Supporting Information for

Sesquiterpenoids from Edible Mushroom *Craterellus odoratus* and Their Immunosuppressive Activity

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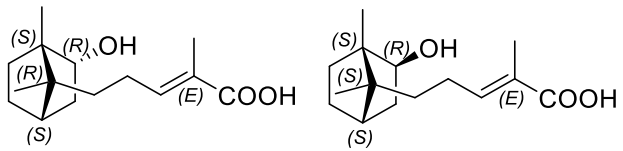
Section S1. Calculational details for 1

S1.1. Computational details for 1 (NMR)



1a **1b**

Conformation search based on molecular mechanics with MMFF force fields were performed for **1a** and **1b** gave 15 and 16 stable conformers with populations higher than 1%, respectively.[1,2] All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package.[3] Gauge Independent Atomic Orbital (GIAO) calculations of their ^{1}H and ^{13}C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The ^{1}H and ^{13}C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by the improved probability DP4+ method.[4]

Table S1. Energy analysis for conformers of **1aA**–**1aO** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
1aA	-811.346396	-811.327397	-811.326453	-811.395115	0	0	19.86%
1aB	-811.345763	-811.326685	-811.325741	-811.395024	0.000091	0.057103	18.03%
1aC	-811.346155	-811.327270	-811.326326	-811.394244	0.000871	0.546561	7.89%
1aD	-811.345542	-811.326569	-811.325625	-811.393639	0.001476	0.926204	4.16%
1aE	-811.346505	-811.327616	-811.326672	-811.394869	0.000246	0.154367	15.30%
1aF	-811.345807	-811.326871	-811.325927	-811.394120	0.000995	0.624372	6.92%
1aG	-811.345696	-811.326792	-811.325848	-811.393802	0.001313	0.823920	4.94%
1aH	-811.346282	-811.327479	-811.326535	-811.394301	0.000814	0.510793	8.38%
1aI	-811.343685	-811.324821	-811.323877	-811.391425	0.003690	2.315510	0.40%
1aJ	-811.344259	-811.325515	-811.324570	-811.391727	0.003388	2.126002	0.55%
1aK	-811.345655	-811.326666	-811.325721	-811.394425	0.000690	0.432982	9.56%

1aL	-811.342392	-811.323667	-811.322723	-811.389609	0.005506	3.455067	0.06%
1aM	-811.345470	-811.326570	-811.325626	-811.393508	0.001607	1.008408	3.62%
1aN	-811.343690	-811.324969	-811.324025	-811.390977	0.004138	2.596634	0.25%
1aO	-811.343007	-811.324371	-811.323427	-811.390108	0.005007	3.141940	0.10%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S1. Main conformers of **1a** in NMR and ECD calculations.

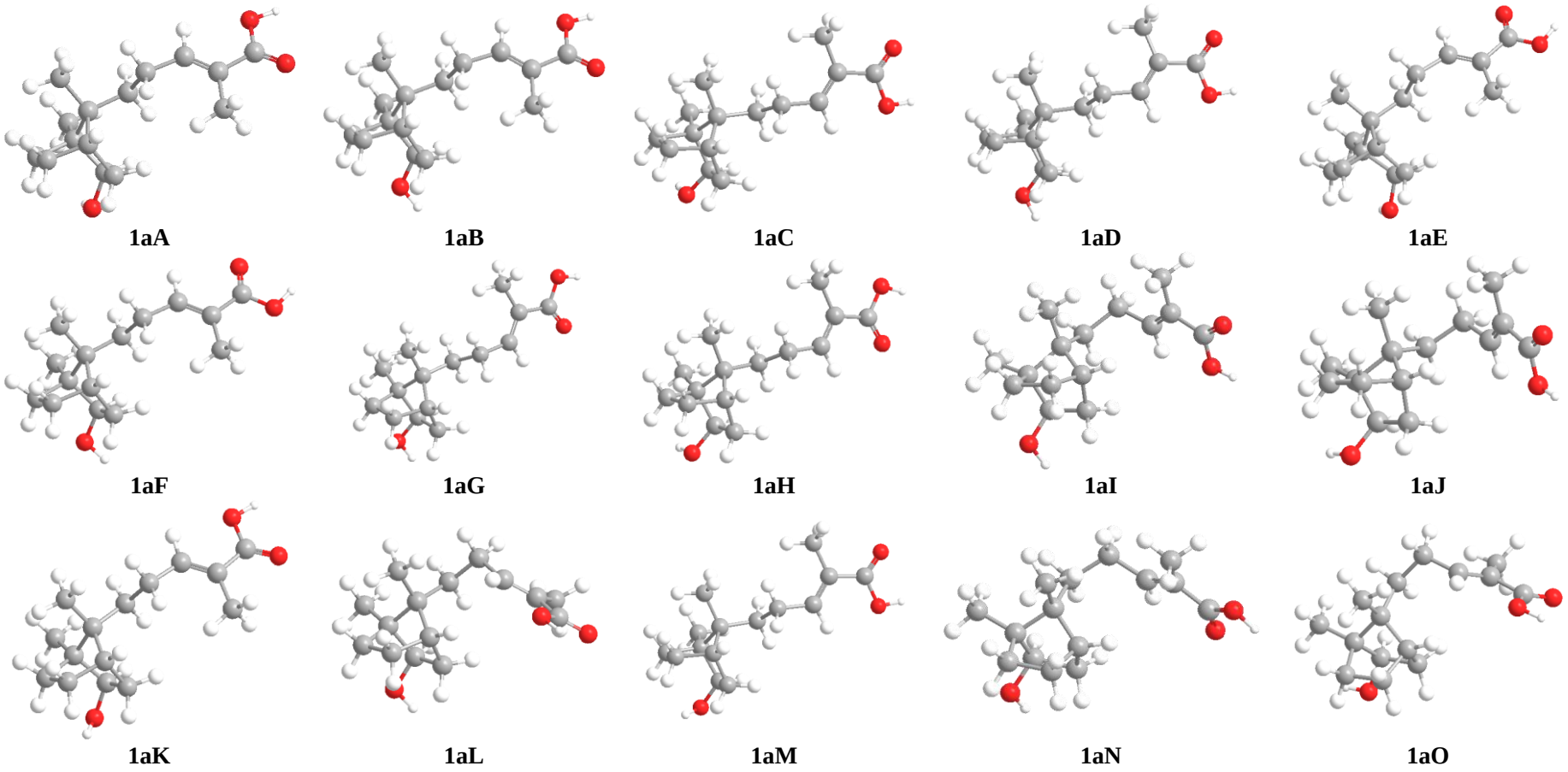
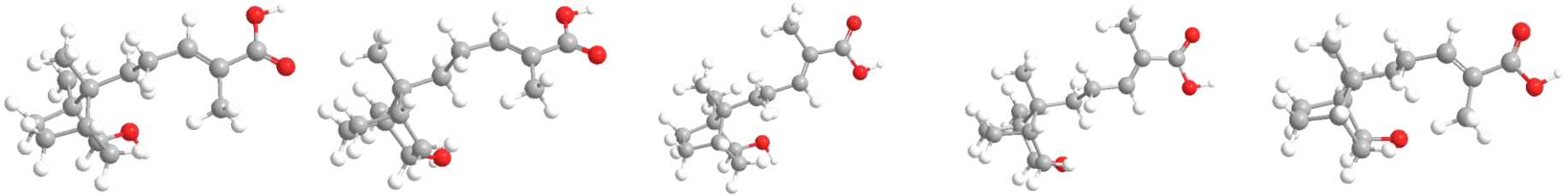


Table S2. Energy analysis for conformers of **1bA**–**1bP** at B3LYP/6-31G(d) level in the gas phase

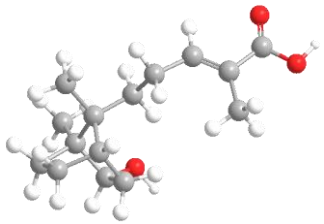
Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
1bA	-811.345766	-811.326731	-811.325786	-811.394434	0.000619	0.388428	14.06%
1bB	-811.346763	-811.327870	-811.326926	-811.395053	0	0	27.10%
1bC	-811.345556	-811.326611	-811.325667	-811.393516	0.001537	0.964482	5.32%
1bD	-811.346640	-811.327785	-811.326841	-811.394428	0.000625	0.392193	13.97%
1bE	-811.346793	-811.328048	-811.327104	-811.394436	0.000617	0.387173	14.09%
1bF	-811.345728	-811.326874	-811.325929	-811.393457	0.001596	1.001505	4.99%
1bG	-811.345653	-811.326791	-811.325847	-811.393483	0.001570	0.985190	5.13%
1bH	-811.343373	-811.324551	-811.323607	-811.390913	0.004140	2.597889	0.34%
1bI	-811.342002	-811.323287	-811.322343	-811.389135	0.005918	3.713601	0.05%
1bJ	-811.346722	-811.327950	-811.327006	-811.394361	0.000692	0.434237	13.02%
1bK	-811.344366	-811.325637	-811.324693	-811.391957	0.003096	1.942769	1.02%
1bL	-811.343380	-811.324693	-811.323749	-811.390469	0.004584	2.876504	0.21%
1bM	-811.343062	-811.324413	-811.323469	-811.390130	0.004923	3.089229	0.15%
1bN	-811.343313	-811.324423	-811.323479	-811.390889	0.004164	2.612950	0.33%
1bO	-811.342109	-811.323443	-811.322498	-811.389226	0.005827	3.656498	0.06%
1bP	-811.343167	-811.324573	-811.323629	-811.390197	0.004856	3.047186	0.16%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

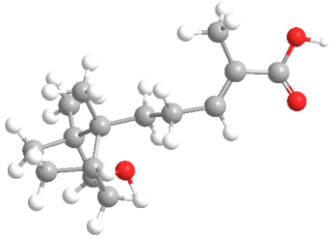
Figure S2. Main conformers of **1b** in NMR calculation.



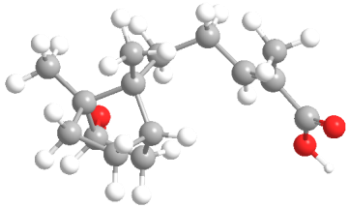
1bA **1bB** **1bC** **1bD** **1bE**



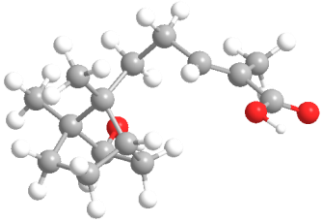
1bF



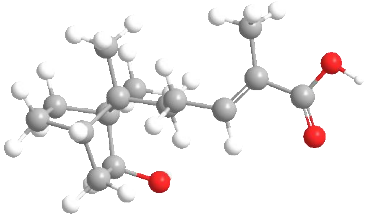
1bG



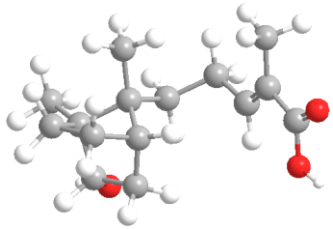
1bH



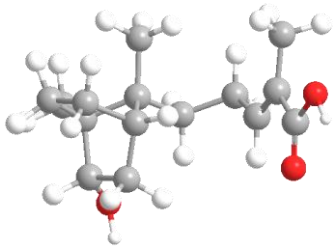
1bI



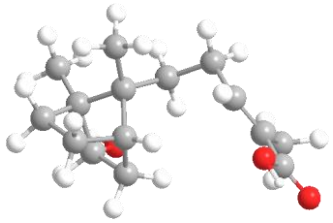
1bJ



1bK



1bL



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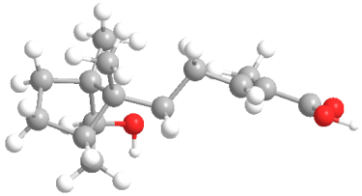
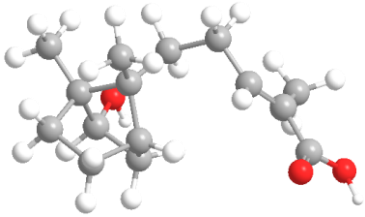
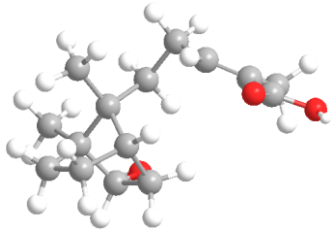


1bN



1bO



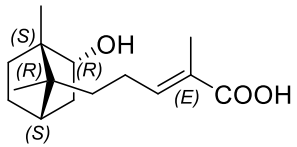
1bP

Table S3. DP4+ analysis results of **1a** (Isomer 1) and **1b** (Isomer 2) with **1**

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
12			DP4+	100.00%	0.00%	–	–	–
14	Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
15	C		49.9	131.3	131.5			
16	C		76.3	106.4	103.1			
17	C		37.6	146.4	145.3			
18	C		41.9	140.7	141.4			
19	C		27.5	156.6	157.3			
20	C		25.8	158.9	150.9			
21	C		50.9	130.1	132.2			
22	C		30.9	153.2	153.3			
23	C		24.5	157.6	158.2			
24	C	x	141.1	29.1	28.4			
25	C	x	128.5	55.5	56.0			
26	C	x	171.3	11.6	11.5			
27	C		11.2	173.4	173.5			
28	C		15.5	169.8	170.0			
29	C		12.3	173.4	175.6			
30								
31	H		4.02	27.67	28.06			
32	H		2.16	29.53	30.00			
33	H		1	30.81	30.13			
34	H		1.79	29.95	29.93			
35	H		1.27	30.05	30.09			
36	H		1.69	30.49	30.70			
37	H		1.23	29.67	30.85			
38	H		1.97	30.47	30.21			
39	H		1.46	30.48	29.21			
40	H		1.17	30.58	30.81			
41	H		2.07	29.42	29.43			
42	H		2.25	29.55	29.49			
43	H	x	6.69	24.30	24.29			
44	H		1.8	29.69	29.65			
45	H		1.8	30.02	30.02			
46	H		1.8	30.05	30.04			
47	H		0.93	31.11	31.10			
48	H		0.93	30.65	30.90			
49	H		0.93	30.64	30.53			
50	H		0.85	30.96	30.67			
51	H		0.85	30.74	30.98			
52	H		0.85	30.99	30.92			

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
4			Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
5	sDP4+ (H data)		100.00%	0.00%	-	-	-	-
6	sDP4+ (C data)		99.96%	0.04%	-	-	-	-
7	sDP4+ (all data)		100.00%	0.00%	-	-	-	-
8	uDP4+ (H data)		99.99%	0.01%	-	-	-	-
9	uDP4+ (C data)		99.99%	0.01%	-	-	-	-
10	uDP4+ (all data)		100.00%	0.00%	-	-	-	-
11	DP4+ (H data)		100.00%	0.00%	-	-	-	-
12	DP4+ (C data)		100.00%	0.00%	-	-	-	-
13	DP4+ (all data)		100.00%	0.00%	-	-	-	-

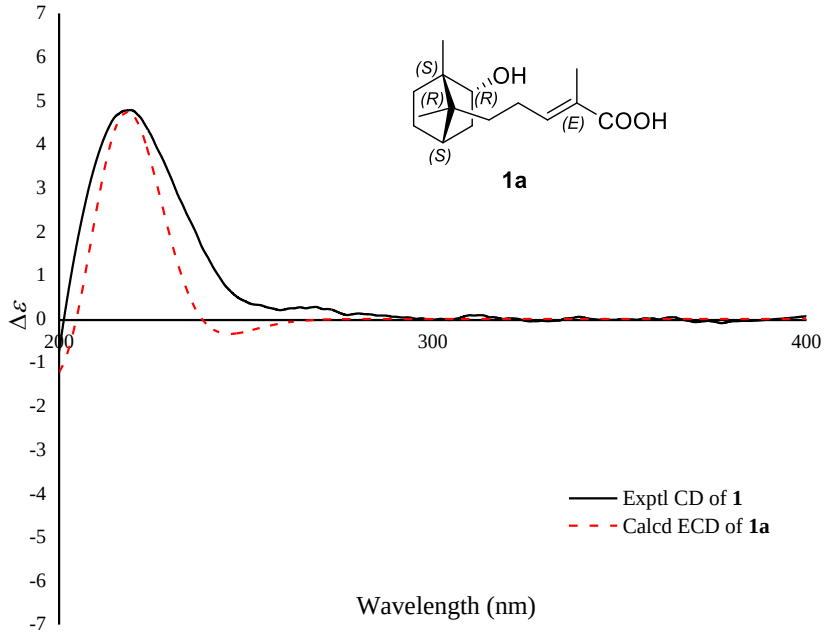
S1.2. Computational details for 1 (ECD)



1a

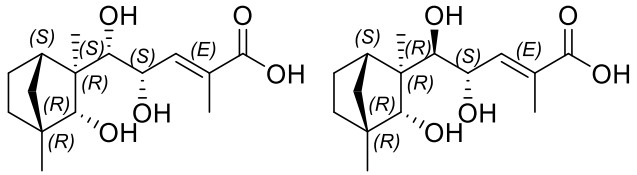
Conformation search based on molecular mechanics with MMFF force fields were performed for **1a** gave 15 stable conformers with populations higher than 1%. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 with σ = 0.30 eV, UV shift -10 nm.[5]

Figure S3. Comparison of the calculated ECD spectra for possible structure with the experimental spectrum of **1** in methanol with PCM model.



Section S2. Calculational details for 6

S2.1. Computational details for 6 (NMR)



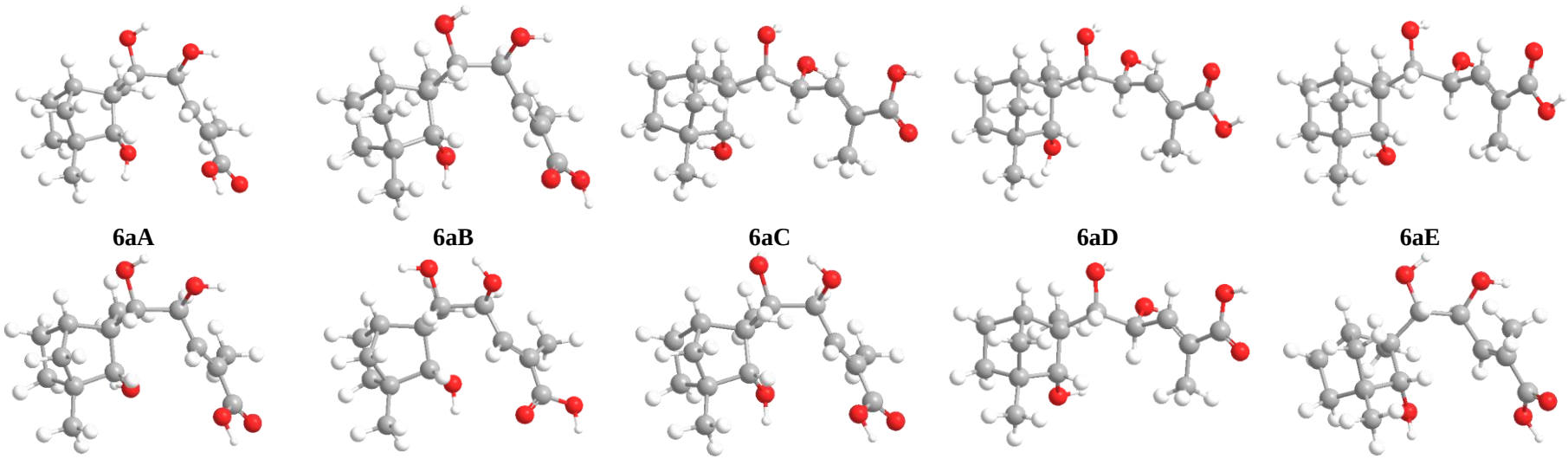
Conformation search based on molecular mechanics with MMFF force fields were performed for **6a** and **6b** gave 14 and 6 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. Gauge Independent Atomic Orbital (GIAO) calculations of their ^{1}H and ^{13}C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The ^{1}H and ^{13}C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by the improved probability DP4+ method.

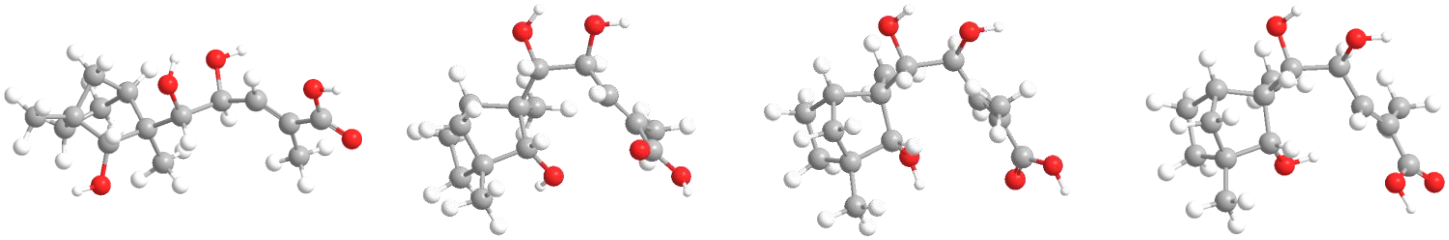
Table S4. Energy analysis for conformers of **6aA**–**6aN** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
6aA	-961.762350	-961.741395	-961.740451	-961.811097	0.002207	1.384913	3.09%
6aB	-961.762329	-961.741476	-961.740532	-961.810880	0.002424	1.521083	2.45%
6aC	-961.763374	-961.742292	-961.741348	-961.813304	0	0	32.01%
6aD	-961.763197	-961.742209	-961.741264	-961.812730	0.000574	0.360190	17.42%
6aE	-961.763360	-961.742398	-961.741453	-961.812880	0.000424	0.266064	20.42%
6aF	-961.762085	-961.741187	-961.740243	-961.810939	0.002365	1.484060	2.61%
6aG	-961.761002	-961.740193	-961.739249	-961.809492	0.003812	2.392066	0.56%
6aH	-961.761637	-961.740848	-961.739904	-961.810356	0.002948	1.849898	1.41%
6aI	-961.762385	-961.741255	-961.740311	-961.812327	0.000977	0.613077	11.37%
6aJ	-961.761694	-961.741115	-961.740171	-961.809567	0.003737	2.345003	0.61%
6aK	-961.761297	-961.740323	-961.739379	-961.810997	0.002307	1.447664	2.78%
6aL	-961.762100	-961.741290	-961.740346	-961.810727	0.002577	1.617092	2.09%
6aM	-961.763188	-961.742920	-961.741975	-961.810351	0.002953	1.853036	1.40%
6aN	-961.761903	-961.741079	-961.740135	-961.810582	0.002722	1.708081	1.79%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S4. Main conformers of **6a** in NMR calculation.





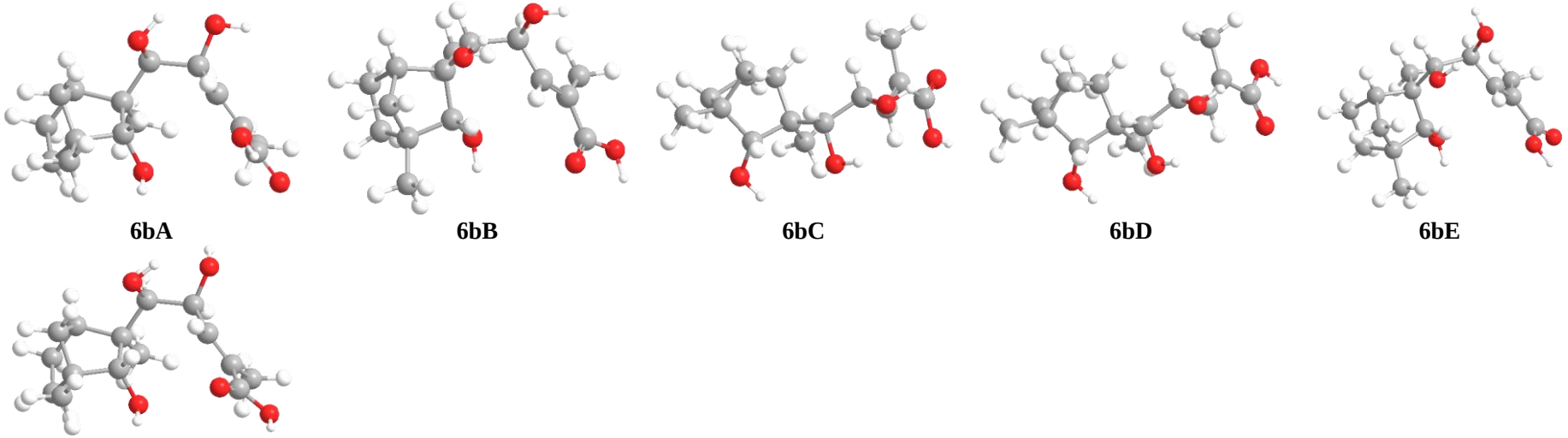
6aK **6aL** **6aM** **6aN**

Table S5. Energy analysis for conformers of **6bA**–**6bF** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
6bA	-961.759791	-961.738977	-961.738032	-961.808480	0.003372	2.115962	1.60%
6bB	-961.759853	-961.739083	-961.738139	-961.808436	0.003416	2.143572	1.53%
6bC	-961.762214	-961.741234	-961.740290	-961.811852	0	0	57.17%
6bD	-961.762236	-961.741352	-961.740407	-961.811482	0.000370	0.232179	38.63%
6bE	-961.758853	-961.738074	-961.737130	-961.807592	0.004260	2.673190	0.63%
6bF	-961.758789	-961.738105	-961.737160	-961.807263	0.004589	2.879641	0.44%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S5. Main conformers of **6b** in NMR and ECD calculations.



6bA **6bB** **6bC** **6bD** **6bE**

6bF

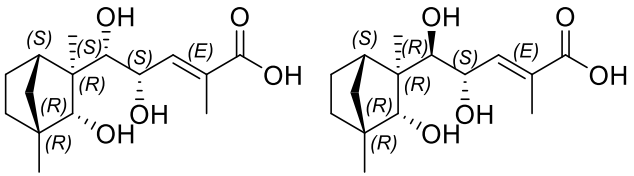
Table S6. DP4+ analysis results of **6a** (Isomer 1) and **6b** (Isomer 2) with **6**

Functional		Solvent?		Basis Set		Type of Data	
mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
		DP4+	0.00%	100.00%	–	–	–
Nuclei	sp2?	xperimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C		49.8	133.4	134.1			
C		82.2	103.1	100.4			
C		47.8	134.1	136.8			
C		44.7	139.4	139.4			
C		27.6	158.2	158.2			
C		26.7	159.4	159.5			
C		41.5	145.1	144.0			
C		80.5	107.7	104.1			
C		70.6	117.3	115.5			
C	x	138.4	36.2	37.0			
C	x	135.7	52.5	51.5			
C	x	176.1	11.3	11.6			
C		14.3	172.7	172.8			
C		19.9	175.0	175.1			
C		12.2	167.4	166.8			

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	–	–	–	–	–	–
sDP4+ (C data)	0.60%	99.40%	–	–	–	–
sDP4+ (all data)	0.60%	99.40%	–	–	–	–
uDP4+ (H data)	–	–	–	–	–	–
uDP4+ (C data)	0.14%	99.86%	–	–	–	–
uDP4+ (all data)	0.14%	99.86%	–	–	–	–
DP4+ (H data)	–	–	–	–	–	–
DP4+ (C data)	0.00%	100.00%	–	–	–	–
DP4+ (all data)	0.00%	100.00%	–	–	–	–

S2.2. Computational details for 6 (ECD)

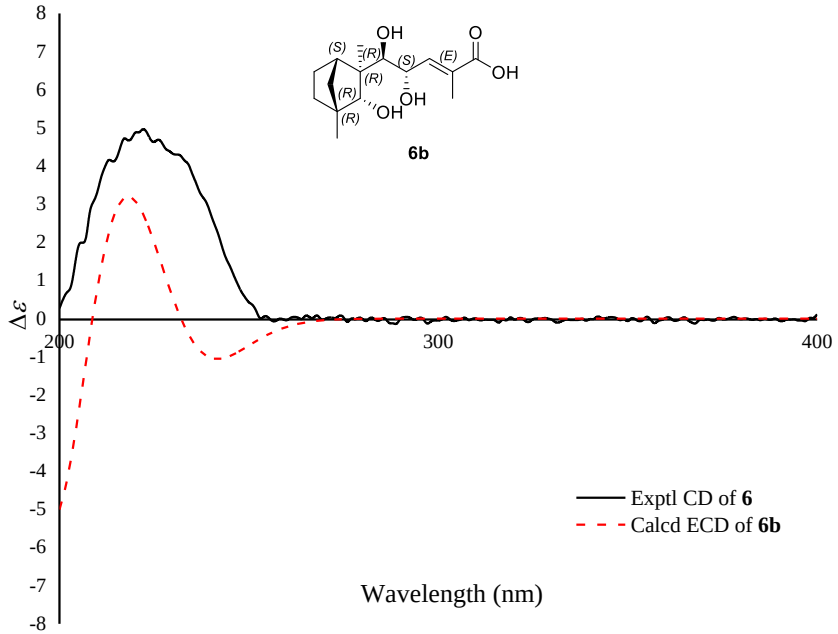


6a

6b

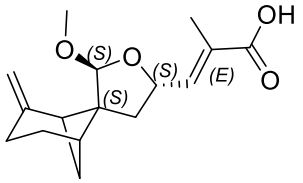
Conformation search based on molecular mechanics with MMFF force fields were performed for **6b** gave 6 stable conformers with populations higher than 1%. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71.

Figure S6. Comparison of the calculated ECD spectra for possible structure with the experimental spectrum of **6** in methanol with PCM model.

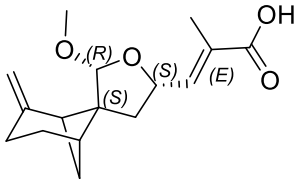


Section S3. Calculational details for 6*S*,9*S*,14*S*-7 and 6*S*,9*S*,14*R*-8

S3.1. Computational details for 6S,9S,14S-7 and 6S,9S,14R-8 (NMR)



7*S*,9*S*,14*S*-**7**



7*S*,9*S*,14*R*-**8**

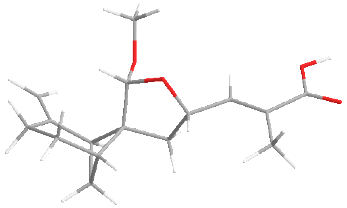
Conformation search based on molecular mechanics with MMFF force fields were performed for 7*S*,9*S*,14*S*-**7** and 7*S*,9*S*,14*R*-**8** gave 5 and 6 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. Gauge Independent Atomic Orbital (GIAO) calculations of their ^{1}H and ^{13}C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The ^{1}H and ^{13}C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by linear correlation coefficients (R^2) and the improved probability DP4+ method.

Table S7. Energy analysis for conformers of 7*S*,9*S*,14*R*-**8A**–7*S*,9*S*,14*R*-**8F** at B3LYP/6-31G(d) level in the gas phase

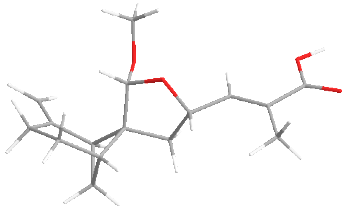
Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
7*S*,9*S*,14*R*-**8A**	-923.429467	-923.409966	-923.409022	-923.478920	0.000002	0.001255	25.87%
7*S*,9*S*,14*R*-**8B**	-923.429467	-923.409966	-923.409022	-923.478922	0	0	25.92%
7*S*,9*S*,14*R*-**8C**	-923.429472	-923.410060	-923.409116	-923.478765	0.000157	0.098519	21.95%
7*S*,9*S*,14*R*-**8D**	-923.429466	-923.409965	-923.409021	-923.478917	0.000005	0.003138	25.78%
7*S*,9*S*,14*R*-**8E**	-923.424220	-923.404699	-923.403755	-923.474439	0.004483	2.813125	0.22%
7*S*,9*S*,14*R*-**8F**	-923.425652	-923.406341	-923.405397	-923.474571	0.004351	2.730294	0.26%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

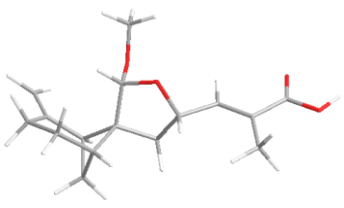
Figure S7. Main conformers of 7*S*,9*S*,14*R*-**8** in NMR and ECD calculations.



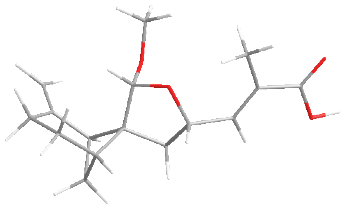
7*S*,9*S*,14*R*-**8A**



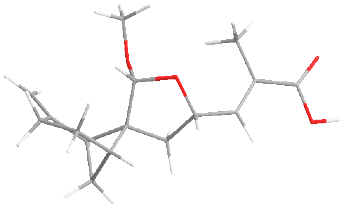
7*S*,9*S*,14*R*-**8B**



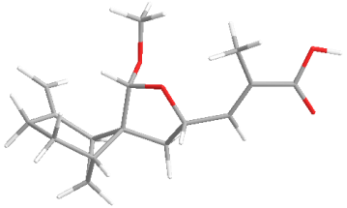
7*S*,9*S*,14*R*-**8C**



7*S*,9*S*,14*R*-**8D**



7*S*,9*S*,14*R*-**8E**

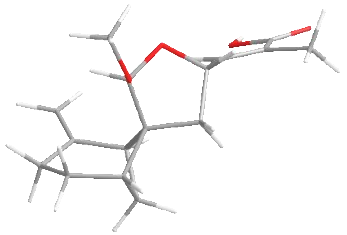


7*S*,9*S*,14*R*-**8F**

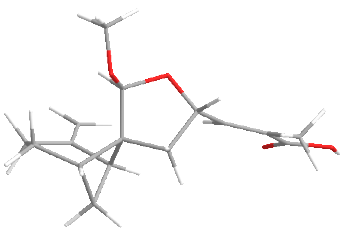
Table S8. Energy analysis for conformers of 6*S*,9*S*,14*S*-**7A**–6*S*,9*S*,14*S*-**7E** at B3LYP/6-31G(d) level in the gas phase

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
7*S*,9*S*,14*S*-**7A**	-923.430034	-923.410552	-923.409608	-923.479402	0	0	46.18%
7*S*,9*S*,14*S*-**7B**	-923.430071	-923.410679	-923.409735	-923.479299	0.000103	0.064633	41.41%
7*S*,9*S*,14*S*-**7C**	-923.427379	-923.407883	-923.406939	-923.477329	0.002073	1.300827	5.13%
7*S*,9*S*,14*S*-**7D**	-923.427568	-923.408186	-923.407242	-923.477005	0.002397	1.504140	3.64%
7*S*,9*S*,14*S*-**7E**	-923.427568	-923.408186	-923.407242	-923.477005	0.002397	1.504140	3.64%

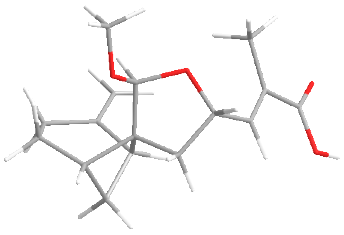
Figure S8. Main conformers of 7*S*,9*S*,14*S*-**7** in NMR and ECD calculations.



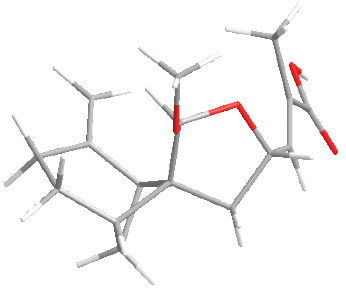
7*S*,9*S*,14*S*-**7A**



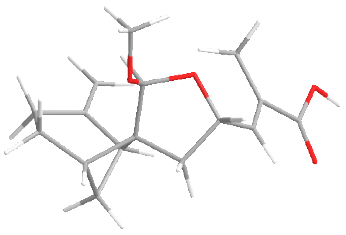
7*S*,9*S*,14*S*-**7B**



7*S*,9*S*,14*S*-**7C**



7*S*,9*S*,14*S*-**7D**



7*S*,9*S*,14*S*-**7E**

Table S9. DP4+ analysis results of 7*S*,9*S*,14*R*-**8** (Isomer 1) and 7*S*,9*S*,14*S*-**7** (Isomer 2) with 7*S*,9*S*,14*R*-**8**

Functional		Solvent?		Basis Set		Type of Data	
mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
		DP4+	86.91%	13.09%	–	–	–
Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C		49.1	134.7	132.2			
C	x	151	24.8	24.2			
C		24.3	159.9	159.5			
C		24.7	160.6	160.3			
C		40.6	144.3	144.2			
C		56.5	126.7	127.2			
C		29.1	159.6	160.2			
C		39.4	146.4	144.3			
C		75.7	108.9	108.9			
C	x	144.2	30.0	30.4			
C	x	130.2	55.0	55.1			
C	x	171.3	11.7	11.5			
C		12.8	173.3	172.9			
C		106.8	78.8	77.3			
C	x	107.8	75.1	74.8			
C		55.4	132.3	132.6			

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	–	–	–	–	–	–
sDP4+ (C data)	89.98%	10.02%	–	–	–	–
sDP4+ (all data)	89.98%	10.02%	–	–	–	–
uDP4+ (H data)	–	–	–	–	–	–
uDP4+ (C data)	42.51%	57.49%	–	–	–	–
uDP4+ (all data)	42.51%	57.49%	–	–	–	–
DP4+ (H data)	–	–	–	–	–	–
DP4+ (C data)	86.91%	13.09%	–	–	–	–
DP4+ (all data)	86.91%	13.09%	–	–	–	–

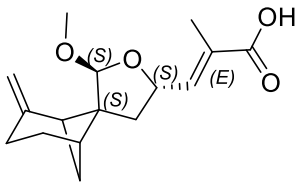
Table S10. DP4+ analysis results of 7*S*,9*S*,14*R*-**8** (Isomer 1) and 7*S*,9*S*,14*S*-**7** (Isomer 2) with 7*S*,9*S*,14*S*-**7**

Functional		Solvent?		Basis Set		Type of Data	
mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
		DP4+	0.11%	99.89%	–	–	–
Nuclei	sp2?	xperimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C		52	134.7	132.2			
C	x	150	24.8	24.2			
C		23.1	159.9	159.5			
C		23.5	160.6	160.3			
C		39.4	144.3	144.2			
C		54.7	126.7	127.2			
C		26.5	159.6	160.2			
C		40.4	146.4	144.3			
C		73.7	108.9	108.9			
C	x	143	30.0	30.4			
C	x	128.1	55.0	55.1			
C	x	169.8	11.7	11.5			
C		11.4	173.3	172.9			
C		106.4	78.8	77.3			
C	x	107	75.1	74.8			
C		53.3	132.3	132.6			

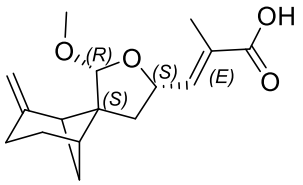
Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-311+G(d,p)	Shielding Tensors

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	–	–	–	–	–	–
sDP4+ (C data)	2.83%	97.17%	–	–	–	–
sDP4+ (all data)	2.83%	97.17%	–	–	–	–
uDP4+ (H data)	–	–	–	–	–	–
uDP4+ (C data)	3.72%	96.28%	–	–	–	–
uDP4+ (all data)	3.72%	96.28%	–	–	–	–
DP4+ (H data)	–	–	–	–	–	–
DP4+ (C data)	0.11%	99.89%	–	–	–	–
DP4+ (all data)	0.11%	99.89%	–	–	–	–

S3.2. Computational details for 7S,9S,14R-8 and 7S,9S,14S-7 (ECD)



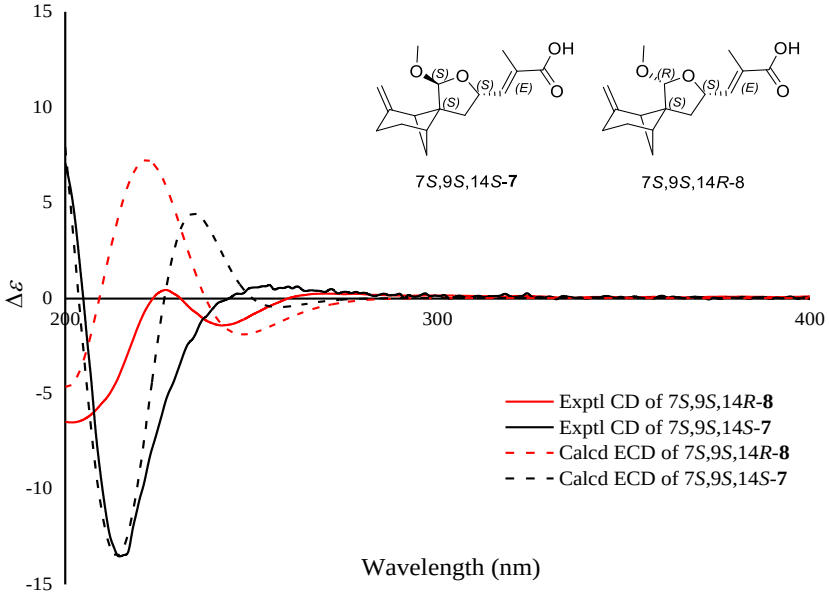
7*S*,9*S*,14*S*-**7**



7*S*,9*S*,14*R*-**8**

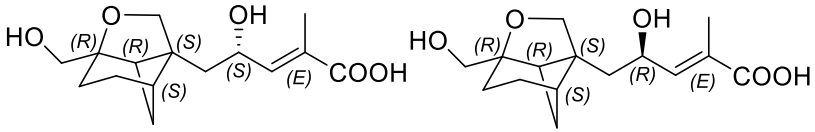
Conformation search based on molecular mechanics with MMFF force fields were performed for 7*S*,9*S*,14*S*-**7** and 7*S*,9*S*,14*R*-**8** gave 5 and 6 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 with σ = 0.30 eV, UV shift -20 and -10 nm, respectively.

Figure S9. Comparison of the calculated ECD spectra for possible structure with the experimental spectrum of 7*S*,9*S*,14*S*-**7** and 7*S*,9*S*,14*R*-**8** in methanol.



Section S4. Calculational details for 10

S4.1. Computational details for 10 (ECD)



10a **10b**

Conformation search based on molecular mechanics with MMFF force fields were performed for **10a** and **10b** gave 9 and 12 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 with σ = 0.30 eV, UV shift -18 and -18 nm, respectively.

Figure S10. Comparison of the calculated ECD spectra for possible structure with the experimental spectrum of **10** in methanol with PCM model.

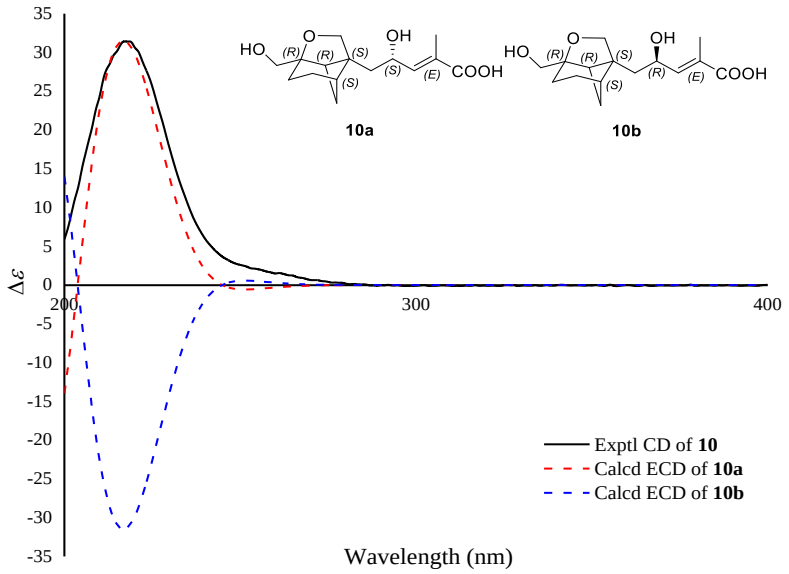


Table S11. Energy analysis for conformers of **10aA**–**10aI** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
10aA	-960.558406	-960.538984	-960.538040	-960.607670	0	0	38.64%
10aB	-960.558367	-960.539069	-960.538125	-960.607301	0.000369	0.231551	26.14%
10aC	-960.556762	-960.537217	-960.536273	-960.606432	0.001238	0.776857	10.41%
10aD	-960.557455	-960.538090	-960.537146	-960.606438	0.001232	0.773092	10.47%
10aE	-960.556308	-960.537096	-960.536152	-960.604867	0.002803	1.758909	1.98%
10aF	-960.556735	-960.537309	-960.536365	-960.605920	0.001750	1.098142	6.05%
10aG	-960.556376	-960.537295	-960.536351	-960.604531	0.003139	1.969752	1.39%
10aH	-960.555902	-960.536542	-960.535598	-960.604874	0.002796	1.754517	2.00%
10aI	-960.556216	-960.536805	-960.535860	-960.605236	0.002434	1.527358	2.93%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S11. Main conformers of **10a** in ECD calculation.

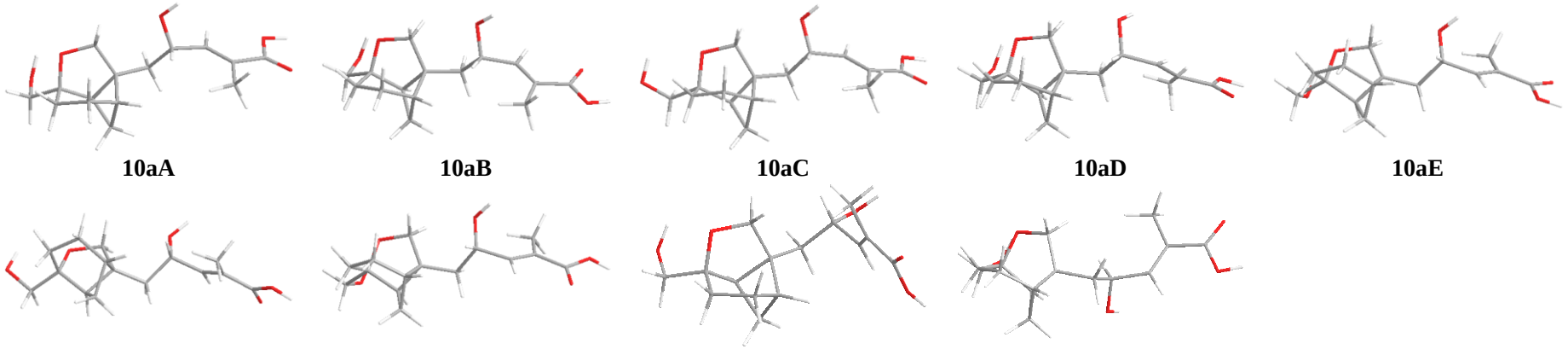


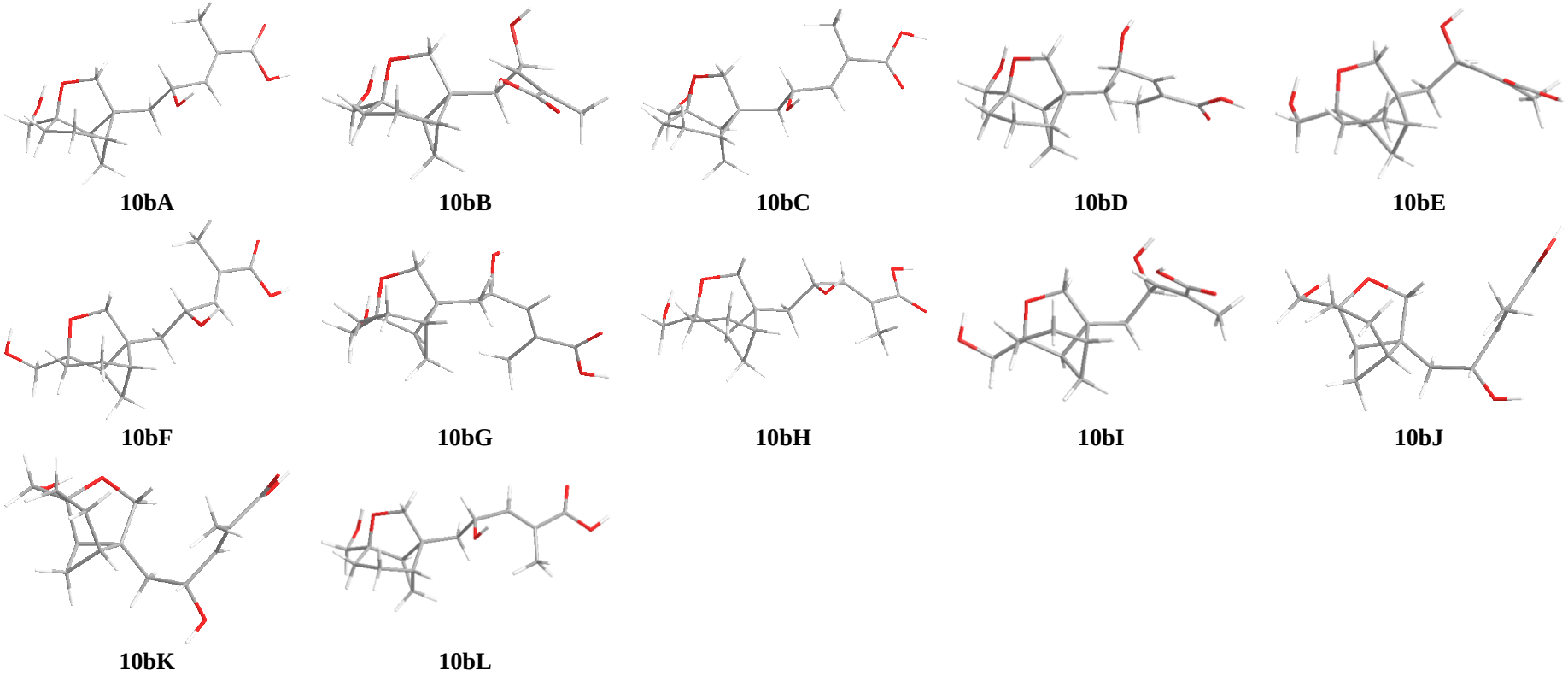
Table S12. Energy analysis for conformers of **10bA**–**10bL** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
10bA	-960.557174	-960.537738	-960.536794	-960.606304	0	0	29.81%
10bB	-960.555406	-960.536074	-960.535130	-960.604205	0.002099	1.317142	3.22%
10bC	-960.557188	-960.537843	-960.536899	-960.606157	0.000147	0.092244	25.51%
10bD	-960.556102	-960.536710	-960.535766	-960.605386	0.000918	0.576054	11.27%
10bE	-960.555361	-960.536147	-960.535203	-960.603769	0.002535	1.590737	2.03%

10bF	-960.555494	-960.535950	-960.535006	-960.604963	0.001341	0.841490	7.20%
10bG	-960.556164	-960.536849	-960.535905	-960.605279	0.001025	0.643197	10.06%
10bH	-960.555043	-960.535766	-960.534822	-960.604090	0.002214	1.389306	2.85%
10bI	-960.553717	-960.534287	-960.533343	-960.602677	0.003627	2.275977	0.64%
10bJ	-960.556008	-960.536753	-960.535809	-960.604568	0.001736	1.089356	4.73%
10bK	-960.554282	-960.534900	-960.533956	-960.602934	0.003370	2.114707	0.84%
10bL	-960.555095	-960.535952	-960.535008	-960.603677	0.002627	1.648467	1.84%

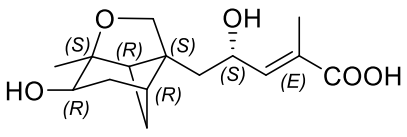
E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S12. Main conformers of **10b** in ECD calculation.

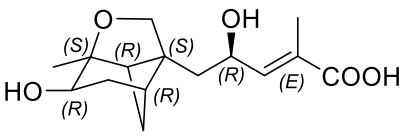


Section S5. Calculational details for 11

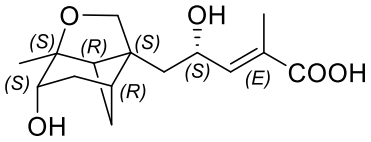
S5.1. Computational details for 11 (NMR)



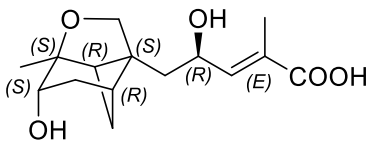
11a



11b



11a



11b

Conformation search based on molecular mechanics with MMFF force fields were performed for **11a**, **11b**, **11c** and **11d** gave 8, 14, 3 and 4 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. Gauge Independent Atomic Orbital (GIAO) calculations of their ^{1}H and ^{13}C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The ^{1}H and ^{13}C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by the improved probability DP4+ method.

Table S13. Energy analysis for conformers of **11aA**–**11aH** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
11aA	-960.564000	-960.544556	-960.543611	-960.612659	0	0	33.74%
11aB	-960.564017	-960.544659	-960.543714	-960.612494	0.000165	0.103539	28.33%
11aC	-960.561967	-960.542677	-960.541733	-960.610252	0.002407	1.510415	2.63%
11aD	-960.563096	-960.543659	-960.542715	-960.611756	0.000903	0.566641	12.96%
11aE	-960.562085	-960.542885	-960.541941	-960.610227	0.002432	1.526103	2.56%
11aF	-960.563234	-960.543882	-960.542938	-960.611794	0.000865	0.542796	13.49%
11aG	-960.561573	-960.542129	-960.541185	-960.610009	0.002650	1.662900	2.03%
11aH	-960.561958	-960.542440	-960.541496	-960.610703	0.001956	1.227409	4.25%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S13. Main conformers of **11a** in NMR calculation.

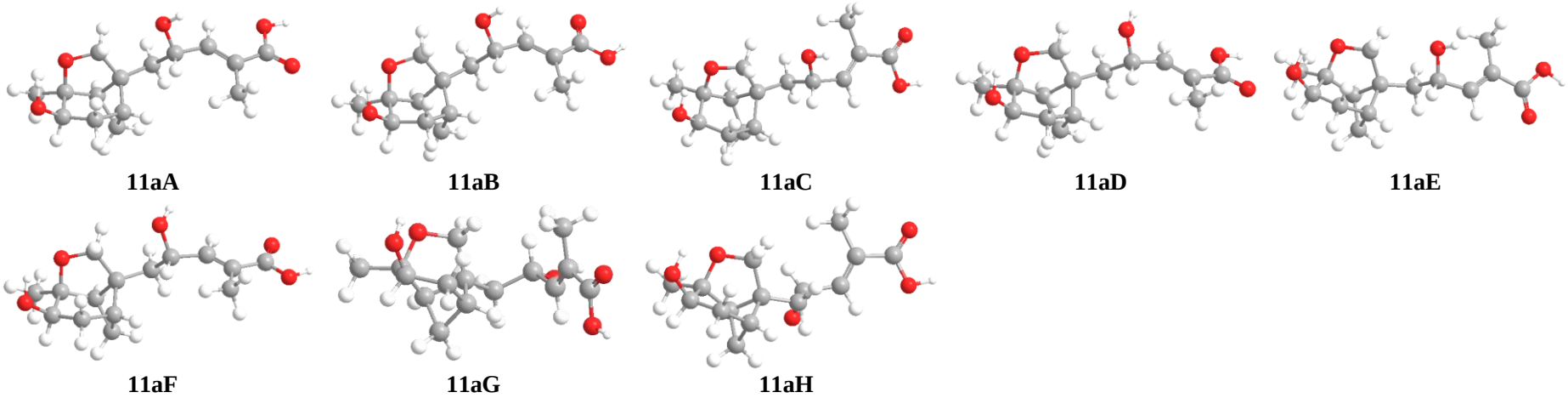


Table S14. Energy analysis for conformers of **11bA**–**11bN** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
11bA	-960.562876	-960.543336	-960.542392	-960.611789	0.000304	0.190763	22.95%
11bB	-960.561084	-960.541698	-960.540754	-960.609465	0.002628	1.649095	1.96%
11bC	-960.562955	-960.543476	-960.542532	-960.612093	0	0	31.68%
11bD	-960.561578	-960.542164	-960.541220	-960.609996	0.002097	1.315887	3.43%
11bE	-960.561044	-960.541770	-960.540825	-960.609041	0.003052	1.915159	1.25%
11bF	-960.561830	-960.542299	-960.541354	-960.611060	0.001033	0.648217	10.60%
11bG	-960.560382	-960.540978	-960.540034	-960.608983	0.003110	1.951555	1.17%
11bH	-960.560787	-960.541426	-960.540482	-960.609337	0.002756	1.729416	1.71%
11bI	-960.561946	-960.542458	-960.541514	-960.610675	0.001418	0.889808	7.05%
11bJ	-960.561607	-960.542290	-960.541345	-960.609776	0.002317	1.453940	2.72%
11bK	-960.562044	-960.542663	-960.541719	-960.610520	0.001573	0.987072	5.98%
11bL	-960.560888	-960.541631	-960.540687	-960.609218	0.002875	1.804090	1.50%
11bM	-960.561806	-960.542394	-960.541450	-960.610718	0.001375	0.862826	7.38%
11bN	-960.559956	-960.540460	-960.539516	-960.608382	0.003711	2.328688	0.62%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S14. Main conformers of **11b** in NMR calculation.

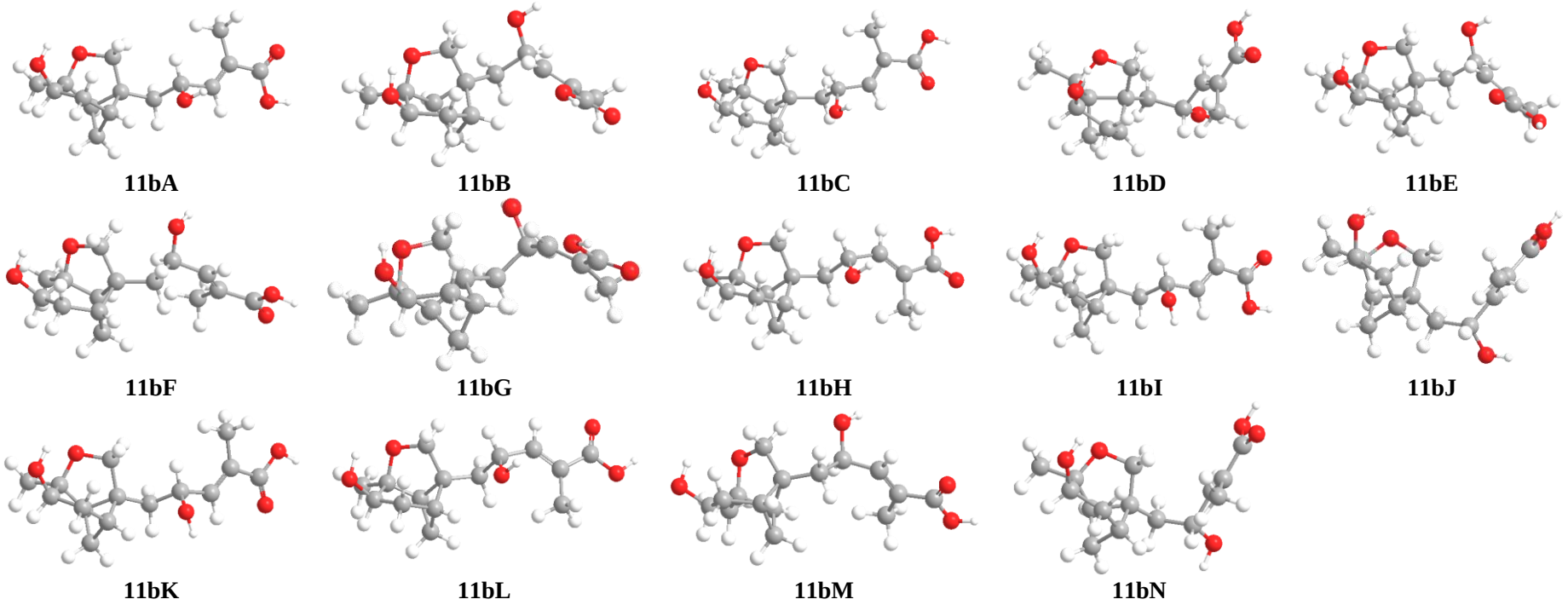
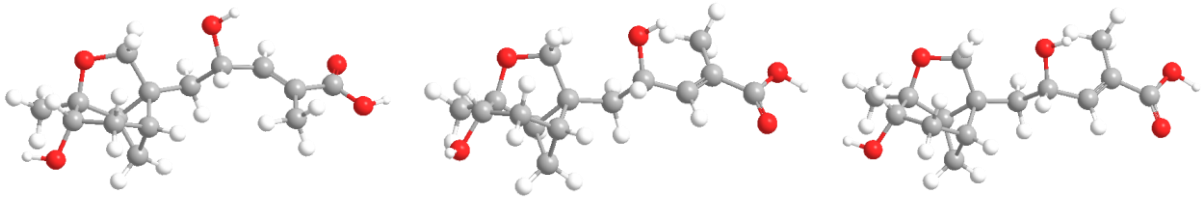


Table S15. Energy analysis for conformers of **11cA**–**11cC** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
11cA	-960.559341	-960.539753	-960.538809	-960.608210	0	0	89.73%
11cB	-960.557064	-960.537596	-960.536652	-960.605459	0.002751	1.726279	4.86%
11cC	-960.557322	-960.537958	-960.537014	-960.605559	0.002651	1.663528	5.40%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S15. Main conformers of **11c** in NMR and ECD calculations.



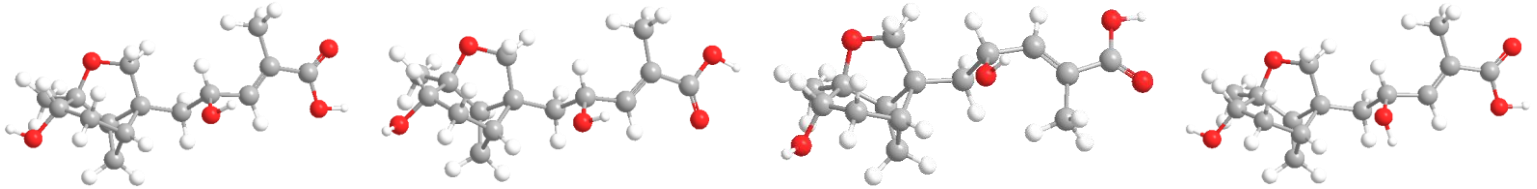
11cA **11cB** **11cC**

Table S16. Energy analysis for conformers of **11dA**–**11dD** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
11dA	-960.558201	-960.538472	-960.537528	-960.607671	0	0	43.87%
11dB	-960.557972	-960.538260	-960.537316	-960.607436	0.000235	0.147465	34.20%
11dC	-960.555786	-960.536186	-960.535242	-960.604696	0.002975	1.866841	1.87%
11dD	-960.557404	-960.537690	-960.536745	-960.606932	0.000739	0.463730	20.05%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S16. Main conformers of **11d** in NMR calculation.



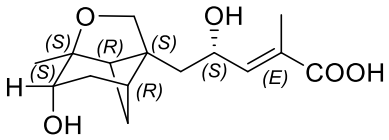
11dA **11dB** **11dC** **11dD**

Table S17. DP4+ analysis results of **11a** (Isomer 1), **11b** (Isomer 2), **11c** (Isomer 3) and **11d** (Isomer 4) with **11**

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	▪PW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
12			DP4+	0.00%	0.00%	100.00%	0.00%	-
14	Nuclei	sp2?	xperimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
15	C		87.4	95.4	93.9	96.6	94.6	
16	C		72.3	114.6	114.6	109.3	109.5	
17	C		32.9	149.9	150.3	151.9	151.4	
18	C		37.9	145.5	143.2	146.5	144.0	
19	C		22.8	163.2	163.7	162.9	163.5	
20	C		51.3	133.1	133.0	132.7	132.0	
21	C		54.7	128.4	128.6	127.8	128.1	
22	C		71.5	111.2	113.5	111.6	114.1	
23	C		21	165.5	165.4	165.7	165.1	
24	C		40.1	146.1	147.1	146.1	146.0	
25	C		65.8	116.5	114.9	116.9	114.1	
26	C	x	141.8	30.7	30.6	29.6	30.5	
27	C	x	129.3	54.6	54.5	54.5	54.7	
28	C	x	172.2	11.6	11.6	11.5	11.6	
29	C		11.8	172.8	172.8	172.8	172.8	
30								
31	H		3.63	28.11	28.15	28.07	28.03	
32	H		2.25	29.36	29.43	29.43	29.40	
33	H		1.85	30.25	30.26	29.85	30.00	
34	H		2.27	29.45	29.32	29.45	29.14	
35	H		2.12	29.82	29.78	29.84	29.75	
36	H		2.06	30.32	30.38	29.61	29.61	
37	H		2.1	29.53	29.53	29.71	29.73	
38	H		3.85	28.07	27.90	28.08	28.13	
39	H		3.61	27.78	27.86	27.76	27.74	
40	H		1.31	30.03	30.01	30.53	30.52	
41	H		1.31	30.85	30.83	30.69	30.72	
42	H		1.31	30.61	30.61	30.23	30.17	
43	H		2	29.90	29.68	29.90	29.62	
44	H		1.81	30.00	30.22	30.00	30.35	
45	H		4.42	27.13	27.16	27.02	27.25	
46	H	x	6.57	24.54	24.55	24.47	24.56	
47	H		1.83	30.03	29.87	29.65	29.92	
48	H		1.83	29.85	29.99	29.96	29.93	
49	H		1.83	29.82	29.90	29.84	30.04	

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
4			Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
5	sDP4+ (H data)		0.16%	0.12%	98.00%	1.72%	-	-
6	sDP4+ (C data)		11.64%	0.05%	86.80%	1.51%	-	-
7	sDP4+ (all data)		0.02%	0.00%	99.95%	0.03%	-	-
8	uDP4+ (H data)		0.33%	0.60%	75.68%	23.40%	-	-
9	uDP4+ (C data)		38.20%	0.41%	59.62%	1.77%	-	-
10	uDP4+ (all data)		0.27%	0.01%	98.81%	0.91%	-	-
11	DP4+ (H data)		0.00%	0.00%	99.46%	0.54%	-	-
12	DP4+ (C data)		7.91%	0.00%	92.04%	0.05%	-	-
13	DP4+ (all data)		0.00%	0.00%	100.00%	0.00%	-	-

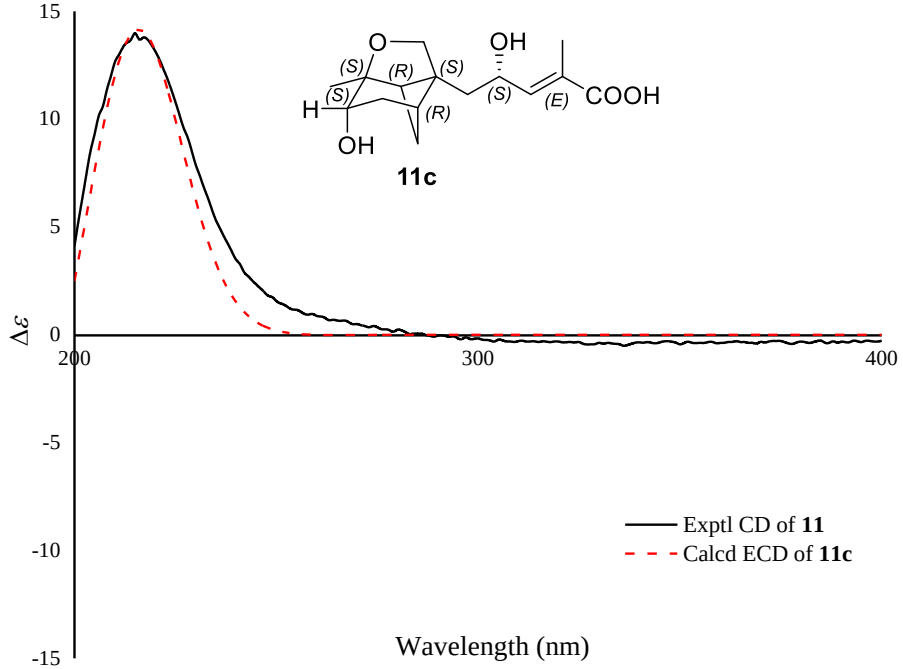
S5.2. Computational details for 11 (ECD)



11c

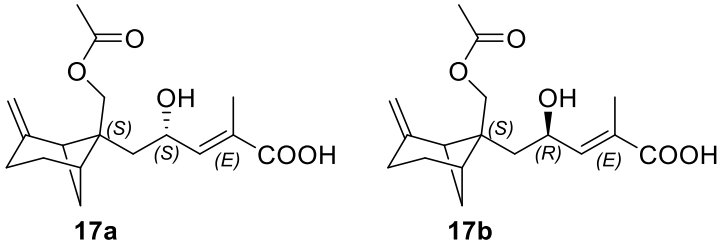
Conformation search based on molecular mechanics with MMFF force fields were performed for **11c** gave 3 stable conformers with populations higher than 1%. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71.

Figure S17. Comparison of the calculated ECD spectra for possible structure with the experimental spectrum of **11** in methanol with PCM model.



Section S6. Calculational details for 17

S6.1. Computational details for 17 (ECD)



Conformation search based on molecular mechanics with MMFF force fields were performed for **17a** and **17b** gave 19 and 13 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 with σ = 0.30 eV, UV shift -30, and -27 nm, respectively.

Figure S18. Comparison of the calculated ECD spectra for possible structure with the experimental spectrum of **17** in methanol with PCM model.

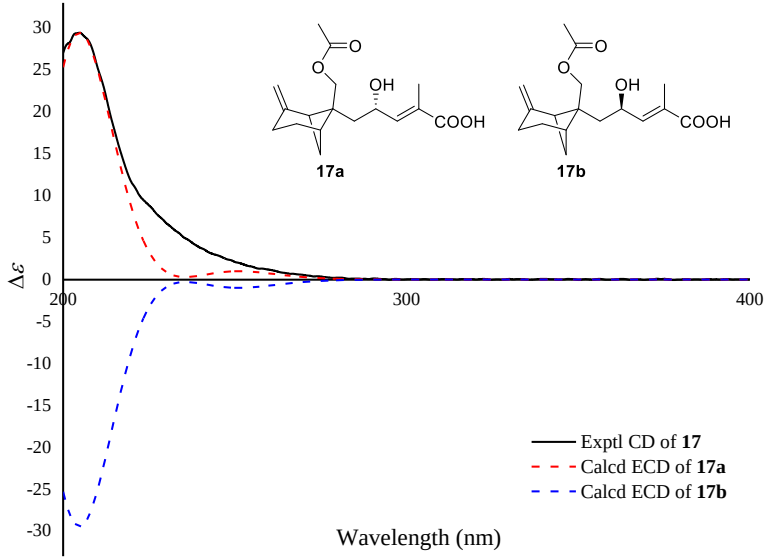
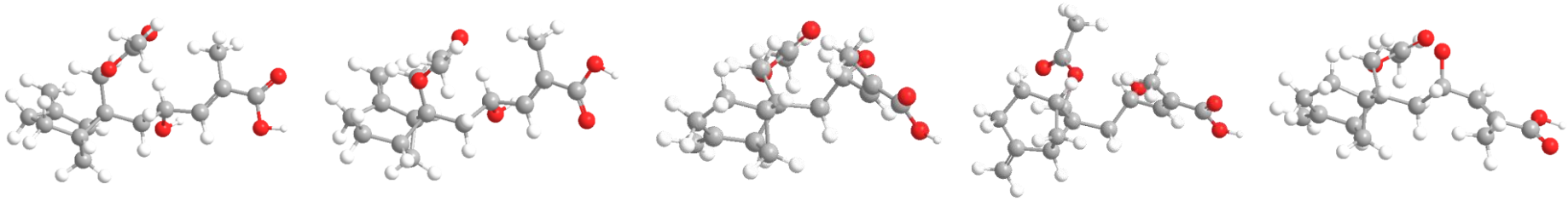


Table S18. Energy analysis for conformers of **17aA**–**17aS** at B3LYP/6-31G(d) level in the gas phase

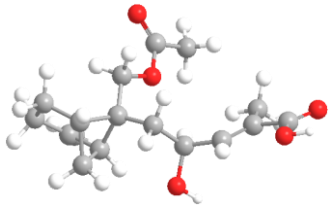
Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
17aA	-1037.954922	-1037.931906	-1037.930962	-1038.009872	0.000998	0.626254	8.07%
17aB	-1037.954900	-1037.931995	-1037.931051	-1038.009603	0.001267	0.795055	6.07%
17aC	-1037.952727	-1037.929956	-1037.929012	-1038.008229	0.002641	1.657253	1.41%
17aD	-1037.954573	-1037.931695	-1037.930751	-1038.009911	0.000959	0.601782	8.41%
17aE	-1037.956899	-1037.934403	-1037.933459	-1038.010870	0	0	23.23%
17aF	-1037.952910	-1037.929807	-1037.928863	-1038.007908	0.002962	1.858683	1.01%
17aG	-1037.952671	-1037.930038	-1037.929093	-1038.007451	0.003419	2.145455	0.62%
17aH	-1037.954512	-1037.931415	-1037.930470	-1038.010222	0.000648	0.406626	11.69%
17aI	-1037.952702	-1037.929941	-1037.928997	-1038.006025	0.004845	3.040284	0.14%
17aJ	-1037.956917	-1037.934534	-1037.933590	-1038.010575	0.000295	0.185115	16.99%
17aK	-1037.952971	-1037.930055	-1037.929111	-1038.007230	0.003640	2.284135	0.49%
17aL	-1037.954477	-1037.931736	-1037.930792	-1038.009324	0.001546	0.970130	4.51%
17aM	-1037.952423	-1037.929553	-1037.928609	-1038.007503	0.003367	2.112824	0.66%
17aN	-1037.952905	-1037.929889	-1037.928945	-1038.007778	0.003092	1.940259	0.88%
17aO	-1037.953996	-1037.931149	-1037.930205	-1038.008502	0.002368	1.485942	1.89%
17aP	-1037.951652	-1037.928838	-1037.927894	-1038.005231	0.005639	3.538526	0.06%
17aQ	-1037.954566	-1037.931535	-1037.930591	-1038.010238	0.000632	0.396586	11.89%
17aR	-1037.952907	-1037.929841	-1037.928897	-1038.008204	0.002666	1.672940	1.38%
17aS	-1037.954282	-1037.931902	-1037.930958	-1038.007455	0.003415	2.142945	0.62%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

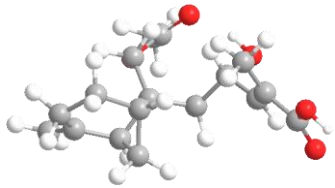
Figure S19. Main conformers of **17a** in NMR calculation.



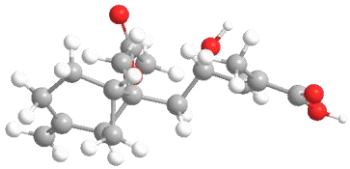
17aA **17aB** **17aC** **17aD** **17aE**



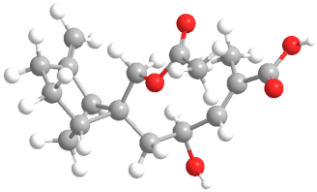
17aF



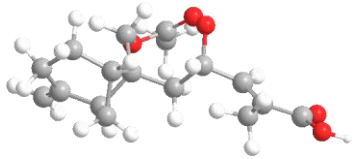
17aG



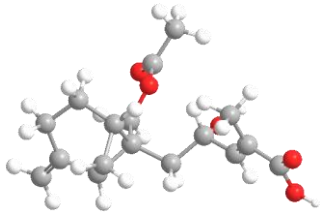
17aH



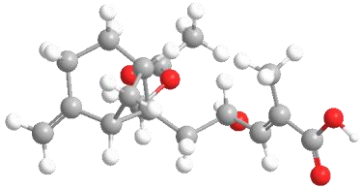
17aI



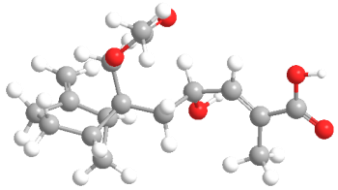
17aJ



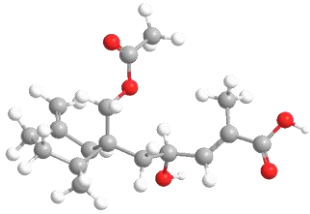
17aK



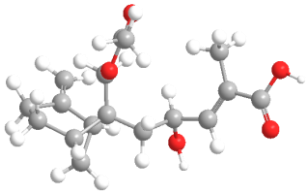
17aL



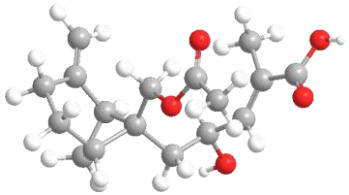
17aM



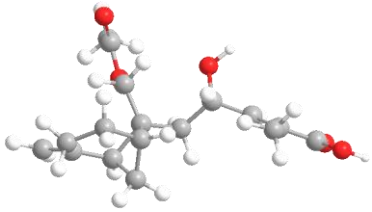
17aN



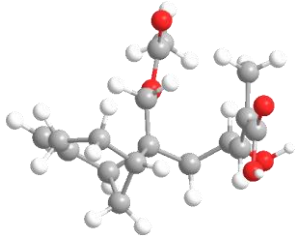
17aO



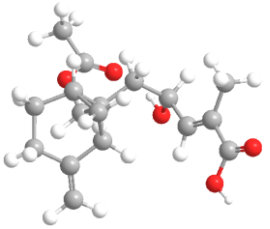
17aP



17aQ



17aR



17aS

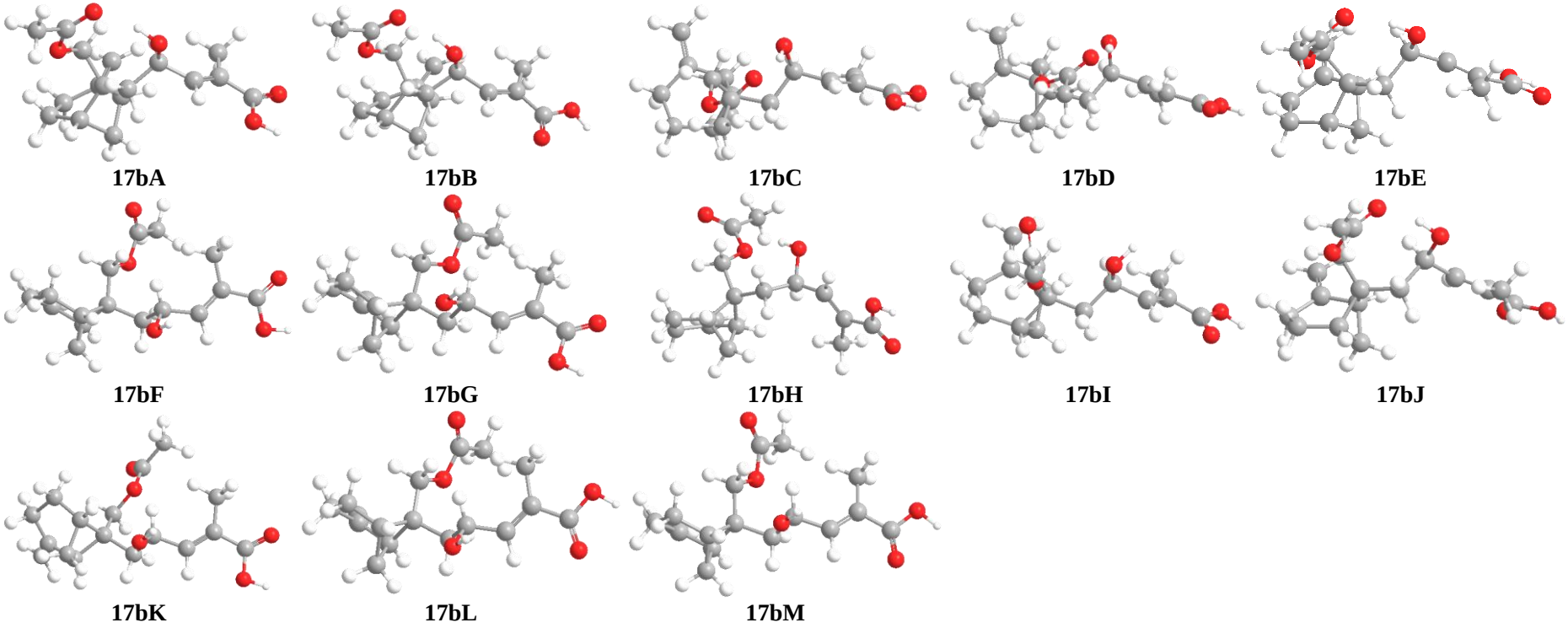
Table S19. Energy analysis for conformers of **17bA**–**17bM** at B3LYP/6-31G(d) level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
17bA	-1037.953692	-1037.931004	-1037.930060	-1038.008273	0.003730	2.340610	0.63%
17bB	-1037.953707	-1037.931091	-1037.930147	-1038.008255	0.003748	2.351906	0.61%
17bC	-1037.957696	-1037.935163	-1037.934219	-1038.012003	0	0	32.61%
17bD	-1037.957682	-1037.935279	-1037.934335	-1038.011465	0.000538	0.337600	18.44%
17bE	-1037.952088	-1037.929485	-1037.928541	-1038.007015	0.004988	3.130017	0.17%
17bF	-1037.955135	-1037.931994	-1037.931050	-1038.010634	0.001369	0.859061	7.64%
17bG	-1037.955134	-1037.931994	-1037.931049	-1038.010630	0.001373	0.861571	7.61%
17bH	-1037.953943	-1037.931073	-1037.930129	-1038.009434	0.002569	1.612072	2.14%
17bI	-1037.955129	-1037.932096	-1037.931152	-1038.010980	0.001023	0.641942	11.03%
17bJ	-1037.952229	-1037.929774	-1037.928830	-1038.006576	0.005427	3.405494	0.10%
17bK	-1037.953621	-1037.930410	-1037.929466	-1038.009994	0.002009	1.260667	3.88%
17bL	-1037.955175	-1037.932115	-1037.931171	-1038.010661	0.001342	0.842118	7.87%

17bM	-1037.955170	-1037.932116	-1037.931172	-1038.010586	0.001417	0.889181	7.26%

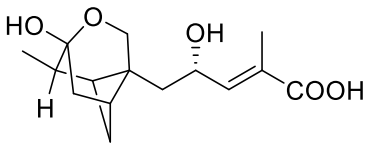
E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S20. Main conformers of **17b** in NMR calculation.

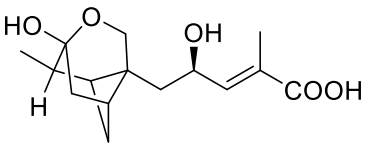


Section S7. Calculational details for 18

S7.1. Computational details for 18 (ECD)



18a



18b

Conformation search based on molecular mechanics with MMFF force fields were performed for **18a** and **18b** gave 15 and 15 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 with σ = 0.30 eV, UV shift -15 nm, respectively.

Figure S21. Comparison of the calculated ECD spectra for possible structure with the experimental spectrum of **18** in methanol with PCM model.

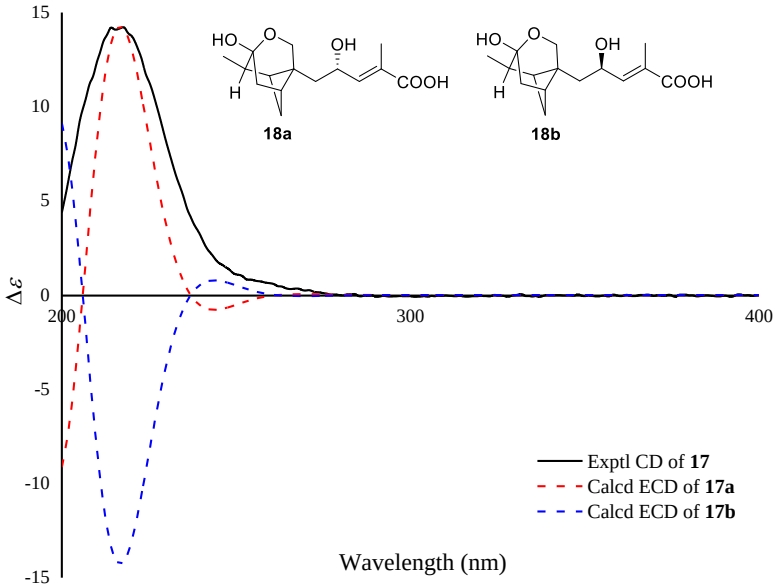
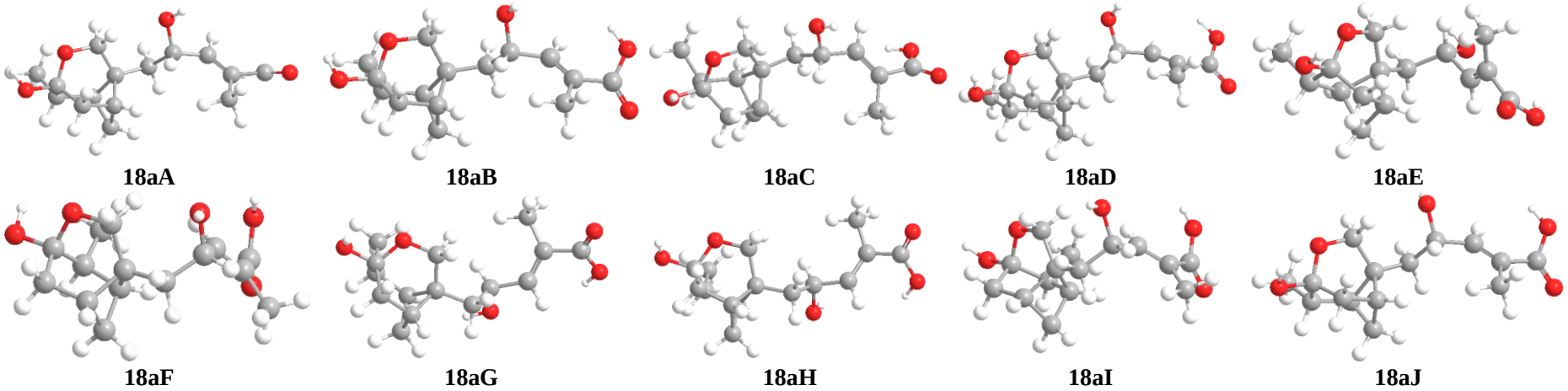


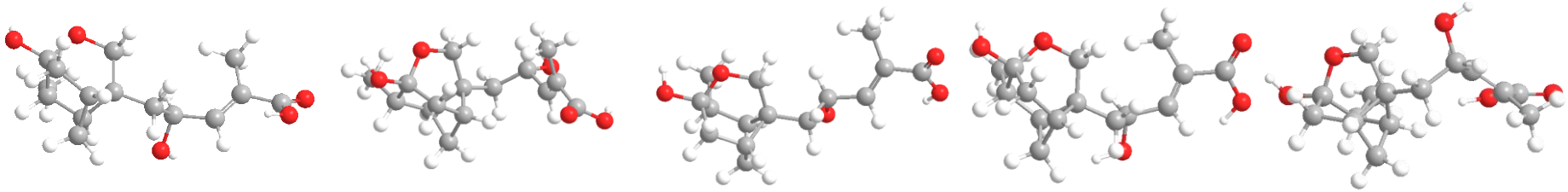
Table S20. Energy analysis for conformers of **18aA**–**18aO** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
18aA	-960.561201	-960.541471	-960.540527	-960.610254	0.000720	0.451807	12.44%
18aB	-960.561263	-960.541510	-960.540566	-960.610561	0.000413	0.259161	17.22%
18aC	-960.561689	-960.541944	-960.540999	-960.610974	0	0	26.68%
18aD	-960.561723	-960.541980	-960.541036	-960.610728	0.000246	0.154367	20.56%
18aE	-960.557772	-960.538018	-960.537074	-960.606245	0.004729	2.967492	0.18%
18aF	-960.557257	-960.537630	-960.536686	-960.605515	0.005459	3.425574	0.08%
18aG	-960.559111	-960.539480	-960.538535	-960.607200	0.003774	2.368221	0.49%
18aH	-960.560759	-960.541057	-960.540113	-960.609676	0.001298	0.814507	6.74%
18aI	-960.557588	-960.538003	-960.537059	-960.605721	0.005253	3.296307	0.10%
18aJ	-960.560599	-960.540903	-960.539959	-960.609559	0.001415	0.887926	5.95%
18aK	-960.560580	-960.540882	-960.539938	-960.609372	0.001602	1.005270	4.88%
18aL	-960.557152	-960.537439	-960.536495	-960.605472	0.005502	3.452557	0.08%
18aM	-960.560295	-960.540578	-960.539634	-960.609233	0.001741	1.092494	4.22%
18aN	-960.558630	-960.538988	-960.538044	-960.606814	0.004160	2.610440	0.32%
18aO	-960.557747	-960.538275	-960.537331	-960.605187	0.005787	3.631397	0.06%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

Figure S22. Main conformers of **18a** in ECD calculation.





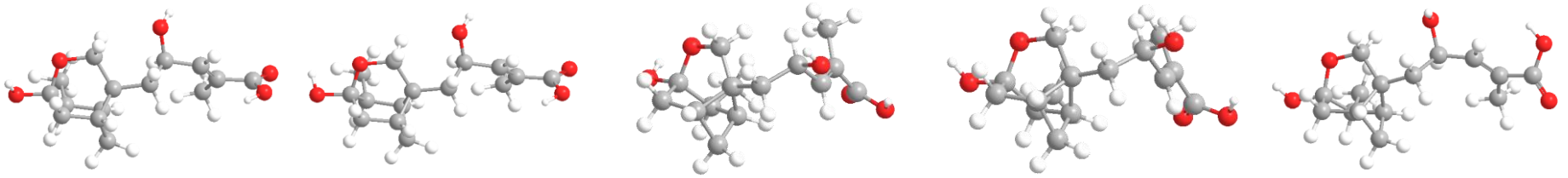
18aK **18aL** **18aM** **18aN** **18aO**

Table S21. Energy analysis for conformers of **18bA**–**18bO** at B3LYP/6-31G(d) level in the gas phase

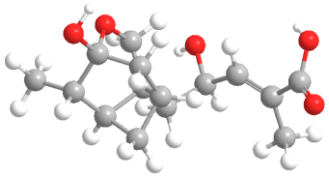
Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
18bA	-960.561660	-960.541916	-960.540972	-960.610939	0	0	30.89%
18bB	-960.561246	-960.541492	-960.540548	-960.610729	0.000210	0.131777	24.73%
18bC	-960.557222	-960.537523	-960.536579	-960.605340	0.005599	3.513426	0.08%
18bD	-960.557619	-960.537922	-960.536977	-960.605701	0.005238	3.286895	0.12%
18bE	-960.560570	-960.540854	-960.539910	-960.609889	0.001050	0.658885	10.15%
18bF	-960.557739	-960.538128	-960.537183	-960.605867	0.005072	3.182728	0.14%
18bG	-960.561247	-960.541528	-960.540584	-960.610209	0.000730	0.458082	14.25%
18bH	-960.560178	-960.540471	-960.539527	-960.609523	0.001416	0.888553	6.89%
18bI	-960.558765	-960.539080	-960.538136	-960.607242	0.003697	2.319903	0.61%
18bJ	-960.560659	-960.540957	-960.540013	-960.609619	0.001320	0.828313	7.63%
18bK	-960.558814	-960.539218	-960.538274	-960.606926	0.004013	2.518196	0.44%
18bL	-960.559207	-960.539530	-960.538586	-960.607645	0.003294	2.067016	0.94%
18bM	-960.557203	-960.537608	-960.536663	-960.605332	0.005607	3.518446	0.08%
18bN	-960.559270	-960.539651	-960.538707	-960.607454	0.003485	2.186871	0.77%
18bO	-960.559280	-960.539695	-960.538751	-960.608480	0.002459	1.543046	2.28%

E, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

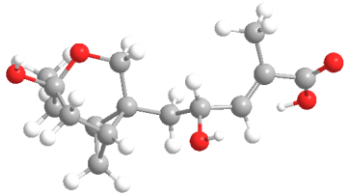
Figure S23. Main conformers of **18b** in ECD calculation.



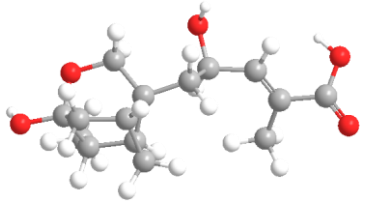
18bA **18bB** **18bC** **18bD** **18bE**



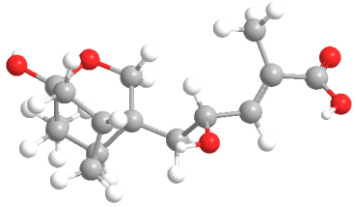
18bF



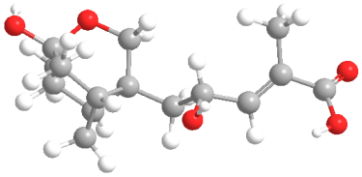
18bG



18bH



18bI



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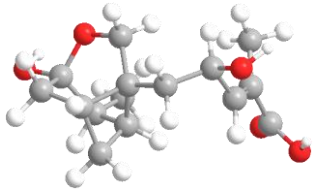

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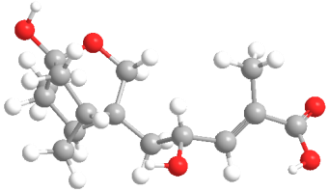
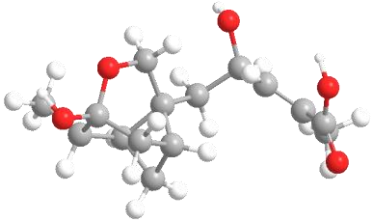
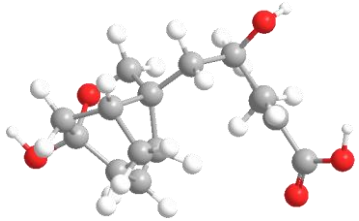


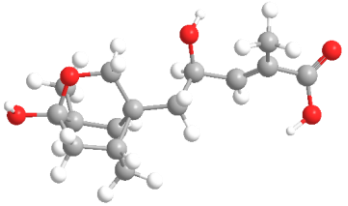
18bL



18bM



18bN



18bO

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Section S8. NMR and MS spectra for 1

Figure S24. ^{1}H NMR of compound **1** in CD_3OD

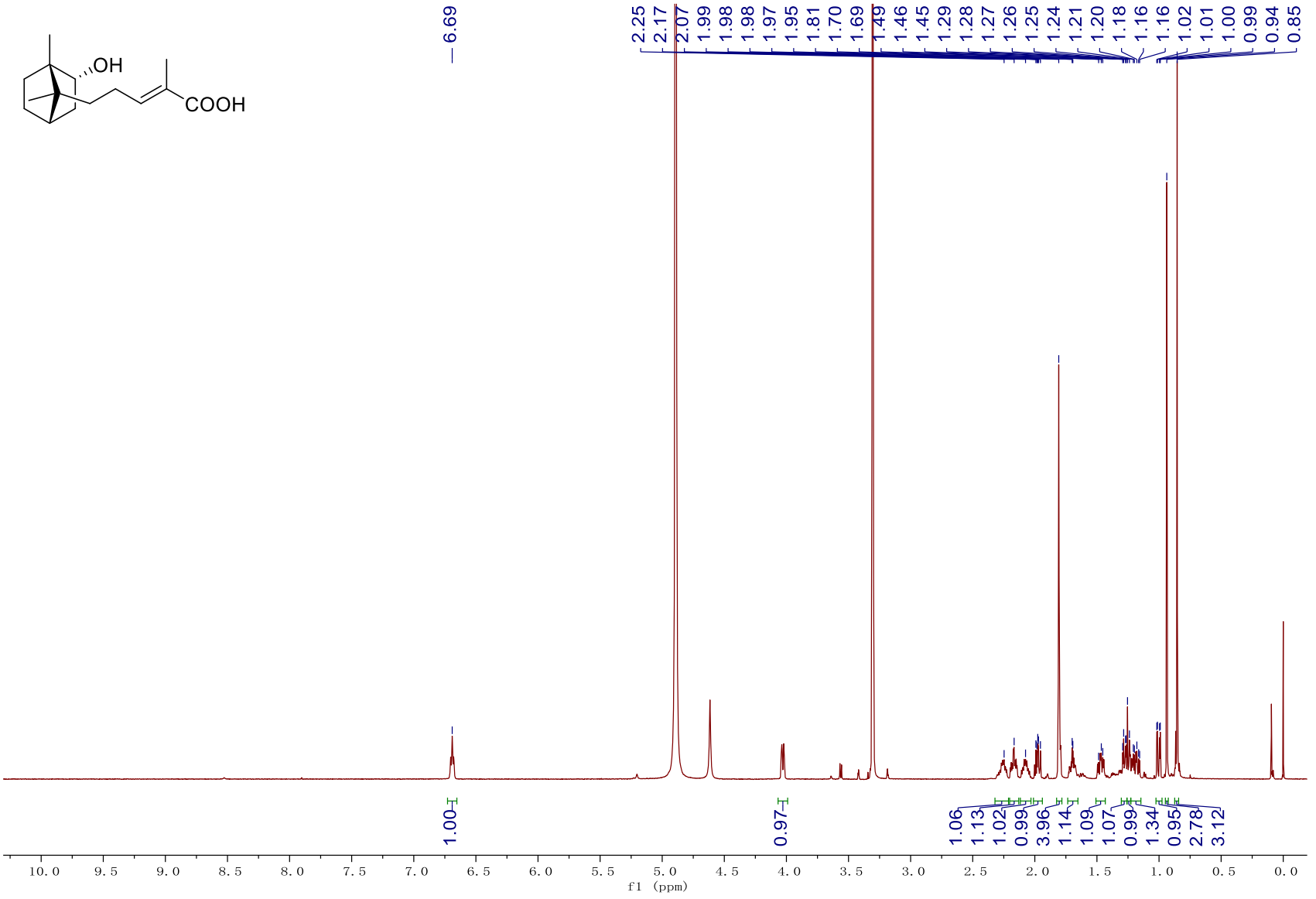


Figure S25. ^{13}C NMR and DEPT of compound **1** in CD_3OD

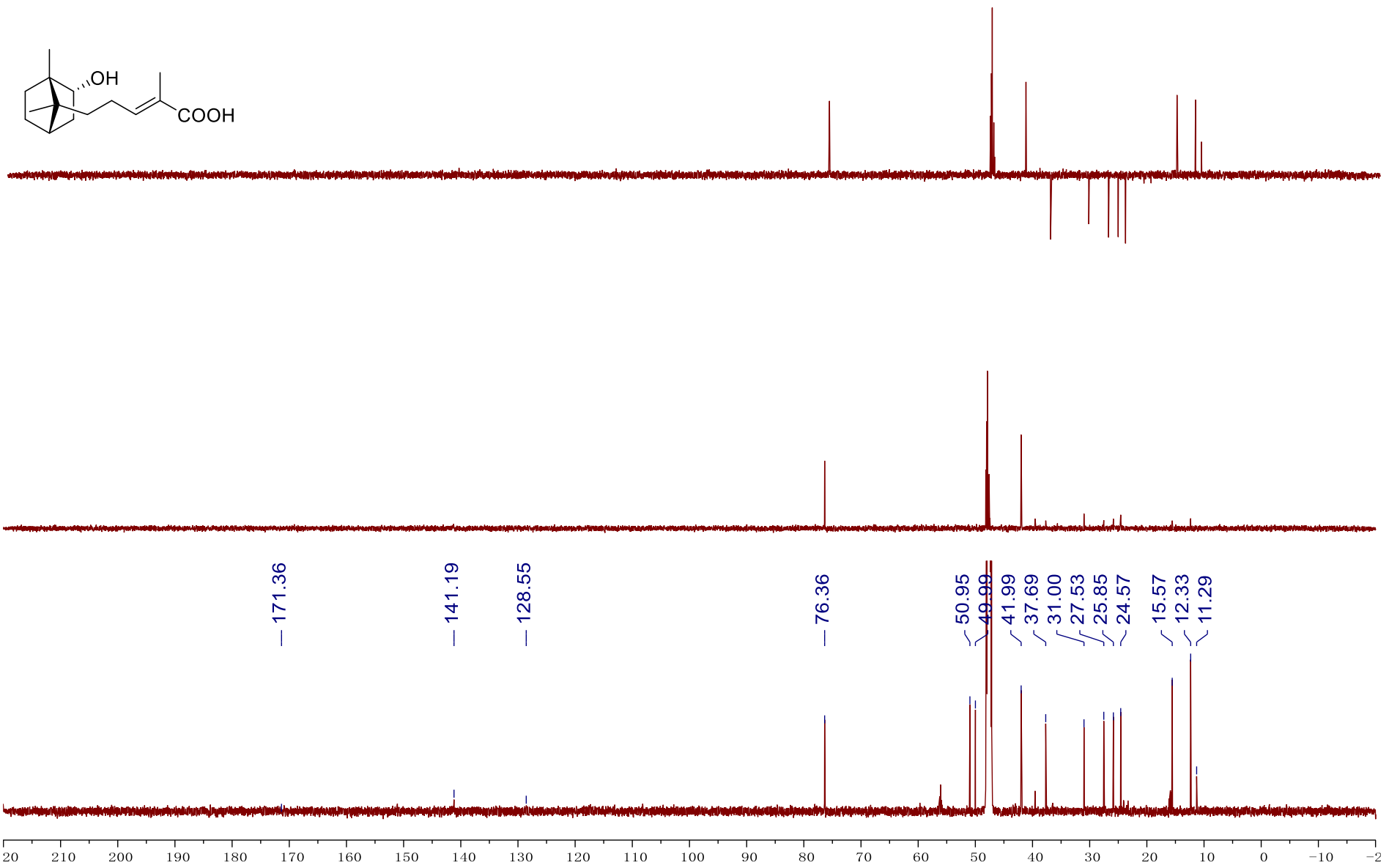


Figure S26. HSQC of compound **1** in CD_3OD

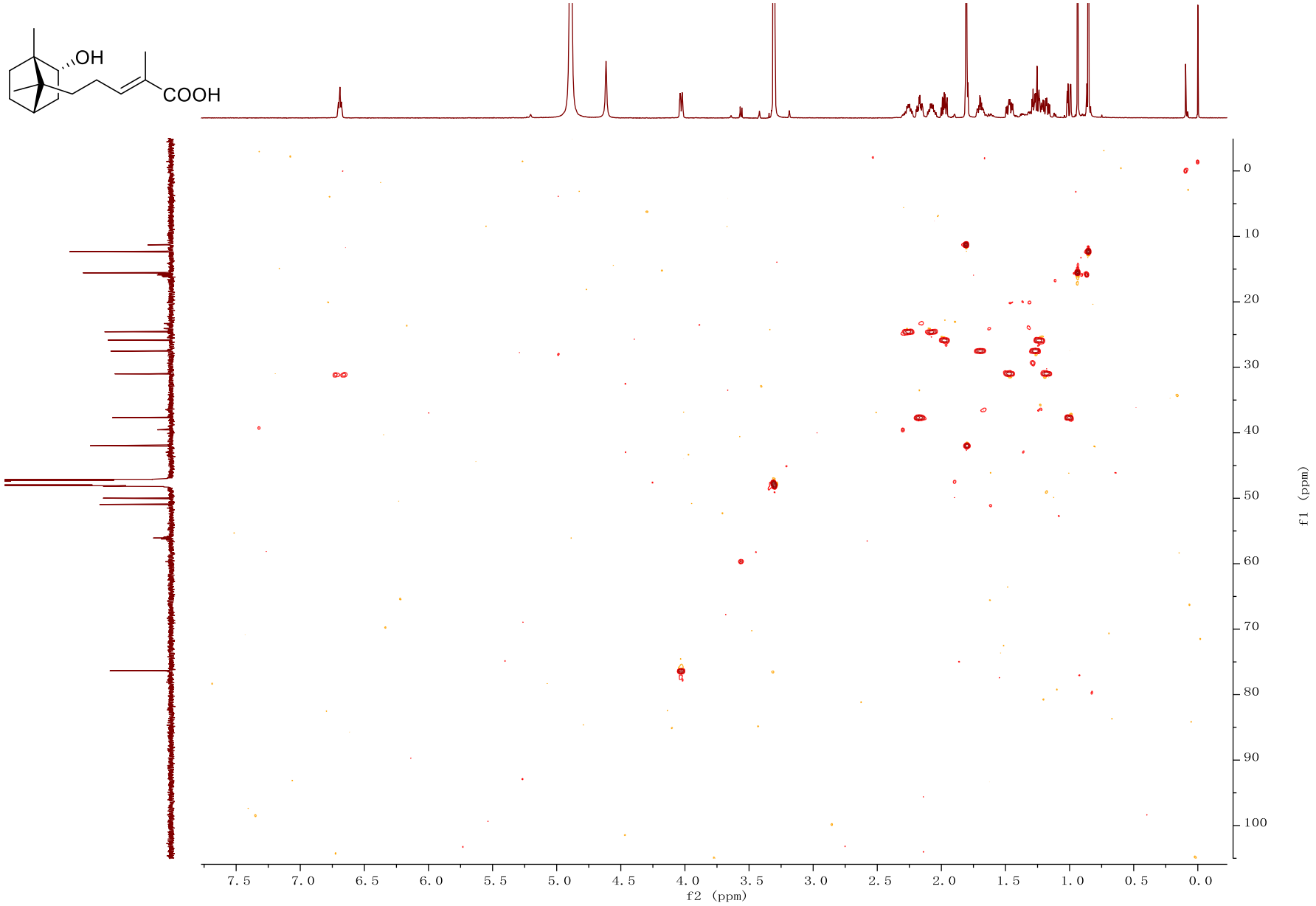


Figure S27. HMBC of compound **1** in CD_3OD

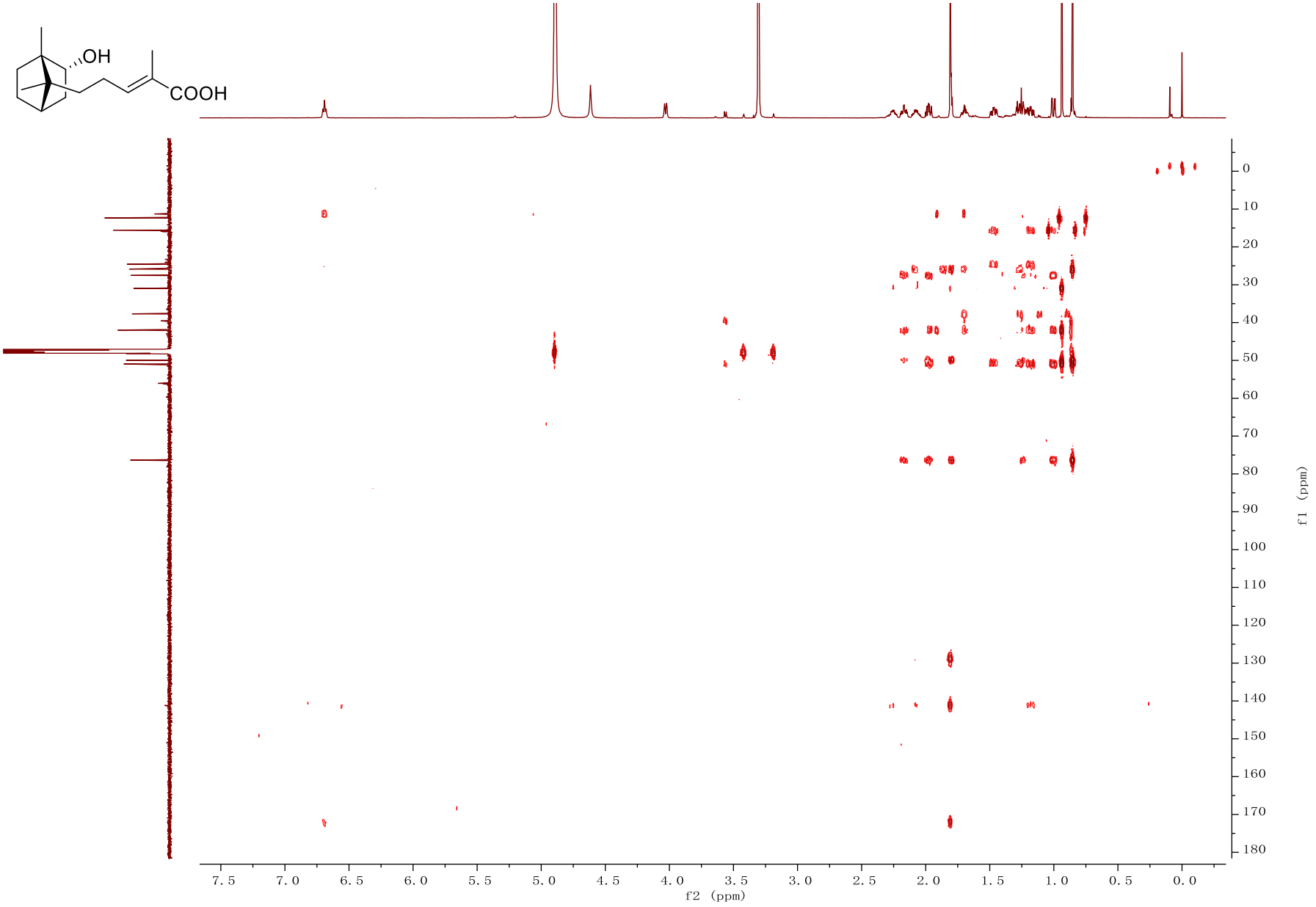


Figure S28. ^{1}H-^{1}H COSY of compound **1** in CD_3OD

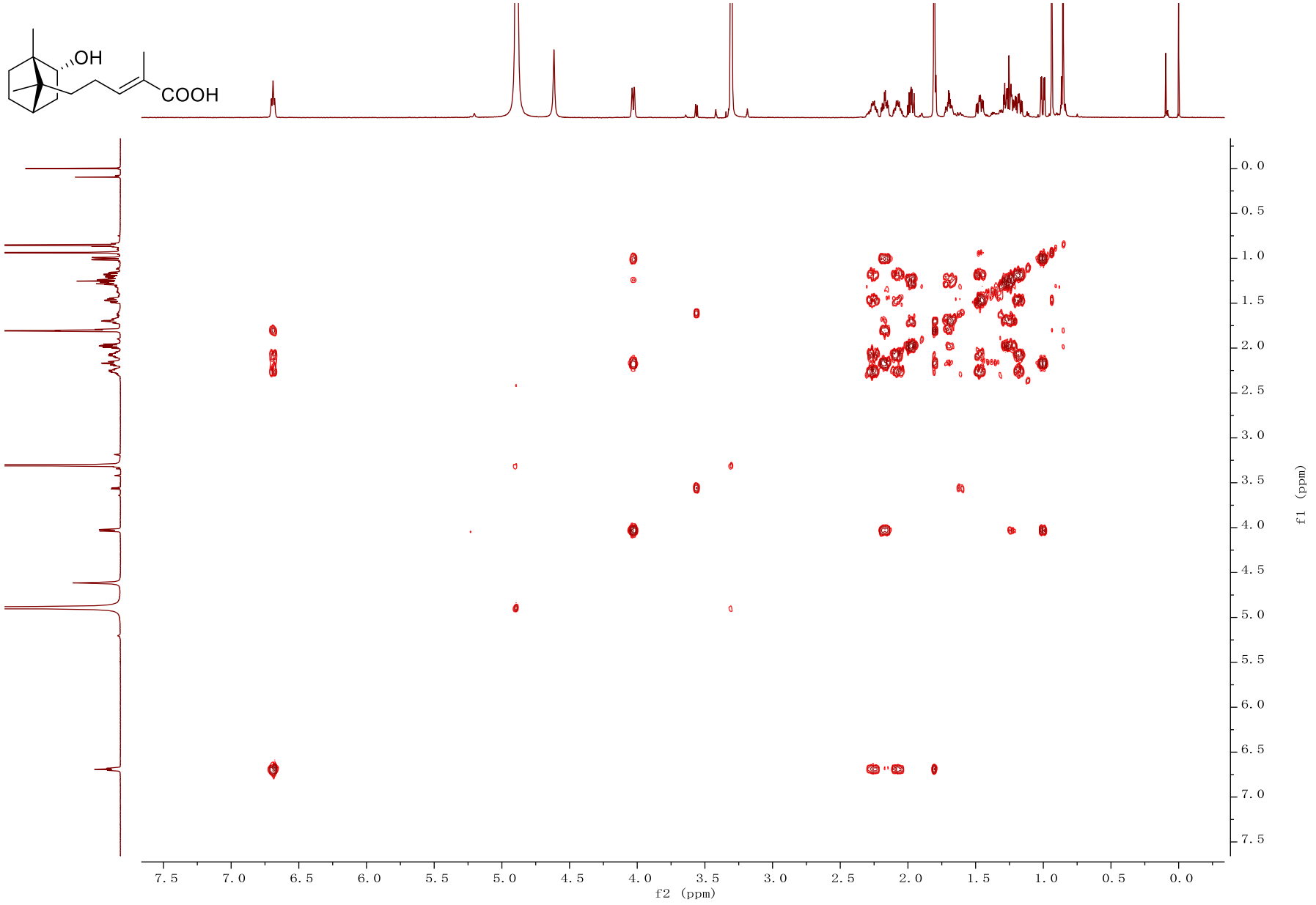


Figure S29. ROESY of compound **1** in CD_3OD

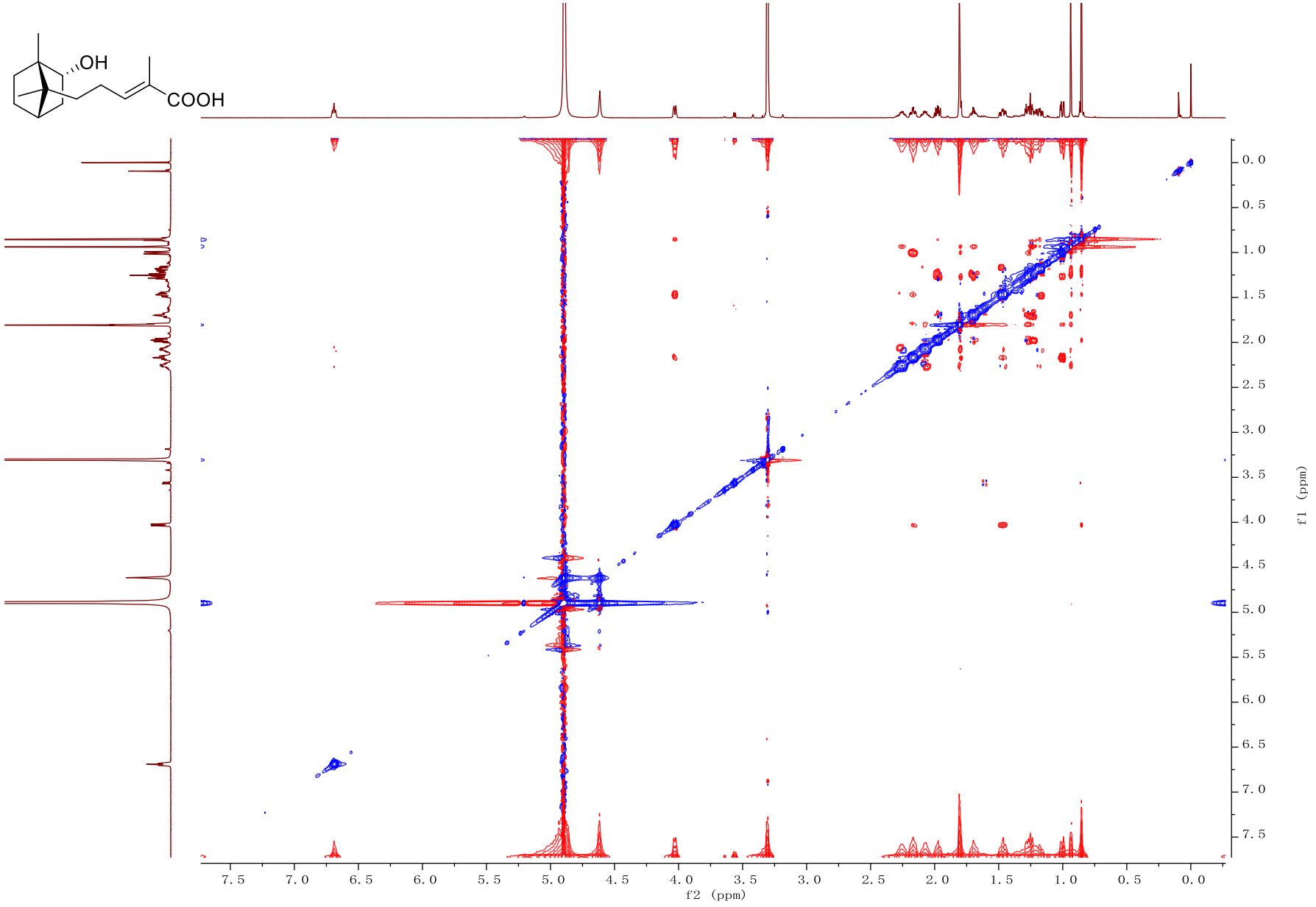
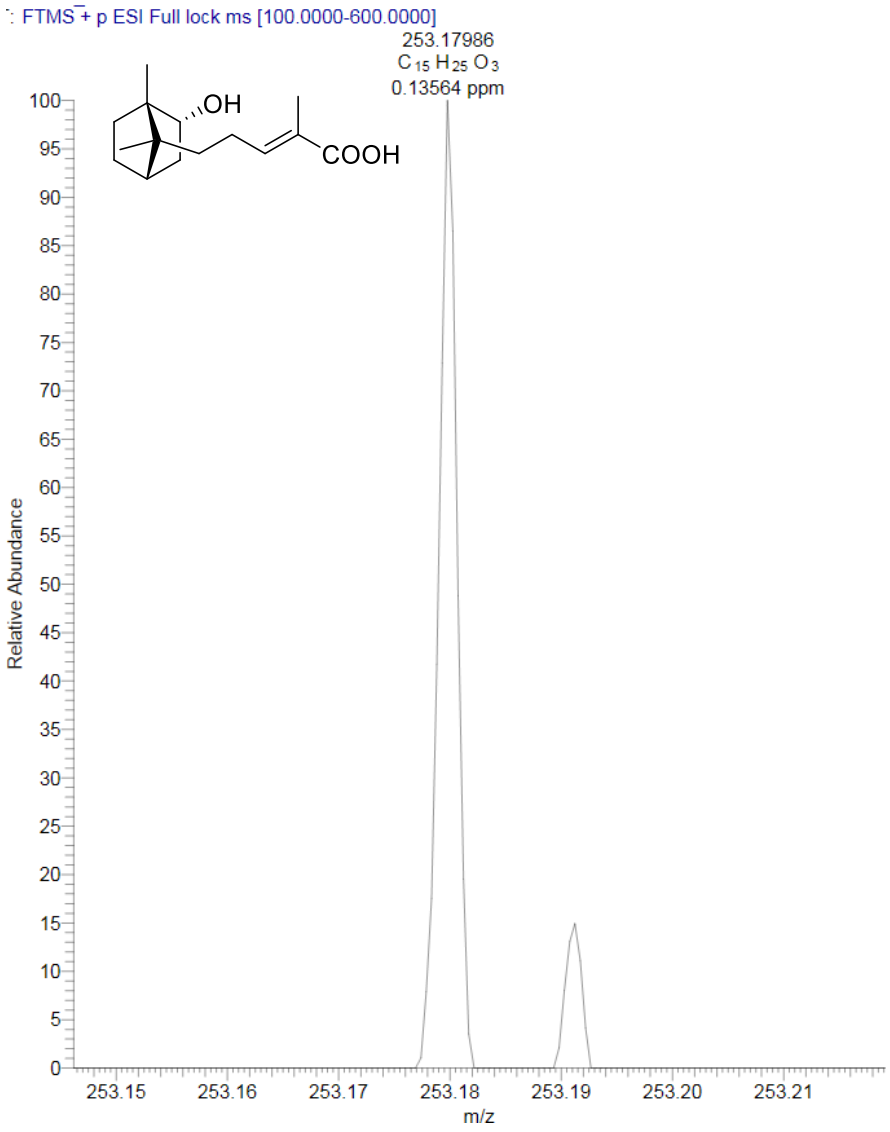


Figure S30. HR-ESIMS of compound **1**



Section S9. NMR and MS spectra for 2

Figure S31. ^{1}H NMR of compound **2** in CD_3OD

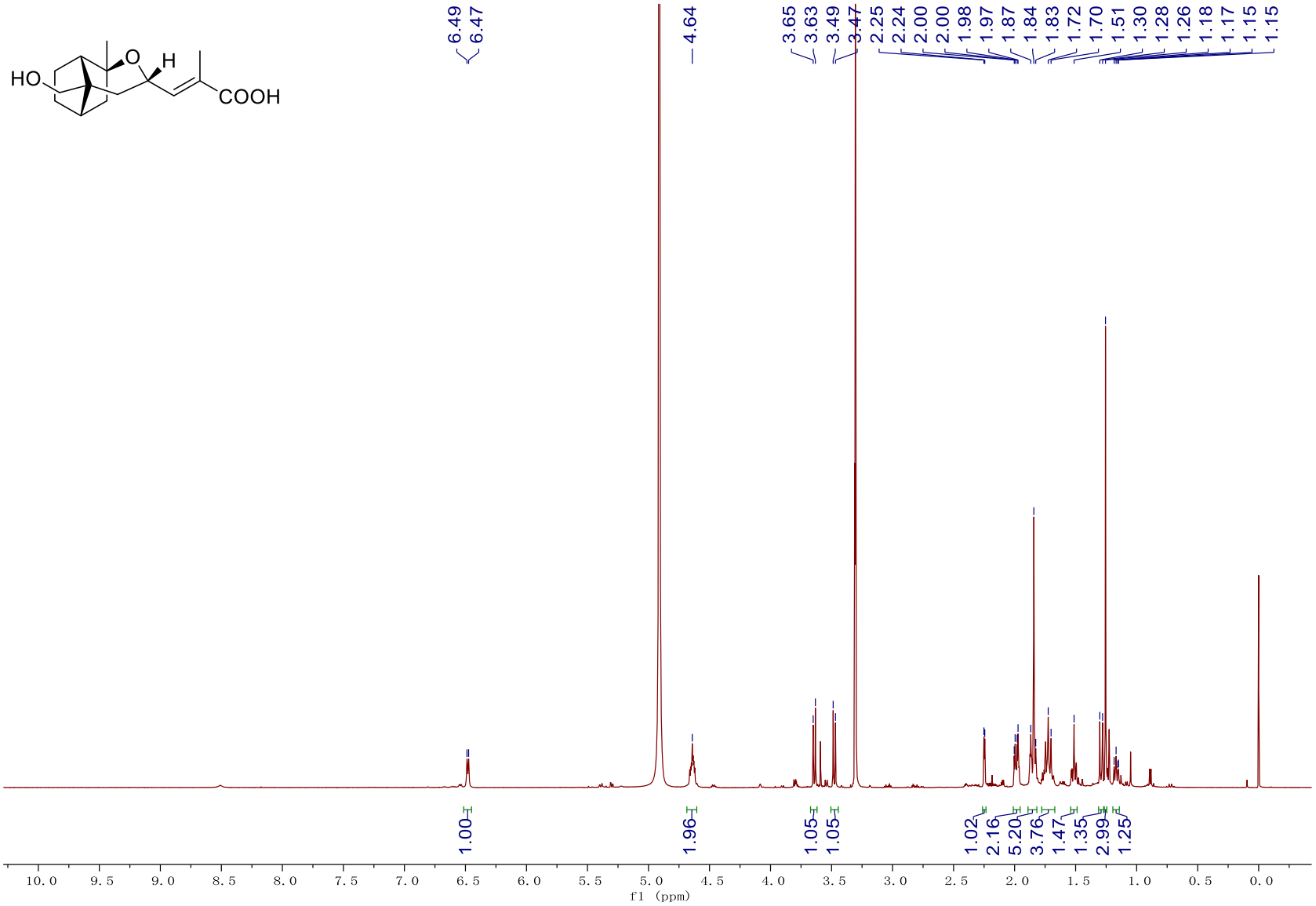


Figure S32. ^{13}C NMR and DEPT of compound **2** in CD_3OD

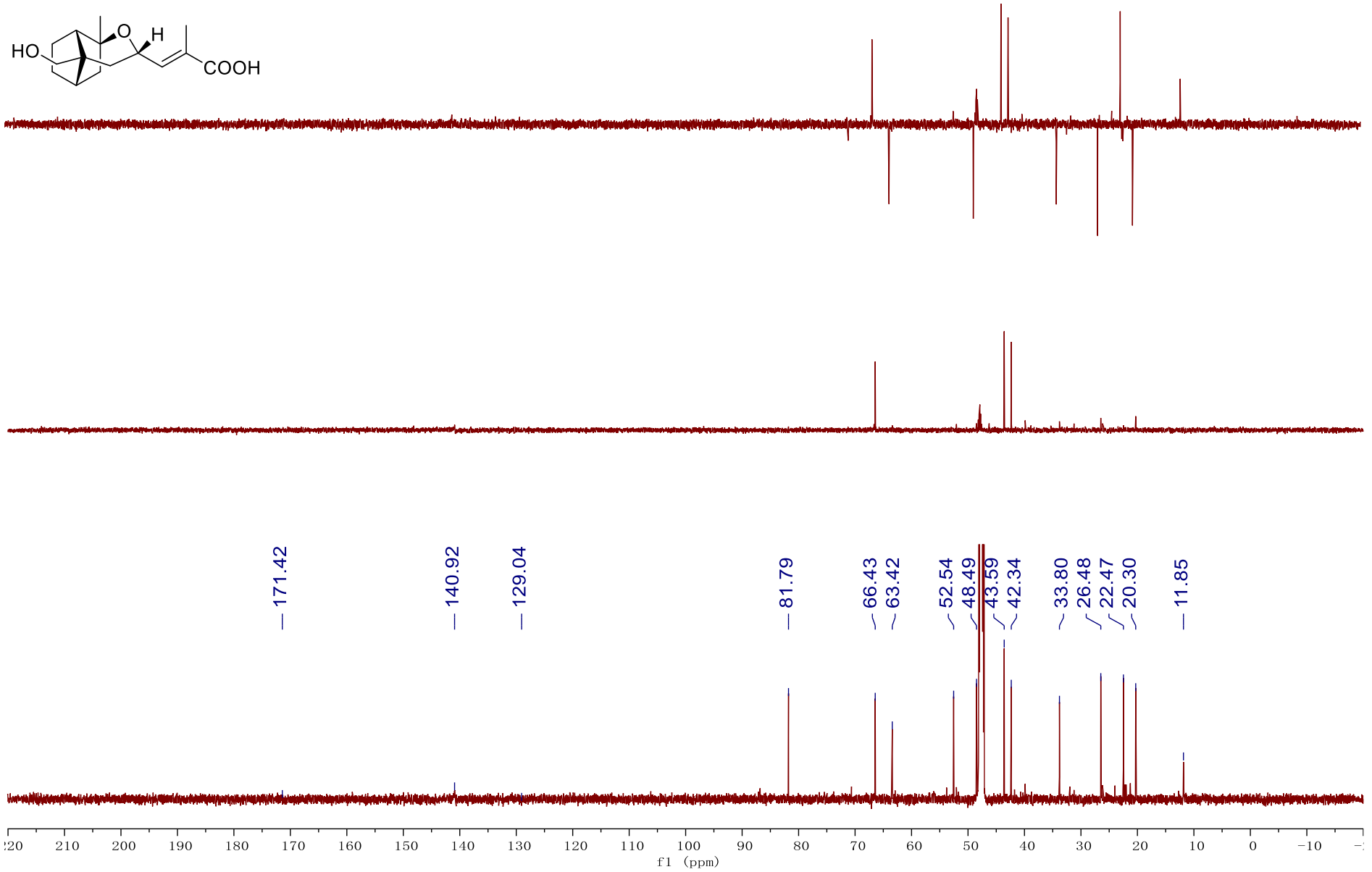


Figure S33. HSQC of compound **2** in CD_3OD

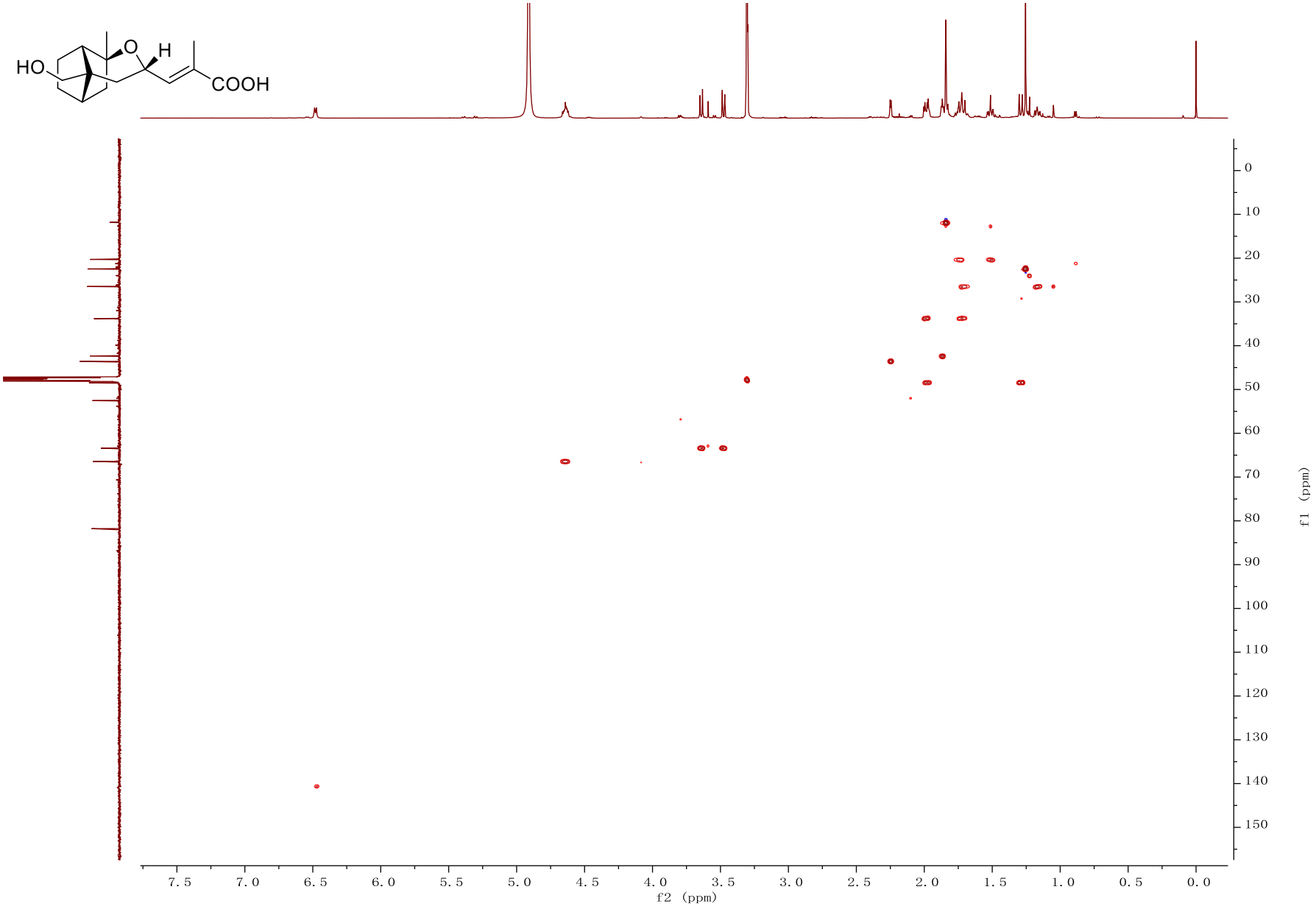


Figure S34. HMBC of compound **2** in CD_3OD

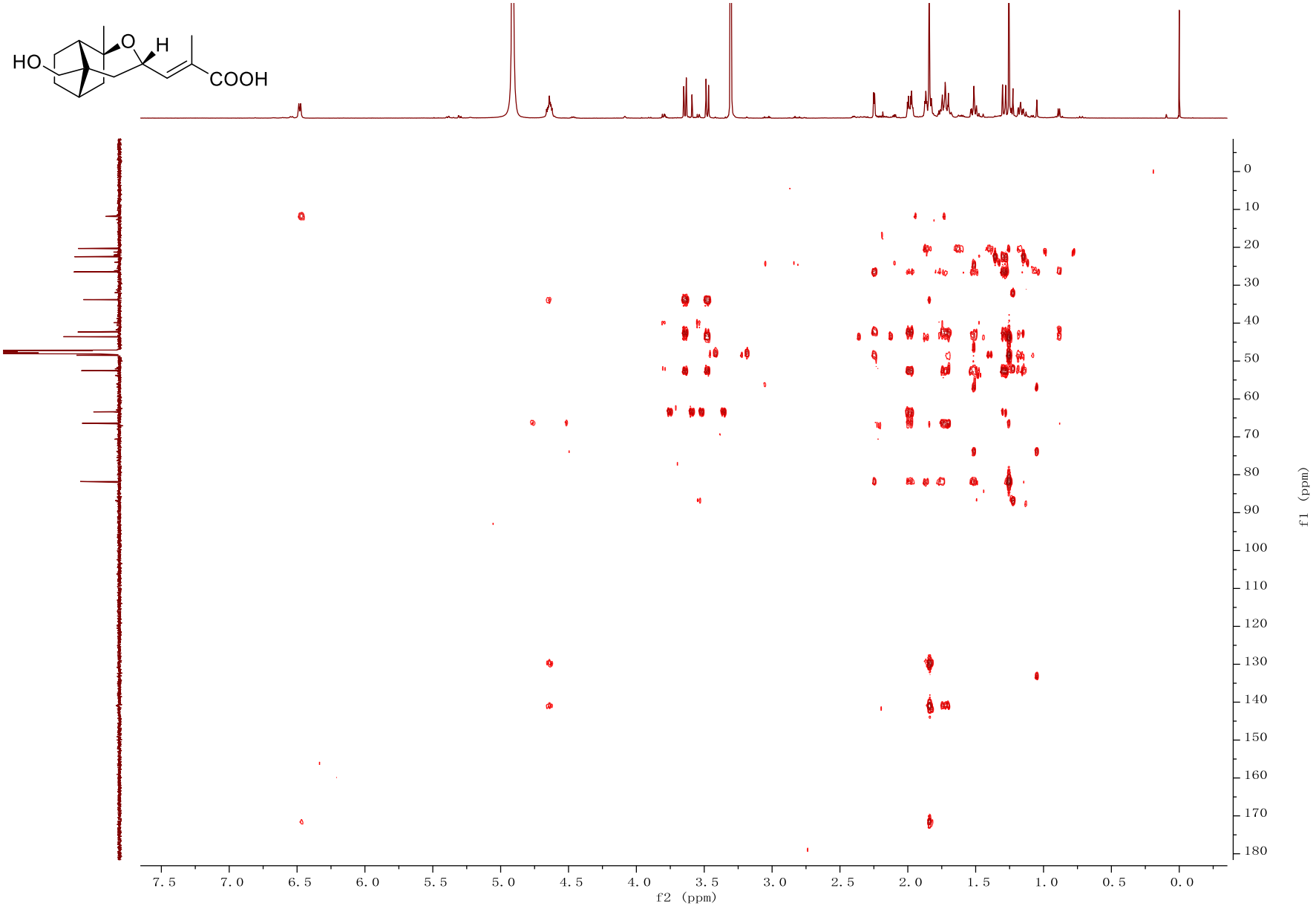


Figure S35. ^{1}H-^{1}H COSY of compound **2** in CD_3OD

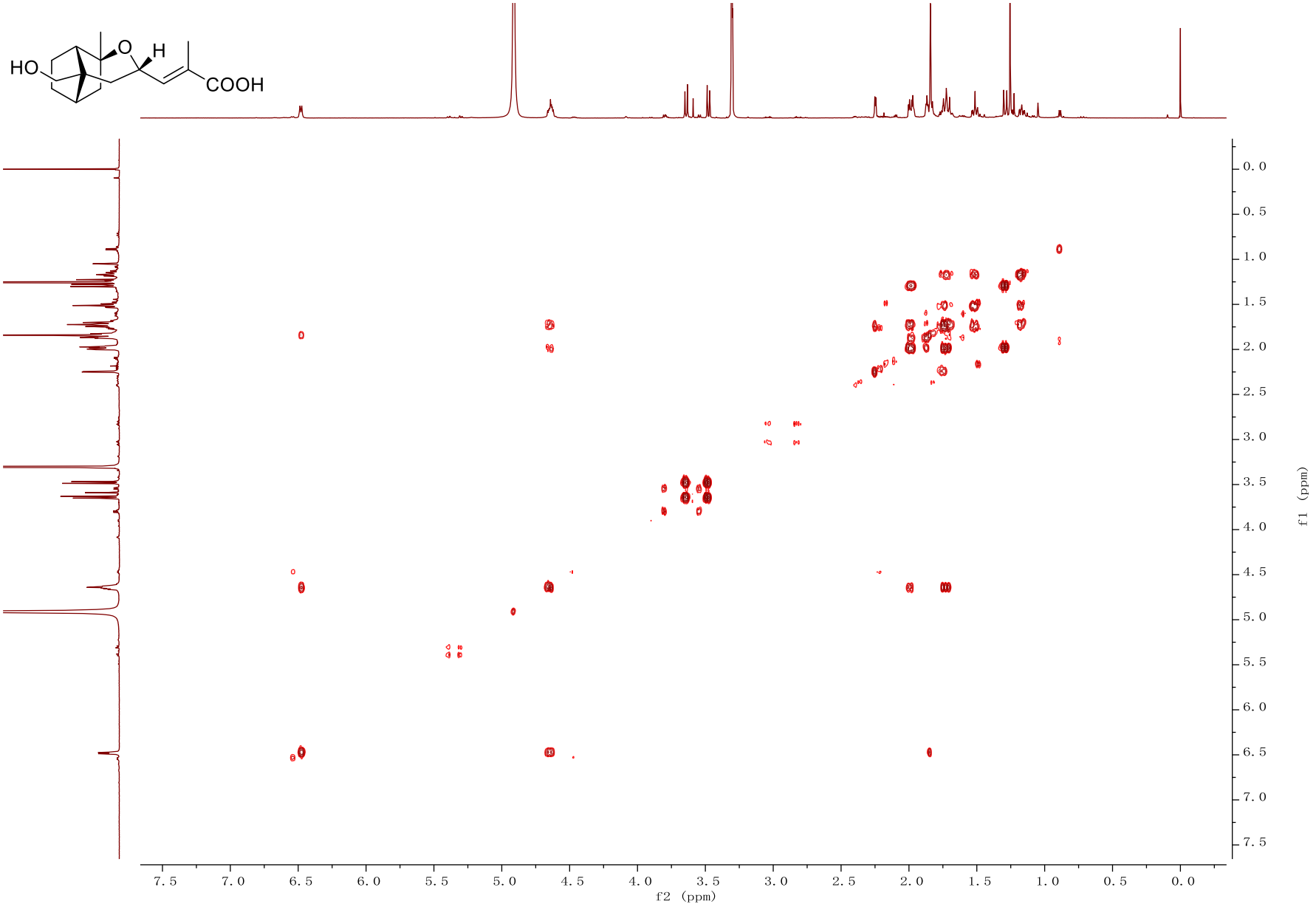


Figure S36. ROESY of compound **2** in CD_3OD

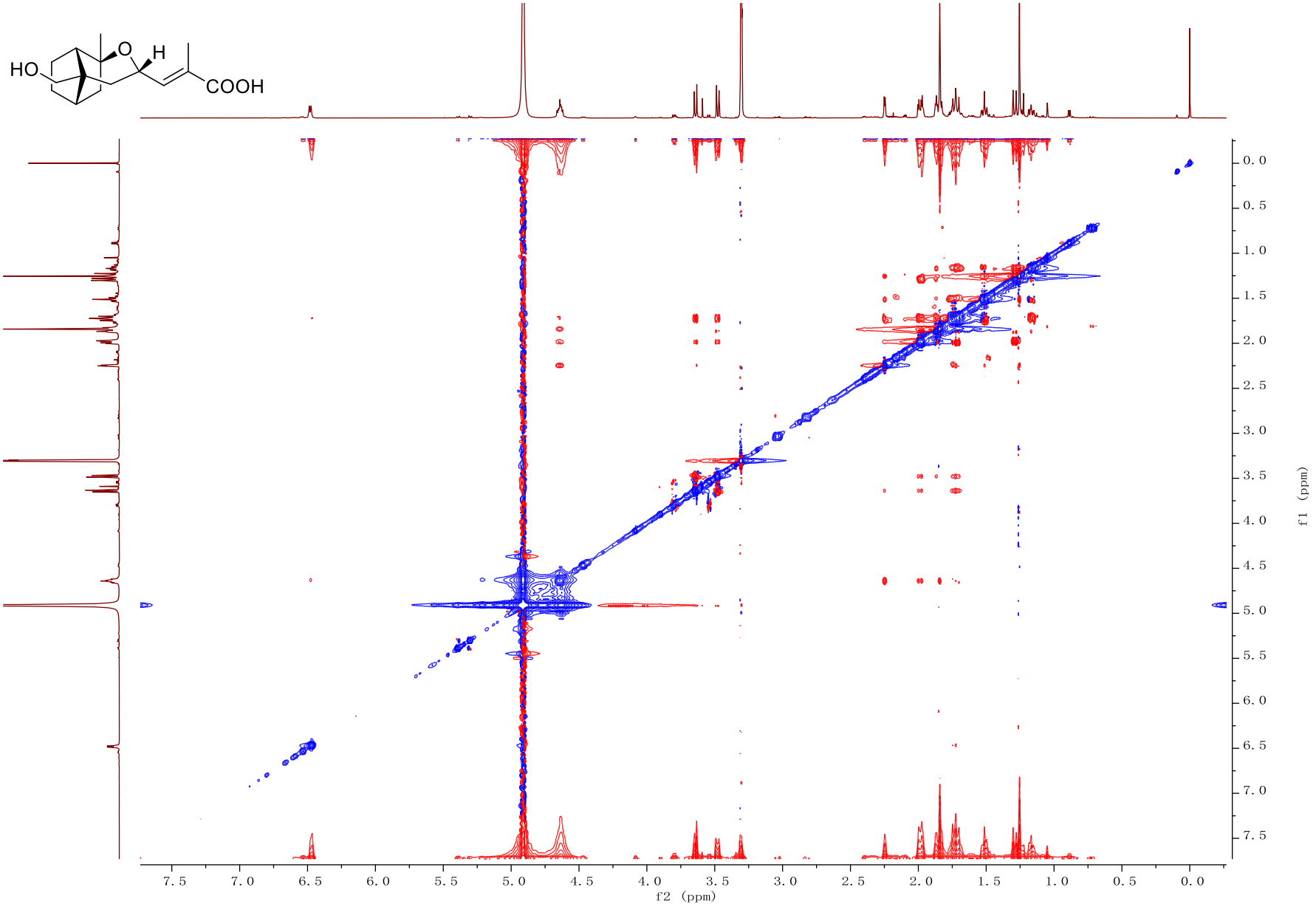
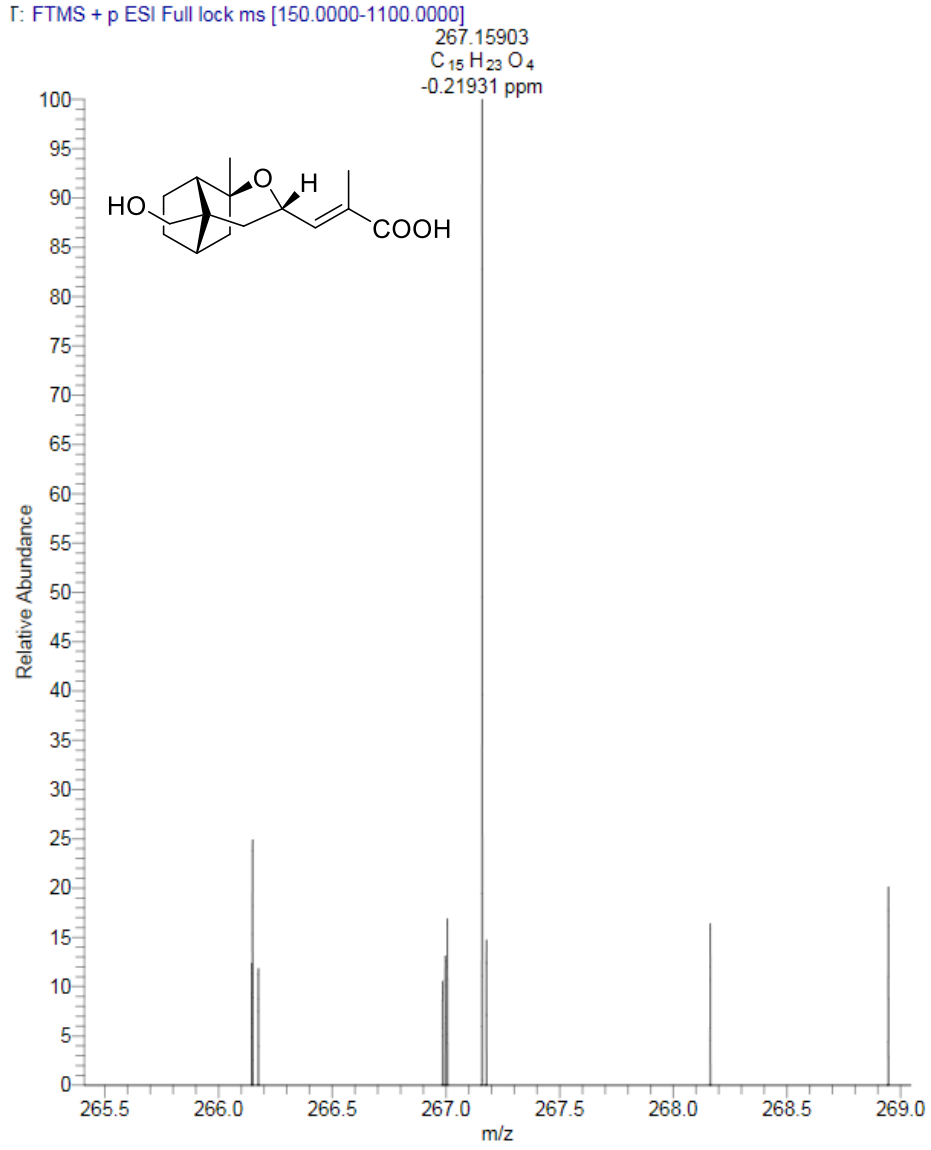


Figure S37. HR-ESIMS of compound **2**



Section S10. NMR and MS spectra for 3

Figure S38. ^{1}H NMR of compound **3** in CD_3OD

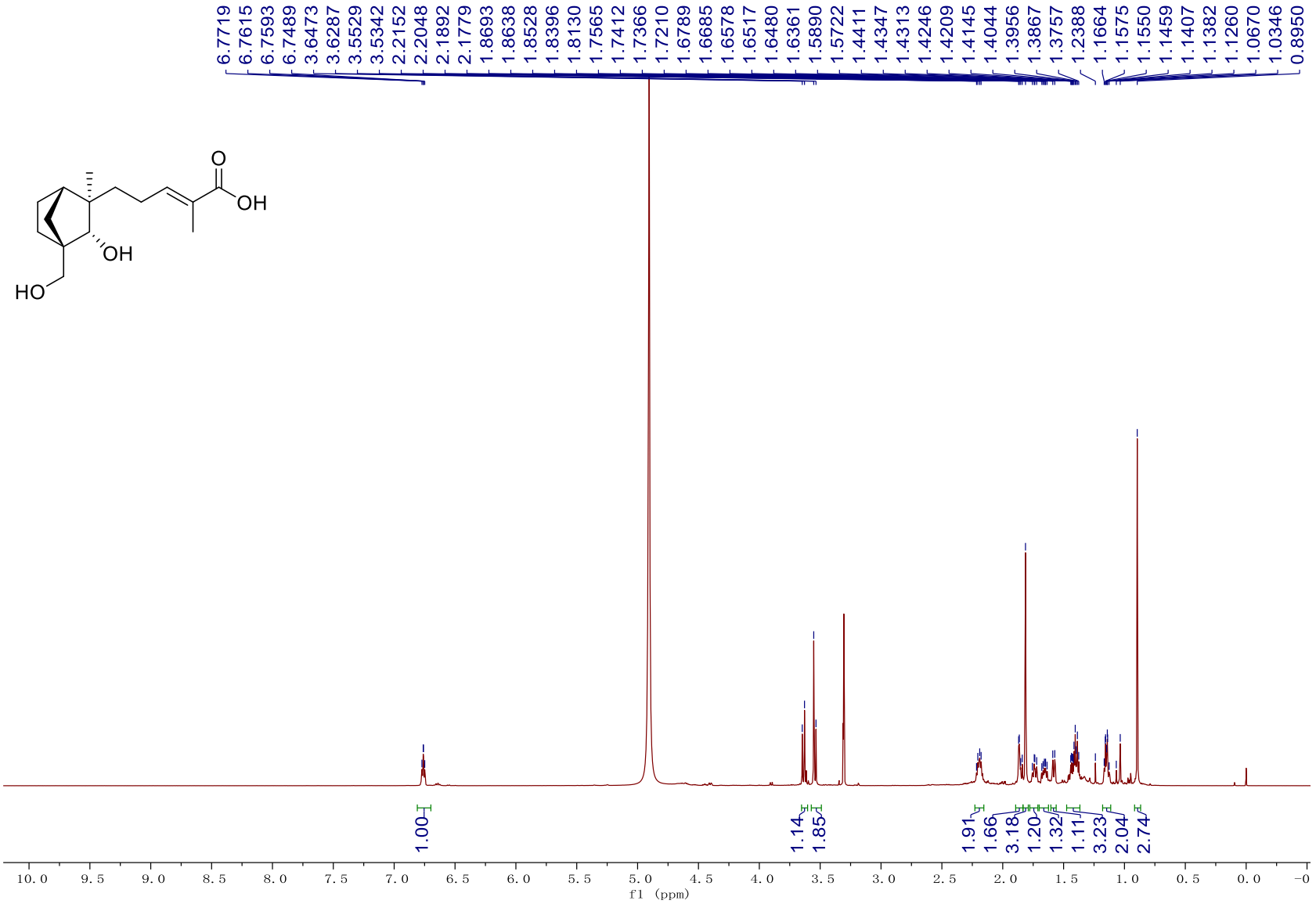


Figure S39. ^{13}C NMR and DEPT of compound **3** in CD_3OD

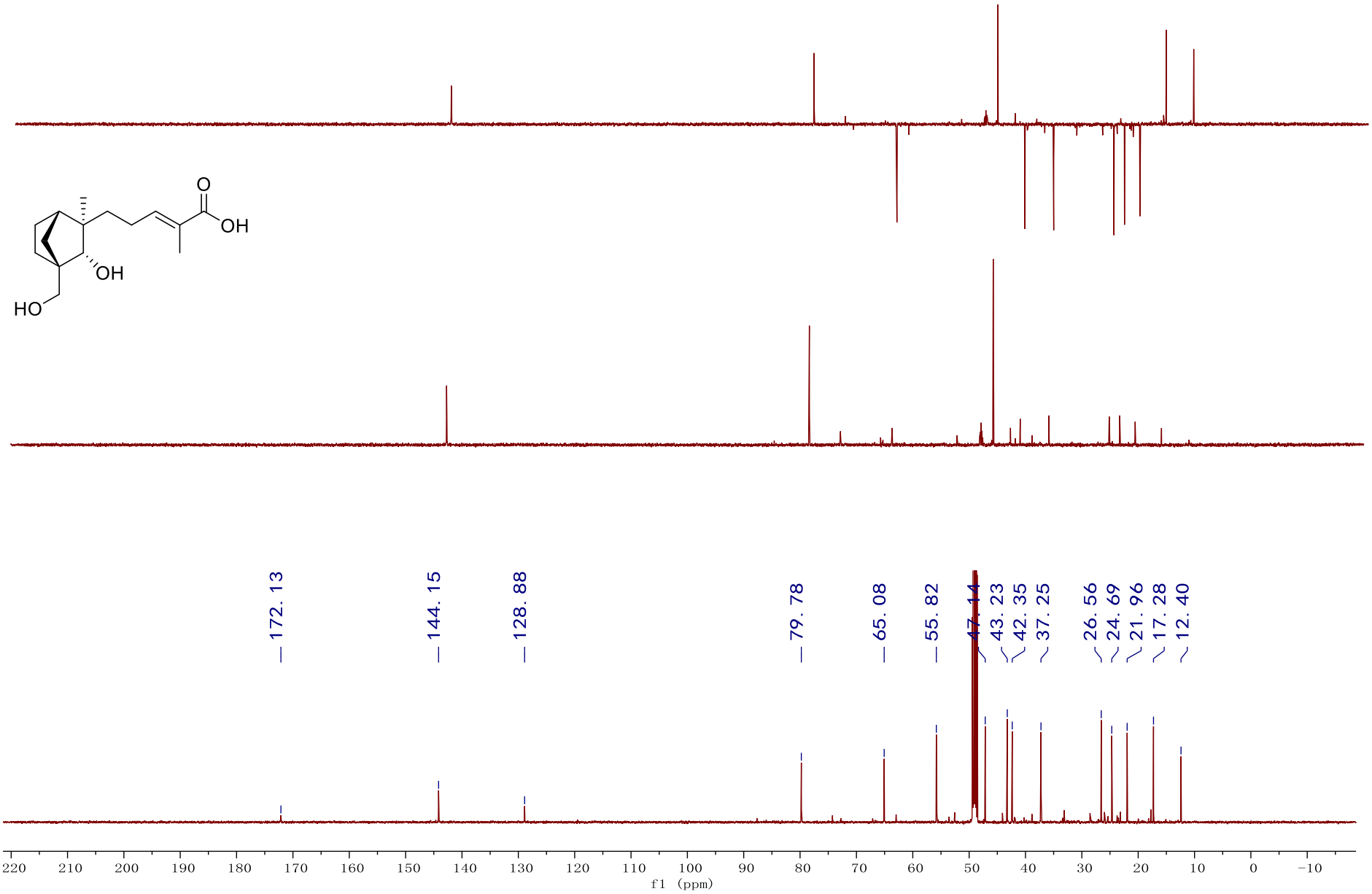


Figure S40. HSQC of compound **3** in CD_3OD

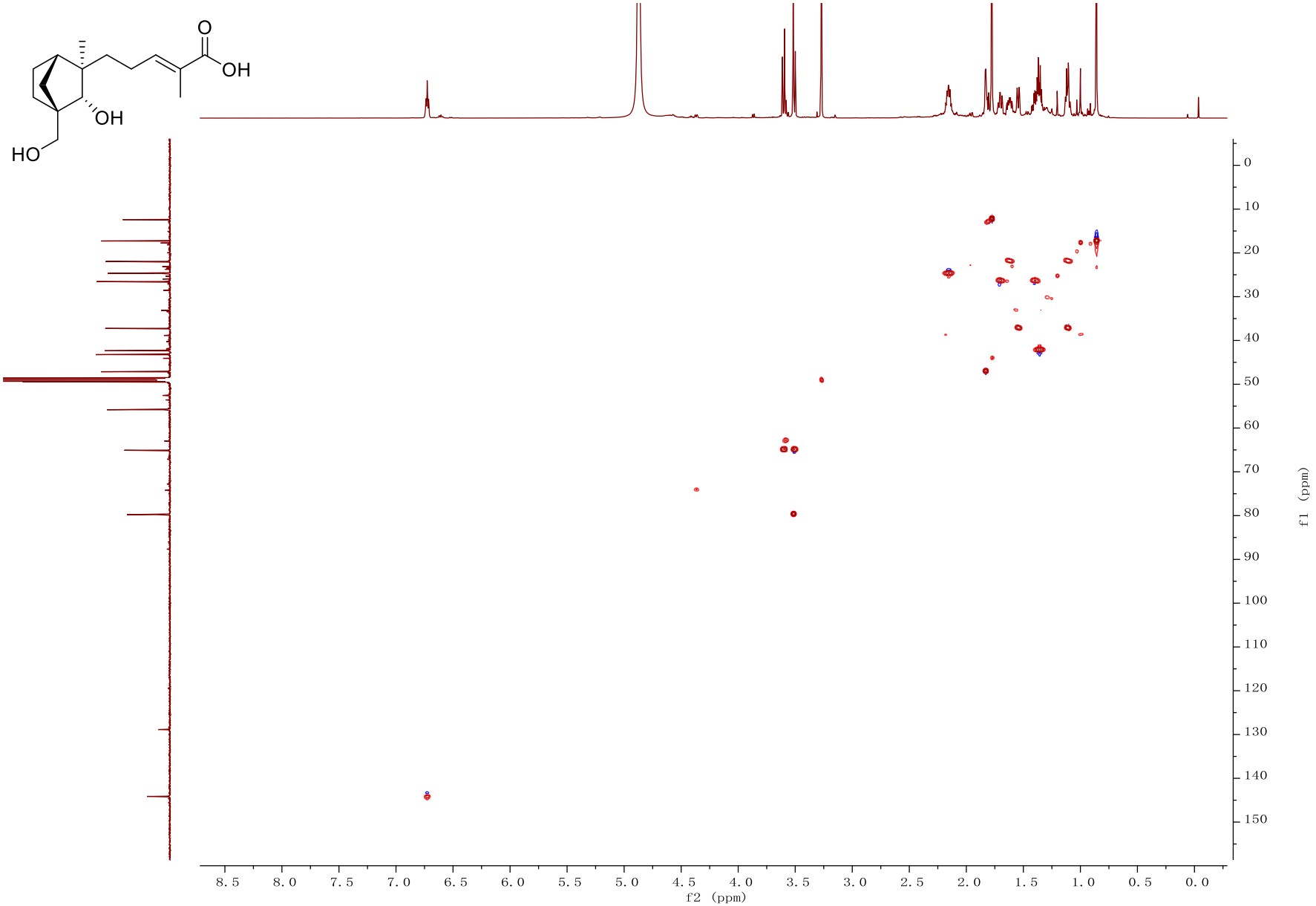


Figure S41. HMBC of compound **3** in CD_3OD

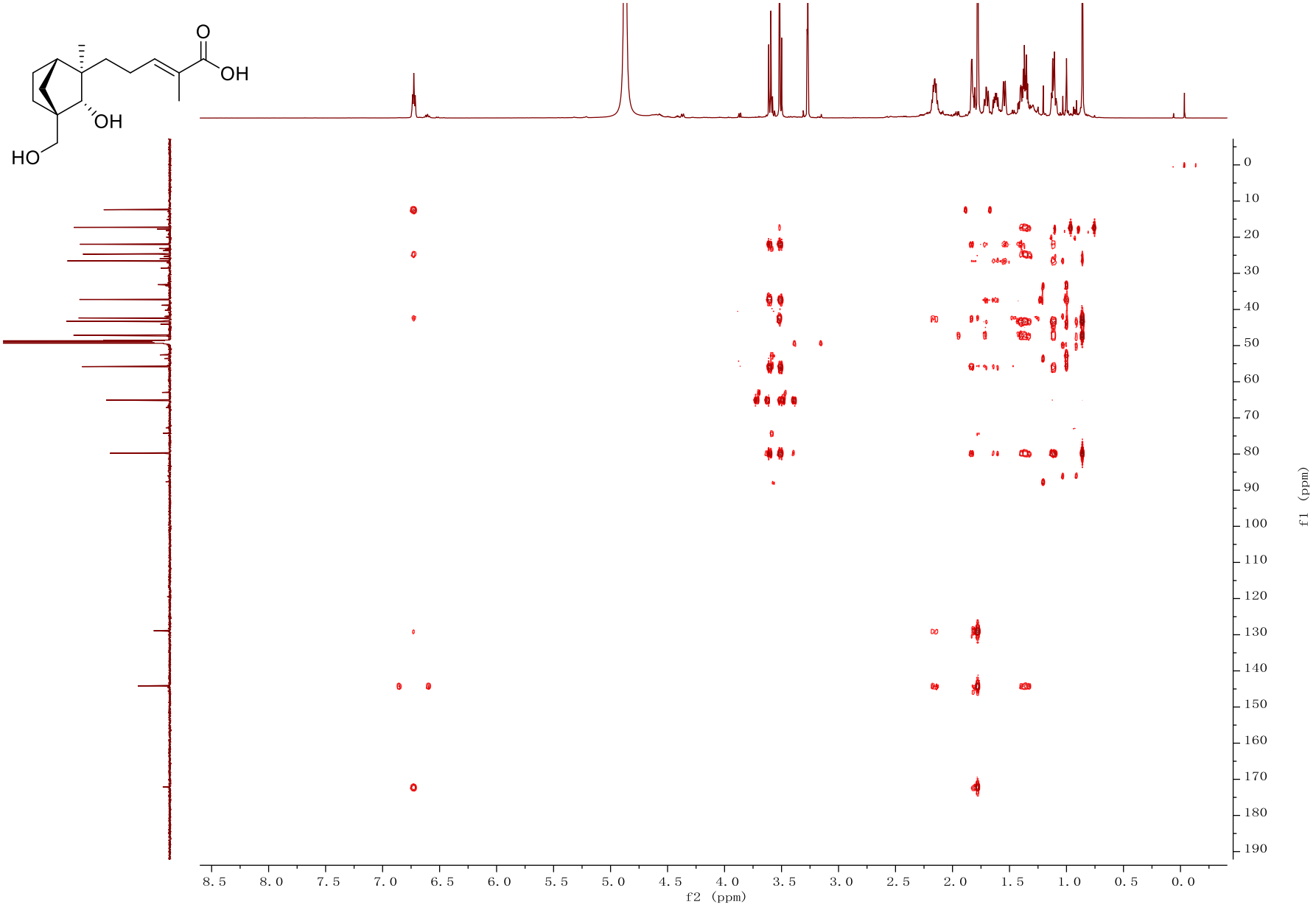


Figure S42. ^{1}H-^{1}H COSY of compound **3** in CD_3OD

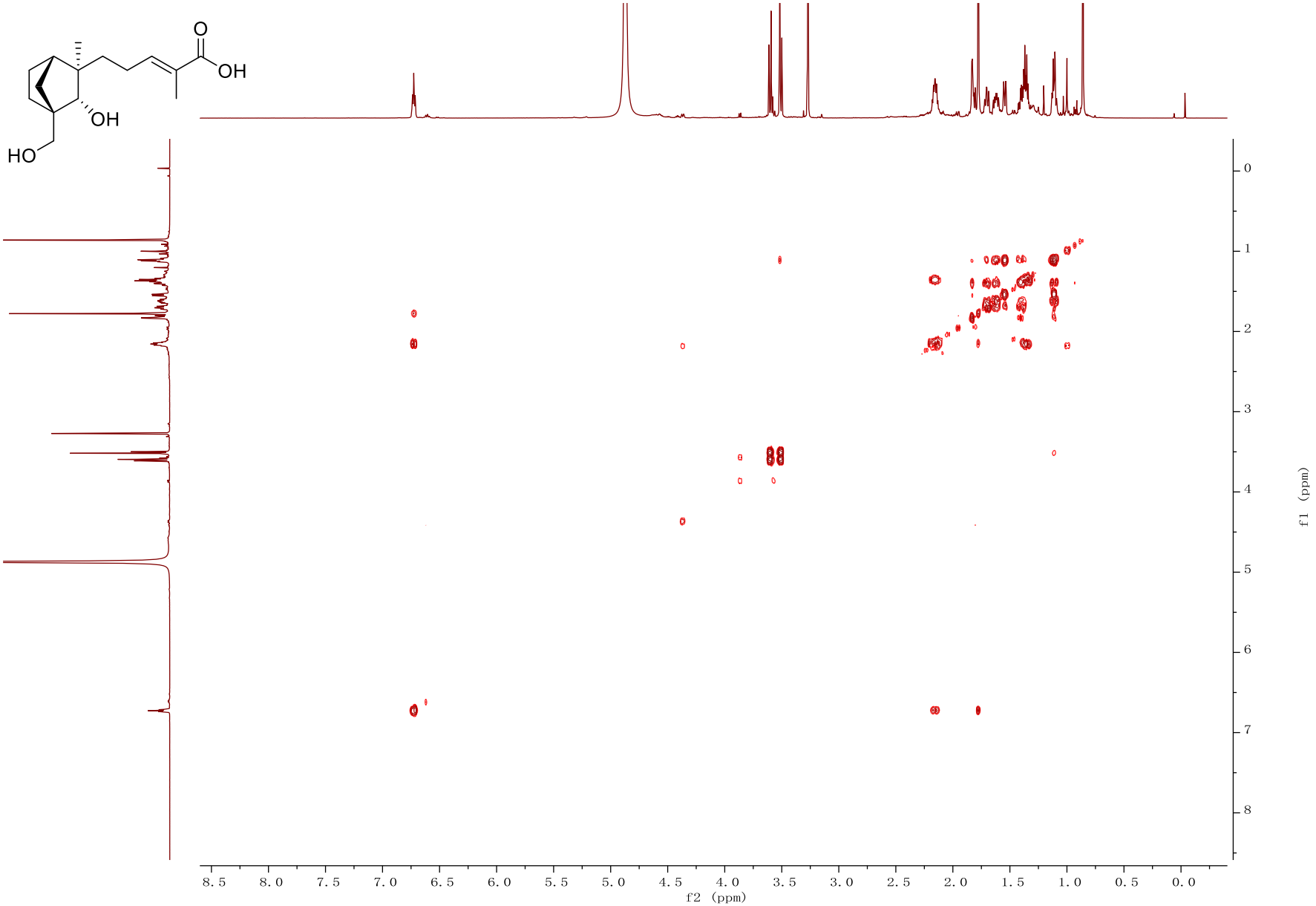


Figure S43. ROESY of compound **3** in CD_3OD

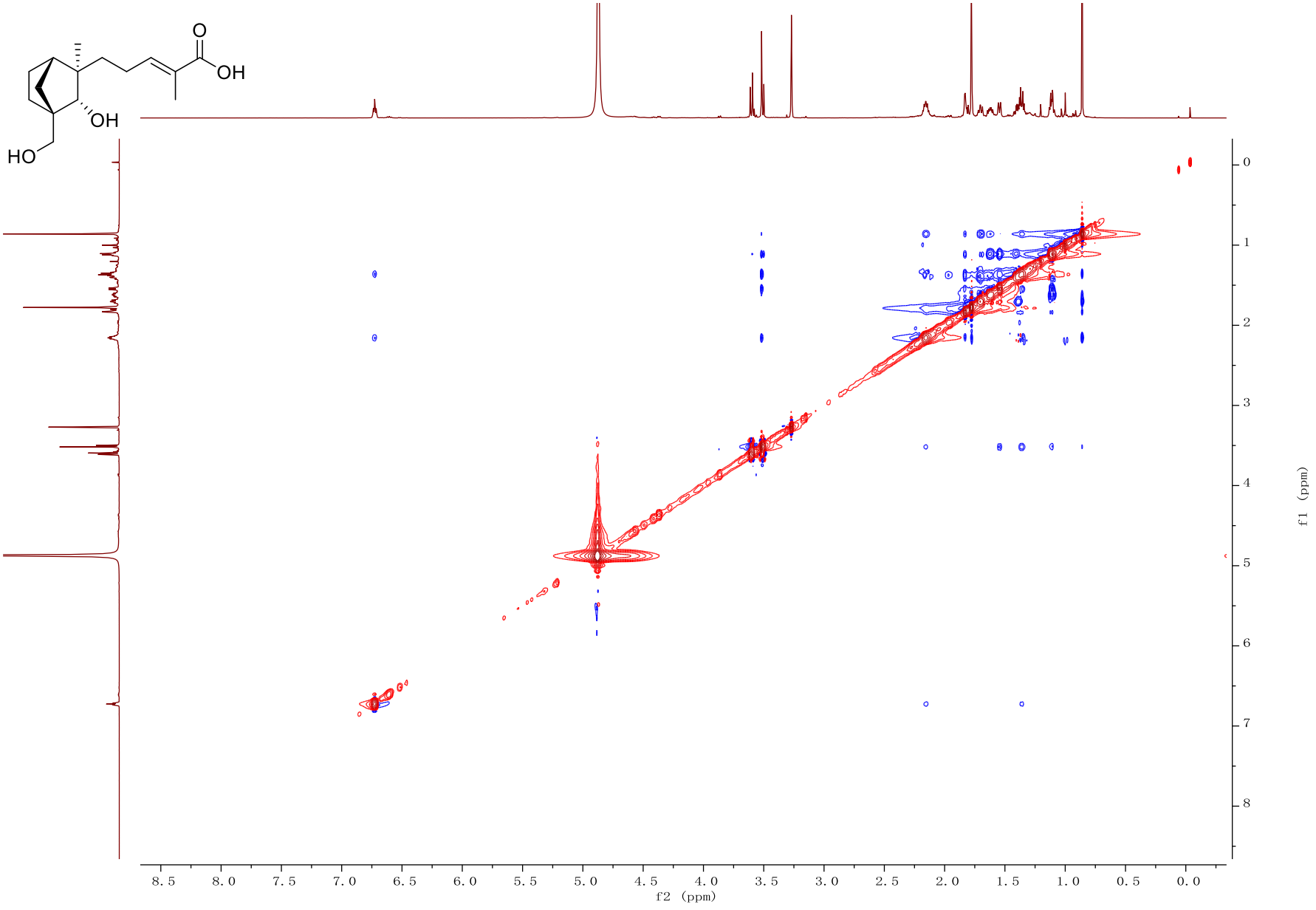
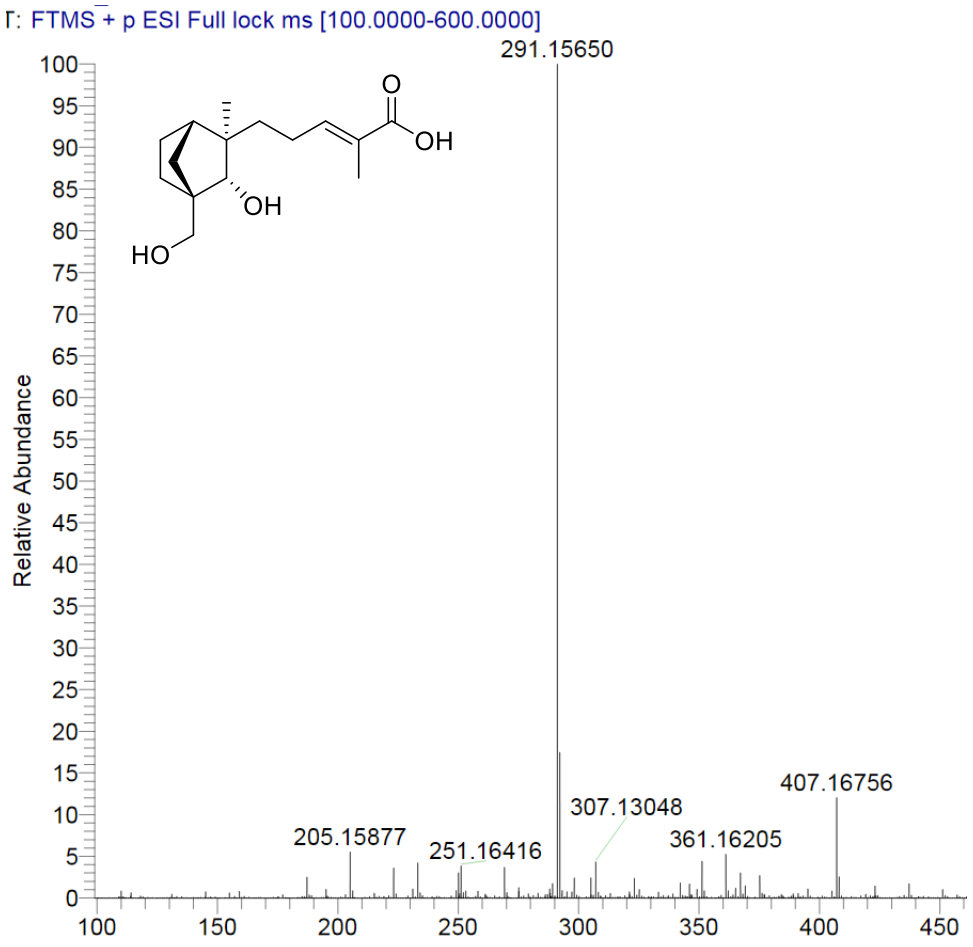


Figure S44. HR-ESIMS of compound **3**



Section S11. NMR and MS spectra for 4

Figure S45. ^{1}H NMR of compound **4** in CD_3OD

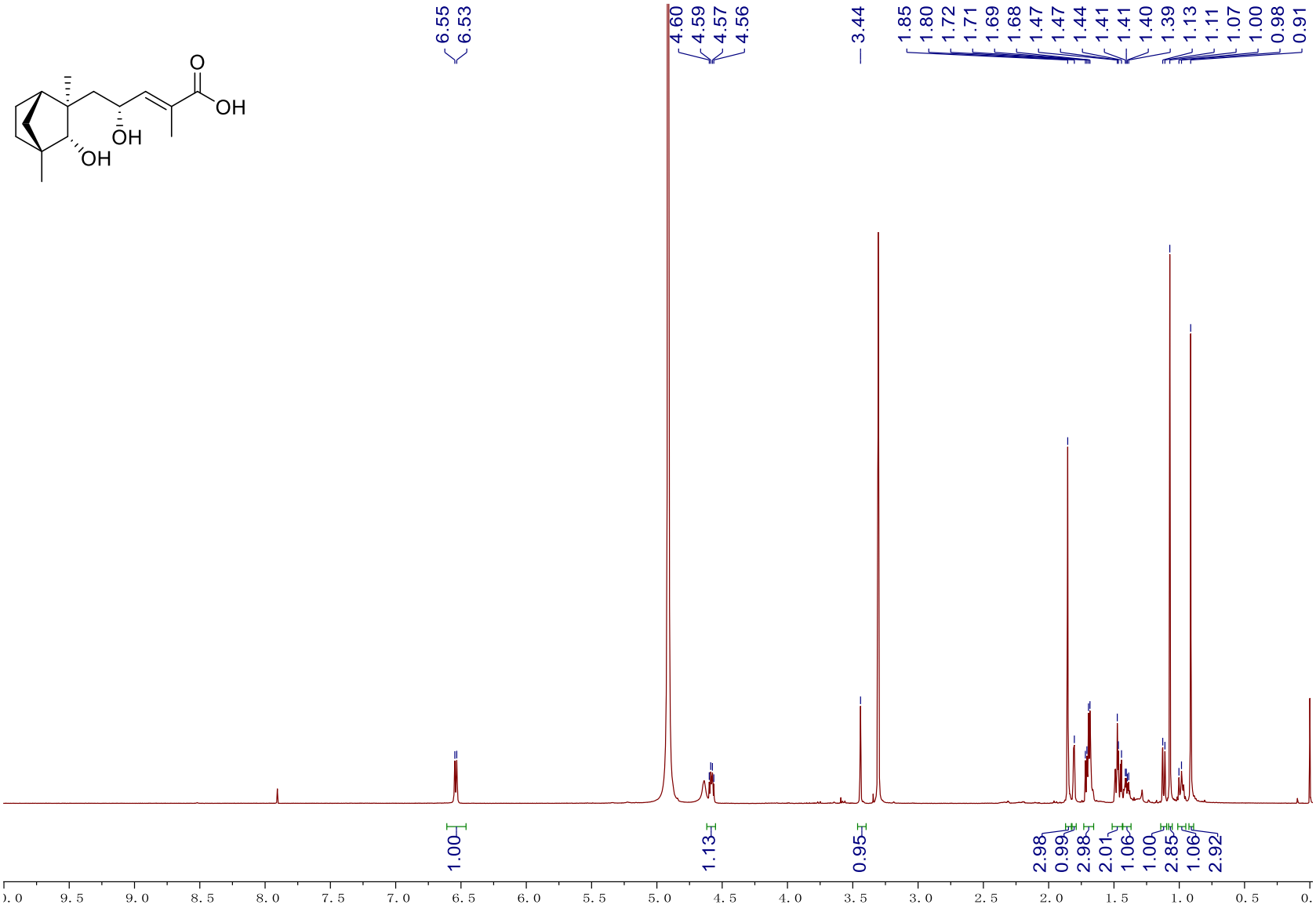


Figure S46. ^{13}C NMR and DEPT of compound **4** in CD_3OD

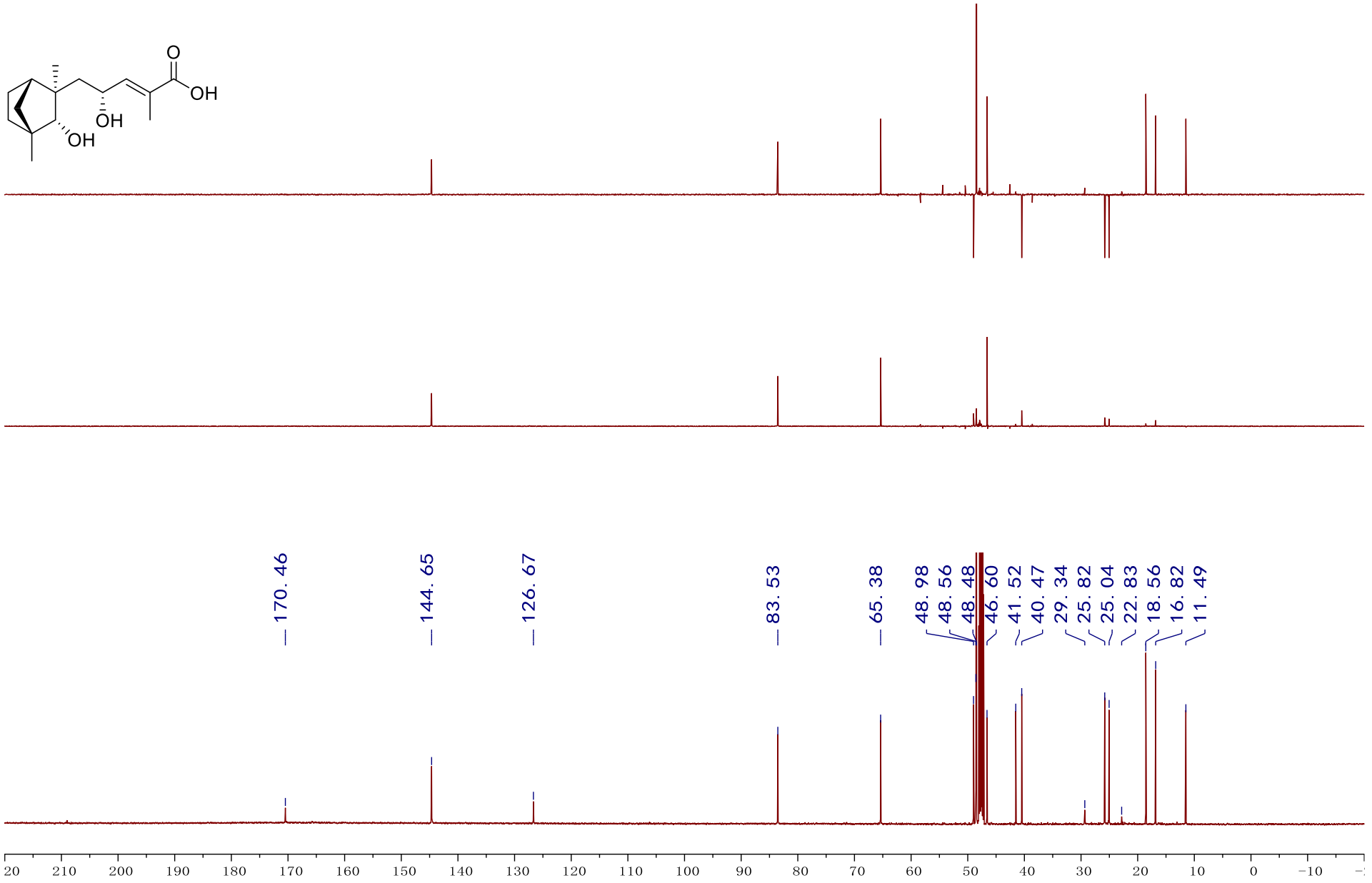


Figure S47. HSQC of compound **4** in CD_3OD

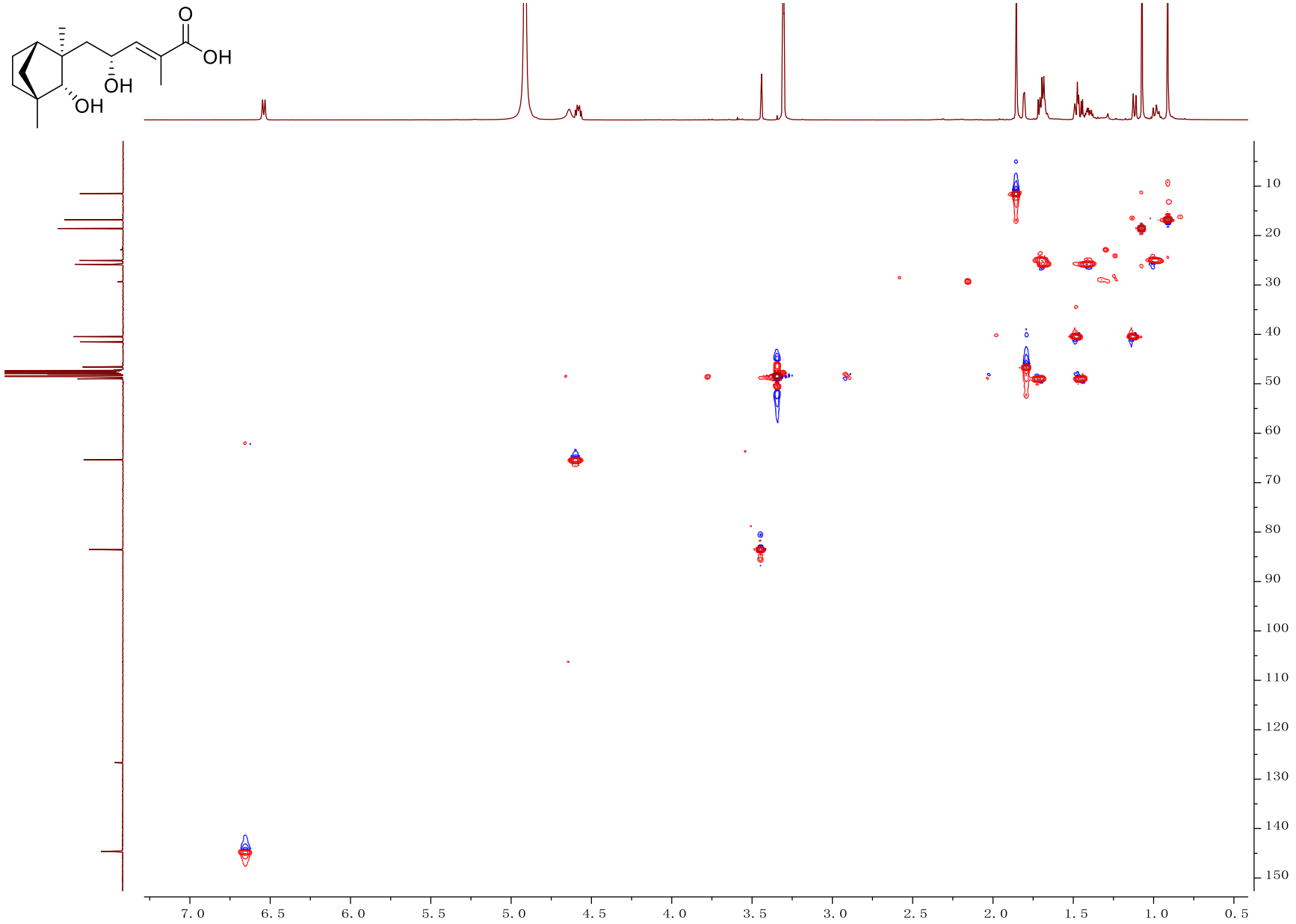


Figure S48. HMBC of compound **4** in CD_3OD

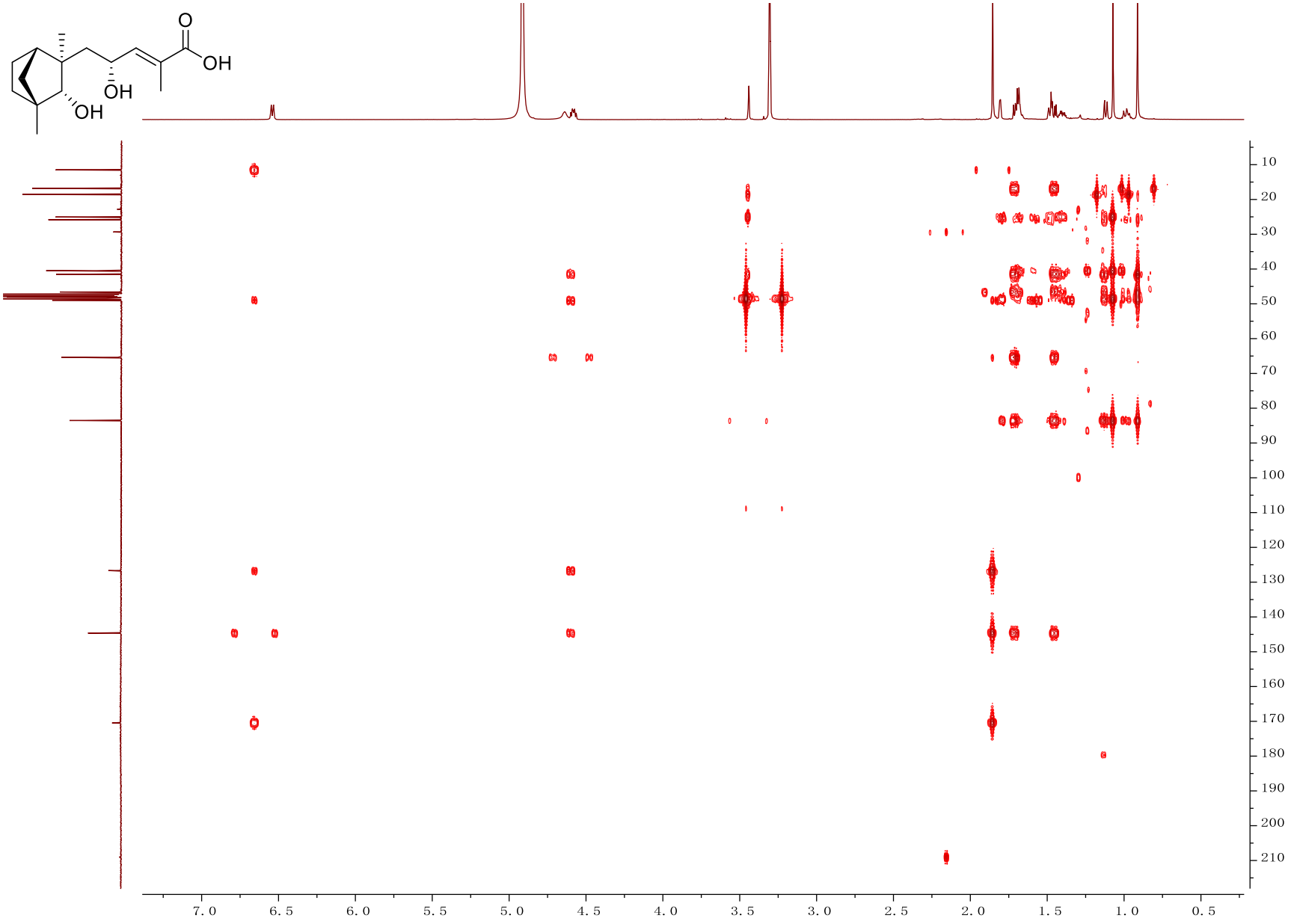


Figure S49. ^{1}H-^{1}H COSY of compound **4** in CD_3OD

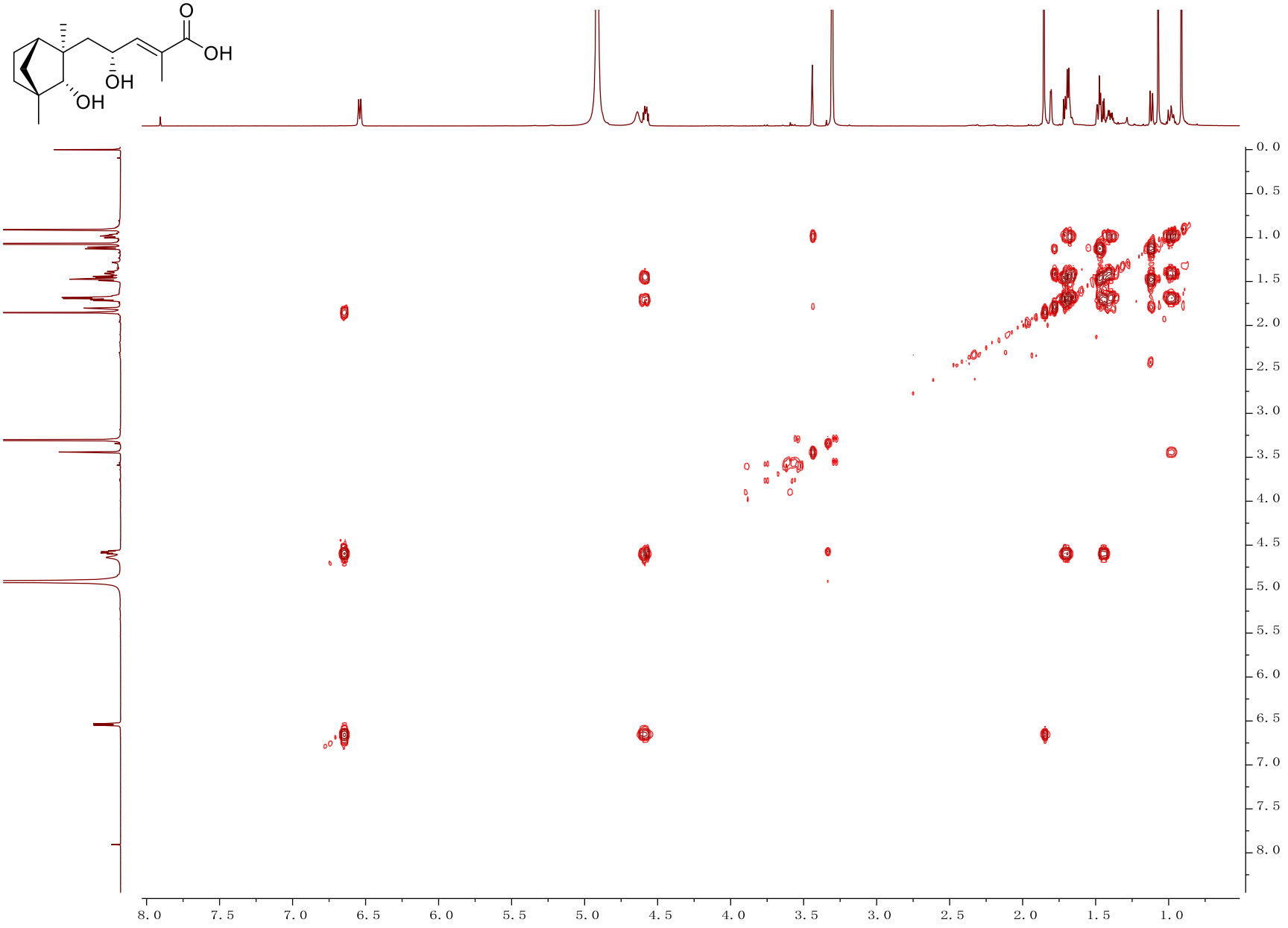


Figure S50. ROESY of compound **4** in CD_3OD

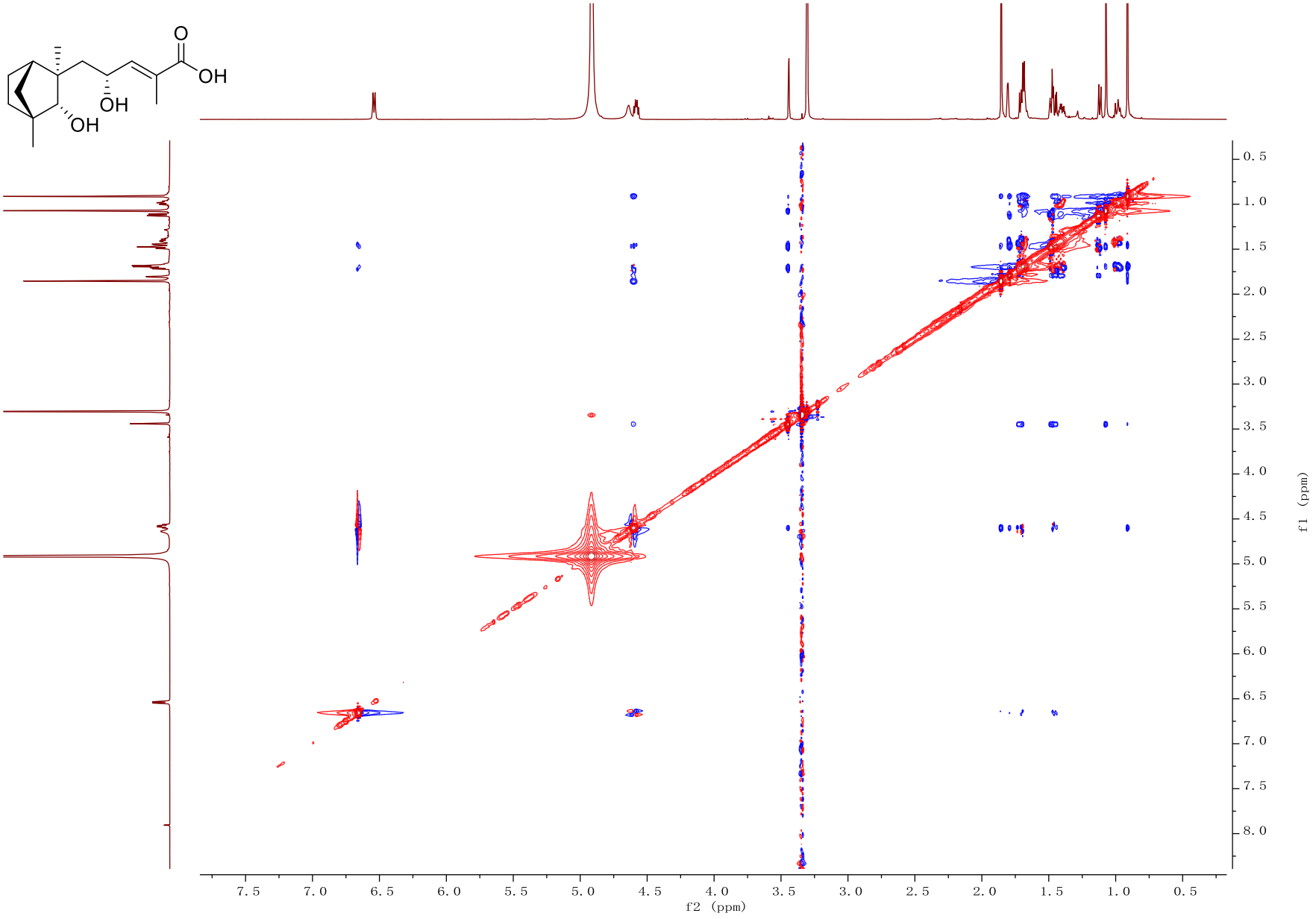
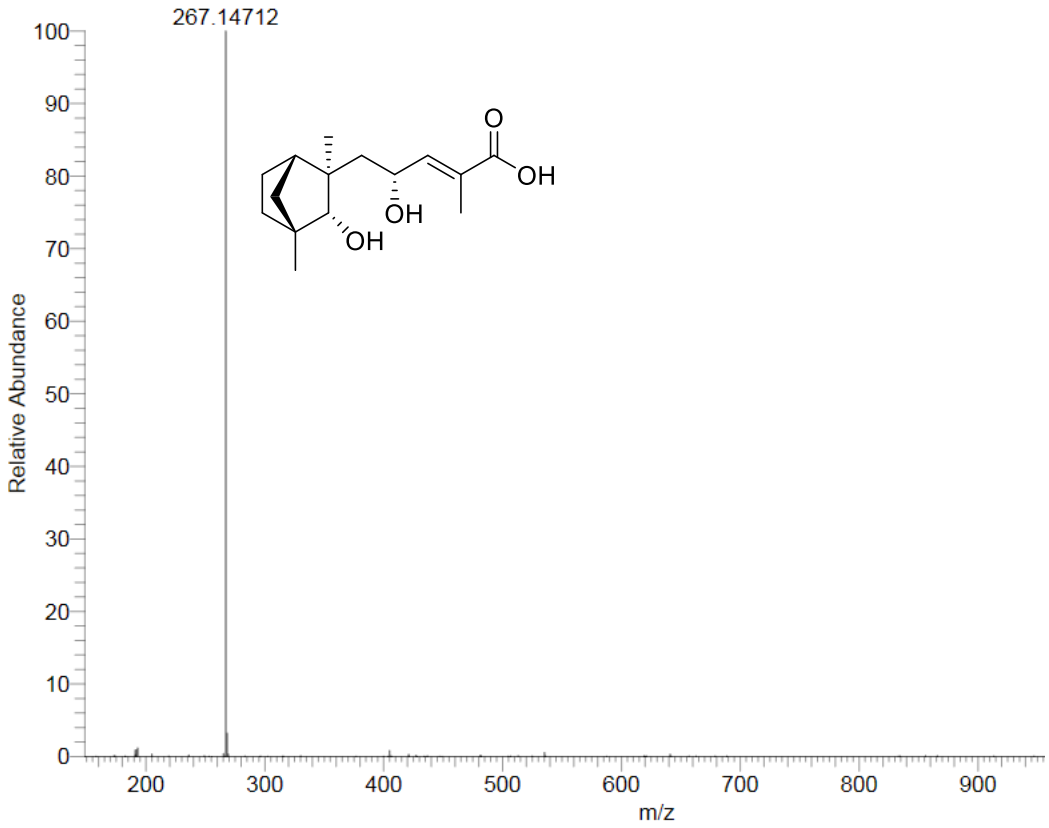


Figure S51. HR-ESIMS of compound **4**



Section S12. NMR and MS spectra for 5

Figure S52. ^{1}H NMR of compound **5** in CD_3OD

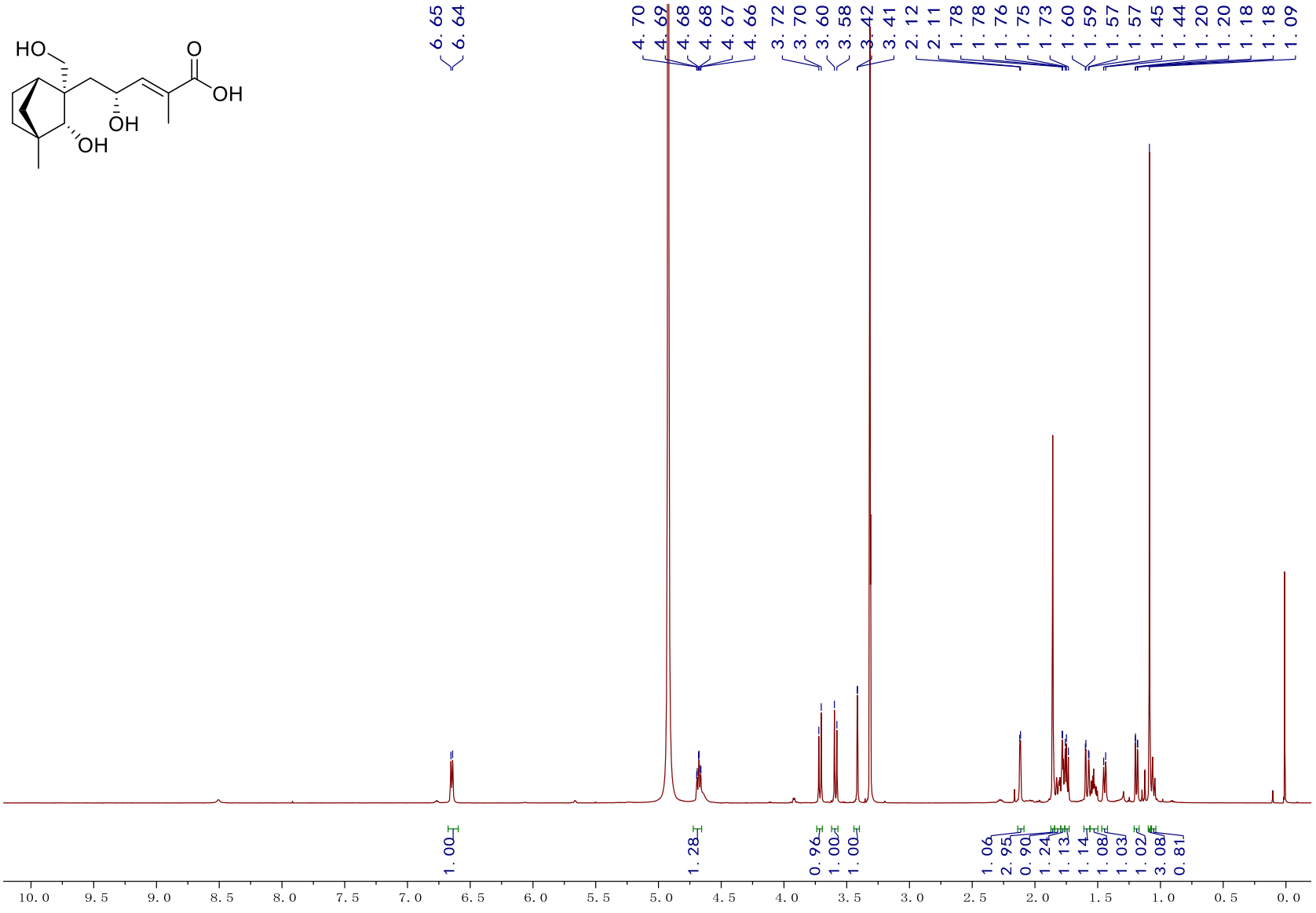


Figure S53. ^{13}C NMR and DEPT of compound **5** in CD_3OD

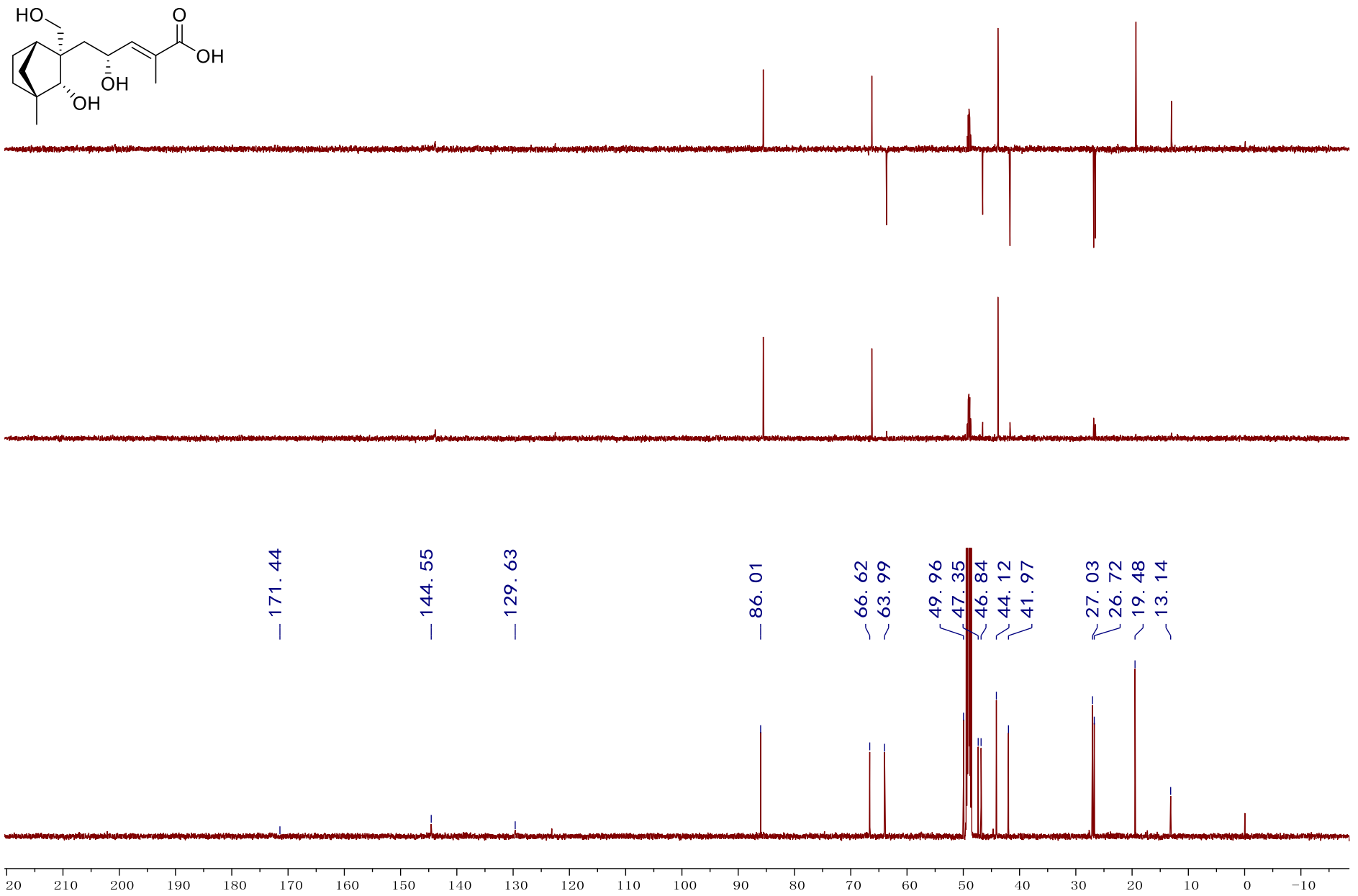


Figure S54. HSQC of compound **5** in CD_3OD

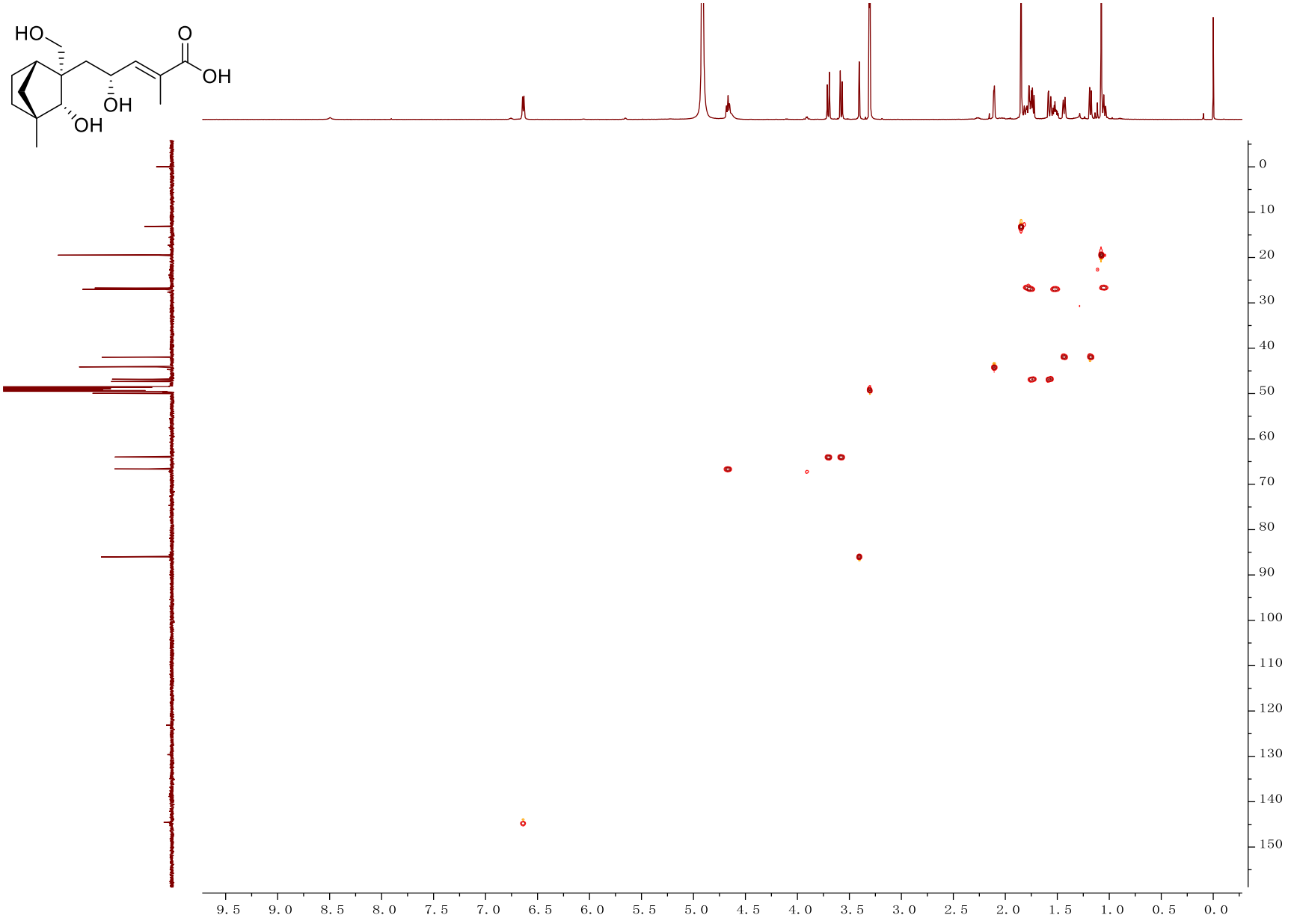


Figure S55. HMBC of compound **5** in CD_3OD

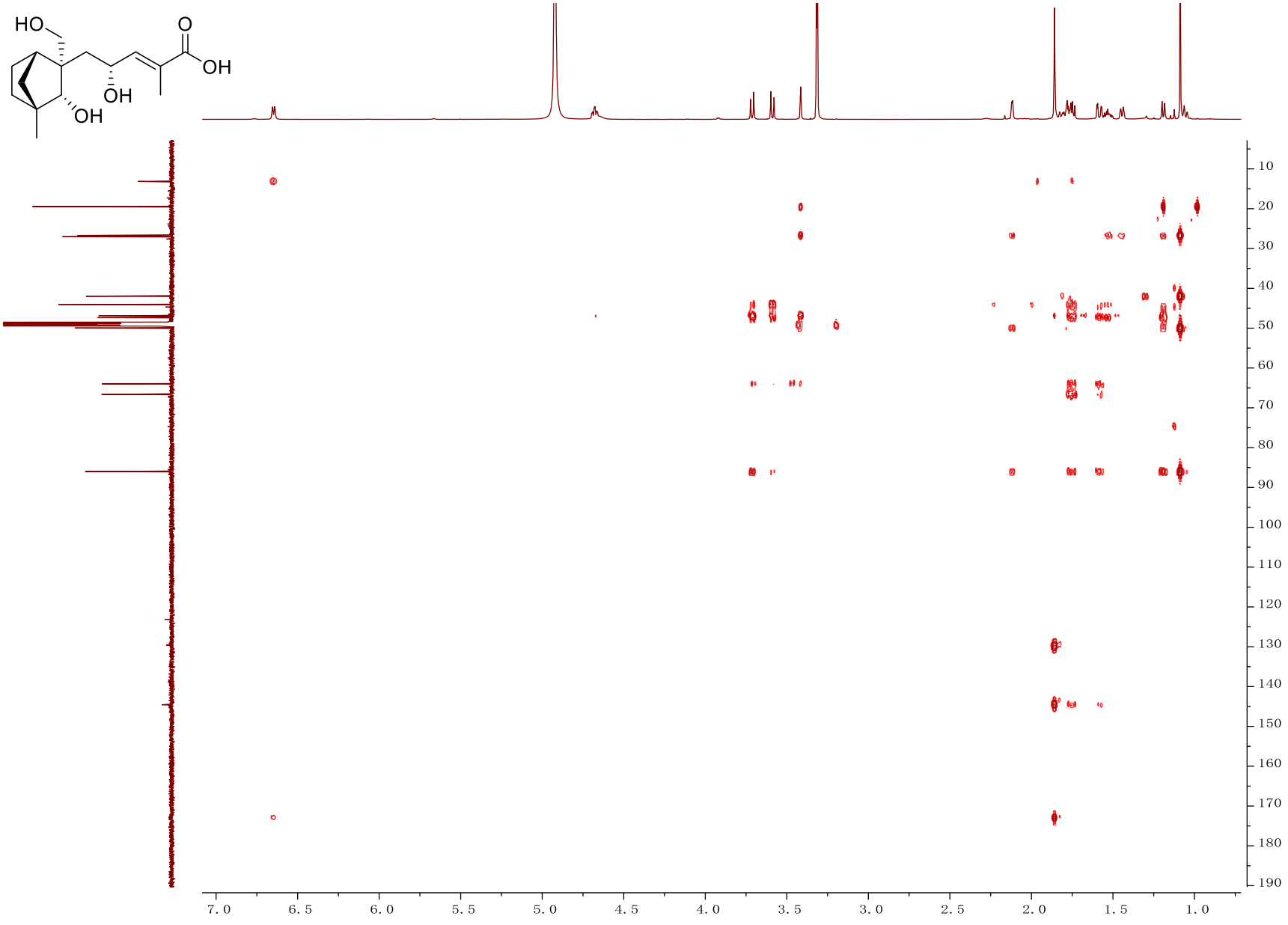


Figure S56. ^{1}H-^{1}H COSY of compound **5** in CD_3OD

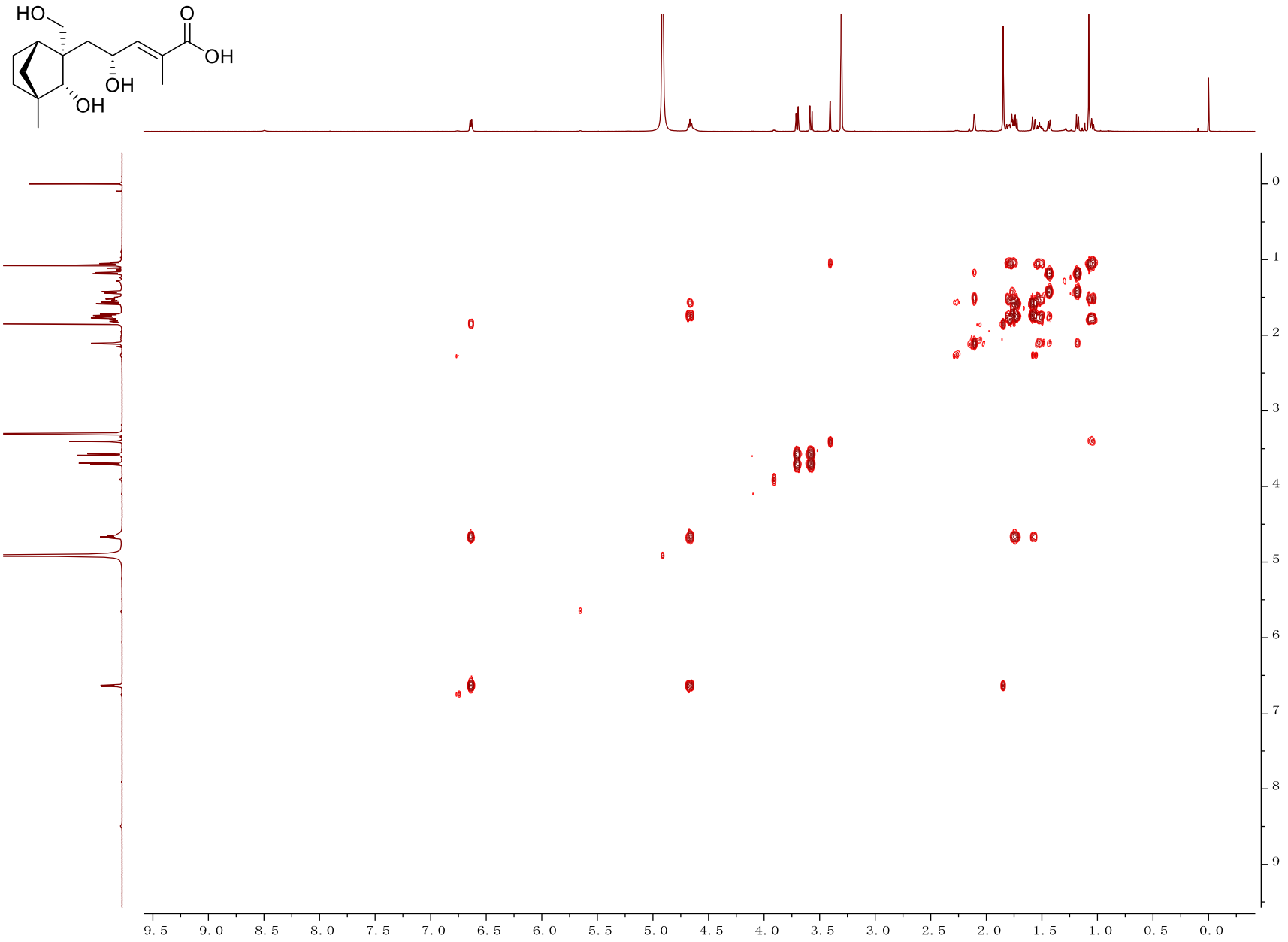


Figure S57. ROESY of compound **5** in CD_3OD

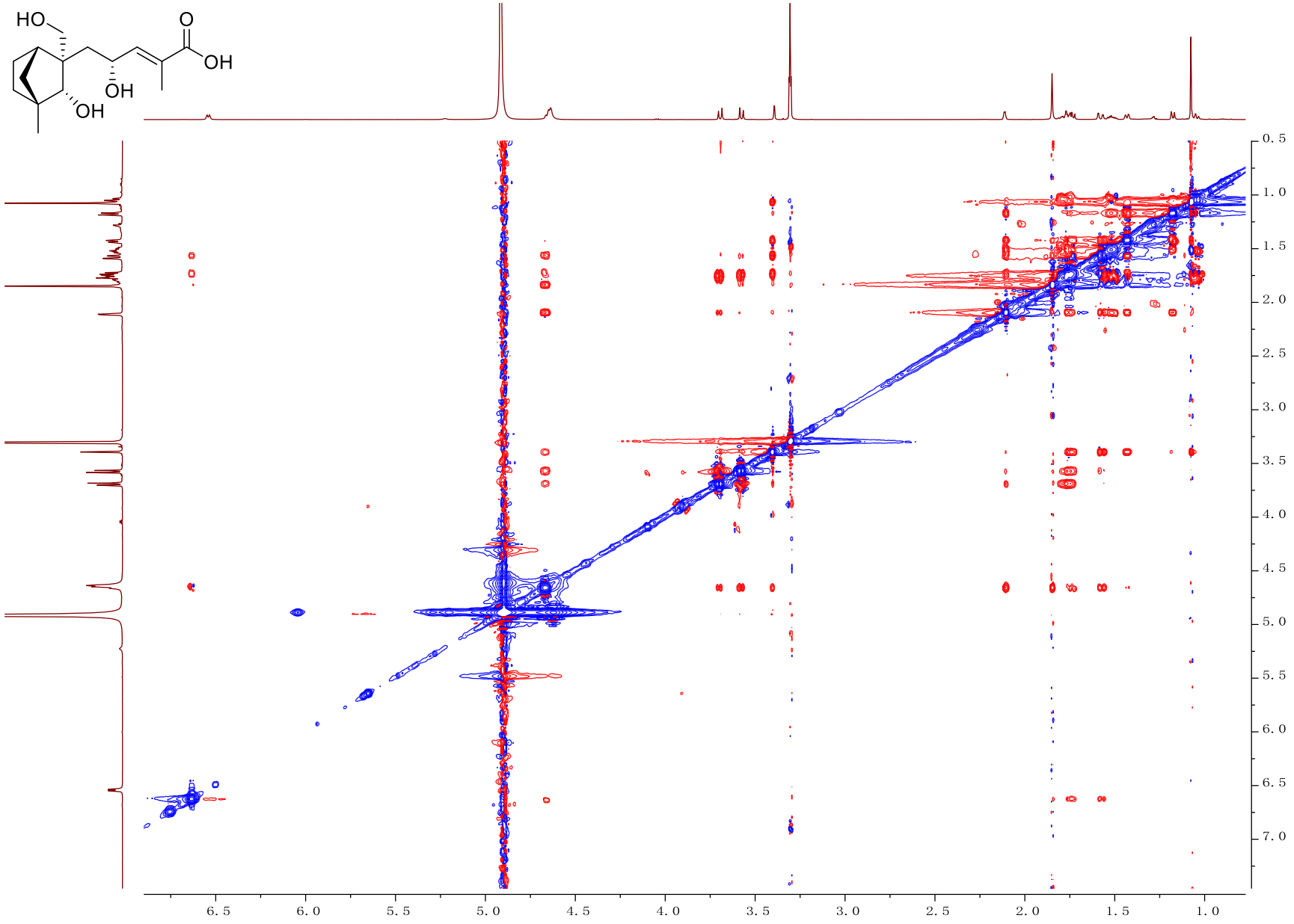
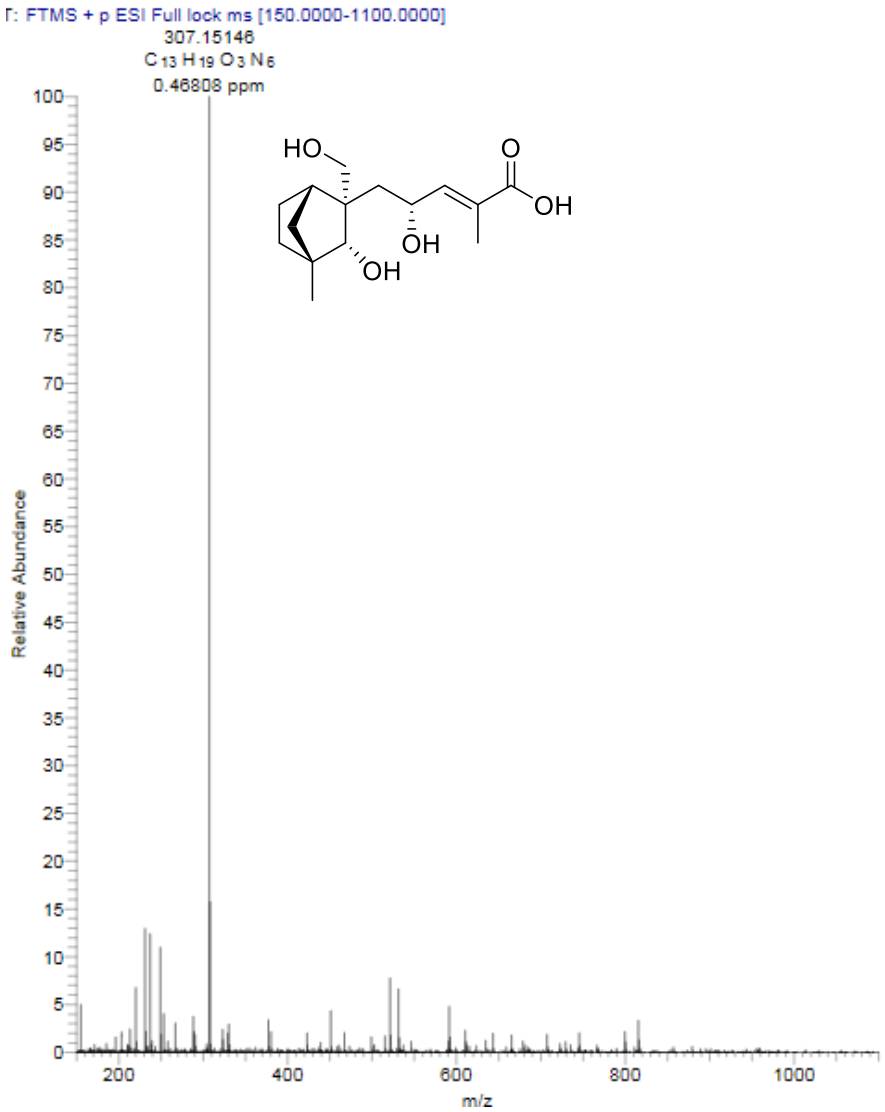


Figure S58. HR-ESIMS of compound **5**



Section S13. NMR and MS spectra for 6

Figure S59. ^{1}H NMR of compound **6** in CD_3OD

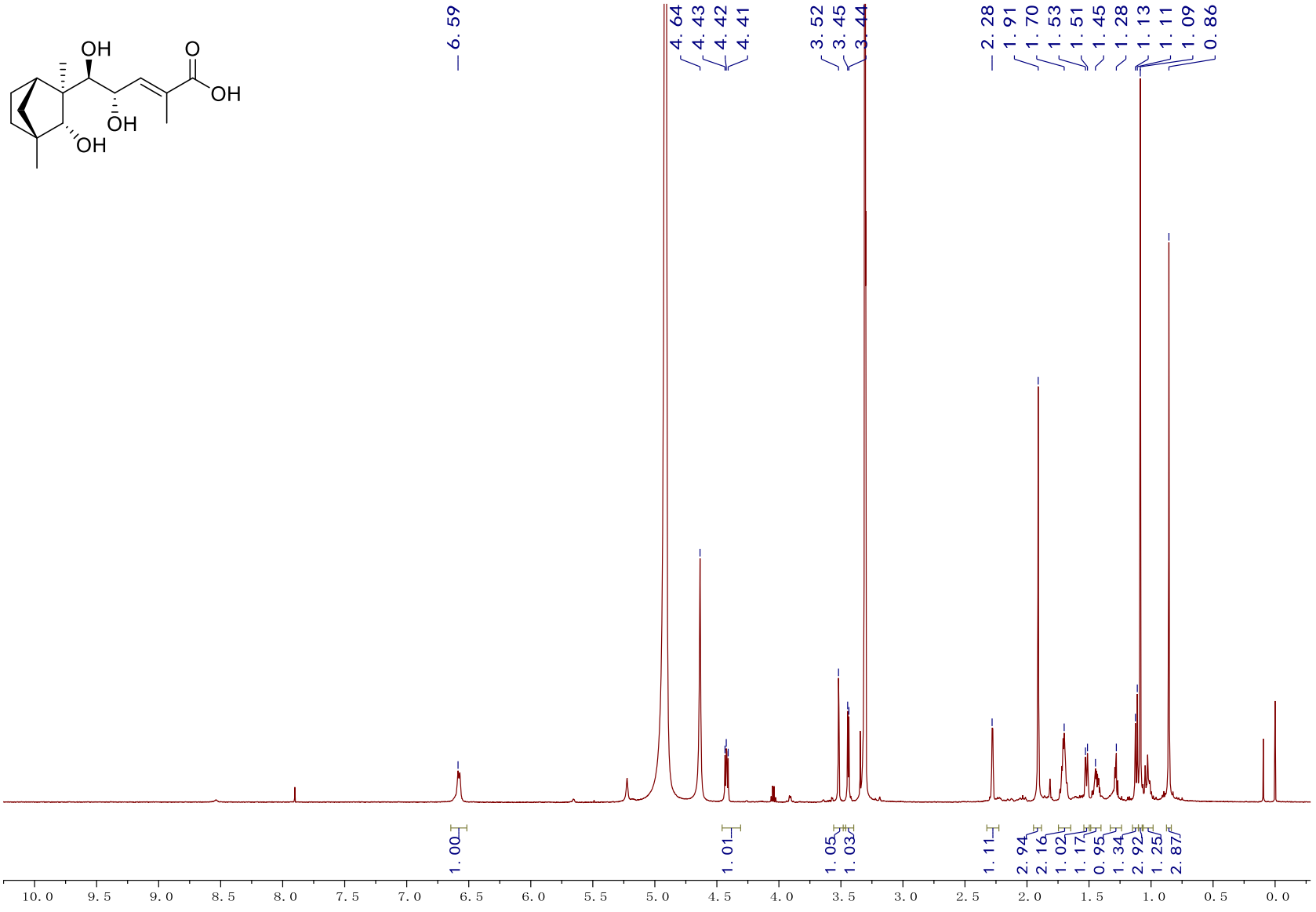
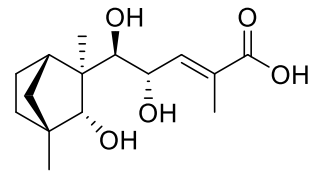


Figure S60. ^{13}C NMR and DEPT of compound **6** in CD_3OD



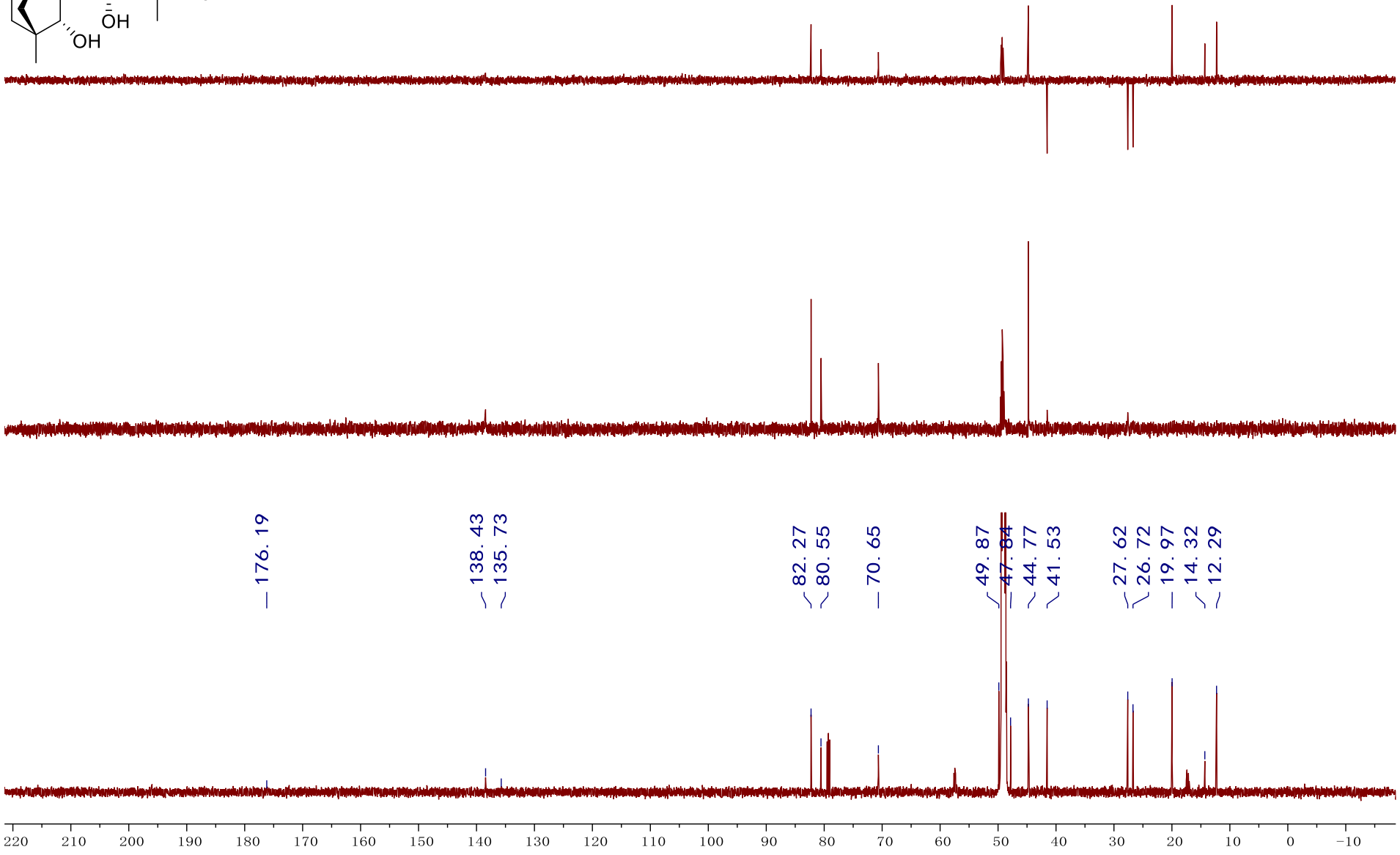


Figure S61. HSQC of compound **6** in CD_3OD

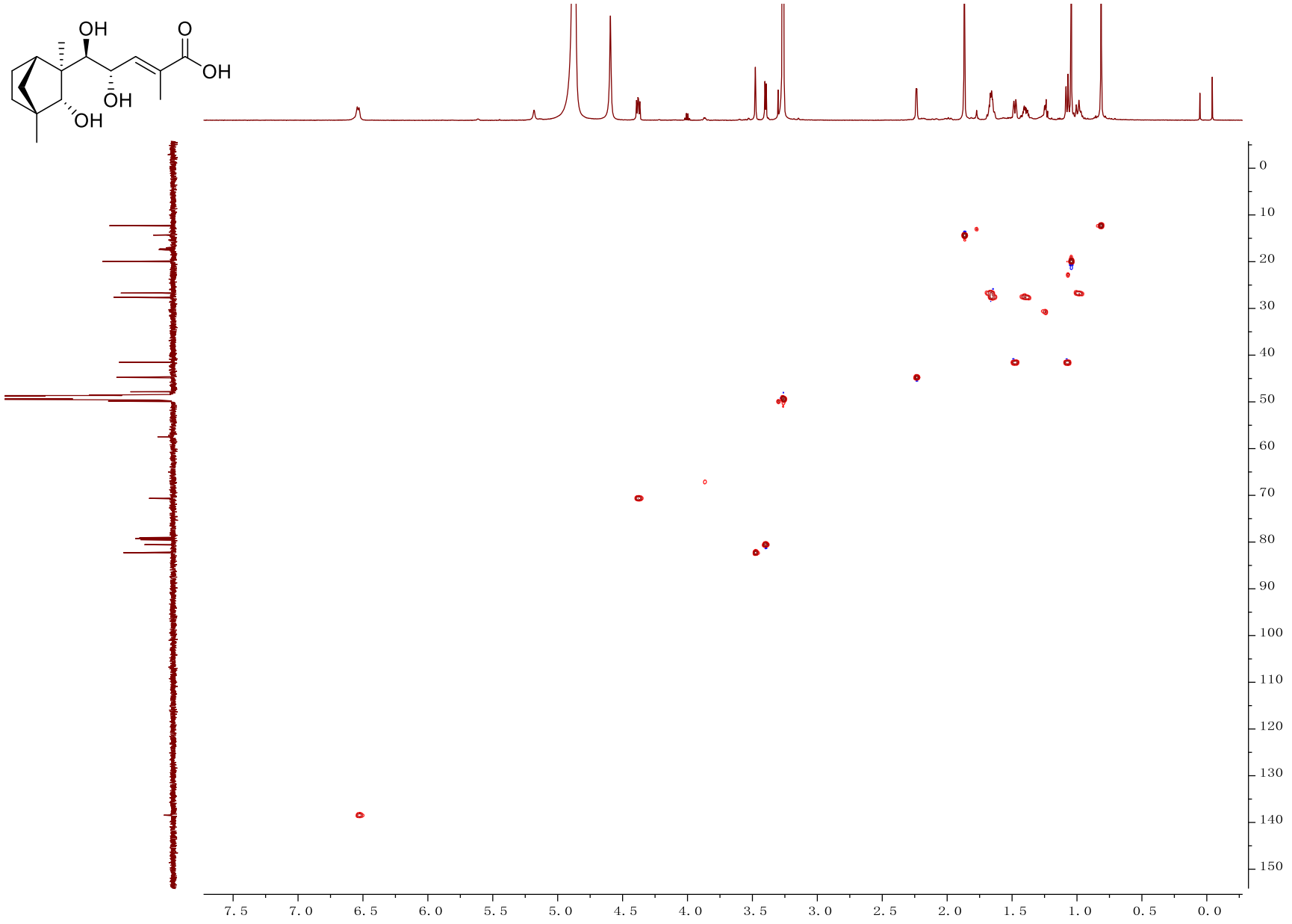


Figure S62. HMBC of compound **6** in CD_3OD

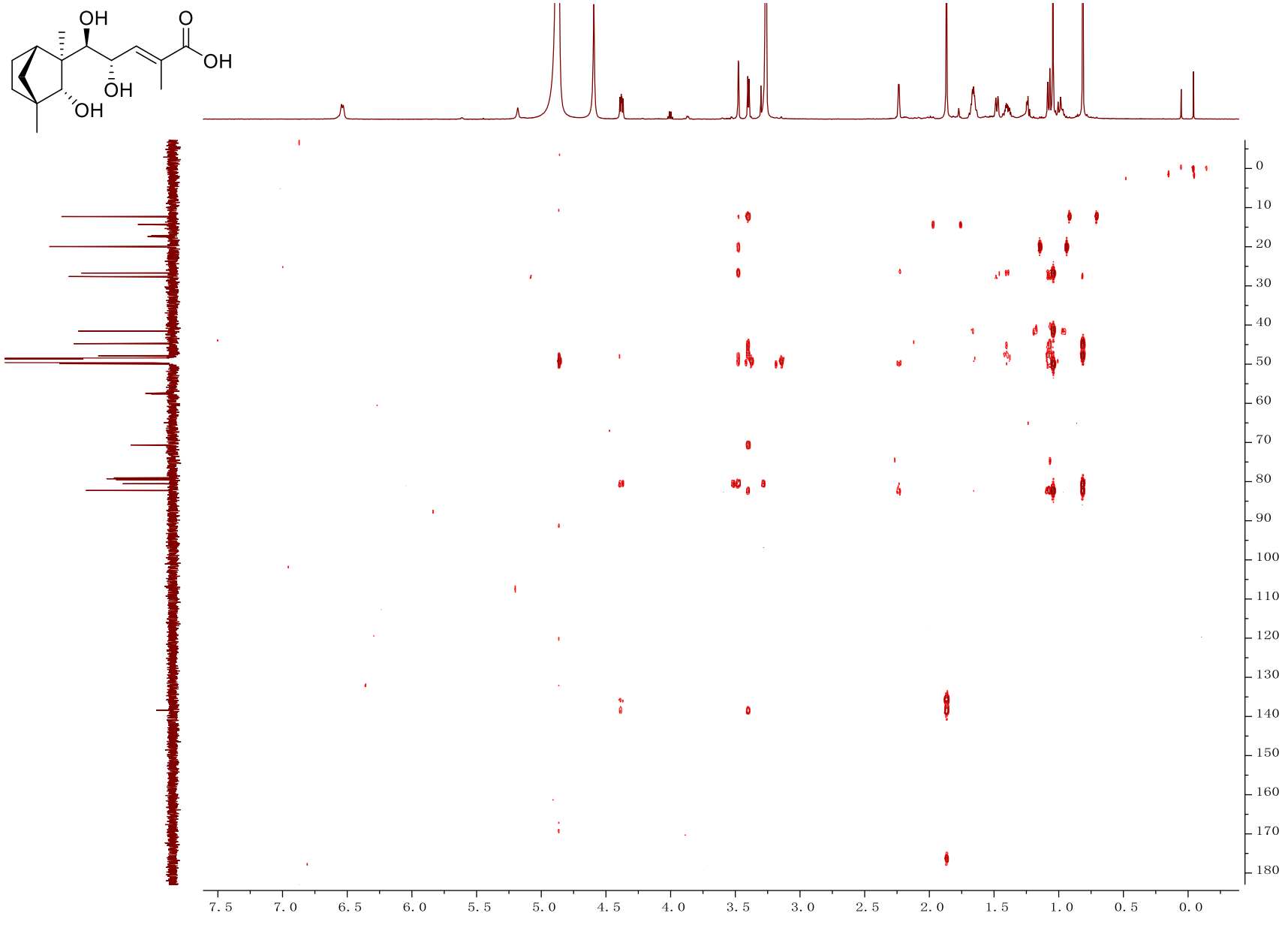


Figure S63. ^{1}H-^{1}H COSY of compound **6** in CD_3OD

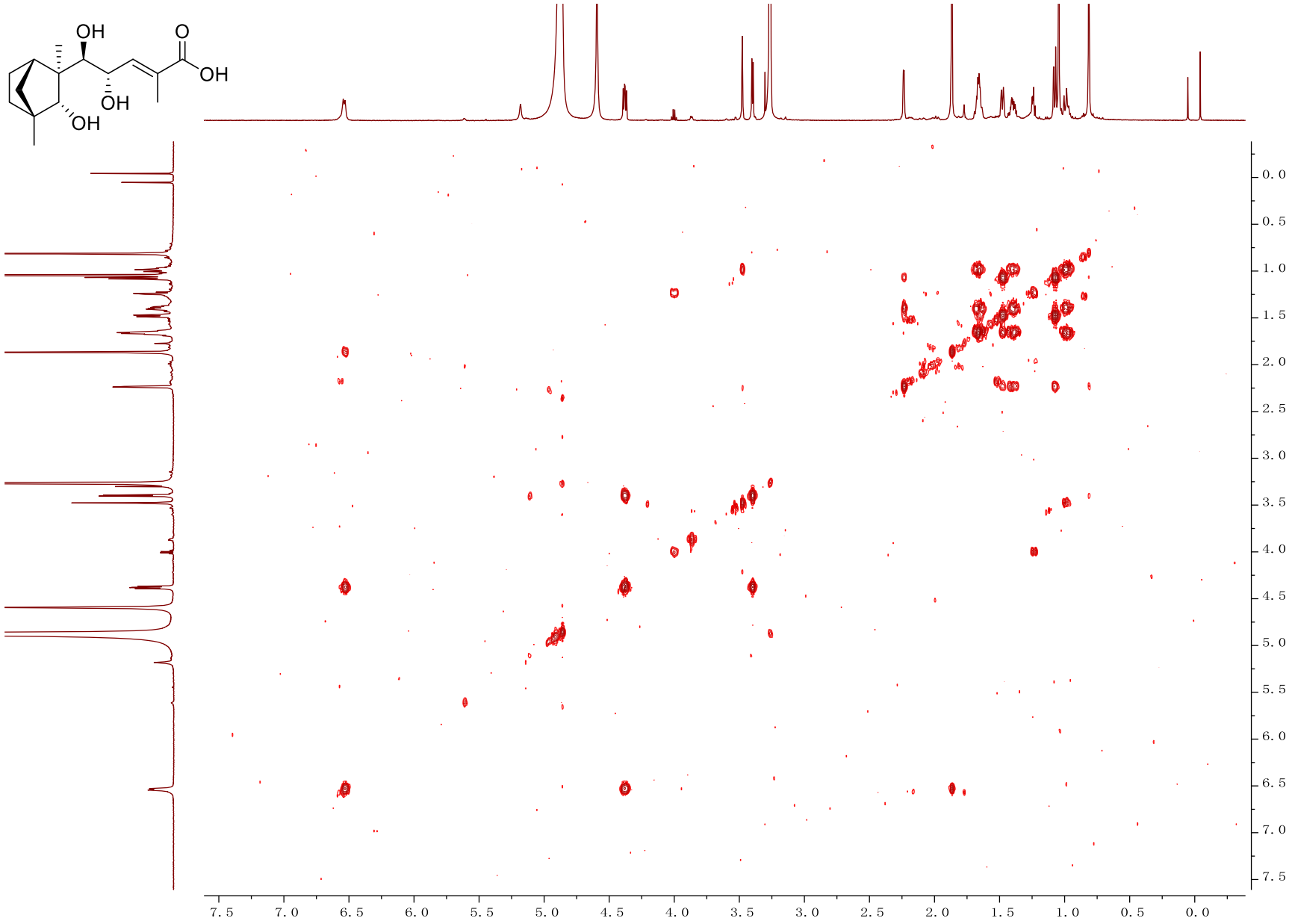


Figure S64. ROESY of compound **6** in CD_3OD

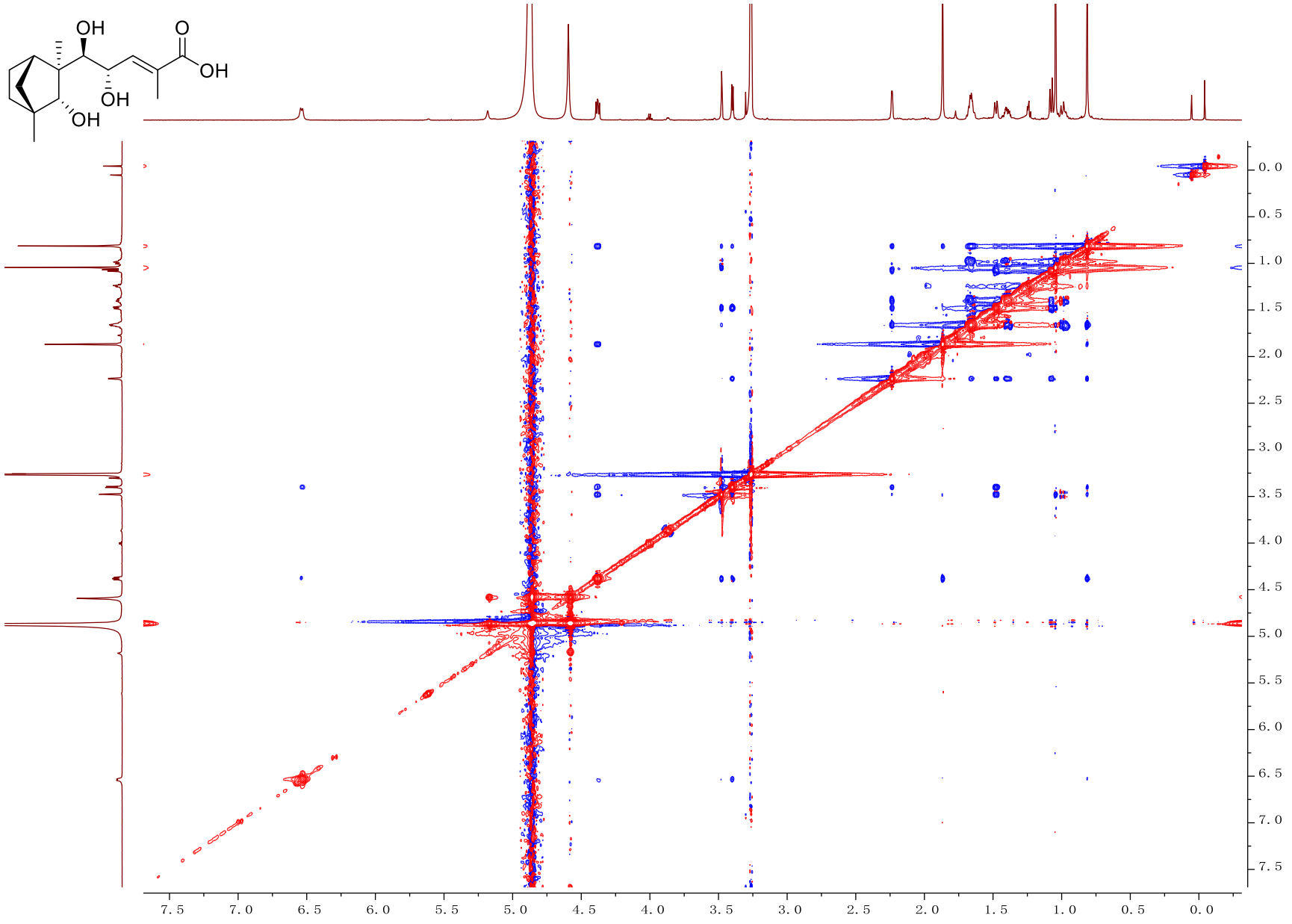
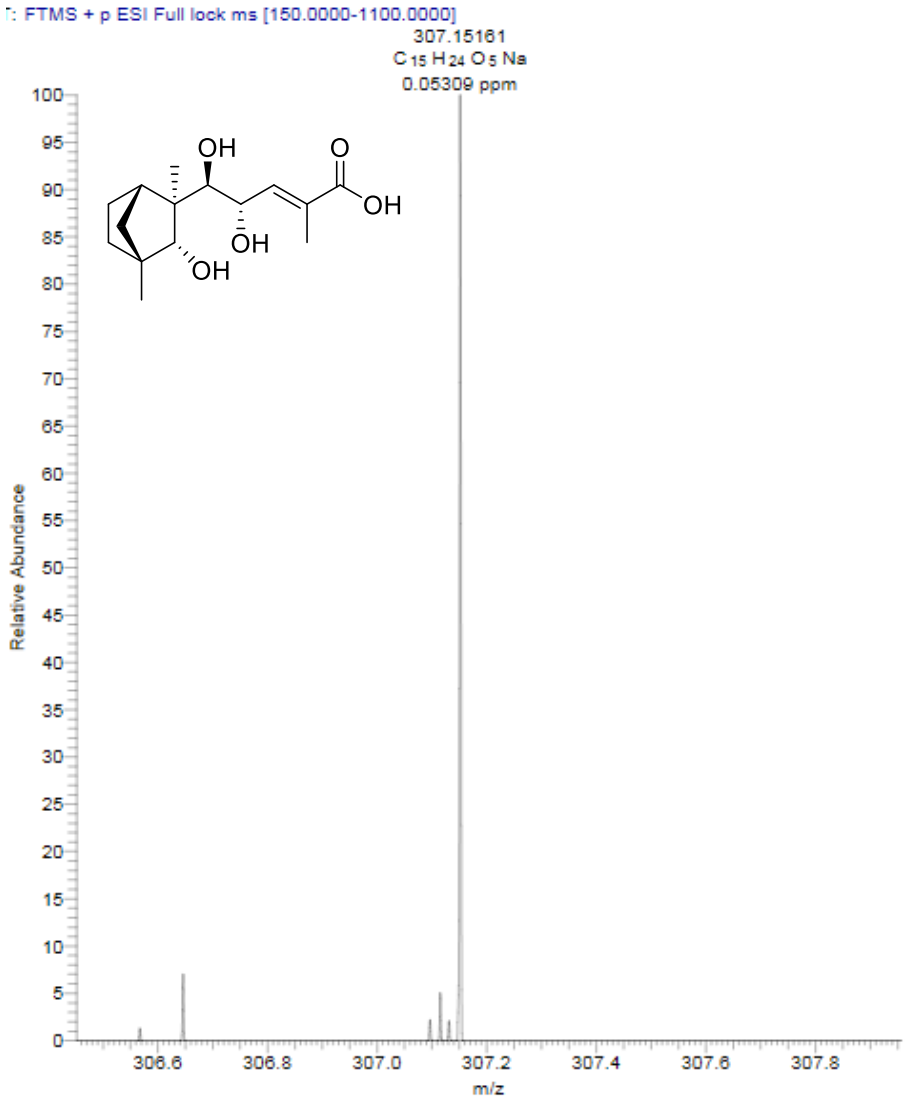


Figure S65. HR-ESIMS of compound **6**



Section S14. NMR and MS spectra for 7*S*,9*S*,14*S*-7

Figure S66. ^{1}H NMR of compound 7*S*,9*S*,14*S*-**7** in CD_3OD

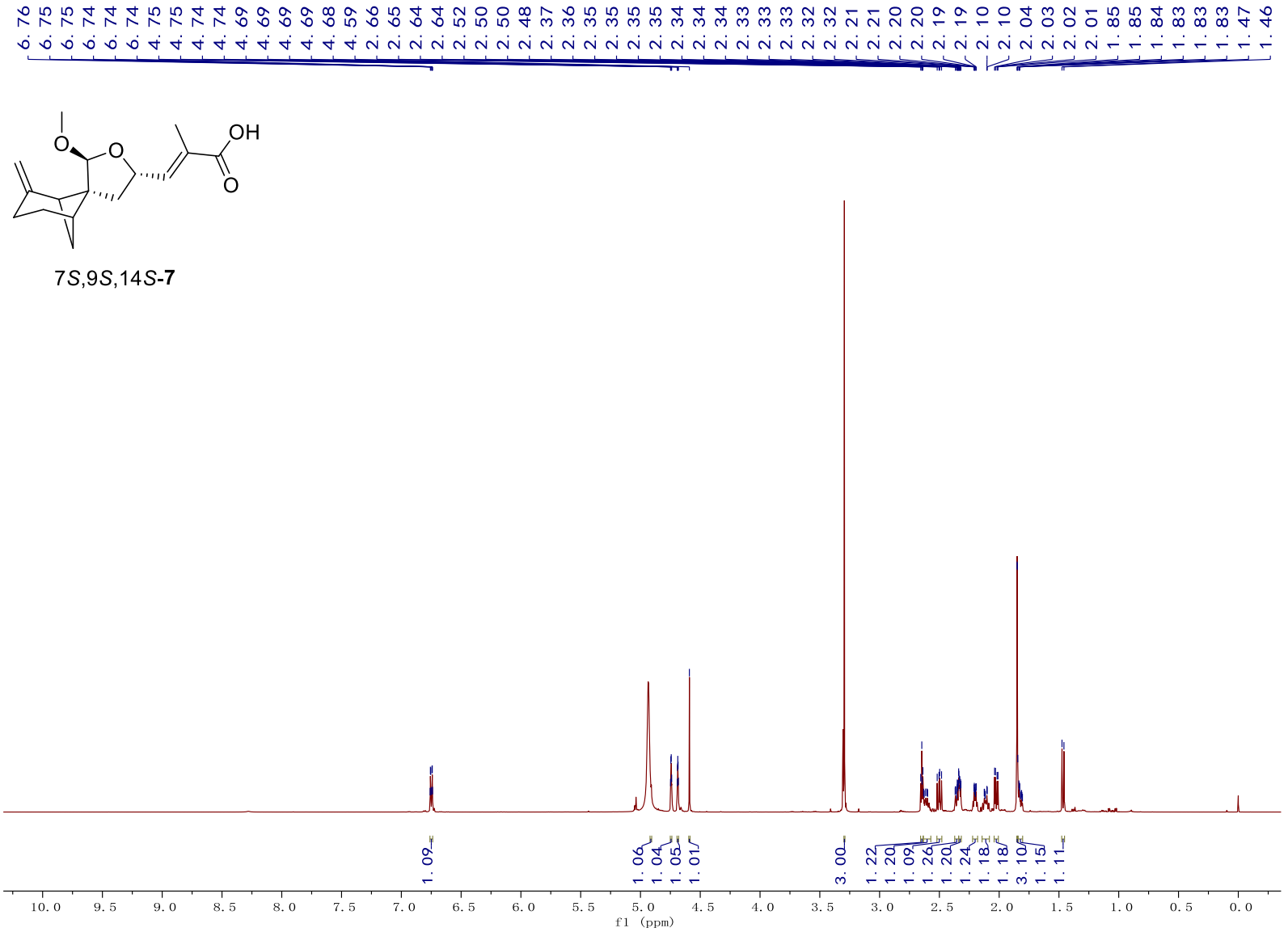


Figure S67. ^{13}C NMR and DEPT of compound 7*S*,9*S*,14*S*-**7** in CD_3OD

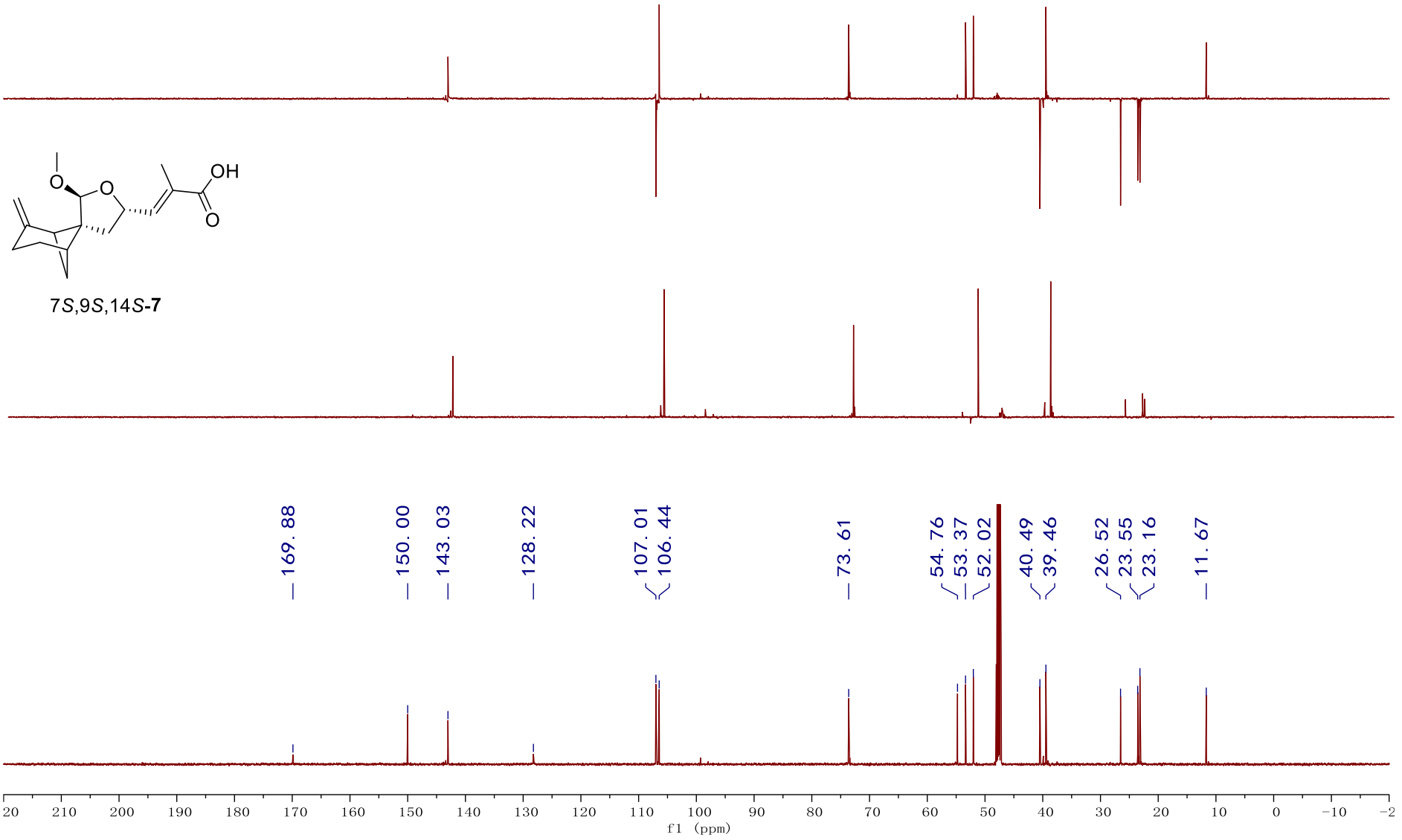


Figure S68. HSQC of compound 7*S*,9*S*,14*S*-**7** in CD_3OD

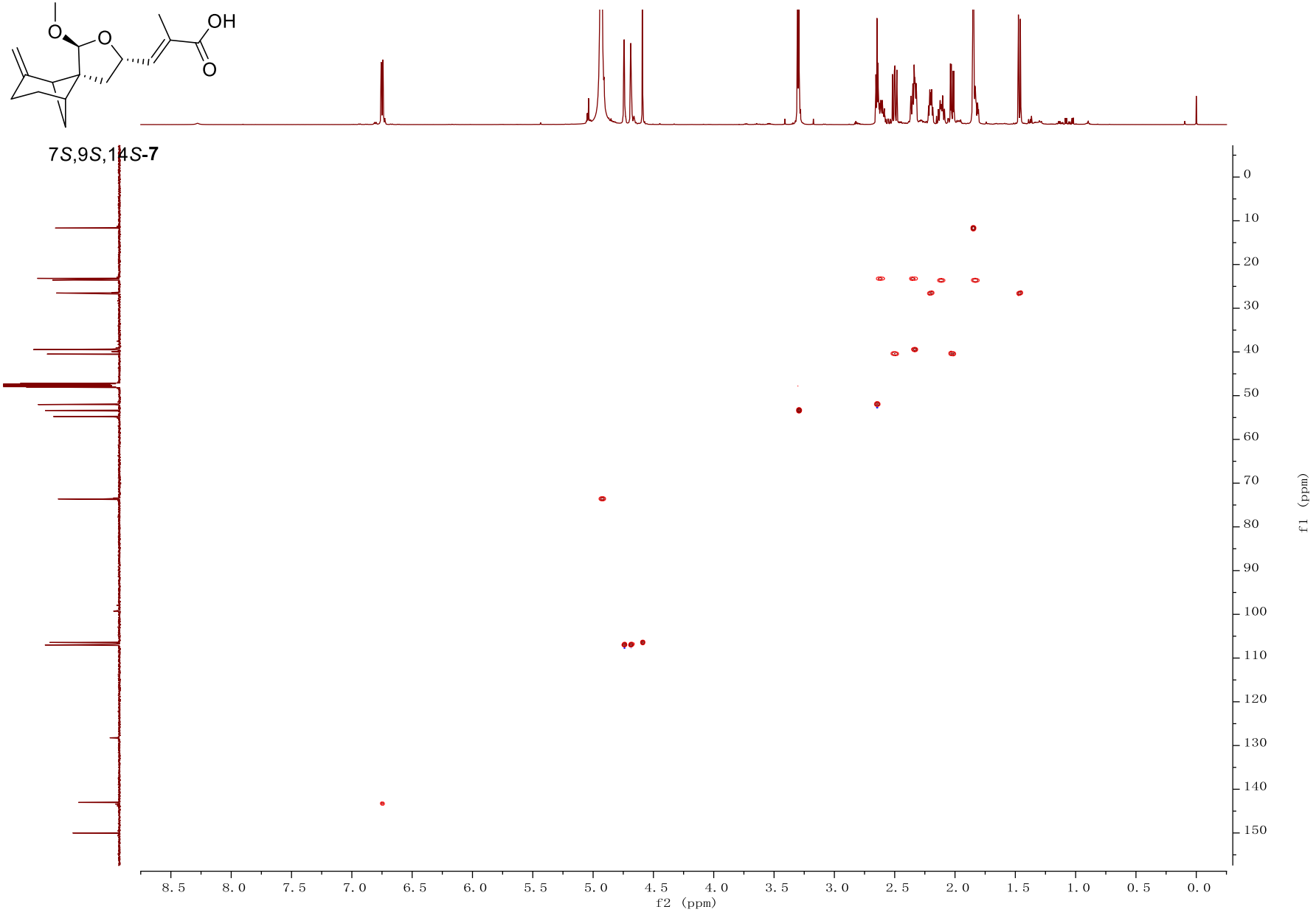


Figure S69. HMBC of compound 7*S*,9*S*,14*S*-**7** in CD_3OD

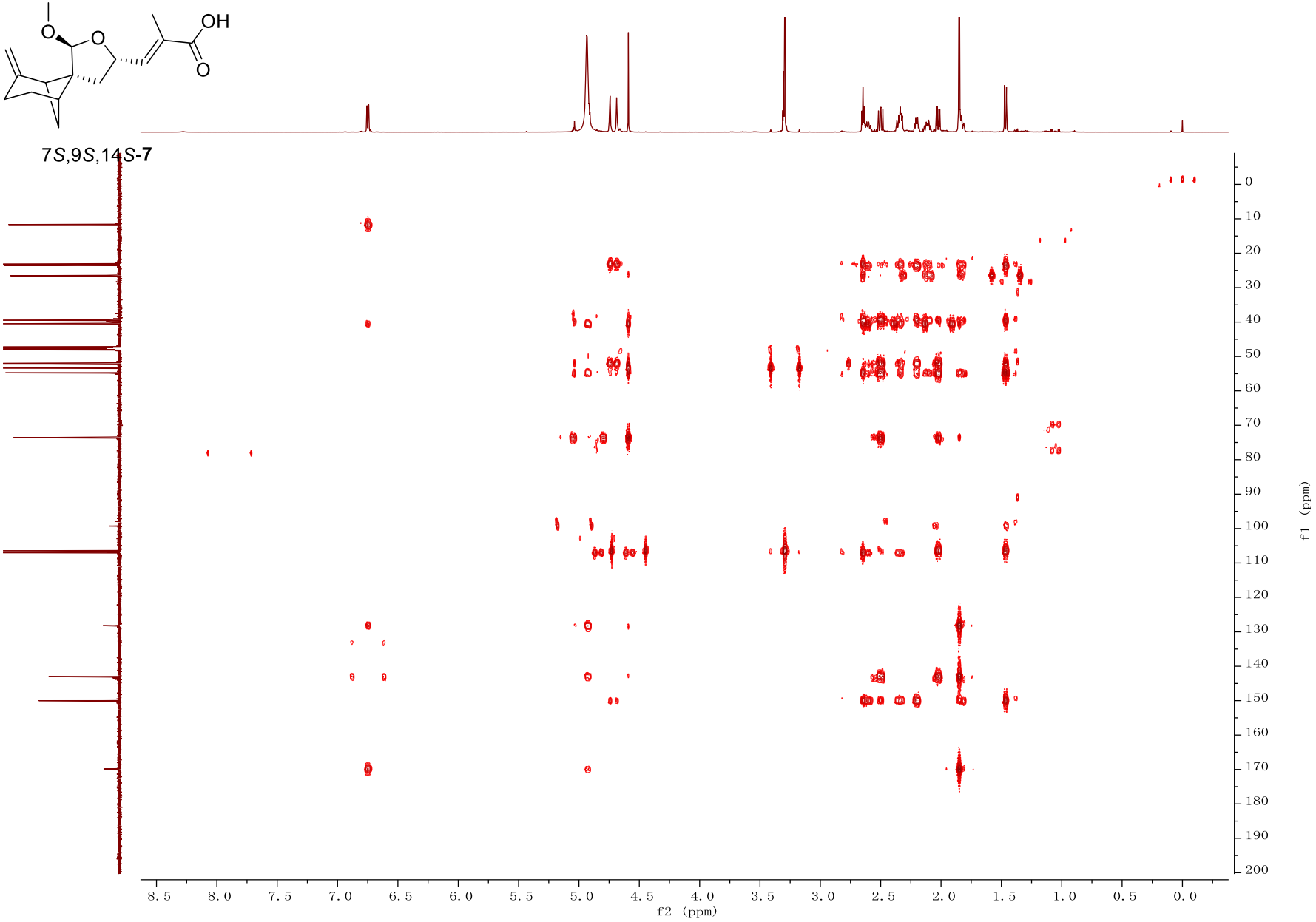


Figure S70. ^{1}H-^{1}H COSY of compound 7*S*,9*S*,14*S*-**7** in CD_3OD

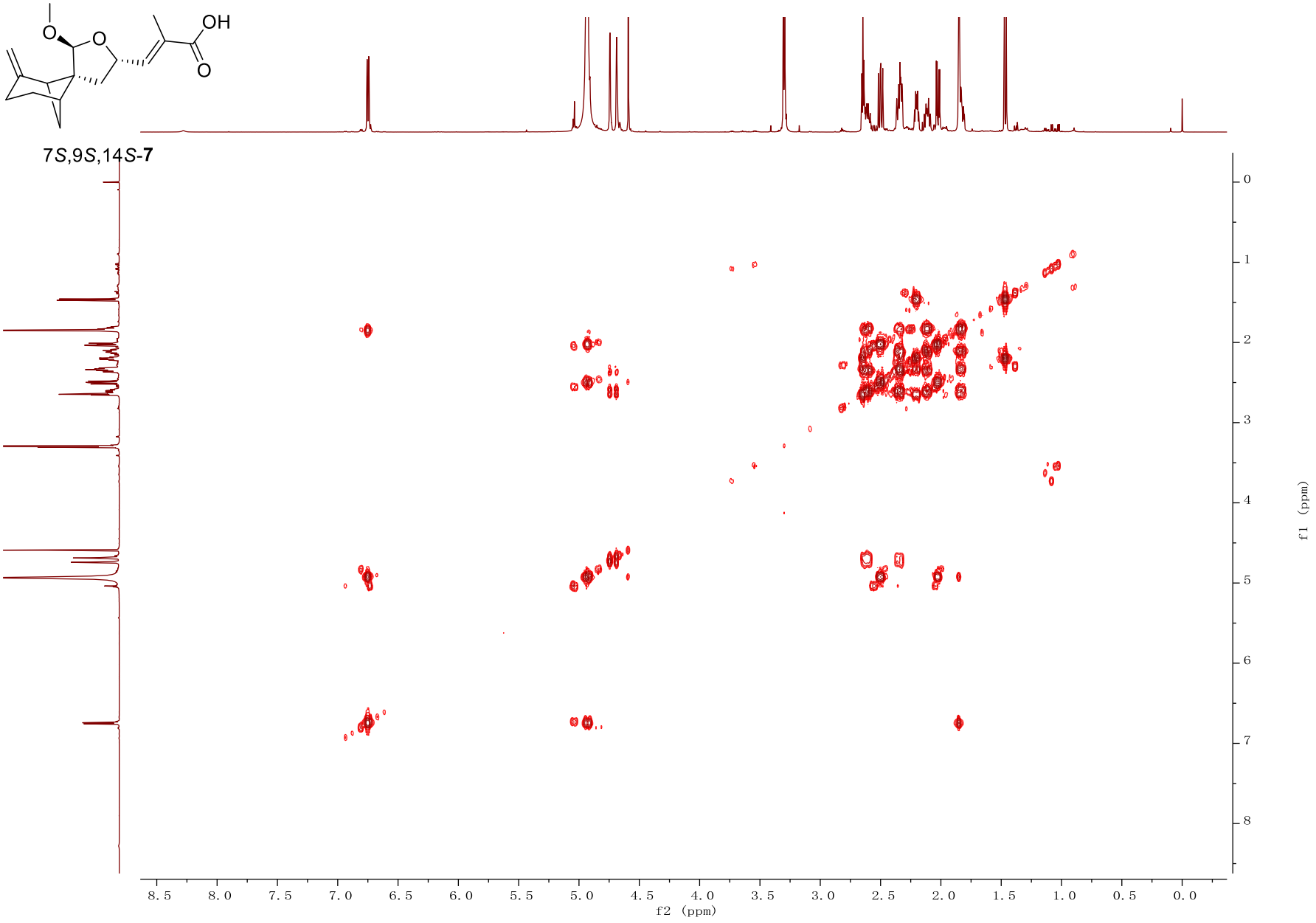


Figure S71. ROESY of compound 7*S*,9*S*,14*S*-**7** in CD_3OD

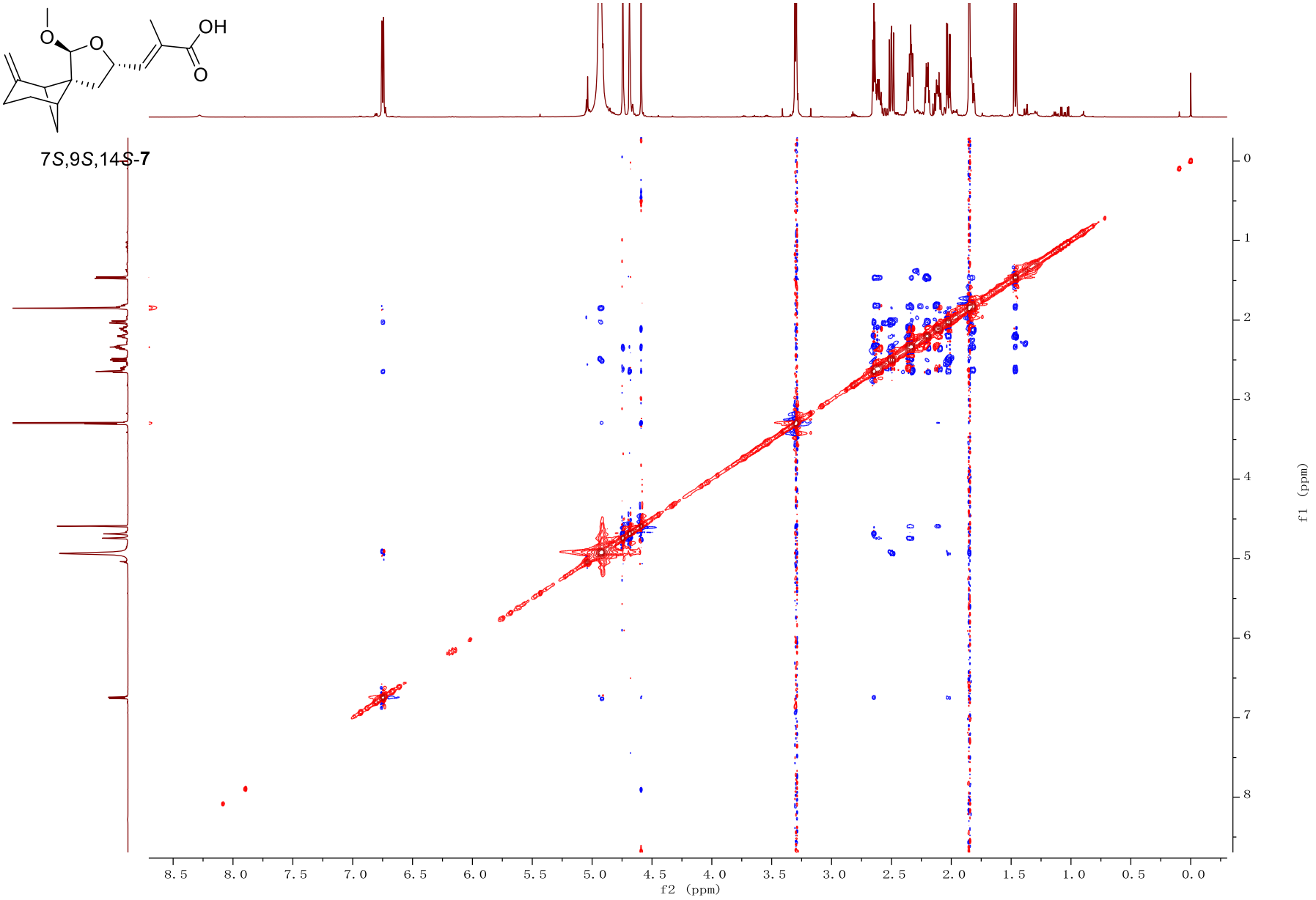
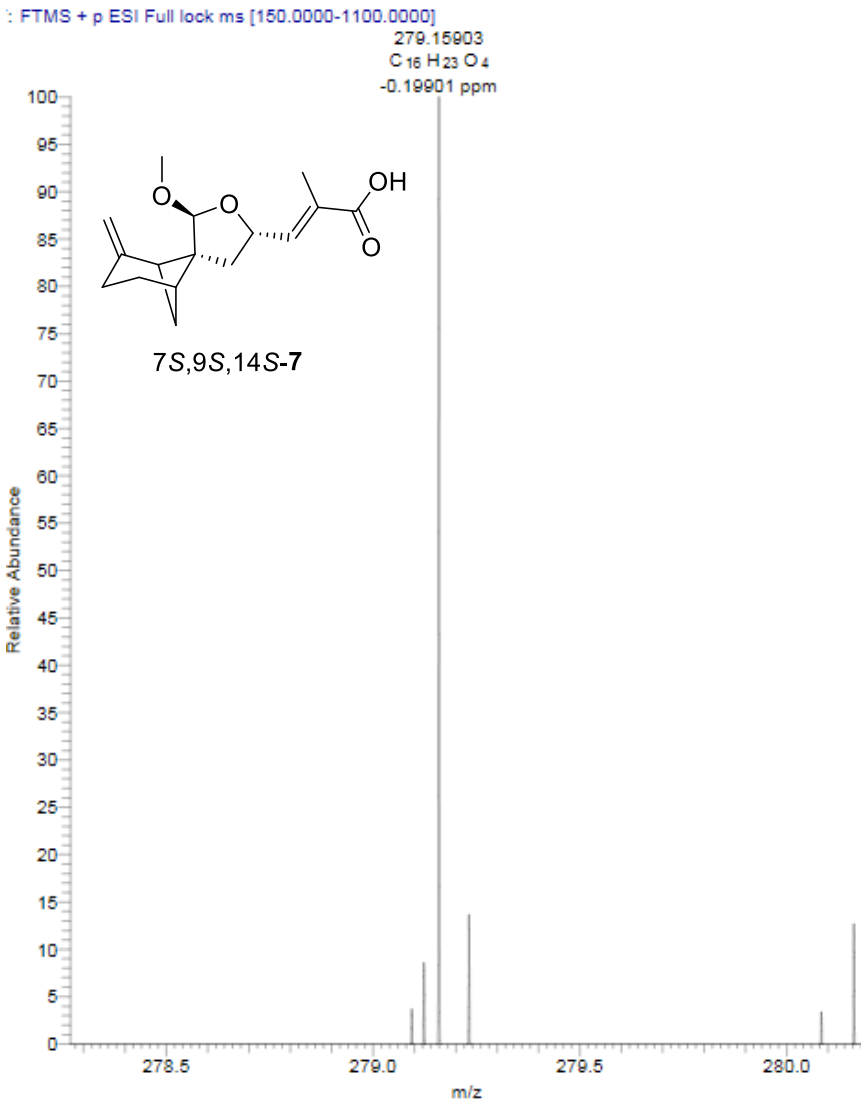


Figure S72. HR-ESIMS of compound 7*S*,9*S*,14*S*-**7**



Section S15. NMR and MS spectra for 7*S*,9*S*,14*R*-8

Figure S73. ^{1}H NMR of compound 7*S*,9*S*,14*R*-**8** in CD_3OD

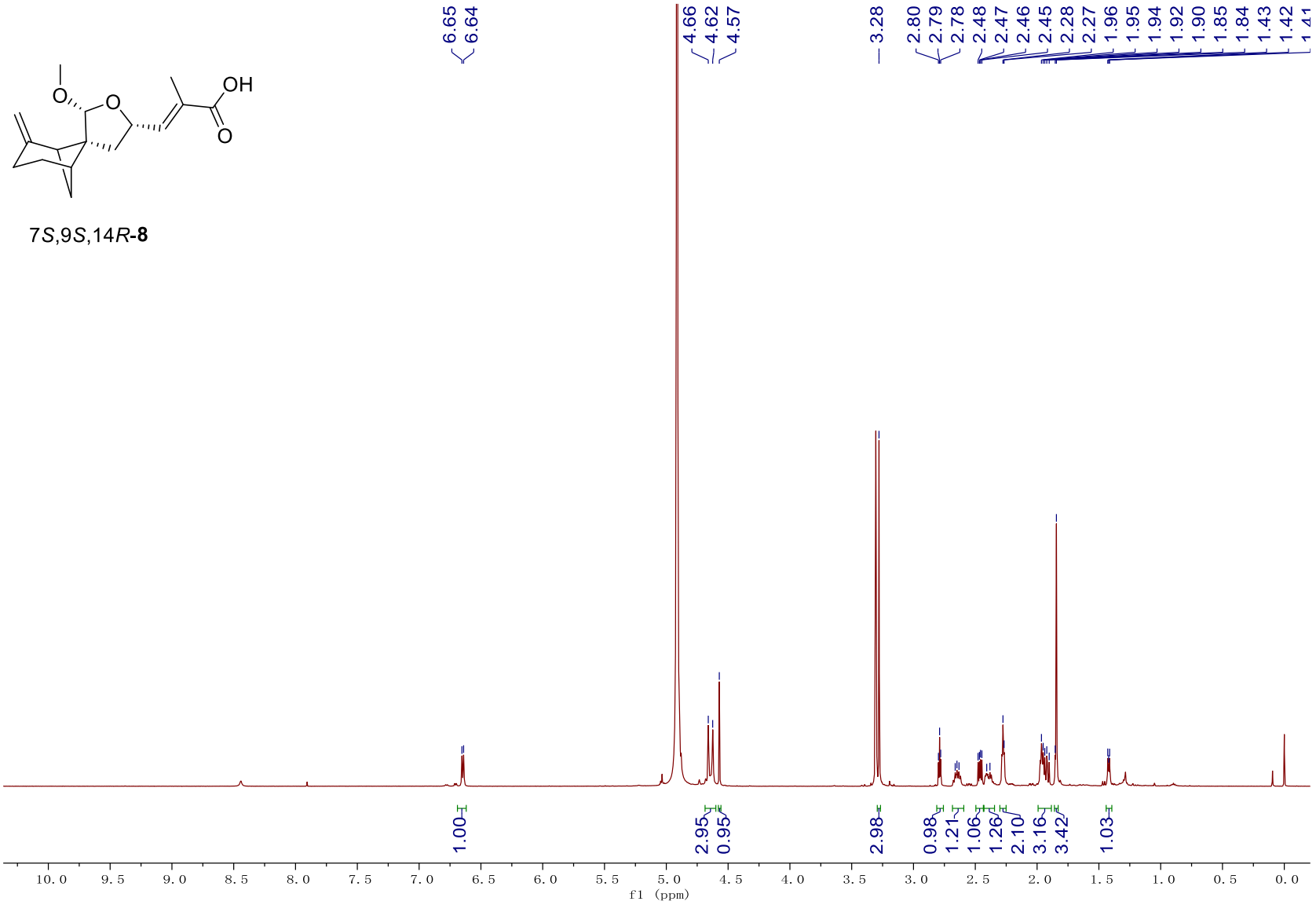
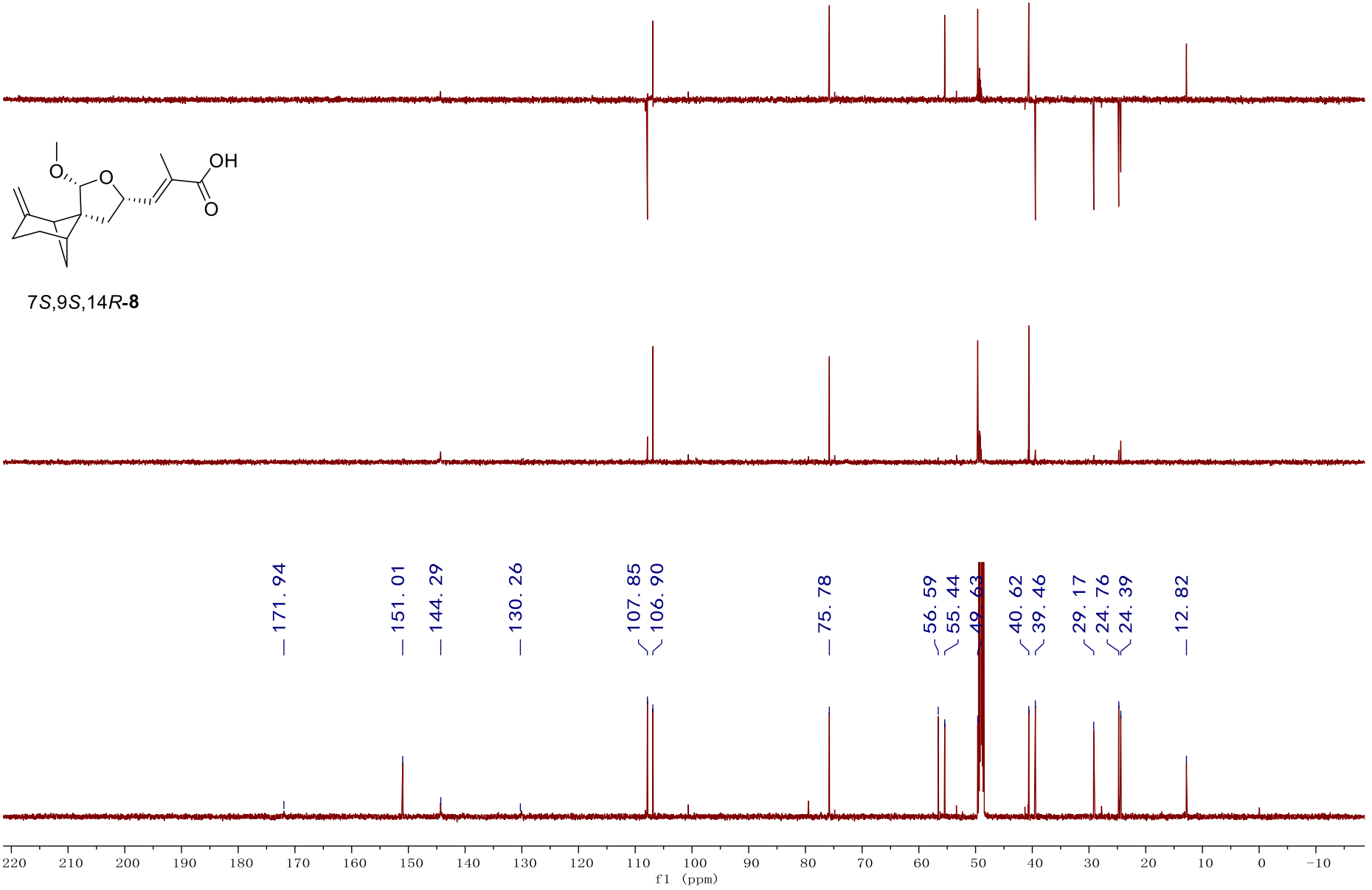


Figure S74. ^{13}C NMR and DEPT of compound 7*S*,9*S*,14*R*-**8** in CD_3OD



7*S*,9*S*,14*R*-**8**

Figure S75. HSQC of compound 7*S*,9*S*,14*R*-**8** in CD_3OD

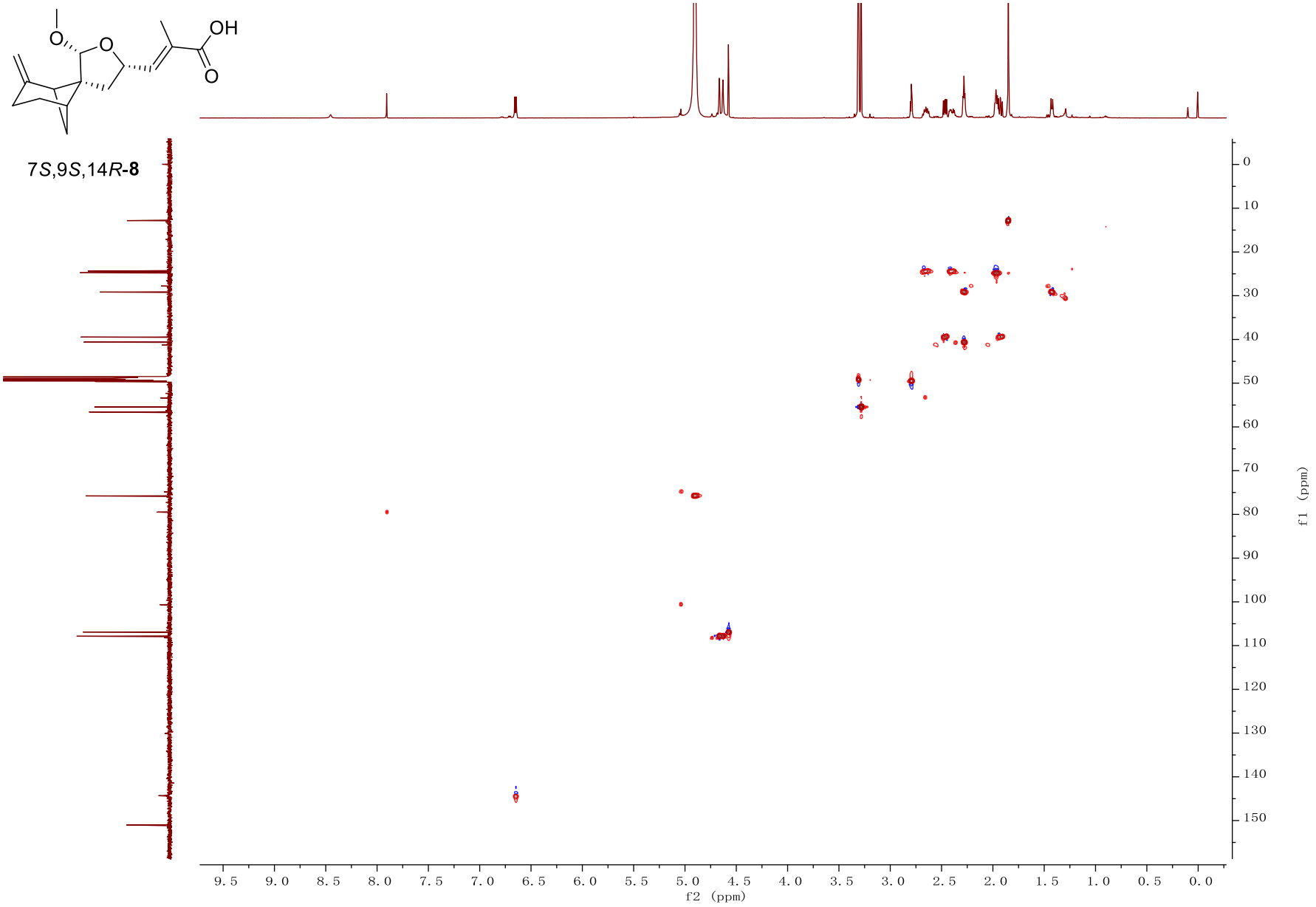


Figure S76. HMBC of compound 7*S*,9*S*,14*R*-**8** in CD_3OD

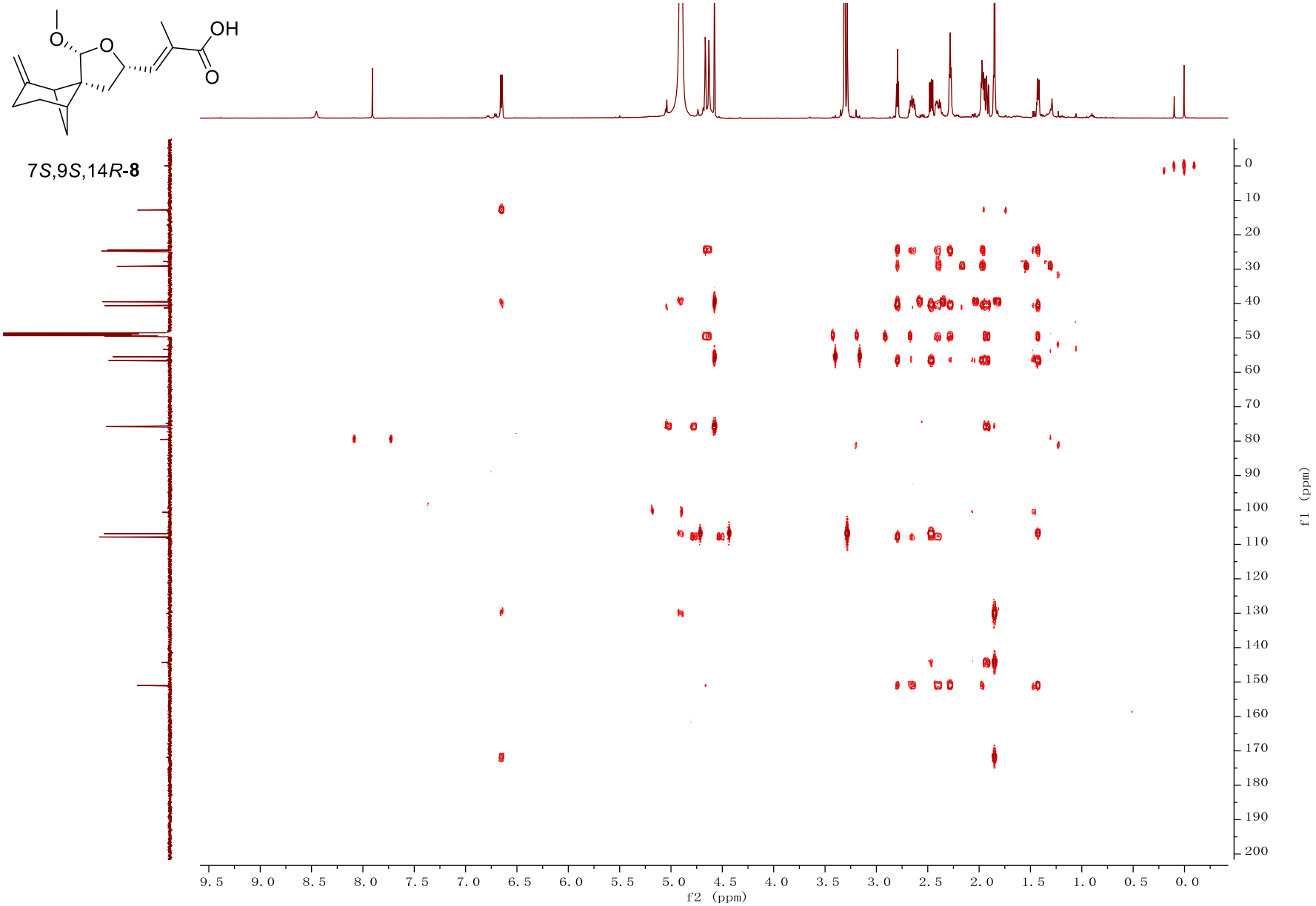


Figure S77. ^{1}H-^{1}H COSY of compound 7*S*,9*S*,14*R*-**8** in CD_3OD

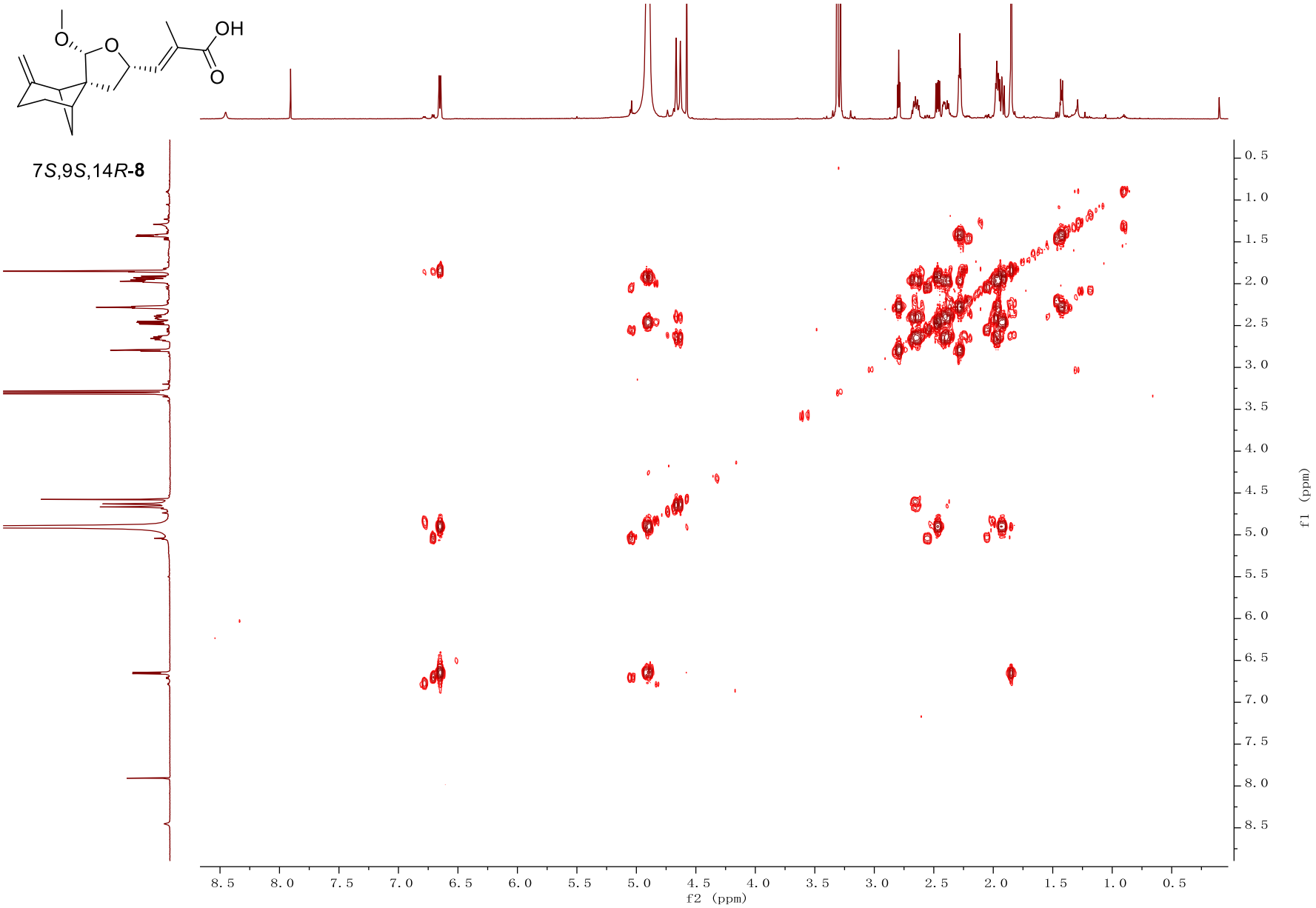


Figure S78. ROESY of compound 7*S*,9*S*,14*R*-**8** in CD_3OD

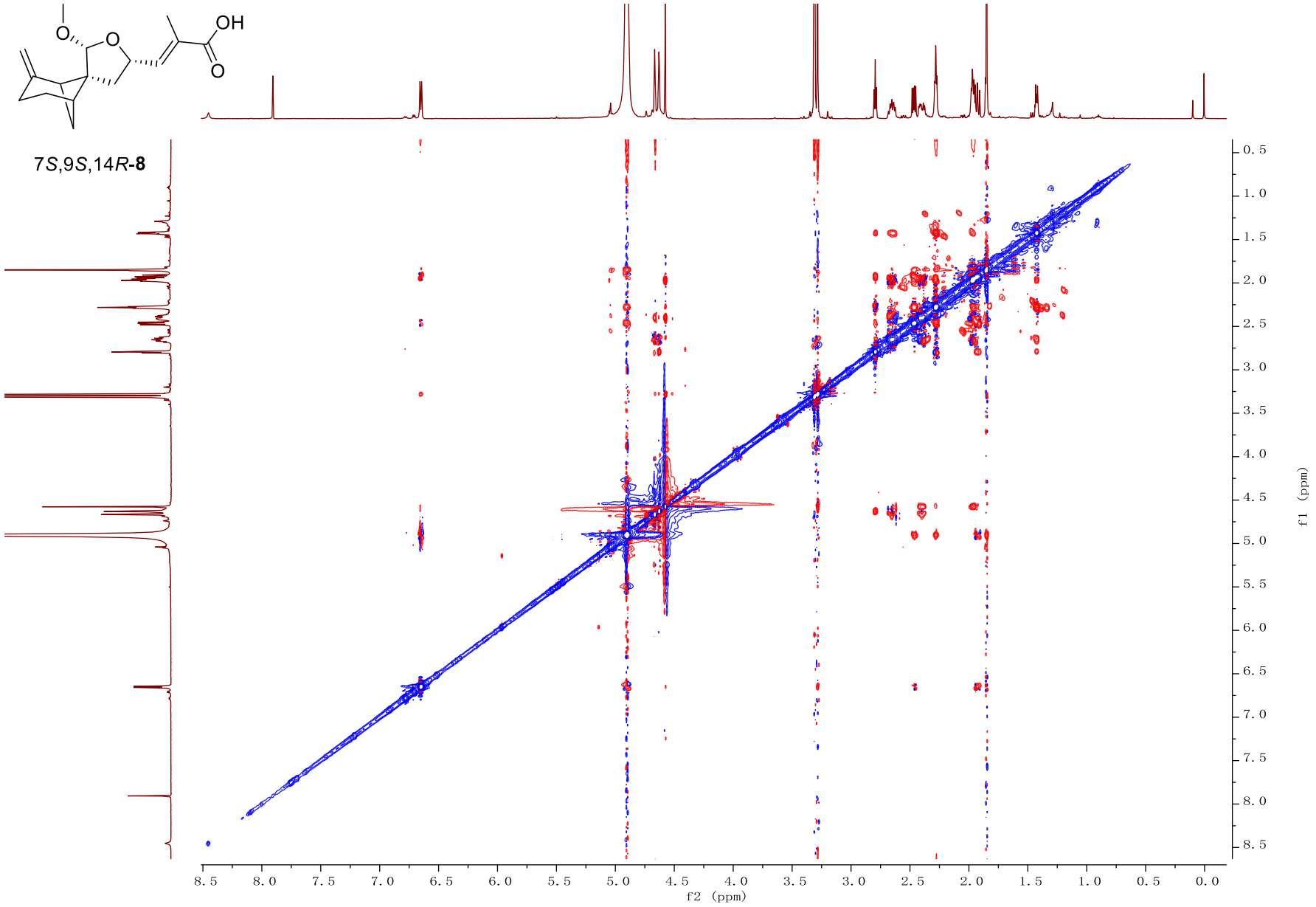
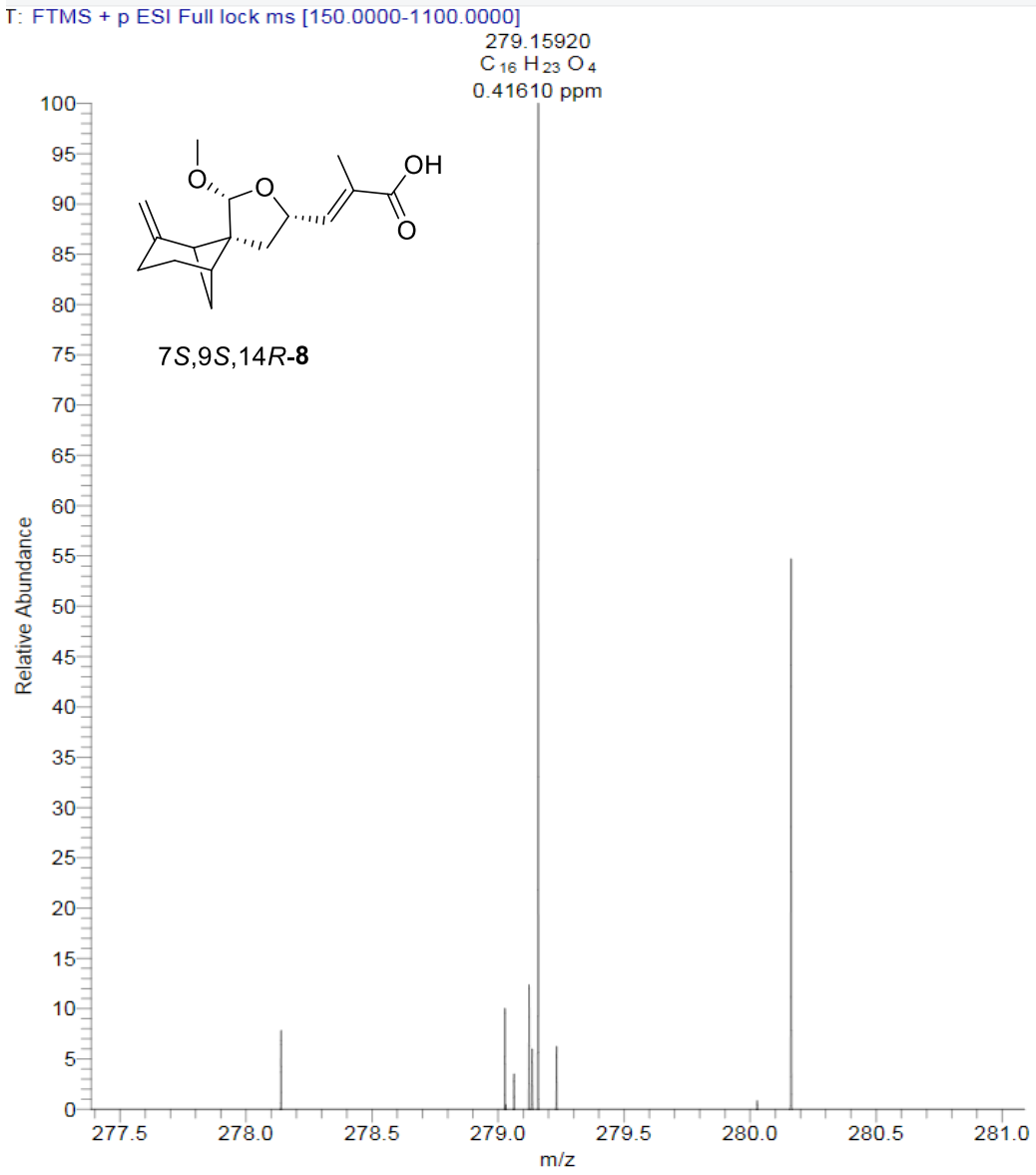


Figure S79. HR-ESIMS of compound 7*S*,9*S*,14*R*-**8**



Section S16. NMR and MS spectra for 9

Figure S80. ^{1}H NMR of compound **9** in CD_3OD

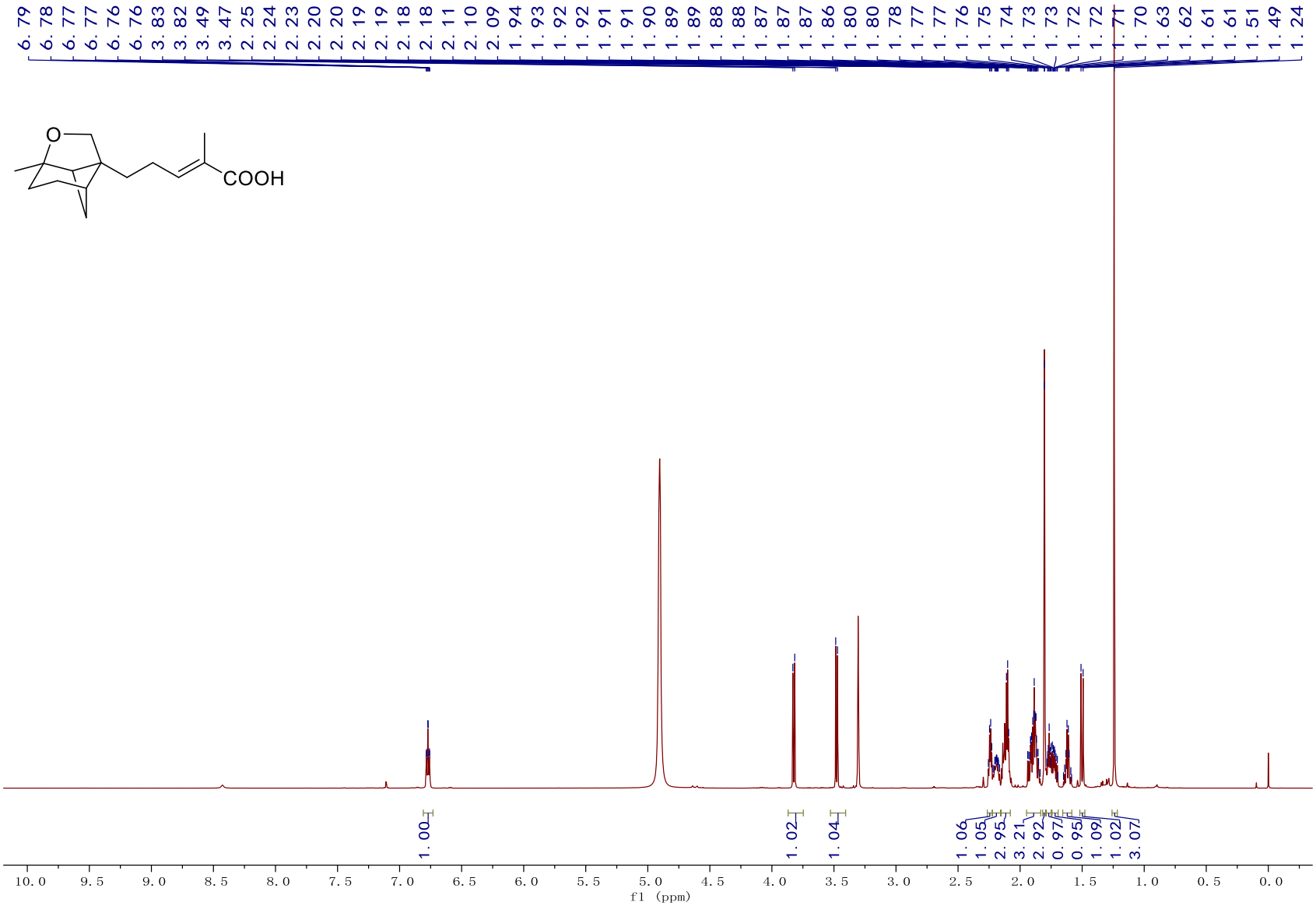


Figure S81. ^{13}C NMR and DEPT of compound **9** in CD_3OD

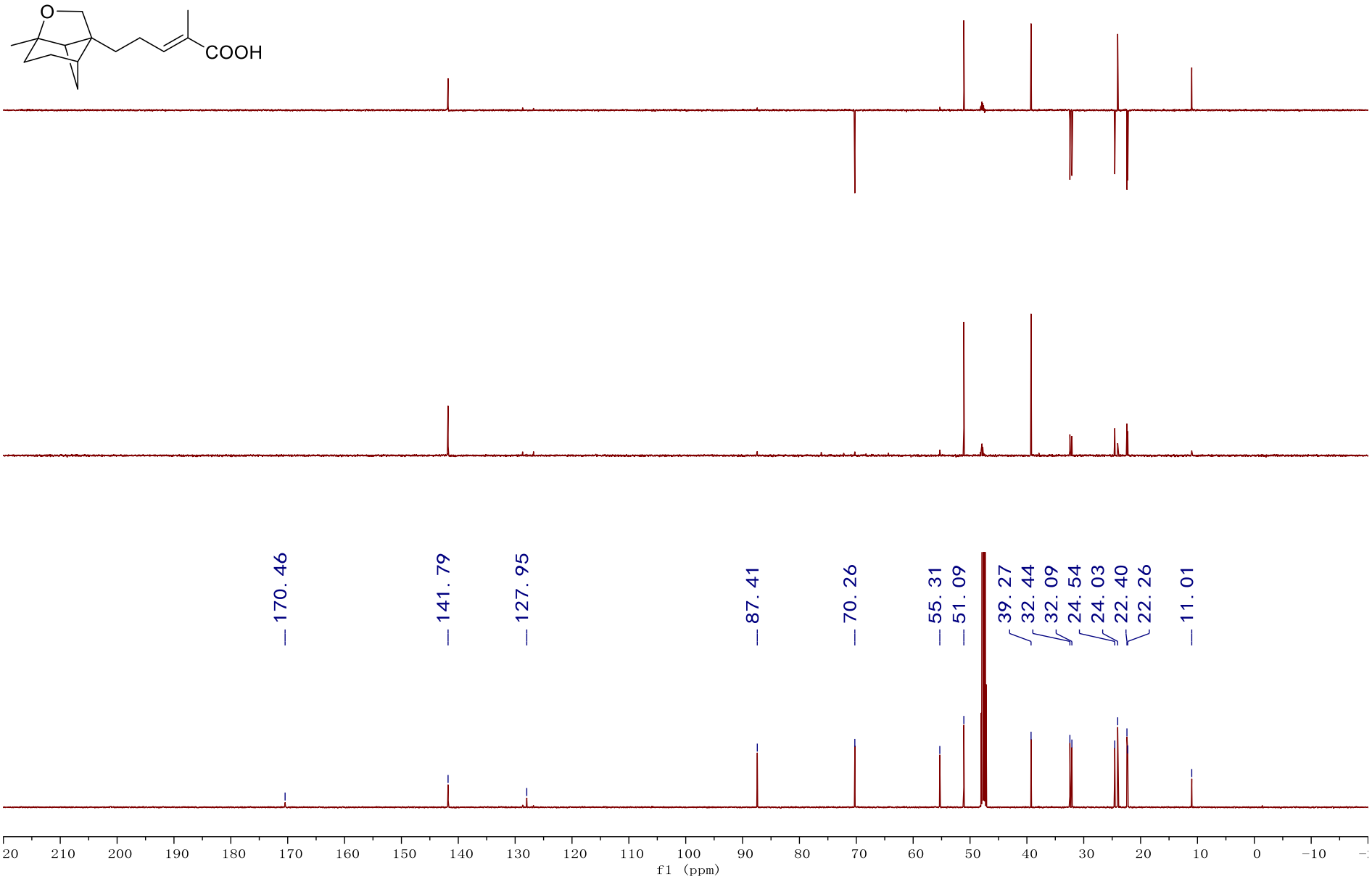


Figure S82. HSQC of compound **9** in CD_3OD

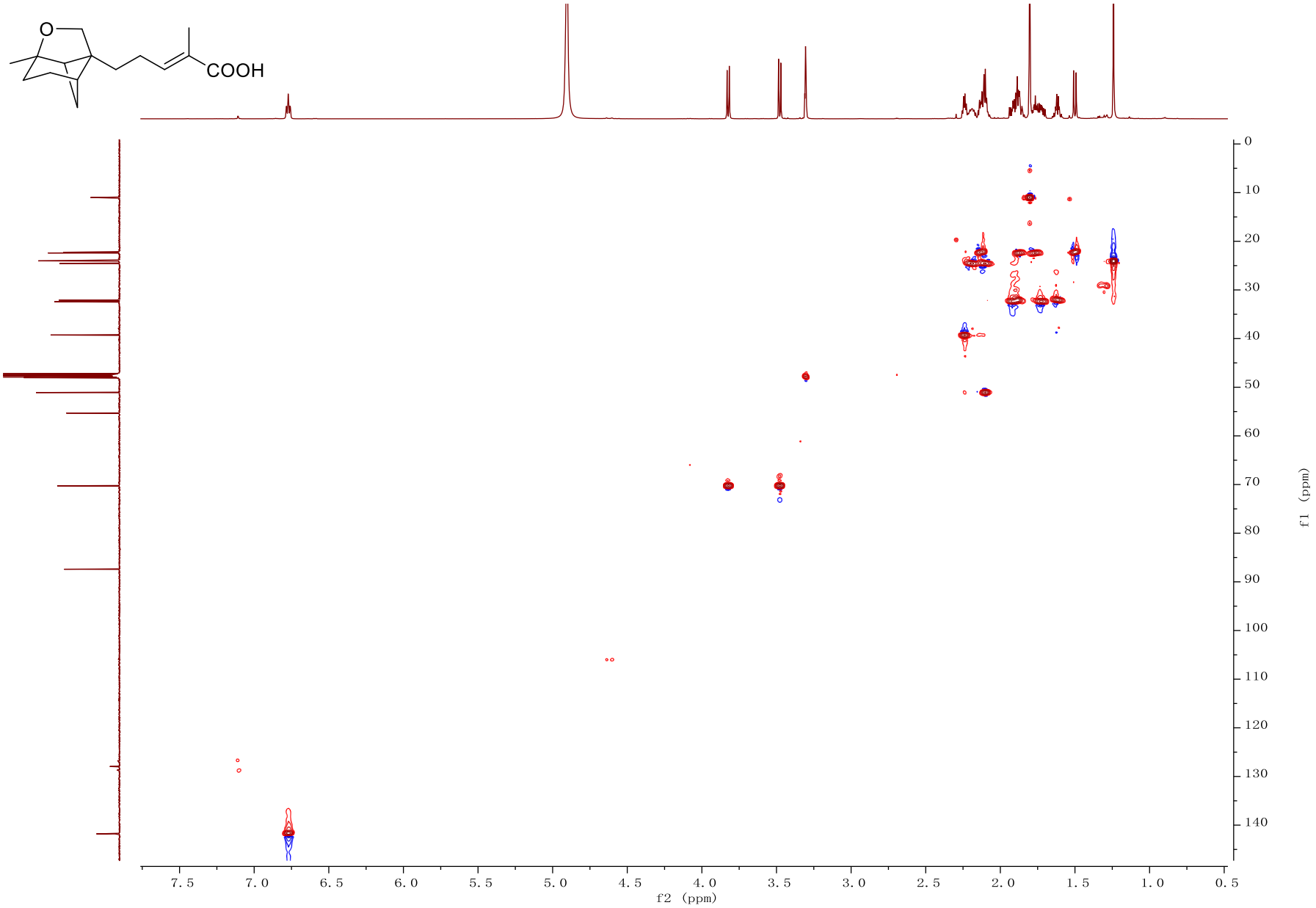


Figure S83. HMBC of compound **9** in CD_3OD

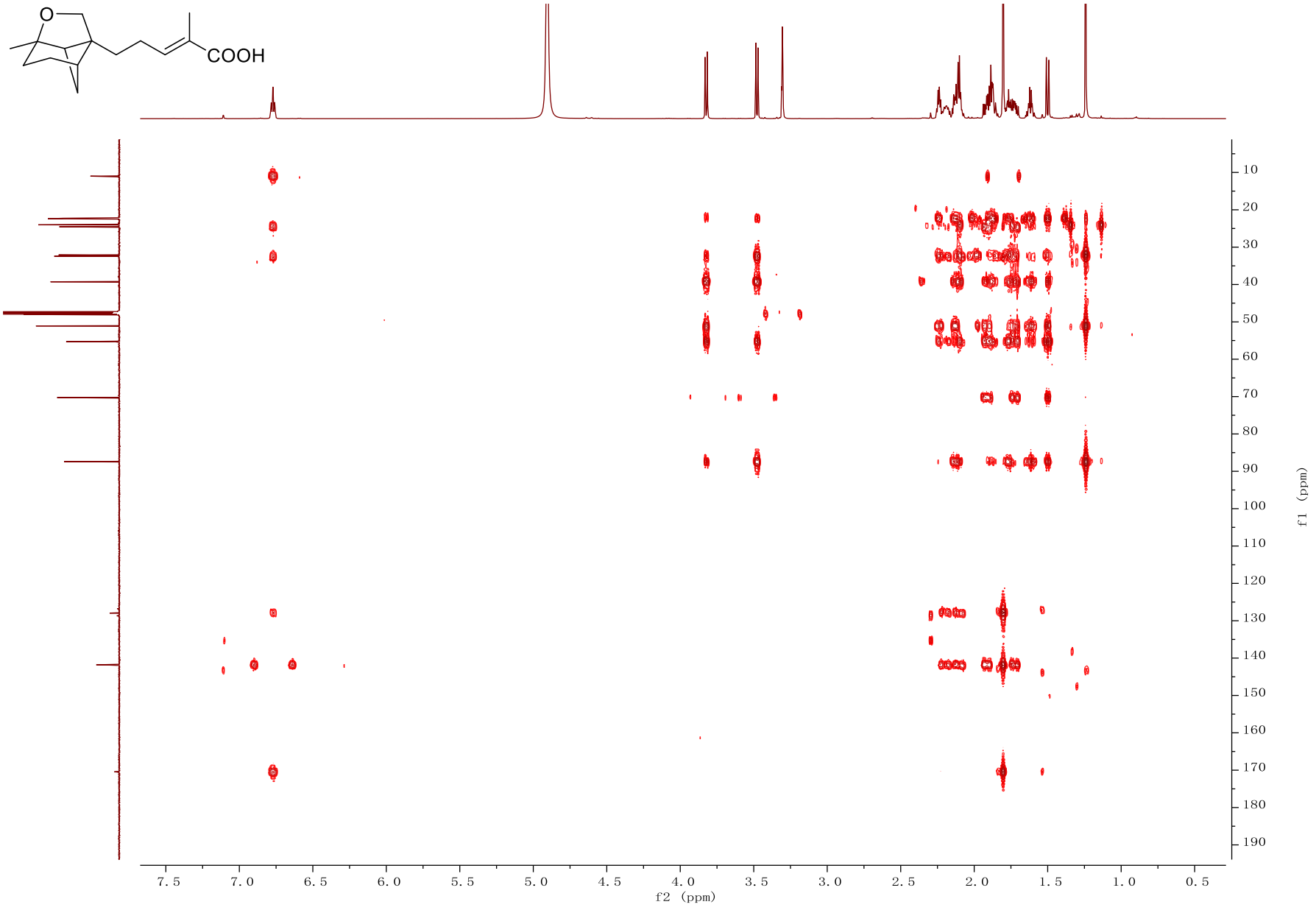


Figure S84. ^{1}H-^{1}H COSY of compound **9** in CD_3OD

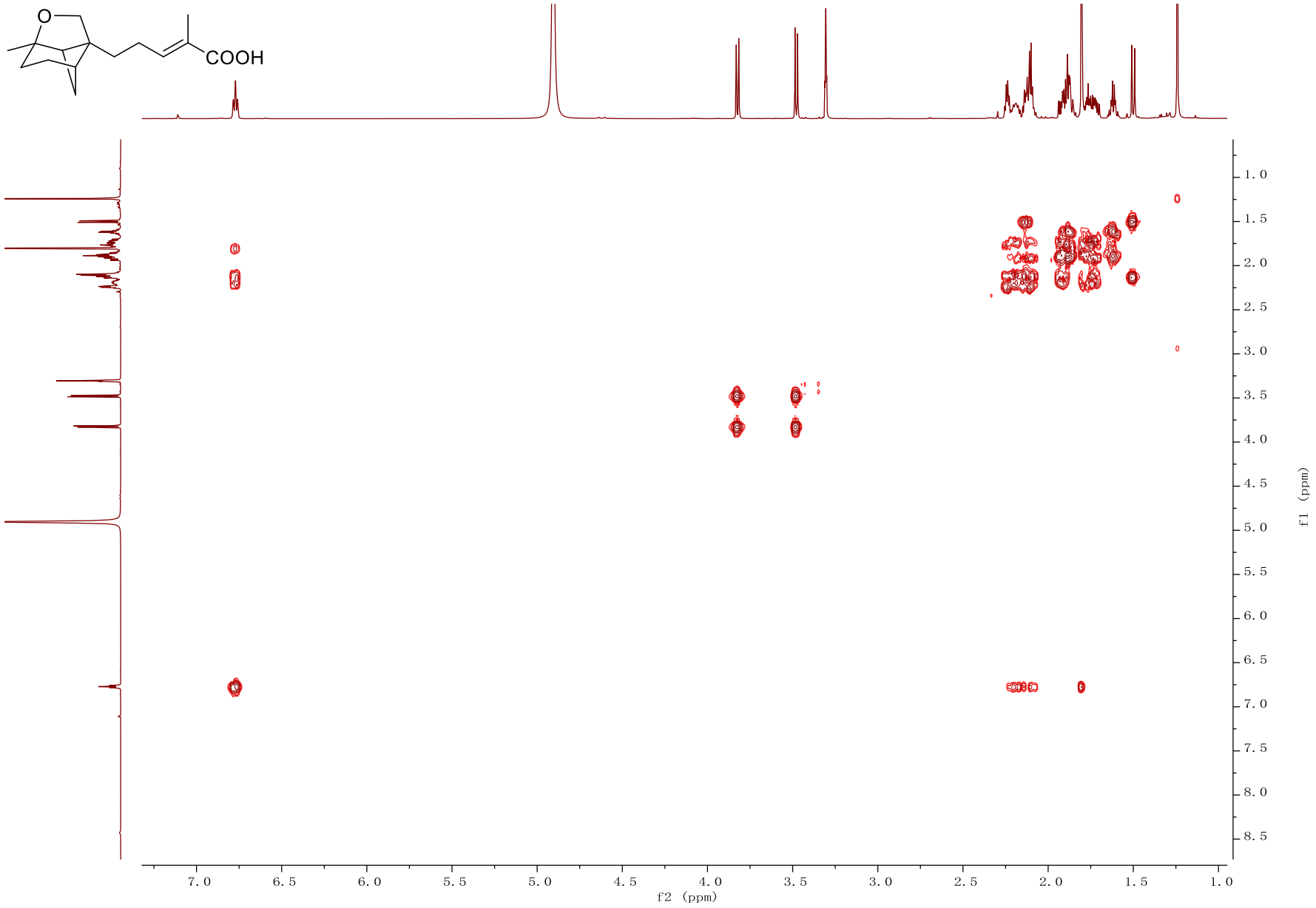


Figure S85. ROESY of compound **9** in CD_3OD

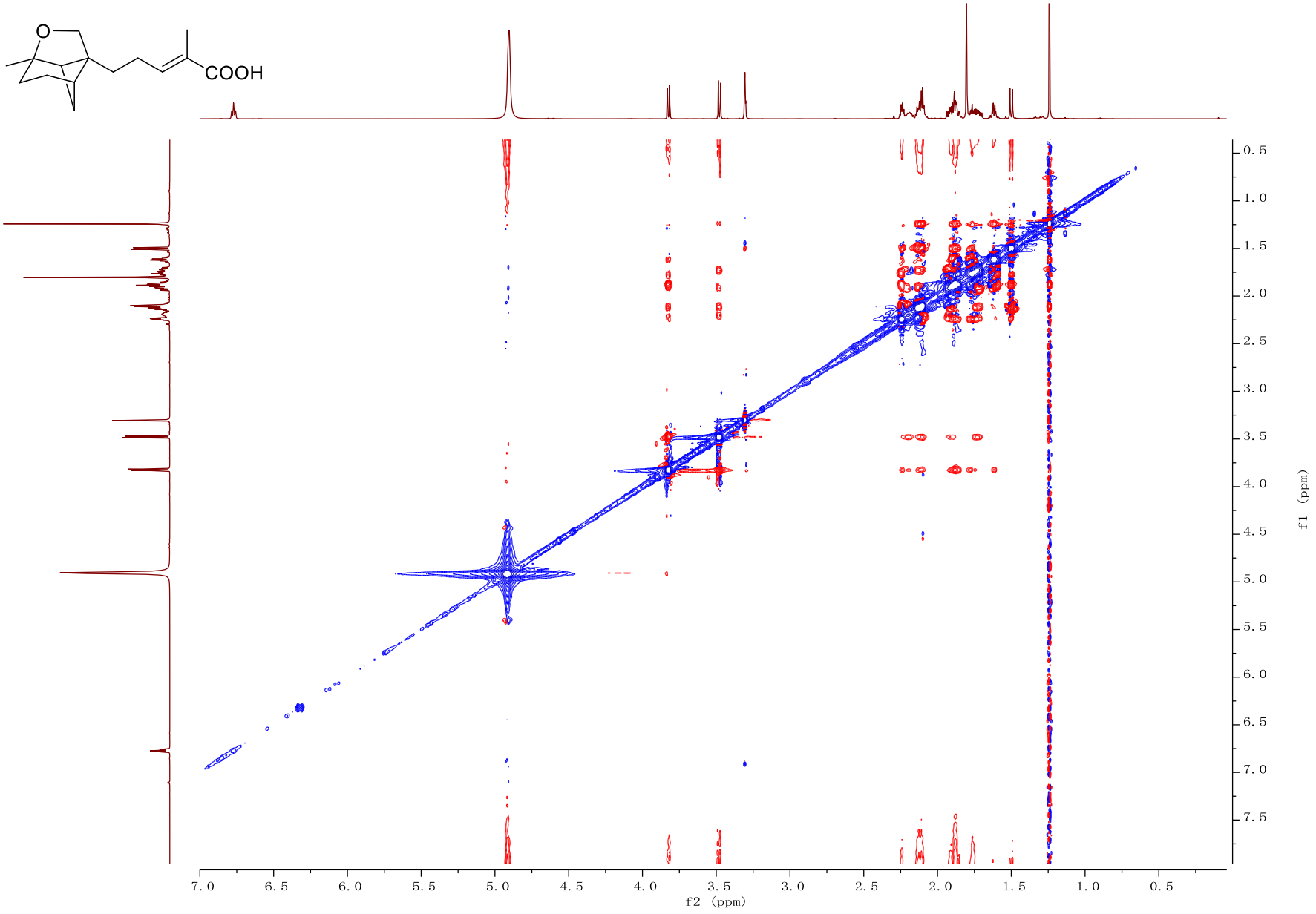
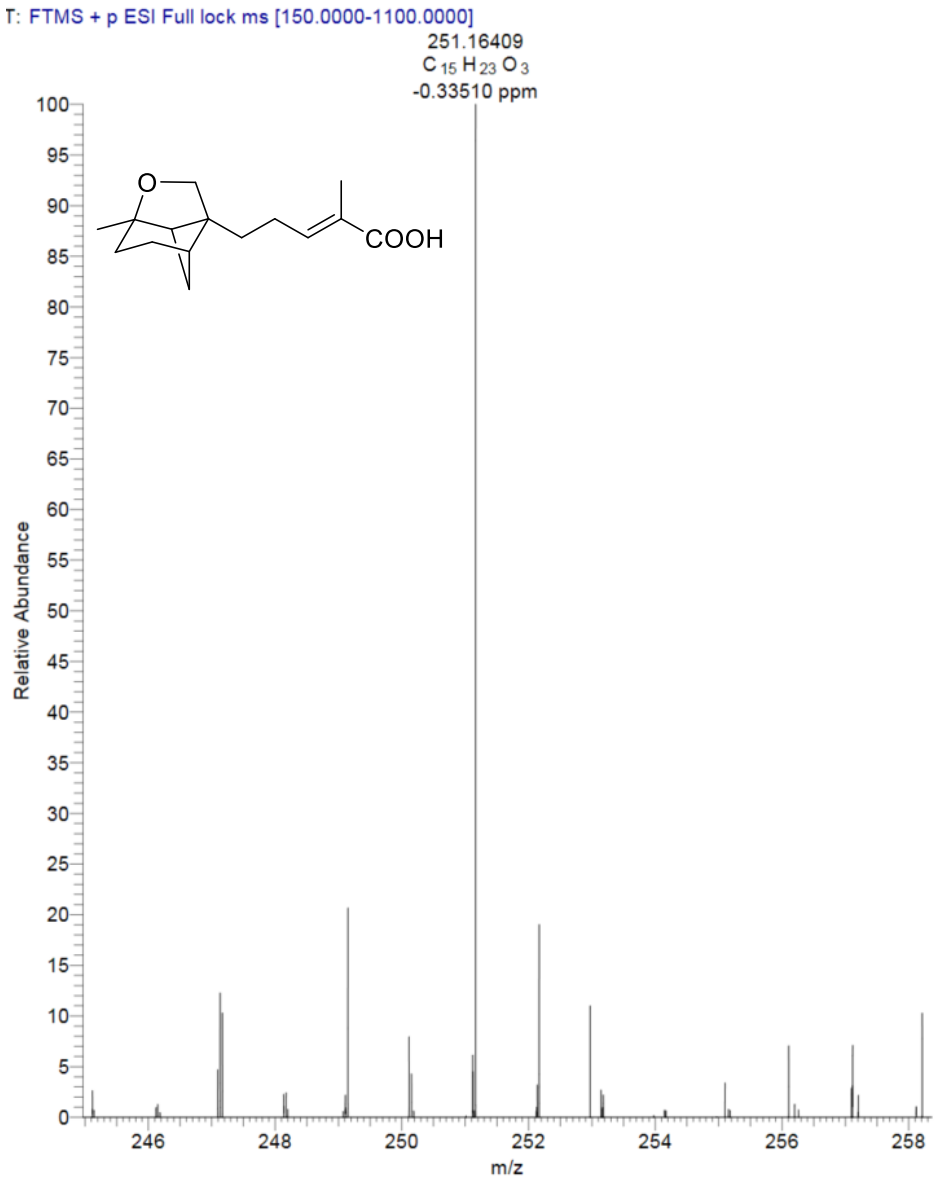


Figure S86. HR-ESIMS of compound **9**



Section S17. NMR and MS spectra for 10

Figure S87. ^{1}H NMR of compound **10** in CD_3OD

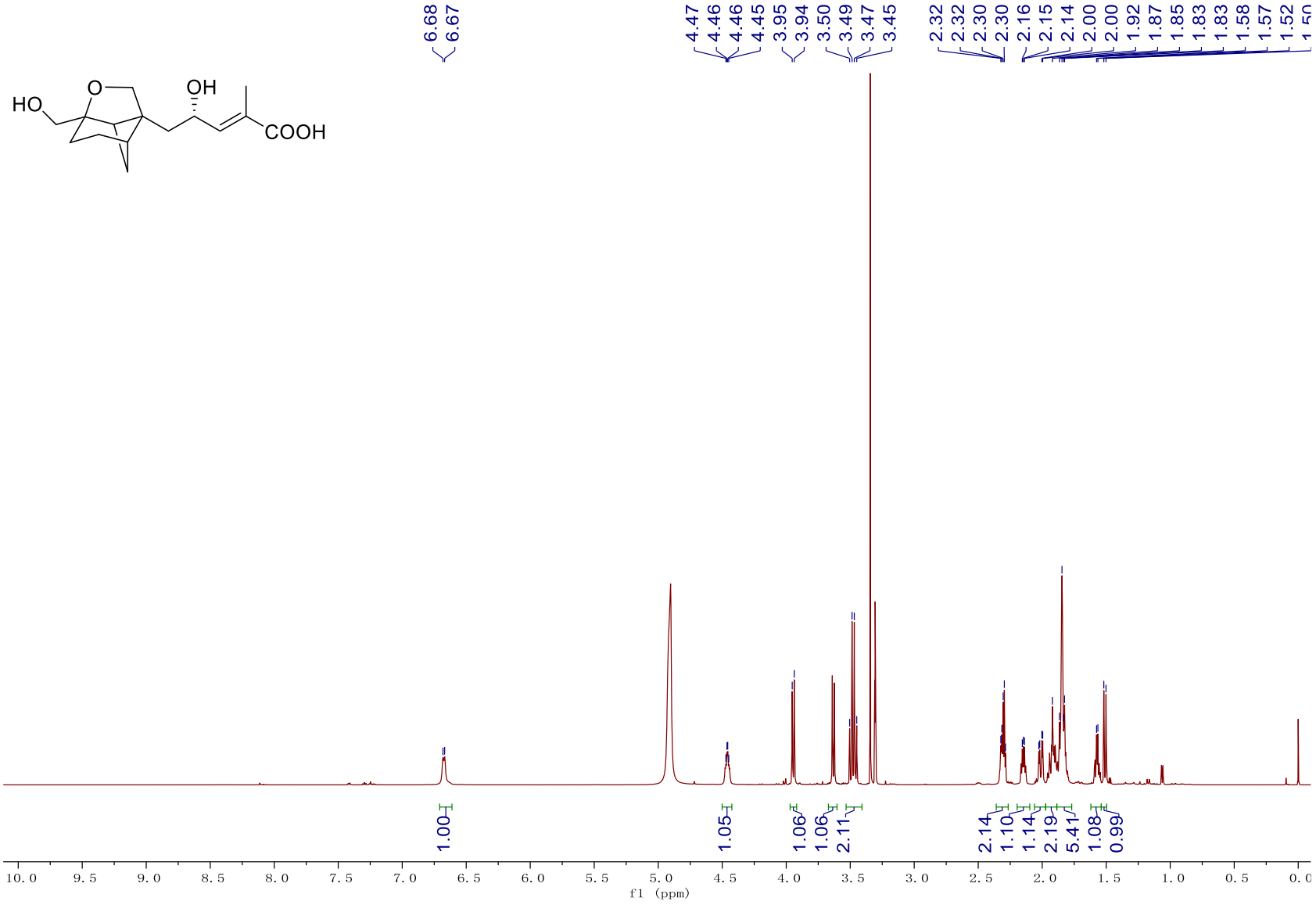


Figure S88. ^{13}C NMR and DEPT of compound **10** in CD_3OD

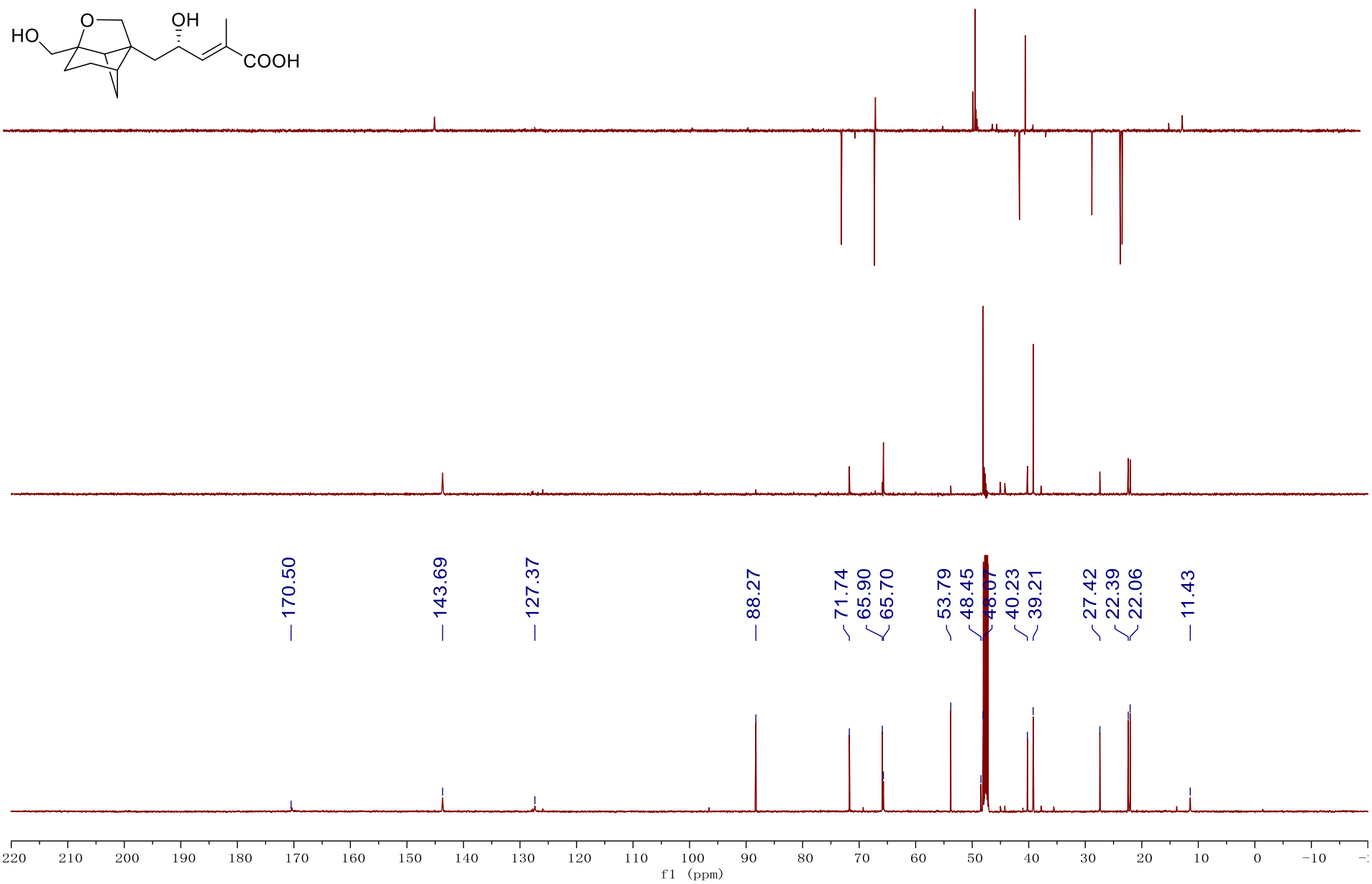


Figure S89. HSQC of compound **10** in CD_3OD

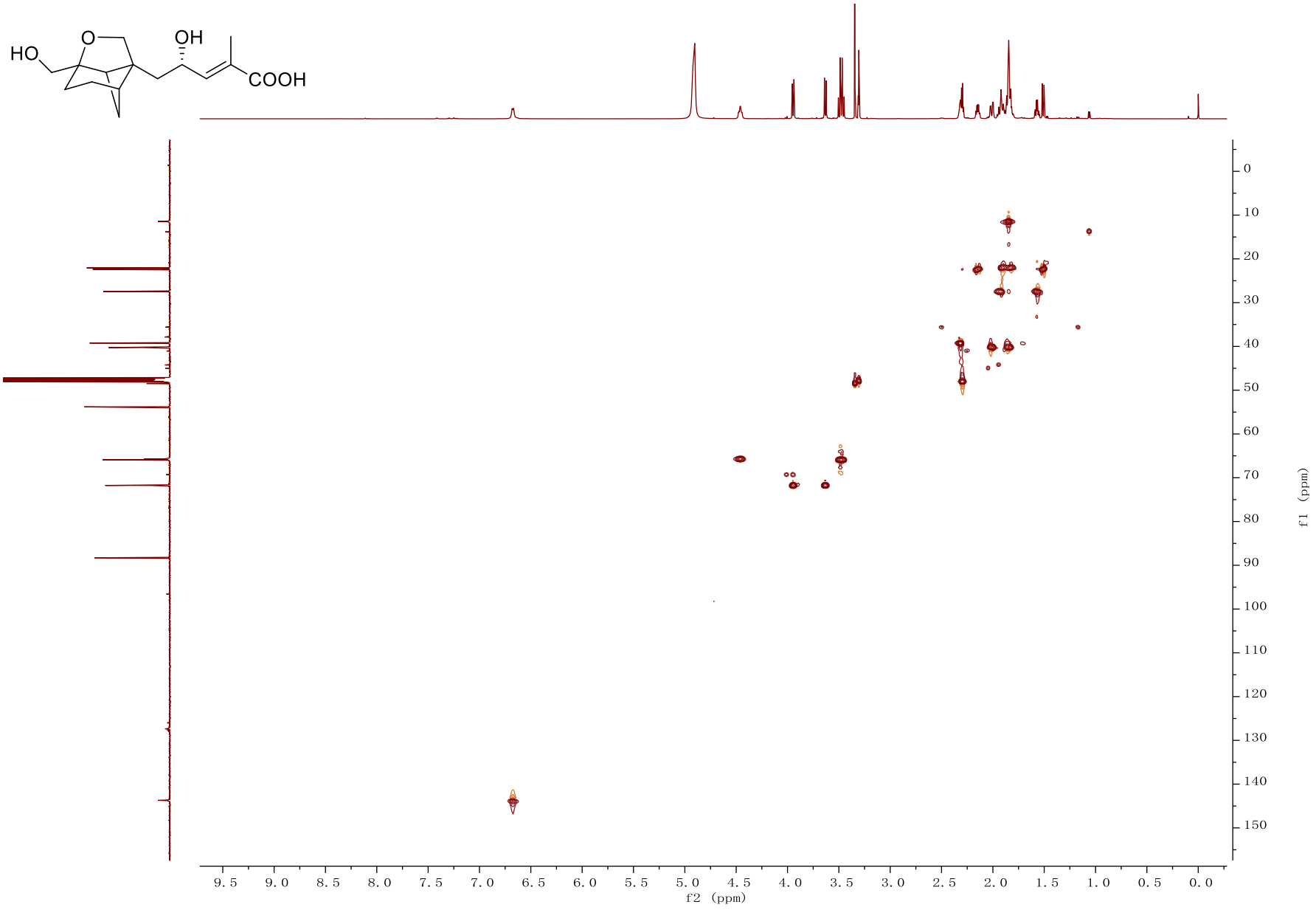


Figure S90. HMBC of compound **10** in CD_3OD

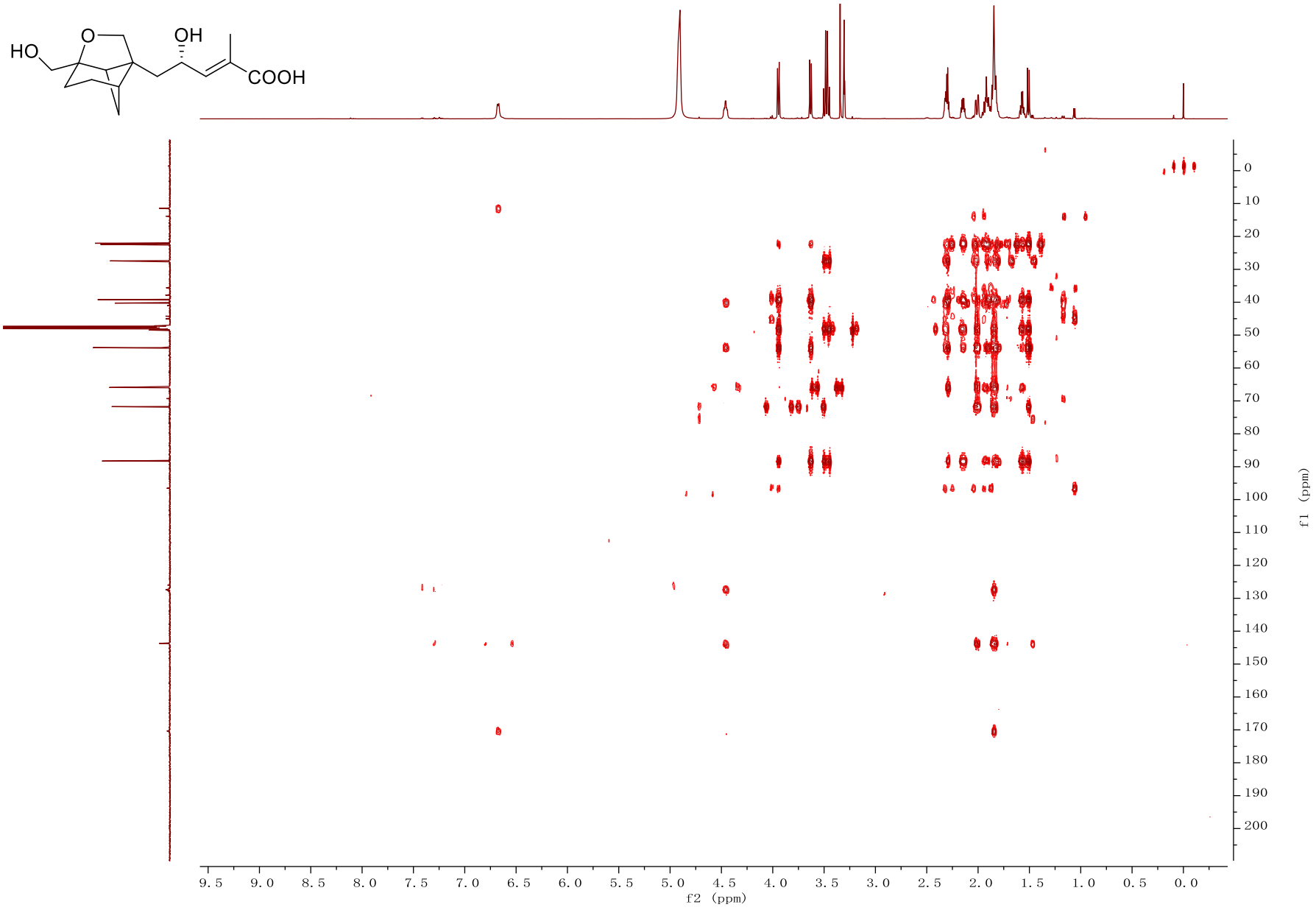


Figure S91. ^{1}H-^{1}H COSY of compound **10** in CD_3OD

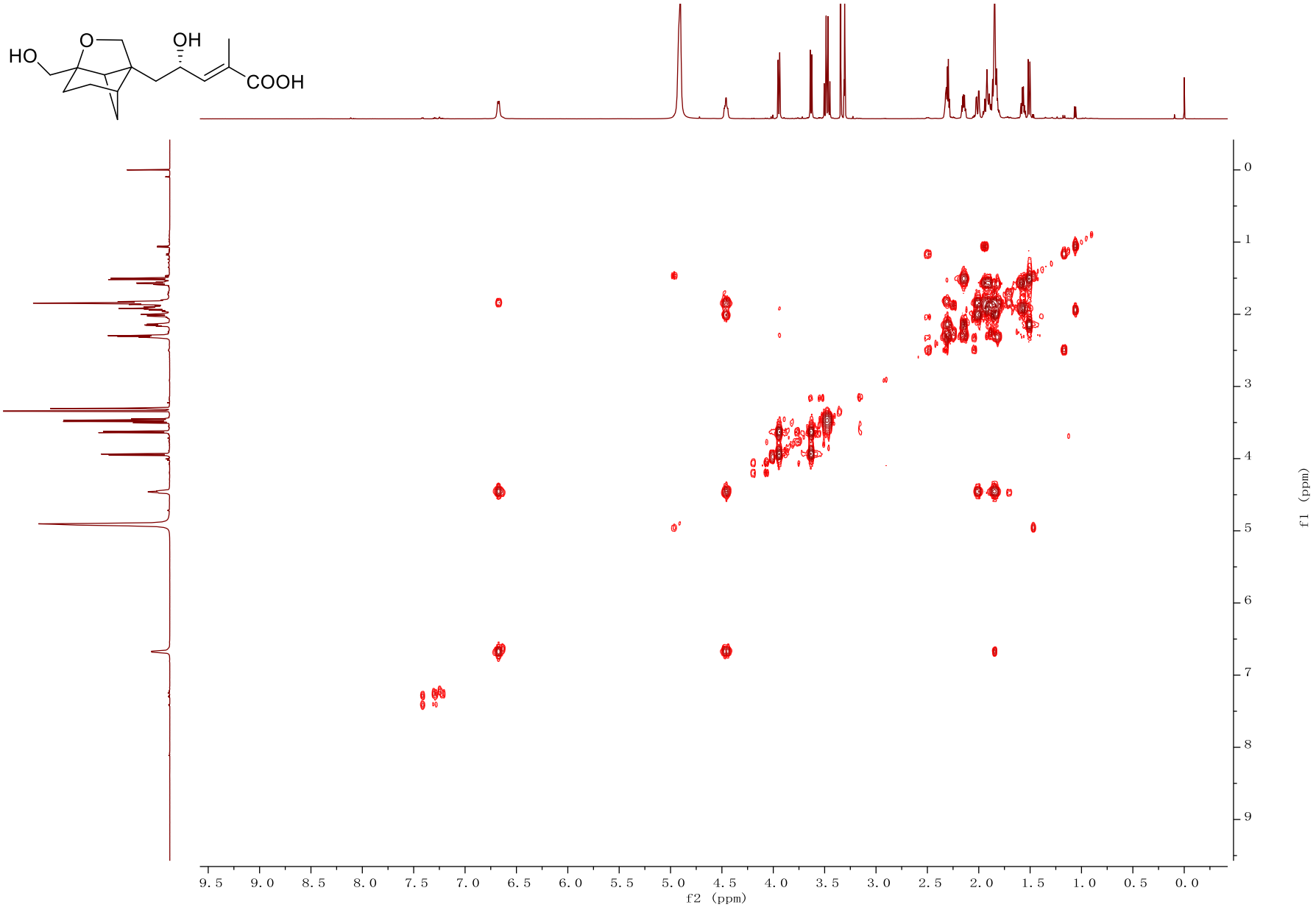


Figure S92. ROESY of compound **10** in CD_3OD

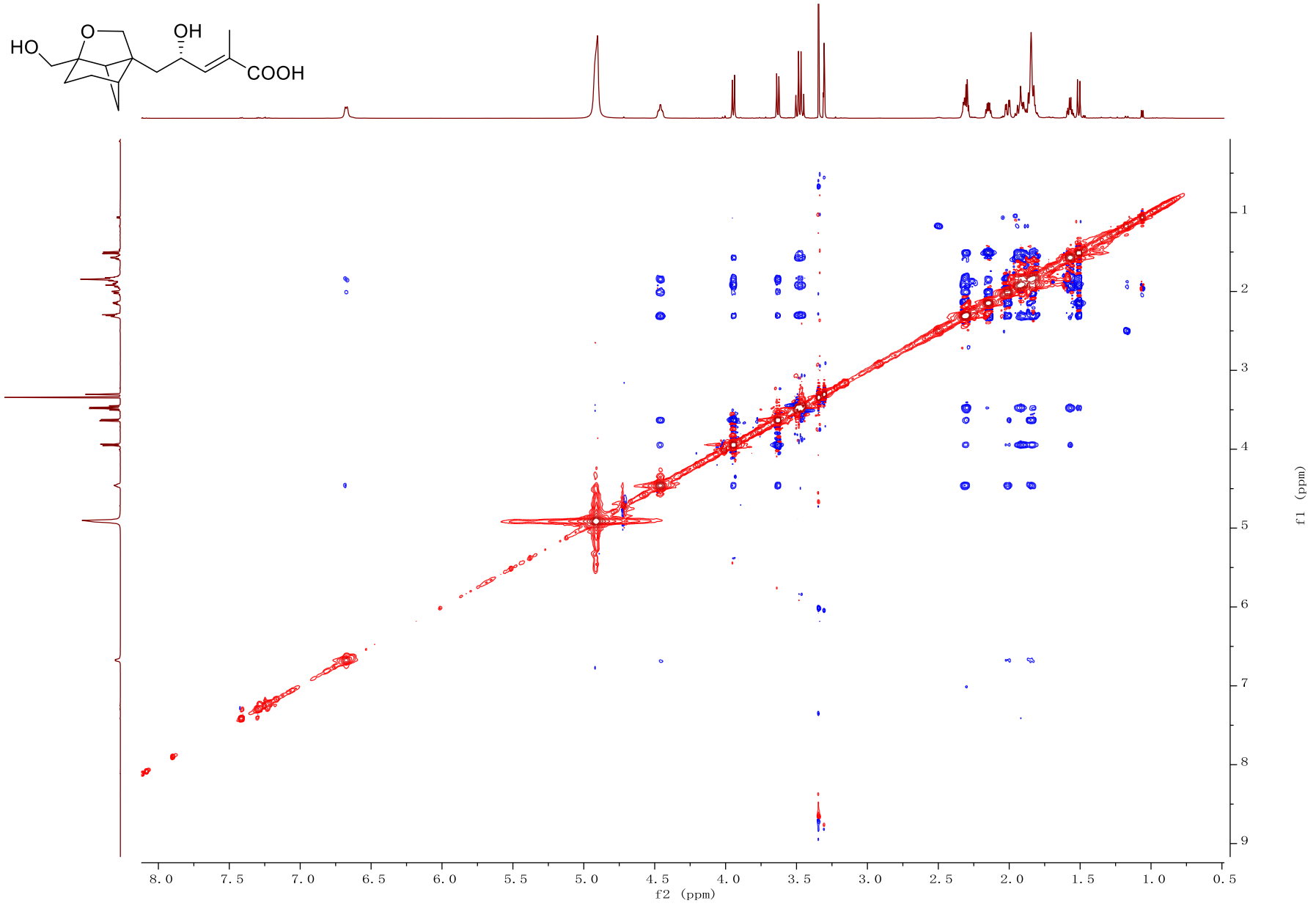
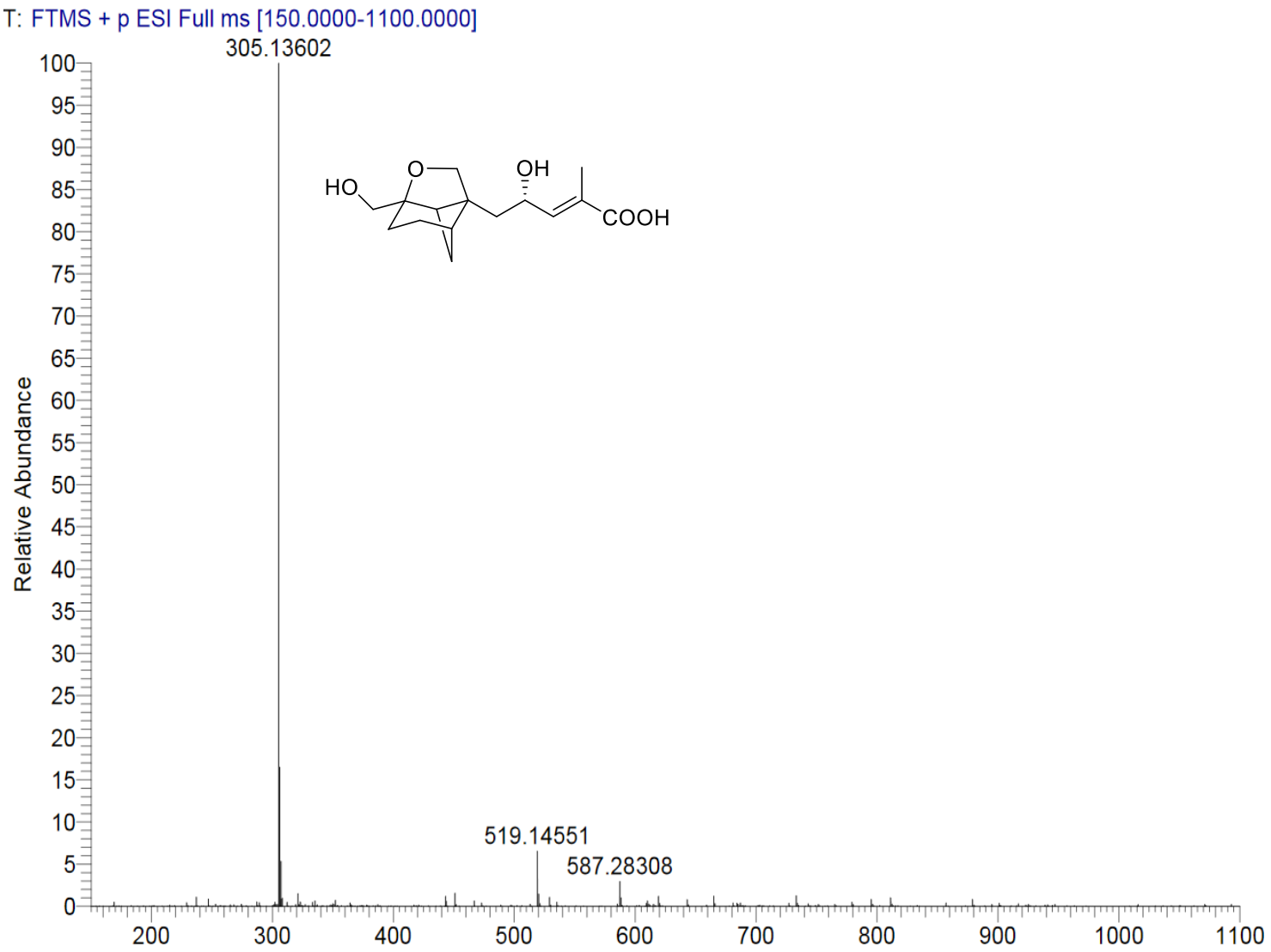


Figure S93. HR-ESIMS of compound **10**



Section S18. NMR and MS spectra for 11

Figure S94. ^{1}H NMR of compound **11** in CD_3OD

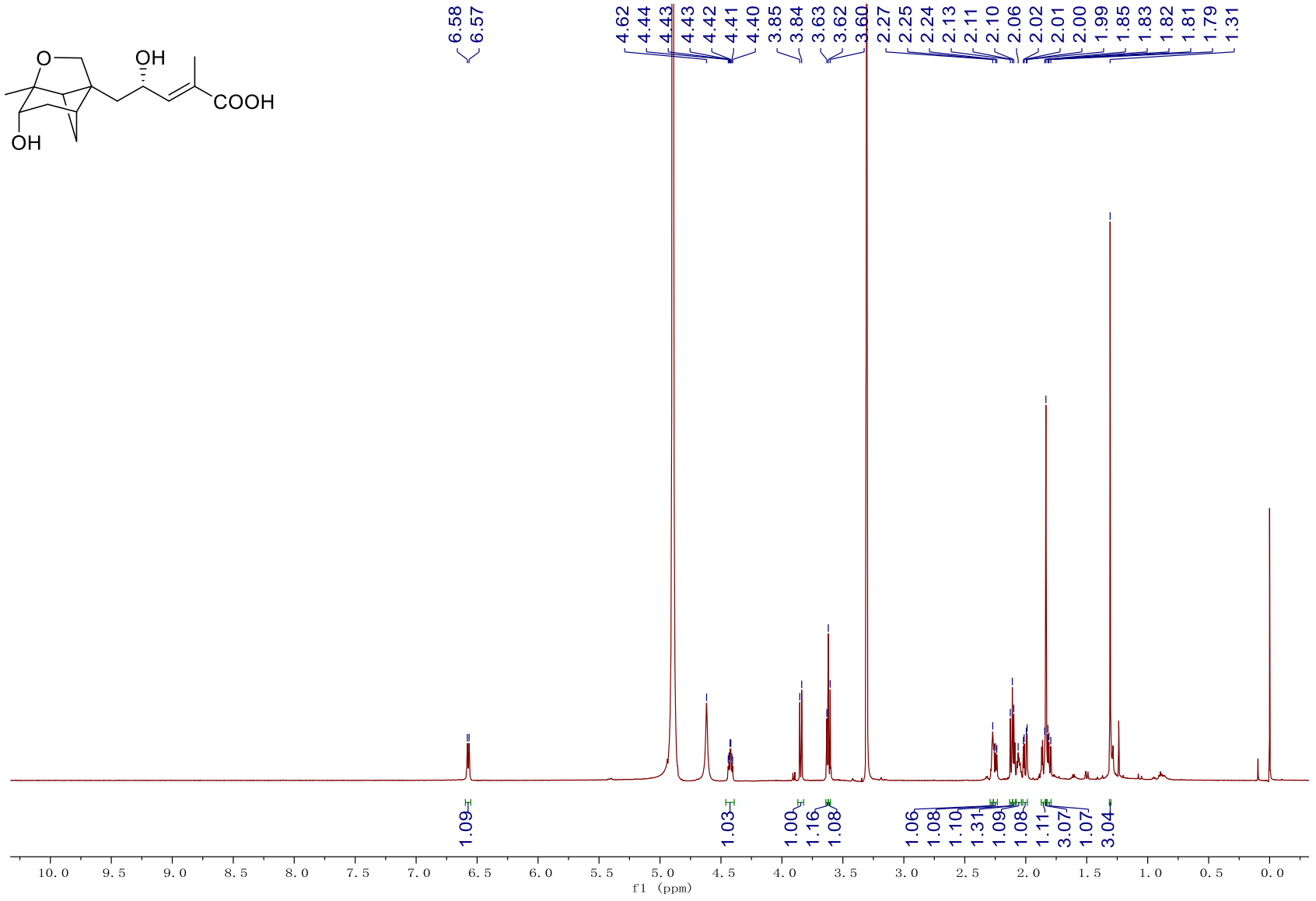


Figure S95. ^{13}C NMR and DEPT of compound **11** in CD_3OD

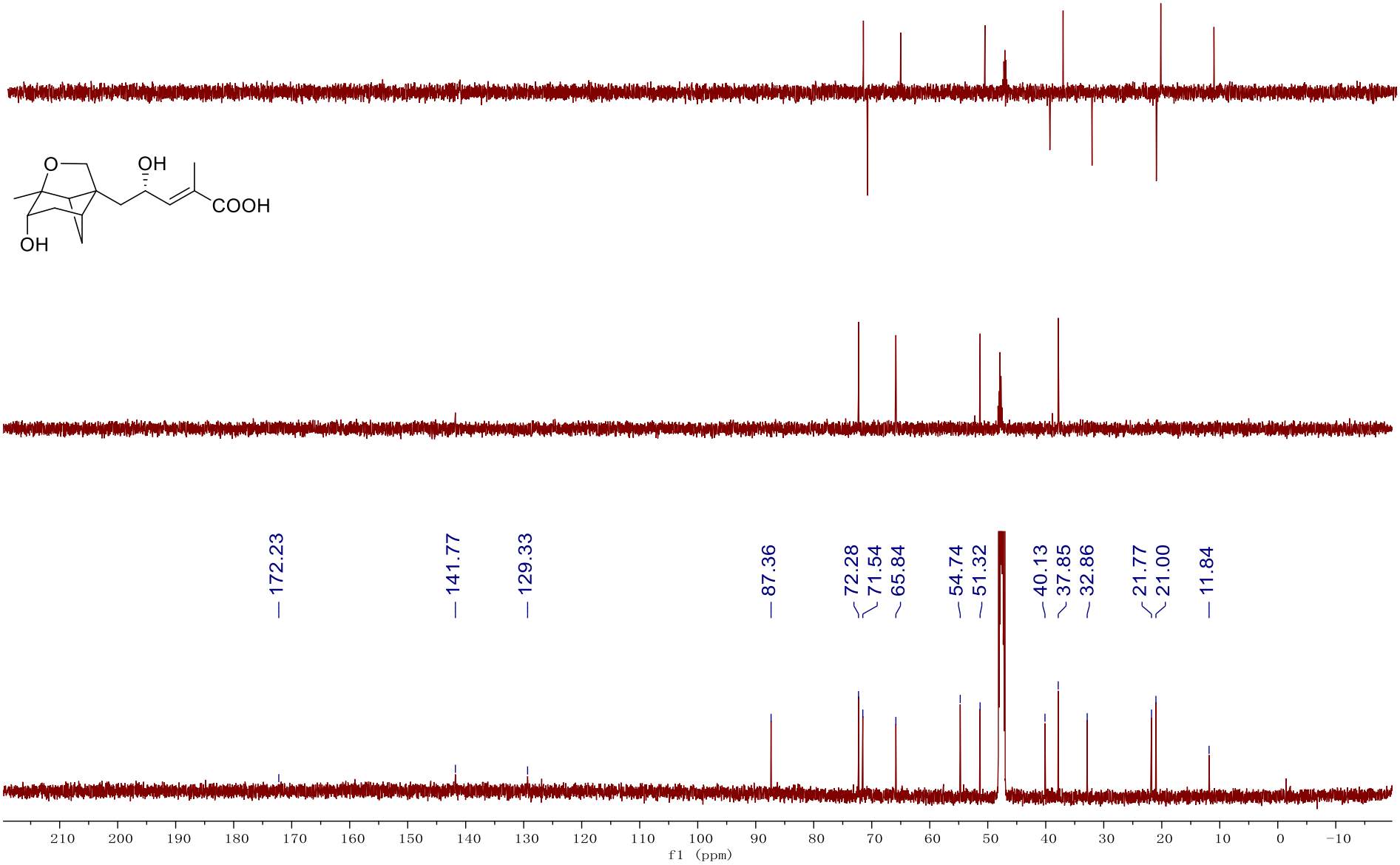


Figure S96. HSQC of compound **11** in CD_3OD

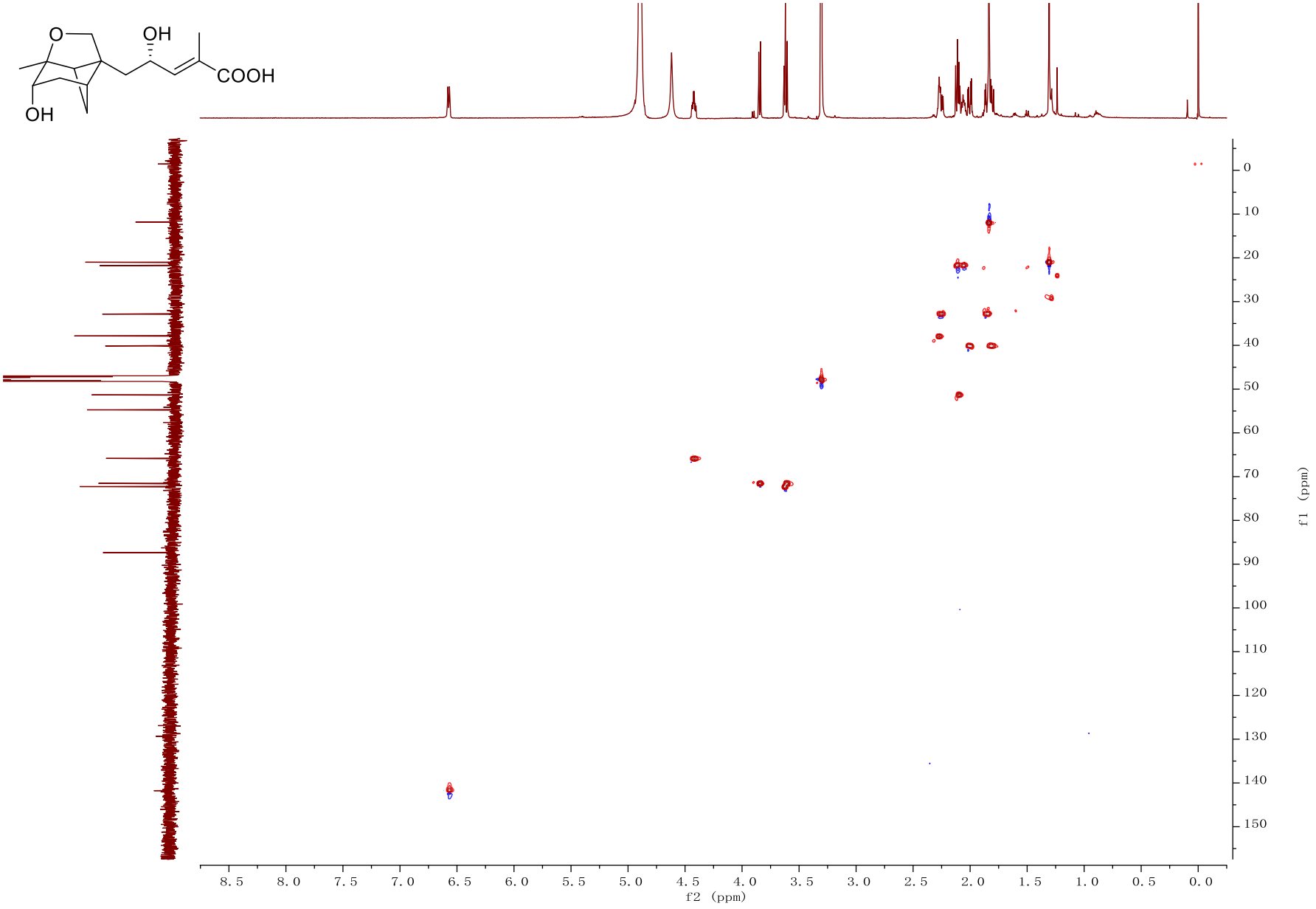


Figure S97. HMBC of compound **11** in CD_3OD

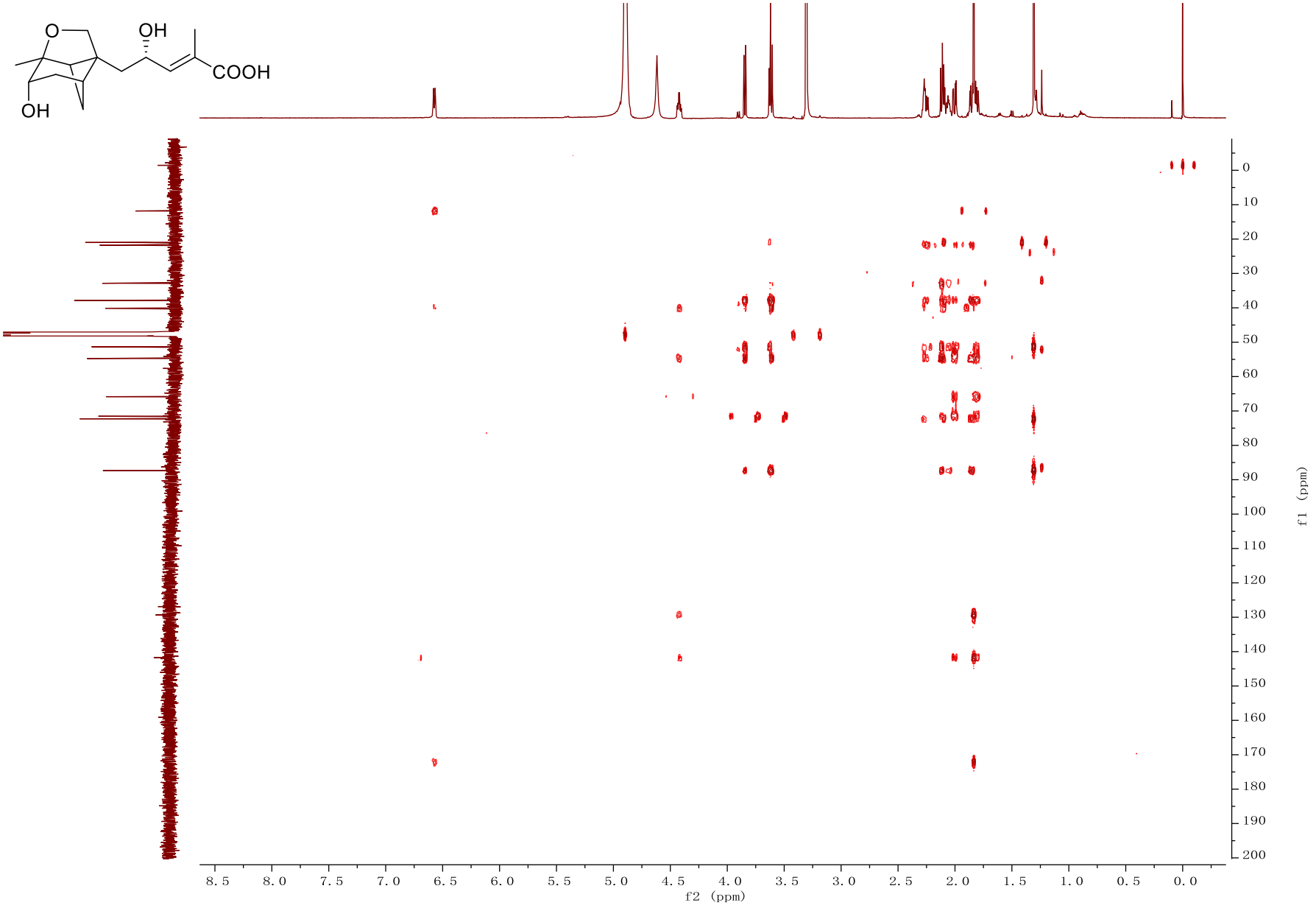


Figure S98. ^{1}H-^{1}H COSY of compound **11** in CD_3OD

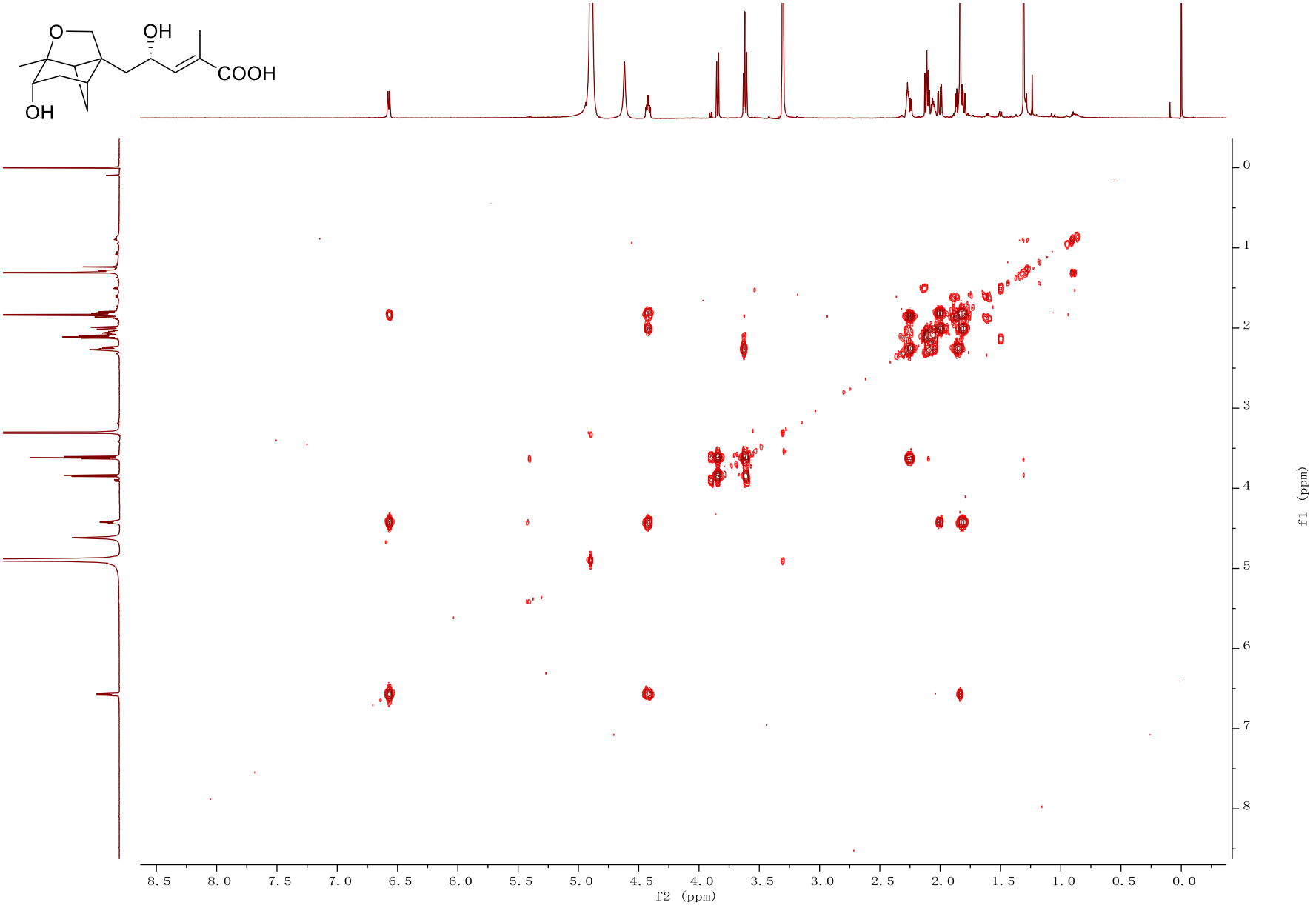


Figure S99. ROESY of compound **11** in CD_3OD

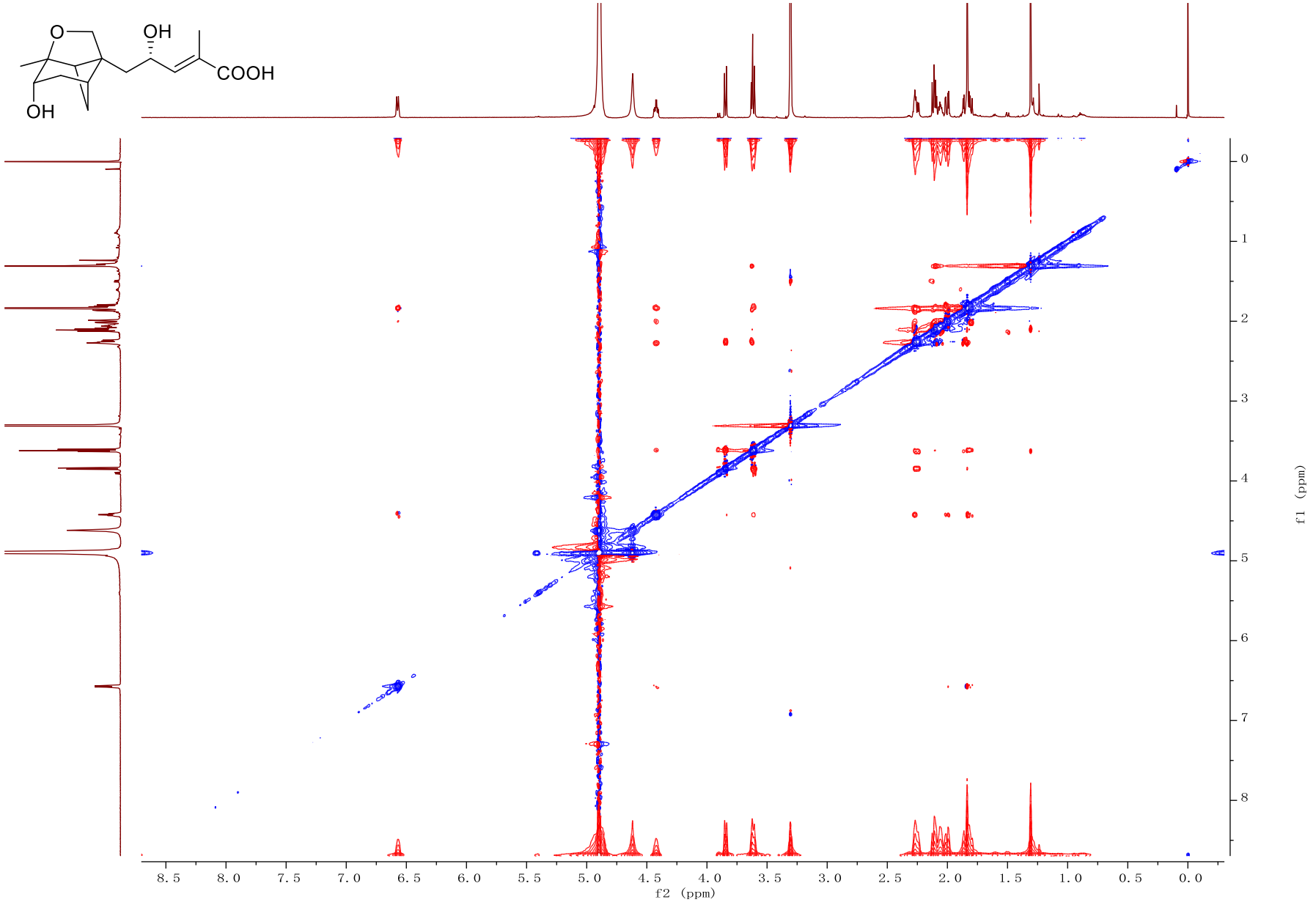
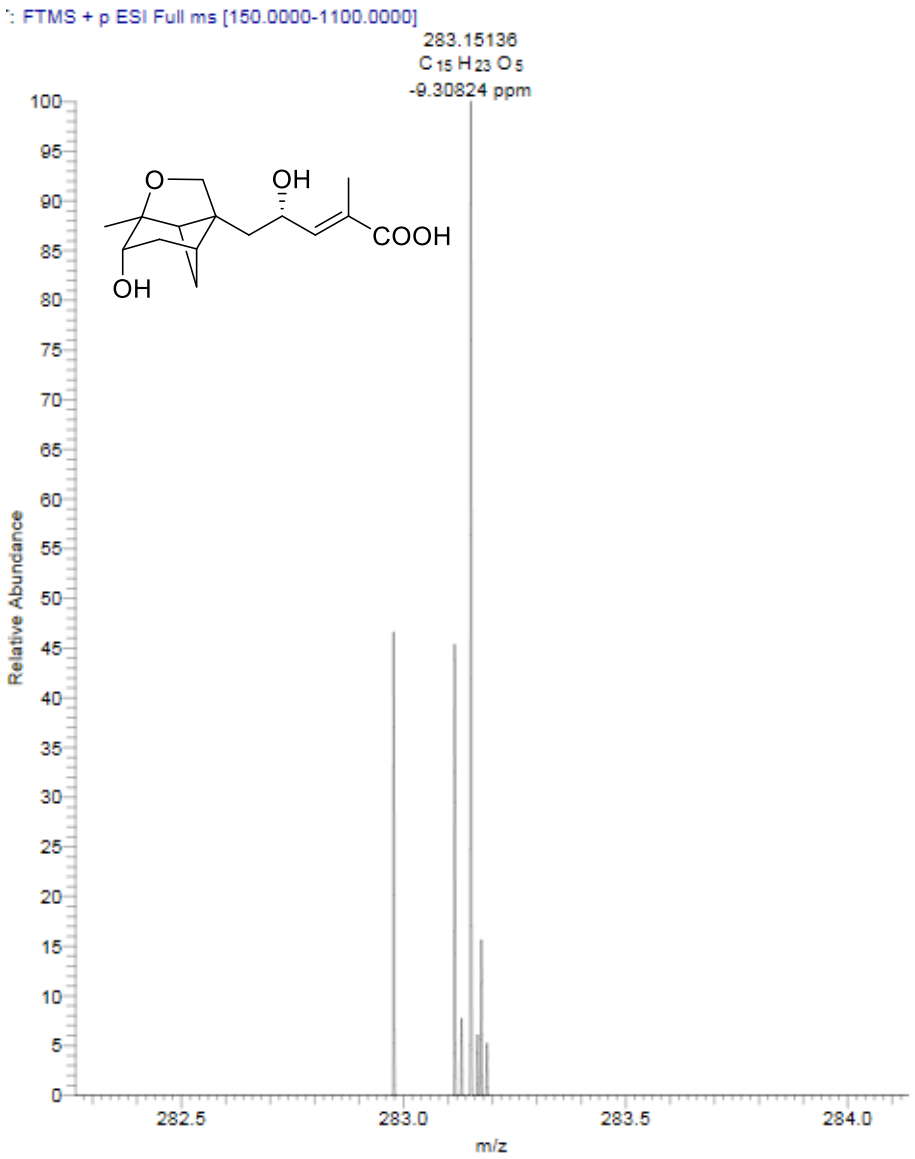


Figure S100. HR-ESIMS of compound **11**



Section S19. NMR and MS spectra for 12

Figure S101. ^{1}H NMR of compound **12** in CD_3OD

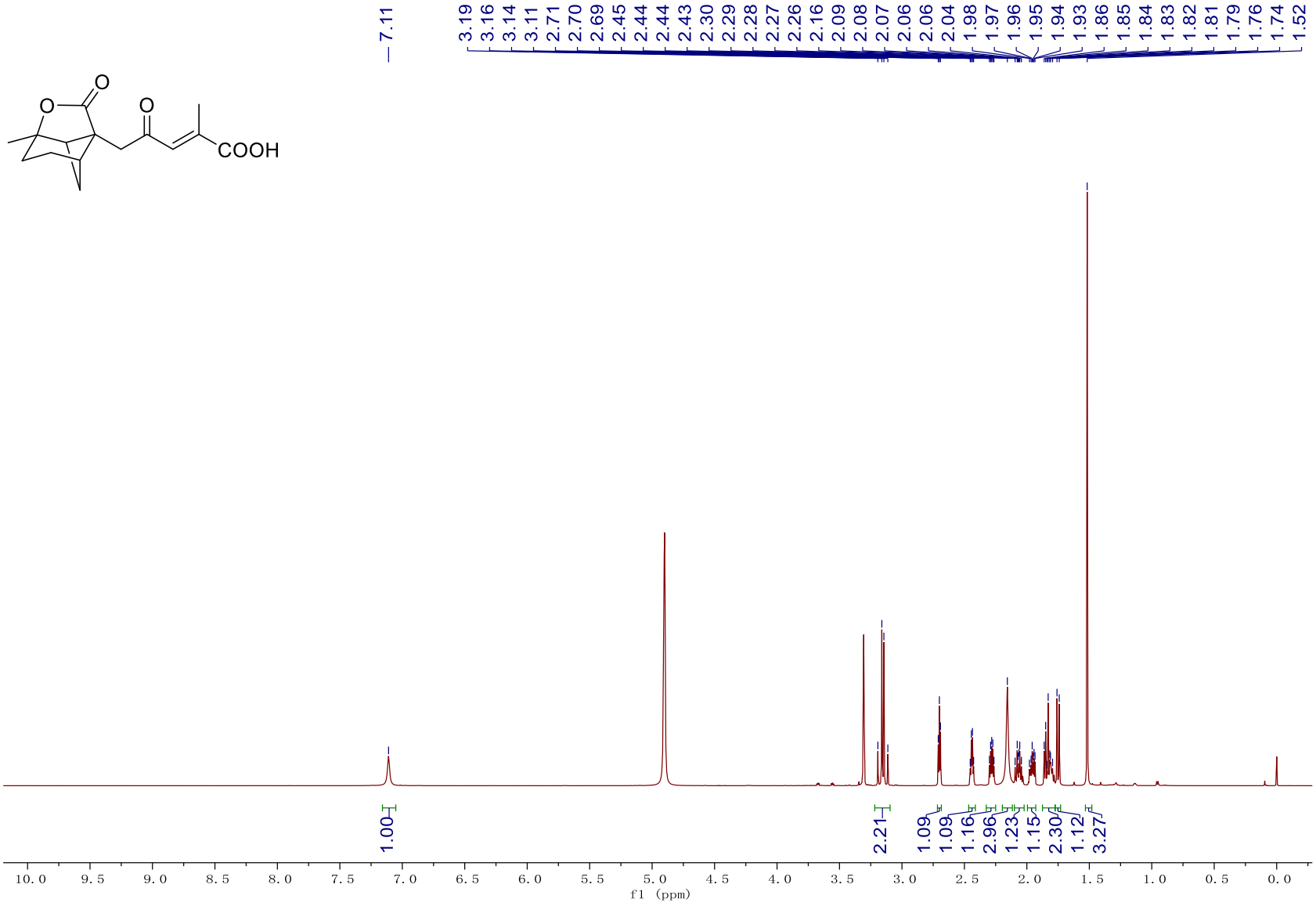


Figure S102. ^{13}C NMR and DEPT of compound **12** in CD_3OD

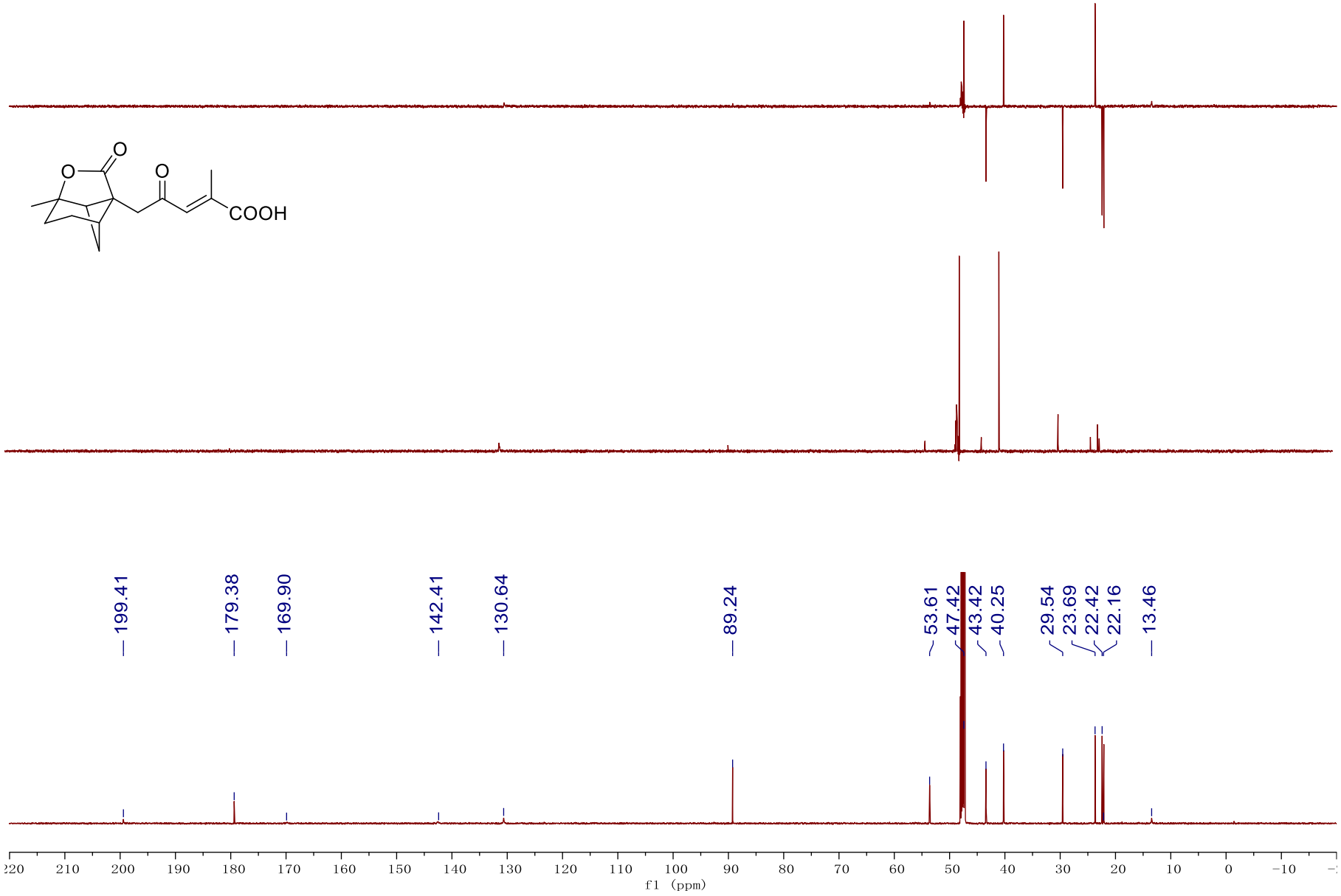


Figure S103. HSQC of compound **12** in CD_3OD

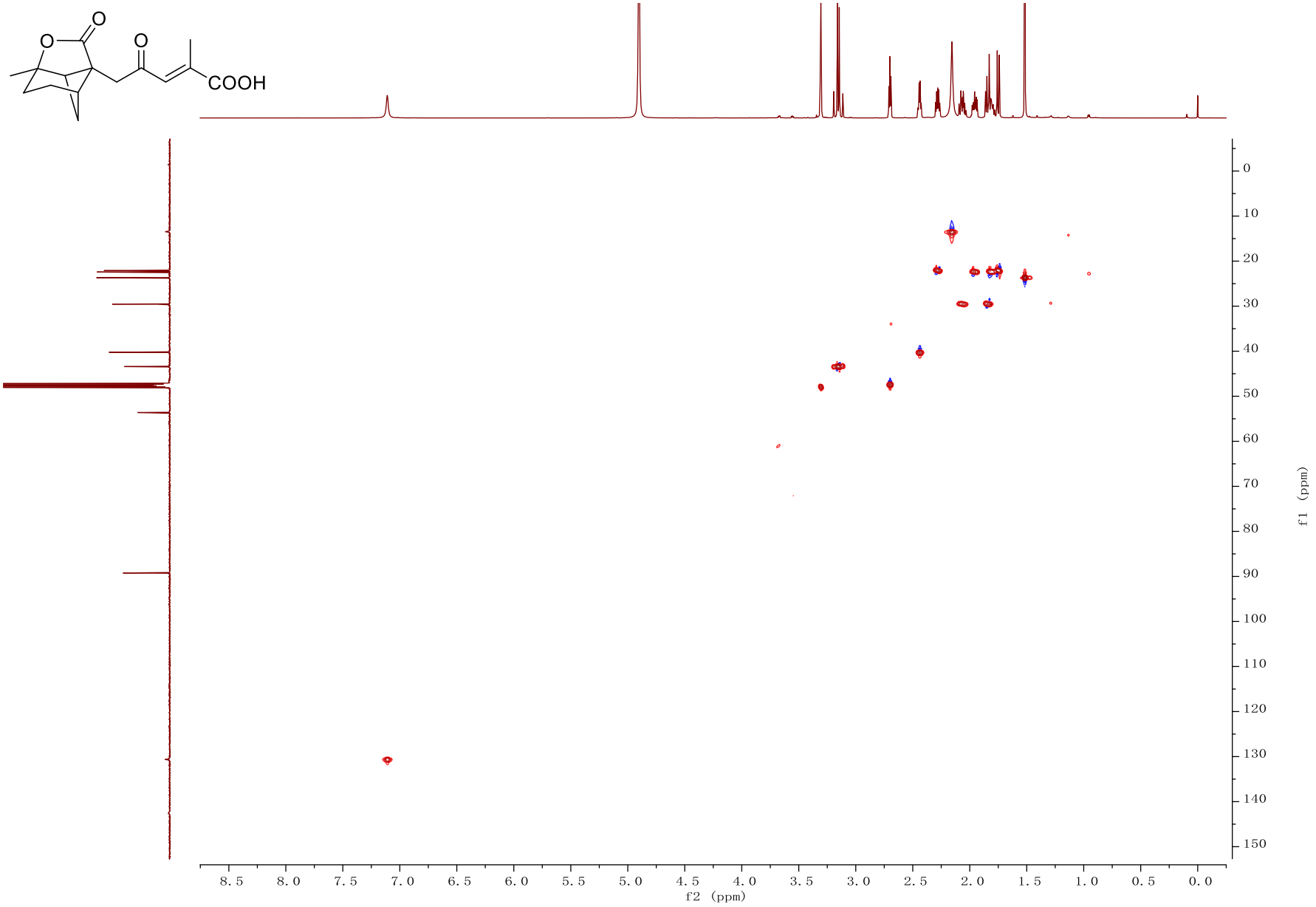


Figure S104. HMBC of compound **12** in CD_3OD

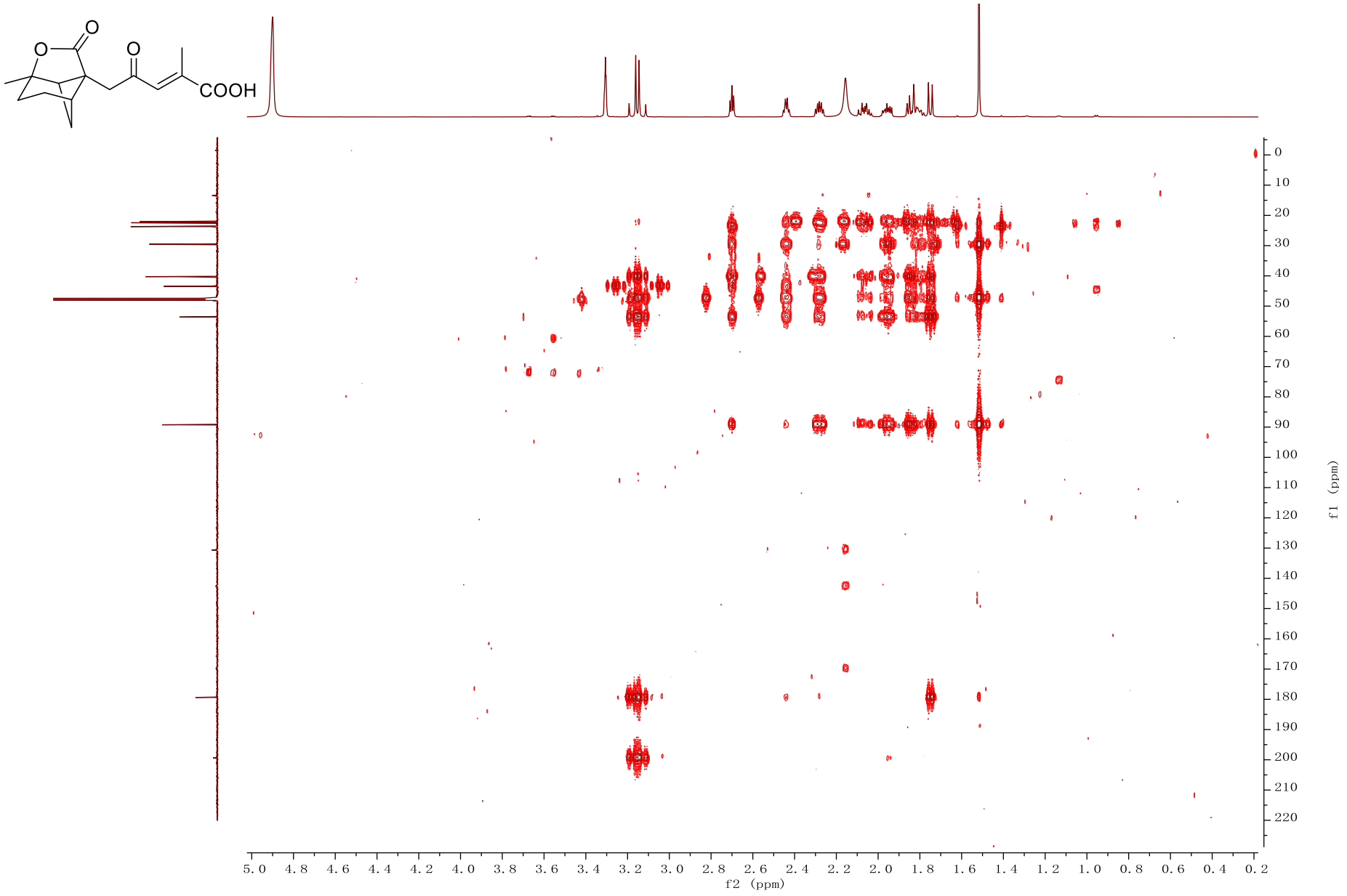


Figure S105. ^{1}H-^{1}H COSY of compound **12** in CD_3OD

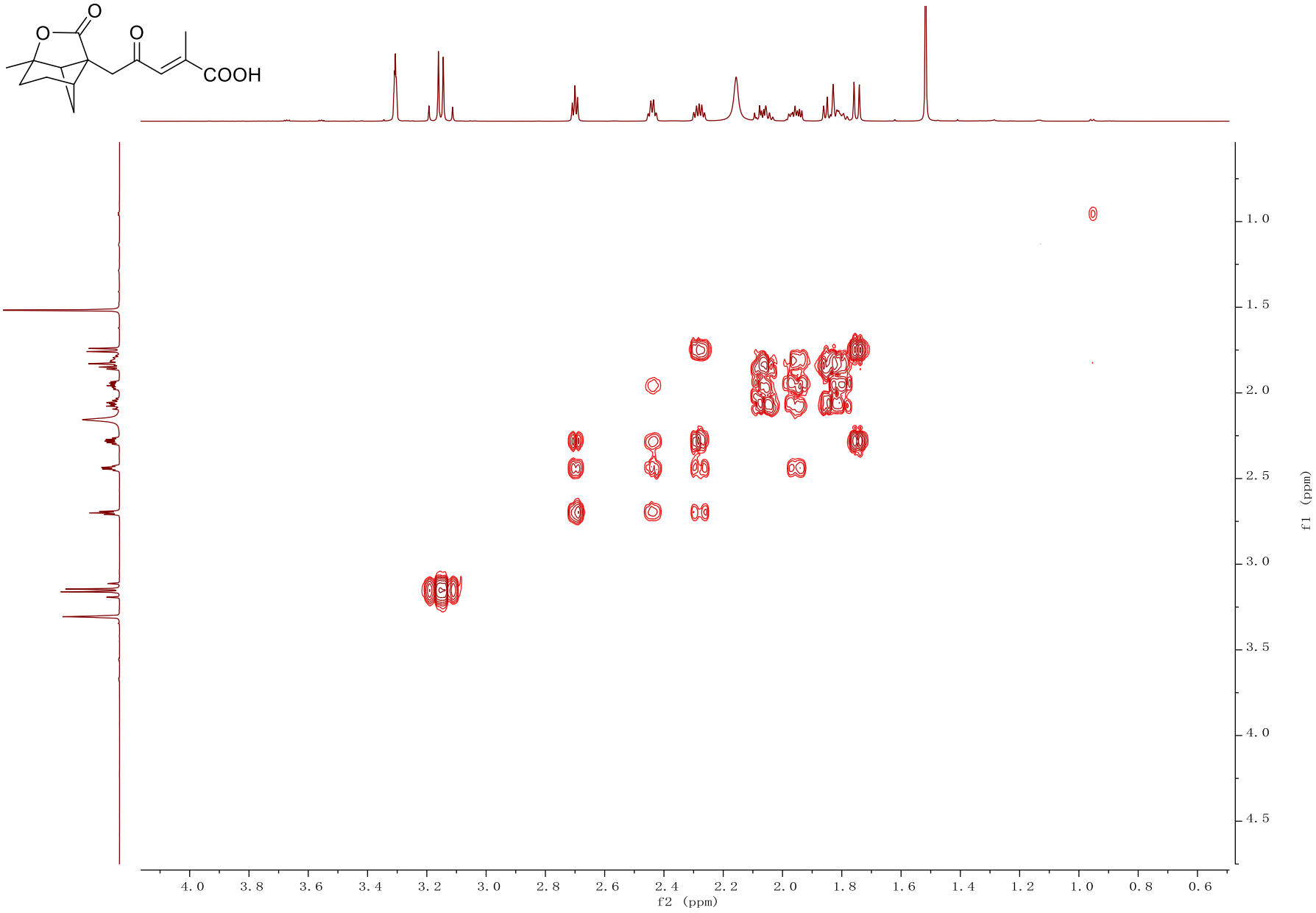


Figure S106. ROESY of compound **12** in CD_3OD

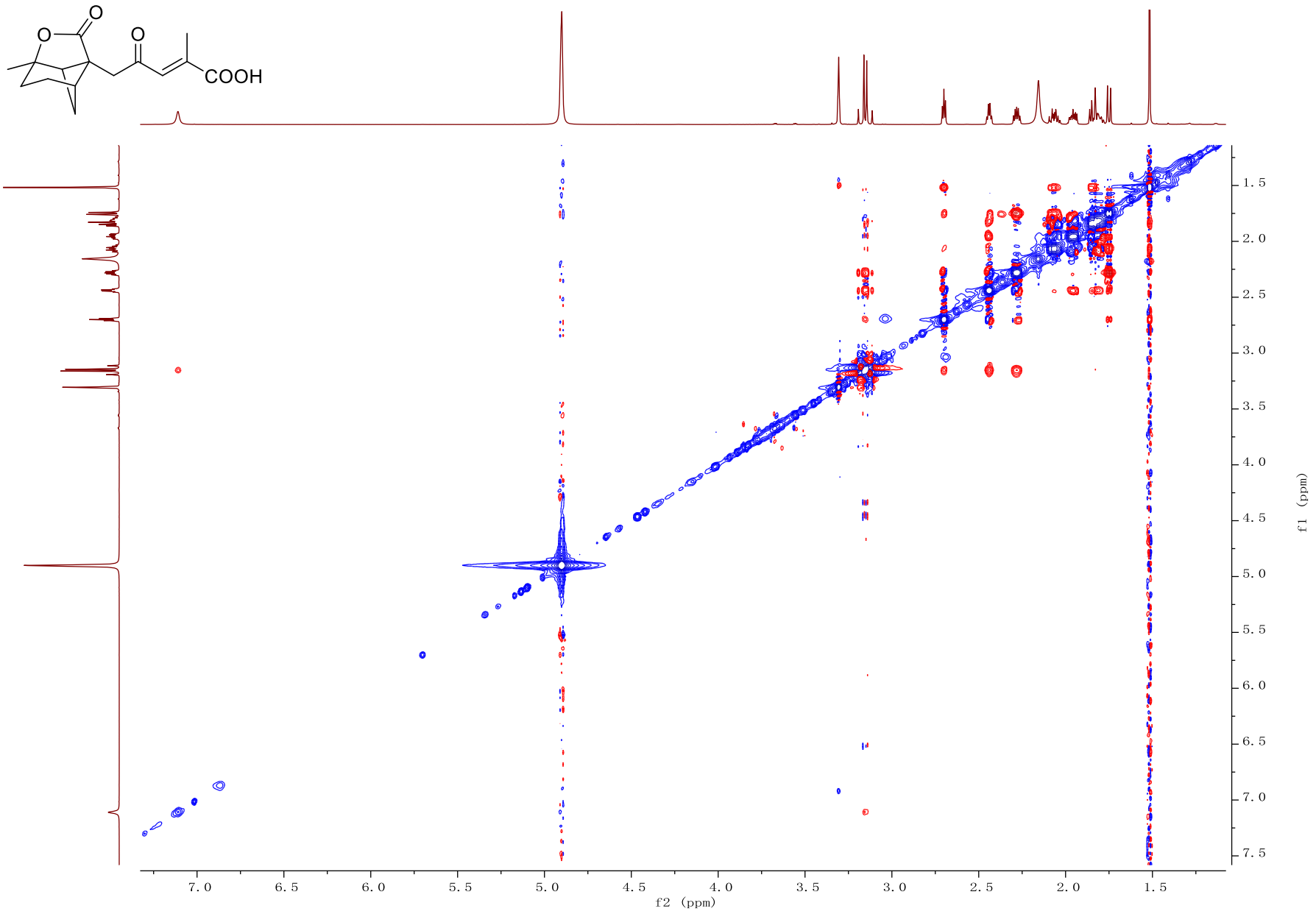
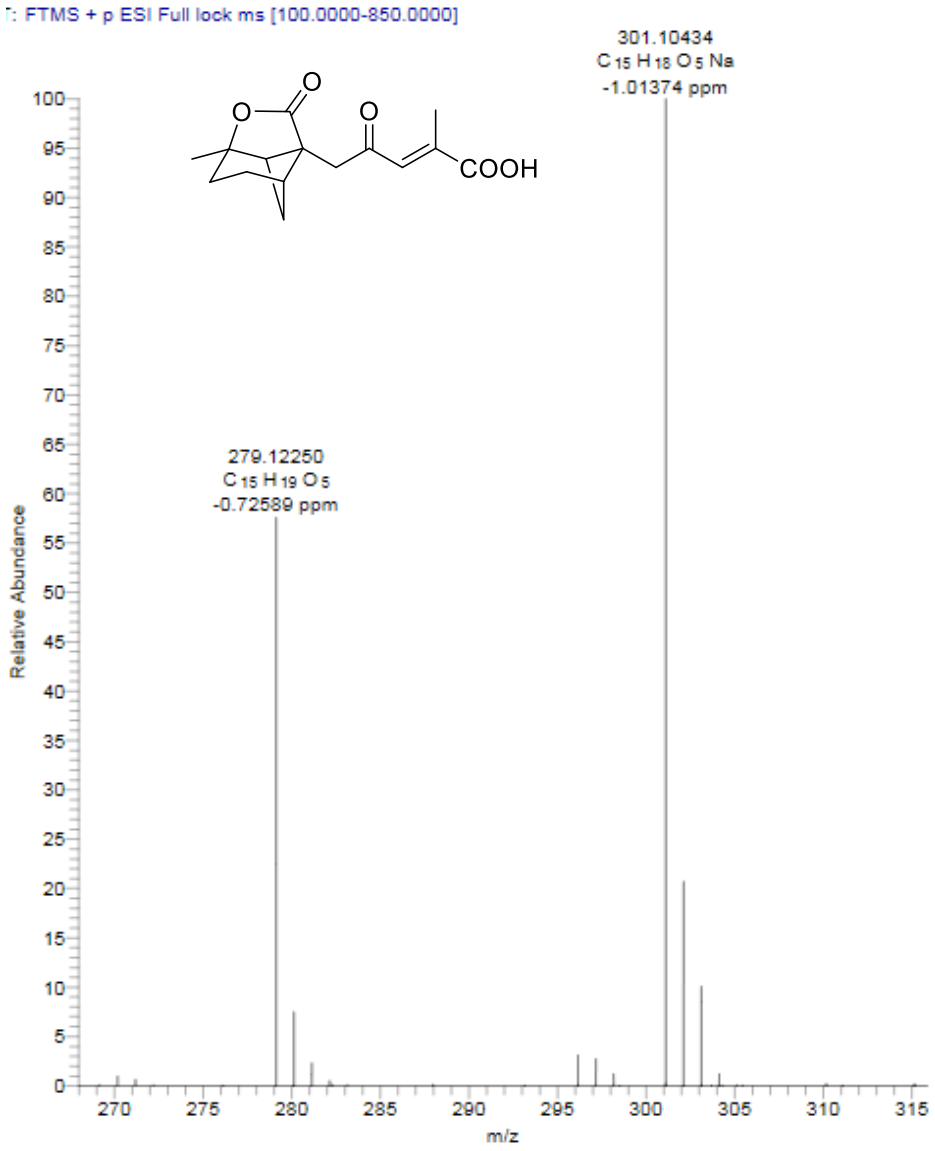


Figure S107. HR-ESIMS of compound **12**



Section S20. NMR and MS spectra for 13

Figure S108. ^{1}H NMR of compound **13** in CD_3OD

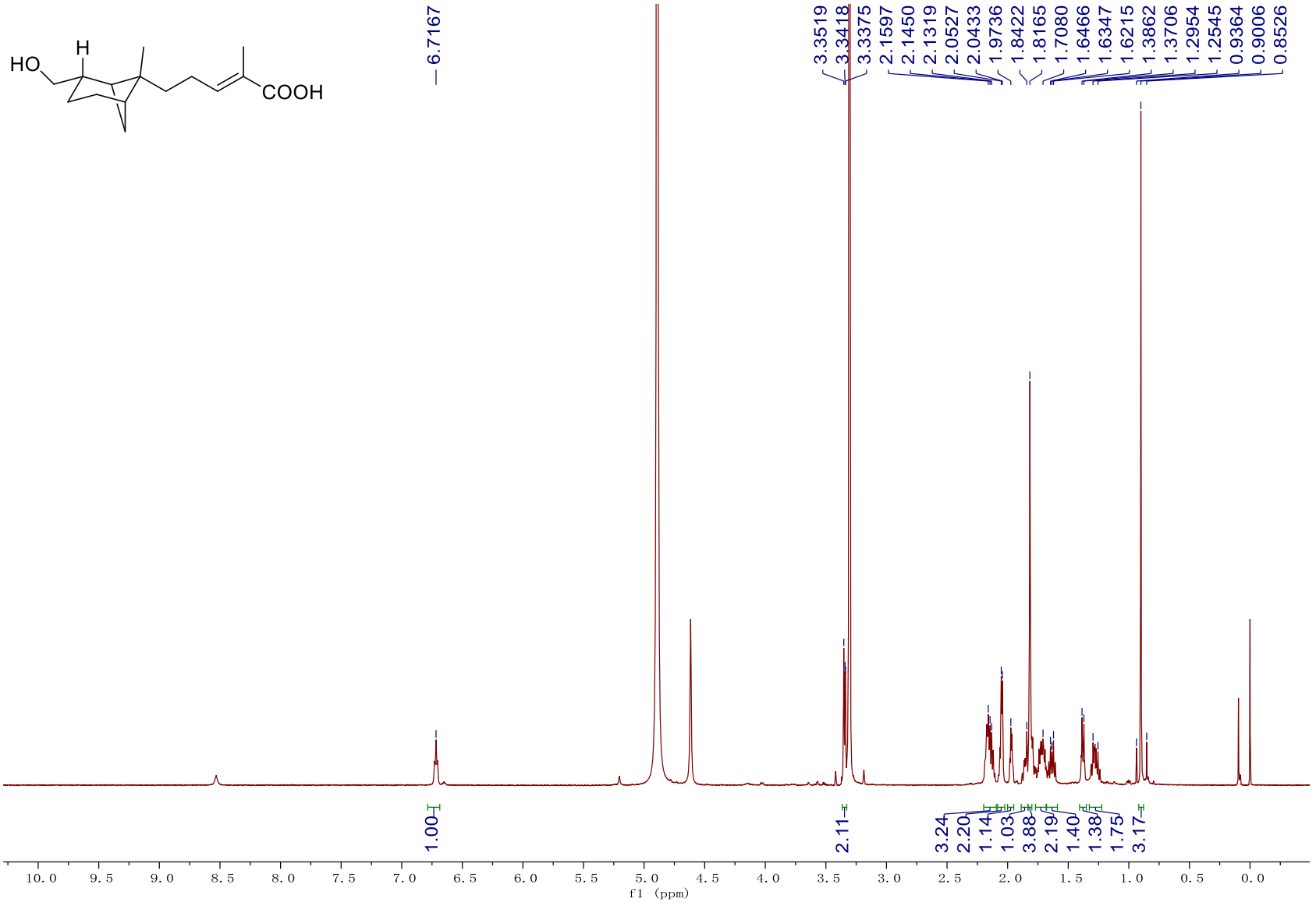


Figure S109. ^{13}C NMR and DEPT of compound **13** in CD_3OD

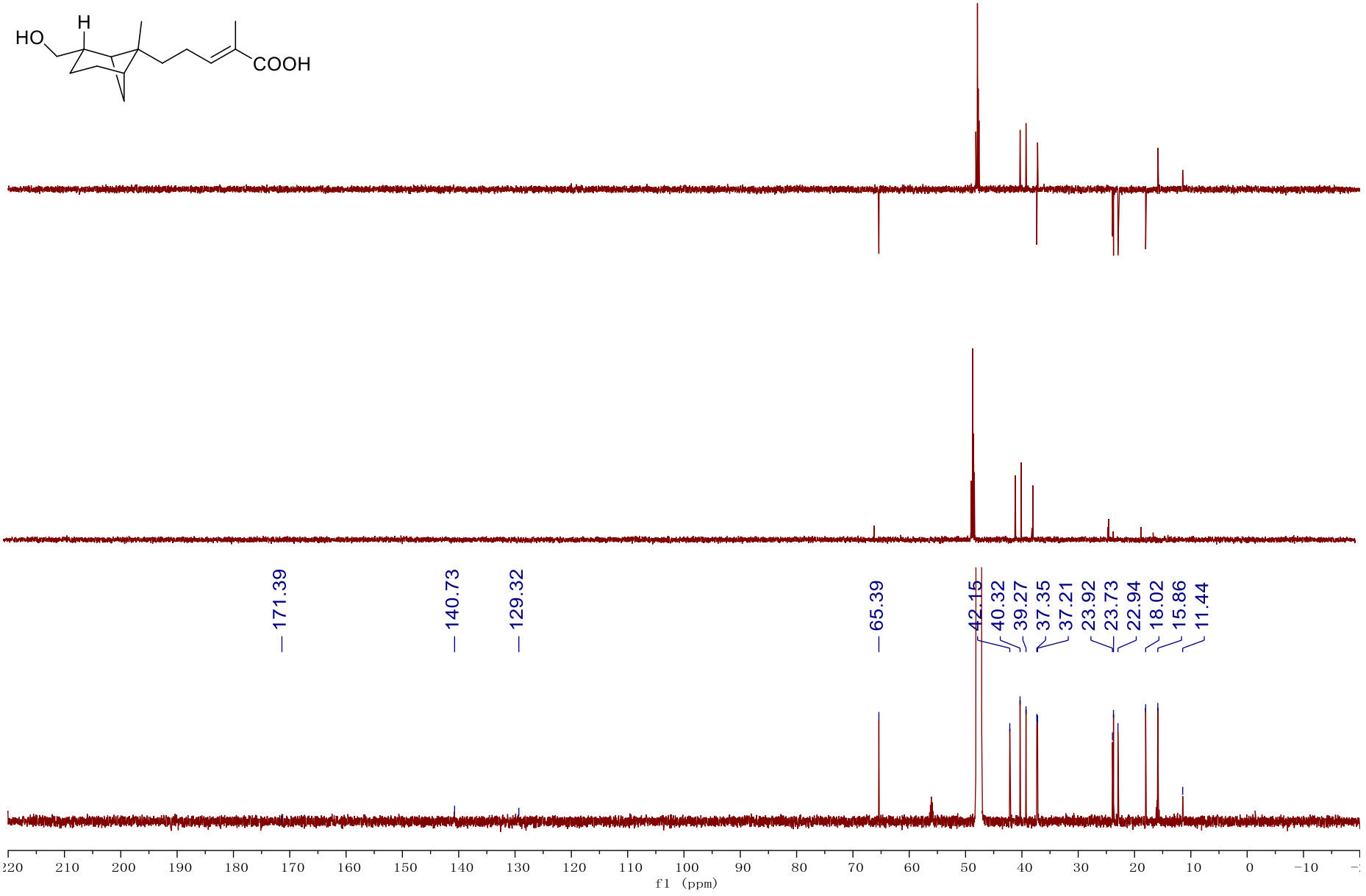


Figure S110. HSQC of compound **13** in CD_3OD

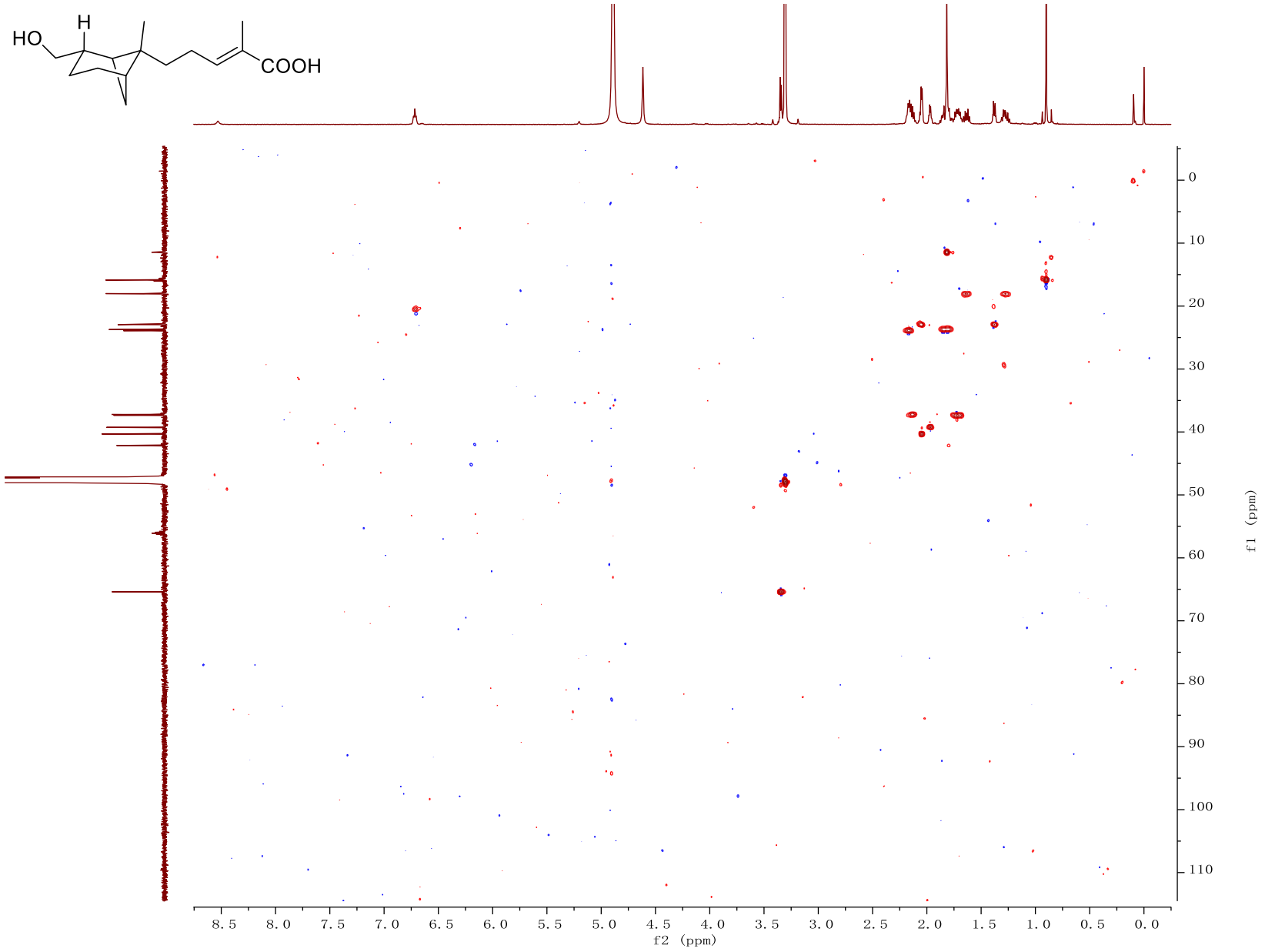


Figure S111. HMBC of compound **13** in CD_3OD

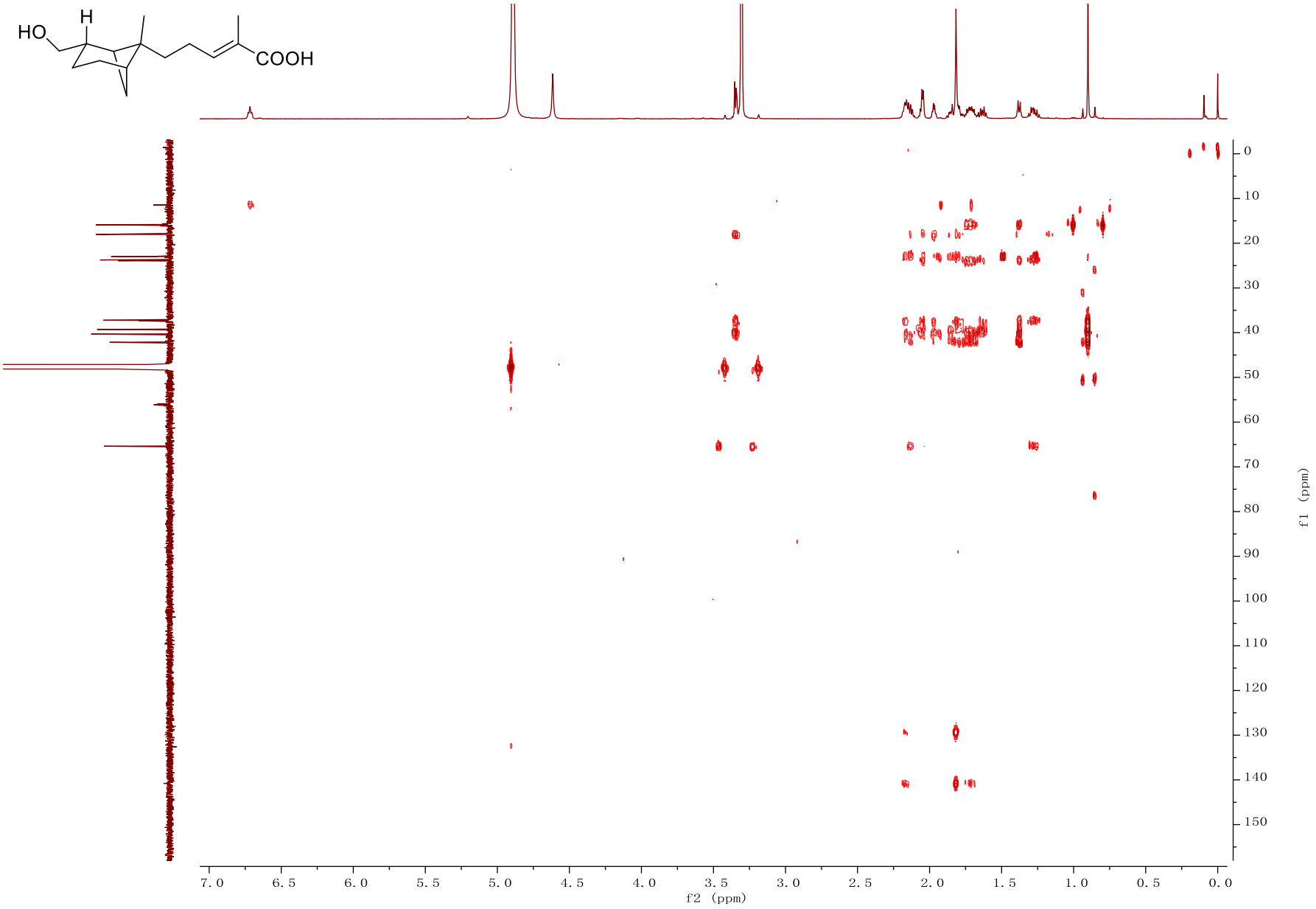


Figure S112. ^{1}H-^{1}H COSY of compound **13** in CD_3OD

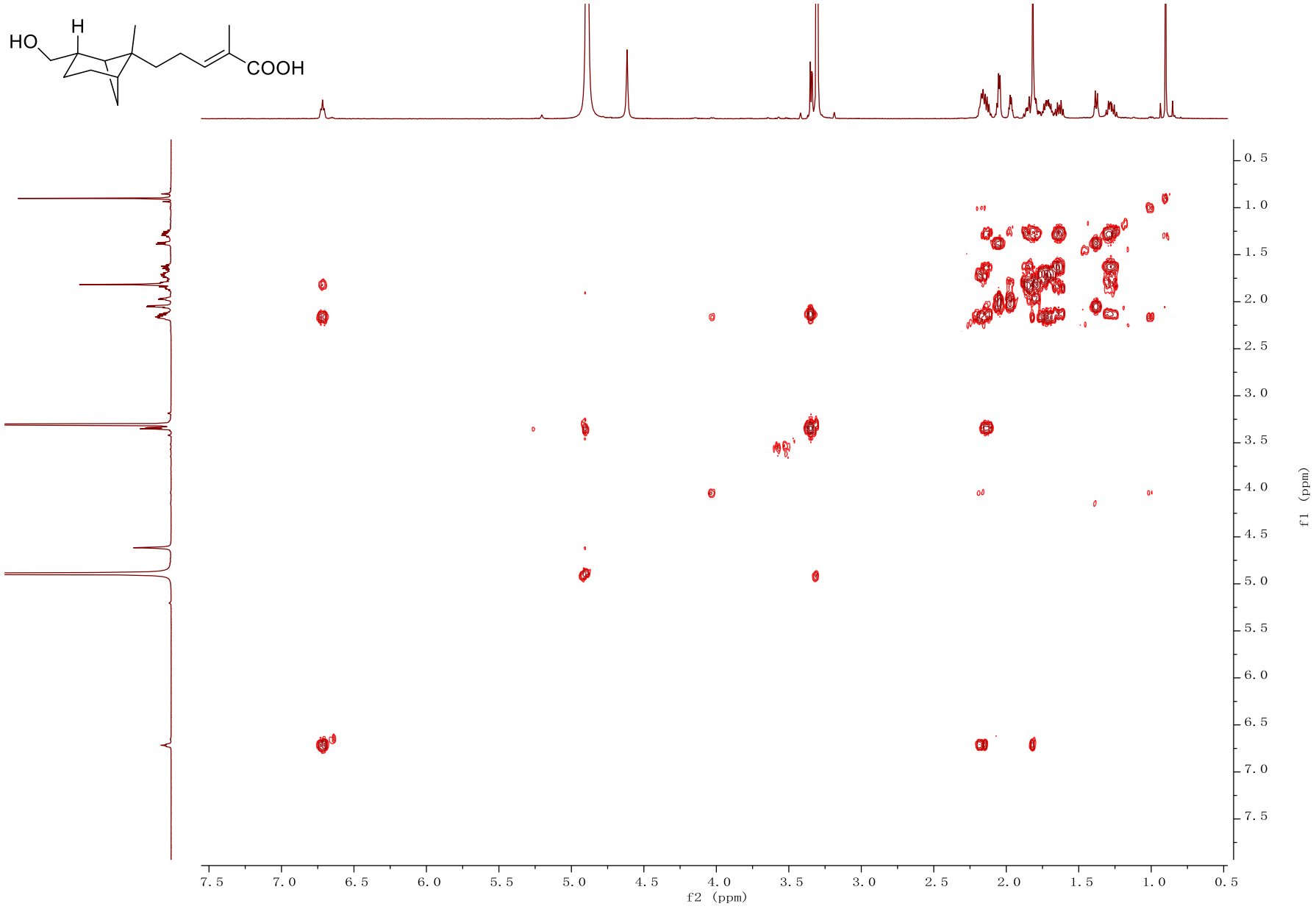


Figure S113. ROESY of compound **13** in CD_3OD

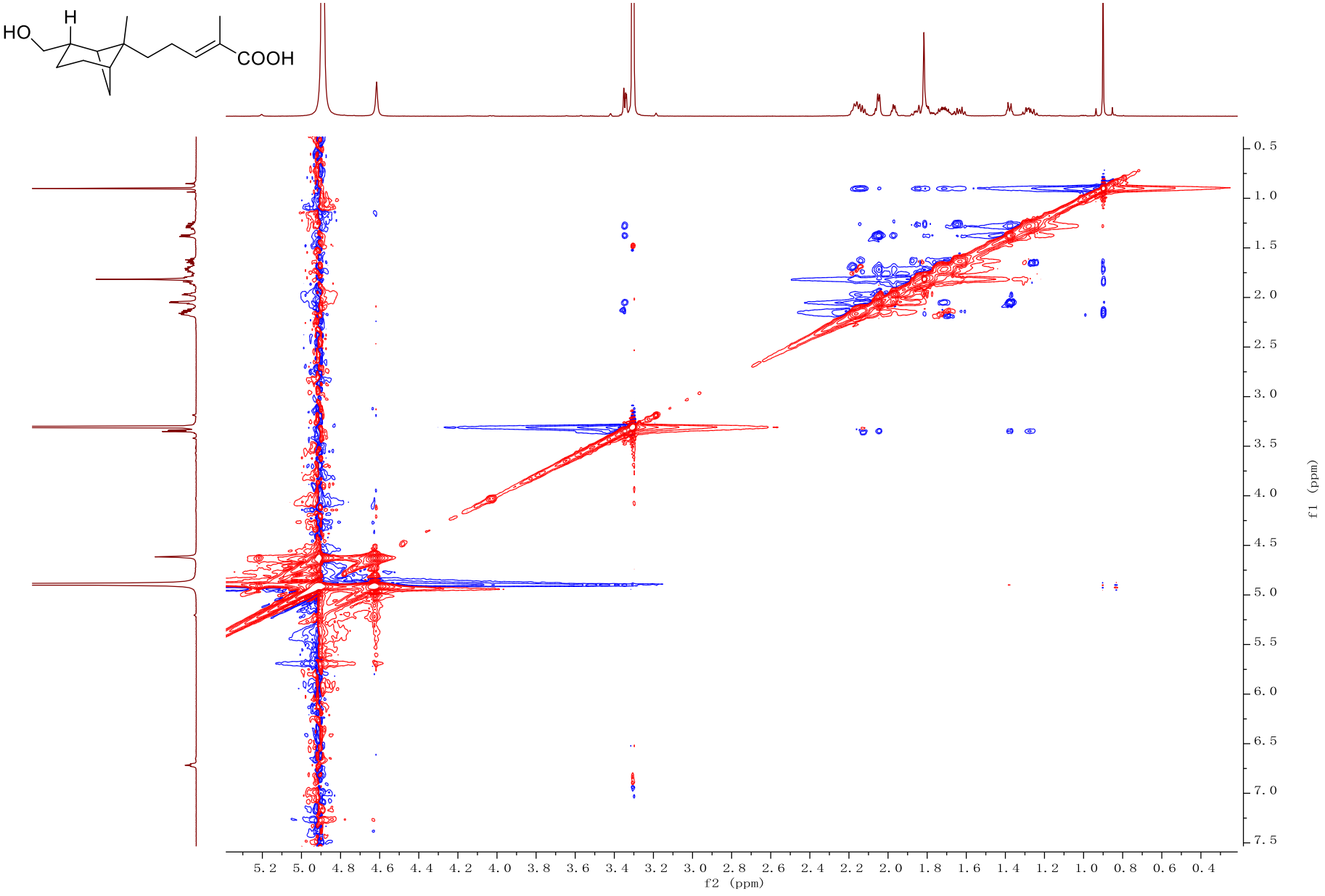
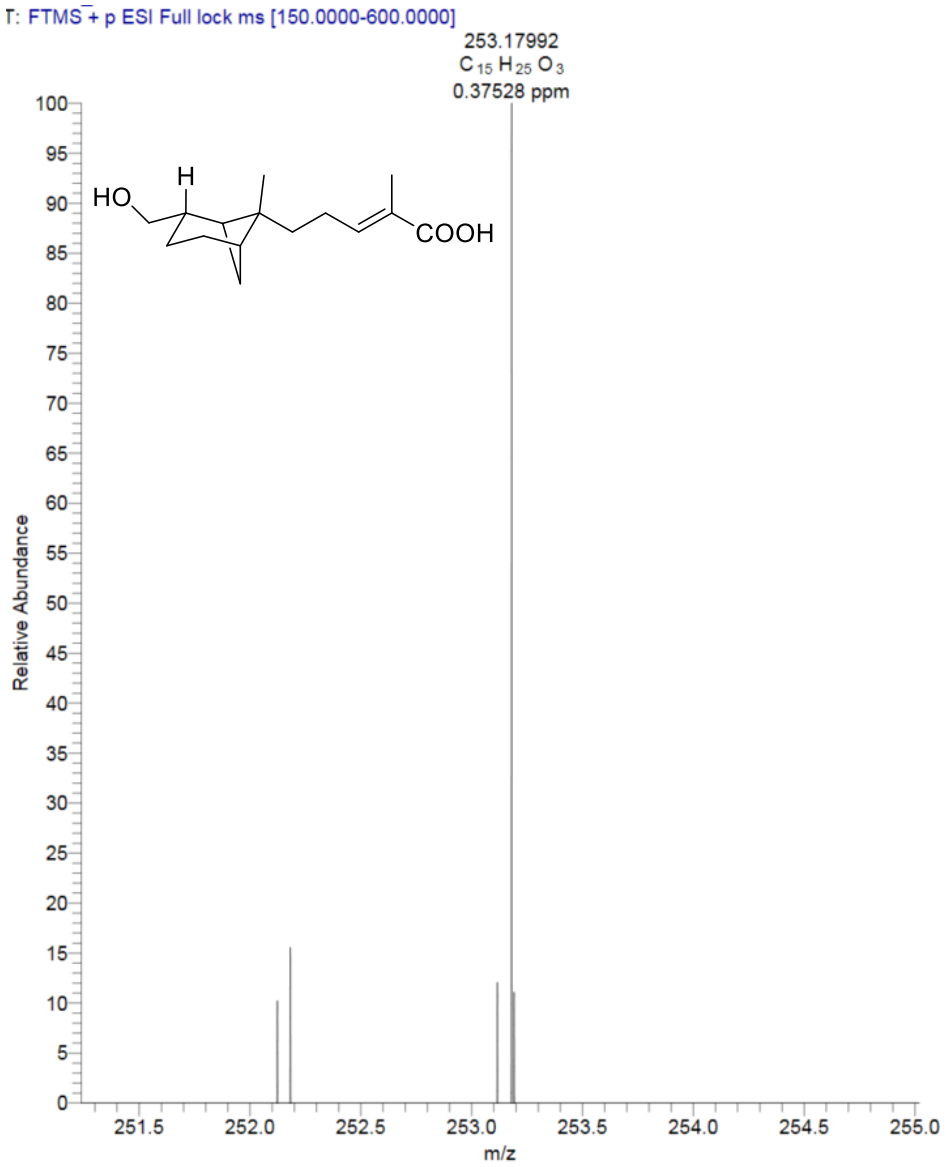


Figure S114. HR-ESIMS of compound **13**



Section S21. NMR and MS spectra for 14

Figure S115. ^{1}H NMR of compound **14** in CD_3OD

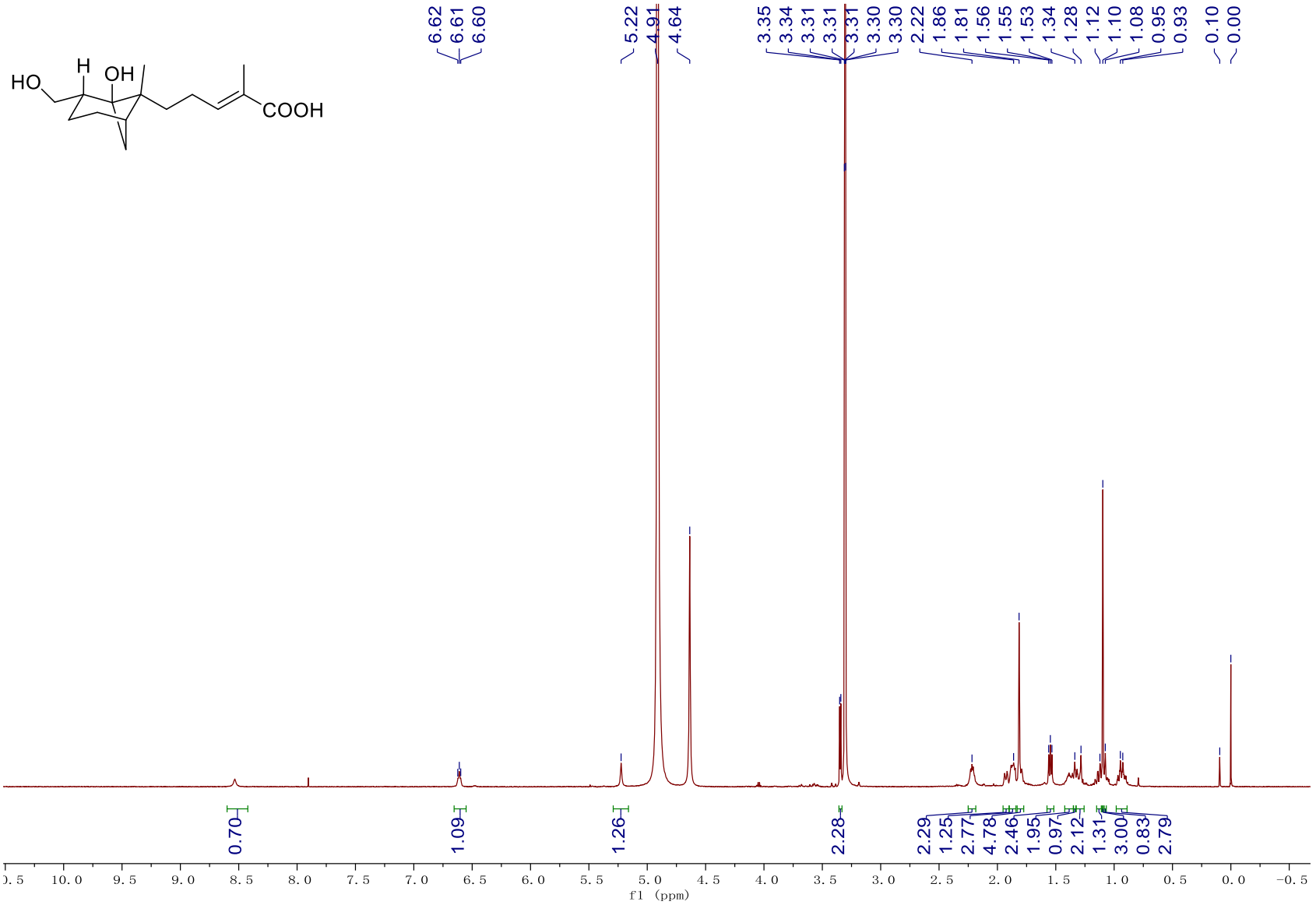


Figure S116. ^{13}C NMR and DEPT of compound **14** in CD_3OD

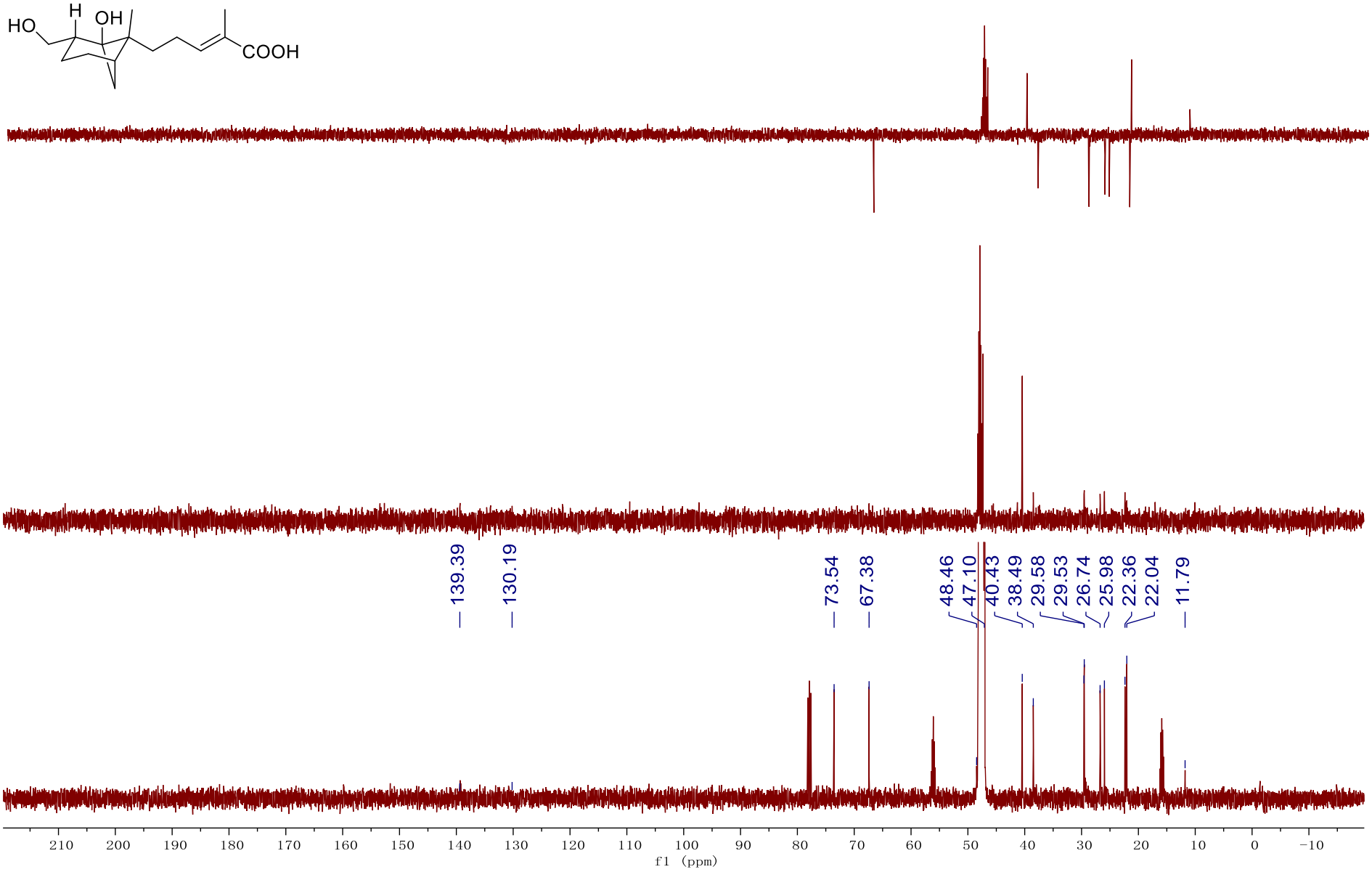


Figure S117. HSQC of compound **14** in CD_3OD

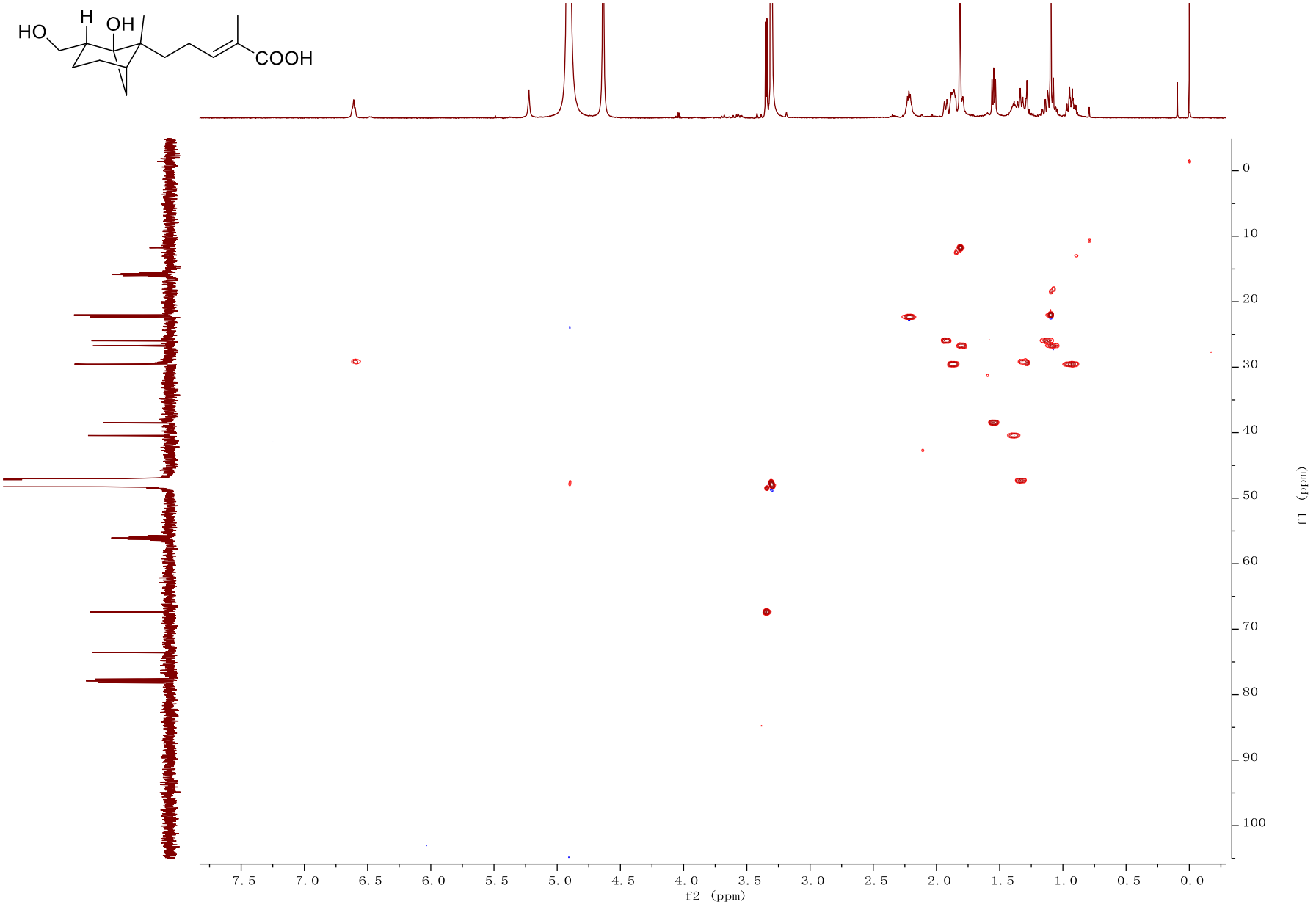


Figure S118. HMBC of compound **14** in CD_3OD

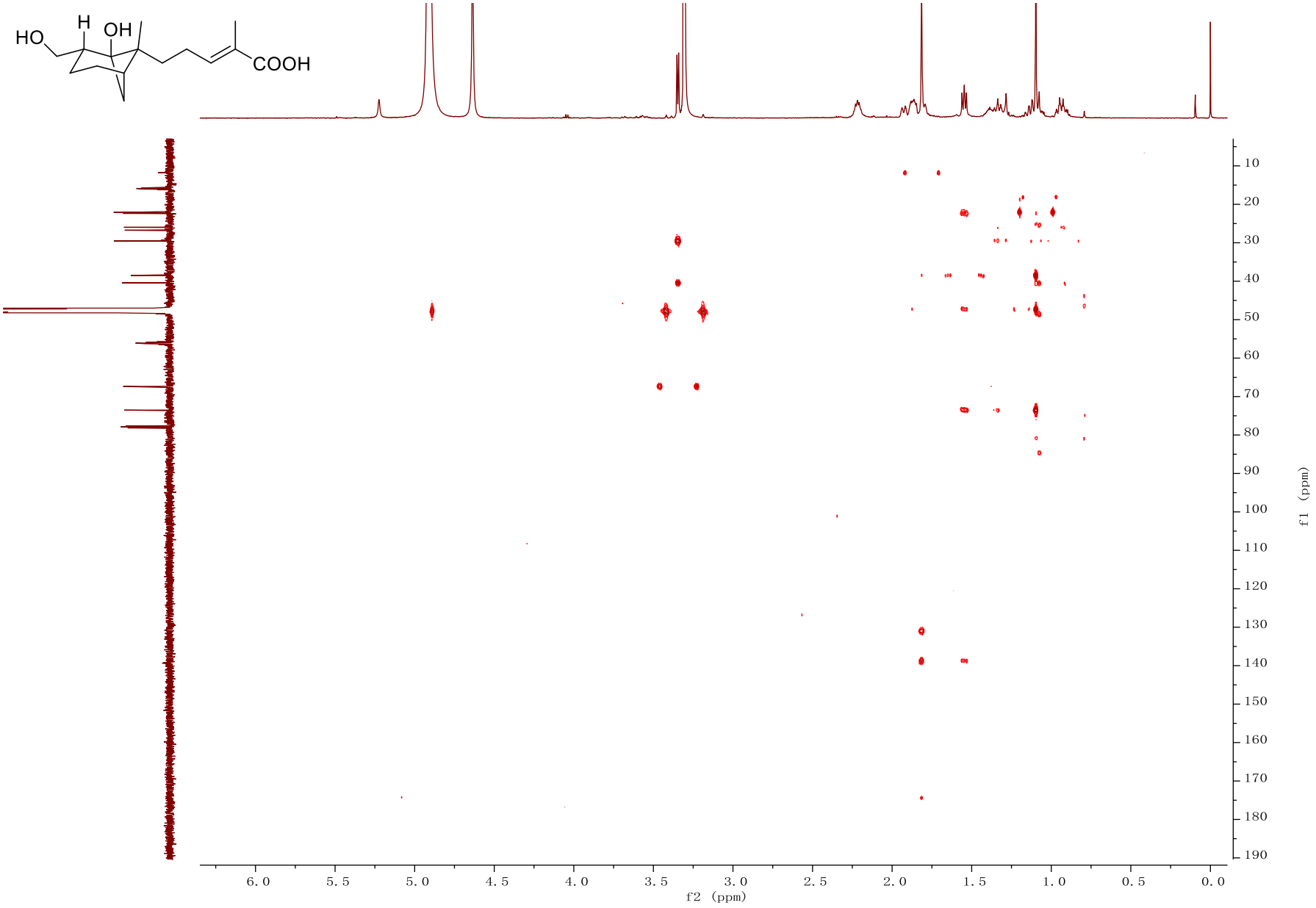


Figure S119. ^{1}H-^{1}H COSY of compound **14** in CD_3OD

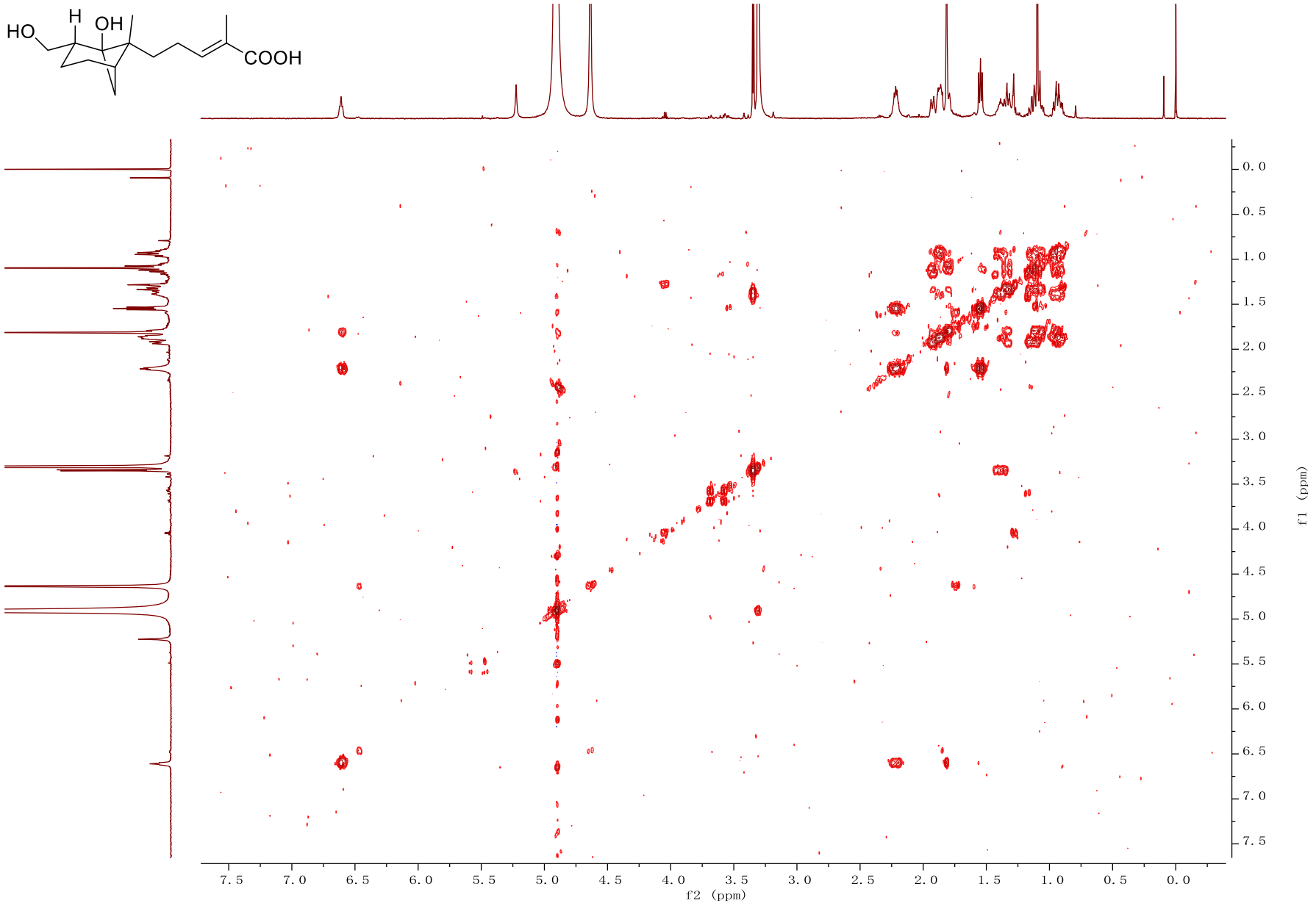


Figure S120. ROESY of compound **14** in CD_3OD

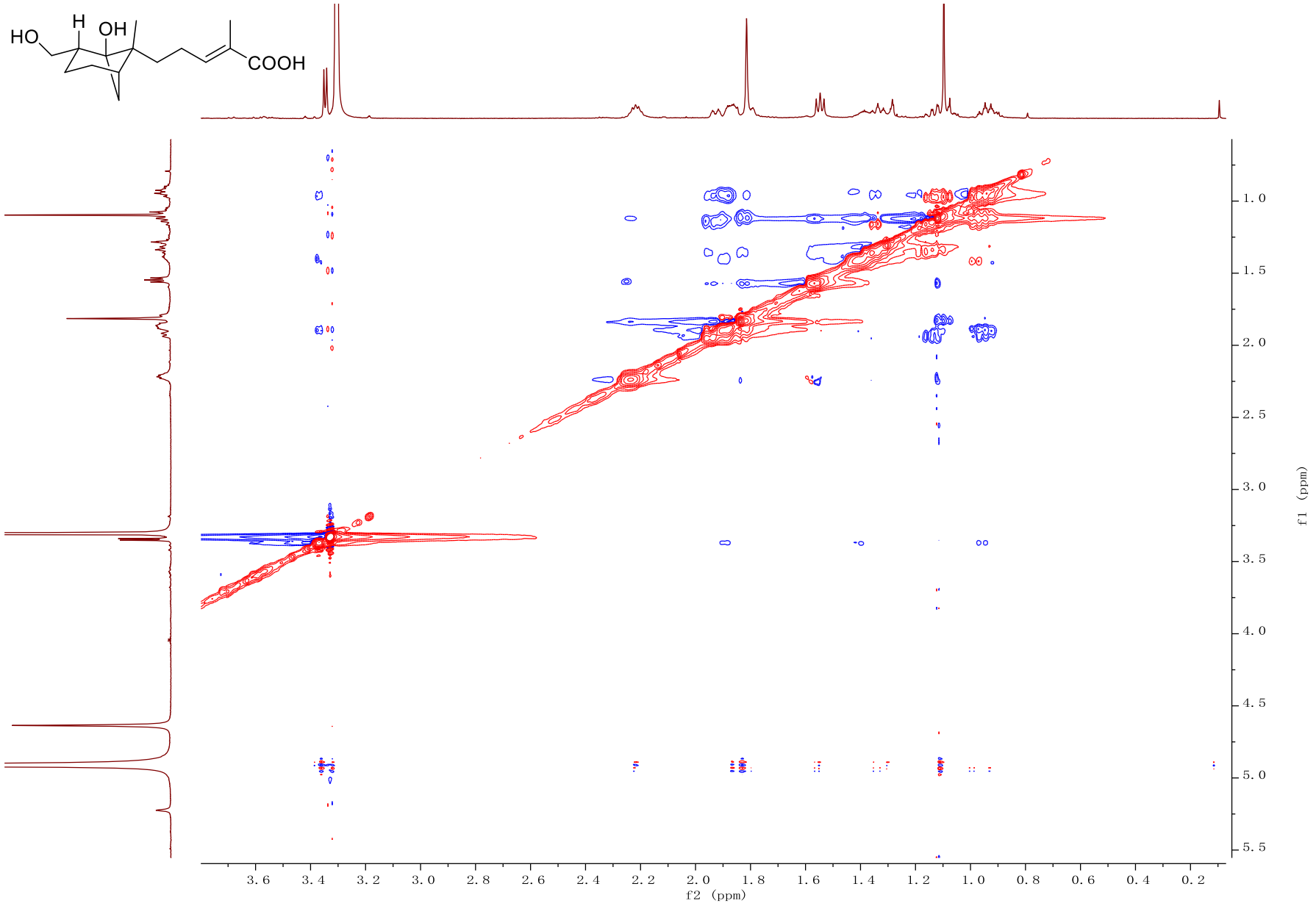
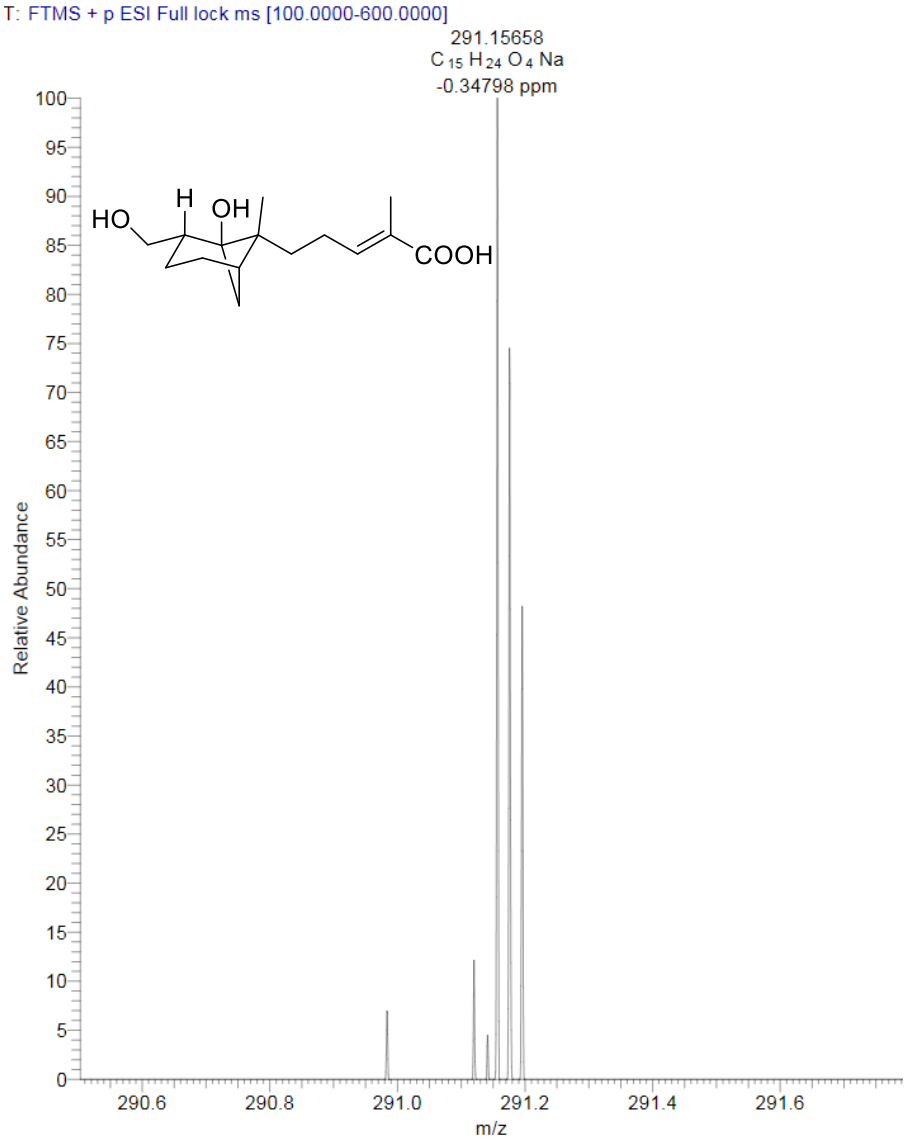


Figure S121. HR-ESIMS of compound **14**



Section S22. NMR and MS spectra for 15

Figure S122. ^{1}H NMR of compound **15** in CD_3OD

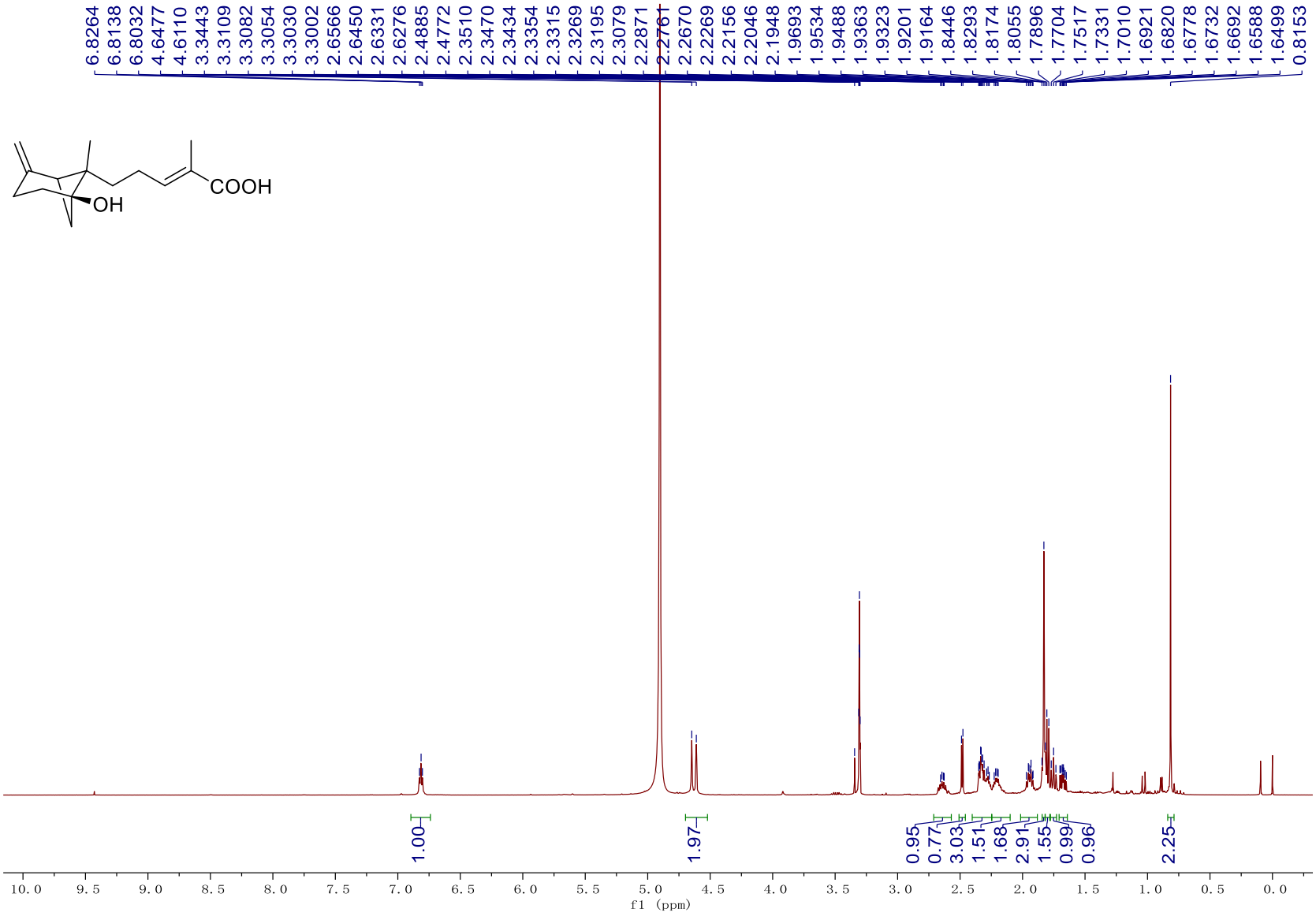


Figure S123. ^{13}C NMR and DEPT of compound **15** in CD_3OD

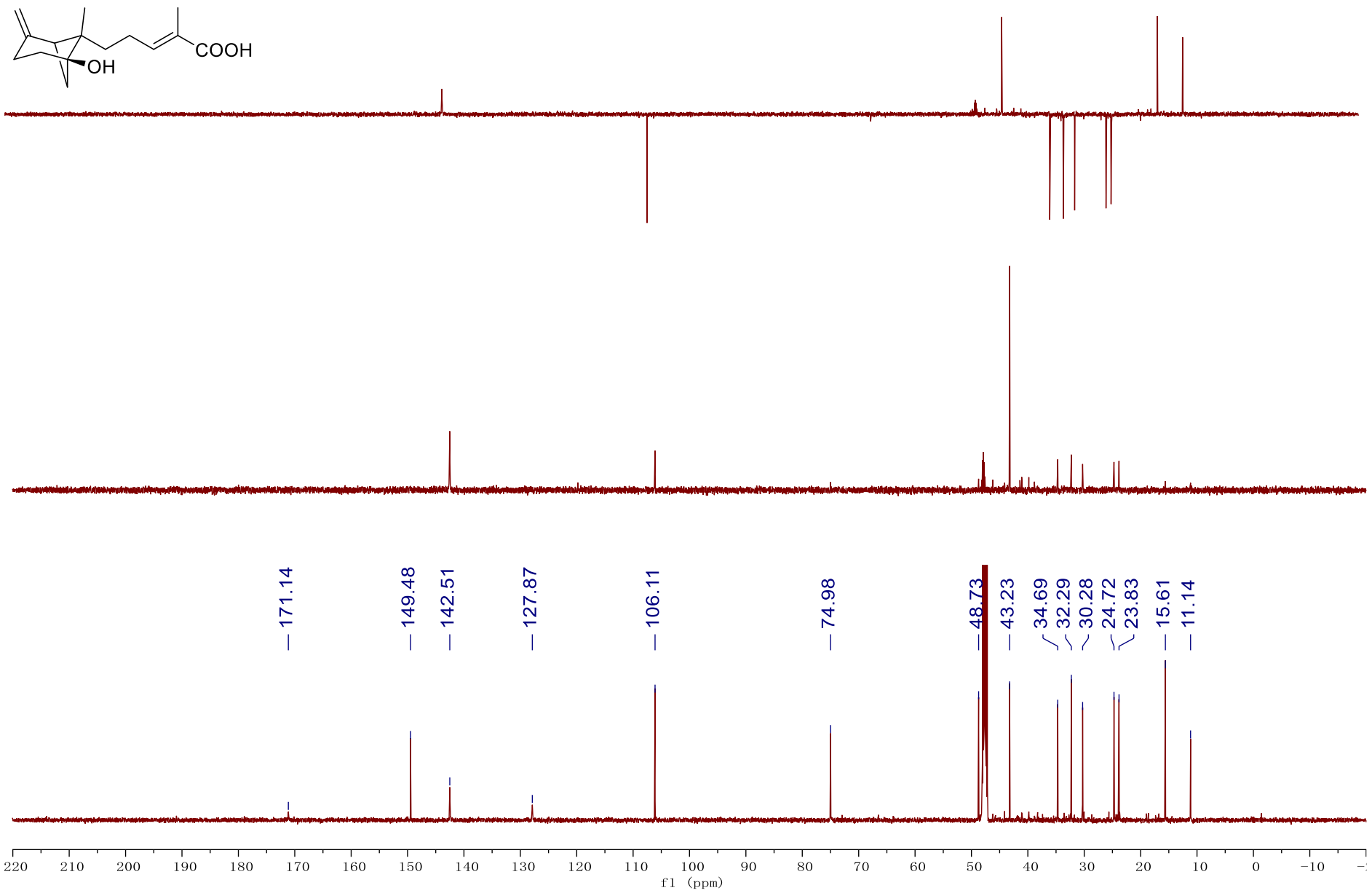


Figure S124. HSQC of compound **15** in CD_3OD

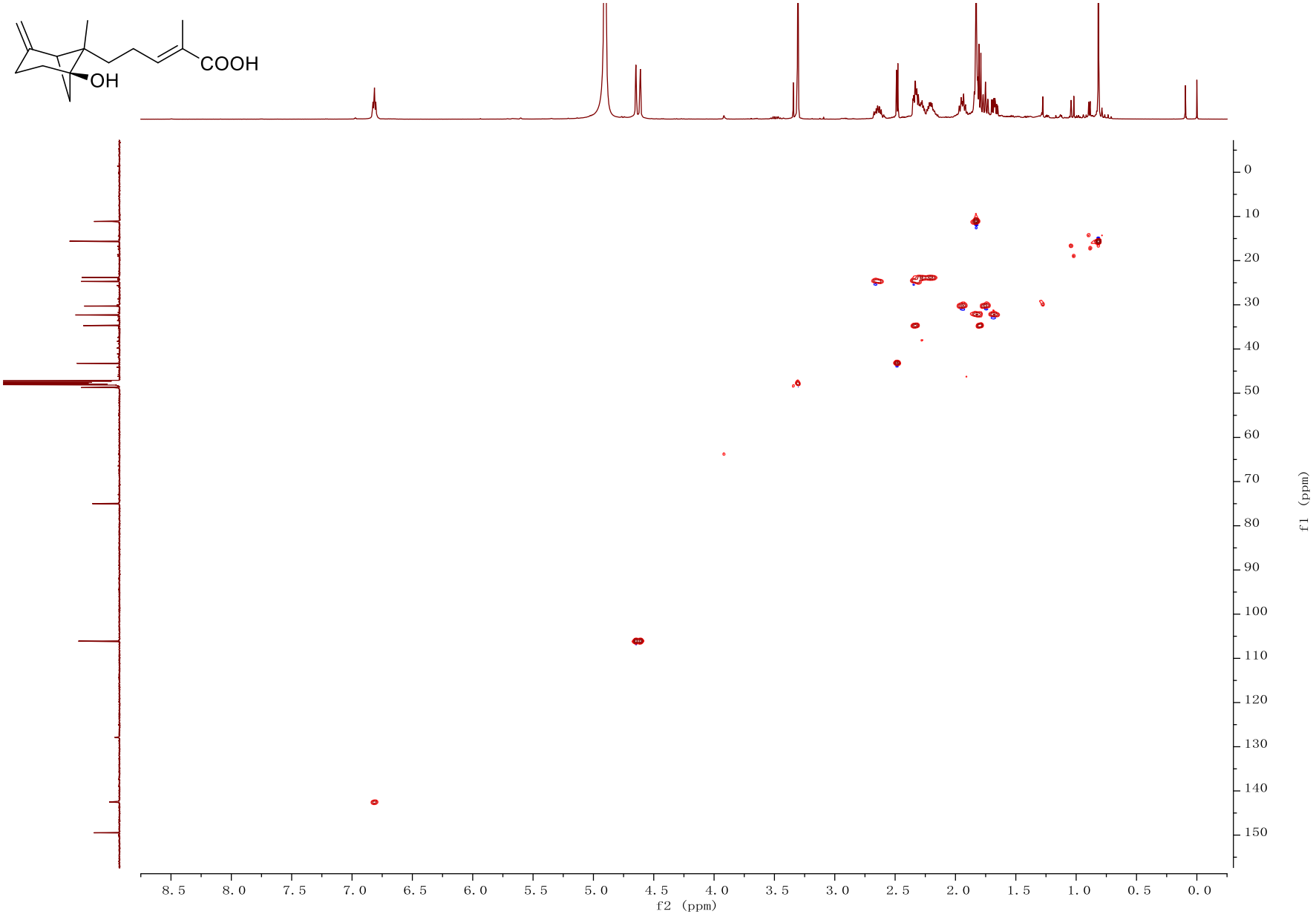


Figure S125. HMBC of compound **15** in CD_3OD

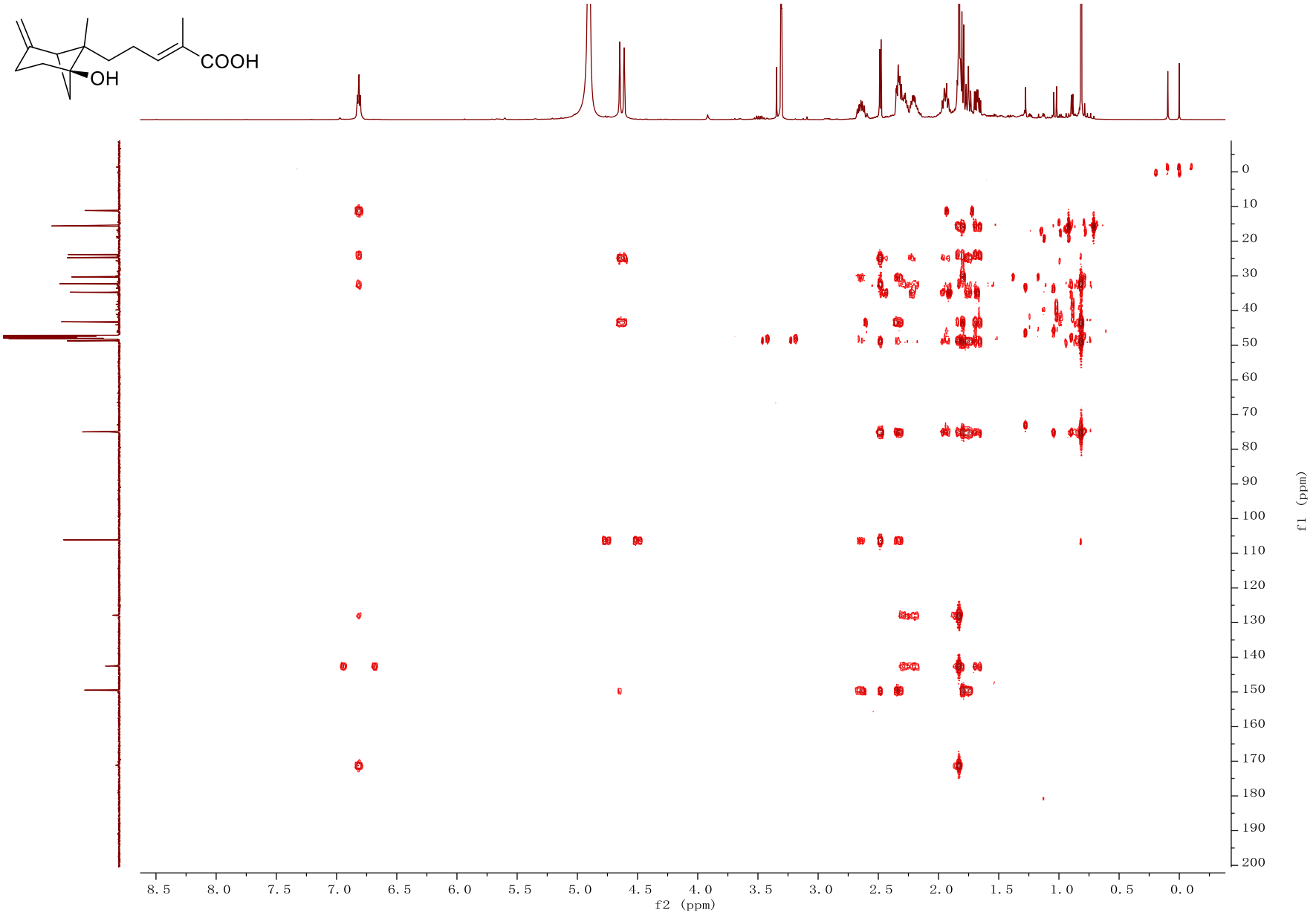


Figure S126. ^{1}H-^{1}H COSY of compound **15** in CD_3OD

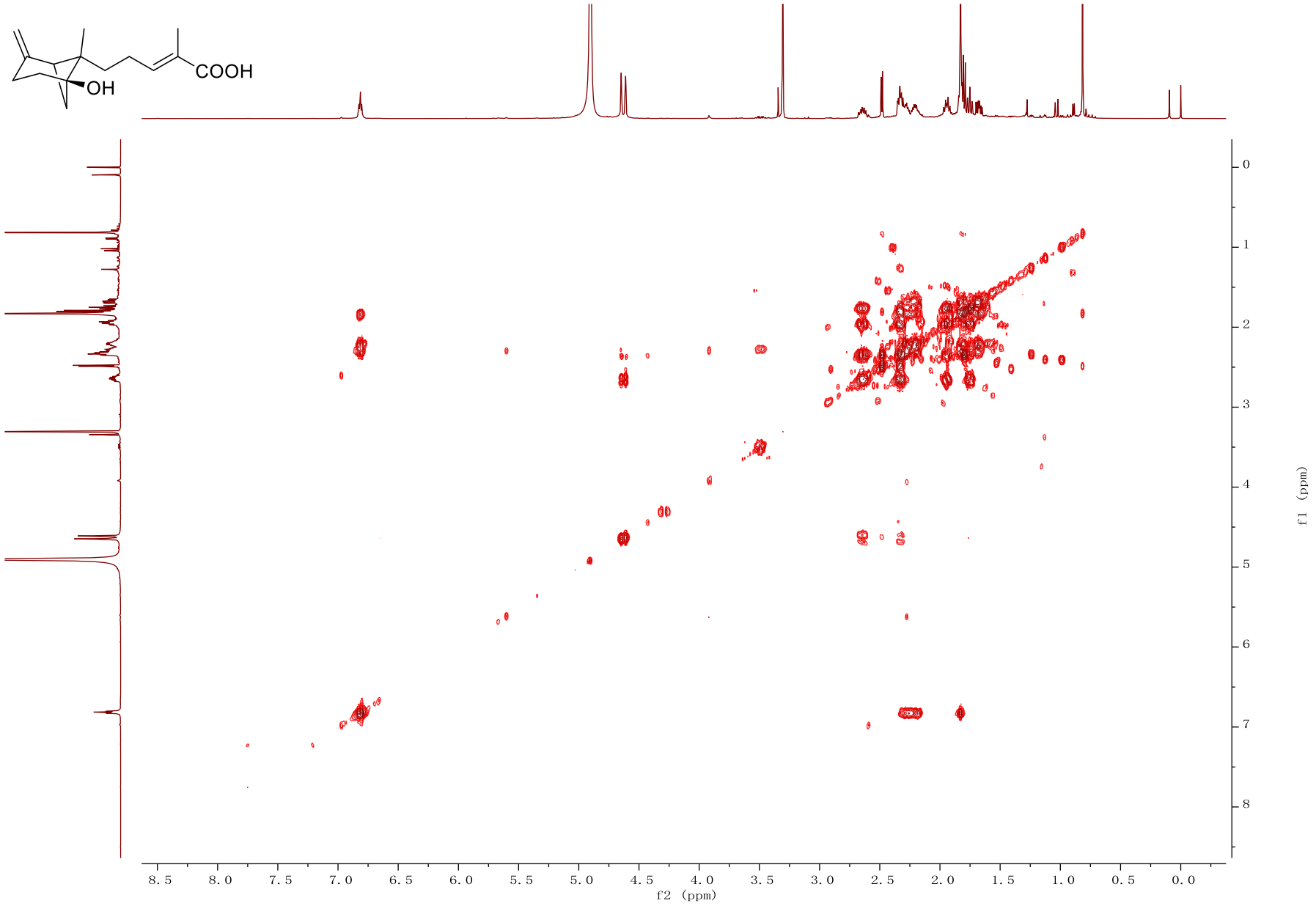


Figure S127. ROESY of compound **15** in CD_3OD

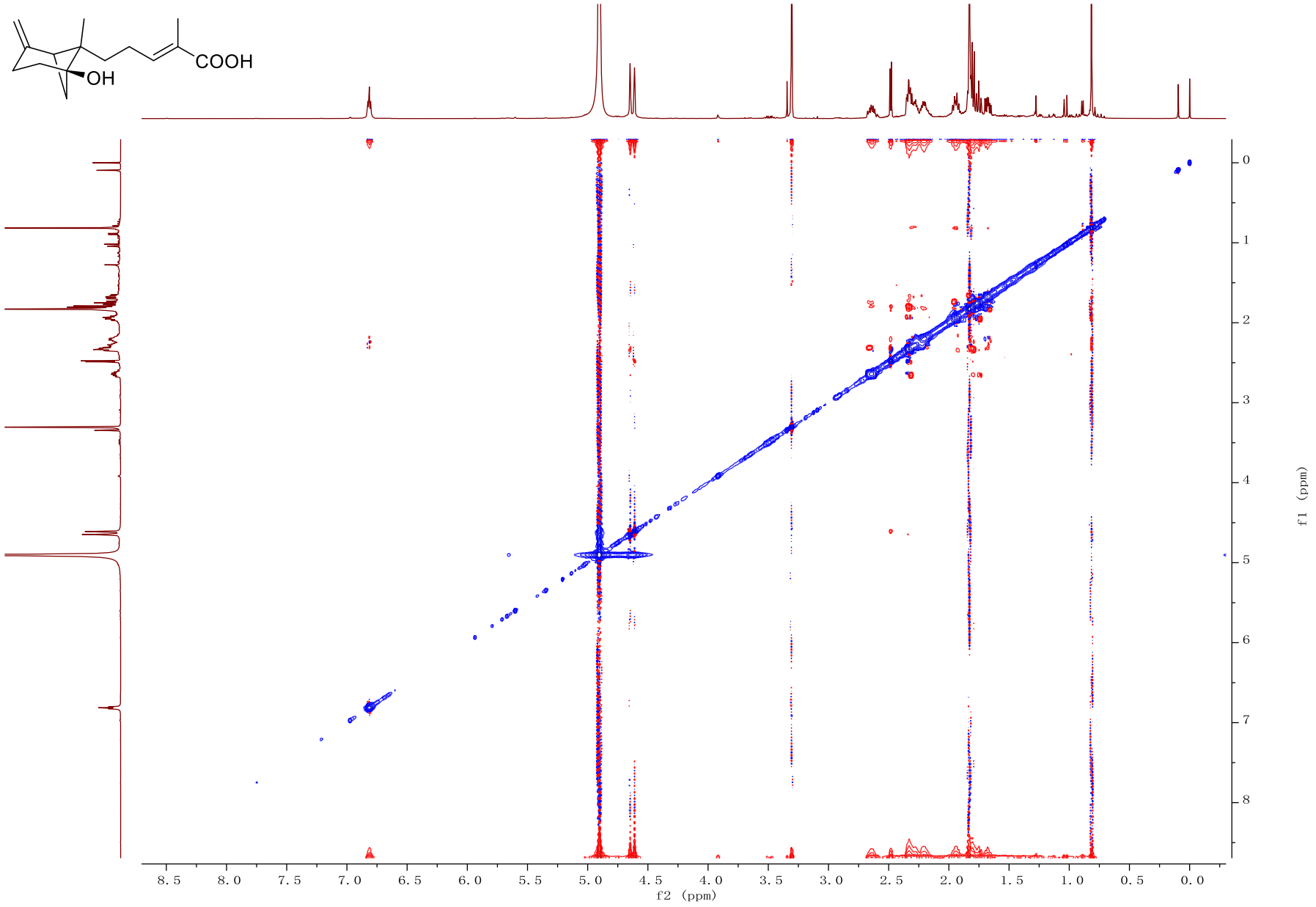
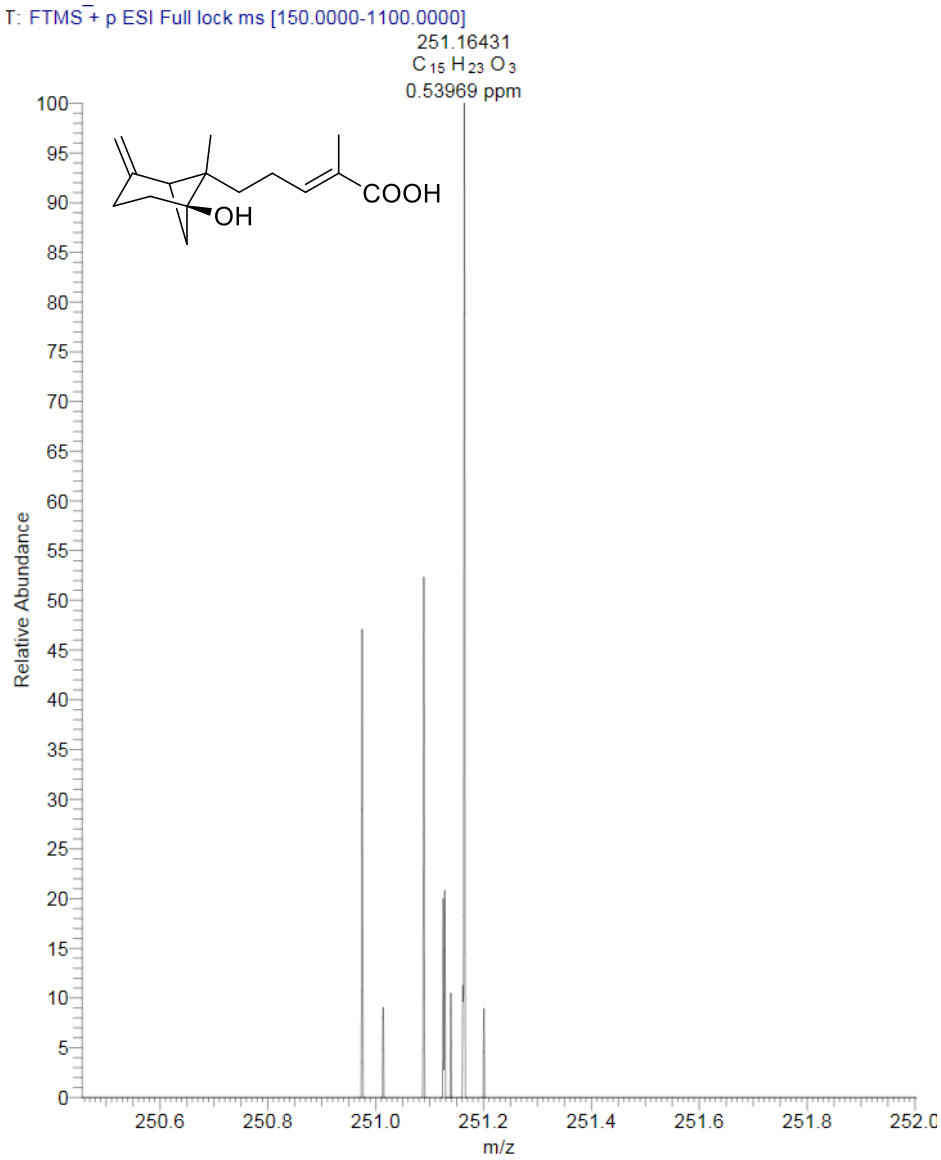


Figure S128. HR-ESIMS of compound **15**



Section S23. NMR and MS spectra for 16

Figure S129. ^{1}H NMR of compound **16** in CD_3OD

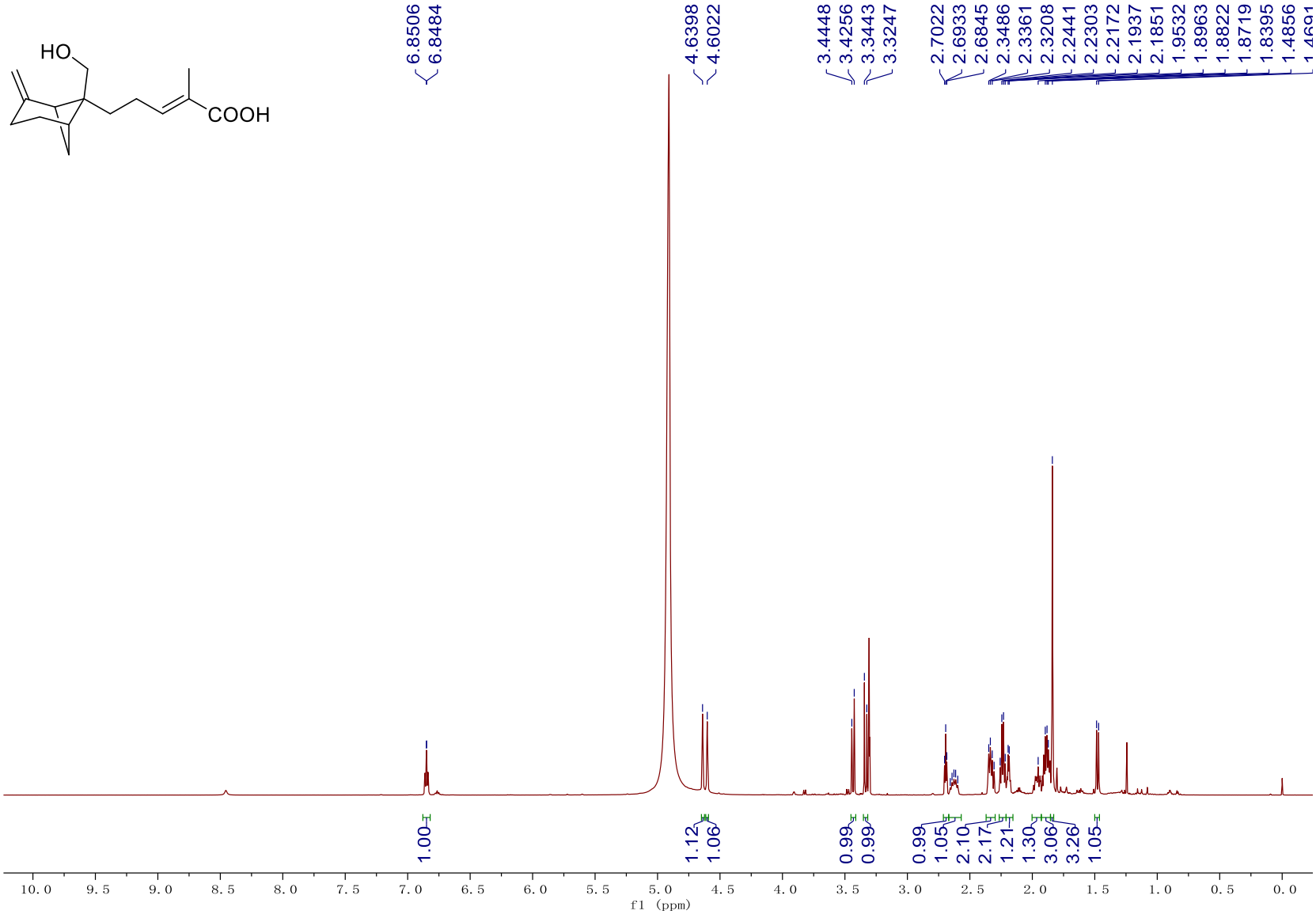


Figure S130. ^{13}C NMR and DEPT of compound **16** in CD_3OD

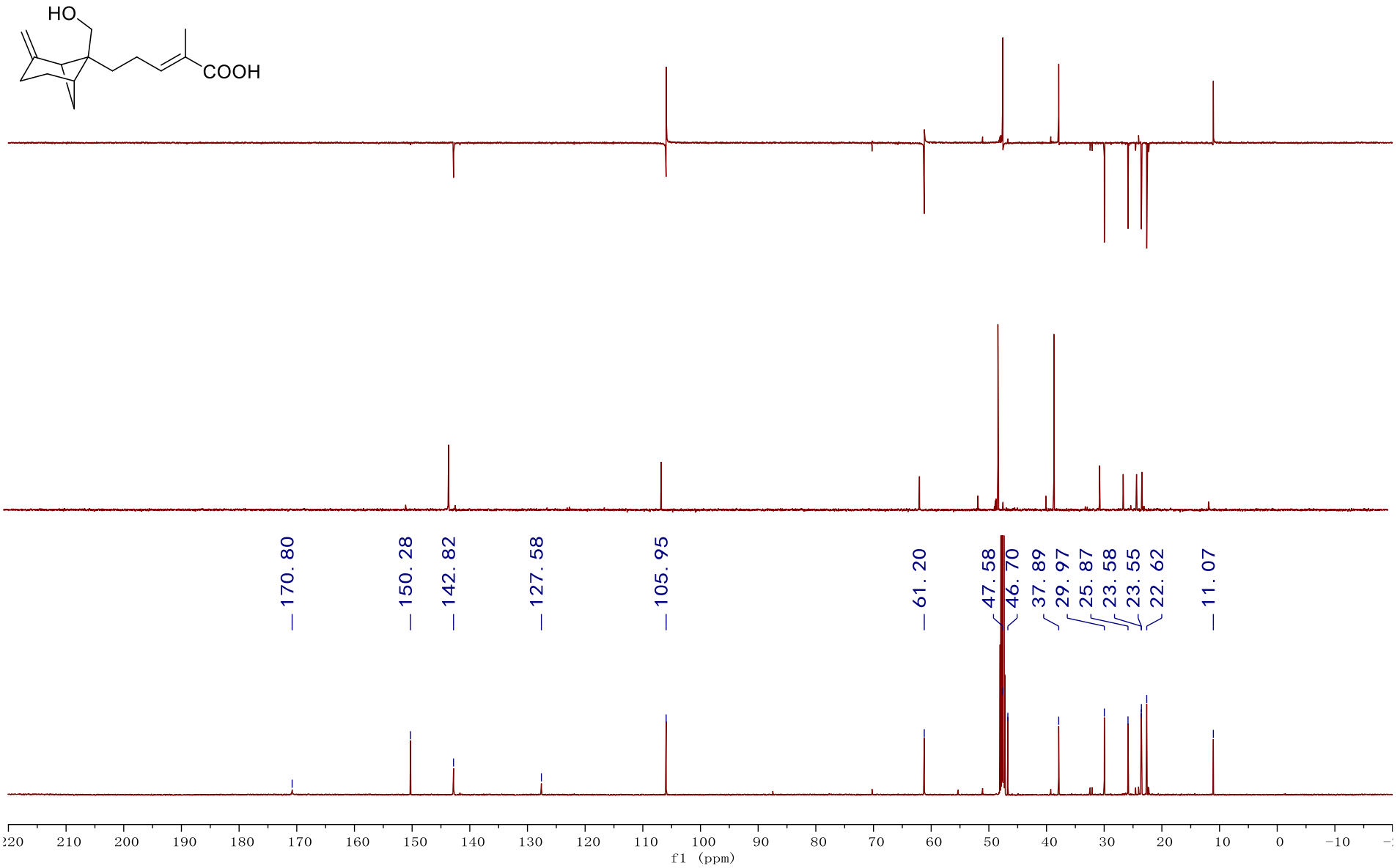


Figure S131. HSQC of compound **16** in CD_3OD

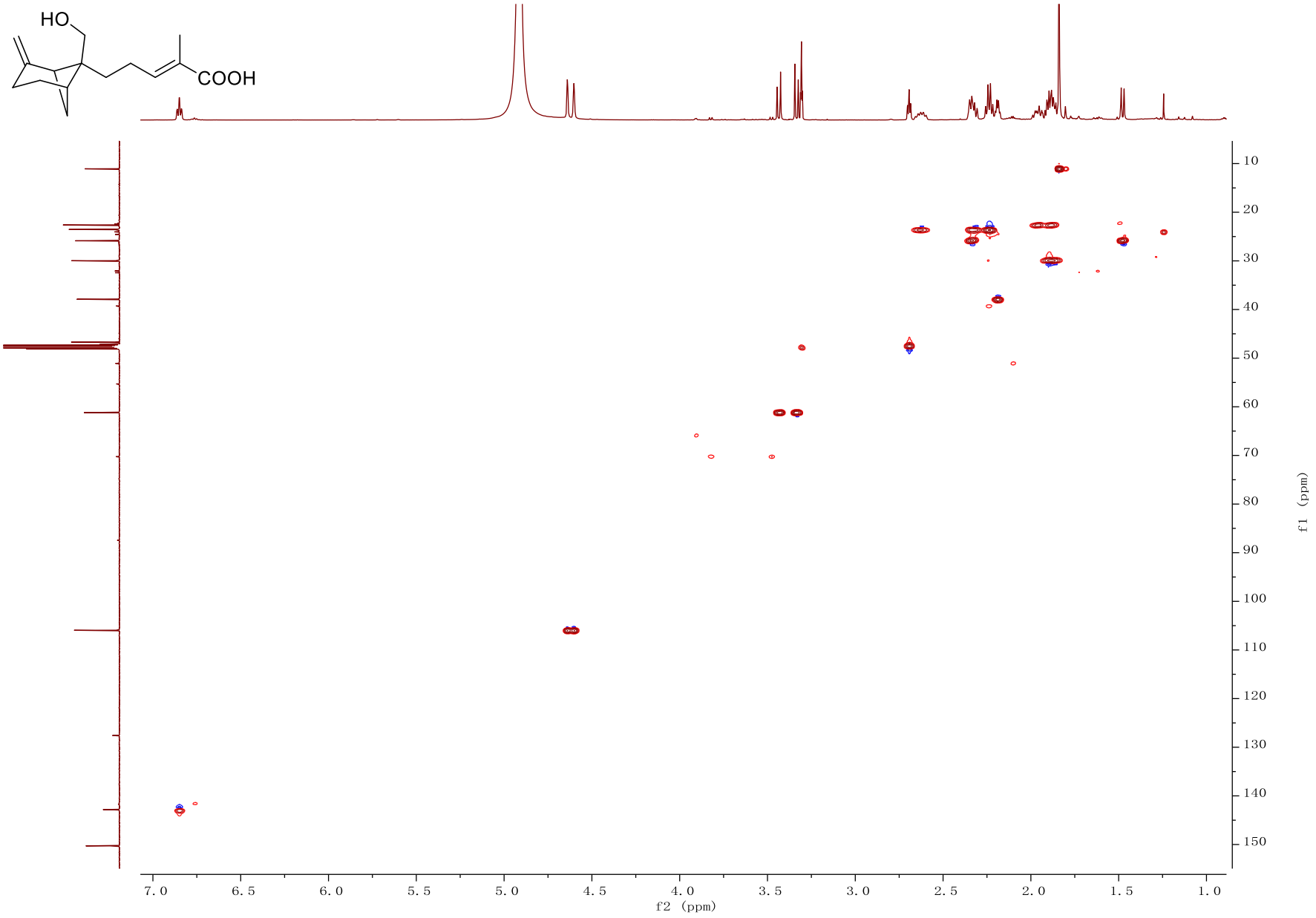


Figure S132. HMBC of compound **16** in CD_3OD

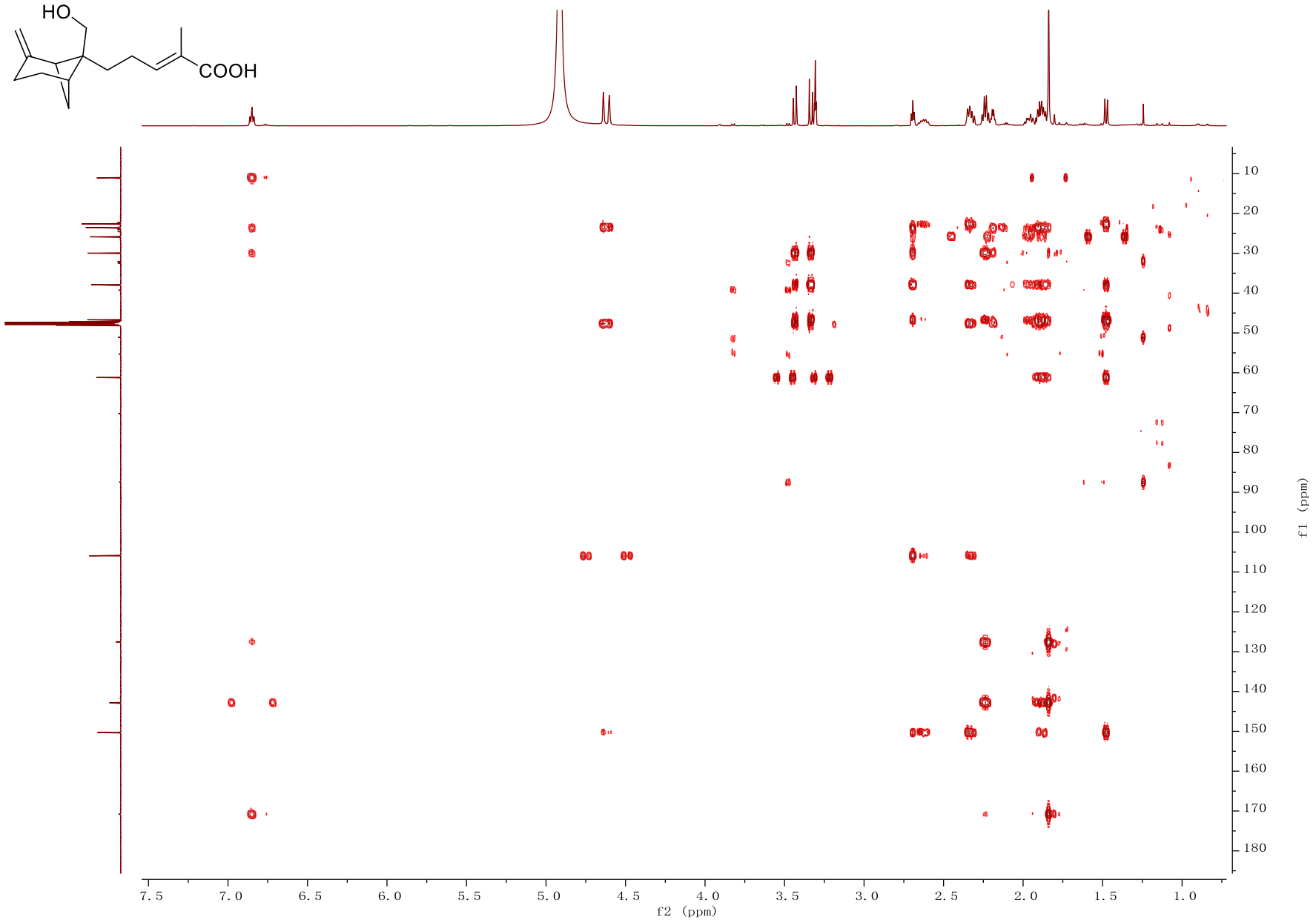


Figure S133. ^{1}H-^{1}H COSY of compound **16** in CD_3OD

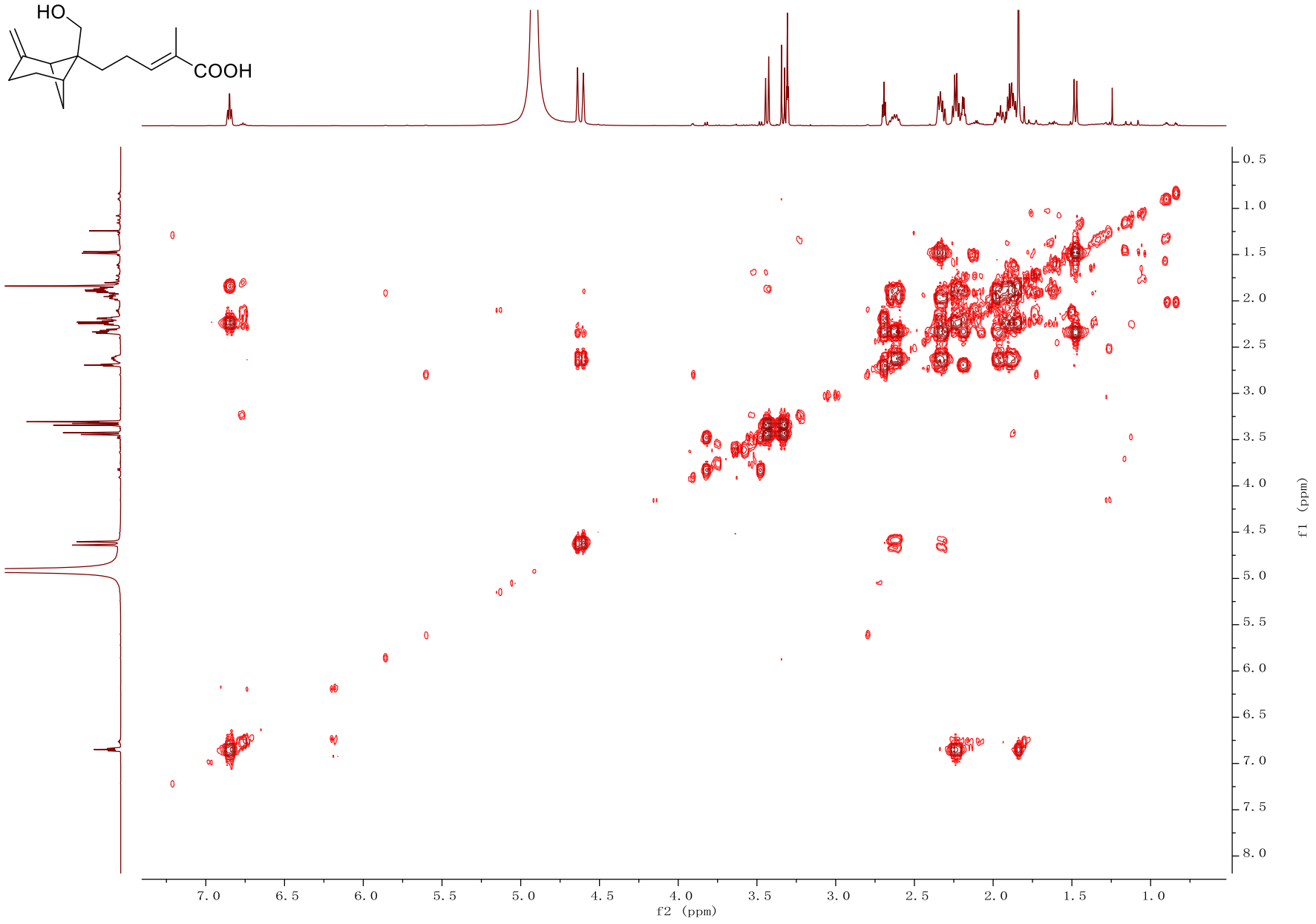


Figure S134. ROESY of compound **16** in CD_3OD

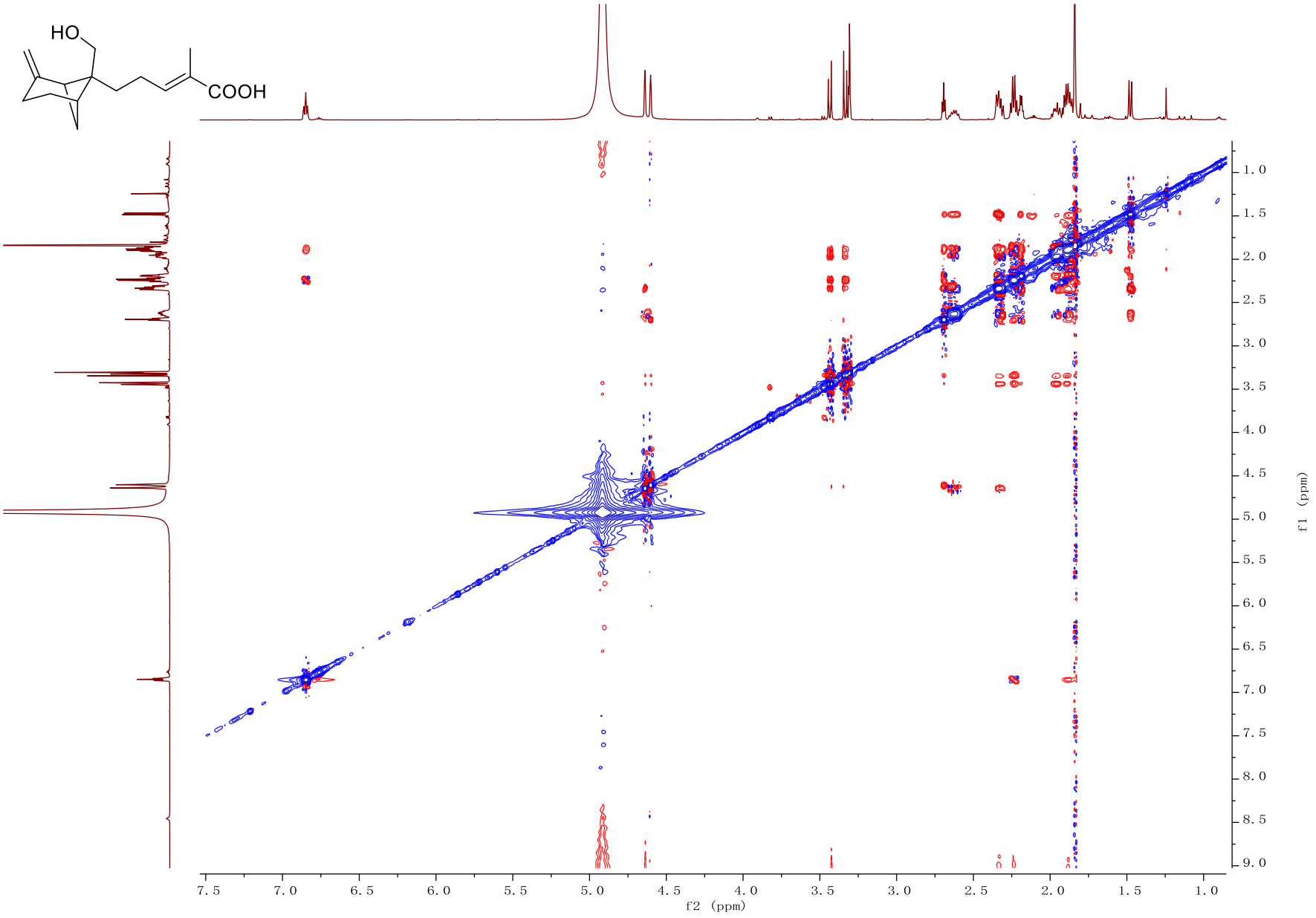
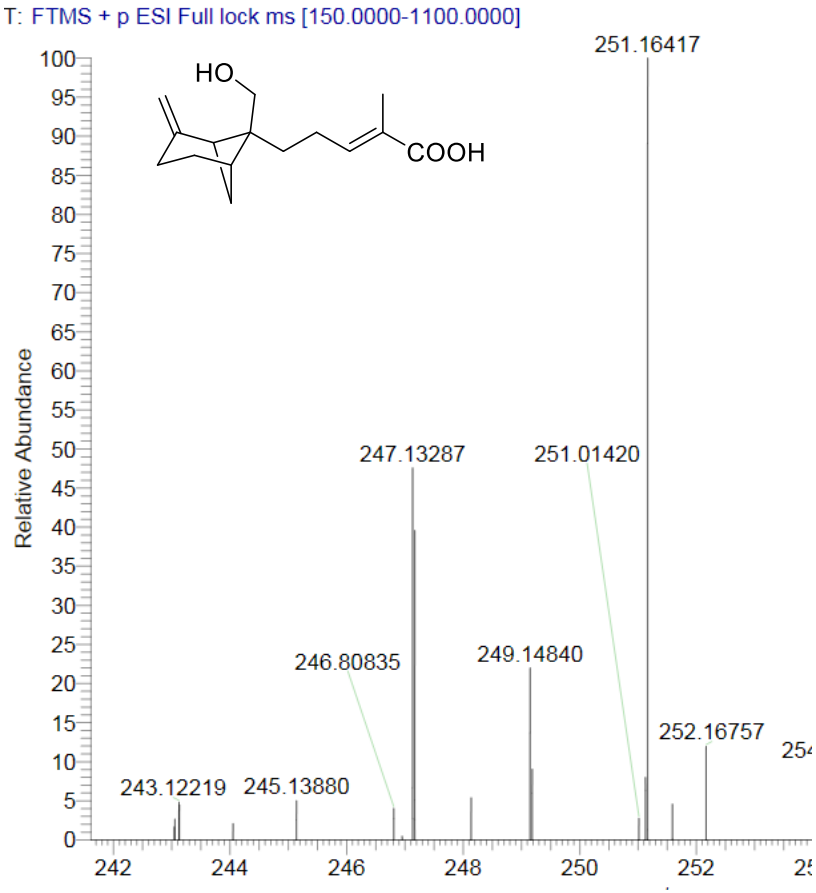


Figure S135. HR-ESIMS of compound **16**



Section S24. NMR and MS spectra for 17

Figure S136. ^{1}H NMR of compound **17** in CD_3OD

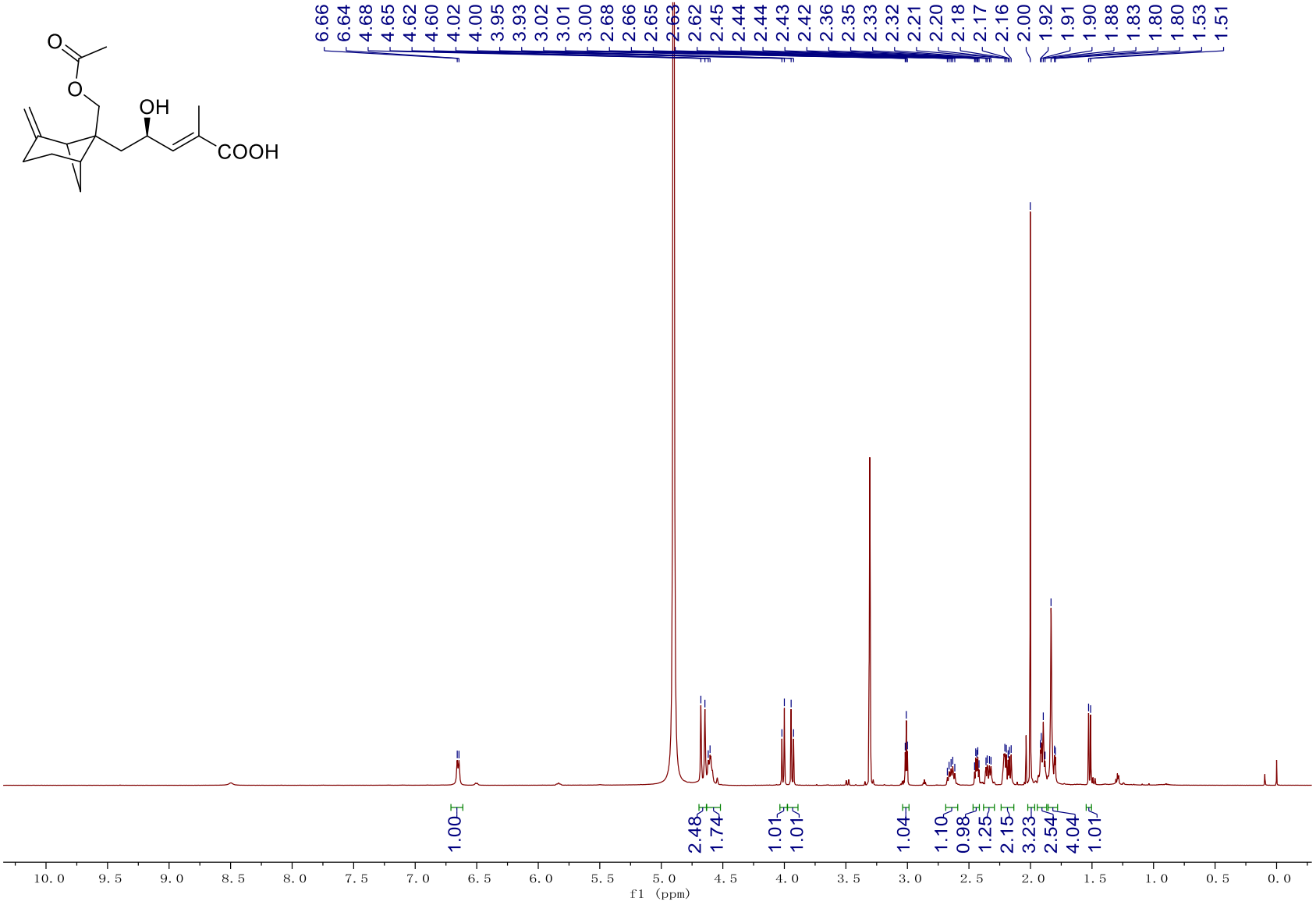


Figure S137. ^{13}C NMR and DEPT of compound **17** in CD_3OD

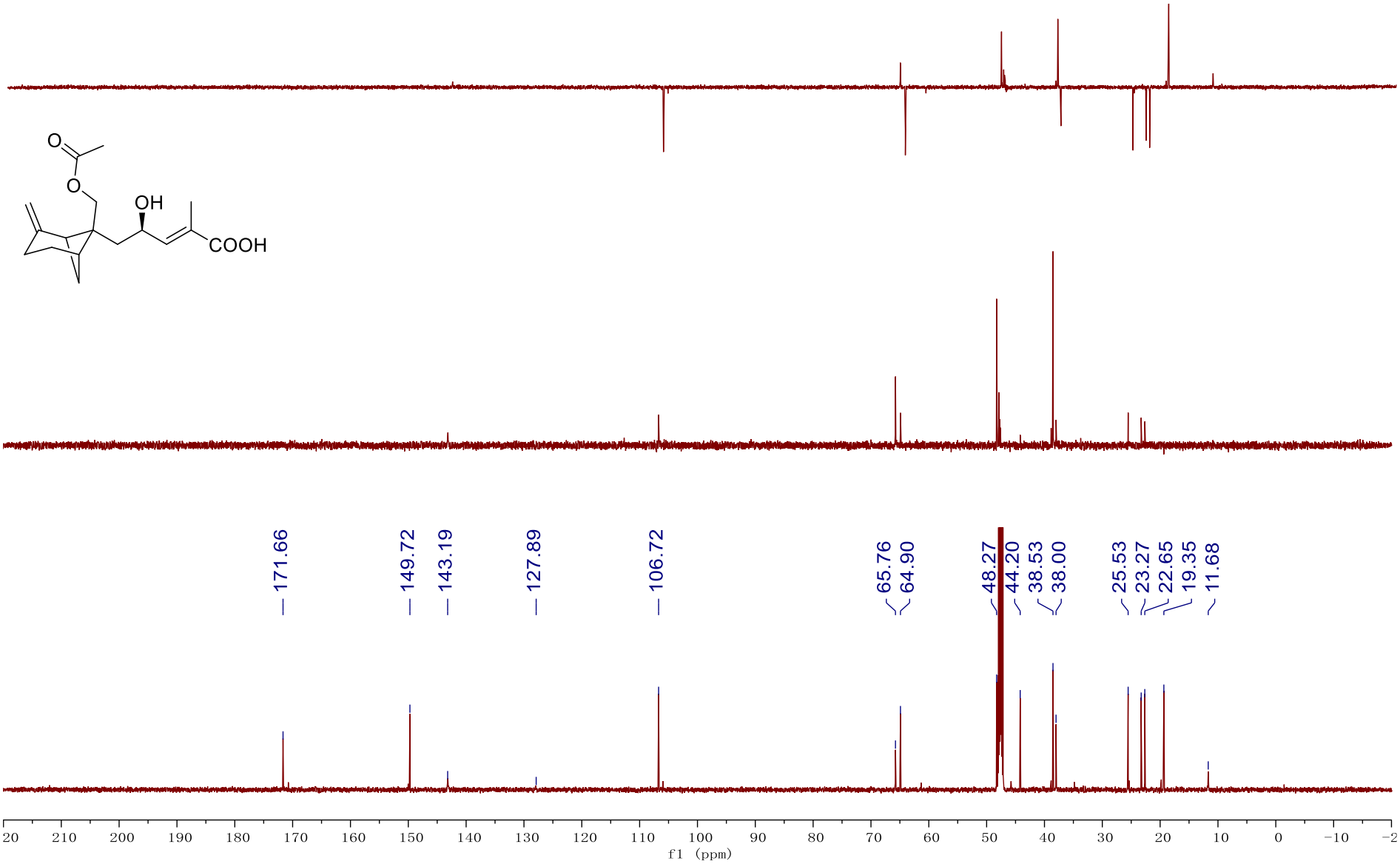


Figure S138. HSQC of compound **17** in CD_3OD

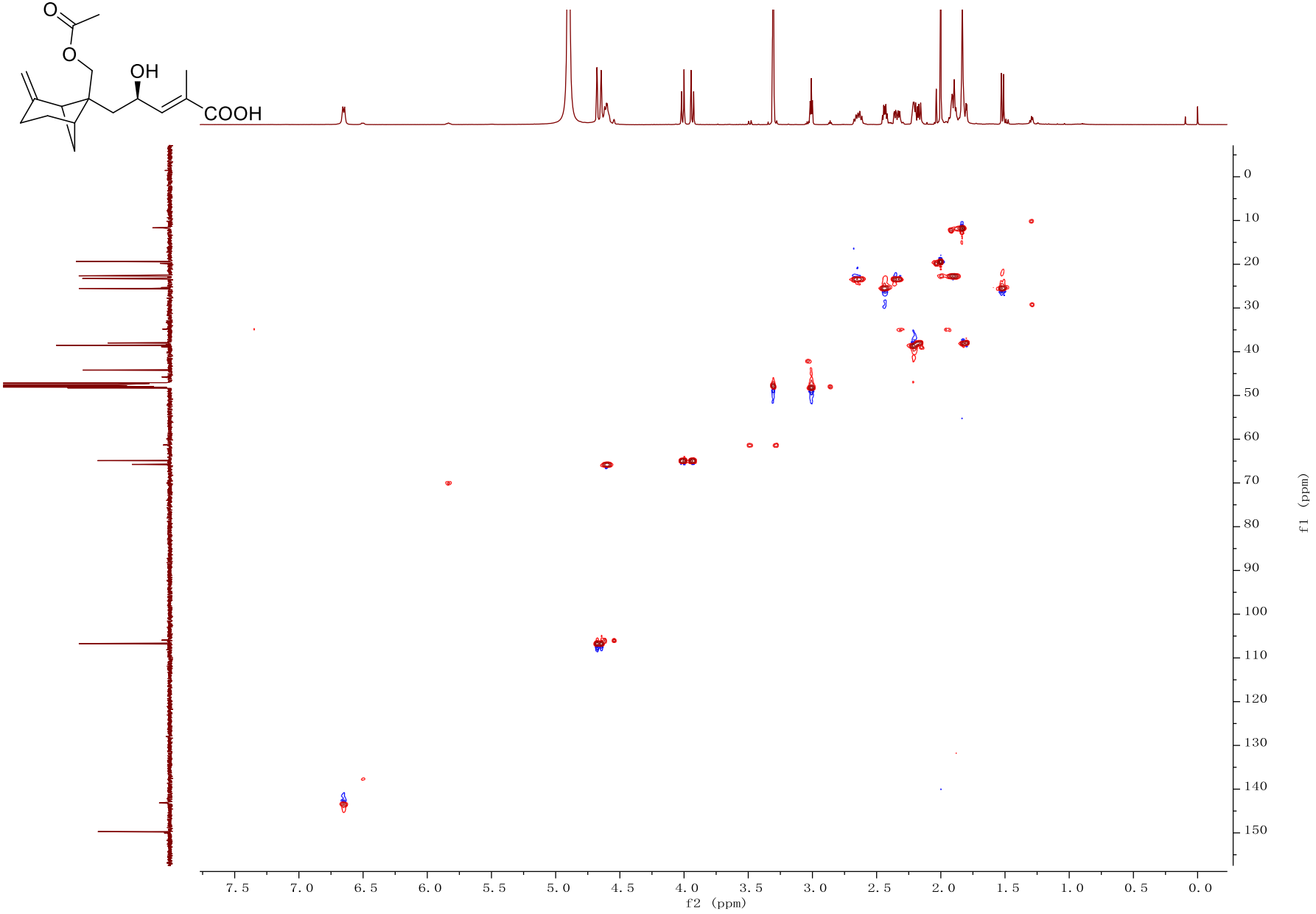


Figure S139. HMBC of compound **17** in CD_3OD

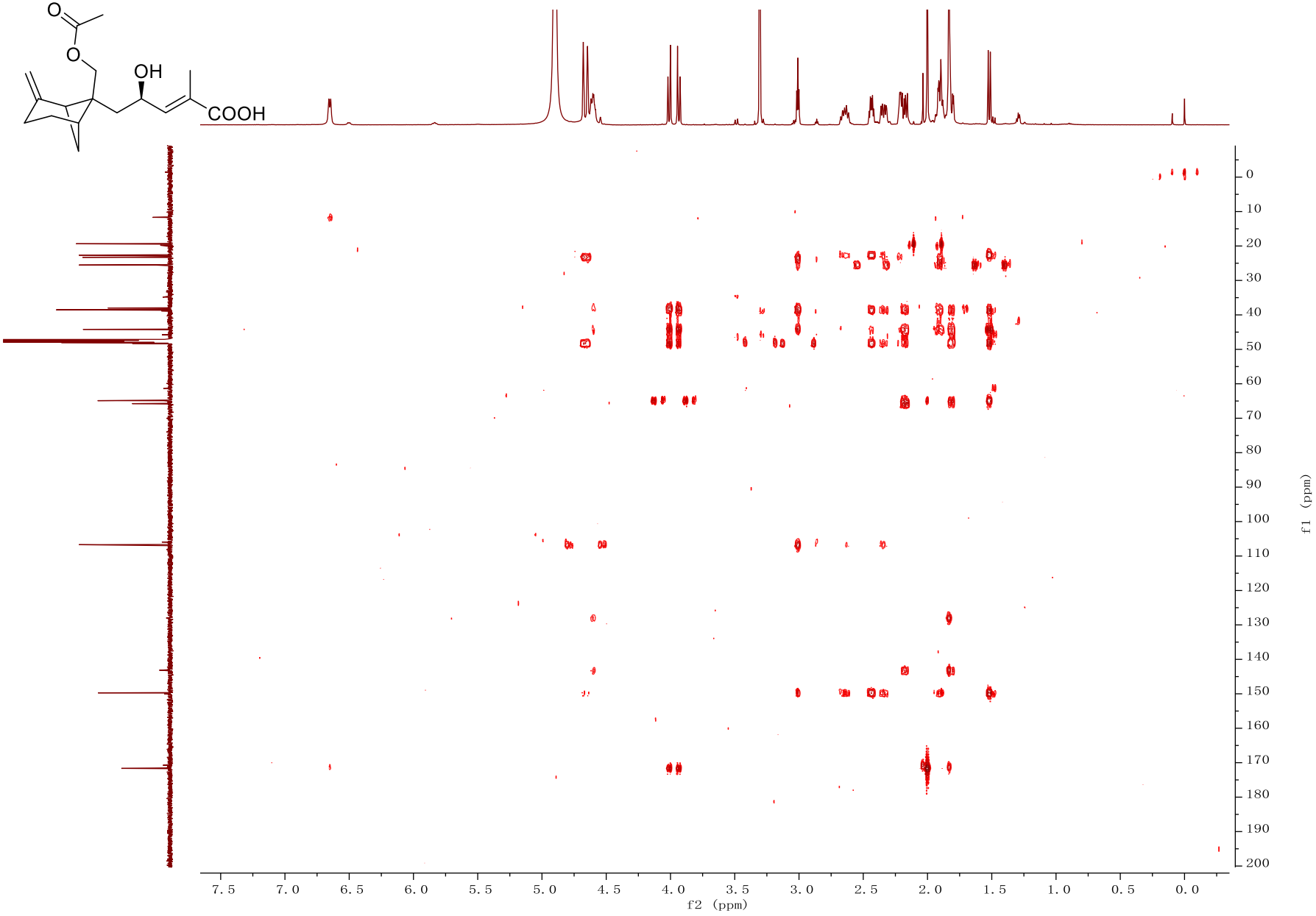


Figure S140. ^{1}H-^{1}H COSY of compound **17** in CD_3OD

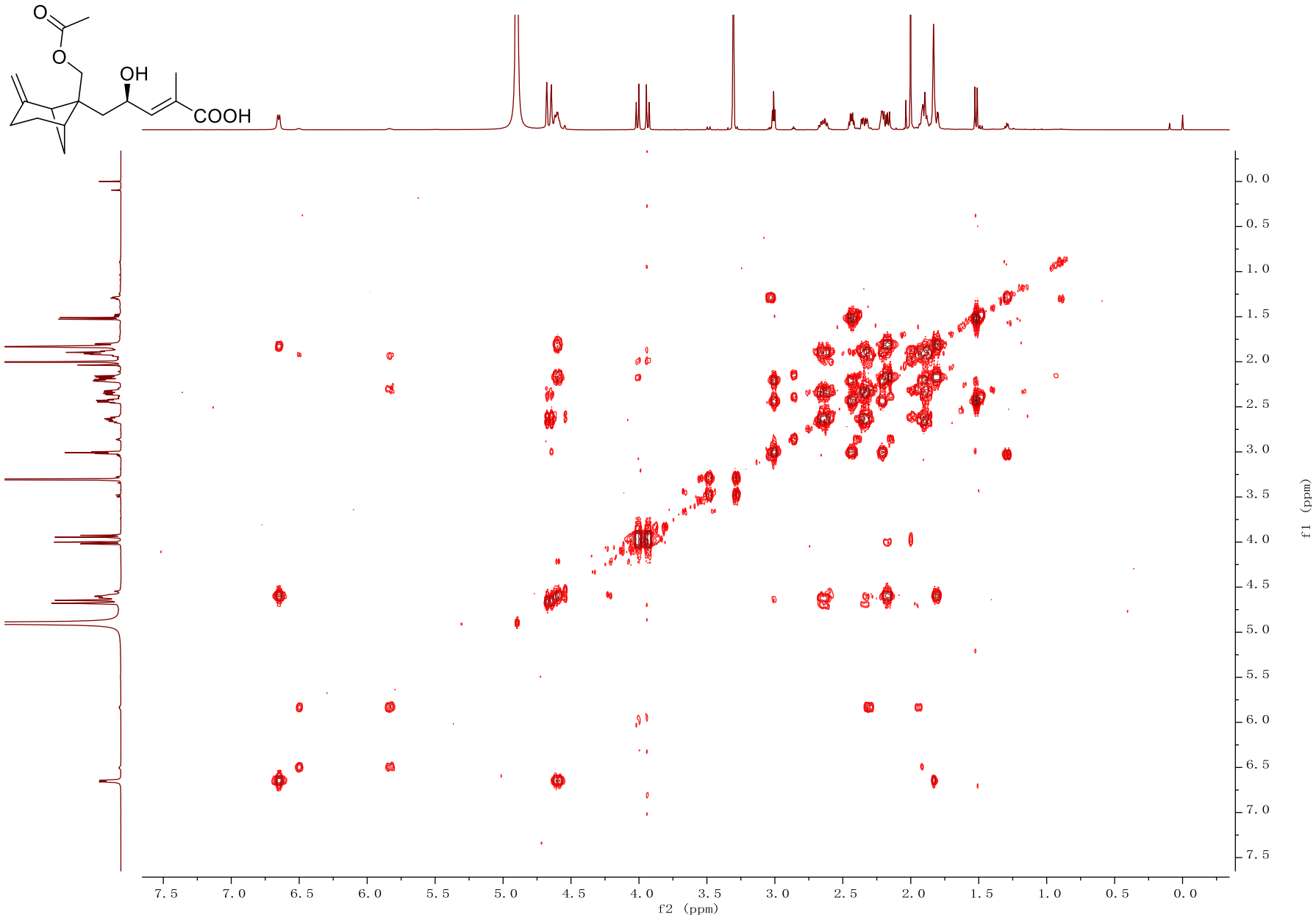


Figure S141. ROESY of compound **17** in CD_3OD

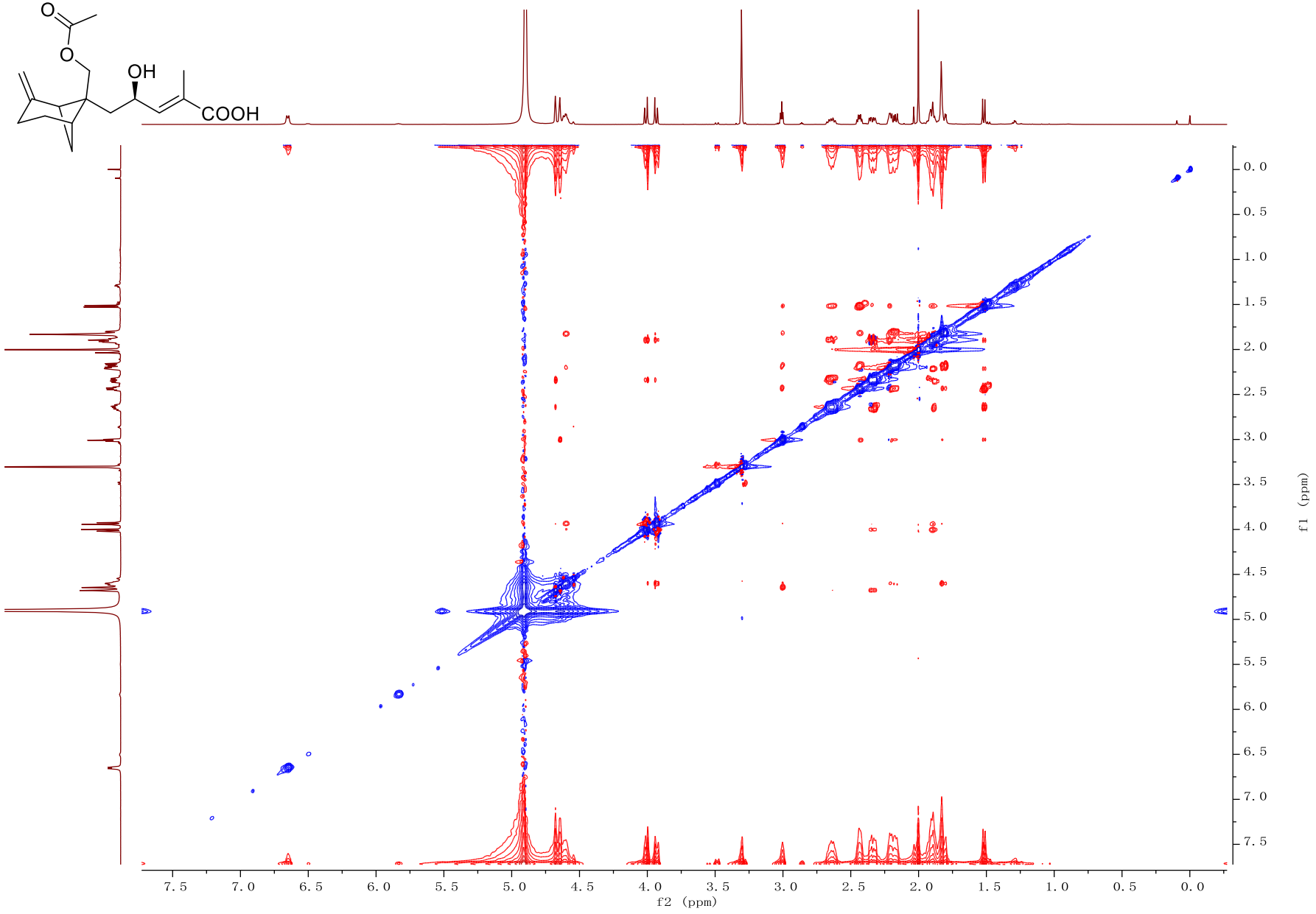
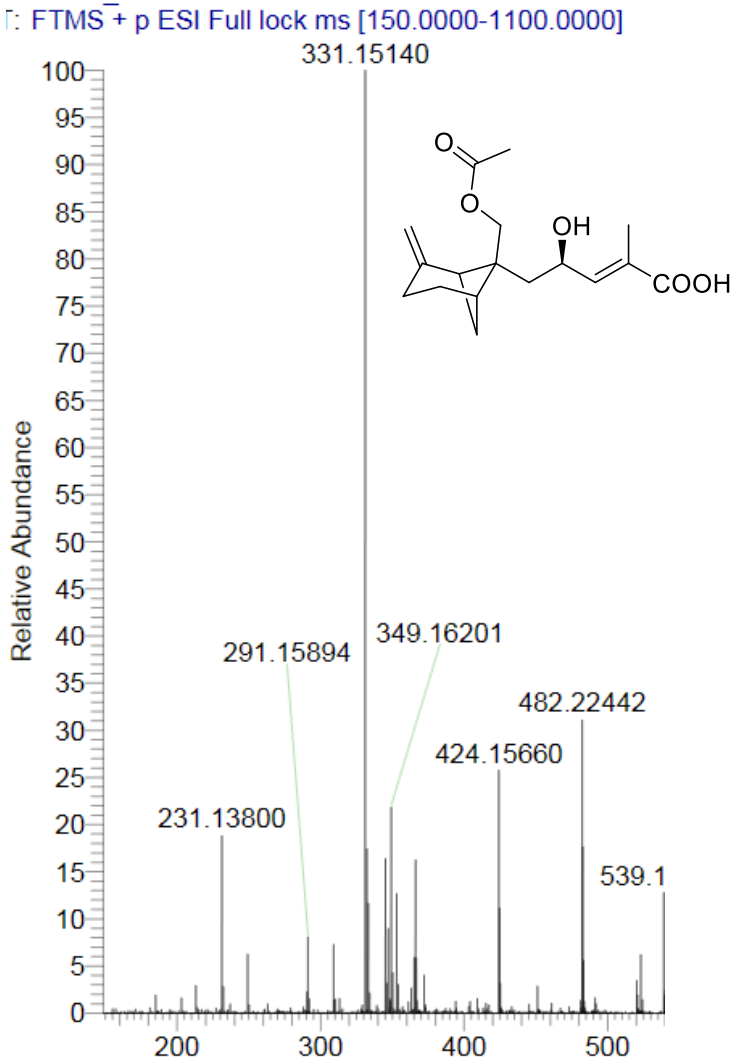


Figure S142. HR-ESIMS of compound **17**



Section S25. NMR and MS spectra for 18

Figure S143. ^{1}H NMR of compound **18** in CD_3OD

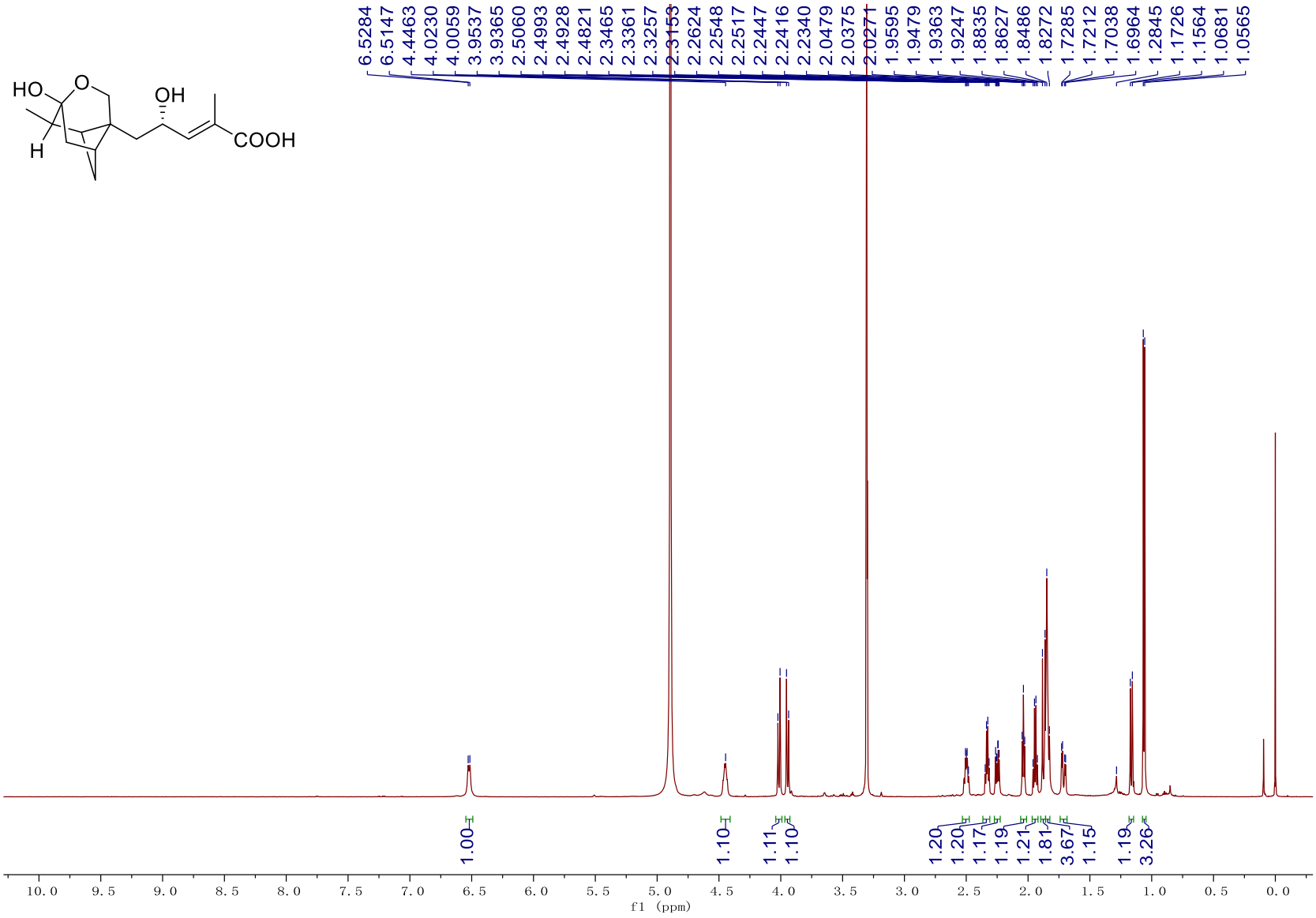


Figure S144. ^{13}C NMR and DEPT of compound **18** in CD_3OD

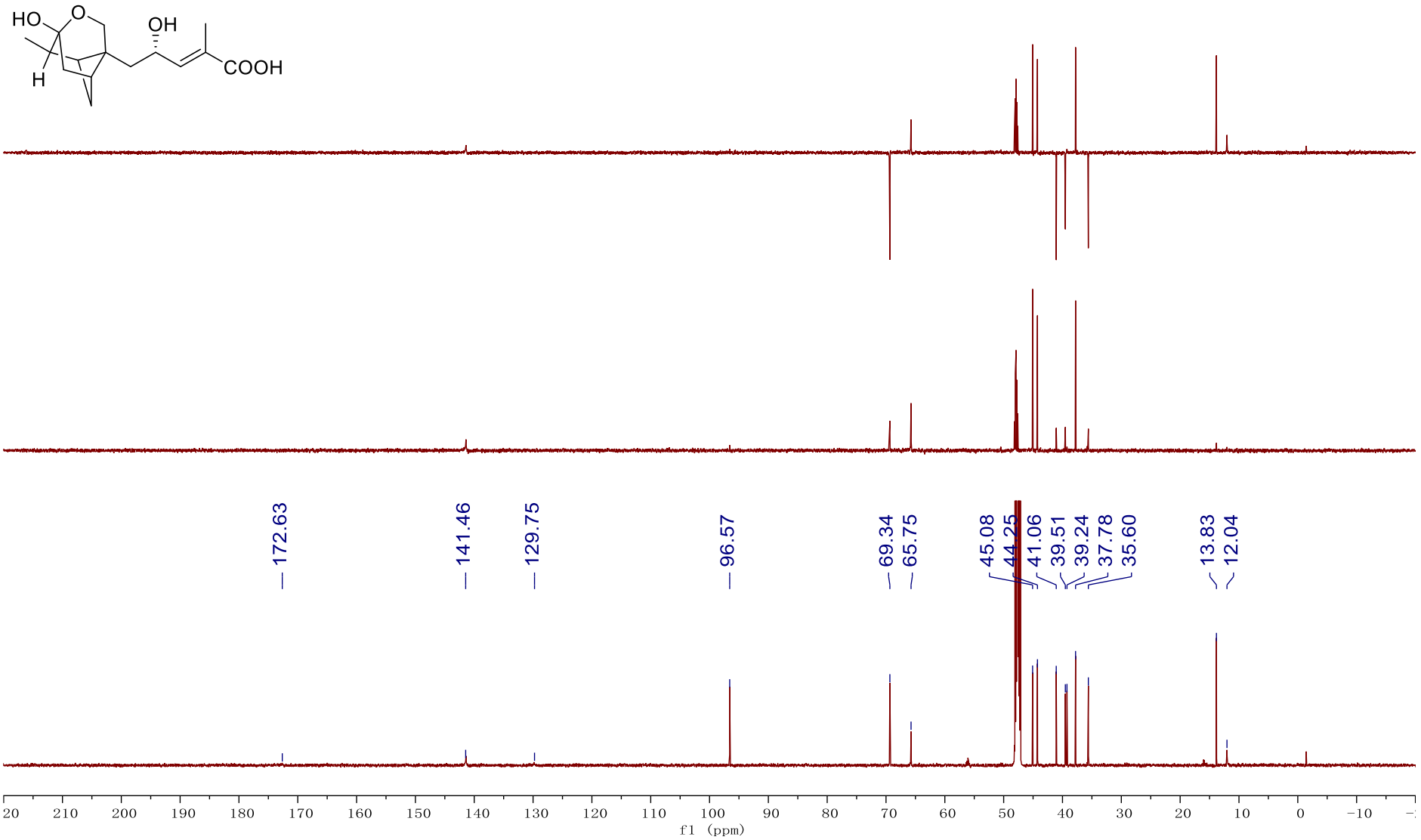


Figure S145. HSQC of compound **18** in CD_3OD

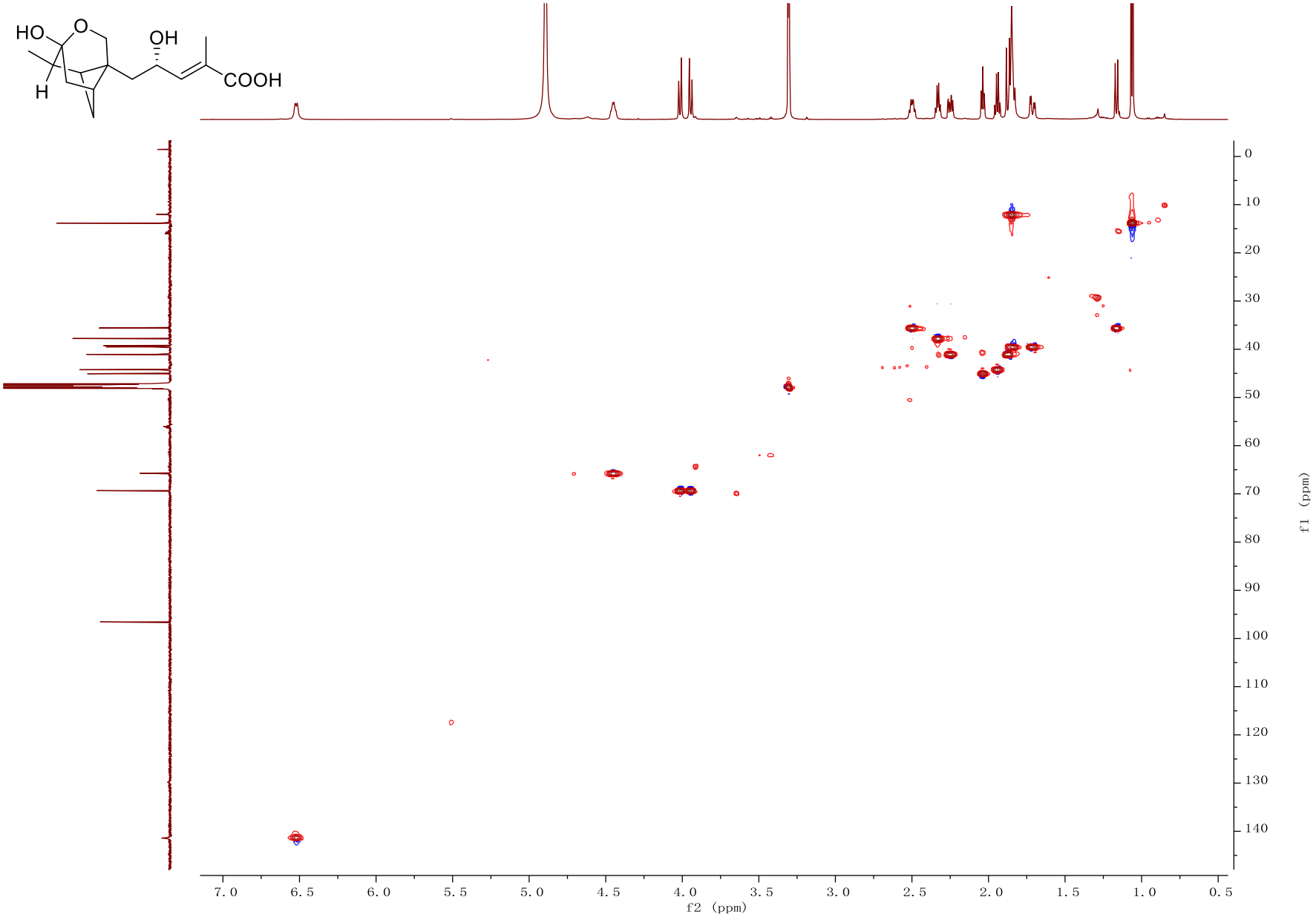


Figure S146. HMBC of compound **18** in CD_3OD

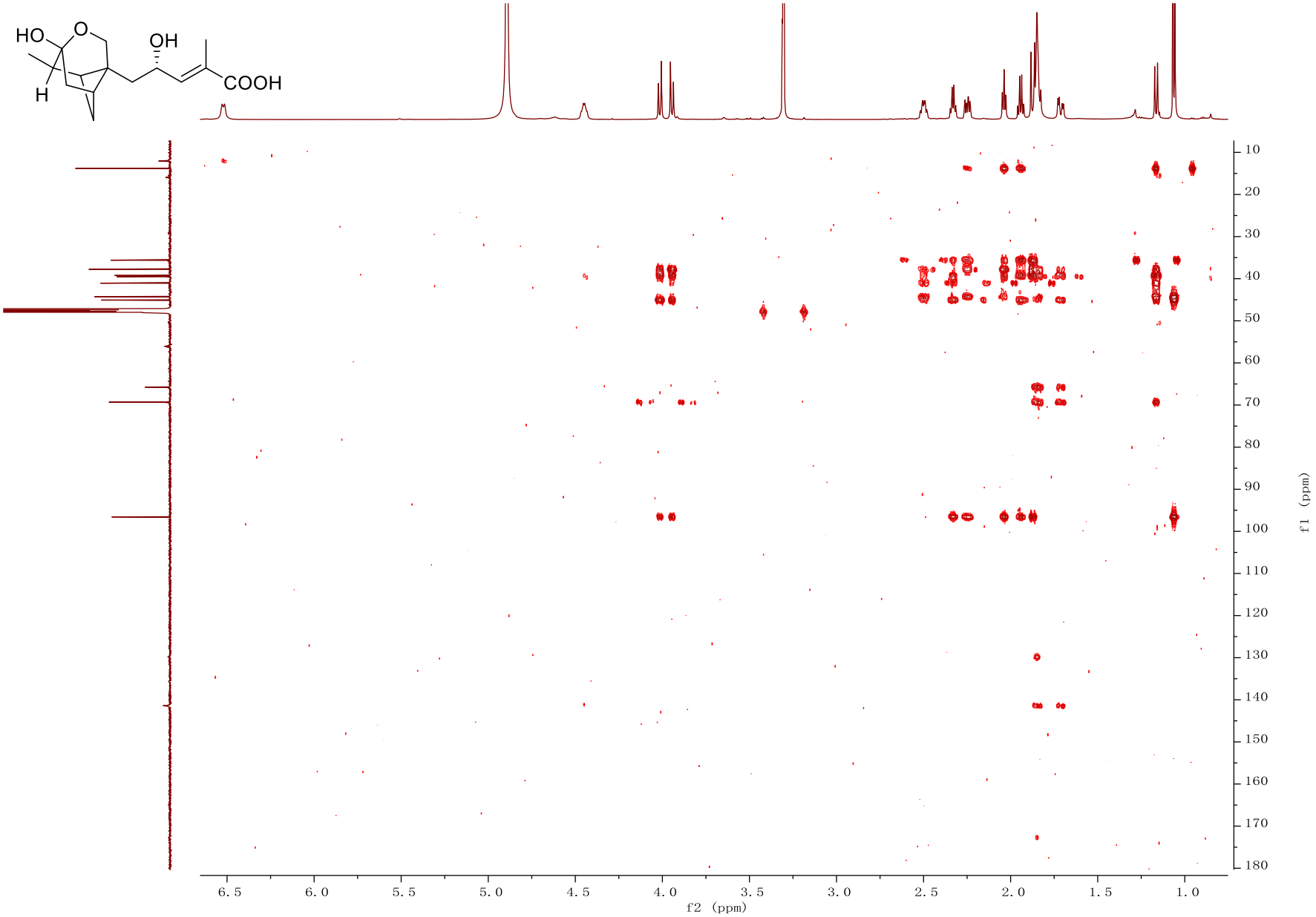


Figure S147. ^{1}H-^{1}H COSY of compound **18** in CD_3OD

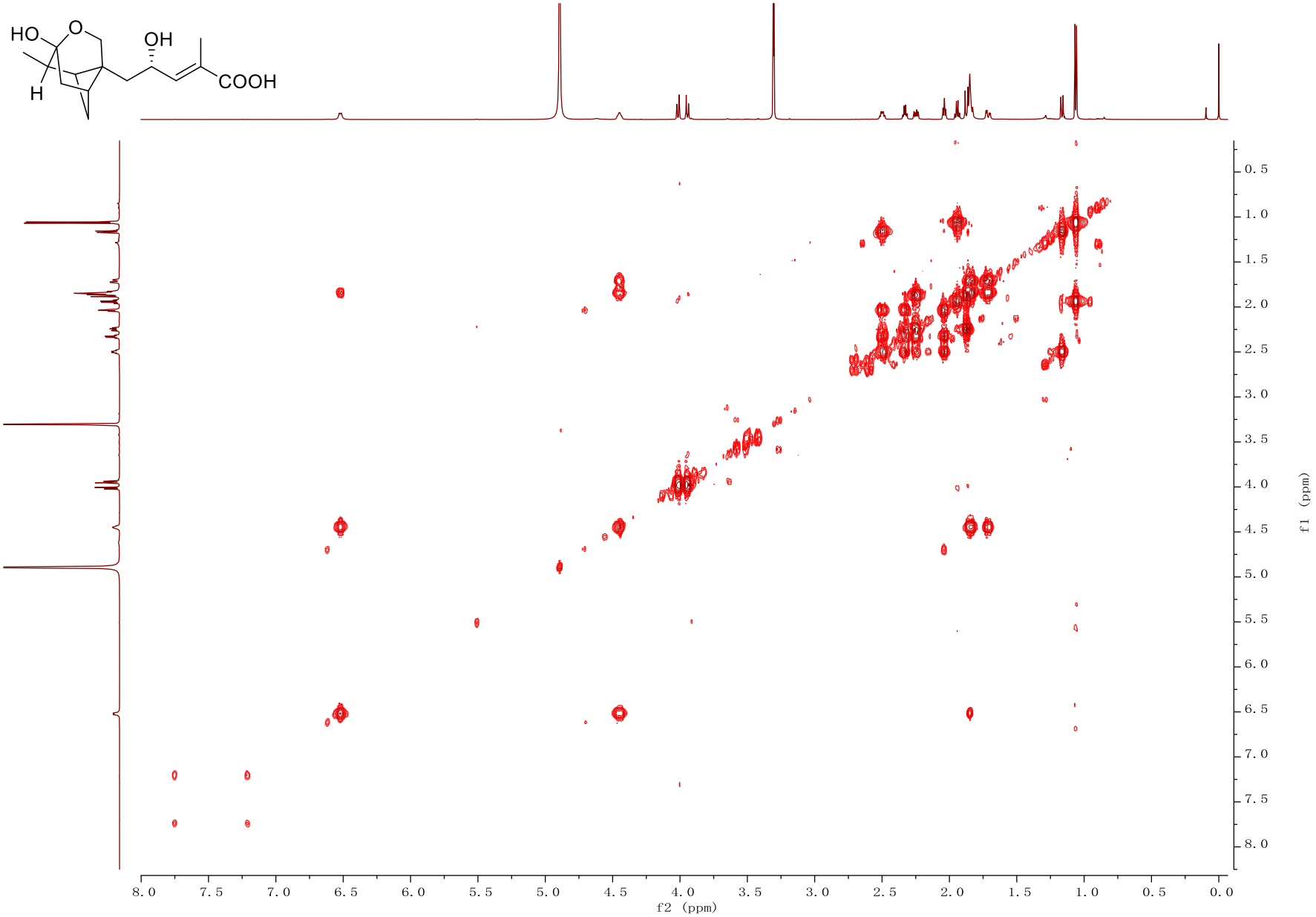


Figure S148. ROESY of compound **18** in CD_3OD

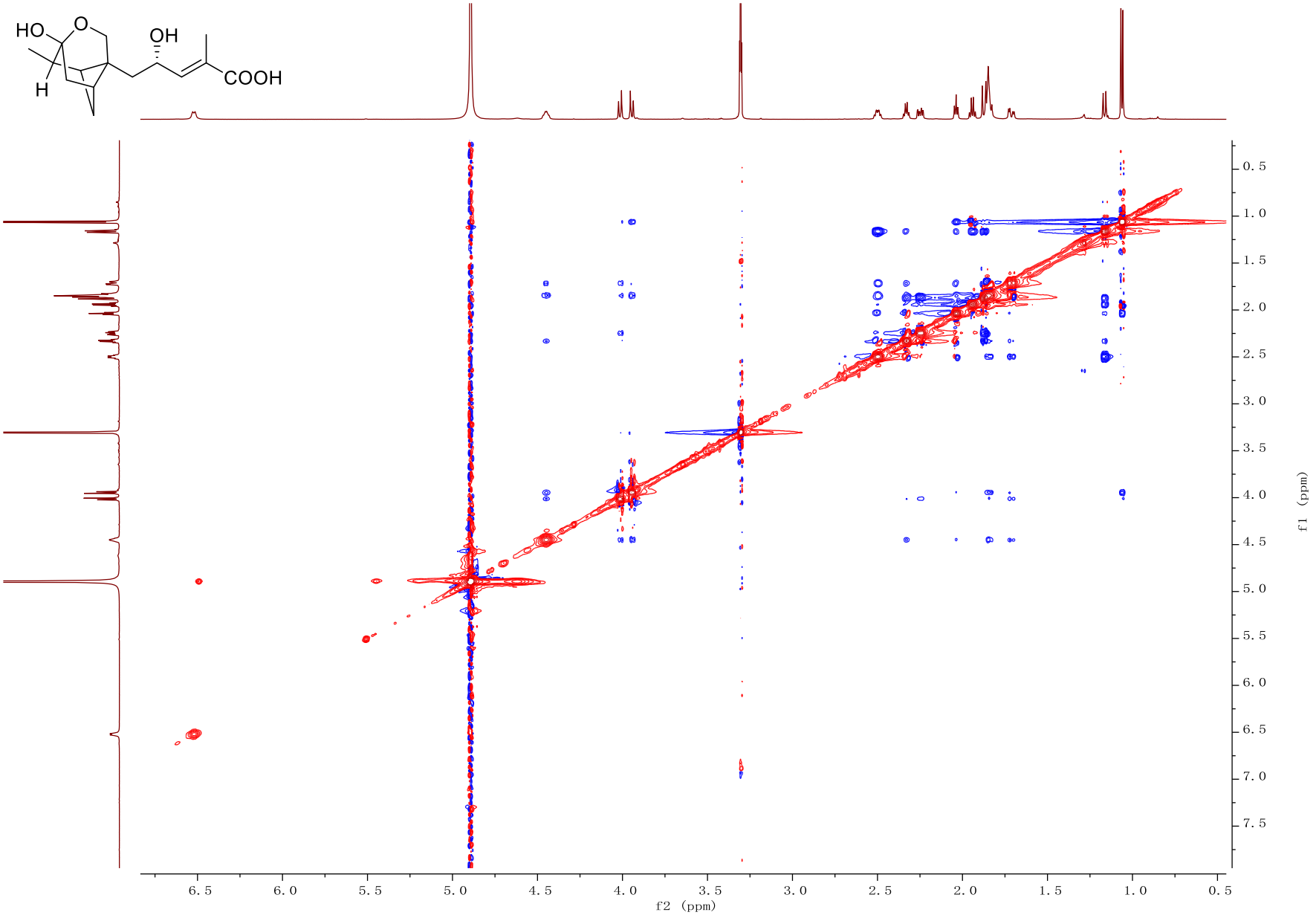
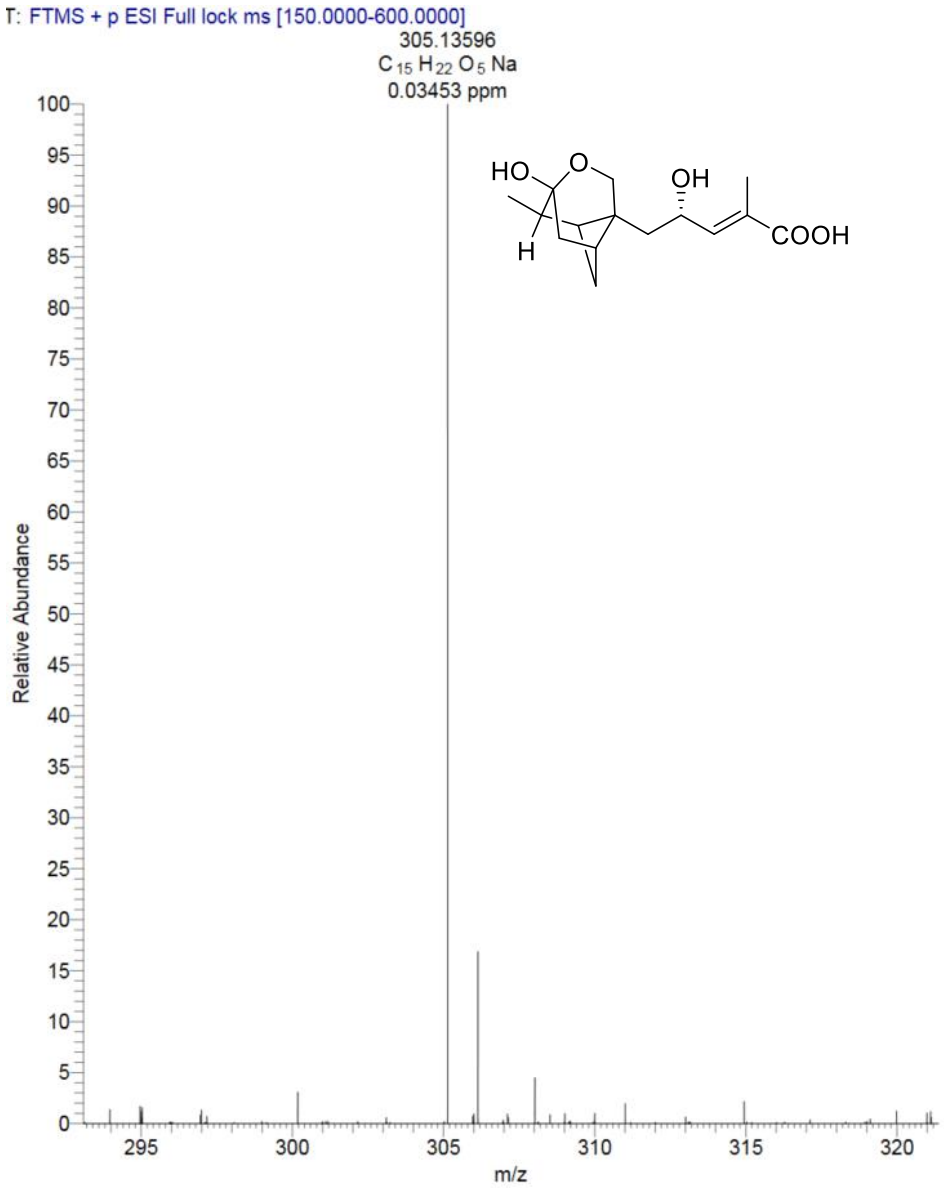


Figure S149. HR-ESIMS of compound **18**



Section S26. NMR and MS spectra for 19

Figure S150. ^{1}H NMR of compound **19** in CD_3OD

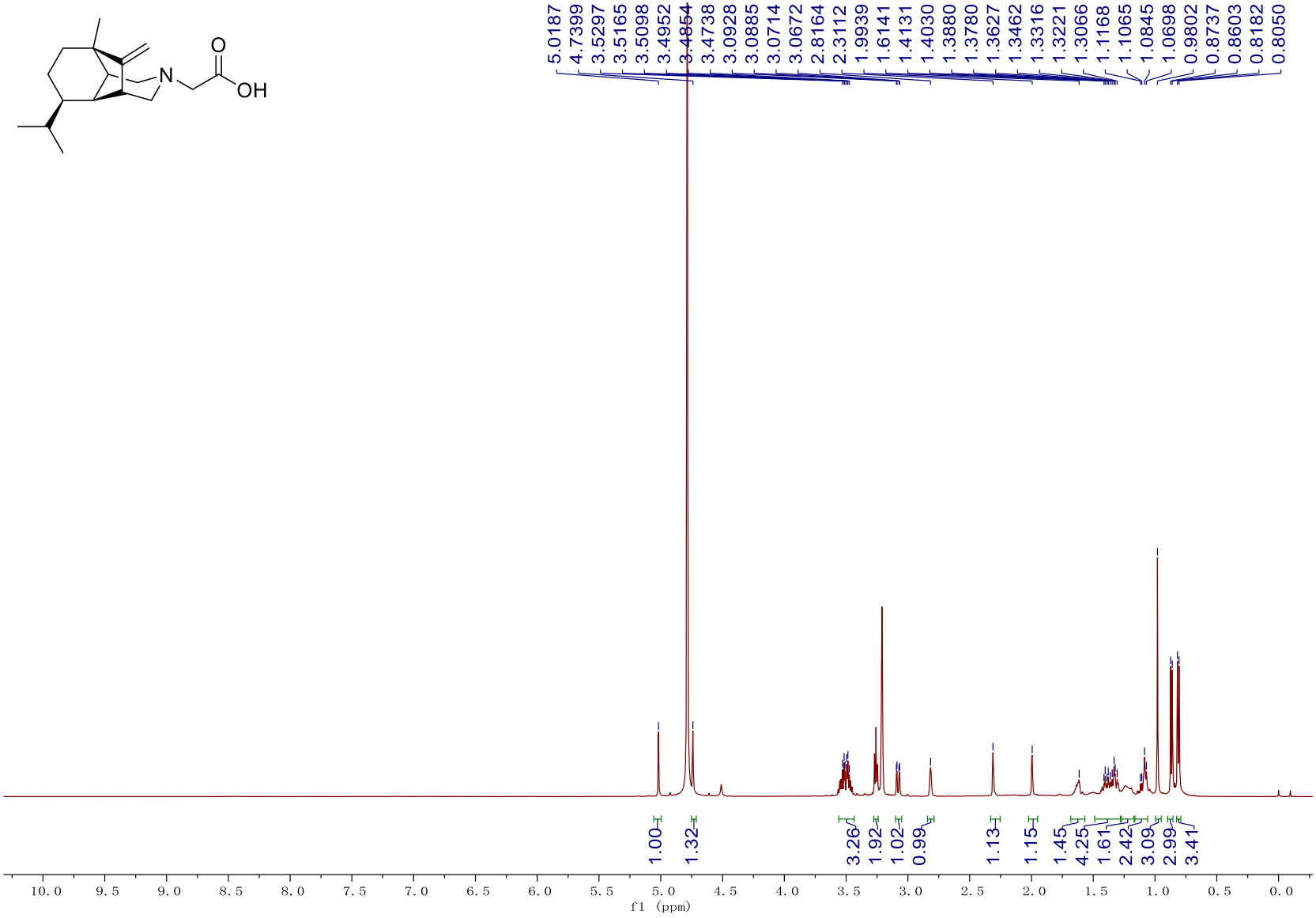


Figure S151. ^{13}C NMR and DEPT of compound **19** in CD_3OD

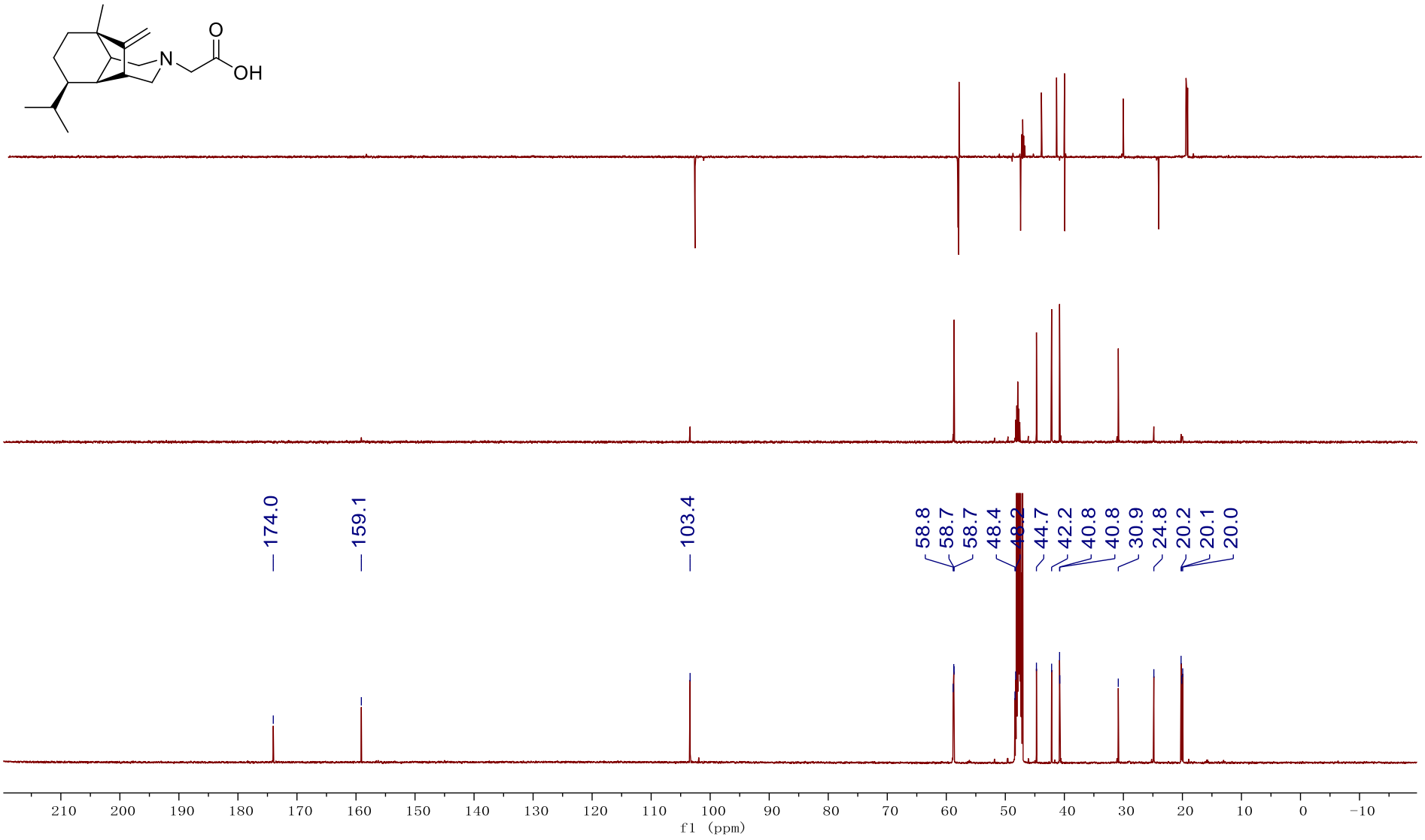


Figure S152. HSQC of compound **19** in CD_3OD

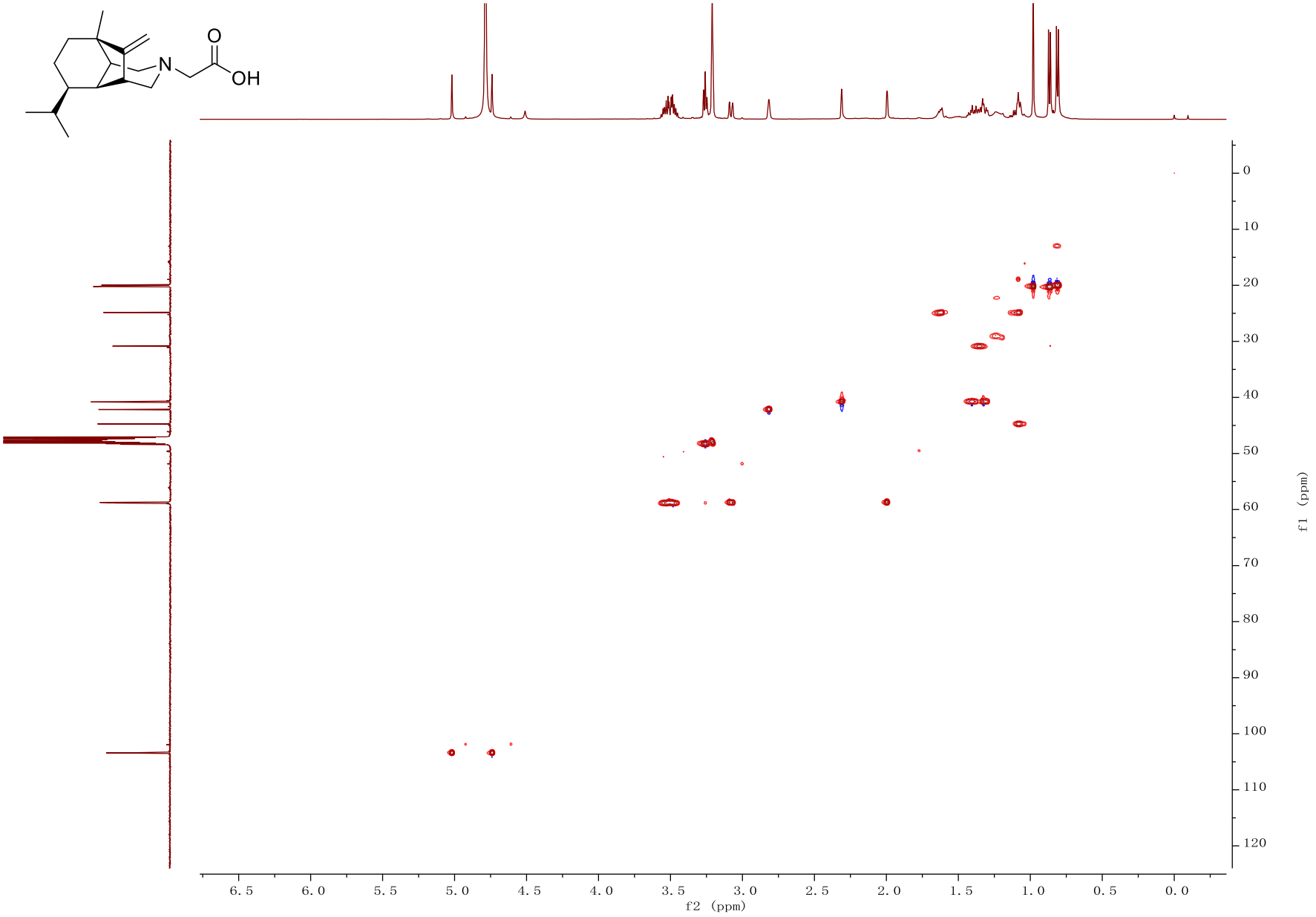


Figure S153. HMBC of compound **19** in CD_3OD

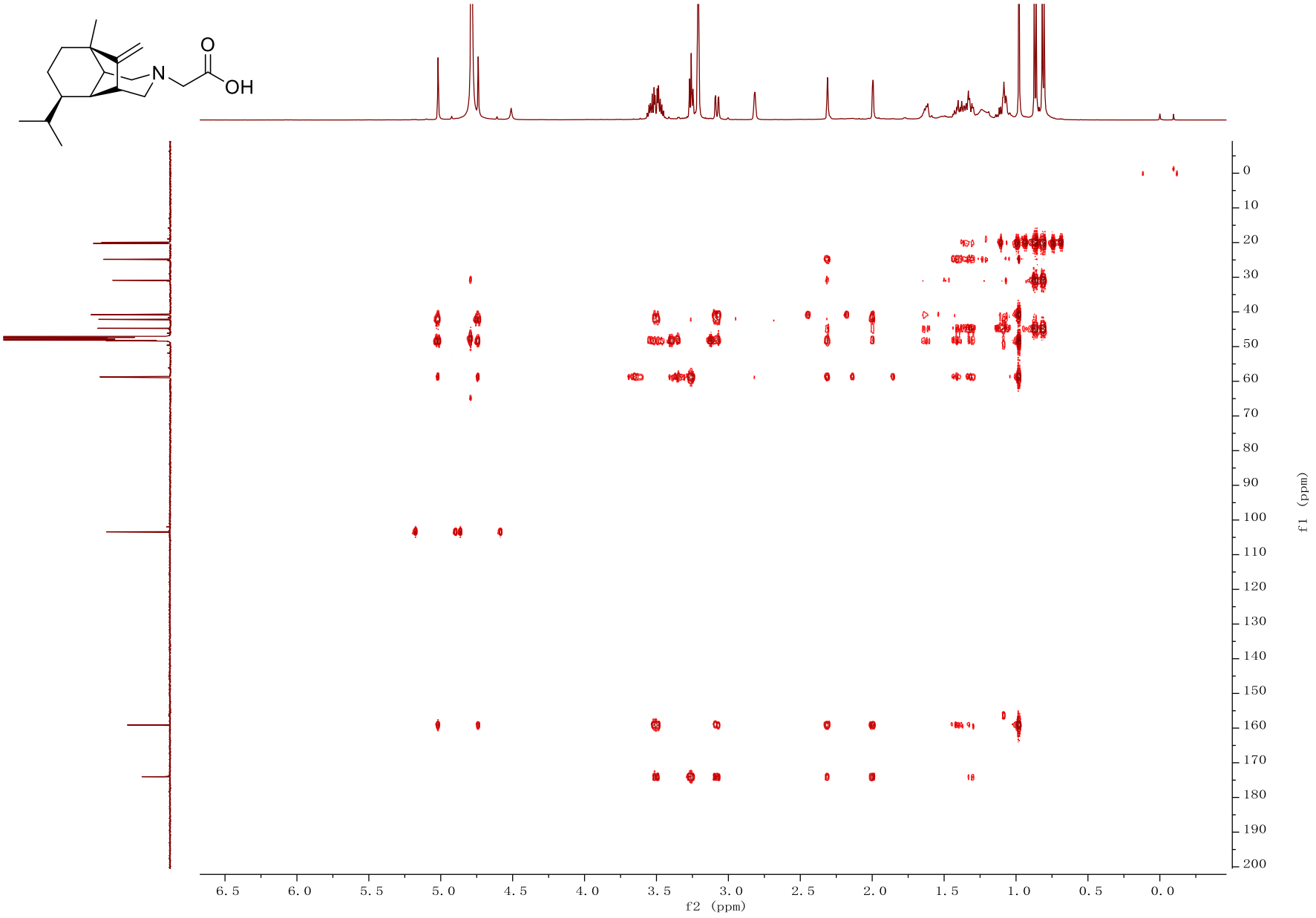


Figure S154. ^{1}H-^{1}H COSY of compound **19** in CD_3OD

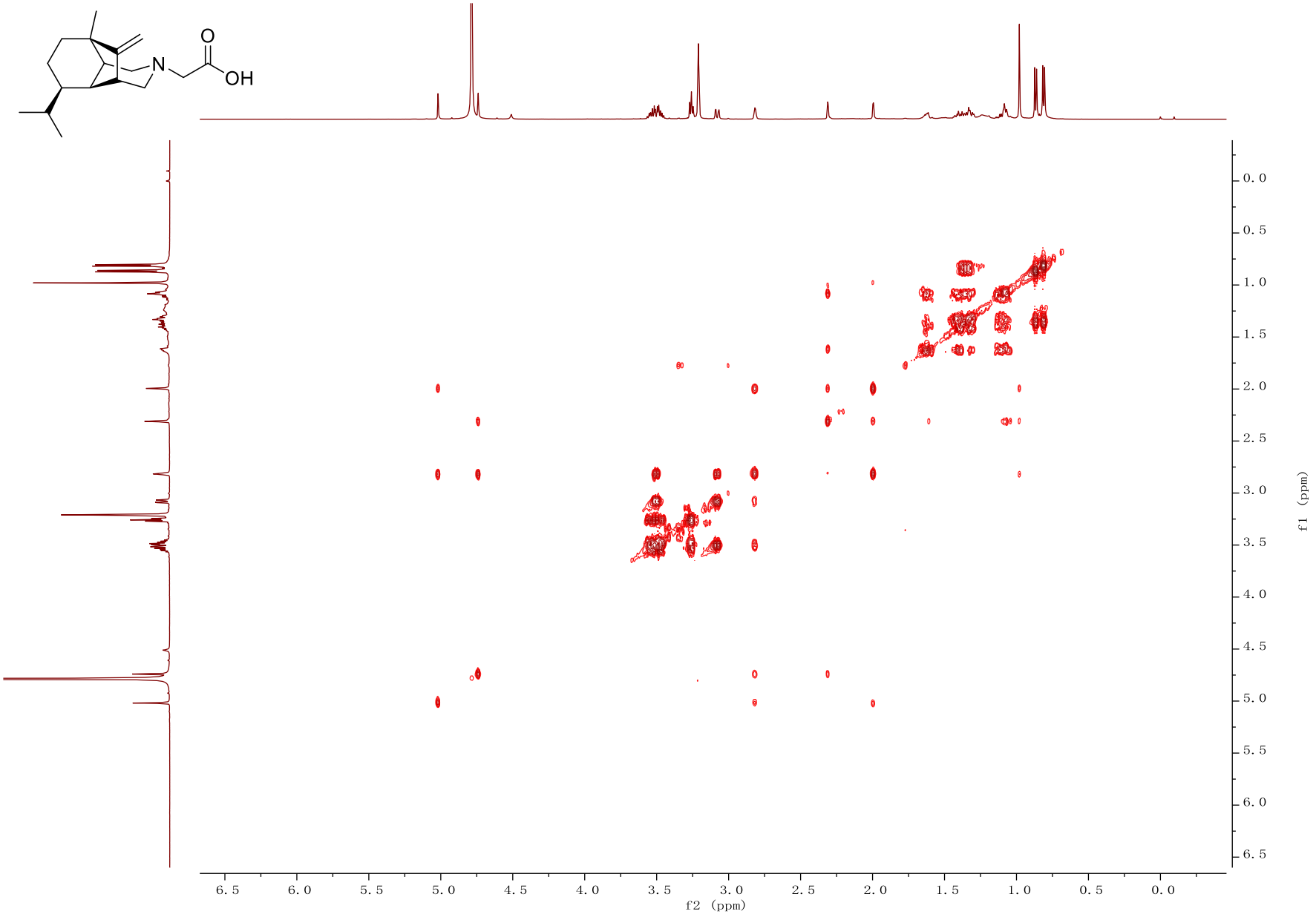


Figure S155. ROESY of compound **19** in CD_3OD

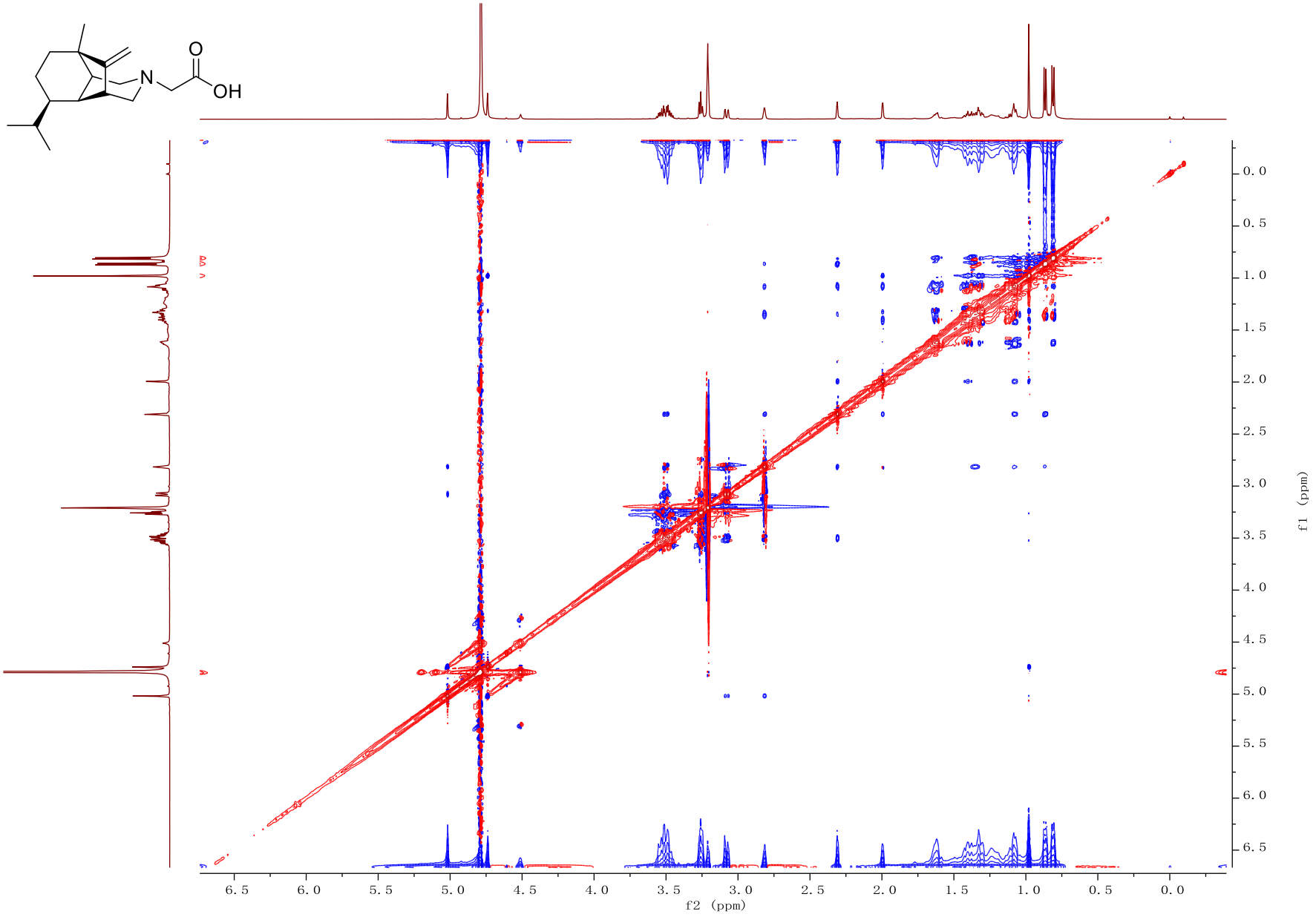


Figure S156. HR-ESIMS of compound **19**