Supporting Information

Diterpenes and Sesquiterpenes from the Marine Algicolous Fungus *Trichoderma harzianum* X-5

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Table S1. Cartesian coordinates of the energy-minimized conformer **1a** optimized at the B3LYP/6-31G(d) level in MeOH.

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Table S4. Cartesian coordinates of the energy-minimized conformer **2a** optimized at the B3LYP/6-31G(d) level in MeOH.

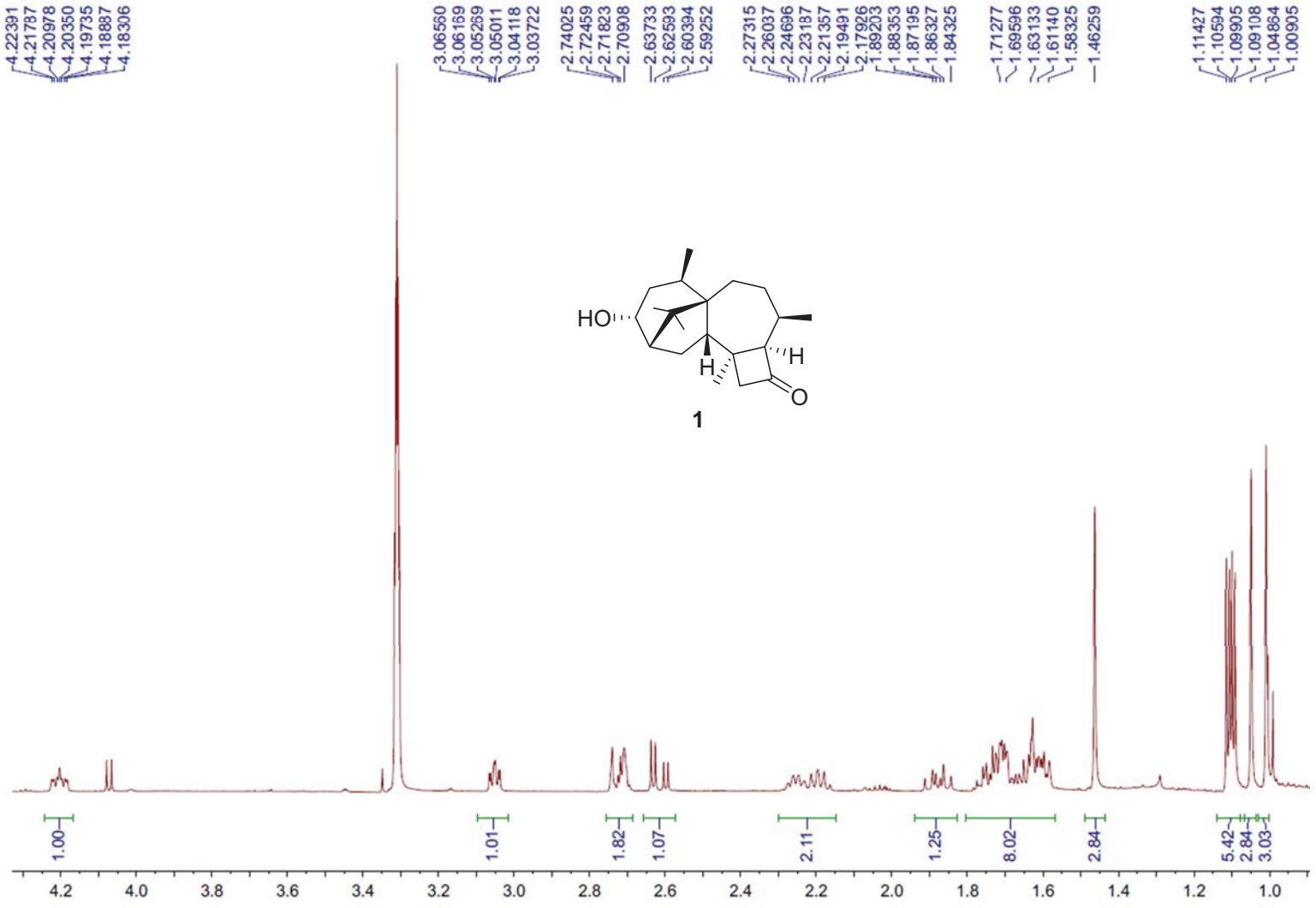


Figure S1. ^{1}H NMR spectrum of compound **1** in CD_3OD.

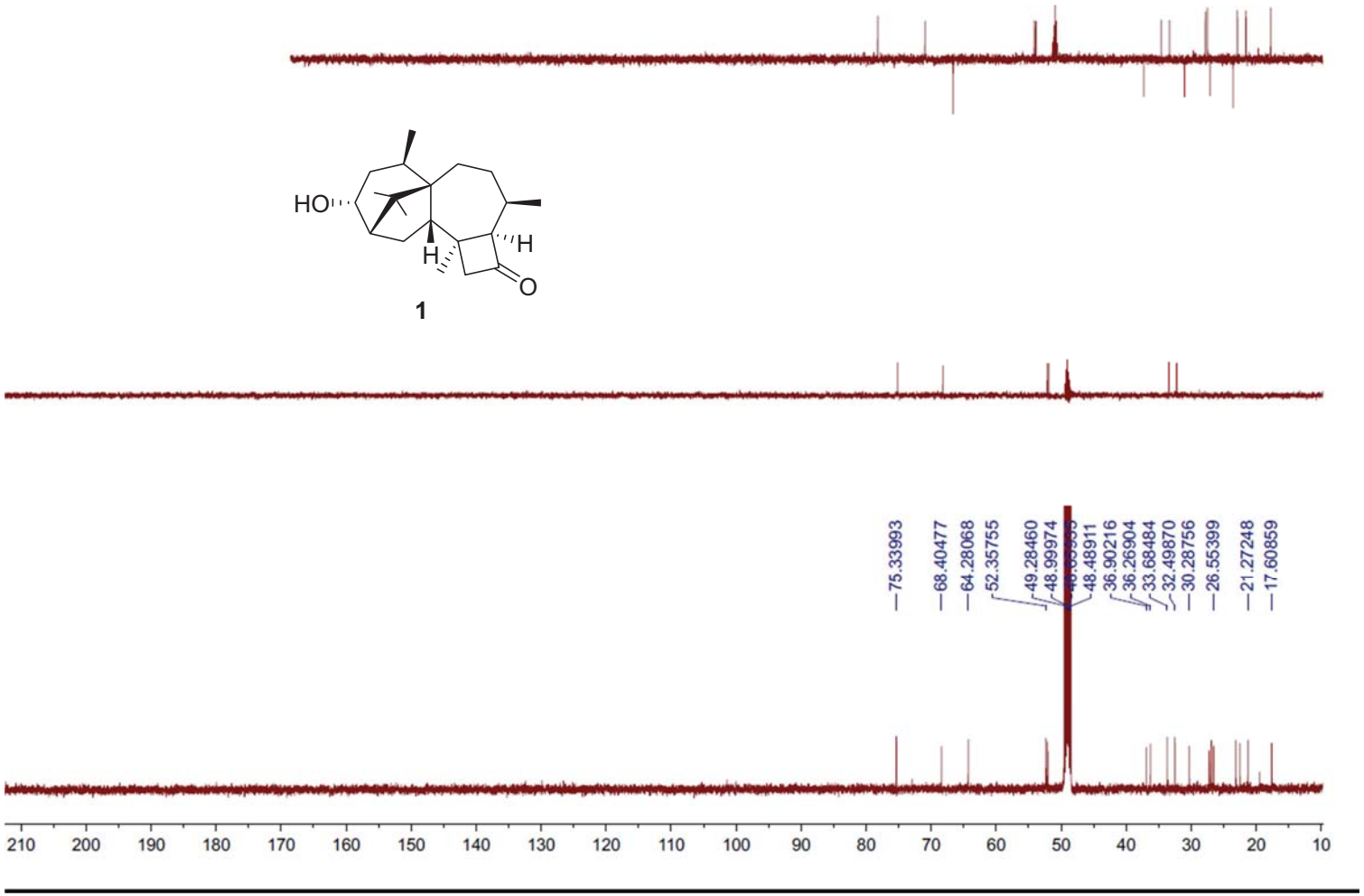


Figure S2. ^{13}C NMR and DEPT spectra of compound **1** in CD_3OD.

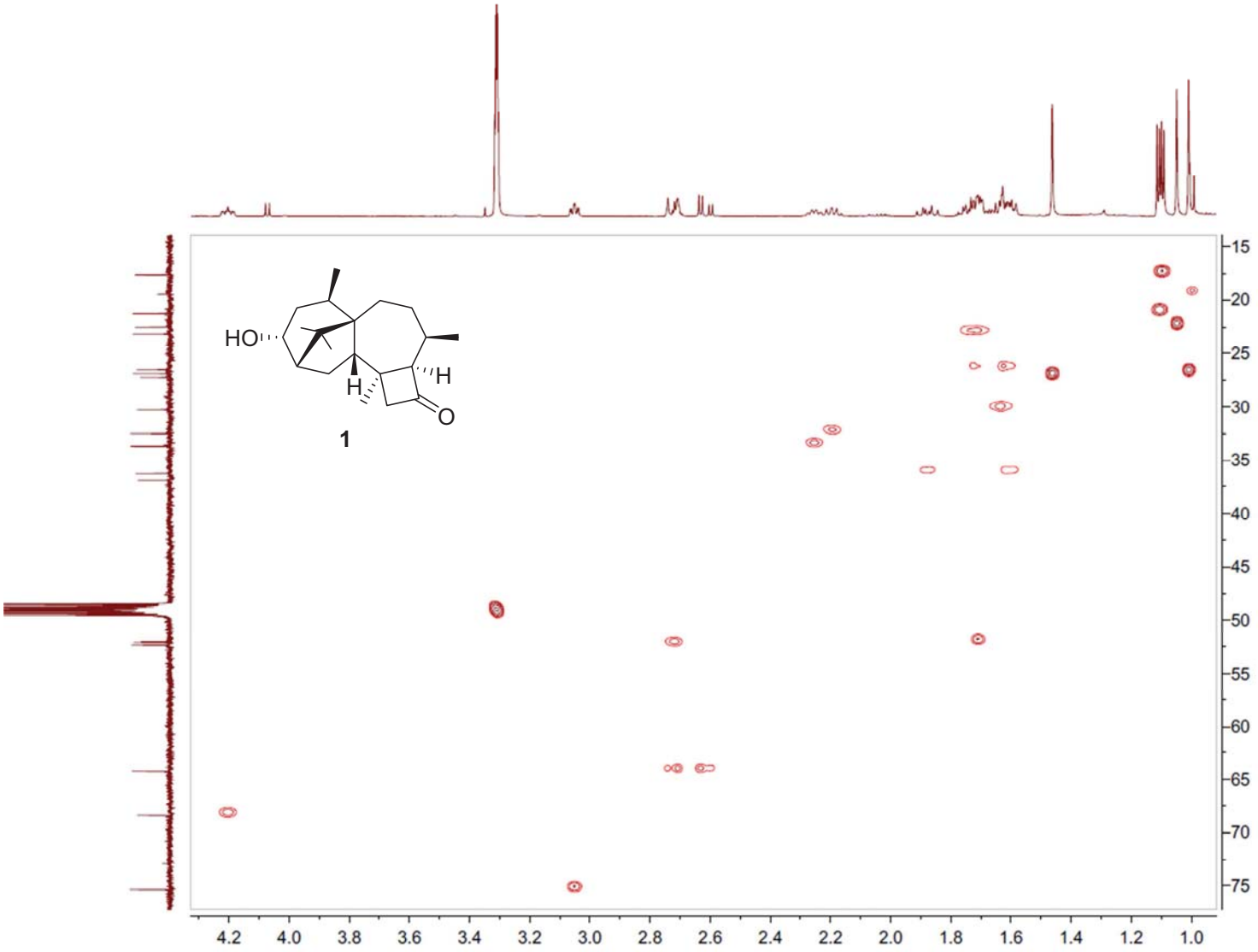


Figure S3. HSQC spectrum of compound **1** in CD_3OD.

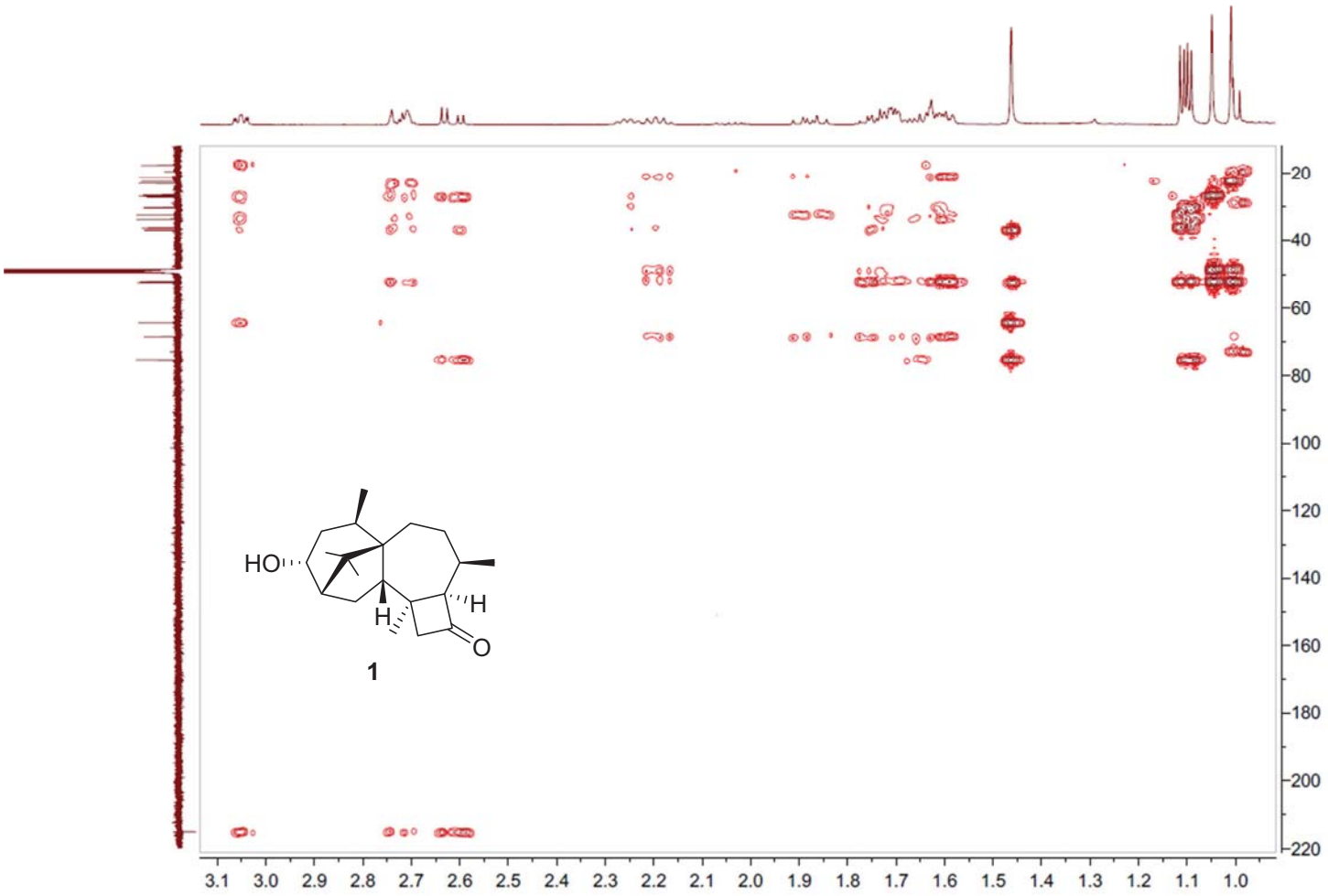


Figure S4. HMBC spectrum of compound **1** in CD_3OD.

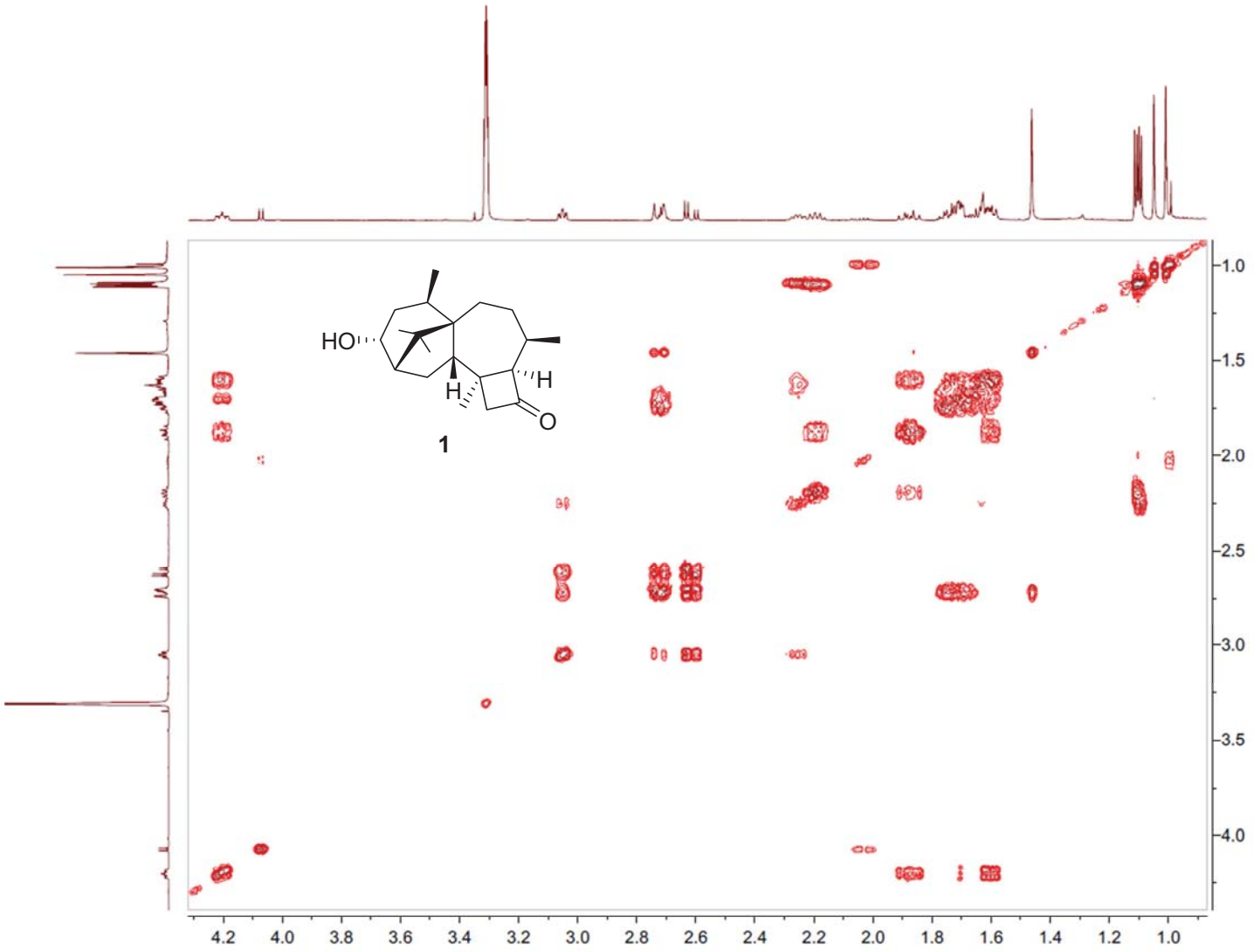


Figure S5. COSY spectrum of compound **1** in CD_3OD.

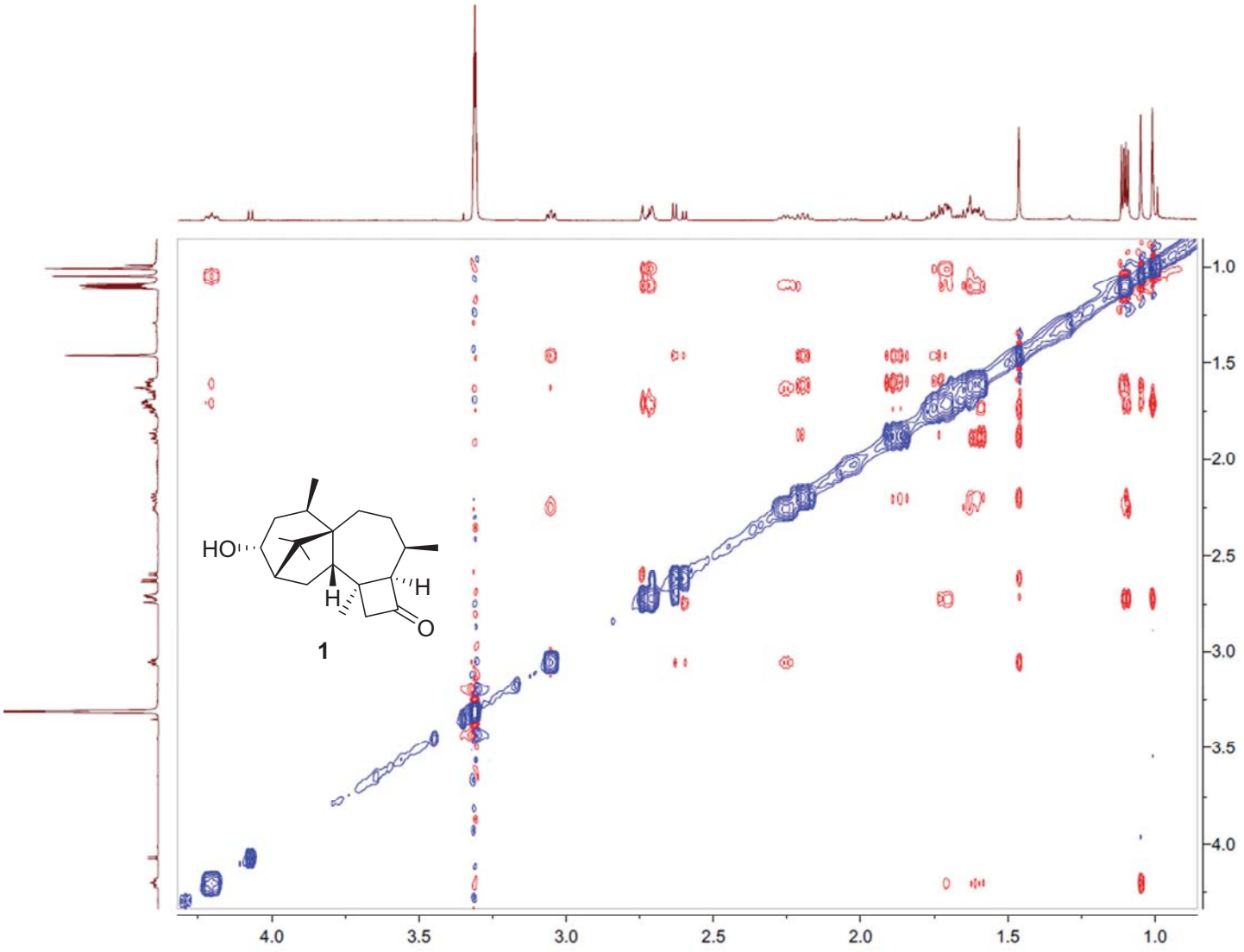
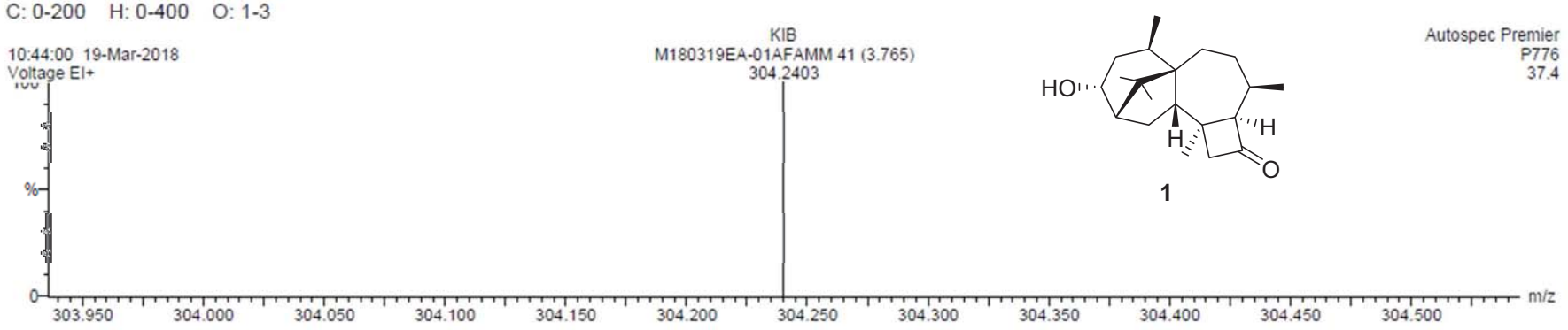


Figure S6. NOESY spectrum of compound **1** in CD_3OD.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 1-3



1

Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
304.2403	304.2402	0.1	0.3	5.0	5546035.0	C20 H32 O2

Figure S7. HREIMS spectrum of compound **1**.

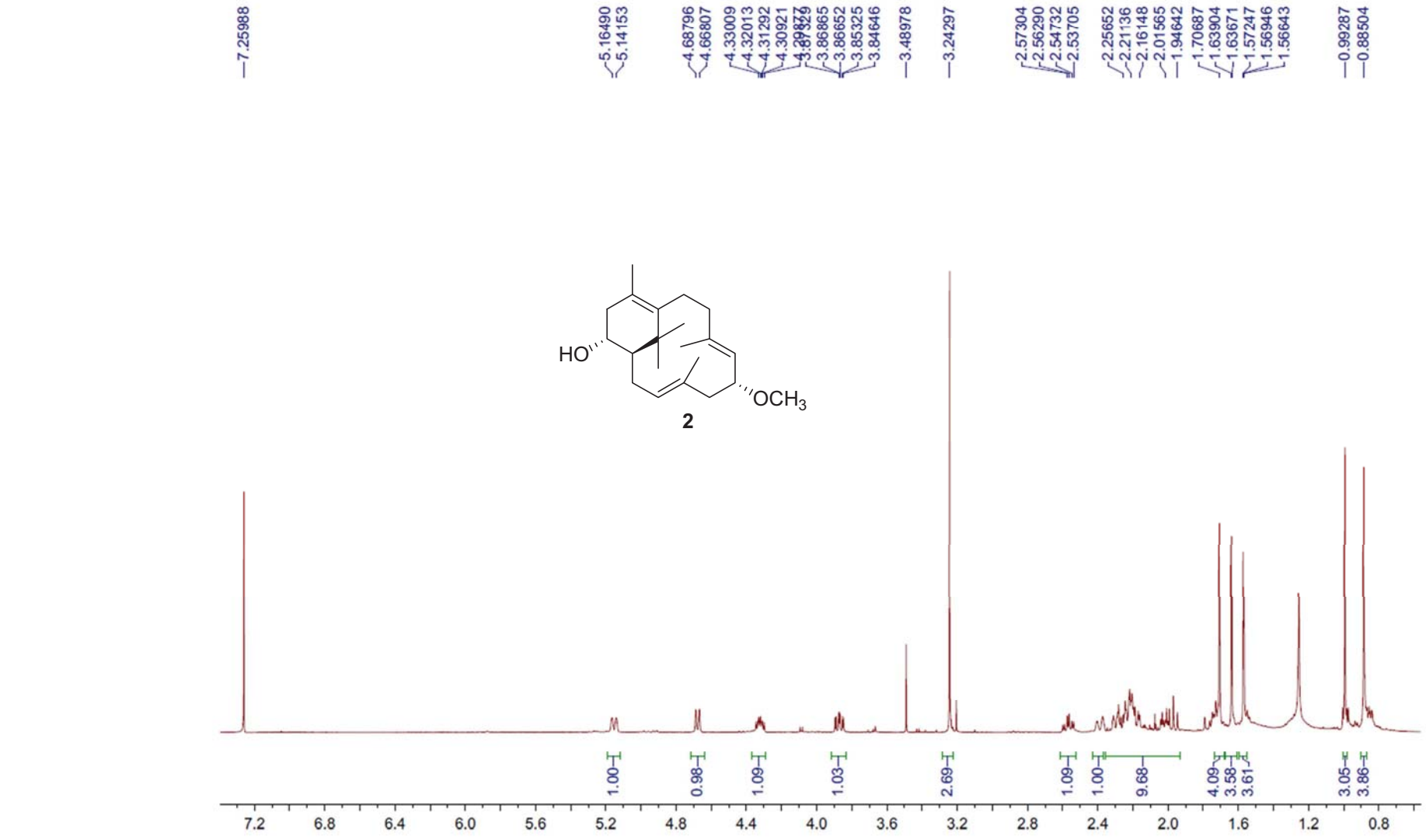


Figure S8. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

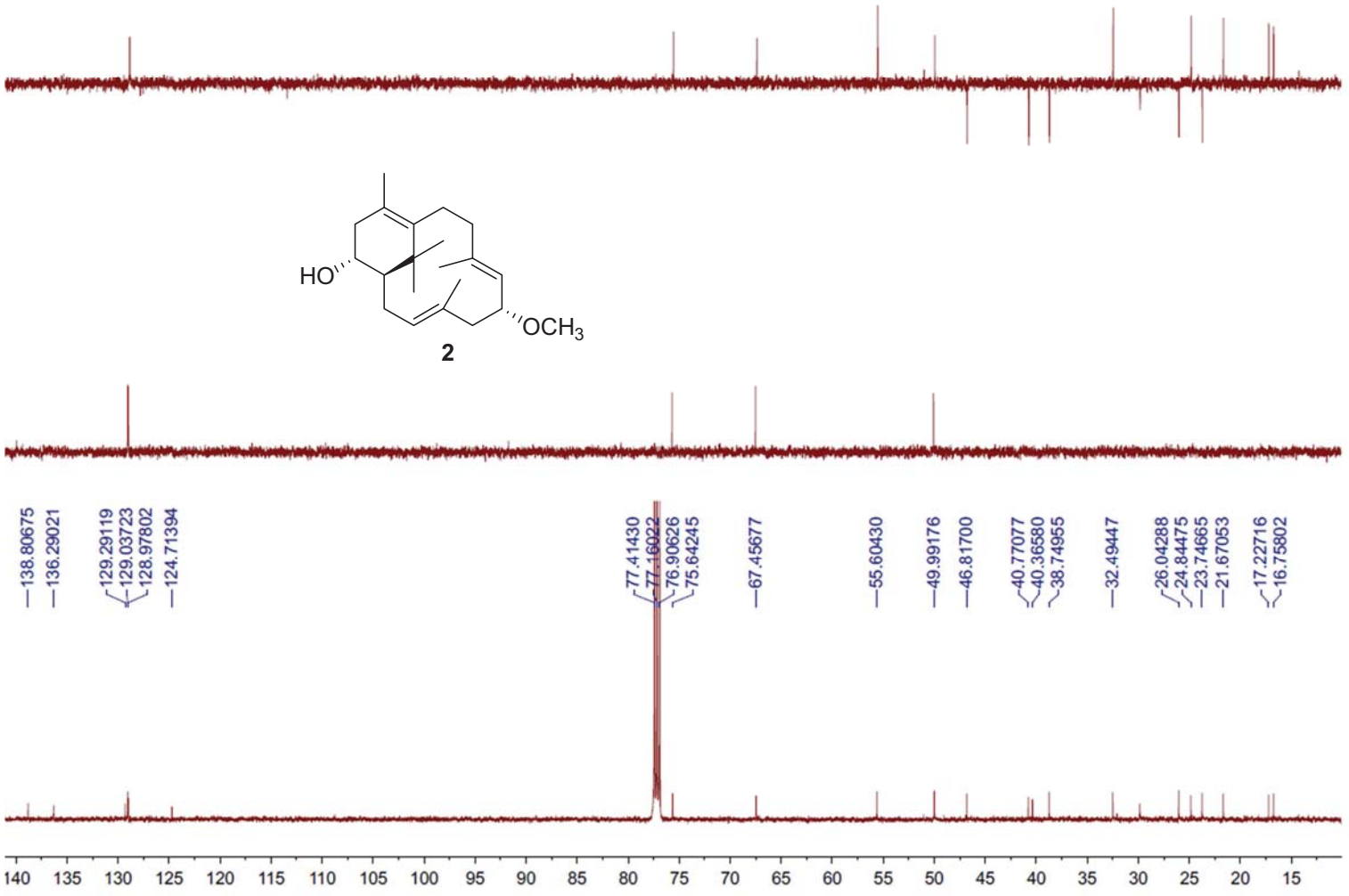


Figure S9. ^{13}C NMR and DEPT spectra of compound **2** in $CDCl_3$.

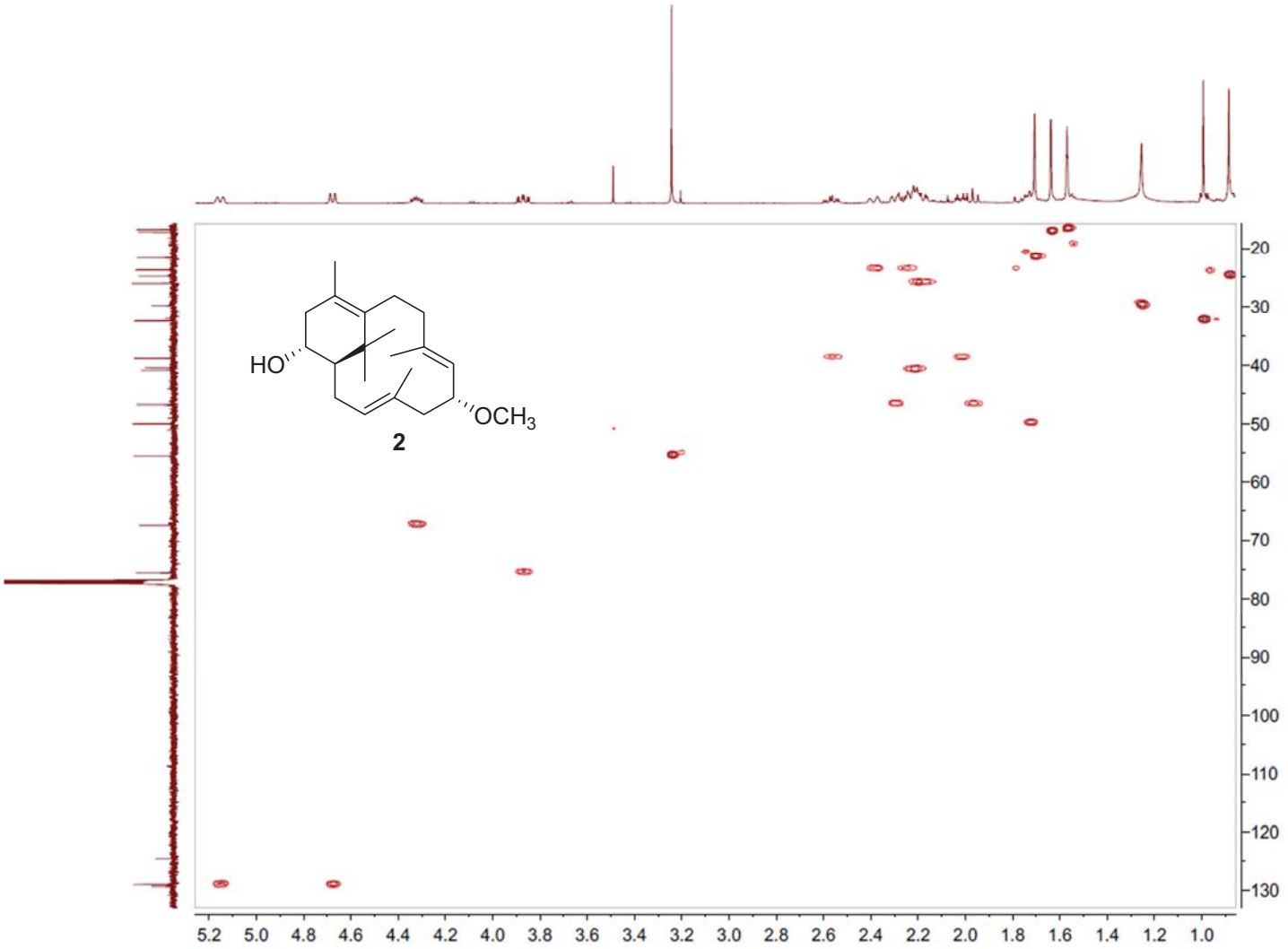


Figure S10. HSQC spectrum of compound **2** in $CDCl_3$.

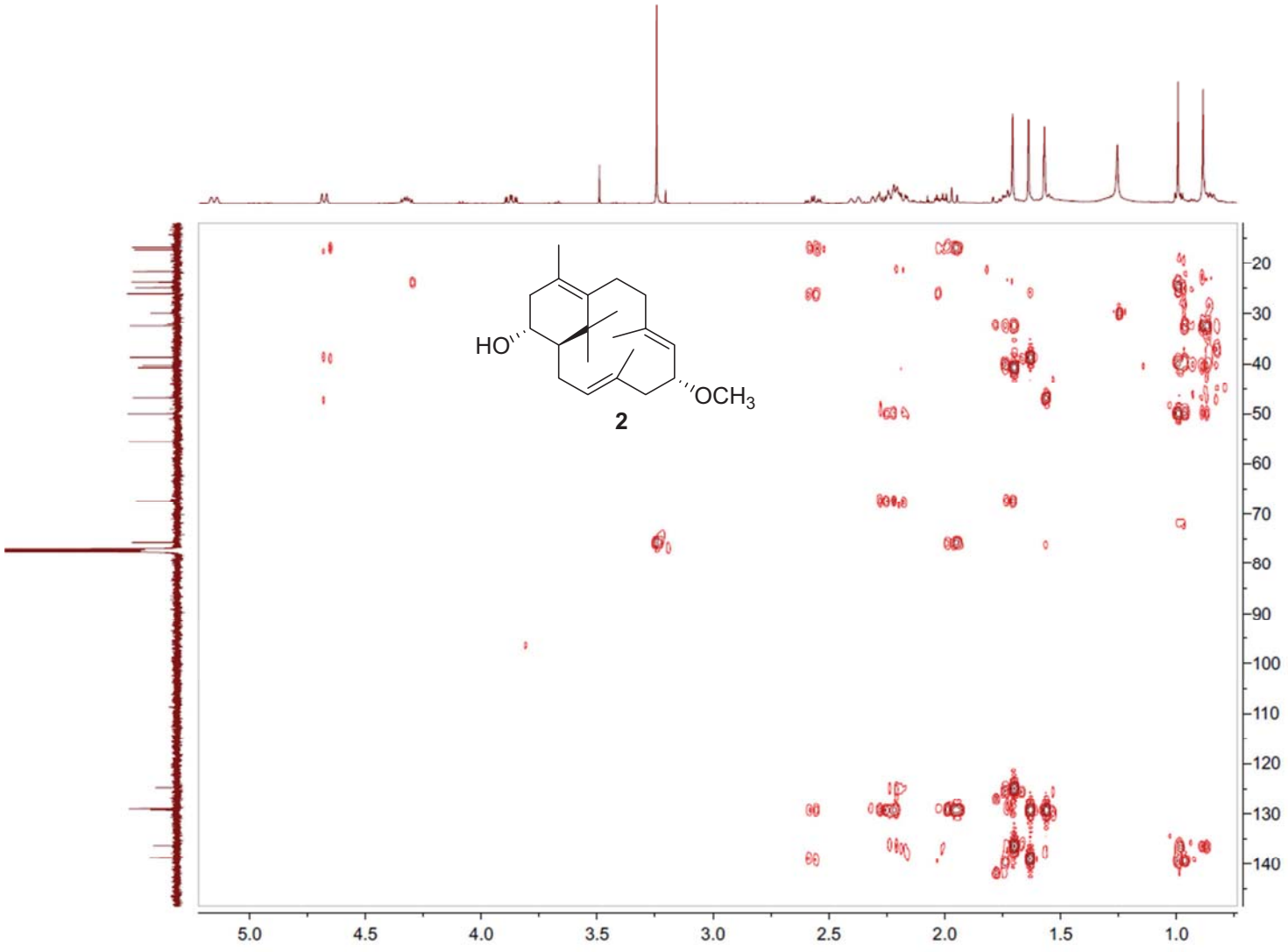


Figure S11. HMBC spectrum of compound **2** in $CDCl_3$.

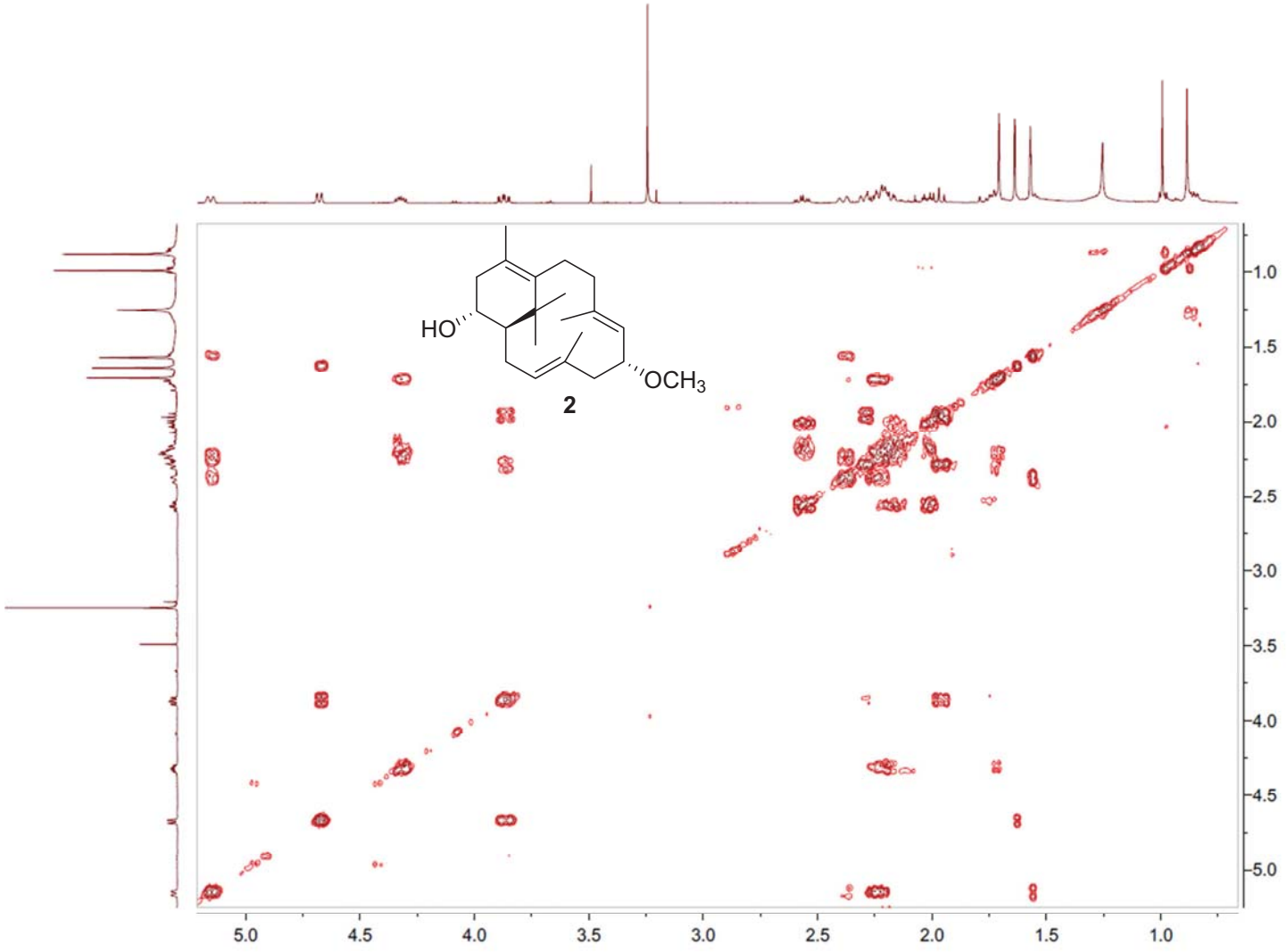


Figure S12. COSY spectrum of compound **2** in $CDCl_3$.

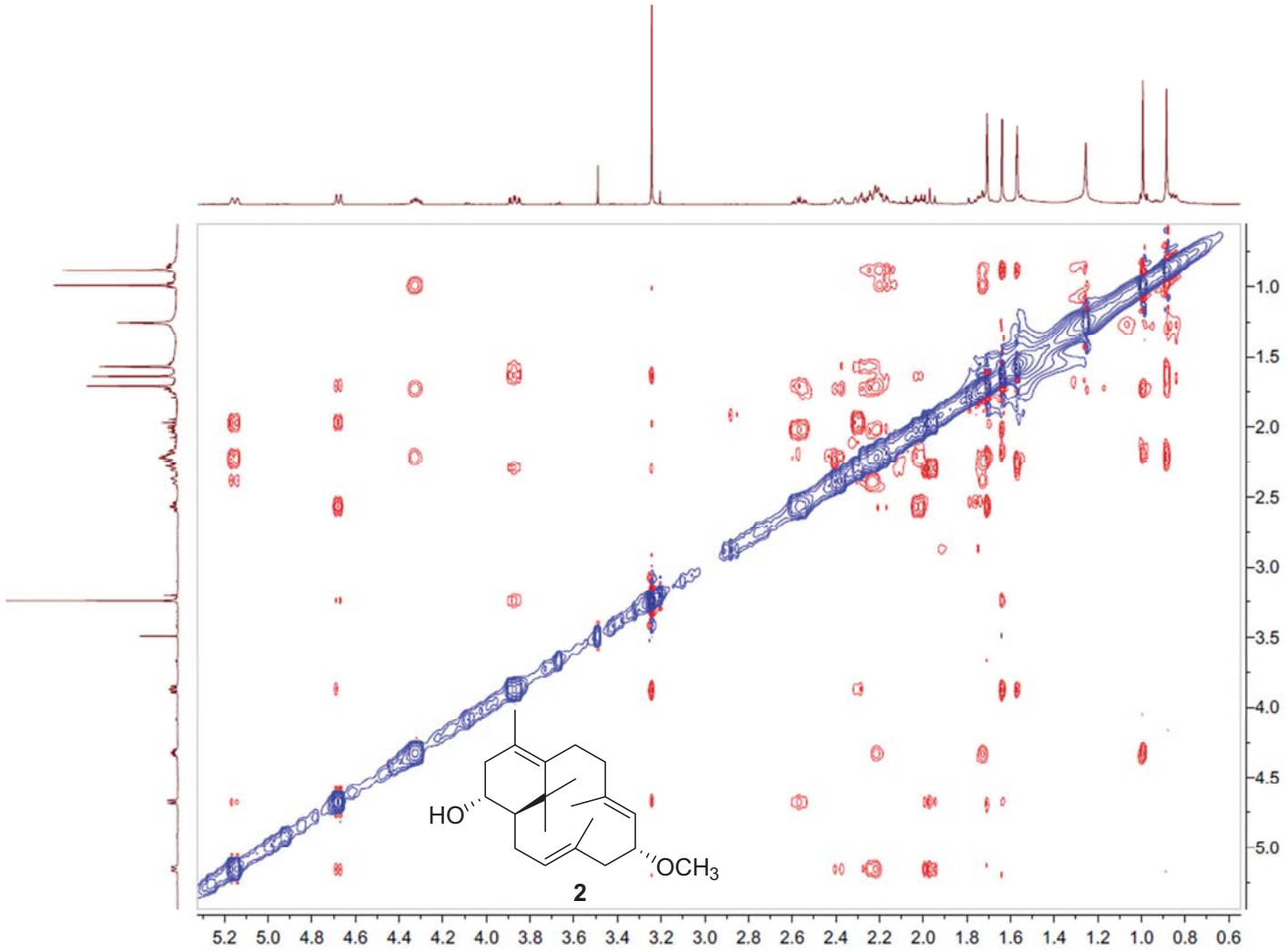
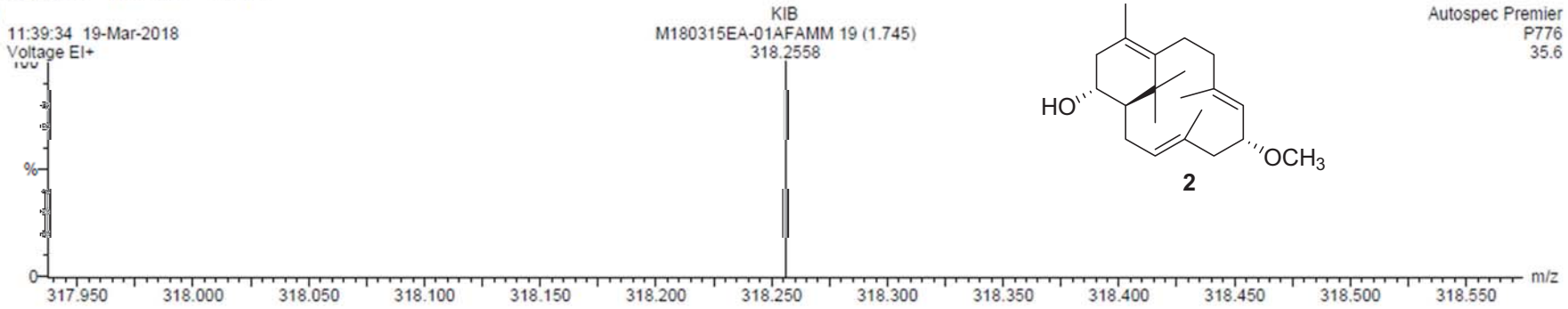


Figure S13. NOESY spectrum of compound **2** in $CDCl_3$.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
26 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 1-5



2

Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
318.2558	318.2559	-0.1	-0.3	5.0	5546034.5	C21 H34 O2

Figure S14. HREIMS spectrum of compound **2**.

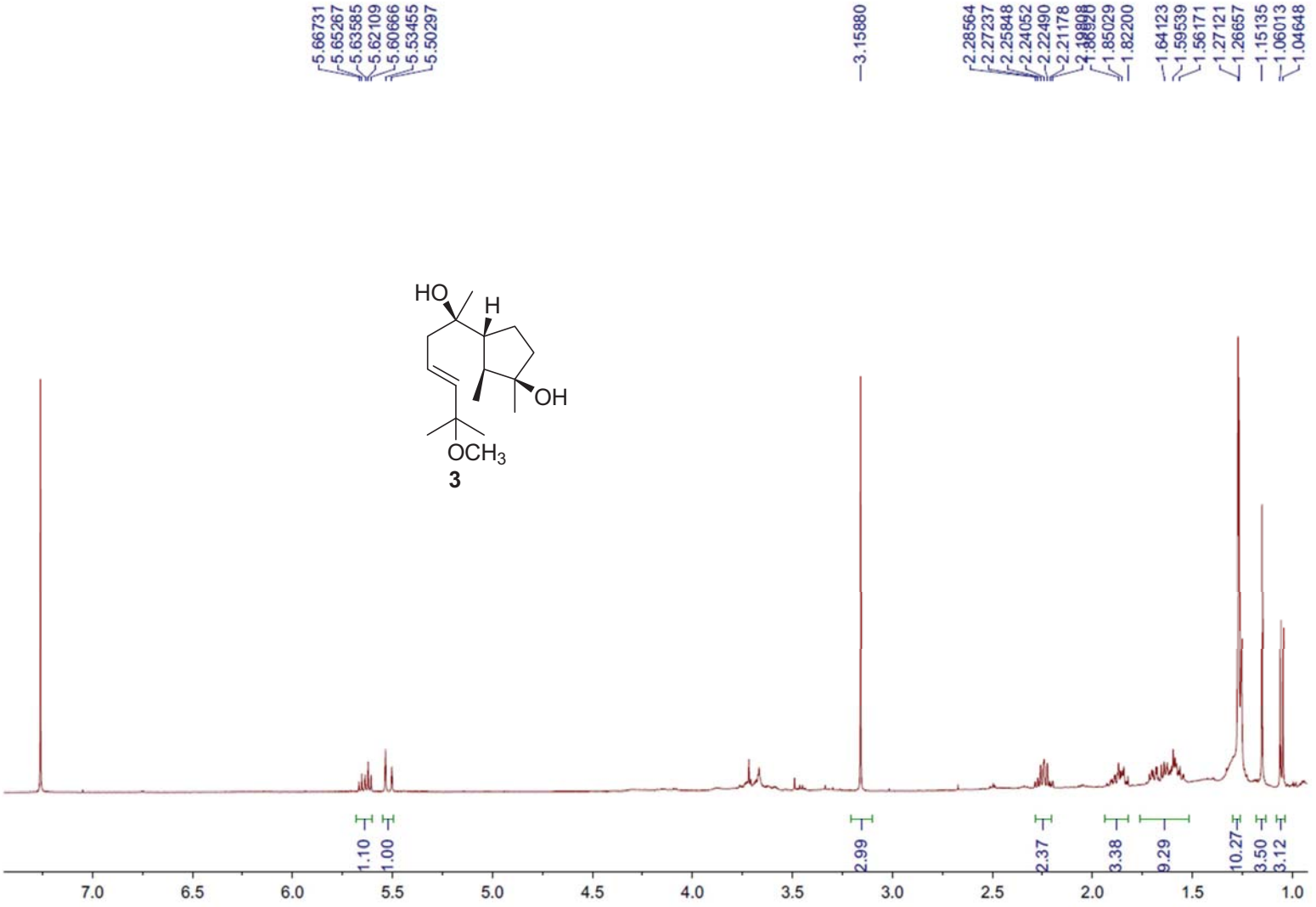


Figure S15. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

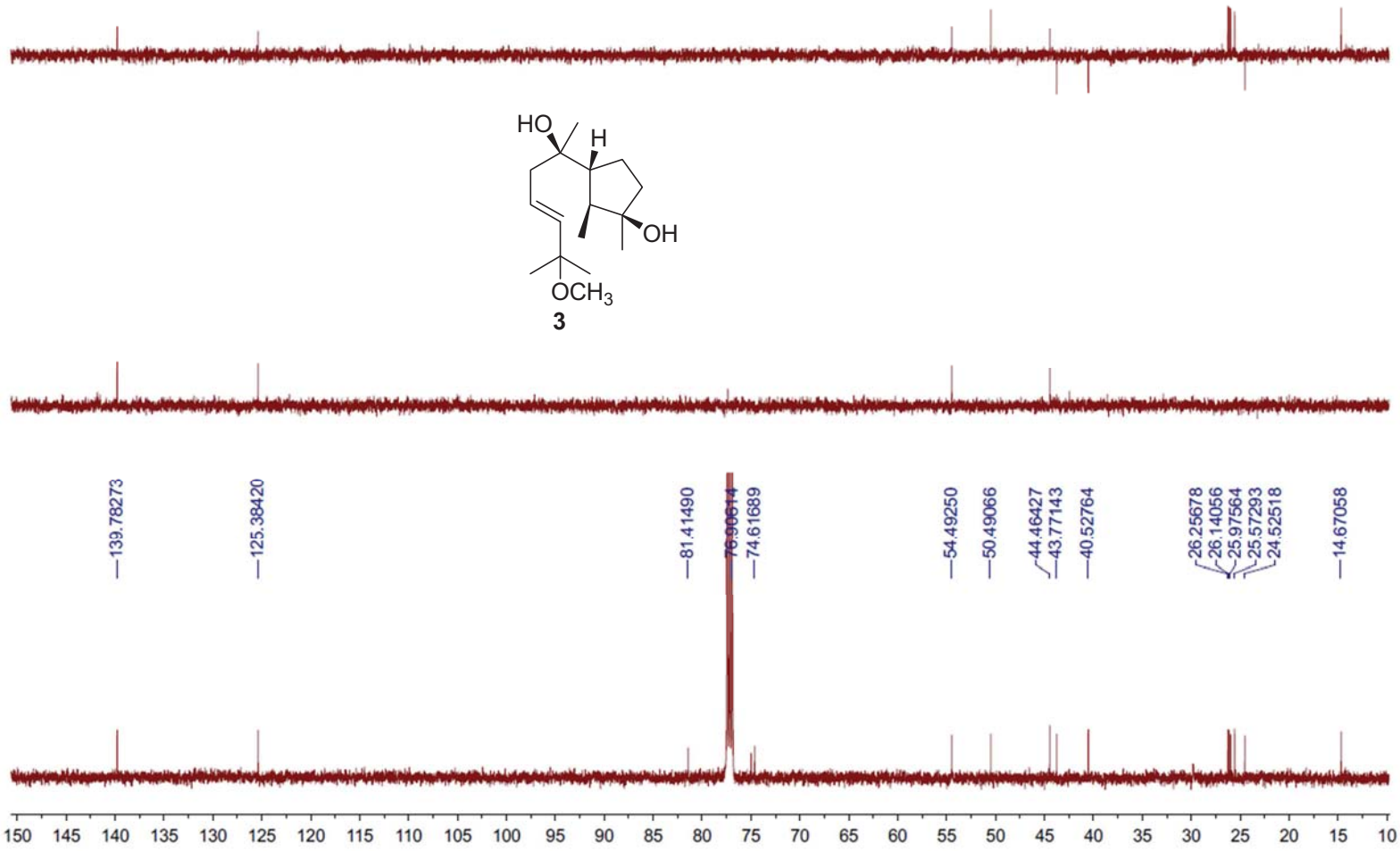


Figure S16. ^{13}C NMR and DEPT spectra of compound **3** in $CDCl_3$.

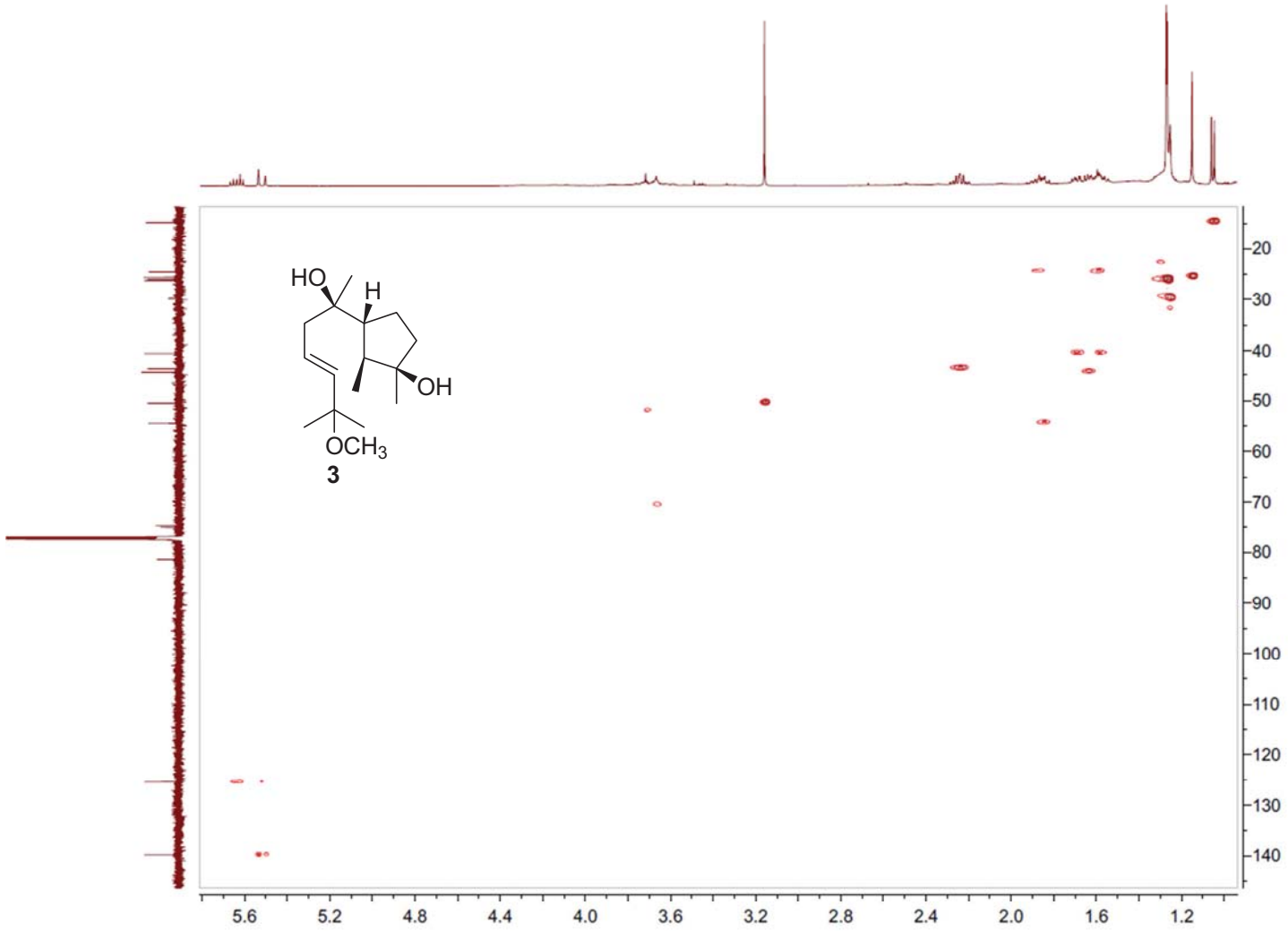


Figure S17. HSQC spectrum of compound **3** in $CDCl_3$.

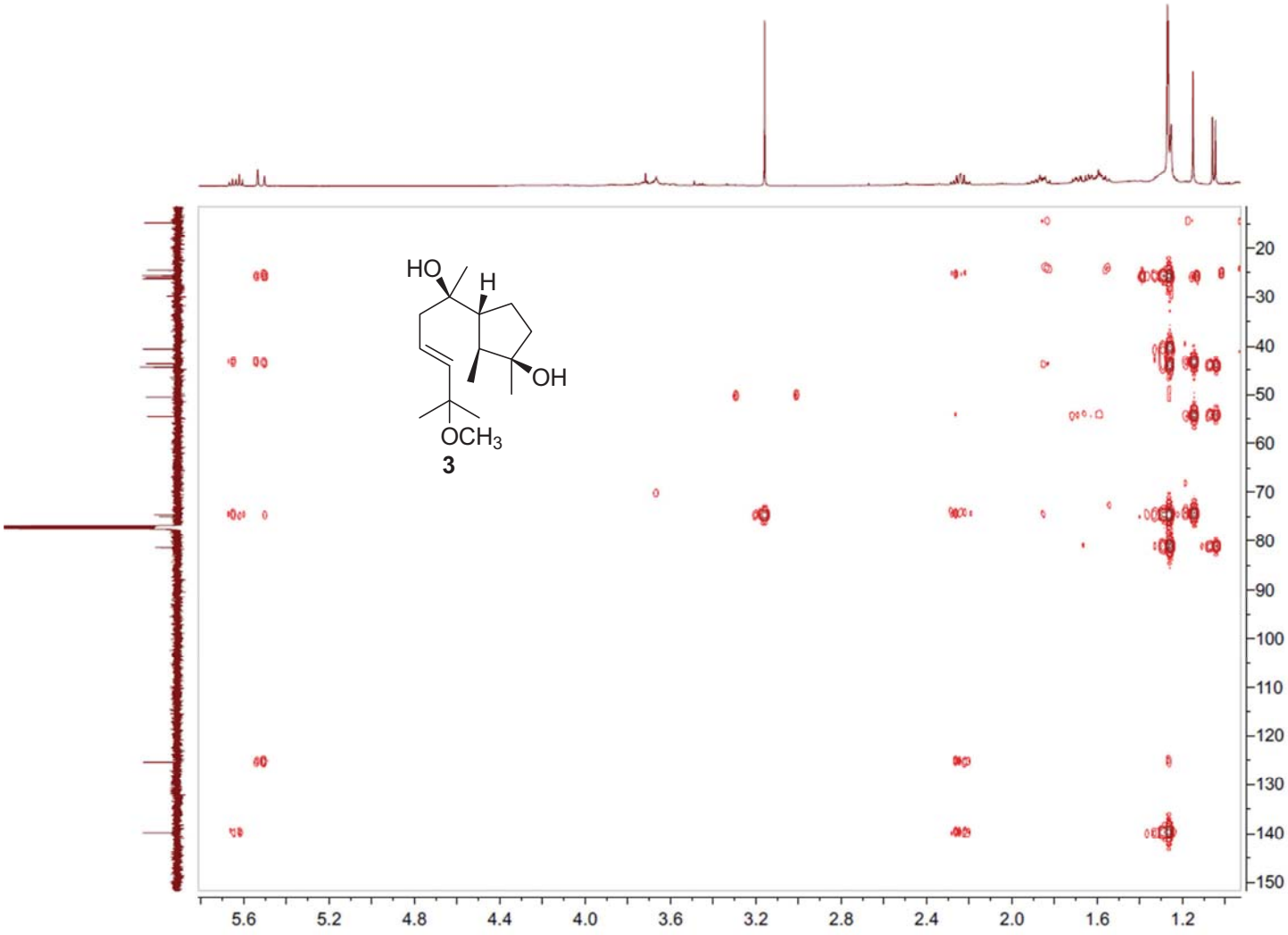


Figure S18. HMBC spectrum of compound **3** in $CDCl_3$.

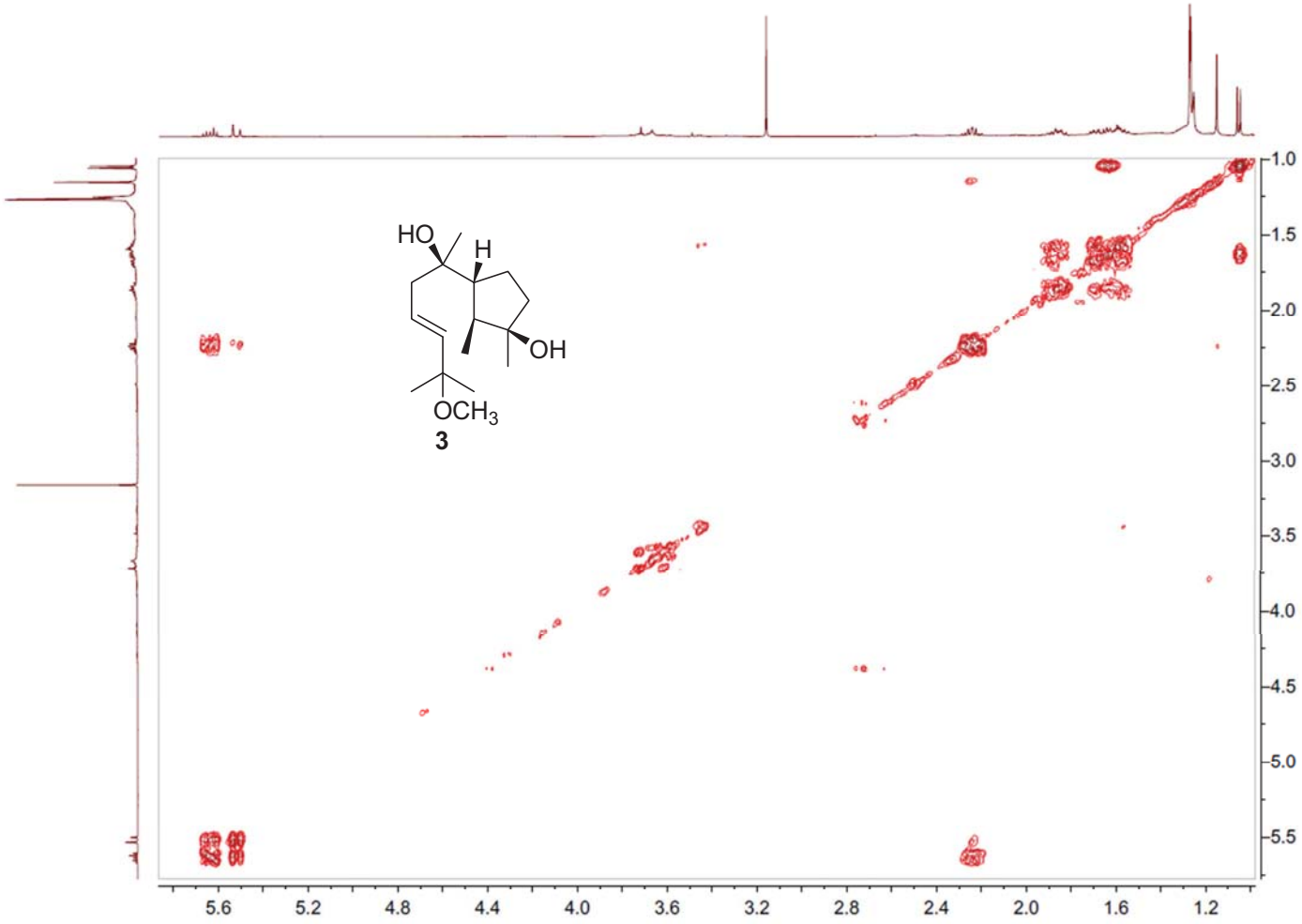


Figure S19. COSY spectrum of compound **3** in $CDCl_3$.

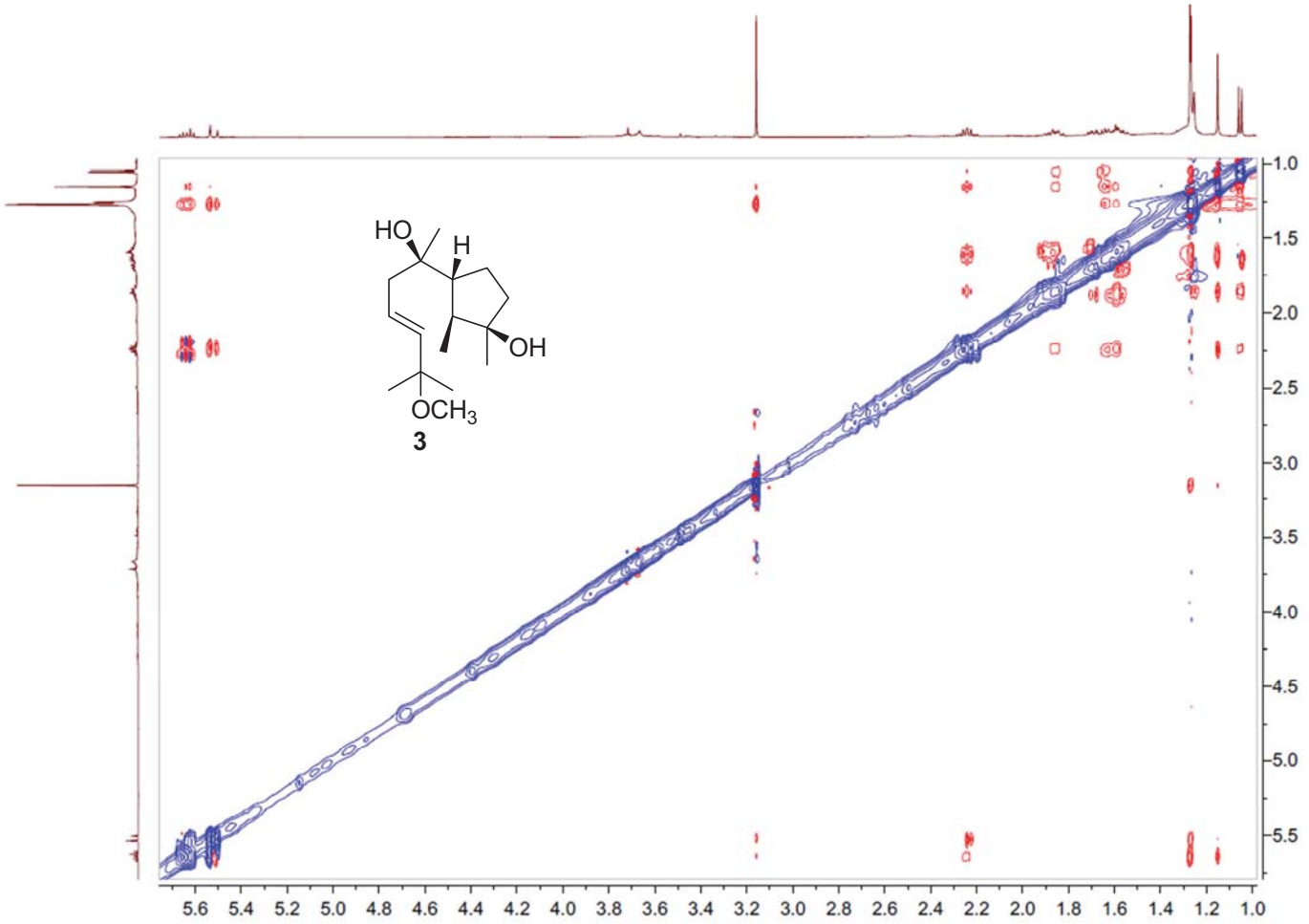
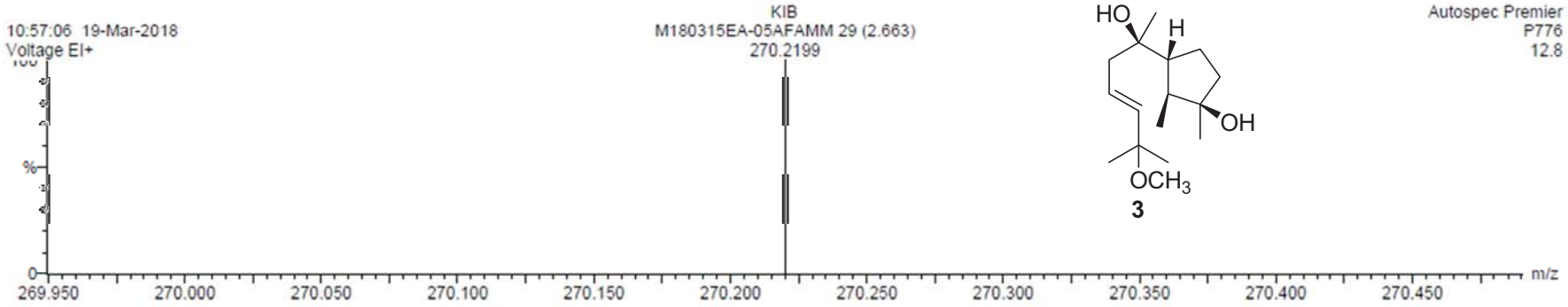


Figure S20. NOESY spectrum of compound **3** in $CDCl_3$.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 1-4



3

Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
270.2199	270.2195	0.4	1.5	2.0	5546026.0	C16 H30 O3

Figure S21. HREIMS spectrum of compound **3**.

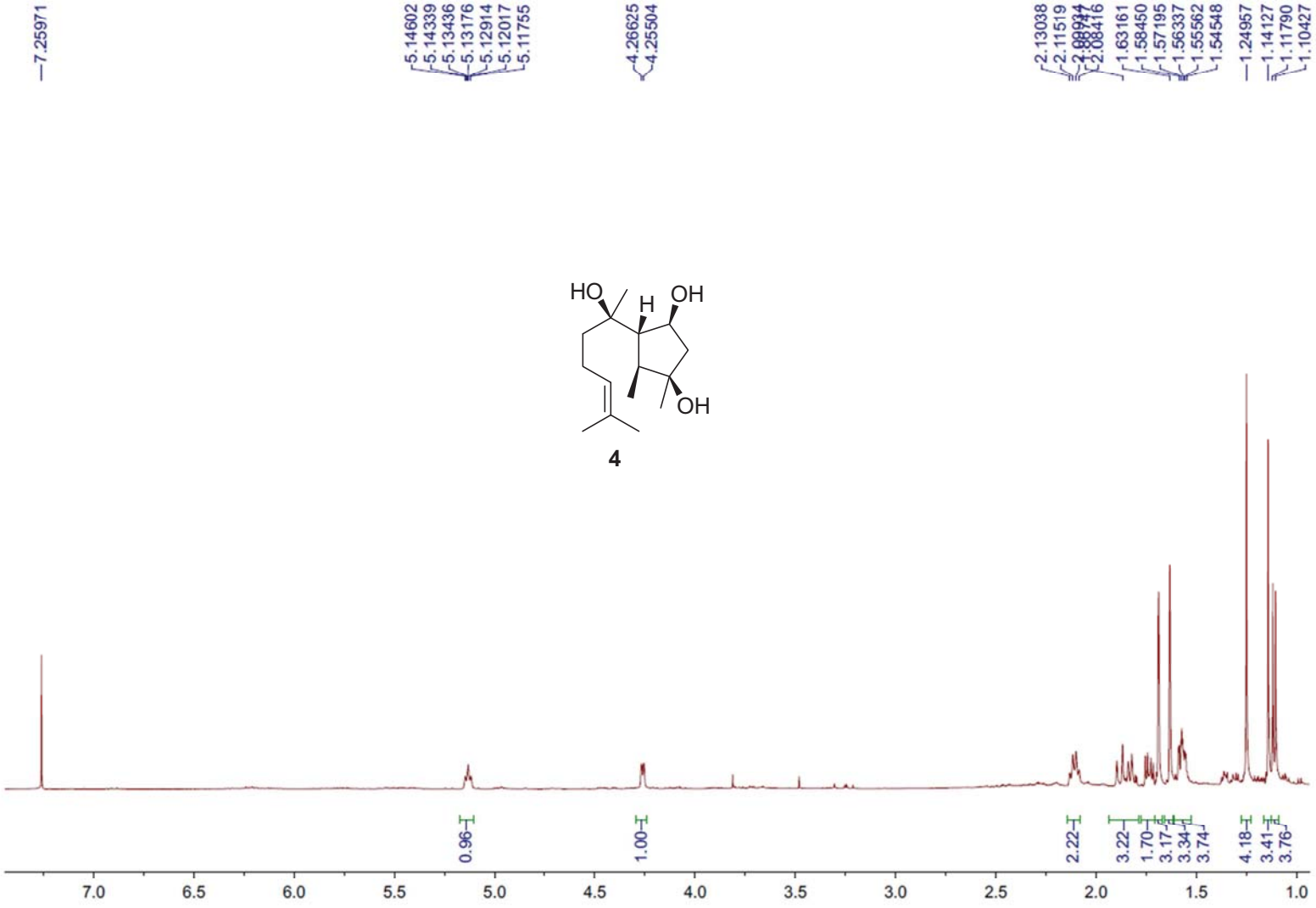


Figure S22. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

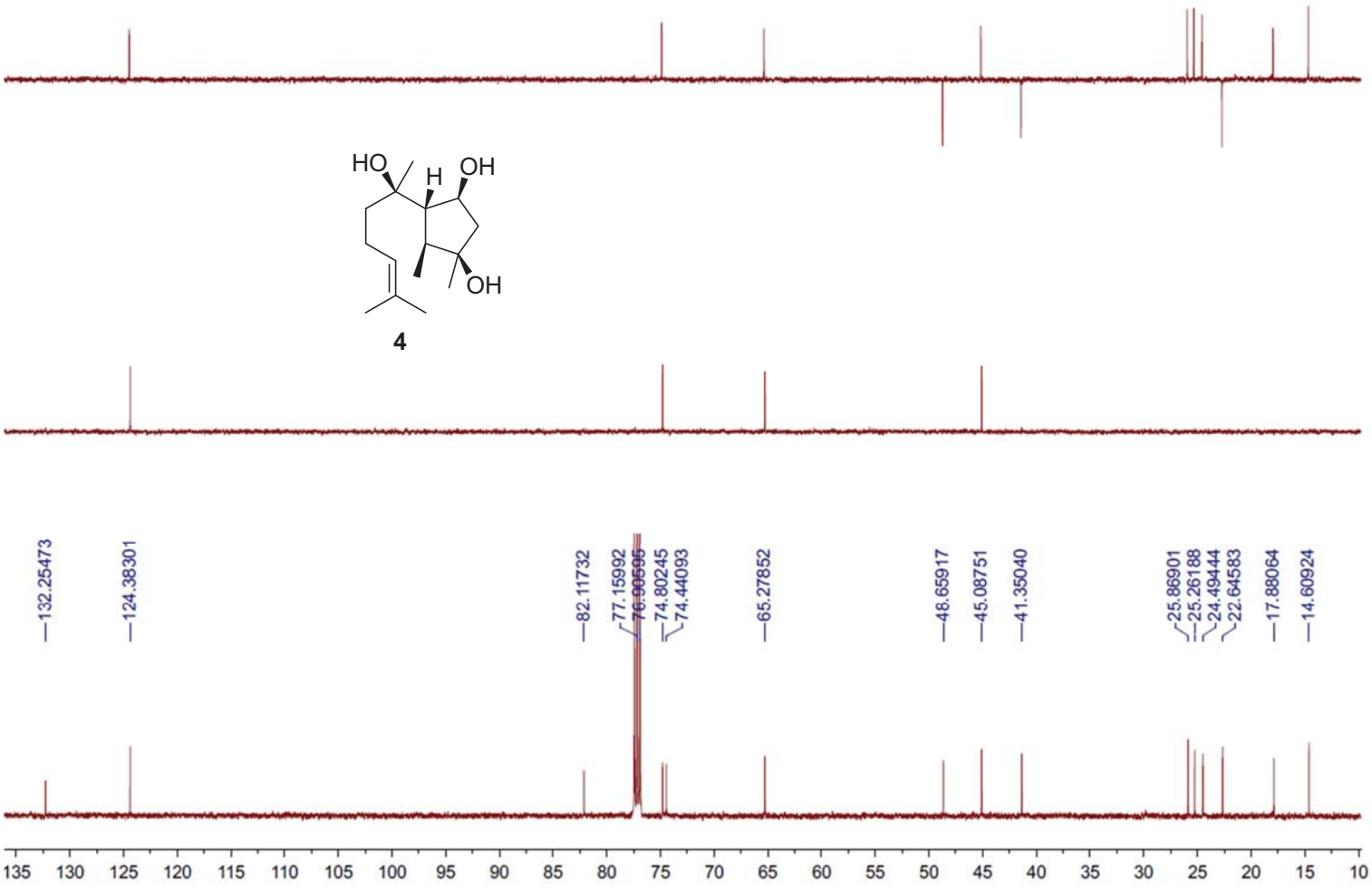


Figure S23. ^{13}C NMR and DEPT spectra of compound **4** in $CDCl_3$.

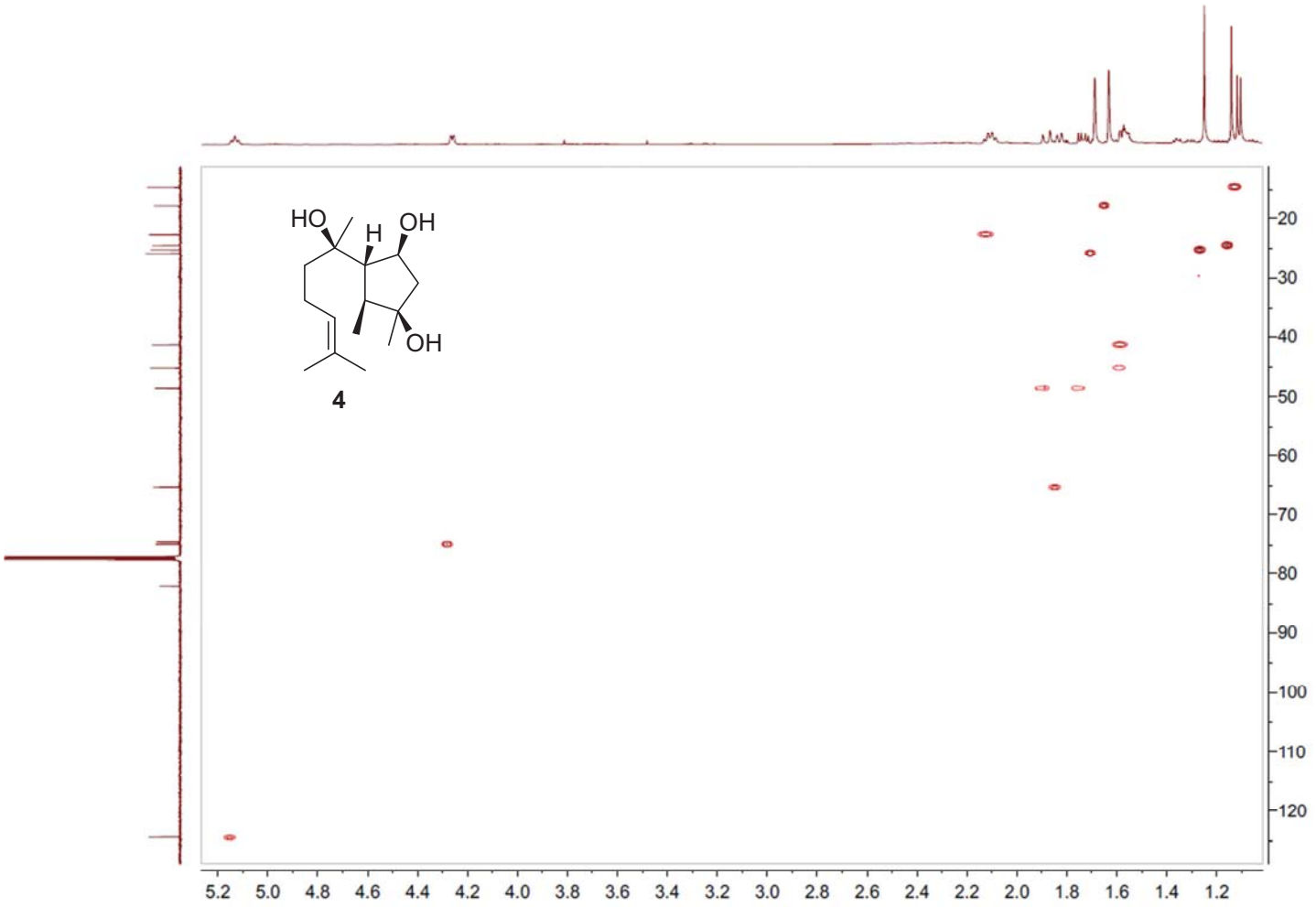


Figure S24. HSQC spectrum of compound **4** in $CDCl_3$.

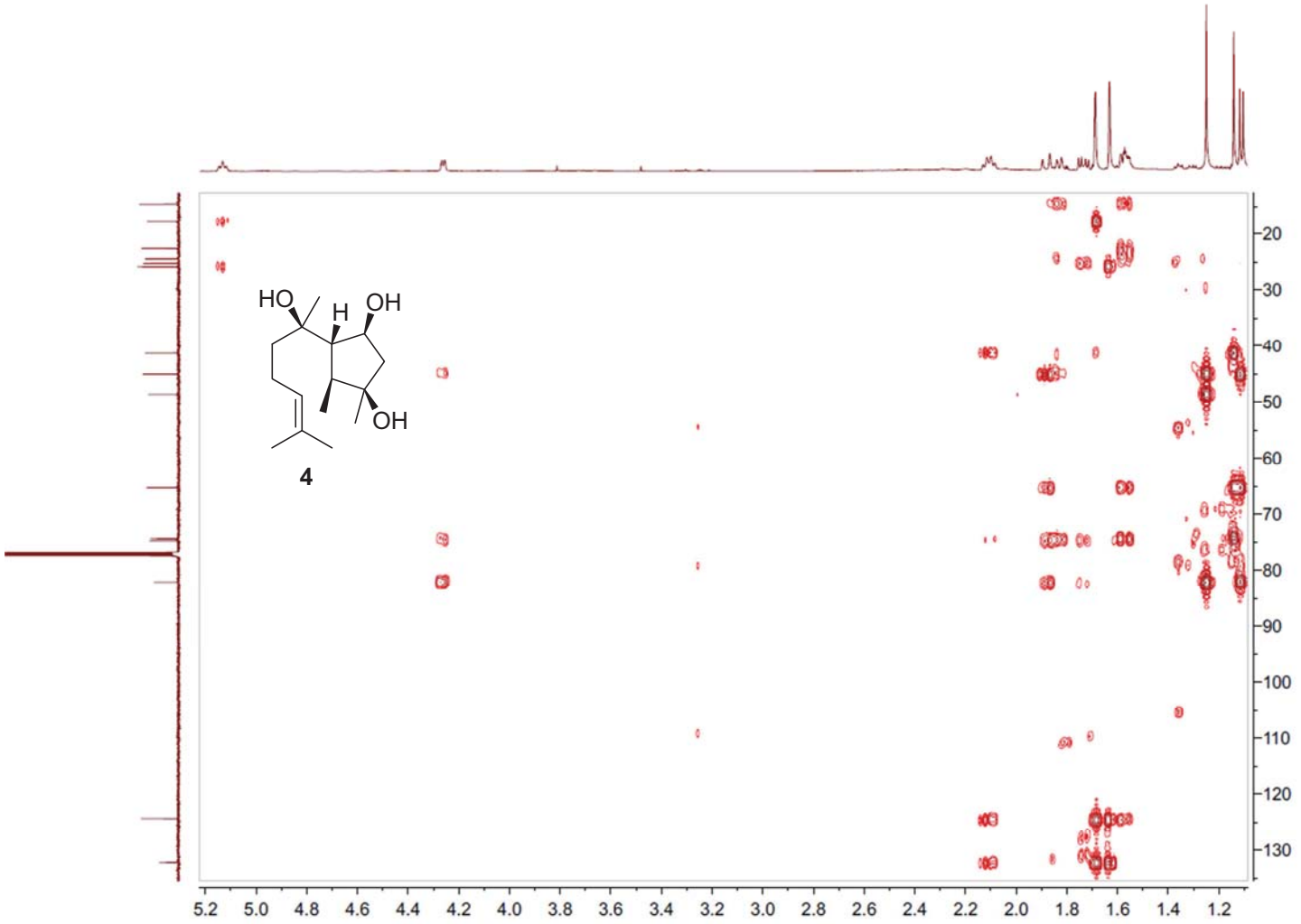


Figure S25. HMBC spectrum of compound **4** in $CDCl_3$.

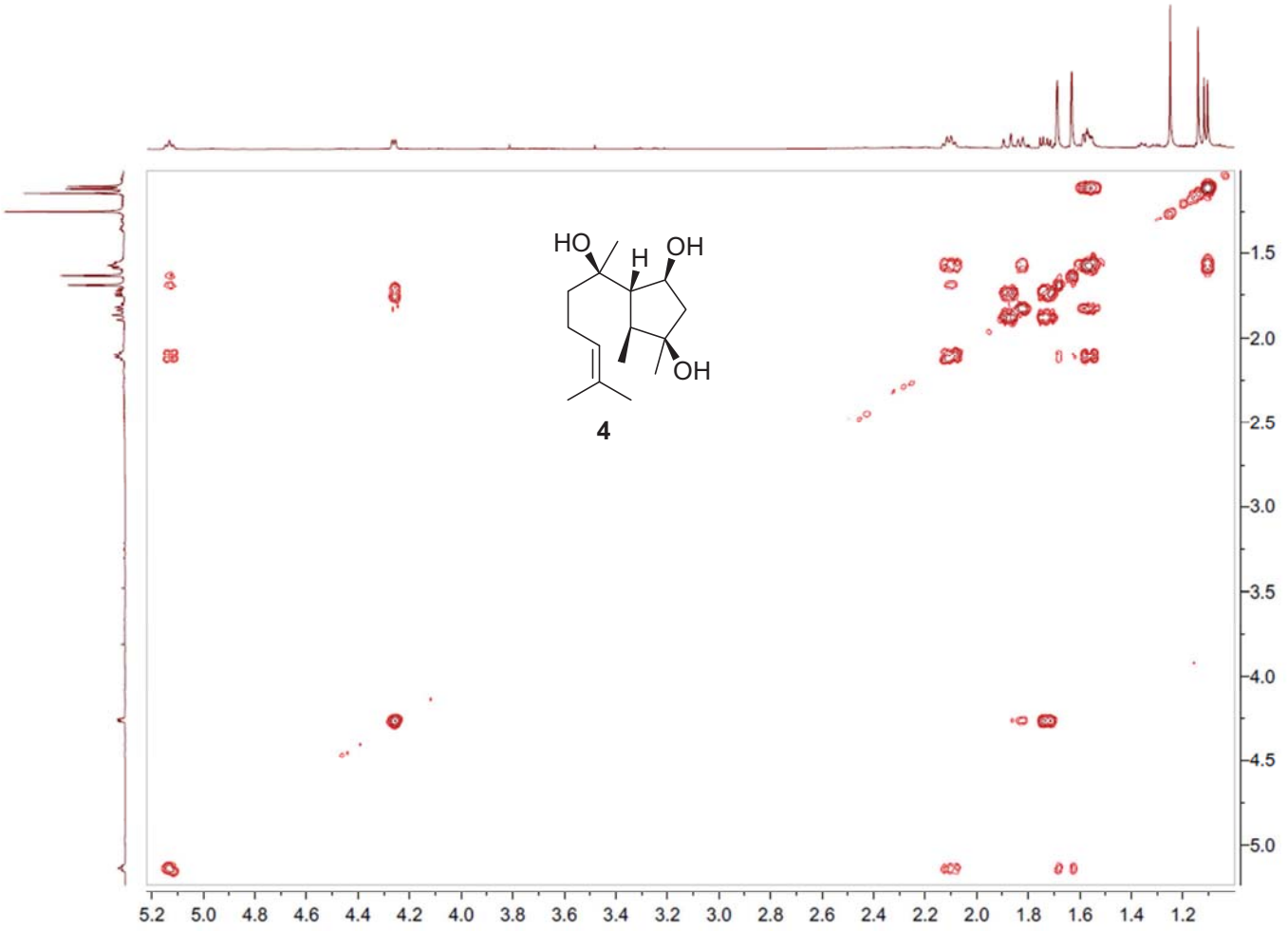


Figure S26. COSY spectrum of compound **4** in $CDCl_3$.

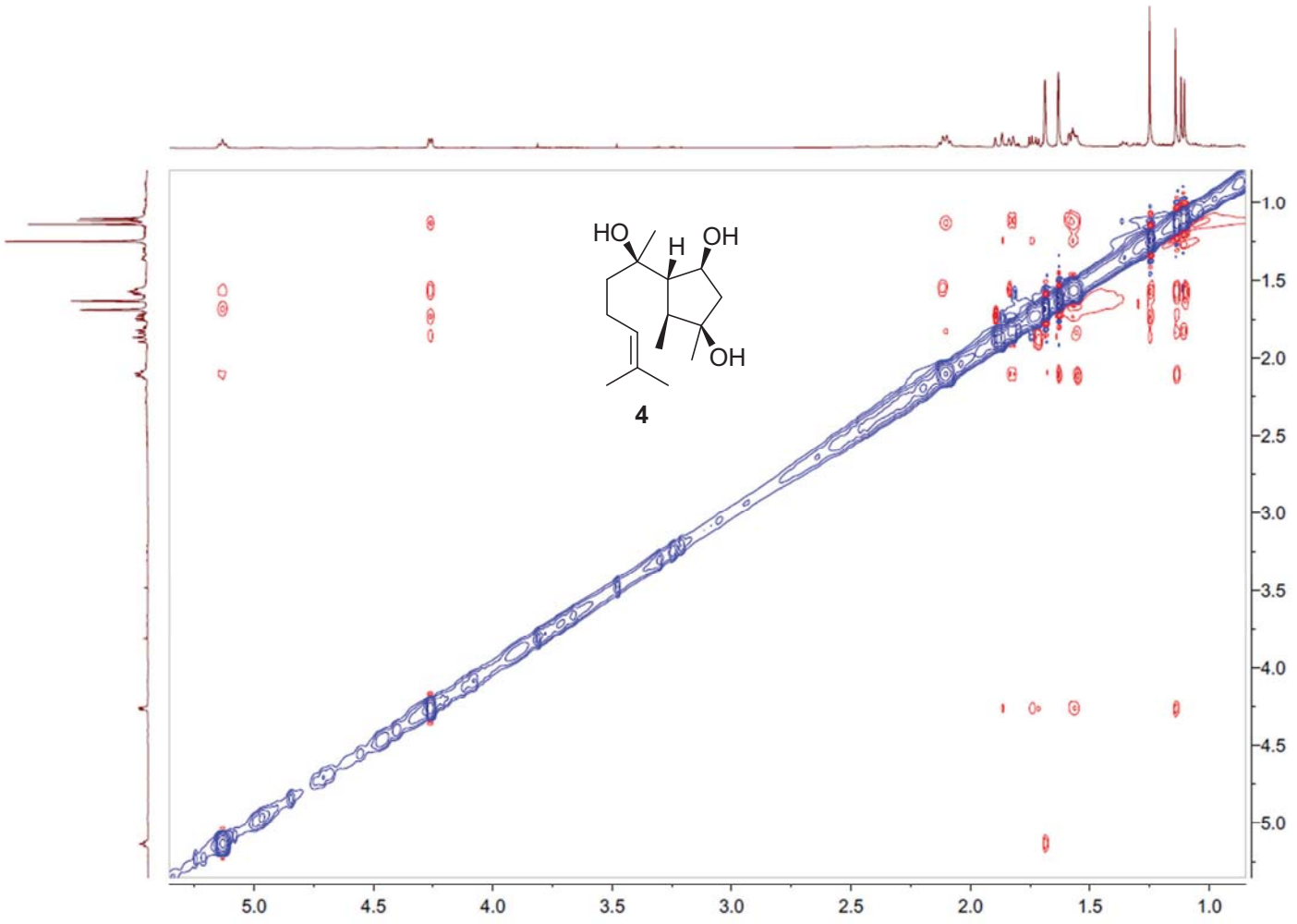
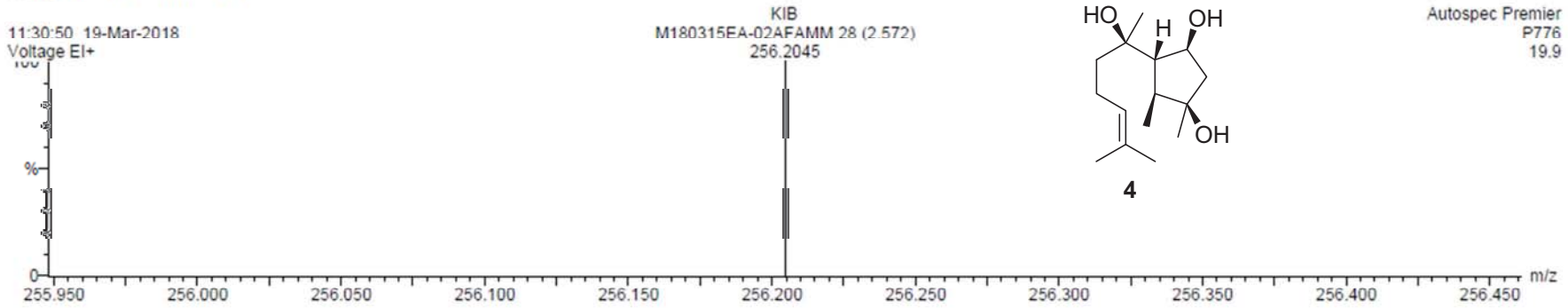


Figure S27. NOESY spectrum of compound **4** in $CDCl_3$.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 1-5



4

Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
256.2045	256.2038	0.7	2.7	2.0	5546027.0	C15 H28 O3

Figure S28. HREIMS spectrum of compound **4**.

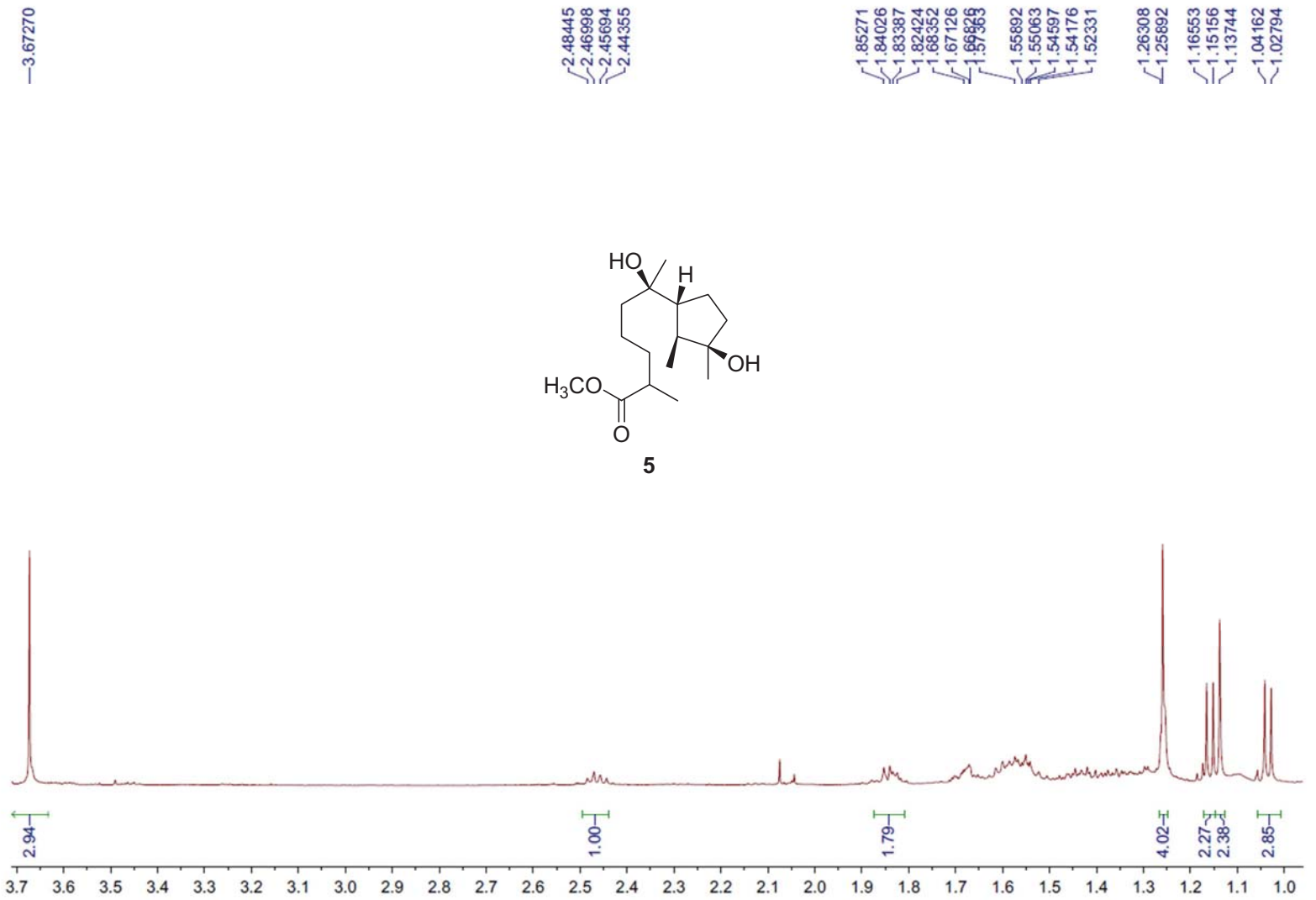


Figure S29. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

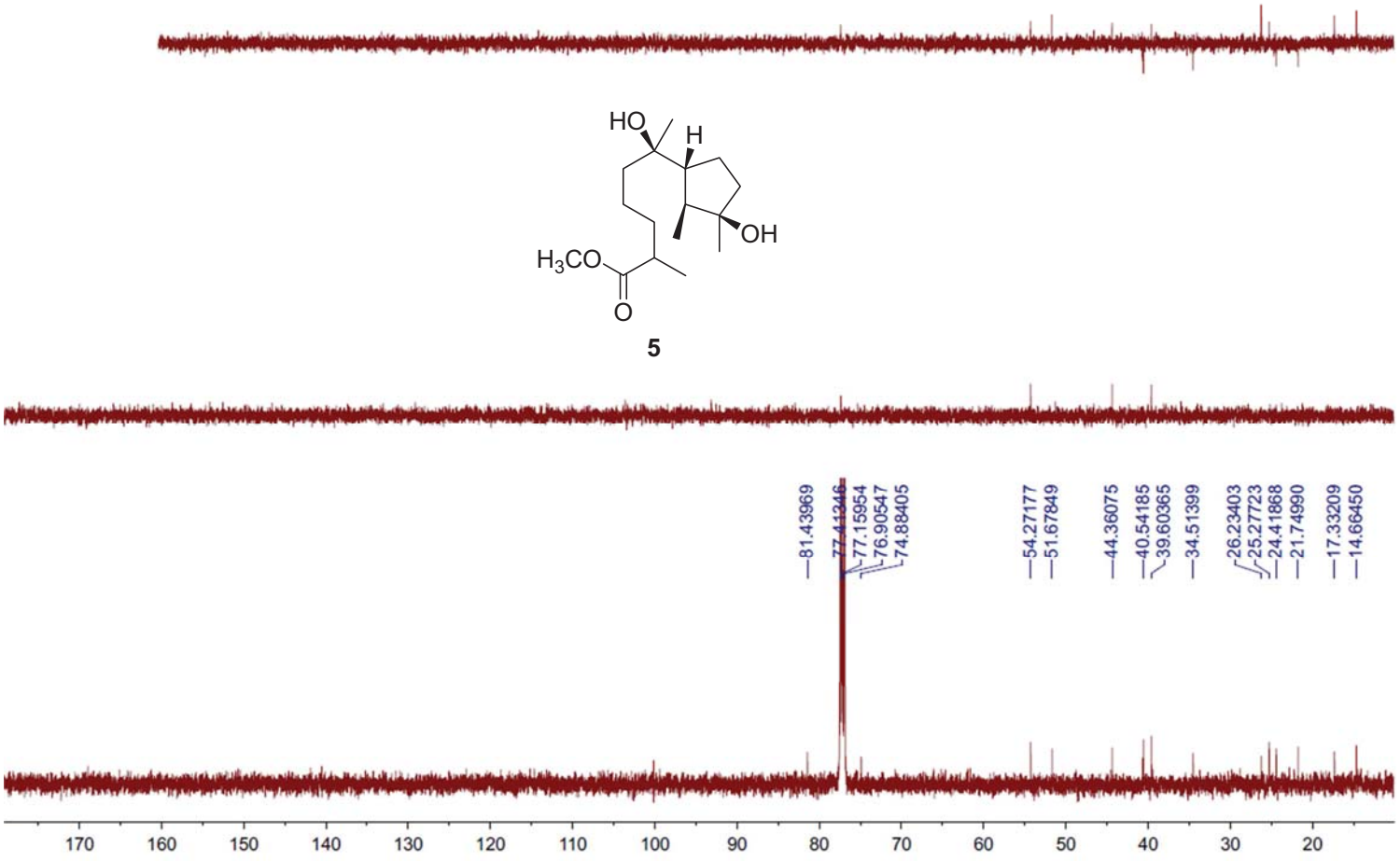


Figure S30. ^{13}C NMR and DEPT spectra of compound **5** in $CDCl_3$.

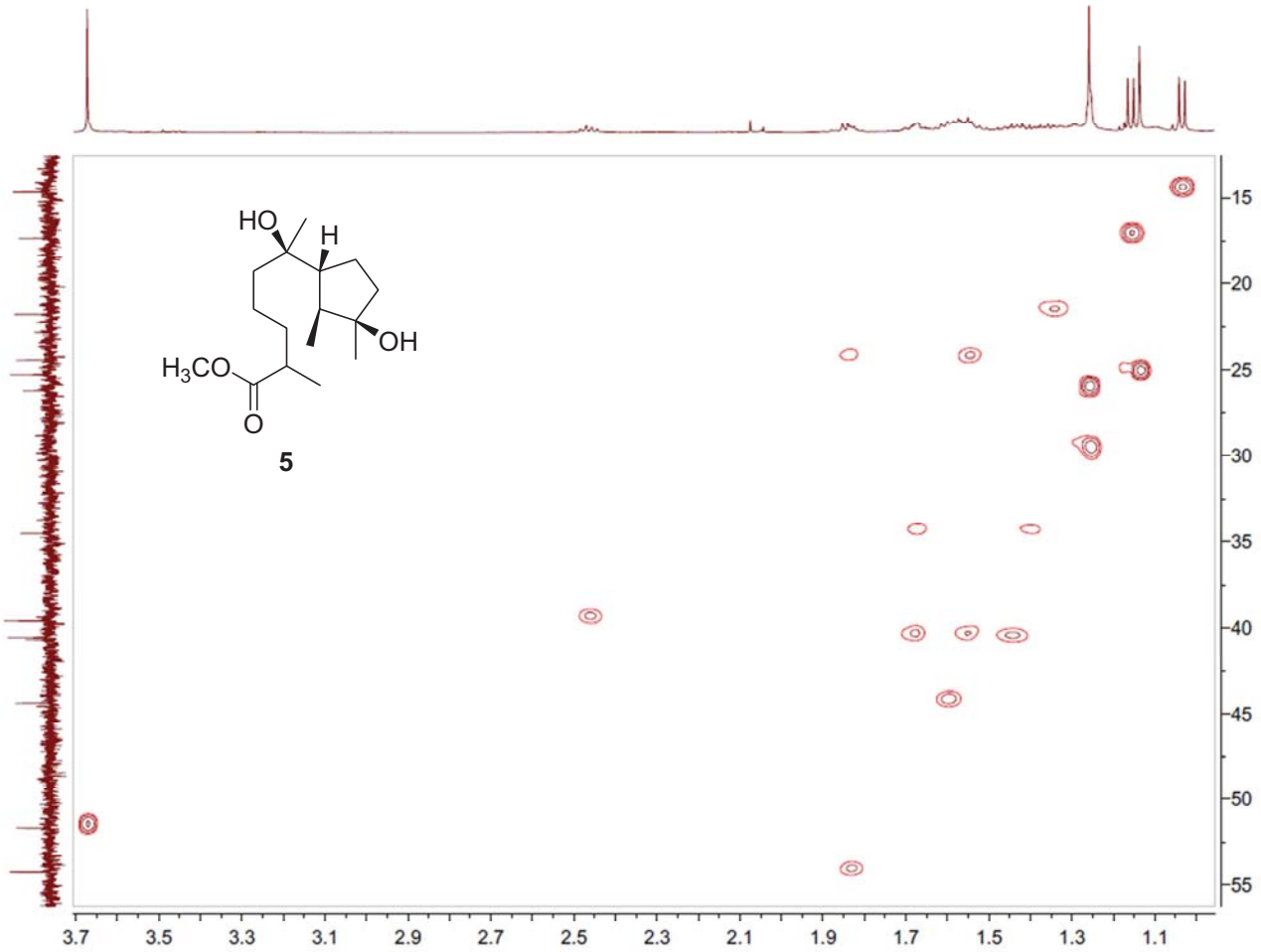


Figure S31. HSQC spectrum of compound **5** in $CDCl_3$.

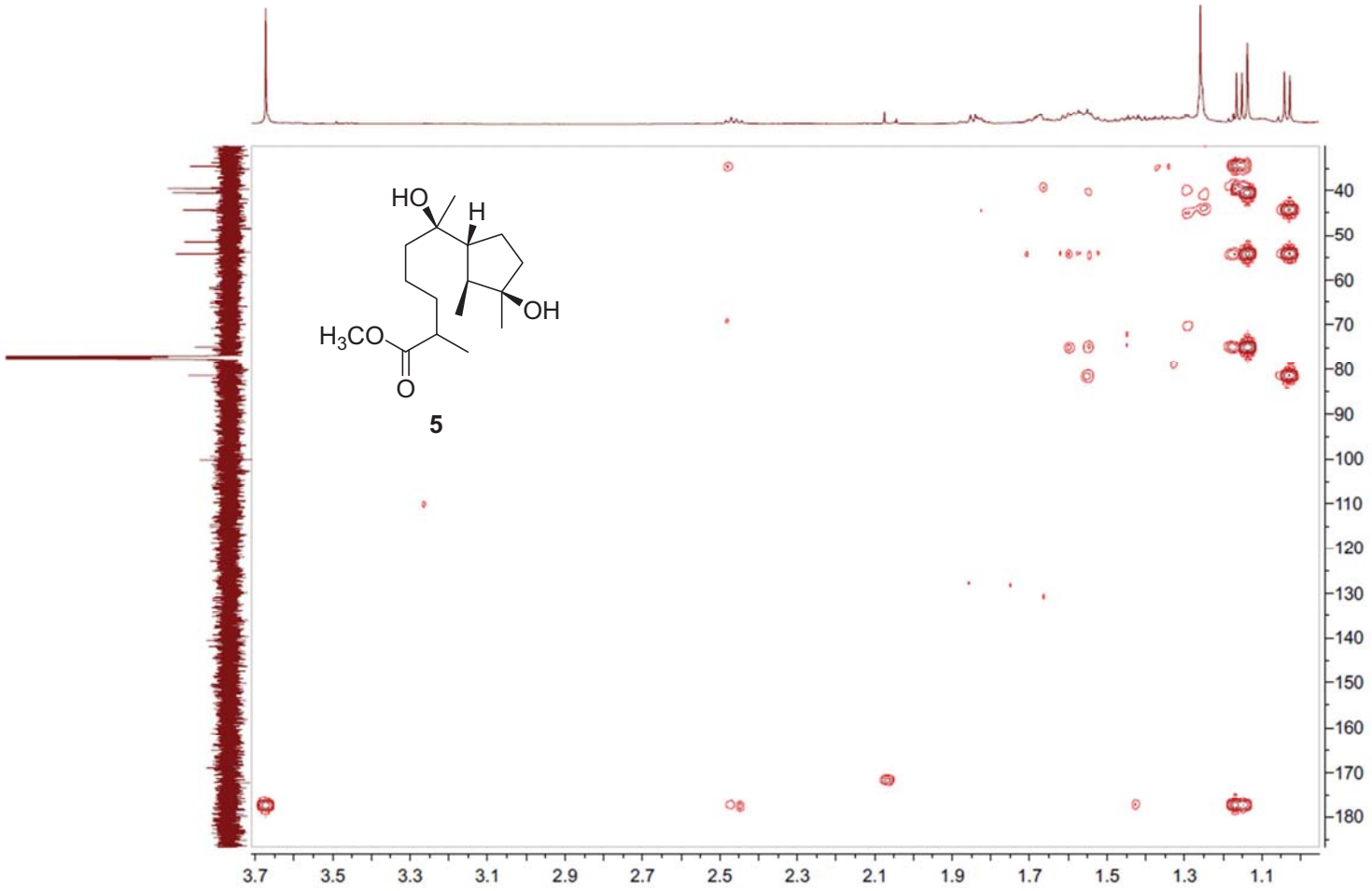


Figure S32. HMBC spectrum of compound **5** in $CDCl_3$.

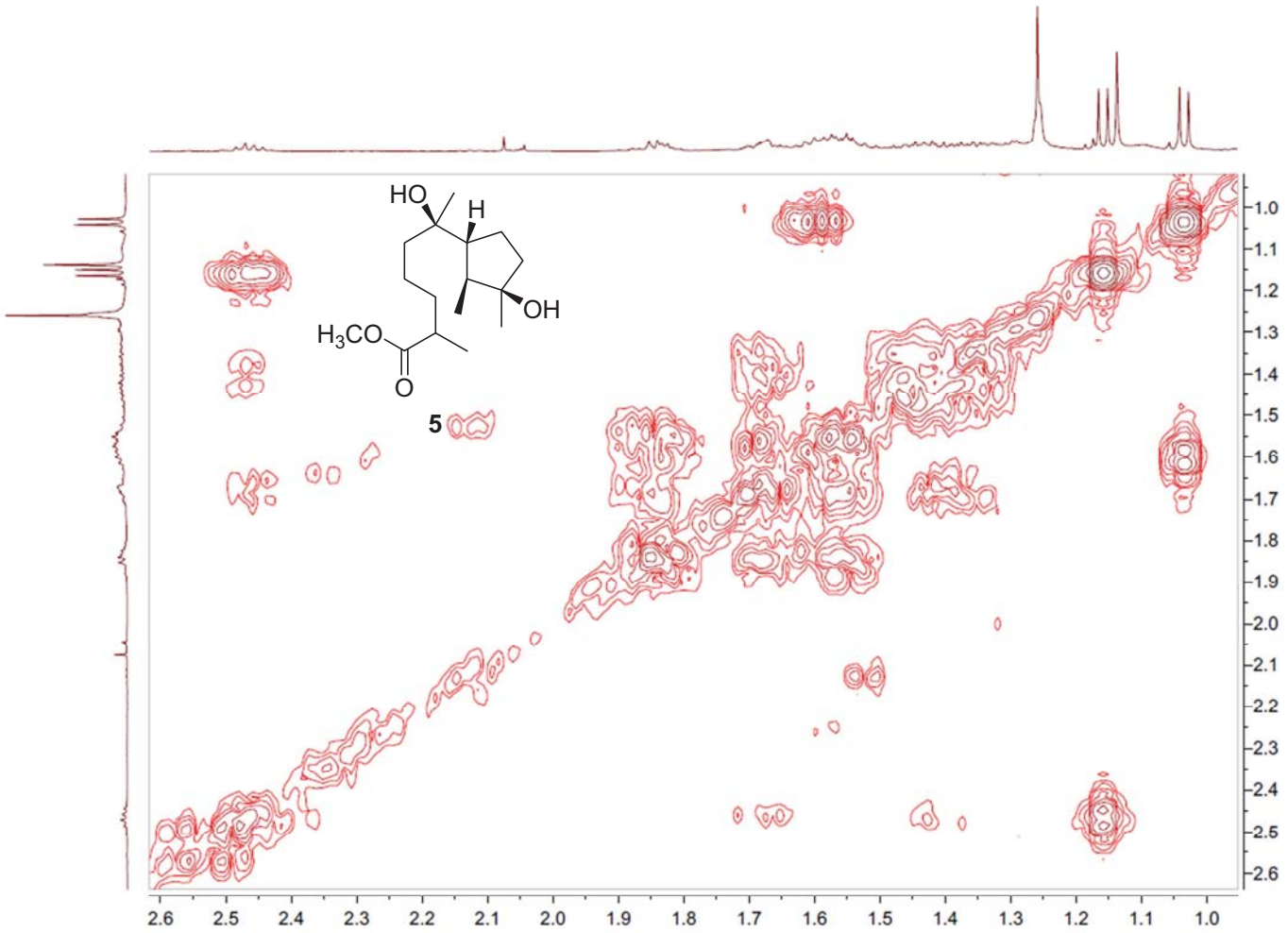


Figure S33. COSY spectrum of compound **5** in $CDCl_3$.

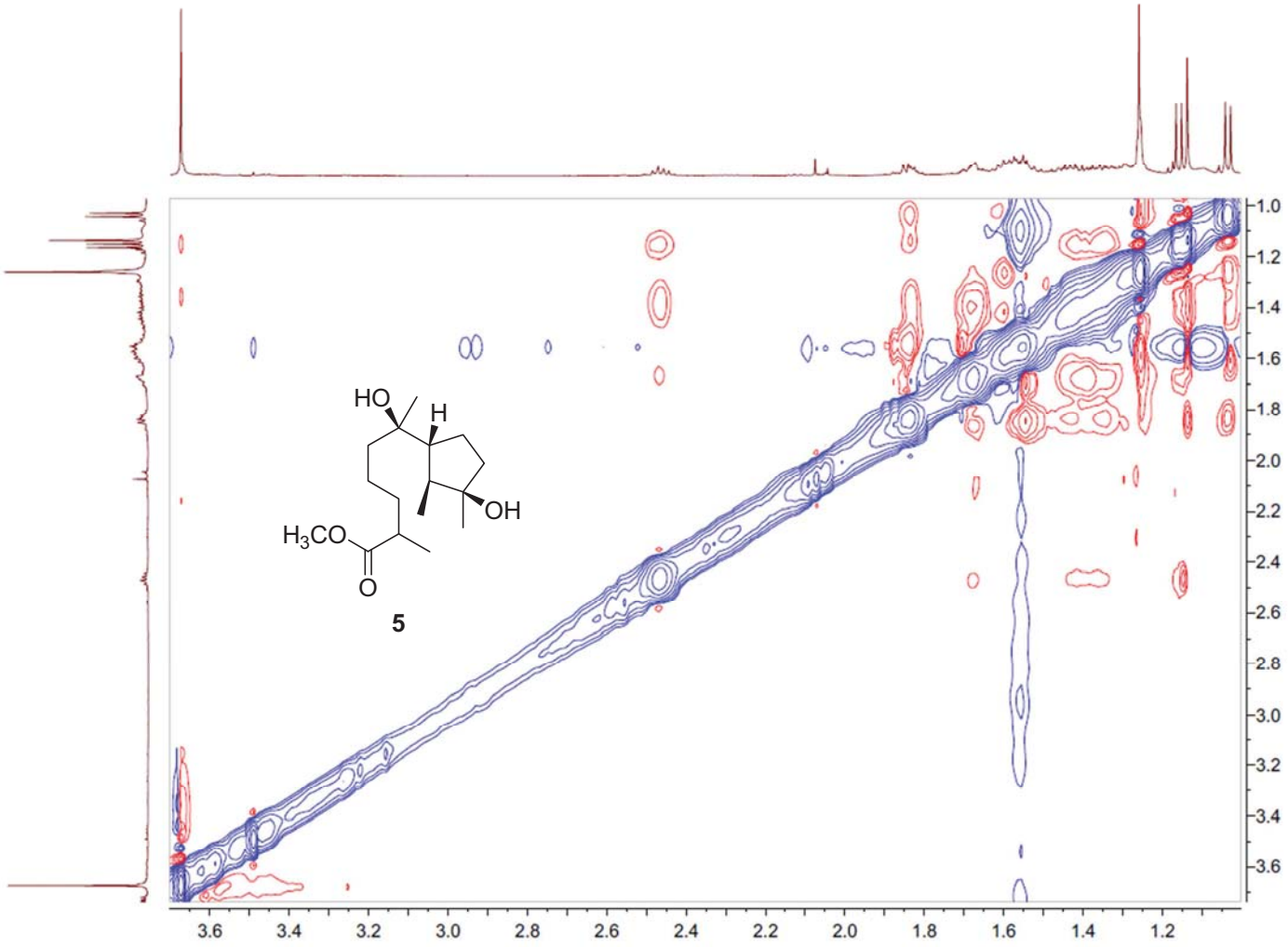
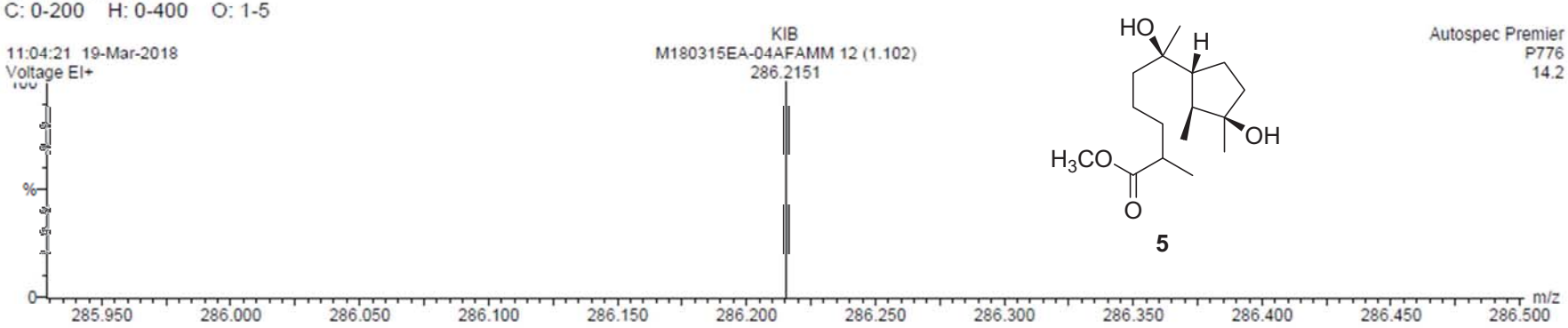


Figure S34. NOESY spectrum of compound **5** in $CDCl_3$.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 1-5



5

Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
286.2151	286.2144	0.7	2.4	2.0	5546026.0	C16 H30 O4

Figure S35. HREIMS spectrum of compound **5**.

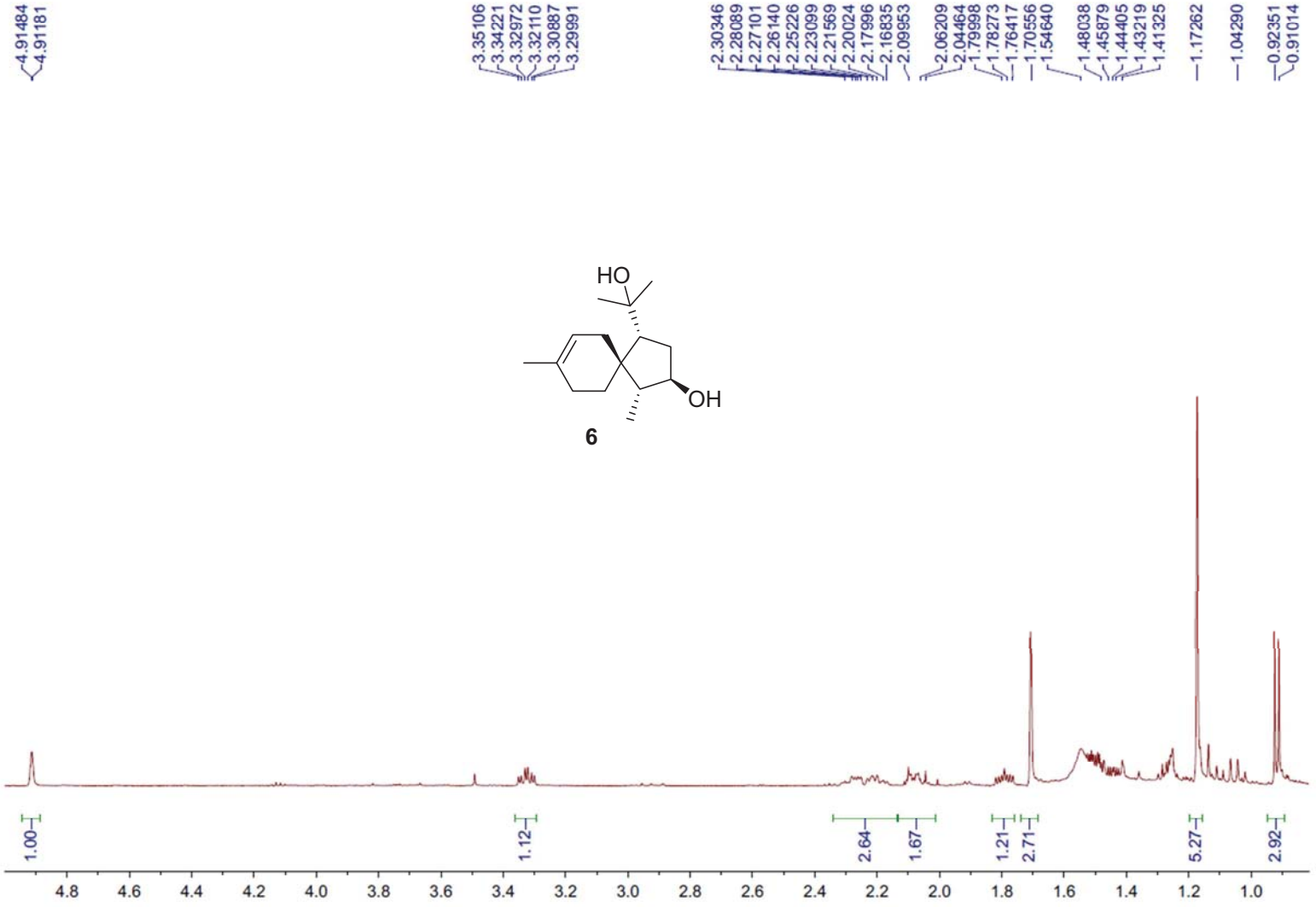


Figure S36. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

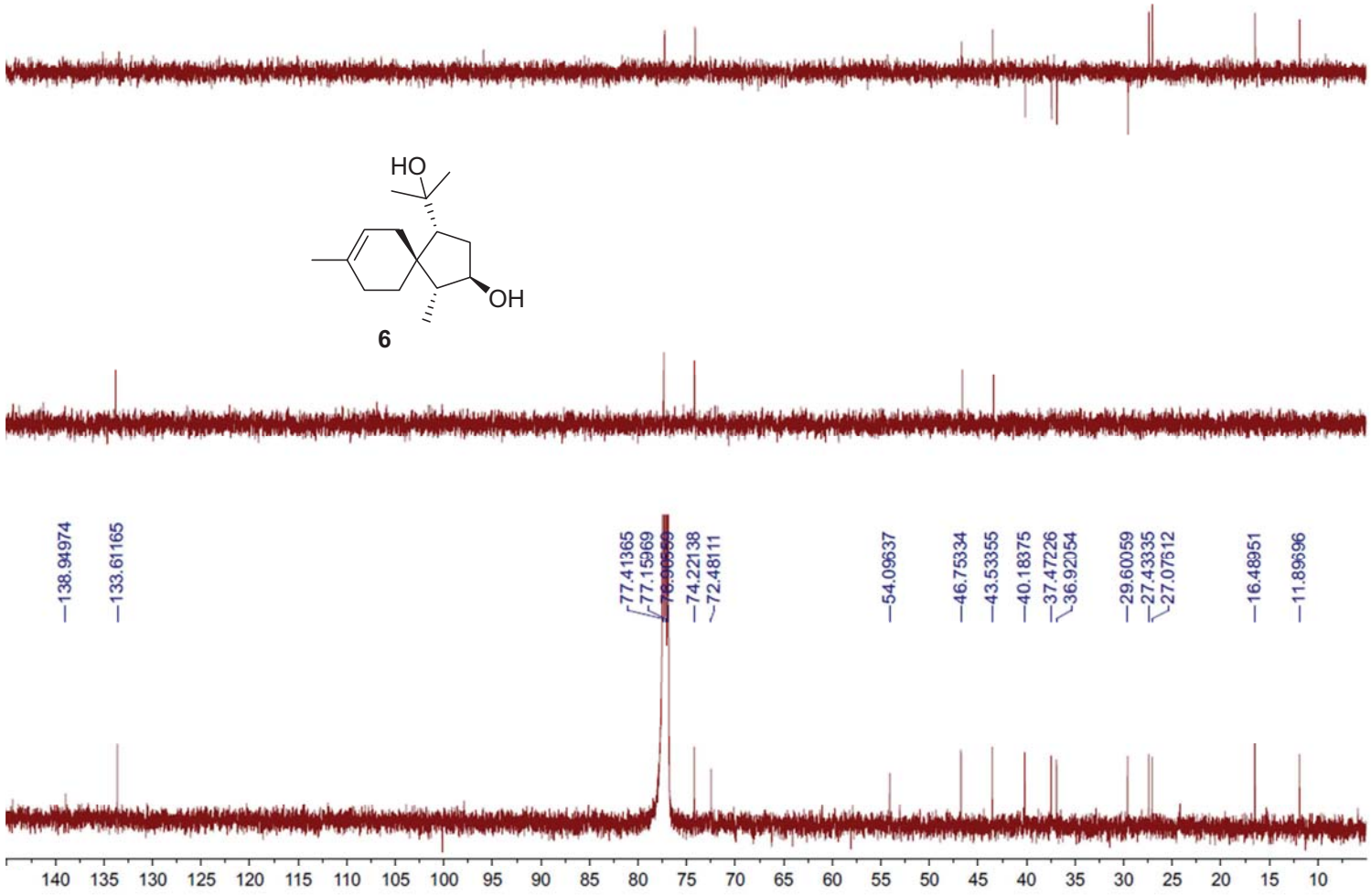


Figure S37. ^{13}C NMR and DEPT spectra of compound **6** in $CDCl_3$.

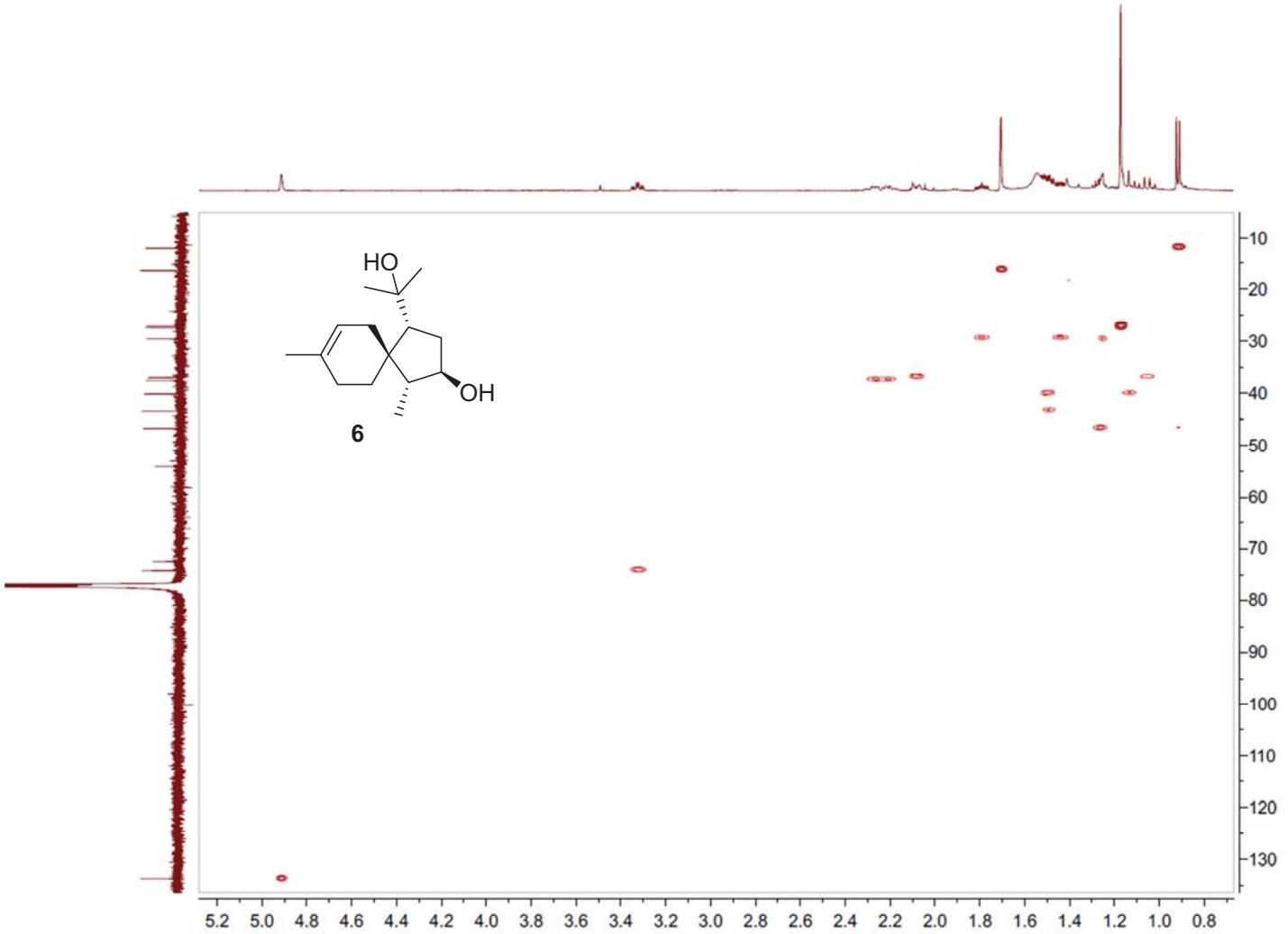


Figure S38. HSQC spectrum of compound **6** in $CDCl_3$.

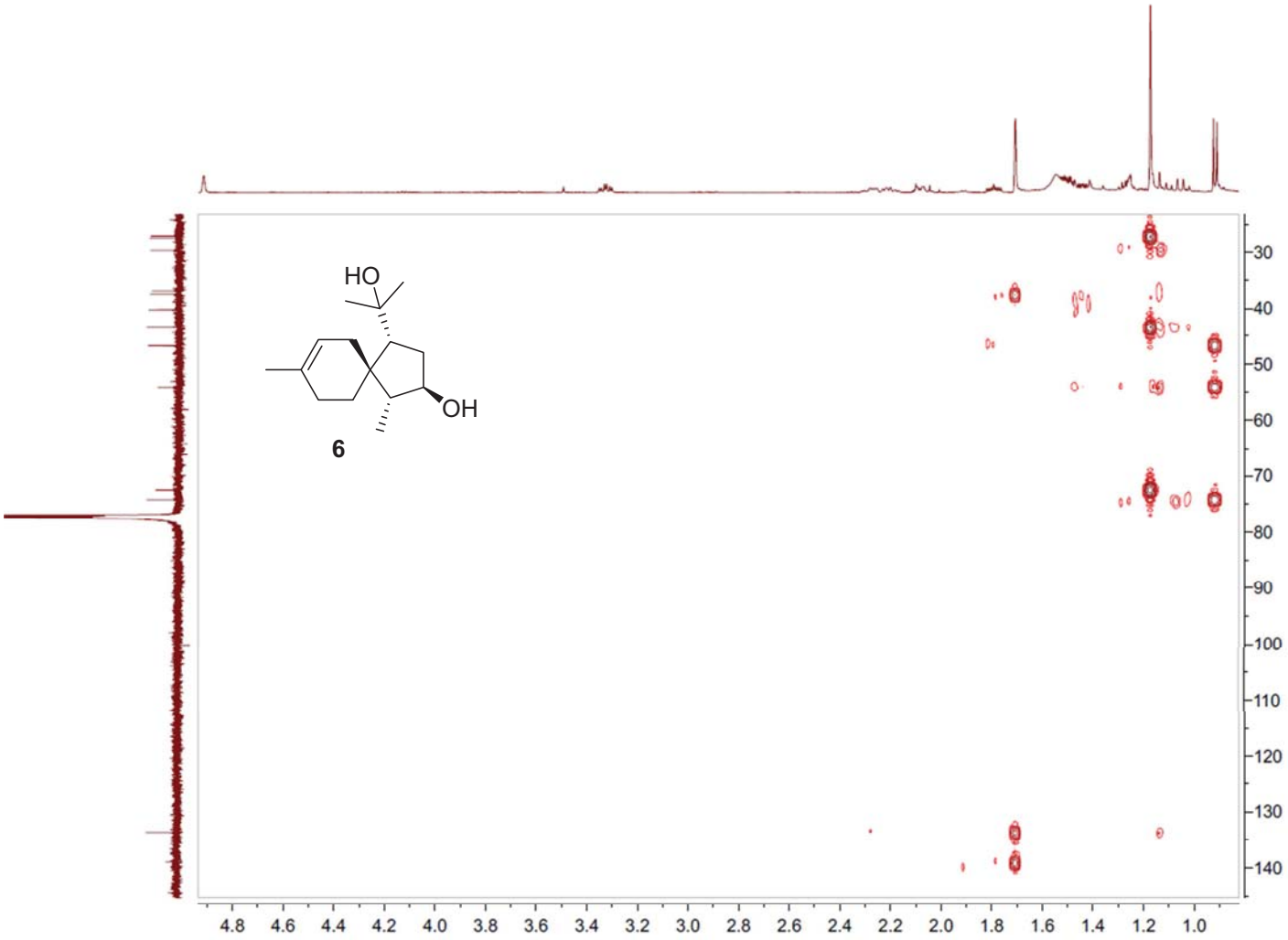


Figure S39. HMBC spectrum of compound **6** in $CDCl_3$.

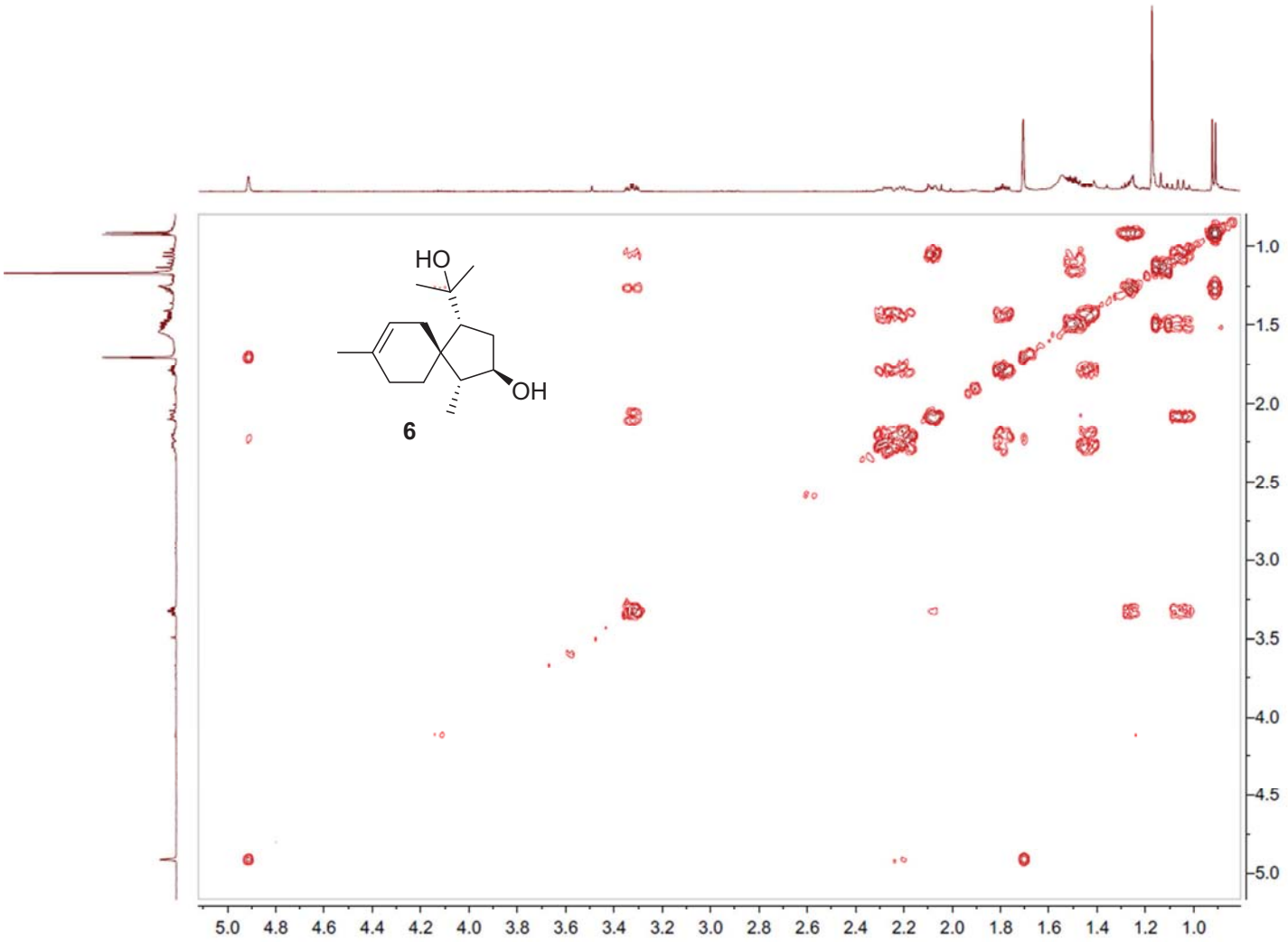


Figure S40. COSY spectrum of compound **6** in $CDCl_3$.

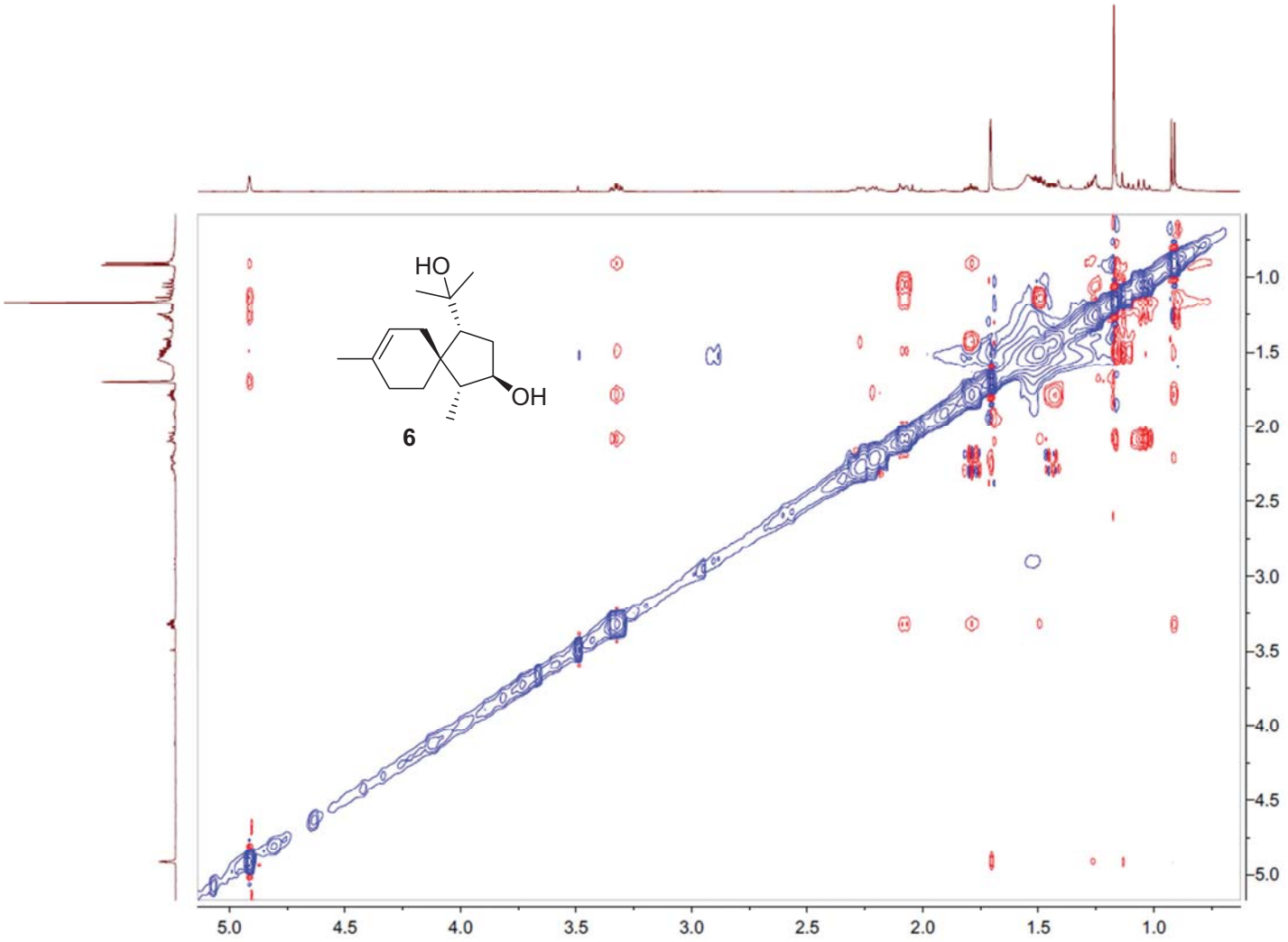
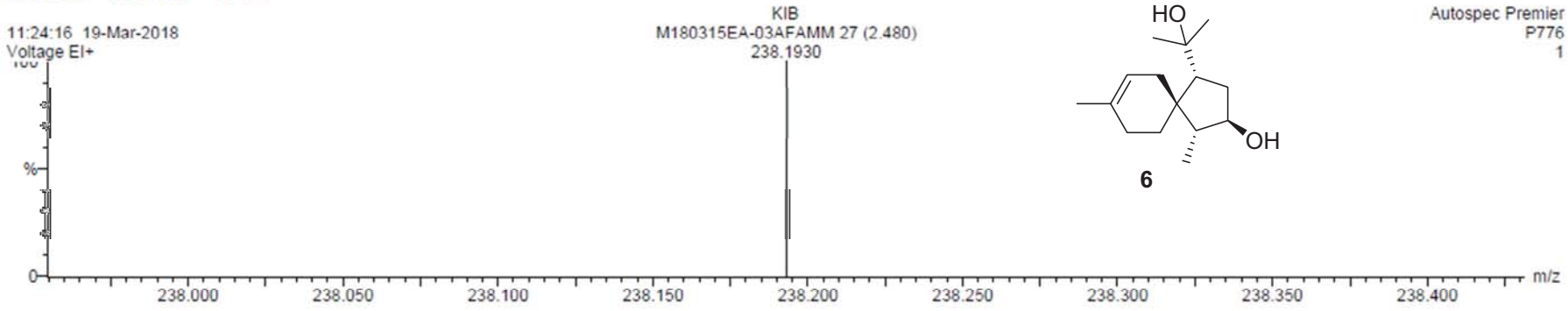


Figure S41. NOESY spectrum of compound **6** in $CDCl_3$.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

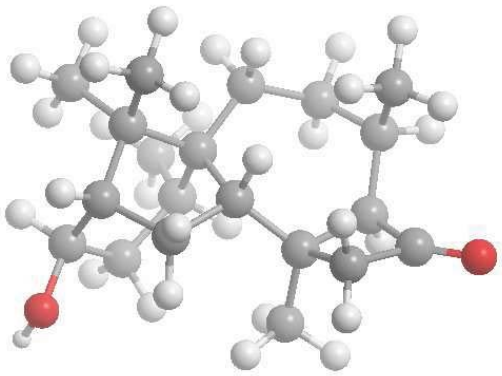
Monoisotopic Mass, Odd and Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 1-5



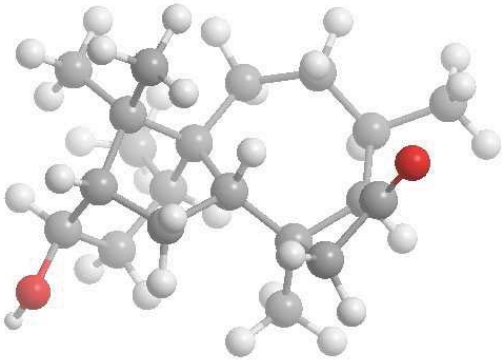
6

Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
238.1930	238.1933	-0.3	-1.3	3.0	5546026.0	C15 H26 O2

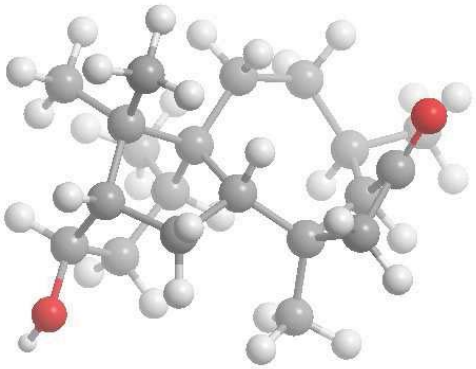
Figure S42. HREIMS spectrum of compound **6**.



1a (59.4%)

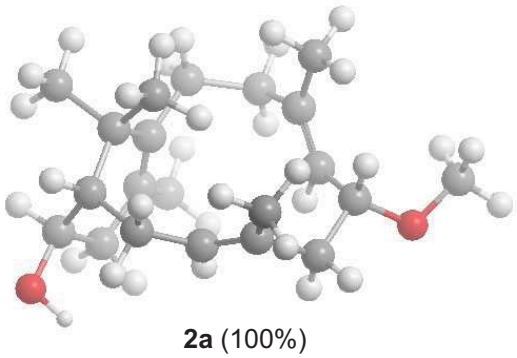


1b (40.0%)



1c (0.6%)

Figure S43. Energy-minimized conformers (**1a**–**1c** with Boltzmann populations) of compound **1** within a 3 kcal/mol energy threshold from the global minimum optimized at the B3LYP/6-31G(d) level in MeOH.



2a (100%)

Figure S44. Energy-minimized conformer (**2a** with Boltzmann populations) of compound **2** within a 3 kcal/mol energy threshold from the global minimum optimized at the B3LYP/6-31G(d) level in MeOH.

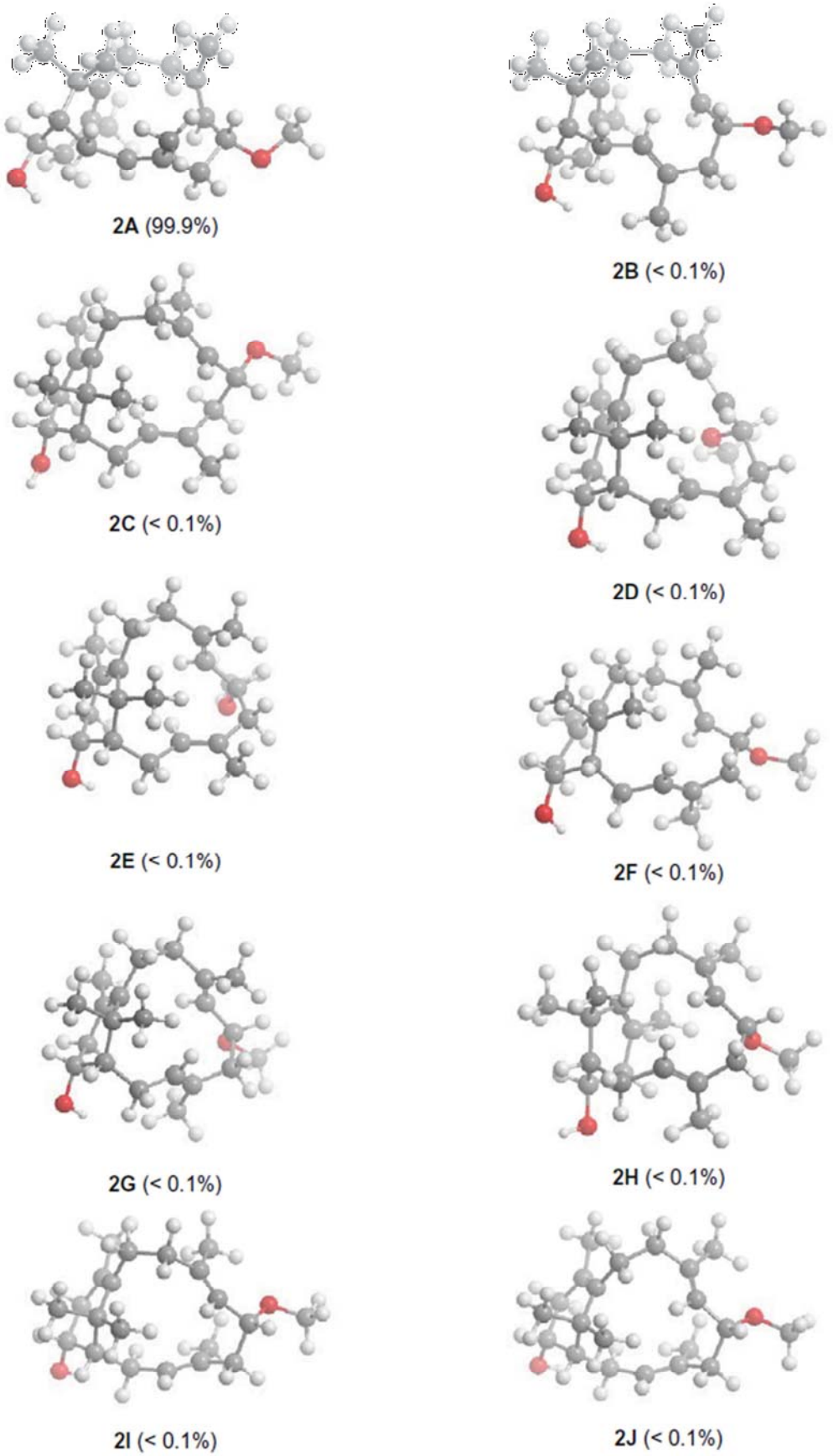
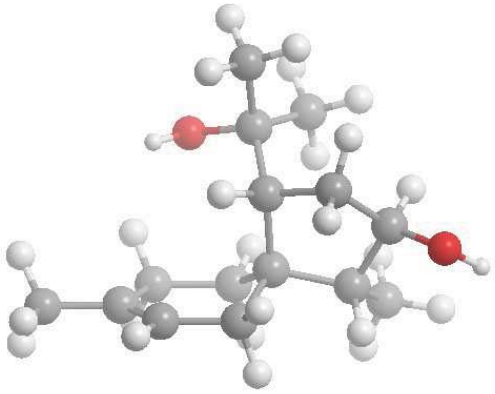
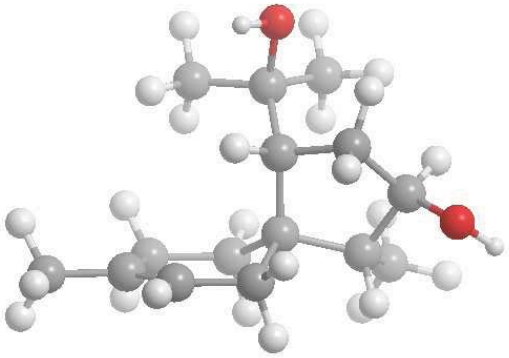


Figure S45. Energy-minimized conformers (**2A-2J** with Boltzmann populations) of compound **2** optimized at the B3LYP/6-31G(d) level in $CHCl_3$.



6A (97.2%)



6B (2.8%)

Figure S46. Energy-minimized conformers (**6A** and **6B** with Boltzmann populations) of compound **3** optimized at the B3LYP/6-31G(d) level in $CHCl_3$.

Table S1. Cartesian coordinates of the energy-minimized conformer **1a** optimized at the B3LYP/6-31G(d) level in MeOH.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.680605	0.746897	0.075602
2	6	0	-0.171298	-0.372201	-0.647598
3	6	0	-1.366900	-1.086597	0.042302
4	6	0	-2.510098	-0.191194	0.690302
5	6	0	-2.614793	1.344406	0.497202
6	6	0	-1.383591	2.090203	1.058802
7	6	0	-0.105591	2.071499	0.199602
8	6	0	1.190404	0.247295	1.478502
9	6	0	2.112900	-1.007207	1.374802
10	6	0	2.987300	-1.128710	0.113102
11	6	0	2.252401	-0.618608	-1.130898
12	6	0	0.881699	-1.321504	-1.304098
13	6	0	-2.424602	-1.638594	-0.991298
14	6	0	-3.514200	-1.009491	-0.130098
15	6	0	-3.004092	1.810407	-0.918498
16	6	0	1.884805	0.880793	-0.962098
17	6	0	1.459507	1.450395	-2.342098
18	6	0	3.067808	1.773190	-0.528498
19	1	0	-0.649597	0.164401	-1.471098
20	6	0	1.777807	1.309394	2.435602
21	8	0	3.341596	-2.501911	-0.124698
22	6	0	-1.056903	-2.233098	1.025302
23	8	0	-4.718000	-1.139788	-0.076998
24	1	0	-2.605598	-0.378694	1.767802
25	1	0	-3.458492	1.631009	1.141402
26	1	0	-1.673588	3.143104	1.181602
27	1	0	-1.177392	1.717802	2.070602
28	1	0	0.567811	2.843697	0.591102
29	1	0	-0.375190	2.411300	-0.805598
30	1	0	0.289903	-0.091902	2.002302
31	1	0	1.495298	-1.908805	1.389702
32	1	0	2.749300	-1.066309	2.267902
33	1	0	3.916401	-0.557612	0.233802
34	1	0	2.904001	-0.778309	-1.999298
35	1	0	0.907496	-2.315704	-0.853298
36	1	0	0.651199	-1.472403	-2.364298
37	1	0	-2.478105	-2.720794	-1.151398
38	1	0	-2.373000	-1.142794	-1.969398
39	1	0	-2.279693	1.524405	-1.686898
40	1	0	-3.976993	1.400310	-1.209798
41	1	0	-3.087689	2.903508	-0.939898
42	1	0	1.204810	2.513695	-2.278498
43	1	0	0.615106	0.932897	-2.804098
44	1	0	2.305807	1.363792	-3.034198
45	1	0	3.571207	1.447689	0.380302
46	1	0	3.822708	1.788088	-1.324698
47	1	0	2.740011	2.807791	-0.374698
48	1	0	1.075409	2.128196	2.618102
49	1	0	2.716108	1.751291	2.095502
50	1	0	1.975505	0.835393	3.404702
51	1	0	3.776195	-2.827512	0.680202
52	1	0	-1.991205	-2.727196	1.320402
53	1	0	-0.424006	-3.002600	0.573302
54	1	0	-0.581502	-1.887800	1.946402

Table S2. Cartesian coordinates of the energy-minimized conformer **1b** optimized at the B3LYP/6-31G(d) level in MeOH.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.601401	0.764899	-0.059395
2	6	0	0.151103	-0.554799	0.389005
3	6	0	1.224205	-1.299496	-0.460495
4	6	0	2.564902	-0.458393	-0.612195
5	6	0	2.665398	1.063408	-0.782795
6	6	0	1.823896	1.882605	0.218905
7	6	0	0.338896	2.007801	-0.166995
8	6	0	-1.351600	0.570097	-1.436795
9	6	0	-2.337297	-0.627106	-1.424095
10	6	0	-3.131997	-0.782508	-0.117195
11	6	0	-2.222597	-0.580305	1.102305
12	6	0	-0.960495	-1.472102	0.990305
13	6	0	2.006507	-2.252294	0.530905
14	6	0	3.055104	-1.155691	0.656905
15	6	0	4.146997	1.484812	-0.742595
16	6	0	-1.646801	0.864796	1.140105
17	6	0	-2.707904	1.978093	1.029405
18	6	0	-0.975402	1.114498	2.517805
19	1	0	0.737902	-0.218097	1.248105
20	6	0	-2.047904	1.809095	-2.062095
21	8	0	-3.696493	-2.100509	-0.017895
22	6	0	0.793407	-2.020697	-1.740695
23	8	0	3.869904	-0.881489	1.513105
24	1	0	3.130104	-0.925491	-1.434395
25	1	0	2.285398	1.298507	-1.788495
26	1	0	2.227694	2.904206	0.230805
27	1	0	1.961697	1.503206	1.239205
28	1	0	0.339395	2.364801	-1.202895
29	1	0	-0.093406	2.832300	0.413005
30	1	0	-0.552900	0.320199	-2.143095
31	1	0	-3.030797	-0.542907	-2.272395
32	1	0	-1.793695	-1.562404	-1.573495
33	1	0	-3.952699	-0.054310	-0.078895
34	1	0	-2.805897	-0.805507	2.004105
35	1	0	-0.659494	-1.843501	1.975405
36	1	0	-1.161993	-2.356802	0.380305
37	1	0	2.414609	-3.134693	0.023205
38	1	0	1.513708	-2.572995	1.452805
39	1	0	4.578898	1.297913	0.245505
40	1	0	4.739499	0.926713	-1.477795
41	1	0	4.249994	2.552512	-0.968395
42	1	0	-3.342804	1.917892	0.148905
43	1	0	-2.234907	2.967495	1.026105
44	1	0	-3.367404	1.941092	1.905405
45	1	0	-1.752102	1.162996	3.290005
46	1	0	-0.271100	0.339000	2.826705
47	1	0	-0.444804	2.073599	2.533405
48	1	0	-1.553406	2.755896	-1.829695
49	1	0	-3.094304	1.902792	-1.761295
50	1	0	-2.046803	1.700595	-3.153295
51	1	0	-4.220793	-2.247011	-0.821895
52	1	0	1.641408	-2.585995	-2.145795
53	1	0	-0.009492	-2.740399	-1.549995
54	1	0	0.459105	-1.335898	-2.524595

Table S3. Cartesian coordinates of the energy-minimized conformer **1c** optimized at the B3LYP/6-31G(d) level in MeOH.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.507918	0.652394	0.291195
2	6	0	0.032887	-0.815004	0.493595
3	6	0	1.196889	-1.420500	-0.357805
4	6	0	2.465286	-0.475096	-0.497305
5	6	0	2.478181	1.006205	-0.889605
6	6	0	1.819777	2.021102	0.070495
7	6	0	0.519979	1.671798	0.841195
8	6	0	-0.920219	0.905893	-1.202705
9	6	0	-2.045915	-0.057911	-1.692205
10	6	0	-3.082514	-0.505915	-0.645705
11	6	0	-2.433613	-0.727413	0.724995
12	6	0	-1.239009	-1.710409	0.628895
13	6	0	2.061793	-2.304397	0.627195
14	6	0	2.956888	-1.073094	0.813395
15	6	0	3.927279	1.451810	-1.170905
16	6	0	-1.794418	0.591390	1.238395
17	6	0	-2.736822	1.812386	1.188095
18	6	0	-1.455617	0.431991	2.745595
19	1	0	0.467687	-0.763903	1.496095
20	6	0	-1.205424	2.367992	-1.612305
21	8	0	-3.696609	-1.744617	-1.040305
22	6	0	0.837392	-2.114001	-1.675705
23	8	0	3.661287	-0.678291	1.717895
24	1	0	3.084688	-0.988593	-1.251605
25	1	0	1.942881	1.056203	-1.847205
26	1	0	1.660374	2.931102	-0.521605
27	1	0	2.561876	2.302005	0.829795
28	1	0	0.820380	1.299799	1.826295
29	1	0	0.008475	2.621896	1.040795
30	1	0	-0.039518	0.633296	-1.791705
31	1	0	-2.560917	0.391187	-2.552105
32	1	0	-1.589512	-0.978710	-2.066405
33	1	0	-3.875416	0.245682	-0.543905
34	1	0	-3.207712	-1.094115	1.410995
35	1	0	-1.174107	-2.336008	1.525895
36	1	0	-1.380407	-2.394209	-0.209805
37	1	0	1.578494	-2.715099	1.518095
38	1	0	2.602195	-3.105995	0.109495
39	1	0	4.545580	1.347312	-0.271805
40	1	0	4.383382	0.852311	-1.967505
41	1	0	3.958176	2.502610	-1.481705
42	1	0	-3.176723	2.008285	0.211995
43	1	0	-2.213525	2.722688	1.503195
44	1	0	-3.567421	1.659383	1.888595
45	1	0	-2.386816	0.261187	3.298895
46	1	0	-0.790214	-0.404307	2.973995
47	1	0	-1.000720	1.341292	3.152295
48	1	0	-0.431626	3.054594	-1.256605
49	1	0	-2.167725	2.746788	-1.261605
50	1	0	-1.217324	2.432192	-2.707305
51	1	0	-4.083110	-1.604218	-1.919905
52	1	0	0.482689	-1.406102	-2.431605
53	1	0	1.727294	-2.605098	-2.086805
54	1	0	0.071895	-2.885504	-1.550705

Table S4. Cartesian coordinates of the energy-minimized conformer **2a** optimized at the B3LYP/6-31G(d) level in MeOH.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.538703	-0.055682	-1.803489
2	6	0	3.331696	0.686626	-0.733489
3	6	0	2.515594	0.936418	0.550211
4	6	0	1.984907	-0.421887	1.125411
5	6	0	1.380715	-1.340992	0.033911
6	6	0	1.703814	-1.204289	-1.271189
7	6	0	-1.856283	-1.509822	0.449111
8	6	0	-0.929273	-2.639514	0.044511
9	6	0	0.553226	-2.537100	0.517411
10	6	0	-1.054018	2.215885	0.138111
11	6	0	-2.255015	1.911774	-0.735989
12	6	0	-3.042203	0.650767	-0.309889
13	6	0	-2.202592	-0.588426	-0.465289
14	6	0	1.488783	2.107809	0.434811
15	6	0	0.180885	1.889797	-0.282389
16	8	0	3.941185	1.876431	-1.252989
17	6	0	3.177414	-1.198676	1.757511
18	6	0	1.007804	-0.115796	2.283611
19	6	0	-2.348383	-1.543827	1.876611
20	6	0	-1.381424	2.877582	1.456711
21	6	0	1.271623	-2.165693	-2.358689
22	8	0	-4.188103	0.616156	-1.179489
23	1	0	3.243691	1.309325	1.285011
24	6	0	-5.174394	-0.322453	-0.786089
25	1	0	3.237707	-0.427675	-2.564889
26	1	0	1.885897	0.652912	-2.340889
27	1	0	4.189202	0.064634	-0.458389
28	1	0	-0.949172	-2.735214	-1.044289
29	1	0	-1.319264	-3.585817	0.447811
30	1	0	0.569527	-2.582900	1.609211
31	1	0	1.040735	-3.465195	0.188211
32	1	0	-2.961523	2.752767	-0.724489
33	1	0	-1.942914	1.767477	-1.777489
34	1	0	-3.394004	0.767363	0.724911
35	1	0	-1.807691	-0.708722	-1.475989
36	1	0	2.030776	2.929914	-0.057689
37	1	0	1.295480	2.473907	1.446211
38	1	0	0.250590	1.440297	-1.270889
39	1	0	3.254181	2.382125	-1.716089
40	1	0	3.966416	-1.415568	1.031311
41	1	0	2.839923	-2.157379	2.167811
42	1	0	3.617209	-0.622972	2.581911
43	1	0	1.461197	0.618808	2.960211
44	1	0	0.060200	0.287495	1.923011
45	1	0	0.798212	-1.005898	2.884411
46	1	0	-2.996291	-0.701933	2.131311
47	1	0	-1.514183	-1.549419	2.587711
48	1	0	-2.913774	-2.469232	2.053911
49	1	0	-0.509625	3.026290	2.097411
50	1	0	-1.841233	3.861178	1.285911
51	1	0	-2.115018	2.290275	2.024911
52	1	0	0.950032	-3.137396	-1.978389
53	1	0	0.446319	-1.753901	-2.957889
54	1	0	2.100125	-2.342786	-3.056389
55	1	0	-4.787385	-1.351049	-0.780889
56	1	0	-5.989395	-0.251561	-1.511889
57	1	0	-5.570096	-0.095857	0.216611