Supporting Information Section

Structures, Biogenesis, and Biological Activities of Pyrano[4,3-*c*]isochromene-4-one Derivatives from the Fungus *Phellinus igniarius*:

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Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College (Key Laboratory of Bioactive Substances and Resources Utilization of Chinese Herbal Medicine, Ministry of Education), Beijing 100050, China, Key Laboratory for Atmospheric Chemistry (LAC), Centre for Atmosphere Watch and Services (CAWAS), Chinese Academy of Meteorological Sciences (CAMS), Beijing 100081, China, and Department of Chemistry, Beijing Normal University, Beijing 100875, China

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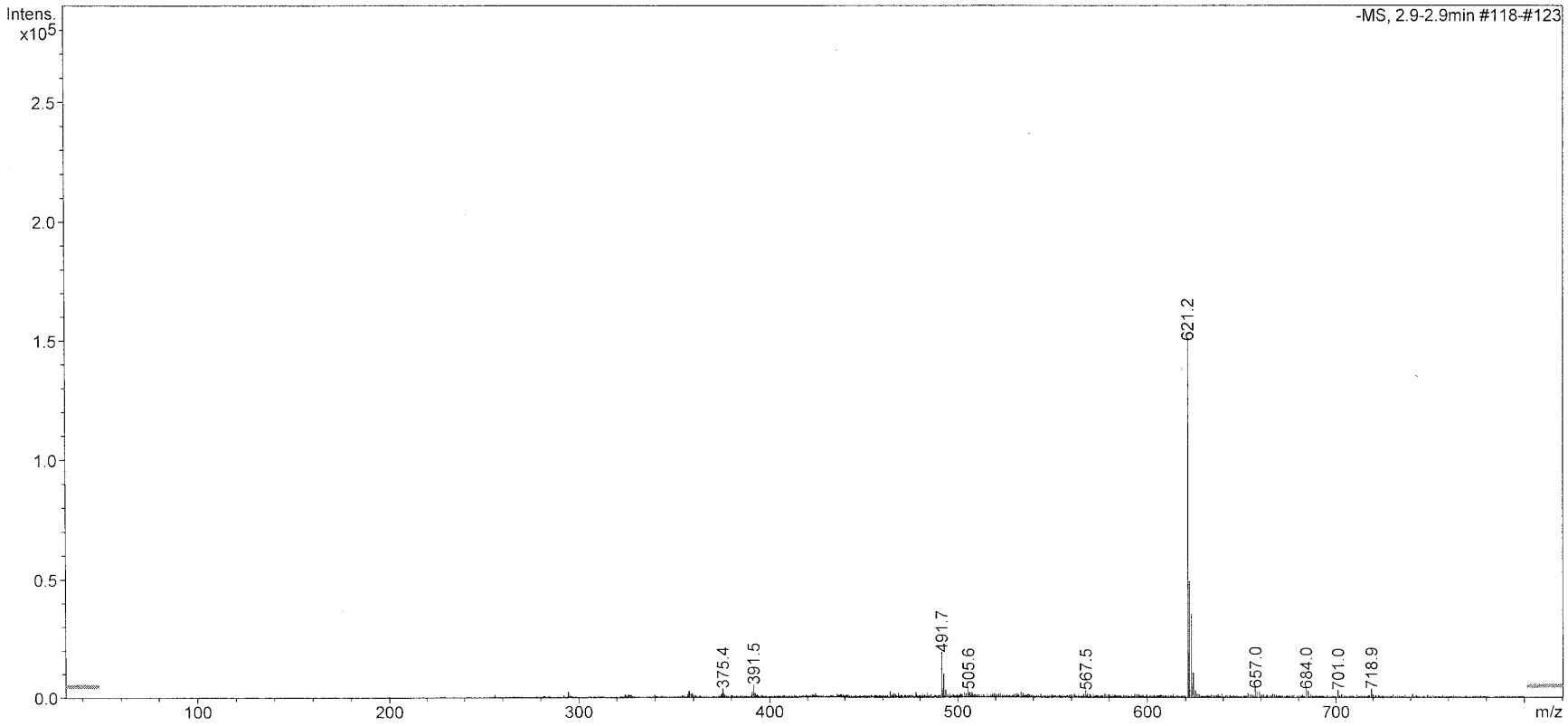
List of Supporting Information

Display Report - Selected Window Selected Analysis

Analysis Name: E13C35D.d
Method: Copy of TEST.MS
Sample Name: E13C35D
Analysis Info:

Instrument: LC-MSD-Trap-SL
Operator: Administrator

Print Date: 2006-3-24 8:12:52
Acq. Date: 2004-2-17 14:59:52



ESI-MS of Phelligridin H (**1**)

Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

SIOC

Instrument:

IonSpec 4.7 Tesla FTMS

Card Serial Number: I041198

Sample Serial Number: SH-W6 C15

Operator: Hua Qin Date: 2004/08/03

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 623.0808 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
O	15.994915	0	30

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

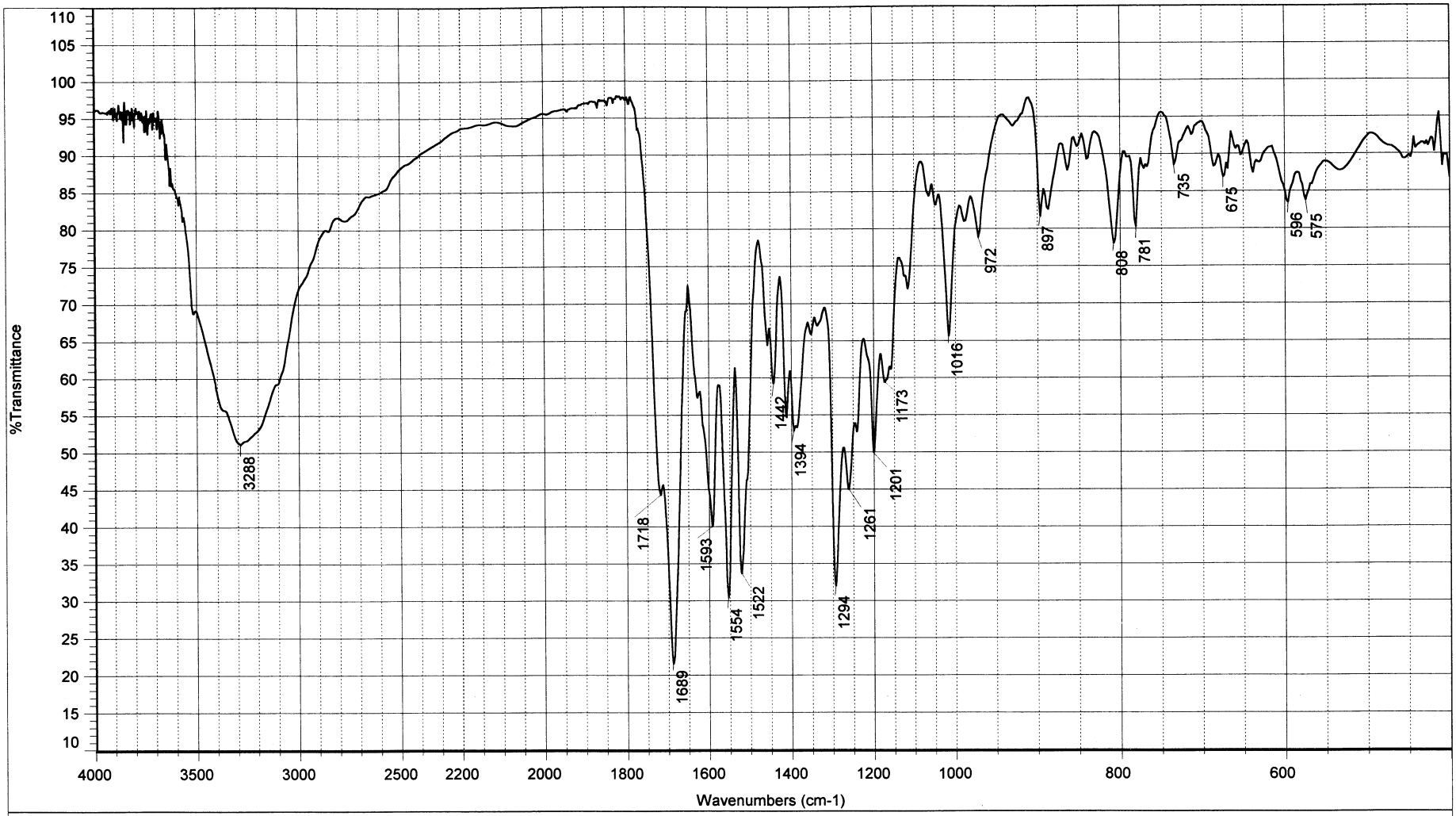
Search Results:

Number of Hits = 2

m/z	Delta m/z	DBE	Formula
623.08202	-0.00122	24.5	$C_{33}H_{19}O_{13}^{+1}$
623.07852	0.00228	2.5	$C_{15}H_{27}O_{26}^{+1}$

HR-MS of Phelligridin H (**1**)

IR spectrum of Phelligridin H (**1**)



Date: Wed Nov 10 10:02:00 2004 Sample Name: C155 (KBr)

Scans: 64 检测单位：国家药物及代谢产物分析研究中心

Resolution: 4.000 检测仪器：美国尼高力公司傅立叶变换红外光谱仪: IMPACT - 400

THERMO SPECTRONIC ~ VISION32 SOFTWARE V1.25

Batch Information - scan003

Batch Type	Scan	Operator Name	(None Entered)
Instrument ID	110514	Aborted	No

Results Table - scan003

Data Mode Absorbance

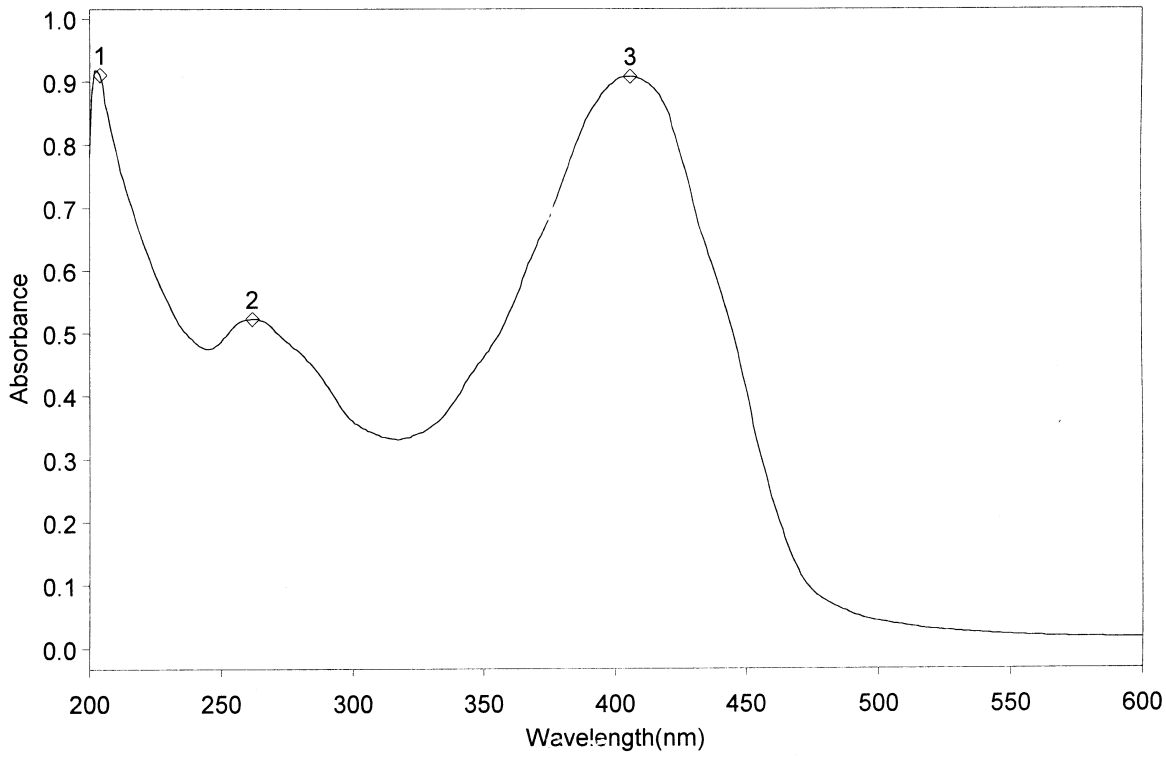
	A	B	C	D	E
1	**C155**		**1**	**2**	**3**
2	Cycle01	nm	204.0	262.0	406.0
3	Manual	A	.911	.522	.908

All calculations have been performed to double precision as defined by ANSI/IEEE STD 754-1985 but have been rounded for display purposes.

C155

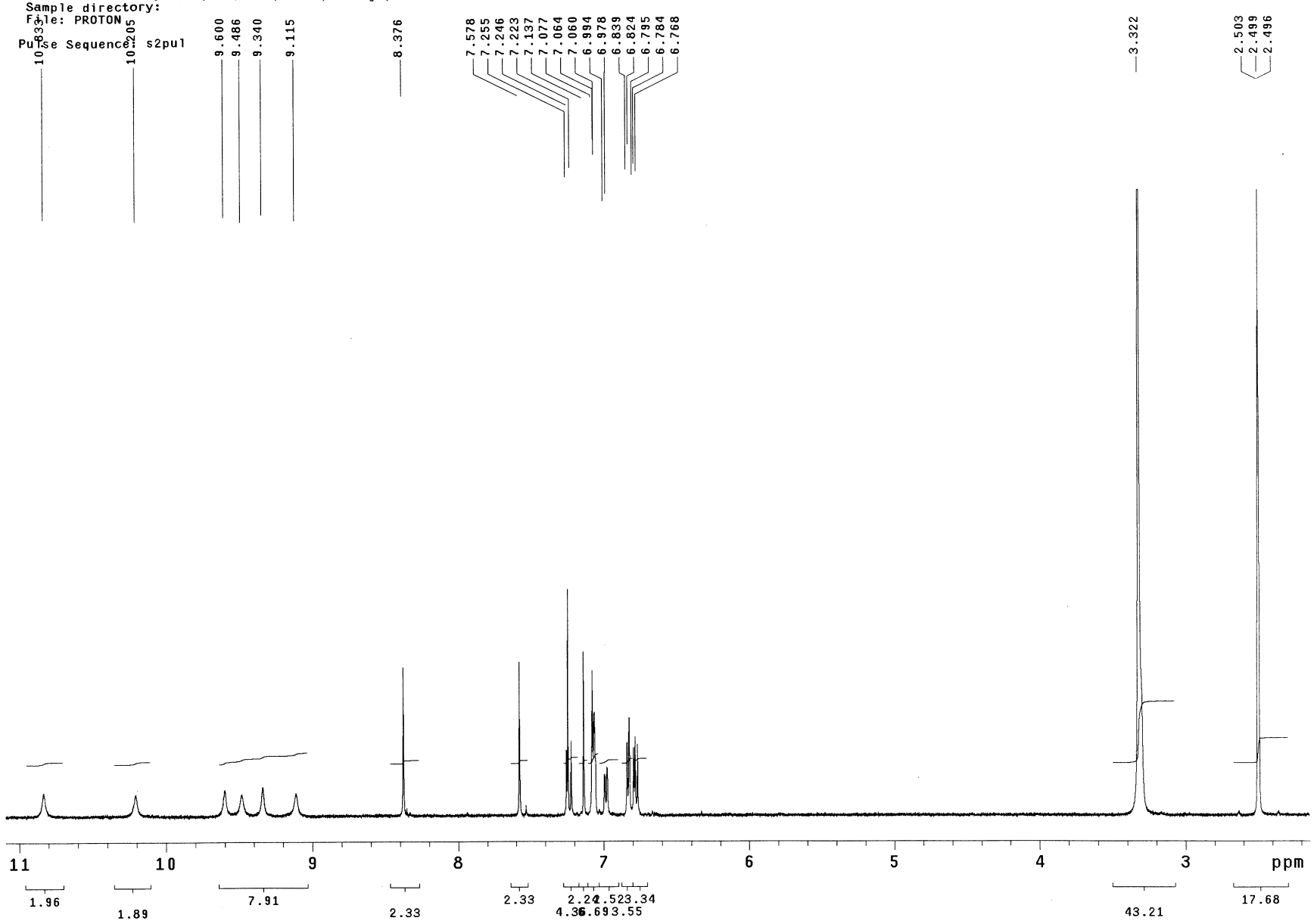
Description MeOH溶液

C155,Cycle01

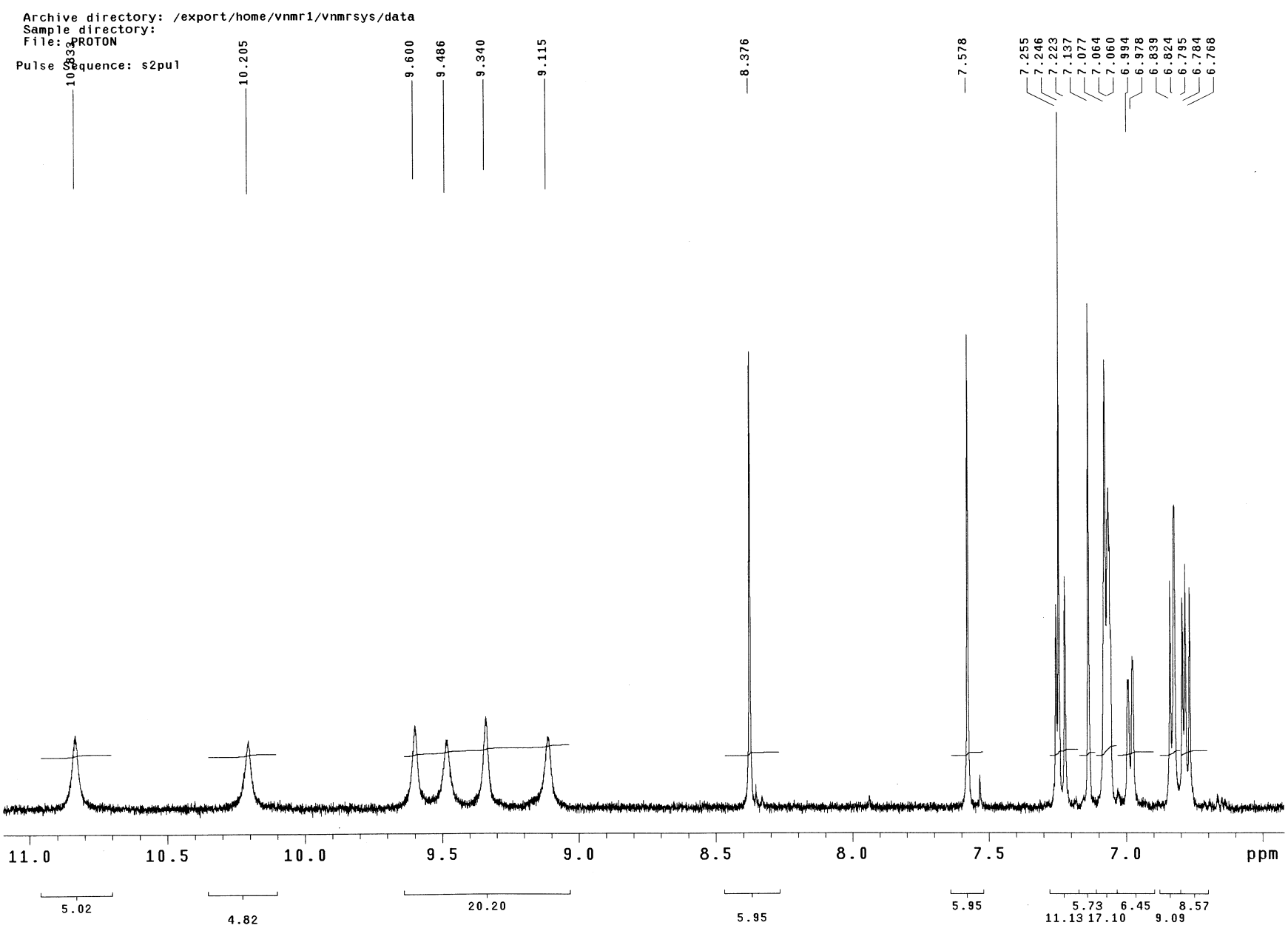


UV spectrum of Phelligridin H (**1**)

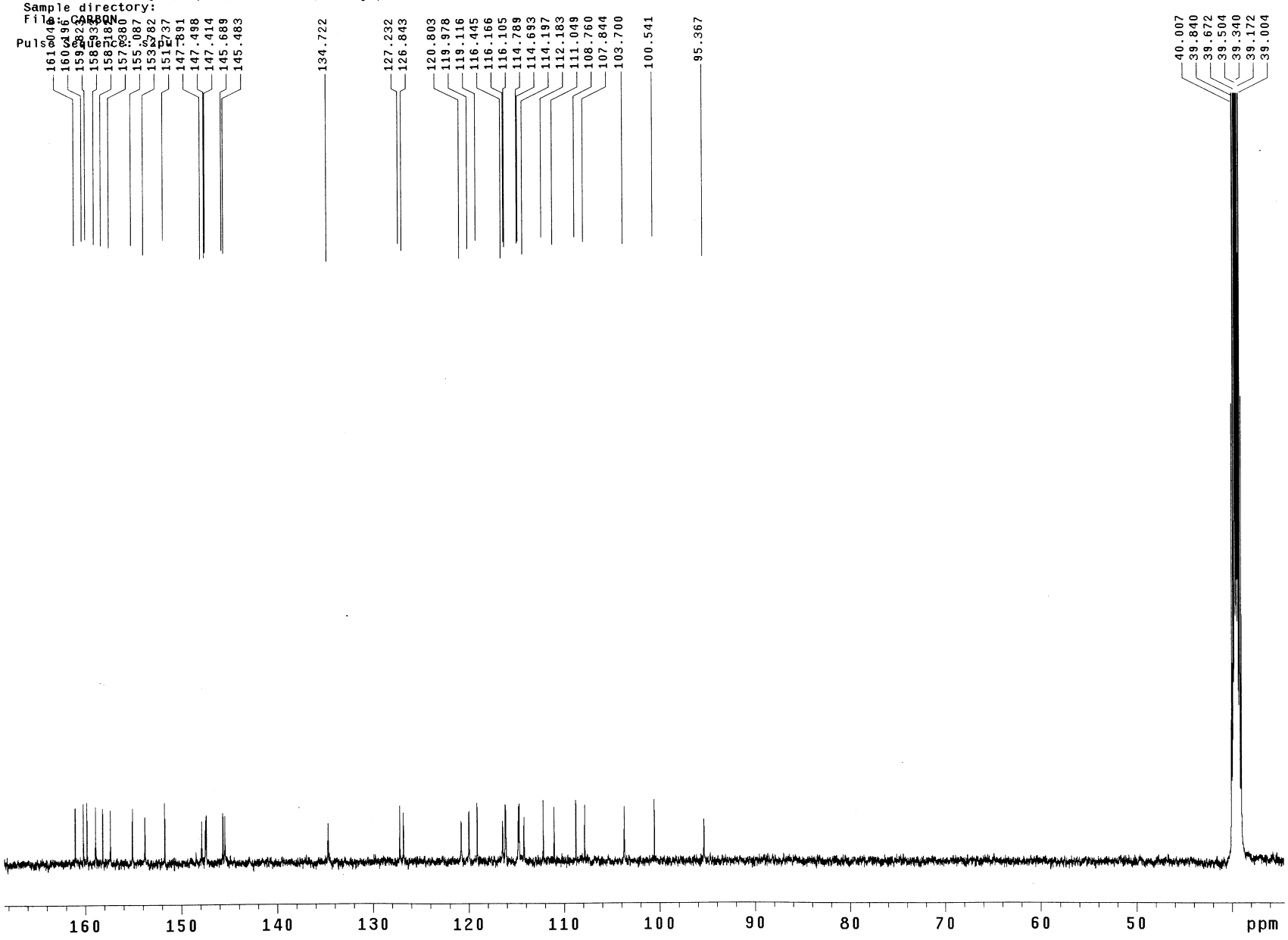
^{1}H NMR spectrum of Phelligridin H (**1**)



Regional enlarged ^{1}H NMR spectrum of Phelligridin H (**1**)



^{13}C NMR spectrum of Phelligridin H (**1**)

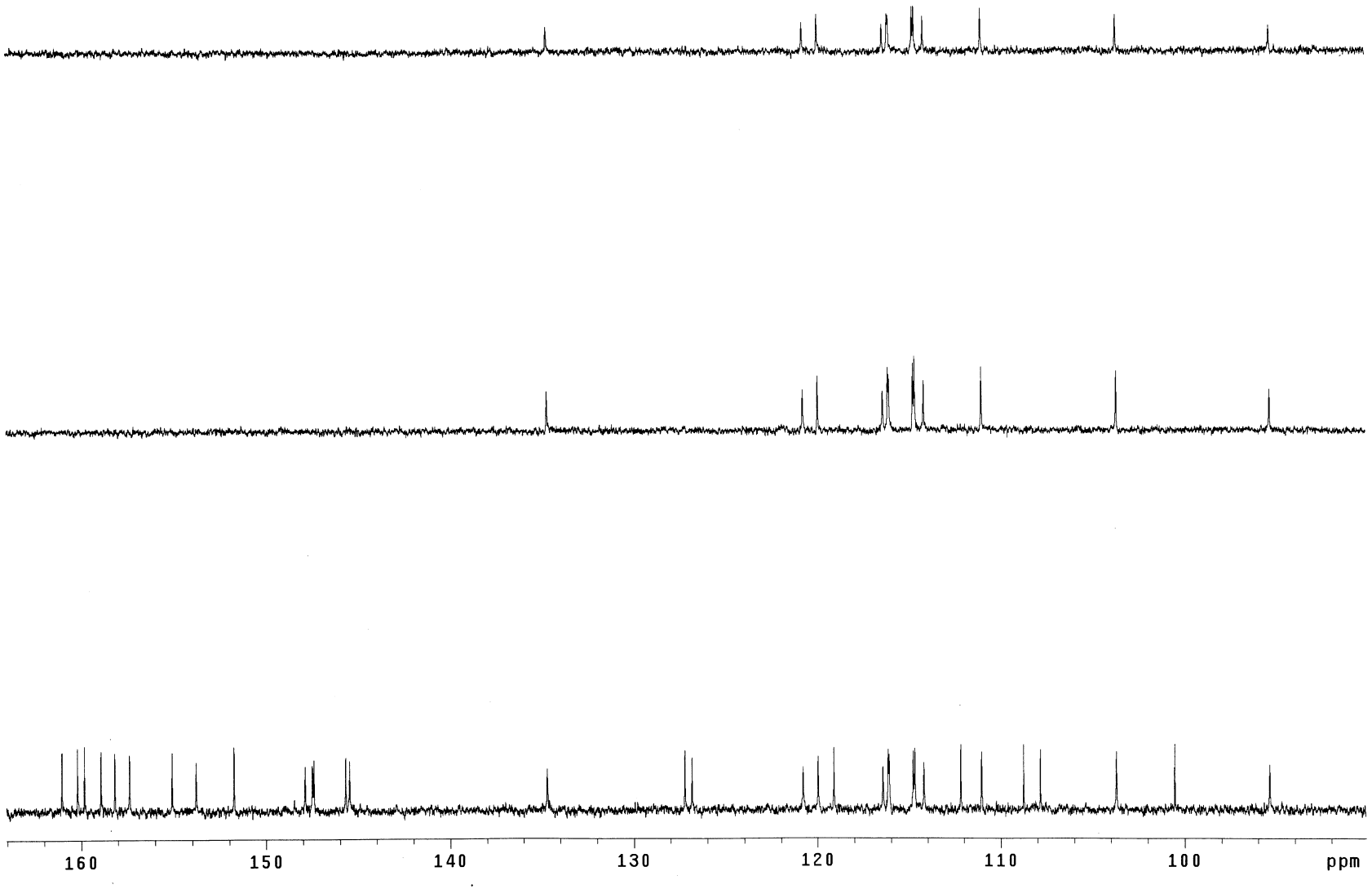


DEPT spectrum of Phelligridin H (**1**)

INOVA-500 DEPT-NMR C155 IN DMSO 06.01

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: DEPT



^{1}H-^{1}H COSY spectrum of Phelligridin H (**1**)

```
INOVA-501 gCOSY B96G IN DMSO 04.04.30

 File: PROTON

 Solvent: DMSO
 Temp. 25.0 C / 298.1 K
INOVA-500  "NMR501"

 Relax. delay 1.000 sec
 Acq. time 0.229 sec
 Width     4473.3 Hz
 2D Width 4473.3 Hz
 2 repetitions
 300 increments
OBSERVE    H1, 499.7474033 MHz
DATA PROCESSING
 Sine bell 0.114 sec
F1 DATA PROCESSING
 Sine bell 0.033 sec
FT size 2048 x 2048
Total time 13 min, 5 sec
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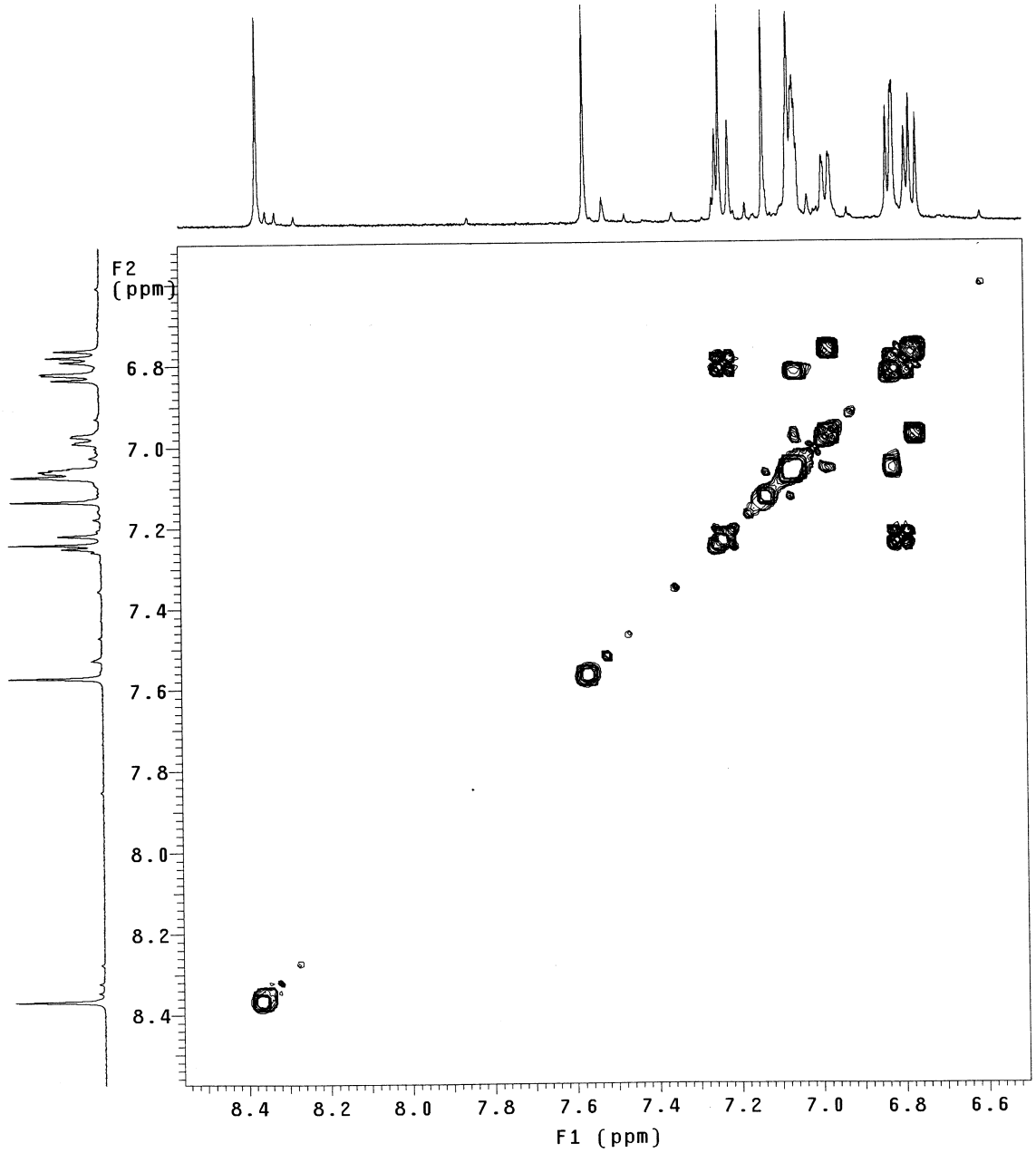
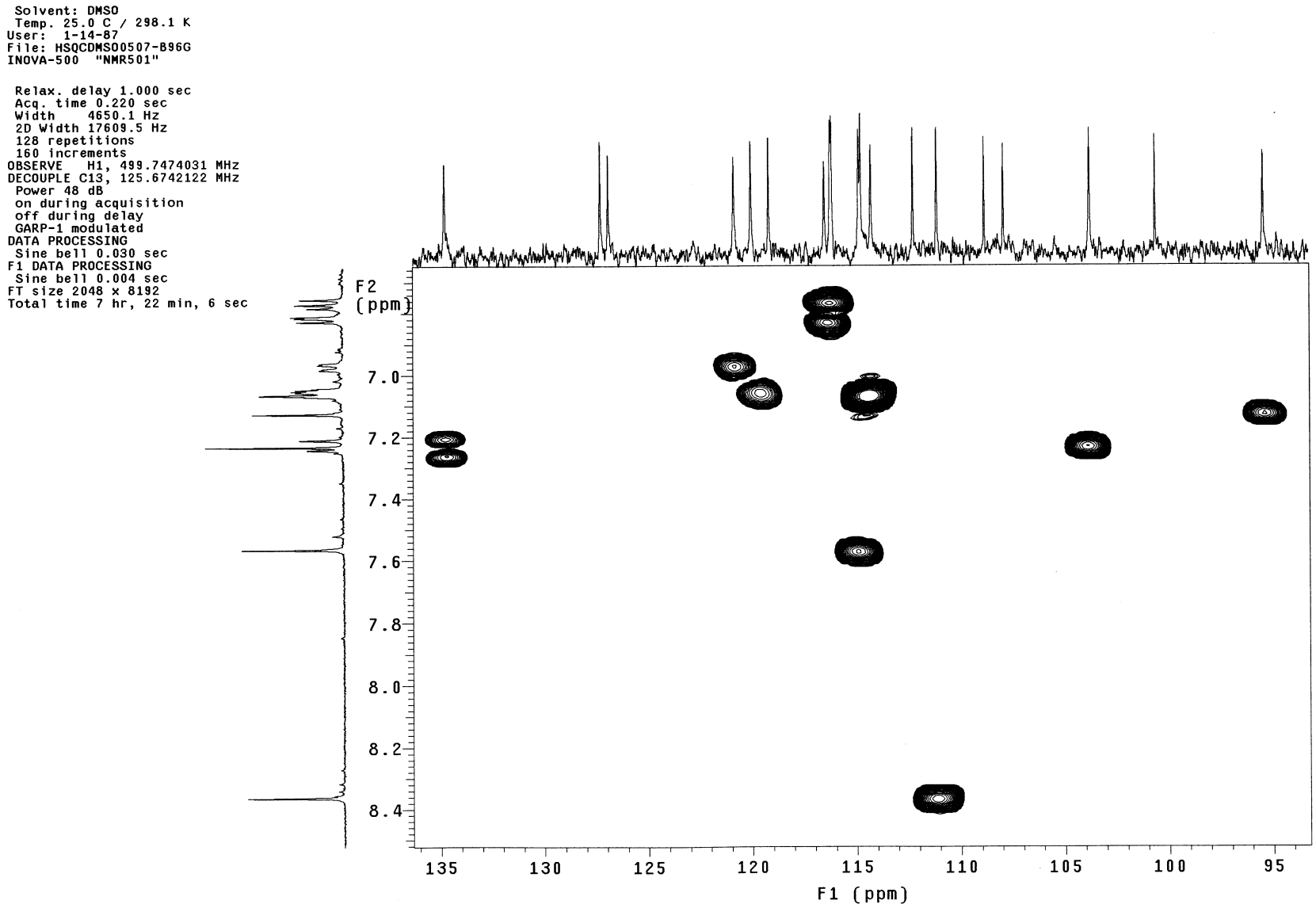


HSQC spectrum of Phelligridin H

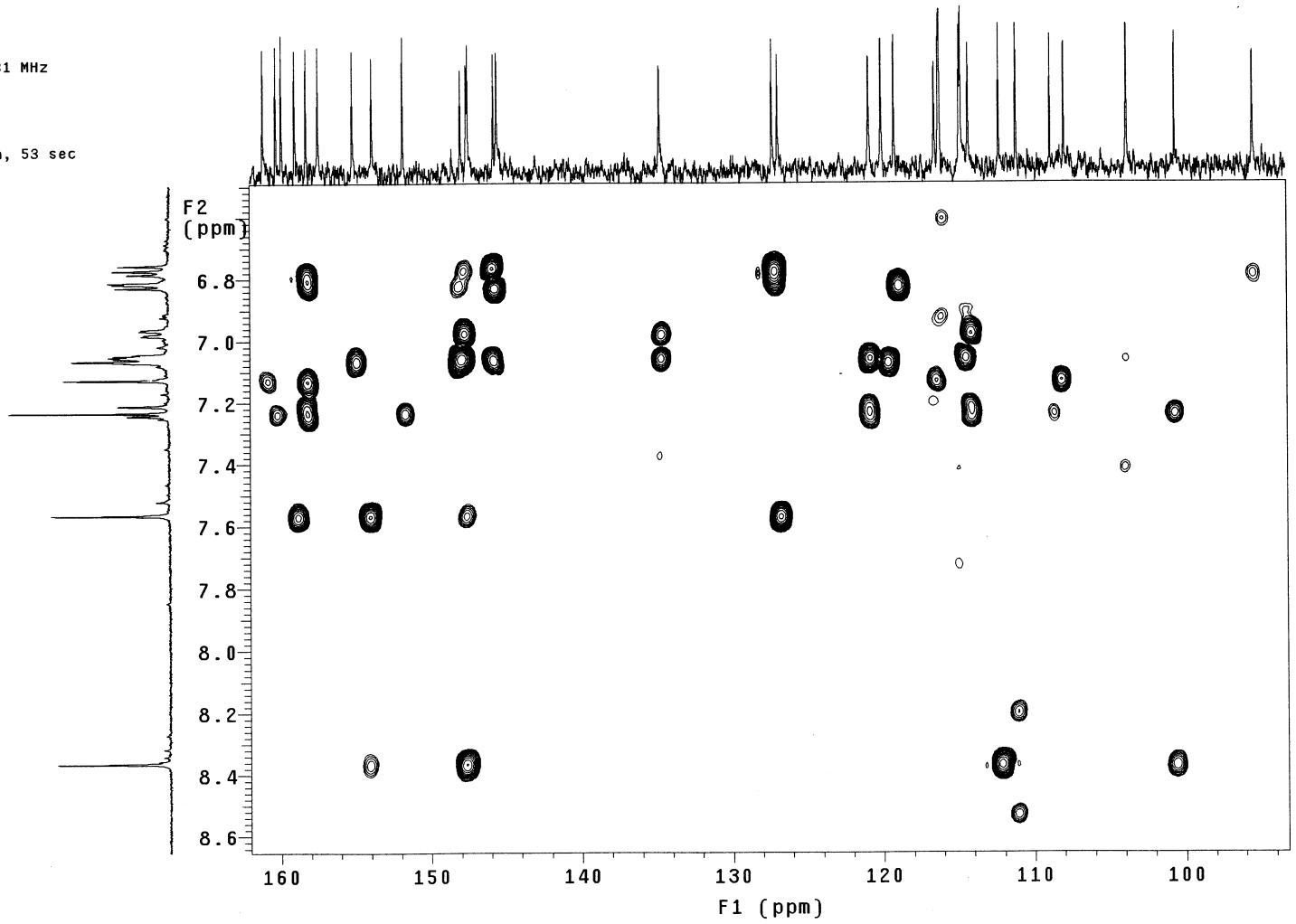


INOVA-501 gHMBC B96G IN DMSO 04.05.07

HMBC spectrum of Phelligridin H (**1**)

Solvent: DMSO
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: HMBCDMSO0507-B96G
INOVA-500 "NMR501"

Relax. delay 1.000 sec
Acq. time 0.214 sec
Width 4782.4 Hz
2D Width 22624.4 Hz
192 repetitions
320 increments
OBSERVE H1, 499.7474031 MHz
DATA PROCESSING
Sine bell 0.032 sec
F1 DATA PROCESSING
Sine bell 0.007 sec
FT size 2048 x 8192
Total time 22 hr, 14 min, 53 sec

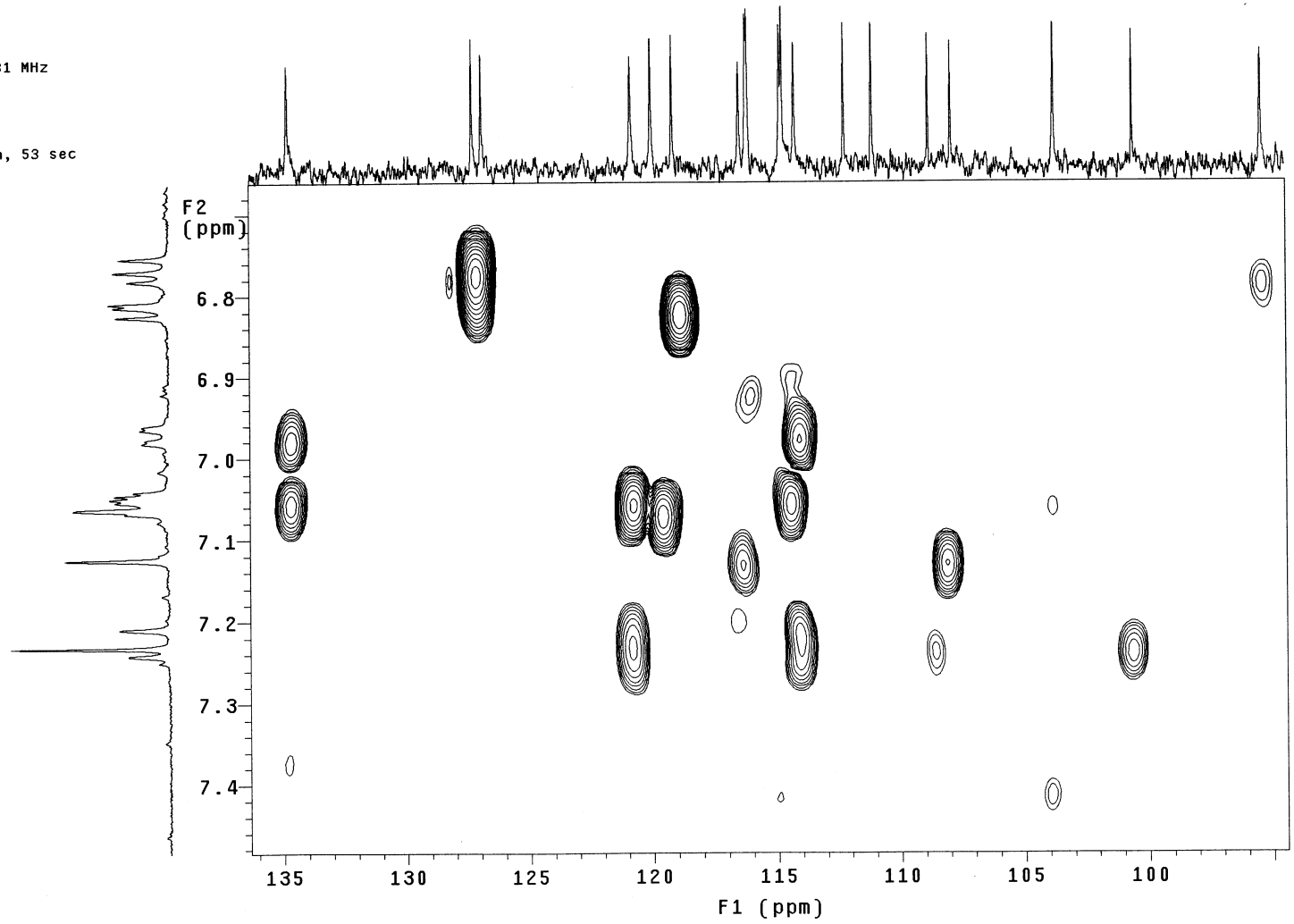


INOVA-501 gHMBC B96G IN DMSO 04.05.07

Regional enlarged HMBC spectrum of Phelligridin H (**1**)

Solvent: DMSO
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: HMBCDMSO0507-B96G
INOVA-500 "NMR501"

Relax. delay 1.000 sec
Acq. time 0.214 sec
Width 4782.4 Hz
2D Width 22624.4 Hz
192 repetitions
320 increments
OBSERVE H1, 499.7474031 MHz
DATA PROCESSING
Sine bell 0.032 sec
F1 DATA PROCESSING
Sine bell 0.007 sec
FT size 2048 x 8192
Total time 22 hr, 14 min, 53 sec

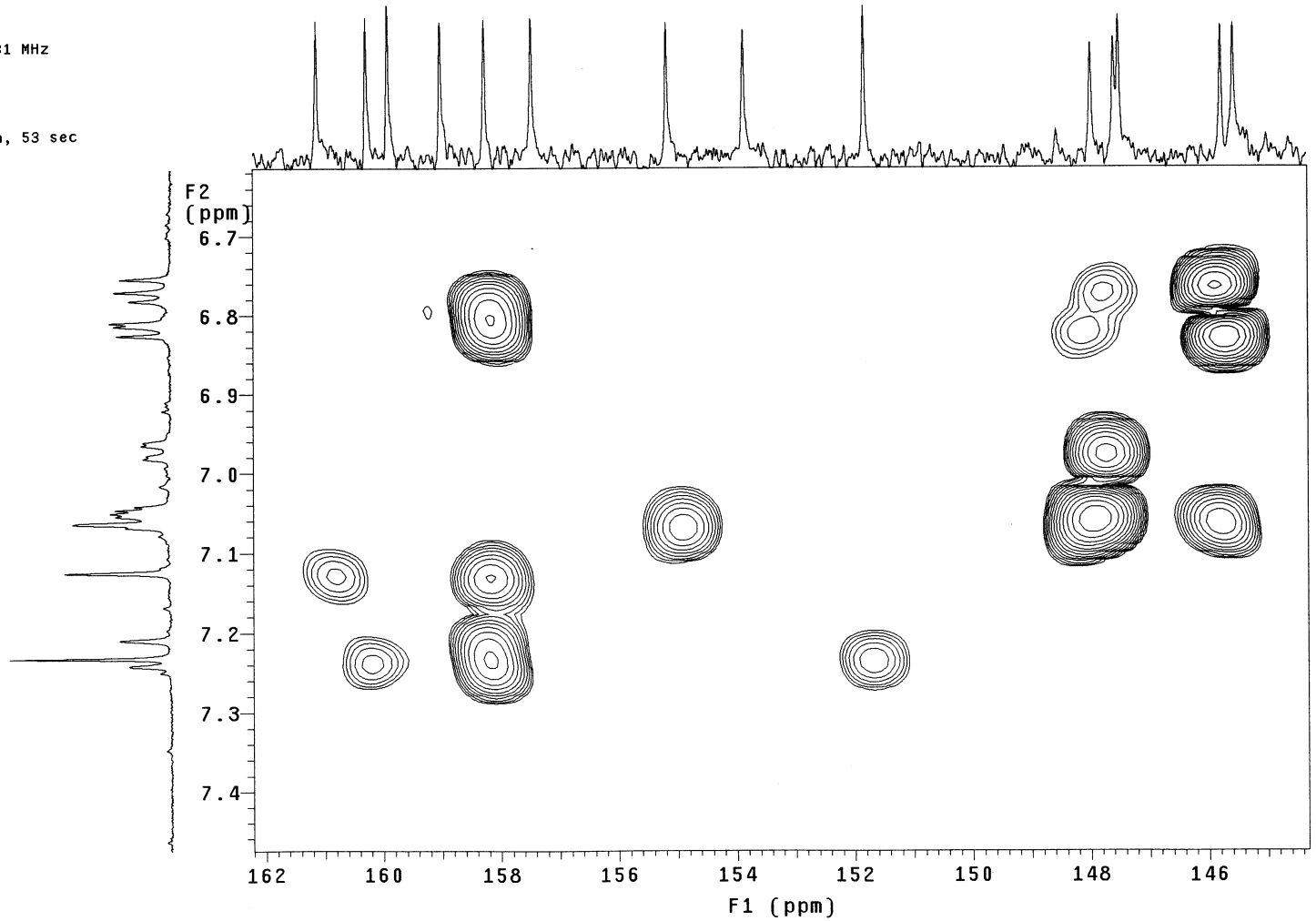


INOVA-501 gHMBC B96G IN DMSO 04.05.07

Regional enlarged HMBC spectrum of Phelligridin H (**1**)

Solvent: DMSO
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: HMBCDMSO0507-B96G
INOVA-500 "NMR501"

Relax. delay 1.000 sec
Acq. time 0.214 sec
Width 4782.4 Hz
2D Width 22624.4 Hz
192 repetitions
320 increments
OBSERVE H1, 499.7474031 MHz
DATA PROCESSING
Sine bell 0.032 sec
F1 DATA PROCESSING
Sine bell 0.007 sec
FT size 2048 x 8192
Total time 22 hr, 14 min, 53 sec

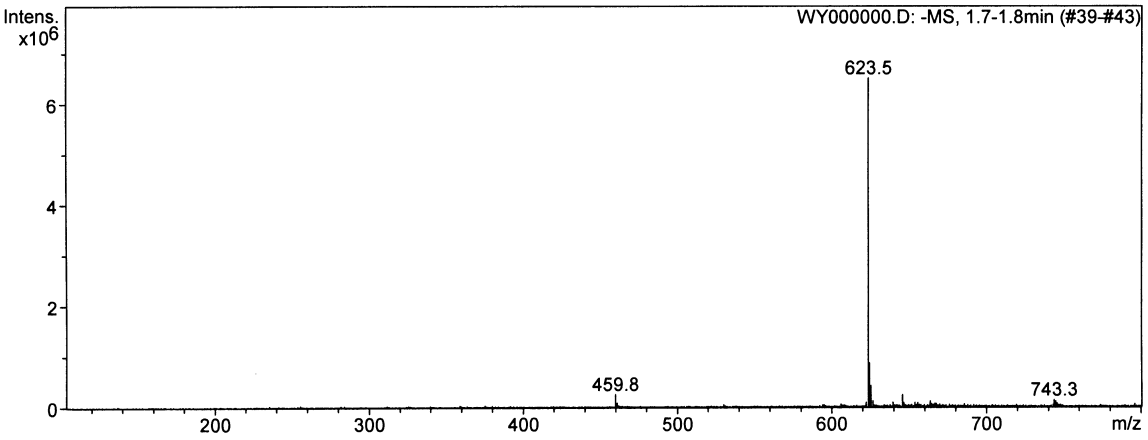


Single Mass Spectrum Deconvolution Report

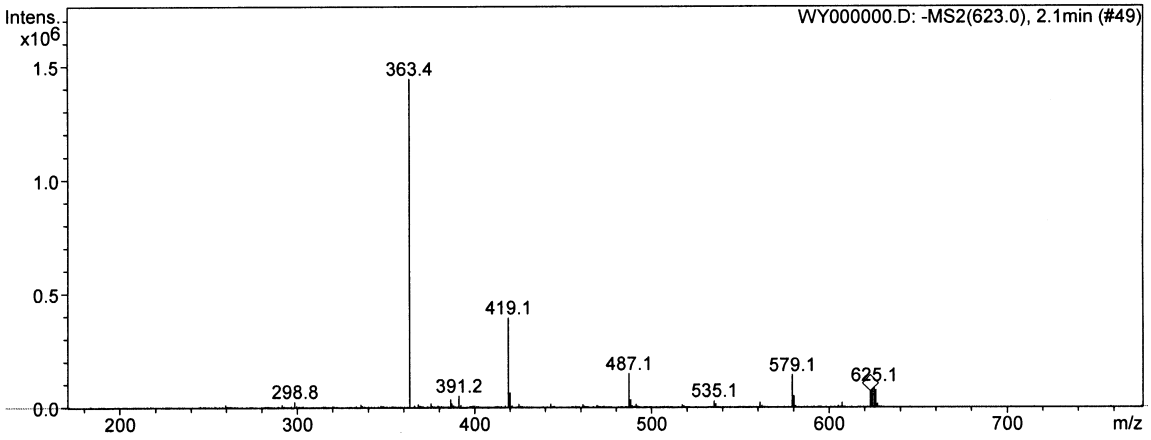
Analysis Name: WY000000.D **Instrument:** LC-MSD-Trap-SL **Print Date:** 11/28/03 17:26:48
Method: Copy of TEST.M **Operator:** Administrator **Acq. Date:** 11/28/03 17:17:24
Sample Name: E13D
Analysis Info:

Acquisition Parameter:

Mass Range Mode	Std/Normal	Trap Drive	61.0	Scan Begin	100 m/z
Ion Polarity	Positive	Skim 1	-40.0 Volt	Scan End	800 m/z
Ion Source Type	ESI	Skim 2	5.0 Volt	Averages	20 Spectra
Dry Temp (Set)	325 °C	Octopole RF Amplitude	150.0 Vpp	Max. Accu Time	300000 µs
Nebulizer (Set)	20.00 psi	Capillary Exit	-137.7 Volt	ICC Target	30000
Dry Gas (Set)	6.00 l/min			Charge Control	on



Component	Deconvoluted Molecule Mass	Absolute Abundance	Relative Abundance



Component	Deconvoluted Molecule Mass	Absolute Abundance	Relative Abundance

ESI-MS of Phelligridin I (**2**)

Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

SIOC

Instrument:

IonSpec 4.7 Tesla FTMS

Card Serial Number: I041195

Sample Serial Number: SH-W2

Operator: Hua Qin Date: 2004/08/03

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 625.0998 ± 0.003
Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
O	15.994915	0	30

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

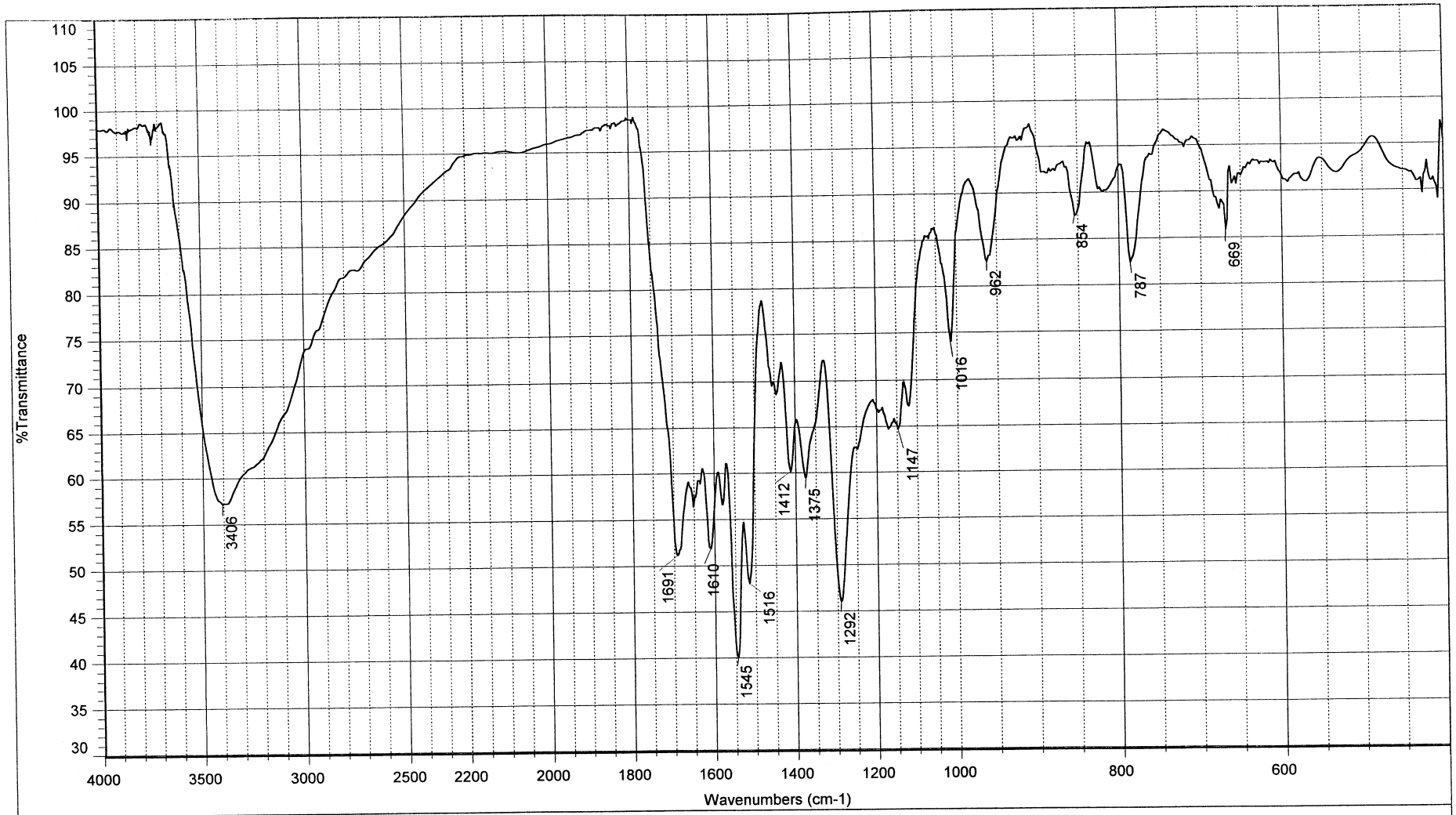
Search Results:

Number of Hits = 2

m/z	Delta m/z	DBE	Formula
625.10118	-0.00138	45.5	$C_{51}H_{13}^{+1}$
625.09767	0.00213	23.5	$C_{33}H_{21}O_{13}^{+1}$

HR-MS of Phelligridin I (**2**)

IR spectrum of Phelligridin I (**2**)



Date: Thu Apr 01 10:23:52 2004

Sample Name: E13D (KBr)

Scans: 64

检测单位：国家药物及代谢产物分析研究中心

Resolution: 4.000

检测仪器：美国尼高力公司傅立叶变换红外光谱仪: IMPACT - 400

THERMO SPECTRONIC ~ VISION32 SOFTWARE V1.25

Batch Information - scan006

Batch Type	Scan	Operator Name	(None Entered)
Instrument ID	110514	Aborted	No

Results Table - scan006

Data Mode Absorbance

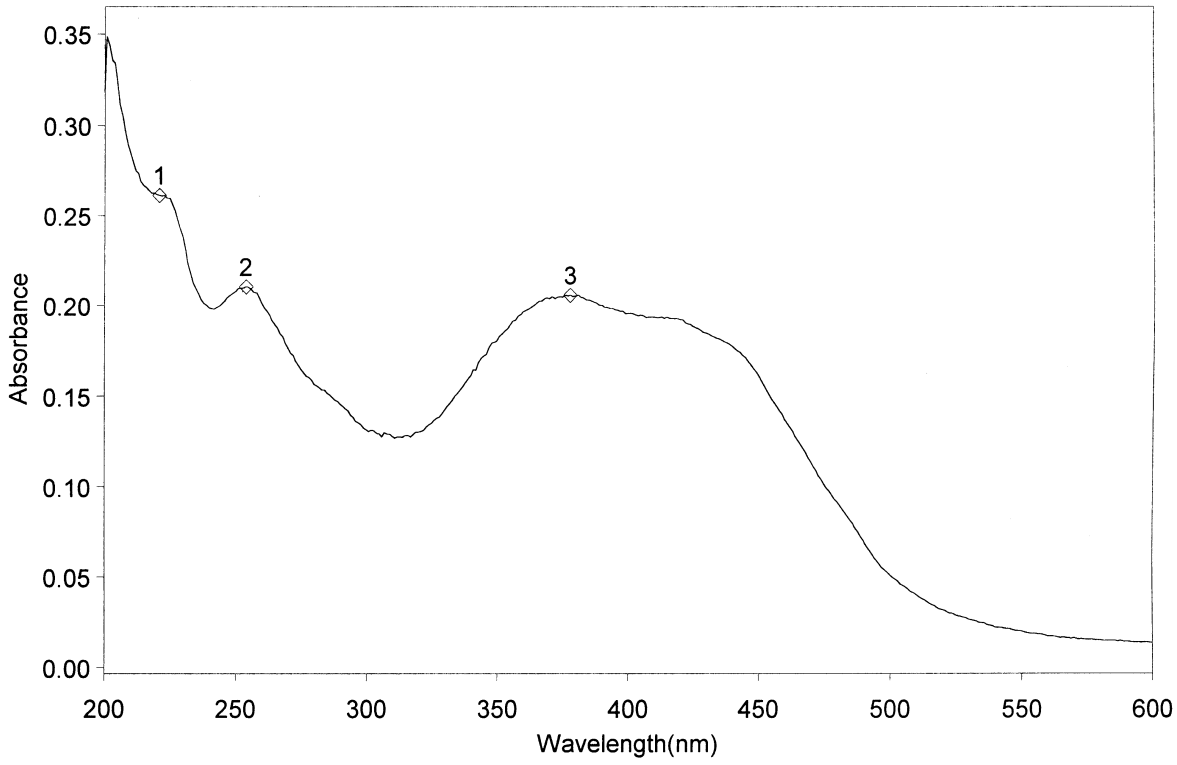
	A	B	C	D	E
1	**E13C4D**		**1**	**2**	**3**
2	Cycle01	nm	221.0	254.0	378.0
3	Manual	A	.261	.210	.206

All calculations have been performed to double precision as defined by ANSI/IEEE STD 754-1985 but have been rounded for display purposes.

E13C4D

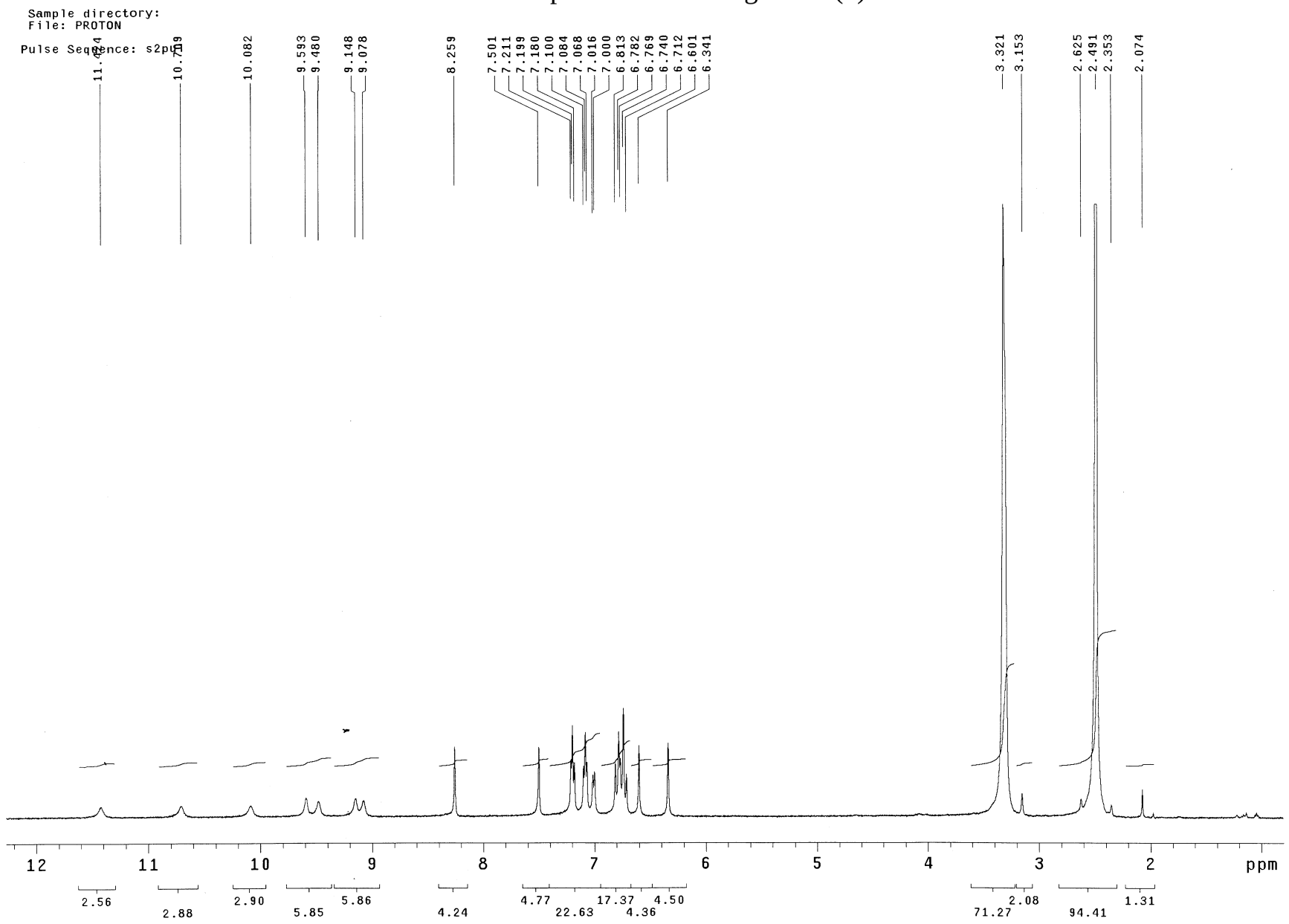
Description 0.074mg/10mlMeOH

E13C4D,Cycle01

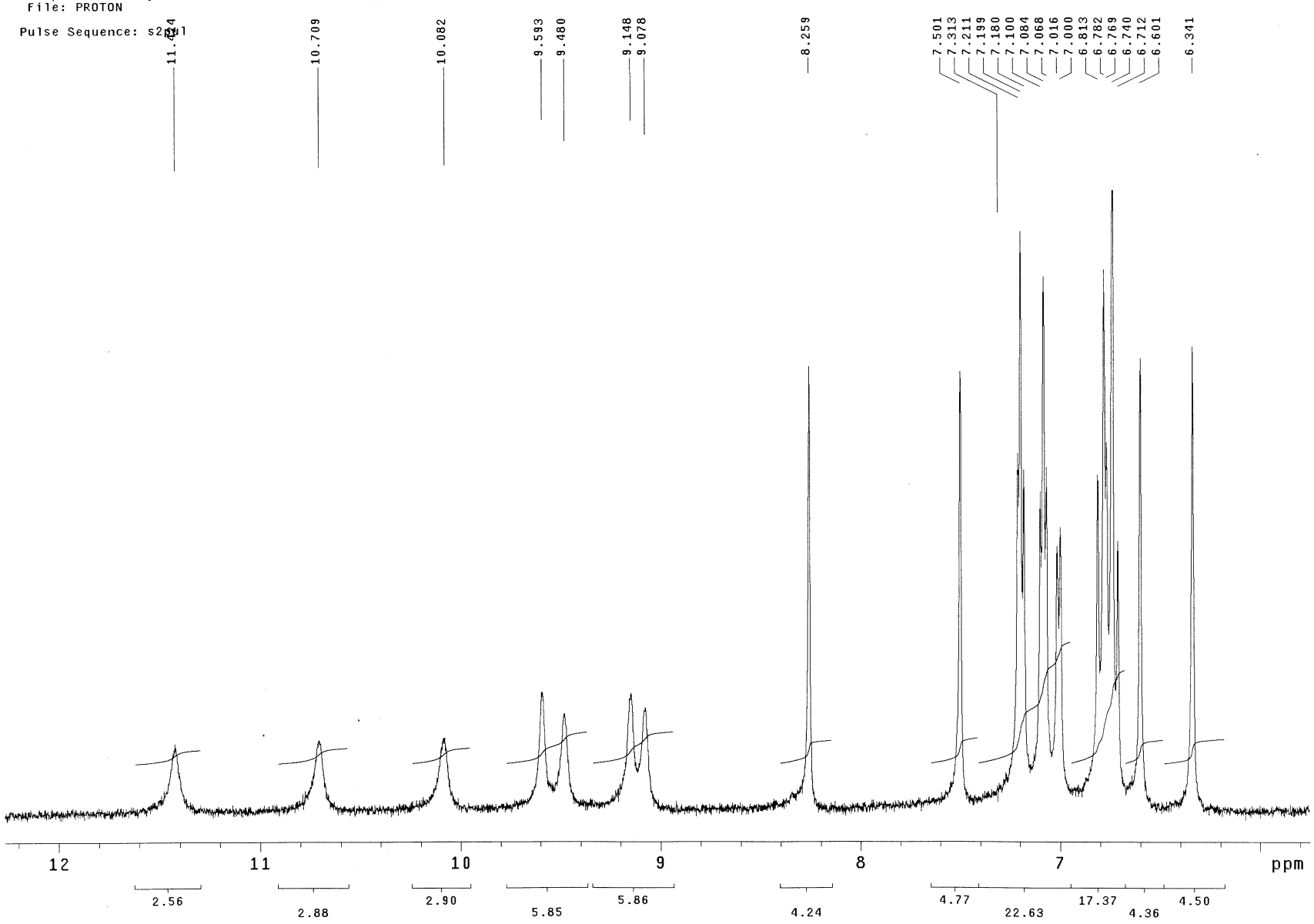


UV spectrum of Phelligridin I (**2**)

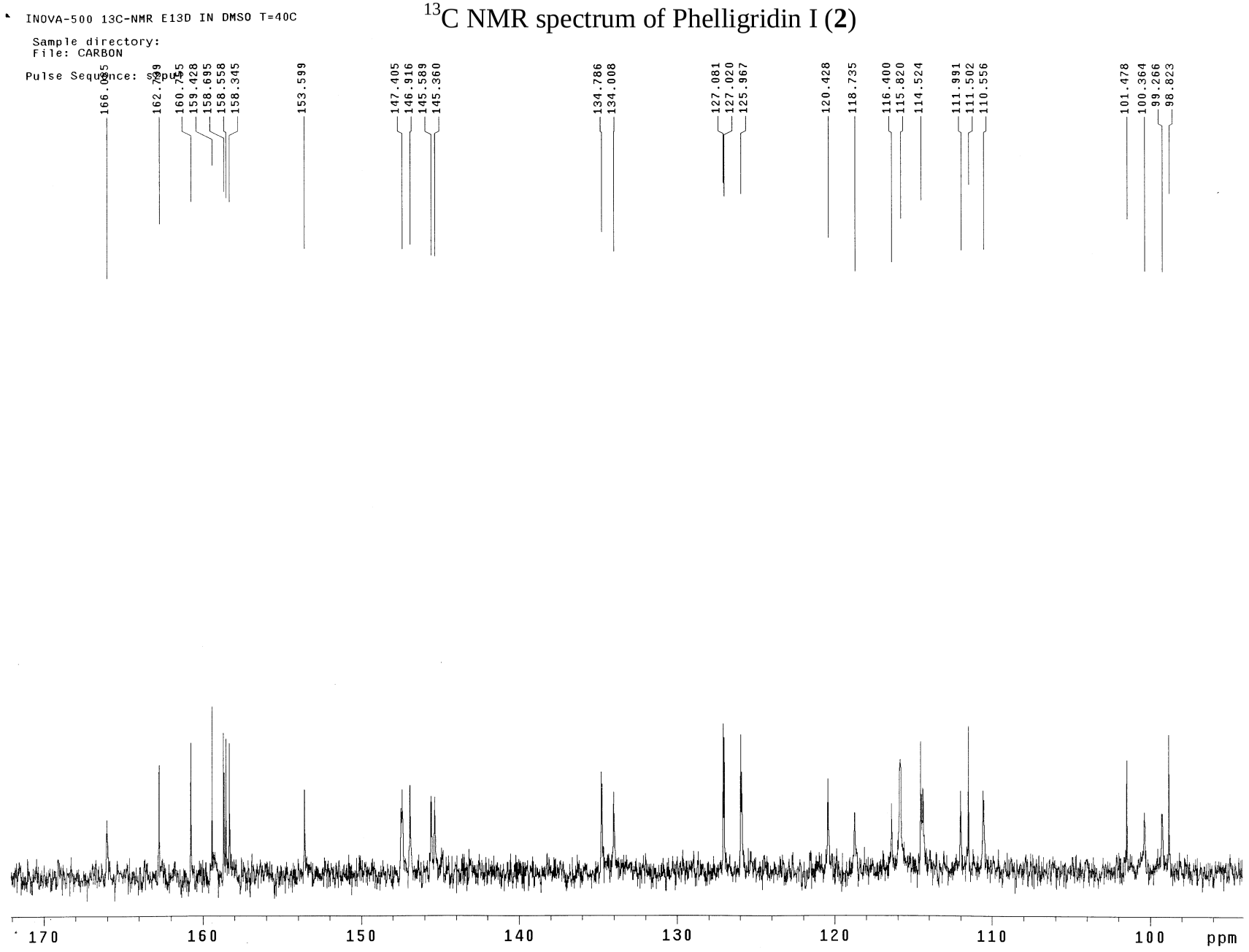
^{1}H NMR spectrum of Phelligridin I (**2**)



Regional enlarged ^{1}H NMR spectrum of Phelligridin I (**2**)



^{13}C NMR spectrum of Phelligridin I (**2**)

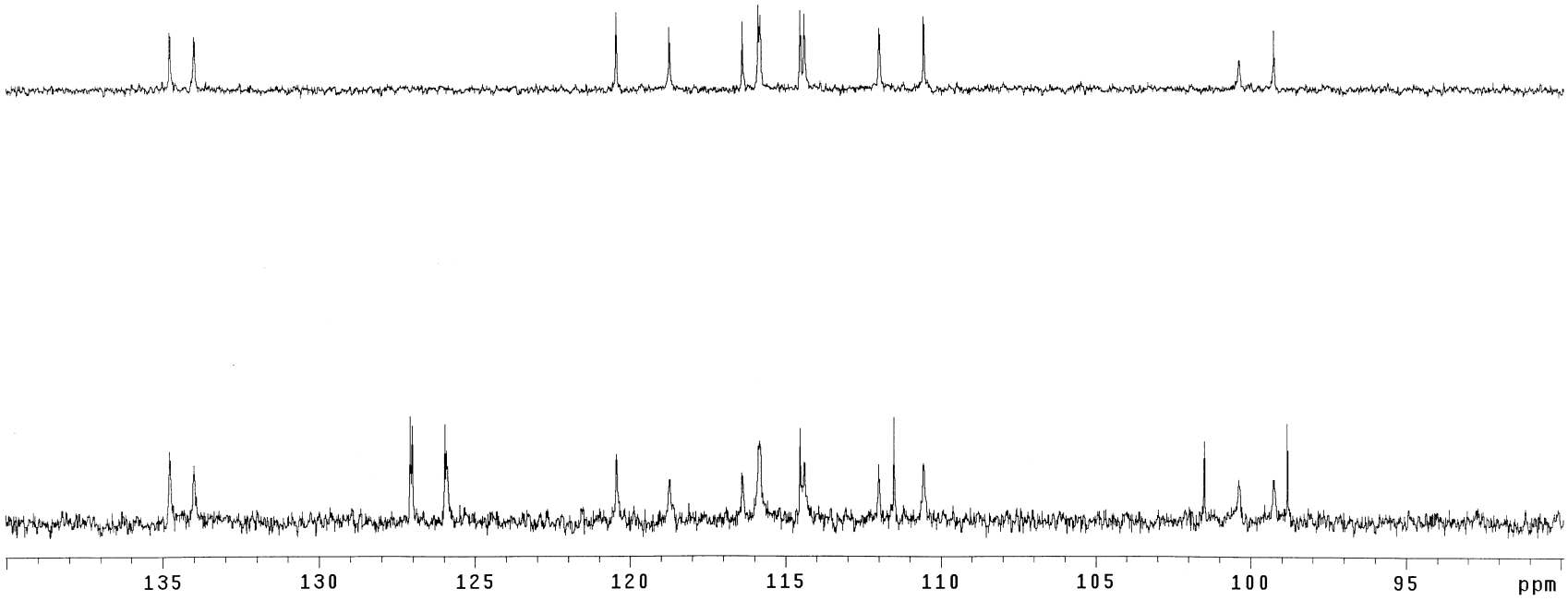


INOVA-500 DEPT-NMR E13D IN DMSO

Sample directory:
File: CARBON

Pulse Sequence: DEPT

DEPT spectrum of Phelligridin I (**2**)



^{1}H-^{1}H COSY spectrum of Phelligridin I (**2**)

```
INOVA-501 gCOSY E13D IN DMSO 03.11.26

 Solvent: DMSO
 Temp. 40.0 C / 313.1 K
INOVA-500  "NMR501"

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 Acq. time 0.196 sec
 Width     5228.8 Hz
 2D Width 5228.8 Hz
 4 repetitions
 256 increments
OBSERVE    H1, 499.7474034 MHz
DATA PROCESSING
 Sq. sine bell 0.098 sec
F1 DATA PROCESSING
 Sq. sine bell 0.015 sec
FT size 2048 x 2048
Total time 21 min, 22 sec
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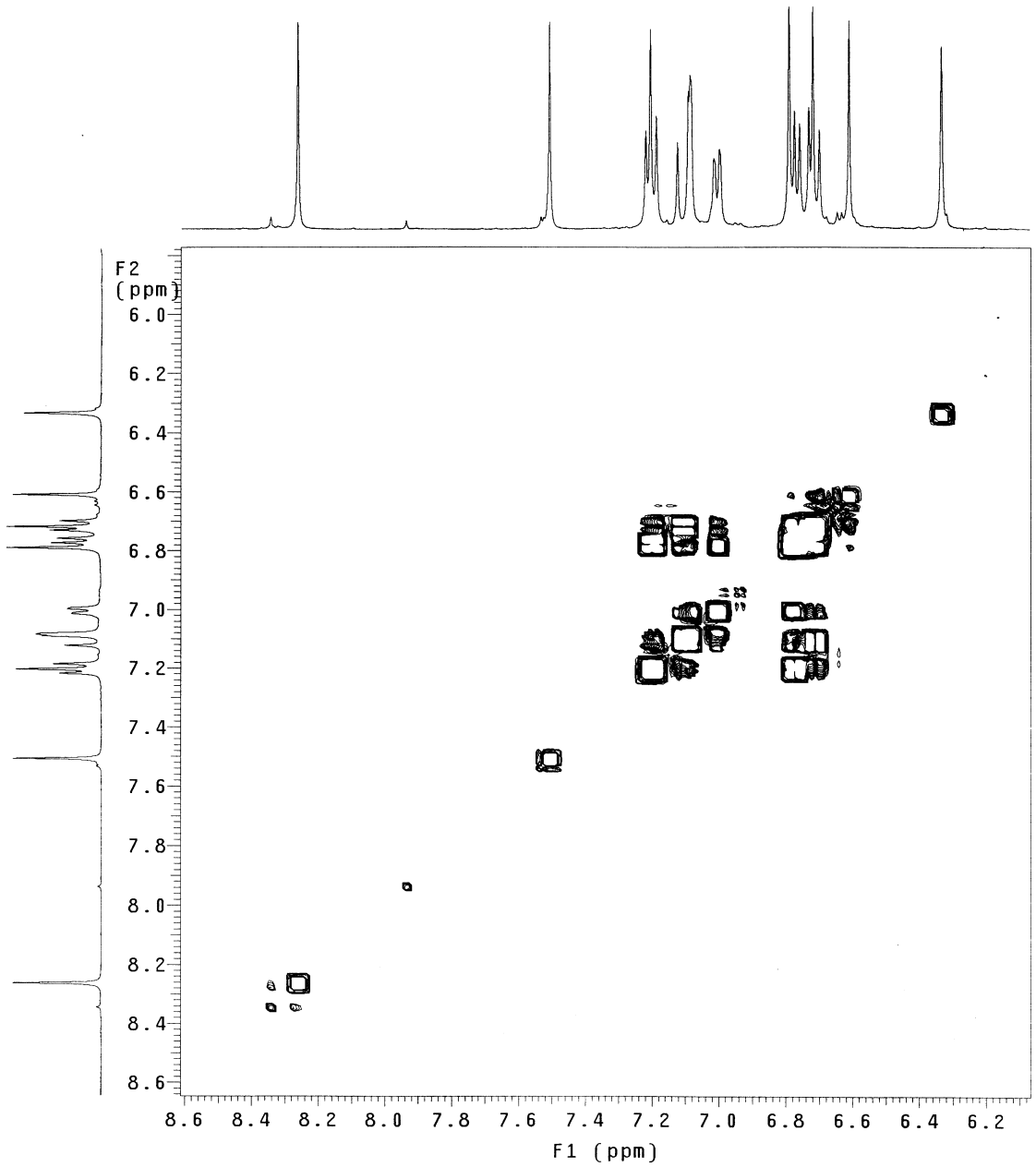
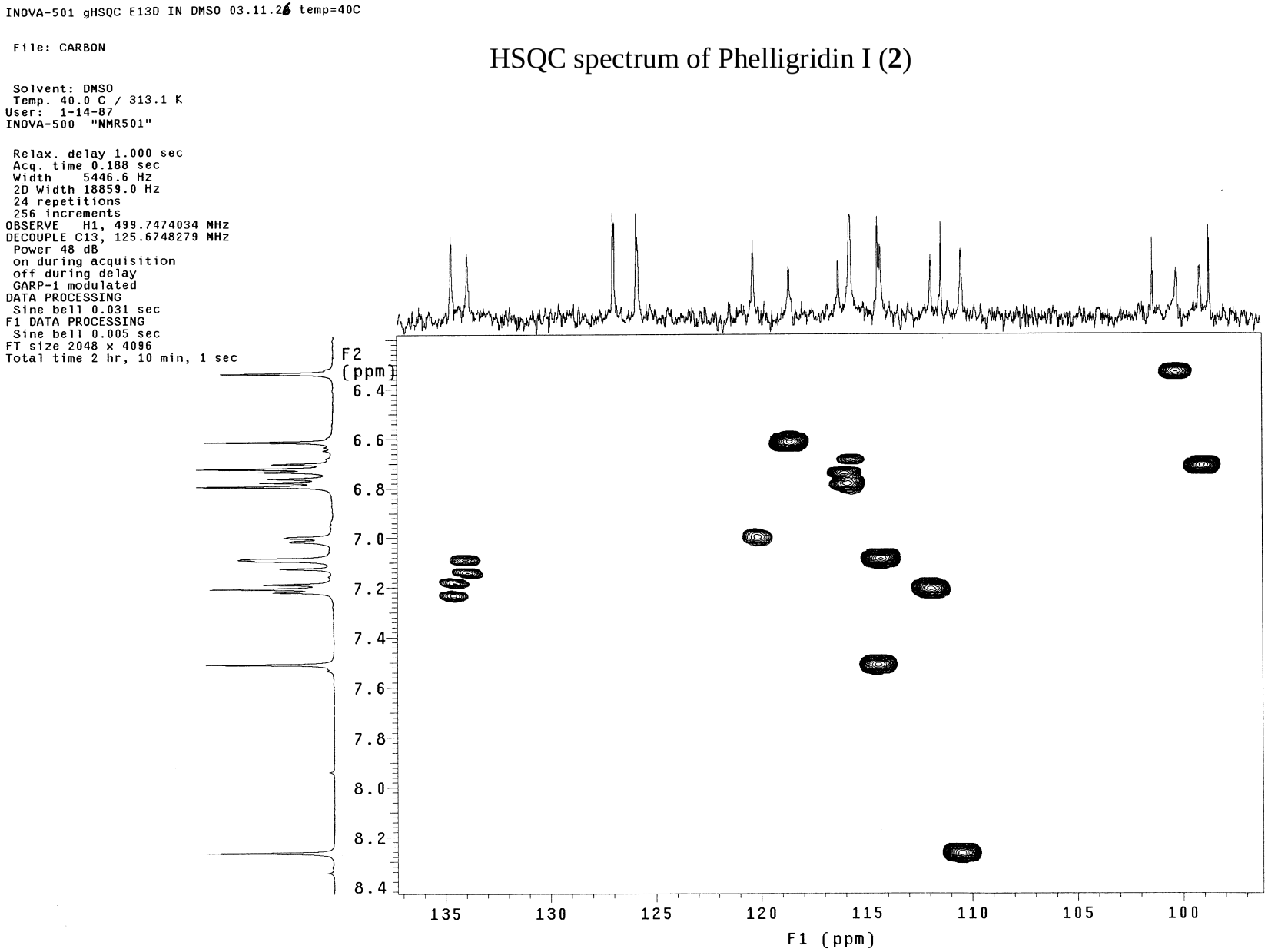


HSQC spectrum of Phelligridin I (**2**)



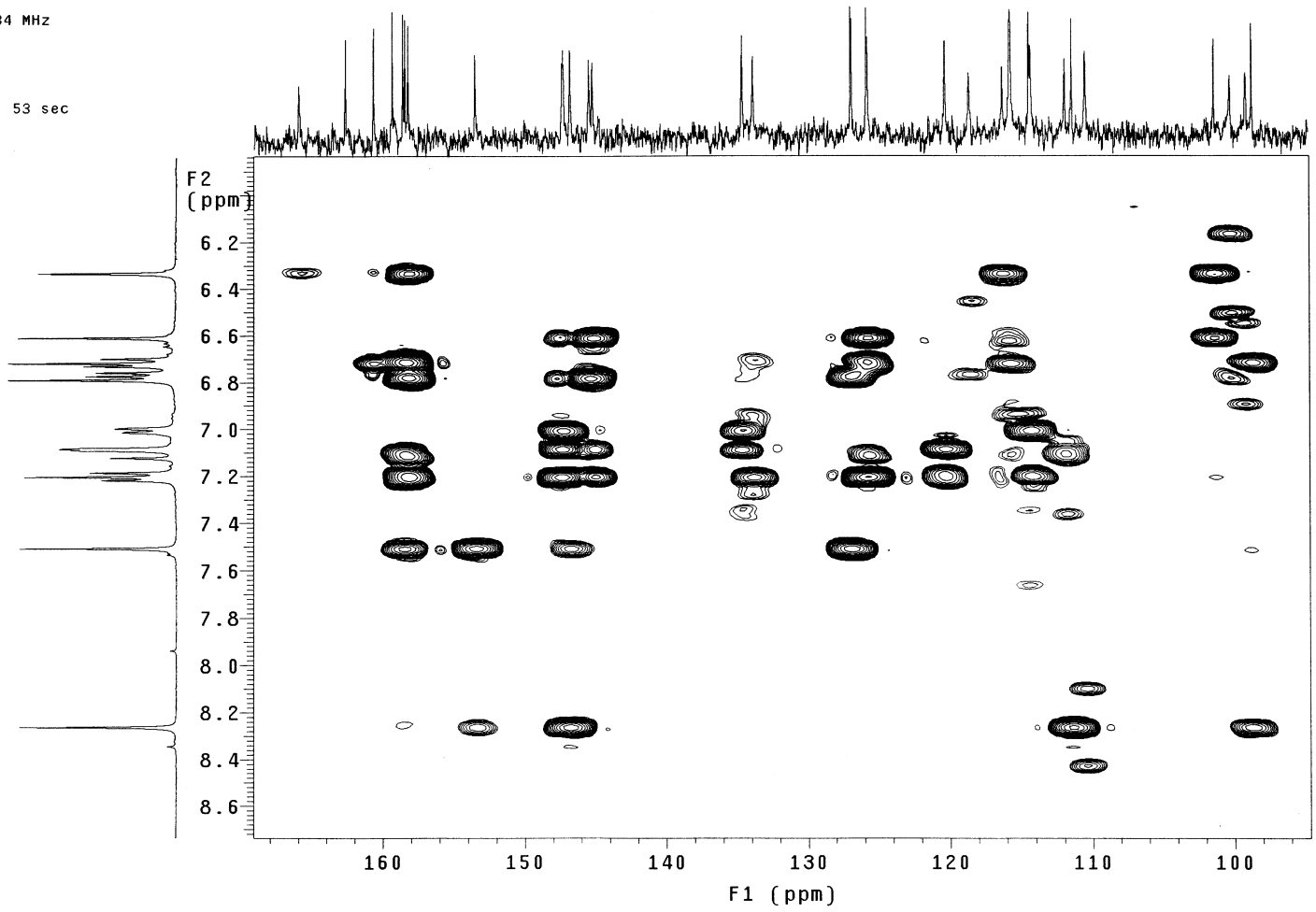
INOVA-501 gHMBC E13D IN DMSO 03.11.2[illegible] temp=40C

File: CARBON

Solvent: DMSO
Temp. 40.0 C / 313.1 K
User: 1-14-87
INOVA-500 "NMR501"

Relax. delay 1.000 sec
Acq. time 0.180 sec
Width 5683.4 Hz
2D Width 18859.0 Hz
32 repetitions
256 increments
OBSERVE H1, 499.7474034 MHz
DATA PROCESSING
Sine bell 0.037 sec
F1 DATA PROCESSING
Sine bell 0.003 sec
FT size 2048 x 4096
Total time 2 hr, 53 min, 53 sec

HMBC spectrum of Phelligridin I (**2**)



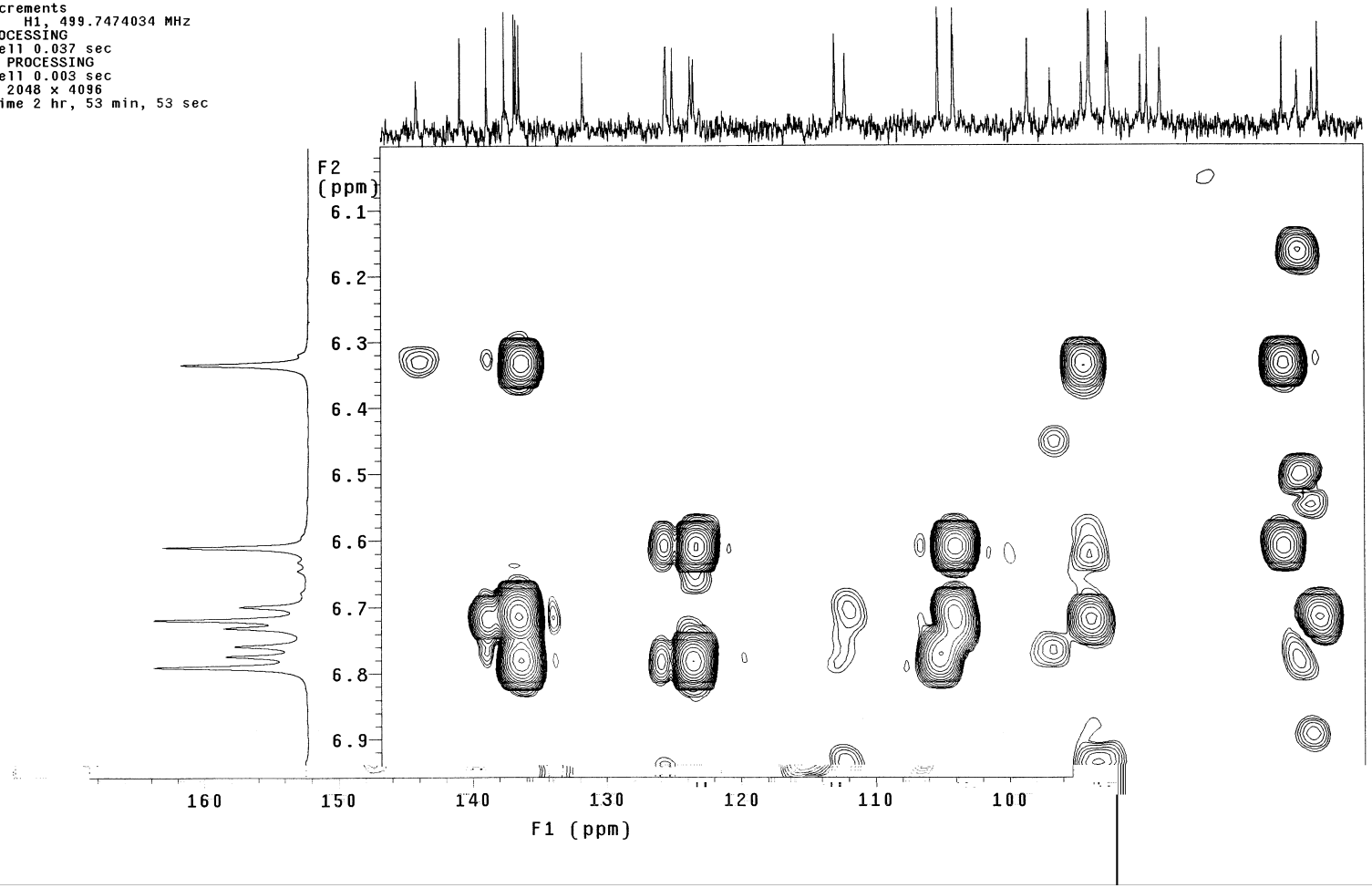
INOVA-501 gHMBC E13D IN DMSO 03.11.2[illegible] temp=40C

File: CARBON

Solvent: DMSO
Temp. 40.0 C / 313.1 K
User: 1-14-87
INOVA-500 "NMR501"

Relax. delay 1.000 sec
Acq. time 0.180 sec
Width 5683.4 Hz
2D Width 18859.0 Hz
32 repetitions
256 increments
OBSERVE H1, 499.7474034 MHz
DATA PROCESSING
Sine bell 0.037 sec
F1 DATA PROCESSING
Sine bell 0.003 sec
FT size 2048 x 4096
Total time 2 hr, 53 min, 53 sec

Regional enlarged HMBC spectrum of Phelligridin I (**2**)



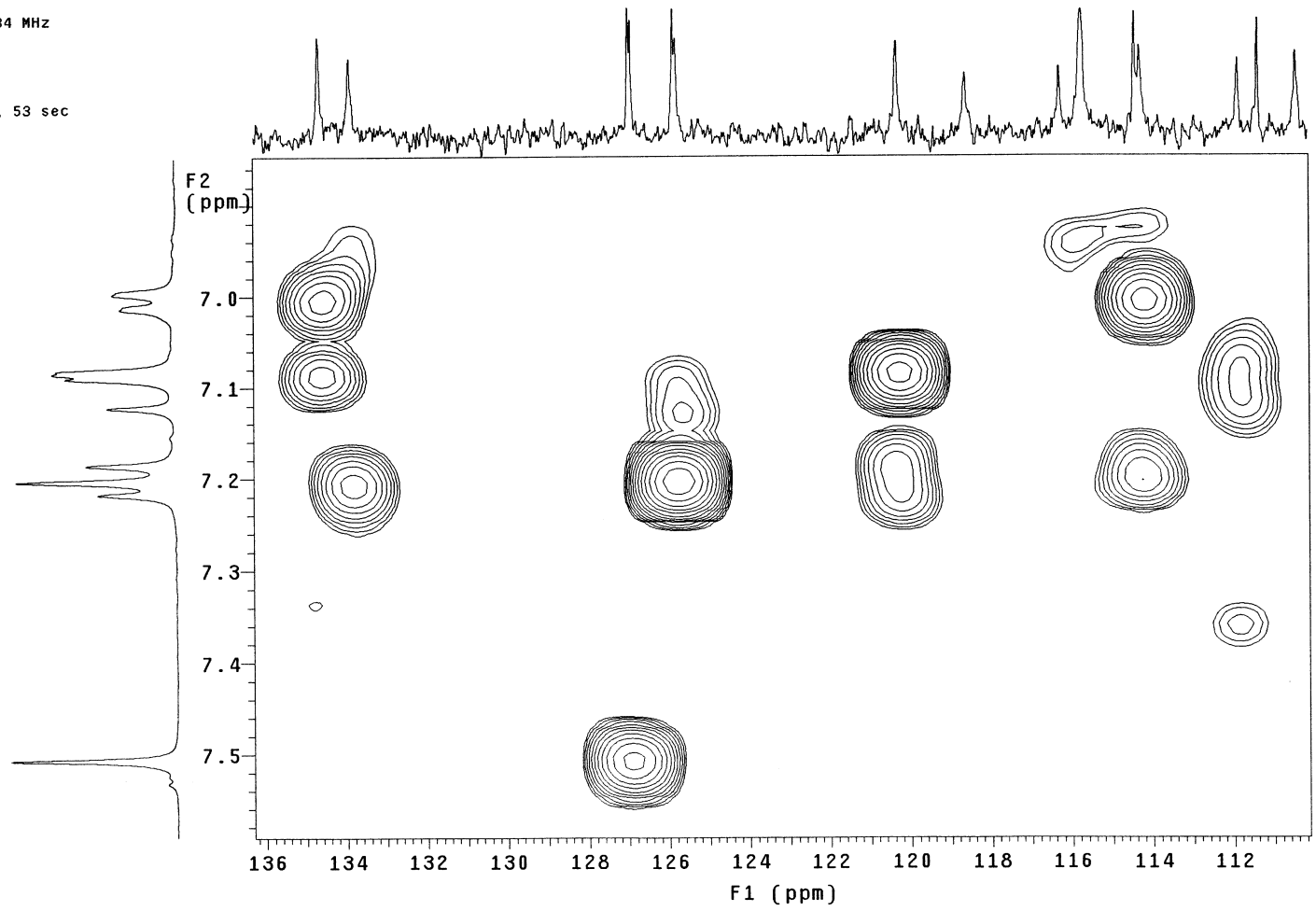
INOVA-501 gHMBC E13D IN DMSO 03.11.2[illegible] temp=40C

File: CARBON

Solvent: DMSO
Temp. 40.0 C / 313.1 K
User: 1-14-87
INOVA-500 "NMR501"

Relax. delay 1.000 sec
Acq. time 0.180 sec
Width 5683.4 Hz
2D Width 18859.0 Hz
32 repetitions
256 increments
OBSERVE H1, 499.7474034 MHz
DATA PROCESSING
Sine bell 0.031 sec
F1 DATA PROCESSING
Sine bell 0.004 sec
FT size 2048 x 4096
Total time 2 hr, 53 min, 53 sec

Regional enlarged HMBC spectrum of Phelligridin I (**2**)



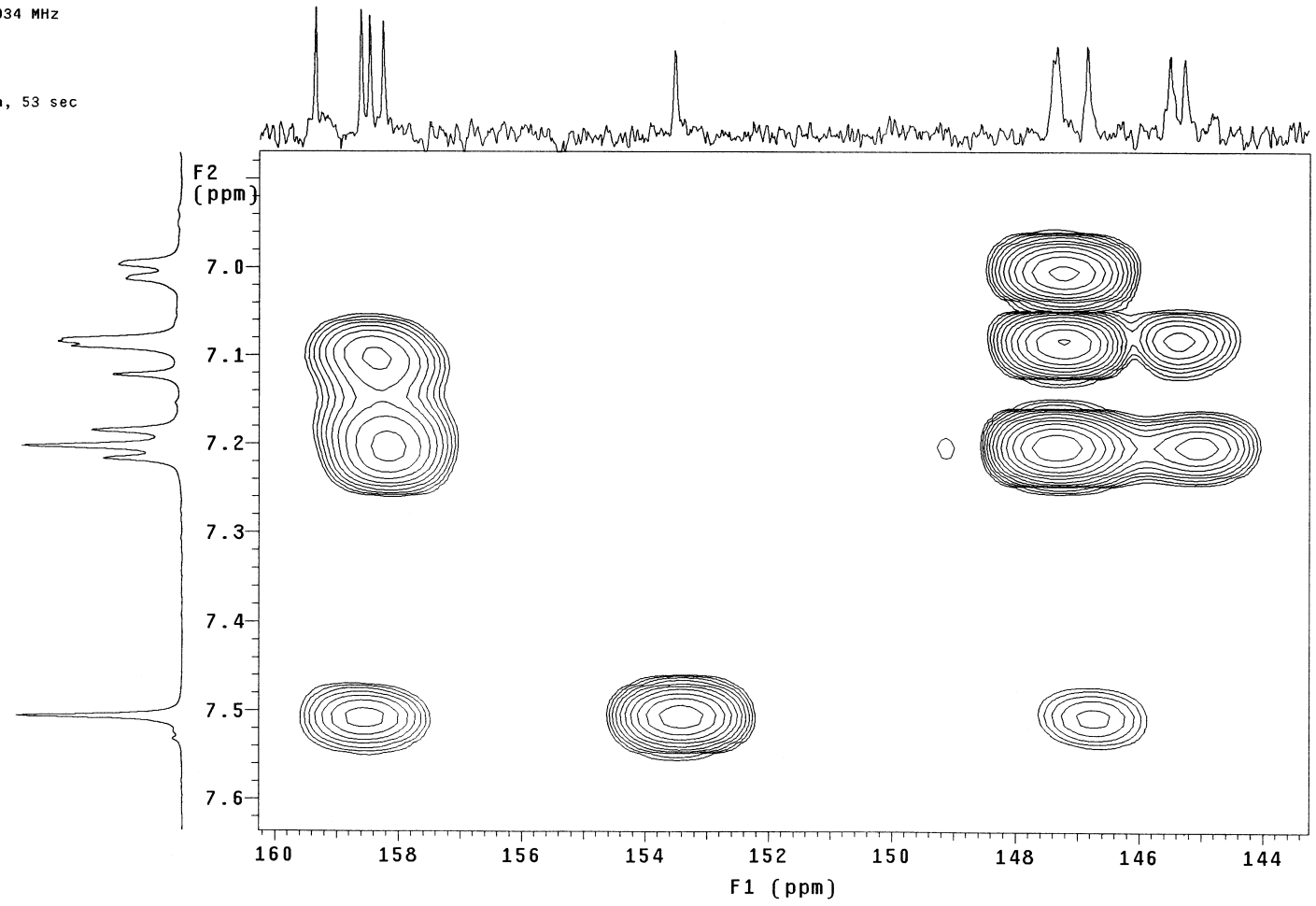
INOVA-501 gHMBC E13D IN DMSO 03.11.26 temp=40C

File: CARBON

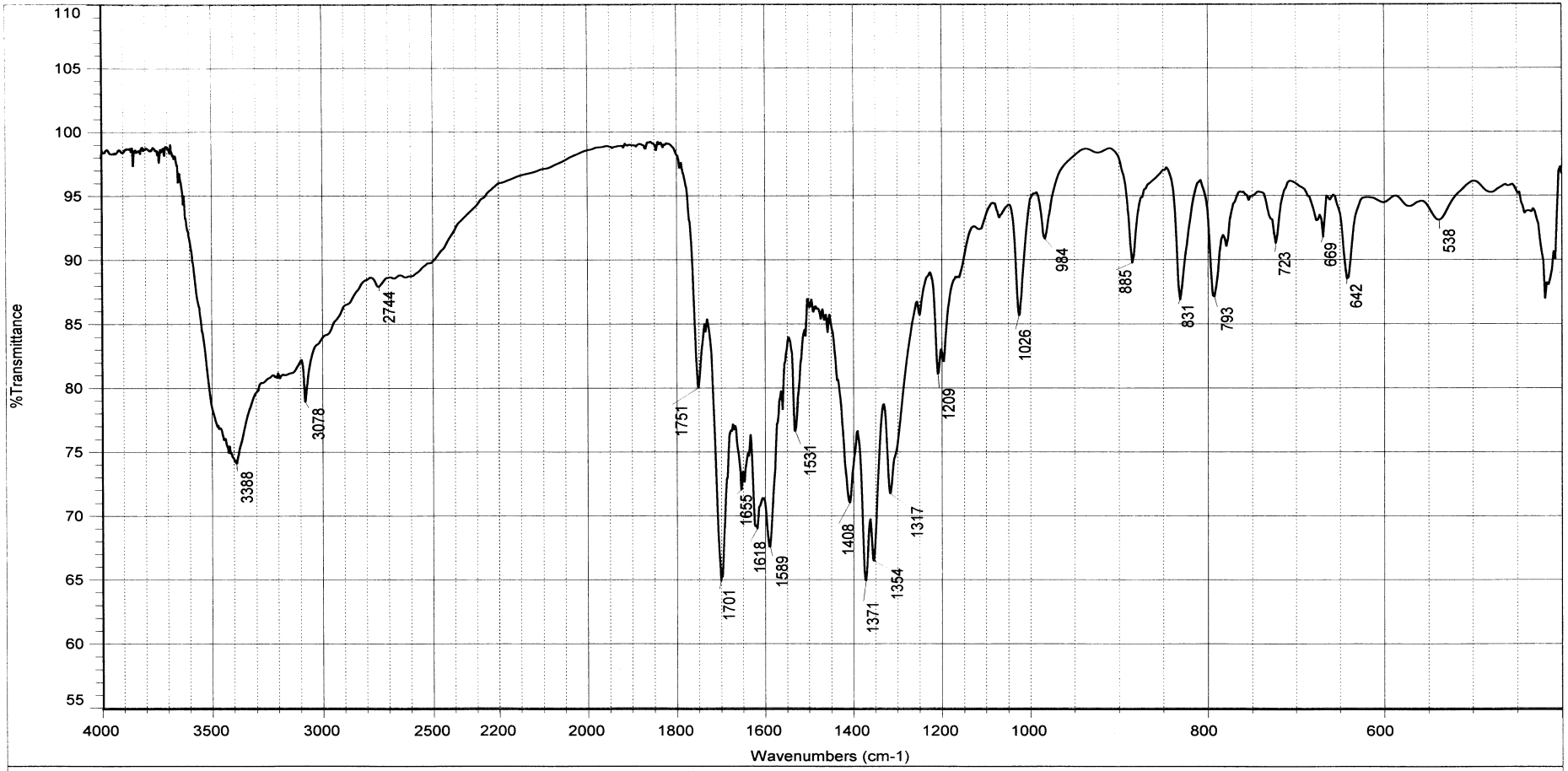
Solvent: DMSO
Temp. 40.0 C / 313.1 K
User: 1-14-87
INOVA-500 "NMR501"

Relax. delay 1.000 sec
Acq. time 0.180 sec
Width 5683.4 Hz
2D Width 18859.0 Hz
32 repetitions
256 increments
OBSERVE H1, 499.7474034 MHz
DATA PROCESSING
Sine bell 0.031 sec
F1 DATA PROCESSING
Sine bell 0.004 sec
FT size 2048 x 4096
Total time 2 hr, 53 min, 53 sec

Regional enlarged HMBC spectrum of Phelligridin I (**2**)



IR spectrum of Phelligridin J (**3**)



Date: Wed Dec 28 09:12:01 2005

Sample Name: shxy - 11 (KBr)

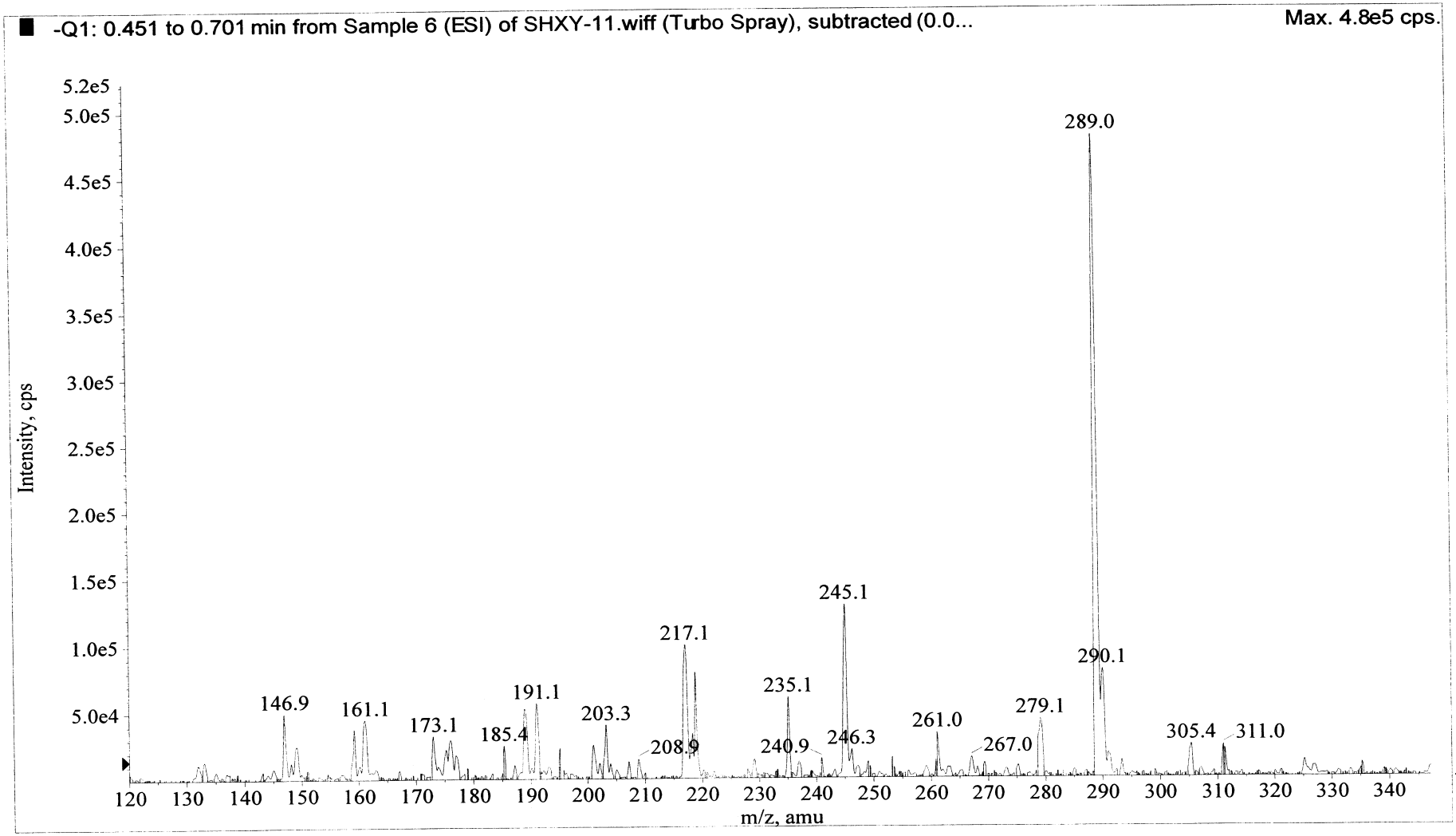
Scans: 64

检测单位：国家药物及代谢产物分析研究中心

Resolution: 4.000

美国尼高力公司(Nicolet Co.)傅立叶变换红外光谱仪: IMPACT - 400

(-)-ESIMS of Phelligridin J (**3**)



(-)-HRESIMS of Phelligridin J (**3**)

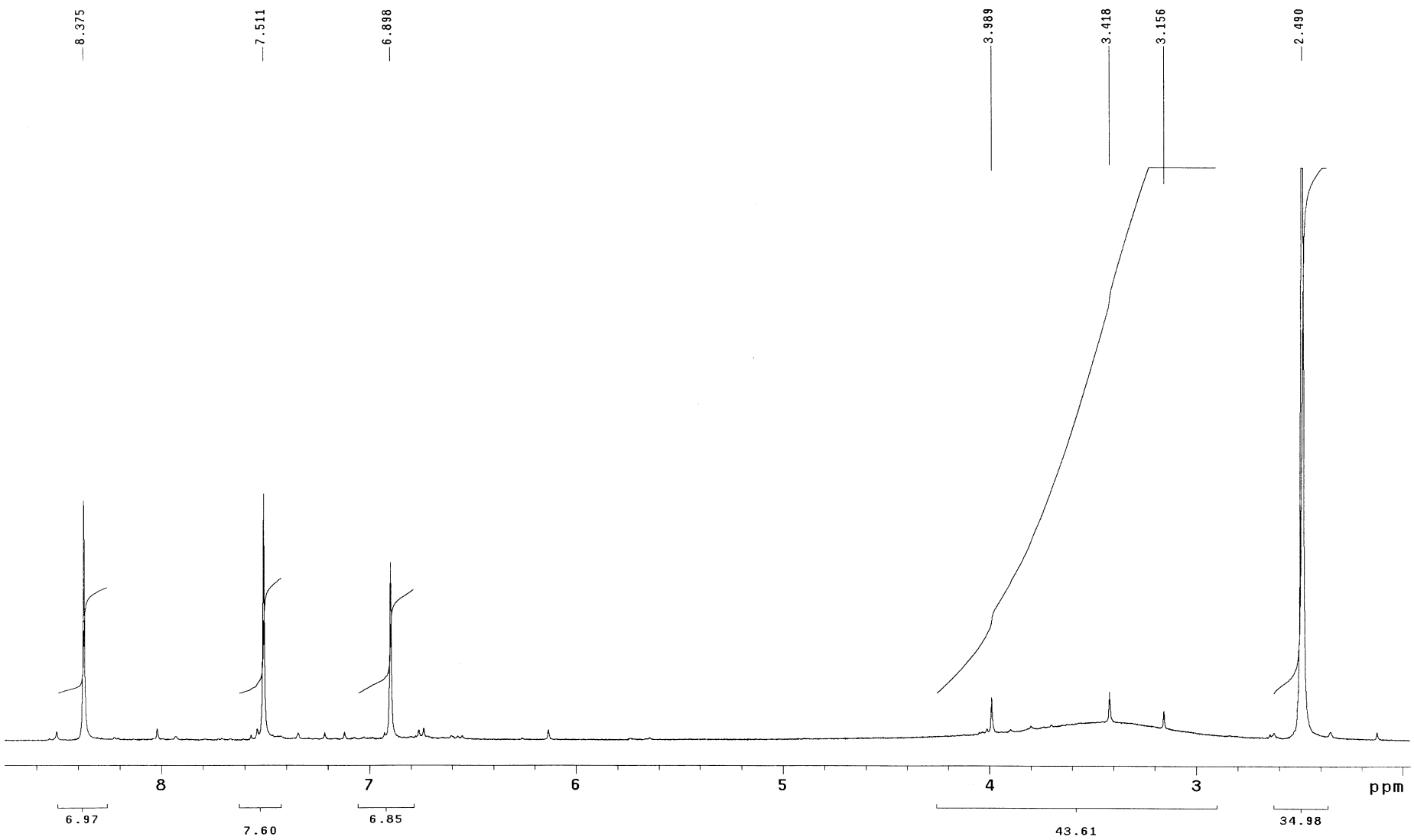
Data:shxy-11
Sample Name:
Description:
Ionization Mode:ESI-
History:Determine m/z[Peak Detect[Centroid,50,Area];Correct Base[]];Correct Base[5.0%];Average(MS[1] 1.4..2.7)

Acquired:12/22/2005 2:01:38 PM
Operator:Accutof
Mass Calibration data:TFANa_ESI-_1000
Created:12/22/2005 2:13:50 PM
Created by:Accutof

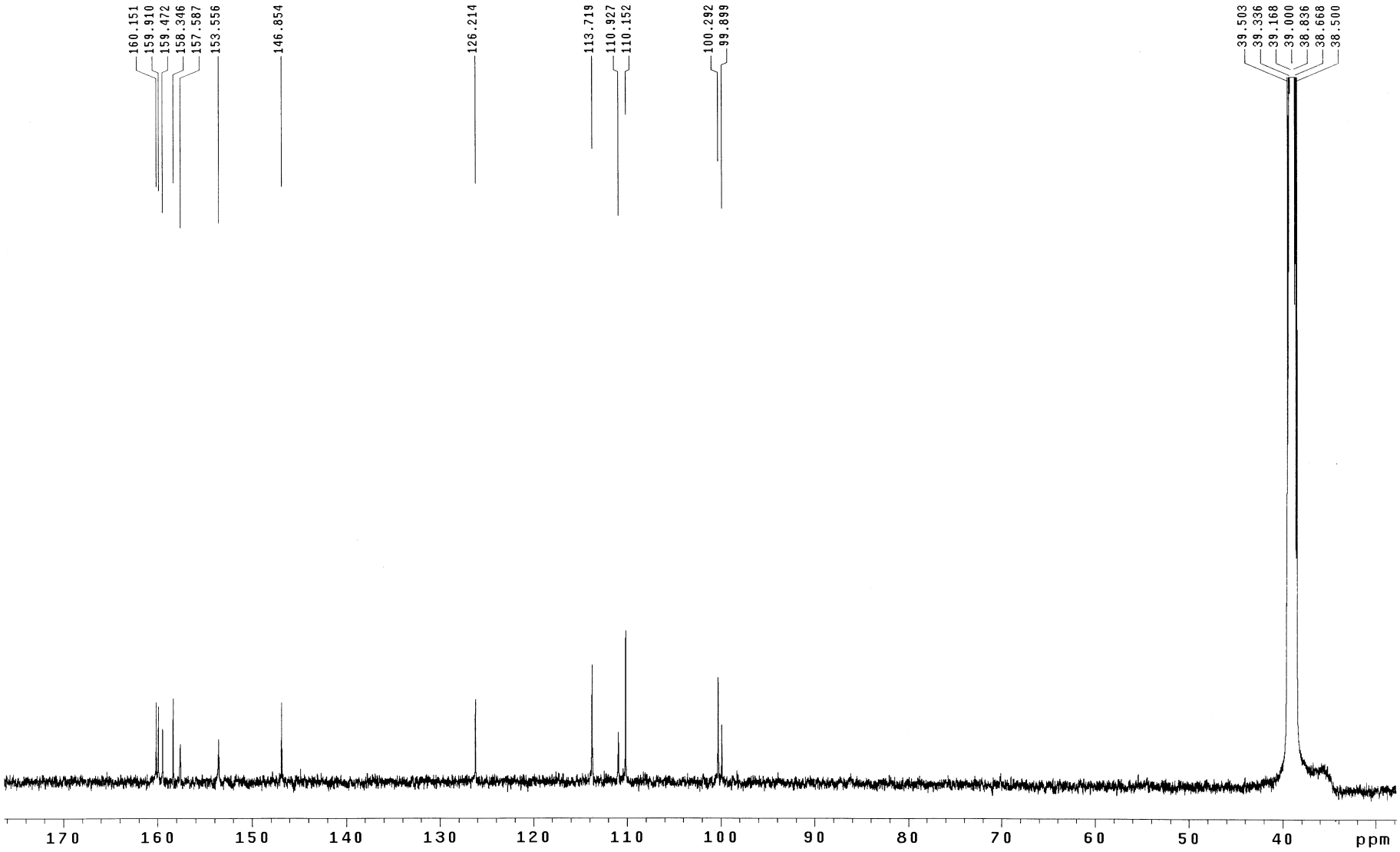
Charge number:1
Tolerance:5.00(mmu)
Unsaturation Number:-1.5 .. 20.0 (Fraction:Both)
Element:^{12}C:0 .. 100, ^{1}H:0 .. 200, ^{16}O:0 .. 10

Mass	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	^{12}C	^{1}H	^{16}O	Unsaturation Number
289.00046	288.99844	2.02	6.98	13	5	8	11.5

^{1}H NMR Spectrum of Phelligridin J (**3**)



^{13}C NMR Spectrum of Phelligridin J (**3**)



INOVA-500 HMBC-NMR SHXY-11 IN DMSO

HMBC Spectrum of Phelligridin J (**3**)

Solvent: DMSO
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Acq. time 0.152 sec
Width 3377.1 Hz
2D Width 9358.9 Hz
400 repetitions
128 increments
OBSERVE H1, 500.0948900 MHz
DATA PROCESSING
Sine bell 0.076 sec
F1 DATA PROCESSING
Sine bell 0.007 sec
FT size 1024 x 4096
Total time 17 hr, 38 min, 56 sec

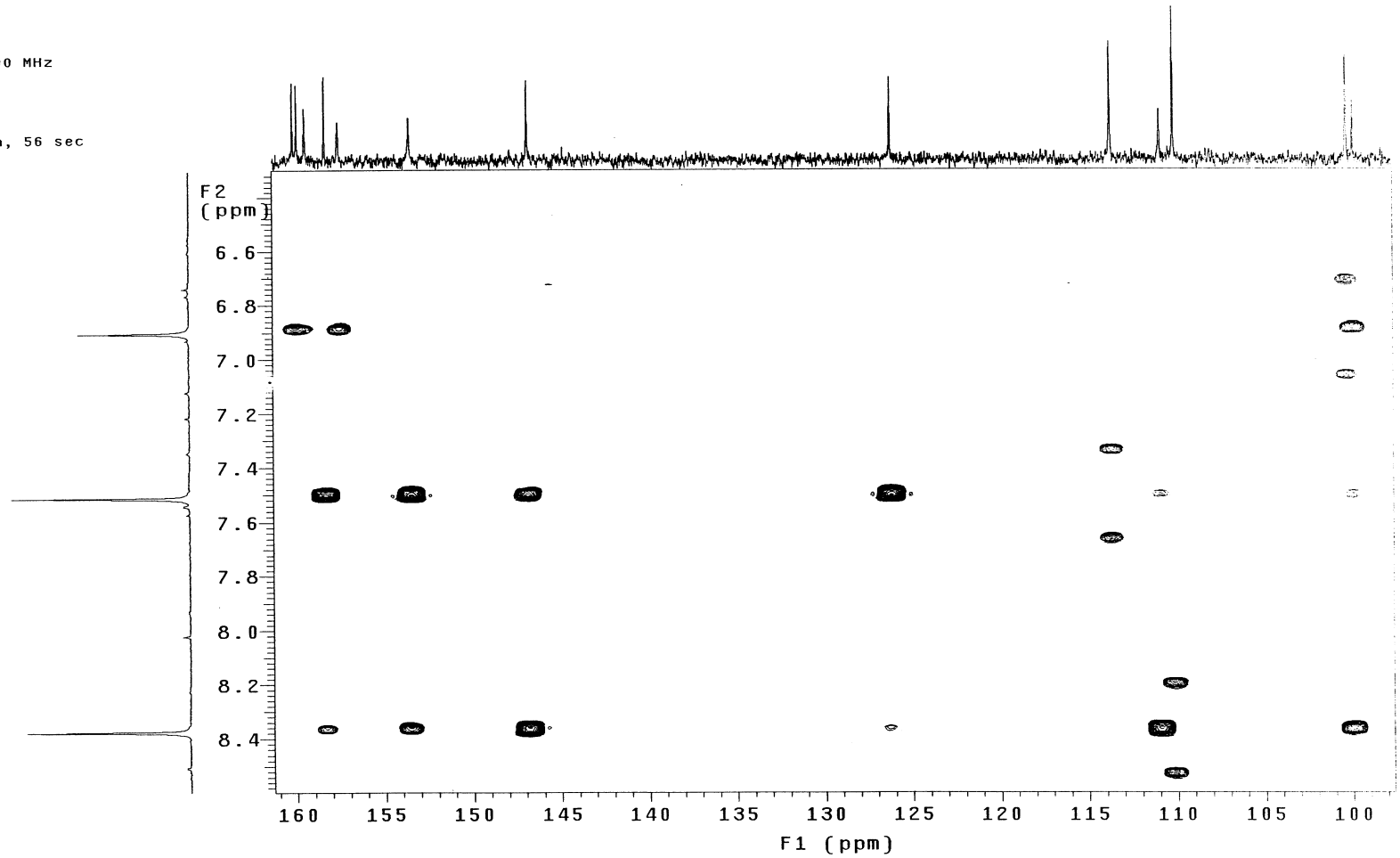


Table 1. ^{1}H and ^{13}C NMR data of compounds **1**-**3**. (Recorded in DMSO-d_6)[a]

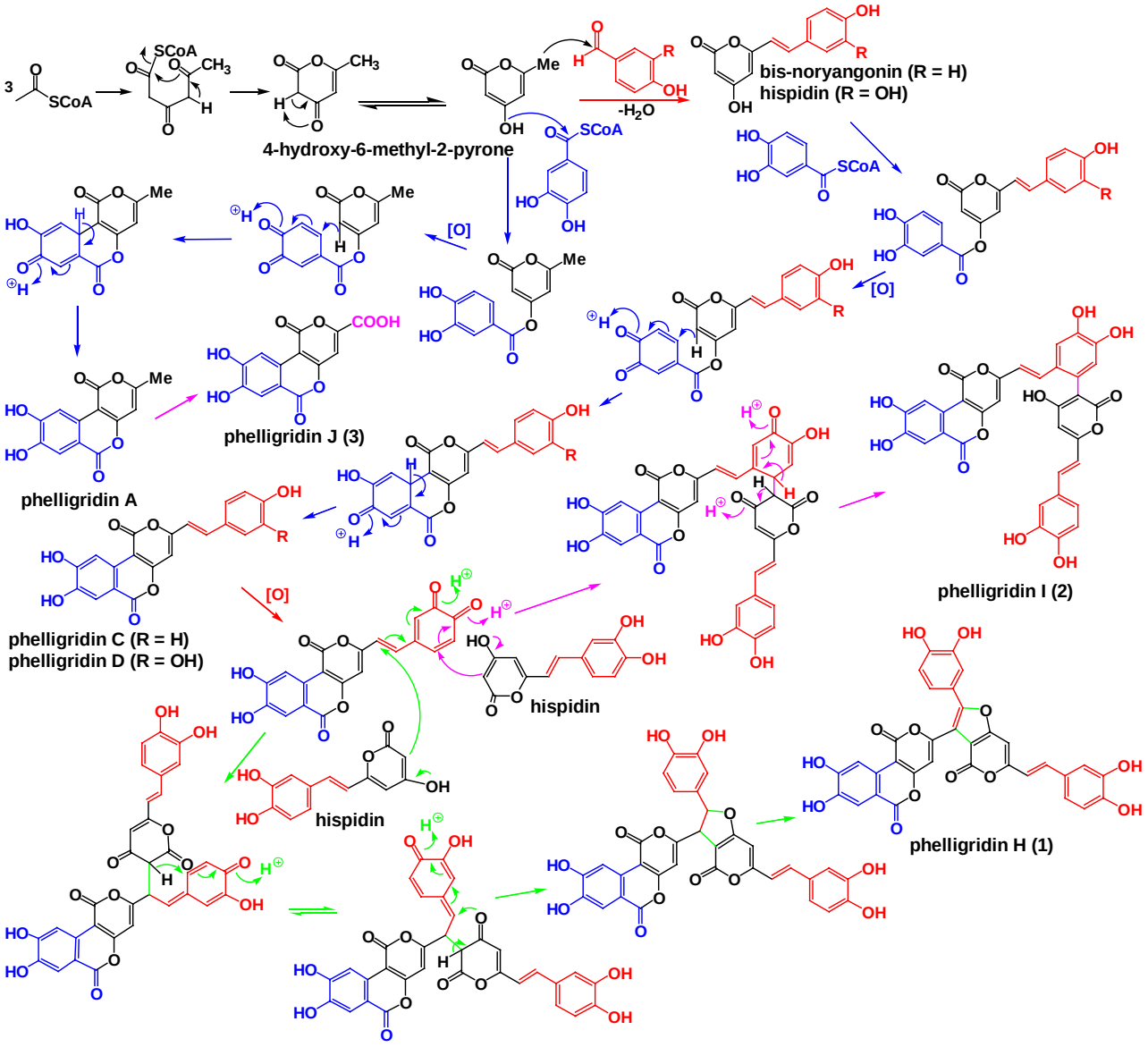
No.	δ_H (**1**)	δ_C (**1**)	δ_H (**2**)	δ_C (**2**)	δ_H (**3**)	δ_C (**3**)
1		159.8 s		159.4 s		159.9 s
3		151.7 s		158.6 s		159.5 s
4	7.25 s	103.7 d	6.74 s	99.3 d	6.90 s	100.3 d
4a		160.2 s		160.8 s		160.2 s
6		158.9 s		158.7 s		158.3 s
6a		112.2 s		111.5 s		110.9 s
7	7.58 s	114.8 d	7.50 s	114.5 d	7.51 s	113.7 d
8		147.4 s		146.9 s		146.9 s
9		153.8 s		153.6 s		153.6 s
10	8.38 s	111.0 d	8.26 s	110.6 d	8.38 s	110.2 d
10a		126.8 s		127.1 s		126.2 s
10b		100.5 s		98.8 s		99.9 s
11						157.6 s
1′		108.8 s	6.73 d (16.0)	115.8 d		
2′		155.1 s	7.08 d (16.0)	134.0 d		
3′		119.1 s		126.0 s		
4′	7.08 d (1.5)	114.7 d	7.20 s	112.0 d		
5′		145.5 s		145.4 s		
6′		147.9 s		147.4 s		
7′	6.83 d (7.5)	116.2 d	6.60 s	118.7 d		
8′	7.07 dd (7.5, 1.5)	120.0 d		126.0 s		
2″		157.4 s		162.7 s		
3″		107.8 s		101.5 s		
4″		161.0 s		166.0 s		
5″	7.14 s	95.4 d	6.34 s	100.4 d		
6″		158.2 s		158.3 s		
7″	6.81 d (16.0)	116.4 d	6.80 d (16.0)	116.4 d		
8″	7.24 d (16.0)	134.7 d	7.20 d (16.0)	134.8 d		
9″		127.2 s		127.0 s		
10″	7.06 d (1.5)	114.2 d	7.08 d (1.5)	114.4 d		
11″		145.7 s		145.6 s		
12″		147.5 s		147.4 s		
13″	6.77 d (8.0)	116.1 d	6.78 d (8.0)	115.8 d		
14″	6.98 dd (8.0, 1.5)	120.8 d	7.01 dd (8.0, 1.5)	120.4 d		

[a]NMR data were measured at 500 MHz for proton and at 125 MHz for carbon. Proton coupling constants (*J*) in Hz are given in parentheses. The assignments were based on DEPT, ^{1}H-^{1}H COSY, HSQC, and HMBC experiments.

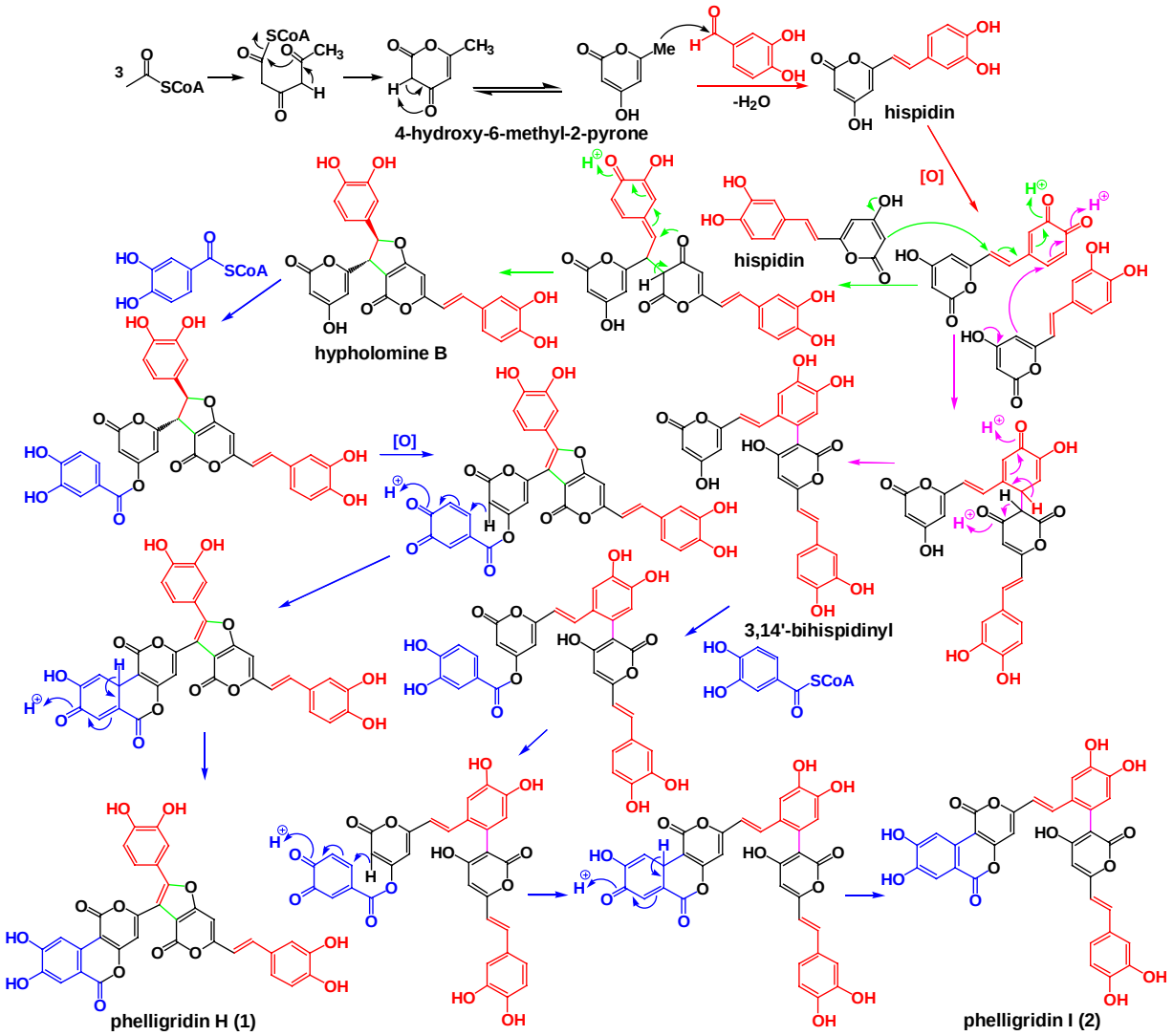
–O*H* of compound **1**: δ9.12 (brs, 11″-O*H*), 9.34 (brs, 5′-O*H*), 9.49 (brs, 6′-O*H*), 9.60 (brs, 12″-O*H*), 10.21 (brs, 8-O*H*), 10.83 (brs, 9-O*H*).

–O*H* of compound **2**: δ9.08 (brs, 5′-O*H*), 9.15 (brs, 11″-O*H*), 9.48 (brs, 6′-O*H*), 9.59 (brs, 12″-O*H*), 10.08 (brs, 8-O*H*), 10.71 (brs, 9-O*H*), 11.42 (brs, 4″-O*H*).

Scheme S1. Biogenetic scheme for phelligridins H (**1**) and I (**2**) involving phelligridin D, and phelligridin **J** (**3**)



Scheme S2. Biogenetic scheme for phelligridins H (**1**) and I (**2**) involving hypholomine B and 3,14'-bihispidinyl.



Scheme S3. Biogenetic scheme for davallialactone (**4**), phelligridin F, and inoscavin A from hispidin and hispilone.