Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Material

Anti-inflammatory fusicoccane-type diterpenoids from the phytopathogenic fungus *Alternaria brassicicola*

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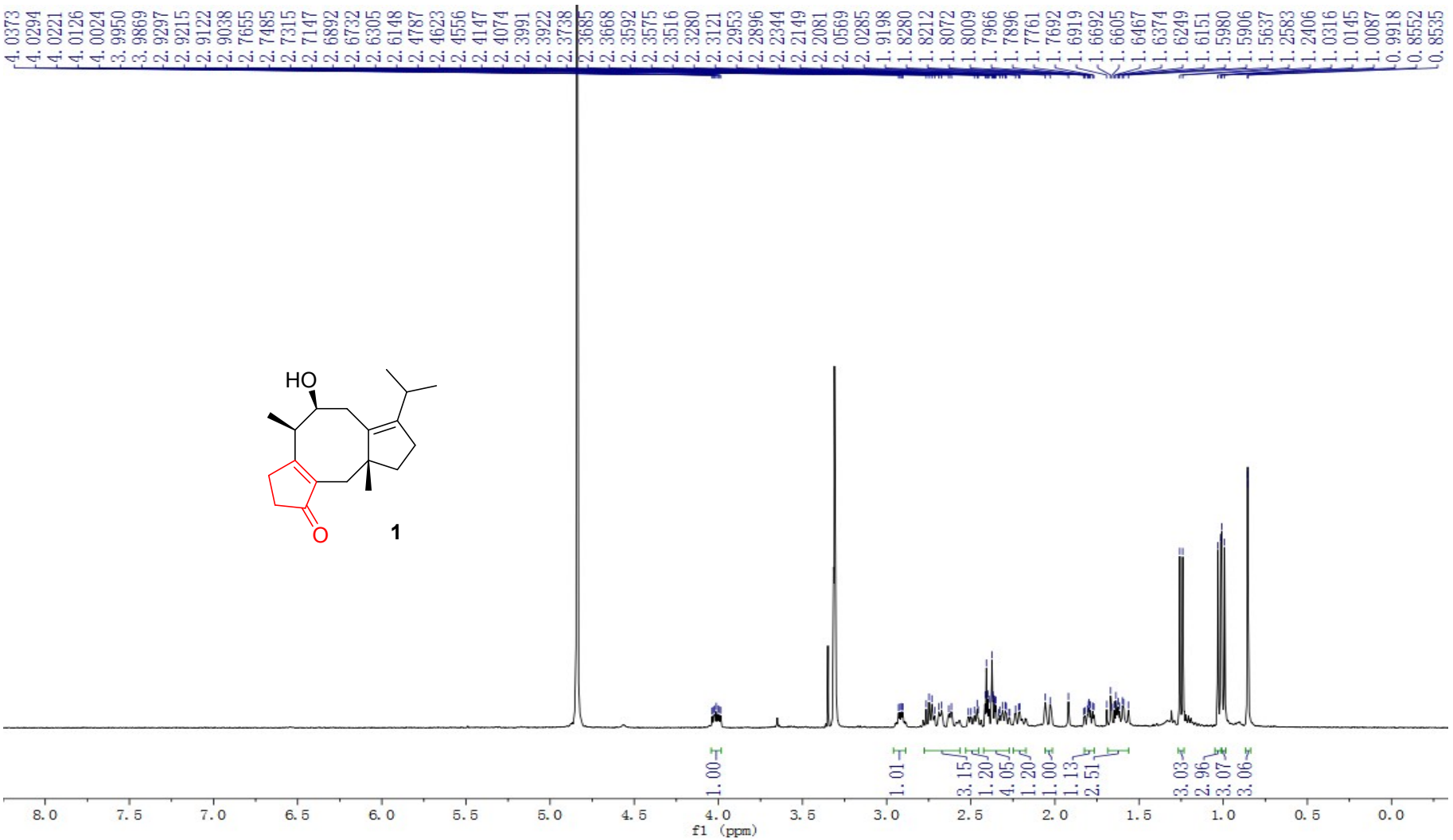


Figure S1. ^{1}H NMR spectrum of compound **1** (Recorded in methanol-d_4)

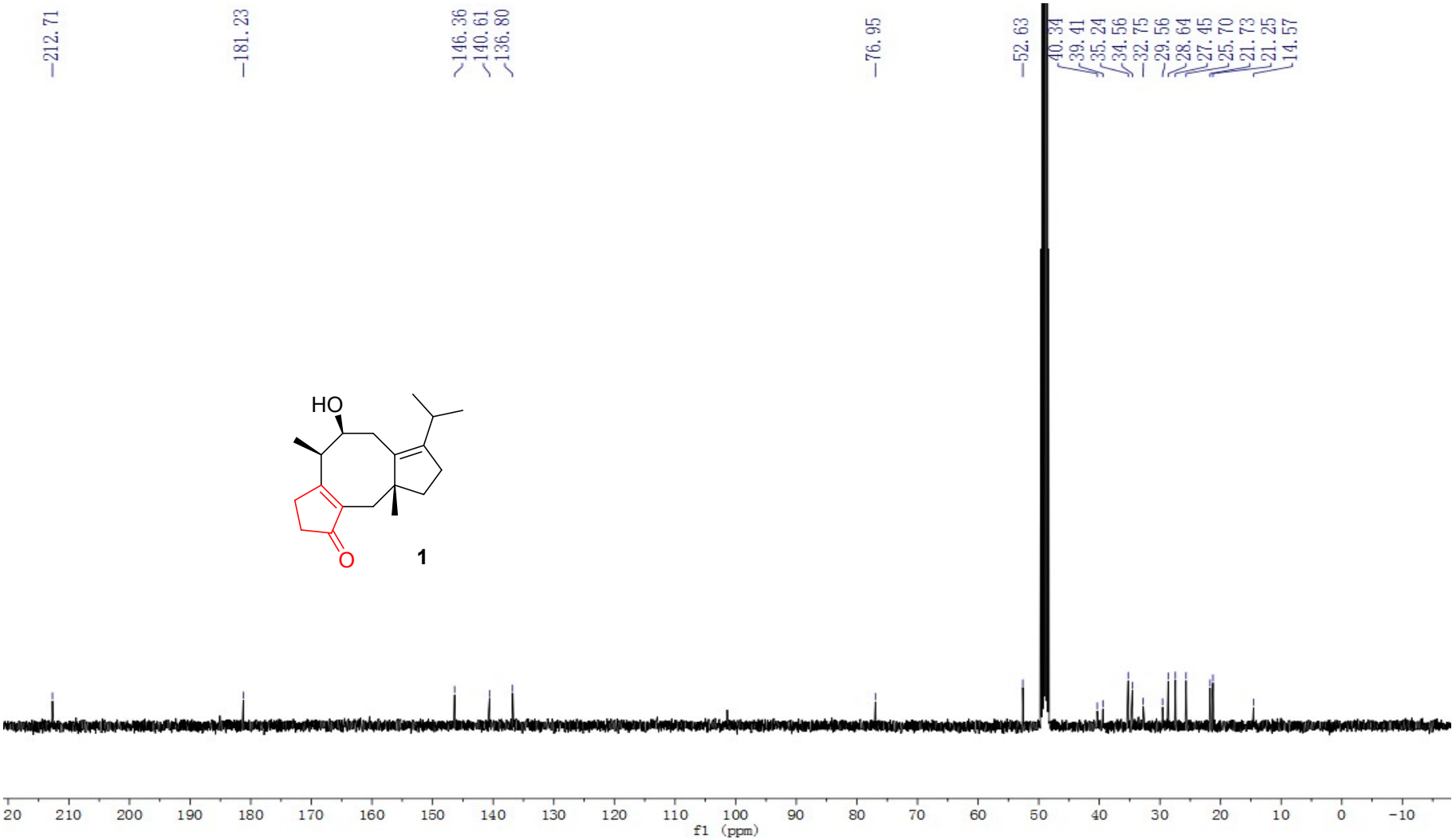


Figure S2. ^{13}C NMR spectrum of compound **1** (Recorded in methanol-d_4)

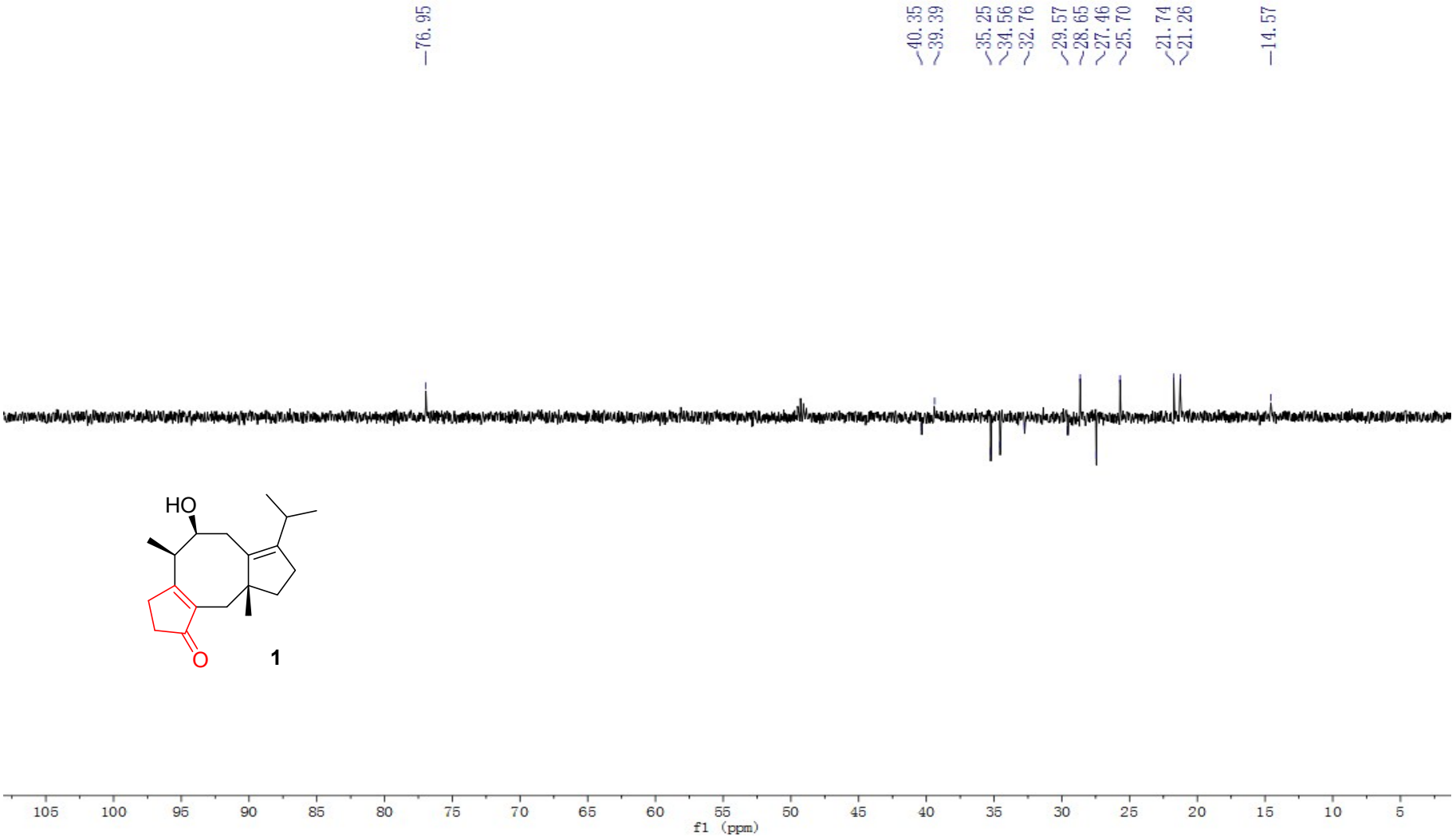


Figure S3. DEPT spectrum of compound **1** (Recorded in methanol-d_4)

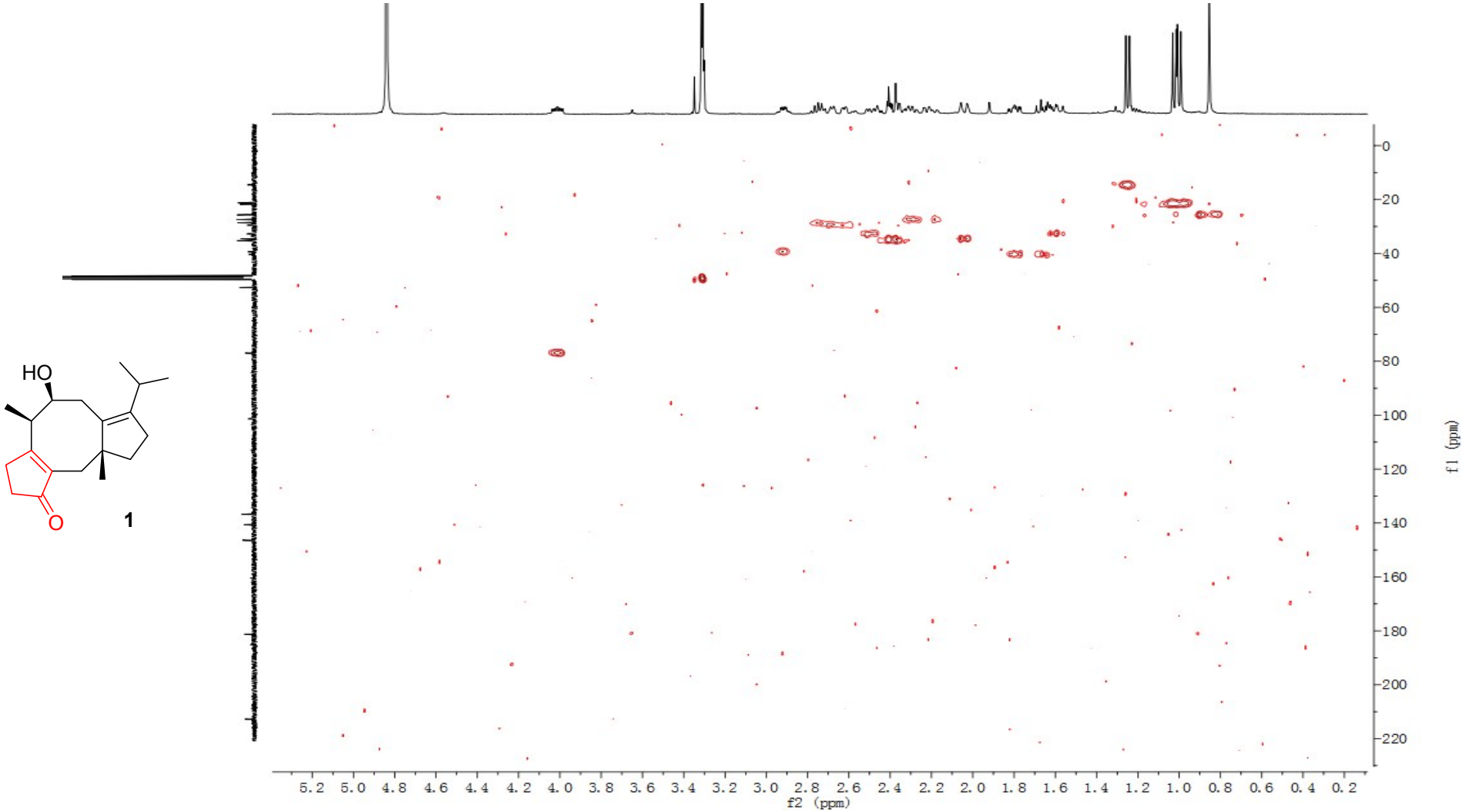


Figure S4. HSQC spectrum of compound **1** (Recorded in methanol-d_4)

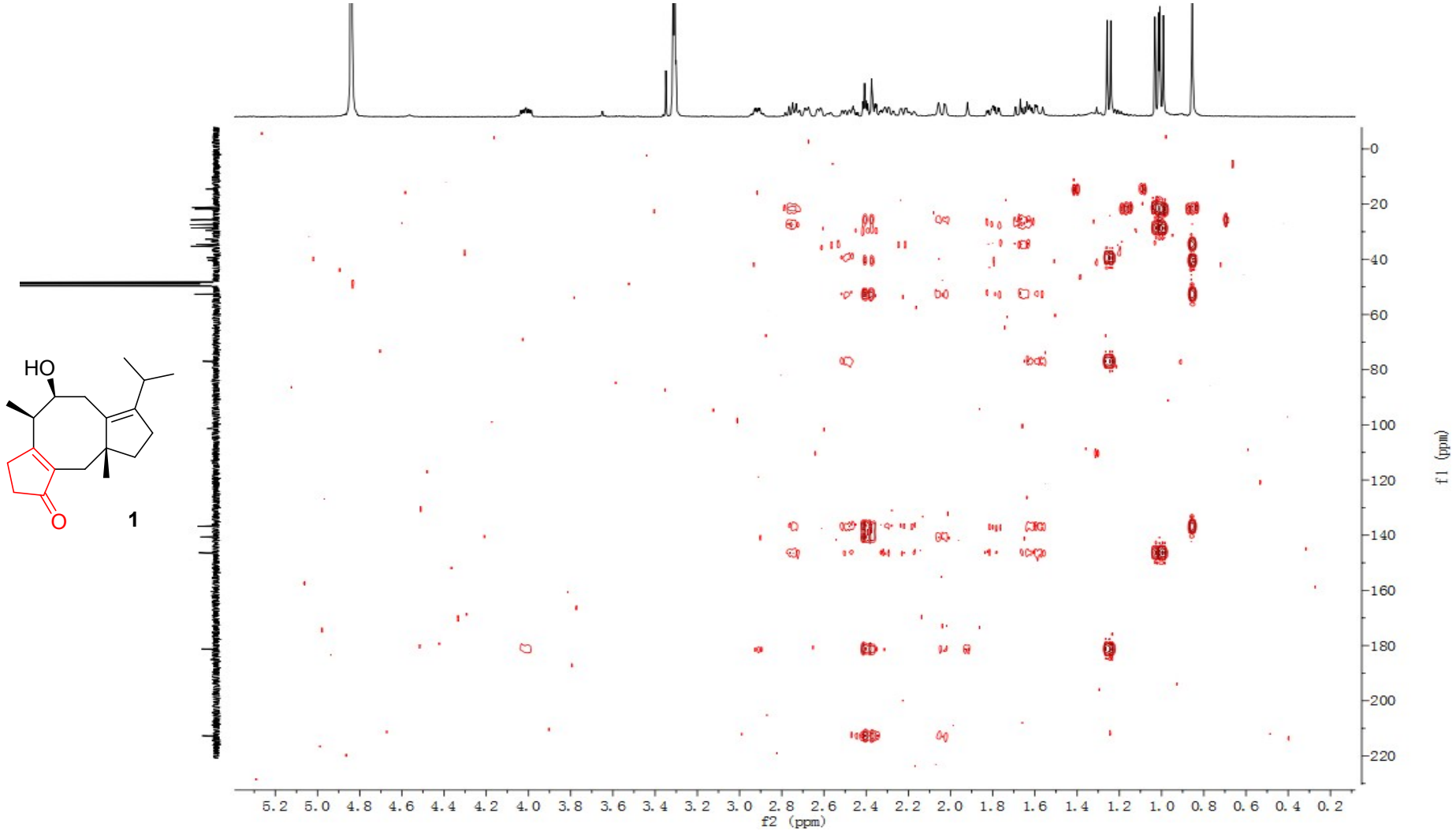


Figure S5. HMBC spectrum of compound **1** (Recorded in methanol-d_4)

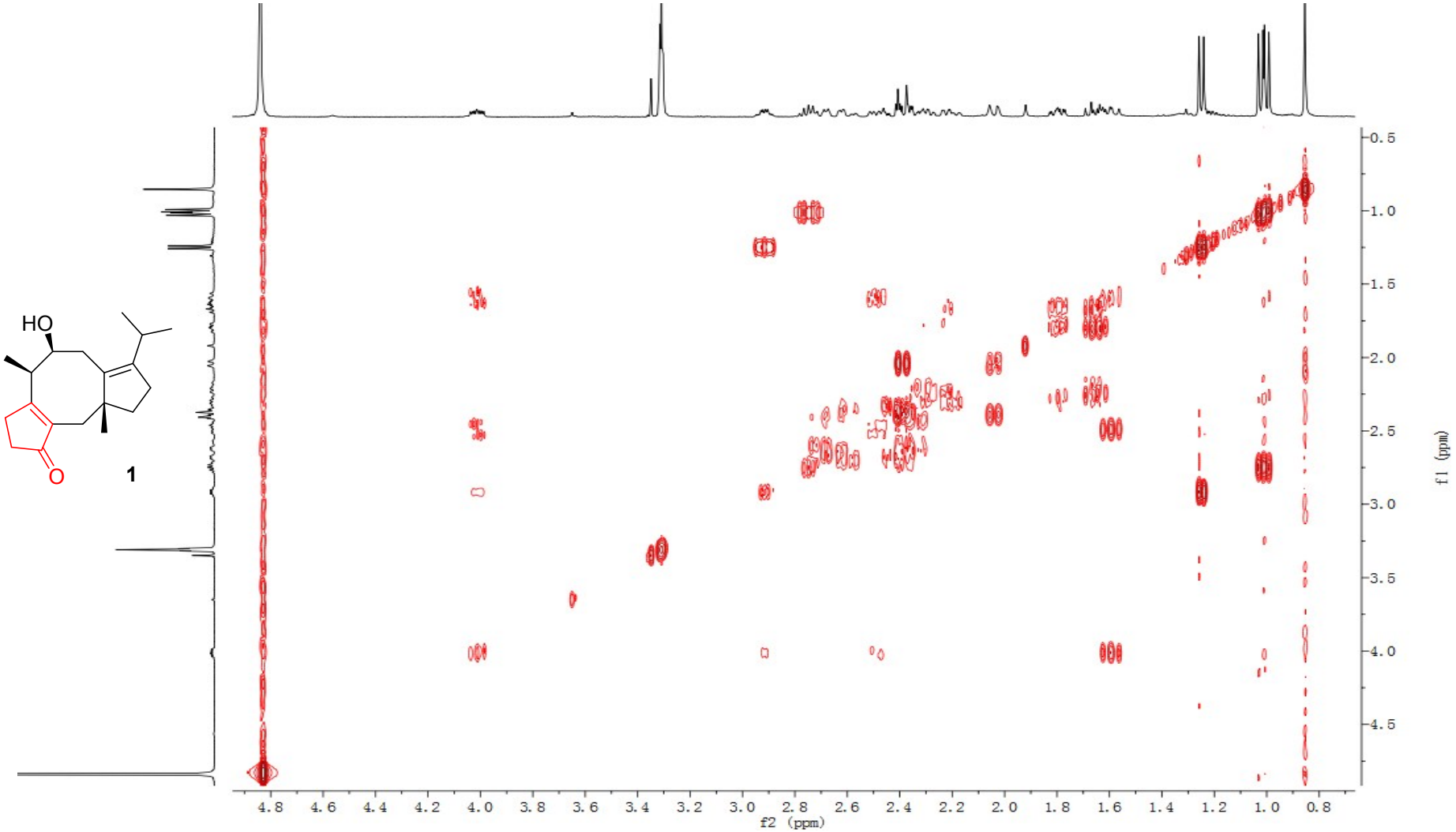


Figure S6. ^{1}H–^{1}H COSY spectrum of compound **1** (Recorded in methanol-d_4)

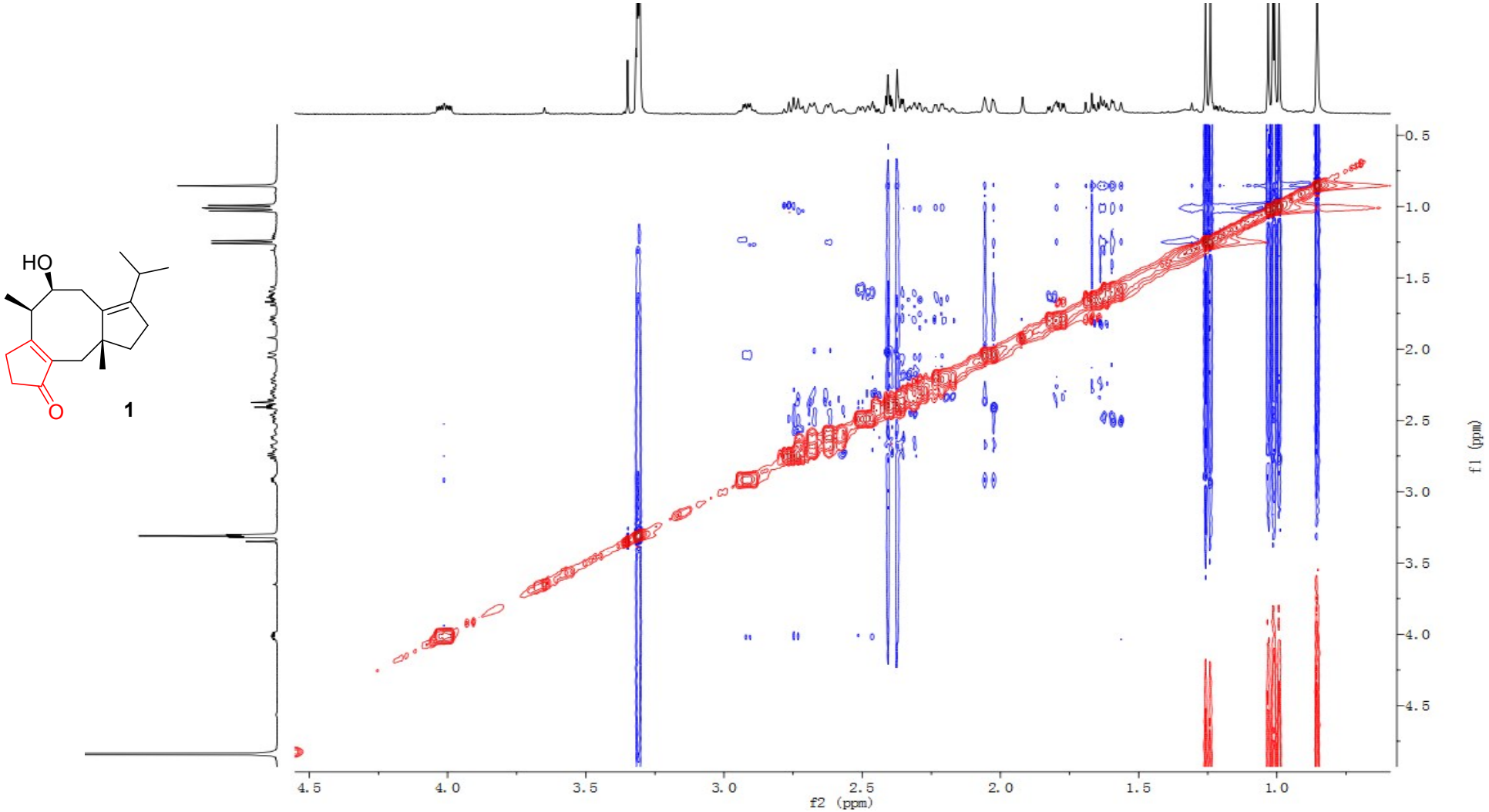


Figure S7. NOESY spectrum of compound **1** (Recorded in methanol-d_4)

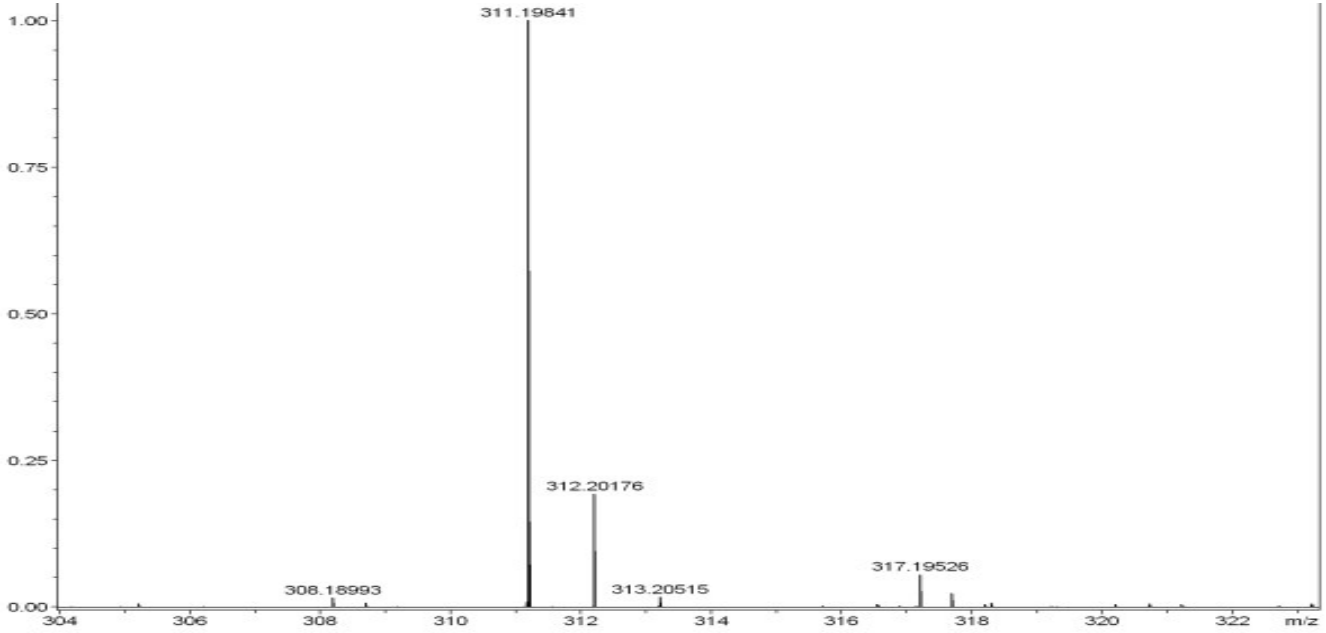
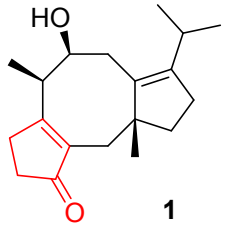


Figure S8. HRESIMS spectrum of compound **1**



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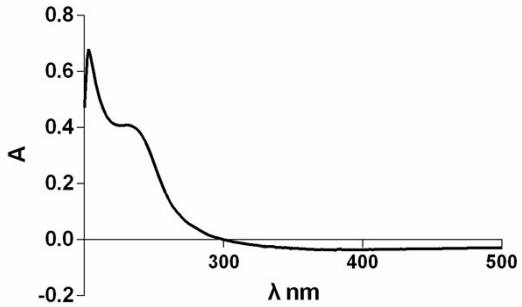

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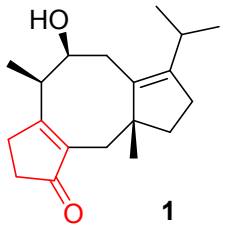

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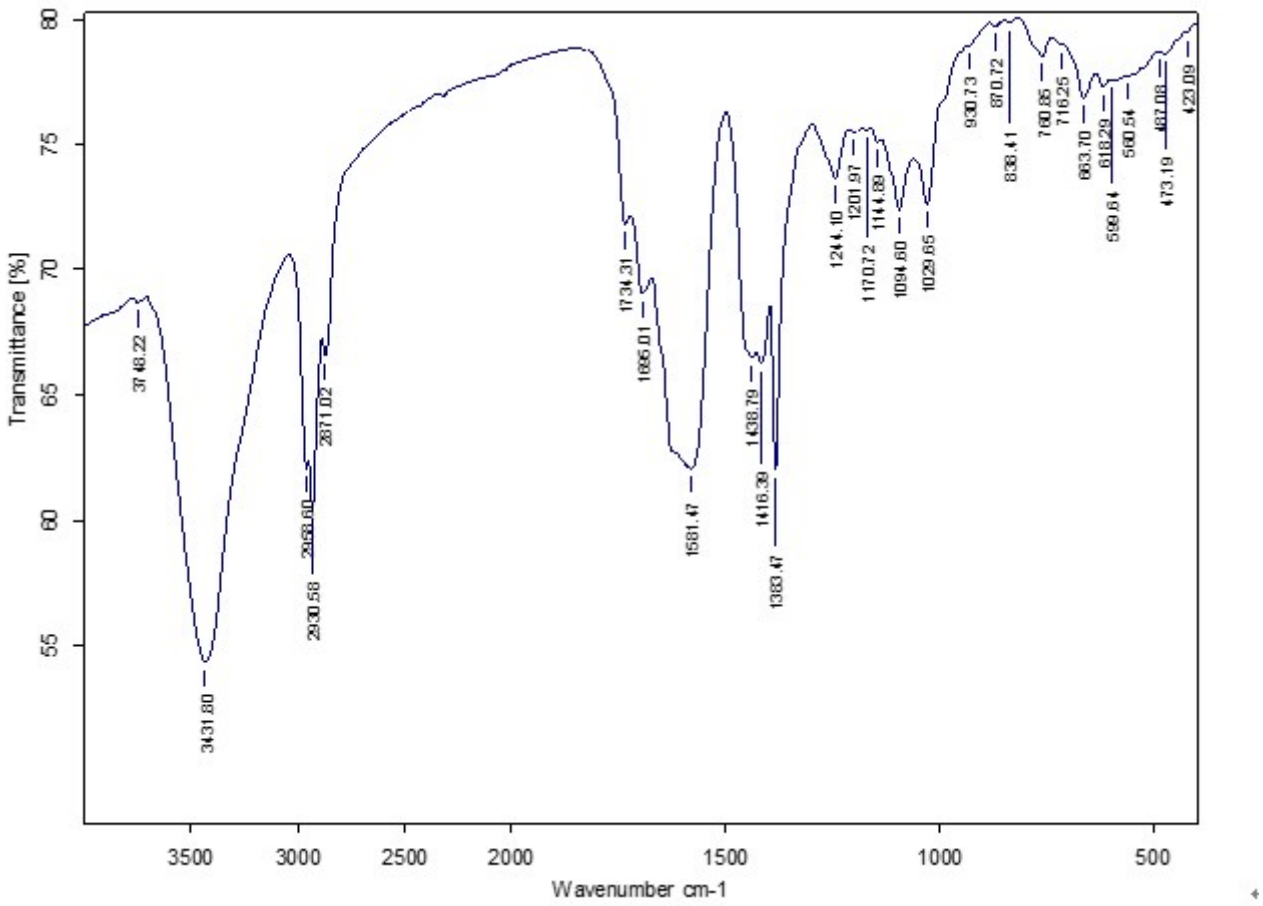


Figure S10. IR spectrum of compound **1**

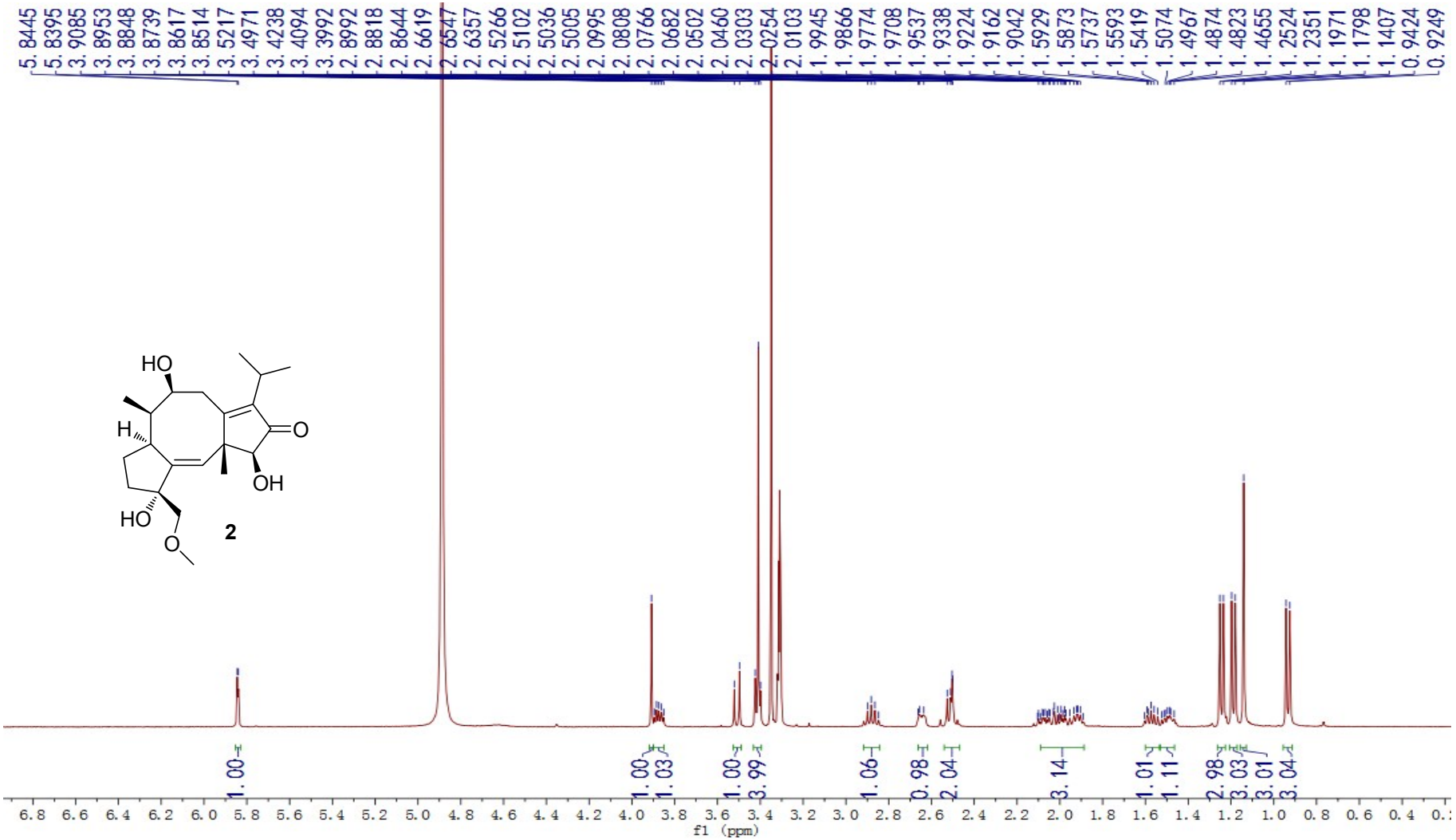


Figure S11. ^{1}H NMR spectrum of compound **2** (Recorded in methanol-d_4)

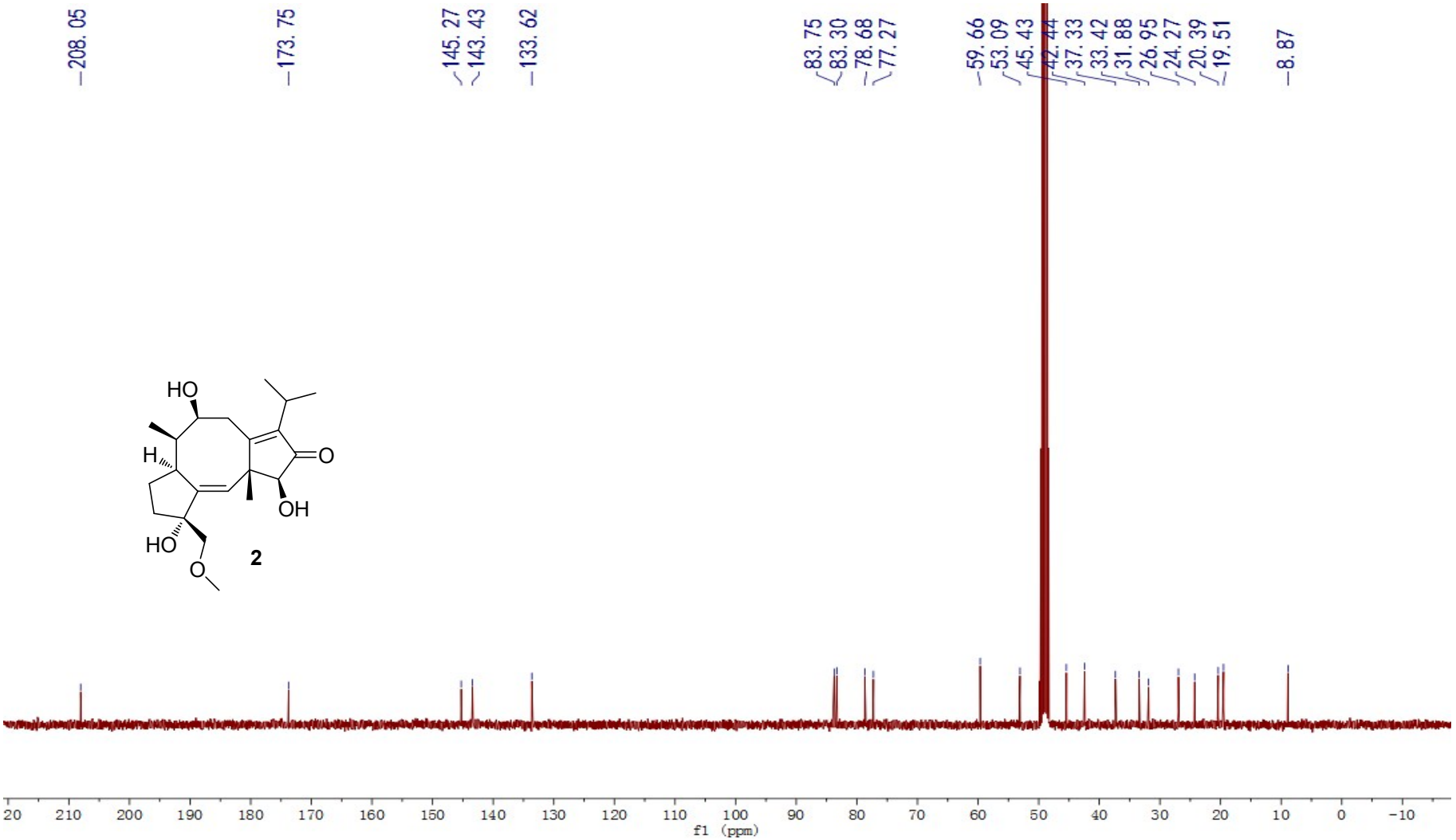


Figure S12. ^{13}C NMR spectrum of compound **2** (Recorded in methanol-d_4)

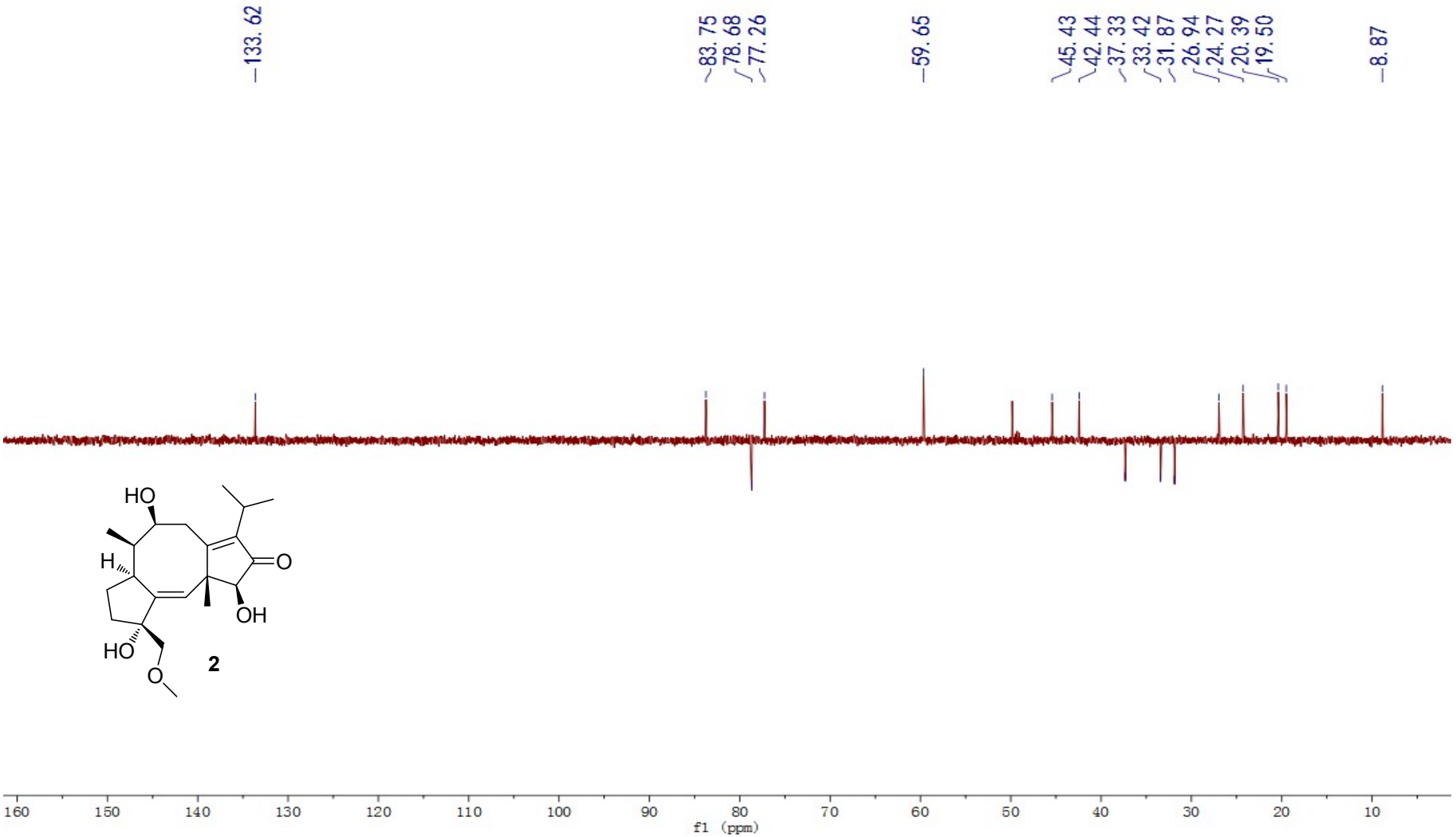


Figure S13. DEPT spectrum of compound **2** (Recorded in methanol-d_4)

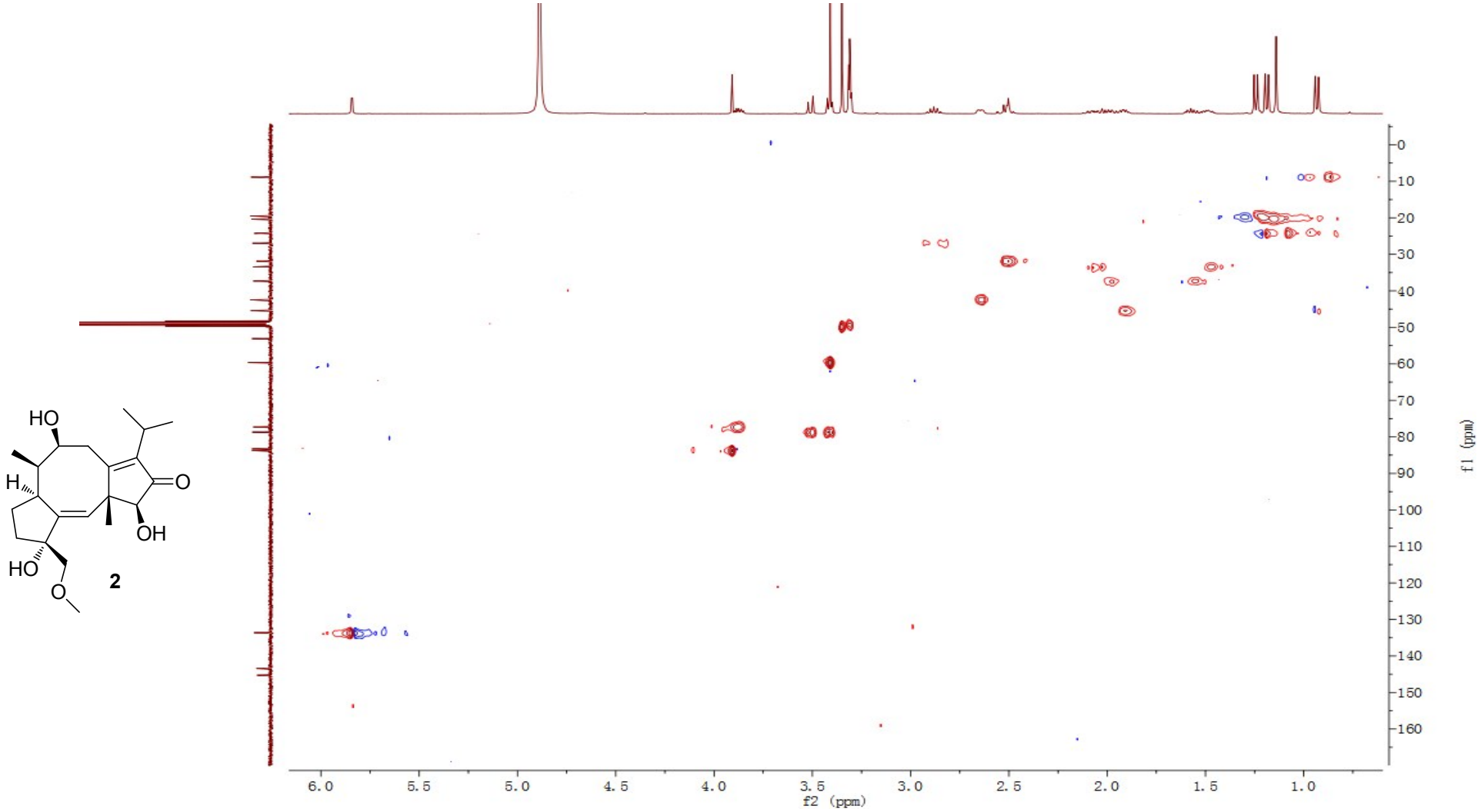


Figure S14. HSQC spectrum of compound **2** (Recorded in methanol-d_4)

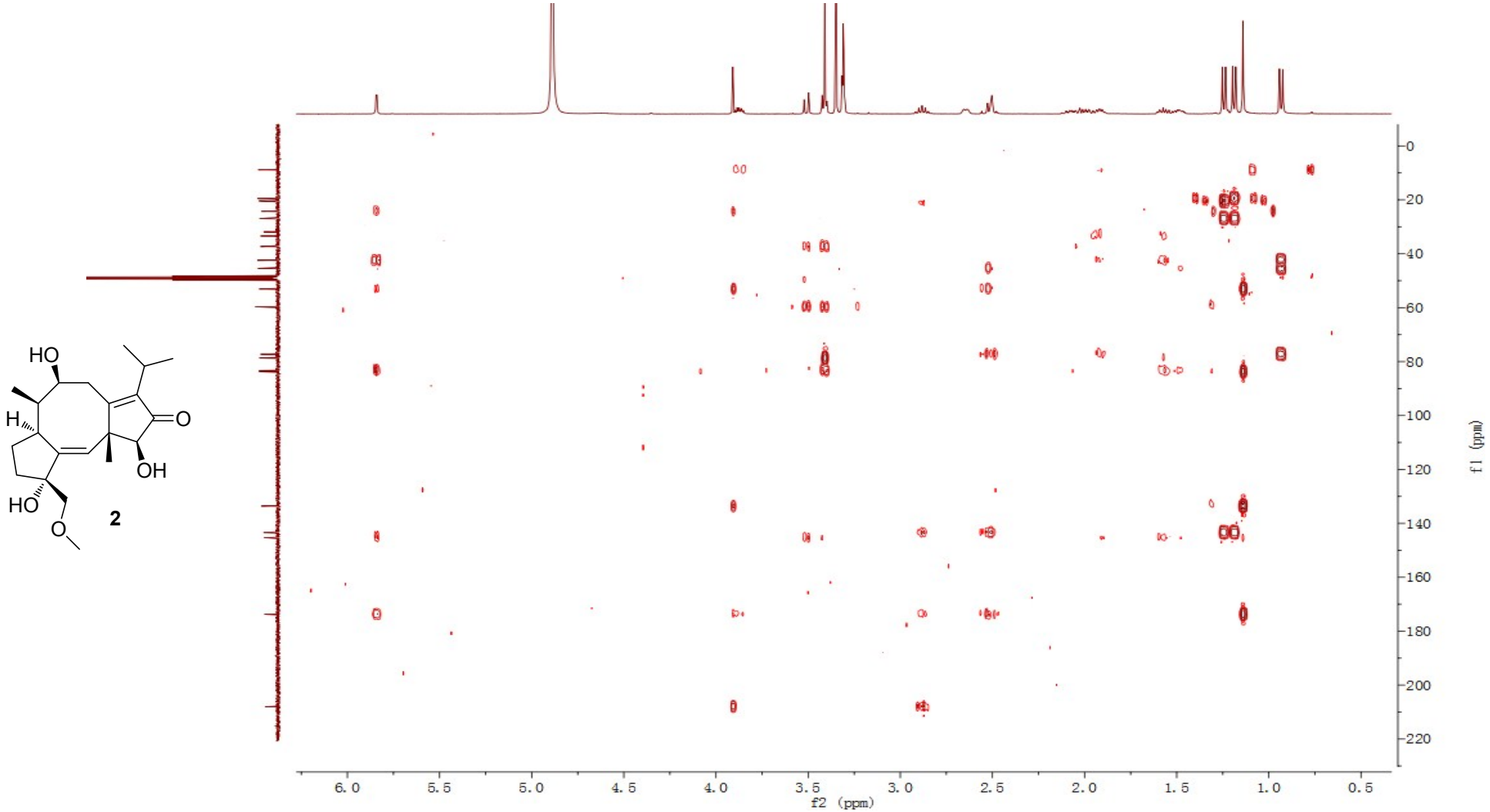


Figure S15. HMBC spectrum of compound **2** (Recorded in methanol-d_4)

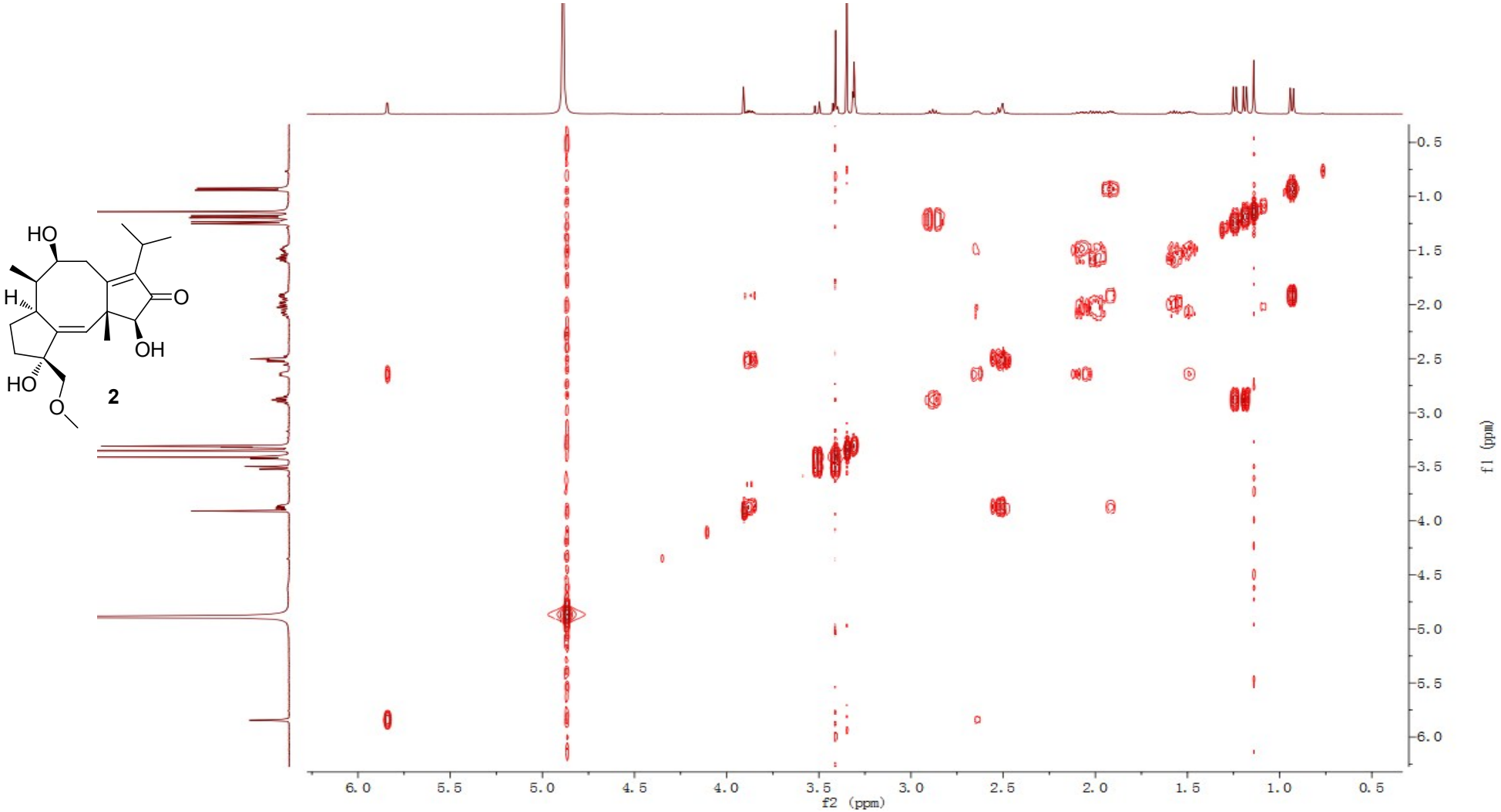
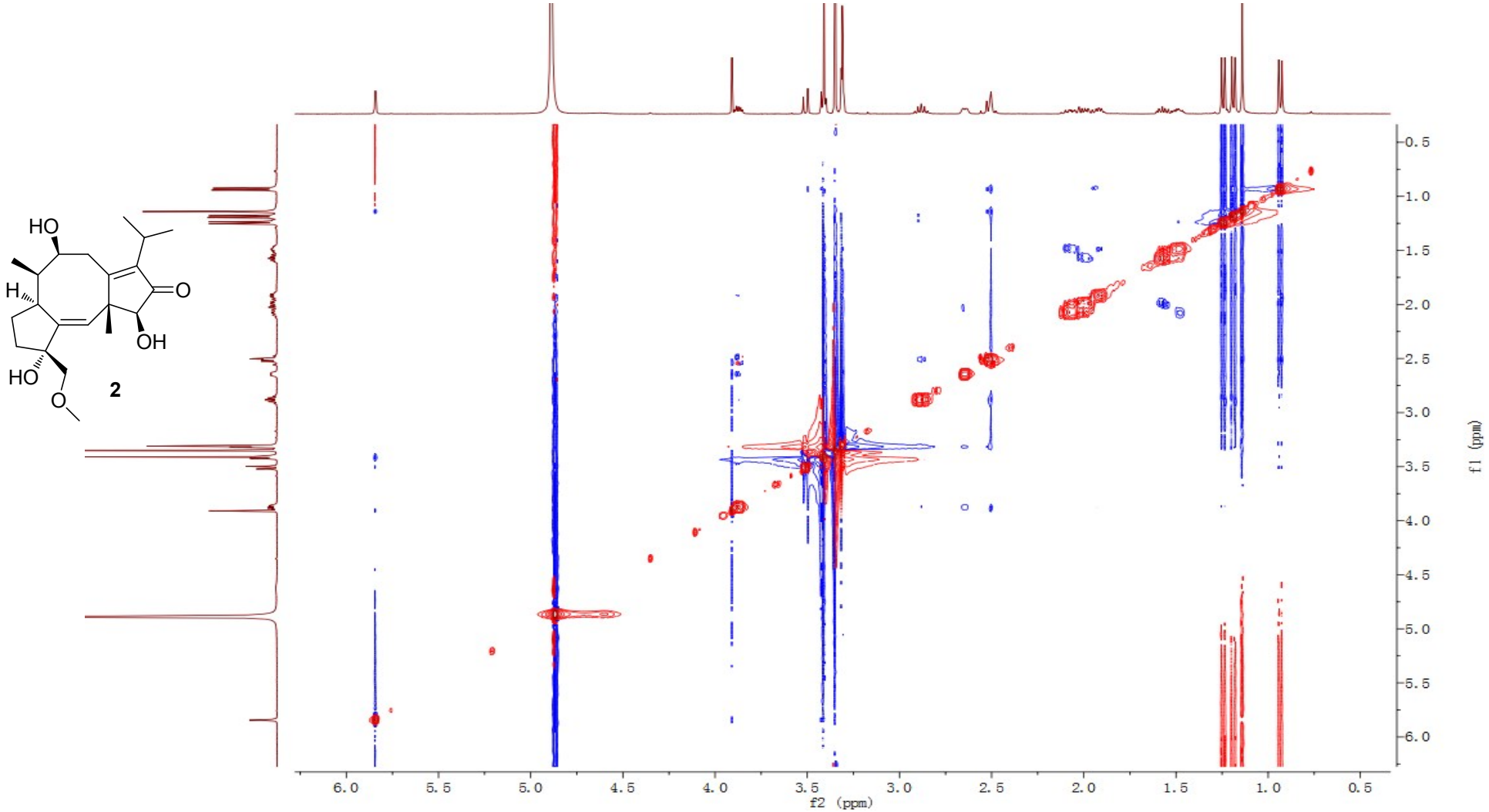


Figure S16. ^{1}H–^{1}H COSY spectrum of compound **2** (Recorded in methanol-d_4)



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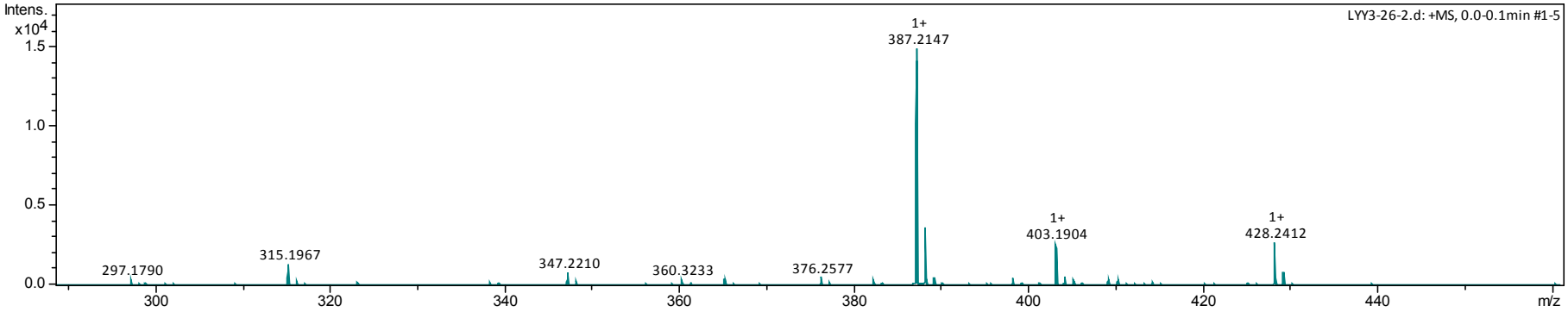
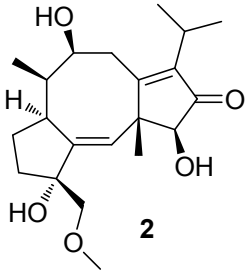


Figure S18. HRESIMS spectrum of compound **2**



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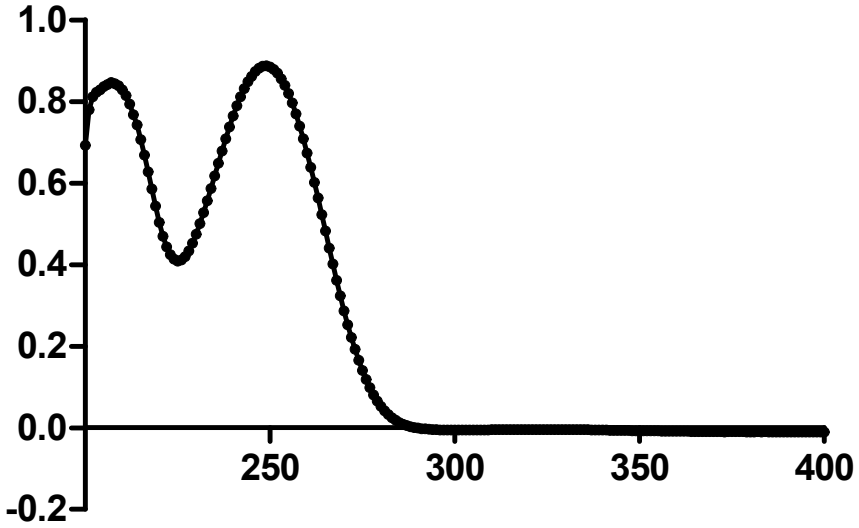


Figure S19. UV spectrum of compound **2**

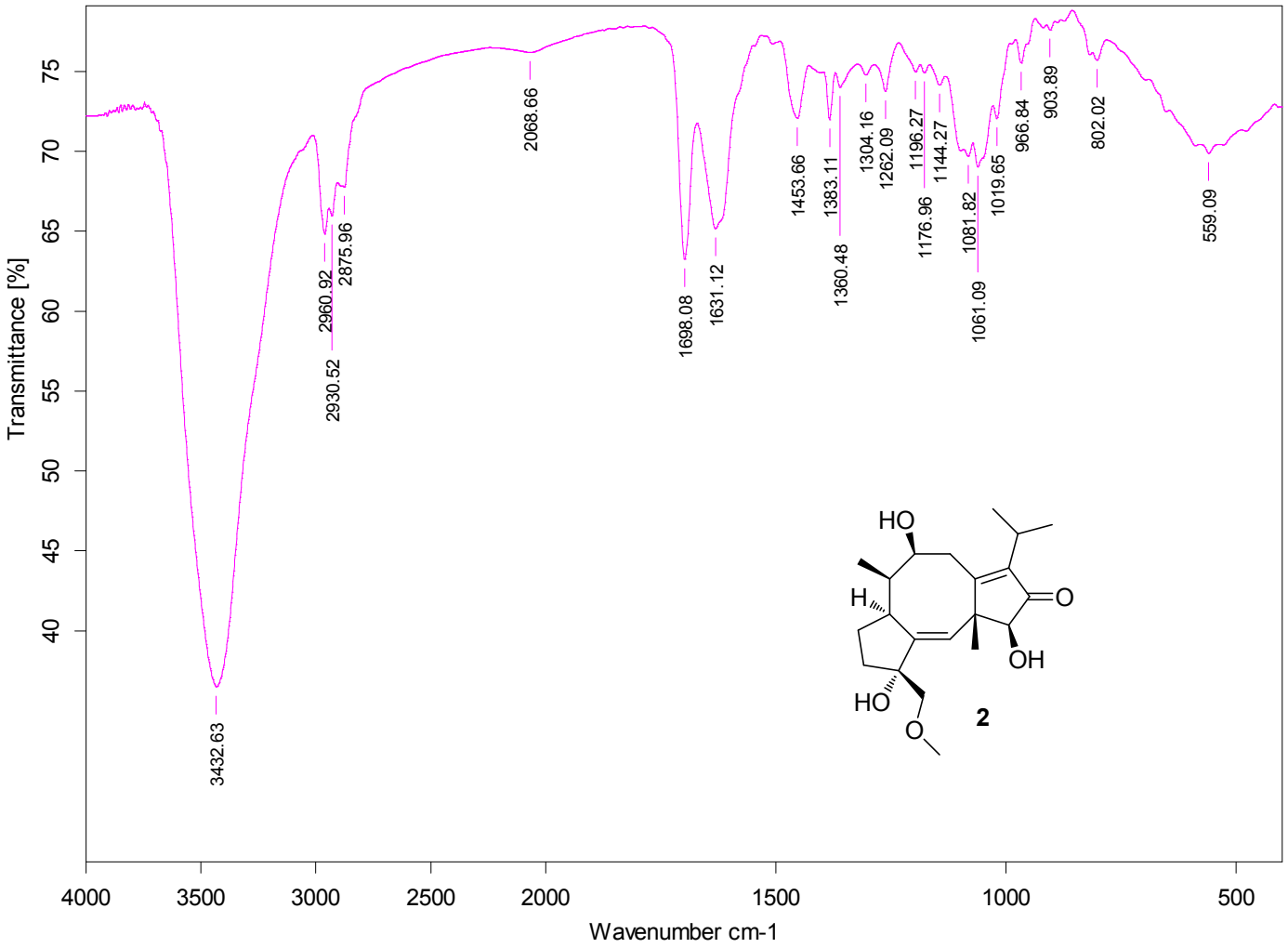


Figure S20. IR spectrum of compound **2**

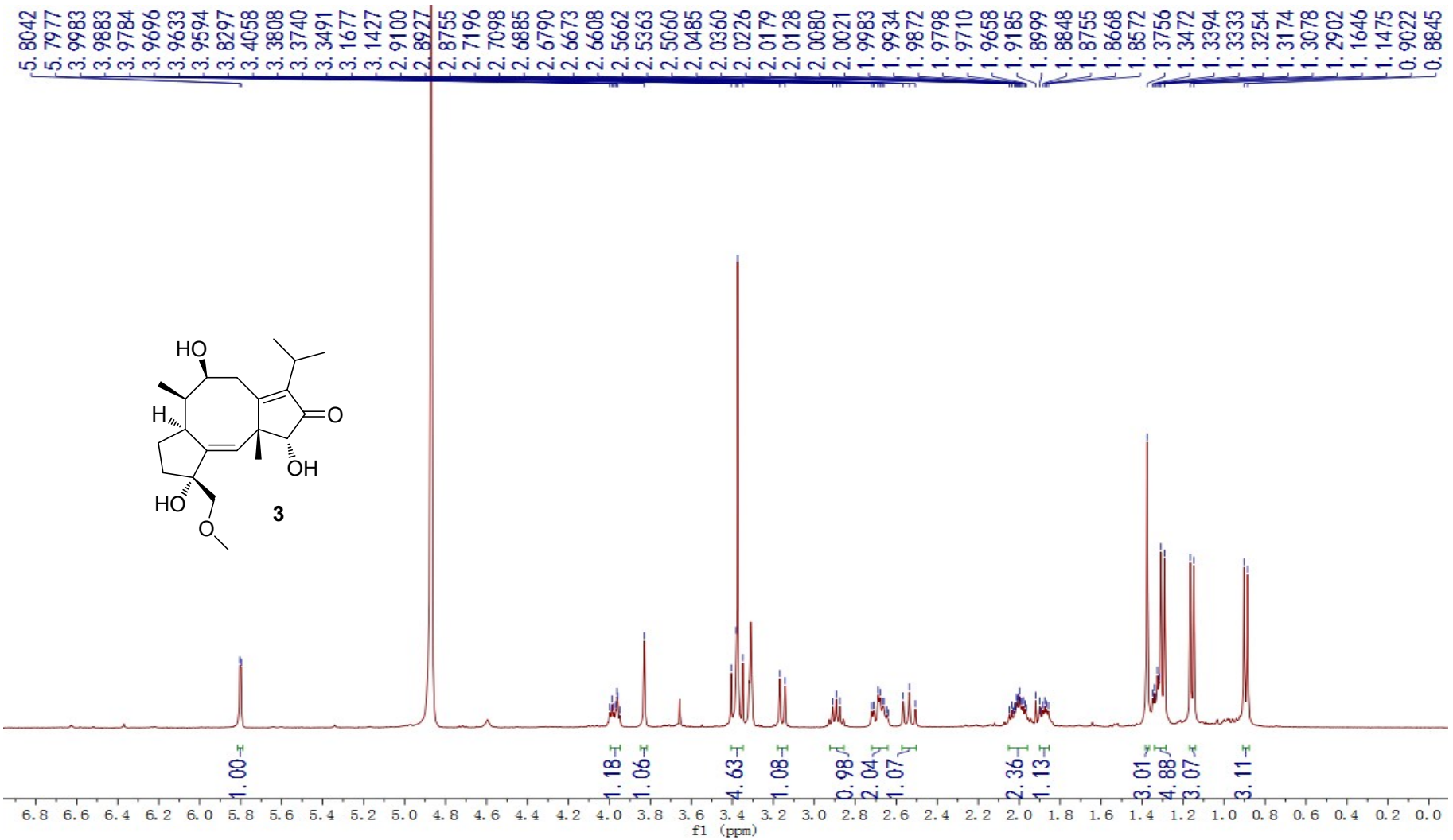


Figure S21. ^{1}H NMR spectrum of compound **3** (Recorded in methanol-d_4)

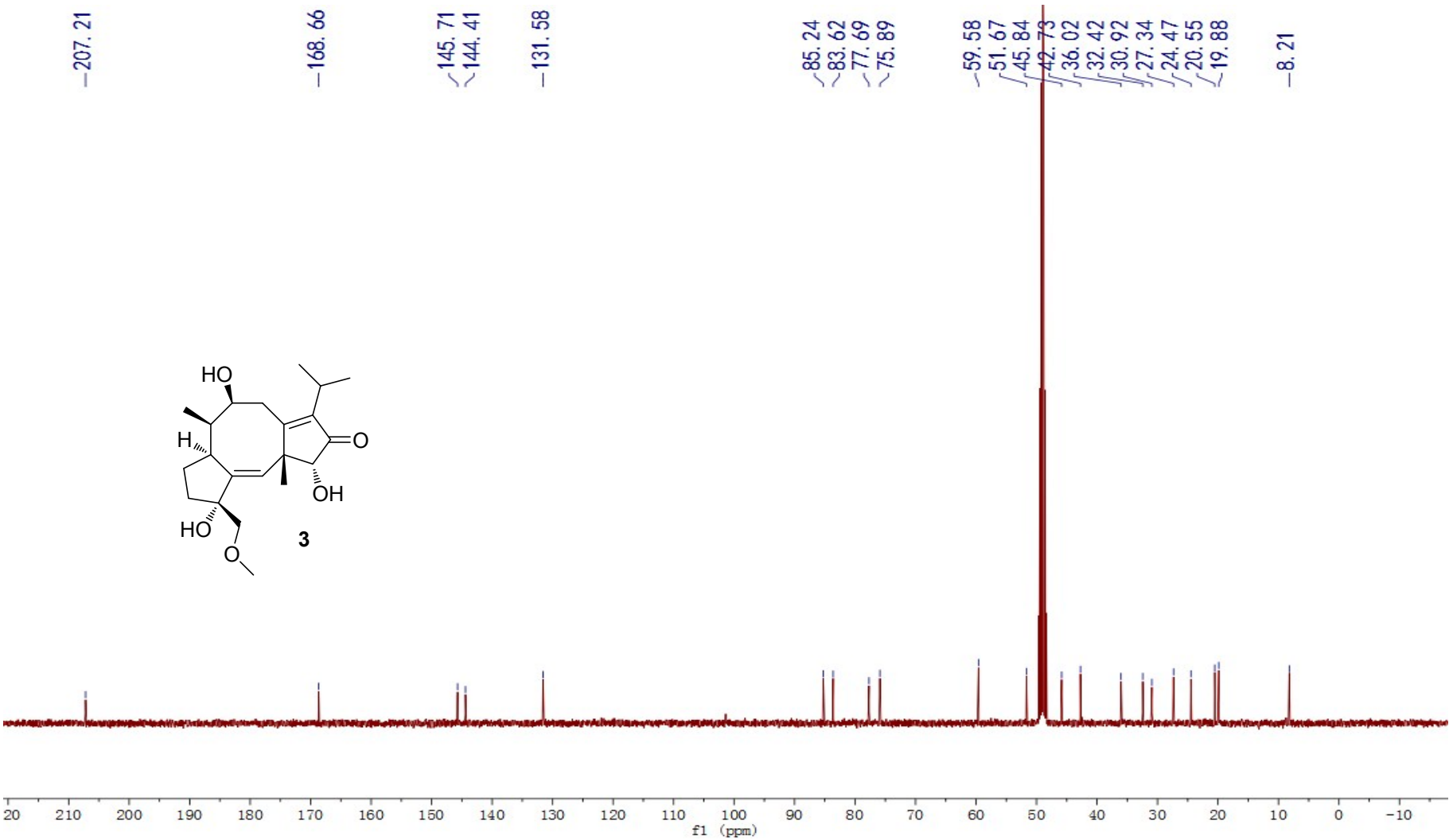


Figure S22. ^{13}C NMR spectrum of compound **3** (Recorded in methanol-d_4)

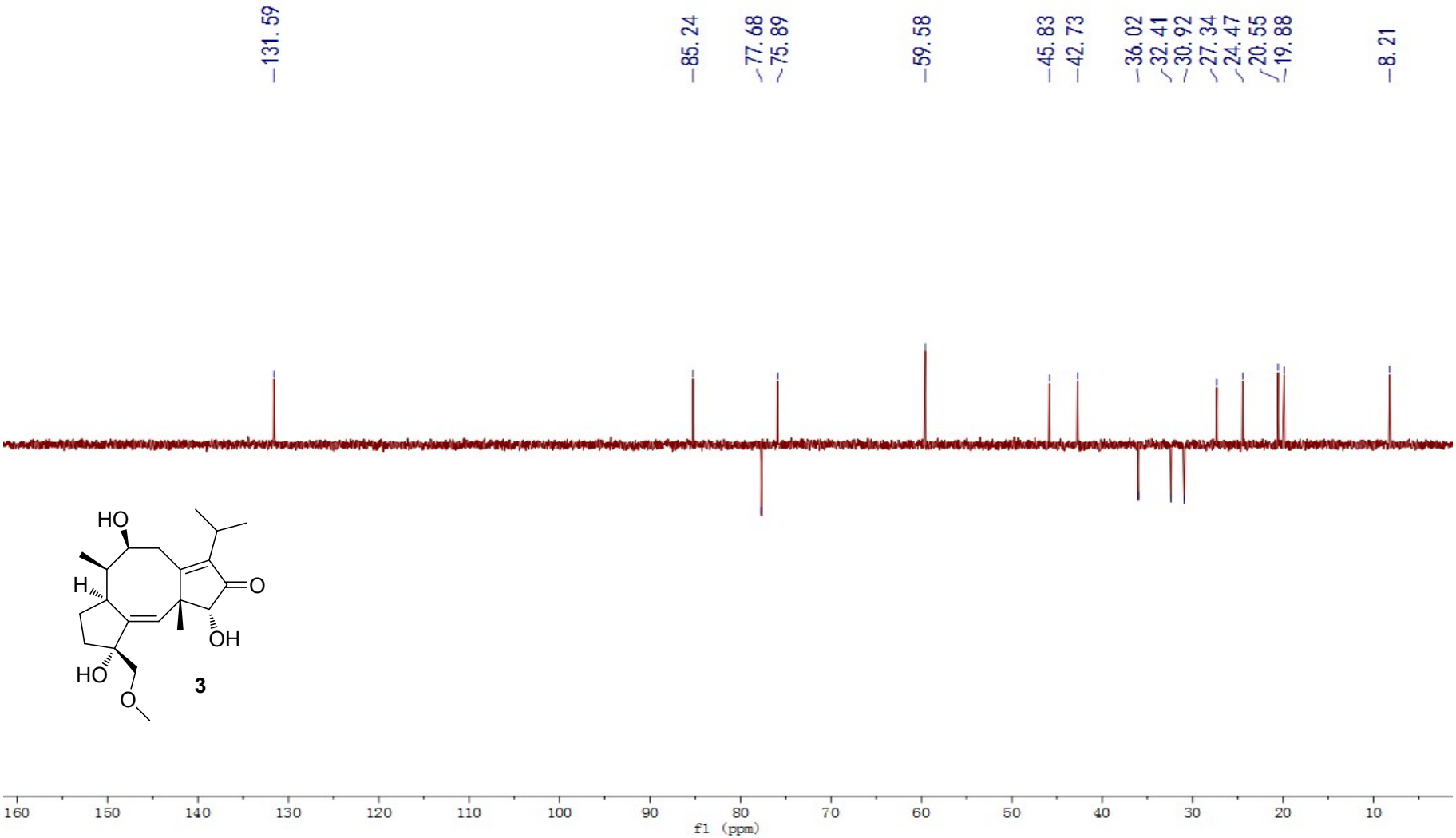


Figure S23. DEPT spectrum of compound **3** (Recorded in methanol-d_4)

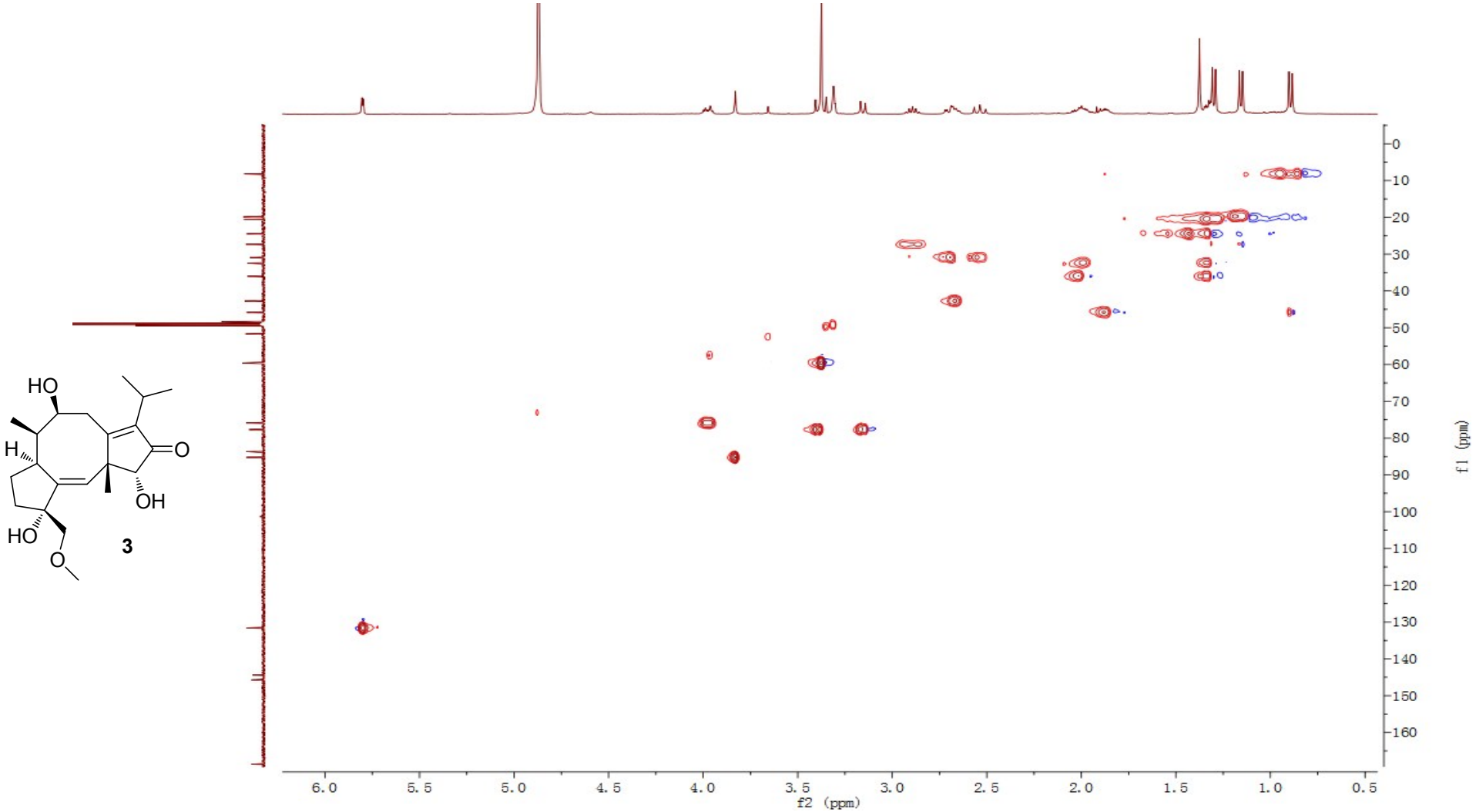


Figure S24. HSQC spectrum of compound **3** (Recorded in methanol-d_4)

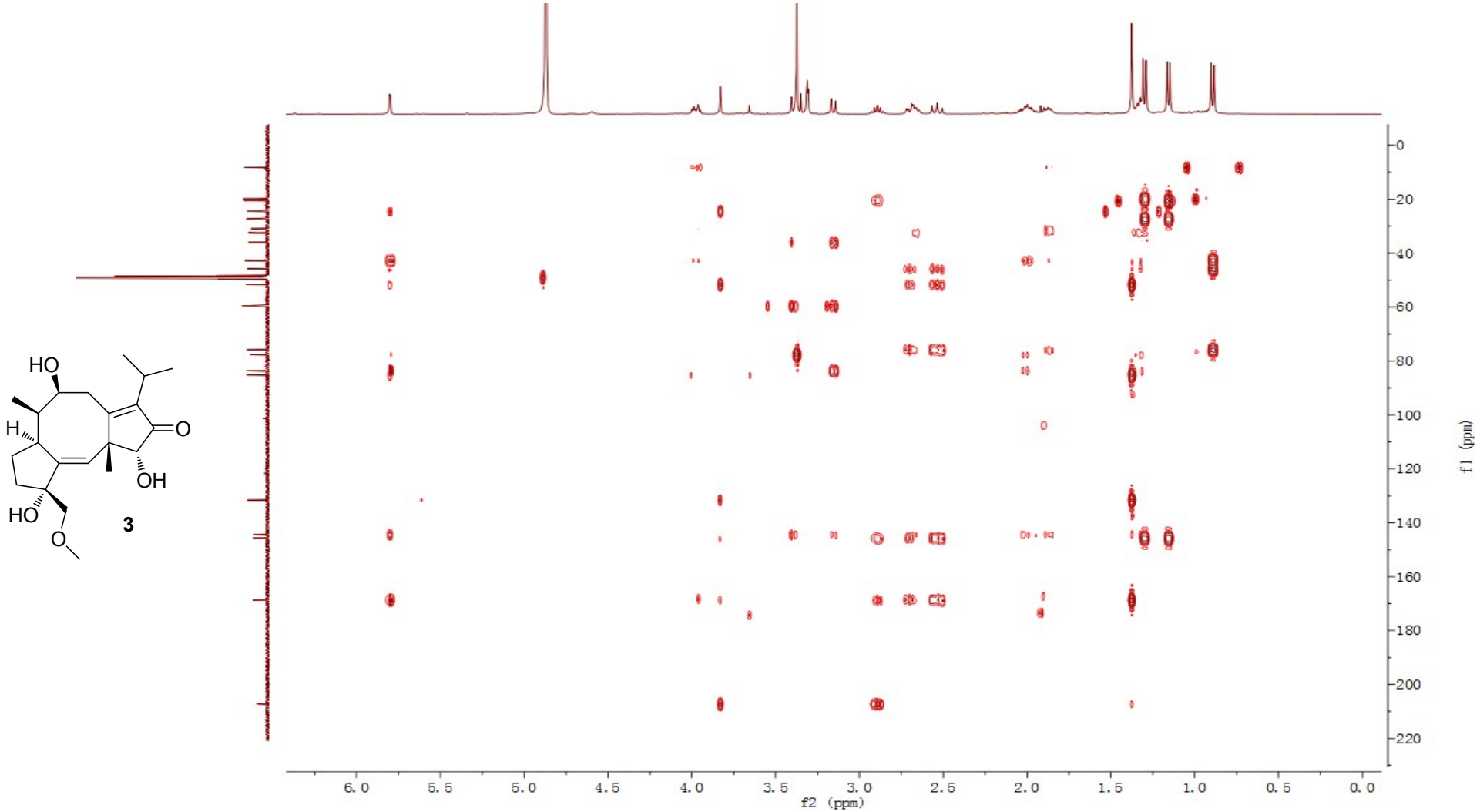


Figure S25. HMBC spectrum of compound **3** (Recorded in methanol-d_4)

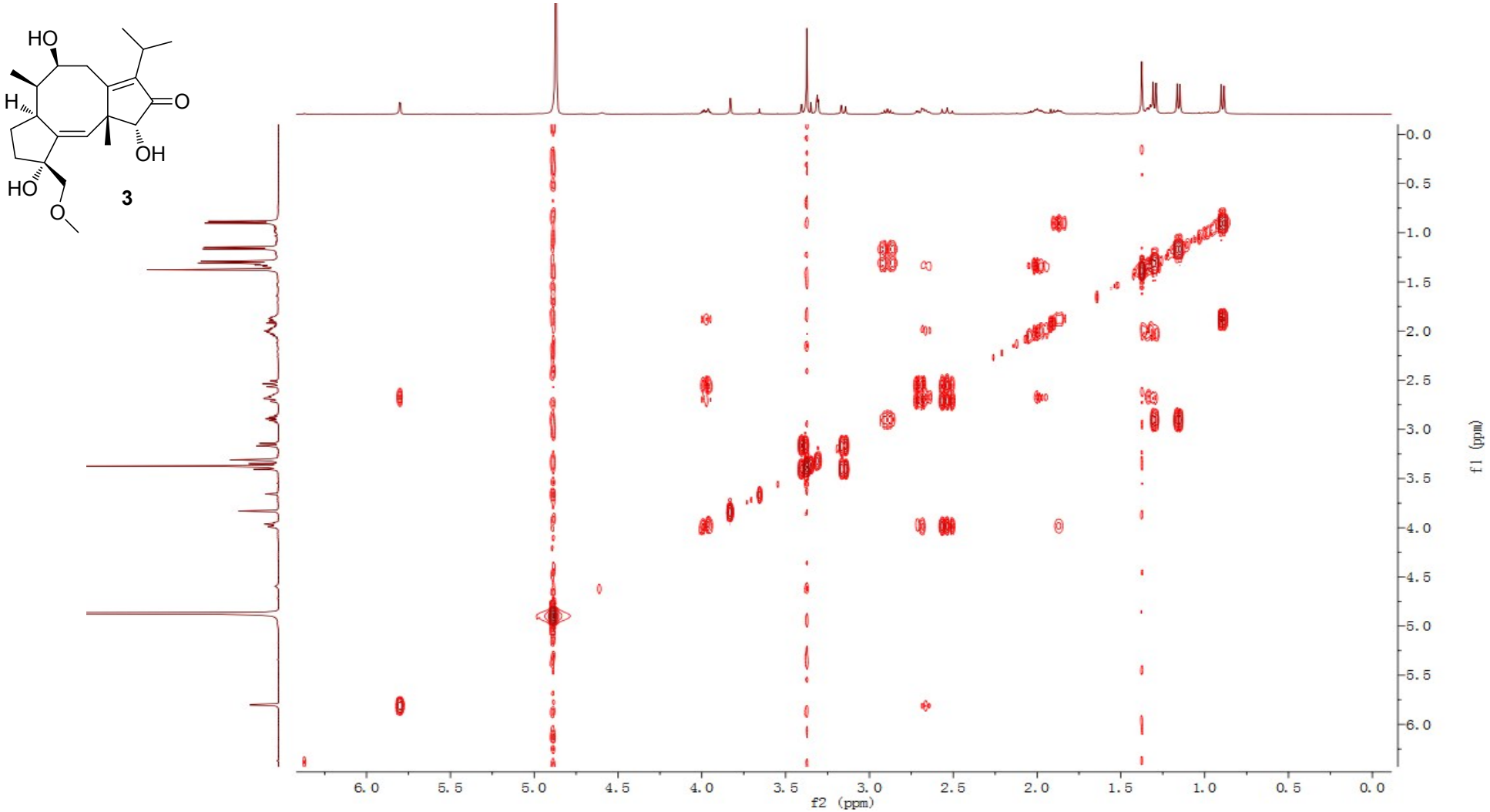


Figure S26. ^{1}H–^{1}H COSY spectrum of compound **3** (Recorded in methanol-d_4)

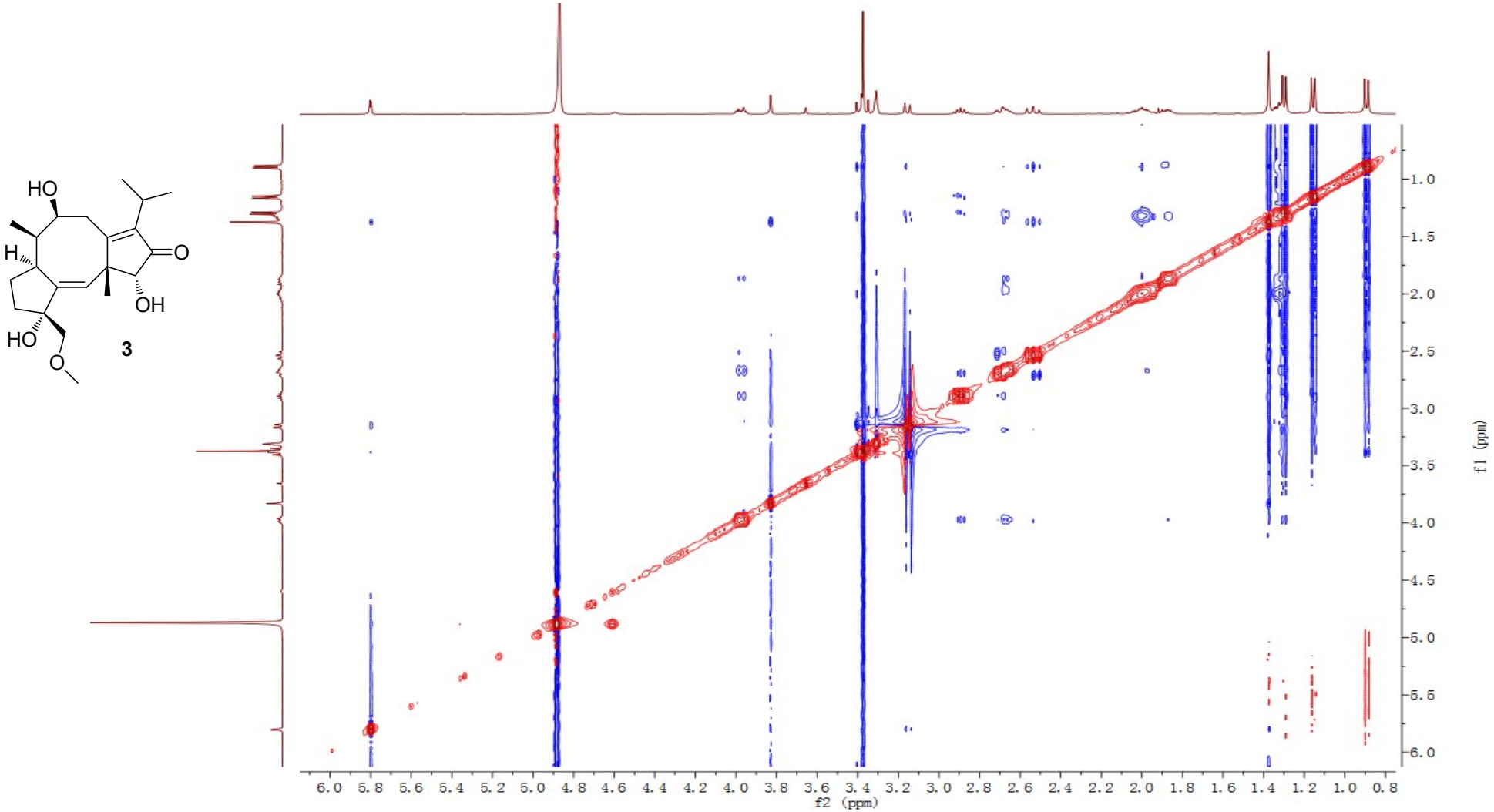


Figure S27. NOESY spectrum of compound **3** (Recorded in methanol-d_4)

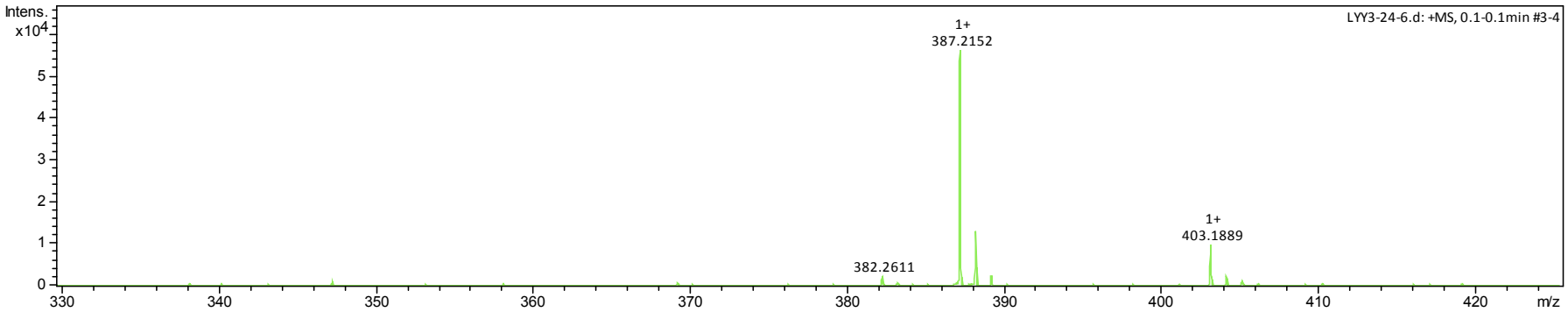
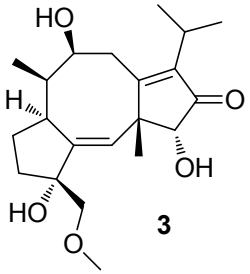


Figure S28. HRESIMS spectrum of compound **3**



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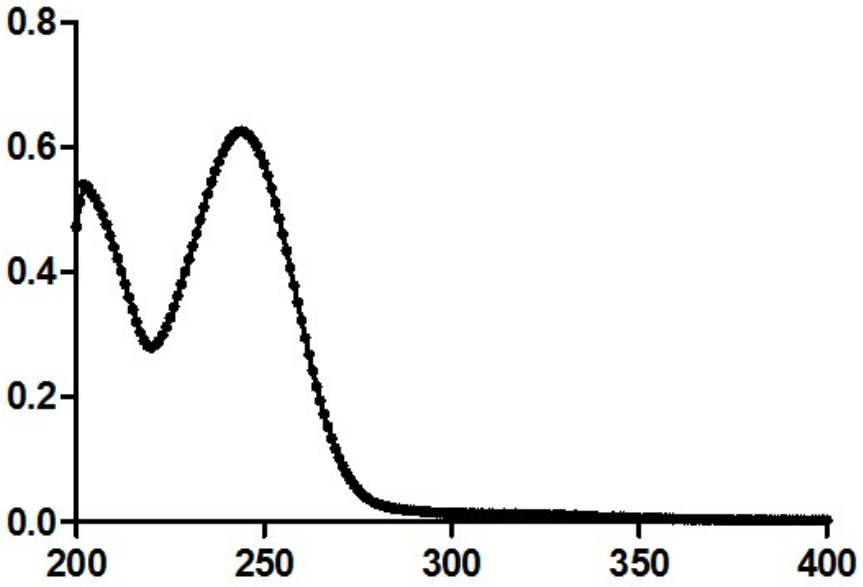


Figure S29. UV spectrum of compound **3**

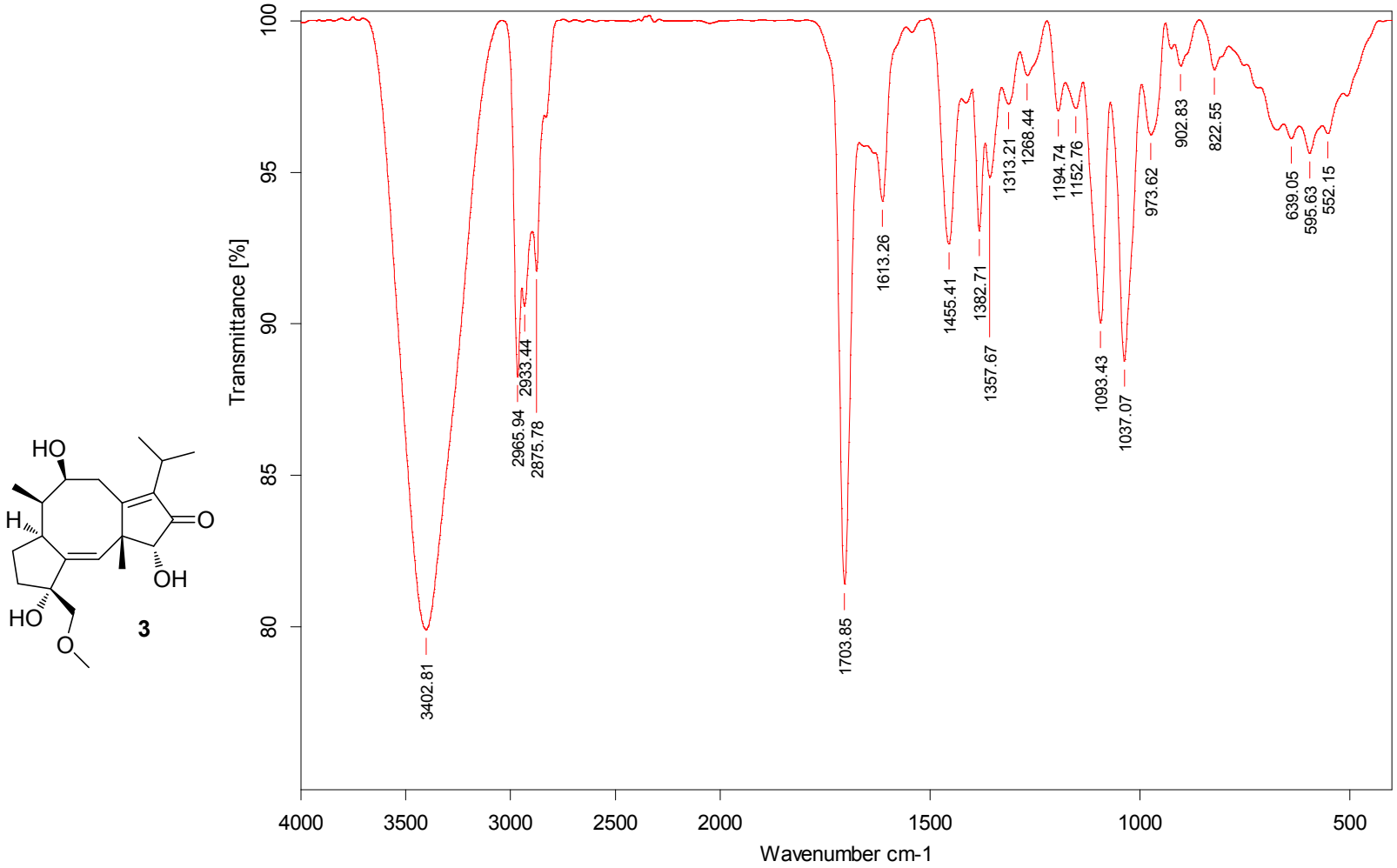


Figure S30. IR spectrum of compound **3**

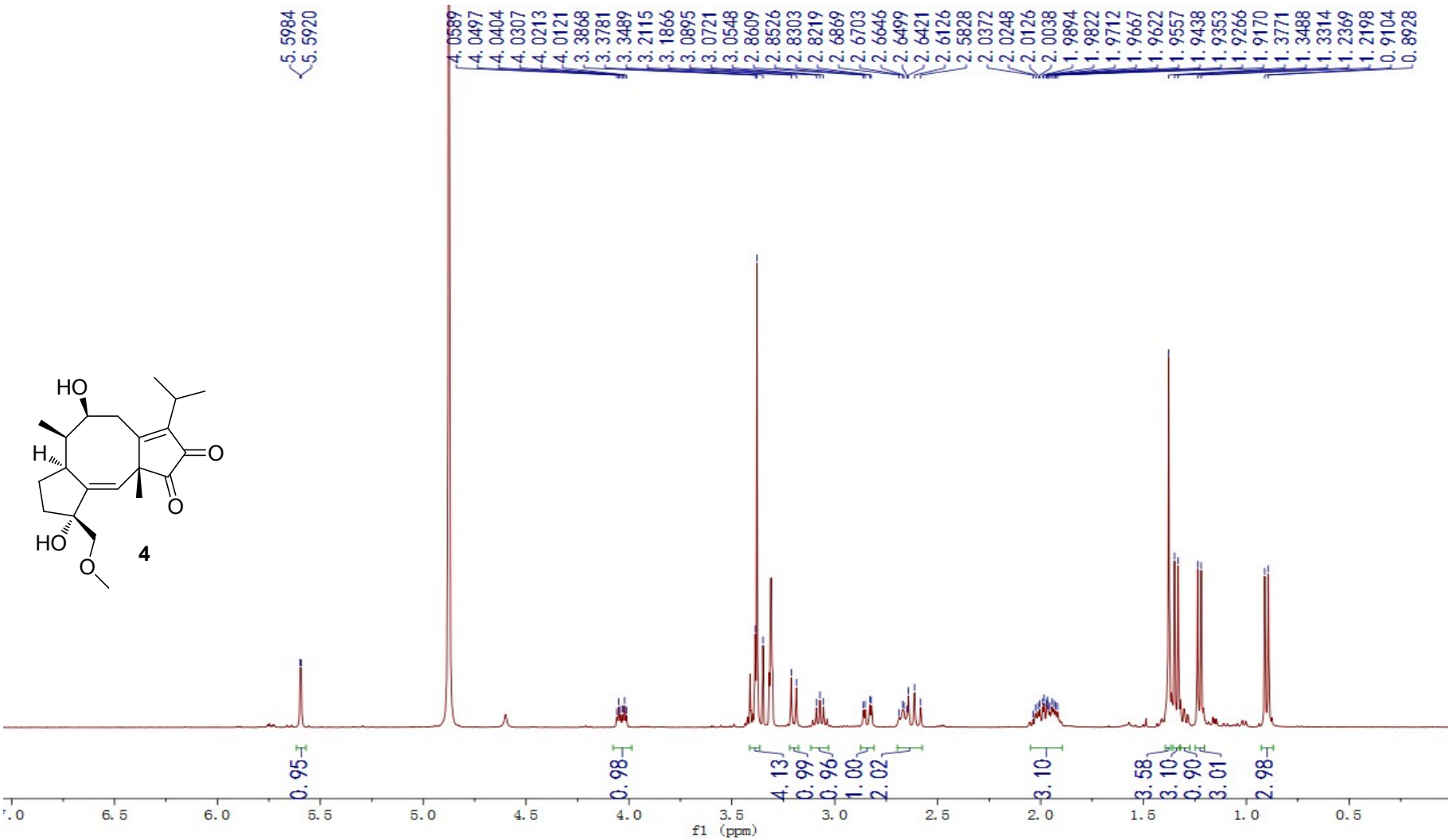


Figure S31. ^{1}H NMR spectrum of compound **4** (Recorded in methanol-d_4)

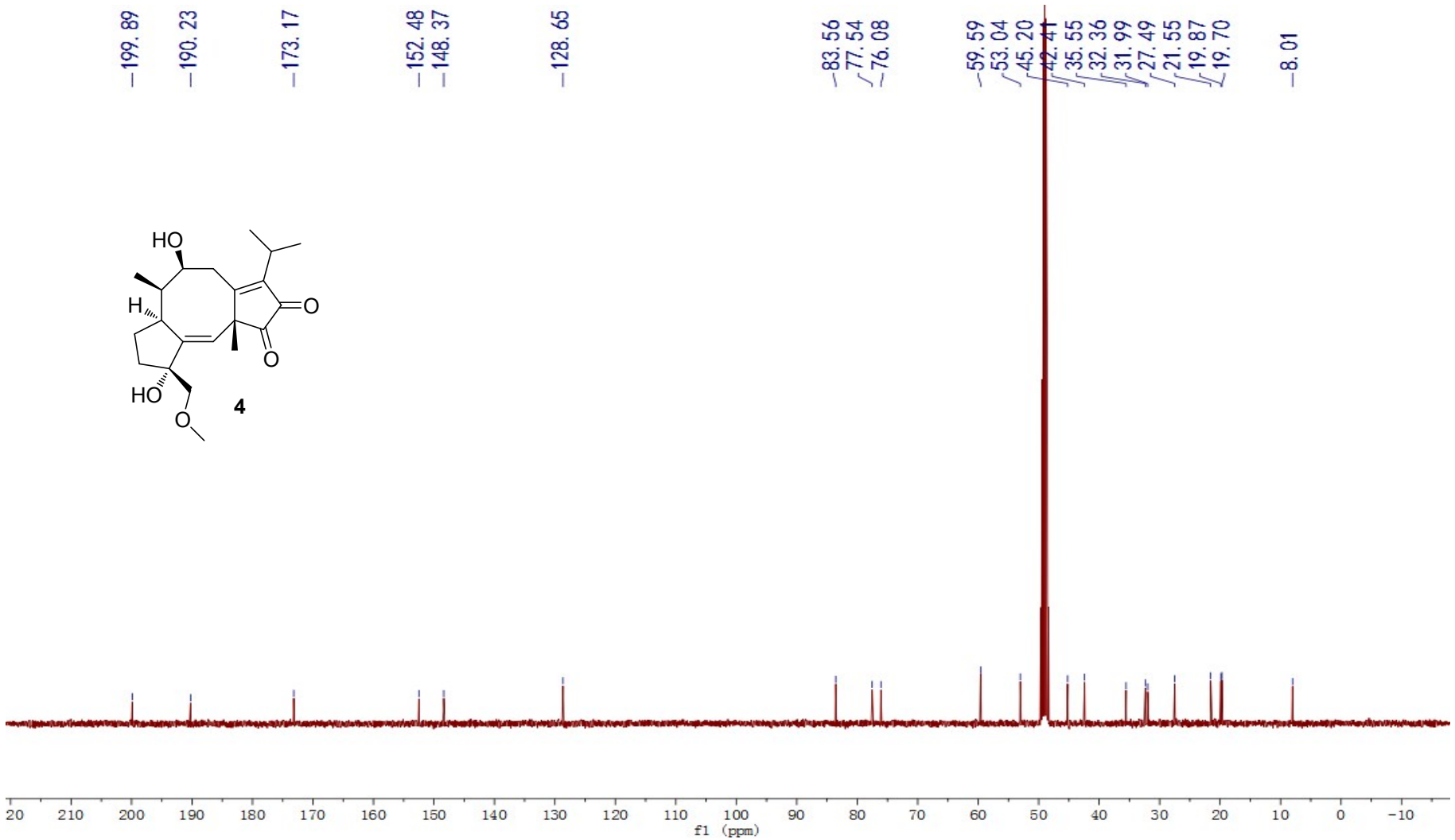


Figure S32. ^{13}C NMR spectrum of compound **4** (Recorded in methanol-d_4)

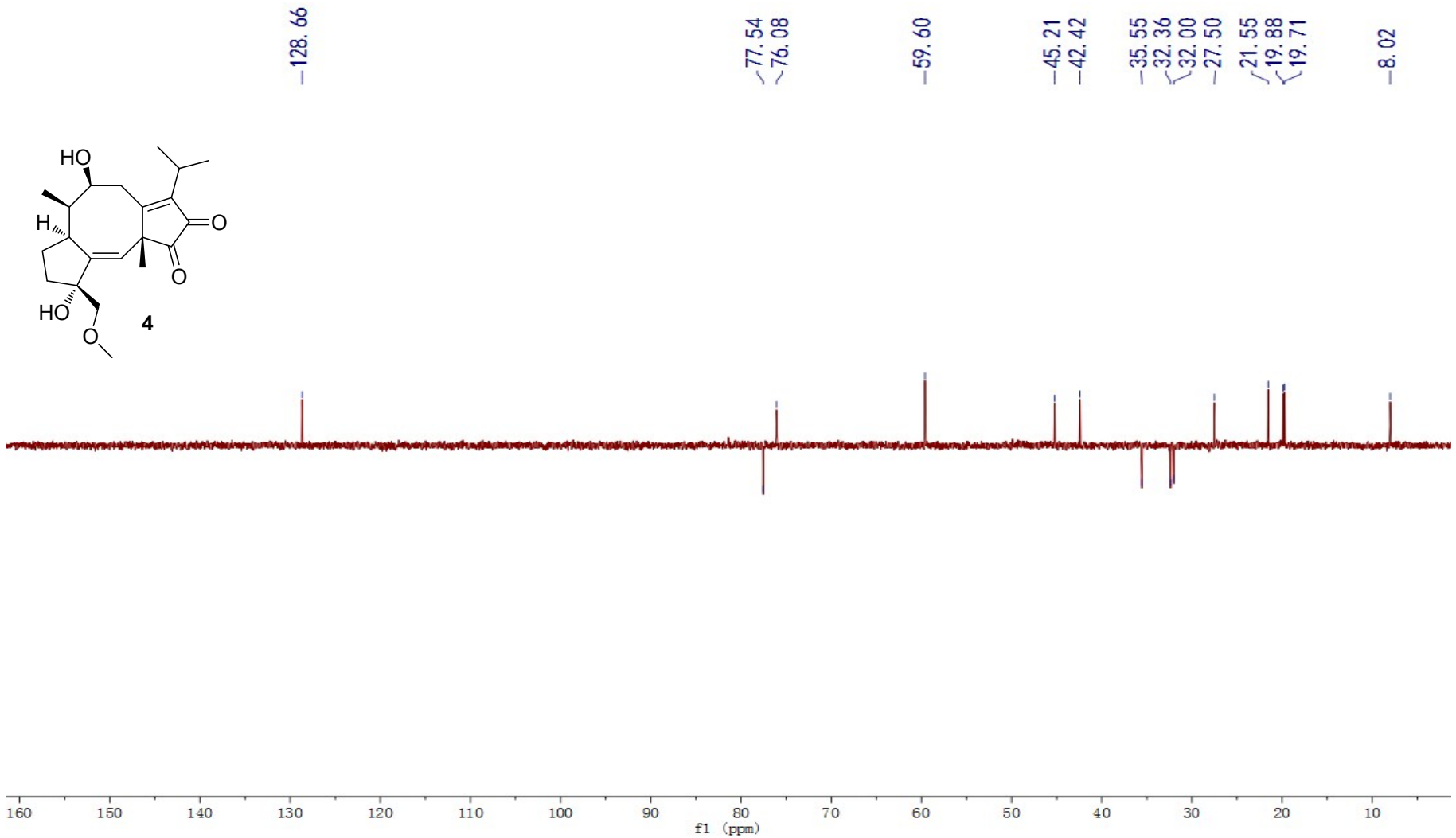


Figure S33. DEPT spectrum of compound **4** (Recorded in methanol-d_4)

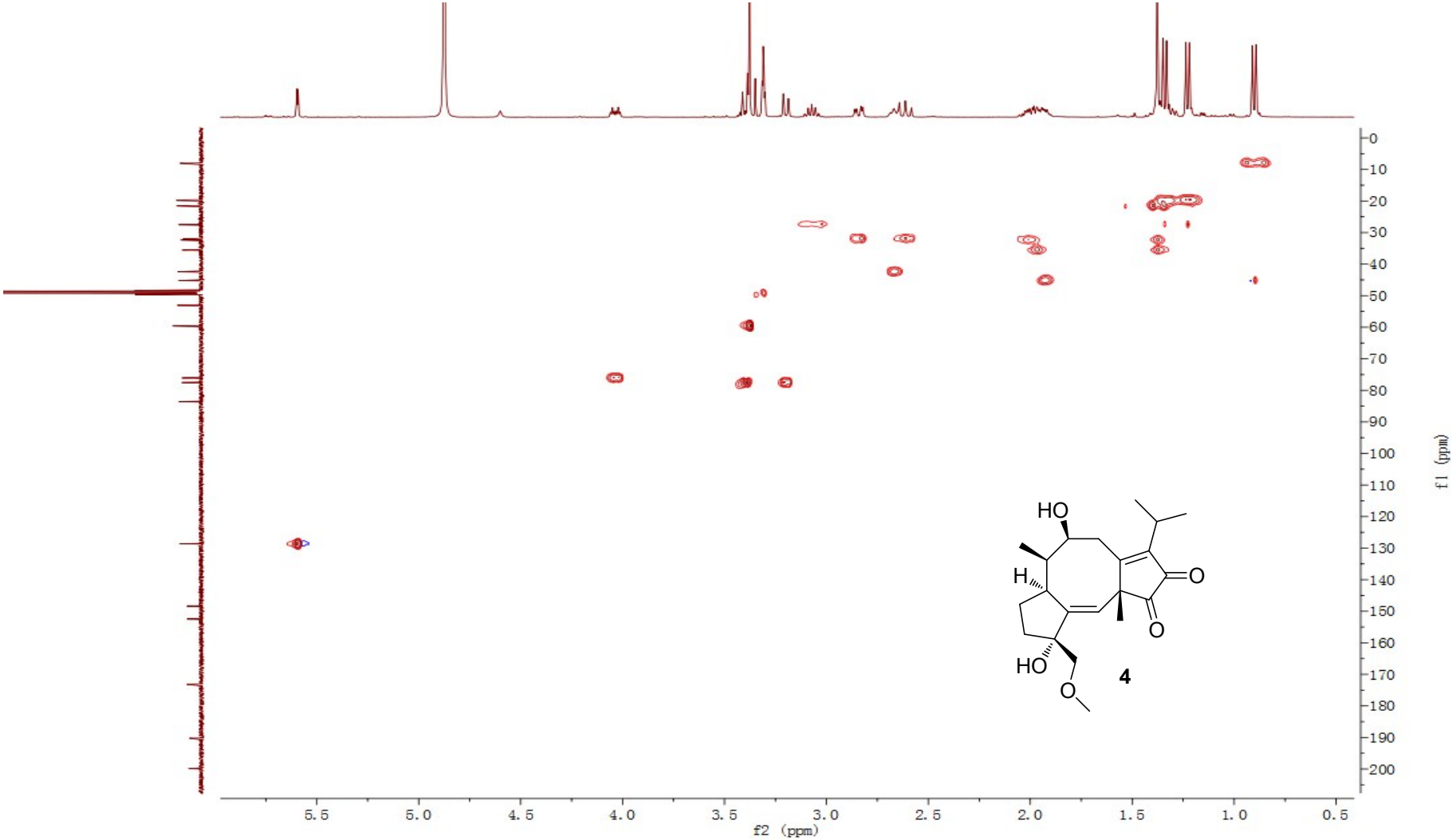


Figure S34. HSQC spectrum of compound **4** (Recorded in methanol-d_4)

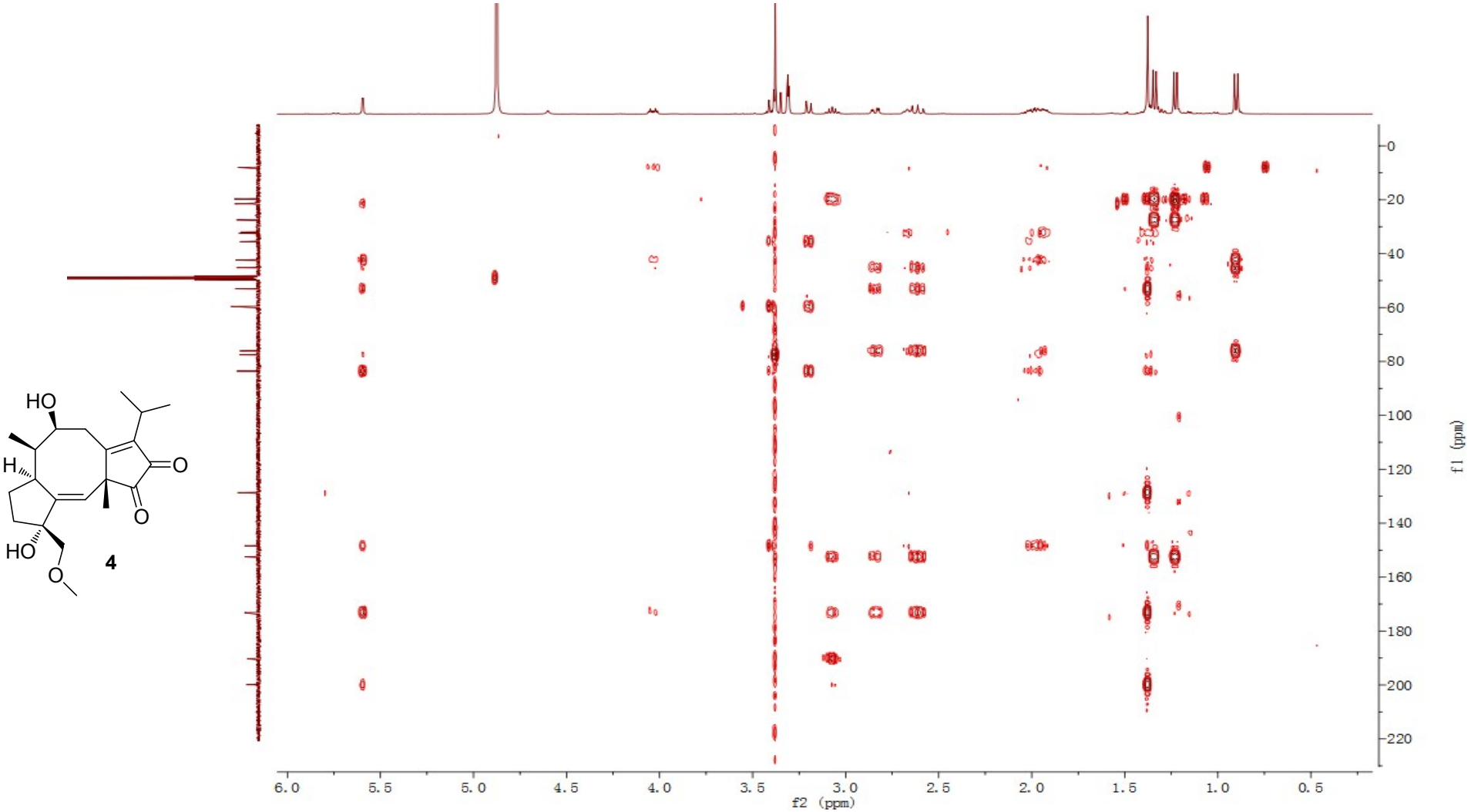


Figure S35. HMBC spectrum of compound **4** (Recorded in methanol-d_4)

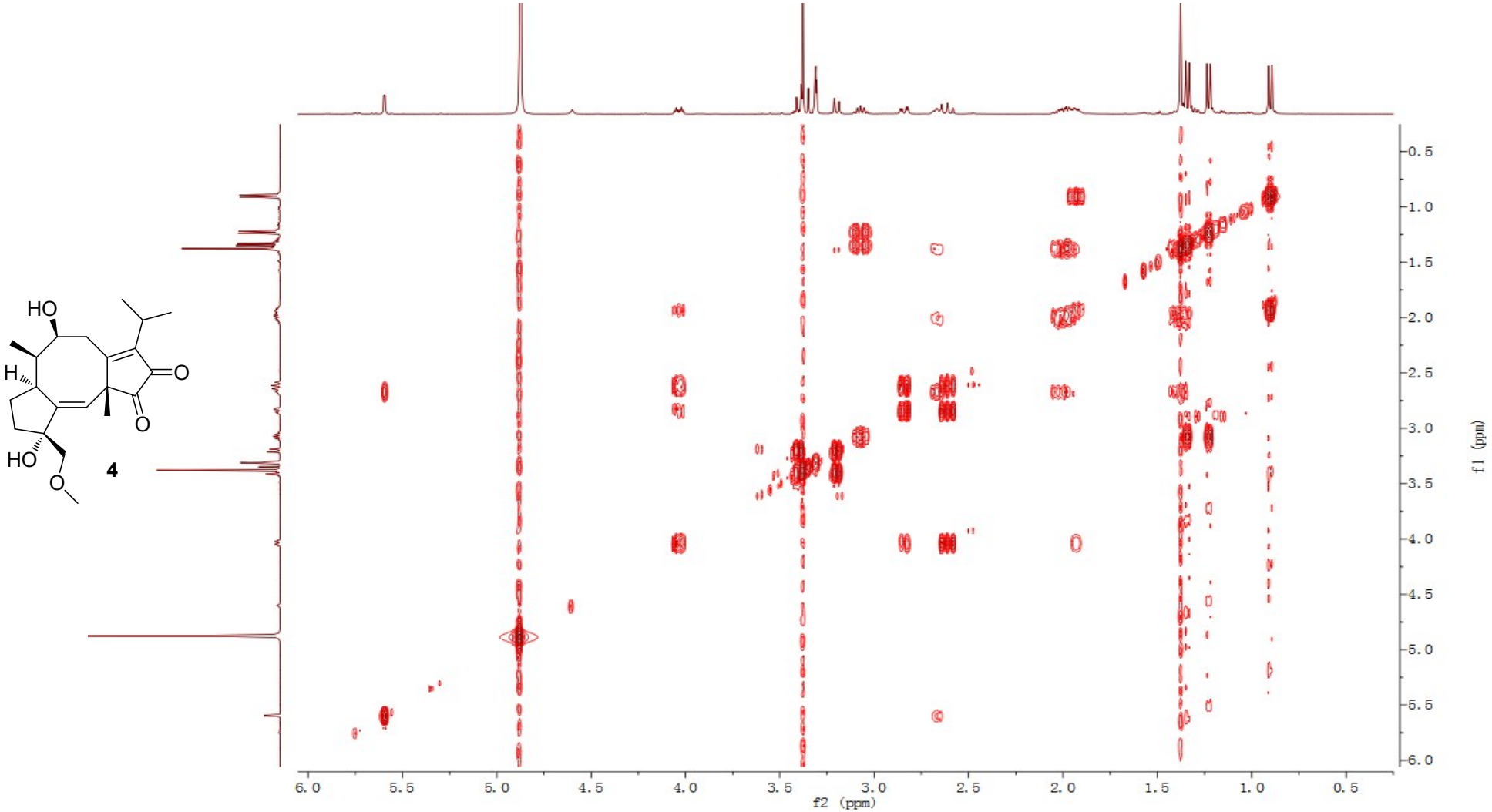


Figure S36. ^{1}H–^{1}H COSY spectrum of compound **4** (Recorded in methanol-d_4)

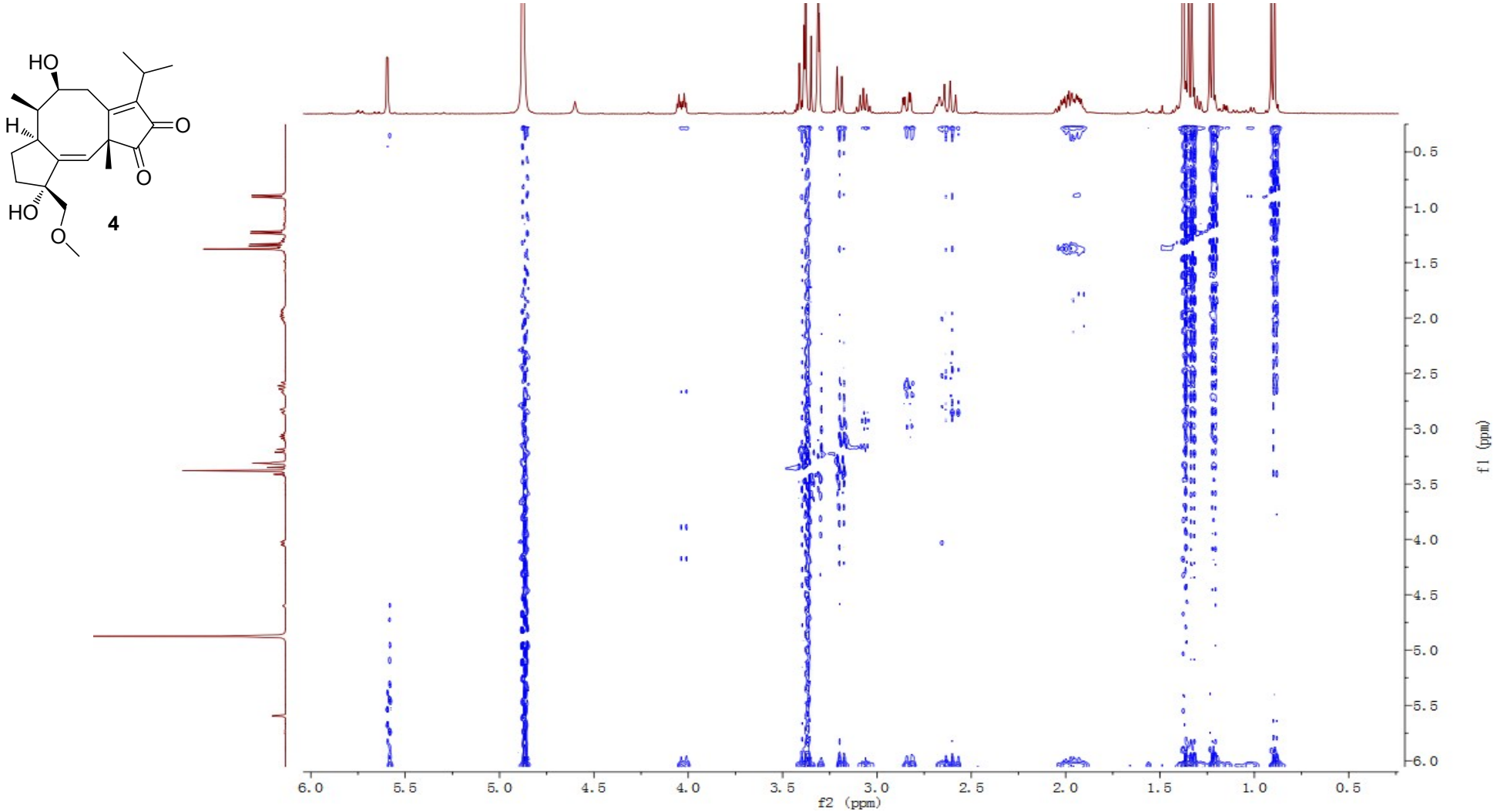


Figure S37. NOESY spectrum of compound **4** (Recorded in methanol-d_4)

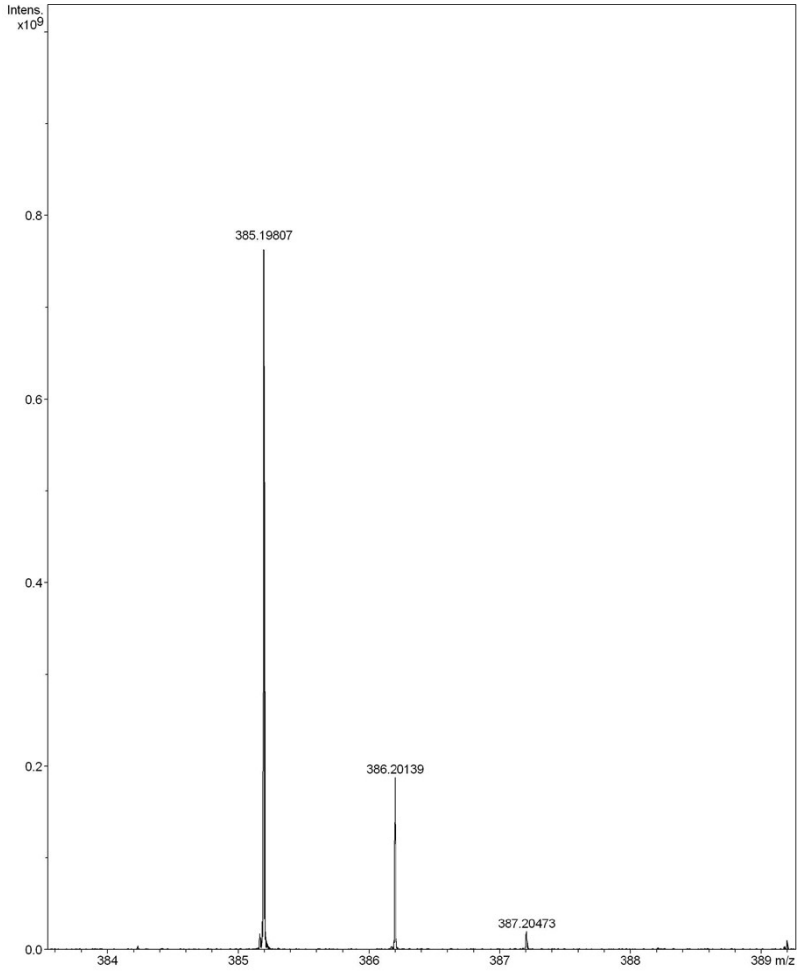
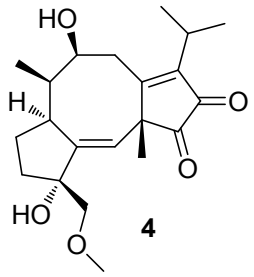


Figure S38. HRESIMS spectrum of compound **4**



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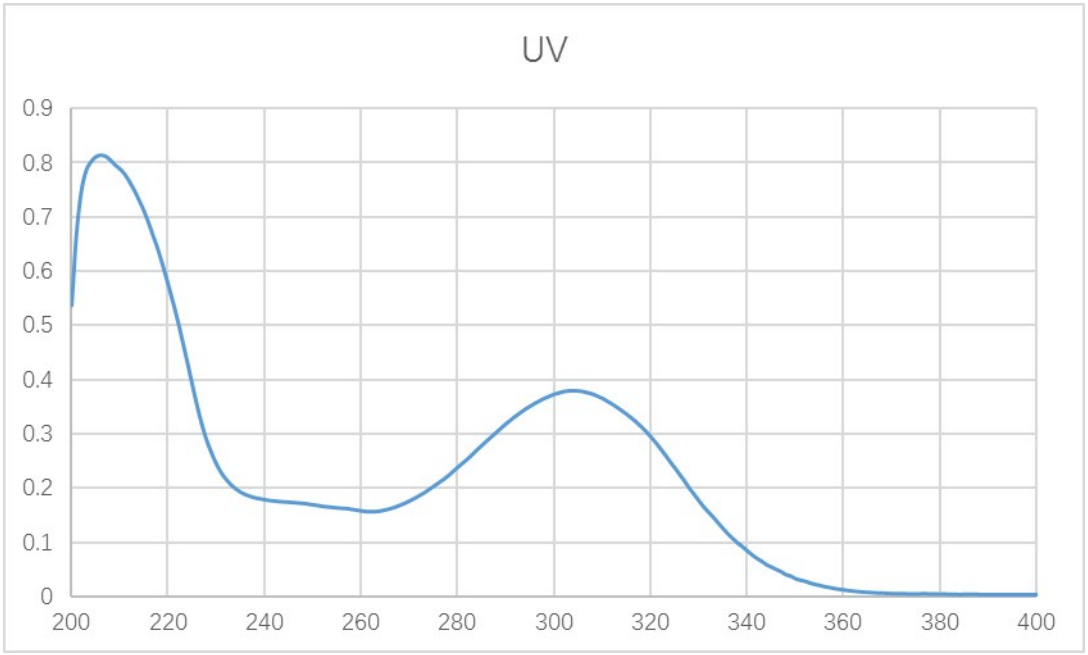


Figure S39. UV spectrum of compound **4**

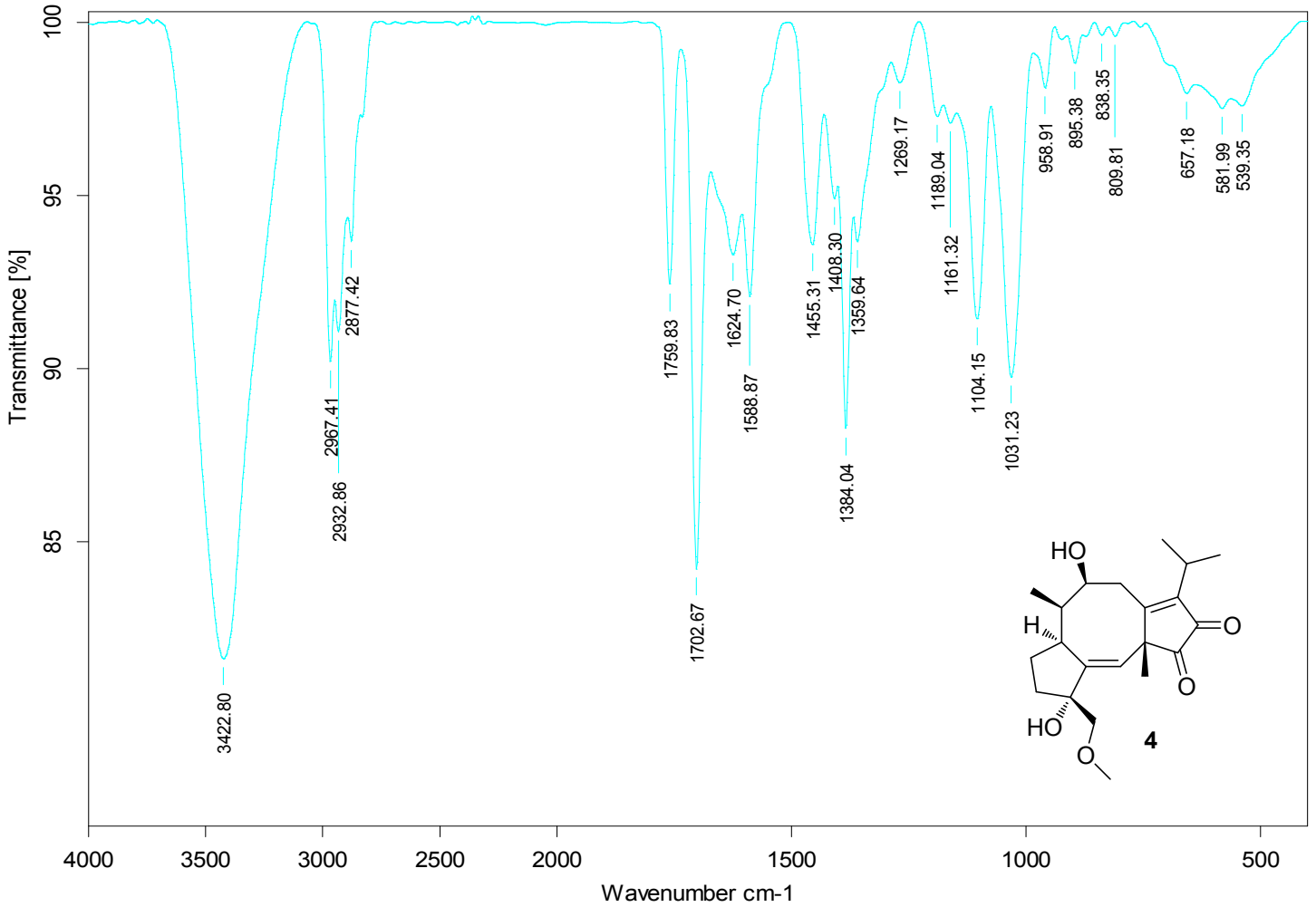


Figure S40. IR spectrum of compound **4**

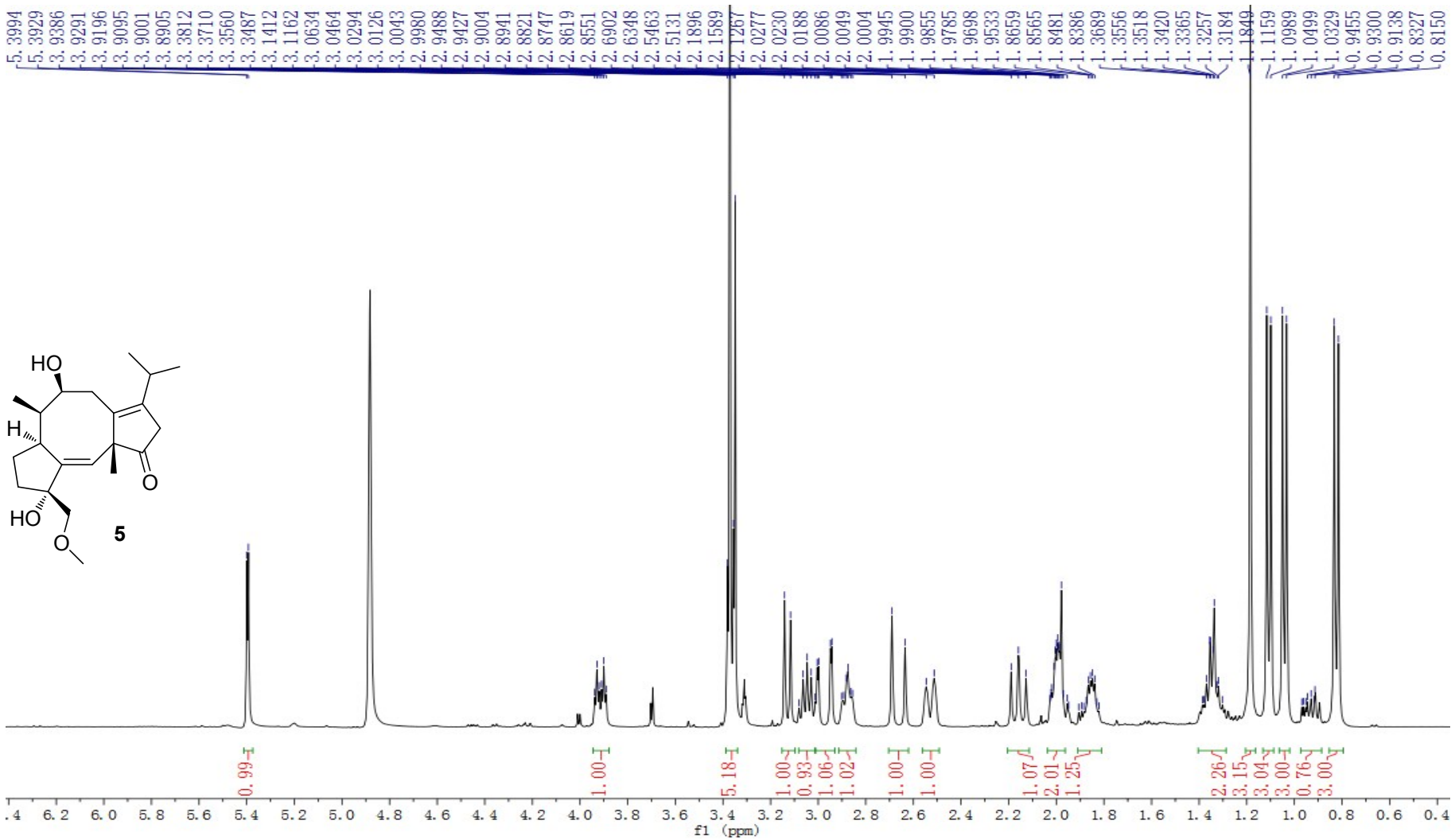


Figure S41. ^{1}H NMR spectrum of compound **5** (Recorded in methanol-d_4)

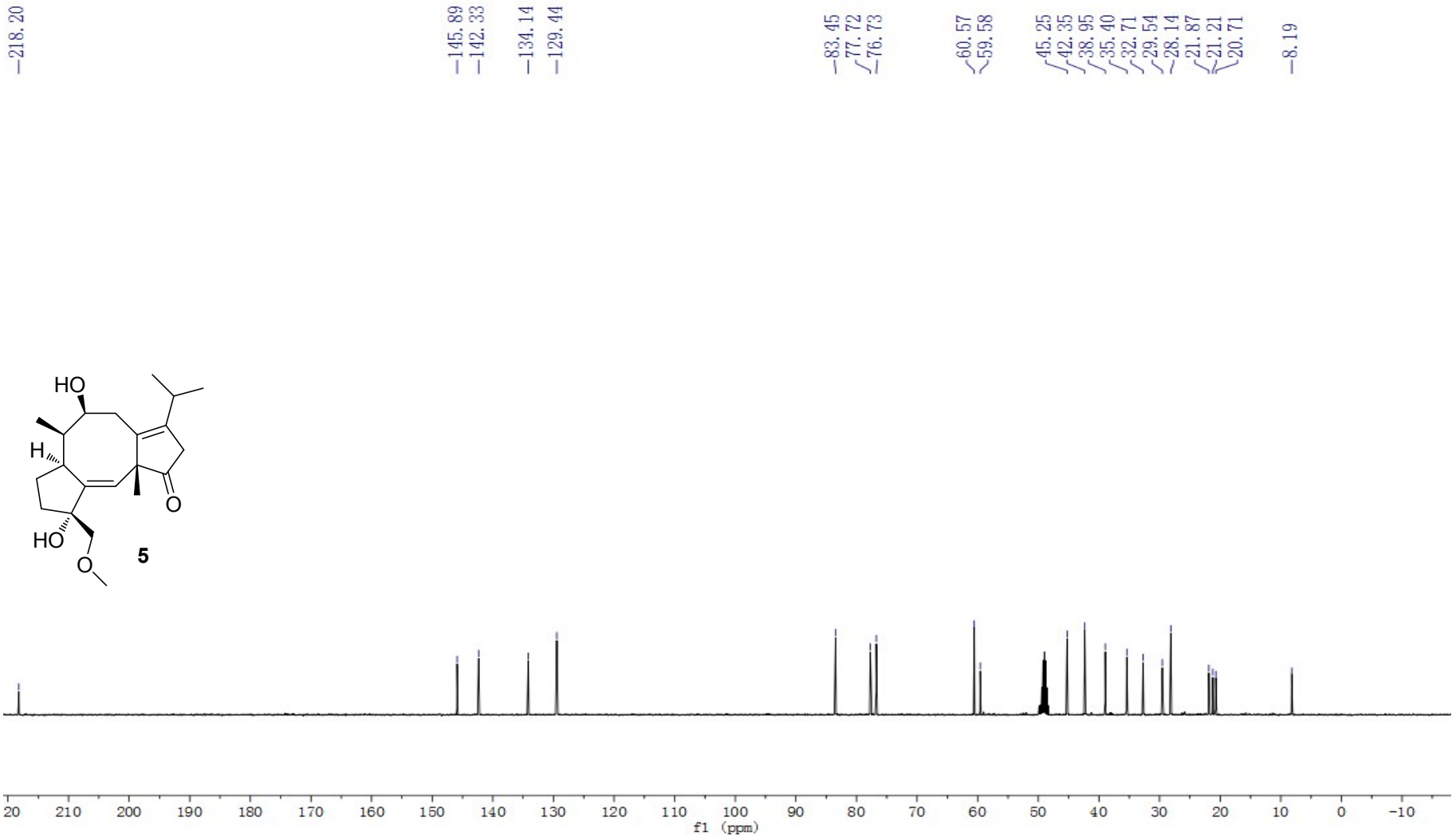


Figure S42. ^{13}C NMR spectrum of compound **5** (Recorded in methanol-d_4)

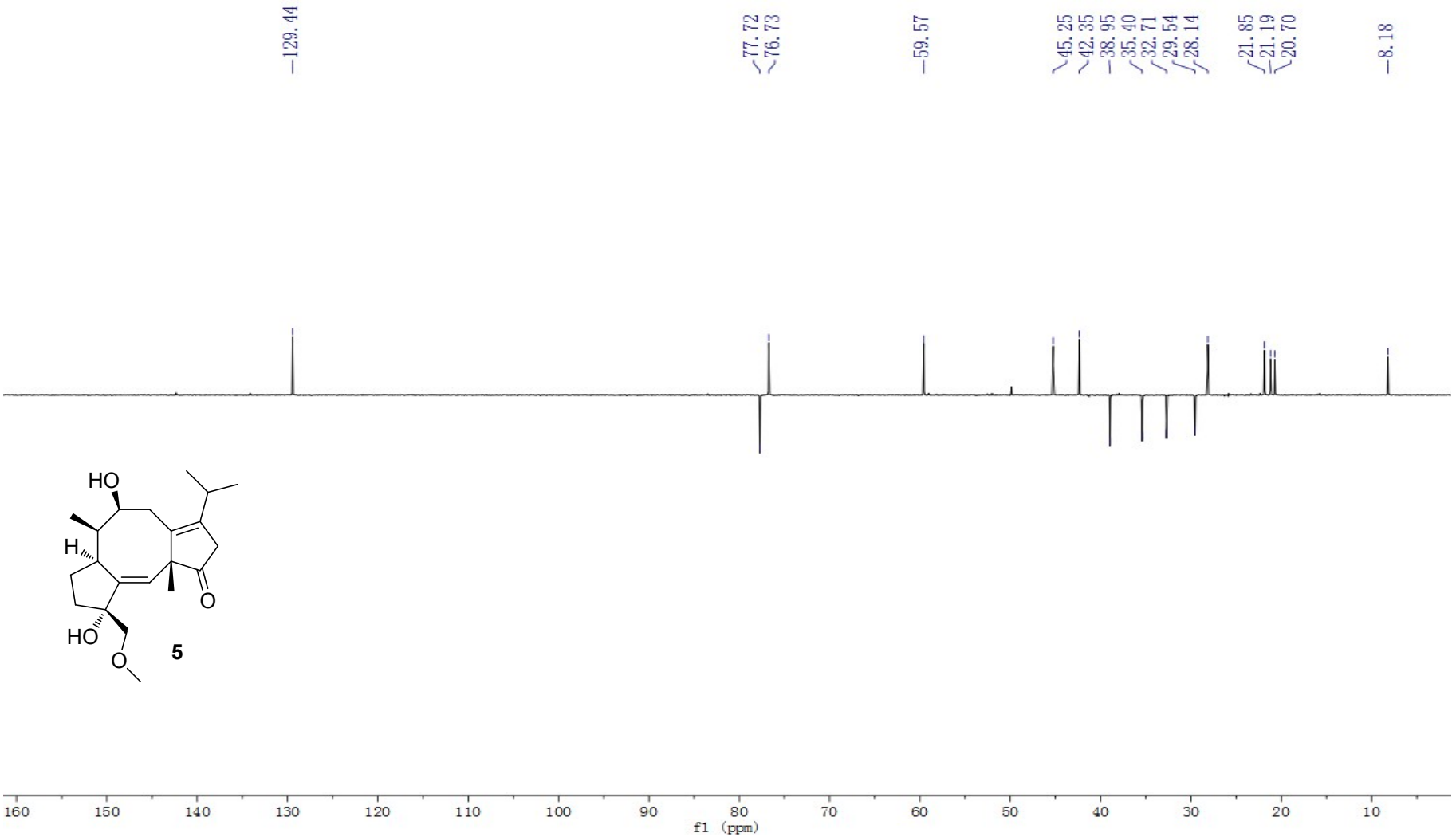


Figure S43. DEPT spectrum of compound **5** (Recorded in methanol-d_4)

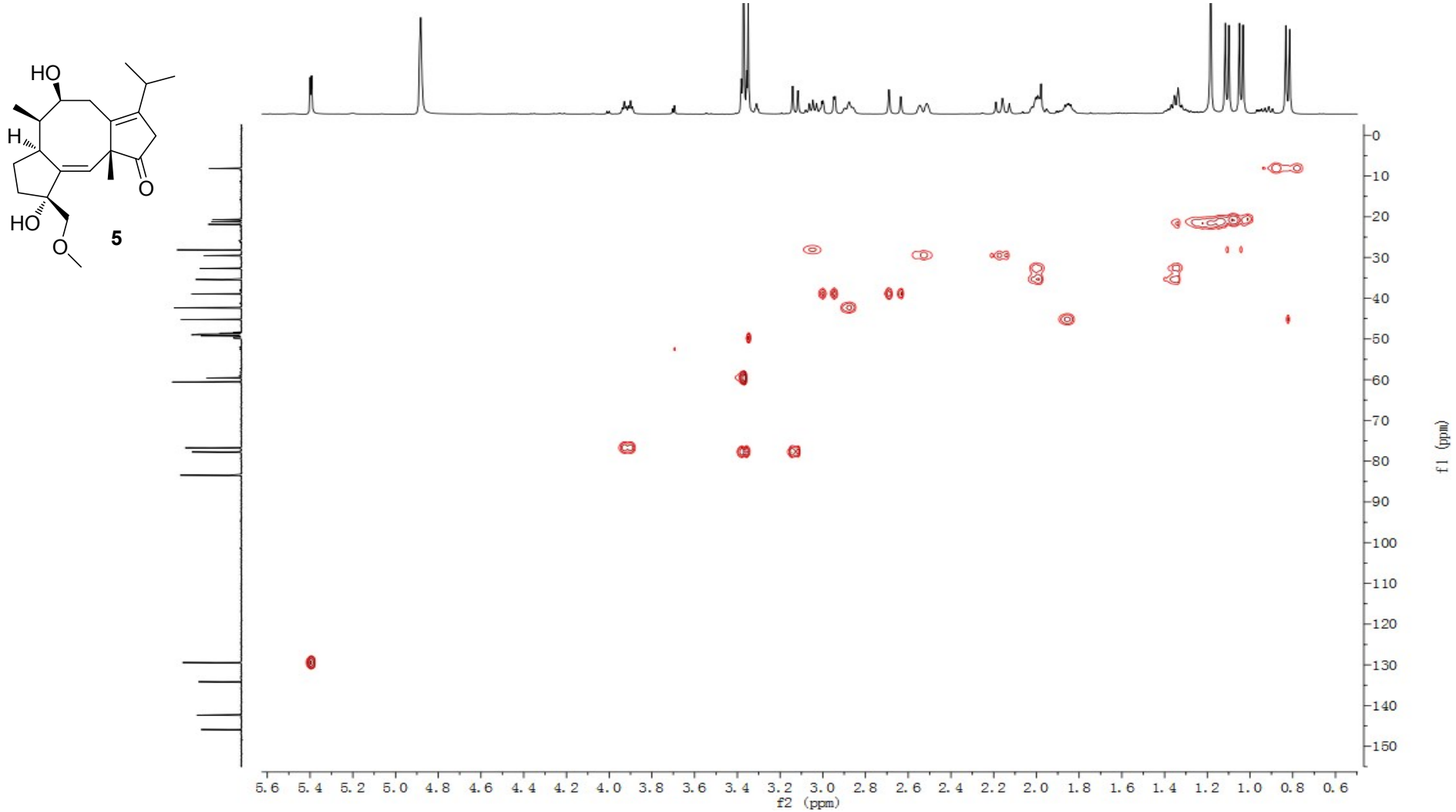


Figure S44. HSQC spectrum of compound **5** (Recorded in methanol-d_4)

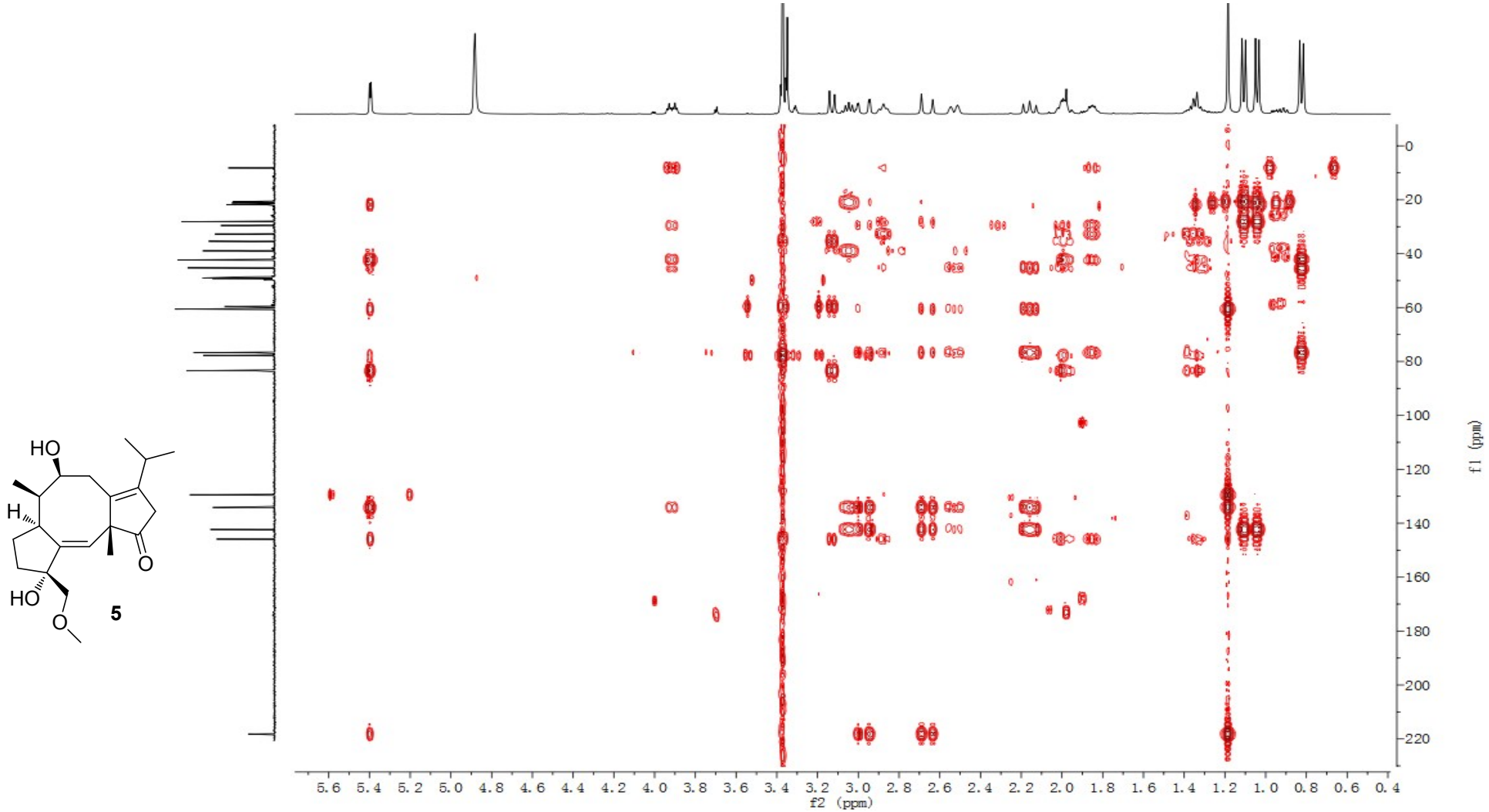


Figure S45. HMBC spectrum of compound **5** (Recorded in methanol-d_4)

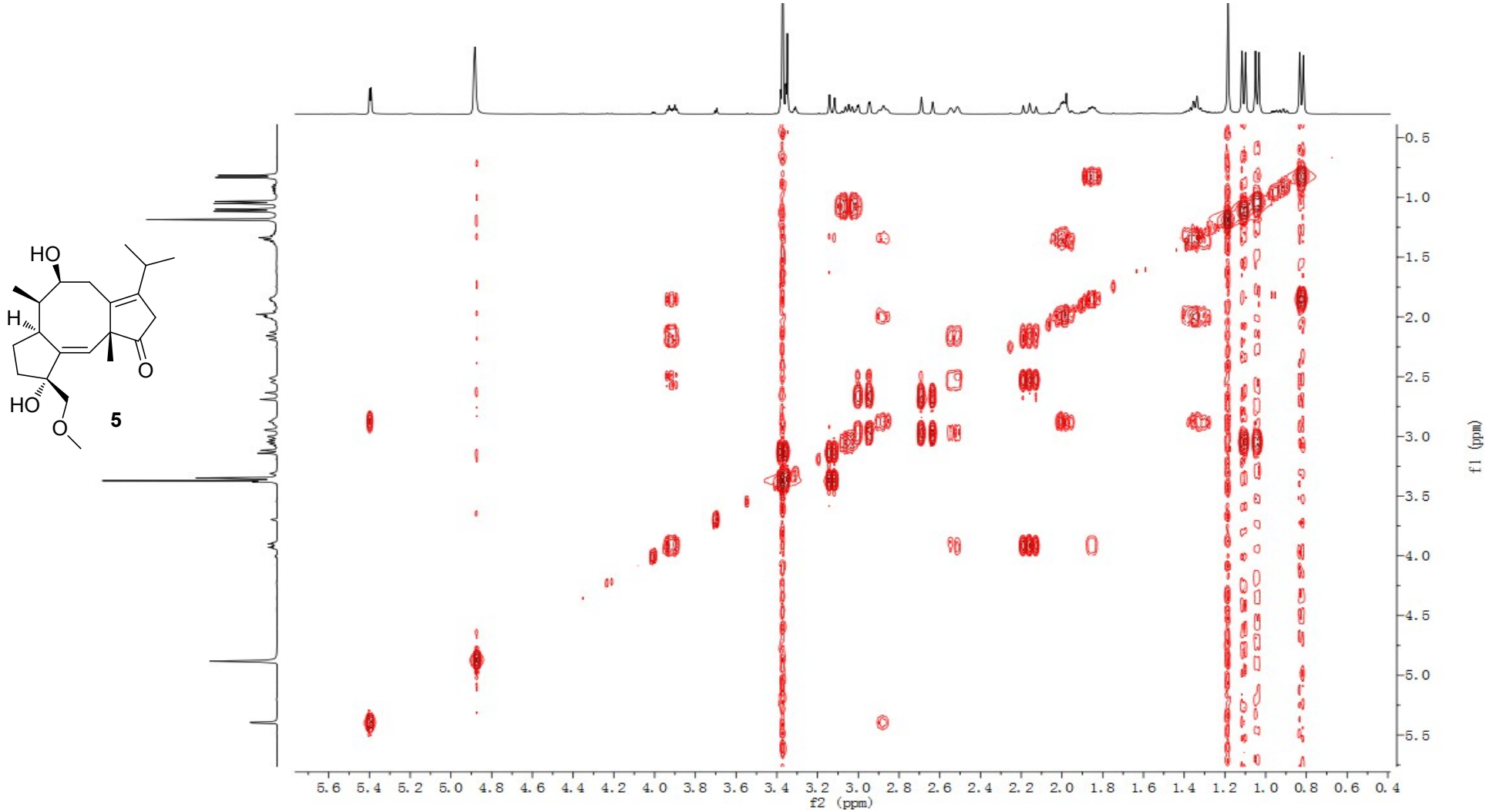


Figure S46. ^{1}H–^{1}H COSY spectrum of compound **5** (Recorded in methanol-d_4)

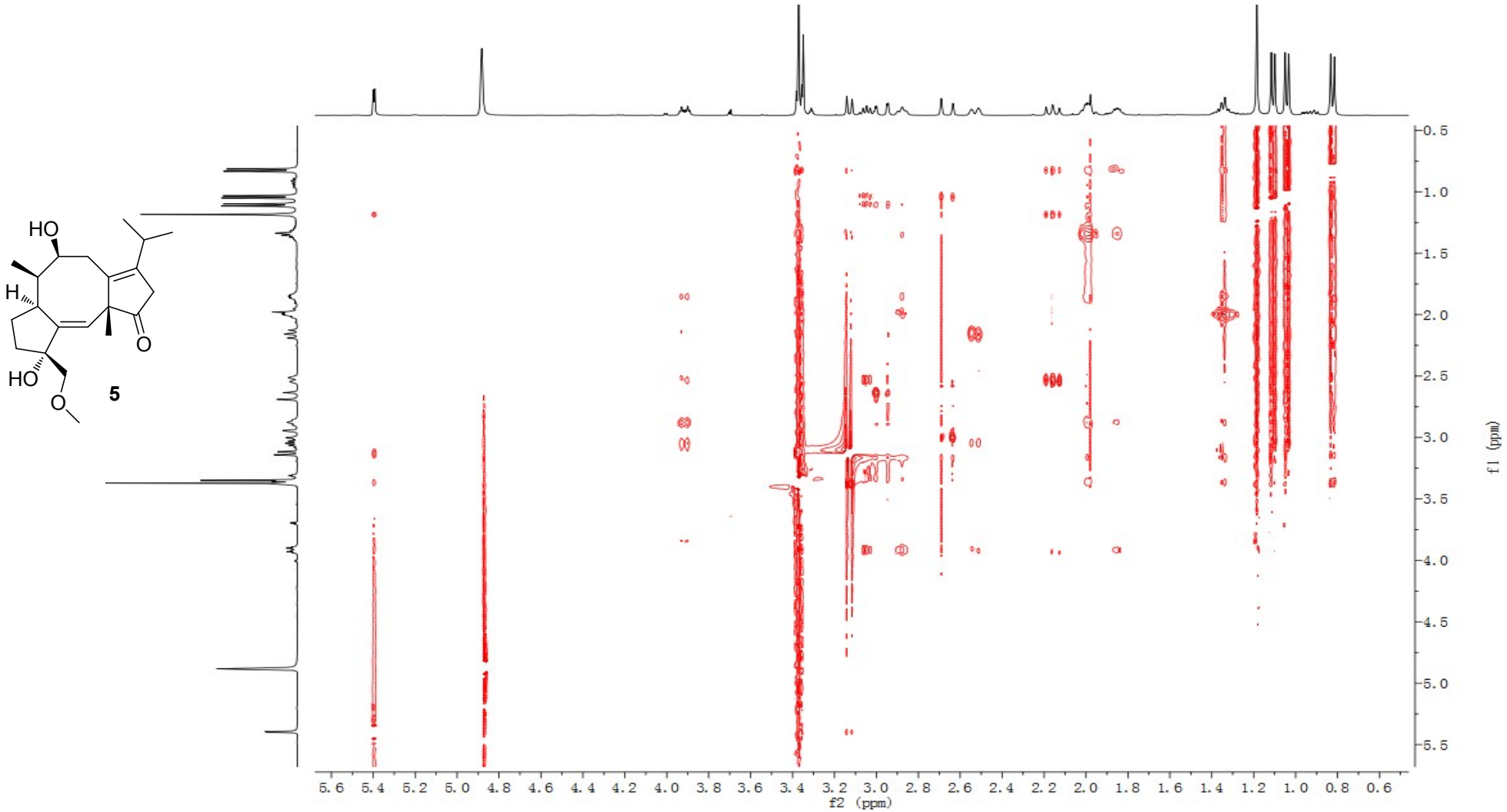


Figure S47. NOESY spectrum of compound **5** (Recorded in methanol-d_4)

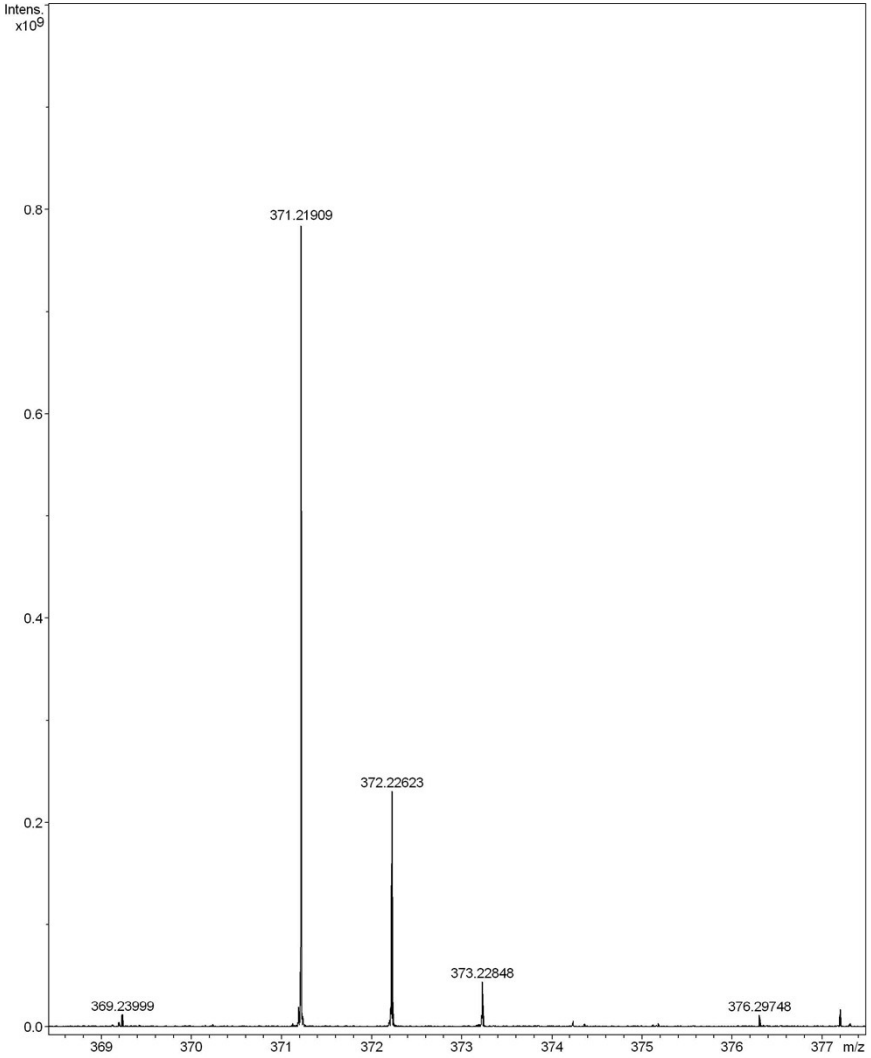
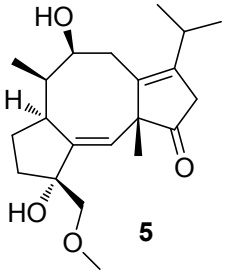


Figure S48. HRESIMS spectrum of compound **5**



5

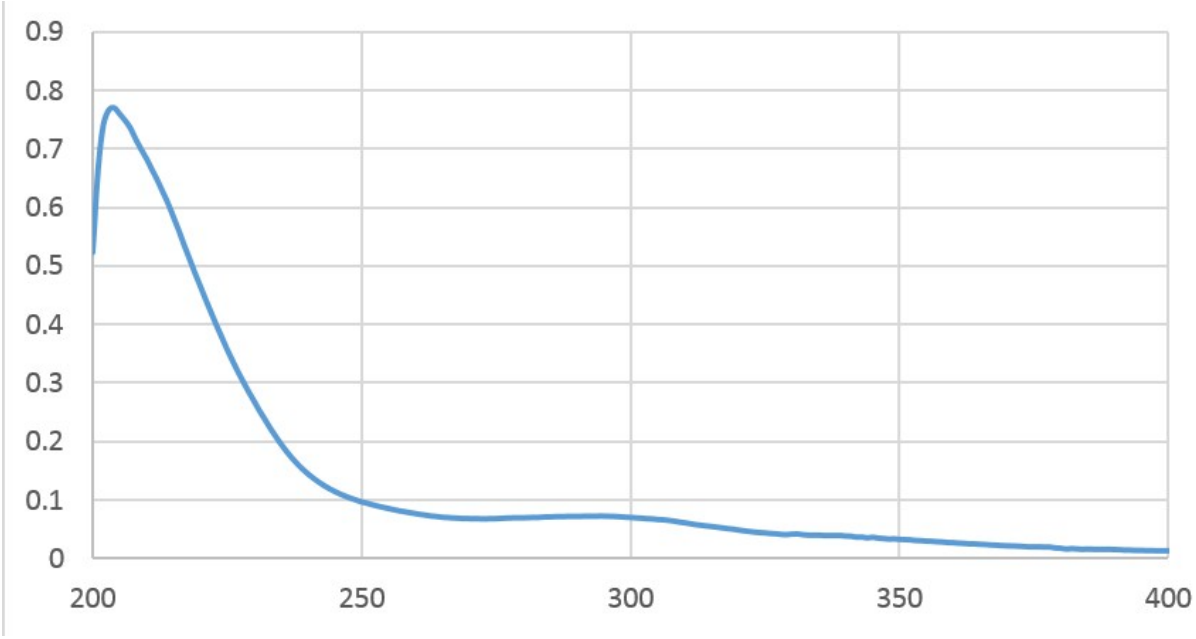


Figure S49. UV spectrum of compound **5**

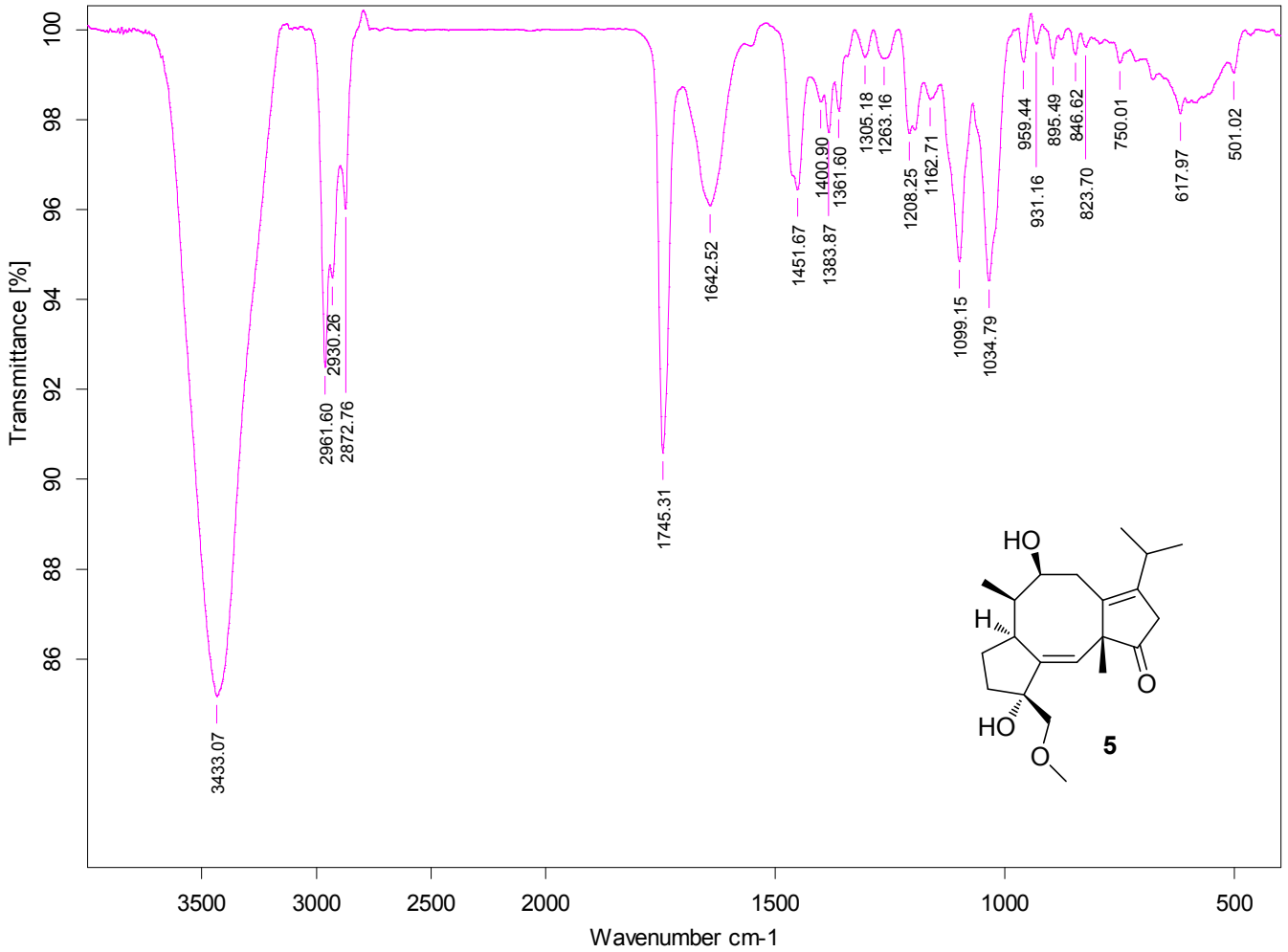


Figure S50. IR spectrum of compound **5**

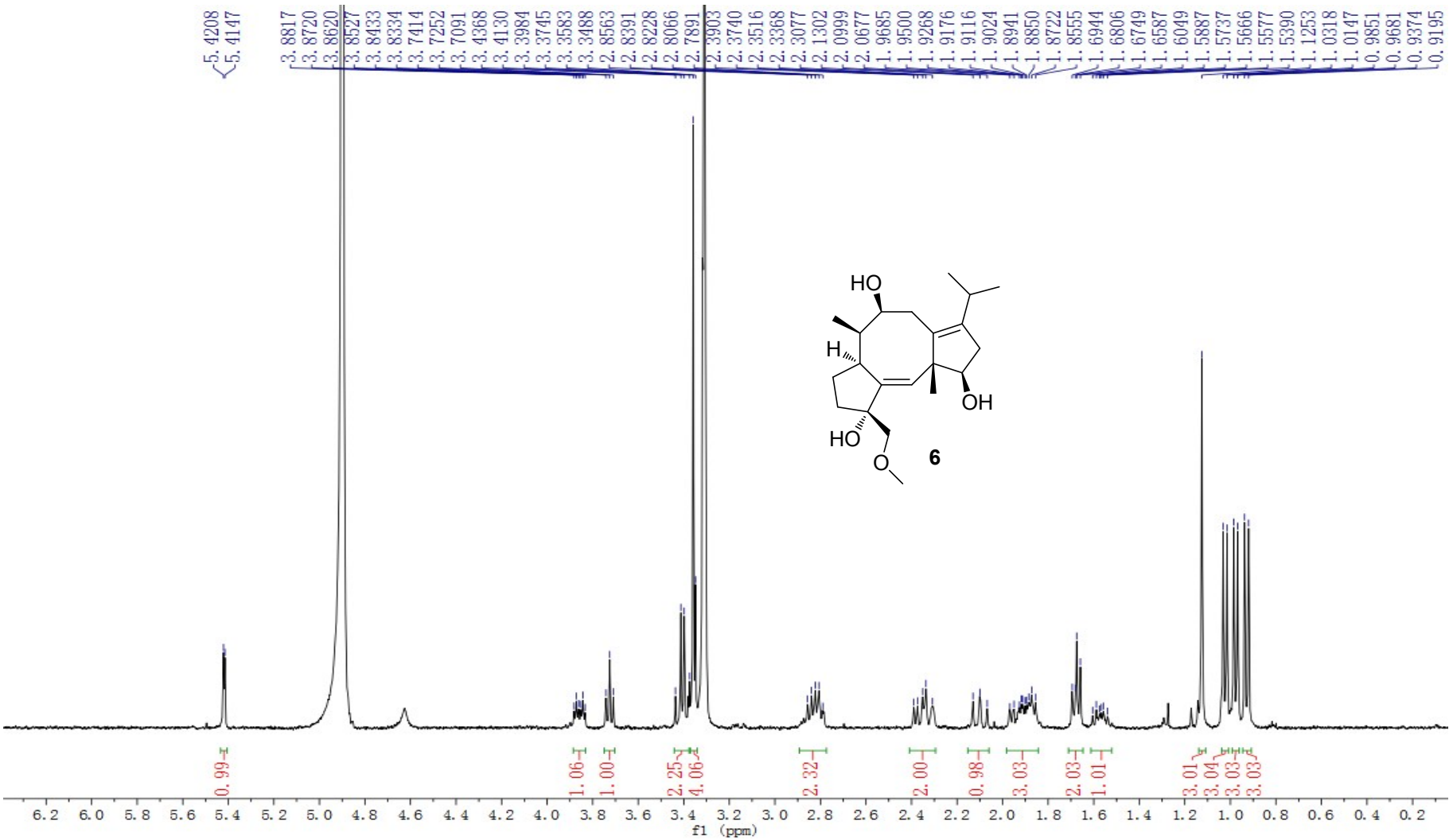


Figure S51. ^{1}H NMR spectrum of compound **6** (Recorded in methanol-d_4)

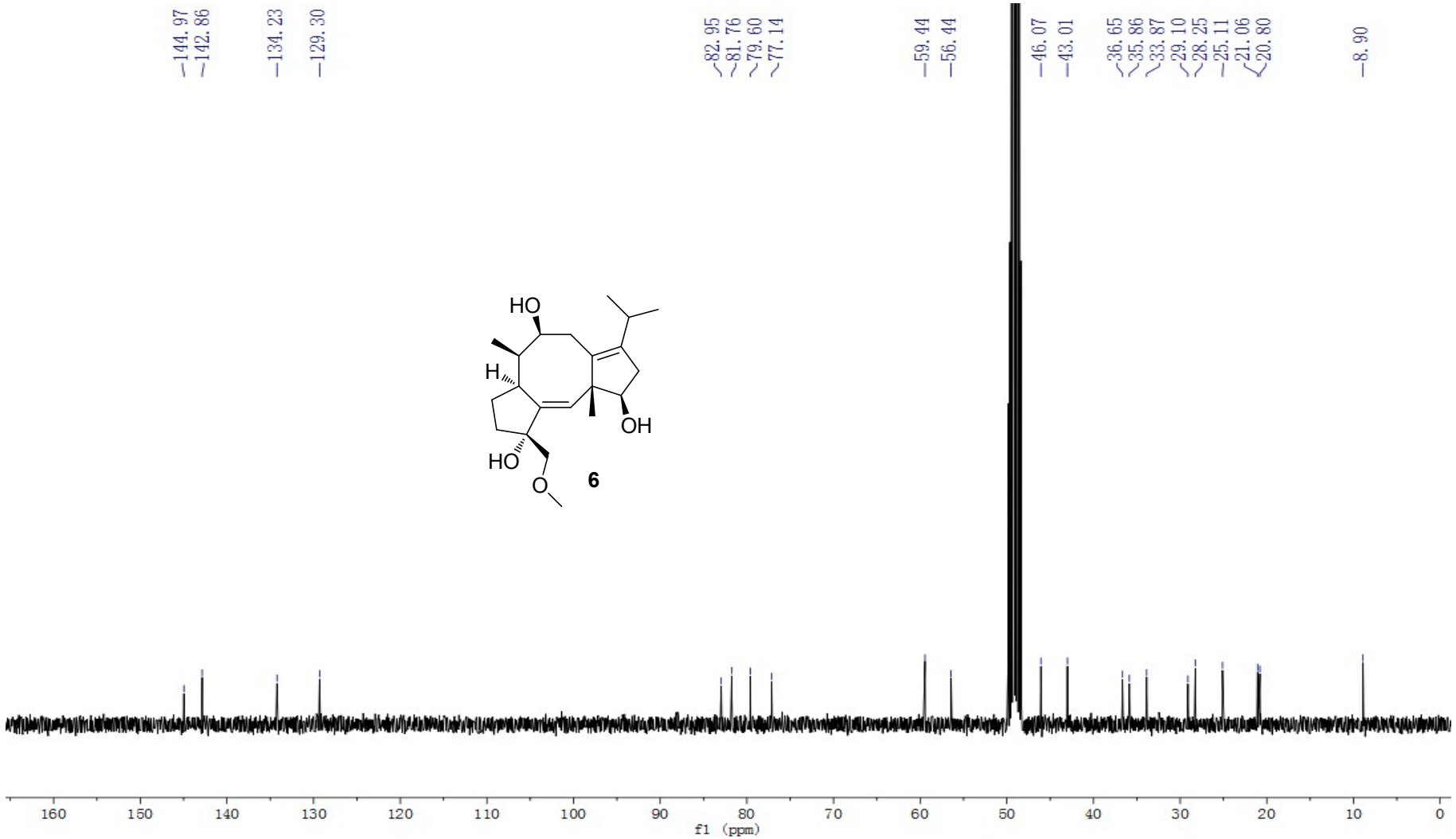


Figure S52. ^{13}C NMR spectrum of compound **6** (Recorded in methanol-d_4)

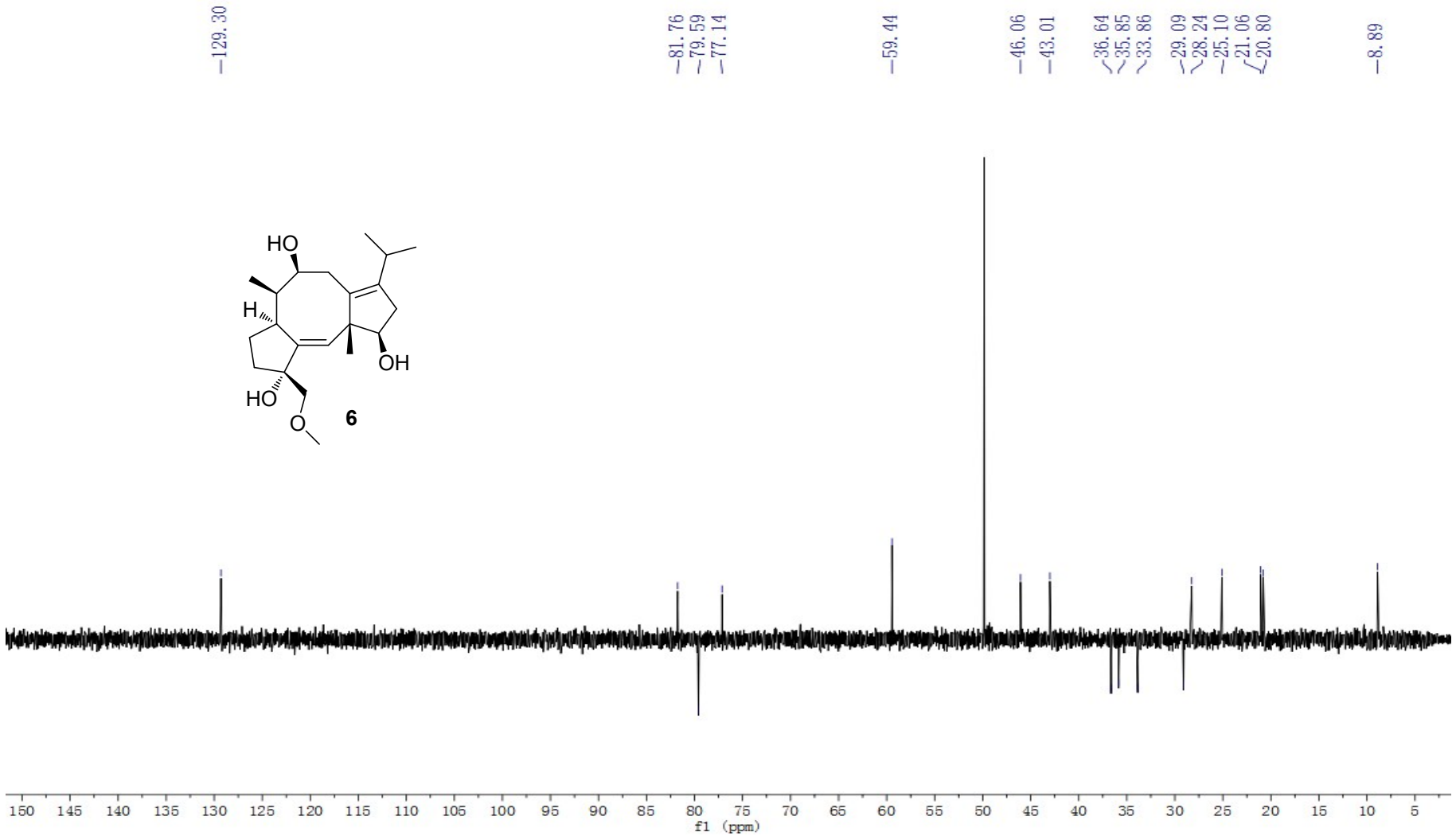


Figure S53. DEPT spectrum of compound **6** (Recorded in methanol-d_4)

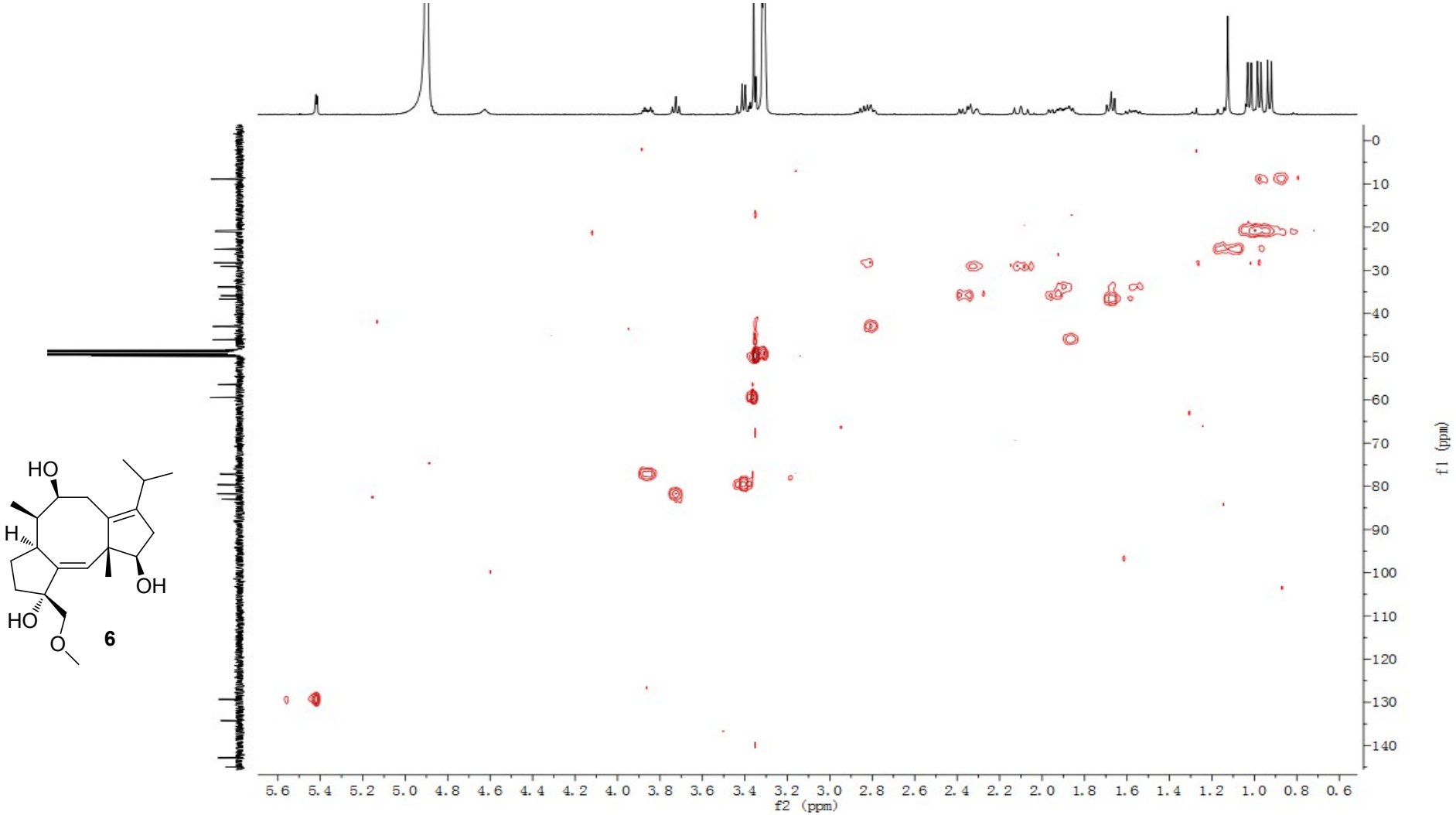


Figure S54. HSQC spectrum of compound **6** (Recorded in methanol-d_4)

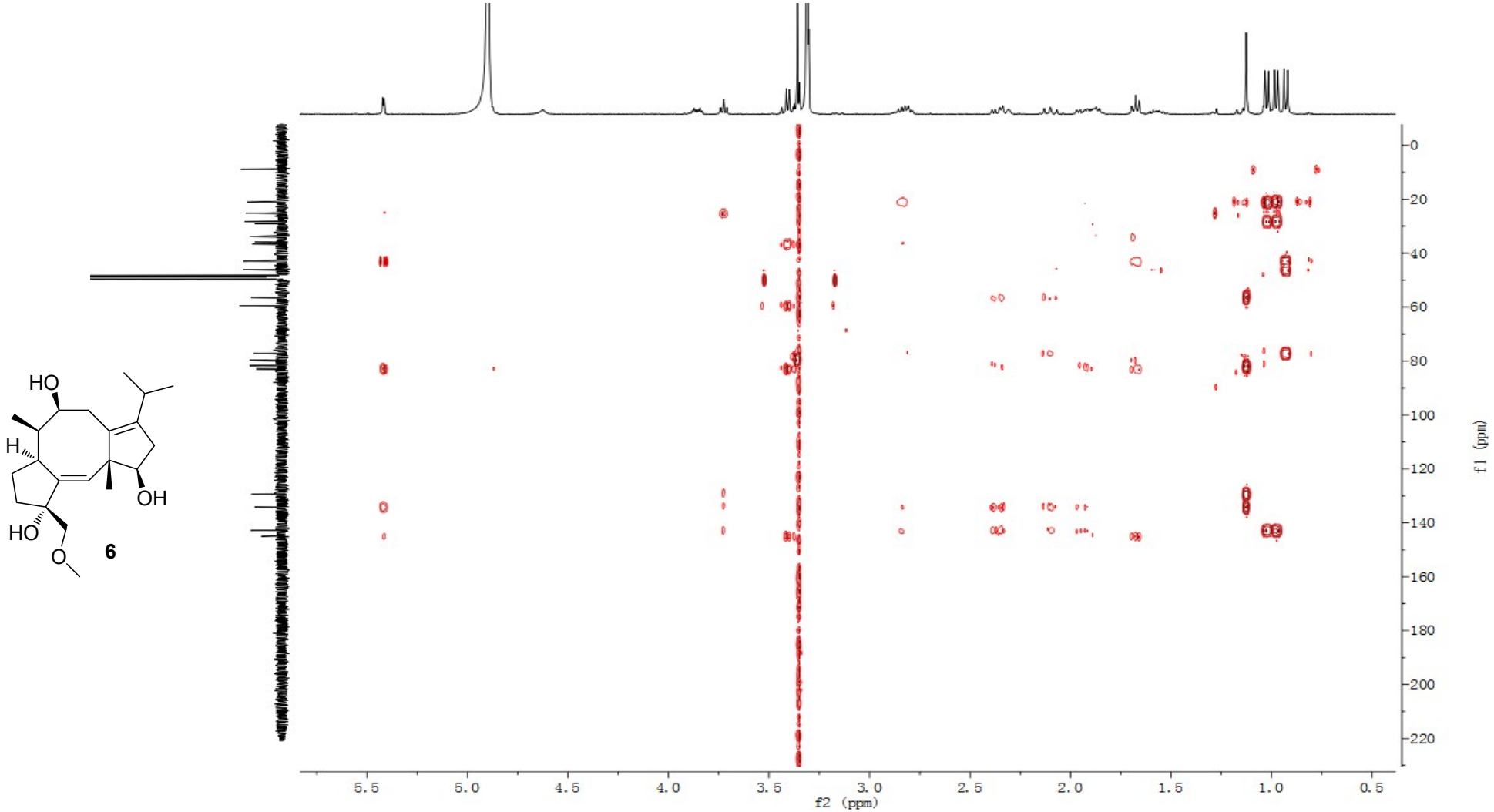


Figure S55. HMBC spectrum of compound **6** (Recorded in methanol-d_4)

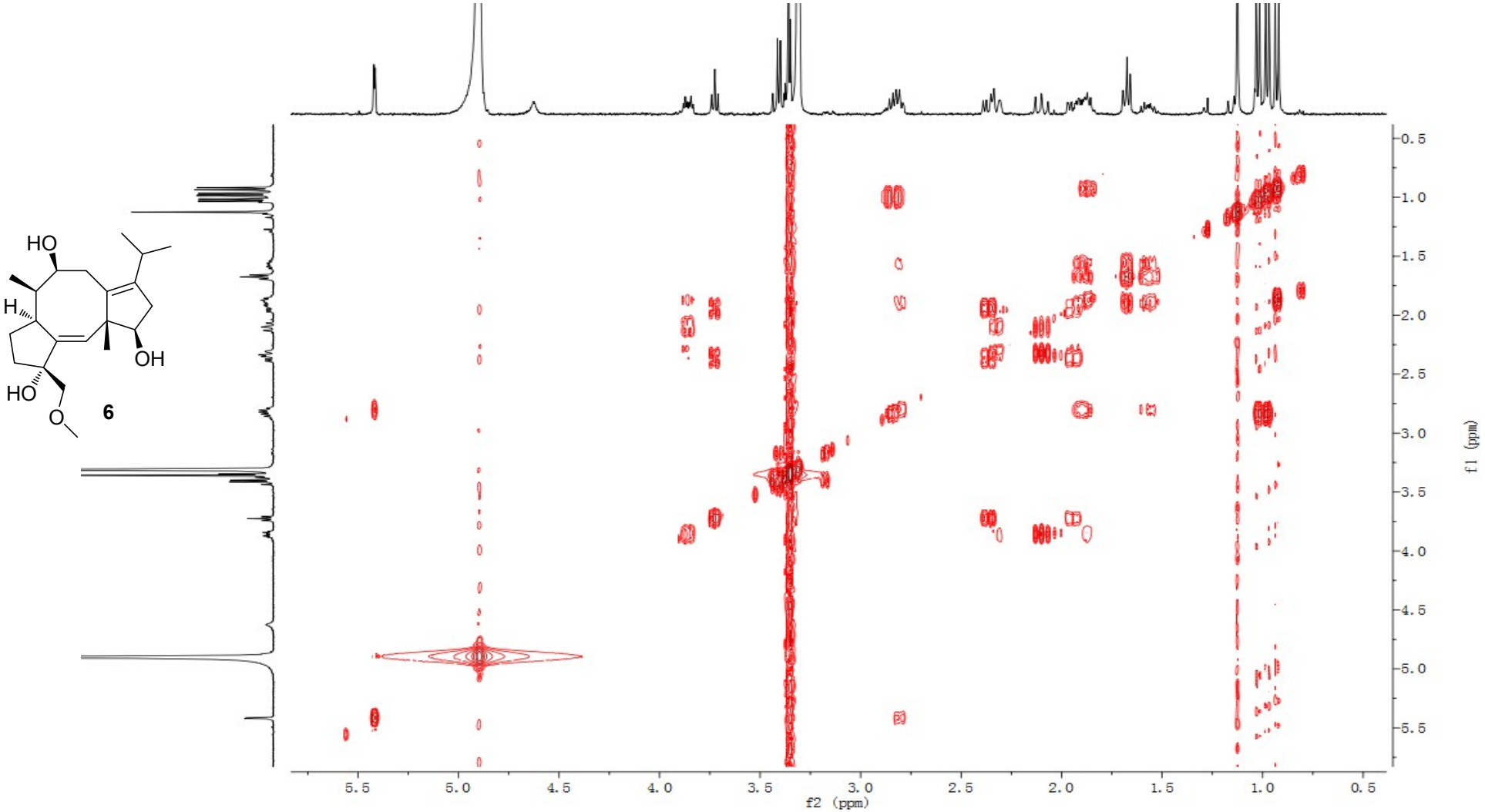


Figure S56. ^{1}H–^{1}H COSY spectrum of compound **6** (Recorded in methanol-d_4)

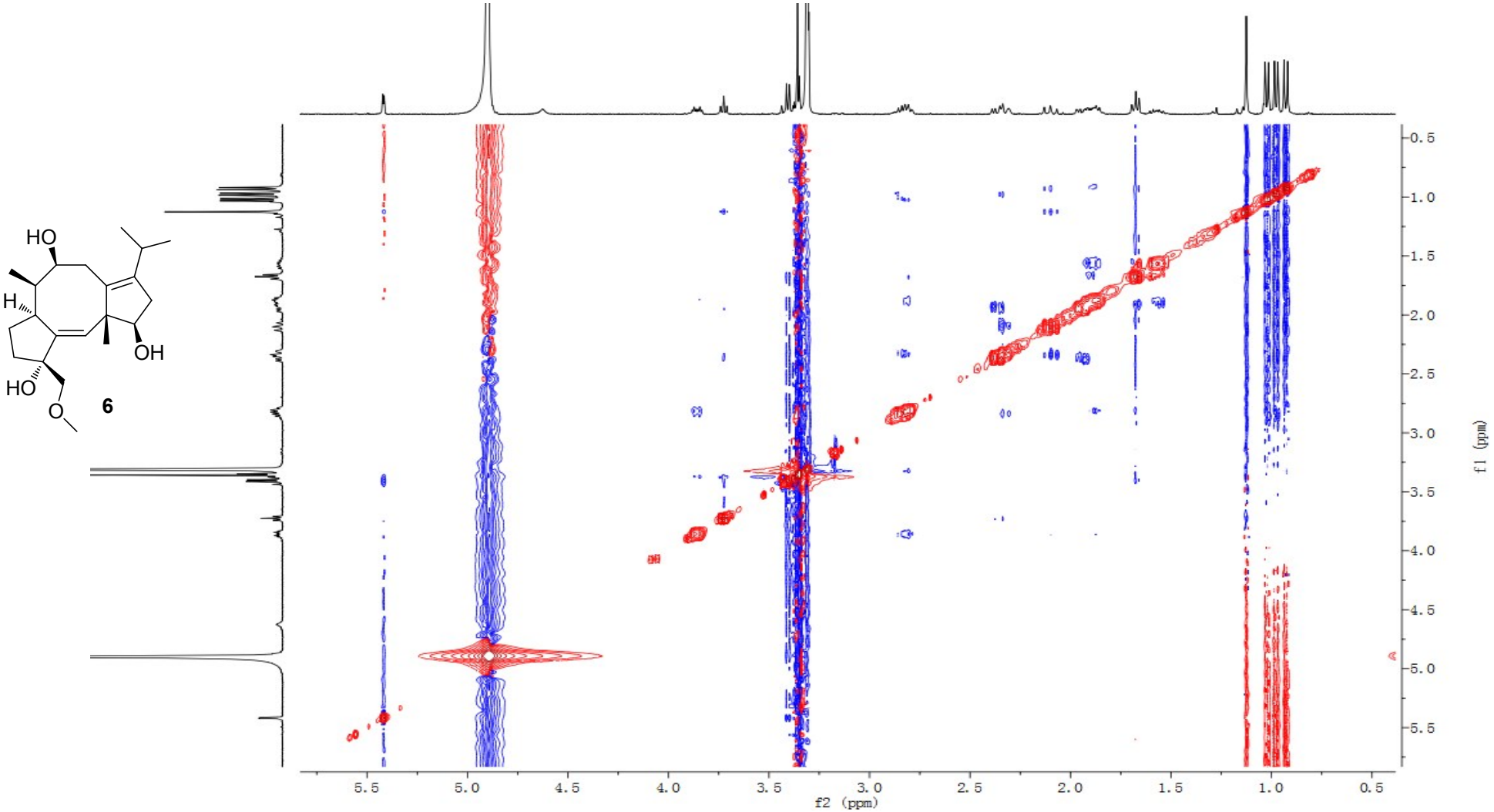


Figure S57. NOESY spectrum of compound **6** (Recorded in methanol-d_4)

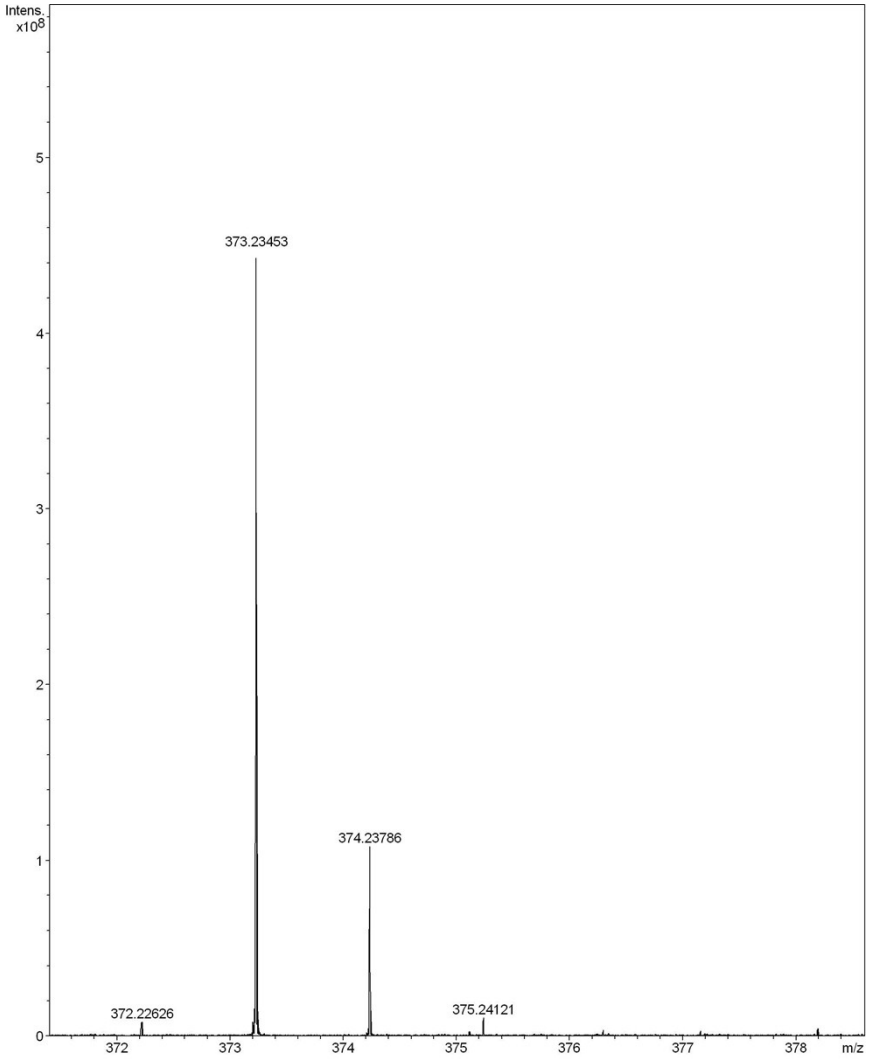
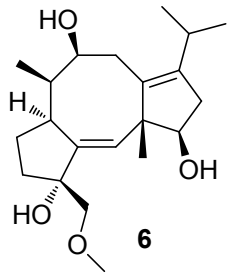


Figure S58. HRESIMS spectrum of compound **6**



6

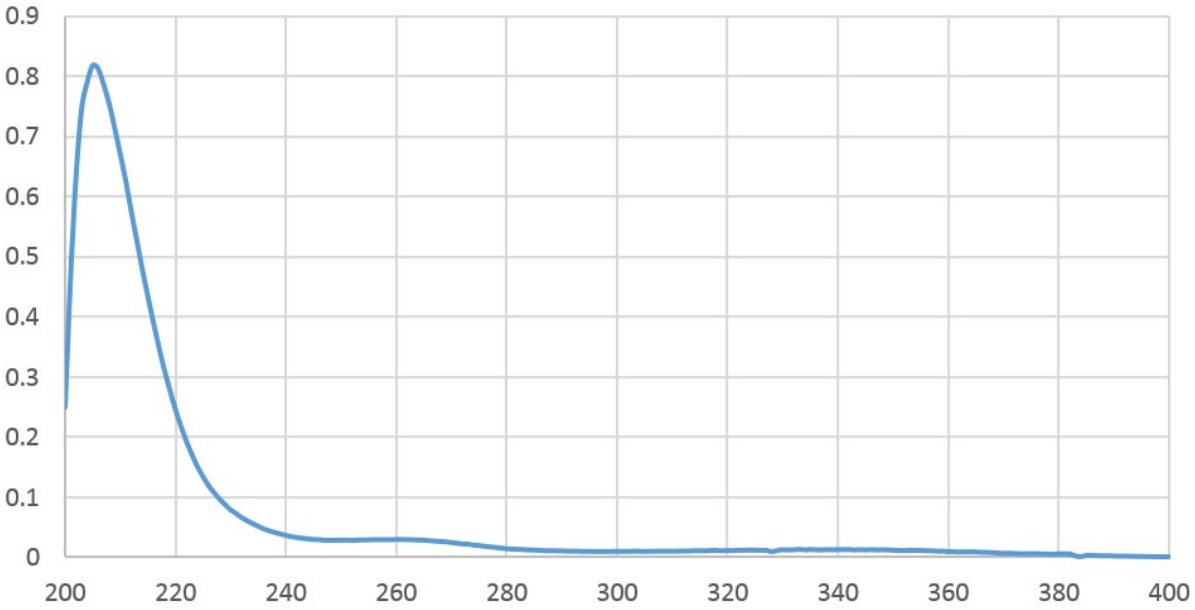
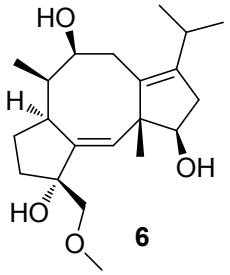


Figure S59. UV spectrum of compound **6**



6

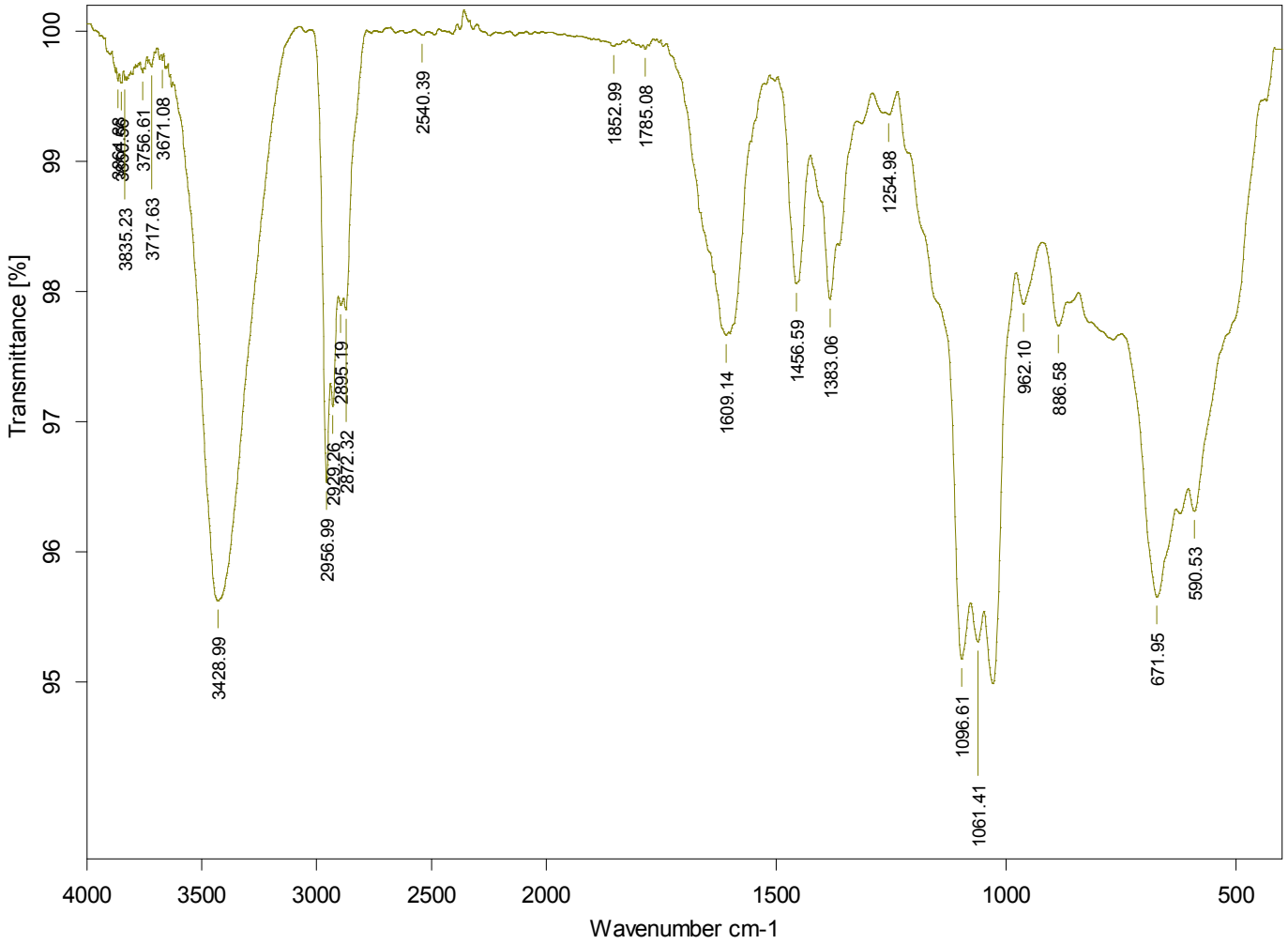


Figure S60. IR spectrum of compound **6**

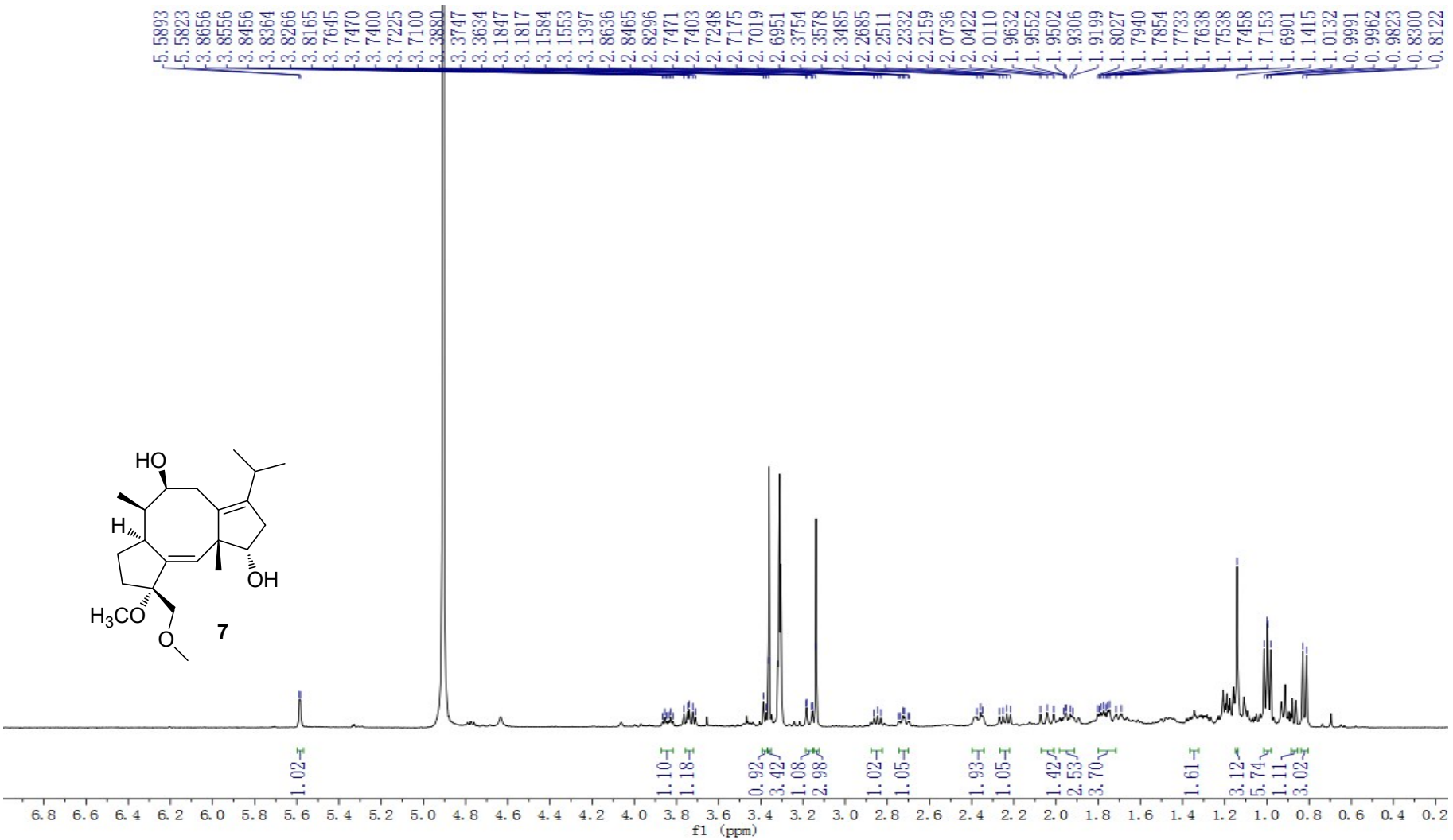


Figure S61. ^{1}H NMR spectrum of compound **7** (Recorded in methanol-d_4)

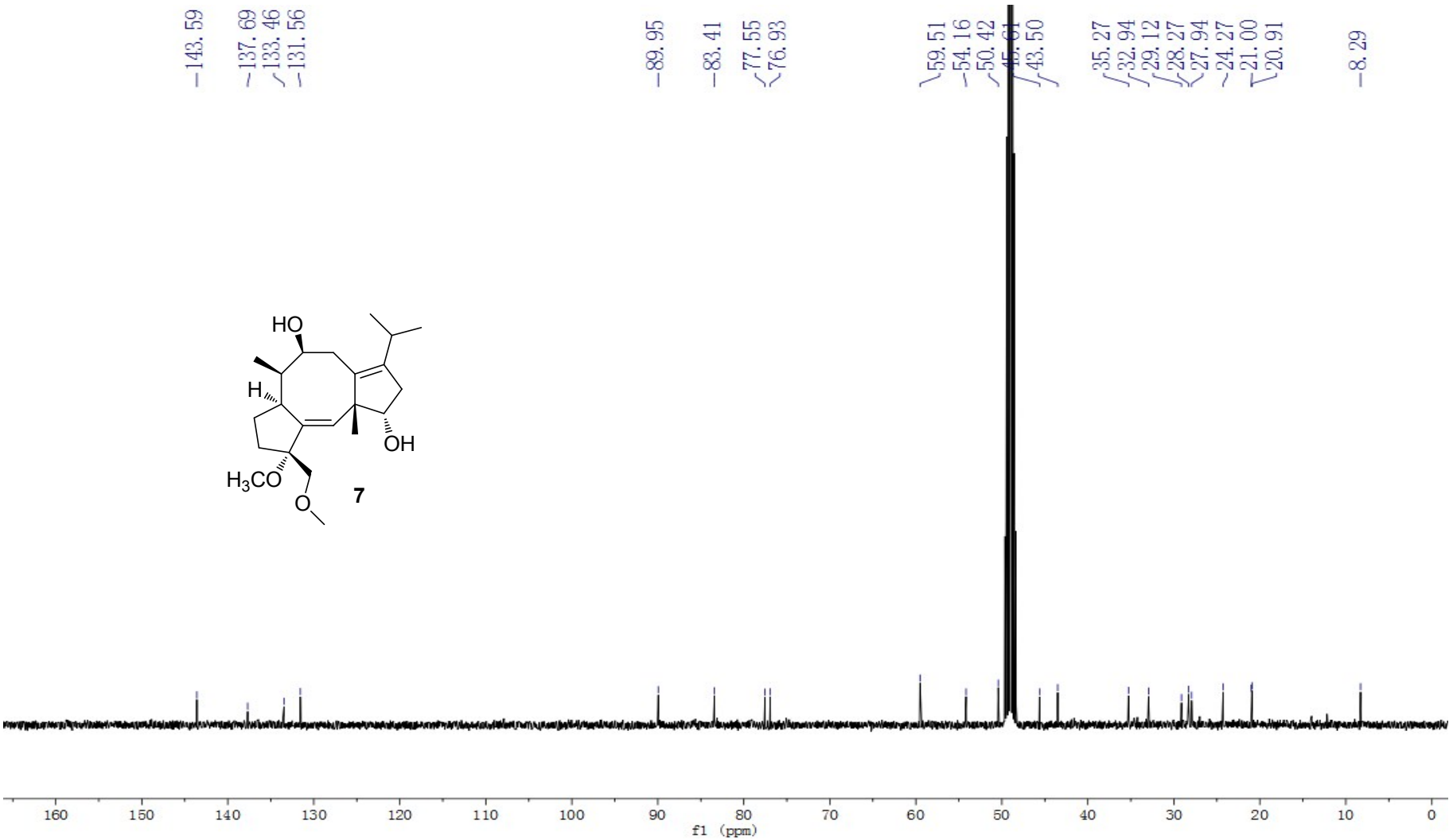


Figure S62. ^{13}C NMR spectrum of compound **7** (Recorded in methanol-d_4)

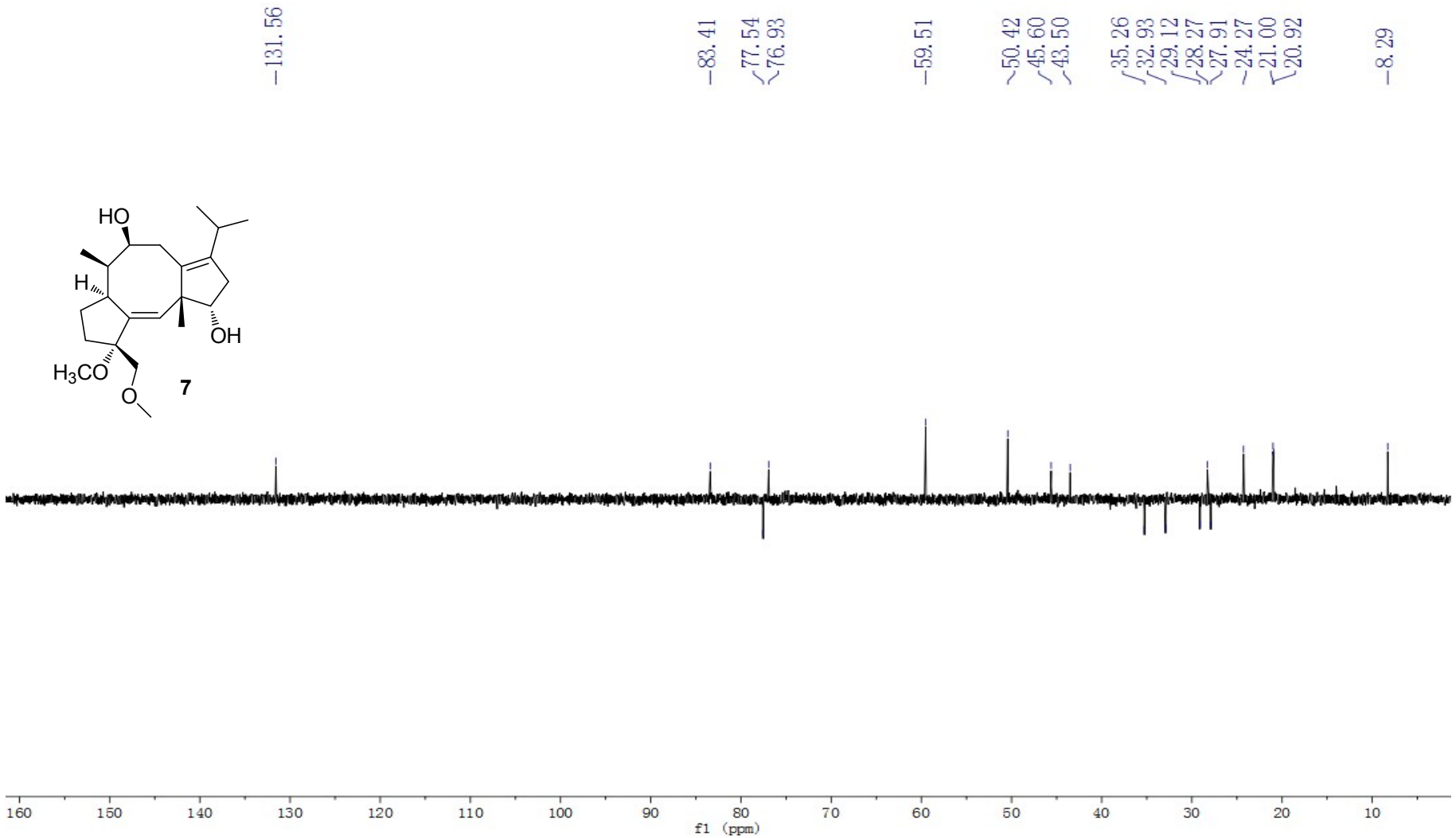


Figure S63. DEPT spectrum of compound **7** (Recorded in methanol-d_4)

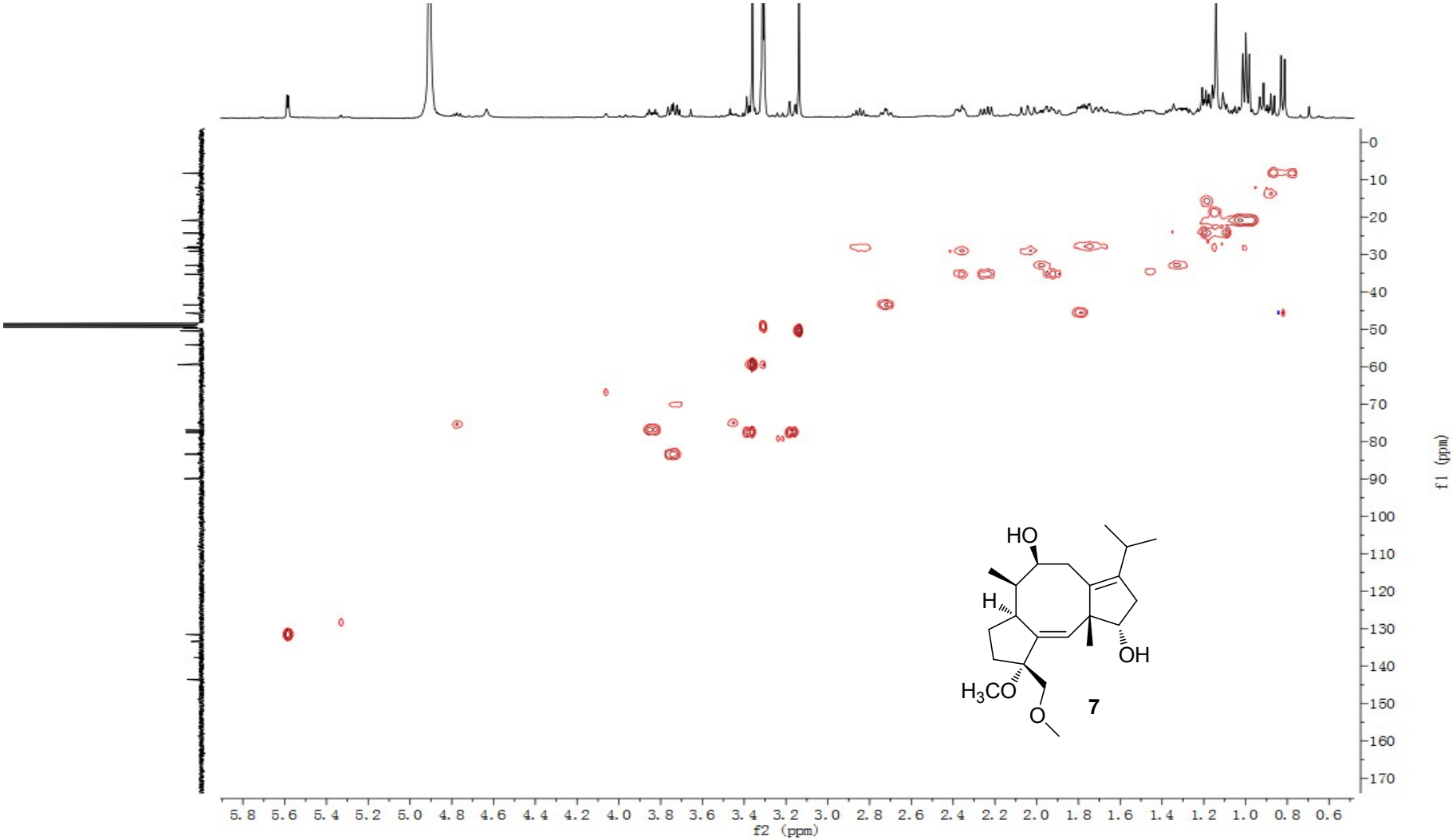


Figure S64. HSQC spectrum of compound **7** (Recorded in methanol-d_4)

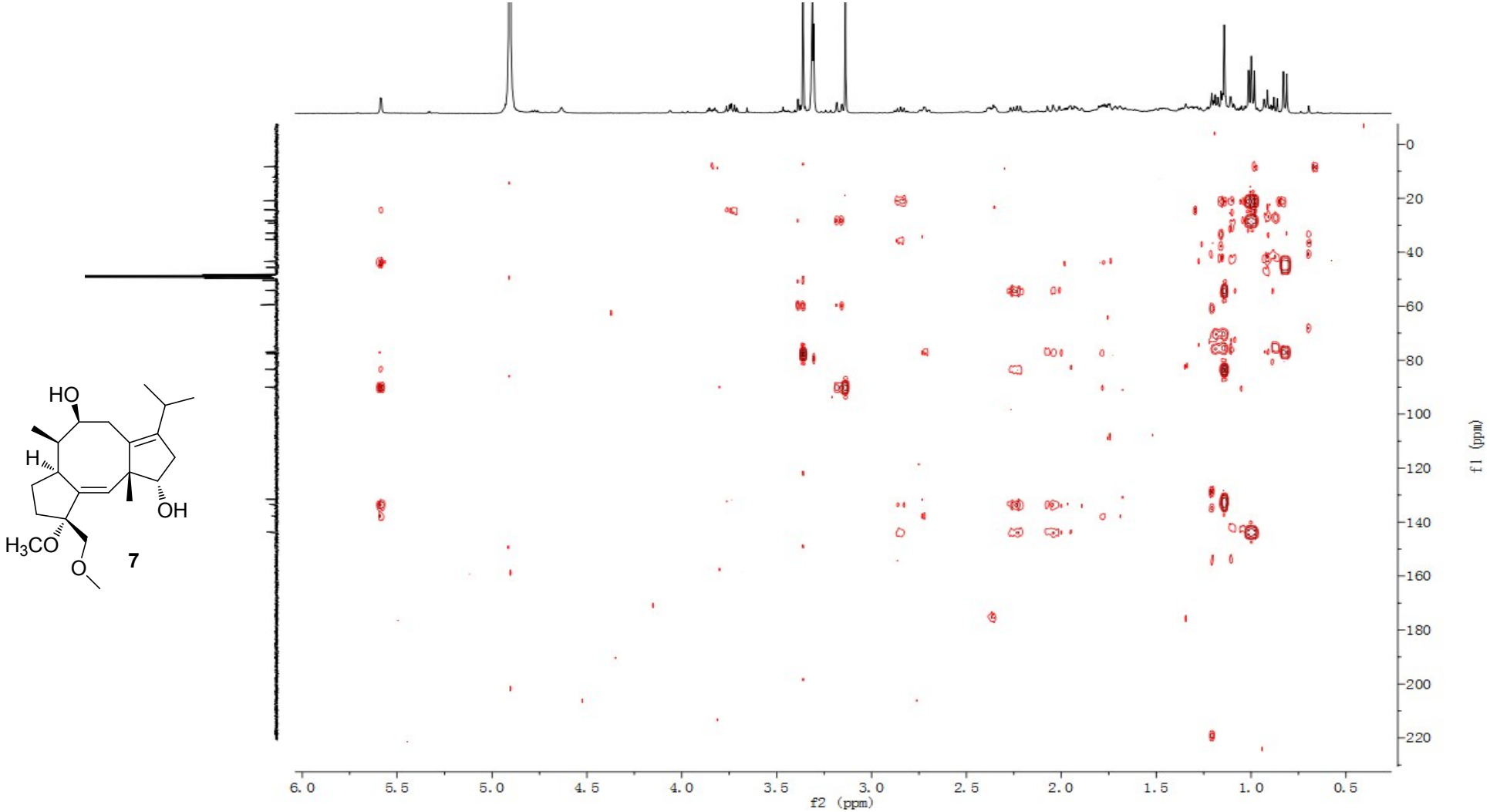


Figure S65. HMBC spectrum of compound **7** (Recorded in methanol-d_4)

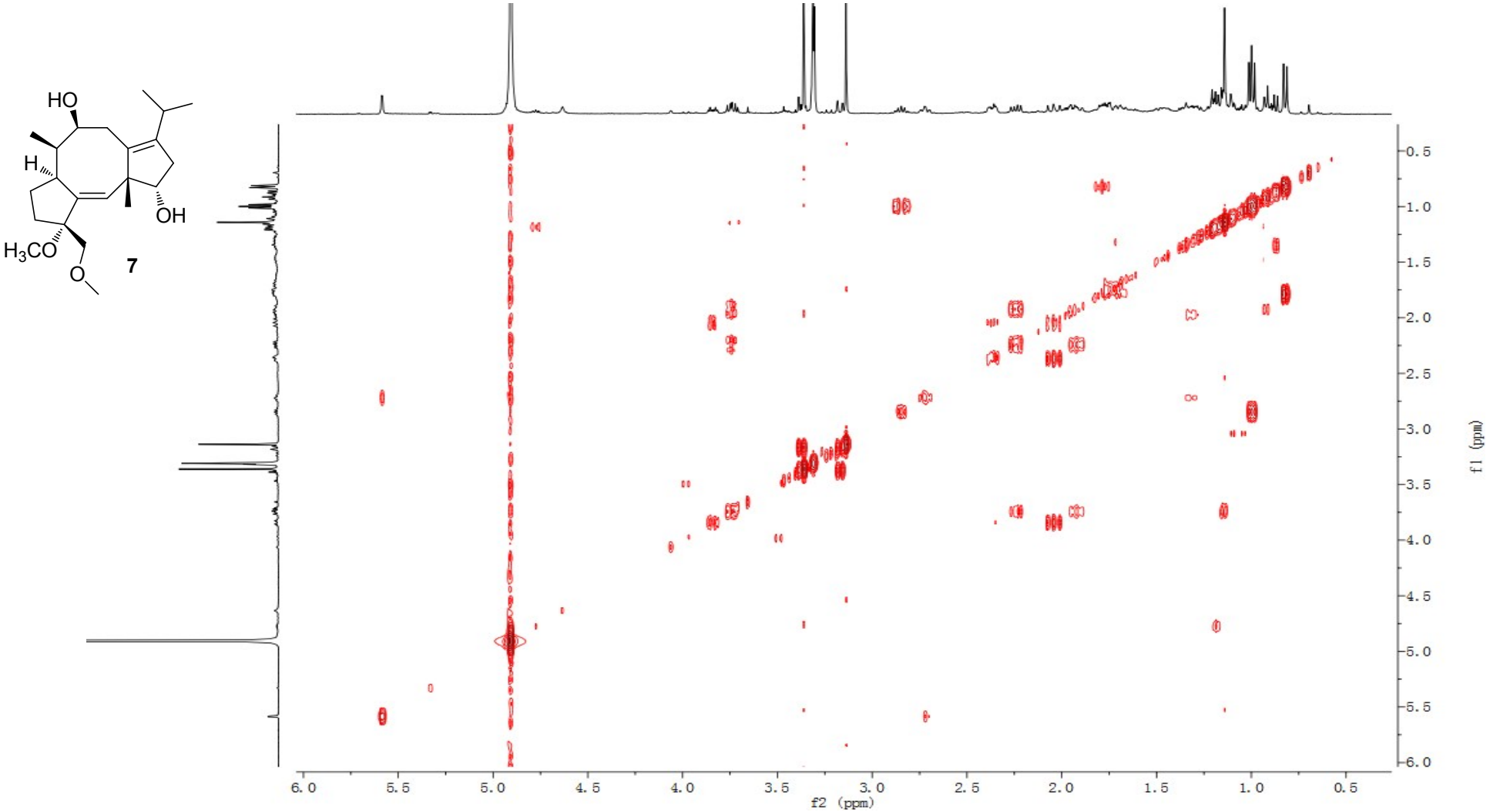


Figure S66. ^{1}H–^{1}H COSY spectrum of compound **7** (Recorded in methanol-d_4)

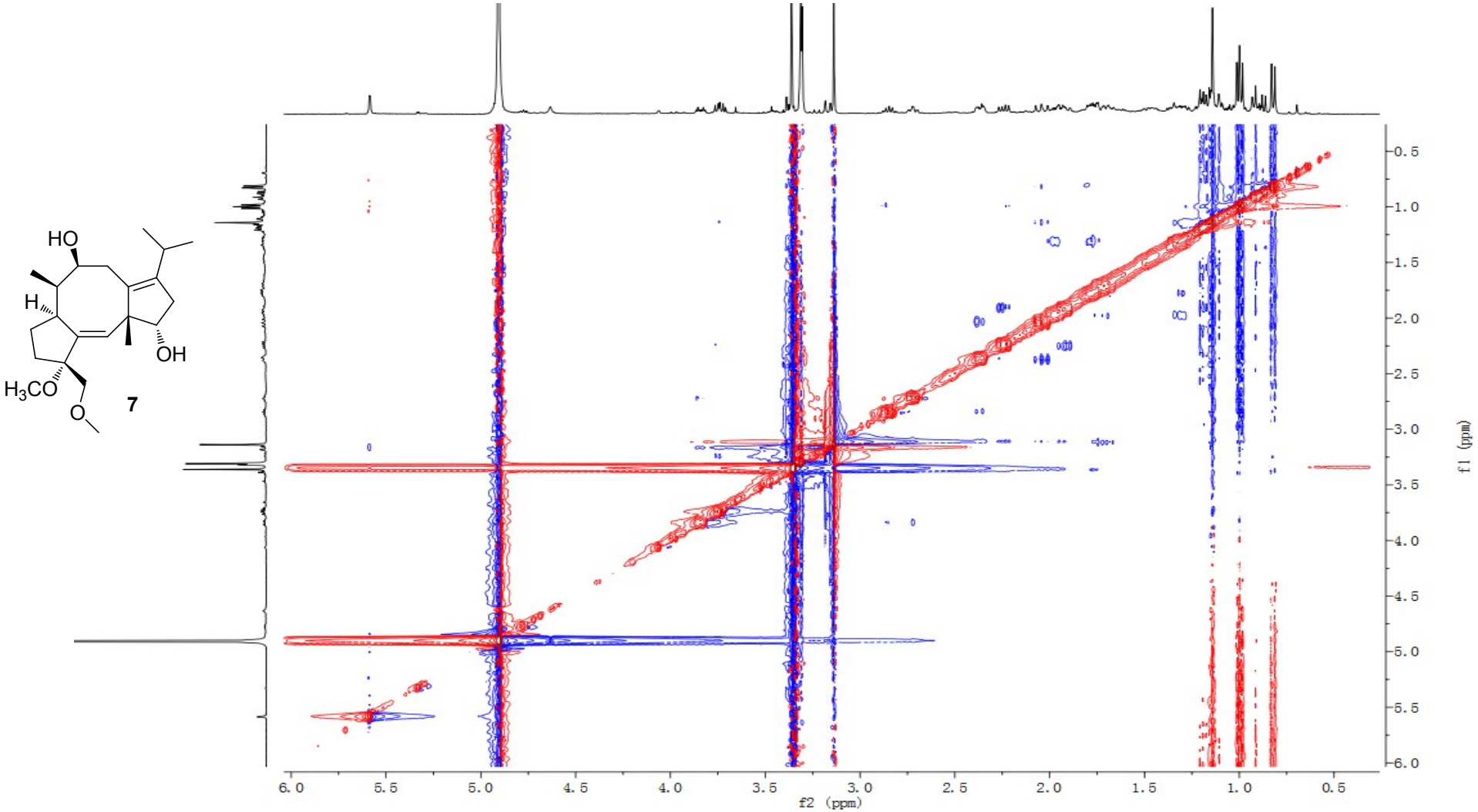


Figure S67. NOESY spectrum of compound **7** (Recorded in methanol-d_4)

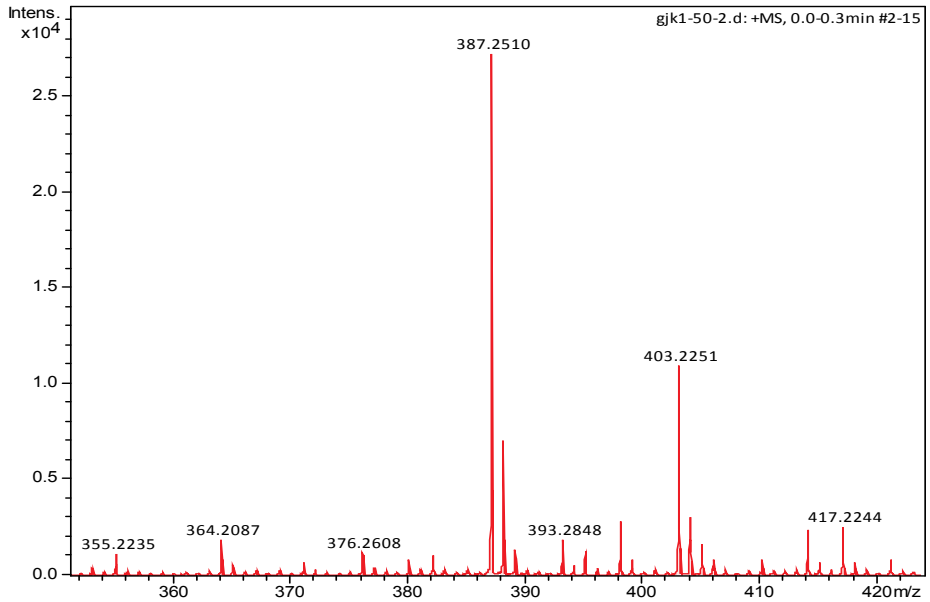
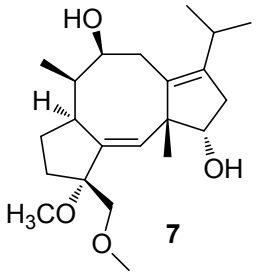


Figure S68. HRESIMS spectrum of compound **7**



7

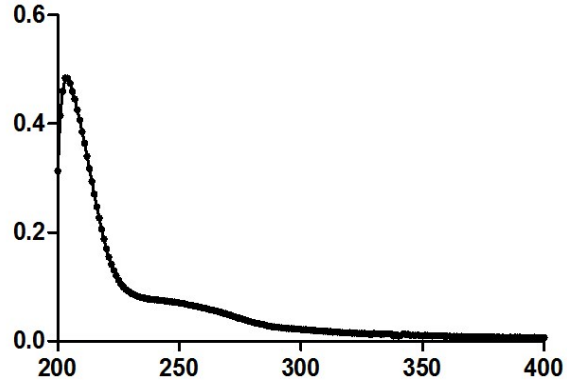
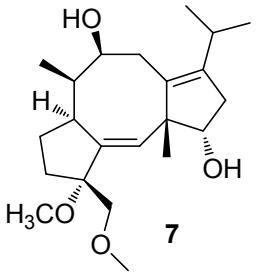


Figure S69. UV spectrum of compound **7**



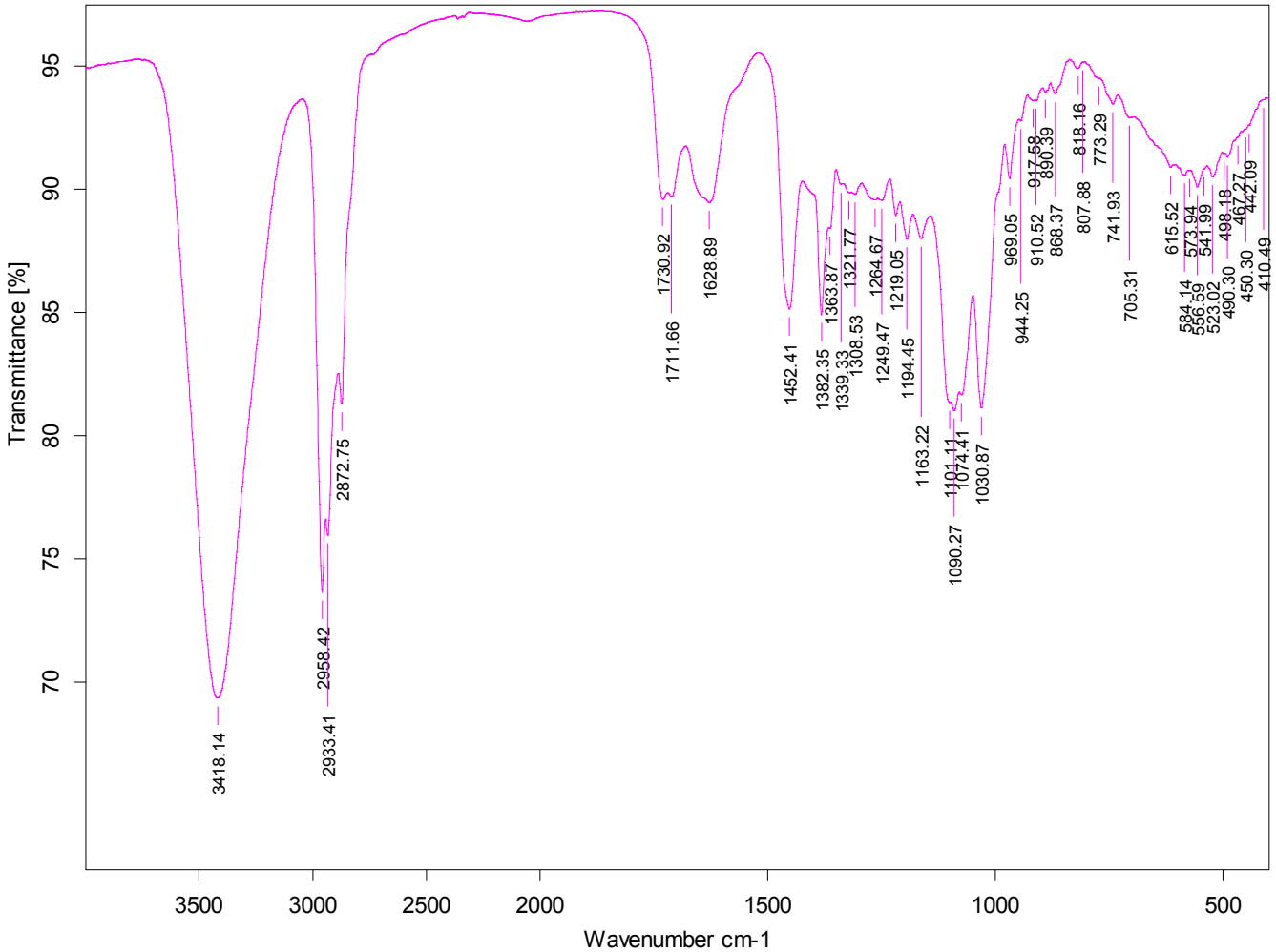


Figure S70. IR spectrum of compound **7**

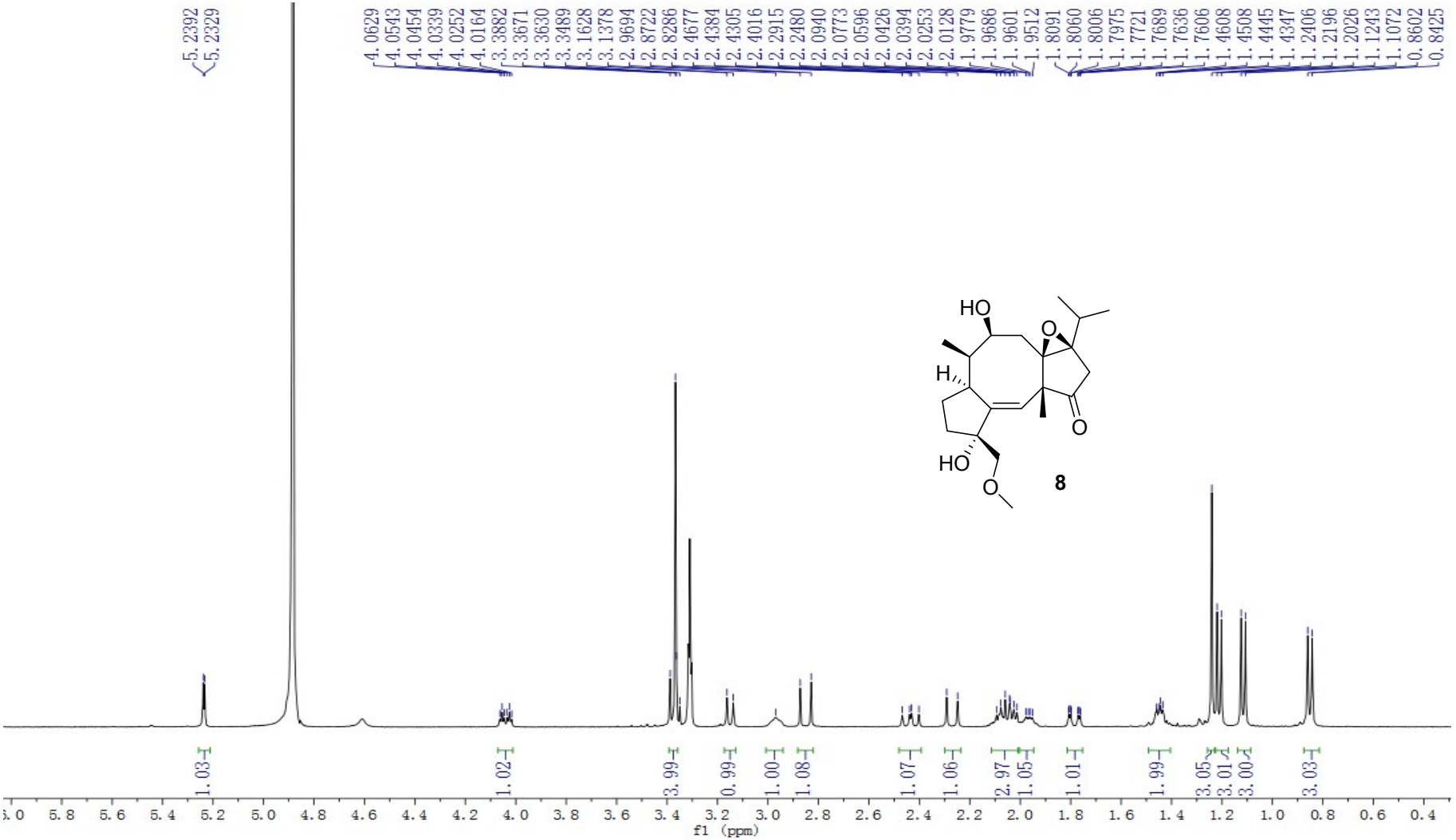


Figure S71. ^{1}H NMR spectrum of compound **8** (Recorded in methanol-d_4)

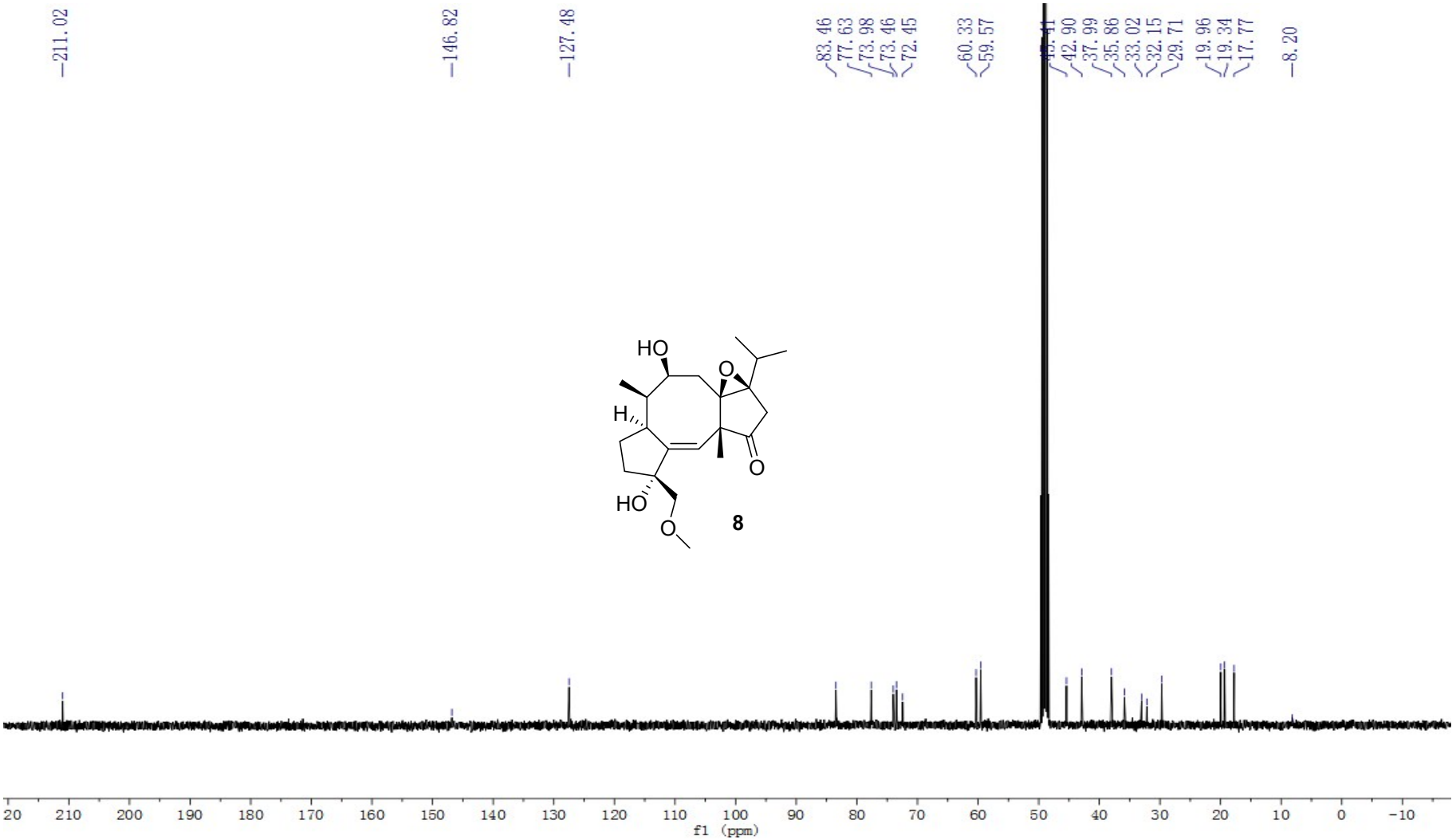


Figure S72. ^{13}C NMR spectrum of compound **8** (Recorded in methanol-d_4)

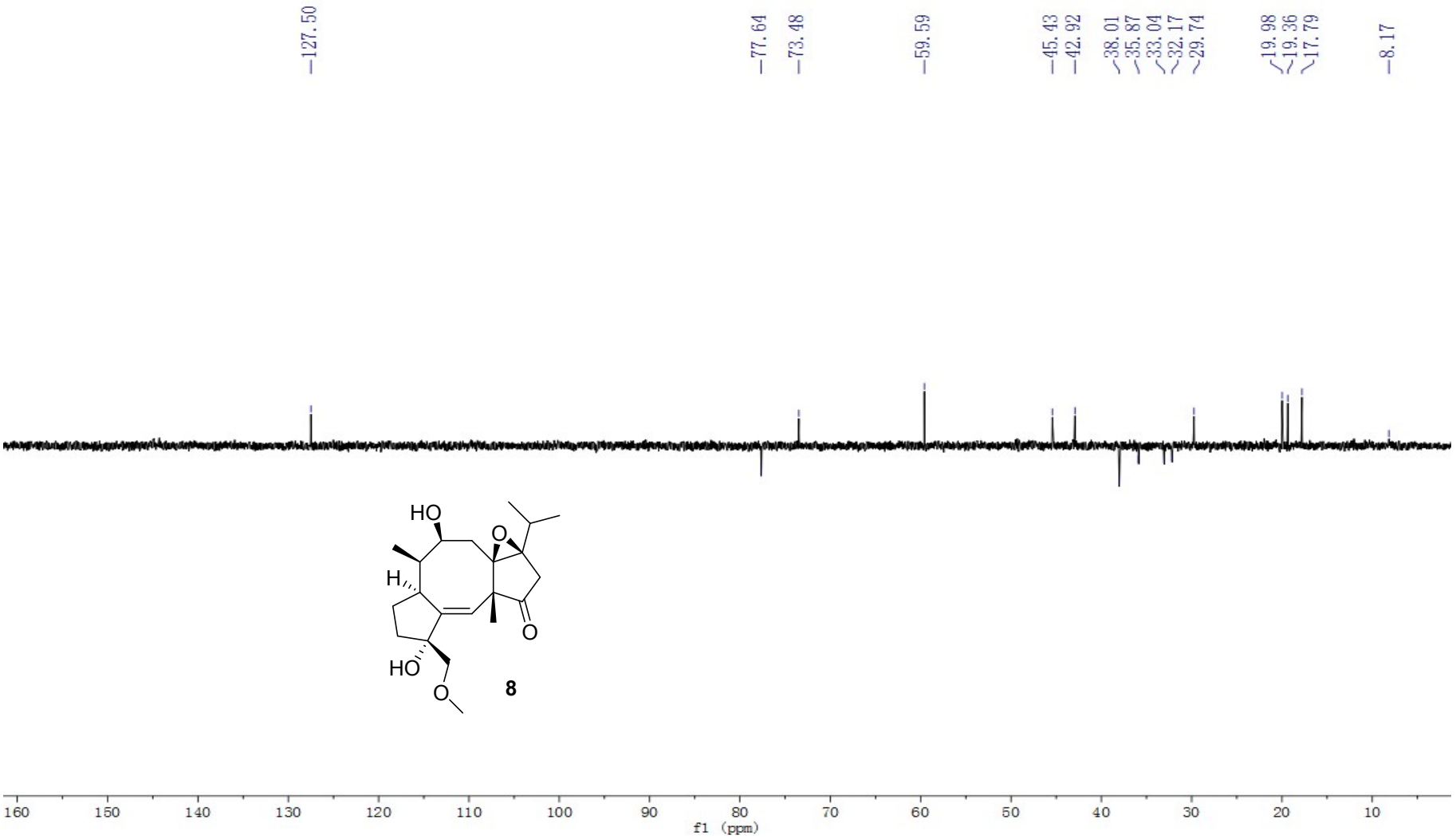


Figure S73. DEPT spectrum of compound **8** (Recorded in methanol-d_4)

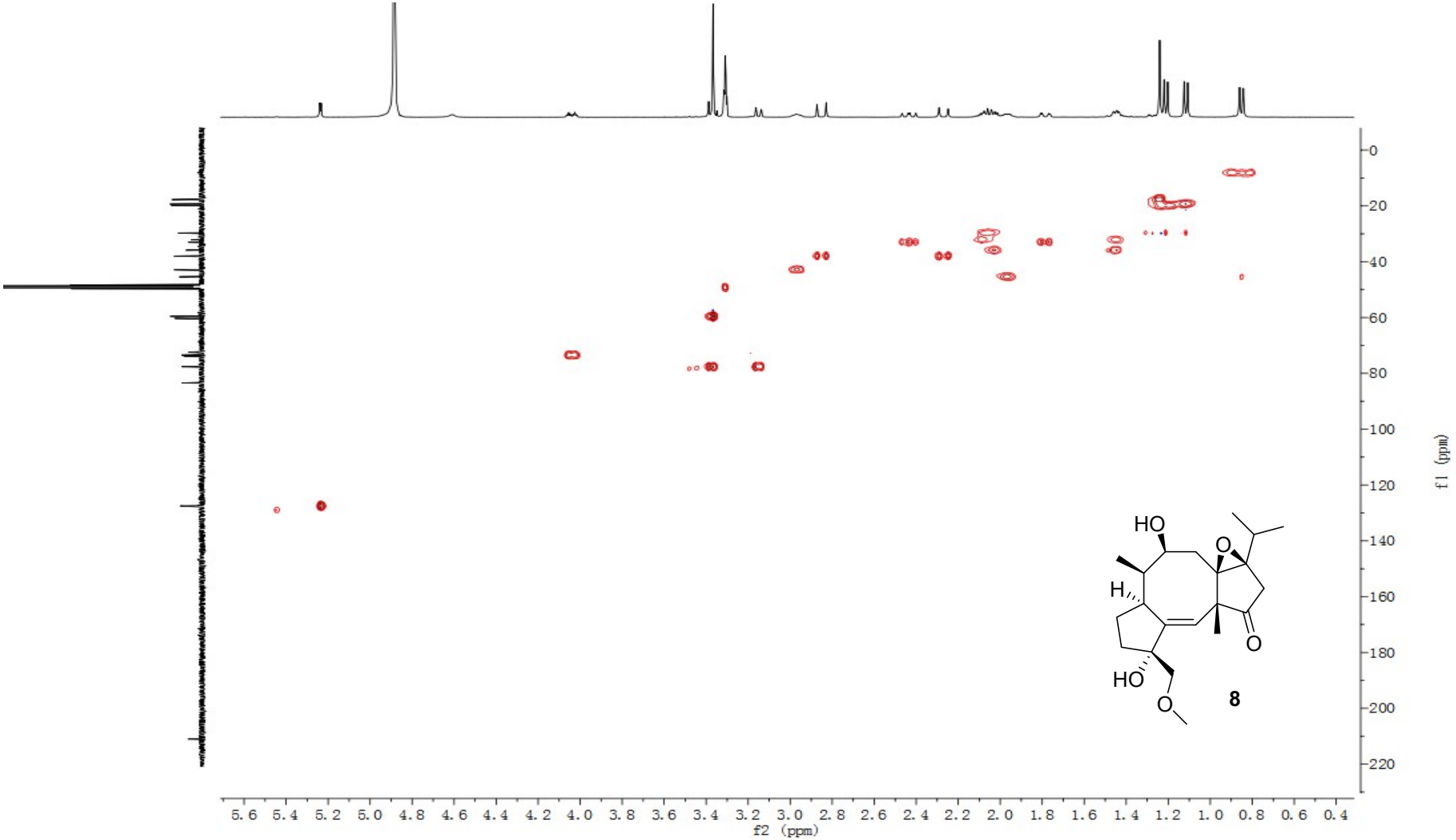


Figure S74. HSQC spectrum of compound **8** (Recorded in methanol-d_4)

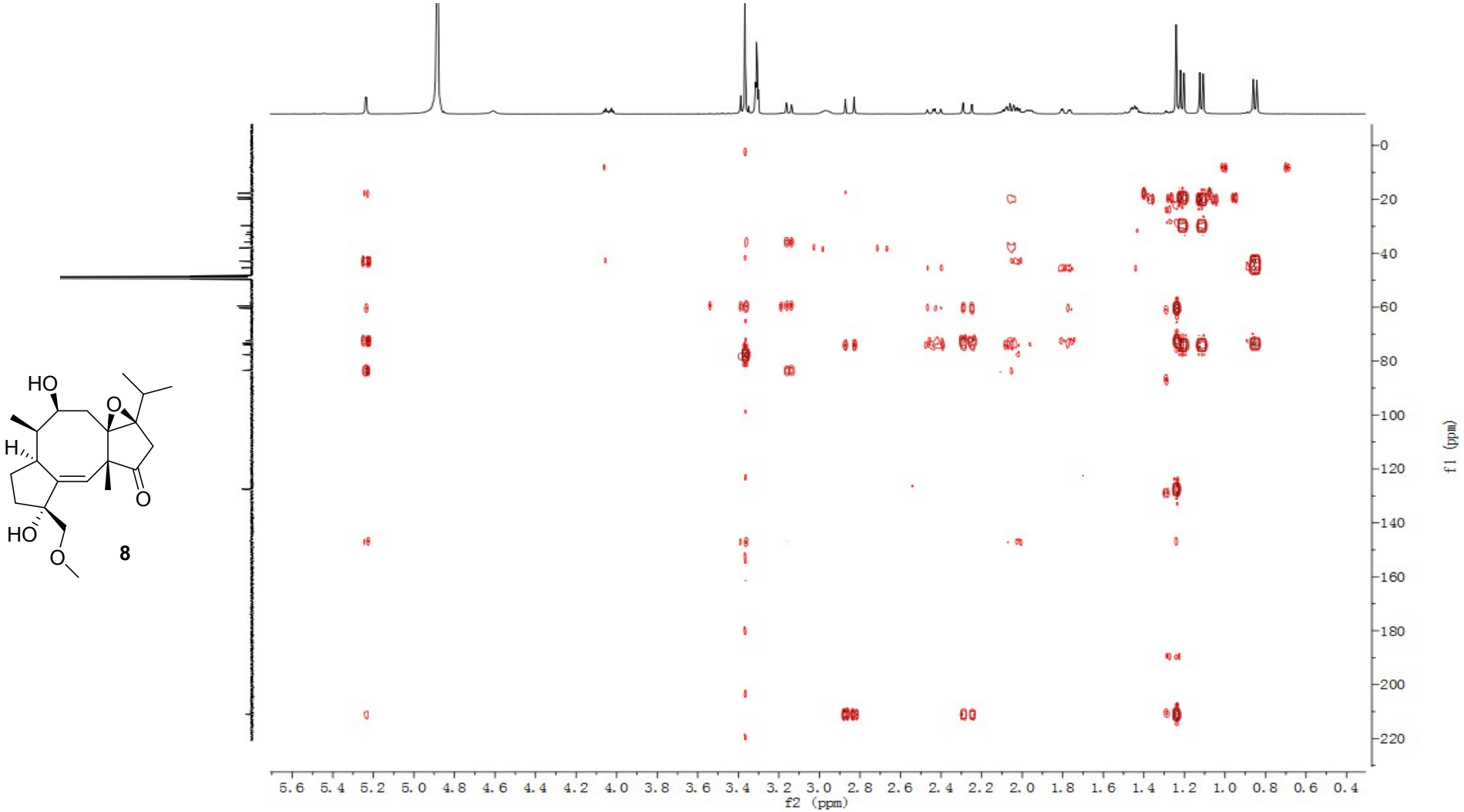


Figure S75. HMBC spectrum of compound **8** (Recorded in methanol-d_4)

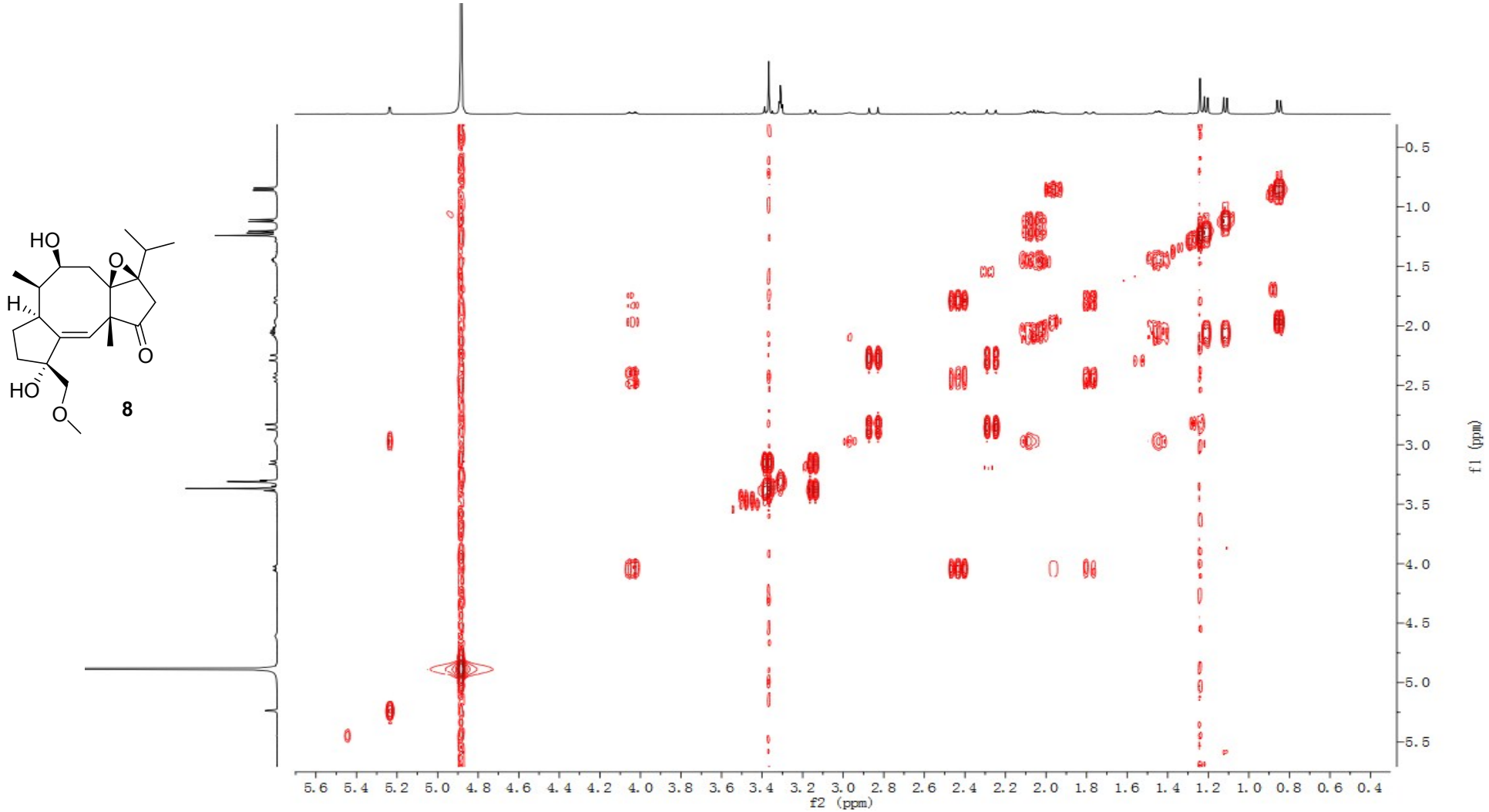


Figure S76. ^{1}H–^{1}H COSY spectrum of compound **8** (Recorded in methanol-d_4)

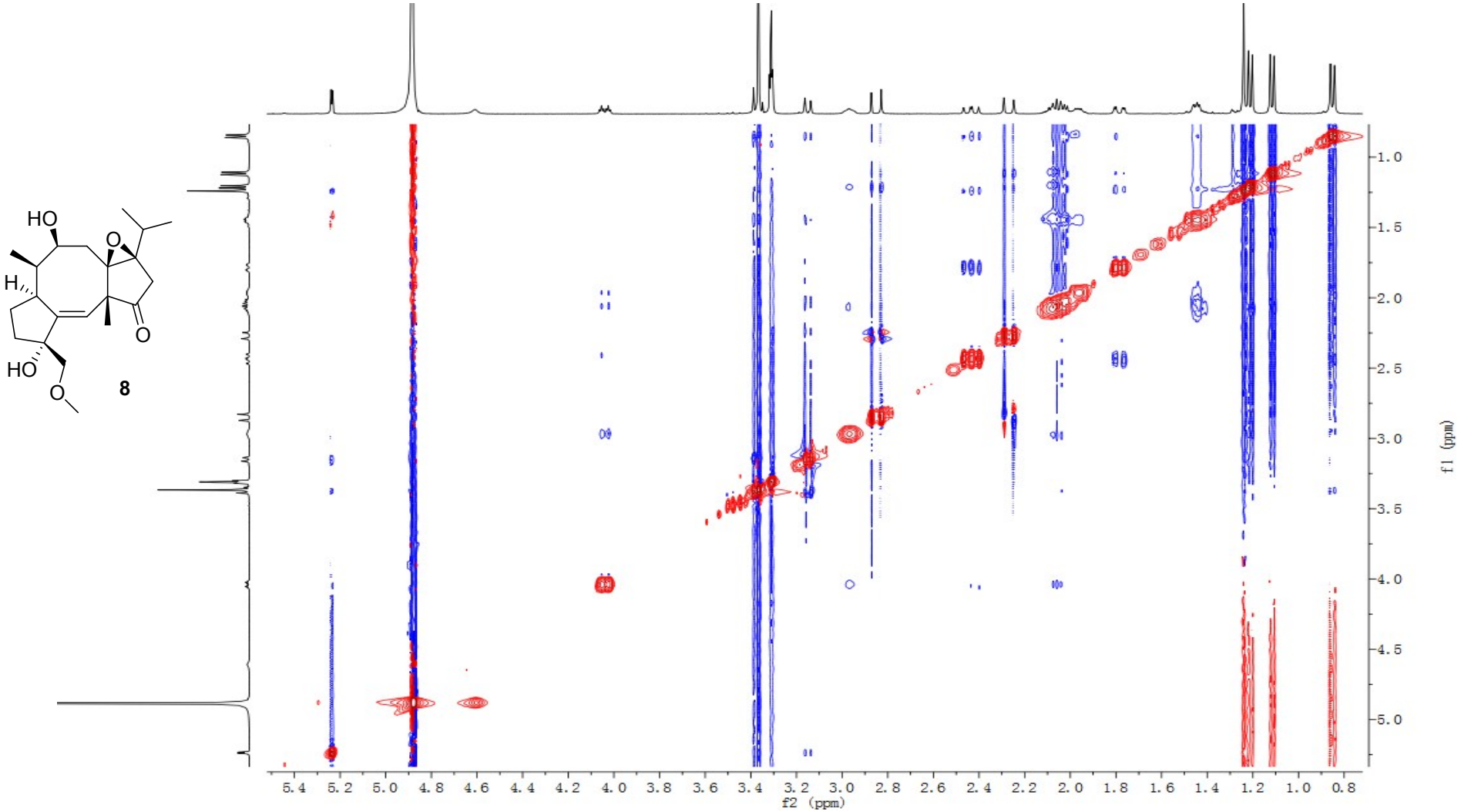


Figure S77. NOESY spectrum of compound **8** (Recorded in methanol-d_4)

Figure S78. HRESIMS spectrum of compound **8**

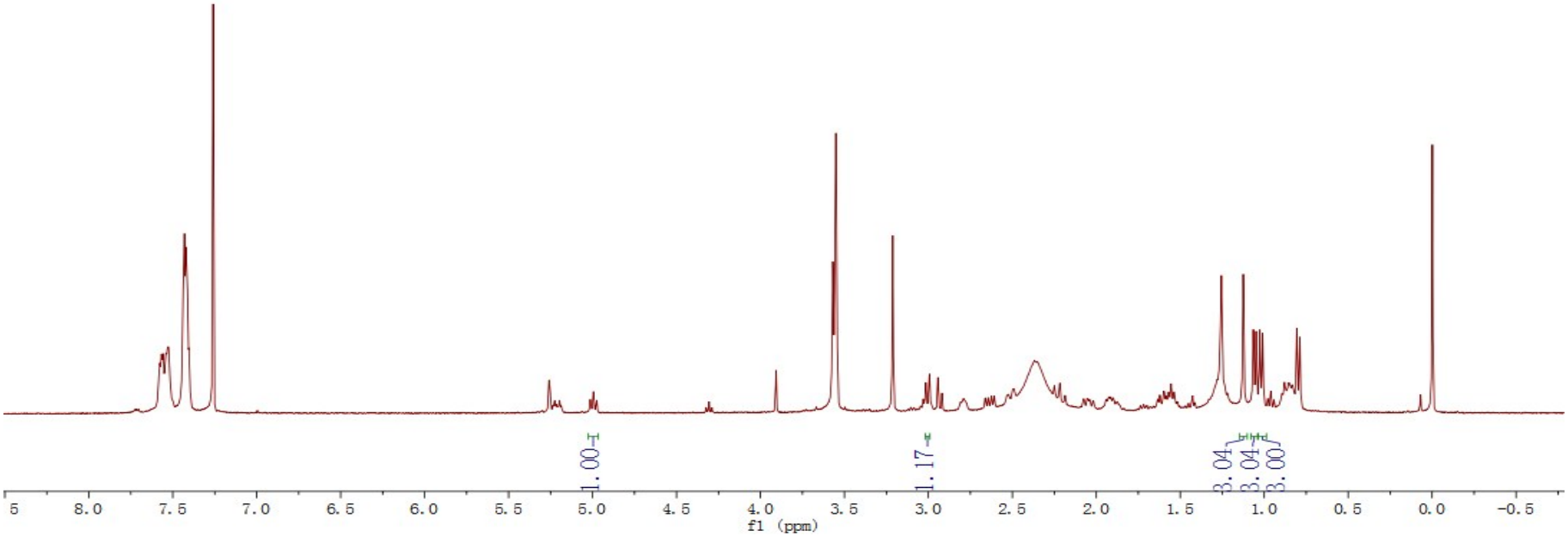


Figure S79. ^{1}H NMR spectrum of the (*S*)-MTPA ester of **6** in $CDCl_3$.

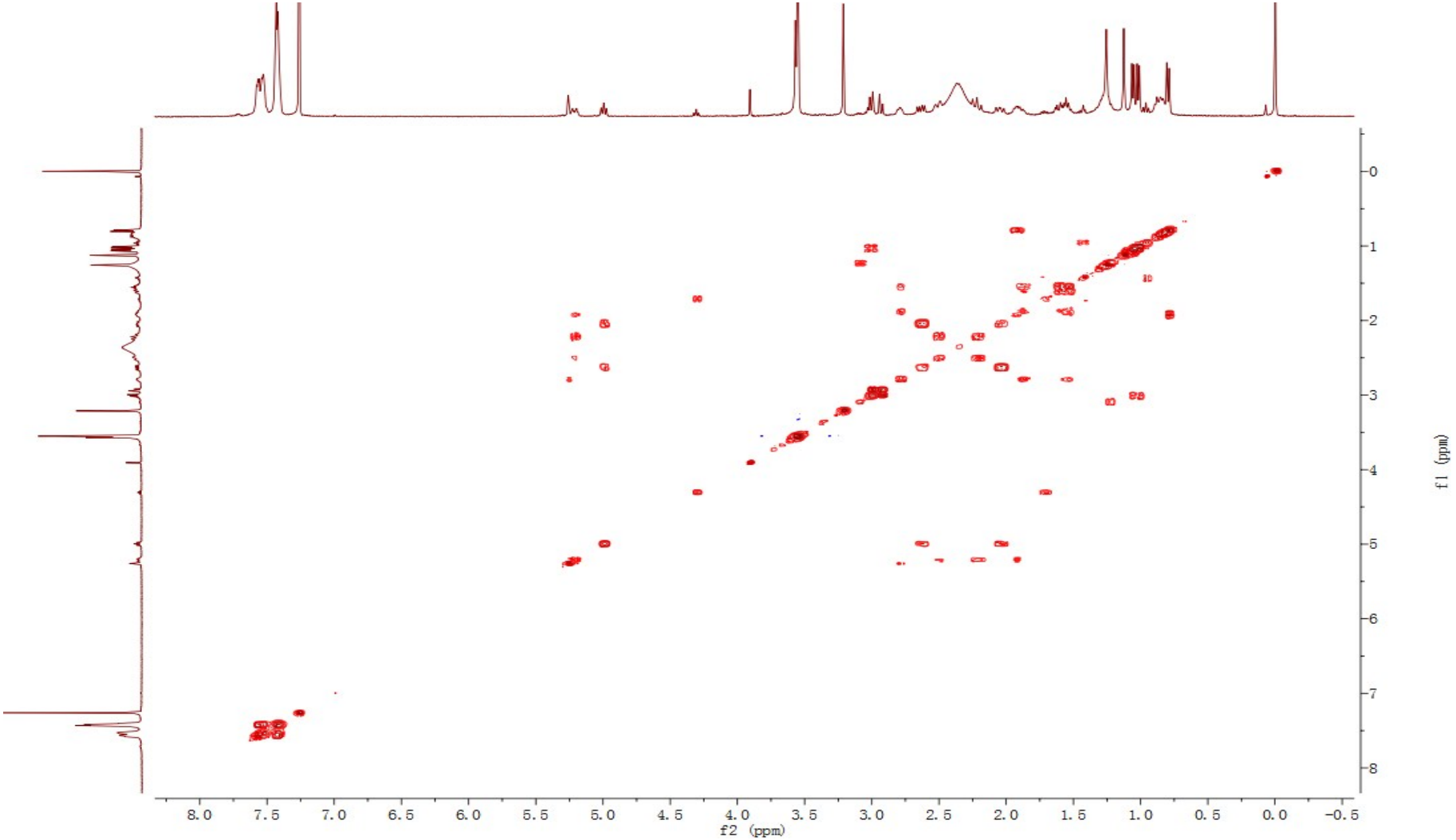


Figure S80. ^{1}H–^{1}H COSY spectrum of the (*S*)-MTPA ester of **6** in $CDCl_3$.

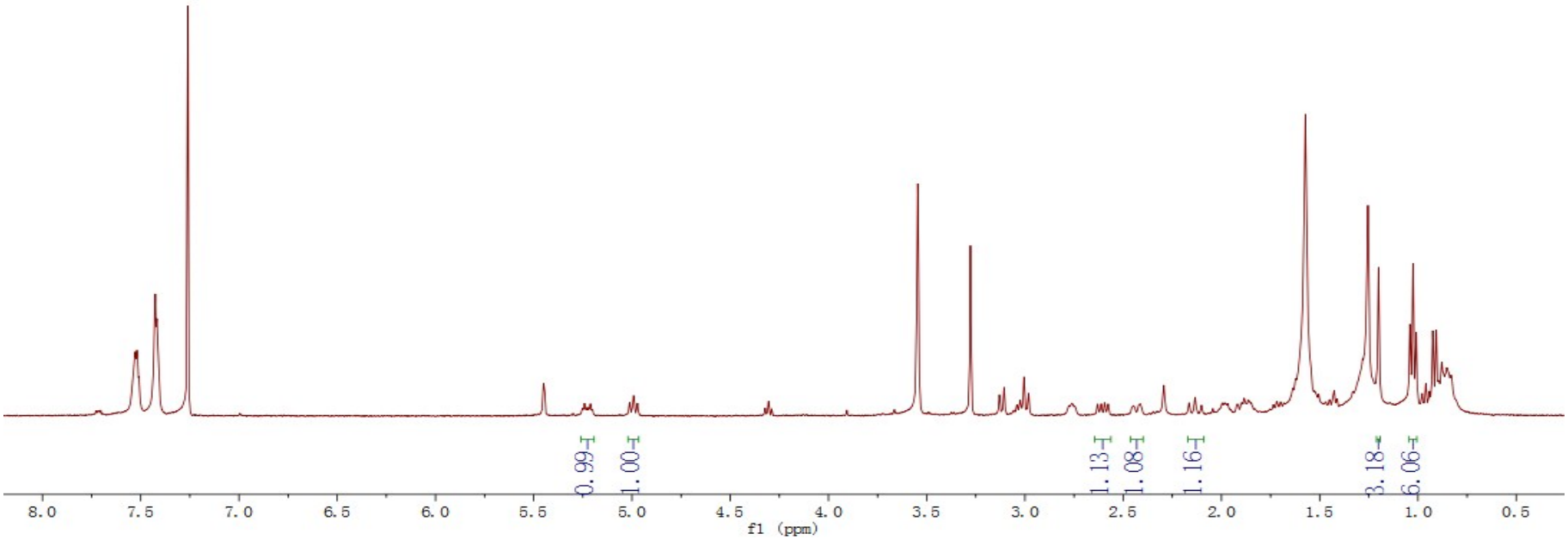


Figure S81. ^{1}H NMR spectrum of the (*R*)-MTPA ester of **6** in $CDCl_3$.

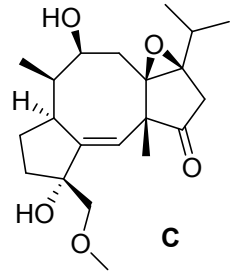
Figure S82. $^{1}H–^{1}H$ COSY spectrum of the (*R*)-MTPA ester of **6** in $CDCl_3$.

Table S1. Experimental and Calculated ^{13}C NMR Data for three possible structures of 8 (δ in ppm).

no.	Compound A			Compound B			Compound C		
	δ_C, exptl[a]	δ_C, (adj_calcd)[b]	$\Delta\delta$[c]	δ_C, exptl[a]	δ_C, (adj_calcd)[b]	$\Delta\delta$[c]	δ_C, exptl[a]	(adj_calcd)[b]	$\Delta\delta$[c]
1	127.5	124.2	3.3	127.5	125.9	1.6	127.5	127.0	0.5
2	146.8	151.8	-5.0	146.8	156.0	-9.2	146.8	152.8	-6.0
3	83.5	80.5	3.0	83.5	79.3	4.2	83.5	81.4	2.1
4	35.9	34.7	1.2	35.9	36.4	-0.5	35.9	38.2	-2.3
5	32.2	23.9	8.3	32.2	29.9	2.3	32.2	31.1	1.1
6	42.9	42.5	0.4	42.9	45.4	-2.5	42.9	43.9	-1.0
7	45.4	43.0	2.4	45.4	47.8	-2.4	45.4	46.7	-1.3
8	73.5	68.9	4.6	73.5	69.9	3.6	73.5	73.7	-0.2
9	33.0	44.8	-11.8	33.0	38.3	-5.3	33.0	32.8	0.2
10	72.5	88.6	-16.1	72.5	85.0	-12.5	72.5	73.0	-0.5
11	60.3	63.7	-3.4	60.3	62.7	-2.4	60.3	61.4	-1.1
12	211.0	212.3	-1.3	211.0	214.8	-3.8	211.0	212.8	-1.8
13	38.0	50.7	-12.7	38.0	51.7	-13.7	38.0	37.4	0.6
14	74.0	83.3	-9.3	74.0	79.7	-5.7	74.0	73.9	0.1
15	29.7	35.3	-5.6	29.7	35.1	-5.4	29.7	30.2	-0.5
16	77.6	73.2	4.4	77.6	74.7	2.9	77.6	76.0	1.6
17	8.2	5.9	2.3	8.2	7.6	0.6	8.2	11.0	-2.8
18	17.8	24.2	-6.4	17.8	24.2	-6.4	17.8	17.2	0.6
19	20.0	15.6	4.4	20.0	15.5	4.5	20.0	17.2	2.8
20	19.3	15.3	4.0	19.3	14.8	4.5	19.3	16.9	2.4
21	59.6	55.0	4.6	59.6	54.8	4.8	59.6	54.8	4.8

[a]Recorded in methanol-d_4 at 100 MHz. [b]Calculated in methanol-d_4. [c]$\Delta\delta = \delta_{exptl} - \delta_{adj\_calcd}$.

^{13}C NMR Calculation Data



C

Table S2. Important thermodynamic parameters (a.u.) and boltzmann distribution of the optimized compound **C** at B3LYP/6-31G(d) level in methanol.

Conformation	Internal Energy	%
1	-1195.370421	47.21%
2	-1195.370222	38.19%
3	-1195.369139	12.17%
4	-1195.367604	2.38%

Table S3. Optimized coordinates of compound **C** at B3LYP/6-31G(d) level in methanol.

Conformation 1							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	0.492	1.11	0.386	H	0.859	-1.265	-2.717
C	1.071	0.066	-0.231	H	1.281	-2.806	-1.969
C	-1.553	2.292	-0.121	H	3.282	-1.823	-0.939
C	-2.481	1.536	-1.064	H	3.262	-1.008	-2.502
C	1.288	-1.722	-1.817	H	-2.394	-1.909	1.31
C	2.697	-1.153	-1.578	H	-2.033	-0.911	2.699

C	-1.698	-1.149	1.681	H	-0.579	-1.112	-0.903
C	0.452	-1.281	-0.588	H	-0.316	-3.117	0.16
C	0.36	-2.344	0.552	H	-0.513	-2.701	2.46
C	-0.315	-1.817	1.842	H	2.419	-2.354	1.322
C	-0.922	1.314	0.914	H	2.112	-3.567	0.061
C	2.467	0.202	-0.86	H	1.487	-3.803	1.694
C	-1.901	0.125	0.869	H	-1.901	2.183	2.652
C	-2.839	0.278	-0.292	H	-0.344	2.931	2.248
C	1.676	-3.049	0.921	H	-0.386	1.331	3.029
C	-0.883	1.981	2.304	H	-5.25	0.5	-1.727
C	-5.147	-0.354	-1.047	H	-5.539	-0.061	-0.068
C	-3.149	-1.255	-2.314	H	-5.77	-1.166	-1.437
C	5.851	1.172	0.2	H	-3.197	-0.439	-3.044
C	3.568	0.534	0.154	H	-3.759	-2.078	-2.699
C	-3.681	-0.815	-0.94	H	-2.112	-1.605	-2.266
O	-1.311	3.479	-0.171	H	6.708	1.29	-0.468
O	-3.249	0.648	1.048	H	6.104	0.449	0.988
O	0.572	-1.034	2.653	H	5.622	2.14	0.671
O	2.402	1.285	-1.805	H	3.686	-0.272	0.894
O	4.765	0.713	-0.591	H	3.317	1.46	0.693
H	1.08	2.024	0.466	H	-3.662	-1.685	-0.273
H	-3.351	2.15	-1.316	H	0.945	-0.338	2.087
H	-1.946	1.317	-1.997	H	3.333	1.477	-2.022
Conformation 2							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	0.702	-1.067	-0.471	H	1.331	1.068	2.877
C	1.234	-0.088	0.272	H	1.531	2.675	2.17

C	-1.257	-2.455	-0.071	H	3.372	1.852	0.734
C	-2.294	-1.878	0.885	H	3.696	1.036	2.265
C	1.58	1.603	1.954	H	-0.951	1.017	-2.403
C	2.961	1.147	1.464	H	-2.597	1.388	-1.935
C	-1.617	1.111	-1.537	H	-0.372	0.931	1.292
C	0.592	1.178	0.834	H	0.407	3.253	0.356
C	0.314	2.313	-0.209	H	-1.784	2.322	0.236
C	-1.161	2.294	-0.67	H	0.972	3.193	-2.072
C	-0.697	-1.338	-0.999	H	2.306	2.648	-1.048
C	2.686	-0.206	0.788	H	1.35	1.467	-1.952
C	-1.781	-0.252	-0.882	H	-0.084	-1.134	-3.089
C	-2.756	-0.603	0.197	H	-0.009	-2.791	-2.46
C	1.295	2.403	-1.388	H	-1.581	-2.069	-2.855
C	-0.588	-1.863	-2.447	H	-4.03	1.459	2.71
C	-3.319	0.734	2.298	H	-3.306	-0.132	2.969
C	-5.15	-0.295	0.884	H	-2.325	1.193	2.323
C	6.002	-0.779	-0.729	H	-5.179	-1.199	1.504
C	3.699	-0.55	-0.307	H	-5.464	-0.565	-0.129
C	-3.745	0.337	0.875	H	-5.879	0.412	1.293
O	-0.892	-3.613	-0.099	H	5.979	-0.068	-1.57
O	-3.056	-0.893	-1.189	H	6.971	-0.705	-0.227
O	-1.457	3.448	-1.47	H	5.886	-1.796	-1.134
O	2.738	-1.189	1.844	H	3.593	0.156	-1.146
O	5.007	-0.483	0.233	H	3.508	-1.561	-0.704
H	1.36	-1.899	-0.73	H	-3.799	1.245	0.263
H	-1.815	-1.677	1.853	H	-1.192	4.231	-0.96
H	-3.1	-2.598	1.055	H	2.276	-1.981	1.523

Conformation 3							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	0.476	1.281	-0.199	H	0.762	-1.65	-2.764
C	1.068	0.173	-0.664	H	1.39	-2.982	-1.792
C	-1.756	2.139	-0.561	H	3.364	-1.632	-1.149
C	-2.709	1.091	-1.126	H	3.166	-1.225	-2.856
C	1.314	-1.891	-1.848	H	-1.84	-1.593	1.97
C	2.679	-1.184	-1.875	H	-1.284	-0.252	2.942
C	-1.155	-0.737	1.966	H	-0.503	-1.263	-0.842
C	0.569	-1.268	-0.638	H	0.012	-2.902	0.609
C	0.726	-2.071	0.701	H	0.272	-2.037	2.771
C	0.286	-1.294	1.962	H	2.893	-1.966	1.07
C	-0.842	1.5	0.521	H	2.384	-3.399	0.156
C	2.373	0.274	-1.469	H	2.062	-3.297	1.886
C	-1.654	0.262	0.934	H	-1.583	2.654	2.213
C	-2.779	0.039	-0.032	H	-0.255	3.43	1.329
C	2.103	-2.712	0.96	H	0.083	2.053	2.407
C	-0.635	2.473	1.698	H	-5.408	-0.292	-0.974
C	-5.083	-0.945	-0.154	H	-5.333	-0.455	0.792
C	-3.24	-1.962	-1.558	H	-5.657	-1.875	-0.223
C	4.677	0.897	1.378	H	-3.505	-1.35	-2.428
C	3.505	0.952	-0.682	H	-3.812	-2.894	-1.625
C	-3.574	-1.245	-0.24	H	-2.179	-2.22	-1.636
O	-1.693	3.298	-0.916	H	4.667	0.377	2.338
O	-3.013	0.697	1.239	H	4.521	1.972	1.546
O	1.239	-0.316	2.395	H	5.654	0.754	0.896
O	2.088	1.089	-2.622	H	3.276	2.023	-0.572
O	3.631	0.341	0.593	H	4.453	0.868	-1.239

H	0.982	2.227	-0.394	H	-3.329	-1.922	0.587
H	-3.679	1.542	-1.358	H	1.737	0.021	1.629
H	-2.292	0.694	-2.061	H	2.879	1.076	-3.188
Conformation 4							
Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
C	0.902	-0.997	-0.15	H	0.987	1.479	2.941
C	1.307	0.117	0.475	H	1.138	3.041	2.138
C	-1.011	-2.449	0.256	H	3.204	2.335	1.018
C	-2.162	-1.829	1.041	H	3.408	1.608	2.615
C	1.308	1.967	2.012	H	-2.393	1.021	-2.187
C	2.773	1.615	1.724	H	-0.689	0.737	-2.463
C	-1.435	0.885	-1.674	H	-0.483	1.082	1.184
C	0.509	1.371	0.823	H	0.257	3.382	0.104
C	0.279	2.382	-0.35	H	-1.846	2.316	-0.106
C	-1.134	2.209	-0.938	H	1.513	1.423	-1.894
C	-0.429	-1.417	-0.751	H	2.326	2.732	-1.027
C	2.725	0.202	1.089	H	1.085	3.112	-2.225
C	-1.578	-0.399	-0.868	H	-1.094	-2.425	-2.57
C	-2.629	-0.682	0.159	H	0.473	-2.987	-1.952
C	1.365	2.407	-1.437	H	0.366	-1.428	-2.79
C	-0.156	-2.106	-2.107	H	-5.129	-1.275	1.319
C	-5.091	-0.454	0.592	H	-5.292	-0.867	-0.401
C	-3.461	0.859	2.018	H	-5.894	0.248	0.842
C	5.007	-1.421	-1.355	H	-3.461	0.082	2.791
C	3.898	0.036	0.117	H	-4.246	1.578	2.272
C	-3.729	0.264	0.626	H	-2.501	1.384	2.068
O	-0.587	-3.576	0.404	H	4.962	-2.447	-1.731

O	-2.782	-1.157	-1.2	H	5.981	-1.26	-0.867
O	-1.321	3.298	-1.851	H	4.925	-0.724	-2.202
O	2.907	-0.82	2.088	H	4.831	0.234	0.672
O	3.937	-1.263	-0.441	H	3.818	0.792	-0.678
H	1.639	-1.792	-0.235	H	-3.778	1.087	-0.098
H	-2.94	-2.575	1.232	H	-2.237	3.262	-2.17
H	-1.789	-1.479	2.013	H	2.072	-0.899	2.577