Supporting Information for

Bungsteroid A, One Unusual C_{34} Pentacyclic Steroid Analogue from *Zanthoxylum bungeanum* Maxim.

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Author Contributions

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EXPERIMENTAL SECTION

Analysis of the purity of bungsteroid A

The purity of bungsteroid A has been analyzed by HPLC with a refractive index detector (AZURA RID 2.1L, KNAUER, German). The Analysis of purity of bungsteroid A by HPLC was shown as Figure S1, it's purity is 96.6%.

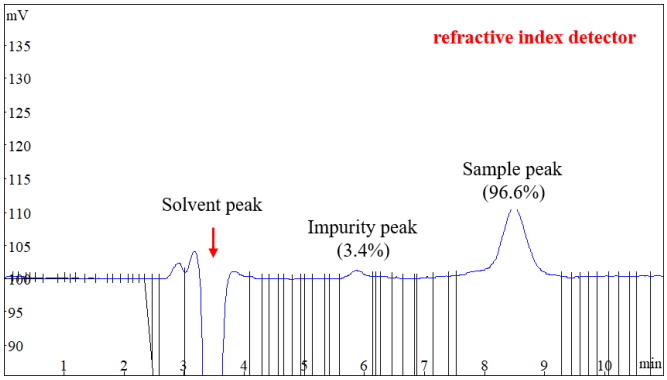


Figure S1. Analysis of the purity of bungsteroid A by HPLC with a refractive index detector.

The Quantum-chemical ^{13}C NMR, ECD Calculations, and Calculations of Optical Rotations.

All of the quantum-chemical ^{13}C NMR, ECD calculations, and calculations of optical rotations were determined by quantum chemical TDDFT calculations of using Gaussian 16 (Revision A.03)[1] series of programs.

Firstly, conformational analyses were carried out via molclus software,[2] and then using xtb software (GFN1-xTB)[3] for initial optimization and removal of energy overlap. In the energy window of 2 Kcal/mol, the results showed six lowest energy conformers for compound **1a-1d** (Figure S1), respectively. The conformers were then re-optimized using TDDFT at the BLYP/6-31g** level in vacuum in the Gaussian 16 program, and vibrational frequencies analysis is performed at the same level to ensure their stability and none of imaginary frequencies. The solvent model used in the process is SMD implicit solvent model. In order to obtain more accurate single-point energy, we use the M06-2X/Def2-TZVP method to calculate the single-point energy of each stable structure. This is because the TZVP base group can effectively avoid the calculation errors caused by the overlapping errors (BBSE) of the units. NMR calculations are performed at the B972/Def2-TZVP level and corrected using the

scaling method (TMS, TMS is optimized at the same level and NMR is calculated). ECD is calculated at the PBE1PBE/TZVP level. OR calculation uses the following base group: pbe1pbe/aug-cc-pVTZ polar = Optrot CPHF = RdFreq scrf = (smd, solvent = methanol) (reference: https://pubs.acs.org/doi/abs/10.1021/np070502r),[4] in order to calculate the result more accurately, nstates is set to 20.

References

(1) (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

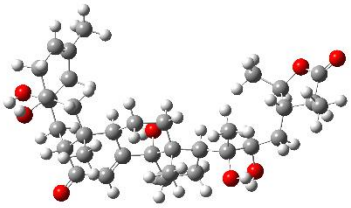
(2) Tian Lu, molclus program, Version 1.9. http://www.keinsci.com/research/molclus.html (accessed 2019-Nov-5).

(3) Grimme, S.; Bannwarth, C.; Shushkov, P. A Robust and accurate tight-binding quantum chemical method for structures, vibrational frequencies, and noncovalent interactions of large molecular systems parametrized for all spd-block elements (*Z* = 1−86). *J. Chem. Theory Comput.* **2017**, *13*, 1989–2009.

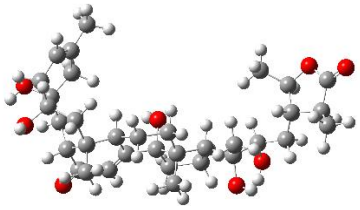
(4) Stephens, P. J.; Pan, J. J.; Devlin, F. J.; Cheeseman, J. R. Determination of the absolute configurations of natural products using TDDFT optical rotation calculations: the iridoid oruwacin. *J. Nat. Prod.* **2008**, *71*, 285–288.

Figure S2. Low-energy 3D conformers in the energy window of 2 Kcal/mol of

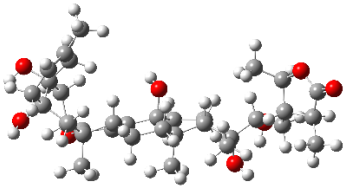
compounds **1a-1d**.



1a1



1a2



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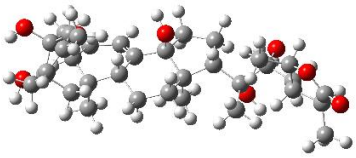

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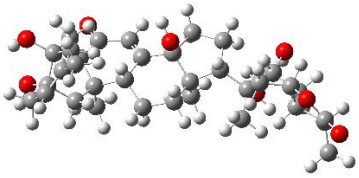

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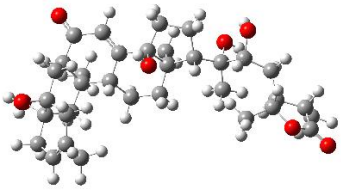

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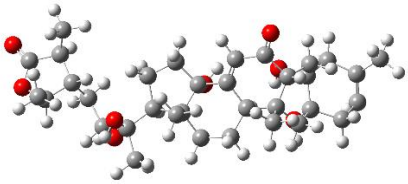

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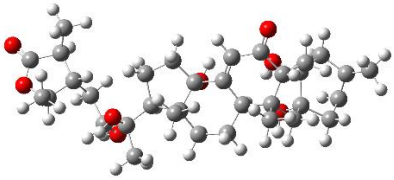

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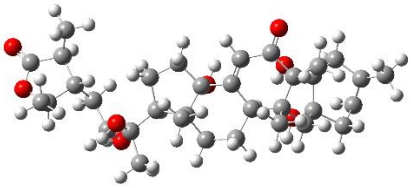

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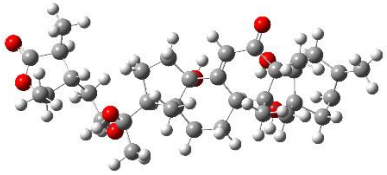

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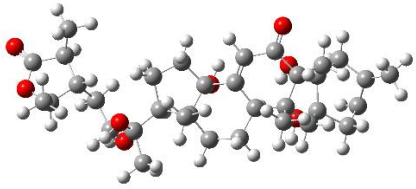

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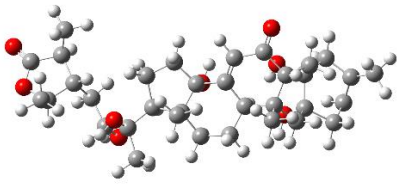

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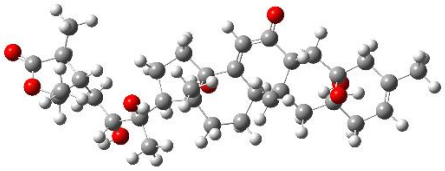

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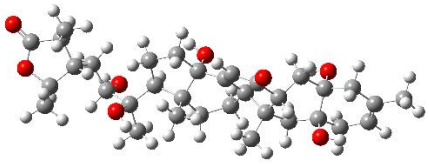

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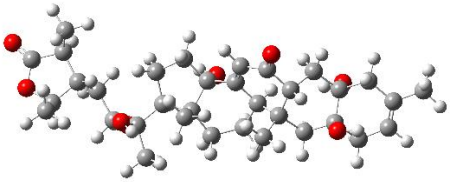

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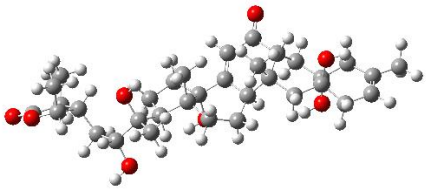

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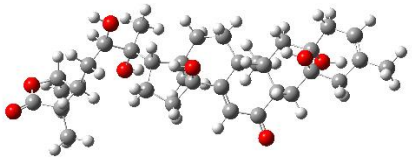

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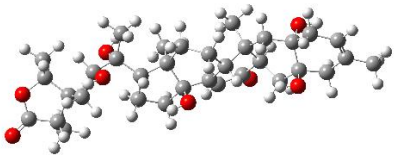

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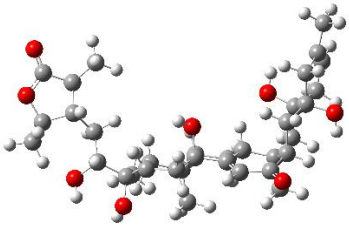

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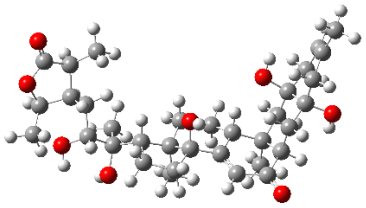

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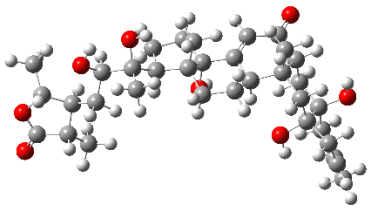

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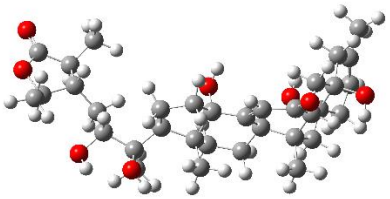

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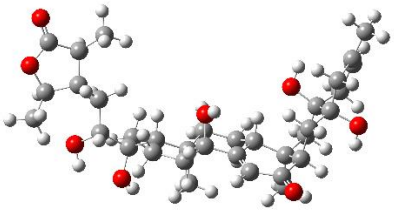

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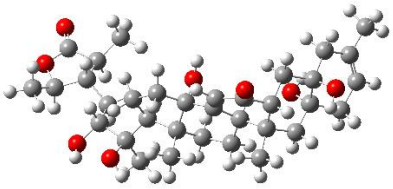


1d6

Table S1. The coordinate for the lowest-energy conformer of **1a** in the quantum-chemical ^{13}C NMR, ECD calculations, and calculations of optical rotations.

Atom	X	Y	Z	Atom	X	Y	Z
H	4.31055	2.87533	-0.26628	O	8.68059	3.12708	0.40769
H	3.75532	1.61572	-1.38523	C	4.54903	2.34129	-1.19144
H	4.56042	3.05936	-2.01686	C	7.82272	0.79627	2.05997
H	7.18281	1.44696	2.66478	H	5.4149	1.07463	0.93978
H	8.86571	1.04597	2.27467	C	5.89195	1.64949	-1.0678
H	7.65025	-0.23813	2.37025	O	6.8972	2.70793	-0.87338
H	6.1627	1.14129	-1.99963	C	7.79283	2.36497	0.07098
H	8.19063	0.31458	-0.0085	C	7.52224	0.96563	0.57531
H	4.46409	-3.11504	-0.81657	C	6.06763	0.70962	0.14263
H	6.55299	-1.08894	-0.89396	O	4.64983	-2.41018	-1.46319
H	6.02866	-1.35975	0.75663	C	5.81466	-0.77545	-0.14736
H	4.32351	-0.4959	1.97218	H	1.9713	-0.40619	-0.97084
H	2.59782	-0.70111	2.22168	C	3.35082	-0.44779	1.47646
H	3.18199	0.57956	1.14551	C	4.45083	-1.19856	-0.72373
H	4.11805	-0.45219	-1.44897	O	3.45795	-2.77167	0.83368
H	4.172	-2.74651	1.48923	C	3.28853	-1.43154	0.31155
H	-3.19071	-1.15445	3.15517	O	-4.87938	-3.47998	-0.90453
H	-3.2881	-2.55769	2.08096	H	-2.36683	0.35664	-0.23379
H	-4.76418	-1.75927	2.64294	C	-3.73524	-1.58509	2.31168
H	-0.87202	-0.59774	-2.45453	H	-5.61799	-1.56054	0.54432

H	1.02293	-2.26717	2.28039	O	-0.35495	-0.39668	-1.65982
H	0.89654	-3.42348	0.96191	C	0.47829	-2.49893	1.36146
H	-7.41551	0.95262	-0.71729	O	-6.76138	1.42777	-1.25596
H	-6.91569	0.53552	2.14132	O	-6.69466	0.3488	1.2168
H	2.12073	-2.1876	-2.46341	C	1.93127	-1.35951	-0.43657
H	2.23346	-3.40147	-1.20688	C	1.71412	-2.48851	-1.49646
H	-0.07344	-3.69436	-1.10002	C	0.18945	-2.74707	-1.5769
H	-0.1852	-2.78596	-2.60402	C	-1.26484	-0.06484	1.54042
H	-1.30212	-0.76482	2.37745	C	0.18043	-0.0062	1.02494
H	-1.54294	0.91211	1.94719	C	0.58245	-1.33363	0.35648
C	-5.48258	1.09003	-0.68905	C	-0.41816	-1.5758	-0.81195
H	0.29627	0.81214	0.30817	C	-3.76643	4.56047	-1.34498
H	0.83003	0.21883	1.87254	C	-2.319	-0.47393	0.48131
H	-4.17922	4.73162	-2.34795	C	-1.85683	-1.65417	-0.34866
H	-2.71703	4.27	-1.4886	C	-2.68862	-2.62689	-0.77191
H	-3.78605	5.50866	-0.79971	C	-4.12892	-2.56463	-0.54398
H	-2.32991	-3.46414	-1.36293	C	-4.29536	0.74975	1.52522
H	-3.54435	1.52356	1.34333	C	-3.74645	-0.64679	1.08848
H	-4.47794	0.75629	2.60509	C	-4.69137	-1.28661	0.0407
H	-4.22868	-0.27797	-1.83133	C	-5.06436	-0.34398	-1.12656
H	-5.89759	-0.79178	-1.67423	C	-5.95402	2.6464	1.25393
H	-5.81884	2.7491	2.3386	C	-5.5926	1.20821	0.84737
H	-7.02729	2.78638	1.06699	C	-4.48976	2.1176	-1.25117
H	-3.46912	1.72724	-1.16596	C	-4.53036	3.48606	-0.62293
H	-4.68217	2.19007	-2.32991	C	-5.17519	3.70461	0.52842
H	-5.17556	4.70291	0.96308	H	-0.55982	-2.70246	1.63777

Table S2. The coordinate for the lowest-energy conformer of **1b** in the quantum-chemical ^{13}C NMR, ECD calculations, and calculations of optical rotations.

Atom	X	Y	Z	Atom	X	Y	Z
C	6.98753	-0.4849	-2.35463	H	6.22108	-0.41947	-3.13373
C	7.34718	0.72432	-1.83252	H	6.30788	2.63926	-1.43202
C	6.15439	1.61489	-1.79109	H	5.63558	1.64668	-2.75342
C	5.13748	0.86355	-0.77979	H	6.30727	-2.45358	-1.58423
C	5.15098	-0.74653	-0.84219	H	7.21189	-1.45799	-0.4231
C	6.53537	-1.42448	-1.27966	H	6.33178	0.8643	0.99966
C	5.38184	1.28394	0.66466	H	5.47644	2.37156	0.72448
C	4.26132	0.82806	1.63771	H	5.67262	-1.42785	1.12653
C	3.70881	-0.61208	1.37037	H	4.44326	-2.39153	0.34638
C	4.76198	-1.35749	0.52357	H	1.13801	2.46877	1.71652
C	3.21938	1.91498	1.8199	H	-0.21109	-3.05142	0.3057
C	1.81836	1.63874	1.5517	H	0.323	-1.97675	-0.97872
C	1.40383	0.50001	0.96358	H	2.24495	-2.79089	0.34786
C	2.3235	-0.64997	0.64193	H	1.47863	-2.27094	1.83264

C	0.02531	0.39982	0.34274	H	-0.82116	2.39918	0.19387
C	-0.68681	-0.949	0.6365	H	-1.05661	1.62829	1.76073
C	0.22358	-2.07047	0.10717	H	-3.12387	0.8946	0.95191
C	1.60325	-2.01579	0.77888	H	-2.70955	1.30216	-0.70472
C	-1.03227	1.44419	0.68377	H	8.97653	-0.04032	-0.6345
C	-2.35015	0.79599	0.19157	H	9.19946	1.59464	-1.25691
C	-2.04476	-0.71055	-0.10587	H	8.13085	1.34642	0.10756
C	8.45578	0.90073	-0.83794	H	3.93886	-1.99089	-1.77942
O	4.18386	-1.05772	-1.86135	H	3.49846	0.75806	-1.80527
O	3.83598	1.35031	-1.11243	H	2.85084	-0.85095	3.37082
O	3.57595	3.0465	2.17883	H	3.39804	-2.37704	2.65432
C	3.62135	-1.3115	2.74247	H	4.57764	-1.22147	3.26751
H	4.74756	0.80131	2.61997	H	0.02694	-0.80367	2.70979
C	-0.87944	-1.08072	2.16391	H	-1.68803	-0.44706	2.52955
O	0.26178	0.4443	-1.09166	H	-1.12327	-2.10972	2.43858
C	-3.23441	-1.67684	0.13524	H	0.62647	1.32141	-1.28478
C	-2.80316	-3.14757	0.23784	H	-3.69462	-3.78304	0.3014
O	-3.88012	-1.31314	1.37051	H	-2.22834	-3.46682	-0.63179
C	-4.29563	-1.60786	-1.00811	H	-2.21072	-3.31544	1.13693
C	-4.94779	-0.26731	-1.36821	H	-4.53327	-2.00042	1.57066
C	-5.78012	0.44012	-0.2911	H	-5.08953	-2.30356	-0.69384
O	-3.65498	-2.1294	-2.18307	H	-4.18097	0.41534	-1.74212
C	-6.36167	1.76707	-0.82056	H	-5.61295	-0.4714	-2.22088
C	-7.82395	1.46091	-1.06993	H	-4.30351	-2.11144	-2.90156
O	-8.15753	0.25161	-0.58252	H	-5.92013	2.0343	-1.78644
C	-7.03237	-0.36723	0.12912	H	-7.00167	-1.39556	-0.23628
C	-7.32763	-0.34467	1.61647	H	-8.27027	-0.85471	1.83595
C	-6.21948	2.96462	0.12868	H	-6.5217	-0.85452	2.15249
O	-8.64856	2.16906	-1.61919	H	-7.38864	0.68355	1.98637
H	2.51527	-0.53464	-0.42551	H	-5.16133	3.19857	0.2758
H	-1.82432	-0.80657	-1.1717	H	-6.71456	3.84665	-0.28829
H	-5.16731	0.6203	0.58918	H	-6.6624	2.75035	1.10596

Table S3. The coordinate for the lowest-energy conformer of **1c** in the quantum-chemical ^{13}C NMR, ECD calculations, and calculations of optical rotations.

Atom	X	Y	Z	Atom	X	Y	Z
H	-0.88265	0.06813	-2.40526	H	7.35037	1.69375	0.41965
H	-7.00633	2.83627	0.8392	H	9.02852	-1.86106	-0.56825
H	-7.42711	3.54356	-0.7336	H	-2.14353	-1.19433	-1.35804
H	-5.73872	3.14108	-0.36225	H	4.86824	-0.1861	-2.18207
H	-7.35778	0.94172	2.34168	H	2.64781	-0.06793	-1.2513
H	-6.35534	-0.49396	2.64204	C	-6.77653	2.82196	-0.23062
H	-8.12697	-0.62872	2.67207	C	-7.28111	-0.13845	2.18091
H	-7.18671	-1.54285	0.55113	C	-7.25228	-0.46325	0.70054

H	-6.73583	1.45173	-1.88806	O	-8.54086	-0.08062	0.11015
H	-4.89541	-2.80025	-2.21527	C	-8.41678	0.98932	-0.69527
H	-6.2073	-1.0441	-1.77287	C	-6.96965	1.41762	-0.81853
H	3.64929	-0.82026	2.83631	O	-4.12773	-2.52944	-1.69136
H	9.84114	1.27085	-1.76493	C	-6.17526	0.30166	-0.10879
H	1.37484	-1.82998	-1.5818	C	-5.44534	-0.59193	-1.12065
H	-4.8241	0.02818	-1.76938	C	-4.61325	-1.76315	-0.57893
H	-5.27251	-2.39334	0.03417	O	-3.90953	-0.78574	1.46488
H	-3.30249	-0.90902	2.207	C	-2.88433	-2.8701	0.80515
H	-2.08726	-2.77913	1.5448	C	-3.37548	-1.49451	0.33054
H	-2.51407	-3.47113	-0.02599	O	-0.01709	0.15109	-1.98199
H	-3.71618	-3.40582	1.27334	C	-0.9045	-0.18373	1.72465
H	-1.21389	-1.02039	2.35577	H	4.51487	1.16248	1.7864
H	0.07396	0.13114	2.08917	O	3.12778	3.26352	1.64221
H	2.30576	-1.71304	2.11205	O	5.77021	0.13467	-2.03571
H	2.09844	-0.0165	2.57765	O	6.18806	-0.4205	1.598
H	7.1518	-0.31415	1.61815	C	9.78138	0.71968	-0.81723
H	10.02471	1.43939	-0.0244	C	-2.2618	-0.68502	-0.39601
H	4.17018	-1.66237	-0.72333	C	-2.61556	0.81552	-0.66106
H	-5.45677	0.73564	0.58411	C	-1.29636	1.6268	-0.55663
C	2.80034	-0.73812	2.15043	C	1.46066	-1.674	-0.50653
H	10.5513	-0.05742	-0.82254	C	0.05911	-1.88354	0.12026
H	-3.05974	0.93857	-1.65038	C	-0.83276	-0.61799	0.24356
O	-9.39057	1.50305	-1.21627	C	-0.21495	0.55088	-0.60551
H	-1.60043	0.64061	1.89225	C	2.15621	-0.29683	-0.29437
H	-3.34284	1.17612	0.06617	C	1.17077	0.834	-0.09584
H	-1.25705	2.18471	0.38013	C	1.50703	1.98304	0.52223
H	-1.167	2.34266	-1.37253	C	2.83651	2.20109	1.07688
H	2.11737	-2.46504	-0.13526	C	4.40219	-1.30718	0.28452
H	-0.44838	-2.64068	-0.48256	C	3.30133	-0.30506	0.76344
H	0.17453	-2.32103	1.11614	C	3.88909	1.1256	0.89348
H	0.79587	2.79322	0.64789	C	4.76733	1.53971	-0.3061
H	4.40703	-2.19564	0.92338	C	6.8227	-1.78178	-0.29611
H	4.1418	1.66599	-1.19624	C	5.82212	-0.75057	0.24128
H	5.19638	2.52304	-0.09232	C	5.88659	0.52561	-0.65051
H	6.45333	-2.20629	-1.23731	C	7.27938	1.14809	-0.52999
H	6.88003	-2.61025	0.4203	C	8.40724	0.14384	-0.61846
H	7.38544	1.90371	-1.31867	C	8.18614	-1.17424	-0.50336

Table S4. The coordinate for the lowest-energy conformer of **1d** in the quantum-chemical ^{13}C NMR, ECD calculations, and calculations of optical rotations.

Atom	X	Y	Z	Atom	X	Y	Z
C	6.45059	2.84744	-1.43631	C	4.60892	-0.55709	-1.4165

C	6.36533	3.2336	-0.15447	H	7.63746	4.47491	1.06259
C	5.76211	2.34162	0.90786	O	-5.73765	-1.73087	-1.1223
C	5.55218	0.894	0.45778	H	4.80632	2.76713	1.23903
C	4.96785	0.86841	-0.98422	H	6.40824	2.33091	1.79471
C	5.97969	1.50873	-1.94356	H	6.83516	0.83693	-2.08435
C	4.64261	0.13418	1.4309	H	5.50349	1.61872	-2.92537
C	4.39596	-1.31628	0.96317	H	3.69208	0.66553	1.52968
C	3.74106	-1.38685	-0.43835	H	5.547	-1.10469	-1.56565
C	-4.8335	0.44372	-0.72303	H	1.5664	-2.34371	2.75049
C	3.58535	-2.0395	2.01773	H	-0.16734	0.34613	-1.45611
C	2.13365	-1.97294	1.90216	H	1.62561	-2.04793	-2.06231
C	1.52283	-1.40378	0.84211	H	-0.67906	-1.20598	2.91143
C	2.27347	-0.85945	-0.35727	H	-0.62445	-2.75872	2.08107
C	0.04194	-1.09781	0.85836	H	-2.87178	-2.3962	1.52502
C	-0.6691	-1.50669	-0.46227	H	-2.79405	-0.68929	1.94125
C	-0.00583	-0.72515	-1.6071	H	7.21635	5.19024	-0.50812
C	1.49788	-1.02968	-1.68841	H	6.02636	5.13214	0.80925
C	-0.84513	-1.69672	1.948	H	-5.50416	1.00486	1.24564
C	-2.27917	-1.48765	1.40108	C	-7.72373	-0.41568	1.05434
C	-2.1397	-1.12099	-0.10984	H	4.13286	-0.50874	-2.40047
C	6.83813	4.58017	0.3173	H	4.00875	2.57978	-0.99907
O	3.75183	1.64452	-1.01258	H	6.8186	-0.58727	0.10176
O	6.87096	0.31097	0.45756	H	3.09594	-3.48697	-0.34018
O	4.13673	-2.58153	2.98335	H	3.52031	-2.94474	-1.96904
H	5.36404	-1.82921	0.92506	H	4.79117	-3.25744	-0.78782
C	-7.32799	2.99345	0.37972	H	0.54983	-3.32962	-0.5611
H	2.32065	0.21888	-0.18052	H	-1.08836	-3.61379	0.01593
H	5.11605	0.12158	2.41818	H	-0.79239	-3.29902	-1.69746
C	-0.49264	-3.02344	-0.68153	H	0.30682	0.59579	1.81648

O	-0.04428	0.35038	0.94699	H	-4.05641	-1.62341	-2.99884
C	-3.30852	-1.64897	-0.97432	H	-2.89219	-0.32809	-2.65457
C	-3.13314	-1.37747	-2.46783	H	-2.32677	-1.98714	-2.88289
O	-3.51597	-3.07033	-0.76919	H	-2.97989	-3.55418	-1.41147
C	-4.65678	-1.05108	-0.47141	H	-4.71397	-1.24667	0.60754
C	-5.82919	1.14338	0.20553	H	-3.87239	0.95096	-0.60458
C	-5.92487	2.65355	-0.06912	H	1.95246	-0.36854	-2.43149
O	-8.08376	1.88216	0.44421	H	-5.48731	-2.67045	-1.09133
C	-7.29602	0.68272	0.10476	H	-5.91839	2.81743	-1.15753
C	-4.85969	3.52716	0.58243	H	-7.55361	0.4317	-0.92923
O	-7.78599	4.08813	0.65357	H	-8.80155	-0.59005	0.98008
H	-0.46095	-0.98528	-2.56583	H	-7.20823	-1.34302	0.79803
C	3.78087	-2.85349	-0.91151	H	-7.48189	-0.14415	2.08675
H	-5.14054	0.58622	-1.76562	H	-3.86667	3.26669	0.20532
H	-2.17541	-0.0325	-0.19355	H	-5.04043	4.5839	0.36582
H	6.88887	3.52655	-2.16577	H	-4.86019	3.39402	1.66916

Table S5. The single point energy for the lowest-energy conformer of **1a-1d** in the quantum-chemical ^{13}C NMR, ECD calculations, and calculations of optical rotations.

Conf.	Single Point Energy (Hartree)	Conf.	Single Point Energy (Hartree)
1a	-1927.848096	1c	-1927.832446
1b	-1927.750437	1d	-1927.865250

Table S6. The imaginary frequencies for the lowest-energy conformer of **1a**.

No.	Freq. (Hz)	IR	No.	Freq. (Hz)	IR
1	13.33	1.9789	136	1137.16	100.2822
2	14.27	0.6479	137	1146.62	9.713
3	22.4	0.3415	138	1147.9	30.2841
4	27.16	1.2366	139	1153.97	34.5225
5	38.28	0.5223	140	1156.9	24.2336
6	45.52	0.1694	141	1165.78	34.1131
7	46.03	6.2454	142	1166.42	33.9573
8	68.57	0.4578	143	1173.47	14.9703
9	82.78	1.089	144	1177.85	41.7251

10	98.29	6.786	145	1185.86	65.4279
11	100.85	5.2069	146	1194.94	7.2717
12	112.11	0.9504	147	1208.56	284.8761
13	124.33	2.8891	148	1208.91	20.4939
14	132.35	3.8117	149	1225.36	28.5745
15	136.74	1.8241	150	1231.28	30.1756
16	144.95	1.4706	151	1239.46	11.4925
17	156.15	2.9512	152	1242.01	14.94
18	174.54	5.1033	153	1253.58	1.5491
19	176.52	6.1457	154	1259.97	38.1939
20	187.44	10.4867	155	1263.56	5.7172
21	193.67	5.7927	156	1265.66	69.7397
22	203.14	139.9447	157	1268.83	53.9745
23	213.21	5.855	158	1273.79	14.1784
24	214.49	27.5769	159	1275.7	30.5647
25	220.69	8.3003	160	1280.7	7.865
26	231.04	2.8911	161	1297.29	93.801
27	233.82	0.1076	162	1309.38	23.6654
28	236.34	0.0891	163	1312.44	20.3038
29	241.83	1.7528	164	1316.86	1.3755
30	251.25	1.7308	165	1321.43	3.8392
31	254.38	4.8888	166	1324.39	62.8755
32	257.52	3.9744	167	1326.39	30.525
33	264.9	1.0468	168	1332.49	32.2261
34	278.83	16.8018	169	1339.03	51.6825
35	281.9	4.8313	170	1344.53	38.7129
36	286.15	4.9626	171	1349.31	20.2355
37	289.93	23.9659	172	1351.42	13.7643
38	294.37	2.3601	173	1357.92	47.5524
39	300.77	2.409	174	1360.7	8.3113
40	310.09	0.7744	175	1366.34	28.4883
41	326.32	3.5438	176	1371.22	69.2547
42	331.49	40.0537	177	1372.84	28.7979
43	335.37	172.1407	178	1377.97	1.9823
44	339.18	48.344	179	1379.83	19.6015
45	348.42	22.1186	180	1384.34	22.693
46	361.38	12.0299	181	1387.99	16.3217
47	365.83	5.0283	182	1394.12	6.5618
48	368.18	7.1653	183	1395.9	54.6745
49	372.98	8.947	184	1405.45	21.3961
50	383.76	50.9936	185	1408.33	0.0041
51	387.69	0.7581	186	1409.71	5.4143
52	393.86	12.0303	187	1411.94	31.5792
53	400.76	3.2279	188	1417.36	7.0232

54	406.04	14.8103	189	1419.98	11.8331
55	419	23.4813	190	1420.19	9.2829
56	421.76	16.5522	191	1423.59	15.2574
57	436.06	68.0197	192	1425.65	10.2786
58	437.25	7.9128	193	1428.67	35.2029
59	443.95	32.6353	194	1431.85	5.2189
60	448.24	6.5369	195	1444.07	98.0216
61	457.71	40.2431	196	1463.28	7.9666
62	463.6	40.9341	197	1475.2	3.4215
63	473.61	11.3583	198	1476.21	9.2426
64	493.44	6.0973	199	1481	3.5293
65	508.61	2.6729	200	1483.81	0.3001
66	525.17	19.4054	201	1485.36	5.4422
67	531.69	12.4264	202	1487.92	9.844
68	547.66	113.8354	203	1488.45	2.9363
69	553.44	204.0345	204	1489.3	4.3168
70	559.93	8.2353	205	1494.95	3.9276
71	567.43	31.074	206	1495.55	15.7738
72	570.4	11.8981	207	1495.91	2.3501
73	585.47	7.2422	208	1496.69	4.3942
74	606.05	14.478	209	1496.92	4.7373
75	610.17	26.4945	210	1498.53	4.5963
76	620.08	11.4401	211	1499.18	2.3905
77	646.99	6.6486	212	1501.06	20.1151
78	657.05	10.0875	213	1507.95	4.6058
79	671.57	8.0476	214	1511.27	3.0791
80	677.19	9.4866	215	1515.7	3.2615
81	682.91	1.9725	216	1523.29	12.1133
82	708.42	10.2776	217	1680.91	191.1193
83	714.89	15.0577	218	1697.19	788.706
84	725.59	6.1984	219	1756.62	5.1995
85	732.55	28.5804	220	1794.68	735.3869
86	743.13	1.2784	221	3021.8	59.3306
87	770.54	8.0767	222	3022.54	10.5608
88	790.79	4.3099	223	3023.43	49.3104
89	801.03	28.6739	224	3033.95	32.7801
90	814.93	19.7265	225	3037.19	53.2148
91	821.83	21.282	226	3045.87	44.3731
92	837.59	2.5189	227	3048.79	7.5804
93	849.37	10.0488	228	3052.11	31.9594
94	857.97	20.58	229	3053.79	11.8905
95	867.64	6.1401	230	3056.76	95.2785
96	881.56	5.6985	231	3056.93	12.9535
97	888.8	32.0456	232	3058.39	13.6888

98	894.09	72.141	233	3063.38	22.8503
99	901.43	85.1993	234	3068.41	34.5096
100	909.24	15.9582	235	3070.32	7.7514
101	916.01	25.6177	236	3070.65	29.2735
102	922.87	1.8878	237	3070.79	64.2997
103	925.4	6.0875	238	3070.93	39.247
104	935.85	8.2907	239	3074.43	30.0802
105	945.31	13.2662	240	3075.43	35.04
106	951.39	87.5454	241	3075.58	18.339
107	958.81	43.4801	242	3078.94	58.4157
108	963.48	38.9899	243	3099.92	98.91
109	976.97	34.6147	244	3100.16	5.8541
110	977.5	11.8453	245	3102.51	97.0966
111	985.24	16.799	246	3102.62	19.7325
112	987.73	35.1724	247	3108.32	35.5688
113	992.26	14.1268	248	3112.88	41.2978
114	1012.82	7.0305	249	3115.61	27.0678
115	1015.66	9.4154	250	3116.22	61.7275
116	1027.31	8.8417	251	3118.68	41.9101
117	1034.14	11.2942	252	3125.68	44.8155
118	1039.45	115.733	253	3126.68	115.1942
119	1044.07	65.3331	254	3127.96	22.754
120	1055.76	34.5018	255	3130.72	47.8847
121	1058.37	115.0012	256	3131.04	50.214
122	1063.46	48.9174	257	3131.68	34.5675
123	1064.75	26.6268	258	3134.9	54.5691
124	1066.18	10.2229	259	3140.85	21.841
125	1068.25	35.5342	260	3146.02	26.2892
126	1070.03	37.9353	261	3148.53	42.6078
127	1084.76	25.2024	262	3152.72	48.0034
128	1090.42	86.4851	263	3155.64	48.1699
129	1093.54	42.5437	264	3163.05	37.1947
130	1096.52	39.169	265	3196.82	11.2318
131	1099.72	40.3564	266	3674.4	160.0602
132	1111.95	6.8765	267	3740.48	89.8993
133	1115.95	33.5693	268	3771.82	63.2612
134	1128.97	40.3698	269	3780.82	64.5494
135	1132.98	15.9692	270	3787.85	77.0028

Table S7. The imaginary frequencies for the lowest-energy conformer of **1b**.

No.	Freq. (Hz)	IR	No.	Freq. (Hz)	IR
1	8.45	0.0299	136	1131.34	129.5555
2	23.66	0.5327	137	1135.39	42.8618
3	27.02	0.8559	138	1143.53	21.6319

4	31.46	2.1835	139	1147.58	65.8873
5	37.56	1.8808	140	1156.39	10.7452
6	48.97	3.5704	141	1160.42	50.0718
7	58.31	7.7359	142	1164.48	6.6611
8	62.09	0.8469	143	1169.3	57.668
9	81.68	1.5185	144	1173.2	20.2018
10	92.81	1.9282	145	1180.55	36.5632
11	109.82	0.4181	146	1185.3	34.1066
12	117.14	3.0158	147	1192.37	45.1867
13	122.47	4.6593	148	1200.9	62.2184
14	128.36	0.911	149	1215.93	336.2503
15	130.15	7.2151	150	1225.58	43.5475
16	156.38	7.5273	151	1233.72	22.7069
17	158.55	5.3864	152	1238.58	2.7694
18	169.65	4.2208	153	1244.72	10.4934
19	182.84	3.3064	154	1249.11	14.0096
20	198.58	1.8295	155	1249.87	40.9927
21	199.97	2.1977	156	1256.58	3.2935
22	217	18.4415	157	1260.28	23.1749
23	223.31	0.7356	158	1262.01	27.0975
24	226.25	13.3769	159	1273.09	2.519
25	232.58	123.3819	160	1274.98	11.9421
26	237	61.7705	161	1276.96	44.0419
27	239.51	73.9344	162	1289.14	8.2135
28	241.43	132.1618	163	1293.99	52.8971
29	246.05	17.0525	164	1300.57	45.1257
30	251.21	3.6204	165	1305.7	26.4814
31	257.13	7.0814	166	1313.49	11.4314
32	260.43	16.0454	167	1325.38	53.1547
33	263.77	11.9223	168	1330.35	6.852
34	272.02	19.073	169	1333.38	13.7688
35	281.44	16.9479	170	1337.07	17.7498
36	284.92	4.8437	171	1341.6	9.5412
37	299.4	4.1877	172	1348.74	14.1161
38	305.07	10.8505	173	1353.42	55.1121
39	310.28	10.8768	174	1357.8	20.6957
40	315.71	50.1309	175	1360.64	70.4183
41	321.67	41.5526	176	1363.88	21.4861
42	323.75	161.1369	177	1367.73	33.2305
43	327.08	31.2581	178	1371.75	27.5357
44	331.39	6.1255	179	1379.91	7.2514
45	341.15	8.2286	180	1383.33	39.4287
46	347.34	0.8215	181	1389.18	21.3258
47	365.26	133.6781	182	1389.27	27.8453

48	368.24	28.7121	183	1398.03	97.8796
49	372.96	32.4626	184	1399.34	4.1312
50	374.93	18.0403	185	1403.93	27.0574
51	382.3	18.8639	186	1408.7	5.0117
52	393.24	7.2261	187	1408.81	11.6111
53	401.88	24.2989	188	1411.74	96.9221
54	408.62	2.0292	189	1414.36	25.826
55	413.62	18.7353	190	1419.09	8.8869
56	418.15	14.3878	191	1424.33	4.5449
57	429.59	27.4183	192	1426.49	8.6099
58	445.93	9.253	193	1426.8	13.2429
59	448.17	5.4121	194	1433.33	7.0849
60	459.54	12.2765	195	1446.61	30.5414
61	468.68	76.4686	196	1467.27	19.1433
62	482.1	29.6007	197	1477.65	12.6552
63	491.76	64.9018	198	1481.5	5.9732
64	501.23	19.7438	199	1487.79	0.6431
65	509.86	55.8256	200	1488.73	1.2963
66	518.22	13.8492	201	1490.12	3.1911
67	524.34	16.5326	202	1490.72	20.9014
68	530.02	20.6697	203	1491.87	4.8447
69	548.05	19.701	204	1494.03	5.7364
70	555.9	11.096	205	1494.96	1.0016
71	563.26	31.4261	206	1495.76	1.9885
72	566.7	3.4542	207	1495.99	2.3622
73	575.67	4.1551	208	1496.4	9.5217
74	593.63	11.2998	209	1500.08	4.3502
75	603.76	10.716	210	1501.4	7.8784
76	615.85	11.5418	211	1503.04	2.1146
77	639.46	10.6843	212	1503.87	13.368
78	652.18	1.265	213	1508.77	8.6929
79	656.47	27.8836	214	1510.7	2.5691
80	665.78	30.4212	215	1515.45	6.7991
81	686.64	0.4675	216	1519.63	2.6691
82	713.49	1.2568	217	1606.13	30.7364
83	714.2	1.3116	218	1680.75	852.2706
84	715.05	12.4738	219	1685.25	97.7137
85	724.83	13.5151	220	1791.11	735.6795
86	746.15	17.8341	221	2982.54	108.3241
87	775.84	3.4632	222	3006.2	56.5181
88	788.74	9.7984	223	3018.87	37.2466
89	816.24	17.5851	224	3036.93	111.7494
90	820.07	9.5765	225	3041.31	2.6348
91	826.96	4.7284	226	3044.12	98.7977

92	828.65	28.2066	227	3044.97	33.9195
93	848.61	3.4598	228	3049.51	42.3739
94	861.58	23.5543	229	3049.96	54.883
95	869.08	37.4495	230	3052.76	16.978
96	882.16	5.3227	231	3055.51	26.4804
97	887.24	46.107	232	3058.89	66.8224
98	898.79	36.0061	233	3062.81	19.7486
99	904.39	48.5912	234	3066.15	76.676
100	909.5	33.2152	235	3072.06	74.7025
101	912.53	14.3585	236	3074.64	32.0249
102	924.01	109.1262	237	3074.94	10.4414
103	928.15	18.8388	238	3077.24	19.0581
104	933.19	33.624	239	3085.8	13.2033
105	936.65	4.9367	240	3088.38	41.8288
106	946.36	30.5715	241	3094.9	23.6579
107	960.88	44.8936	242	3102.33	57.1786
108	965.42	117.8871	243	3108.63	52.2847
109	969.06	46.6065	244	3111.48	13.0697
110	978.08	29.849	245	3112.22	35.0272
111	980.17	3.7062	246	3112.7	78.655
112	992.93	35.0457	247	3113.6	20.3729
113	995.03	26.5319	248	3115.83	48.9864
114	996.58	17.4864	249	3122.08	66.9348
115	1011.65	27.3536	250	3124.17	2.5618
116	1017.69	26.8095	251	3125.15	129.7528
117	1021.42	48.0077	252	3127.23	51.1637
118	1034.67	12.7152	253	3129.44	41.4817
119	1039.12	10.8591	254	3129.96	73.111
120	1043.85	61.8013	255	3132.4	40.3609
121	1045.16	52.4743	256	3135.08	15.7282
122	1048.31	123.5005	257	3136.43	26.3341
123	1051.11	35.4101	258	3137.29	15.6461
124	1054.05	101.3224	259	3138.8	61.121
125	1062.86	17.1465	260	3139	21.766
126	1064.02	13.0022	261	3153.03	34.6444
127	1068.44	15.6485	262	3156.54	31.317
128	1074.53	14.2053	263	3160.87	33.9738
129	1082.07	60.8092	264	3174.95	26.8298
130	1085.63	8.2056	265	3194.43	13.1956
131	1091.05	39.8466	266	3721.52	146.2848
132	1102.78	2.8161	267	3780.13	59.4522
133	1105.26	32.4695	268	3783.45	55.8316
134	1108.41	28.3538	269	3788.85	57.4225
135	1115.01	10.9876	270	3791.43	83.8887

Table S8. The imaginary frequencies for the lowest-energy conformer of **1c**.

No.	Freq. (Hz)	IR	No.	Freq. (Hz)	IR
1	14.22	2.0187	136	1129.21	81.5846
2	16.82	3.3657	137	1138.93	31.5709
3	20.51	0.3014	138	1145.15	63.449
4	32.37	0.4959	139	1149.61	65.0354
5	37.14	6.2932	140	1160.4	20.5865
6	45.67	2.0672	141	1163.33	8.2509
7	53.14	3.9404	142	1168.14	5.3294
8	73.72	2.1906	143	1178.7	34.1962
9	85.03	0.9502	144	1180.87	21.1143
10	98.38	9.6565	145	1186.24	47.8618
11	107.33	0.2565	146	1195.95	2.4998
12	111.88	49.3192	147	1198.71	87.289
13	118.37	1.4365	148	1212.87	26.812
14	119.9	93.8804	149	1216.88	321.824
15	127.99	14.4491	150	1233.04	18.8073
16	128.94	19.6859	151	1234.31	11.1933
17	138.47	3.1047	152	1238.75	13.0813
18	140.64	12.9943	153	1246.82	30.9875
19	159.89	1.0074	154	1259.5	15.3323
20	171.02	2.618	155	1266.2	24.7946
21	185.31	0.8248	156	1268.07	33.9167
22	203.09	13.1284	157	1270.62	38.4655
23	211.28	15.5743	158	1282.21	4.0189
24	217.38	9.5093	159	1290.96	81.3466
25	227.91	3.2928	160	1294.39	37.7472
26	233.79	12.5705	161	1295.65	87.2817
27	235.17	3.4892	162	1301.9	10.7712
28	244.31	2.1383	163	1305.1	45.4513
29	247.99	189.429	164	1310.66	42.6436
30	253.08	8.2248	165	1322.68	65.8508
31	258.08	4.8291	166	1326.84	23.6482
32	262.29	6.5571	167	1329.99	15.877
33	266.23	5.8376	168	1332.31	3.8135
34	267.86	13.6754	169	1332.77	30.9656
35	279.91	15.8354	170	1336.76	15.1613
36	287.39	5.61	171	1341.5	31.3049
37	294.83	22.6841	172	1345.18	7.214
38	298	9.0437	173	1347.61	7.8975
39	301.39	12.1679	174	1360.97	113.9648
40	303.87	10.3822	175	1367.6	51.8817
41	307.31	99.5047	176	1370.67	17.5831

42	310.63	3.4007	177	1371.14	31.3794
43	316.43	0.6389	178	1381.91	23.3916
44	317.15	74.4698	179	1384.38	22.4443
45	337.32	9.7744	180	1388.43	11.2137
46	346.7	1.2636	181	1388.99	31.9666
47	353.13	21.3537	182	1394.73	37.5589
48	364.9	12.731	183	1397.23	4.6195
49	366.07	13.7485	184	1399.64	79.154
50	373.93	39.6603	185	1407.91	5.535
51	390.12	54.3121	186	1413.41	12.8653
52	393.58	63.784	187	1413.91	10.2903
53	397.21	22.946	188	1420.55	4.5263
54	400.43	105.1352	189	1421.49	14.7393
55	405.35	35.8093	190	1421.83	3.5642
56	411.68	29.1054	191	1426.36	18.3143
57	415.23	10.9559	192	1427.84	1.7543
58	437.3	4.5126	193	1432.2	15.4349
59	445.42	0.9259	194	1434.45	8.3147
60	452.96	4.7178	195	1456.95	33.5818
61	456.08	6.0867	196	1461.92	3.9565
62	464.47	10.8562	197	1464.92	8.411
63	480.11	1.8211	198	1475.41	9.7129
64	495.61	2.5719	199	1486.27	7.1724
65	510.26	7.2875	200	1486.96	5.3837
66	515.84	3.9702	201	1487.47	11.698
67	525.07	18.1982	202	1488.26	8.5688
68	534.24	21.9324	203	1490.87	3.8594
69	550.31	6.1678	204	1494.41	8.1873
70	555.88	4.4488	205	1494.68	0.6058
71	572.22	1.2618	206	1494.98	4.3071
72	576.57	12.9596	207	1495.74	5.4171
73	593.48	12.2455	208	1496.99	2.1362
74	602.47	6.0665	209	1498.24	5.5153
75	604.65	0.988	210	1503.18	0.6843
76	606.62	8.2526	211	1505.09	6.873
77	628.31	34.8702	212	1505.27	5.3547
78	655.03	24.4542	213	1508.63	0.3786
79	682.76	4.4613	214	1510.65	15.6268
80	691.88	2.3042	215	1517.82	5.0808
81	704.27	2.5673	216	1541.35	13.8853
82	710.32	1.3425	217	1685.69	503.3146
83	714	17.9029	218	1690.27	464.5367
84	727.56	25.158	219	1738.55	5.649
85	740.15	0.7548	220	1789.8	736.822

86	751.64	0.4138	221	3007.07	22.1593
87	775.24	8.2277	222	3010.27	80.4876
88	790.79	3.7271	223	3017.94	67.2666
89	801.94	2.0464	224	3023.31	43.186
90	813.08	23.1116	225	3037.12	62.3532
91	827.1	7.9507	226	3042.12	37.8631
92	837.01	1.9649	227	3050.42	28.9359
93	844.08	6.6712	228	3051.67	18.6879
94	853.94	15.018	229	3053.24	26.9668
95	866.71	24.1252	230	3056.56	49.2018
96	881.15	6.6292	231	3061.2	20.8471
97	887.63	20.7782	232	3062.88	55.8238
98	891.36	13.0075	233	3063.65	17.8218
99	901.61	53.3815	234	3066.66	29.0527
100	908.27	116.3376	235	3070.41	12.5225
101	913.48	26.0581	236	3073.14	56.9843
102	917.19	10.3254	237	3073.21	11.4881
103	929.68	14.8088	238	3075.45	69.675
104	937.91	2.598	239	3076.91	19.0428
105	950.82	21.1112	240	3083.68	39.8936
106	953.73	14.8972	241	3085.6	69.2421
107	966	113.8818	242	3095.33	48.8646
108	967.99	32.662	243	3098.12	21.4947
109	972.49	20.7058	244	3102.6	26.5526
110	976.92	15.0349	245	3104.22	50.5871
111	979.48	26.301	246	3107.58	19.2527
112	984.03	4.0587	247	3115.94	20.0043
113	991.4	38.7826	248	3119.64	39.763
114	999.19	3.8381	249	3120.55	76.1312
115	1021.45	16.2005	250	3127.55	16.5744
116	1031.21	7.6968	251	3128.33	49.9395
117	1039.24	13.7415	252	3128.92	111.3789
118	1040.06	1.7287	253	3129.15	5.1174
119	1046.5	80.4903	254	3131.39	29.6479
120	1048.59	245.0919	255	3132.33	20.0603
121	1050.61	30.1023	256	3133.09	68.5929
122	1057.03	12.1713	257	3134.98	58.6763
123	1059.51	127.637	258	3139.7	29.3441
124	1065.33	2.9736	259	3140.87	38.223
125	1070.45	31.7428	260	3148.55	14.9116
126	1074.24	13.889	261	3153.74	54.7321
127	1088.4	8.1769	262	3156.16	49.5838
128	1090.82	35.3767	263	3161.19	25.025
129	1098.42	26.2455	264	3165.13	31.9498

130	1101.69	8.5644	265	3200.83	11.548
131	1106.71	9.415	266	3758.9	89.4843
132	1110.36	77.5013	267	3793.02	49.613
133	1112.91	31.3625	268	3793.4	67.9172
134	1116.58	4.7257	269	3806.38	63.4199
135	1120.87	24.0121	270	3811.32	86.8544

Table S9. The imaginary frequencies for the lowest-energy conformer of **1d**.

No.	Freq. (Hz)	IR	No.	Freq. (Hz)	IR
1	13.35	0.8155	136	1130.67	83.0949
2	17.98	2.2142	137	1137.9	26.4223
3	29.14	0.9523	138	1145.39	11.7919
4	33.77	0.8387	139	1160.75	6.9417
5	42.43	0.2708	140	1166.93	18.4954
6	56.56	2.0433	141	1171.91	9.9221
7	66.1	2.6432	142	1174.05	37.1301
8	73.75	3.2395	143	1178.37	7.0065
9	81.87	2.0186	144	1184.9	11.1736
10	97.9	0.8211	145	1197.92	12.7038
11	103.25	3.8341	146	1206.26	2.5289
12	117.48	1.38	147	1209.98	289.2695
13	127.46	3.2118	148	1216.78	49.9782
14	132.68	1.0037	149	1226.76	12.5938
15	151.99	3.3819	150	1227.39	17.5859
16	159.3	11.5743	151	1233.16	5.6614
17	171	2.2354	152	1239.46	11.8754
18	179.07	1.4811	153	1256.24	29.8631
19	183.35	4.3462	154	1259.23	31.0592
20	193.02	2.0806	155	1263.37	10.2677
21	202.48	1.0893	156	1269.15	8.7533
22	208.44	0.24	157	1274.46	23.6772
23	212.49	2.6609	158	1275.57	29.9026
24	216.95	3.7666	159	1292.04	172.2925
25	225.85	8.8089	160	1300.68	131.7769
26	227.82	0.5109	161	1304.57	8.7622
27	243.96	0.963	162	1307.88	3.2457
28	247.28	0.2074	163	1314.29	2.2281
29	253.44	5.2925	164	1321.73	8.5996
30	267.5	0.3061	165	1324.18	19.0388
31	271.58	5.4683	166	1325.46	7.3872
32	273.16	8.0472	167	1330.11	125.4345
33	276.99	3.7746	168	1332.63	17.0967
34	281.29	11.3676	169	1342.48	20.1892
35	283.3	28.9098	170	1348.21	38.393

36	290.92	20.4598	171	1349.64	86.5715
37	301.29	9.4499	172	1353.89	56.0472
38	306.25	10.7629	173	1356.06	11.1422
39	313.68	7.6179	174	1359.17	21.9538
40	319.54	27.1132	175	1362.22	37.0018
41	328.51	35.906	176	1364.55	50.1033
42	332.8	219.1026	177	1367.81	22.5276
43	337.29	9.713	178	1377.31	2.8883
44	343.21	44.0048	179	1380.21	6.803
45	355.37	20.4978	180	1383.49	7.2177
46	358.31	8.0031	181	1384.77	51.0511
47	366.81	22.0851	182	1387.75	10.5868
48	369.54	46.1093	183	1396.37	30.9154
49	376.77	4.8865	184	1397.66	8.9528
50	378.7	28.7359	185	1401.3	101.7323
51	389.12	90.024	186	1404.14	12.8459
52	395.17	11.7075	187	1413.84	10.7775
53	404.6	165.3983	188	1418.07	9.5876
54	408.87	20.6877	189	1421.49	2.0554
55	419.79	35.1886	190	1422.55	4.2954
56	424.75	4.2689	191	1422.67	4.7345
57	436.11	9.0716	192	1423.6	48.5334
58	439.15	24.9767	193	1427.43	2.3821
59	447.2	10.8872	194	1432.74	11.5697
60	455.97	26.5261	195	1448.49	36.2831
61	476.01	26.0573	196	1462.01	5.8723
62	483.76	117.8212	197	1462.57	4.641
63	486.26	0.6426	198	1475.7	9.3338
64	495.65	21.8997	199	1476.69	10.2282
65	505.75	12.5223	200	1488.27	7.8551
66	506.5	4.1526	201	1488.97	4.2075
67	517.98	22.7436	202	1489.6	6.656
68	525.2	27.914	203	1490.66	1.9971
69	526.66	11.0928	204	1492.47	2.5516
70	551.72	5.1845	205	1493.35	15.1492
71	553.3	17.325	206	1495.34	14.5524
72	577.78	68.0637	207	1496.55	5.8454
73	592.35	10.1325	208	1497.12	9.8786
74	598.24	10.9679	209	1497.9	5.3821
75	602.31	7.355	210	1498.05	2.127
76	621.41	25.0036	211	1500.56	4.6888
77	633.45	1.2583	212	1505.24	4.6723
78	654.43	11.2061	213	1507.44	5.0618
79	685.35	1.2498	214	1509.41	6.0723

80	692.99	3.9947	215	1518.04	4.0382
81	697.64	19.5068	216	1532.49	4.5385
82	711.42	7.9073	217	1674.16	210.4911
83	720.47	9.6421	218	1698.09	793.2012
84	728.01	7.6386	219	1738.98	5.5879
85	749.62	0.2151	220	1794.14	731.768
86	752.58	2.3372	221	3019.14	7.0708
87	780.04	1.3368	222	3024.01	43.5227
88	802.94	1.293	223	3030.46	44.4612
89	805.93	17.2084	224	3036.69	36.661
90	813.05	14.7202	225	3038.4	70.0806
91	831.34	3.0525	226	3040.14	21.3945
92	832.82	17.0172	227	3047.97	13.9701
93	842.11	6.6943	228	3050.8	24.0577
94	857.28	20.2958	229	3052.62	32.7901
95	864.41	19.0394	230	3054.99	91.2727
96	877.06	22.5207	231	3056.59	30.2608
97	891.23	97.5094	232	3057.59	22.3782
98	895.95	27.4918	233	3058.81	20.2931
99	900.54	17.8281	234	3062.41	32.0826
100	906.39	12.4333	235	3064.46	44.747
101	913.34	13.2278	236	3071.03	7.568
102	927.16	66.3149	237	3071.66	55.3437
103	931.88	9.6474	238	3072.31	21.8192
104	936.06	18.22	239	3073.96	68.8004
105	942.35	39.8347	240	3075.63	26.0984
106	955.44	10.3178	241	3077.08	31.4116
107	961.59	2.7072	242	3081.63	20.6887
108	967.53	15.0116	243	3081.94	100.8237
109	971.45	116.9727	244	3082.53	46.8768
110	973.66	14.5145	245	3093.92	45.9319
111	980.71	4.9333	246	3098.76	41.3968
112	989.4	10.0184	247	3112.33	29.756
113	993.28	7.8932	248	3113.91	29.7809
114	1013.45	12.2398	249	3115.92	47.8129
115	1014.99	19.9939	250	3116.15	5.3669
116	1019.87	18.6193	251	3116.73	76.9924
117	1035.36	21.6667	252	3120.53	39.1025
118	1041.23	1.906	253	3120.58	99.7003
119	1043.78	76.6535	254	3124.69	55.1704
120	1049.03	95.8798	255	3126.17	38.9472
121	1053.46	1.4479	256	3127.45	51.6685
122	1059.69	5.979	257	3131.61	29.3709
123	1064.55	2.7578	258	3132.05	39.6274

124	1067.24	273.7799	259	3132.94	77.4222
125	1069.69	78.2664	260	3137.93	26.9268
126	1073.82	7.9215	261	3142.45	42.9544
127	1084.19	14.1282	262	3149.56	34.1607
128	1086.57	4.3844	263	3156.47	48.3481
129	1089.26	59.895	264	3160.48	8.137
130	1097.31	13.3969	265	3197.06	10.5554
131	1104.07	57.8124	266	3710.76	136.0735
132	1110.39	17.9578	267	3751.26	91.0403
133	1113.28	57.0896	268	3775.52	64.0695
134	1116.99	140.2729	269	3815.54	47.8282
135	1124.69	18.6006	270	3829.77	78.0354

Table S10. The experimental ^{13}C NMR data of **1** in methanol at 100 MHz and the calculated ^{13}C NMR data of **1a**, **1b**, **1c**, and **1d** in methanol at the B972/Def2-TZVP level.

	1 (δ_C, ppm)	**1a** (δ_C, ppm)	**1b** (δ_C, ppm)	**1c** (δ_C, ppm)	**1d** (δ_C, ppm)
1	38.3	40.0	40.0	39.8	35.6
2	119.4	118.9	120.1	118.3	118.0
3	131.3	137.4	137.9	139.7	139.2
4	43.6	42.2	44.4	41.9	37.6
5	72.1	71.0	78.4	71.9	72.4
6	36.5	36.9	36.9	39.1	35.6
7	53.2	53.7	68.4	50.2	51.6
8	39.2	41.7	42.7	40.3	35.9
9	44.2	43.0	44.7	43.2	42.2
10	73.2	74.0	78.7	74.3	73.1
11	35.7	36.9	36.5	38.5	33.0
12	169.2	177.3	188.6	177.6	179.2
13	122.7	119.0	136.3	119.8	119.3
14	206.0	210.4	209.2	209.4	209.7
15	21.5	20.4	23.5	21.0	19.1
16	32.4	30.0	29.7	32.7	29.6
17	48.6	46.8	48.2	43.4	47.5
18	85.1	85.8	89.8	89.4	85.9
19	31.8	29.4	29.5	28.0	29.5
20	21.5	20.3	20.8	19.8	19.1
21	50.4	50.8	62.0	48.8	50.5
22	18.0	13.0	15.3	18.0	13.4
23	26.1	21.6	25.2	25.1	19.9
24	23.1	21.5	24.6	21.3	19.2
25	77.7	77.2	83.3	80.0	79.5
26	20.6	19.0	20.0	19.7	16.2
27	75.0	75.8	82.6	76.6	73.4

28	34.8	36.0	34.0	35.9	31.3
29	49.7	48.9	50.6	46.8	47.9
30	43.5	41.8	43.5	40.5	37.1
31	181.8	185.9	190.1	188.4	185.9
32	15.9	9.7	14.0	15.5	9.7
33	81.8	83.1	86.1	83.0	84.0
34	19.6	18.4	18.2	19.5	15.5

Table S11. The NMR data of **1** in pyridine-d_5 at 600 MHz and The NMR data of cyasterone and 18-*epi*-cyasterone in pyridine-d_5.

	1 (pyridine-d_5)		**cyasterone** (pyridine-d_5)		**18-*epi*-cyasterone** (pyridine-d_5)	
No.	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	2.88 d (10.8) 1.99 d (10.8)	38.0				
2	5.24 s	119.3				
3		130.5				
4	2.93 d (19.2) 2.61 d (19.2)	43.3				
5		71.2	4.21 (1H, brs)	68.0	4.21 (1H, brs)	68.0
6	1.76 overlap 1.50 d (13.2)	35.7	1.79 (2H, m)	32.5	1.79 (2H, m)	32.5
7	3.31 d (13.2)	52.5	3.00 (1H, dd, 10.2, 2.8)	51.4	3.00 (1H, dd, J = 10.2, 2.8)	51.4
8		38.3		38.7		38.7
9	2.15 d (13.2) 1.94 d (13.2)	44.4	2.14 (1H, d, 13.2) 1.92 (1H, m)	38.0	2.14 (1H, d, *J* = 13.2) 1.92 (1H, m)	38.0
10		71.9	4.16 (1H, d, 11.5)	68.1	4.16 (1H, d, *J* = 11.5)	68.1
11	3.82 t (8.4)	34.6	3.59 (1H, m)	34.5	3.59 (1H, m)	34.5
12		166.5		165.7		165.7
13	6.34 s	122.1	6.28 (1H, s)	121.8	6.28 (1H, s)	121.8
14		202.6		203.4		203.4
15	2.00 m 1.77 m	21.2	1.76 (2H, m)	21.0	1.76 (2H, m)	21.0
16	2.27 overlap 2.00 overlap	32.0	2.63 (1H, m) 2.06 (1H, m)	32.1	2.63 (1H, m) 2.06 (1H, m)	32.1
17		47.9		48.2		48.2
18		83.9		84.1		84.1
19	2.65 dd (12.6, 4.2) 2.07 d (12.6)	31.9	2.22 (2H, m)	31.9	2.22 (2H, m)	31.9
20	2.49 t (10.2) 1.75 d (10.2)	20.8	2.46 (1H, m) 2.06 (1H, m)	21.4	2.46 (1H, m) 2.06 (1H, m)	21.4
21	2.89 overlap	49.9	2.87 (1H, brt, 9.6)	50.1	2.87 (1H, brt, *J* = 9.6)	50.1
22	1.26 s (3H)	17.7	1.24 (3H, s)	17.9	1.24 (3H, s)	17.9
23	1.10 s (3H)	25.8	1.07 (3H, s)	24.5	1.07 (3H, s)	24.5
24	1.65 s (3H)	23.0				
25		76.6		76.8		76.8
26	1.60 s (3H)	20.8	1.57 (3H, s)	21.0	1.57 (3H, s)	21.0
27	3.98 d (10.8)	73.8	3.94 (1H, d, 9.9)	74.1	3.88 (1H, d, *J* = 10.6)	76.5
28	1.78 m (2H)	34.3	1.76 (2H, m)	34.5	1.79 (2H, m)	30.9
29	2.28 dd (12.0, 7.2)	48.6	2.22 (1H, m)	48.8	2.46 (1H, m)	46.1
30	2.45 dq (10.8, 7.2)	42.3	2.35 (1H, dq, 11.5, 6.5)	42.5	2.33 (1H, dq, *J* = 11.5, 6.5)	38.7
31		179.0		179.1		179.1
32	1.38 d (7.2, 3H)	15.8	1.36 (3H, d, 7.1)	15.9	1.30 (3H, d, *J* = 6.5)	16.4
33	4.08 dq (9.0, 6.0)	79.7	4.03 (1H, dd, 9.3, 6.0)	79.9	4.98 (1H, t, *J* = 6.8)	78.7
34	1.34 d (6.0, 3H)	19.2	1.32 (3H, d, 6.0)	19.4	1.17 (3H, d, *J* = 7.0)	14.4

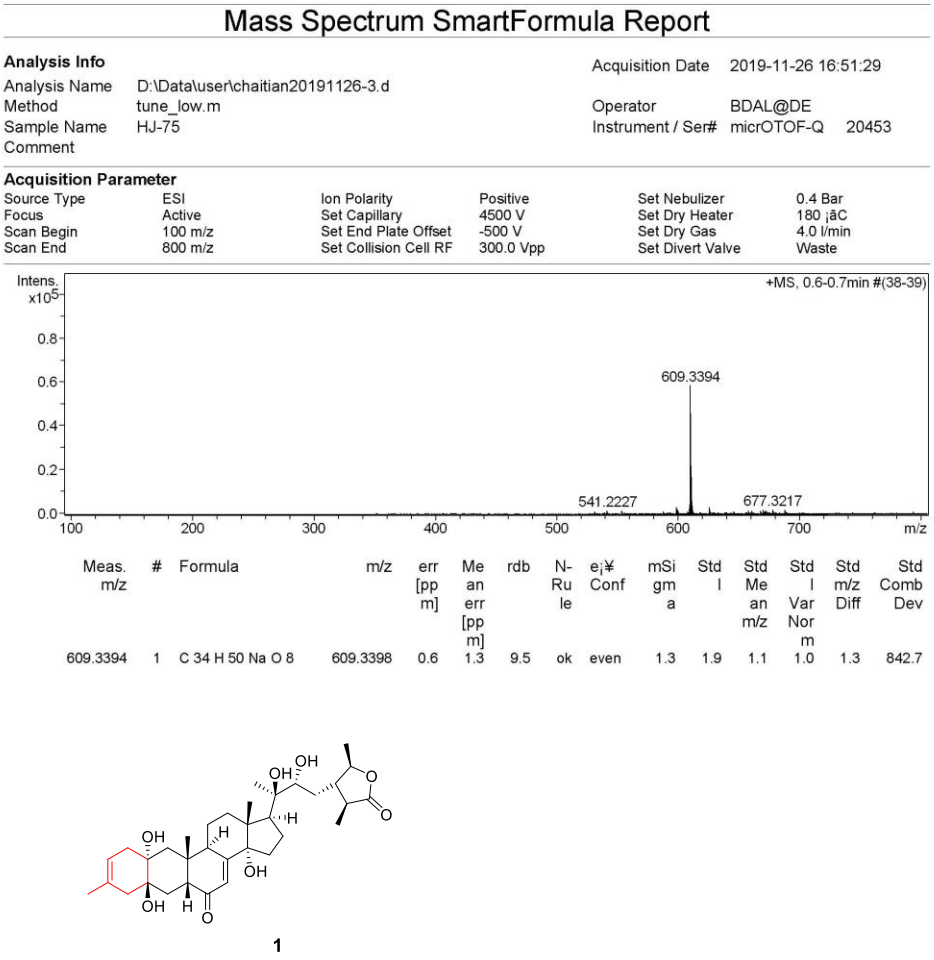


Figure S3. HRESIMS Spectrum of **1**

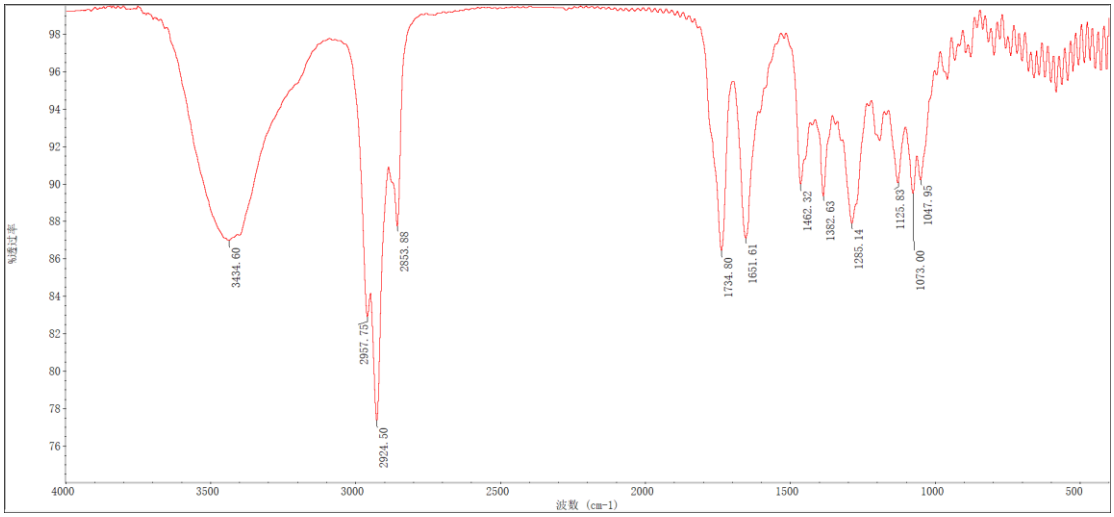
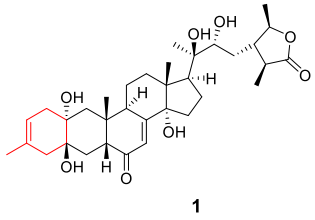


Figure S4. IR Spectrum of **1**



1

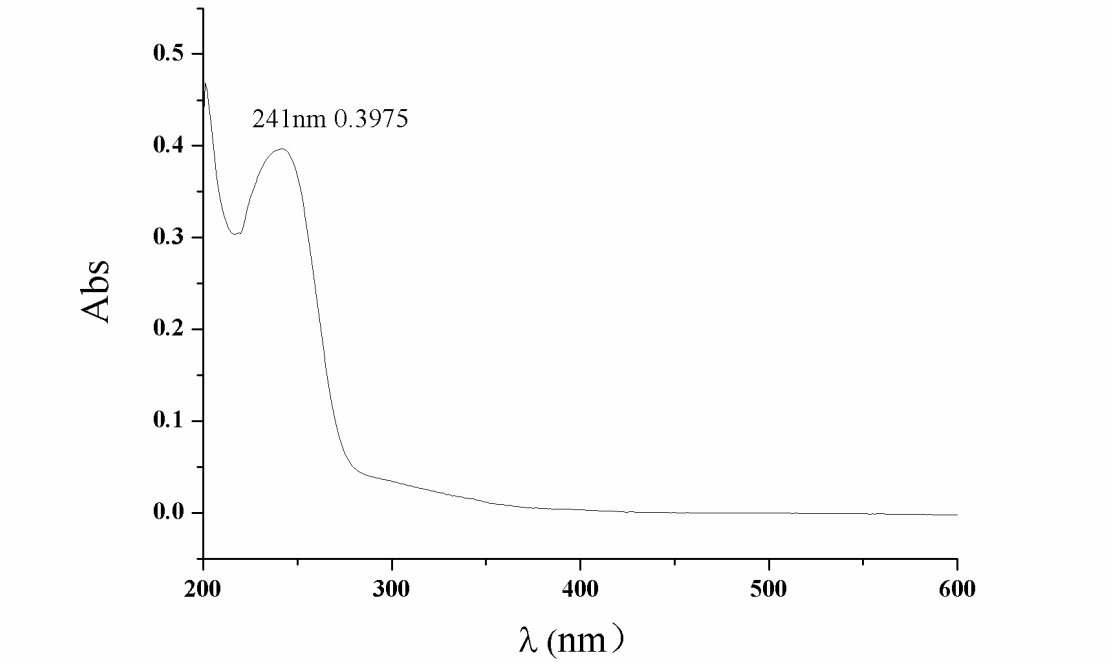


Figure S5. UV Spectrum of **1** (MeOH)

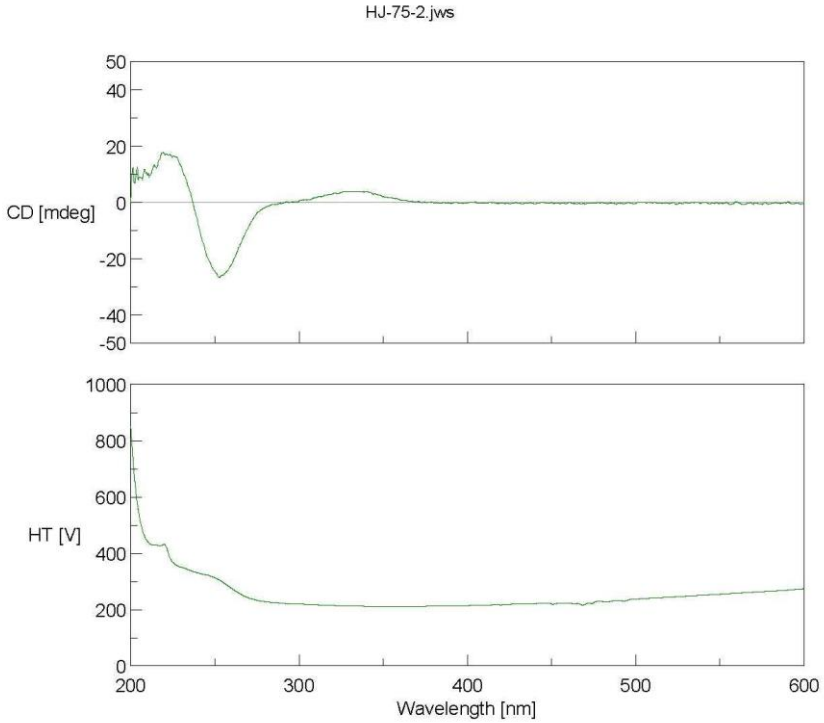


Figure S6. CD Spectrum of **1** (MeOH)

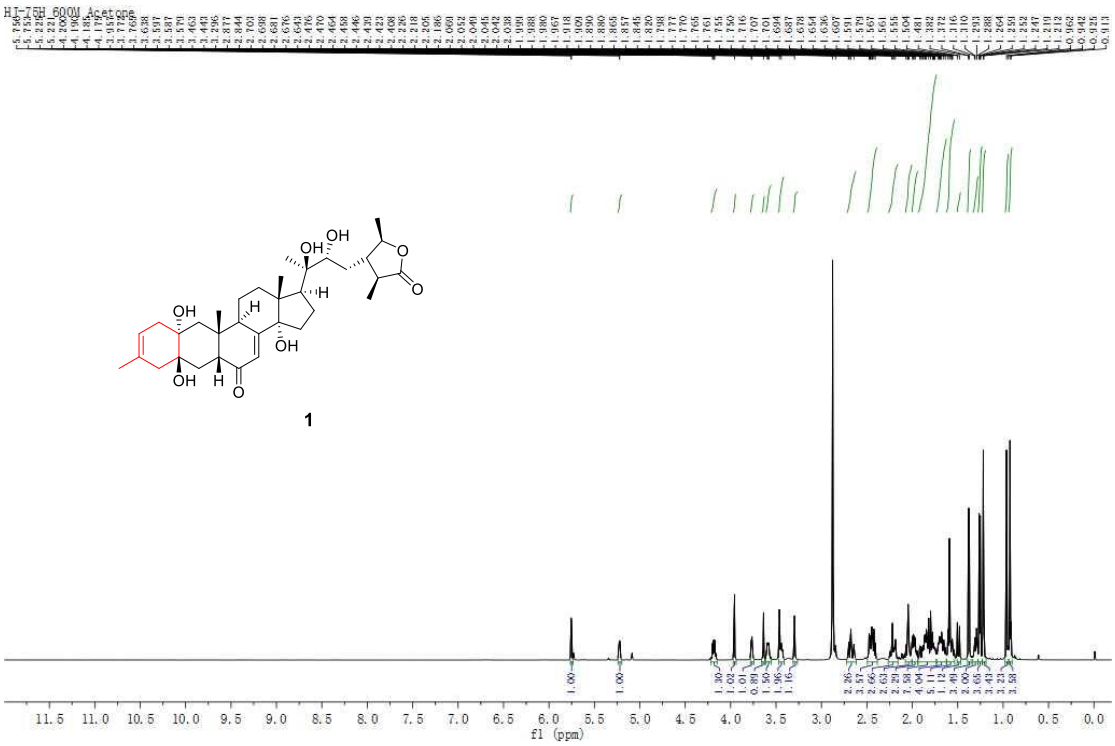


Figure S7. ^{1}H NMR Spectrum of **1** (600 MHz, acetone-d_6)

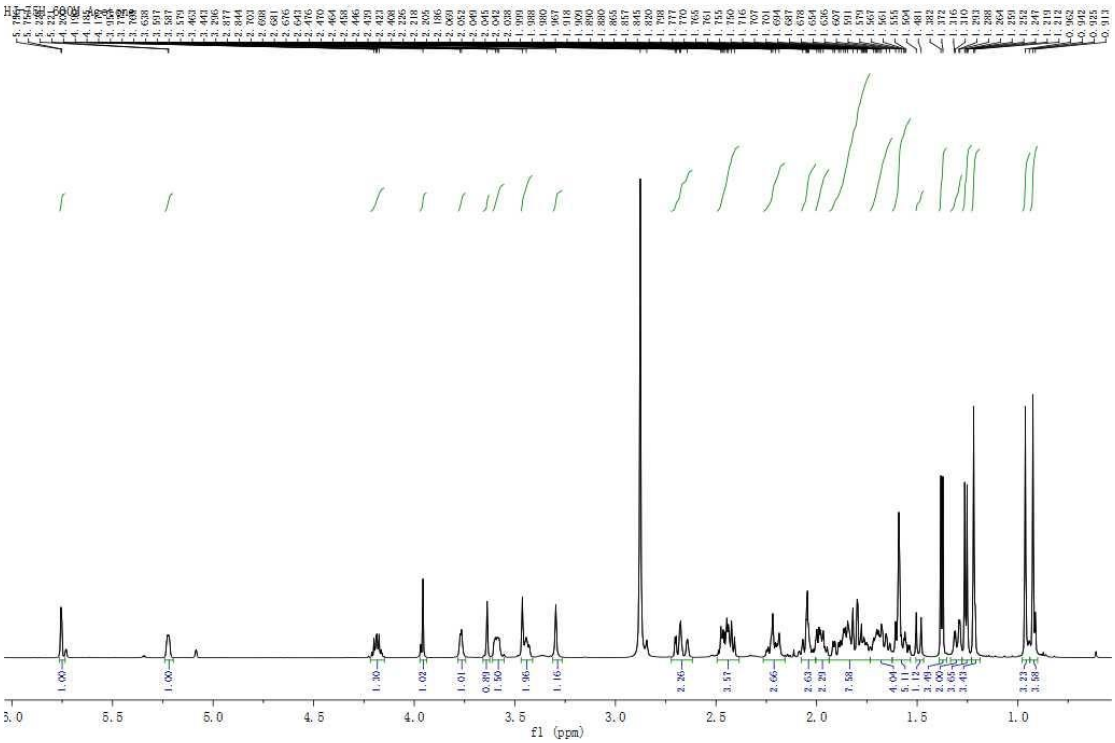


Figure S8. An expansion of the 0.5−5.8 ppm region of the ^{1}H NMR Spectrum of **1** (600 MHz, acetone-d_6)

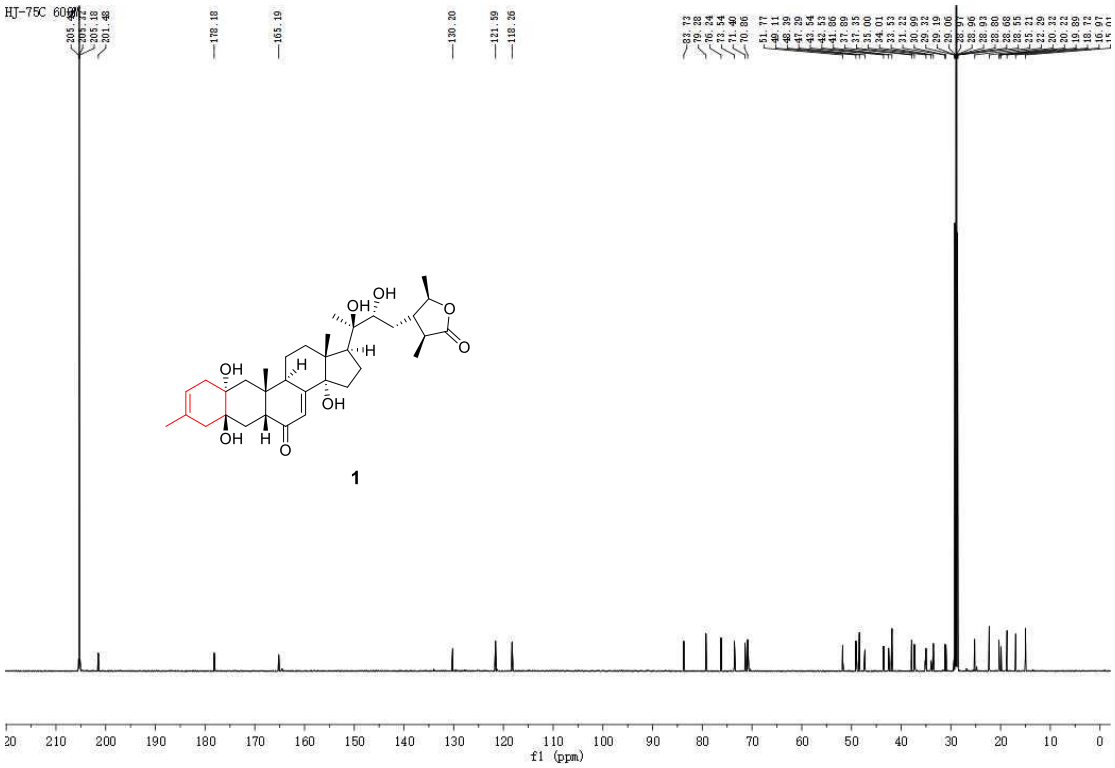


Figure S9. ^{13}C NMR Spectrum of **1** (150 MHz, acetone-d_6)

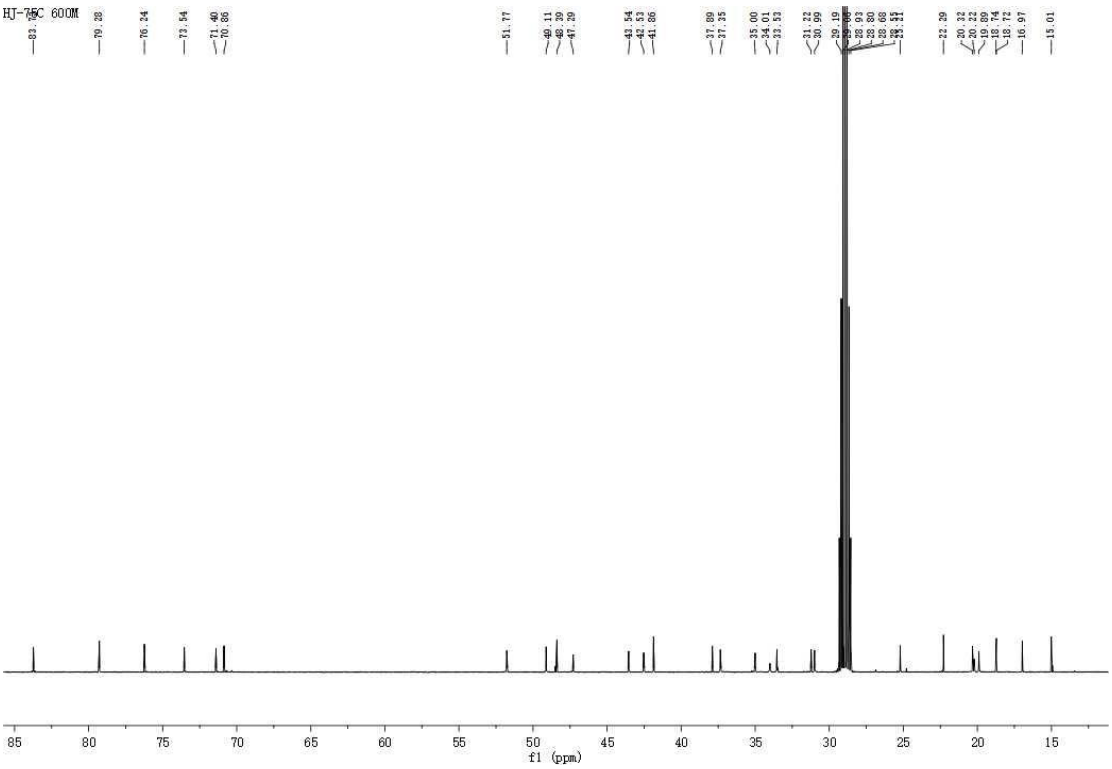


Figure S10. An expansion of the 10−85ppm region of the ^{13}C NMR Spectrum of **1** (150 MHz, acetone-d_6)

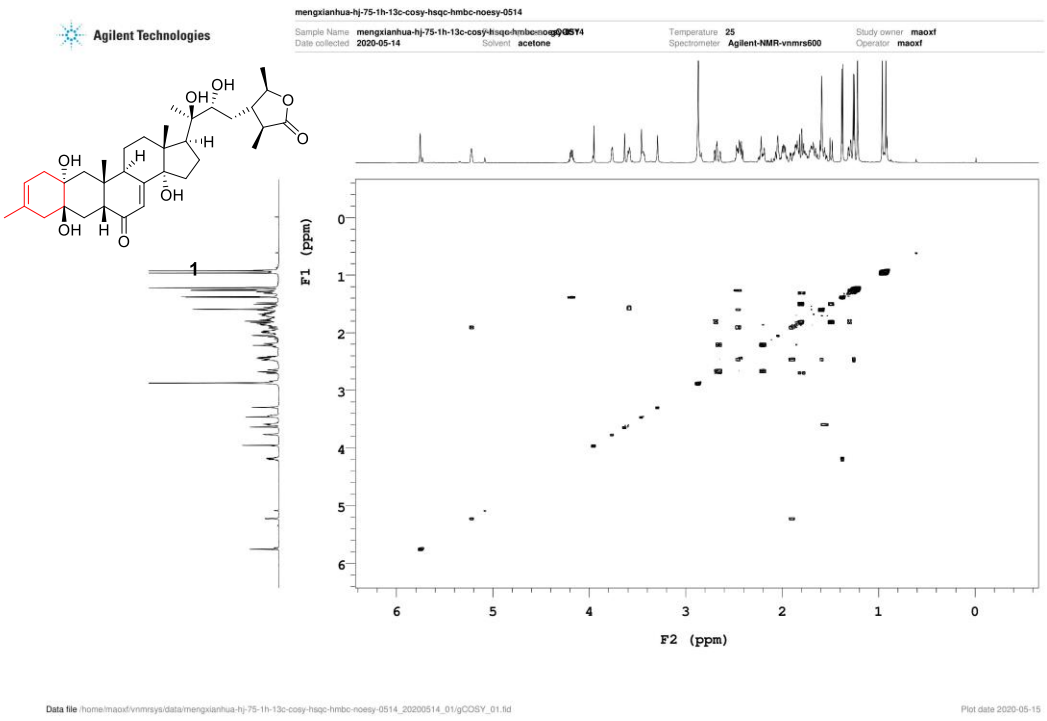


Figure S11. ^{1}H-^{1}H COSY Spectrum of **1** (600 MHz, acetone-d_6)

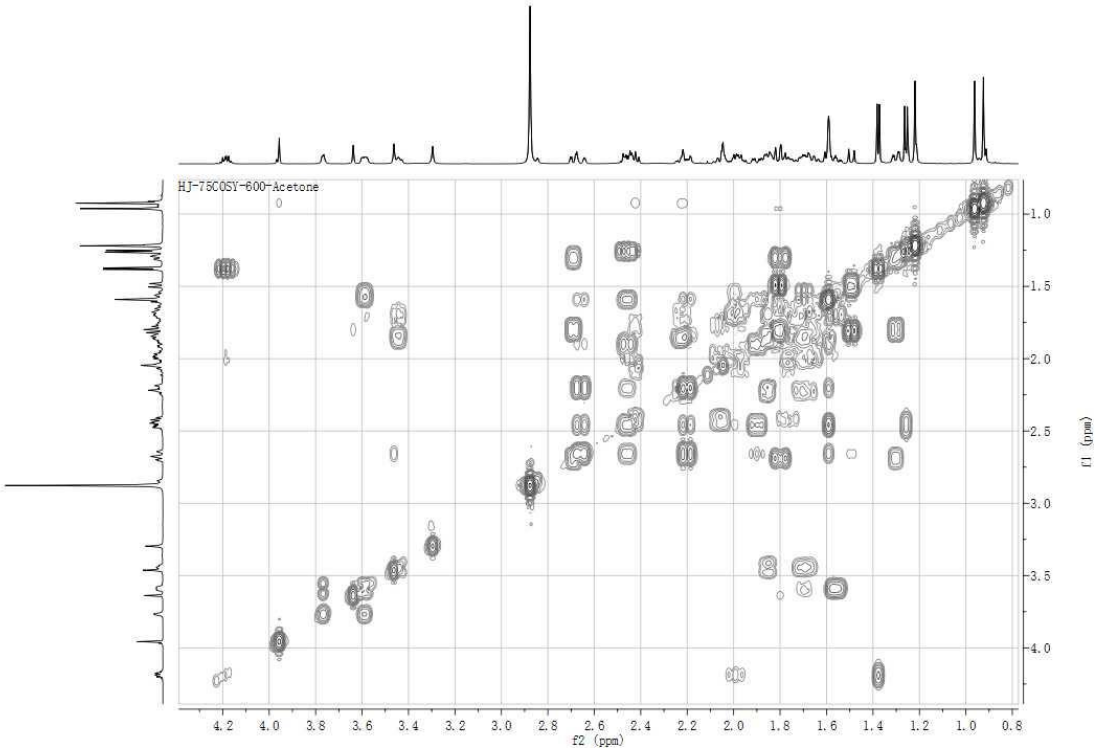


Figure S12. An expansion of the 0.8−4.4 ppm region of the ^{1}H-^{1}H COSY Spectrum of **1** (600 MHz, acetone-d_6)

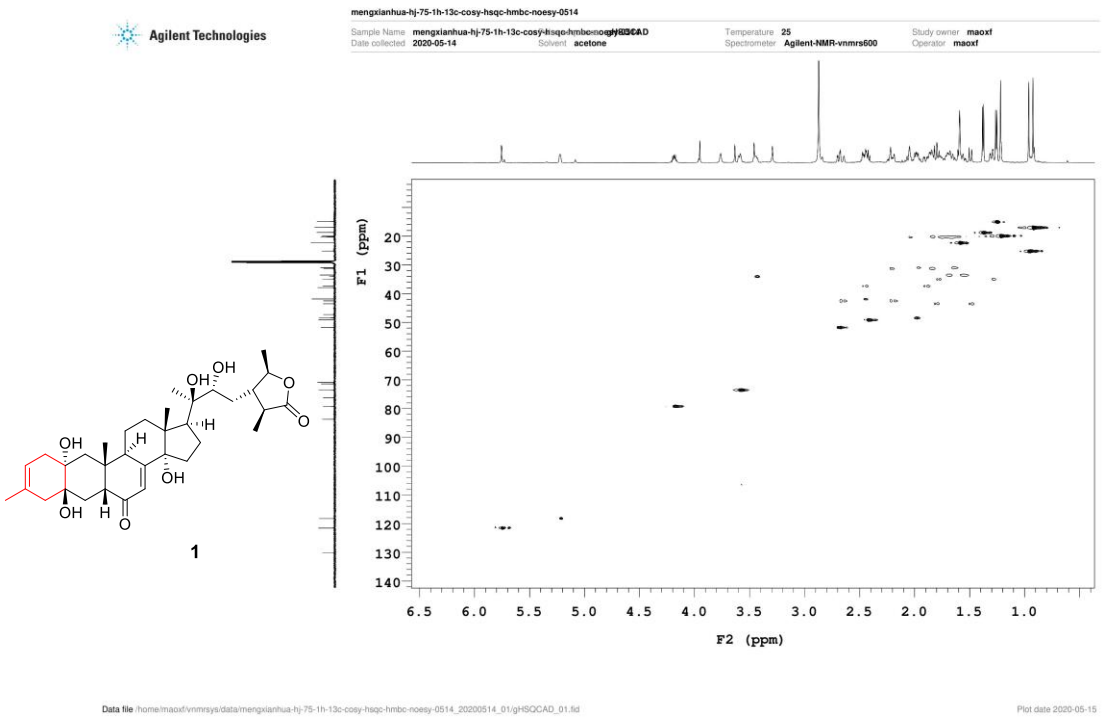


Figure S13. HSQC Spectrum of **1** (600 MHz for ^{1}H NMR, acetone-d_6)

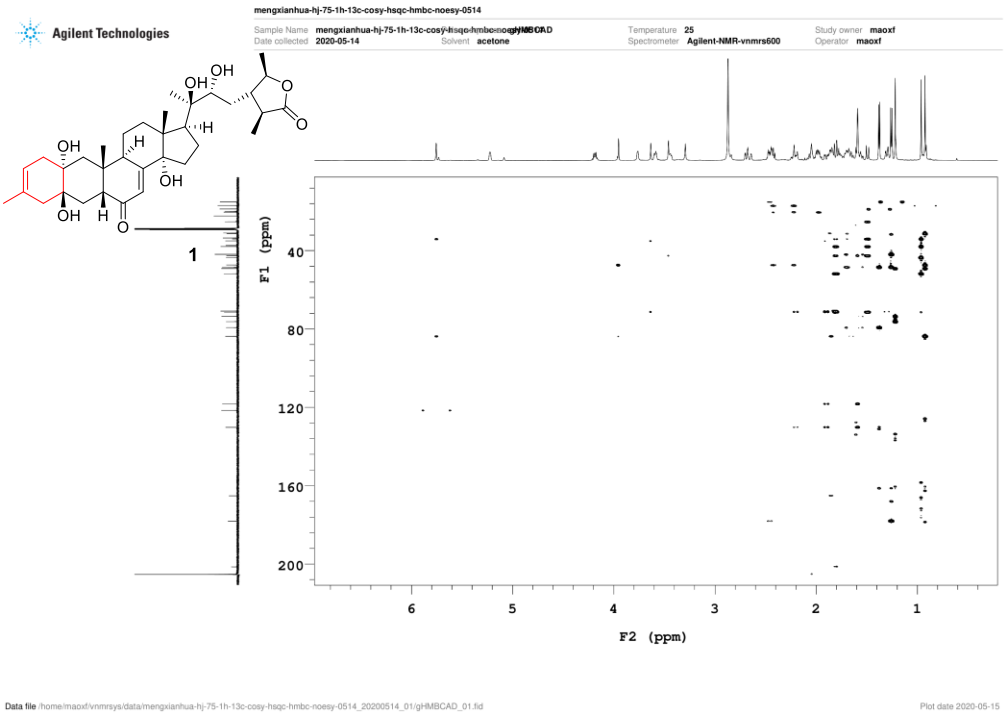


Figure S14. HMBC Spectrum of **1** (600 MHz for ^{1}H NMR, acetone-d_6)

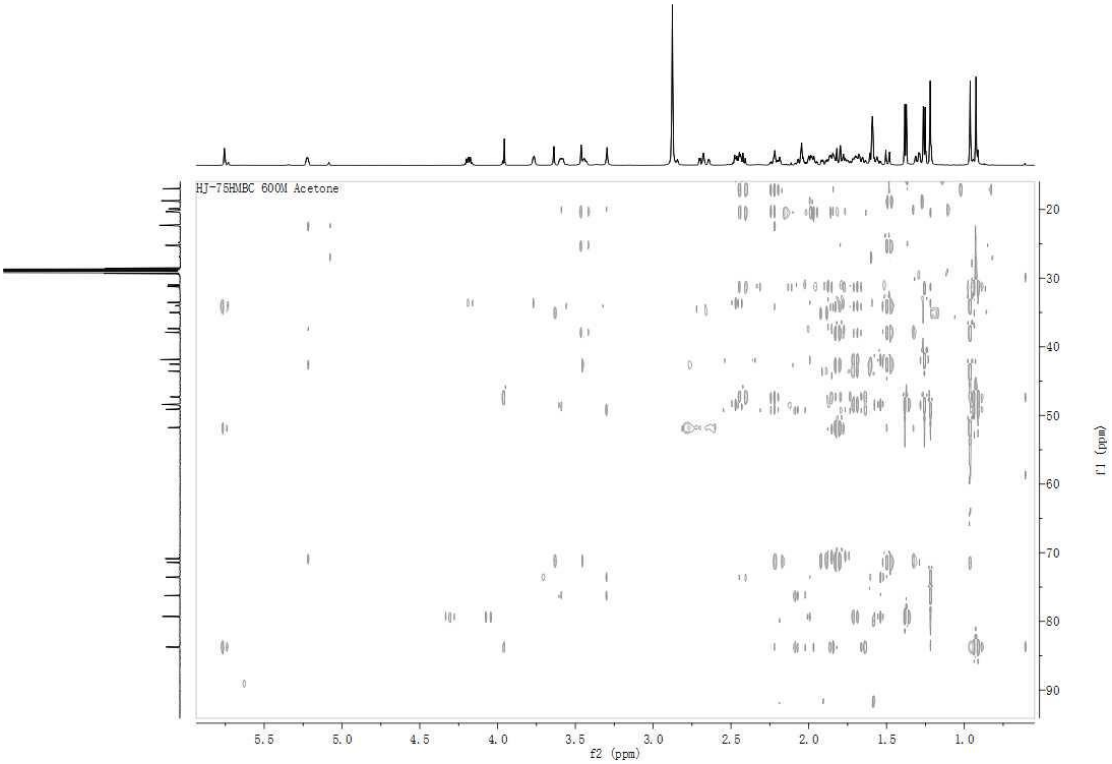


Figure S15. An expansion of 0.5-6.0 (^{1}H)/ 15-95 (^{13}C) ppm region of the HMBC Spectrum of **1** (600 MHz for ^{1}H NMR, acetone-d_6)

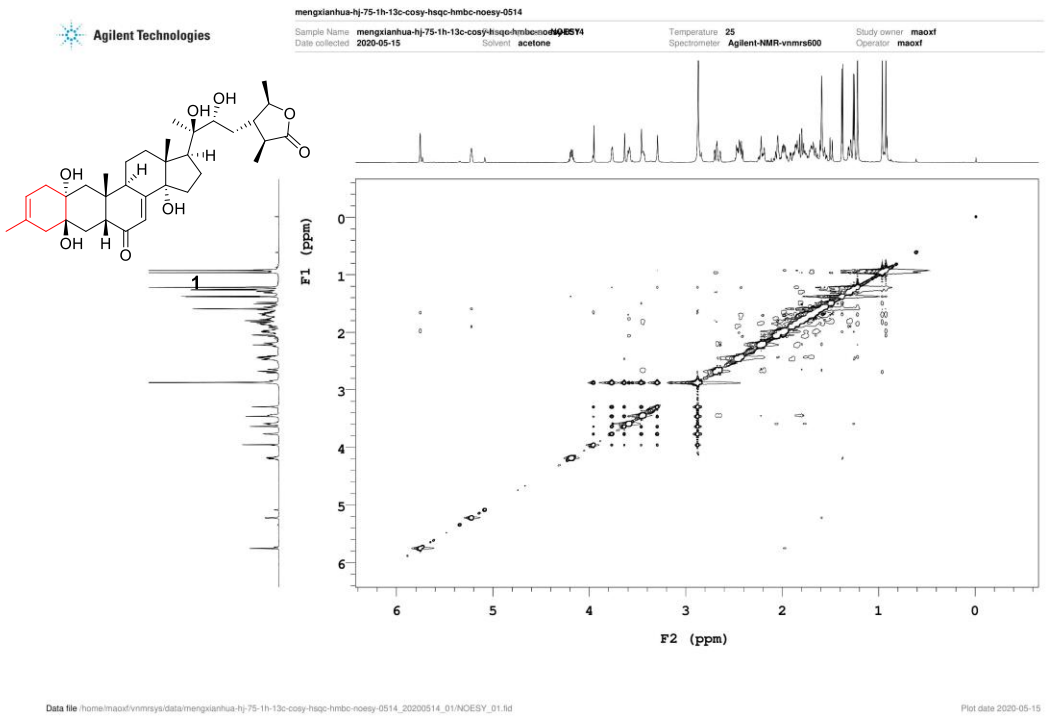


Figure S16. NOESY Spectrum of **1** (600 MHz, acetone-d_6)

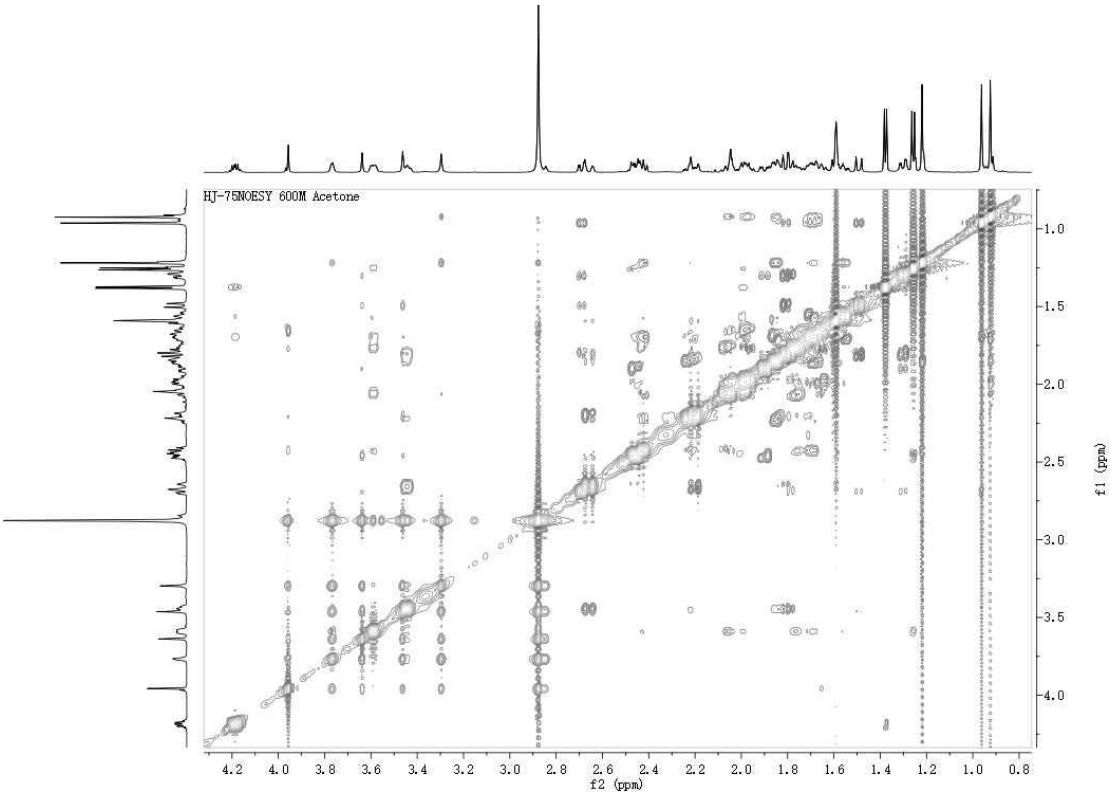


Figure S17. An expansion of 0.8-4.3 ppm region of the NOESY Spectrum of **1** (600 MHz, acetone-d_6)

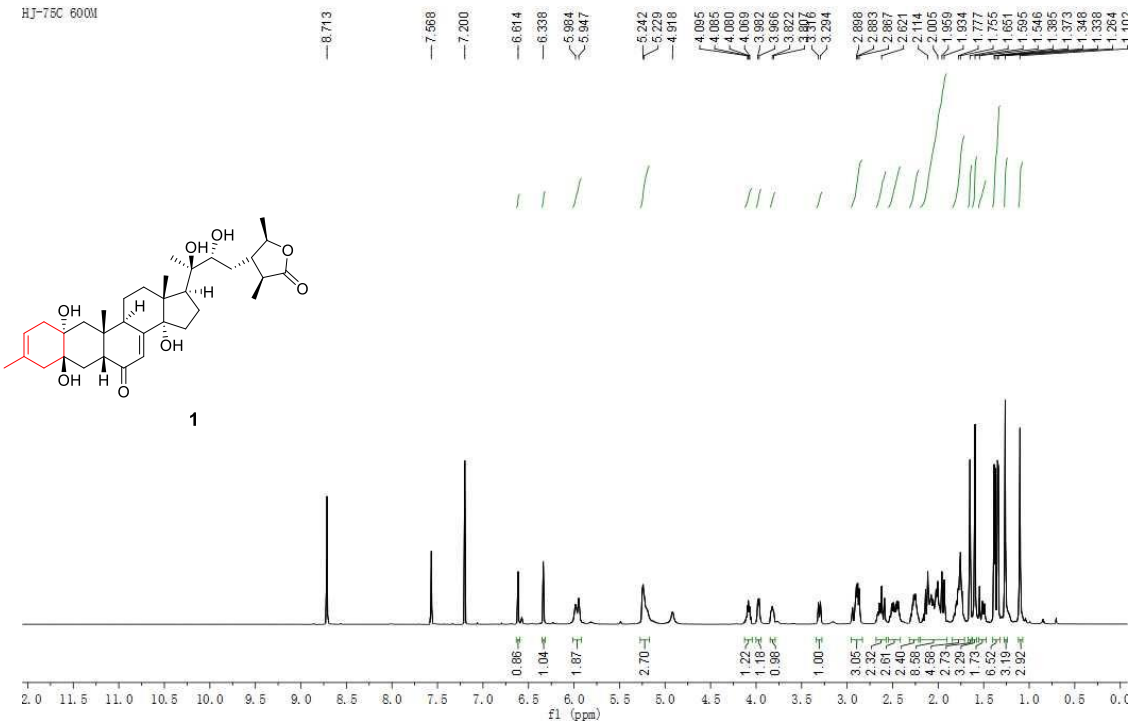


Figure S18. ^{1}H NMR Spectrum of **1** (600 MHz, pyridine-d_5)

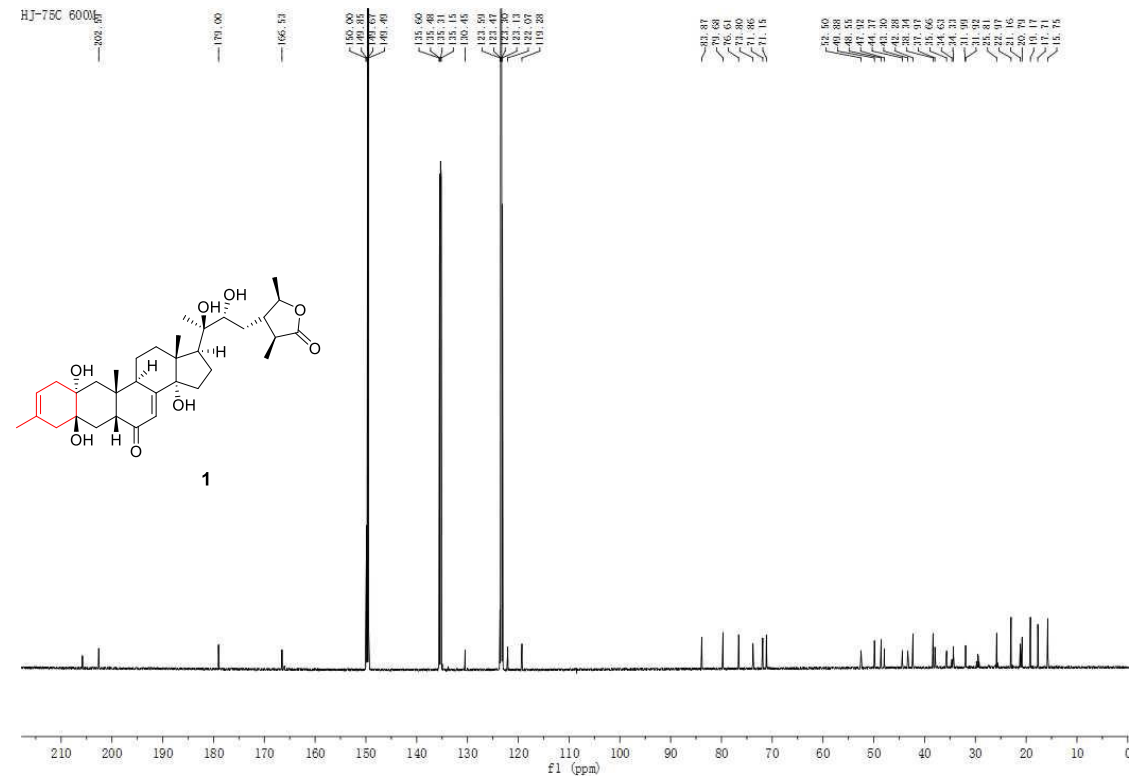


Figure S19. ^{13}C NMR Spectrum of **1** (150 MHz, pyridine-d_5)

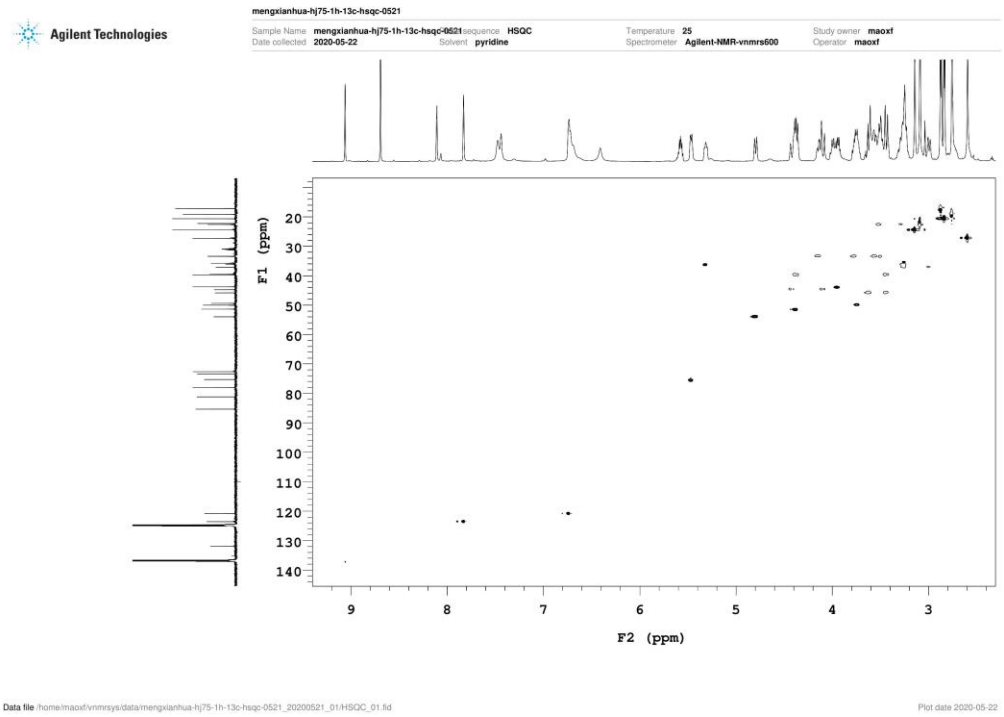


Figure S20. HSQC Spectrum of **1** (600 MHz for ^{1}H NMR, pyridine-d_5)

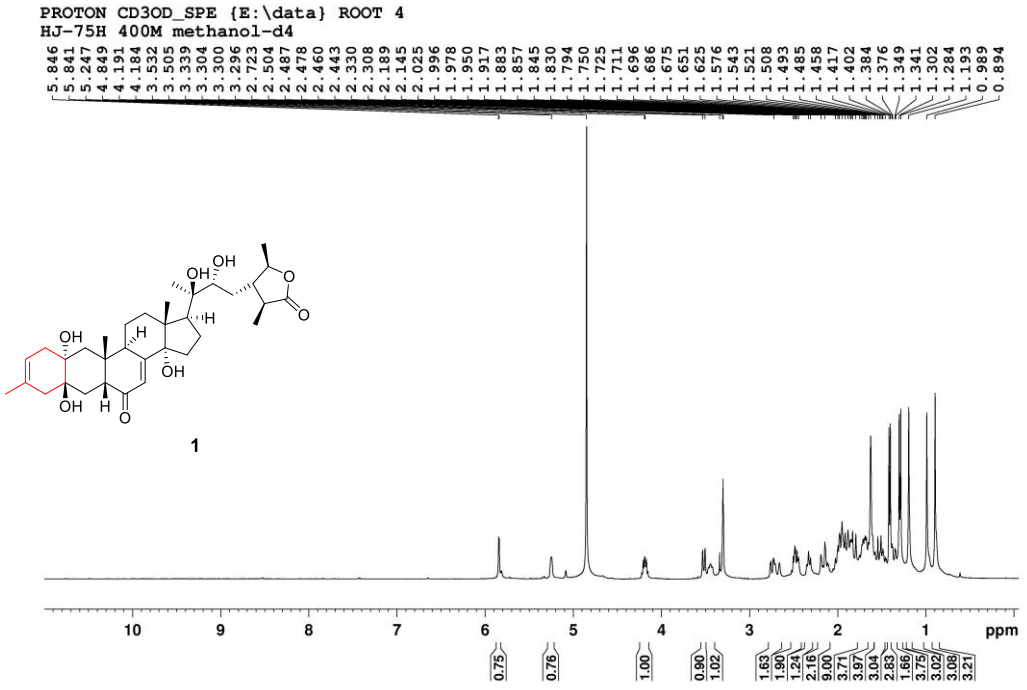


Figure S21. ^{1}H NMR Spectrum of **1** (400 MHz, methanol-d_4)

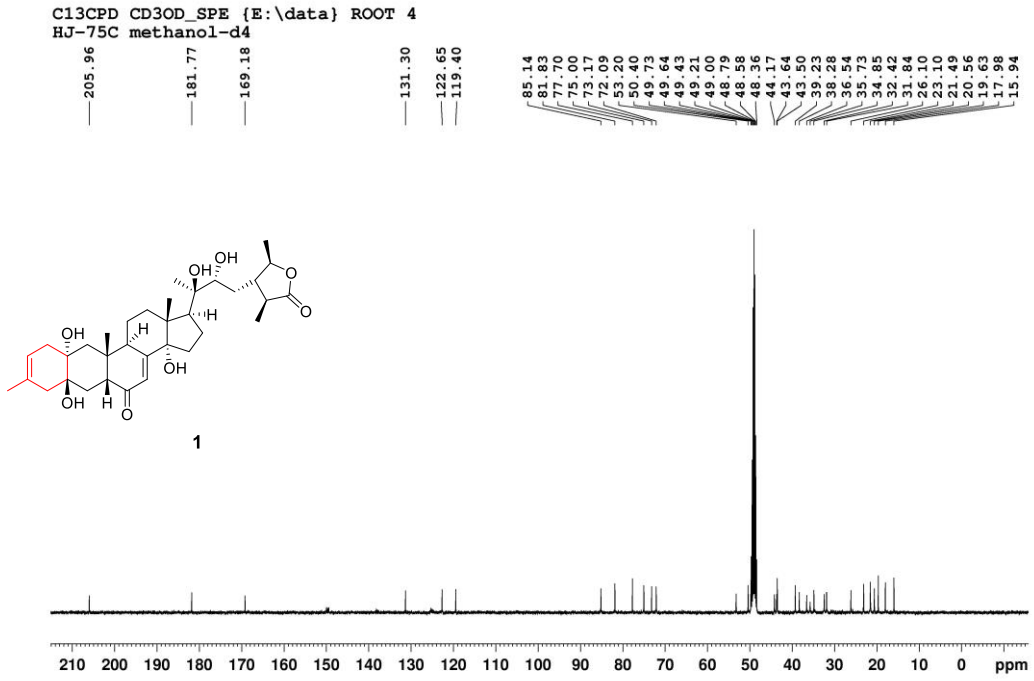


Figure S22. ^{13}C NMR Spectrum of **1** (100 MHz, methanol-d_4)

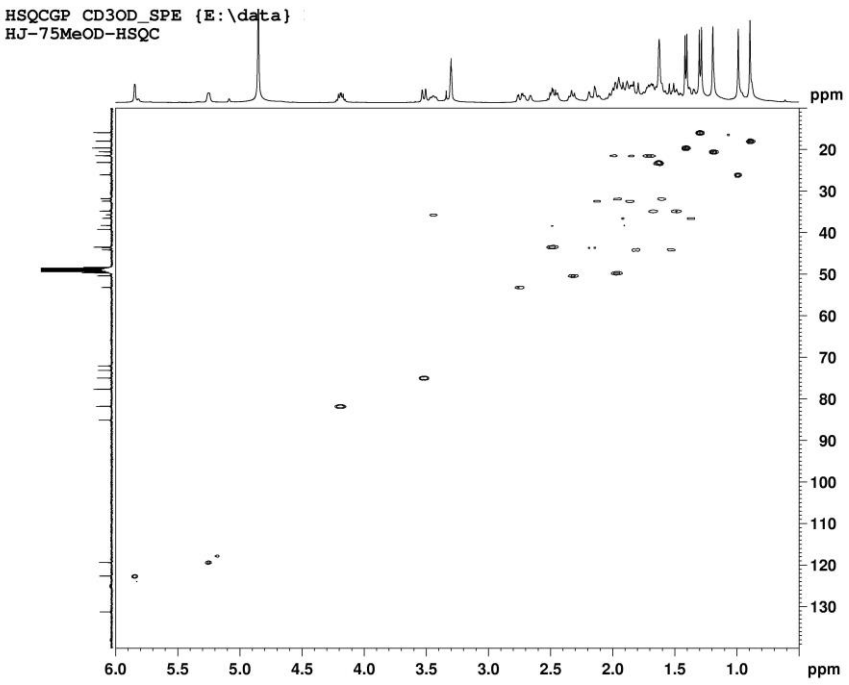
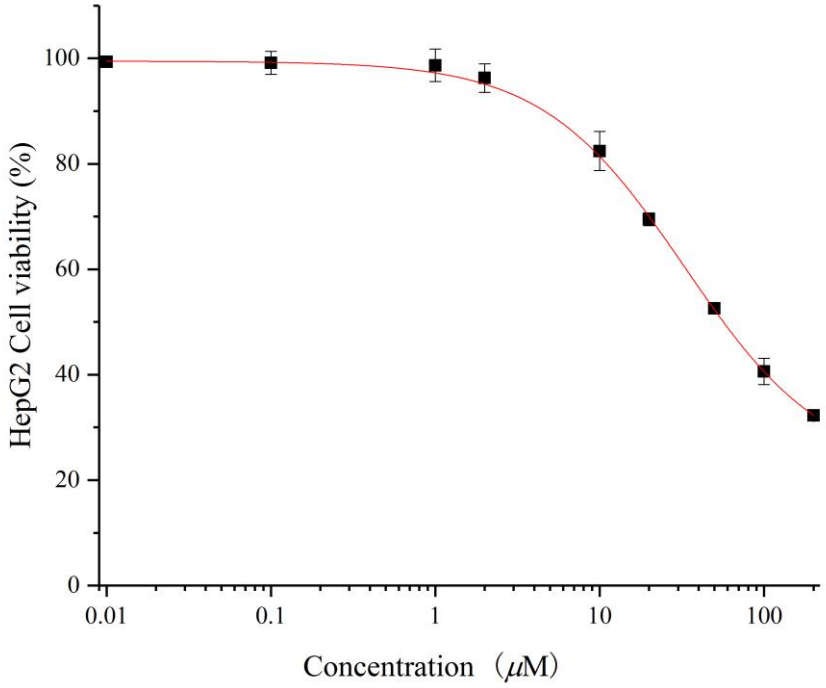
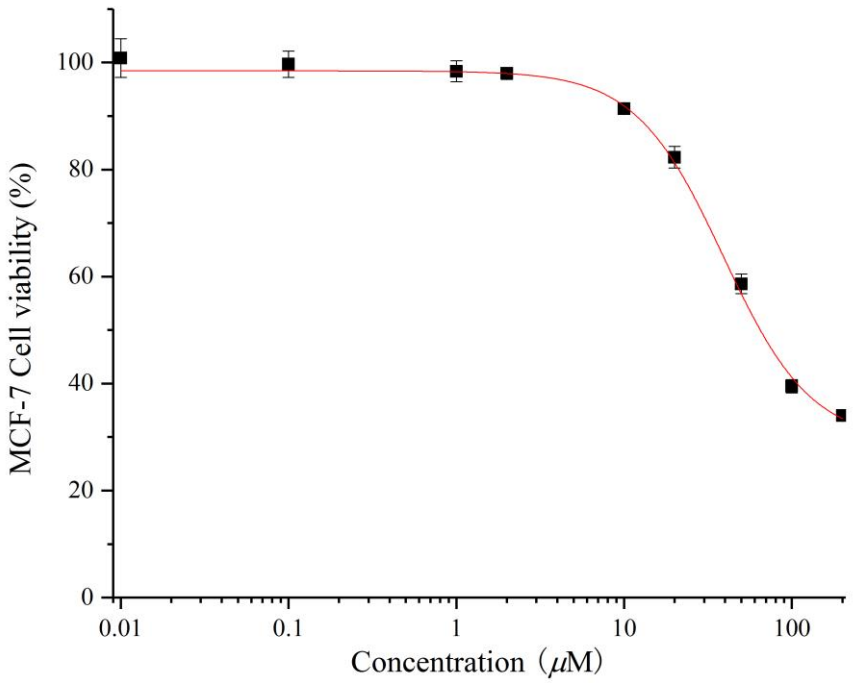


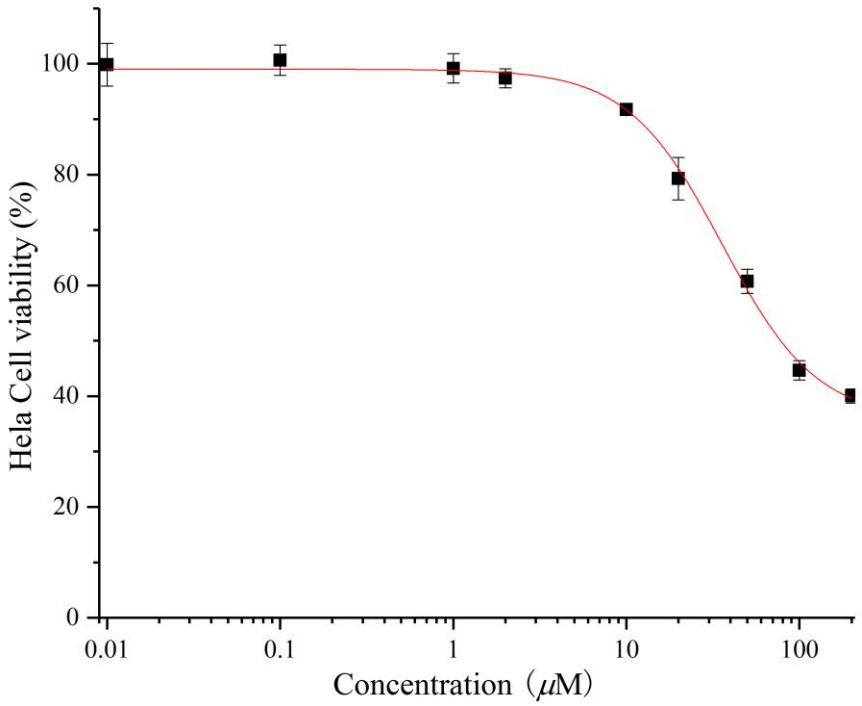
Figure S23. HSQC Spectrum of **1** (400 MHz for ^{1}H NMR, methanol-d_4)


HepG2 Cell viability (%)
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration（μM）

A


MCF-7 Cell viability (%)
100
80
60
40
20
0
0.01
0.1
1
10
100
Concentration（μM）

B



C

Figure S24. Antiproliferative activities against HepG2 (A), MCF-7 (B) and HeLa (C) cell lines of compounds **1**