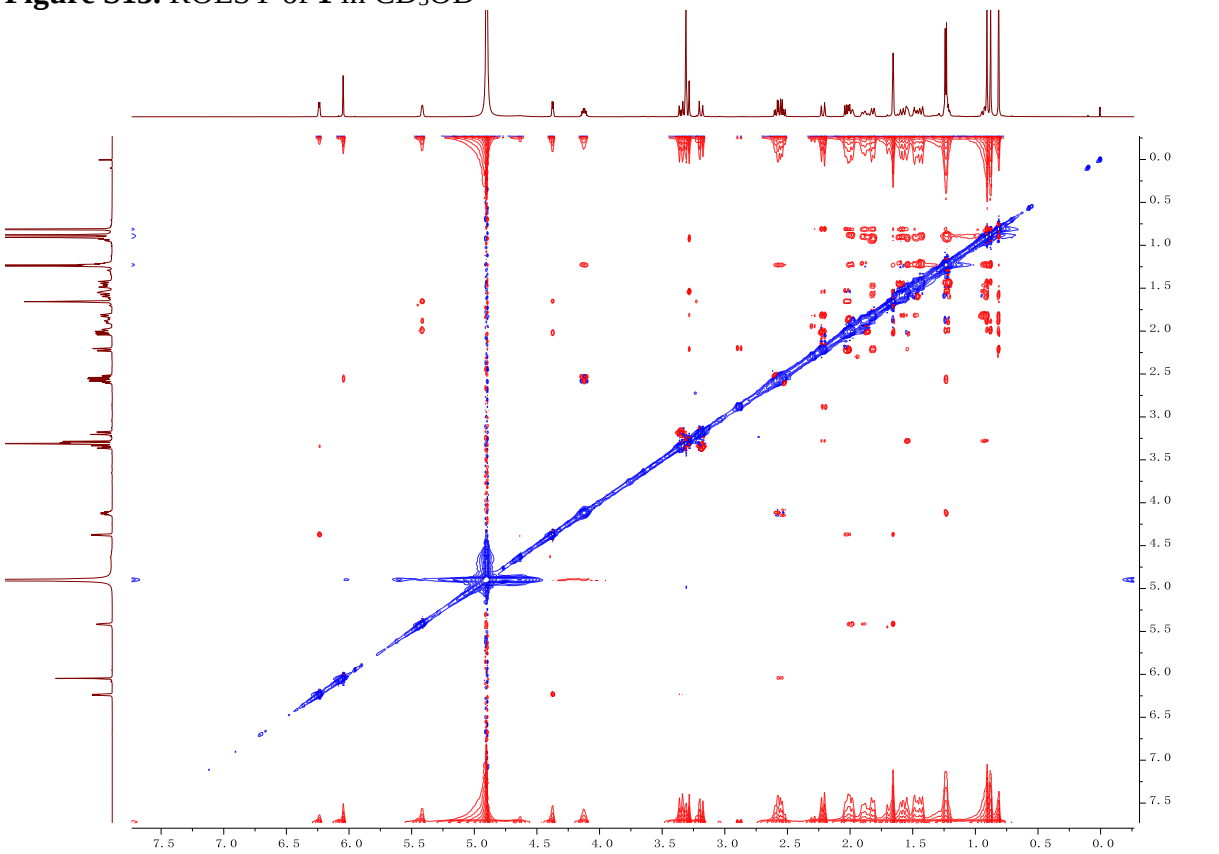


Figure S14. HRESIMS of **1**

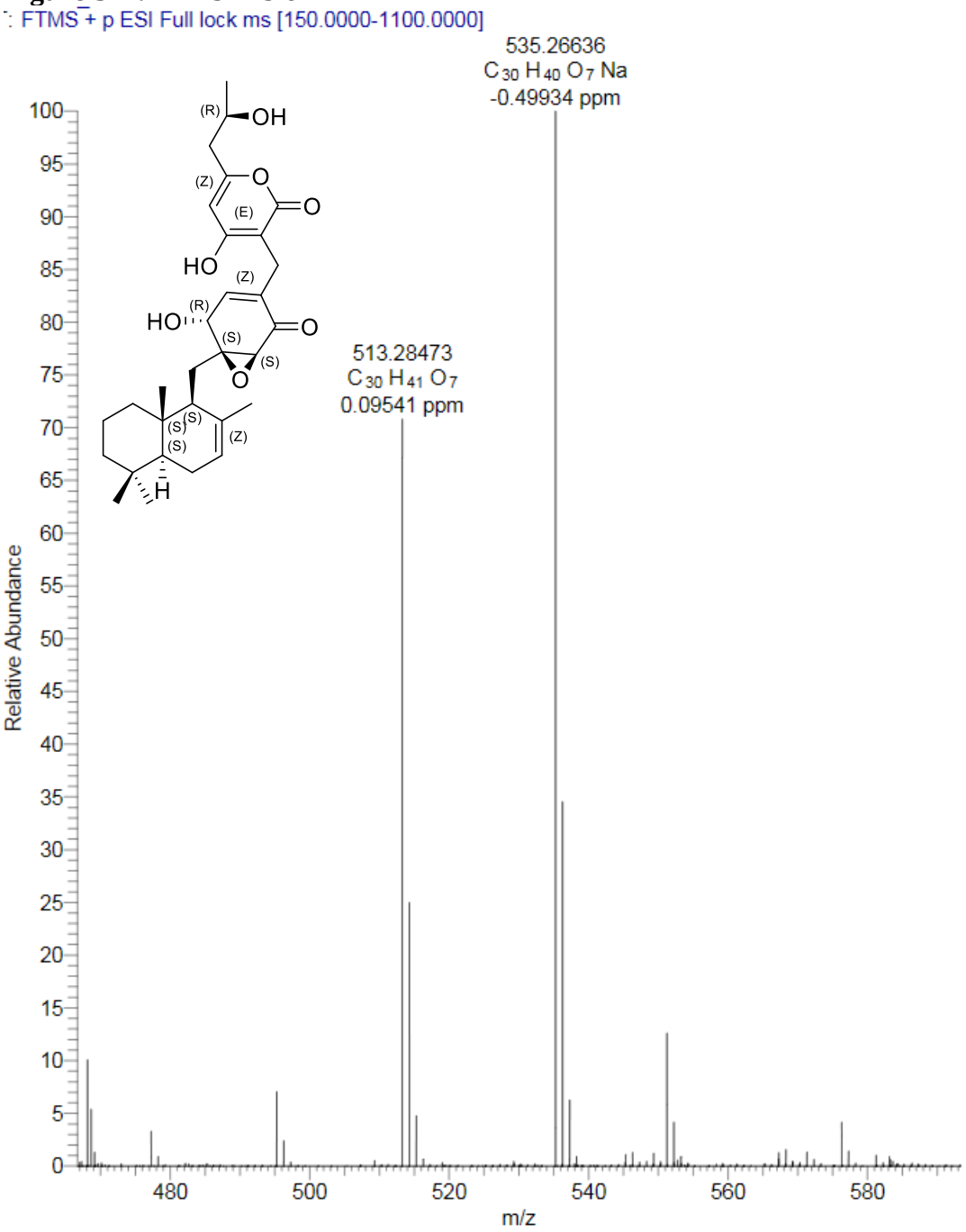


Figure S15. UV of **1**

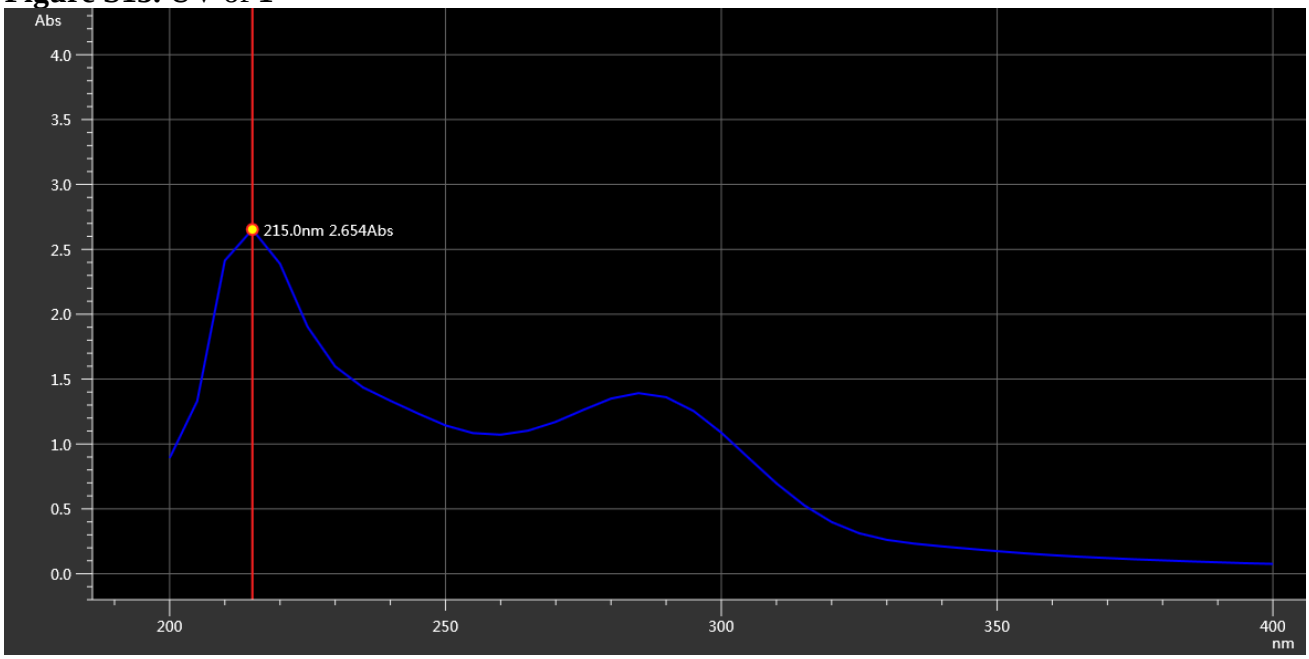
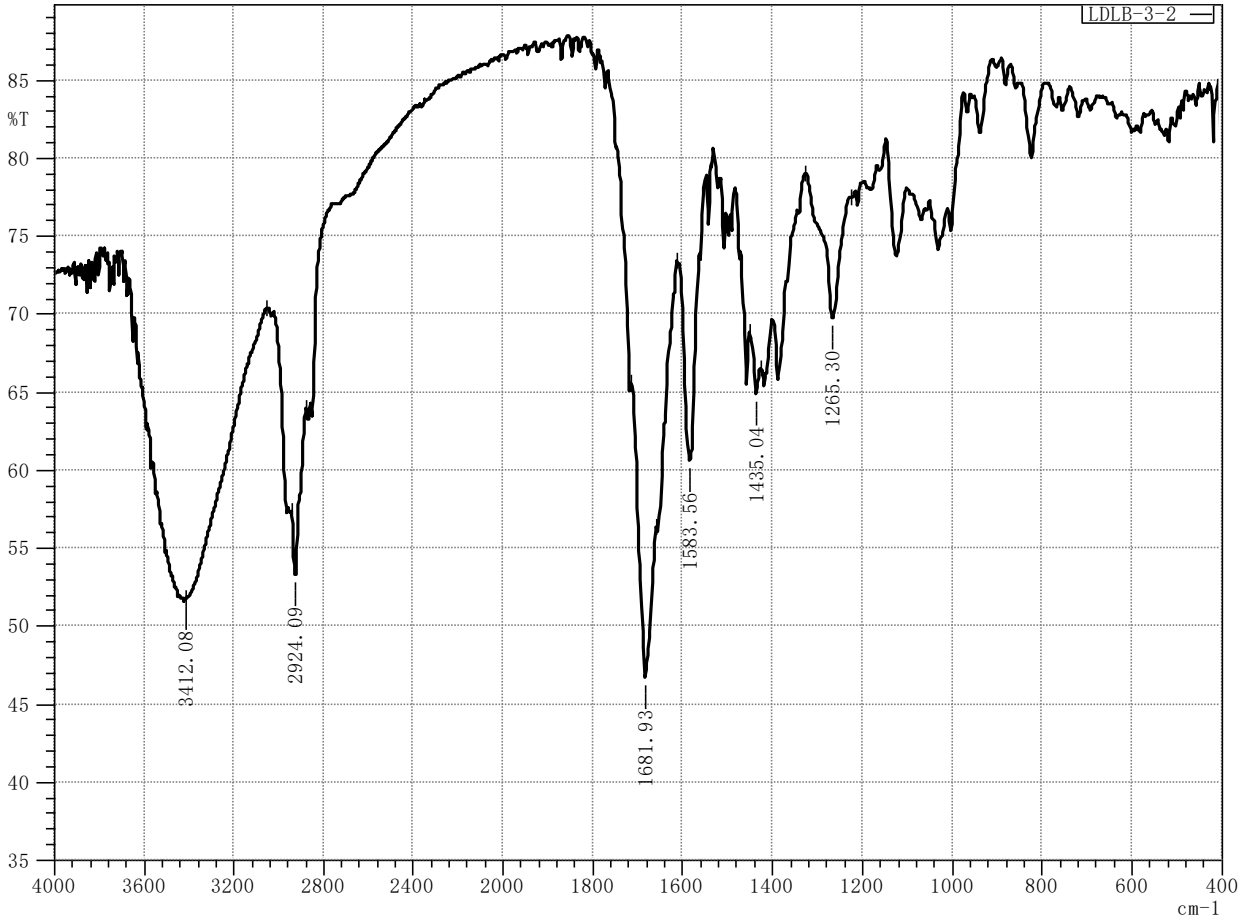


Figure S16. IR of **1**



Section S4. NMR and MS spectra of 2

Figure S17. ^{1}H NMR of **2** in CD_3OD

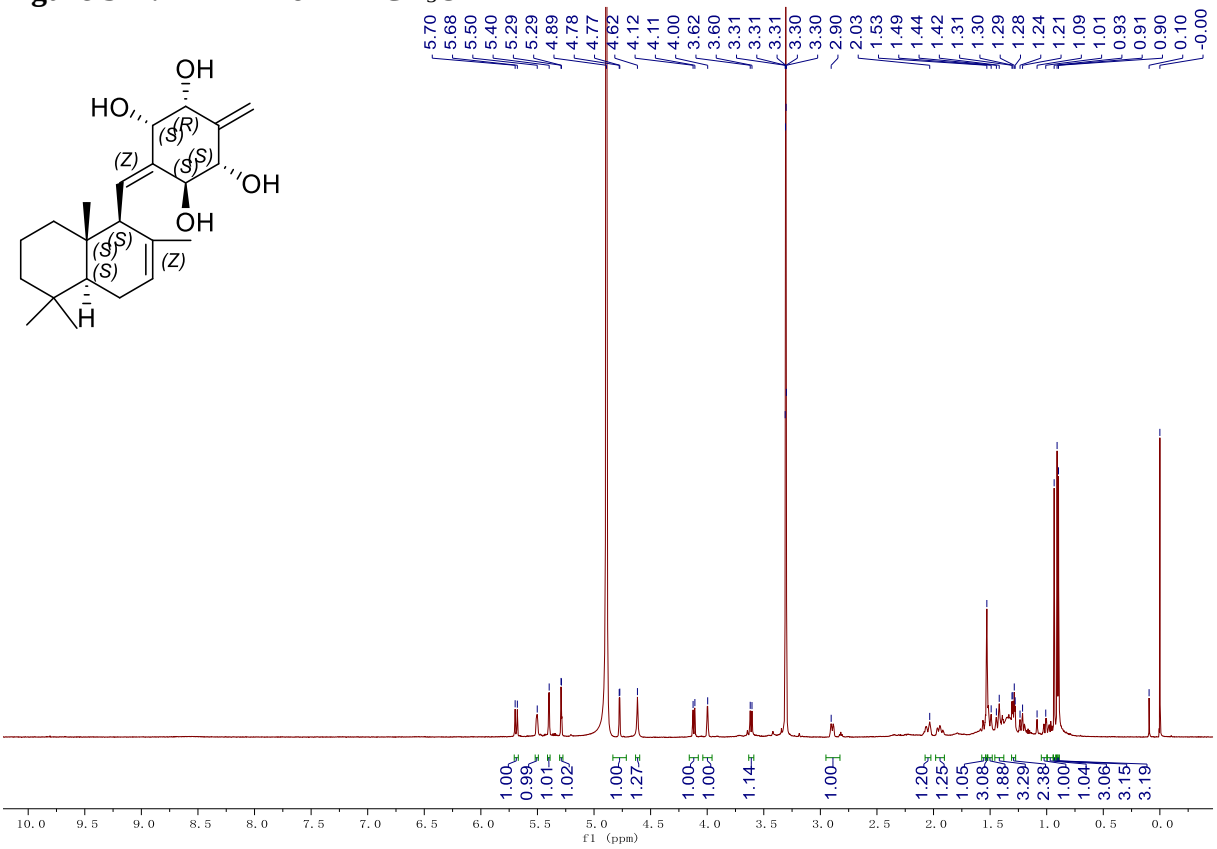


Figure S18. ^{13}C NMR and DEPT of **2** in CD_3OD

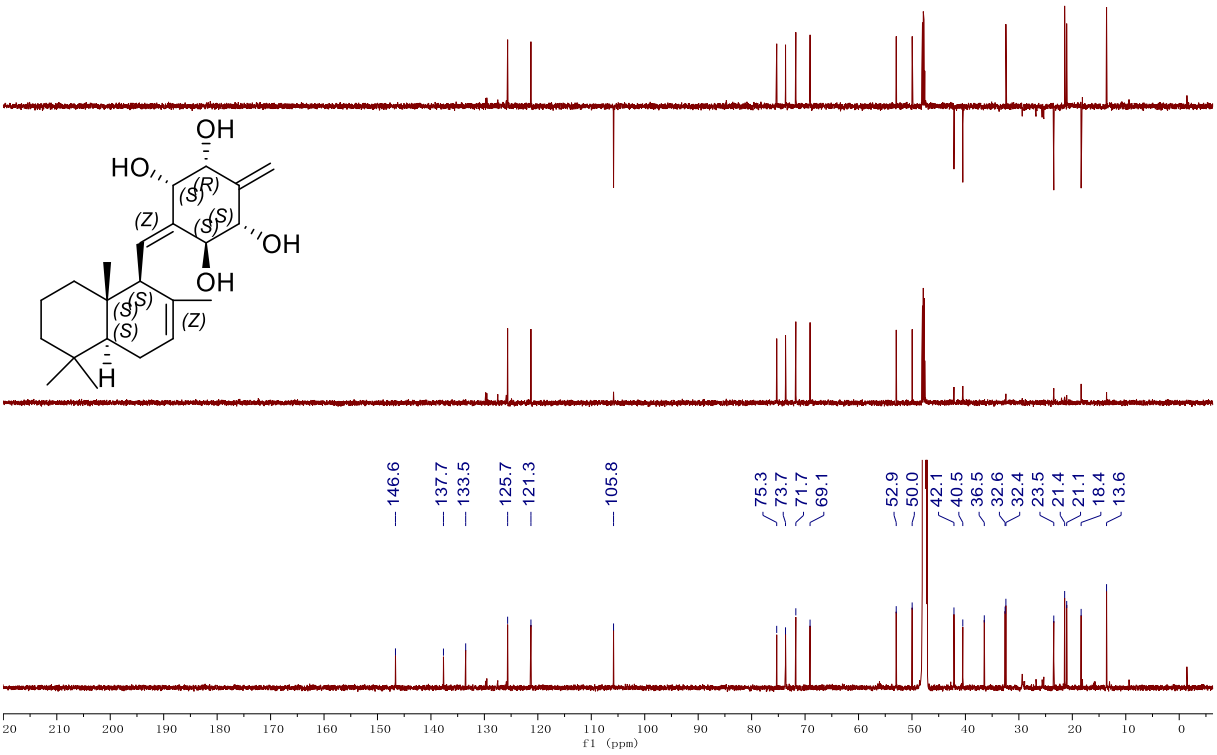


Figure S19. HSQC of **2** in CD_3OD

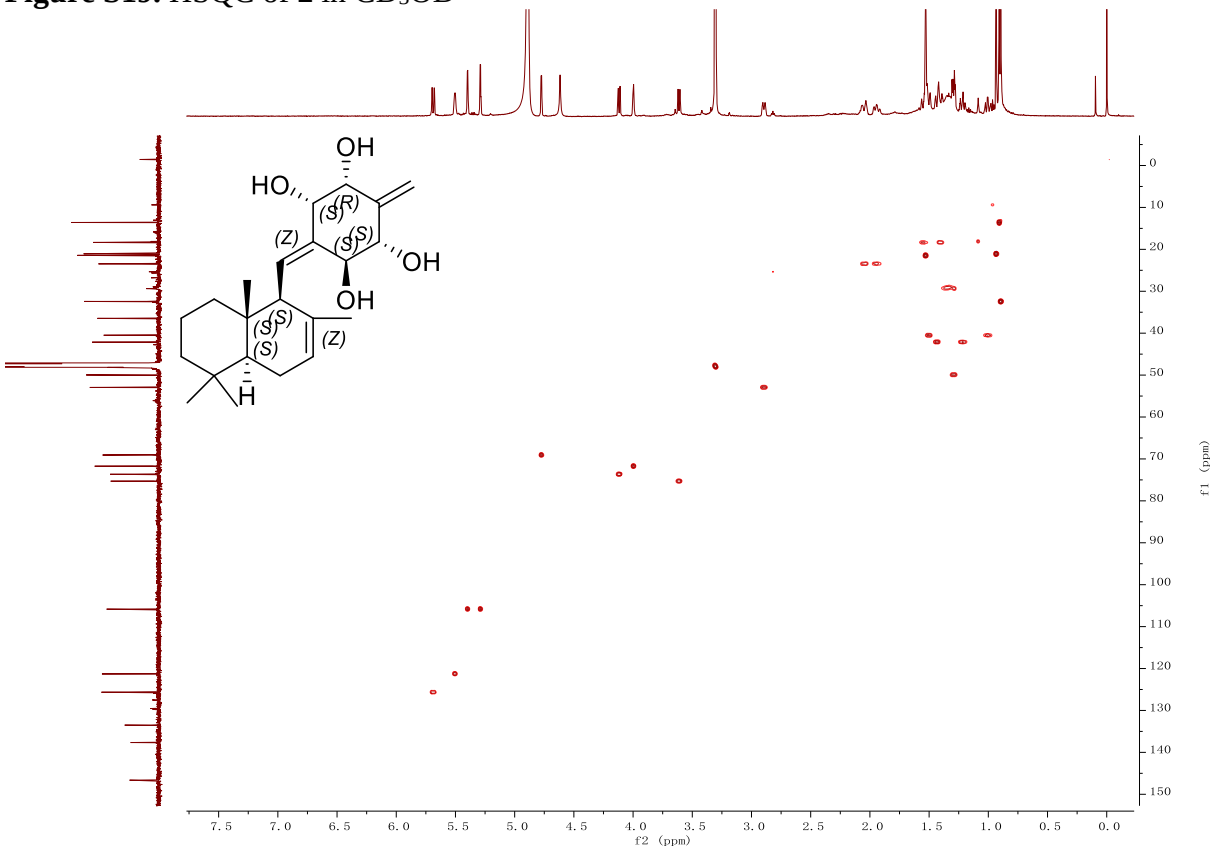


Figure S20. HMBC of **2** in CD_3OD

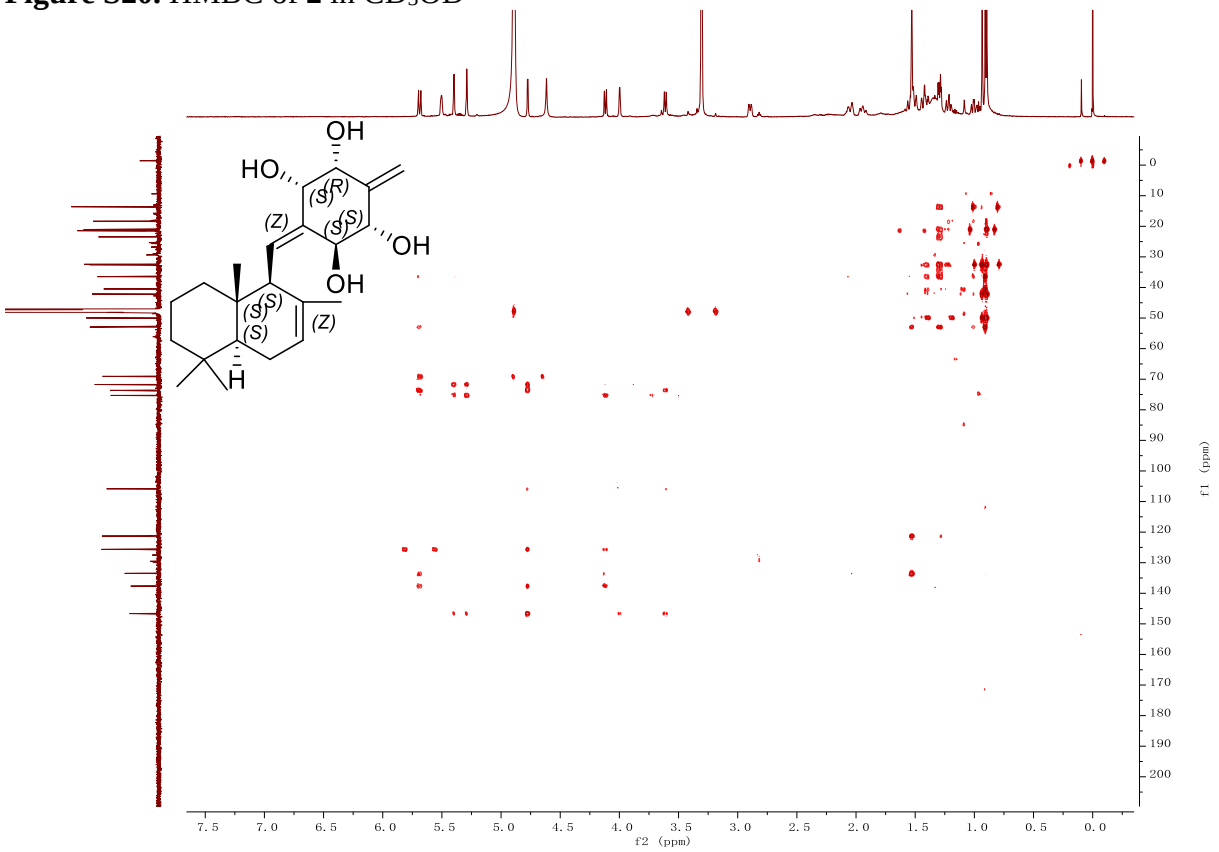


Figure S21. ^{1}H-^{1}H COSY of **2** in CD_3OD

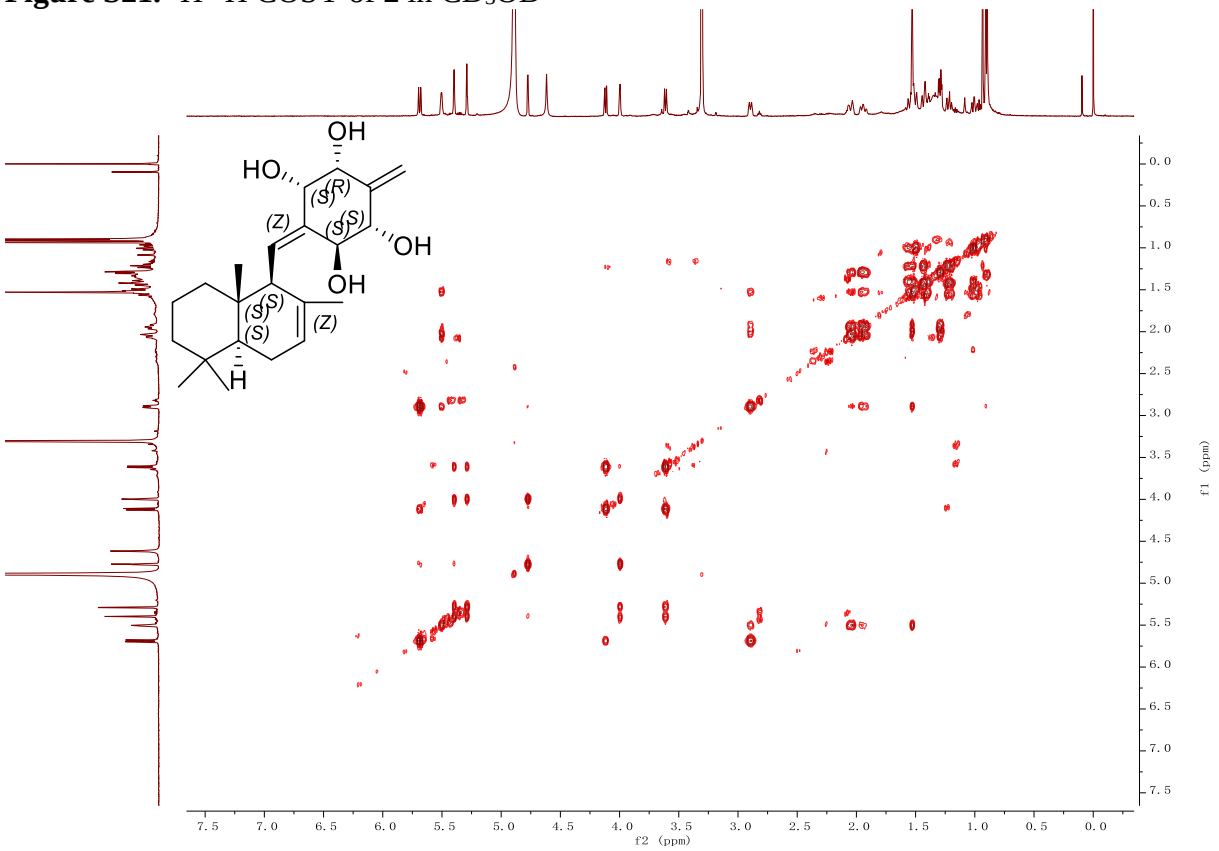


Figure S22. ROESY of **2** in CD_3OD

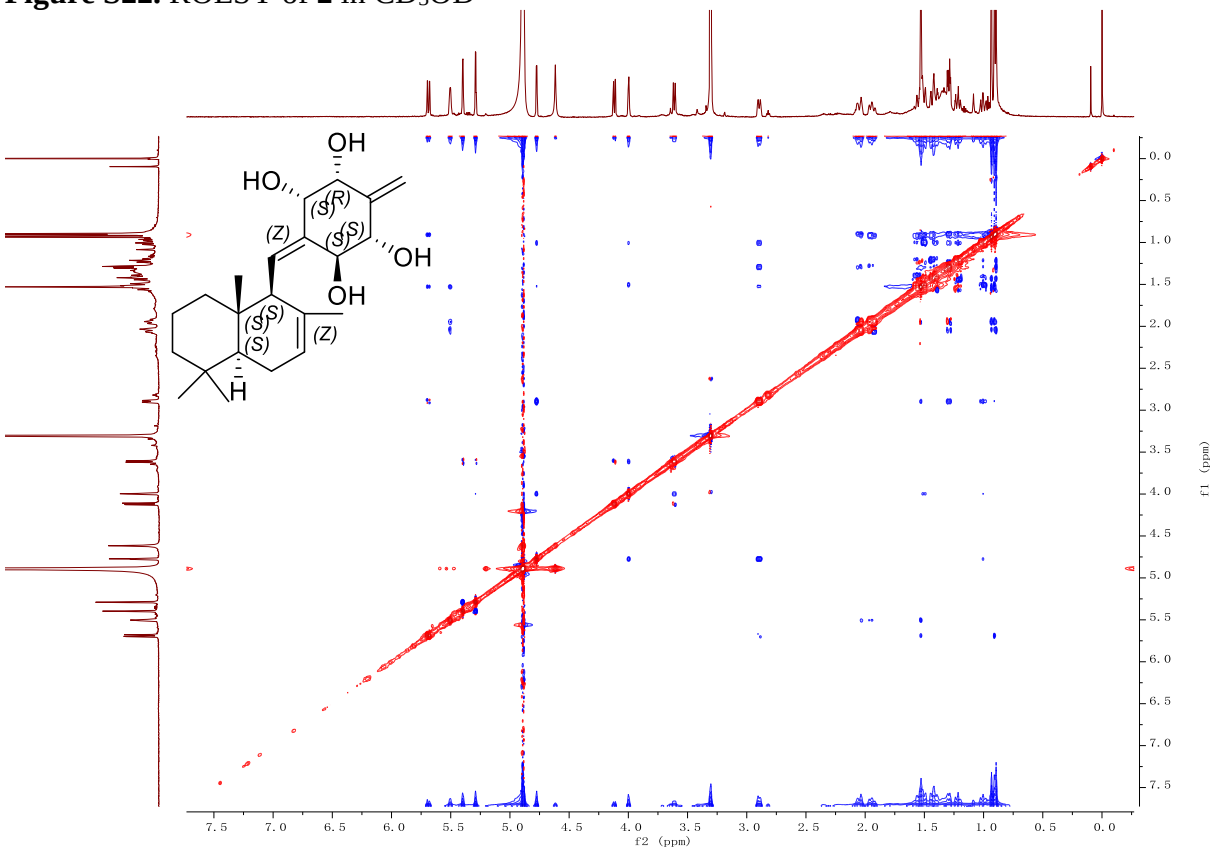


Figure S23. HRESIMS of **2**

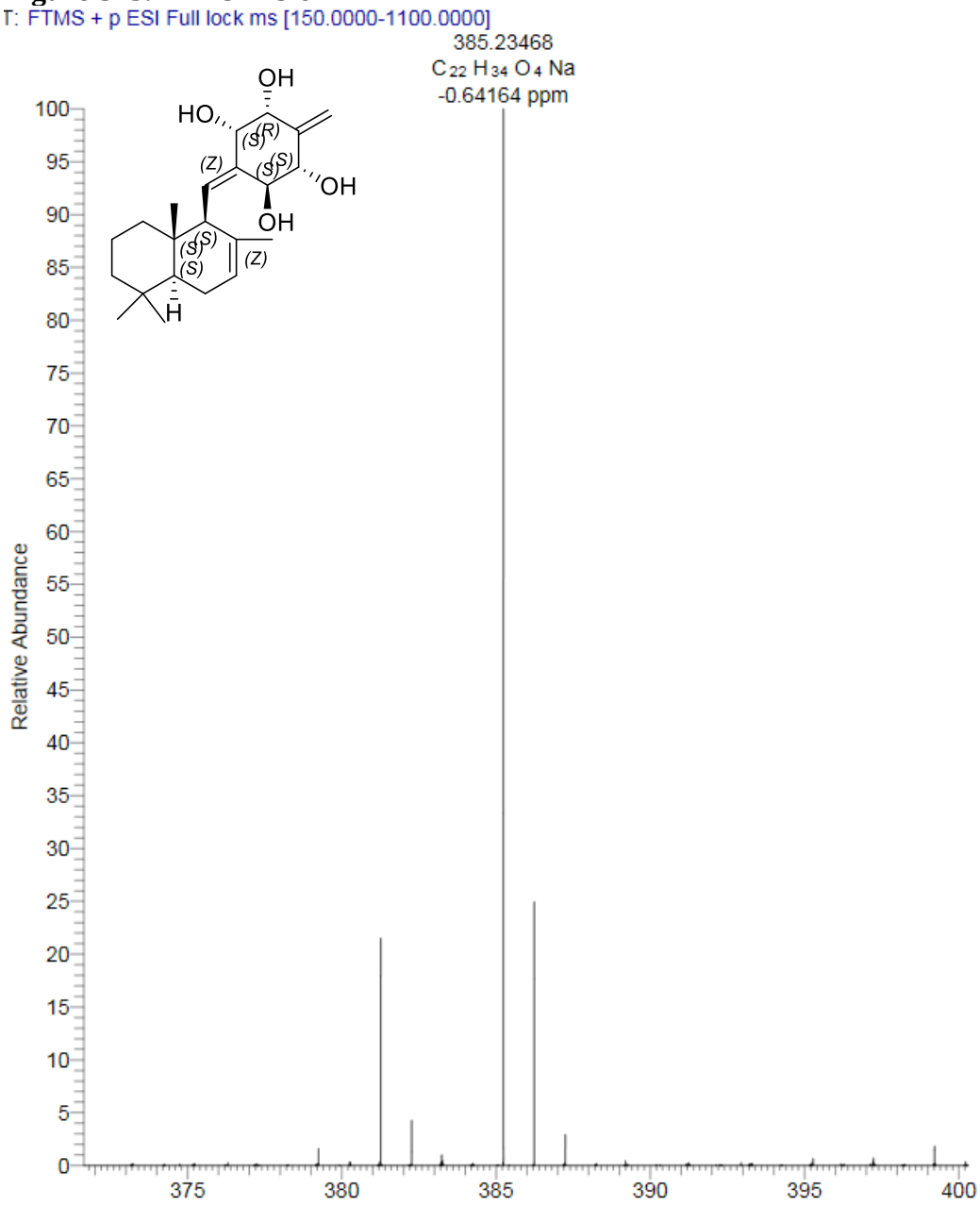


Figure S24. UV of **2**

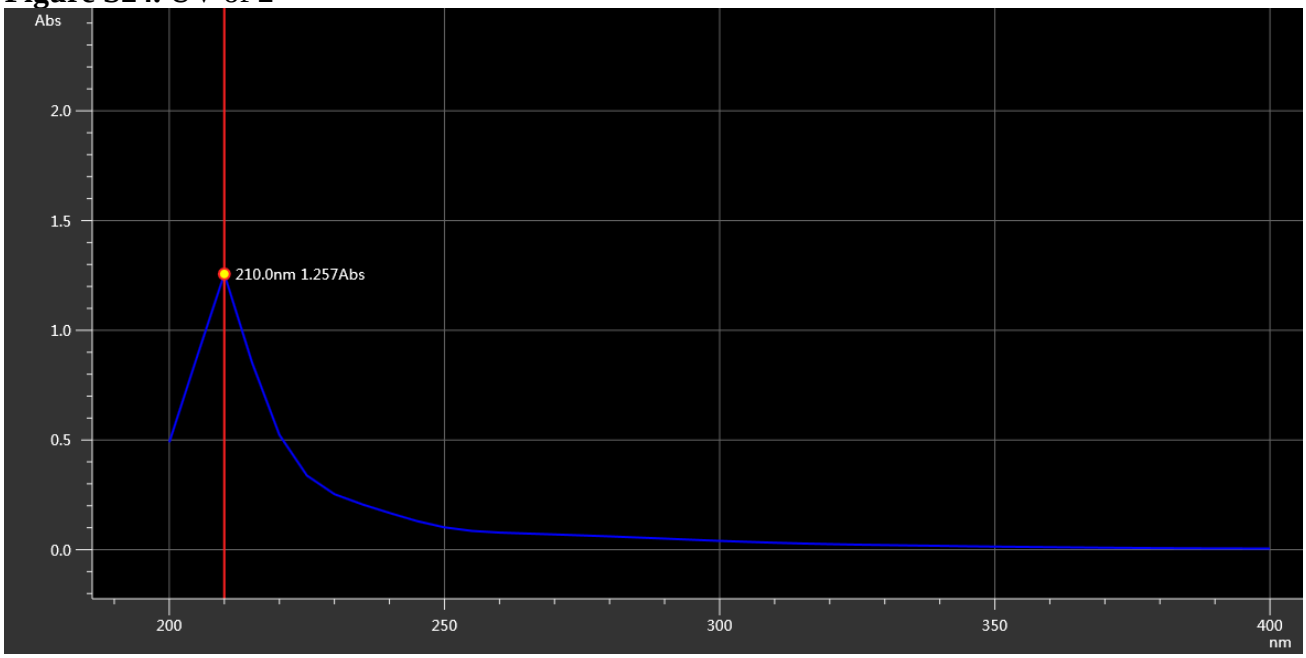


Figure S25. IR of **2**