Supporting Information

Peyssonnosides A−B, Unusual Diterpene Glycosides with a Sterically Encumbered Cyclopropane Motif: Structure Elucidation Using an Integrated Spectroscopic and Computational Workflow

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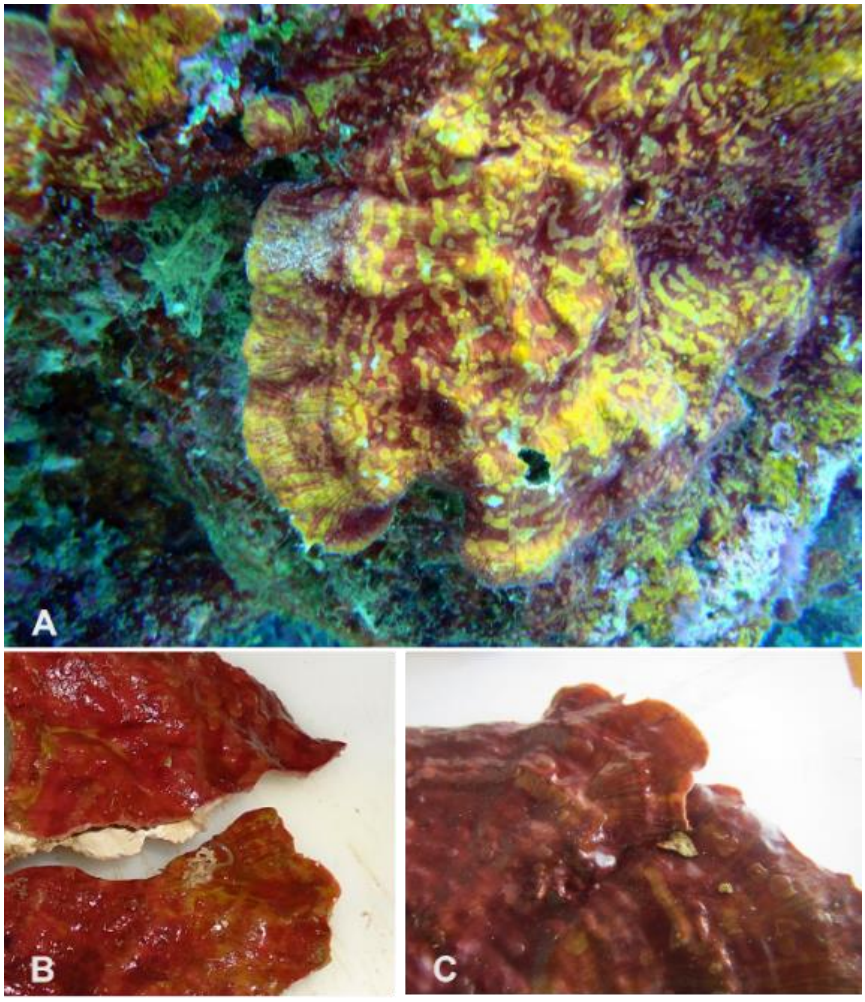


Figure S1. A: *Peyssonnelia* sp. (G-1163) growing on a reef slope. **B:** Close-up of the surface of G-1163, **C**: Surface of G-1588 showing analogous morphology with calcified texture and intermittent tinges of yellow on a red surface.

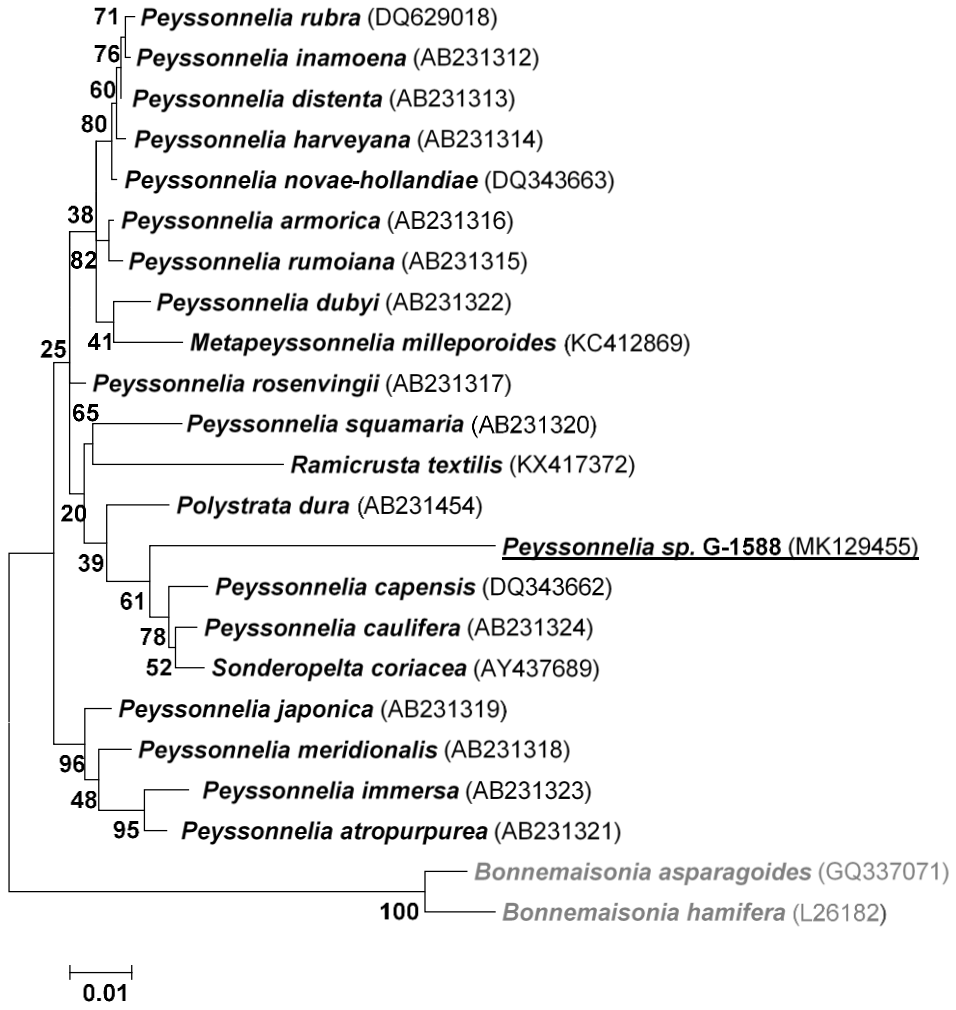


Figure S2. Evolutionary relationship of *Peyssonnelia* sp. G-1588 with related red algal species from family Peyssonneliaceae was inferred by the 18S small subunit (SSU) rRNA sequences using the Maximum Likelihood method based on the Kimura 2-parameter model [1] in MEGA X.[2] The percentage of replicate trees in which the associated species clustered together in the bootstrap test (1000 iterations) is shown next to the branches. The accession numbers of the SSU rRNA of respective red algae are mentioned in parentheses. The outgroup taxa are represented in gray. The SSU rRNA sequence from *Peyssonnelia* sp. used in this study is underlined. The tree is drawn to scale, with branch lengths measured in the number of substitutions per site.

Table S1. Bioassay results for peyssonnosides A-B (**1**−**2**).

Strain/cell line	**1**[a]	**2**[a]	Positive Control
Methicillin-resistant *Staphylococcus aureus* (MRSA, ATCC 33591)	16.7±0.3	>50	<1
Vancomycin-resistant *Enterococcus faecium* (VREF, ATCC 700221)	>50	>50	<7.8
Escherichia coli (EC, ATCC 25922)	>50	>50	<7.8
Multidrug-resistant *Escherichia coli* (MDREC, ATCC BAA-1743)	>50	>50	<15.6
Amphotericin B-resistant *Candida albicans* (ARCA, ATCC 90873)	>50	>50	>50
Enterobacter cloacae (CDC0008)	>50	>50	<0.5
Klebsiella pneumoniae (CDC0016)	>50	>50	<0.5
Acinetobacter baumannii (CDC0033)	>50	>50	>50
Enterococcus faecium (HM-959)	>50	>50	32
Pseudomonas aeruginosa (PA01)	>50	>50	<0.5
Mycobacterium tuberculosis (H37Rv)	>50	>50	0.07
Plasmodium berghei (exoerythrocytic stage)	2.4	5.8	0.0003
Plasmodium falciparum (Dd2L)	>6.25	>6.25	0.003
Plasmodium falciparum (D10)	>6.25	>6.25	0.007
HEK293T cell line	>10	>9	1.3

[a] Antibacterial activity reported as MIC (μg/ml), antiplasmodial activity reported as EC_{50} (μM), cytotoxicity against HEK293T cell line reported as CC_{50} (μM)

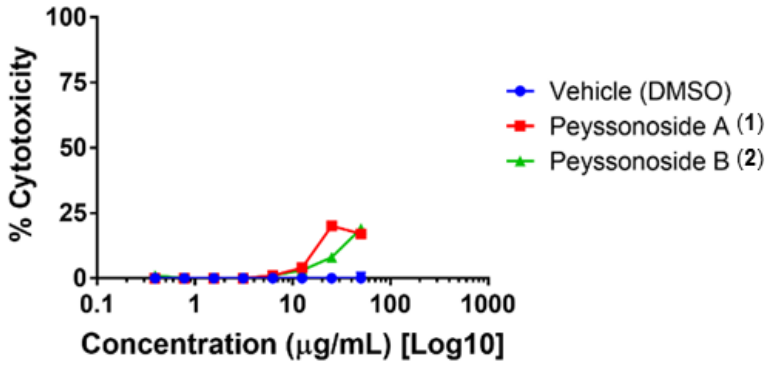


Figure S3. Cytotoxicity of **1**–**2** against human keratinocytes (HaCaT). Relative cytotoxicity (%) were less than 25% for both **1**–**2** at highest concentration of 50 μg/ml.

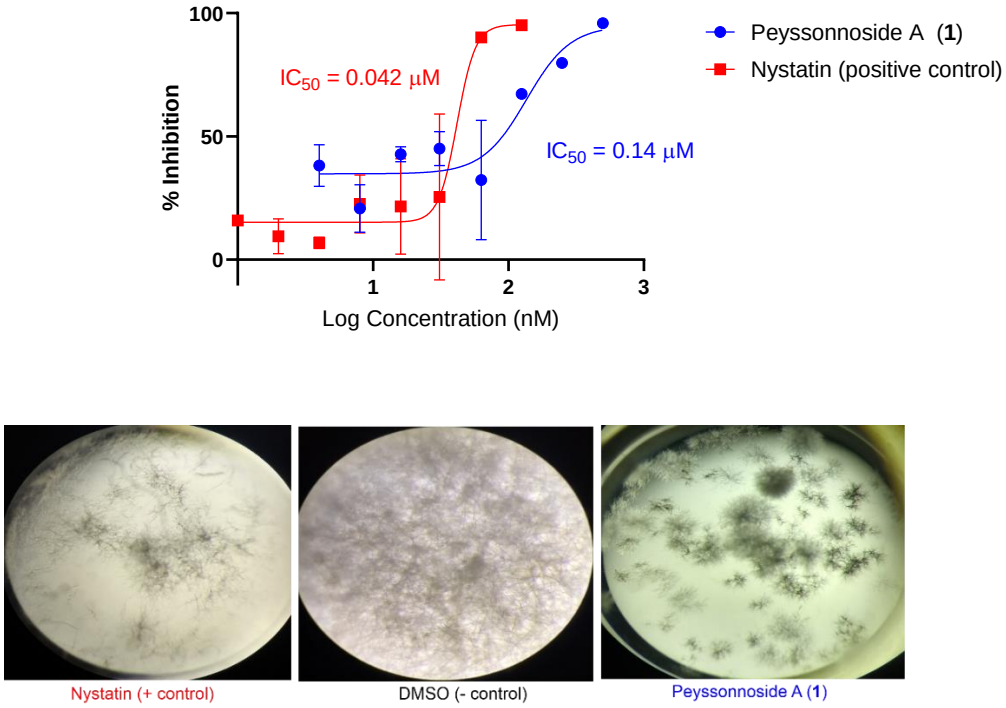


Figure S4. Top: Percent growth inhibition after 3 days incubation of the fungus *D. salina* with peyssonnoside A (**1**) and the antifungal drug nystatin (n = 3, mean ± standard error). **Bottom:** Comparison of fungal growth in the presence of nystatin, DMSO, and **1** showing the morphological change in the fungus exposed to **1**.

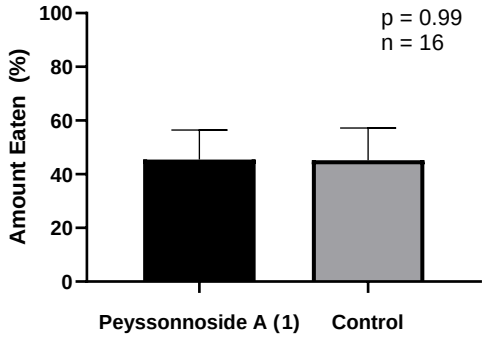


Figure S5. Response of hermit crabs *Clibanarius striolatus* to food laced with 1 mg/mL peyssonnoside A (**1**). These data indicate that **1** does not deter hermit crab feeding (mean ± standard error).

HRESIMS spectra of peyssonnosides A–B (1–2)

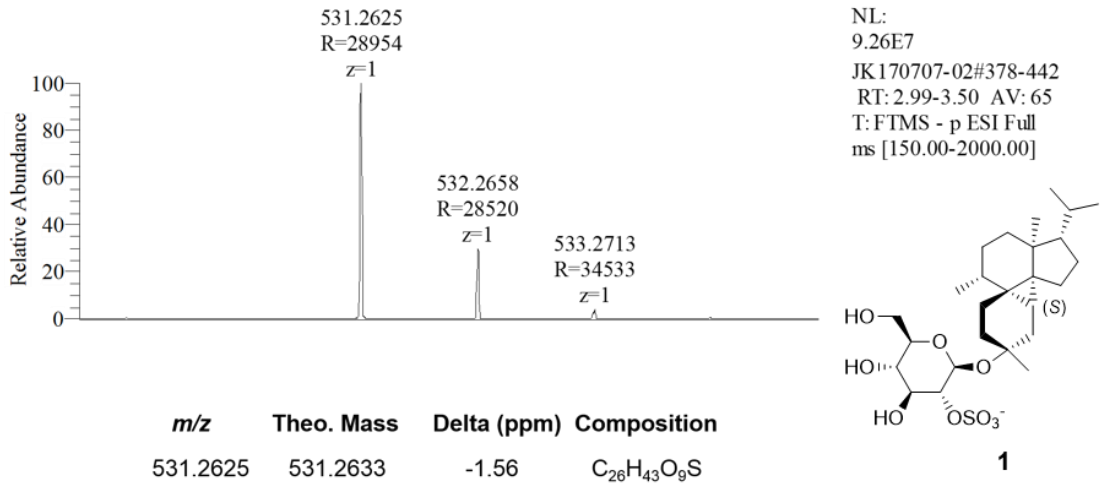


Figure S6. Negative ionization mode HRESIMS spectrum of peyssonnoside A (**1**)

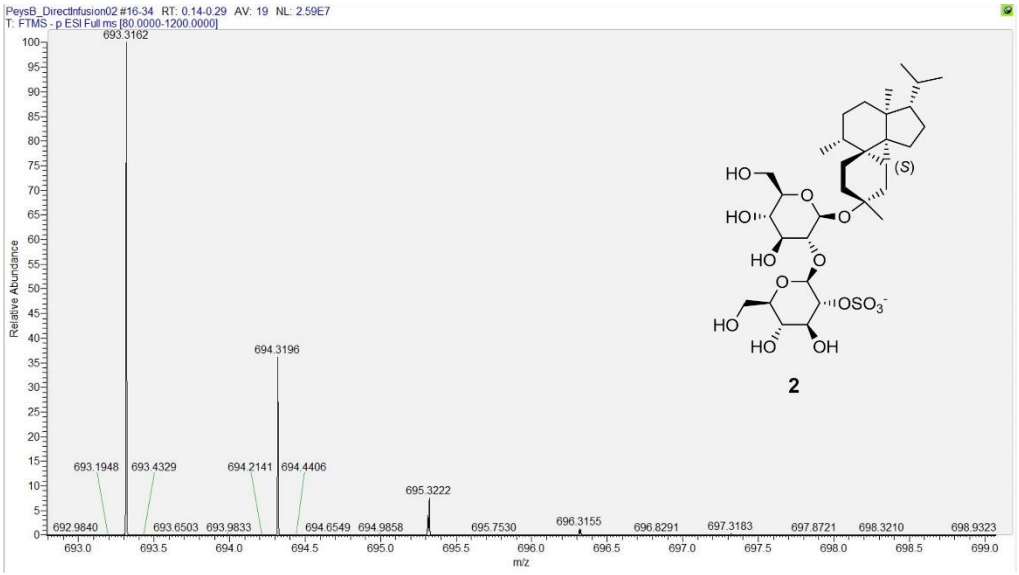
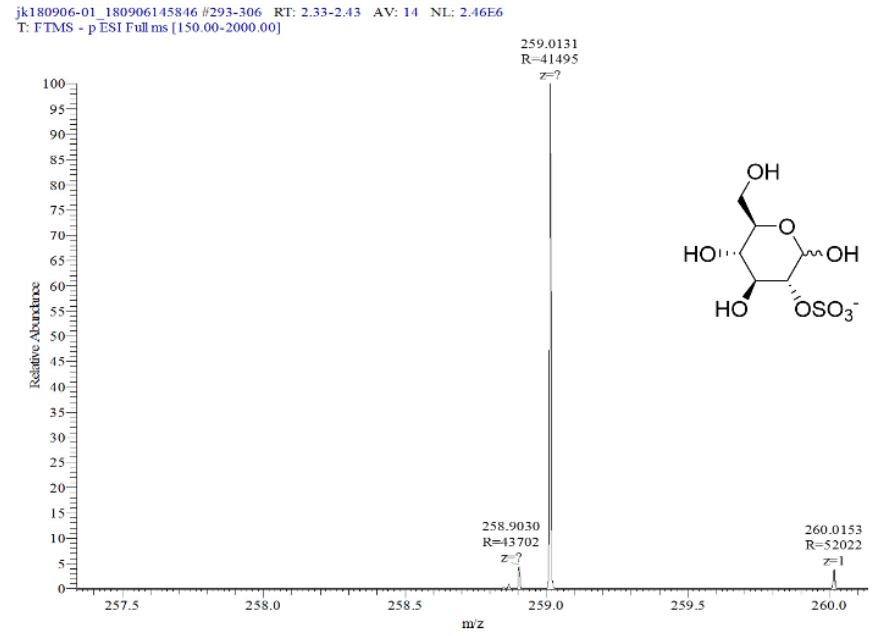


Figure S7. Negative ionization mode HRESIMS spectrum of peyssonnoside B (**2**)



m/z	Theo. Mass	Composition
259.0131	259.0129	$C_6H_{11}O_9S$

Figure S8. Negative ionization mode HRESIMS spectrum of the glycone from peyssonnoside A (**1**)

DFT calculation result for peyssonnoside A (1)

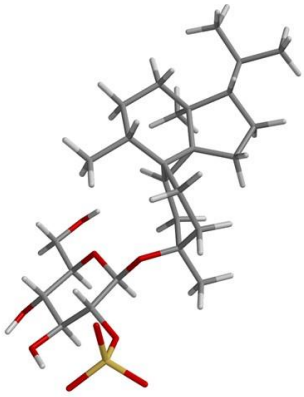
Table S2. Electronic energies (ΔE), free energies (ΔG), and Boltzmann population for conformers of **1** obtained from DFT calculations suing B3LYP/ 6-311++G(2d,2p) level of theory in DMSO.

Conformers	Energies (Hartree)		Abundance (%)
	Δ*E*	Δ*G*	
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*-**1a**	−2092.56129910	−2091.949211	23.2
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1b**	−2092.56084250	−2091.947305	3.1
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1c**	−2092.56069863	−2091.950226	68.1
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1d**	−2092.56092083	−2091.947645	4.4
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1e**	−2092.55665119	−2091.946428	1.2

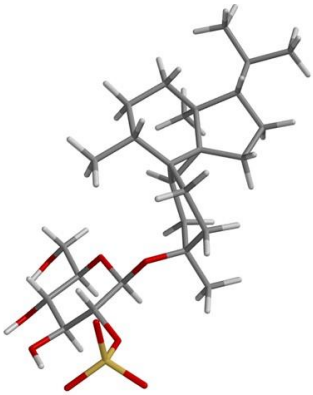
Table S3. Electronic energies (ΔE), free energies (ΔG), and Boltzmann population for conformers of **1** obtained from DFT calculations suing B3LYP/ 6-311++G(2d,2p) level of theory in DMSO.

Conformers	Energies (Hartree)		Abundance (%)
	Δ*E*	Δ*G*	
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* -**1a**	−2092.56127660	−2091.948773	34.0
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1b**	−2092.56063950	−2091.948144	17.5
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1c**	−2092.55989244	−2091.948091	16.5
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1d**	−2092.55890251	−2091.947022	5.3
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1e**	−2092.56055234	−2091.948548	26.8

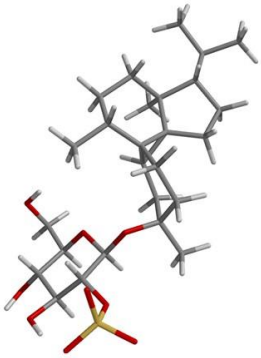
Lowest energy conformations of peyssonnoside A (1)



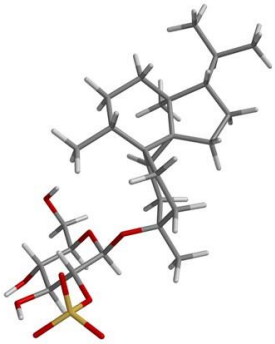
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*-**1a**



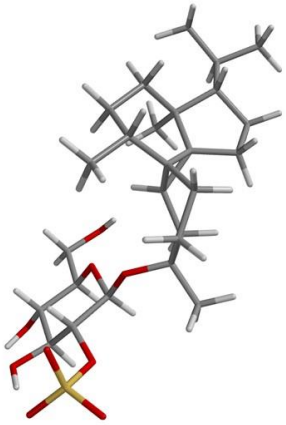
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1b**



1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1c**

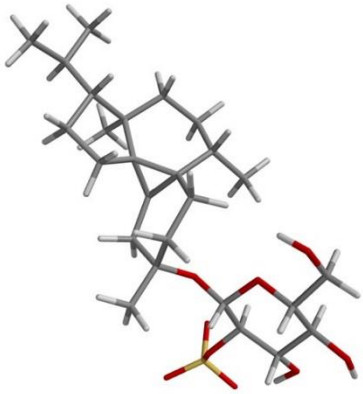


1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1d**

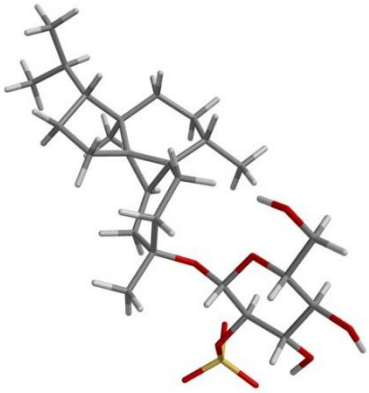


1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,*11S*,14*S*-**1e**

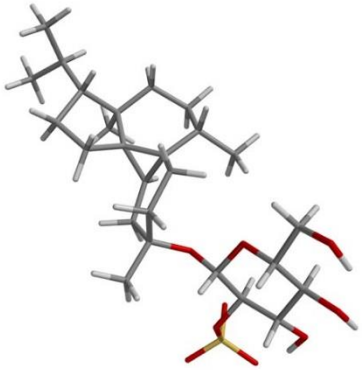
Figure S9. Lowest energy conformations of 1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S* – peyssonnoside A (**1**).



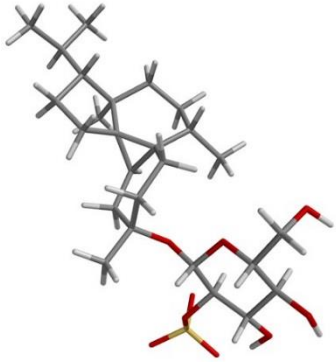
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* -**1a**



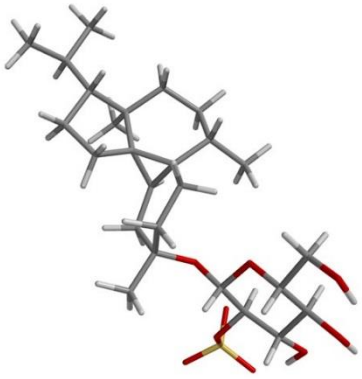
1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1b**



1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1c**



1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1d**



1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R*-**1e**

Figure S10. Lowest energy conformations of 1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* – peyssonnoside A (**1**)

Overlay of lowest energy conformations of peyssonnoside A (1)

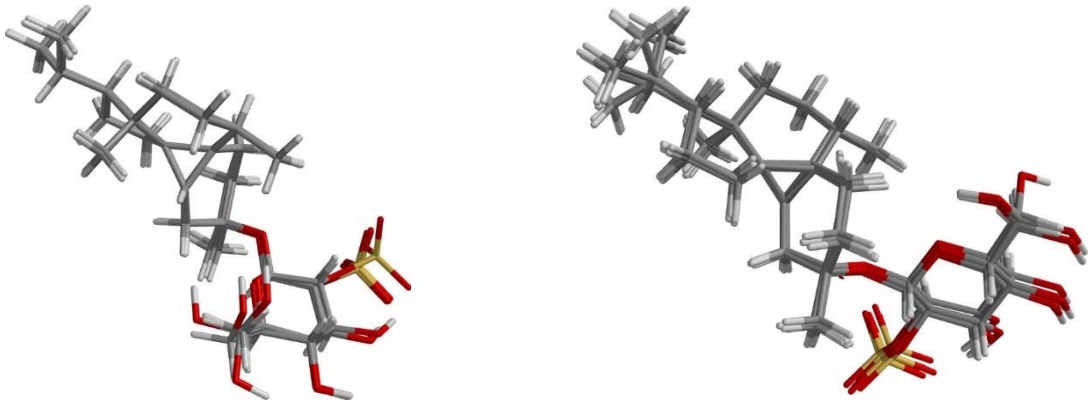


Figure S11. Left: Overlay of lowest energy conformations of 1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S* – peyssonnoside A (**1**) and right: 1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* – peyssonnoside A (**1**)

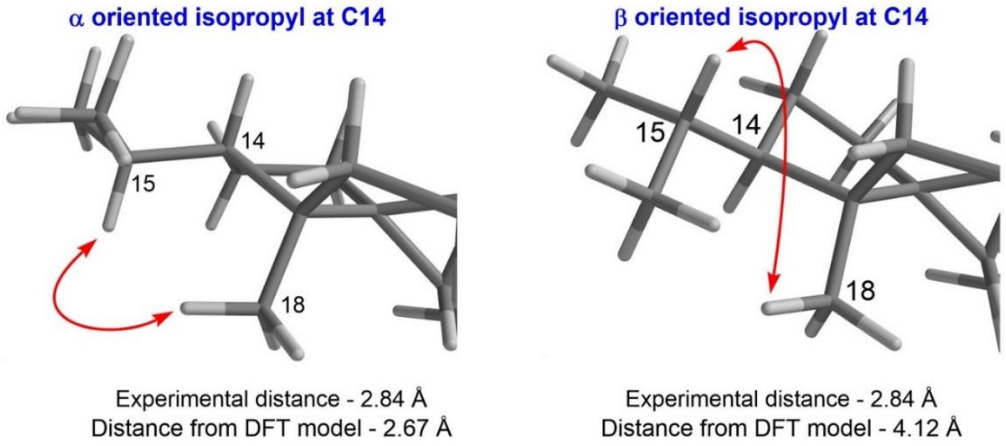


Figure S12. Experimental and calculated distances between H-15 and H_3-18 with isopropyl oriented α or β at C-14 for **1**.

Table S4. Atomic coordinates and NMR shielding tensors for peyssonnoside A (**1**), obtained from DFT calculations at B3LYP/6-311++G(2d,2p) level of theory using DMSO as solvent.

	1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*-**1a**				1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*-**1b**			
Atom	***x***	***y***	***z***	Shielding	***x***	***y***	***z***	Shielding
C	1.6780	-0.4133	-1.1156	140.267	3.1060	-0.4057	-0.1335	140.058
C	1.7370	-1.6623	-2.0037	154.202	3.5650	-1.5426	-1.0535	154.149
H	0.7649	-1.9706	-2.3843	30.461	2.9421	-1.6621	-1.9378	30.524
H	2.1349	-2.5097	-1.4401	30.366	3.5384	-2.4965	-0.5208	30.387
C	2.6962	-1.3196	-3.1417	149.469	5.0083	-1.2153	-1.4296	149.132
H	3.1547	-2.2120	-3.5642	29.904	5.5673	-2.1097	-1.6990	29.900
H	2.1679	-0.8146	-3.9553	30.428	5.0407	-0.5440	-2.2924	30.430
C	2.8297	0.5534	-1.5817	134.931	4.3834	0.4213	0.2700	135.213
C	3.7150	-0.3639	-2.5080	115.126	5.5723	-0.5036	-0.1933	115.435
H	4.3447	-0.9613	-1.8366	30.730	5.6932	-1.2634	0.5893	30.760
C	3.6275	1.0814	-0.3710	140.129	4.4134	0.6740	1.7914	139.946
H	4.3084	0.2992	-0.0228	30.792	4.7298	-0.2417	2.2998	30.915
H	4.2516	1.9216	-0.6737	30.294	5.1587	1.4325	2.0290	30.303
C	2.7447	1.5022	0.7987	153.813	3.0631	1.0962	2.3599	153.300
H	2.0398	2.2783	0.4872	30.998	2.7062	2.0046	1.8655	31.002
H	3.3604	1.9574	1.5779	30.610	3.1747	1.3583	3.4145	30.603
C	1.9865	0.3174	1.4055	142.803	2.0121	-0.0118	2.2410	143.471
H	2.7421	-0.3403	1.8539	30.384	2.3377	-0.8243	2.9030	30.402
C	1.2578	-0.5317	0.3522	153.185	1.9360	-0.6191	0.8314	152.690
C	0.3426	0.1512	-0.6354	164.998	1.7692	0.2982	-0.3559	164.865
H	0.3151	1.2291	-0.5572	31.263	1.7709	1.3524	-0.1182	31.327
C	0.8247	-1.8939	0.8952	158.547	1.1843	-1.9507	0.8100	158.216
H	1.6690	-2.5892	0.8620	30.418	1.8575	-2.7586	1.1129	30.444
H	0.5846	-1.7701	1.9499	29.670	0.4107	-1.9070	1.5750	29.731
C	-0.3870	-2.5513	0.2149	145.568	0.5096	-2.3388	-0.5160	145.379
H	-0.0878	-3.0483	-0.7057	30.863	1.2339	-2.7729	-1.2024	30.853
H	-0.7864	-3.3272	0.8703	30.332	-0.2377	-3.1107	-0.3237	30.345
C	-1.5193	-1.5835	-0.1378	101.503	-0.1689	-1.1765	-1.2461	101.659
C	-0.9976	-0.4519	-1.0420	150.735	0.8423	-0.0472	-1.5162	151.135
H	-1.7506	0.3343	-1.0774	29.632	0.2923	0.8454	-1.8096	29.493
H	-0.9421	-0.8506	-2.0576	30.662	1.4246	-0.3402	-2.3931	30.758
C	4.6608	0.2928	-3.5426	147.796	6.9682	0.1210	-0.4315	147.613
H	4.0513	0.8939	-4.2235	30.229	6.8675	0.8873	-1.2054	30.229
C	5.3664	-0.7775	-4.3935	158.496	7.9553	-0.9319	-0.9652	158.393
H	5.9416	-1.4599	-3.7622	31.182	8.0496	-1.7673	-0.2663	31.201
H	6.0616	-0.3094	-5.0922	30.925	8.9466	-0.4933	-1.0902	30.941
H	4.6654	-1.3727	-4.9761	30.509	7.6505	-1.3357	-1.9291	30.514
C	5.7266	1.2126	-2.9288	160.824	7.5825	0.7837	0.8101	160.861
H	6.3222	0.6791	-2.1843	31.102	7.6451	0.0764	1.6404	31.120
H	5.2991	2.0886	-2.4467	30.438	7.0151	1.6467	1.1504	30.442
H	6.4083	1.5675	-3.7038	30.990	8.5957	1.1258	0.5915	31.017
C	-2.6571	-2.3453	-0.8227	156.522	-0.7873	-1.6772	-2.5539	156.629
H	-3.4374	-1.6829	-1.1971	30.174	-1.1813	-0.8669	-3.1670	30.166
H	-3.1073	-3.0589	-0.1339	30.881	-1.5921	-2.3829	-2.3509	30.918
H	-2.2639	-2.8934	-1.6779	31.022	-0.0258	-2.1850	-3.1445	31.003
O	-1.9572	-1.0687	1.1647	201.426	-1.2179	-0.7448	-0.3145	201.014
C	-3.0815	-0.2724	1.2527	82.032	-2.1473	0.1970	-0.7065	81.823
H	-3.7768	-0.4411	0.4255	26.982	-2.3150	0.1918	-1.7875	26.995
O	-2.6809	1.1052	1.2364	223.909	-1.6799	1.4997	-0.3279	226.660
C	-3.7870	-0.5661	2.5868	98.371	-3.4716	-0.0937	0.0193	98.218
H	-3.0460	-0.5127	3.3840	27.757	-3.2594	-0.2163	1.0811	27.805
C	-4.9326	0.4194	2.8293	100.309	-4.4866	1.0298	-0.2120	100.924
H	-5.7172	0.2069	2.0928	27.974	-4.7972	0.9920	-1.2631	27.931
C	-4.4819	1.8626	2.6342	105.473	-3.8633	2.3938	0.0509	99.144
H	-3.7730	2.1158	3.4299	28.337	-3.6379	2.4765	1.1188	28.021
C	-3.7804	2.0201	1.2884	102.635	-2.5577	2.5509	-0.7270	106.702

H	-4.4848	1.8008	0.4770	28.197	-2.7602	2.4911	-1.8034	28.228
C	-3.2030	3.4096	1.0833	114.356	-1.8407	3.8681	-0.4379	111.388
H	-4.0021	4.1451	1.1228	27.740	-1.7138	3.9847	0.6431	27.757
H	-2.4903	3.6268	1.8848	28.019	-0.8530	3.8379	-0.8940	27.880
O	-2.5807	3.5465	-0.1930	303.181	-2.5215	4.9895	-0.9963	301.252
H	-1.9115	2.8568	-0.2608	29.951	-3.4500	4.9189	-0.7349	28.704
O	-4.3081	-1.9072	2.4891	100.624	-3.9743	-1.3300	-0.5265	100.936
O	-5.4722	0.3382	4.1431	274.055	-5.6275	0.9341	0.6320	274.684
H	-5.5843	-0.6019	4.3847	25.521	-5.9399	0.0084	0.6390	25.518
O	-5.5985	2.7496	2.6782	290.675	-4.7576	3.4445	-0.3332	290.537
H	-6.1006	2.5368	3.4735	29.492	-5.5829	3.3214	0.1496	29.159
C	2.2512	1.7347	-2.3846	165.254	4.4186	1.7649	-0.4845	165.247
H	1.6527	1.3915	-3.2291	31.119	4.3645	1.6221	-1.5644	31.131
H	3.0428	2.3758	-2.7719	31.231	5.3308	2.3189	-0.2638	31.184
H	1.6083	2.3594	-1.7668	30.959	3.5820	2.4017	-0.2025	30.953
C	1.0700	0.8114	2.5330	163.972	0.6604	0.4985	2.7586	164.118
H	1.6522	1.3537	3.2805	31.031	0.7611	0.8582	3.7844	31.016
H	0.5547	-0.0014	3.0422	30.344	-0.1091	-0.2720	2.7535	30.415
H	0.3118	1.4914	2.1429	31.190	0.3034	1.3285	2.1475	31.309
S	-4.2963	-2.8840	3.8269	121.367	-4.7638	-2.3956	0.4660	121.340
O	-5.3723	-2.3588	4.6943	93.450	-4.8213	-3.5816	-0.3799	115.525
O	-2.9660	-2.7586	4.4203	111.323	-6.0853	-1.7811	0.7152	93.298
O	-4.6037	-4.1802	3.2346	115.575	-3.9490	-2.5179	1.6737	111.380

Table S5. Atomic coordinates and NMR shielding tensors for peyssonnoside A (**1**), obtained from DFT calculations at B3LYP/6-311++G(2d,2p) level of theory using DMSO as solvent.

	1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*-**1c**				1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*-**1d**			
Atom	***x***	***y***	***z***	Shielding	***x***	***y***	***z***	Shielding
C	3.0675	-0.4531	-0.1125	140.810	3.0478	-0.4071	-0.1884	140.509
C	3.5127	-1.7279	-0.8371	154.457	3.5597	-1.4960	-1.1371	154.219
H	2.8841	-1.9839	-1.6881	30.515	2.9815	-1.5772	-2.0556	30.566
H	3.4803	-2.5827	-0.1566	30.336	3.5139	-2.4743	-0.6516	30.359
C	4.9578	-1.4784	-1.2608	149.359	5.0179	-1.1442	-1.4208	149.031
H	5.5068	-2.4093	-1.3917	29.905	5.5950	-2.0199	-1.7122	29.880
H	4.9960	-0.9455	-2.2151	30.422	5.0901	-0.4236	-2.2404	30.419
C	4.3552	0.4108	0.1616	134.015	4.2986	0.3952	0.3318	134.897
C	5.5297	-0.5953	-0.1449	115.460	5.5125	-0.5048	-0.1171	115.101
H	5.6313	-1.2281	0.7459	30.738	5.5896	-1.3084	0.6262	30.719
C	4.3845	0.8991	1.6247	140.578	4.2417	0.5605	1.8647	139.458
H	4.6838	0.0694	2.2718	30.857	4.5253	-0.3848	2.3367	30.923
H	5.1418	1.6732	1.7443	30.238	4.9745	1.2994	2.1876	30.319
C	3.0392	1.4259	2.1124	153.131	2.8614	0.9579	2.3776	152.811
H	2.6978	2.2499	1.4790	30.920	2.5354	1.8930	1.9126	30.984
H	3.1511	1.8488	3.1134	30.548	2.9123	1.1622	3.4495	30.614
C	1.9736	0.3267	2.1628	142.179	1.8183	-0.1377	2.1373	143.108
H	2.2833	-0.3727	2.9497	30.464	2.0996	-0.9840	2.7768	30.384
C	1.8955	-0.4985	0.8696	154.239	1.8291	-0.6732	0.6976	152.558
C	1.7370	0.2183	-0.4494	164.553	1.7214	0.3047	-0.4480	164.478
H	1.7459	1.2972	-0.3816	31.309	1.7051	1.3450	-0.1555	31.346
C	1.1342	-1.8092	1.0642	158.479	1.0914	-2.0063	0.5680	158.134
H	1.8040	-2.5677	1.4806	30.339	1.7631	-2.8274	0.8364	30.451
H	0.3728	-1.6402	1.8240	29.708	0.2974	-2.0179	1.3125	29.744
C	0.4352	-2.3904	-0.1753	145.214	0.4551	-2.3111	-0.7985	144.988
H	1.1406	-2.9493	-0.7876	30.858	1.1974	-2.7080	-1.4892	30.877
H	-0.3260	-3.1035	0.1457	30.377	-0.3009	-3.0886	-0.6748	30.310
C	-0.2267	-1.3479	-1.0811	101.061	-0.1917	-1.0986	-1.4742	101.710
C	0.8050	-0.3010	-1.5389	151.838	0.8519	0.0163	-1.6664	150.769

H	0.2727	0.5398	-1.9811	29.656	0.3335	0.9273	-1.9583	29.321
H	1.3792	-0.7501	-2.3528	30.772	1.4704	-0.2663	-2.5216	30.809
C	6.9398	-0.0411	-0.4616	147.507	6.9195	0.1275	-0.2408	147.706
H	6.8625	0.5995	-1.3447	30.215	6.8626	0.9386	-0.9723	30.227
C	7.9085	-1.1836	-0.8145	158.580	7.9341	-0.8960	-0.7802	158.289
H	7.9795	-1.9004	0.0078	31.159	7.6819	-1.2424	-1.7810	30.534
H	8.9097	-0.7897	-0.9959	30.929	7.9899	-1.7707	-0.1268	31.211
H	7.6026	-1.7278	-1.7064	30.490	8.9308	-0.4543	-0.8255	30.918
C	7.5583	0.7900	0.6720	160.702	7.4636	0.7123	1.0709	160.780
H	7.5909	0.2186	1.6027	31.087	7.4736	-0.0427	1.8606	31.110
H	7.0130	1.7105	0.8669	30.420	6.8815	1.5587	1.4274	30.421
H	8.5834	1.0665	0.4194	30.908	8.4895	1.0578	0.9320	31.001
C	-0.8682	-2.0445	-2.2843	156.671	-0.7987	-1.5119	-2.8163	157.288
H	-1.2515	-1.3389	-3.0211	30.268	-0.0384	-2.0092	-3.4174	30.912
H	-1.6859	-2.6874	-1.9606	30.943	-1.1572	-0.6596	-3.3933	30.222
H	-0.1242	-2.6611	-2.7871	31.066	-1.6251	-2.2070	-2.6691	30.914
O	-1.2583	-0.7451	-0.2289	202.827	-1.2356	-0.6877	-0.5281	201.850
C	-2.1527	0.1590	-0.7669	81.966	-2.2007	0.2245	-0.9005	81.442
H	-2.2886	0.0165	-1.8430	26.969	-2.4637	0.1424	-1.9593	26.945
O	-1.6610	1.4873	-0.5458	226.107	-1.7162	1.5530	-0.6581	226.067
C	-3.5044	-0.0029	-0.0546	97.961	-3.4516	-0.0177	-0.0413	97.875
H	-3.3304	0.0110	1.0209	27.780	-3.1478	-0.0632	1.0040	27.727
C	-4.4773	1.1020	-0.4726	100.266	-4.4913	1.0829	-0.2674	100.103
H	-4.7411	0.9340	-1.5240	28.059	-4.8842	0.9681	-1.2851	28.002
C	-3.8399	2.4813	-0.3586	109.531	-3.8751	2.4722	-0.1511	109.314
H	-3.6653	2.7011	0.6982	27.797	-3.5777	2.6380	0.8879	27.770
C	-2.4996	2.5119	-1.0883	103.364	-2.6358	2.5818	-1.0351	103.535
H	-2.6642	2.3396	-2.1596	28.429	-2.9279	2.4635	-2.0862	28.417
C	-1.7439	3.8236	-0.9388	117.613	-1.8933	3.9027	-0.9019	117.749
H	-0.8268	3.7681	-1.5309	27.679	-1.0622	3.9093	-1.6119	27.664
H	-2.3543	4.6372	-1.3232	27.802	-2.5649	4.7215	-1.1480	27.802
O	-1.4442	4.1439	0.4191	314.056	-1.4213	4.1439	0.4228	315.769
H	-0.9481	3.4061	0.7900	30.350	-0.8695	3.3954	0.6745	30.288
O	-4.0202	-1.2905	-0.4517	100.114	-3.9877	-1.2931	-0.4516	101.268
O	-5.6597	1.1346	0.3190	273.577	-5.5634	1.0366	0.6679	273.150
H	-5.9987	0.2243	0.4217	25.551	-5.8730	0.1138	0.7511	25.521
O	-4.6906	3.4762	-0.9278	292.064	-4.8110	3.4719	-0.5542	291.757
H	-5.5661	3.3558	-0.5426	29.488	-5.6284	3.3086	-0.0701	29.420
C	4.4146	1.6174	-0.7953	164.992	4.3738	1.7795	-0.3421	165.384
H	4.3670	1.3062	-1.8393	31.140	4.3819	1.6980	-1.4296	31.107
H	5.3339	2.1859	-0.6554	31.191	5.2704	2.3196	-0.0386	31.155
H	3.5856	2.3024	-0.6256	30.895	3.5208	2.3999	-0.0729	30.931
C	0.6250	0.9272	2.5808	162.786	0.4355	0.3486	2.5914	163.512
H	0.7205	1.4436	3.5378	30.969	-0.3336	-0.4147	2.4851	30.257
H	-0.1561	0.1761	2.6847	30.227	0.1227	1.2159	2.0082	31.271
H	0.2852	1.6540	1.8415	31.336	0.4655	0.6468	3.6413	30.969
S	-4.8777	-2.1973	0.6363	121.494	-4.6901	-2.2838	0.6741	121.464
O	-4.9194	-3.4880	-0.0406	115.638	-3.7954	-2.2973	1.8305	110.882
O	-6.1968	-1.5364	0.7314	93.256	-4.7822	-3.5356	-0.0677	115.396
O	-4.1245	-2.1641	1.8892	111.213	-6.0033	-1.6681	0.9608	93.238

Table S6. Atomic coordinates and NMR shielding tensors for peyssonnoside A (**1**), obtained from DFT calculations at B3LYP/6-311++G(2d,2p) level of theory using DMSO as solvent.

1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*-**1e**									
Atom	***x***	***y***	***z***	Shielding		***x***	***y***	***z***	Shielding
C	3.0717	-0.7250	-0.2851	138.344	H	8.1295	1.6950	0.9771	30.958
C	3.7199	-1.3754	-1.5123	153.596	C	-1.2393	-1.8938	-2.3810	155.583
H	3.0822	-1.3898	-2.3945	30.368	H	-0.5801	-2.5155	-2.9865	30.965
H	3.9702	-2.4168	-1.2950	30.353	H	-1.5367	-1.0429	-2.9939	30.332
C	5.0102	-0.5976	-1.7546	150.236	H	-2.1282	-2.4736	-2.1357	30.649
H	5.7386	-1.1879	-2.3075	29.967	O	-1.4460	-0.8130	-0.1816	189.964
H	4.8170	0.3064	-2.3388	30.516	C	-2.1041	0.3359	-0.5745	82.262
C	4.1561	0.1996	0.3878	134.073	H	-2.1769	0.4242	-1.6627	27.083
C	5.4871	-0.2212	-0.3454	115.231	O	-1.3857	1.4713	-0.0714	224.369
H	5.8237	-1.1471	0.1378	30.601	C	-3.5145	0.3249	0.0383	97.929
C	4.2277	-0.0491	1.9089	139.268	H	-3.4237	0.0864	1.0976	27.778
H	4.7876	-0.9703	2.0953	30.728	C	-4.2215	1.6675	-0.1644	100.084
H	4.7849	0.7539	2.3907	30.112	H	-4.4453	1.7699	-1.2333	27.975
C	2.8583	-0.1833	2.5693	151.958	C	-3.3343	2.8381	0.2436	106.042
H	2.2570	0.7154	2.4034	30.883	H	-3.1876	2.8041	1.3285	28.358
H	2.9825	-0.2617	3.6518	30.648	C	-1.9732	2.7251	-0.4362	102.241
C	2.1063	-1.4213	2.0742	140.287	H	-2.0995	2.7735	-1.5245	28.205
H	2.7017	-2.2895	2.3851	30.212	C	-1.0023	3.8091	-0.0049	114.425
C	2.0334	-1.4914	0.5447	151.002	H	-1.4272	4.7851	-0.2243	27.785
C	1.6086	-0.2933	-0.2719	162.267	H	-0.8345	3.7369	1.0740	27.990
H	1.3902	0.6073	0.2830	31.062	O	0.2340	3.7321	-0.7130	301.511
C	1.4720	-2.7978	-0.0159	155.376	H	0.5896	2.8471	-0.5785	29.928
H	1.9938	-3.0796	-0.9297	30.739	O	-4.2420	-0.7191	-0.6403	100.833
H	1.6502	-3.6144	0.6870	30.463	O	-5.4215	1.7854	0.5908	273.724
C	-0.0407	-2.7272	-0.3139	141.375	H	-5.9384	0.9618	0.4953	25.556
H	-0.3314	-3.6251	-0.8603	30.124	O	-3.9350	4.0779	-0.1270	290.597
H	-0.6019	-2.7404	0.6166	29.975	H	-4.8449	4.0600	0.1915	29.437
C	-0.5064	-1.4740	-1.1049	97.799	C	3.8449	1.6858	0.1222	164.402
C	0.6723	-0.5434	-1.4396	150.190	H	3.7250	1.8907	-0.9419	31.199
H	0.2859	0.3994	-1.8268	29.811	H	4.6401	2.3270	0.5012	31.224
H	1.2051	-1.0049	-2.2708	30.994	H	2.9266	1.9955	0.6185	30.889
C	6.6932	0.7484	-0.3440	147.611	C	0.7422	-1.5337	2.7691	162.526
H	6.3771	1.6837	-0.8144	30.227	H	0.2645	-2.4949	2.5848	30.393
C	7.8483	0.1858	-1.1910	158.712	H	0.0616	-0.7517	2.4304	30.961
H	7.5752	0.0647	-2.2378	30.481	H	0.8632	-1.4325	3.8495	30.972
H	8.1698	-0.7885	-0.8134	31.141	S	-5.3350	-1.6347	0.2020	121.590
H	8.7089	0.8553	-1.1505	30.940	O	-5.5934	-2.7113	-0.7466	115.285
C	7.2300	1.0820	1.0556	160.024	O	-6.4957	-0.7446	0.4180	93.760
H	7.4970	0.1723	1.5986	31.255	O	-4.6737	-2.0306	1.4442	111.383
H	6.5141	1.6325	1.6615	30.370					

Table S7. Atomic coordinates for peyssonnoside A (**1**), obtained from DFT calculations at B3LYP/6-311++G(2d,2p) level of theory using DMSO as solvent.

1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* -**1a**					1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* -**1**b			
Atom	***x***	***y***	***z***	Shielding	***x***	***y***	***z***	Shielding
C	0.2323	-2.0075	0.6727	141.536	-1.8638	1.0132	-0.1255	142.806
C	1.0061	-2.8747	1.7344	133.514	-2.7374	2.1118	0.5742	132.779
C	2.4625	-2.3869	1.8749	139.858	-2.6734	1.9946	2.1088	141.675
H	2.9245	-2.8389	2.7522	30.180	-3.1155	2.8843	2.5641	30.219
H	3.0386	-2.7287	1.0099	30.873	-3.2837	1.1450	2.4291	30.980
C	2.5833	-0.8693	1.9634	152.842	-1.2555	1.7857	2.6285	152.815
H	2.0017	-0.4886	2.8078	30.927	-0.6066	2.6073	2.3121	30.930
H	3.6199	-0.5933	2.1699	30.510	-1.2508	1.8074	3.7205	30.480
C	2.1429	-0.1771	0.6696	143.727	-0.6678	0.4459	2.1659	143.077
H	2.8867	-0.4392	-0.0936	30.420	-1.2358	-0.3383	2.6822	30.392
C	0.7934	-0.6871	0.1419	153.885	-0.8496	0.1826	0.6613	153.534
C	-0.3984	-0.6732	1.0663	164.611	-0.3637	1.2212	-0.3193	165.036
H	-0.1856	-0.3546	2.0771	31.320	0.0275	2.1238	0.1294	31.378
C	0.5628	-0.3166	-1.3239	157.613	-0.6493	-1.2889	0.2973	157.692
H	1.0560	-1.0491	-1.9701	30.390	-1.5747	-1.8422	0.4837	30.411
H	1.0680	0.6311	-1.4990	29.575	0.0909	-1.6940	0.9843	29.516
C	-0.8969	-0.1522	-1.7814	148.613	-0.1669	-1.5926	-1.1313	148.624
H	-1.3380	-1.1193	-2.0206	30.926	-1.0021	-1.5816	-1.8309	30.870
H	-0.9157	0.4212	-2.7100	30.279	0.2355	-2.6067	-1.1628	30.275
C	-1.8160	0.5158	-0.7528	100.494	0.8802	-0.6123	-1.6715	100.321
C	-1.7784	-0.2449	0.5833	147.077	0.3567	0.8323	-1.6040	146.910
H	-2.2387	0.3968	1.3345	29.770	1.2111	1.4931	-1.7508	29.762
H	-2.4324	-1.1134	0.4866	30.545	-0.2961	0.9876	-2.4649	30.496
C	0.2992	-2.8208	3.1027	165.597	-2.2969	3.5248	0.1497	163.739
H	-0.7431	-3.1330	3.0294	31.119	-2.2856	3.6395	-0.9341	31.079
H	0.3048	-1.8138	3.5164	30.866	-1.2930	3.7516	0.5064	30.828
H	0.7938	-3.4671	3.8274	31.286	-2.9622	4.2811	0.5667	31.351
C	2.1777	1.3464	0.8536	163.705	0.7957	0.3376	2.6165	163.676
H	1.9285	1.8843	-0.0592	30.084	1.4011	1.1121	2.1415	31.269
H	3.1723	1.6670	1.1705	30.975	0.8705	0.4733	3.6974	30.943
H	1.4680	1.6557	1.6233	31.312	1.2398	-0.6249	2.3697	30.099
C	-3.2594	0.5797	-1.2588	156.472	1.2587	-0.9464	-3.1165	156.393
H	-3.3431	1.0903	-2.2174	30.269	0.3836	-0.8435	-3.7568	30.953
H	-3.8939	1.0930	-0.5370	30.757	1.6200	-1.9680	-3.2278	30.244
H	-3.6428	-0.4303	-1.3982	30.975	2.0303	-0.2658	-3.4751	30.747
O	-1.3401	1.8613	-0.4059	203.356	2.0800	-0.5920	-0.8246	203.594
C	-1.3273	2.8537	-1.3672	81.873	2.8688	-1.7218	-0.7229	81.894
H	-2.0448	2.6631	-2.1704	27.027	2.7580	-2.3850	-1.5855	27.020
O	-0.0151	2.9290	-1.9388	223.962	2.4937	-2.4437	0.4569	224.106
C	0.1009	3.9079	-2.9762	101.996	3.2313	-3.6555	0.6444	102.098
H	-0.6630	3.7300	-3.7427	28.256	3.1525	-4.2815	-0.2528	28.261
C	-0.1000	5.2901	-2.3622	105.546	4.6934	-3.2987	0.8949	105.478
H	0.6845	5.4589	-1.6167	28.334	4.7544	-2.6939	1.8061	28.333
C	-1.4545	5.3637	-1.6660	99.914	5.2412	-2.4795	-0.2685	99.973
H	-2.2340	5.2970	-2.4349	28.002	5.2725	-3.1277	-1.1529	27.998
C	-1.6556	4.1970	-0.6950	97.924	4.3383	-1.2871	-0.5958	97.901
H	-1.0217	4.3049	0.1849	27.729	4.4035	-0.5214	0.1768	27.731
C	1.4752	3.7274	-3.5959	114.396	2.5893	-4.3820	1.8127	114.395
H	1.6218	4.4673	-4.3783	27.789	2.6407	-3.7495	2.7041	28.005
H	2.2405	3.8761	-2.8281	28.002	3.1309	-5.3033	2.0105	27.780
O	1.6203	2.4472	-4.2089	302.456	1.2391	-4.7508	1.5355	302.452
H	1.4346	1.7824	-3.5367	29.996	0.7621	-3.9468	1.3023	29.985
O	-0.0095	6.2719	-3.3933	291.138	5.4414	-4.5023	1.0598	291.017
H	-0.2783	7.1143	-3.0087	29.523	6.3741	-4.2580	1.0769	29.541
O	-1.5143	6.6355	-1.0311	274.103	6.5630	-2.0964	0.0926	274.166

H	-2.2814	6.6527	-0.4261	25.523	6.8786	-1.4158	-0.5333	25.517
O	-3.0403	4.1246	-0.2975	99.796	4.7095	-0.7300	-1.8735	99.842
S	-3.5226	4.8435	1.1140	121.687	5.7345	0.5694	-1.9296	121.687
O	-3.5162	6.2942	0.8288	93.386	7.0660	0.0240	-1.5900	93.575
O	-2.5483	4.4525	2.1314	112.217	5.2383	1.5307	-0.9463	112.279
O	-4.8603	4.2858	1.2733	115.670	5.6063	0.9709	-3.3253	115.639
C	0.9312	-4.3290	1.1299	115.452	-4.1784	1.7721	0.0619	116.858
H	1.7152	-4.3840	0.3642	30.773	-4.4705	0.8887	0.6398	30.464
C	-0.4151	-4.3404	0.3945	149.821	-3.9531	1.2747	-1.3676	156.781
H	-1.2308	-4.4663	1.1122	30.412	-3.7333	2.1052	-2.0403	30.282
H	-0.4976	-5.1486	-0.3297	29.967	-4.8141	0.7454	-1.7776	30.254
C	-0.4906	-2.9704	-0.2748	154.579	-2.7261	0.3686	-1.2234	154.584
H	-1.5201	-2.6834	-0.4814	30.455	-2.2013	0.2505	-2.1699	30.354
H	0.0223	-3.0099	-1.2391	30.380	-3.0477	-0.6294	-0.9158	30.393
C	1.1303	-5.5474	2.0634	147.018	-5.3049	2.8152	0.2851	151.303
H	0.3695	-5.5004	2.8477	30.205	-5.0580	3.3751	1.1920	30.027
C	2.5061	-5.5985	2.7437	160.532	-6.6437	2.1077	0.5513	157.251
H	2.6095	-6.5222	3.3157	30.924	-7.4402	2.8315	0.7341	30.836
H	2.6670	-4.7713	3.4312	30.357	-6.5802	1.4517	1.4206	30.853
H	3.3086	-5.5776	2.0025	31.111	-6.9423	1.4987	-0.3053	30.767
C	0.9113	-6.8650	1.2994	158.573	-5.4886	3.8334	-0.8511	162.601
H	1.0917	-7.7182	1.9553	30.931	-6.2400	4.5734	-0.5695	30.949
H	1.6018	-6.9453	0.4555	31.189	-5.8378	3.3463	-1.7634	31.248
H	-0.1018	-6.9560	0.9114	30.493	-4.5723	4.3686	-1.0911	30.652

Table S8. Atomic coordinates for peyssonnoside A (**1**), obtained from DFT calculations at B3LYP/6-311++G(2d,2p) level of theory using DMSO as solvent.

1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* **-1c**					1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* **-1d**			
Atom	***x***	***y***	***z***	Shielding	***x***	***y***	***z***	Shielding
C	3.1835	-0.0550	-0.1654	143.411	-3.1349	-0.1188	0.2522	141.836
C	4.4723	-0.1910	0.7167	132.670	-4.4111	-0.2826	-0.6526	133.079
C	4.4670	0.8106	1.8874	141.463	-4.3858	0.7293	-1.8170	139.505
H	5.2593	0.5538	2.5948	30.211	-5.1394	0.4652	-2.5582	30.132
H	4.7015	1.8089	1.5061	30.971	-4.6579	1.7183	-1.4364	30.835
C	3.1224	0.8774	2.6037	152.918	-3.0239	0.8331	-2.4960	152.851
H	2.8432	-0.1084	2.9862	30.950	-2.7126	-0.1438	-2.8772	30.930
H	3.1985	1.5251	3.4801	30.506	-3.0982	1.4819	-3.3717	30.531
C	2.0128	1.4194	1.6925	143.555	-1.9490	1.3963	-1.5607	143.801
H	2.2463	2.4761	1.5110	30.426	-2.2140	2.4448	-1.3738	30.398
C	1.9725	0.7482	0.3093	153.576	-1.9269	0.7105	-0.1866	154.192
C	1.8895	-0.7564	0.2396	165.154	-1.8193	-0.7929	-0.1317	164.576
H	1.9311	-1.2603	1.1954	31.403	-1.8299	-1.2846	-1.0944	31.323
C	1.1672	1.5541	-0.7102	158.382	-1.1591	1.5189	0.8606	158.660
H	1.8011	2.3346	-1.1424	30.502	-1.8202	2.2739	1.2974	30.515
H	0.3751	2.0705	-0.1739	29.504	-0.3736	2.0664	0.3451	29.397
C	0.5056	0.7647	-1.8531	148.781	-0.4912	0.7273	1.9983	148.326
H	1.2214	0.5670	-2.6506	30.934	-1.2100	0.5014	2.7857	31.000
H	-0.2783	1.3795	-2.2988	30.277	0.2762	1.3512	2.4590	30.267
C	-0.0811	-0.5898	-1.4393	99.856	0.1276	-0.6078	1.5678	100.569
C	0.9922	-1.4628	-0.7673	146.947	-0.9284	-1.4936	0.8852	146.844
H	0.4778	-2.2873	-0.2735	29.797	-0.4005	-2.3125	0.3965	29.793
H	1.5937	-1.9139	-1.5587	30.538	-1.5342	-1.9503	1.6701	30.624
C	4.6189	-1.6213	1.2680	163.623	-4.5052	-1.7181	-1.2060	165.447
H	4.5824	-2.3690	0.4758	31.077	-4.4907	-2.4591	-0.4061	31.116
H	3.8213	-1.8594	1.9705	30.840	-3.6731	-1.9454	-1.8703	30.894
H	5.5612	-1.7369	1.8039	31.320	-5.4207	-1.8608	-1.7796	31.247
C	0.6635	1.3567	2.4221	163.701	-0.5834	1.3766	-2.2613	163.603
H	0.7209	1.8921	3.3722	31.004	-0.2848	0.3516	-2.4890	31.315

H	-0.1467	1.7930	1.8409	30.177	-0.6339	1.9251	-3.2043	30.998
H	0.3941	0.3214	2.6400	31.325	0.2031	1.8232	-1.6561	30.028
C	-0.6586	-1.3355	-2.6449	156.176	0.7202	-1.3550	2.7650	156.650
H	0.1367	-1.5518	-3.3571	30.933	-0.0734	-1.6078	3.4670	30.967
H	-1.4135	-0.7541	-3.1729	30.250	1.4517	-0.7587	3.3092	30.250
H	-1.1061	-2.2780	-2.3309	30.772	1.1990	-2.2782	2.4396	30.818
O	-1.1096	-0.4355	-0.4016	203.473	1.1475	-0.4171	0.5294	203.131
C	-2.2742	0.2491	-0.6892	81.855	2.3182	0.2549	0.8257	81.834
H	-2.5008	0.2516	-1.7595	27.035	2.5845	0.1750	1.8843	27.026
O	-2.1288	1.6069	-0.2545	227.629	2.1563	1.6392	0.5014	222.380
C	-3.2675	2.4163	-0.5407	106.464	3.3093	2.4266	0.8029	103.461
H	-3.5195	2.3578	-1.6068	28.306	3.6054	2.2684	1.8485	28.574
C	-4.4366	1.8946	0.2933	98.914	4.4434	1.9764	-0.1134	108.587
H	-4.1682	1.9822	1.3508	28.032	4.1309	2.1260	-1.1514	27.894
C	-4.7129	0.4309	-0.0224	100.679	4.7286	0.4938	0.0901	100.045
H	-5.0774	0.3671	-1.0548	27.995	5.1248	0.3568	1.1037	27.999
C	-3.4346	-0.4077	0.0776	97.881	3.4492	-0.3386	-0.0311	97.582
H	-3.1306	-0.5330	1.1166	27.791	3.1081	-0.3818	-1.0650	27.748
C	-2.8879	3.8578	-0.2083	111.396	2.9485	3.9001	0.6656	116.401
H	-1.9574	4.1023	-0.7171	27.947	3.7558	4.4990	1.0888	27.465
H	-2.7220	3.9525	0.8696	27.763	2.0458	4.0856	1.2452	28.012
O	-3.8653	4.7931	-0.6586	301.623	2.6604	4.3142	-0.6704	313.661
H	-4.7266	4.4738	-0.3556	28.721	3.4910	4.4538	-1.1350	30.650
O	-5.5902	2.6996	0.0237	290.017	5.6014	2.7633	0.1636	293.431
H	-6.3216	2.3532	0.5473	29.185	6.3330	2.3794	-0.3336	29.504
O	-5.7306	0.0049	0.8753	274.736	5.7207	0.1350	-0.8652	273.982
H	-5.7995	-0.9689	0.8350	25.538	5.7906	-0.8389	-0.8995	25.488
O	-3.6460	-1.6976	-0.5321	100.187	3.6818	-1.6737	0.4648	99.753
S	-4.0774	-2.9860	0.4145	121.742	4.0765	-2.8792	-0.5992	121.393
O	-3.1675	-2.9815	1.5587	112.231	3.1369	-2.7721	-1.7144	112.044
O	-3.9107	-4.0921	-0.5205	115.749	3.9257	-4.0610	0.2414	115.849
O	-5.4852	-2.7348	0.7898	93.448	5.4763	-2.6052	-0.9891	93.683
C	5.6129	0.1621	-0.2979	116.731	-5.5957	0.0031	0.3475	115.037
H	5.5570	1.2510	-0.4014	30.507	-5.6650	1.0947	0.4362	30.783
C	5.1112	-0.4070	-1.6269	156.779	-5.0639	-0.5219	1.6875	150.136
H	5.2069	-1.4938	-1.6461	30.294	-5.1376	-1.6126	1.7168	30.426
H	5.6528	-0.0194	-2.4906	30.268	-5.6166	-0.1400	2.5439	29.957
C	3.6337	-0.0020	-1.6347	154.877	-3.6033	-0.0768	1.7104	154.672
H	3.0451	-0.6424	-2.2896	30.388	-3.0051	-0.6965	2.3762	30.495
H	3.5398	1.0150	-2.0230	30.417	-3.5448	0.9435	2.0984	30.315
C	7.0791	-0.1508	0.1016	151.115	-7.0157	-0.5095	0.0046	147.300
H	7.1438	-0.0835	1.1916	30.039	-6.9665	-1.5972	-0.0989	30.194
C	8.0274	0.9180	-0.4660	157.274	-7.5926	0.0630	-1.2981	160.346
H	9.0604	0.7212	-0.1732	30.820	-8.6244	-0.2675	-1.4301	30.968
H	7.7615	1.9143	-0.1098	30.875	-7.0366	-0.2503	-2.1787	30.367
H	7.9918	0.9337	-1.5580	30.775	-7.5961	1.1554	-1.2765	31.169
C	7.5838	-1.5433	-0.3073	162.699	-7.9976	-0.2086	1.1504	158.583
H	8.5900	-1.7049	0.0837	30.943	-9.0025	-0.5424	0.8868	30.922
H	7.6373	-1.6385	-1.3934	31.234	-8.0477	0.8655	1.3482	31.204
H	6.9520	-2.3469	0.0649	30.650	-7.7180	-0.7061	2.0775	30.499

Table S9. Atomic coordinates for peyssonnoside A (**1**), obtained from DFT calculations at B3LYP/6-311++G(2d,2p) level of theory using DMSO as solvent.

1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* -**1e**									
Atom	***x***	***y***	***z***	Shielding		***x***	***y***	***z***	Shielding
C	-3.1796	-0.0887	0.2323	141.734	H	3.5301	2.3814	1.5761	28.295
C	-4.4797	-0.2647	-0.6366	133.124	C	4.4179	1.9068	-0.3348	98.957
C	-4.4718	0.7141	-1.8288	139.654	H	4.1324	1.9858	-1.3886	28.031
H	-5.2515	0.4428	-2.5401	30.180	C	4.7061	0.4463	-0.0146	100.648
H	-4.7159	1.7178	-1.4683	30.866	H	5.0870	0.3898	1.0123	27.993
C	-3.1287	0.7750	-2.5489	152.894	C	3.4299	-0.3983	-0.0904	97.924
H	-2.8435	-0.2177	-2.9090	30.941	H	3.1076	-0.5262	-1.1235	27.778
H	-3.2171	1.3988	-3.4413	30.540	C	2.8666	3.8655	0.1751	111.383
C	-2.0195	1.3484	-1.6610	143.863	H	2.6823	3.9494	-0.9007	27.762
H	-2.2609	2.4073	-1.5034	30.436	H	1.9432	4.1094	0.6971	27.948
C	-1.9734	0.7101	-0.2645	153.821	O	3.8461	4.8101	0.6007	301.579
C	-1.8812	-0.7917	-0.1587	164.985	H	4.7040	4.4926	0.2868	28.726
H	-1.9201	-1.3171	-1.1027	31.367	O	5.5719	2.7188	-0.0891	290.022
C	-1.1716	1.5462	0.7338	158.176	H	6.2971	2.3702	-0.6199	29.168
H	-1.8122	2.3263	1.1566	30.492	O	5.7118	0.0209	-0.9260	274.747
H	-0.3927	2.0638	0.1794	29.570	H	5.7943	-0.9513	-0.8741	25.526
C	-0.4862	0.7902	1.8855	148.593	O	3.6564	-1.6869	0.5162	99.986
H	-1.1867	0.6096	2.7006	30.997	S	4.0897	-2.9715	-0.4352	121.746
H	0.3011	1.4212	2.3016	30.273	O	3.9191	-4.0822	0.4936	115.834
C	0.1027	-0.5708	1.4973	100.235	O	5.4992	-2.7198	-0.8041	93.071
C	-0.9748	-1.4660	0.8627	146.984	O	3.1840	-2.9601	-1.5827	112.035
H	-0.4638	-2.3054	0.3910	29.821	C	-5.6370	0.0622	0.3833	115.215
H	-1.5685	-1.8921	1.6736	30.579	H	-5.6976	1.1565	0.4384	30.794
C	-4.6028	-1.7137	-1.1469	165.503	C	-5.0757	-0.4233	1.7260	149.948
H	-4.5785	-2.4321	-0.3269	31.119	H	-5.1581	-1.5119	1.7929	30.414
H	-3.7887	-1.9699	-1.8230	30.883	H	-5.6034	-0.0085	2.5828	29.990
H	-5.5326	-1.8609	-1.6956	31.268	C	-3.6115	0.0078	1.6991	154.675
C	-0.6732	1.2794	-2.3950	163.696	H	-3.0040	-0.5969	2.3703	30.489
H	0.1374	1.7290	-1.8247	30.179	H	-3.5316	1.0398	2.0501	30.420
H	-0.7375	1.7984	-3.3538	31.031	C	-7.0680	-0.4518	0.0926	147.319
H	-0.3999	0.2419	-2.5970	31.368	H	-7.0259	-1.5416	0.0107	30.191
C	0.7003	-1.2829	2.7135	156.441	C	-7.6785	0.0956	-1.2055	160.532
H	1.4609	-0.6854	3.2146	30.270	H	-8.7139	-0.2351	-1.3041	30.940
H	1.1454	-2.2329	2.4188	30.795	H	-7.1459	-0.2360	-2.0939	30.374
H	-0.0840	-1.4820	3.4427	30.976	H	-7.6794	1.1882	-1.2054	31.128
O	1.1160	-0.4368	0.4419	203.298	C	-8.0165	-0.1222	1.2585	158.607
C	2.2825	0.2572	0.6971	81.857	H	-9.0301	-0.4546	1.0287	30.928
H	2.5329	0.2704	1.7620	27.031	H	-8.0548	0.9559	1.4365	31.213
O	2.1212	1.6108	0.2540	227.576	H	-7.7145	-0.6032	2.1873	30.507
C	3.2599	2.4290	0.5140	106.405					

VCD spectra of peyssonnoside A (1)

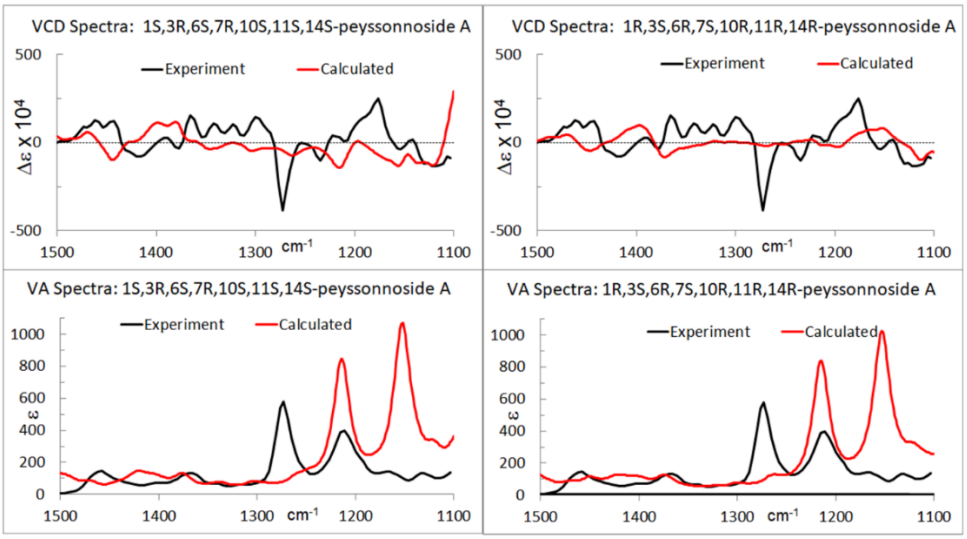


Figure S13. Comparison of experimental and calculated vibrational absorption (VA) and vibrational circular dichroism (VCD) spectra of 1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*S*,3*R*,6*S*,7*R*,10*S*,11*S*,14*S*- peyssonnoside A (**1**) and 1′*S*,2′*R*,3′*S*,4′*S*,5′*R*,1*R*,3*S*,6*R*,7*S*,10*R*,11*R*,14*R* - peyssonnoside A (**1**) with experimental spectra.

Table S10. ^{1}H, ^{13}C, COSY, HMBC, ROESY NMR correlations for peyssonnoside B (**2**).

No	δC	δH (mult, *J* Hz)	COSY	HMBC	ROESY
1	13.9 (CH)	0.66 dd (9.6, 2.2)	H-2a, H-2b	C-3, C-5, C-6, C-7, C-10, C-11, C-12	H-2b, H-19, H-6′a
2a	30.5 (CH_2)	0.81 dd (14.8, 2.2)	H-1	C-1, C-4, C-11	H-2b, H-12, H-20
2b		2.39 ddd (14.6, 9.3, 1.7)	H-1, H-4b	C-1, C-3, C-4, C-11, C-20	H-1, H-2a, H-20, H-1′, H-5′ H-6′b
3	73.0 (C)				
4a	34.2 (CH_2)	0.75 m	H-5a, H-5b	C-1, C-5 C-20, C-1′	H-4b, H-12
4b		1.38 m	H-2b, H-5b	C-2, C-3, C-6	H-4a, H-5a, H-5b, H-20, H-1′′, H-5′′, H-6′′b
5a	21.6 (CH_2)	1.25 m	H-4a	C-1, C-3, C-4, C-6	H-4b, H-5b
5b		1.86 ddd (13.7, 12.9, 7.7)	H-4a, H-4b	C-4, C-6, C-7, C-11	H-4a, H-4b, H-5a, H-7, H-19, H-1′′
6	23.9 (C)				
7	34.9 (CH)	1.39 m	H-8a, H-19	C-1, C-5, C-8, C-9, C-19	H-5b, H-8a, H-8b, H-9a, H-19
8a	26.6 (CH_2)	0.75 m	H-7, H-9a, H-9b	C-7, C-9, C-10	H-7, H-8b, H-9b, H-18, H-19
8b		1.18 m	H-9a, H-9b	C-6, C-7, C-10	H-7, H-8a, H-9b
9a	39.1 (CH_2)	0.91 m	H-8a, H-8b	C-7, C-8, C-10, C-18	H-7, H-9b, H-14
9b		1.49 m	H-8a, H-8b	C-7, C-8, C-10, C-11, C-15, C-18	H-8a, H-8b, H-9a, H-18
10	41.5 (C)				
11	36.3 (C)				
12	24.9 (CH_2)	1.28 m	H-13b	C-1, C-6, C-10, C-11, C-13, C-14	H-2a, H-4a, H-13b
13a	27.9 (CH_2)	1.20 m		C-14	H-13b, H-18
13b		1.72 m	H-12, H-14	C-10, C-11, C-12, C-14	H-12, H-13a, H-17
14	61.5 (CH)	1.19 m	H-13b, H-15	C-9, C-13 C-18	H-9a, H-15
15	28.5 (CH)	1.56 o (6.7)	H-14, H-16, H-17	C-10, C-13, C-14, C-16, C-17	H-14, H-16, H-17, H-18
16	23.3 (CH_3)	0.91 d (6.6)	H-15	C-14, C-15, C-17	H-15
17	23.0 (CH_3)	0.88 d (6.6)	H-15	C-14, C-15, C-16	H-13b, H-15
18	19.0 (CH_3)	0.65 s		C-1, C-9, C-10, C-11, C-14, C-15	H-8a, H-9b, H-13a, H-15
19	19.5 (CH_3)	1.02 d (6.3)	H-7	C-6, C-7, C-8, C-9	H-1, H-5b, H-7, H-8a, H-2′, H-6′a, H-1′′
20	24.5 (CH_3)	1.13 s		C-1, C-2, C-3, C-4, C-5, C-1′	H-2a, H-2b, H-4b, H-1′, H-6′′b
1′	96.6 (CH)	4.44 d (7.6)	H-2′	C-3, C-2′ C-5′	H-2b, H-20, H-3′, H-5′
2′	83.3 (CH)	3.13 t (8.0)	H-1′, H-3′	C-1′, C-3′, C-1′′	H-19, H-1′′, OH (4.94)
3′	75.6 (CH)	3.25 t (8.7)	H-2′, H-4′	C-1′, C-2′, C-4′	H-1′, H-5′,OH (4.94)
4′	70.4 (CH)	3.0 m	H-3′, H-5′	C-3′, C-5′, C-6′	
5′	76.1 CH)	3.11 m	H-4′, H-6′a, H-6′b	C-1′, C-3′, C-4′, C-6′	H-2b, H-1′, H-3′, H-6′b
6′a	61.8 (CH_2)	3.35 m	H-5′	C-5′	H-1, H-19, H-6′b
6′b		3.73 dd (11.5, 1.5)	H-5′	C-4′	H-2b, H-5′, H-6′a
1′′	100.9 (CH)	4.53 d (7.7)	H-2′′	C-2′, C-2′′, C-3′′, C-5′′	H-4b, H-5b, H-19, H-2′, H-3′′
2′′	79.7 (CH)	3.7 dd (9.2, 8.0)	H-1′′, H-3′′	C-1′′, C-3′′, C-4′′	H-4′′, OH (4.94)
3′′	75.7 (CH)	3.37 t (9.0)	H-2′′, H-4′′	C-1′′, C-2′′, C-4′′	H-1′′, H-5′′
4′′	69.4 (CH)	3.29 t (9.3)	H-3′′, H-5′′	C-3′′, C-5′′, C-6′′	H-2′′
5′′	76.4 (CH)	3.0 m	H-4′′, H-6′′a, H-6′′b	C-1′′, C-4′′	H-4b, H-3′′
6′′a	60 (CH_2)	3.55 dd (11.6, 3.0)	H-5′′	C-4′′, C-5′′	
6′′b		3.62 dd (11.7, 1.5)	H-5′′	C-4′′, C-5′′	H-4b, H-20
OH		4.1 brs			
OH		4.28 brs			
OH		4.47 brs			
OH		4.94 s		C-2′, C-3′, C-4′	H-2′, H-3′, H-2′′
OH		5.03 brs			
OH		5.17 brs			

NMR spectra for peyssonnoside A (1)

Figure S14. ^{1}H NMR spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

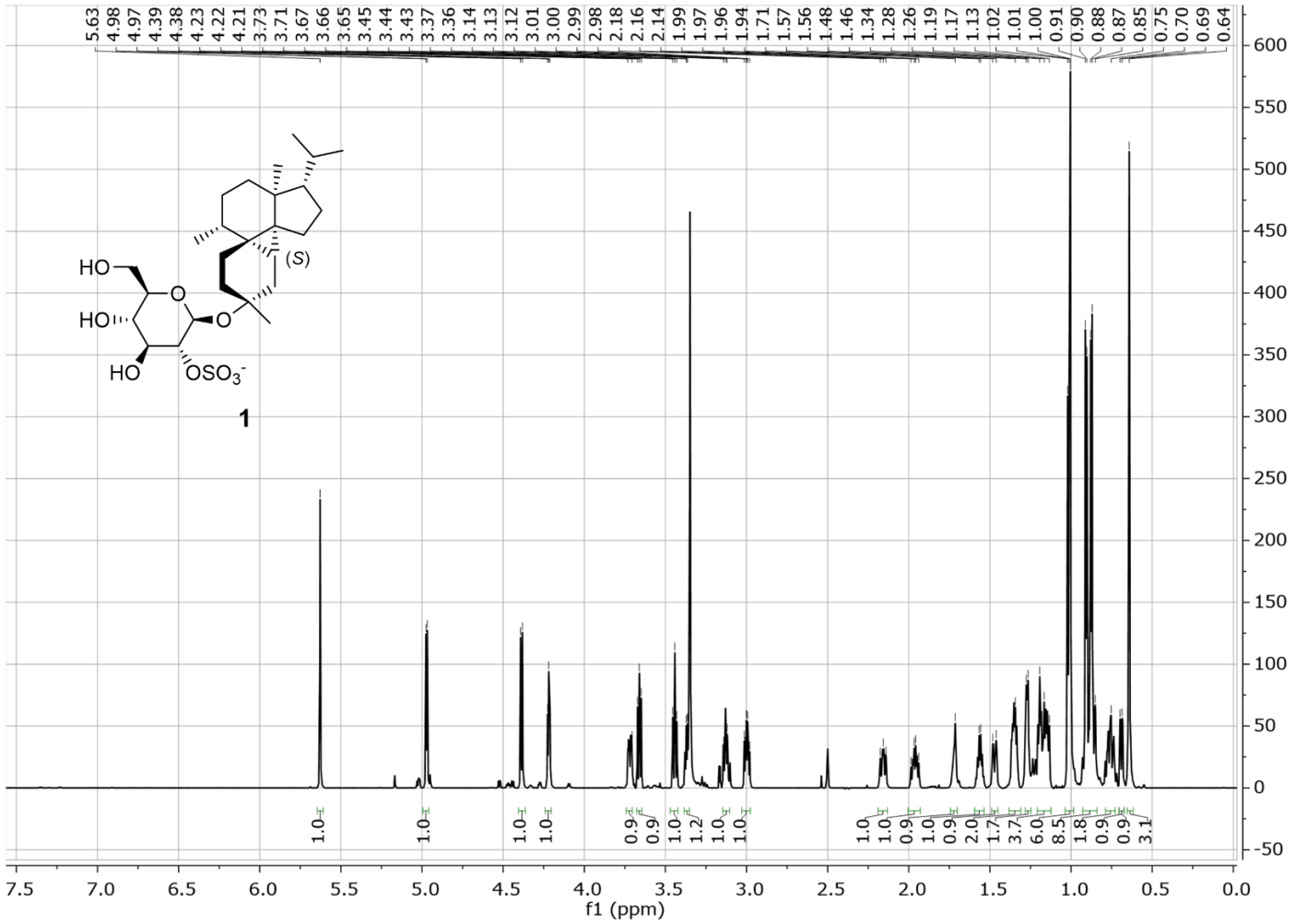


Figure S15. ^{13}C NMR spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

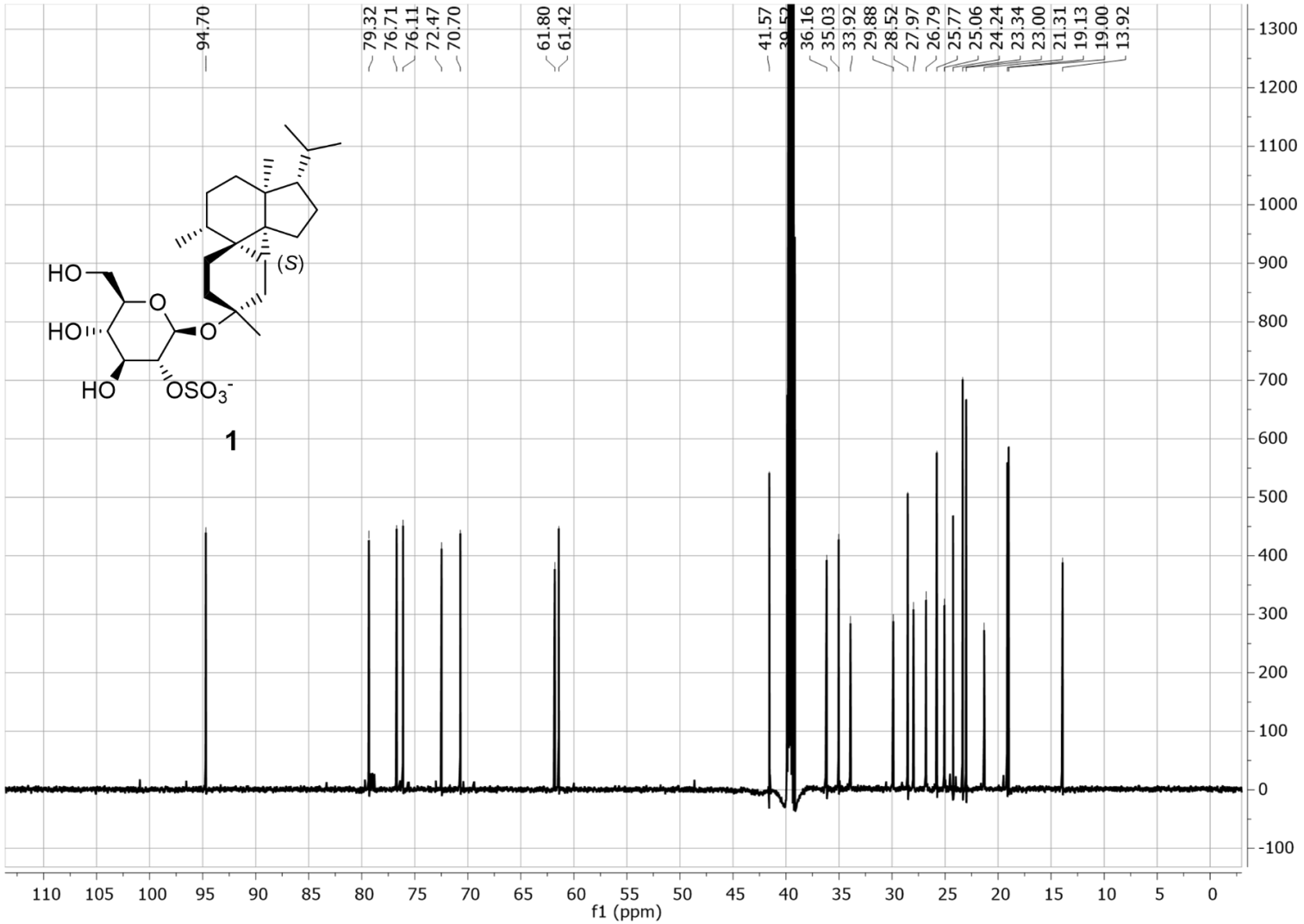


Figure S16. HSQC spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

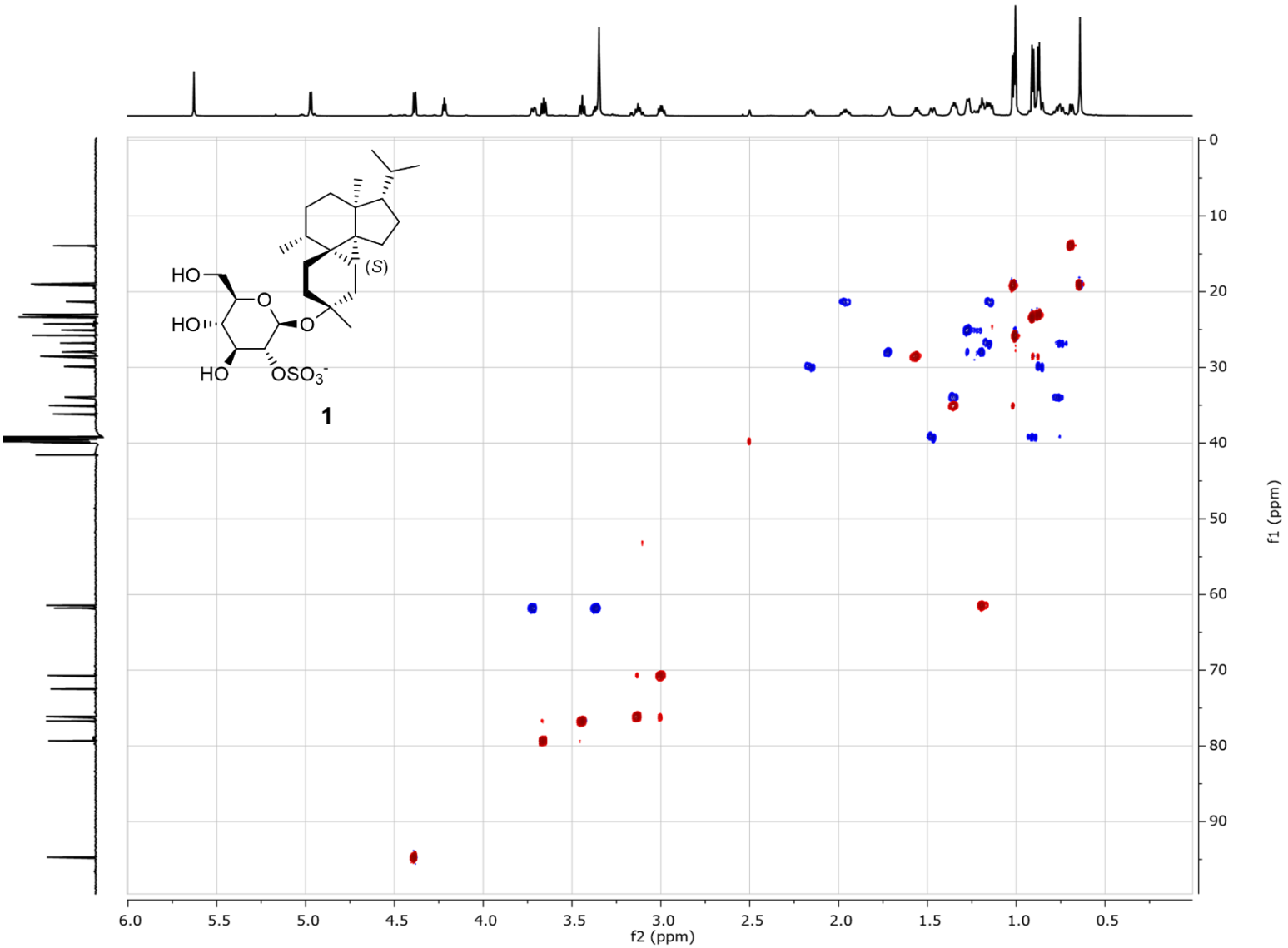


Figure S17. COSY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

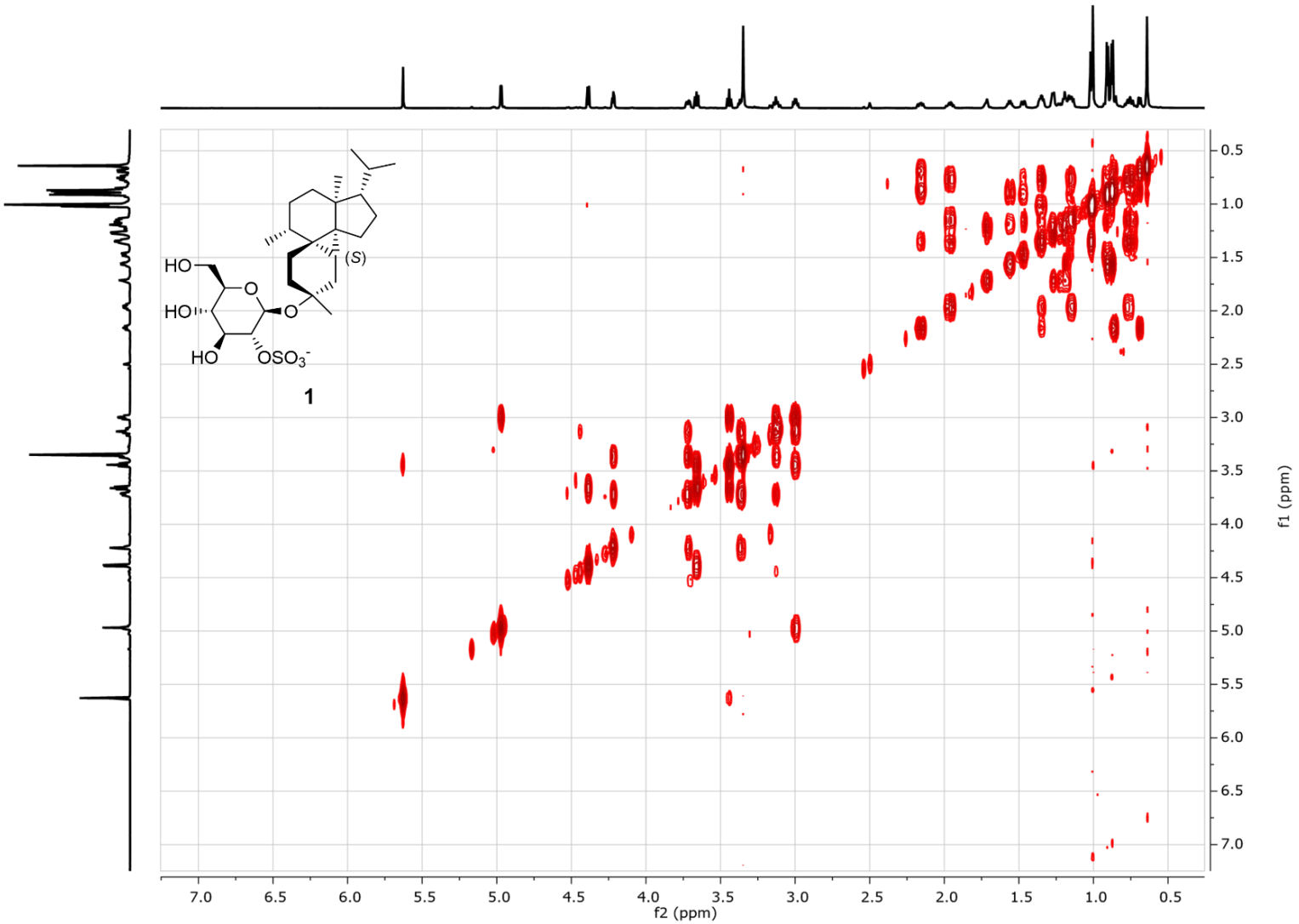


Figure S18. HMBC spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

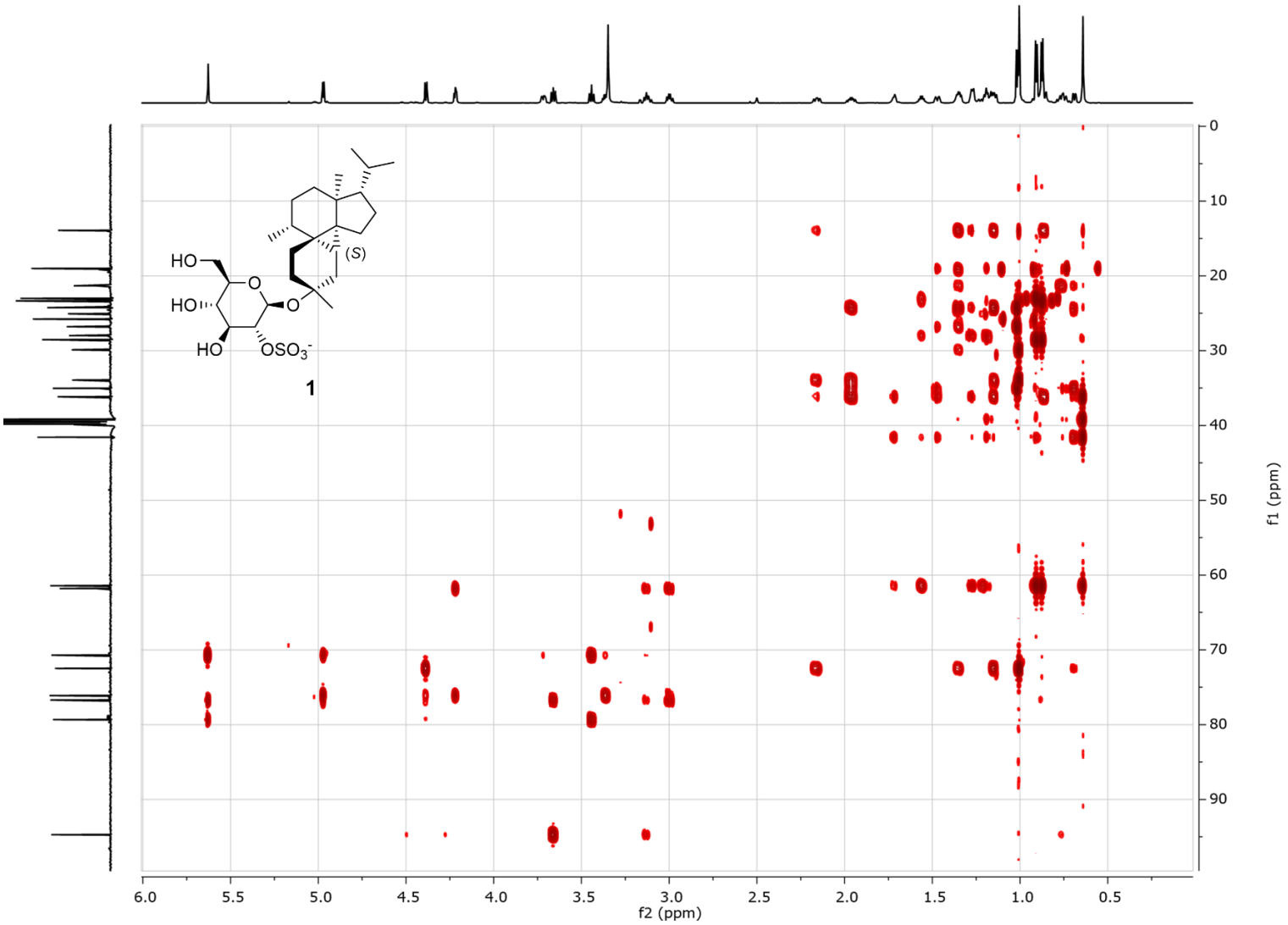


Figure S19. J_{CH} coupled HSQC spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

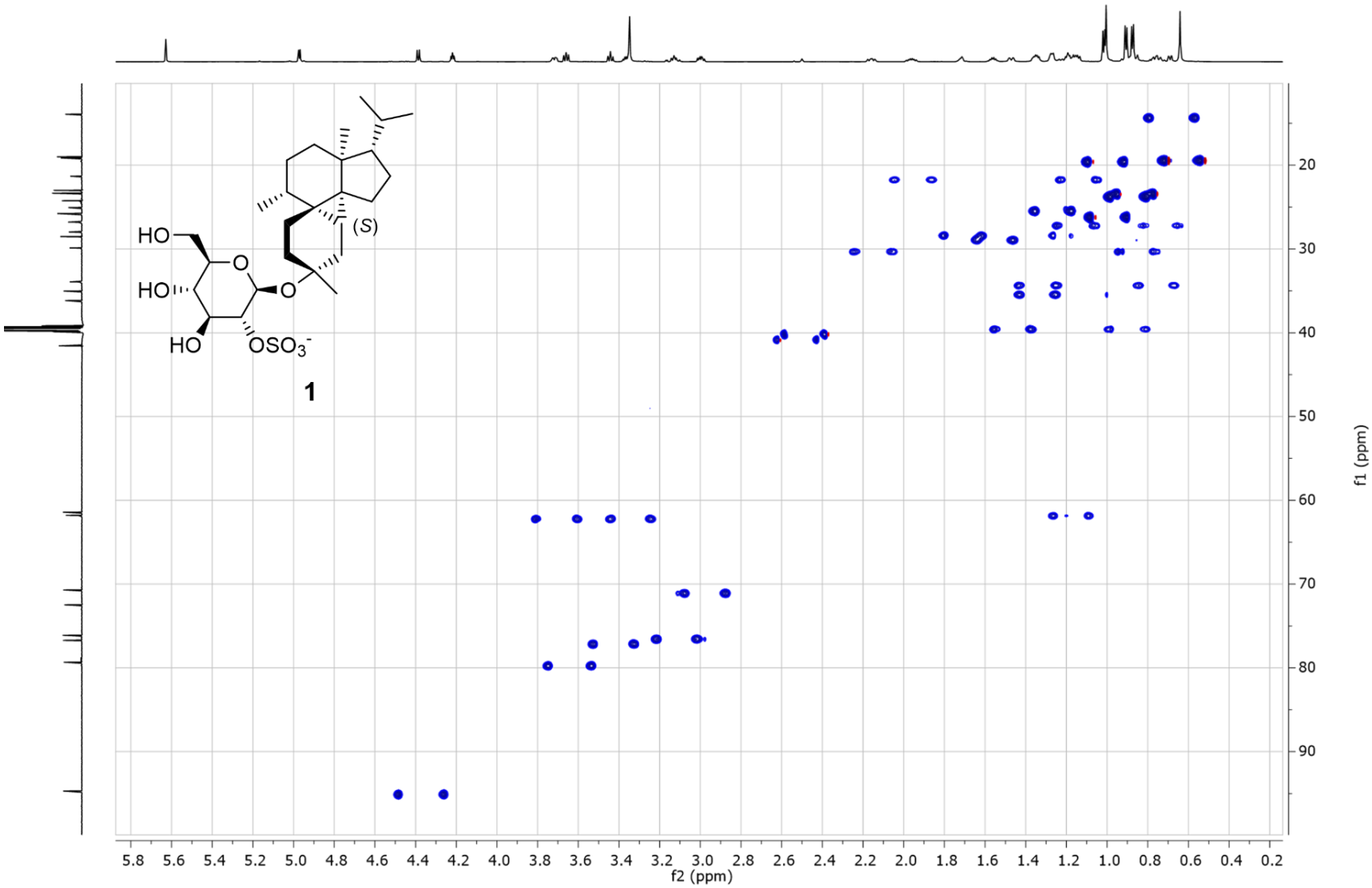


Figure S20. HSQC-ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

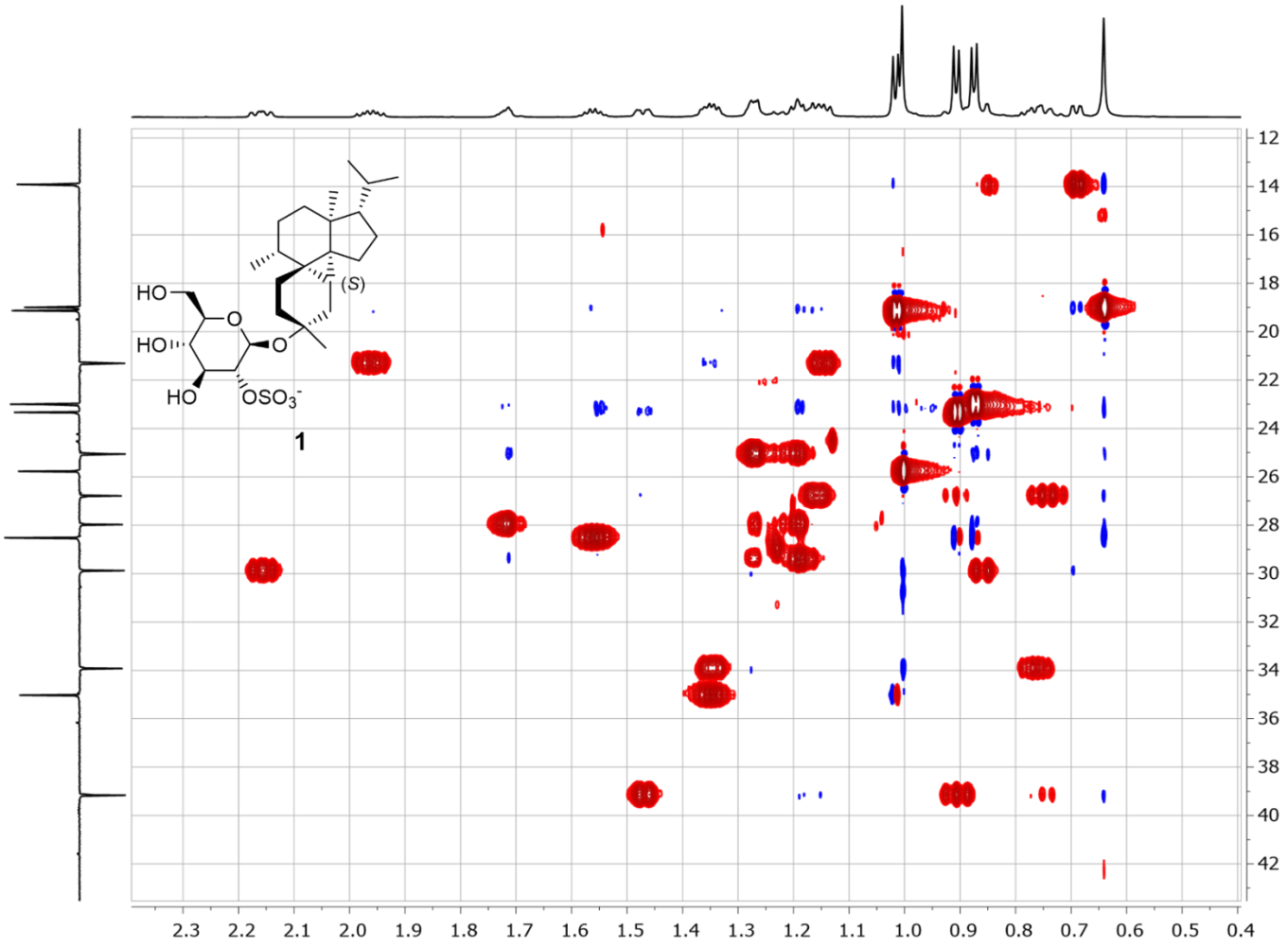
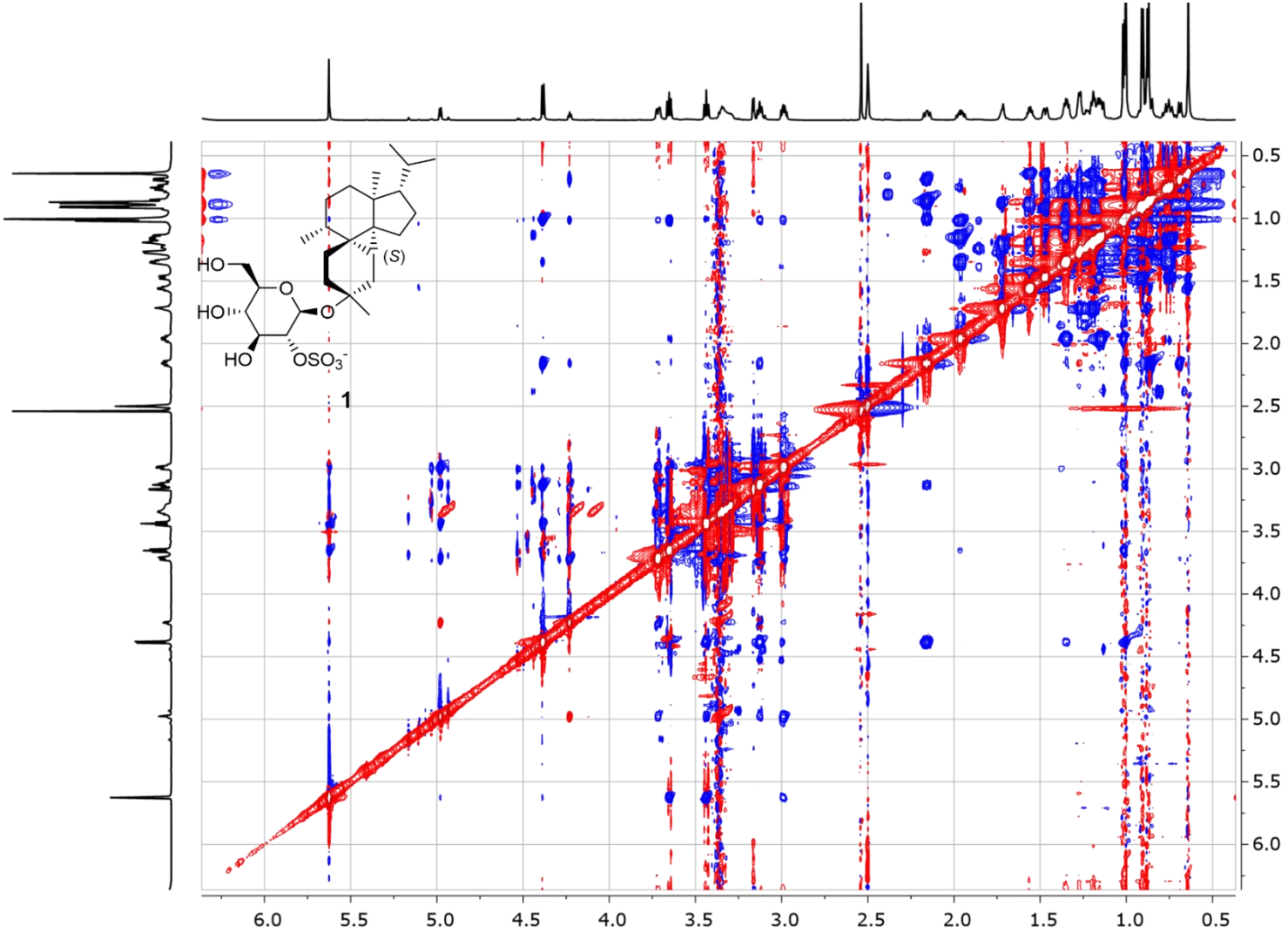


Figure S21. ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6



NMR spectra for peyssonnoside B (2)

Figure S22. ^{1}H NMR spectrum of peyssonnoside B (**2**) at 800 MHz in DMSO-d_6

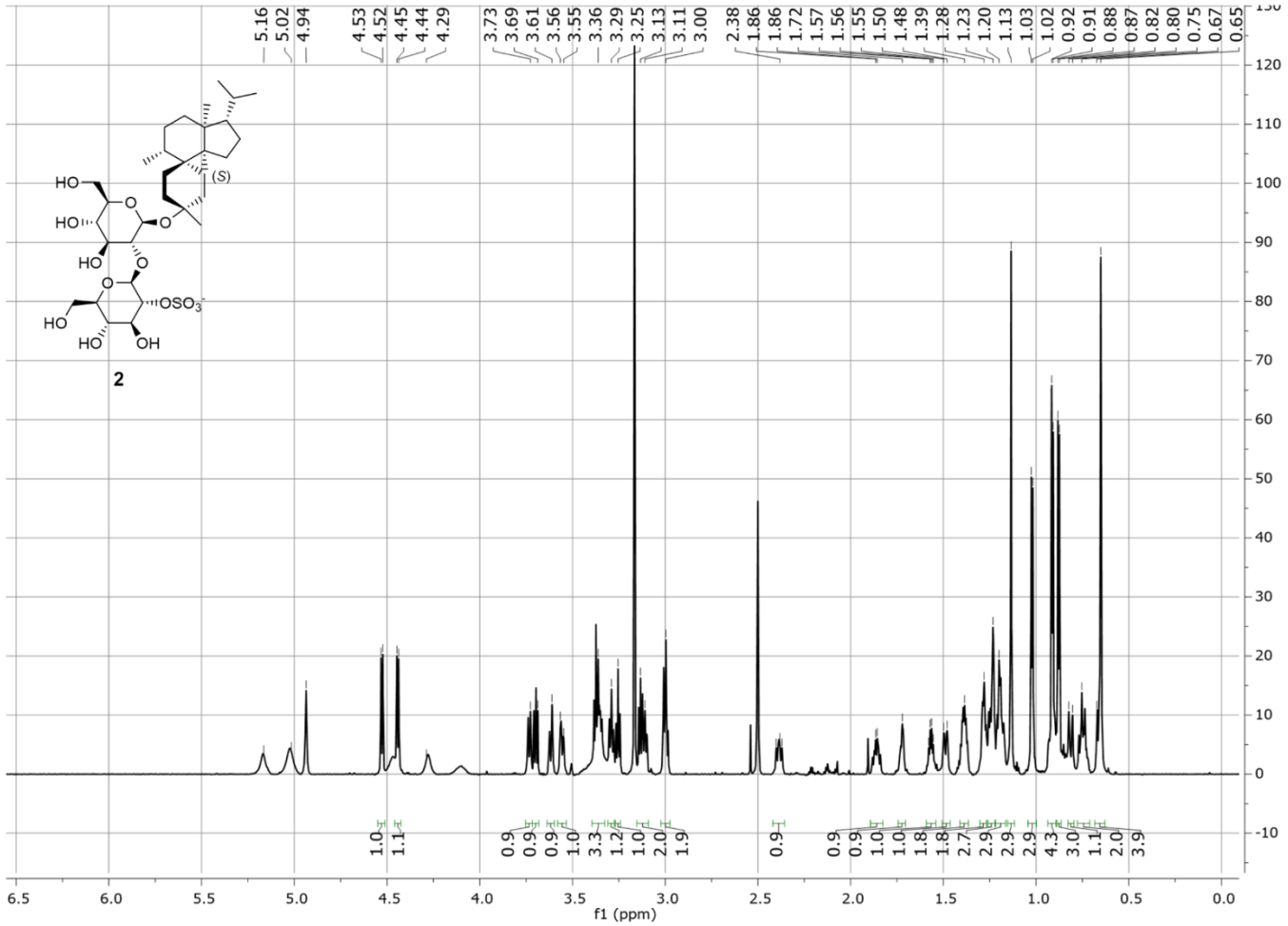


Figure S23. ^{13}C spectrum of peyssonnoside B (**2**) at 800 MHz in DMSO-d_6

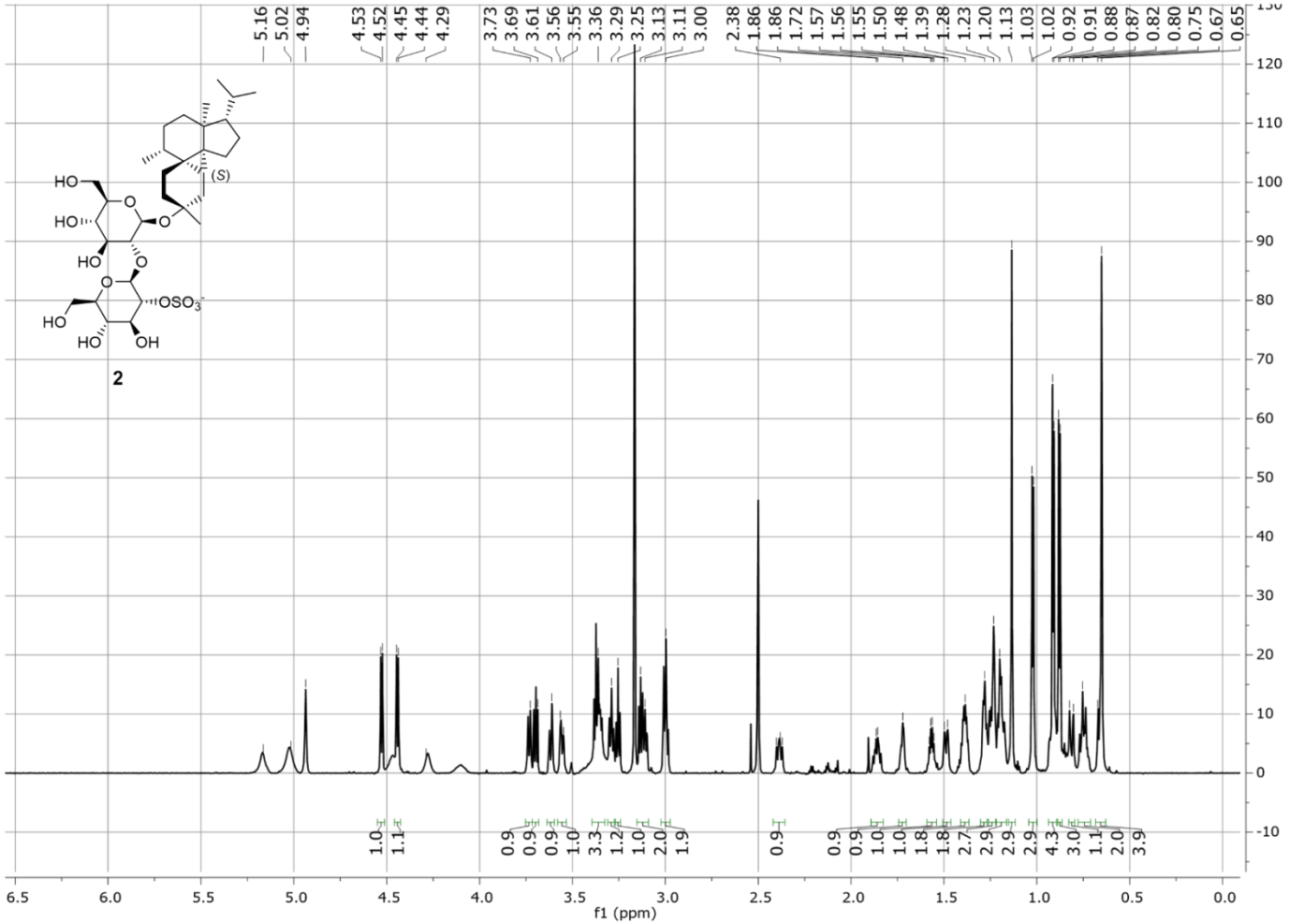


Figure S24. HSQC spectrum of peyssonnoside B (**2**) at 800 MHz in DMSO-d_6

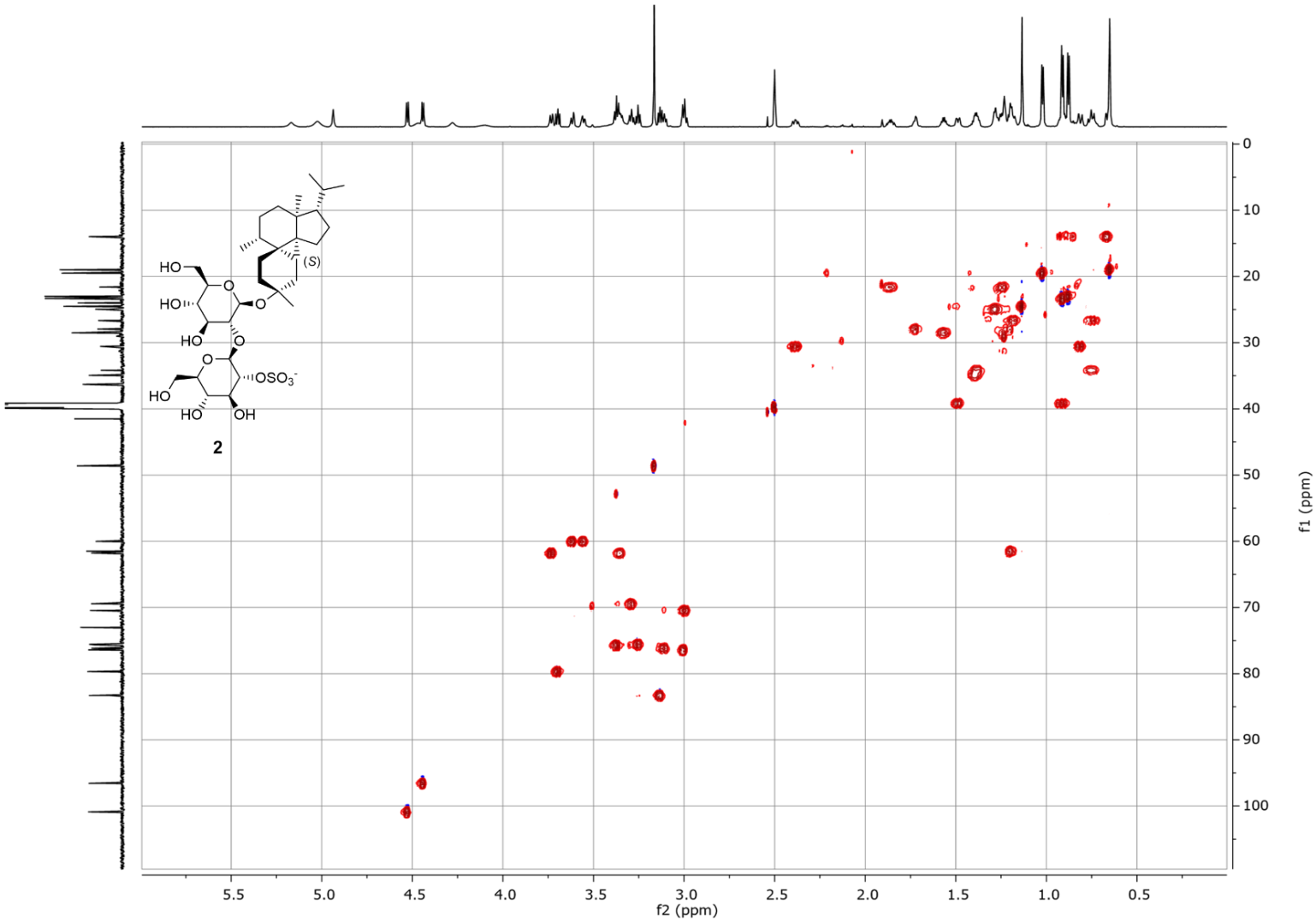


Figure S25. COSY spectrum of peyssonnoside B (**2**) at 800 MHz in DMSO-d_6

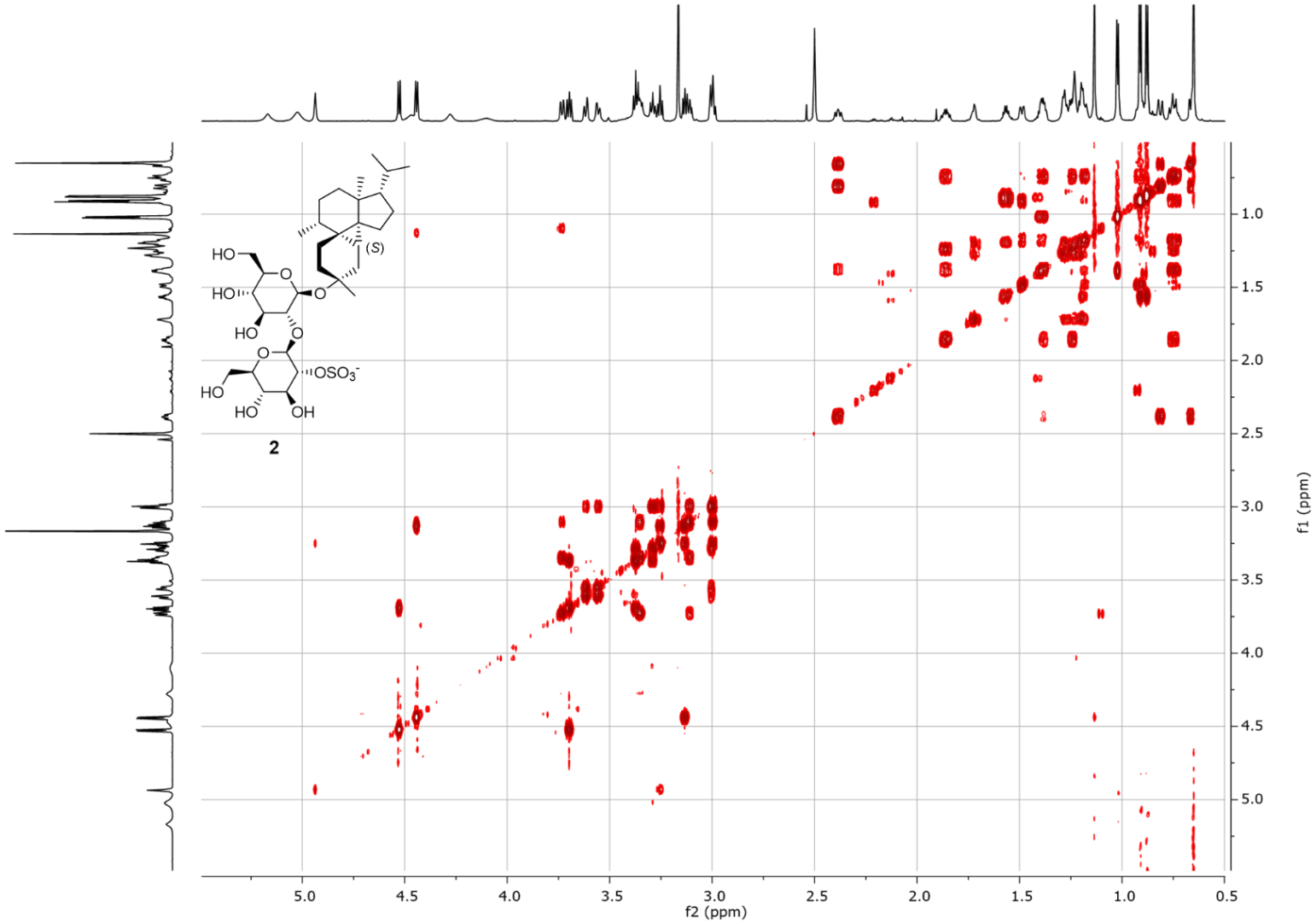


Figure S26. HMBC spectrum of peyssonnoside B (**2**) at 800 MHz in DMSO-d_6

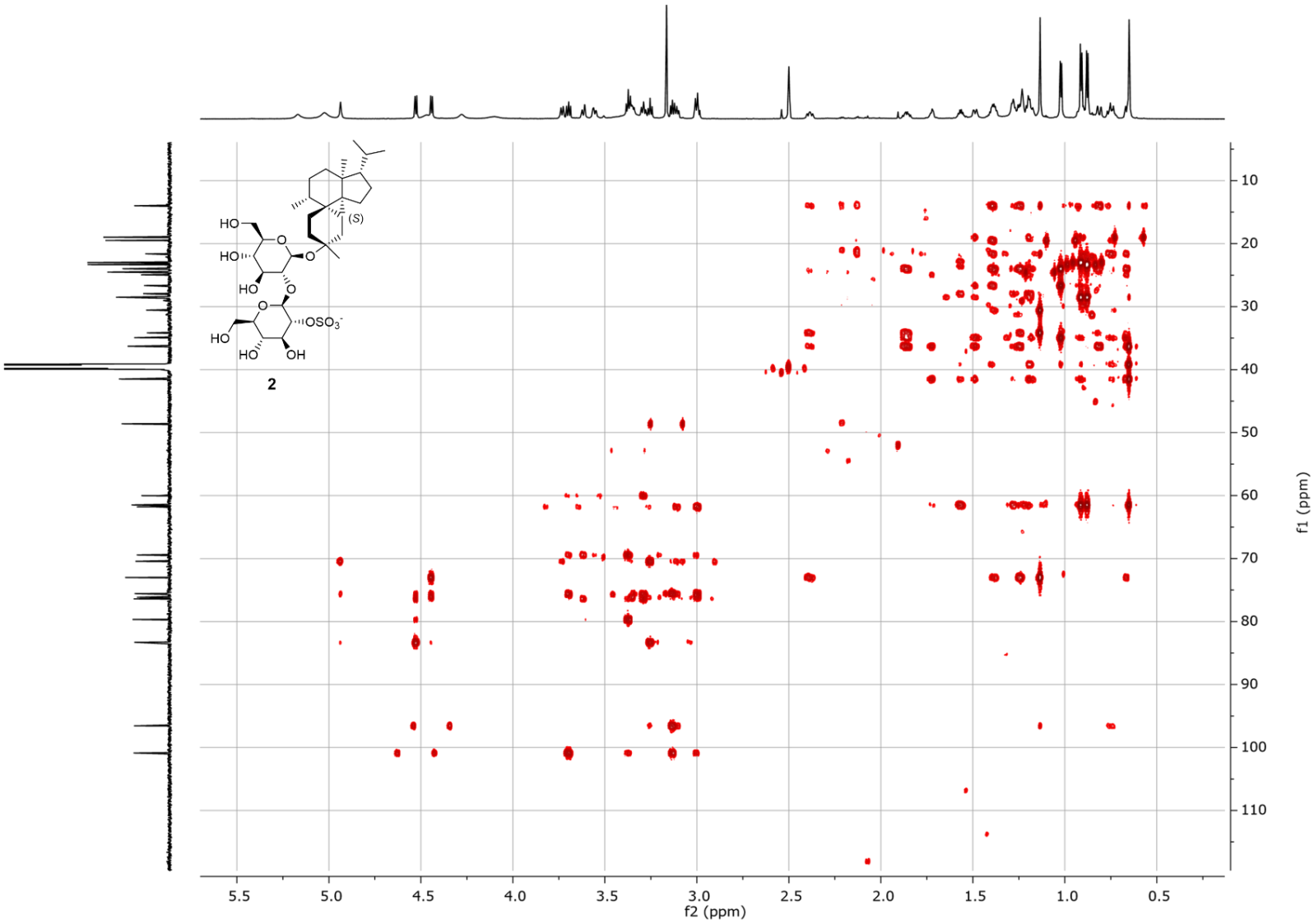


Figure S27. TOCSY spectrum of peyssonnoside B (**2**) at 800 MHz in DMSO-d_6

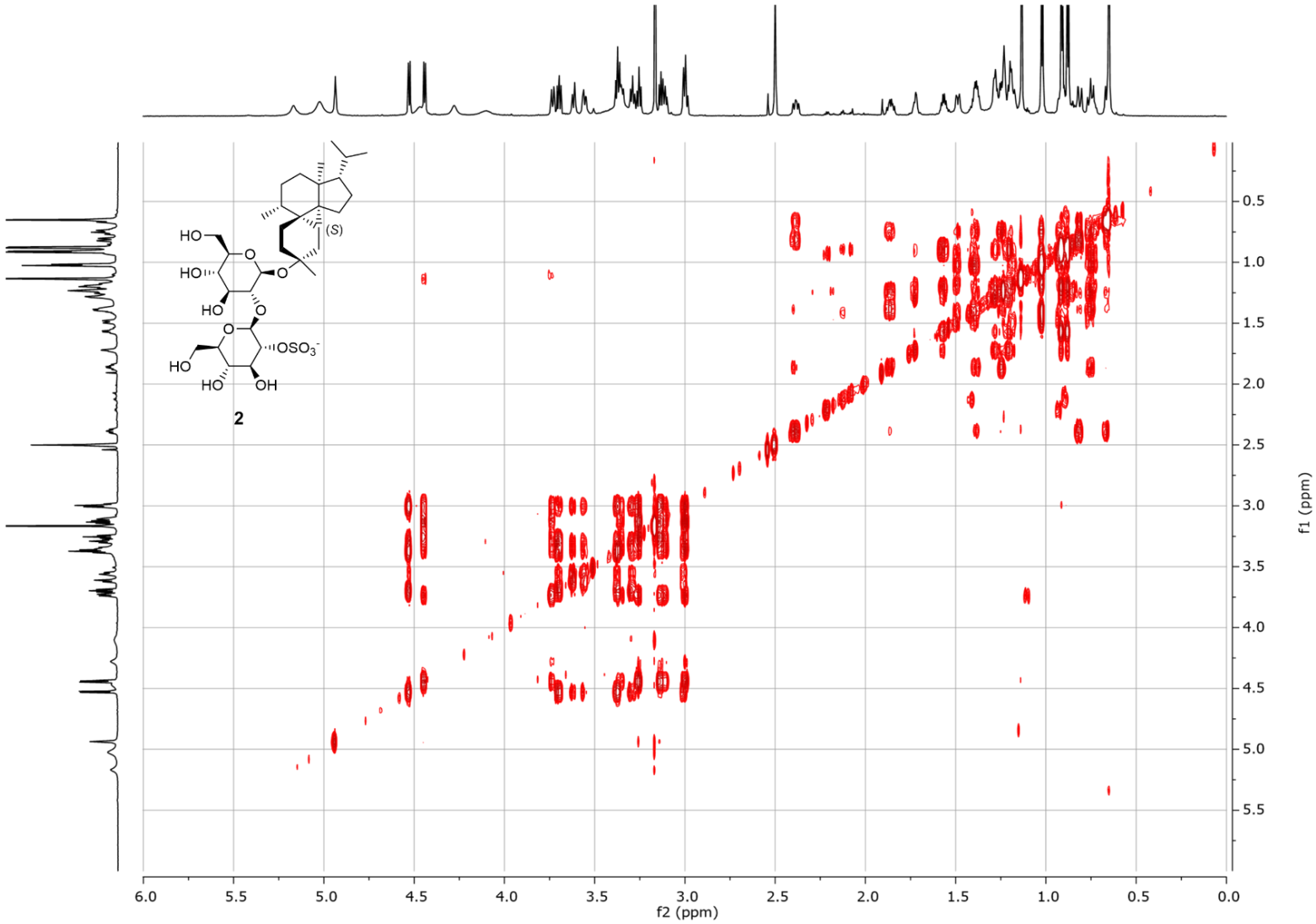


Figure S28. ROESY spectrum of peyssonnoside B (**2**) at 800 MHz in DMSO-d_6

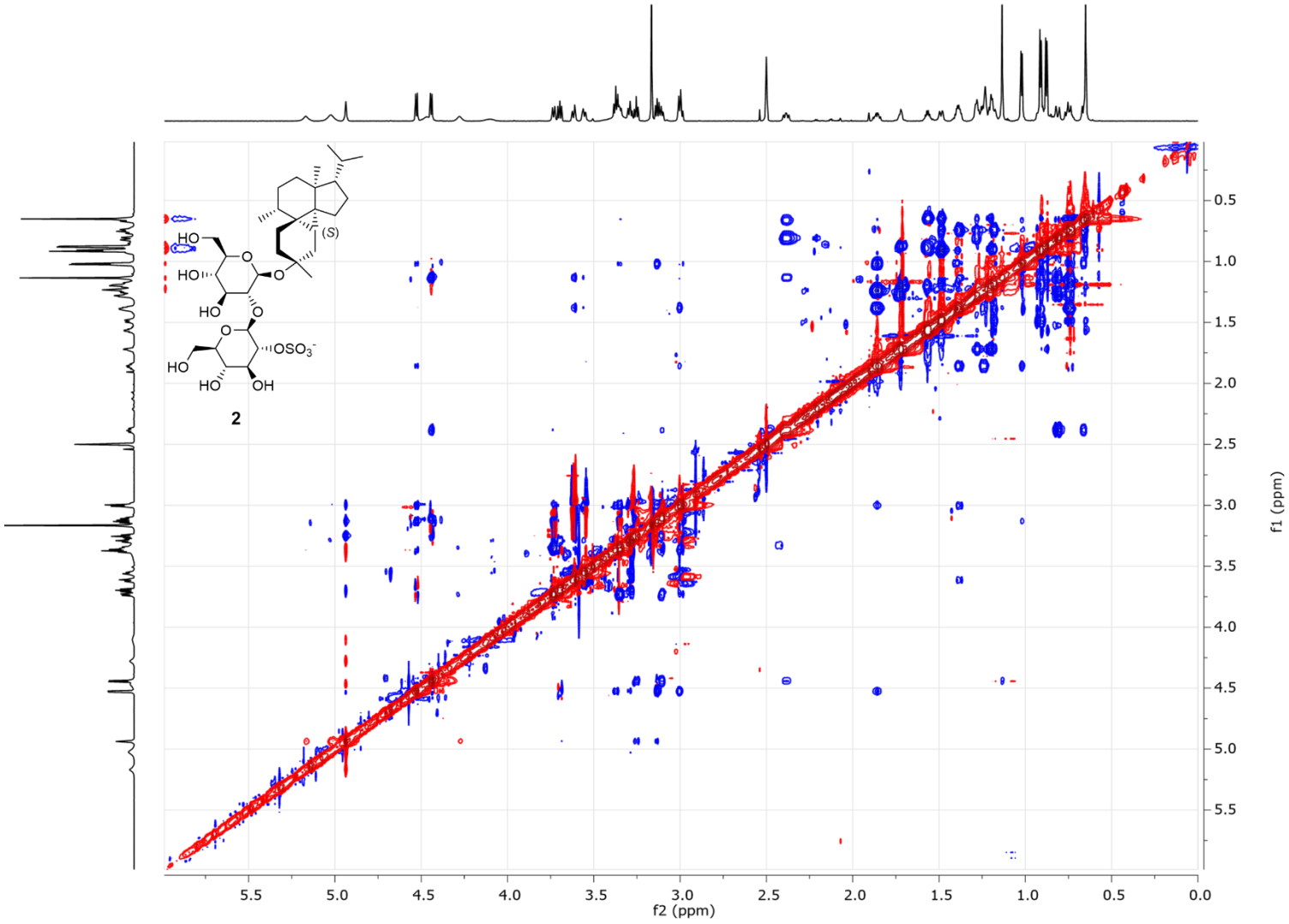


Figure S29. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

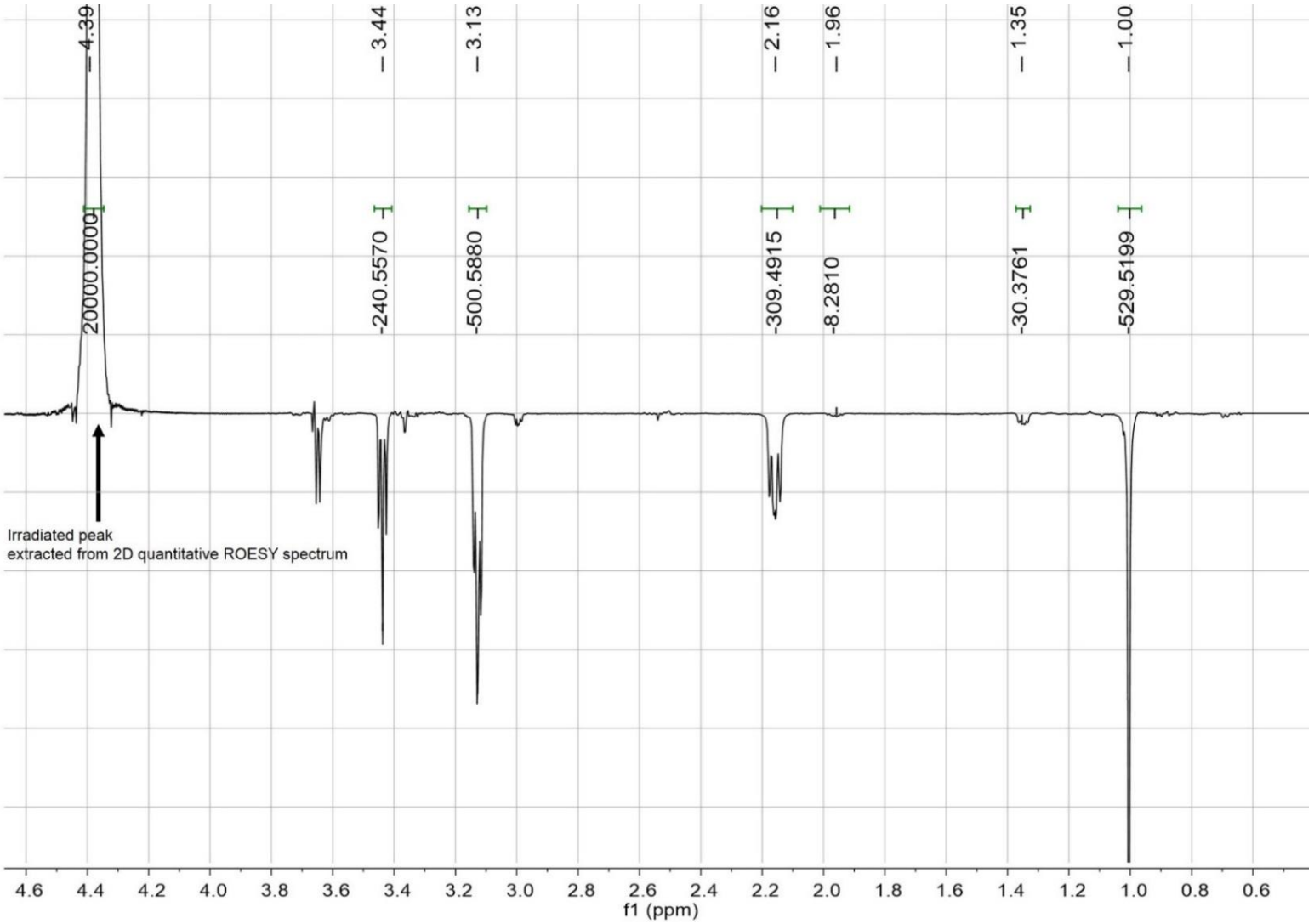


Figure S30. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

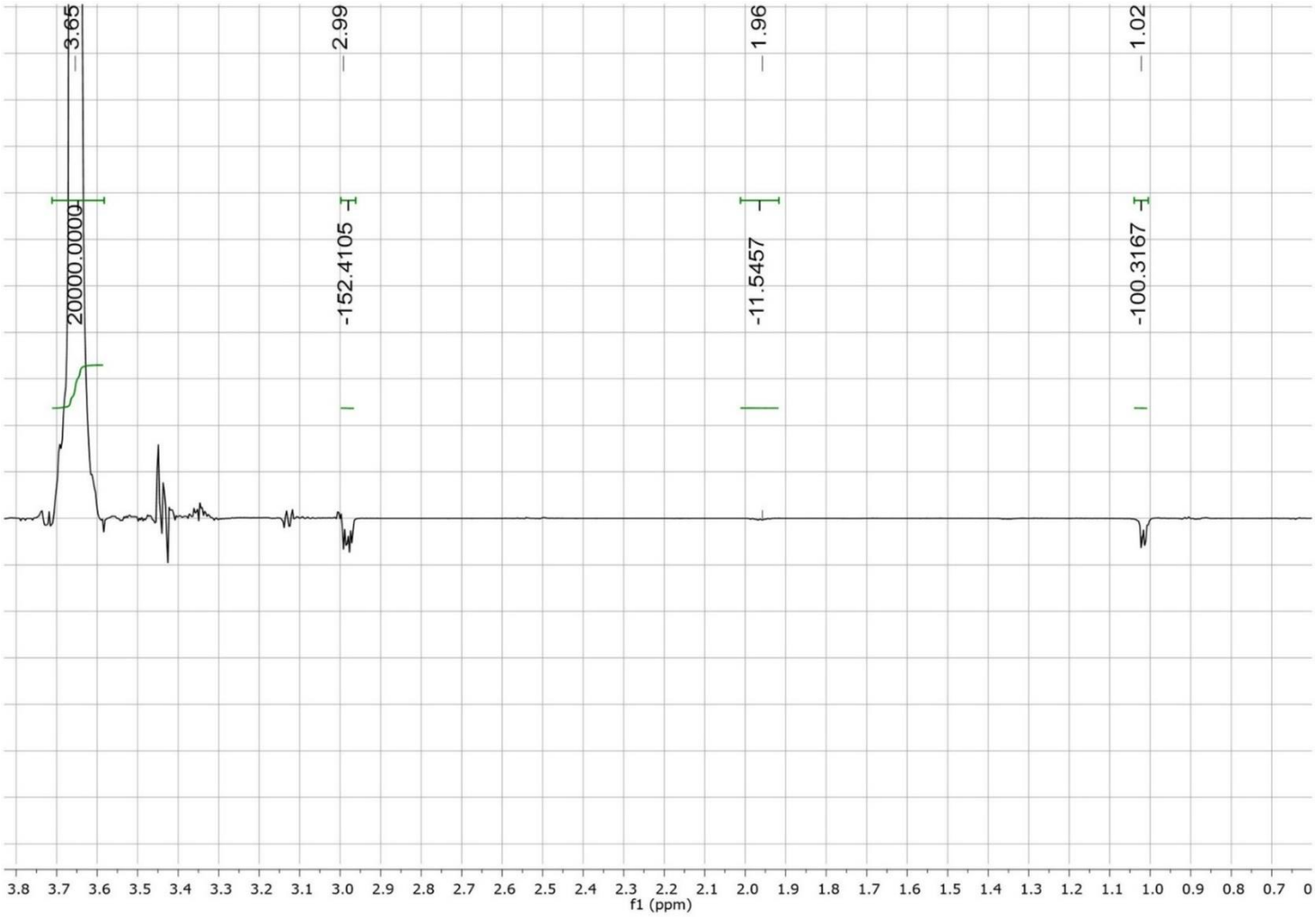


Figure S31. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

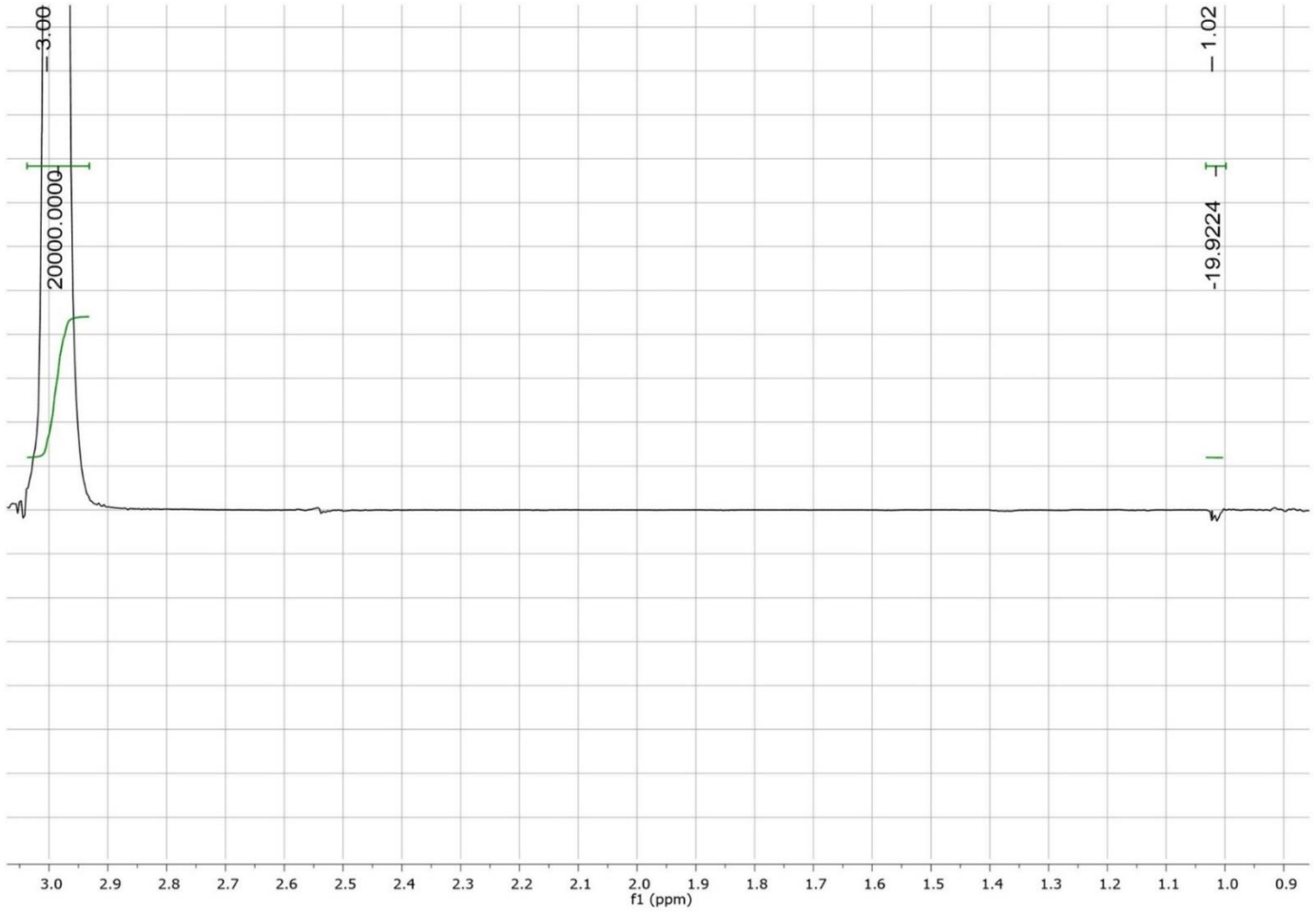


Figure S32. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

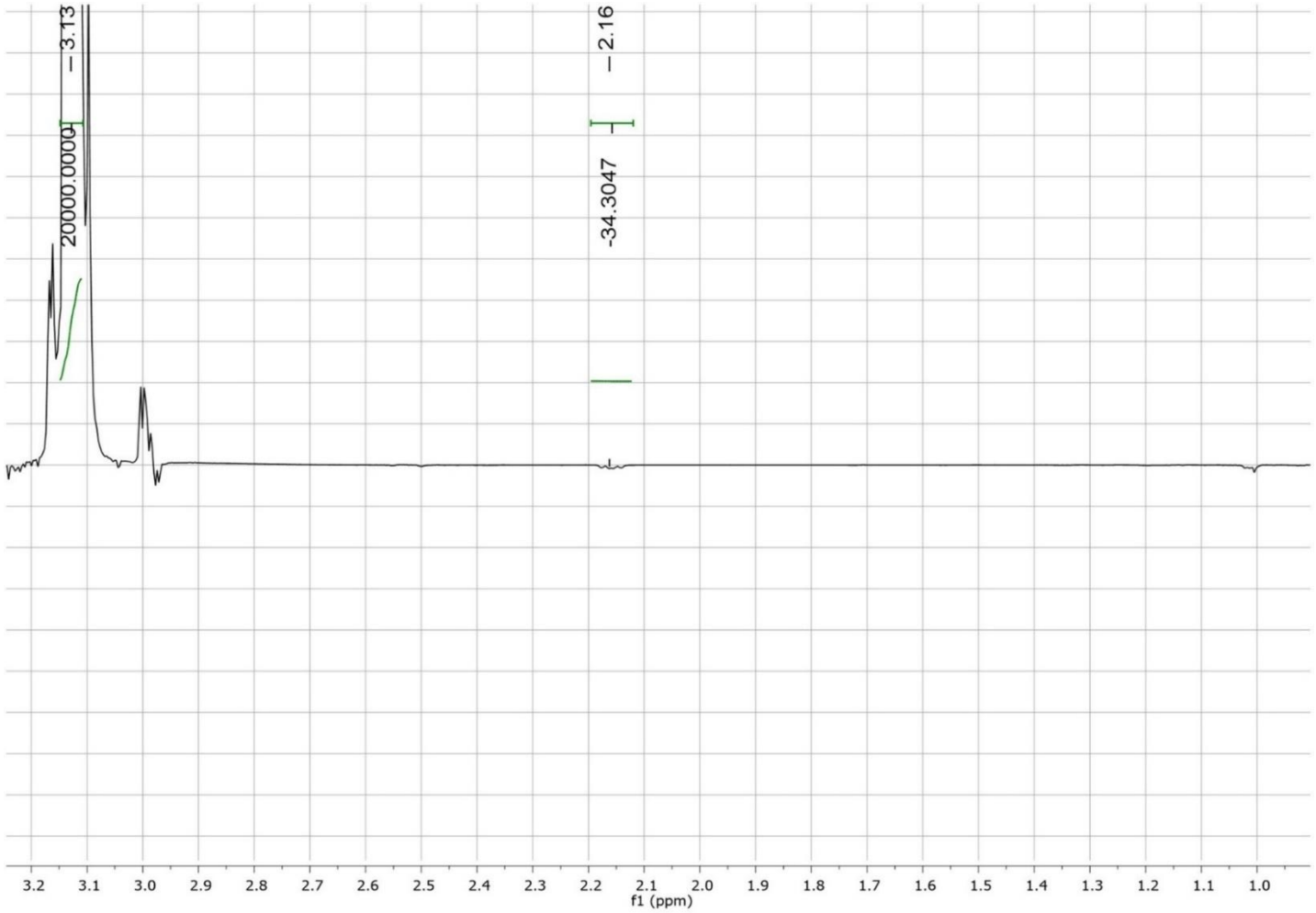


Figure S33. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

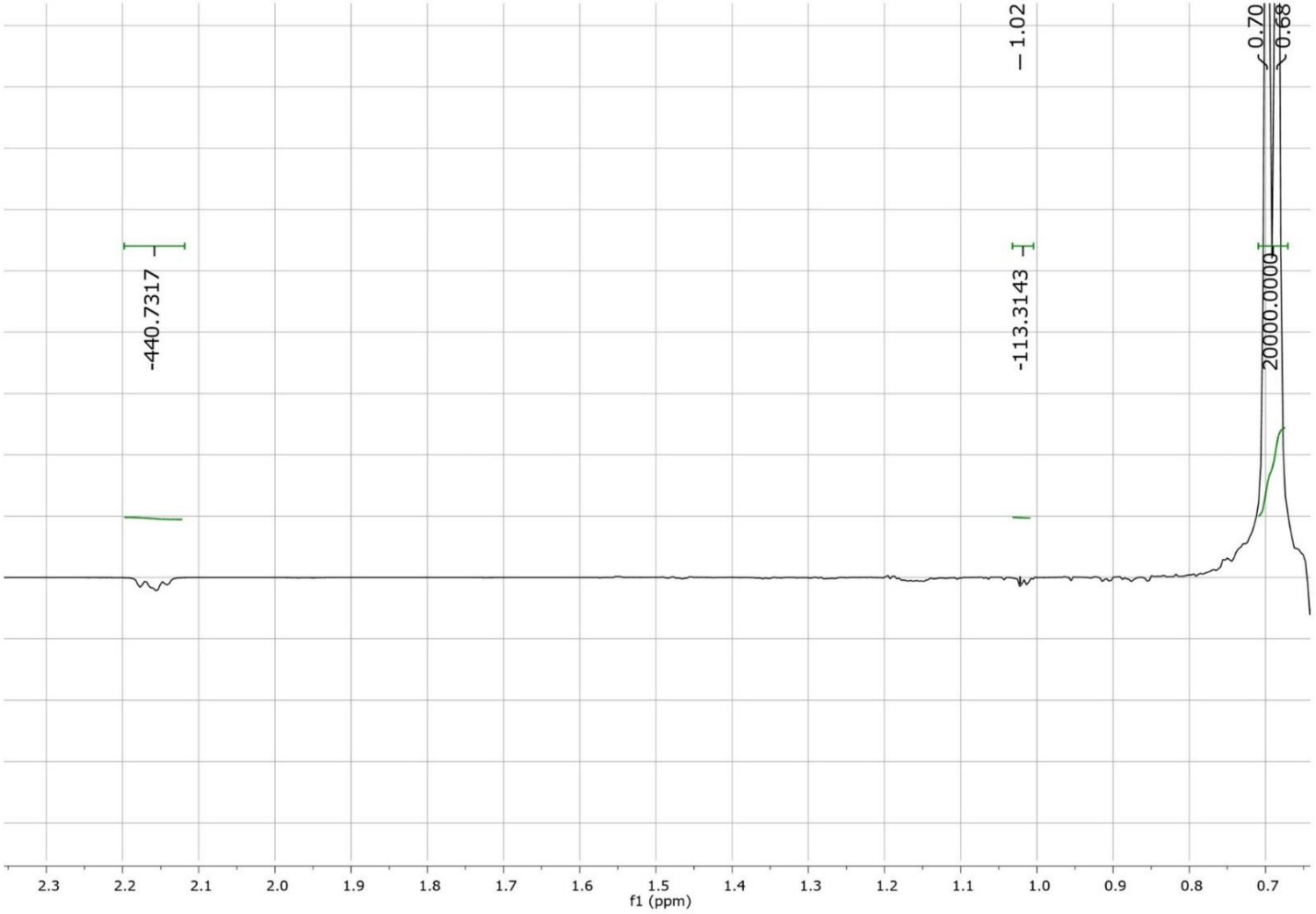


Figure S34. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

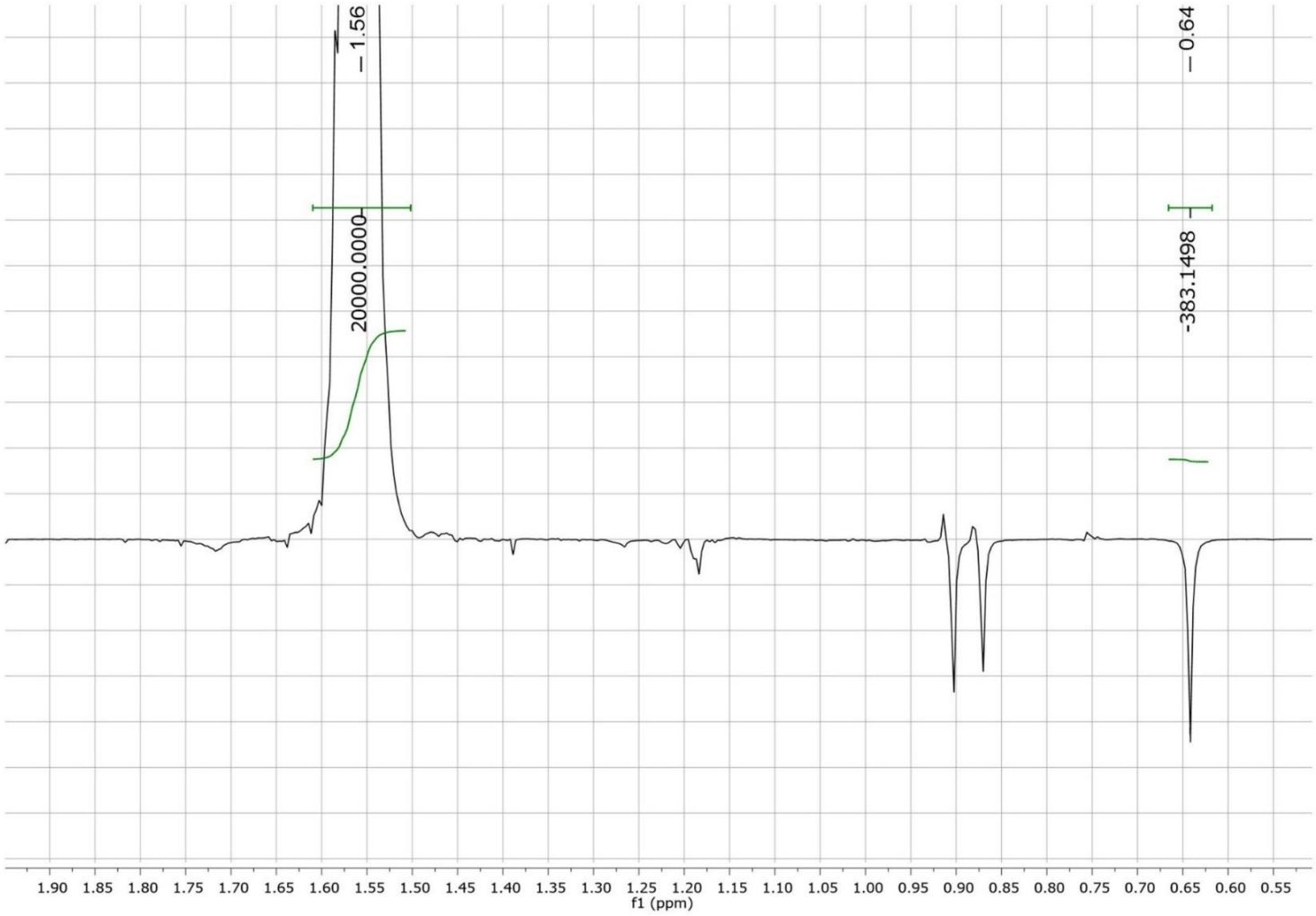


Figure S35. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

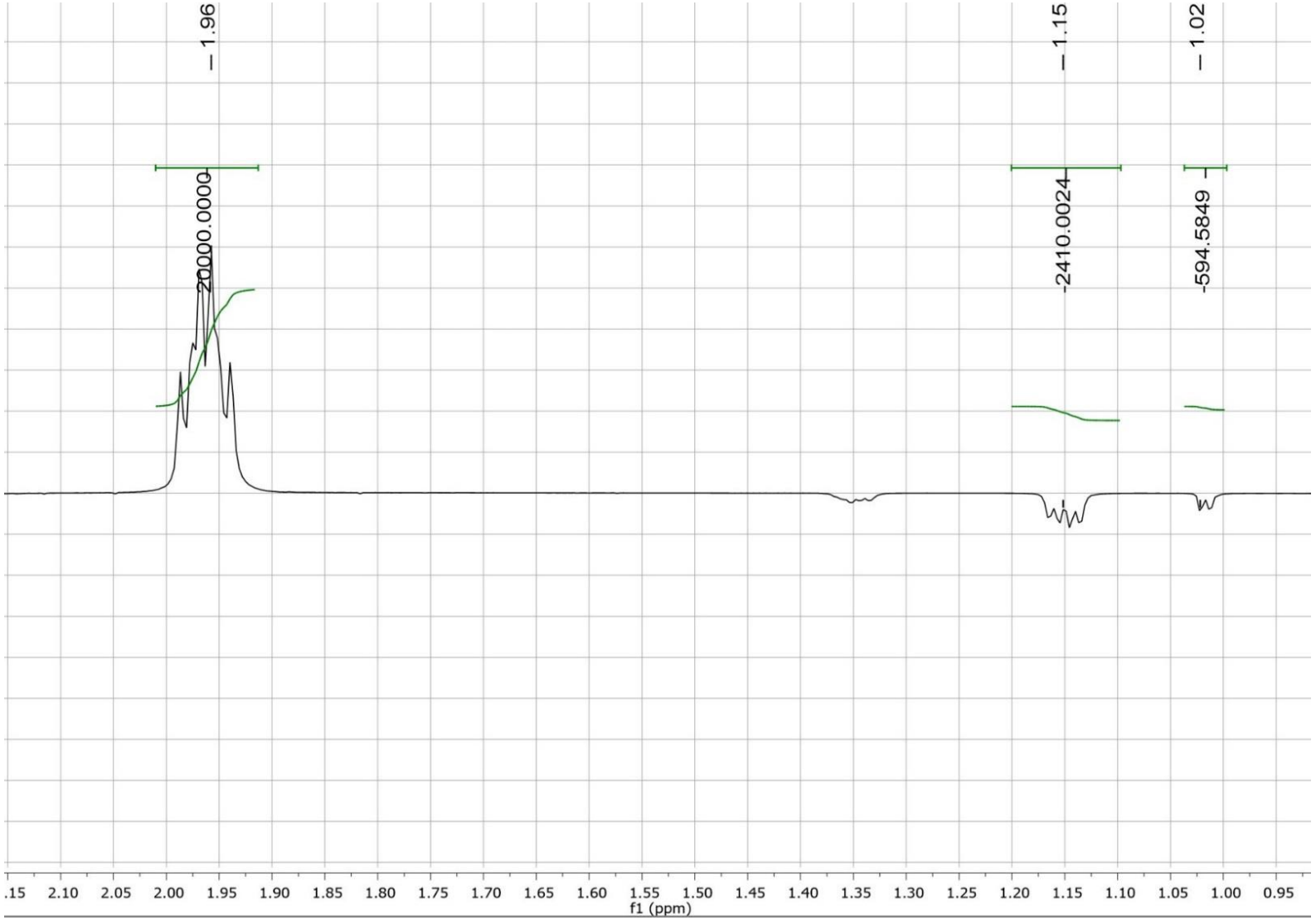


Figure S36. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

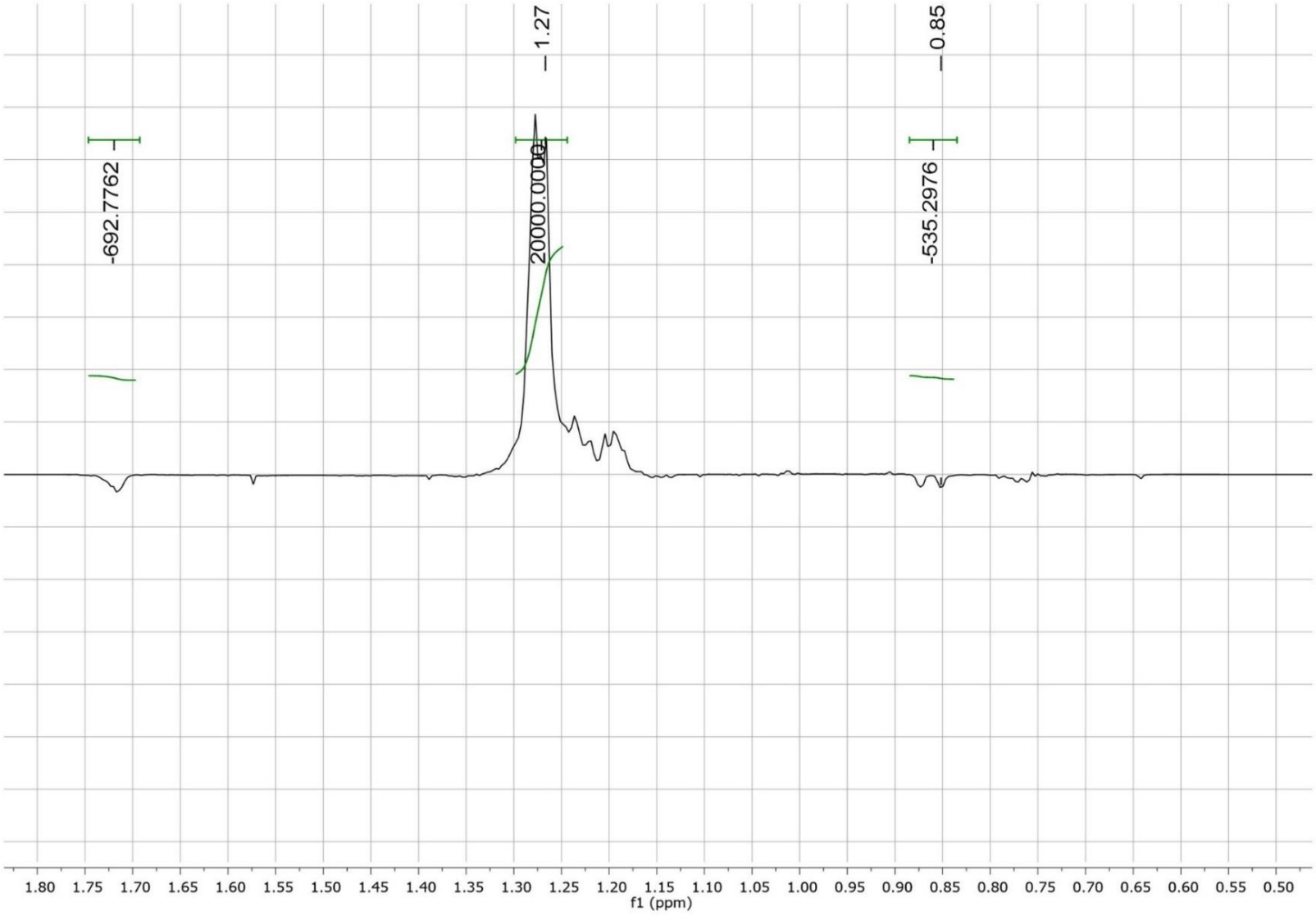


Figure S37. 1D ROESY slice extracted from 2D ROESY spectrum of peyssonnoside A (**1**) at 700 MHz in DMSO-d_6

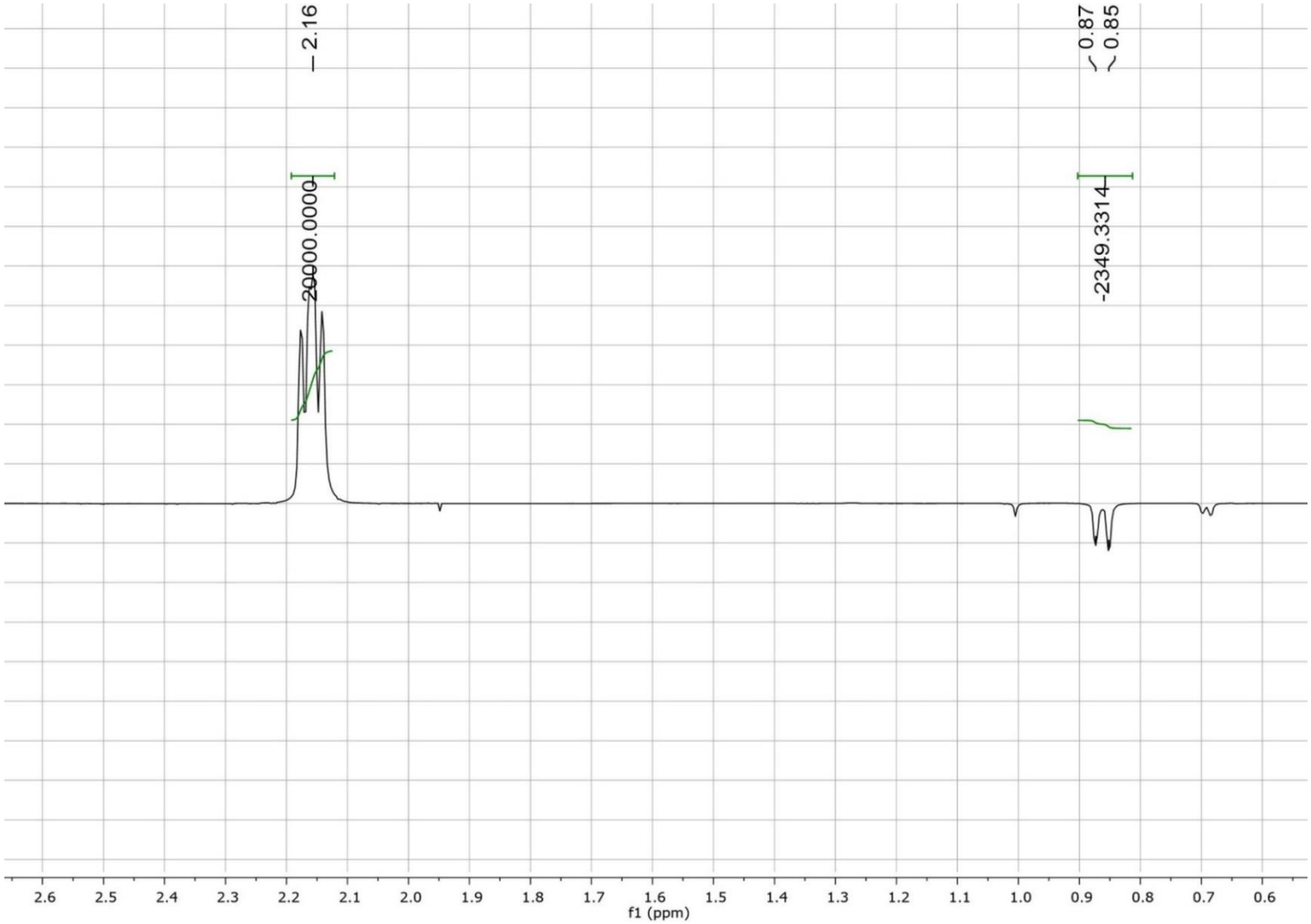
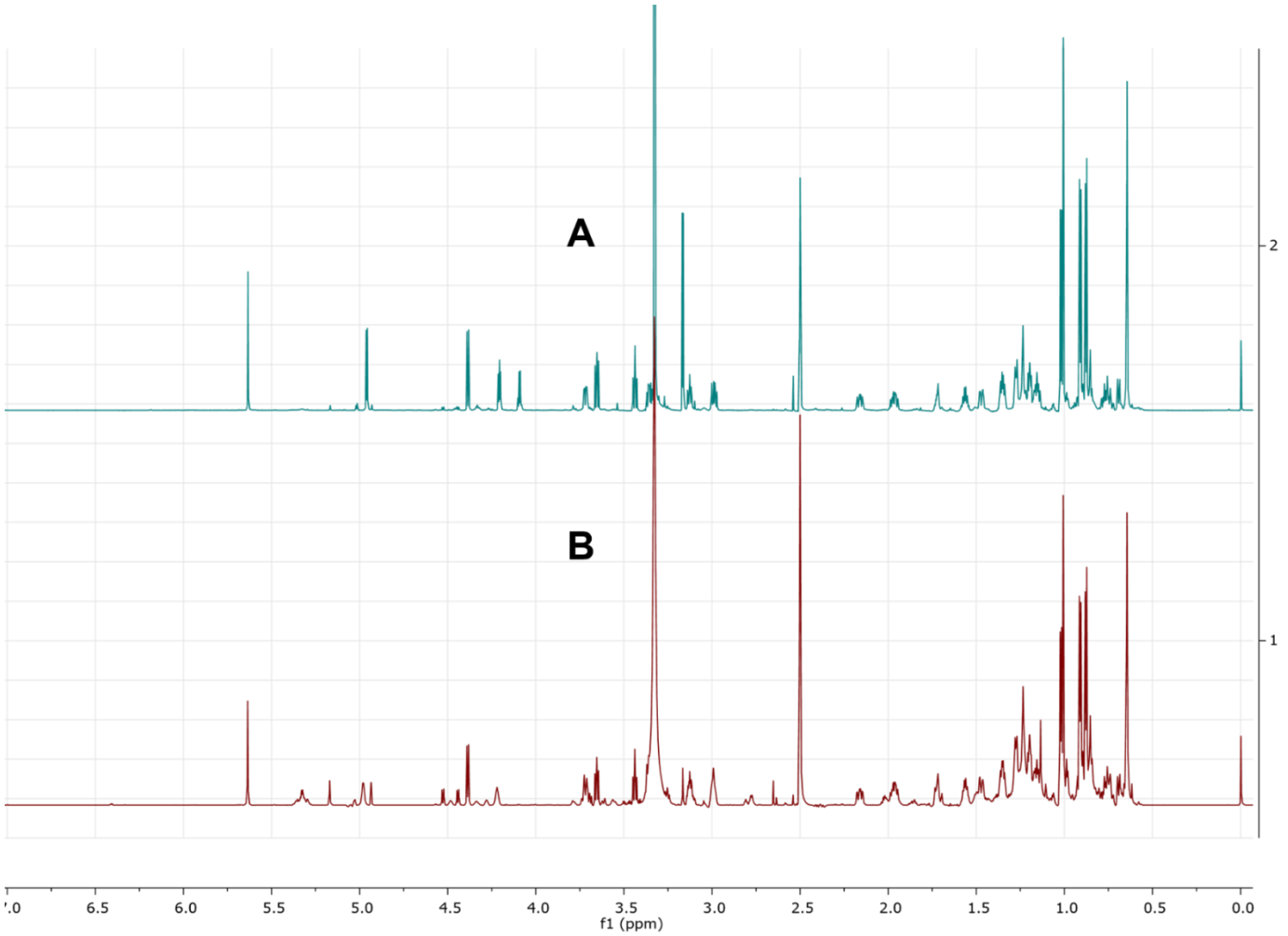


Figure S38. Comparison of ^{1}H NMR spectra of HP20SS fractions eluting with 80% aqueous methanol for **A** (collection G-1163) and **B** (collection G-1588) at 800 MHz in DMSO-d_6



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(1) Kimura, M. A simple method for estimating evolutionary rates of base substitutions through comparative studies of nucleotide sequences. *J. Mol. Evol.* **1980**, *16*, 111-120.
(2) Kumar, S.; Stecher, G.; Li, M.; Knyaz, C.; Tamura, K., MEGA X: Molecular Evolutionary Genetics Analysis across Computing Platforms. *Mol. Biol. Evol.* **2018**, *35*, 1547-1549.