

Supporting Information

Ganolearic acid A, a Hexanorlanostane Triterpenoid with a 3/5/6/5-Fused Tetracyclic Skeleton from *Ganoderma cochlear*

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Contents

- *HPLC and UPLC-MS total ion chromatograms of Fr. I-2 and HRESI
MS spectra of peak A.....S3*
- *NMR, MS, CD, and UV Spectra of Ganolearic acid A (1).....S4*
- *Computational Data of 1-1 and 1-2.....S18*
- *NMR and MS Spectra of Fornicatin M (2).....S49*

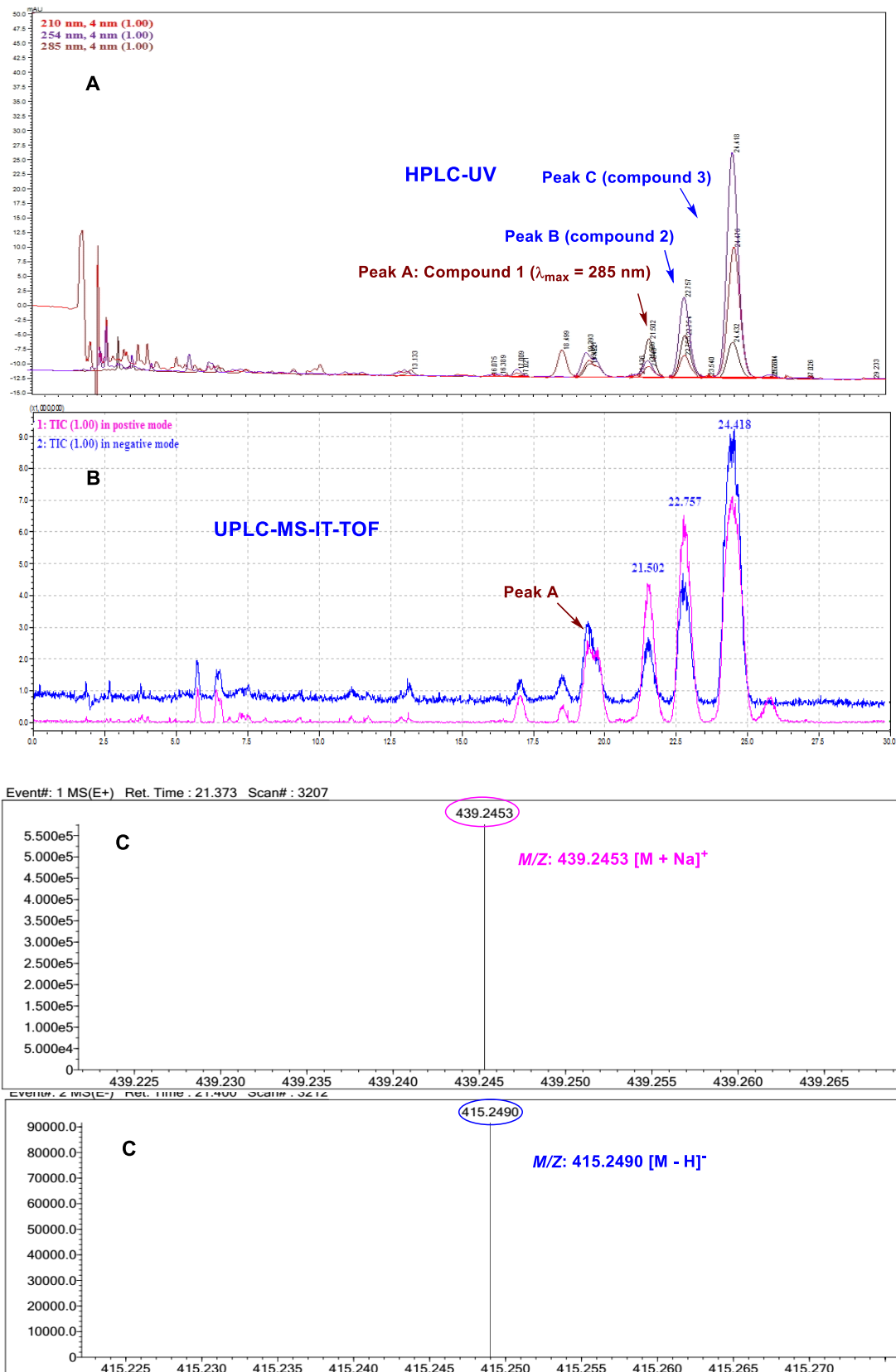


Figure S1. A: HPLC chromatogram of Fr. I-2 and the maximum wavelength of peak A is 285 nm; B: UPLC-MS total ion chromatogram of Fr. I-2; C: HRESI MS spectra of peak A.

NMR, MS, ECD, and UV Spectra of Ganolearic acid A (1)

kgar34-1

PROTON-sxhuo Pyr D:\\ root 9

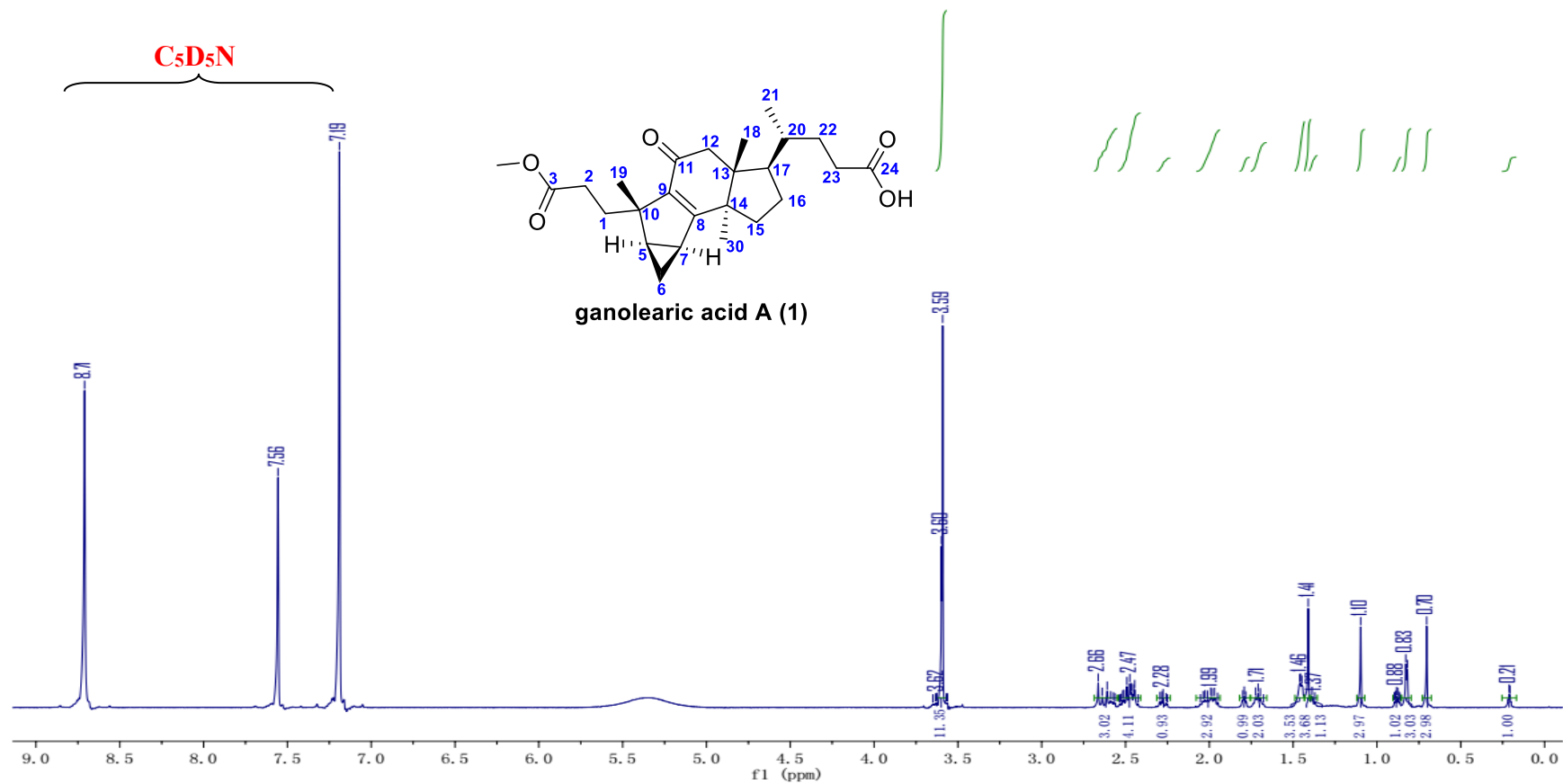


Figure S2. ¹H NMR (600 MHz, C₅D₅N) spectrum of ganolearic acid A (1).

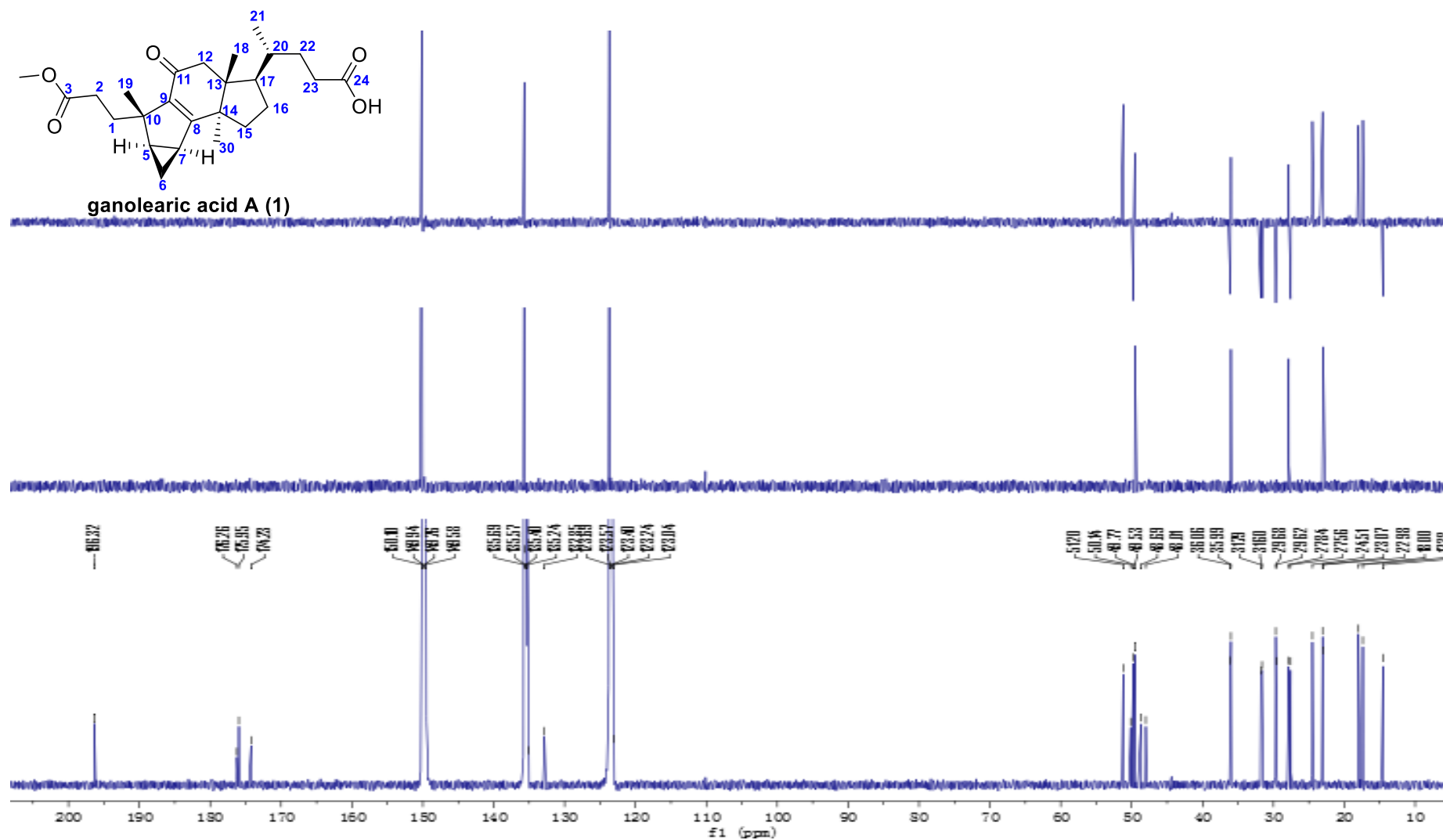


Figure S3. ^{13}C NMR (150 MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of ganolearic acid A (1).

kgar34-1a

PROTON-sxhuo MeOD D:\\ root 7

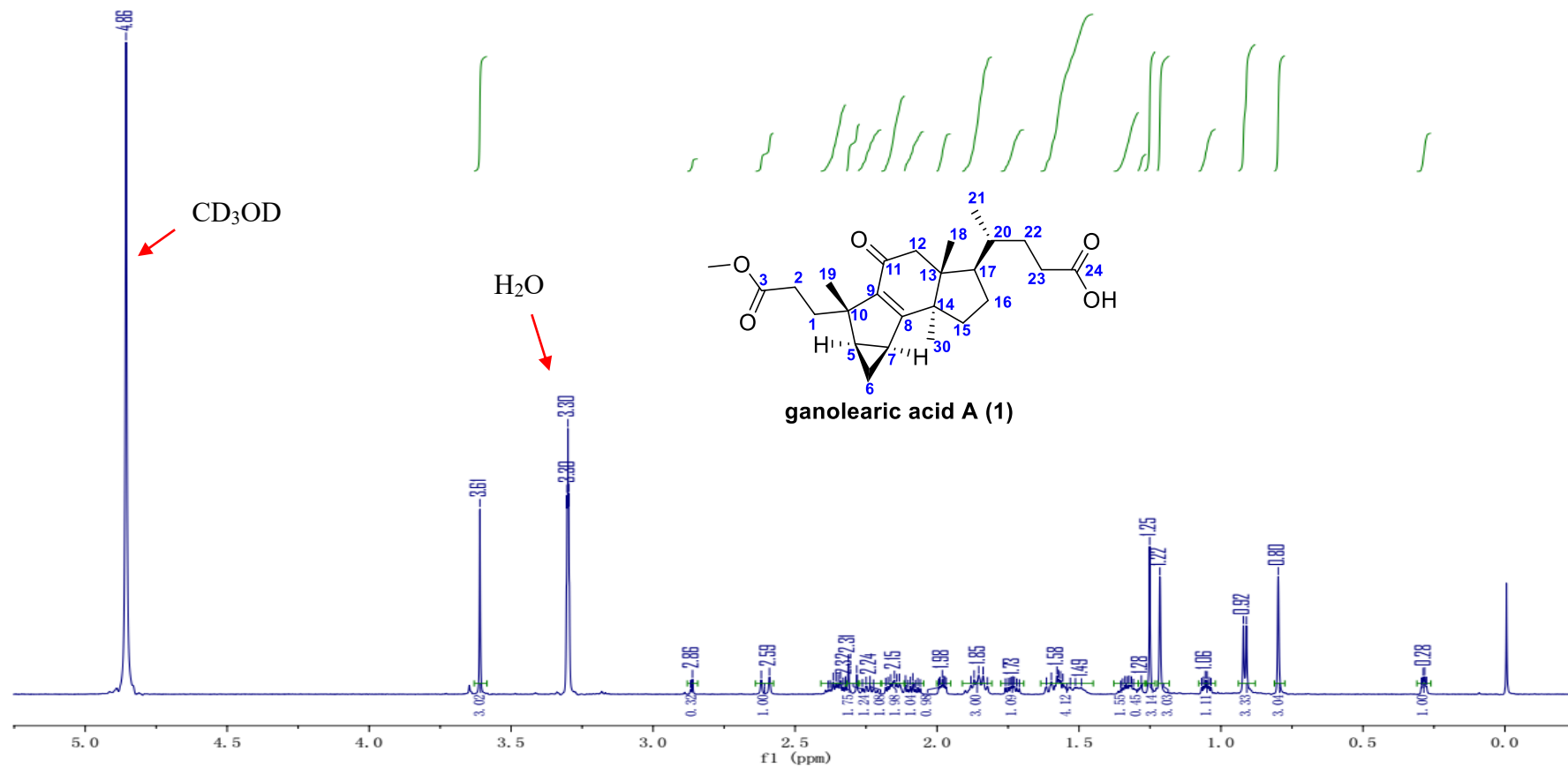


Figure S4. ¹H NMR (800 MHz, CD₃OD) spectrum of ganolearic acid A (1).

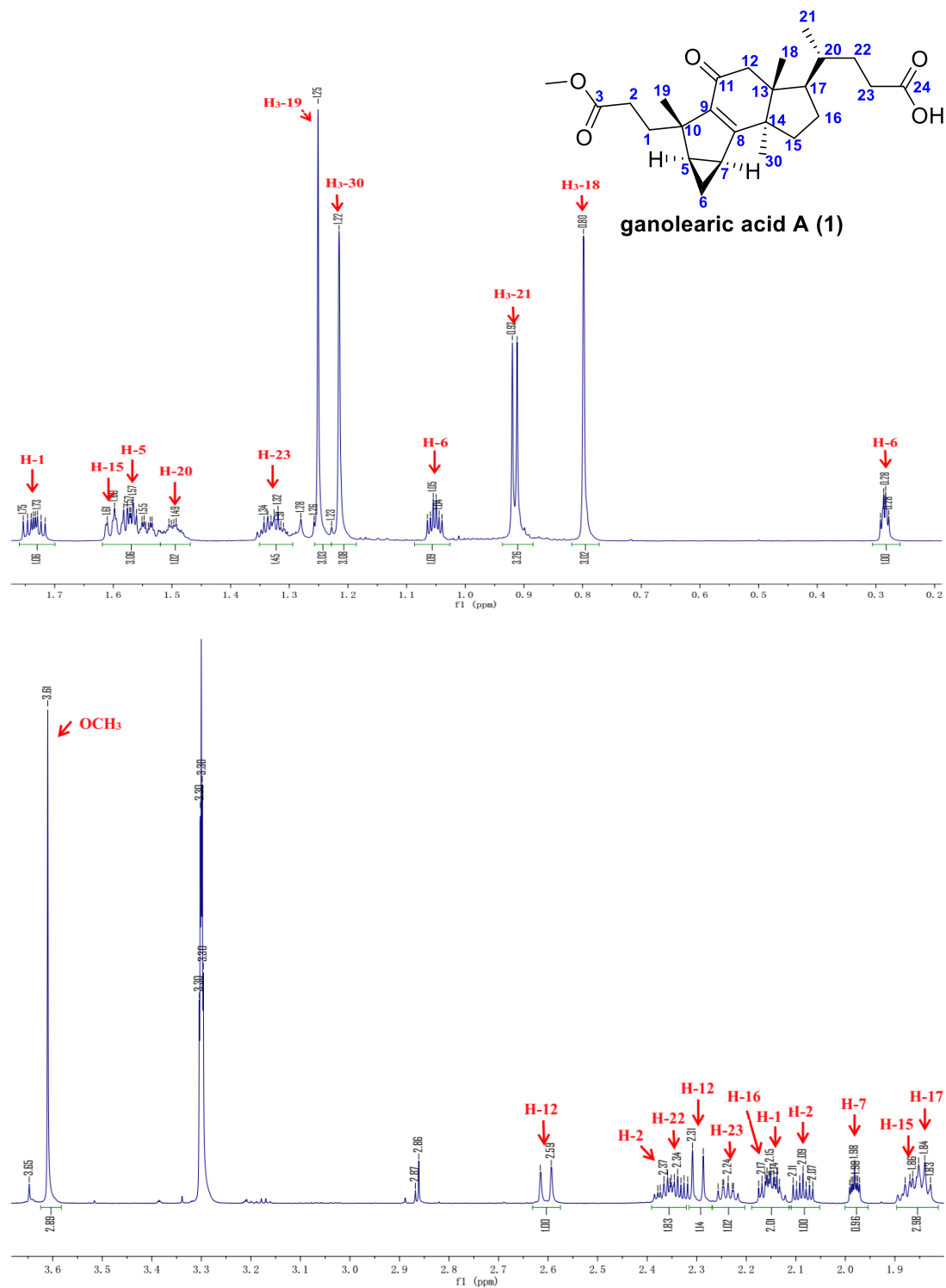


Figure S5. Expanded ^1H NMR spectrum of ganolearic acid A (1) in CD_3OD .

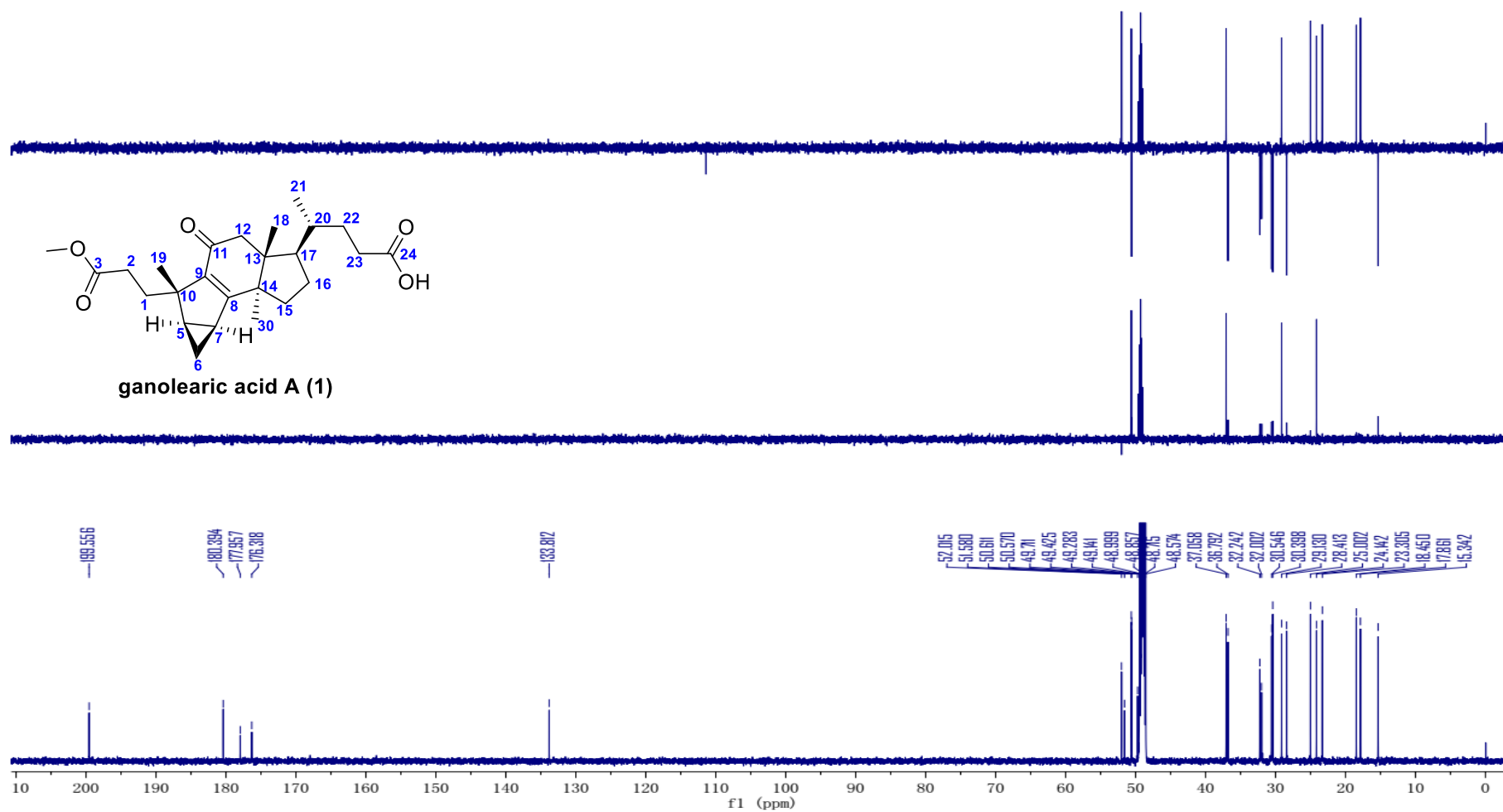


Figure S6. ^{13}C NMR (200 MHz, CD_3OD) spectrum of ganolearic acid A (1).

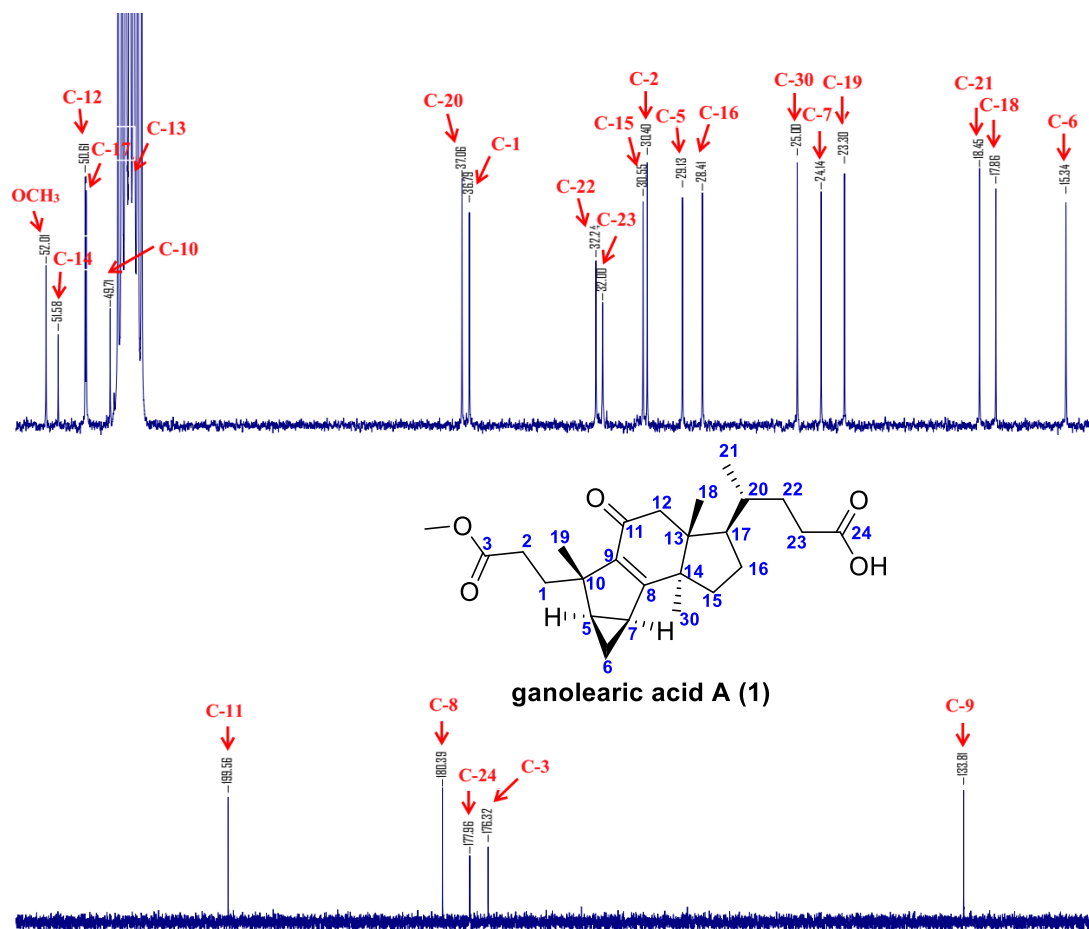


Figure S7. Expanded ^{13}C NMR spectrum of ganolearic acid A (1) in CD_3OD .

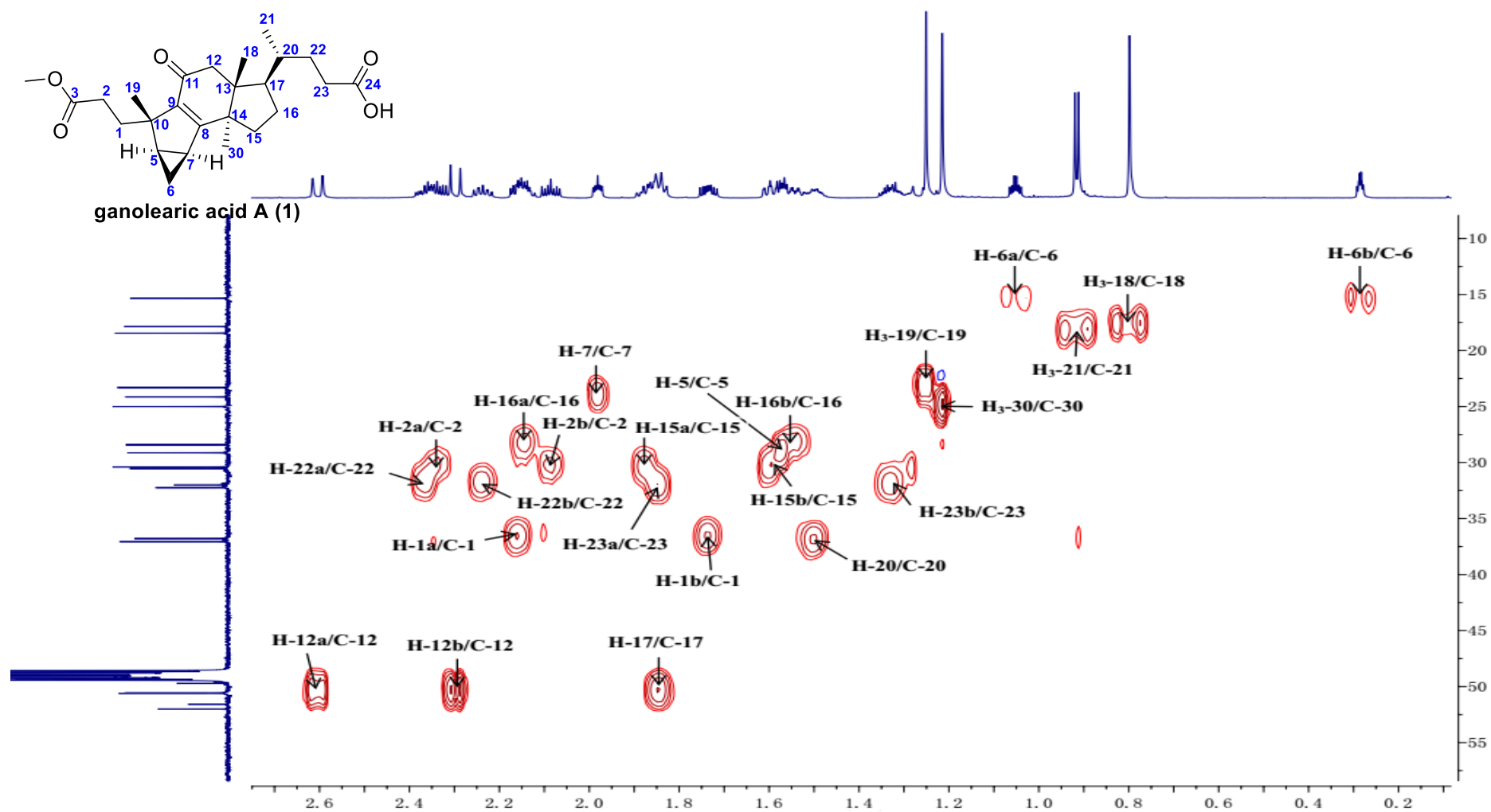


Figure S8. HSQC (800/200 MHz, CD_3OD) spectrum of ganolearic acid A (1).

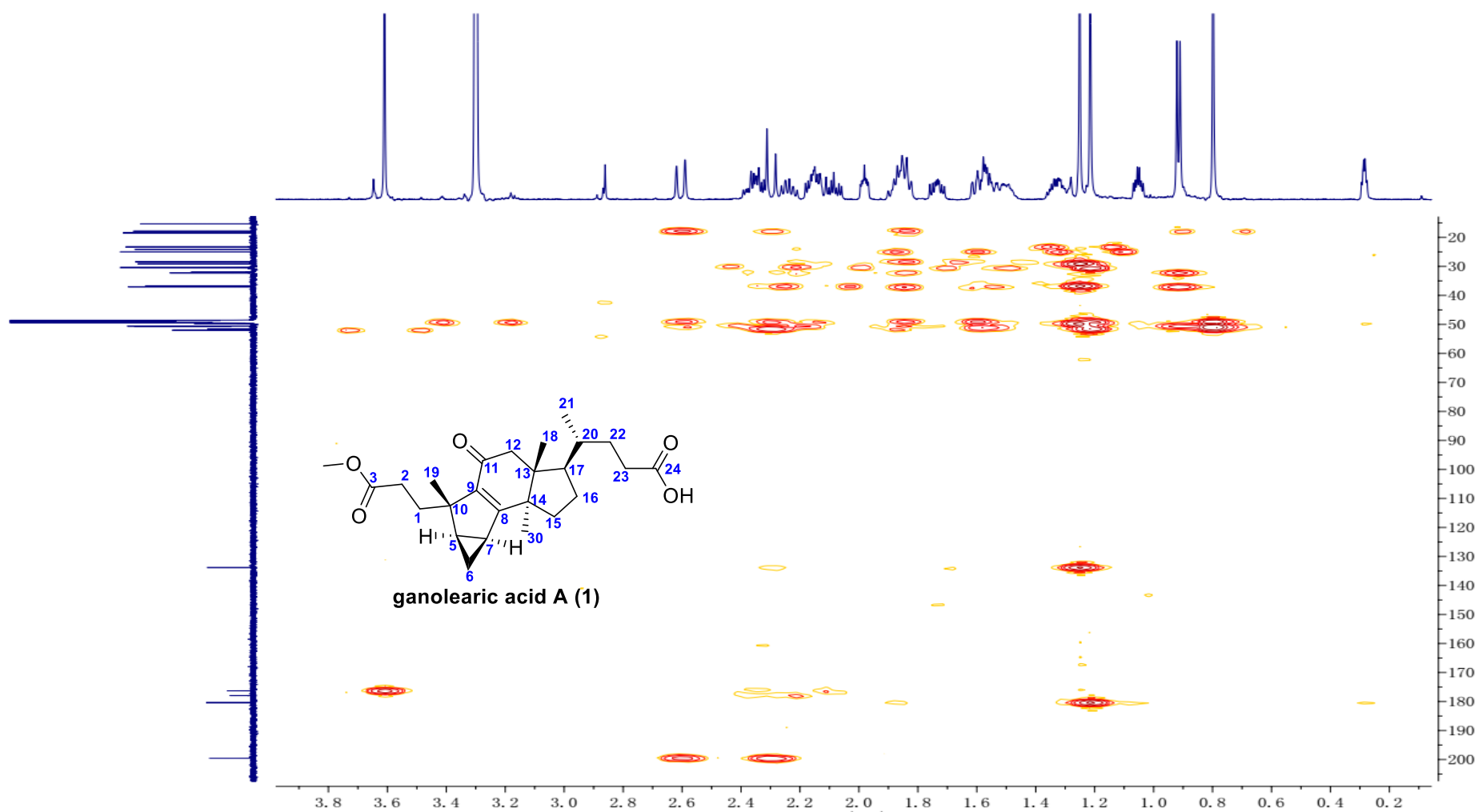


Figure S9. HMBC (800/200 MHz, CD₃OD) spectrum of ganolearic acid A (1).

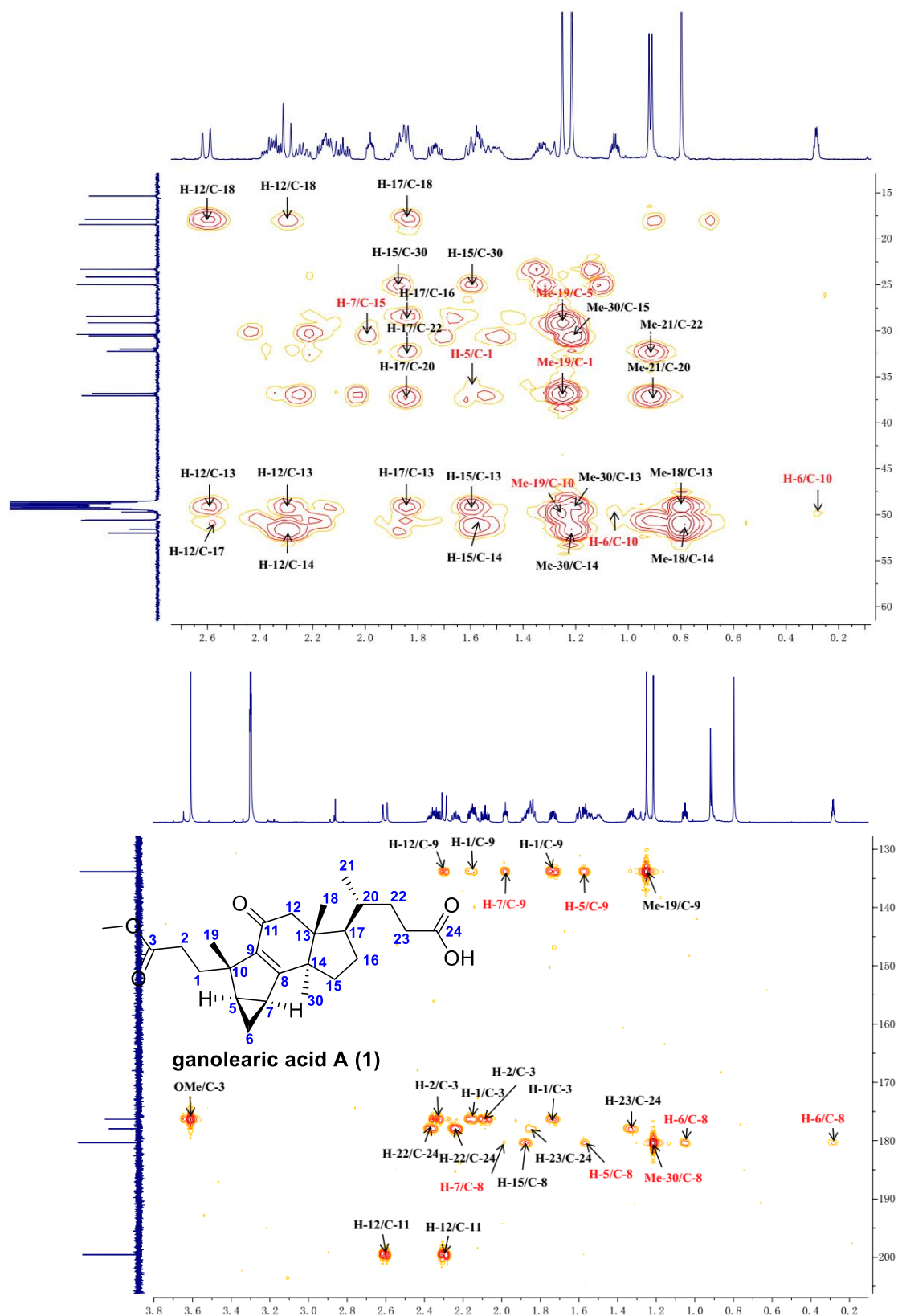


Figure S10. Expanded HMBC spectrum of ganolearic acid A (1) in CD_3OD .

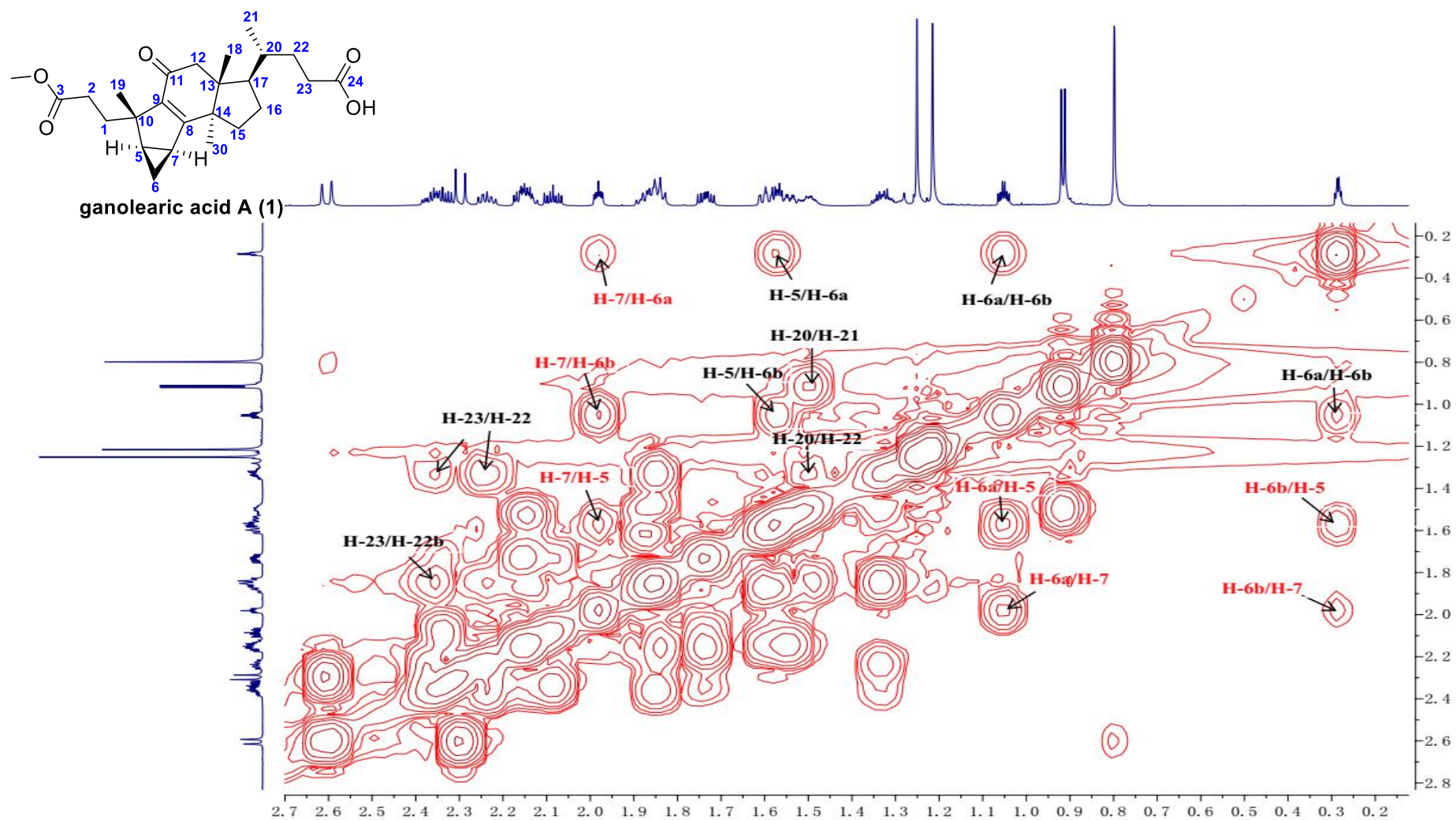


Figure S11. ^1H - ^1H COSY (800/200 MHz, CD_3OD) spectrum of ganolearic acid A (1).

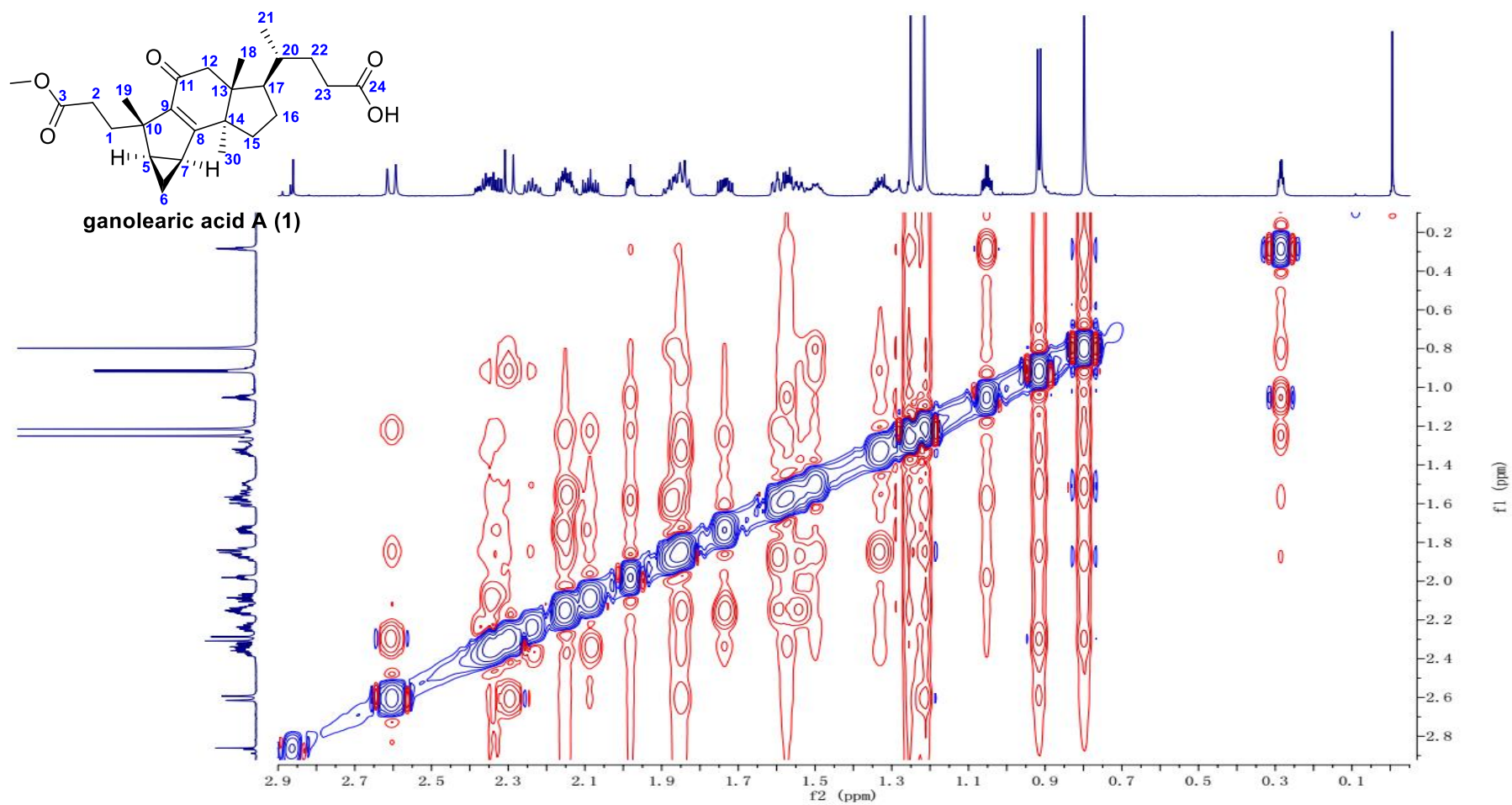


Figure S12. ROESY spectrum of ganolearic acid A (1) in CD₃OD.

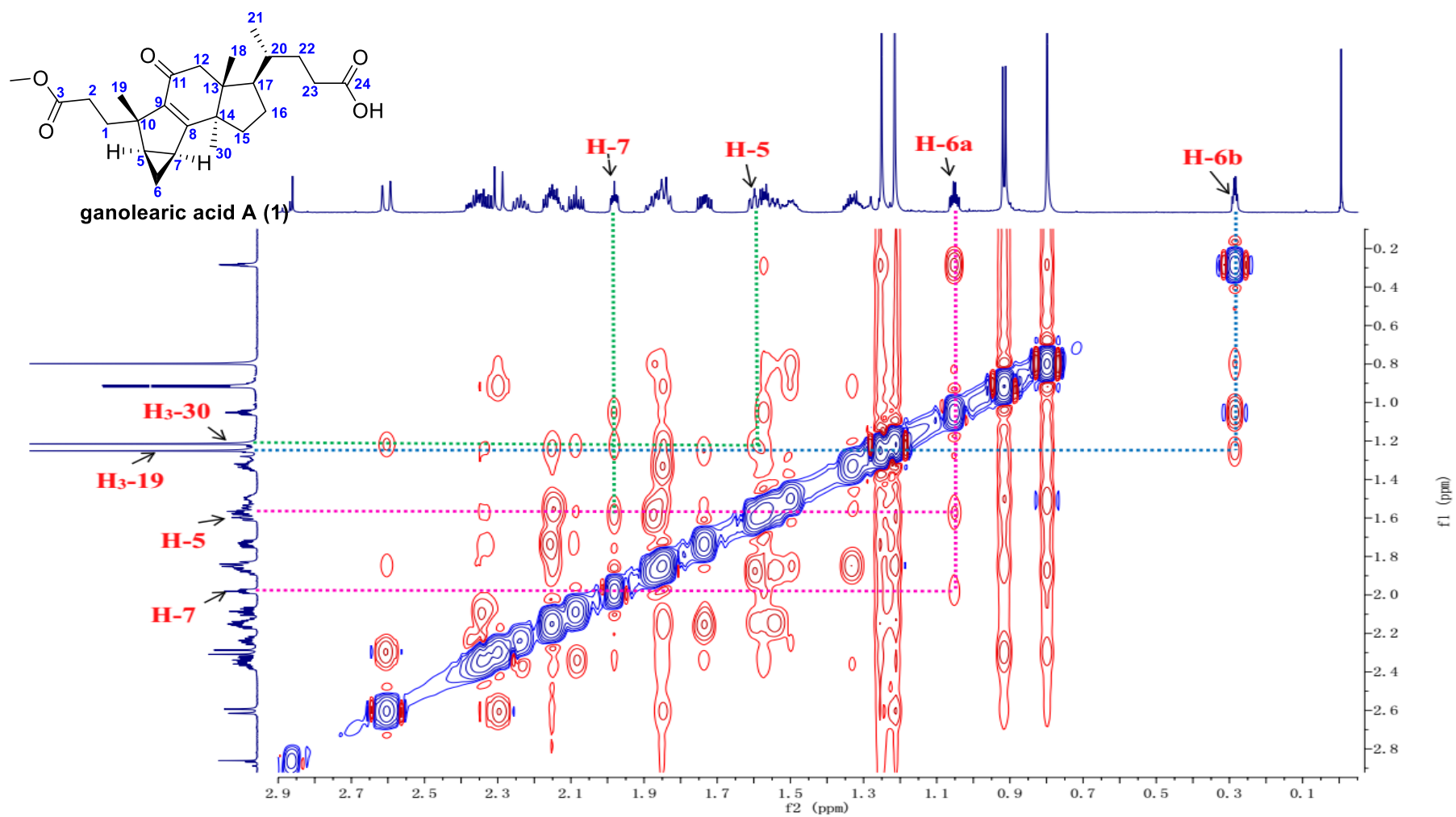


Figure S13. Expanded ROESY spectrum of ganolearic acid A (1) in CD₃OD.

Data File: E:\DATA\2018\0206\LCMS\Kgar34-5u.lcd

Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	O	2	0	50	Si	4	0	0	Br	1	0	0	Na
C	4	0	100	F	1	0	0	S	2	0	0	I	3	0	0	
N	3	0	0	Na	1	0	0	Cl	1	0	0					

Error Margin (ppm): 10

HC Ratio: unlimited

Max Isotopes: all

MSn Iso RI (%): 75.00

DBE Range: -2.0 - 100.0

Apply N Rule: yes

Isotope RI (%): 1.00

MSn Logic Mode: AND

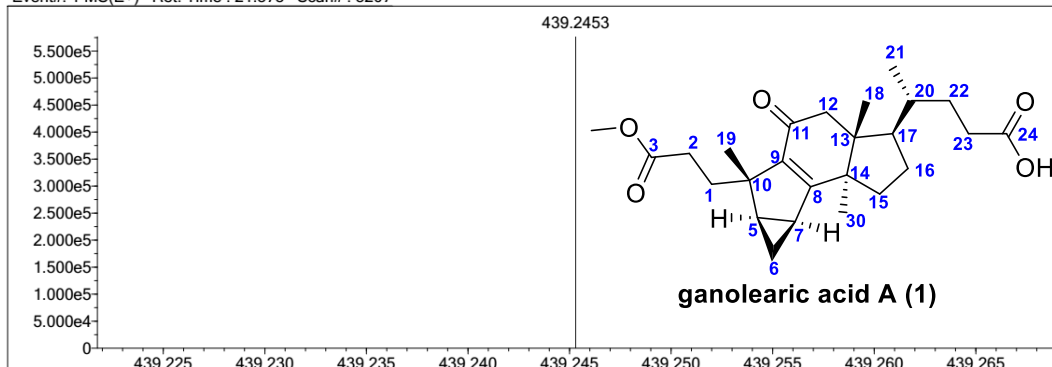
Electron Ions: both

Use MSn Info: yes

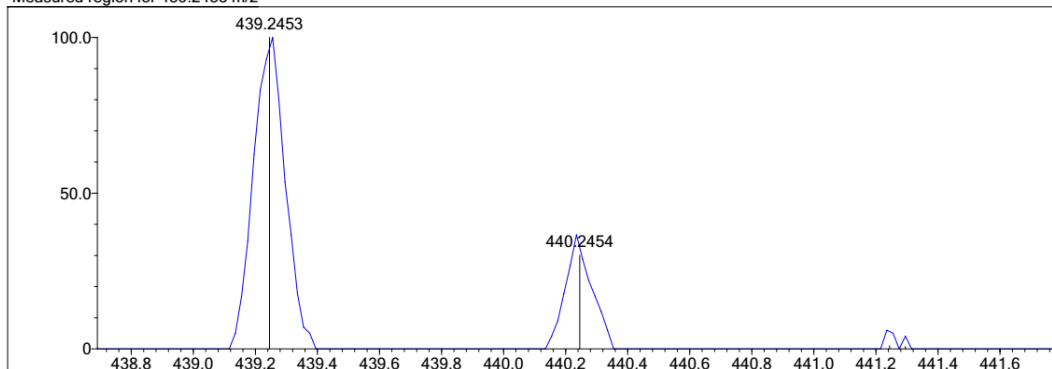
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Max Results: 10

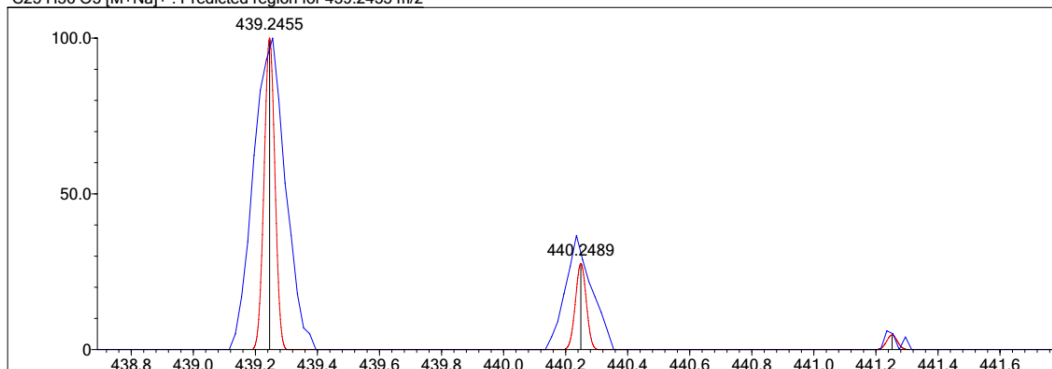
Event#: 1 MS(E+) Ret. Time : 21.373 Scan#: 3207



Measured region for 439.2453 m/z

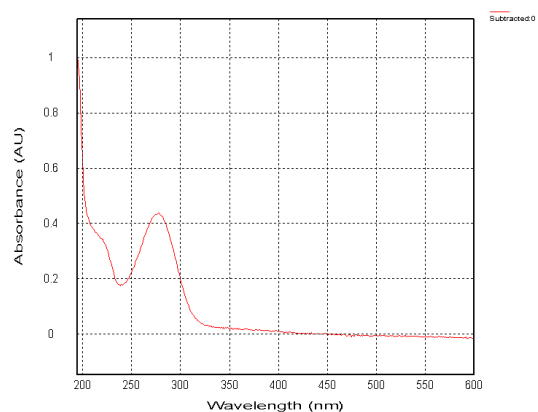
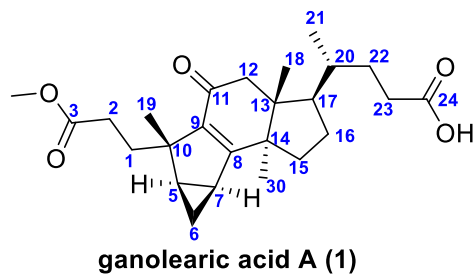
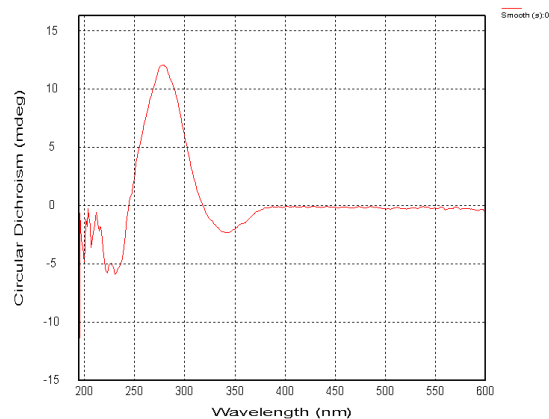


C25 H36 O5 [M+Na]+ : Predicted region for 439.2455 m/z



Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	DBE
C25 H36 O5	[M+Na]+	439.2453	439.2455	-0.2	-0.46	8.0

Figure S14. HRESIMS spectrum of ganolearic acid B (1).



File: CD KGAR34-1-1mm(195-600)18022802.dsx

ProBinaryX

Attributes :

- Time Stamp :Wed Feb 28 16:53:30 2018
- File ID : {CB7C1510-0671-4ec8-A737-C6C209B394D5}
- Is CFR Compliant : false
- Original unaltered data

Remarks:

- HV (CDDC channel): 0 v
- Time per point: 1 s
- Description: Sample 1
- Concentration: 0.4563 mg/mL MeOH
- Pathlength: 1 mm

Settings:

- Time-per-point: 1s (25us x 40000)
- Wavelength: 195nm - 600nm
- Step Size: 1nm
- Bandwidth: 2nm

Figure S15. CD and UV spectra of ganolearic acid B (1).

Calculations Data of 1-1 and 1-2

1. ECD calculation

The theoretical calculations of compound **1** were performed using Gaussian 09.¹ Conformational analysis was carried out. The optimized conformation geometries and thermodynamic parameters of all conformations were provided. The 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. The ECD spectra of compound **1** were obtained by weighing the Boltzmann distribution rate of each geometric conformation.

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

$$\Delta\varepsilon(E) = \frac{1}{2.297 \times 10^{-39}} \times \frac{1}{\sqrt{2\pi}\sigma} \sum_i^A \Delta E_i R_i e^{-[(E-E_i)/(2\sigma)]^2} \quad (1)$$

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.

2. NMR calculation

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.² The solvent effect was considered by using pyridine in the calculations to resemble the experimental condition. The polarized continuum model (PCM) of Tomasi et al. was used.³ The calculated ^{13}C NMR chemical shifts were analyzed by subtracting the isotopic shifts for TMS calculated with the same methods.² 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.⁴ The

differences $\Delta\delta$ were determined by subtracting the experimental chemical shifts δ_{exptl} from the calculated chemical shifts δ_{calcd} .

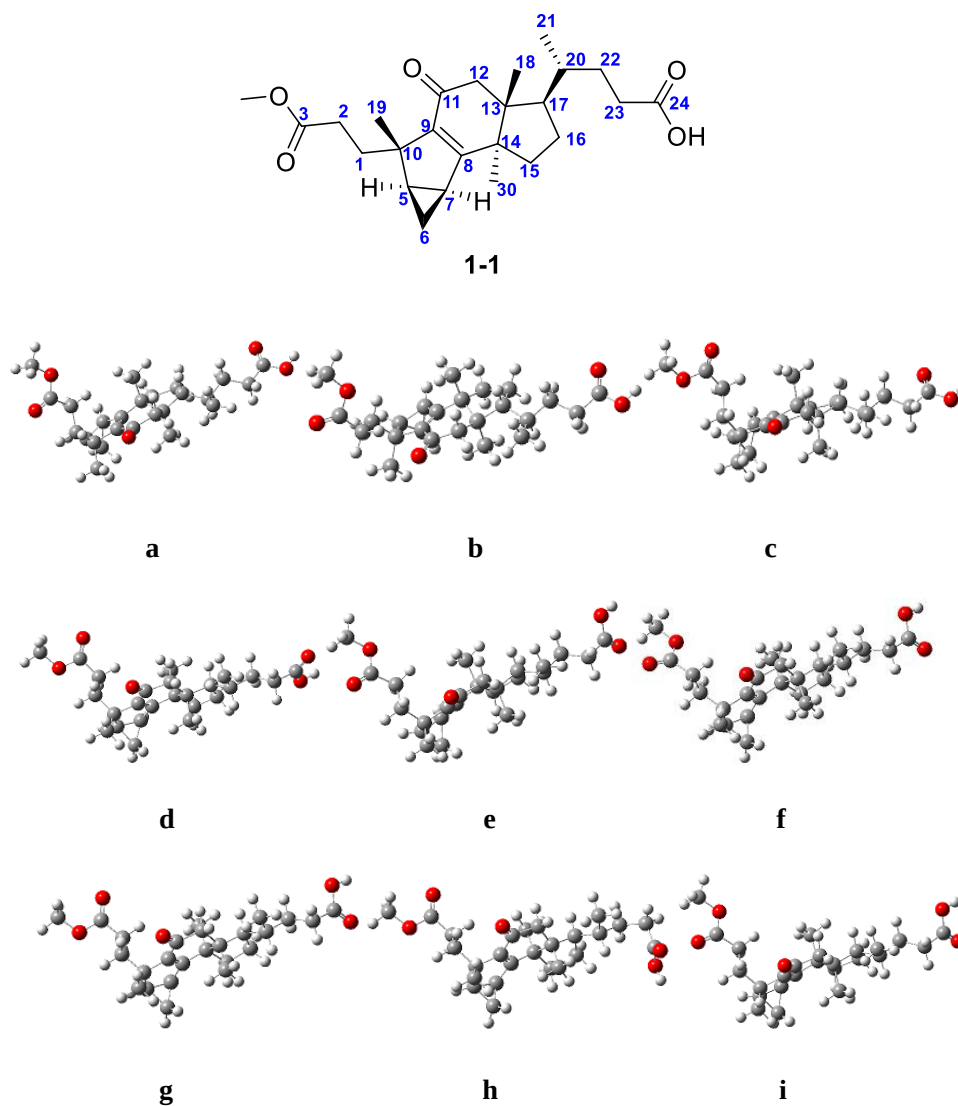


Figure S16. Optimized geometries of predominant conformers for compound **1-1** at the B3LYP/6-31G(d,p) level in the gas phase.

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

Conformations	E+ZPE	G	%
1-1-a	-1349.929681	-1349.993937	40.6
1-1-b	-1349.927091	-1349.992374	7.8
1-1-c	-1349.928725	-1349.993514	25.9

1-1-d	-1349.926637	-1349.991261	2.4
1-1-e	-1349.927745	-1349.992425	8.2
1-1-f	-1349.925045	-1349.990288	0.8
1-1-g	-1349.926803	-1349.991690	3.8
1-1-h	-1349.926820	-1349.991234	2.3
1-1-i	-1349.927747	-1349.992426	8.2

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 **1-1** in the gas phase (Å) at B3LYP/6-31G(d,p) level

1-1-a				1-1-b			
C	1.150736	-0.85508	0.823869	C	-1.05188	1.268775	0.587938
C	1.769392	-0.96483	-0.38054	C	-1.79493	0.72143	-0.41212
C	-0.17491	-0.15861	0.975289	C	0.296824	0.724819	0.974051
C	-1.07094	-0.46553	-0.28957	C	1.072109	0.288676	-0.33007
C	-0.31585	0.01814	-1.54333	C	0.218187	-0.76295	-1.06155
C	1.131799	-0.51007	-1.62634	C	-1.23665	-0.31028	-1.30197
C	-1.10709	-0.55646	2.137493	C	1.31747	1.654902	1.660337
C	-2.51215	-0.0962	1.651042	C	2.684874	0.965677	1.37878
C	-2.40672	0.237683	0.120171	C	2.453595	-0.12731	0.274321
C	-1.33111	-1.9863	-0.44865	C	1.282794	1.485432	-1.29327
C	-3.71138	-0.0897	-0.65154	C	3.677461	-0.29774	-0.66274
C	-3.60167	0.186192	-2.16029	C	3.43927	-1.32919	-1.77777
C	-4.88768	0.704621	-0.03761	C	4.919797	-0.67944	0.175106
C	0.159552	1.354866	1.152454	C	0.009139	-0.45146	1.957354
O	1.713107	-0.51945	-2.70811	O	-1.87731	-0.82293	-2.21718
C	3.172053	-1.57373	-0.27665	C	-3.20471	1.334608	-0.49813

O	5.245543	2.904422	0.274473	O	-5.1843	-2.34048	1.017315
C	5.480655	1.61079	-0.05244	C	-5.71245	-1.69183	-0.05293
C	4.2477	0.760515	0.179211	C	-4.66508	-0.85715	-0.75663
C	4.277428	-0.541	-0.62707	C	-4.28771	0.378553	0.0844
C	3.359582	-2.79519	-1.20019	C	-3.58718	1.810481	-1.91168
O	6.554501	1.21227	-0.44961	O	-6.88086	-1.77914	-0.36421
C	-6.26867	0.300489	-0.56104	C	6.239785	-0.66219	-0.60093
C	-7.39797	0.952247	0.207743	C	7.446108	-0.83178	0.297731
O	-8.59928	0.705742	-0.37342	O	8.583356	-0.99266	-0.42485
O	-7.29071	1.607691	1.220944	O	7.444468	-0.8192	1.509179
C	3.234108	-1.95764	1.219482	C	-3.0869	2.511342	0.498723
C	1.978301	-1.43643	1.911943	C	-1.75875	2.398765	1.235425
C	6.371508	3.785687	0.132494	C	-6.11172	-3.14259	1.763777
C	2.236177	-2.93163	1.774479	C	-2.042	3.565562	0.293395
H	1.976001	-0.99468	2.904326	H	-1.63711	2.598729	2.29575
H	4.198278	-1.89811	1.717423	H	-3.98371	2.797908	1.040443
H	-0.79747	-0.28793	-2.4748	H	0.612241	-1.02551	-2.04554
H	-0.264	1.113736	-1.57853	H	0.175186	-1.70058	-0.49281
H	-0.81903	-0.07712	3.078262	H	1.121787	1.761603	2.731903
H	-1.08195	-1.63541	2.312882	H	1.285362	2.660277	1.231803
H	-3.25167	-0.88649	1.81841	H	3.42135	1.701704	1.039255
H	-2.86115	0.771977	2.216452	H	3.096908	0.519358	2.287761
H	-2.25389	1.319083	0.006639	H	2.316346	-1.09852	0.767715
H	-0.40294	-2.55089	-0.55533	H	0.336804	1.943633	-1.58909
H	-1.88374	-2.41212	0.392332	H	1.910891	2.269176	-0.86301

H	-1.92407	-2.16776	-1.34964	H	1.773754	1.143128	-2.20876
H	-3.93038	-1.15886	-0.51366	H	3.88561	0.674353	-1.13398
H	-4.55654	0.021049	-2.66807	H	4.339453	-1.48051	-2.38071
H	-2.87095	-0.46243	-2.64694	H	2.648676	-1.02079	-2.46431
H	-3.30358	1.22466	-2.34847	H	3.156114	-2.30176	-1.35763
H	-4.90034	0.584177	1.048295	H	5.029137	0.001193	1.022726
H	-4.73451	1.777203	-0.21635	H	4.771146	-1.67652	0.610608
H	0.67313	1.777248	0.286257	H	-0.58092	-1.24848	1.500438
H	-0.73109	1.955846	1.35296	H	0.926379	-0.88585	2.363015
H	0.826101	1.472214	2.013461	H	-0.56838	-0.06875	2.805552
H	4.206466	0.555169	1.2573	H	-3.78431	-1.4714	-0.95218
H	3.363097	1.362939	-0.04408	H	-5.08772	-0.56014	-1.7177
H	4.197081	-0.30481	-1.6922	H	-5.19767	0.975583	0.237381
H	5.254395	-1.01657	-0.48405	H	-3.95878	0.048474	1.075965
H	4.360189	-3.22141	-1.06967	H	-4.59934	2.230412	-1.91317
H	3.239693	-2.49892	-2.2445	H	-3.54553	0.98635	-2.62541
H	2.629522	-3.58003	-0.98188	H	-2.90257	2.58952	-2.26014
H	-6.40963	0.541531	-1.61967	H	6.290857	-1.43763	-1.37208
H	-6.41491	-0.78612	-0.48571	H	6.369205	0.290385	-1.13362
H	-9.26304	1.141802	0.187383	H	9.303433	-1.07556	0.223144
H	6.012286	4.772664	0.423744	H	-5.53389	-3.5868	2.574468
H	7.193632	3.470868	0.78034	H	-6.92237	-2.52791	2.163637
H	6.725118	3.796061	-0.90133	H	-6.54488	-3.92178	1.131539
H	2.517267	-3.46181	2.680019	H	-2.22052	4.531571	0.756898
H	1.600216	-3.49913	1.101565	H	-1.49042	3.609741	-0.64119

1-1-c				1-1-d			
C	1.108519	0.947169	-0.67982	C	1.09496	1.002179	-0.60336
C	1.745316	0.77009	0.50691	C	1.74026	0.734161	0.561381
C	-0.2331	0.325293	-0.96014	C	-0.252	0.409662	-0.91879
C	-1.10511	0.355325	0.355949	C	-1.11202	0.336238	0.40402
C	-0.34429	-0.41032	1.456271	C	-0.34288	-0.51581	1.432674
C	1.112823	0.065065	1.6334	C	1.11547	-0.05537	1.634969
C	-1.1717	0.991123	-1.98611	C	-1.19706	1.157925	-1.88013
C	-2.57798	0.449611	-1.59586	C	-2.60294	0.596463	-1.51738
C	-2.46042	-0.21718	-0.17879	C	-2.47388	-0.18776	-0.16293
C	-1.33417	1.806241	0.853623	C	-1.33386	1.742168	1.020155
C	-3.74841	-0.04794	0.668229	C	-3.75209	-0.08647	0.709628
C	-3.62374	-0.64805	2.078345	C	-3.61679	-0.80932	2.059582
C	-4.94607	-0.67209	-0.08495	C	-4.963	-0.63552	-0.08288
C	0.070119	-1.11437	-1.47871	C	0.040947	-0.98503	-1.5547
O	1.705288	-0.1663	2.683969	O	1.715705	-0.3681	2.659573
C	3.162336	1.353112	0.513732	C	3.159908	1.3086	0.600365
O	6.498048	-1.34946	-0.38237	O	6.472923	-1.34415	-0.5067
C	5.251165	-1.88358	-0.38495	C	5.221813	-1.866	-0.55039
C	4.193602	-0.81035	-0.5351	C	4.17266	-0.77572	-0.61368
C	4.236722	0.232633	0.596605	C	4.229201	0.18001	0.59188
C	3.403889	2.323559	1.688138	C	3.414382	2.187463	1.842372
O	5.041617	-3.07294	-0.284	O	5.002166	-3.05781	-0.54516
C	-6.31341	-0.36867	0.533785	C	-6.32924	-0.3675	0.58139
C	-7.46291	-0.81879	-0.34214	C	-7.48724	-0.85119	-0.26241

O	-8.6515	-0.70303	0.302525	O	-7.55655	-0.19555	-1.45148
O	-7.38014	-1.22497	-1.4805	O	-8.27643	-1.71757	0.042373
C	3.21236	2.069068	-0.85527	C	3.20318	2.124393	-0.71128
C	1.934083	1.745226	-1.62223	C	1.917418	1.864482	-1.49054
C	7.568842	-2.29516	-0.23277	C	7.536099	-2.30748	-0.43488
C	2.228296	3.163567	-1.14882	C	2.222935	3.242303	-0.91586
H	1.906484	1.544086	-2.68923	H	1.88117	1.742894	-2.56925
H	4.166687	2.107162	-1.37363	H	4.153703	2.196542	-1.23292
H	-0.81065	-0.31761	2.439592	H	-0.80075	-0.50259	2.424136
H	-0.30967	-1.4857	1.240408	H	-0.31039	-1.57039	1.130979
H	-0.90248	0.736897	-3.01608	H	-0.94013	0.981638	-2.92932
H	-1.13096	2.081102	-1.90887	H	-1.14876	2.238597	-1.72082
H	-3.30957	1.264288	-1.57495	H	-3.32644	1.412837	-1.4188
H	-2.94306	-0.26837	-2.33515	H	-2.98334	-0.05377	-2.30997
H	-2.32972	-1.29949	-0.31091	H	-2.34665	-1.2552	-0.38651
H	-0.39391	2.324305	1.05325	H	-0.39128	2.237071	1.262291
H	-1.90208	2.412032	0.143385	H	-1.89902	2.407477	0.363016
H	-1.8984	1.792673	1.790562	H	-1.89878	1.652007	1.952242
H	-3.95101	1.028559	0.770637	H	-3.94877	0.977472	0.906446
H	-4.56866	-0.58212	2.625719	H	-4.55664	-0.79369	2.61844
H	-2.8742	-0.13252	2.68173	H	-2.86284	-0.34837	2.700334
H	-3.34318	-1.70707	2.031085	H	-3.33631	-1.85954	1.9161
H	-4.96875	-0.31938	-1.11887	H	-4.98685	-0.19057	-1.08062
H	-4.81036	-1.7602	-0.14397	H	-4.83798	-1.71804	-0.22446
H	0.577647	-1.73268	-0.73542	H	0.550743	-1.66355	-0.86789

H	-0.83264	-1.63714	-1.8042	H	-0.86604	-1.47637	-1.91544
H	0.731374	-1.04528	-2.34895	H	0.696265	-0.84823	-2.42137
H	4.347582	-0.32096	-1.504	H	4.326625	-0.21758	-1.54476
H	3.229562	-1.32064	-0.56611	H	3.204785	-1.27554	-0.67808
H	4.113955	-0.27415	1.558988	H	4.110125	-0.39566	1.515084
H	5.226274	0.704022	0.602781	H	5.221115	0.645139	0.625739
H	4.409456	2.753801	1.626315	H	4.422413	2.614908	1.806852
H	3.30537	1.796888	2.639636	H	3.317681	1.59188	2.752583
H	2.685466	3.148437	1.679485	H	2.701654	3.015242	1.899941
H	-6.44831	-0.83014	1.517333	H	-6.42059	-0.8653	1.547559
H	-6.439	0.710954	0.696842	H	-6.45013	0.71187	0.737627
H	-9.32952	-0.99356	-0.33084	H	-8.31587	-0.57893	-1.92216
H	8.486292	-1.70672	-0.24151	H	8.458283	-1.72763	-0.39777
H	7.472732	-2.84132	0.708821	H	7.436261	-2.92644	0.460107
H	7.566901	-3.01416	-1.05587	H	7.527667	-2.95819	-1.31293
H	2.506106	3.884192	-1.91271	H	2.499822	4.015627	-1.62676
H	1.617186	3.569769	-0.34833	H	1.619239	3.59263	-0.08382
1-1-e				1-1-f			
C	-1.1431	-0.90639	-0.7856	C	1.040173	1.268566	-0.62179
C	-1.7639	-0.94379	0.422011	C	1.786956	0.738228	0.3846
C	0.192089	-0.23613	-0.9711	C	-0.3169	0.728092	-0.98324
C	1.082712	-0.48958	0.309113	C	-1.0835	0.325668	0.336661
C	0.334182	0.068772	1.535183	C	-0.23124	-0.7173	1.082259
C	-1.12164	-0.43142	1.642756	C	1.22834	-0.26938	1.301737
C	1.119758	-0.70639	-2.10927	C	-1.33646	1.652253	-1.67901

C	2.529955	-0.23722	-1.64626	C	-2.7061	0.978242	-1.37258
C	2.428304	0.174784	-0.13387	C	-2.47369	-0.09236	-0.24628
C	1.322965	-2.00346	0.545814	C	-1.27642	1.543826	1.276538
C	3.726398	-0.13373	0.657345	C	-3.68774	-0.22981	0.709278
C	3.615386	0.212124	2.150924	C	-3.44519	-1.23715	1.844675
C	4.915524	0.620942	0.014853	C	-4.94544	-0.62297	-0.10279
C	-0.12118	1.270737	-1.22577	C	-0.04827	-0.47076	-1.94481
O	-1.70489	-0.37245	2.721785	O	1.872265	-0.76589	2.223343
C	-3.17304	-1.5419	0.349536	C	3.201788	1.342392	0.446038
O	-5.21554	2.91515	-0.44599	O	5.150867	-2.42293	-0.9481
C	-5.45481	1.646992	-0.03334	C	5.694858	-1.70232	0.066623
C	-4.23	0.775142	-0.22447	C	4.649937	-0.85088	0.753298
C	-4.26814	-0.48279	0.648172	C	4.274557	0.364134	-0.11862
C	-3.37082	-2.71282	1.334545	C	3.596763	1.850222	1.845057
O	-6.52609	1.282487	0.401485	O	6.874196	-1.74346	0.344673
C	6.299576	0.191542	0.545836	C	-6.26532	-0.53297	0.692246
C	7.423461	0.884948	-0.18935	C	-7.46637	-0.81784	-0.17995
O	7.45549	2.216046	0.08326	O	-7.50799	-2.11972	-0.5677
O	8.208402	0.362293	-0.94926	O	-8.30065	-0.01259	-0.52977
C	-3.24025	-2.00167	-1.12479	C	3.086088	2.495332	-0.57864
C	-1.97743	-1.53377	-1.84254	C	1.75126	2.376339	-1.30225
C	-6.33432	3.811528	-0.34845	C	6.075387	-3.24514	-1.67624
C	-2.25527	-3.01619	-1.62832	C	2.051768	3.563249	-0.39131
H	-1.96948	-1.14425	-2.85654	H	1.623047	2.550942	-2.3663
H	-4.20354	-1.95509	-1.62574	H	3.981079	2.760664	-1.13398

H	0.810188	-0.19701	2.481771	H	-0.61909	-0.95725	2.074393
H	0.299861	1.165377	1.514816	H	-0.19892	-1.66649	0.532193
H	0.838123	-0.27482	-3.07478	H	-1.1494	1.736682	-2.75407
H	1.082821	-1.79277	-2.22643	H	-1.29389	2.665484	-1.27049
H	3.261053	-1.04262	-1.77384	H	-3.43603	1.725842	-1.04454
H	2.886319	0.598087	-2.25545	H	-3.12558	0.514624	-2.26973
H	2.290231	1.262622	-0.07406	H	-2.34855	-1.07548	-0.71893
H	0.386865	-2.5501	0.674068	H	-0.32427	2.001456	1.552412
H	1.875203	-2.47784	-0.26904	H	-1.90382	2.322778	0.836775
H	1.907867	-2.14718	1.45879	H	-1.75947	1.224608	2.204476
H	3.93417	-1.20959	0.56661	H	-3.88261	0.755074	1.157766
H	4.567693	0.065396	2.668686	H	-4.34239	-1.3768	2.454562
H	2.880487	-0.41073	2.664006	H	-2.65325	-0.91231	2.521885
H	3.322229	1.259421	2.290729	H	-3.16207	-2.21803	1.444734
H	4.910649	0.459466	-1.06774	H	-5.03804	0.031614	-0.97511
H	4.789973	1.699601	0.171127	H	-4.82684	-1.64344	-0.48788
H	-0.629	1.743799	-0.38279	H	0.542558	-1.2612	-1.47782
H	0.778102	1.848239	-1.45514	H	-0.97272	-0.90846	-2.33017
H	-0.78556	1.354046	-2.09239	H	0.521254	-0.10978	-2.80778
H	-4.19347	0.515245	-1.29092	H	3.768502	-1.4575	0.967033
H	-3.3398	1.380897	-0.03436	H	5.076522	-0.52811	1.704335
H	-4.18301	-0.19248	1.699392	H	5.187435	0.950533	-0.29328
H	-5.24948	-0.95663	0.532119	H	3.936677	0.009811	-1.09897
H	-4.37423	-3.13802	1.224188	H	4.612161	2.261901	1.829845
H	-3.25042	-2.36427	2.362527	H	3.553346	1.044452	2.579325

H	-2.64588	-3.51268	1.158144	H	2.920522	2.643045	2.178247
H	6.39517	0.428013	1.610363	H	-6.26806	-1.2505	1.51892
H	6.445381	-0.88378	0.415504	H	-6.39852	0.47057	1.104133
H	8.188418	2.578251	-0.44286	H	-8.29264	-2.2037	-1.13558
H	-5.97531	4.77273	-0.71614	H	5.485224	-3.74767	-2.44278
H	-7.16945	3.455992	-0.95734	H	6.859187	-2.6362	-2.1341
H	-6.66931	3.8987	0.687993	H	6.545115	-3.97714	-1.01442
H	-2.5434	-3.58813	-2.50582	H	2.234788	4.516144	-0.87951
H	-1.6269	-3.55781	-0.92737	H	1.507723	3.63469	0.545929
1-1-g				1-1-h			
C	1.103365	0.981904	-0.65637	C	0.94766	0.94777	-0.57499
C	1.742541	0.767243	0.522835	C	1.531929	0.6045	0.602198
C	-0.24587	0.381707	-0.94735	C	-0.29689	0.262545	-1.07243
C	-1.11277	0.387535	0.372387	C	-1.23894	-0.05773	0.153894
C	-0.35663	-0.41443	1.449703	C	-0.45839	-0.94653	1.142295
C	1.10678	0.039109	1.632655	C	0.922417	-0.37183	1.519479
C	-1.18072	1.083611	-1.95238	C	-1.24723	1.019011	-2.02231
C	-2.5914	0.547625	-1.57067	C	-2.60029	0.267996	-1.8539
C	-2.47647	-0.15652	-0.17146	C	-2.48855	-0.64763	-0.58121
C	-1.32435	1.827828	0.907492	C	-1.65978	1.234183	0.901324
C	-3.75796	0.006604	0.687301	C	-3.83465	-0.76882	0.178939
C	-3.63242	-0.62966	2.080924	C	-3.74209	-1.61046	1.461587
C	-4.96762	-0.58906	-0.073	C	-4.90689	-1.34776	-0.77573
C	0.040211	-1.04743	-1.50362	C	0.195511	-1.00766	-1.83201
O	1.700882	-0.2283	2.673566	O	1.478829	-0.74826	2.547424

C	3.166406	1.333014	0.538509	C	2.869353	1.314764	0.832206
O	6.460103	-1.39612	-0.42369	O	6.543916	-0.77995	-0.30041
C	5.204811	-1.90839	-0.45827	C	5.376695	-1.44205	-0.49819
C	4.165928	-0.81275	-0.57474	C	4.199915	-0.48917	-0.51588
C	4.227144	0.197319	0.585235	C	4.060025	0.31638	0.788678
C	3.425291	2.267971	1.737668	C	2.926814	2.054691	2.184723
O	4.974434	-3.09713	-0.40795	O	5.315547	-2.64318	-0.64744
C	-6.33749	-0.25536	0.554923	C	-6.3396	-1.41897	-0.20508
C	-7.48102	-0.76958	-0.28901	C	-6.84954	-0.08177	0.282192
O	-7.54078	-2.12721	-0.27954	O	-6.91777	0.830618	-0.7236
O	-8.2581	-0.09313	-0.92571	O	-7.15892	0.190641	1.421209
C	3.218494	2.085179	-0.81071	C	2.917869	2.286207	-0.36795
C	1.933795	1.795591	-1.58086	C	1.731247	1.994353	-1.28152
C	7.513876	-2.36506	-0.30422	C	7.717903	-1.60668	-0.26219
C	2.245412	3.197596	-1.071	C	1.836283	3.314698	-0.52843
H	1.900053	1.623187	-2.6527	H	1.789825	2.003815	-2.36604
H	4.171035	2.12694	-1.33203	H	3.890673	2.519443	-0.79244
H	-0.81798	-0.34101	2.436957	H	-0.98595	-1.09953	2.086266
H	-0.3354	-1.48442	1.206902	H	-0.29002	-1.94802	0.726658
H	-0.91817	0.852914	-2.98956	H	-0.89266	1.003846	-3.05774
H	-1.12827	2.170677	-1.84759	H	-1.33913	2.069997	-1.73515
H	-3.31416	1.369327	-1.52706	H	-3.42345	0.981342	-1.74074
H	-2.96504	-0.14773	-2.32744	H	-2.83227	-0.32672	-2.74191
H	-2.35861	-1.23663	-0.33095	H	-2.22967	-1.6659	-0.90171
H	-0.3777	2.329528	1.118091	H	-0.79808	1.791094	1.274653

H	-1.88664	2.458136	0.214372	H	-2.24664	1.911813	0.276457
H	-1.8867	1.796909	1.845042	H	-2.27725	0.977985	1.766714
H	-3.9499	1.081704	0.81504	H	-4.15538	0.244295	0.460255
H	-4.57585	-0.57678	2.631899	H	-4.71315	-1.67668	1.959507
H	-2.88209	-0.12909	2.695709	H	-3.04938	-1.17903	2.185979
H	-3.35262	-1.68719	2.006757	H	-3.40326	-2.6303	1.242121
H	-4.97392	-0.21447	-1.10149	H	-4.94321	-0.75425	-1.6929
H	-4.8574	-1.67881	-0.13669	H	-4.61169	-2.36368	-1.07053
H	0.543591	-1.68975	-0.77816	H	0.728512	-1.70752	-1.18494
H	-0.86899	-1.55248	-1.83927	H	-0.62451	-1.54256	-2.31754
H	0.699195	-0.96307	-2.3742	H	0.890691	-0.70226	-2.62123
H	4.327187	-0.29946	-1.53009	H	4.334505	0.19068	-1.36551
H	3.193628	-1.30602	-0.61946	H	3.310342	-1.09174	-0.70658
H	4.101702	-0.3343	1.533743	H	3.945637	-0.37541	1.629086
H	5.222519	0.655883	0.600383	H	4.985672	0.879138	0.955778
H	4.435695	2.687633	1.682534	H	3.877945	2.588492	2.287274
H	3.325064	1.716707	2.674977	H	2.832949	1.343795	3.008292
H	2.717055	3.101464	1.755528	H	2.119952	2.78766	2.274153
H	-6.42458	-0.70012	1.551227	H	-7.01296	-1.77117	-0.99511
H	-6.46578	0.826208	0.64577	H	-6.41444	-2.11482	0.631699
H	-8.28394	-2.36563	-0.85925	H	-7.24105	1.651949	-0.31589
H	8.440877	-1.79221	-0.28116	H	8.552747	-0.92689	-0.09195
H	7.400282	-2.94749	0.613348	H	7.648632	-2.33848	0.546371
H	7.507471	-3.0496	-1.15615	H	7.845025	-2.14065	-1.20727
H	2.528423	3.935095	-1.81665	H	2.077418	4.193839	-1.1193

H	1.641664	3.589367	-0.25779	H	1.136132	3.497141	0.281463
1-1-i							
C	-1.14315	-0.90641	-0.78573				
C	-1.76392	-0.94377	0.421897				
C	0.191996	-0.23603	-0.97125				
C	1.082658	-0.48951	0.308916				
C	0.334206	0.068706	1.535099				
C	-1.12178	-0.43109	1.642544				
C	1.119658	-0.70623	-2.10944				
C	2.529848	-0.23698	-1.64647				
C	2.428219	0.174931	-0.13405				
C	1.322927	-2.00341	0.54542				
C	3.726325	-0.13361	0.657123				
C	3.615272	0.212127	2.150732				
C	4.915471	0.62115	0.014773				
C	-0.12133	1.270851	-1.22583				
O	-1.70511	-0.37186	2.721523				
C	-3.17299	-1.54201	0.349504				
O	-5.21567	2.914824	-0.44629				
C	-5.45492	1.646806	-0.03316				
C	-4.23031	0.774734	-0.22483				
C	-4.26821	-0.483	0.648043				
C	-3.37059	-2.71278	1.334727				
O	-6.52597	1.282615	0.402453				
C	6.299453	0.191226	0.545387				

C	7.423946	0.884905	-0.18869				
O	7.452559	2.216827	0.080217				
O	8.2123	0.361653	-0.94464				
C	-3.24022	-2.00201	-1.12479				
C	-1.97747	-1.53396	-1.84257				
C	-6.33415	3.811498	-0.34807				
C	-2.2551	-3.01643	-1.62822				
H	-1.96956	-1.14463	-2.85664				
H	-4.20356	-1.95554	-1.62563				
H	0.81012	-0.19748	2.481621				
H	0.300196	1.165319	1.515076				
H	0.837969	-0.27467	-3.07493				
H	1.082802	-1.79262	-2.2266				
H	3.260997	-1.04232	-1.77412				
H	2.886131	0.598385	-2.25564				
H	2.290126	1.262764	-0.07419				
H	0.386827	-2.55004	0.673775				
H	1.875005	-2.47772	-0.26959				
H	1.907989	-2.14724	1.458278				
H	3.934096	-1.20947	0.566306				
H	4.567563	0.065383	2.668522				
H	2.880352	-0.41074	2.663771				
H	3.322129	1.259423	2.290584				
H	4.910356	0.460228	-1.0679				
H	4.790153	1.699753	0.17154				

H	-0.62905	1.743861	-0.38276				
H	0.777922	1.848371	-1.45526				
H	-0.78581	1.3542	-2.09237				
H	-4.19439	0.514773	-1.29128				
H	-3.33994	1.380412	-0.03522				
H	-4.18304	-0.19246	1.699185				
H	-5.24948	-0.95706	0.532166				
H	-4.37395	-3.13814	1.224485				
H	-3.25022	-2.36402	2.362646				
H	-2.64555	-3.51259	1.158481				
H	6.395011	0.426885	1.610128				
H	6.445301	-0.88401	0.414435				
H	8.186503	2.578951	-0.44454				
H	-5.97449	4.773132	-0.71399				
H	-7.16895	3.457303	-0.95821				
H	-6.6699	3.897099	0.688249				
H	-2.54301	-3.58849	-2.50571				
H	-1.62668	-3.55784	-0.92715				

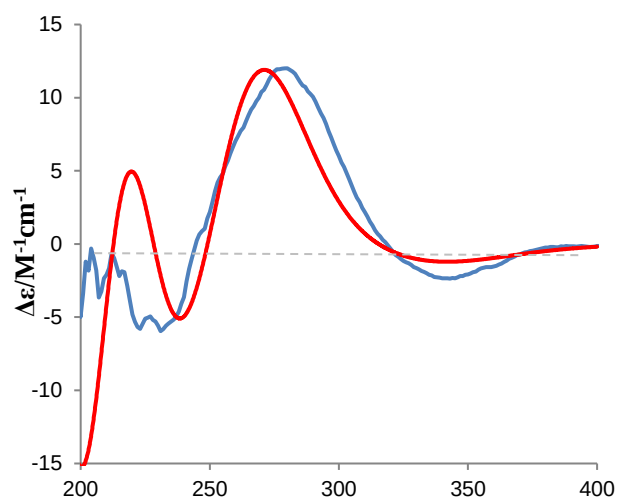


Figure S17. Calculated and experimental ECDs of **1-1** (red, calculated at the B3LYP-PCM/6-31G(d,p)/B3LYP/6-31G(d,p) level in CH₃OH; blue, experimental in CH₃OH).

Table S3. The computed ¹³C NMR data for **1-1**.

No.	1-1	δ_{exptl}	pyridine	
			δ_{calcd}	$\Delta\delta$
1	8	175.9	177.1	1.2
2	9	132.8	132.5	-0.3
3	14	50.1	54.4	4.3
4	13	48	52.6	4.6
5	12	49.7	50.7	1.0
6	11	196.3	192.3	-4.0
7	15	29.6	31.7	2.1
8	16	27.5	30.5	3.0
9	17	49.5	51.4	1.9
10	18	17.3	18.5	1.2
11	20	35.9	39.5	3.6
12	21	17.9	18.6	0.7
13	22	31.5	32.4	0.9
14	30	24.5	26.1	1.6
15	10	48.6	52.2	3.6
16	3	174.2	170.6	-3.6
17	2	29.6	31.9	2.3
18	1	36	37.5	1.5
19	19	23	24.9	1.9
20	23	31.7	33.1	1.4
21	24	176.2	169.8	-6.4
22	5	27.8	31.6	3.8
23	7	22.9	27.9	5.0
24	-OCH ₃	51.1	51.9	0.8

25	6	14.5	18.5	4.0
	LAD^a			6.4
	MAD^b			2.59

^aLAD = largest absolute deviation. ^bMAD = mean absolute deviation, computed as $(1/n) \sum_i^n$

$$|\delta_{\text{calcd}} - \delta_{\text{exptl}}|$$

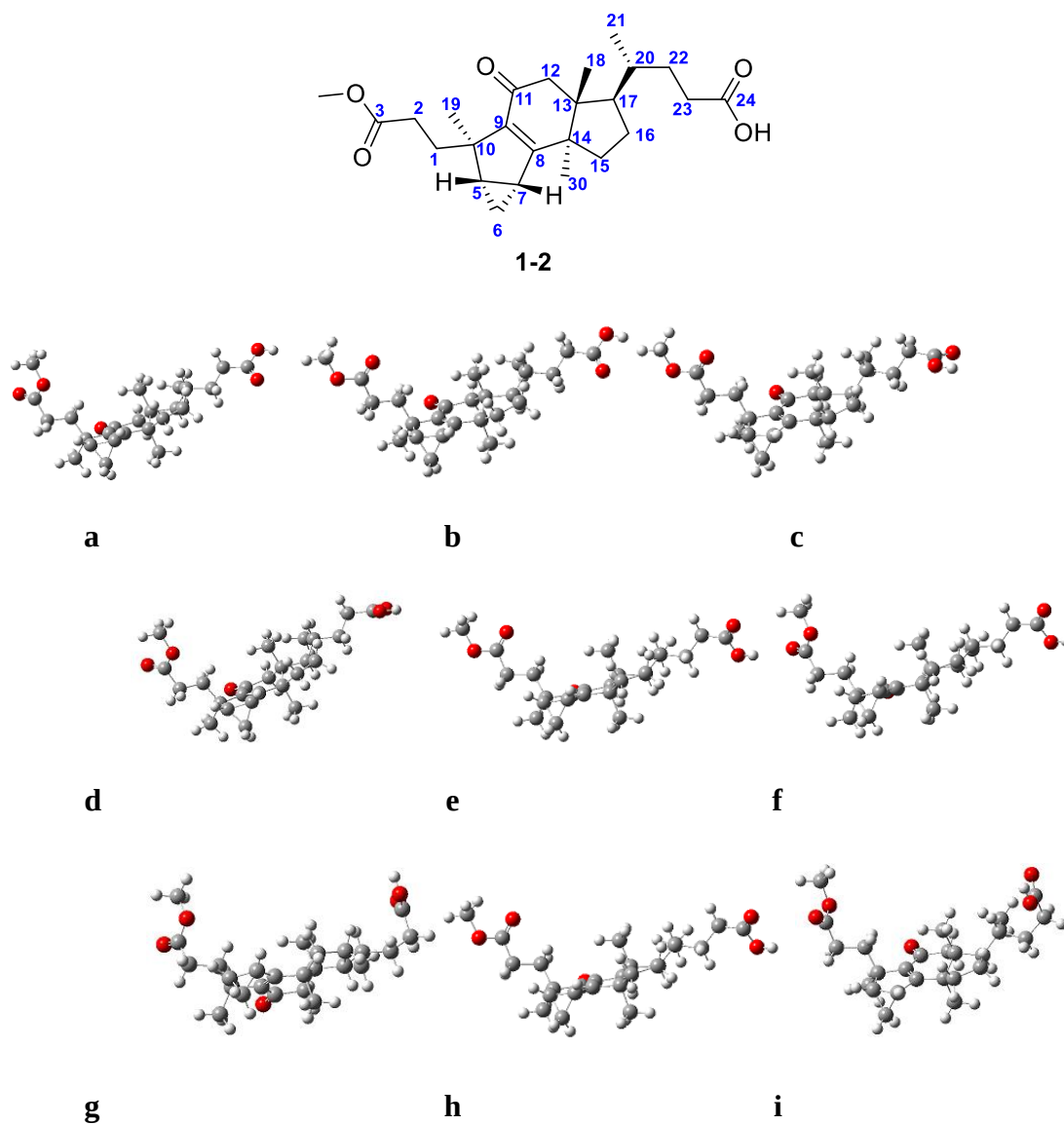


Figure S18. Optimized geometries of predominant conformers for compound **1-2** at the B3LYP/6-31G(d,p) level in the gas phase.

Table S4. Important thermodynamic parameters (a.u.) and Boltzmann distributions of the optimized compound **1-2** at B3LYP/6-31G(d,p) level in the gas phase

Conformations	E+ZPE	G	%
1-2-a	-1349.927398	-1349.991779	12.6
1-2-b	-1349.928808	-1349.993067	49.2
1-2-c	-1349.926857	-1349.991190	6.7
1-2-d	-1349.925443	-1349.990210	2.4
1-2-e	-1349.926941	-1349.991600	10.4
1-2-f	-1349.925432	-1349.990311	2.6
1-2-g	-1349.925202	-1349.989627	1.3
1-2-h	-1349.926939	-1349.991596	10.4
1-2-i	-1349.925805	-1349.990779	4.4

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 S5. Optimized Z-matrixes of compound **2-2** in the gas phase (Å) at B3LYP/6-31G(d,p) level

1-2-a				1-2-b			
C	1.01509	-1.43997	-0.47829	C	0.907208	-1.49613	-0.37357
C	1.711524	-1.00146	0.601762	C	1.622496	-0.94902	0.642392
C	-0.48961	-1.48154	-0.49302	C	-0.59784	-1.52279	-0.36294
C	-1.06299	-0.26132	0.325213	C	-1.14458	-0.2094	0.317946
C	-0.49656	-0.33732	1.756944	C	-0.56242	-0.13458	1.743496
C	1.041169	-0.44825	1.790354	C	0.973572	-0.26843	1.774987
C	-1.23675	-1.34931	-1.83549	C	-1.36154	-1.53488	-1.70286
C	-2.66436	-0.897	-1.40997	C	-2.77604	-1.01084	-1.31752
C	-2.5996	-0.44881	0.094885	C	-2.68623	-0.39857	0.126311
C	-0.62504	1.093299	-0.29157	C	-0.69557	1.061494	-0.45084
C	-3.56721	0.721559	0.409406	C	-3.63393	0.813227	0.320796
C	-3.47235	1.203504	1.866188	C	-3.51504	1.449565	1.715051
C	-5.01523	0.29904	0.069212	C	-5.09154	0.378459	0.042806
C	-0.86783	-2.87401	0.103219	C	-0.98323	-2.83306	0.393655
O	1.657578	-0.06751	2.781875	O	1.605878	0.199248	2.718516
C	3.231197	-1.08714	0.406774	C	3.138411	-1.05942	0.431297
O	5.300803	2.347749	-1.3271	O	6.950488	2.0393	-0.29794

C	5.776404	1.882789	-0.14439	C	5.654709	1.787863	-0.59899
C	5.322716	0.459332	0.105826	C	5.219193	0.446837	-0.03948
C	3.79266	0.357523	0.276227	C	3.698593	0.360244	0.138647
C	3.927047	-1.85195	1.551175	C	3.852745	-1.70337	1.637302
O	6.469951	2.545175	0.595821	O	4.96649	2.54241	-1.2524
C	-6.03956	1.43582	0.126863	C	-6.09984	1.530028	-0.00482
C	-7.39372	1.028499	-0.41317	C	-7.4647	1.09112	-0.49017
O	-8.32491	1.990554	-0.19195	O	-8.38219	2.081358	-0.35024
O	-7.65515	-0.00672	-0.98565	O	-7.74504	0.010496	-0.9608
C	3.327982	-1.82657	-0.94693	C	3.210634	-1.93763	-0.83918
C	1.923476	-1.987	-1.51742	C	1.795995	-2.15444	-1.36378
C	5.665028	3.700662	-1.64329	C	7.474051	3.270913	-0.82137
C	2.739471	-3.1999	-1.08056	C	2.620072	-3.31651	-0.81814
H	1.688775	-1.86755	-2.57089	H	1.542574	-2.14498	-2.41964
H	4.149308	-1.57452	-1.61071	H	4.018634	-1.75594	-1.5415
H	-0.74403	0.536899	2.36265	H	-0.7888	0.806151	2.249847
H	-0.89948	-1.20396	2.296745	H	-0.97353	-0.92782	2.380975
H	-1.24922	-2.28994	-2.39458	H	-1.39598	-2.53397	-2.14807
H	-0.76389	-0.60289	-2.48056	H	-0.88633	-0.87681	-2.43621
H	-3.0071	-0.07003	-2.0407	H	-3.11025	-0.25293	-2.03391
H	-3.38913	-1.70417	-1.54585	H	-3.51751	-1.81334	-1.35512
H	-2.92639	-1.28647	0.725032	H	-3.01648	-1.15653	0.848913
H	0.460516	1.179448	-0.36467	H	0.390208	1.129696	-0.53766
H	-1.03644	1.254434	-1.29099	H	-1.11057	1.111371	-1.46041
H	-0.97417	1.917759	0.336938	H	-1.0344	1.955521	0.080802
H	-3.3084	1.564653	-0.24792	H	-3.37165	1.575987	-0.42707
H	-4.20944	1.983572	2.078602	H	-4.23135	2.266269	1.845179
H	-2.49246	1.624739	2.09739	H	-2.52341	1.869489	1.89231
H	-3.65443	0.378181	2.565022	H	-3.71055	0.71086	2.501764
H	-5.05877	-0.13055	-0.93447	H	-5.1538	-0.15097	-0.91111
H	-5.32887	-0.50308	0.750509	H	-5.40682	-0.34499	0.806515
H	-0.52062	-2.99925	1.131118	H	-0.6245	-2.8429	1.425057
H	-1.9445	-3.05887	0.077232	H	-2.06211	-3.00689	0.40142
H	-0.39135	-3.65335	-0.49956	H	-0.52247	-3.68221	-0.1207
H	5.65437	-0.15119	-0.74262	H	5.583083	-0.31492	-0.74335
H	5.846287	0.116138	0.999339	H	5.757905	0.27276	0.895561
H	3.499087	0.915319	1.171081	H	3.401418	1.018661	0.960709
H	3.311917	0.838845	-0.58231	H	3.222237	0.750342	-0.76675
H	4.987992	-2.00839	1.333285	H	4.911087	-1.87983	1.420821
H	3.832286	-1.29919	2.488127	H	3.769588	-1.05819	2.514332

H	3.473871	-2.83685	1.695827	H	3.40399	-2.66878	1.888116
H	-6.19137	1.821097	1.140325	H	-6.23648	2.017044	0.966046
H	-5.70352	2.297272	-0.4671	H	-5.75769	2.322533	-0.68506
H	-9.15163	1.658005	-0.58079	H	-9.21677	1.72451	-0.69866
H	5.202674	3.913906	-2.60708	H	8.51136	3.314638	-0.48986
H	5.294506	4.388922	-0.8796	H	7.419574	3.281801	-1.91289
H	6.751157	3.803021	-1.70873	H	6.911655	4.123999	-0.43407
H	3.133645	-3.8334	-1.87013	H	2.998793	-4.02929	-1.54526
H	2.414776	-3.73549	-0.19367	H	2.313186	-3.75686	0.125702
1-2-c				1-2-d			
C	-0.88433	1.490797	-0.3611	C	1.09496	1.002179	-0.60336
C	-1.60575	0.947524	0.652478	C	1.74026	0.734161	0.561381
C	0.621035	1.500928	-0.34999	C	-0.252	0.409662	-0.91879
C	1.15296	0.17874	0.325537	C	-1.11202	0.336238	0.40402
C	0.570054	0.104628	1.750779	C	-0.34288	-0.51581	1.432674
C	-0.96444	0.255554	1.782619	C	1.11547	-0.05537	1.634969
C	1.38445	1.50917	-1.69001	C	-1.19706	1.157925	-1.88013
C	2.793527	0.969614	-1.30629	C	-2.60294	0.596463	-1.51738
C	2.69692	0.351207	0.134747	C	-2.47388	-0.18776	-0.16293
C	0.689666	-1.08364	-0.44887	C	-1.33386	1.742168	1.020155
C	3.628282	-0.87446	0.323714	C	-3.75209	-0.08647	0.709628
C	3.502415	-1.51395	1.715345	C	-3.61679	-0.80932	2.059582
C	5.092738	-0.45845	0.0456	C	-4.963	-0.63552	-0.08288
C	1.021304	2.803623	0.411713	C	0.040947	-0.98503	-1.5547
O	-1.60185	-0.20875	2.724195	O	1.715705	-0.3681	2.659573
C	-3.12031	1.073805	0.440601	C	3.159908	1.3086	0.600365
O	-6.95718	-1.99032	-0.30416	O	6.472923	-1.34415	-0.5067
C	-5.66131	-1.74394	-0.60819	C	5.221813	-1.866	-0.55039
C	-5.21486	-0.41112	-0.03757	C	4.17266	-0.77572	-0.61368
C	-3.69356	-0.33929	0.141631	C	4.229201	0.18001	0.59188
C	-3.8297	1.719776	1.648407	C	3.414382	2.187463	1.842372
O	-4.98035	-2.49603	-1.27201	O	5.002166	-3.05781	-0.54516
C	6.084267	-1.63824	-0.02924	C	-6.32924	-0.3675	0.58139
C	7.48146	-1.19131	-0.39618	C	-7.48724	-0.85119	-0.26241
O	7.530999	-0.66123	-1.6473	O	-7.55655	-0.19555	-1.45148
O	8.462377	-1.26891	0.309704	O	-8.27643	-1.71757	0.042373
C	-3.18277	1.957593	-0.82648	C	3.20318	2.124393	-0.71128
C	-1.76554	2.162147	-1.3493	C	1.917418	1.864482	-1.49054
C	-7.49069	-3.21345	-0.83758	C	7.536099	-2.30748	-0.43488
C	-2.57839	3.330328	-0.79983	C	2.222935	3.242303	-0.91586

H	-1.5117	2.154062	-2.40508	H	1.88117	1.742894	-2.56925
H	-3.99195	1.786557	-1.53012	H	4.153703	2.196542	-1.23292
H	0.785696	-0.84068	2.253226	H	-0.80075	-0.50259	2.424136
H	0.989935	0.89048	2.39168	H	-0.31039	-1.57039	1.130979
H	1.42915	2.50904	-2.13253	H	-0.94013	0.981638	-2.92932
H	0.902695	0.857792	-2.42497	H	-1.14876	2.238597	-1.72082
H	3.121595	0.212618	-2.02649	H	-3.32644	1.412837	-1.4188
H	3.54162	1.766449	-1.3391	H	-2.98334	-0.05377	-2.30997
H	3.035726	1.101561	0.861377	H	-2.34665	-1.2552	-0.38651
H	-0.39658	-1.13635	-0.53968	H	-0.39128	2.237071	1.262291
H	1.10741	-1.13616	-1.45718	H	-1.89902	2.407477	0.363016
H	1.013884	-1.9841	0.080943	H	-1.89878	1.652007	1.952242
H	3.357324	-1.62956	-0.42841	H	-3.94877	0.977472	0.906446
H	4.211519	-2.33653	1.844719	H	-4.55664	-0.79369	2.61844
H	2.506887	-1.92607	1.888429	H	-2.86284	-0.34837	2.700334
H	3.702201	-0.77929	2.504599	H	-3.33631	-1.85954	1.9161
H	5.152063	0.083151	-0.90185	H	-4.98685	-0.19057	-1.08062
H	5.422679	0.239294	0.827774	H	-4.83798	-1.71804	-0.22446
H	0.662069	2.81369	1.442896	H	0.550743	-1.66355	-0.86789
H	2.102209	2.964775	0.421202	H	-0.86604	-1.47637	-1.91544
H	0.570928	3.660158	-0.09955	H	0.696265	-0.84823	-2.42137
H	-5.57155	0.359227	-0.73577	H	4.326625	-0.21758	-1.54476
H	-5.75242	-0.23971	0.898578	H	3.204785	-1.27554	-0.67808
H	-3.40277	-1.00395	0.960955	H	4.110125	-0.39566	1.515084
H	-3.22064	-0.72978	-0.7654	H	5.221115	0.645139	0.625739
H	-4.88621	1.906426	1.431654	H	4.422413	2.614908	1.806852
H	-3.75321	1.070727	2.523173	H	3.317681	1.59188	2.752583
H	-3.37254	2.680228	1.903086	H	2.701654	3.015242	1.899941
H	6.166483	-2.16633	0.921678	H	-6.42059	-0.8653	1.547559
H	5.742688	-2.35	-0.79111	H	-6.45013	0.71187	0.737627
H	8.455217	-0.39365	-1.78608	H	-8.31587	-0.57893	-1.92216
H	-8.52707	-3.25356	-0.50278	H	8.458283	-1.72763	-0.39777
H	-7.44005	-3.21412	-1.92933	H	7.436261	-2.92644	0.460107
H	-6.93251	-4.07382	-0.46044	H	7.527667	-2.95819	-1.31293
H	-2.9494	4.049548	-1.52458	H	2.499822	4.015627	-1.62676
H	-2.26789	3.764182	0.145847	H	1.619239	3.59263	-0.08382
1-2-e				1-2-f			
C	-0.88837	1.477746	-0.41066	C	0.994315	-1.42737	-0.52481
C	-1.60137	0.958816	0.621502	C	1.690445	-1.02402	0.569015
C	0.61701	1.4839	-0.41437	C	-0.51095	-1.44766	-0.5477

C	1.152266	0.17504	0.284158	C	-1.06971	-0.23464	0.291112
C	0.582754	0.133139	1.716196	C	-0.51427	-0.34779	1.724365
C	-0.95095	0.28902	1.759686	C	1.020947	-0.48827	1.766032
C	1.367851	1.461337	-1.76126	C	-1.24881	-1.27817	-1.89095
C	2.779883	0.929078	-1.37831	C	-2.67145	-0.81136	-1.46434
C	2.694784	0.339883	0.075852	C	-2.60798	-0.3923	0.049066
C	0.678913	-1.10213	-0.459	C	-0.60634	1.124169	-0.29785
C	3.624839	-0.88443	0.281109	C	-3.55452	0.790877	0.381194
C	3.505255	-1.49903	1.684376	C	-3.45708	1.24309	1.846919
C	5.089265	-0.47523	-0.00816	C	-5.01144	0.403345	0.030324
C	1.027639	2.801867	0.314976	C	-0.9129	-2.84509	0.020467
O	-1.58019	-0.15326	2.717232	O	1.636105	-0.14227	2.770834
C	-3.11756	1.086361	0.422628	C	3.209869	-1.1238	0.37965
O	-6.97713	-1.97237	-0.22331	O	5.324014	2.345215	-1.23131
C	-5.68059	-1.74322	-0.53786	C	5.79462	1.830361	-0.06759
C	-5.22288	-0.39951	-0.00274	C	5.321381	0.405042	0.131408
C	-3.69964	-0.33034	0.160189	C	3.78949	0.316954	0.290846
C	-3.81172	1.760899	1.623663	C	3.889824	-1.92701	1.507354
O	-5.00732	-2.5169	-1.18444	O	6.49874	2.454896	0.695186
C	6.076397	-1.65977	-0.08104	C	-6.00748	1.581864	0.073285
C	7.462247	-1.20817	-0.48035	C	-7.38614	1.166744	-0.3861
O	8.055348	-0.47952	0.501883	O	-7.98183	0.330925	0.504747
O	8.006772	-1.42741	-1.53975	O	-7.92309	1.497507	-1.42011
C	-3.18977	1.943325	-0.86227	C	3.304876	-1.82886	-0.99222
C	-1.7774	2.130762	-1.40417	C	1.901255	-1.9593	-1.57305
C	-7.52121	-3.20496	-0.72327	C	5.707291	3.703617	-1.49828
C	-2.57981	3.313792	-0.87136	C	2.70185	-3.19176	-1.16358
H	-1.5346	2.098822	-2.46209	H	1.673203	-1.81021	-2.6242
H	-4.00688	1.760843	-1.5537	H	4.132132	-1.56912	-1.64561
H	0.800797	-0.80145	2.23739	H	-0.7492	0.519777	2.344354
H	1.010586	0.931861	2.335534	H	-0.93724	-1.21614	2.245733
H	1.409438	2.450877	-2.22668	H	-1.27365	-2.20756	-2.46814
H	0.8788	0.794102	-2.47683	H	-0.76138	-0.52722	-2.51957
H	3.102203	0.157999	-2.08605	H	-2.99808	0.0321	-2.08174
H	3.527159	1.725547	-1.43309	H	-3.40671	-1.60592	-1.61902
H	3.04211	1.103524	0.784327	H	-2.95267	-1.23554	0.662156
H	-0.40816	-1.15279	-0.54041	H	0.480773	1.19289	-0.36443
H	1.088782	-1.17795	-1.46903	H	-1.01008	1.310939	-1.29587
H	1.004005	-1.99207	0.087775	H	-0.94408	1.942731	0.344319
H	3.348429	-1.65187	-0.45598	H	-3.27852	1.639823	-0.26053

H	4.215381	-2.31908	1.825304	H	-4.18939	2.022698	2.075764
H	2.510921	-1.90941	1.868001	H	-2.47491	1.655331	2.084414
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H	5.429992	0.228914	0.761239	H	-5.35504	-0.38228	0.714849
H	0.67792	2.835656	1.34894	H	-0.57261	-2.99456	1.047361
H	2.108961	2.960402	0.311023	H	-1.99222	-3.01291	-0.01404
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H	-5.58354	0.356132	-0.71481	H	5.650082	-0.18049	-0.73567
H	-5.75075	-0.20435	0.93433	H	5.836157	0.025288	1.015152
H	-3.40375	-0.97824	0.991041	H	3.497525	0.853644	1.199033
H	-3.23725	-0.74294	-0.74247	H	3.319562	0.827597	-0.55666
H	-4.86933	1.9486	1.413264	H	4.949853	-2.09122	1.290742
H	-3.73013	1.129568	2.510875	H	3.797313	-1.39753	2.457872
H	-3.34731	2.723962	1.854356	H	3.423666	-2.90952	1.624048
H	6.149069	-2.16283	0.888313	H	-6.09272	1.978487	1.089898
H	5.74793	-2.38836	-0.82658	H	-5.67757	2.387887	-0.58705
H	8.922998	-0.21629	0.151063	H	-8.84476	0.10225	0.119716
H	-8.55642	-3.22935	-0.38339	H	5.244768	3.959501	-2.45152
H	-7.4752	-3.23373	-1.81485	H	5.349835	4.368236	-0.70792
H	-6.96734	-4.05932	-0.32664	H	6.794594	3.792137	-1.56429
H	-2.95571	4.019057	-1.60721	H	3.09286	-3.80923	-1.96729
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C	-0.58151	-1.68194	-0.60207	C	-0.61708	-1.48385	-0.41416
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C	0.895799	-0.7561	1.758347	C	0.950956	-0.28888	1.759725
C	-1.35399	-1.49085	-1.92238	C	-1.36796	-1.46159	-1.76103
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C	5.065625	0.649996	0.135361	C	5.222906	0.399478	-0.00262
C	3.552586	0.407495	0.313918	C	3.699655	0.330369	0.160236
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O	6.083473	2.746849	0.821724	O	5.007517	2.516688	-1.18464
C	-6.36898	0.693765	0.380638	C	-6.07655	1.659873	-0.08087
C	-6.16209	2.034566	-0.28678	C	-7.46214	1.207872	-0.48061
O	-6.07748	1.919015	-1.63892	O	-8.05645	0.481499	0.502587
O	-6.06736	3.103139	0.275681	O	-8.00543	1.424832	-1.54111
C	3.243944	-1.67674	-1.1172	C	3.189703	-1.94332	-0.86218
C	1.84774	-1.89582	-1.68855	C	1.777312	-2.13079	-1.40403
C	5.098556	4.086304	-1.23497	C	7.52146	3.204605	-0.72363
C	2.765972	-3.07417	-1.38031	C	2.579748	-3.31379	-0.87118
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H	4.031064	-1.29418	-1.75977	H	4.006792	-1.76085	-1.55364
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H	-0.98522	-1.68385	2.202722	H	-1.01073	-0.93114	2.335766
H	-1.30254	-2.37671	-2.56291	H	-1.40962	-2.45125	-2.22618
H	-0.94807	-0.65643	-2.50185	H	-0.87892	-0.79456	-2.4768
H	-3.21881	-0.33766	-2.00376	H	-3.10219	-0.15816	-2.08602
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H	-1.30793	1.584918	0.529738	H	-1.00404	1.9922	0.087274
H	-3.60682	1.110506	-0.08215	H	-3.34848	1.651956	-0.45617
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H	-2.7747	0.993308	2.268448	H	-2.51097	1.909643	1.867853
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H	-5.43497	-1.22052	0.675304	H	-5.42997	-0.22894	0.761009
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H	5.423952	0.161921	-0.77915	H	5.583552	-0.35625	-0.71463
H	5.63522	0.255193	0.977908	H	5.75075	0.204388	0.934471
H	3.233217	0.846069	1.264585	H	3.403734	0.978295	0.991054
H	3.017588	0.932595	-0.48472	H	3.237339	0.742955	-0.74247
H	4.949632	-1.94459	1.122096	H	4.869281	-1.94856	1.413345

H	3.75713	-1.45178	2.349591	H	3.730076	-1.12948	2.510941
H	3.513782	-2.92735	1.408931	H	3.347244	-2.72388	1.854467
H	-7.29755	0.26153	-0.01027	H	-6.14941	2.162614	0.888609
H	-6.51333	0.884693	1.444859	H	-5.74805	2.38863	-0.82624
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H	6.170405	4.274066	-1.33703	H	6.967953	4.059122	-0.32683
H	3.196598	-3.5931	-2.23202	H	2.955595	-4.01908	-1.60703
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C	0.869403	-1.65586	-0.42257				
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C	-0.62848	-1.78884	-0.35116				
C	-1.23949	-0.51768	0.355142				
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O	1.569038	0.0845	2.644572				
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C	5.062915	0.561221	-0.26655				
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C	3.893452	-1.6662	1.4778				
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C	-6.36579	0.806073	0.365756				
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O	-6.07881	3.15913	-0.16992				
C	3.178179	-1.94377	-0.97433				
C	1.762353	-2.25397	-1.4464				
C	5.525905	4.21823	0.002868				

C	2.680593	-3.35829	-0.93152				
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H	6.534866	4.354756	-0.39449				
H	4.80614	4.565776	-0.74239				
H	3.079018	-4.04616	-1.67188				
H	2.438397	-3.81492	0.023314				

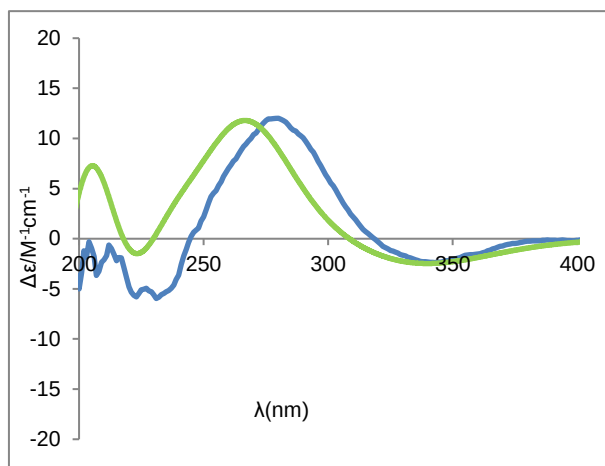


Figure S19. Calculated and experimental ECDs of **1-2** (green, calculated at the B3LYP-PCM/6-31G(d,p)//B3LYP/6-31G(d,p) level in CH₃OH; blue, experimental in CH₃OH).

Table S6. The computed ¹³C NMR data for **1-2**.

No.	1-2	δ_{exptl}	Pyridine	
			δ_{calcd}	$\Delta\delta$
1	8	175.9	175.0	-0.9
2	9	132.8	134.0	1.2
3	14	50.1	48.4	-1.7
4	13	48	46.4	-1.6
5	12	49.7	45.1	-4.6
6	11	196.3	192.5	-3.8
7	15	29.6	25.0	-4.6
8	16	27.5	23.6	-3.9
9	17	49.5	45.5	-4.0
10	18	17.3	10.7	-6.6
11	20	35.9	32.7	-3.2
12	21	17.9	11.2	-6.7
13	22	31.5	26.1	-5.4
14	30	24.5	19.0	-5.5
15	10	48.6	46.3	-2.3
16	3	174.2	169.4	-4.8
17	2	29.6	24.1	-5.5
18	1	36	28.7	-7.3
19	19	23	13.9	-9.1
20	23	31.7	26.6	-5.1
21	24	176.2	168.6	-7.6
22	5	27.8	23.0	-4.8

23	7	22.9	20.4	-2.5
24	-OCH3	51.1	46.1	-5.0
25	6	14.5	12.9	-1.6

LAD^a 9.1

MAD^b 4.37

^aLAD = largest absolute deviation. ^b MAD = mean absolute deviation, computed as $(1/n) \sum$

$$\frac{n}{i} |\delta_{\text{calcd}} - \delta_{\text{exptl}}|$$

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NMR and MS Spectra of Fornicatin M (2)

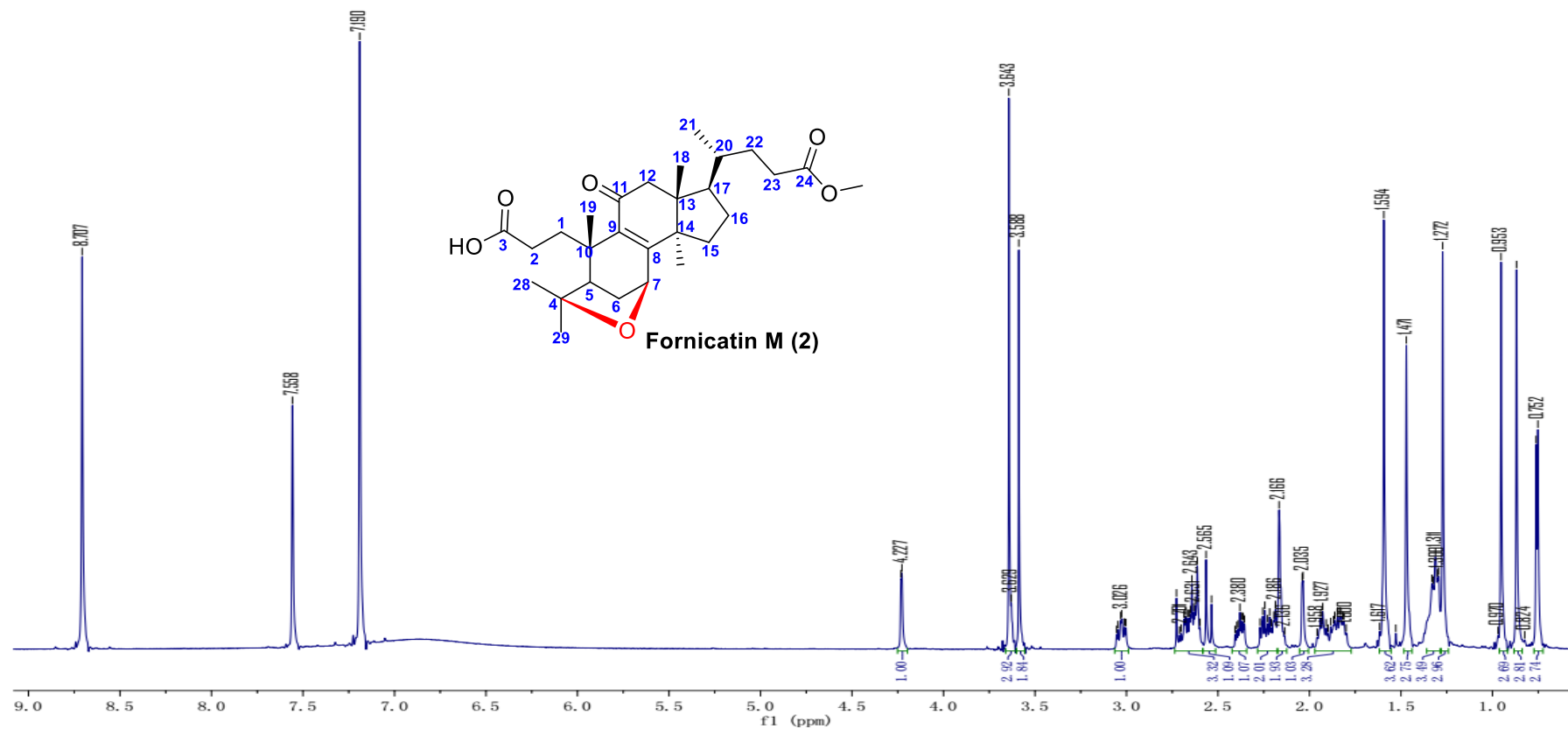


Figure S20. ¹H NMR (600 MHz, C₅D₅N) spectrum of fornicatin M (2).

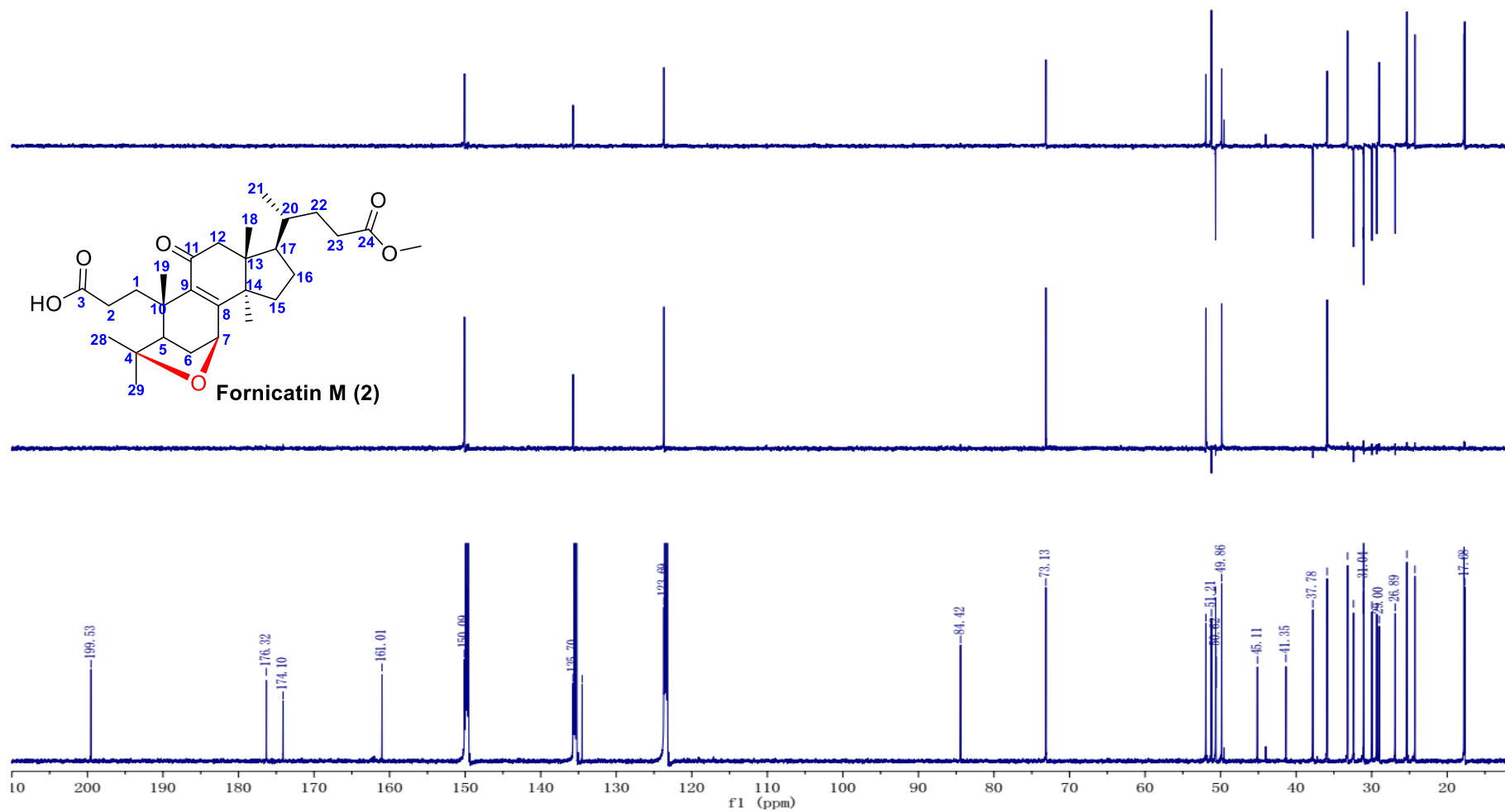


Figure S21. ^{13}C NMR (150 MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of fornicatin M (2).

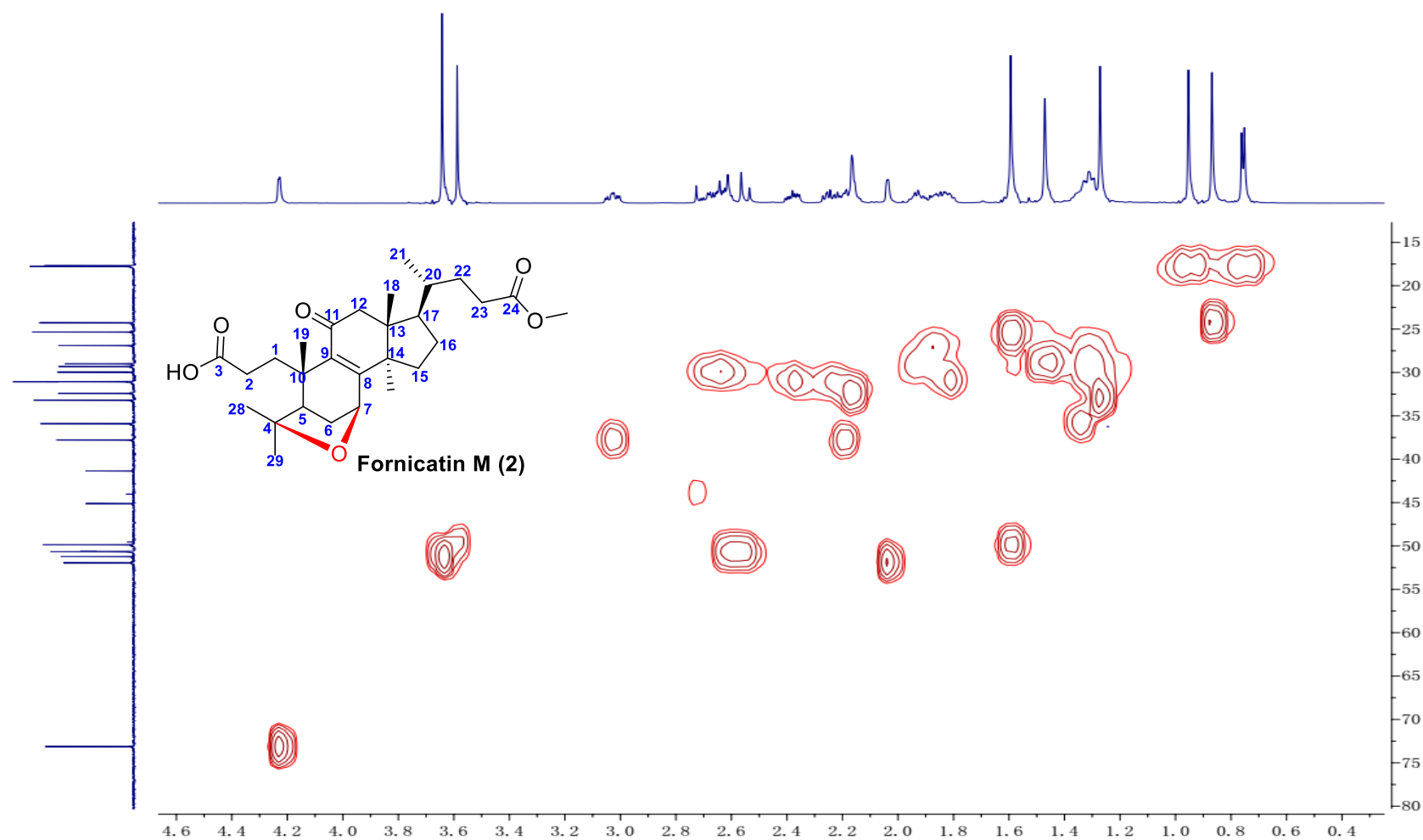


Figure S22. HSQC (600/150 MHz, C₅D₅N) spectrum of fornicatin M (2).

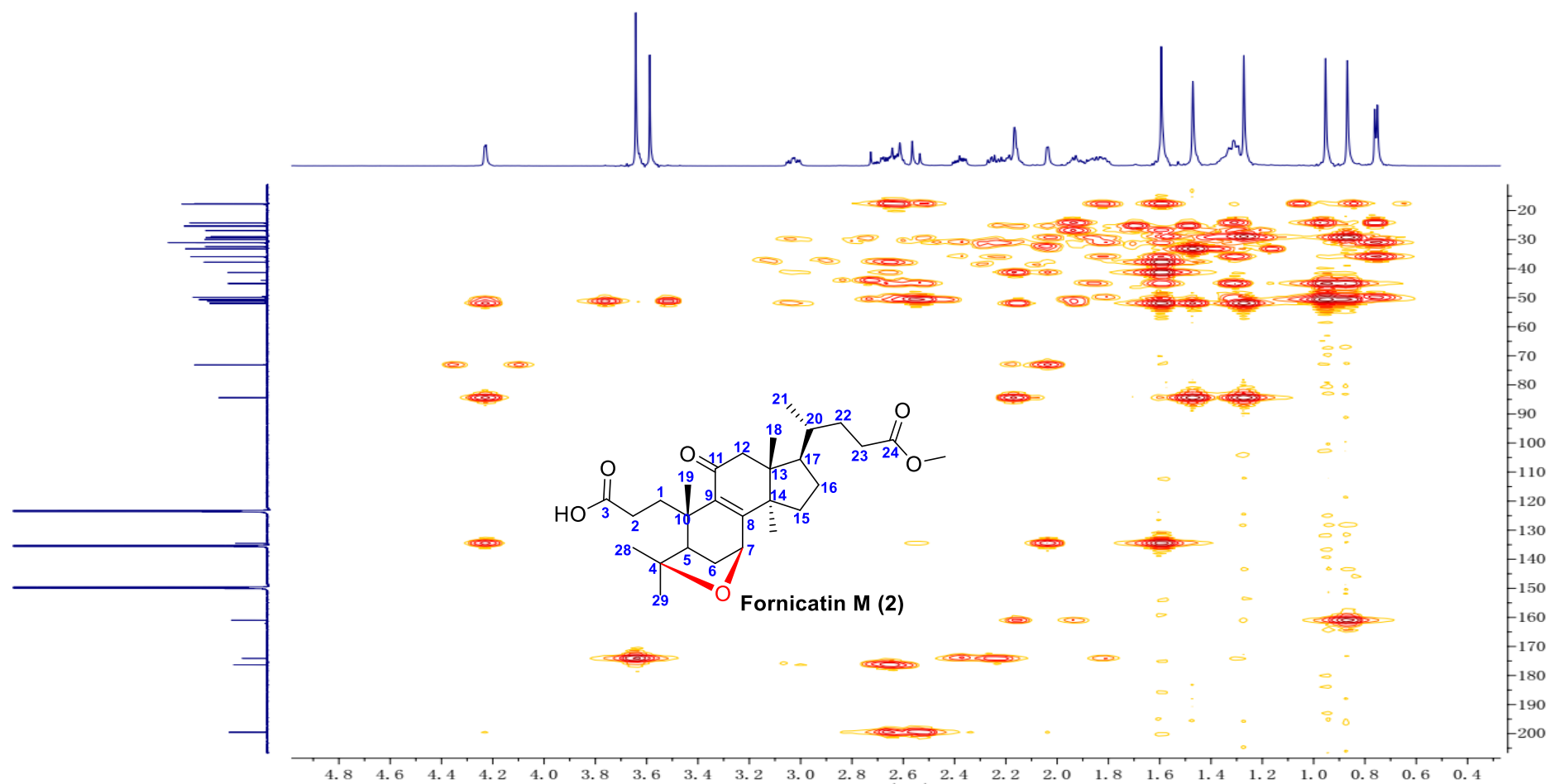


Figure S23. HMBC (600/150 MHz, C₅D₅N) spectrum of fornicatin M (2).

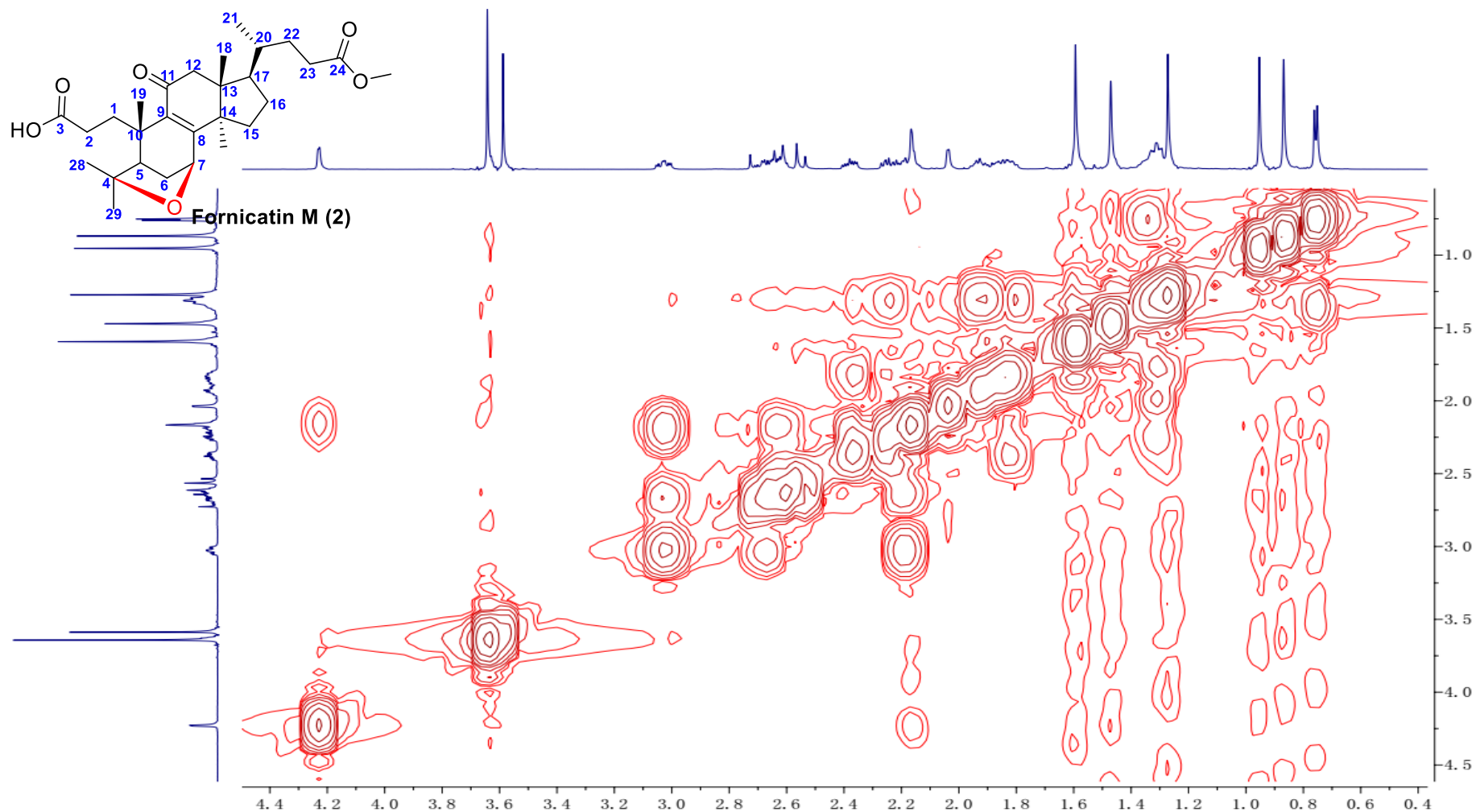


Figure S24. ^1H - ^1H COSY (150 MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of fornicatin M (2).

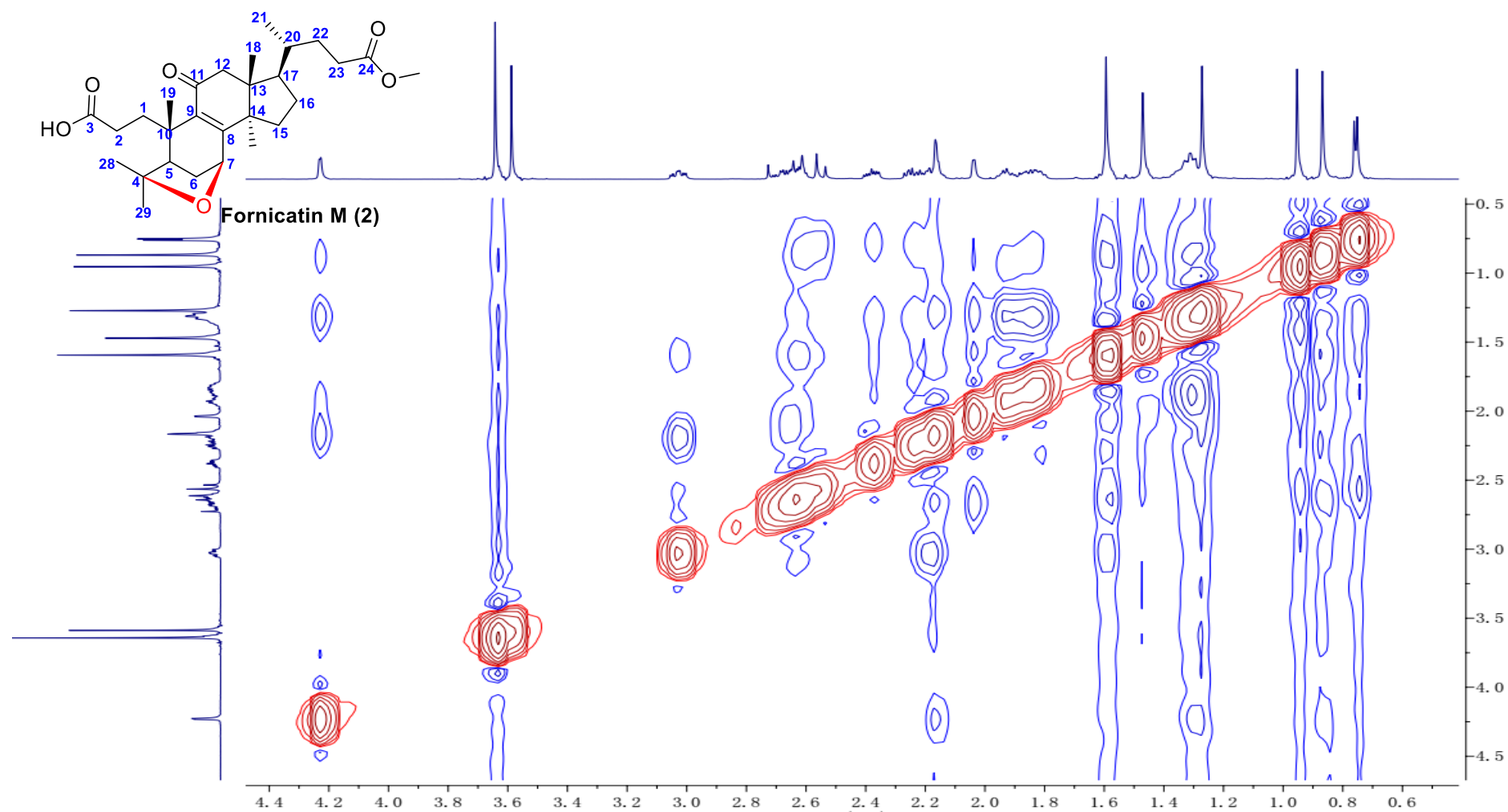


Figure S25. ROESY (150 MHz, C₅D₅N) spectrum of fornicatin M (2).

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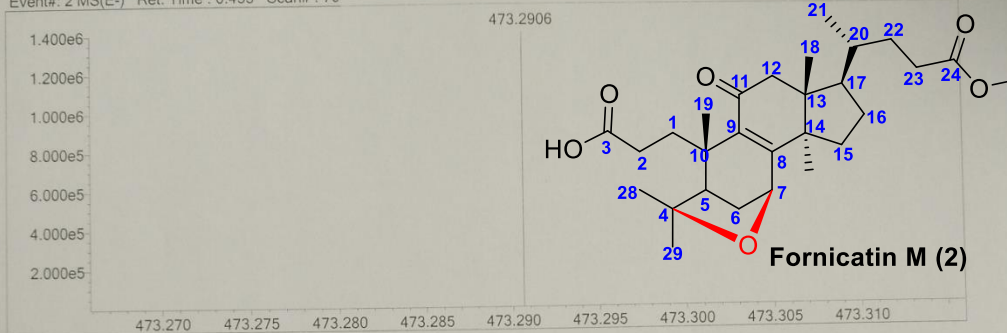
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C	4	0	100	F	1	0	0	S	2	0	0	I	3	0	0	
N	3	0	0	Na	1	0	0	Cl	1	0	0					

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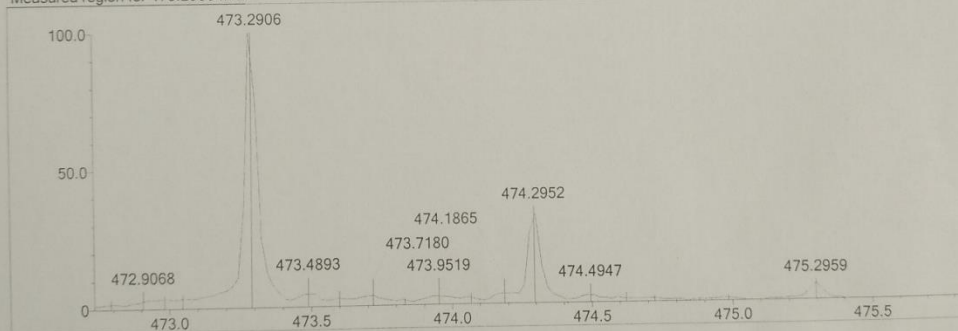
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Electron Ions: both
Use MSn Info: yes
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Max Results: 10

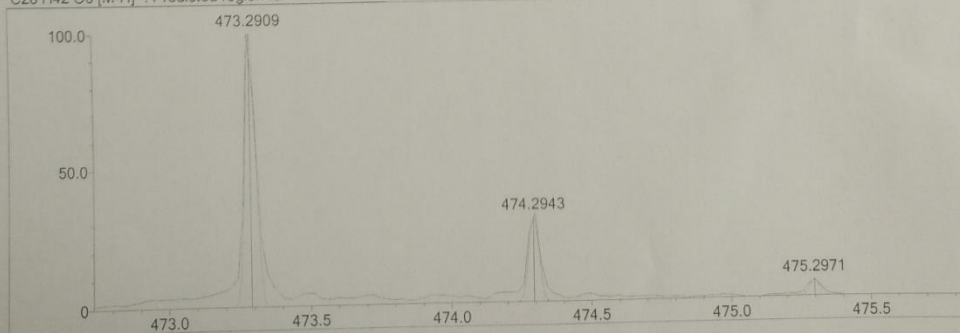
Event#: 2 MS(E-) Ret. Time : 0.453 Scan# : 70



Measured region for 473.2906 m/z



C28 H42 O6 [M-H]- : Predicted region for 473.2909 m/z



Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	DBE
C28 H42 O6	[M-H]-	473.2906	473.2909	-0.3	-0.63	8.0

Figure S26. HRESIMS spectrum of fornicatin M (2).