Supporting Information for:

An Approach for Expanding Triterpenoid Complexity via Divergent Norrish-Yang Photocyclization

Vasily A. Ignatenko and Gregory P. Tochtrop*

Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, United States

*E-mail: tochtrop@case.edu

Table of Contents:

General experimental details

All reactions were run in an atmosphere of dry argon unless otherwise stated. THF was distilled from benzophenone ketyl solution with sodium prior to use. C_6D_6 was deoxygenated by purging with argon gas under stirring for 15 min. Quick syringe transfers were done with disposable syringes and needles.

Photochemical reactions were performed in a multilamp chamber photoreactor equipped with a cooling fan.

Column chromatography was performed with silica gel (particle size 32-63 μm). Analytical and semi-preparative HPLC separations were performed using acetonitrile and water (for HPLC, 99.9%). Analytical thin-layer chromatography (TLC) was carried out using glass-coated silica gel 0.25 mm plates with fluorescent indicator. All reactions that were monitored by TLC were visualized with a 254 nm UV-lamp or using phosphomolybdic acid (PMA) and 1,4-dinitrophenylhydrazine (DNP) stain solutions prepared by well-known protocols.

Chemical shifts of all ^{1}H and ^{13}C NMR spectra reported in δ units, part per million (ppm) with reference to the residual solvent peak ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.16 ppm, center of triplet, for ^{13}C NMR). DEPT, COSY, NOESY, HMQC, HMBC spectra were recorded using standard 2-D NMR pulse sequences.

For the HRMS measurements, Linear ion Trap Quadrupole (LTQ) mass spectrometer was used with Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass analyzer (100 000 resolving power at m/z 400).

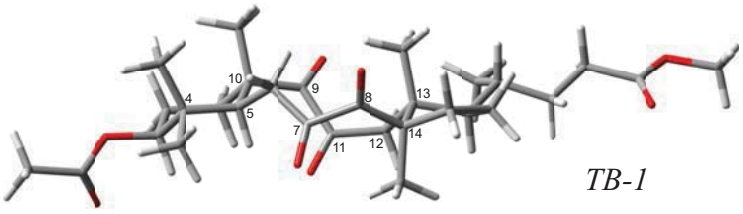
Complete reference 59

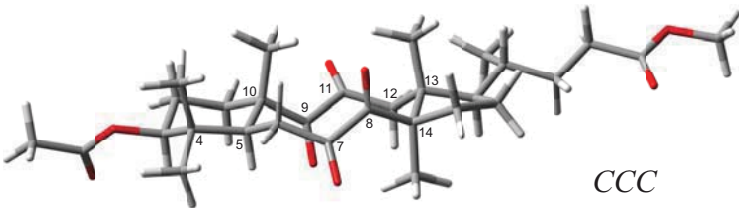
Reference 59. Gaussian 09, Revision A.02,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,
K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand,
K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,
V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

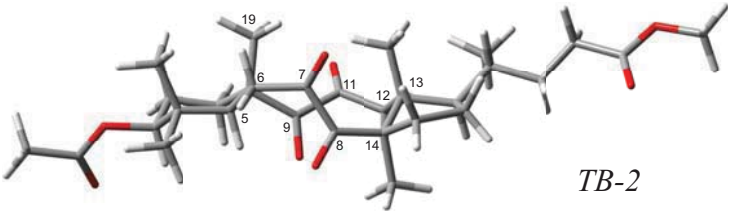
Conformational analyses of tetraketone **1** and triketone **5** were reported in the Supporting Information for reference 18

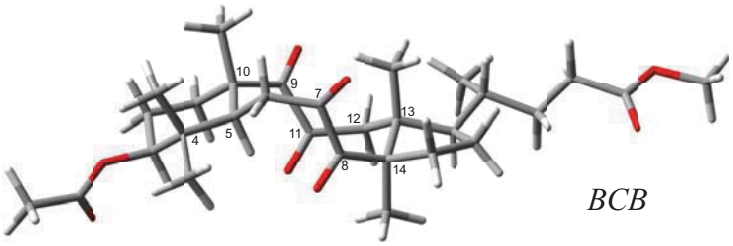
Figure S1. Conformational analysis of tetraketone **14**.

CCC = 'chair-chair-chair'
BCB = 'boat (with bow at C-5 and stern between C-8 and C-11)-chair- boat (with bow between C-7 and C-9 and stern at C-13)'
TB = 'twist-boat'







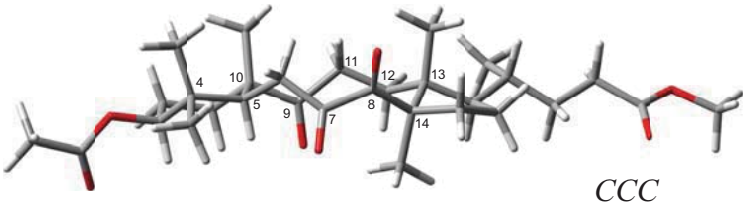


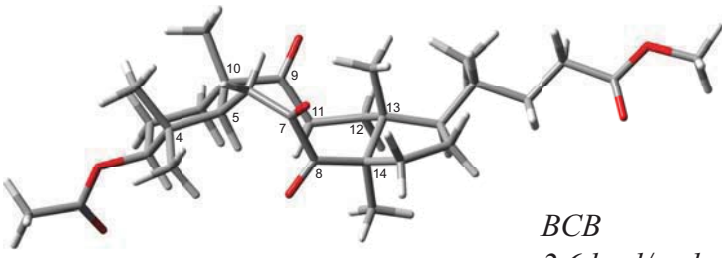
Lowest energy conformations and electronic energies were determined using Gaussian (R) 09 software package using B3LYP/6-311G(d,p) level of theory

Conformer TB-1: E_{tot} = -1771.94425083 A.U.
Conformer CCC: E_{tot} = -1771.94356416 A.U.
Conformer BCB: E_{tot} = -1771.93998494 A.U.
Conformer TB-2: E_{tot} = -1771.93504760 A.U.

Figure S2. Conformational analysis of triketone **17**.

CCC = 'chair-chair-chair'
BCB = 'boat (with bow at C-5 and stern between C-8 and C-11)-chair- boat (with bow between C-7 and C-9 and stern at C-13)'





Lowest energy conformations and electronic energies were determined using Gaussian (R) 09 software package using B3LYP/6-311G(d,p) level of theory

Conformer CCC: E_{tot} = -1697.91972184 A.U.
Conformer BCB: E_{tot} = -1697.9156057 A.U.

FigureS3. ^{13}C VT NMR of tetraketone **14**.

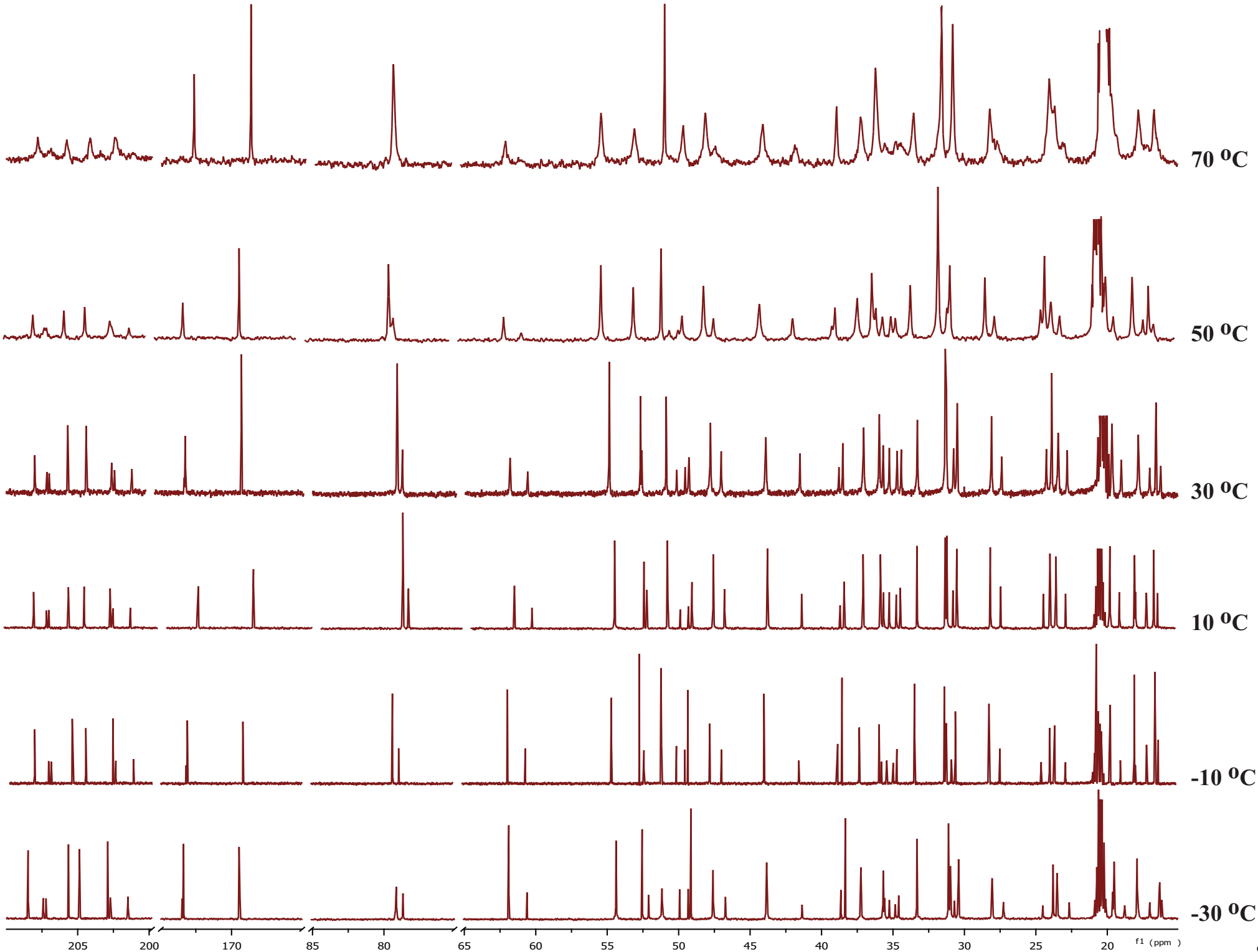


Table S1. Atomic coordinates for the optimized geometry of tetraketone **1**.

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.061069	0.422968	-0.249239
2	6	0	-1.007891	-0.418035	0.669170
3	6	0	1.622114	1.064495	2.182556
4	6	0	2.746460	0.664214	1.202261
5	6	0	2.305045	-0.586593	0.347810
6	6	0	1.231151	-0.229517	-0.710062
7	1	0	1.853483	-1.284937	1.052335
8	1	0	1.628036	0.433126	-1.477736
9	1	0	0.915997	-1.156251	-1.195367
10	6	0	0.895909	-0.008781	3.071728
11	6	0	-2.009079	0.195420	1.677846
12	6	0	-0.411002	0.396199	3.723924
13	1	0	-0.516210	1.477879	3.682617
14	1	0	-0.292149	0.105485	4.768910
15	6	0	3.466108	-1.430820	-0.322625
16	6	0	3.084122	1.911825	0.362462
17	1	0	3.935257	1.731661	-0.291691
18	1	0	2.242578	2.234570	-0.251886
19	1	0	3.332670	2.743080	1.022594
20	6	0	3.961556	0.316517	2.124459
21	1	0	4.320761	1.242003	2.583336
22	1	0	3.635194	-0.340495	2.931609
23	6	0	5.094935	-0.381516	1.373701
24	1	0	5.886054	-0.638419	2.081768
25	1	0	5.536903	0.263395	0.609779
26	6	0	4.561912	-1.661465	0.746545
27	1	0	4.159626	-2.294913	1.541358
28	6	0	2.903268	-2.818181	-0.709353
29	1	0	2.175883	-2.754760	-1.521126
30	1	0	3.713680	-3.463628	-1.052742
31	1	0	2.417846	-3.302614	0.142433
32	6	0	4.070274	-0.796353	-1.593652
33	1	0	4.517358	0.181983	-1.419535
34	1	0	4.852071	-1.447771	-1.985910
35	1	0	3.316206	-0.682170	-2.374453
36	8	0	5.648288	-2.396813	0.115906
37	6	0	6.394197	-3.207404	0.904361
38	8	0	6.218533	-3.345622	2.088022
39	6	0	7.456514	-3.907706	0.092728
40	1	0	8.105334	-4.472720	0.758582
41	1	0	6.985995	-4.585082	-0.624232
42	1	0	8.038243	-3.180258	-0.476601
43	6	0	-1.707850	-0.307454	3.174367
44	6	0	-1.505322	-1.830993	3.258166
45	1	0	-2.418644	-2.380499	3.040163
46	1	0	-0.744463	-2.192780	2.572657
47	1	0	-1.165667	-2.096053	4.256573
48	6	0	-2.893551	0.181435	4.126357
49	1	0	-2.741898	1.262615	4.178949
50	6	0	-3.392516	-0.367459	1.247270
51	1	0	-3.563305	-0.115536	0.195264
52	1	0	-3.371175	-1.456369	1.300408
53	6	0	-4.518980	0.215449	2.088485
54	6	0	-4.375990	0.009145	3.616117
55	6	0	-2.786571	-0.265035	5.625945
56	1	0	-3.167783	0.574378	6.213400
57	1	0	-1.745308	-0.371729	5.931351
58	6	0	-4.944344	-1.382291	3.990712
59	6	0	-5.247786	1.104061	4.279127
60	1	0	-6.290356	0.999933	3.961379
61	1	0	-5.233361	1.071841	5.369017
62	1	0	-4.908694	2.098799	3.976205
63	1	0	-4.399409	-2.170630	3.466740
64	1	0	-5.977457	-1.436486	3.628604
65	6	0	-4.938637	-1.663786	5.493179
66	6	0	-3.553255	-1.522530	6.151689
67	1	0	-5.336729	-2.661086	5.687257
68	1	0	-5.616934	-0.964050	5.990139
69	6	0	-3.733737	-1.354062	7.683752
70	1	0	-4.258719	-2.213591	8.111414
71	1	0	-2.766654	-1.263890	8.180513
72	1	0	-4.325727	-0.459507	7.892868
73	6	0	-2.677485	-2.778817	6.027510
74	8	0	-1.565732	-2.863238	6.493591
75	8	0	-3.281816	-3.808319	5.402333
76	6	0	-2.513103	-5.024245	5.314064
77	1	0	-2.238808	-5.374242	6.309735
78	1	0	-3.162271	-5.741528	4.816970
79	1	0	-1.606036	-4.857881	4.731851
80	6	0	-2.028313	1.740048	1.586991
81	1	0	-2.638211	2.174557	2.377203
82	1	0	-1.038502	2.183117	1.663003
83	1	0	-2.445270	2.056729	0.631650
84	1	0	-4.601990	1.283919	1.872385
85	1	0	-5.471246	-0.222515	1.769044
86	8	0	1.329224	2.221355	2.390480
87	8	0	-1.007675	-1.602220	0.401583
88	8	0	-0.468812	1.448304	-0.745648
89	8	0	1.432467	-1.072569	3.293382

Table S2. Atomic coordinates for the optimized geometry of triketone **5**.

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.120732	0.511694	-0.323127
2	6	0	-0.918633	-0.374160	0.677983
3	6	0	1.547280	1.146165	2.136999
4	6	0	2.774526	0.677918	1.302944
5	6	0	2.278051	-0.457151	0.320659
6	6	0	1.276458	0.060500	-0.734073
7	1	0	1.740256	-1.177142	0.943181
8	1	0	1.685578	0.884300	-1.317911
9	1	0	1.073554	-0.749554	-1.440718
10	6	0	0.966116	0.217447	3.204447
11	1	0	1.666854	0.311762	4.043862
12	1	0	1.049328	-0.826557	2.901264
13	6	0	-1.980378	0.176210	1.652087
14	6	0	-0.443644	0.571635	3.722236
15	1	0	-0.600692	1.641114	3.575761
16	1	0	-0.419117	0.417615	4.800453
17	6	0	3.406112	-1.333229	-0.367505
18	6	0	3.344226	1.924893	0.599561
19	1	0	4.254717	1.701689	0.046950
20	1	0	2.626396	2.376005	-0.083582
21	1	0	3.583126	2.685885	1.345398
22	6	0	3.837770	0.097029	2.273300
23	1	0	4.230885	0.905480	2.897794
24	1	0	3.375824	-0.624949	2.951995
25	6	0	4.980233	-0.616374	1.549383
26	1	0	5.679533	-1.021459	2.284489
27	1	0	5.543228	0.066602	0.908160
28	6	0	4.410287	-1.764961	0.729734
29	1	0	3.912407	-2.460850	1.411012
30	6	0	2.762099	-2.625815	-0.923084
31	1	0	2.134893	-2.432593	-1.795150
32	1	0	3.544453	-3.318423	-1.239055
33	1	0	2.144777	-3.123488	-0.170324
34	6	0	4.132094	-0.631465	-1.534440
35	1	0	4.706590	0.240185	-1.224595
36	1	0	4.826375	-1.330349	-2.002597
37	1	0	3.423192	-0.307848	-2.298794
38	8	0	5.491022	-2.496975	0.087312
39	6	0	6.113658	-3.454699	0.815435
40	8	0	5.822349	-3.734756	1.950686
41	6	0	7.207105	-4.109814	0.008326
42	1	0	7.724740	-4.839723	0.626949
43	1	0	6.778826	-4.602644	-0.867633
44	1	0	7.909406	-3.355147	-0.351745
45	6	0	-1.666911	-0.234960	3.174551
46	6	0	-1.363250	-1.738807	3.330952
47	1	0	-2.241300	-2.362579	3.174167
48	1	0	-0.611960	-2.093458	2.630197
49	1	0	-0.985806	-1.928467	4.334580
50	6	0	-2.914766	0.190066	4.078123
51	1	0	-2.844917	1.281234	4.095883
52	6	0	-3.300787	-0.523193	1.217516
53	1	0	-3.465203	-0.336643	0.150948
54	1	0	-3.191461	-1.603226	1.326076
55	6	0	-4.491244	0.006391	2.004598
56	6	0	-4.369754	-0.112683	3.543826
57	6	0	-2.814844	-0.192403	5.598995
58	1	0	-3.268714	0.638435	6.145872
59	1	0	-1.777067	-0.214020	5.930635
60	6	0	-4.849748	-1.521761	3.971308
61	6	0	-5.333710	0.946262	4.133406
62	1	0	-6.359952	0.747382	3.807048
63	1	0	-5.335756	0.973263	5.223806
64	1	0	-5.063792	1.946113	3.782022
65	1	0	-4.241816	-2.293487	3.493442
66	1	0	-5.867993	-1.663007	3.590886
67	6	0	-4.860825	-1.737638	5.484082
68	6	0	-3.501339	-1.480588	6.159044
69	1	0	-5.202382	-2.748017	5.715497
70	1	0	-5.590237	-1.058897	5.935959
71	6	0	-3.720226	-1.272041	7.681391
72	1	0	-4.189532	-2.151469	8.132890
73	1	0	-2.771451	-1.092651	8.189474
74	1	0	-4.378615	-0.415882	7.847570
75	6	0	-2.540501	-2.676954	6.095430
76	8	0	-1.424620	-2.663119	6.560741
77	8	0	-3.073892	-3.777361	5.528783
78	6	0	-2.229165	-4.944106	5.508993
79	1	0	-1.915821	-5.205185	6.520285
80	1	0	-2.837162	-5.735021	5.075624
81	1	0	-1.344591	-4.761717	4.897336
82	6	0	-2.133536	1.708207	1.495061
83	1	0	-2.780142	2.119465	2.267975
84	1	0	-1.181308	2.229805	1.554103
85	1	0	-2.574397	1.947095	0.527828
86	1	0	-4.651585	1.053011	1.733208
87	1	0	-5.398270	-0.520930	1.687726
88	8	0	1.089459	2.258260	1.978321
89	8	0	-0.755017	-1.564557	0.487807
90	8	0	-0.703686	1.366091	-0.948899

Table S3. Atomic coordinates for the optimized geometry of conformer TB-1 of tetraketone **14**.

Z-Matrix orientation:

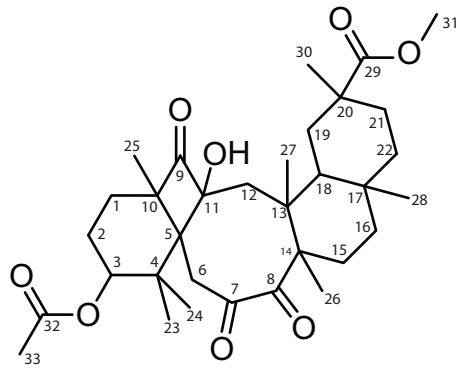
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.812566	-0.722522	-0.423906
2	6	0	-0.717347	-0.536445	-0.368889
3	6	0	1.420077	0.360409	2.872863
4	6	0	2.708069	0.865851	2.174261
5	6	0	2.882323	0.222028	0.754300
6	6	0	1.659558	0.516839	-0.156596
7	1	0	2.882618	-0.854682	0.927684
8	6	0	0.871881	-1.082772	2.663589
9	6	0	-1.630285	-1.406945	0.506954
10	6	0	-1.729997	-0.830359	2.004827
11	6	0	-0.596650	-1.341128	2.950977
12	1	0	-0.769497	-0.903122	3.933730
13	1	0	-0.676350	-2.423334	3.052734
14	6	0	4.271697	0.468720	0.057953
15	6	0	2.644065	2.407721	2.192602
16	1	0	3.622222	2.851431	2.028516
17	1	0	1.969701	2.802652	1.429362
18	1	0	2.277369	2.744227	3.161756
19	6	0	3.880315	0.377250	3.081501
20	1	0	3.809162	0.869283	4.055511
21	1	0	3.776180	-0.697710	3.252714
22	6	0	5.249431	0.650493	2.450098
23	1	0	6.027785	0.225320	3.087941
24	1	0	5.447011	1.723230	2.376536
25	6	0	5.351631	0.008074	1.069699
26	1	0	5.282333	-1.076747	1.186239
27	6	0	4.365695	-0.456234	-1.176846
28	1	0	3.687941	-0.139775	-1.973200
29	1	0	5.379128	-0.427111	-1.581693
30	1	0	4.115028	-1.489232	-0.926928
31	6	0	4.521873	1.914017	-0.419480
32	1	0	4.704179	2.615486	0.392639
33	1	0	5.398305	1.937848	-1.068754
34	1	0	3.673314	2.289550	-0.997492
35	8	0	6.654599	0.299831	0.492510
36	6	0	7.687894	-0.501895	0.845024
37	8	0	7.594065	-1.423679	1.615065
38	6	0	8.952049	-0.082413	0.136008
39	1	0	9.787631	-0.670859	0.508876
40	1	0	8.840589	-0.241774	-0.939366
41	1	0	9.137549	0.981980	0.292060
42	6	0	-1.186539	-2.886951	0.471391
43	1	0	-1.892073	-3.501781	1.035343
44	1	0	-1.186466	-3.248515	-0.558701
45	1	0	-0.188297	-3.052660	0.871771
46	6	0	-1.818926	0.708666	1.983948
47	1	0	-2.673038	1.045155	1.393548
48	1	0	-1.922979	1.110239	2.991114
49	1	0	-0.934194	1.177082	1.552177
50	6	0	-3.083738	-1.288302	-0.001589
51	6	0	-3.103691	-1.447058	2.492004
52	6	0	-3.994026	-1.514792	1.218325
53	1	0	-3.242617	-0.300297	-0.431466
54	1	0	-3.266884	-2.008569	-0.802113
55	1	0	-4.774501	-0.750169	1.254159
56	1	0	-4.508762	-2.475371	1.160386
57	1	0	-2.883223	-2.473258	2.808360
58	6	0	-3.861074	-0.779571	3.678169
59	1	0	-4.176744	0.218744	3.346734
60	6	0	-3.047343	-0.613196	4.973041
61	1	0	-2.641808	-1.572290	5.311669
62	1	0	-2.219437	0.088615	4.868862
63	1	0	-3.677495	-0.225654	5.776624
64	6	0	-5.144205	-1.593726	3.971002
65	1	0	-5.675886	-1.816660	3.046404
66	1	0	-4.861979	-2.564708	4.396416
67	6	0	-6.137129	-0.901713	4.909430
68	1	0	-5.768260	-0.807468	5.932480
69	1	0	-6.337074	0.121966	4.567044
70	6	0	-7.476489	-1.609271	4.962546
71	8	0	-7.882588	-2.416316	4.163989
72	8	0	-8.191924	-1.199705	6.032580
73	6	0	-9.506253	-1.772343	6.162051
74	1	0	-9.442986	-2.857403	6.256418
75	1	0	-9.927421	-1.333012	7.063514
76	1	0	-10.118658	-1.527089	5.292884
77	8	0	0.852516	1.012671	3.722467
78	8	0	-1.130768	0.336433	-1.104365
79	1	0	1.971290	0.871047	-1.143456
80	1	0	1.029579	1.313060	0.242497
81	8	0	1.279422	-1.775857	-0.790212
82	8	0	1.655926	-1.985821	2.464329

Table S4. Atomic coordinates for the optimized geometry of conformer CCC of triketone **17**.

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.866529	-0.524835	-0.269061
2	6	0	-0.599834	-0.142602	0.048354
3	6	0	1.813780	-0.439810	2.723734
4	6	0	3.077633	0.335871	2.237161
5	6	0	3.171103	0.024516	0.690149
6	6	0	1.934436	0.549193	-0.089960
7	1	0	3.120544	-1.067926	0.638846
8	6	0	0.549960	0.336725	3.086066
9	6	0	-1.529456	-1.025340	0.882573
10	6	0	-1.871962	-0.355055	2.309316
11	6	0	-0.717142	-0.508830	3.335106
12	1	0	-1.106084	-0.238310	4.314039
13	1	0	-0.423505	-1.556543	3.411591
14	6	0	4.533935	0.372605	-0.015007
15	6	0	3.006615	1.832351	2.601947
16	1	0	3.960339	2.325843	2.427005
17	1	0	2.251890	2.387416	2.042771
18	1	0	2.784304	1.953091	3.665514
19	6	0	4.302743	-0.304990	2.938897
20	1	0	4.293238	-0.037739	4.001015
21	1	0	4.195827	-1.390666	2.888855
22	6	0	5.636656	0.104313	2.310623
23	1	0	6.450162	-0.423333	2.814111
24	1	0	5.830860	1.174488	2.428523
25	6	0	5.660222	-0.268788	0.833629
26	1	0	5.585326	-1.356343	0.751225
27	6	0	4.554976	-0.316701	-1.399355
28	1	0	3.868462	0.156008	-2.104942
29	1	0	5.556032	-0.247450	-1.829269
30	1	0	4.279555	-1.371736	-1.325468
31	6	0	4.774987	1.880388	-0.231315
32	1	0	4.978558	2.423898	0.690412
33	1	0	5.635271	2.025262	-0.886397
34	1	0	3.911378	2.349166	-0.710124
35	8	0	6.933555	0.123068	0.247654
36	6	0	7.971151	-0.738793	0.370869
37	8	0	7.904033	-1.799686	0.937601
38	6	0	9.203872	-0.183916	-0.299824
39	1	0	10.036231	-0.868014	-0.149481
40	1	0	9.018212	-0.054097	-1.368598
41	1	0	9.444068	0.798445	0.112128
42	6	0	-0.980815	-2.463027	1.026971
43	1	0	-1.682782	-3.085719	1.582890
44	1	0	-0.853227	-2.906707	0.039762
45	1	0	-0.018094	-2.512698	1.532464
46	6	0	-2.273150	1.129609	2.172928
47	1	0	-3.168366	1.256945	1.563099
48	1	0	-2.485060	1.548113	3.159501
49	1	0	-1.500029	1.745005	1.714817
50	6	0	-2.927422	-1.093368	0.225214
51	6	0	-3.148331	-1.192314	2.719339
52	6	0	-3.895047	-1.447825	1.372346
53	1	0	-3.174181	-0.130465	-0.221474
54	1	0	-2.939904	-1.833998	-0.577602
55	1	0	-4.797432	-0.833587	1.309219
56	1	0	-4.225640	-2.485558	1.303702
57	1	0	-2.782566	-2.150947	3.103617
58	6	0	-4.123068	-0.642138	3.802489
59	1	0	-4.577797	0.275341	3.406395
60	6	0	-3.479738	-0.305098	5.158012
61	1	0	-2.932822	-1.164266	5.560010
62	1	0	-2.790054	0.537376	5.099529
63	1	0	-4.241663	-0.030477	5.891271
64	6	0	-5.263267	-1.668092	4.010578
65	1	0	-5.657156	-1.999428	3.050333
66	1	0	-4.853235	-2.564432	4.492224
67	6	0	-6.448606	-1.152250	4.832149
68	1	0	-6.207044	-0.993638	5.884771
69	1	0	-6.783012	-0.178726	4.450163
70	6	0	-7.647614	-2.076955	4.763285
71	8	0	-7.839047	-2.925943	3.928742
72	8	0	-8.515041	-1.814837	5.765694
73	6	0	-9.719138	-2.603405	5.770386
74	1	0	-9.481328	-3.664272	5.861334
75	1	0	-10.287103	-2.262340	6.633056
76	1	0	-10.284806	-2.444753	4.850844
77	1	0	0.805378	0.900970	3.991198
78	1	0	0.390230	1.117109	2.338819
79	8	0	1.847991	-1.649162	2.799048
80	8	0	-0.960924	0.890578	-0.481292
81	1	0	2.218381	0.827915	-1.107011
82	1	0	1.503831	1.446004	0.352131
83	8	0	1.112170	-1.588216	-0.790290

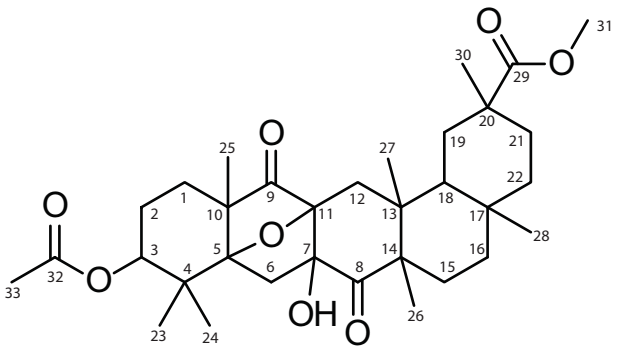
Table S5. ^{1}H and ^{13}C NMR Data, HMQC and HMBC Correlations of **3.**



position	δ_C	δ_H (mult, *J* in Hz)	HMBC (from ^{1}H to ^{13}C)
1	29.1	1.84 (m)	C-3, C-5, C-9, C-10, C-25
		1.96 (m)	C-3, C-5, C-9, C-10, C-25
2	23.2	2.03 (m)	C-1, C-3, C-4, C-10
		1.53 (m)	C-3, C-10
3	72.4	5.70 (dd, 12, 12)	C-1, C-2, C-4, C-5, C-23, C-24, C-32
4	43.8		
5	56.9		
6	41.2	2.75 (d, 12)	C-4, C-5, C-7, C-8, C-10, C-11
		3.40 (d, 12)	C-4, C-5, C-7, C-10, C-11
7	210.0		
8	211.5		
9	218.9		
10	62.3		
11	92.2		
12	42.4	1.73 (d, 18)	C-5, C-9, C-11, C-13, C-14, C-18, C-27
		2.25 (d, 18)	C-9, C-11, C-13, C-14, C-18, C-27
13	40.6		
14	55.4		
15	24.5	2.17 (ddd, 18, 18, 6)	C-8, C-13, C-14, C-16, C-17, C-26
		1.23 (m)	C-14, C-17, C-26
16	35.4	1.65 (m)	C-14, C-15, C-22, C-28
		1.41 (m)	C-14, C-15, C-18
17	32.7		
18	47.0	1.52 (m)	C-12, C-13, C-14, C-17, C-19, C-20, C-27, C-28
19	31.2	1.82 (m)	C-13, C-17, C-18, C-20, C-29, C-30
		2.35 (d, 18)	C-13, C-17, C-18, C-20, C-21, C-29, C-30
20	40.7		
21	29.8	2.26 (m)	C-17, C-19, C-29
		1.40 (m)	C-17, C-20, C-30
22	33.4	0.95 (m)	C-16, C-17, C-18, C-20, C-21, C-28
		1.88 (m)	C-16, C-17, C-18, C-20, C-21, C-28
23	21.8	1.16 (s)	C-3, C-4, C-5, C-24
24	21.6	1.02 (s)	C-3, C-4, C-5, C-23
25	22.4	1.32 (s)	C-1, C-5, C-9, C-10
26	17.2	1.35 (s)	C-8, C-13, C-14, C-15
27	19.0	1.06 (s)	C-12, C-13, C-14, C-18
28	31.2	1.04 (s)	C-16, C-17, C-18
29	178.7		
30	32.8	1.23 (s)	C-19, C-20, C-21, C-29
31	52.4	3.60 (s)	C-29
32	170.4		
33	21.3	2.02 (s)	C-32

m = multiplet, overlapped

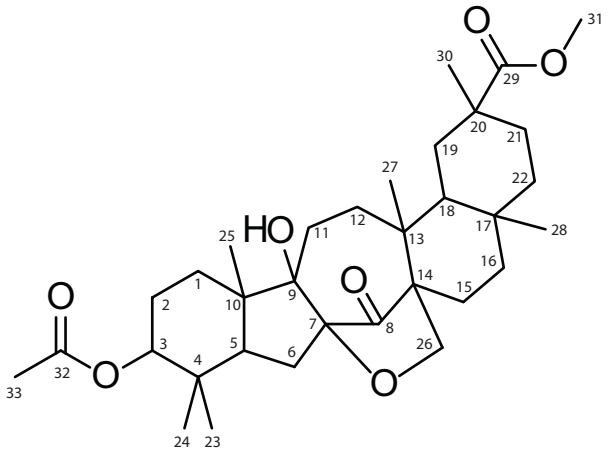
Table S6. ^{1}H and ^{13}C NMR Data, HMQC and HMBC Correlations of **4.**



position	δ_C	δ_H (mult, *J* in Hz)	HMBC (from ^{1}H to ^{13}C)
1	29.87	1.75 (m)	C-3, C-10
		1.53 (m)	C-2, C-5, C-10, C-25
2	23.1	1.72 (m)	C-4
		1.72 (m)	C-4
3	76.5	4.81 (dd, 10.8, 4.8)	C-1, C-2, C-4, C-23, C-24
4	38.5		
5	90.6		
6	39.8	2.69 (d, 14.4)	C-5, C-8, C-11
		1.88 (m)	C-7, C-8, C-10, C-11
7	90.3		
8	212.6		
9	212.4		
10	48.7		
11	77.3		
12	31.1	2.20 (m)	C-7, C-9, C-13, C-14, C-18, C-27
		1.97 (m)	C-7, C-9, C-13, C-14, C-18, C-27
13	40.4		
14	52.5		
15	24.2	1.75 (m)	C-8, C-14, C-16, C-26
		1.48 (m)	C-13, C-14, C-16, C-17
16	35.4	1.42 (m)	C-15, C-17, C-18, C-22, C-28
		1.70 (m)	C-14, C-15, C-17, C-22, C-28
17	31.3		
18	44.3	1.72 (m)	C-13, C-22, C-27
19	30.7	1.73 (m)	C-13, C-18, C-29, C-30
		2.36 (d, 15)	C-13, C-17, C-18, C-20, C-21, C-29
20	40.4		
21	29.91	2.23 (m)	C-29
		1.38 (m)	C-17, C-20, C-22, C-30
22	33.9	0.95 (m)	C-17, C-18, C-21
		1.99 (m)	C-16, C-17, C-20, C-21
23	17.7	1.00 (s)	C-3, C-4, C-5, C-24
24	20.8	0.92 (s)	C-3, C-4, C-5, C-23
25	19.4	1.29 (s)	C-1, C-5, C-9, C-10
26	18.5	1.31 (s)	C-8, C-13, C-14, C-15
27	22.3	0.77 (s)	C-12, C-13, C-14, C-18
28	31.5	1.07 (s)	C-16, C-17, C-18, C-22
29	178.6		
30	32.5	1.19 (s)	C-19, C-20, C-21, C-29
31	51.6	3.61 (s)	C-29
32	170.6		
33	21.4	2.05 (s)	C-32

m = multiplet, overlapped

Table S7. ^{1}H and ^{13}C NMR Data, HMQC and HMBC Correlations of **7.**



position	δ_C	δ_H (mult, *J* in Hz)	HMBC (from ^{1}H to ^{13}C)
1	32.2	1.39 (m)	C-2, C-5, C-25
		1.39 (m)	C-2, C-5, C-25
2	25.3	1.74 (m)	C-1, C-3, C-4, C-10
		1.74 (m)	C-1, C-3, C-4, C-10
3	80.5	4.51 (dd, 11.4, 4.2)	C-2, C-4, C-23, C-24
4	37.3		
5	48.3	1.39 (m)	C-1, C-3, C-4, C-7, C-9, C-10, C-23, C-24, C-25
6	29.2	1.74 (m)	C-5, C-7, C-8, C-9
		1.54 (m)	C-5, C-7, C-8
7	87.3		
8	212.9		
9	78.9		
10	47.4		
11	29.0	1.51 (m)	C-9, C-12, C-13
		1.15 (m)	C-7
12	34.0	1.78 (m)	
		1.66 (m)	C-9, C-11, C-13, C-14, C-27
13	39.7		
14	53.9		
15	25.6	2.06 (m)	C-14, C-16
		1.16 (m)	C-8, C-13, C-14, C-16, C-17, C-26
16	36.8	1.30 (m)	C-14, C-15, C-17, C-22, C-28
		1.57 (m)	C-14, C-15, C-17, C-18, C-22, C-28
17	31.8		
18	46.7	1.18 (m)	C-13, C-14, C-16, C-17, C-19, C-27
19	30.96	1.61 (m)	C-13, C-17, C-18, C-20, C-21, C-29, C-30
		2.32 (m)	C-13, C-17, C-18, C-20, C-21, C-29
20	40.7		
21	29.3	2.25 (m)	C-20, C-22, C-29
		1.38 (m)	C-20, C-22, C-29, C-30
22	33.5	0.96 (m)	C-17, C-18, C-28
		1.93 (m)	C-17, C-21, C-28
23	17.5	0.93 (s)	C-3, C-4, C-5, C-24
24	29.1	0.97 (s)	C-3, C-4, C-5, C-23
25	16.6	1.00 (s)	C-1, C-5, C-9, C-10
26	72.6	4.29 (d, 9.6)	C-13, C-14, C-15
		4.04 (d, 9.6)	C-7, C-8, C-13, C-14, C-15
27	17.2	0.85 (s)	C-12, C-13, C-14, C-18
28	30.9	0.95 (s)	C-16, C-17, C-18, C-22
29	179.3		
30	31.3	1.19 (s)	C-19, C-20, C-21, C-29
31	52.0	3.64 (s)	C-29
32	171.1		
33	21.4	2.05 (s)	C-32

m = multiplet, overlapped

Figure S4. Key HMBC correlations of **11**.

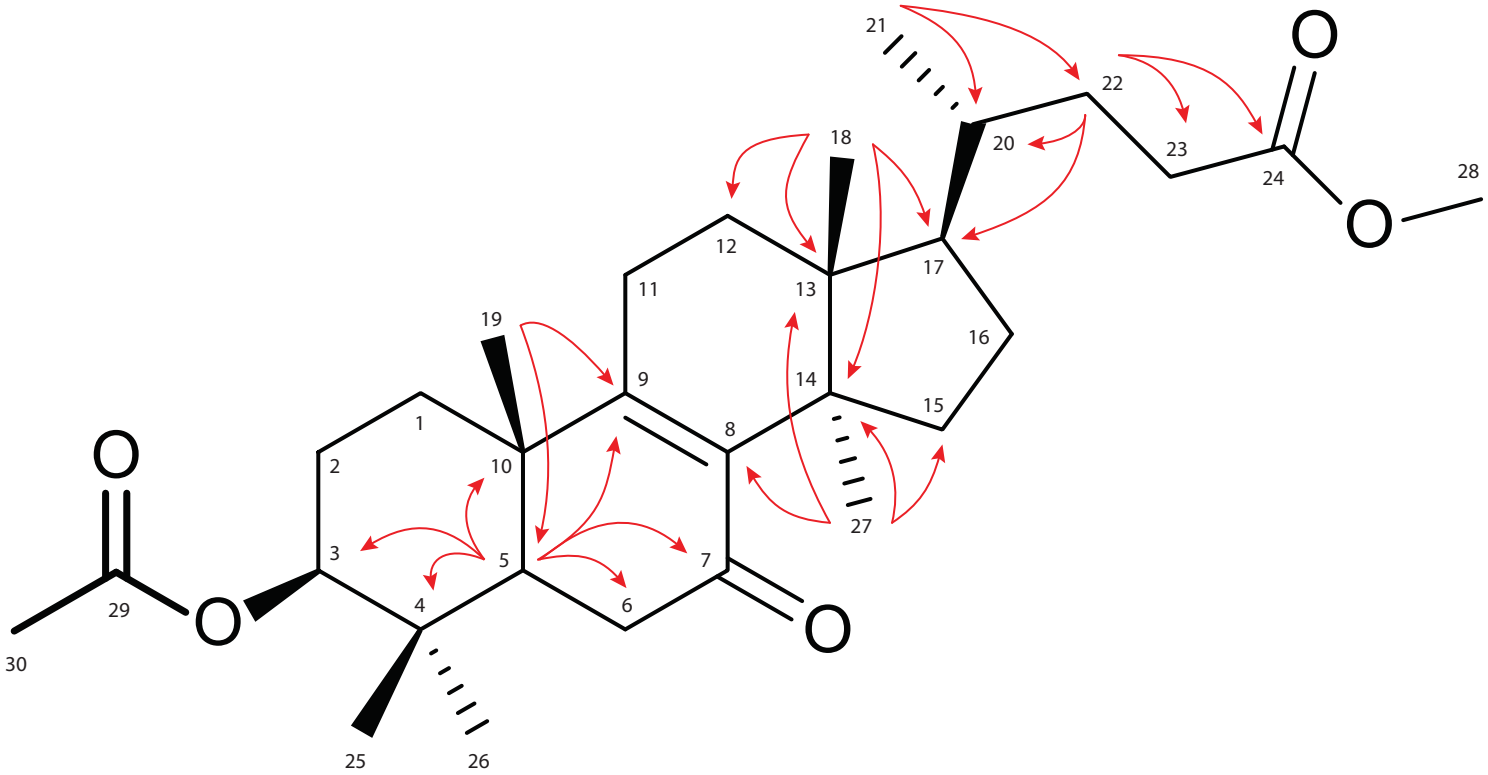


Figure S5. Key HMBC correlations of **12**.

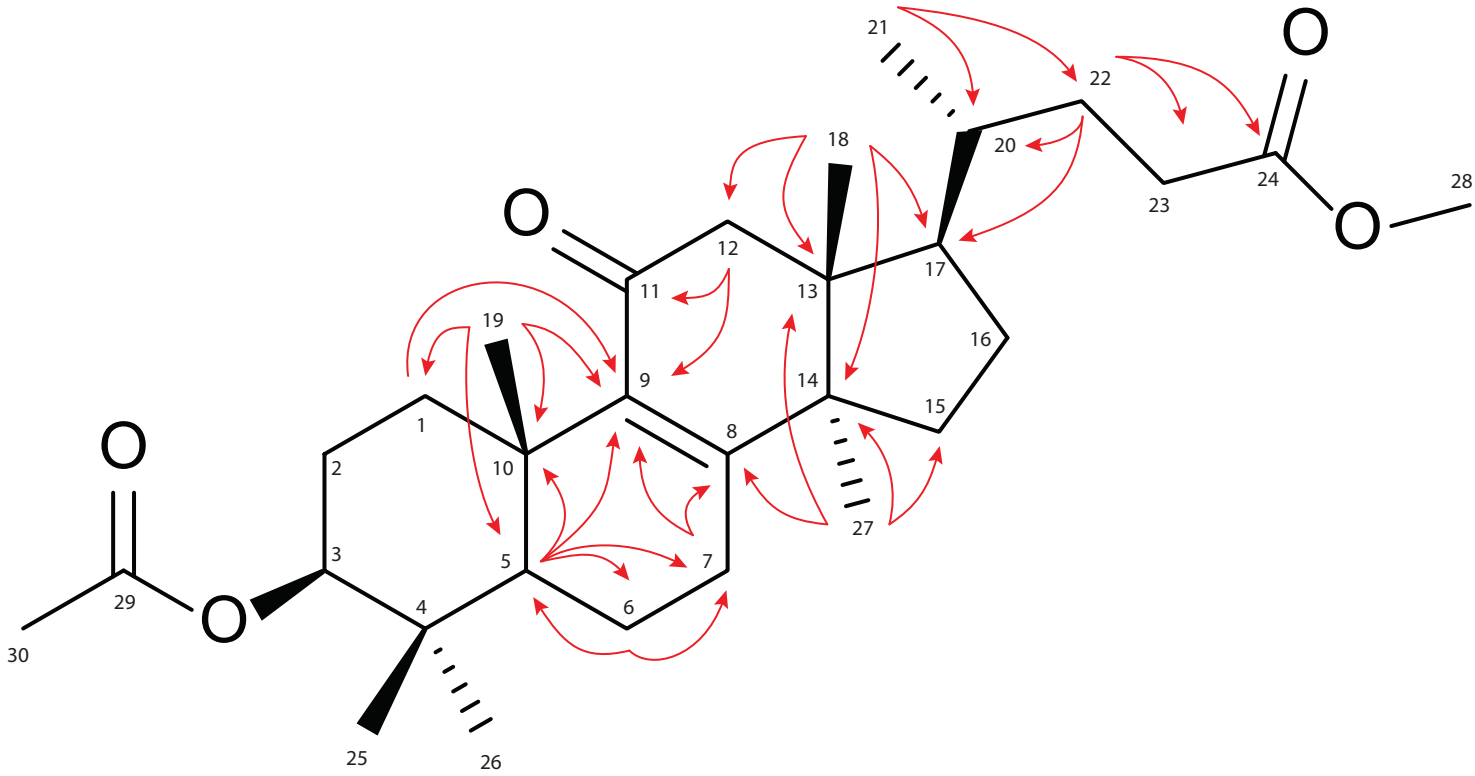


Table S8. ^{1}H and ^{13}C NMR Data, HMQC Correlations of **11.**

№	δ_C	δ_H (mult, *J* in Hz)
1	34.6	1.81 (m)
		1.50 (m)
2	24.0	1.81 (m)
		1.66 (m)
3	79.7	4.52 (dd, 11.6, 4.4)
4	37.9	
5	50.0	1.73 (m)
6	36.6	2.40 (m)
		2.42 (m)
7	198.8	
8	139.1	
9	164.7	
10	39.8	
11	31.4	2.32 (m)
		2.23 (m)
12	30.2	1.80 (m)
		1.80 (m)
13	45.1	
14	47.9	
15	31.4	2.34 (m)
		2.20 (m)
16	28.8	2.05 (m)
		1.40 (m)
17	48.9	1.46 (m)
18	15.9	0.65 (s)
19	18.6	1.18 (s)
20	36.1	1.44 (m)
21	25.1	0.91 (m)
22	32.1	2.07 (m)
		1.81 (m)
23	23.8	2.33 (m)
		2.21 (m)
24	174.8	
25	27.5	0.88 (s)
26	16.5	0.95 (s)
27	18.5	0.91 (s)
28	51.6	3.66 (s)
29	171.0	
30	21.4	2.06 (s)

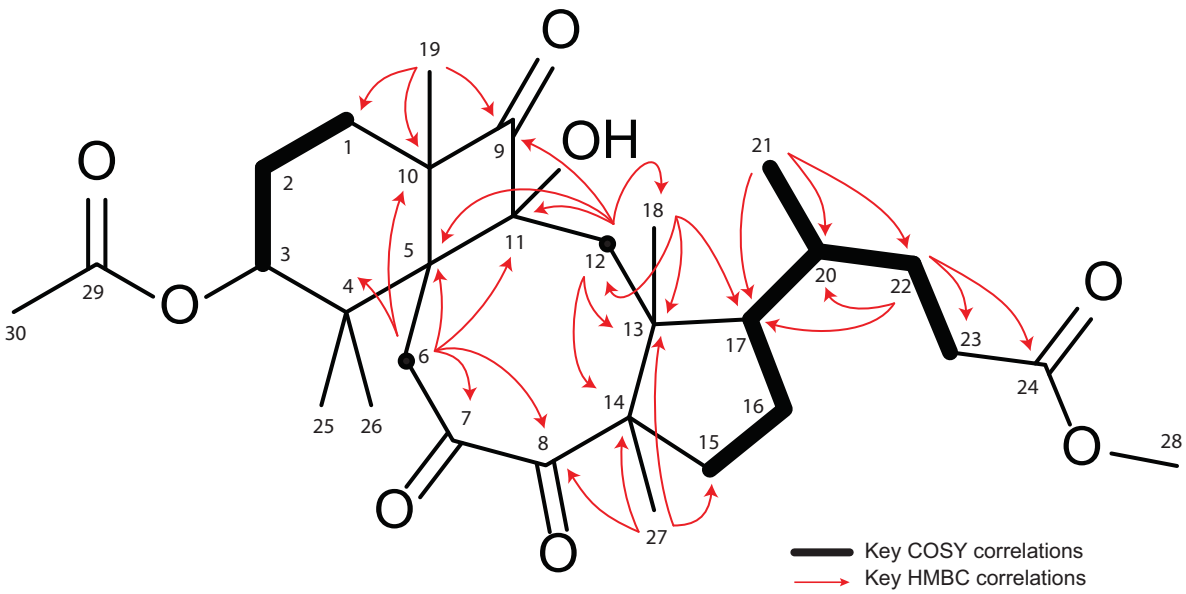
m = multiplet, overlapped

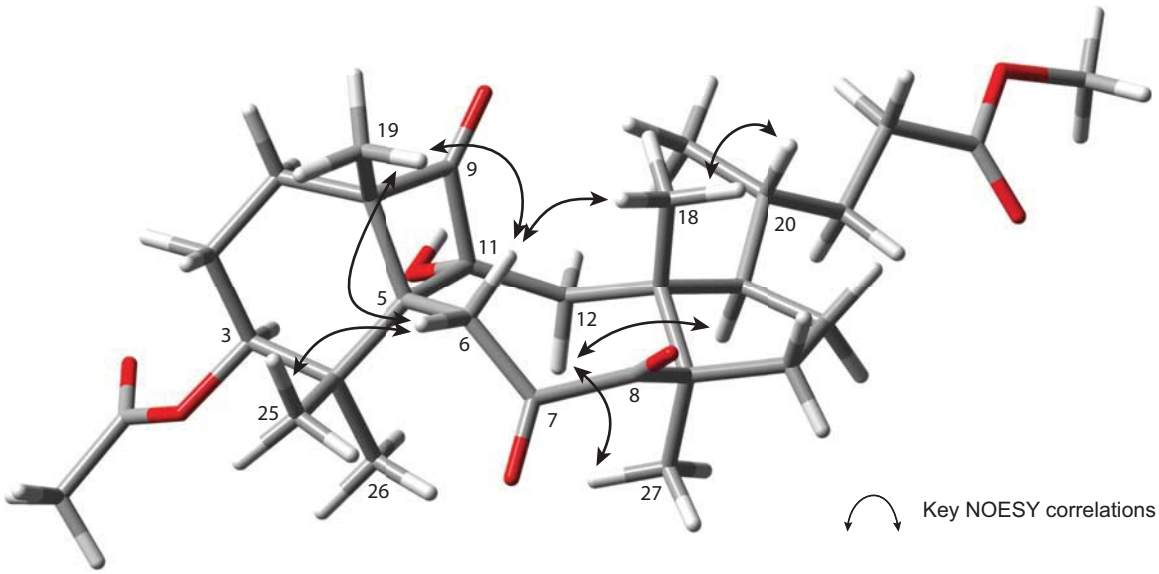
Table S9. ^{1}H and ^{13}C NMR Data, HMQC Correlations of **12.**

№	δ_C	δ_H (mult, *J* in Hz)
1	34.1	2.99 (ddd, 13.8, 3.6, 3.6)
		1.10 (m)
2	24.3	1.67 (m)
		1.67 (m)
3	80.7	4.49 (dd, 10.2, 6)
4	38.0	
5	52.0	0.98 (m)
6	17.3	1.44 (m)
		1.71 (m)
7	29.9	2.22 (m)
		2.32 (m)
8	164.2	
9	139.5	
10	37.6	
11	199.1	
12	51.9	2.64 (d, 16.2)
		2.44 (d, 16.2)
13	51.6	
14	47.4	
15	31.0	1.74 (m)
		1.33 (m)
16	27.0	1.99 (m)
		1.39 (m)
17	50.1	1.68 (m)
18	16.8	0.80 (s)
19	19.1	1.13 (s)
20	35.8	1.39 (m)
21	18.1	0.85 (d, 6.6)
22	31.0	1.80 (m)
		1.28 (m)
23	31.2	2.35 (m)
		2.22 (m)
24	174.6	
25	16.9	0.88 (s)
26	28.4	0.88 (s)
27	25.9	1.10 (s)
28	51.7	3.65 (s)
29	171.0	
30	21.4	2.03 (s)

m = multiplet, overlapped

Figure S6. Key COSY, HMBC, and NOESY correlations of **15**.



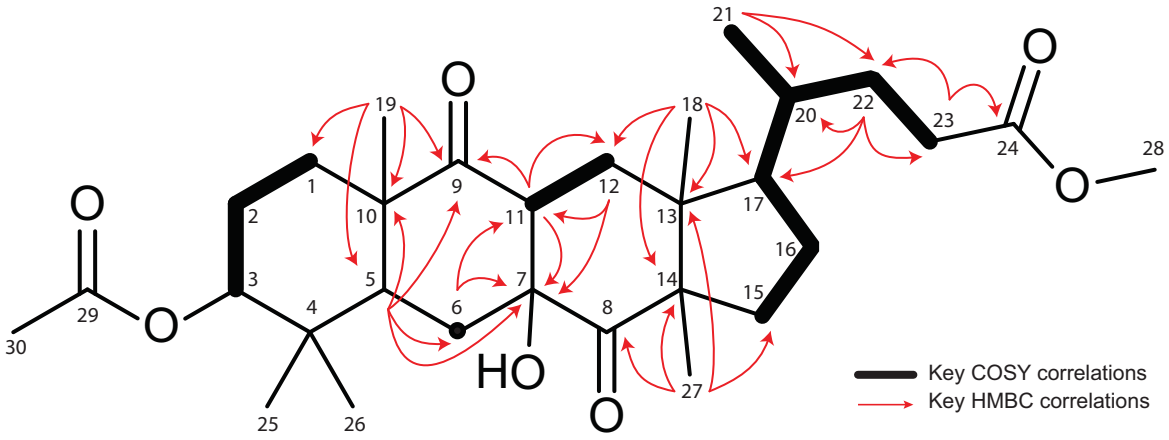


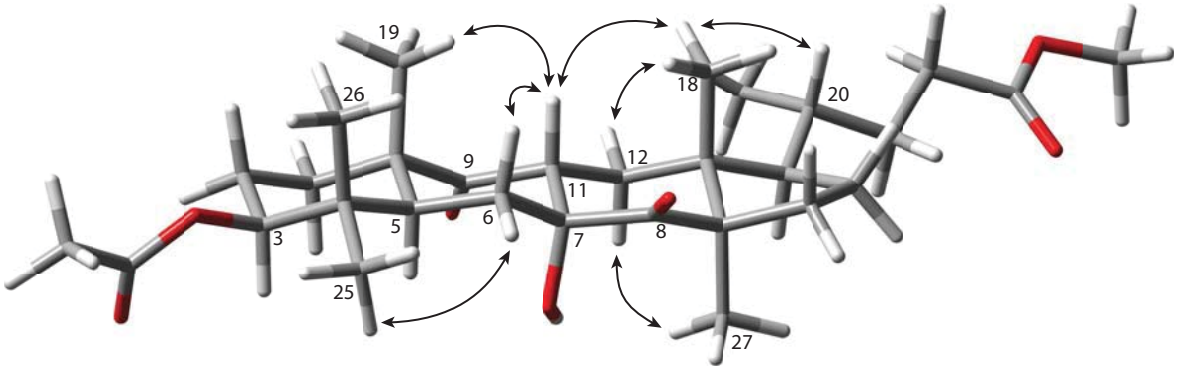
Geometry of **15** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

Table S10. ^{1}H and ^{13}C NMR Data, HMQC Correlations of **15.**

№	δ_C	δ_H (mult, *J* in Hz)
1	35.6	2.55 (m)
		1.70 (m)
2	22.7	1.59 (m)
		1.59 (m)
3	78.7	5.67 (m)
4	40.0	
5	56.2	
6	40.9	2.90 (d, 13.9)
		2.60 (d, 13.9)
7	210.0	
8	209.5	
9	213.3	
10	63.4	
11	94.9	
12	43.1	2.31 (m)
		2.24 (m)
13	48.7	
14	59.5	
15	29.3	2.46 (m)
		1.25 (m)
16	23.0	1.87 (m)
		1.47 (m)
17	53.9	1.69 (m)
18	17.7	0.93 (s)
19	19.5	1.16 (s)
20	34.2	1.56 (m)
21	20.3	1.10 (d, 6.7)
22	30.9	1.85 (m)
		1.33 (m)
23	31.9	2.40 (m)
		2.29 (m)
24	174.5	
25	20.5	1.37 (s)
26	21.4	1.16 (s)
27	19.8	1.28 (s)
28	51.8	3.69 (s)
29	171.4	
30	21.6	2.07(s)

Figure S7. Key COSY, HMBC, and NOESY correlations of **18**.



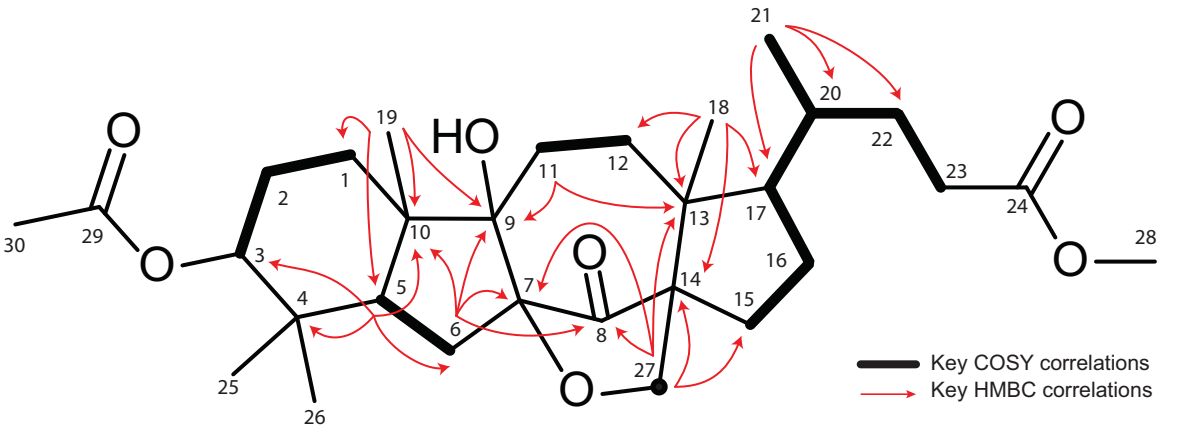


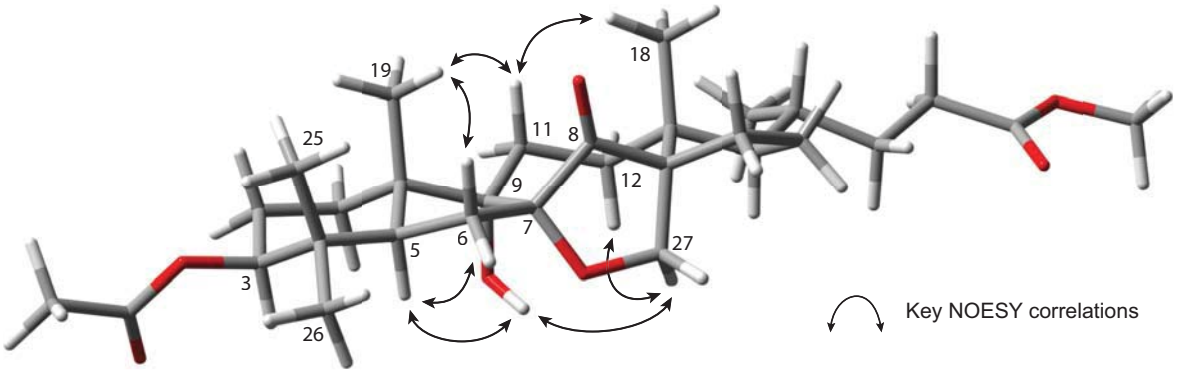
Geometry of **18**was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

Table S11. ^{1}H and ^{13}C NMR Data, HMQC Correlations of **18.**

№	δ_C	δ_H (mult, *J* in Hz)
1	30.7	1.71(m)
		1.62 (m)
2	23.6	1.80 (m)
		1.62 (m)
3	80.0	4.48 (dd, 11.4, 4.6)
4	38.5	
5	45.5	
6	28.9	2.13 (d, 13.3)
		1.84 (m)
7	79.2	
8	211.6	
9	211.8	
10	47.9	
11	50.2	3.10 (dd, 12.4, 2.6)
12	28.4	2.21 (m)
		1.73 (m)
13	59.3	
14	47.3	
15	29.3	1.73 (m)
		1.29 (m)
16	26.9	1.99 (m)
		1.36 (m)
17	49.5	1.70 (m)
18	18.6	0.68 (s)
19	19.5	1.12 (s)
20	35.3	1.43 (m)
21	18.7	0.95 (d, 6.4)
22	31.2	1.81 (m)
		1.34 (m)
23	31.1	2.37 (m)
		2.24 (m)
24	174.6	
25	28.1	0.88 (s)
26	17.3	0.99 (s)
27	22.8	1.28 (s)
28	51.7	3.65 (s)
29	171.0	
30	21.3	2.04(s)

Figure S8. Key COSY, HMBC, and NOESY correlations of **20**.





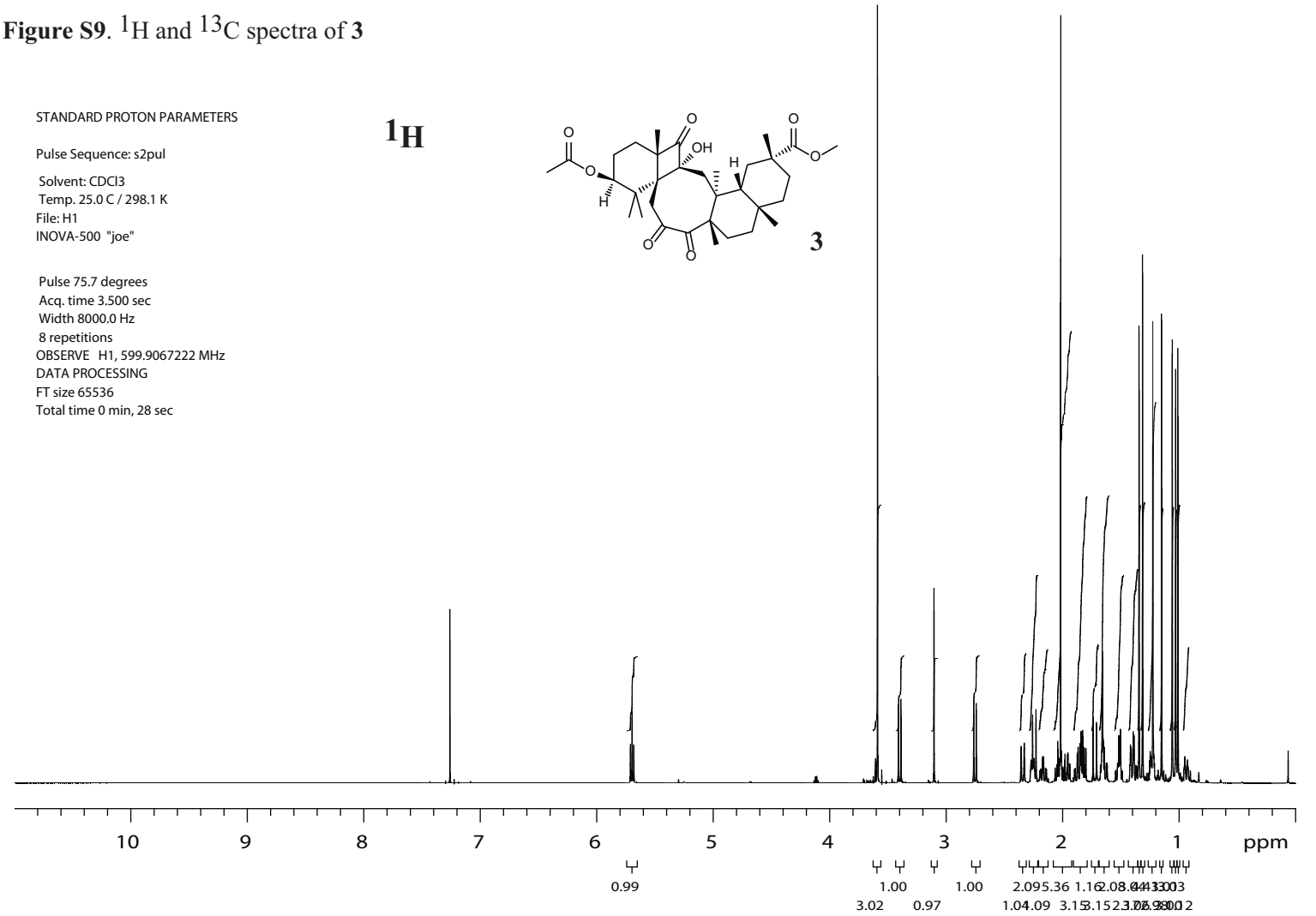
Geometry of **20** was optimized using Gaussian (R) 09 with B3LYP/6-311G(d,p).

Table S12. ^{1}H and ^{13}C NMR Data, HMQC Correlations of **20.**

№	δ_C	δ_H (mult, *J* in Hz)
1	29.7	1.88 (m)
		1.25 (m)
2	24.4	1.74 (m)
		1.61 (m)
3	80.89	4.65 (dd, 11.9, 4.7)
4	37.0	
5	49.2	1.92 (m)
6	30.4	2.21 (m)
		1.42 (m)
7	89.5	
8	209.9	
9	80.88	
10	49.1	
11	26.2	1.41 (m)
		1.36 (m)
12	29.8	1.79 (m)
		1.68 (m)
13	49.9	
14	61.4	
15	29.6	1.38 (m)
		2.20 (m)
16	27.4	1.88 (m)
		1.58 (m)
17	53.5	1.33 (m)
18	15.3	0.85 (s)
19	15.4	0.86 (s)
20	34.8	1.49 (m)
21	19.0	0.92 (d, 6.4)
22	31.2	1.82 (m)
		1.31 (m)
23	31.3	2.35 (m)
		2.24 (m)
24	174.5	
25	29.4	0.88 (s)
26	16.8	0.96 (s)
27	74.1	4.26 (d, 9.3)
		3.80 (d, 9.3)
28	51.7	3.66 (s)
29	171.1	
30	21.4	2.05 (s)

m = multiplet, overlapped

Figure S9. ^{1}H and ^{13}C spectra of **3**



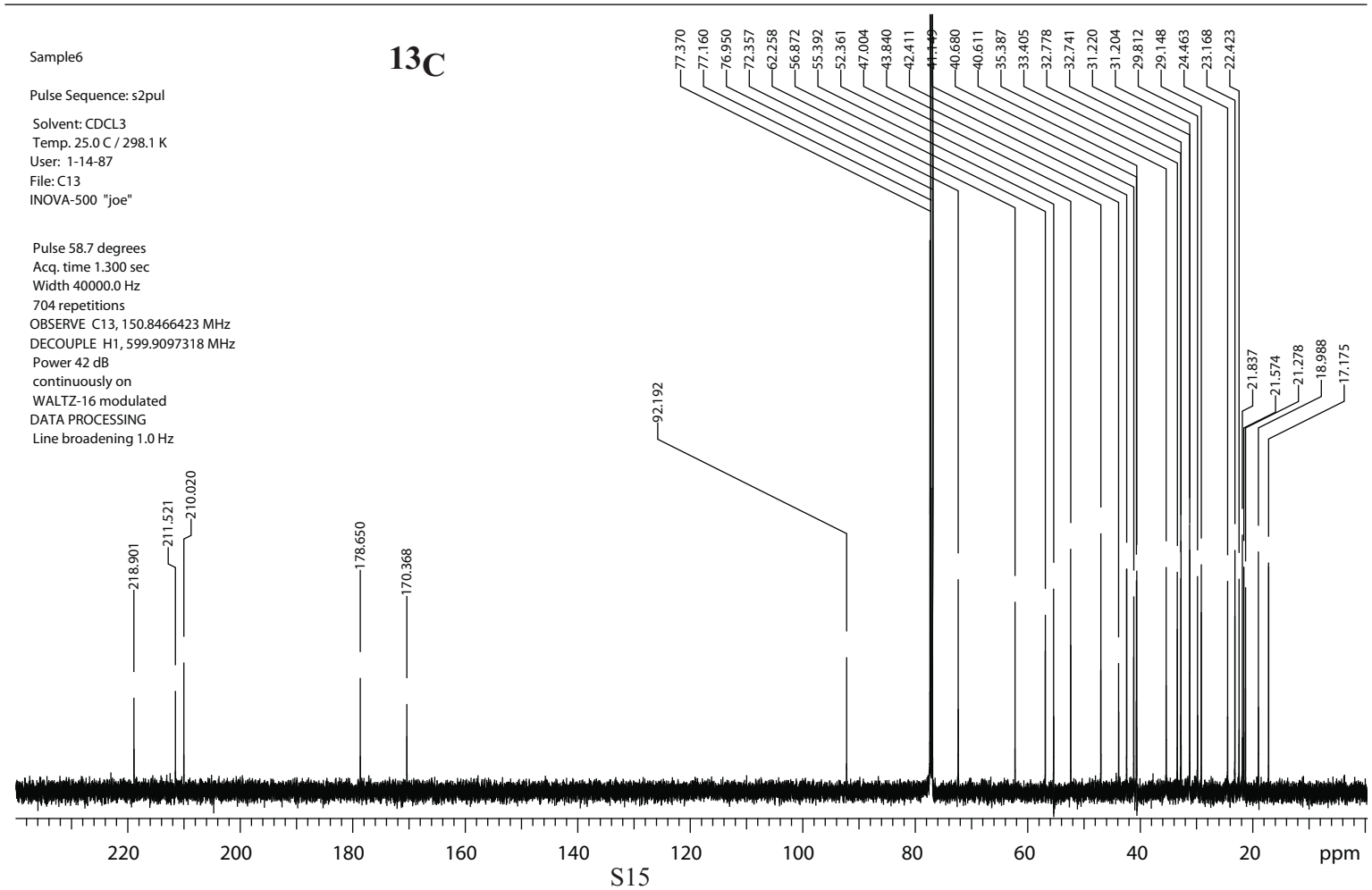
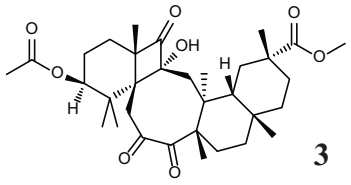


Figure S10. HMQC and HMBC spectra of **3**.



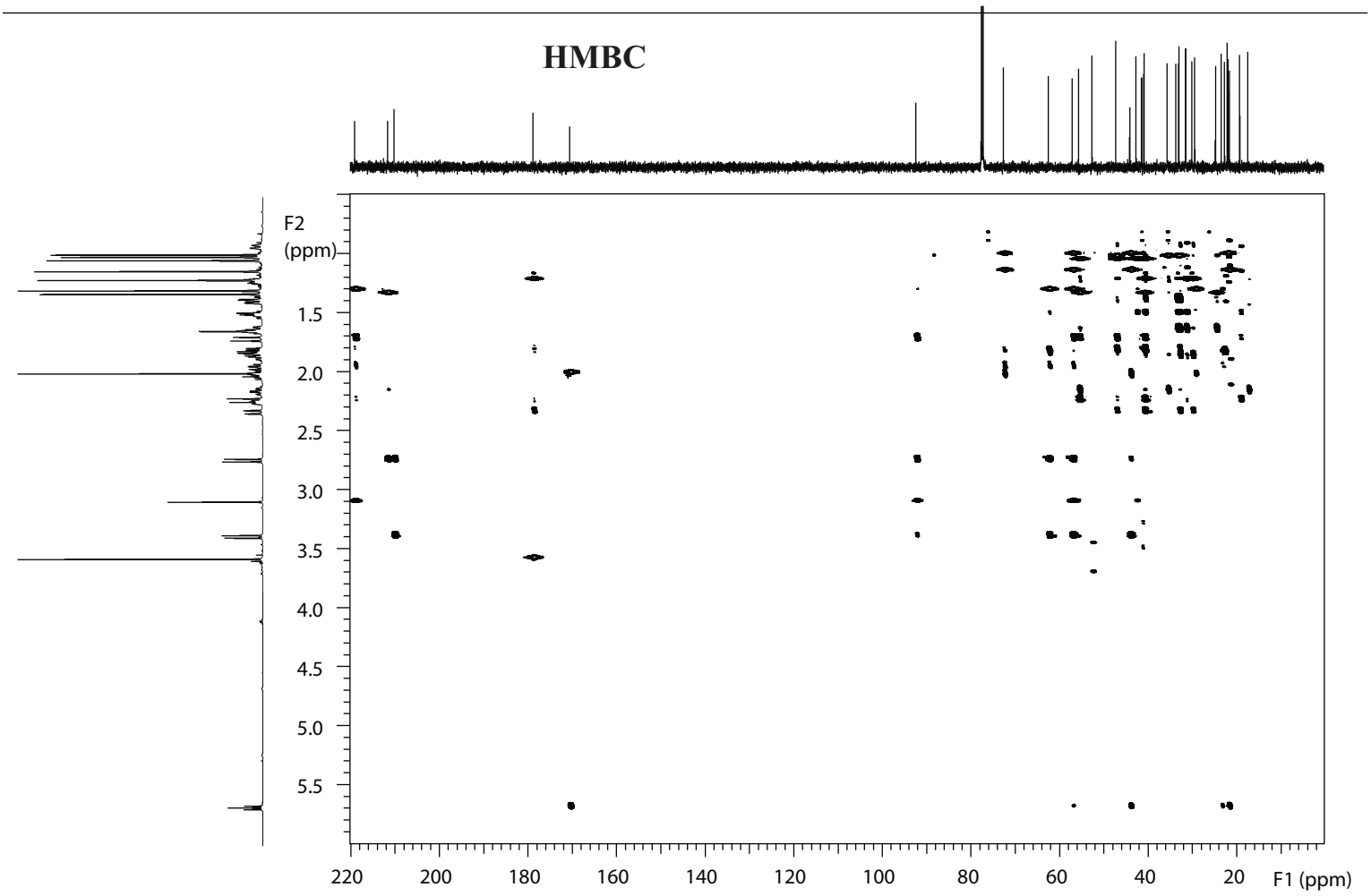
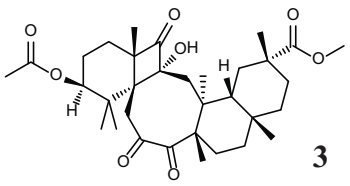
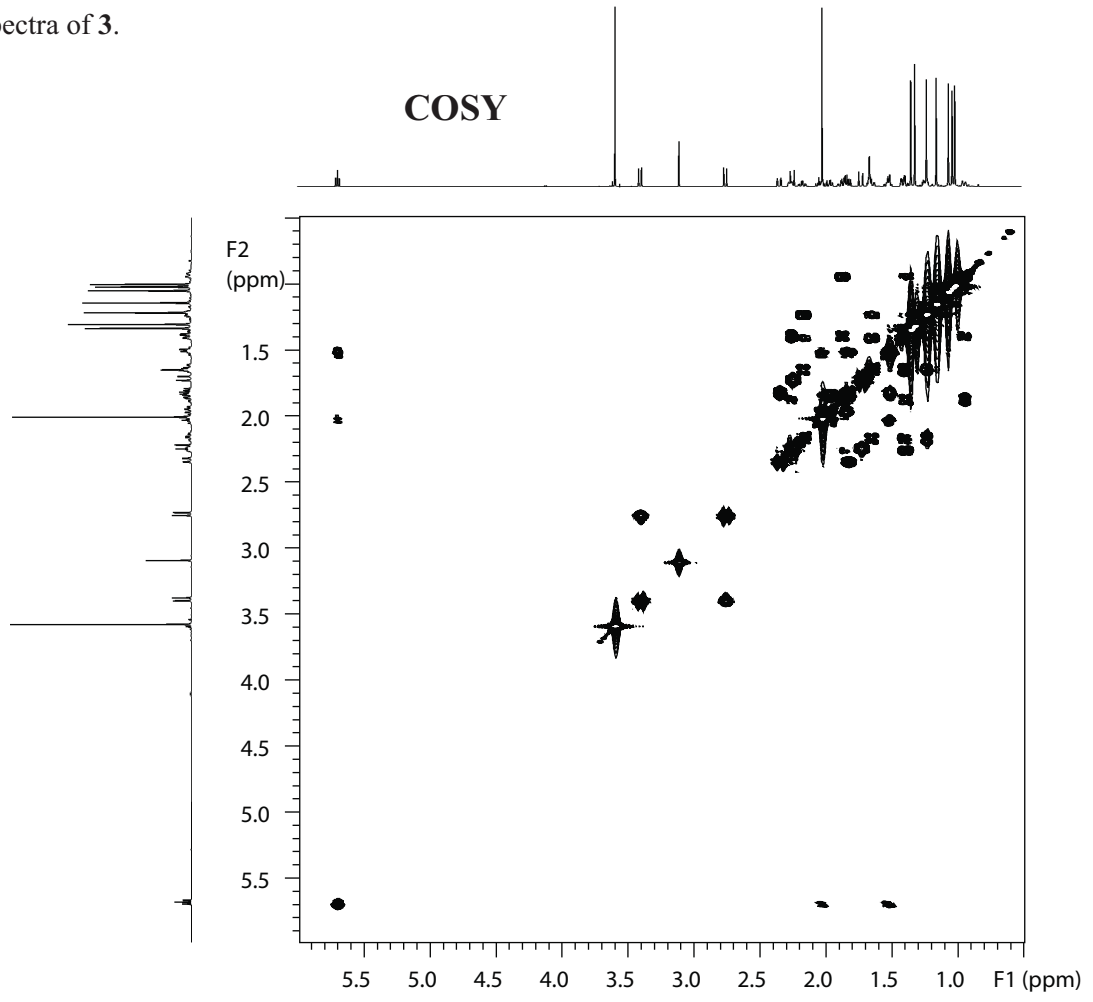


Figure S11. COSY and NOESY spectra of **3**.



3



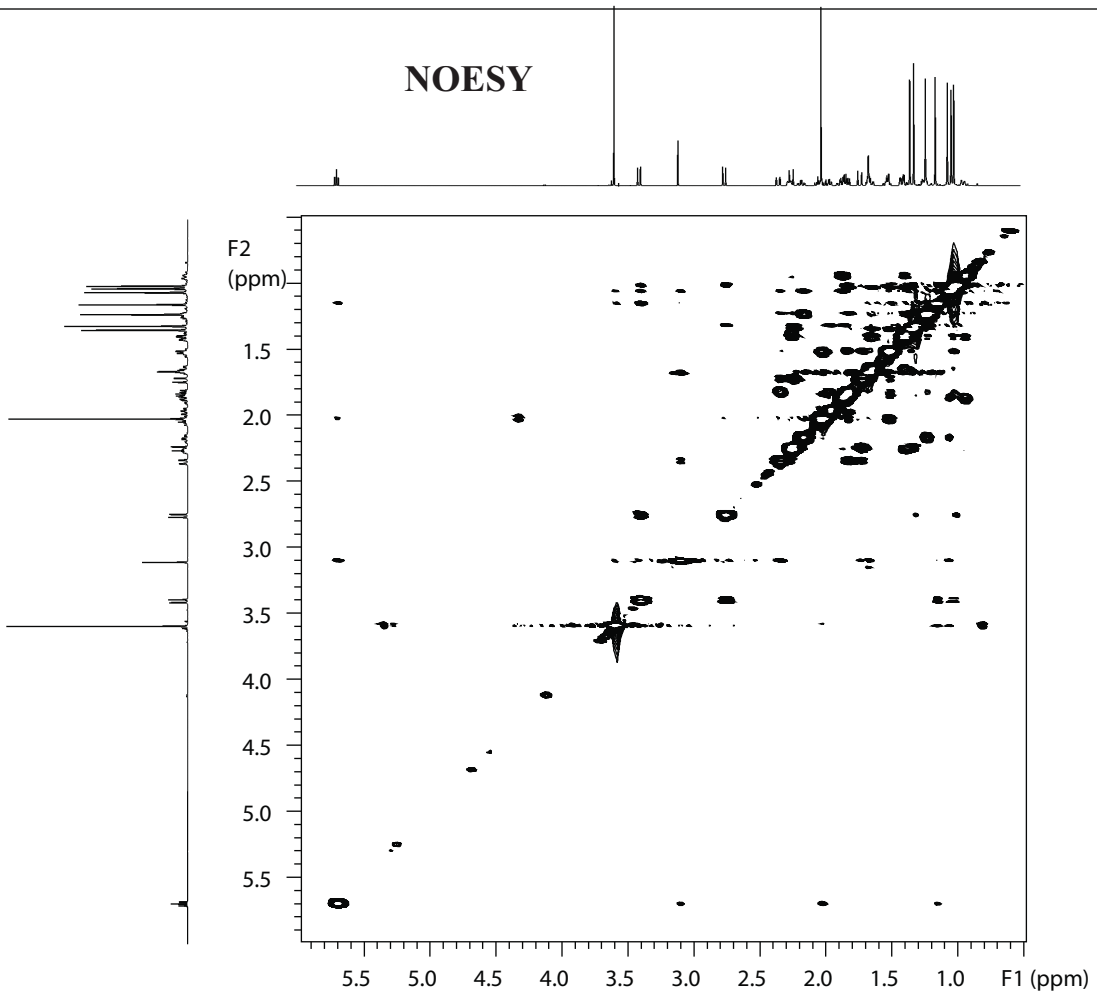
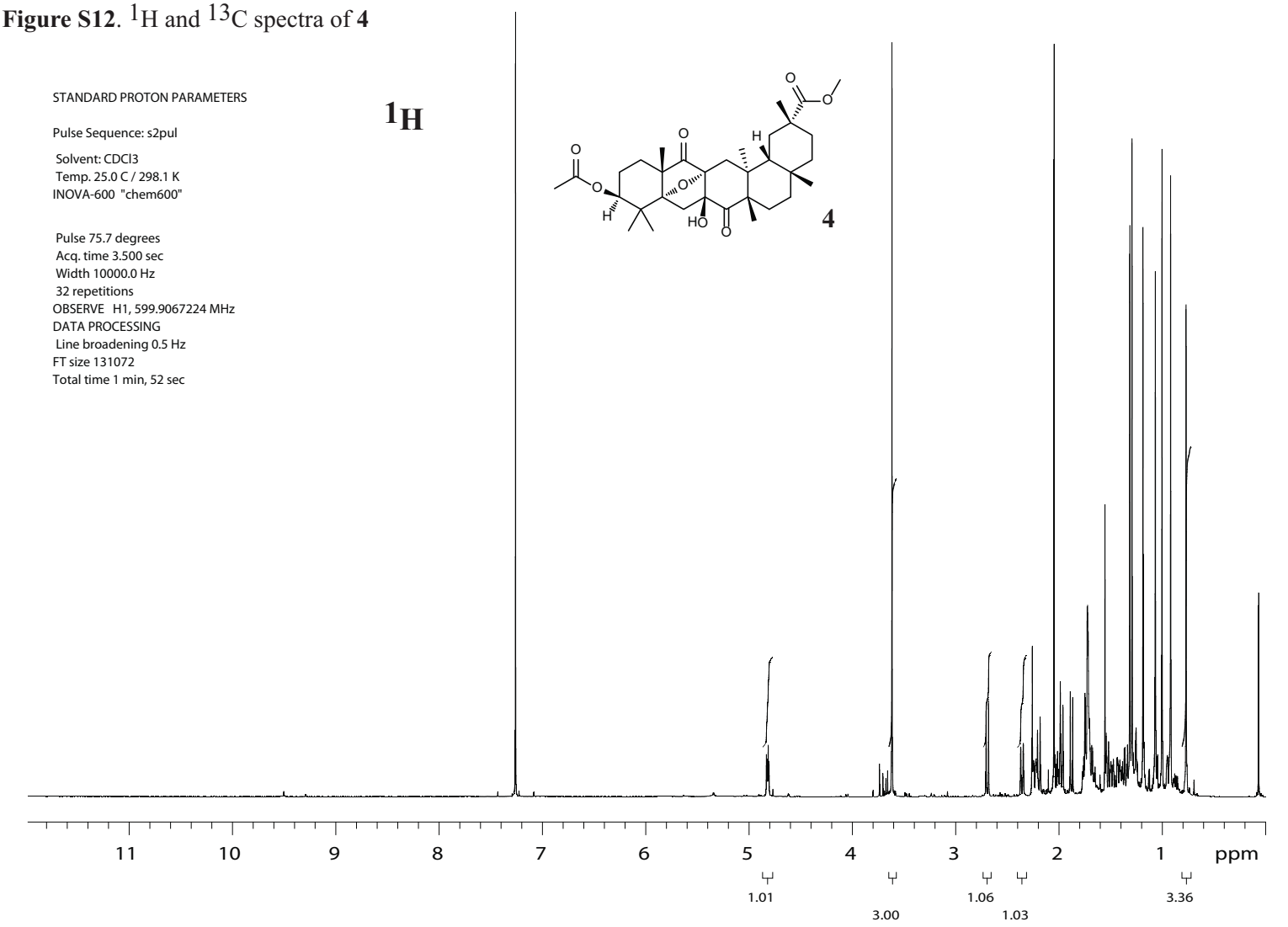


Figure S12. ^{1}H and ^{13}C spectra of **4**



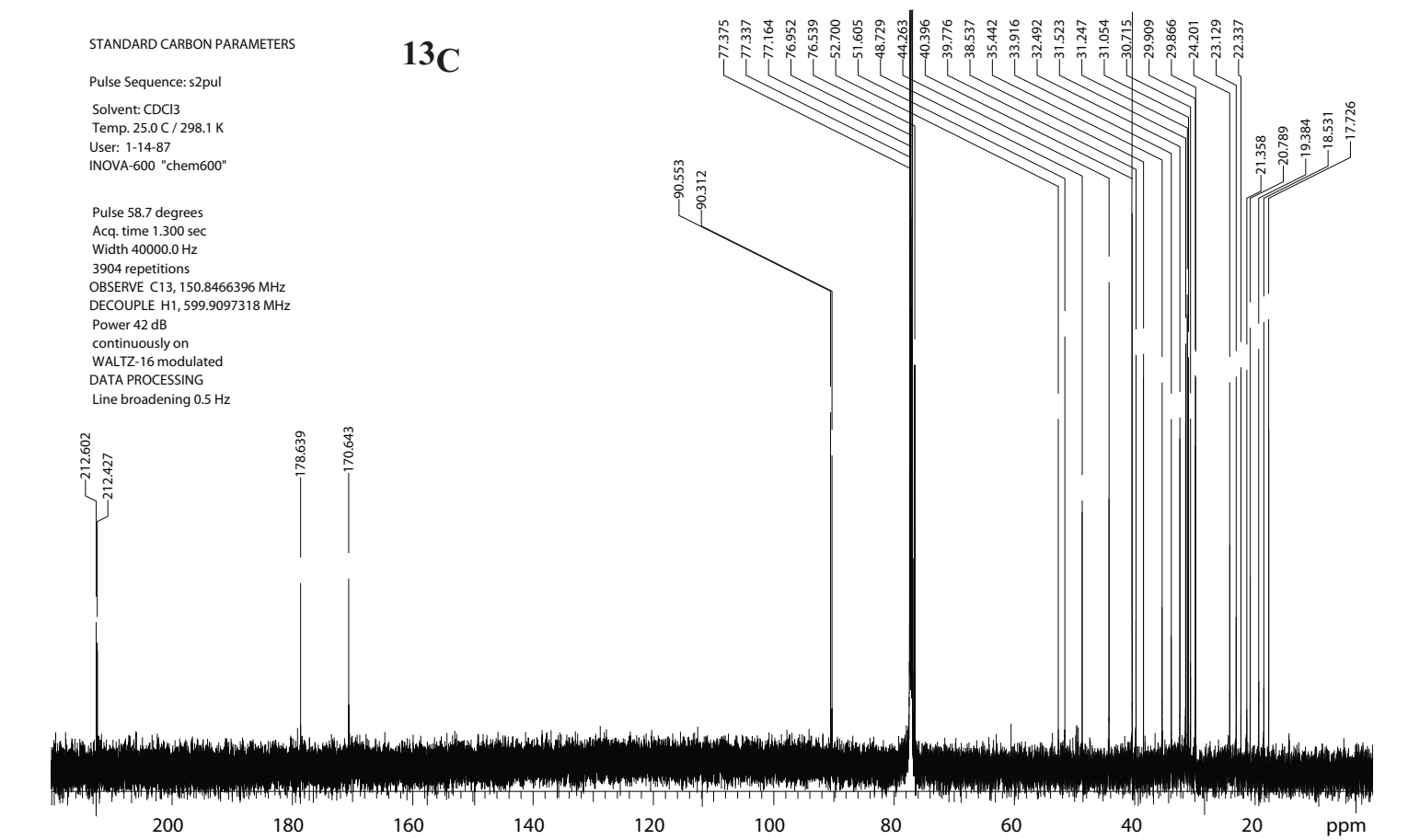
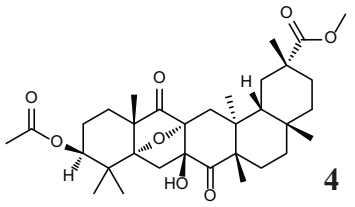


Figure S13. HMQC and HMBC spectra of **4**.



4

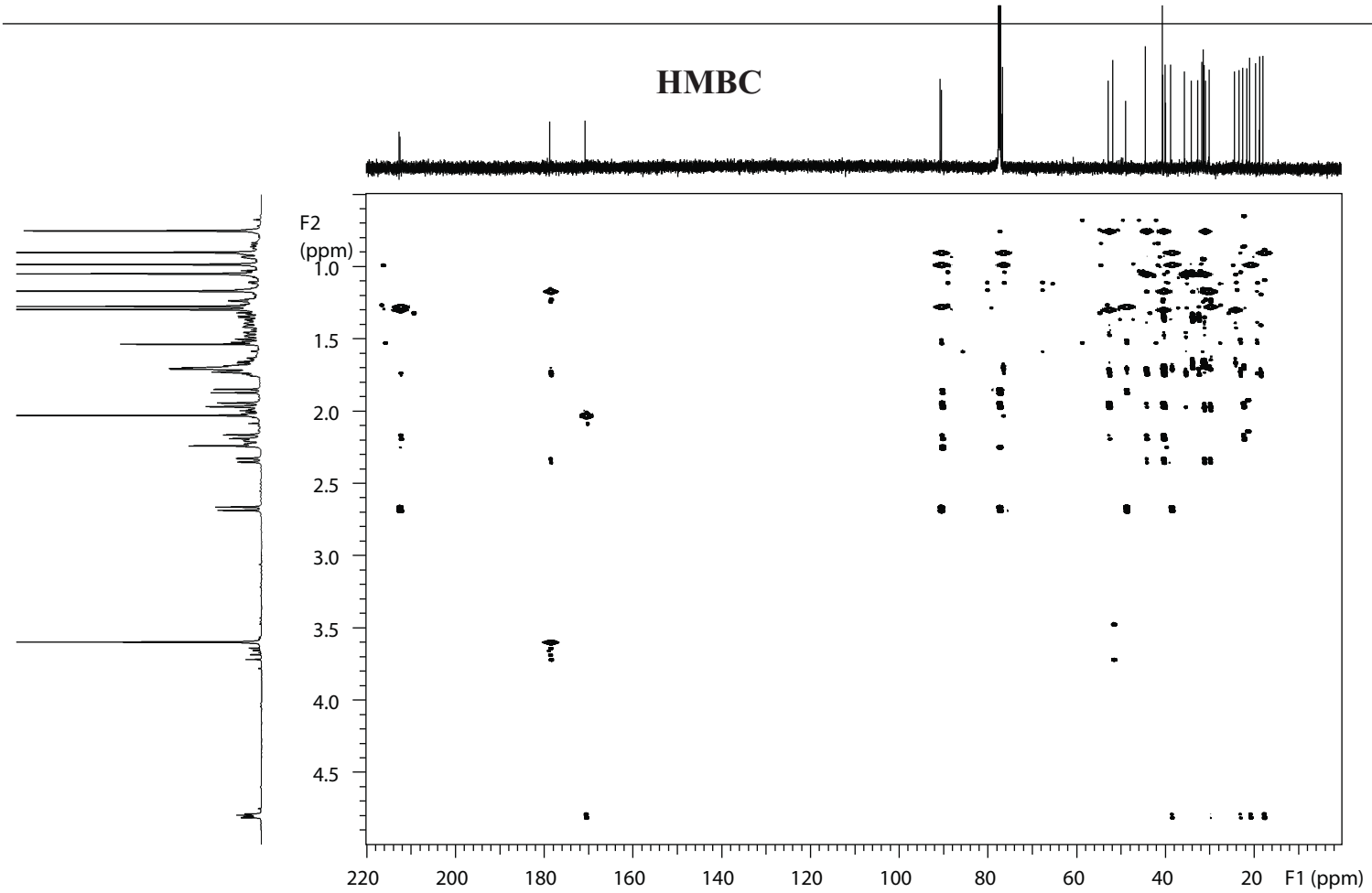
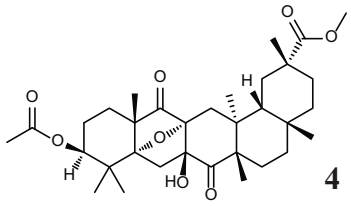
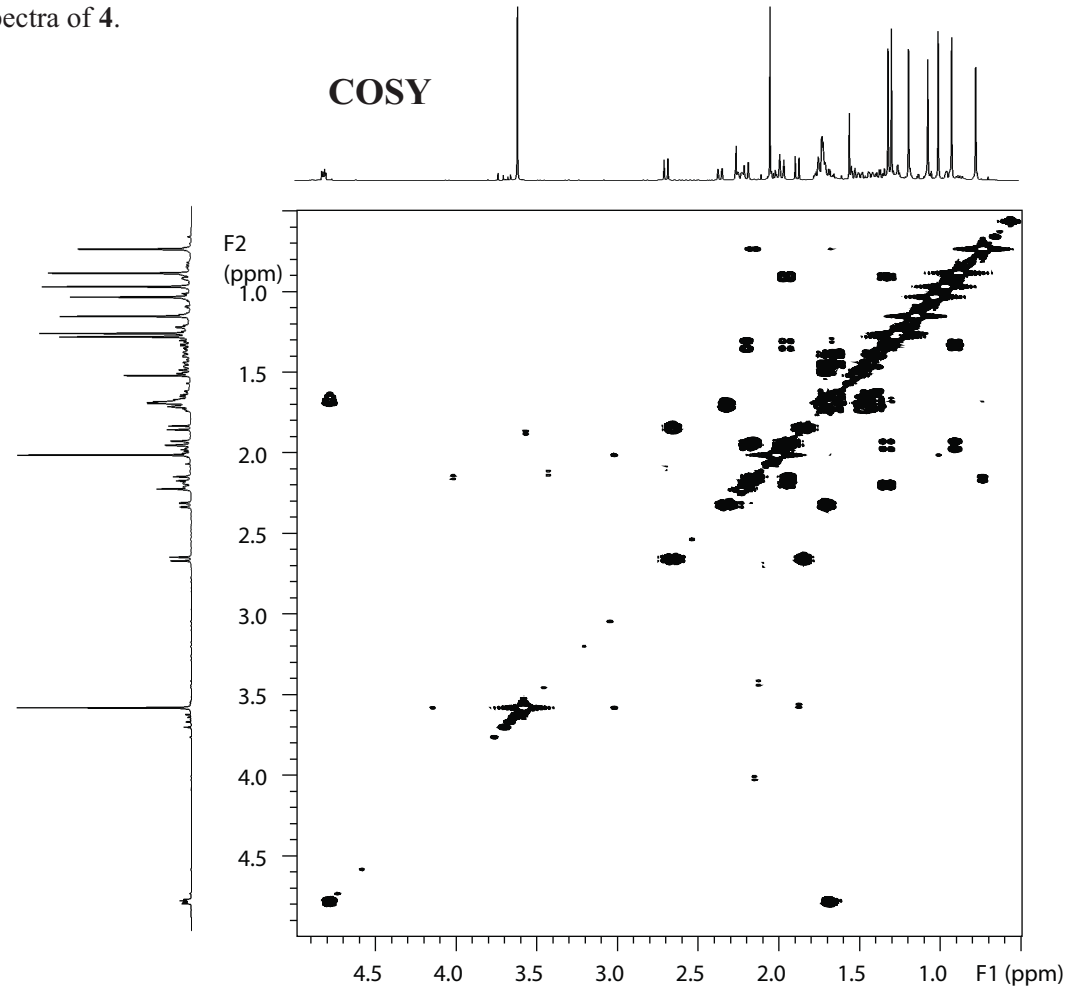


Figure S14. COSY and NOESY spectra of **4**.



4



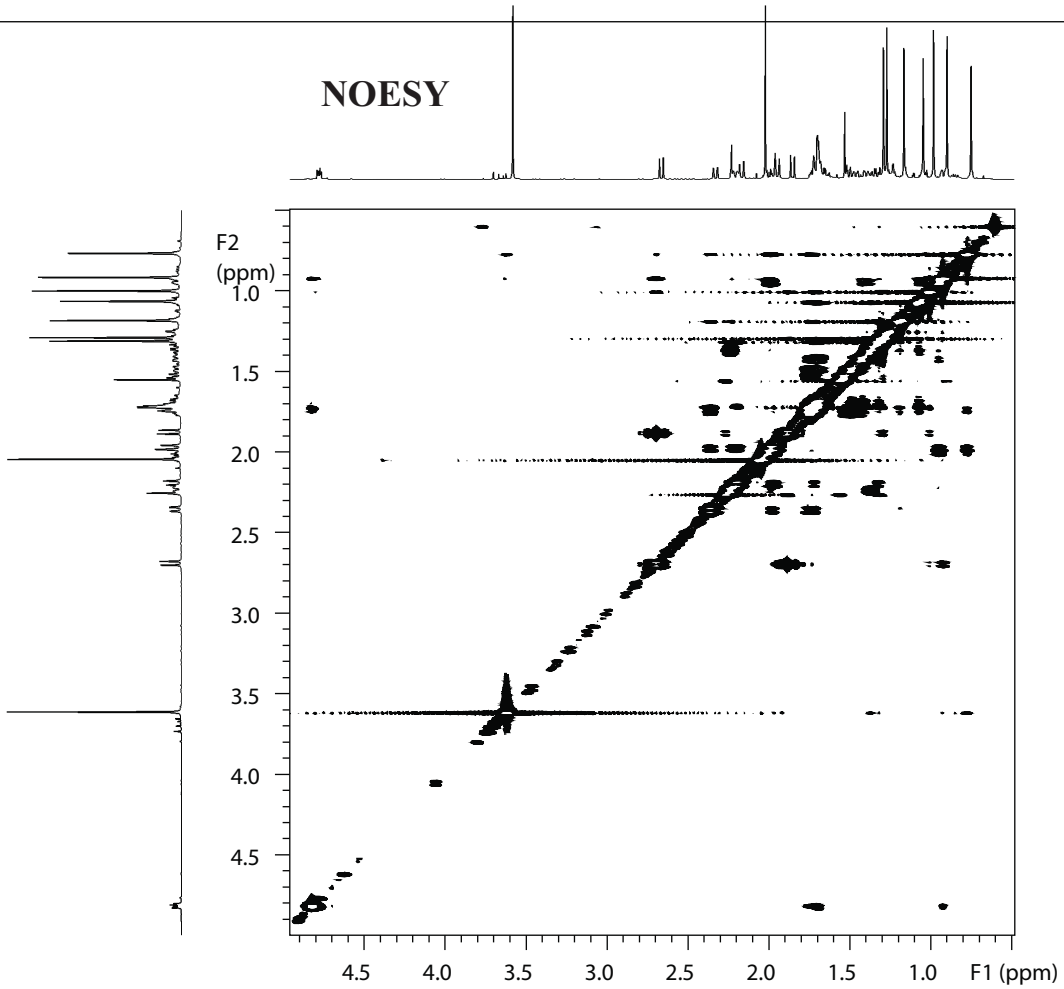
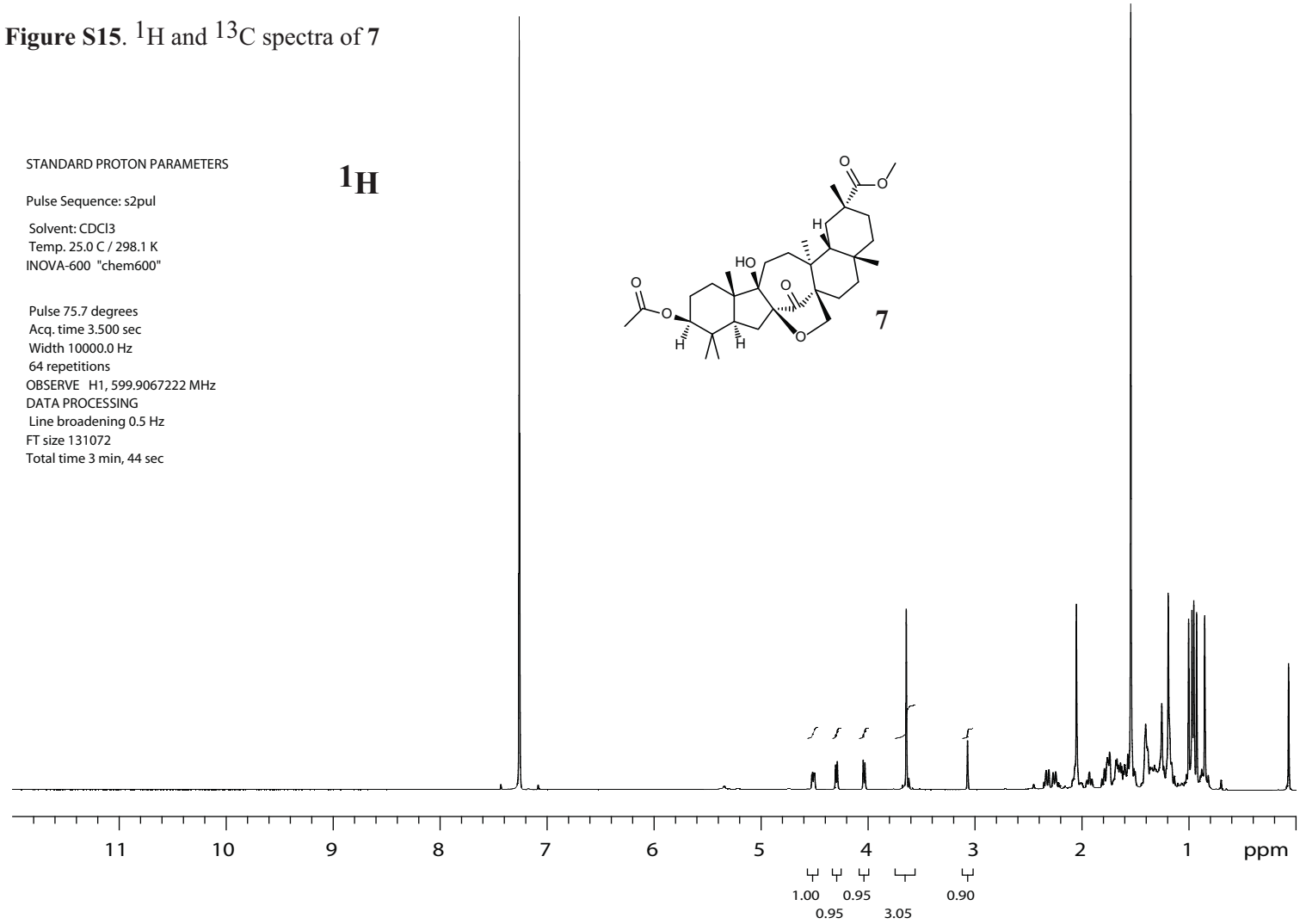


Figure S15. ^{1}H and ^{13}C spectra of **7**



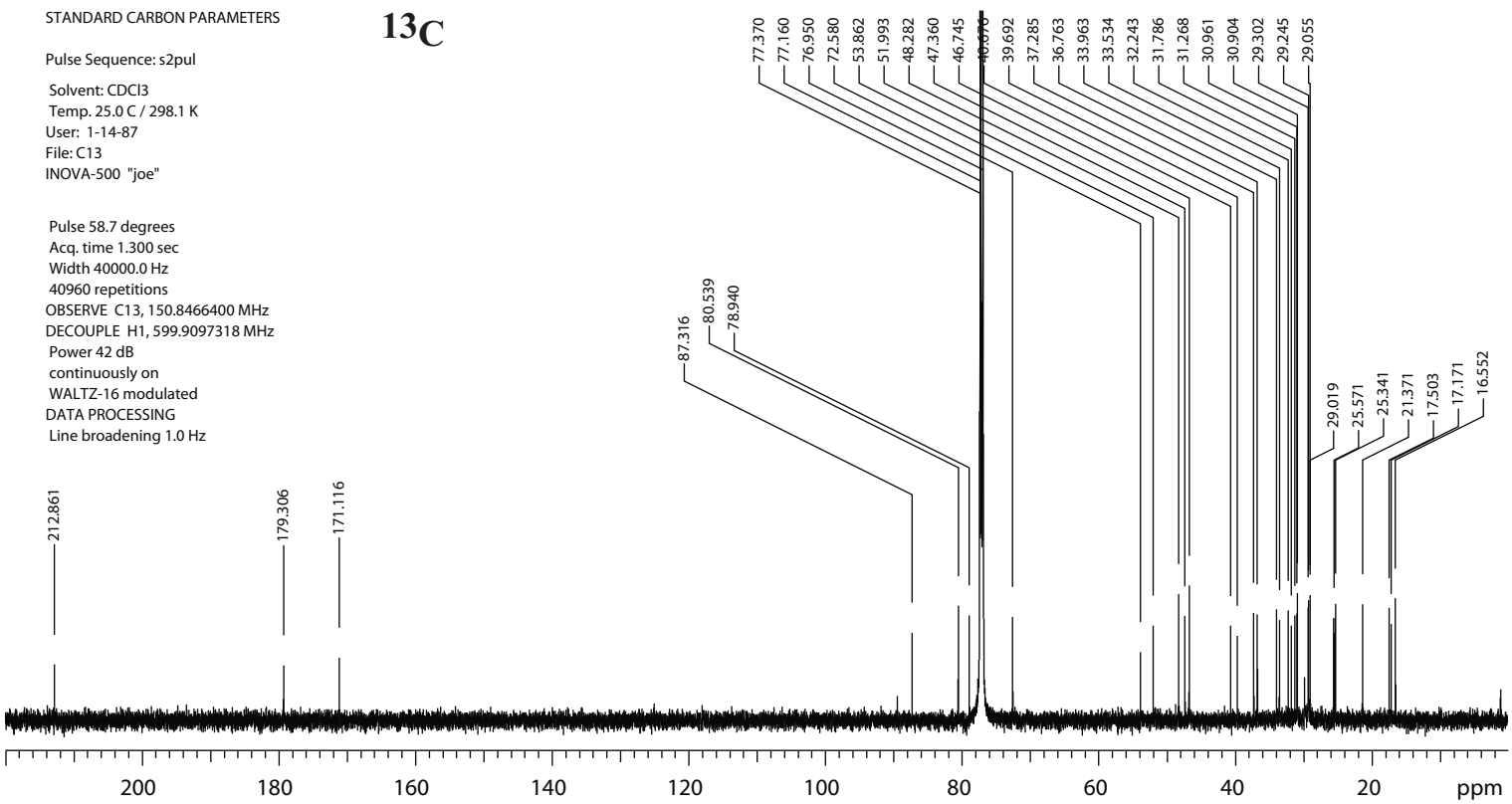
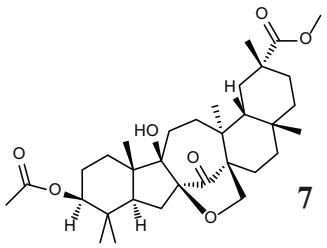


Figure S16. HMQC and HMBC spectra of **7**.



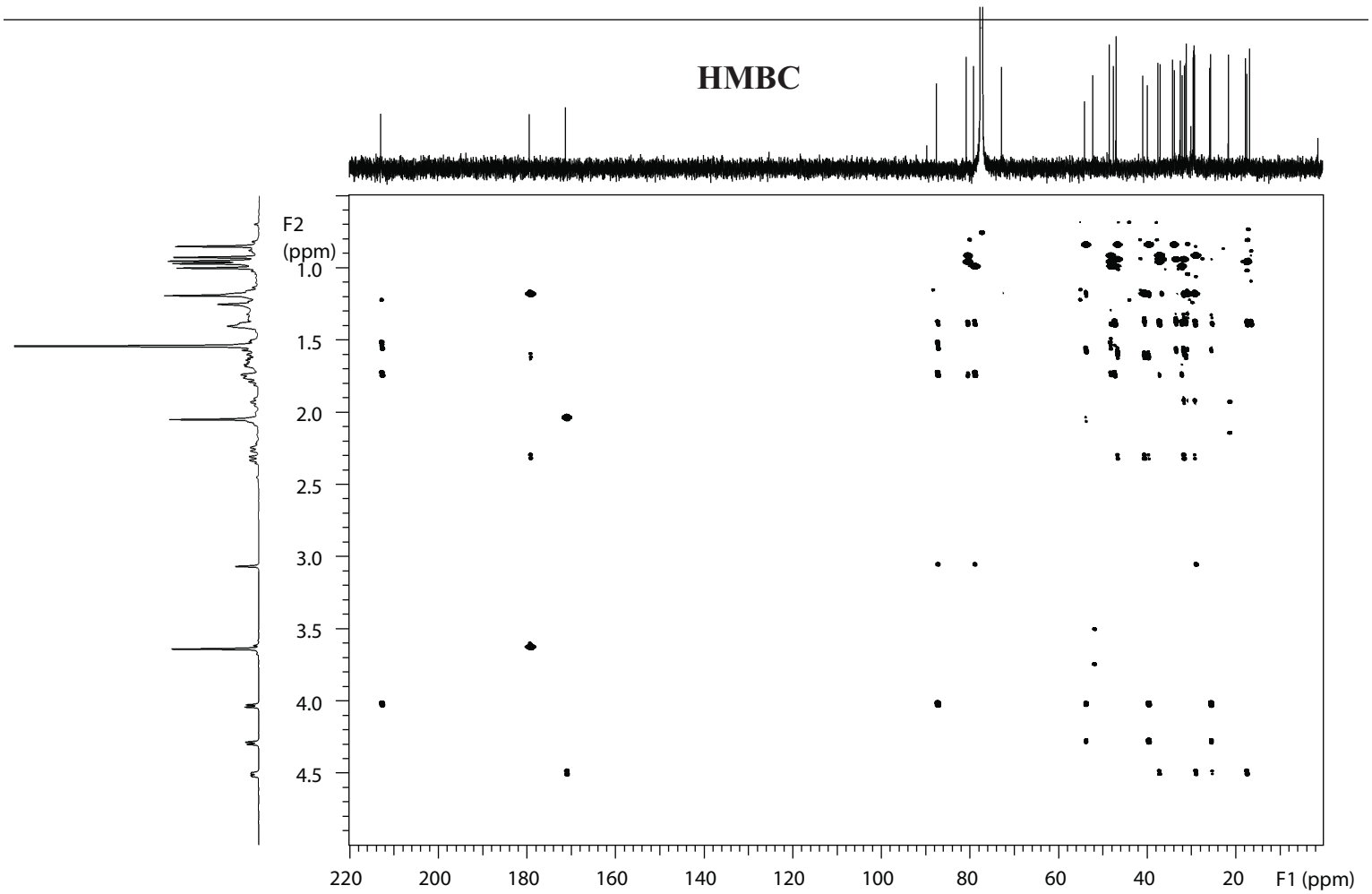
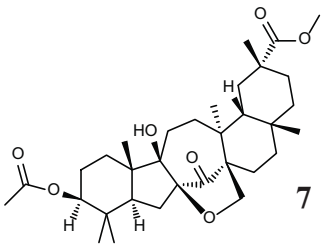


Figure S17. COSY and NOESY spectra of **7**.



7

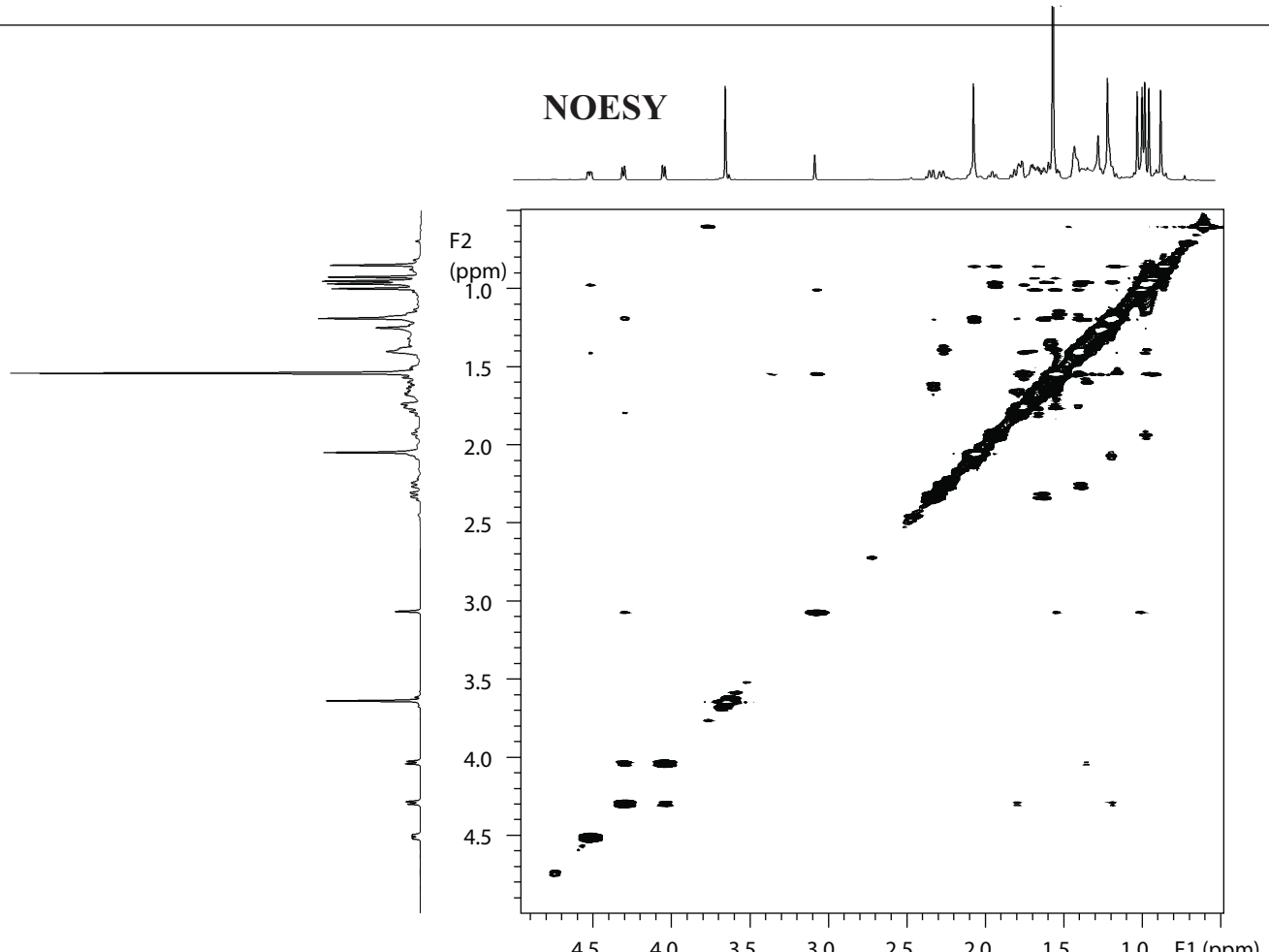
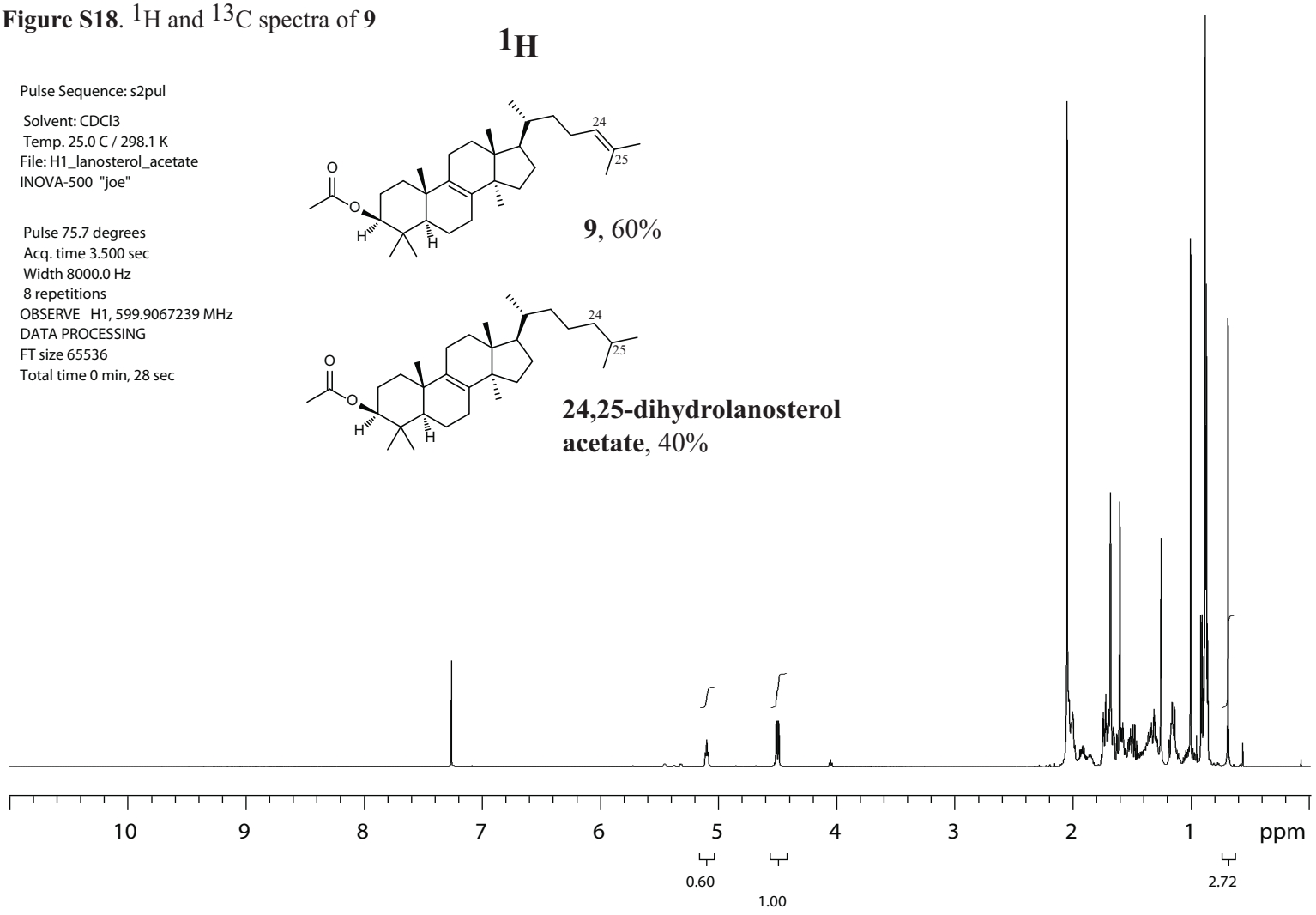


Figure S18. ^{1}H and ^{13}C spectra of **9**



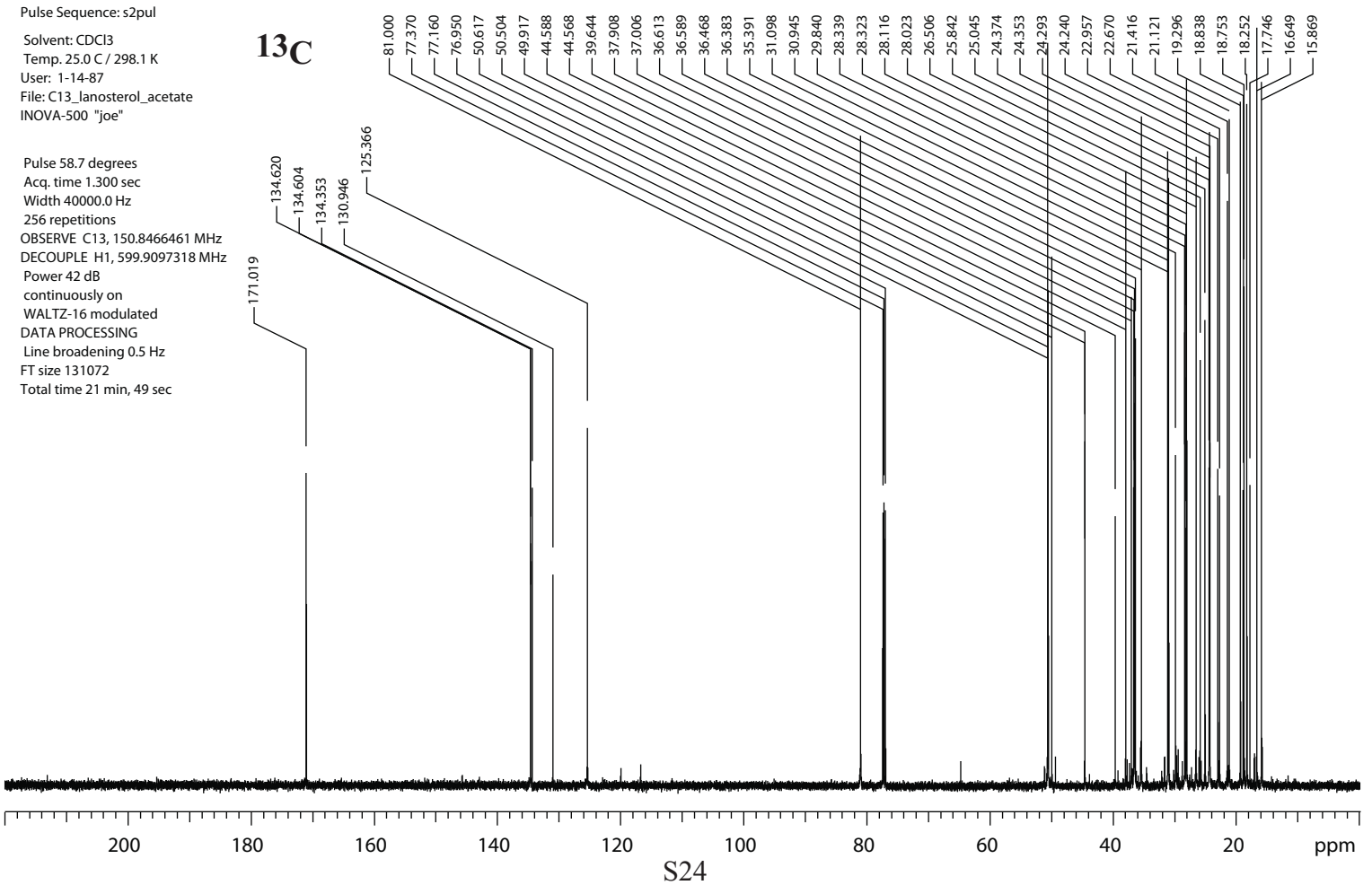
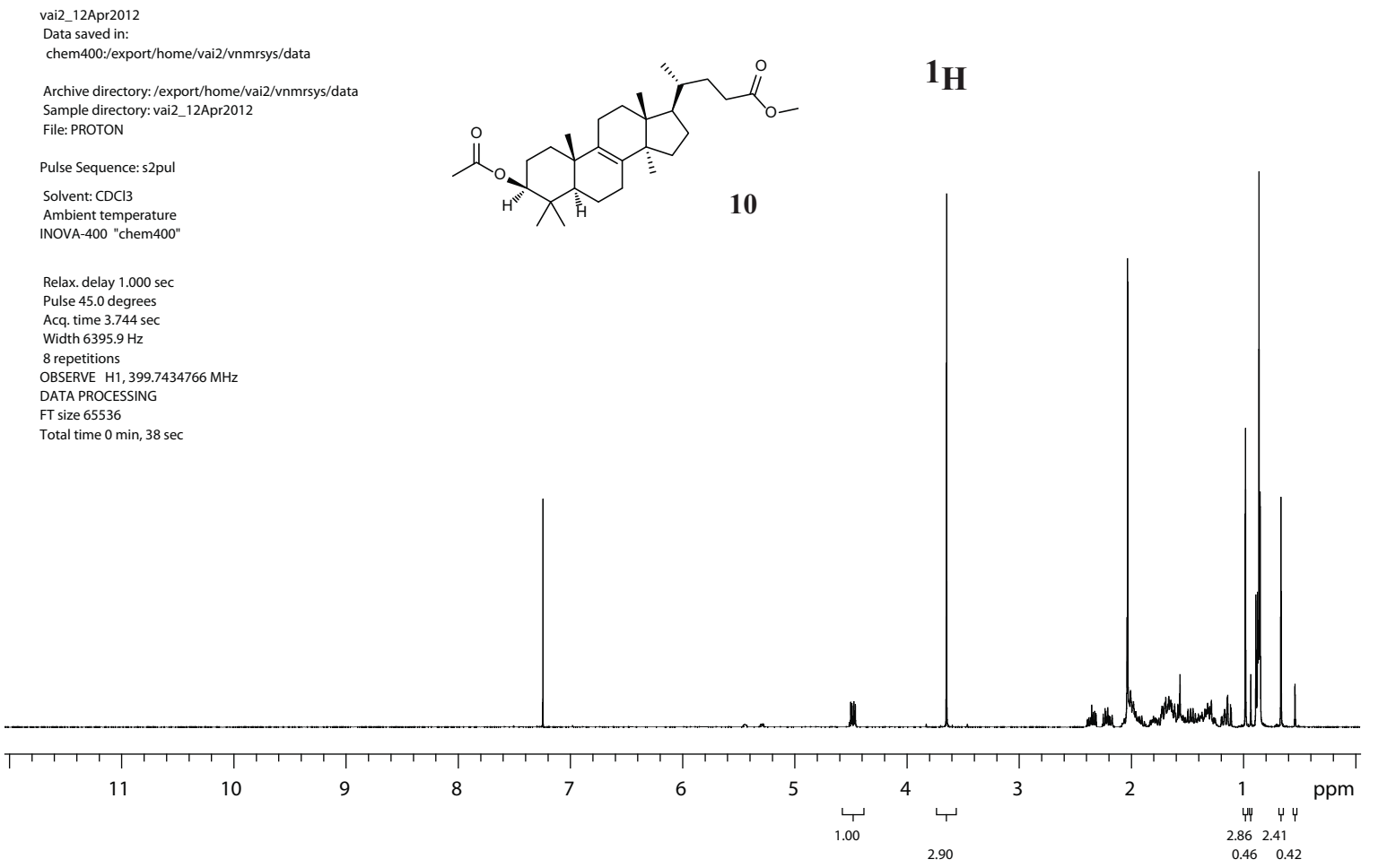


Figure S19. ^{1}H and ^{13}C spectra of **10**



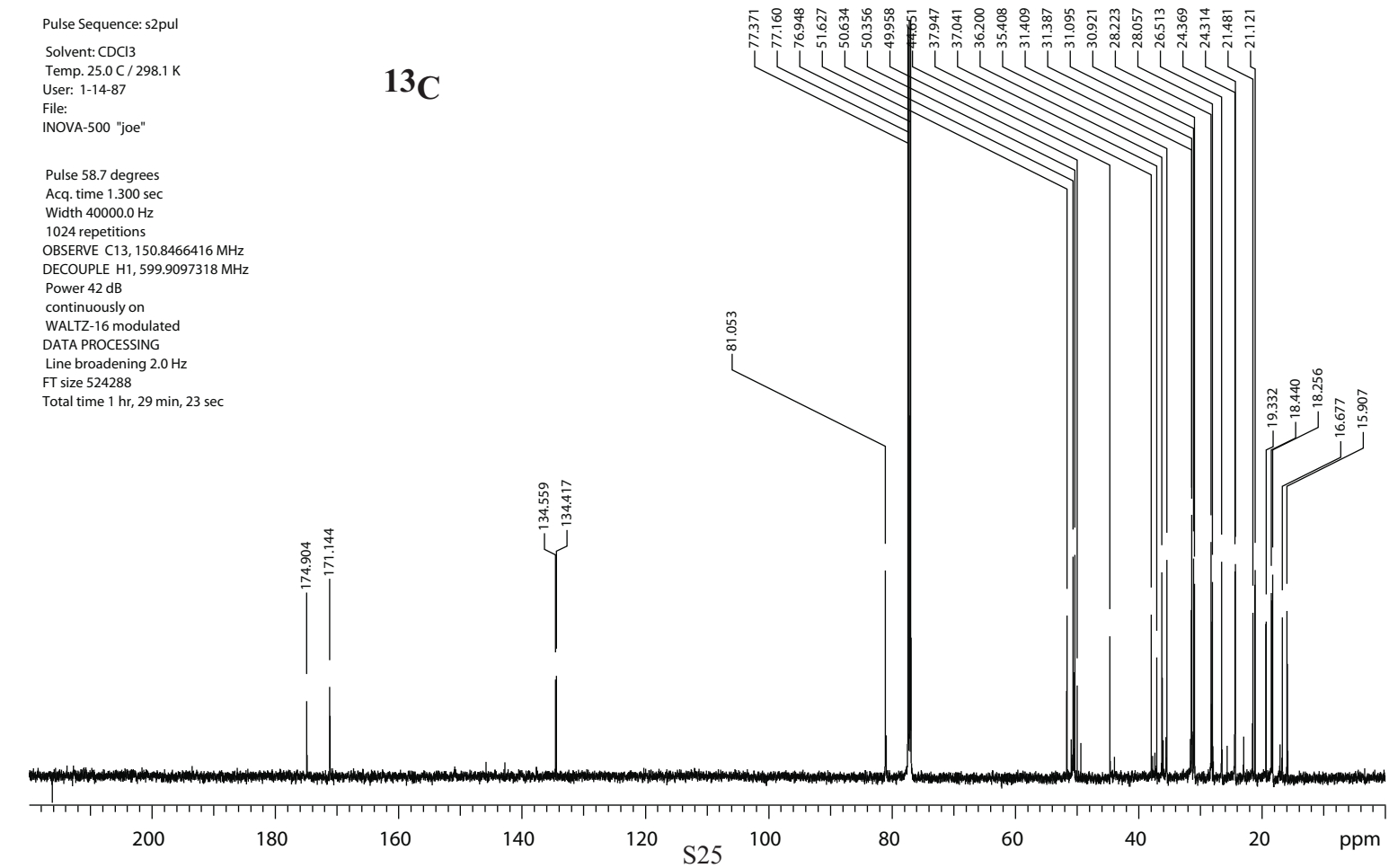
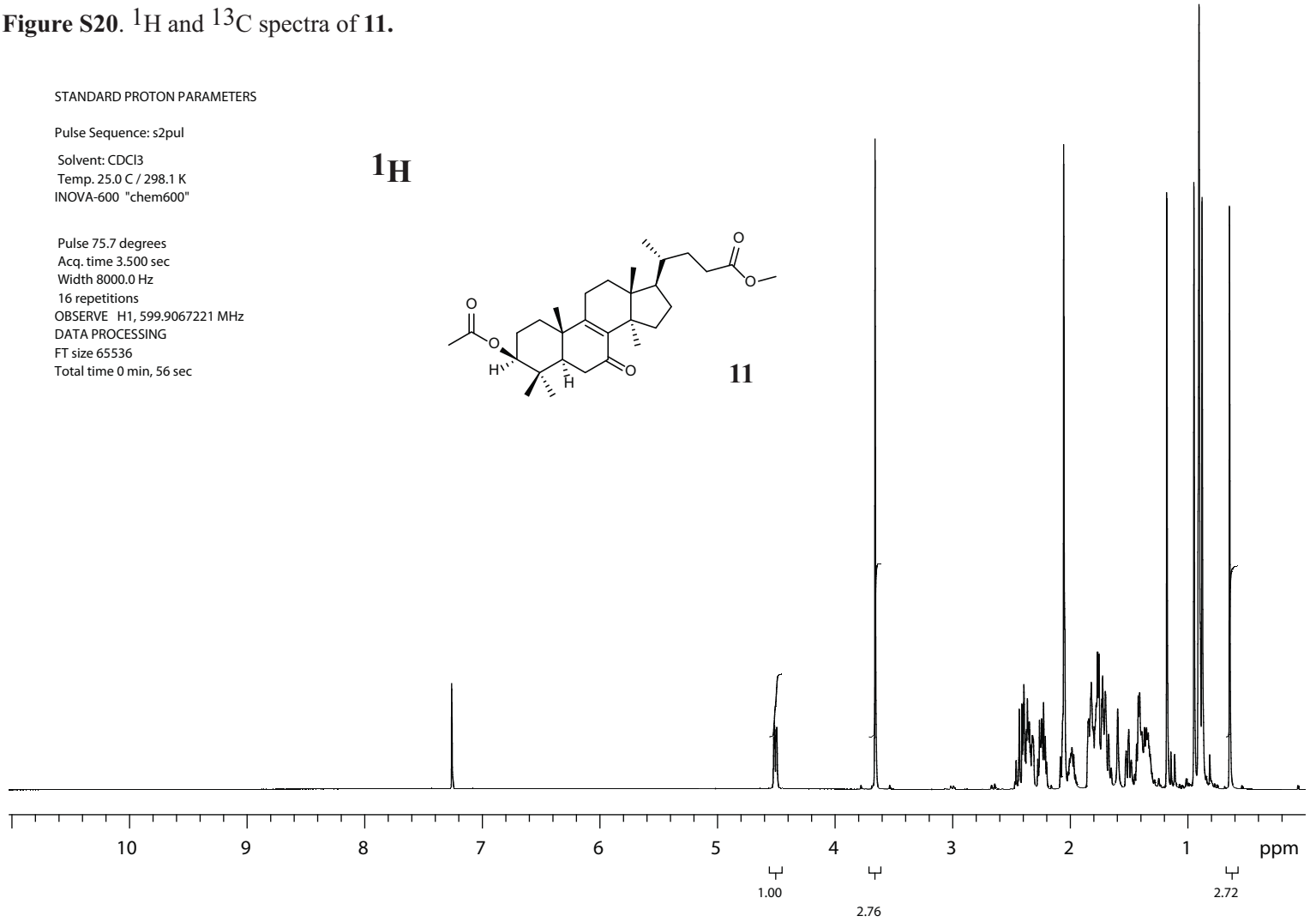


Figure S20. ^{1}H and ^{13}C spectra of **11.**



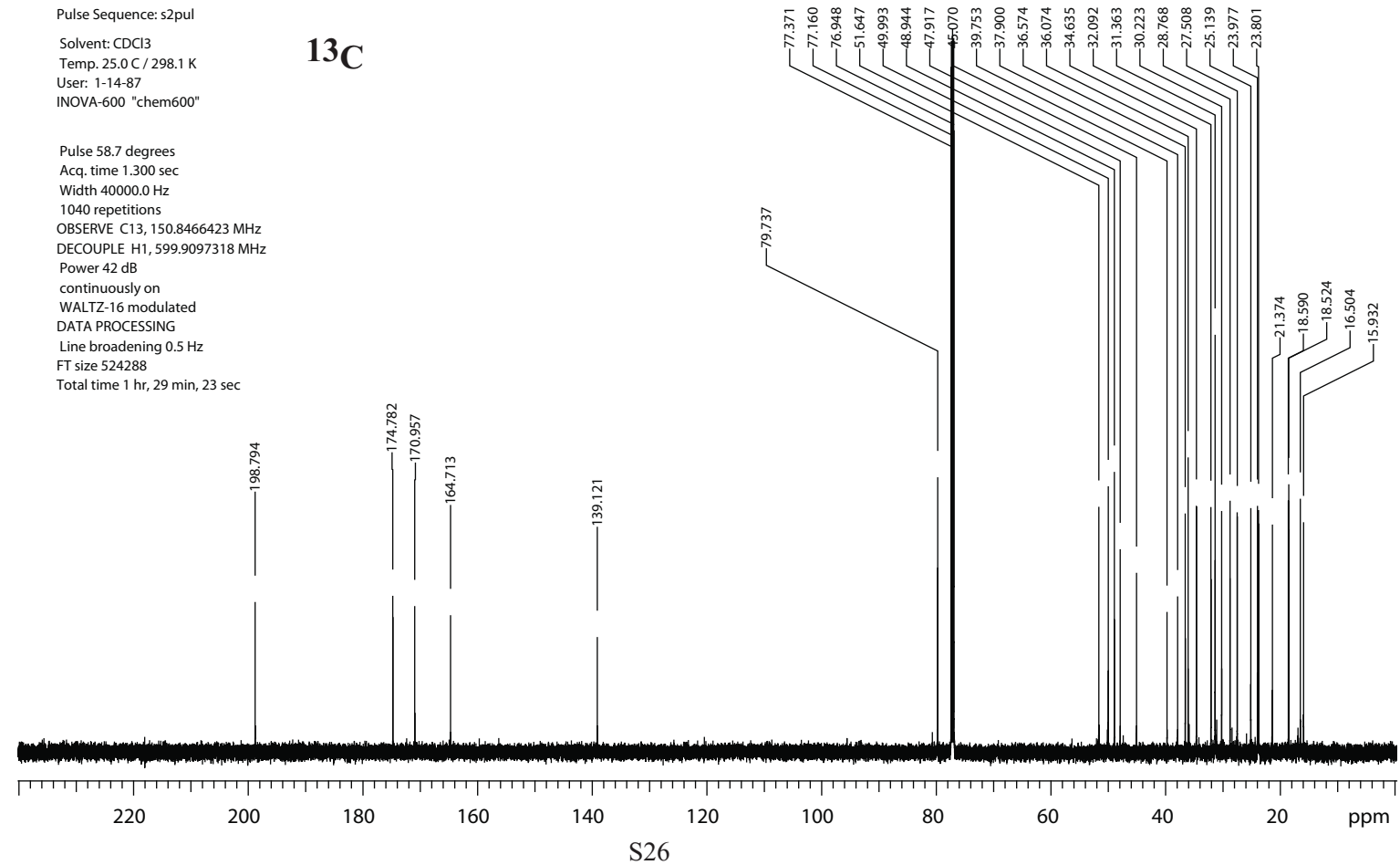
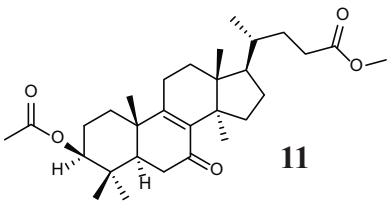


Figure S21. HMQC and HMBC spectra of **11**.



11

HMQC

HMBC

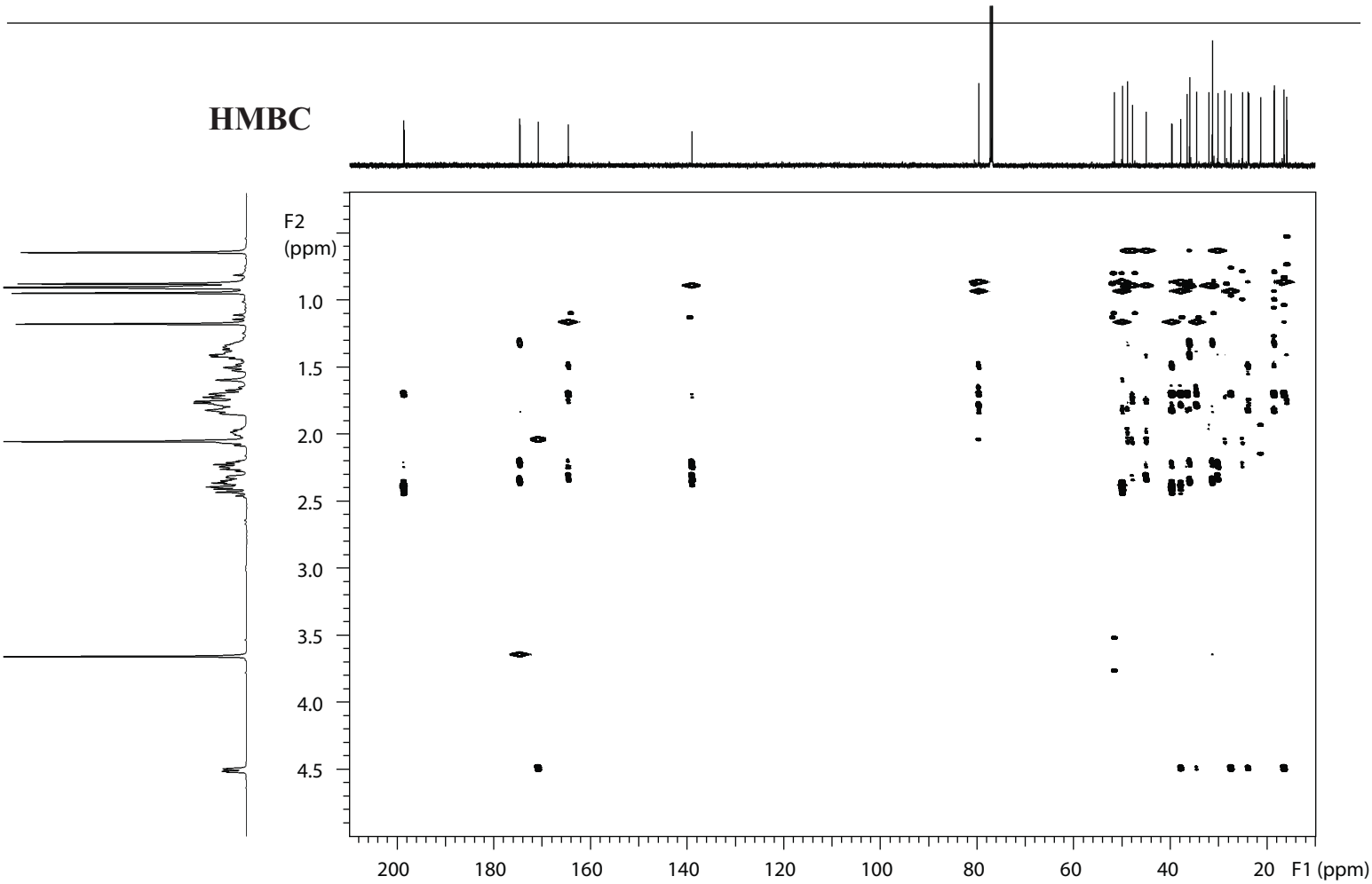
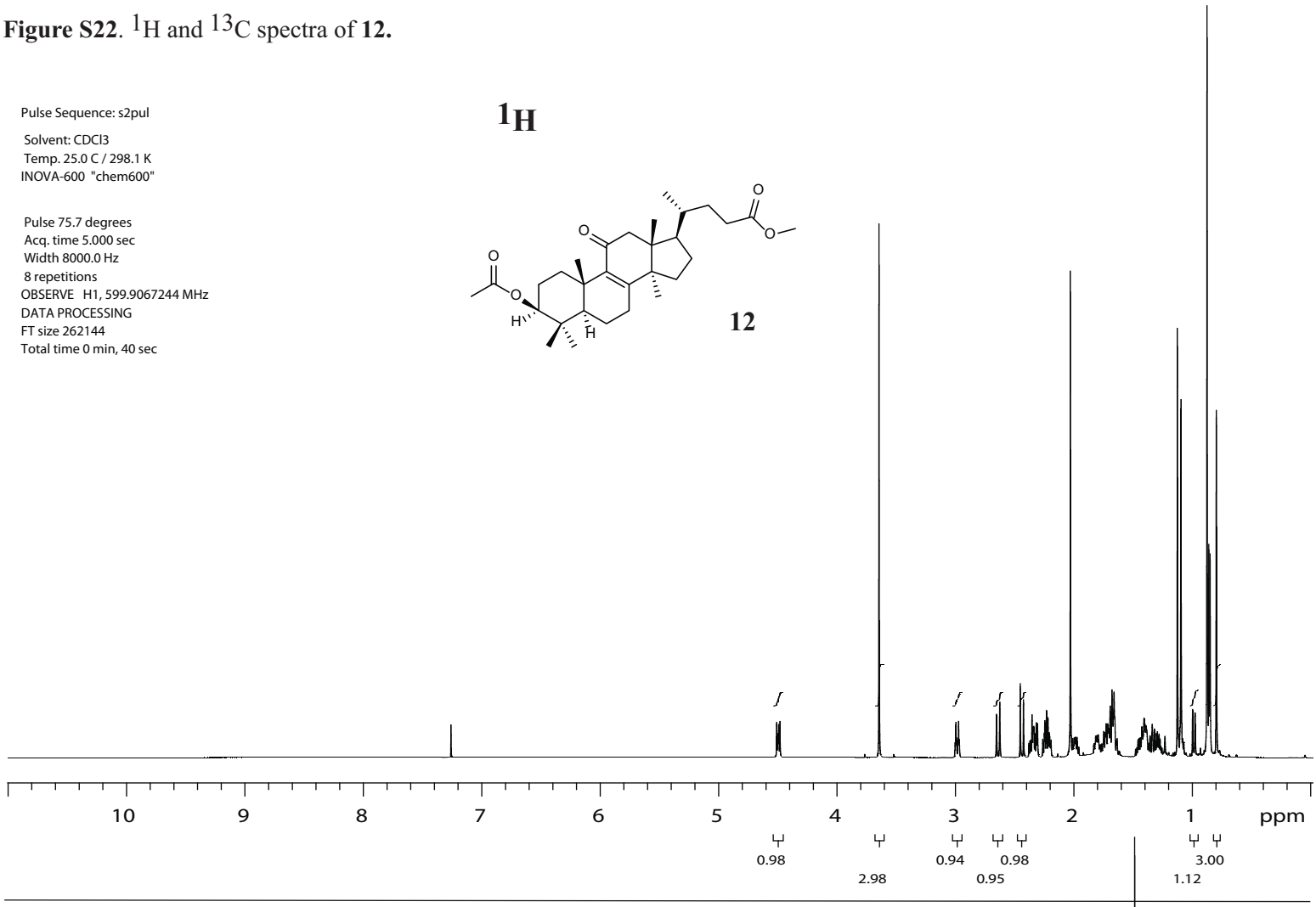


Figure S22. ^{1}H and ^{13}C spectra of **12.**



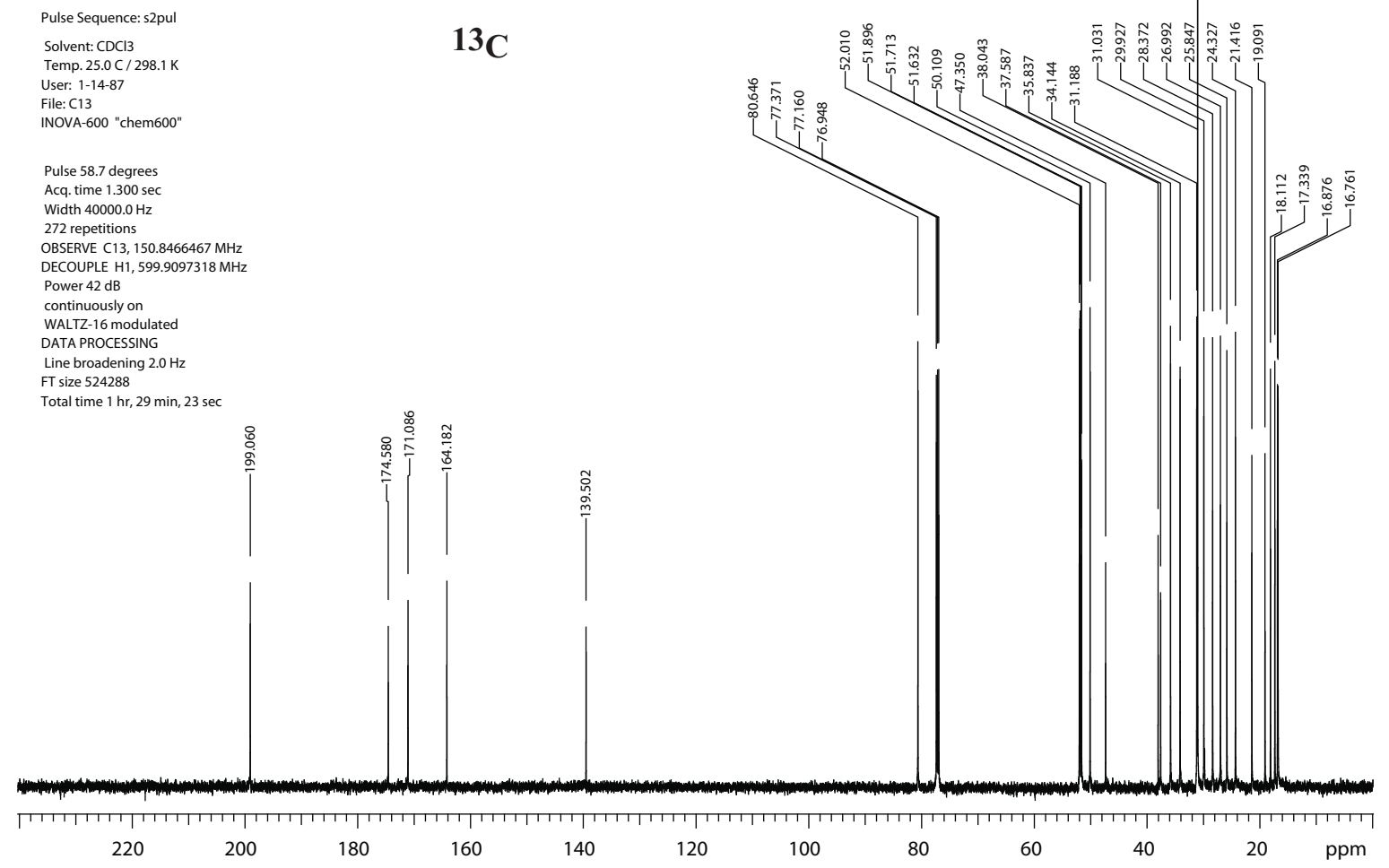
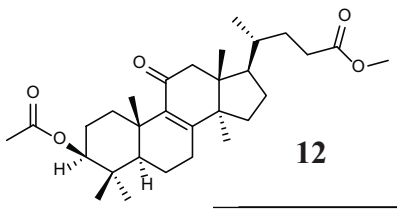


Figure S23. COSY and HMBC spectra of **12**.



12

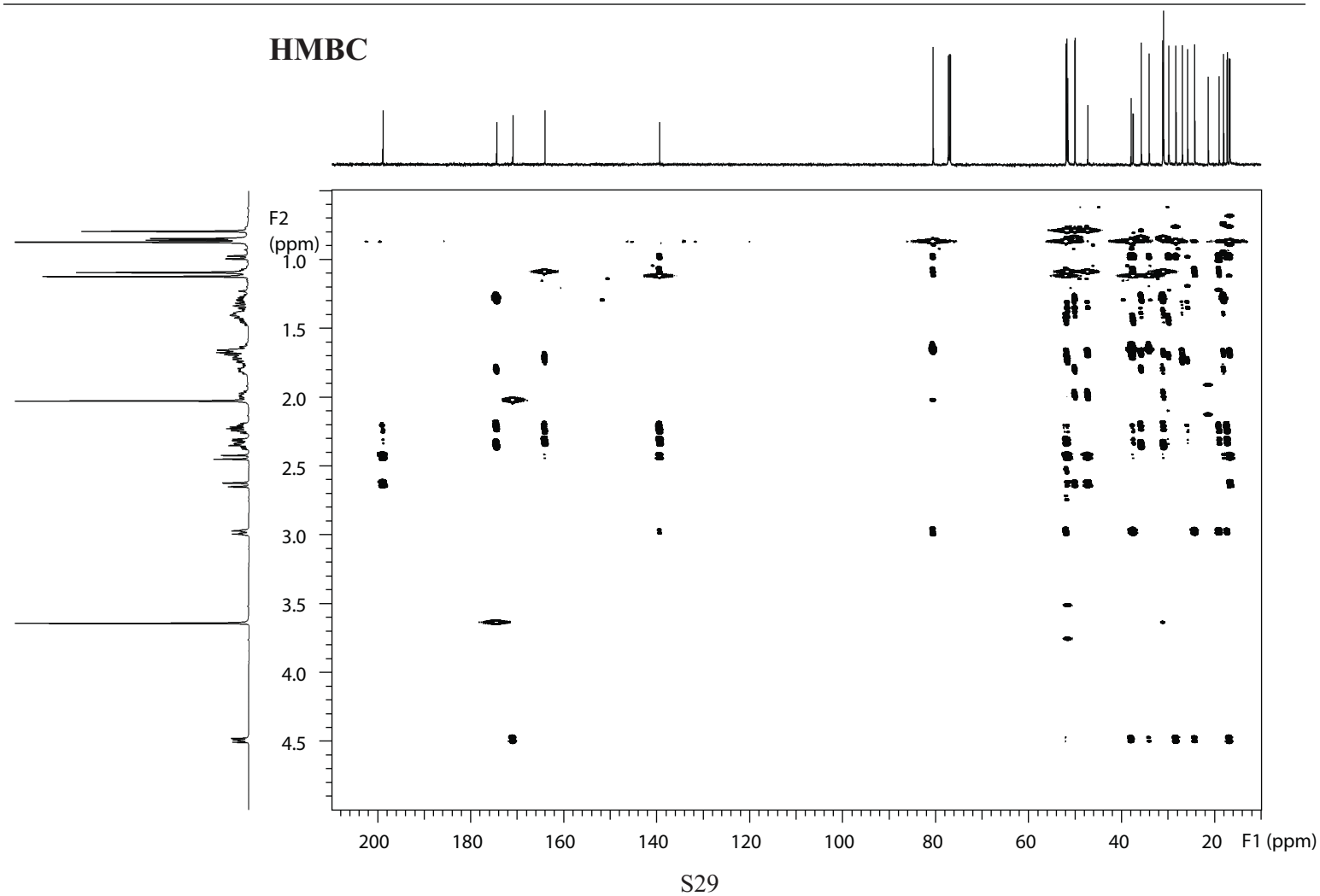
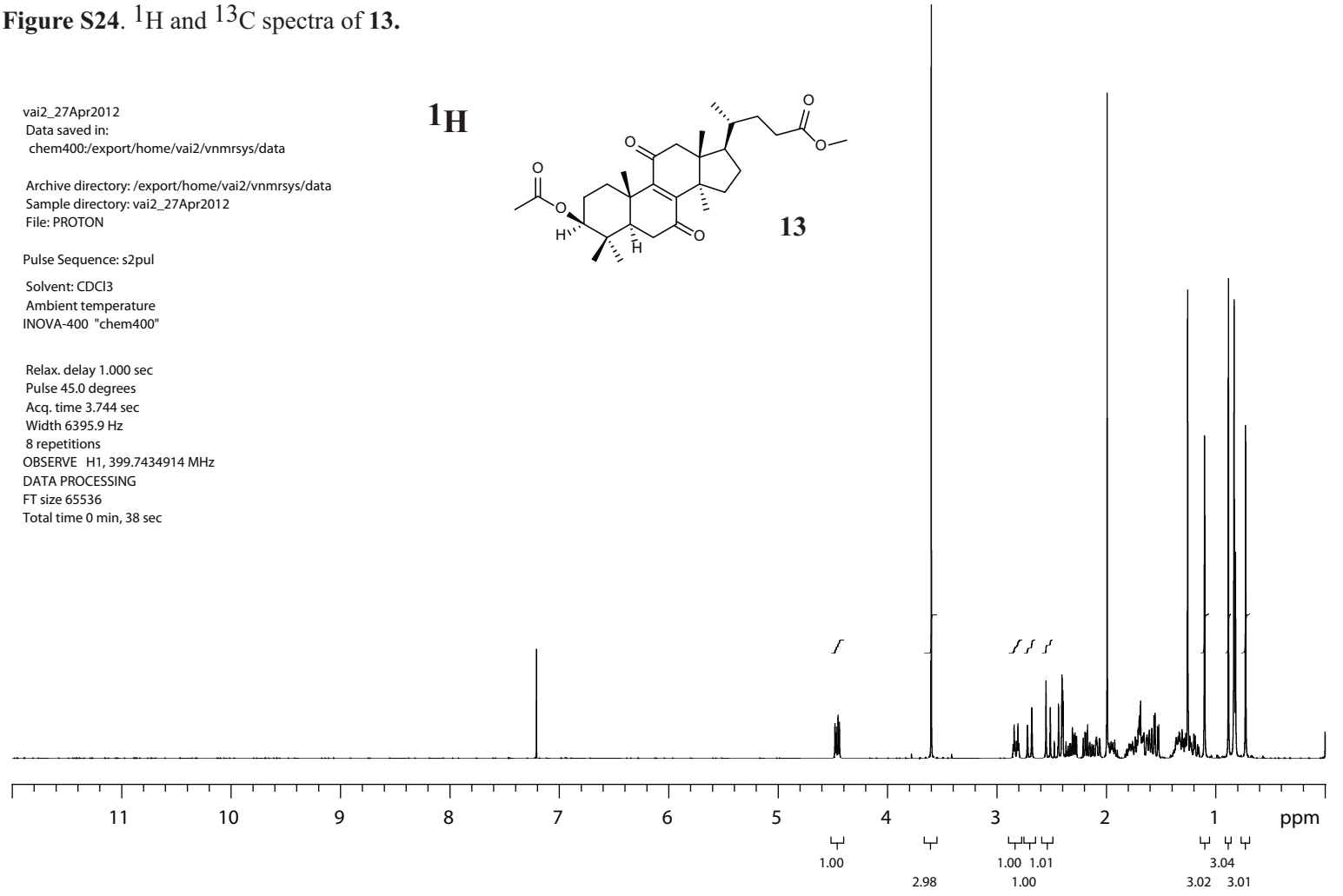


Figure S24. ^{1}H and ^{13}C spectra of **13.**



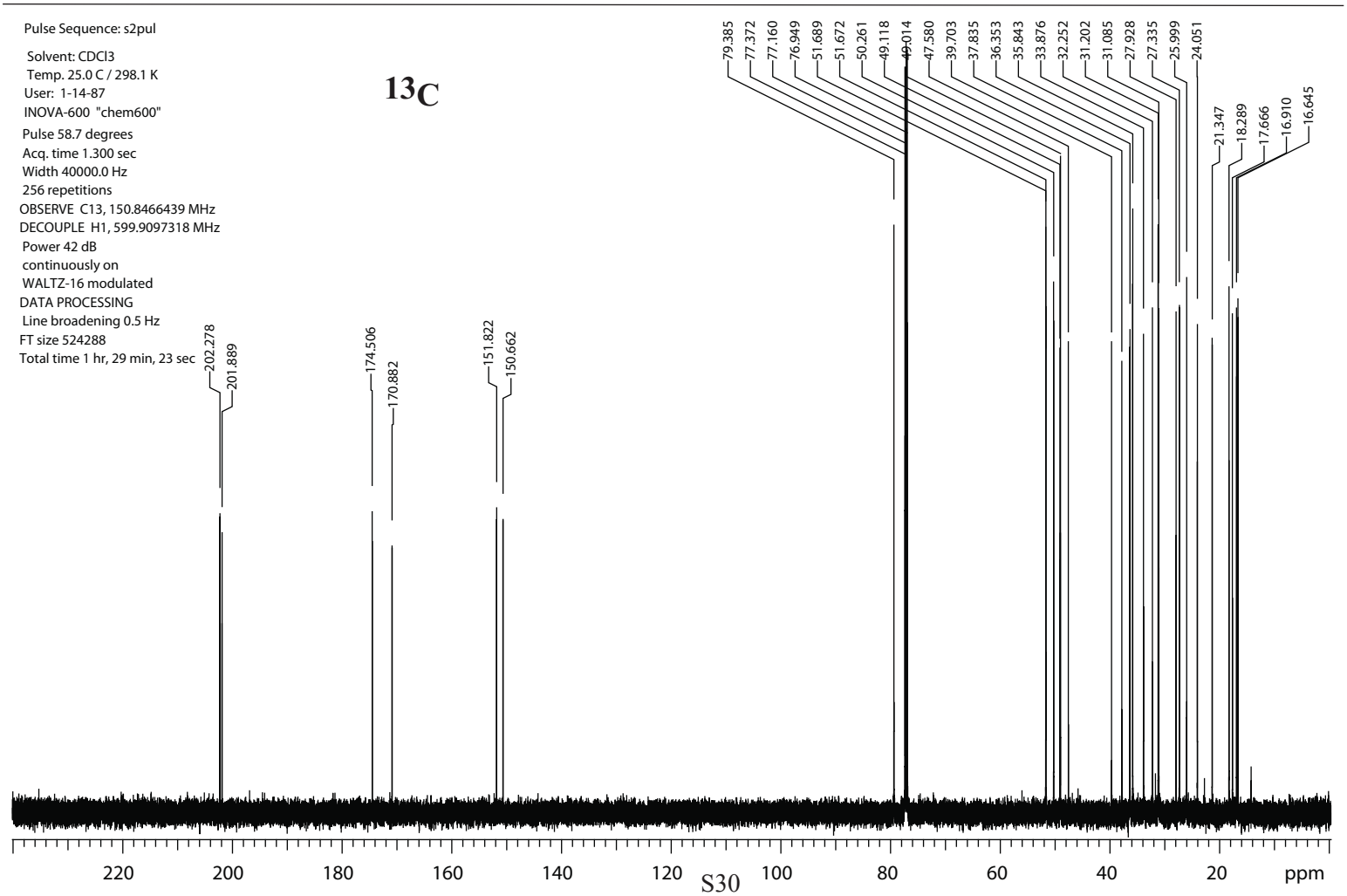
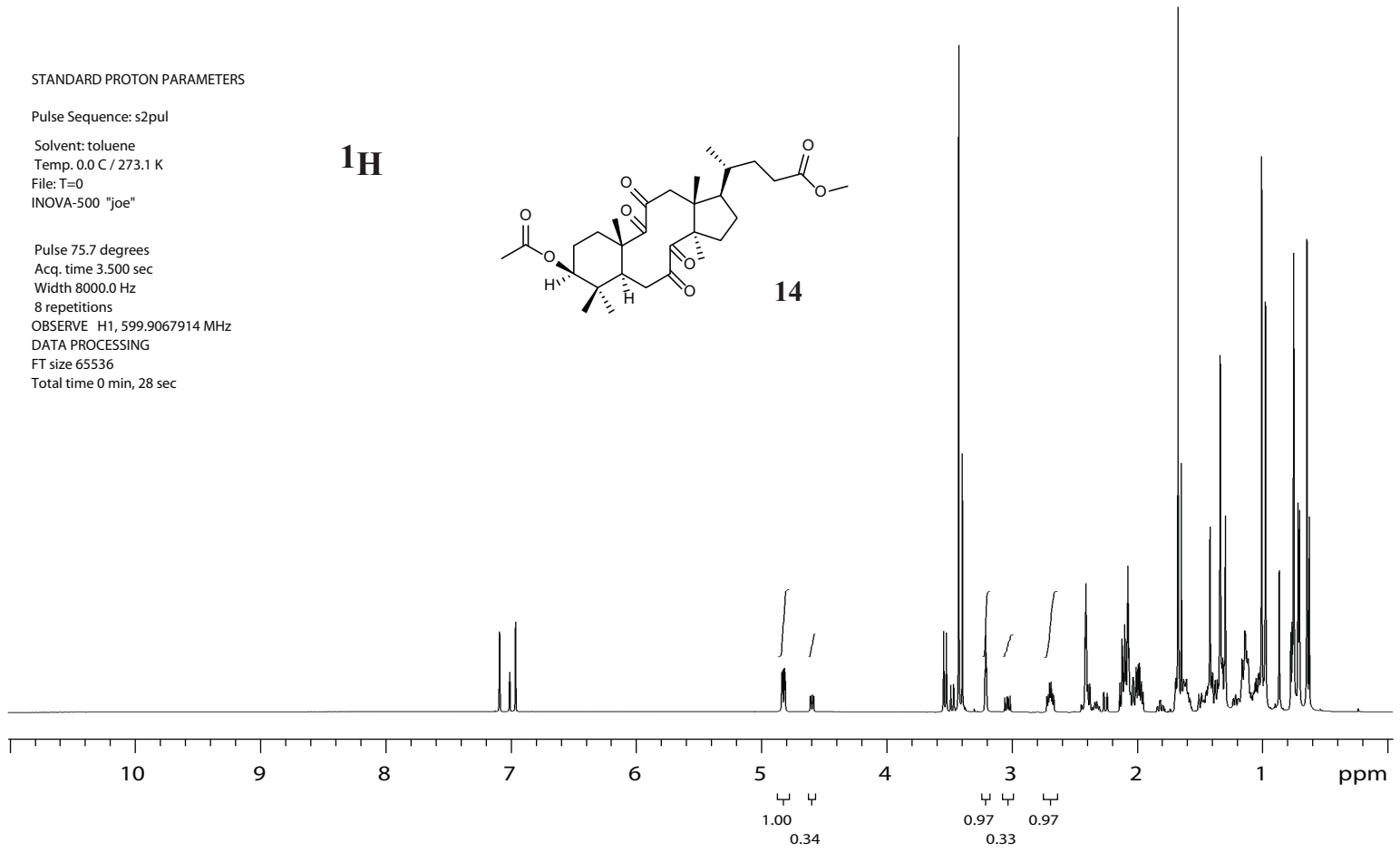


Figure S25. ^{1}H and ^{13}C spectra of **14.**



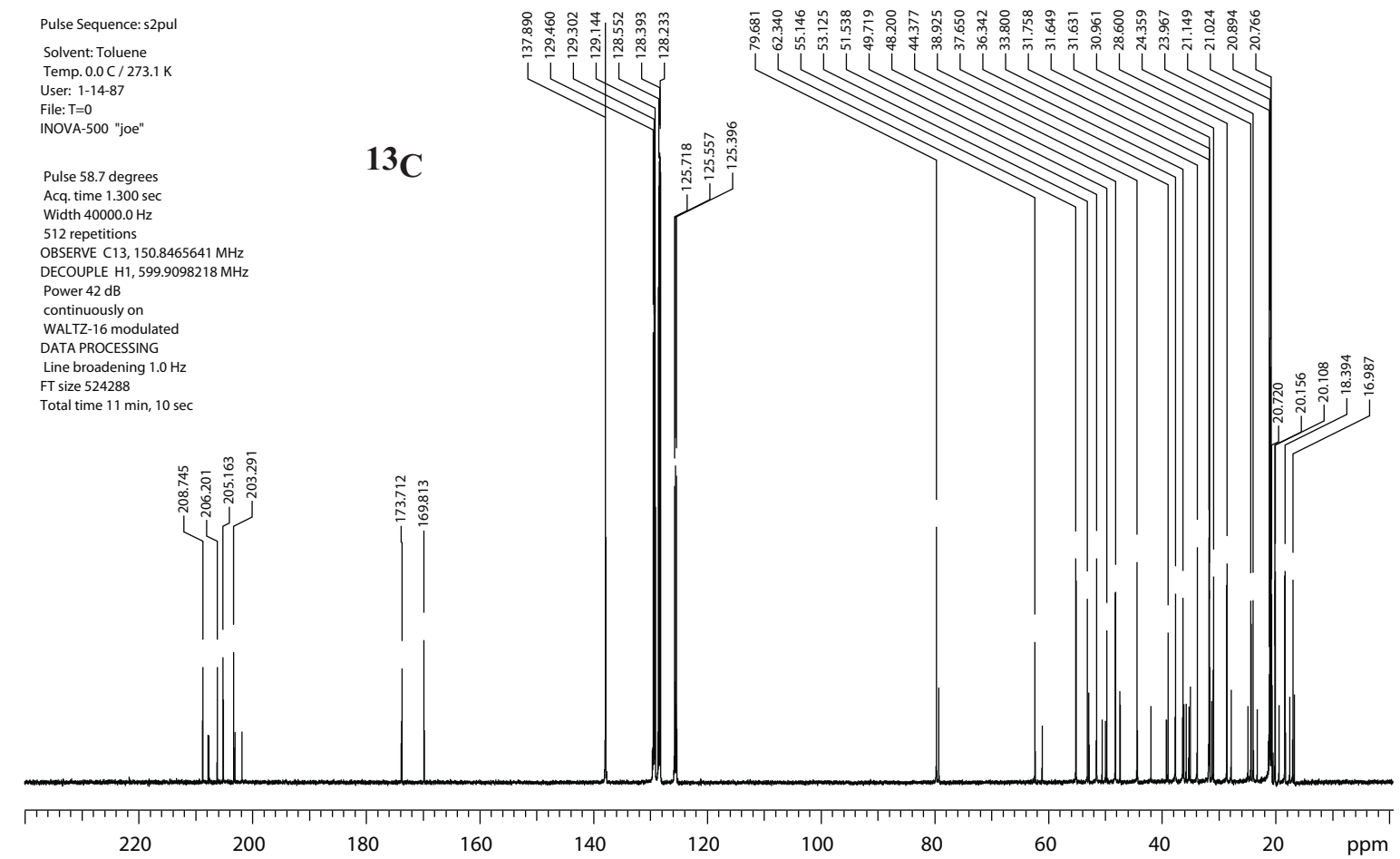
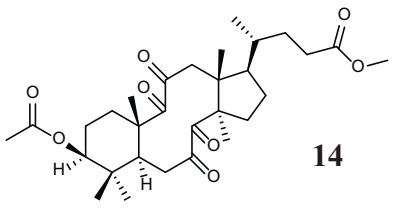


Figure S26. COSY and HMBC spectra of **14**.



14

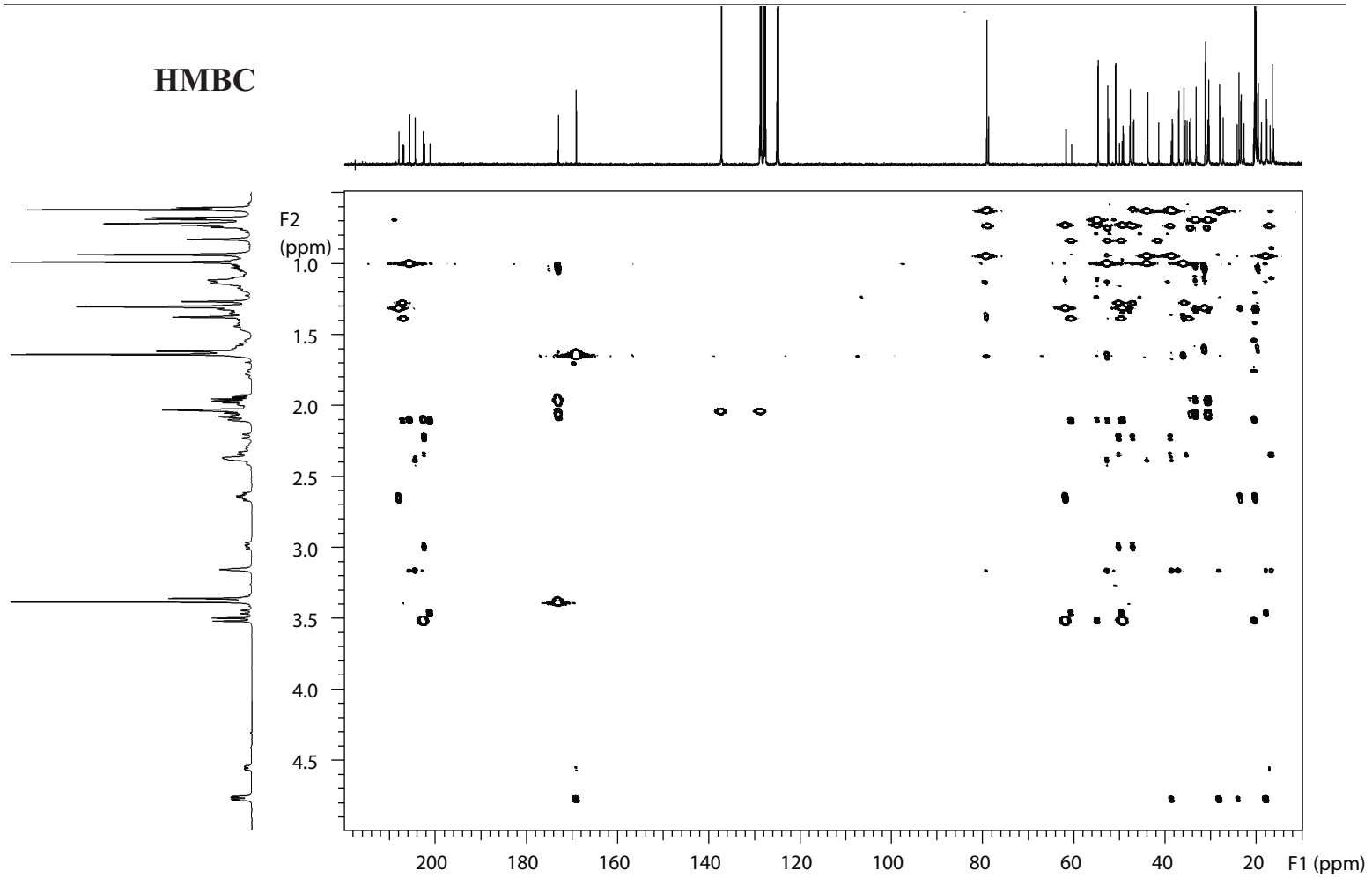
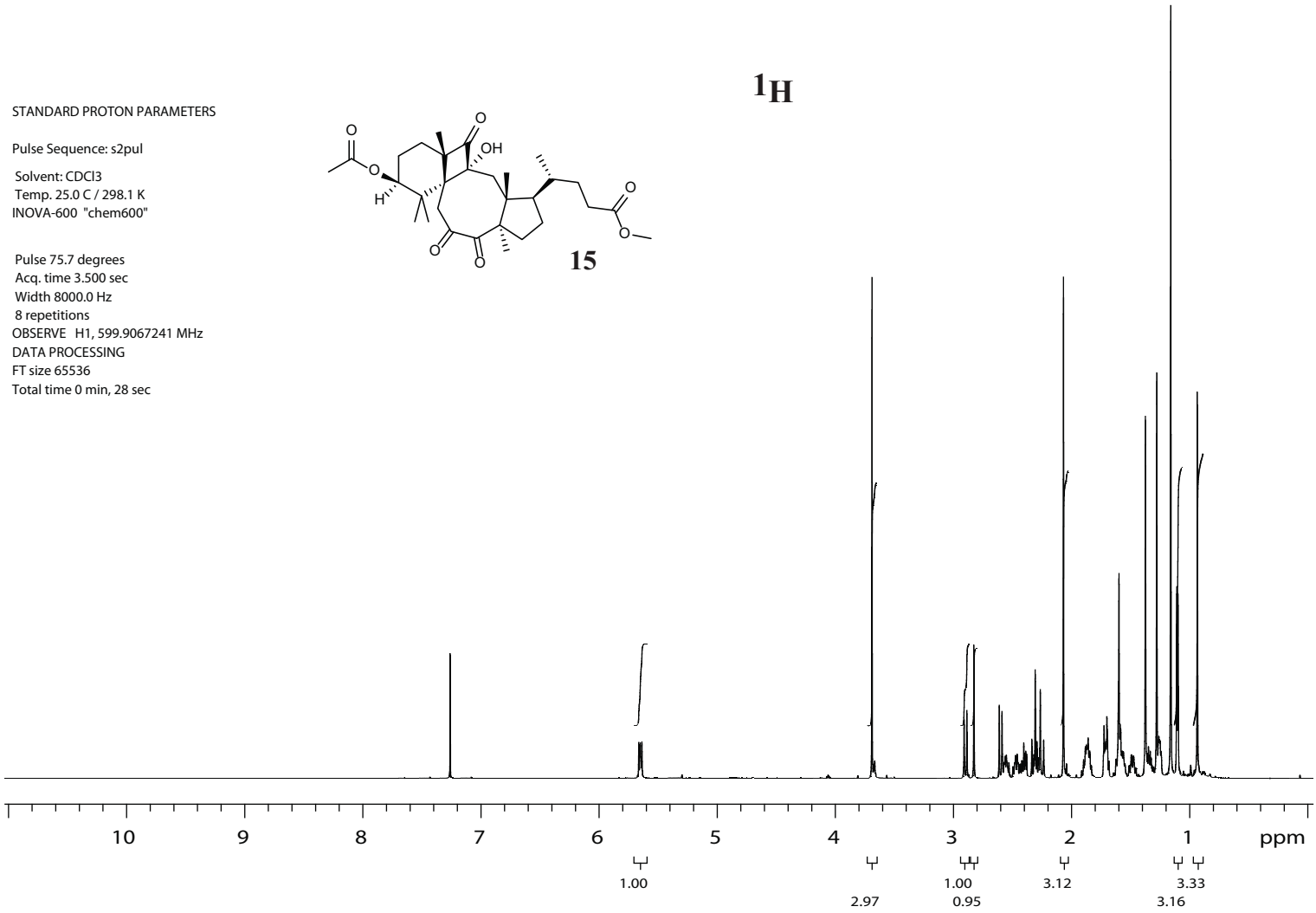


Figure S27. ^{1}H and ^{13}C spectra of **15**



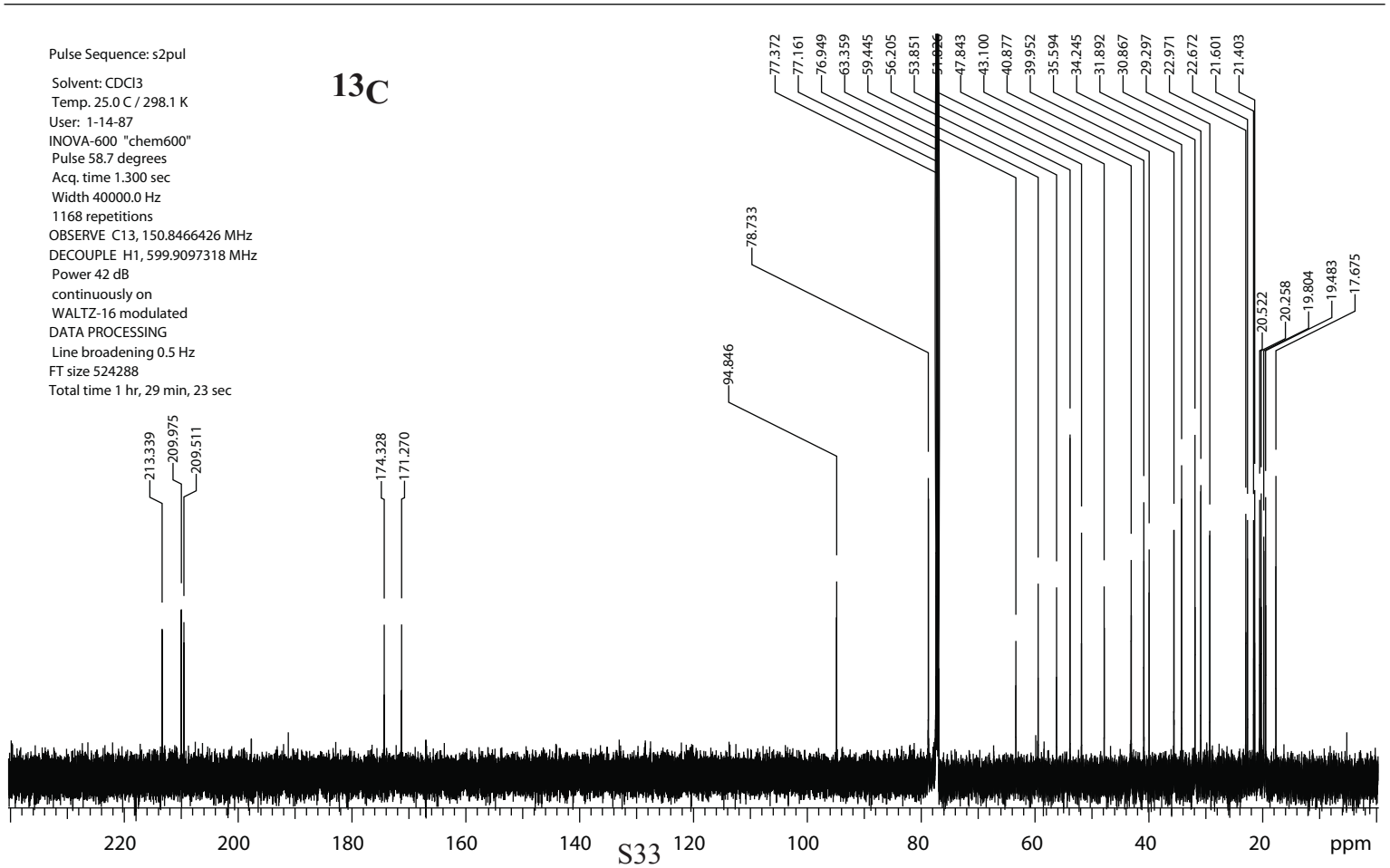
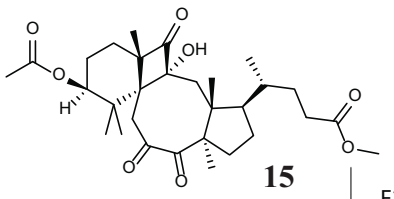


Figure S28. HMQC and HMBC spectra of **15**.



15

HMQC

F2 (ppm)

1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5

80 70 60 50 40 30 20 F1 (ppm)

HMBC

F2 (ppm)

1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5

220 200 180 160 140 120 100 80 60 40 20 F1 (ppm)

Figure S29. COSY and NOESY spectra of **15**.

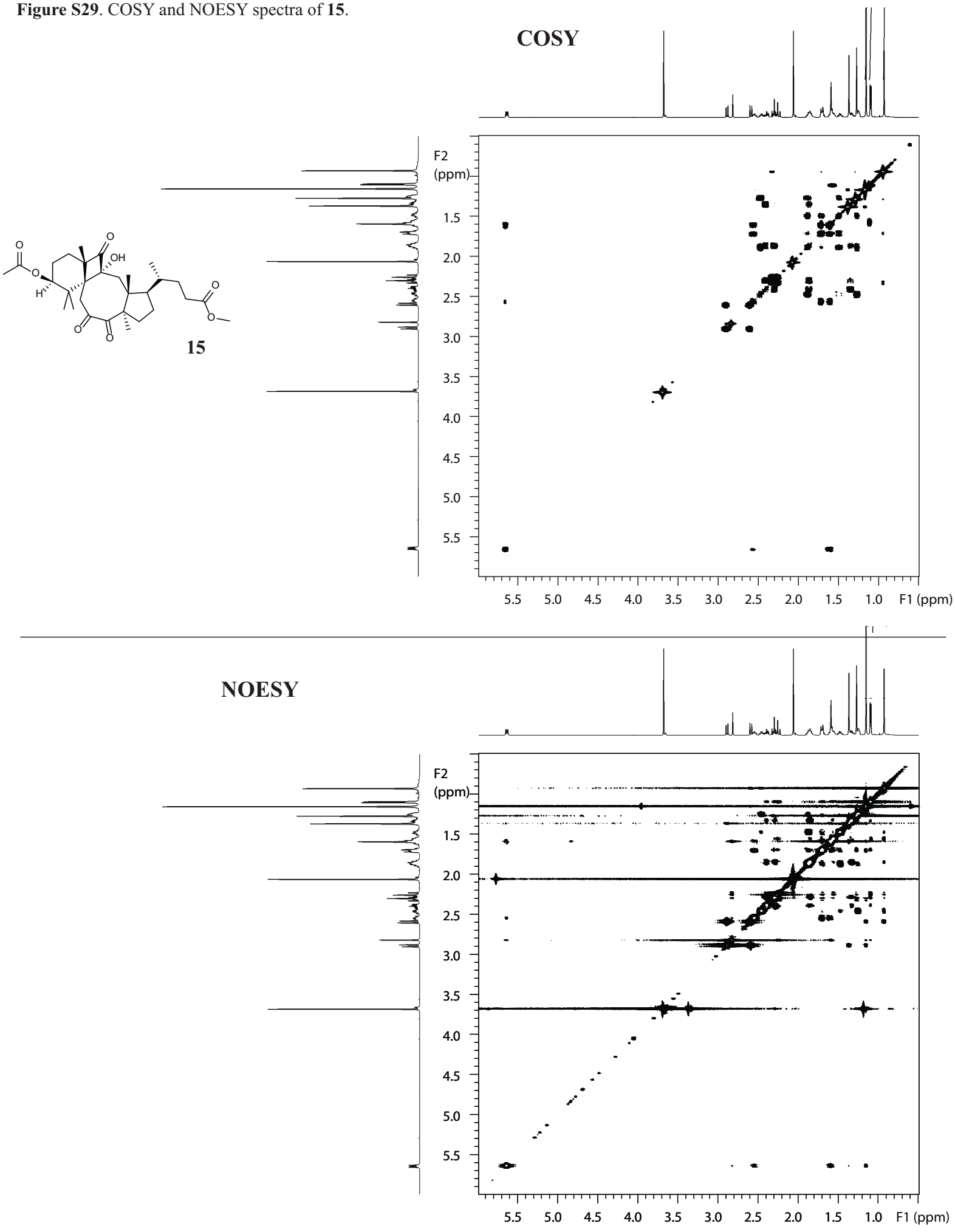
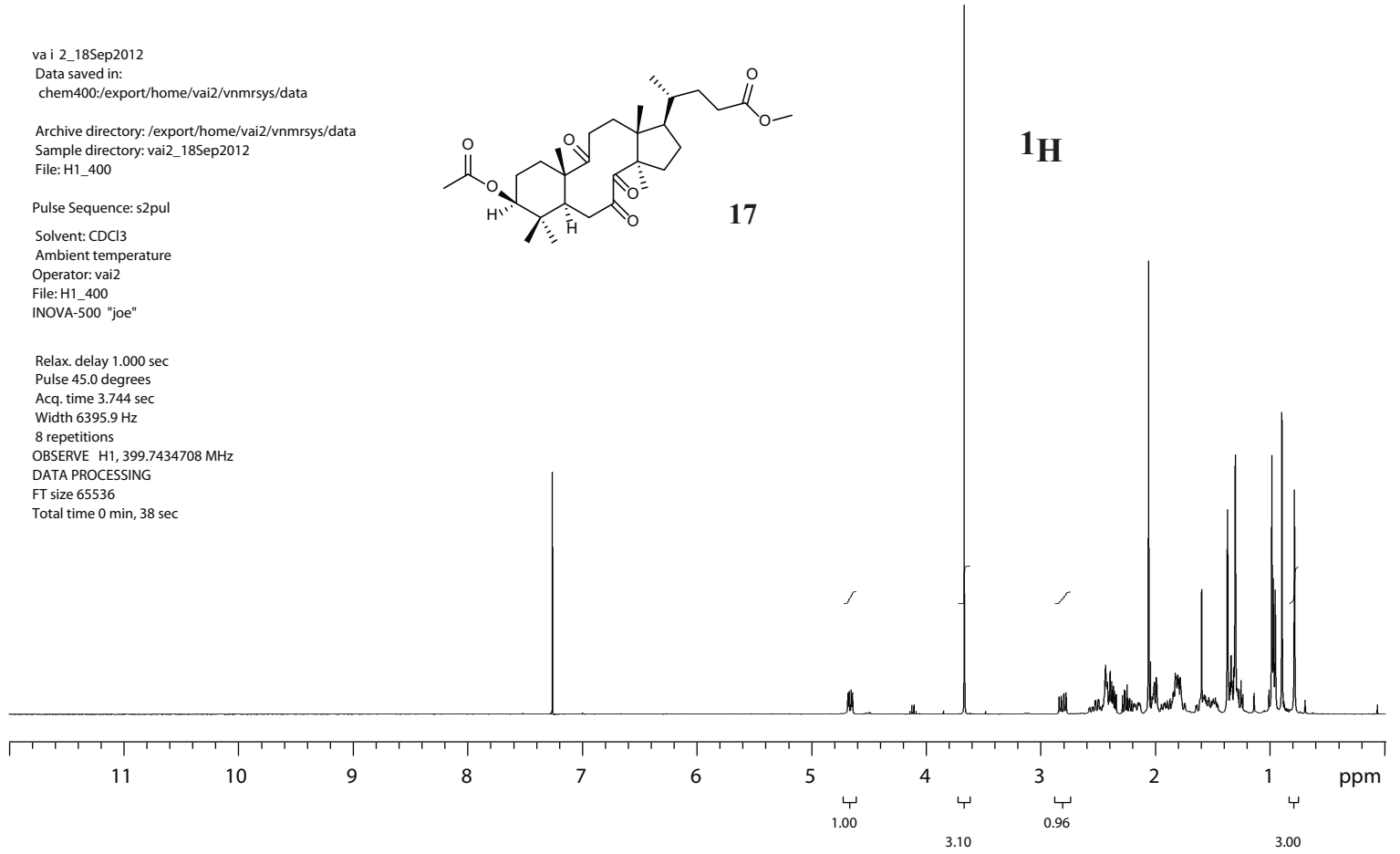


Figure S30. ^{1}H and ^{13}C spectra of **17**



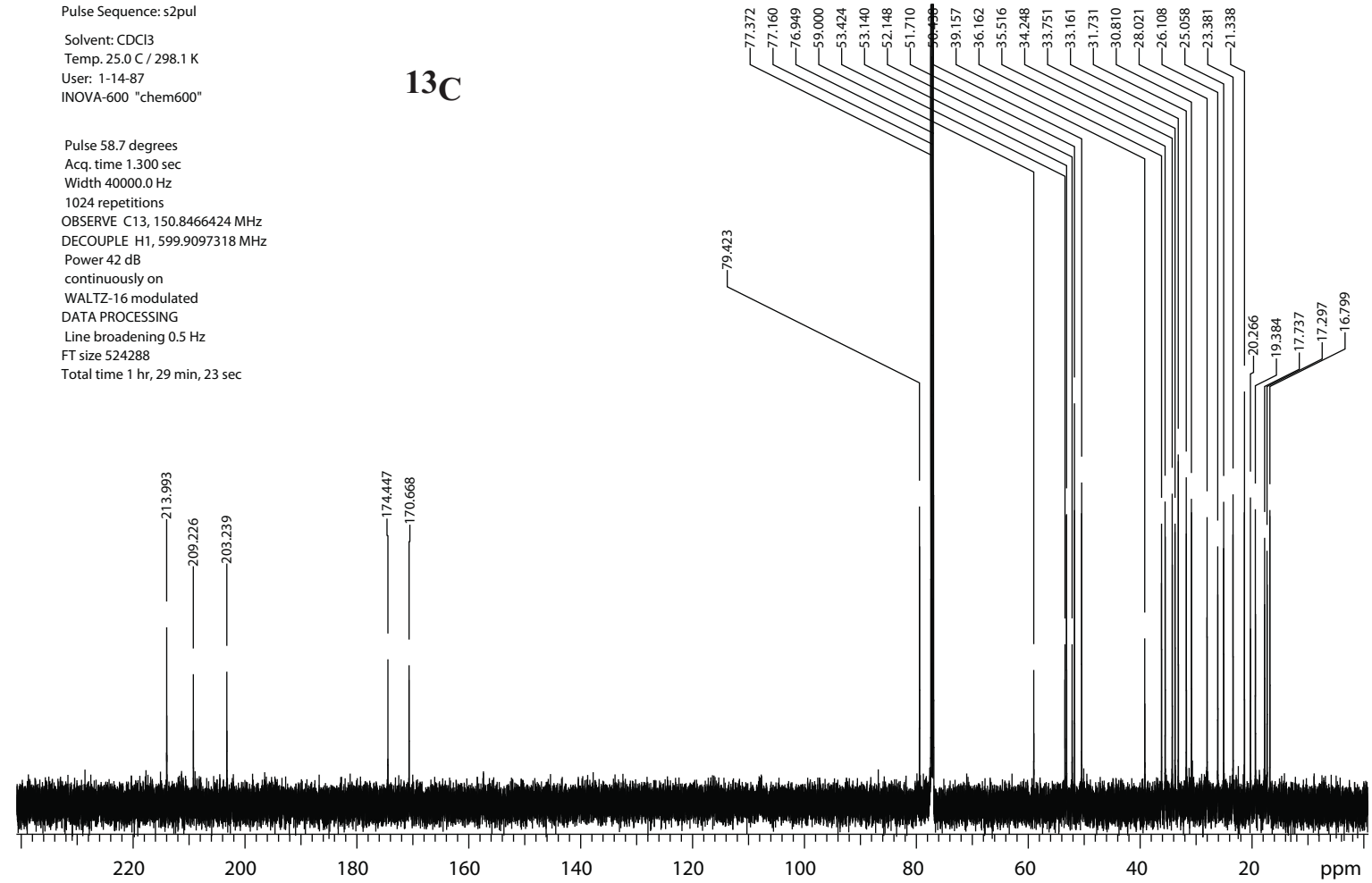
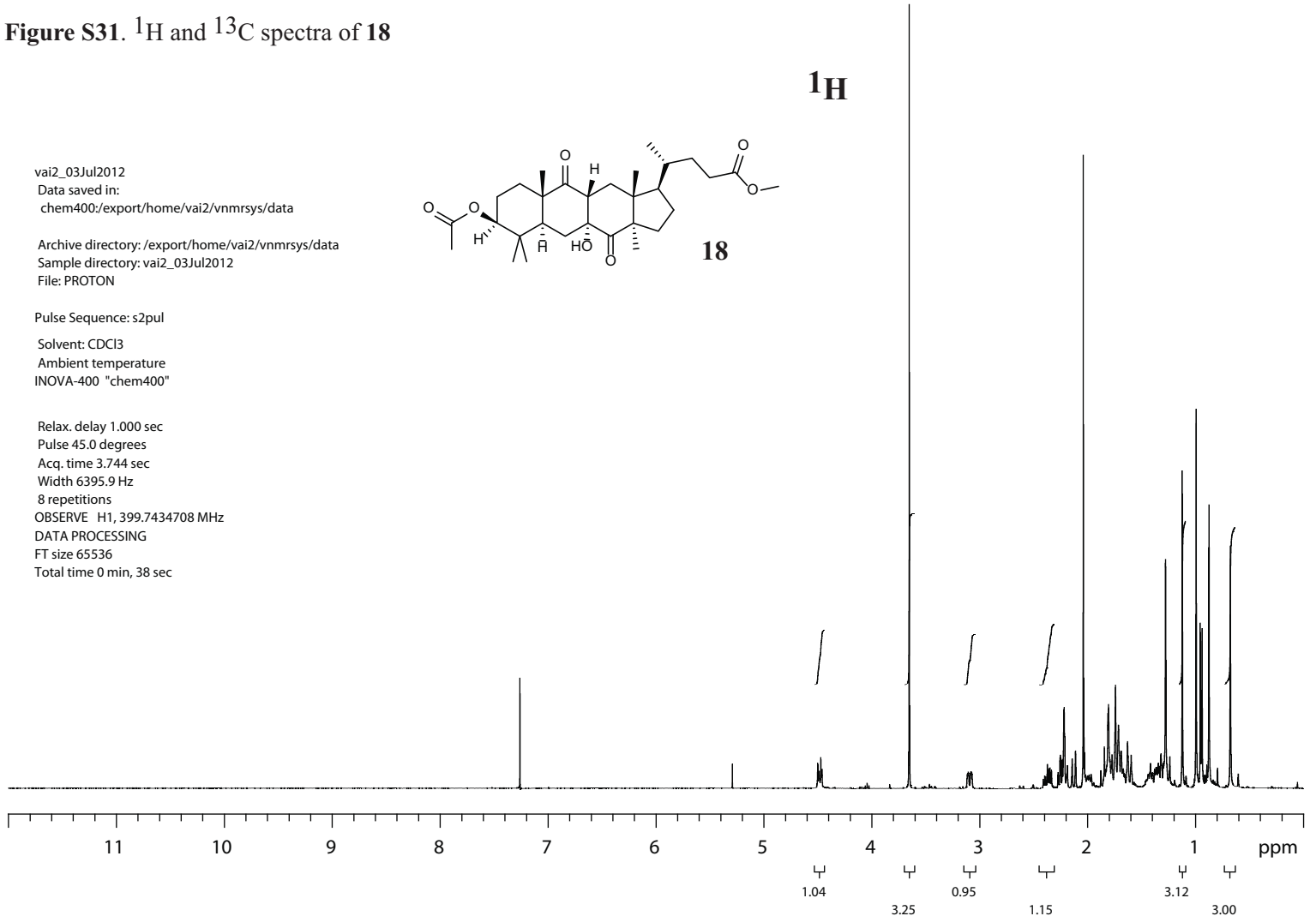


Figure S31. ^{1}H and ^{13}C spectra of **18**



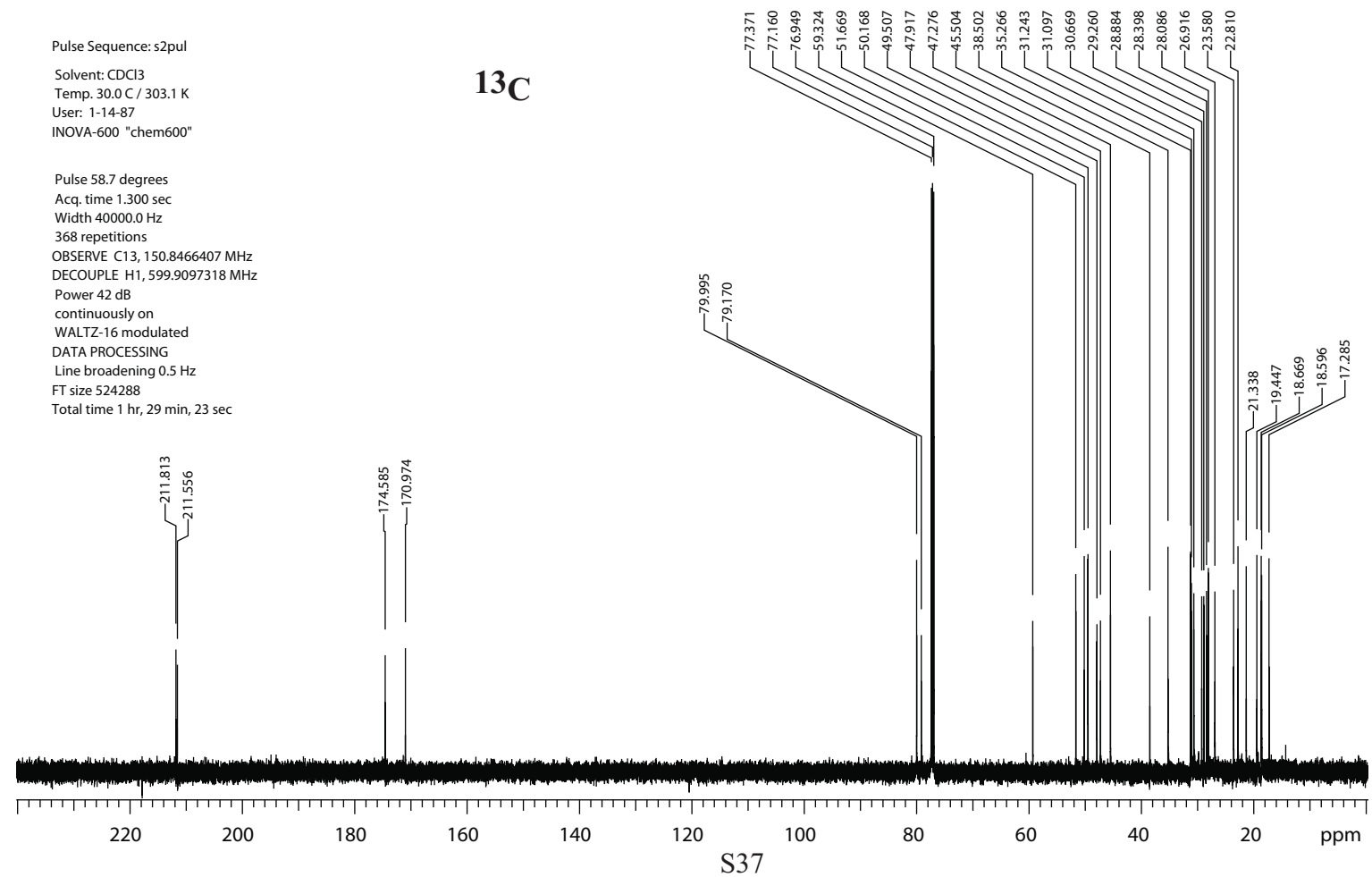
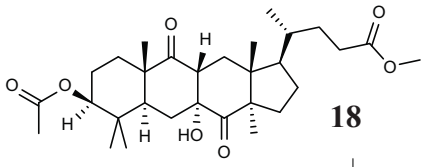


Figure S32. HMQC and HMBC spectra of 1**8**.



18

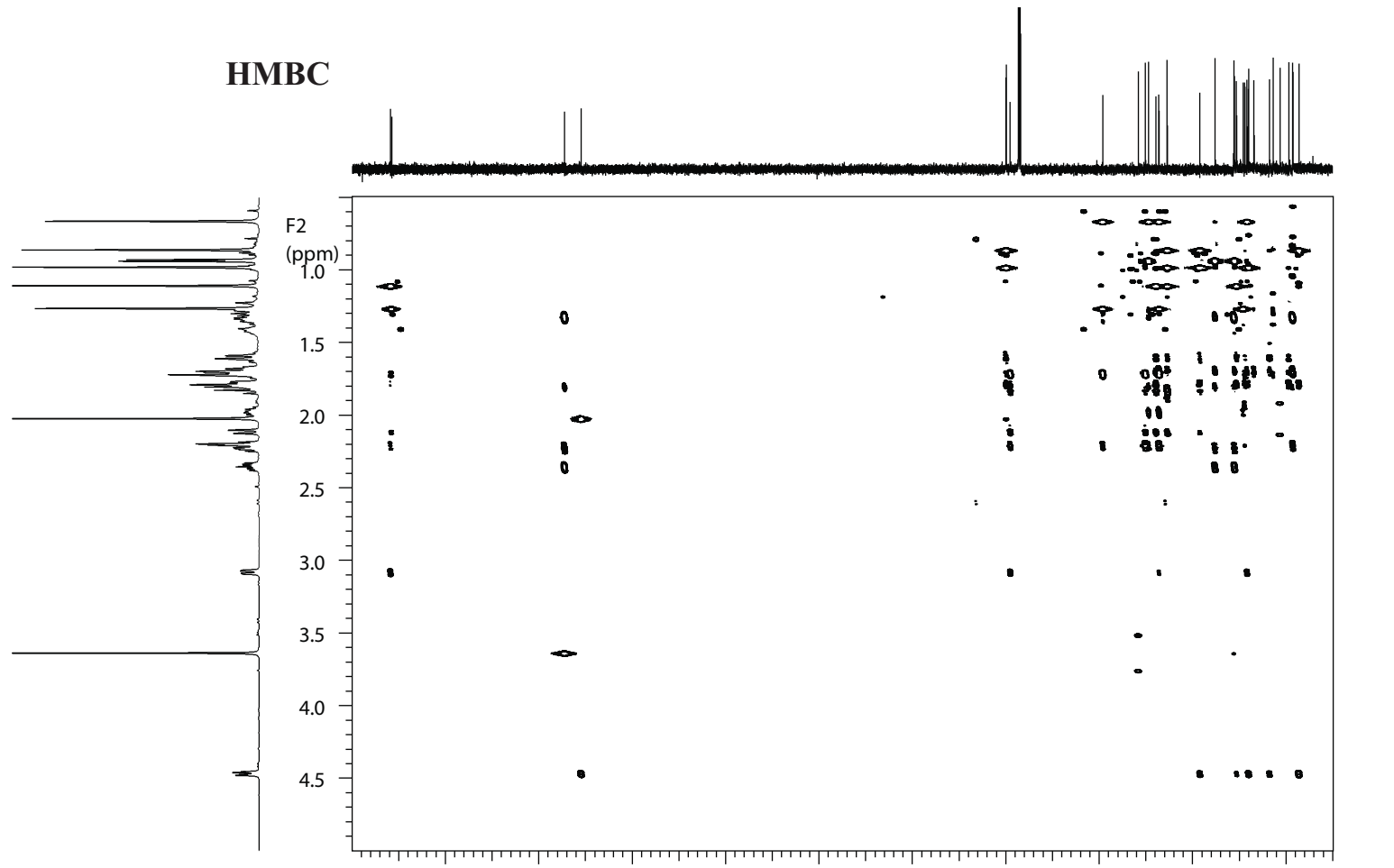
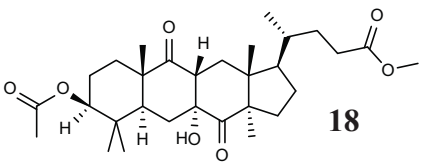
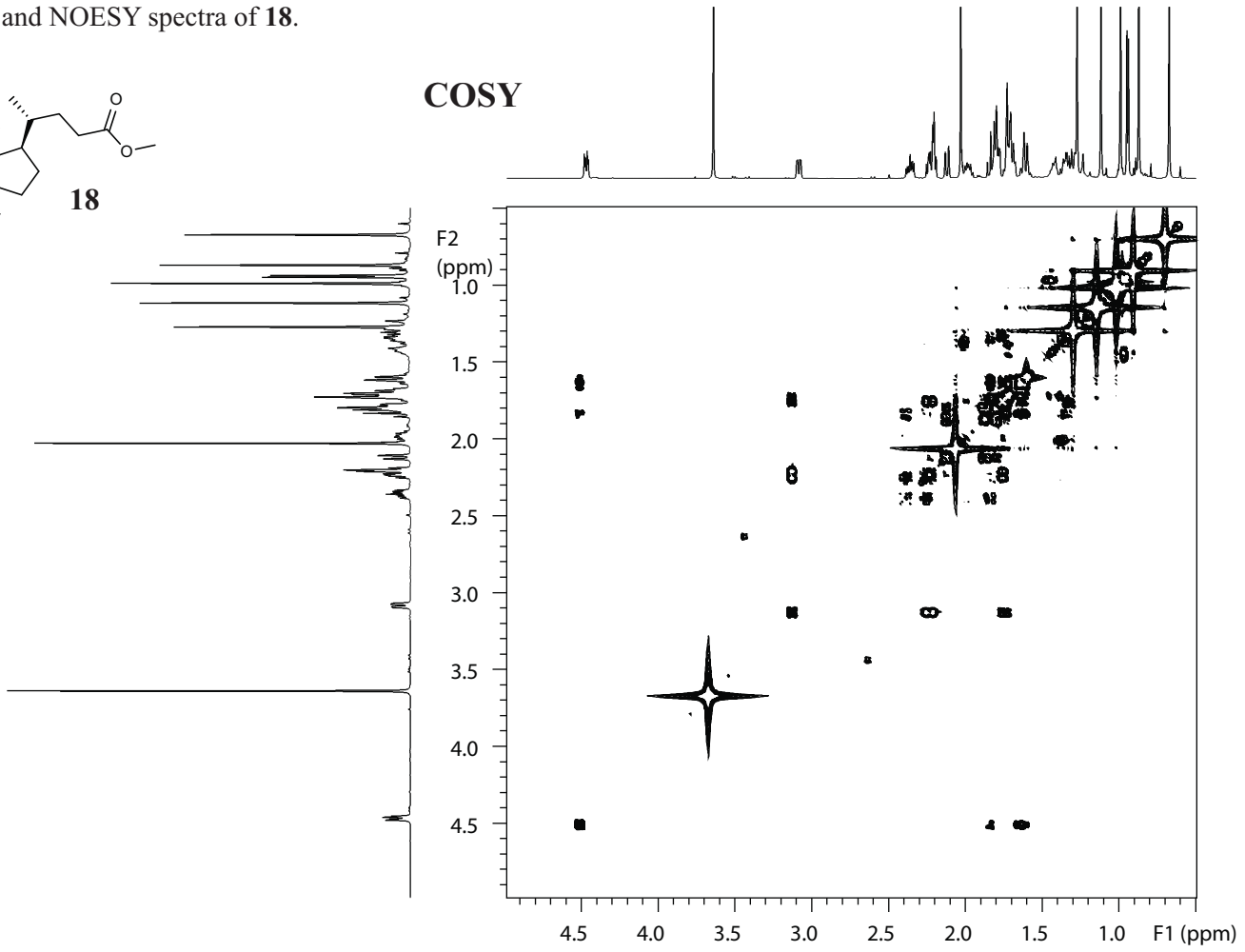


Figure S33. COSY and NOESY spectra of **18**.



18

COSY



NOESY

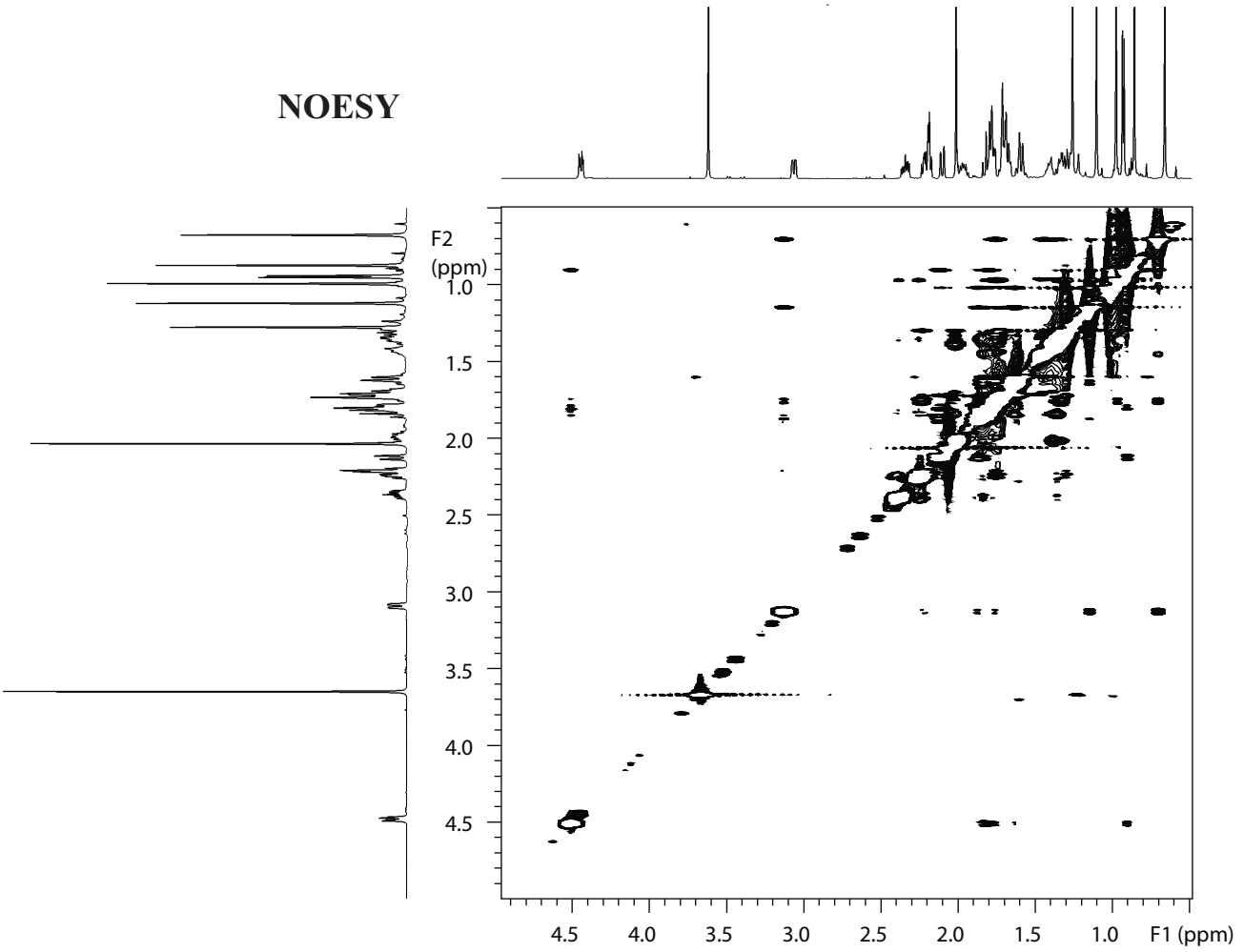
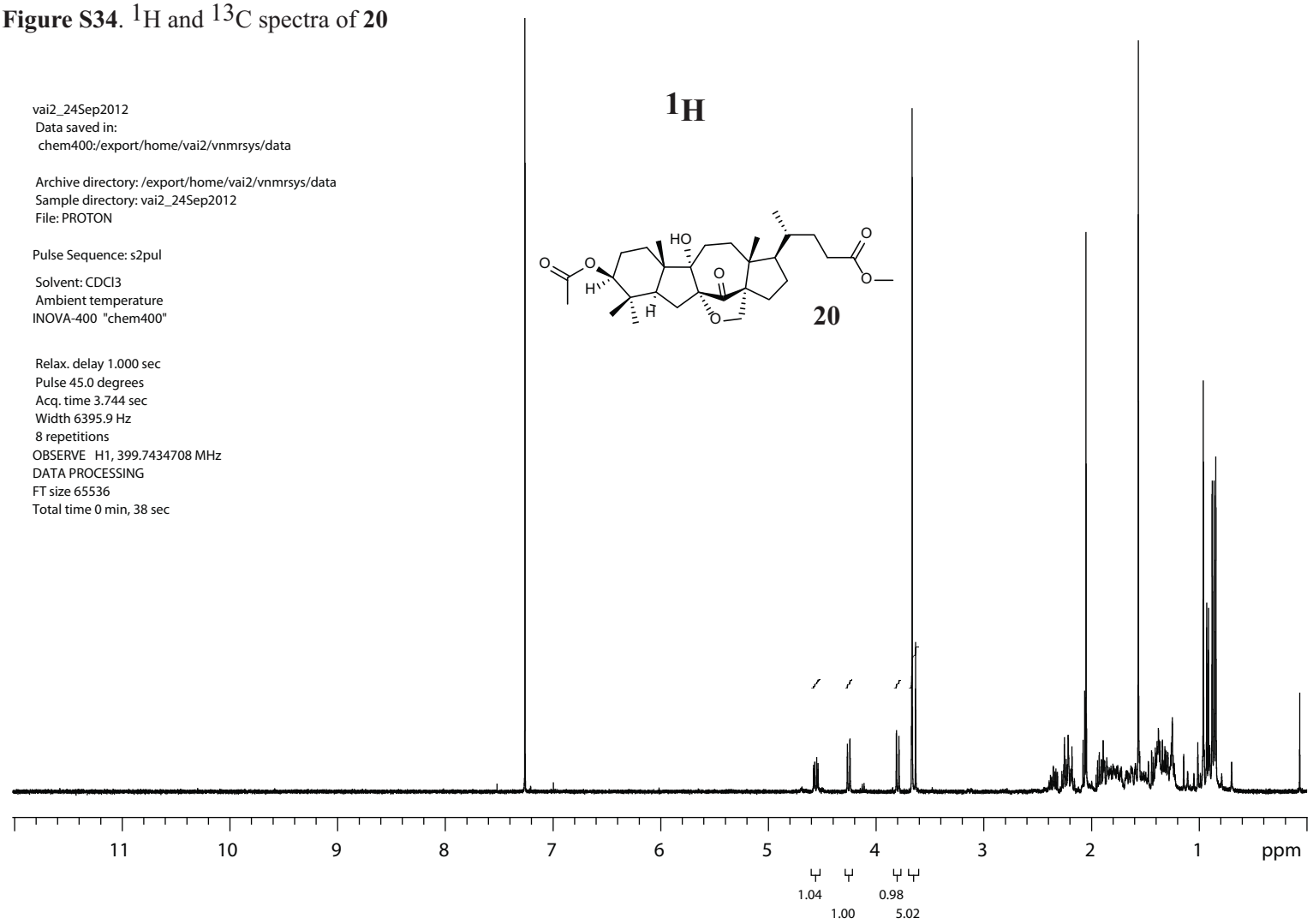


Figure S34. ^{1}H and ^{13}C spectra of **20**



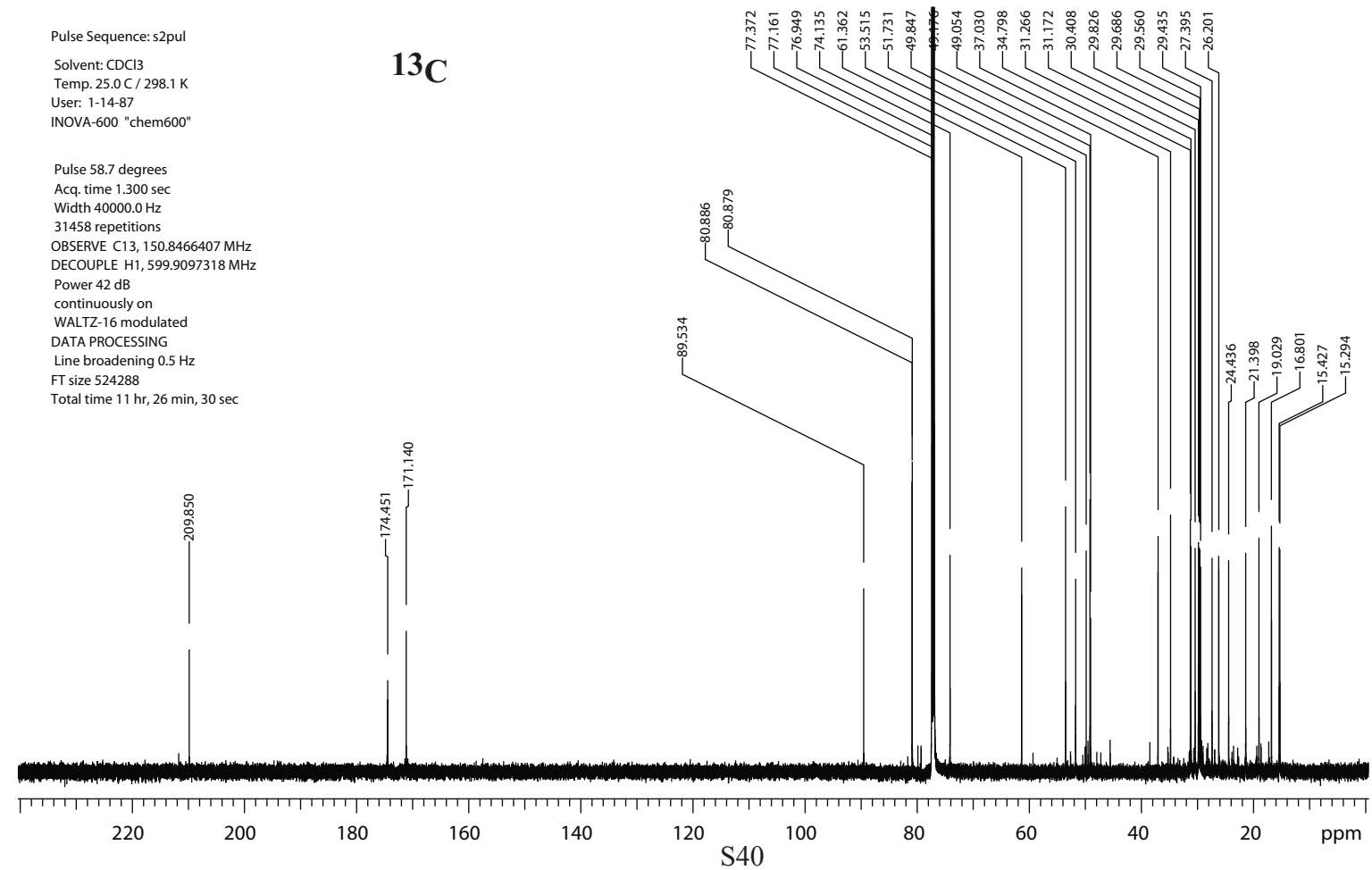
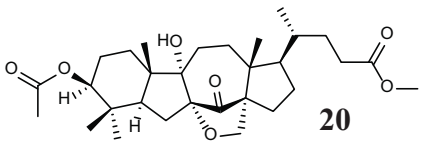
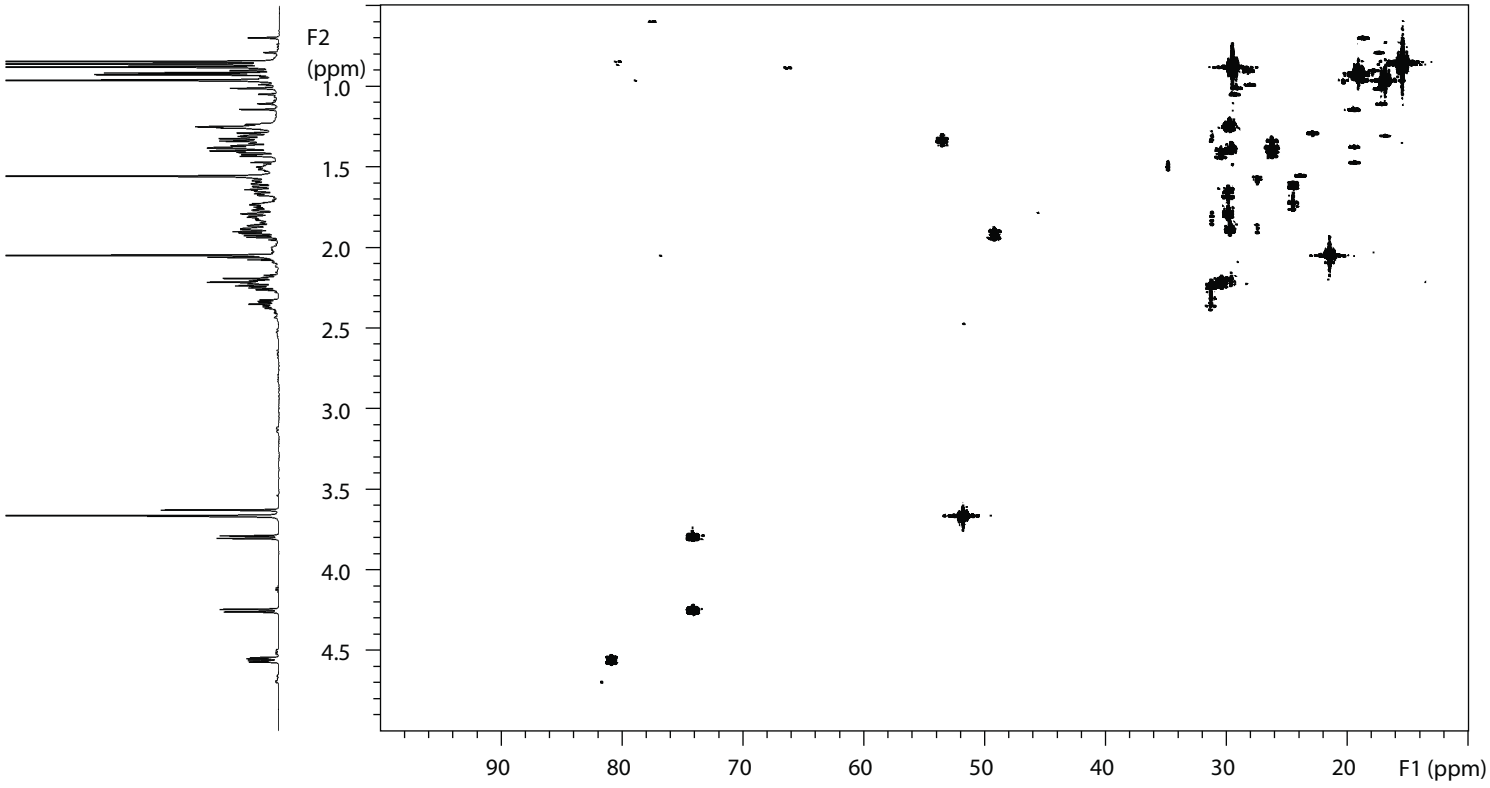


Figure S35. HMQC and HMBC spectra of **20**.



20

HMQC



HMBC

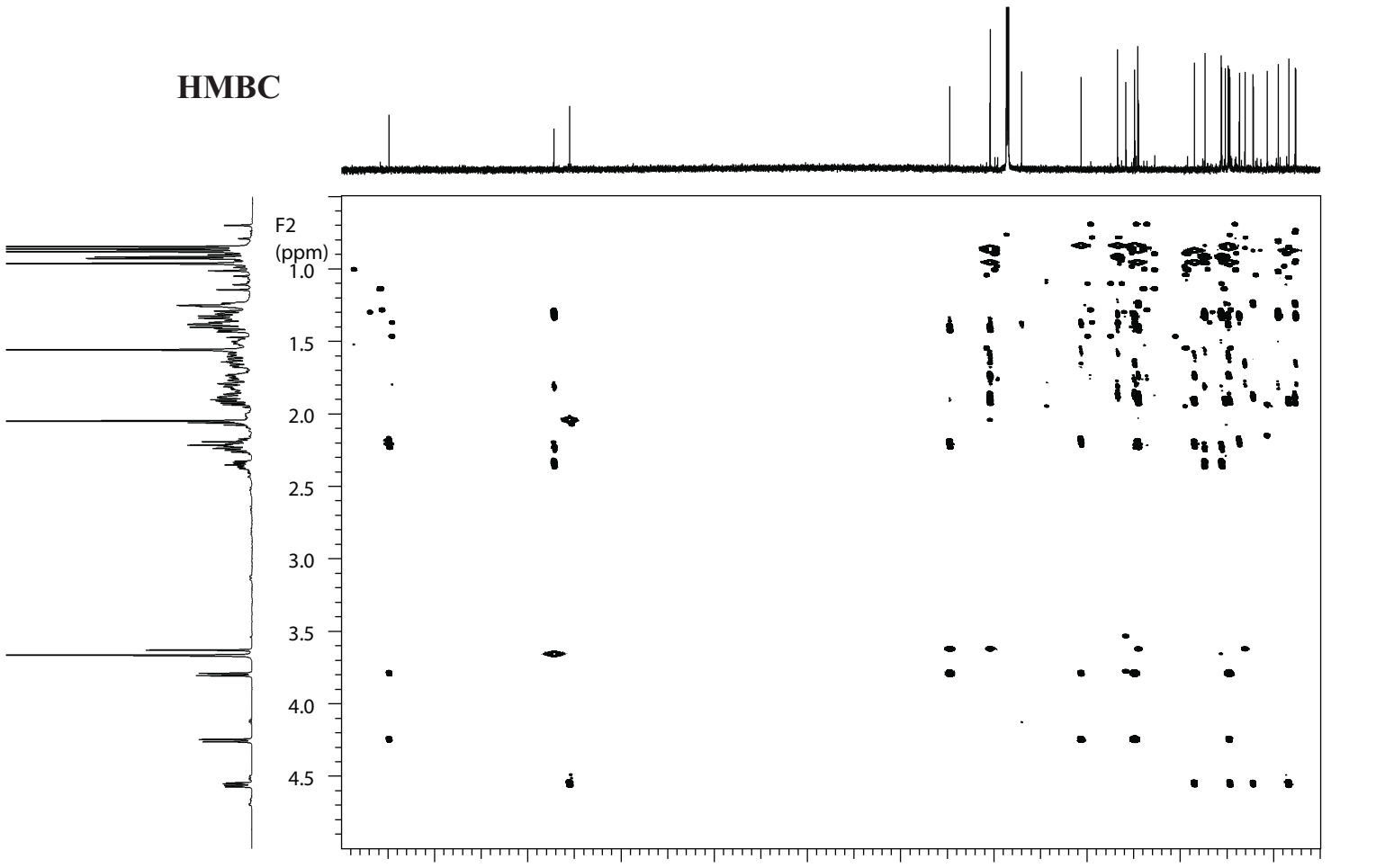
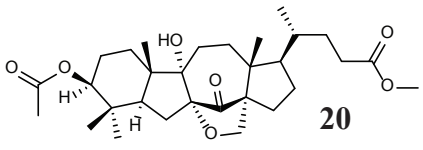
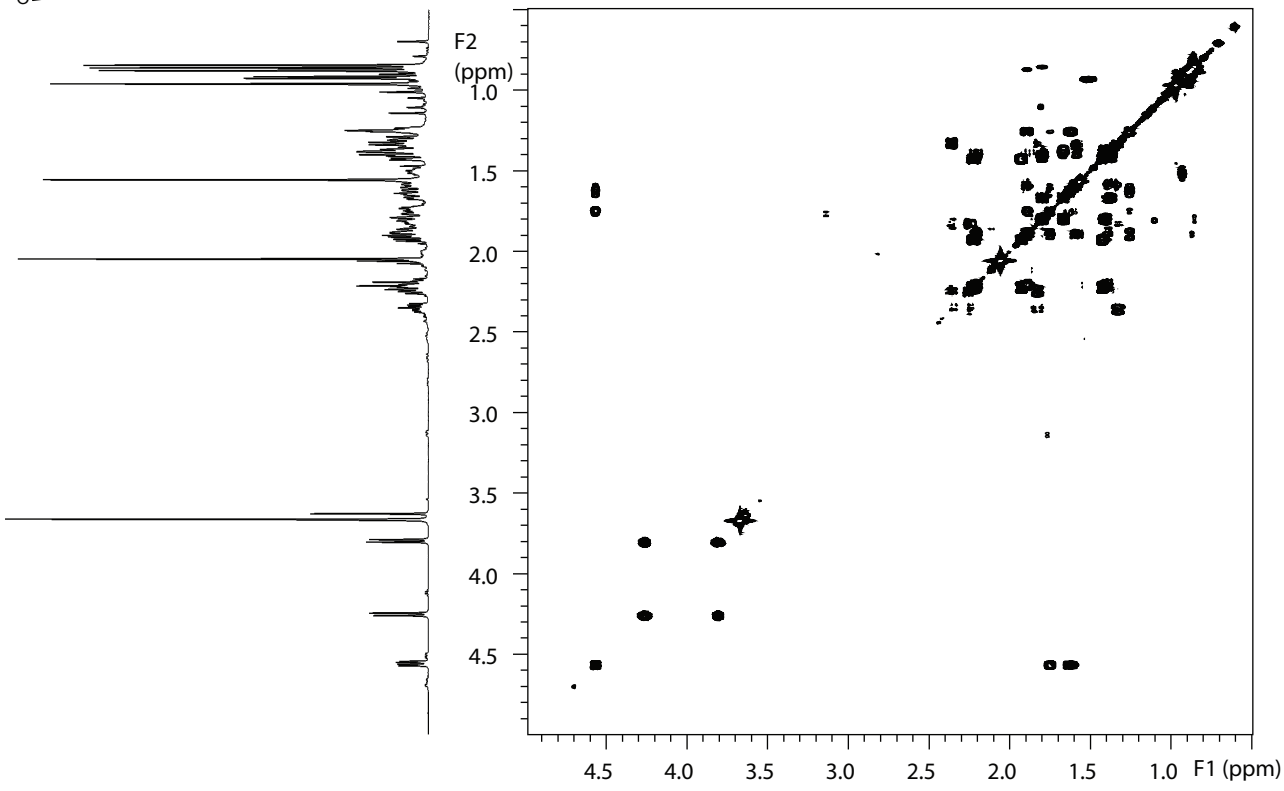


Figure S36. COSY and NOESY spectra of **20**.



20

COSY



NOESY