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

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Electronic supplementary information for

Anti Hepatitis B Virus Activities and Absolute Configurations of Sesquiterpenoid Glycosides from *Phyllanthus emblica*

Jun-Jiang Lv,†[a,b] Ya-Feng Wang,†[c] Jing-Min Zhang,[c,d] Shan Yu,[a,b] Dong Wang,[a] Hong-Tao Zhu,[a] Rong-Rong Cheng,[a] Chong-Ren Yang,[a] Min Xu,[a,*] and Ying-Jun Zhang[a,*]

[a] *State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, People's Republic of China.*

[b] *University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China.*

[c] *School of Pharmaceutical Sciences, Zhengzhou University, Zhengzhou 450001, People's Republic of China.*

[d] *Henan Key Laboratory for Pharmacology of Liver Diseases, Academy of Medical and Pharmaceutical Sciences, Zhengzhou University, 40 Daxue Road, Zhengzhou 450052, People's Republic of China.*

** Tel: +86-871-6522-3235. Fax: +86-871-6522-3235. E-mail: zhangyj@mail.kib.ac.cn (Ying-Jun Zhang) and minxu@mail.kib.ac.cn (Min Xu).*

† These authors contributed equally to this work.

Table of contents

1. Figure S1 HRESIMS of compound **1**

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B	3	0	0	O	2	0	30	S	2	0	0	I	3	0	0	HCOO
C	4	0	60	F	1	0	0	Cl	1	0	0					

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MSn Logic Mode: OR

Electron Ions: both
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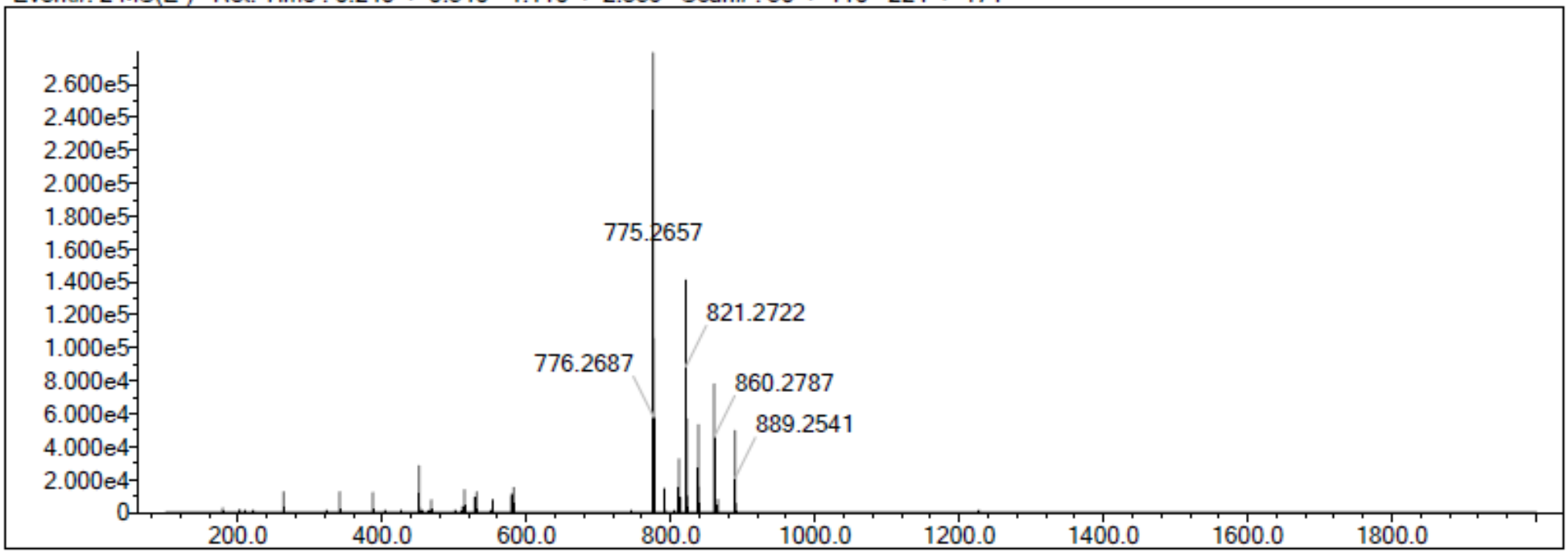
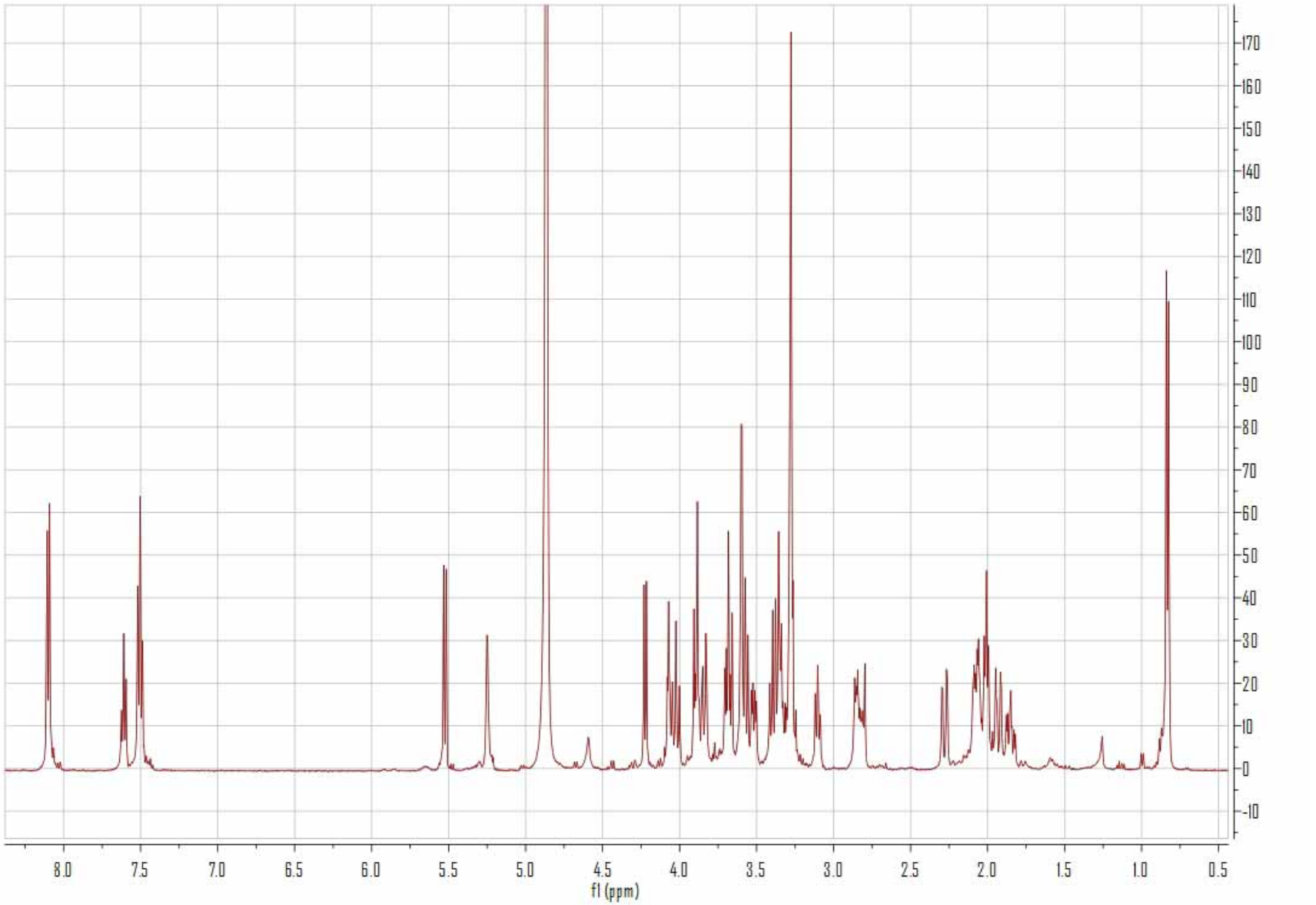
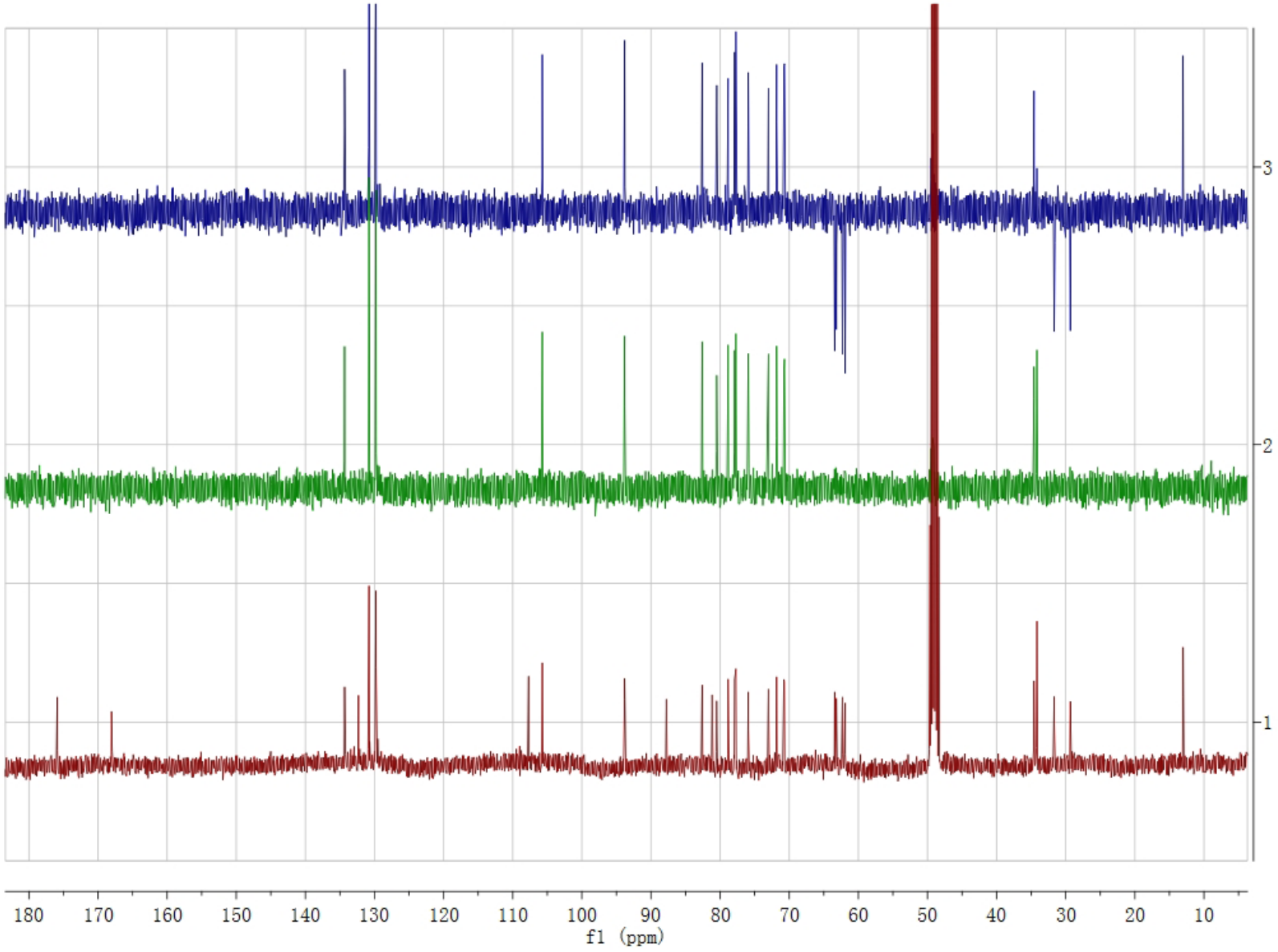


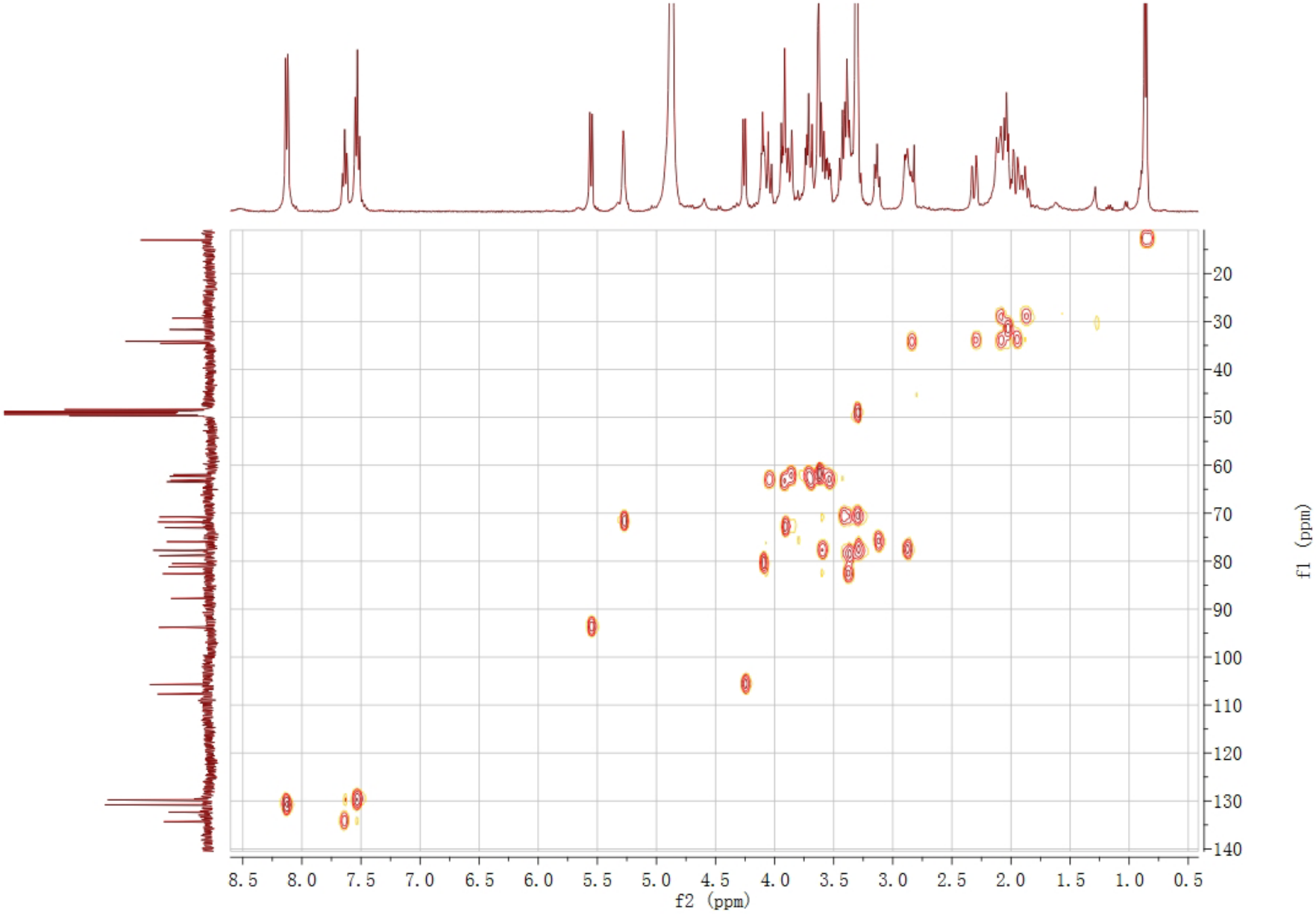
2. Figure S2 ^{1}H NMR (500 MHz) spectrum of phyllaemblicins G1 (**1**) in CD_3OD



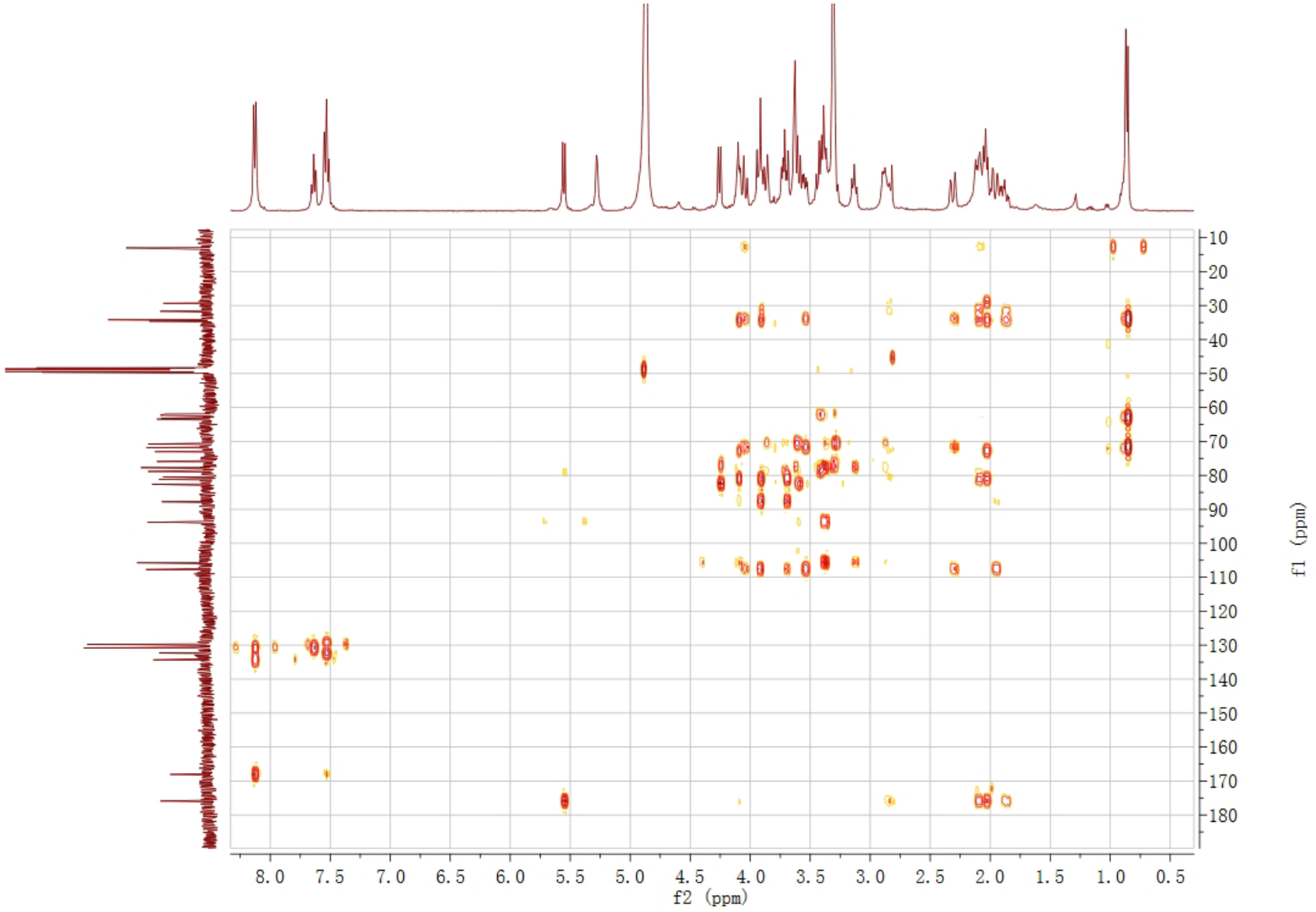
3. Figure S3 ^{13}C NMR (125 MHz) spectrum of phyllaemblicins G1 (**1**) in CD_3OD



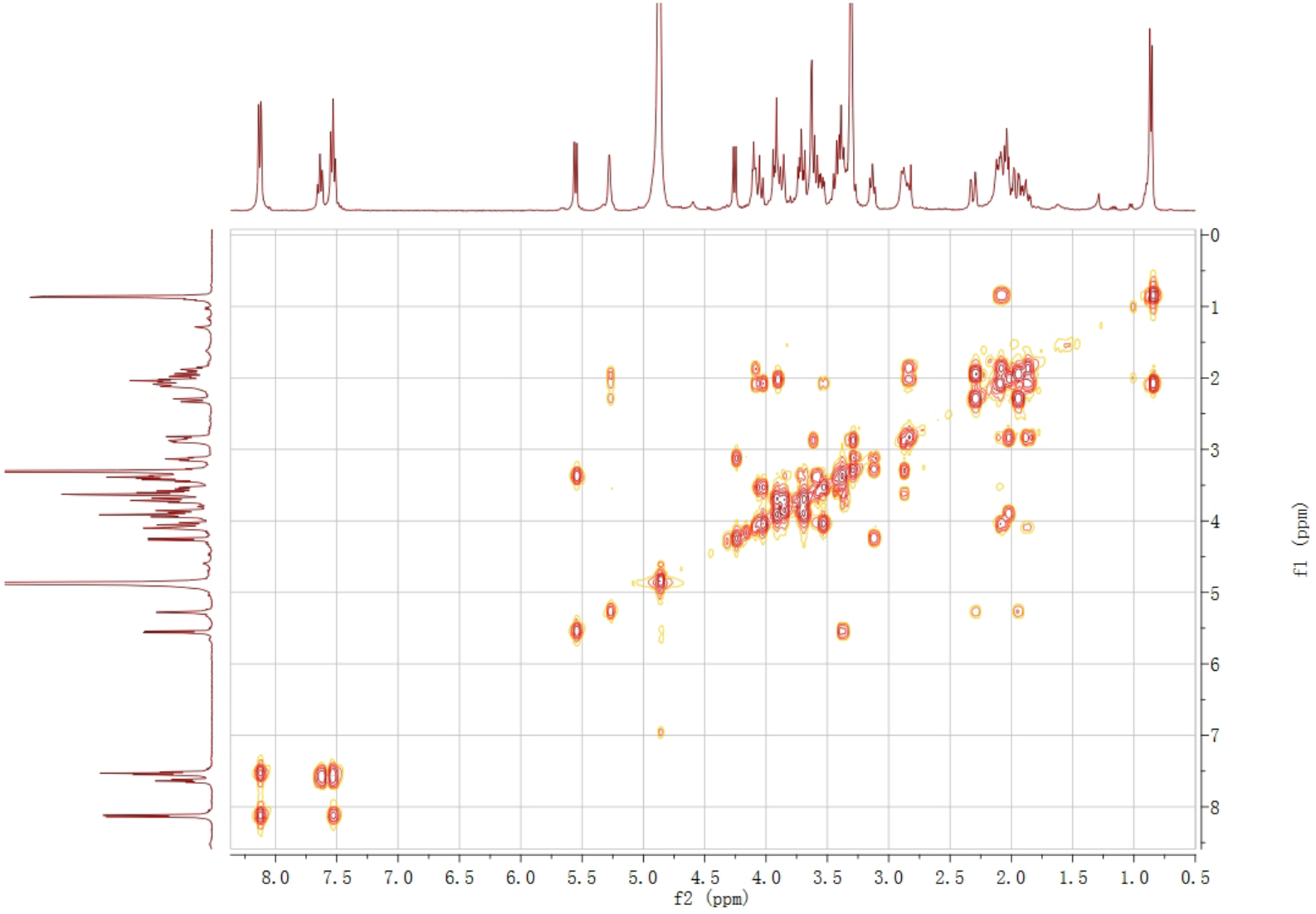
4. Figure S4 HSQC spectrum of phyllaemblicins G1 (**1**) in CD_3OD



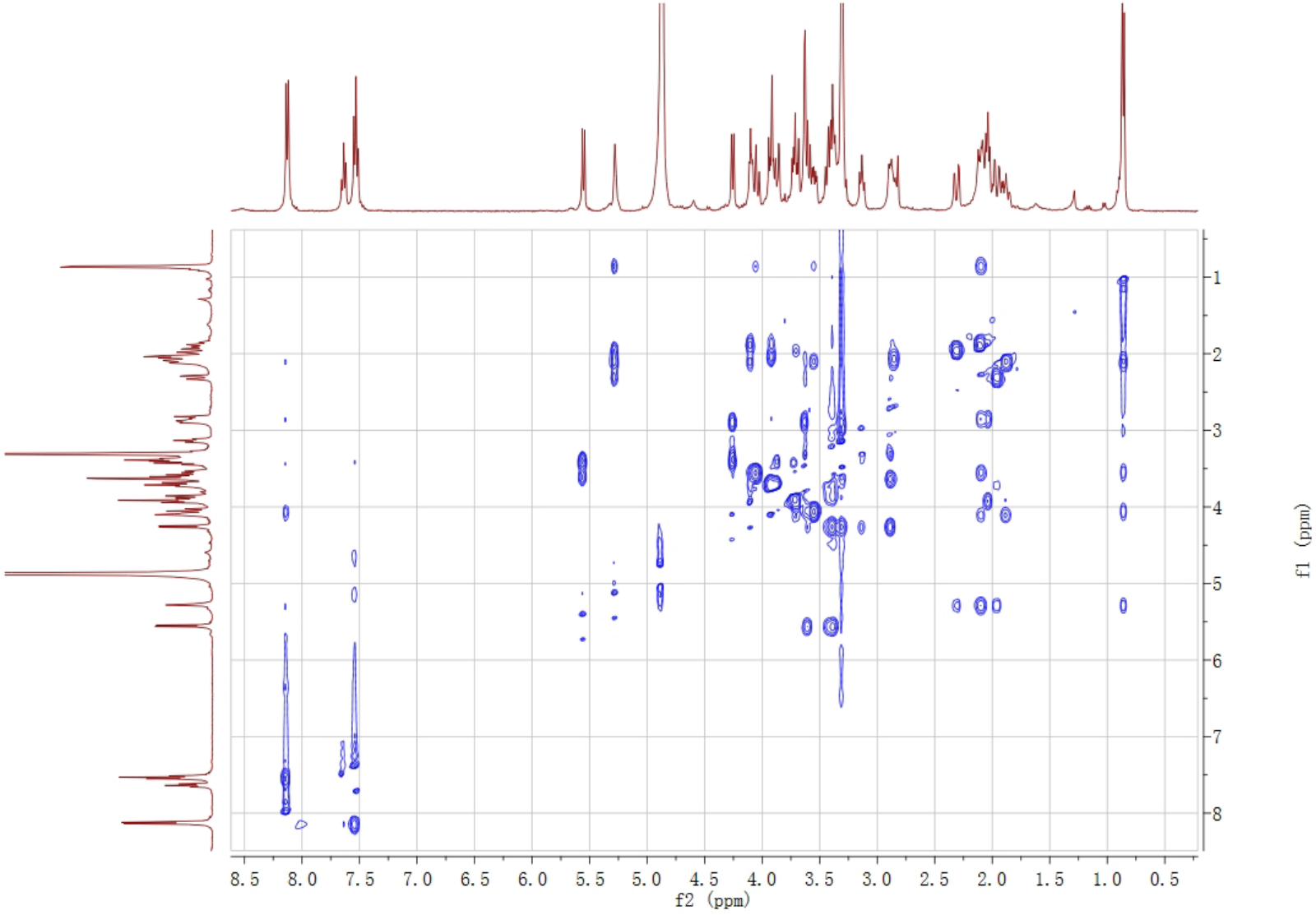
5. Figure S5 HMBC spectrum of phyllaemblicins G1 (**1**) in CD_3OD



6. Figure S6 ^{1}H-^{1}H COSY spectrum of phyllaemblicins G1 (**1**) in CD_3OD



7. Figure S7 ROESY spectrum of phyllaemblicins G1 (**1**) in CD_3OD



8. Figure S8 HRESIMS of phyllaemblicins G2 (**2**)

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B	3	0	0	O	2	0	30	S	2	0	0	I	3	0	0	HCOO
C	4	0	60	F	1	0	0	Cl	1	0	0					

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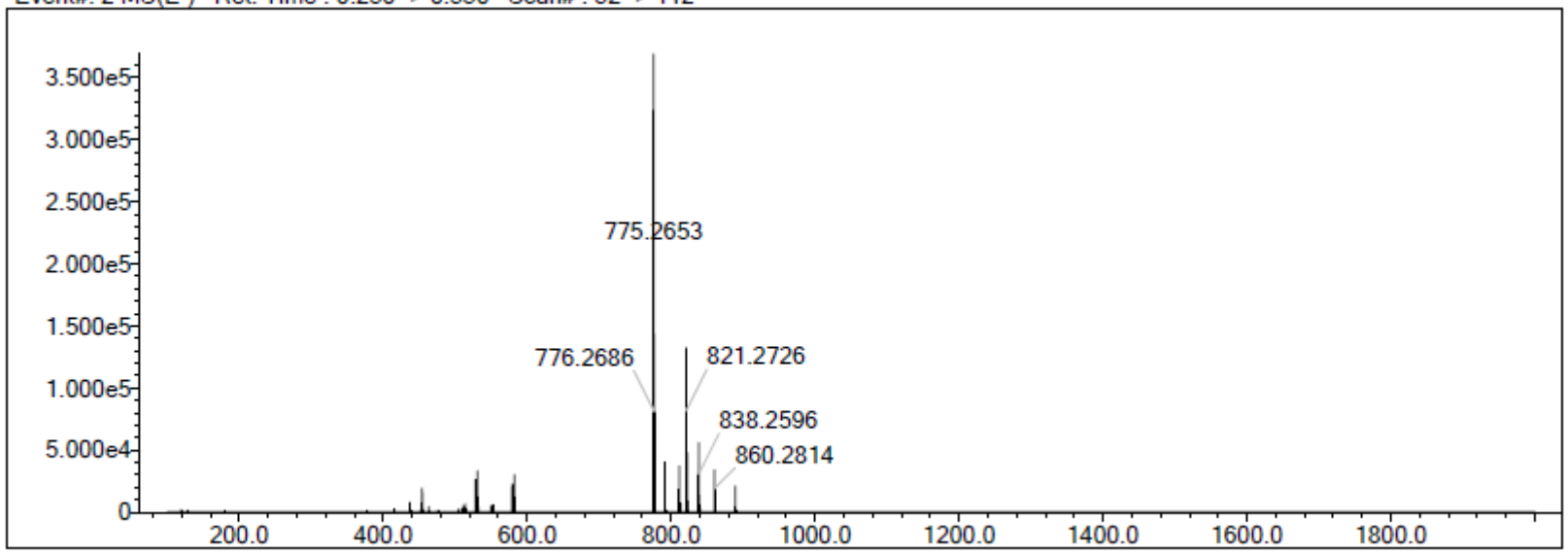
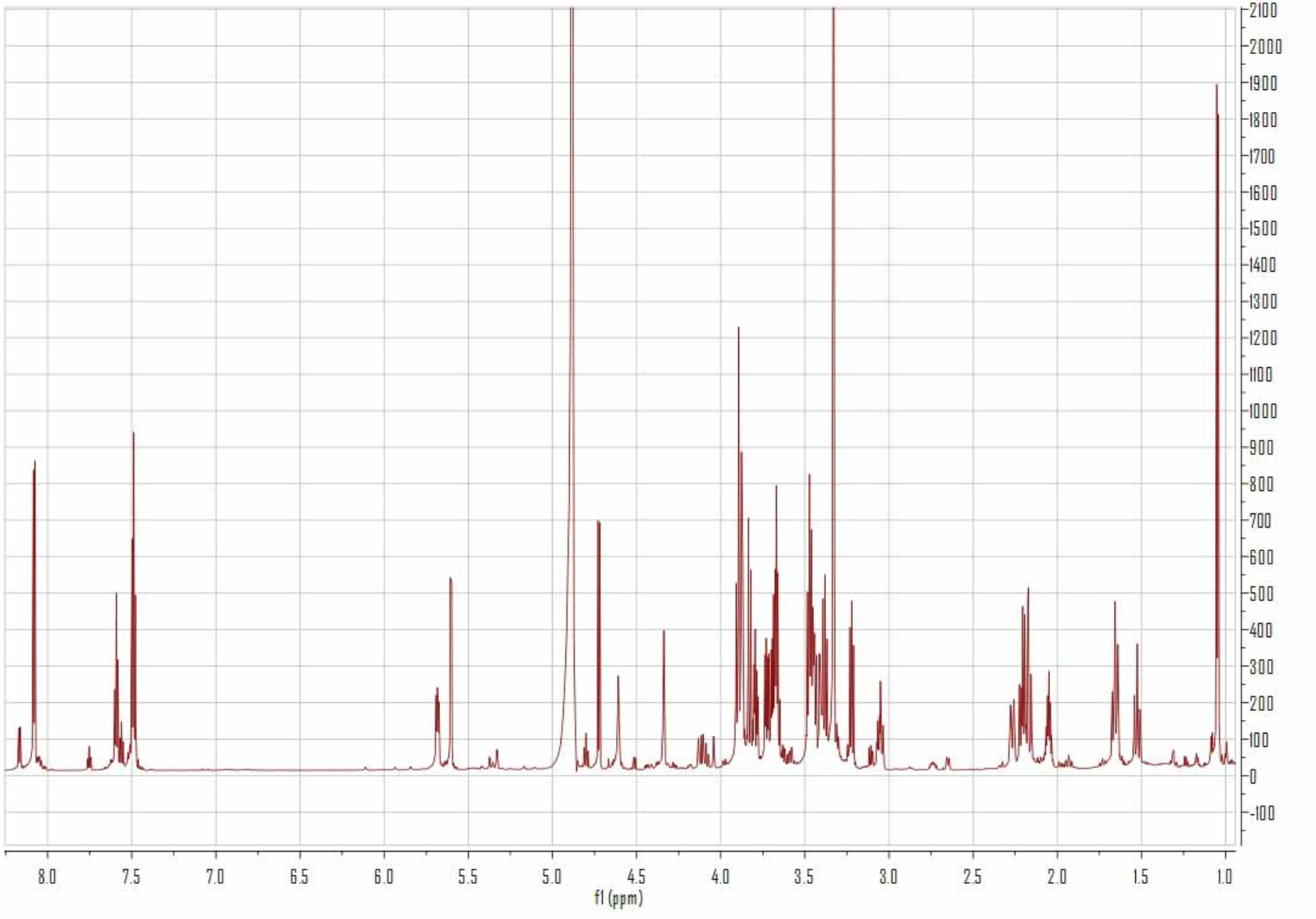
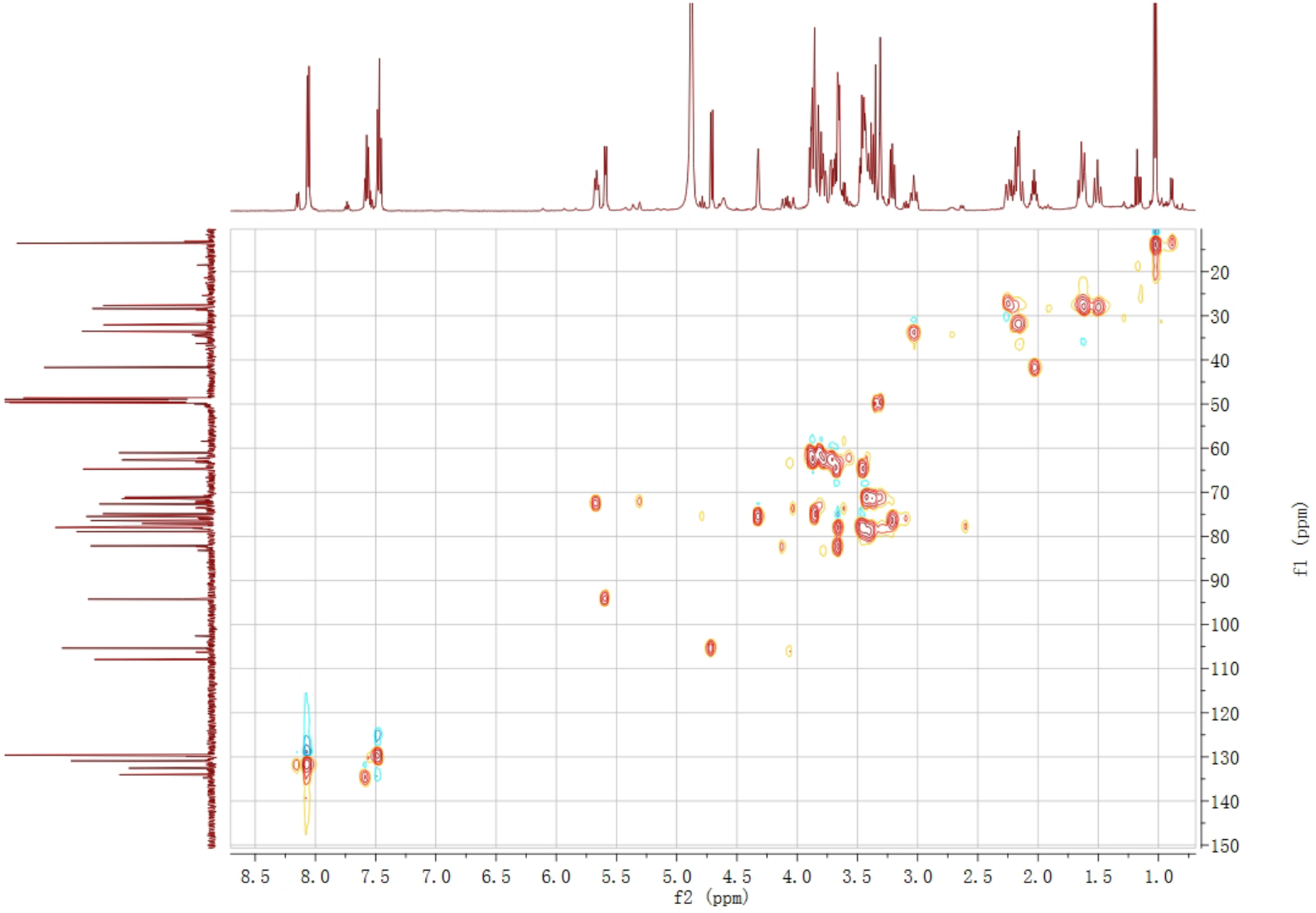


9. Figure S9 ^{1}H NMR (800 MHz) spectrum of phyllaemblicins G2 (**2**) in CD_3OD



10. Figure S10 ^{13}C NMR (125 MHz) spectrum of phyllaemblicins G2 (**2**) in CD_3OD

11. Figure S11 HSQC spectrum of phyllaemblicins G2 (**2**) in CD_3OD



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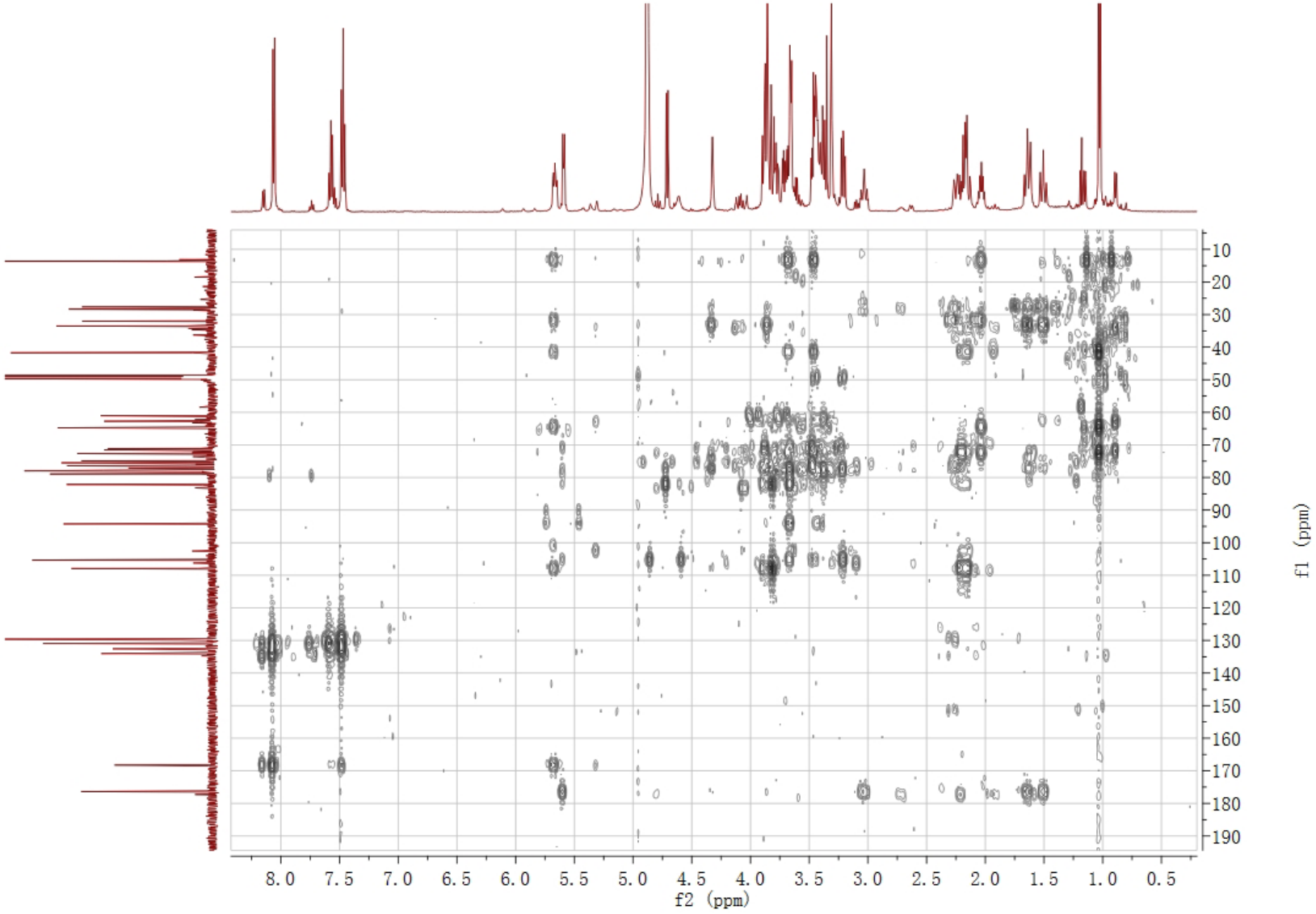
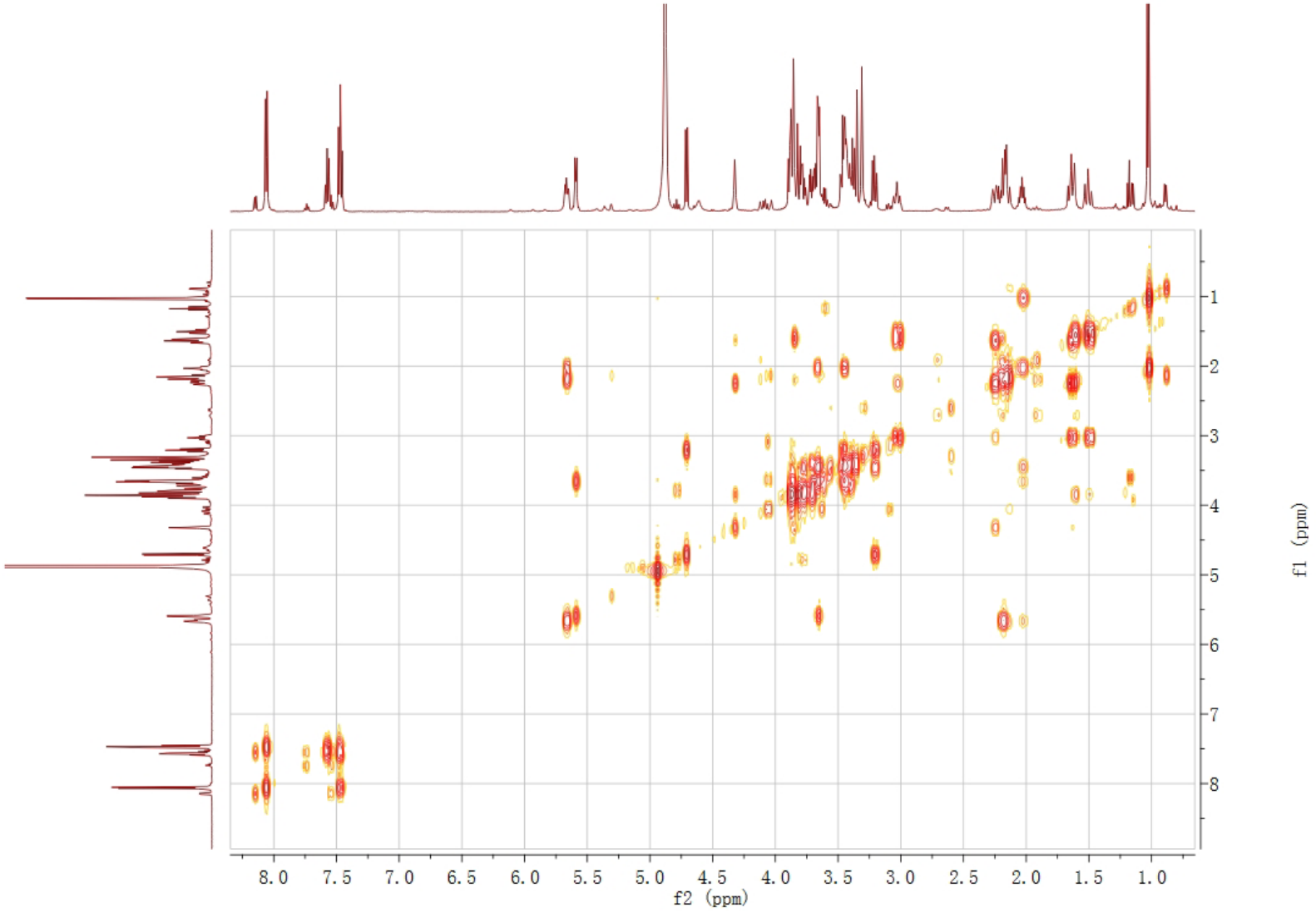


13. Figure S13 ^{1}H-^{1}H COSY spectrum of phyllaemblicins G2 (**2**) in CD_3OD



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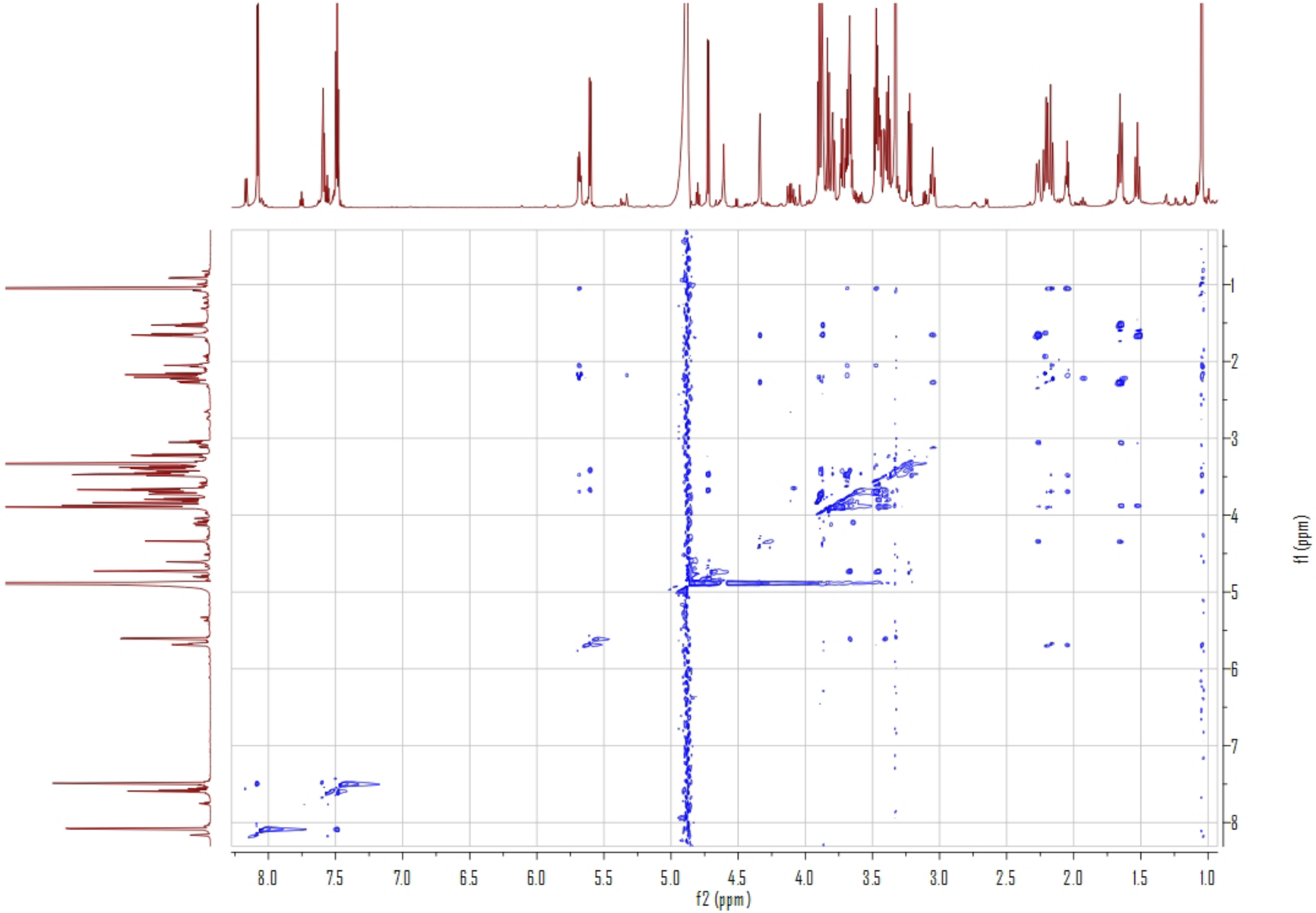

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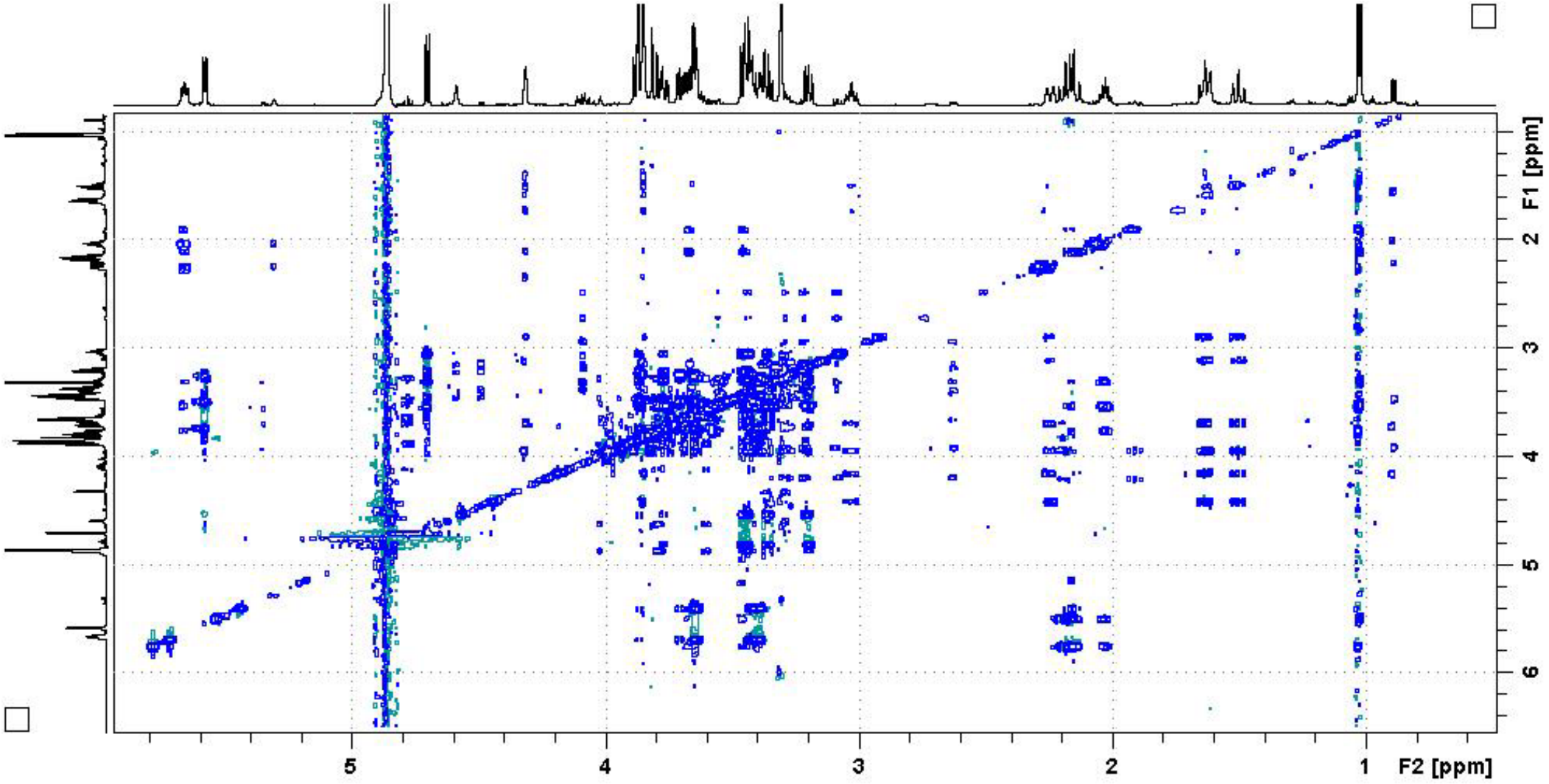
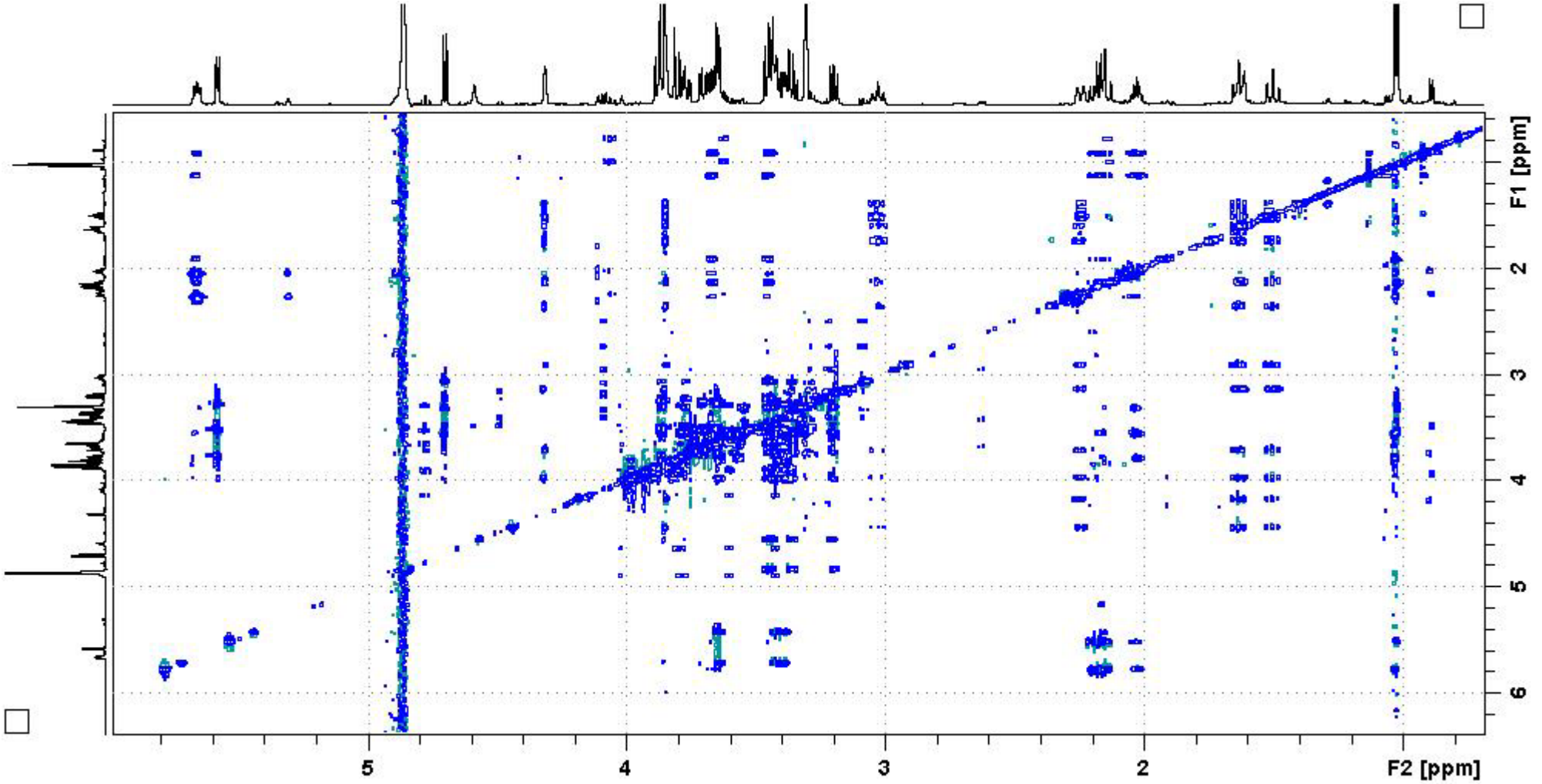
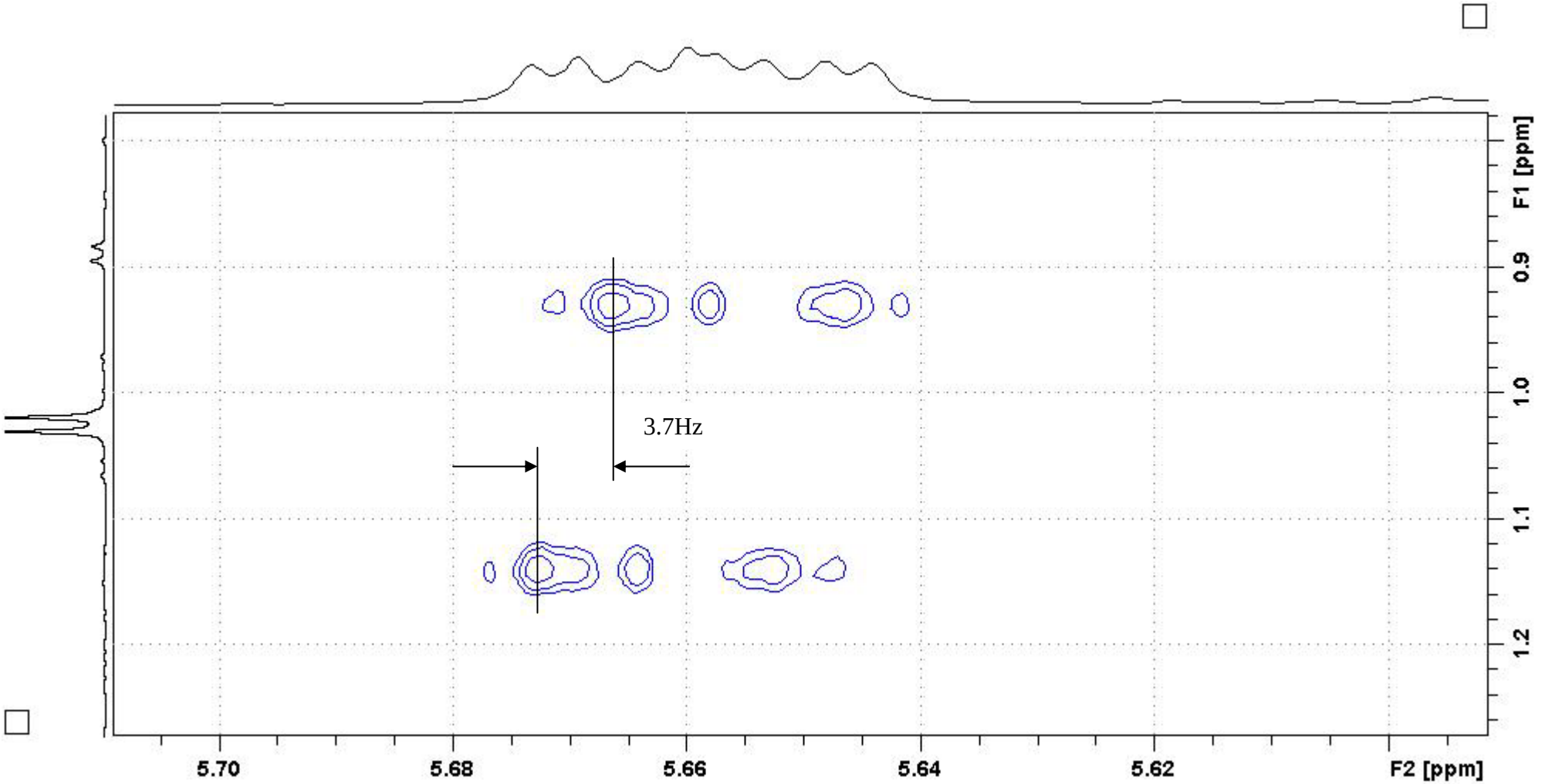


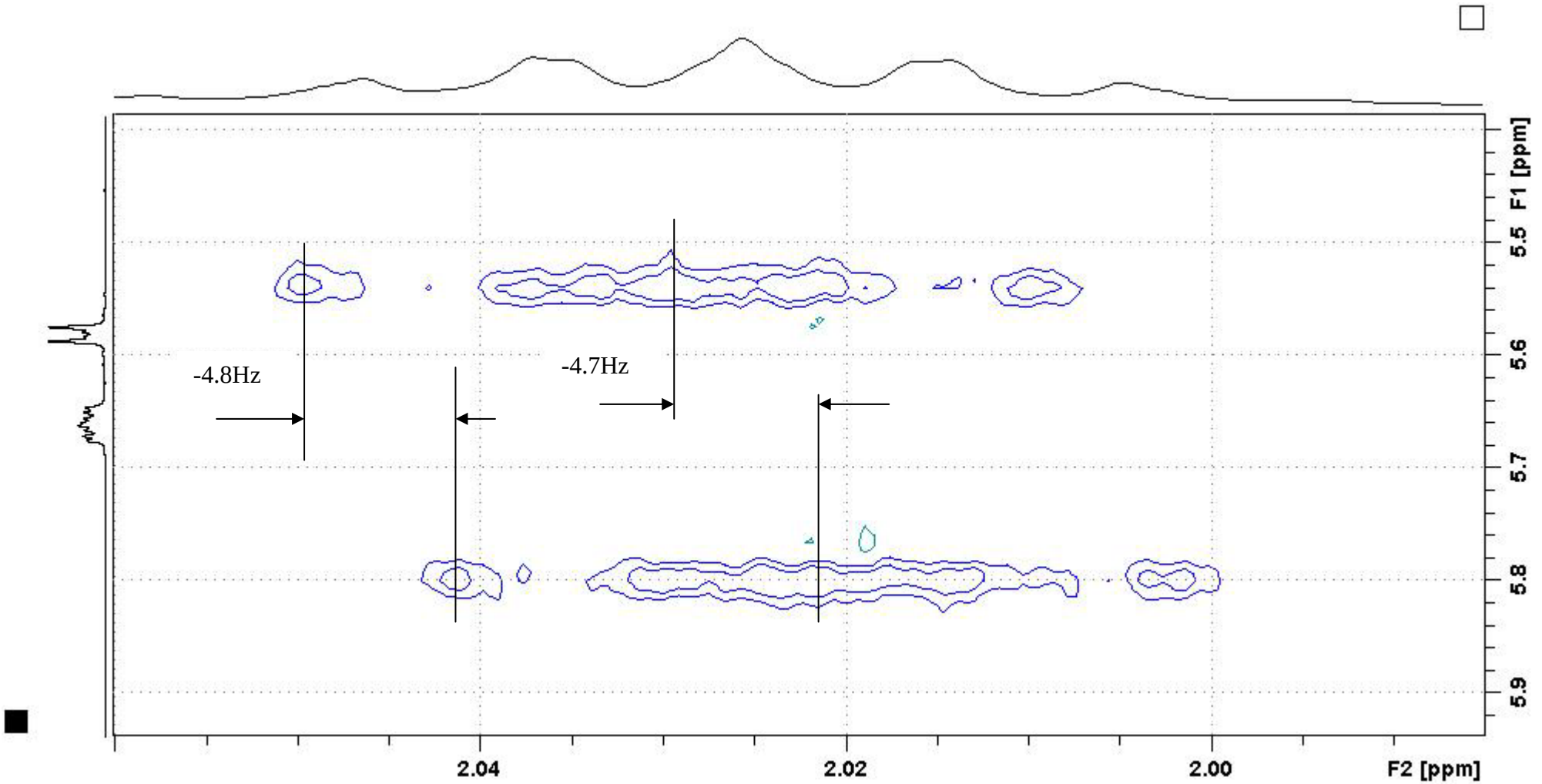
16. Figure S16 HETLOC spectrum of phyllaemblicins G2 (**2**) in CD_3OD



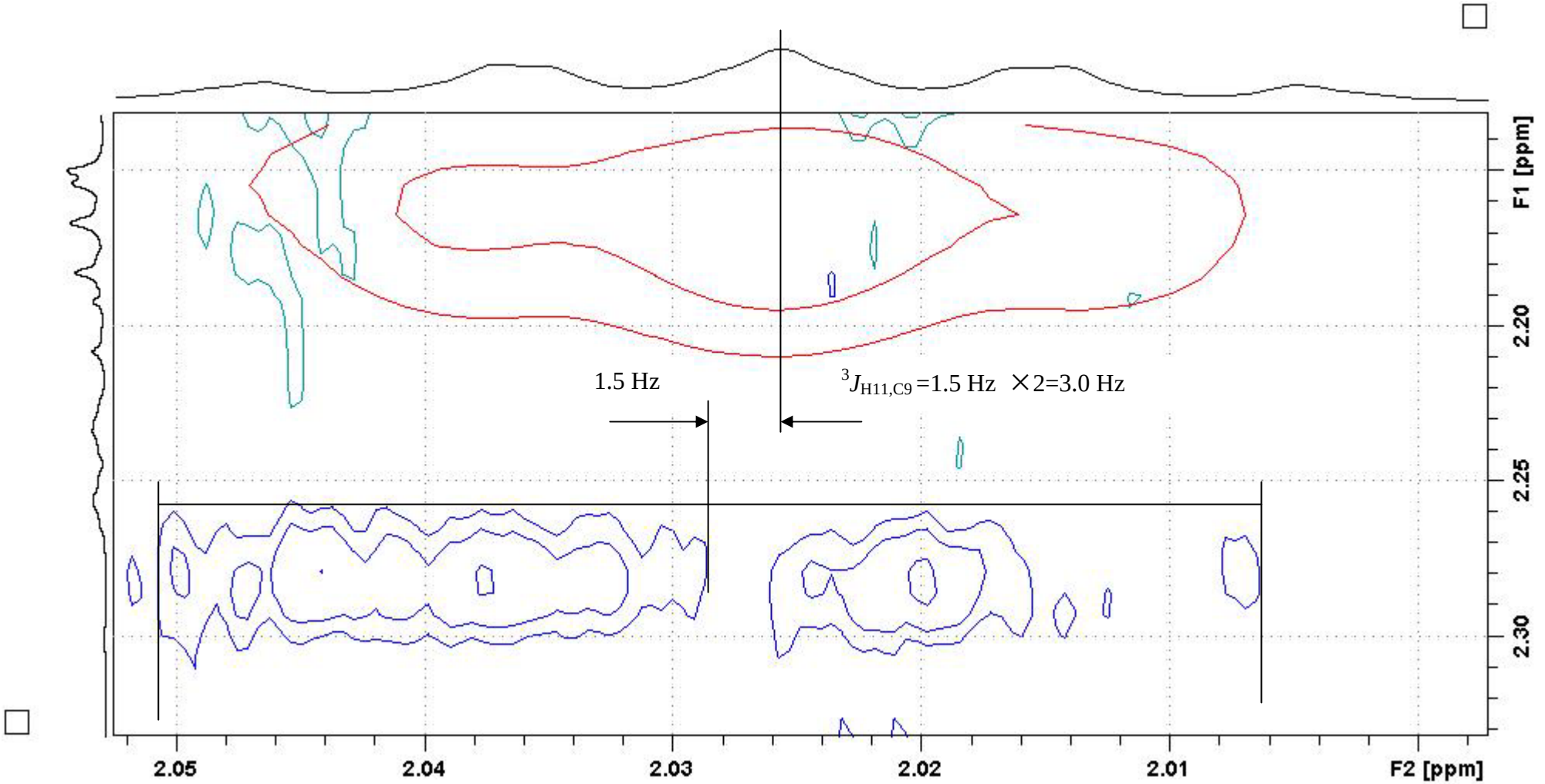
17. Figure S17 $^{3}J_{H10,C14}$ calculation using HETLOC spectrum of phyllaemblicins G2 (**2**) in CD_3OD



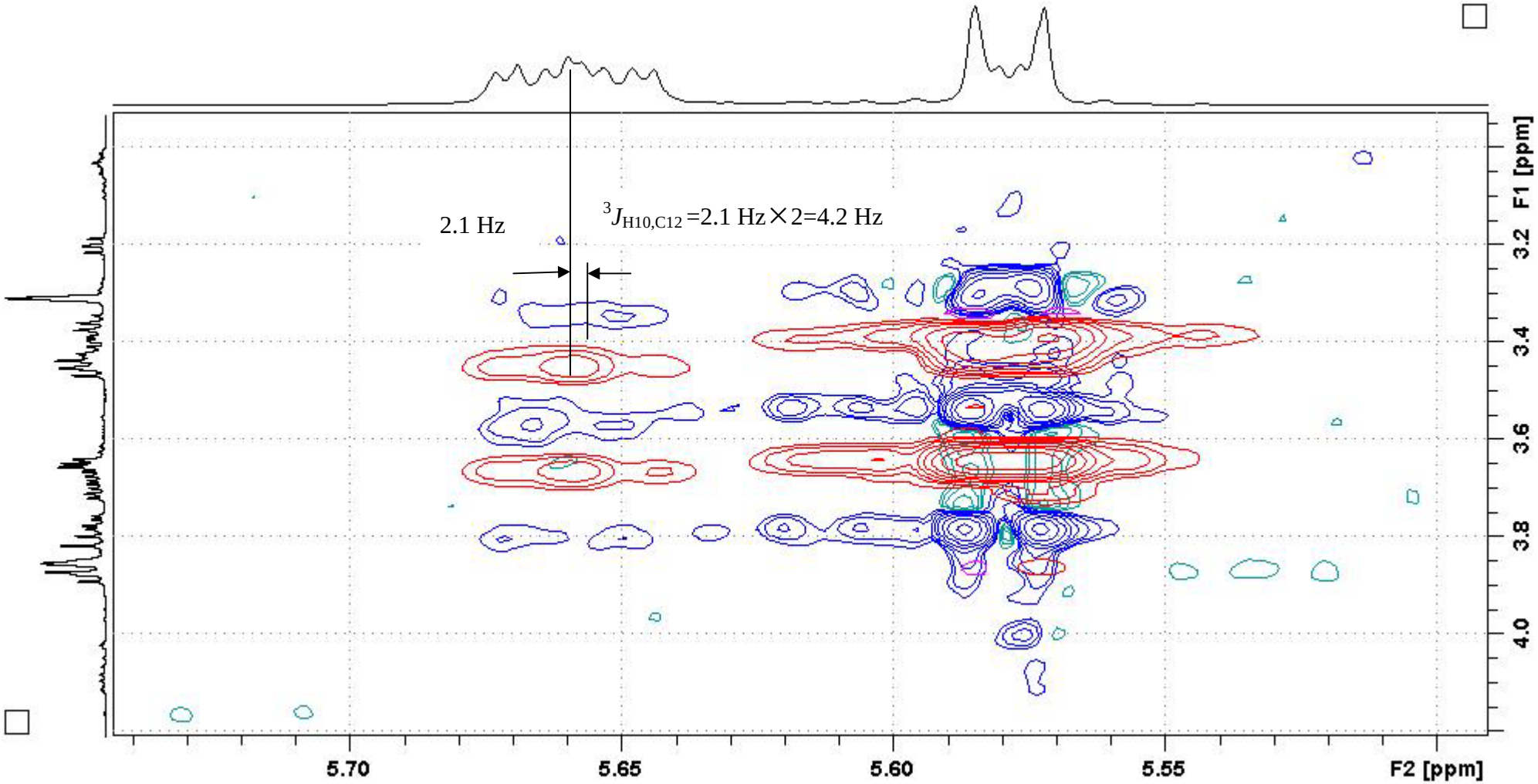
18. Figure S18 $^{2}J_{H11,C10}$ calculation using HETLOC spectrum of phyllaemblicins G2 (**2**) in CD_3OD



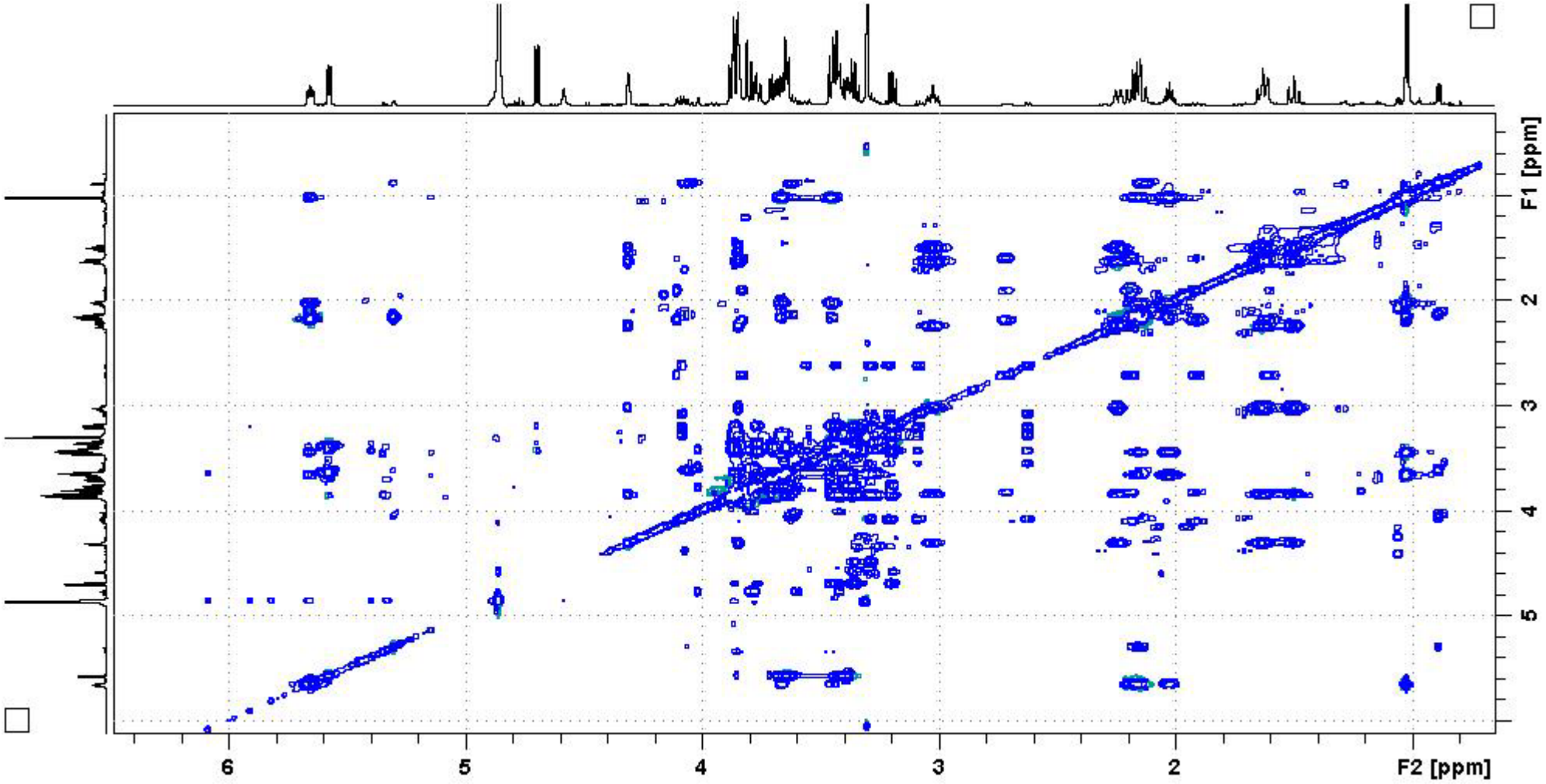
19. Figure S19 $^{3}J_{H11,C9}$ calculation using TOCSY and HETLOC spectrum of phyllaemblicins G2 (**2**) in CD_3OD



20. Figure S20 $^{3}J_{H10,C12}$ calculation using TOCSY and HETLOC spectrum of phyllaemblicins G2 (**2**) in CD_3OD



21. Figure S21 HSQC-TOCSY spectrum of phyllaemblicins G2 (**2**) in CD_3OD



22.Figure S22 HRESIMS of compound **2A**

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IRM Calibration Status	Success	**DA Method**	ESIN.m
Comment			

Sample Group	**Info.**
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User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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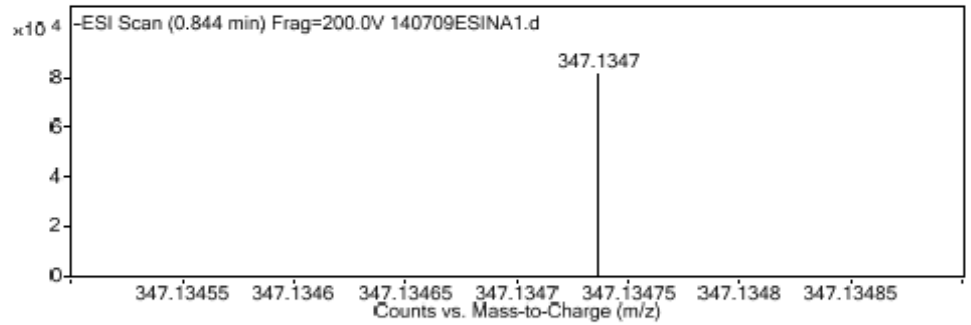

Peak List

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Formula Calculator Element Limits

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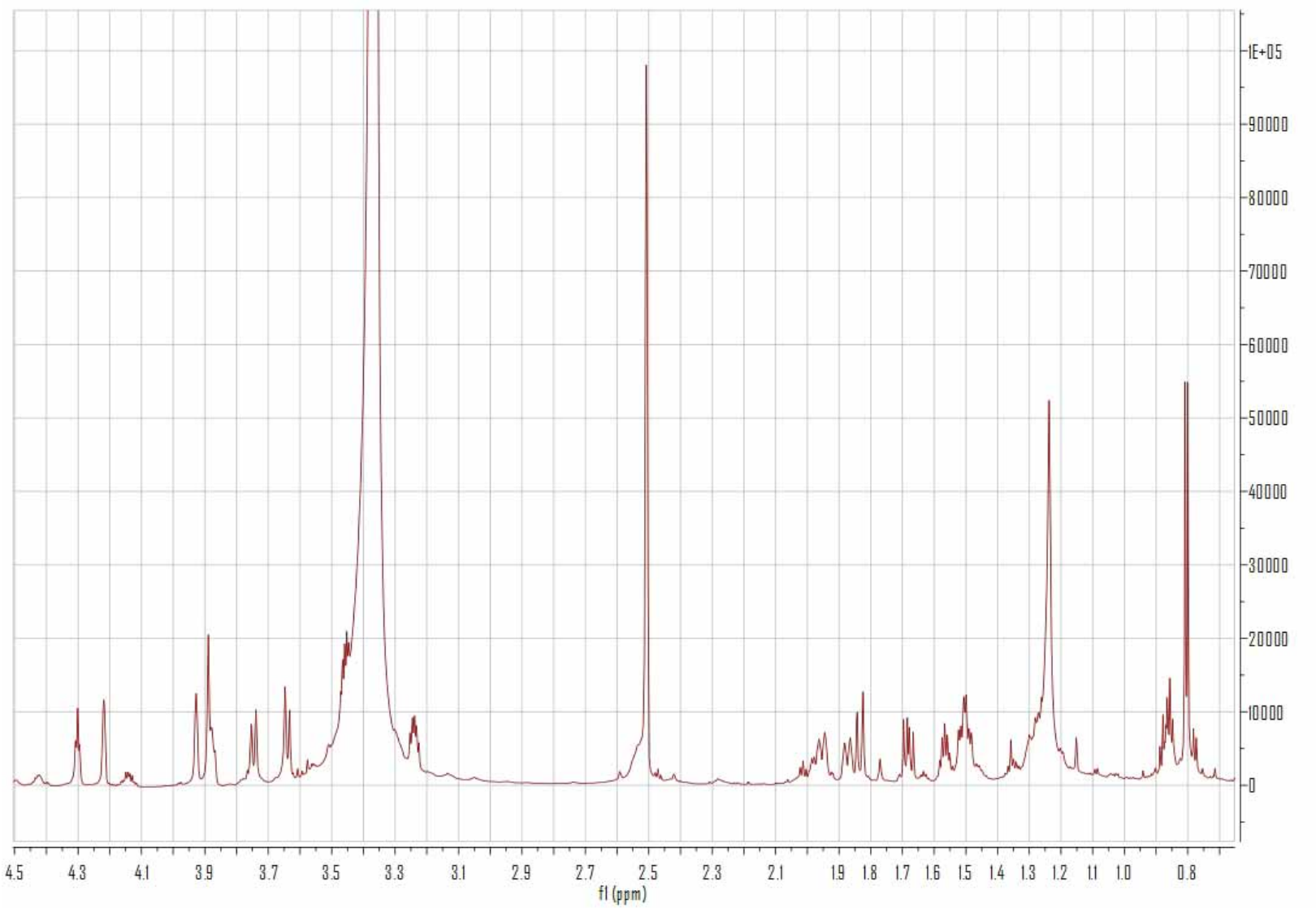
H	0	400
O	1	10

Formula Calculator Results

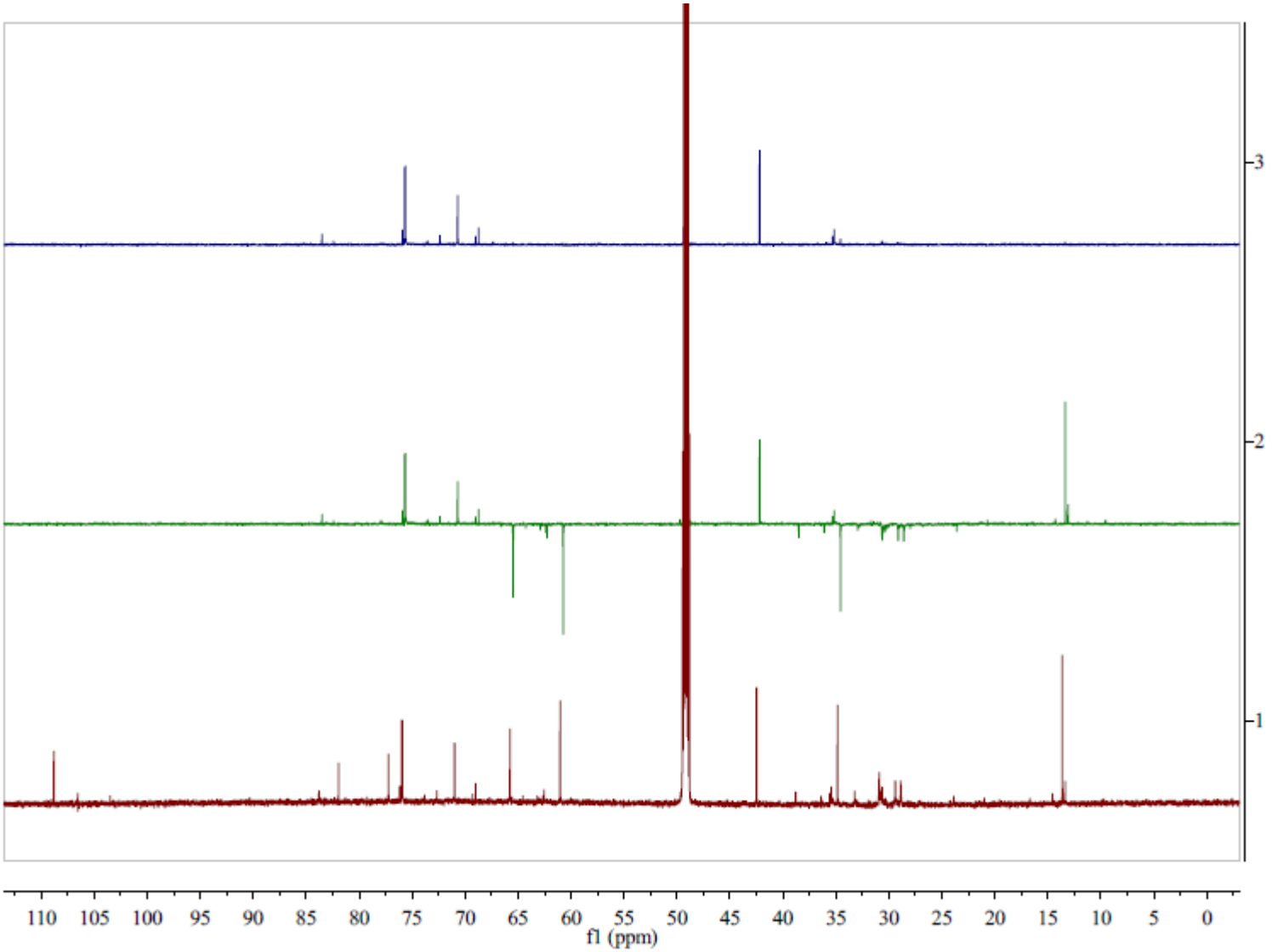
Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C15 H23 O9	347.1342	347.1347	-0.5	1.4	4.5

--- End Of Report ---

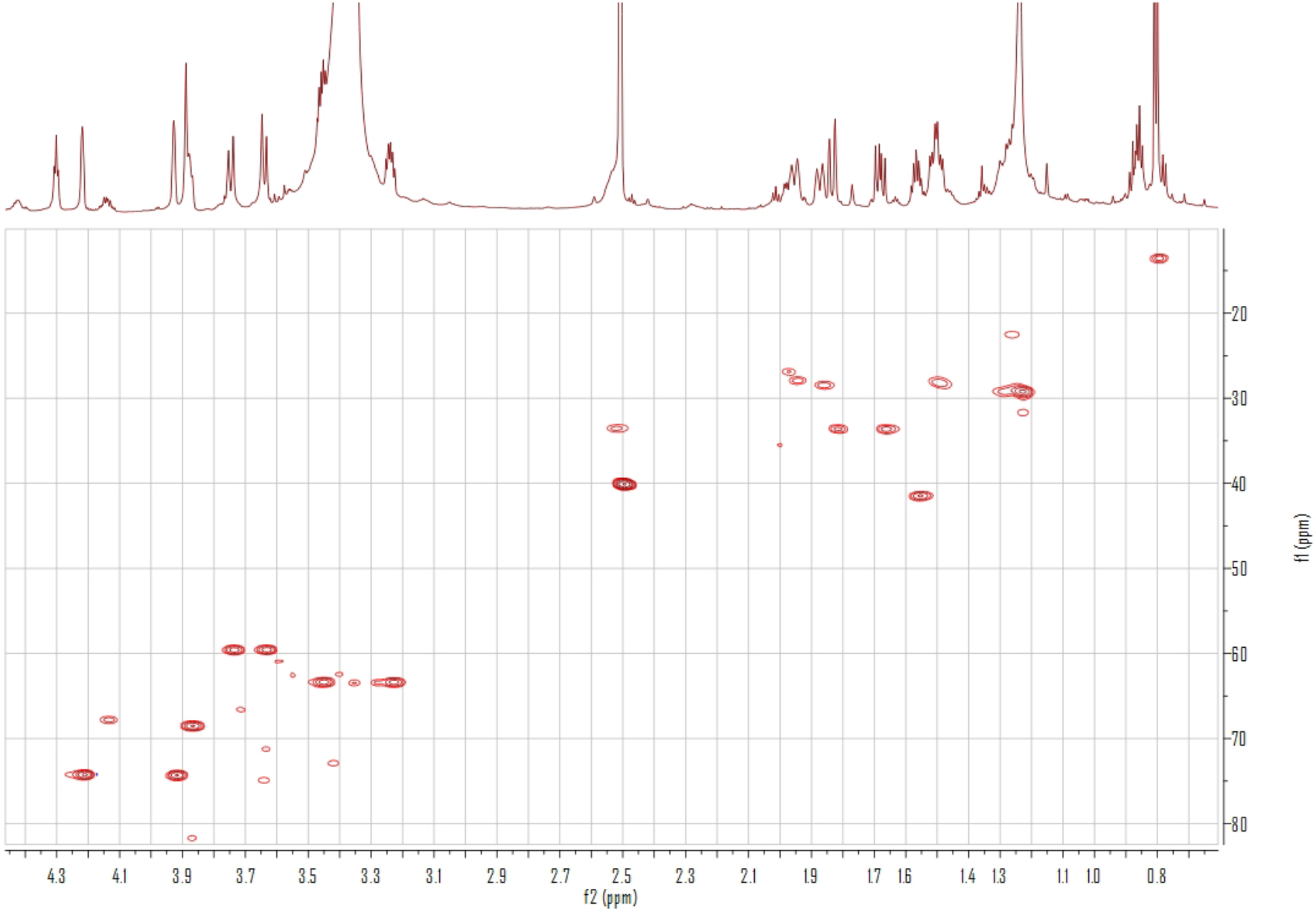
23.Figure S23 ^{1}H NMR (800 MHz) spectrum of compound **2A** in DMSO-d_6



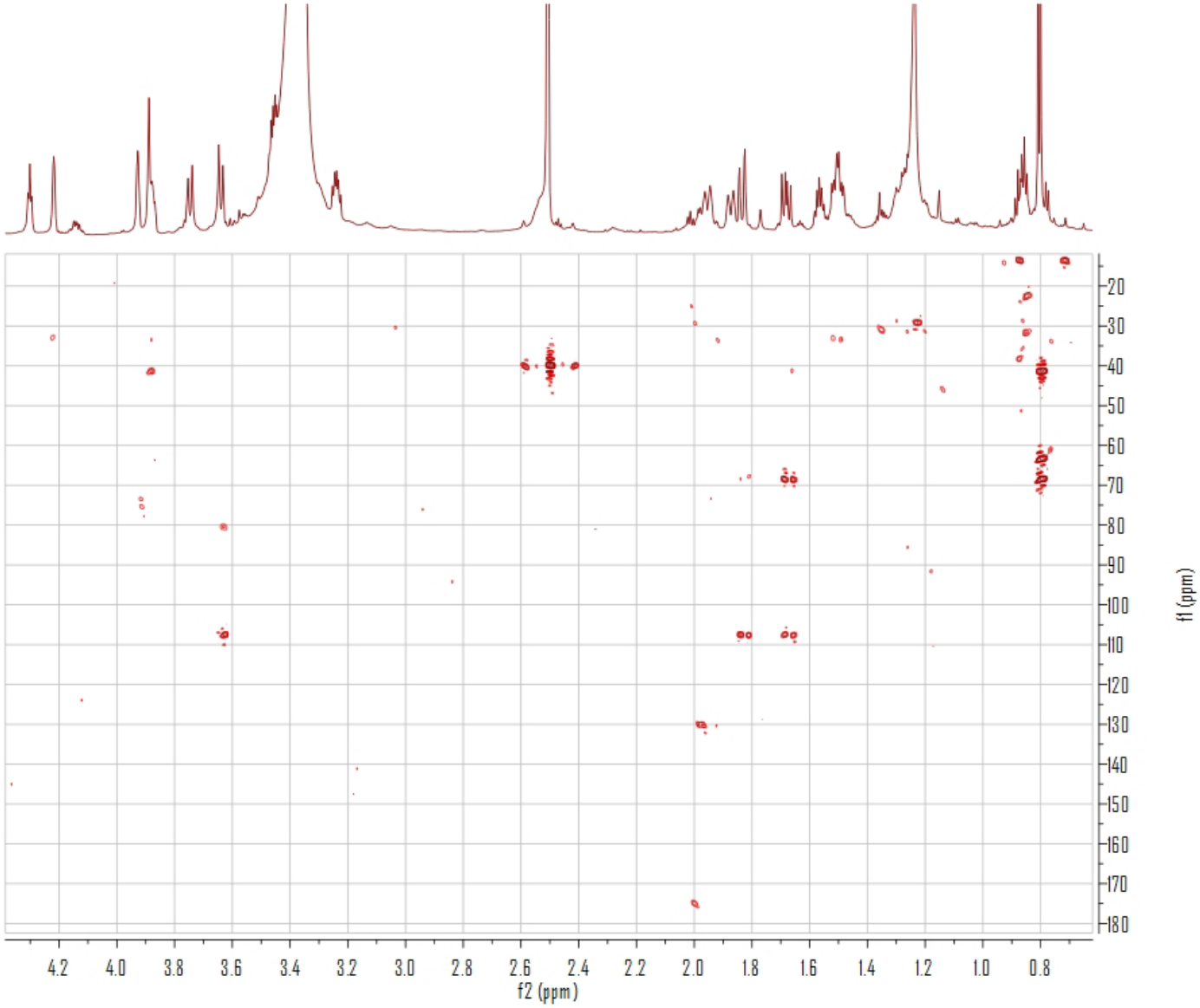
24. Figure S24 ^{13}C NMR (800 MHz) spectrum of compound **2A** in CH_3OD



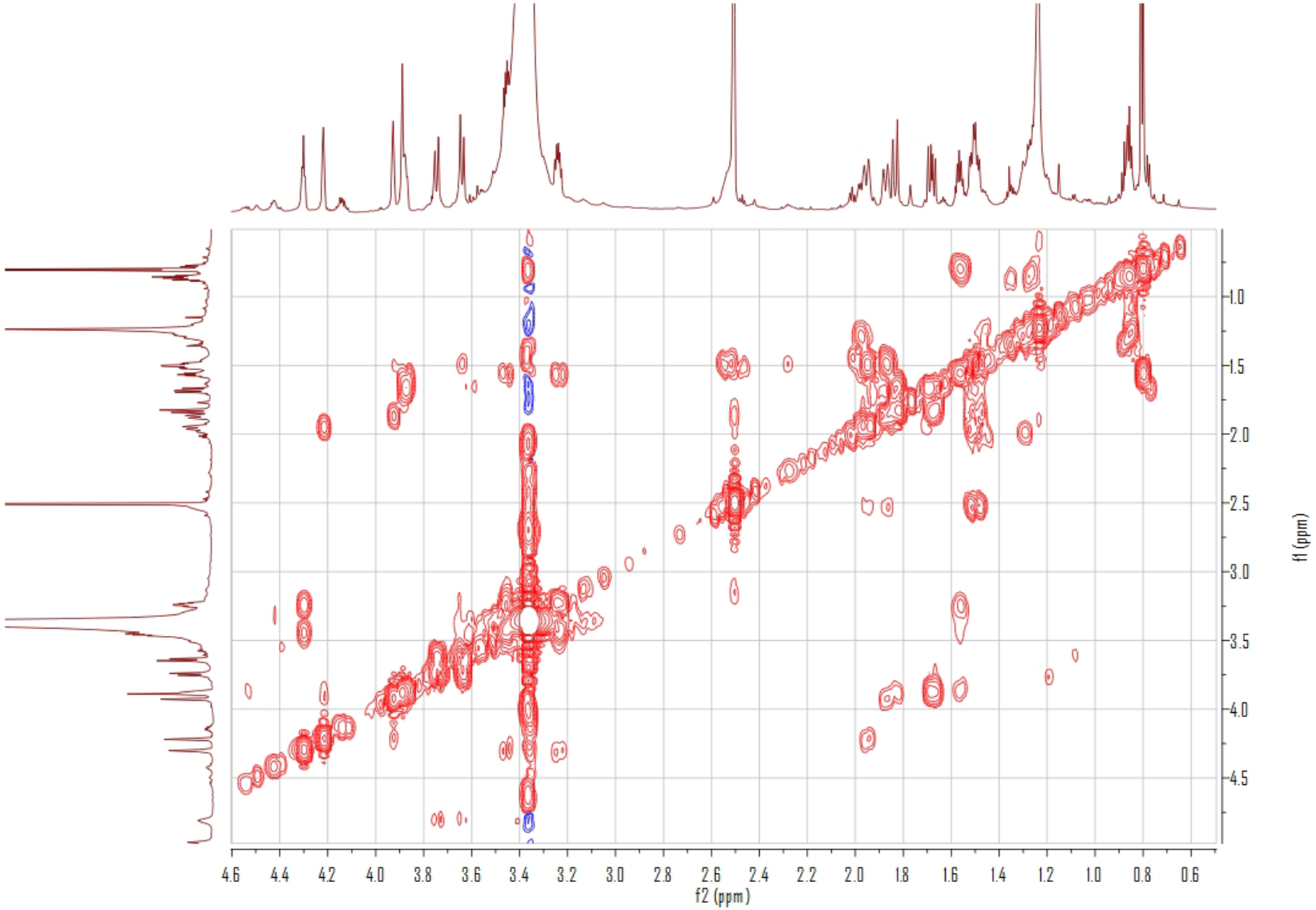
25.Figure S25 HSQC spectrum of compound **2A** in DMSO-d_6



26. Figure S26 HMBC spectrum of compound **2A** in DMSO-d_6



27. Figure S27 ^{1}H-^{1}H COSY spectrum of compound **2A** in DMSO-d_6



28.Figure S28 HRESIMS of phyllaemblicins G3 (**3**)

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User Spectra

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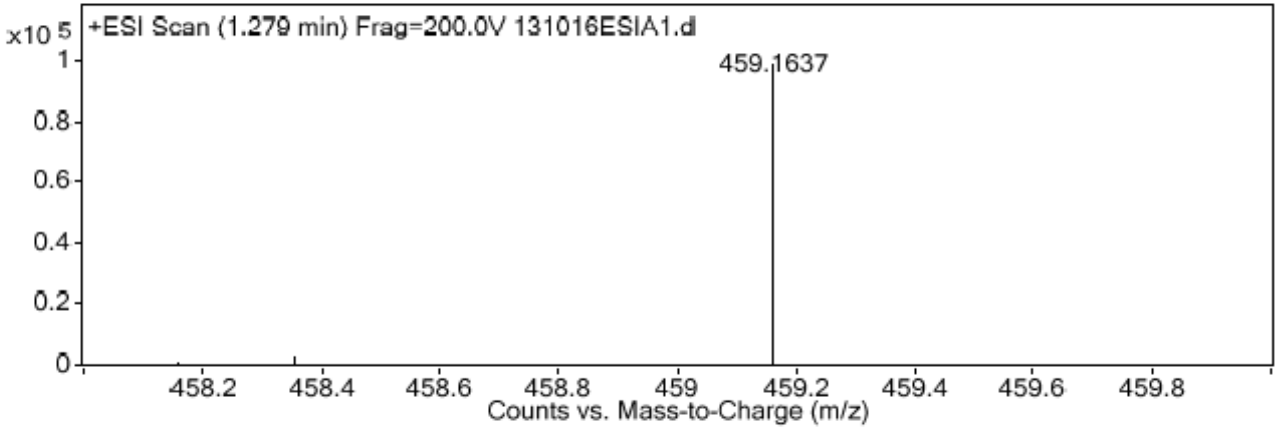

Formula Calculator Element Limits

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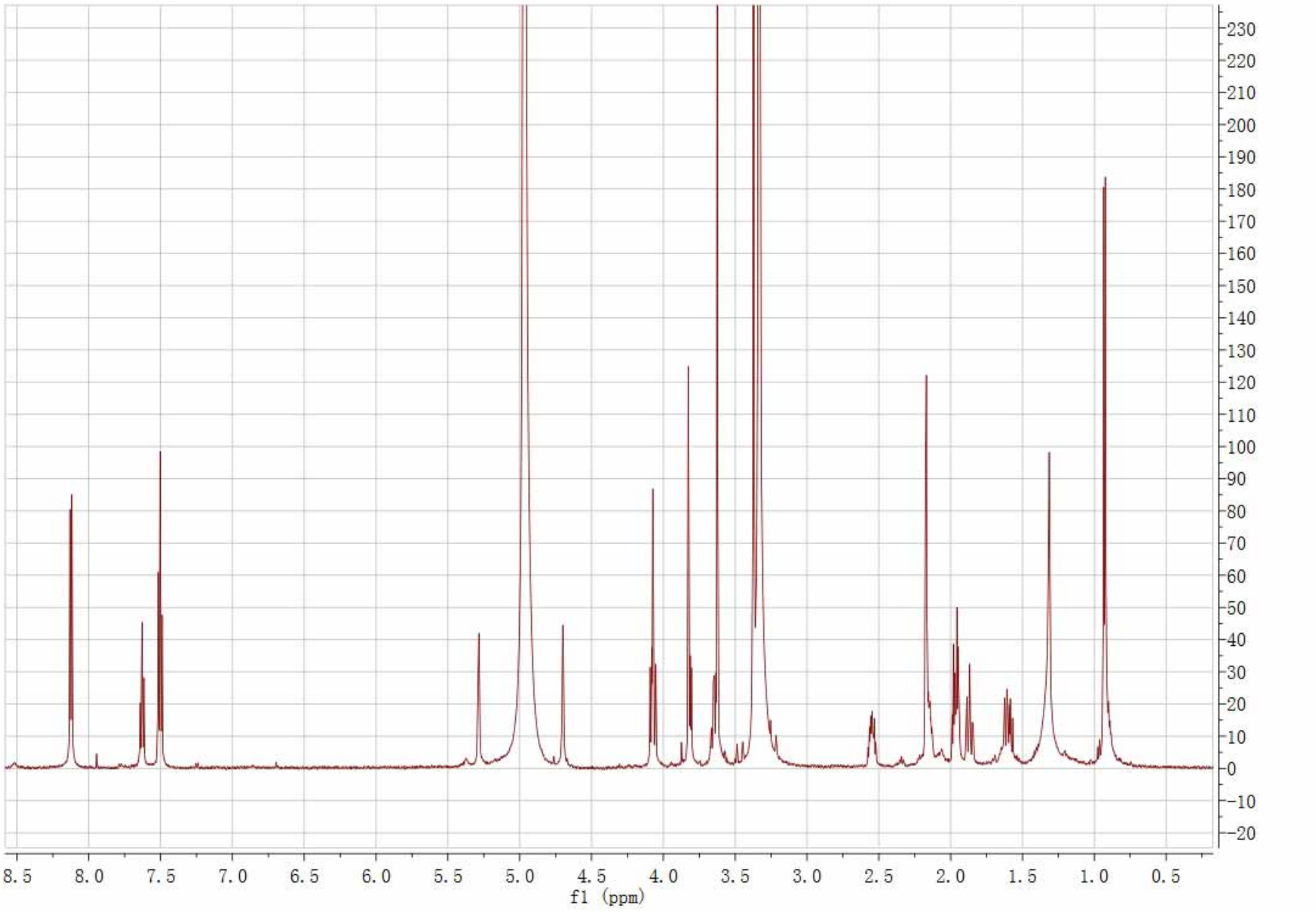
C	0	200
H	0	400
O	8	10
Na	1	1

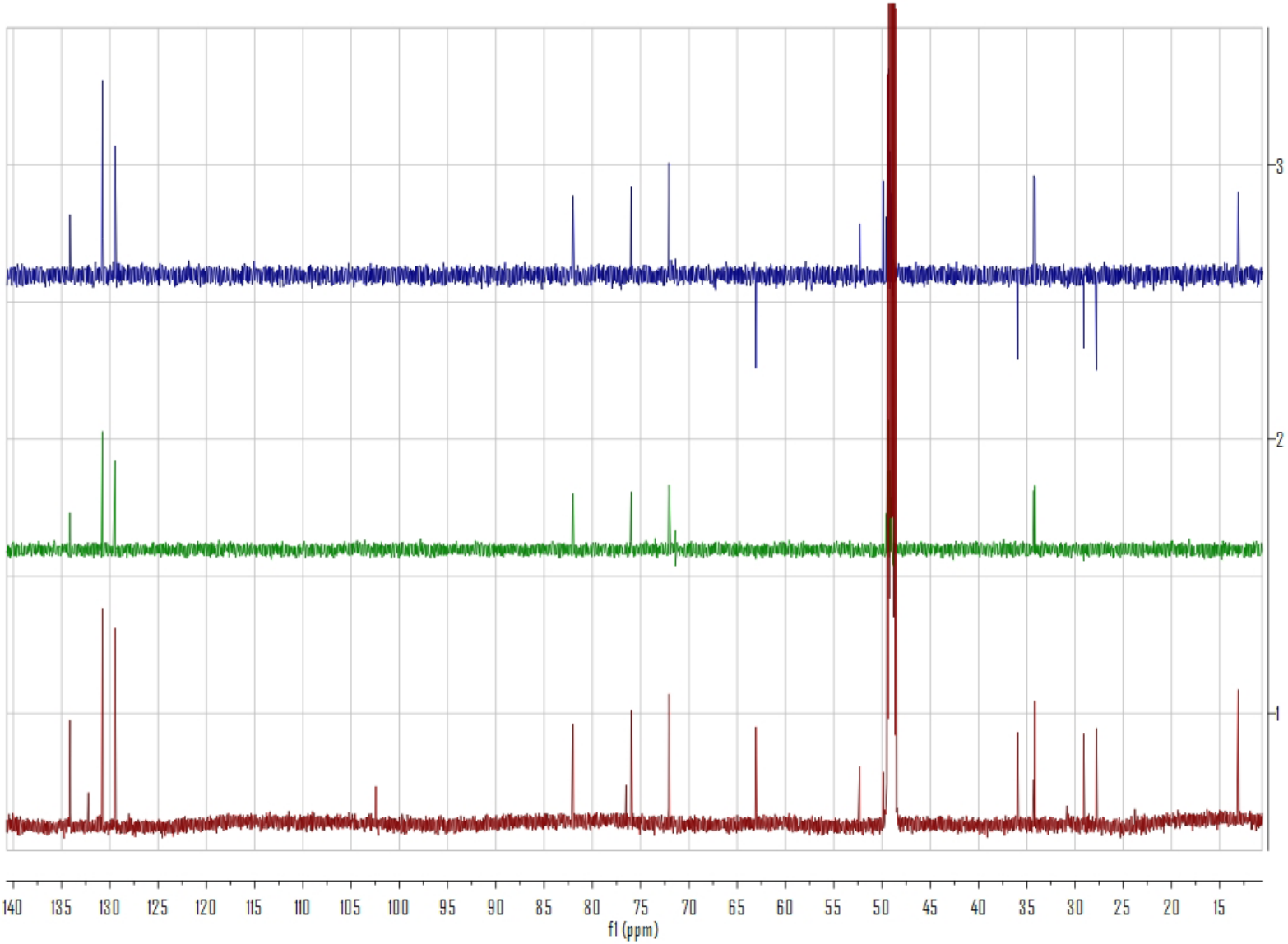
Formula Calculator Results

Formula	Calculated Mass	Measured Mass	Diff. (mDa)	Diff. (ppm)	DBE
C22 H28 Na O9	459.1631	459.1642	-1.1	-2.4	8.5

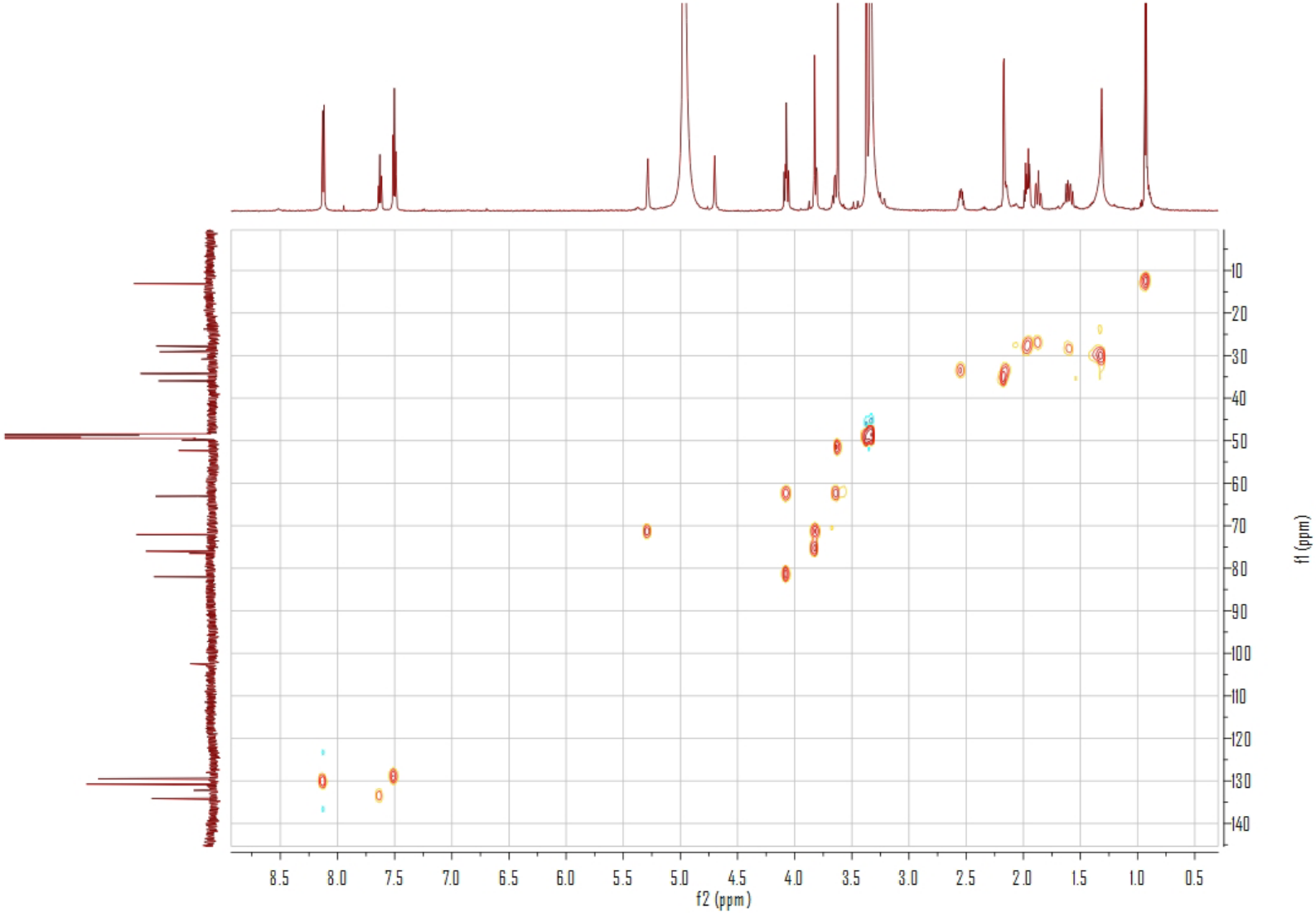
29.Figure S29 ^{1}H NMR (600 MHz) spectrum of phyllaemblicins G3 (**3**) in CD_3OD



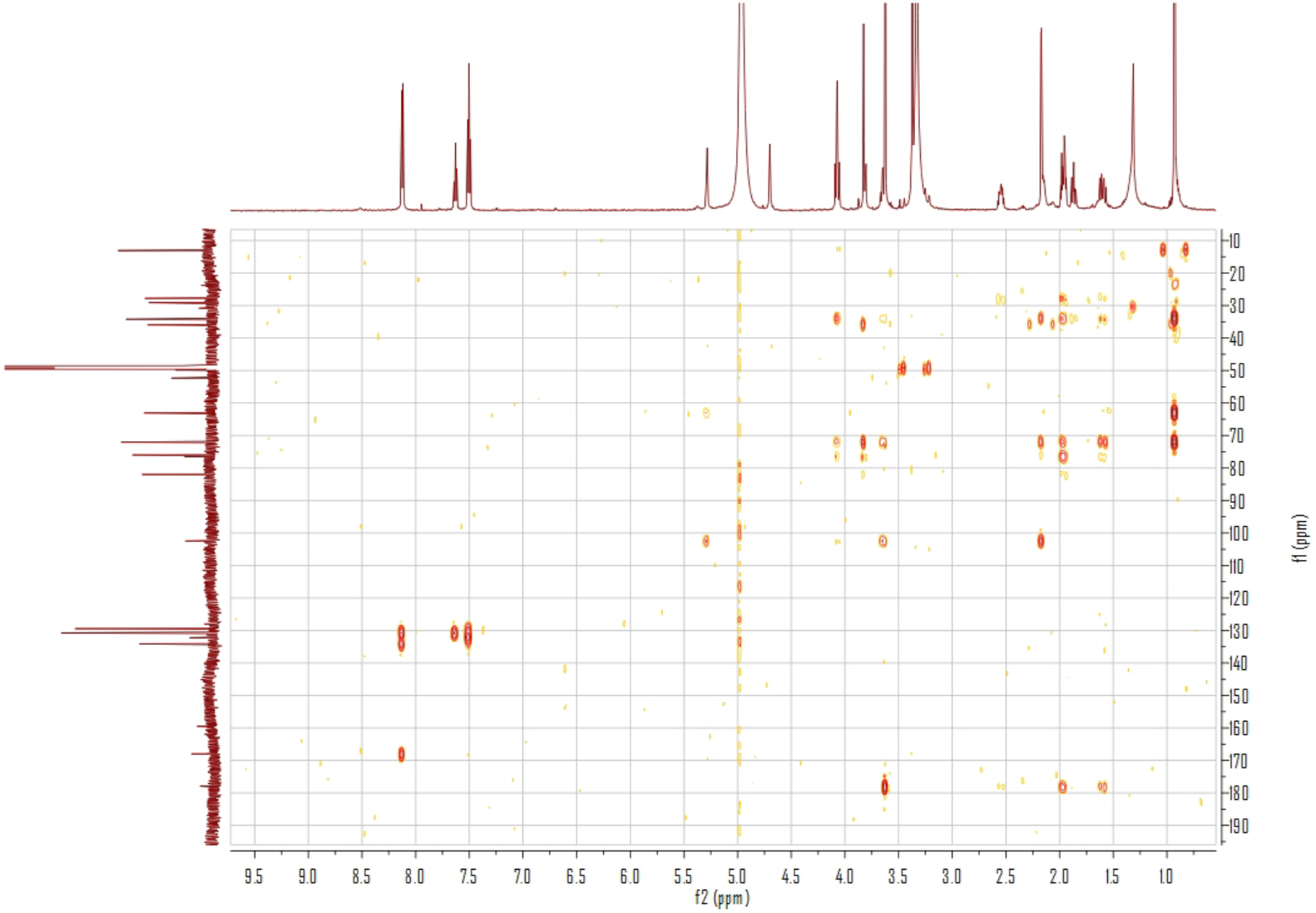
30.Figure S30 ^{13}C NMR (150 MHz) spectrum of phyllaemblicins G3 (**3**) in CD_3OD



31.Figure S31 HSQC spectrum of phyllaemblicins G3 (**3**) in CD_3OD



32.Figure S32 HMBC spectrum of phyllaemblicins G3 (**3**) in CD_3OD



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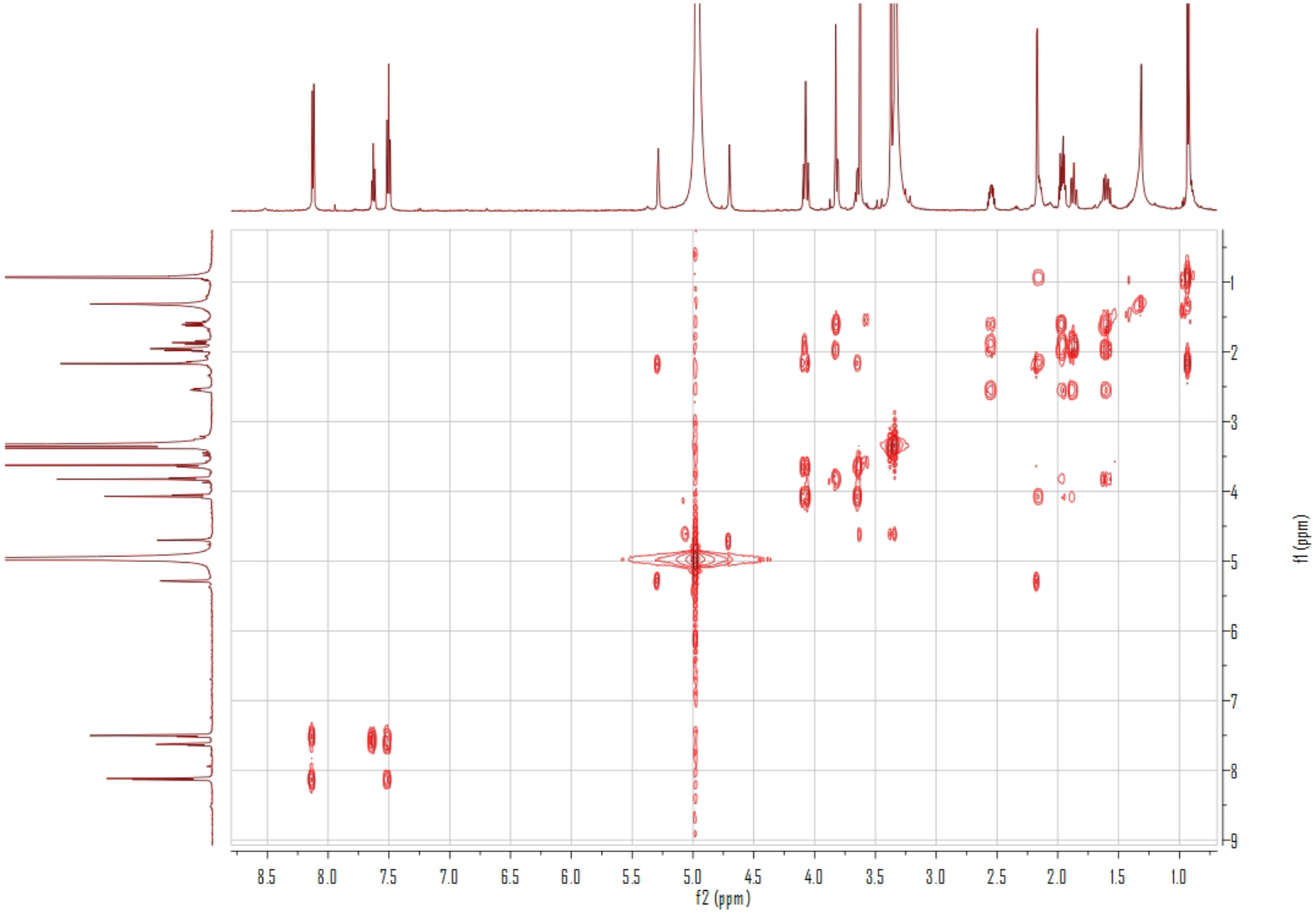
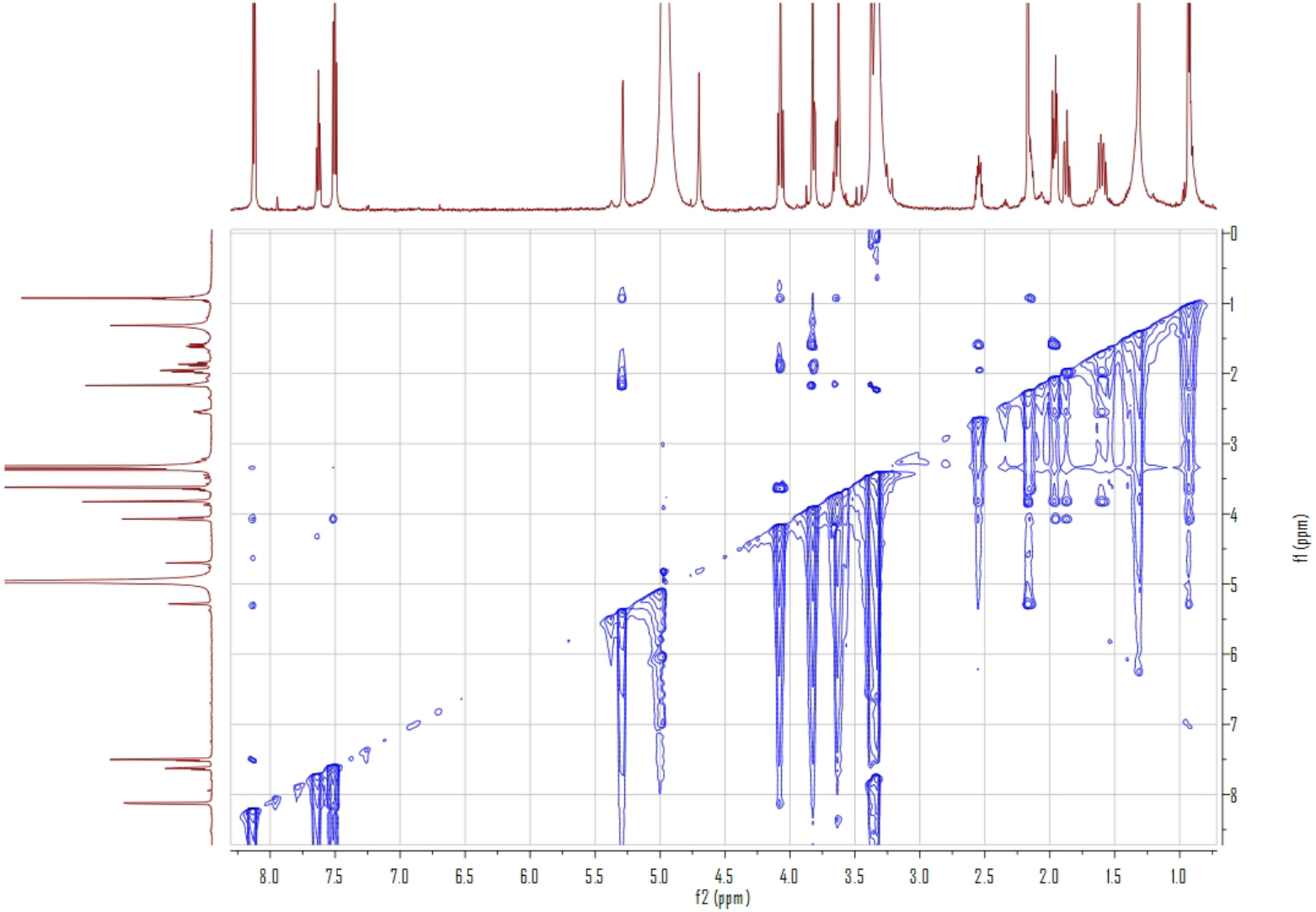


34.Figure S34 ROESY spectrum of phyllaemblicins G3 (**3**) in CD_3OD



35.Figure S35 HRESIMS of phyllaemblicin G4 (**4**)

Formula Predictor Report - gca40_TLJ1811_30.lcd

Data File: D:\分子量测定\2013-01-24\gca40_TLJ1811_30.lcd

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B	3	0	0	O	2	0	30	S	2	0	0	I	3	0	0	HCOO
C	4	0	60	F	1	0	0	Cl	1	0	0					

Error Margin (mDa): 20.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

DBE Range: 0.0 - 30.0
Apply N Rule: no
Isotope RI (%): 1.00
MSn Logic Mode: OR

Electron Ions: both
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Max Results: 800

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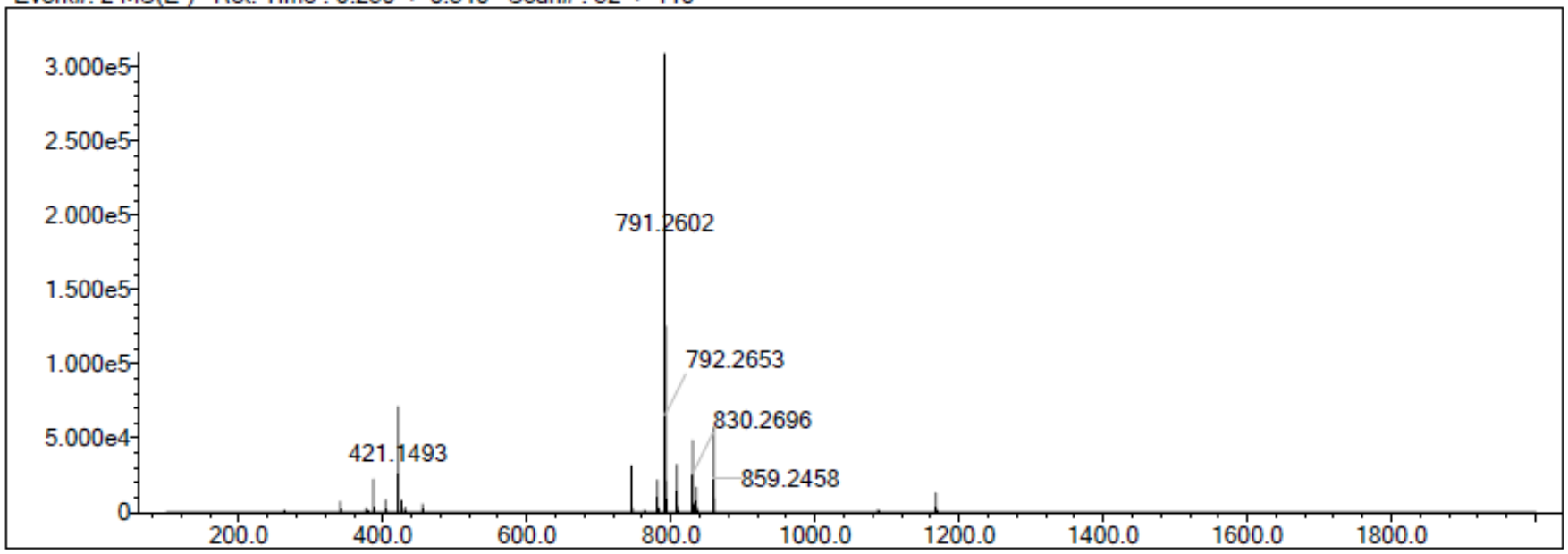
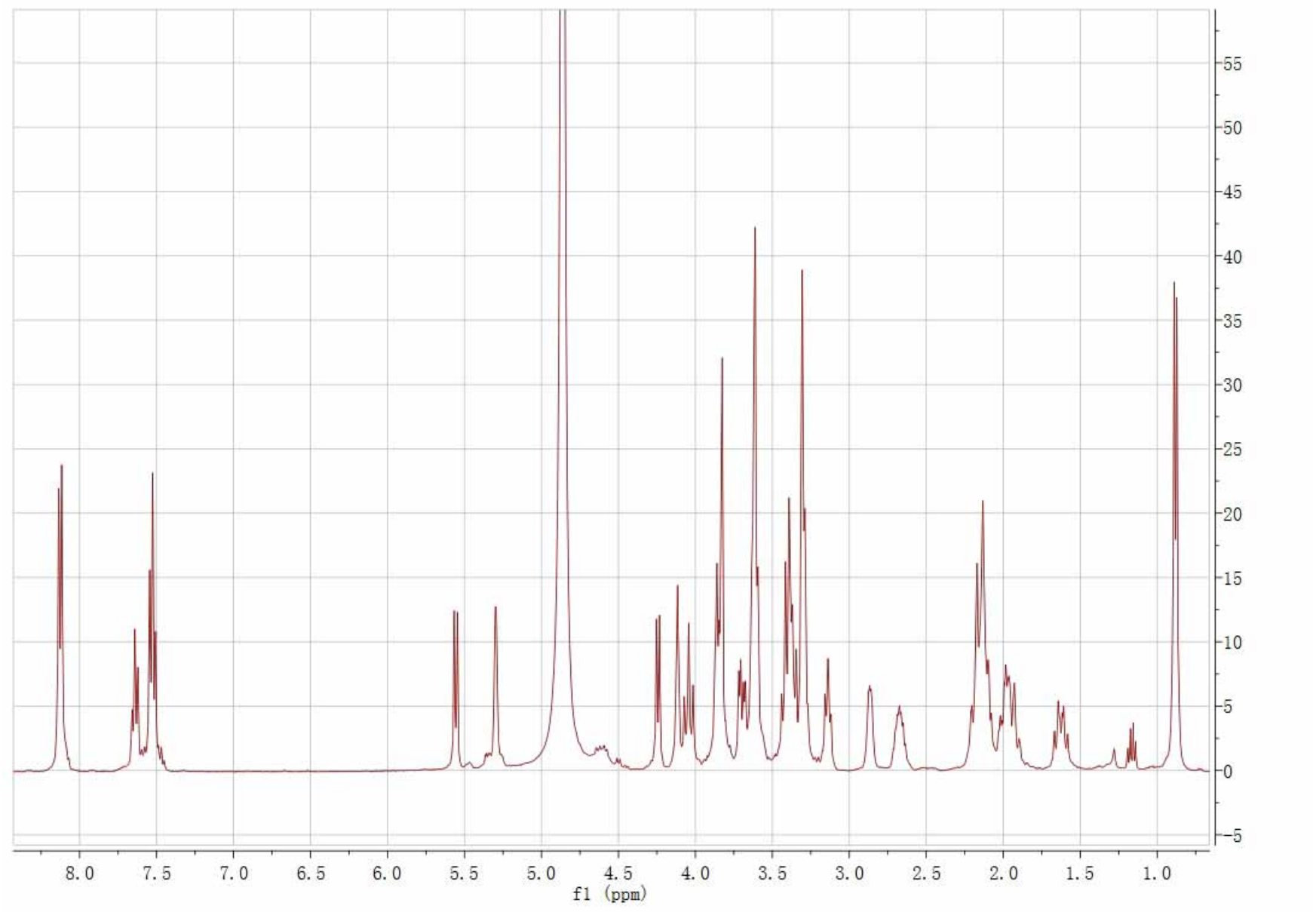
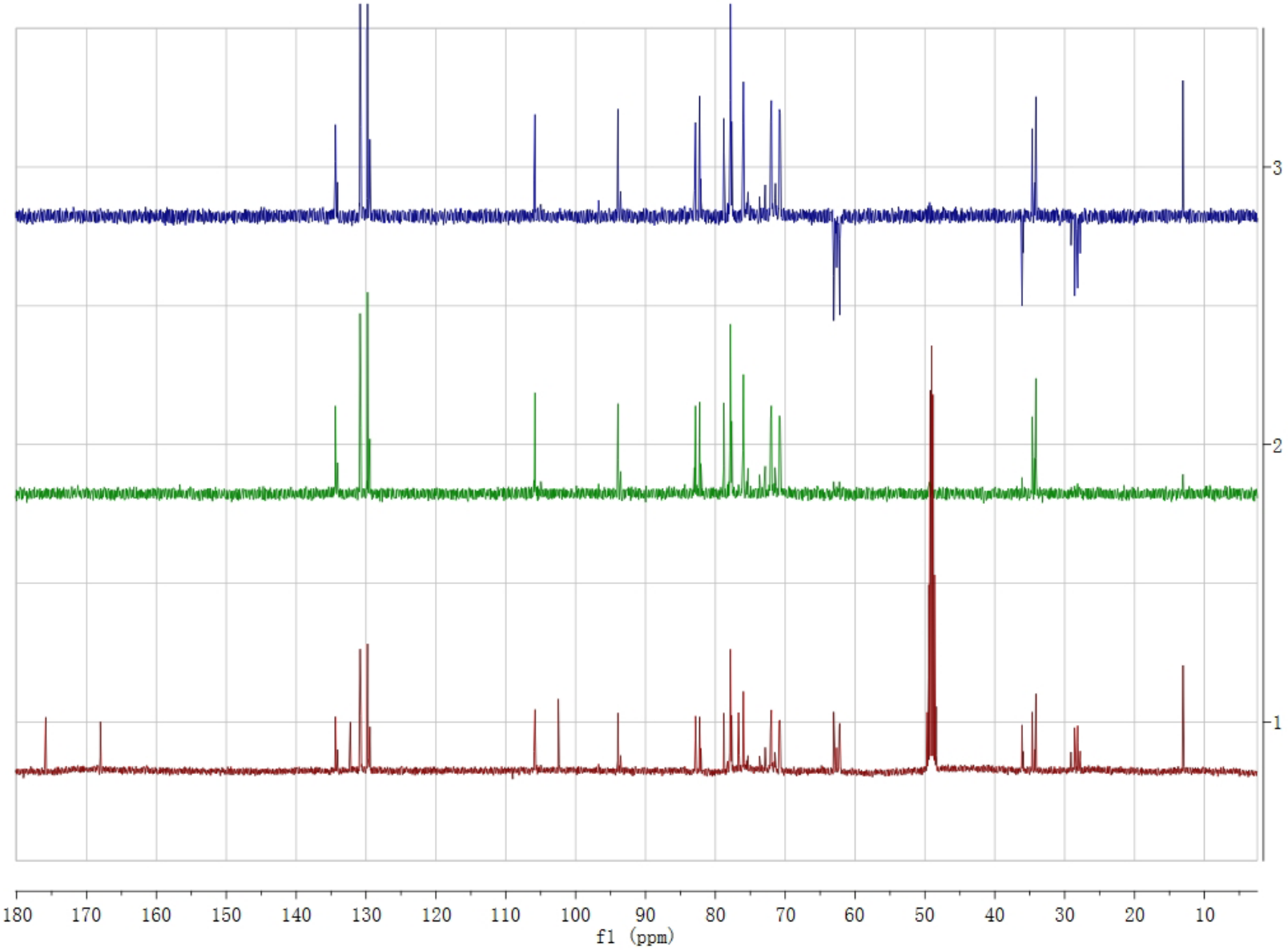


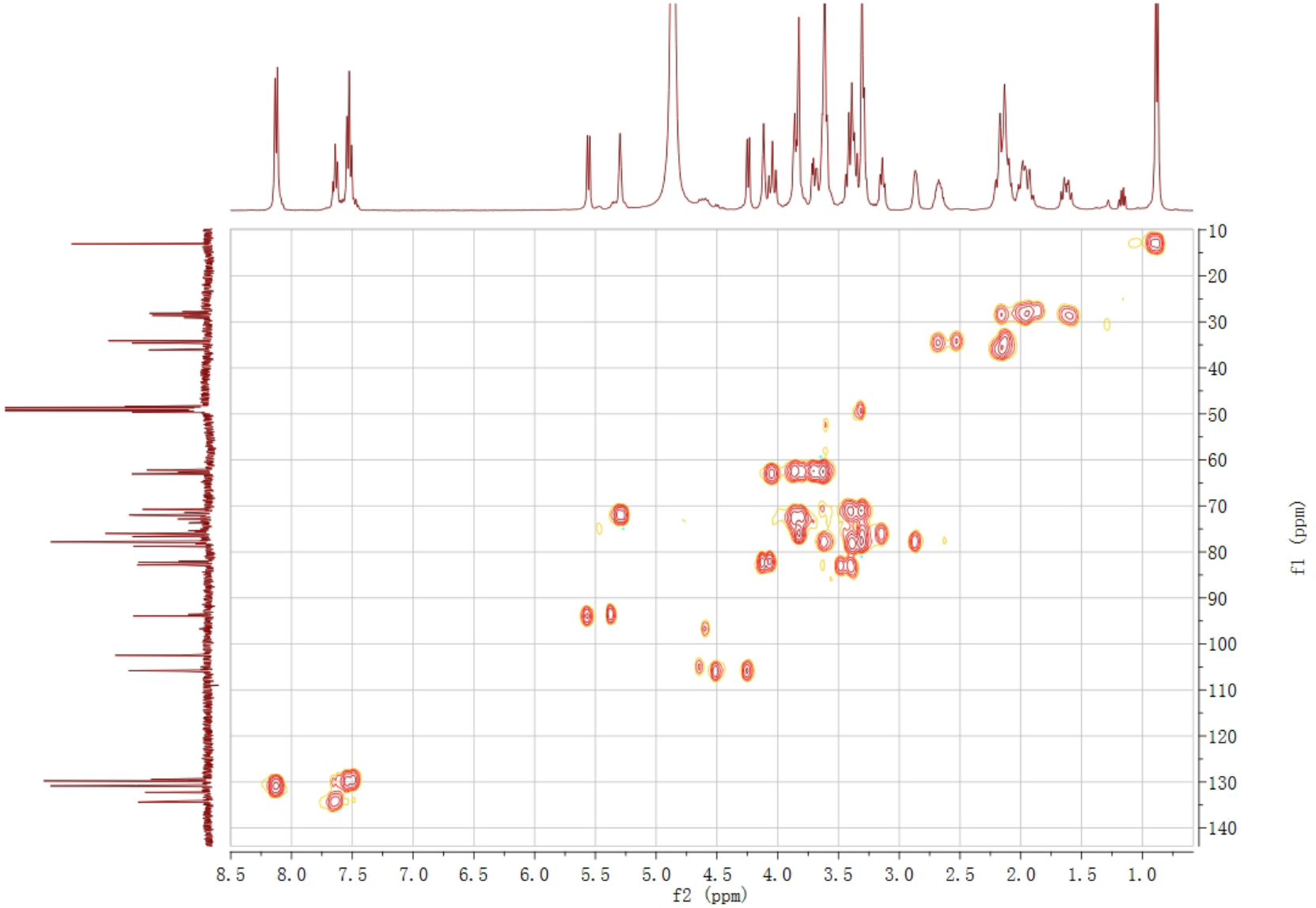
36.Figure S36 ^{1}H NMR (400 MHz) spectrum of phyllaemblicins G4 (**4**) in CD_3OD



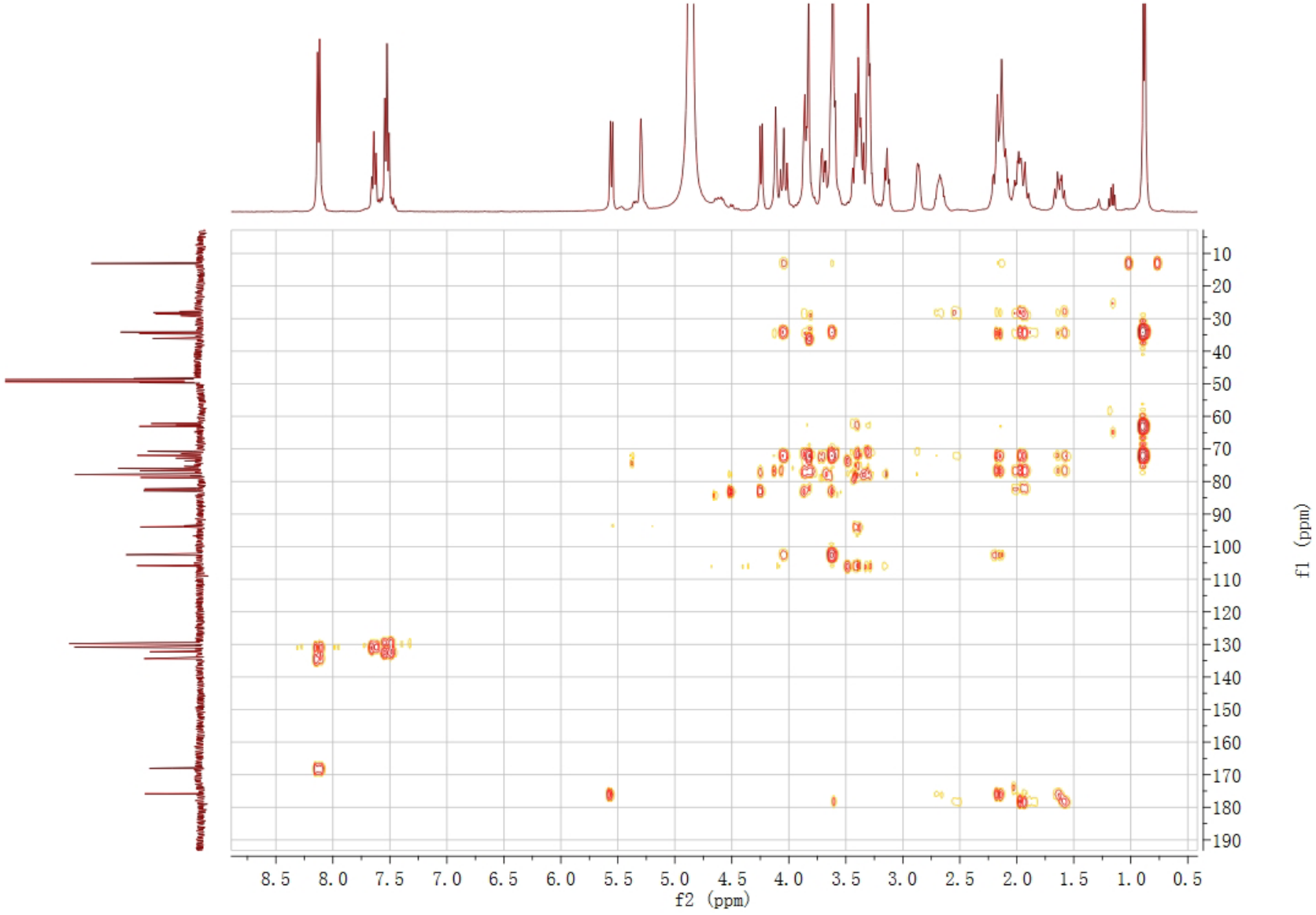
37.Figure S37 ^{13}C NMR (100 MHz) spectrum of phyllaemblicins G4 (**4**) in CD_3OD



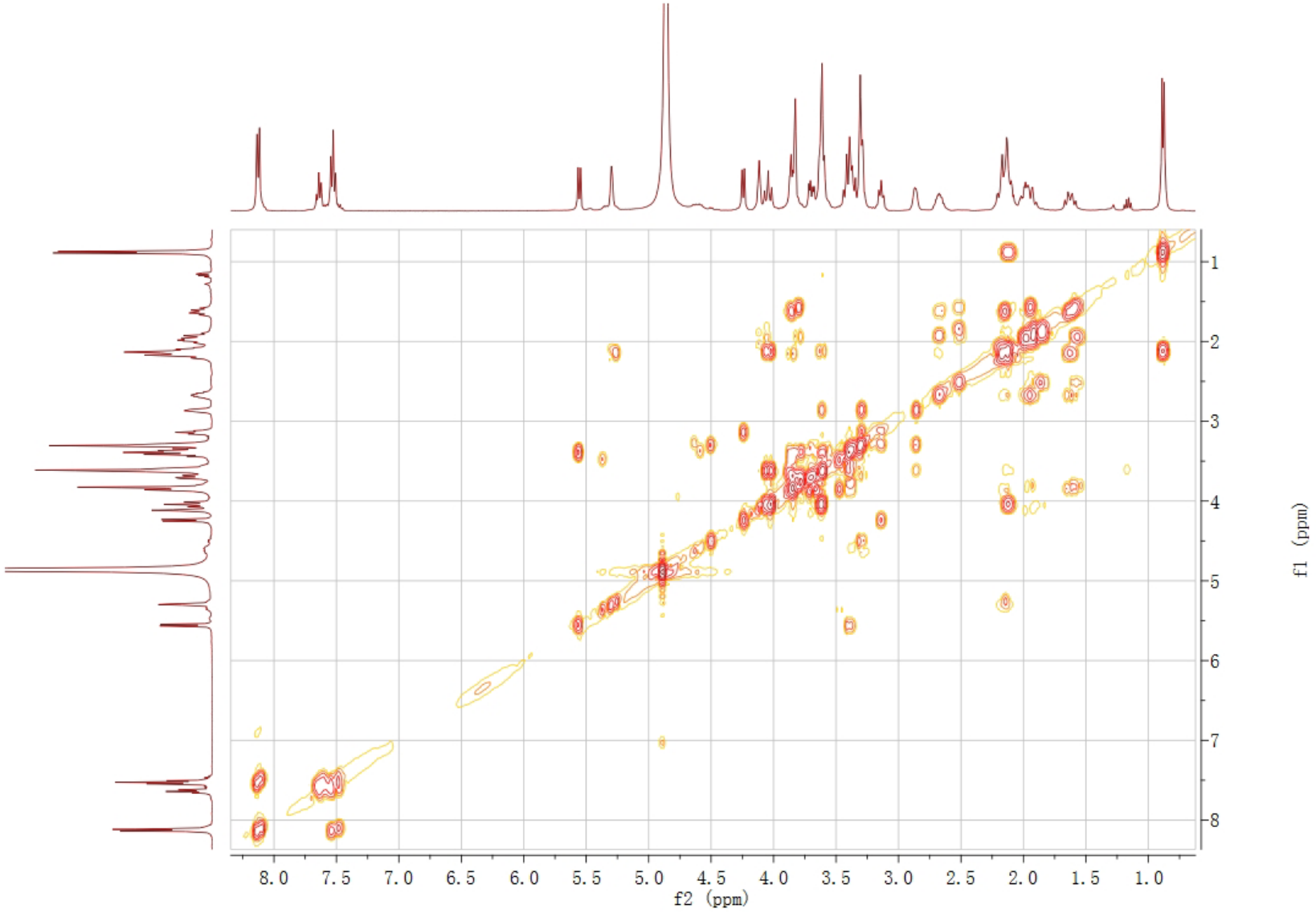
38.Figure S38 HSQC spectrum of phyllaemblicins G4 (**4**) in CD_3OD



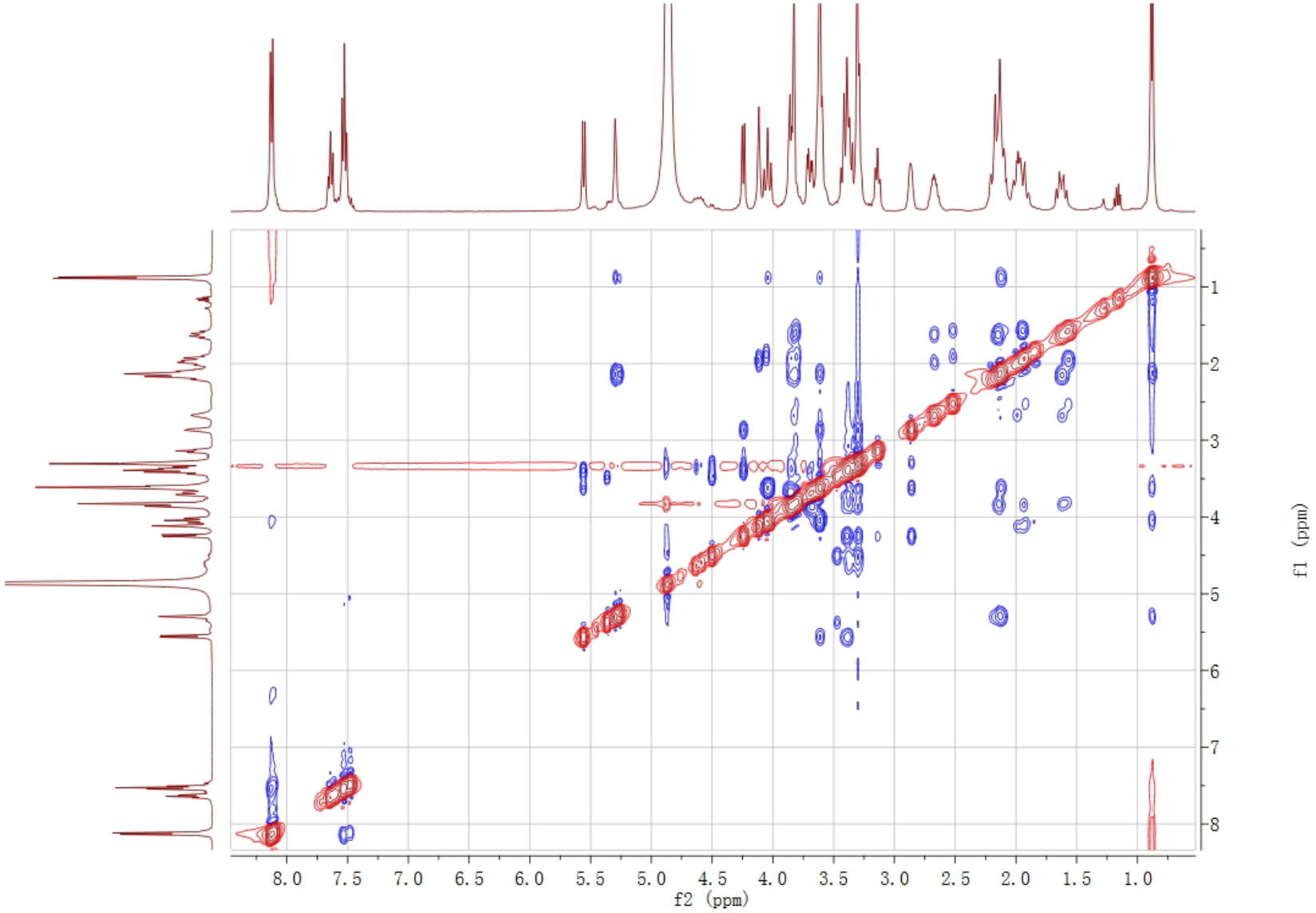
39.Figure S39 HMBC spectrum of phyllaemblicins G4 (**4**) in CD_3OD



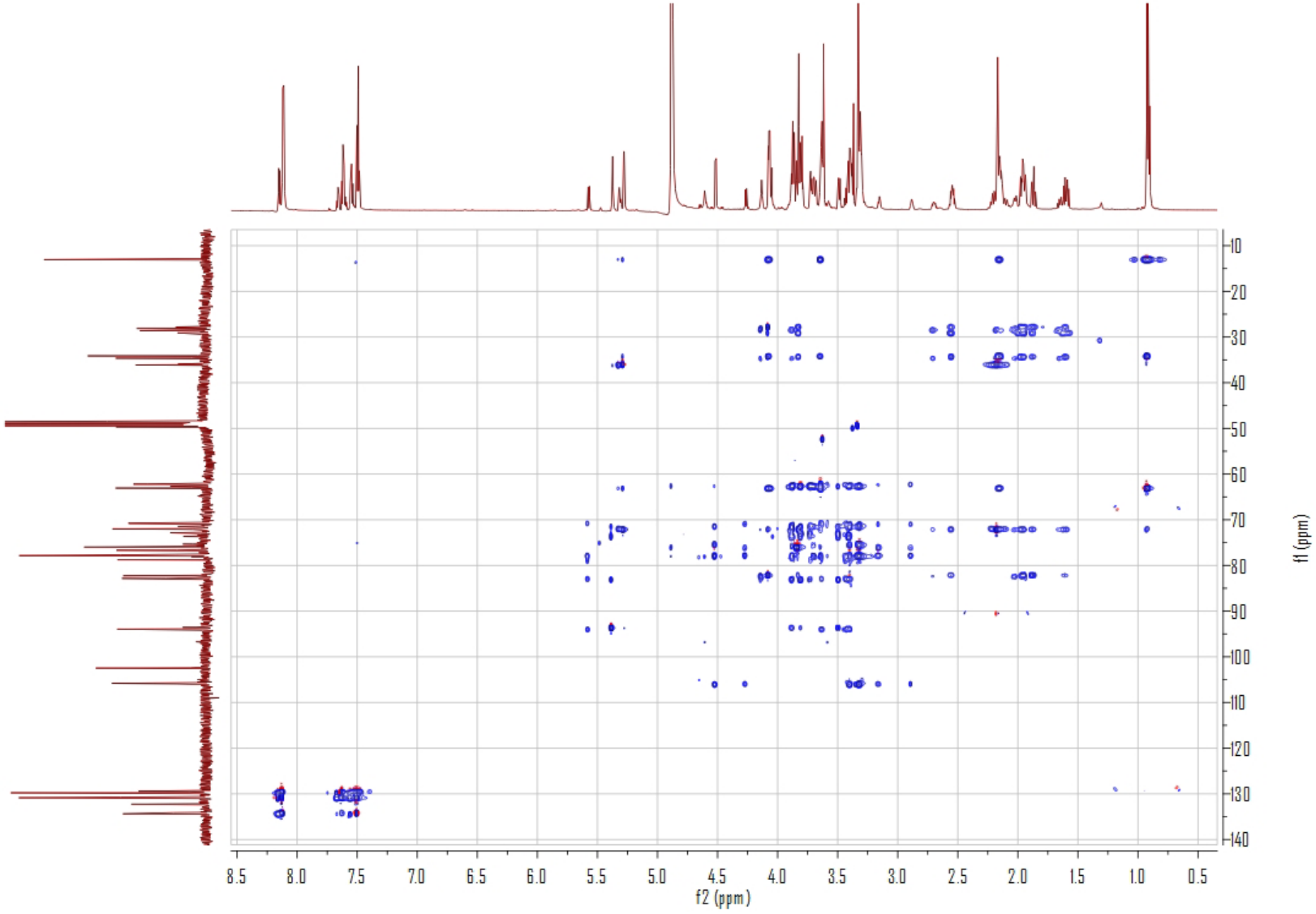
40.Figure S40 ^{1}H-^{1}H COSY spectrum of phyllaemblicins G4 (**4**) in CD_3OD



41.Figure S41 ROESY spectrum of phyllaemblicins G4 (**4**) in CD_3OD



42.Figure S42 HSQC-TOCSY spectrum of phyllaemblicins G4 (**4**) in CD_3OD



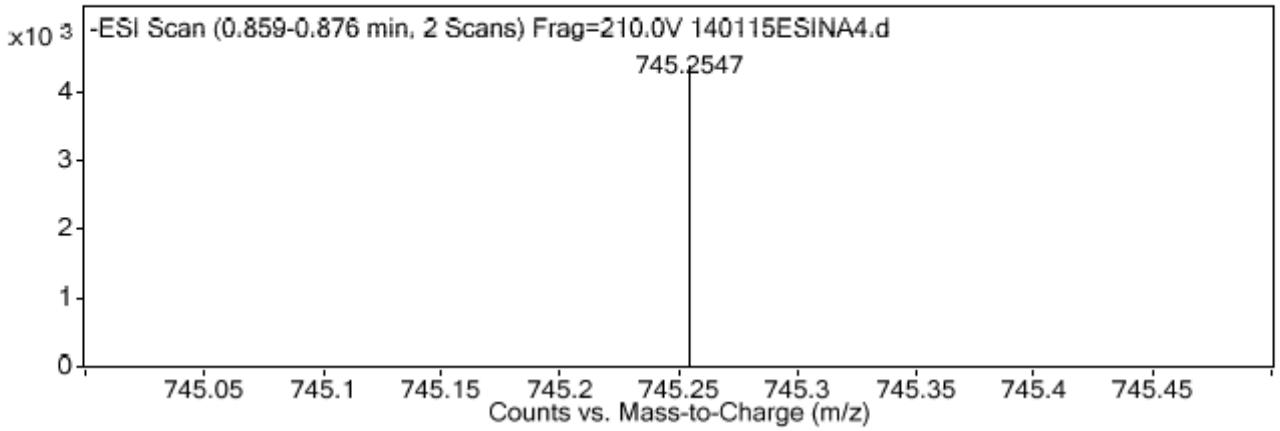
43.Figure S43 HRESIMS of phyllaemblicin G5 (**5**)

Data Filename	140115ESINA4.d	**Sample Name**	YWX1261
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESIN.m	**Acquired Time**	1/15/2014 11:15:39 AM
IRM Calibration Status	Success	**DA Method**	demo1.m
Comment			

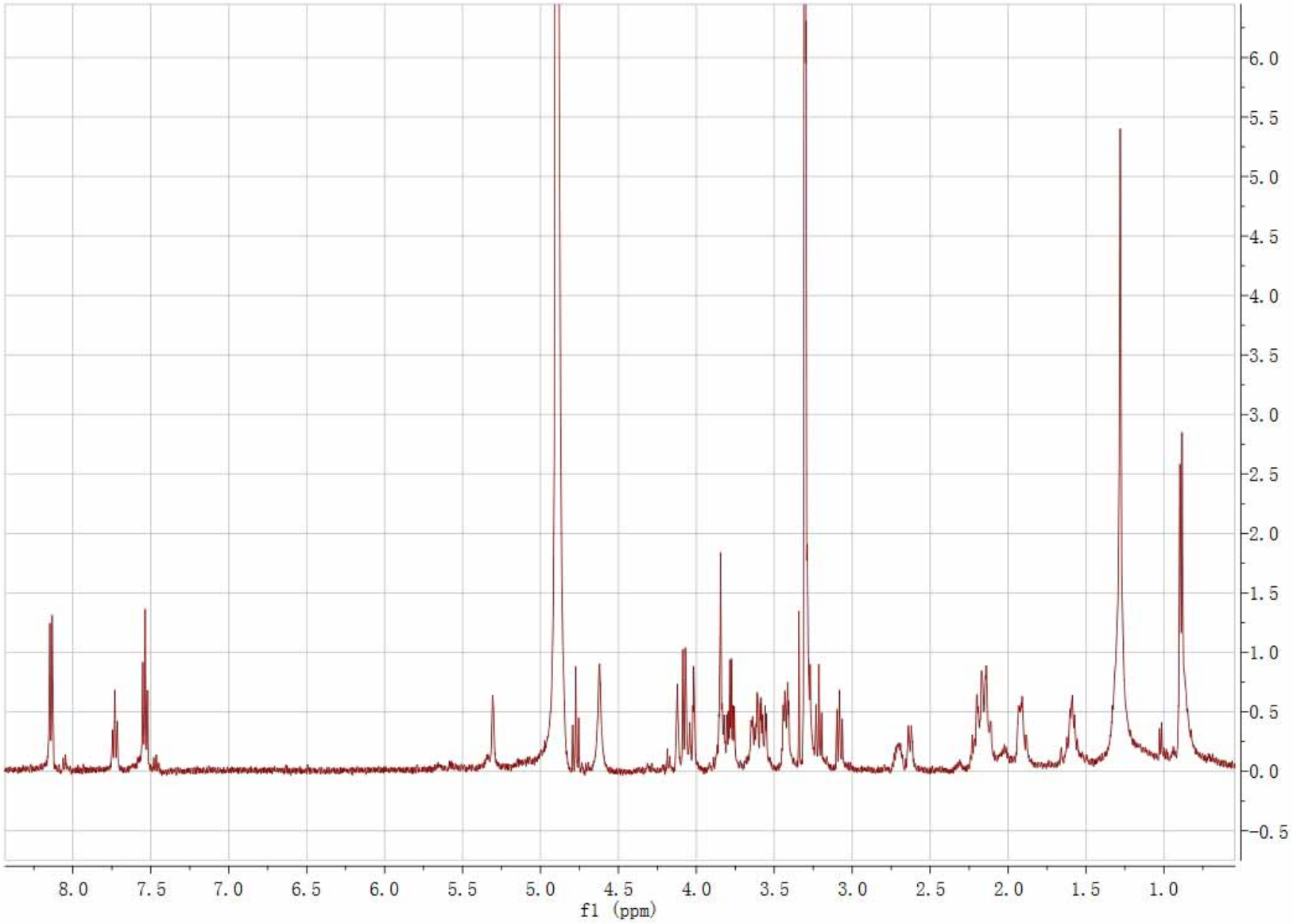
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

User Spectra

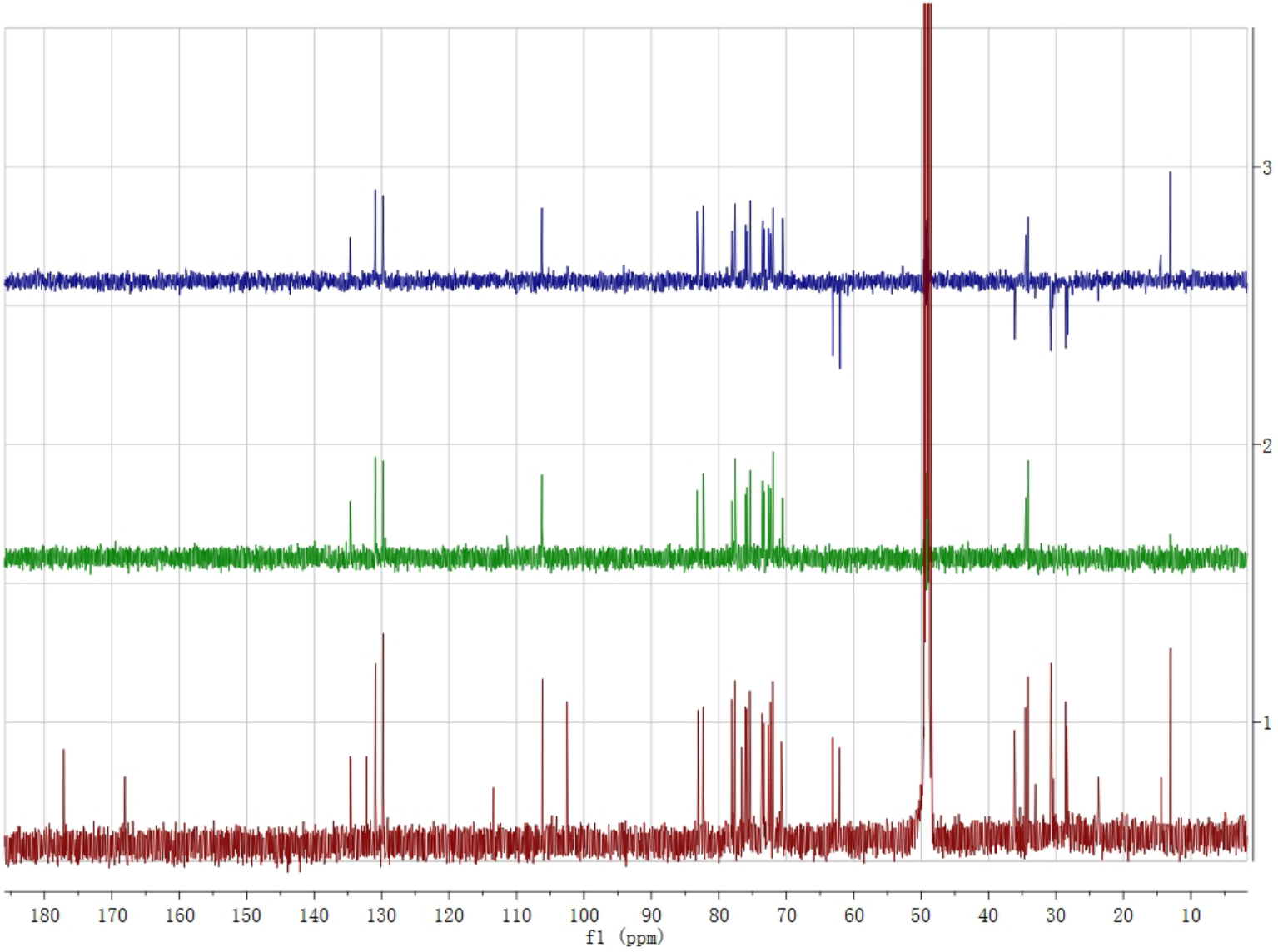
Fragmentor Voltage	Collision Energy	Ionization Mode
210	0	ESI



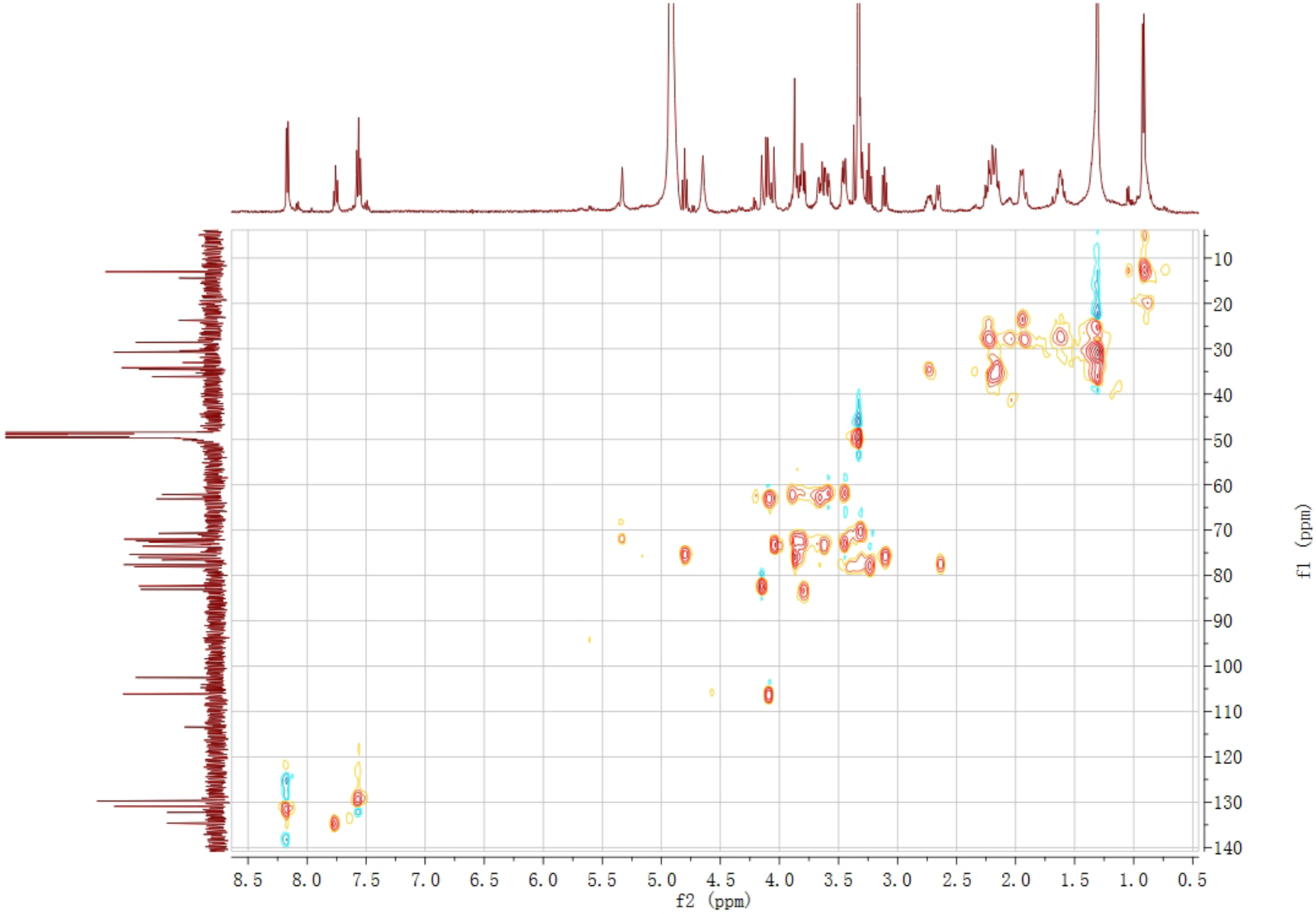
44.Figure S44 ^{1}H NMR (500 MHz) spectrum of phyllaemblicin G5 (**5**) in CD_3OD



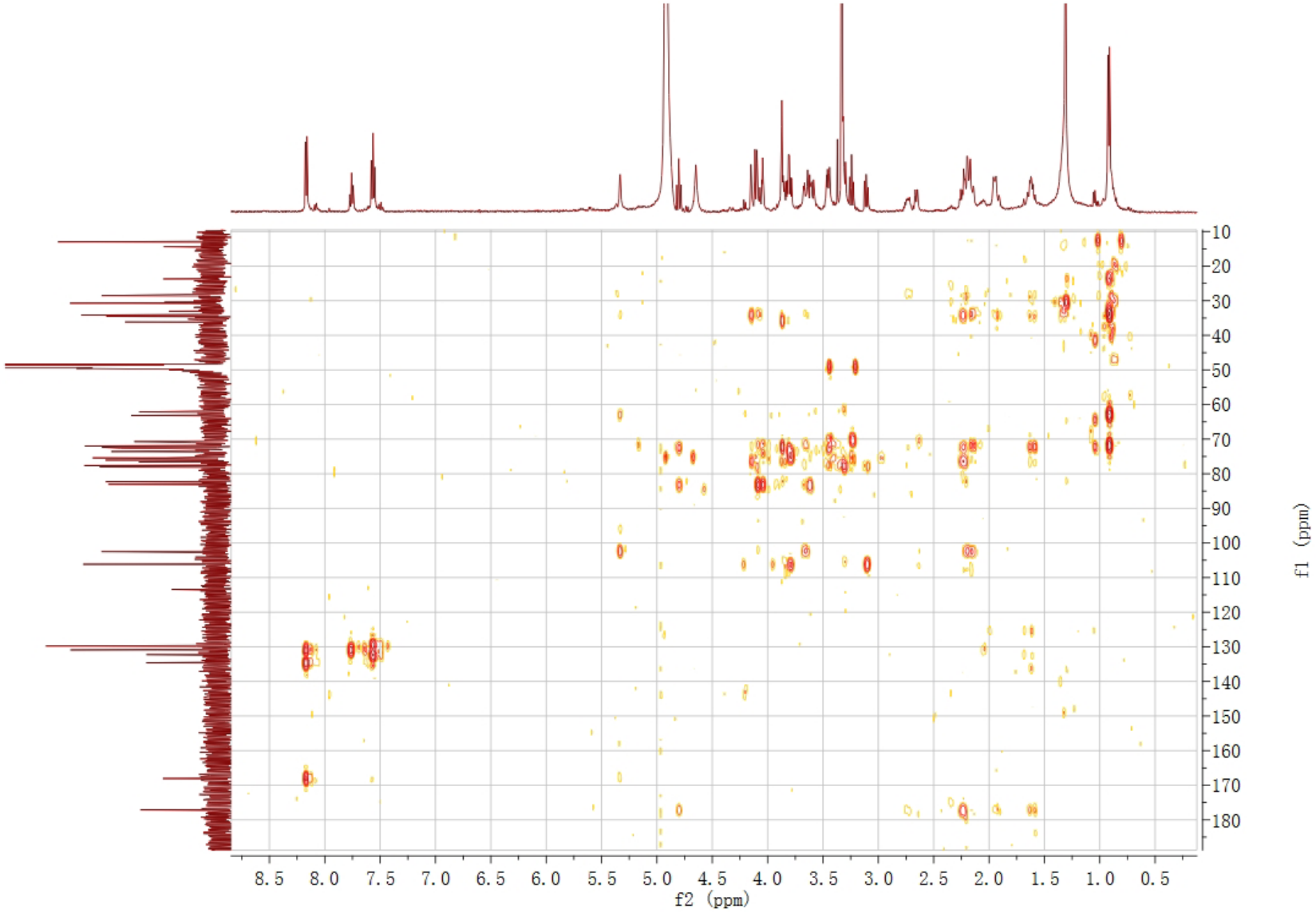
45.Figure S45 ^{13}C NMR (125 MHz) spectrum of phyllaemblicin G5 (**5**) in CD_3OD



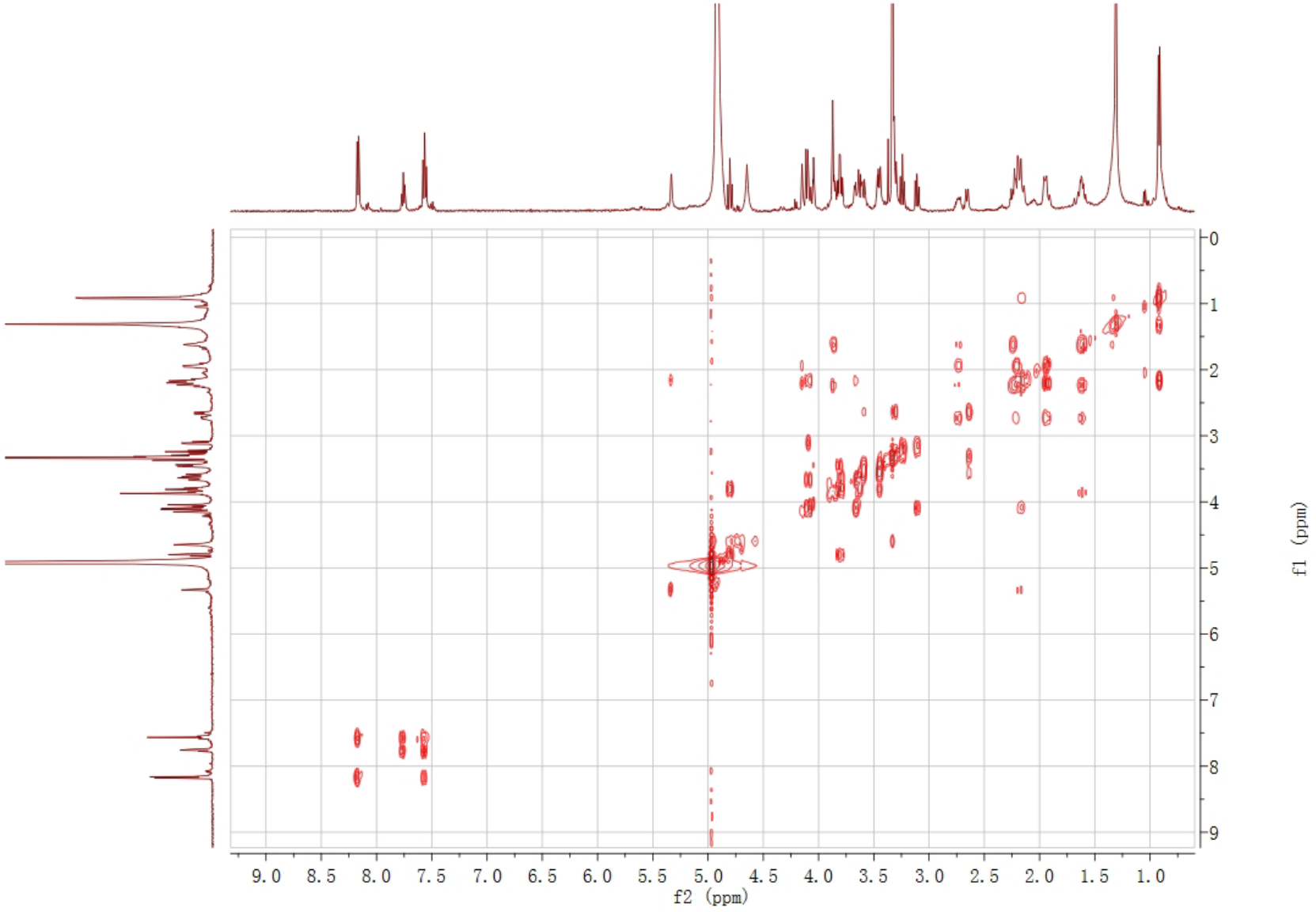
46.Figure S46 HSQC spectrum of phyllaemblicin G5 (**5**) in CD_3OD



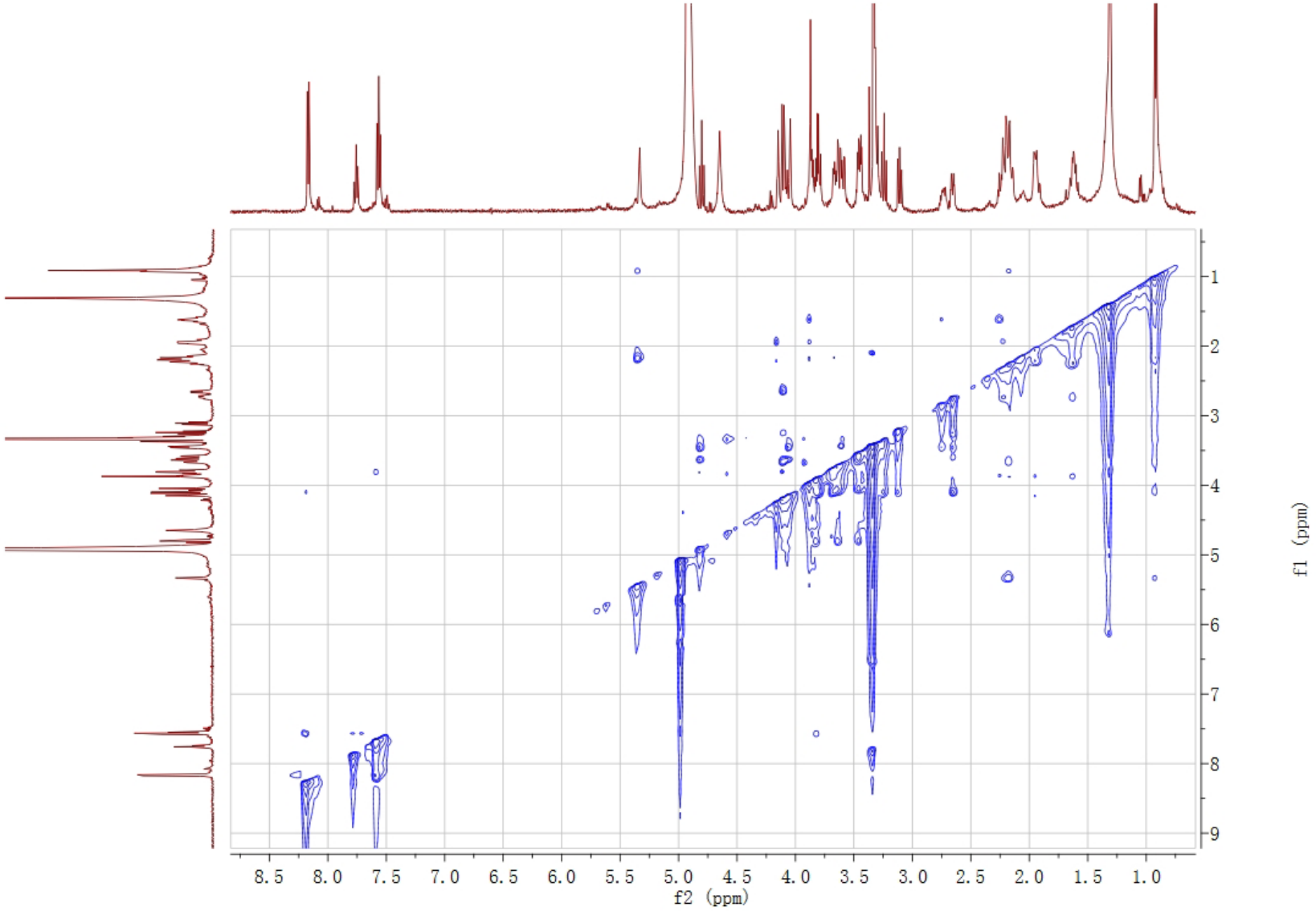
47.Figure S47 HMBC spectrum of phyllaemblicin G5 (**5**) in CD_3OD



48.Figure S48 ^{1}H-^{1}H COSY spectrum of phyllaemblicin G5 (**5**) in CD_3OD



49.Figure S49 ROESY spectrum of phyllaemblicin G5 (**5**) in CD_3OD



50.Figure S50 HRESIMS of phyllaemblicin G6 (**6**)

Formula Predictor Report - gca40_TLJ18851_20.lcd

Data File: D:\分子量测定\2013-01-24\gca40_TLJ18851_20.lcd

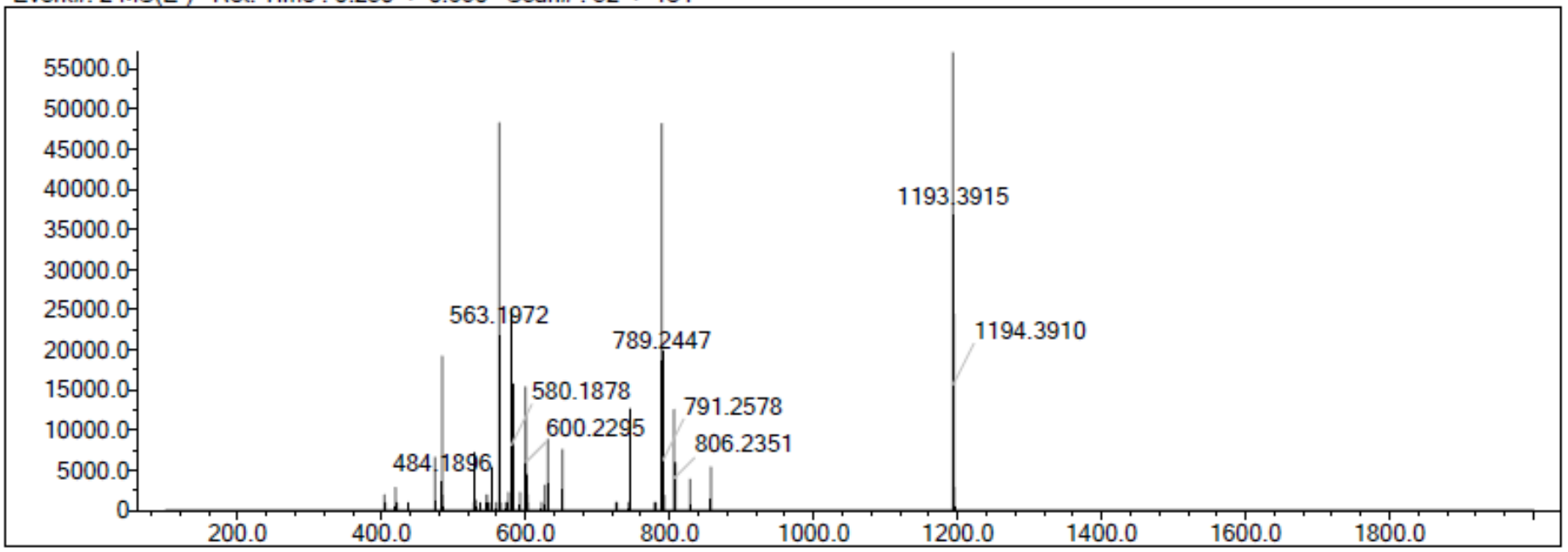
Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	N	3	0	0	P	3	0	0	Br	1	0	0	H
B	3	0	0	O	2	0	30	S	2	0	0	I	3	0	0	HCOO
C	4	0	60	F	1	0	0	Cl	1	0	0					

Error Margin (mDa): 20.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

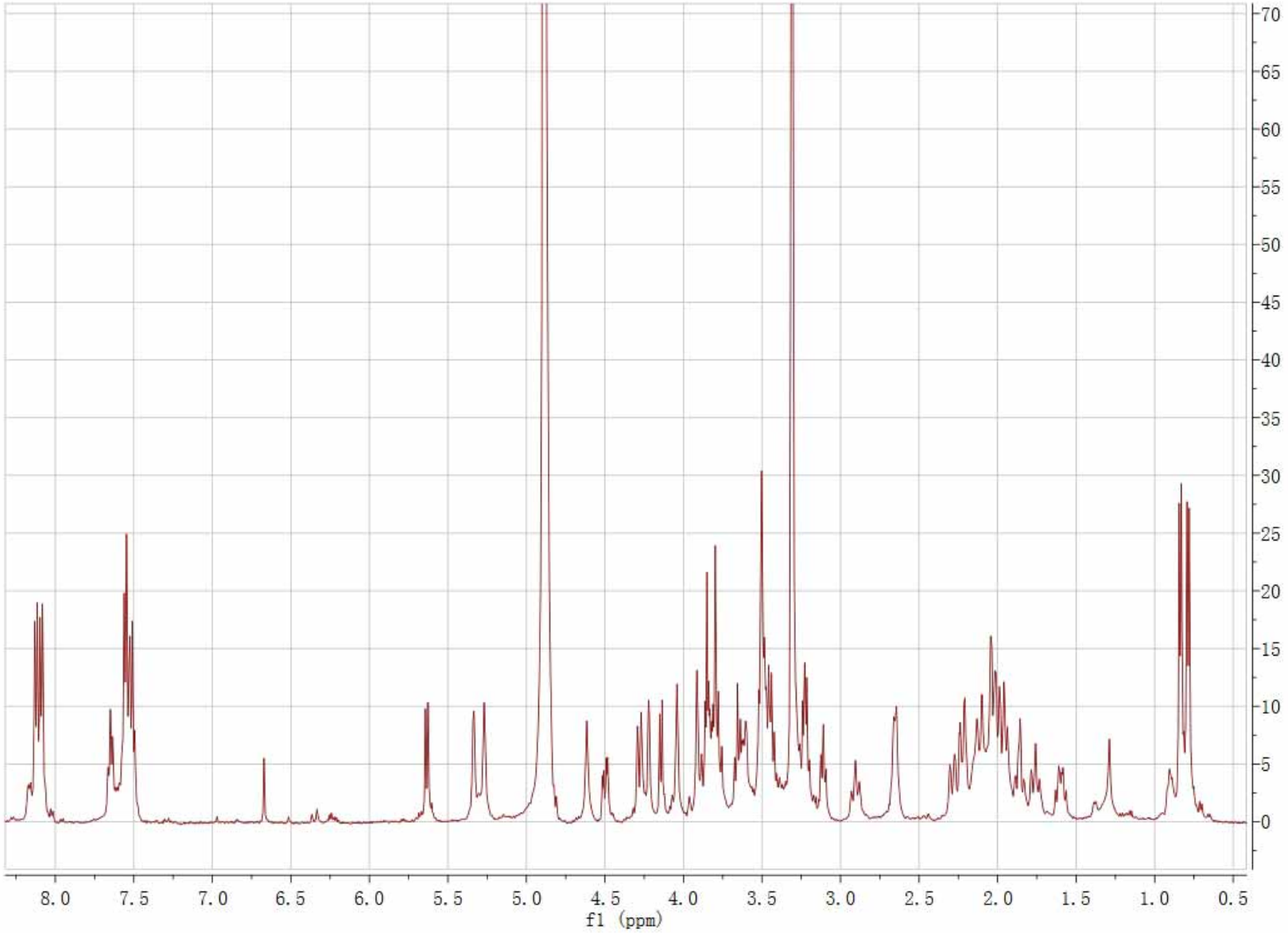
DBE Range: 0.0 - 30.0
Apply N Rule: no
Isotope RI (%): 1.00
MSn Logic Mode: OR

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

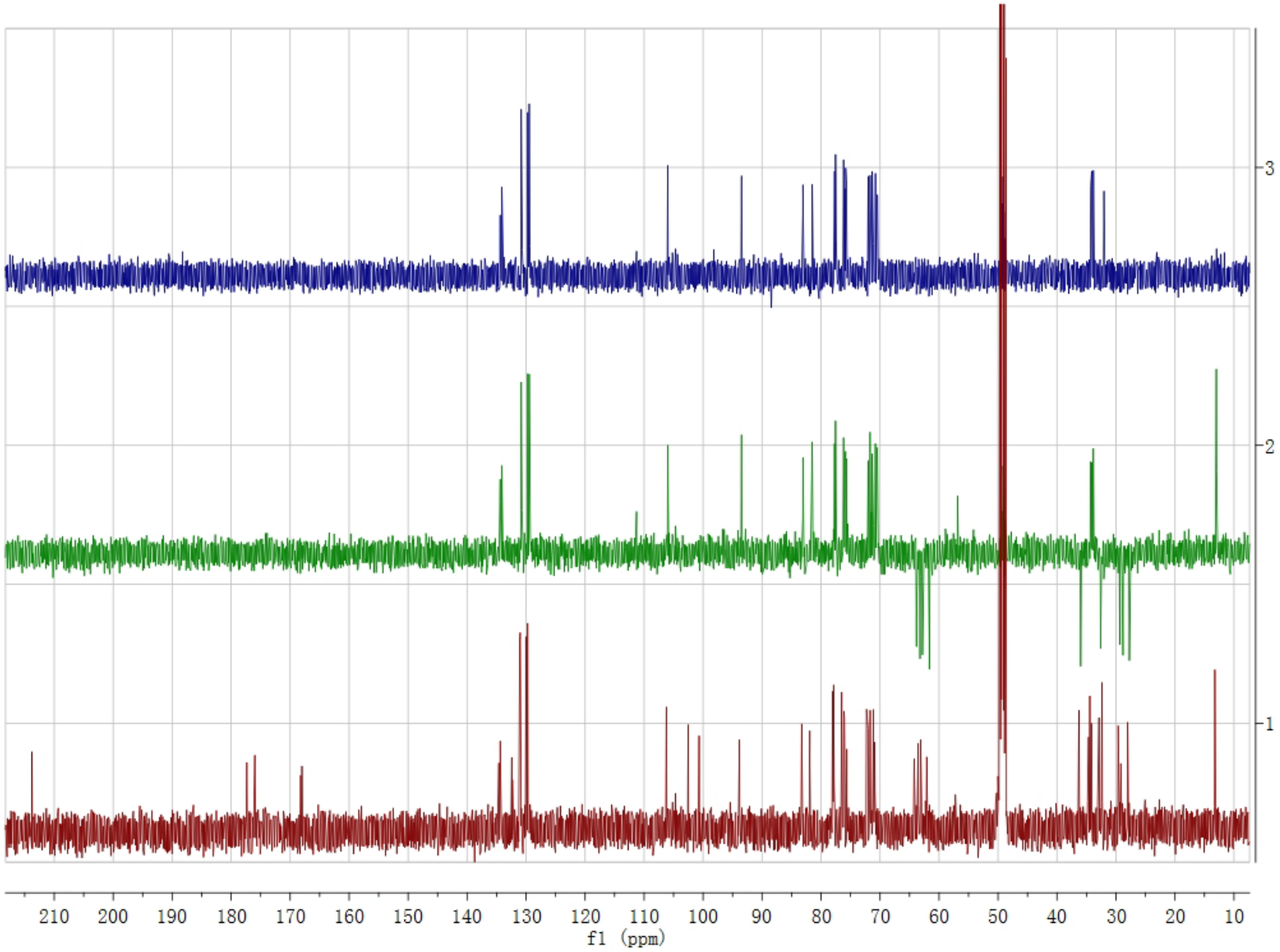
Event#: 2 MS(E-) Ret. Time : 0.250 -> 0.660 Scan# : 52 -> 134



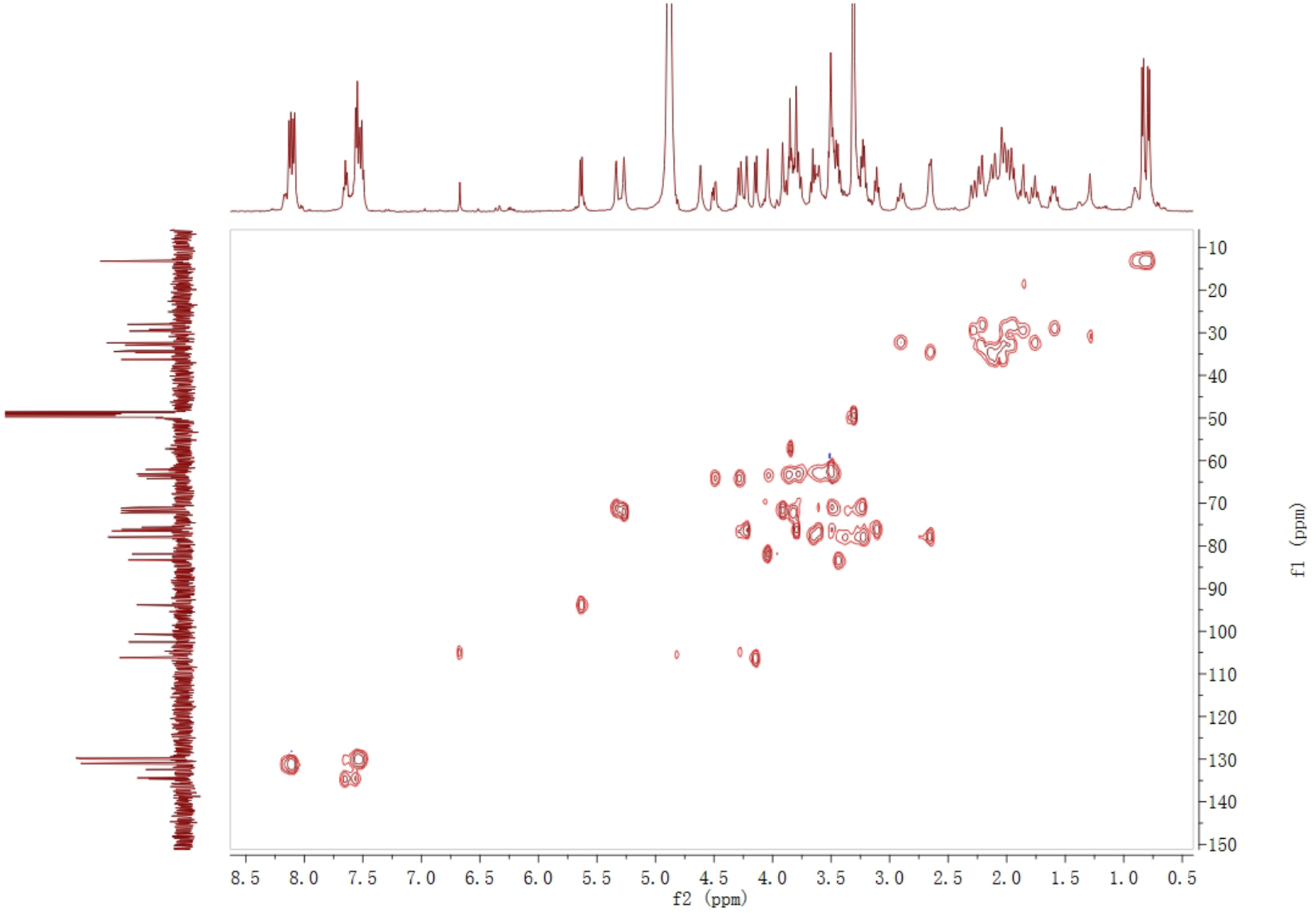
51.Figure S51 ^{1}H NMR (500 MHz) spectrum of phyllaemblicin G6 (**6**) in CD_3OD



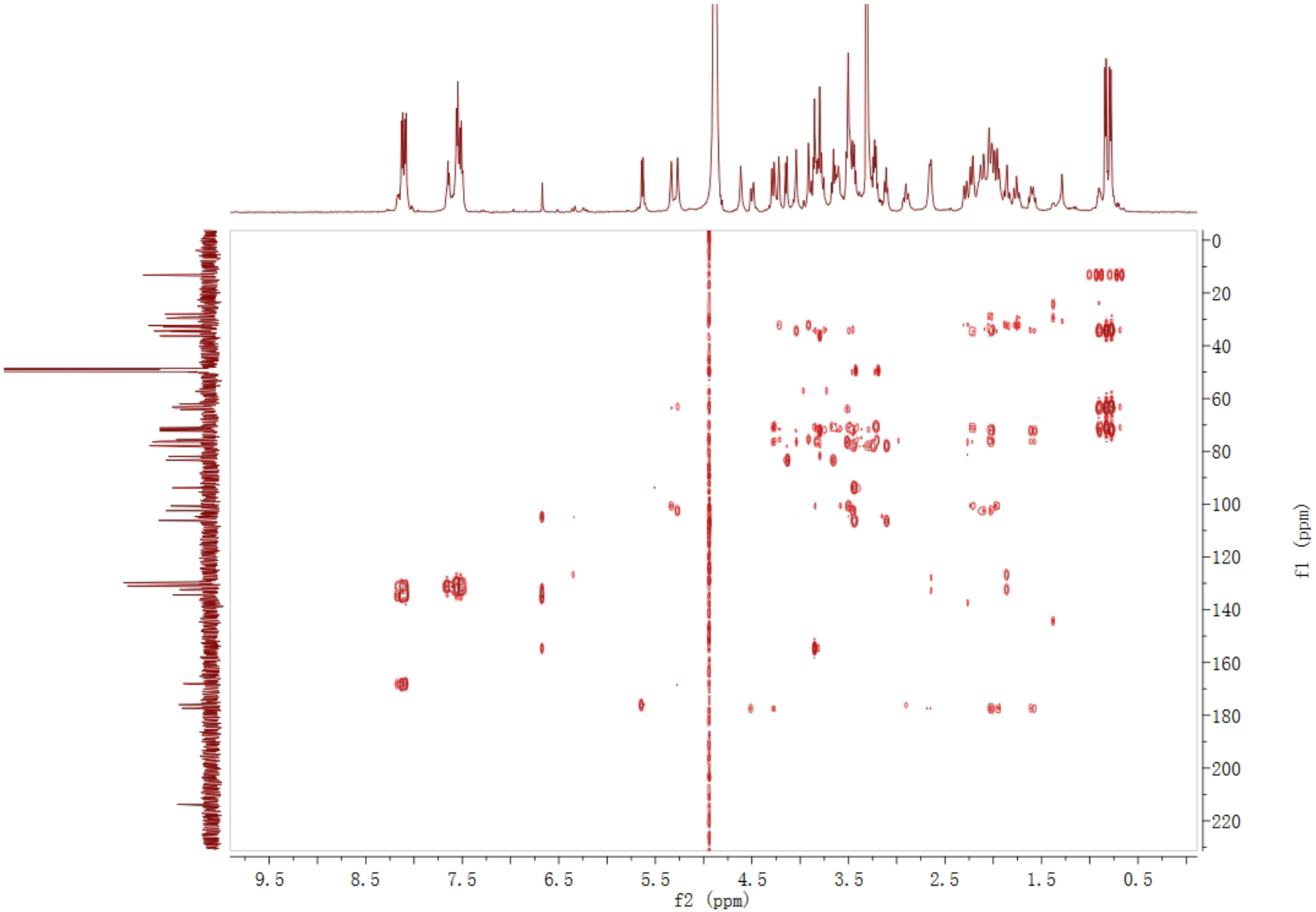
52.Figure S52 ^{13}C NMR (125 MHz) spectrum of phyllaemblicin G6 (**6**) in CD_3OD



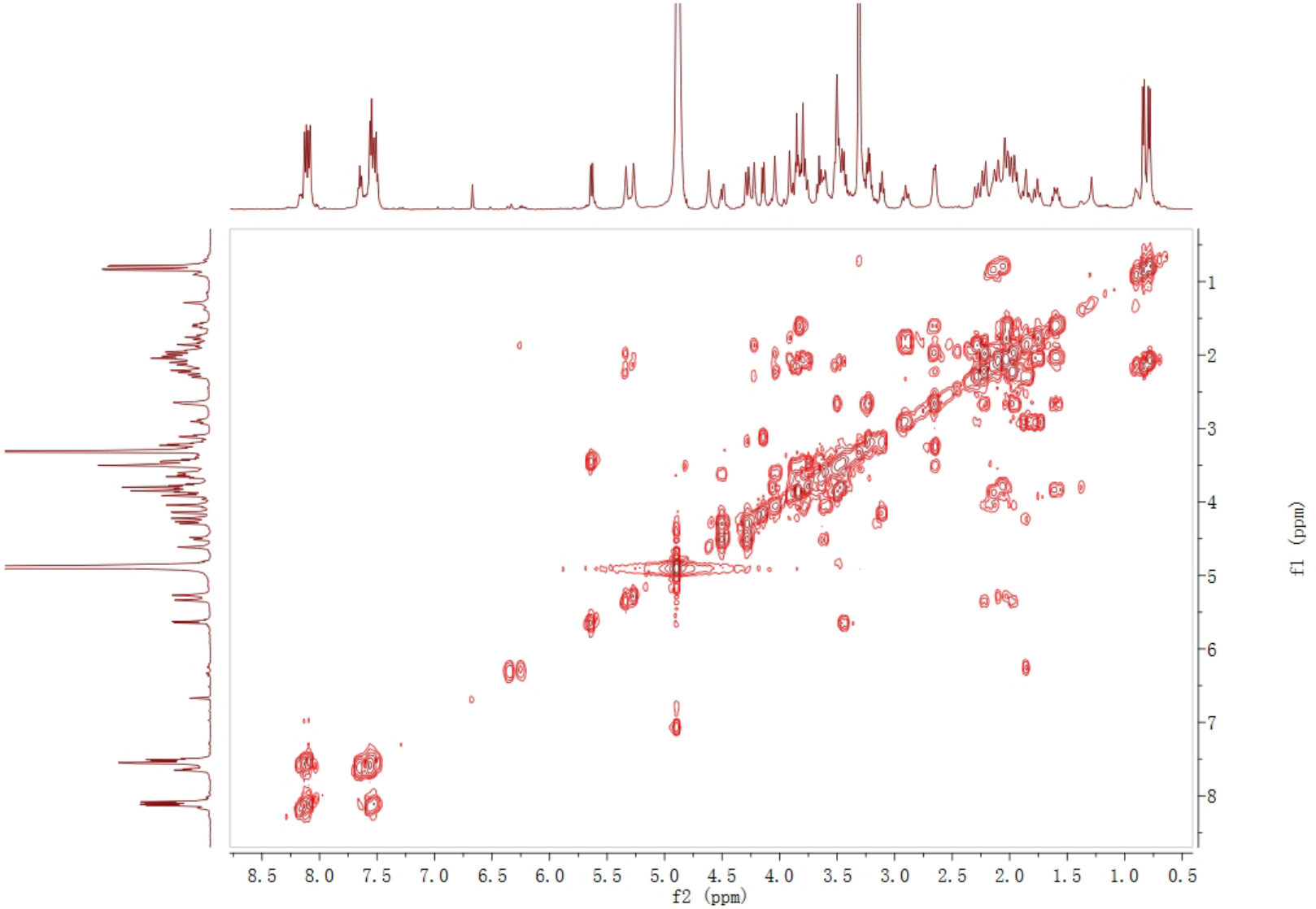
53.Figure S53 HSQC spectrum of phyllaemblicin G6 (**6**) in CD_3OD



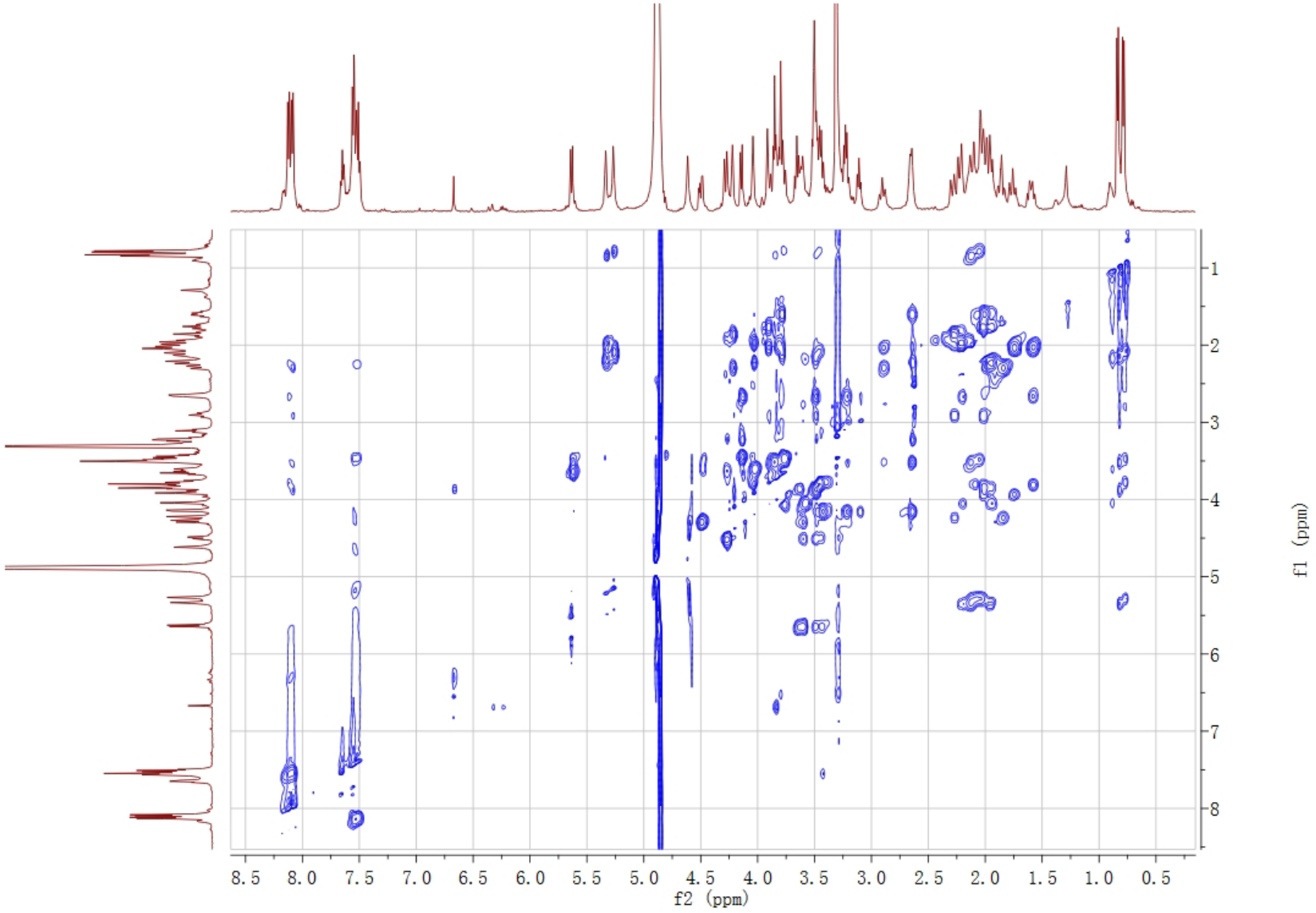
54.Figure S54 HMBC spectrum of phyllaemblicin G6 (**6**) in CD_3OD



55.Figure S55 ^{1}H-^{1}H COSY spectrum of phyllaemblicin G6 (**6**) in CD_3OD



56.Figure S56 ROESY spectrum of phyllaemblicin G6 (**6**) in CD_3OD



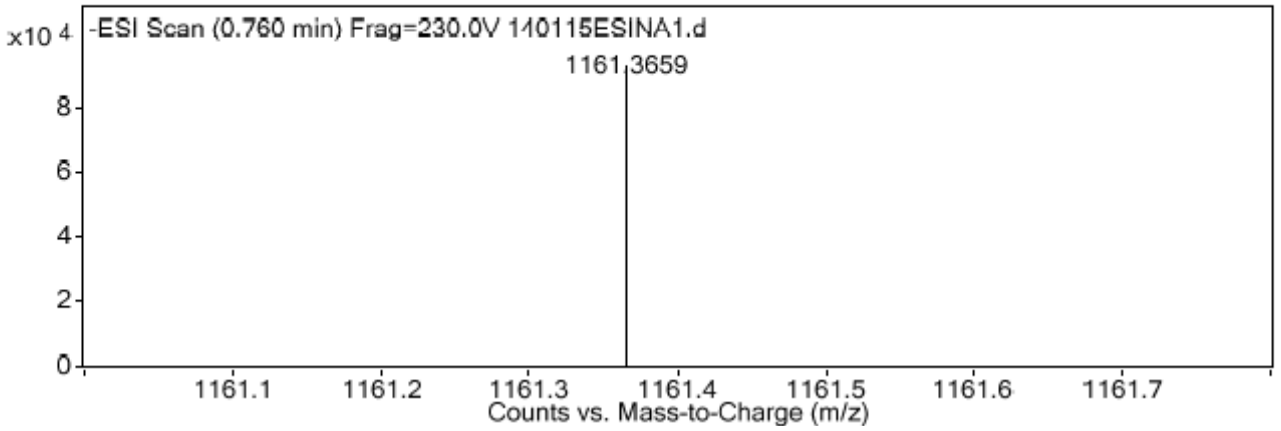
57.Figure S57 HRESIMS of phyllaemblicin G7 (**7**)

Data Filename	140115ESINA1.d	**Sample Name**	YLJ18952
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESIN.m	**Acquired Time**	1/15/2014 10:32:12 AM
IRM Calibration Status	Success	**DA Method**	demo1.m
Comment			

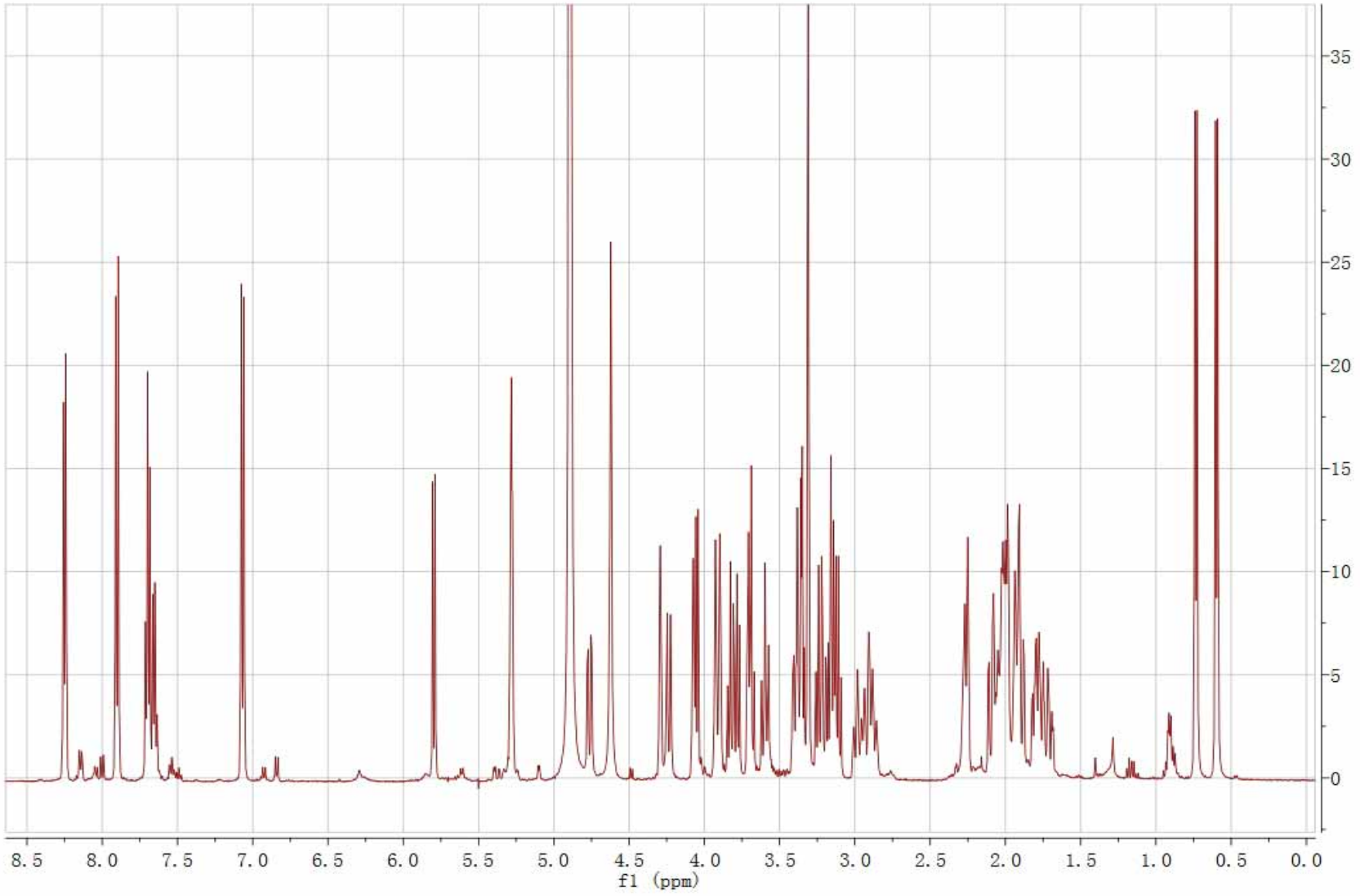
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

User Spectra

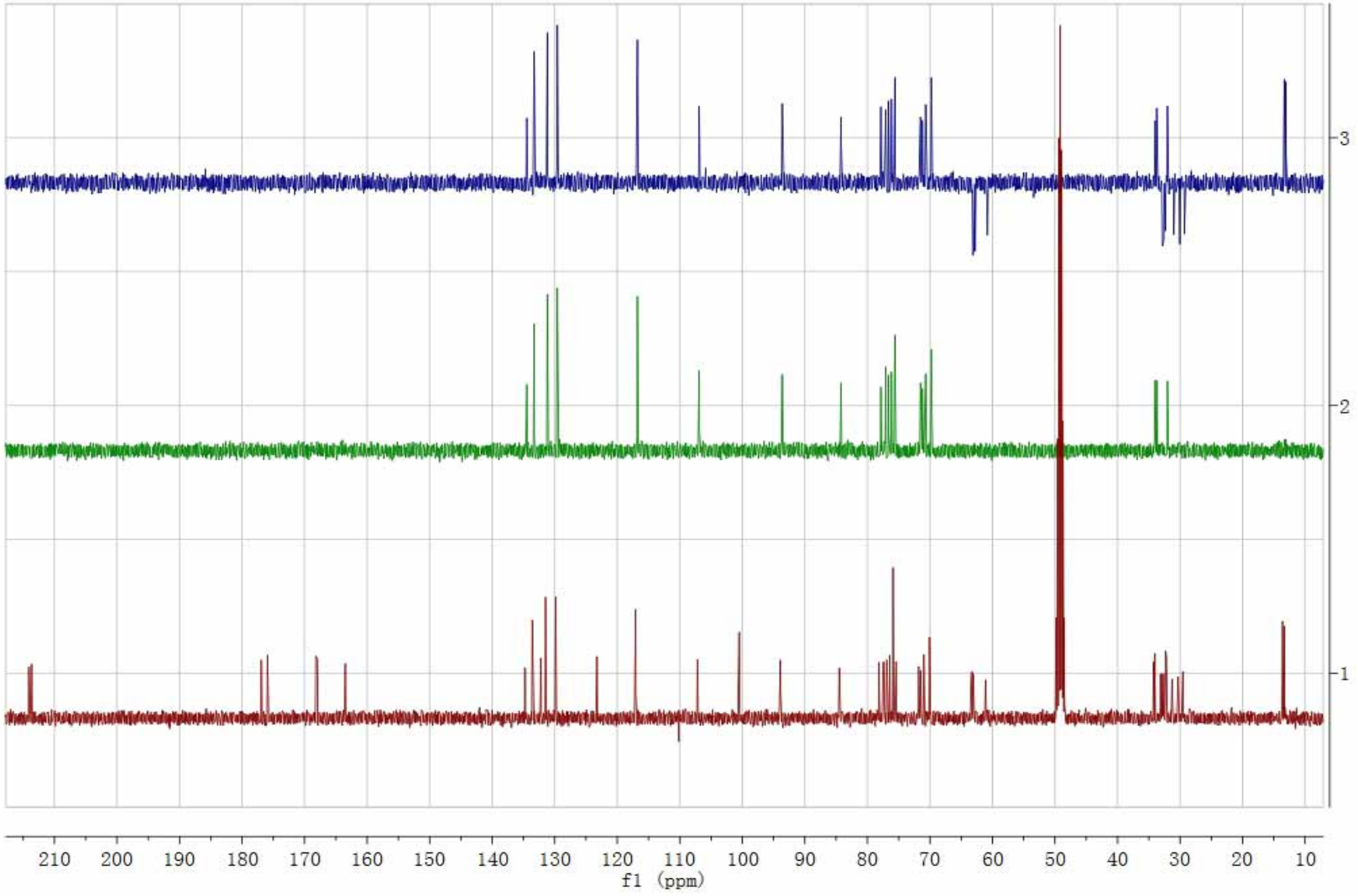
Fragmentor Voltage	Collision Energy	Ionization Mode
230	0	ESI



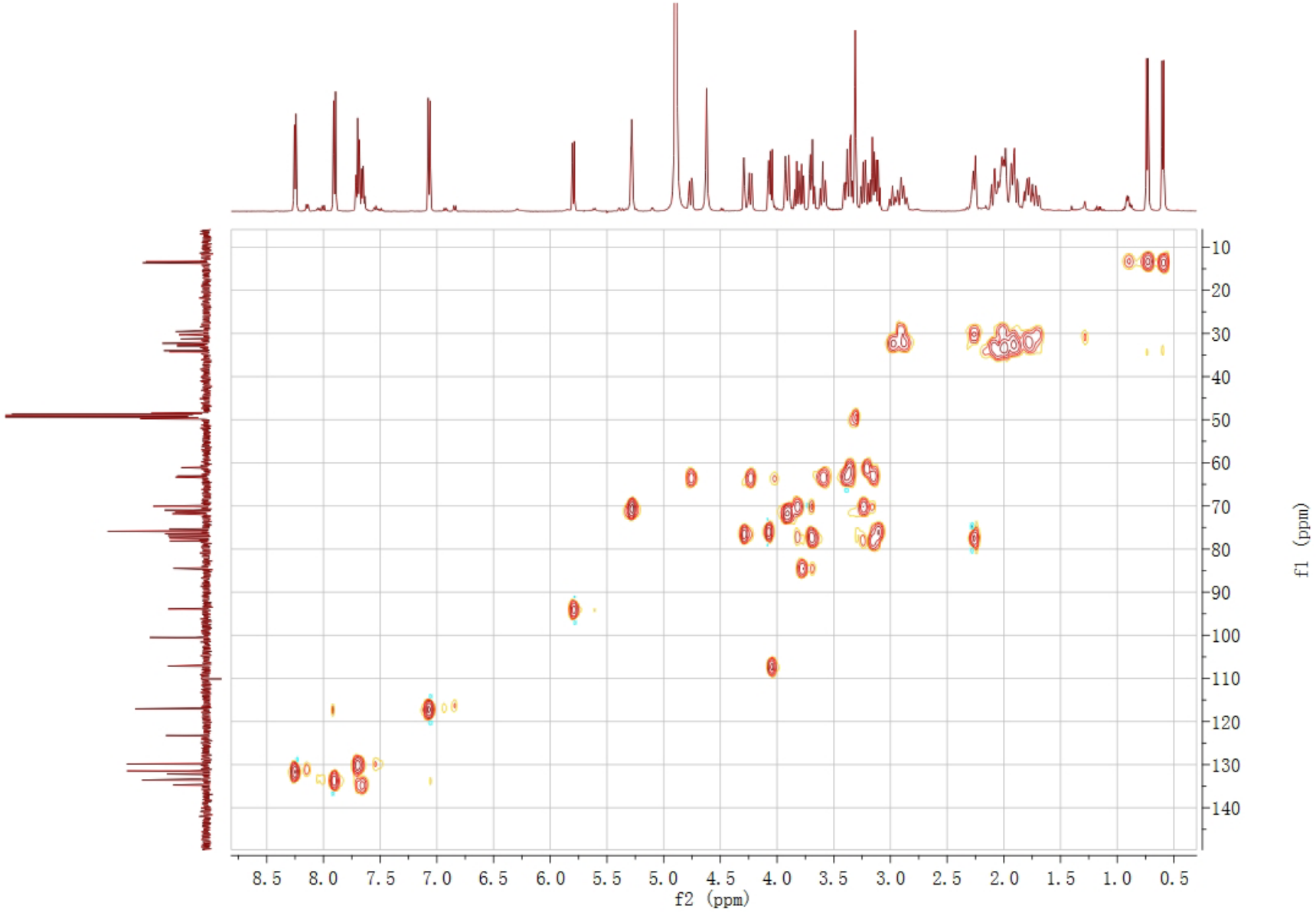
58.Figure S58 ^{1}H NMR (500 MHz) spectrum of phyllaemblicin G7 (**7**) in CD_3OD



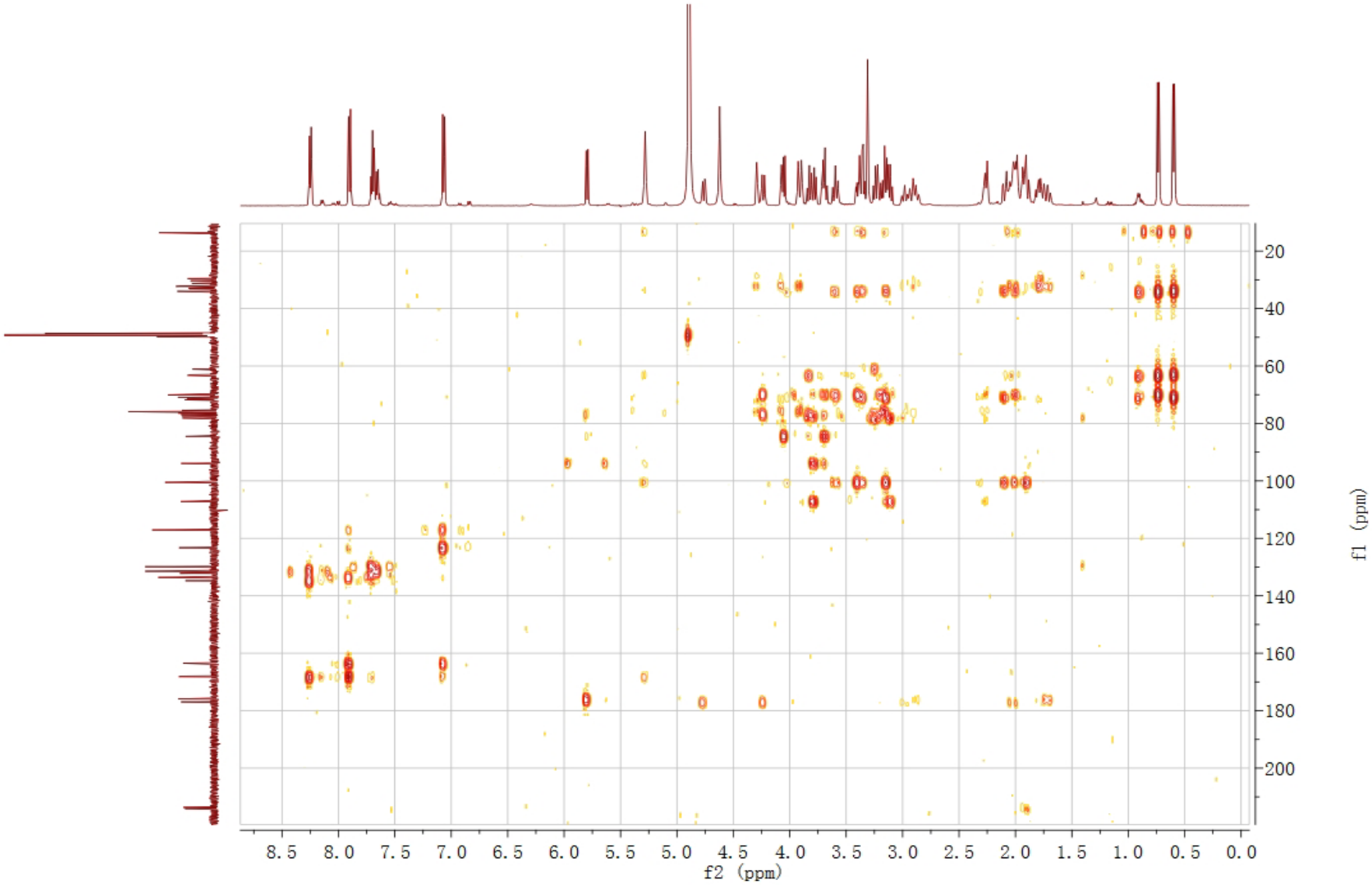
59.Figure S59 ^{13}C NMR (100 MHz) spectrum of phyllaemblicin G7 (**7**) in CD_3OD



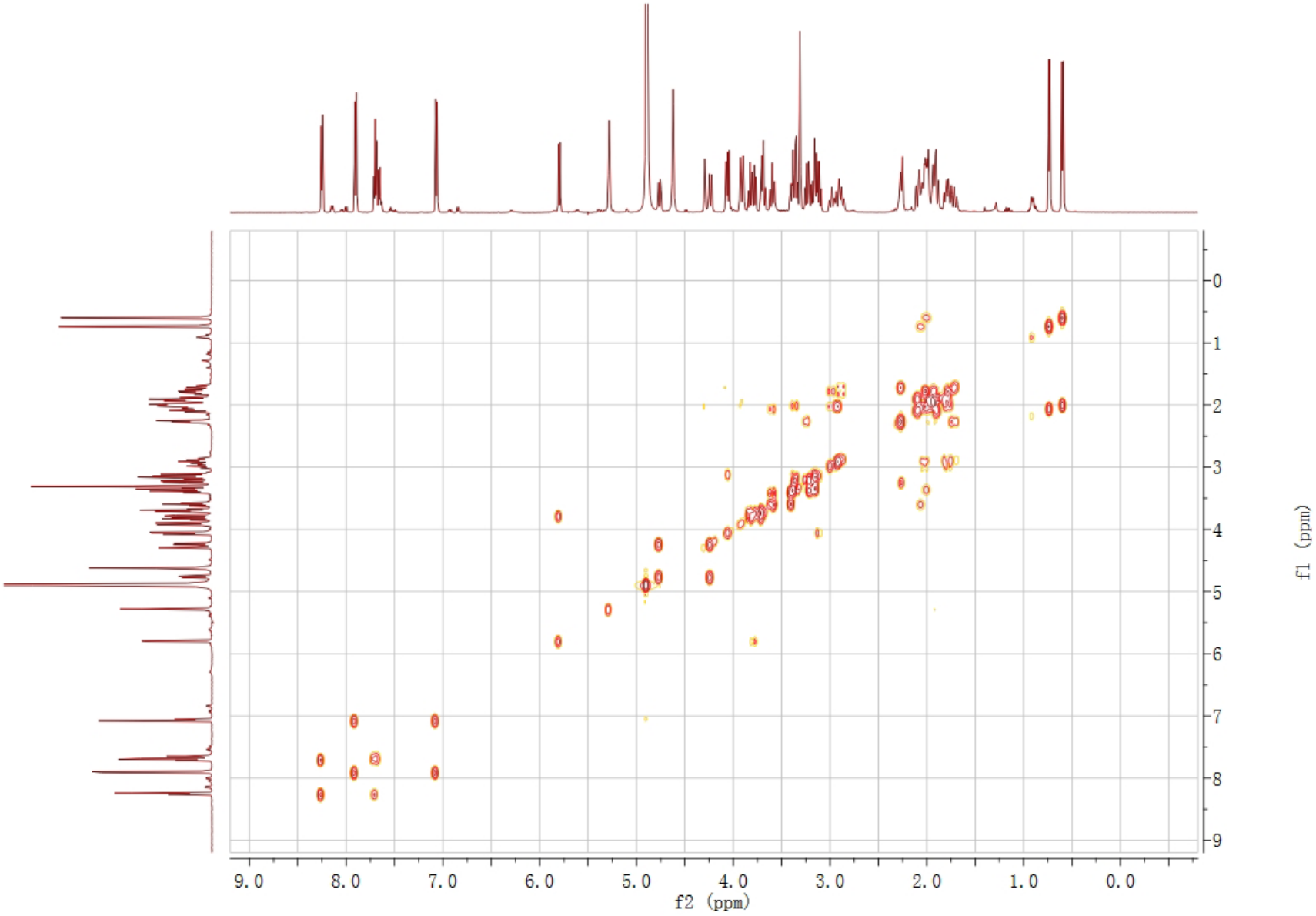
60.Figure S60 HSQC spectrum of phyllaemblicin G7 (**7**) in CD_3OD



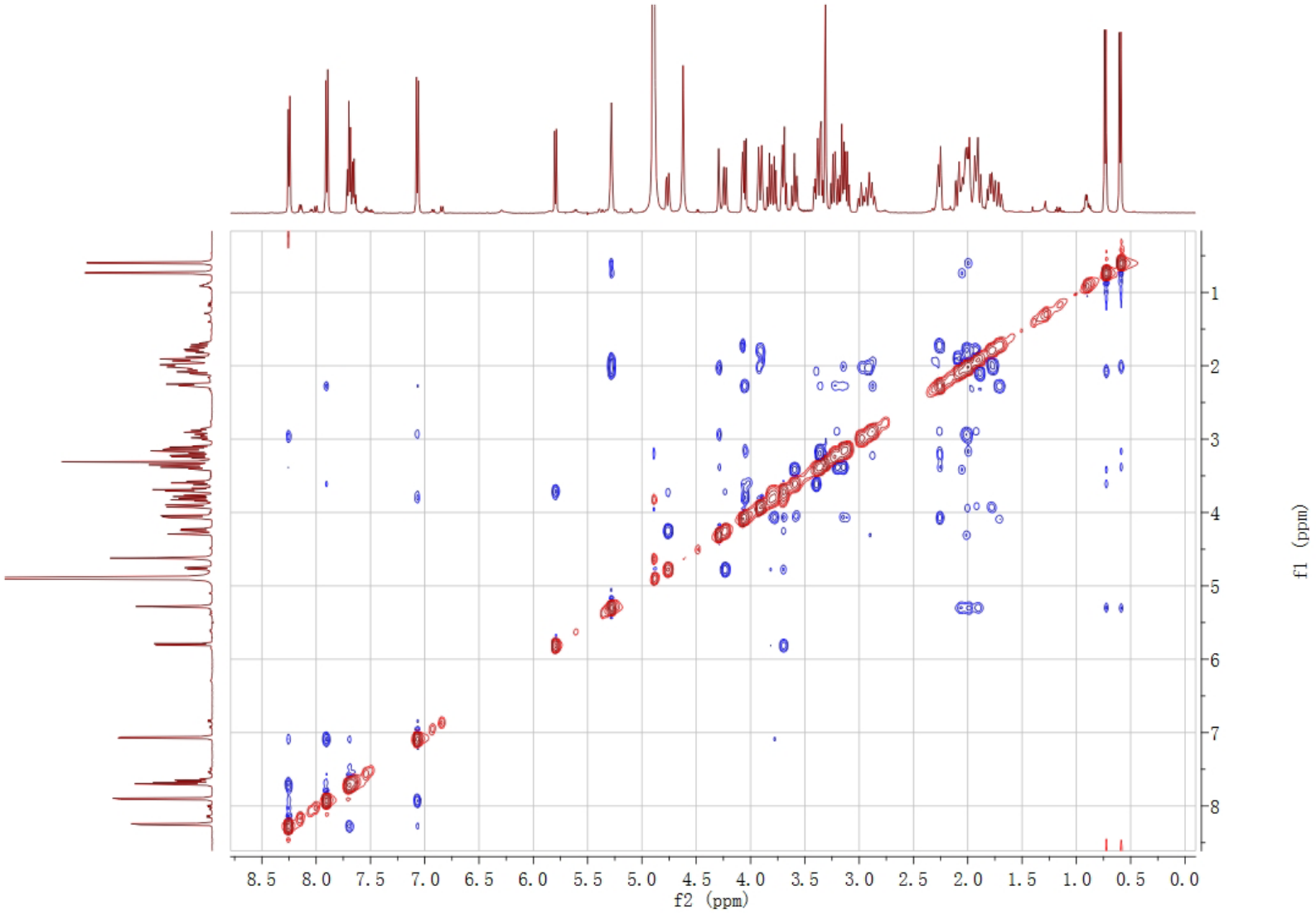
61.Figure S61 HMBC spectrum of phyllaemblicin G7 (**7**) in CD_3OD



62.Figure S62 ^{1}H-^{1}H COSY spectrum of phyllaemblicin G7 (**7**) in CD_3OD



63.Figure S63 ROESY spectrum of phyllaemblicin G7 (**7**) in CD_3OD



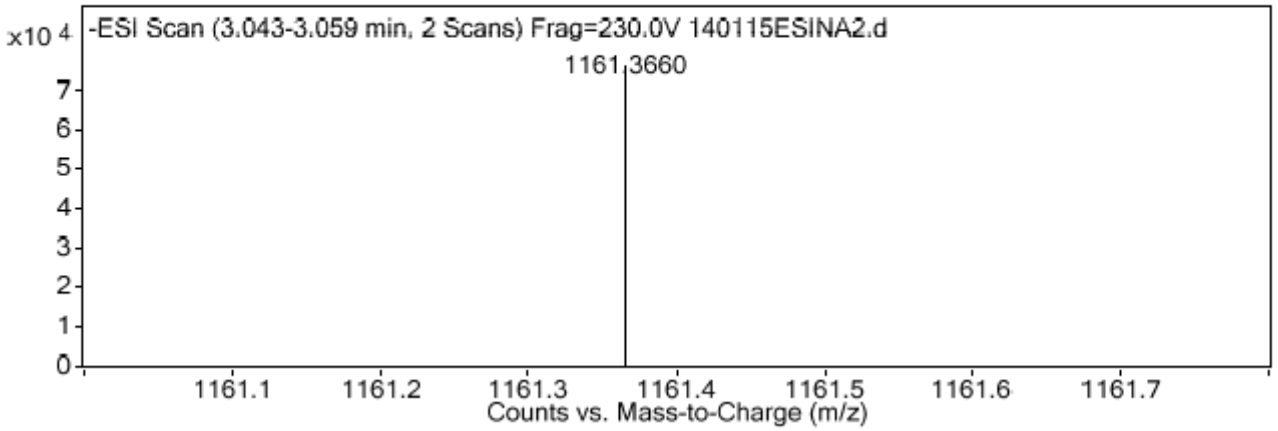
64.Figure S64 HRESIMS of phyllaemblicin G8 (**8**)

Data Filename	140115ESINA2.d	**Sample Name**	YLJ18951
Sample Type	Sample	**Position**	
Instrument Name	Agilent G6230 TOF MS	**User Name**	KIB
Acq Method	ESIN.m	**Acquired Time**	1/15/2014 10:47:25 AM
IRM Calibration Status	Success	**DA Method**	demo1.m
Comment			

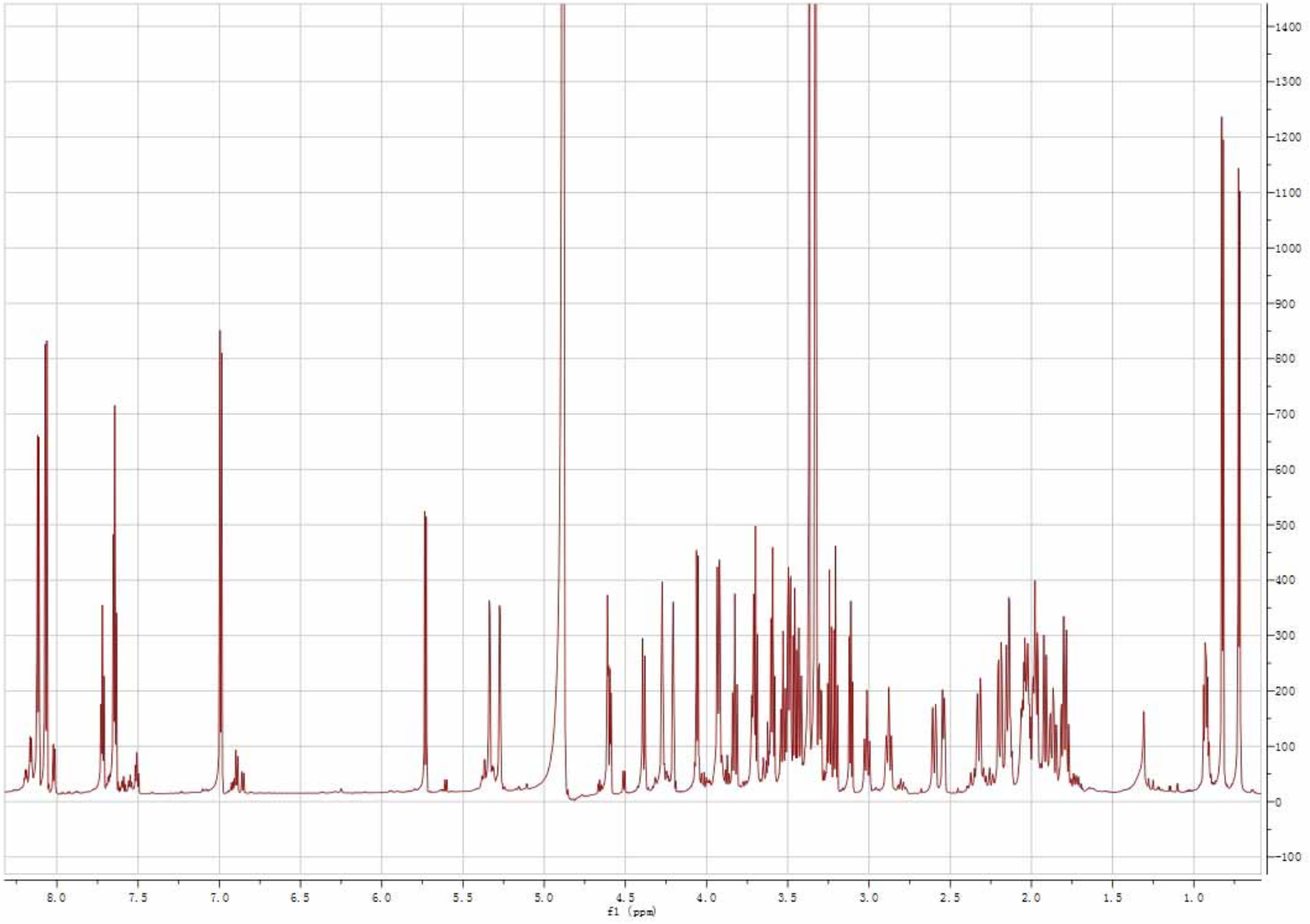
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

User Spectra

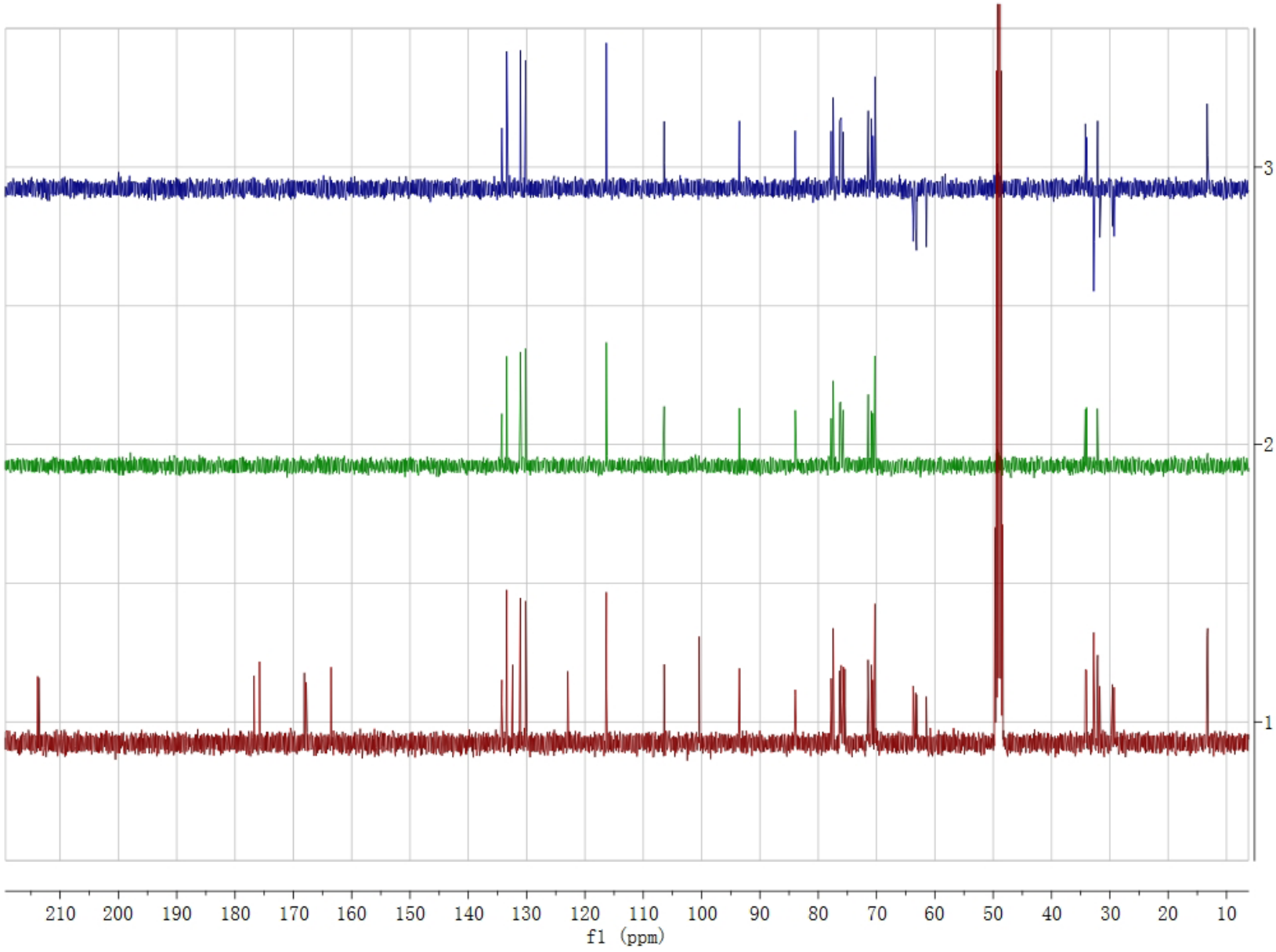
Fragmentor Voltage	Collision Energy	Ionization Mode
230	0	ESI



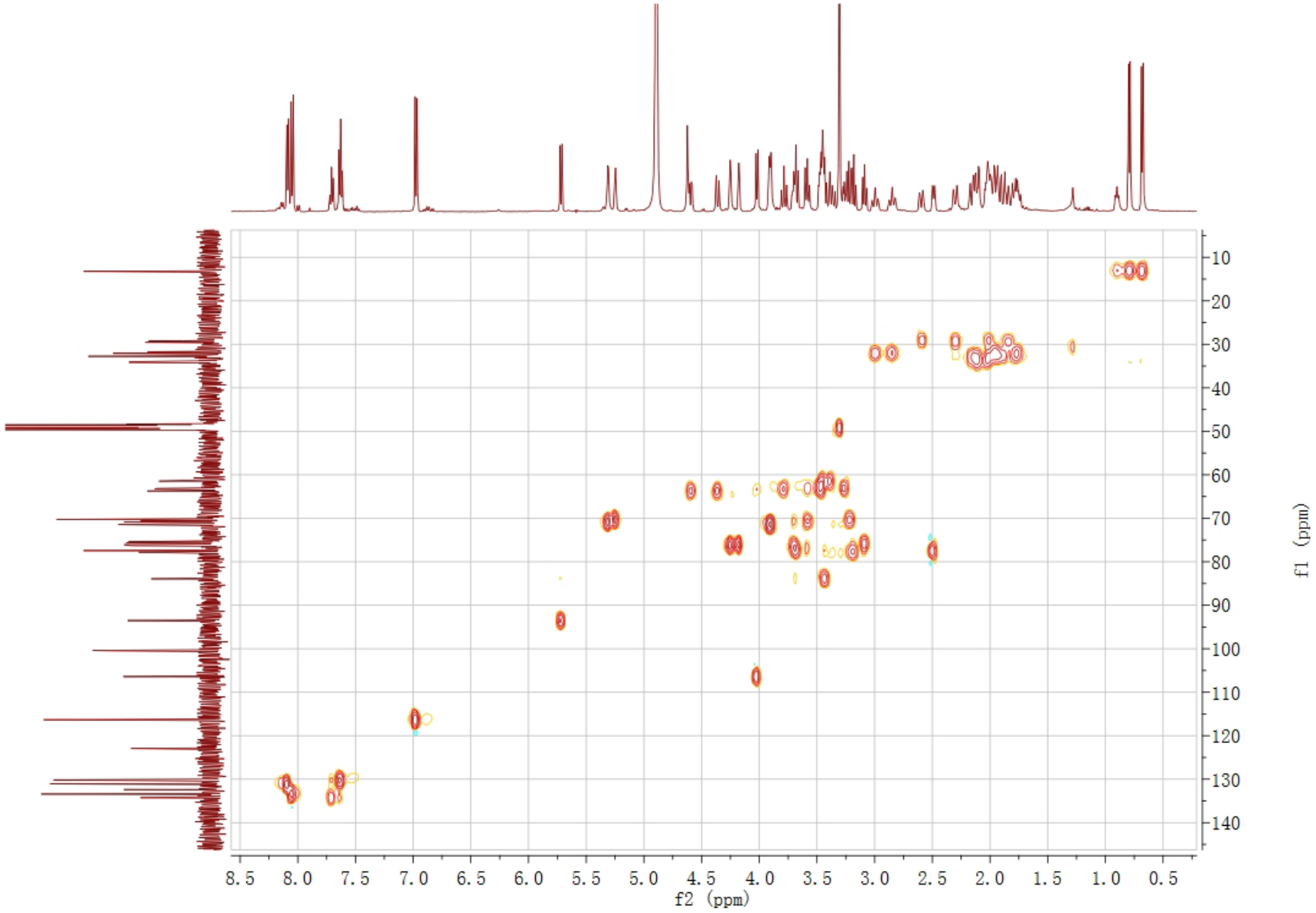
65.Figure S65 ^{1}H NMR (800 MHz) spectrum of phyllaemblicin G8 (**8**) in CD_3OD



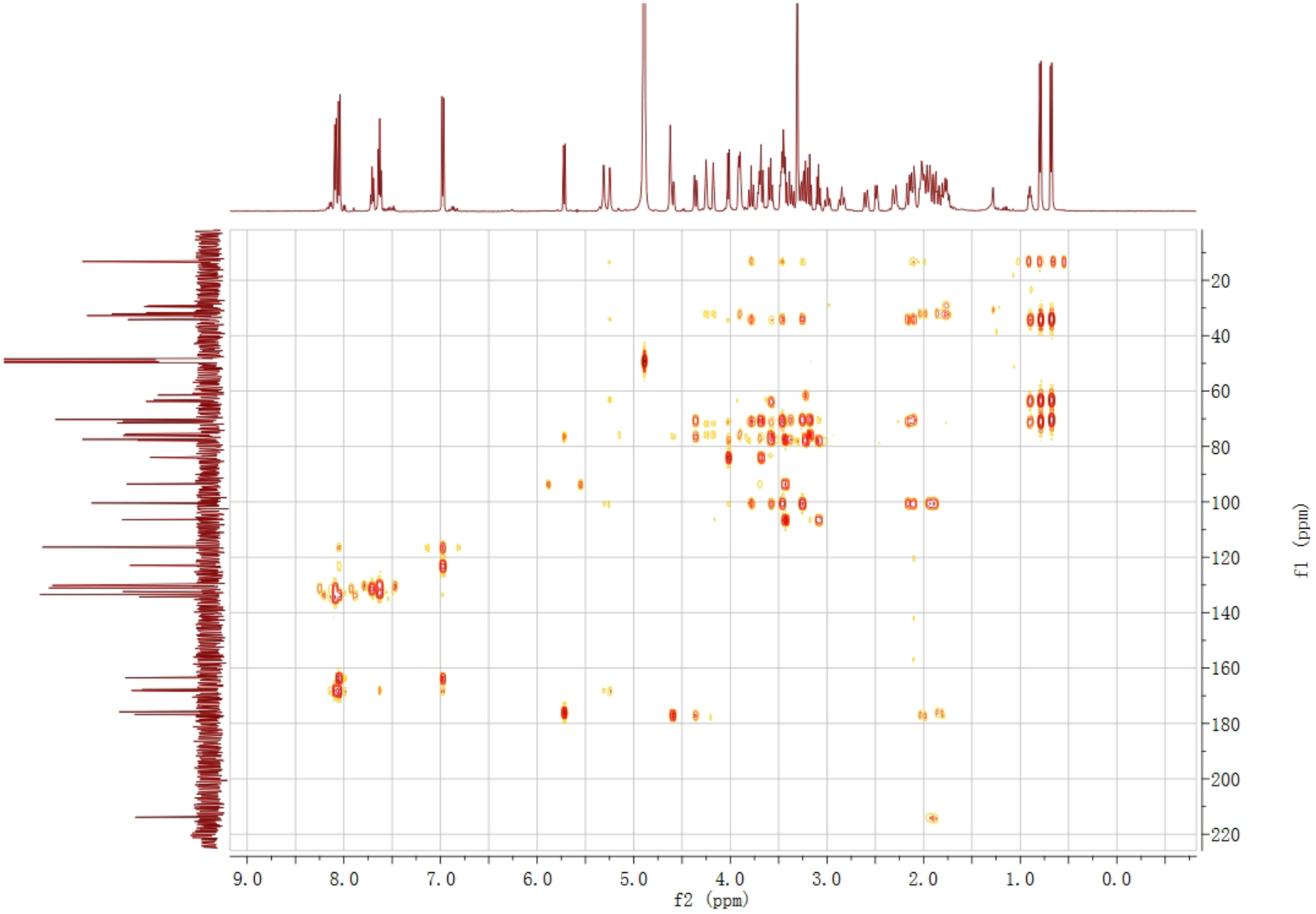
66.Figure S66 ^{13}C NMR (100 MHz) spectrum of phyllaemblicin G8 (**8**) in CD_3OD



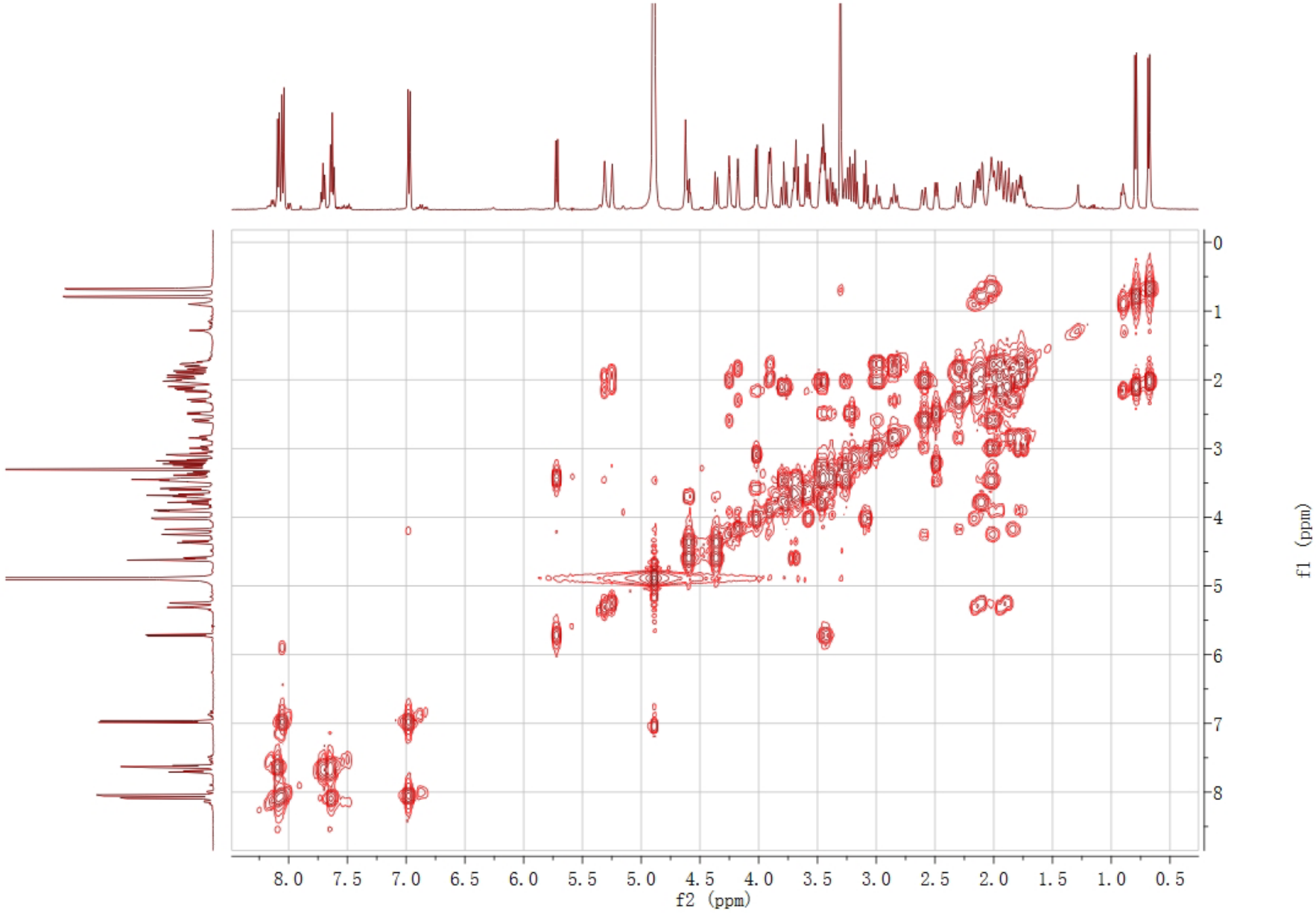
67.Figure S67 HSQC spectrum of phyllaemblicin G8 (**8**) in CD_3OD



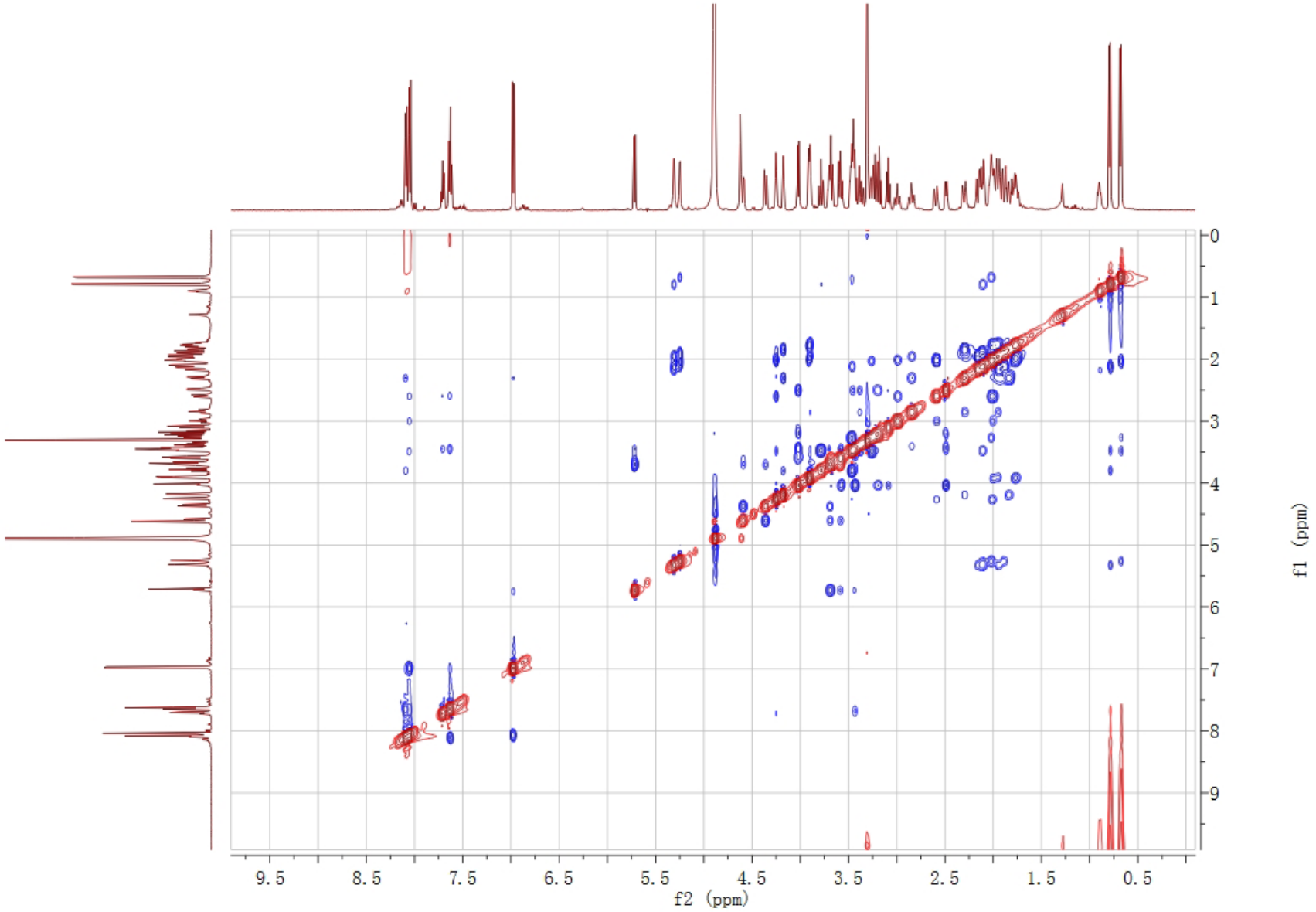
68.Figure S68 HMBC spectrum of phyllaemblicin G8 (**8**) in CD_3OD



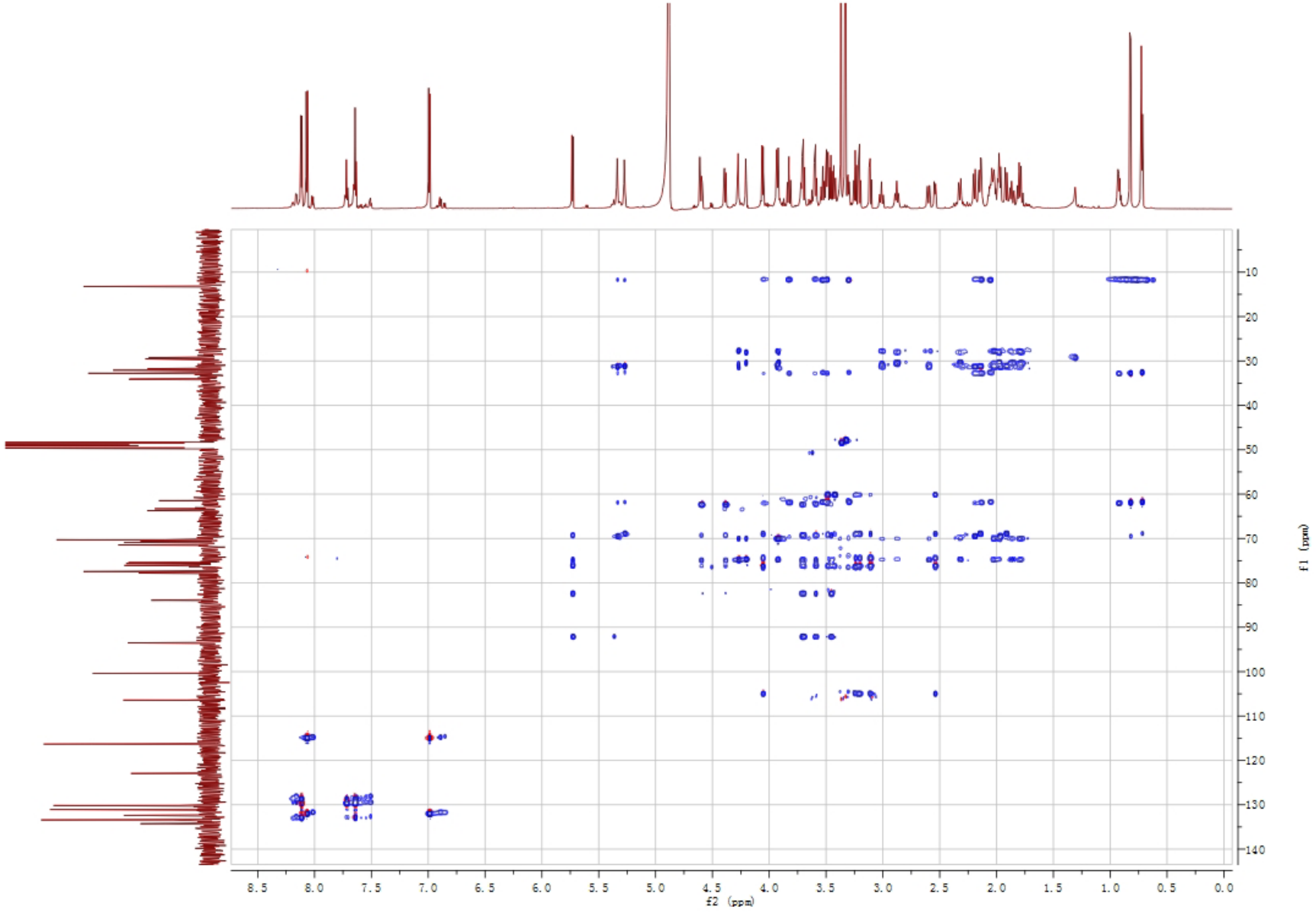
69.Figure S69 ^{1}H-^{1}H COSY spectrum of phyllaemblicin G8 (**8**) in CD_3OD



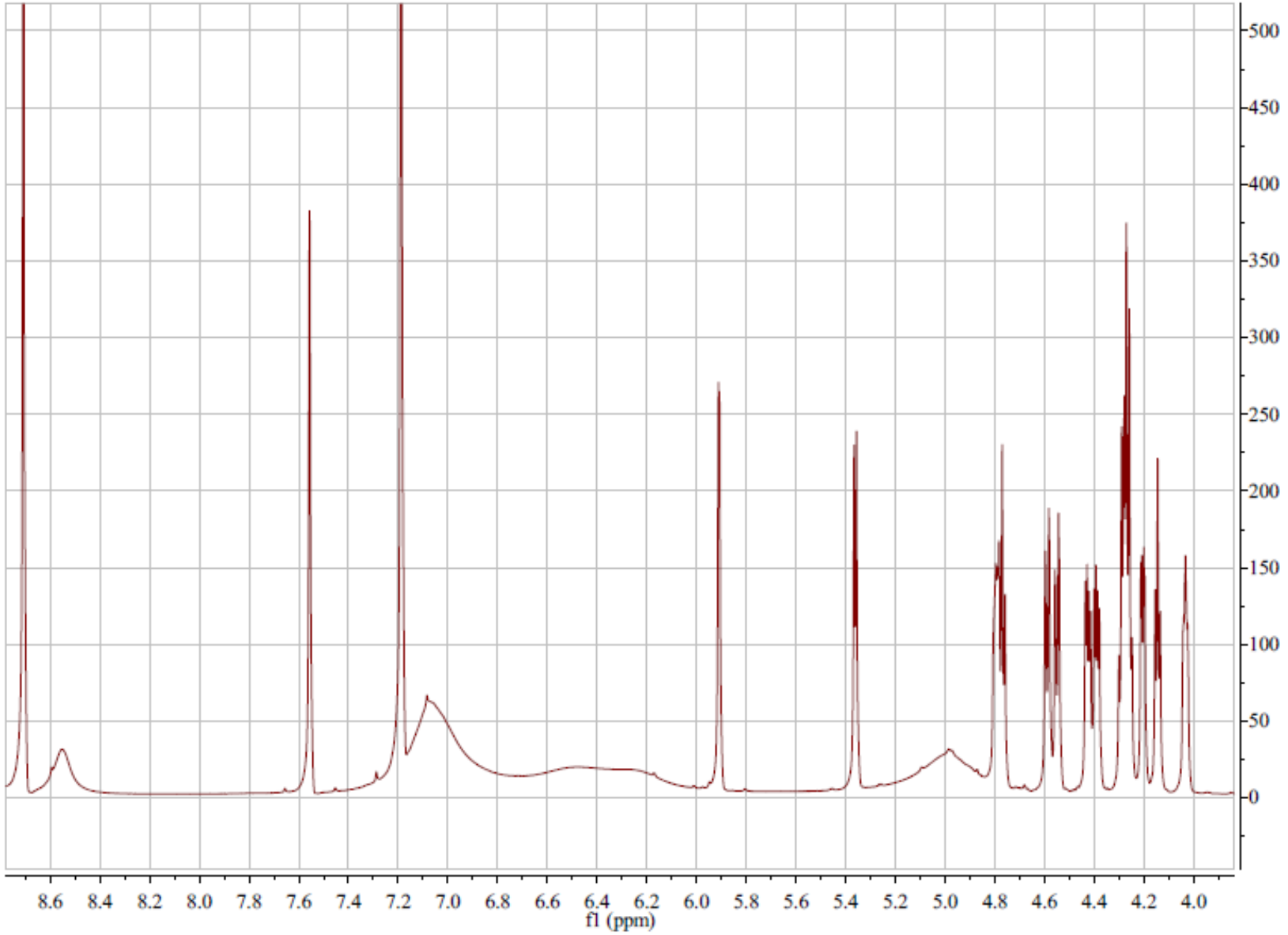
70.Figure S70 ROESY spectrum of phyllaemblicin G8 (**8**) in CD_3OD



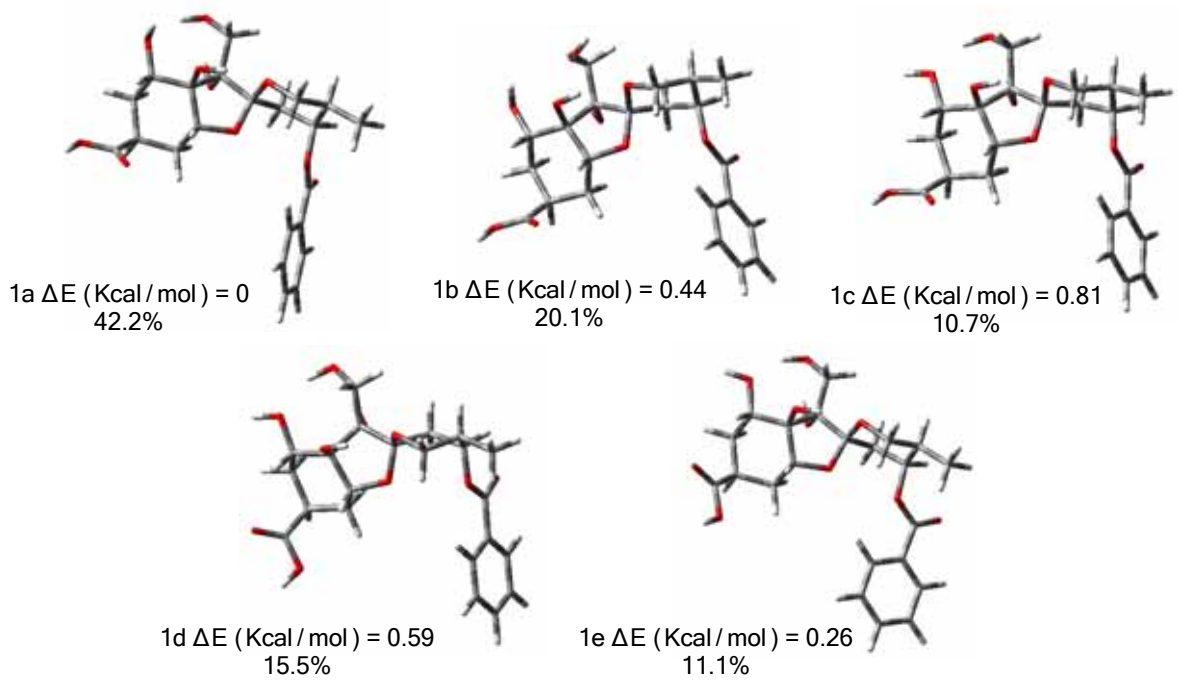
71.Figure S71 HSQC-TOCSY spectrum of phyllaemblicin G8 (**8**) in CD_3OD



72.Figure S72 ^{1}H NMR (800 MHz) spectrum of glucose (hydolysis product of **7**) in pyridine-d_6



73.Figure S73 ECD calculations of phyllaemblicin G1 (**1**)



DFT optimized conformers of the aglycon of 1*S*,3*S*,5*R*,6*R*,7*S*,8*S*,10*S*,11*R*- phyllaemblicin G1 (**1**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

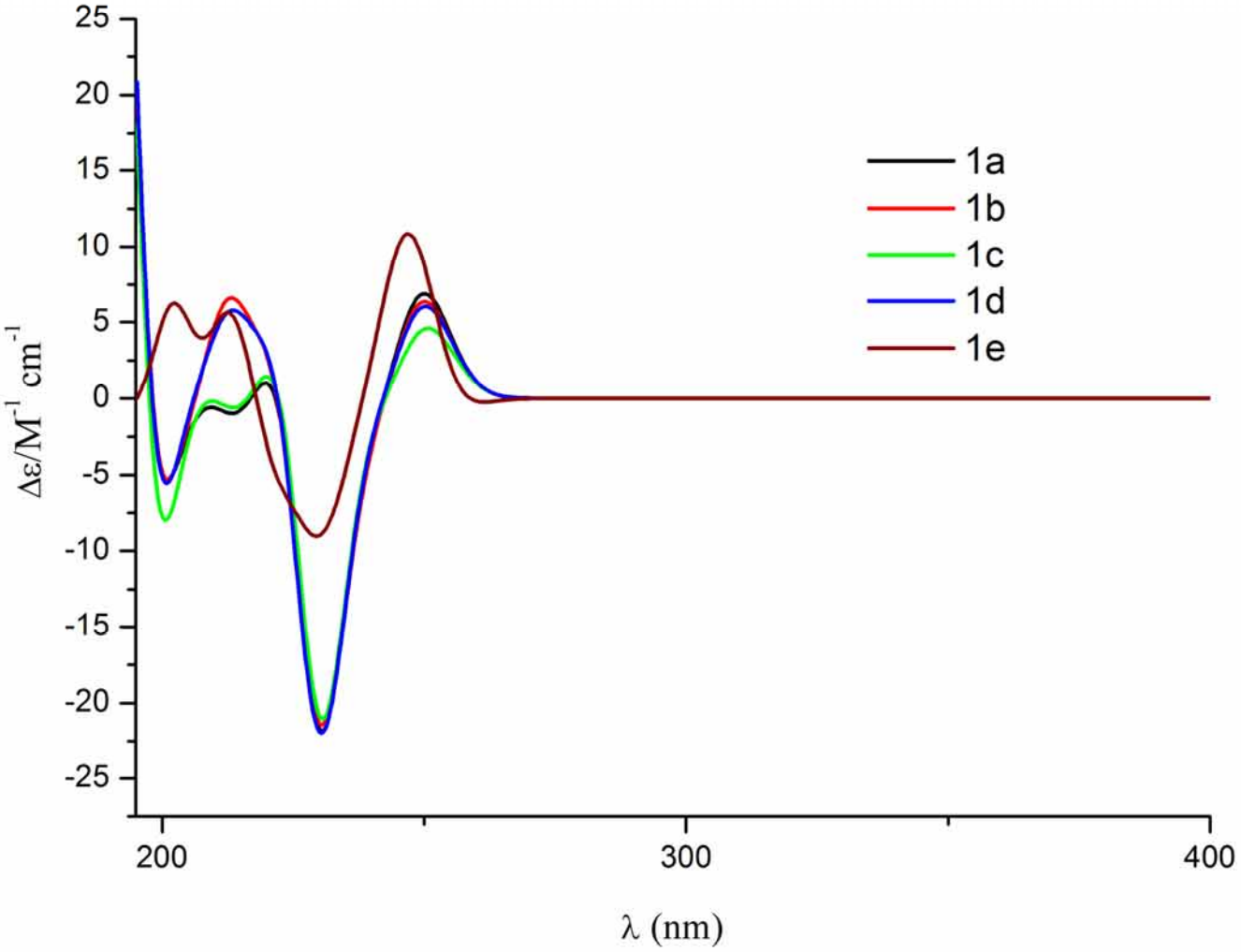
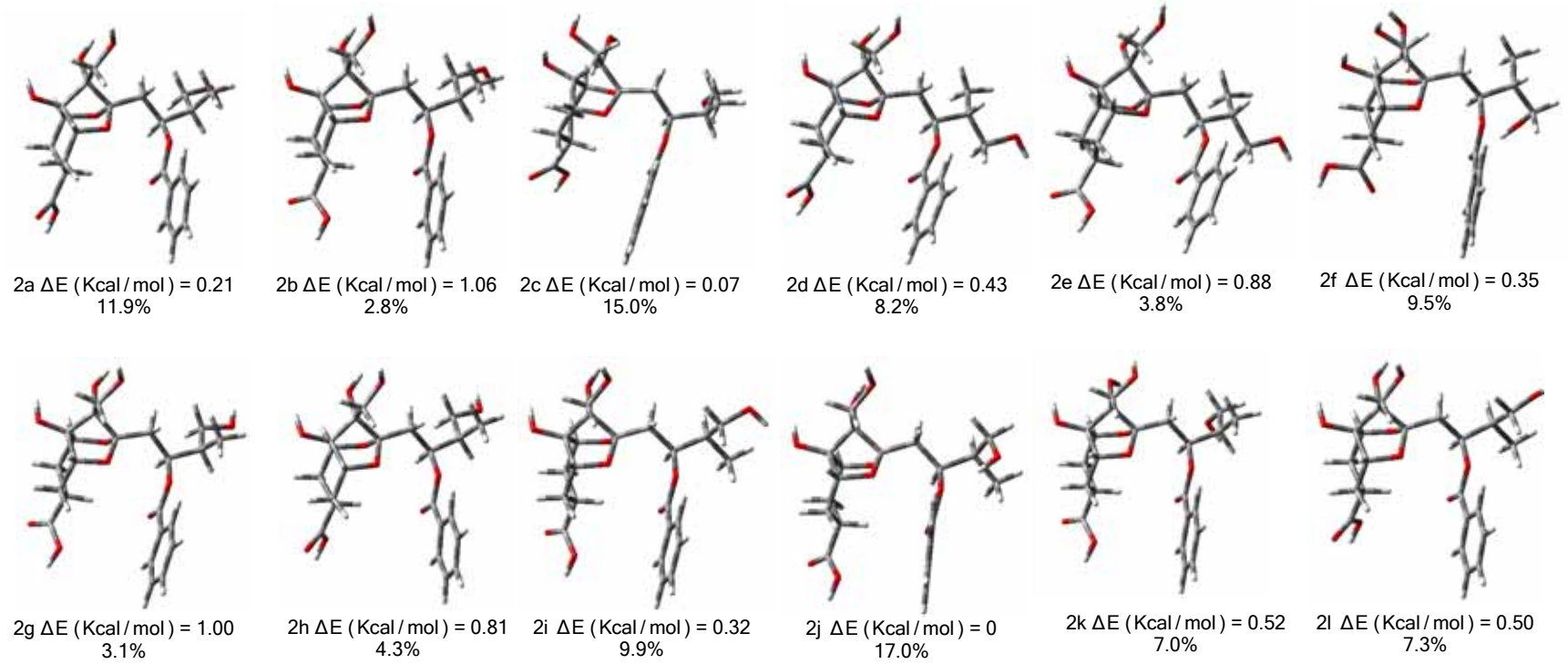


Figure 3. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon 1*S*, 3*S*, 5*R*, 6*R*, 7*S*, 8*S*, 10*S*, 11*R*-phyllaemblicin G1 (**1**), with Gaussian band shape 0.3ev.

74.Figure S74 ECD calculations of phyllaemblicin G2 (**2**)



DFT optimized conformers of the aglycon of 1*S*, 3*S*, 5*R*, 6*S*, 7*S*, 8*R*, 10*S*, 11*R*-phyllaemblicin G2 (**2**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

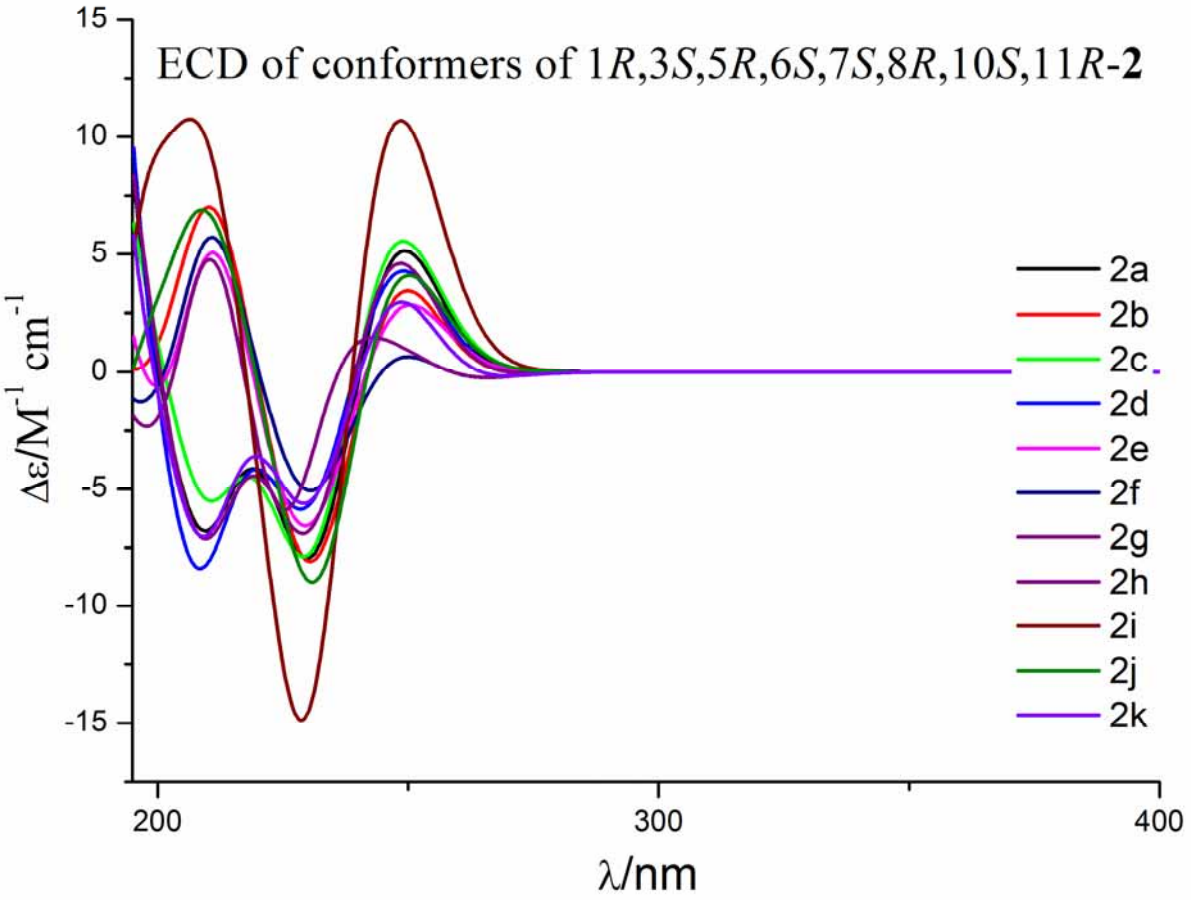
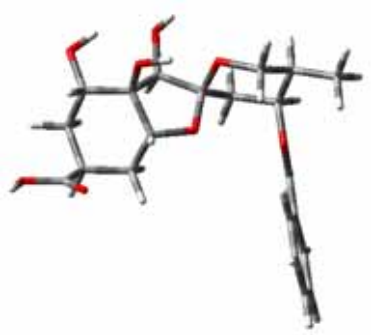
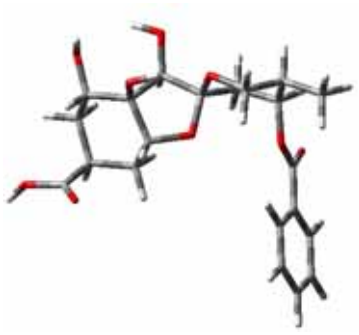


Figure 5. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon 1*S*, 3*S*, 5*R*, 6*S*, 7*S*, 8*R*, 10*S*, 11*R*-phyllaemblicin G2 (**2**), with Gaussian band shape 0.3ev.

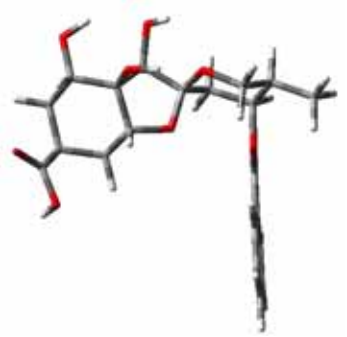
75.Figure S75 ECD calculations of compound **3**



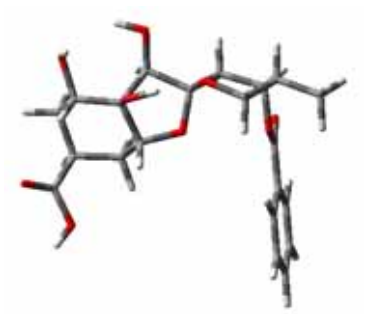
3a ΔE (Kcal / mol) = 0
41.5%



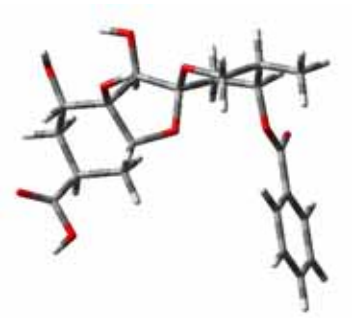
3b ΔE (Kcal / mol) = 1.47
3.5%



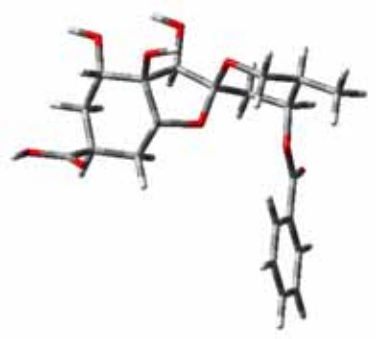
3c ΔE (Kcal / mol) = 0
41.2%



3d ΔE (Kcal / mol) = 1.19
5.6%



3e ΔE (Kcal / mol) = 1.90
1.7%



3f ΔE (Kcal / mol) = 1.33
4.4%

DFT optimized conformers of the aglycon of 1*S*, 3*S*, 5*R*, 6*S*,7*R*, 8*S*, 10*S*, 11*R*-phyllaemblicin G3 (**3**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

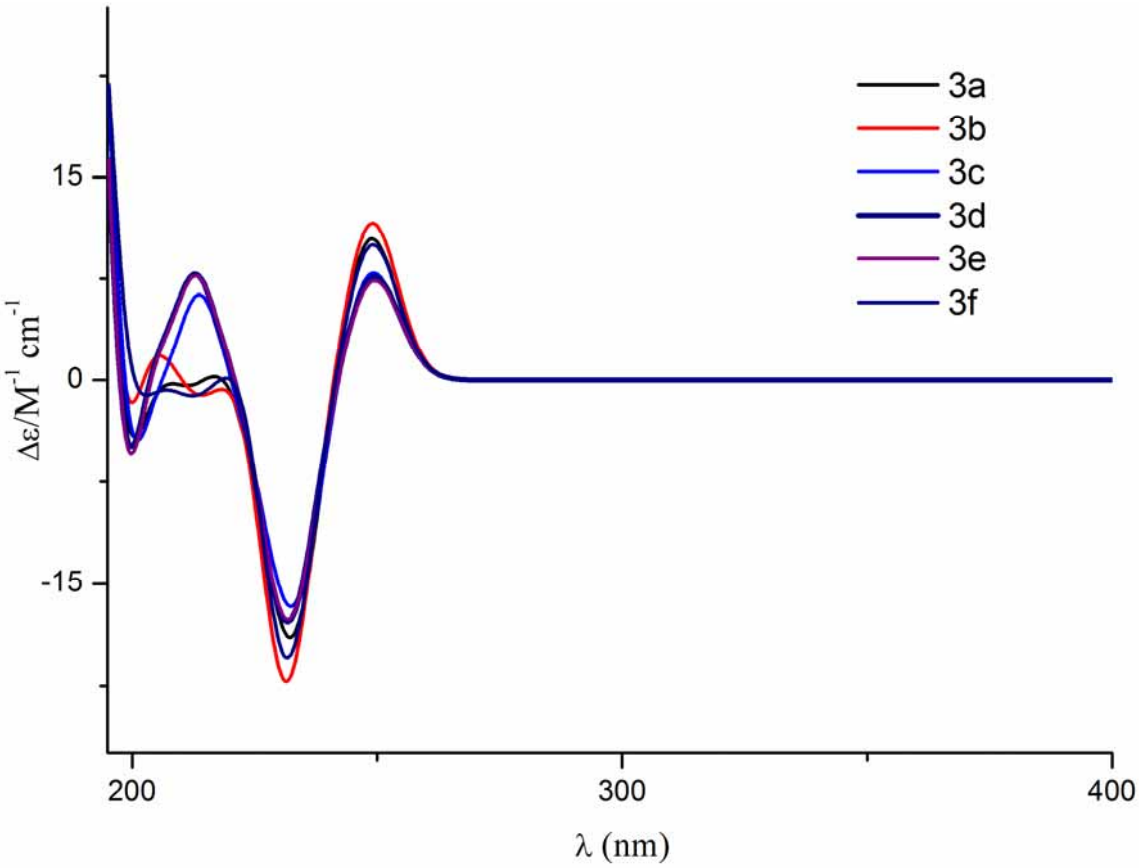
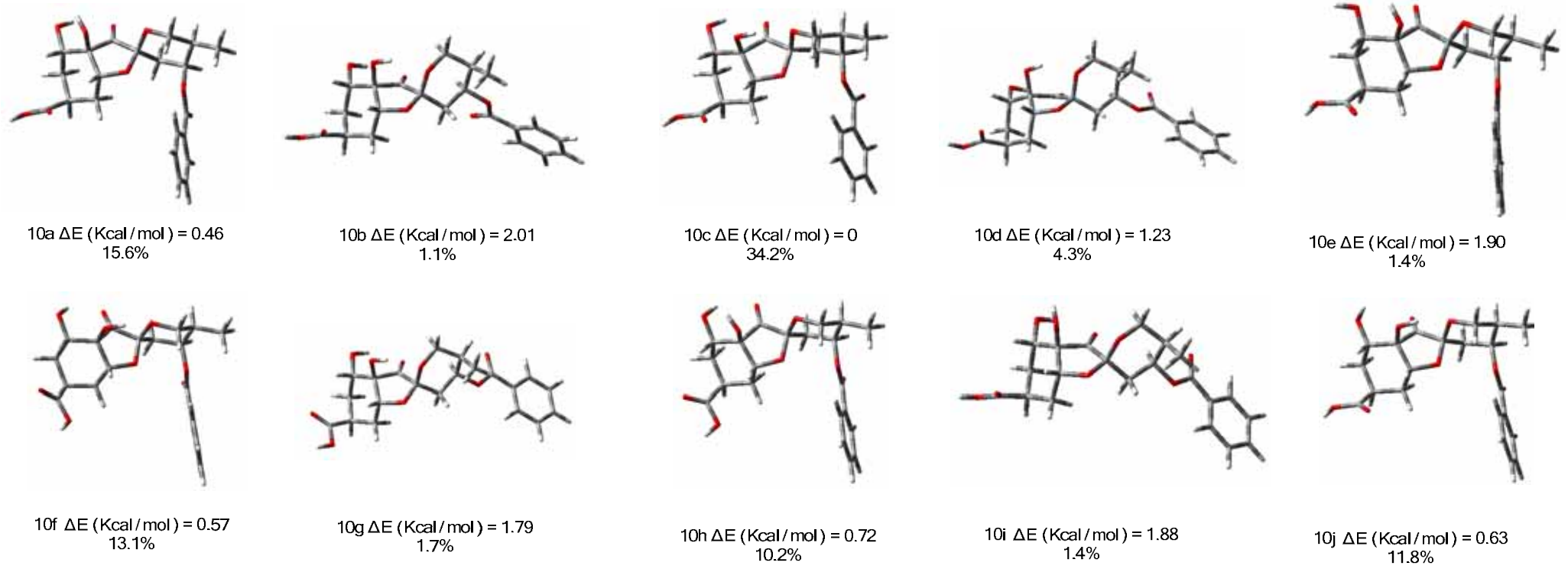
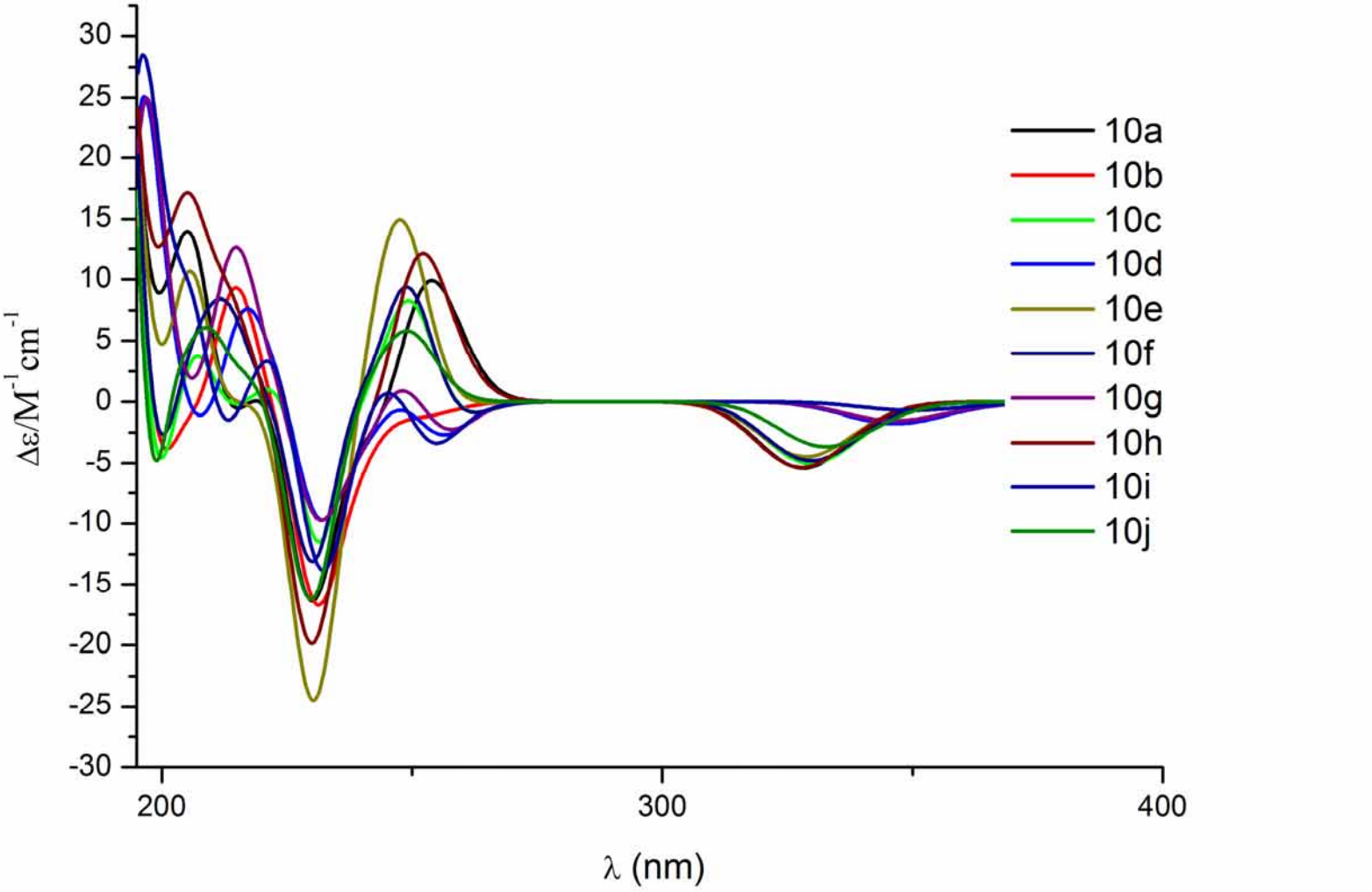


Figure 7. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of 1*S*, 3*S*, 5*R*, 6*S*,7*R*, 8*S*, 10*S*, 11*R*-phyllaemblicin G3 (**3**), with Gaussian band shape 0.3ev.

76.Figure S76 ECD calculations of compound **10**



DFT optimized conformers of the aglycon of 1*S*, 3*S*, 5*R*, 6*R*, 8*S*, 10*S*, 11*R*-phyllaemblic acid (**10**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.



TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon 1*S*, 3*S*, 5*R*, 6*R*, 8*S*, 10*S*, 11*R*-phyllaemblic acid (**10**), with Gaussian band shape 0.3ev.