Supporting information for

Sesquiterpenoids and Xanthones from Kiwi-Associated Fungus *Bipolaris* sp. and Their Anti-Pathogenic Microorganism Activity

Jun-Jie Yu, Ying-Xue Jin, Shan-Shan Huang, and Juan He*

School of Pharmaceutical Sciences, National Demonstration Center for Experimental Ethnopharmacology Education, South-Central University for Nationalities, Wuhan 430074, People's Republic of China; junjieyu98@outlook.com (J. J. Y); Yancy6020@163.com (Y. X. J.); HuangSS1998@126.com (S. S. H.)

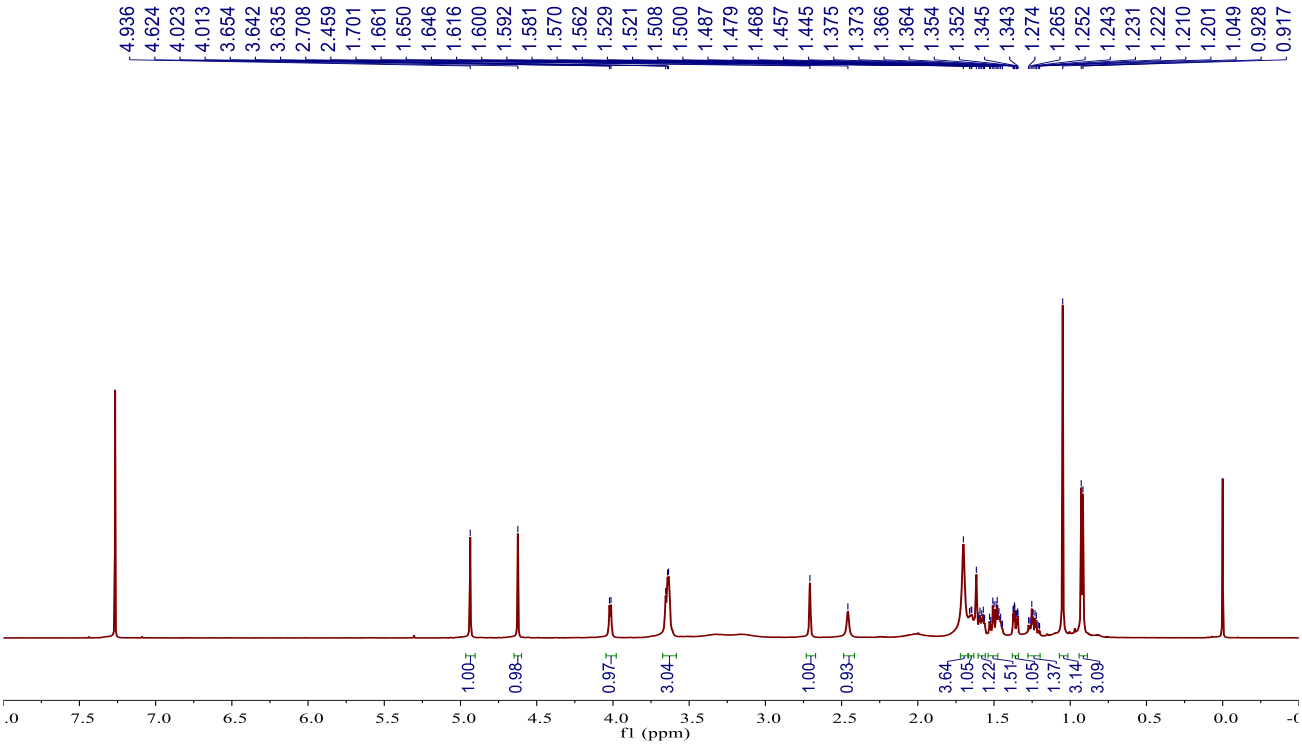
*Correspondence: 2015048@mail.scuec.edu.cn (J. H.)

Content

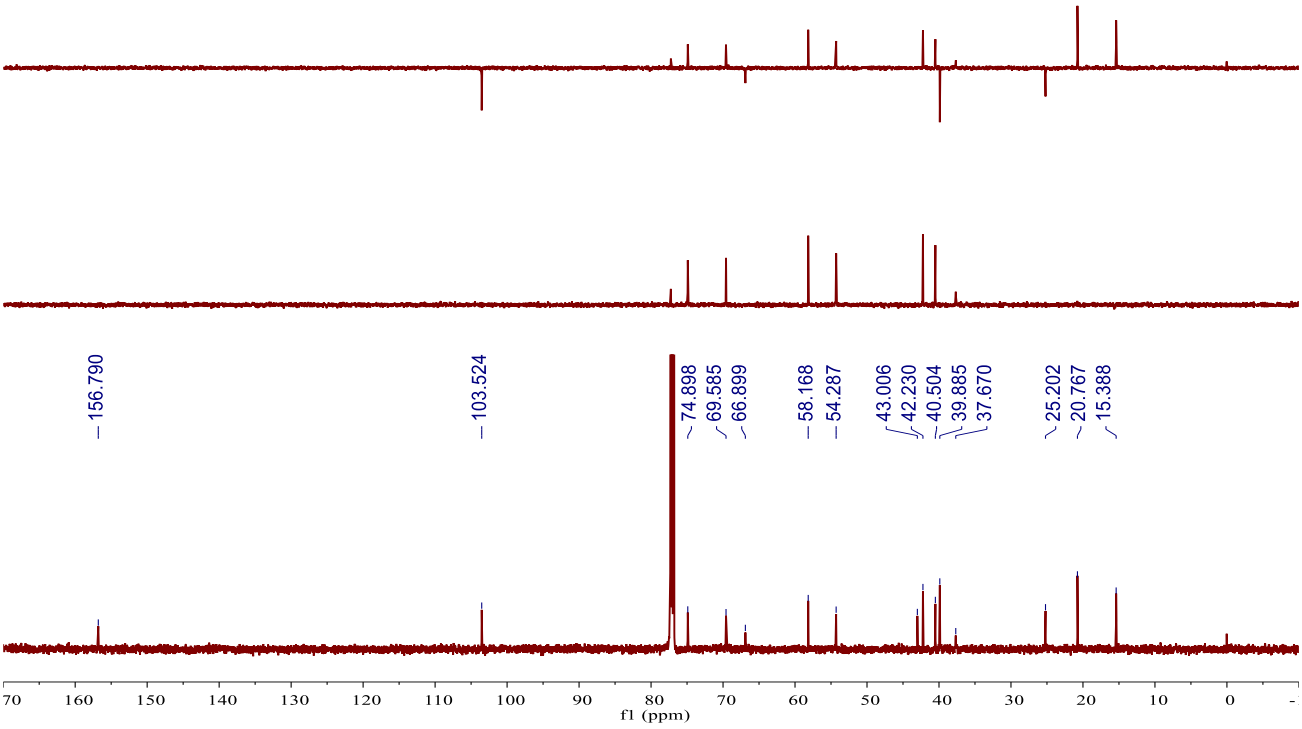
Sections S1. Supplementary of NMR, HRESIMS and CD spectra

S1.1 NMR and HRESIMS spectra of bipolarisorokin A (1)

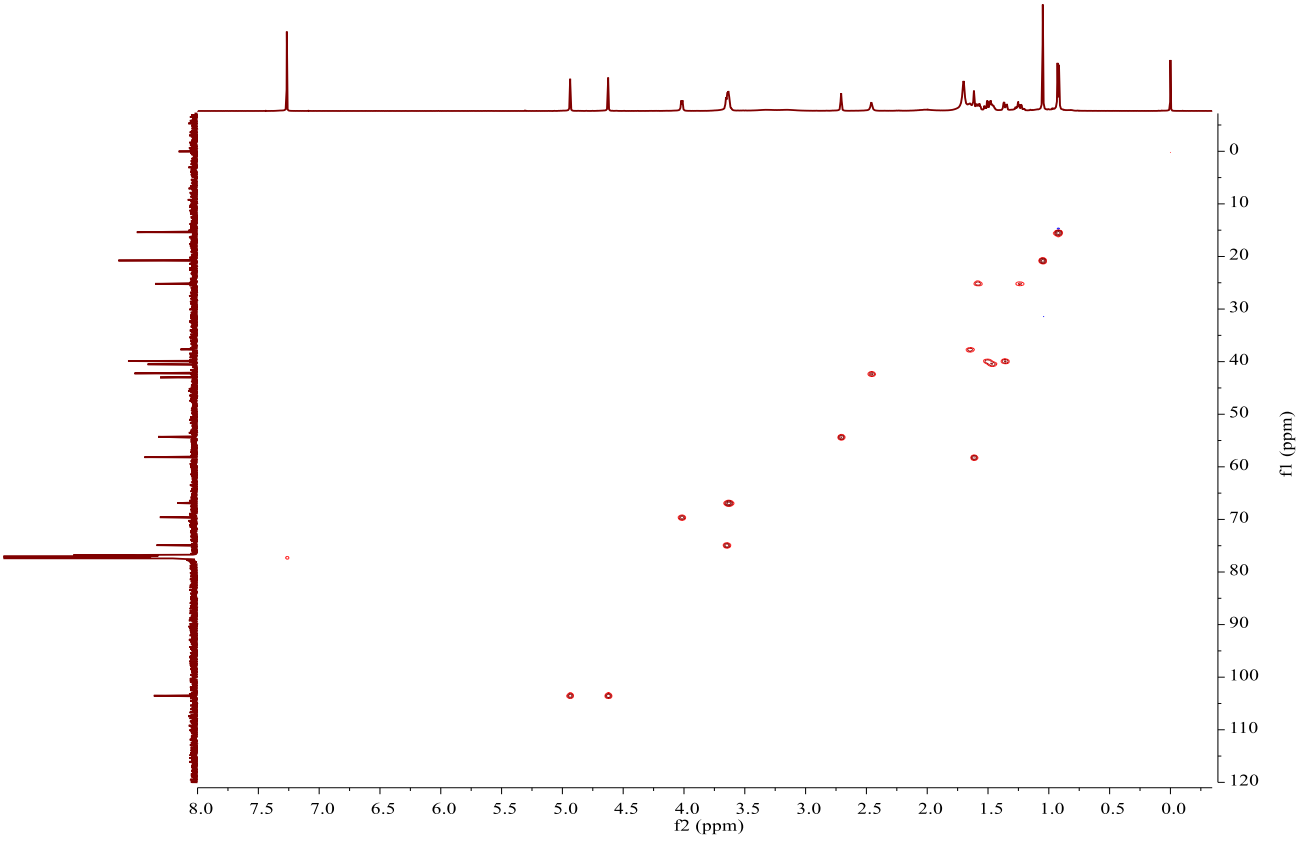
^{1}H NMR spectrum



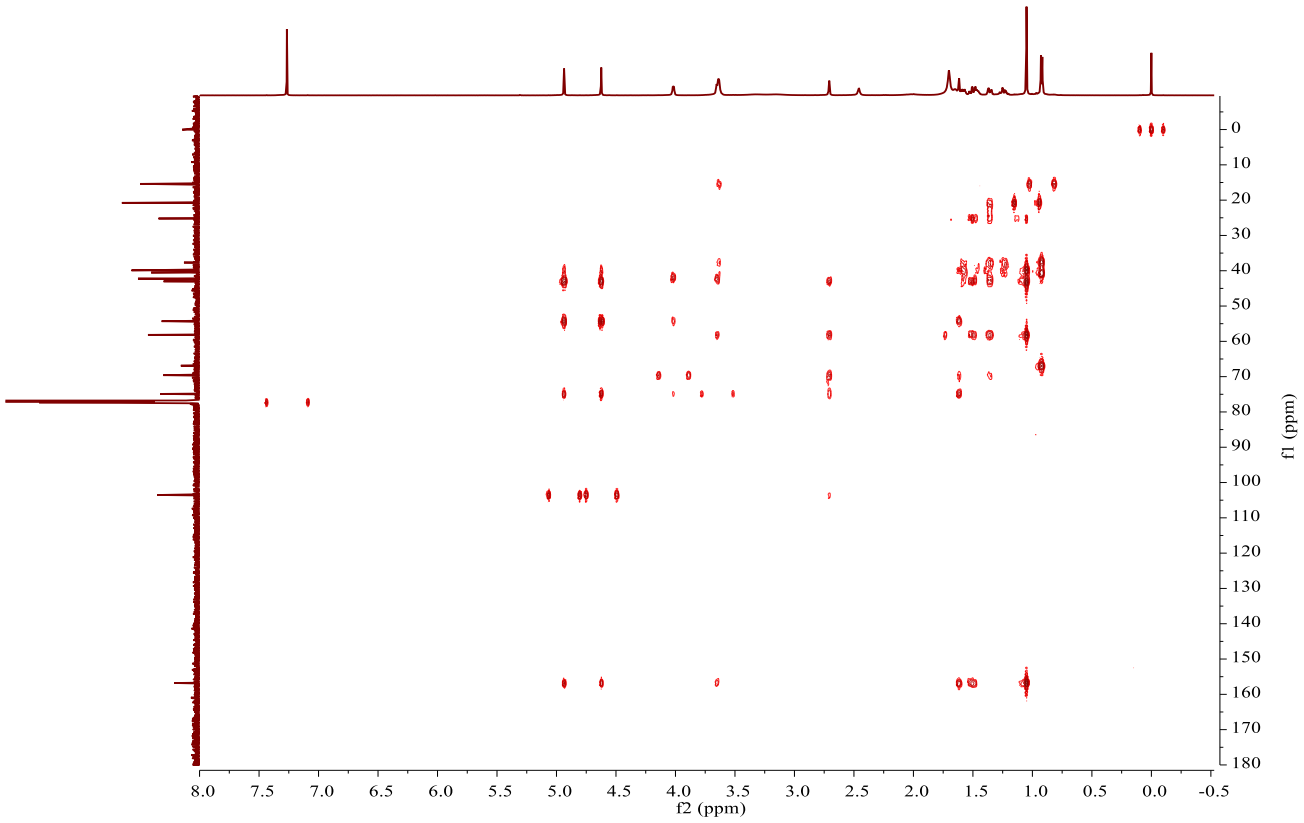
^{13}C NMR and DEPT spectra



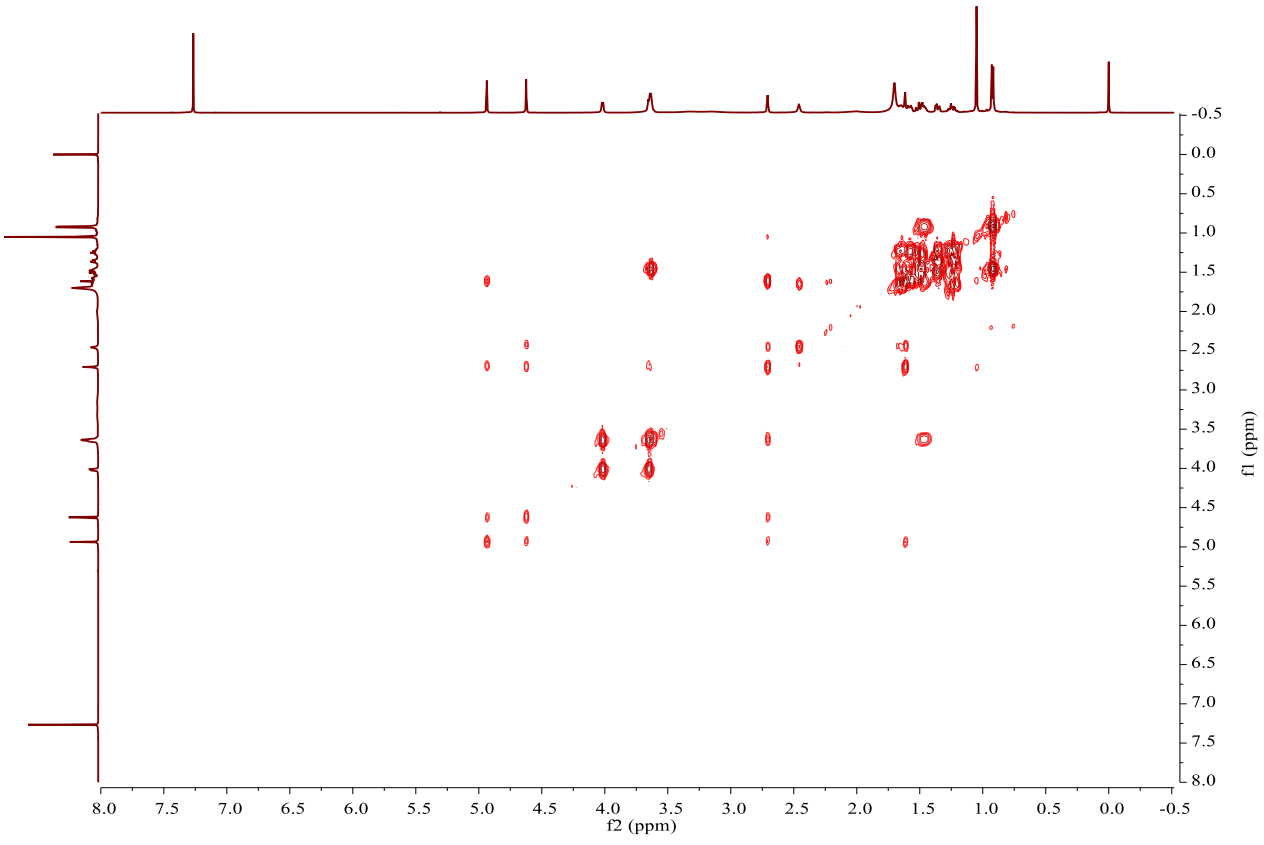
HSQC spectrum



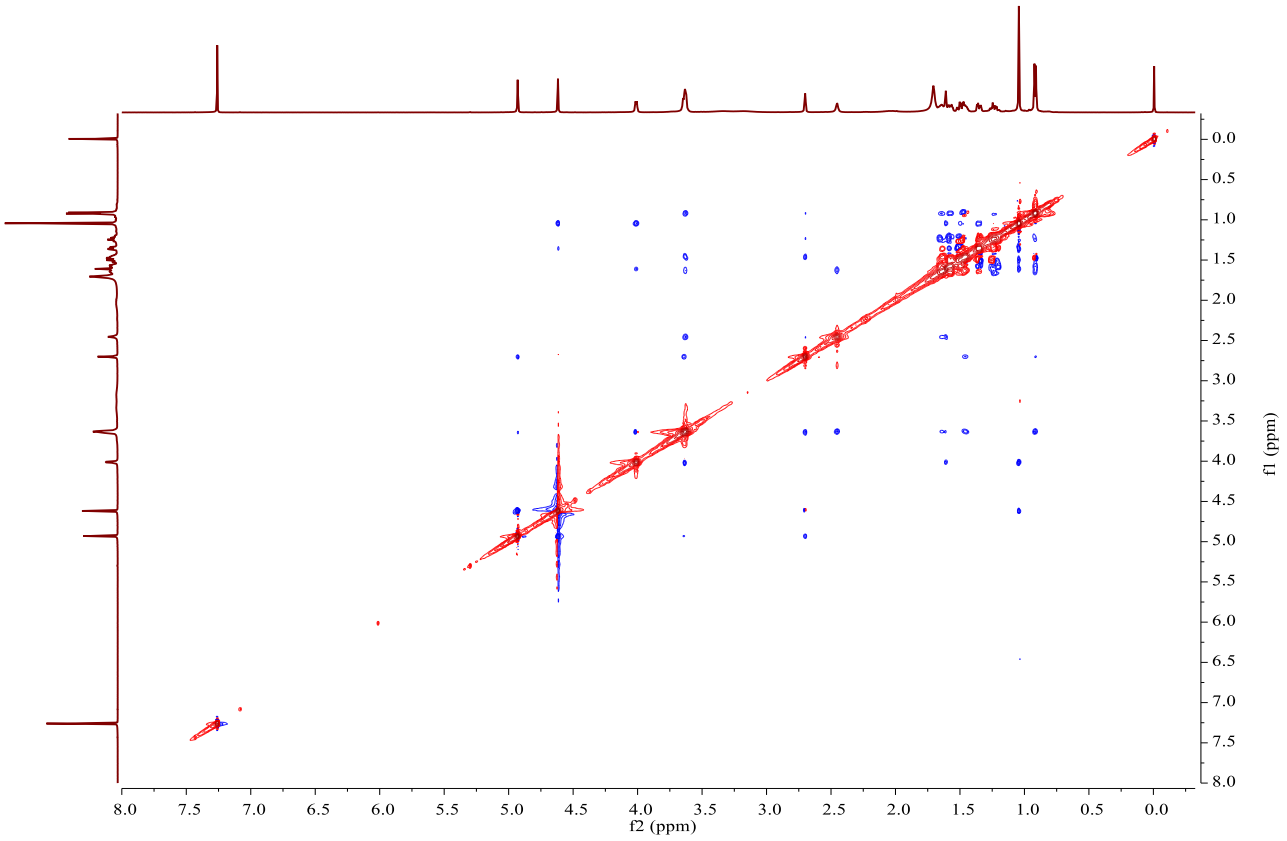
HMBC spectrum



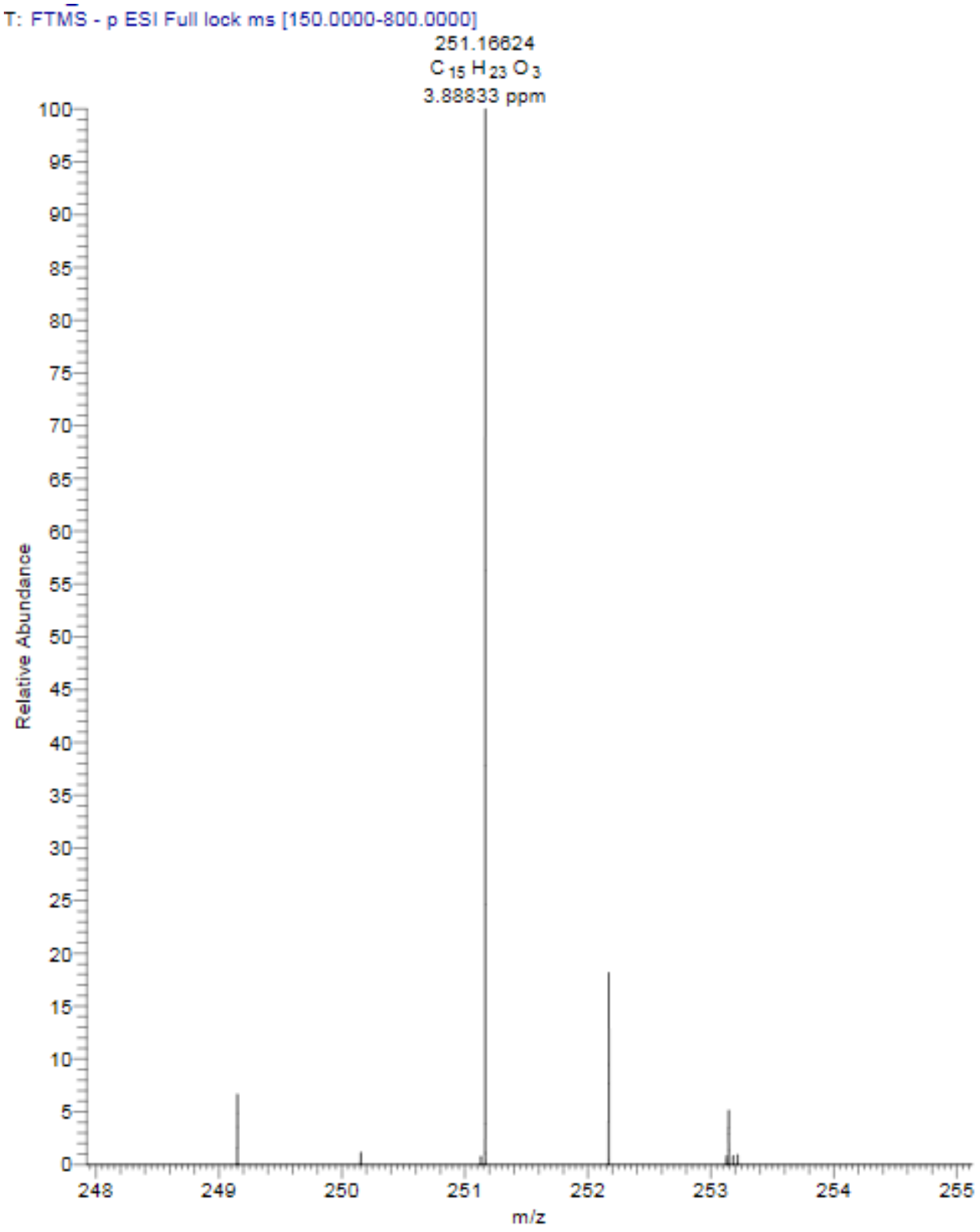
^{1}H-^{1}H COSY spectrum



ROESY spectrum

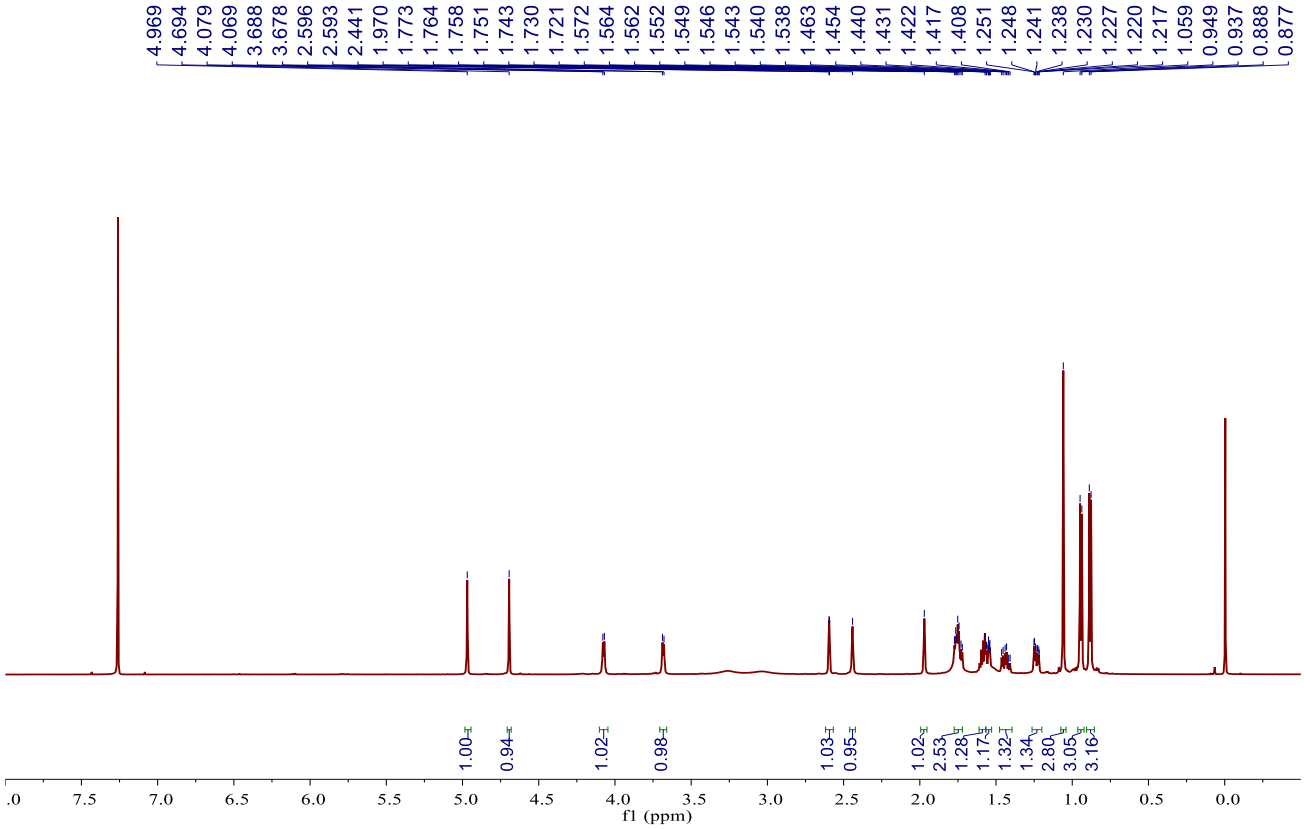


HRESIMS

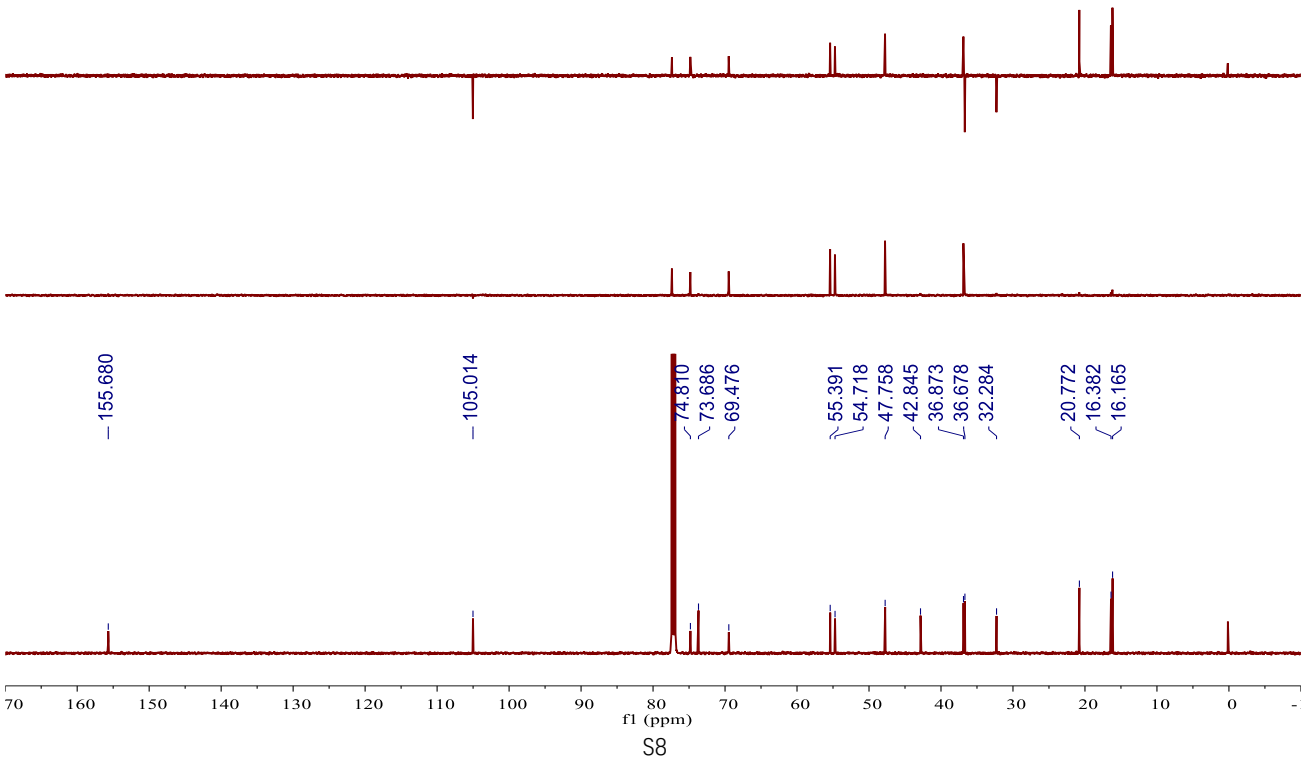

T: FTMS - p ESI Full lock ms [150.0000-800.0000]
251.16624
C 15 H 23 O 3
3.88833 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
248
249
250
251
252
253
254
255

S1.2 NMR and HRESIMS spectra of bipolarisorokin B (2)

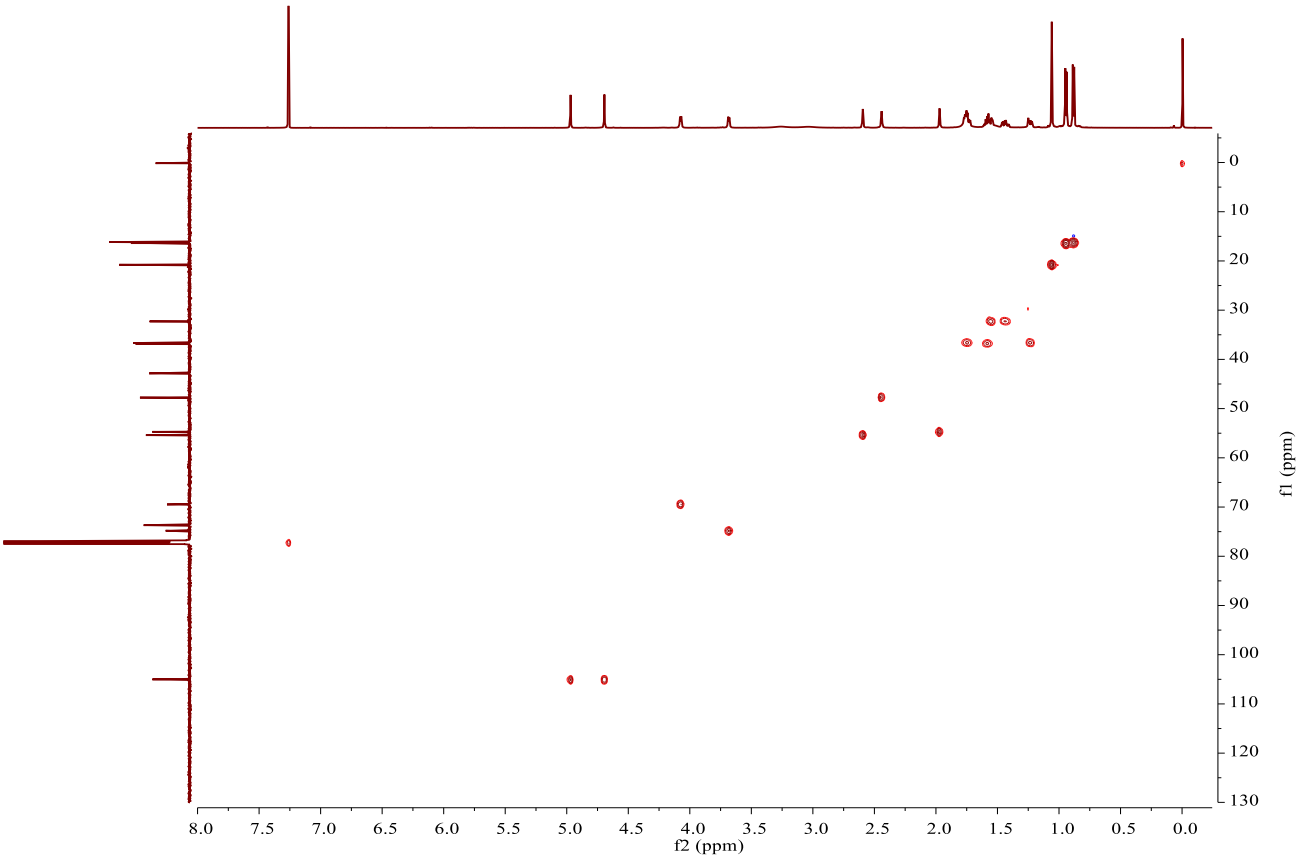
^{1}H NMR spectrum



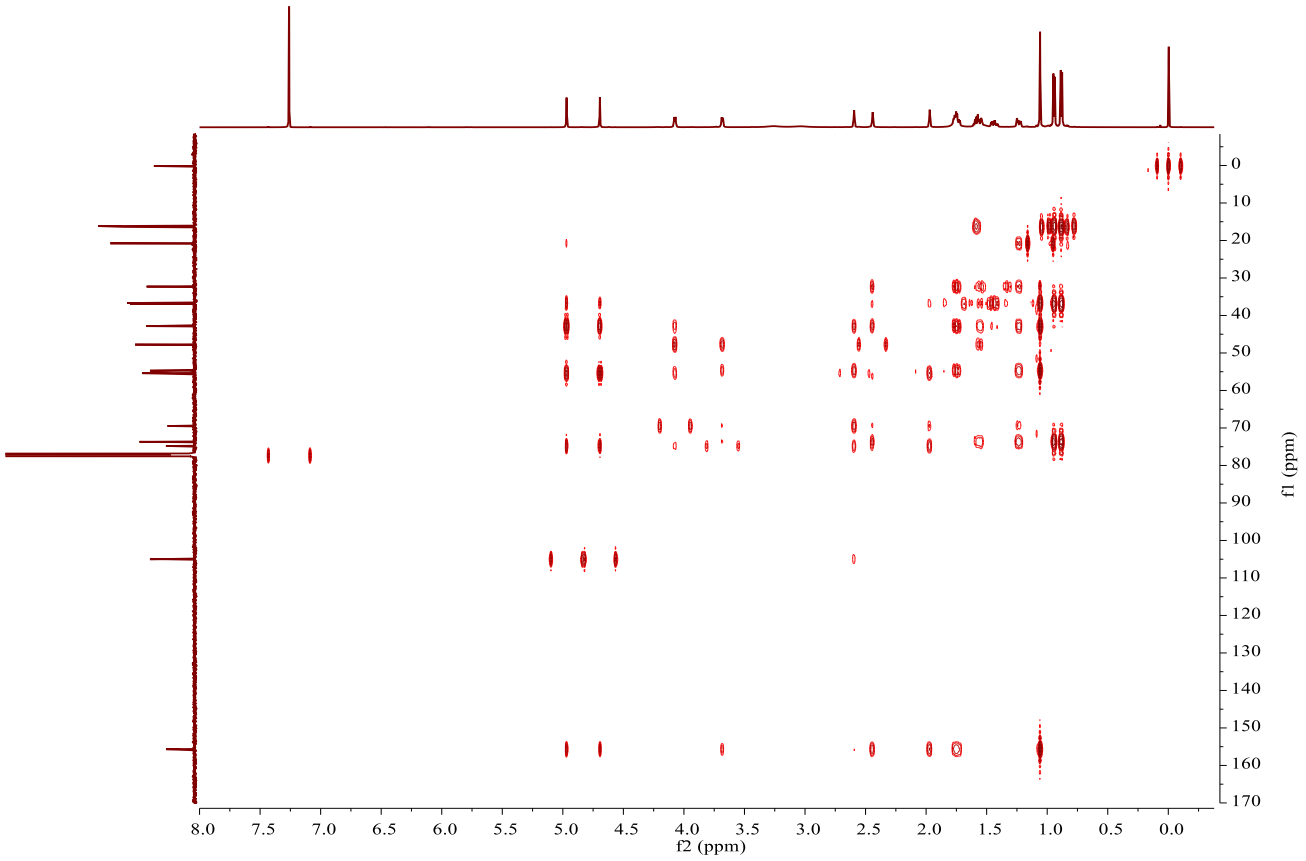
^{13}C NMR and DEPT spectra



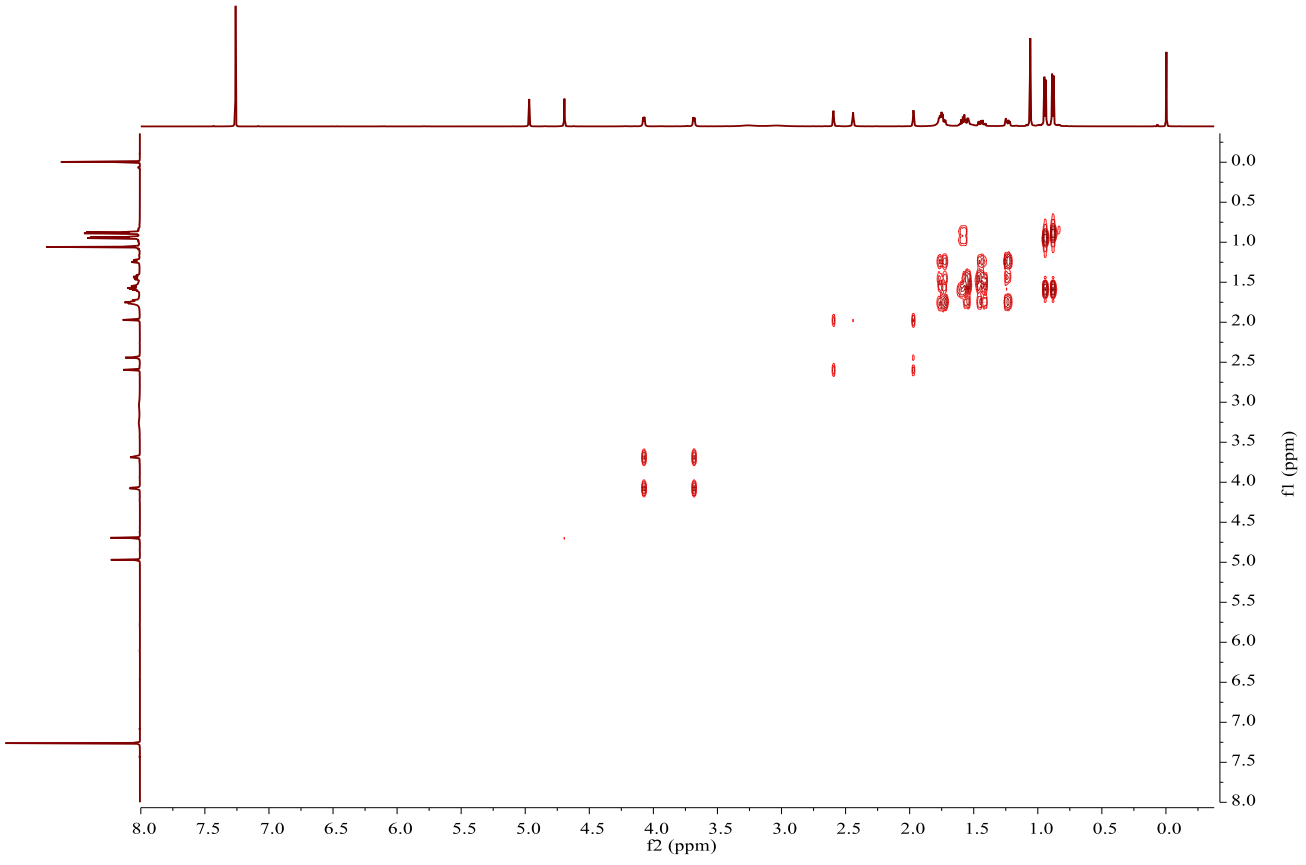
HSQC spectrum



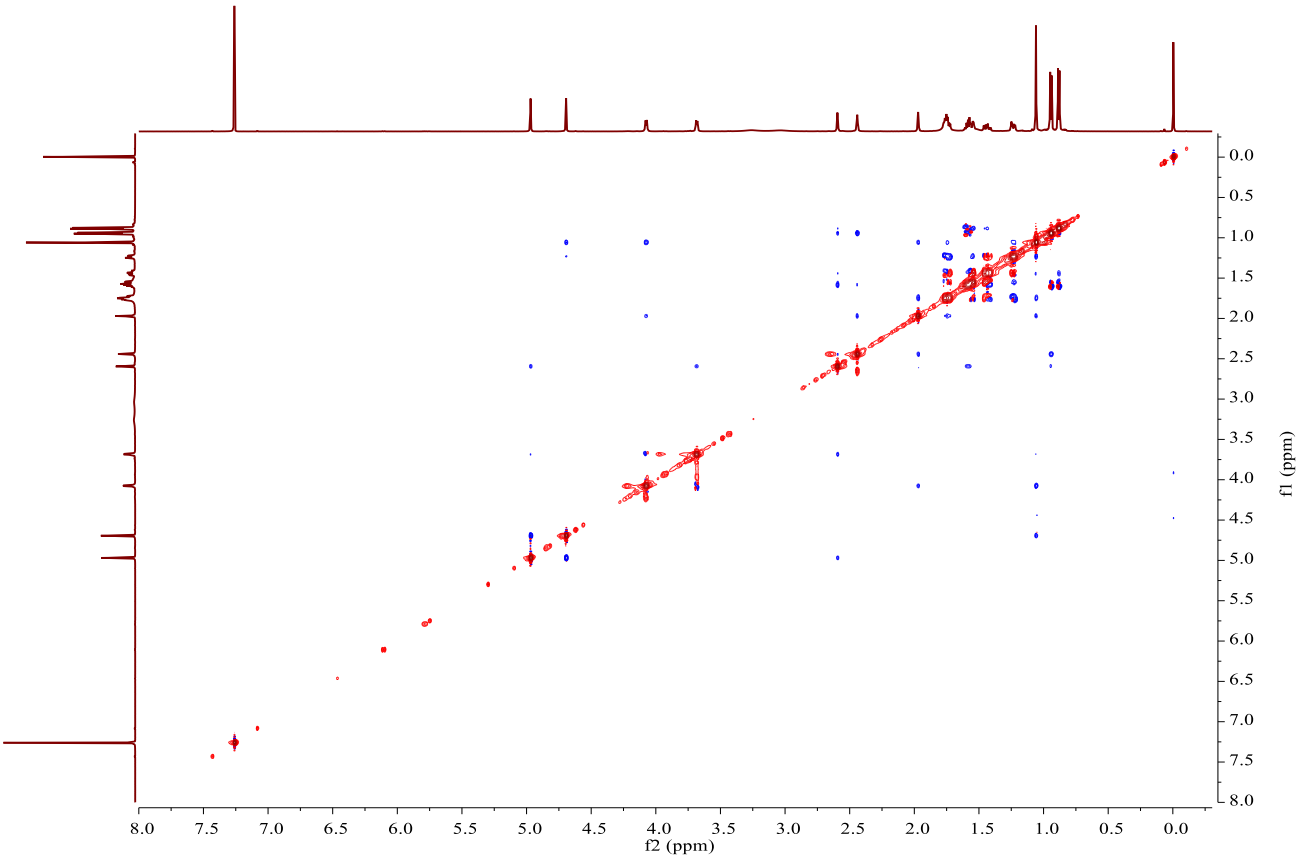
HMBC spectrum



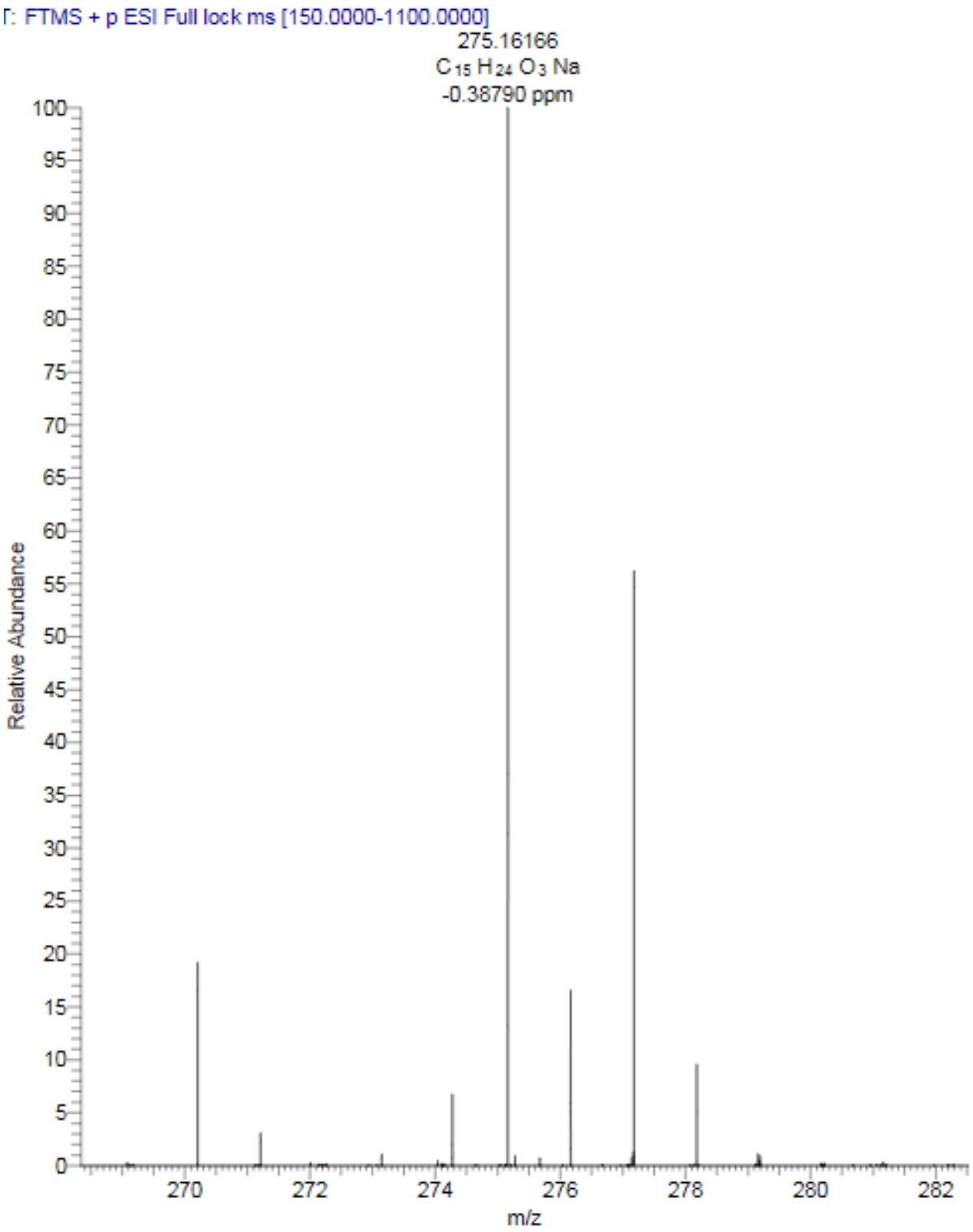
^{1}H-^{1}H COSY spectrum



ROESY spectrum

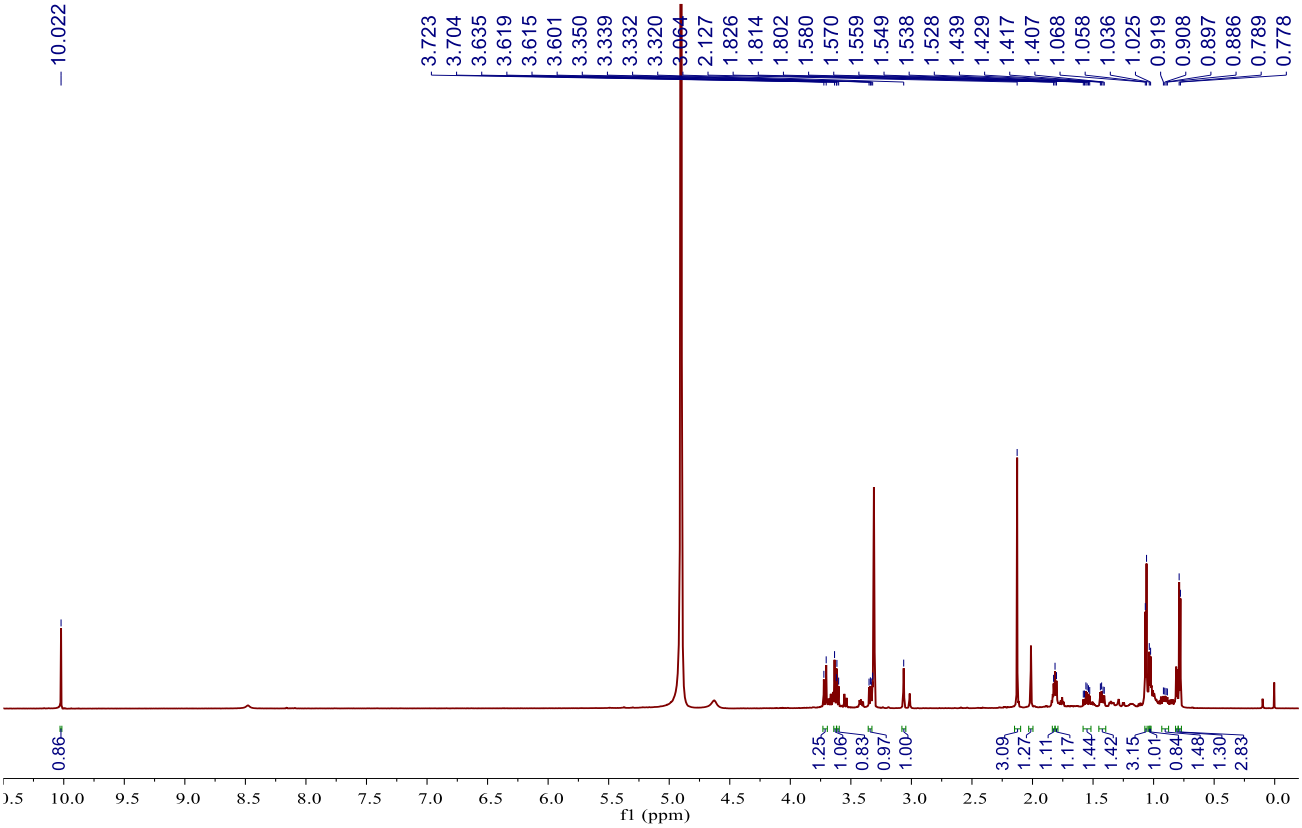


HRESIMS

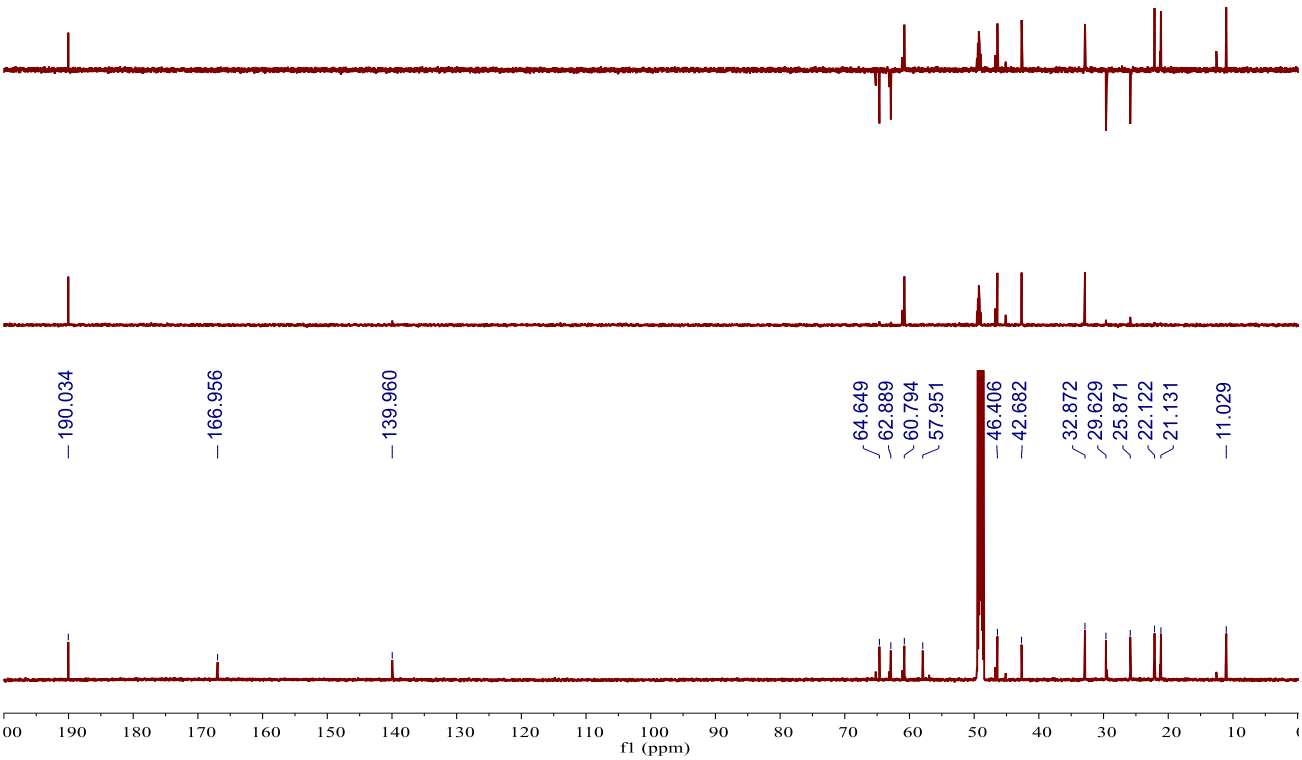

F: FTMS + p ESI Full lock ms [150.0000-1100.0000]
275.16166
C15 H24 O3 Na
-0.38790 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
270
272
274
276
278
280
282

S1.3 NMR, HRESIMS and CD spectra of bipolarisorokin C (3)

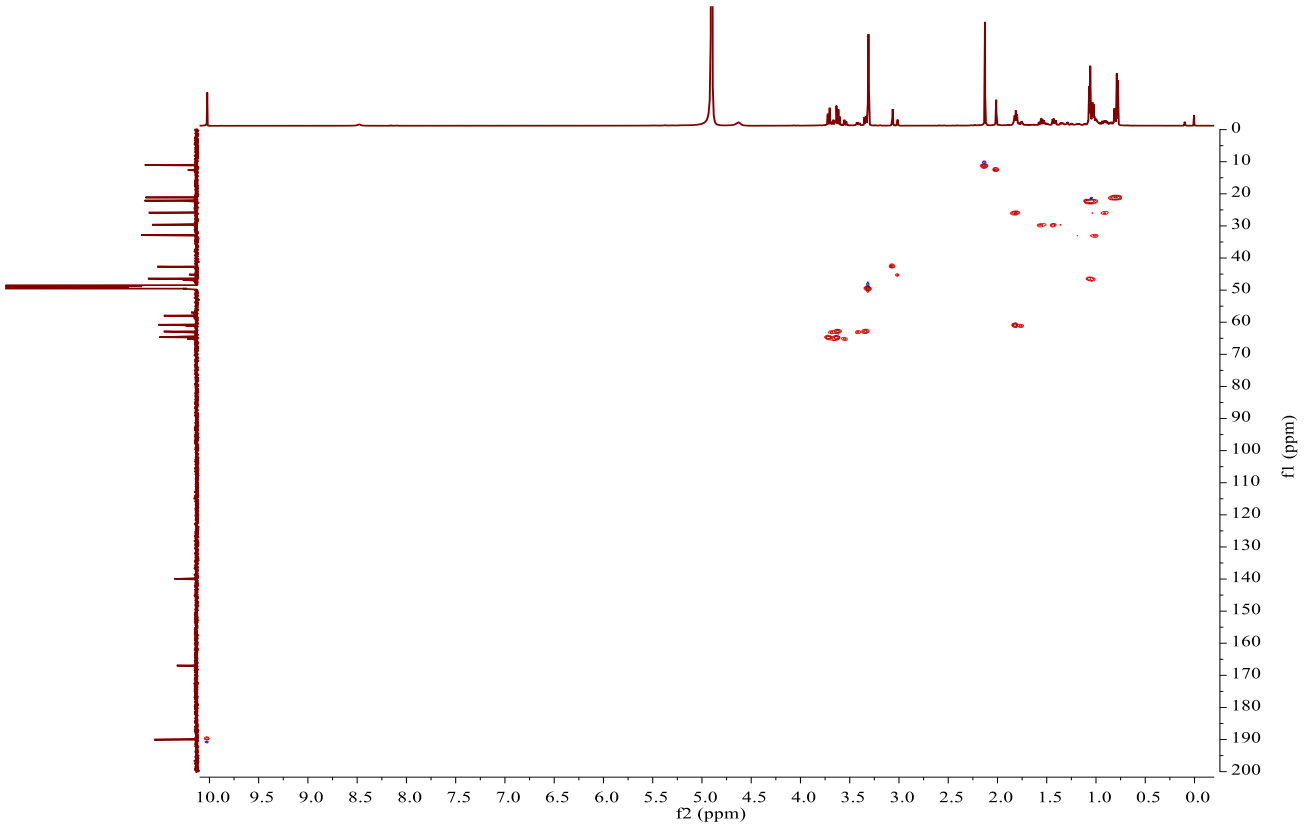
^{1}H NMR spectrum



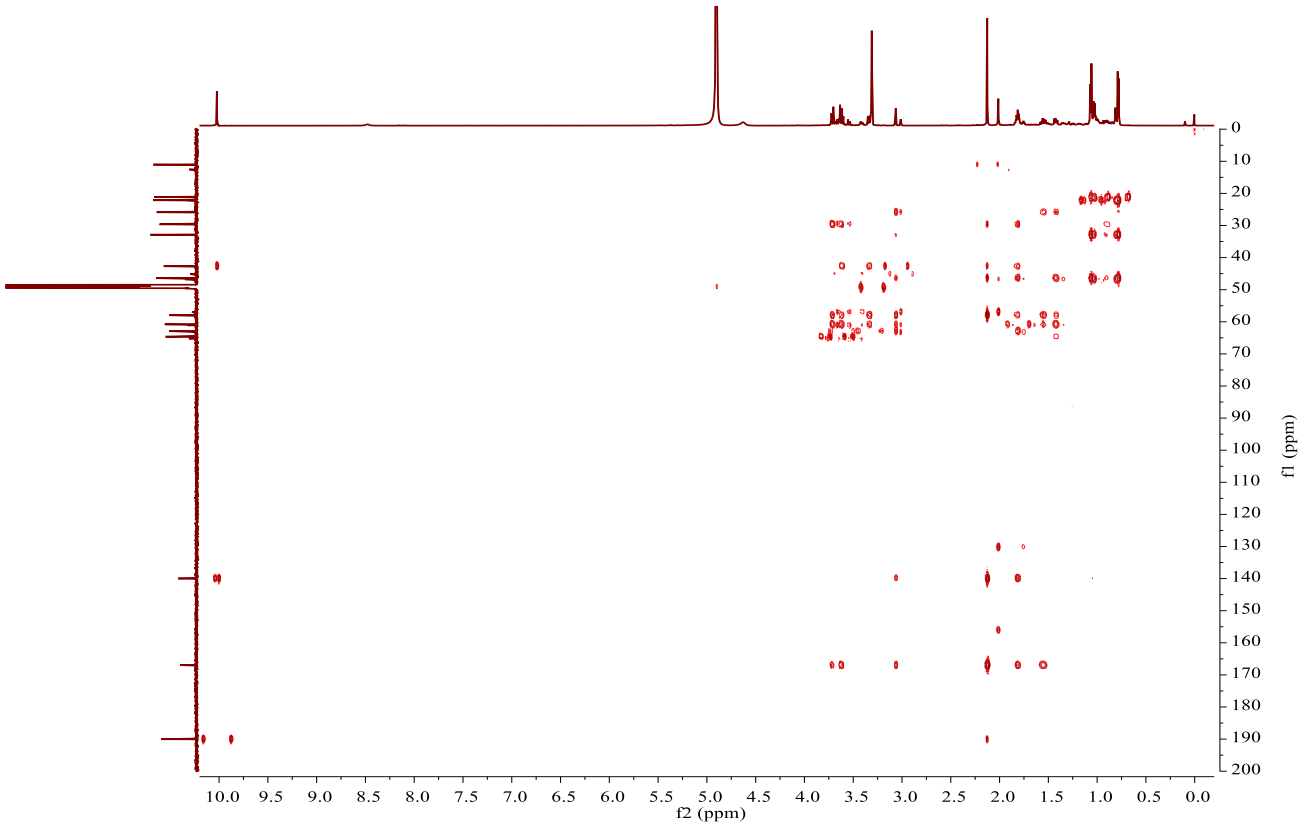
^{13}C NMR and DEPT spectra



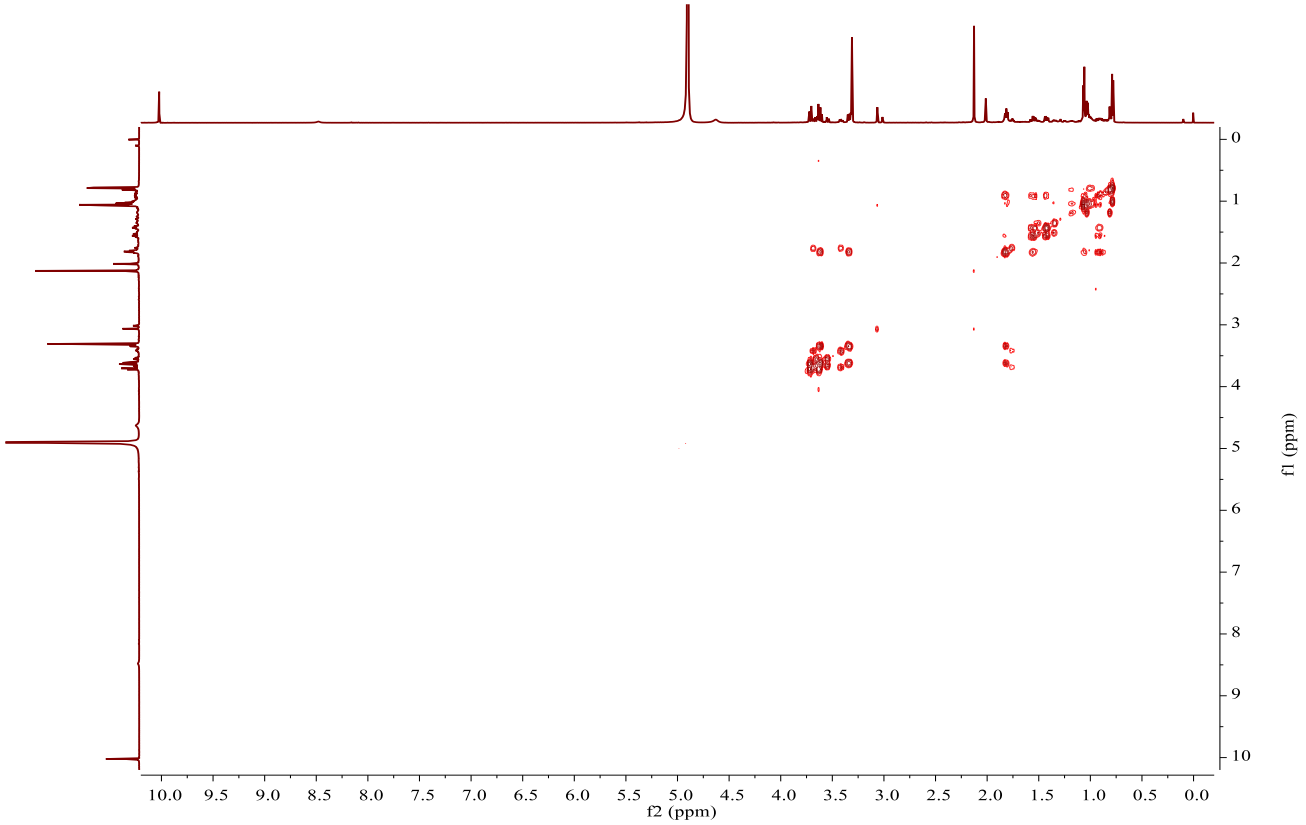
HSQC spectrum



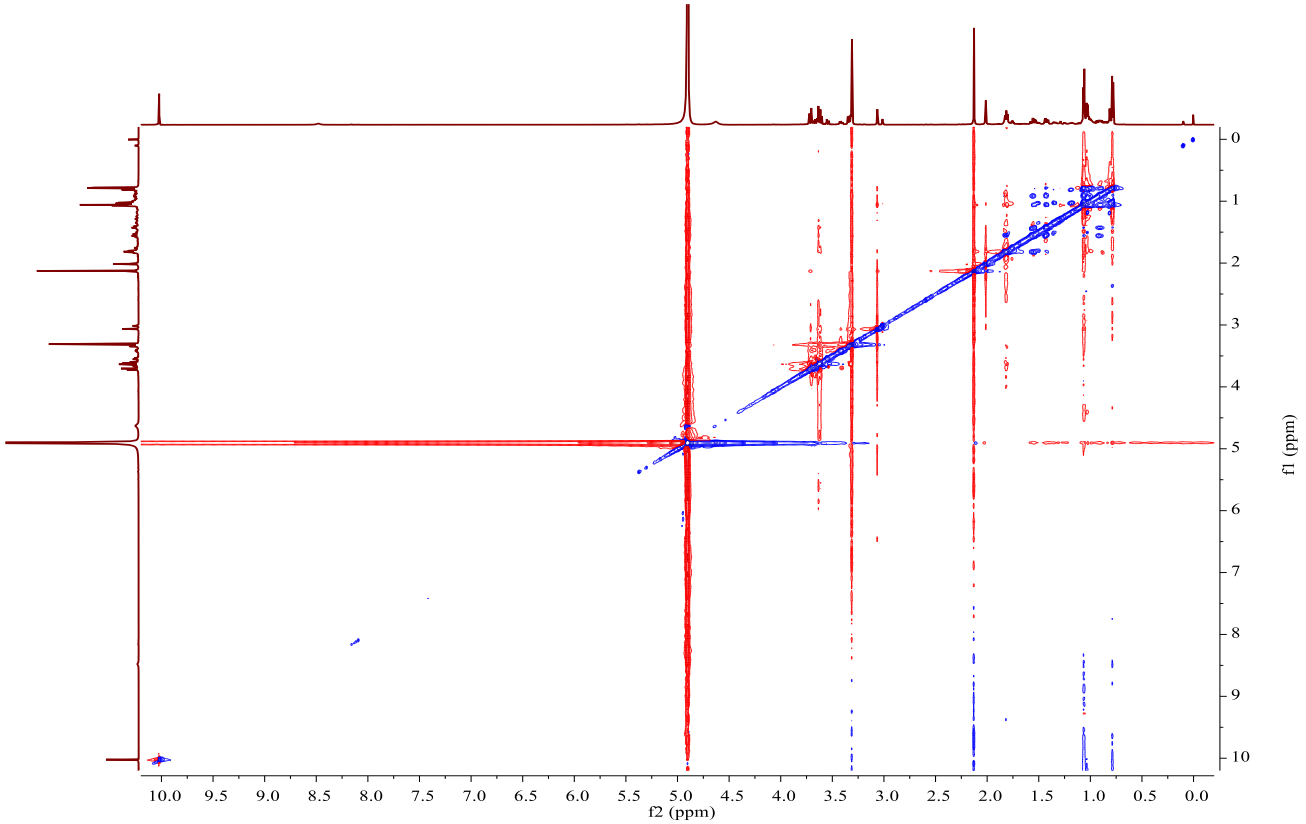
HMBC spectrum



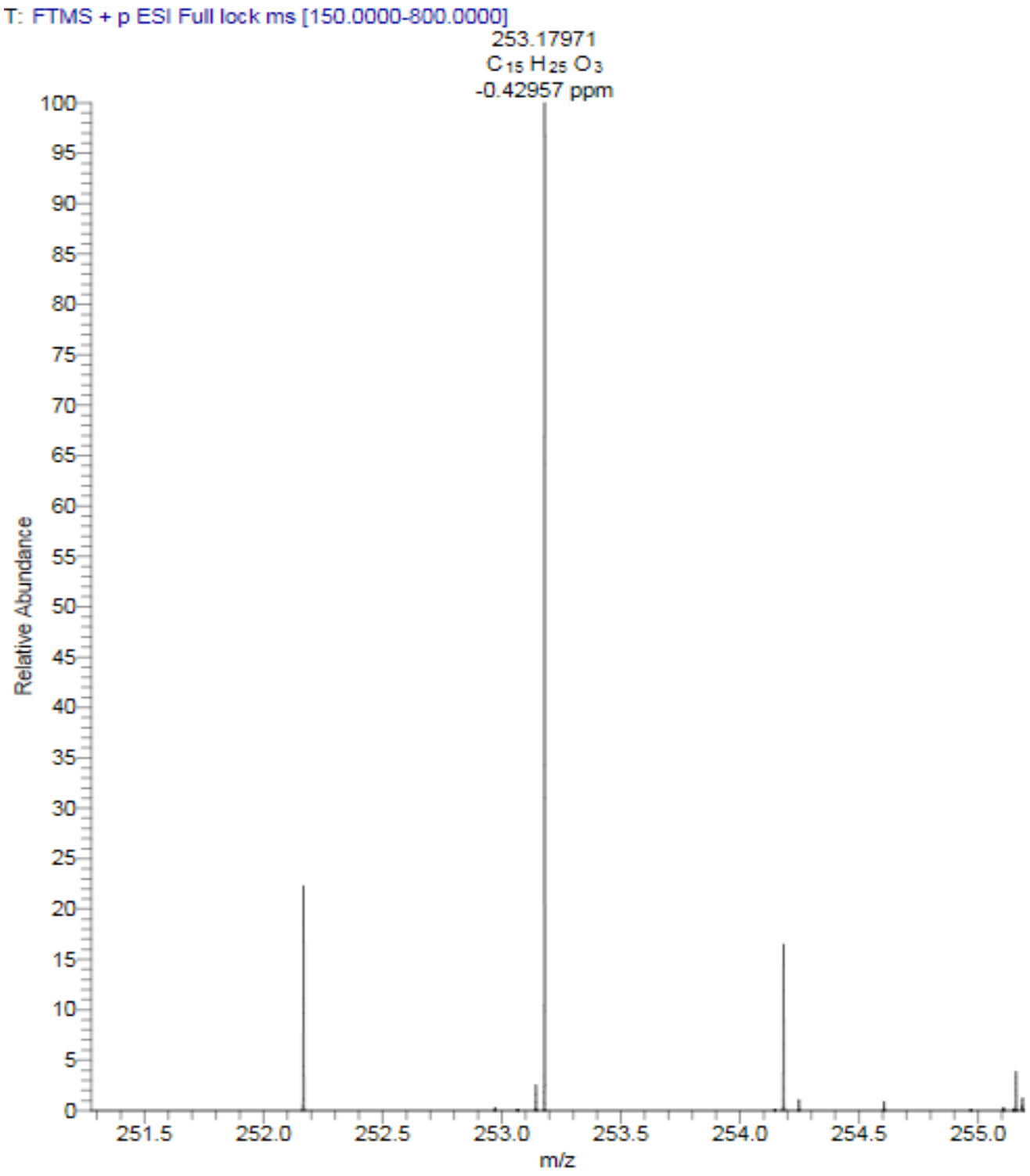
^{1}H-^{1}H COSY spectrum



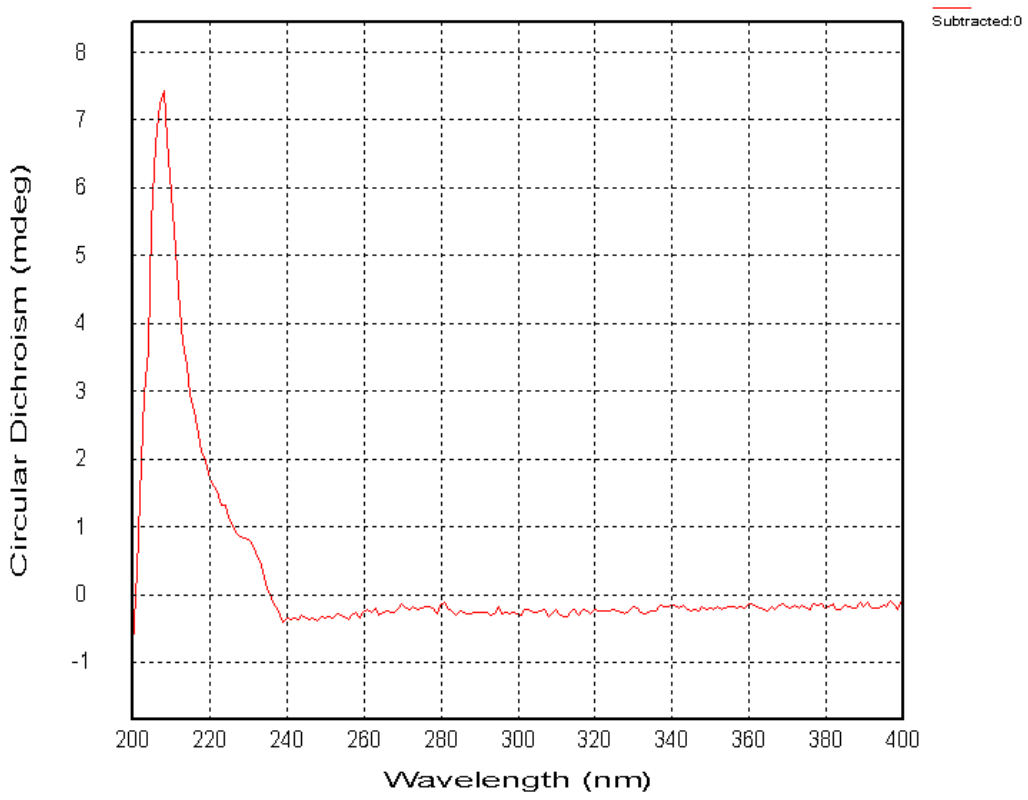
ROESY spectrum



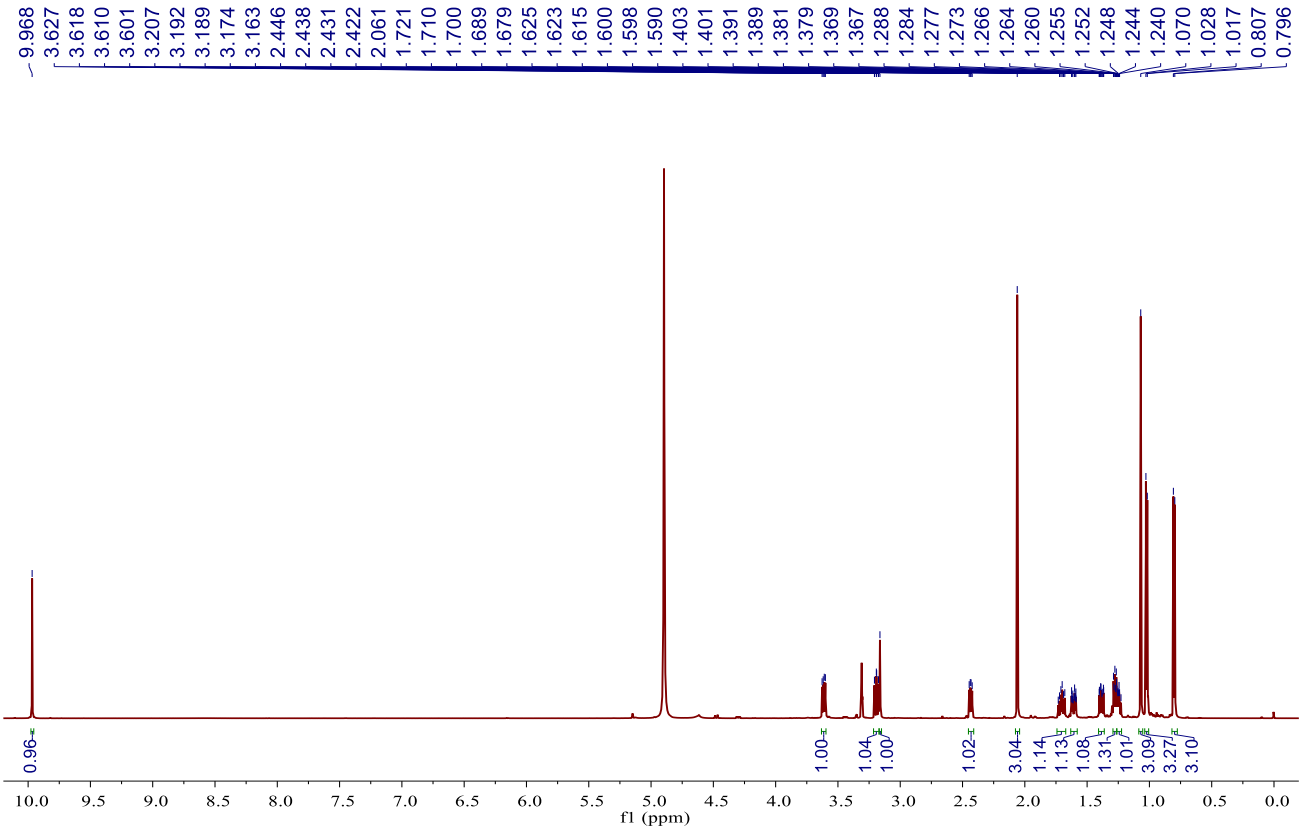
HRESIMS


T: FTMS + p ESI Full lock ms [150.0000-800.0000]
253.17971
C15 H25 O3
-0.42957 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
251.5
252.0
252.5
253.0
253.5
254.0
254.5
255.0

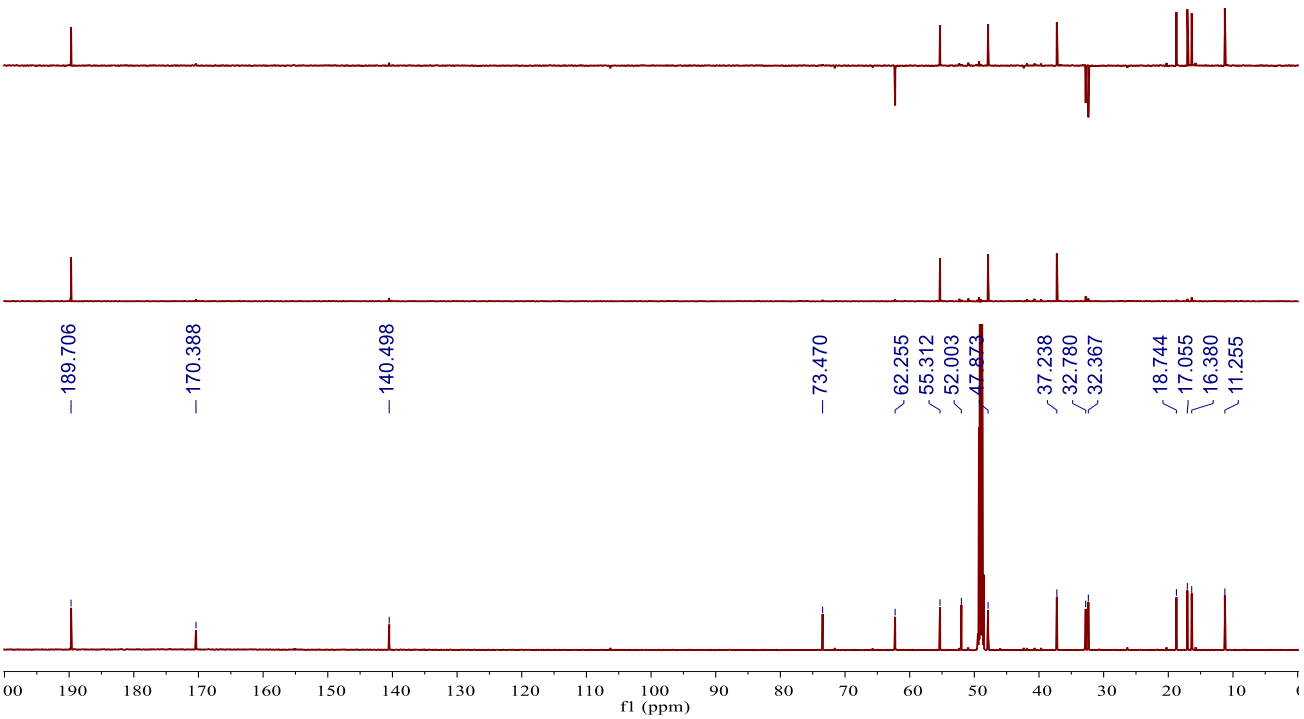
CD spectra


Subtracted:0
Circular Dichroism (mdeg)
8
7
6
5
4
3
2
1
0
-1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

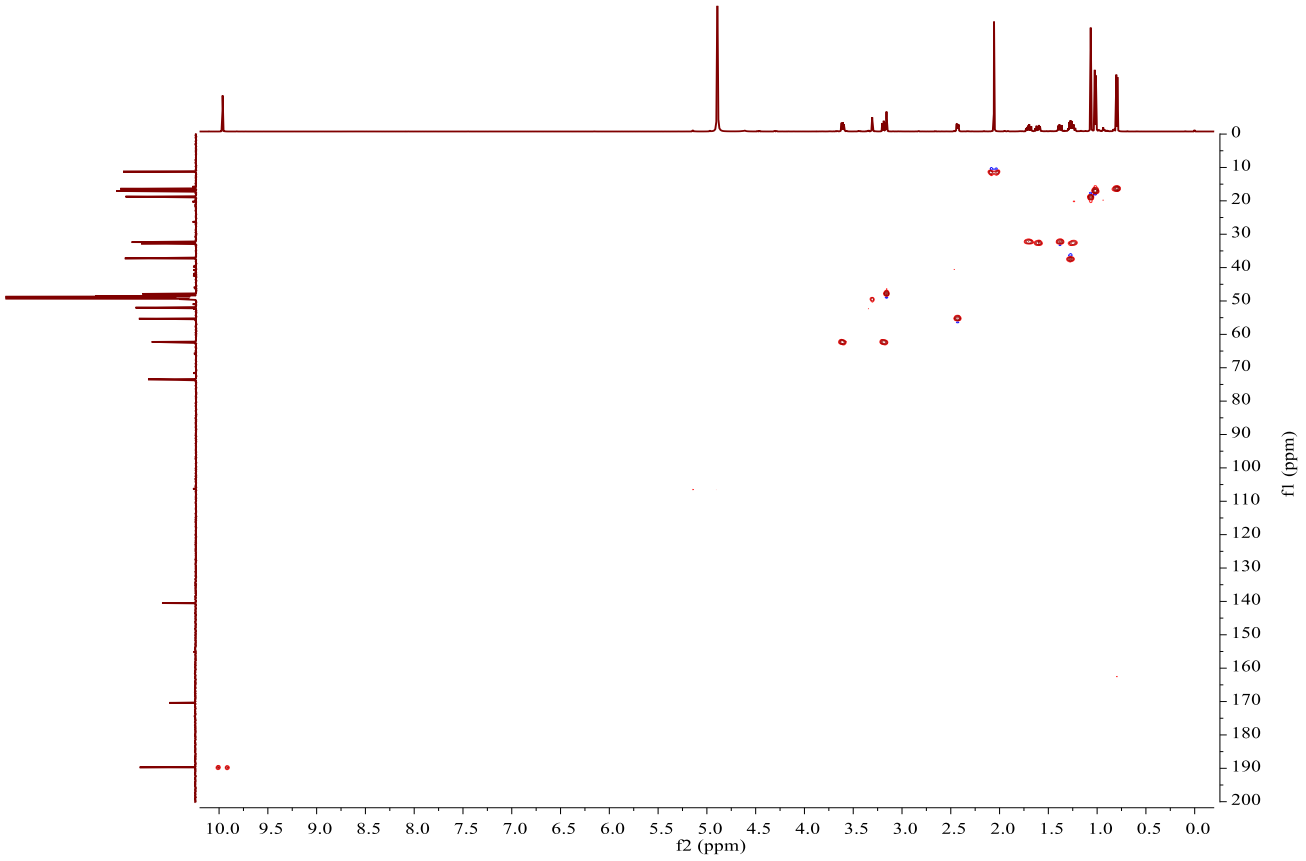
S1.4 NMR, HRESIMS and CD spectra of bipolarisorokin D (4)



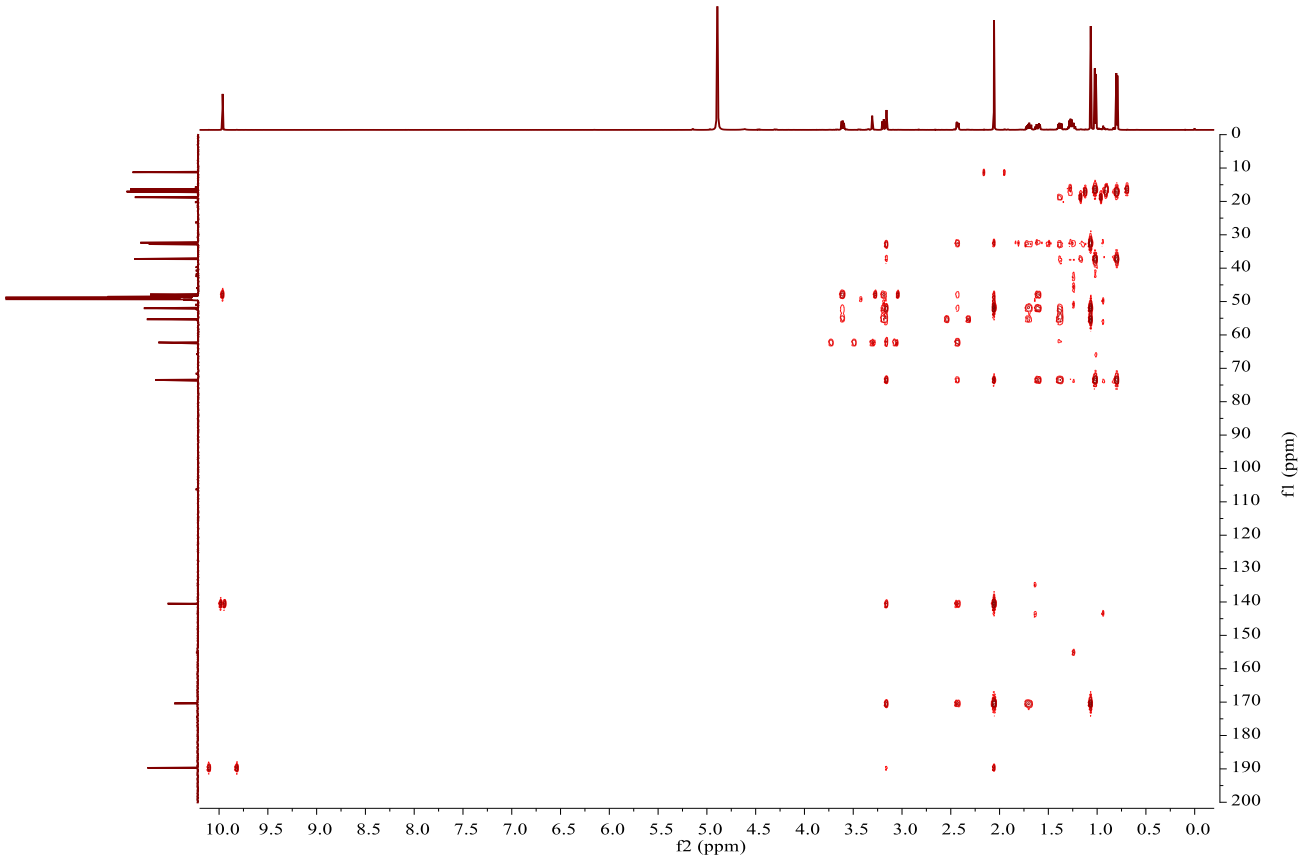
^{13}C NMR and DEPT spectra



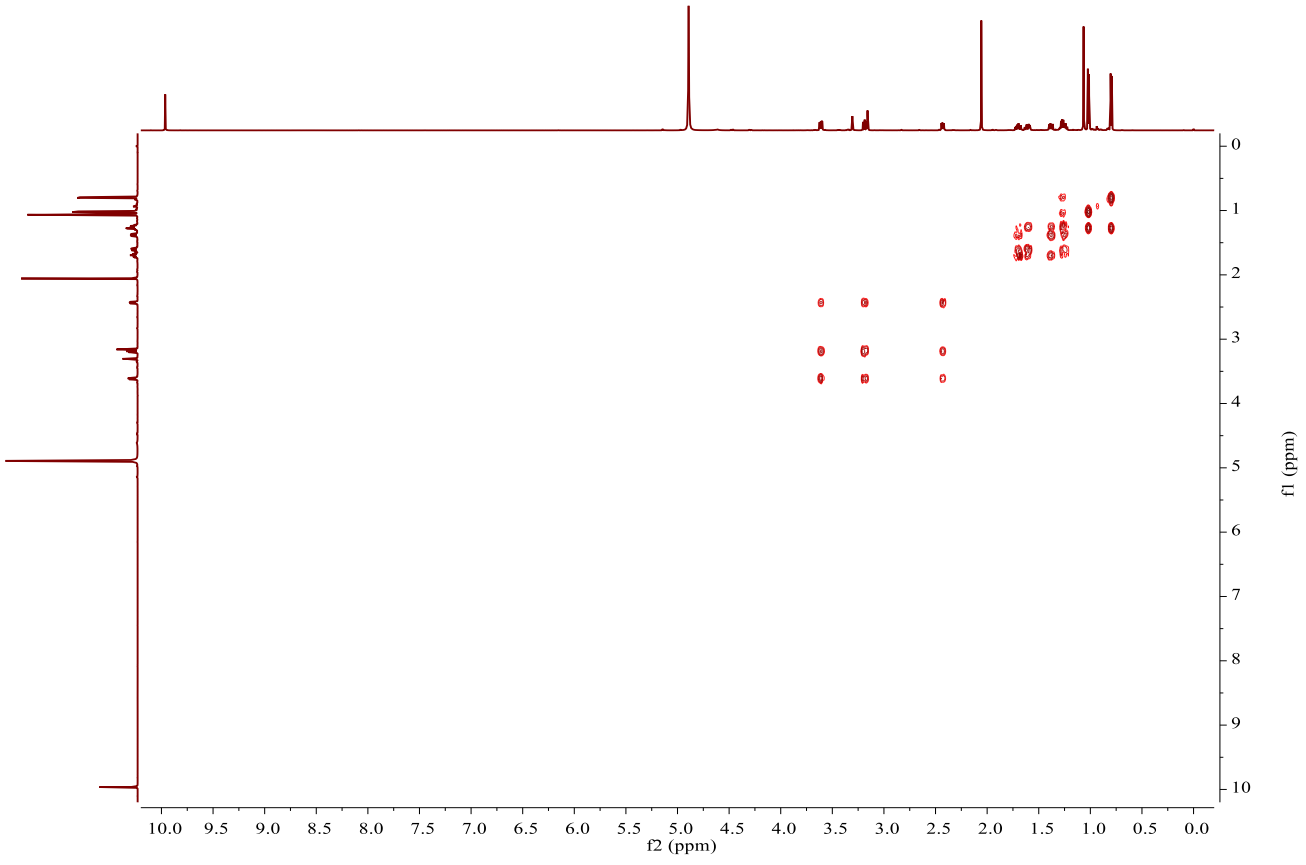
HSQC spectrum



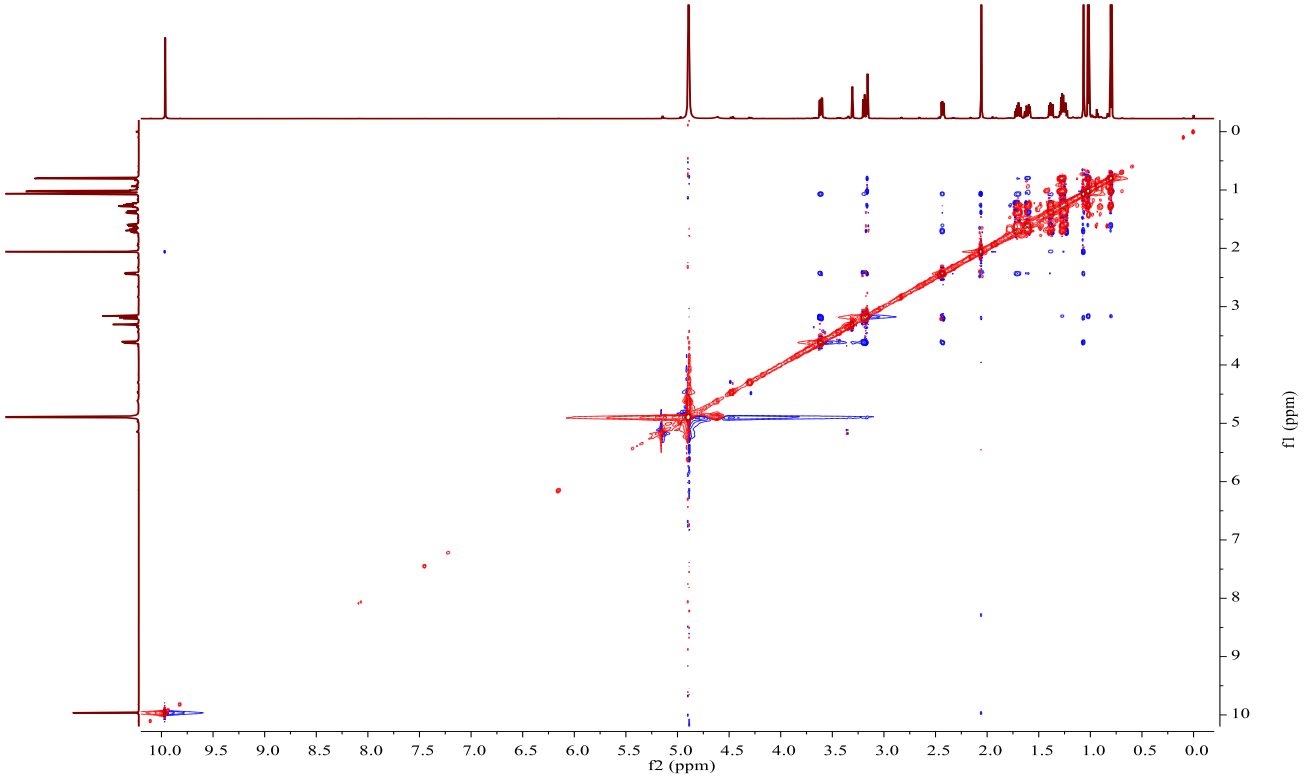
HMBC spectrum



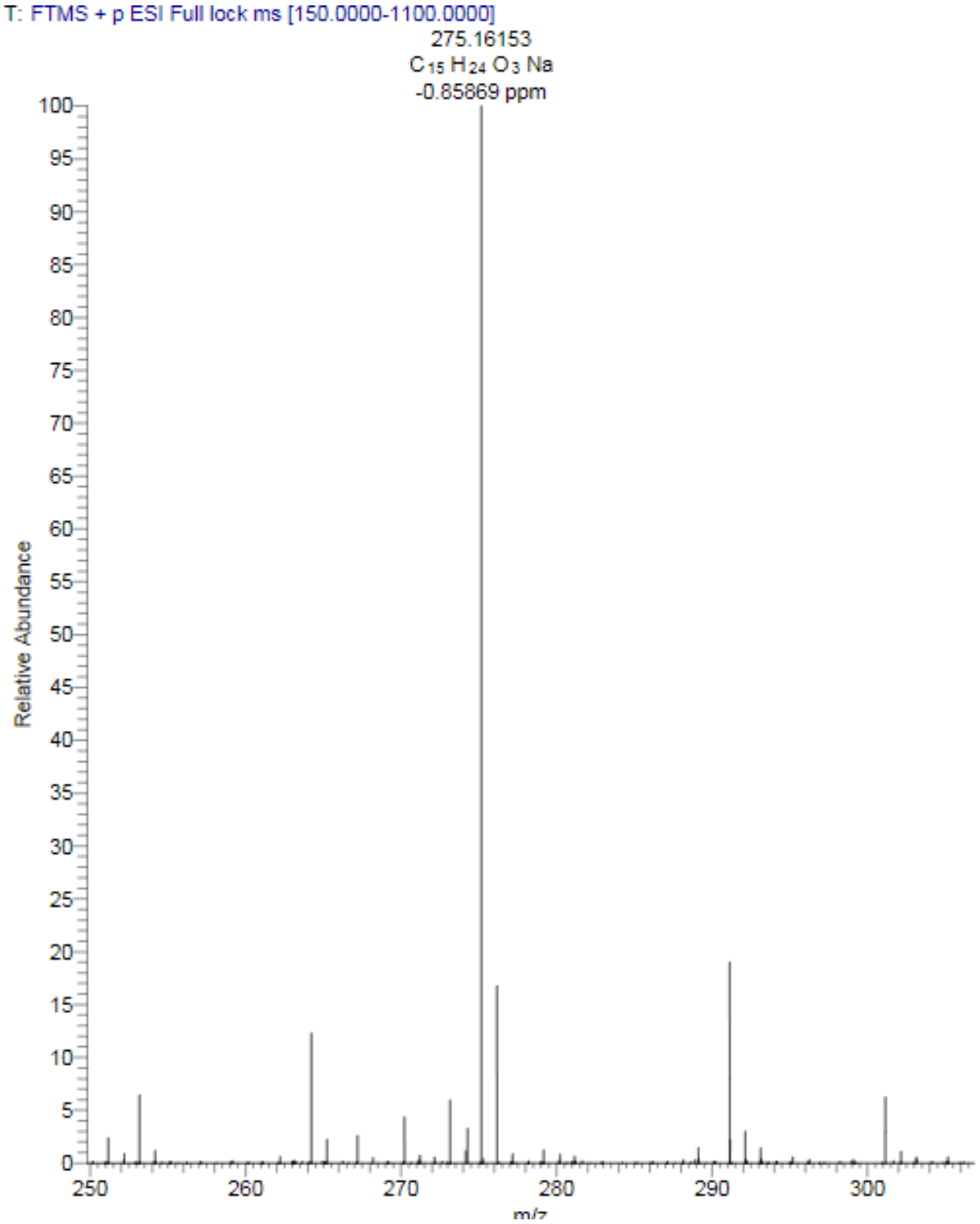
^{1}H-^{1}H COSY spectrum



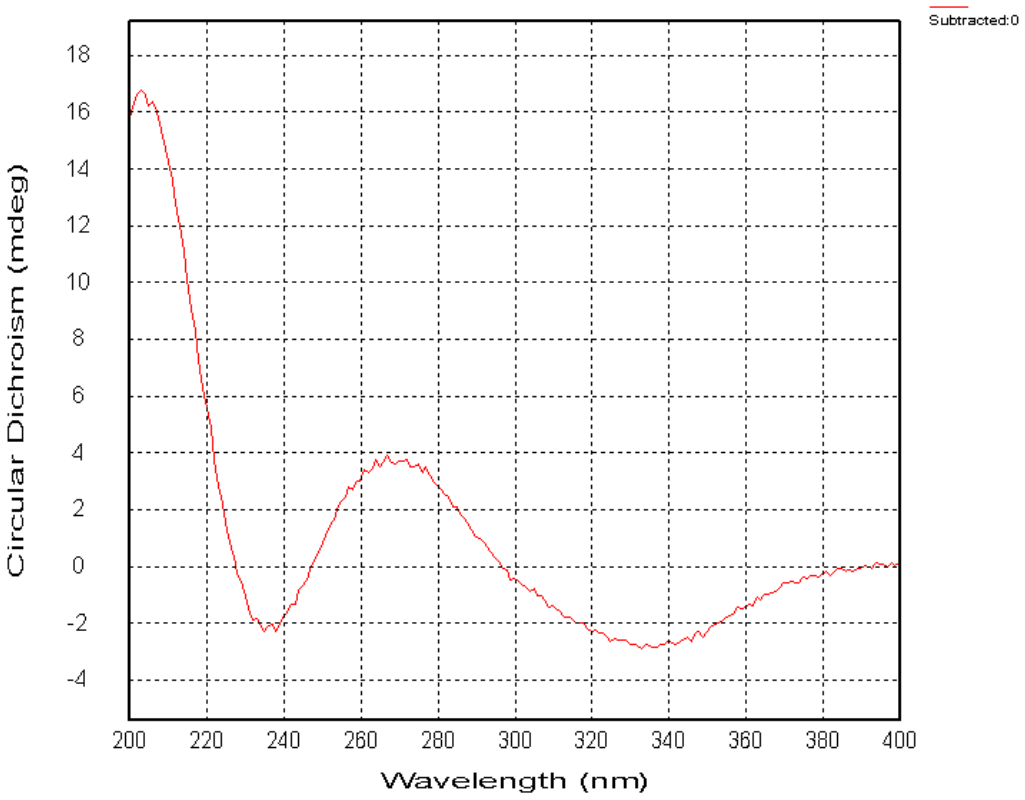
ROESY spectrum



HRESIMS

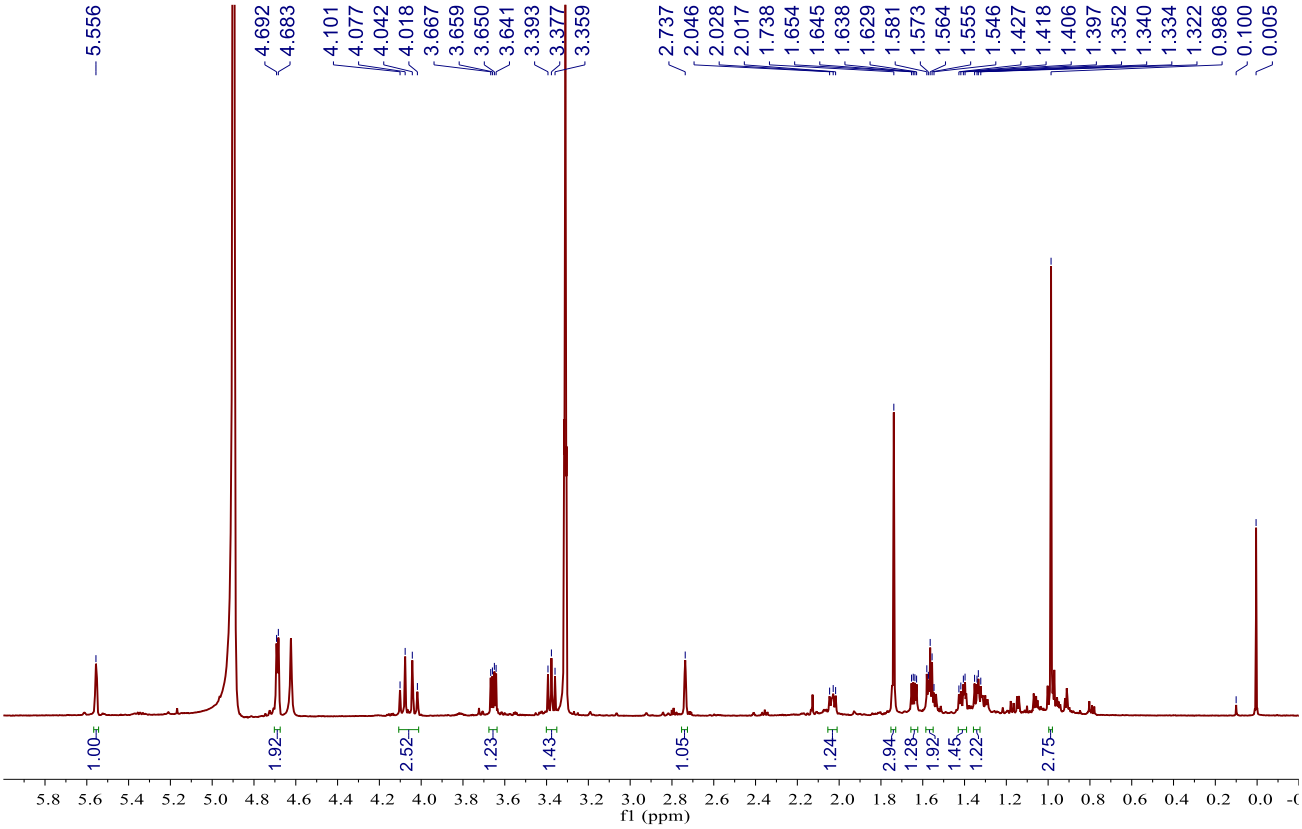

T: FTMS + p ESI Full lock ms [150.0000-1100.0000]
275.16153
C15 H24 O3 Na
-0.85869 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
250
260
270
280
290
300

CD spectra

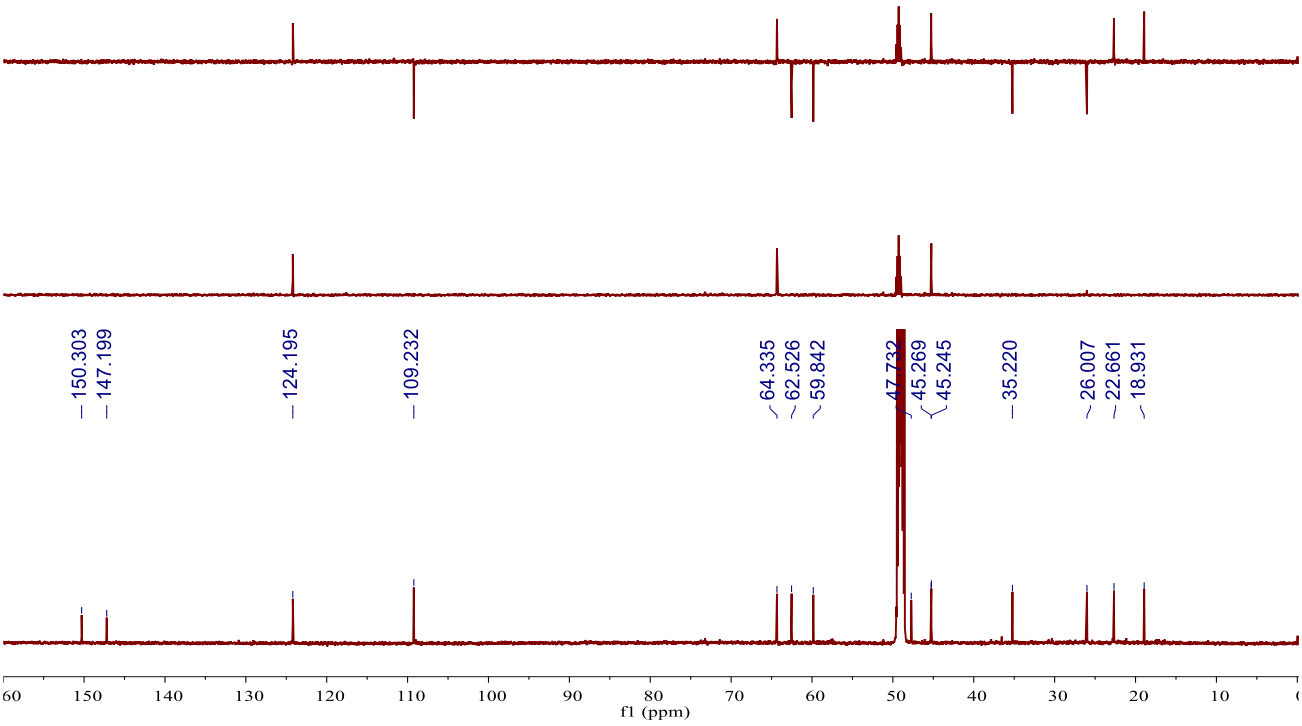

Subtracted:0
Circular Dichroism (mdeg)
18
16
14
12
10
8
6
4
2
0
-2
-4
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

S1.5 NMR, HRESIMS and CD spectra of bipolarisorokin E (5)

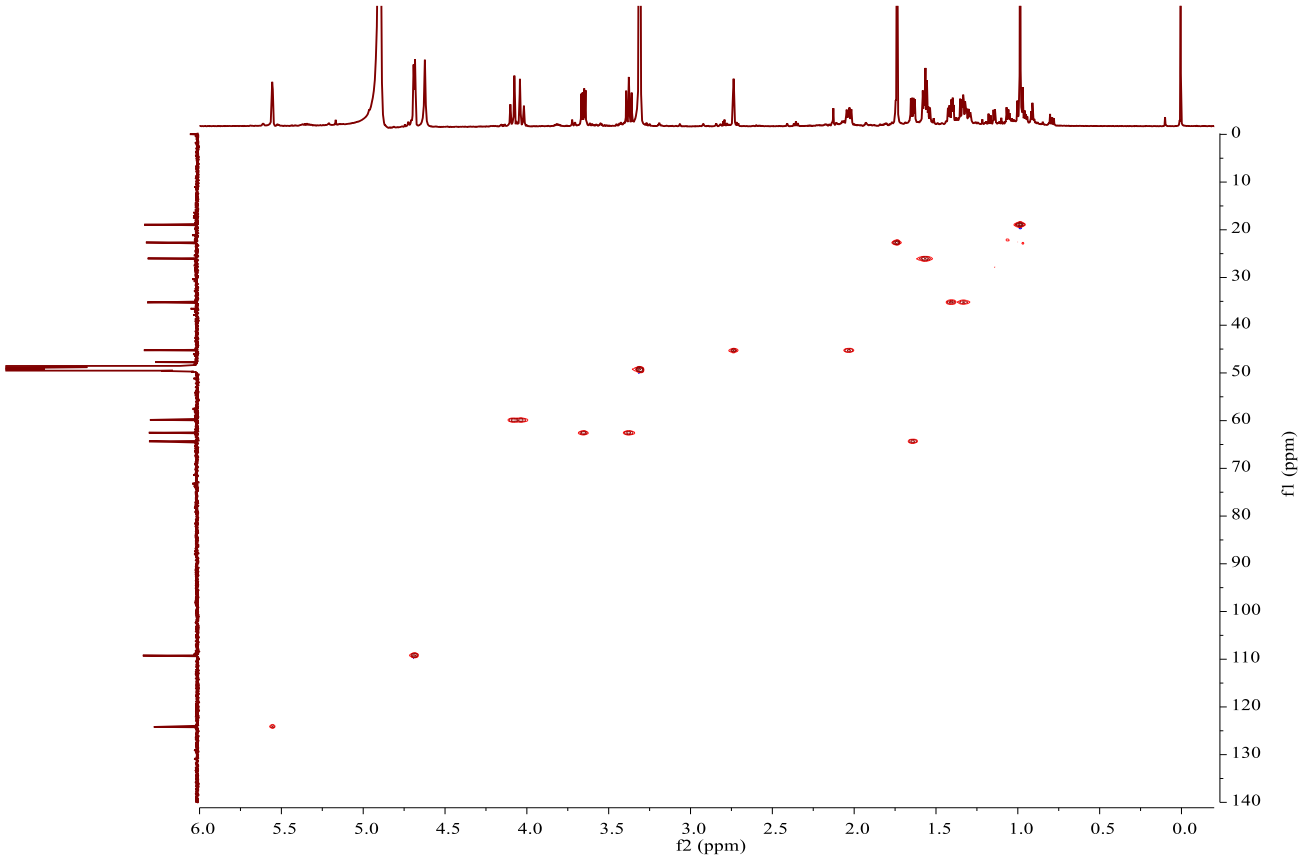
^{1}H NMR spectrum



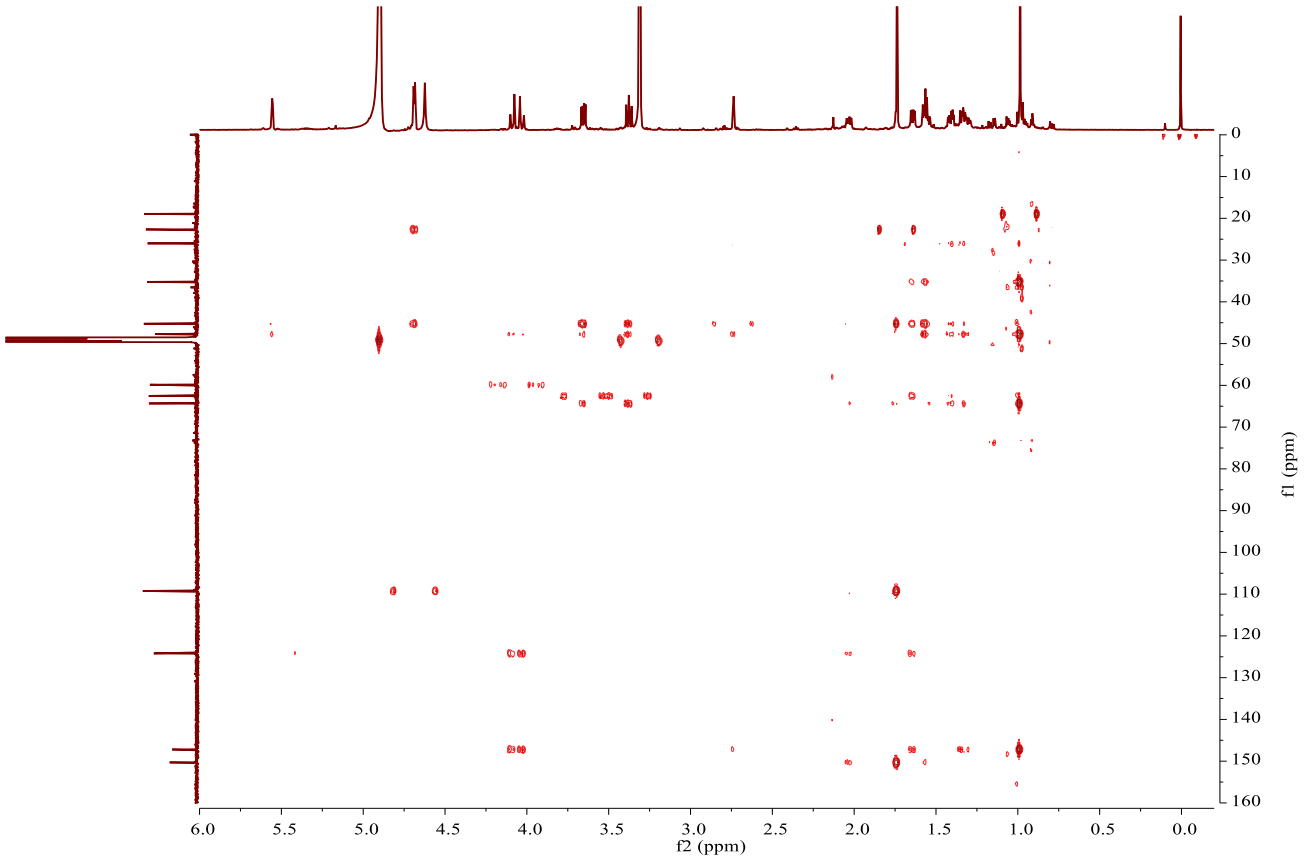
^{13}C NMR and DEPT spectra



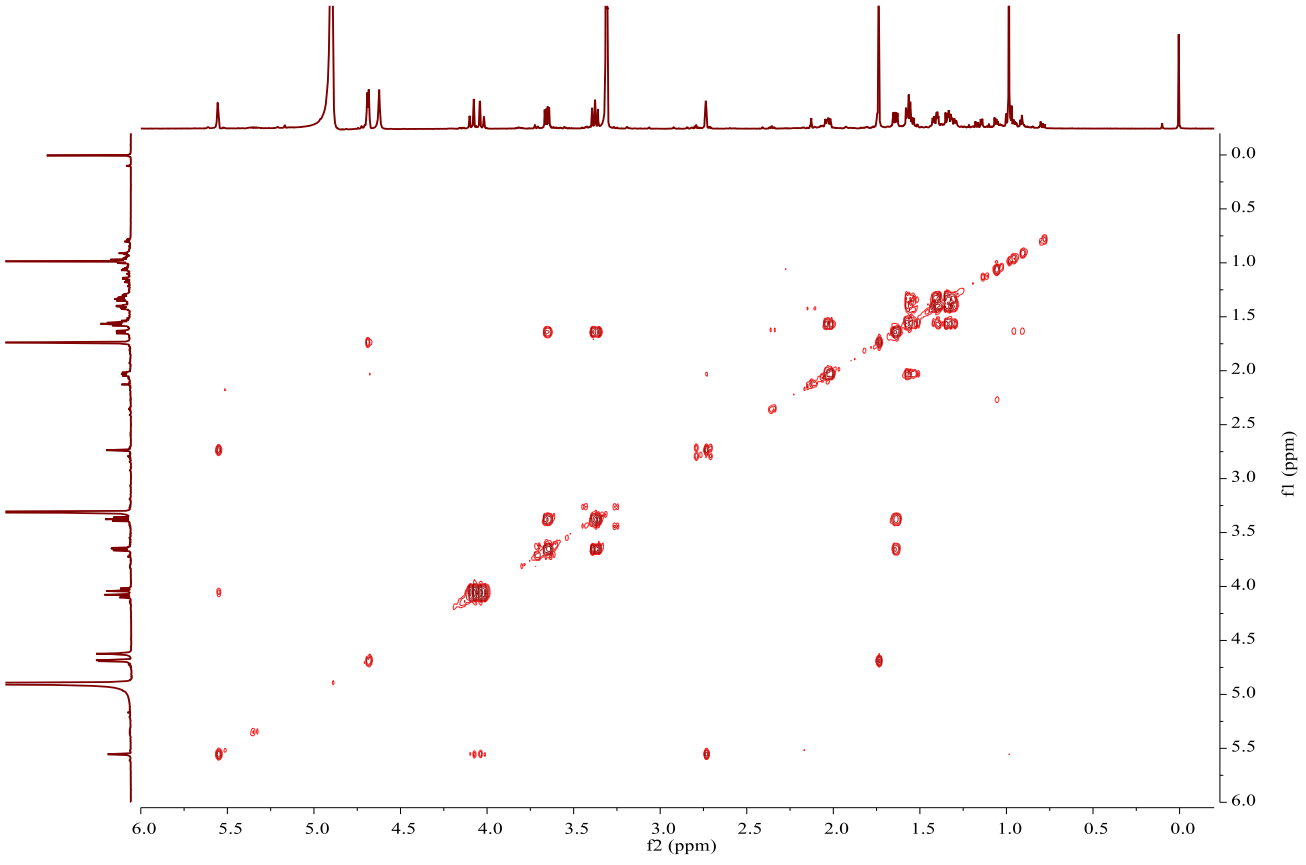
HSQC spectrum



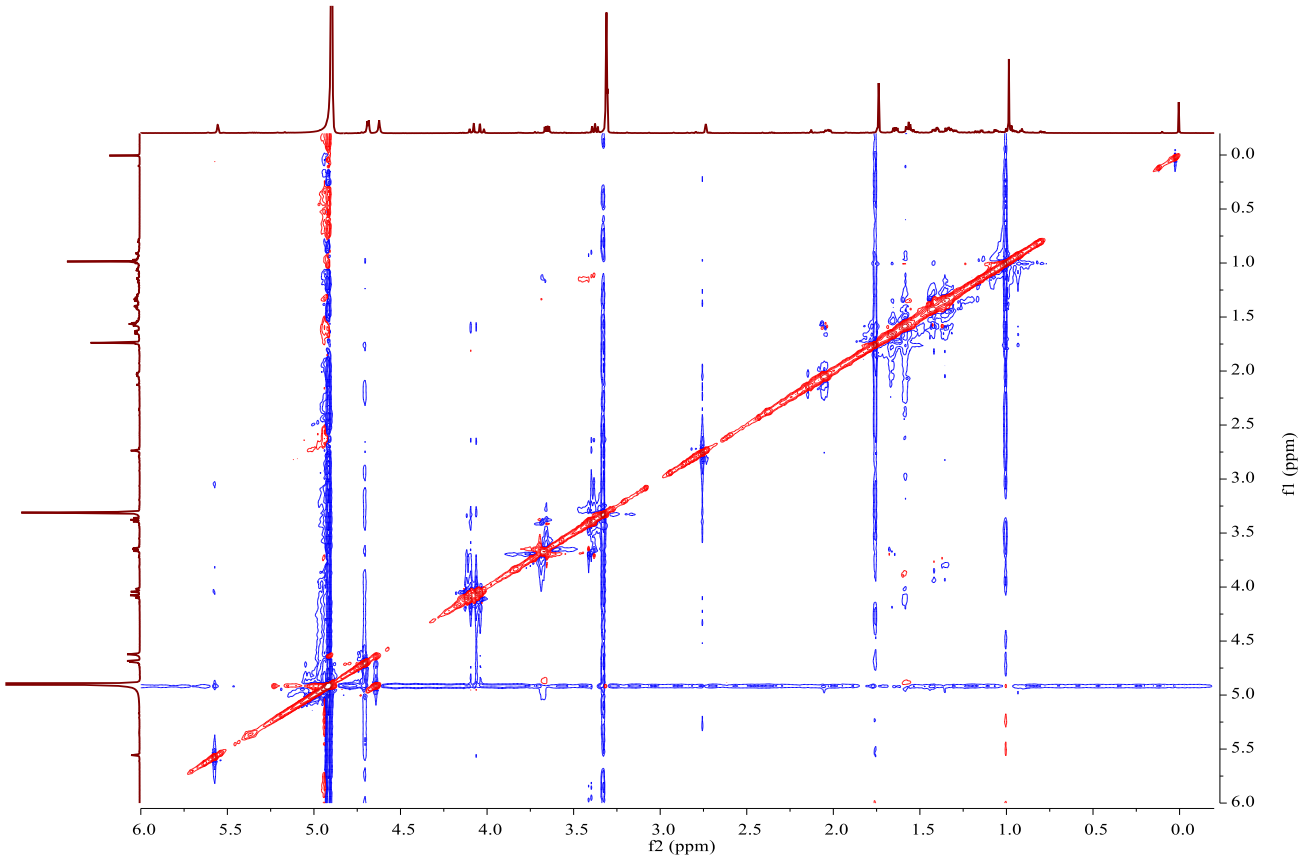
HMBC spectrum



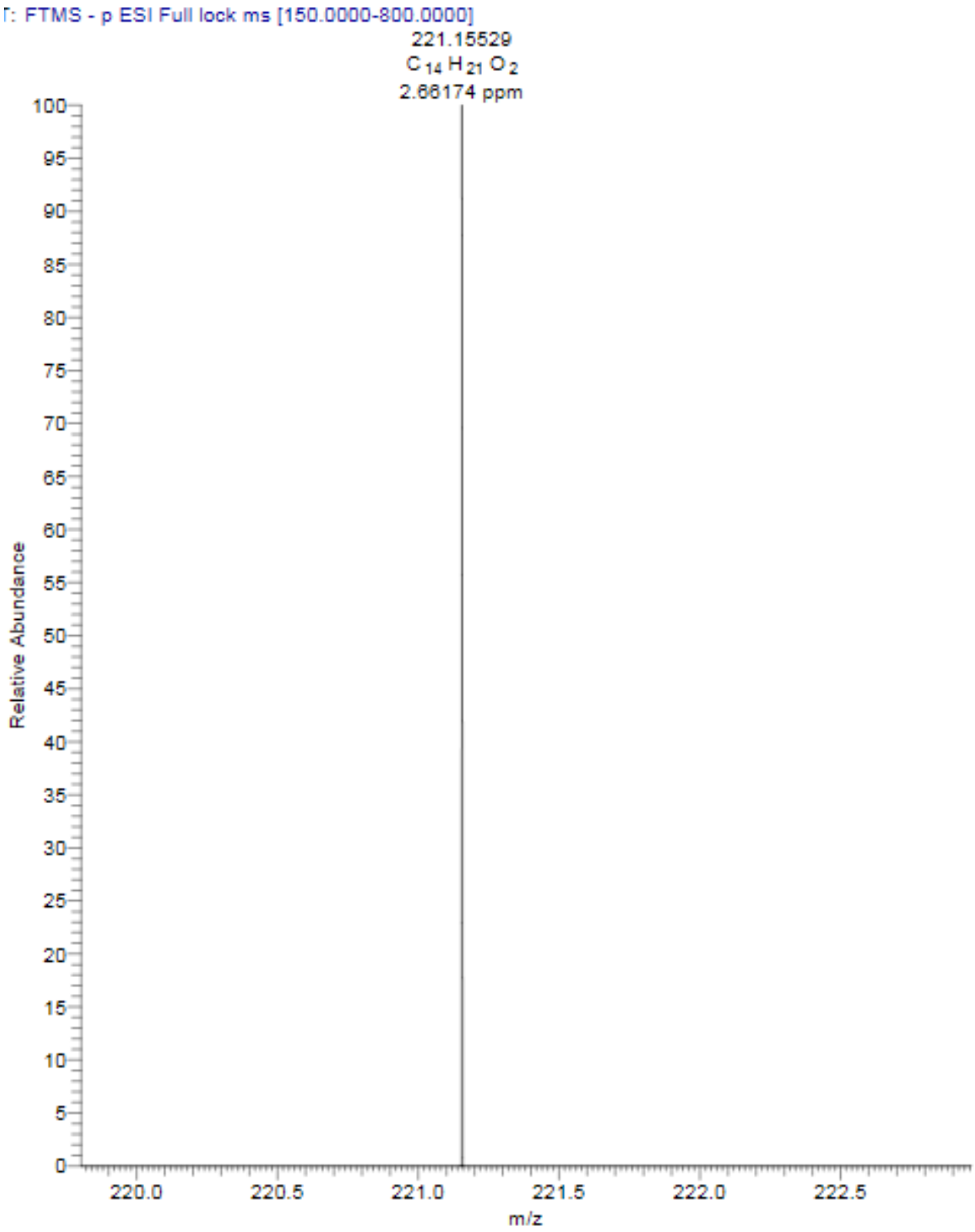
^{1}H-^{1}H COSY spectrum



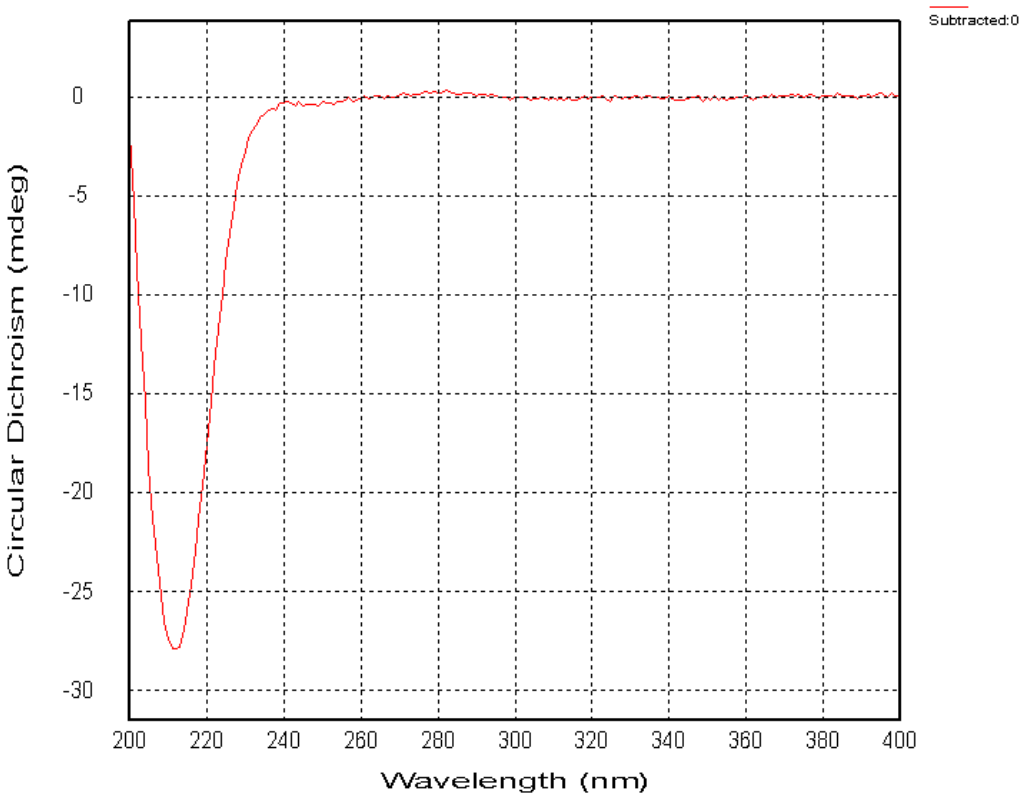
ROESY spectrum



HRESIMS

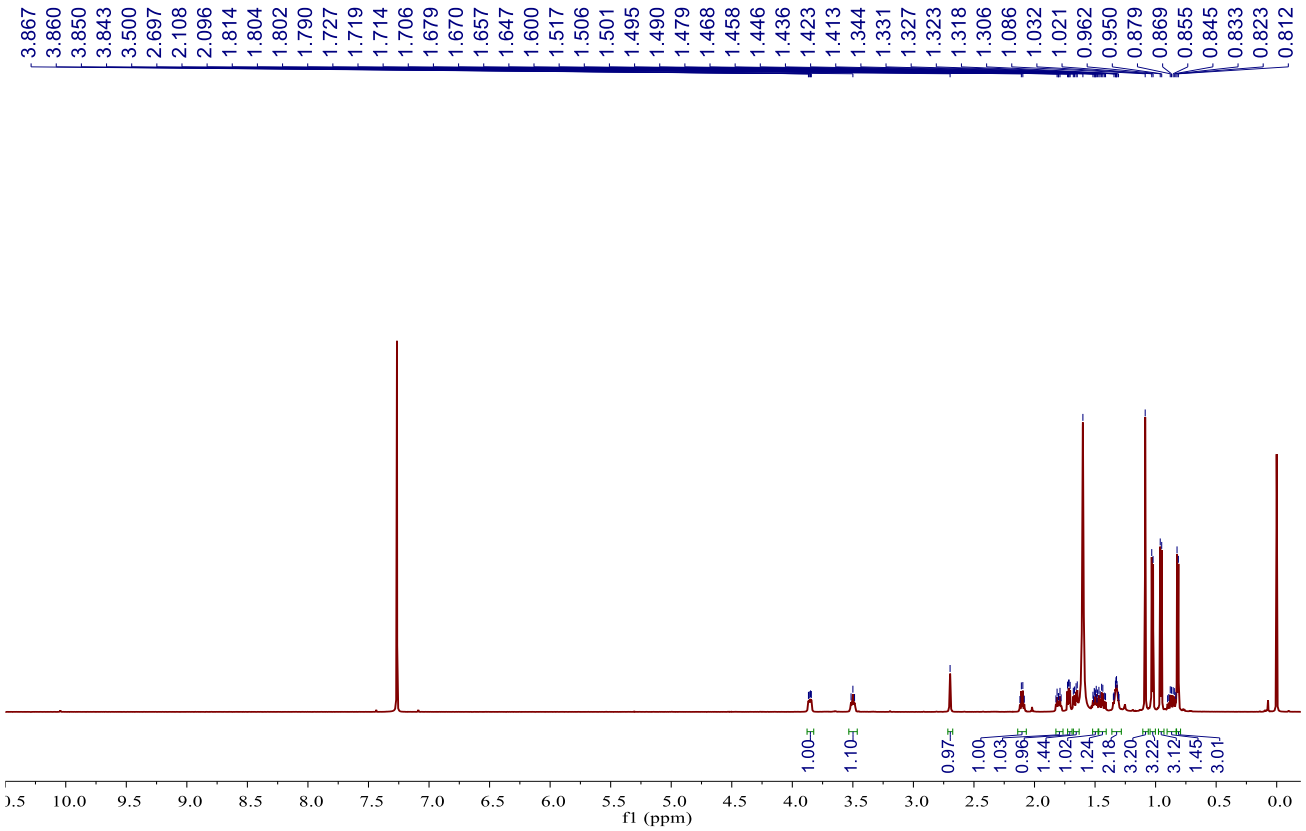

: FTMS - p ESI Full lock ms [150.0000-800.0000]
221.15529
C 14 H 21 O 2
2.66174 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
220.0
220.5
221.0
221.5
222.0
222.5

CD spectra

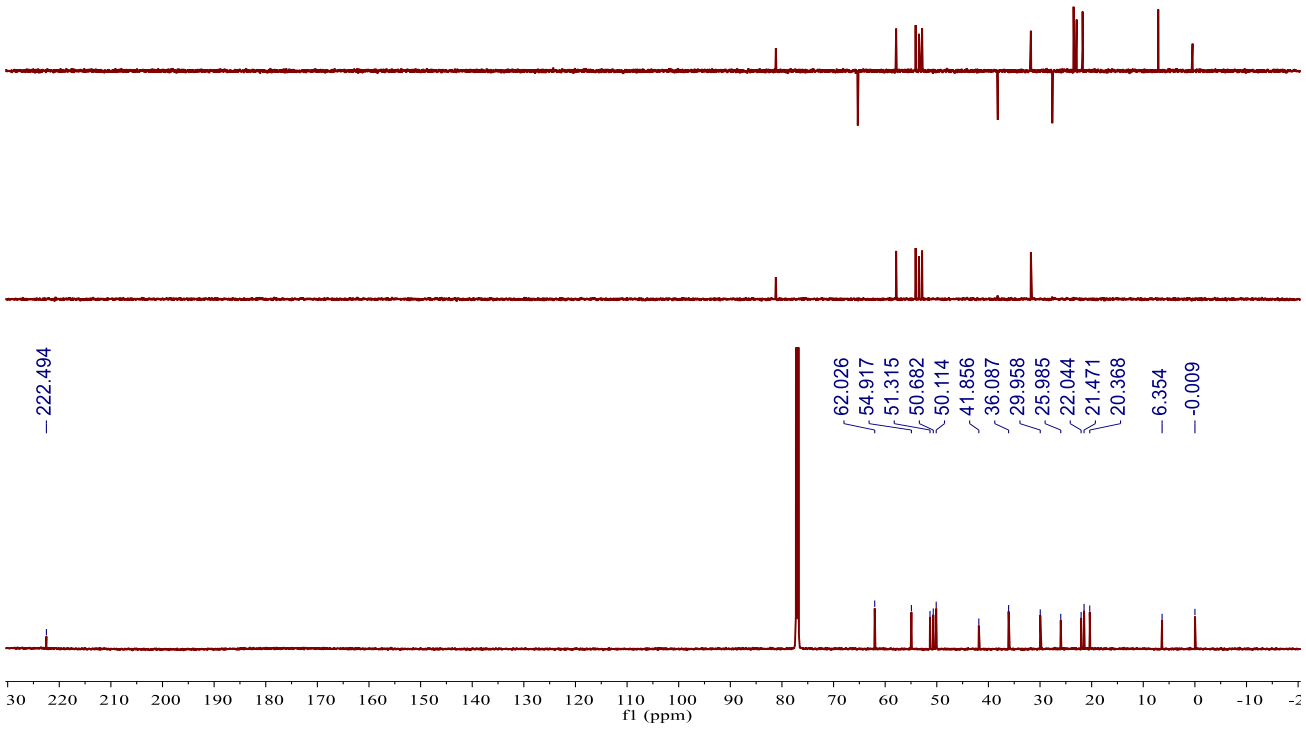

Subtracted:0
Circular Dichroism (mdeg)
0
-5
-10
-15
-20
-25
-30
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

S1.6 NMR and HRESIMS spectra of bipolarisorokin F (6)

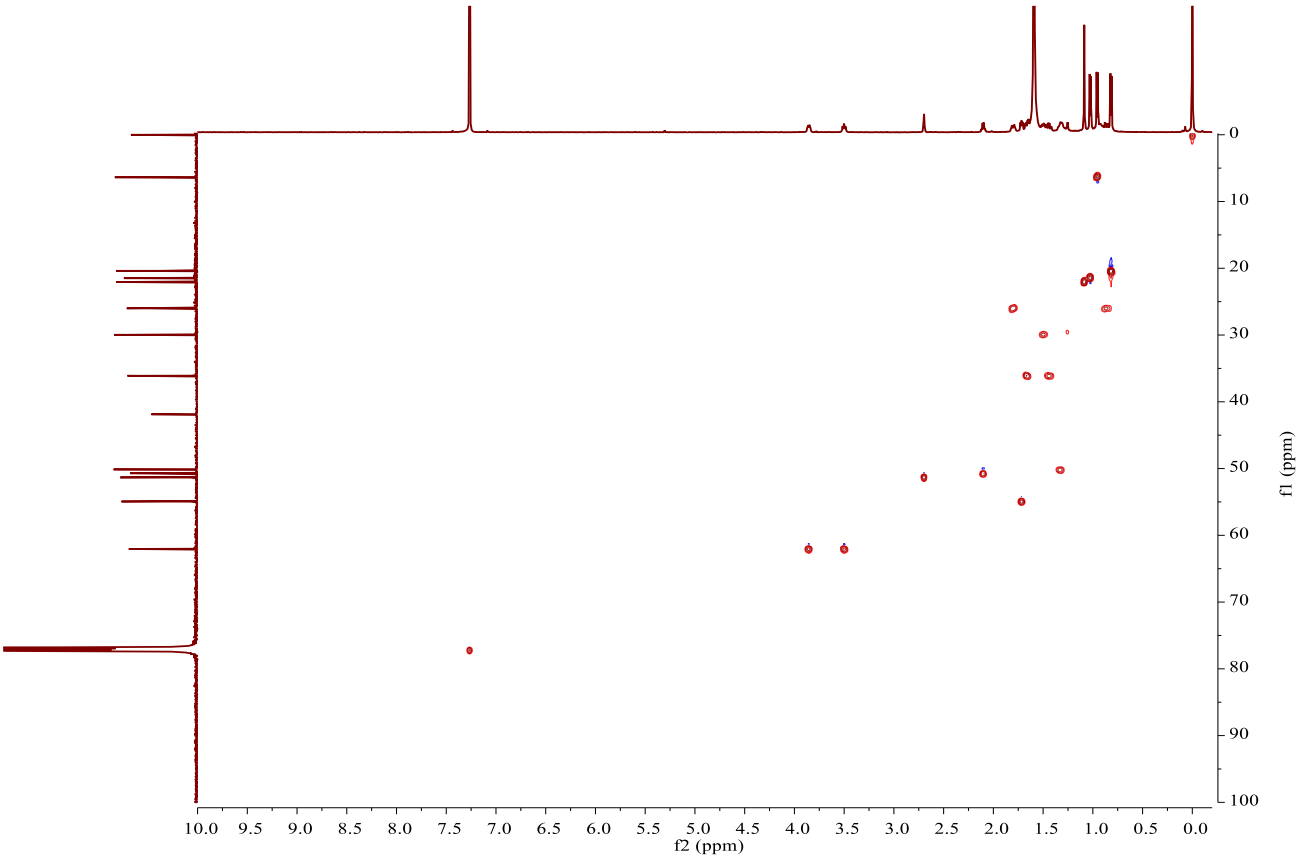
^{1}H NMR spectrum



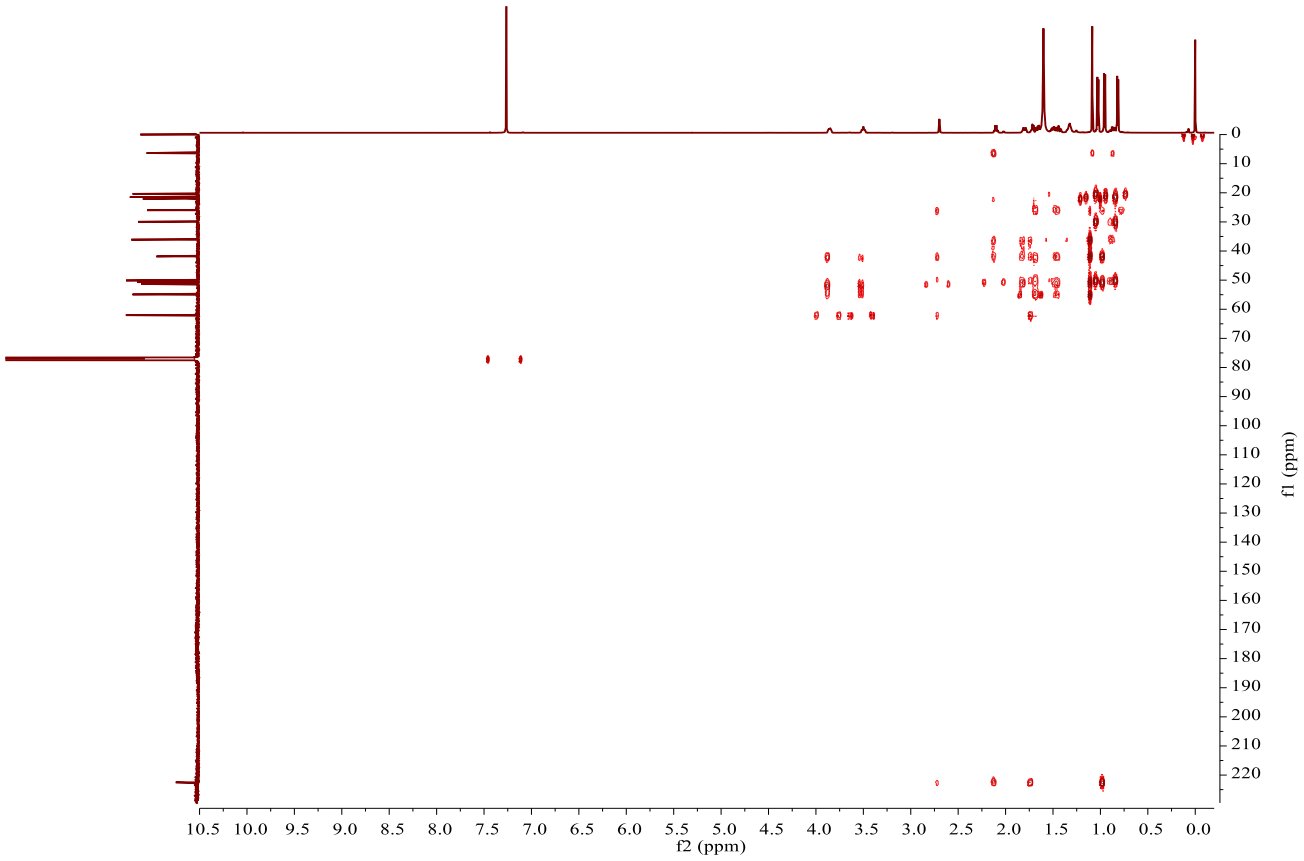
^{13}C NMR and DEPT spectra



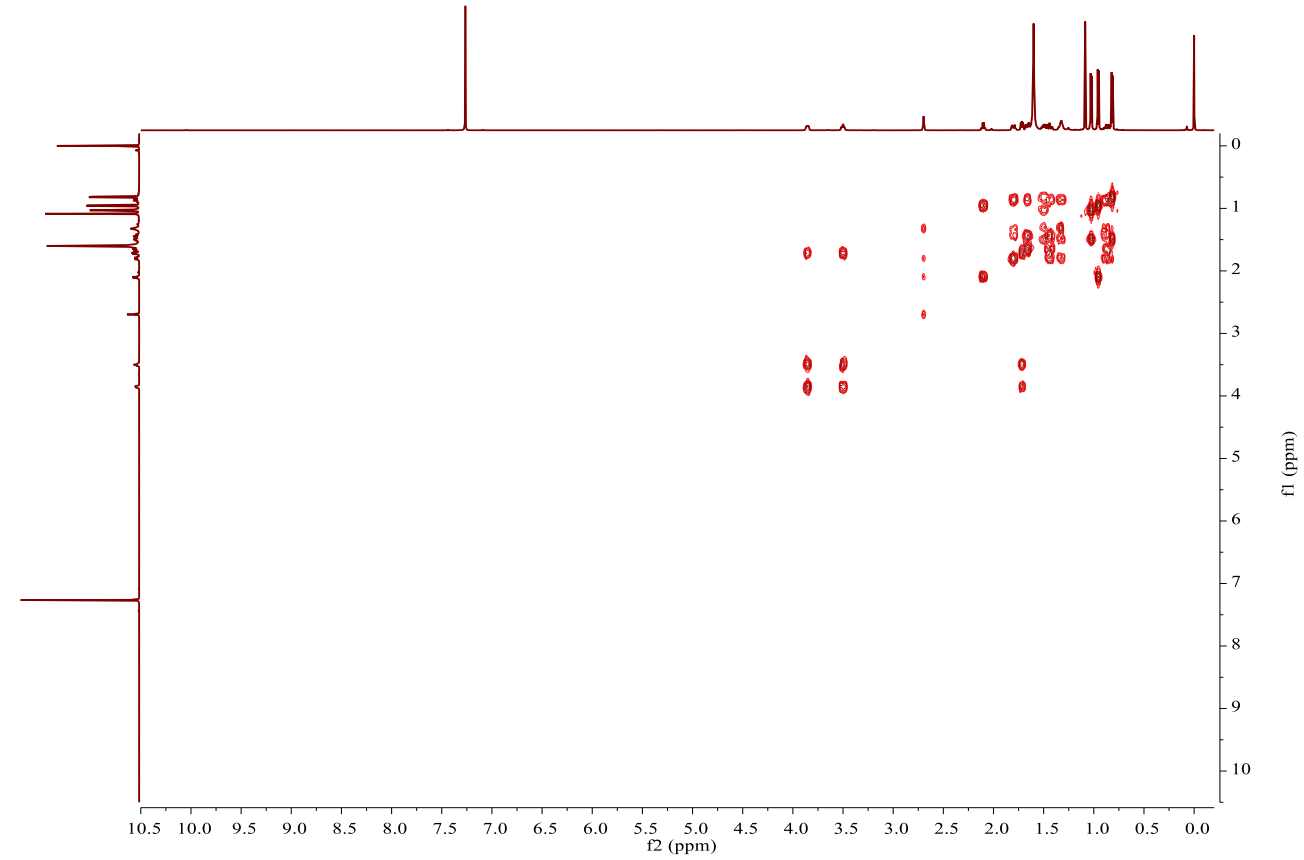
HSQC spectrum



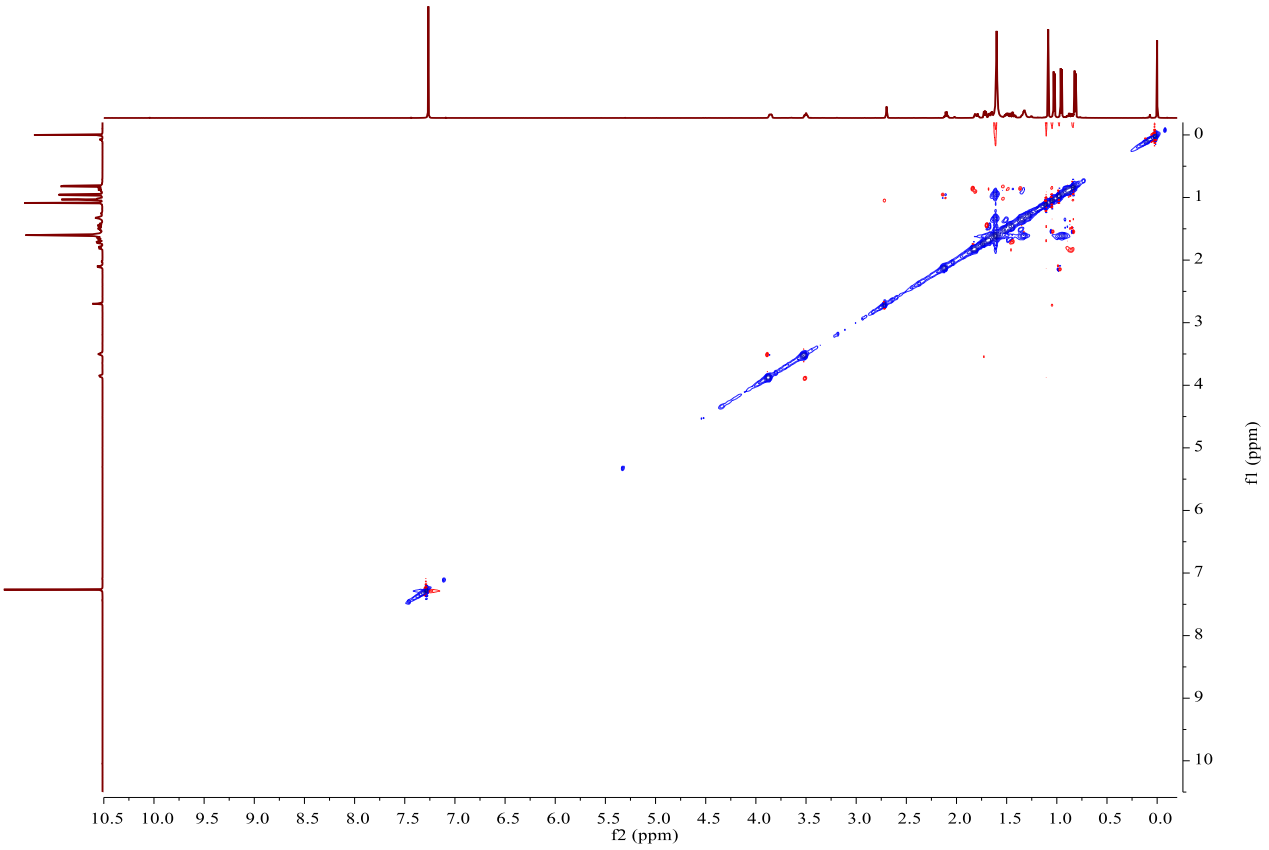
HMBC spectrum



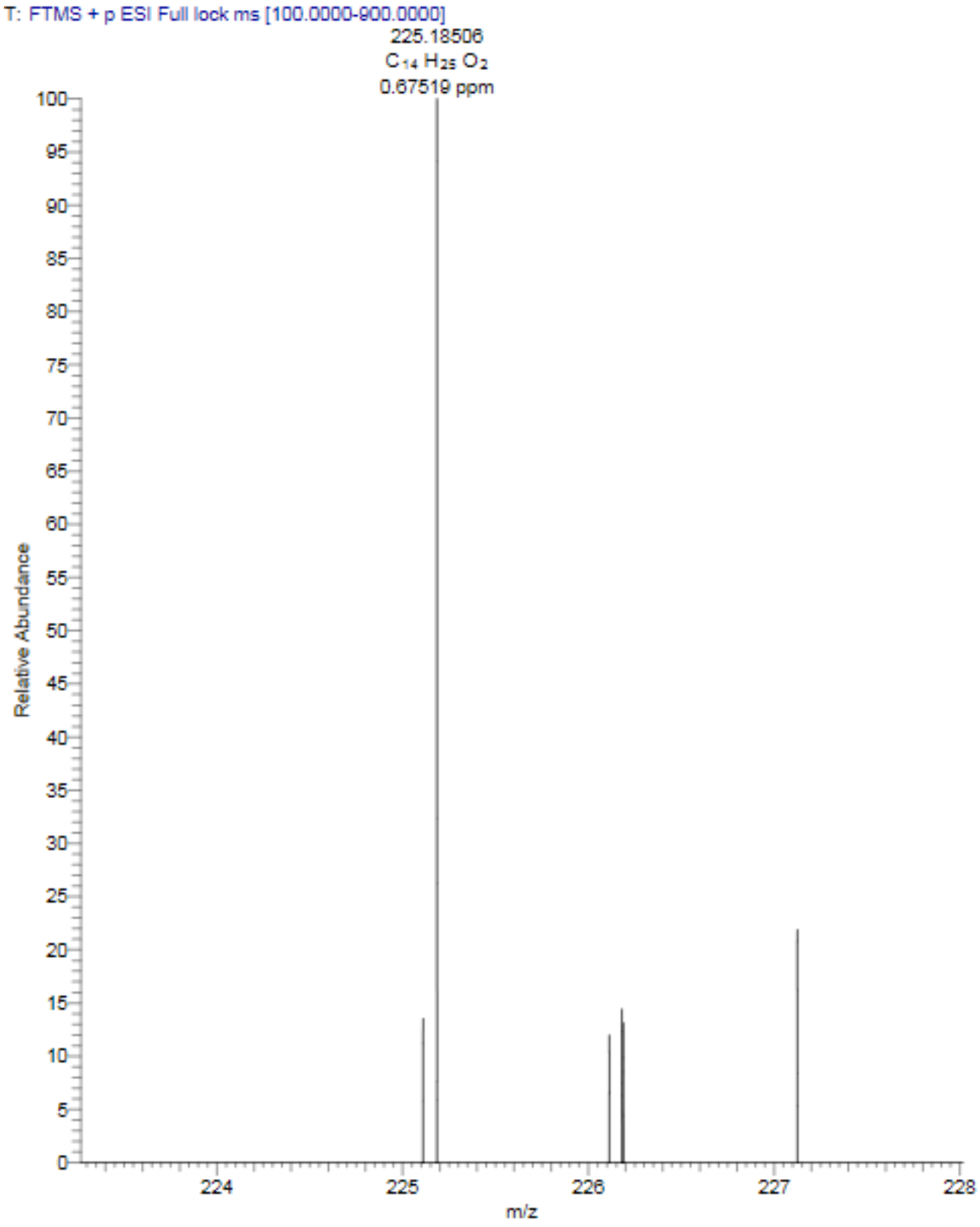
^{1}H-^{1}H COSY spectrum



ROESY spectrum

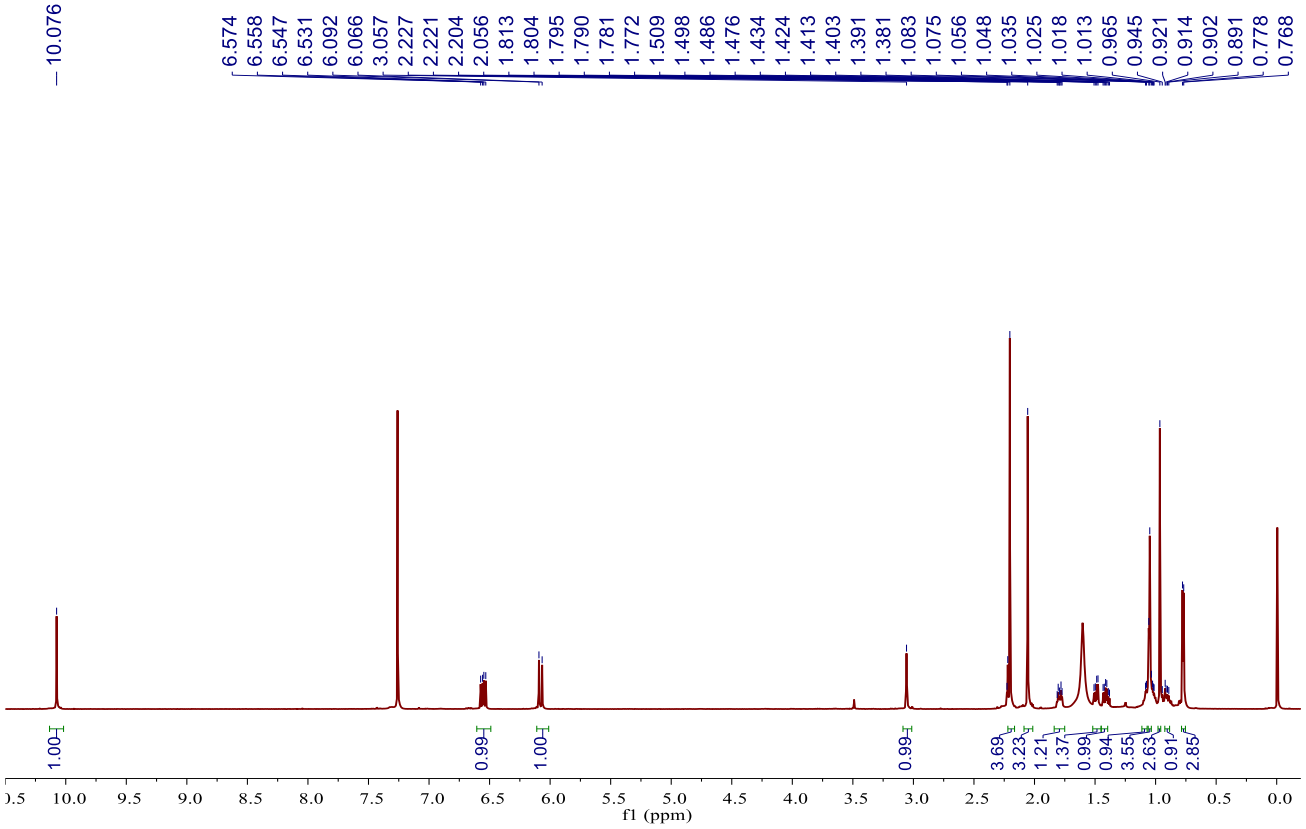


HRESIMS

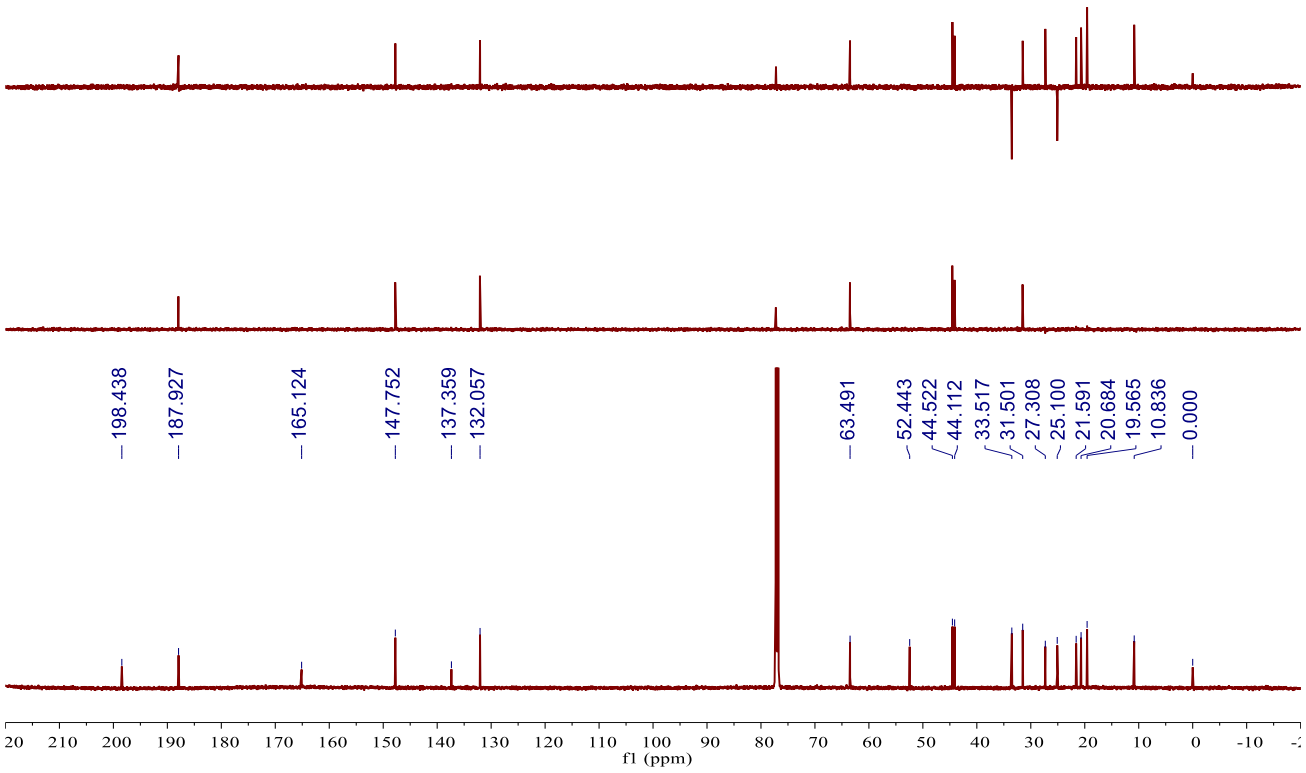

T: FTMS + p ESI Full lock ms [100.0000-900.0000]
225.18506
C14 H25 O2
0.67519 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
224
225
226
227
228

S1.7 NMR, HRESIMS and CD spectra of bipolarisorokin G (7)

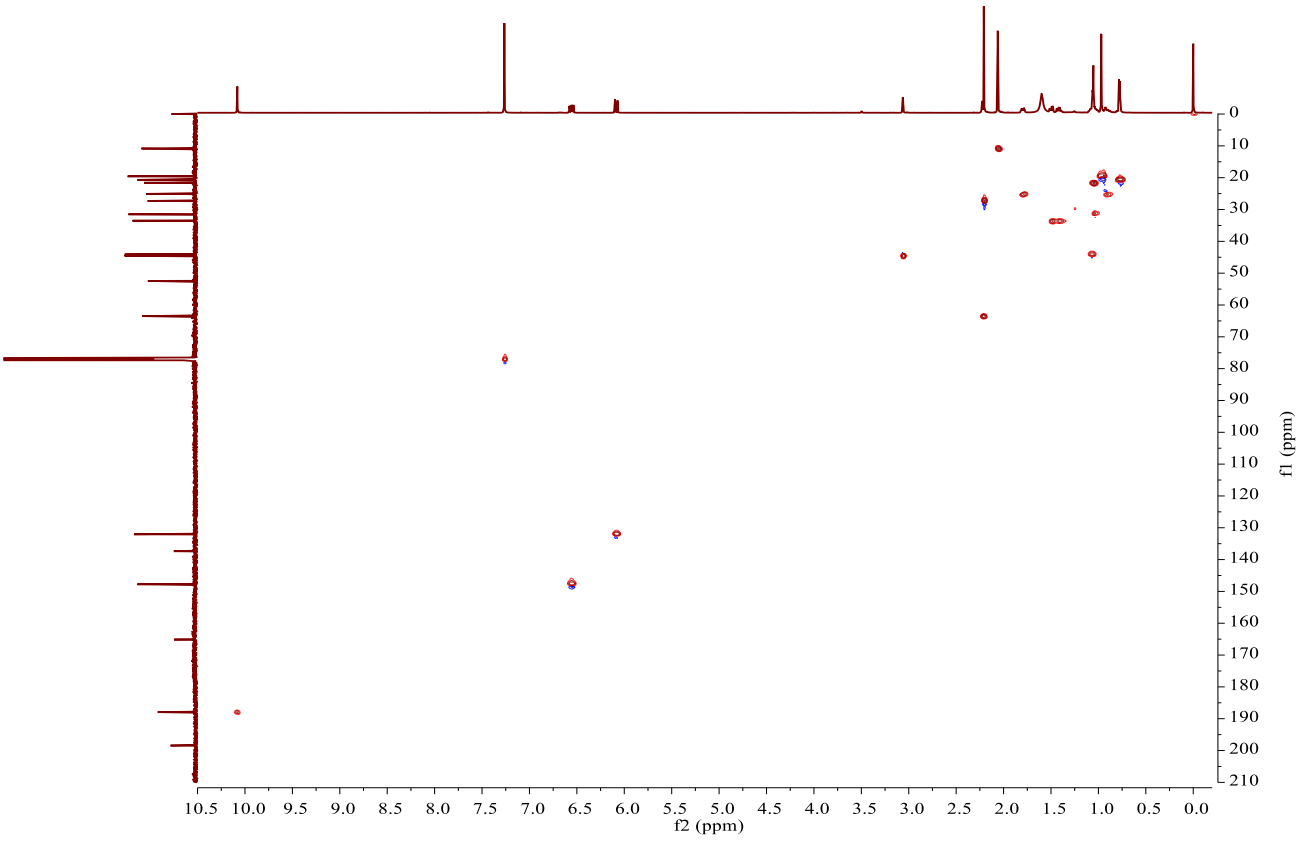
^{1}H NMR spectrum



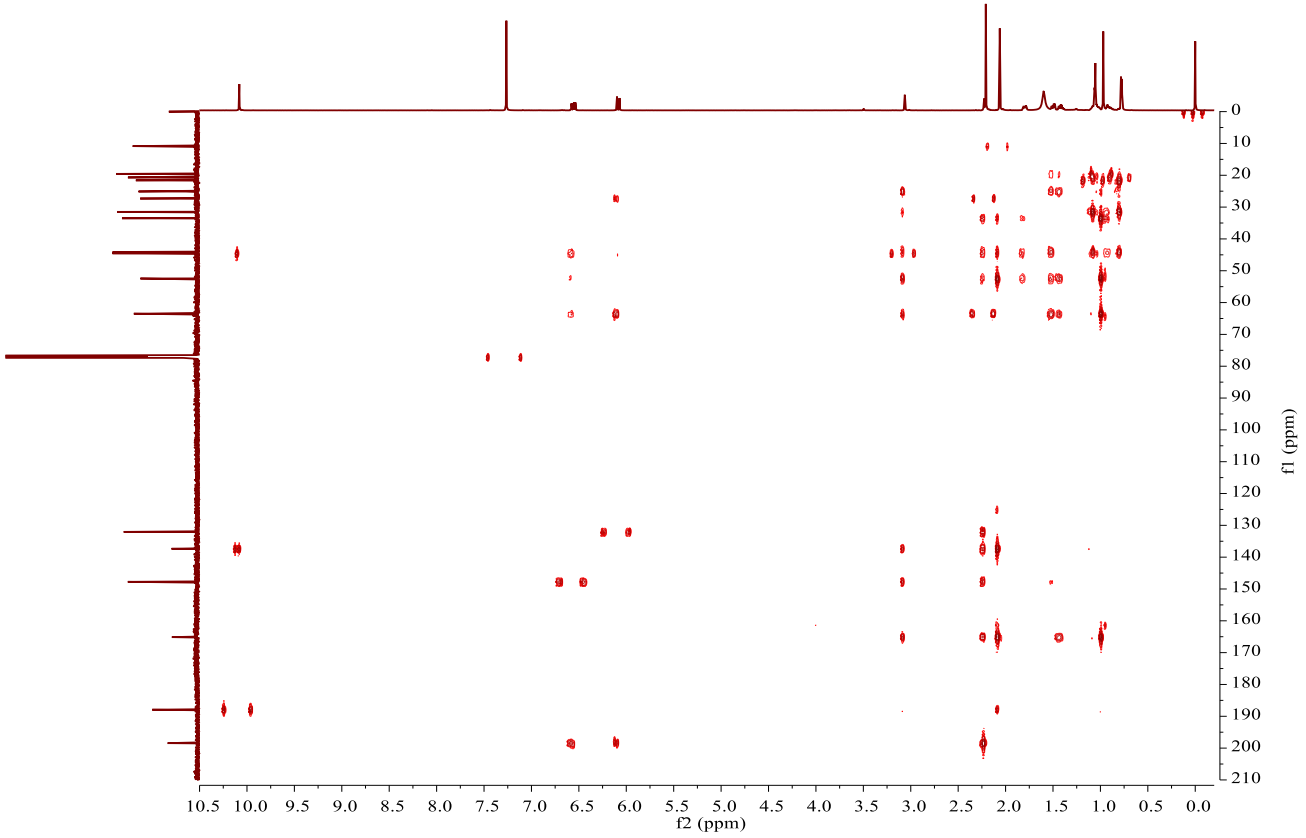
^{13}C NMR and DEPT spectra



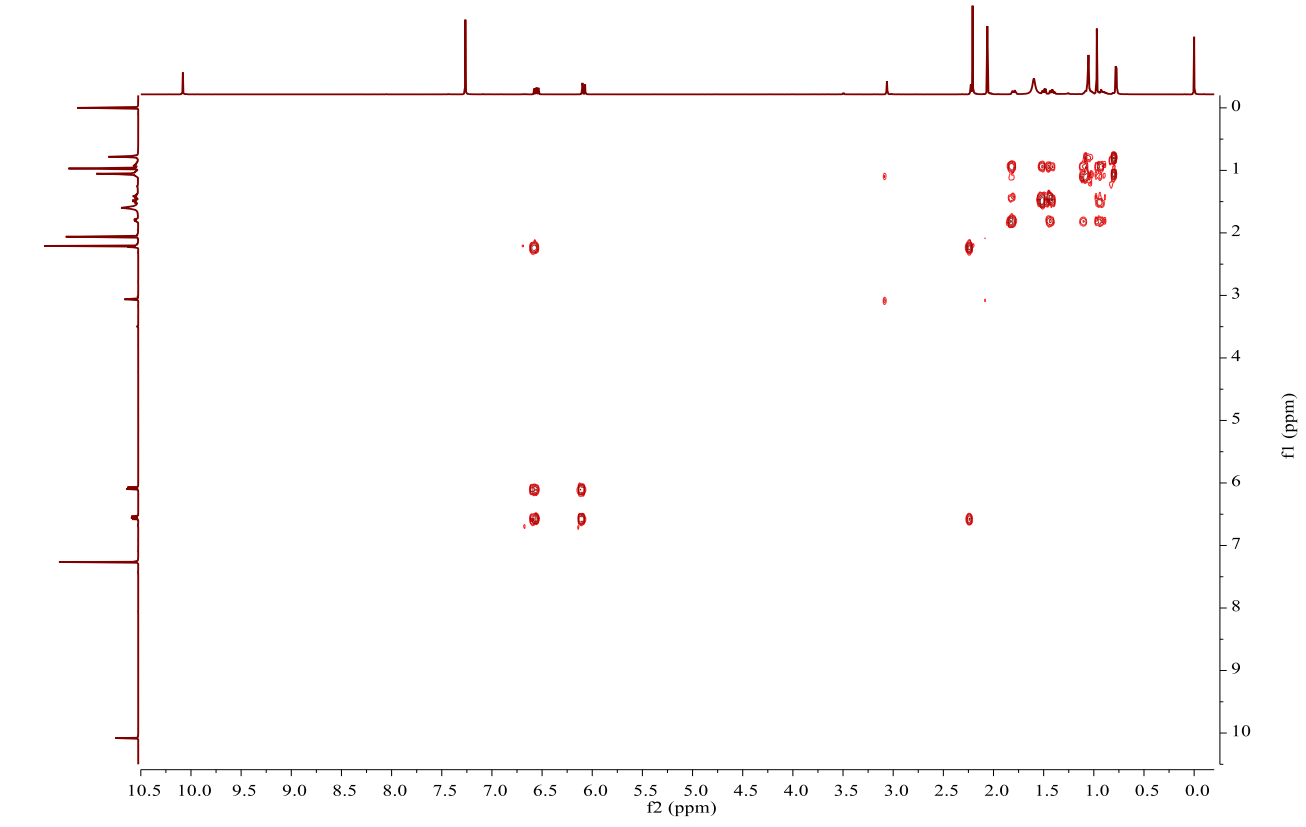
HSQC spectrum



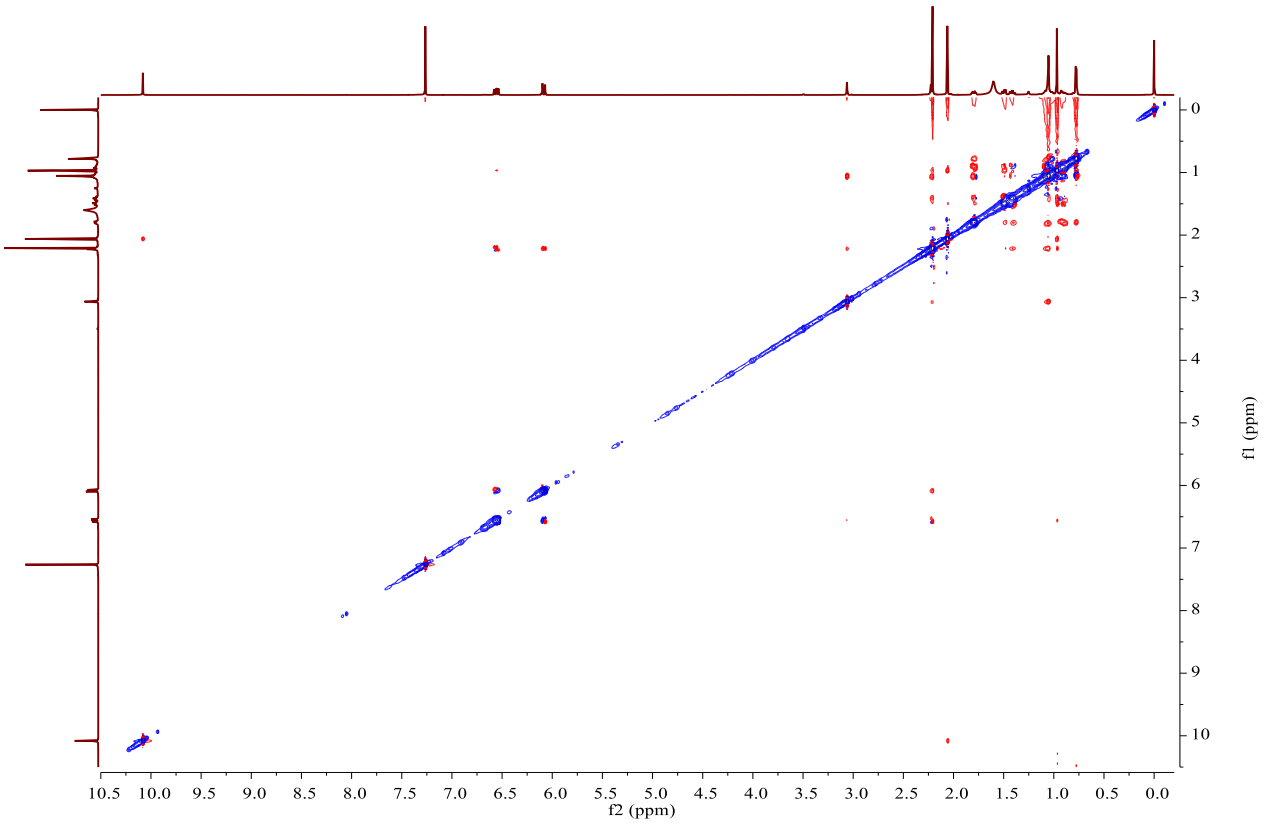
HMBC spectrum



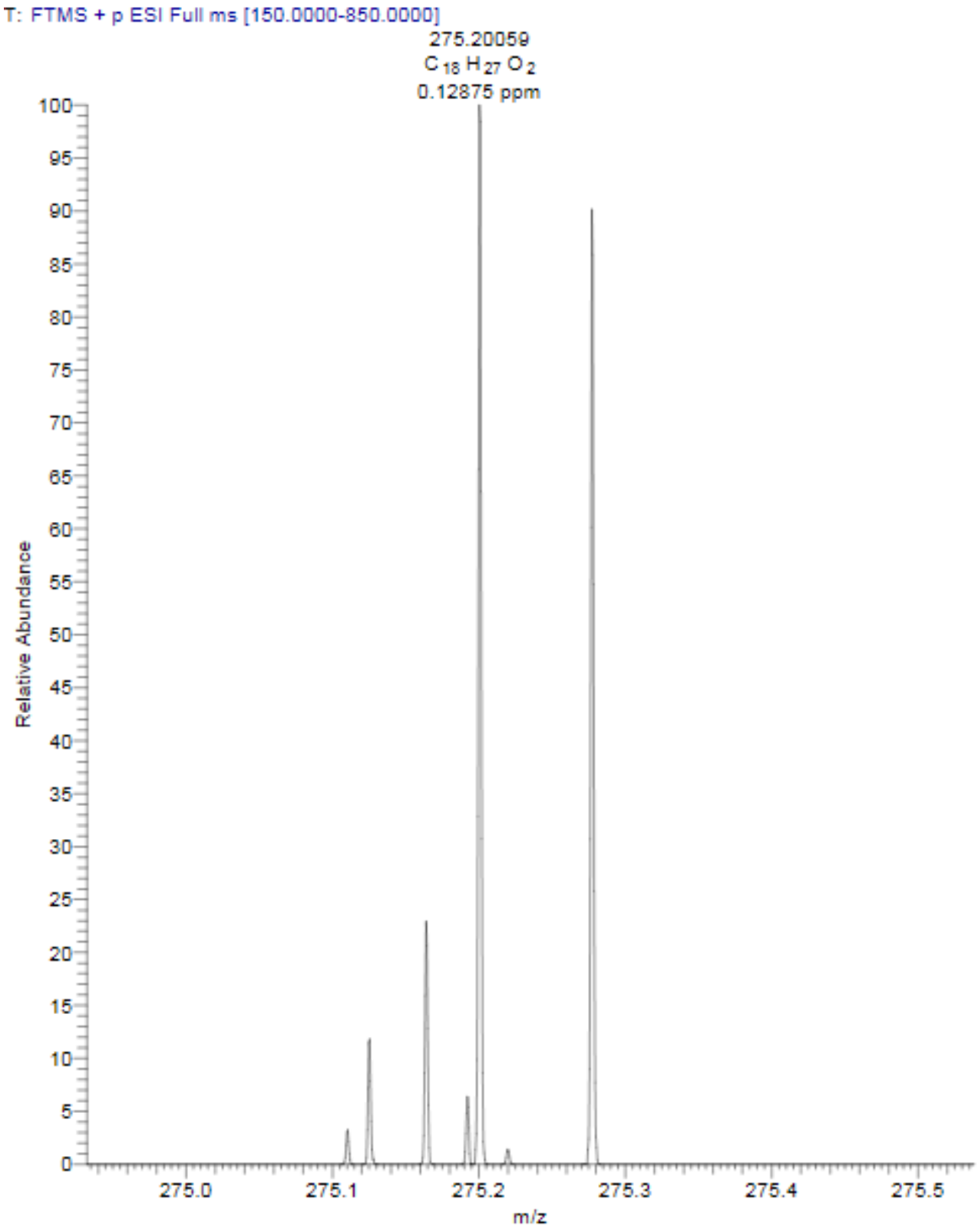
^{1}H-^{1}H COSY spectrum



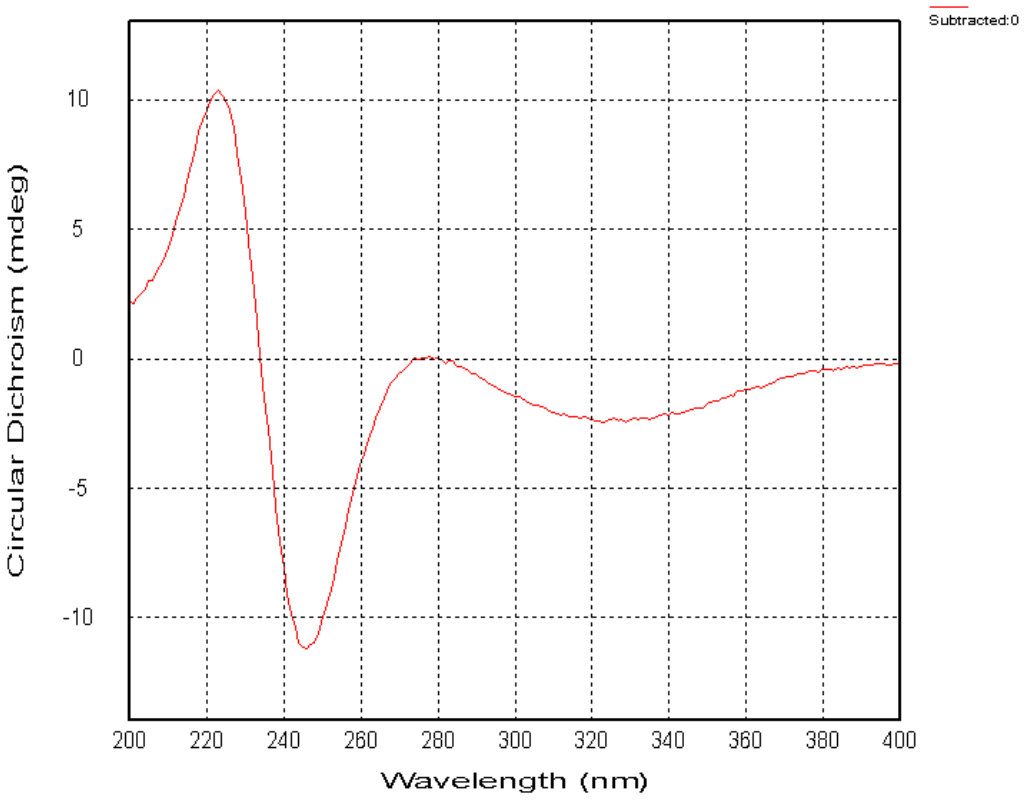
ROESY spectrum



HRESIMS

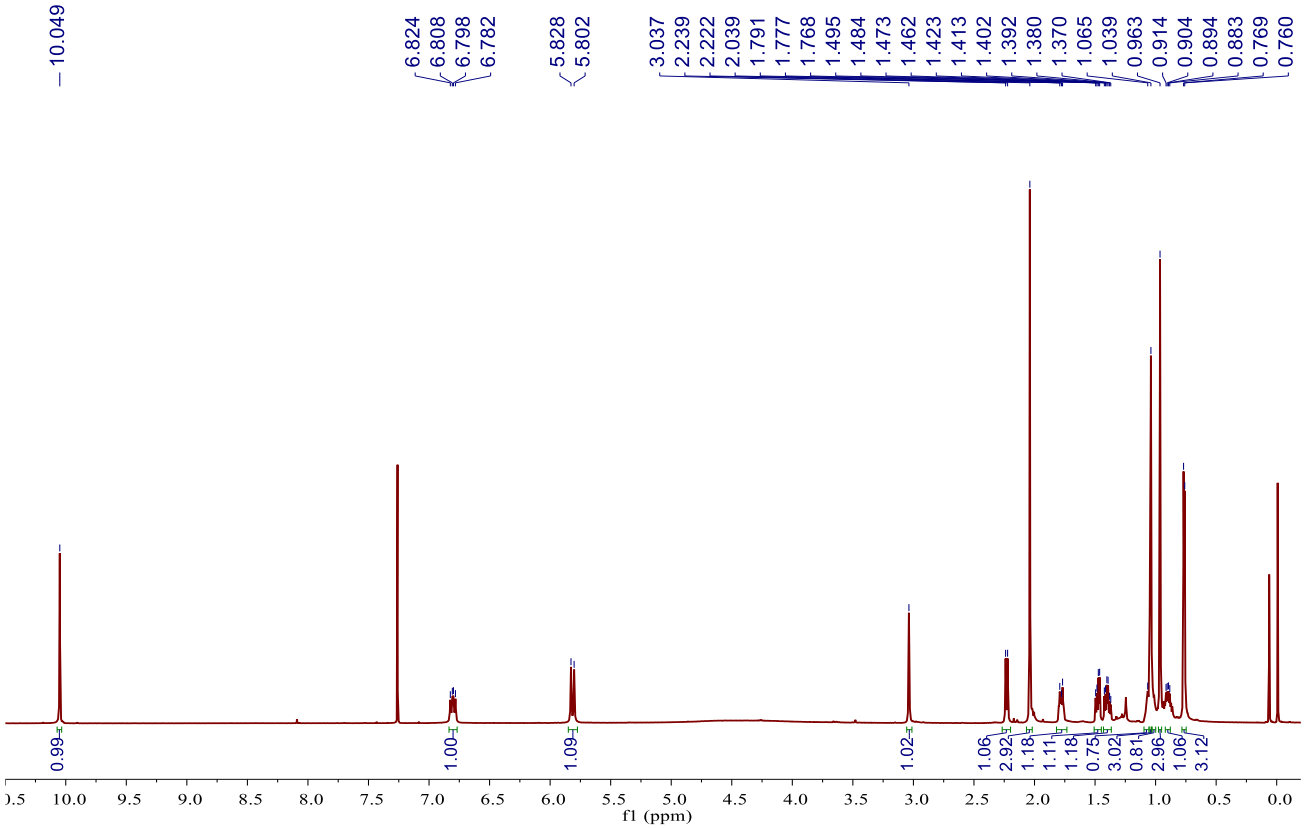

T: FTMS + p ESI Full ms [150.0000-850.0000]
275.20059
C 18 H 27 O 2
0.12875 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
275.0
275.1
275.2
275.3
275.4
275.5

CD spectra

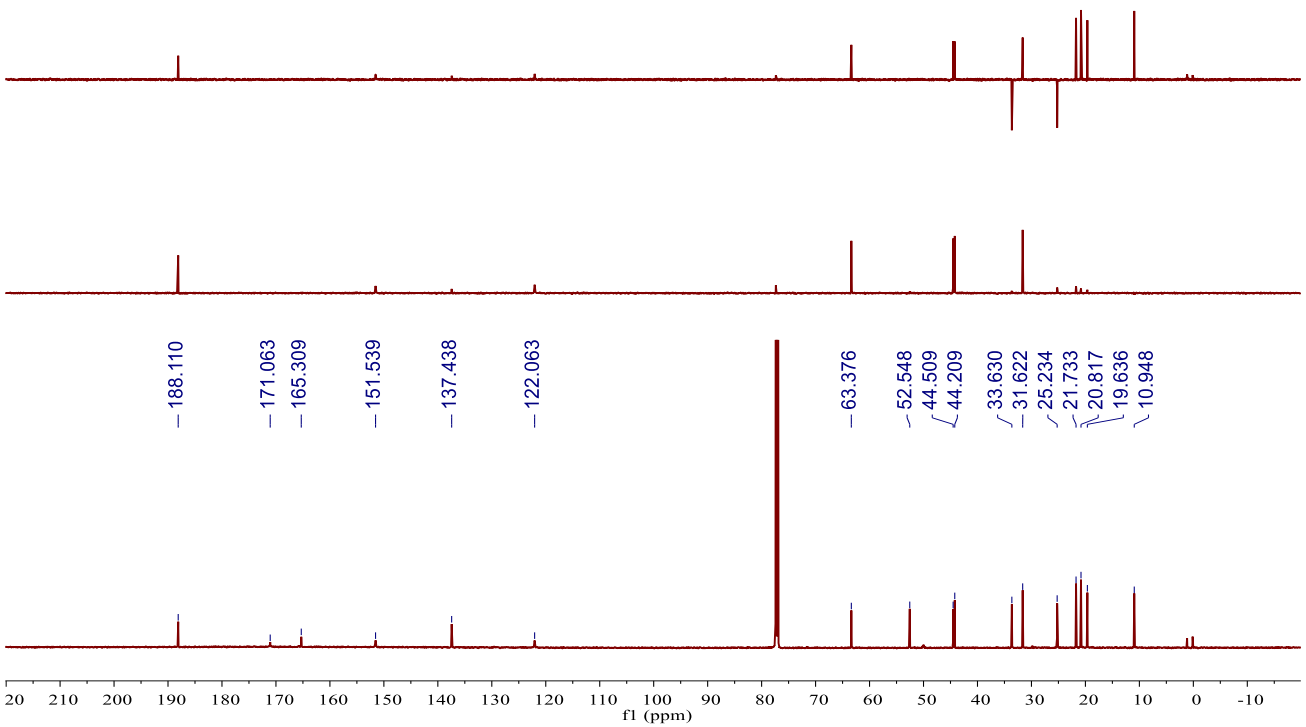

Subtracted:0
Circular Dichroism (mdeg)
10
5
0
-5
-10
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

S1.8 NMR, HRESIMS and CD spectra of bipolarisorokin H (8)

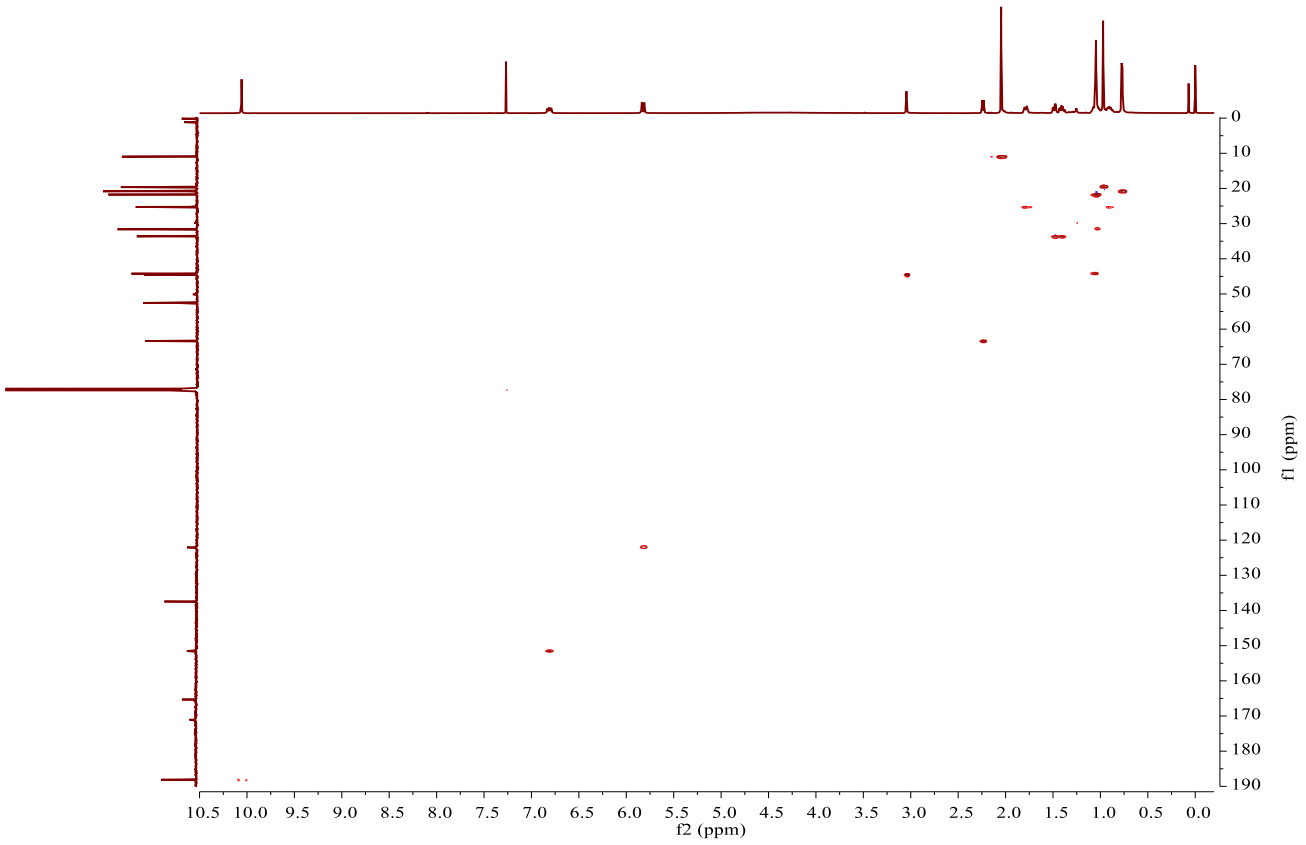
^{1}H NMR spectrum



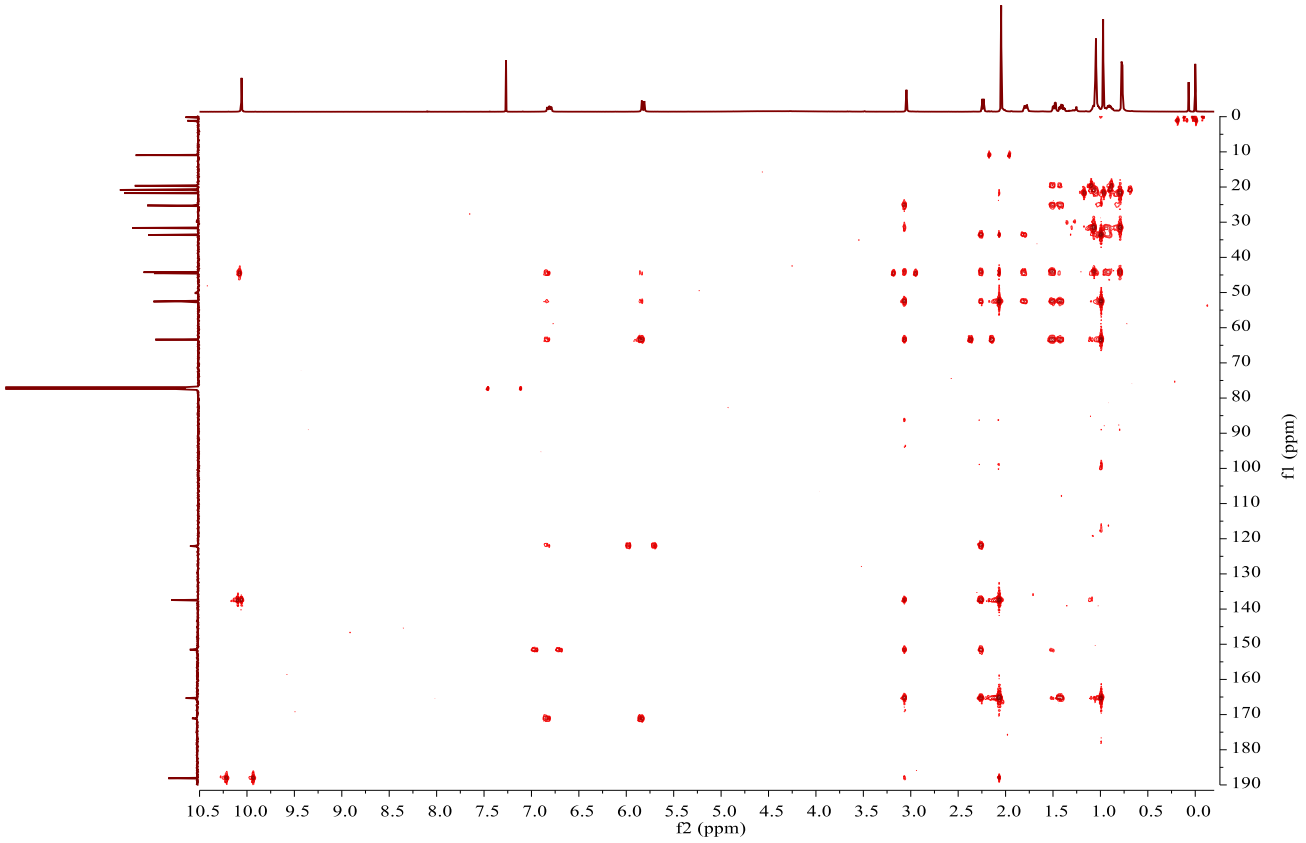
^{13}C NMR and DEPT spectra



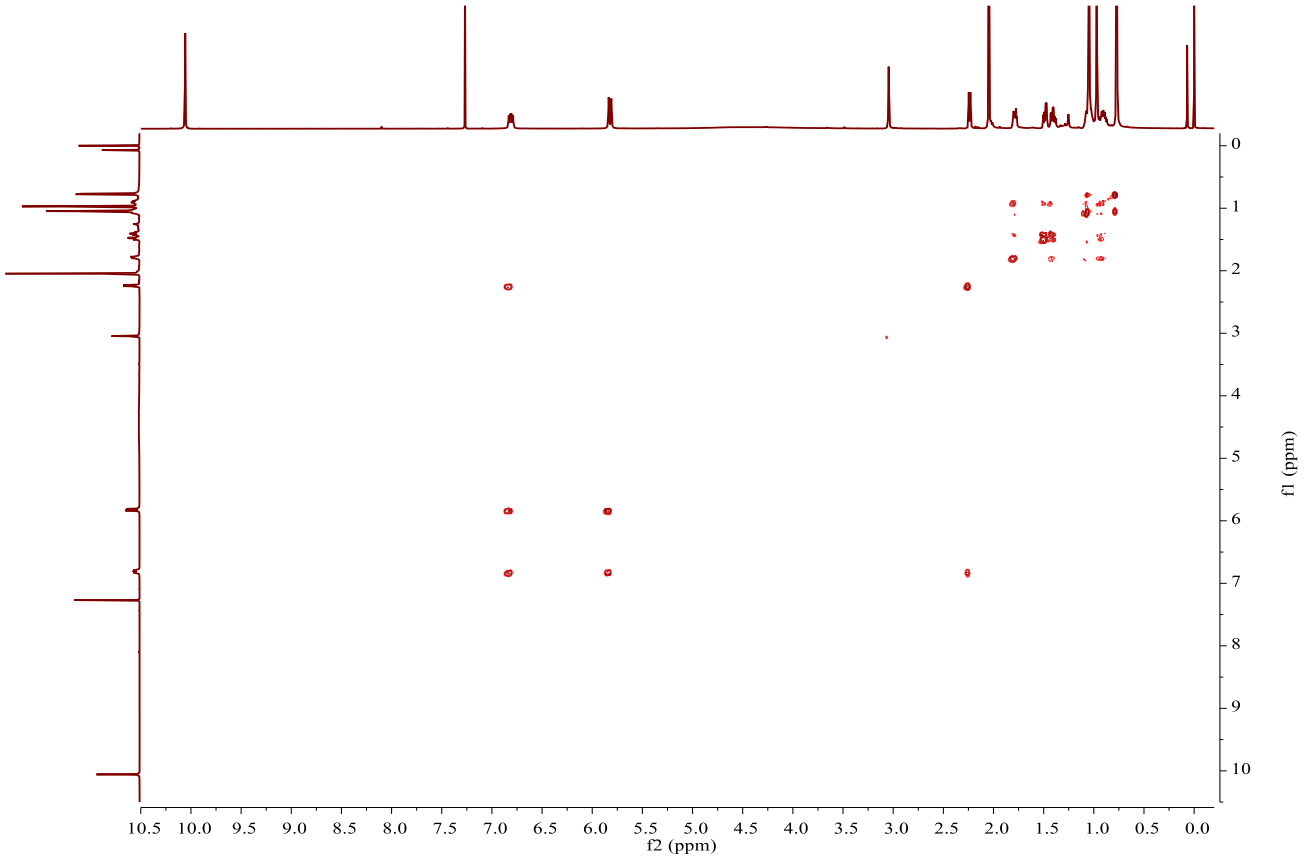
HSQC spectrum



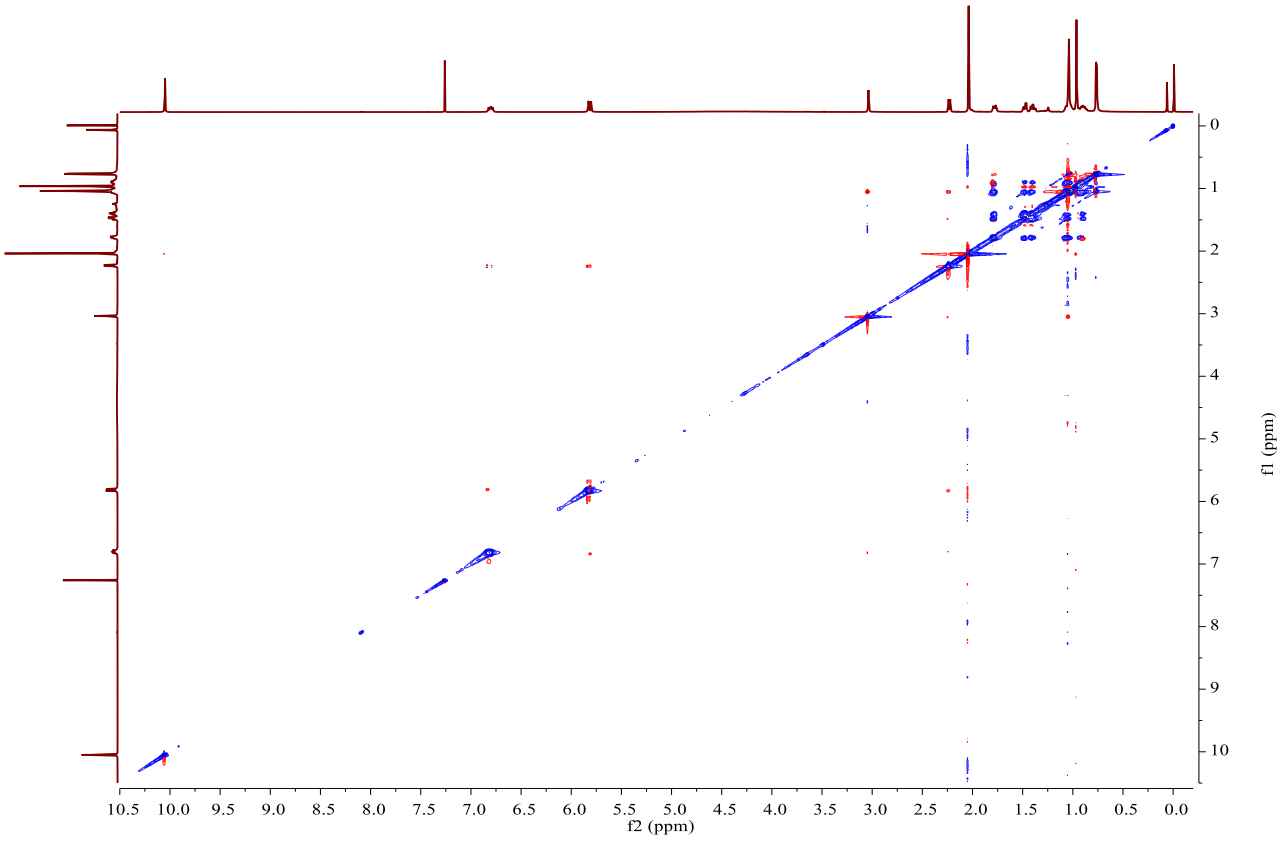
HMBC spectrum



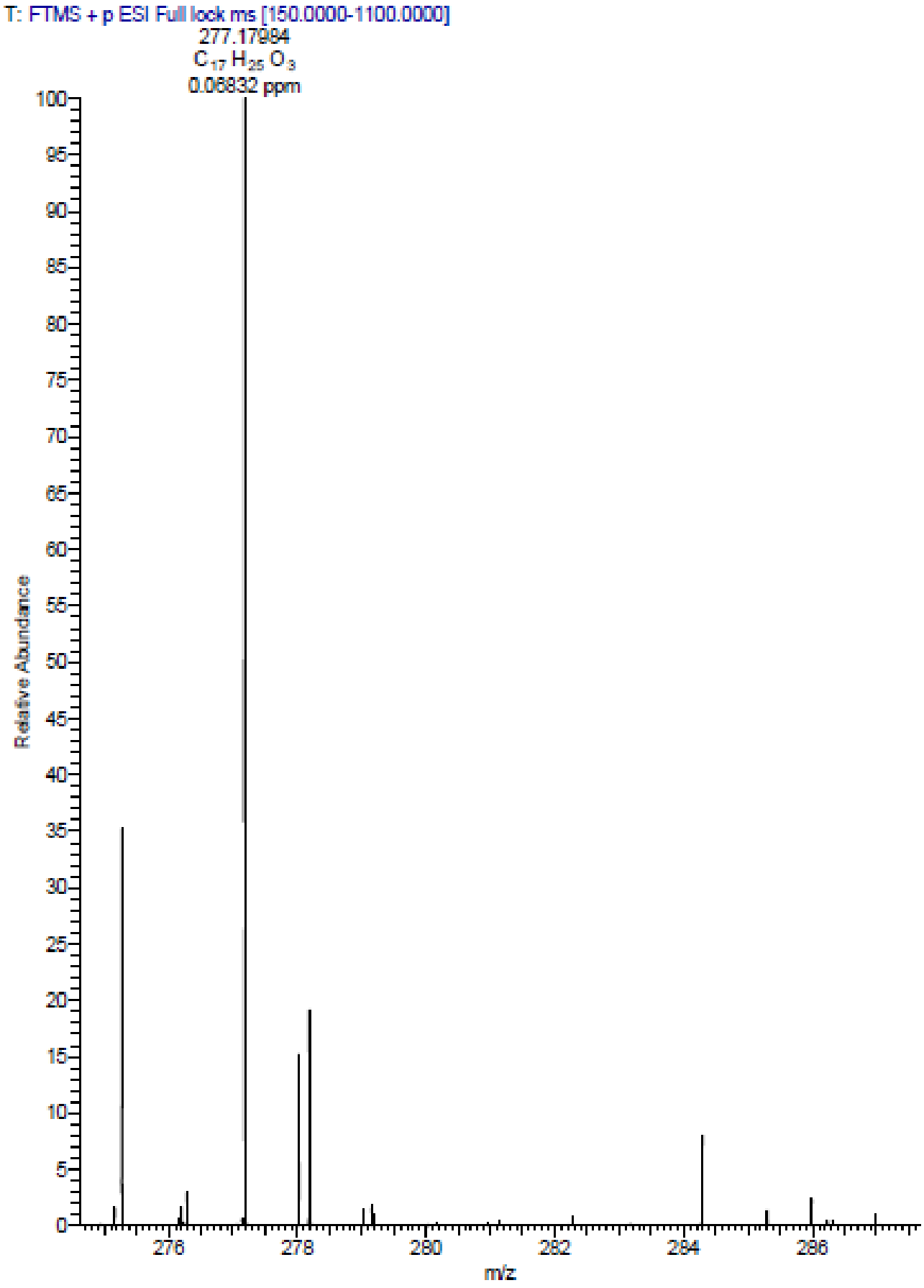
^{1}H-^{1}H COSY spectrum



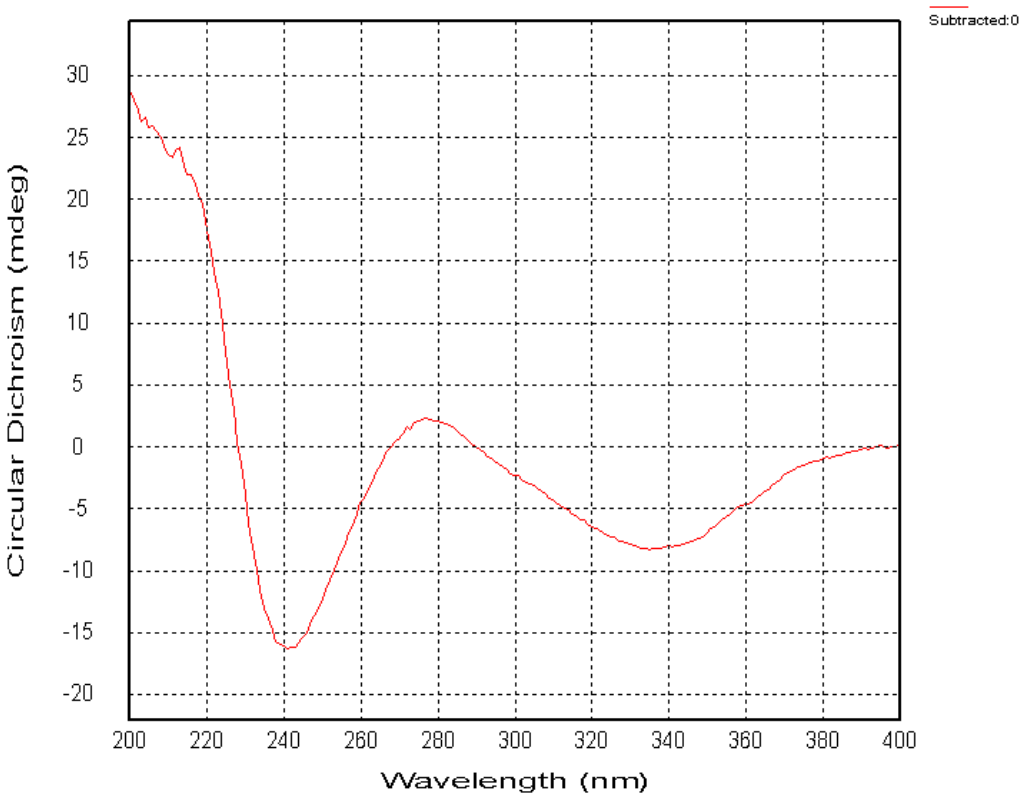
ROESY spectrum



HRESIMS

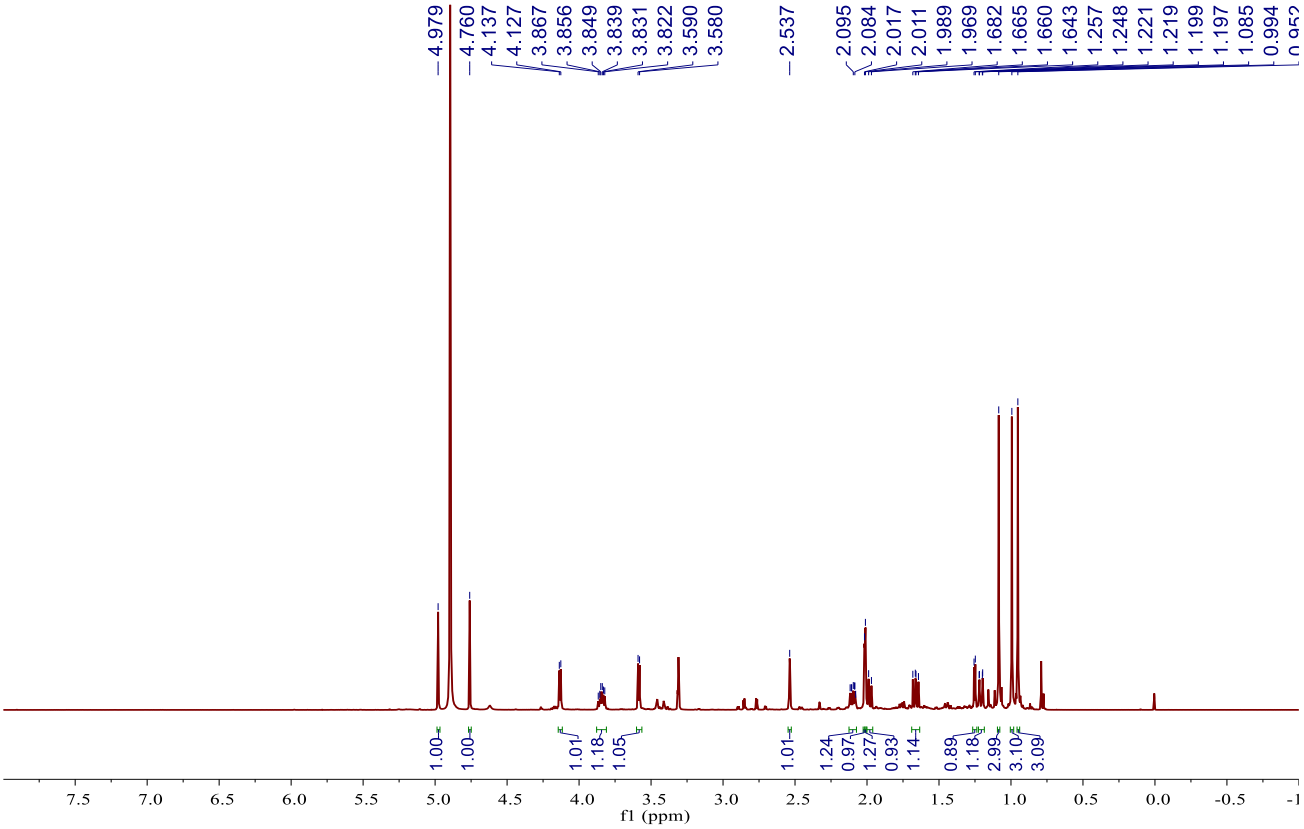

T: FTMS + p ESI Full lock ms [150.0000-1100.0000]
277.17984
C17 H25 O3
0.06832 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
276
278
280
282
284
286

CD spectra

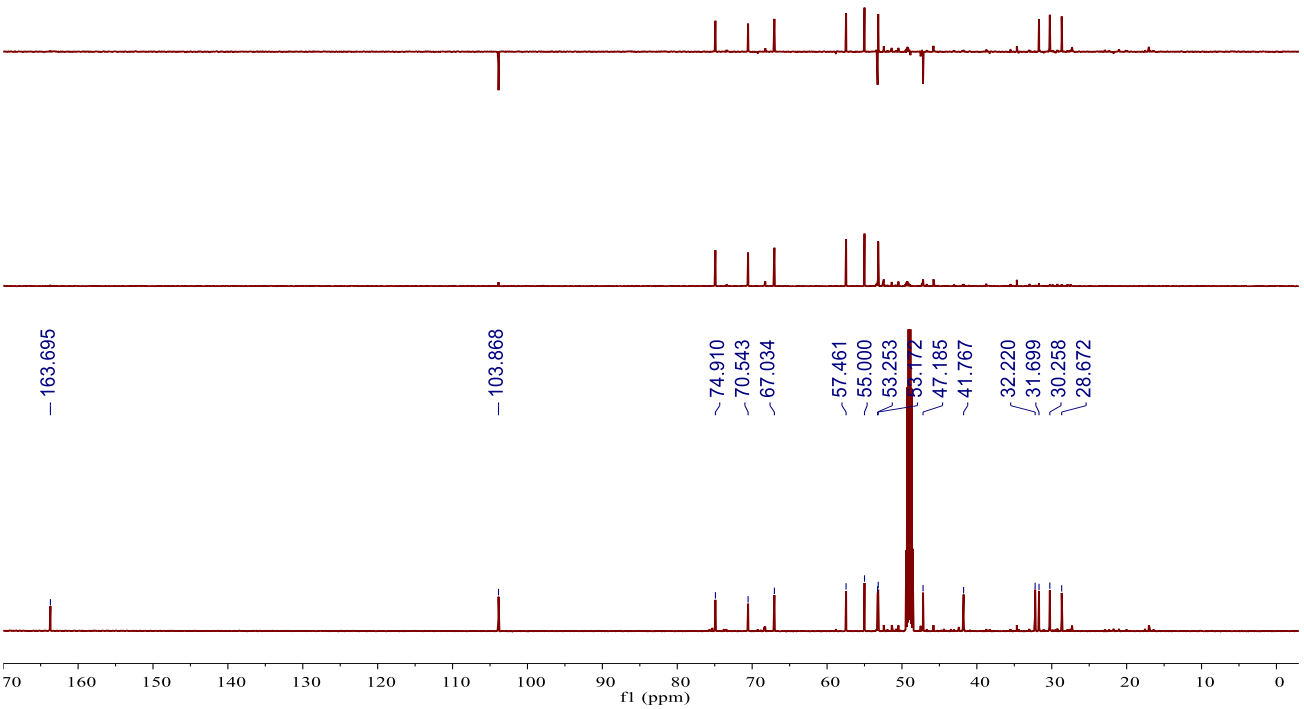

Subtracted:0
Circular Dichroism (mdeg)
30
25
20
15
10
5
0
-5
-10
-15
-20
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

S1.9 NMR and HRESIMS spectra of bipolarisorokin I (9)

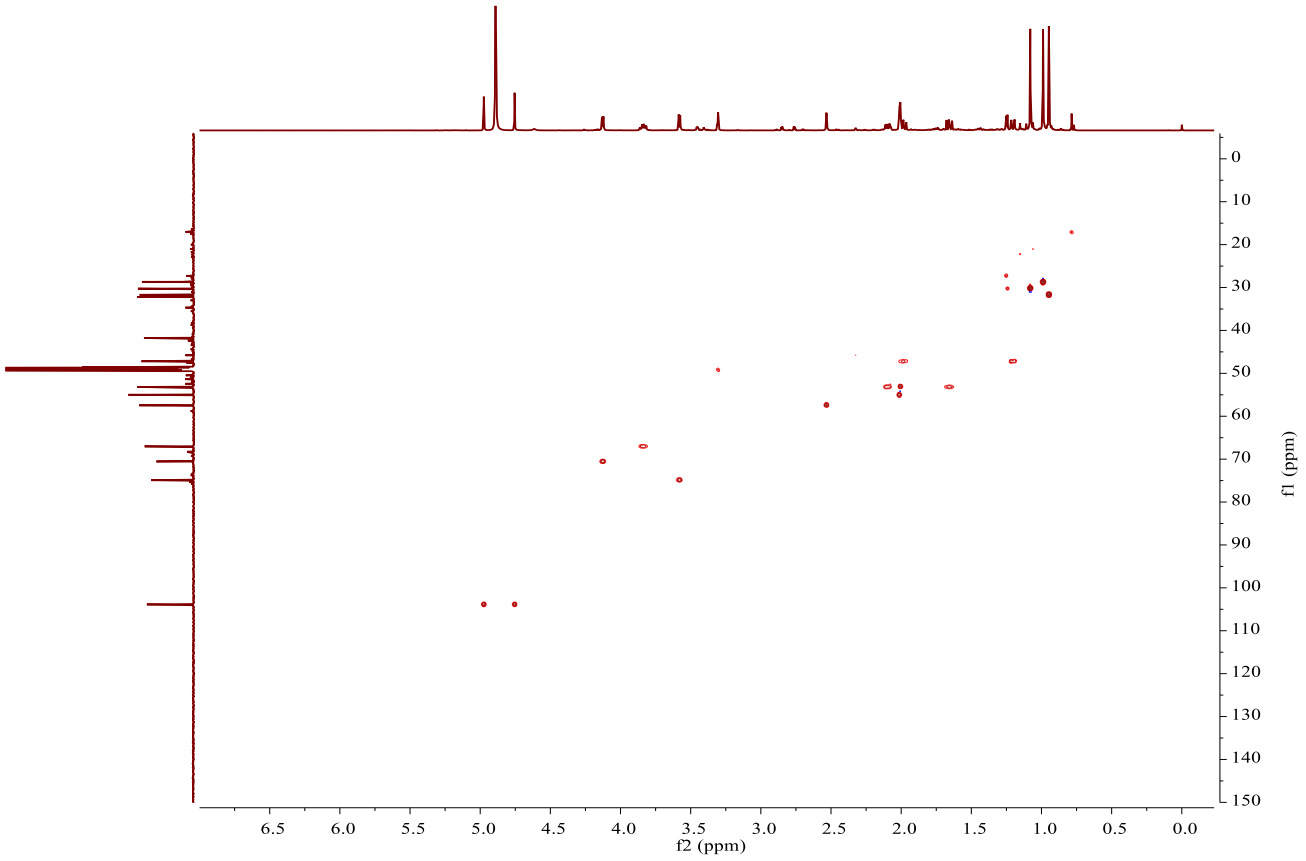
^{1}H NMR spectrum



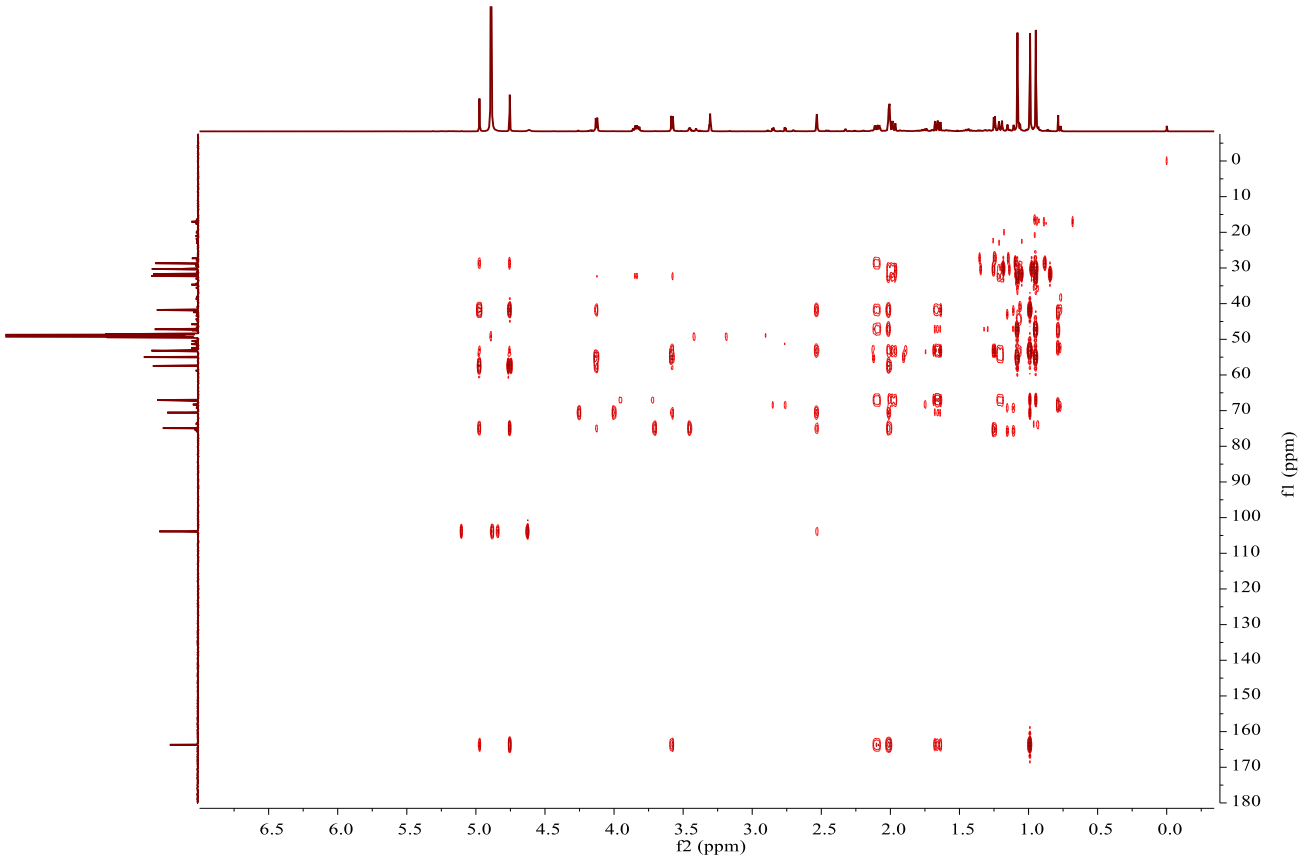
^{13}C NMR and DEPT spectra



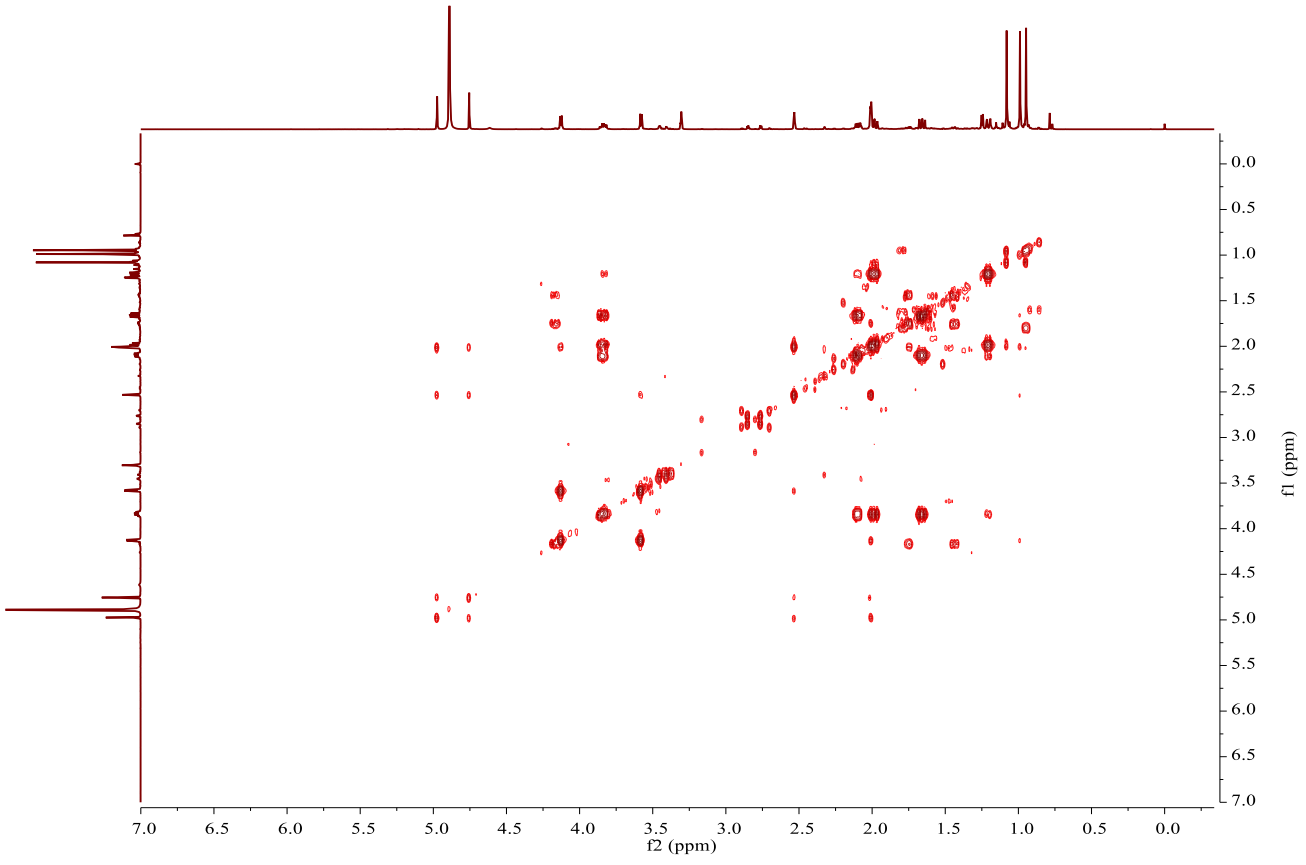
HSQC spectrum



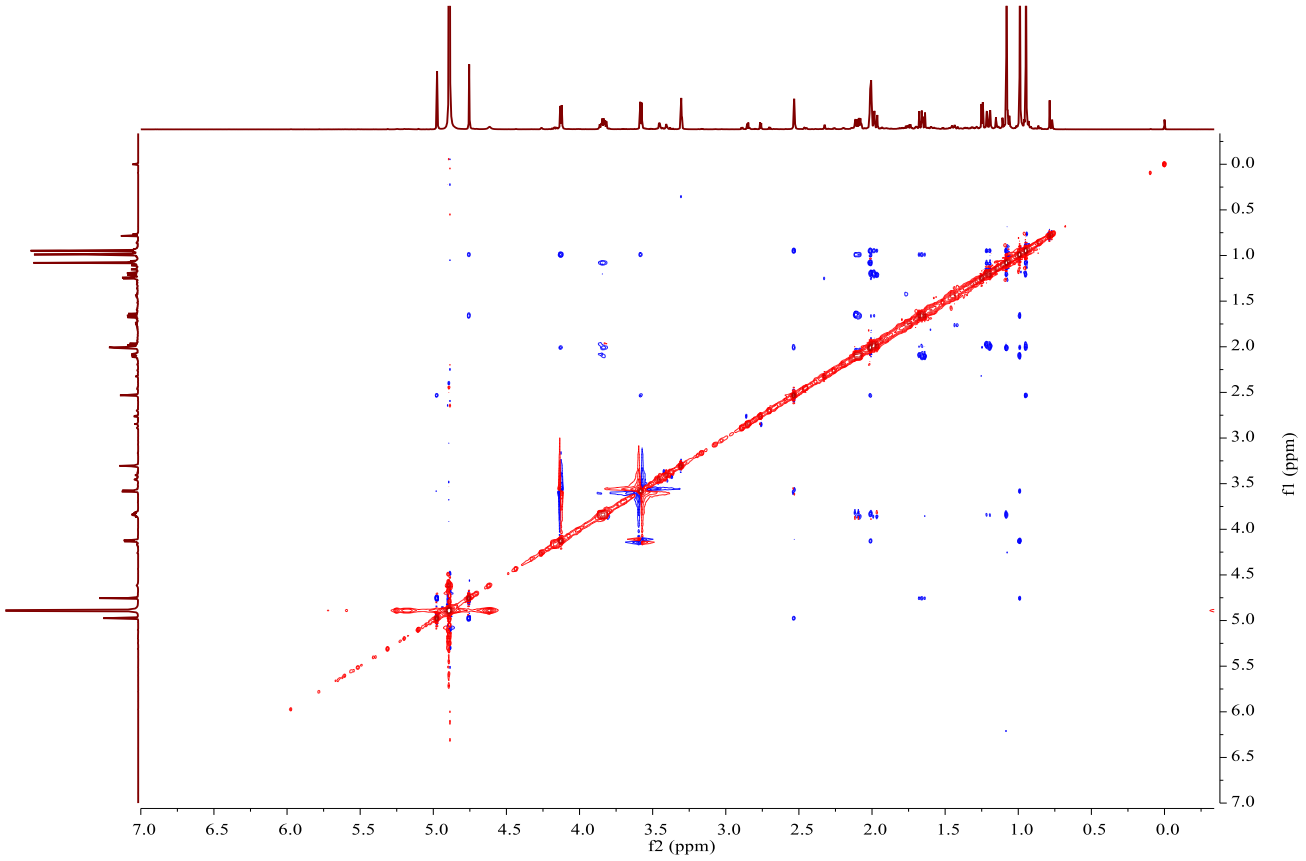
HMBC spectrum



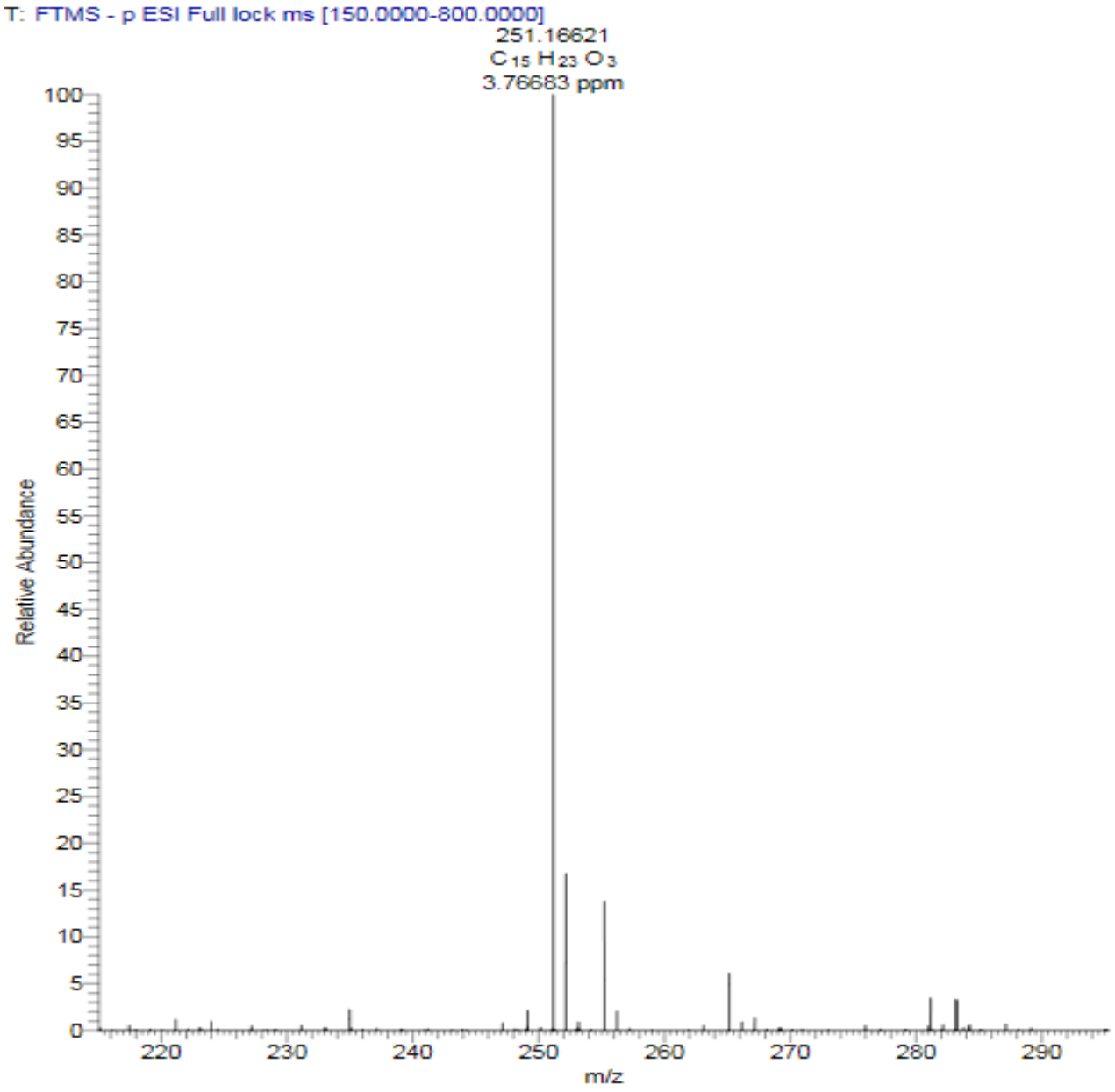
^{1}H-^{1}H COSY spectrum



ROESY spectrum

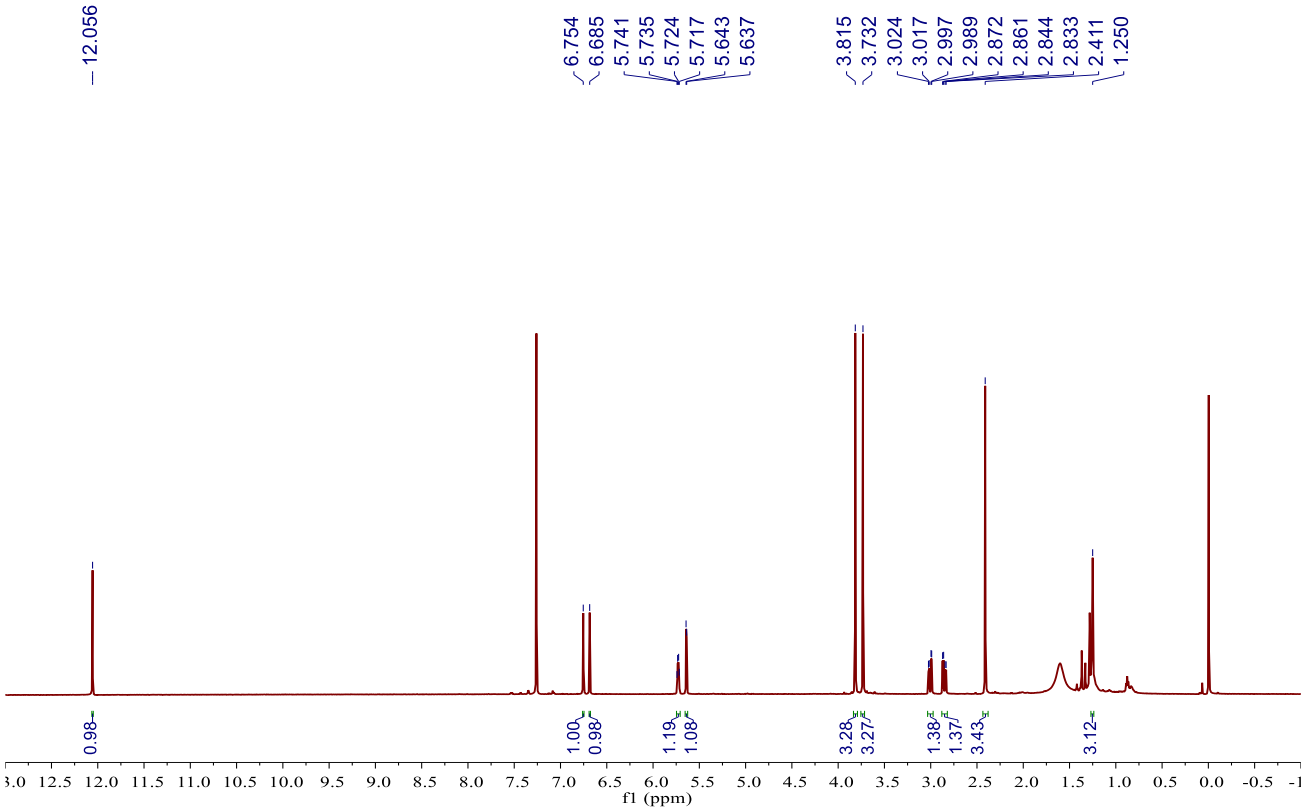


HRESIMS

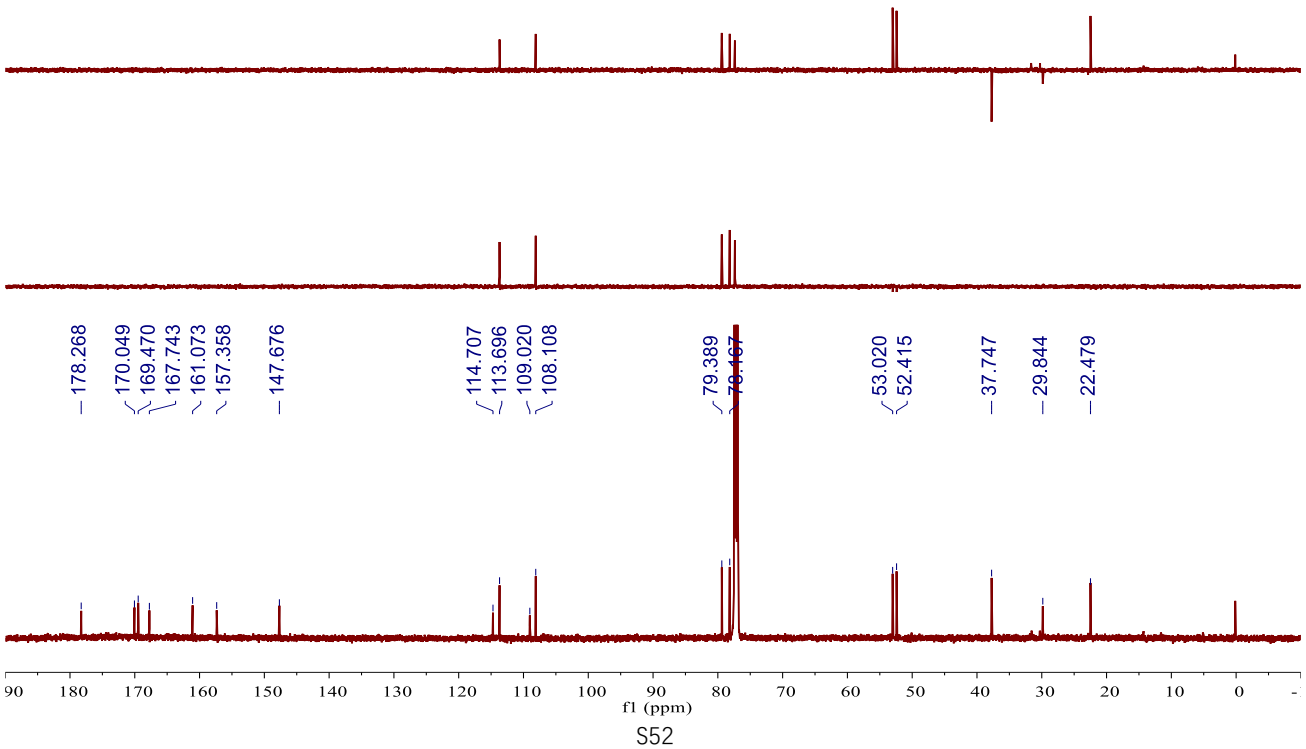

T: FTMS - p ESI Full lock ms [150.0000-800.0000]
251.16621
C15 H23 O3
3.76683 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
220
230
240
250
260
270
280
290

S1.10 NMR, HRESIMS and CD spectra of bipolarithone A (10)

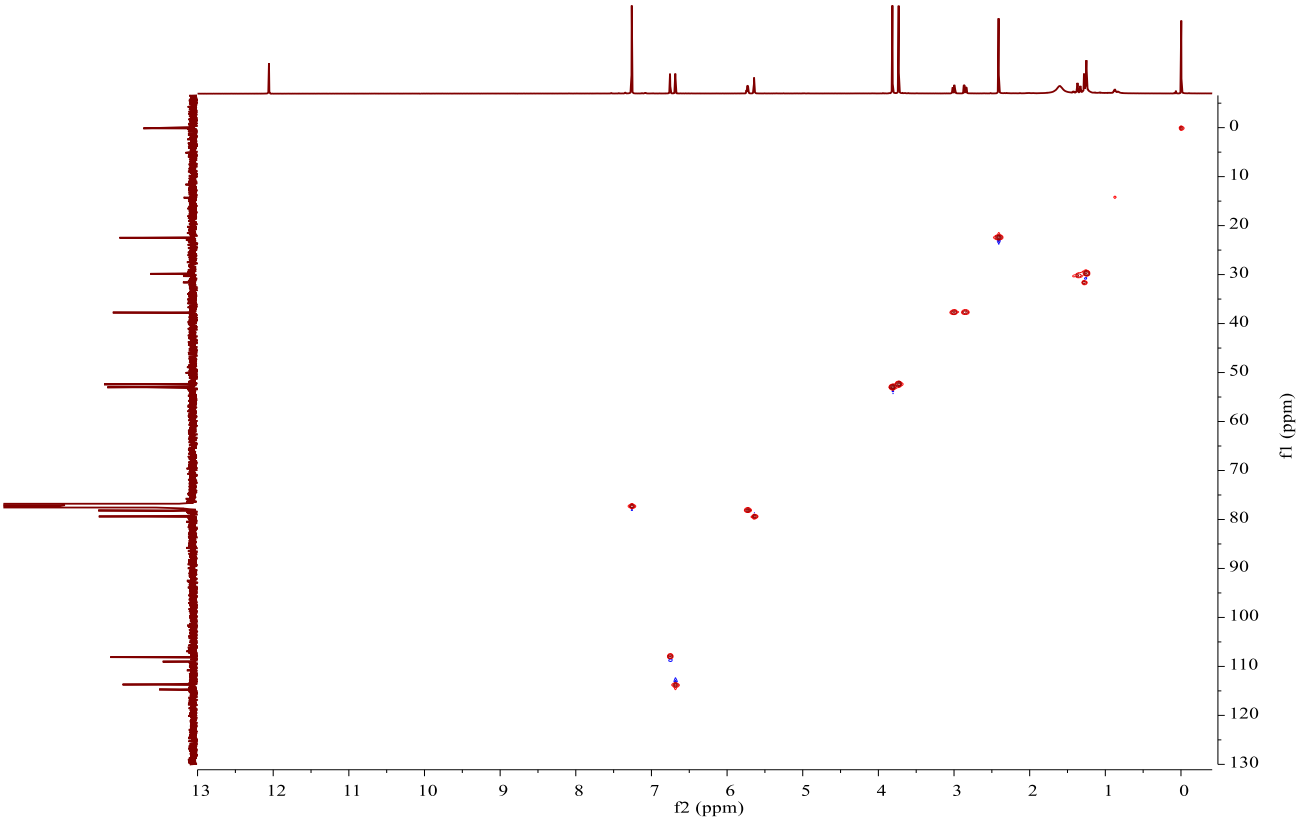
^{1}H NMR spectrum



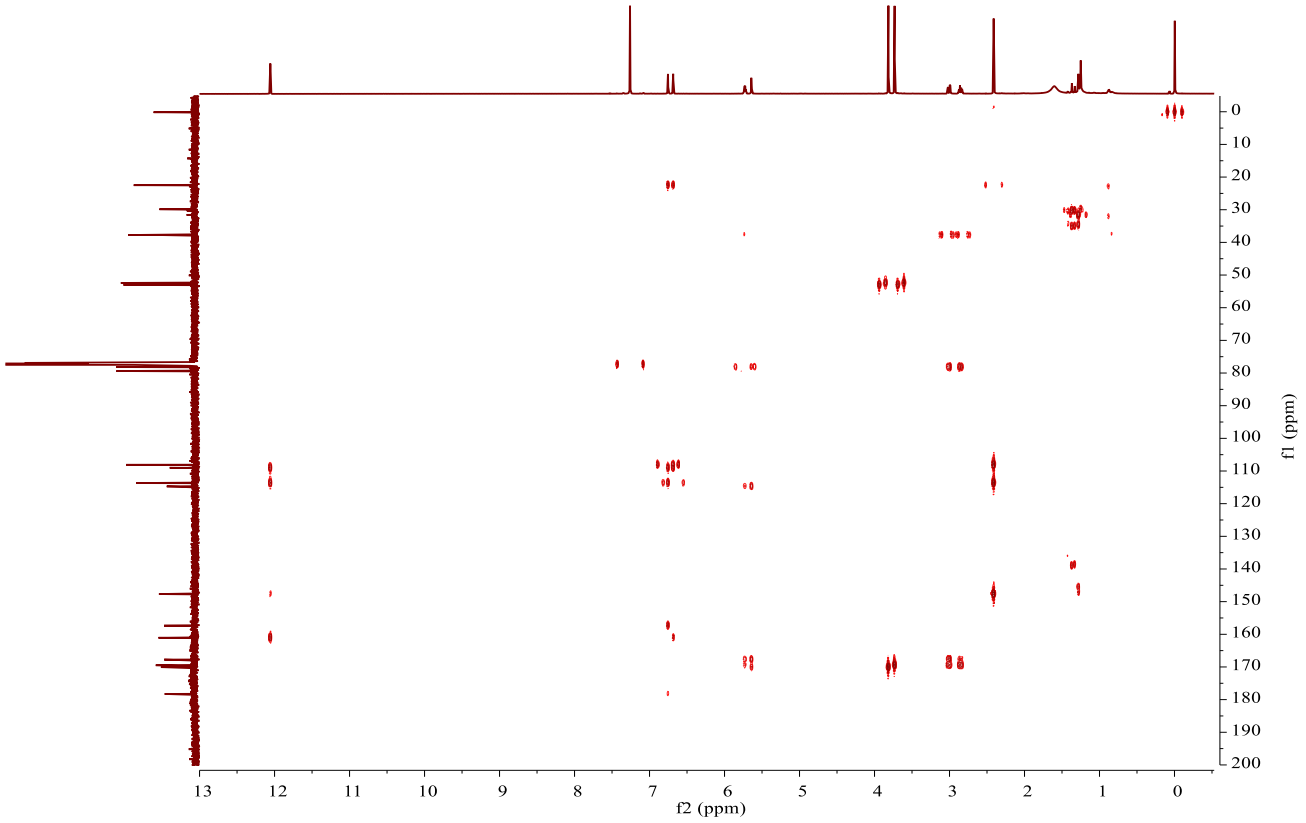
^{13}C NMR and DEPT spectra



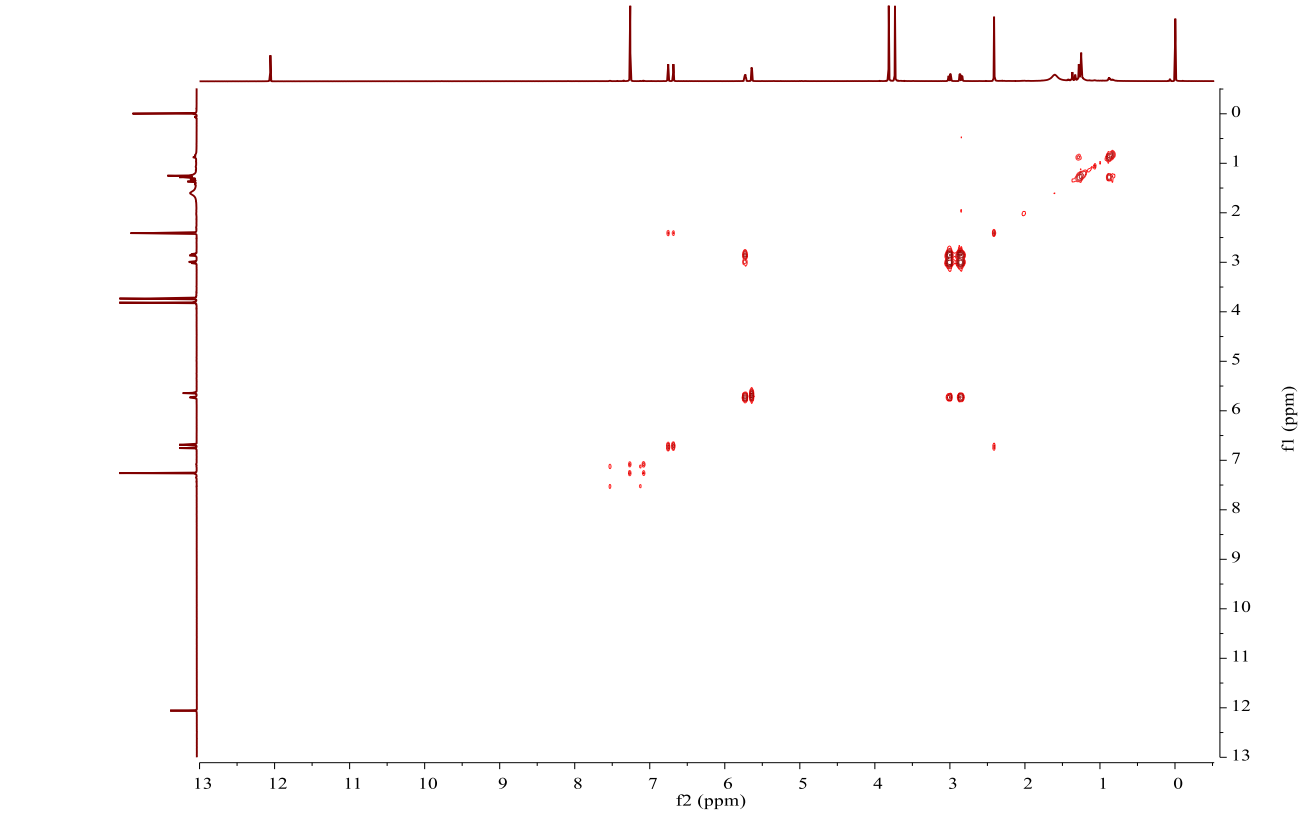
HSQC spectrum



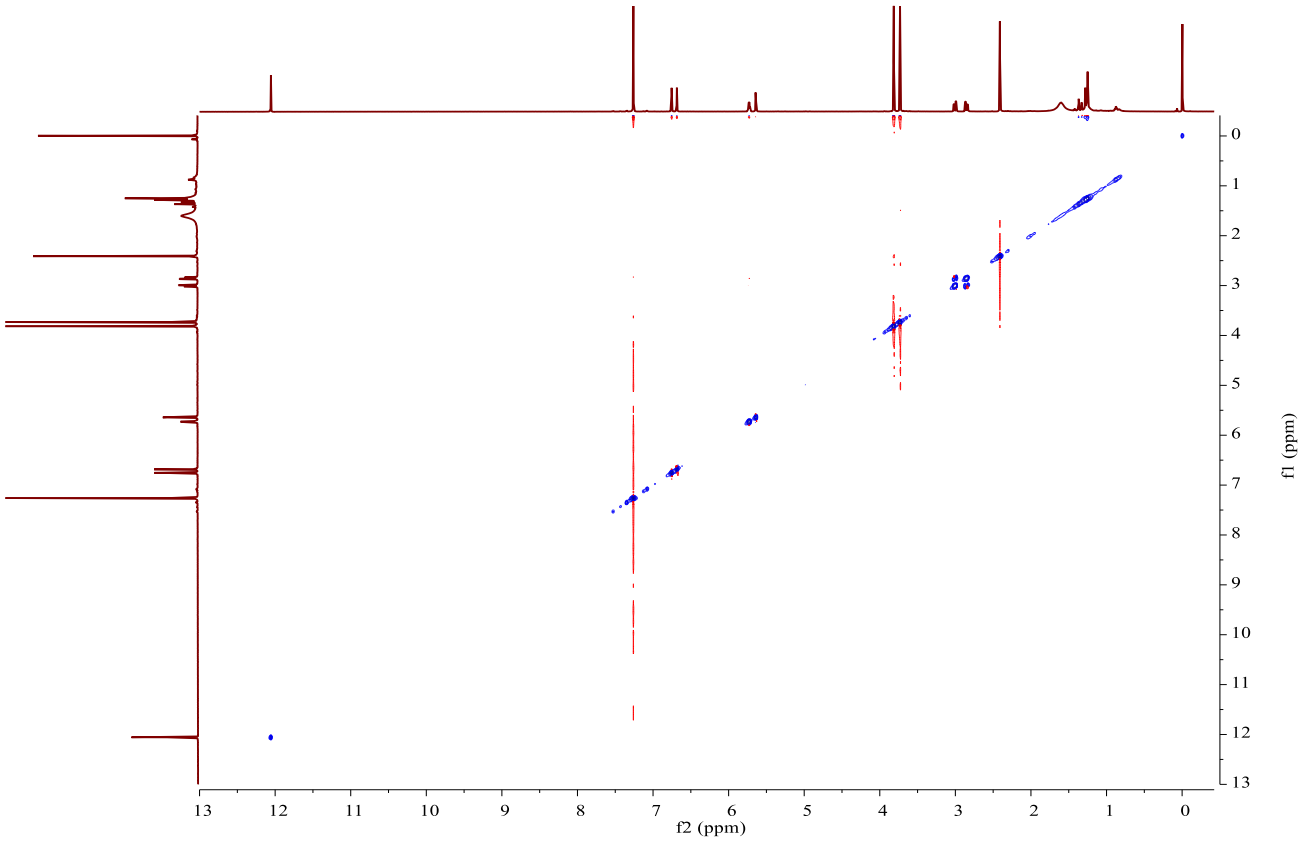
HMBC spectrum



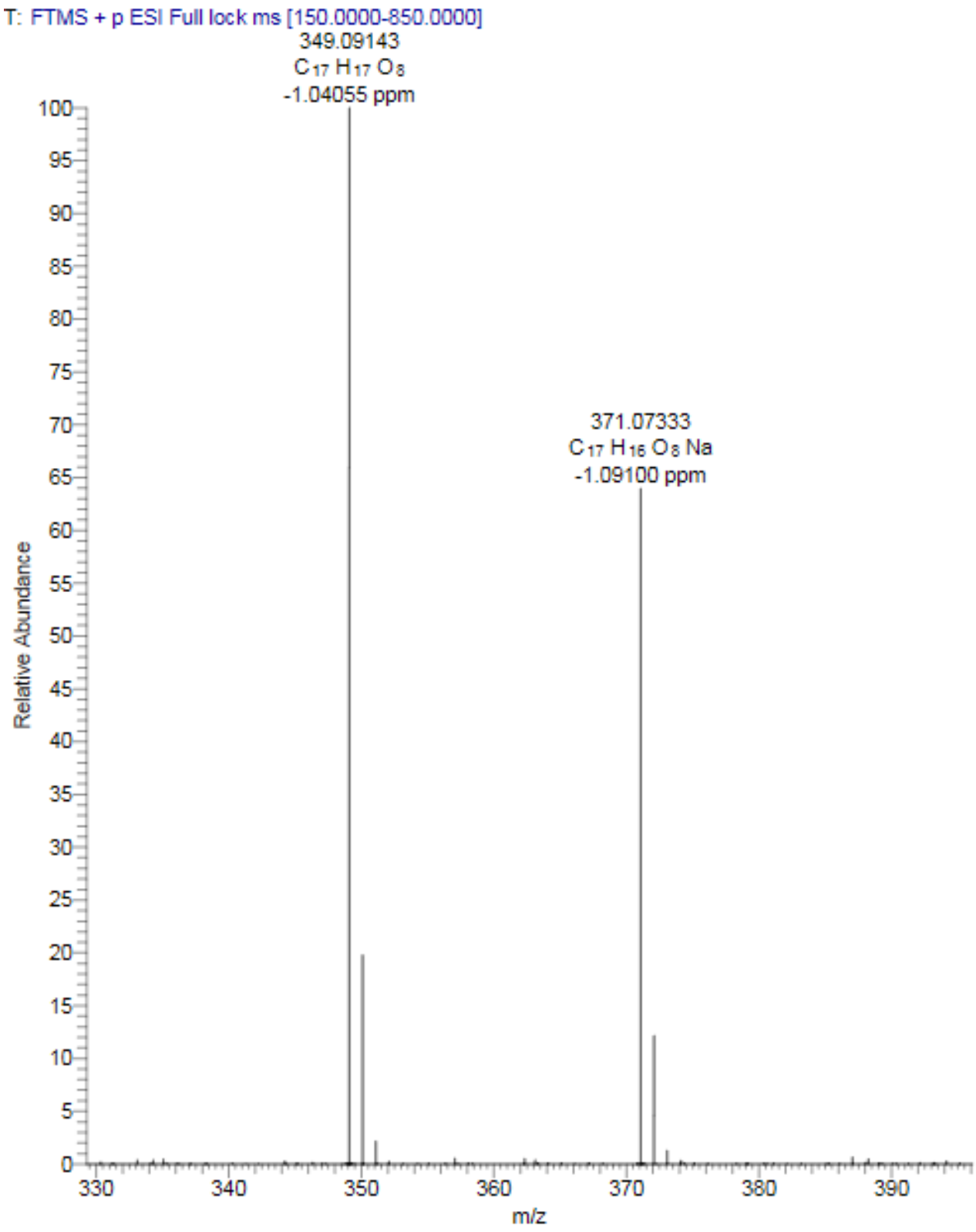
^{1}H-^{1}H COSY spectrum



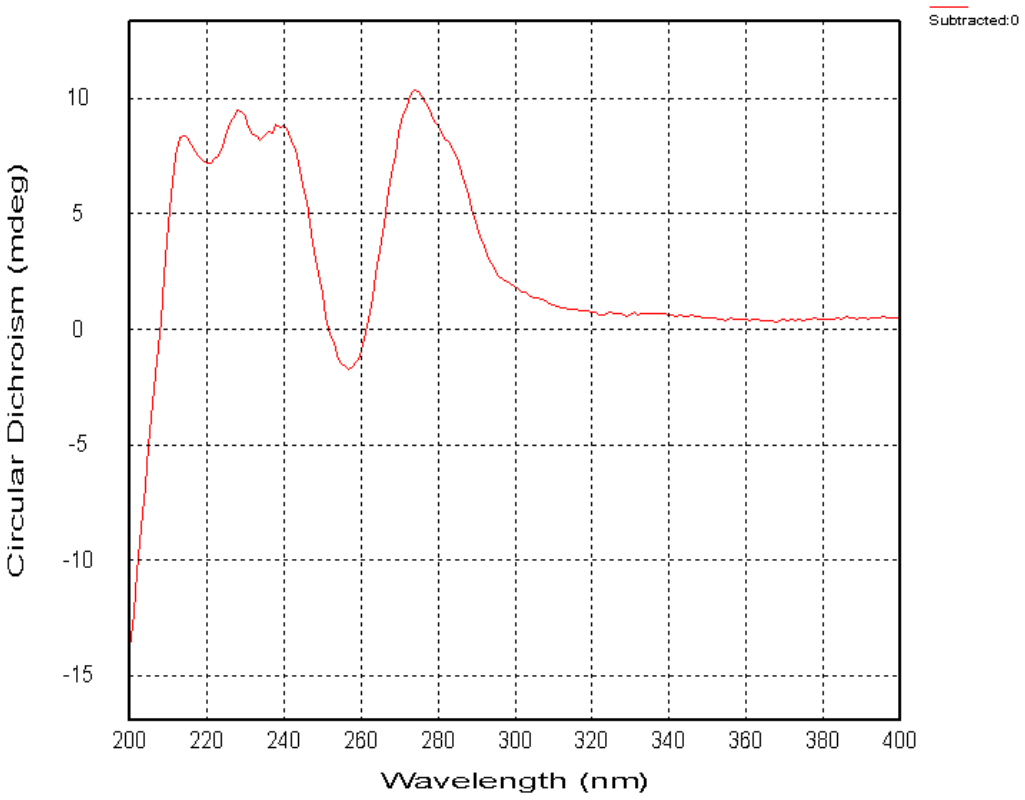
ROESY spectrum



HRESIMS

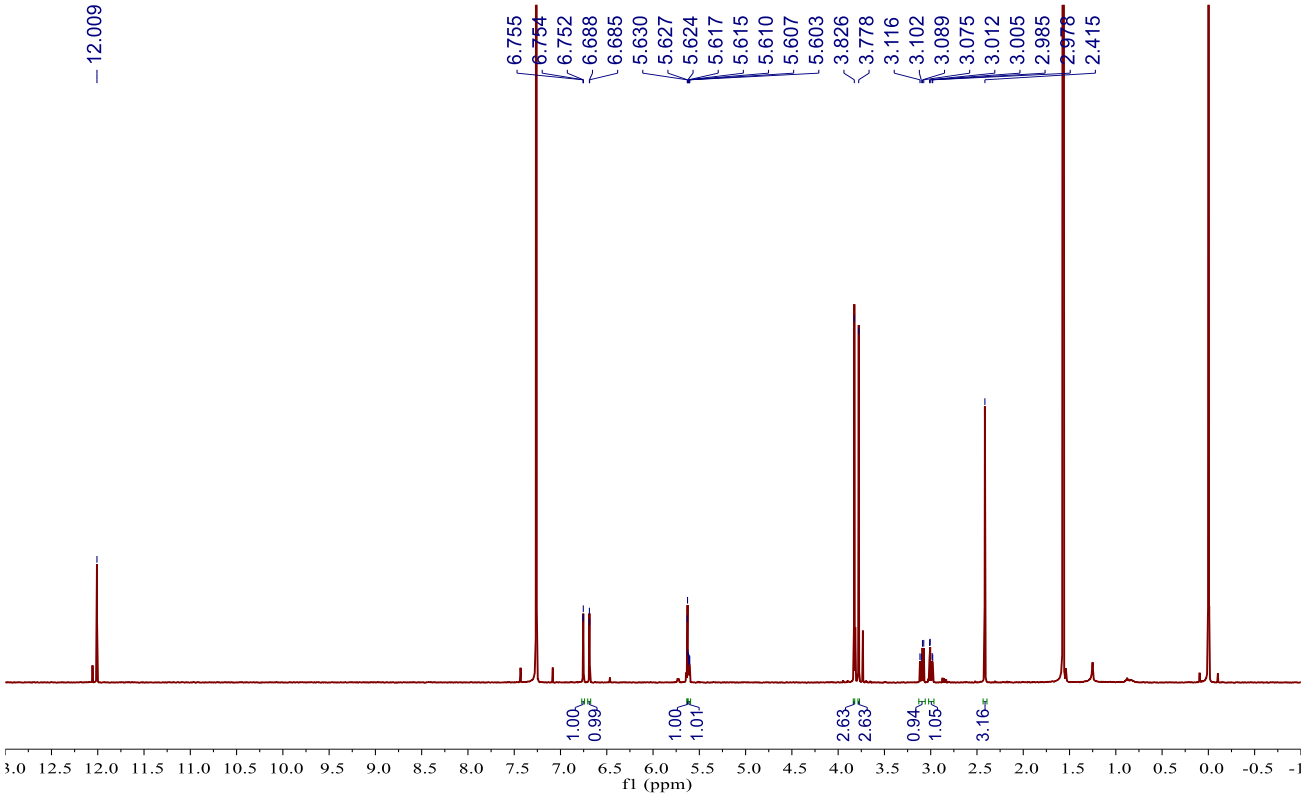

T: FTMS + p ESI Full lock ms [150.0000-850.0000]
349.09143
C17 H17 O8
-1.04055 ppm
371.07333
C17 H16 O8 Na
-1.09100 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
330
340
350
360
370
380
390

CD spectra

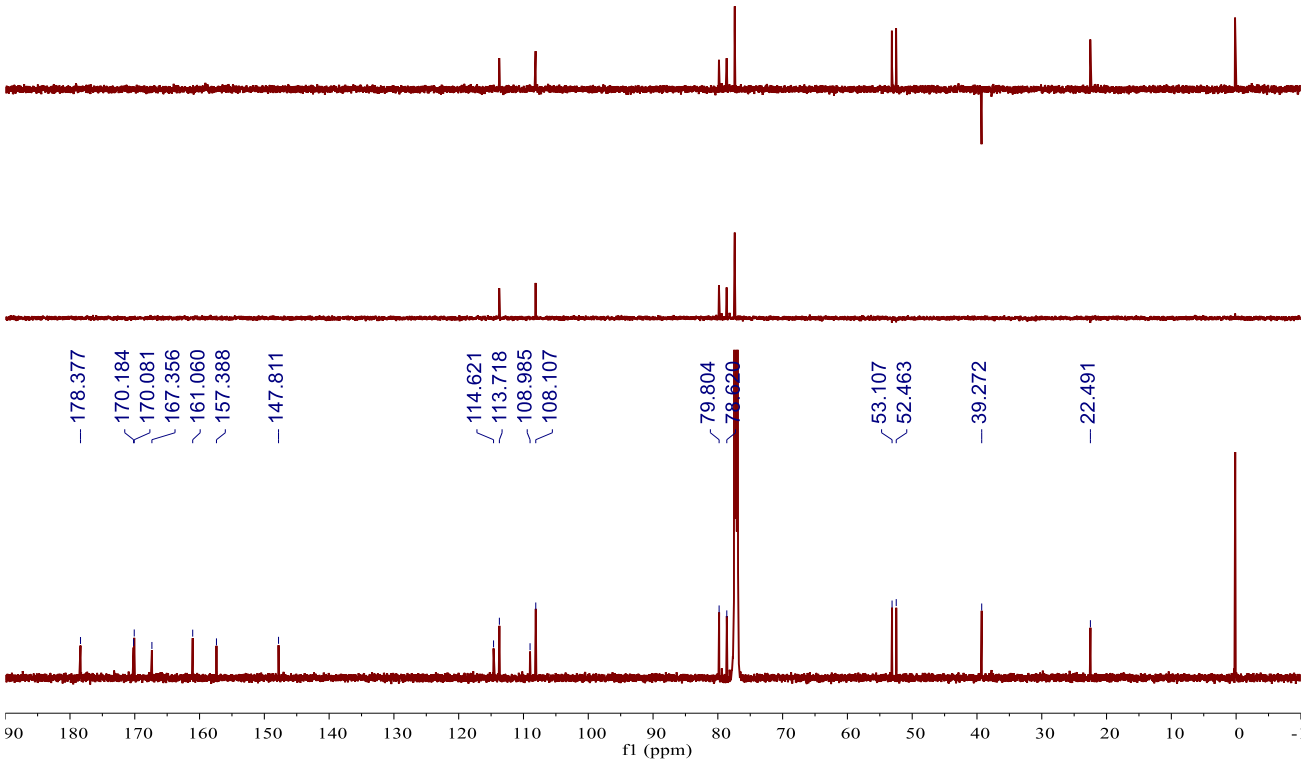

Subtracted:0
Circular Dichroism (mdeg)
10
5
0
-5
-10
-15
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

S1.11 NMR, HRESIMS and CD spectra of bipolarithone B (11)

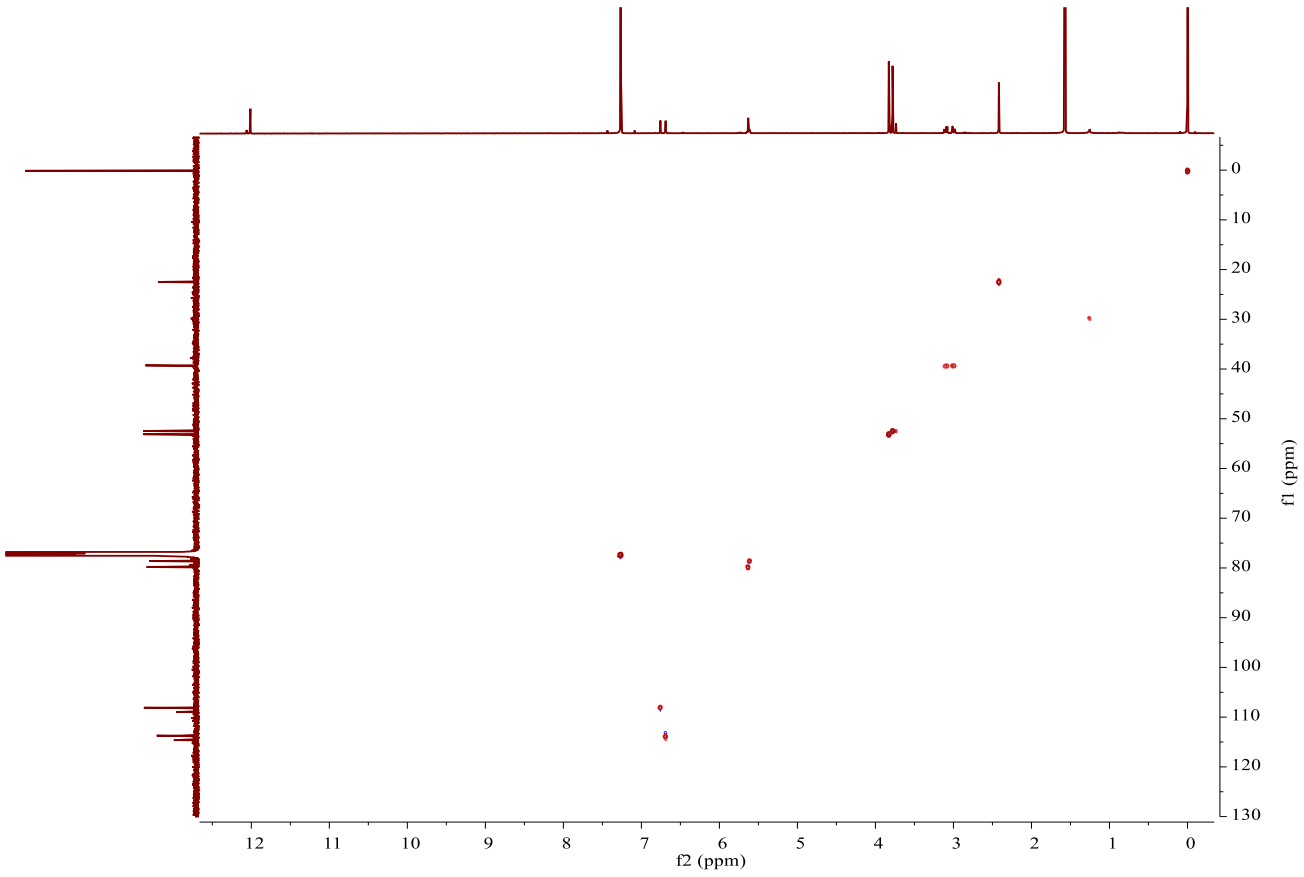
^{1}H NMR spectrum



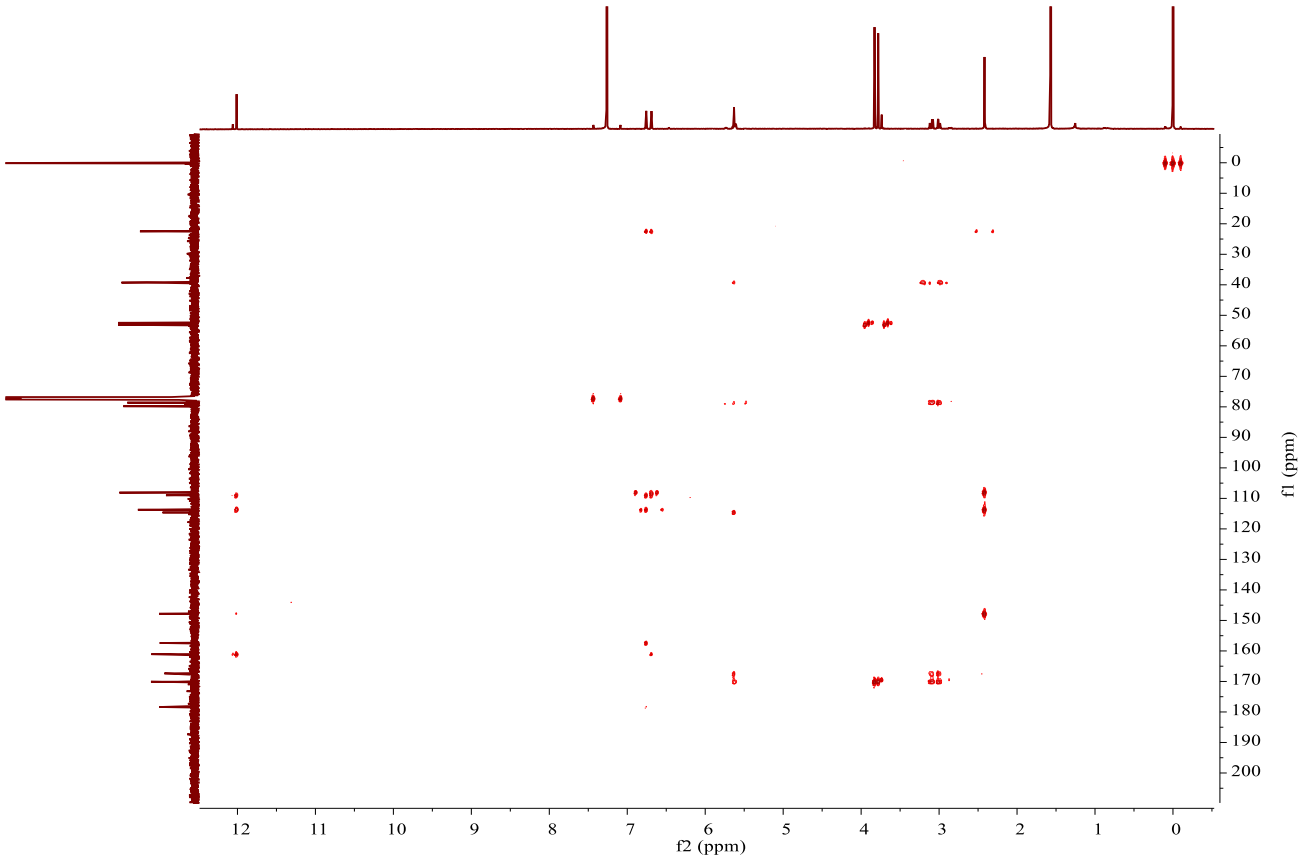
^{13}C NMR and DEPT spectra



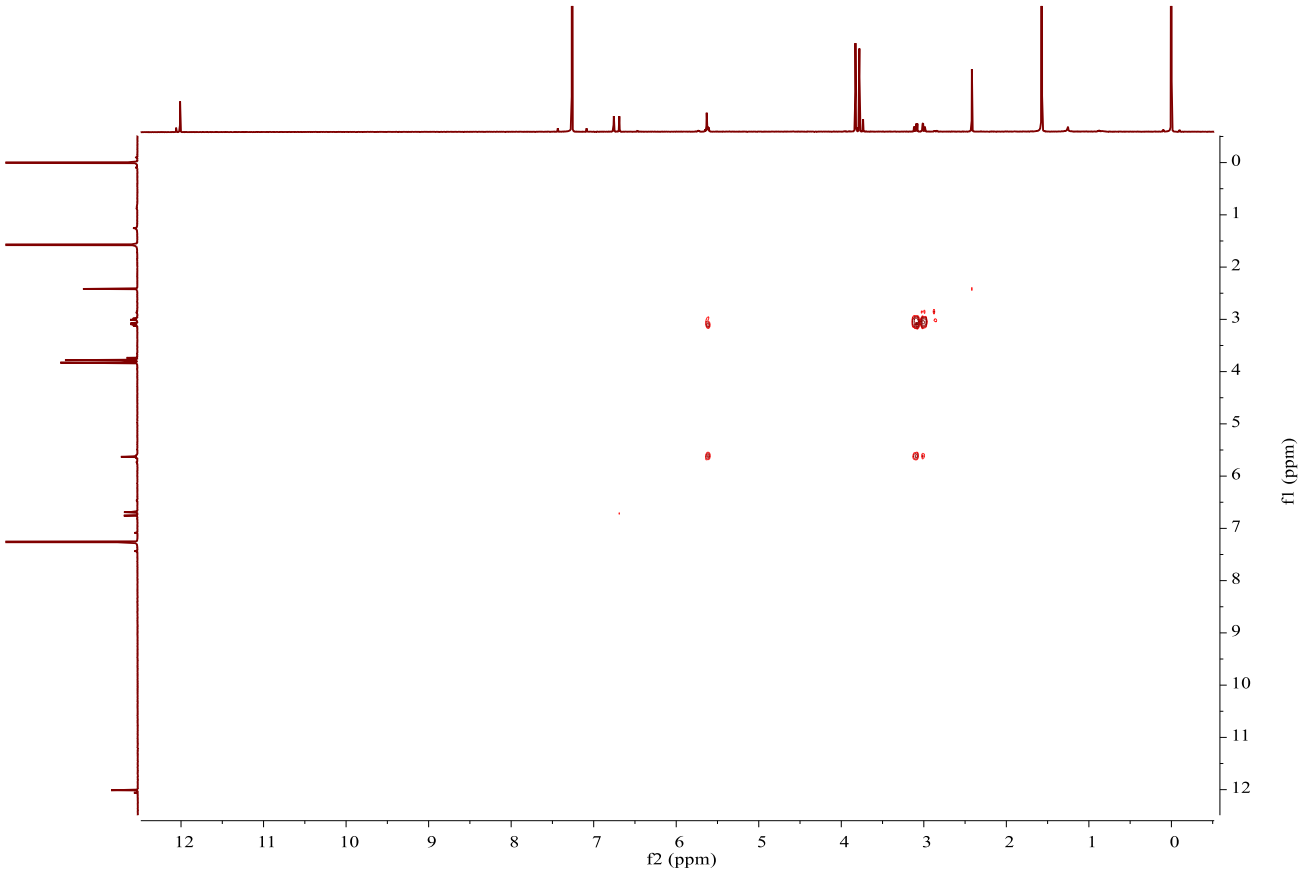
HSQC spectrum



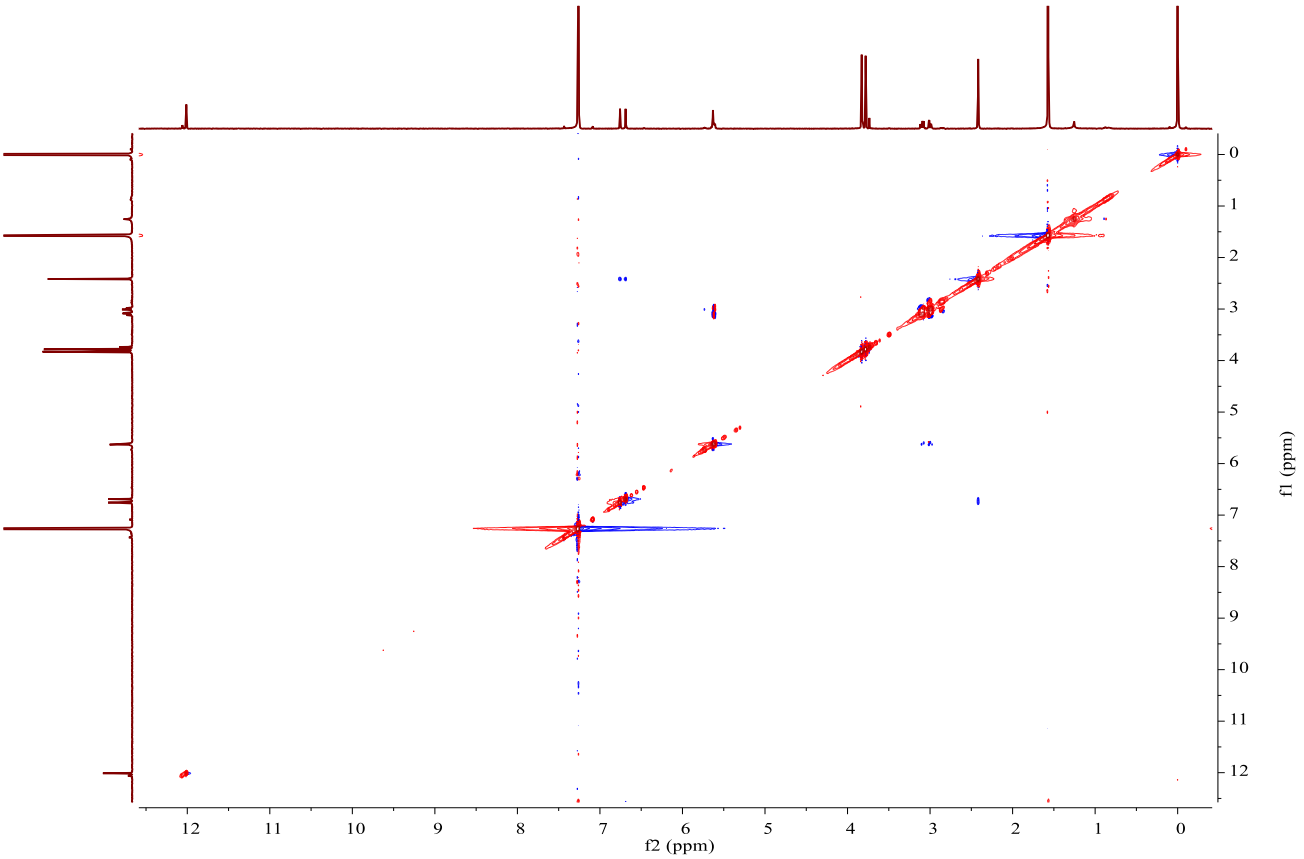
HMBC spectrum



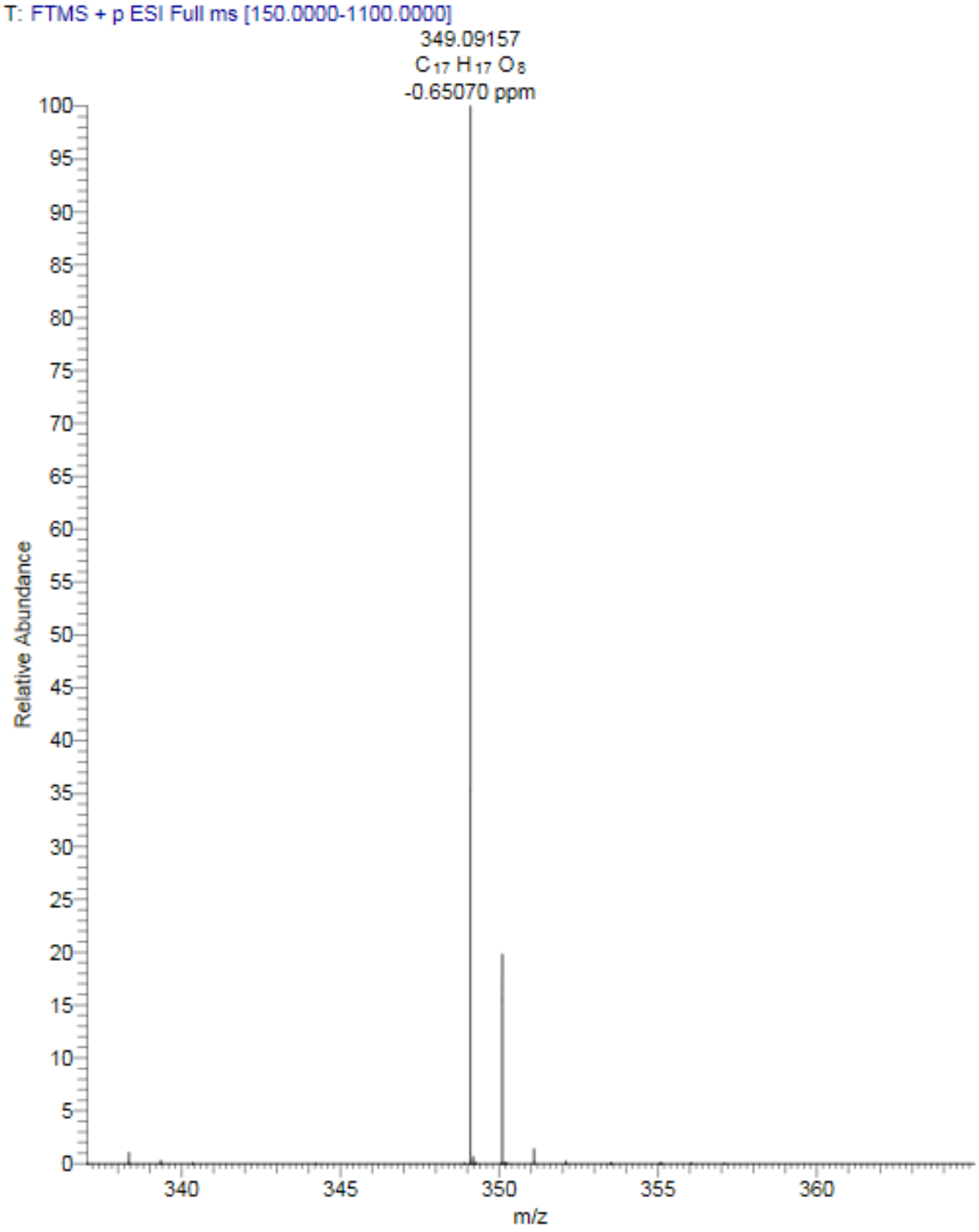
^{1}H-^{1}H COSY spectrum



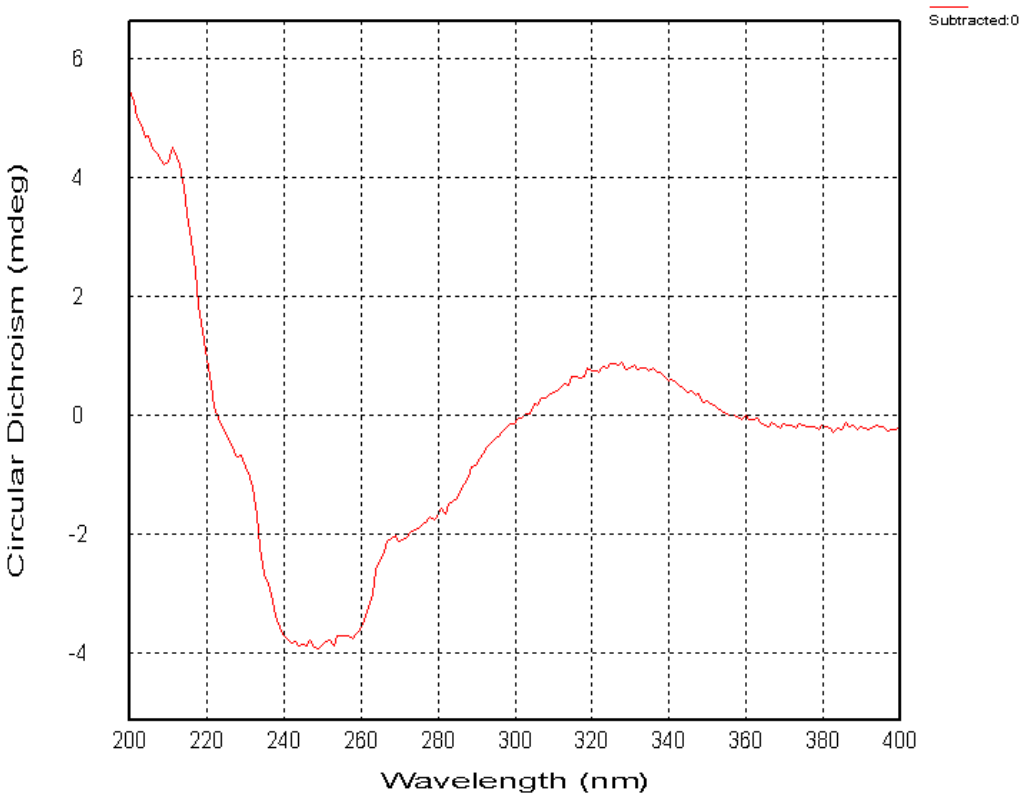
ROESY spectrum



HRESIMS

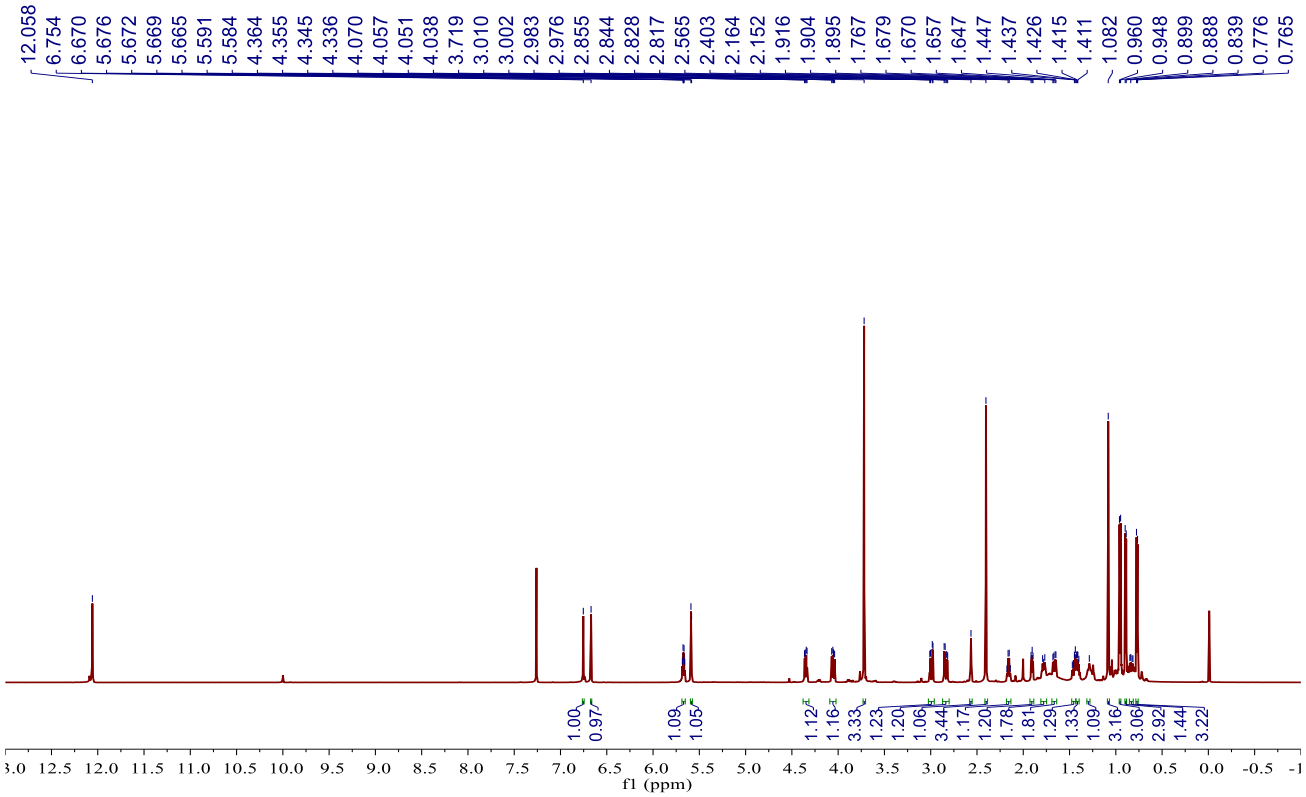

T: FTMS + p ESI Full ms [150.0000-1100.0000]
349.09157
C17 H17 O8
-0.65070 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
340
345
350
355
360

CD spectra

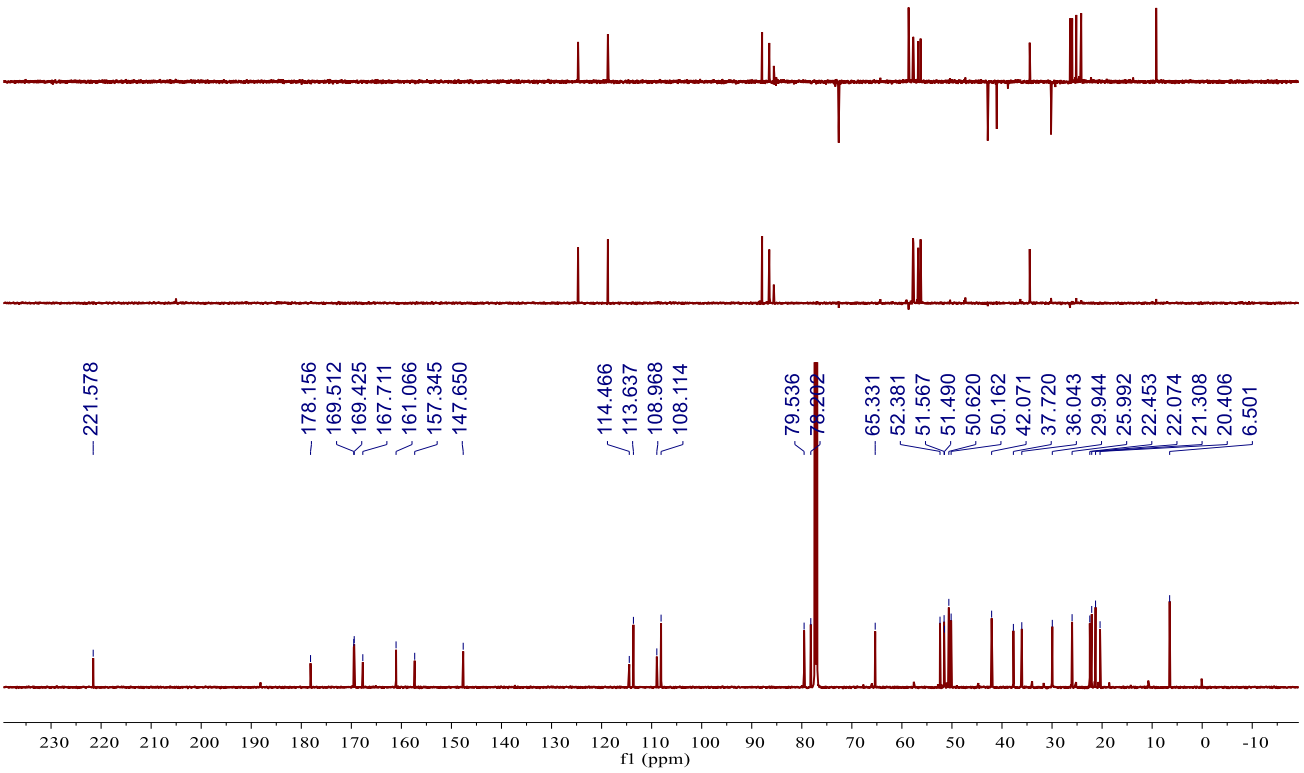

Subtracted:0
Circular Dichroism (mdeg)
6
4
2
0
-2
-4
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

S1.12 NMR, HRESIMS and CD spectra of bipolarithone C (12)

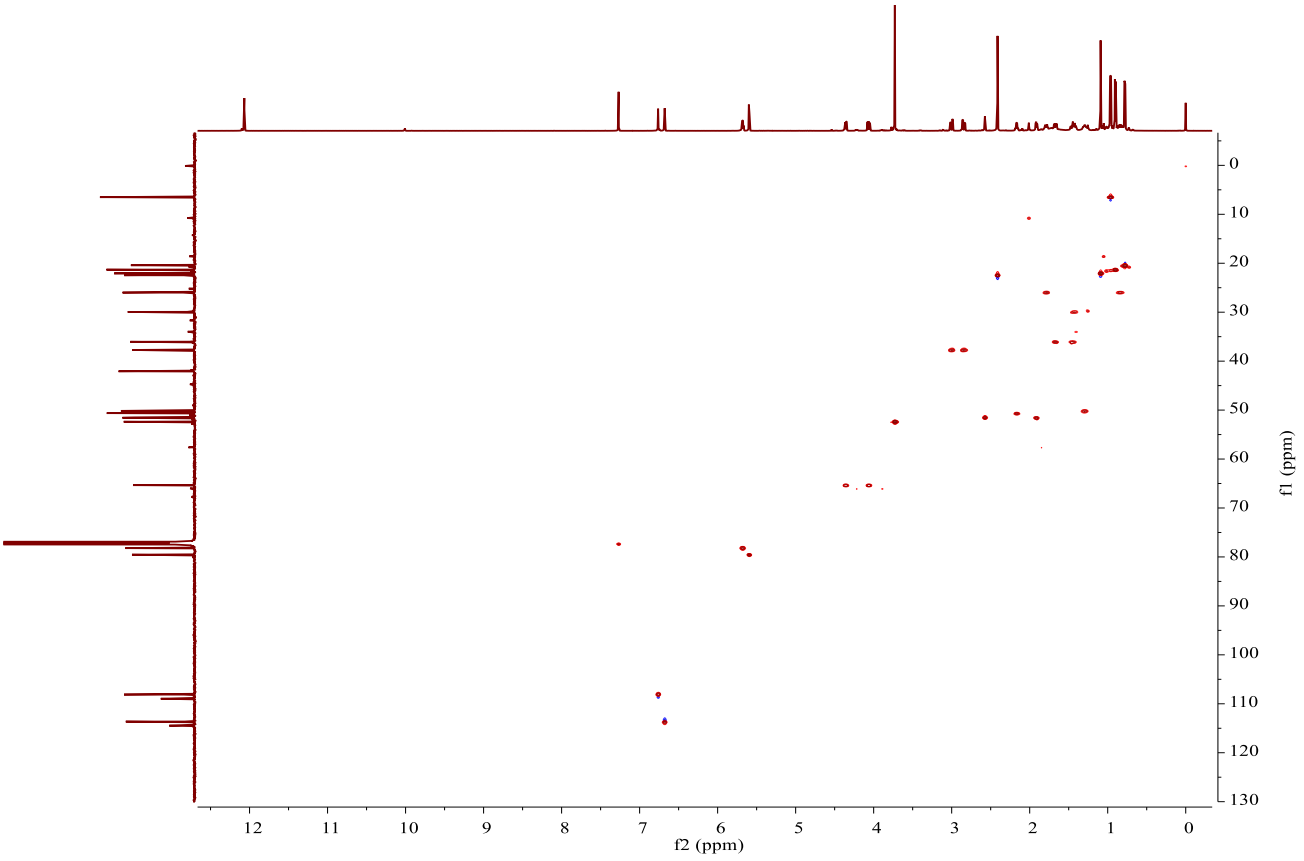
^{1}H NMR spectrum



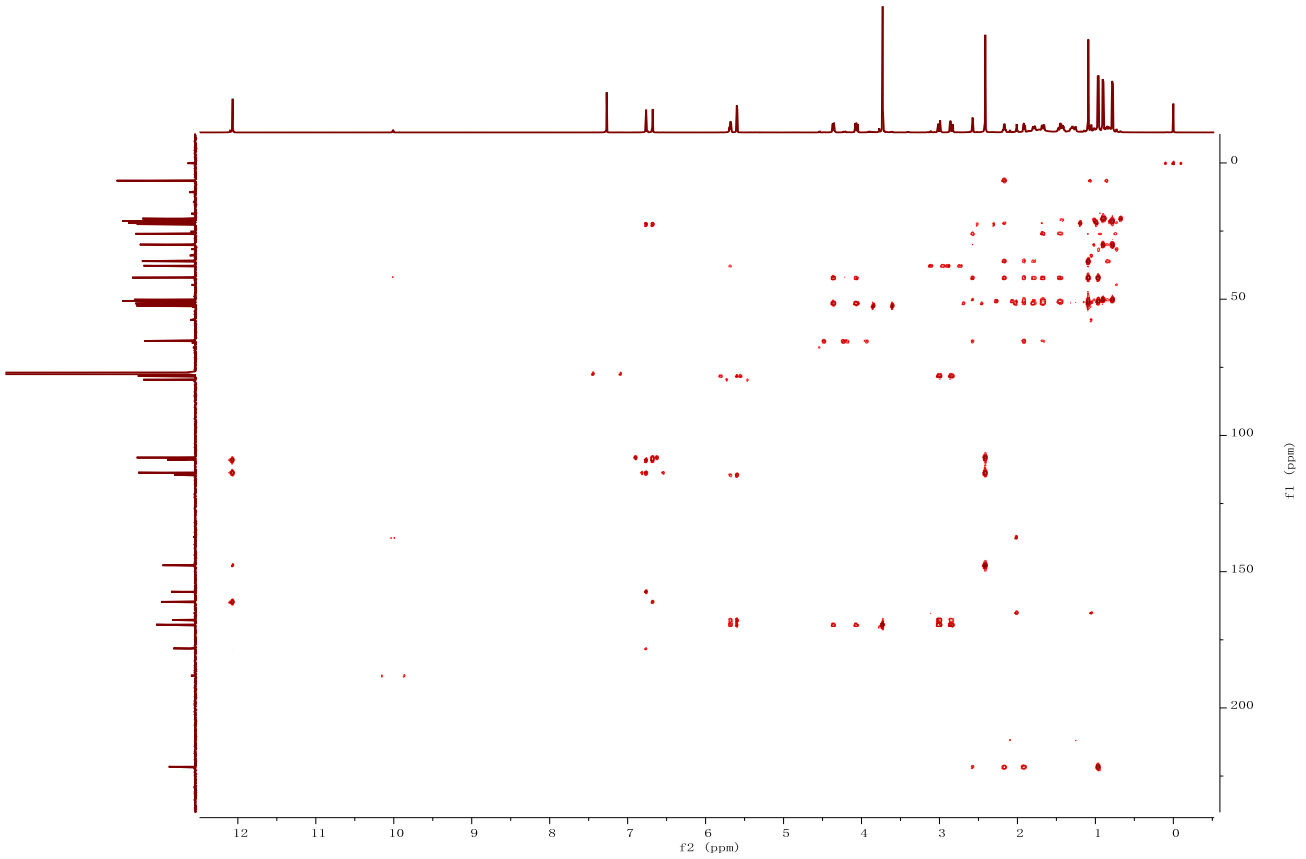
^{13}C NMR and DEPT spectra



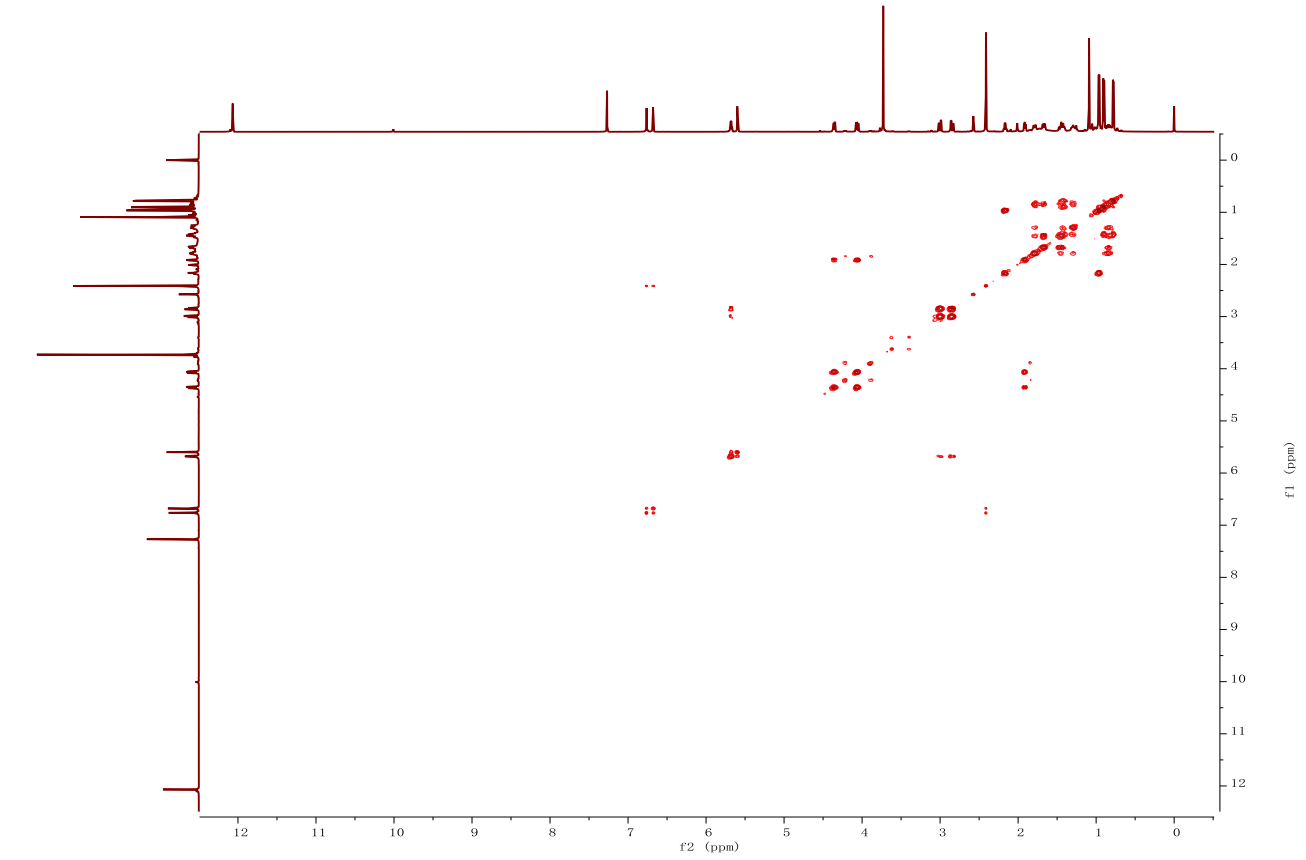
HSQC spectrum



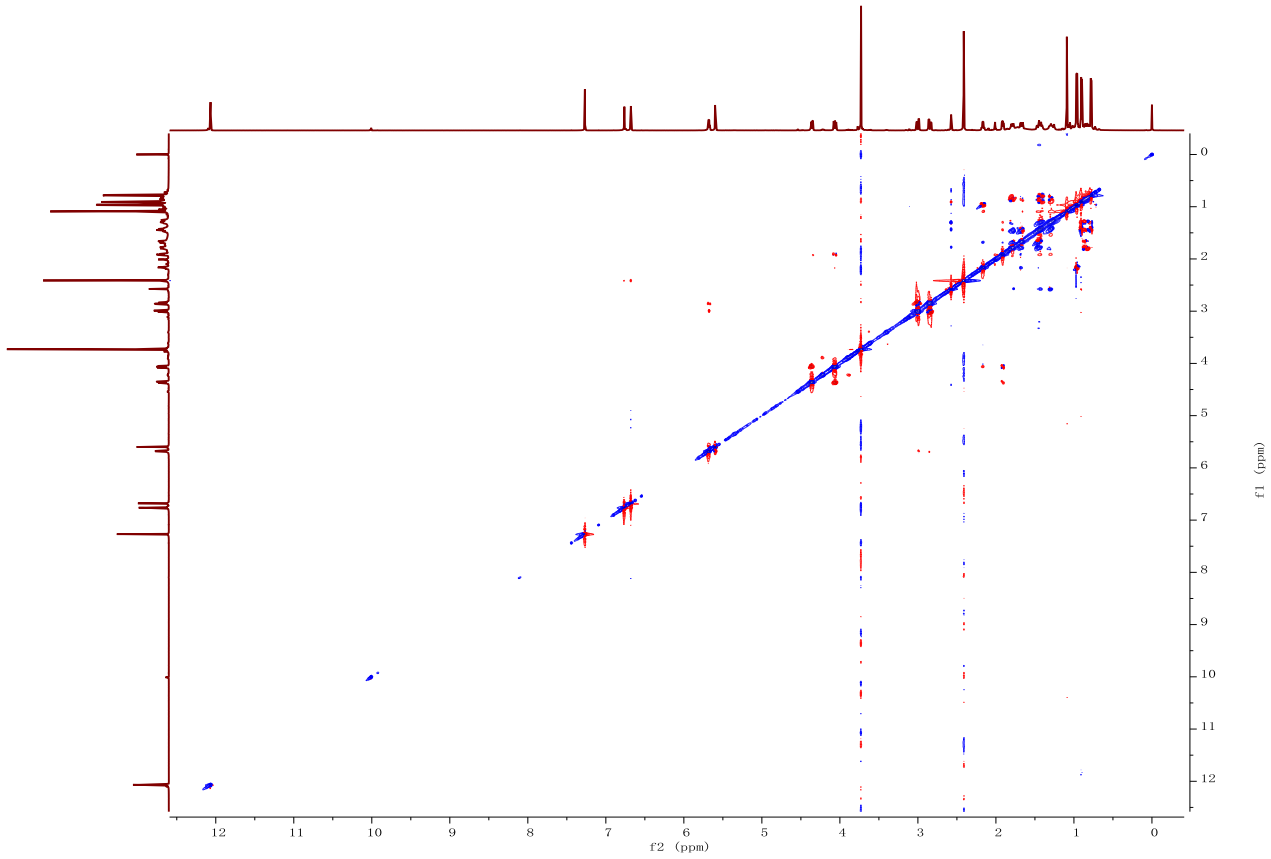
HMBC spectrum



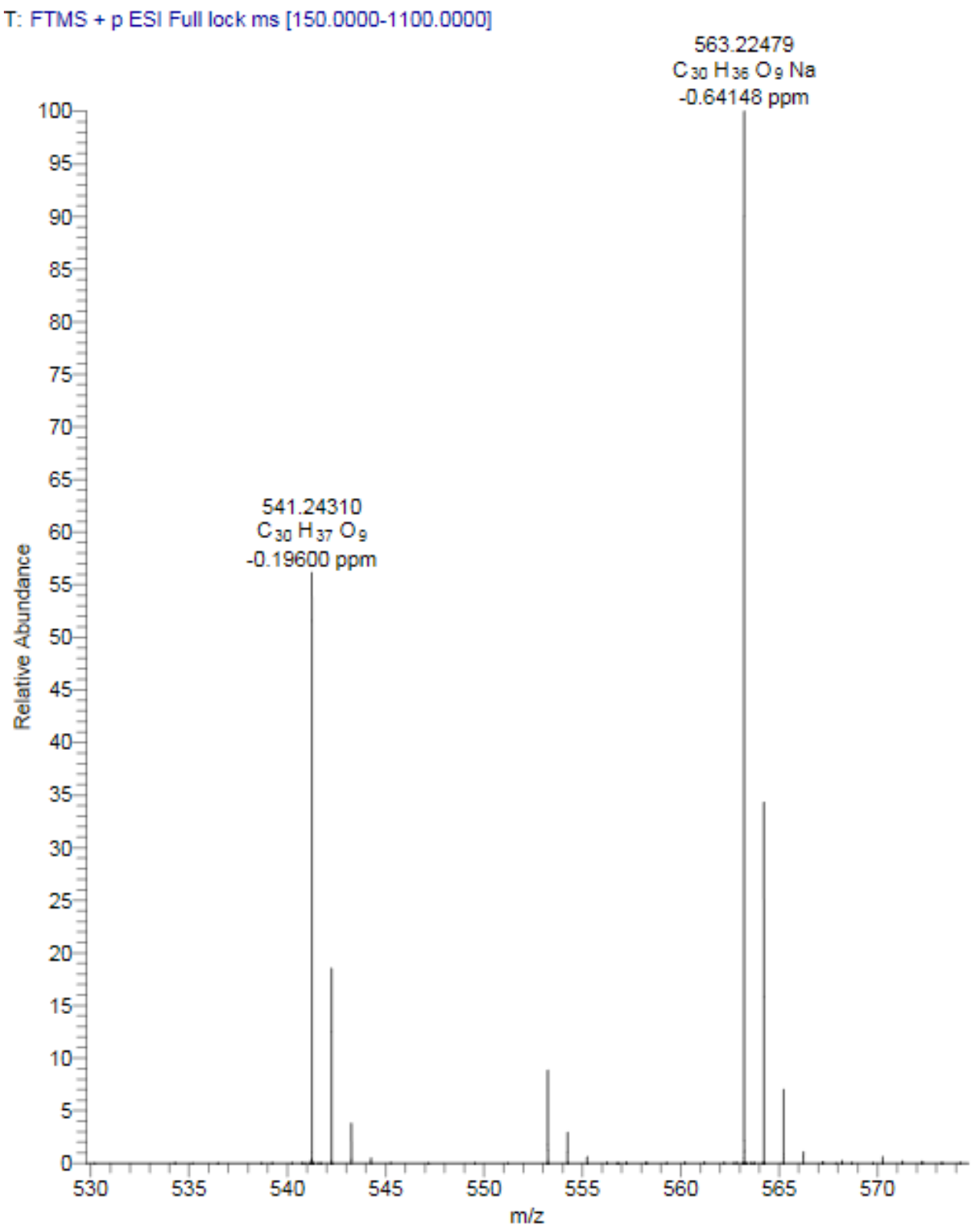
^{1}H-^{1}H COSY spectrum



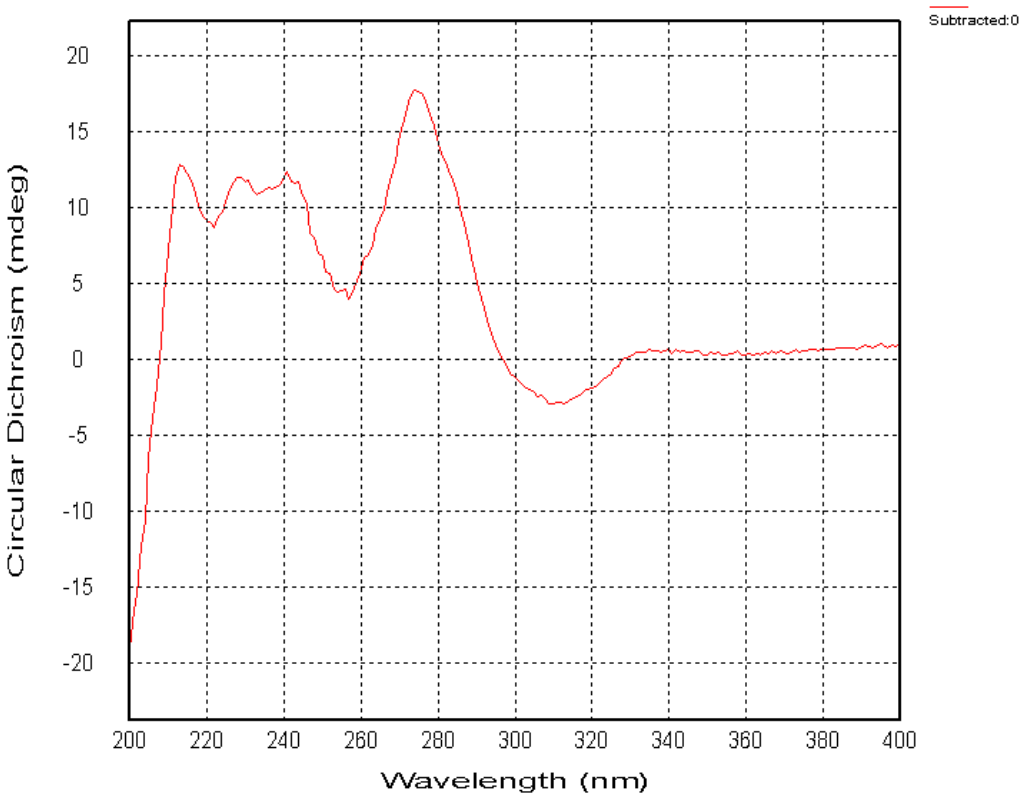
ROESY spectrum



HRESIMS

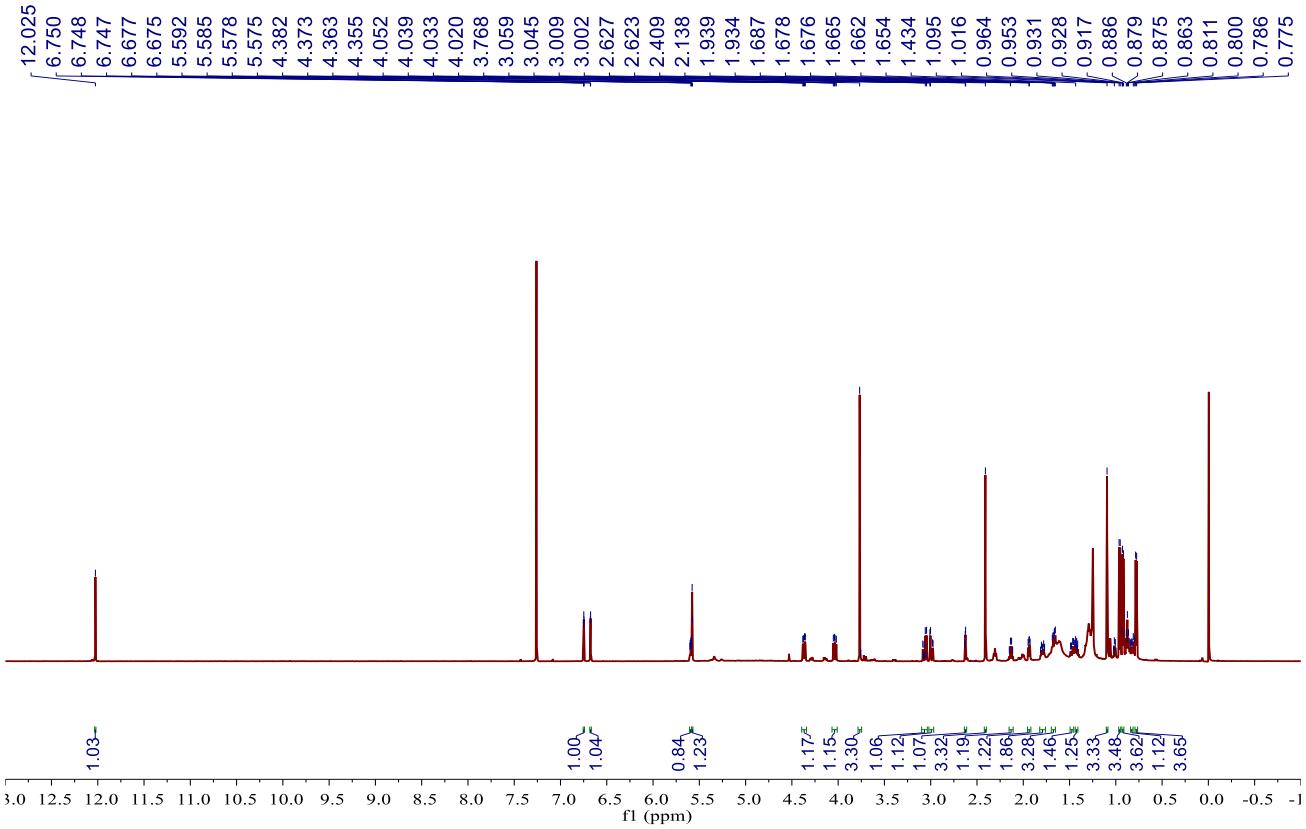

T: FTMS + p ESI Full lock ms [150.0000-1100.0000]
563.22479
C30 H36 O9 Na
-0.64148 ppm
541.24310
C30 H37 O9
-0.19600 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
530
535
540
545
550
555
560
565
570

CD spectra

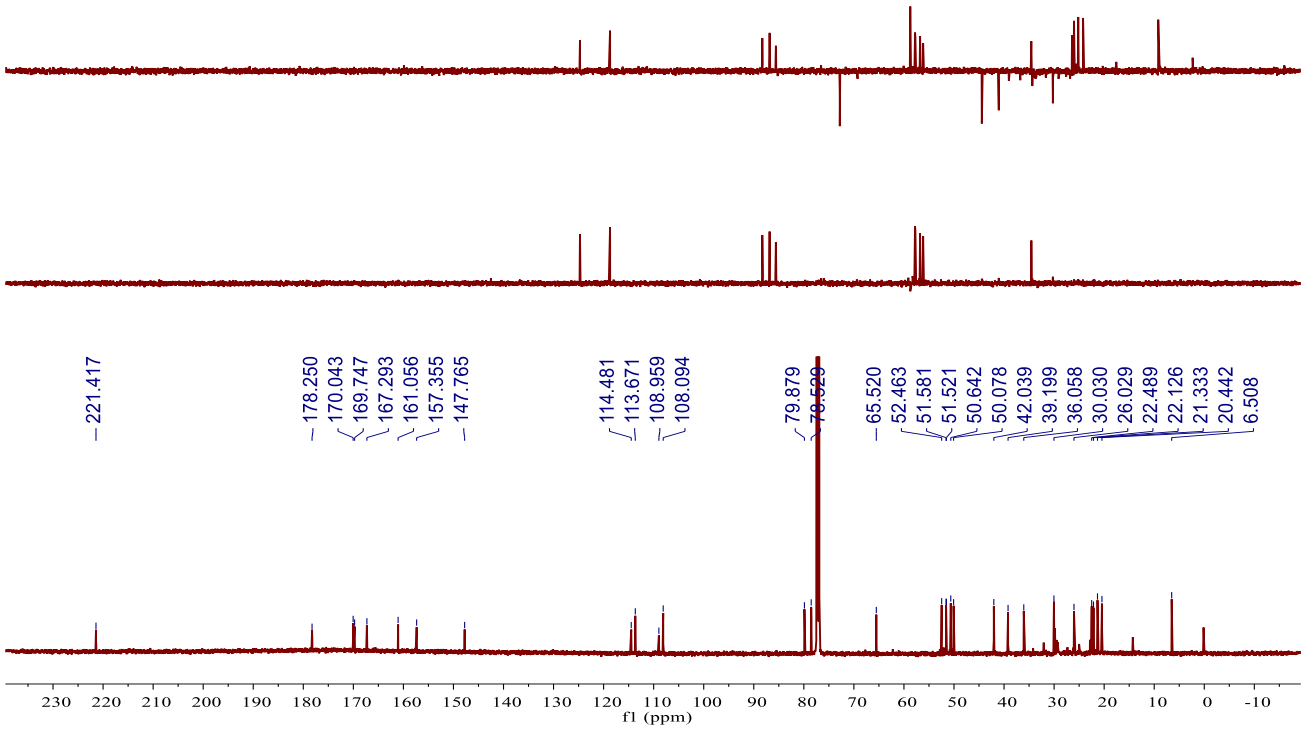

Subtracted:0
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
-20
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

S1.13 NMR, HRESIMS and CD spectra of bipolarithone D (13)

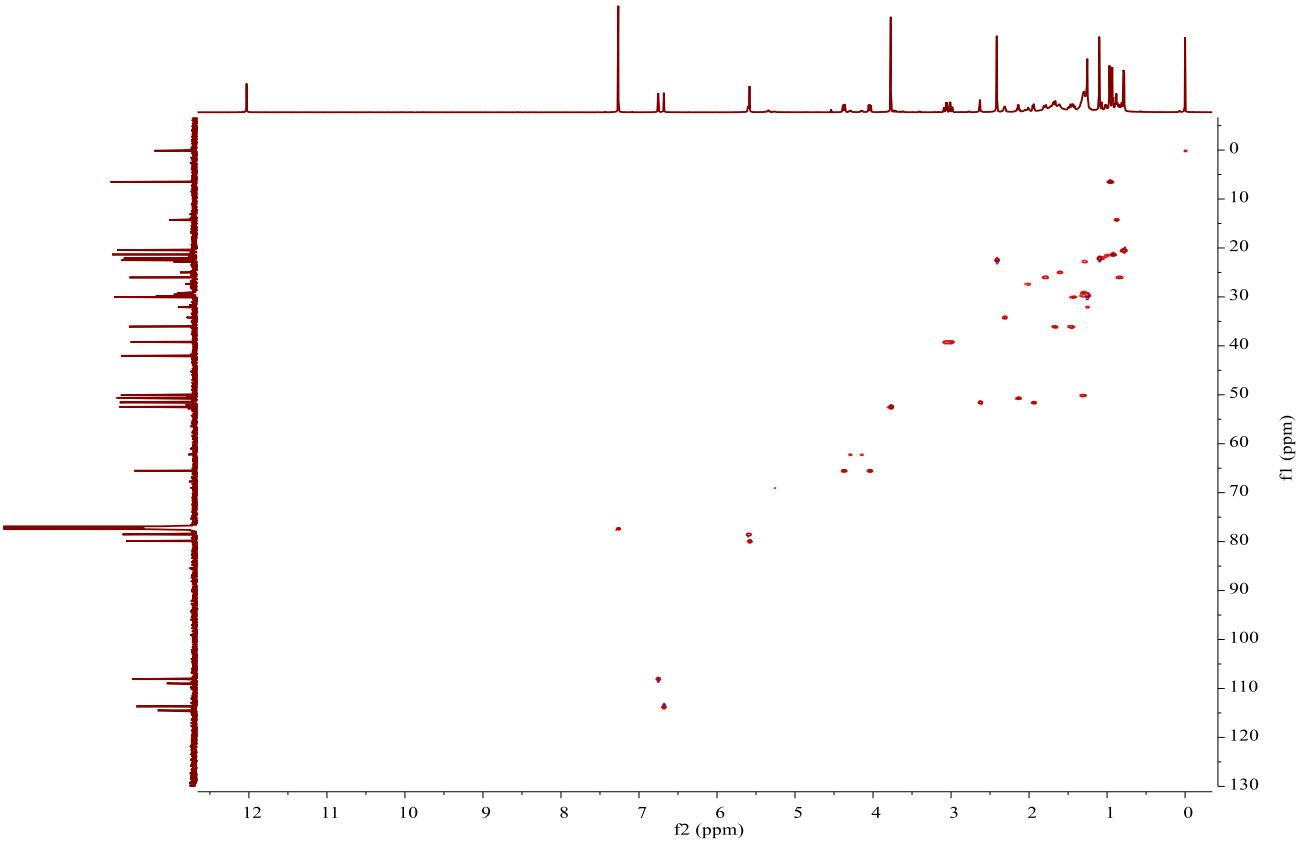
^{1}H NMR spectrum



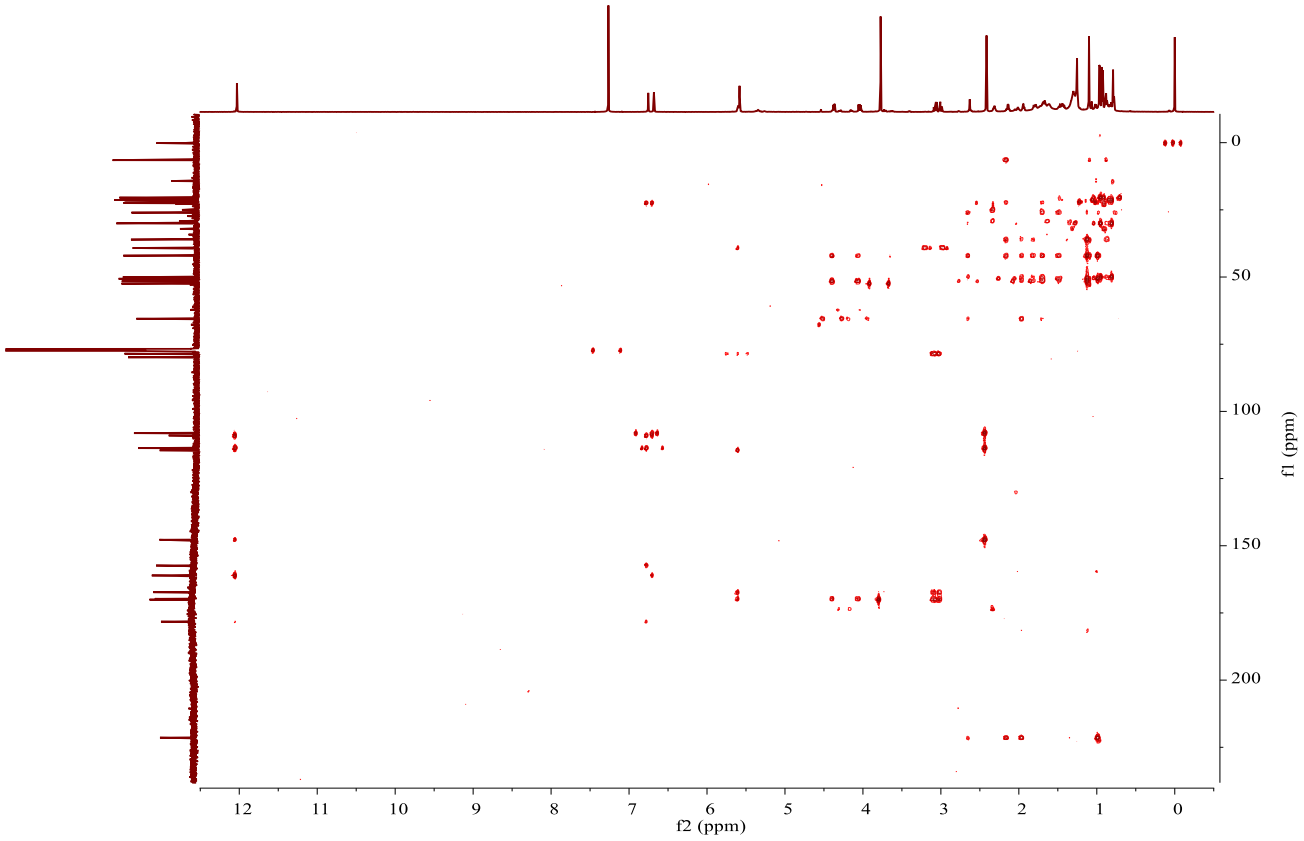
^{13}C NMR and DEPT spectra



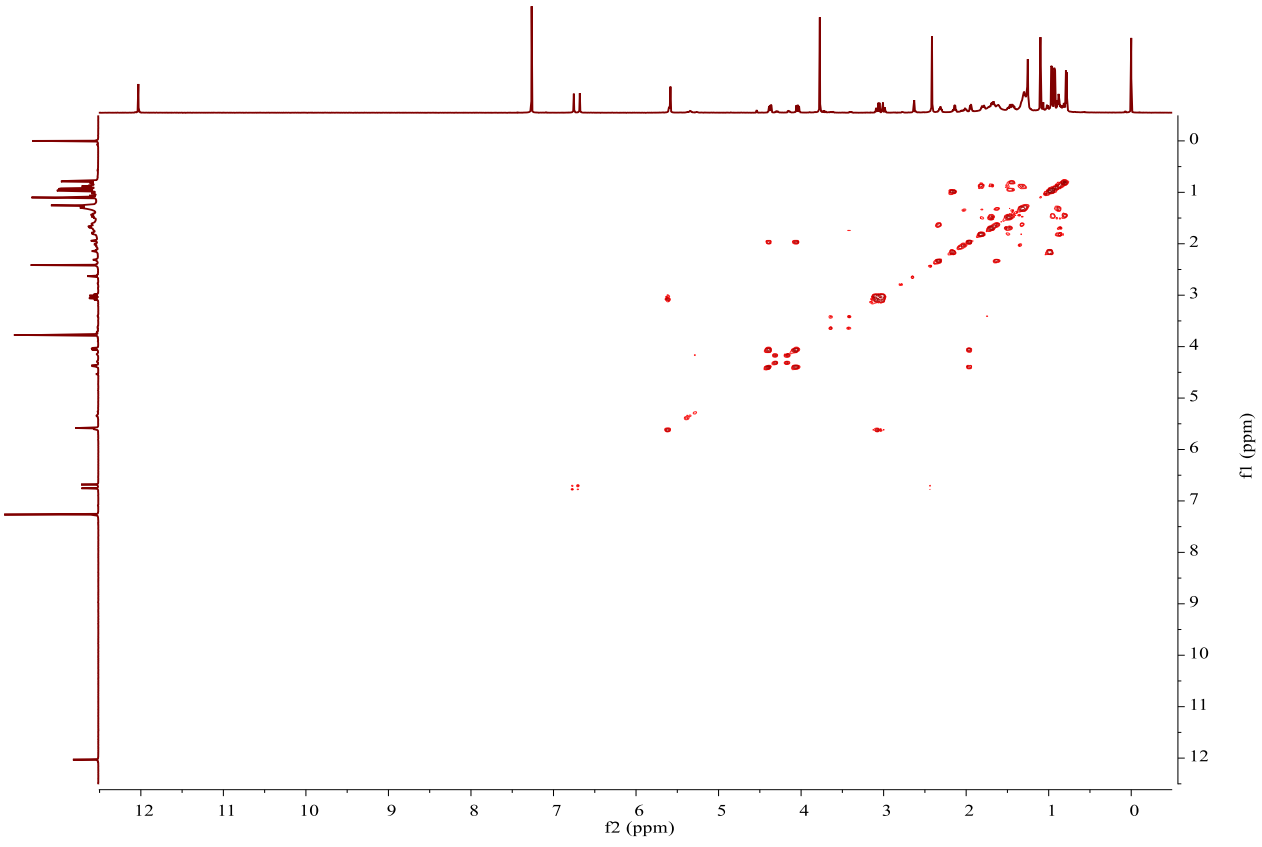
HSQC spectrum



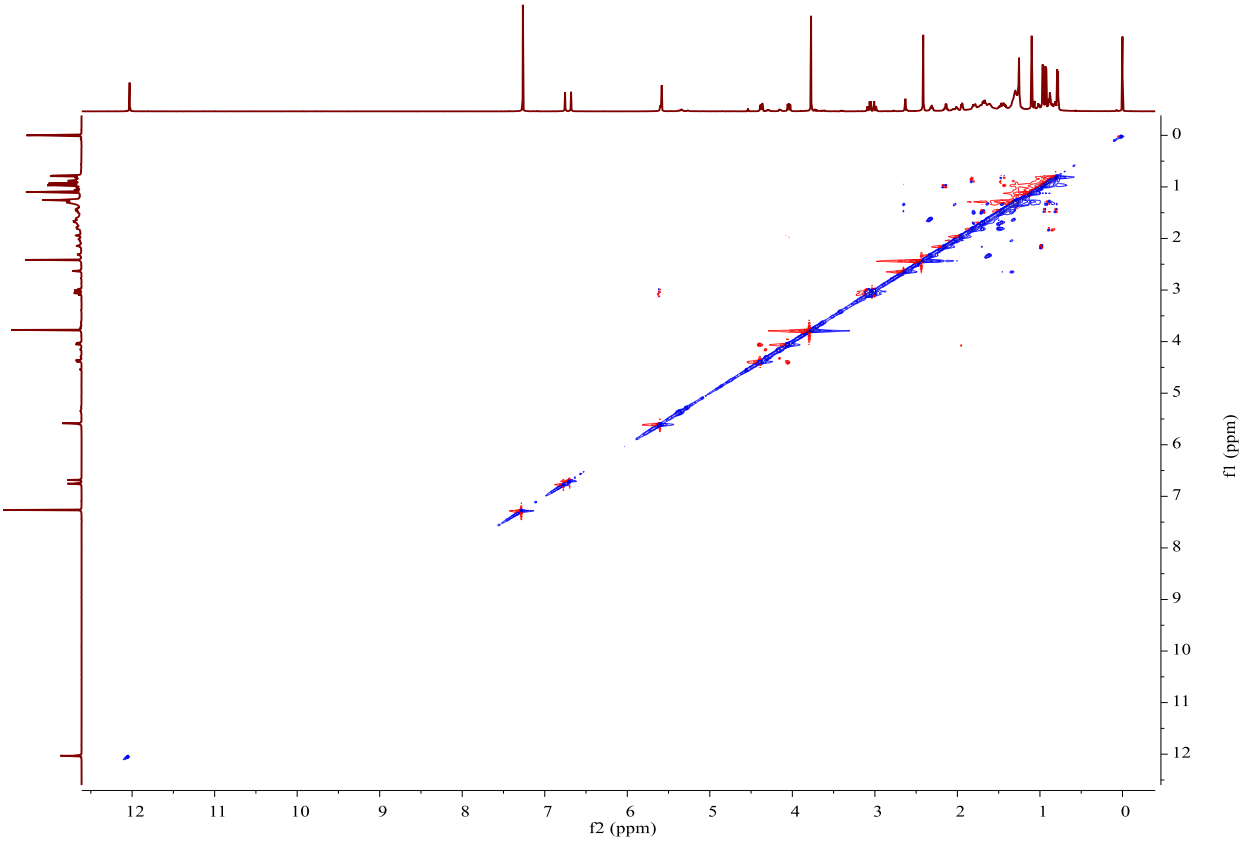
HMBC spectrum



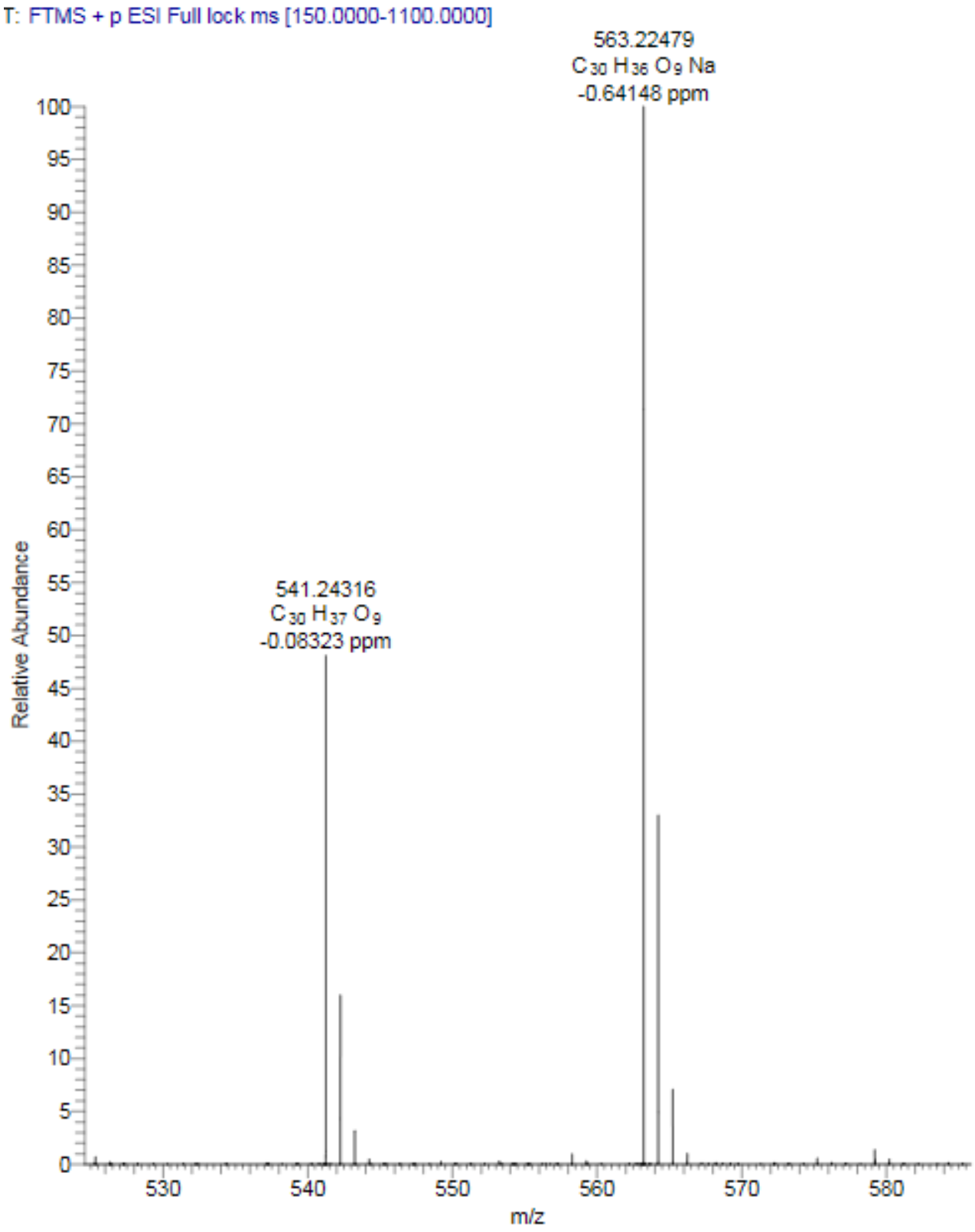
^{1}H-^{1}H COSY spectrum



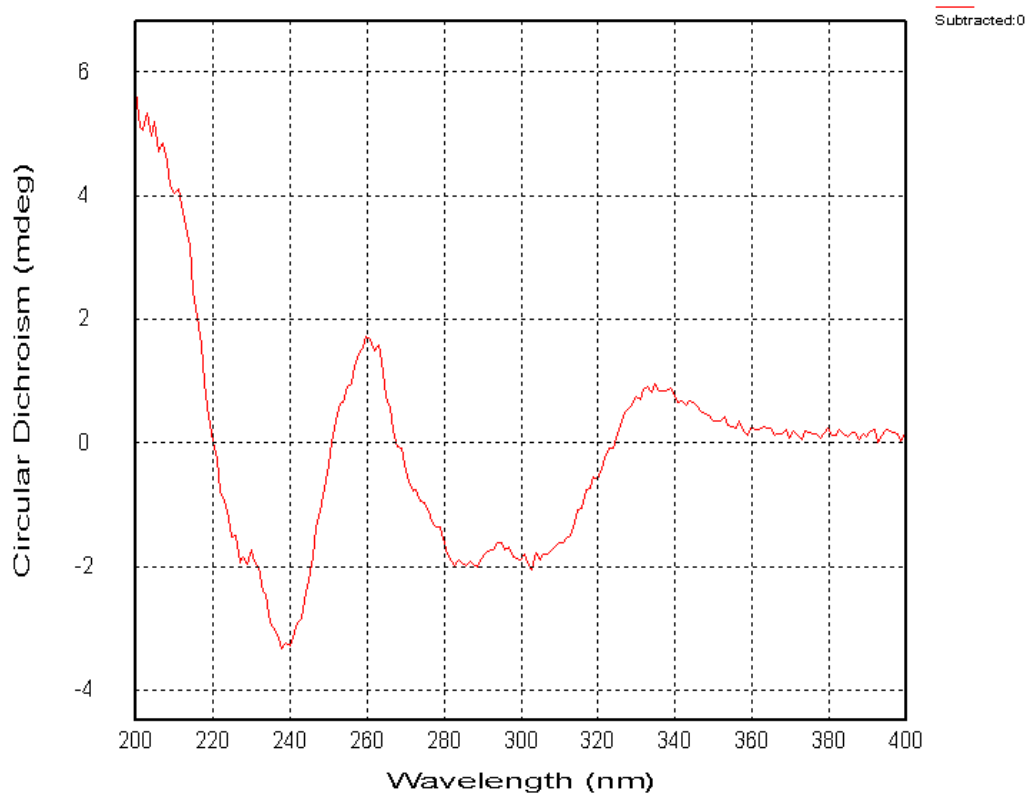
ROESY spectrum



HRESIMS


T: FTMS + p ESI Full lock ms [150.0000-1100.0000]
563.22479
C30 H36 O9 Na
-0.64148 ppm
541.24316
C30 H37 O9
-0.08323 ppm
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
530
540
550
560
570
580

CD spectra


Subtracted:0
Circular Dichroism (mdeg)
6
4
2
0
-2
-4
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

Sections S2. Computational details

S2.1. Computational details for bipolarisorokin C (3) (ECD)

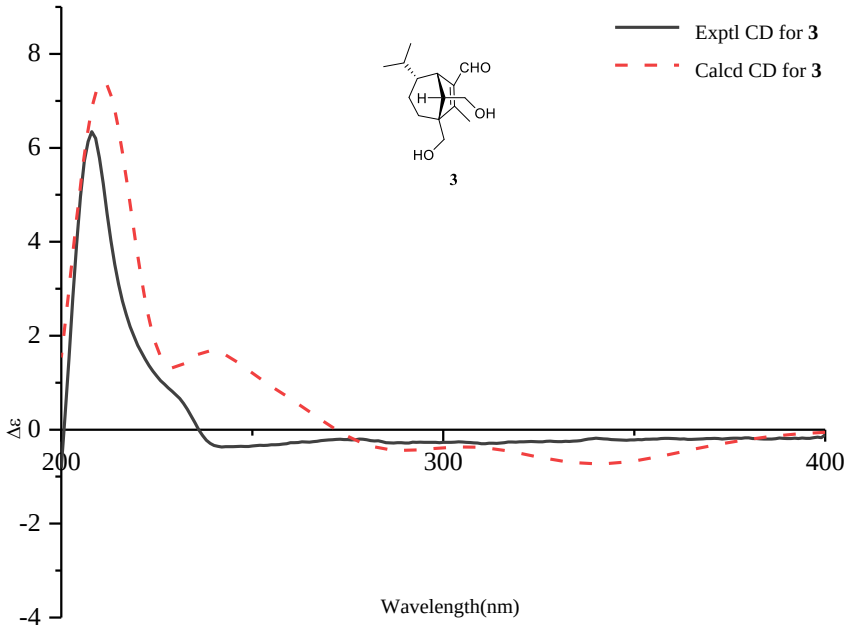


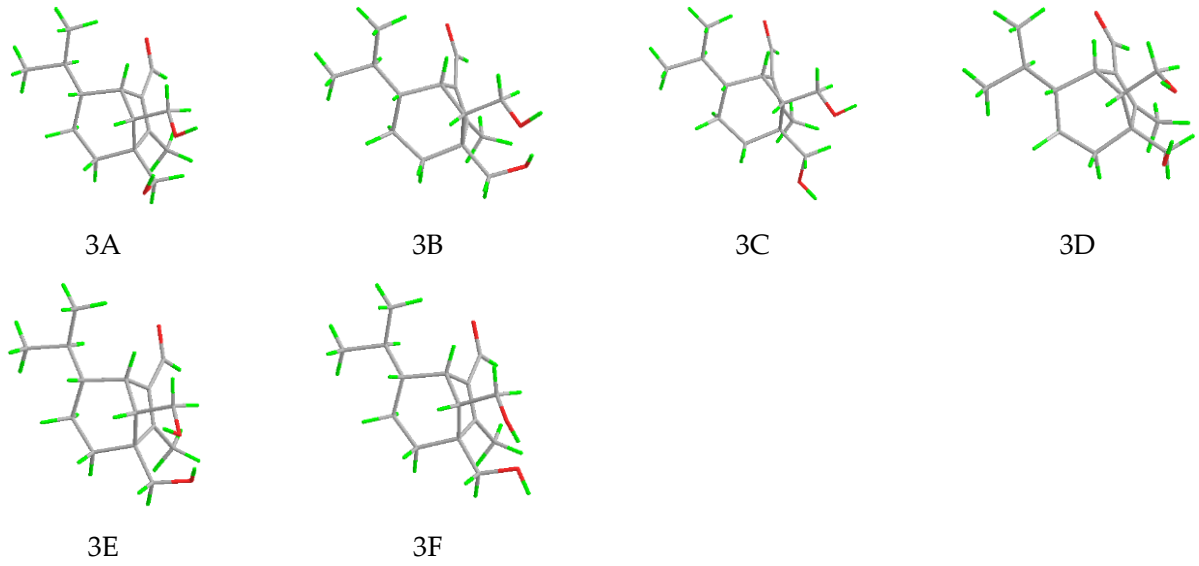
Figure S1. Calculated ECD spectra for **3** at the B3LYP/6-311G(d) level in methanol with IEFPCM model (σ = 0.35 eV, UV shift 7 nm). Experimental CD spectra of **3** (black line) in MeOH.

Table S1. Energy analysis for conformers of **3A~3F** at B3LYP/6-31G(d) level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
3A	-811.401389	-811.382734	-811.38179	-811.445976	0.002106	1.321535	6.80%
3B	-811.403156	-811.384823	-811.383879	-811.447234	0.000848	0.532128	25.79%
3C	-811.394306	-811.375171	-811.374227	-811.439445	0.008637	5.4198	0.01%
3D	-811.400708	-811.382174	-811.38123	-811.445153	0.002929	1.837975	2.84%
3E	-811.403984	-811.385629	-811.384685	-811.448082	0	0	63.34%
3F	-811.400129	-811.381683	-811.380739	-811.444362	0.00372	2.334335	1.23%

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

Figure S2. Main conformers of **3** in ECD



S2.2. Computational details for bipolarisorokin G (7) (ECD)

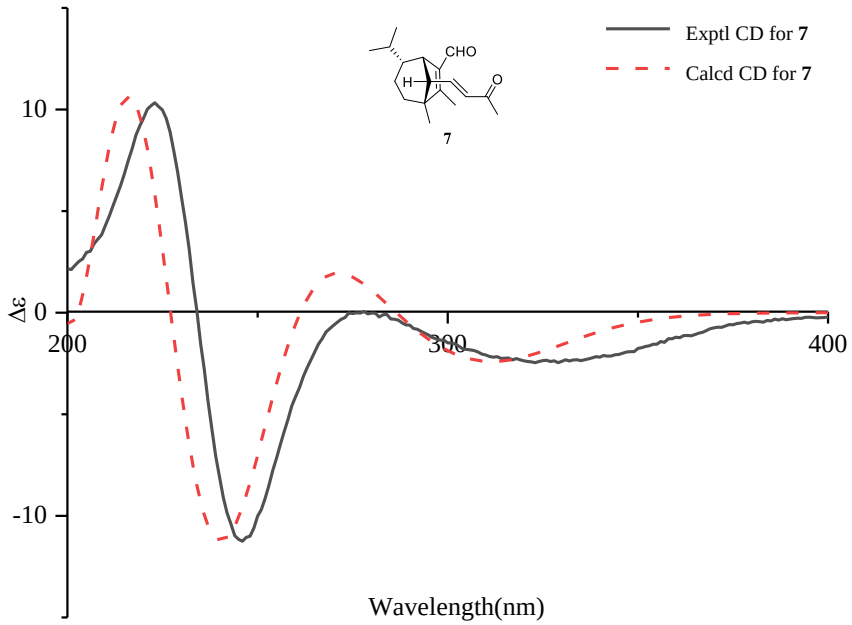


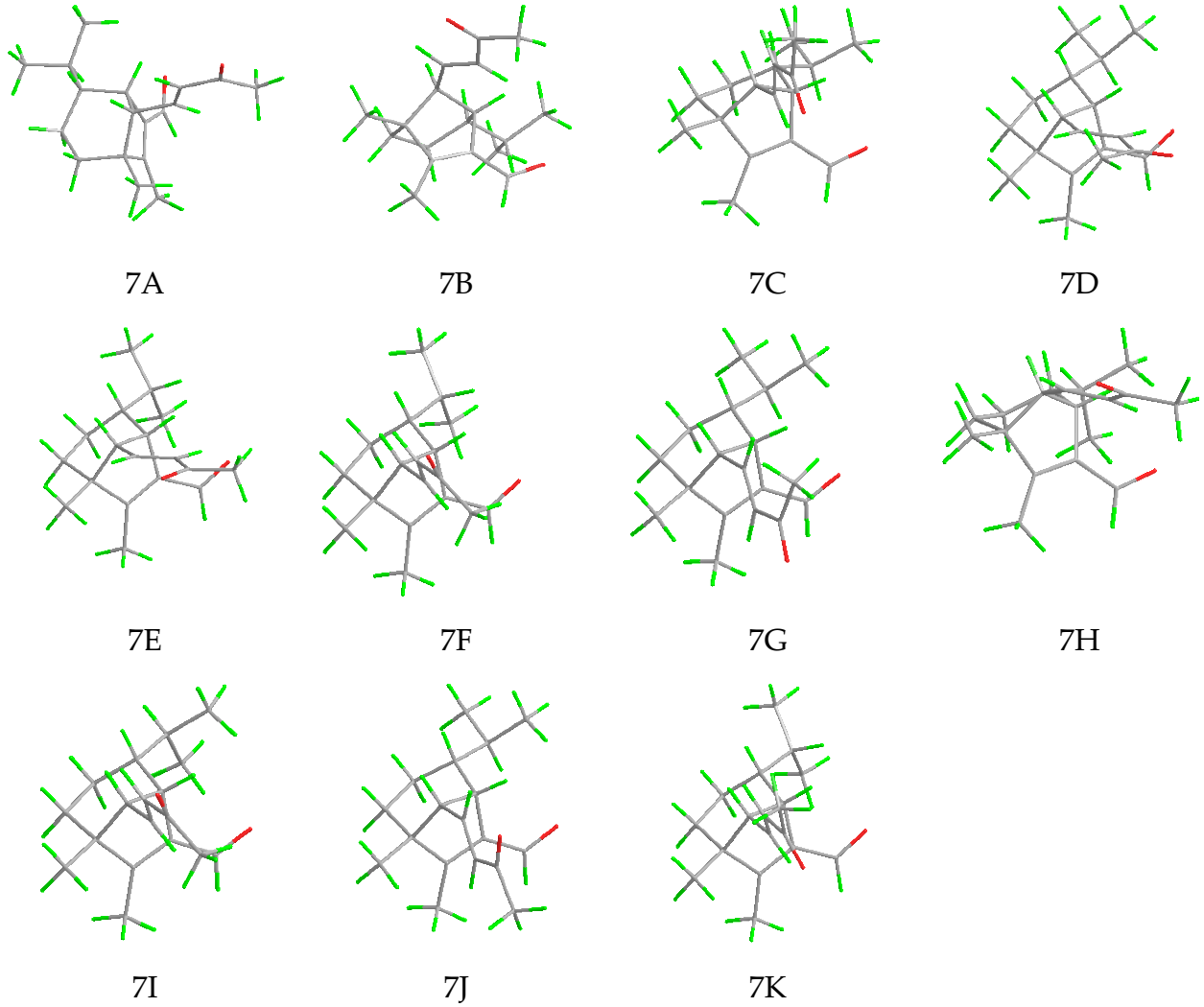
Figure S3. Calculated ECD spectra for **7** at the B3LYP/6-311G(d) level in methanol with IEFPCM model (σ = 0.30 eV, UV shift -**21** nm). Experimental CD spectra of **7** (black line) in MeOH.

Table S2. Energy analysis for conformers of **7A~7K** at B3LYP/6-31G(d) level in the gas phase

Species	*E′=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
7A	-851.689303	-851.667934	-851.66699	-851.738756	0.000753	0.472515	23.63%
7B	-851.689337	-851.668042	-851.667098	-851.738542	0.000967	0.606802	18.83%
7C	-851.689897	-851.668478	-851.667534	-851.739509	0	0	52.48%
7D	-851.687229	-851.66598	-851.665036	-851.736267	0.003242	2.034386	1.69%
7E	-851.685214	-851.663817	-851.662873	-851.735376	0.004133	2.593497	0.66%
7F	-851.684986	-851.663557	-851.662612	-851.734821	0.004688	2.941765	0.36%
7G	-851.685209	-851.663911	-851.662967	-851.734125	0.005384	3.378511	0.17%
7H	-851.686185	-851.665011	-851.664067	-851.73516	0.004349	2.729039	0.52%
7I	-851.685802	-851.664542	-851.663598	-851.73505	0.004459	2.798065	0.47%
7J	-851.685847	-851.664456	-851.663512	-851.735092	0.004417	2.771709	0.49%
7K	-851.685504	-851.664035	-851.663091	-851.735425	0.004084	2.562749	0.69%

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

Figure S4. Main conformers of **7** in ECD



S2.3. Computational details for bipolarithone A (10) (ECD)

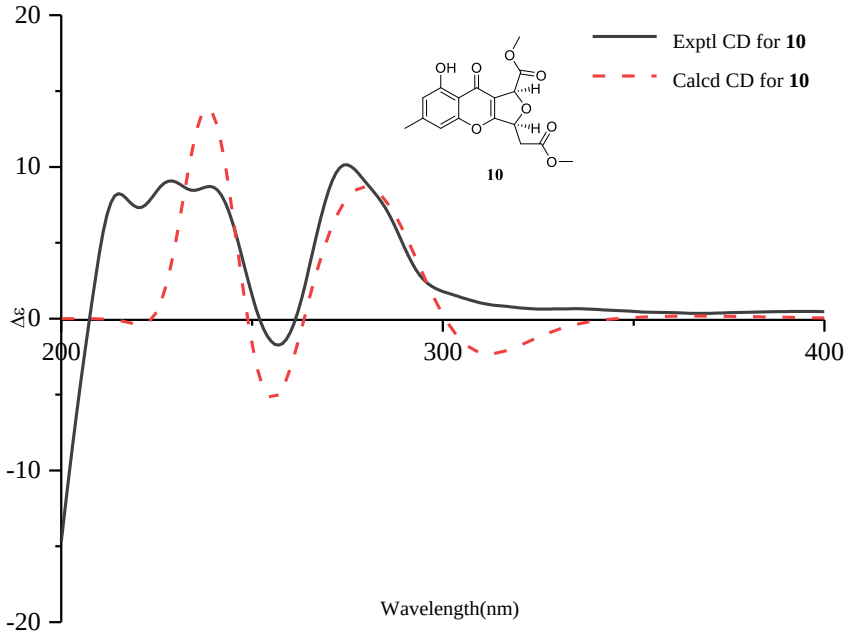


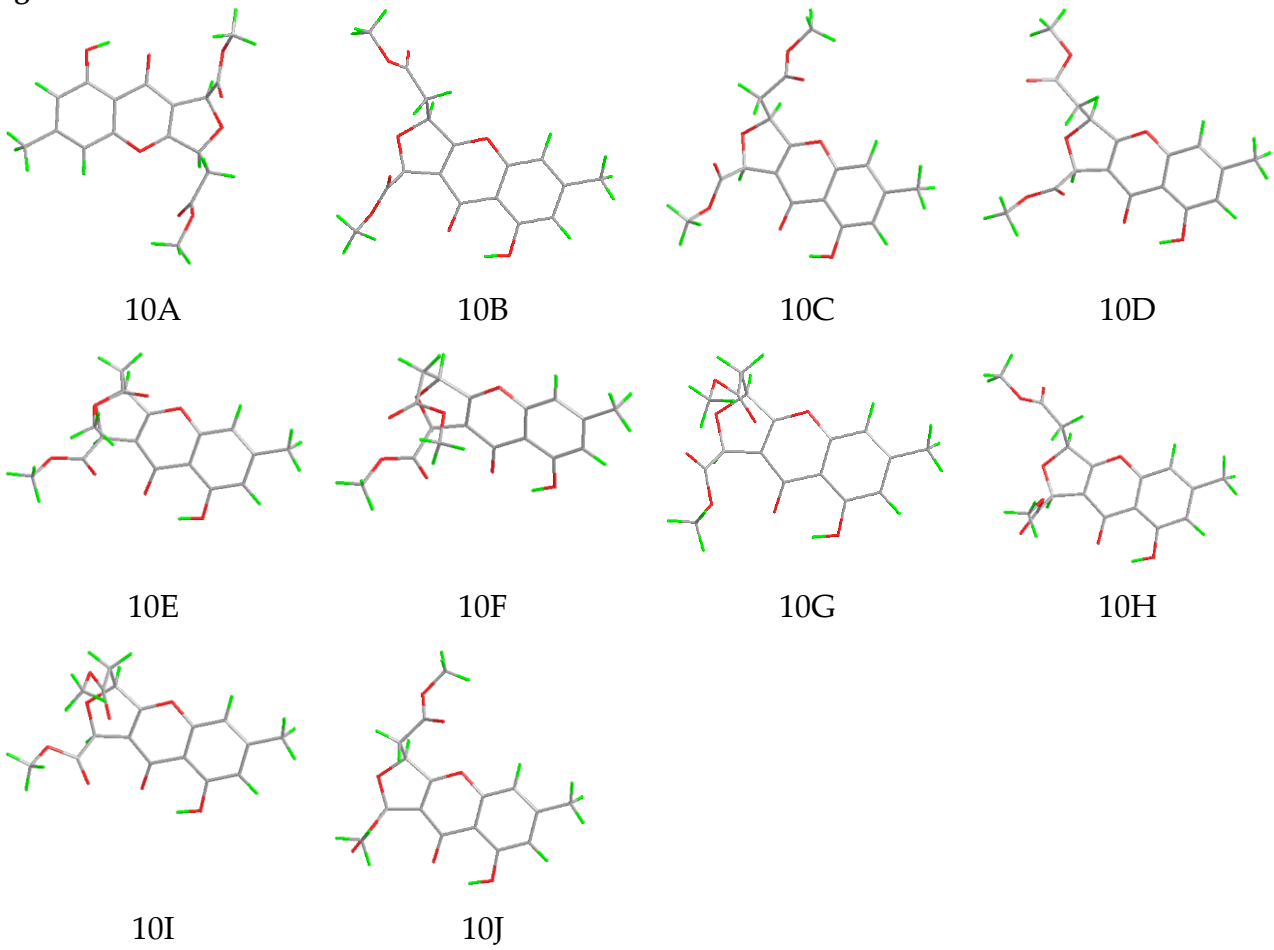
Figure S5. Calculated ECD spectra for **10** at the B3LYP/6-311G(d) level in methanol with IEFPCM model (σ = 0.32 eV, UV shift 29 nm). Experimental CD spectra of **10** (black line) in MeOH.

Table S3. Energy analysis for conformers of **10A~10J** at B3LYP/6-31G(d) level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
10A	-1259.018573	-1258.995248	-1258.994304	-1259.075493	0	0	37.35%
10B	-1259.018243	-1258.994946	-1258.994001	-1259.074519	0.000974	0.611194253	13.30%
10C	-1259.017827	-1258.994525	-1258.99358	-1259.073885	0.001608	1.009035276	6.79%
10D	-1259.016576	-1258.993274	-1258.99233	-1259.072975	0.002518	1.580068921	2.59%
10E	-1259.019921	-1258.996898	-1258.995954	-1259.074685	0.000808	0.507027676	15.86%
10F	-1259.019649	-1258.99674	-1258.995795	-1259.073383	0.00211	1.324045045	3.99%
10G	-1259.019922	-1258.996899	-1258.995955	-1259.074692	0.000801	0.50263511	15.98%
10H	-1259.016416	-1258.993081	-1258.992137	-1259.072682	0.002811	1.763929205	1.90%
10I	-1259.016685	-1258.993481	-1258.992537	-1259.07197	0.003523	2.210715969	0.89%
10J	-1259.016394	-1258.993049	-1258.992105	-1259.072351	0.003142	1.971634849	1.34%

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

Figure S6. Main conformers of **10** in ECD



S2.4. Computational details for bipolarithone B (11) (ECD)

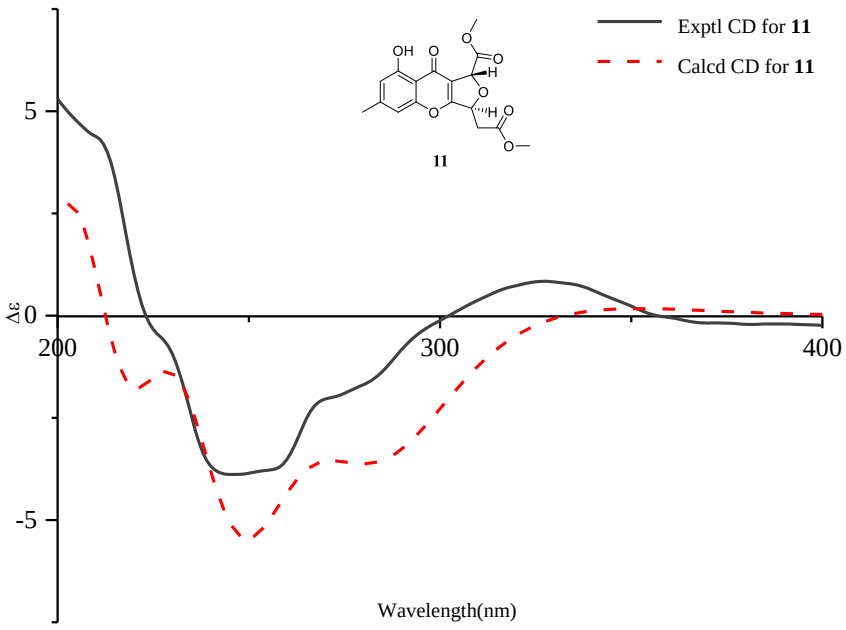


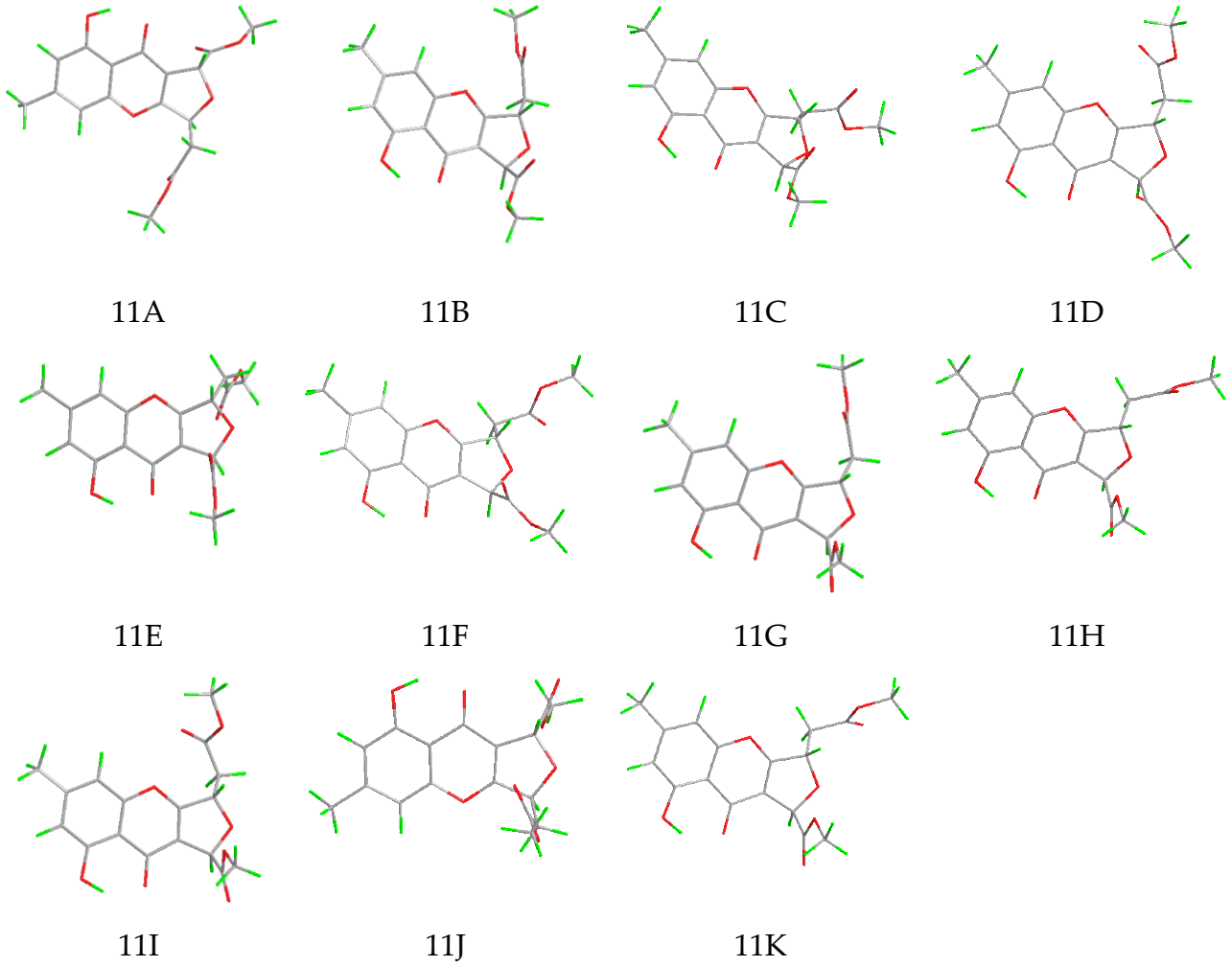
Figure S7. Calculated ECD spectra for **11** at the B3LYP/6-311G(d) level in methanol with IEFPCM model (σ = 0.38 eV, UV shift 2 nm). Experimental CD spectra of **11** (black line) in MeOH.

Table S4. Energy analysis for conformers of **11A~11K** at B3LYP/6-31G(d) level in the gas phase

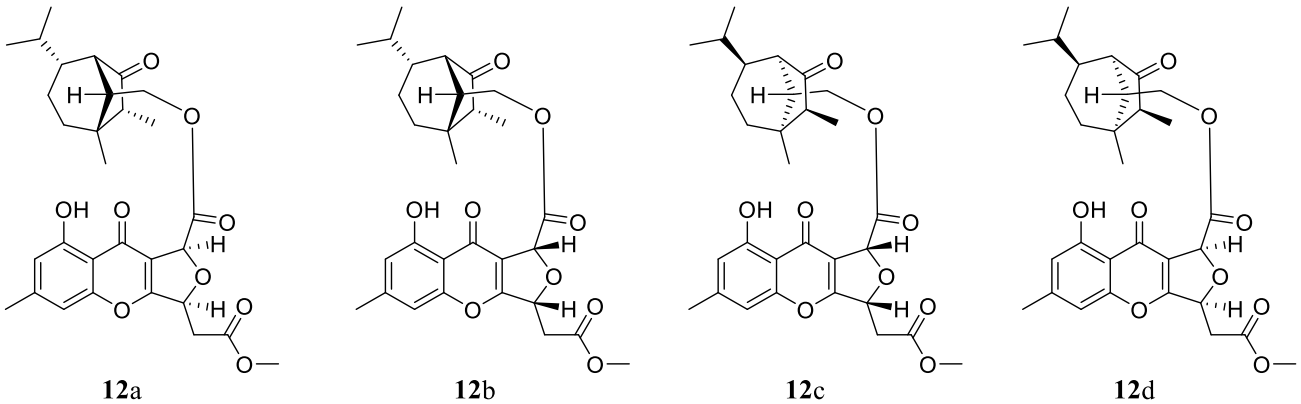
Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
11A	-1259.0163	-1258.99289	-1258.991942	-1259.073522	0.000625	0.392193	16.46%
11B	-1259.0163	-1258.99288	-1258.991935	-1259.073547	0.0006	0.376506	16.90%
11C	-1259.0156	-1258.99216	-1258.991211	-1259.072575	0.001572	0.986445	6.03%
11D	-1259.0161	-1258.99272	-1258.991774	-1259.072775	0.001372	0.860943	7.46%
11E	-1259.0179	-1258.99463	-1258.993688	-1259.074147	0	0	31.92%
11F	-1259.0151	-1258.99163	-1258.990684	-1259.071946	0.002201	1.381148	3.10%
11G	-1259.0157	-1258.99224	-1258.991292	-1259.072508	0.001639	1.028488	5.62%
11H	-1259.0151	-1258.99173	-1258.990784	-1259.071808	0.002339	1.467745	2.68%
11I	-1259.0151	-1258.99172	-1258.990774	-1259.071517	0.00263	1.65035	1.97%
11J	-1259.0169	-1258.99356	-1258.992613	-1259.073068	0.001079	0.677083	10.17%
11K	-1259.0141	-1258.99062	-1258.989679	-1259.070653	0.003494	2.192518	0.79%

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

Figure S8. Main conformers of **11** in ECD



S2.5. Computational details for bipolarithone C (12) (ECD)



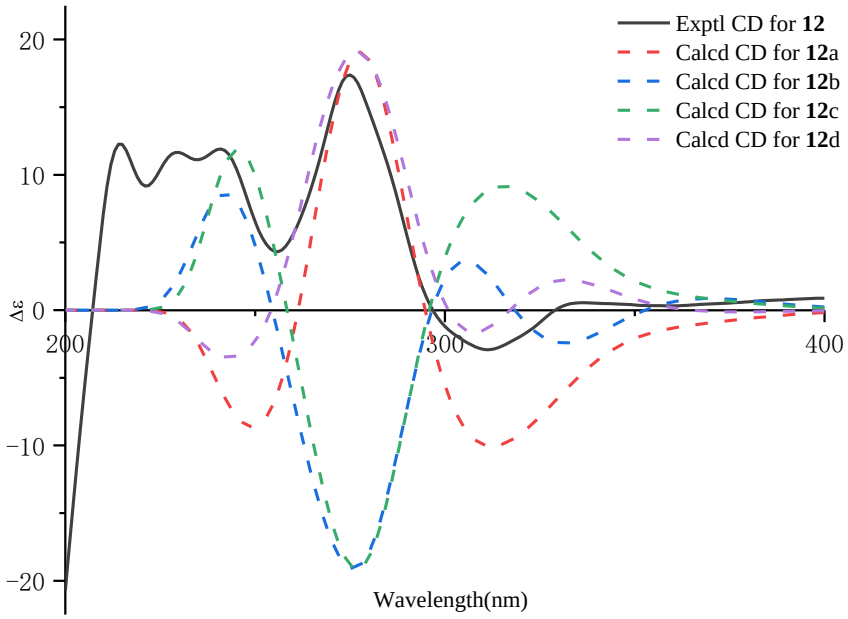


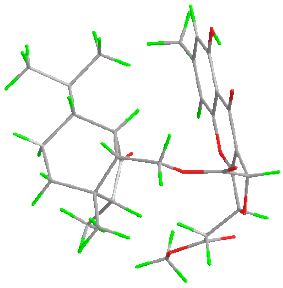
Figure S9. Calculated ECD spectra for **12a–12d** at the B3LYP/6-311G(d) level in methanol with IEFPCM model (σ = 0.30 eV, UV shift 26 nm). Experimental CD spectra of **12** (black line) in MeOH.

Table S5. Energy analysis for conformers of **12aA~12aK** at B3LYP/6-31G(d) level in the gas phase

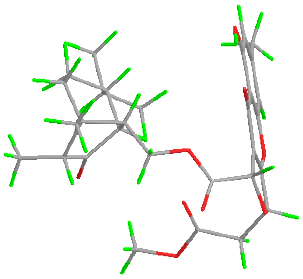
Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
12aA	-1841.477567	-1841.440453	-1841.439509	-1841.547406	0.000796	0.499498	24.42%
12aB	-1841.480266	-1841.443482	-1841.442538	-1841.548202	0	0	56.78%
12aC	-1841.475594	-1841.438502	-1841.437558	-1841.545011	0.003191	2.002383	1.93%
12aD	-1841.469323	-1841.431763	-1841.430818	-1841.542825	0.005377	3.374119	0.19%
12aE	-1841.476806	-1841.439623	-1841.438679	-1841.546971	0.001231	0.772464	15.40%
12aF	-1841.473561	-1841.436386	-1841.435442	-1841.544096	0.004106	2.576554	0.73%
12aG	-1841.471611	-1841.43455	-1841.433605	-1841.541743	0.006459	4.053084	0.06%
12aH	-1841.468618	-1841.431083	-1841.430139	-1841.541659	0.006543	4.105795	0.06%
12aI	-1841.47161	-1841.434552	-1841.433608	-1841.541673	0.006529	4.09701	0.06%
12aJ	-1841.471135	-1841.434062	-1841.433118	-1841.541871	0.006331	3.972763	0.07%
12aK	-1841.474176	-1841.437091	-1841.436147	-1841.54328	0.004922	3.088602	0.31%

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

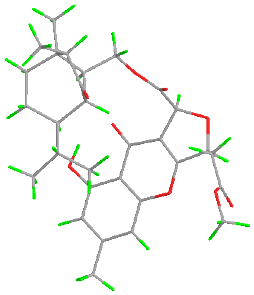
Figure S10. Main conformers of **12a** in ECD



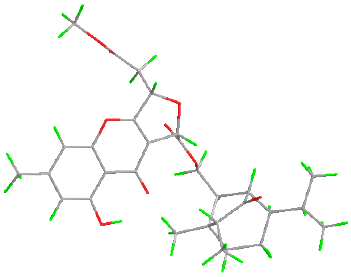
12aA



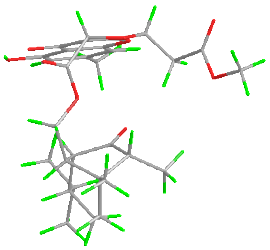
12aB



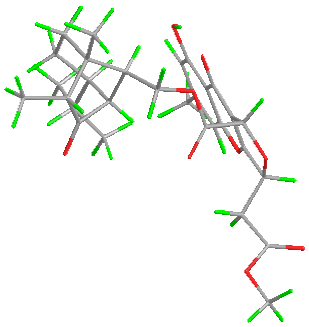
12aC



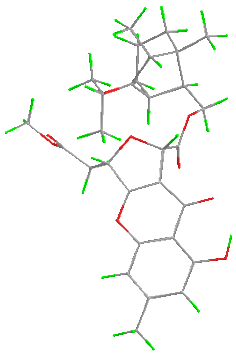
12aD



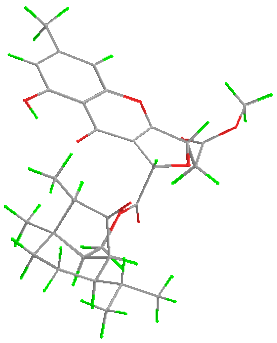
12aE



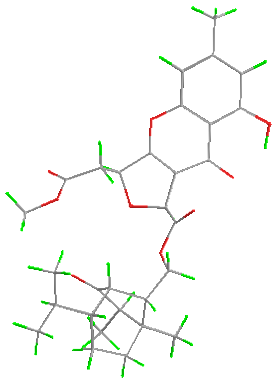
12aF



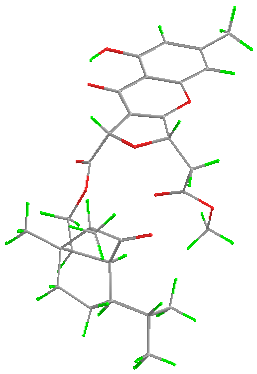
12aG



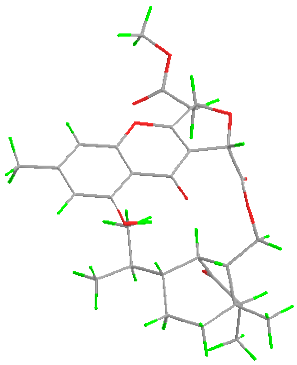
12aH



12aI



12aJ



12aK

Table S6. Energy analysis for conformers of **12bA~12bF** at B3LYP/6-31G(d) level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
12bA	-1841.479288	-1841.442477	-1841.441533	-1841.547737	0.002644	1.659135	4.06%
12bB	-1841.480583	-1841.443646	-1841.442702	-1841.549573	0.000808	0.507028	28.40%
12bC	-1841.479168	-1841.441893	-1841.440948	-1841.550381	0	0	66.88%
12bD	-1841.470431	-1841.433084	-1841.432139	-1841.542772	0.007609	4.77472	0.02%
12bE	-1841.470006	-1841.432677	-1841.431732	-1841.542051	0.00833	5.227154	0.01%
12bF	-1841.475978	-1841.439043	-1841.438098	-1841.545978	0.004403	2.762924	0.63%

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

Figure S11. Main conformers of **12b** in ECD

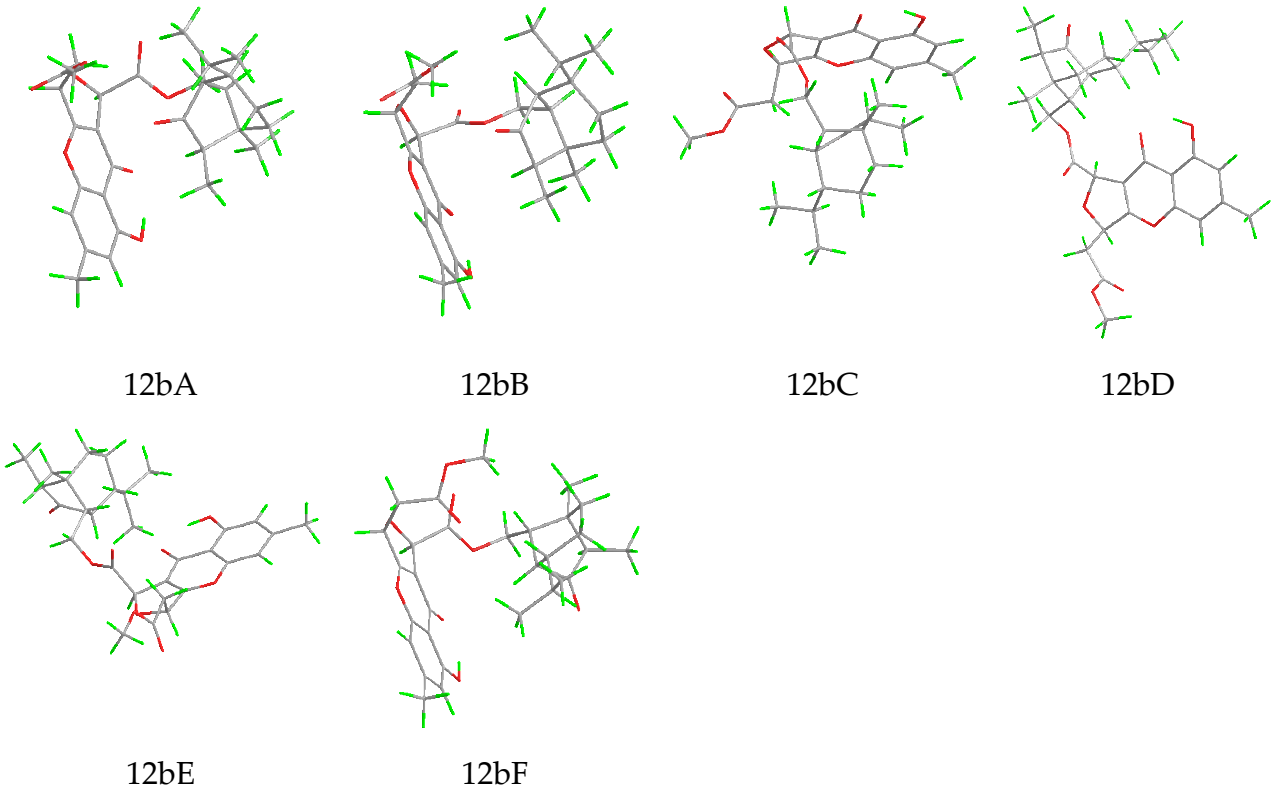


Table S7. Energy analysis for conformers of **12cA~12cM** at B3LYP/6-31G(d) level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
12cA	-1841.477567	-1841.440453	-1841.439509	-1841.547406	0.000798	0.500752581	19.02%
12cB	-1841.480266	-1841.443481	-1841.442537	-1841.548204	0	0	44.31%
12cC	-1841.475594	-1841.438502	-1841.437558	-1841.54501	0.003194	2.004265343	1.50%
12cD	-1841.469323	-1841.431763	-1841.430818	-1841.542825	0.005379	3.3753736	0.15%
12cE	-1841.476806	-1841.439623	-1841.438679	-1841.546969	0.001235	0.774974232	11.97%
12cF	-1841.474586	-1841.437285	-1841.436341	-1841.54594	0.002264	1.420681508	4.02%
12cG	-1841.473561	-1841.436386	-1841.435442	-1841.544093	0.004111	2.579691554	0.57%
12cH	-1841.469825	-1841.43259	-1841.431645	-1841.5412	0.007004	4.395076538	0.03%
12cI	-1841.468618	-1841.431083	-1841.430139	-1841.541659	0.006545	4.107049677	0.04%
12cJ	-1841.477451	-1841.440311	-1841.439367	-1841.547357	0.000847	0.531500547	18.06%
12cK	-1841.471134	-1841.434062	-1841.433118	-1841.541873	0.006331	3.972762645	0.05%
12cL	-1841.474177	-1841.437092	-1841.436147	-1841.543282	0.004922	3.088601759	0.24%
12cM	-1841.467596	-1841.430163	-1841.429219	-1841.541311	0.006893	4.325422983	0.03%

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

Figure S12. Main conformers of **12c** in ECD

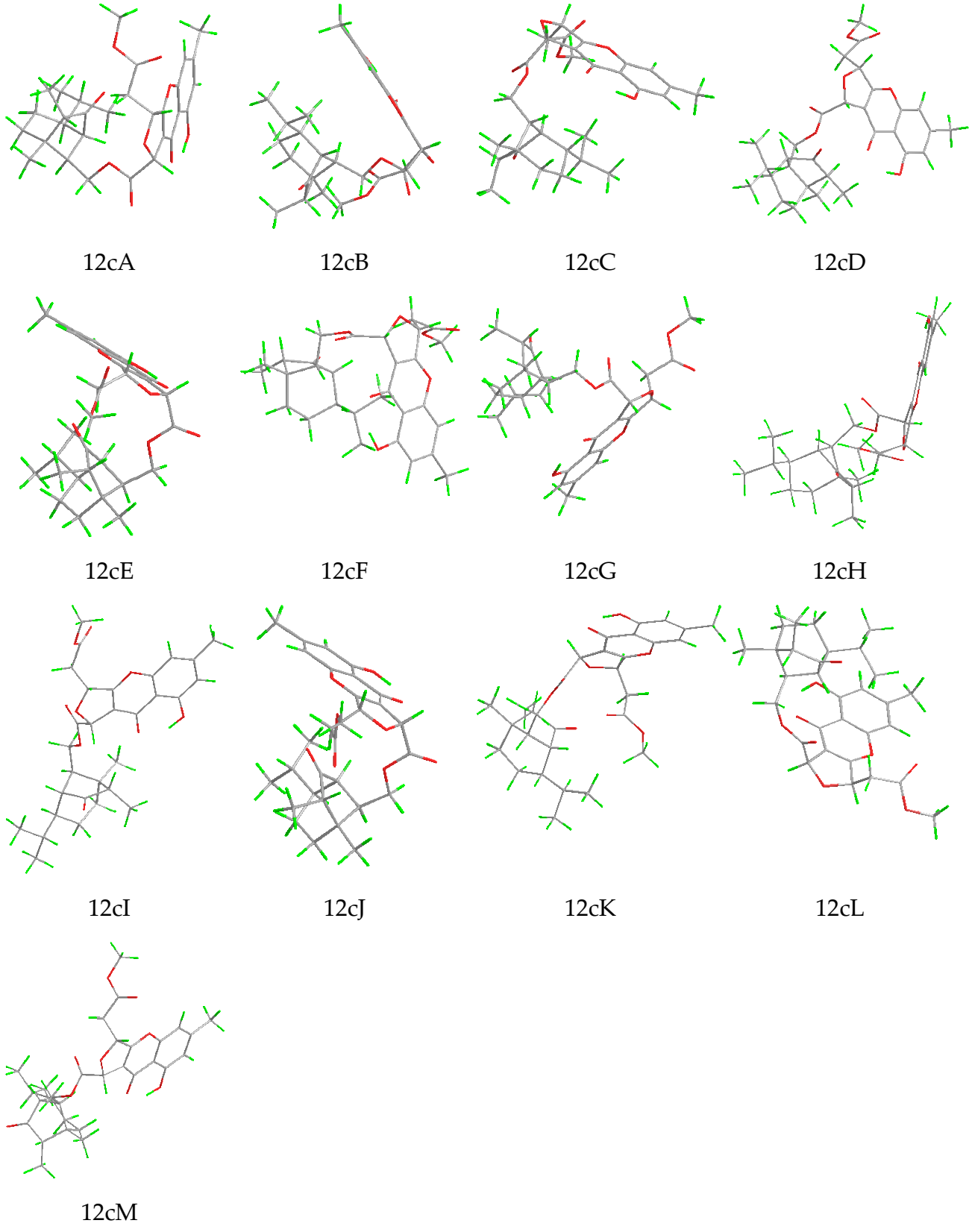
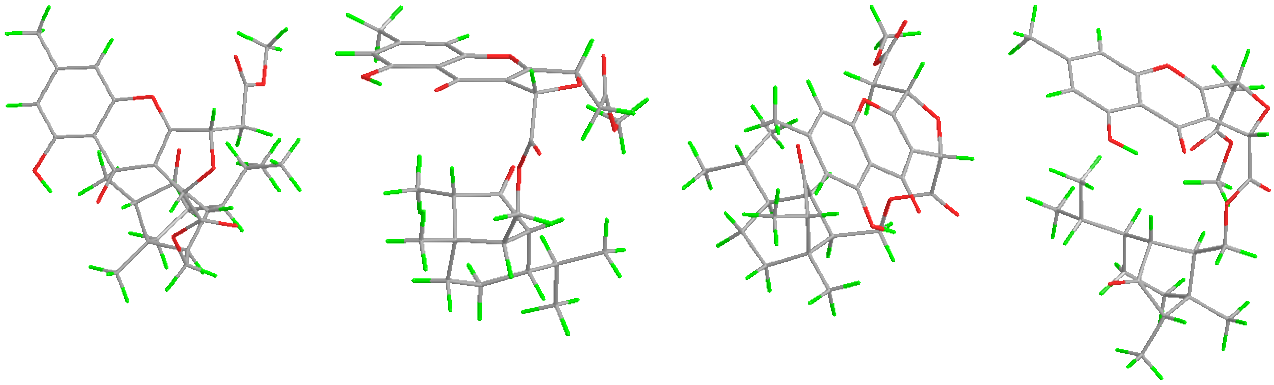


Table S8. Energy analysis for conformers of **12dA~12dF** at B3LYP/6-31G(d) level in the gas phase

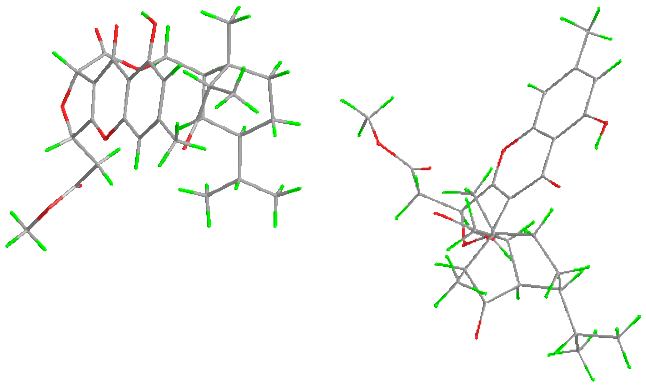
Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
12dA	-1841.479288	-1841.442477	-1841.441533	-1841.547737	0.002647	1.661017646	3.03%
12dB	-1841.480583	-1841.443647	-1841.442703	-1841.54957	0.000814	0.510792733	21.12%
12dC	-1841.479169	-1841.441893	-1841.440949	-1841.550384	0	0	50.05%
12dD	-1841.475978	-1841.439043	-1841.438099	-1841.545975	0.004409	2.766689385	0.47%
12dE	-1841.480098	-1841.44304	-1841.442095	-1841.549741	0.000643	0.403488608	25.32%
12dF	-1841.470432	-1841.43309	-1841.432146	-1841.542697	0.007687	4.823665526	0.01%

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

Figure S13. Main conformers of **12d** in ECD



12dA 12dB 12dC 12dD



12dE 12dF

S2.6. Computational details for 12a and 12d (NMR)

All the optimized conformers were subjected to Gauge Independent Atomic Orbital (GIAO) calculations of their ^{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 ^{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 S9. DP4+ analysis results of **12a** (Isomer 1) and **12d** (Isomer 2)

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

		DP4+	100.00%	0.00%	–	–	–
Nuclei	sp2?	xperimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C	x	221.6	-47.3	-46.8			
C		50.6	131.1	128.2			
C		42.1	141.2	136.6			
C		36.1	148.6	144.6			
C		26.0	157.4	154.0			
C		50.2	135.4	129.2			
C		51.5	131.9	128.0			
C		22.1	163.7	160.1			
C		30.0	152.7	150.1			
C		20.4	166.5	160.5			
C		21.3	164.3	161.8			
C		6.5	178.6	174.9			
C		51.6	131.6	128.7			
C		65.3	120.8	116.1			
C	x	161.1	19.6	18.7			
C	x	113.6	68.7	67.1			
C	x	147.6	32.1	30.8			
C	x	108.1	74.7	72.3			
C	x	157.4	23.2	22.1			
C		78.2	103.4	101.2			
C		37.7	144.9	140.1			
C	x	169.5	9.2	10.9			
C		79.5	102.6	99.4			
C	x	114.5	67.3	64.9			
C	x	178.2	4.1	3.4			
C	x	109.0	73.2	71.7			
C	x	167.7	10.3	10.5			
C		22.5	162.9	158.5			
C	x	169.4	8.3	7.8			
C		52.4	131.8	129.7			

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)	39.00%	61.00%	–	–	–	–
sDP4+ (all data)	39.00%	61.00%	–	–	–	–
uDP4+ (H data)	–	–	–	–	–	–
uDP4+ (C data)	100.00%	0.00%	–	–	–	–
uDP4+ (all data)	100.00%	0.00%	–	–	–	–
DP4+ (H data)	–	–	–	–	–	–
DP4+ (C data)	100.00%	0.00%	–	–	–	–
DP4+ (all data)	100.00%	0.00%	–	–	–	–

S2.7. Computational details for bipolarithone D (13) (ECD)

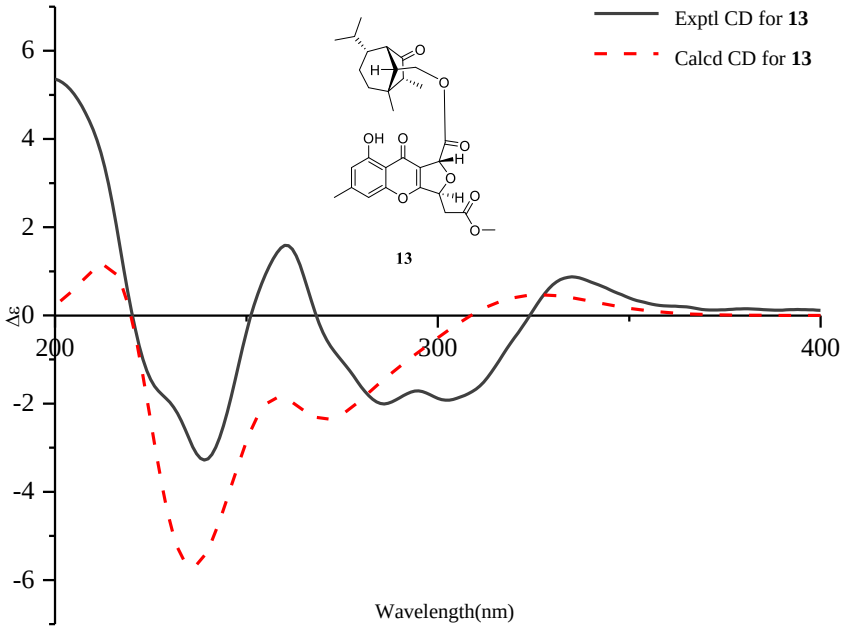


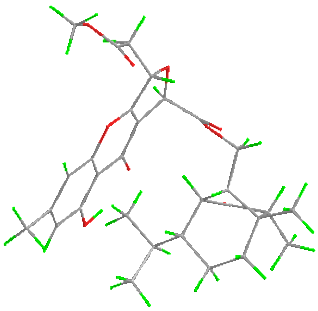
Figure S14. Calculated ECD spectra for **13** at the B3LYP/6-311G(d) level in methanol with IEFPCM model (σ = 0.25 eV, UV shift -7 nm). Experimental CD spectra of **13** (black line) in MeOH.

Table S10. Energy analysis for conformers of **13A~13I** at B3LYP/6-31G(d) level in the gas phase

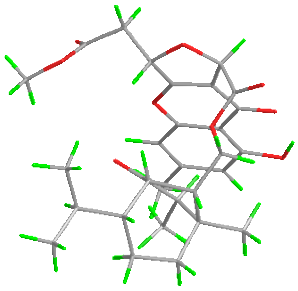
Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
13A	-1841.468163	-1841.430722	-1841.429777	-1841.540899	0.008079	5.06964925	0.01%
13B	-1841.476079	-1841.438801	-1841.437856	-1841.547017	0.001961	1.230546129	9.76%
13C	-1841.472092	-1841.434953	-1841.434009	-1841.543804	0.005174	3.246734153	0.32%
13D	-1841.469919	-1841.43262	-1841.431676	-1841.542167	0.006811	4.273967204	0.06%
13E	-1841.476788	-1841.439463	-1841.438519	-1841.548978	0	0	78.03%
13F	-1841.473712	-1841.436572	-1841.435628	-1841.545092	0.003886	2.438501917	1.27%
13G	-1841.474043	-1841.436633	-1841.435689	-1841.546529	0.002449	1.536770766	5.82%
13H	-1841.472688	-1841.435529	-1841.434585	-1841.544133	0.004845	3.040283527	0.46%
13I	-1841.475408	-1841.438401	-1841.437457	-1841.546233	0.002745	1.722513578	4.25%

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

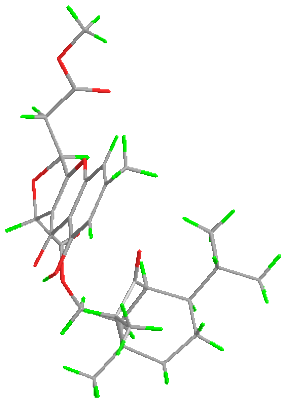
Figure S15. Main conformers of **13** in ECD



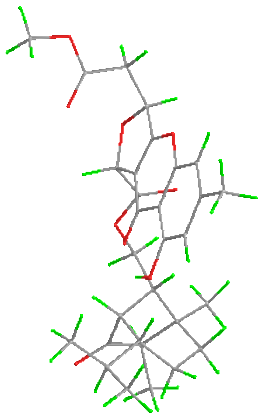
13A



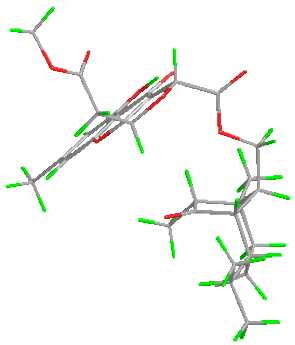
13b



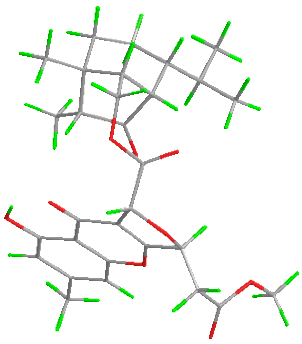
13C



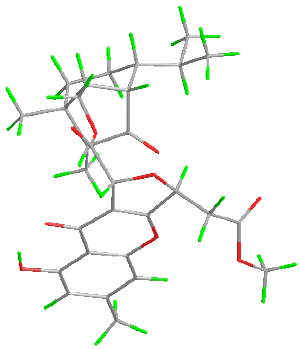
13D



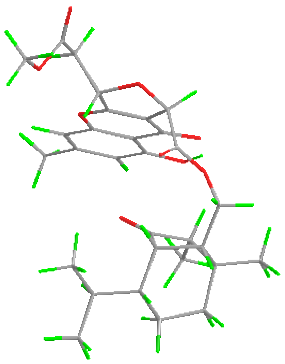
13E



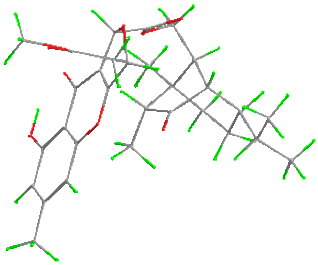
13F



13G



13H



13I