

Supplementary Information

Structural diversity of terpenoids in the Soft Coral *Sinularia flexibilis*, evidence by a collection from the South China Sea

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Figure S36. HRESIMS spectrum of sinulaflexiolide L (**8**)

Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3) of 9 α -hydroxy-flexibilide (**1**).

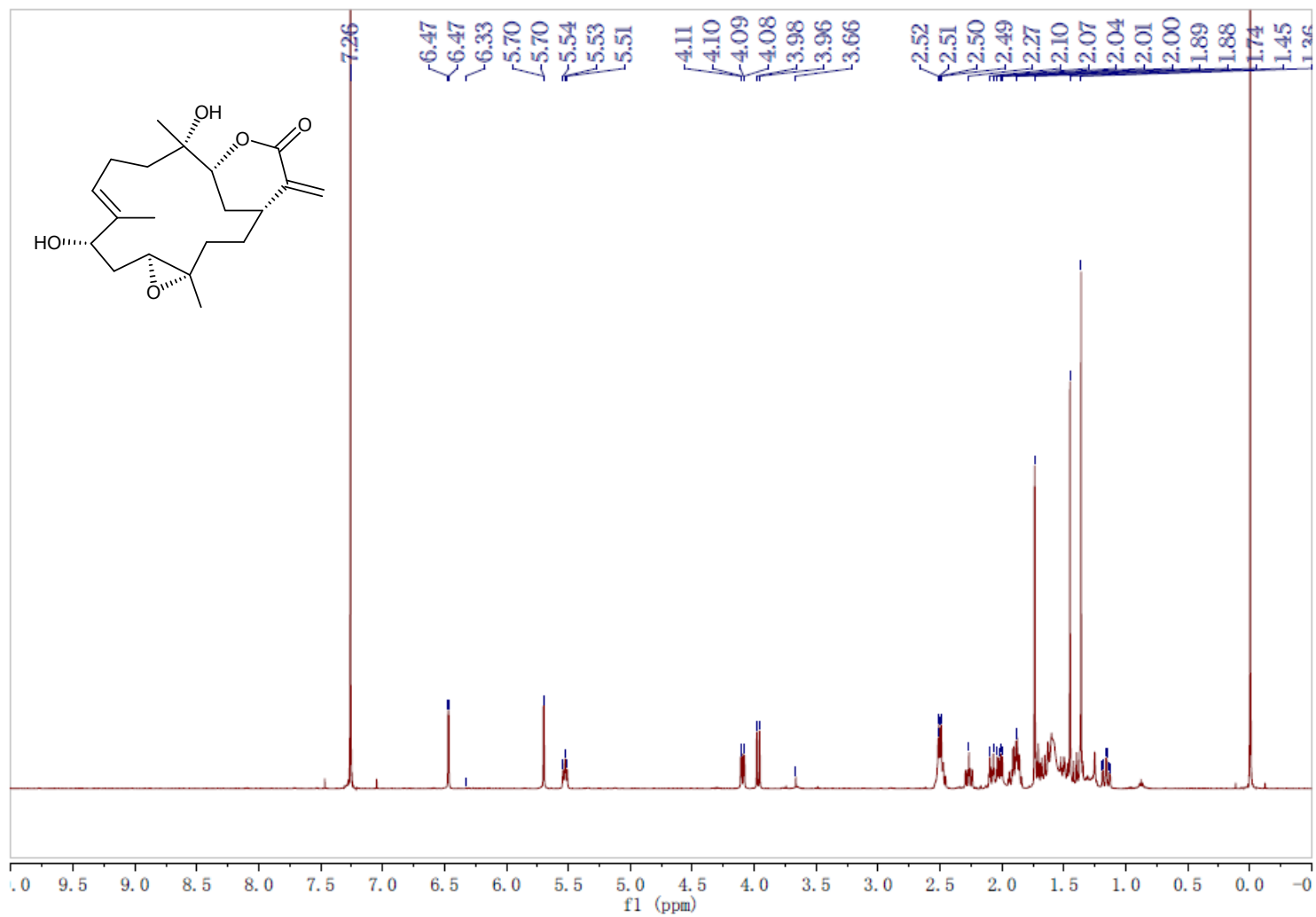


Figure S2. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 9 α -hydroxy-flexibilide (**1**).

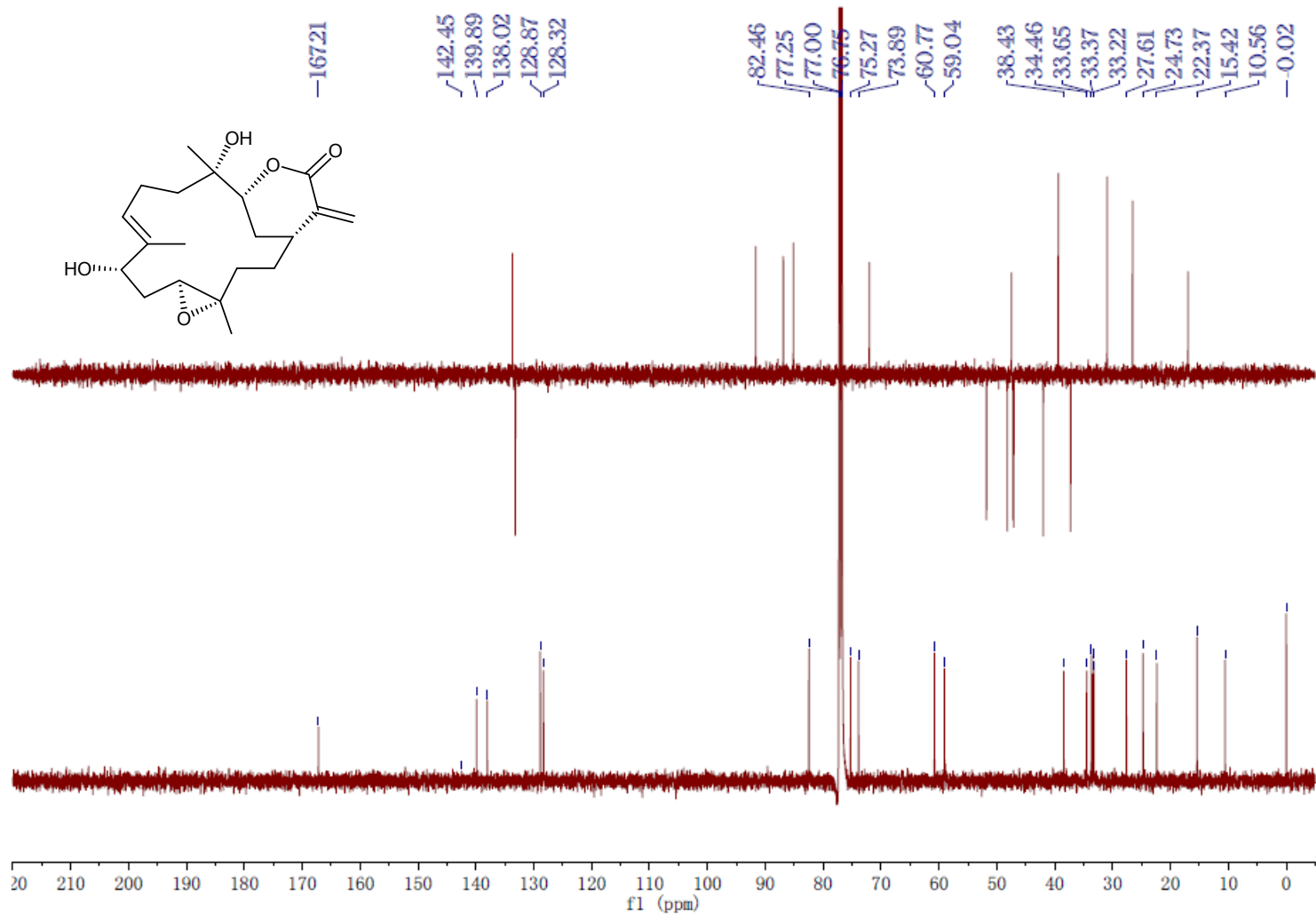


Figure S3. HMQC spectrum (400 MHz, CDCl₃) of 9 α -hydroxy-flexibilide (**1**).

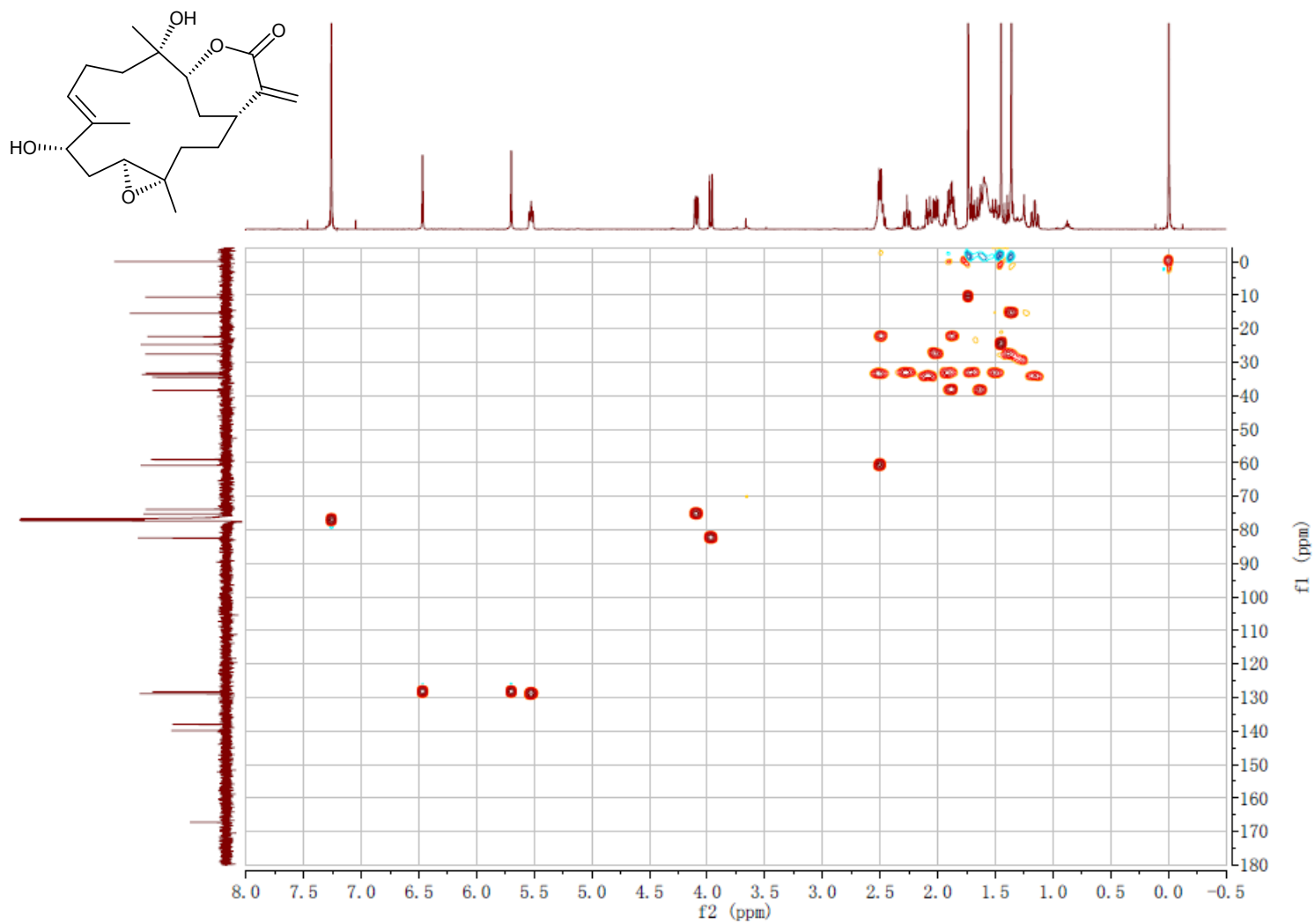


Figure S4. HMBC spectrum (400 MHz, CDCl₃) of 9 α -hydroxy-flexibilide (**1**).

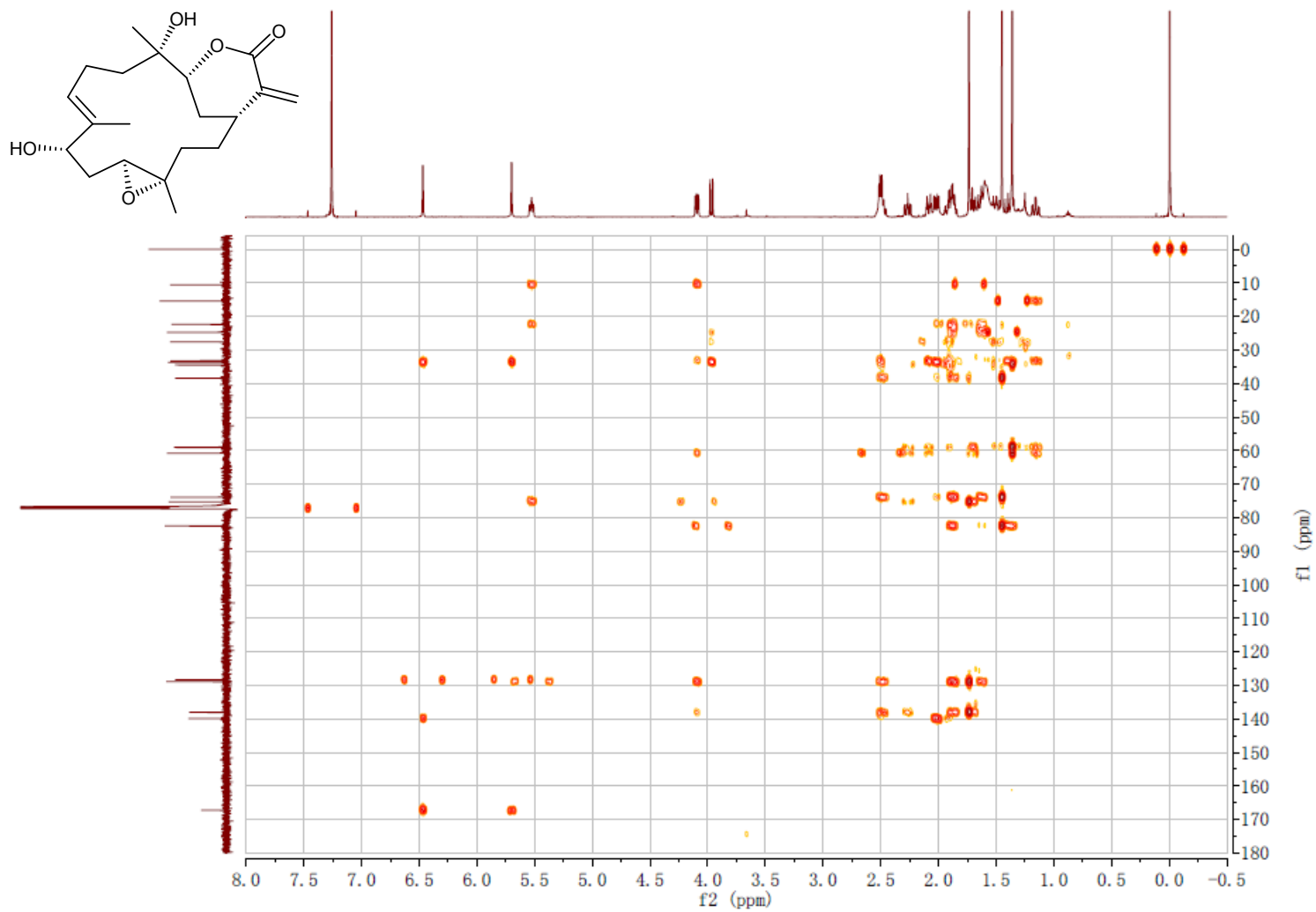


Figure S5. ^1H - ^1H COSY spectrum (400 MHz, CDCl_3) of 9α -hydroxy-flexibilide (**1**).

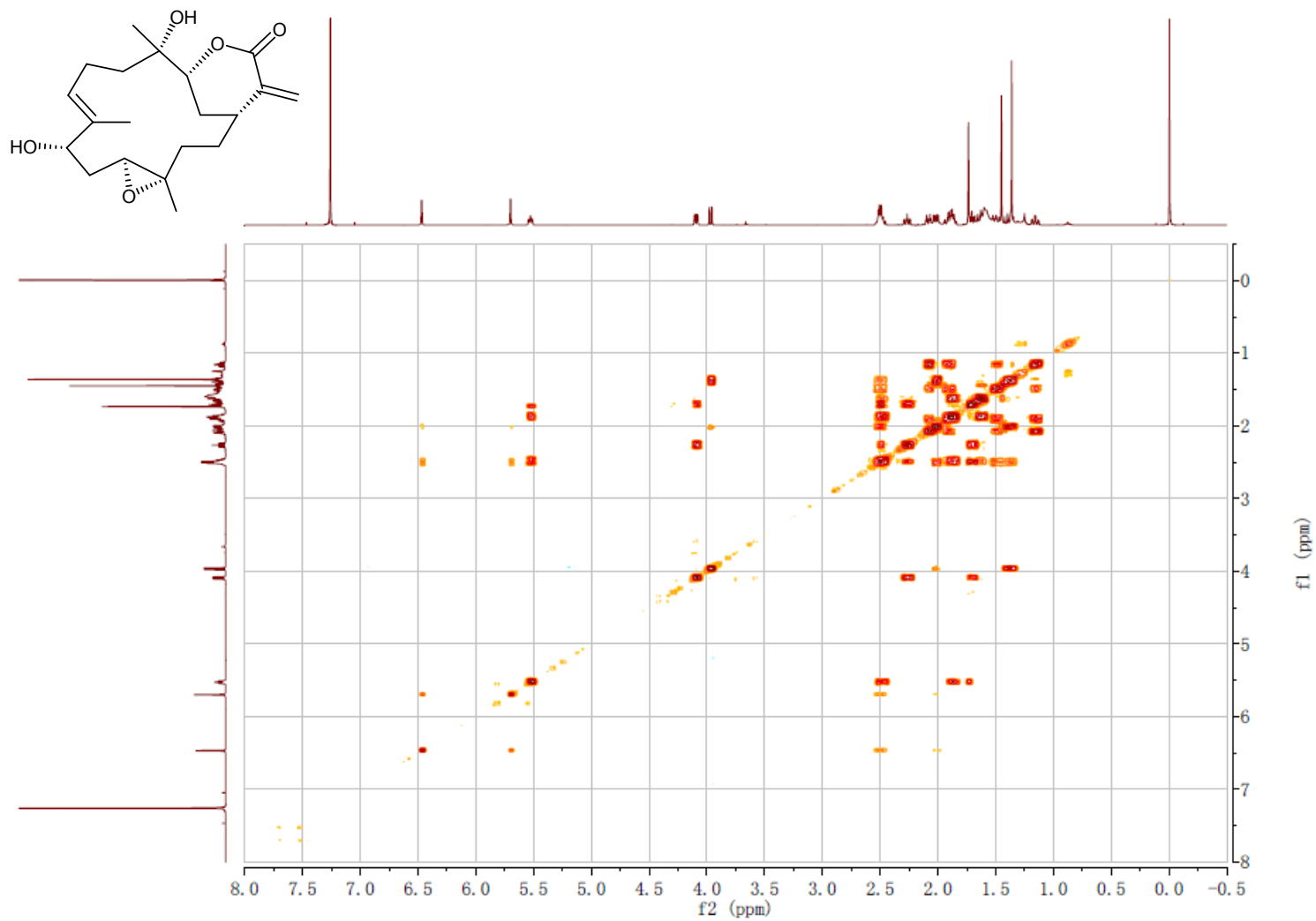


Figure S6. ROESY spectrum (400 MHz, CDCl₃) of 9 α -hydroxy-flexibilide (**1**).

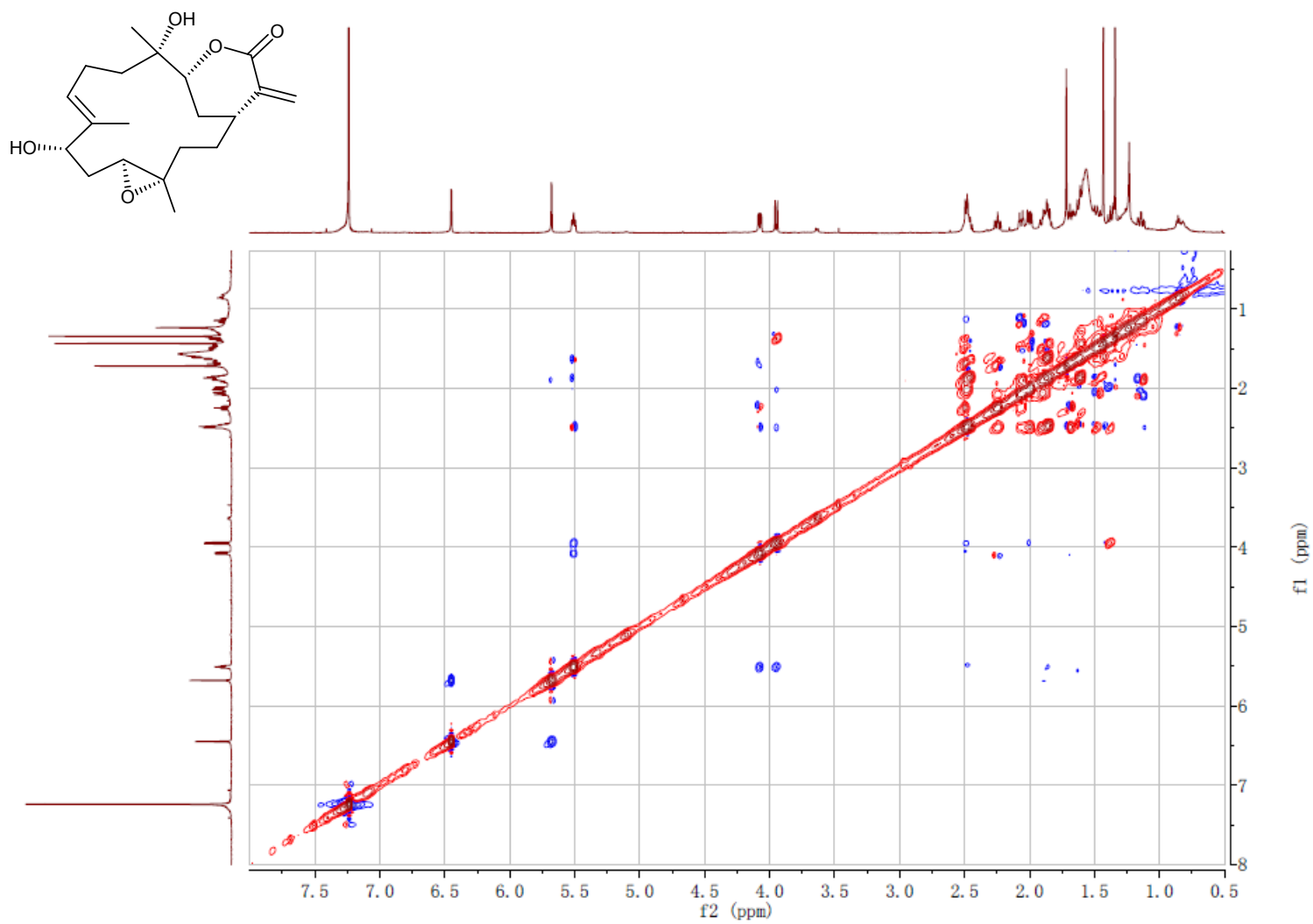
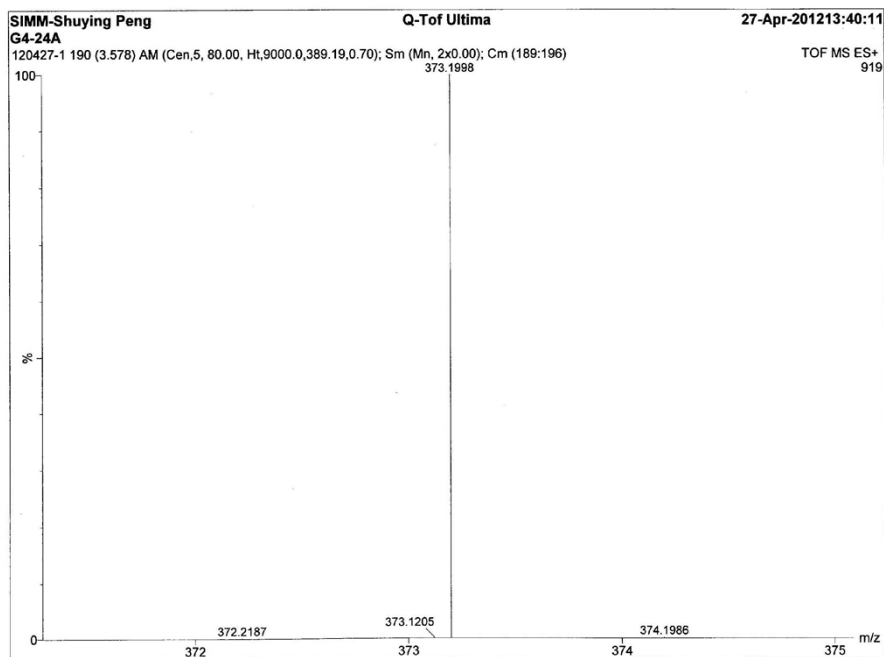


Figure S7. HRESIMS spectrum of 9 α -hydroxy-flexibilide (**1**).

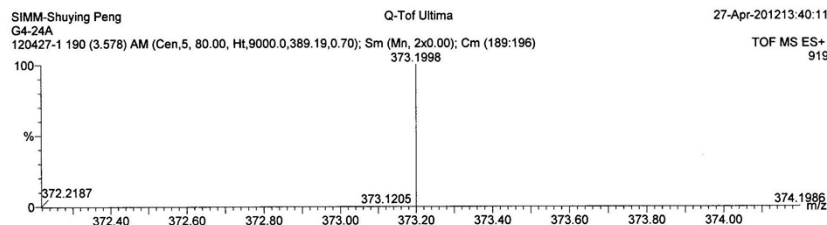


Elemental Composition Report

Page 1

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
 18 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)



Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
373.1998	100.00	373.1991	0.7	1.9	5.5	1	C20 H30 O5 Na

Figure S8. ^1H NMR spectrum (400 MHz, CDCl_3) of 15(17)-dehydromanaarenolide E (**2**)

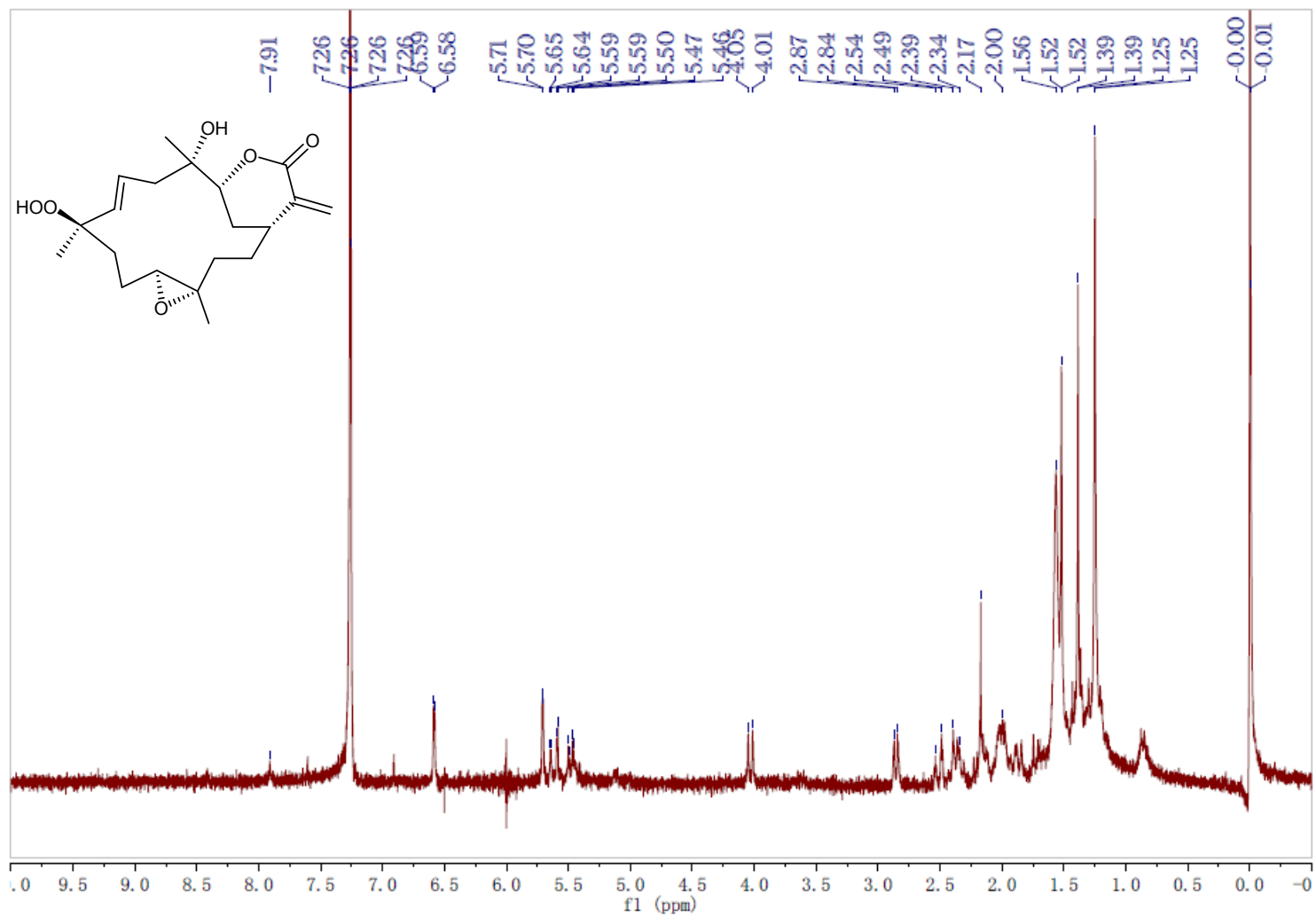


Figure S9. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 15(17)-dehydromanaarenolide E (**2**)

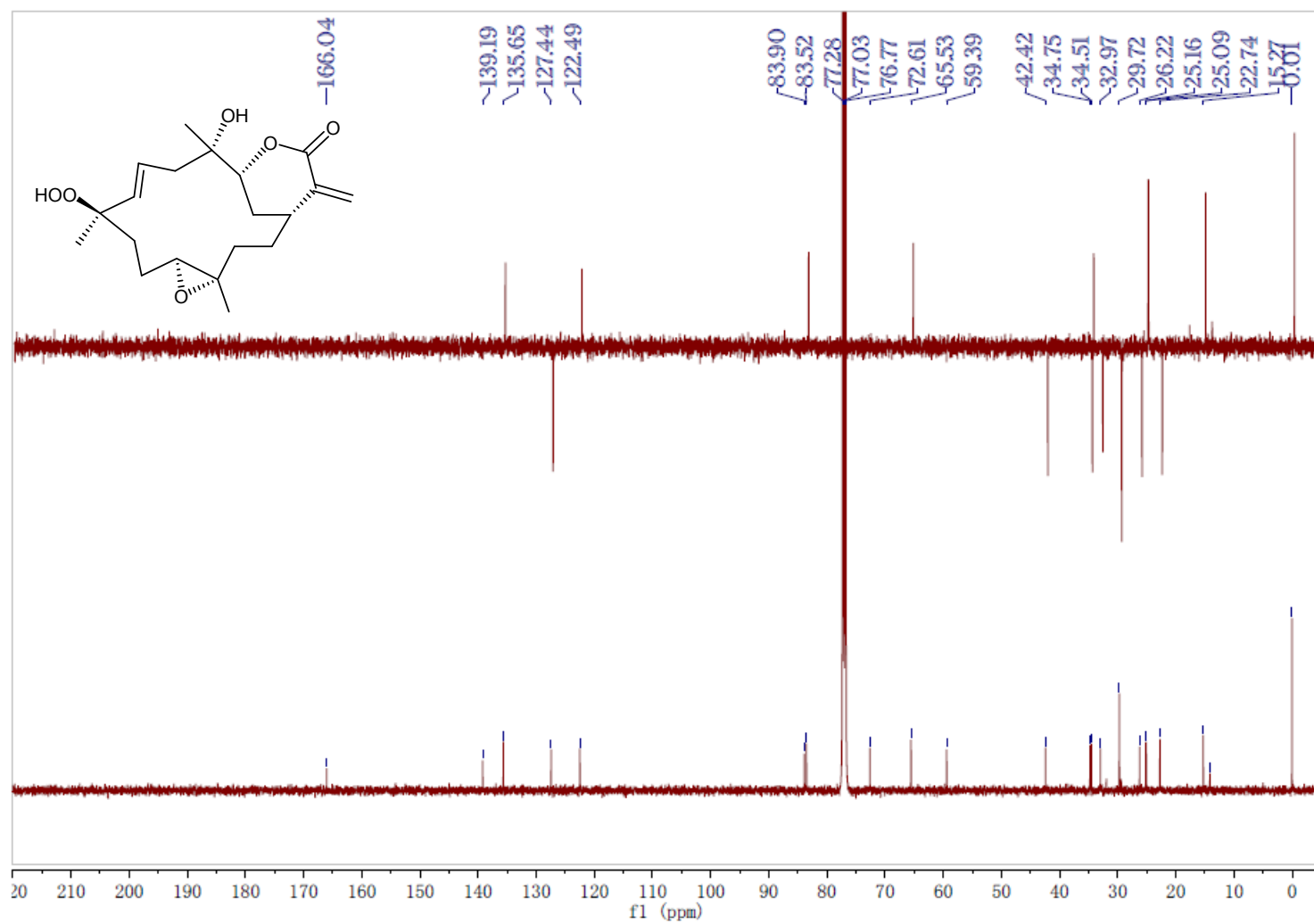
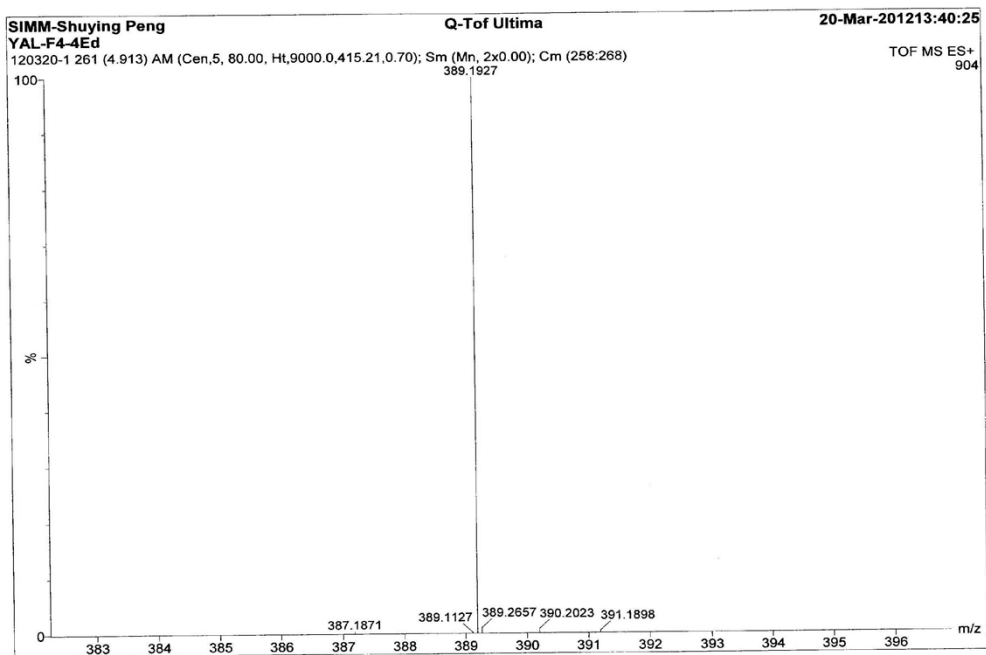


Figure S10. HRESIMS spectrum of 15(17)-dehydromanaarenolide E (2)

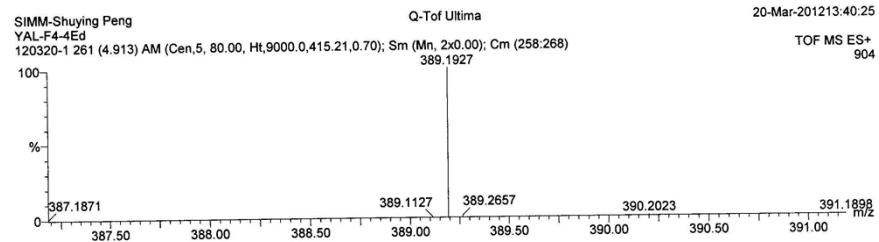


Elemental Composition Report

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Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
 15 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)



Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
389.1927	100.00	389.1940	-1.3	-3.4	5.5	1	C20 H30 O6 Na

Figure S11. ^1H NMR spectrum (400 MHz, CDCl_3) of 8-dehydroxy-15(17)-dehydromanaarenolide E (**3**)

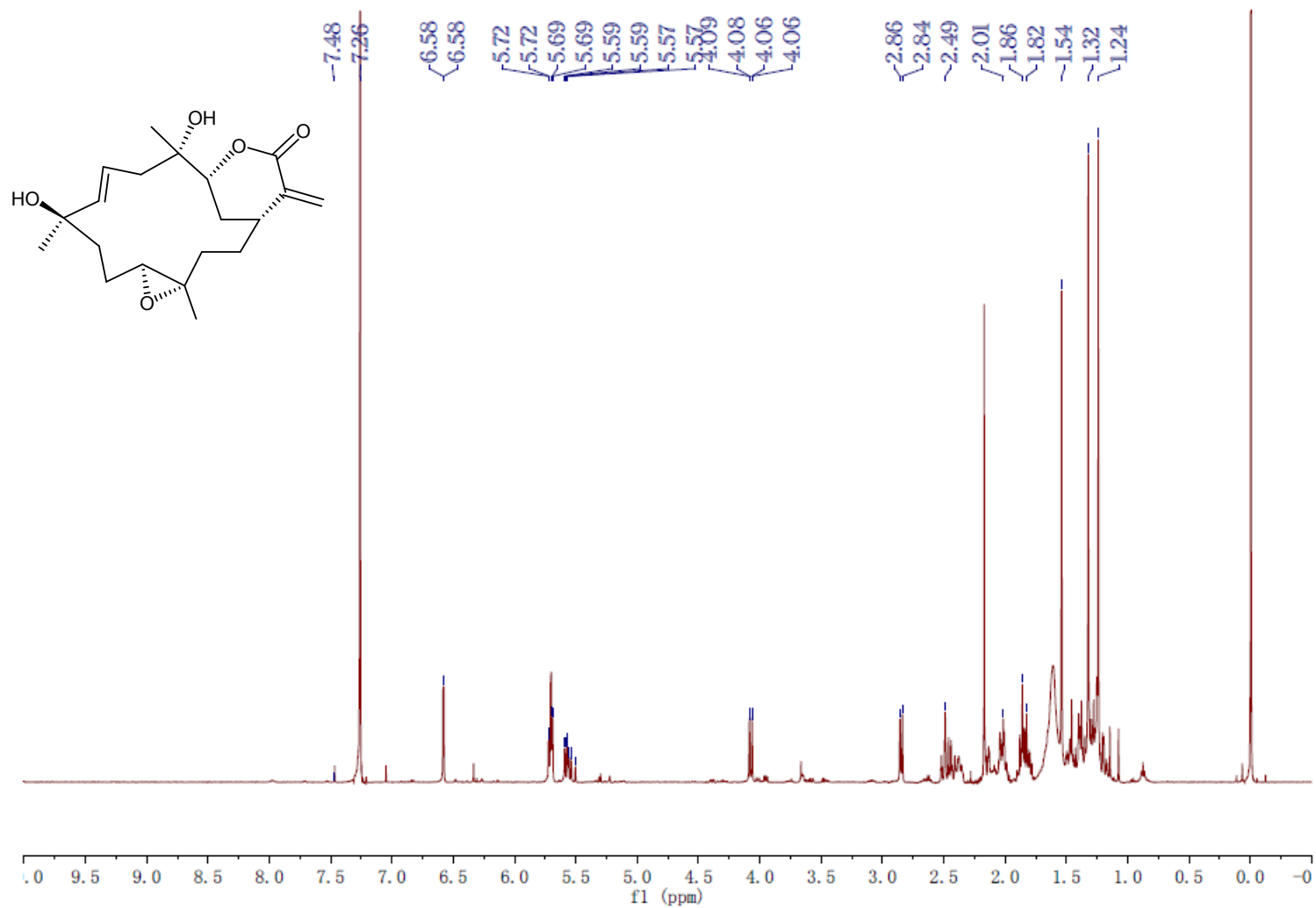


Figure S12. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 8-dehydroxy-15(17)-dehydromanaarenolide E (**3**)

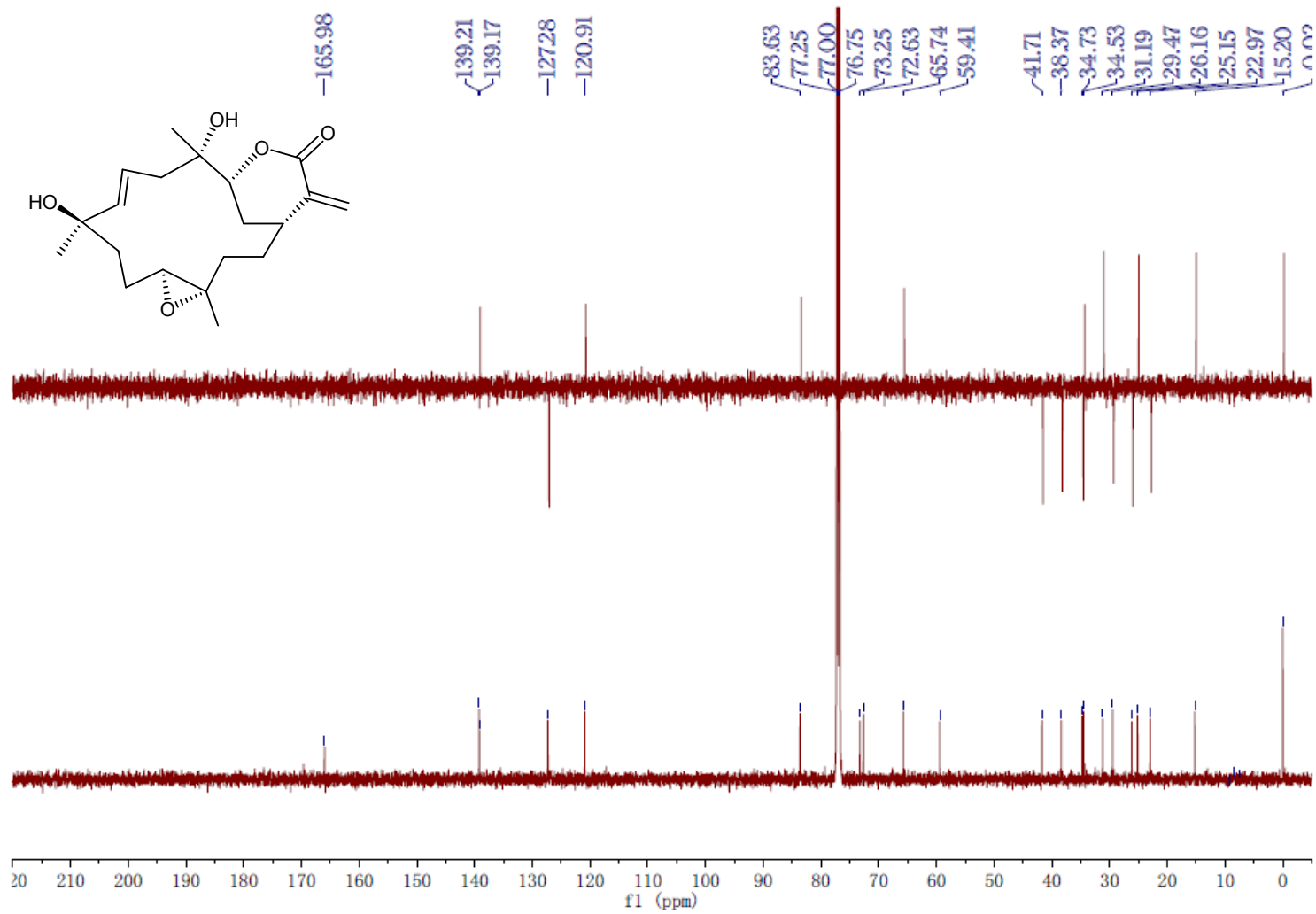


Figure S13. HMQC spectrum (400 MHz, CDCl₃) of 8-dehydroxy-15(17)-dehydromanaarenolide E (**3**)

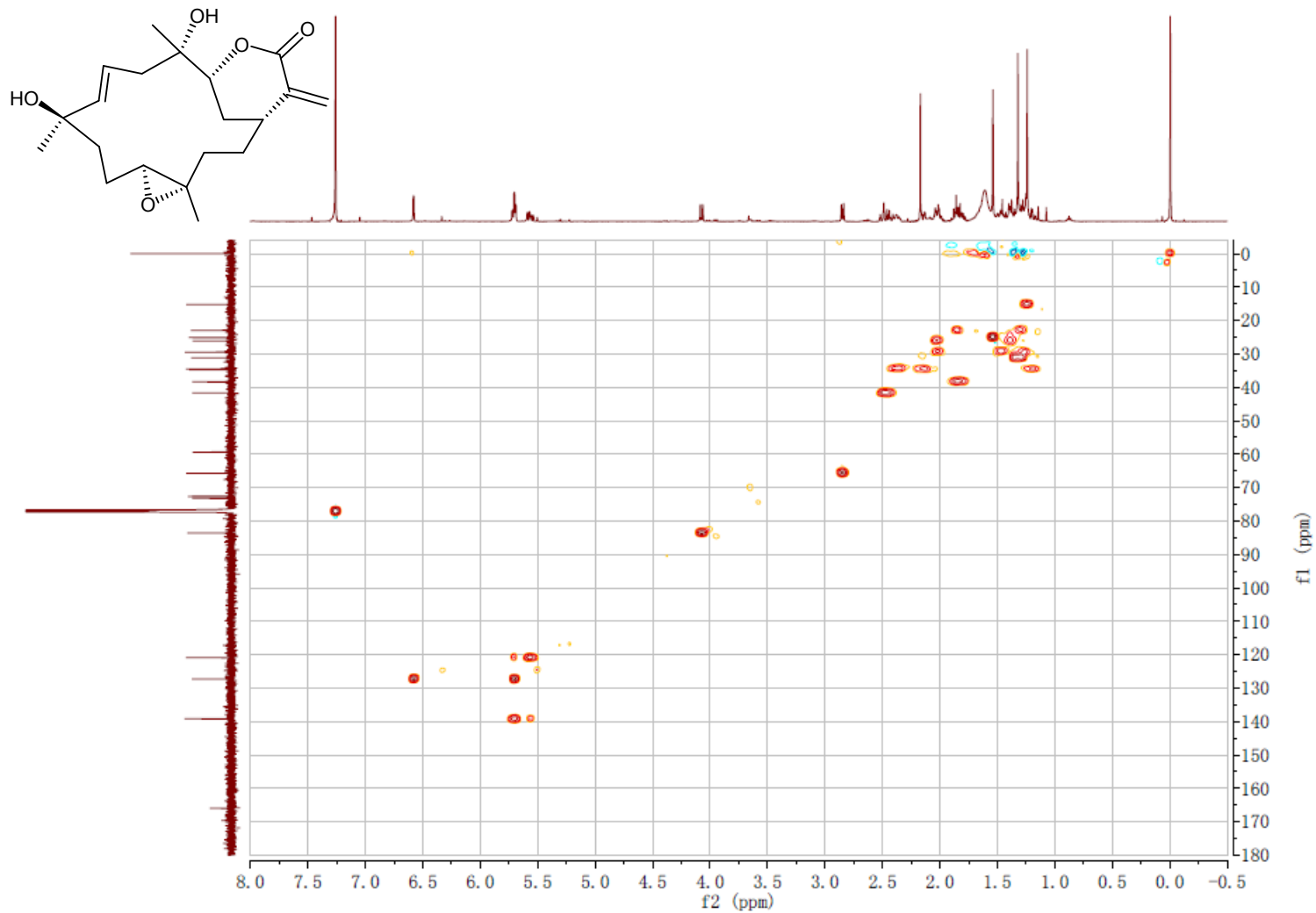


Figure S14. HMBC spectrum (400 MHz, CDCl₃) of 8-dehydroxy-15(17)-dehydromanaarenolide E (**3**)

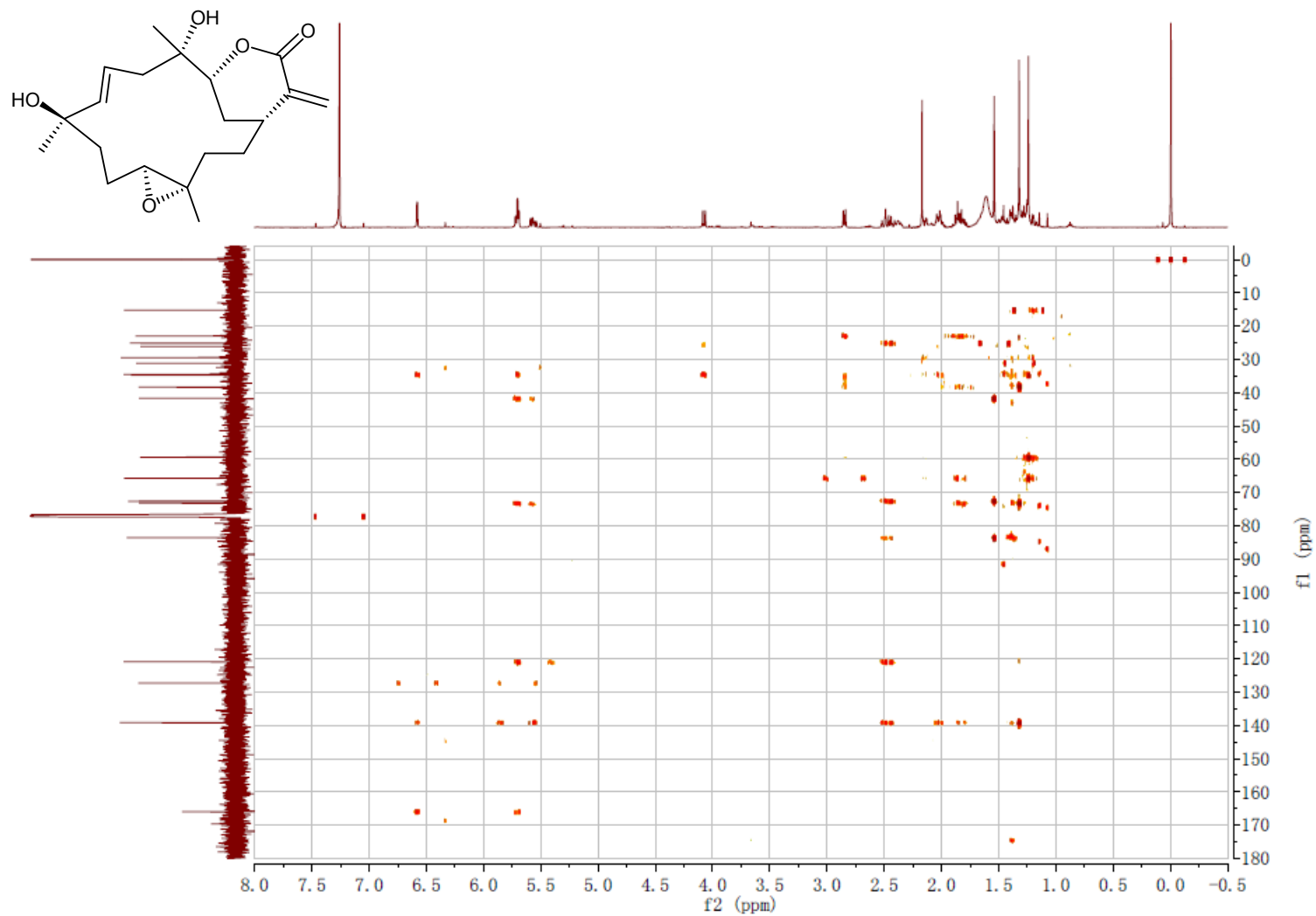


Figure S15. ^1H - ^1H COSY spectrum (400 MHz, CDCl_3) of 8-dehydroxy-15(17)-dehydromanaarenolide E (**3**)

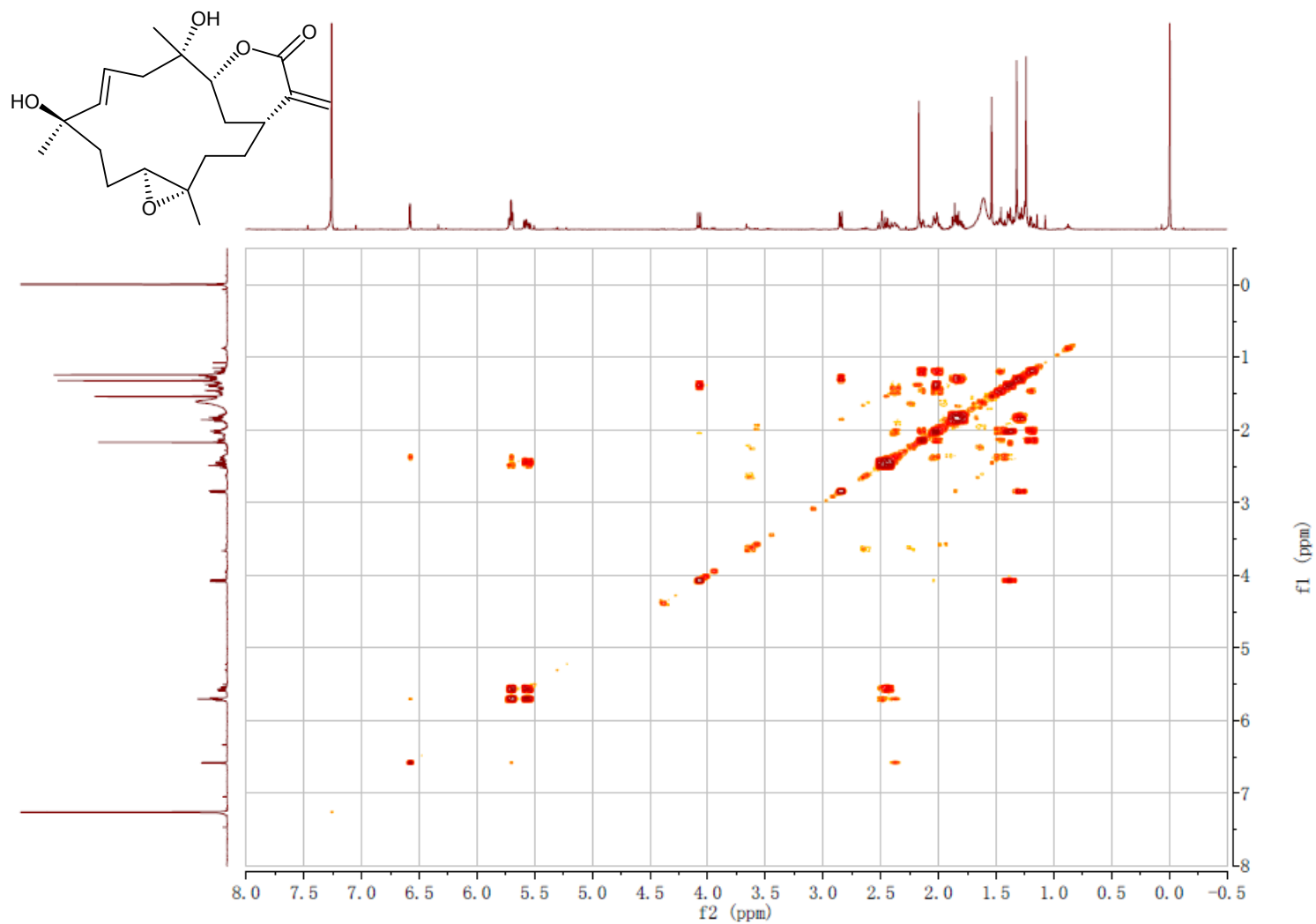
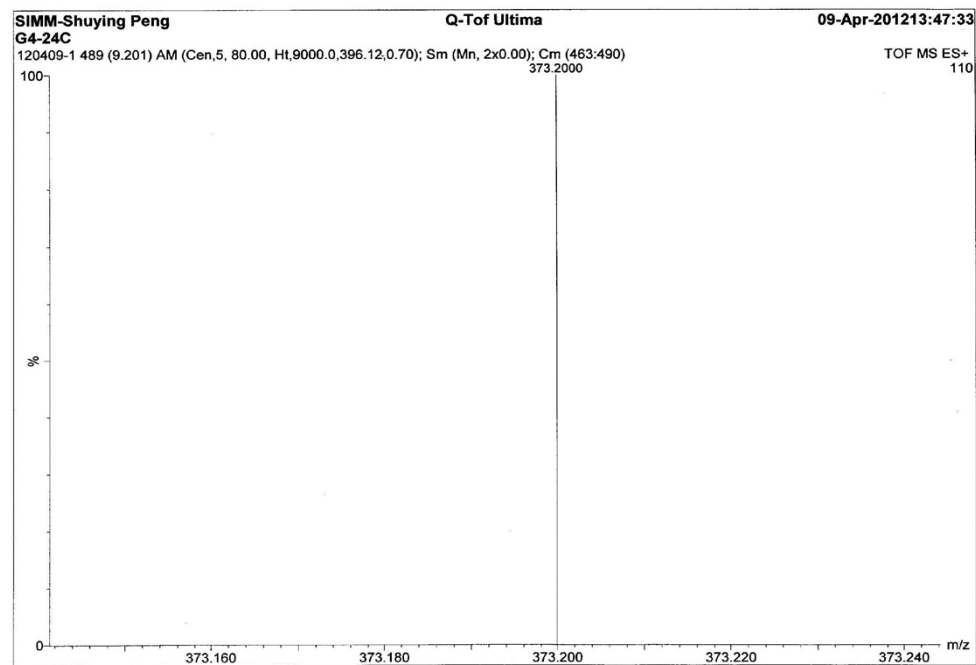


Figure S16. HRESIMS spectrum of 8-dehydroxy-15(17)-dehydromanaarenolide E (3)

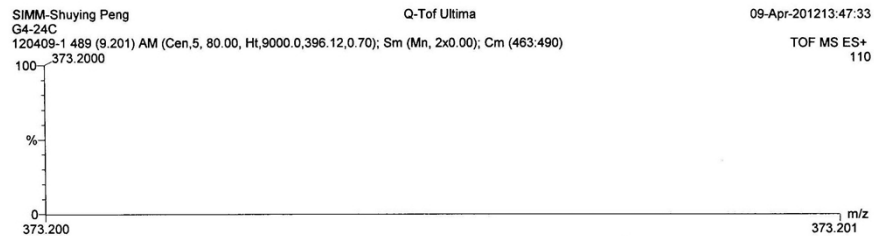


Elemental Composition Report

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Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
 13 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)



Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
373.2000	373.1991	0.9	2.4	5.5	1	C20 H30 O5 Na

Figure S17. ^1H NMR spectrum (400 MHz, CDCl_3) of 15,17-dedihydromanaarenolide A (**4**)

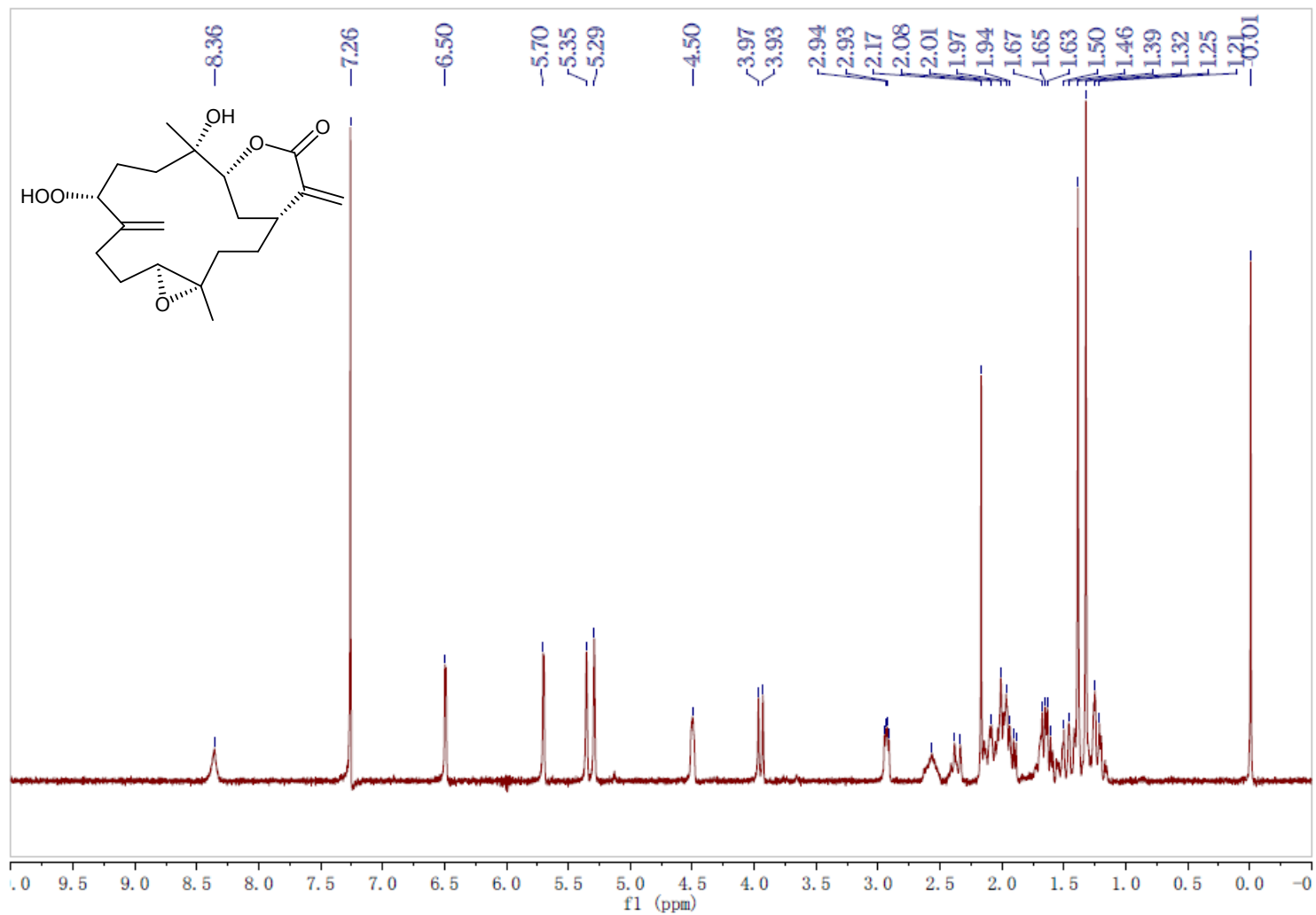


Figure S18. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 15,17-dedihydromanaarenolide A (4)

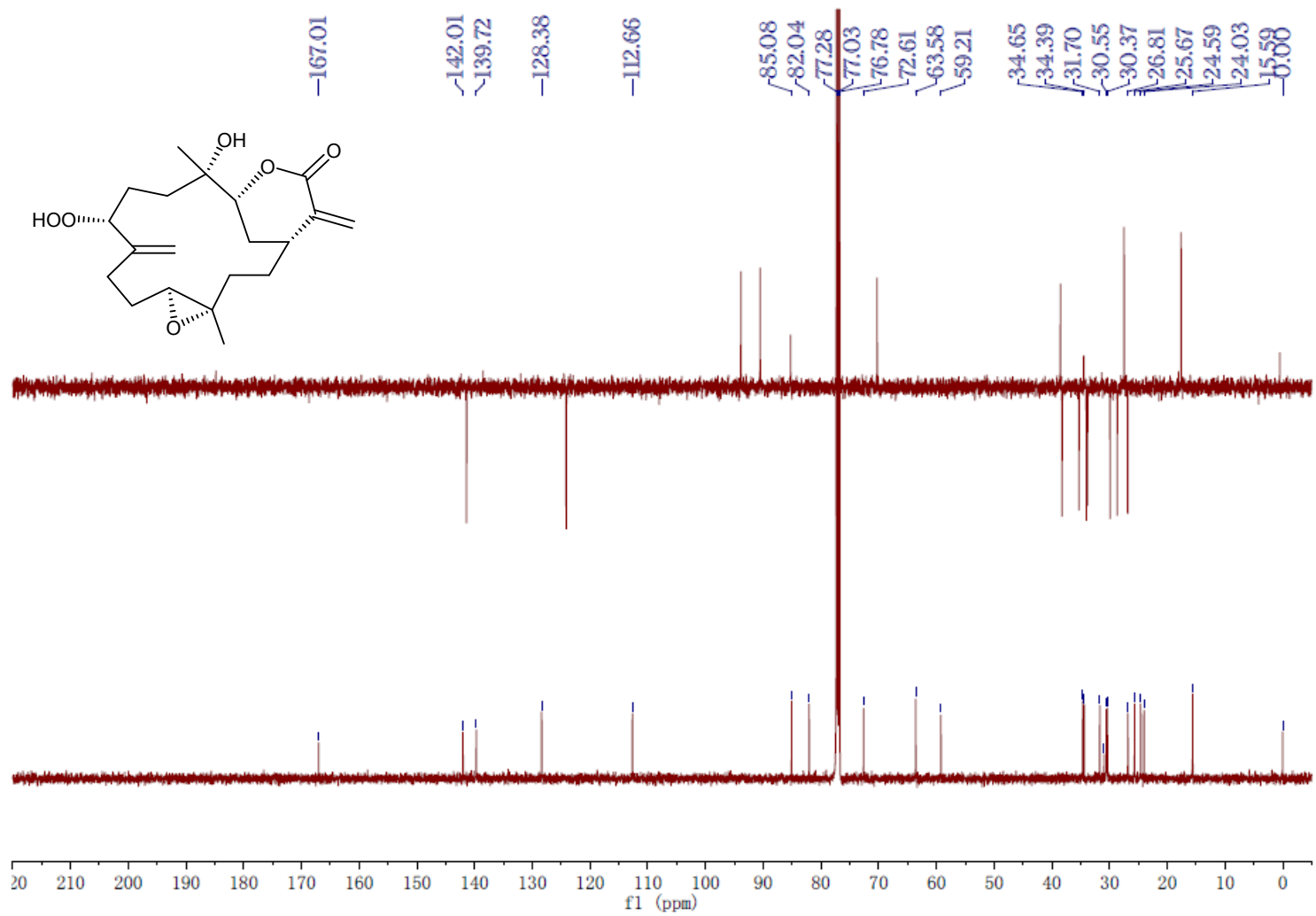
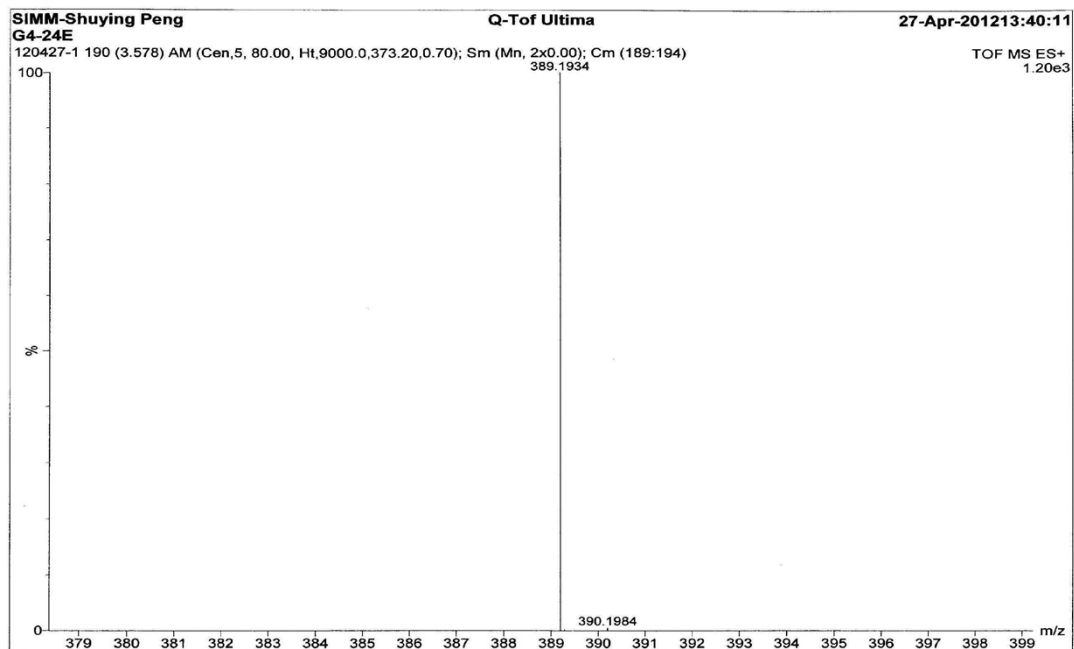


Figure S19. HRESIMS spectrum of 15,17-dedihydrimanaarenolide A (4)

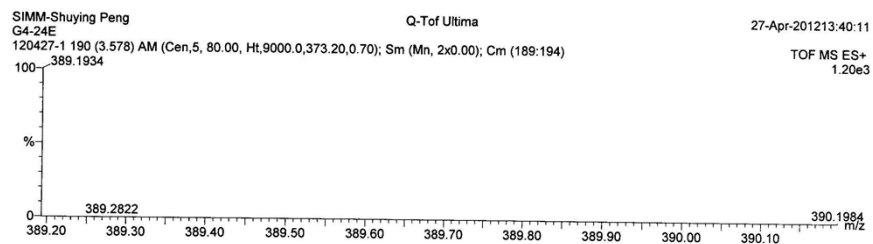


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Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
 15 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)



Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
389.1934	100.00	389.1940	-0.6	-1.6	5.5	1	C20 H30 O6 Na

Figure S20. ¹H NMR spectrum (400 MHz, CDCl₃) of 15,17-dedihydrimanaarenolide C (5)

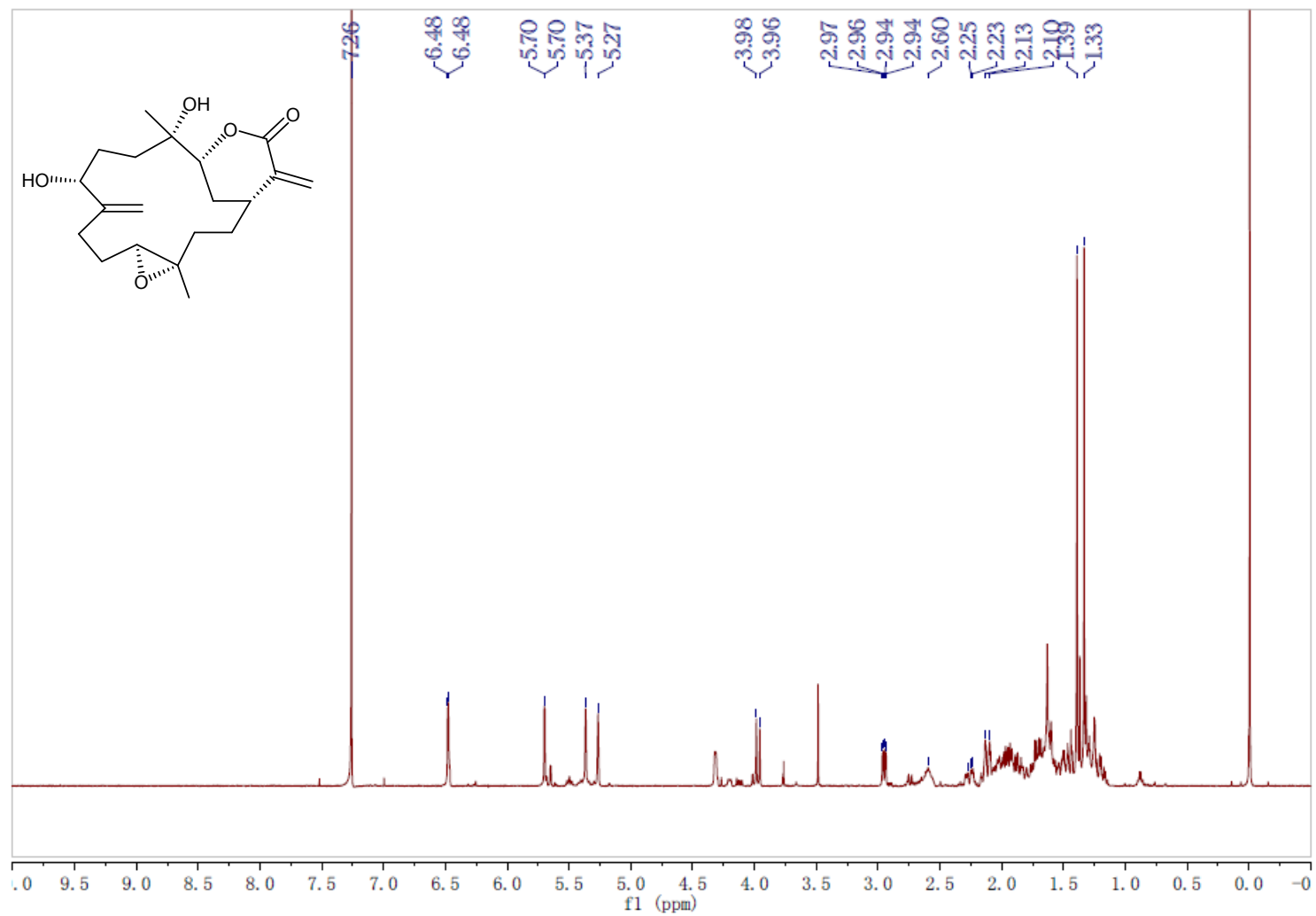


Figure S21. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 15,17-dedihydromanaarenolide C (5)

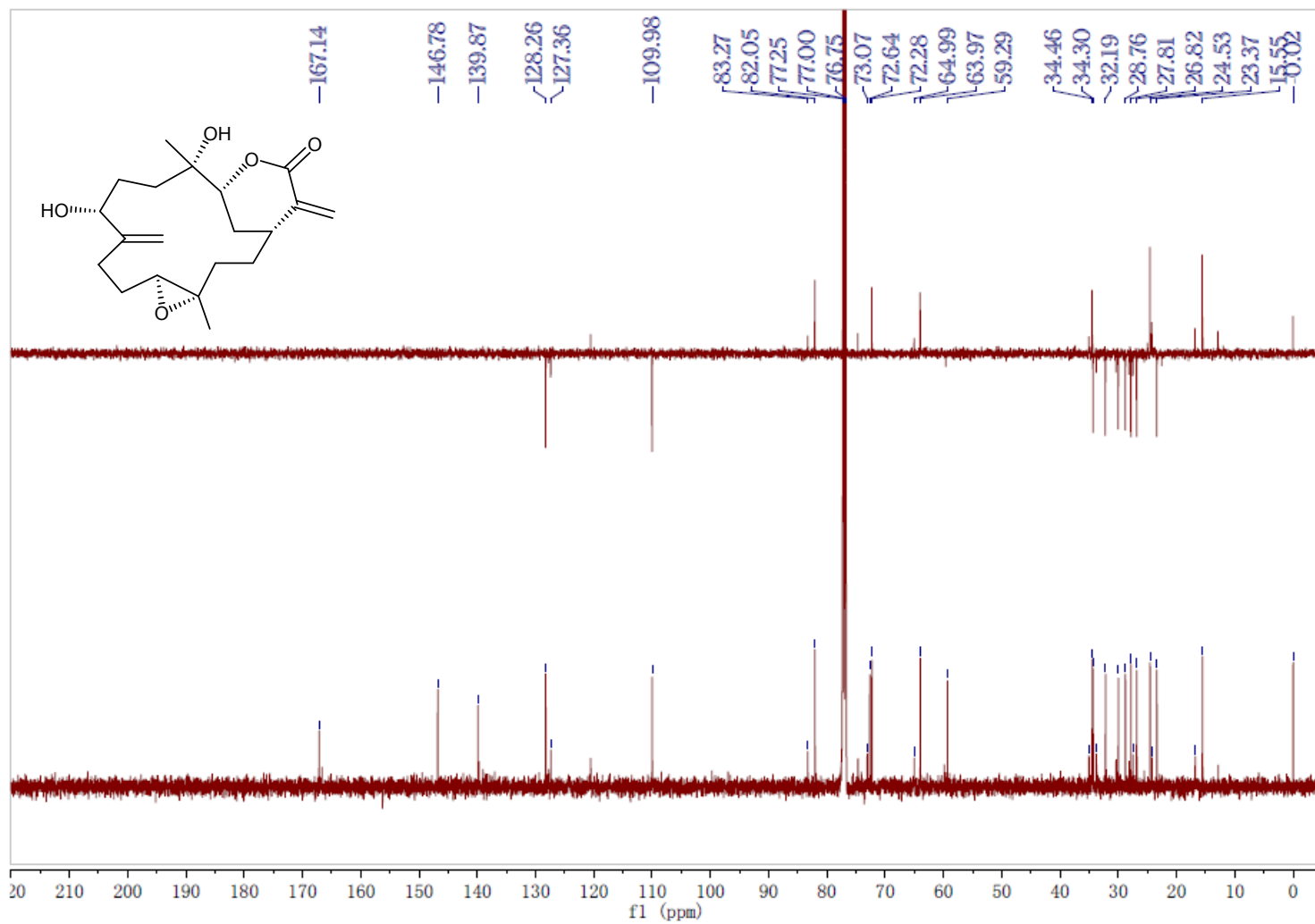
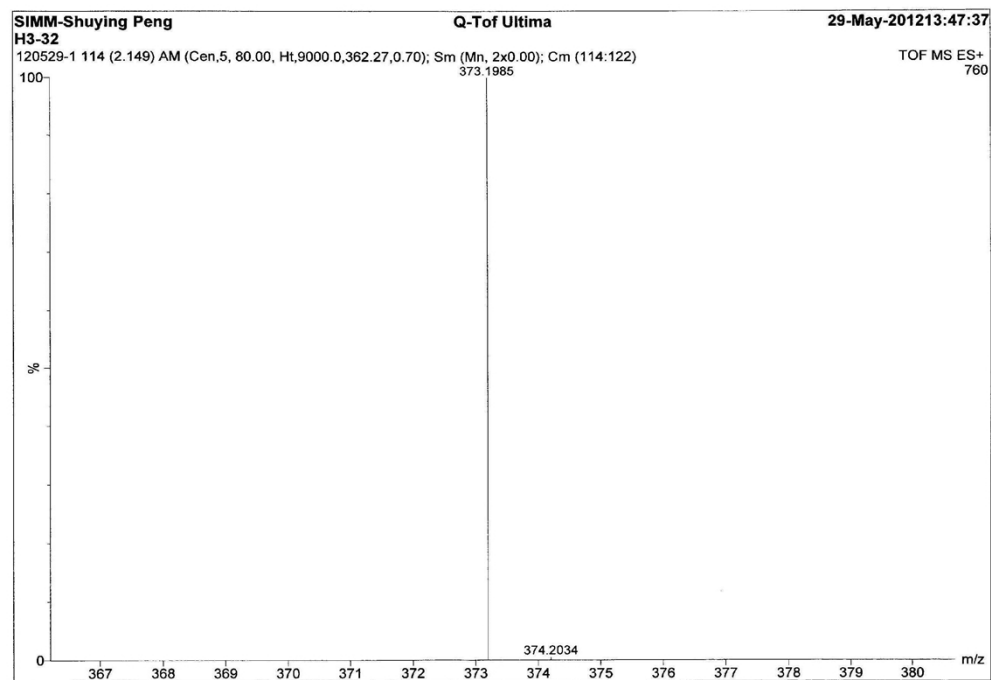


Figure S22. HRESIMS spectrum of 15,17-dedihydrimanaarenolide C (5)



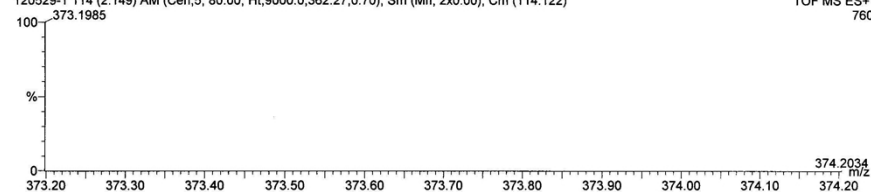
Elemental Composition Report

Page 1

Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
13 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)

SIMM-Shuying Peng Q-ToF Ultima 29-May-201213:47:37
H3-32
120529-1 114 (2.149) AM (Cen,5, 80.00, Ht,9000.0,362.27,0.70); Sm (Mn, 2x0.00); Cm (114:122) TOF MS ES+ 760



Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
373.1985	100.00	373.1991	-0.6	-1.6	5.5	1	C20 H30 O5 Na

Figure S23 ^1H NMR spectrum (400 MHz, CDCl_3) of *epi*-flexilarin A (6)

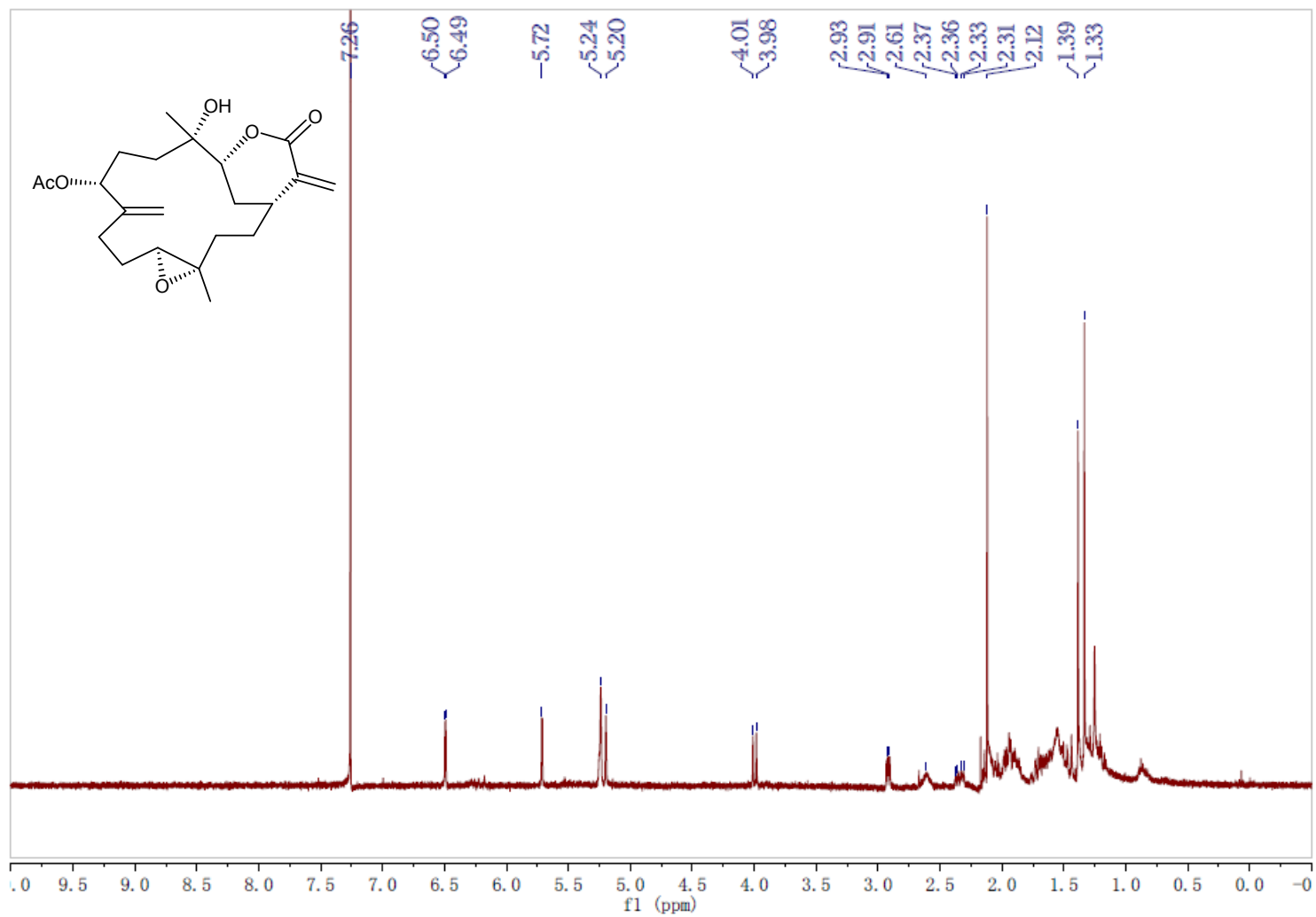
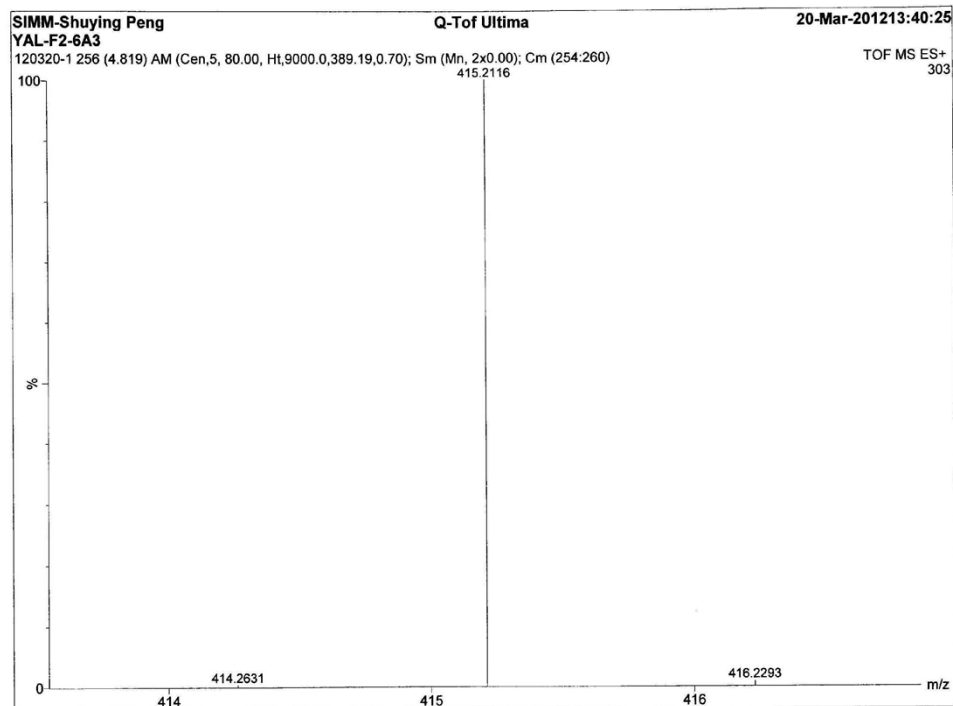


Figure S24 HRESIMS spectrum of *epi*-flexilarin A (6)

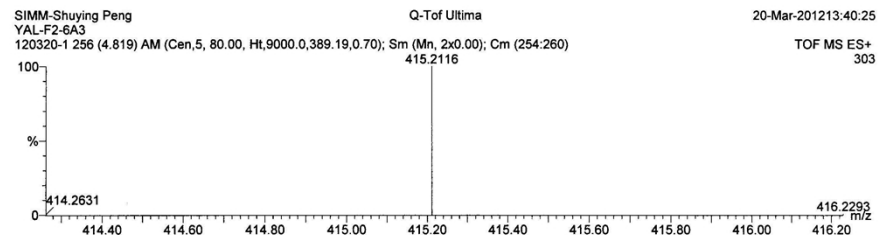


Elemental Composition Report

Page 1

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
 14 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)



Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
415.2116	100.00	415.2097	1.9	4.7	6.5	1	C22 H32 O6 Na

Figure S25. ¹H NMR spectrum (400 MHz, CDCl₃) of epoxyflexibilene (7)

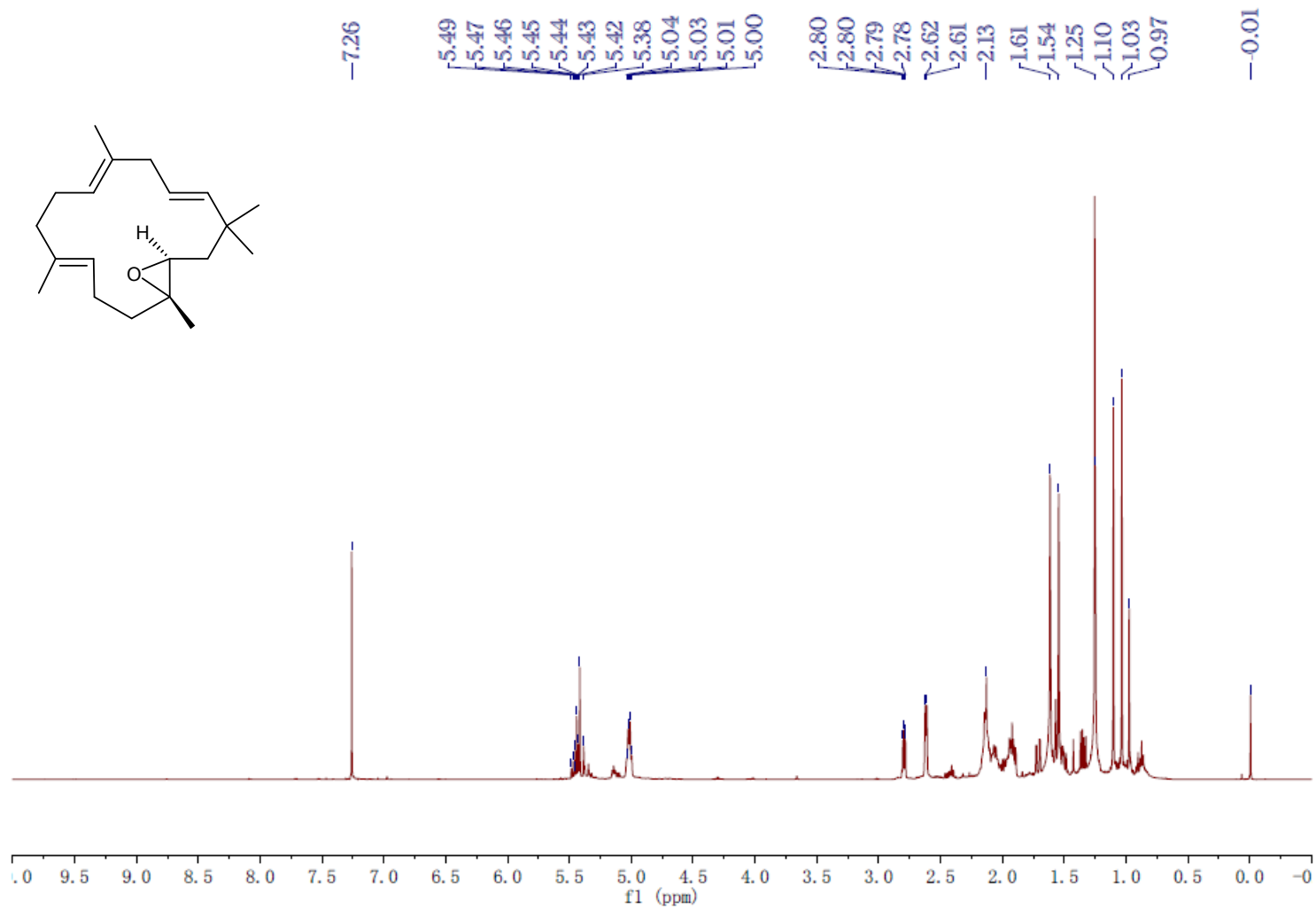


Figure S26. ¹³C NMR spectrum (100 MHz, CDCl₃) of epoxyflexibilene (7)

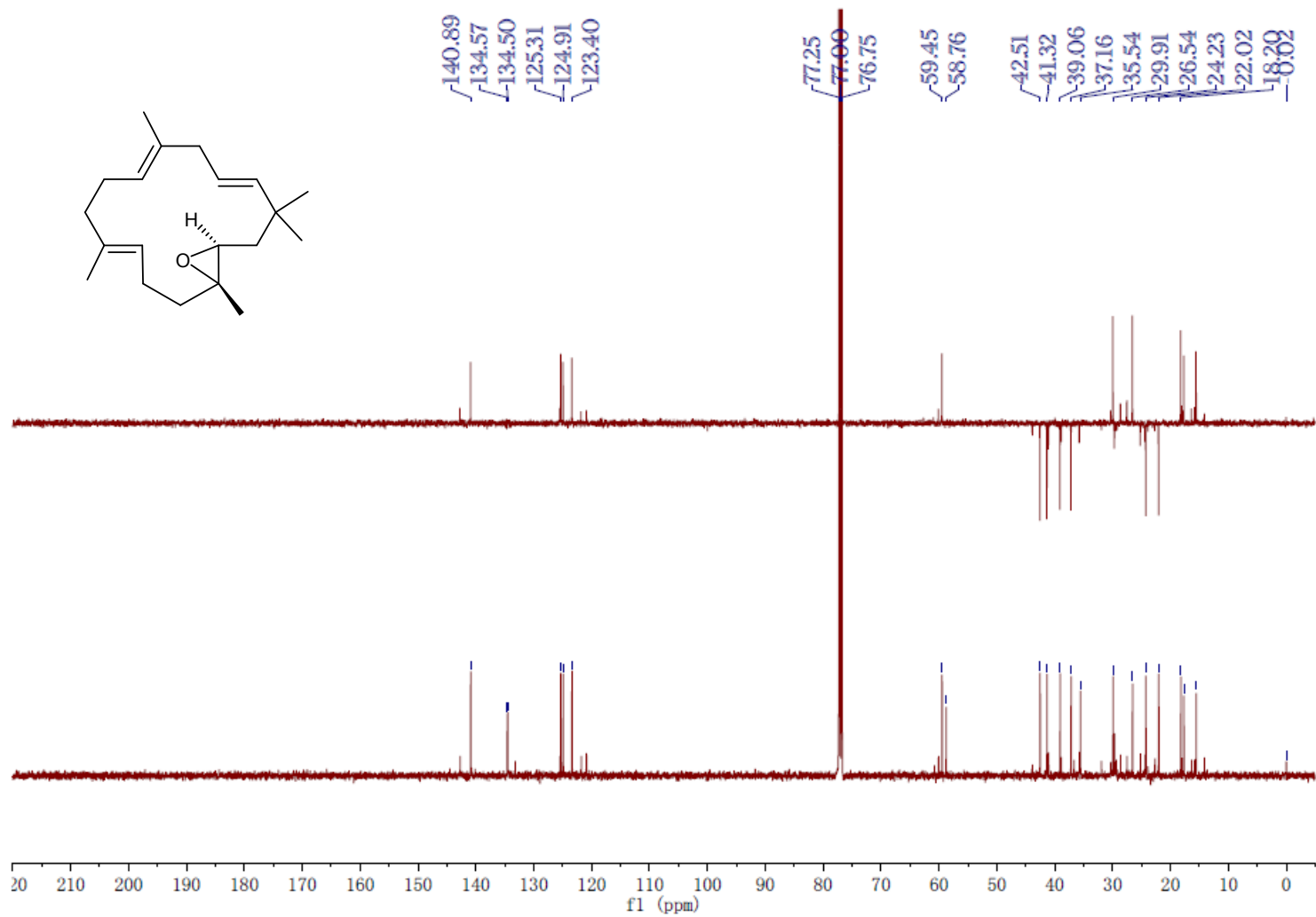


Figure S27. HMQC spectrum (400 MHz, CDCl₃) of epoxyflexibilene (7)

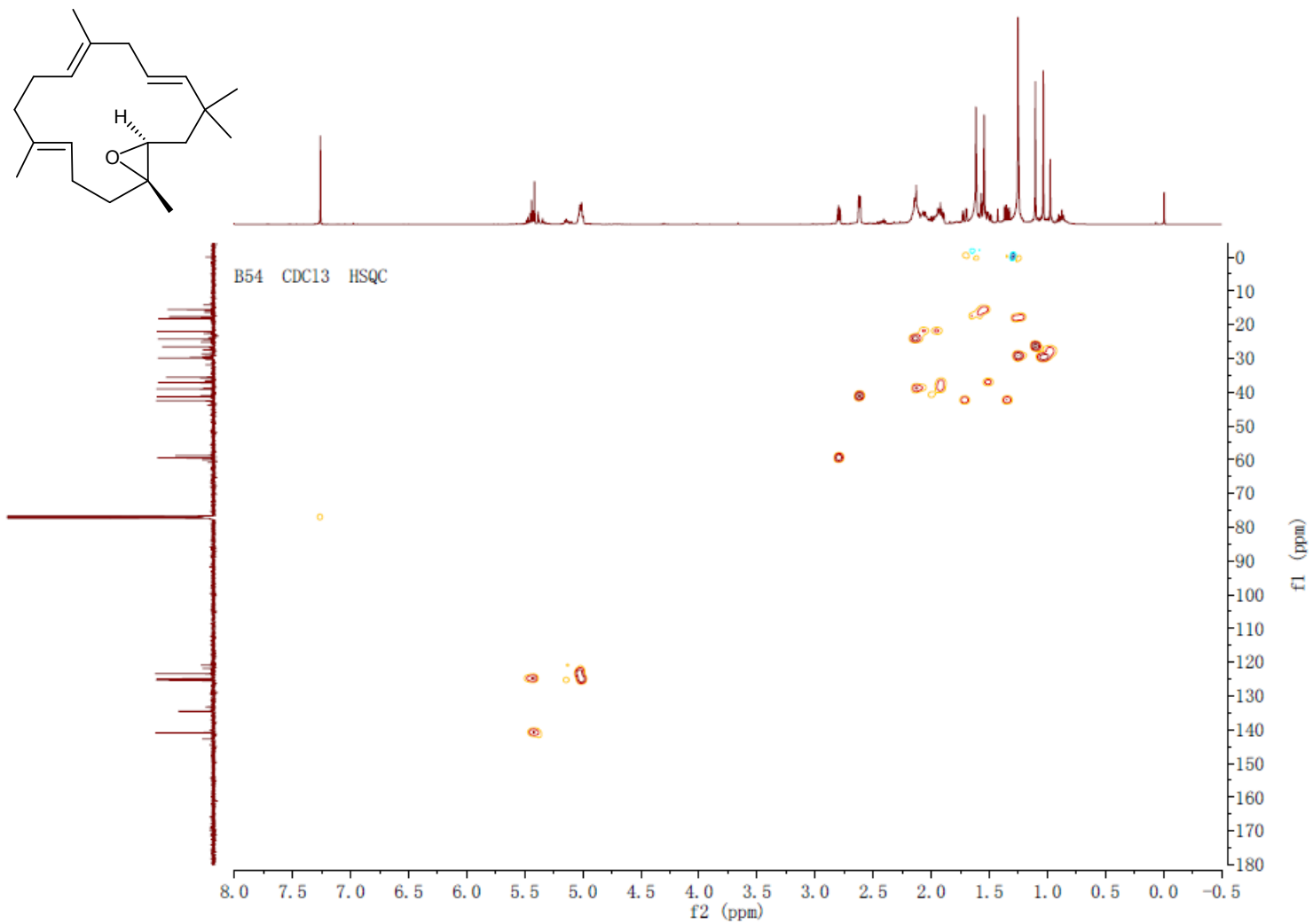


Figure S28. HMBC spectrum (400 MHz, CDCl₃) of epoxyflexibilene (7)

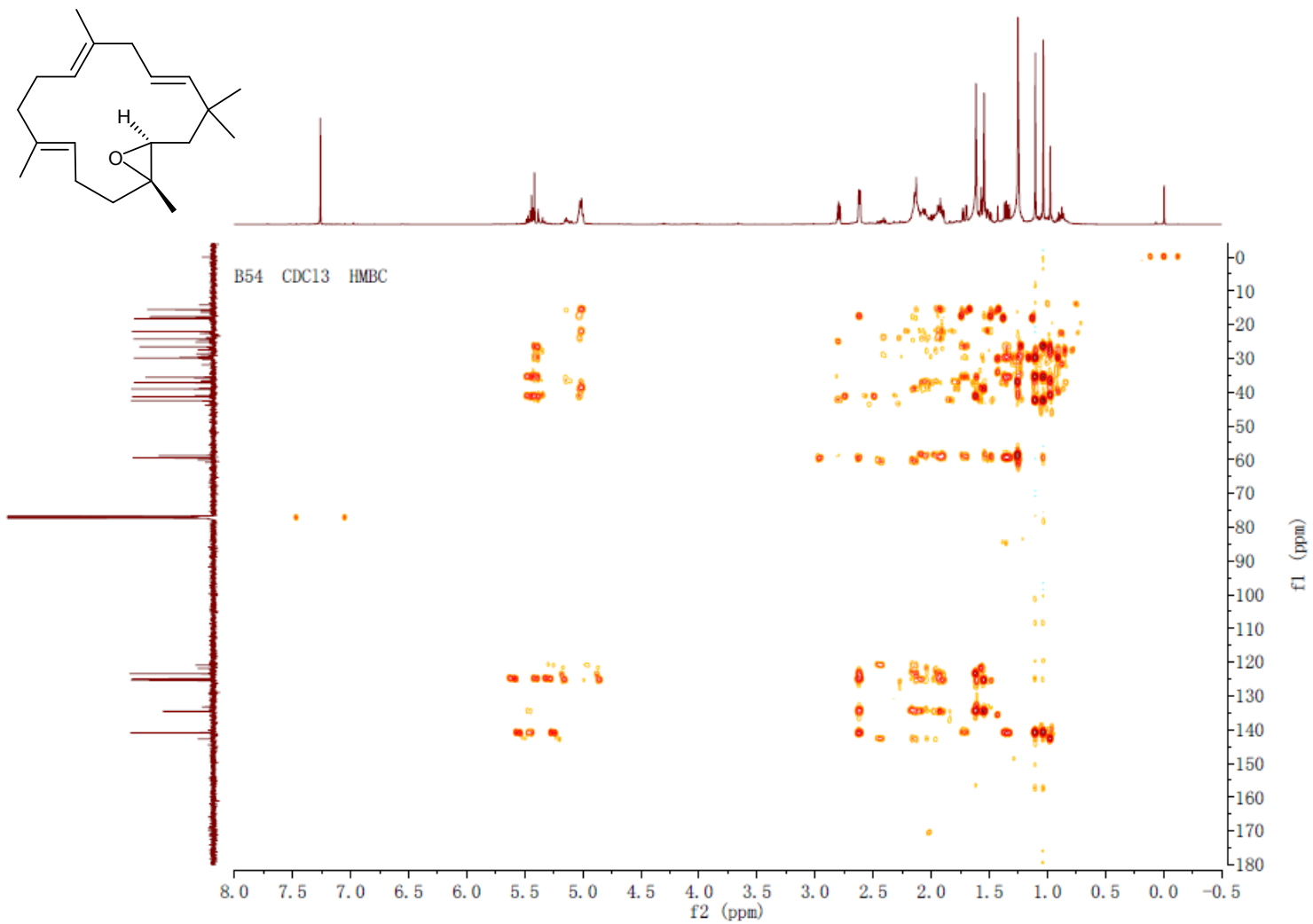


Figure S29. ^1H - ^1H COSY spectrum (400 MHz, CDCl_3) of epoxyflexibilene (7)

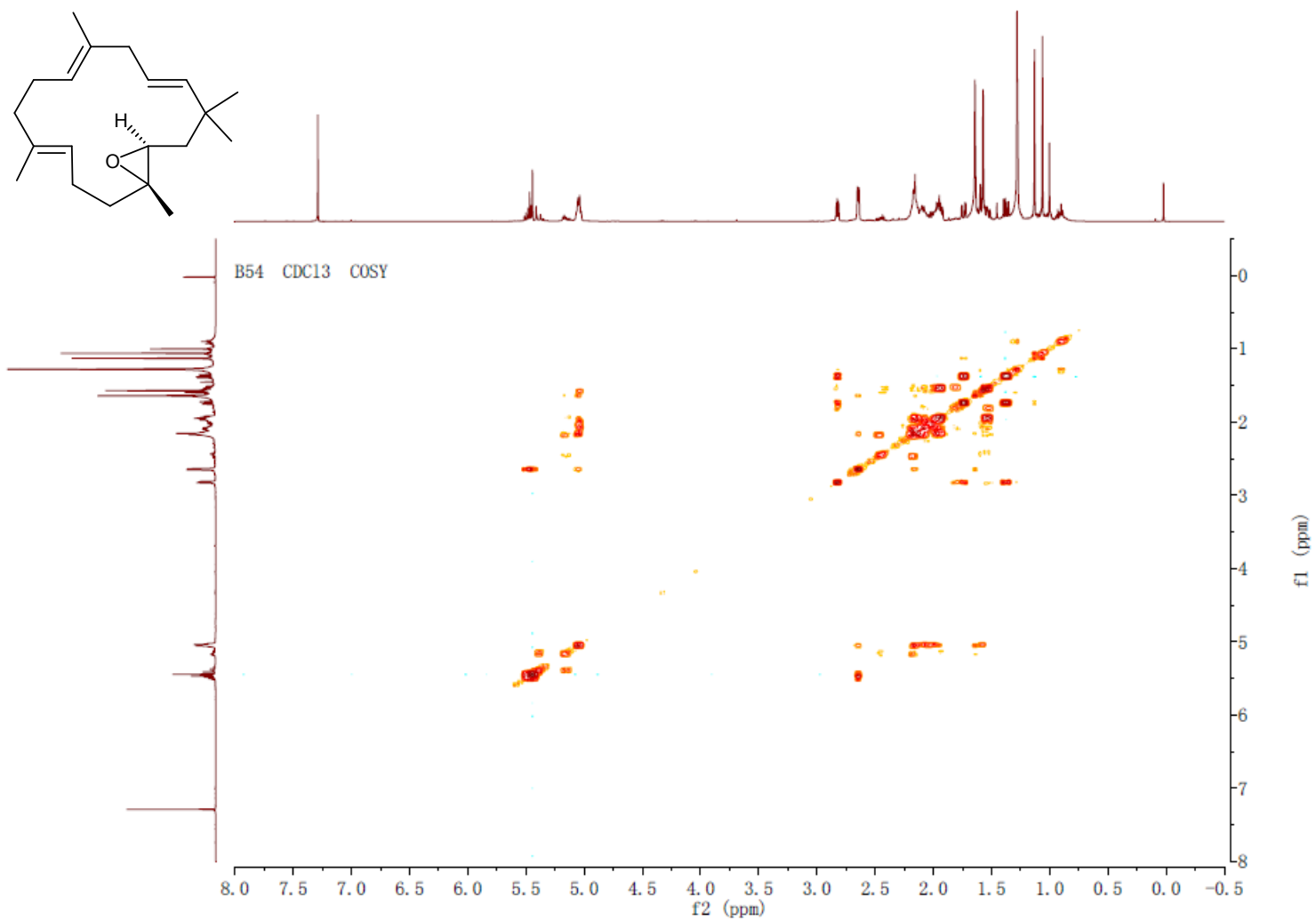
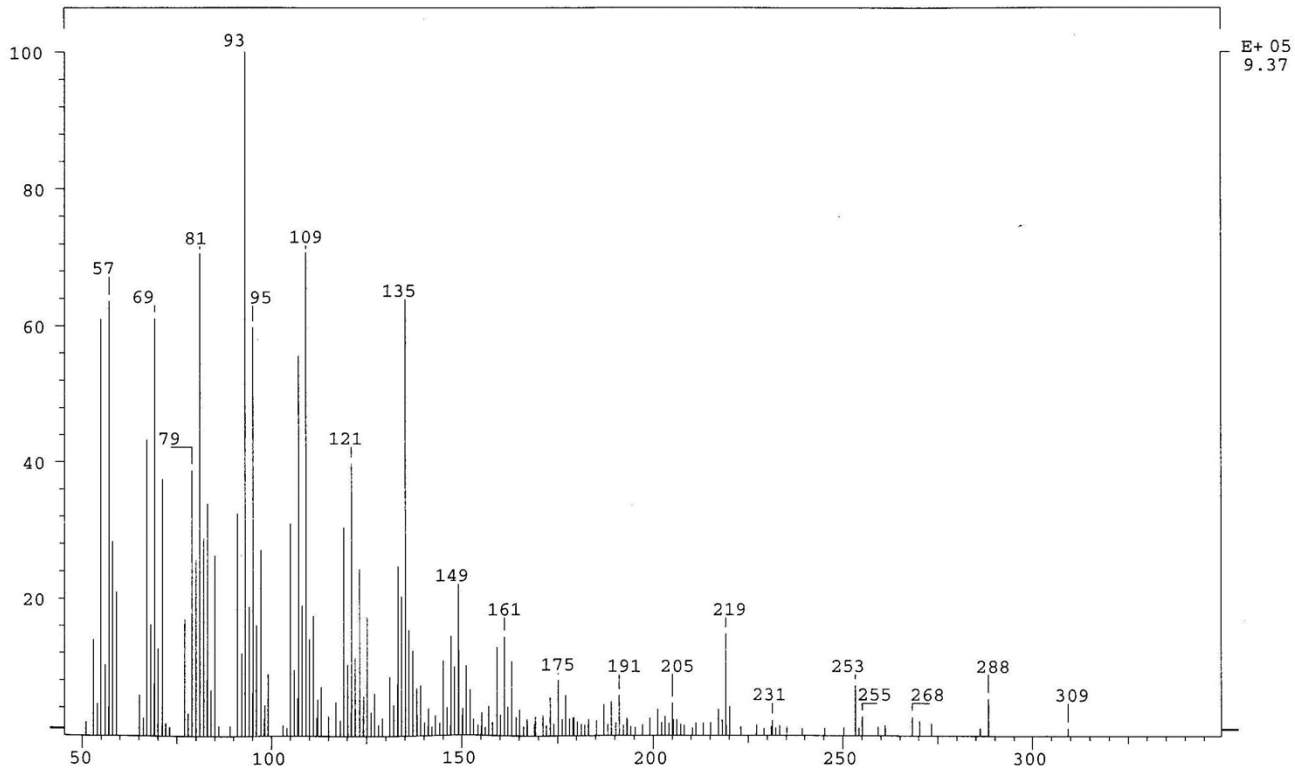


Figure S30. HREIMS spectrum of epoxyflexibilene (7)

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Samp: B54 Start : 14:01:24 23
Comm: Finnigan/MAT95//70eV/Tsou:220c/R:10000
Mode: EI +VE +LMR BSCAN (EXP) UP HR NRM Study : S/N: PT200712-01-01
Oper: WANG_J@SIMM.CAS Inlet :
Base: 93.1 Inten : 937324 Masses: 50 > 800
Norm: 93.1 RIC : 29253695 #peaks: 1540
Peak: 1000.00 mmu
Data: CMASS : converted



LIST: h120684-c1 20-Jul-12 Elapse: 03:28.9 16
 Samp: B54 Start : 14:01:24 23
 Comm: Finnigan/MAT95//70eV/Tsou:220c/R:10000
 Mode: EI +VE +LMR BSCAN (EXP) UP HR NRM Study : S/N: PT200712-01-01
 Oper: WANG_J@SIMM.CAS Inlet :
 Limit: (0)
 : (369) C21.H100.0
 Peak: 1000.00 mmu R+D: -2.0 > 60.0
 Data: CMASS : converted

Mass	Intensity	%RA	%RIC	Delta	R+D	Composition
71.07406	* 208064	9.93	0.55			
77.00519	* 344109	16.42	0.91	-2.5	5.5	C5.H.O
79.01825	* 706990	33.74	1.87	0.1	4.5	C5.H3.O
80.02357	* 607062	28.97	1.60	2.6	4.0	C5.H4.O
81.03134	* 1229042	58.66	3.25	2.7	3.5	C5.H5.O
82.04390	* 414558	19.79	1.09	-2.0	3.0	C5.H6.O
83.02024	* 97072	4.63	0.26			
83.05672	* 323124	15.42	0.85			
85.04997	* 149535	7.14	0.39			
85.08075	* 118914	5.68	0.31			
91.05135	* 528476	25.22	1.40			
92.06045	* 280654	13.40	0.74	2.2	4.0	C7.H8
93.06998	* 2095203	100.00	5.53	0.4	3.5	C7.H9
94.07740	* 378798	18.08	1.00	0.9	3.0	C7.H10
95.08729	* 949957	45.34	2.51	-1.2	2.5	C7.H11
96.05934	* 143325	6.84	0.38	-1.8	3.0	C6.H8.O
96.09433	* 200355	9.56	0.53	-0.4	2.0	C7.H12
97.06630	* 122054	5.83	0.32	-1.0	2.5	C6.H9.O
97.10271	* 170591	8.14	0.45	-1.0	1.5	C7.H13
105.0341	* 517198	24.68	1.37	0.0	5.5	C7.H5.O
106.0372	* 141754	6.77	0.37			
107.0435	* 931328	44.45	2.46			
108.0482	* 312346	14.91	0.82			
109.0204	* 206493	9.86	0.55			
109.0566	* 1316622	62.84	3.48			
110.0277	* 82940	3.96	0.22			
110.0628	* 237542	11.34	0.63			
111.0375	* 169235	8.08	0.45			
111.0735	* 122982	5.87	0.32			
119.0869	* 467091	22.29	1.23	-0.8	4.5	C9.H11
120.0929	* 170020	8.11	0.45	1.0	4.0	C9.H12
121.1021	* 802564	38.30	2.12	-0.4	3.5	C9.H13
122.1075	* 224909	10.73	0.59	2.0	3.0	C9.H14
123.0805	* 163810	7.82	0.43	0.5	3.5	C8.H11.O
123.1168	* 285508	13.63	0.75	0.6	2.5	C9.H15
125.0962	* 318056	15.18	0.84	0.4	2.5	C8.H13.O
133.1021	* 358170	17.09	0.95	-0.3	4.5	C10.H13
134.1091	* 339897	16.22	0.90	0.5	4.0	C10.H14
135.1172	* 1222404	58.34	3.23	0.2	3.5	C10.H15
136.1230	* 304566	14.54	0.80	2.2	3.0	C10.H16
137.0966	* 173374	8.27	0.46	0.0	3.5	C9.H13.O
137.1319	* 153246	7.31	0.40	1.1	2.5	C10.H17
138.1042	* 134902	6.44	0.36	0.3	3.0	C9.H14.O
139.1121	* 122126	5.83	0.32	0.2	2.5	C9.H15.O
145.1009	* 120413	5.75	0.32	0.8	5.5	C11.H13
147.1162	* 232974	11.12	0.62	1.2	4.5	C11.H15
148.1229	* 184938	8.83	0.49	2.3	4.0	C11.H16
149.0226	* 110277	5.26	0.29			
149.1311	* 159170	7.60	0.42	2.0	3.5	C11.H17
151.1116	* 139970	6.68	0.37	0.7	3.5	C10.H15.O
152.1178	* 105566	5.04	0.28	2.3	3.0	C10.H16.O
159.1165	* 135830	6.48	0.36	0.9	5.5	C12.H15
161.1320	* 245037	11.70	0.65	1.0	4.5	C12.H17
163.1477	* 91434	4.36	0.24	1.0	3.5	C12.H19
175.1477	* 109635	5.23	0.29	1.0	4.5	C13.H19
219.1752	* 142183	6.79	0.38	-0.3	4.5	C15.H23.O
288.2466	* 92861	4.43	0.25	-1.3	5.0	C20.H32.O

Figure S31. ^1H NMR spectrum (400 MHz, Pyr- d_5) of sinulaflexiolide L (**8**)

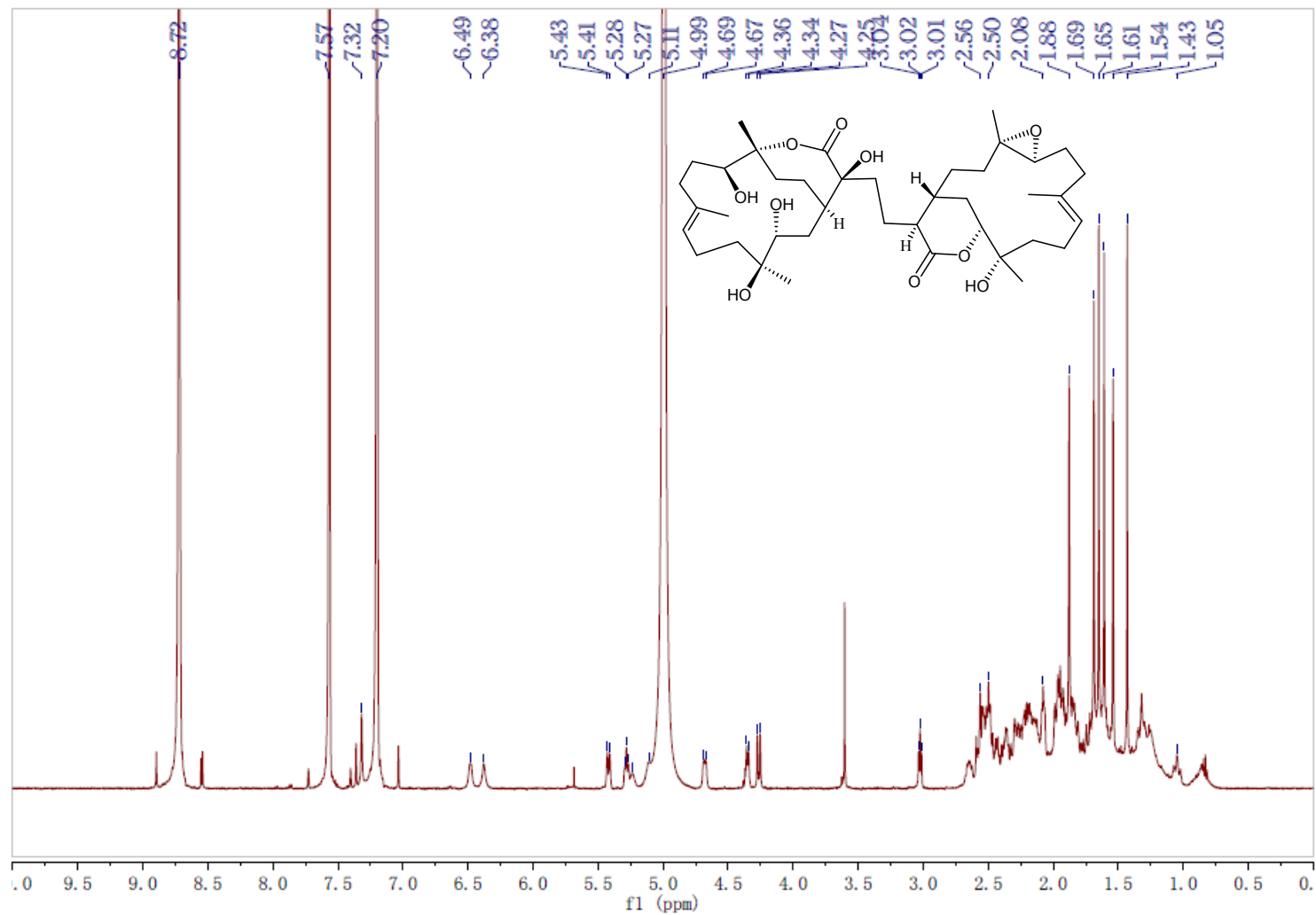


Figure S32. ^{13}C NMR spectrum (100 MHz, Pyr- d_5) of simulaflexiolide L (**8**)

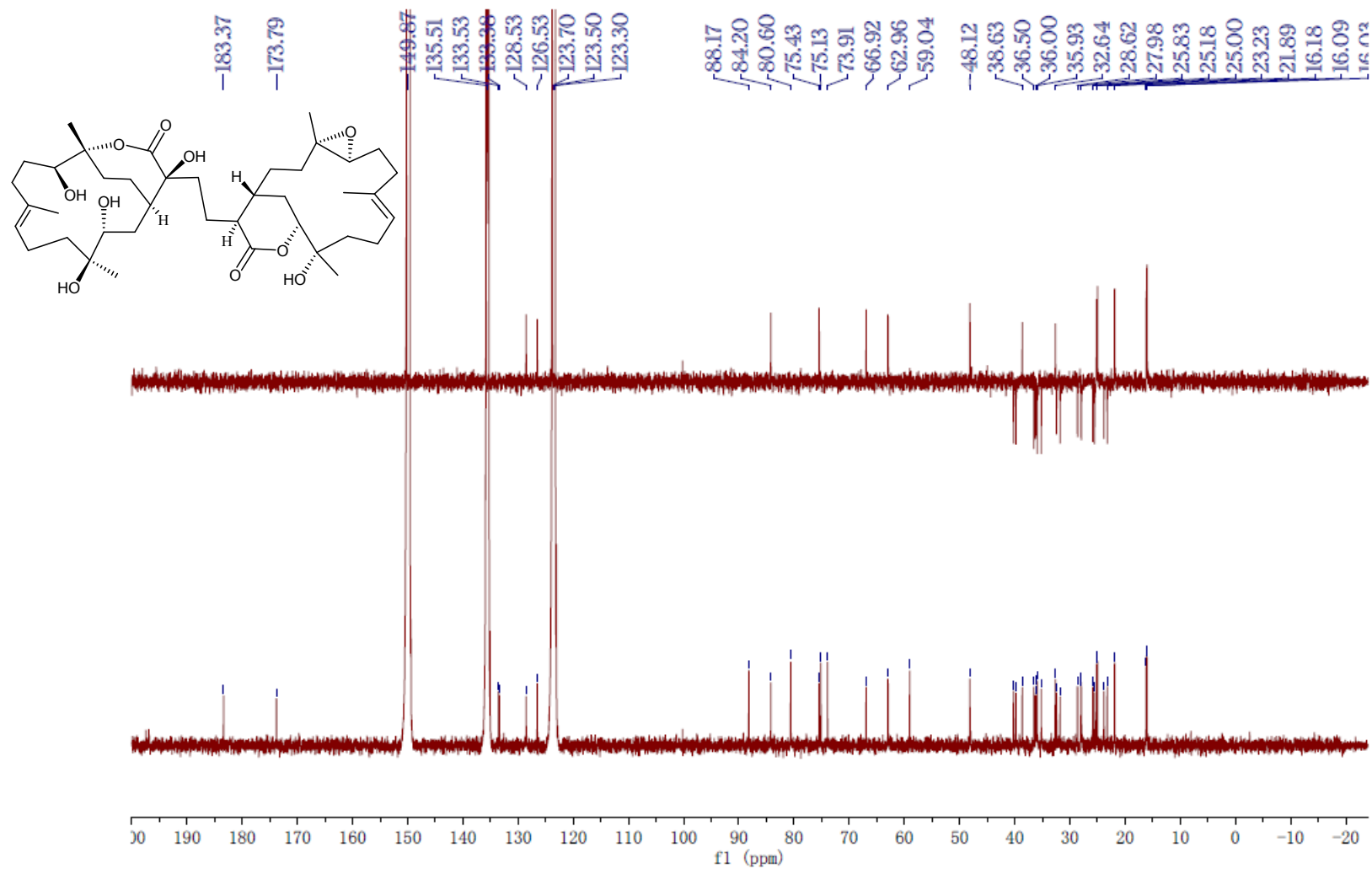


Figure S33. HMQC spectrum (400 MHz, Pyr-d₅) of sinulaflexiolide L (**8**)

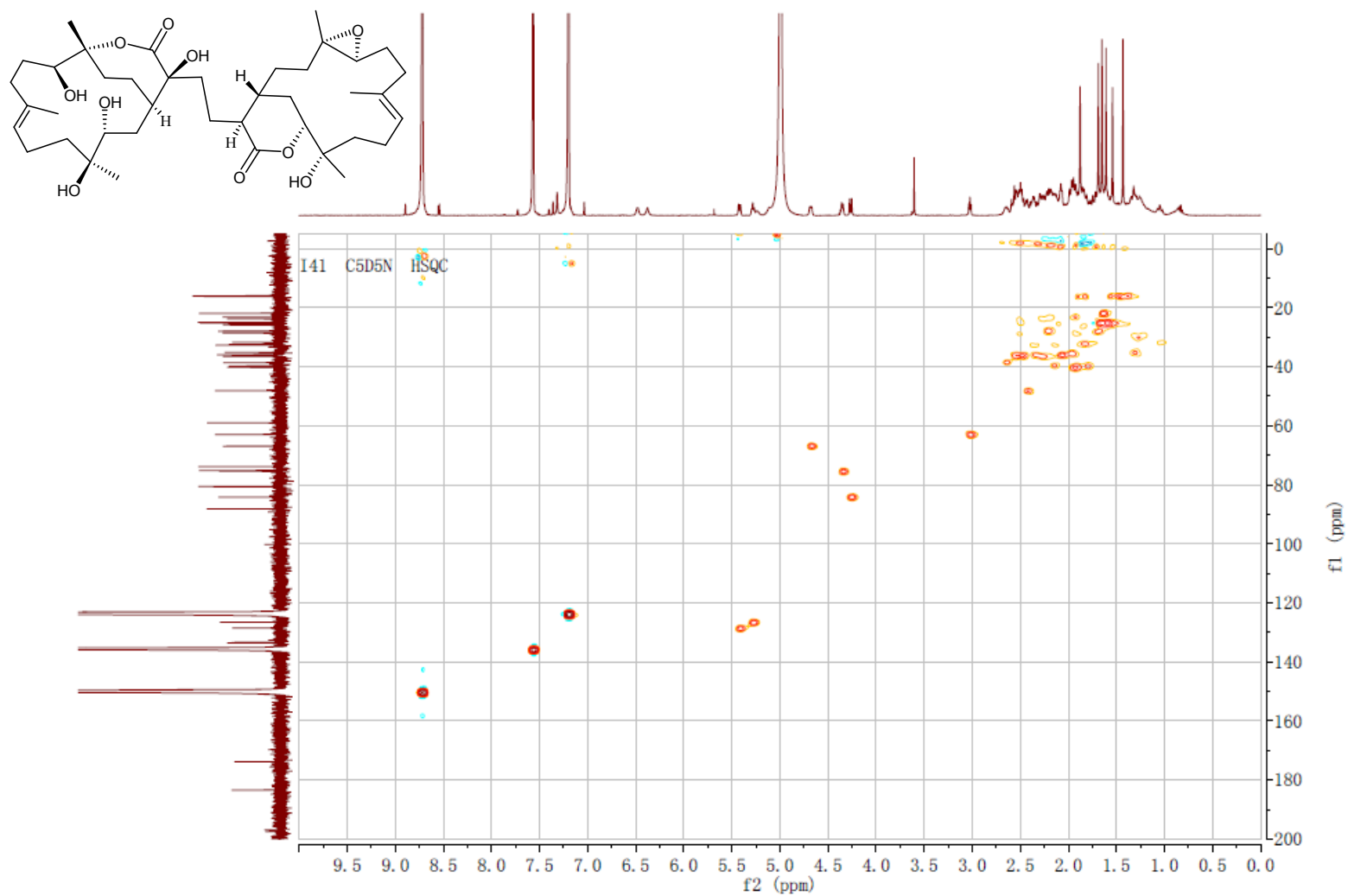


Figure S34. HMBC spectrum (400 MHz, Pyr-d₅) of sinulaflexiolide L (**8**)

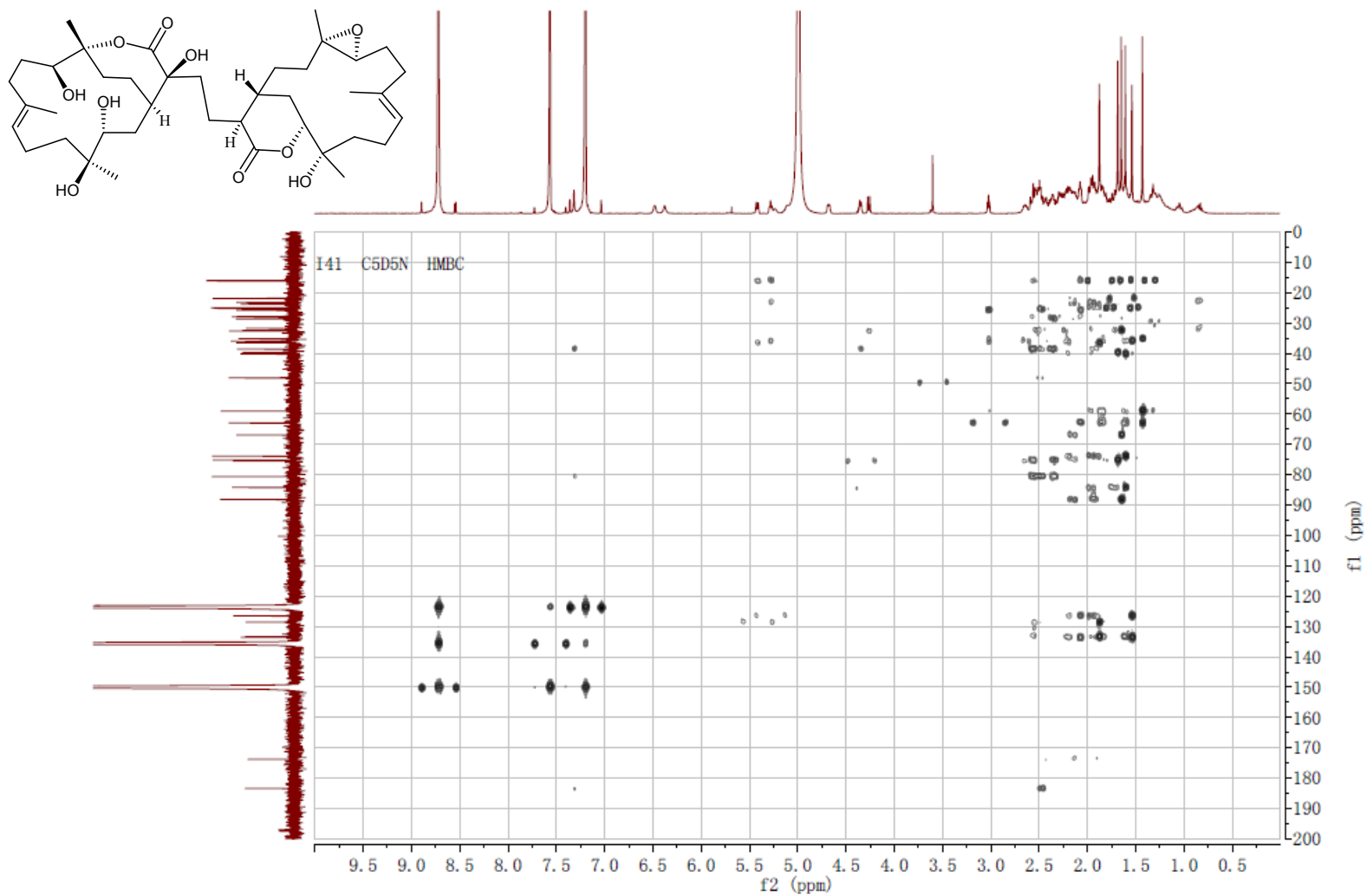


Figure S35. ^1H - ^1H COSY spectrum (400 MHz, Pyr- d_5) of sinulaflexiolide L (**8**)

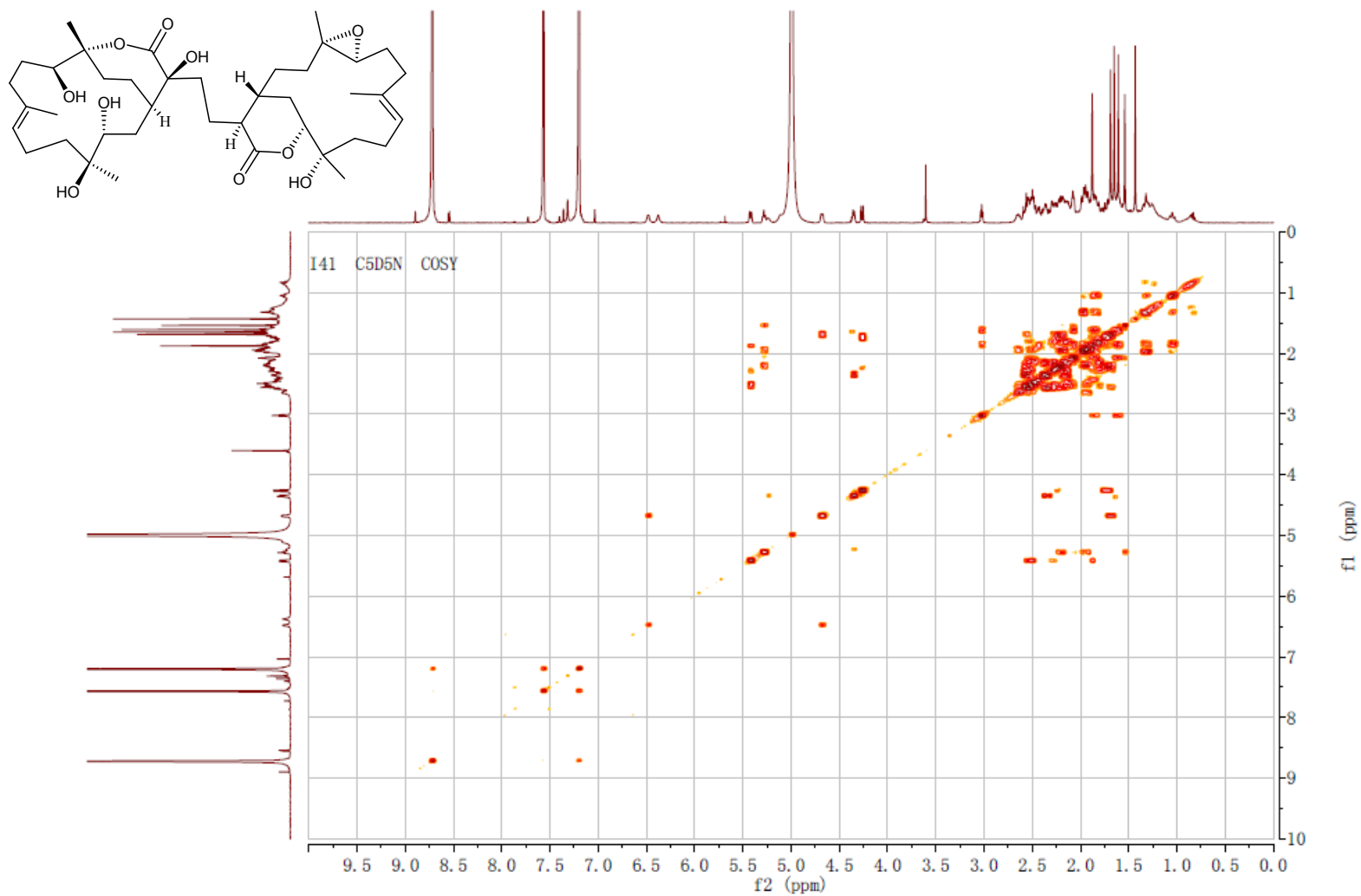
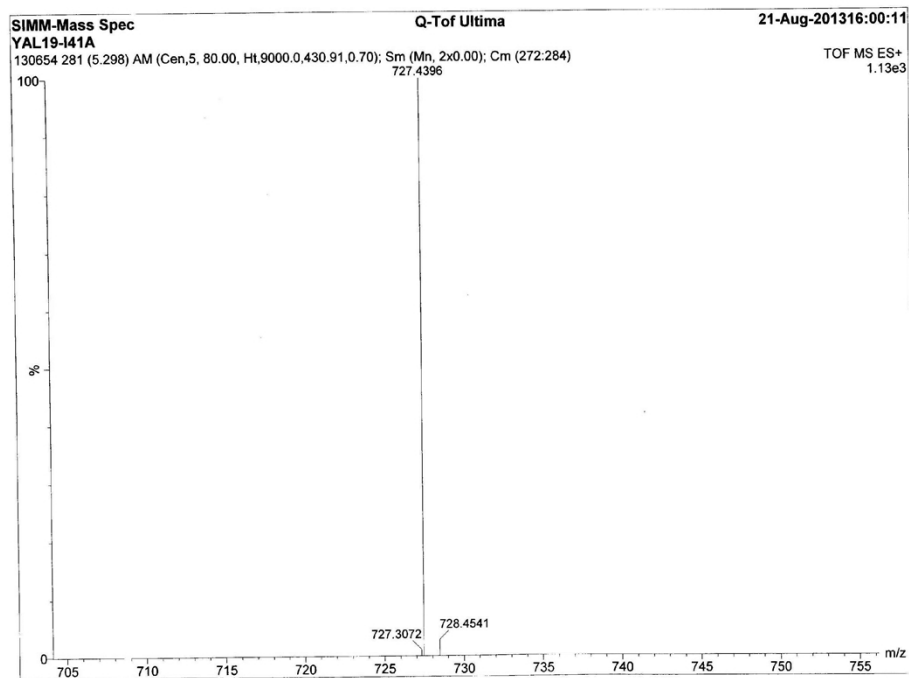


Figure S36. HRESIMS spectrum of sinulaflexiolide L (**8**)

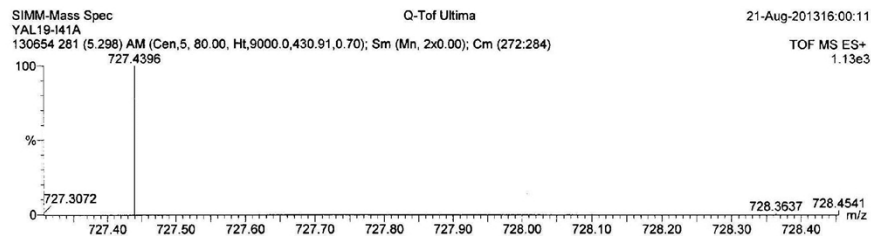


Elemental Composition Report

Page 1

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
 20 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)



Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
727.4396	100.00	727.4397	-0.1	-0.2	8.5	1	C40 H64 O10 Na