Supporting Information

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Ionol Derivatives from *Euphorbia tirucalli*

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1. ECD calculation

The theoretical calculations of compound **1** were performed using Gaussian 09[1] and figured using GaussView 5.0[2]. Conformation search using molecular mechanics calculations was performed in Discovery Studio 3.5 Client with MMFF force field with 20 kcal mol^{-1} upper energy limit.[3]

The optimized conformation geometries and thermodynamic parameters of all selected conformations were provided. The predominant conformers were optimized at B3LYP/6-31G(d,p) level. The theoretical calculation of ECD was performed using time dependent Density Functional Theory (TDDFT) at B3LYP/6-31G(d,p) level in MeOH with PCM model[4]. The ECD spectra of compound **1** were obtained by weighing the Boltzmann distribution rate of each geometric conformation[5].

The ECD spectra were simulated by overlapping Gaussian functions for each transition according to:

$$\Delta\varepsilon(E) = \frac{1}{2.297\times10^{-39}} \times \frac{1}{\sqrt{2\pi\sigma}} \sum_{i}^{A} \Delta E_i R_i e^{-[(E-E_i)/(2\sigma)]^2} \qquad (1)$$

The σ represented the width of the band at $1/e$ height, and ΔE_i and R_i were the excitation energies and rotational strengths for transition i, respectively. R_{vel} had been used in this work.

For the calculations of ^{13}C NMR chemical shifts, B3LYP/6-31G(d,p) method was used to optimize the selected conformations. For all optimized structures, vibrational spectra were calculated to ensure that no imaginary frequencies for energy minimum were obtained. NMR calculations were performed at the levels of mPW1PW91/6-31G(d,p) with the gauge-independent atomic orbital (GIAO) method.[6] The solvent effect was considered by using DMSO for **1** in the calculations to resemble the experimental condition. The polarized continuum model (PCM) of Tomasiet al. was used.[4] The calculated ^{13}C NMR chemical shifts were analyzed by subtracting the isotopic shifts for TMS calculated with the same methods.[6] Different conformers for structure **1** were considered. The ^{13}C NMR chemical shifts in each compound were considered as the average values of the same atoms in the different conformers. The average values were obtained by the Boltzmann distributions, using the relative Gibbs free energies as weighting factors.[5] The differences $\Delta\delta$ were determined by

subtracting the experimental chemical shifts δexptl from the scaled calculated chemical shifts δcalcd.

(1) Gaussian 09, Revision C.01,M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

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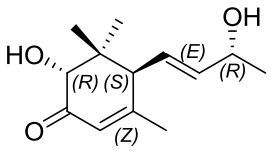
(3) Smith, S. G.; Goodman, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 12946−12959.

(4) (a) Miertus, S.; Scrocc, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117. (b) Miertus, S.; Tomasi, J. *J. Chem. Phys.* **1982**, *65*, 239. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327.

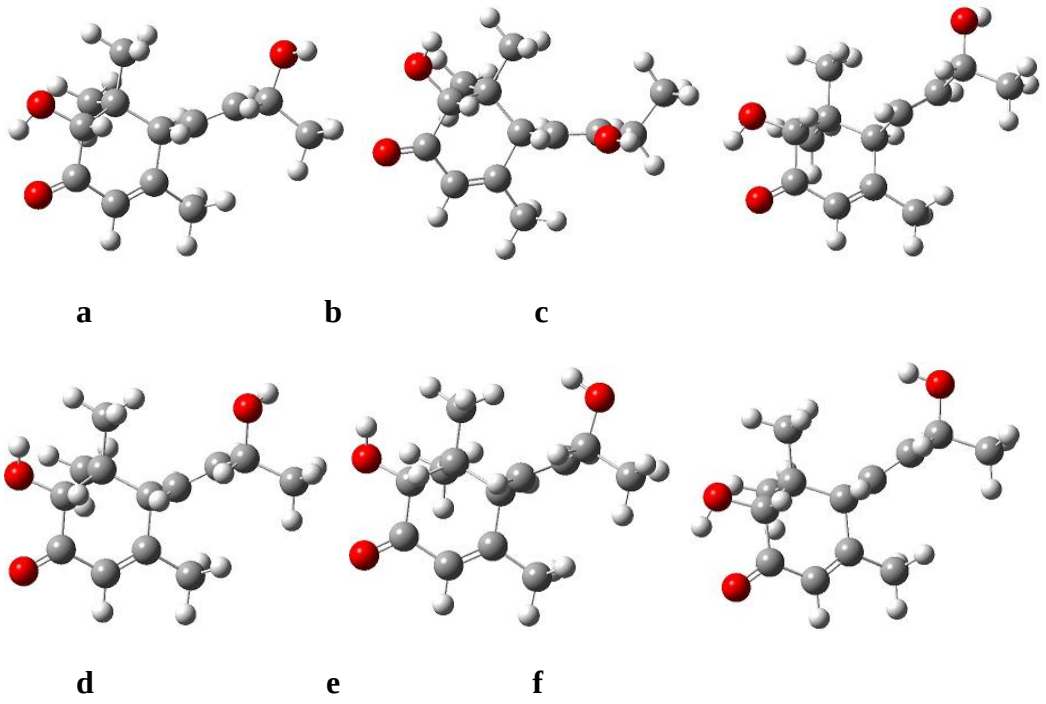
(5) Tähtinen, P.; Bagno, A.; Klika, K. D.; Pihlaja, K. *J. Am. Chem. Soc.* **2003**, *125*, 4609−4618.

(6) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.(b) Rohlfing, C. M.; Allen, L. C.; Ditchfield, R. *Chem. Phys.* **1984**, *87*, 9.(c) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.



(RSR)

1-A



a **b** **c**

d **e** **f**

Figure S1. Optimized geometries of predominant conformers for compound **1-A** at the B3LYP/6-31G(d,p) level in the gas phase.

Table S1. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1-A** at B3LYP/6-31G(d,p) level in the gas phase

Conformations	E+ZPE	G	%
1-A-a	-732.783420	-732.828373	9.6
1-A-b	-732.772609	-732.817797	0.0
1-A-c	-732.783457	-732.828490	10.8
1-A-d	-732.771815	-732.817407	0.0
1-A-e	-732.773554	-732.818865	0.0
1-A-f	-732.785653	-732.830372	79.6

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy in the gas phase at B3LYP/6-31G(d,p) level., %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Table S2. Optimized Z-matrixes of compound **1-A** in the gas phase (Å) at B3LYP/6-31G(d,p) level

1-A-a				**1-A-b**			
C	-1.92819	-0.72521	-0.71699	C	-1.72426	-0.88668	-0.64885
C	-2.51349	0.680645	-0.84894	C	-2.49409	0.4092	-0.93966
C	-1.71532	1.800051	-0.34925	C	-1.87073	1.655413	-0.4578
C	-0.62072	1.61081	0.417286	C	-0.79626	1.688496	0.353668
C	-0.07551	0.215794	0.716265	C	-0.08016	0.413066	0.785543
C	-1.17057	-0.90314	0.621986	C	-1.01532	-0.84229	0.735031
C	-0.53317	-2.30174	0.666989	C	-0.19563	-2.12975	0.935477
C	-2.15114	-0.77162	1.804996	C	-2.06668	-0.75546	1.860547
C	0.139701	2.764447	1.005988	C	-0.22078	2.981479	0.859231
C	1.129855	-0.01288	-0.17884	C	1.186102	0.277266	-0.04026
C	2.386208	-0.13309	0.254815	C	2.422129	0.338902	0.458747
C	3.587232	-0.30669	-0.63478	C	3.688473	0.211941	-0.34724
C	4.496514	0.928987	-0.60525	C	4.576239	-0.92483	0.179255
O	4.282965	-1.4607	-0.15372	O	3.338958	0.002921	-1.71202
O	-2.9473	-1.68115	-0.87761	O	-2.61959	-1.97564	-0.7768
O	-3.62133	0.818972	-1.3615	O	-3.54217	0.413751	-1.56304
H	-1.19193	-0.82371	-1.53738	H	-0.94406	-0.94139	-1.42803
H	-2.0957	2.796408	-0.5589	H	-2.36897	2.57029	-0.7691
H	0.292916	0.220134	1.751515	H	0.22779	0.541033	1.833452
H	0.141965	-2.47165	-0.1763	H	0.513287	-2.29909	0.11886
H	0.04566	-2.43538	1.587599	H	0.381681	-2.08126	1.864993

H	-1.31496	-3.06462	0.636236	H	-0.85922	-2.99727	1.009263
H	-1.6458	-1.00702	2.747647	H	-1.58714	-0.8552	2.840485
H	-2.56986	0.235541	1.890988	H	-2.60951	0.193355	1.846197
H	-2.97868	-1.4726	1.674557	H	-2.79688	-1.56103	1.75066
H	-0.24092	3.727054	0.656943	H	-0.72996	3.848308	0.431703
H	0.071879	2.742412	2.101498	H	-0.30422	3.036492	1.952676
H	1.204215	2.692068	0.757336	H	0.847096	3.047649	0.622129
H	0.937487	-0.05091	-1.25104	H	1.071016	0.150537	-1.11392
H	2.605989	-0.10362	1.322528	H	2.573263	0.481911	1.529138
H	3.242356	-0.47013	-1.66894	H	4.249099	1.159286	-0.24382
H	5.381938	0.773085	-1.23384	H	5.511865	-0.98054	-0.38943
H	3.972353	1.813328	-0.98047	H	4.837223	-0.76988	1.231317
H	4.83506	1.128367	0.416352	H	4.053979	-1.88117	0.085694
H	5.097541	-1.54603	-0.66712	H	4.157731	-0.04143	-2.22152
H	-3.69473	-1.17788	-1.25226	H	-2.09584	-2.76939	-0.93808
1-A-c				**1-A-d**			
C	-1.90836	-0.7643	-0.68792	C	-1.91331	-0.77702	-0.6796
C	-2.53492	0.618835	-0.86341	C	-2.55287	0.602036	-0.89981
C	-1.7665	1.777218	-0.40689	C	-1.78917	1.761872	-0.40231
C	-0.66301	1.645818	0.358697	C	-0.68624	1.658298	0.363472
C	-0.07766	0.277863	0.703135	C	-0.08407	0.301699	0.713748
C	-1.14112	-0.87486	0.652673	C	-1.14336	-0.8519	0.670213
C	-0.46437	-2.25261	0.74203	C	-0.44998	-2.22053	0.7949
C	-2.1201	-0.73015	1.835331	C	-2.13003	-0.69729	1.845792
C	0.069799	2.840208	0.89948	C	0.033501	2.866639	0.893139
C	1.130444	0.052583	-0.18887	C	1.121137	0.074082	-0.1804
C	2.390161	-0.04806	0.241919	C	2.381822	-0.03684	0.245161
C	3.592674	-0.26303	-0.6439	C	3.579027	-0.25582	-0.6467

C	4.632252	0.850677	-0.48425	C	4.631186	0.844806	-0.48181
O	4.18179	-1.54817	-0.41006	O	4.154794	-1.55005	-0.42561
O	-2.89981	-1.75421	-0.81021	O	-2.92491	-1.75932	-0.79429
O	-3.64895	0.708188	-1.37295	O	-3.61551	0.735867	-1.48221
H	-1.17267	-0.86992	-1.50787	H	-1.17889	-0.89068	-1.49656
H	-2.17559	2.754617	-0.64938	H	-2.20669	2.73232	-0.6592
H	0.293295	0.32805	1.736479	H	0.288803	0.35622	1.746558
H	0.219852	-2.42892	-0.09253	H	0.218473	-2.42623	-0.04694
H	0.112233	-2.34249	1.66966	H	0.152628	-2.26831	1.708249
H	-1.22438	-3.03765	0.731576	H	-1.19453	-3.02069	0.855354
H	-1.60384	-0.91537	2.783337	H	-1.62032	-0.87517	2.798969
H	-2.56893	0.26629	1.886938	H	-2.57631	0.29992	1.882974
H	-2.92642	-1.4602	1.735095	H	-2.94003	-1.42388	1.7473
H	-0.34189	3.778932	0.521962	H	-0.39919	3.796238	0.516328
H	0.014292	2.854386	1.995825	H	-0.00842	2.88644	1.990099
H	1.133278	2.789782	0.640684	H	1.094832	2.836092	0.621194
H	0.93805	-0.00278	-1.26043	H	0.926177	0.028812	-1.25228
H	2.597396	0.012677	1.313702	H	2.593499	0.017878	1.316294
H	3.262199	-0.30044	-1.68788	H	3.244487	-0.28089	-1.68981
H	5.502532	0.643849	-1.11342	H	5.496613	0.634839	-1.11665
H	4.217914	1.824635	-0.76381	H	4.225654	1.825405	-0.75049
H	4.971024	0.91916	0.557415	H	4.974886	0.900484	0.559032
H	4.515065	-1.55574	0.498288	H	4.506689	-1.5619	0.475654
H	-3.66337	-1.2866	-1.1981	H	-2.49929	-2.59914	-1.00396
1-A-e				**1-A-f**			
C	-1.93259	-0.74963	-0.69335	C	-1.91558	-0.7482	-0.69691
C	-2.54153	0.647002	-0.88988	C	-2.52916	0.642752	-0.85607
C	-1.75257	1.780593	-0.3731	C	-1.74794	1.787806	-0.38887

C	-0.65167	1.640271	0.389944	C	-0.64458	1.636983	0.373637
C	-0.0783	0.264977	0.717388	C	-0.07365	0.259318	0.705403
C	-1.16161	-0.86418	0.653128	C	-1.14929	-0.88088	0.642063
C	-0.49922	-2.25027	0.750989	C	-0.4893	-2.26769	0.715616
C	-2.14284	-0.71138	1.833614	C	-2.12597	-0.73991	1.827136
C	0.091759	2.823781	0.94209	C	0.100499	2.818162	0.926257
C	1.125567	0.031838	-0.1776	C	1.134734	0.031889	-0.18586
C	2.388869	-0.06309	0.24806	C	2.39623	-0.0565	0.246038
C	3.584737	-0.26859	-0.64584	C	3.595401	-0.26934	-0.64185
C	4.602464	0.86299	-0.52682	C	4.617693	0.857922	-0.52078
O	4.280412	-1.46685	-0.28002	O	4.283171	-1.46943	-0.26904
O	-2.96618	-1.7071	-0.82108	O	-2.91527	-1.72798	-0.83106
O	-3.60084	0.812808	-1.46995	O	-3.64308	0.747364	-1.36278
H	-1.20319	-0.86575	-1.51464	H	-1.18102	-0.85004	-1.51851
H	-2.14933	2.764198	-0.612	H	-2.14688	2.771985	-0.62021
H	0.293931	0.295191	1.751264	H	0.29622	0.296474	1.739515
H	0.152309	-2.45781	-0.10431	H	0.178985	-2.44677	-0.13182
H	0.112242	-2.32649	1.656442	H	0.098352	-2.37112	1.634795
H	-1.26099	-3.03439	0.805369	H	-1.25867	-3.04352	0.708363
H	-1.63596	-0.91943	2.782117	H	-1.61219	-0.94528	2.77227
H	-2.5658	0.294905	1.891161	H	-2.56048	0.261927	1.892583
H	-2.96946	-1.41705	1.722132	H	-2.9425	-1.45707	1.716902
H	-0.32194	3.768394	0.581745	H	-0.30357	3.764643	0.560125
H	0.048113	2.824282	2.039126	H	0.047081	2.820334	2.022755
H	1.152683	2.777442	0.671436	H	1.163011	2.761498	0.665238
H	0.929633	-0.01761	-1.24956	H	0.942451	-0.02746	-1.2576
H	2.61232	-0.00891	1.314879	H	2.615061	0.002326	1.313557
H	3.24127	-0.3314	-1.69175	H	3.256357	-0.33342	-1.68906

H	5.475378	0.644164	-1.14819	H	5.4922	0.633812	-1.13797
H	4.166178	1.812205	-0.85029	H	4.187414	1.808663	-0.84805
H	4.9379	0.964279	0.510027	H	4.949352	0.959645	0.517263
H	3.640909	-2.19115	-0.30681	H	3.641652	-2.19185	-0.30169
H	-2.56173	-2.55182	-1.05148	H	-3.67589	-1.24833	-1.21032

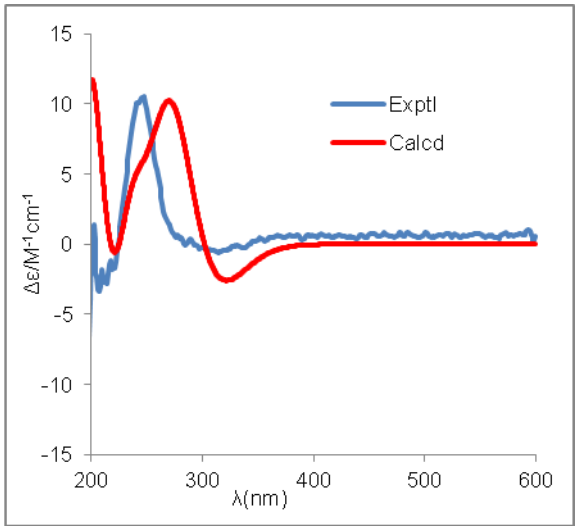
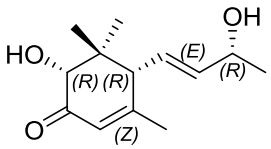
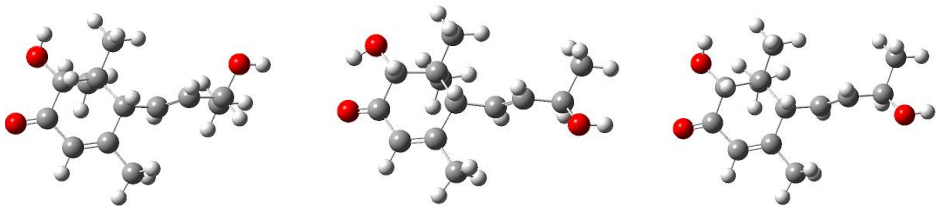


Figure S2. Calculated and experimental ECDs of **1-A** (red, calculated at the B3LYP-PCM/6-31G(d,p)//B3LYP/6-31G(d,p) level in CH_3OH; blue, experimental in CH_3OH).



1-B



a **b** **c**

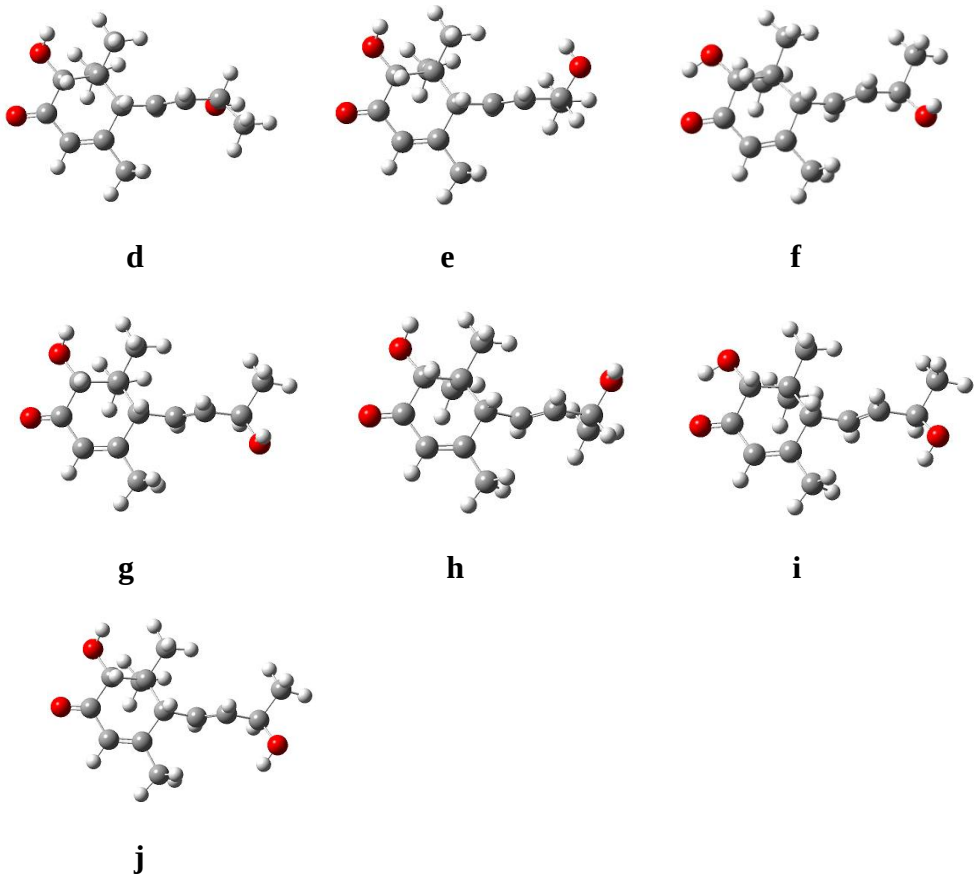


Figure S3. Optimized geometries of predominant conformers for compound **1-B** at the B3LYP/6-31G(d,p) level in the gas phase.

Table S3. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1-B** at B3LYP/6-31G(d,p) level in the gas phase

Conformations	E+ZPE	G	%
1-B-a	-732.769509	-732.814457	0.0
1-B-b	-732.783577	-732.828420	18.1
1-B-c	-732.771076	-732.816377	0.0
1-B-d	-732.771855	-732.816844	0.0
1-B-e	-732.770904	-732.815852	0.0
1-B-f	-732.783541	-732.828354	16.9
1-B-g	-732.771015	-732.816251	0.0
1-B-h	-732.768952	-732.814164	0.0

1-B-i	-732.784995	-732.829629	65.0
1-B-j	-732.772701	-732.817748	0.0

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy in the gas phase at B3LYP/6-31G(d,p) level., %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Table S4. Optimized Z-matrixes of compound **1-B** in the gas phase (Å) at B3LYP/6-31G(d,p) level

1-B-a				**1-B-b**			
C	-2.35198	-0.76405	-0.48805	C	-2.37122	-0.68115	-0.59017
C	-2.99984	0.533782	0.002489	C	-2.98066	0.619896	-0.07823
C	-2.1224	1.716499	-0.0258	C	-2.08893	1.772054	0.014567
C	-0.79305	1.655278	-0.23514	C	-0.74823	1.649115	-0.09057
C	-0.07415	0.324501	-0.46048	C	-0.0752	0.295705	-0.33757
C	-0.89703	-0.912	0.047138	C	-0.97773	-0.93323	0.04006
C	-0.28504	-2.20272	-0.52767	C	-0.39604	-2.22101	-0.56676
C	-0.92298	-1.00722	1.586278	C	-1.12029	-1.10844	1.565074
C	0.033869	2.910484	-0.3133	C	0.140012	2.860418	-0.02403
C	1.333524	0.342744	0.096827	C	1.2927	0.226235	0.304805
C	2.434215	0.152703	-0.63338	C	2.436763	0.036435	-0.35434
C	3.861413	0.158716	-0.1465	C	3.791244	-0.06514	0.292009
C	4.033079	0.126148	1.371462	C	4.403826	-1.45918	0.108732
O	4.479585	-0.97865	-0.76267	O	4.608762	0.935928	-0.32464
O	-3.19009	-1.84455	-0.1337	O	-3.25912	-1.74581	-0.36242
O	-4.17014	0.598956	0.337755	O	-4.17577	0.652807	0.20509
H	-2.28994	-0.66447	-1.58844	H	-2.21767	-0.54092	-1.67873
H	-2.6208	2.669346	0.13448	H	-2.55501	2.737006	0.195896
H	0.01935	0.214472	-1.5543	H	0.082649	0.244447	-1.42834

H	-0.33507	-2.21727	-1.62373	H	-0.30182	-2.13922	-1.65599
H	0.766015	-2.29872	-0.24424	H	0.595085	-2.43618	-0.15782
H	-0.81068	-3.08413	-0.1469	H	-1.05597	-3.06434	-0.35023
H	0.050855	-1.31197	1.980426	H	-0.18327	-1.45171	2.012755
H	-1.19699	-0.05662	2.053162	H	-1.41375	-0.17975	2.064575
H	-1.66121	-1.75395	1.888992	H	-1.88786	-1.85902	1.768107
H	-0.59273	3.802986	-0.24841	H	-0.44527	3.781206	0.029049
H	0.780456	2.950655	0.487757	H	0.80661	2.818922	0.844473
H	0.596494	2.945953	-1.25449	H	0.795613	2.907372	-0.90174
H	1.419989	0.516524	1.167693	H	1.324502	0.338101	1.38874
H	2.344483	-0.02715	-1.70478	H	2.435416	-0.06421	-1.44032
H	4.335368	1.080636	-0.53117	H	3.685922	0.138912	1.37039
H	5.097521	0.107962	1.6299	H	5.401912	-1.50588	0.561712
H	3.597146	1.010745	1.846358	H	3.785311	-2.22713	0.583066
H	3.563711	-0.76854	1.789909	H	4.500639	-1.69579	-0.95548
H	5.42681	-0.93114	-0.57661	H	5.511221	0.816582	0.000826
H	-2.94346	-2.60053	-0.67991	H	-4.09269	-1.31206	-0.09666
1-B-c				**1-B-d**			
C	-2.39651	-0.67932	-0.56546	C	-2.46007	-0.54301	-0.54548
C	-3.01515	0.622914	-0.04811	C	-2.91366	0.80495	0.020849
C	-2.08648	1.762401	0.0355	C	-1.86793	1.840209	0.075097
C	-0.75046	1.649355	-0.09711	C	-0.55979	1.592093	-0.13102
C	-0.07849	0.297618	-0.34484	C	-0.04581	0.184065	-0.43768
C	-0.98546	-0.92149	0.04733	C	-1.05325	-0.94059	-0.00947
C	-0.39877	-2.21072	-0.55578	C	-0.63505	-2.27398	-0.6556
C	-1.1109	-1.09092	1.57514	C	-1.11377	-1.12032	1.521066
C	0.135417	2.86536	-0.06371	C	0.449227	2.708292	-0.12058
C	1.289477	0.230956	0.298901	C	1.33948	-0.04049	0.127298

C	2.434868	0.034788	-0.35643	C	2.413631	-0.34974	-0.6008
C	3.789292	-0.05465	0.292263	C	3.797445	-0.57709	-0.05095
C	4.401096	-1.45297	0.140105	C	4.821338	0.364864	-0.70058
O	4.60811	0.931116	-0.34632	O	3.759494	-0.402	1.361912
O	-3.30089	-1.73603	-0.31707	O	-3.45803	-1.50397	-0.26866
O	-4.20023	0.72582	0.218942	O	-4.06722	1.025291	0.348717
H	-2.26258	-0.52982	-1.65359	H	-2.36327	-0.38638	-1.63685
H	-2.55116	2.729058	0.213043	H	-2.21951	2.845088	0.295481
H	0.080767	0.236815	-1.43502	H	0.040207	0.129238	-1.53694
H	-0.36896	-2.16444	-1.65173	H	-0.66568	-2.21794	-1.75134
H	0.6223	-2.37826	-0.20361	H	0.3831	-2.54564	-0.36566
H	-0.99475	-3.081	-0.26346	H	-1.29565	-3.08517	-0.33333
H	-0.17347	-1.44709	2.012305	H	-0.19719	-1.5806	1.900776
H	-1.38351	-0.15497	2.071159	H	-1.25605	-0.1687	2.041098
H	-1.89003	-1.8252	1.794154	H	-1.95447	-1.7709	1.774982
H	-0.454	3.782878	0.000402	H	-0.03559	3.680183	-0.00268
H	0.827903	2.835772	0.784807	H	1.179377	2.580998	0.686275
H	0.763362	2.912842	-0.96175	H	1.026984	2.716227	-1.05329
H	1.319966	0.357903	1.381093	H	1.45819	0.053473	1.203482
H	2.435616	-0.07772	-1.44126	H	2.329398	-0.45383	-1.68307
H	3.683943	0.173068	1.365852	H	4.08768	-1.61612	-0.29321
H	5.399901	-1.48986	0.592373	H	5.830781	0.15816	-0.32605
H	3.783249	-2.20954	0.633399	H	4.840534	0.240623	-1.7883
H	4.496375	-1.71403	-0.91856	H	4.571016	1.404627	-0.4715
H	5.508534	0.824507	-0.01096	H	4.645727	-0.57531	1.703255
H	-3.06705	-2.46816	-0.89993	H	-3.31027	-2.25808	-0.85193
1-B-e				**1-B-f**			
C	-2.37909	-0.67876	-0.58588	C	-2.40645	-0.67535	-0.55991

C	-2.97876	0.629884	-0.08172	C	-3.01171	0.638141	-0.05534
C	-2.07845	1.776269	0.002998	C	-2.07114	1.768694	0.019122
C	-0.73891	1.642969	-0.10295	C	-0.73643	1.640794	-0.11199
C	-0.07579	0.282935	-0.3406	C	-0.07852	0.279796	-0.34705
C	-0.98724	-0.93707	0.045413	C	-0.99823	-0.9264	0.056008
C	-0.41524	-2.23297	-0.55329	C	-0.42457	-2.22715	-0.53475
C	-1.13	-1.10127	1.571643	C	-1.12604	-1.08015	1.585282
C	0.158274	2.84827	-0.0457	C	0.162142	2.847768	-0.08916
C	1.290647	0.207424	0.304148	C	1.287541	0.203904	0.299607
C	2.435551	-0.01199	-0.34561	C	2.434172	-0.01877	-0.34638
C	3.795848	-0.08997	0.302169	C	3.793951	-0.08709	0.303833
C	4.474667	-1.44139	0.061135	C	4.482433	-1.43433	0.066083
O	4.633406	0.988809	-0.13441	O	4.626093	0.99588	-0.13228
O	-3.27421	-1.73558	-0.35135	O	-3.32186	-1.71989	-0.3017
O	-4.17329	0.67352	0.201853	O	-4.19583	0.756253	0.209055
H	-2.22515	-0.5461	-1.67541	H	-2.27056	-0.53765	-1.64942
H	-2.53729	2.74568	0.178602	H	-2.52592	2.741546	0.188261
H	0.081897	0.222215	-1.43108	H	0.080641	0.206685	-1.43668
H	-0.32209	-2.15931	-1.64328	H	-0.3948	-2.19171	-1.63119
H	0.57461	-2.45252	-0.14365	H	0.594656	-2.40189	-0.18068
H	-1.08097	-3.07004	-0.33046	H	-1.02937	-3.08845	-0.23423
H	-0.19516	-1.44826	2.020925	H	-0.19302	-1.443	2.026267
H	-1.41653	-0.16731	2.065222	H	-1.38813	-0.13663	2.072477
H	-1.90272	-1.84504	1.779949	H	-1.91363	-1.80338	1.810547
H	-0.42003	3.773528	0.005214	H	-0.41733	3.771737	-0.02786
H	0.829076	2.80675	0.819463	H	0.859046	2.81625	0.755561
H	0.809525	2.886866	-0.92719	H	0.785451	2.884227	-0.99112
H	1.322185	0.338585	1.385879	H	1.317315	0.345173	1.380059

H	2.420185	-0.14488	-1.4305	H	2.421222	-0.15808	-1.43067
H	3.684749	0.069394	1.380658	H	3.679922	0.073181	1.381838
H	5.470197	-1.4467	0.513999	H	5.477534	-1.43184	0.519849
H	3.888099	-2.26164	0.486593	H	3.901512	-2.25802	0.492946
H	4.58513	-1.63465	-1.01357	H	4.595644	-1.62876	-1.00815
H	4.822746	0.848107	-1.07279	H	4.805295	0.864013	-1.07392
H	-4.10474	-1.29476	-0.08782	H	-3.09567	-2.46057	-0.87676
1-B-g				**1-B-h**			
C	-2.40645	-0.67535	-0.55991	C	-2.34537	-0.77339	-0.47541
C	-3.01171	0.638141	-0.05534	C	-2.99703	0.527242	0.003671
C	-2.07114	1.768694	0.019122	C	-2.12419	1.713191	-0.03573
C	-0.73643	1.640794	-0.11199	C	-0.79536	1.65615	-0.24904
C	-0.07852	0.279796	-0.34705	C	-0.07302	0.3264	-0.46962
C	-0.99823	-0.9264	0.056008	C	-0.88734	-0.90905	0.05451
C	-0.42457	-2.22715	-0.53475	C	-0.27212	-2.20309	-0.50941
C	-1.12604	-1.08015	1.585282	C	-0.90524	-0.98862	1.594693
C	0.162142	2.847768	-0.08916	C	0.02682	2.9137	-0.33729
C	1.287541	0.203904	0.299607	C	1.33855	0.352465	0.076916
C	2.434172	-0.01877	-0.34638	C	2.437735	0.15865	-0.65524
C	3.793951	-0.08709	0.303833	C	3.871939	0.138119	-0.17384
C	4.482433	-1.43433	0.066083	C	4.054274	0.262469	1.332186
O	4.626093	0.99588	-0.13228	O	4.501803	-1.09516	-0.55201
O	-3.32186	-1.71989	-0.3017	O	-3.17675	-1.85333	-0.10464
O	-4.19583	0.756253	0.209055	O	-4.16719	0.591039	0.339142
H	-2.27056	-0.53765	-1.64942	H	-2.28925	-0.68577	-1.57718
H	-2.52592	2.741546	0.188261	H	-2.62591	2.664983	0.120083
H	0.080641	0.206685	-1.43668	H	0.011562	0.207976	-1.56355
H	-0.3948	-2.19171	-1.63119	H	-0.32461	-2.22803	-1.60538

H	0.594656	-2.40189	-0.18068	H	0.779284	-2.29409	-0.22528
H	-1.02937	-3.08845	-0.23423	H	-0.79503	-3.08217	-0.11996
H	-0.19302	-1.443	2.026267	H	0.07153	-1.28564	1.987399
H	-1.38813	-0.13663	2.072477	H	-1.18075	-0.03444	2.053144
H	-1.91363	-1.80338	1.810547	H	-1.63895	-1.73512	1.908671
H	-0.41733	3.771737	-0.02786	H	-0.60255	3.804304	-0.27384
H	0.859046	2.81625	0.755561	H	0.776987	2.960498	0.460022
H	0.785451	2.884227	-0.99112	H	0.584878	2.946911	-1.28133
H	1.317315	0.345173	1.380059	H	1.433352	0.53258	1.145818
H	2.421222	-0.15808	-1.43067	H	2.322547	-0.01308	-1.72898
H	3.679922	0.073181	1.381838	H	4.400618	0.978905	-0.65789
H	5.477534	-1.43184	0.519849	H	5.118054	0.201655	1.573489
H	3.901512	-2.25802	0.492946	H	3.668728	1.217343	1.700233
H	4.595644	-1.62876	-1.00815	H	3.539409	-0.5525	1.848857
H	4.805295	0.864013	-1.07392	H	4.445769	-1.17772	-1.51333
H	-3.09567	-2.46057	-0.87676	H	-2.93663	-2.61242	-0.64934
1-B-i				**1-B-j**			
C	-2.37093	-0.68614	-0.58575	C	-2.39816	-0.68251	-0.56071
C	-2.98001	0.616798	-0.07949	C	-3.01284	0.624635	-0.05205
C	-2.08806	1.770381	0.004917	C	-2.08074	1.762891	0.022285
C	-0.74803	1.646749	-0.1019	C	-0.74555	1.644575	-0.10984
C	-0.07393	0.292952	-0.34206	C	-0.07668	0.289896	-0.34829
C	-0.97614	-0.93478	0.043905	C	-0.98724	-0.92442	0.053493
C	-0.39599	-2.2259	-0.55722	C	-0.40527	-2.21986	-0.54068
C	-1.11606	-1.10166	1.570056	C	-1.11245	-1.08204	1.582563
C	0.138059	2.860769	-0.04399	C	0.142005	2.86019	-0.0855
C	1.294199	0.222432	0.300425	C	1.290998	0.219065	0.296106
C	2.437631	-0.00866	-0.35052	C	2.436043	-0.01562	-0.351

C	3.794148	-0.09498	0.300298	C	3.792527	-0.08936	0.30171
C	4.467661	-1.44466	0.066914	C	4.474429	-1.43699	0.080753
O	4.676745	0.889491	-0.2537	O	4.669955	0.895045	-0.26
O	-3.25713	-1.75038	-0.35138	O	-3.30516	-1.73436	-0.3041
O	-4.17389	0.652312	0.206983	O	-4.19665	0.733847	0.216665
H	-2.21896	-0.55117	-1.67522	H	-2.26418	-0.54083	-1.64991
H	-2.55443	2.736107	0.181376	H	-2.543	2.731974	0.192867
H	0.082935	0.234187	-1.43261	H	0.081883	0.219731	-1.43804
H	-0.30156	-2.14921	-1.6468	H	-0.37426	-2.18097	-1.63686
H	0.594259	-2.44178	-0.14691	H	0.614266	-2.39082	-0.18603
H	-1.05784	-3.06676	-0.33718	H	-1.00599	-3.08508	-0.24334
H	-0.17819	-1.44222	2.017898	H	-0.17628	-1.43867	2.021881
H	-1.40958	-0.17072	2.065401	H	-1.38177	-0.14175	2.072227
H	-1.88276	-1.85169	1.778055	H	-1.89412	-1.81192	1.806954
H	-0.44861	3.780675	0.007828	H	-0.44581	3.77906	-0.02761
H	0.806528	2.825186	0.823601	H	0.832584	2.836633	0.765133
H	0.786432	2.9067	-0.92754	H	0.766814	2.901637	-0.98645
H	1.327025	0.354084	1.3826	H	1.322225	0.362329	1.376745
H	2.433565	-0.14037	-1.43384	H	2.434364	-0.15495	-1.43344
H	3.679244	0.064322	1.385377	H	3.675664	0.078561	1.38525
H	5.467761	-1.44143	0.509272	H	5.474632	-1.42362	0.522695
H	3.883248	-2.25232	0.516336	H	3.895431	-2.24409	0.538323
H	4.568624	-1.63809	-1.0055	H	4.576538	-1.63985	-0.98987
H	4.252542	1.751042	-0.14427	H	4.239457	1.754785	-0.16103
H	-4.09135	-1.31763	-0.08662	H	-3.07597	-2.4711	-0.88303

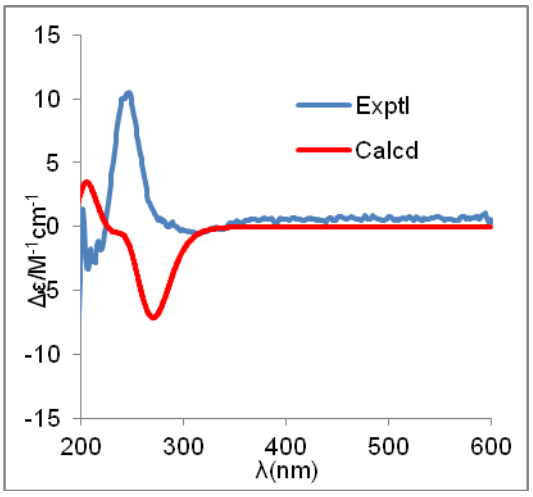
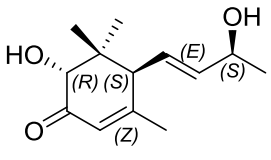
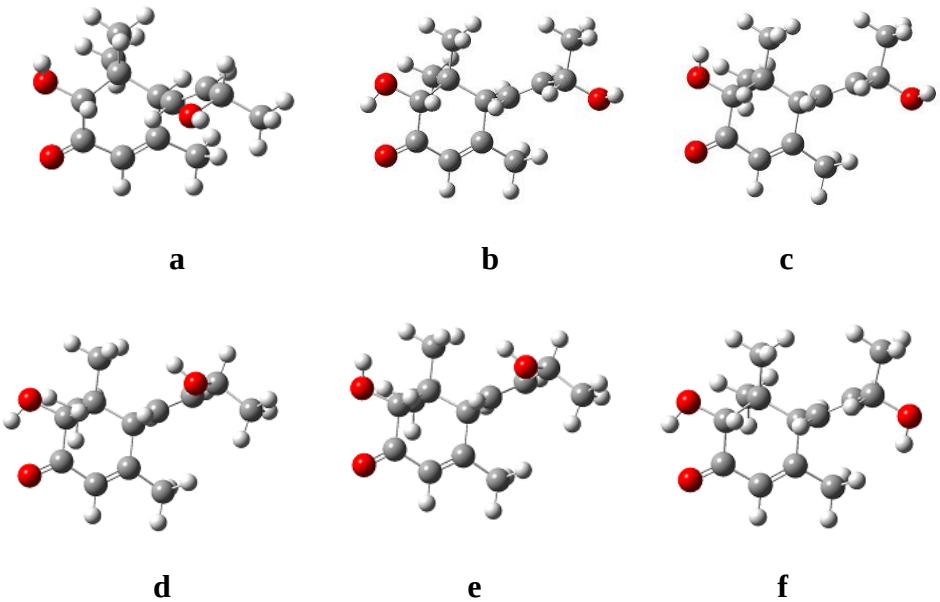


Figure S4. Calculated and experimental ECDs of **1-B** (red, calculated at the B3LYP-PCM/6-31G(d,p)//B3LYP/6-31G(d,p) level in CH_3OH; blue, experimental in CH_3OH).



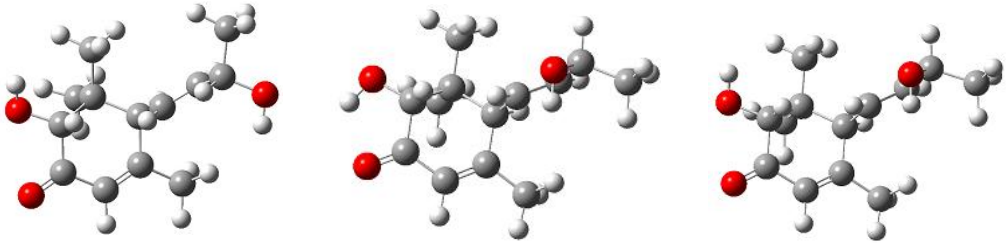
(R,S,S)

1-C

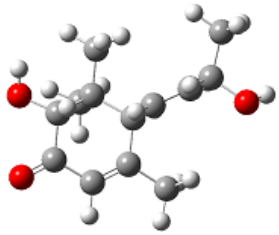


a **b** **c**

d **e** **f**



g **h** **i**



j

Figure S5. Optimized geometries of predominant conformers for compound **1-C** at the B3LYP/6-31G(d,p) level in the gas phase.

Table S5. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1-C** at B3LYP/6-31G(d,p) level in the gas phase

Conformations	E+ZPE	G	%
1-C-a	-732.772617	-732.817804	0.0
1-C-b	-732.784020	-732.828924	8.7
1-C-c	-732.771909	-732.817454	0.0
1-C-d	-732.785609	-732.830110	30.5
1-C-e	-732.773280	-732.818352	0.0
1-C-f	-732.785464	-732.830316	38.0
1-C-g	-732.773593	-732.819055	0.0
1-C-h	-732.785274	-732.829836	22.8
1-C-i	-732.773597	-732.818700	0.0
1-C-j	-732.771802	-732.817371	0.0

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy in the gas phase at B3LYP/6-31G(d,p) level., %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Table S6. Optimized Z-matrixes of compound **1-C** in the gas phase (Å) at B3LYP/6-31G(d,p) level

1-C-a				**1-C-b**			
C	-1.87594	-0.73752	-0.64582	C	-1.90486	-0.77961	-0.68213
C	-2.37286	0.671887	-0.99743	C	-2.54819	0.596095	-0.85692
C	-1.53713	1.791226	-0.5252	C	-1.78726	1.763101	-0.41276
C	-0.49984	1.644197	0.321255	C	-0.67524	1.64588	0.343473
C	-0.05316	0.269472	0.80696	C	-0.07803	0.284518	0.69616
C	-1.21111	-0.78368	0.760205	C	-1.13	-0.87778	0.654609
C	-0.66155	-2.19702	1.024635	C	-0.44007	-2.24893	0.744519
C	-2.2587	-0.45881	1.845197	C	-2.10442	-0.74002	1.841868
C	0.296233	2.819072	0.815579	C	0.057596	2.849183	0.863452
C	1.182731	-0.13266	0.023263	C	1.132881	0.072247	-0.19505
C	2.396376	-0.28601	0.556314	C	2.394055	0.032297	0.238941
C	3.637359	-0.66138	-0.21039	C	3.598369	-0.16481	-0.64035
C	4.727811	0.41113	-0.07466	C	4.307256	-1.49152	-0.34181
O	3.283937	-0.86865	-1.5742	O	4.466736	0.945715	-0.38714
O	-2.96046	-1.63795	-0.7739	O	-2.88534	-1.78127	-0.79882
O	-3.38132	0.856526	-1.65775	O	-3.66752	0.669563	-1.35797
H	-1.09973	-0.96732	-1.39659	H	-1.17203	-0.87768	-1.50565
H	-1.8425	2.774157	-0.87552	H	-2.20533	2.735735	-0.65866
H	0.248377	0.368074	1.859993	H	0.293937	0.345989	1.728325
H	0.031216	-2.52418	0.242924	H	0.234095	-2.42273	-0.09921
H	-0.12062	-2.23115	1.97646	H	0.149009	-2.32847	1.66512

H	-1.48168	-2.91924	1.090447	H	-1.19238	-3.04144	0.746044
H	-1.83776	-0.61881	2.843836	H	-1.58168	-0.91849	2.787599
H	-2.60701	0.575855	1.787719	H	-2.56079	0.252902	1.893411
H	-3.12731	-1.11148	1.728582	H	-2.90522	-1.47695	1.747295
H	-0.02598	3.753856	0.351013	H	-0.37352	3.781775	0.492465
H	0.193169	2.920809	1.903975	H	0.027915	2.866352	1.960728
H	1.363633	2.67461	0.613608	H	1.115044	2.808835	0.57953
H	1.069656	-0.27825	-1.04806	H	0.940632	-0.01138	-1.26462
H	2.546188	-0.14012	1.626479	H	2.612604	0.137378	1.302212
H	4.026587	-1.60087	0.223742	H	3.273249	-0.16273	-1.69363
H	5.643182	0.102254	-0.59344	H	5.196752	-1.60571	-0.97356
H	4.985648	0.584173	0.975296	H	3.647752	-2.34289	-0.53514
H	4.381373	1.352829	-0.51005	H	4.625378	-1.52584	0.704883
H	4.090099	-1.09198	-2.05611	H	5.288636	0.789673	-0.87168
H	-2.59517	-2.52212	-0.89703	H	-3.65758	-1.3203	-1.17798
1-C-c				**1-C-d**			
C	-1.91638	-0.78816	-0.67521	C	-1.83909	-0.74557	-0.64434
C	-2.56475	0.58749	-0.89224	C	-2.33925	0.657841	-0.98551
C	-1.8019	1.750784	-0.40411	C	-1.51639	1.791819	-0.56627
C	-0.69162	1.653808	0.352412	C	-0.48788	1.647645	0.295804
C	-0.08372	0.300037	0.706103	C	-0.04658	0.277645	0.806956
C	-1.13702	-0.85791	0.669043	C	-1.19568	-0.78963	0.76332
C	-0.43595	-2.22305	0.789348	C	-0.65	-2.20161	1.031476
C	-2.11657	-0.7089	1.851313	C	-2.25214	-0.46225	1.838468
C	0.032702	2.865839	0.866609	C	0.29984	2.828276	0.787041
C	1.123735	0.084364	-0.18807	C	1.206549	-0.11926	0.046723
C	2.386431	0.035215	0.240997	C	2.414536	-0.26366	0.597217
C	3.587589	-0.15903	-0.64336	C	3.670589	-0.6365	-0.15894

C	4.292589	-1.49108	-0.35854	C	4.650949	0.535131	-0.24433
O	4.461629	0.944921	-0.38279	O	3.410973	-1.04593	-1.49781
O	-2.92372	-1.77614	-0.783	O	-2.89073	-1.67033	-0.77403
O	-3.6327	0.713448	-1.46699	O	-3.40153	0.78047	-1.59
H	-1.18693	-0.8981	-1.49736	H	-1.0485	-0.9725	-1.3846
H	-2.22378	2.719111	-0.66158	H	-1.82272	2.770973	-0.92498
H	0.290813	0.360936	1.737756	H	0.241036	0.395788	1.861205
H	0.218229	-2.4282	-0.06433	H	0.067341	-2.51445	0.267308
H	0.182218	-2.26406	1.692455	H	-0.14387	-2.24532	2.002484
H	-1.1748	-3.02734	0.863672	H	-1.47229	-2.92114	1.037297
H	-1.59954	-0.88477	2.800901	H	-1.83406	-0.60421	2.840749
H	-2.56584	0.286774	1.891586	H	-2.61397	0.567777	1.768671
H	-2.92459	-1.43841	1.758033	H	-3.10922	-1.13031	1.726333
H	-0.41217	3.792345	0.496399	H	-0.01288	3.757502	0.305497
H	0.011223	2.886994	1.964121	H	0.176997	2.941939	1.872016
H	1.088671	2.839481	0.574618	H	1.370094	2.678925	0.606482
H	0.928393	0.012364	-1.25828	H	1.109522	-0.25913	-1.02843
H	2.608919	0.133339	1.304098	H	2.544444	-0.10835	1.669398
H	3.259512	-0.14635	-1.69571	H	4.16545	-1.45362	0.395689
H	5.180421	-1.60282	-0.99303	H	5.565824	0.221734	-0.75433
H	3.629967	-2.33876	-0.55805	H	4.912369	0.899135	0.753769
H	4.612865	-1.53585	0.687087	H	4.198401	1.354985	-0.80946
H	5.278285	0.794115	-0.87774	H	2.847712	-1.83089	-1.4593
H	-2.49446	-2.61516	-0.98815	H	-3.58417	-1.18173	-1.25677
1-C-e				**1-C-f**			
C	-1.85915	-0.73913	-0.64659	C	-1.89659	-0.77998	-0.68985
C	-2.34853	0.668136	-1.01919	C	-2.53768	0.596849	-0.86296
C	-1.51749	1.790953	-0.54744	C	-1.78213	1.761947	-0.4026

C	-0.49048	1.651516	0.312763	C	-0.67824	1.639857	0.36415
C	-0.05046	0.280627	0.816131	C	-0.0772	0.277589	0.704444
C	-1.20925	-0.77166	0.766436	C	-1.12868	-0.88581	0.65065
C	-0.66696	-2.1834	1.053111	C	-0.43873	-2.25715	0.736182
C	-2.26748	-0.43371	1.83723	C	-2.10878	-0.75484	1.833942
C	0.299368	2.8308	0.806524	C	0.036542	2.840433	0.915225
C	1.198111	-0.12407	0.053382	C	1.133876	0.068412	-0.18806
C	2.407816	-0.27146	0.599853	C	2.396814	-0.0047	0.242535
C	3.663441	-0.63878	-0.15959	C	3.598719	-0.19348	-0.64737
C	4.635478	0.539095	-0.25298	C	4.38519	-1.45476	-0.30104
O	3.401759	-1.05487	-1.49642	O	4.512639	0.899787	-0.49015
O	-2.94518	-1.63662	-0.77675	O	-2.87683	-1.78045	-0.81544
O	-3.34792	0.846287	-1.69434	O	-3.65194	0.674985	-1.37367
H	-1.07575	-0.9787	-1.38748	H	-1.15951	-0.87533	-1.50992
H	-1.81814	2.770764	-0.91011	H	-2.20229	2.735639	-0.64111
H	0.238317	0.388335	1.871574	H	0.293731	0.328711	1.737525
H	0.028219	-2.52485	0.279176	H	0.238026	-2.42767	-0.10599
H	-0.13087	-2.20798	2.007811	H	0.147217	-2.34114	1.658344
H	-1.48953	-2.90227	1.122612	H	-1.19124	-3.0494	0.731883
H	-1.85745	-0.58454	2.841759	H	-1.5907	-0.93881	2.781144
H	-2.6122	0.601114	1.765463	H	-2.56645	0.237318	1.889247
H	-3.1366	-1.08515	1.718089	H	-2.9086	-1.49165	1.731072
H	-0.02018	3.761529	0.332266	H	-0.37864	3.775913	0.533499
H	0.185362	2.940011	1.893058	H	-0.03378	2.852668	2.010694
H	1.369102	2.688141	0.61603	H	1.104174	2.800409	0.672431
H	1.098546	-0.25833	-1.0226	H	0.940135	-0.00301	-1.2589
H	2.540462	-0.11652	1.67175	H	2.61738	0.078018	1.308164
H	4.166353	-1.45081	0.395433	H	3.260261	-0.25882	-1.69452

H	5.550282	0.230349	-0.76599	H	5.272226	-1.52509	-0.93666
H	4.898661	0.907718	0.742925	H	3.770598	-2.34711	-0.44807
H	4.174687	1.354169	-0.81824	H	4.713834	-1.42226	0.742392
H	2.839059	-1.83974	-1.45212	H	4.029512	1.711064	-0.69674
H	-2.58413	-2.52515	-0.87911	H	-3.64559	-1.32024	-1.20204
1-C-g				**1-C-h**			
C	-1.90901	-0.78719	-0.68405	C	-1.8806	-0.71819	-0.66594
C	-2.55257	0.591127	-0.89806	C	-2.3718	0.705305	-0.92668
C	-1.79457	1.750718	-0.39191	C	-1.53203	1.810348	-0.46365
C	-0.69244	1.646595	0.375084	C	-0.49123	1.614113	0.37275
C	-0.08284	0.290622	0.715343	C	-0.04922	0.215865	0.798898
C	-1.13707	-0.867	0.664358	C	-1.20614	-0.84076	0.722841
C	-0.4383	-2.23375	0.778851	C	-0.66108	-2.26728	0.9015
C	-2.12264	-0.72498	1.84247	C	-2.2366	-0.56543	1.836973
C	0.0162	2.854577	0.920261	C	0.308902	2.761979	0.919045
C	1.124544	0.077748	-0.18027	C	1.181922	-0.14973	-0.01097
C	2.388795	-0.00579	0.244944	C	2.404343	-0.31831	0.498878
C	3.587247	-0.18896	-0.65068	C	3.635306	-0.66217	-0.31192
C	4.374899	-1.45306	-0.31684	C	4.834915	0.210564	0.080322
O	4.50277	0.901896	-0.48928	O	3.400234	-0.61901	-1.71562
O	-2.91841	-1.77126	-0.80236	O	-2.94634	-1.62389	-0.81582
O	-3.61421	0.72399	-1.48234	O	-3.44231	0.870138	-1.50604
H	-1.17544	-0.89498	-1.50273	H	-1.11017	-0.918	-1.43453
H	-2.21703	2.72098	-0.64127	H	-1.83884	2.809078	-0.76346
H	0.290453	0.33965	1.748055	H	0.263096	0.274843	1.851062
H	0.219477	-2.43495	-0.07284	H	0.040352	-2.53895	0.107699
H	0.17531	-2.28202	1.684674	H	-0.13734	-2.3653	1.859195
H	-1.17914	-3.03689	0.844537	H	-1.48656	-2.98307	0.884683

H	-1.6109	-0.90805	2.793521	H	-1.79672	-0.76061	2.820797
H	-2.57209	0.270438	1.887558	H	-2.59571	0.468073	1.829061
H	-2.93042	-1.4534	1.739696	H	-3.09867	-1.22417	1.70972
H	-0.41533	3.784876	0.543873	H	0.007132	3.716775	0.482435
H	-0.03947	2.867444	2.016643	H	0.185144	2.825426	2.008019
H	1.081314	2.830151	0.663074	H	1.378072	2.608987	0.734724
H	0.927789	0.019726	-1.25164	H	1.051731	-0.26914	-1.08478
H	2.613358	0.068338	1.310287	H	2.561365	-0.21994	1.573918
H	3.244755	-0.24644	-1.69712	H	3.896039	-1.71112	-0.1126
H	5.260278	-1.51837	-0.95531	H	5.713519	-0.07662	-0.50311
H	3.760267	-2.34458	-0.46941	H	5.07271	0.105741	1.144107
H	4.706456	-1.42899	0.725893	H	4.621139	1.269348	-0.11038
H	4.017213	1.715978	-0.67858	H	3.202949	0.300919	-1.9437
H	-2.49163	-2.60993	-1.01413	H	-3.64201	-1.10804	-1.26531
1-C-i				**1-C-j**			
C	-1.89095	-0.71798	-0.66256	C	-1.92898	-0.7719	-0.6858
C	-2.37623	0.706492	-0.96861	C	-2.56579	0.612663	-0.87754
C	-1.53343	1.804856	-0.45939	C	-1.78857	1.760889	-0.37593
C	-0.49654	1.623558	0.380748	C	-0.6771	1.6415	0.375373
C	-0.05426	0.229665	0.813349	C	-0.08327	0.276685	0.710066
C	-1.21851	-0.81467	0.737474	C	-1.14785	-0.87039	0.655919
C	-0.67578	-2.23906	0.951817	C	-0.46097	-2.24444	0.75305
C	-2.25791	-0.51973	1.838726	C	-2.12446	-0.73037	1.841784
C	0.301977	2.776439	0.921036	C	0.063664	2.839215	0.900113
C	1.17281	-0.15027	0.005273	C	1.122856	0.061321	-0.186
C	2.397667	-0.31685	0.509861	C	2.385428	-0.02236	0.240094
C	3.623999	-0.66846	-0.30468	C	3.592345	-0.18265	-0.65077
C	4.819148	0.224079	0.055093	C	4.382436	-1.455	-0.33153

O	3.375008	-0.66061	-1.70686	O	4.436269	0.974332	-0.58045
O	-2.98466	-1.60302	-0.81199	O	-2.94454	-1.74965	-0.80665
O	-3.38217	0.920473	-1.62341	O	-3.63575	0.758168	-1.44354
H	-1.12168	-0.93227	-1.42513	H	-1.20223	-0.8743	-1.51118
H	-1.83614	2.800866	-0.7733	H	-2.20014	2.737277	-0.61927
H	0.257102	0.288409	1.86619	H	0.290317	0.318702	1.743269
H	0.010797	-2.54459	0.155937	H	0.191693	-2.44185	-0.10353
H	-0.13068	-2.30823	1.899312	H	0.155734	-2.308	1.655945
H	-1.49975	-2.95827	0.997293	H	-1.20881	-3.04152	0.812676
H	-1.83139	-0.71278	2.829062	H	-1.60851	-0.9275	2.787818
H	-2.60277	0.517441	1.816212	H	-2.56324	0.269172	1.899181
H	-3.12959	-1.1653	1.707163	H	-2.94011	-1.44976	1.737302
H	-0.00908	3.728267	0.484309	H	-0.37766	3.7751	0.549961
H	0.186999	2.843257	2.010879	H	0.056406	2.84349	1.998033
H	1.371202	2.631981	0.728164	H	1.115206	2.809211	0.592471
H	1.038526	-0.27734	-1.06743	H	0.928587	0.018292	-1.25807
H	2.561373	-0.20635	1.582785	H	2.594384	0.034643	1.311591
H	3.89695	-1.71001	-0.08356	H	3.261417	-0.21579	-1.6948
H	5.695213	-0.06934	-0.52912	H	5.266345	-1.51876	-0.97245
H	5.067202	0.147521	1.118928	H	3.771034	-2.35031	-0.48174
H	4.593589	1.275832	-0.15912	H	4.716107	-1.45261	0.714086
H	3.175085	0.253267	-1.95613	H	4.811693	1.006627	0.31076
H	-2.63045	-2.48556	-0.97327	H	-2.52458	-2.58595	-1.03998

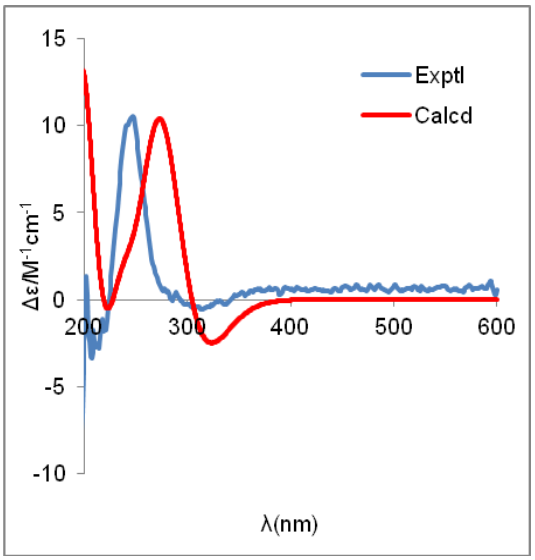
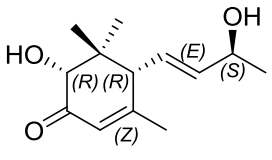
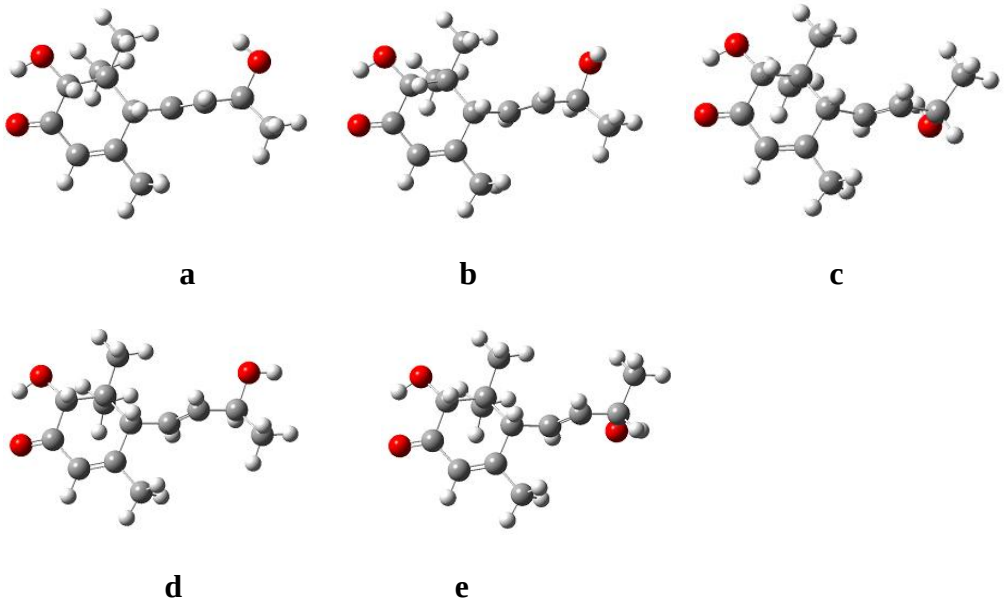


Figure S6. Calculated and experimental ECDs of **1-C** (red, calculated at the B3LYP-PCM/6-31G(d,p)//B3LYP/6-31G(d,p) level in CH_3OH; blue, experimental in CH_3OH).



(R,R,S)

1-D



a **b** **c**

d **e**

Figure S7. Optimized geometries of predominant conformers for compound **1-D** at the B3LYP/6-31G(d,p) level in the gas phase.

Table S7. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1-D** at B3LYP/6-31G(d,p) level in the gas phase

Conformations	E+ZPE	G	%
1-D-a	-732.785256	-732.830053	42.5
1-D-b	-732.783208	-732.827989	4.8
1-D-c	-732.785395	-732.829810	32.9
1-D-d	-732.783123	-732.828020	5.0
1-D-e	-732.784380	-732.829057	14.8

E+ZPE, G: total energy with zero point energy (ZPE) and Gibbs free energy in the gas phase at B3LYP/6-31G(d,p) level., %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors

Table S8. Optimized Z-matrixes of compound **1-D** in the gas phase (Å) at B3LYP/6-31G(d,p) level

1-D-a				**1-D-b**			
C	-2.38963	-0.65123	-0.58776	C	-2.37025	-0.67442	-0.59233
C	-2.9668	0.666766	-0.08277	C	-2.98075	0.627047	-0.08315
C	-2.04663	1.797552	0.002624	C	-2.08917	1.780374	0.009409
C	-0.70977	1.641105	-0.10271	C	-0.74873	1.657189	-0.09347
C	-0.06936	0.270156	-0.34031	C	-0.07545	0.304676	-0.3391
C	-1.00274	-0.93373	0.044966	C	-0.97736	-0.92544	0.040185
C	-0.45444	-2.23996	-0.5534	C	-0.39185	-2.21332	-0.56323
C	-1.1512	-1.09529	1.571023	C	-1.12018	-1.09793	1.565515
C	0.206815	2.831949	-0.04542	C	0.139342	2.86891	-0.02459
C	1.295251	0.167138	0.305105	C	1.290591	0.225476	0.305329
C	2.439631	-0.0543	-0.34748	C	2.431048	-0.02031	-0.34272

C	3.791074	-0.1793	0.307757	C	3.784431	-0.15389	0.309877
C	4.781366	0.869591	-0.19211	C	4.805957	0.831082	-0.26611
O	4.376536	-1.45125	0.005307	O	4.265996	-1.50103	0.218683
O	-3.30224	-1.69305	-0.35424	O	-3.25787	-1.73898	-0.36534
O	-4.16016	0.731393	0.201009	O	-4.17575	0.661654	0.19918
H	-2.23254	-0.52051	-1.67701	H	-2.21509	-0.535	-1.68094
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H	0.862321	2.856535	-0.92431	H	0.792669	2.918589	-0.90418
H	1.326273	0.279384	1.389416	H	1.323597	0.357838	1.386837
H	2.43692	-0.1765	-1.4319	H	2.412567	-0.15941	-1.42688
H	3.669668	-0.06493	1.397858	H	3.678644	0.024843	1.385837
H	5.759181	0.705948	0.269369	H	5.780043	0.681027	0.207811
H	4.436889	1.877736	0.054986	H	4.491993	1.867791	-0.10772
H	4.899024	0.793845	-1.27757	H	4.924001	0.680676	-1.34683
H	3.746672	-2.13191	0.278058	H	4.409648	-1.69699	-0.71793
H	-4.12609	-1.23918	-0.09213	H	-4.09204	-1.30659	-0.09987
1-D-c				**1-D-d**			
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C	-2.13534	1.71411	-0.04715	C	-2.04965	1.795018	-0.00752
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C	-0.06787	0.3301	-0.46095	C	-0.07181	0.267191	-0.34305
C	-0.87651	-0.92333	0.0325	C	-1.0028	-0.9367	0.049271
C	-0.26333	-2.209	-0.54731	C	-0.45077	-2.24341	-0.54489
C	-0.91648	-1.0263	1.569886	C	-1.14573	-1.09181	1.576544
C	0.023303	2.914739	-0.26776	C	0.203086	2.83034	-0.07022
C	1.34059	0.363375	0.089938	C	1.290827	0.165689	0.30615
C	2.44672	0.188495	-0.63612	C	2.427012	-0.09767	-0.3412
C	3.855011	0.202714	-0.0828	C	3.779115	-0.20561	0.3093
C	4.672986	-0.99483	-0.58402	C	4.720088	0.916665	-0.14716
O	3.888109	0.294932	1.337998	O	4.300612	-1.4871	-0.057
O	-3.12912	-1.87417	-0.18739	O	-3.30422	-1.69868	-0.33896
O	-4.14398	0.49895	0.316931	O	-4.1612	0.728593	0.206503
H	-2.23684	-0.68487	-1.62204	H	-2.23809	-0.53304	-1.67066
H	-2.64161	2.660795	0.12199	H	-2.49257	2.773111	0.16105
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H	0.76161	-2.35131	-0.19347	H	0.539929	-2.47206	-0.14304
H	-0.86083	-3.07357	-0.24874	H	-1.12547	-3.07051	-0.31177
H	-1.6281	-1.80365	1.858052	H	-1.93247	-1.81961	1.788686
H	0.063442	-1.29734	1.973218	H	-0.21713	-1.45611	2.024713
H	-1.22731	-0.08894	2.041602	H	-1.41339	-0.15054	2.067294
H	-0.60724	3.804604	-0.20624	H	-0.35999	3.765592	-0.03193
H	0.748559	2.941528	0.552896	H	0.868724	2.788317	0.799206
H	0.611564	2.963376	-1.19219	H	0.856137	2.847749	-0.95117
H	1.450251	0.549347	1.156671	H	1.322322	0.300669	1.387382
H	2.366838	0.019797	-1.71109	H	2.421594	-0.25342	-1.42059

H	4.350418	1.122104	-0.42595	H	3.652662	-0.14223	1.402695
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H	4.216456	-1.9372	-0.25817	H	4.847584	0.888014	-1.23386
H	3.509949	-0.52563	1.685599	H	5.203829	-1.54381	0.282975
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1-D-e							
C	-2.32283	-0.77502	-0.50199				
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C	-0.78398	1.649109	-0.24605				
C	-0.06532	0.315429	-0.47031				
C	-0.8798	-0.92604	0.042866				
C	-0.27916	-2.22237	-0.52619				
C	-0.90803	-1.01157	1.581642				
C	0.048239	2.900177	-0.29832				
C	1.347679	0.341391	0.068995				
C	2.441483	0.16495	-0.67373				
C	3.854341	0.167819	-0.15257				
C	4.558938	-1.16648	-0.43709				
O	3.824678	0.449623	1.243111				
O	-3.14228	-1.8617	-0.153				
O	-4.135	0.524389	0.332821				
H	-2.24924	-0.69441	-1.60506				
H	-2.61671	2.671629	0.109908				
H	0.0095	0.206171	-1.56608				
H	-0.26102	-2.20294	-1.62243				
H	0.745406	-2.3686	-0.17341				

H	-0.88283	-3.0788	-0.2165				
H	-1.6207	-1.78269	1.883976				
H	0.074391	-1.28064	1.979313				
H	-1.21228	-0.06766	2.044712				
H	-0.57355	3.79611	-0.23425				
H	0.78304	2.922368	0.513853				
H	0.627004	2.938899	-1.22925				
H	1.4717	0.511457	1.13528				
H	2.351542	-0.00542	-1.74709				
H	4.405406	0.96521	-0.68482				
H	5.601096	-1.13479	-0.09757				
H	4.567215	-1.39028	-1.50874				
H	4.045557	-1.97856	0.085457				
H	4.733639	0.422091	1.567205				
H	-3.97581	-1.44882	0.144063				

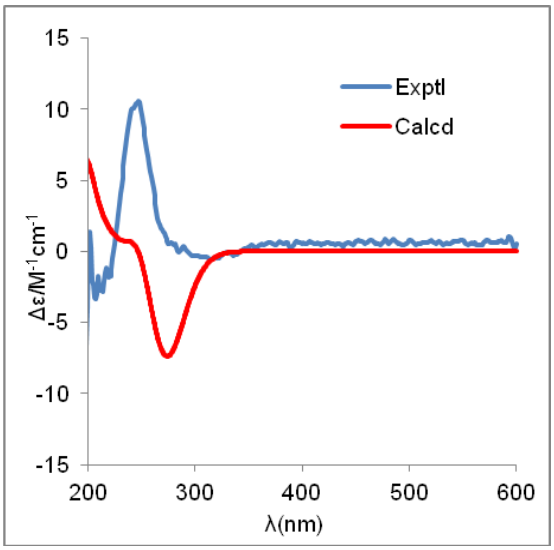


Figure S8. Calculated and experimental ECDs of **1-D** (red, calculated at the B3LYP-PCM/6-31G(d,p)//B3LYP/6-31G(d,p) level in CH_3OH; blue, experimental in CH_3OH).

Table S9. The computed ^{13}C NMR data for **1-A**.

1-A	δexptl	DMSO	
		δcalcd	$\Delta\delta$
1	41.1	46.6	5.5
2	75.5	76.2	0.7
3	198.7	196.3	-2.4
4	123.7	121.0	-2.7
5	162	167.1	5.1
6	56.1	58.8	2.7
7	124.3	127.1	2.8
8	139.8	138.5	-1.3
9	66.2	70.8	4.6
10	23.9	23.5	-0.4
11	20.8	26.4	5.6
12	24.6	21.2	-3.4
13	22.9	25.4	2.5

Table S10. The computed ^{13}C NMR data for **1-C**.

1-C	δexptl	DMSO	
		δcalcd	$\Delta\delta$
1	41.1	46.7	5.6
2	75.5	76.2	0.7
3	198.7	196.4	-2.3
4	123.7	120.9	-2.8
5	162	167.3	5.3
6	56.1	58.7	2.6
7	124.3	124.6	0.3
8	139.8	139.2	-0.6
9	66.2	69.5	3.3
10	23.9	23.8	-0.1
11	20.8	26.5	5.7
12	24.6	21.2	-3.4
13	22.9	25.5	2.6

(6*S*,9*R*)-6,9-dihydroxy-3-oxo-*α*-ionol (**2**): colorless powder (MeOH), ESI-MS *m/z*: 269 $[M+COOH]^+$. ^{1}H-NMR (DMSO, 400 MHz) *δ*: 5.78 (1H, br s, H-4), 5.68 (1H, overlap, H-8), 5.66 (1H, overlap, H-7), 4.17 (1H, m, H-9), 2.35 (1H, d, *J* = 16.7 Hz, H-2a), 2.06 (1H, d, *J* = 16.7 Hz, H-2b), 1.81 (3H, s, H-13), 1.11 (3H, d, *J* = 9.5 Hz, Me-10), 0.93 (3H, s, Me-12), 0.91 (3H, s, Me-11); ^{13}C-NMR (DMSO, 100 MHz) see Table 1.

(6*R*,9*S*)-3-oxo-*α*-ionol *β*-D-glucopyranoside (**3**): colorless powder (MeOH), ESI-MS *m/z*: 393 $[M+Na]^+$. ^{1}H-NMR (CD_3OD, 600 MHz) *δ*: 5.89 (1H, s, H-4), 5.75 (1H, dd, *J* = 15.4, 9.6 Hz, H-7), 5.58 (1H, dd, *J* = 15.4, 7.6 Hz, H-8), 4.48 (1H, br t, *J* = 6.7 Hz, H-9), 4.28 (1H, d, *J* = 8.3 Hz, H-1'), 3.85 (1H, br d, *J* = 11.8 Hz, H-6'a), 3.62 (1H, dd, *J* = 11.8, 6.1 Hz, H-6'b), 3.35 (1H, m, H-3'), 3.29 (1H, m, H-4'), 3.18 (1H, t, *J* = 8.3 Hz, H-2'), 3.15 (1H, m, H-5'), 2.69 (1H, d, *J* = 9.5 Hz, H-6), 2.48 (1H, br d, *J* = 16.7 Hz, H-2a), 2.05 (1H, br d, *J* = 16.7 Hz, H-2b), 1.98 (3H, s, Me-13), 1.29 (3H, d, *J* = 6.2 Hz, Me-10), 1.03 (3H, s, Me-12), 0.99 (3H, s, Me-11); ^{13}C-NMR (CD_3OD, 150 MHz) see Table 1.

(6*R*,9*R*)-3-oxo-*α*-ionol *β*-D-glucopyranoside (**4**): colorless powder (MeOH). ^{1}H-NMR (CD_3OD, 600 MHz) *δ*: 5.87 (1H, s, H-4), 5.76 (1H, dd, *J* = 15.4, 6.5 Hz, H-7), 5.64 (1H, dd, *J* = 15.4, 9.2 Hz, H-8), 4.39 (1H, br t, *J* = 6.4 Hz, H-9), 4.34 (1H, d, *J* = 7.8 Hz, H-1'), 3.80 (1H, dd, *J* = 11.8, 1.9 Hz, H-6'a), 3.65 (1H, dd, *J* = 11.8, 5.4 Hz, H-6'b), 3.33 (1H, m, H-3'), 3.29 (1H, m, H-4'), 3.21 (1H, m, H-5'), 3.16 (1H, t, *J* = 8.7 Hz, H-2'), 2.67 (1H, d, *J* = 9.2 Hz, H-6), 2.42 (1H, br d, *J* = 16.7 Hz, H-2a), 2.03 (1H, br d, *J* = 16.7 Hz, H-2b), 1.93 (3H, s, Me-13), 1.28 (3H, d, *J* = 6.3 Hz, Me-10), 1.02 (3H, s, Me-12), 1.00 (3H, s, Me-11); ^{13}C-NMR (CD_3OD, 150 MHz) see Table 1.

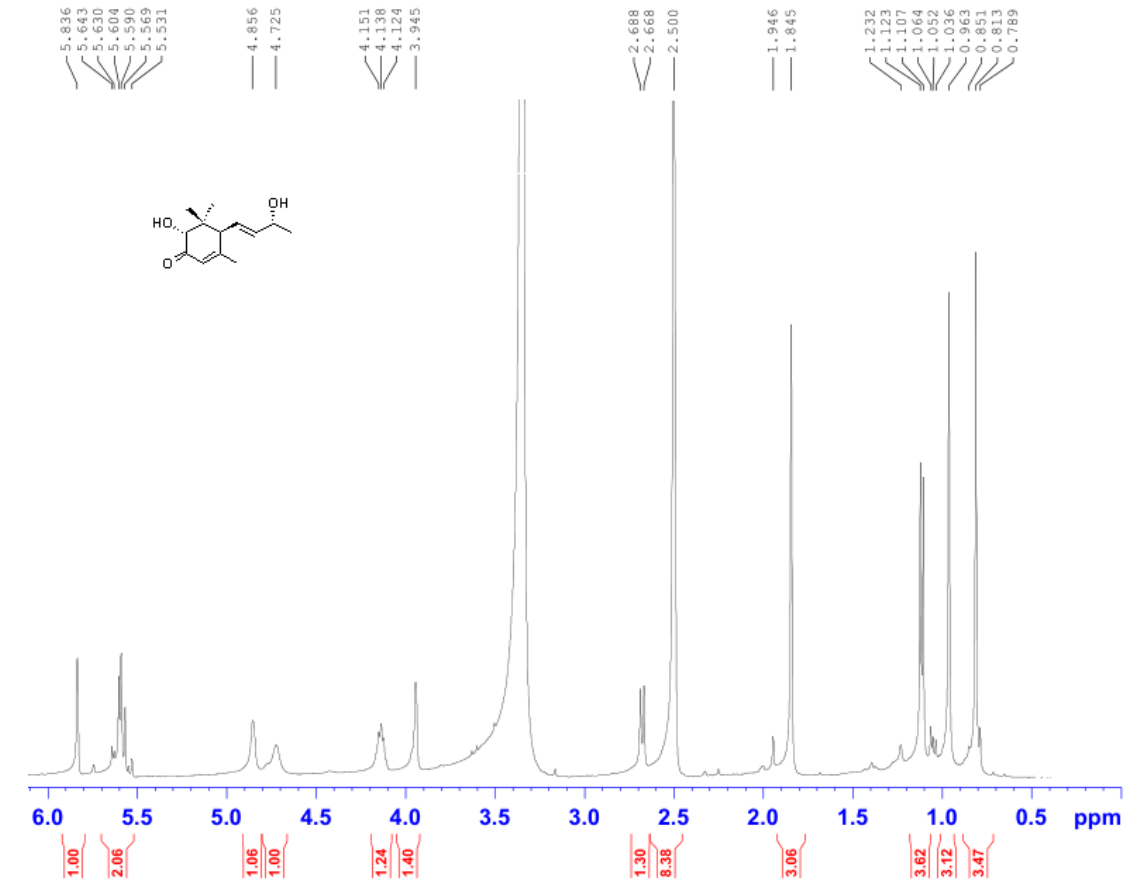


Figure S9. ^{1}H NMR spectrum of compound **1** recorded in DMSO at 600 MHz

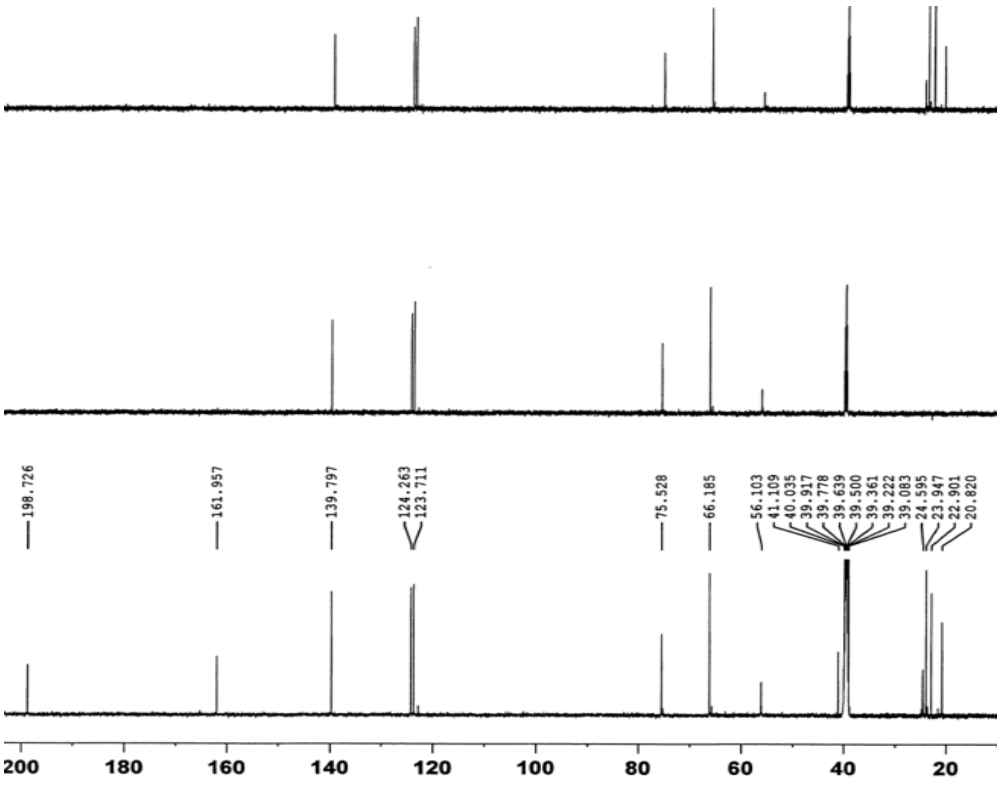


Figure S10. ^{13}C NMR spectrum of compound **1** recorded in DMSO at 150 MHz

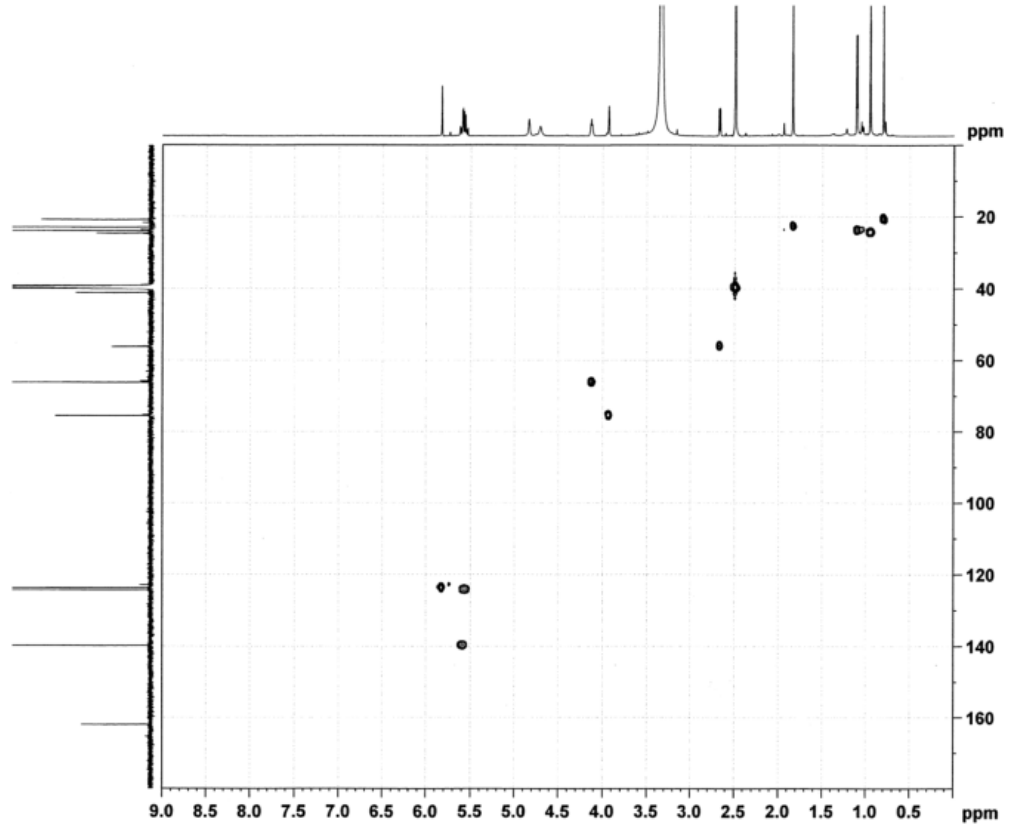


Figure S11. HSQC spectrum of compound **1** recorded in DMSO

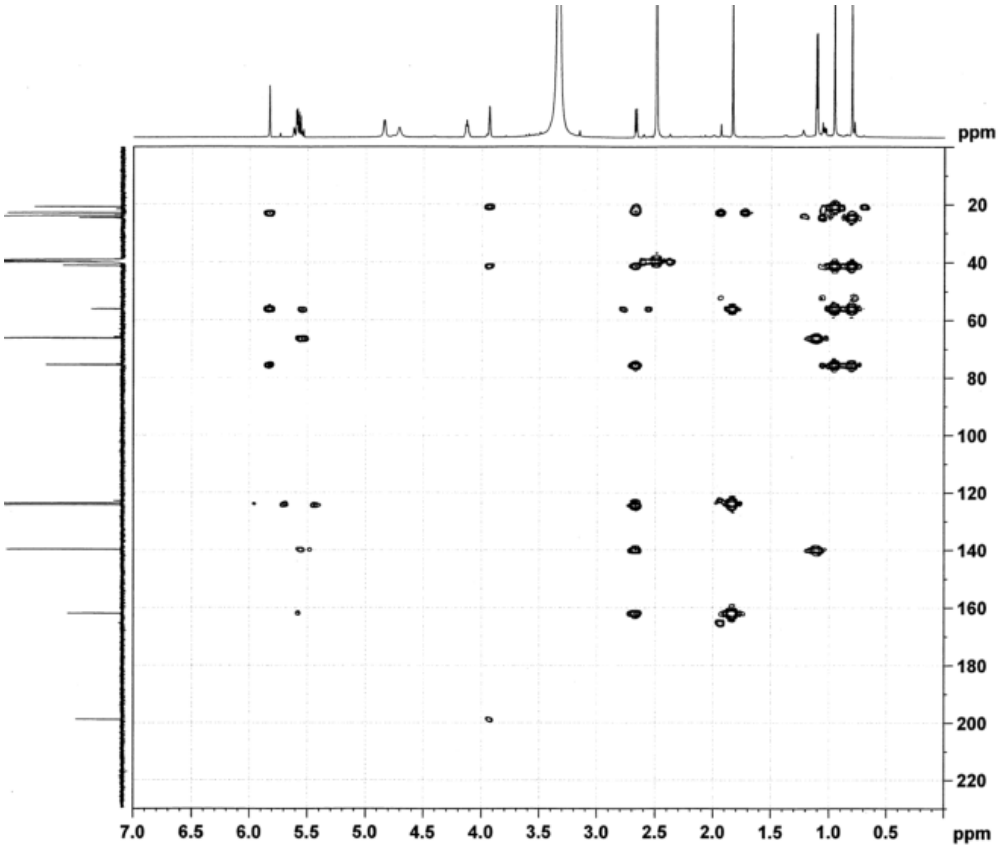


Figure S12. HMBC spectrum of compound **1** recorded in DMSO

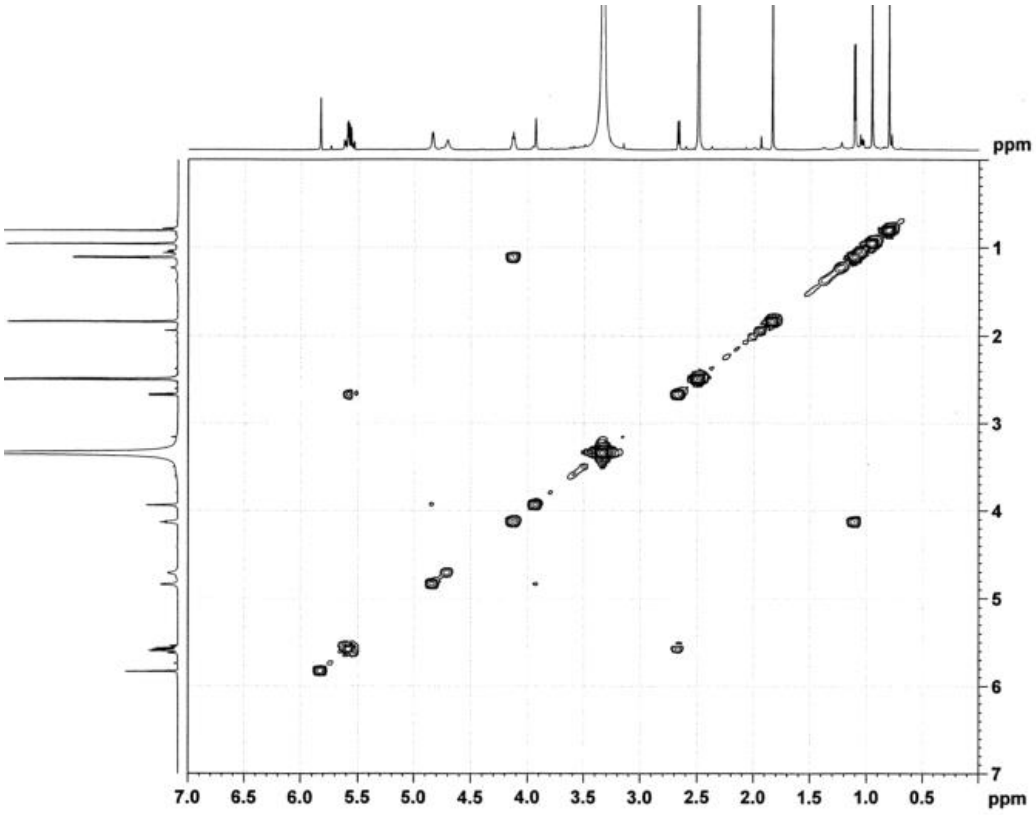


Figure S13. ^{1}H-^{1}H COSY spectrum of compound **1** recorded in DMSO

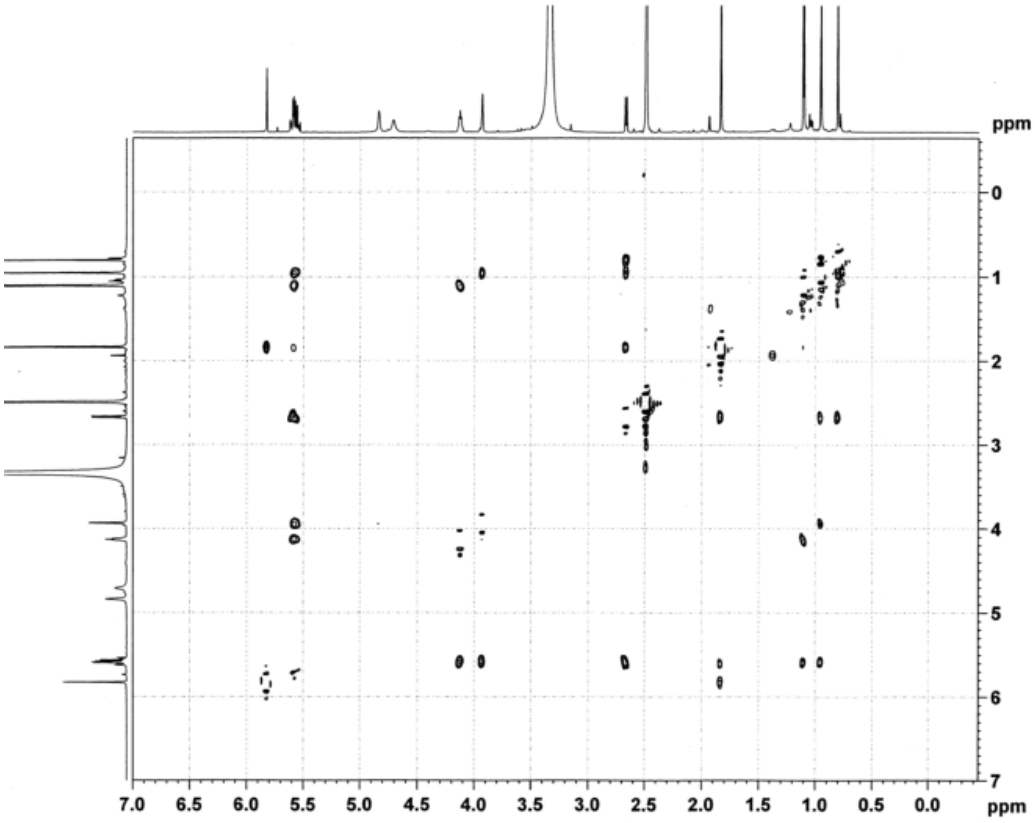
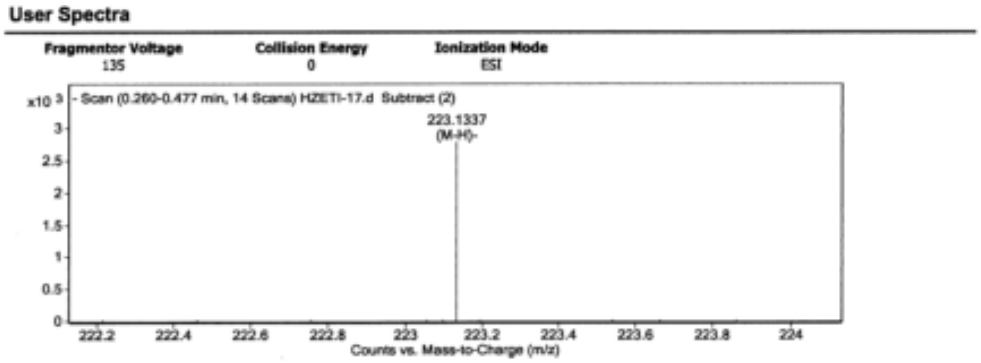


Figure S14. ROESY spectrum of compound **1** recorded in DMSO



Peak List

m/z	z	Abund	Formula	Ion
97.9996		733.98		
209.0815		718.9		
223.1337	1	2796.25	C13 H20 O3	(M-H)-
225.9264		719.85		
253.1075	1	678.62		
255.1237	1	2099.42		
325.1838	1	969.7		
339.1995	1	854.61		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C13 H20 O3	224.1412	223.1340	223.1337	0.1	0.3	4.0000

Figure S15. HR-ESI-MS spectrum of compound **1**

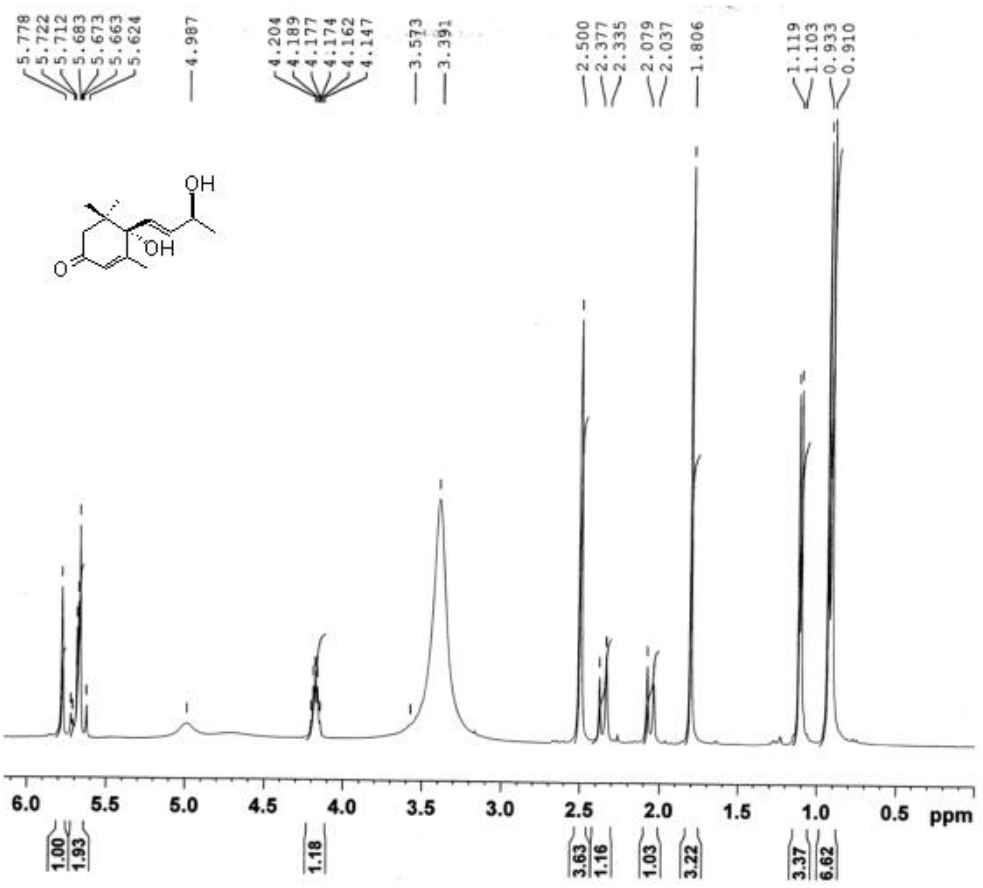


Figure S16. ^{1}H NMR spectrum of compound **2** recorded in DMSO at 400 MHz

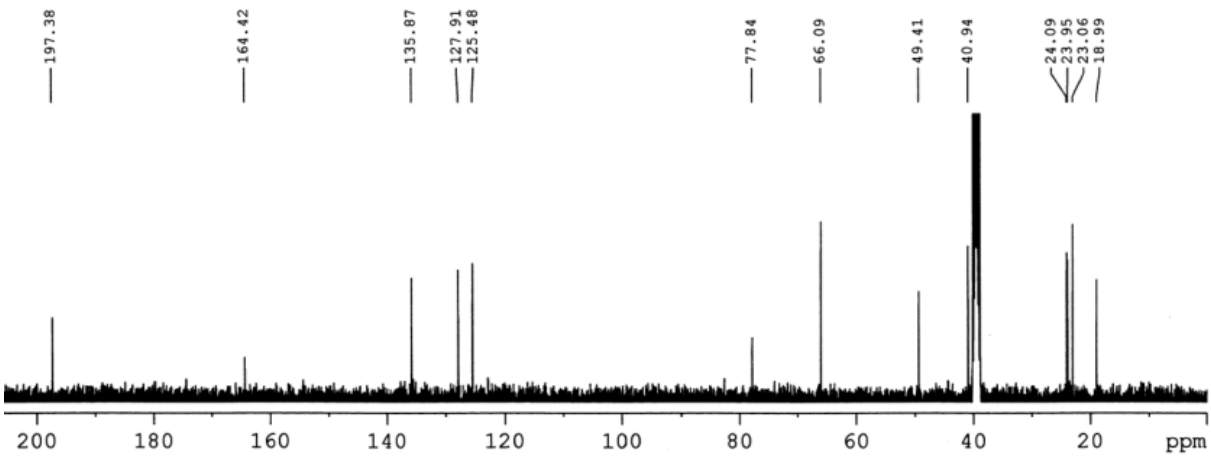


Figure S17. ^{13}C NMR spectrum of compound **2** recorded in DMSO at 100 MHz

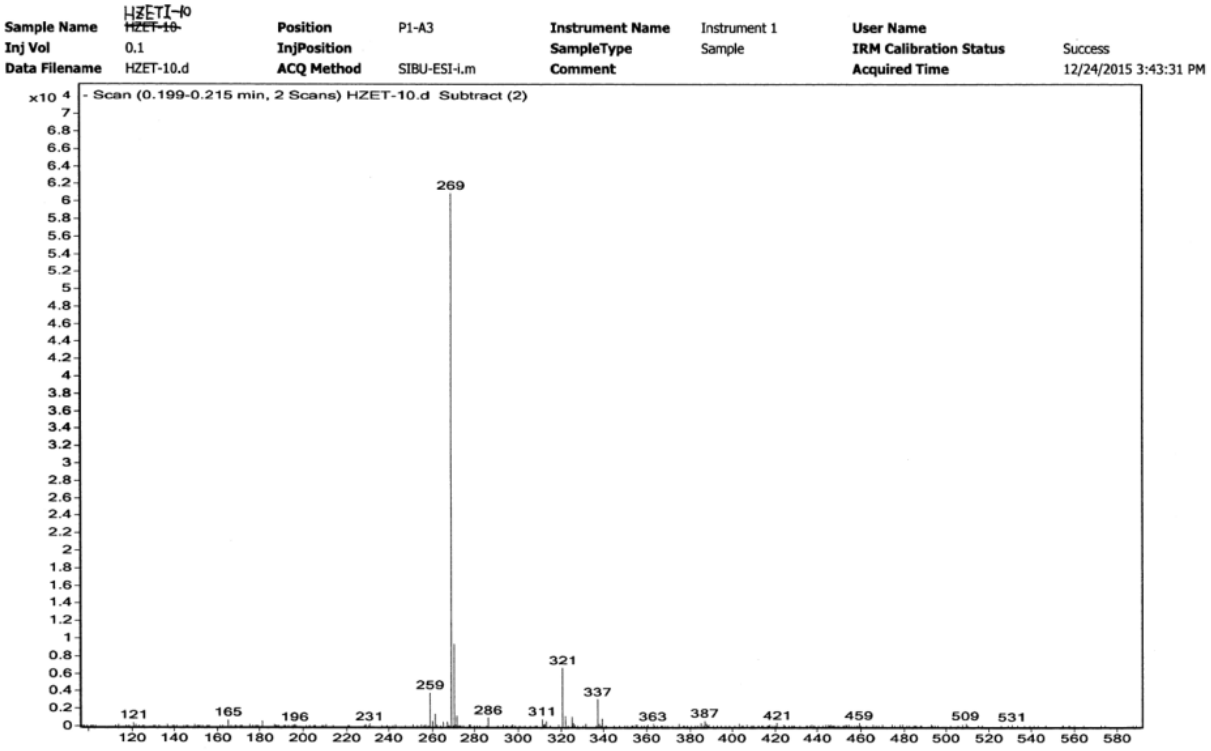


Figure S18. ESI-MS spectrum of compound **2**

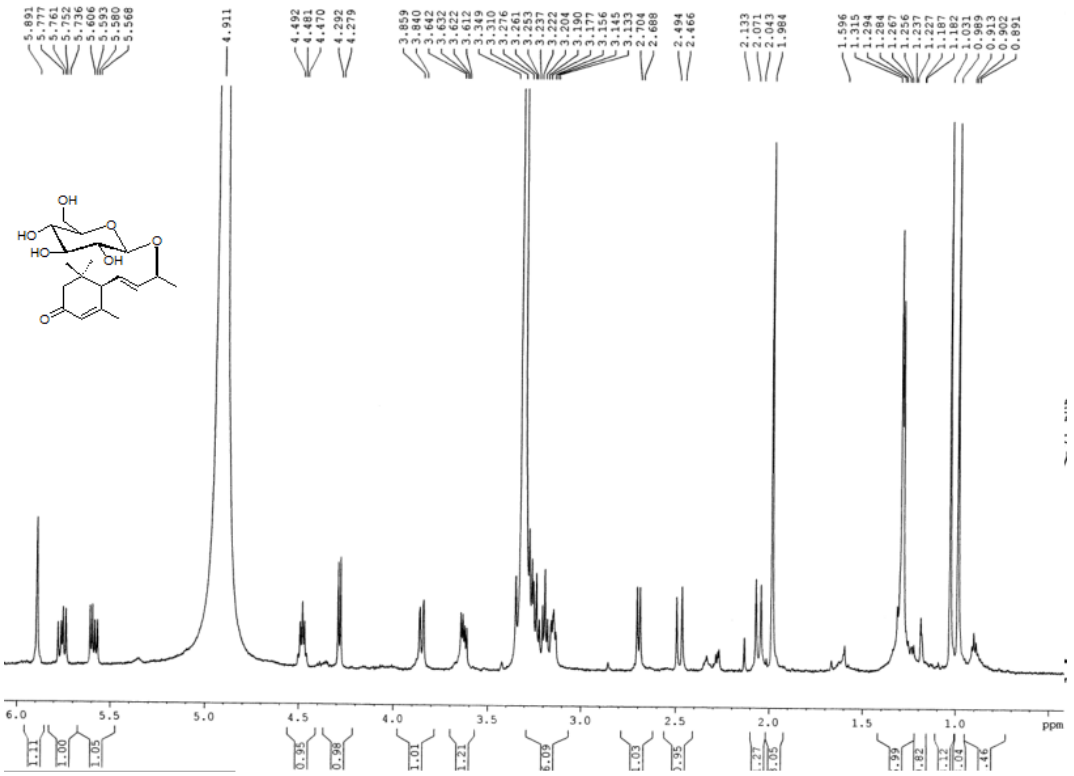


Figure S19. ^{1}H NMR spectrum of compound **3** recorded in CD_3OD at 600 MHz

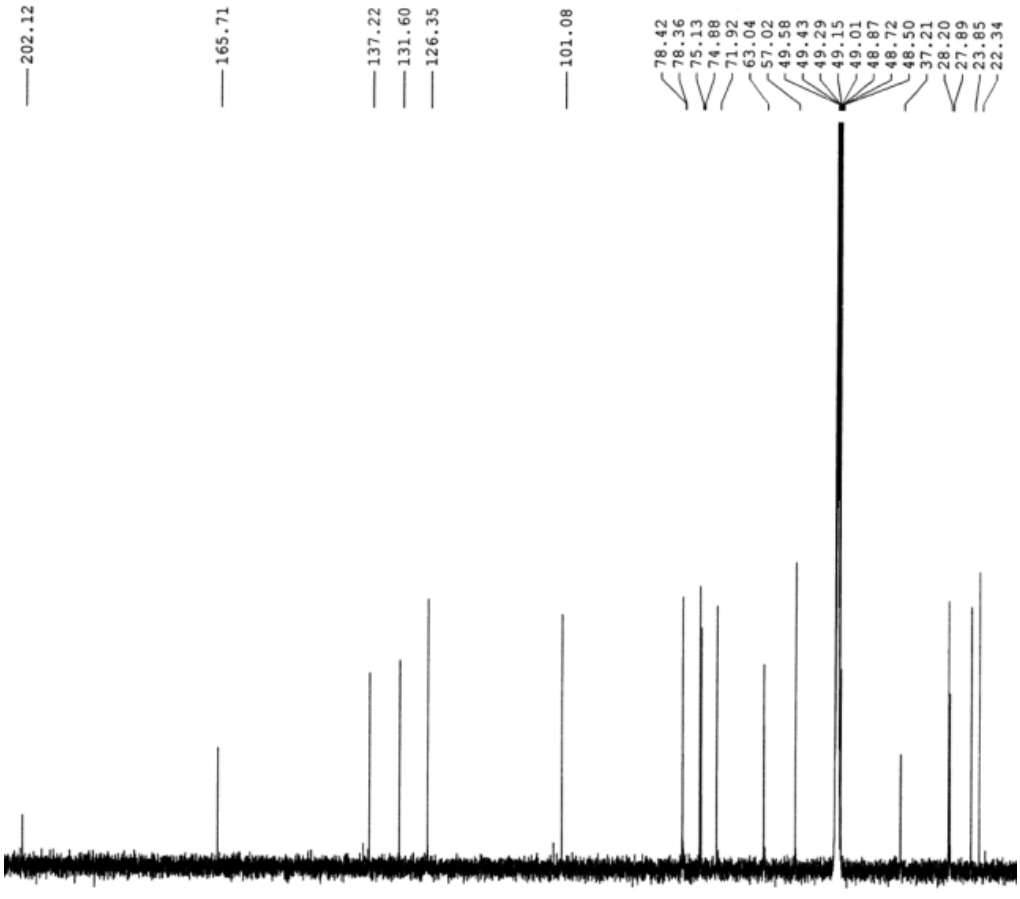


Figure S20. ^{13}C NMR spectrum of compound **3** recorded in CD_3OD at 150 MHz

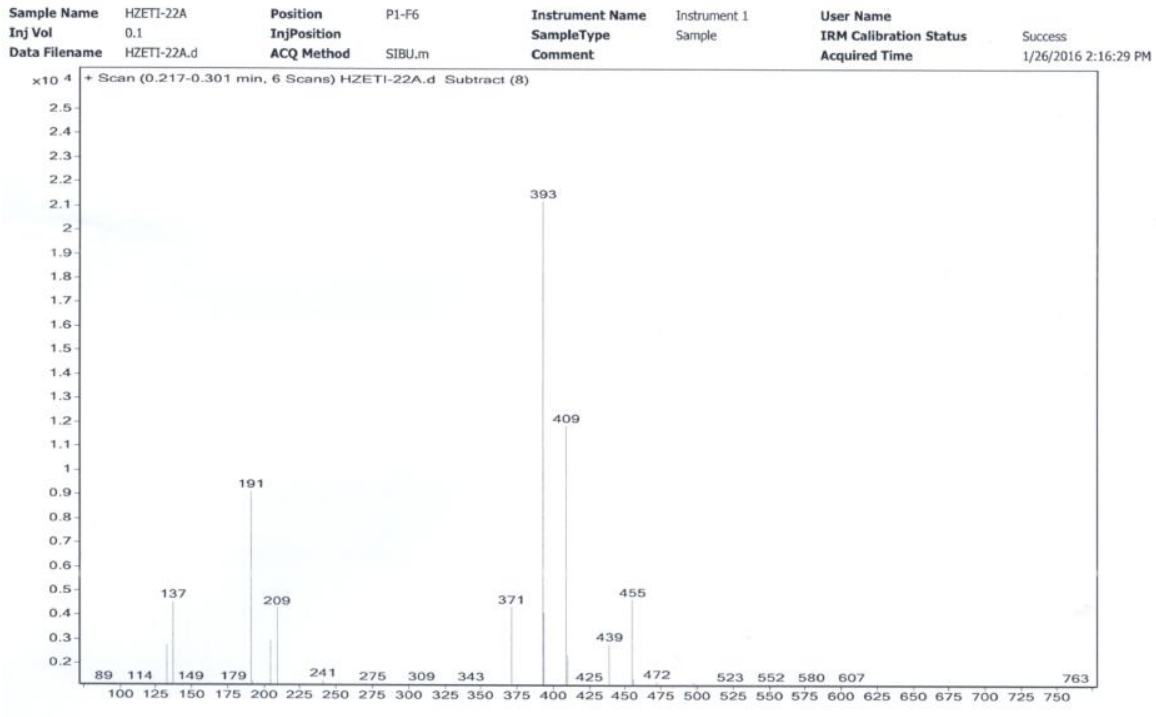


Figure S21. ESI-MS spectrum of compound **3**

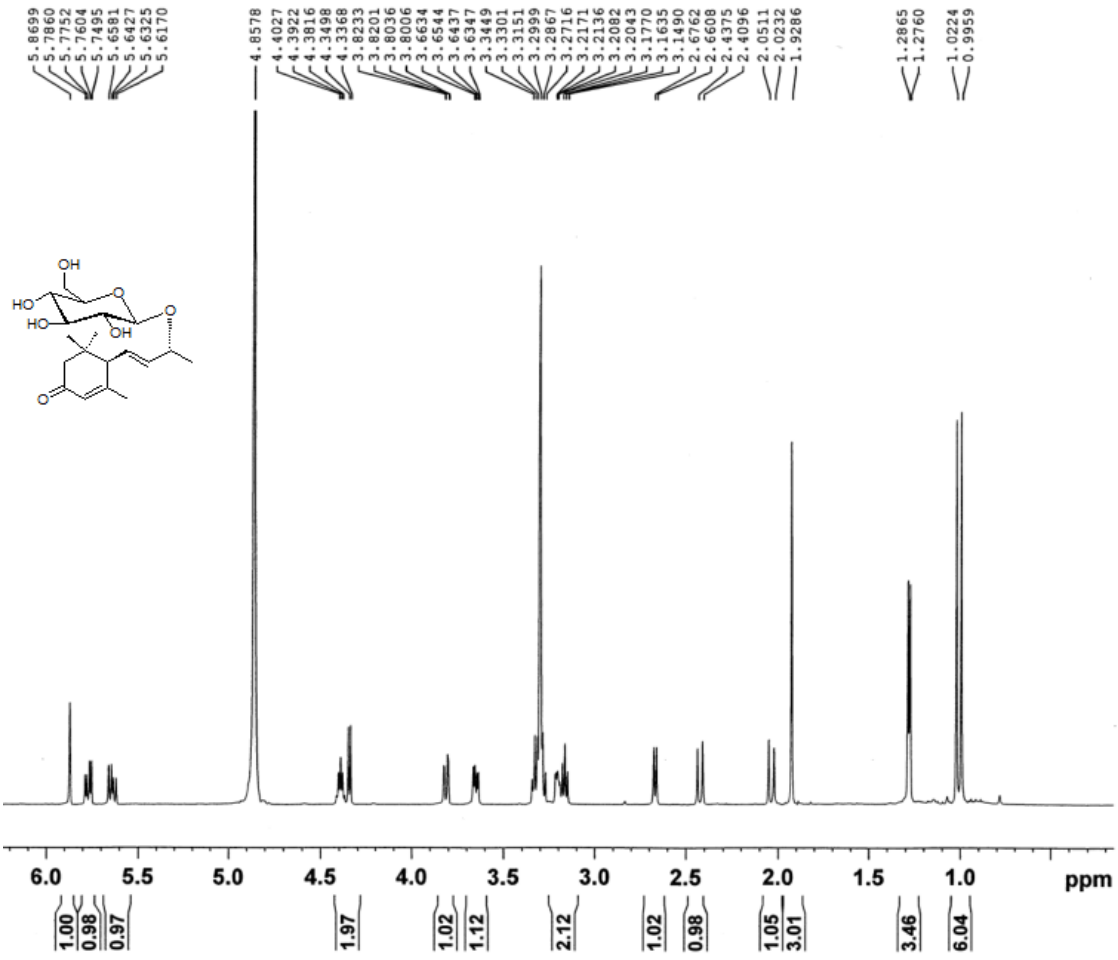


Figure S22. ^{1}H NMR spectrum of compound **4** recorded in CD_3OD at 600 MHz

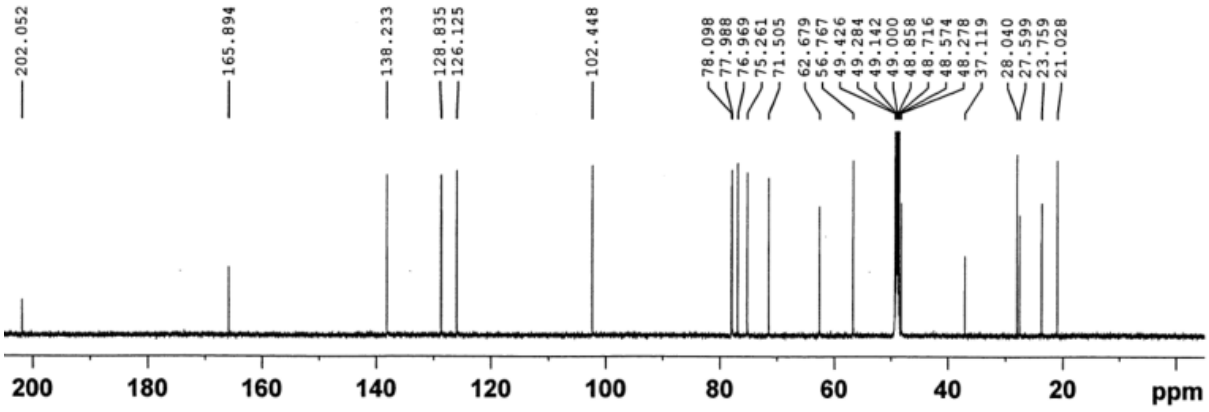


Figure S23. ^{13}C NMR spectrum of compound **4** recorded in CD_3OD at 150 MHz