

## Possibility of [1,5] Sigmatropic Shifts in Bicyclo[4.2.0]octa-2,4-dienes

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Data 1: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (M06-2X/6-31+G(d,p)) of transition state **TS-a1**.

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.408780
C	1.404028	0.000000	-0.596698
C	1.404435	-0.155559	-2.111633
C	1.842153	-1.345916	-2.704301
C	3.030672	-1.943851	-2.305155
C	4.111945	-1.191974	-1.806952
C	4.158694	0.203138	-1.813259
C	3.091793	1.125627	-1.747108
C	2.197170	1.291803	-0.521039
C	2.982676	1.590062	0.743354
O	2.053785	1.935592	1.769627
H	5.065590	-1.711018	-1.743079
H	3.254744	-2.956017	-2.632589
H	1.323545	-1.747304	-3.573108
H	0.613292	0.400276	-2.620447
H	3.308838	2.069810	-2.255361
H	5.131033	0.613658	-2.092486
H	1.975791	-0.821648	-0.148509
H	1.518072	2.136956	-0.705044
H	3.675735	2.423661	0.563049
H	3.567822	0.703495	1.024477
H	-0.526569	-0.907705	-0.314128
H	-0.559818	0.863772	-0.398791
H	2.516358	2.043175	2.607475
H	0.550782	0.739199	1.711453

Energy = -539.6277051 hartree

Frequencies(cm-1): -570.5325, 54.8382, 103.3543, ...

Data 2: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (M06-2X/6-31+G(d,p)) of transition state **TS-a2**.

C	-0.000093	-0.000540	-0.000176
C	-0.000196	-0.000181	1.495342
C	1.447837	0.000243	2.018445
O	2.301629	-0.916509	1.373700
C	-1.054051	0.195560	-0.811853
C	-2.460685	0.481736	-0.539688
C	-3.278944	0.469877	0.545027
C	-3.135995	0.143218	1.960410
C	-2.192875	-0.552462	2.616692
C	-0.961262	-1.165815	2.028878
C	-0.367767	-2.105379	3.072250
O	0.698891	-2.854987	2.501222
H	-0.450984	0.934047	1.848044
H	0.953494	-0.242387	-0.465233
H	-0.839021	0.150625	-1.877785
H	-2.982914	0.776600	-1.449061
H	-4.290123	0.802024	0.314603
H	-3.957056	0.519229	2.568060
H	-2.302613	-0.624648	3.700038
H	-1.237910	-1.777241	1.163582
H	-0.016798	-1.537917	3.946552
H	-1.160093	-2.787454	3.406175
H	1.023807	-3.495592	3.142716
H	1.459546	-0.144648	3.108980
H	1.870560	0.990798	1.823405
H	1.984020	-1.803991	1.597673

Energy = -539.6558237 hartree

Frequencies(cm-1): -26.5829, 47.9381, 142.0644, ...

Data 3: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (M06-2X/6-31+G(d,p)) of transition state **TS-a3**.

C	0.000155	0.000084	0.000090
C	0.000142	-0.000108	1.517320
C	1.341500	-0.000334	2.227143
C	2.064946	1.327863	2.429482
O	2.674074	1.803078	1.250892
O	0.451054	1.279544	-0.440292
C	-0.556623	-1.288668	2.105397
C	-1.821935	-1.309493	2.704701
C	-2.186367	-0.329530	3.619549
C	-1.235084	0.324330	4.426033
C	0.108015	-0.046703	4.506908
C	0.921134	-0.669115	3.534393
H	-1.630413	0.902888	5.257736
H	-3.224898	-0.249438	3.930934
H	-2.479033	-2.166493	2.567613
H	-0.221235	-2.196198	1.597886
H	1.707140	-1.292603	3.970786
H	0.516968	-0.012145	5.518483
H	-0.607231	0.845744	1.861787
H	2.023368	-0.681740	1.698456
H	2.865585	1.197535	3.166400
H	1.351779	2.059299	2.843850
H	-1.016462	-0.191829	-0.368266
H	0.666442	-0.791296	-0.374094
H	1.992987	1.851770	0.561980
H	0.472114	1.307065	-1.402732

Energy = -539.6276665 hartree

Frequencies(cm-1): -572.3146, 61.2232, 99.3000, ...

Data 4: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (UM06-2X/6-31+G(d,p)) of transition state **TS-b**.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.384943
C	1.212046	0.000000	2.082041
C	2.386531	0.199767	1.352869
C	2.349909	0.217769	-0.033639
C	1.213705	-0.421369	-0.806239
C	1.047315	0.496365	-2.011182
C	1.054023	1.739347	-1.120245
C	-0.090761	2.714568	-1.157892
O	0.123248	3.661441	-2.197482
C	2.078651	0.531019	-3.121287
O	1.700791	1.631253	-3.947562
H	3.310301	0.444695	1.869457
H	1.226665	0.008111	3.167001
H	-0.938571	0.092072	1.924122
H	-0.956230	0.005307	-0.520539
H	1.313099	-1.515477	-0.956220
H	3.280168	0.411337	-0.563914
H	1.994423	2.292709	-1.132274
H	0.065611	0.360007	-2.486344
H	2.066383	-0.404574	-3.695592
H	3.090424	0.684022	-2.722476
H	-0.152839	3.283025	-0.225543
H	-1.045628	2.191025	-1.303223
H	0.455353	3.181797	-2.972138
H	2.354821	1.768655	-4.640402

Energy = -539.5732337 hartree

Frequencies(cm-1): -508.5975, 90.2498, 109.1816, ...

Data 5: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (UM06-2X/6-31+G(d,p)) of transition state **TS-c1**.

C	-1.239615	-0.040941	-0.724590
C	0.006194	0.002286	-0.007071
C	-0.000456	0.017577	1.383013
C	-1.195679	0.008226	2.093815
C	-2.544026	-0.150832	1.421170
C	-2.429090	-0.103830	-0.082204
C	-3.330923	1.030883	2.027616
C	-2.305356	2.138638	2.089464
C	-2.256212	3.108717	3.224991
O	-3.164188	4.191974	3.042925
C	-4.620086	1.412158	1.310427
O	-5.265740	2.401838	2.108745
H	-3.606929	0.754678	3.055676
H	-1.899619	2.470468	1.134043
H	-1.181339	-0.053354	3.178805
H	0.937993	0.073657	1.927203
H	0.941605	0.029538	-0.554327
H	-1.216970	-0.035279	-1.810910
H	-3.349105	-0.172488	-0.658595
H	-3.022677	-1.106923	1.699378
H	-1.263081	3.560133	3.300926
H	-2.466997	2.589118	4.172637
H	-4.028541	3.804372	2.835807
H	-5.267790	0.530217	1.199970
H	-4.394028	1.812340	0.313049
H	-6.064044	2.708447	1.665781

Energy = -539.5931415 hartree

Frequencies(cm-1): -494.5999, 53.7188, 69.3139, ...

Data 6: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (UM06-2X/6-31+G(d,p)) of transition state **TS-c2**.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.353488
C	1.223764	0.000000	2.104764
C	2.446073	0.010565	1.431763
C	2.503623	0.059011	0.049696
C	1.264429	-0.007002	-0.823896
C	1.360716	1.260531	-1.697206
C	2.010960	2.287576	-0.794203
C	1.245075	3.007358	0.262867
O	1.662083	4.356498	0.419769
C	2.178383	1.023739	-2.956960
O	2.251933	2.252620	-3.658698
H	3.371616	0.024872	2.000444
H	1.190907	-0.014907	3.188288
H	-0.945029	0.005960	1.889500
H	-0.939985	-0.006218	-0.547535
H	1.266176	-0.917086	-1.453791
H	3.468466	0.004725	-0.445637
H	2.957322	2.730243	-1.095583
H	0.359651	1.601750	-2.012576
H	1.691568	0.249446	-3.566681
H	3.184887	0.667092	-2.688691
H	1.387852	2.544461	1.251860
H	0.164457	2.944616	0.049125
H	1.570581	4.802321	-0.430141
H	2.788551	2.142379	-4.450070

Energy = -539.5884695 hartree

Frequencies(cm-1): -469.3218, 68.0634, 82.6795, ...



Data 7: Cartesian coordinates and energy of the optimized geometry (UM06-2X/6-31+G(d,p)) of intermediate **Int-c**.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.501119
C	1.389268	0.000000	2.070475
C	2.503486	-0.115384	1.292411
C	2.412846	-0.194606	-0.119954
C	1.138158	-0.111509	-0.739283
C	-0.864389	-1.197559	2.026493
C	-0.332230	-2.516478	1.566373
C	-1.219318	-3.696056	1.337526
O	-1.382332	-4.493813	2.508351
C	-1.004066	-1.129525	3.551536
O	-2.002490	-2.071057	3.937579
H	-1.305627	-0.115653	3.851947
H	-0.048224	-1.375627	4.031481
H	-1.880647	-1.064671	1.624523
H	0.742673	-2.676096	1.619650
H	-2.200296	-3.360375	0.968012
H	-0.786109	-4.362460	0.586332
H	-2.116618	-2.043992	4.893675
H	-1.713274	-3.898069	3.197254
H	-0.525007	0.905929	1.855839
H	1.496514	0.095433	3.147906
H	3.483077	-0.130504	1.762122
H	3.309358	-0.290406	-0.721083
H	1.072718	-0.135081	-1.823292
H	-0.968152	0.055780	-0.492263

Energy = -539.5993408 hartree

Data 8: Cartesian coordinates and energy of the optimized geometry (M06-2X/6-31+G(d,p)) of  
endiandric acid 1.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.401947
C	1.238885	0.000000	2.062756
C	2.428249	0.005626	1.344161
C	2.411630	0.009314	-0.051869
C	1.190631	0.005637	-0.721805
C	-1.287638	-0.003908	2.109331
C	-1.484098	0.070626	3.437232
C	-2.803282	0.056214	4.051700
C	-3.015925	0.130573	5.374002
C	-4.368797	0.170892	6.018349
C	-4.623921	1.521300	6.680830
C	-6.041060	1.847394	7.205829
C	-6.310608	1.624842	8.681553
C	-7.660449	2.150075	9.103652
O	-7.924896	1.866035	10.390453
C	-9.182366	2.341554	10.876767
C	-4.709448	2.772710	5.765641
C	-5.874080	3.296331	6.659083
C	-5.419025	4.304901	7.674723
C	-4.208155	4.880194	7.630772
C	-3.239413	4.580686	6.563966
C	-3.479580	3.621872	5.658710
O	-8.423125	2.763940	8.394025
H	-2.772855	3.415257	4.858508
H	-2.330305	5.173154	6.514620
H	-3.937190	5.626235	8.372978
H	-6.137671	4.601587	8.437269
H	-6.764294	3.676291	6.146155
H	-5.072124	2.475105	4.774142
H	-6.797742	1.325547	6.606714
H	-3.881913	1.706000	7.470642
H	-5.553625	2.130153	9.295906
H	-6.259098	0.560709	8.940903
H	-9.227041	2.040196	11.921742
H	-10.001269	1.893606	10.309800
H	-9.238121	3.428328	10.784281
H	-4.455528	-0.625482	6.771066
H	-5.143393	-0.010453	5.261616
H	-2.155224	0.216128	6.040357
H	-3.658567	-0.021947	3.378342
H	-0.637135	0.150028	4.117838
H	-2.167022	-0.072593	1.468083
H	1.276493	-0.009839	3.147636
H	3.375555	0.003824	1.874689
H	3.342924	0.011970	-0.609365
H	1.163282	0.005656	-1.807139
H	-0.950651	-0.002437	-0.527347

Energy = -1002.7902601 hartree

Data 9: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (M06-2X/6-31+G(d,p)) of transition state **TS-a1''**.

C	0.000006	0.000118	-0.000002
C	-0.000008	0.000232	1.389600
C	1.206147	0.000168	2.108953
C	2.406082	-0.005856	1.383942
C	2.408211	-0.006510	-0.008576
C	1.203502	-0.002441	-0.707651
C	1.264826	0.004572	3.576966
C	0.226471	0.066857	4.428727
C	0.377264	0.066037	5.875987
C	-0.649225	0.139538	6.735711
C	-0.517377	0.122594	8.228322
C	-1.274544	-1.044448	8.871426
C	-1.148336	-1.179979	10.371923
C	-2.083963	-0.318681	11.211740
C	-1.889723	-0.536395	12.692649
O	-2.907739	-0.028239	13.407148
C	-2.789819	-0.168041	14.824853
C	-0.747428	-2.414797	8.467780
C	-1.505711	-3.248013	7.639245
C	-2.856923	-3.461594	7.887576
C	-3.391291	-3.418711	9.189841
C	-2.617295	-3.313649	10.348203
C	-1.366842	-2.687273	10.522814
O	-0.938436	-1.084483	13.198906
H	-1.900736	0.354461	15.184597
H	-3.692598	0.275399	15.240823
H	-2.716410	-1.223419	15.095607
H	-3.130155	-0.526324	10.961221
H	-1.912304	0.748386	11.015249
H	-0.112146	-0.970696	10.667008
H	-0.764676	-3.128291	11.319980
H	-2.951669	-3.954287	11.166777
H	-4.390820	-3.831792	9.307893
H	-3.467764	-3.945879	7.129637
H	-1.018673	-3.834680	6.862352
H	0.339964	-2.467562	8.379146
H	-2.335283	-0.988166	8.592826
H	-0.908795	1.061802	8.646252
H	0.543263	0.065382	8.507170
H	-1.664962	0.192101	6.338558
H	1.395113	0.003599	6.264561
H	-0.794252	0.124471	4.052335
H	2.268631	-0.044617	4.000355
H	3.348950	-0.008160	1.925051
H	3.351361	-0.009501	-0.546353
H	1.199474	-0.002598	-1.793055
H	-0.943834	-0.000084	-0.536689
H	-0.948242	-0.004063	1.917991

Energy = -1002.7454438 hartree

Frequencies(cm-1): -559.6712, 16.8850, 22.4899, ...

Data 10: Cartesian coordinates and energy of the optimized geometry (M06-2X/6-31+G(d,p)) of intermediate **Int-a1'**.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.389735
C	1.206172	0.000000	2.108301
C	2.406168	0.006715	1.383141
C	2.408300	0.006772	-0.009145
C	1.203613	0.002645	-0.707812
C	1.268232	-0.004076	3.576068
C	0.235574	-0.083747	4.433370
C	0.400911	-0.079395	5.879136
C	-0.612839	-0.142188	6.754173
C	-0.454601	-0.129386	8.245729
C	-1.173623	-1.311393	8.931282
C	-0.852568	-1.398831	10.433261
C	-1.102955	-0.066508	11.163583
C	-0.631552	-0.086180	12.598887
O	-1.310837	0.790128	13.355768
C	-0.879496	0.887106	14.715835
C	-0.791951	-2.594490	8.241096
C	-1.632961	-3.592591	7.943076
C	-3.036489	-3.626964	8.355019
C	-3.484842	-3.380682	9.600287
C	-2.703929	-3.198771	10.835361
C	-1.618197	-2.478119	11.163208
O	0.270981	-0.766869	13.027489
H	-0.541115	0.747443	10.690580
H	-3.767102	-3.926474	7.605146
H	-4.556148	-3.488327	9.766752
H	-3.109639	-3.795130	11.654220
H	-1.265110	-2.617444	12.184435
H	0.244083	-2.665371	7.908003
H	-1.273027	-4.425232	7.340922
H	0.218308	-1.622640	10.542703
H	-2.257061	-1.164574	8.823643
H	-0.863623	0.813293	8.630077
H	0.614288	-0.147255	8.502920
H	-2.162384	0.207599	11.133250
H	-1.534286	1.621614	15.180818
H	-0.970165	-0.081799	15.211047
H	0.161706	1.213617	14.759339
H	-1.634259	-0.212460	6.374888
H	1.423878	-0.017727	6.254141
H	-0.786359	-0.160212	4.064133
H	2.272709	0.061785	3.995437
H	3.349324	0.009004	1.923829
H	3.351274	0.009253	-0.547212
H	1.199055	0.004221	-1.793174
H	-0.944152	0.001813	-0.536179
H	-0.947564	0.006809	1.919492

Energy = -1002.780151 hartree

Data 11: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (M06-2X/6-31+G(d,p)) of transition state **TS-a2''**.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.392251
C	1.199107	0.000000	2.118914
C	2.406383	-0.008344	1.402272
C	2.408450	-0.008065	0.012592
C	1.205730	-0.003043	-0.696865
C	1.135820	0.003934	3.586704
C	2.167656	0.100536	4.443157
C	2.005193	0.090583	5.889275
C	3.021313	0.170784	6.760591
C	2.870179	0.160173	8.252618
C	3.519397	1.399121	8.893445
C	3.529517	1.402953	10.488719
C	2.889362	0.162509	11.137564
C	2.747816	0.392680	12.623728
O	3.509374	-0.446382	13.347376
C	3.453747	-0.248210	14.763029
C	2.868425	2.653344	8.413333
C	3.414160	3.877400	8.492639
C	4.733598	4.276078	8.975914
C	5.663562	3.749805	9.816119
C	5.789418	2.563172	10.663692
C	4.934553	1.574646	10.981925
O	2.049446	1.244332	13.120072
H	4.111135	-1.002179	15.192135
H	2.430820	-0.375064	15.123001
H	3.798113	0.757086	15.014805
H	3.486677	-0.736017	10.961829
H	1.882007	0.002069	10.744425
H	2.936435	2.264263	10.810178
H	5.321610	0.785005	11.627162
H	6.773866	2.487722	11.121256
H	6.550908	4.375814	9.895936
H	5.029428	5.246039	8.577764
H	2.822785	4.706259	8.108775
H	1.853714	2.567383	8.023940
H	4.569863	1.421398	8.580532
H	3.340158	-0.745077	8.657649
H	1.803439	0.113743	8.505790
H	4.039133	0.260443	6.376127
H	0.984801	0.006969	6.266970
H	3.187434	0.195398	4.072426
H	0.132380	-0.076766	4.005885
H	3.353041	-0.023224	1.933408
H	3.353341	-0.016760	-0.522175
H	1.211786	-0.005102	-1.782220
H	-0.942160	0.002878	-0.539408
H	-0.943934	0.003384	1.931554

Energy = -1002.7714668 hartree

Frequencies(cm<sup>-1</sup>): -44.2653, 17.5746, 20.0714, ...

Data 12: Cartesian coordinates and energy of the optimized geometry (M06-2X/6-31+G(d,p)) of intermediate **Int-a2'**.

C	0.308164	-0.419496	0.139203
H	0.119029	-0.415285	1.225346
C	1.831023	-0.644383	-0.050371
H	2.056039	-0.678248	-1.124130
H	2.096271	-1.619954	0.374524
C	2.677426	0.394156	0.622190
C	-0.043612	0.948551	-0.392789
H	0.496426	1.744856	0.117868
C	-0.777101	1.357122	-1.442634
H	-0.704583	2.426511	-1.646863
C	-1.667487	0.688516	-2.406882
H	-1.608680	1.098978	-3.414250
C	-2.649568	-0.202095	-2.175035
H	-3.319538	-0.444654	-2.997854
C	-2.929836	-0.825088	-0.881808
H	-3.968833	-0.850321	-0.556994
C	-1.990125	-1.370487	-0.099831
H	-2.284016	-1.787816	0.864570
C	-0.542119	-1.542021	-0.479353
H	-0.449788	-1.481717	-1.570712
C	-0.074638	-2.947362	-0.047191
H	0.925039	-3.155282	-0.435213
H	-0.063871	-3.033553	1.044528
C	-0.995151	-3.986731	-0.639926
O	-1.772093	-4.572612	0.287509
O	-1.057458	-4.250662	-1.817249
C	-2.724473	-5.508928	-0.222794
H	-3.266479	-5.880851	0.644871
H	-3.401884	-5.010971	-0.920235
H	-2.215383	-6.324200	-0.740777
C	3.530899	1.217547	-0.003311
H	2.578507	0.469224	1.707671
C	4.349296	2.208920	0.678691
H	3.631184	1.156287	-1.087897
C	5.203976	3.026897	0.040103
H	4.241489	2.259490	1.761641
C	6.065881	4.052338	0.643489
H	5.284392	2.933858	-1.043400
C	6.941088	4.770717	-0.183222
C	7.783088	5.750696	0.335883
C	7.764919	6.034578	1.699252
C	6.896441	5.330076	2.535169
C	6.057138	4.352289	2.015192
H	6.959253	4.552425	-1.248035
H	8.451816	6.292708	-0.325759
H	8.418482	6.798176	2.108981
H	6.873223	5.546921	3.598784
H	5.387633	3.820169	2.683861

Energy = -1002.7793984 hartree

Data 13: Cartesian coordinates, energy, imaginary and low frequencies of the optimized geometry (M06-2X/6-31+G(d,p)) of transition state **TS-a3''**.

C	-0.140590	0.115279	-0.323384
C	-0.031258	0.005965	1.198695
H	1.000703	0.024862	1.559240
C	-0.937705	0.606410	2.096253
H	-0.494064	1.246572	2.861503
C	-2.292989	0.334240	2.294163
H	-2.833904	1.008995	2.953893
C	-2.884759	-0.926279	2.083877
H	-3.798319	-1.132454	2.635625
C	-2.184993	-1.978883	1.505987
H	-2.358938	-2.988537	1.874252
C	-1.156517	-1.733265	0.589158
H	-0.485711	-2.559549	0.345298
C	-1.363985	-0.743263	-0.548409
H	-2.271312	-0.159870	-0.351053
H	0.732248	-0.401542	-0.749901
C	-0.183093	1.551331	-0.860818
H	-1.057006	2.058832	-0.434311
H	-0.321887	1.508945	-1.950756
C	1.063921	2.317722	-0.539389
C	-1.490353	-1.402672	-1.927403
H	-1.595571	-0.632297	-2.697485
H	-0.605485	-2.010619	-2.138999
C	-2.728610	-2.263269	-1.962344
O	-2.441021	-3.567468	-1.802345
O	-3.856274	-1.843957	-2.071074
C	-3.575623	-4.432959	-1.721042
H	-3.172703	-5.438212	-1.611648
H	-4.189988	-4.164480	-0.858283
H	-4.179865	-4.352964	-2.627012
C	1.119130	3.381593	0.275004
H	1.991009	1.951219	-0.985661
C	2.345327	4.095021	0.599367
H	0.198478	3.750198	0.730225
C	2.384794	5.169505	1.406320
H	3.259084	3.716473	0.142249
C	3.575210	5.942699	1.785996
H	1.443837	5.530859	1.822399
C	3.406298	7.157191	2.465890
C	4.500918	7.932869	2.838103
C	5.792642	7.504900	2.540835
C	5.977499	6.292767	1.873134
C	4.883675	5.519426	1.503272
H	2.400071	7.497160	2.697584
H	4.344496	8.871781	3.360283
H	6.649106	8.105194	2.830984
H	6.981119	5.945469	1.647409
H	5.049539	4.571456	1.000772

Energy = -1002.7439882 hartree

Frequencies(cm-1): -564.4111, 8.3133, 14.1581, ...

Data 14: Cartesian coordinates and energy of the optimized geometry (M06-2X/6-31+G(d,p)) of endiandric acid **2**.

C	0.220015	-0.046846	-0.023734
H	0.169324	-0.059655	1.072029
C	1.642588	-0.064513	-0.496923
H	2.382098	0.491664	0.070456
C	1.972783	-0.698428	-1.629529
H	2.995743	-0.677465	-1.993825
C	0.971699	-1.444925	-2.407157
H	1.279105	-1.879573	-3.354655
C	-0.277927	-1.635868	-1.960900
H	-0.978212	-2.239707	-2.534617
C	-0.752479	-1.099695	-0.639389
H	-1.035830	-1.939257	0.007758
C	-1.827668	0.023629	-0.729809
H	-2.437597	0.005437	0.185208
C	-2.743429	0.115261	-1.945882
H	-2.140360	0.109147	-2.862454
H	-3.265288	1.083180	-1.909244
C	-3.750881	-0.995134	-1.986385
C	-0.705173	1.075372	-0.575573
H	-0.337859	1.392594	-1.559965
C	-1.016032	2.280528	0.290692
H	-1.380402	1.960246	1.276380
H	-1.817664	2.890062	-0.144301
C	0.175450	3.176573	0.527169
O	-0.176776	4.295769	1.184086
O	1.311781	2.939266	0.193100
C	0.893422	5.198266	1.474236
H	0.441193	6.026092	2.017439
H	1.652150	4.703236	2.084104
H	1.353658	5.548869	0.547999
C	-3.884014	-1.877912	-2.987319
H	-4.409977	-1.084667	-1.120080
C	-4.862952	-2.954531	-2.998848
H	-3.228738	-1.799193	-3.856617
C	-4.987069	-3.830255	-4.011441
H	-5.516171	-3.021224	-2.129484
C	-5.942642	-4.942571	-4.104885
H	-4.323971	-3.715126	-4.869352
C	-6.031239	-5.659211	-5.306794
C	-6.925204	-6.716720	-5.451399
C	-7.749901	-7.082815	-4.390379
C	-7.667961	-6.383822	-3.184435
C	-6.774470	-5.329160	-3.041765
H	-5.391221	-5.375828	-6.138547
H	-6.977390	-7.254766	-6.392898
H	-8.447213	-7.907632	-4.497478
H	-8.300419	-6.668272	-2.349014
H	-6.716979	-4.807950	-2.091243

Energy = -1002.7882955 hartree



Table 1. Natural orbital occupation numbers (NOON) of transition states and intermediates for the thermal rearrangement of bicyclo[4.2.0]octa-2,4-diene diol **9** (CASSCF(6,6)/6-31+G(d,p)//UM06-2X/6-31+G(d,p)).

	Singlet						Triplet					
	<b>9</b>	1.983	1.938	1.900	0.103	0.058	0.017	1.982	1.912	1.026	0.975	0.087
<b>TS-a1</b>	1.947	1.880	1.864	0.137	0.120	0.051	1.915	1.895	1.013	0.988	0.106	0.084
<b>Int-a1</b>	1.933	1.915	1.899	0.110	0.080	0.062	1.926	1.887	1.005	0.996	0.115	0.071
<b>TS-a2</b>	1.939	1.917	1.873	0.133	0.083	0.055	1.915	1.900	1.018	0.984	0.103	0.080
<b>Int-a2</b>	1.933	1.915	1.898	0.111	0.081	0.063	1.925	1.888	1.006	0.995	0.114	0.072
<b>TS-a3</b>	1.947	1.881	1.864	0.137	0.120	0.051	1.915	1.895	1.013	0.988	0.106	0.084
<b>TS-b</b>	1.943	1.880	1.730	0.272	0.120	0.055	1.903	1.817	1.061	0.939	0.185	0.094
<b>TS-c1</b>	1.933	1.888	1.544	0.458	0.112	0.064	1.921	1.894	1.027	0.974	0.108	0.076
<b>Int-c</b>	1.931	1.885	1.001	1.000	0.116	0.067	1.922	1.894	1.028	0.974	0.108	0.076
<b>TS-c2</b>	1.934	1.890	1.536	0.467	0.110	0.064	1.931	1.884	1.006	0.995	0.117	0.067
<b>10</b>	1.983	1.938	1.900	0.103	0.058	0.017	1.981	1.912	1.025	0.977	0.087	0.019

As expected, the NOON for the first two bonding orbitals are close to 2.0 and those for the last two antibonding orbitals are close to 0.0 for all structures. Furthermore, the NOON for the principal bonding/antibonding pair are close to 1.0/1.0 for all triplet structures. However, while the NOON for the principal bonding/antibonding pair for the singlet structures of the electrocyclic process are close to 2.0/0.0, indicating very little diradical character, they are further off for the sigmatropic processes. More in particular, the concerted sigmatropic transition state has some diradical character (NOON for the principal bonding/antibonding pair = 1.7/0.3), the sigmatropic stepwise transition states have even higher diradical character (NOON for the principal bonding/antibonding pair = 1.5/0.5) and the sigmatropic stepwise intermediate is obviously a pure diradical (NOON for the principal bonding/antibonding pair = 1.0/1.0).

Data 15: Full references of *Gaussian 09* (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.

Figure 1: copy of  $^1\text{H}$  NMR spectrum recorded for (E)-pent-2-en-4-yn-1-ol **11** ( $\text{CDCl}_3$ , 300MHz, residual solvent and TMSOH).

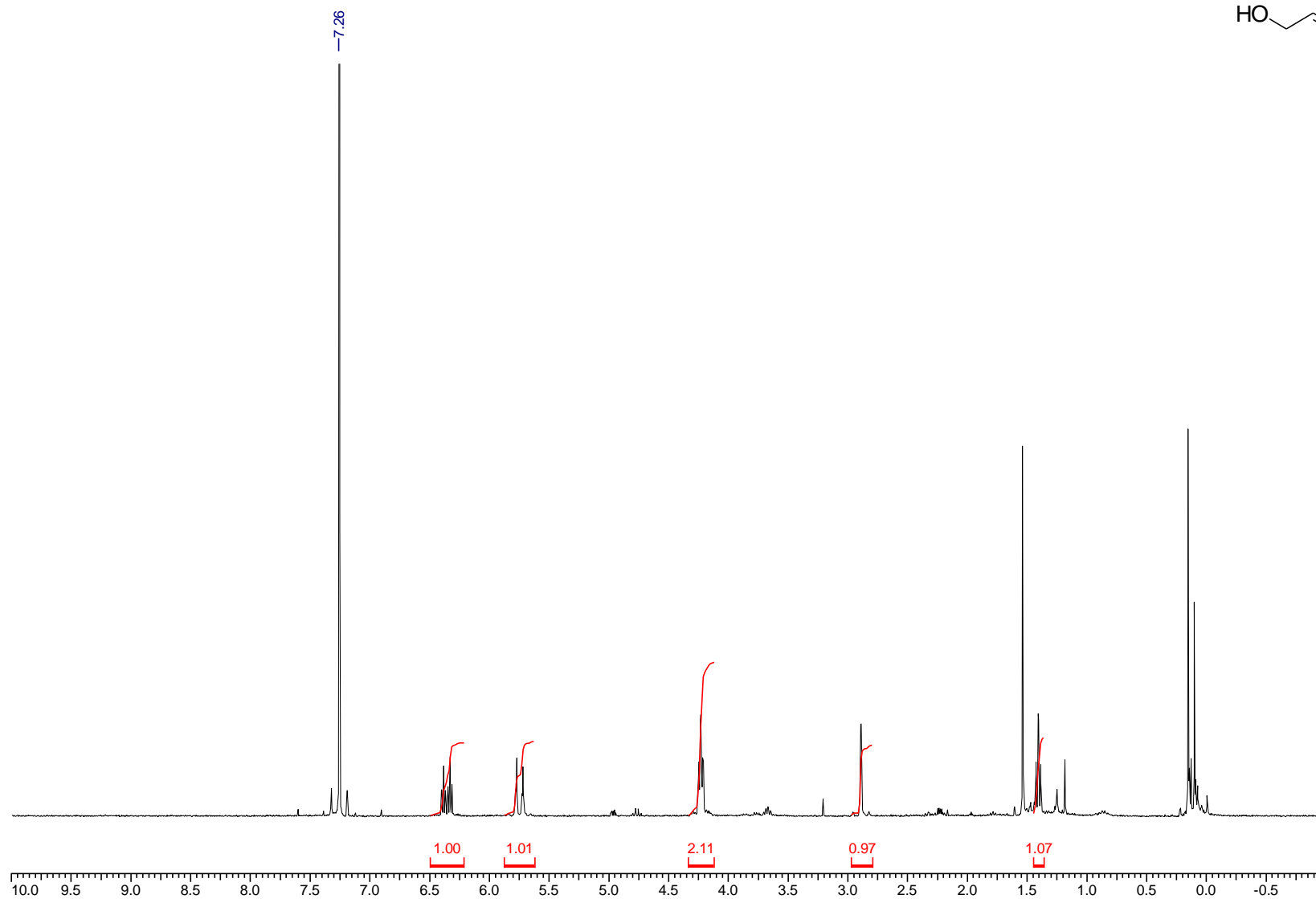
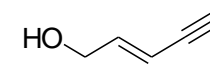


Figure 2: copy of  $^1\text{H}$  NMR spectrum recorded for (2*E*,8*E*)-Deca-2,8-diene-4,6-diyne-1,10-diol **12**. (DMSO- $d_6$ , 300 MHz).

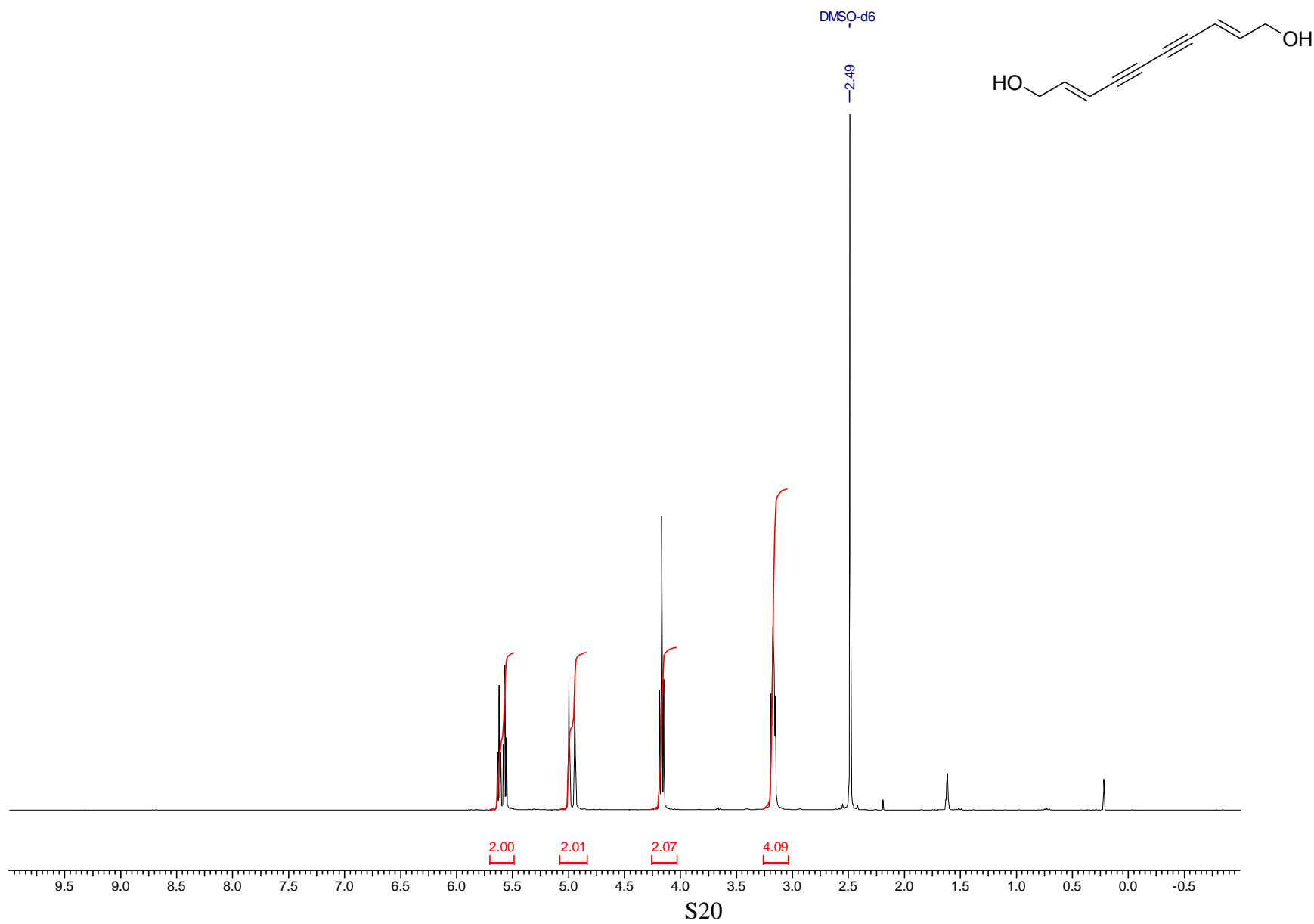


Figure 3: copy of  $^{13}\text{H}$  NMR spectrum (APT) recorded for (2*E*,8*E*)-Deca-2,8-diene-4,6-diyne-1,10-diol **12**. (DMSO- $\text{d}_6$ , 75 MHz).

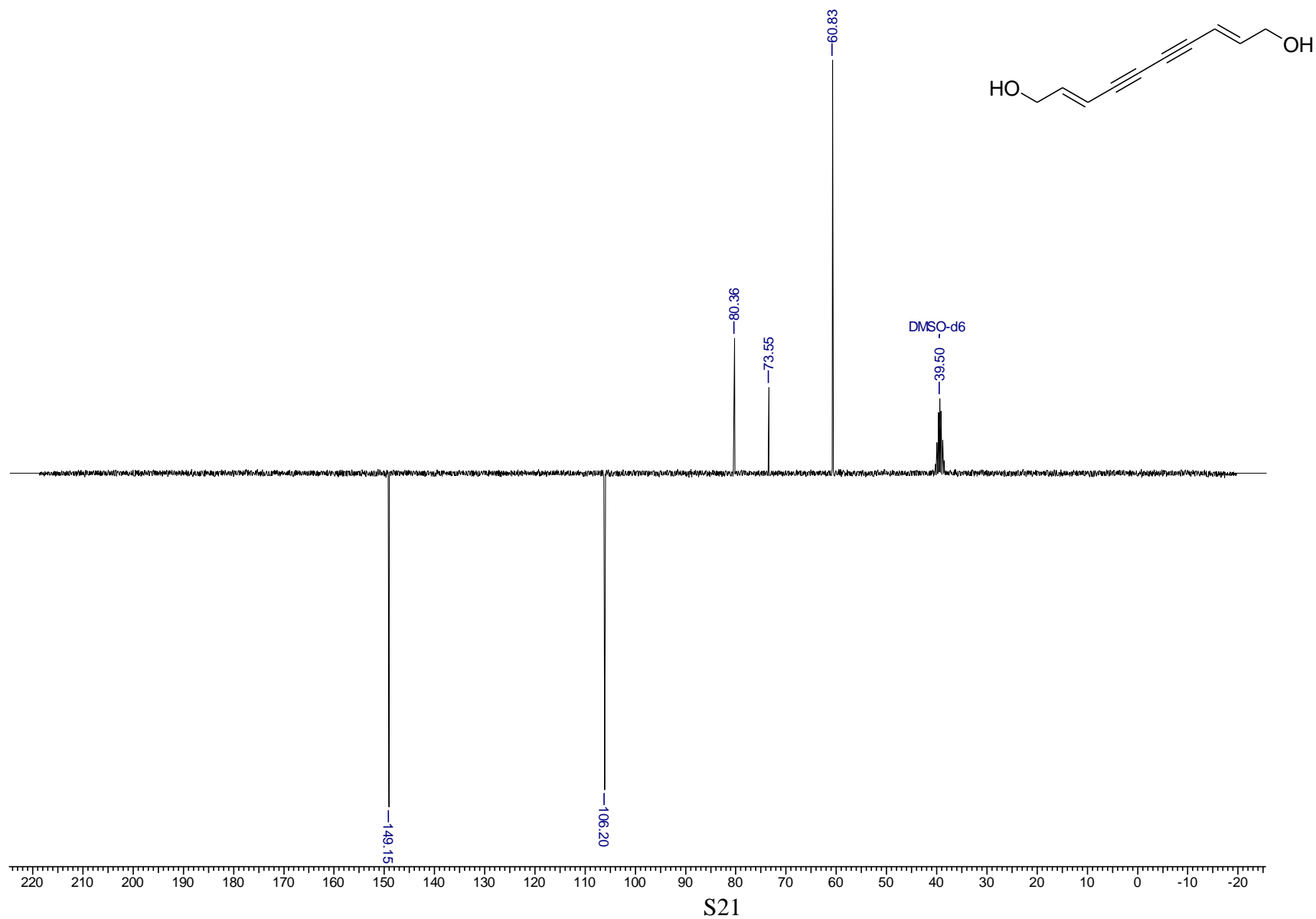


Figure 4: copy of  $^1\text{H}$  NMR spectrum recorded for (8-Hydroxymethyl-bicyclo[4.2.0]octa-2,4-dien-7-yl)-methanol **9**. ( $\text{CDCl}_3$ , 300 MHz, residual MTBE and water).

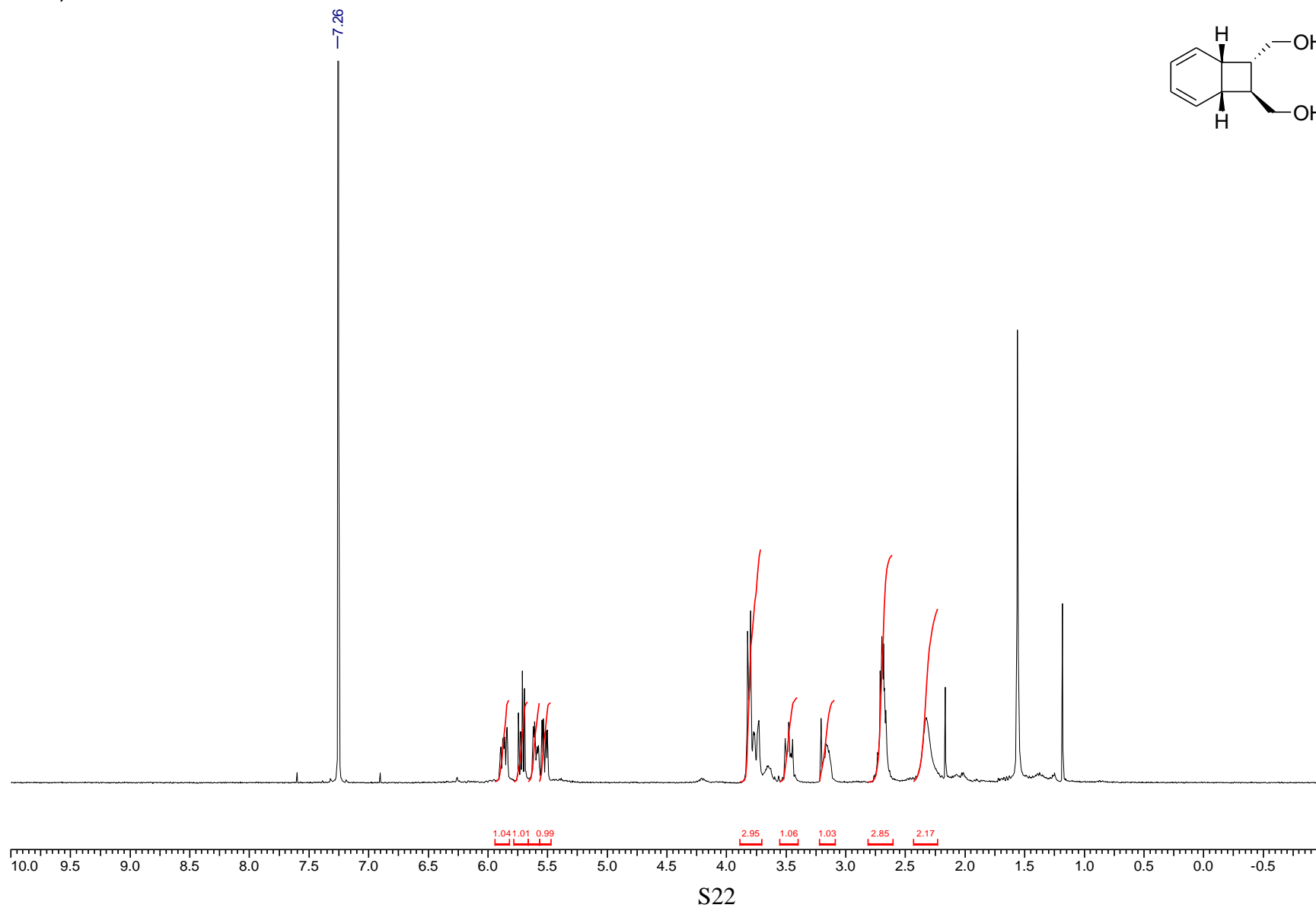
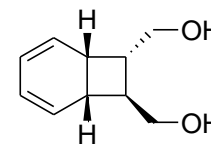


Figure 5: copy of  $^{13}\text{C}$  NMR spectrum (APT) recorded for (8-Hydroxymethyl-bicyclo[4.2.0]octa-2,4-dien-7-yl)-methanol **9**. ( $\text{CDCl}_3$ , 75 MHz, residual MTBE).

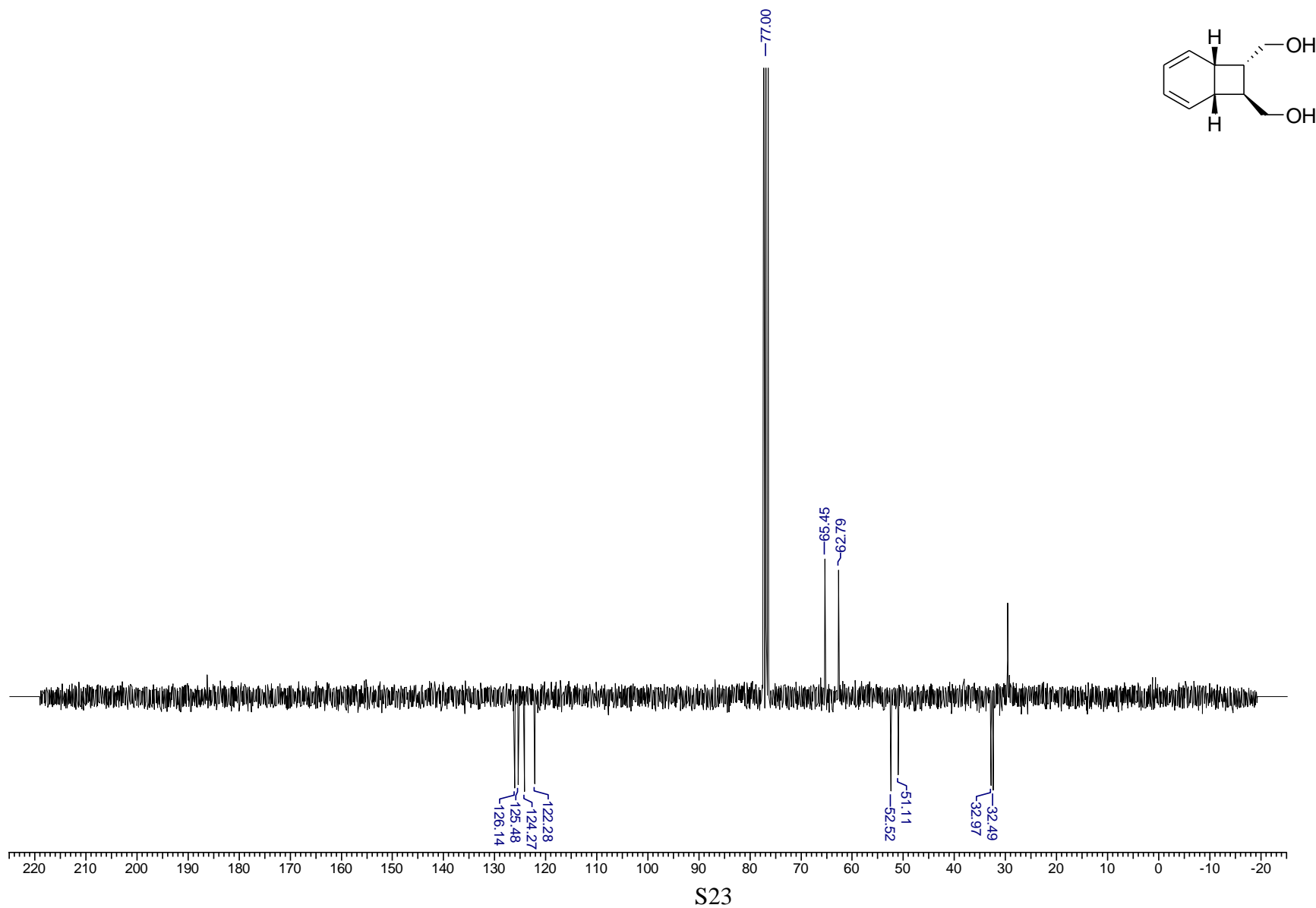


Figure 6: copy of HSQC(EDETGP) and COSY(GPQF) 2D NMR spectrum recorded for (8-Hydroxymethyl-bicyclo[4.2.0]octa-2,4-dien-7-yl)-methanol 9. (DMSO-d<sub>6</sub>, 300 MHz, residual MTBE).

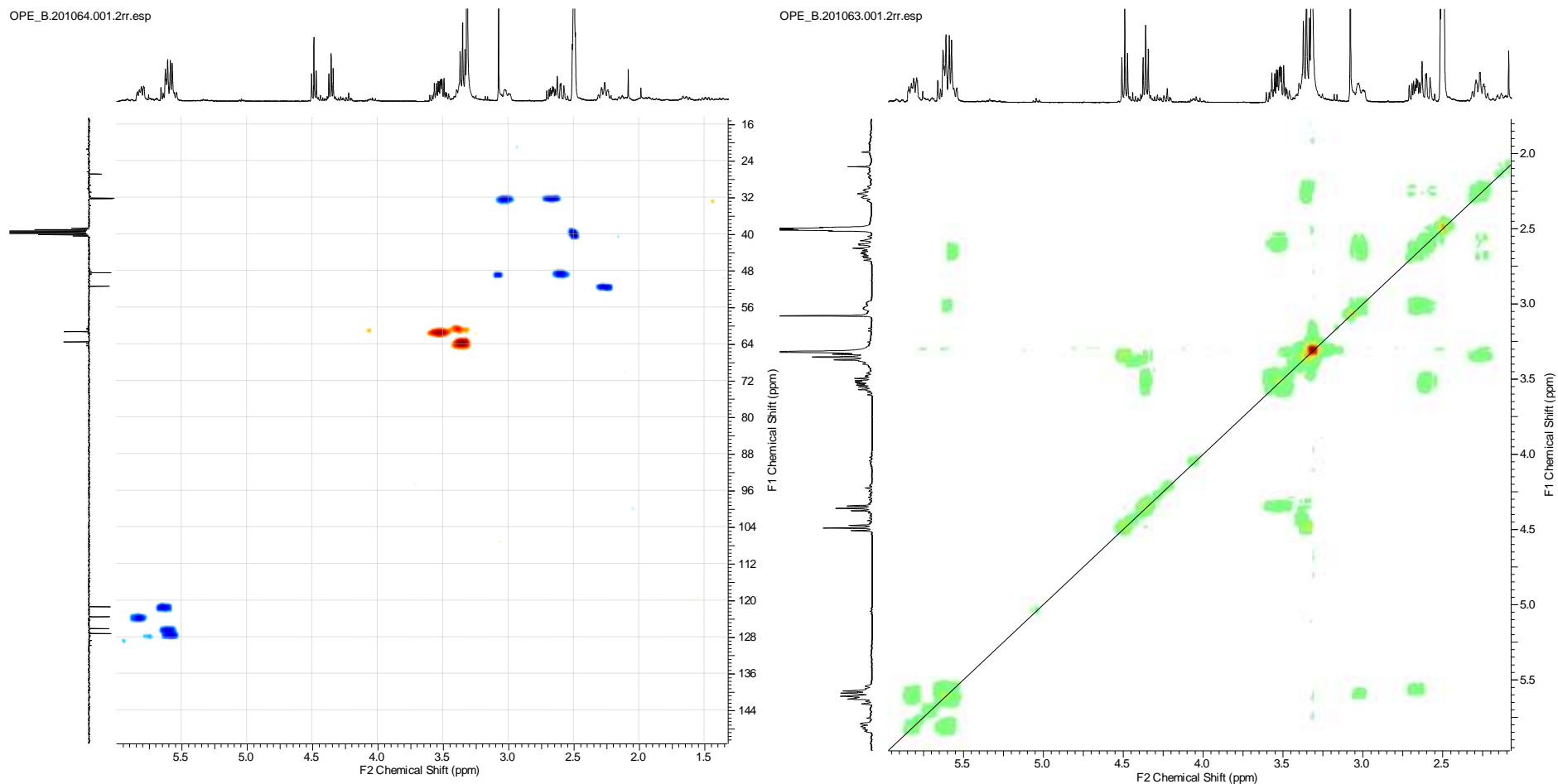




Figure 7: copy of COSY(GPQF) and HSQC(EDETGP) 2D NMR spectrum recorded for (8-Hydroxymethyl-bicyclo[4.2.0]octa-2,4-dien-7-yl)-methanol 9. (CDCl<sub>3</sub>, 300 MHz, residual MTBE and light petroleum).

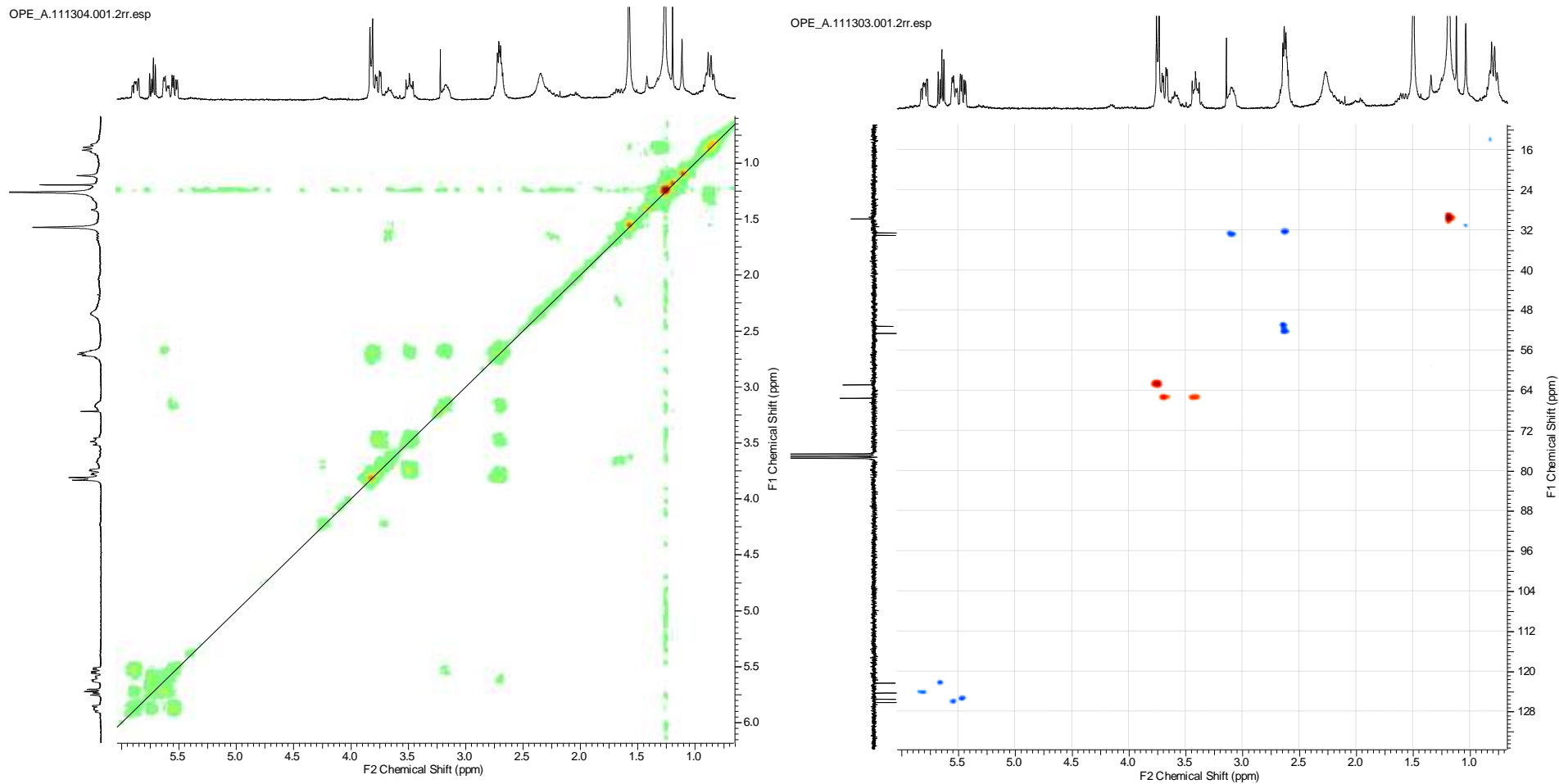


Figure 8: copy of  $^1\text{H}$  NMR spectrum recorded for  $[2,3,4,5\text{-}^2\text{H}_4]\text{-(8-Hydroxymethyl-bicyclo[4.2.0]octa-2,4-dien-7-yl)-methanol-9-d}_4$ . ( $\text{CDCl}_3$ , 300 MHz, res. MTBE and water).

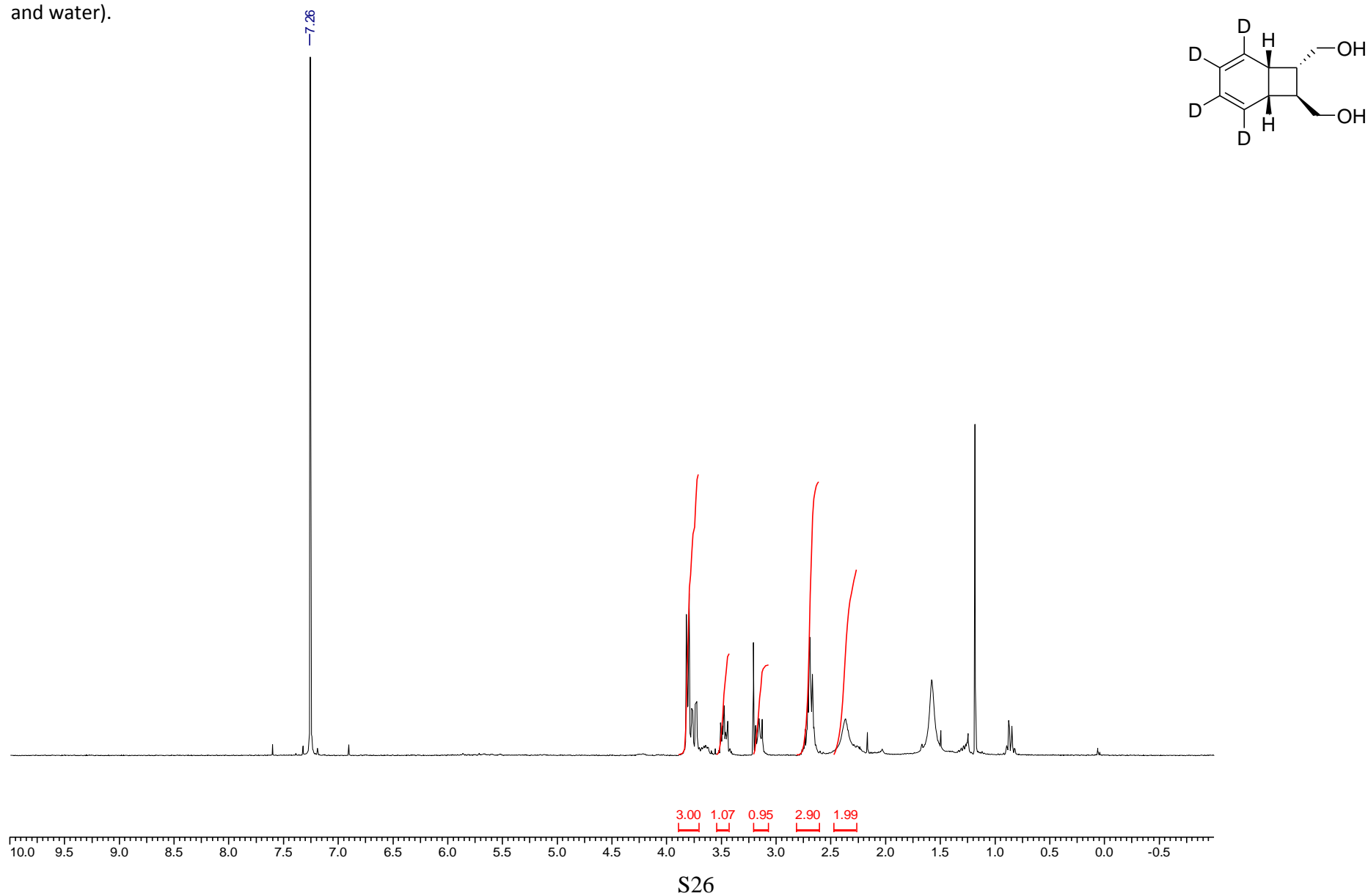


Figure 9: copy of  $^{13}\text{C}$  NMR spectrum (APT) recorded for [2,3,4,5- $2\text{H}_4$ ]-[8-Hydroxymethyl-bicyclo[4.2.0]octa-2,4-dien-7-yl)-methanol 9- $\text{d}_4$ . ( $\text{CDCl}_3$ , 125 MHz, residual MTBE).

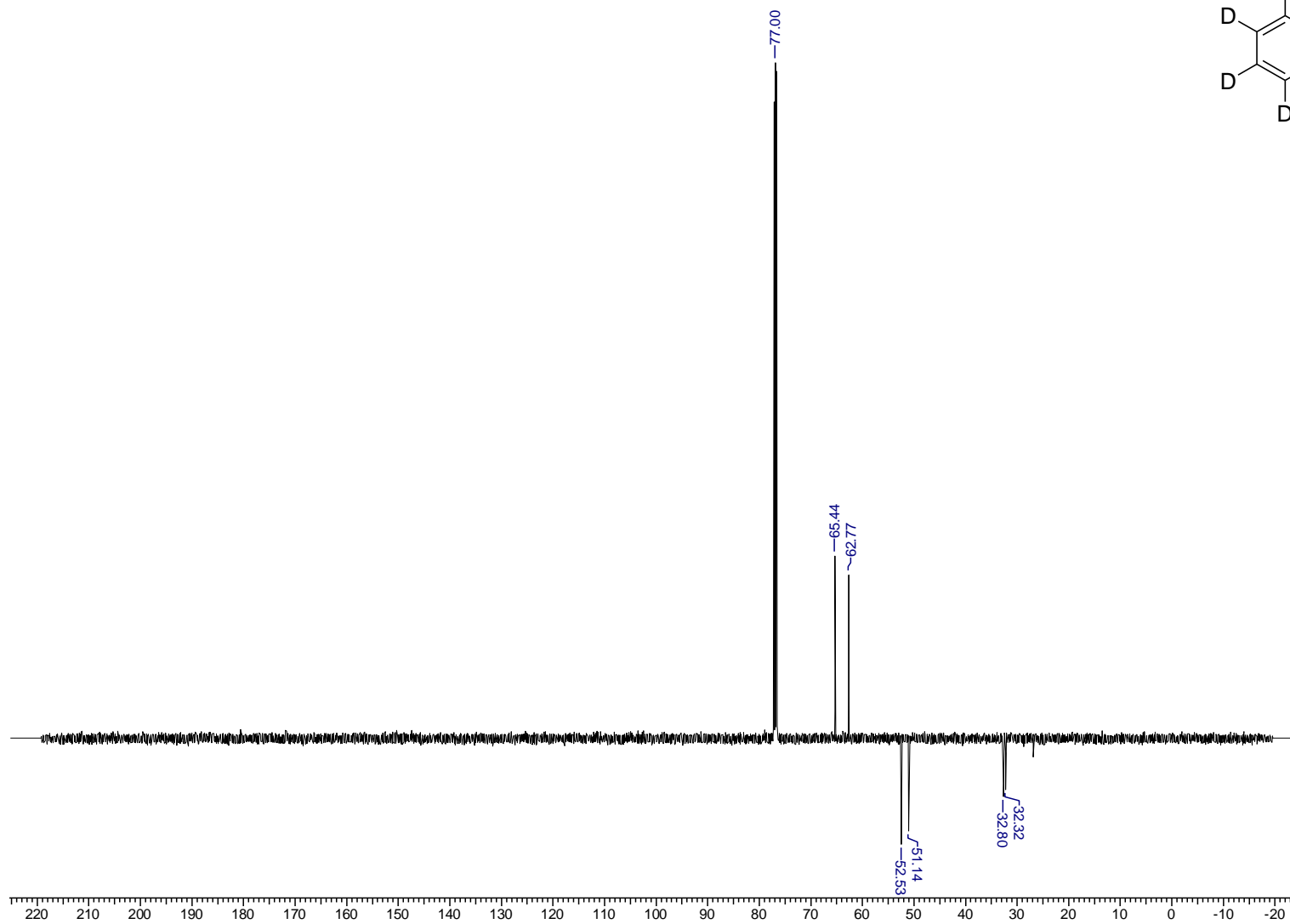
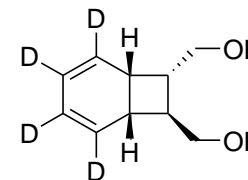


Figure 10: copy of  $^1\text{H}$  NMR spectrum recorded for [2,3,4,5- $2\text{H}_4$ ]-[8-Hydroxymethyl-bicyclo[4.2.0]octa-2,4-dien-7-yl]-methanol  $9\text{-d}_4$ , recovered unchanged by FC after 2 h thermal equilibration at 190-195°C ( $\text{CDCl}_3$ , 300 MHz, residual MTBE).

