Electronic Supplementary Material (ESI) for RSC Advances

Longeracemine, an Unprecedented C-7/C-9 Bonding Alkaloid from *Daphniphyllum longeracemosum*

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Figure S1: ^{1}H NMR (400 MHz) of **1** in CD3OD

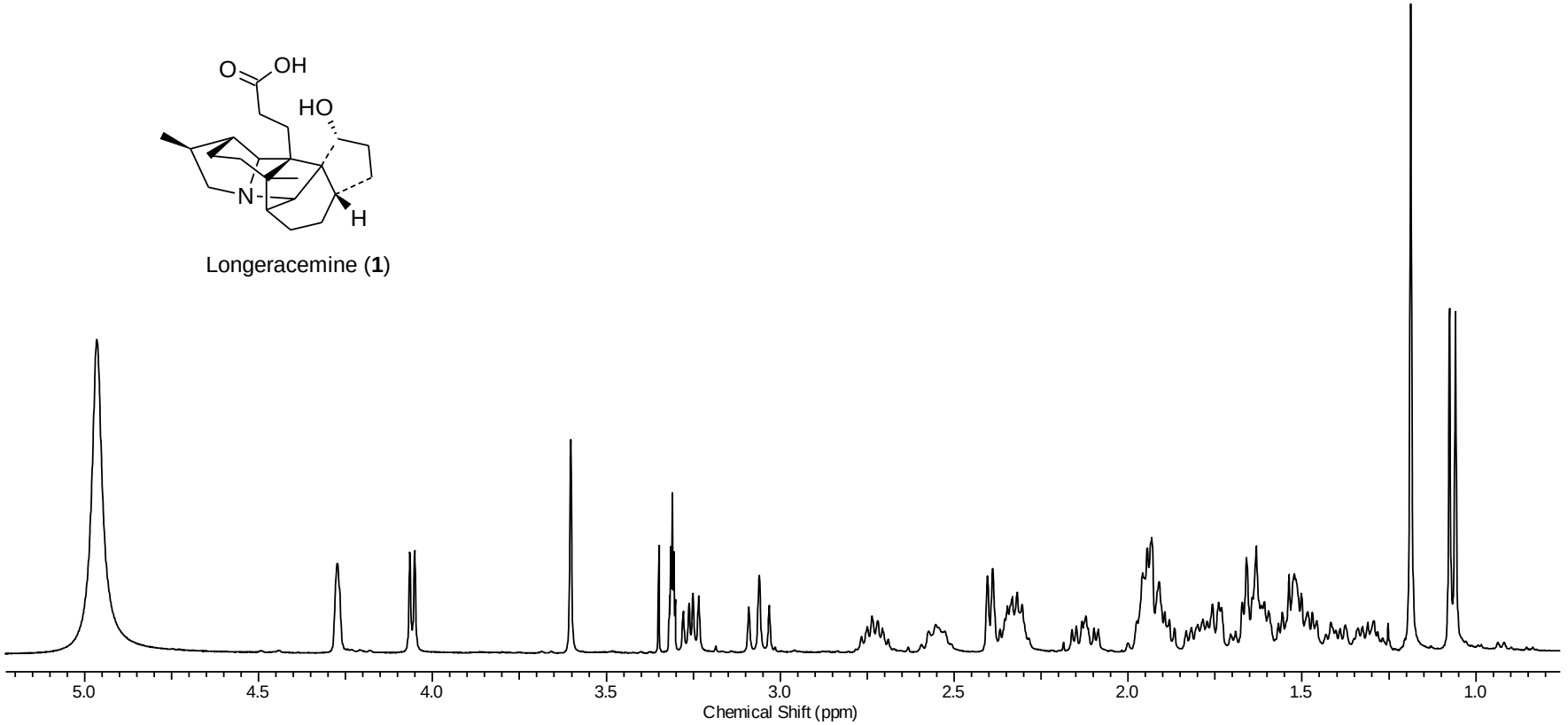


Figure S2: ^{13}C and DEPT NMR (100 MHz) of **1** in CD3OD

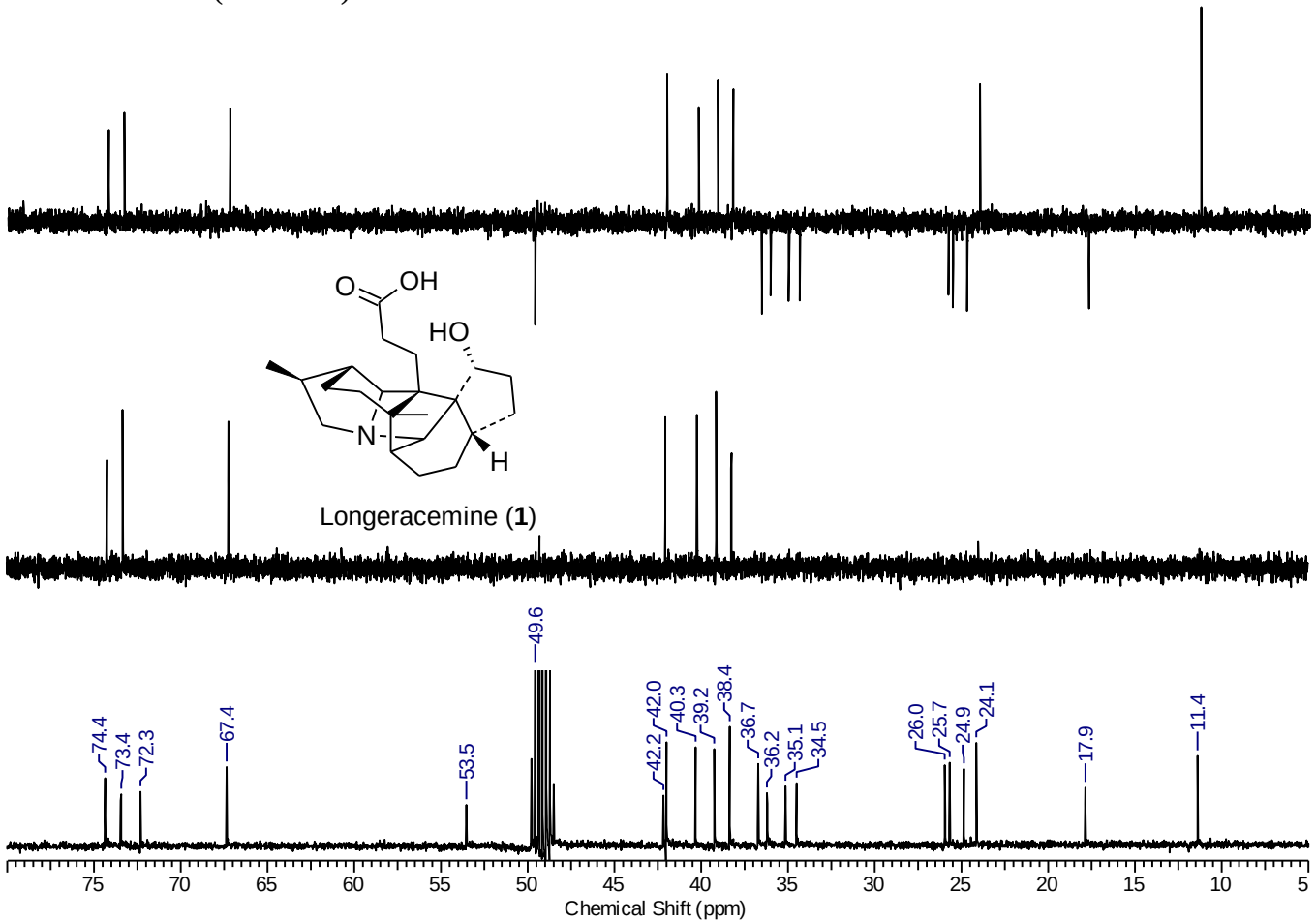


Figure S3: HSQC (500 MHz) of **1** in CD3OD

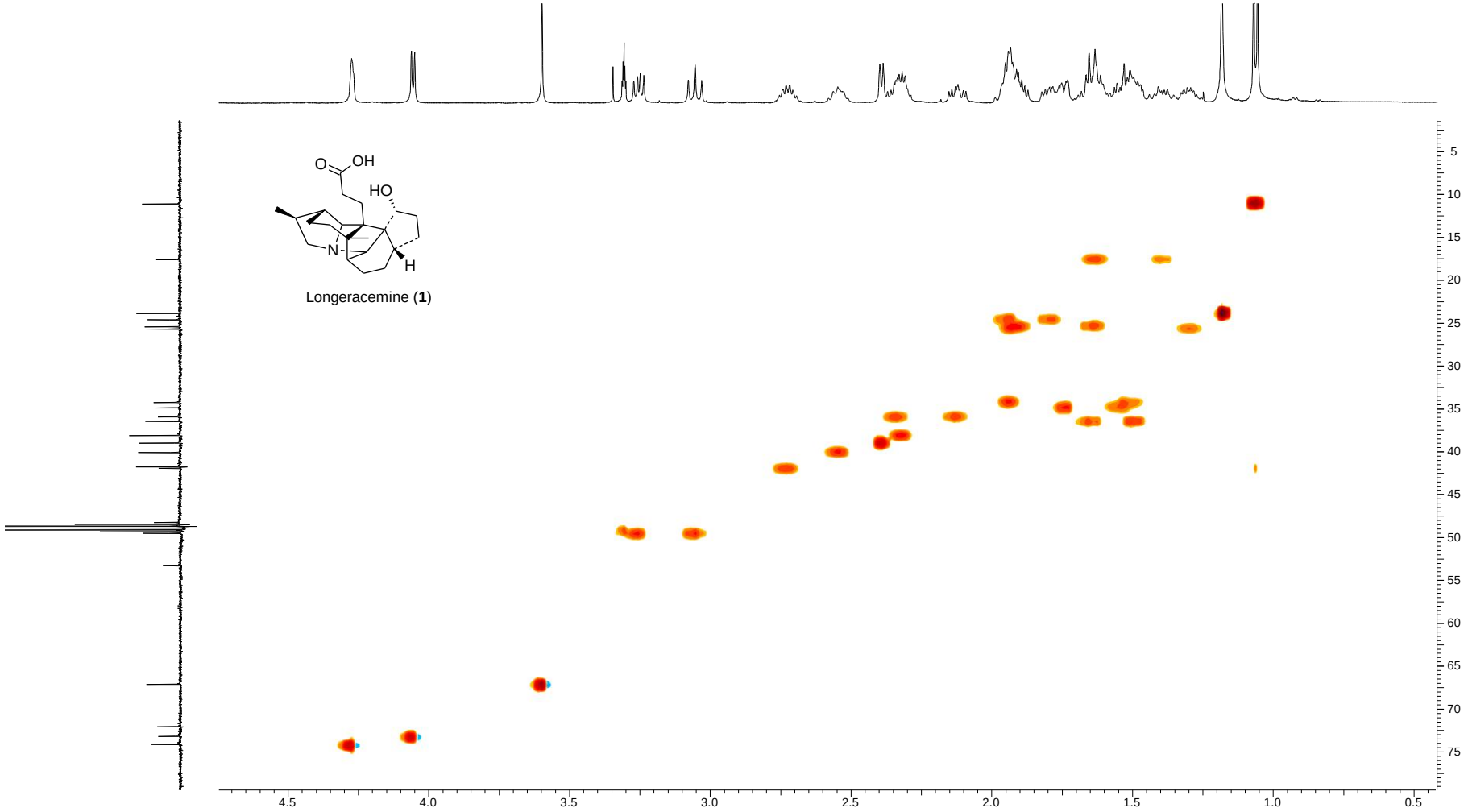


Figure S4: ^{1}H-^{1}H COSY (500 MHz) of **1** in CD3OD

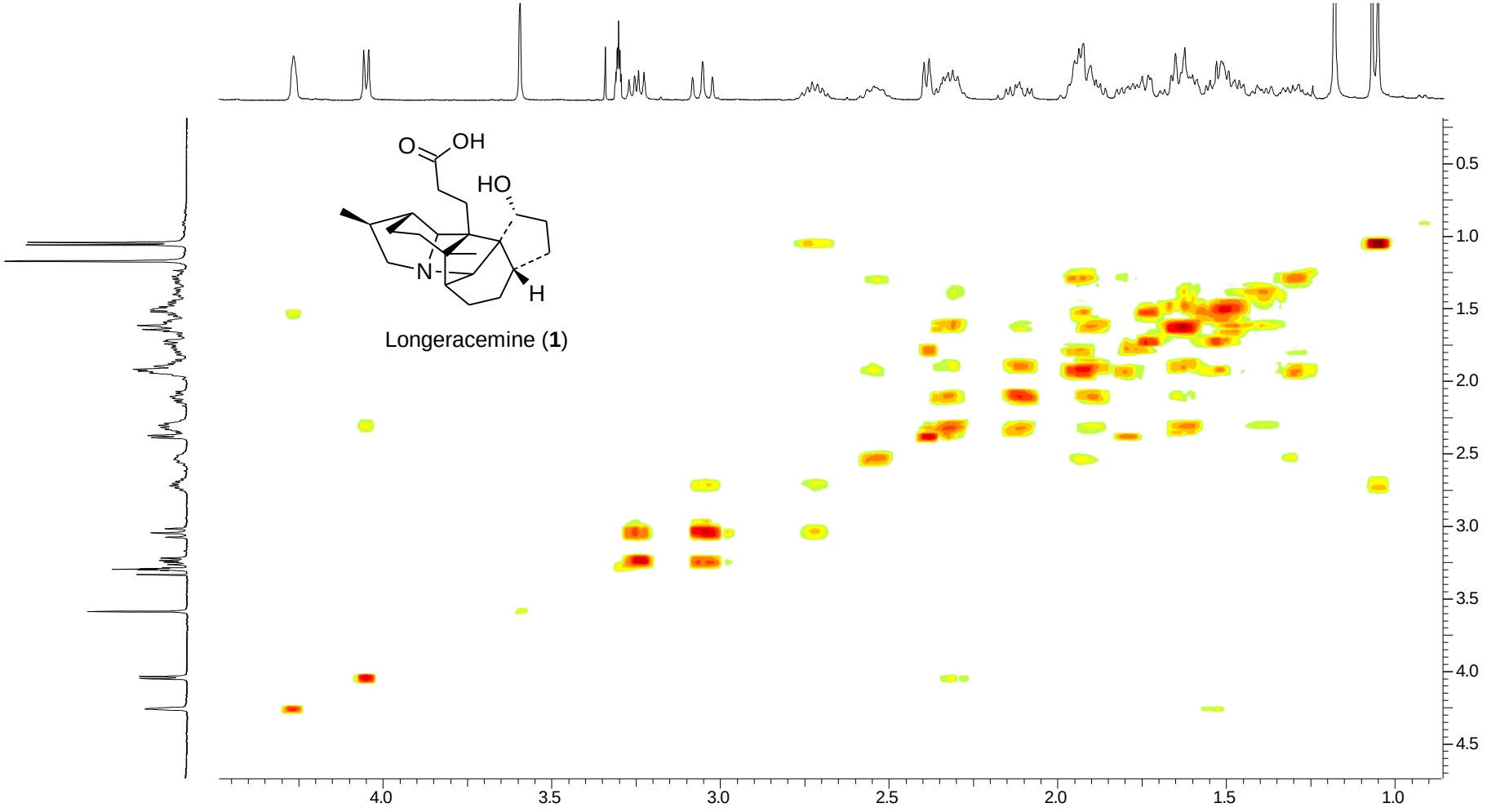


Figure S5: TOCSY (500 MHz) of **1** in CD3OD

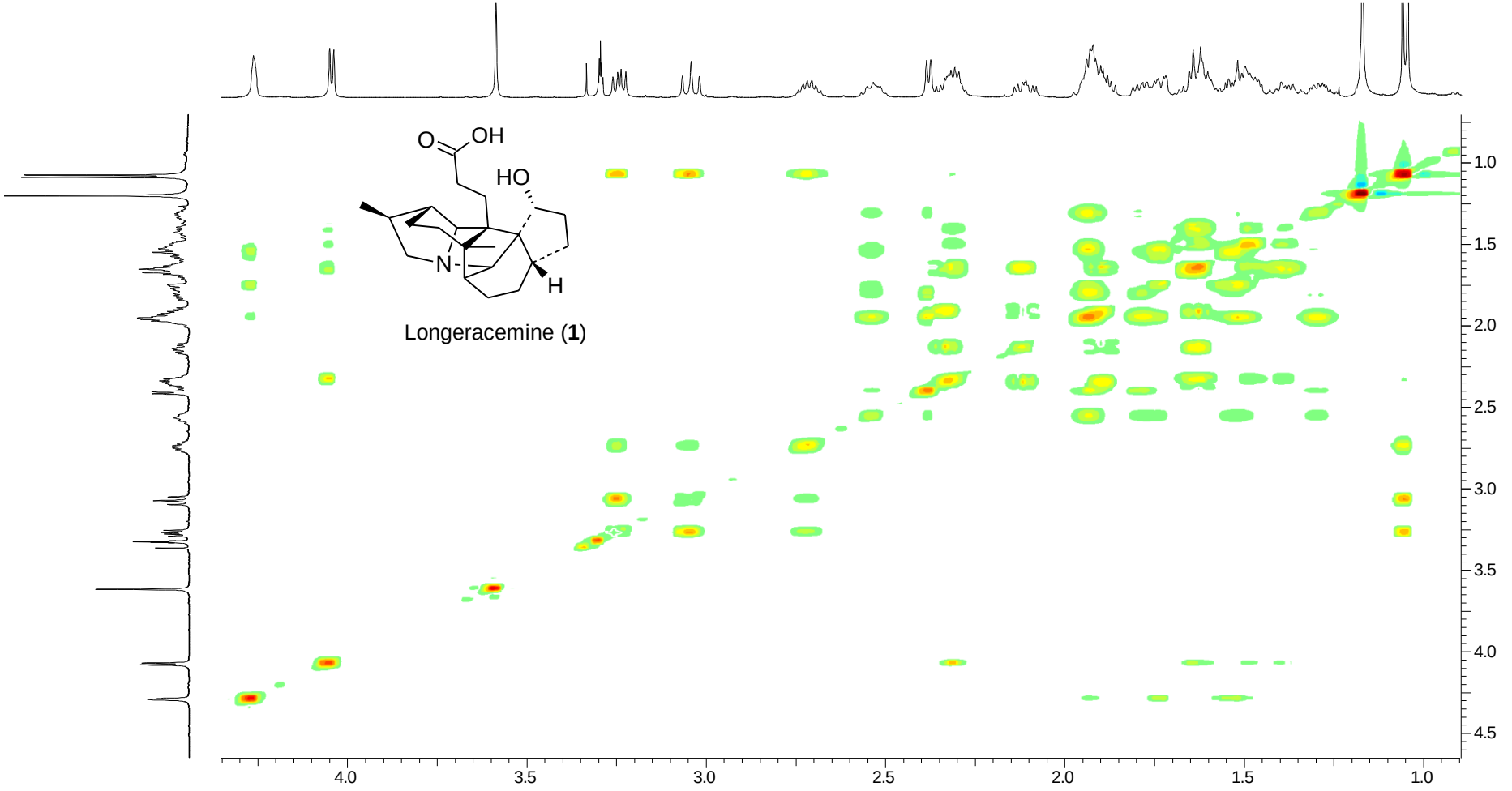


Figure S6: HMBC (500 MHz) of **1** in CD3OD

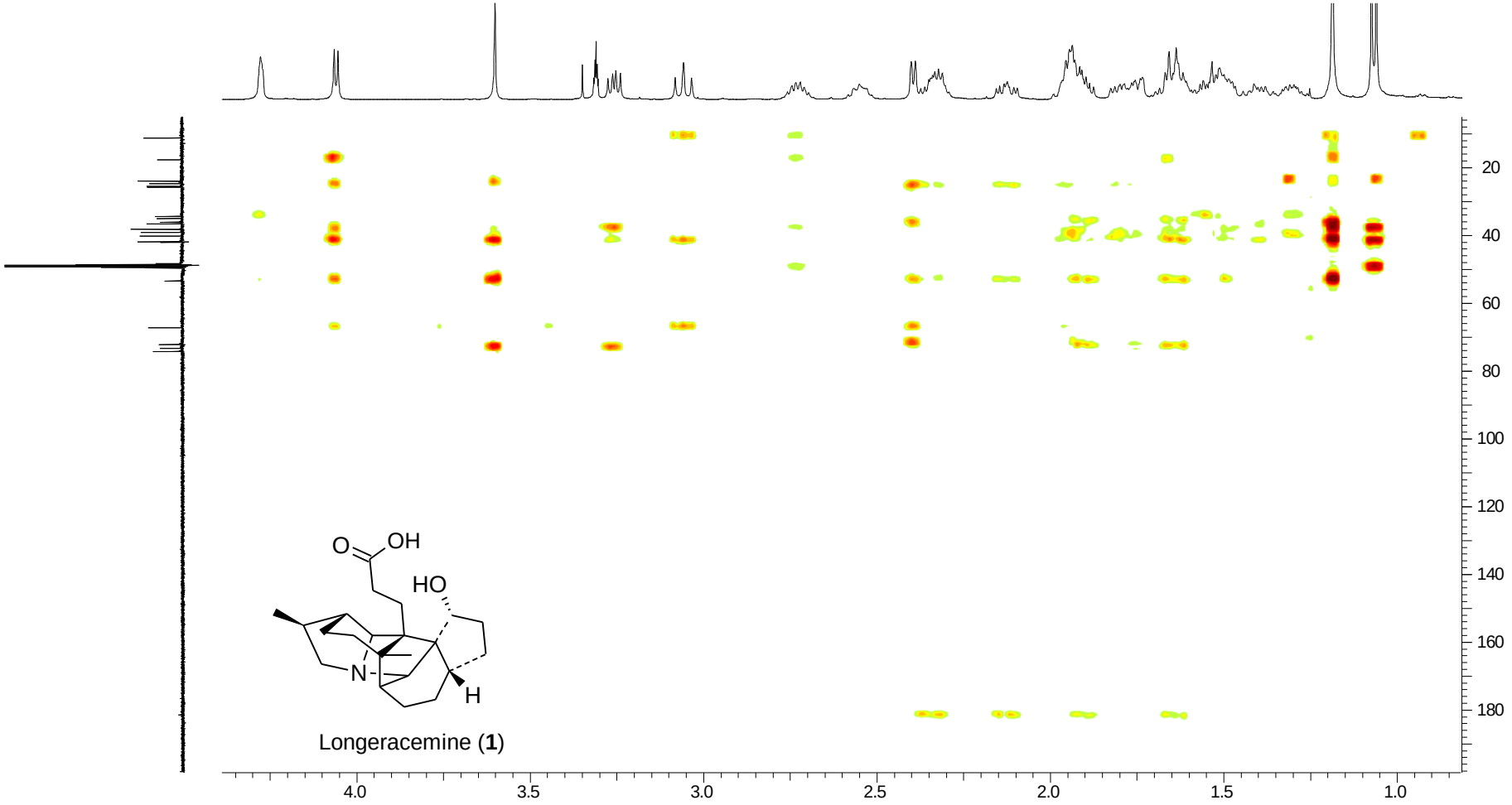


Figure S7: ROESY (500 MHz) of **1** in CD3OD

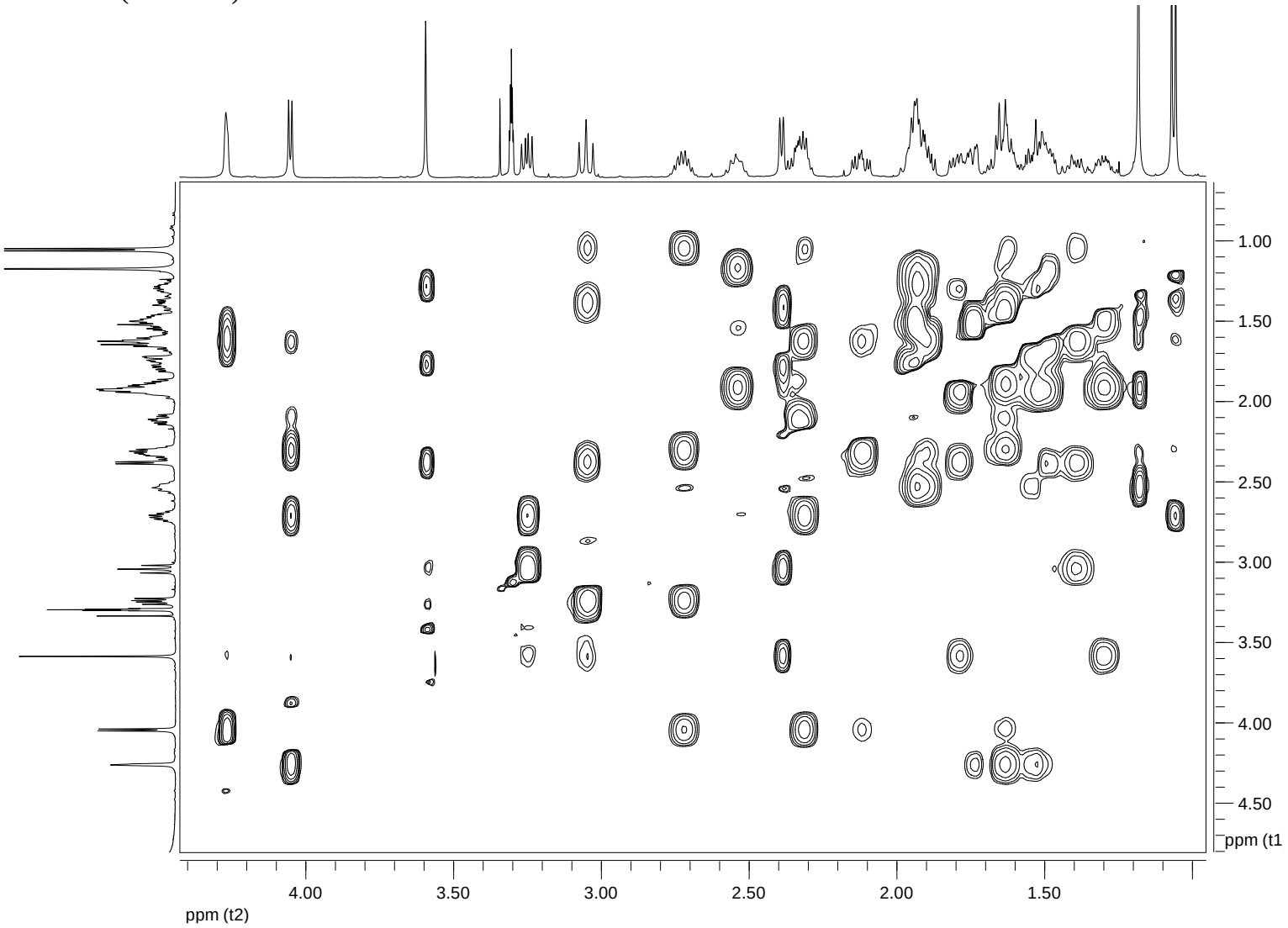


Figure S8: ESI$^+$ Mass Spectrometry of **1**

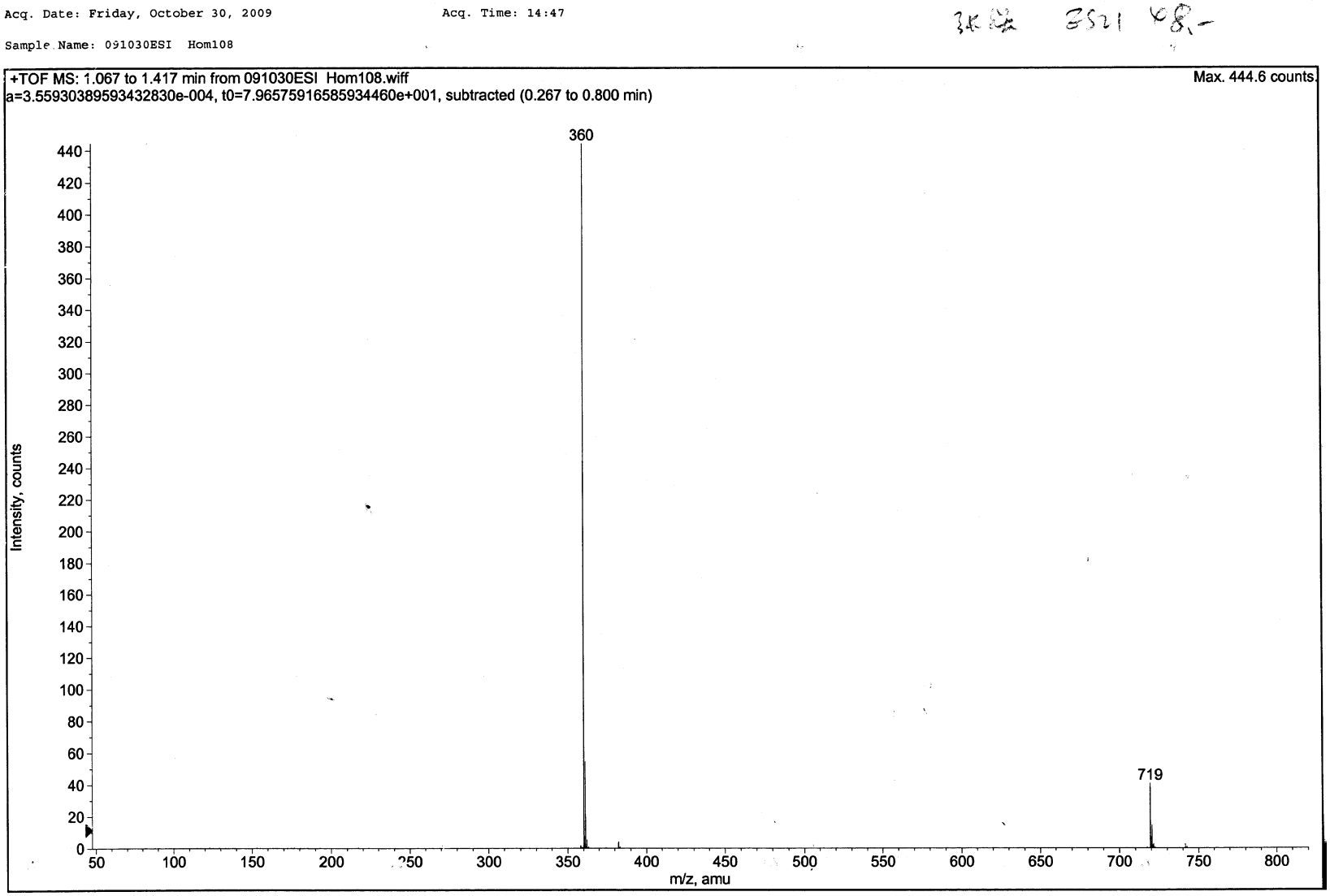
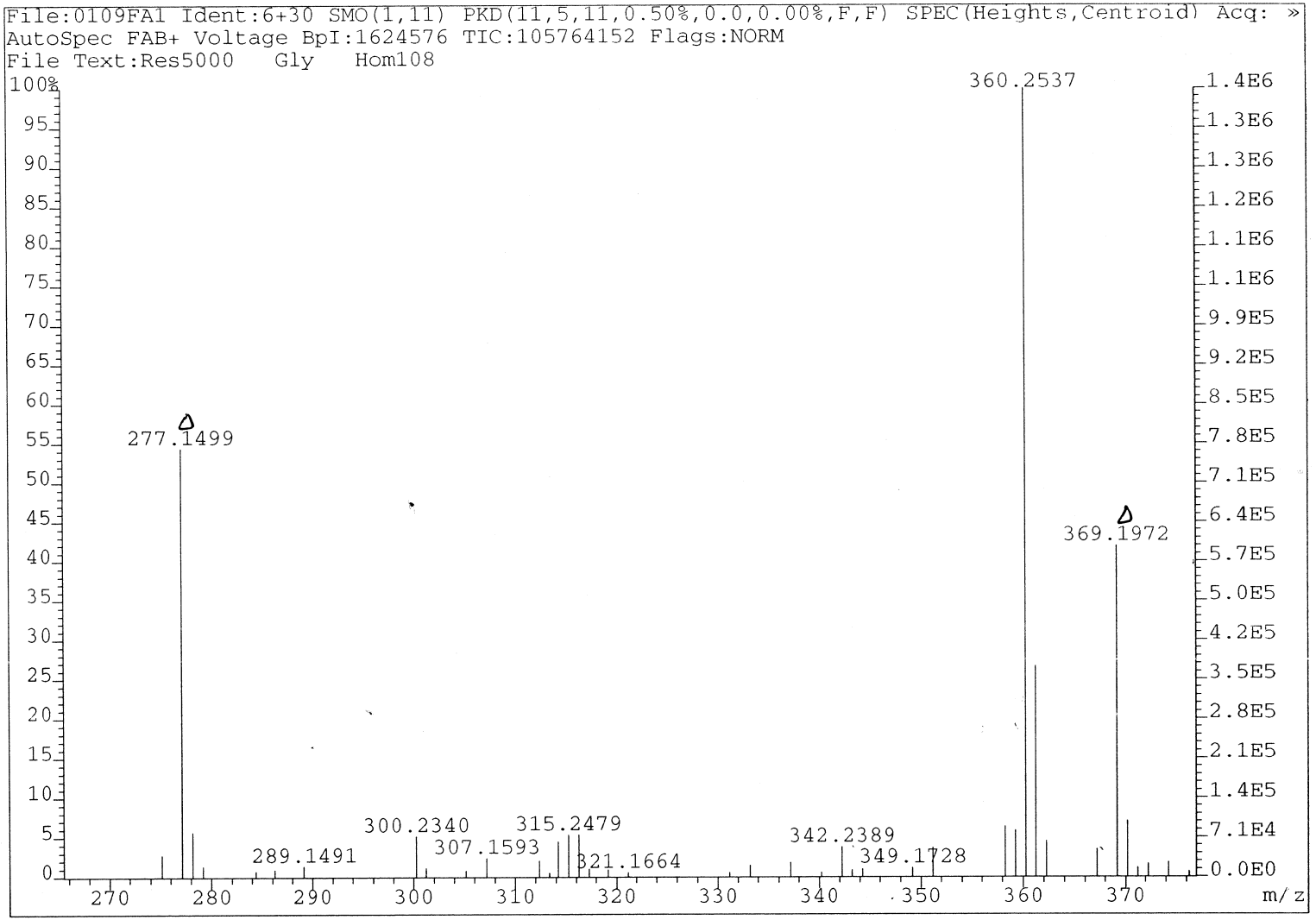


Figure S9: HRESI Mass Spectrometry of **1**



Coordinate **1a** (With 15-OH at *β*-Orientation)

Optimized at b3lyp/6-311+g(d,p) level
E= -1138.930371 a. u.
C,0,0.444007,-0.246031,1.539893
C,0,1.23495,1.131732,1.457457
C,0,0.60253,2.305758,2.236056
C,0,-0.563244,2.959819,1.455787
C,0,-1.299126,2.030819,0.45966
C,0,-0.3002,1.136391,-0.373448
C,0,-0.079501,-0.386426,0.052669
C,0,-0.638601,1.436167,-1.858546
C,0,-1.167536,-1.455198,-0.175089
C,0,-2.091358,2.86108,-0.584115
C,0,-1.201842,2.859571,-1.832174
C,0,1.171371,-0.710448,-0.842351
N,0,1.881052,0.588057,-0.950794
C,0,2.277561,-1.703411,-0.426985
C,0,2.577821,-1.686752,1.080861
C,0,1.339986,-1.451671,1.932409
C,0,3.327012,0.390186,-0.954764
C,0,3.470551,-1.123131,-1.237097
C,0,4.853532,-1.70691,-0.954832
C,0,1.182393,1.495312,-0.056034
C,0,-0.652411,-0.273502,2.630213
C,0,-2.628966,-1.097962,0.111674
C,0,-3.55855,-2.263873,-0.121138
O,0,-3.255024,-3.374939,-0.479863
O,0,-4.852695,-1.921471,0.130163
O,0,-1.641842,0.507677,-2.324165
H,0,-2.002929,1.40794,1.004801
H,0,2.263046,0.997783,1.803514
H,0,1.373371,3.063965,2.410633
H,0,0.278418,1.98044,3.22606
H,0,-1.292079,3.390798,2.14958
H,0,-0.167564,3.806443,0.884325
H,0,0.252759,1.343387,-2.480487
H,0,-0.90362,-2.342529,0.409709
H,0,-1.122376,-1.770616,-1.218216
H,0,-3.041343,2.372926,-0.815276
H,0,-2.321592,3.865927,-0.219866
H,0,-1.735848,3.110731,-2.753942
H,0,-0.378718,3.57529,-1.72981
H,0,0.800676,-1.016597,-1.830237
H,0,2.031429,-2.719601,-0.751679
H,0,3.048272,-2.63027,1.375016
H,0,3.313765,-0.910959,1.309362
H,0,1.644982,-1.326994,2.977878
H,0,0.713252,-2.351674,1.914056

H,0,3.810961,0.993579,-1.73183
H,0,3.803347,0.656998,0.001584
H,0,3.249369,-1.276919,-2.30061
H,0,5.61277,-1.215587,-1.571265
H,0,4.884347,-2.775532,-1.187711
H,0,5.148768,-1.583314,0.090273
H,0,1.470706,2.532125,-0.248926
H,0,-1.411292,0.500554,2.555333
H,0,-0.188349,-0.172612,3.615929
H,0,-1.158941,-1.241547,2.625505
H,0,-2.960868,-0.29097,-0.545057
H,0,-2.802983,-0.75997,1.135391
H,0,-5.389411,-2.709915,-0.039971
H,0,-1.795477,0.68106,-3.258218

Coordinate **1b** (With 15-OH at *α*-Orientation)

Optimized at b3lyp/6-311+g(d,p) level
E=-1138.933831 a.u.

C,0.3 14768,-0.374148,1.55334
C,1.111151,1.008242,1.578139
C,0.451351,2.1398 ,2.396874
C,-0.688942,2.831514,1.612782
C,-1.387263,1.937523,0.563279
C,-0.35023,1.126887,-0.309129
C,-0.145733,-0.415885,0.03993
C,-0.74796 9,1.486891,-1.788534
C,-1.237099,-1.435358,-0.337325
C,-2.232433,2.786 133,-0.424238
C,-1.38151,2.87704,-1.687366
C,1.14255,-0.705358,-0.8129 2
N,1.851706,0.607043,-0.83767
C,2.238079,-1.713255,-0.408831
C,2.4745 11,-1.784119,1.106979
C,1.195742,-1.604083,1.907989
C,3.303203,0.40476 4,-0.779652
C,3.460657,-1.089244,-1.138476
C,4.832233,-1.686343,-0.829896
C,1.112847,1.467505,0.089839
C,-0.814517,-0.471048,2.607905
C,-2.7 04438,-1.101026,-0.045575
C,-3.632014,-2.23821,-0.410921
O,-3.310325,- 3.357228,-0.723296
O,-4.933825,-1.856138,-0.330633
O,0.265881,1.451006 ,-2.776729
H,-2.057659,1.258063,1.079684
H,2.124408,0.851102,1.956114
H,1.215434,2.886153,2.637969

H,0.094205,1.760364,3.355792
H,-1.440479, 3.227779,2.303105
H,-0.281327,3.703156,1.089581
H,-1.533891,0.779525,- 2.096339
H,-1.002489,-2.394042,0.1354
H,-1.162561,-1.630737,-1.411355
H,-3.178389,2.280847,-0.646828
H,-2.490088,3.761459,-0.002788
H,-1.945 866,3.132821,-2.586804
H,-0.58245,3.618952,-1.580253
H,0.819903,-0.953 34,-1.831506
H,2.007626,-2.708851,-0.800855
H,2.936349,-2.741749,1.366 535
H,3.19469,-1.020515,1.413575
H,1.447234,-1.551093,2.973242
H,0.572 67,-2.500235,1.796697
H,3.818661,1.055192,-1.493582
H,3.719647,0.61732 9,0.214802
H,3.283977,-1.185038,-2.216763
H,5.614667,-1.164141,-1.3888 2
H,4.874079,-2.741213,-1.116557
H,5.083831,-1.617252,0.231513
H,1.412 781,2.510083,-0.035046
H,-1.57157,0.306409,2.569141
H,-0.376904,-0.437 516,3.61009
H,-1.318956,-1.437155,2.524473
H,-3.041132,-0.217483,-0.59 2816
H,-2.889477,-0.885078,1.009193
H,-5.472171,-2.629497,-0.557215
H, 1.099789,1.225949,-2.305568

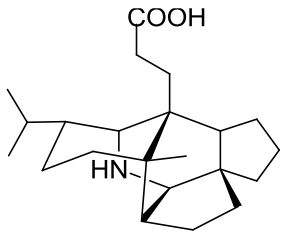
Coordinate Intermediate D

Optimized at B3LYP/6-31+G(d)
E=1062.559997 a. u.

C	0.31477	-0.37415	1.55334
C	1.11115	1.00824	1.57814
C	0.45135	2.1398	2.39687
C	-0.68894	2.83151	1.61278
C	-1.38726	1.93752	0.56328
C	-0.35023	1.12689	-0.30913
C	-0.14573	-0.41589	0.03993
C	-0.74797	1.48689	-1.78853
C	-1.2371	-1.43536	-0.33733
C	-2.23243	2.78613	-0.42424
C	-1.38151	2.87704	-1.68737
C	1.14255	-0.70536	-0.81292
N	1.85171	0.60704	-0.83767

C	2.23808	-1.71326	-0.40883
C	2.47451	-1.78412	1.10698
C	1.19574	-1.60408	1.90799
C	3.3032	0.40476	-0.77965
C	3.46066	-1.08924	-1.13848
C	4.83223	-1.68634	-0.8299
C	1.11285	1.46751	0.08984
C	-0.81452	-0.47105	2.60791
C	-2.70444	-1.10103	-0.04558
C	-3.63201	-2.23821	-0.41092
O	-3.31033	-3.35723	-0.7233
O	-4.93383	-1.85614	-0.33063
O	0.26588	1.45101	-2.77673
H	-2.05766	1.25806	1.07968
H	2.12441	0.8511	1.95611
H	1.21543	2.88615	2.63797
H	0.09421	1.76036	3.35579
H	-1.44048	3.22778	2.30311
H	-0.28133	3.70316	1.08958
H	-1.53389	0.77953	-2.09634
H	-1.00249	-2.39404	0.1354
H	-1.16256	-1.63074	-1.41136
H	-3.17839	2.28085	-0.64683
H	-2.49009	3.76146	-0.00279
H	-1.94587	3.13282	-2.5868
H	-0.58245	3.61895	-1.58025
H	0.8199	-0.95334	-1.83151
H	2.00763	-2.70885	-0.80086
H	2.93635	-2.74175	1.36654
H	3.19469	-1.02052	1.41358
H	1.44723	-1.55109	2.97324
H	0.57267	-2.50023	1.7967
H	3.81866	1.05519	-1.49358
H	3.71965	0.61733	0.2148
H	3.28398	-1.18504	-2.21676
H	5.61467	-1.16414	-1.38882
H	4.87408	-2.74121	-1.11656
H	5.08383	-1.61725	0.23151
H	1.41278	2.51008	-0.03505
H	-1.57157	0.30641	2.56914
H	-0.3769	-0.43752	3.61009
H	-1.31896	-1.43716	2.52447
H	-3.04113	-0.21748	-0.59282
H	-2.88948	-0.88508	1.00919
H	-5.47217	-2.6295	-0.55722
H	1.09979	1.22595	-2.30557

NMR and MS Data of homodaphniphyllate (**3**)



homodaphniphyllate (**3**)

^{1}H NMR ($CDCl_3$, 500MHz) δ (ppm) 0.89 (d, 6.4 Hz, 3 H), 0.99 (d, 6.4 Hz, 3 H), 1.23 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm) 62.9 (C-1), 38.0 (C-2), 19.1 (C-3), 25.4 (C-4), 37.0 (C-5), 40.9 (C-6), 46.7 (C-7), 47.8 (C-8), 51.2 (C-9), 77.3 (C-10), 26.7 (C-11), 22.4 (C-12), 28.4 (C-13), 30.9 (C-14), 32.5 (C-15), 25.9 (C-16), 36.5 (C-17), 30.6 (C-18), 21.5 (C-19), 21.0 (C-20), 25.6 (C-21), 174.1 (C-22); ESI MS *m/z* 346 $[M+H]^+$. These data were consistent to those reported (*Chem. & Biodiver.*, 2009, **6**, 105-110.).