Supporting Information for

Expanstines A-D: four unusual isoprenoid epoxycyclohexenones generated by *Penicillium expansum* YJ−15 fermentation and photopromotion

Jia-Peng Wang‡, Yan Shu‡, Shi-Xi Liu, Jun-Tao Hu, Cheng-Tong Sun, Hao Zhou, Dong Gan, Xue-Yun Cai, Wei Pu, Le Cai* and Zhong-Tao Ding*

Functional Molecules Analysis and Biotransformation Key Laboratory of Universities in Yunnan Province, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, School of Chemical Science and Technology, Yunnan University, Kunming 650091, P.R. China.

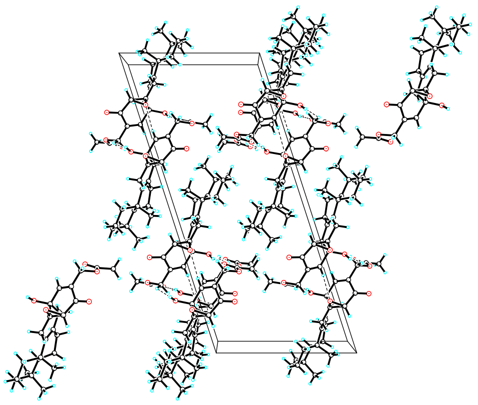
Contents

4′-oxomacrophorin A 7′-acetate (**5**): light yellow powder, $C_{24}H_{32}O_5$, ^{1}H NMR (600 MHz, $CDCl_3$) δ_H: 6.49 (1H, s, H-2′), 4.95 (1H, d, J = 16.2 Hz, H-7′a), 4.82 (1H, s, H-12a), 4.59 (1H, d, J = 16.2 Hz, H-7′b), 4.49 (1H, s, H-12b), 3.73 (1H, s, H-5′), 0.85 (3H, s, H-13), 0.79 (3H, s, H-14), 0.72 (3H, s, H-15); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 192.3 (s, C-4′), 191.8 (s, C-1′), 1670.0 (s, C-8′), 148.8 (s, C-8), 142.8 (s, C-3′), 132.7 (d, C-2′), 107.0 (t, C-12), 62.7 (s, C-6′), 59.4 (t, C-7′), 59.0 (d, C-5′), 55.6 (d, C-5), 51.5 (d, C-9), 42.1 (t, C-3), 39.9 (s, C-10), 39.0 (t, C-1), 38.1 (t, C-7), 33.7 (s, C-4), 33.6 (q, C-13), 24.5 (t, C-6), 21.8 (q, C-14), 20.7 (q, C-9′), 20.2 (t, C-11), 19.4 (t, C-2), 14.6 (q, C-15).

4′-oxomacrophorin A (**6**)[1]: light yellow powder, $C_{22}H_{30}O_4$, ^{1}H NMR (600 MHz, $CDCl_3$) δ_H: 6.58 (1H, s, H-2′), 4.80 (1H, s, H-12a), 4.57 (1H, d, J = 16.2 Hz, H-7′b), 4.50 (1H, s, H-12b), 4.32 (1H, d, J = 16.2 Hz, H-7′a), 3.71 (1H, s, H-5′), 0.84 (3H, s, H_3-13), 0.79 (3H, s, H_3-14), 0.73 (3H, s, H_3-15); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 193.5 (s, C-4′), 192.2 (s, C-1′), 149.0 (s, C-8), 145.8 (s, C-3′), 132.4 (d, C-2′), 106.7 (t, C-12), 62.8 (s, C-6′), 59.4 (t, C-7′), 59.1 (d, C-5′), 55.5 (d, C-5), 51.4 (d, C-9), 42.3 (t, C-3), 40.0 (s, C-10), 38.9 (t, C-1), 38.1 (t, C-7), 33.5 (s, C-4), 33.5 (q, C-13), 24.5 (t, C-6), 21.9 (q, C-14), 20.2 (t, C-11), 19.3 (t, C-2), 14.4 (q, C-15).

Crystallographic data of 1.

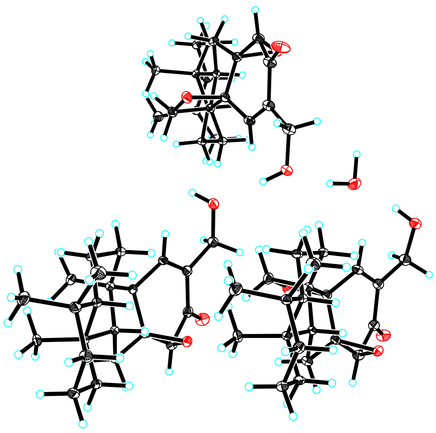
Crystals of **1** (colorless prism) was obtained from $CHCl_3$ and the crystal data of **1** was collected on a Bruker Apex DUO diffractometer using graphin-monochromated Cu Kα radiation (λ = 1.54178 Å). The crystallographic data have been deposited in the Cambridge Crystallographic Data Centre with the deposition number CCDC 1861546. A copy of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1233-336033 or e-mail: deposit@ccdc.cam.ac.uk).



View of the pack drawing of expanstine A (**1**). Hydrogen-bonds are shown as dashed lines

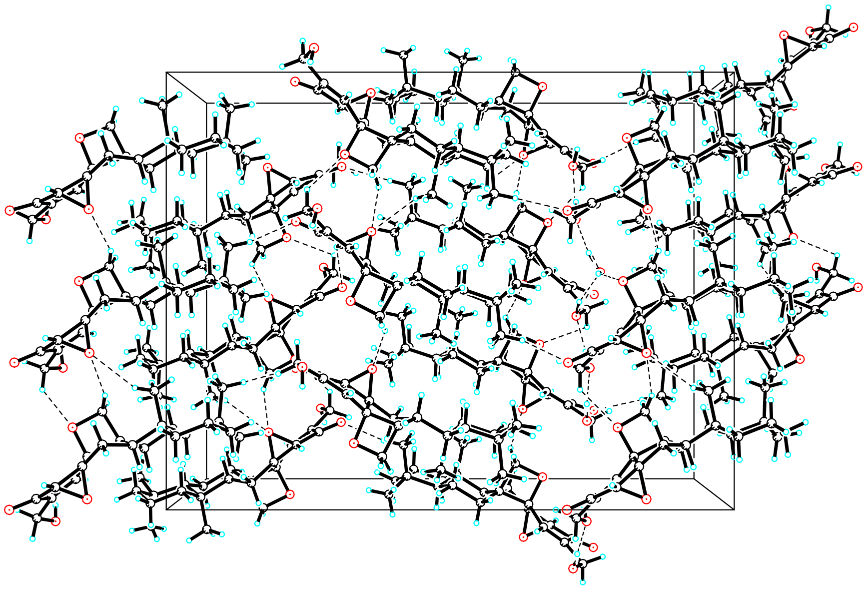
Crystallographic data of 3.

Orthorhombic crystals of **3** was obtained from a mixture solution (petroleum ether : acetone = 3:1) and the crystal data was collected on a Bruker Apex DUO diffractometer using graphin-monochromated Cu Kα radiation (λ = 1.54178 Å). The crystallographic data have been deposited in the Cambridge Crystallographic Data Centre with the deposition number CCDC 1901871. A copy of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1233-336033 or e-mail: deposit@ccdc.cam.ac.uk).



View of the molecules in an asymmetric unit.

Displacement ellipsoids are drawn at the 30% probability level.

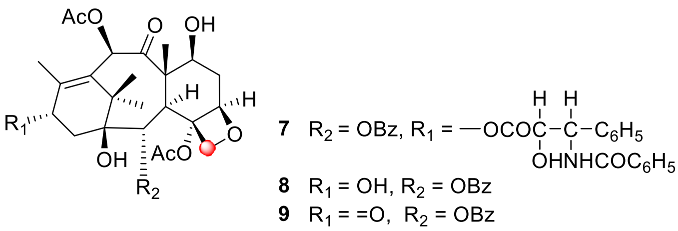


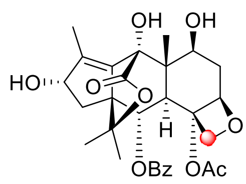
View of the pack drawing of expanstine C (**3**).

Hydrogen-bonds are shown as dashed lines.

Table S1. ^{1}H and ^{13}C NMR data (recorded in $CDCl_3$) for methylene of oxetane ring in compounds **3** and **7-10.**

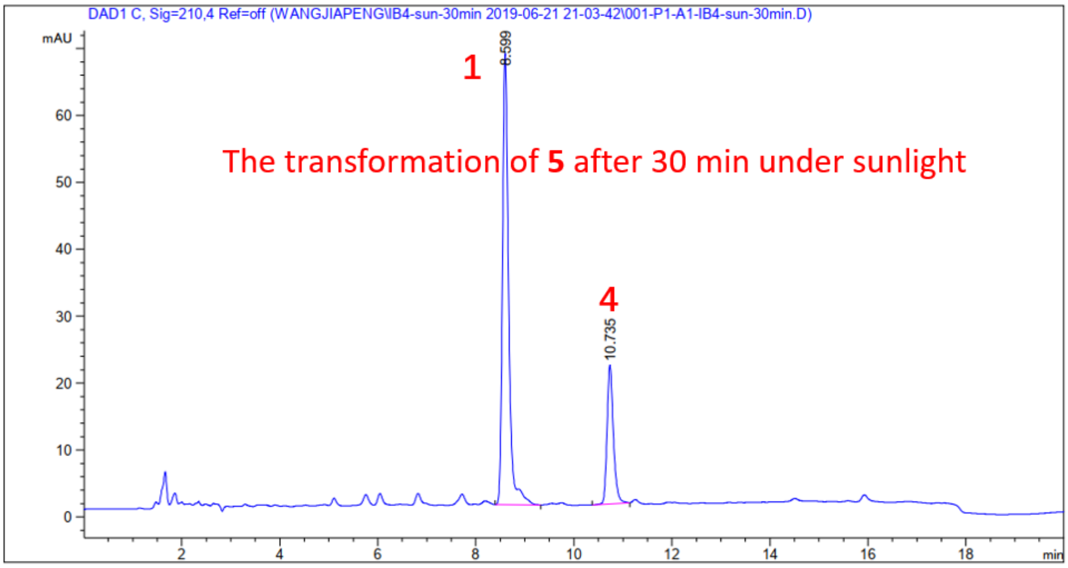
compound	δ_C	δ_H (J in Hz)
3	75.8	4.29 (1H, d, J = 8.4); 4.82 (1H, d, J = 8.4)
7 (taxol)[2]	76.6	4.24 (2H, dd, J = 29.7, 8.4)
8 (baccatin V)[3]	77.6	4.00 (1H, d, J = 8.5); 4.34 (1H, d, J = 8.0)
9 (13-oxobaccatin III)[4]	77.2	4.14 (1H, d, J = 8.0); 4.35 (1H, d, J = 8.0)
10 (wallifoliol)[5]	74.2	4.20 (1H, d, J = 8.5); 4.66 (1H, d, J = 8.5)





10

Figure S1. Structures of compounds **7-10**.



==

面积百分比报告

==

排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 C, Sig=210,4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.599	BB	0.1317	588.30194	67.46300	75.9185
2	10.735	BB	0.1368	186.61043	20.78205	24.0815
总量 :				774.91237	88.24505	

==

All Optimized Cartesian Coordinates

Compound 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	3.012667	-0.633163	0.202335
2	6	0	3.441801	0.887096	0.176432
3	6	0	3.276643	-1.206794	-1.217135
4	6	0	4.895286	1.202139	-0.327568
5	6	0	4.725662	-0.998406	-1.676719
6	6	0	5.113329	0.481687	-1.681789
7	6	0	1.523084	-0.714741	0.575254
8	6	0	0.901222	0.265825	1.262683
9	6	0	3.056908	1.583322	1.491465
10	6	0	1.537489	1.570084	1.668495
11	6	0	0.703325	-1.969329	0.215764
12	6	0	-0.768289	-1.677121	-0.164733
13	6	0	-0.598803	0.186852	1.340519
14	6	0	-1.075970	-0.188028	-0.119351
15	6	0	-1.897468	-2.590974	0.120400
16	6	0	-3.300513	-2.037155	0.293995
17	6	0	-2.503331	0.199311	-0.284825
18	6	0	-3.537897	-0.616141	-0.046344
19	6	0	6.006220	0.822918	0.675743
20	6	0	5.028987	2.719296	-0.599098
21	6	0	3.724846	-1.511123	1.259889
22	8	0	-0.375471	0.515781	-1.137229
23	8	0	-1.337208	-2.462046	-1.207389
24	8	0	-4.200670	-2.752387	0.713296
25	6	0	-4.971909	-0.164941	-0.004981
26	8	0	-5.028776	1.247428	-0.278648
27	6	0	-6.273179	1.789249	-0.296805
28	6	0	-6.214114	3.262748	-0.621246
29	8	0	-7.279247	1.153312	-0.080267
30	1	0	-1.741691	-3.556530	0.600021
31	1	0	3.048171	-2.277199	-1.246030
32	1	0	2.598598	-0.723962	-1.935564
33	1	0	5.406104	-1.568381	-1.033088
34	1	0	4.849148	-1.414701	-2.683400
35	1	0	4.511017	0.994132	-2.445576
36	1	0	6.160476	0.600014	-1.988469
37	1	0	3.532909	1.081703	2.341202
38	1	0	3.411818	2.617361	1.507099
39	1	0	1.080870	2.362811	1.054930
40	1	0	1.259342	1.810610	2.704005
41	1	0	1.145135	-2.503517	-0.626180
42	1	0	0.723918	-2.666276	1.063752
43	1	0	-0.958792	-0.587877	2.026400

44	1	0	-1.034701	1.134861	1.668245
45	1	0	-2.664203	1.242552	-0.536159
46	1	0	6.965478	1.225442	0.331579
47	1	0	5.815299	1.244822	1.667606
48	1	0	6.134435	-0.253850	0.792934
49	1	0	4.211635	3.090018	-1.228029
50	1	0	5.043695	3.310689	0.321186
51	1	0	5.968790	2.920403	-1.125056
52	1	0	4.783167	-1.674835	1.053784
53	1	0	3.636318	-1.082020	2.260963
54	1	0	3.250873	-2.498173	1.290379
55	1	0	-5.587936	-0.707655	-0.729055
56	1	0	-5.404056	-0.371335	0.979665
57	1	0	-5.609076	3.789075	0.122818
58	1	0	-5.739714	3.414038	-1.595199
59	1	0	-7.224595	3.669355	-0.632643
60	1	0	2.795996	1.331021	-0.600203
61	1	0	0.566586	0.455042	-0.914289

Compound 4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.490388	-0.037503	1.127389
2	6	0	5.123417	0.692703	-1.268031
3	6	0	3.650946	0.702509	-1.690297
4	6	0	2.792897	-0.342448	-0.933582
5	6	0	3.012458	-0.219417	0.614770
6	6	0	5.233972	0.983795	0.230662
7	6	0	1.275696	-0.118415	-1.251560
8	6	0	0.270714	-0.923732	-0.319969
9	6	0	0.734754	-1.232512	1.111102
10	6	0	2.249040	-1.349132	1.331637
11	6	0	0.747808	1.354518	-1.343017
12	6	0	-0.580883	1.342976	-0.618073
13	6	0	-1.034994	-0.085698	-0.437407
14	6	0	-0.494066	-1.923113	-1.212645
15	8	0	-1.380605	-0.848517	-1.650987
16	6	0	-1.528128	2.444701	-0.371119
17	6	0	-2.935245	2.091941	0.047261
18	6	0	-3.120801	0.743566	0.659528
19	6	0	-2.205085	-0.231806	0.489857

20	6	0	-4.409787	0.512911	1.409022
21	8	0	-5.474422	0.084982	0.520283
22	8	0	-3.844536	2.900053	-0.058815
23	6	0	-5.568014	-1.243832	0.287466
24	8	0	-4.841315	-2.076804	0.788828
25	6	0	-6.689233	-1.534564	-0.680074
26	1	0	3.268441	1.710883	-1.496641
27	1	0	3.552018	0.537976	-2.771403
28	1	0	2.514247	0.722966	0.895355
29	1	0	4.817054	1.983983	0.417292
30	1	0	6.286066	1.029006	0.539984
31	1	0	1.132986	-0.524036	-2.257053
32	1	0	0.376072	-0.408533	1.741593
33	1	0	0.226359	-2.132792	1.477667
34	1	0	2.614861	-2.324822	0.997454
35	1	0	2.434953	-1.313957	2.409754
36	1	0	1.385272	2.086114	-0.843768
37	1	0	0.649189	1.658589	-2.387646
38	1	0	-1.399087	3.430133	-0.815040
39	1	0	-2.404159	-1.216704	0.904533
40	1	0	-4.274842	-0.239039	2.187879
41	1	0	-4.775398	1.447451	1.833794
42	1	0	-7.607624	-1.034194	-0.363115
43	1	0	-6.426713	-1.142225	-1.667522
44	1	0	-6.844026	-2.611046	-0.744117
45	8	0	-0.564166	2.063472	0.633407
46	1	0	-1.052167	-2.691699	-0.661046
47	1	0	0.033977	-2.385078	-2.052319
48	6	0	5.299412	-1.351964	1.198119
49	1	0	6.273822	-1.158516	1.660873
50	1	0	4.795419	-2.106866	1.808703
51	1	0	5.491361	-1.792910	0.217698
52	6	0	4.447683	0.552348	2.555813
53	1	0	5.461668	0.785898	2.899392
54	1	0	3.863891	1.478887	2.586073
55	1	0	4.012703	-0.142809	3.280580
56	1	0	5.596760	-0.265544	-1.513079
57	1	0	5.672102	1.454158	-1.835072
58	6	0	3.147400	-1.745222	-1.494391
59	1	0	3.043221	-1.739792	-2.584928
60	1	0	4.171014	-2.046322	-1.268659
61	1	0	2.488828	-2.530313	-1.113705

Compound 5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.927337	0.138145	-0.554706
2	6	0	-3.523528	-0.406100	0.802778
3	6	0	-2.815449	-1.048436	-1.546634
4	6	0	-4.826935	-1.280695	0.715763
5	6	0	-4.119598	-1.840424	-1.701425
6	6	0	-4.613901	-2.375719	-0.357463
7	6	0	-1.477013	0.689543	-0.202931
8	6	0	-1.598542	1.801010	0.832151
9	6	0	-3.586880	0.693495	1.880193
10	6	0	-2.203831	1.324084	2.129763
11	6	0	-0.603691	1.043241	-1.429330
12	6	0	0.887322	0.903894	-1.184526
13	6	0	-1.312790	3.093318	0.639231
14	6	0	1.434611	-0.503917	-1.005854
15	6	0	1.731406	2.008518	-0.655911
16	6	0	2.996819	1.705142	0.096287
17	6	0	2.848274	-0.657496	-0.588228
18	6	0	3.586375	0.344770	-0.073051
19	6	0	-6.114346	-0.480858	0.420277
20	6	0	-5.042040	-2.006874	2.064453
21	6	0	-3.743053	1.273890	-1.209905
22	8	0	0.739660	-1.486012	-1.219078
23	8	0	1.752028	1.673039	-2.049144
24	8	0	3.517110	2.541196	0.818193
25	6	0	4.989948	0.192178	0.434792
26	8	0	5.405335	-1.168598	0.269325
27	6	0	6.684021	-1.440791	0.648886
28	6	0	7.005361	-2.898394	0.434053
29	8	0	7.432849	-0.602855	1.094235
30	1	0	1.274687	2.959880	-0.398897
31	1	0	-2.510022	-0.684475	-2.533755
32	1	0	-2.019396	-1.724826	-1.209682
33	1	0	-4.891273	-1.217017	-2.169909
34	1	0	-3.952459	-2.675851	-2.391970
35	1	0	-3.873452	-3.094038	0.023116
36	1	0	-5.547630	-2.938055	-0.488172
37	1	0	-4.289873	1.481557	1.587522
38	1	0	-3.960376	0.279977	2.821664
39	1	0	-1.549374	0.564120	2.582316

40	1	0	-2.282303	2.148082	2.846649
41	1	0	-0.835934	0.368956	-2.255448
42	1	0	-0.790998	2.057473	-1.789137
43	1	0	-0.937206	3.488532	-0.298221
44	1	0	-1.470070	3.820673	1.430680
45	1	0	3.246675	-1.663807	-0.659121
46	1	0	-6.985941	-1.138413	0.516043
47	1	0	-6.249901	0.342020	1.129015
48	1	0	-6.138965	-0.058496	-0.585599
49	1	0	-4.131512	-2.520522	2.393453
50	1	0	-5.353994	-1.326275	2.862235
51	1	0	-5.828928	-2.762340	1.960353
52	1	0	-4.702932	0.925402	-1.592431
53	1	0	-3.934637	2.103263	-0.526224
54	1	0	-3.192401	1.682540	-2.064491
55	1	0	5.669317	0.863418	-0.103347
56	1	0	5.047992	0.485207	1.488414
57	1	0	6.319729	-3.523261	1.013726
58	1	0	6.875547	-3.160778	-0.619872
59	1	0	8.032549	-3.089734	0.741449
60	1	0	-2.761385	-1.122816	1.150789
61	1	0	-0.982617	-0.153685	0.298640

Reference

1. H. Fujimoto, E. Nakamura, Y.-P. Kim, E. Okuyama, M. Ishibashi and T. Sassa, *Journal of Natural Products*, 2001, **64**, 1234-1237.
2. B. Louage, L. Nuhn, M. D. P. Risseeuw, N. Vanparijs, R. De Coen, I. Karalic, S. Van Calenbergh and B. G. De Geest, *Angewandte Chemie International Edition*, 2016, **128**, 11967-11973.
3. J. Zhan, *Chinese Journal of Applied and Environmental Microbiology*, 2003, **9**, 429-432.
4. M. Zhang, X. Lu, J. Zhang, S. Zhang, M. Dong, C. Huo, Q. Shi, Y. Gu and B. Cong, *Chemistry of Natural Compounds*, 2010, **46**, 53-58.
5. D. G. V. Velde, G. I. Georg, S. R. Gollapudi, H. B. Jampani, X.-Z. Liang, L. A. Mitscher and Q.-M. Ye, *Journal of Natural Products*, 1994, **57**, 862-867.

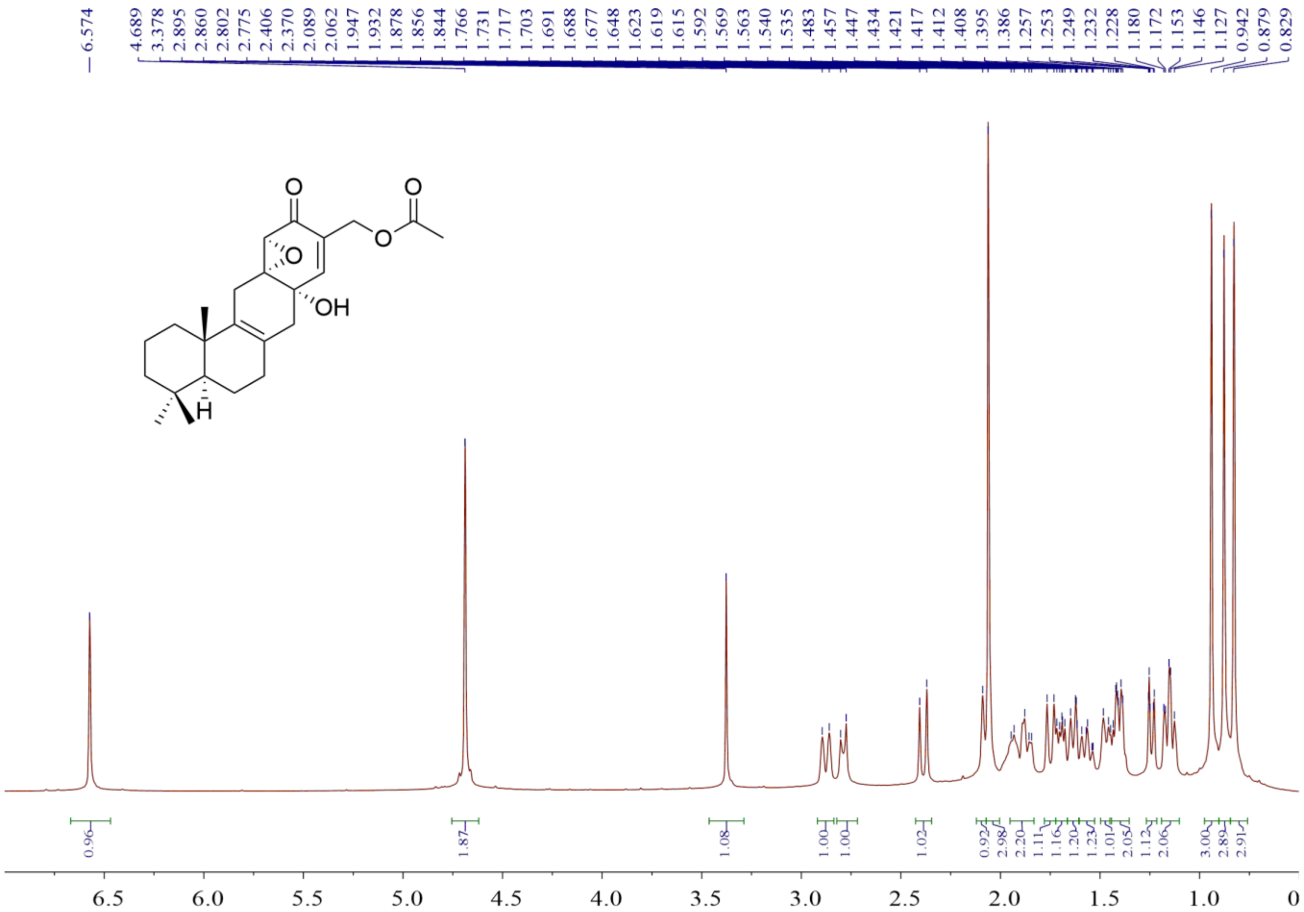


Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of expanstine A (**1**).

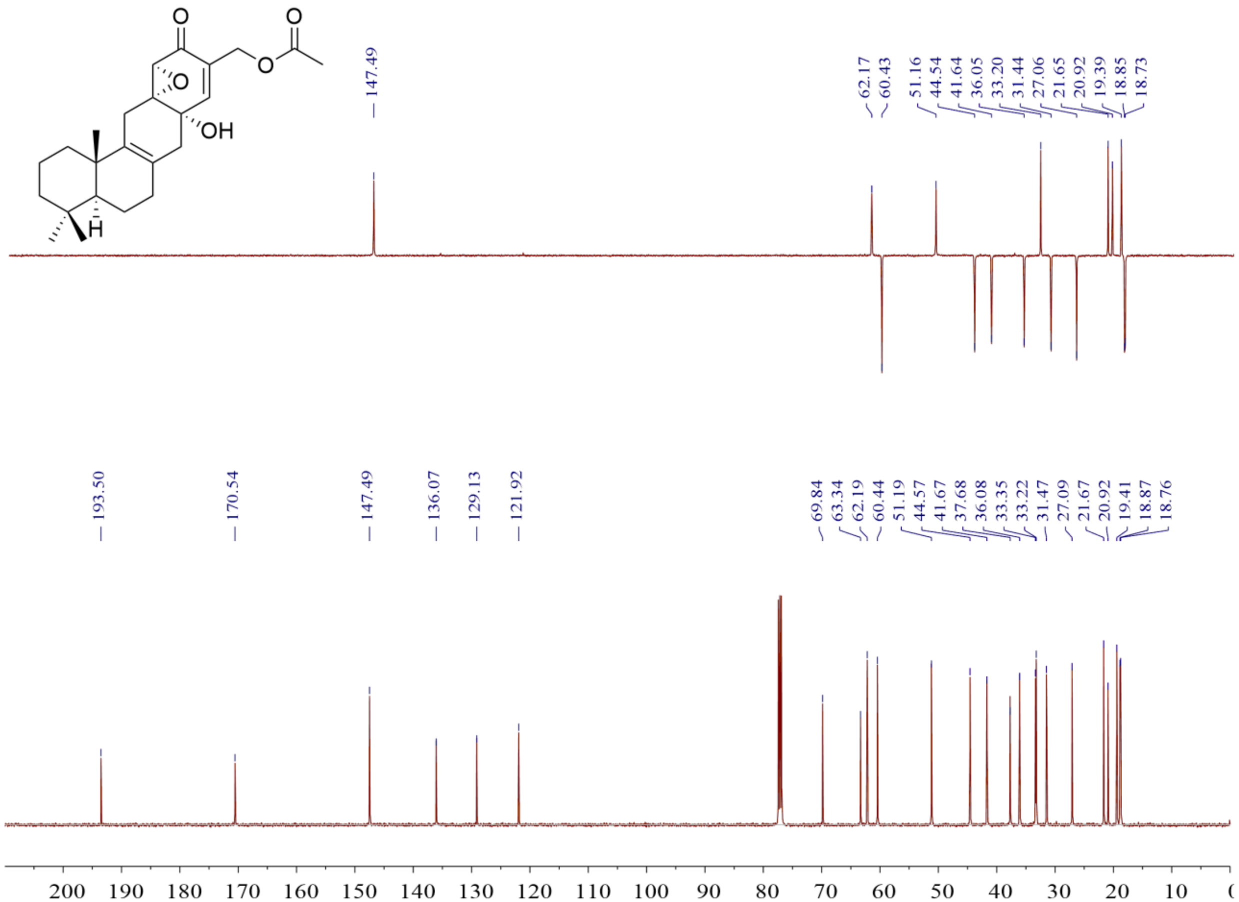


Figure S3. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of expanstine A (**1**).

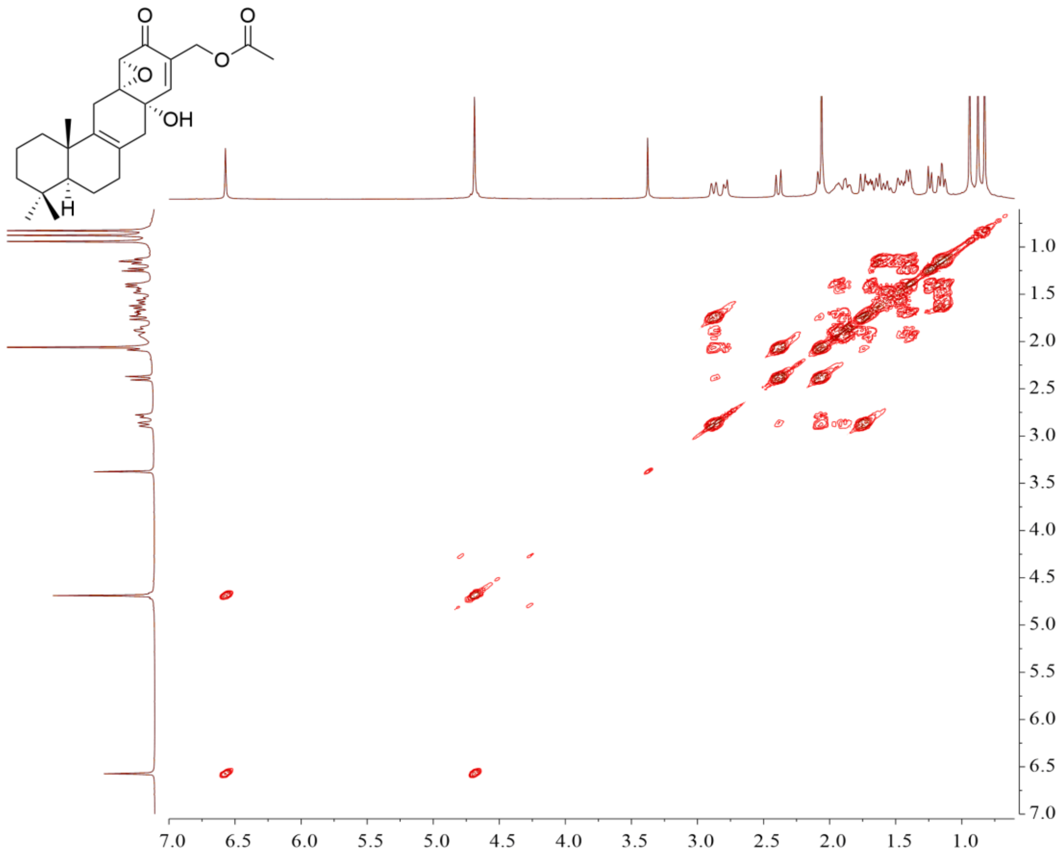


Figure S4. [1]H-[1]H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine A (**1**).

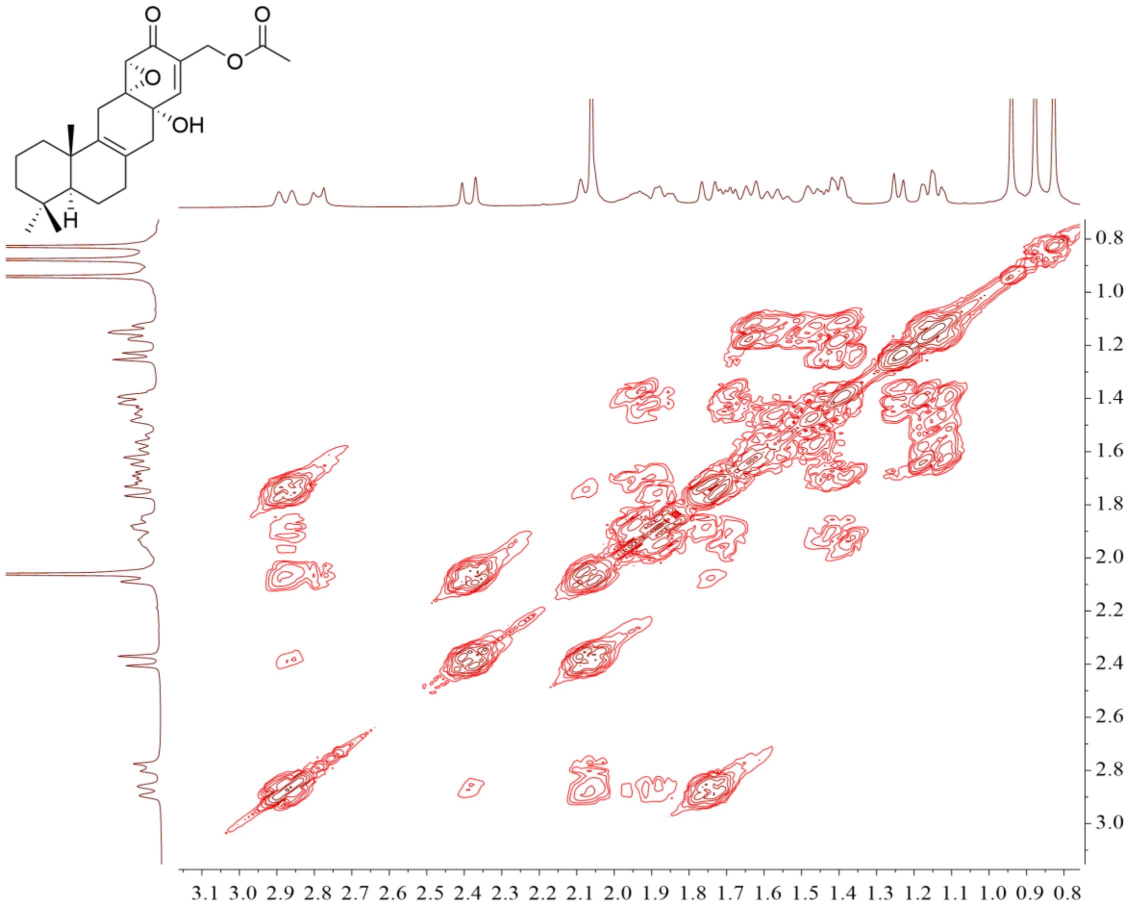


Figure S5. Enlarged ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine A (**1**).

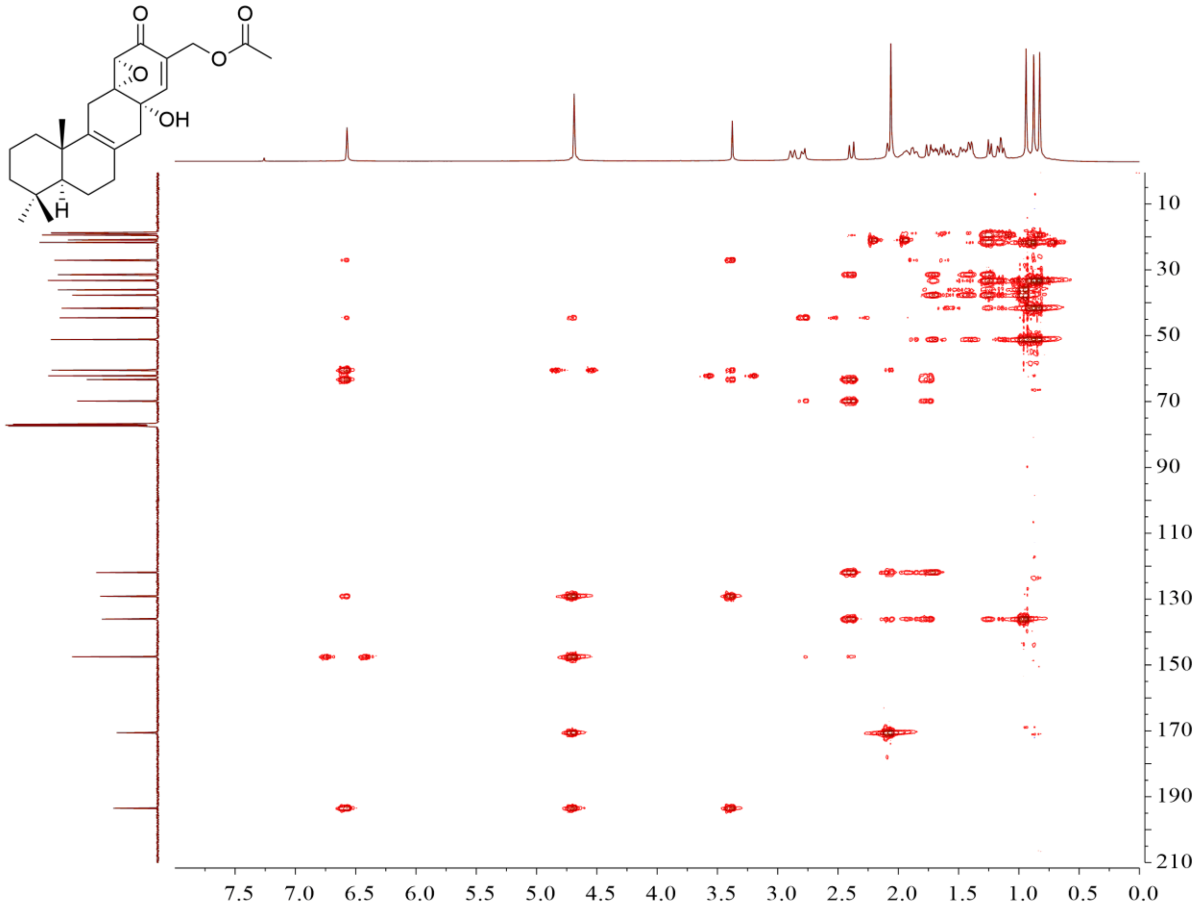


Figure S6. HMBC spectrum ($CDCl_3$, 600 MHz) of expanstine A (**1**).

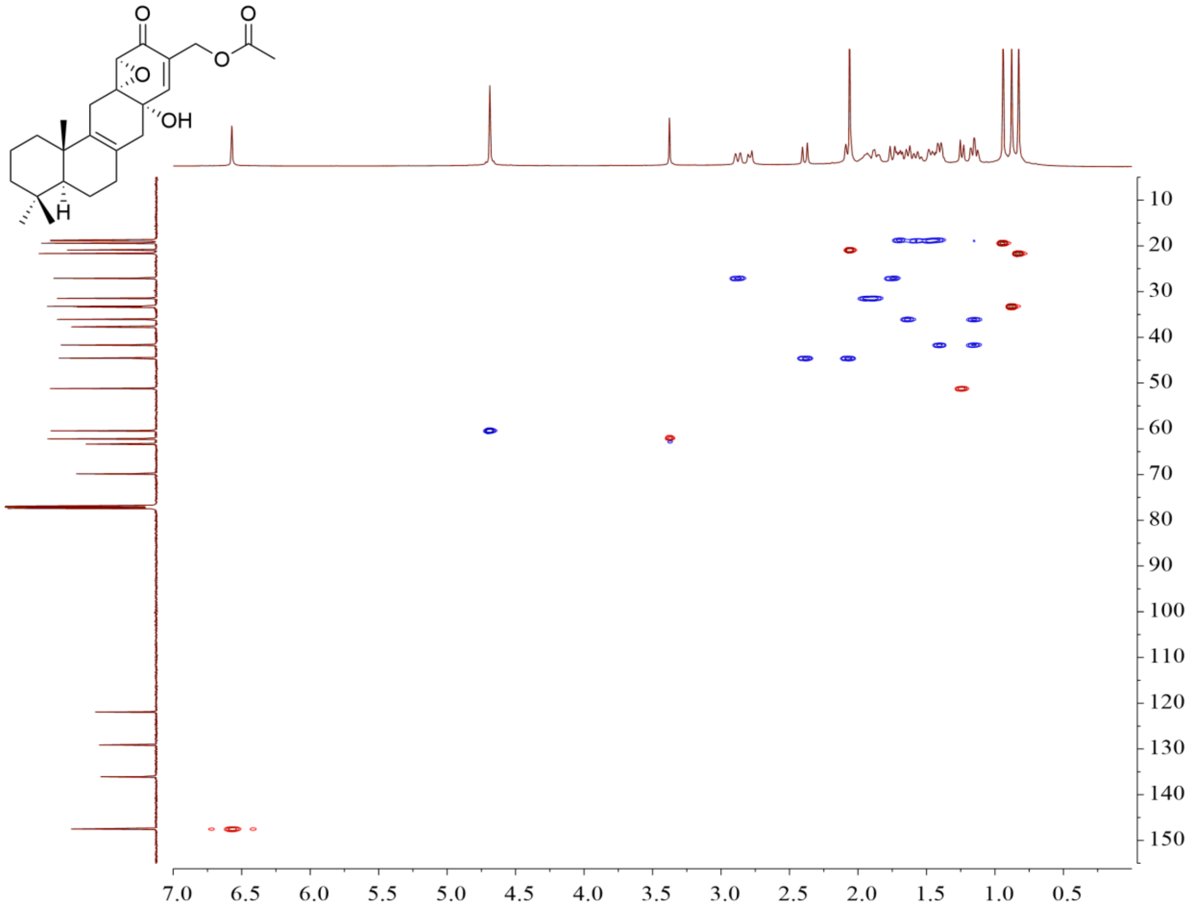


Figure S7. HSQC spectrum ($CDCl_3$, 600 MHz) of expanstine A (**1**).

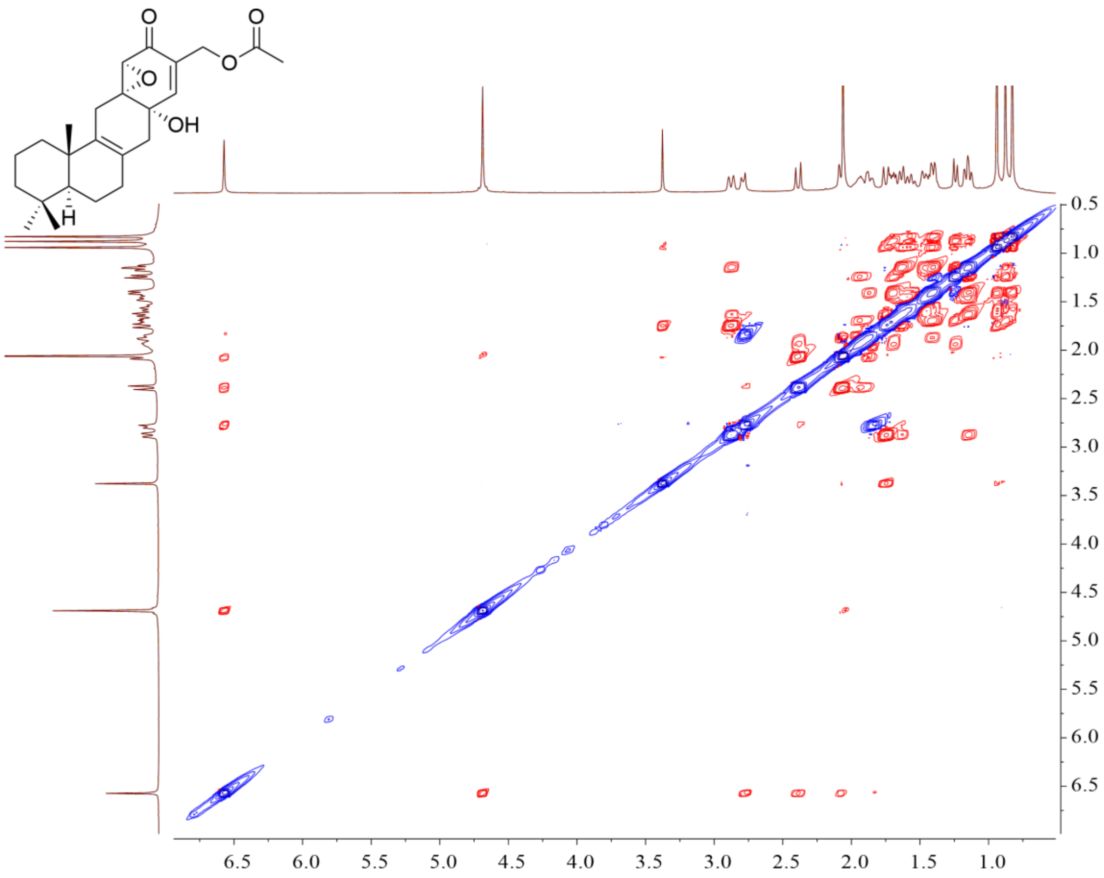


Figure S8. NOESY spectrum ($CDCl_3$, 600 MHz) of expanstine A (**1**).

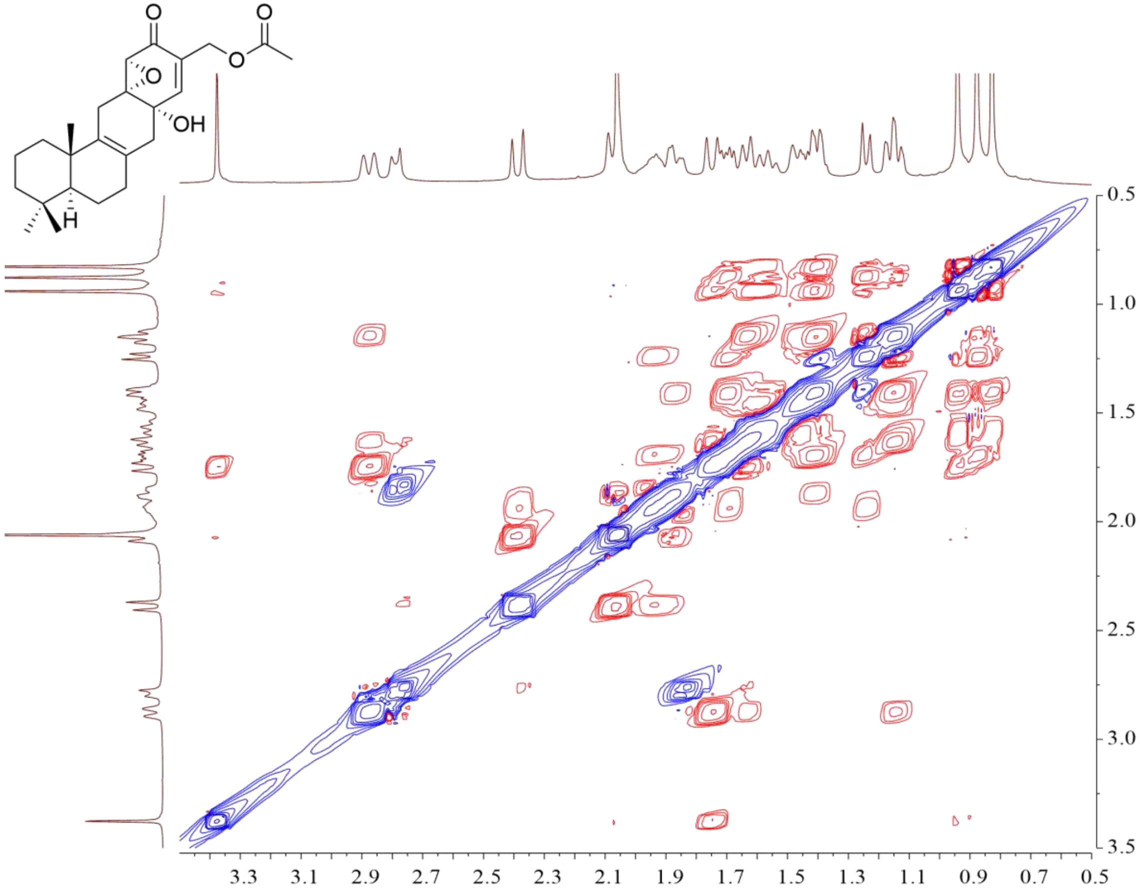


Figure S9. Enlarged NOESY spectrum ($CDCl_3$, 600 MHz) of expanstine A (**1**).

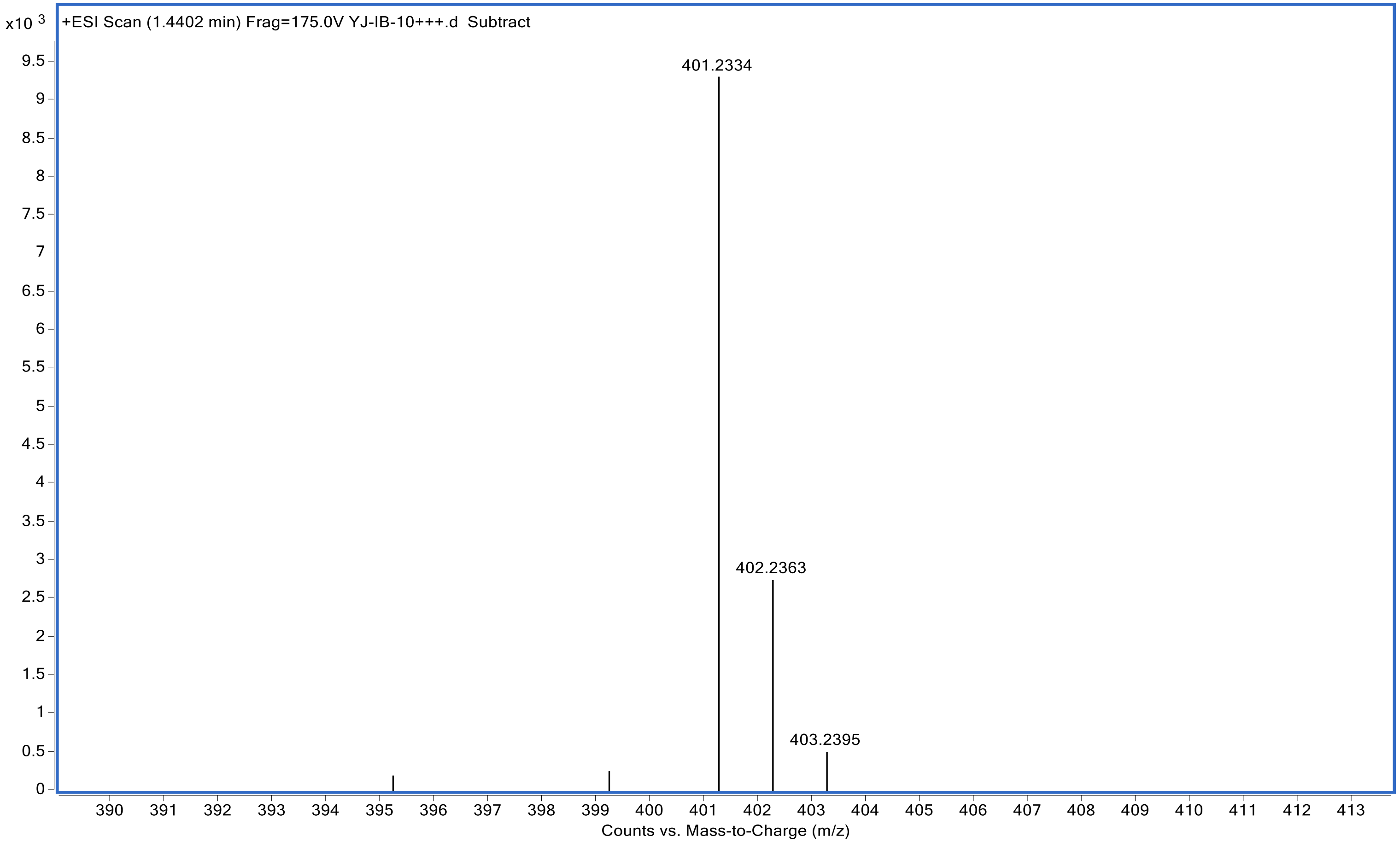


Figure S10. (+)-HR-ESI-MS $[M + H]^+$ of expanstine A (**1**).

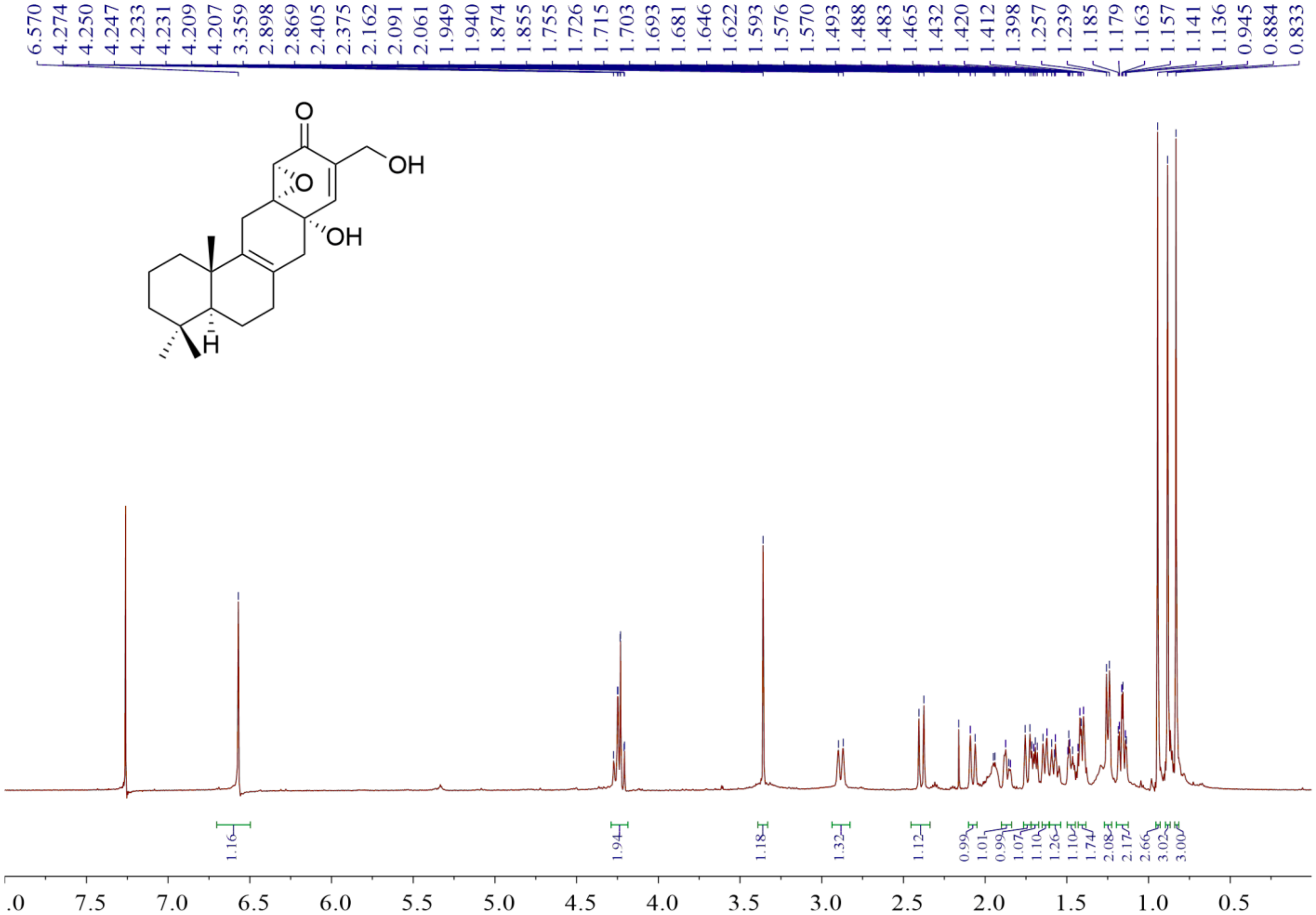


Figure S11. [1]H NMR spectrum ($CDCl_3$, 600 MHz) of expanstine B (**2**).

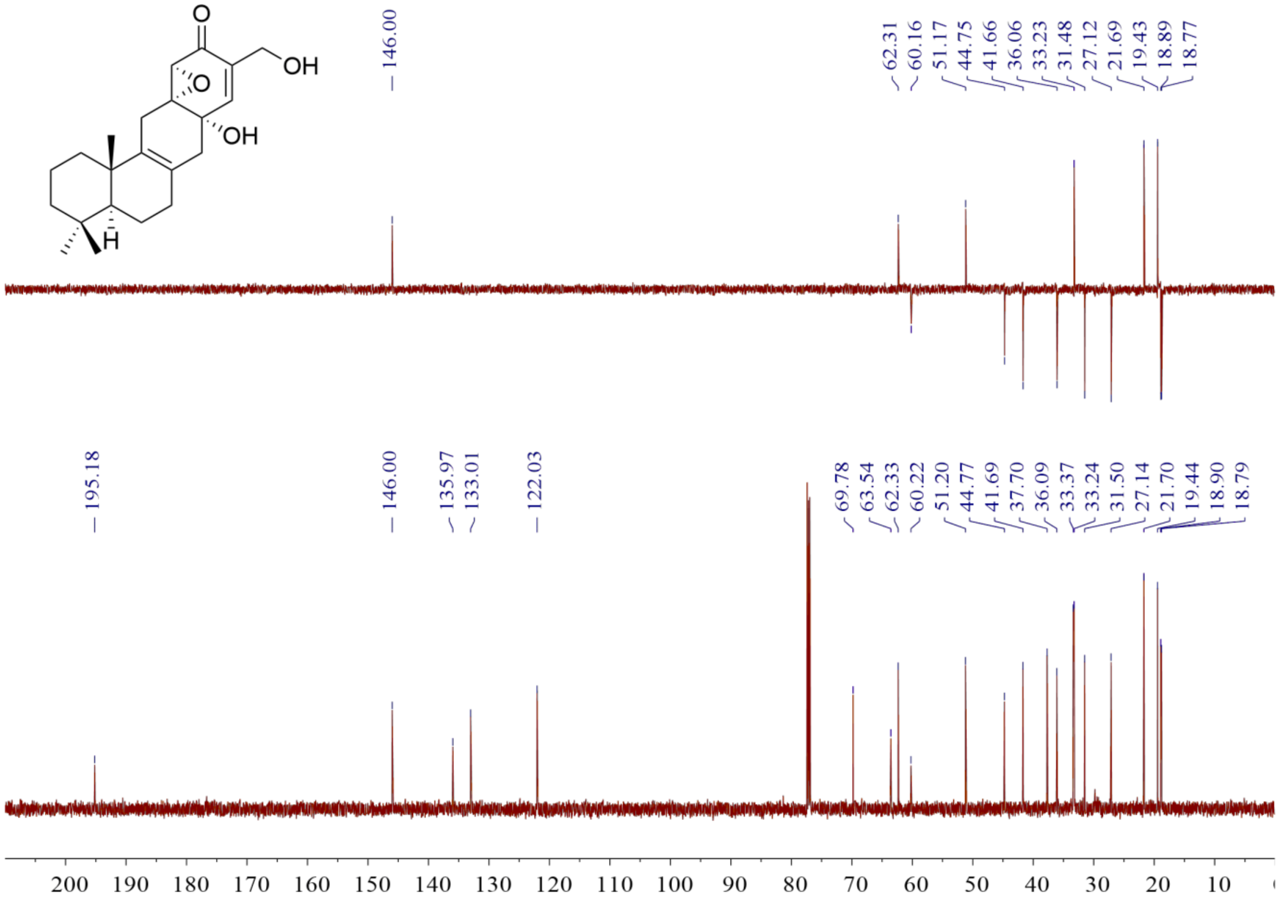


Figure S12. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of expanstine B (**2**).

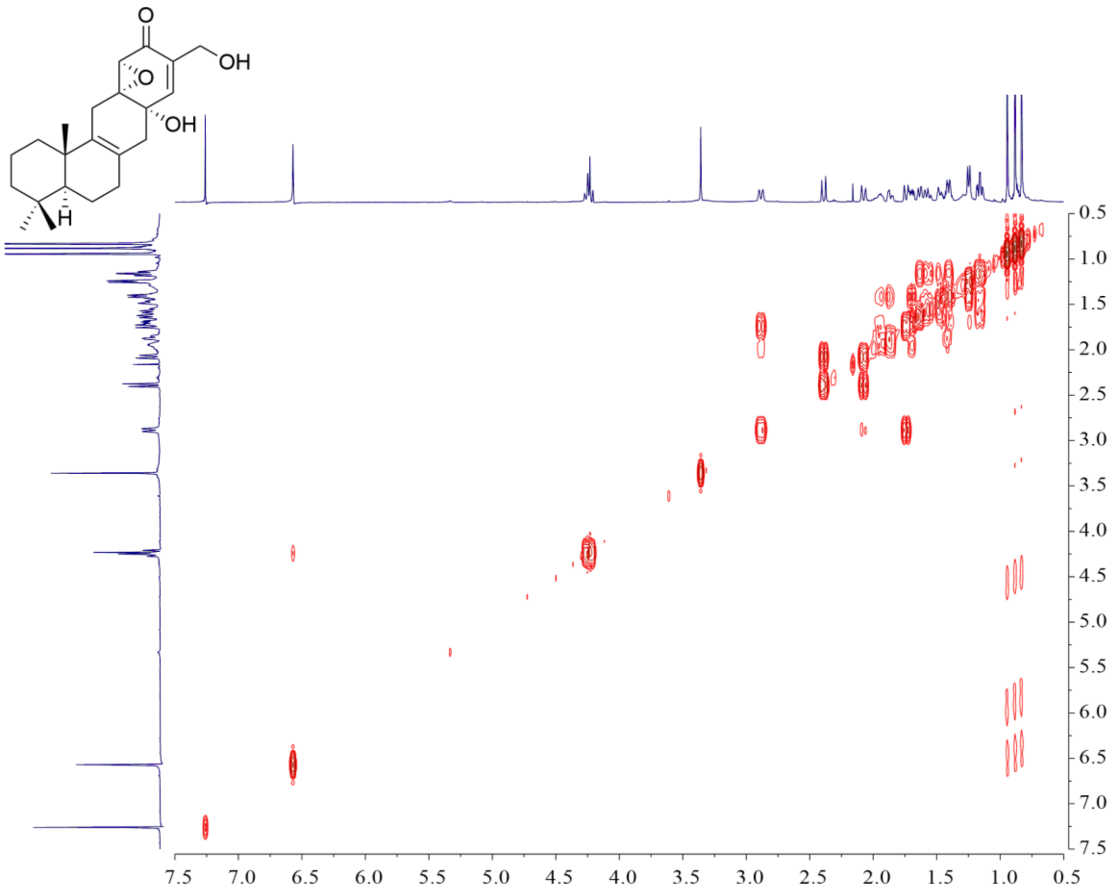


Figure S13. ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine B (**2**).

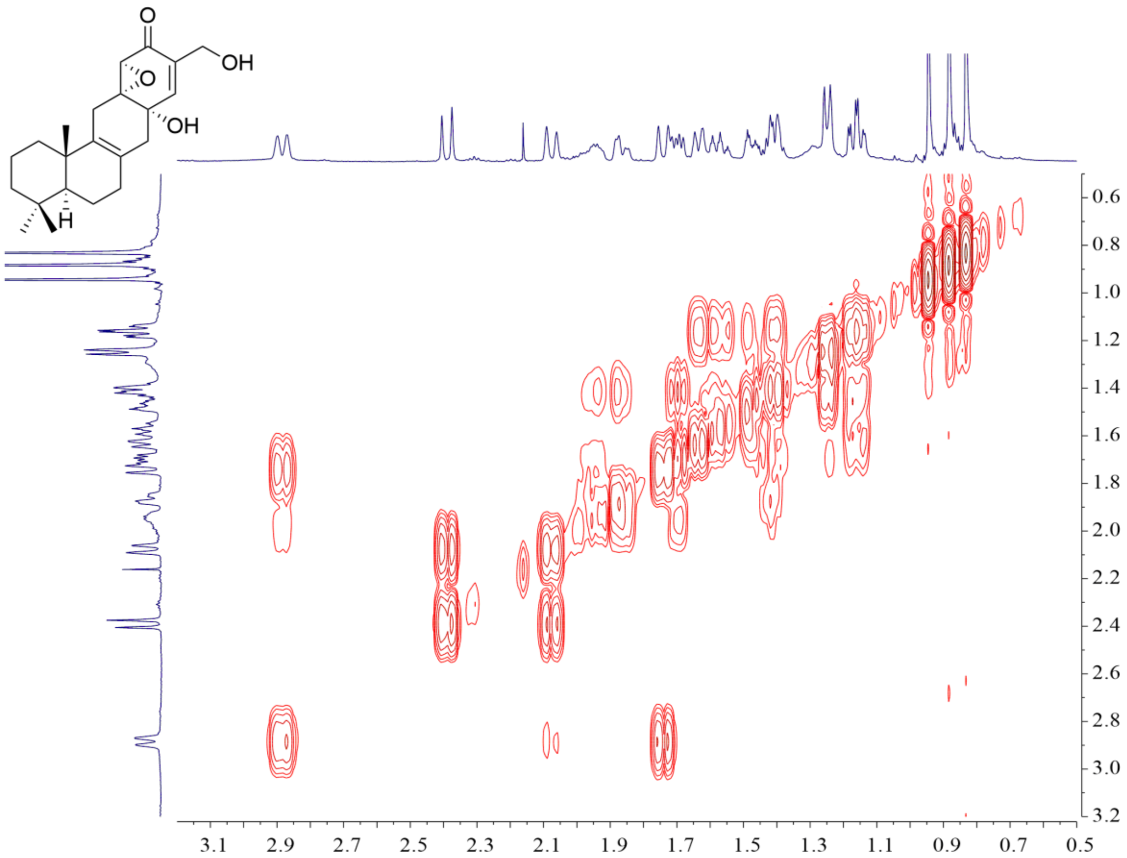


Figure S14. Enlarged ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine B (**2**).

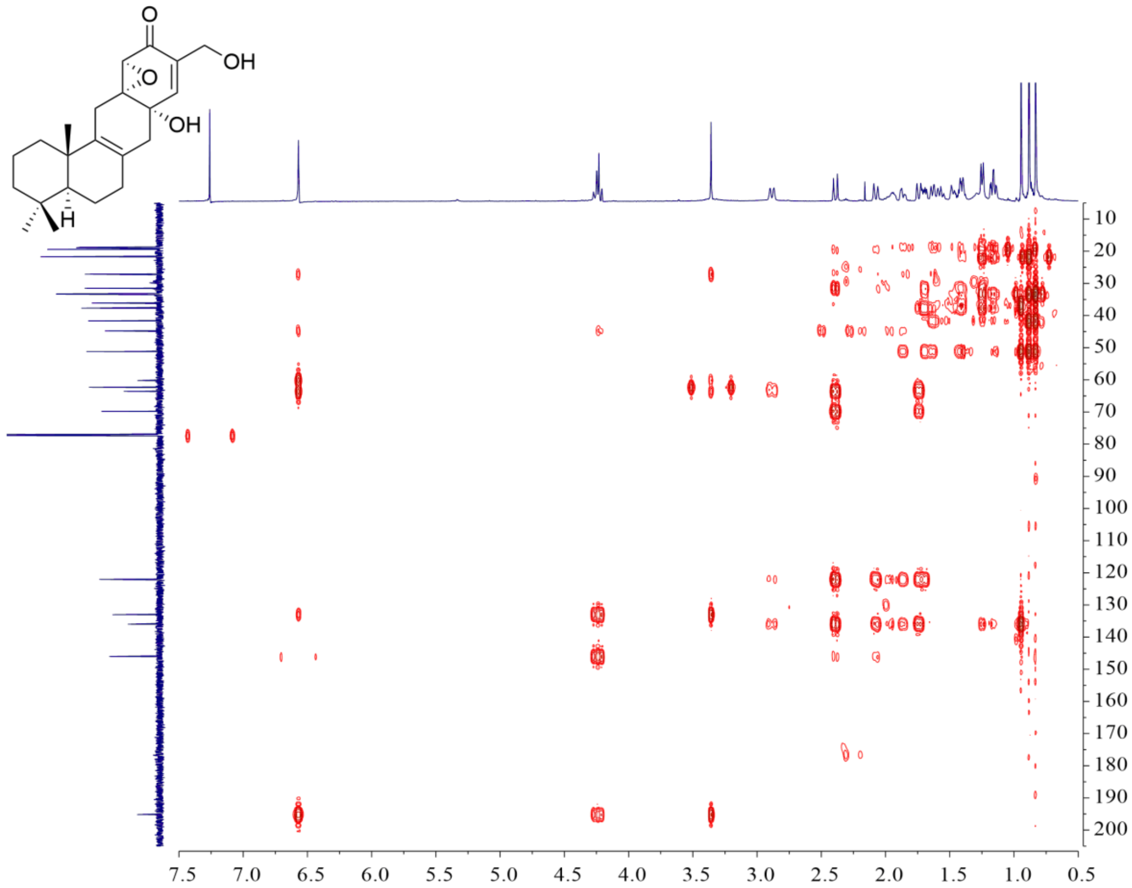


Figure S15. HMBC spectrum ($CDCl_3$, 600 MHz) of expanstine B (**2**).

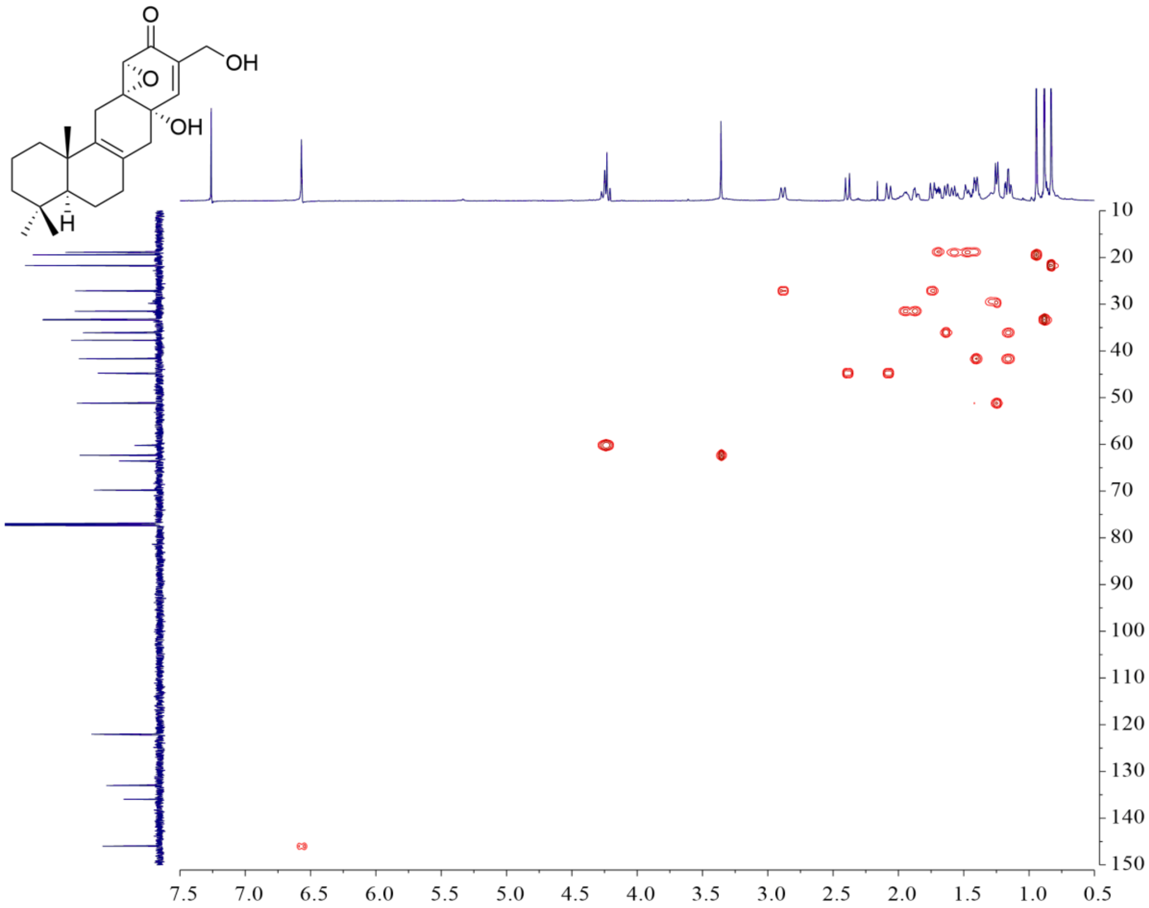


Figure S16. HSQC spectrum ($CDCl_3$, 600 MHz) of expanstine B (**2**).

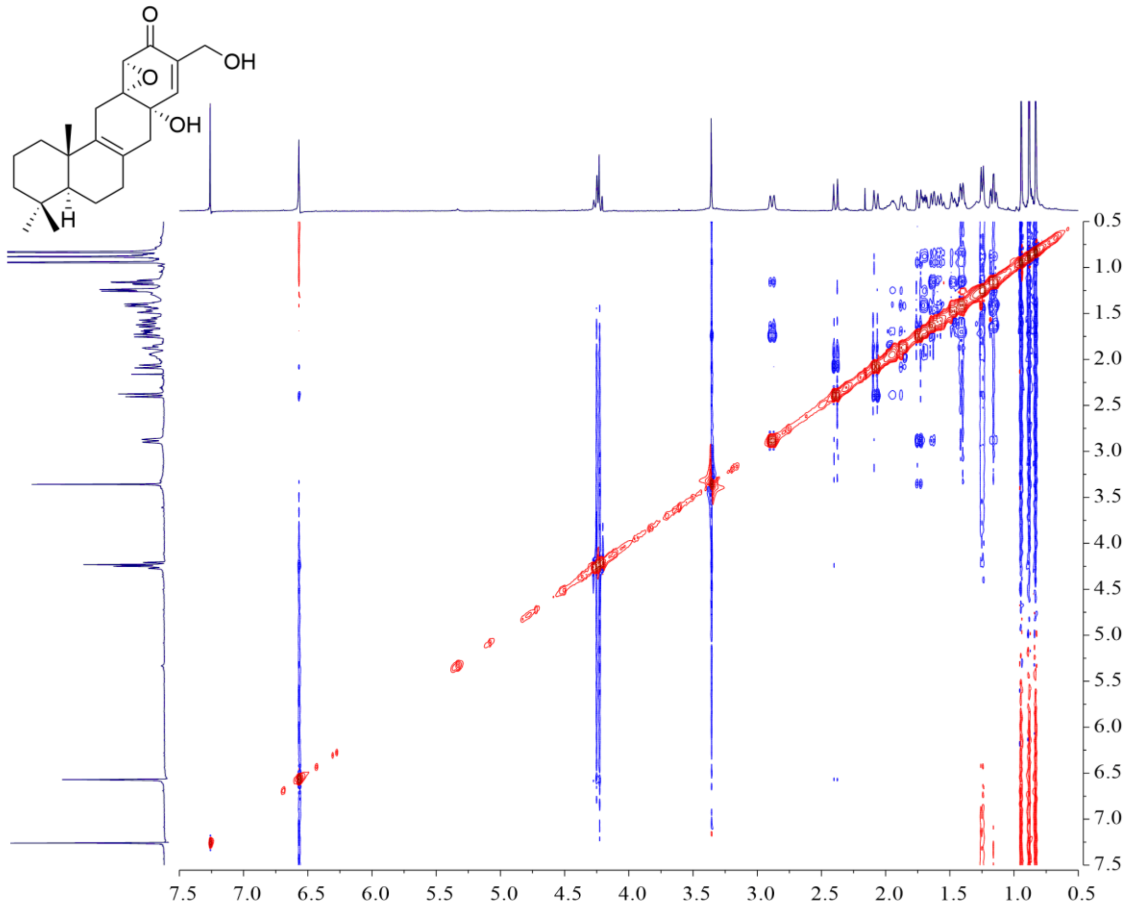


Figure S17. ROESY spectrum ($CDCl_3$, 600 MHz) of expanstine B (**2**).

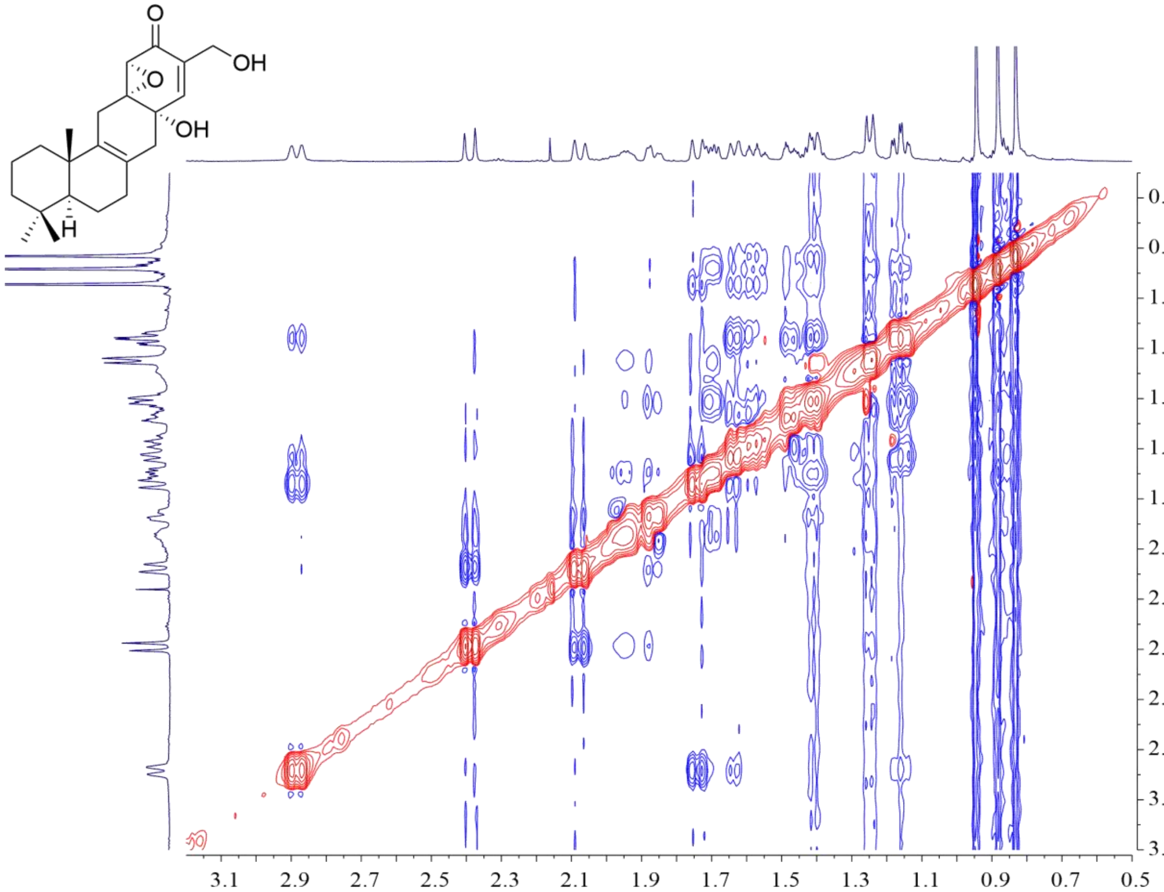


Figure S18. Enlarged ROESY spectrum ($CDCl_3$, 600 MHz) of expanstine B (**2**).

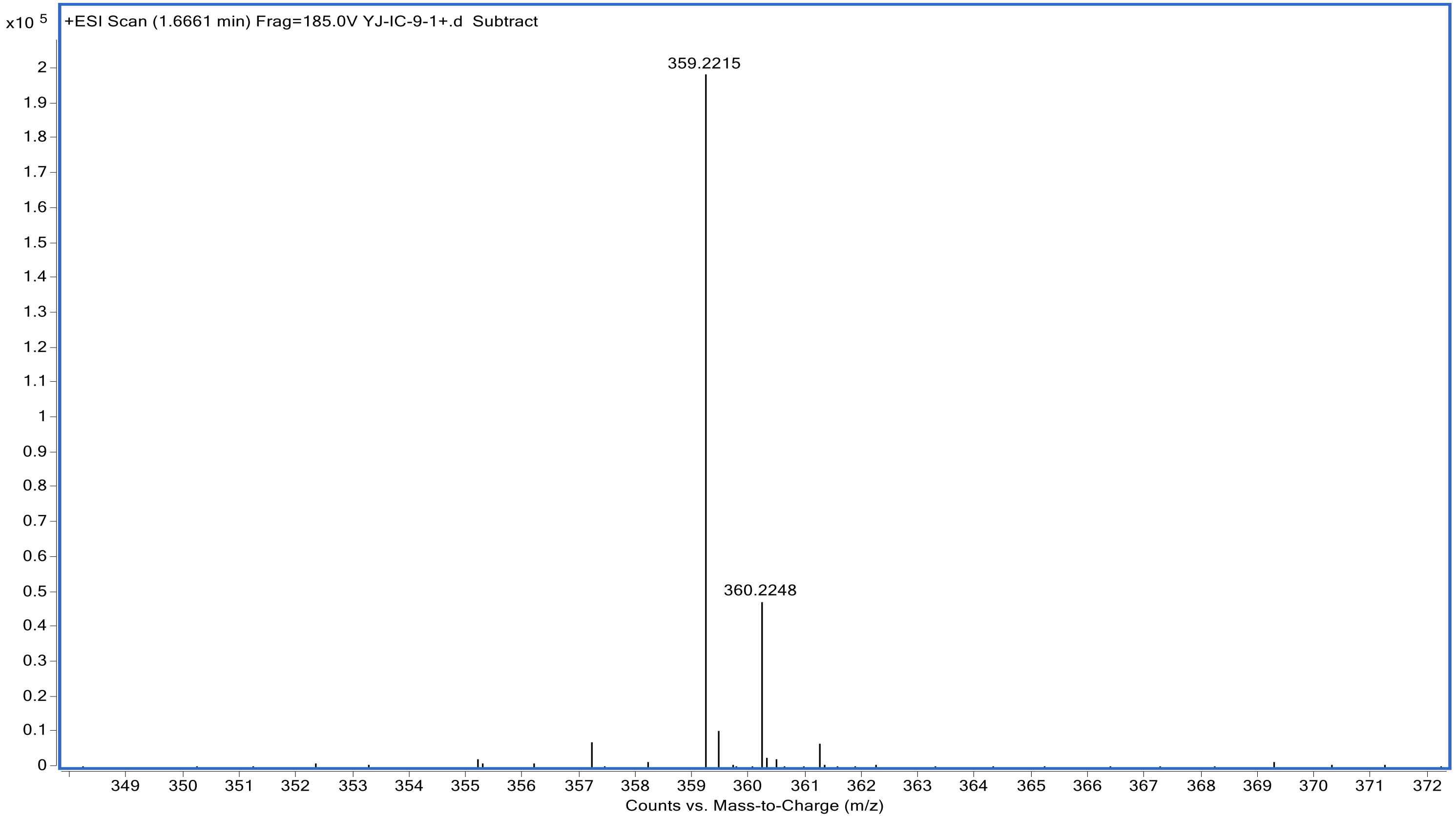


Figure S19. (+)-HR-ESI-MS $[M + H]^+$ of expanstine B (**2**).

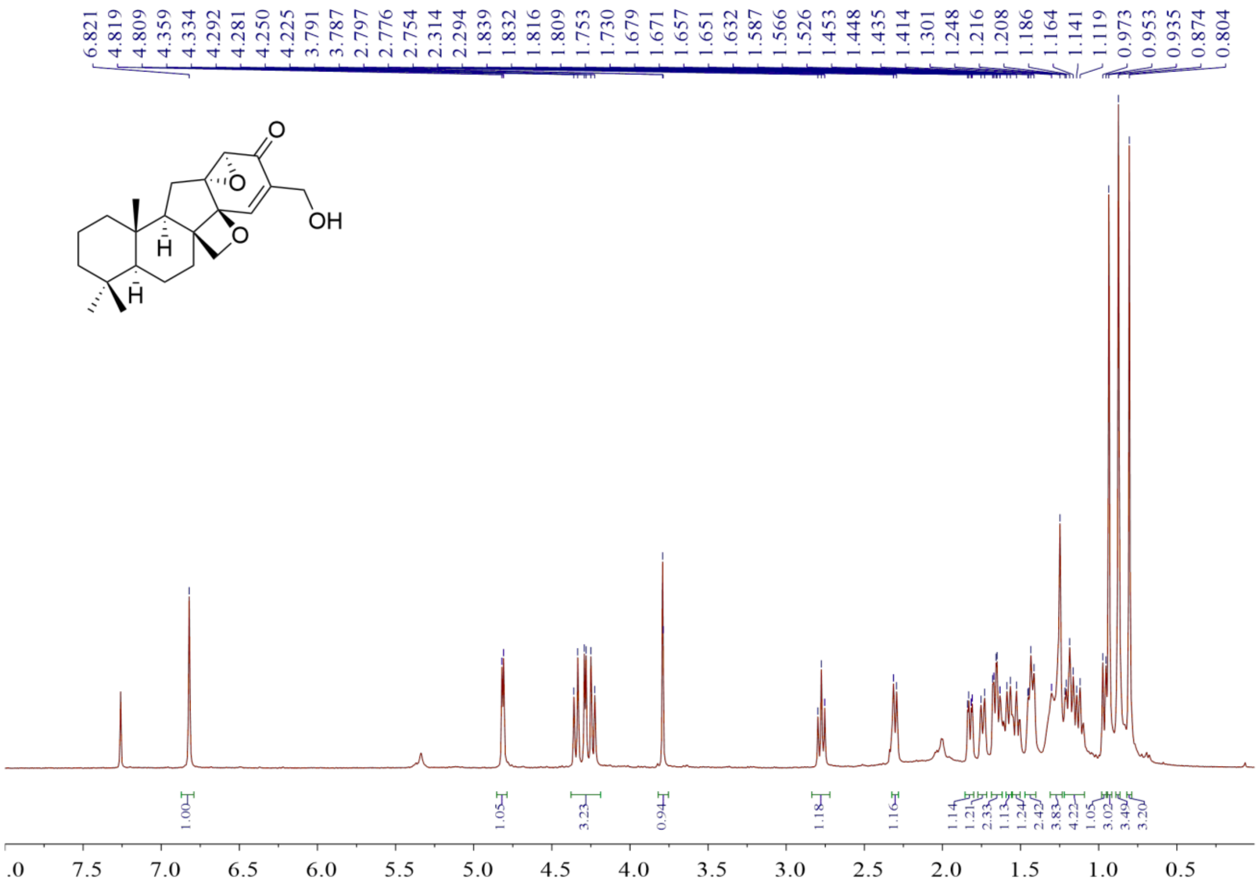


Figure S20. [1]H NMR spectrum ($CDCl_3$, 600 MHz) of expanstine C (**3**).

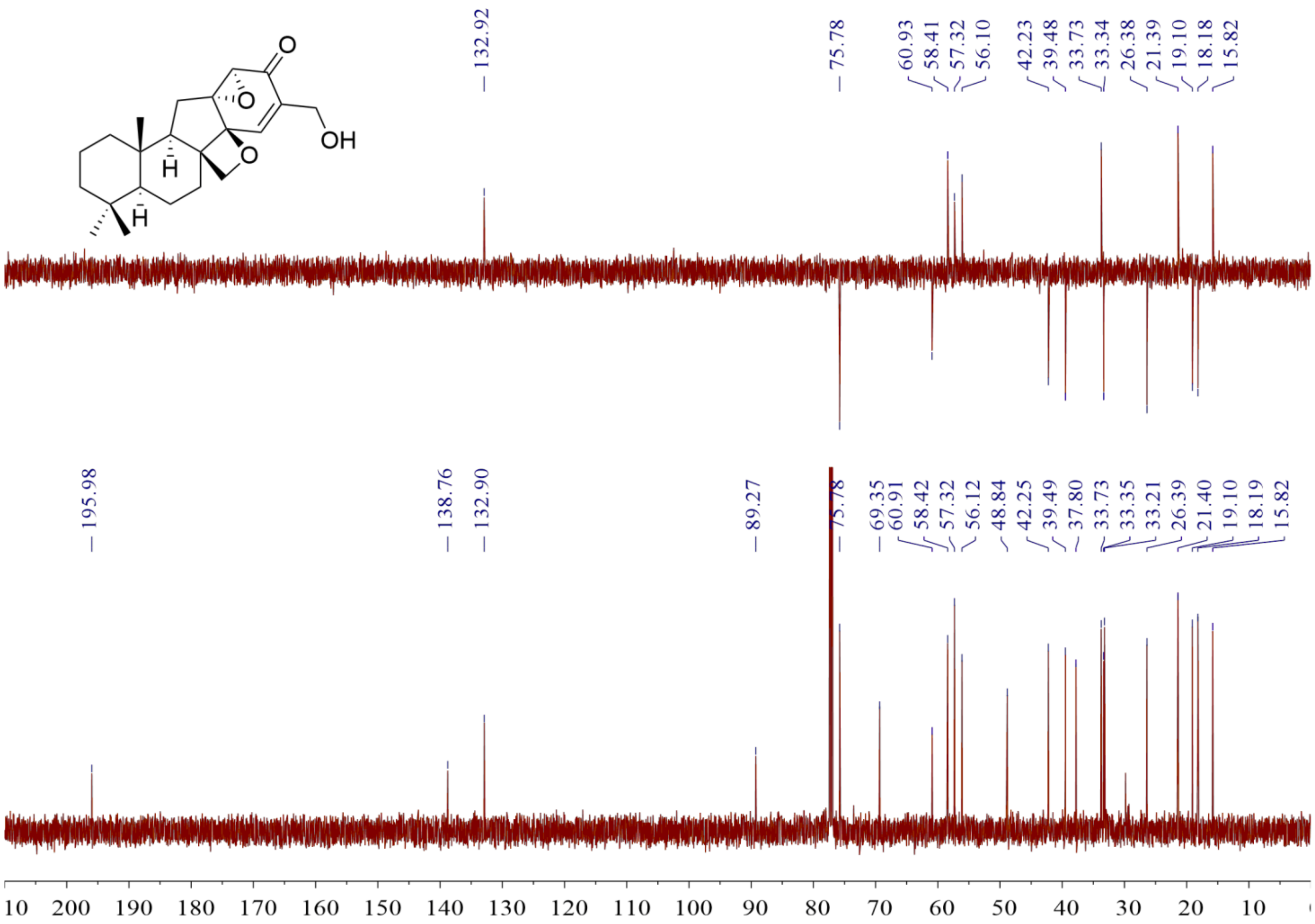


Figure S21. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of expanstine C (**3**).

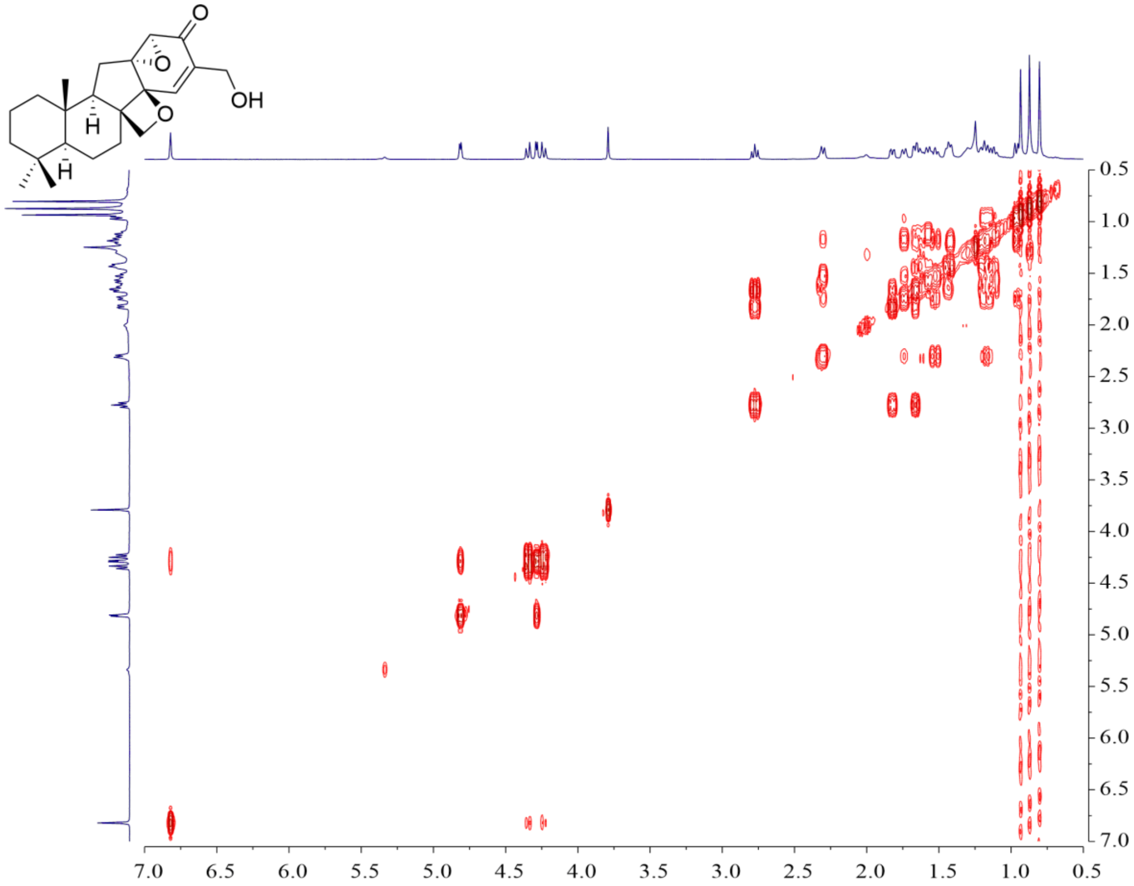


Figure S22. [1]H-[1]H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine C (**3**).

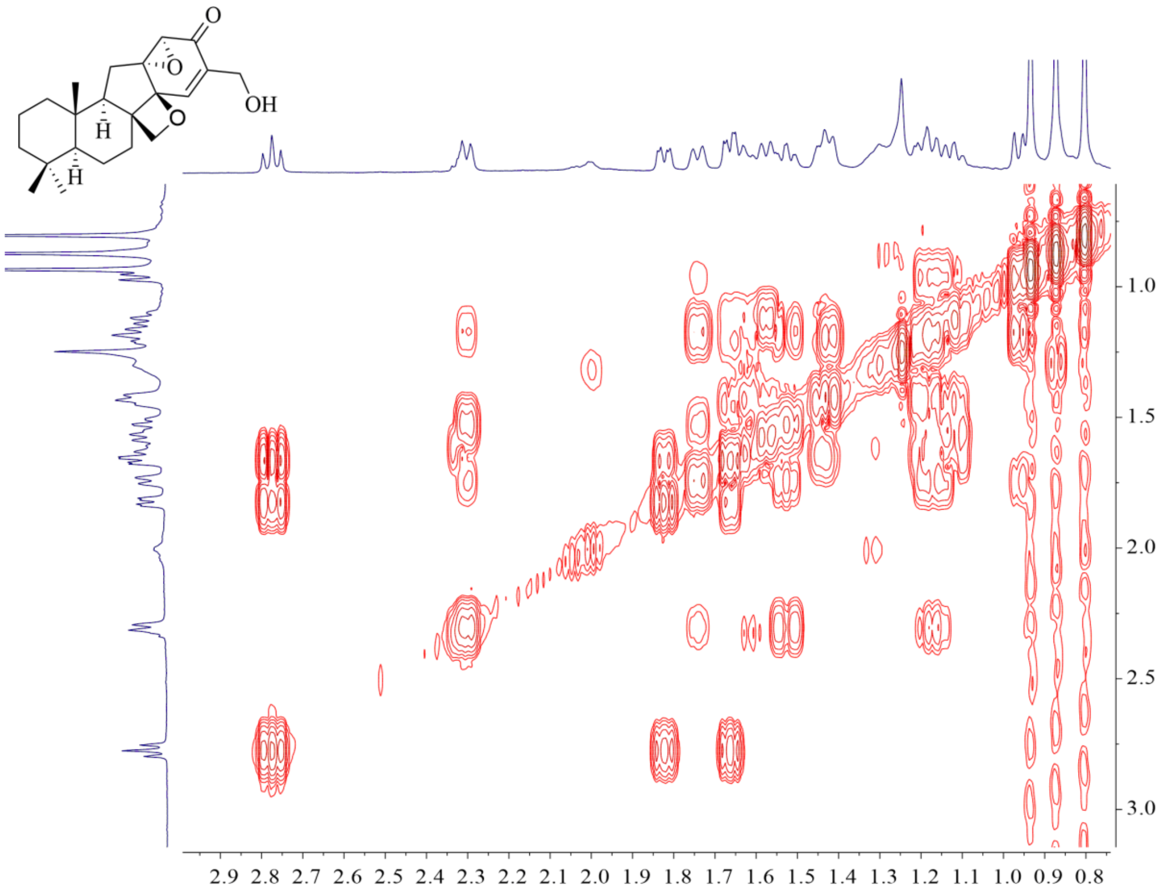


Figure S23. Enlarged ^1H-^1H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine C (**3**).

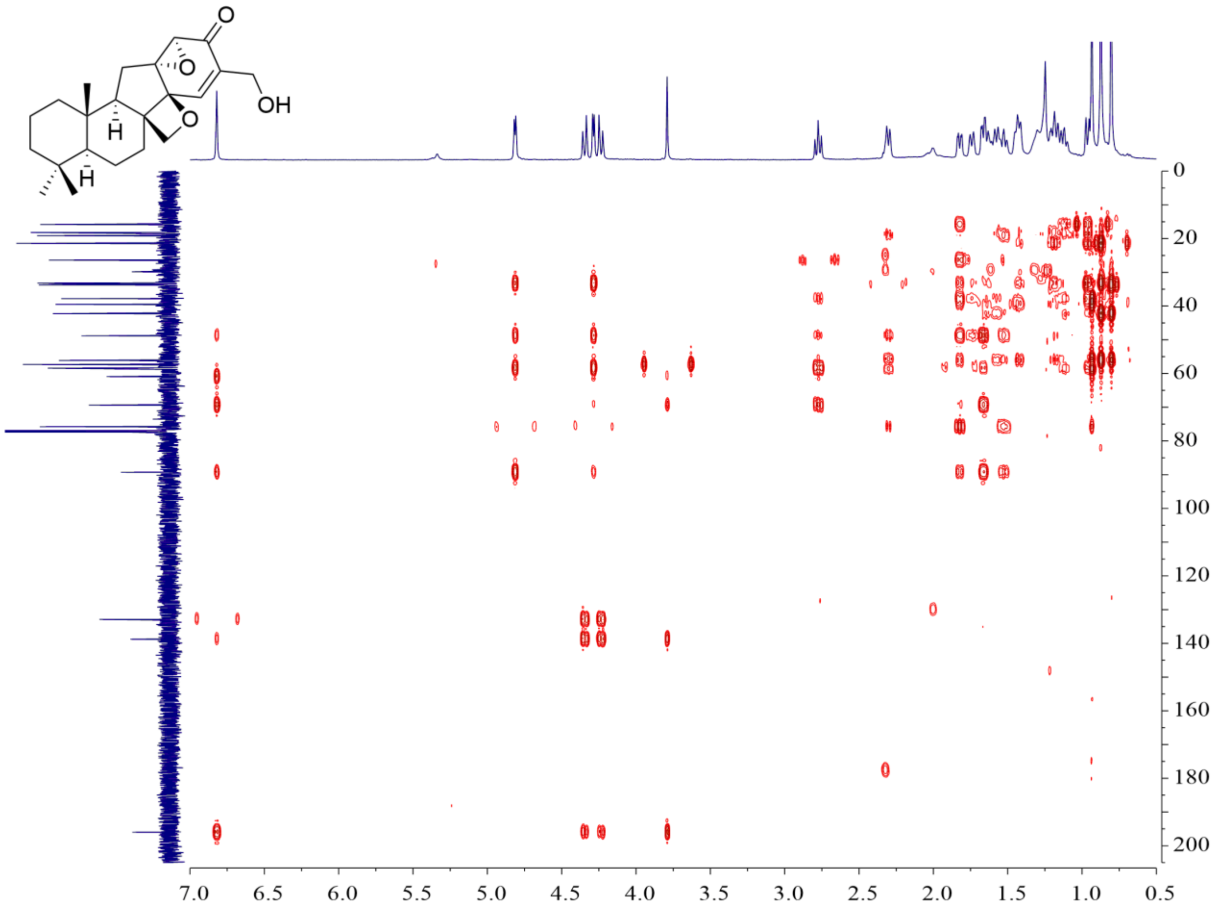


Figure S24. HMBC spectrum ($CDCl_3$, 600 MHz) of expanstine C (**3**).

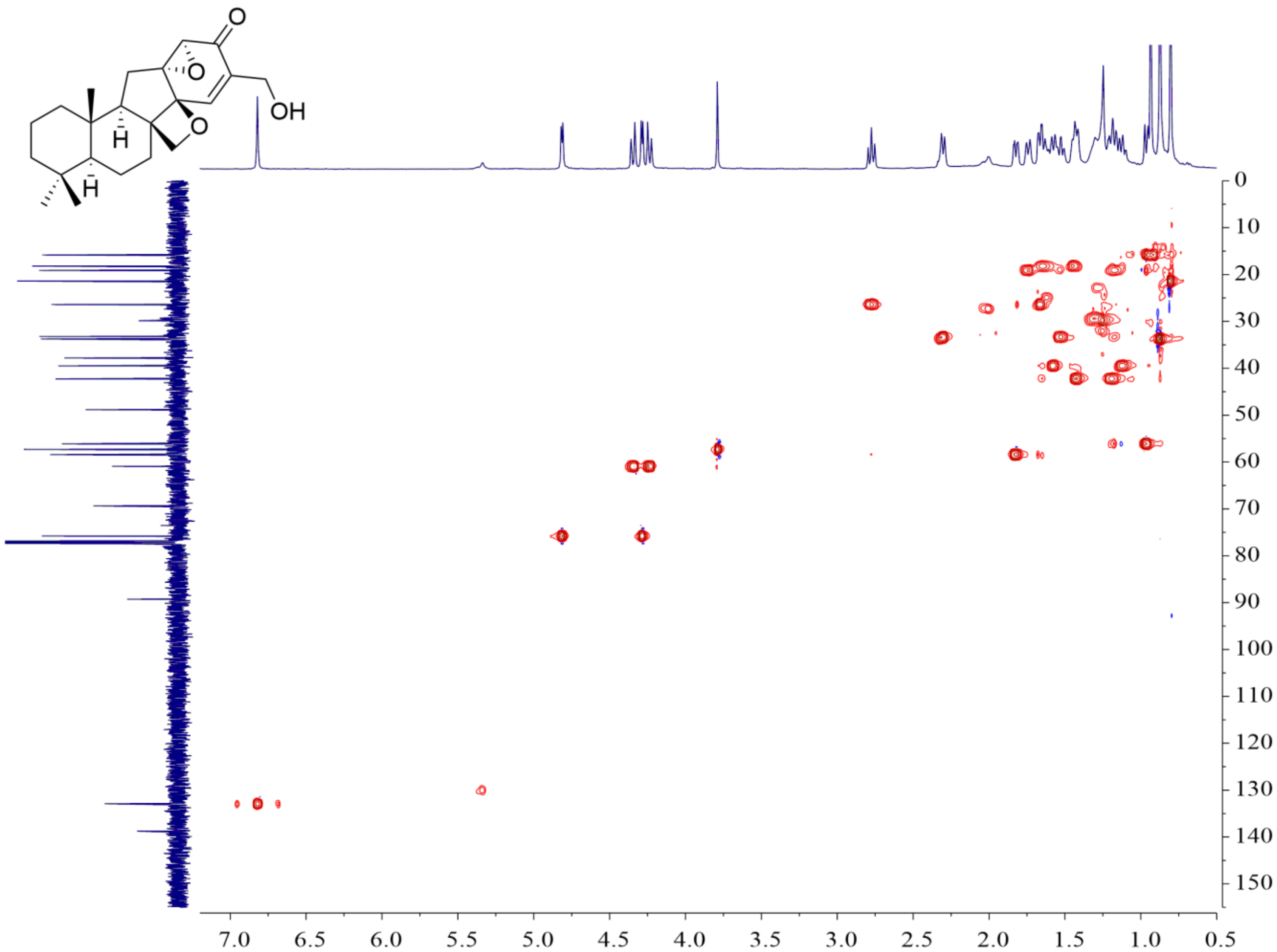


Figure S25. HSQC spectrum ($CDCl_3$, 600 MHz) of expanstine C (**3**).

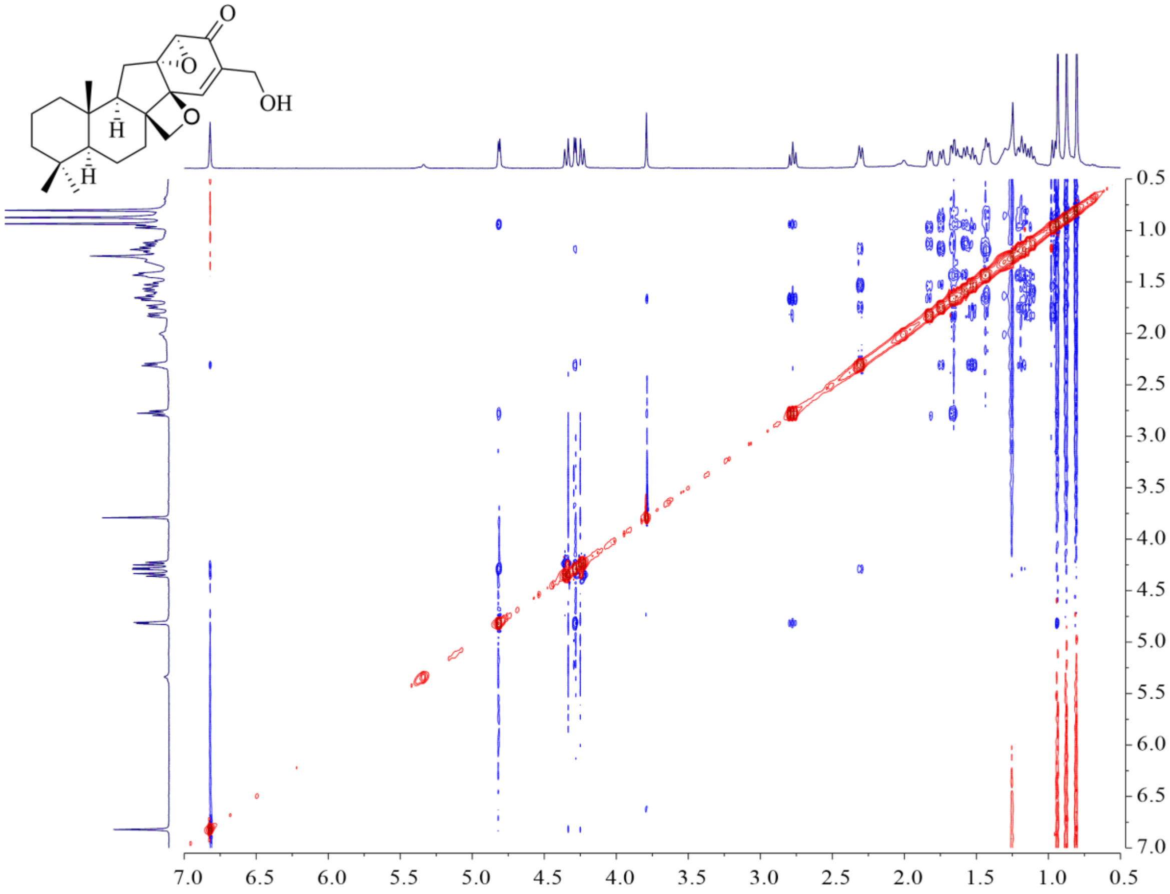


Figure S26. NOESY spectrum ($CDCl_3$, 600 MHz) of expanstine C (**3**).

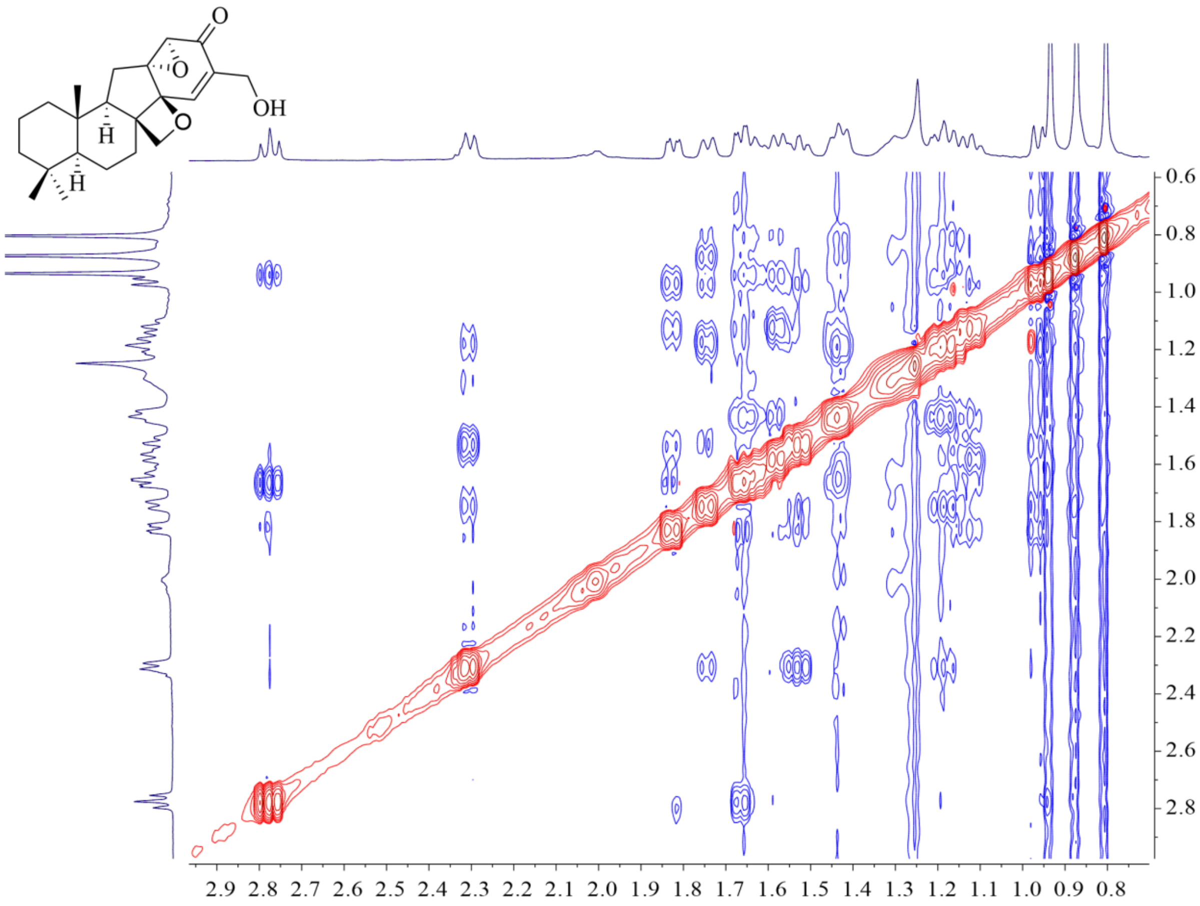


Figure S27. Enlarged ROESY spectrum ($CDCl_3$, 600 MHz) of expanstine C (**3**).

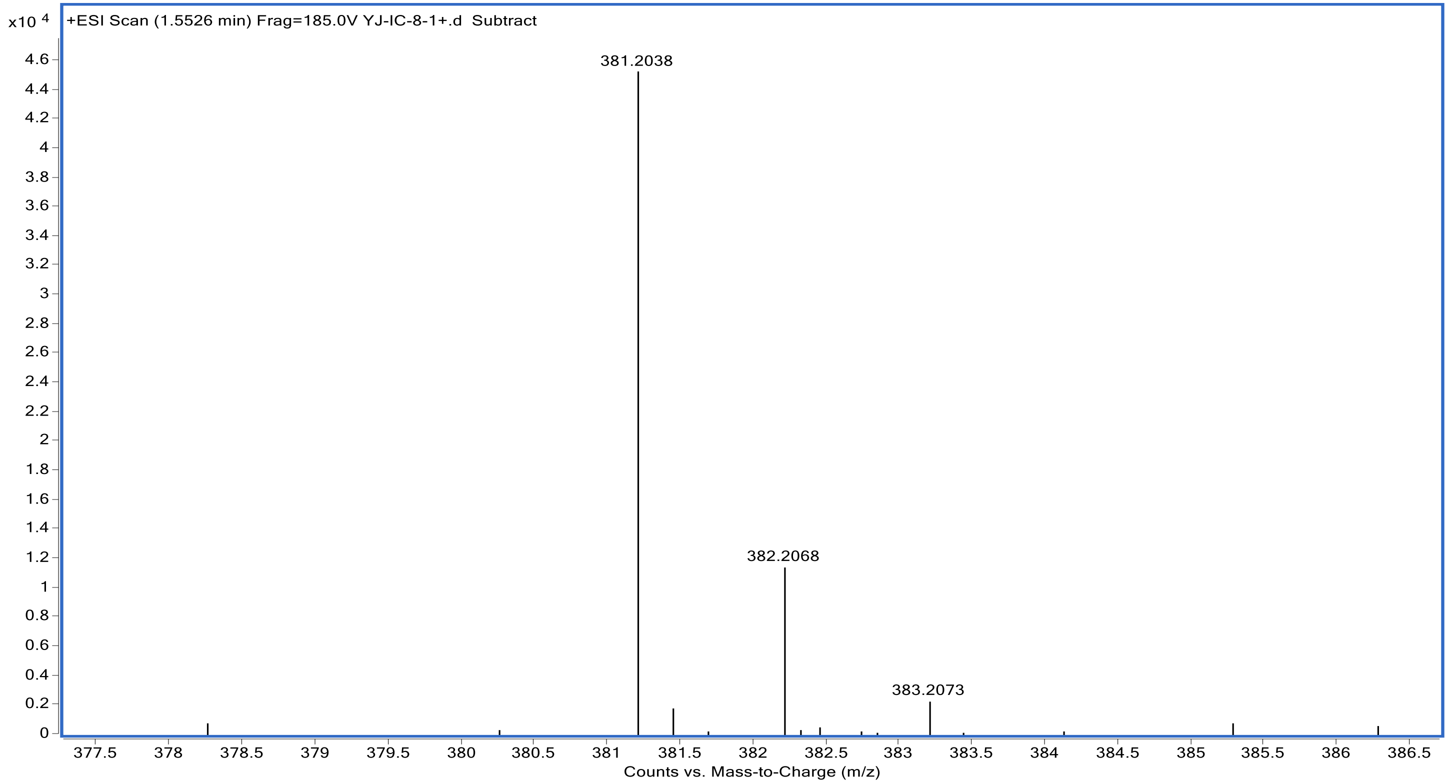


Figure S28. (+)-HR-ESI-MS $[M + Na]^+$ of expanstine C (**3**).

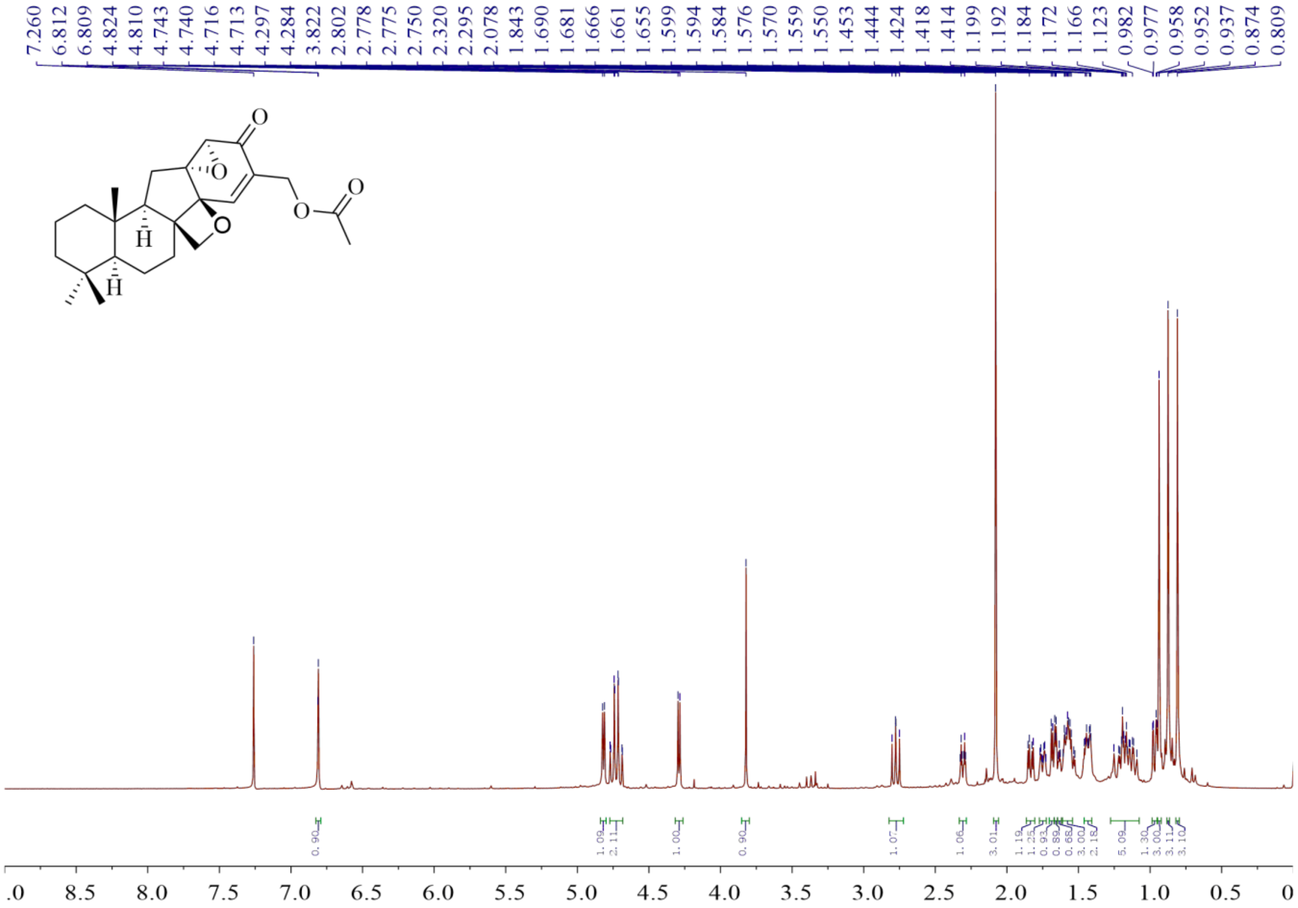


Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of expanstine D (**4**).

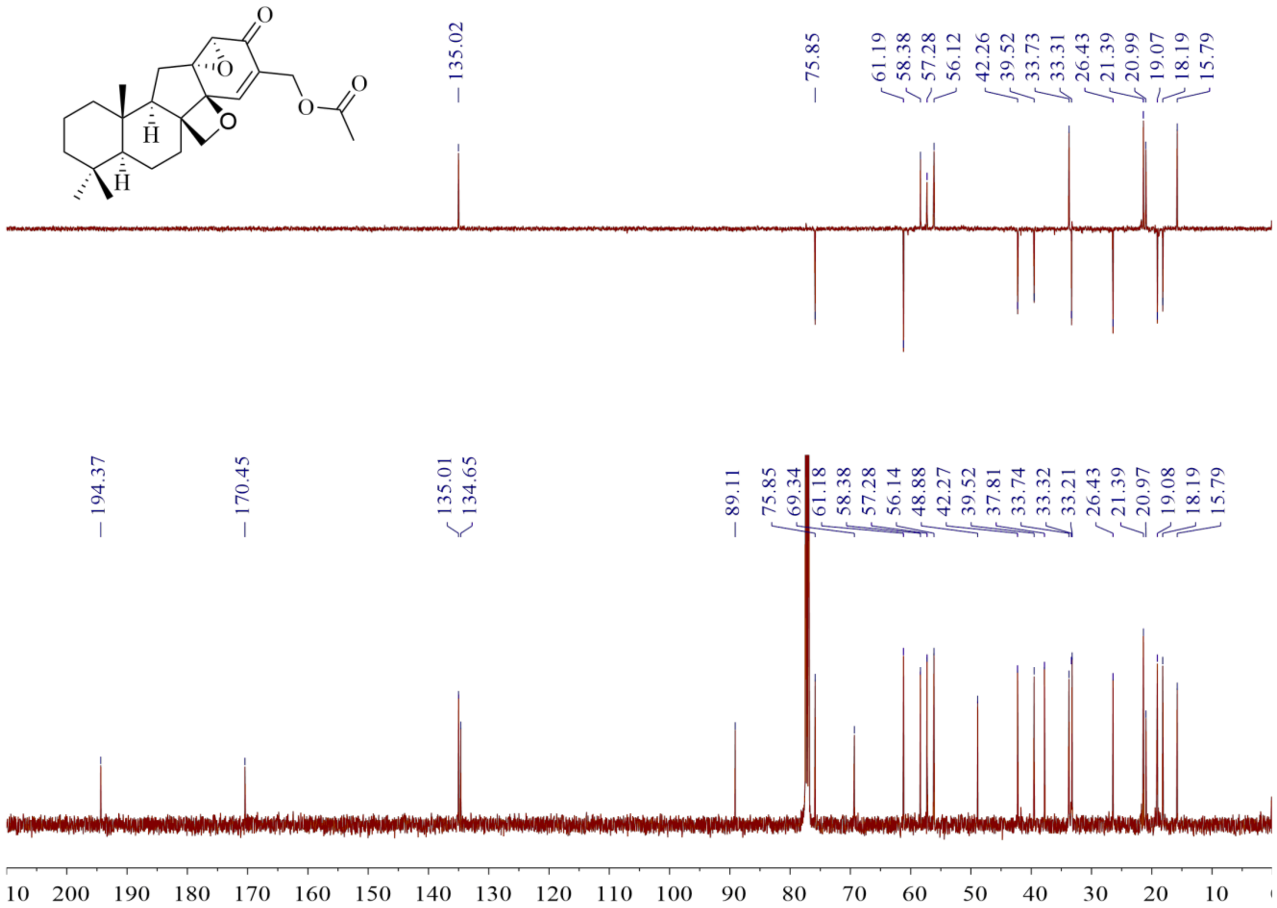


Figure S30. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of expanstine D (**4**).

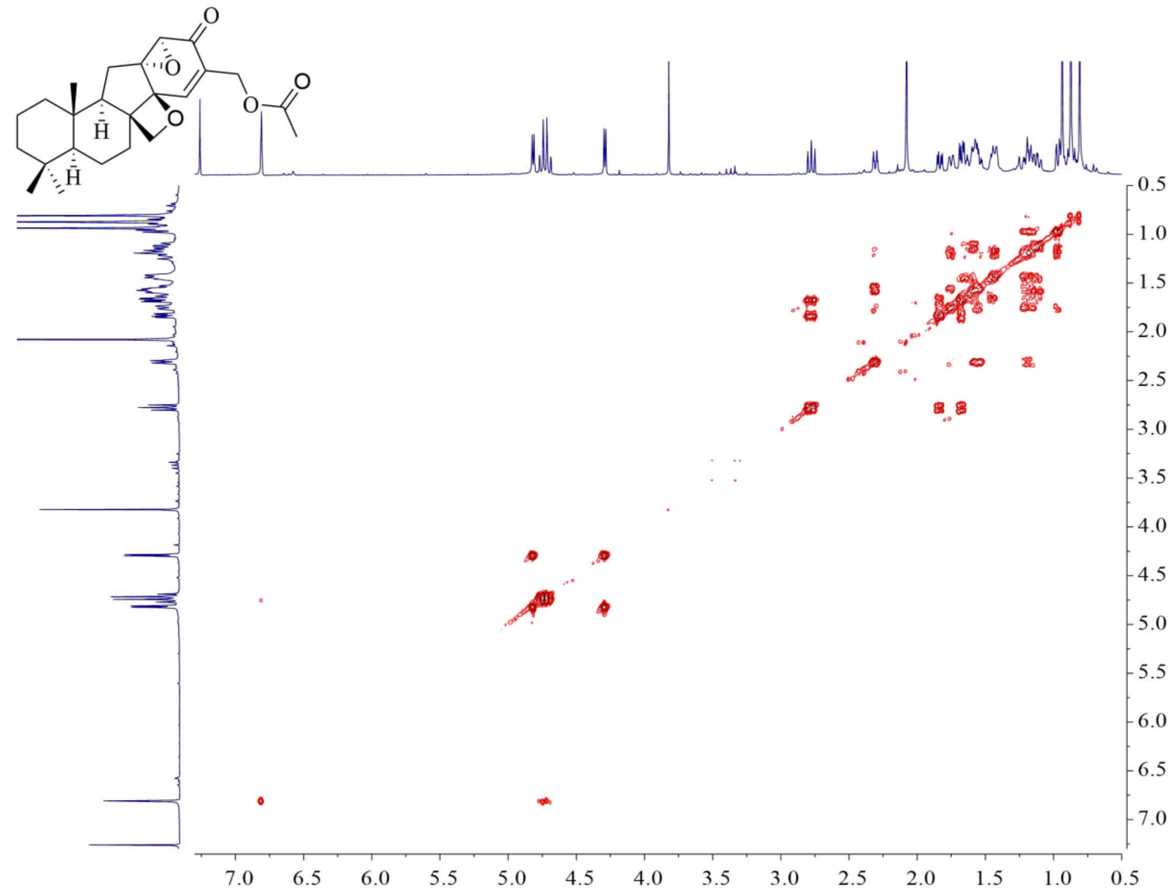


Figure S31. ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine D (**4**).

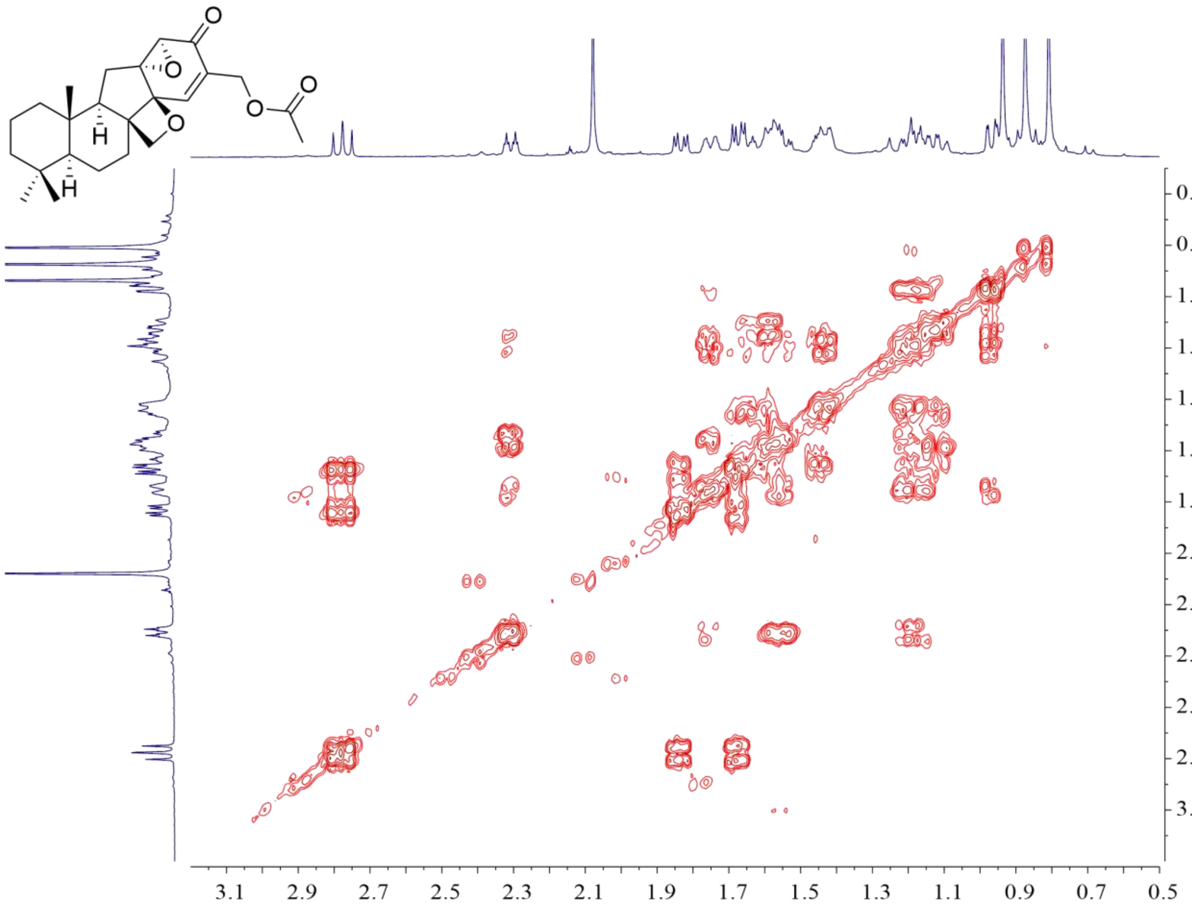


Figure S32. Enlarged ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 600 MHz) of expanstine D (**4**).

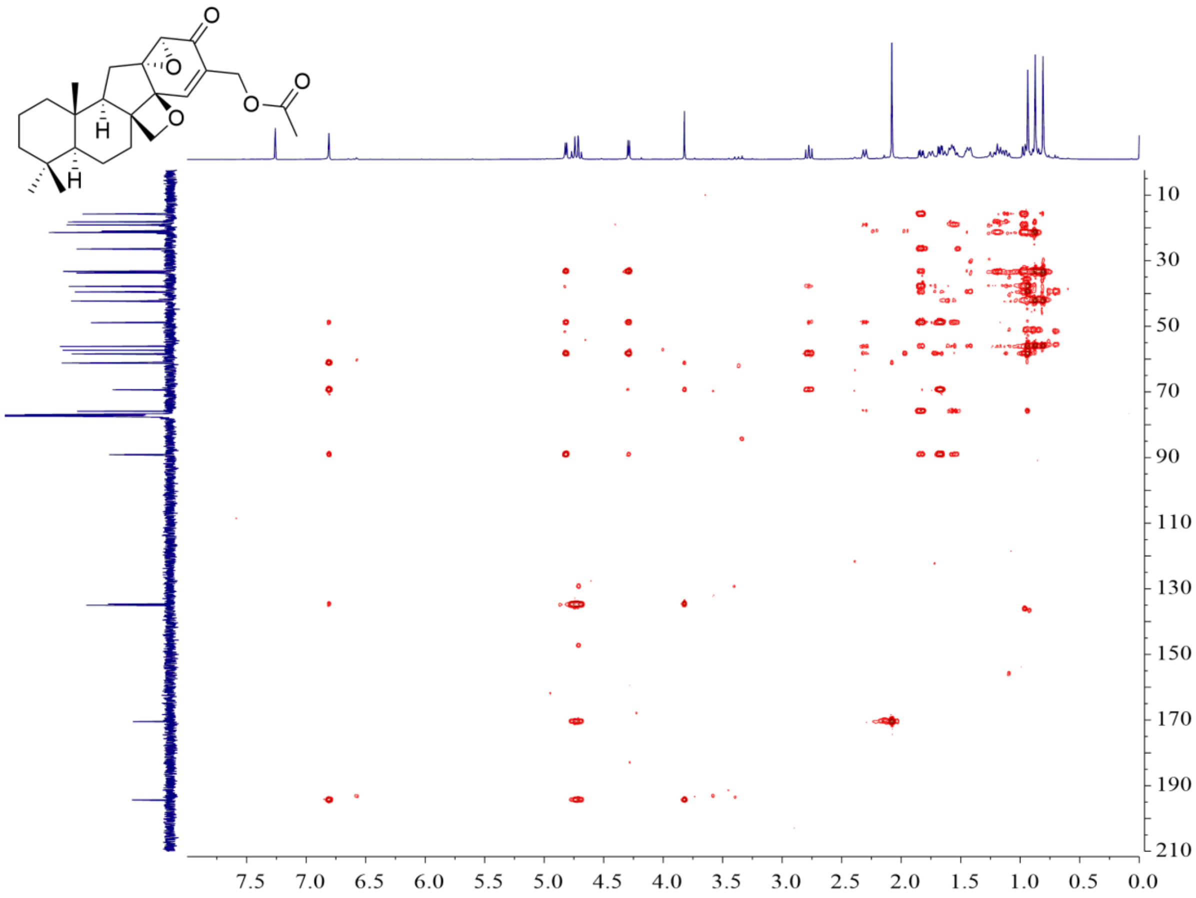


Figure S33. HMBC spectrum ($CDCl_3$, 600 MHz) of expanstine D (**4**).

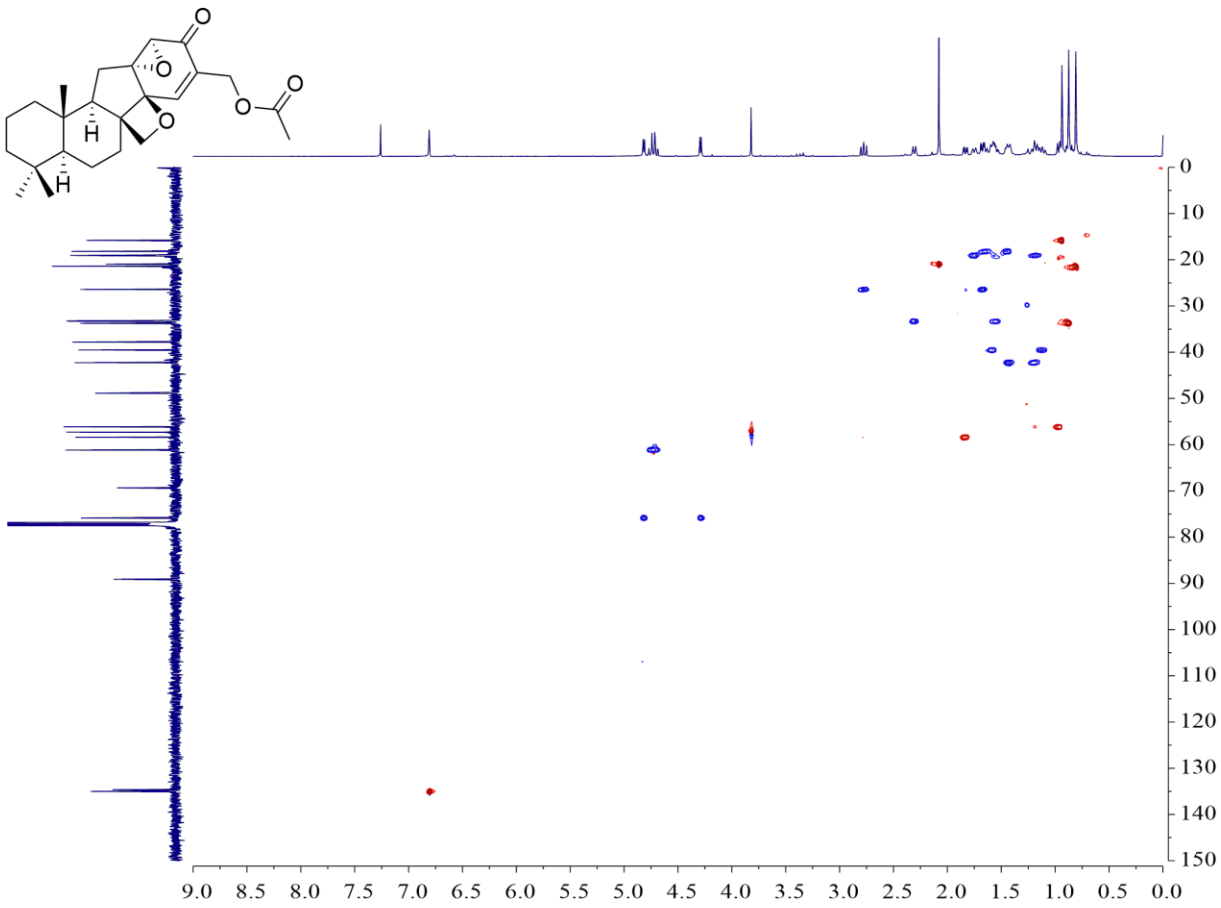


Figure S34. HSQC spectrum ($CDCl_3$, 600 MHz) of expanstine D (**4**).

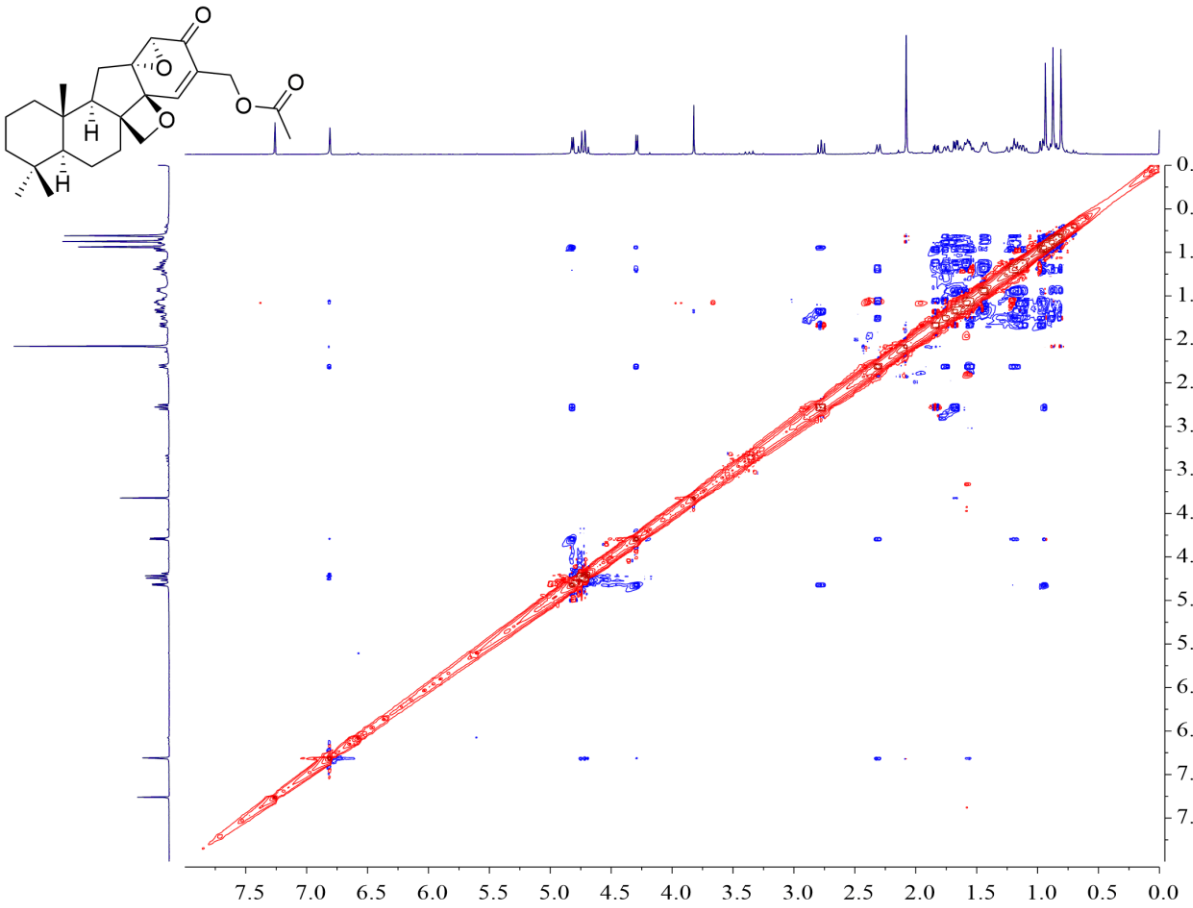


Figure S35. NOESY spectrum ($CDCl_3$, 600 MHz) of expanstine D (**4**).

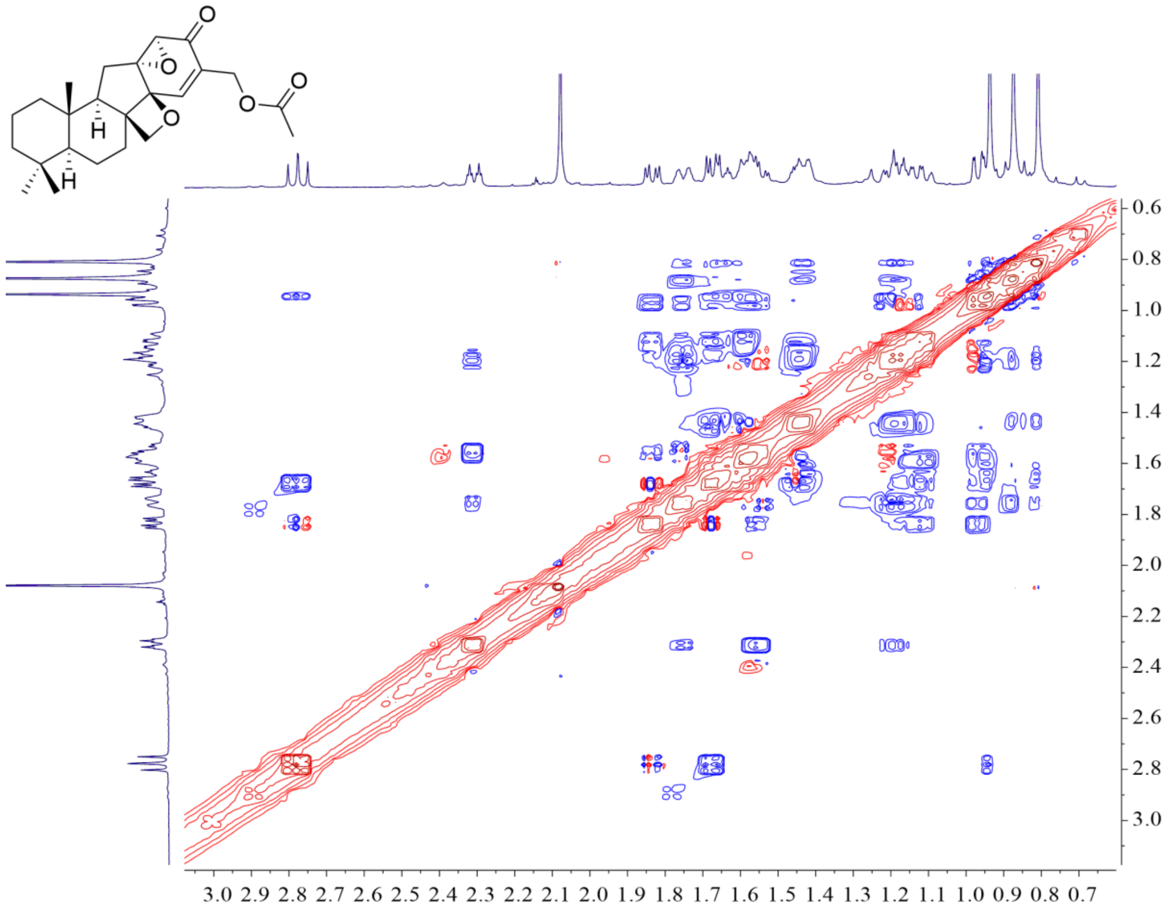


Figure S36. Enlarged NOESY spectrum ($CDCl_3$, 600 MHz) of expanstine D (**4**).

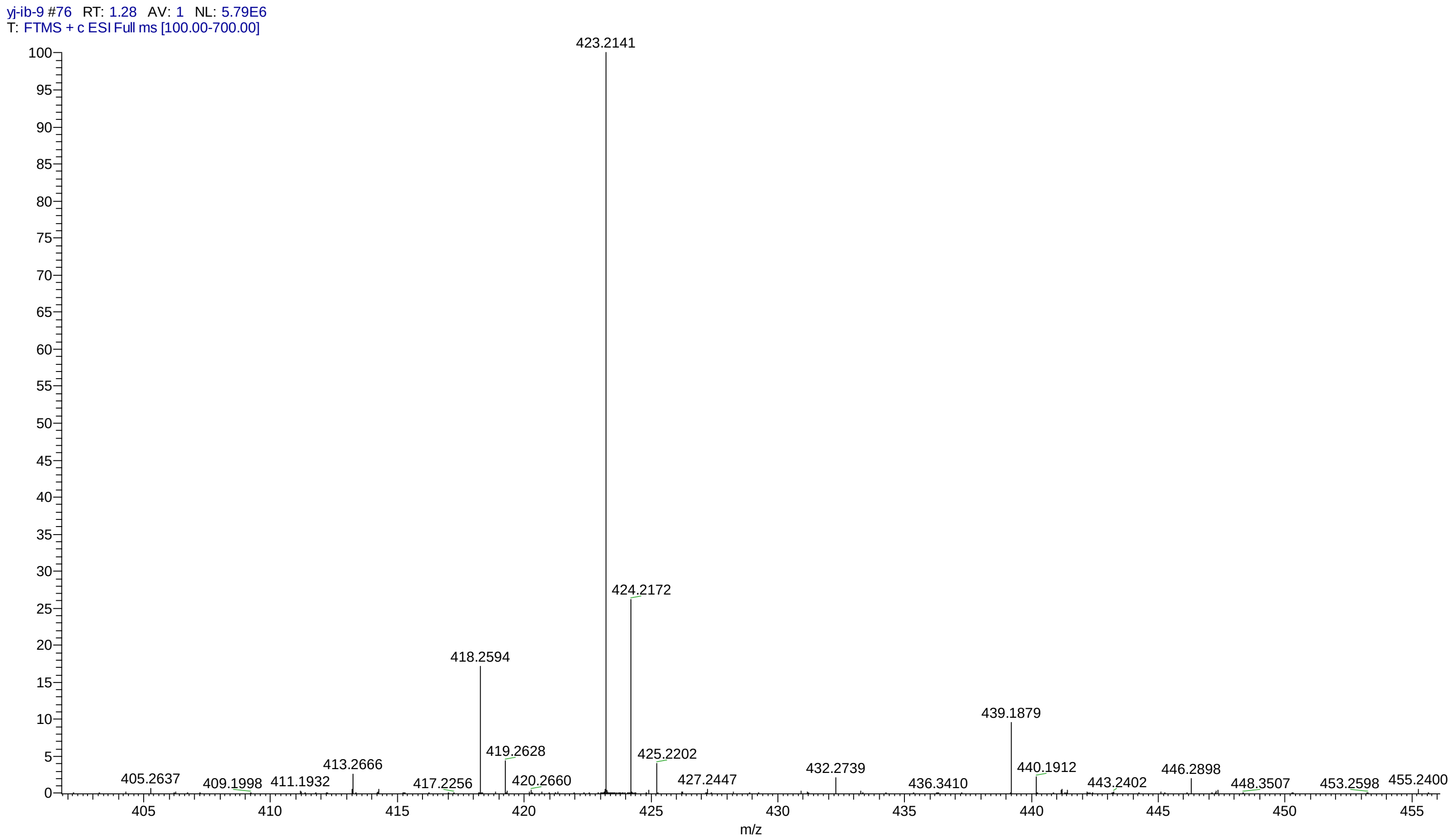


Figure S37. (+)-HR-ESI-MS [M + Na]$^+$ of expanstine D (**4**).

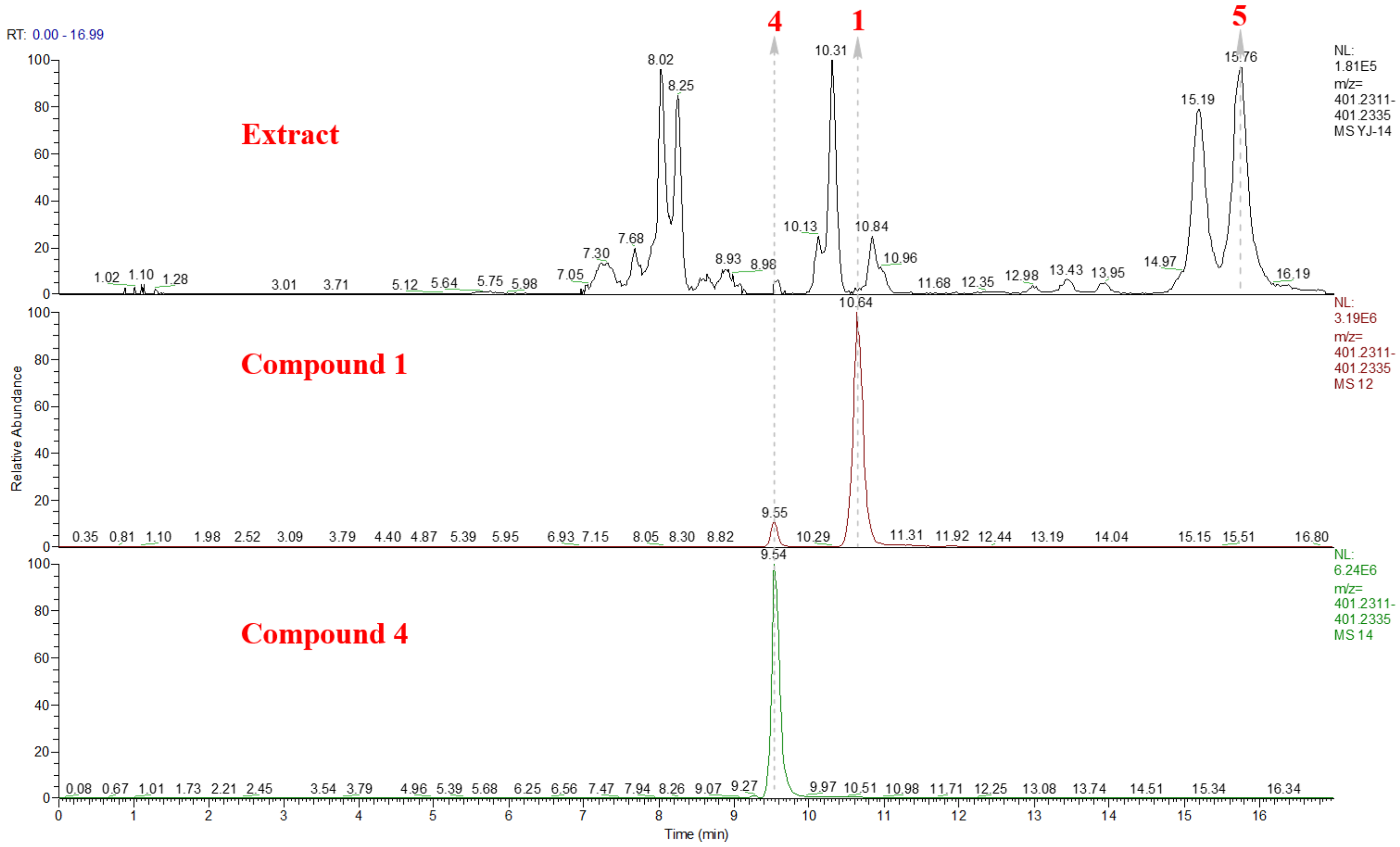


Figure S38. Extracted ion chromatogram (EIC, $[M + H]^+$) of compounds **1**, **4**, and **5** of the MeOH extract and purified compounds **1** and **4**.

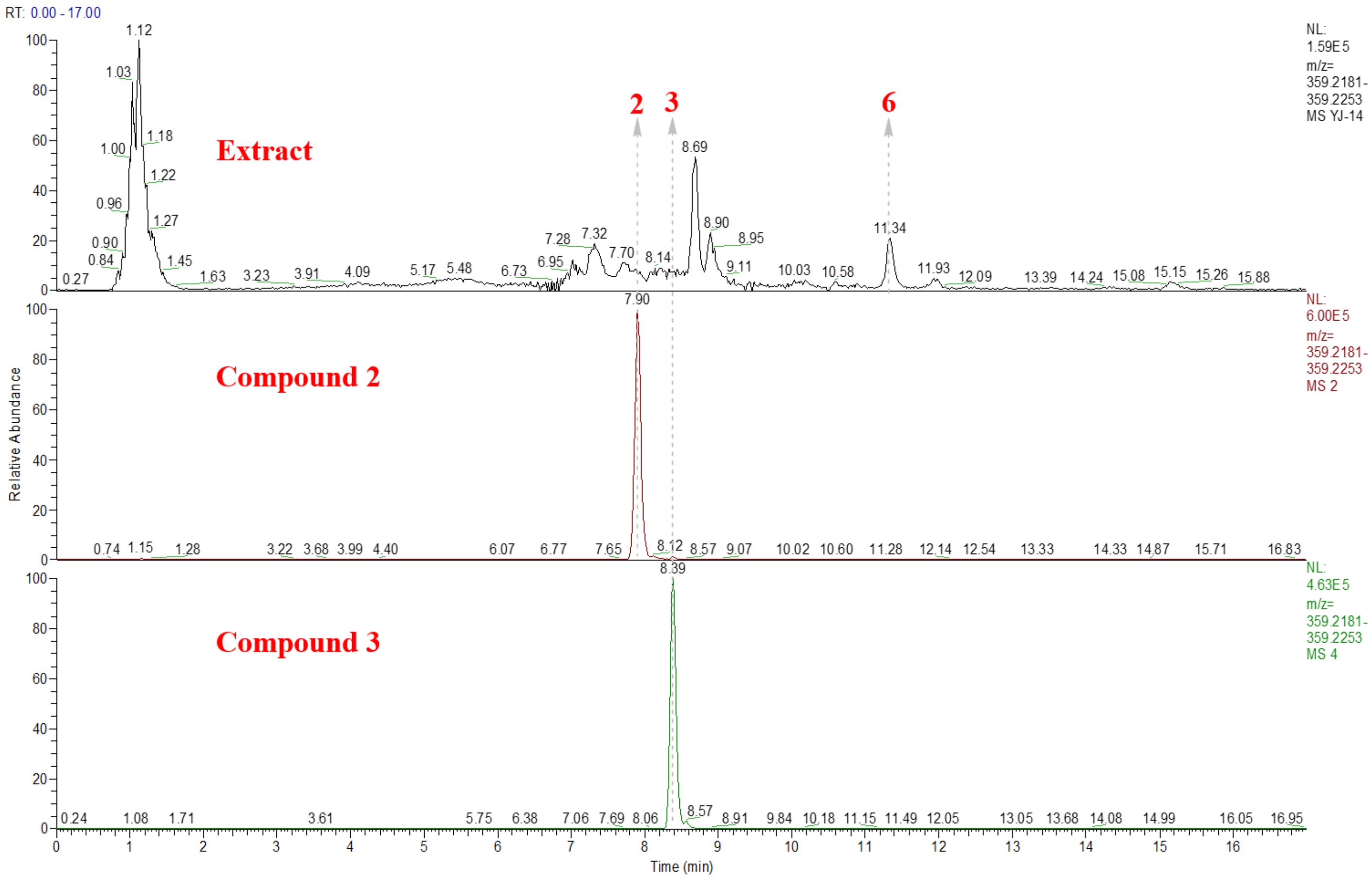


Figure S39. Extracted ion chromatogram (EIC, $[M + H]^+$) of compounds **2**, **3**, and **6** of the MeOH extract and purified compounds **2** and **3**.