

Supporting Information for

Limonoids and Triterpenoids as 11 β -HSD1 Inhibitors from
Walsura robusta

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Figure S39. IR spectrum of walsunoid D (**4**)

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Figure S45. (–)-ESIMS spectrum of walsunoid E (**5**)

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Figure S50. HSQC spectrum of walsunoid F (**6**) in $\text{C}_5\text{D}_5\text{N}$

Figure S51. HMBC spectrum of walsunoid d F (**6**) in $\text{C}_5\text{D}_5\text{N}$

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Figure S53. (+)-ESIMS spectrum of walsunoid F (**6**)

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Figure S57. ^1H NMR spectrum of walsunoid G (**7**) in $\text{C}_5\text{D}_5\text{N}$

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Figure S59. HSQC spectrum of walsunoid G (**7**) in $\text{C}_5\text{D}_5\text{N}$

Figure S60. HMBC spectrum of walsunoid G (**7**) in $\text{C}_5\text{D}_5\text{N}$

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Figure S64. (–)-HRESIMS spectrum of walsunoid G (**7**)

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Figure S70. NOESY spectrum of walsunoid H (**8**) in CDCl_3

Figure S71. (+)-ESIMS spectrum of walsunoid H (**8**)

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Figure S76. ^{13}C NMR spectrum of walsunoid I (**9**) in CDCl_3

Figure S77. HSQC spectrum of walsunoid I (**9**) in CDCl_3

Figure S78. HMBC spectrum of walsunoid I (**9**) in CDCl_3

Figure S79. ^1H - ^1H COSY spectrum of walsunoid I (**9**) in CDCl_3

Figure S80. NOESY spectrum of walsunoid I (**9**) in CDCl_3

Figure S81. (+)-ESIMS spectrum of walsunoid I (**9**)

Figure S82. (–)-ESIMS spectrum of walsunoid I (**9**)

Figure S83. (–)-HRESIMS spectrum of walsunoid I (**9**)

Figure S84. IR spectrum of walsunoid I (**9**)

Figure S85. ^1H NMR spectrum of compound **10** in CDCl_3

Figure S86. ^{13}C NMR spectrum of compound **10** in CDCl_3

Figure S87. ^1H NMR spectrum of compound **10** in $\text{C}_5\text{D}_5\text{N}$

Figure S88. ^{13}C NMR spectrum of compound **10** in $\text{C}_5\text{D}_5\text{N}$

Figure S89. HSQC spectrum of compound **10** in CDCl_3

Figure S90. HMBC spectrum of compound **10** in CDCl_3

Figure S91. (–)-HRESIMS spectrum of **10**

Figure S92. LC-ESI(\pm)MS analysis of **2**

Figure S93. LC-ESI(\pm)MS analysis of **4**

Figure S94. LC-ESI(\pm)MS analysis of **10**

Figure S95. LC-ESI(\pm)MS analysis of ethanolic crude extract

Table S1. ^1H and ^{13}C NMR spectroscopic data of compounds **2** and **10** in CDCl_3 at 500

MHz

position	2		10	
	^1H (<i>J</i> in Hz)	^{13}C	^1H (<i>J</i> in Hz)	^{13}C
1	6.96, d (9.9)	151.7	6.96, d (9.9)	151.7
2	6.13, d (9.9)	127.6	6.13, d (9.9)	127.6
3		203.5		203.5
4		48.7		48.7
5		135.0		135.0
6		140.8		140.9
7		197.4		197.4
8		45.9		45.9
9	2.44, s	45.4	2.45, s	45.4
10		41.0		41.0
11	4.63, dd (8.8,6.3)	67.1	4.64, dd (8.5,6.4)	67.1
12 α	2.11, dd (15.7,6.3)	46.8	2.10, dd (15.9,6.4)	46.6
12 β	2.41, d (15.7)		2.41, d (15.9)	
13		41.3		41.2
14		69.5		69.6
15	3.98, s	58.1	3.98, s	58.0
16 α	2.02, dd (13.5,10.9)	30.9	2.02, dd (13.5,11.0)	31.1
16 β	2.32, dd (13.5,6.5)		2.30, dd (13.5,6.5)	
17	2.74, dd (10.9,6.5)	43.0	2.71, dd (11.0,6.5)	43.0
18	0.71, s	22.3	0.74, s	22.3
19	1.54, s	25.7	1.54, s	25.7
20		137.7		137.6
21		170.8		170.7
22	6.78, t (1.4)	145.1	6.78, t (1.5)	145.0
23	5.79, t (1.0)	102.6	5.73, t (1.5)	102.5
28	1.55, s	27.0	1.55, s	27.0
29	1.49, s	21.3	1.49, s	21.3
30	1.36, s	22.8	1.36, s	22.8
11-OH	2.38, d (8.8)		2.37, d (8.5)	
6-OH	6.38, s		6.38, s	
OMe	3.56, s	57.4	3.54, s	57.2

Table S2. Preliminary assay results of tested compounds against human 11 β -HSD1 at 10 μ M.

Compds no.	Expt. 1	Expt. 1	Expt. 1	Average	SD
1	33.45%	23.37%	39.50%	32.11%	8.15%
2	12.01%	11.26%	17.47%	13.58%	3.39%
3	8.64%	9.32%	15.29%	11.09%	3.66%
4	1.26%	2.46%	0.90%	1.53%	0.82%
5	11.50%	5.95%	15.86%	11.11%	4.96%
6	15.04%	12.23%	12.27%	13.18%	1.61%
7	21.89%	10.87%	17.64%	16.80%	5.55%
8	56.59%	63.21%	58.83%	59.54%	3.36%
9	1.35%	4.47%	13.08%	6.30%	6.08%
10	14.25%	6.86%	13.69%	11.60%	4.12%
11	49.28%	47.47%	45.23%	47.33%	2.03%
12	50.05%	42.55%	43.59%	45.40%	4.06%
13	42.47%	48.50%	42.37%	47.78%	5.08%
14	72.33%	69.29%	77.83%	73.17%	4.32%
16	12.54%	9.71%	13.66%	11.97%	2.03%
17	35.20%	43.10%	32.58%	36.96%	5.48%
18	15.38%	23.04%	24.20%	20.87%	4.79%
19	30.32%	47.17%	38.47%	38.65%	8.43%
20	37.65%	35.28%	46.48%	39.80%	5.90%
Glycyrrhetic acid 1 nM	15.45%	11.05%	8.86%	11.79%	3.36%
Glycyrrhetic acid 10 nM	56.78%	51.97%	59.55%	56.10%	3.87%
Glycyrrhetic acid 100 nM	94.66%	88.87%	89.99%	91.17%	3.07%
Activity of 15 was already reported in our previous article. (<i>J. Nat. Prod.</i> 2013, 76, 1319)					

Table S3. Preliminary assay results of tested compounds against mouse 11 β -HSD1 at 10 μ M.

Compds no.	Expt. 1	Expt. 1	Expt. 1	Average	SD
1	14.10%	27.18%	27.40%	22.89%	7.62%
2	39.05%	38.18%	31.10%	36.11%	4.36%
3	8.53%	7.23%	2.65%	6.14%	3.09%
4	15.38%	22.07%	19.60%	19.01%	3.38%
5	15.16%	4.22%	7.78%	9.06%	5.58%
6	16.80%	15.47%	28.08%	20.12%	6.93%
7	17.65%	14.99%	14.70%	15.78%	1.63%
8	6.88%	5.90%	7.03%	6.60%	0.61%
9	30.60%	30.93%	21.95%	27.83%	5.09%
10	7.88%	5.17%	7.72%	6.93%	1.52%
11	84.54%	89.58%	84.73%	86.28%	2.85%
12	77.43%	73.01%	69.82%	73.42%	3.82%
13	84.31%	88.76%	85.61%	86.23%	2.29%
14	96.00%	95.62%	87.11%	92.91%	5.02%
16	-2.61%	4.51%	5.68%	2.53	4.49%
17	19.22%	11.70%	14.92%	15.28%	3.78%
18	15.08%	20.42%	23.76%	19.75%	4.37%
19	50.38%	52.89%	44.80%	49.35%	4.14%
20	25.99%	22.95%	19.15%	22.69%	3.43%
Glycyrrhetic acid 1 nM	12.58%	11.04%	12.13%	11.91%	0.79%
Glycyrrhetic acid 10 nM	58.83%	59.77%	66.01%	61.53%	3.90%
Glycyrrhetic acid 100 nM	93.51%	105.80%	99.43%	99.58%	6.15%
Activity of 15 was already reported in our previous article. (<i>J. Nat. Prod.</i> 2013, 76, 1319)					

Table S4. X-ray crystallographic data for walsunoid D (**4**)^a

Empirical formula	C ₂₇ H ₃₄ O ₈
Formula weight	486.54
Temperature	296.15 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	$a = 7.4553 (2) \text{ Å}, \quad \alpha = 90^\circ$ $b = 12.0869 (4) \text{ Å}, \quad \beta = 90.180(2)^\circ$ $c = 28.1295 (7) \text{ Å}, \quad \gamma = 90^\circ$
Volume	2534.78 (13) Å ³
Z	4
Calculated density	1.275 Mg/m ³
Absorption coefficient	0.770 mm ⁻¹
F(000)	1040
Crystal size	0.15 * 0.05 * 0.03 mm ³
Theta range for data collection	3.142 to 69.998 °
Index ranges	-8 ≤ h ≤ 6, -12 ≤ k ≤ 14, -32 ≤ l ≤ 33
Reflections collected	15958
Independent reflections	6961 [R(int) = 0.0486]
Completeness to theta = 67.679 °	88.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5340
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6961 / 1 / 647
Goodness-of-fit on F ²	1.025
Final R indices [I > 2σ(I)]	R1 = 0.0432, wR2 = 0.1106
R indices (all data)	R1 = 0.0477, wR2 = 0.1147
Absolute structure parameter	-0.04(9)
Largest diff. peak and hole	0.169 and -0.228 e. Å ⁻³

^a Colorless crystals of walsunoid D (**4**) were obtained in methanol solvent.

Table S5. X-ray crystallographic data for compound **10**^a

Empirical formula	C ₂₇ H ₃₂ O ₈
Formula weight	484.52
Temperature	140 (2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 21
Unit cell dimensions	$a = 7.50130 (10) \text{ Å}, \quad \alpha = 90^\circ$ $b = 11.6919 (2) \text{ Å}, \quad \beta = 90^\circ$ $c = 14.6190 (2) \text{ Å}, \quad \gamma = 90^\circ$
Volume	1244.70 (3) Å ³
Z	2
Calculated density	1.293 Mg/m ³
Absorption coefficient	0.784 mm ⁻¹
F(000)	516
Crystal size	0.250 * 0.120 * 0.100 mm ³
Theta range for data collection	3.114 to 69.460 °
Index ranges	-7 ≤ h ≤ 8, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	9728
Independent reflections	4294 [R(int) = 0.0486]
Completeness to theta = 67.679 °	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.4701
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4294 / 1 / 324
Goodness-of-fit on F ²	1.062
Final R indices [I > 2σ(I)]	R1 = 0.0423, wR2 = 0.1051
R indices (all data)	R1 = 0.0424, wR2 = 0.1053
Absolute structure parameter	-0.01(7)
Largest diff. peak and hole	0.284 and -0.254 e. Å ⁻³

^a Colorless crystals of **10** were obtained in methanol solvent.

Figure S1. ^1H NMR spectrum of walsunoid A (**1**) in CDCl_3

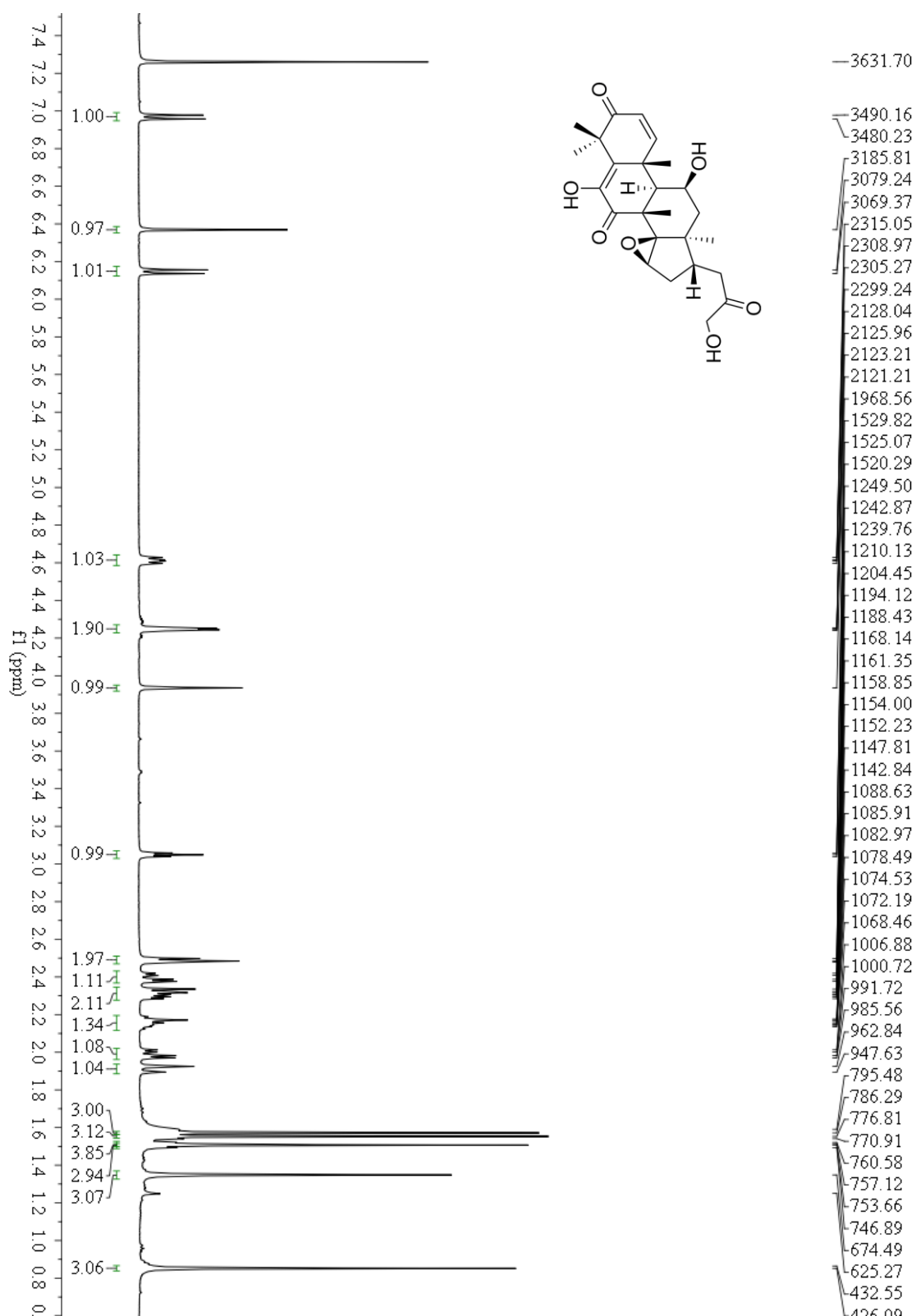


Figure S2. ^{13}C NMR spectrum of walsunoid A (**1**) in CDCl_3

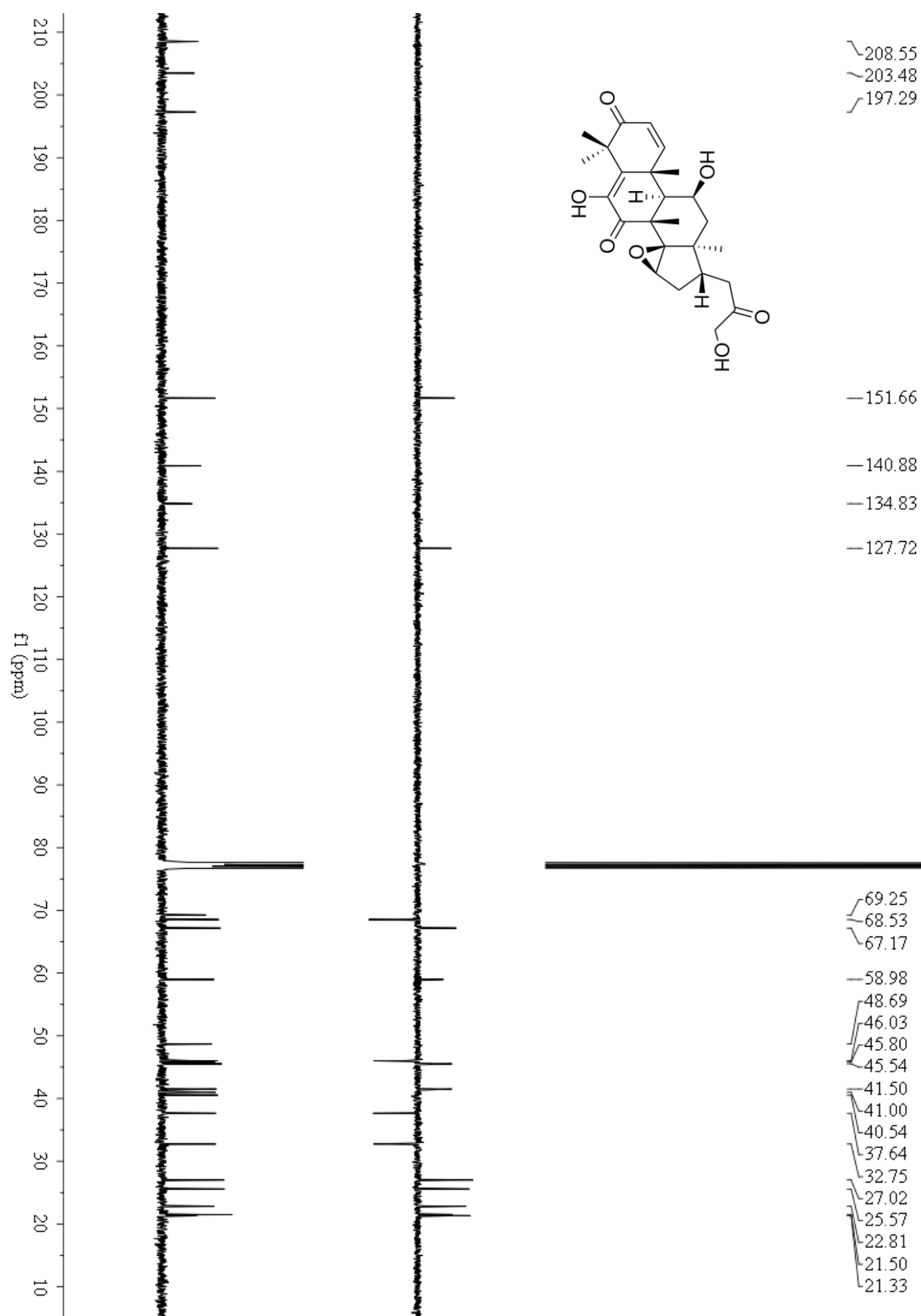


Figure S3. HSQC spectrum of walsunoid A (**1**) in CDCl₃

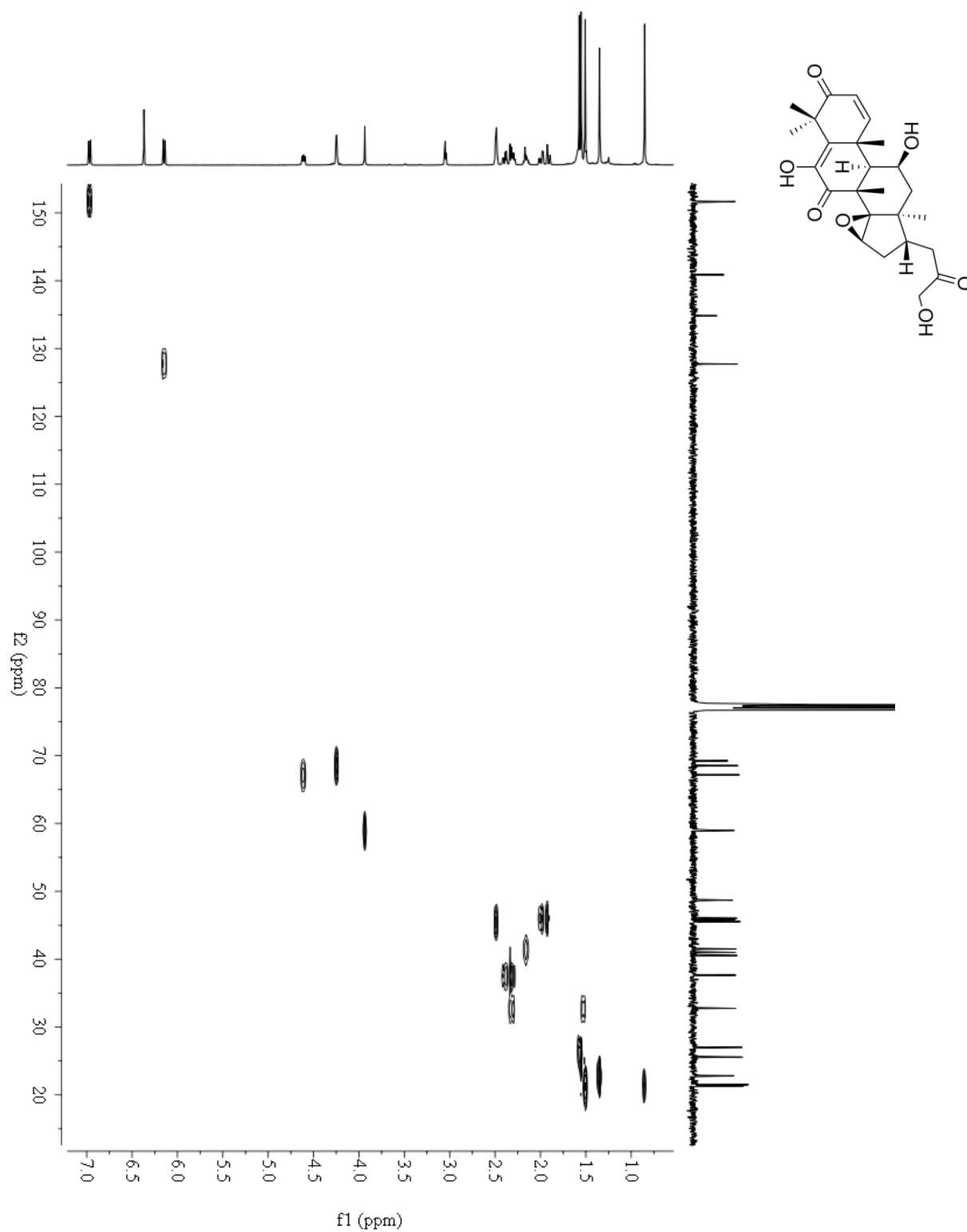


Figure S4. HMBC spectrum of walsunoid A (**1**) in CDCl₃

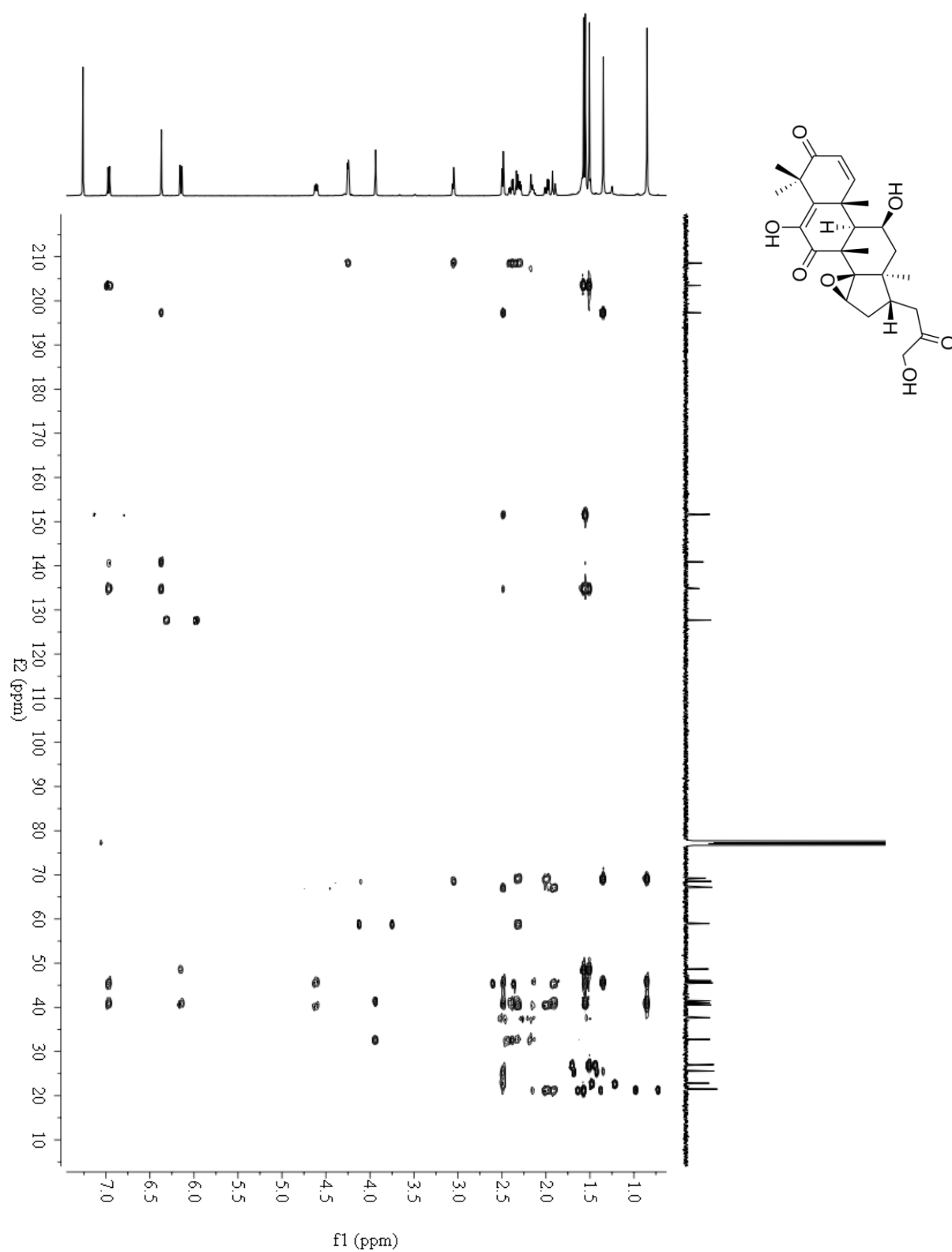


Figure S5. ^1H - ^1H COSY spectrum of walsunoid A (**1**) in CDCl_3

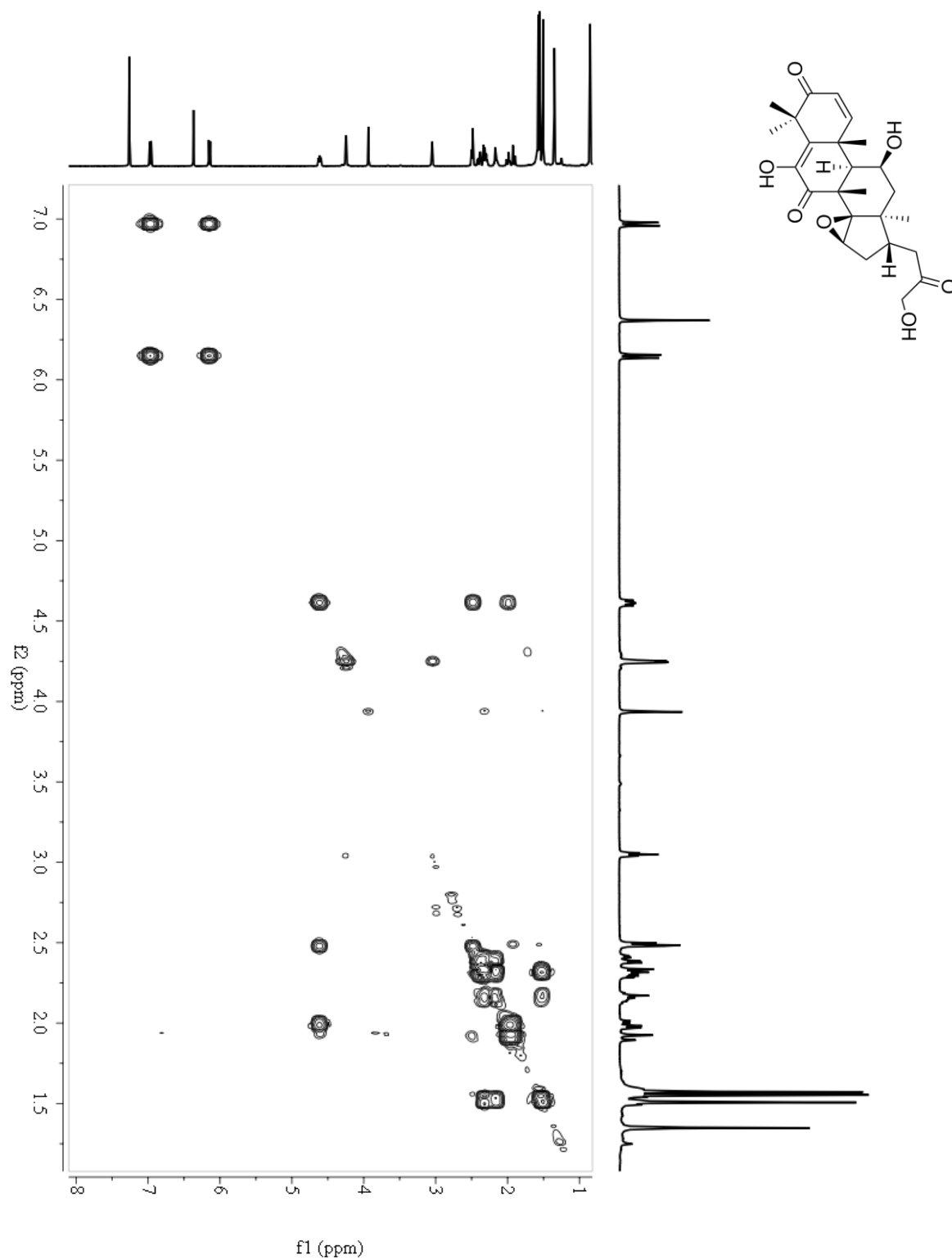


Figure S6. ROESY spectrum of walsunoid A (**1**) in CDCl₃

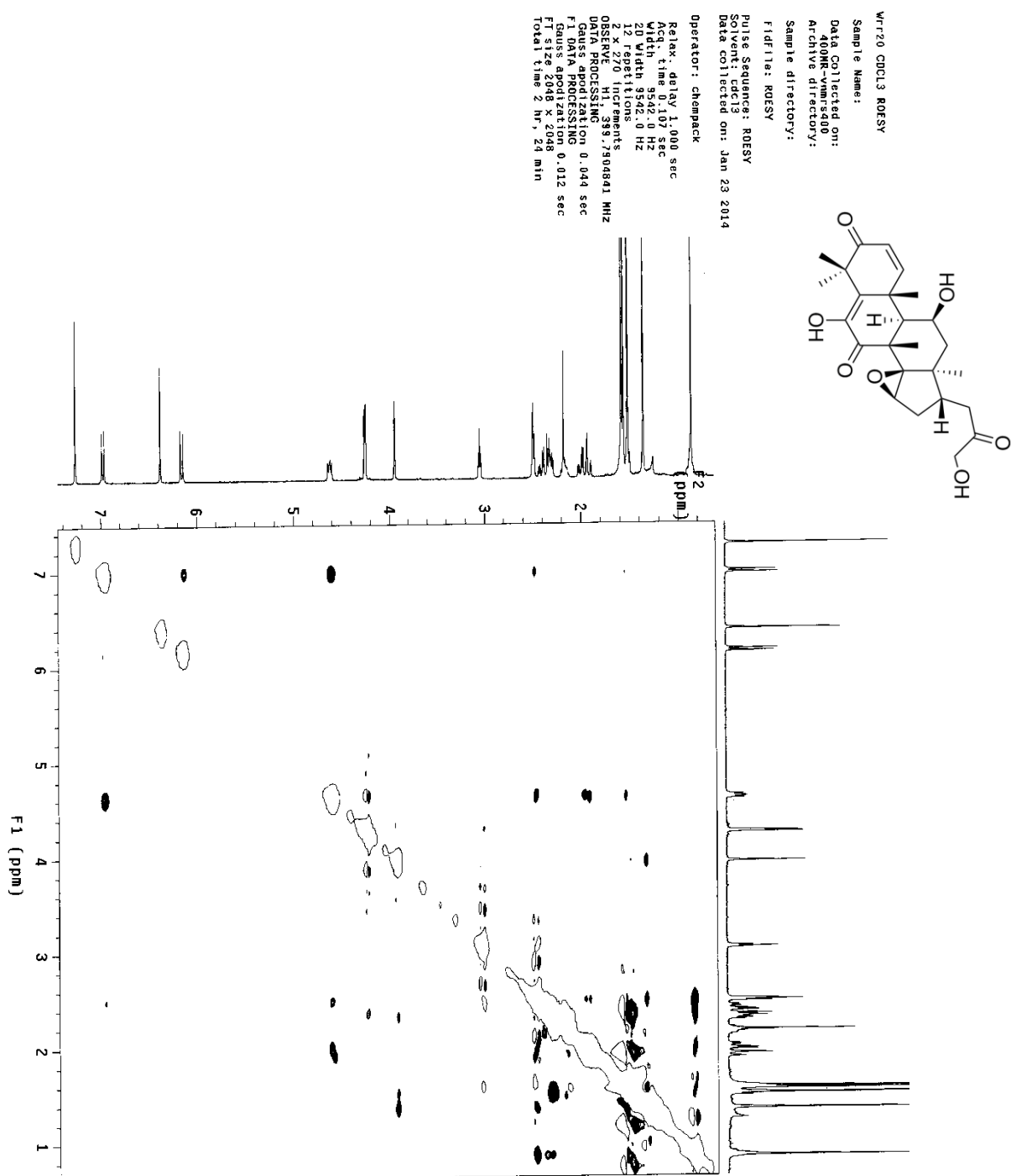


Figure S7. ESI(+)MS spectrum of walsunoid A (1)

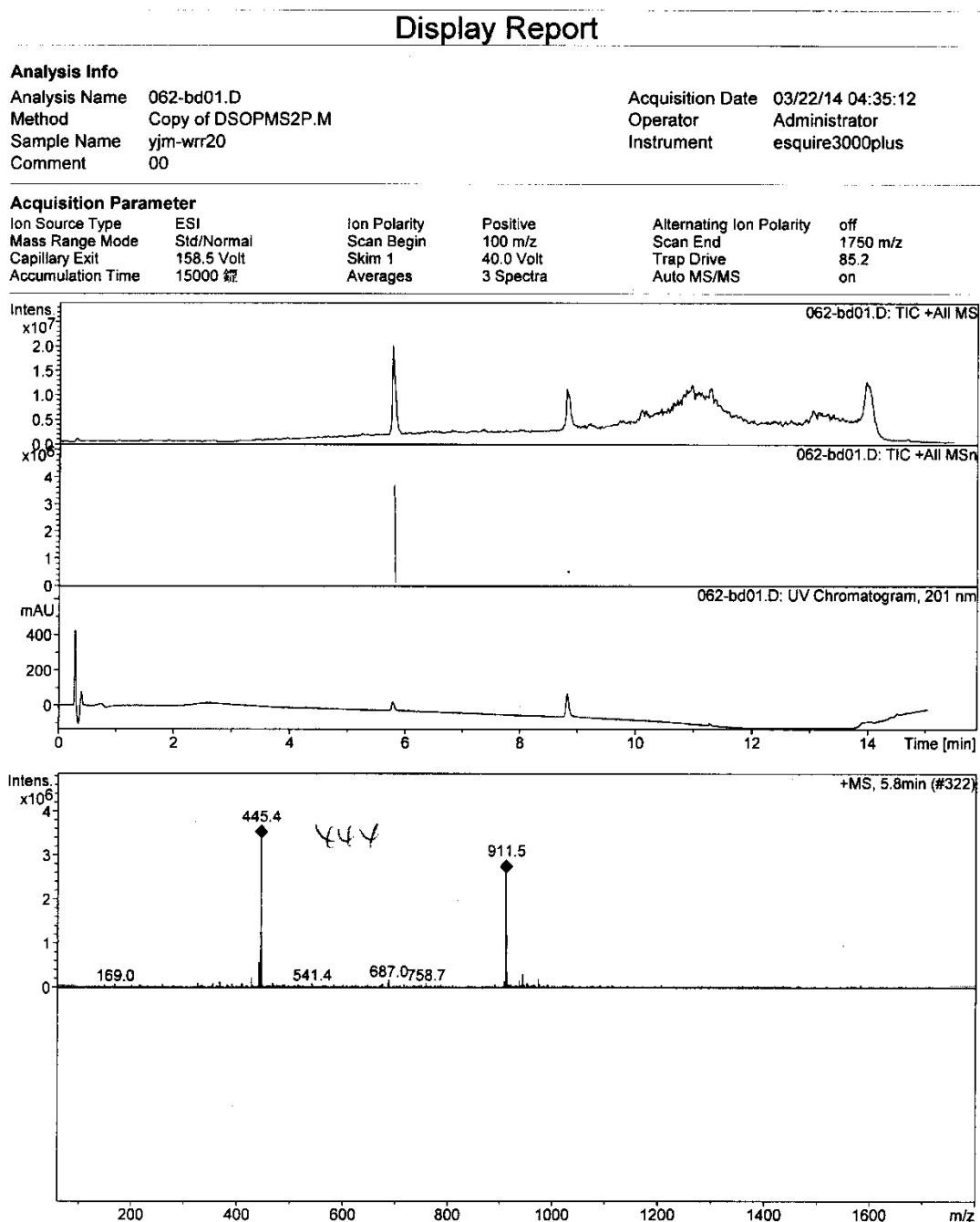


Figure S8. (-)-ESIMS spectrum of walsunoid A (1)

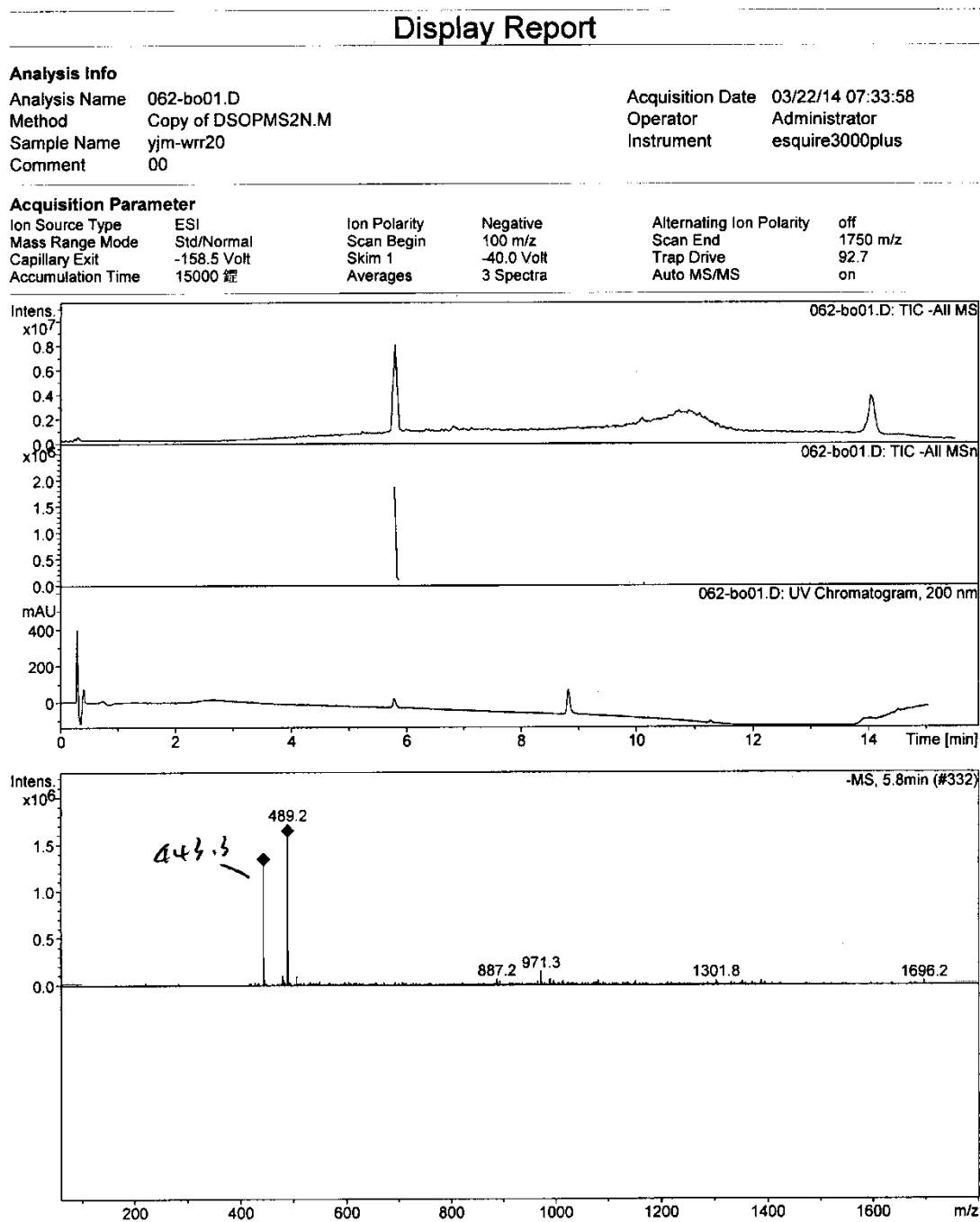


Figure S9. (-)-HRESIMS spectrum of walsunoid A (1)

Elemental Composition Report

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Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

252 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 N: 0-2 O: 0-20

wrr20

LCT PXE KE324

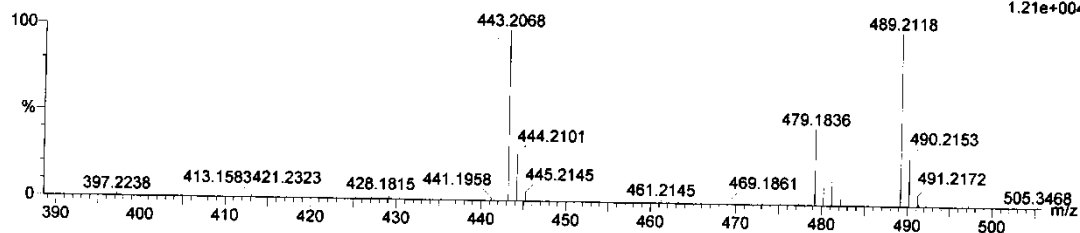
03-Apr-2014

15:09:11

1: TOF MS ES-

1.21e+004

wrr20_0403 18 (0.372) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (7:25)



Minimum:

Maximum:

5.0 5.0 -1.5
50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
443.2068	443.2070	-0.2	-0.5	10.5	132.8	0.0	C25 H31 O7

Figure S10. IR spectrum of walsunoid A (**1**)

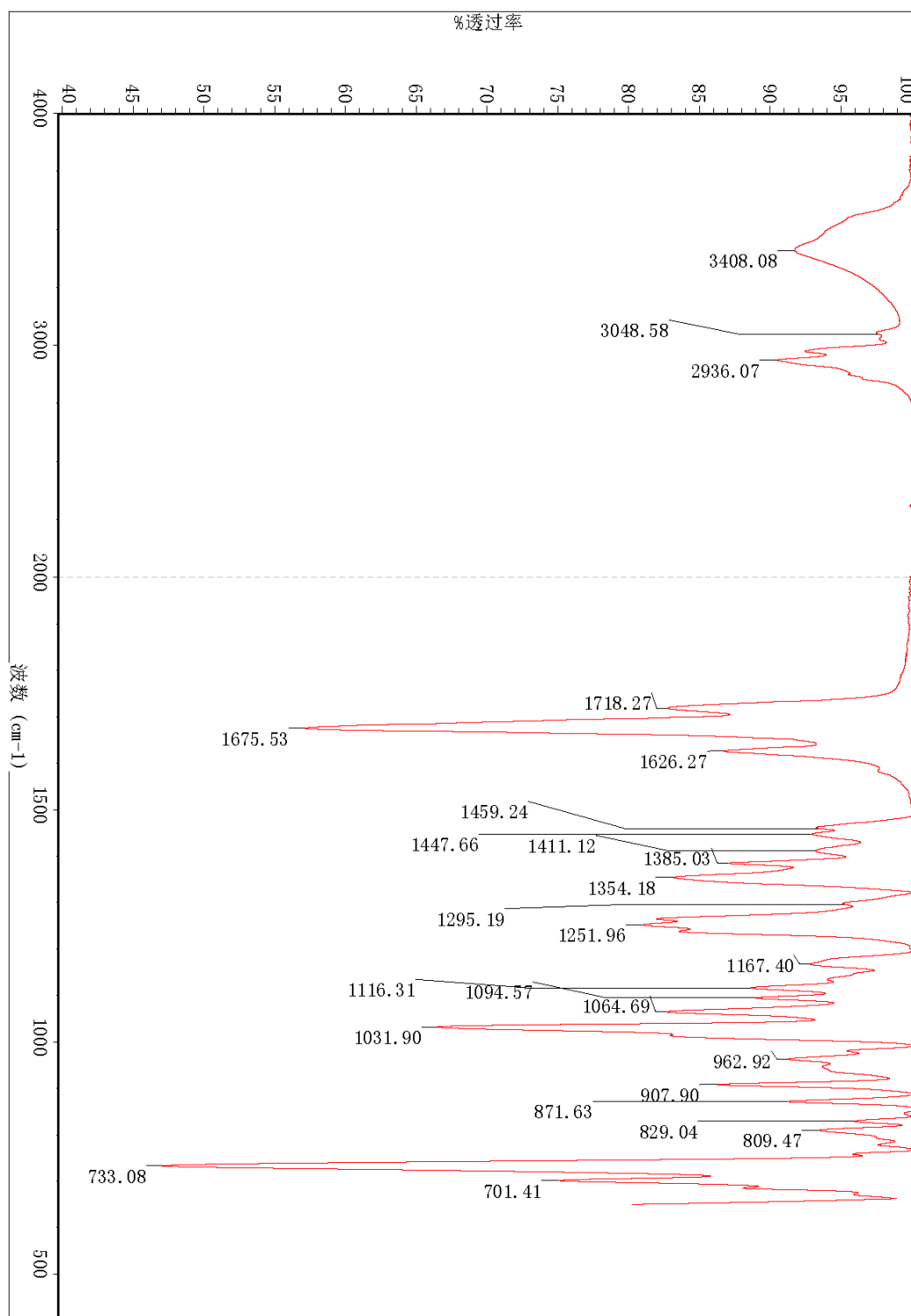


Figure S11. ^1H NMR spectrum of walsunoid B (**2**) in CDCl_3

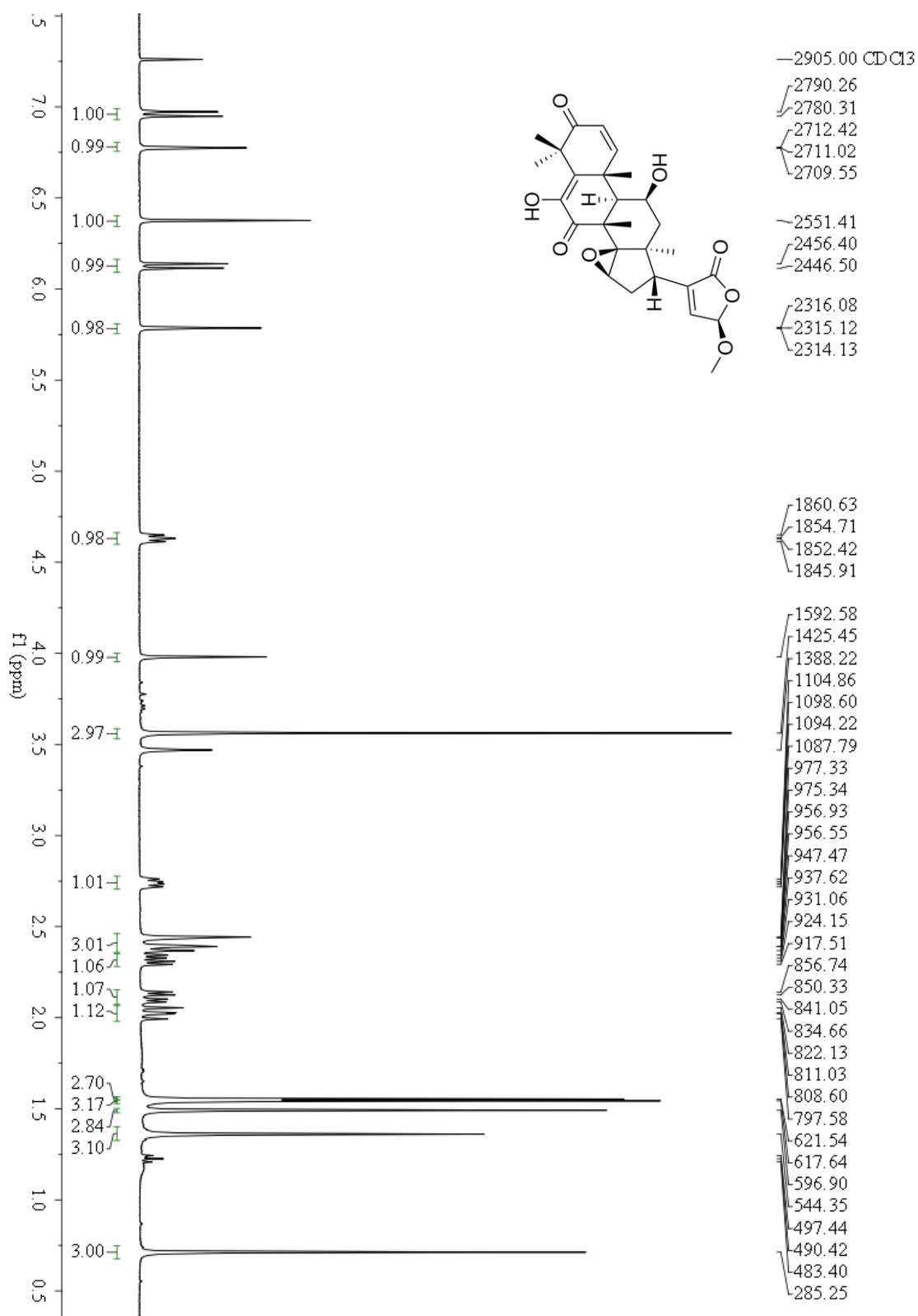
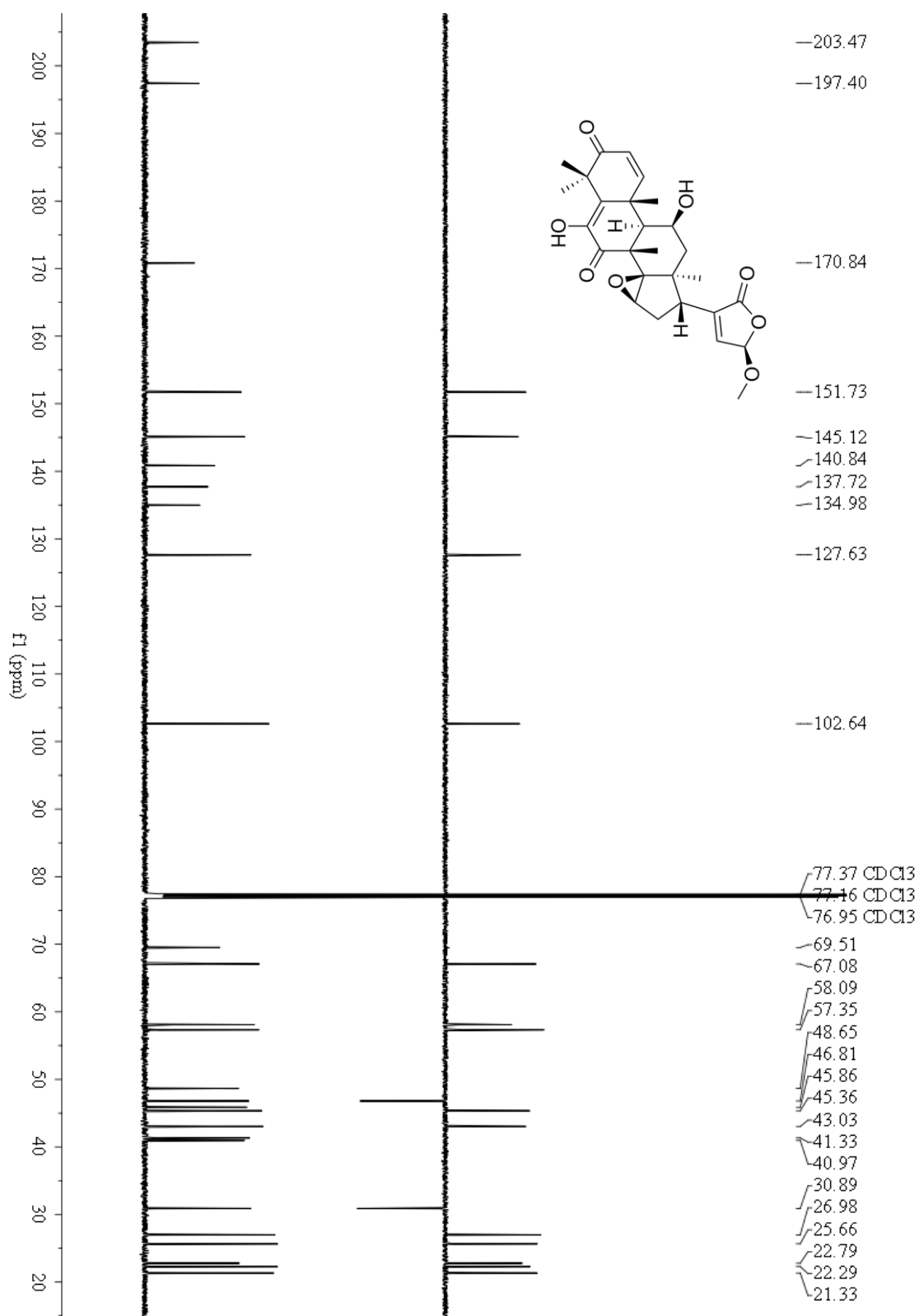


Figure S12. ^{13}C NMR spectrum of walsunoid B (**2**) in CDCl_3



Chemical structure of **1** is shown. The ¹H NMR spectrum (CDCl₃) of **1** is displayed, with the chemical shift (ppm) and integration values for each peak listed on the right and left sides, respectively.

Figure S14. ^{13}C NMR spectrum of walsunoid B (**2**) in $\text{C}_5\text{D}_5\text{N}$

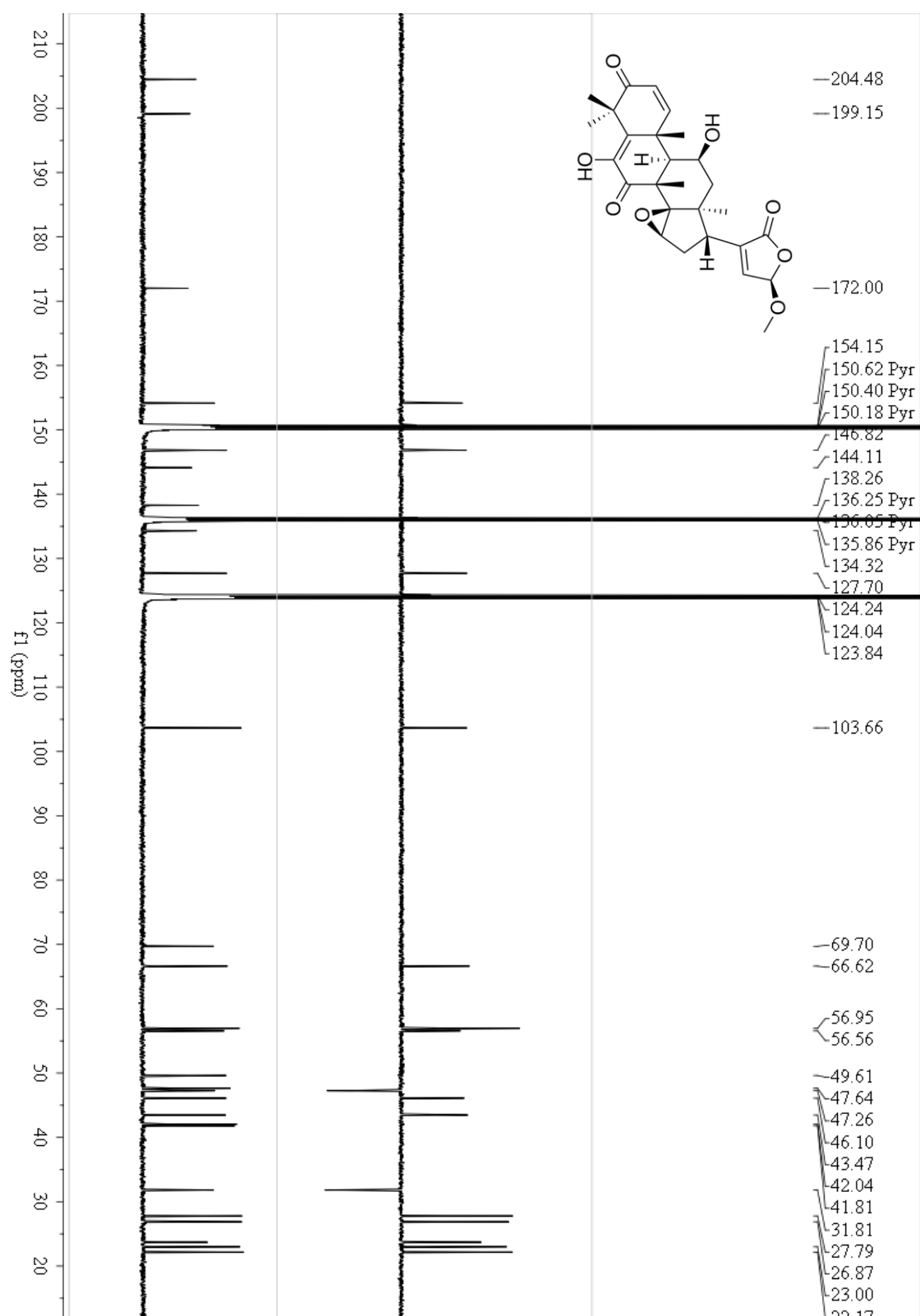


Figure S15. HSQC spectrum of walsunoid B (**2**) in C₅D₅N

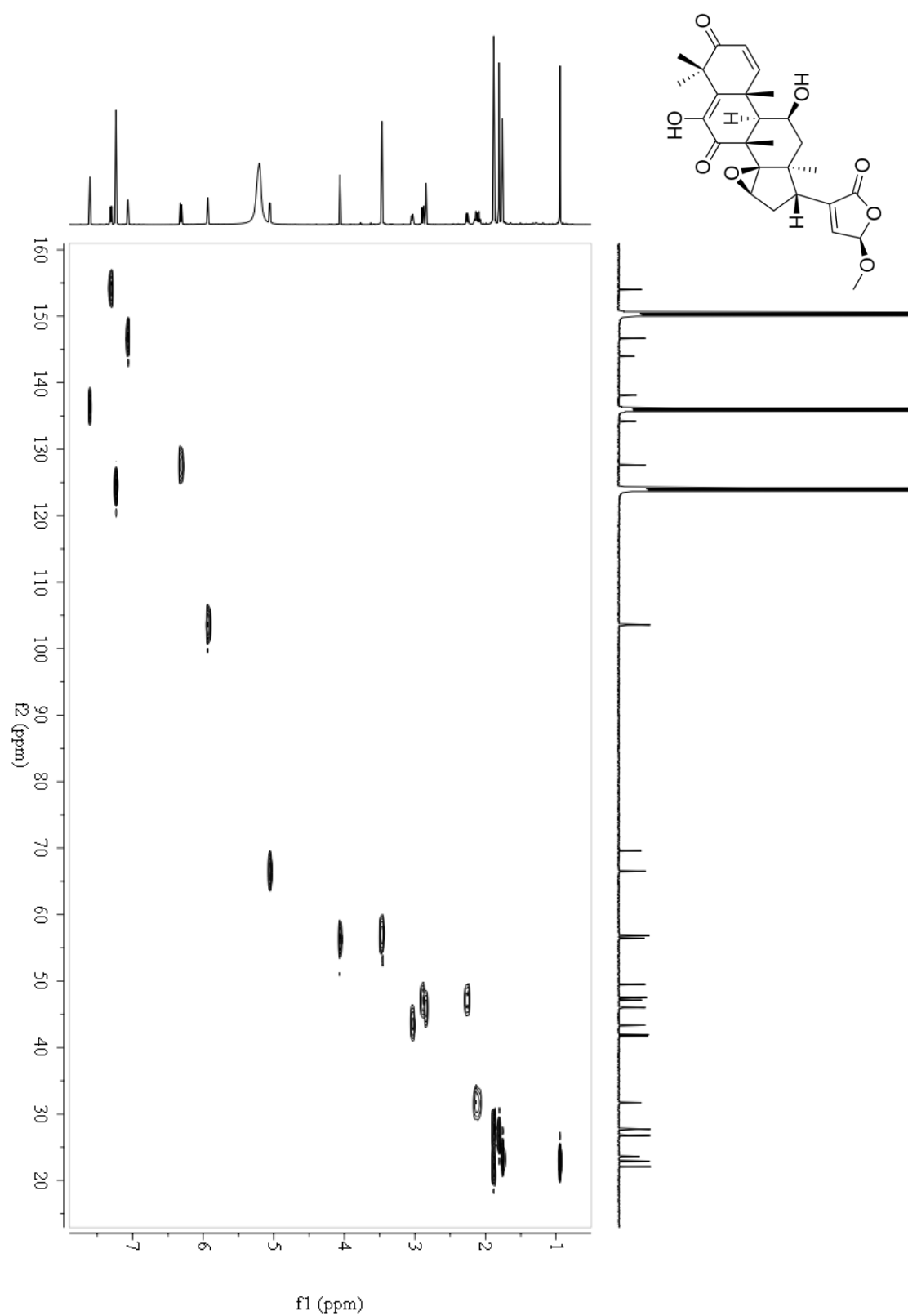


Figure S16. HMBC spectrum of walsunoid B (**2**) in C₅D₅N

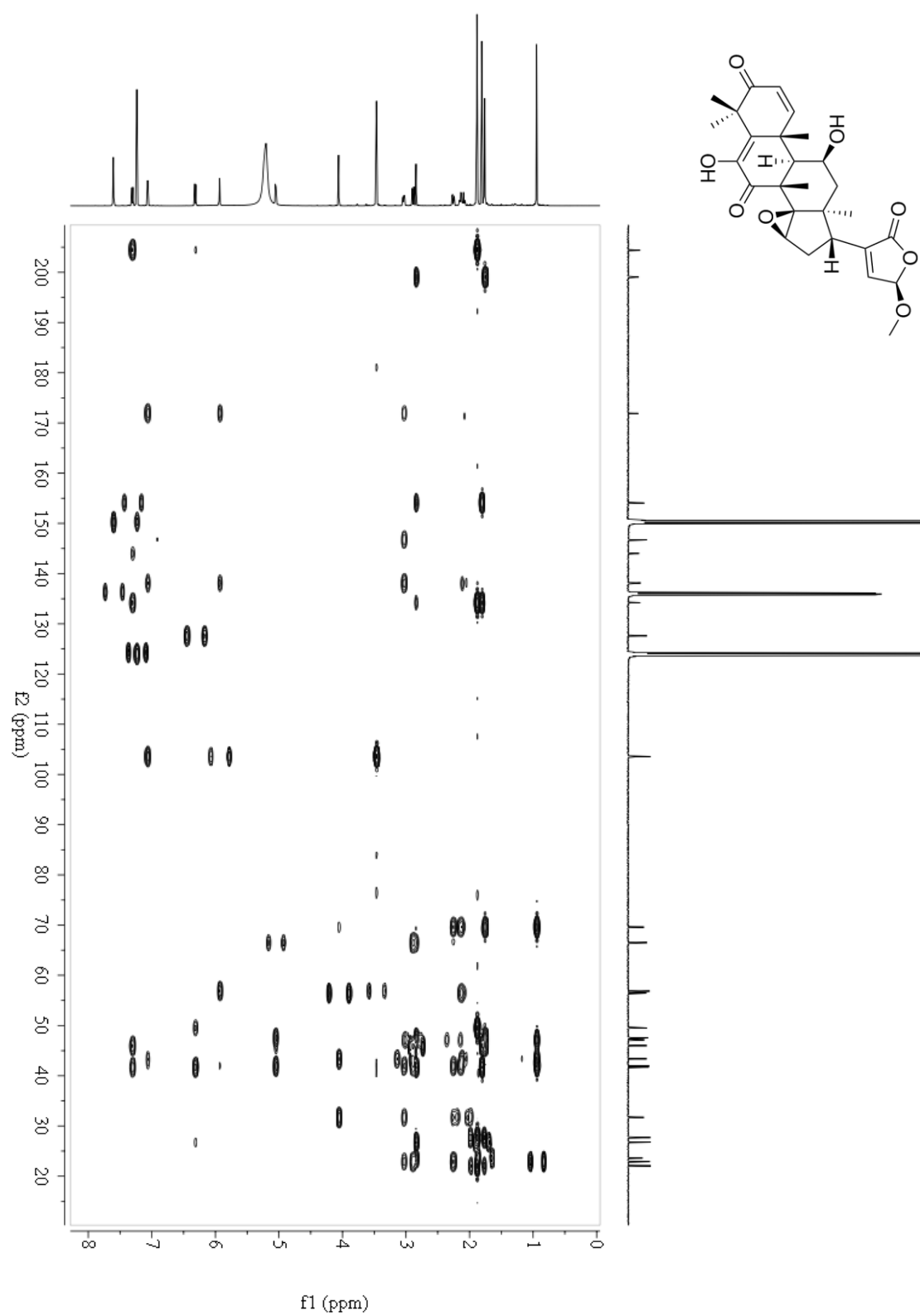


Figure S17. NOESY spectrum of walsunoid B (**2**) in C₅D₅N

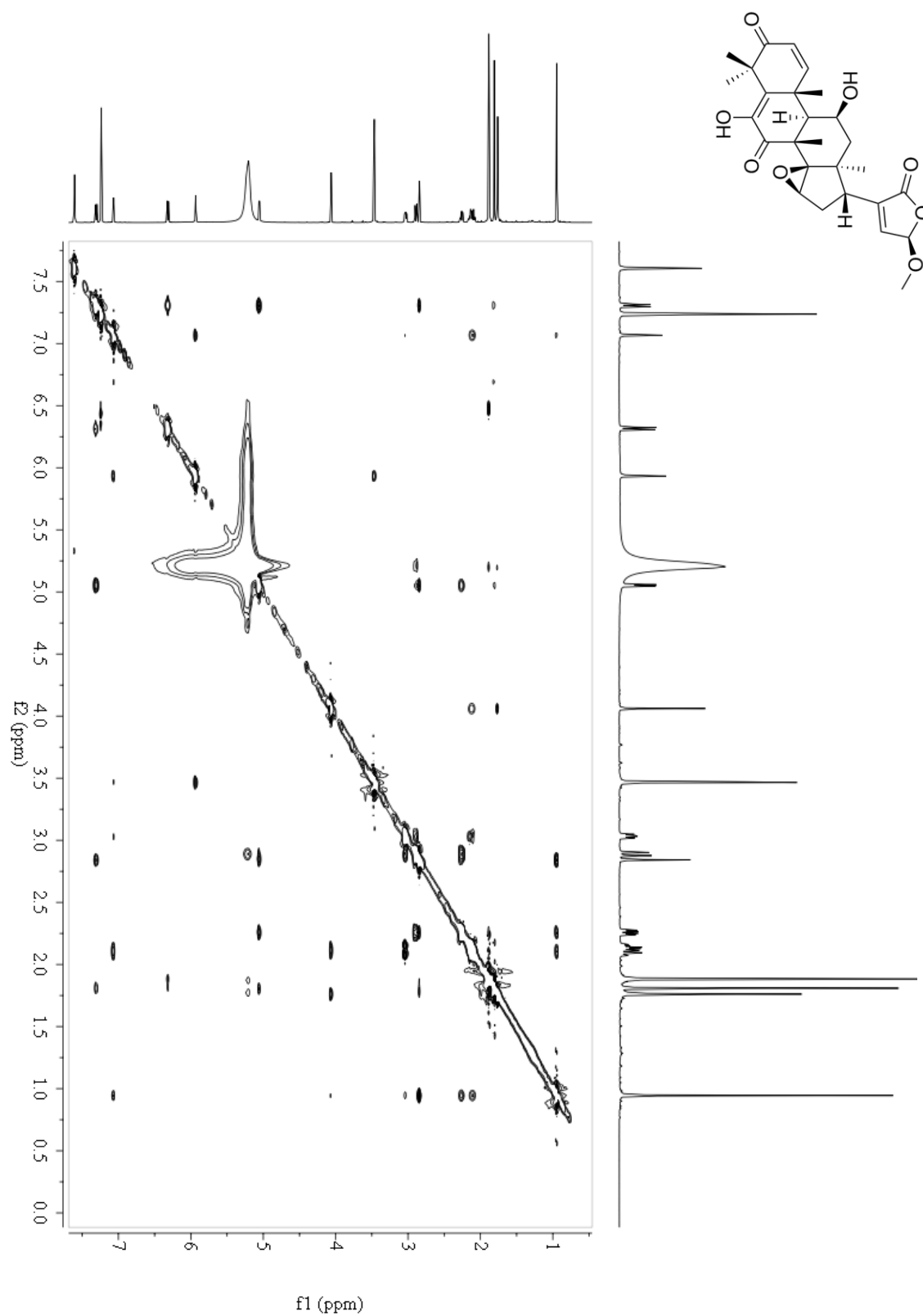


Figure S18. (+)-ESIMS spectrum of walsunoid B (2)

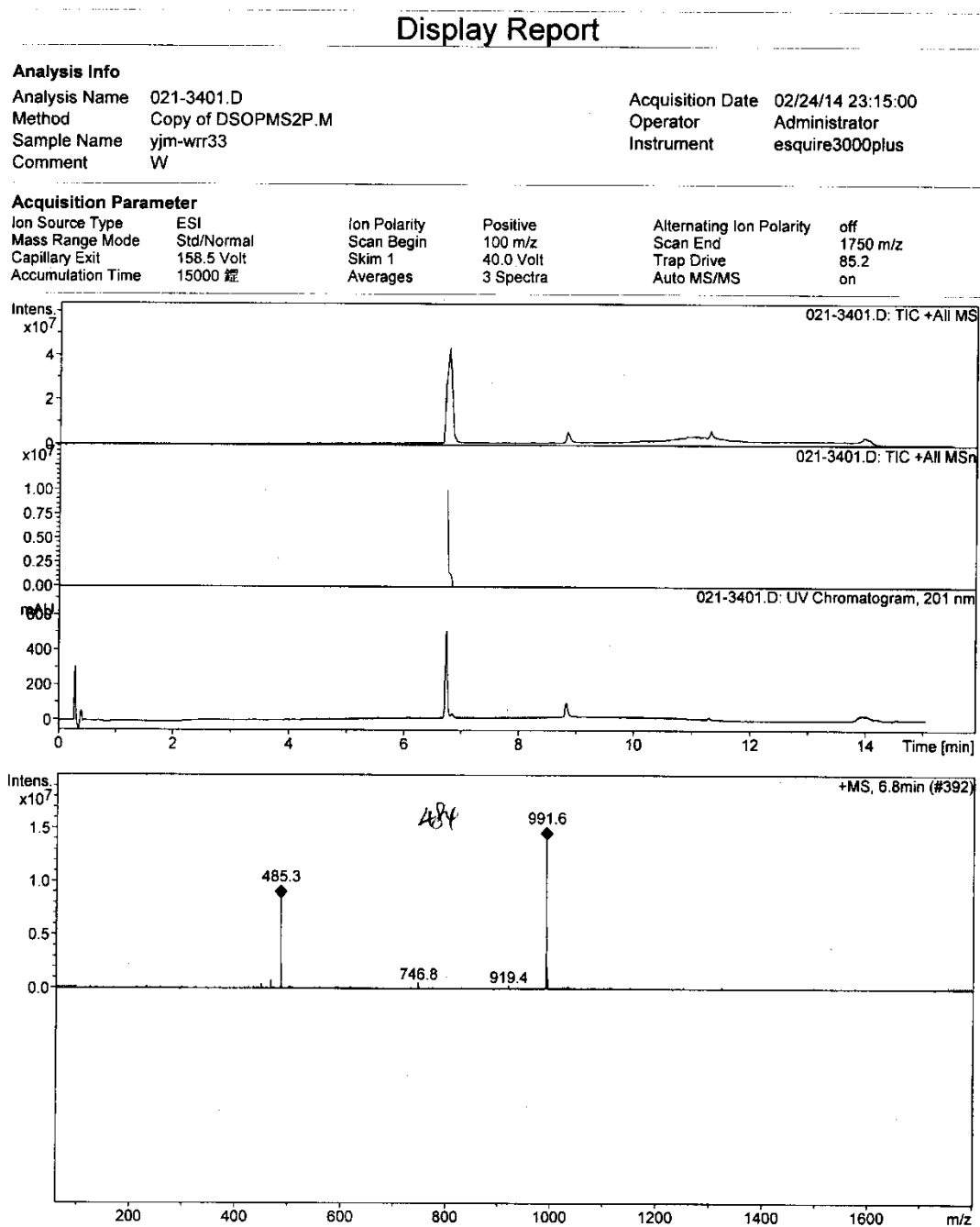


Figure S19. (-)-ESIMS spectrum of walsunoid B (2)

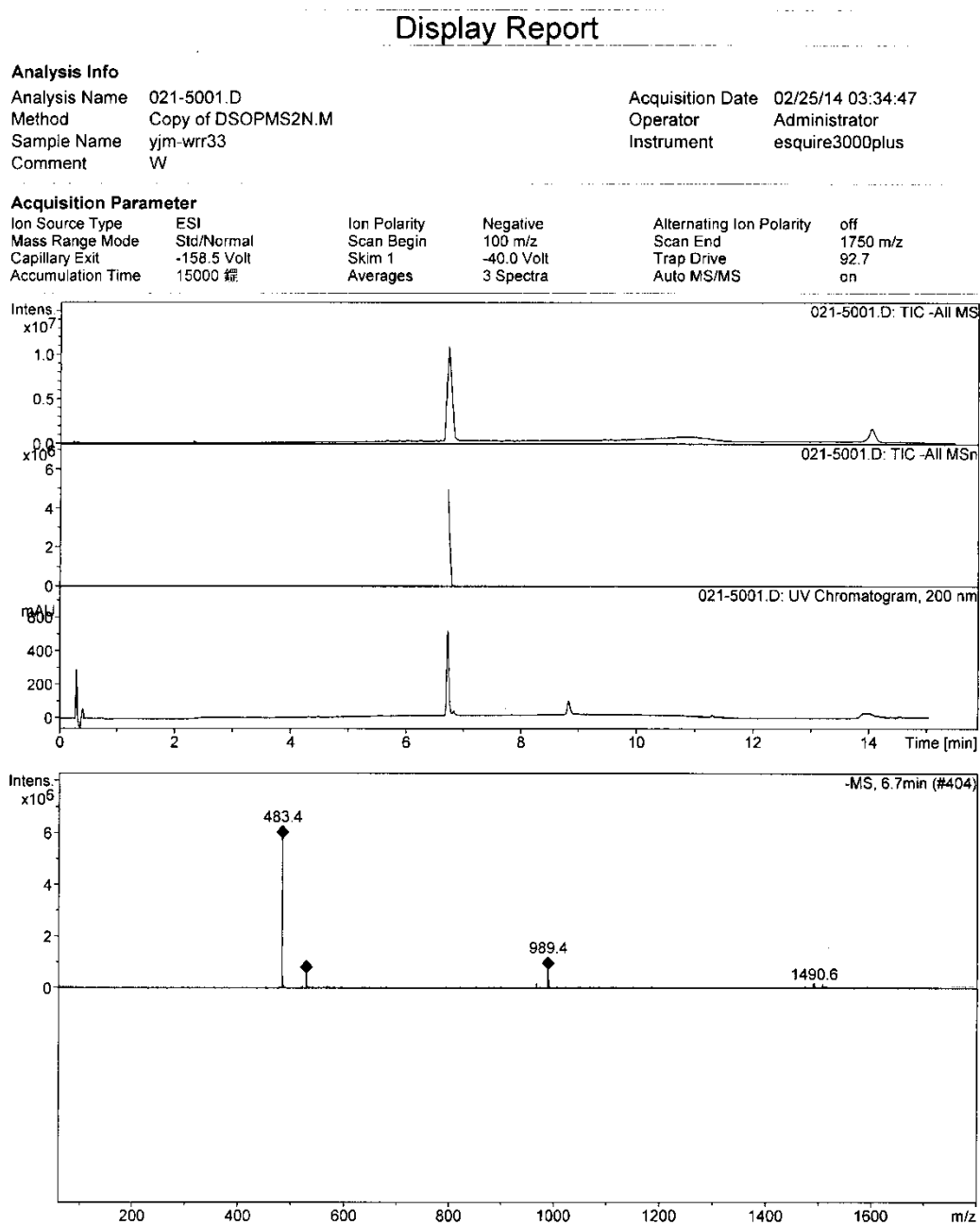


Figure S20. (-)-HRESIMS spectrum of walsunoid B (2)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

97 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 O: 0-20

wrr33

LCT PXE KE324

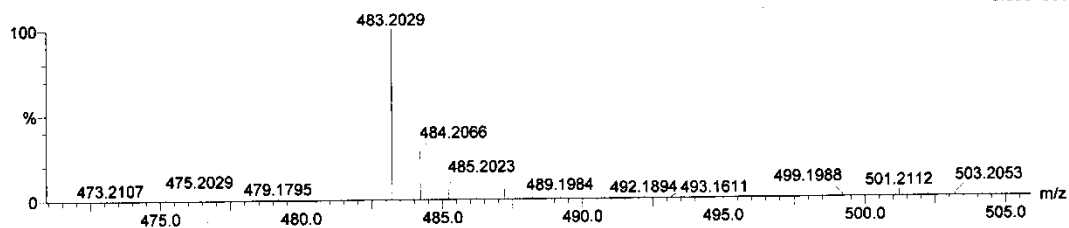
03-Apr-2014

15:31:04

1: TOF MS ES-

9.63e+003

wrr33_0403 13 (0.284) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (9:23)



Minimum: -1.5
Maximum: 5.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
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Figure S21. IR spectrum of walsunoid B (**2**)

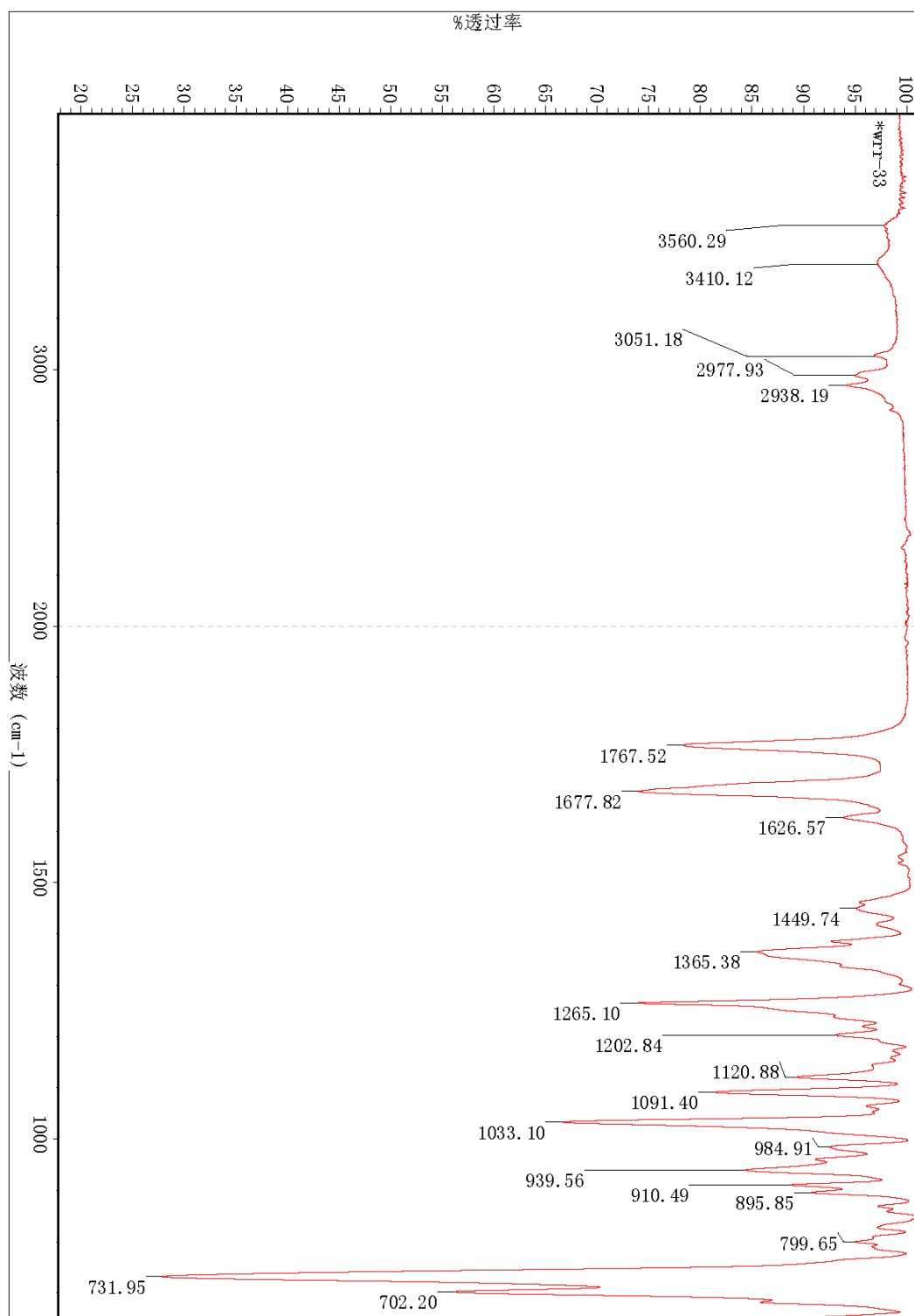


Figure S22. ^1H NMR spectrum of walsunoid C (**3**) in $\text{C}_5\text{D}_5\text{N}$

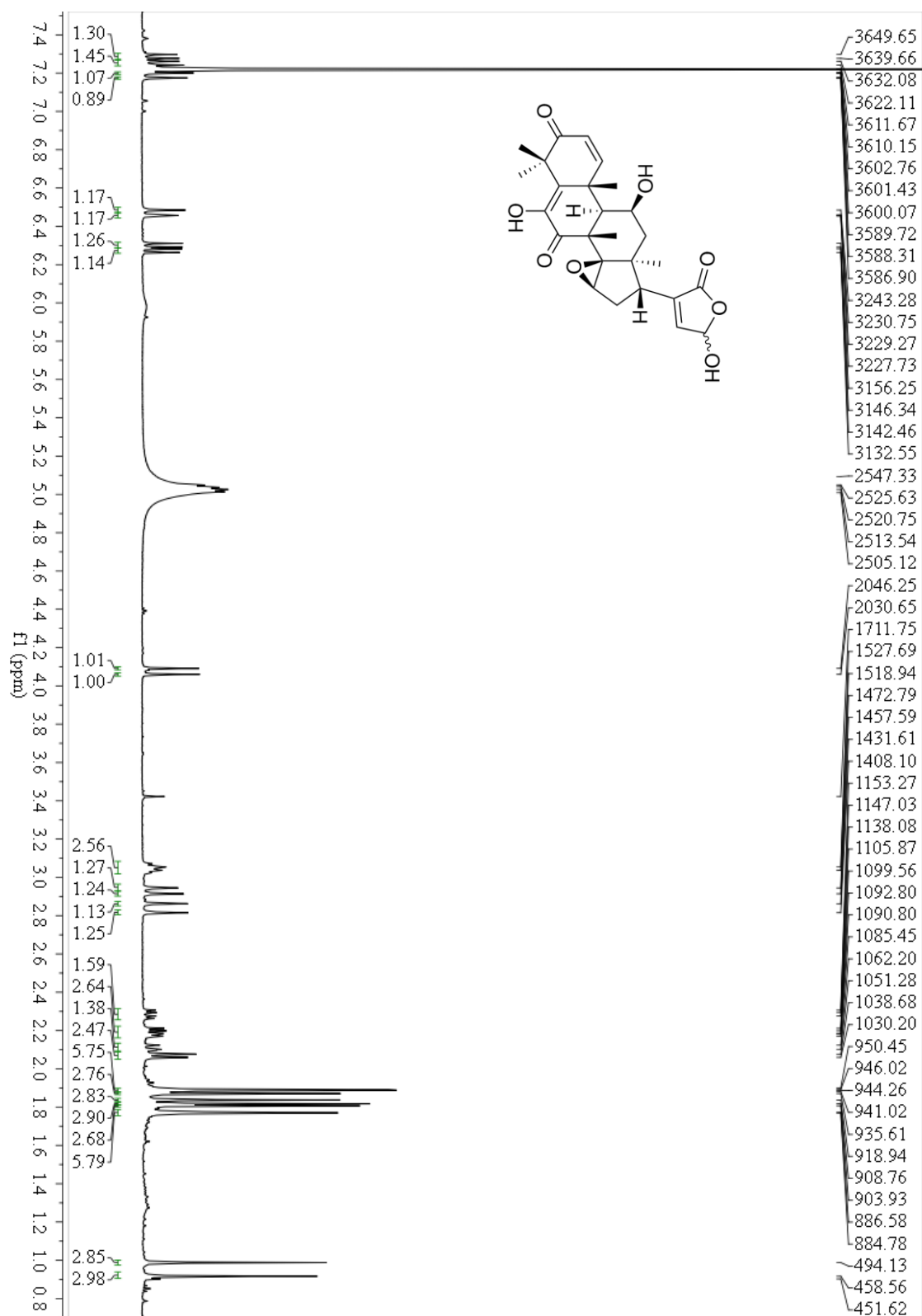


Figure S23. ^{13}C NMR spectrum of walsunoid C (**3**) in $\text{C}_5\text{D}_5\text{N}$

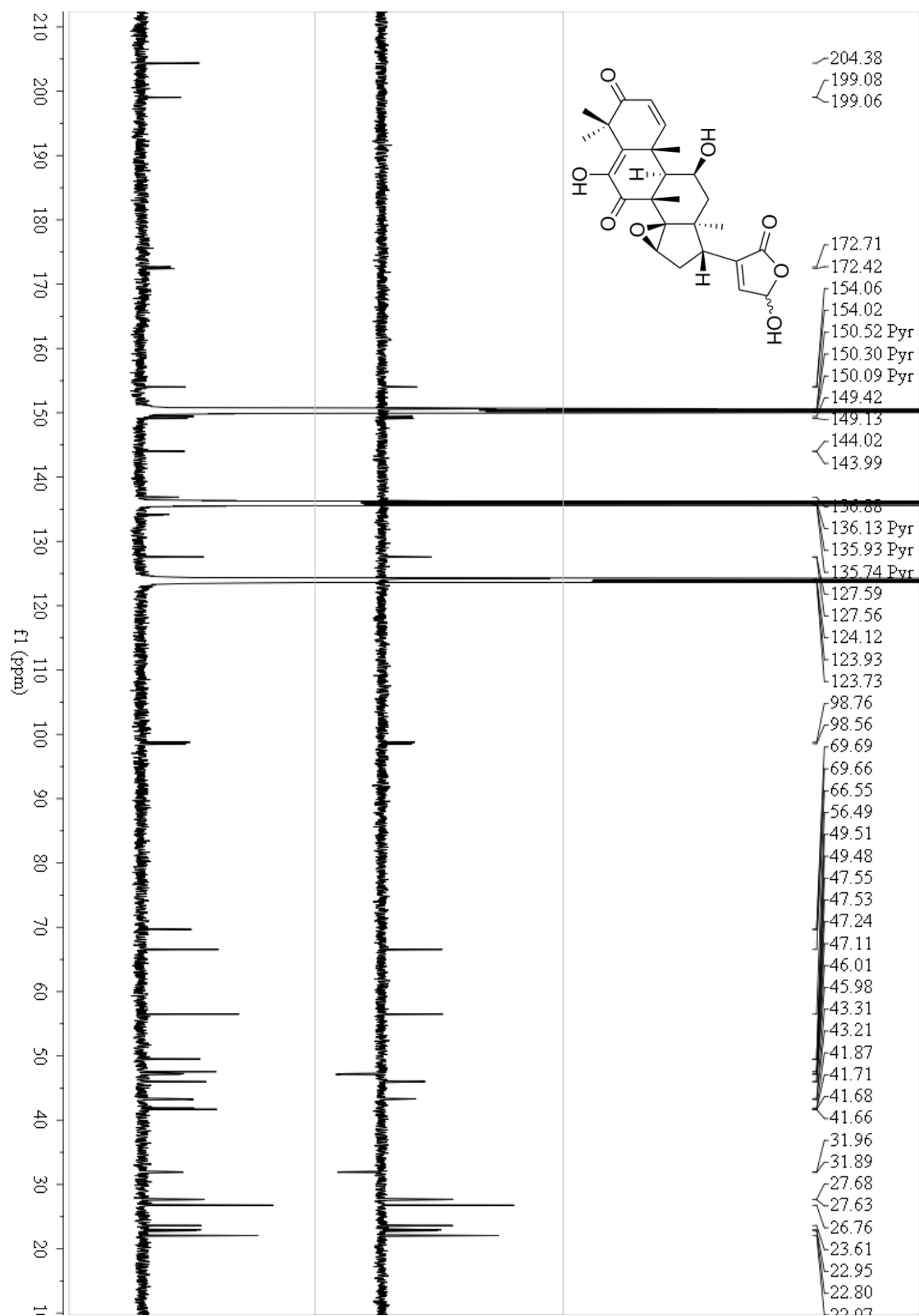


Figure S24. HSQC spectrum of walsunoid C (**3**) in C₅D₅N

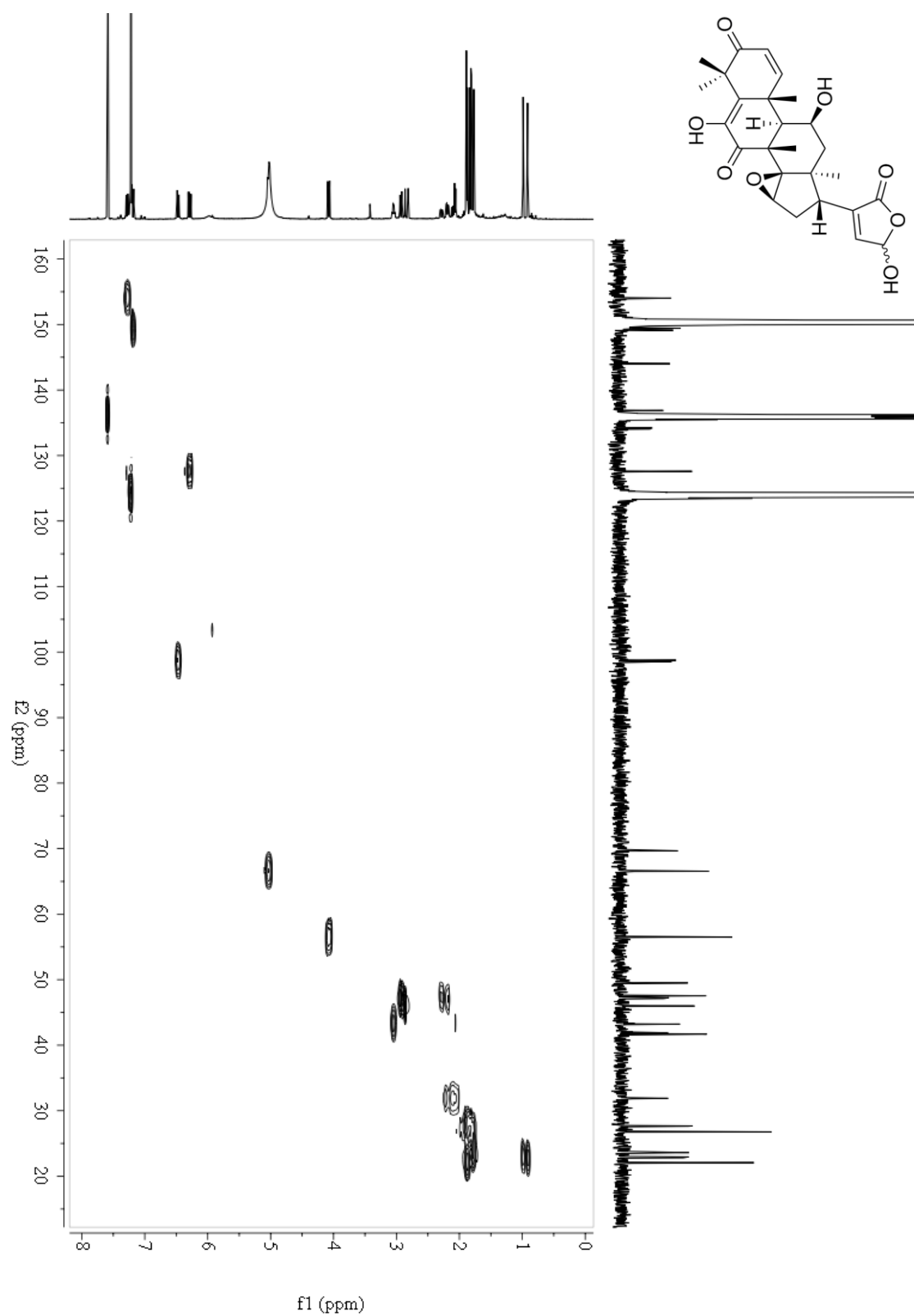
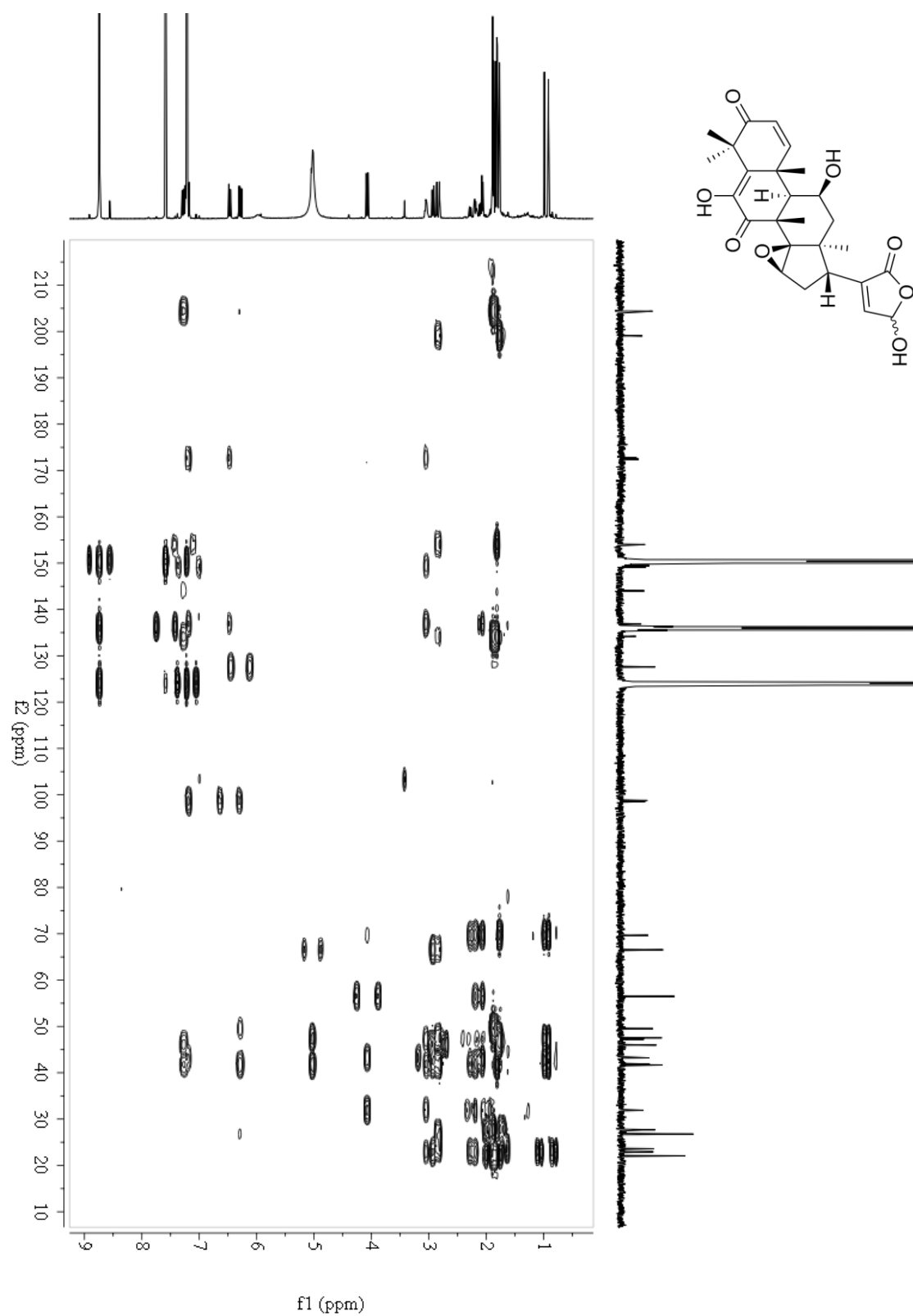


Figure S25. HMBC spectrum of walsunoid C (**3**) in C₅D₅N



The figure displays the chemical structure of compound **1** and its corresponding NMR spectra. The chemical structure is a complex polycyclic molecule featuring a quinone-like core, a fused cyclohexane ring, and a side chain containing a carboxylic acid group. The structure is labeled with stereochemistry (R/S) and various functional groups (OH, O, COOH).

The NMR spectra are shown below the structure. The ¹H NMR spectrum (top) is recorded in CDCl₃ and shows peaks in the aromatic region (6.5–7.5 ppm), a broad peak for the carboxylic acid proton (~11.5 ppm), and aliphatic protons (1.5–4.5 ppm). The ¹³C NMR spectrum (bottom) shows peaks from 10 to 170 ppm, including carbonyl carbons and aliphatic carbons. The chemical shift ranges for both spectra are indicated on the axes.

36

Figure S27. (+)-ESIMS spectrum of walsunoid C (3)

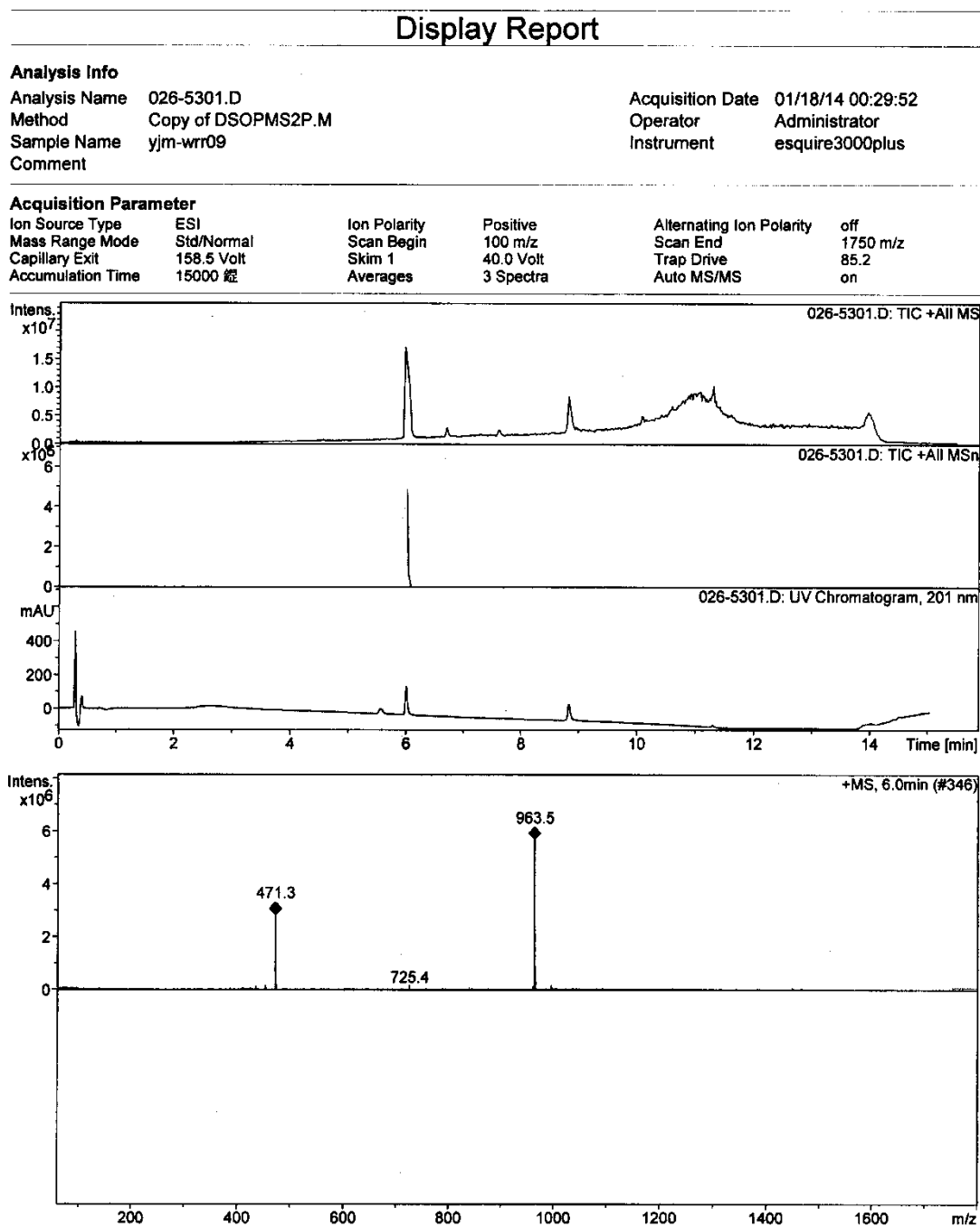


Figure S28. (-)-ESIMS spectrum of walsunoid C (3)

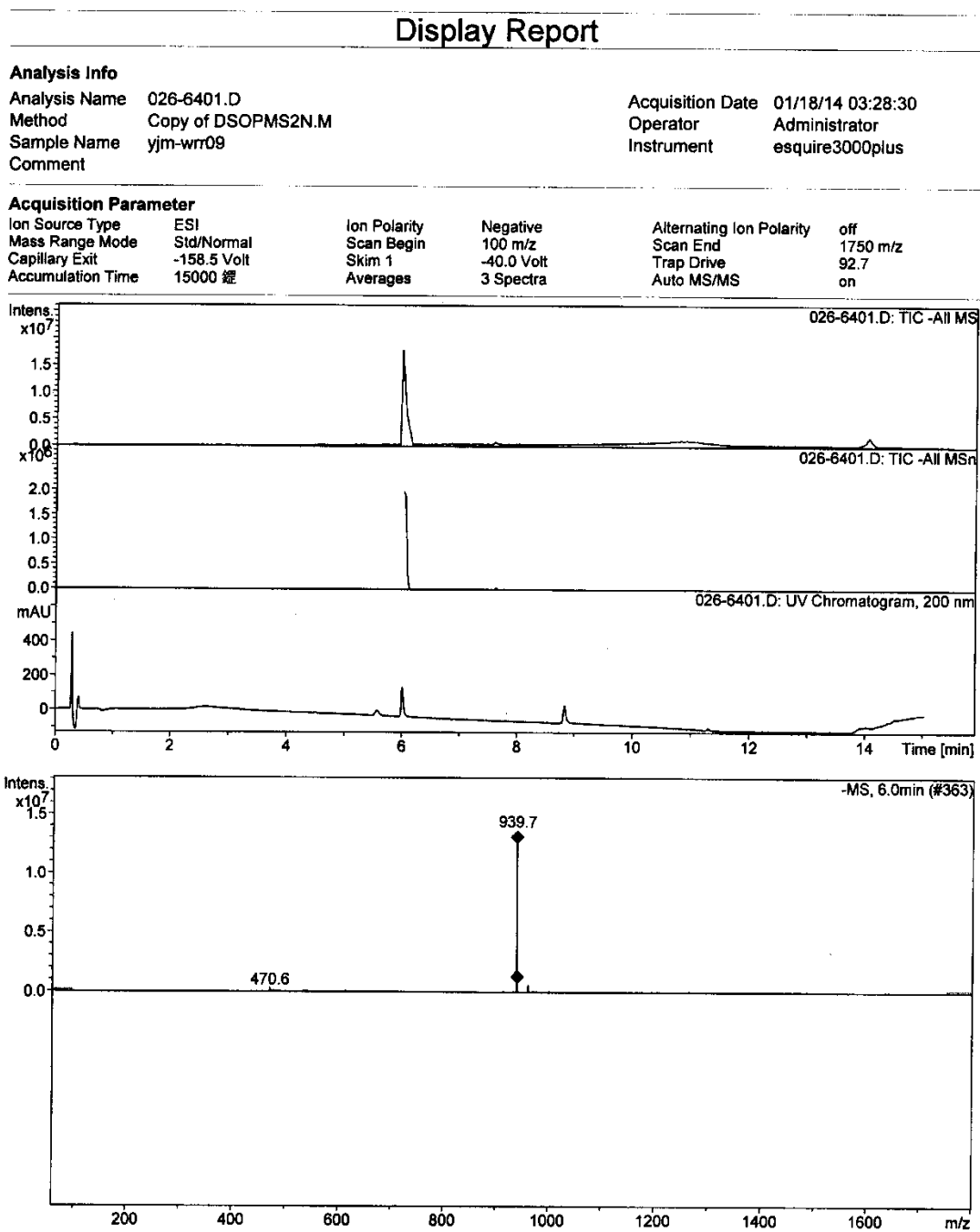


Figure S29. (-)-HRESIMS spectrum of walsunoid C (3)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

90 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 O: 0-20

wrr09

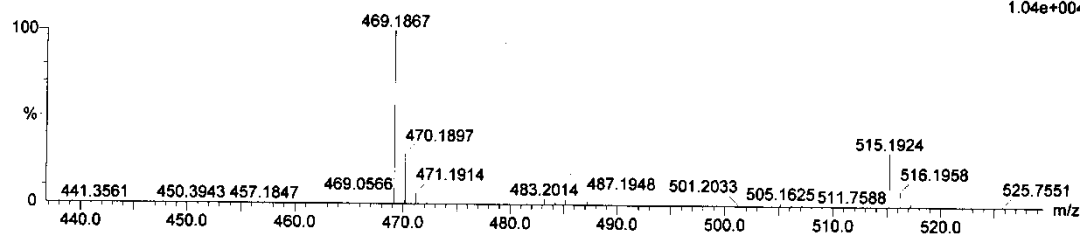
LCT PXE KE324

03-Apr-2014

15:43:20

wrr09_0403 18 (0.372) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (5.22)

1: TOF MS ES-
1.04e+004



Minimum:

Maximum:

5.0

5.0

50.0

Mass

Calc. Mass

mDa

PPM

DBE

i-FIT

i-FIT (Norm)

Formula

469.1867

469.1862

0.5

1.1

12.5

119.6

0.0

C26 H29 O8

Figure S30. IR spectrum of walsunoid C (**3**)

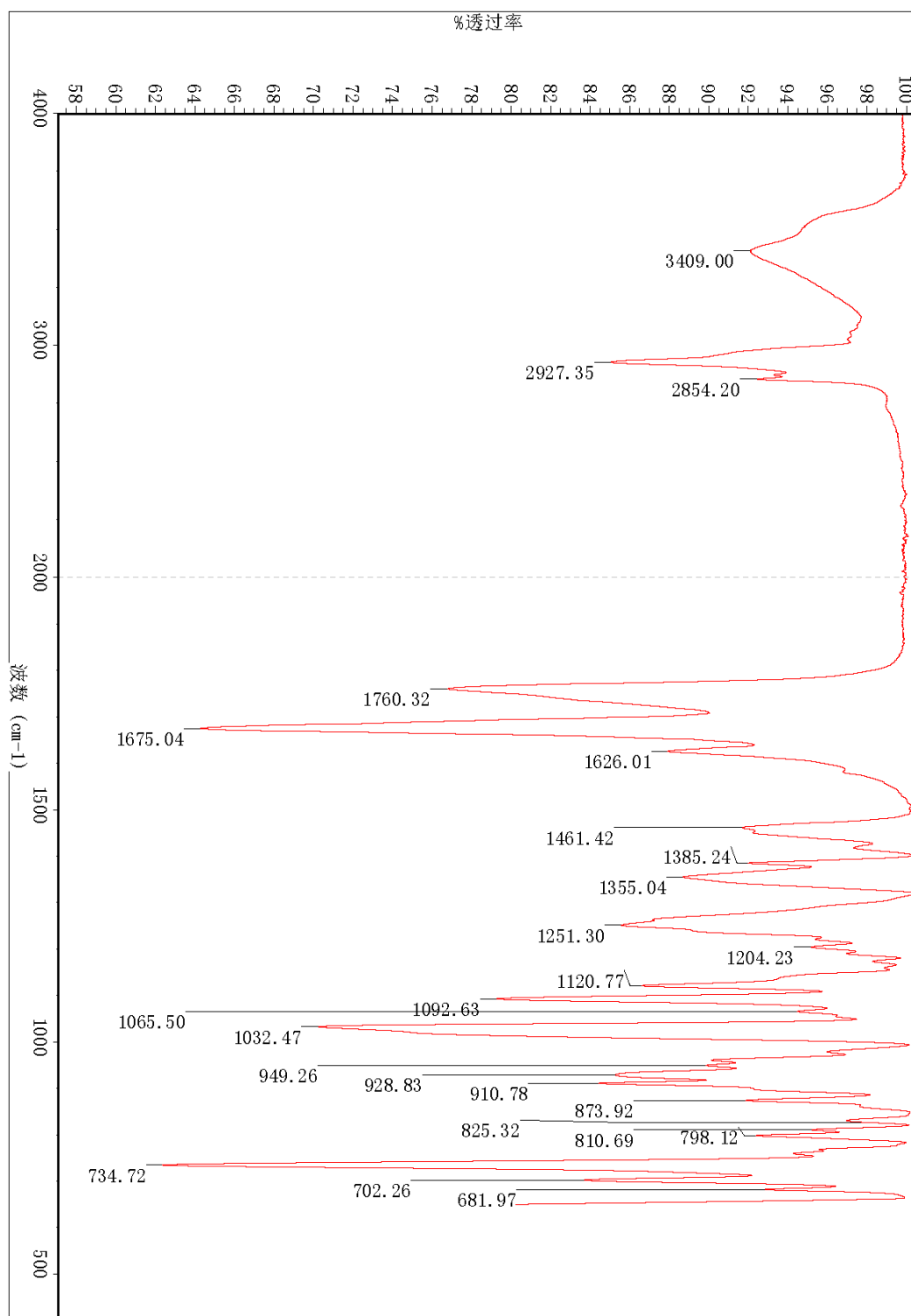


Figure S31. ^1H NMR spectrum of walsunoid D (**4**) in CDCl_3

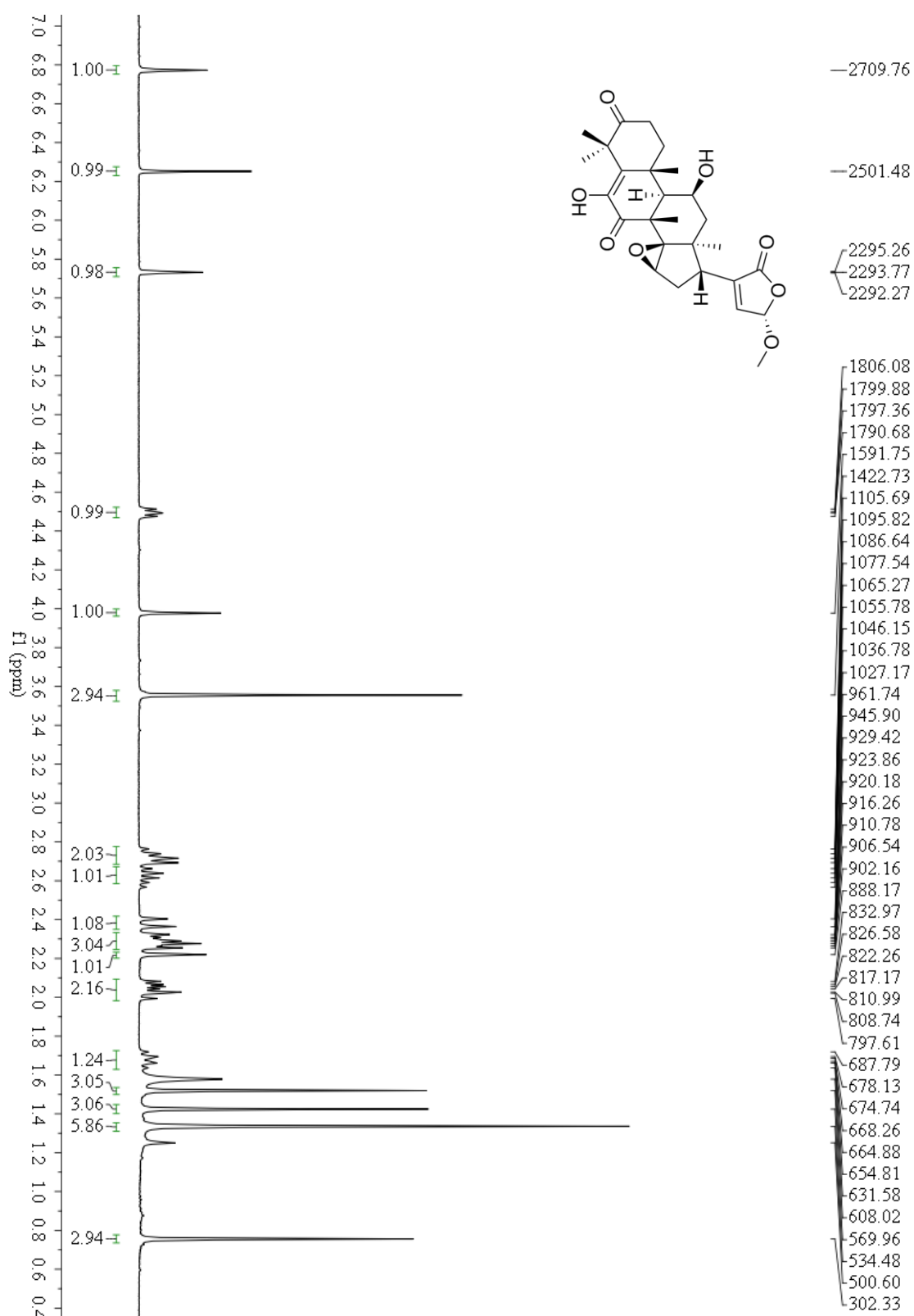


Figure S32. ^{13}C NMR spectrum of walsunoid D (**4**) in CDCl_3

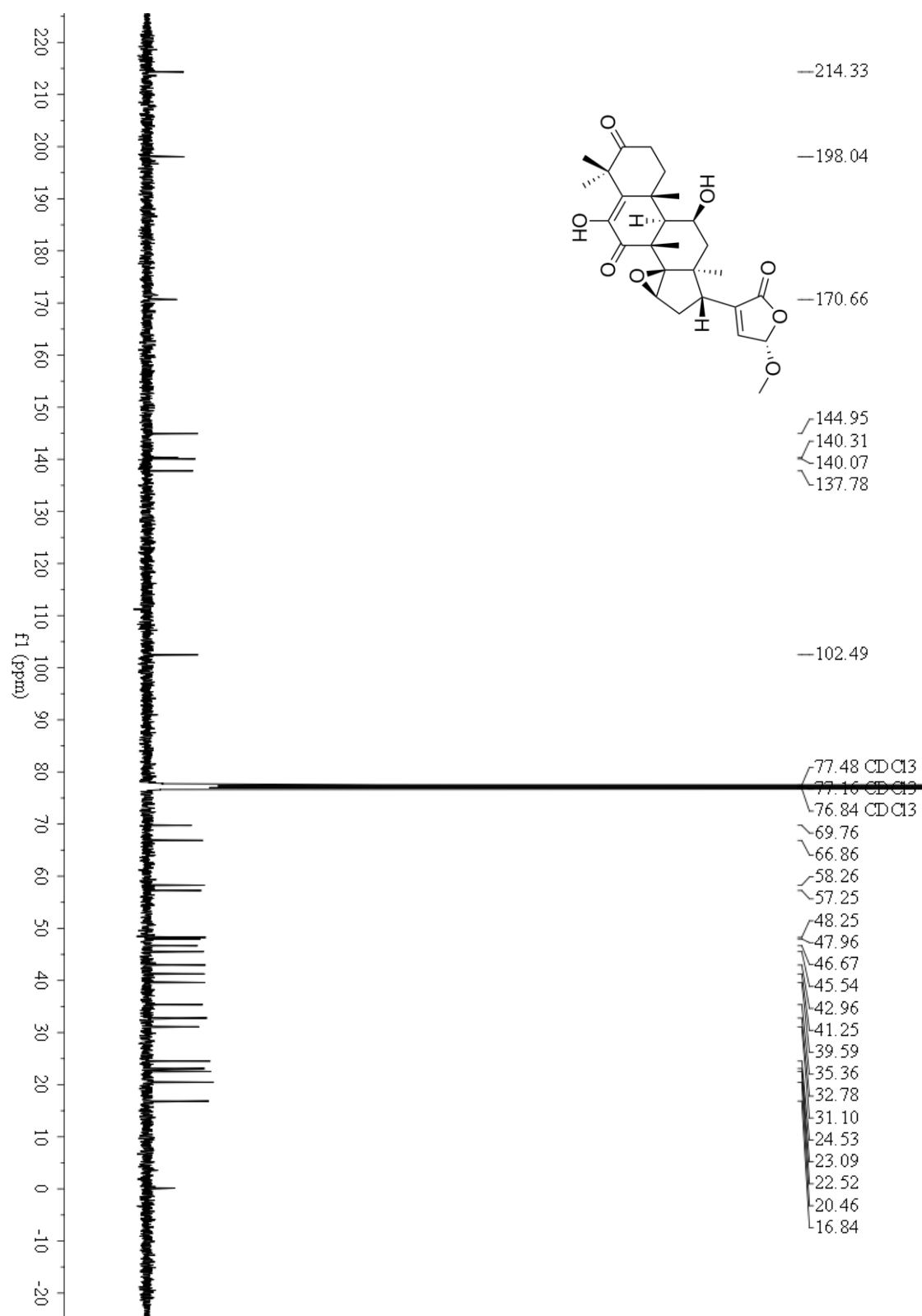


Figure S33. HSQC spectrum of walsunoid D (**4**) in CDCl₃

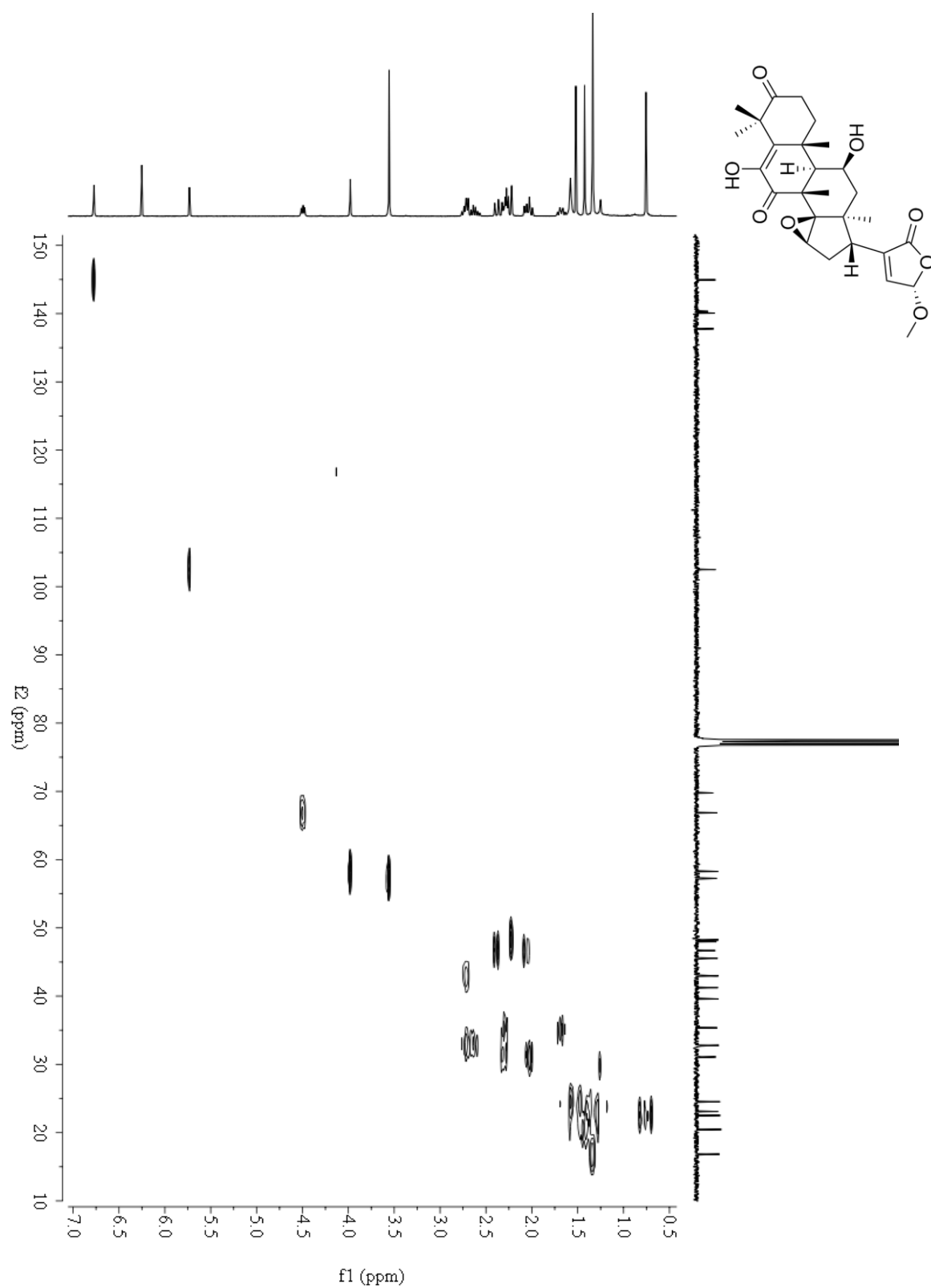


Figure S34. HMBC spectrum of walsunoid D (**4**) in CDCl₃

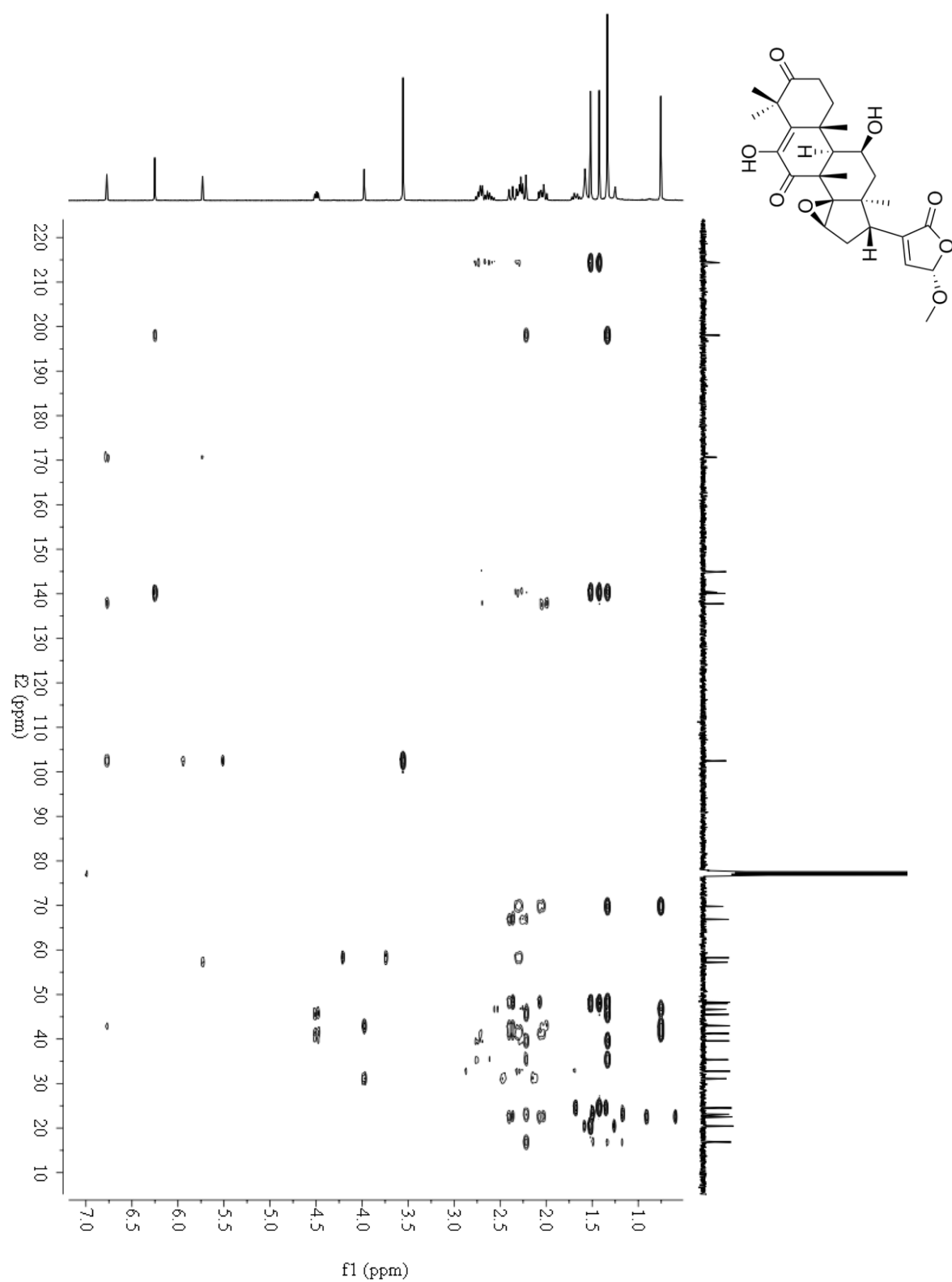
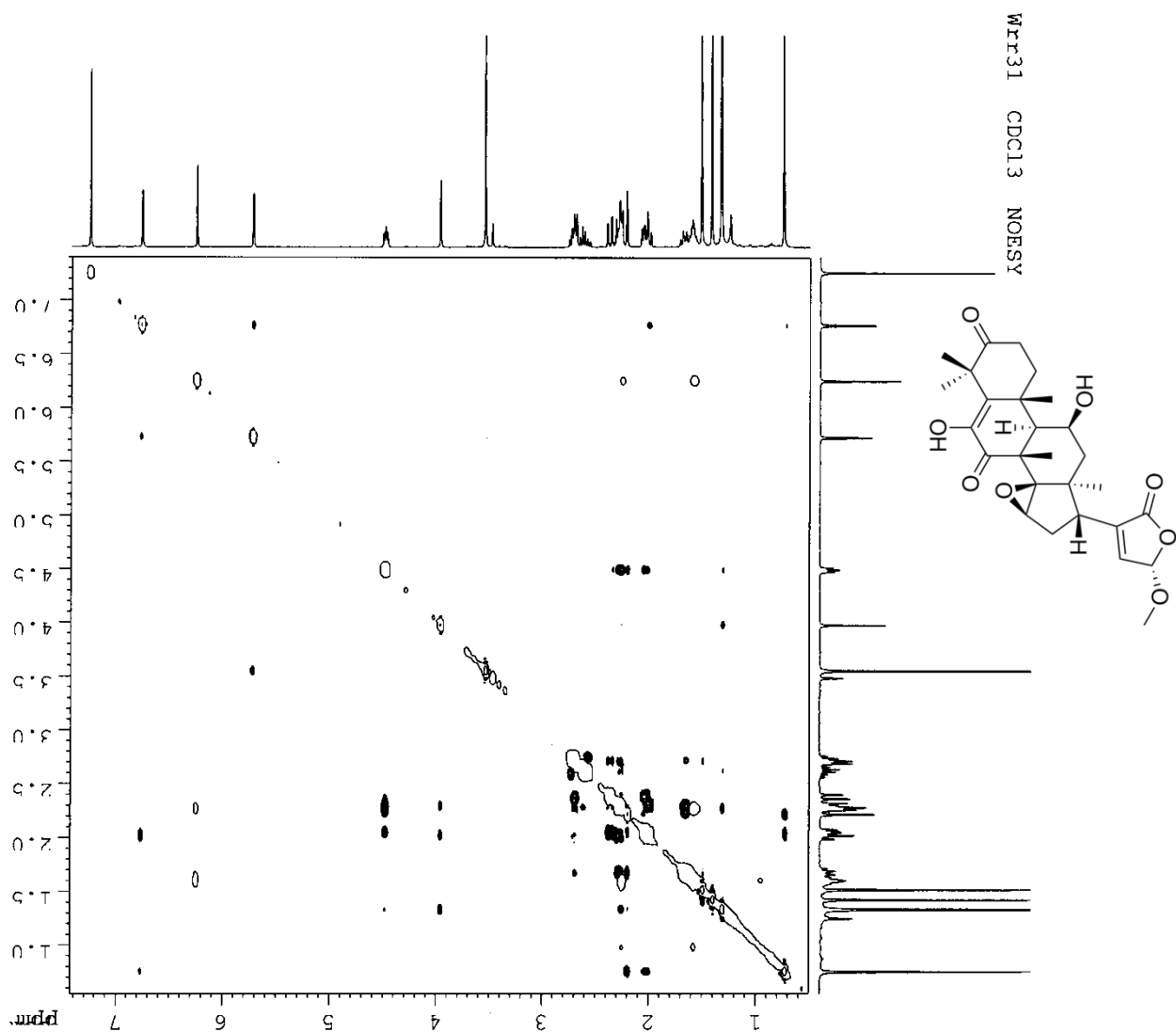


Figure S35. NOESY spectrum of walsunoid D (**4**) in CDCl₃



```

Current Data Parameters
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EXPNO         19
PROCNO        1

F2 - Acquisition Parameters
Date_         20140318
Time          10.56
INSTRUM       spect
PROBHD        5 mm PABUL 13C
PULPROG       noesyphpp
TD            2048
SOLVENT       CDCl3
NS            4
DS            16
SWH           6393.862 Hz
FIDRES        3.12503 Hz
AQ            0.1602036 sec
RG            35.6
DM            78.200 usec
DE            6.50 usec
TE            296.9 K
D0            0.00006600 sec
D1            1.00000000 sec
D8            0.60000002 sec
DECI          0.00000000 sec
D12           0.0002000 sec
INO           0.00015620 sec

===== CHANNEL f1 =====
NUC1          1H
P1            9.50 usec
PL1           2500.00 usec
PLW1          25.00000000 W
PLW10         3.33759999 W
SFO1          400.1328009 MHz

F1 - Acquisition parameters
TD            320
SFO1          400.1328 MHz
FIDRES        20.006580 Hz
SW            16.000 ppm
FMODE         States-TPPI

F2 - Processing parameters
SI            1024
SF            400.130097 MHz
WDW           Q5SINC
SSB           0.65
GB            0
PC            1.00

F1 - Processing parameters
SI            1024
MC2           States-TPPI
SF            400.1300071 MHz
WDW           States-TPPI
SSB           2
GB            0
PC            0 Hz
  
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Figure S36. (+)-ESIMS spectrum of walsunoid D (4)

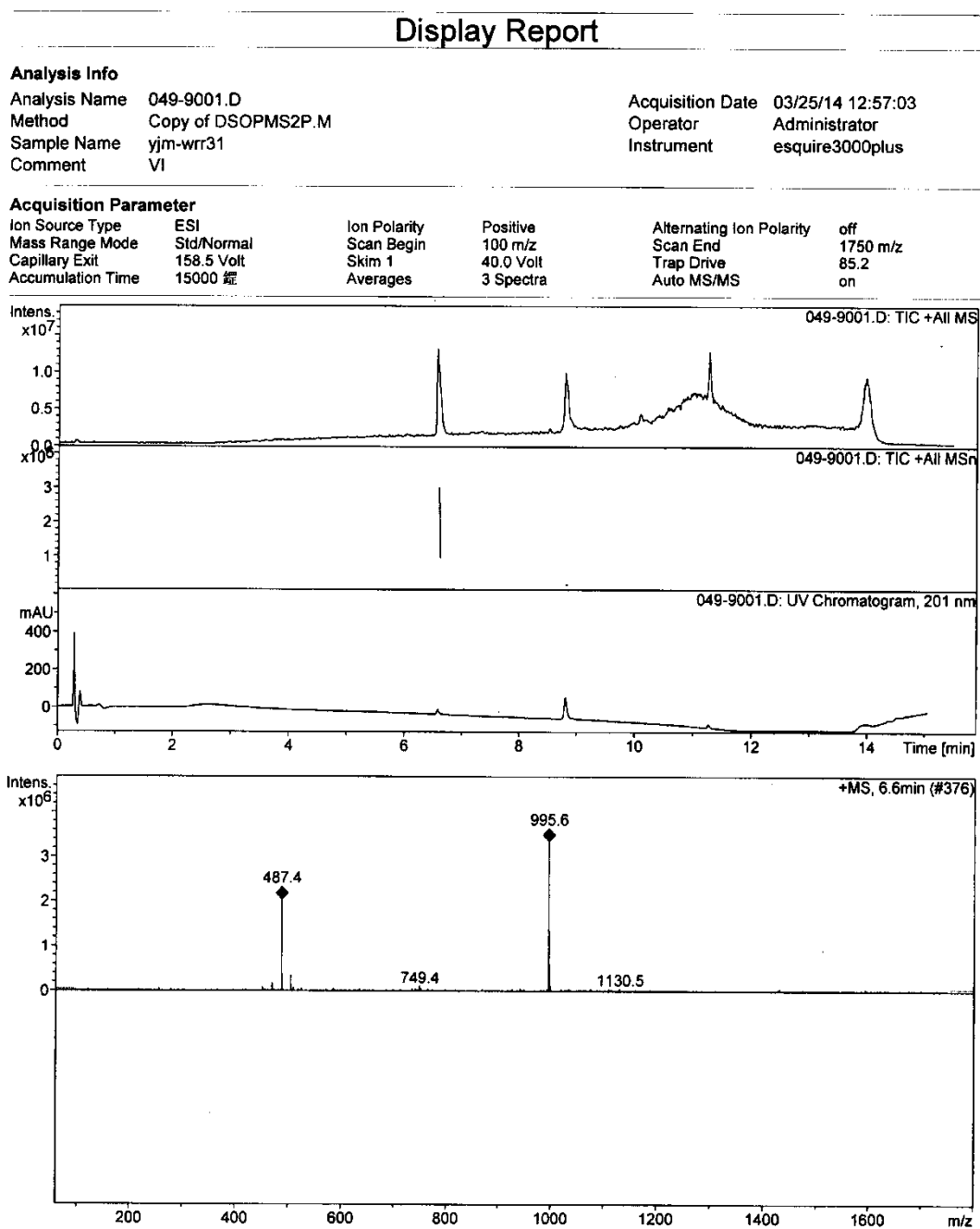


Figure S37. (-)-ESIMS spectrum of walsunoid D (4)

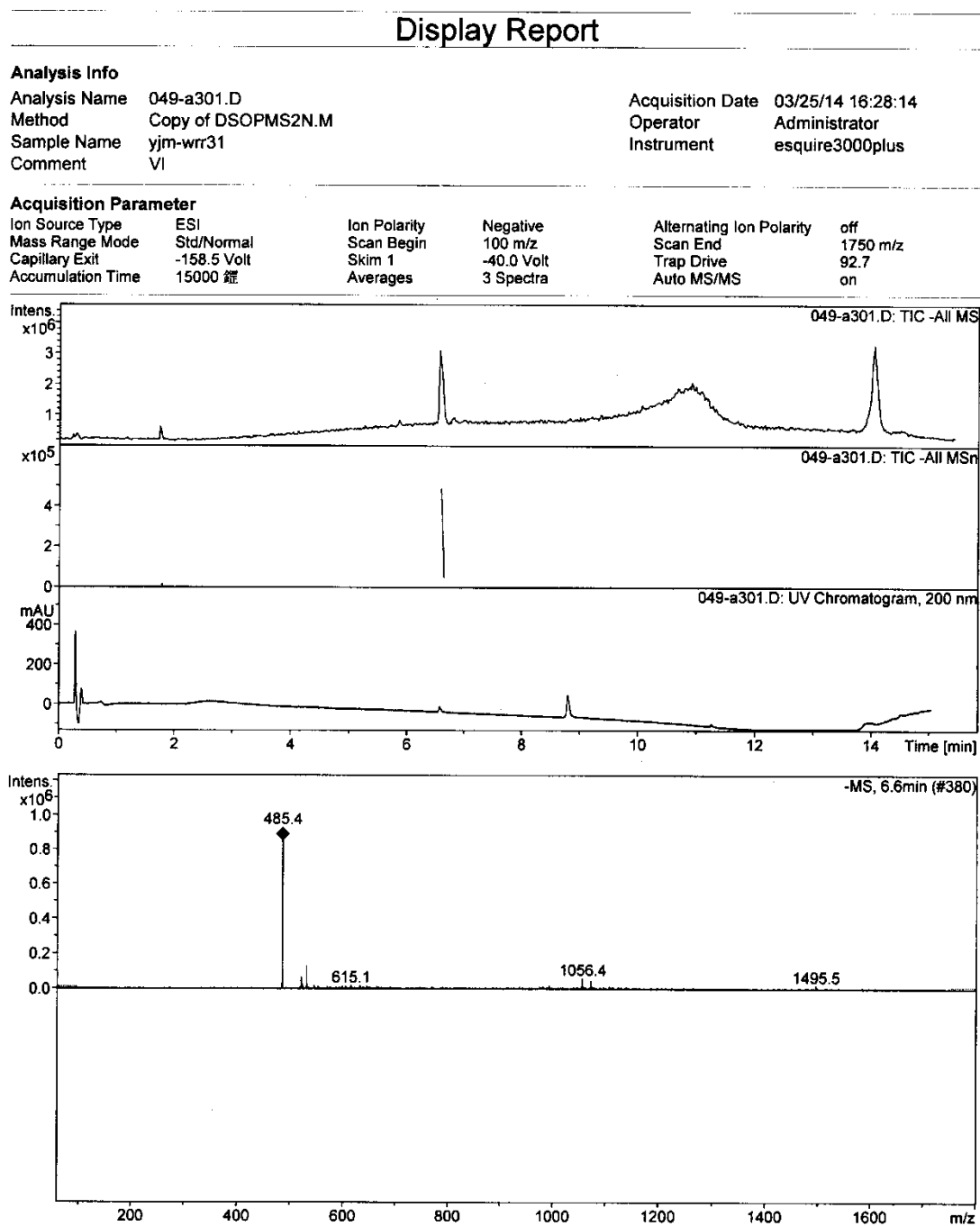


Figure S38. (+)-HRESIMS spectrum of walsunoid D (4)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

406 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 O: 0-20 Na: 0-1

wrr31

LCT PXE KE324

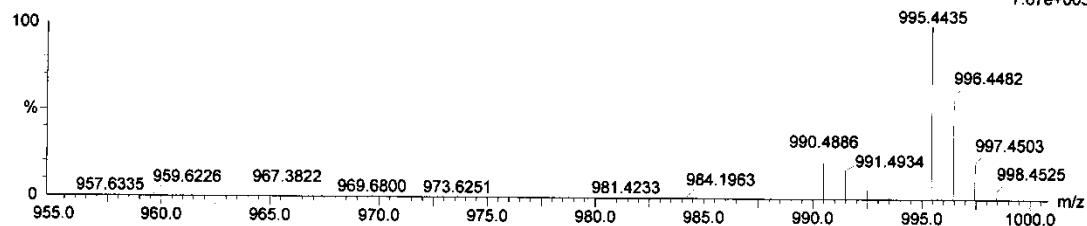
03-Apr-2014

16:53:07

1: TOF MS ES+

7.87e+003

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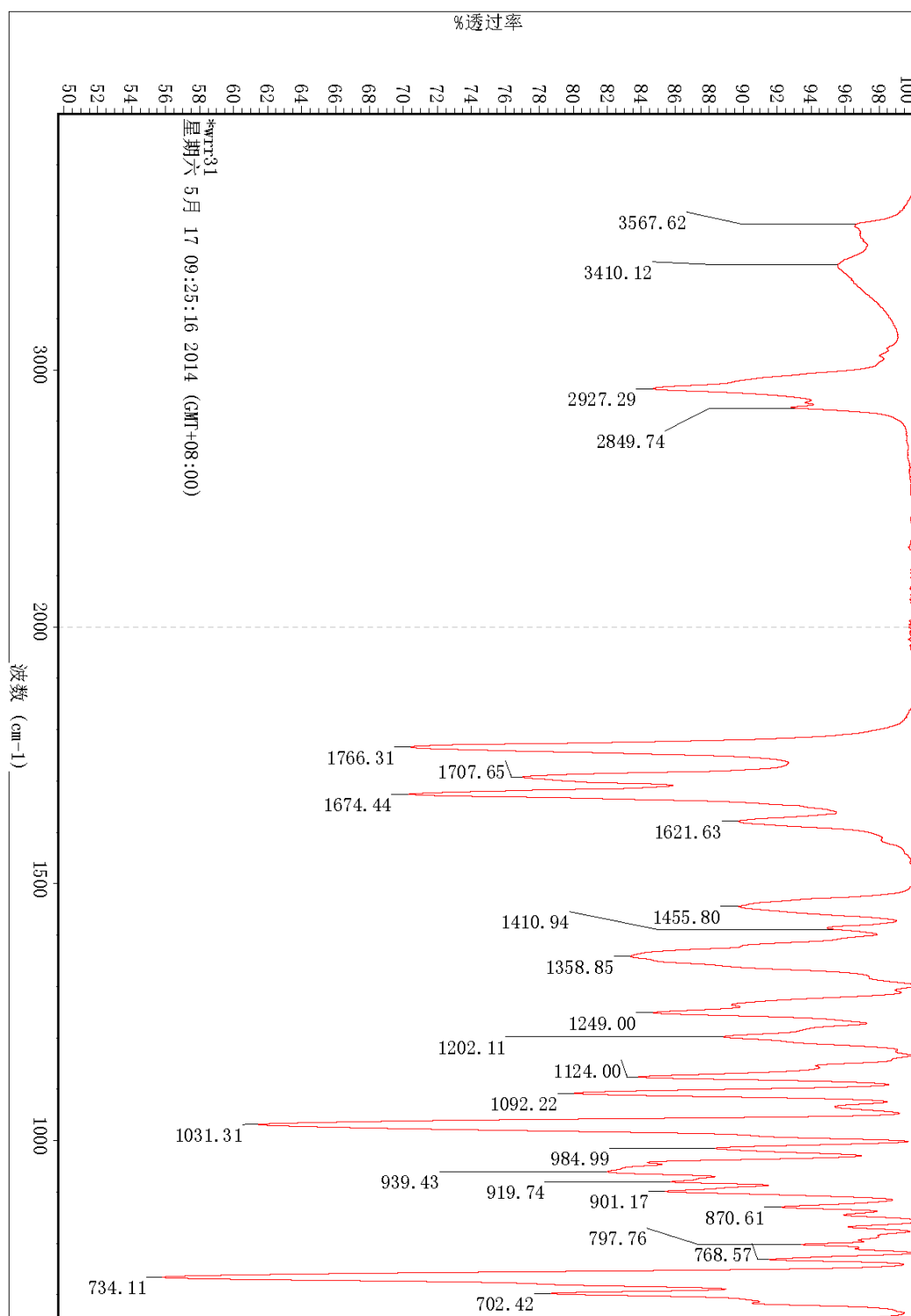
Minimum:

Maximum: 5.0 5.0 -1.5

Maximum: 5.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
995.4435	995.4440	-0.5	-0.5	42.5	62.8	7.1	C72 H60 O3 Na
	995.4429	0.6	0.6	23.5	57.1	1.4	C56 H67 O16
	995.4464	-2.9	-2.9	45.5	64.1	8.4	C74 H59 O3
	995.4405	3.0	3.0	20.5	55.9	0.3	C54 H68 O16 Na

Figure S39. IR spectrum of walsunoid D (4)



Chemical structure of **1** is shown above the spectrum. The ¹³C NMR spectrum (CDCl₃) displays peaks from 439.63 to 912.70 ppm. Key peaks are labeled with their chemical shifts (ppm): 912.70, 857.23, 808.24, 805.13, 804.09, 800.66, 751.85, 750.21, 439.63, 4273.85, 4272.10, 4270.38, 4268.67, 3752.65, 2904.02, 2902.30, 2900.60, 2898.12, 2896.36, 2895.62, 2893.89, 2698.14, 2695.53, 2390.90, 2105.30, 1640.72, 1639.56, 1631.33, 1630.10, 1621.90, 1620.68, 1582.81, 1581.56, 1572.62, 1454.34, 1438.53, 1392.38, 1391.18, 1385.34, 1384.25, 1382.59, 1381.29, 1378.84, 1377.78, 1375.68, 1368.83, 1366.61, 1336.46, 1253.36, 1252.44, 1250.71, 1244.20, 1242.32, 1241.46, 1239.74, 1238.80, 1234.91, 1228.63, 1227.80, 912.70, 857.23, 808.24, 805.13, 804.09, 800.66, 751.85, 750.21, 439.63.

Figure S41. ^{13}C NMR spectrum of e walsunoid E (**5**) in CDCl_3

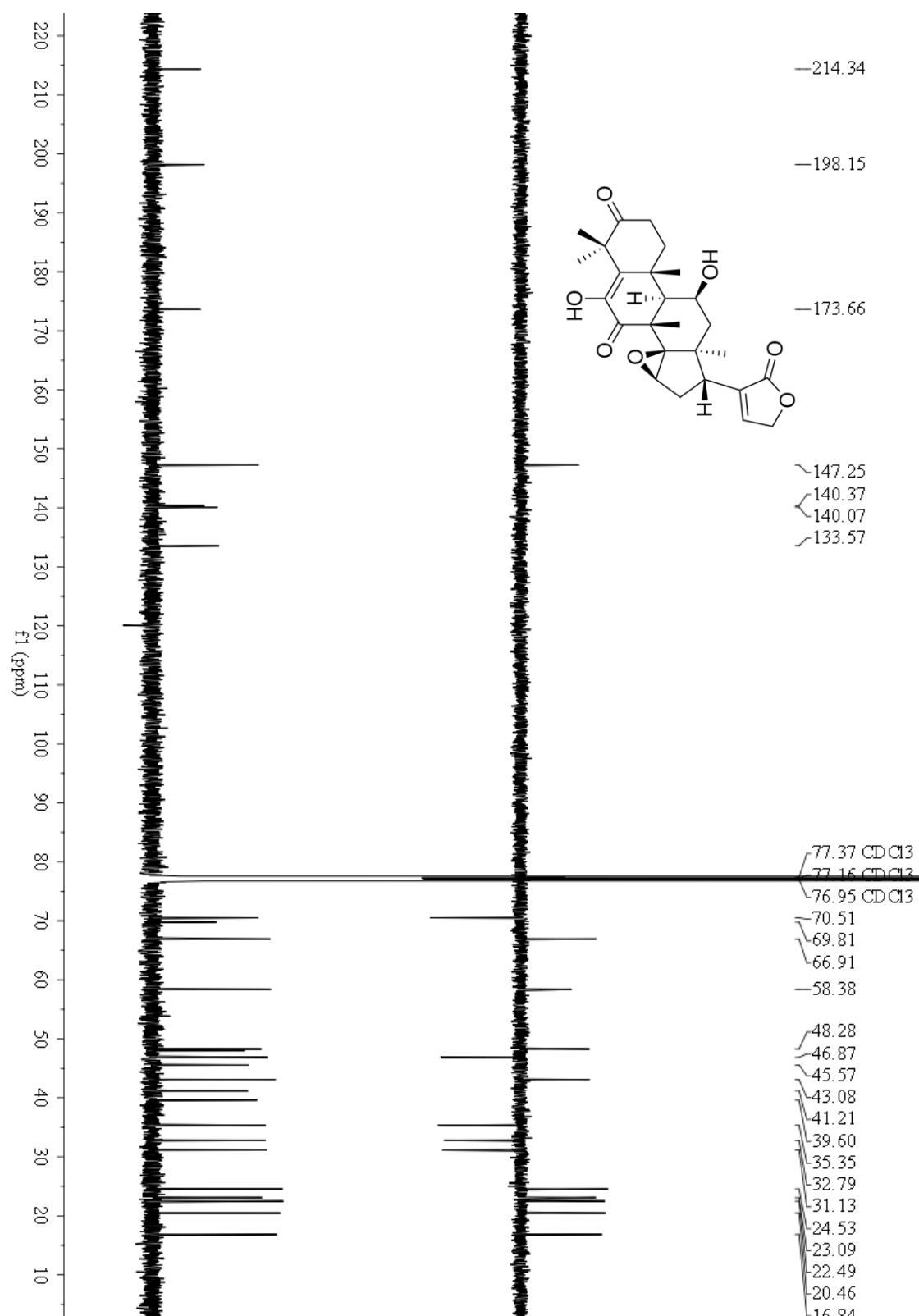


Figure S42. HSQC spectrum of walsunoid E (**5**) in CDCl₃

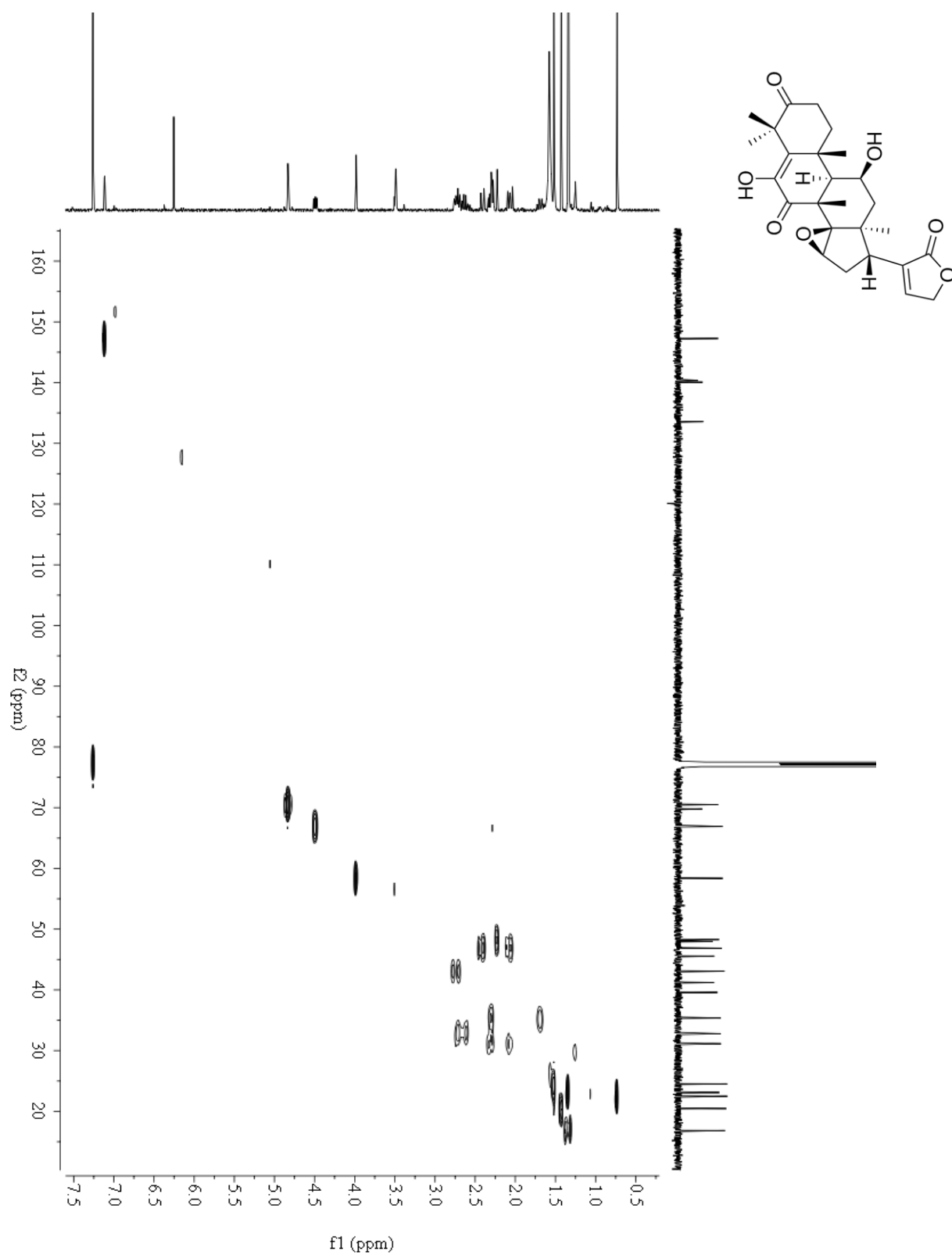


Figure S43. HMBC spectrum of walsunoid E (**5**) in CDCl₃

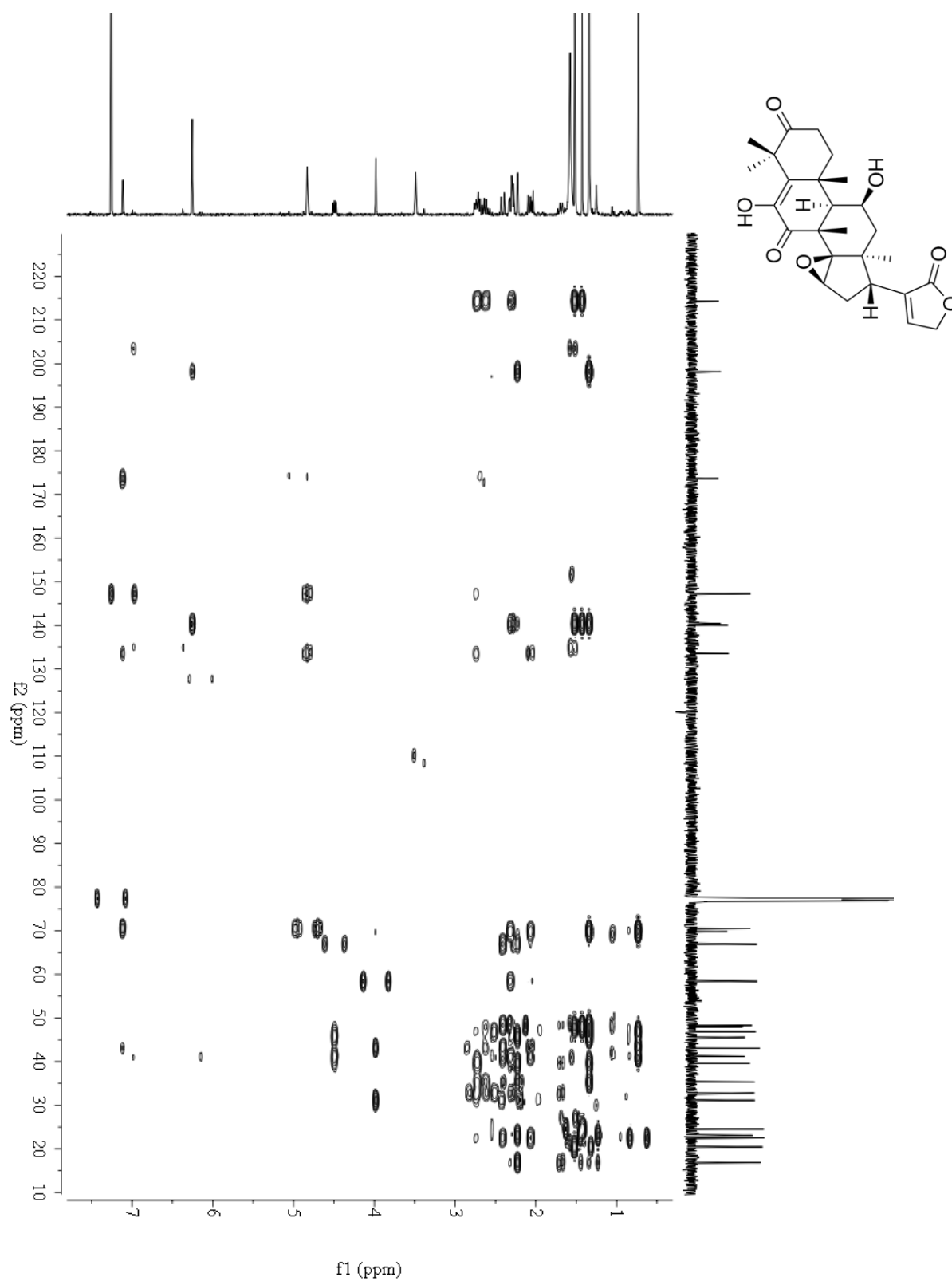


Figure S44. (+)-ESIMS spectrum of walsunoid E (5)

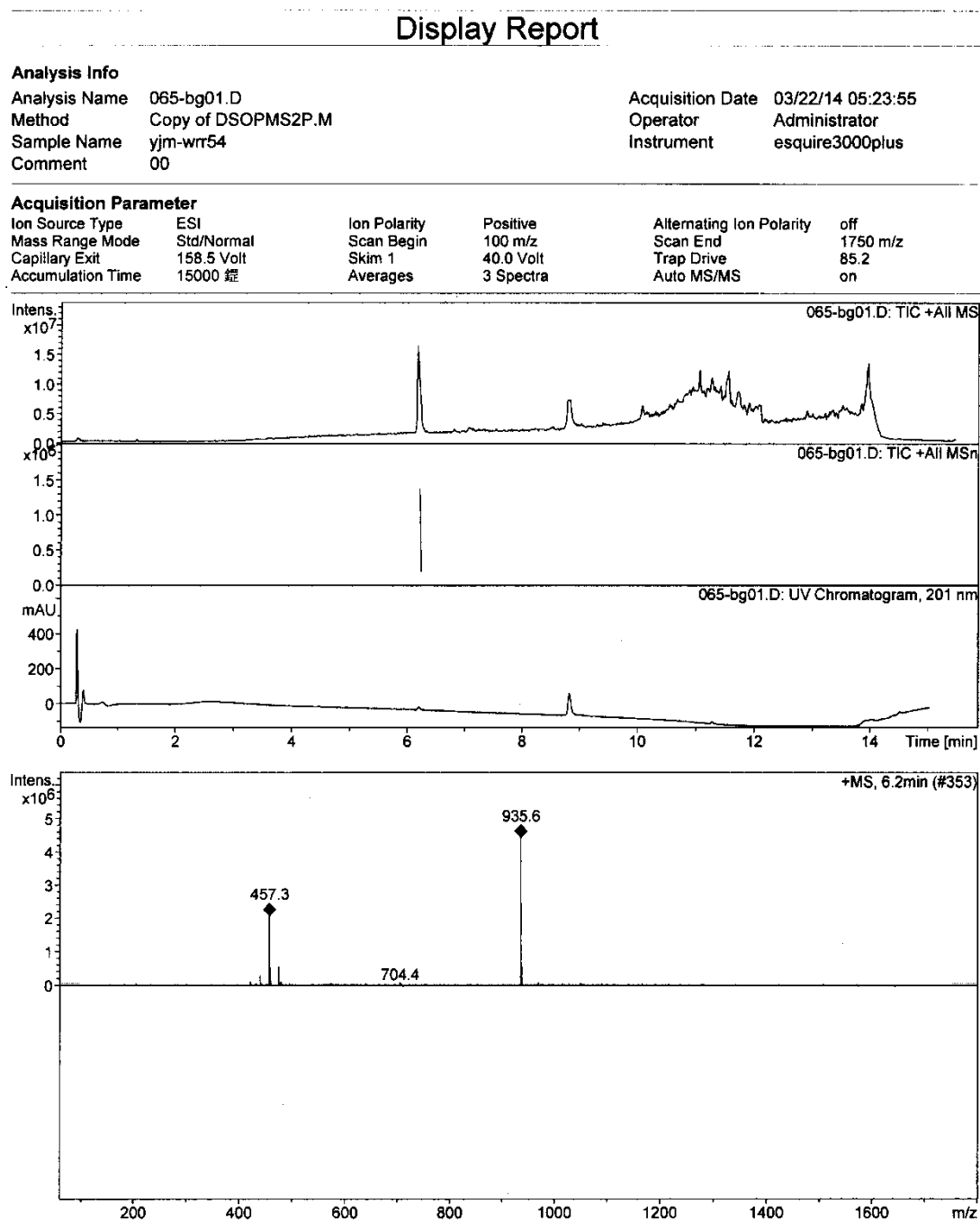


Figure S45. (-)-ESIMS spectrum of walsunoid E (5)

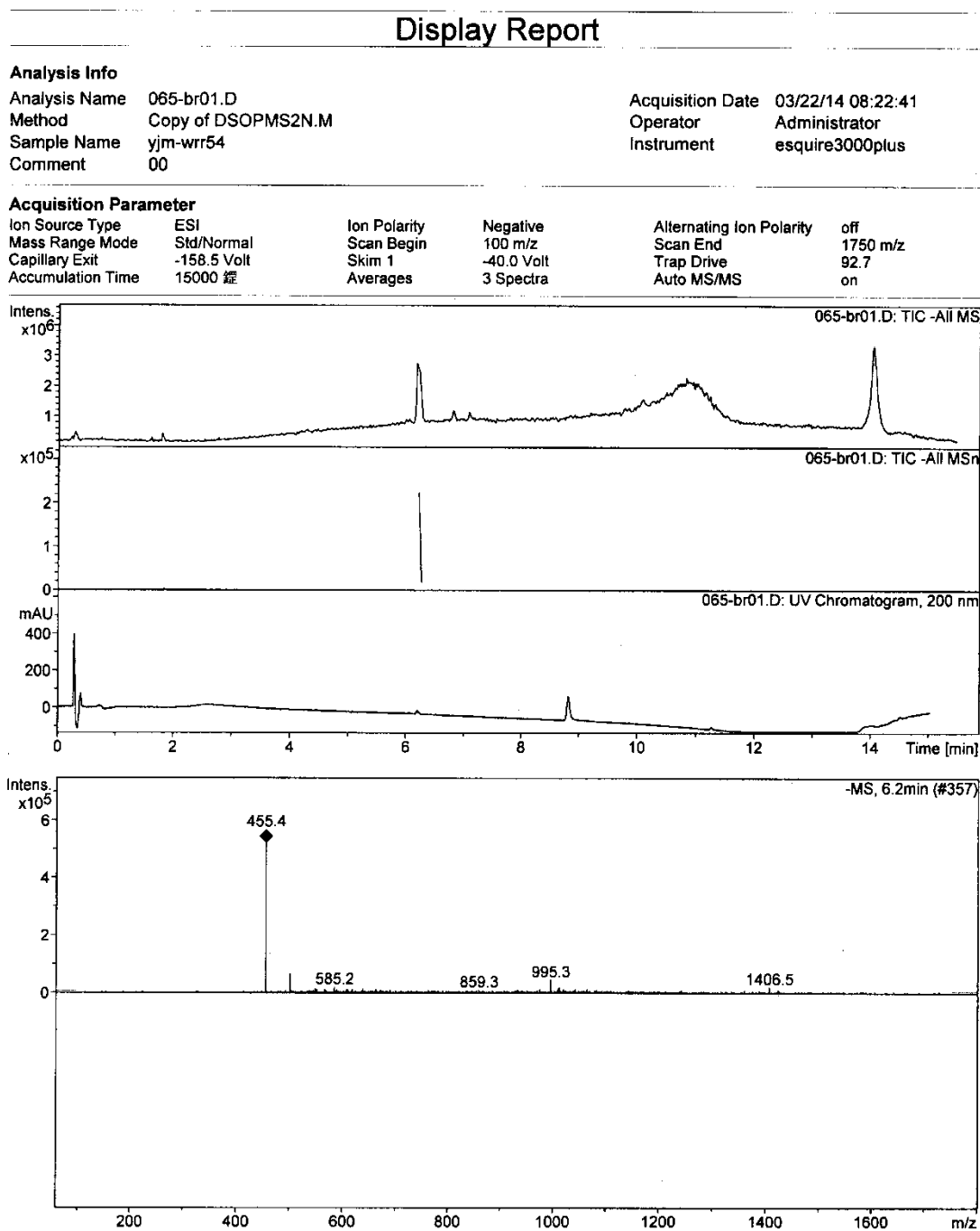


Figure S46. (+)-HRESIMS spectrum of walsunoid E (5)

Elemental Composition Report

Page 1

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

10 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)

SIMM-Mass Spec

Q-ToF Ultima

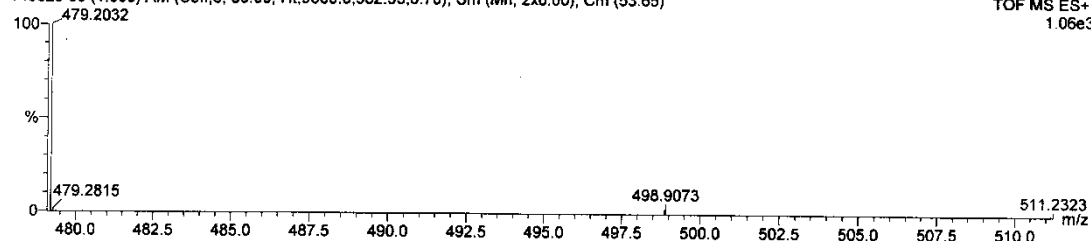
06-May-2014 14:37:37

wrr54

140623 53 (1.000) AM (Cen, 5, 80.00, Ht. 9000.0, 362.93, 0.70); Sm (Mn, 2x0.00); Cm (53:65)

TOF MS ES+

1.06e3



Minimum:	50.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
479.2032	100.00	479.2046	-1.4	-2.9	10.5	1	C26 H32 O7 Na

Figure S47. IR spectrum of walsunoid E (5)

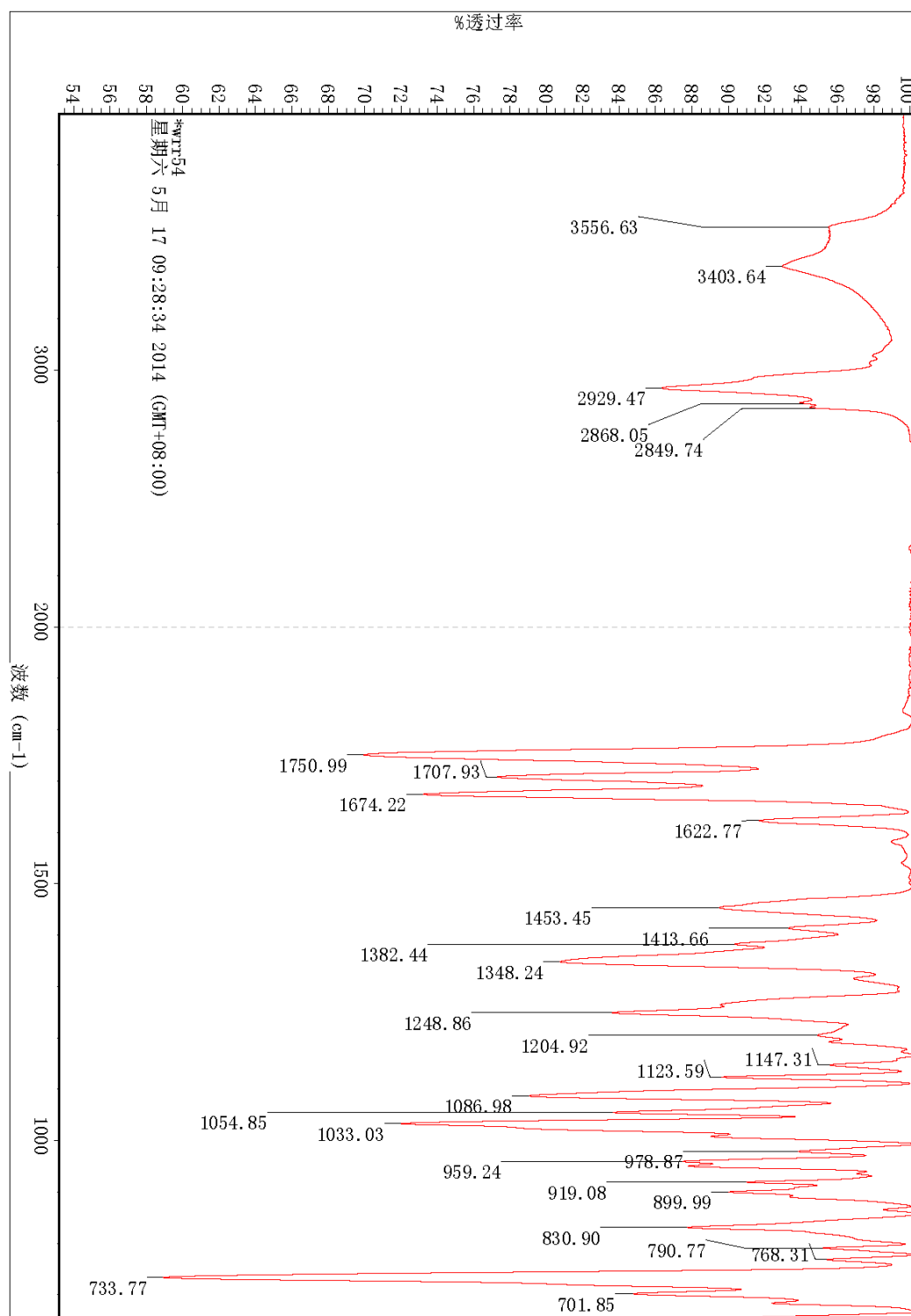


Figure S48. ^1H NMR spectrum of walsunoid F (**6**) in $\text{C}_5\text{D}_5\text{N}$

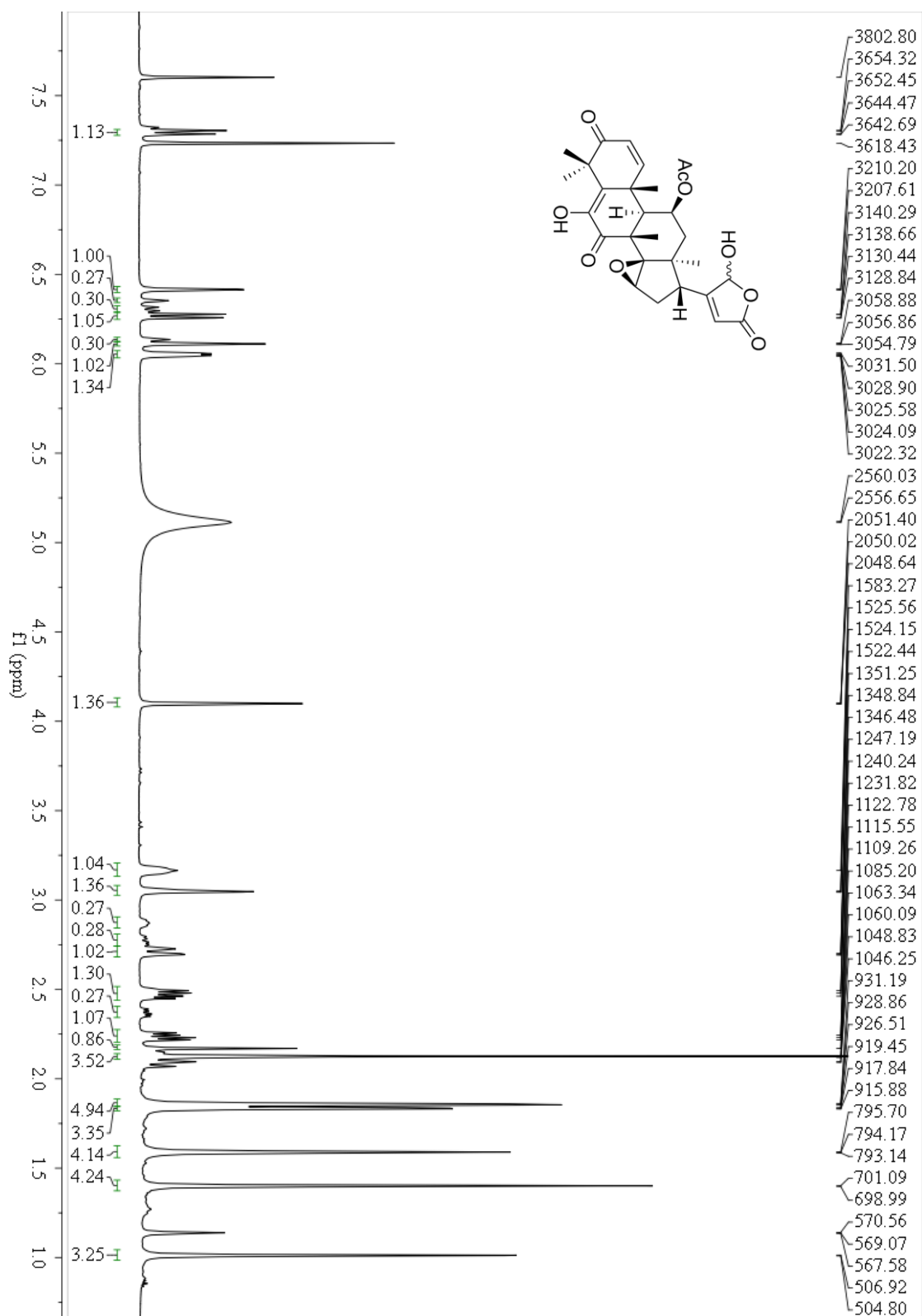


Figure S49. ^{13}C NMR spectrum of walsunoid F (**6**) in $\text{C}_5\text{D}_5\text{N}$

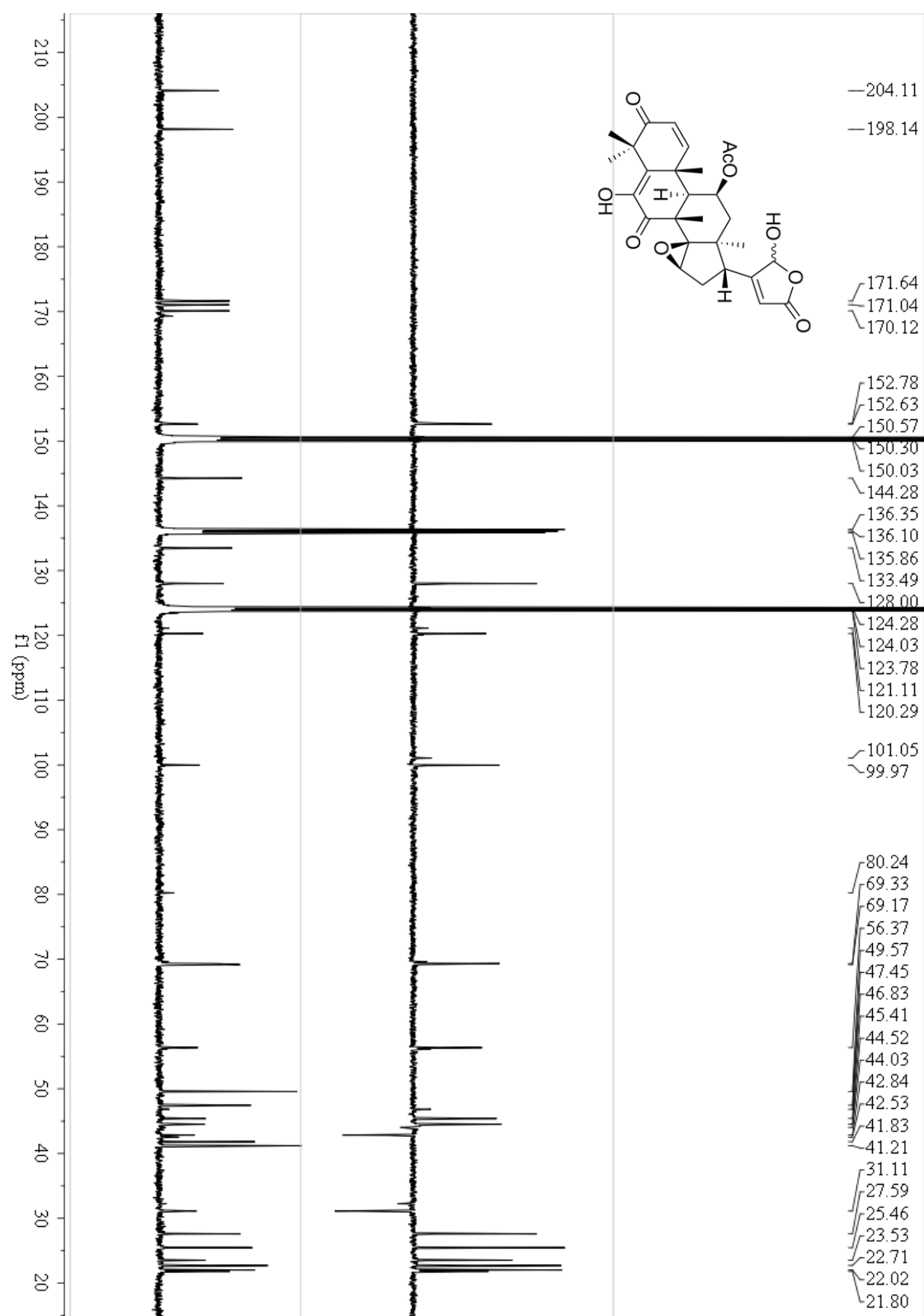


Figure S50. HSQC spectrum of walsunoid F (**6**) in C₅D₅N

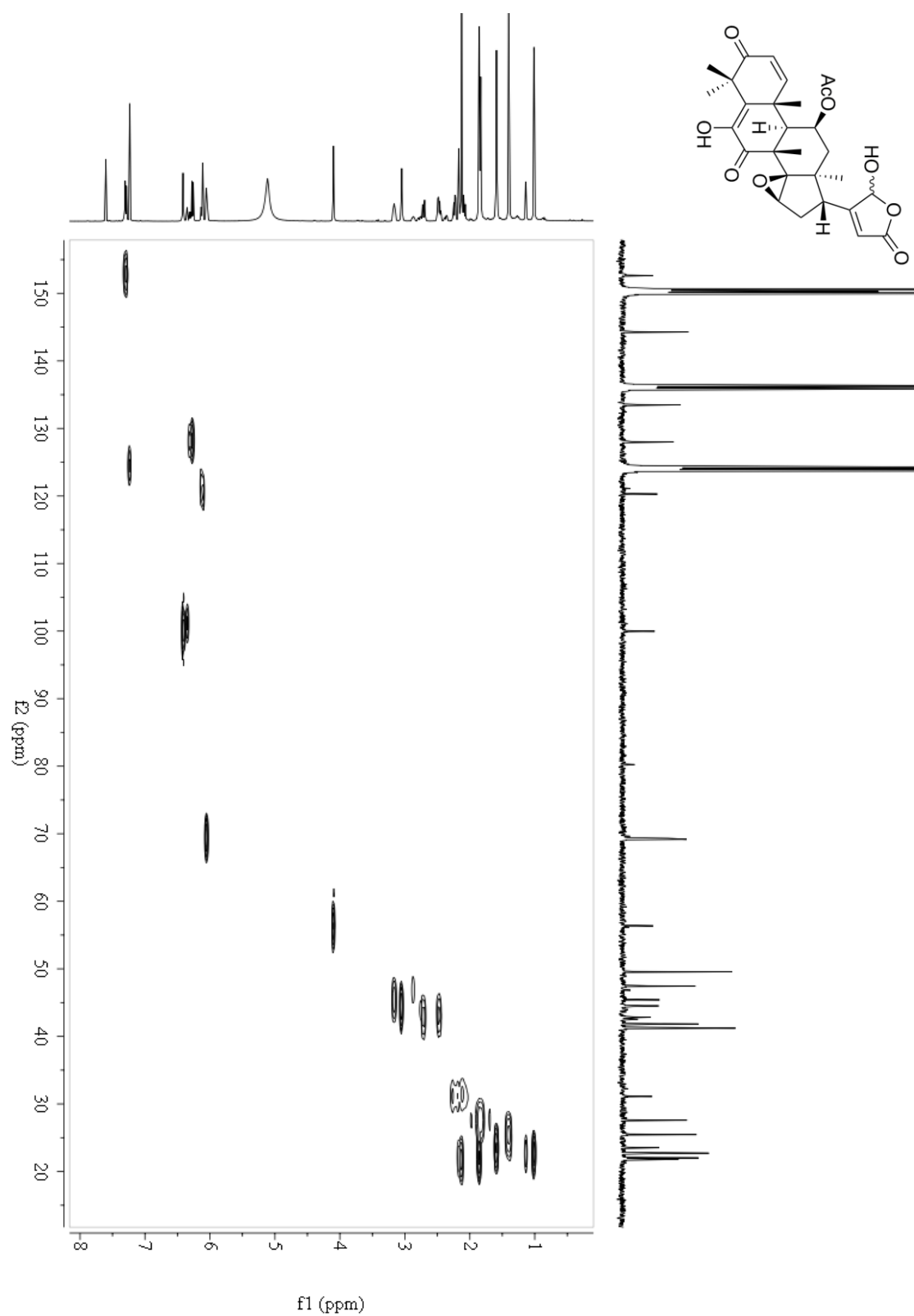


Figure S51. HMBC spectrum of walsunoid d F (**6**) in C_5D_5N

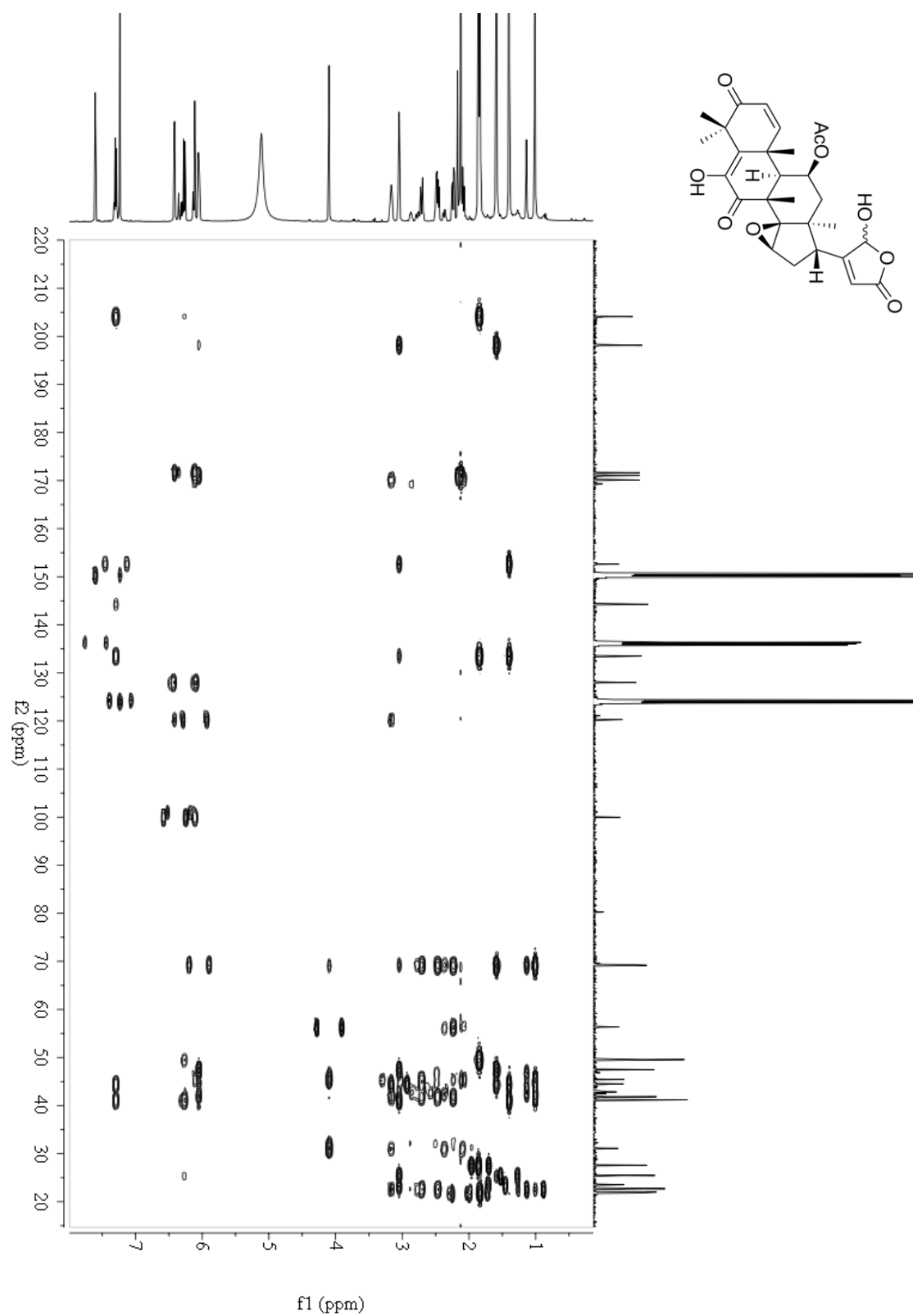


Figure S52. NOESY spectrum of walsunoid F (6) in C₅D₅N

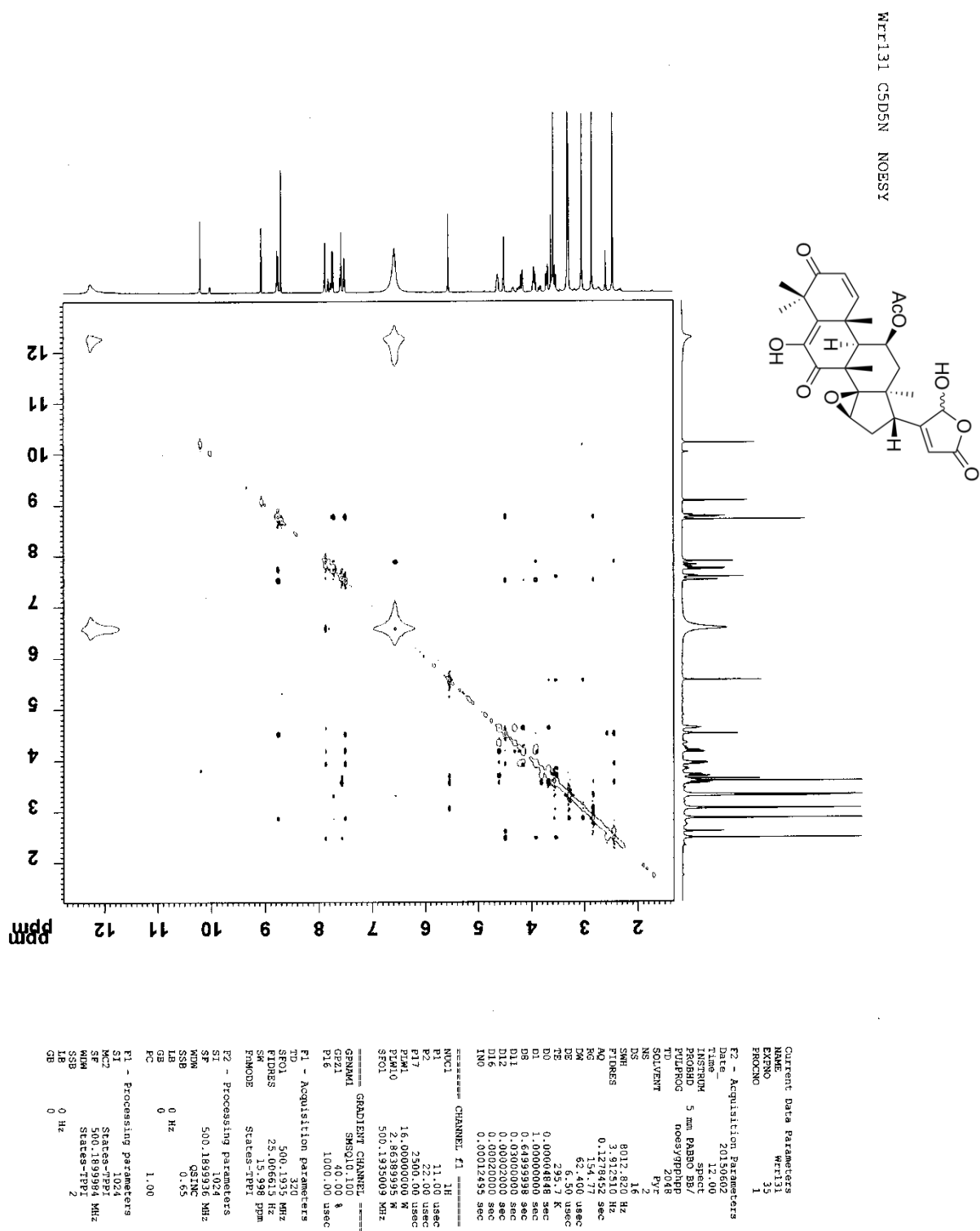


Figure S53. (+)-ESIMS spectrum of walsunoid F (6)

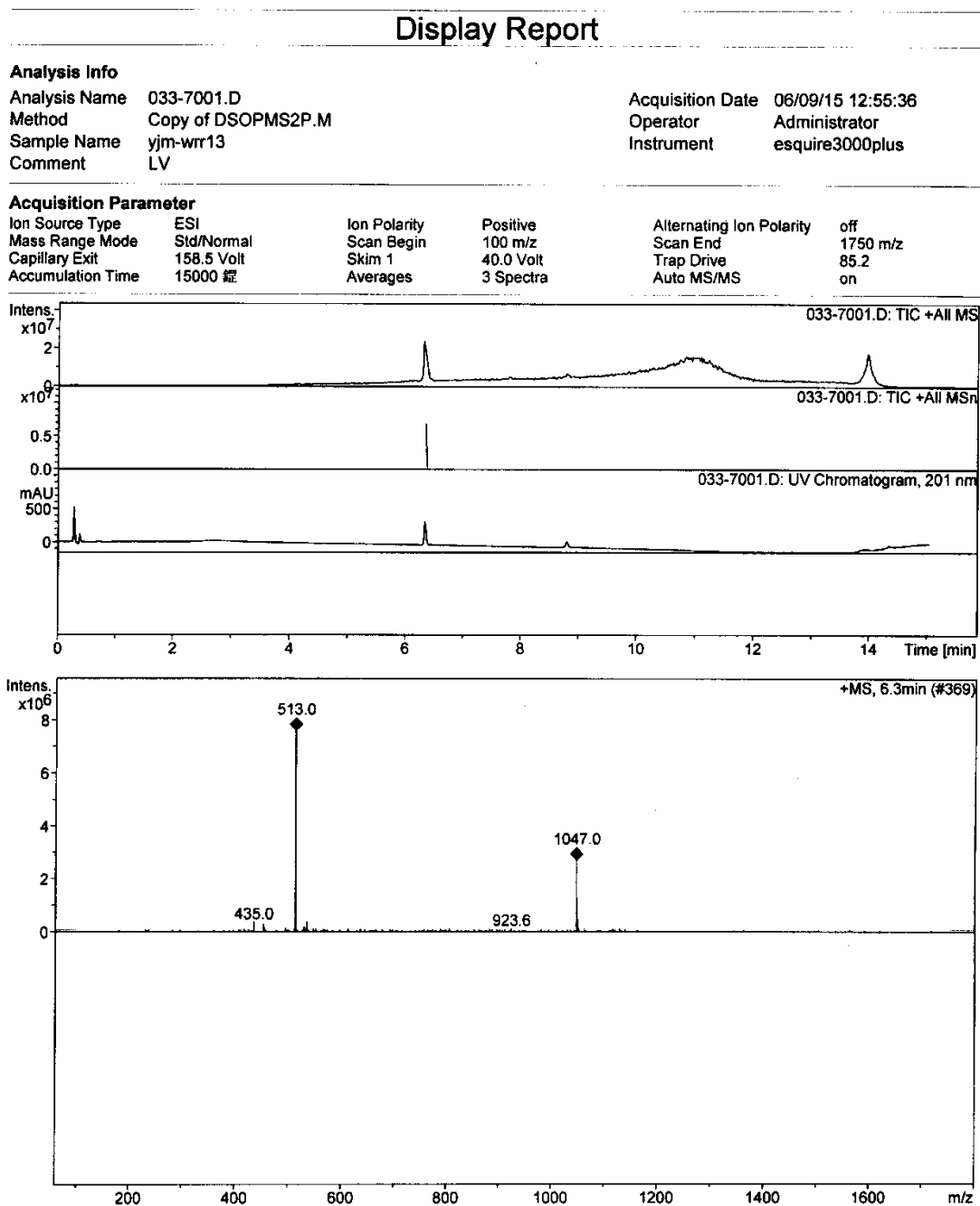


Figure S54. (–)-ESIMS spectrum of walsunoid F (**6**)

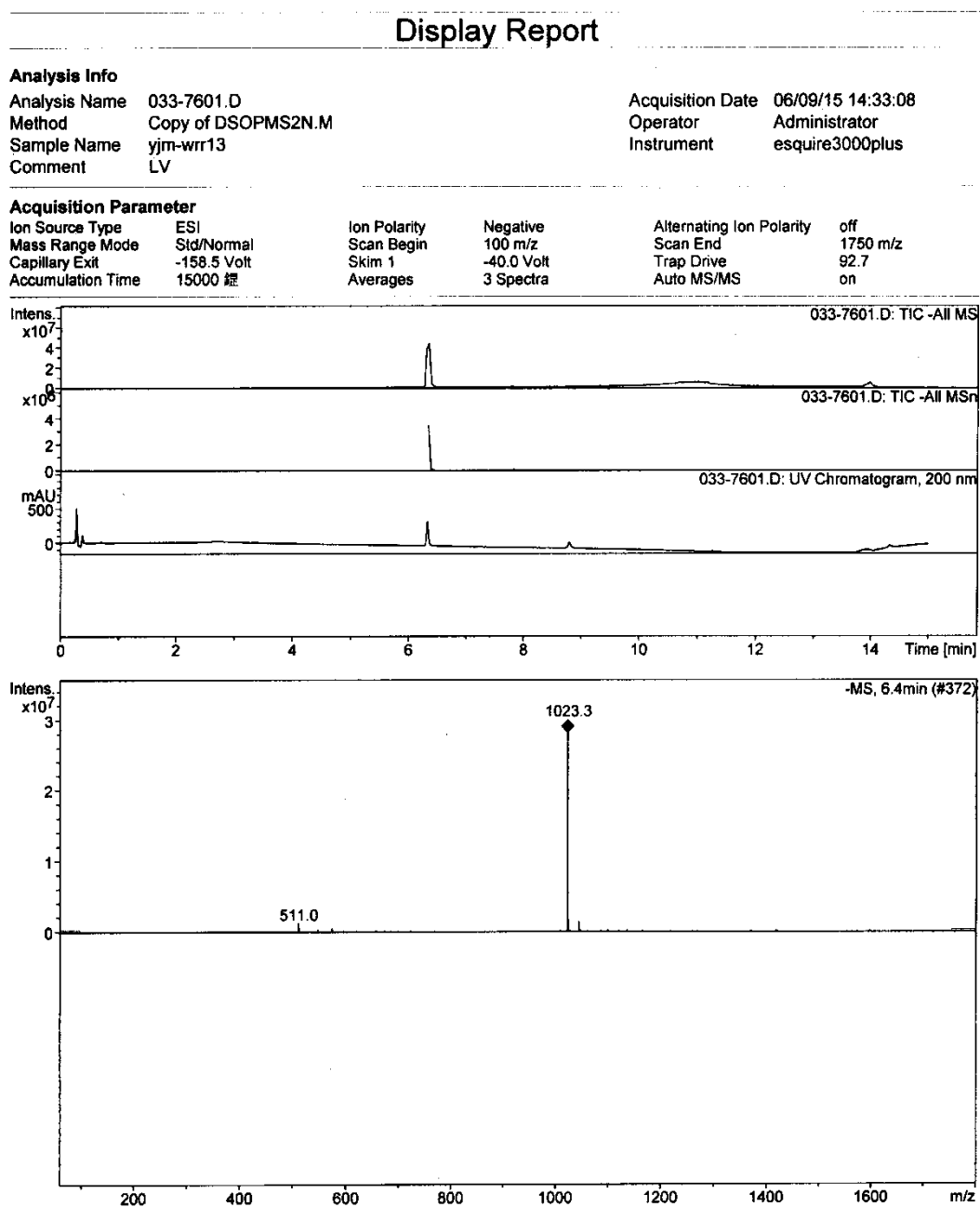


Figure S55. (-)-HRESIMS spectrum of walsunoid F (6)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

104 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 O: 0-20

wrr13

LCT PXE KE324

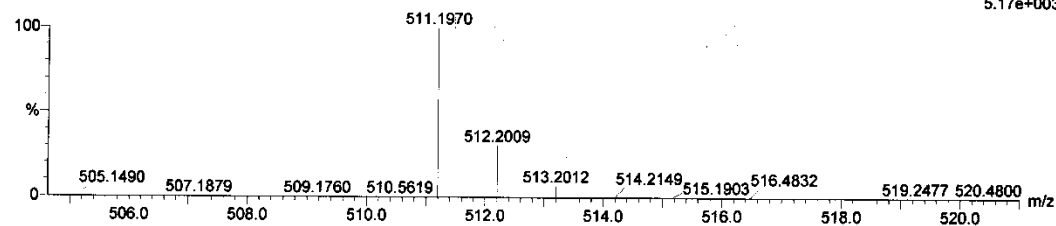
11-Jun-2015

13:56:02

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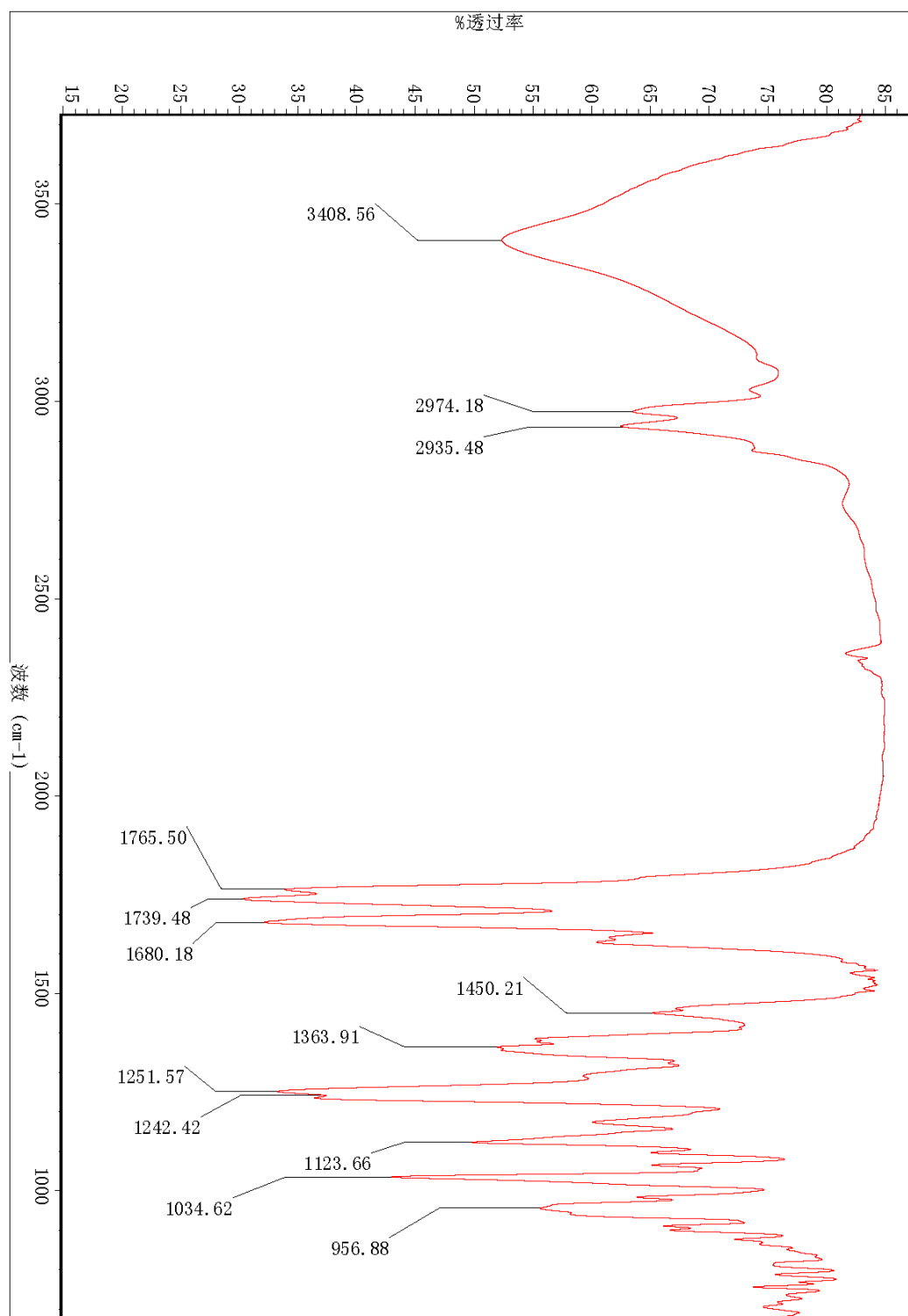
5.17e+003

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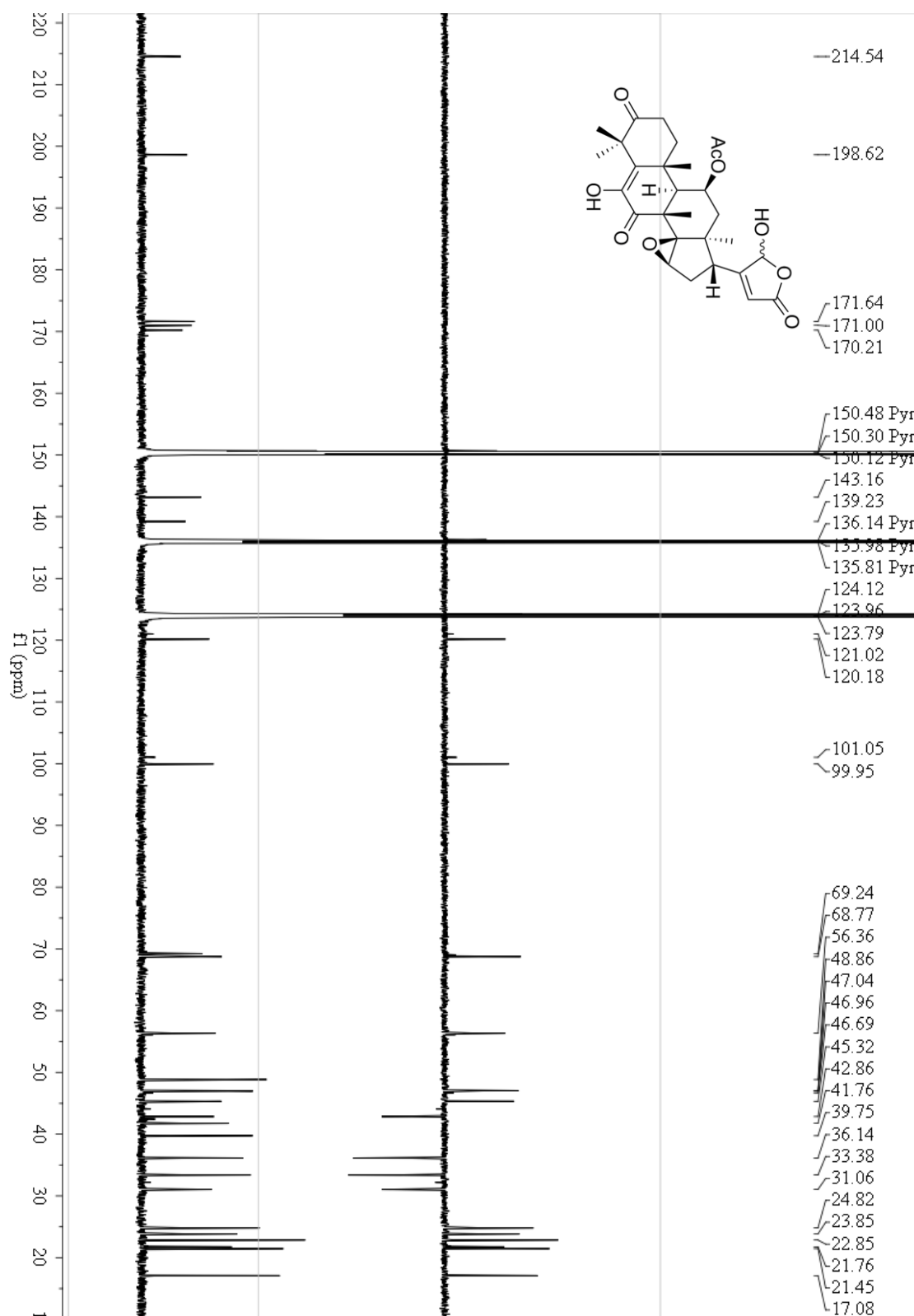
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Maximum:				50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
511.1970	511.1968	0.2	0.4	13.5	47.6	0.0	C28 H31 O9

Figure S56. IR spectrum of walsunoid d F (6)



Chemical structure of **1** is shown. The ¹H NMR spectrum (400 MHz, CDCl₃) displays peaks at δ 7.14 (s, 1H), 6.81 (s, 1H), 6.43 (s, 1H), 6.22 (s, 1H), 6.03 (s, 1H), 5.81 (s, 1H), 5.21 (s, 1H), 5.03 (s, 1H), 4.81 (s, 1H), 4.63 (s, 1H), 4.41 (s, 1H), 4.21 (s, 1H), 4.03 (s, 1H), 3.81 (s, 1H), 3.63 (s, 1H), 3.41 (s, 1H), 3.21 (s, 1H), 3.03 (s, 1H), 2.81 (s, 1H), 2.63 (s, 1H), 2.41 (s, 1H), 2.23 (s, 1H), 2.03 (s, 1H), 1.81 (s, 1H), 1.63 (s, 1H), 1.41 (s, 1H), 1.23 (s, 1H), 1.03 (s, 1H), and 0.81 (s, 1H). The ¹³C NMR spectrum (100 MHz, CDCl₃) displays peaks at δ 386.1, 381.3, 368.9, 366.5, 366.4, 350.7, 350.1, 303.2, 302.3, 301.8, 244.3, 190.3, 189.6, 189.3, 188.6, 169.4, 168.5, 167.5, 166.6, 163.1, 162.5, 160.2, 158.7, 157.6, 156.7, 155.7, 154.7, 147.5, 142.2, 141.5, 140.7, 140.0, 135.4, 134.5, 134.1, 133.4, 133.2, 132.7, 132.0, 129.5, 129.5, 128.7, 126.7, 125.4, 125.1, 124.1, 113.5, 112.6, 112.5, 112.2, 111.2, 109.2, 109.1, 104.7, 104.6, 103.9, 92.8, 71.4, 68.9, and 60.8 ppm.

Figure S58. ^{13}C NMR spectrum of walsunoid G (**7**) in $\text{C}_5\text{D}_5\text{N}$



The figure displays the chemical structure of compound **1** and its corresponding ¹H and ¹³C NMR spectra. The chemical structure is a complex polycyclic molecule featuring a central ring system with multiple methyl groups, a ketone, a hydroxyl group, and an acetate (AcO) group. A side chain includes a carboxylic acid group and a furan ring. The ¹H NMR spectrum (top) shows peaks in the aromatic region (6.5-7.5 ppm), a broad peak for the hydroxyl group (around 10 ppm), and several peaks in the aliphatic region (1.5-5.5 ppm). The ¹³C NMR spectrum (bottom) shows peaks from 15 to 125 ppm, including carbonyl carbons (around 170-200 ppm) and various aliphatic carbons. The x-axis for the ¹³C NMR spectrum is labeled 'f2 (ppm)' and ranges from 15 to 125. The y-axis for the ¹H NMR spectrum is labeled 'f1 (ppm)' and ranges from 1 to 7. The chemical structure is labeled with 'H' and 'AcO' groups.

Figure S60. HMBC spectrum of walsunoid G (**7**) in C₅D₅N

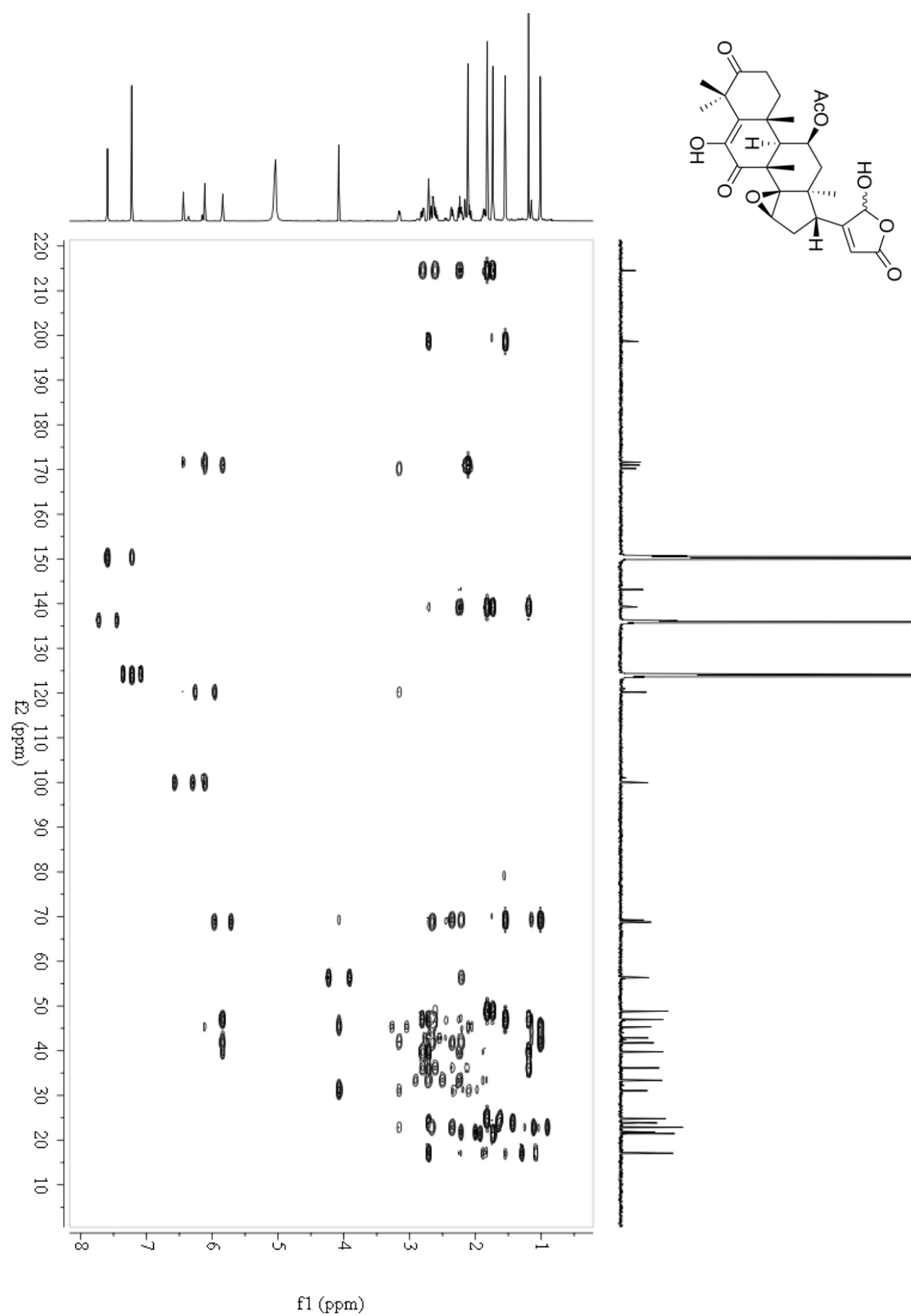


Figure S61. NOESY spectrum of walsunoid G (**7**) in C₅D₅N

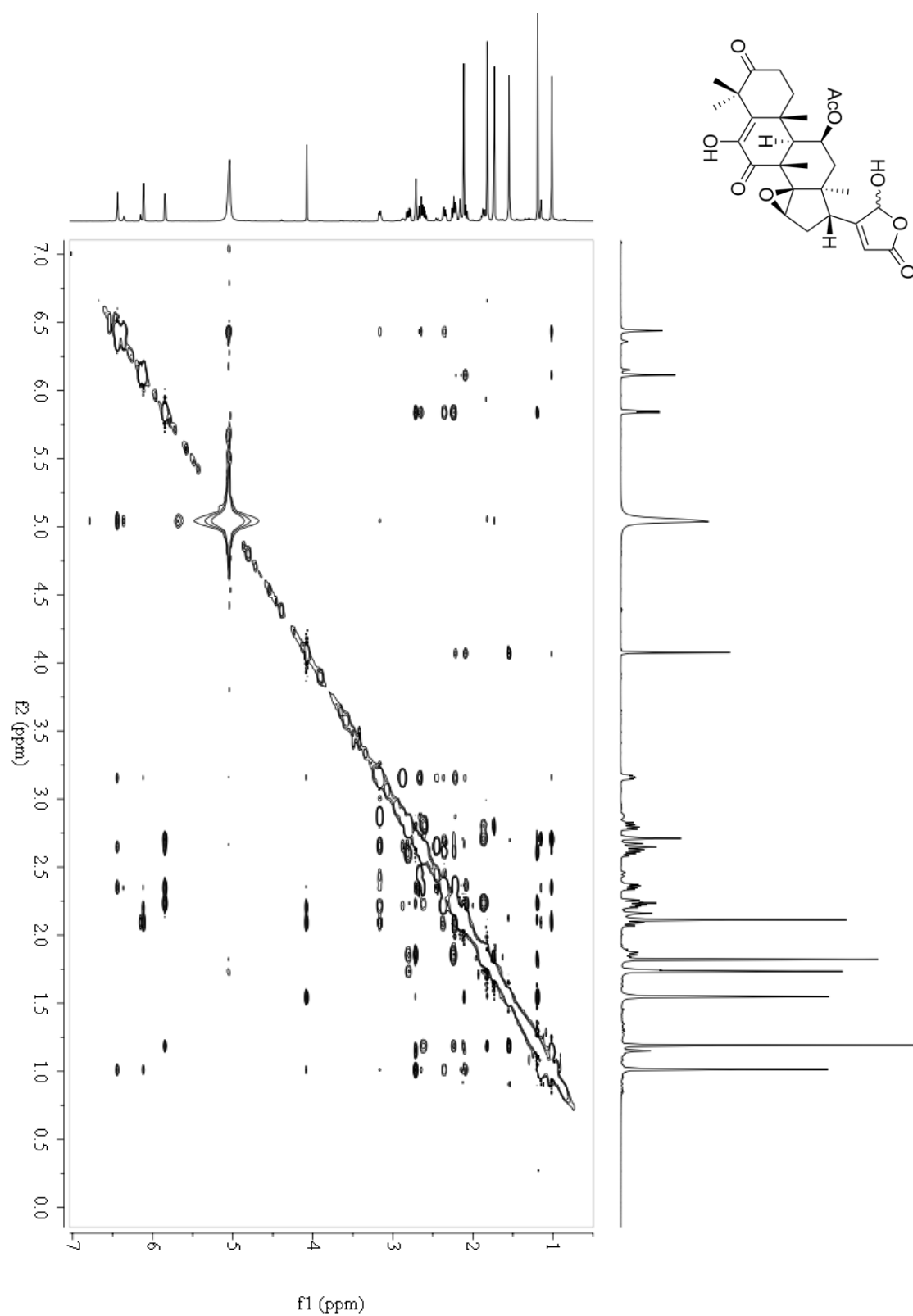


Figure S62. (+)-ESIMS spectrum of walsunoid G (7)

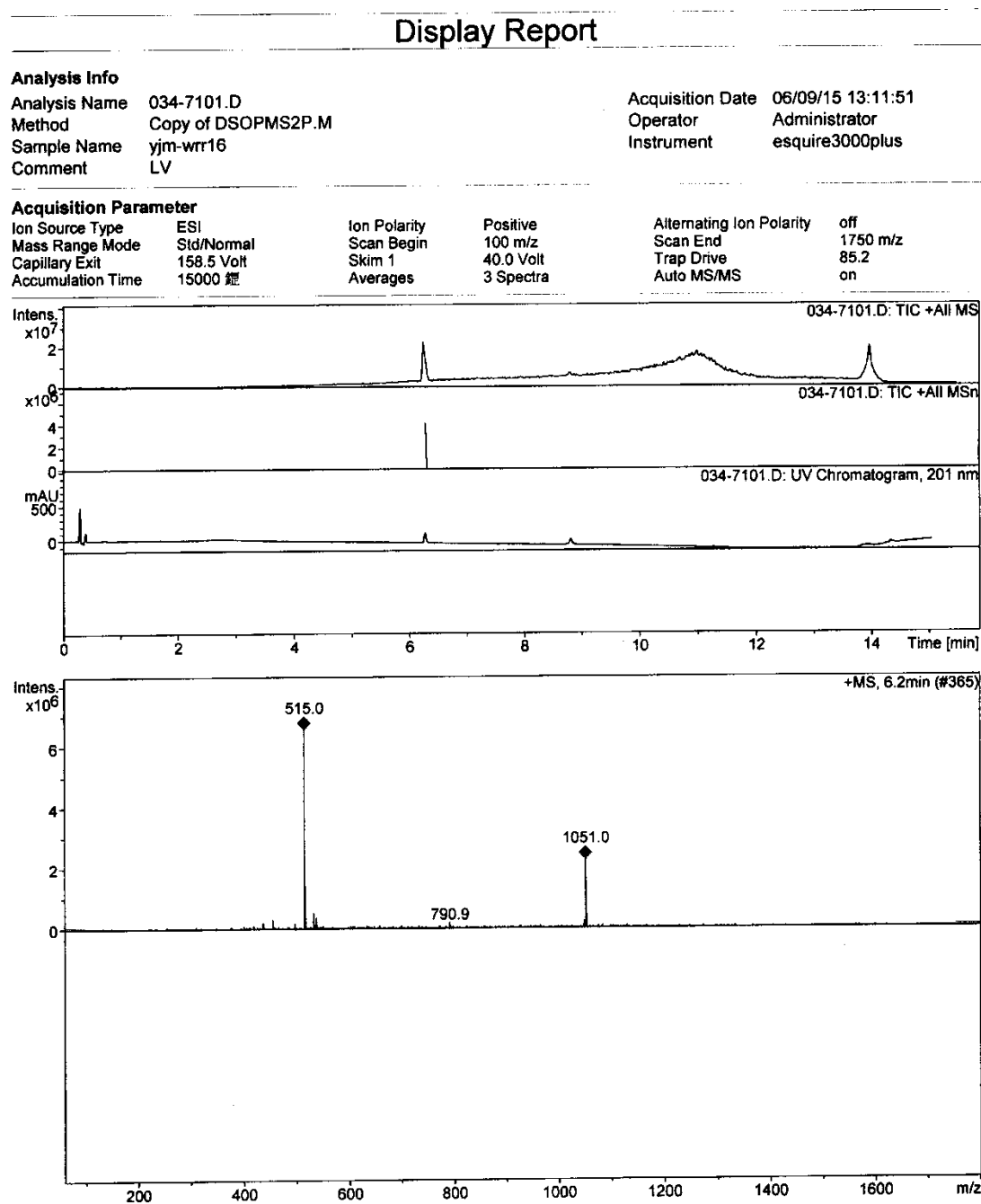


Figure S63. (-)-ESIMS spectrum of walsunoid G (7)

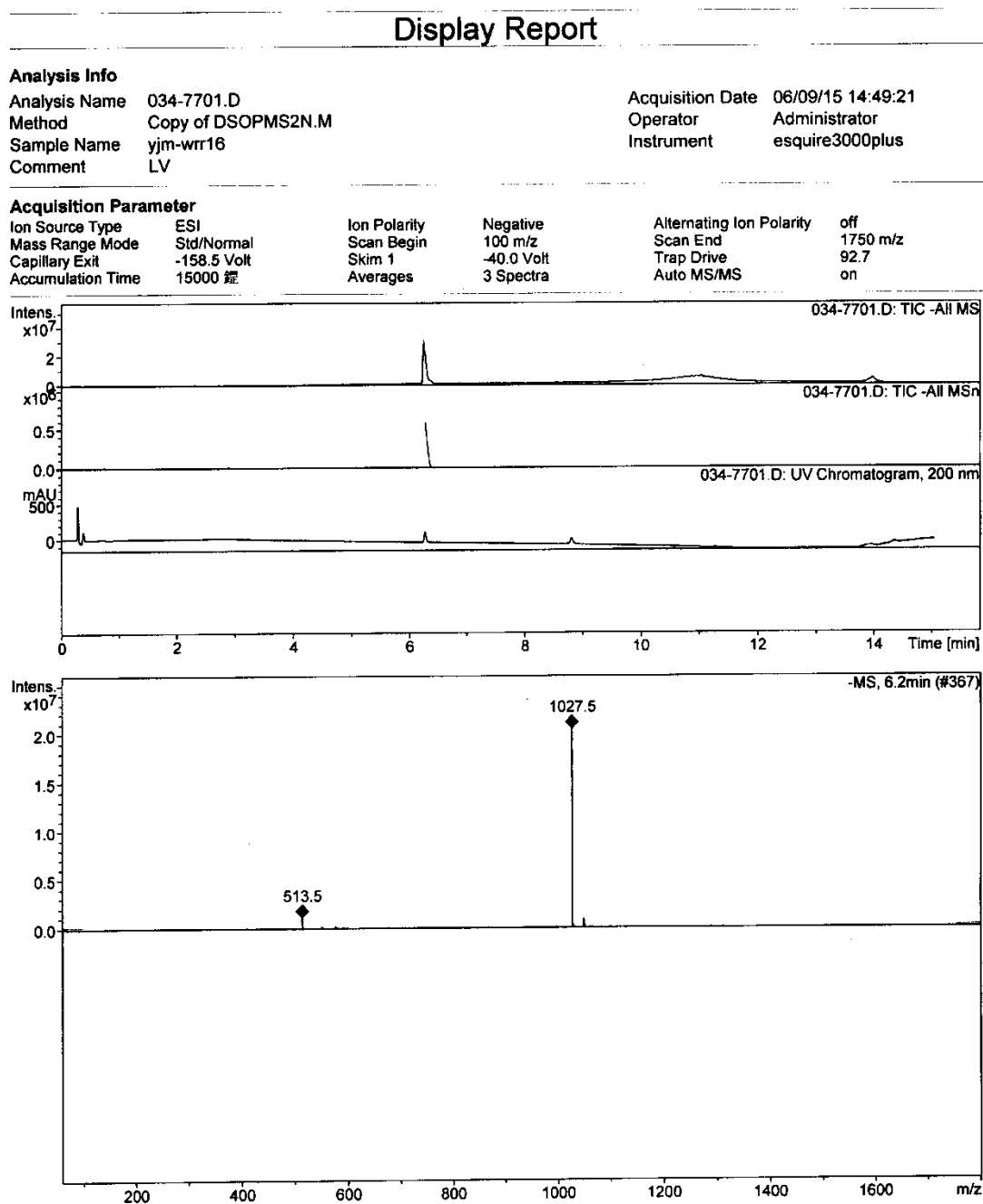


Figure S64. (-)-HRESIMS spectrum of walsunoid G (7)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

101 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 O: 0-20

wrr16

LCT PXE KE324

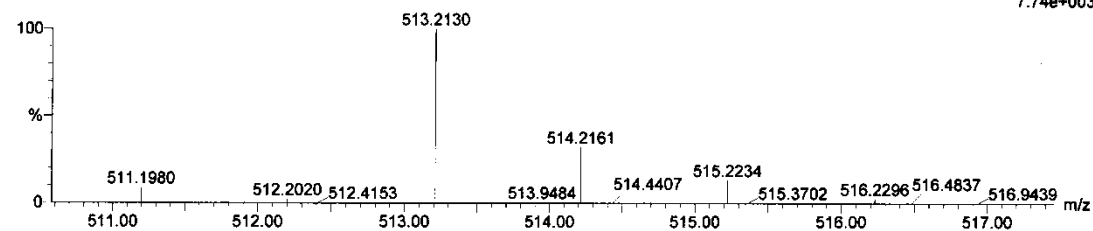
11-Jun-2015

14:02:29

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1: TOF MS ES-

7.74e+003



Minimum:

-1.5

Maximum:

5.0

5.0

50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
513.2130	513.2125	0.5	1.0	12.5	63.7	0.0	C28 H33 O9

Figure S65. IR spectrum of walsunoid G (**7**)

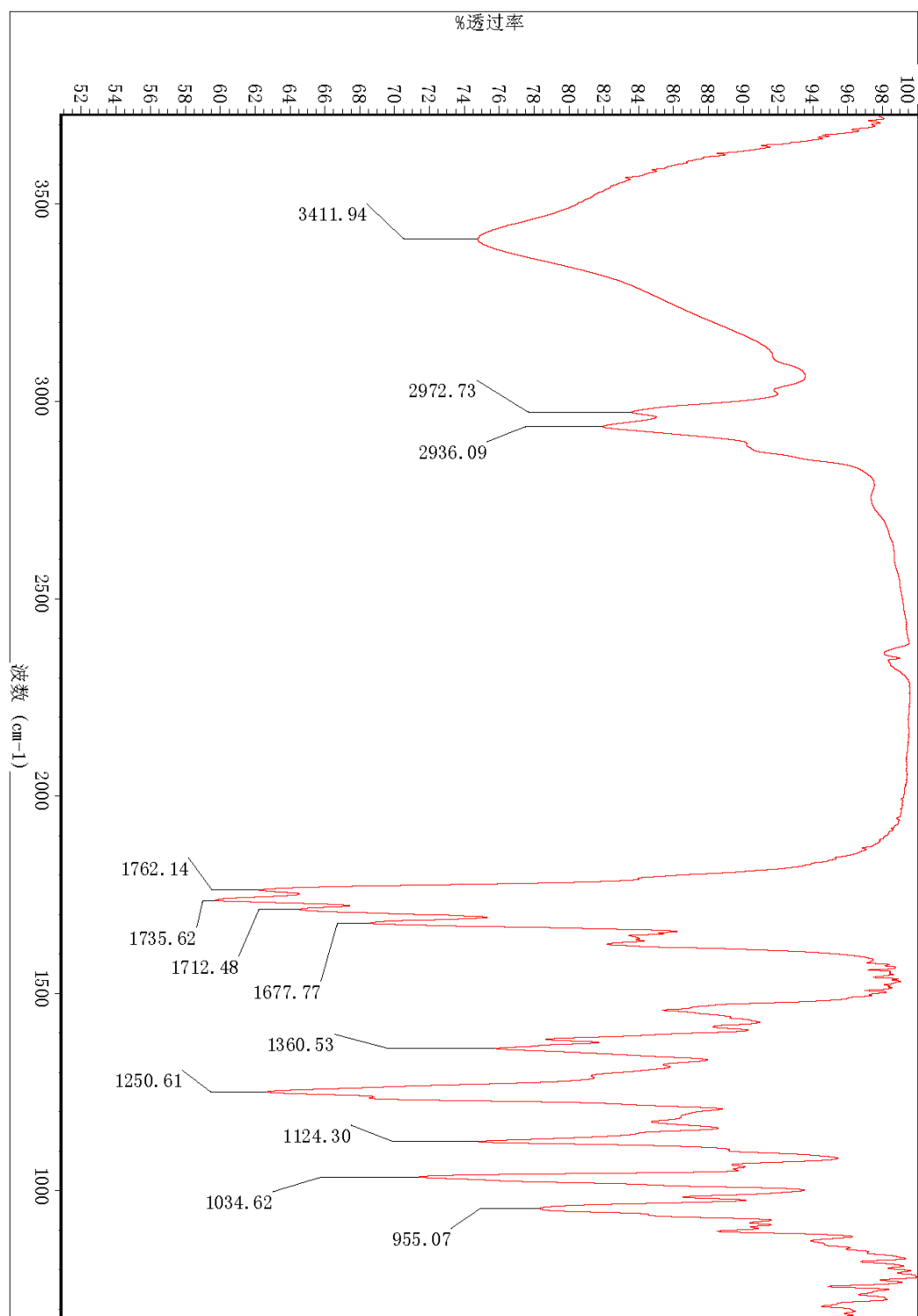


Figure S66. ^1H NMR spectrum of walsunoid H (**8**) in CDCl_3

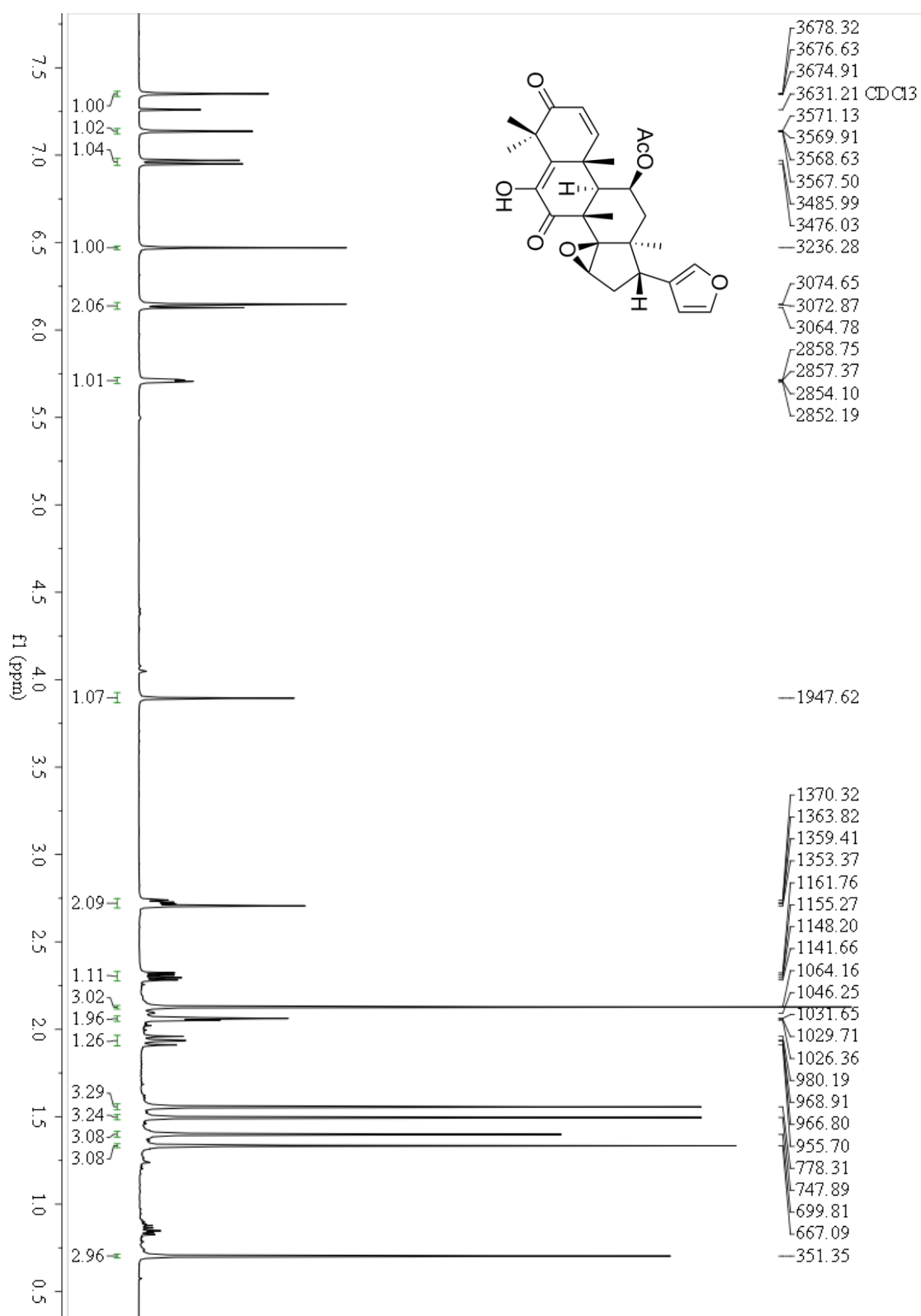


Figure S67. ^{13}C NMR spectrum of walsunoid H (**8**) in CDCl_3

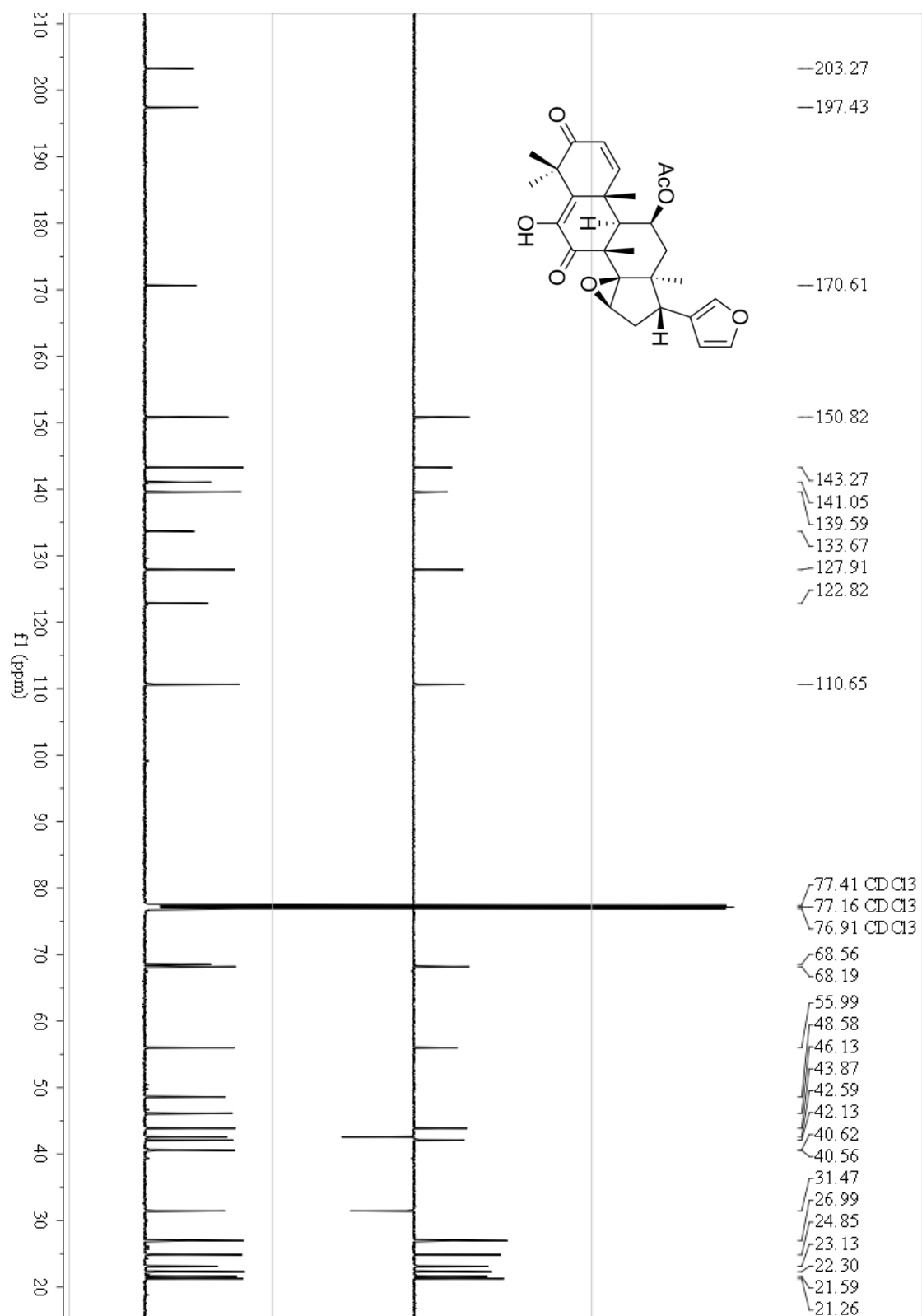


Figure S68. HSQC spectrum of walsunoid H (**8**) in CDCl₃

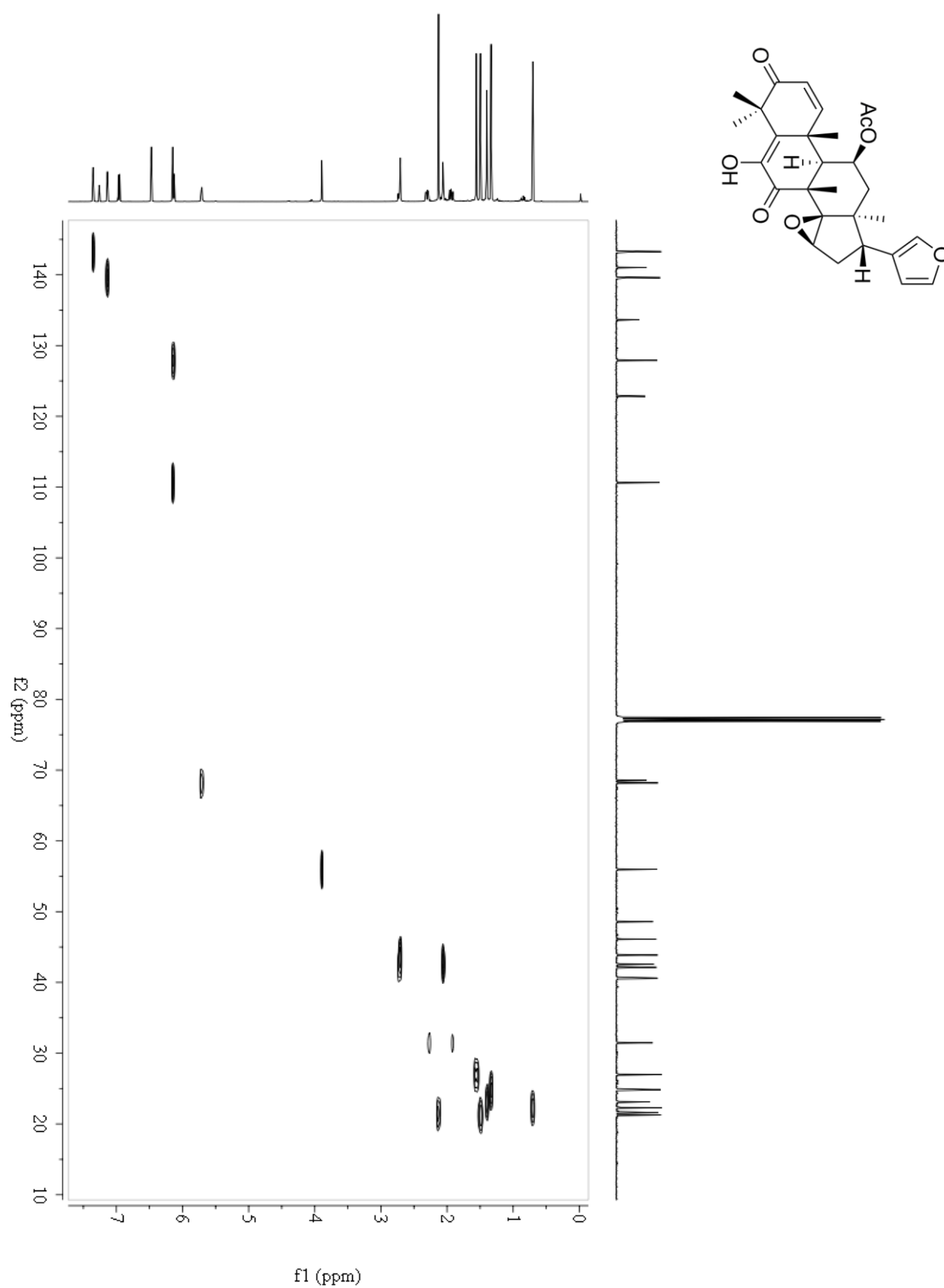
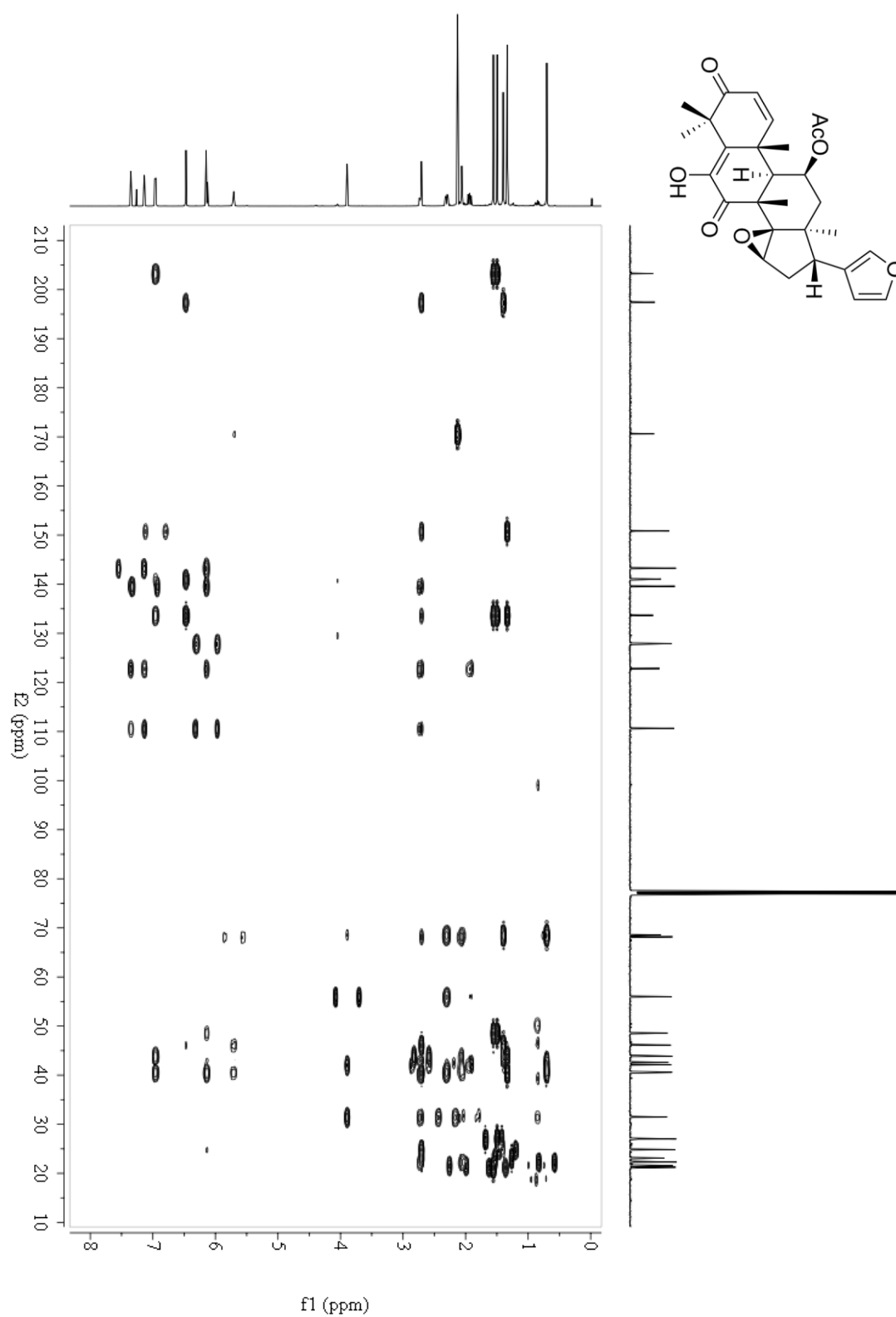
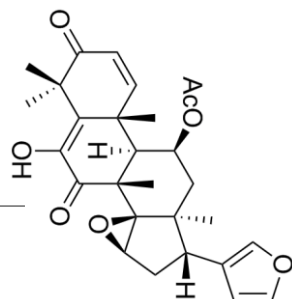
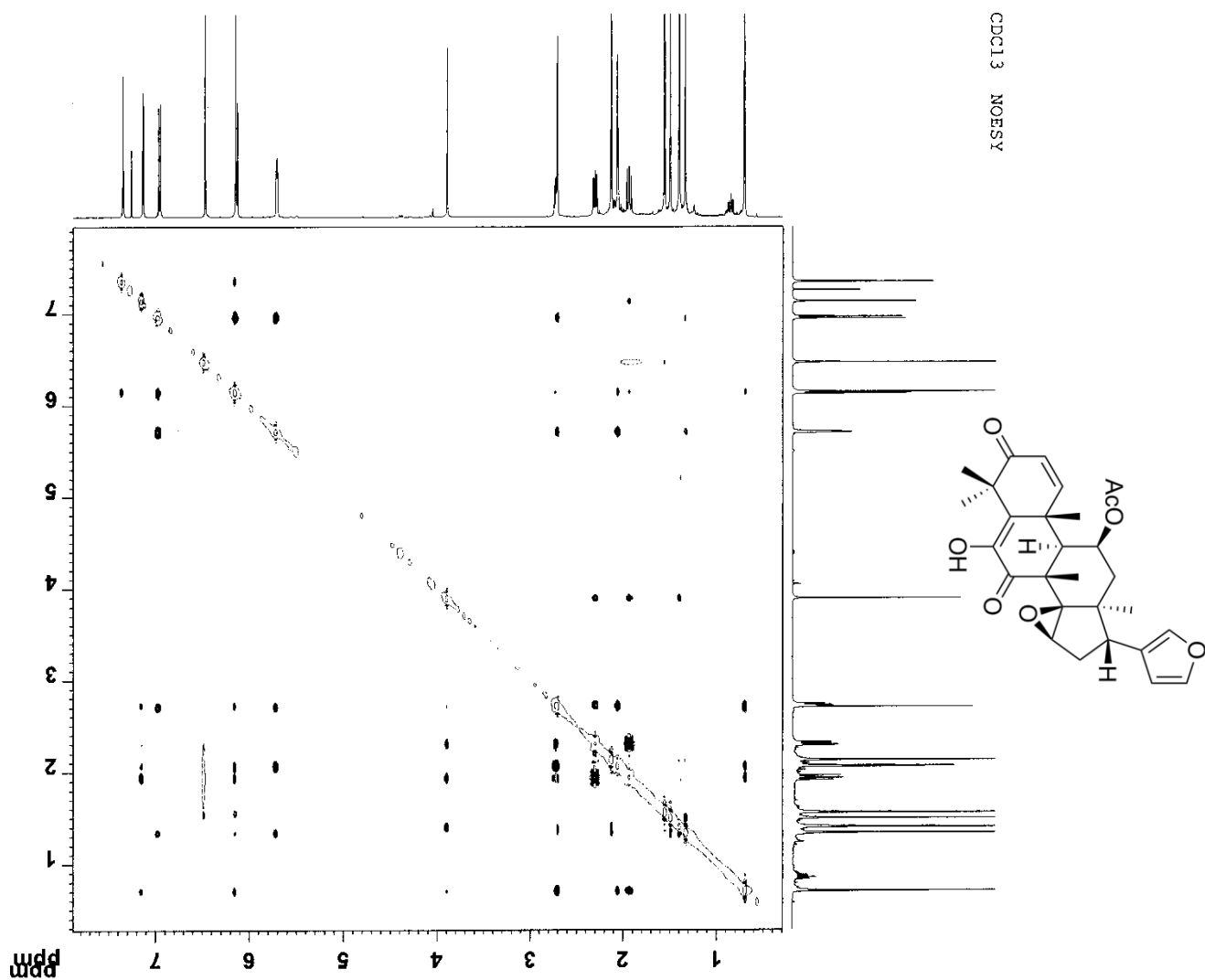


Figure S69. HMBC spectrum of walsunoid H (**8**) in CDCl₃



```
WRR28  CDCL3  NOESY
```



Current Data Parameters		Acquisition Parameters	
NAME	W128	Date	20150605
EXNO	1	Time	12.23
FIDNO	1	INSTRUM	5 mm CPDQ 13C
PROCNO	9	PROBHD	spec
		PULPROG	zgpg30pphph
		TD	2048
		DELTA	2.08
		NS	CCCL2
		DS	16
		SWH	8012.870 Hz
		AQ	3.912510 Hz
		TE	0.178452 sec
		RG	61.53
		RG2	62.460 usec
		TE2	101.8 Hz
		TE3	101.8 Hz
		D1	0.00049931 sec
		D8	1.00000000 sec
		D81	0.6493998 sec
		D11	0.0300000 sec
		D12	0.0002000 sec
		D13	0.0002000 sec
		TK0	0.00012495 sec
===== CHANNEL: F1 =====			
MUCL	1H		
F1	10.75 usec		
F2	25.70 usec		
F3	12.000000 usec		
F4	12.000000 usec		
F5	1.9016000 Hz		
FID10	500 1135009 KHz		
===== GRADIENT CHANNEL: =====			
GRANA1	SHG10:100		
GPZ1	40.00 V		
P16	1000.00 usec		
===== Acquisition parameters =====			
F1	320		
TD	500,135 Hz		
SFO1	25.00659 Hz		
FIDRES	16.000 ppm		
SW	Stable-TFPI		
PRMODE	Stable-TFPI		
===== Processing parameters =====			
S1	500,1350075 MHz		
SI	1024		
MSW	OSINE		
SSB	2		
PC	1.00		
LB	0 Hz		
GB	0 Hz		
===== Processing parameters =====			
F1	Processing parameters		
S1	1024		
MS2	Stable-TFPI		
SF	500.1300104 MHz		
MMW			
SSB	2		
LB	0 Hz		
GB	0 Hz		

Figure S71. (+)-ESIMS spectrum of walsunoid H (**8**)

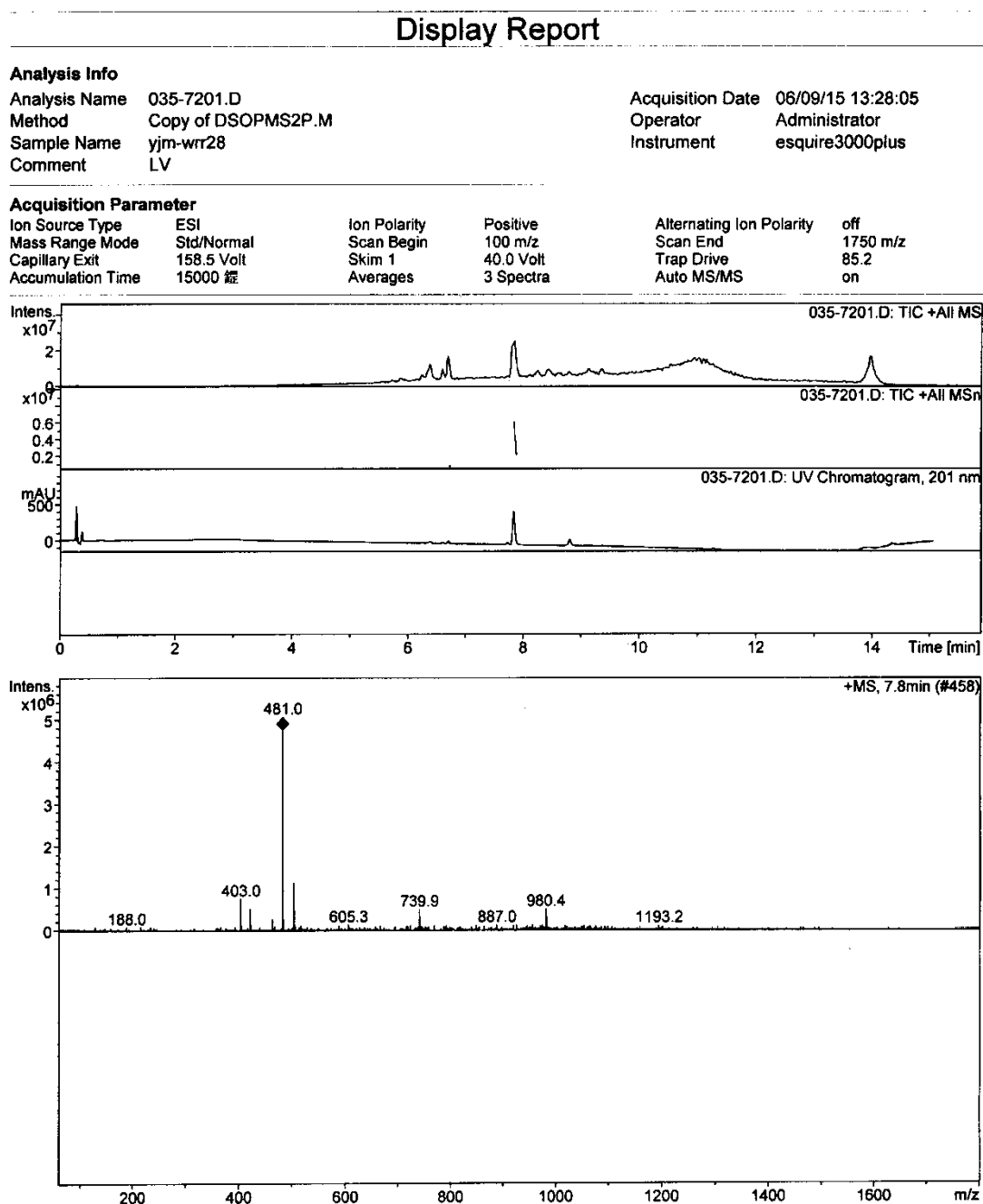


Figure S72. (-)-ESIMS spectrum of walsunoid H (8)

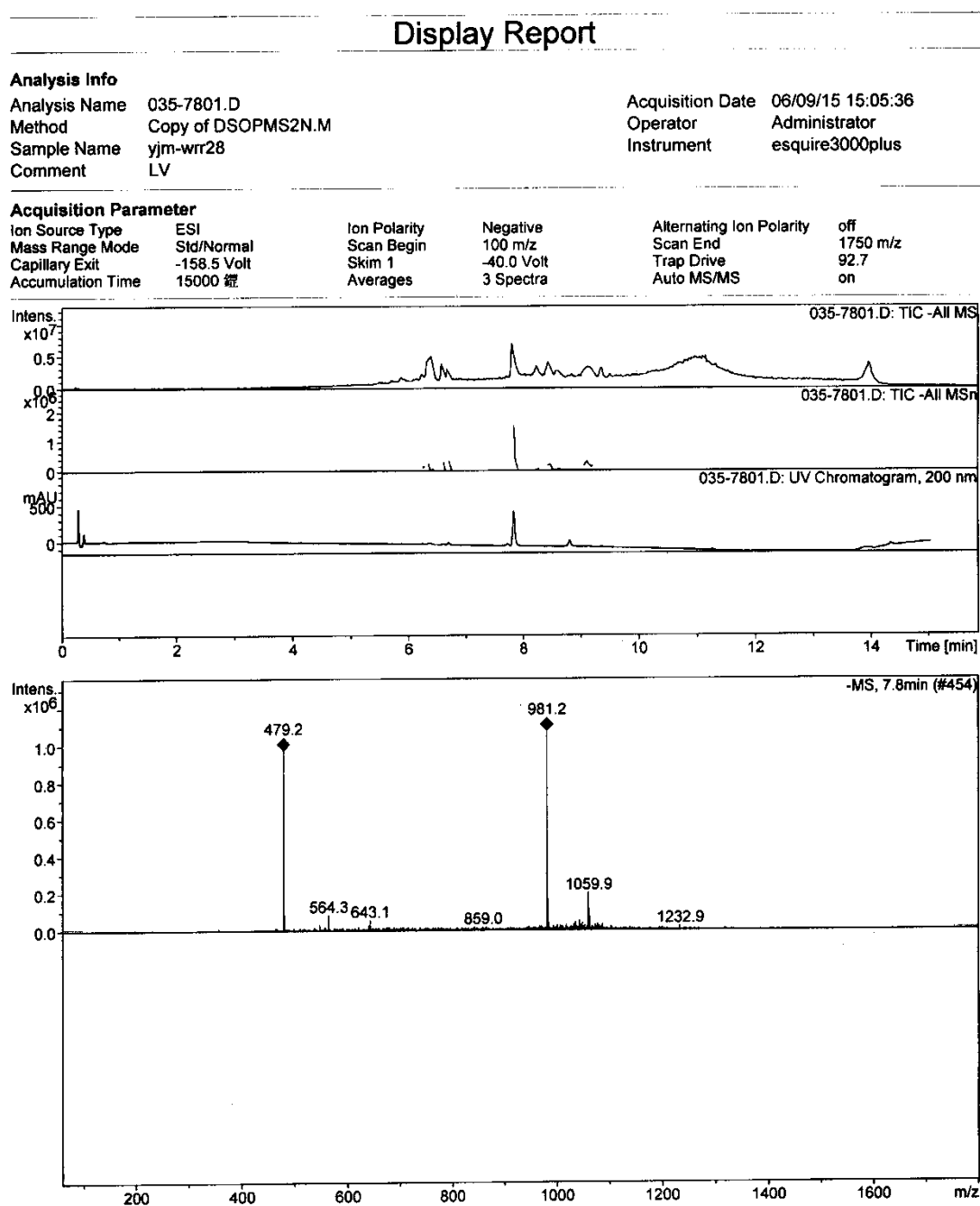


Figure S73. (-)-HRESIMS spectrum of walsunoid H (**8**)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

96 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 O: 0-20

wrr28

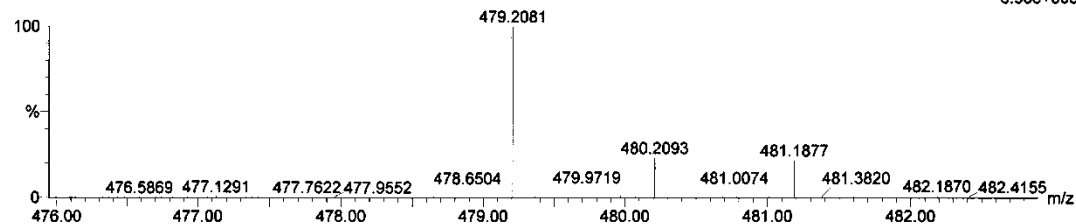
LCT PXE KE324

11-Jun-2015

14:10:05

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1: TOF MS ES-
6.98e+003



Minimum: -1.5
Maximum: 5.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
479.2081	479.2070	1.1	2.3	13.5	123.7	0.0	C28 H31 O7

Figure S74. IR spectrum of walsunoid H (**8**)

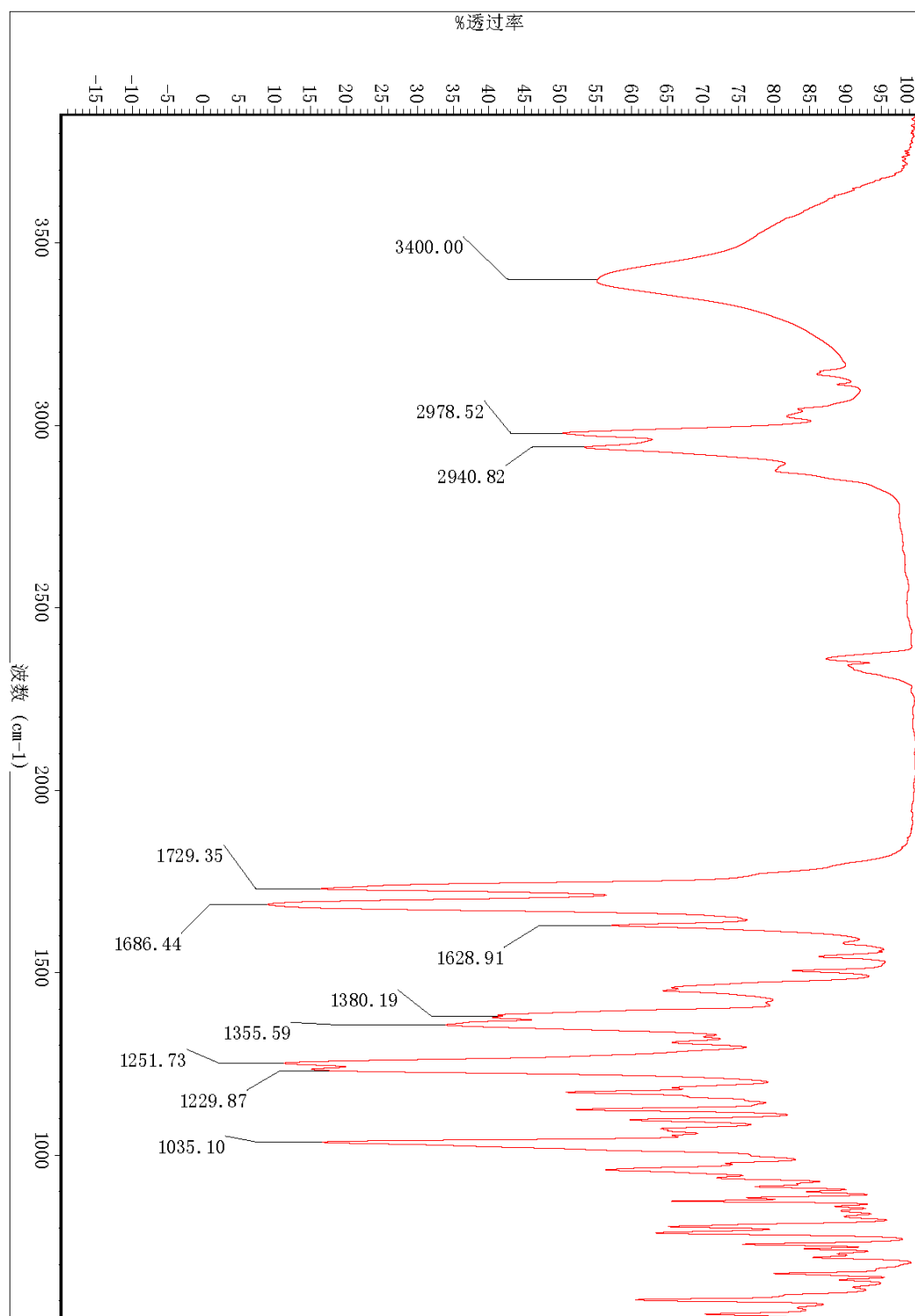


Figure S75. ^1H NMR spectrum of walsunoid I (**9**) in CDCl_3

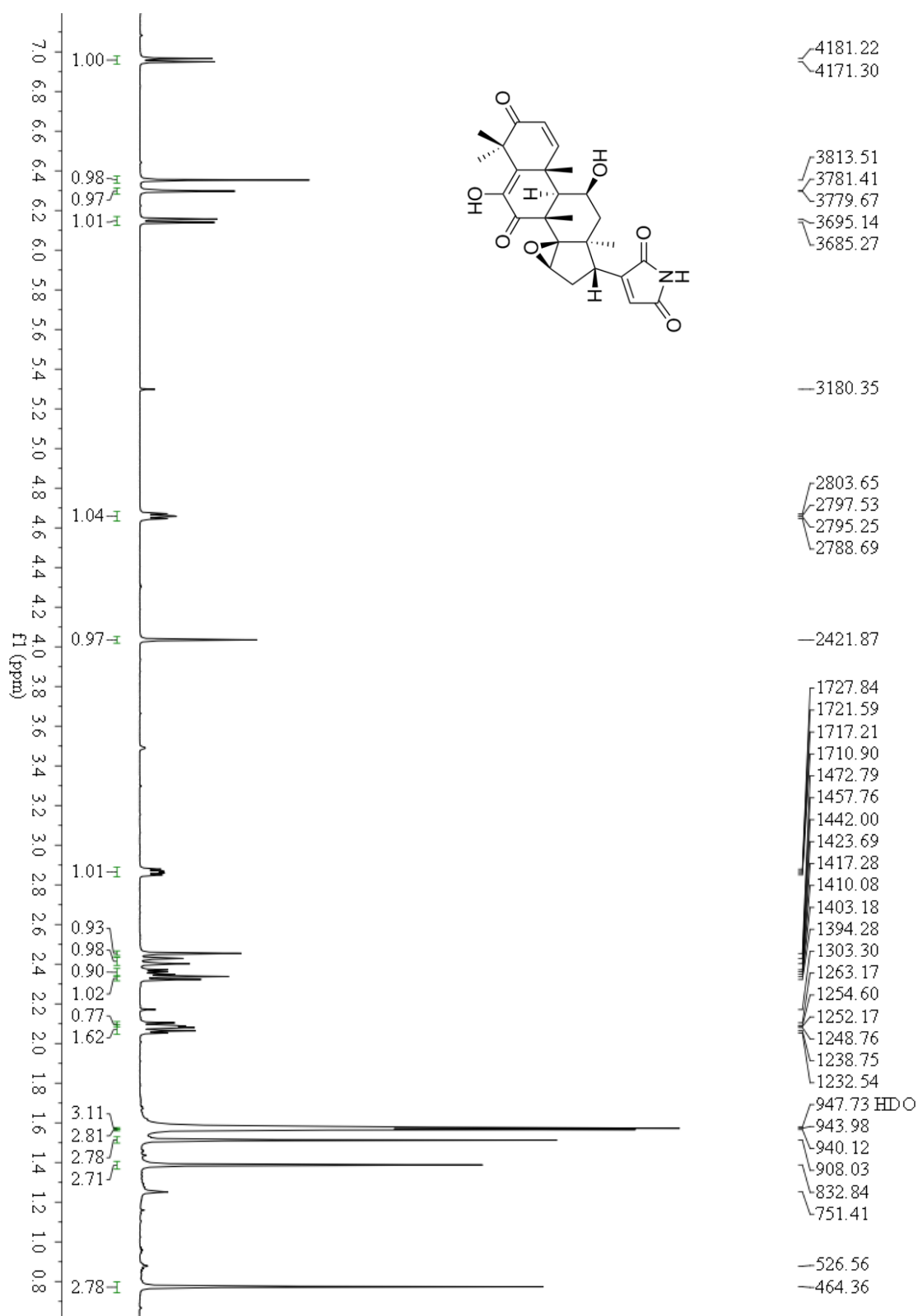


Figure S76. ^{13}C NMR spectrum of walsunoid I (**9**) in CDCl_3

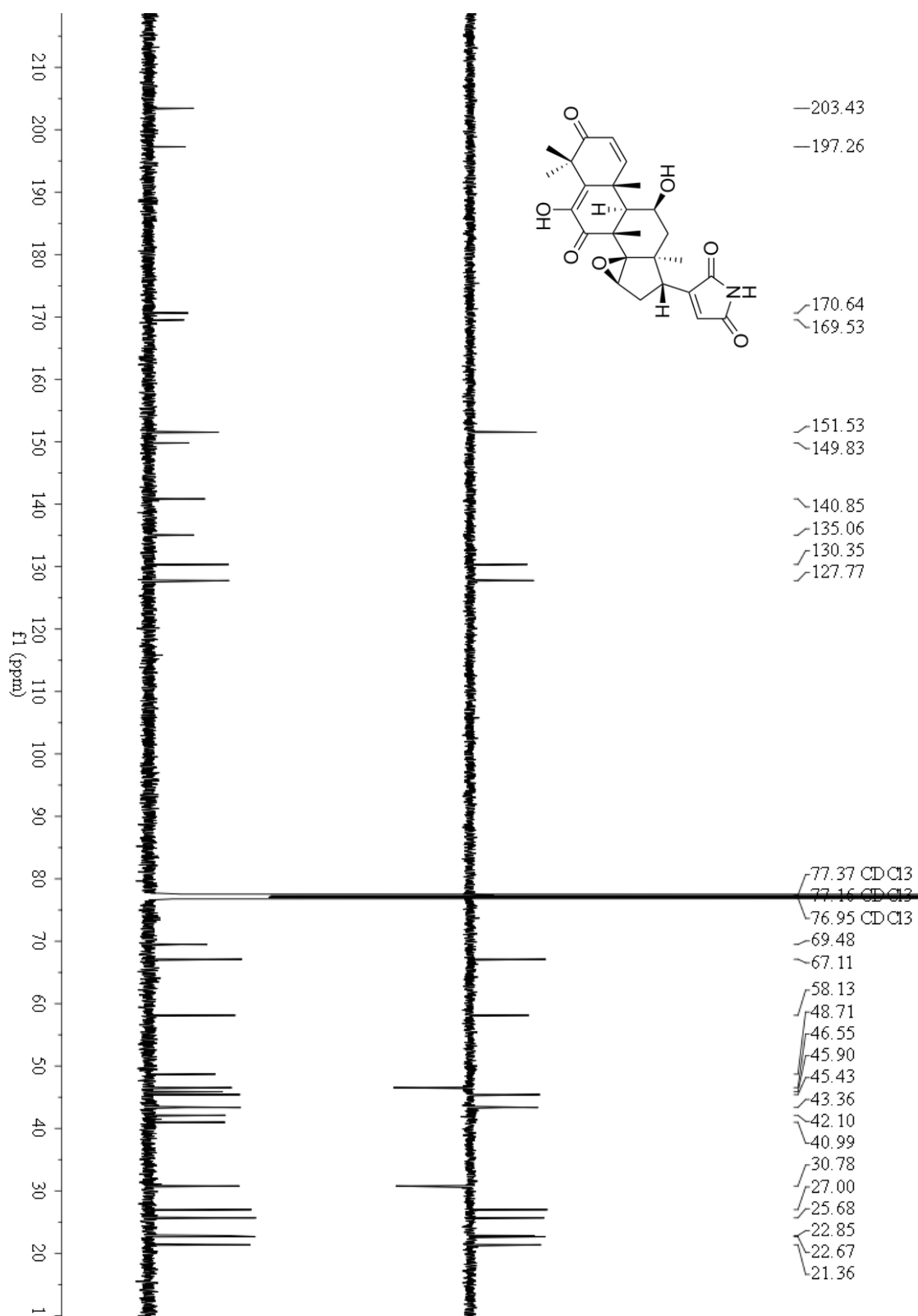


Figure S77. HSQC spectrum of walsunoid I (**9**) in CDCl₃

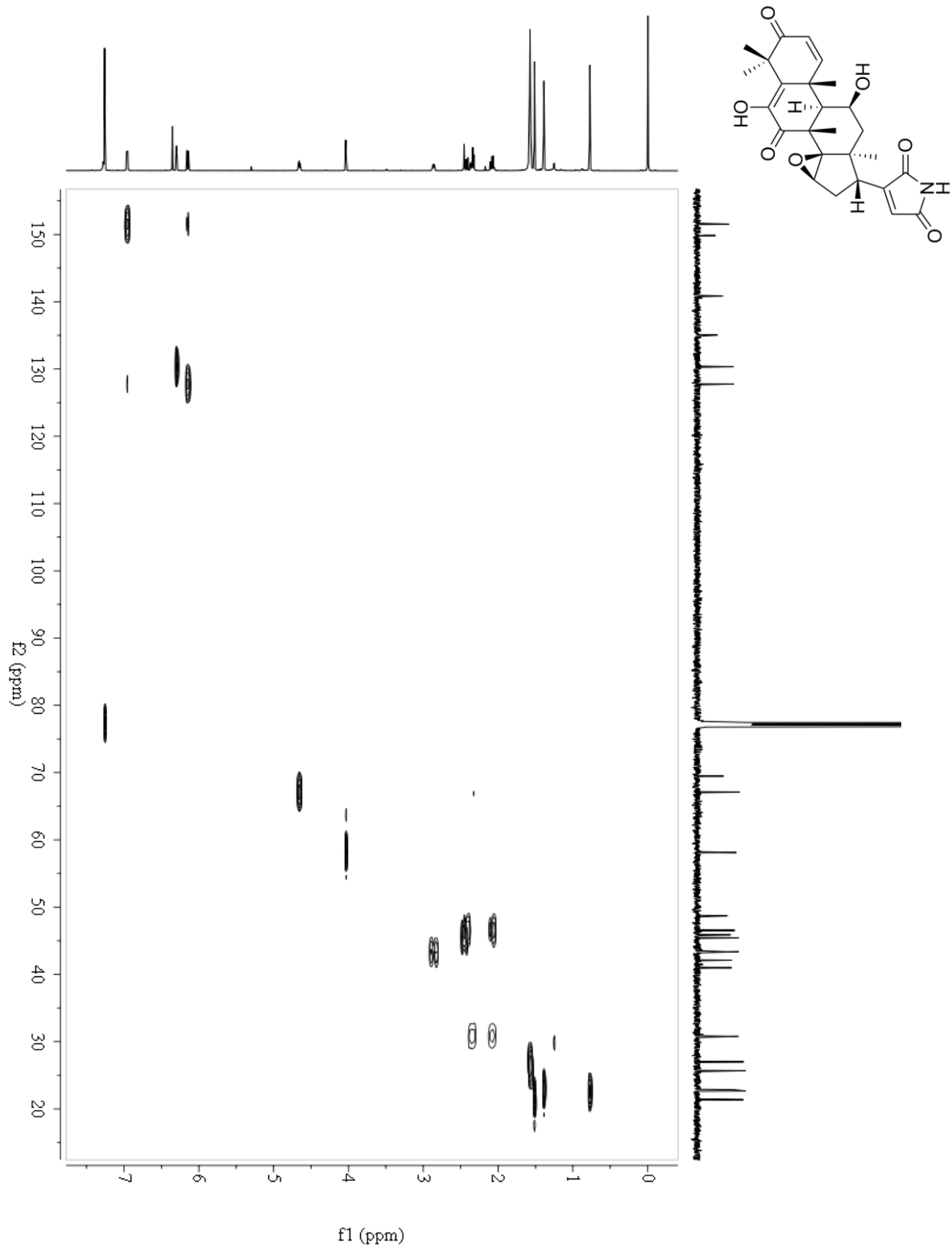


Figure S79. ^1H - ^1H COSY spectrum of walsunoid I (**9**) in CDCl_3

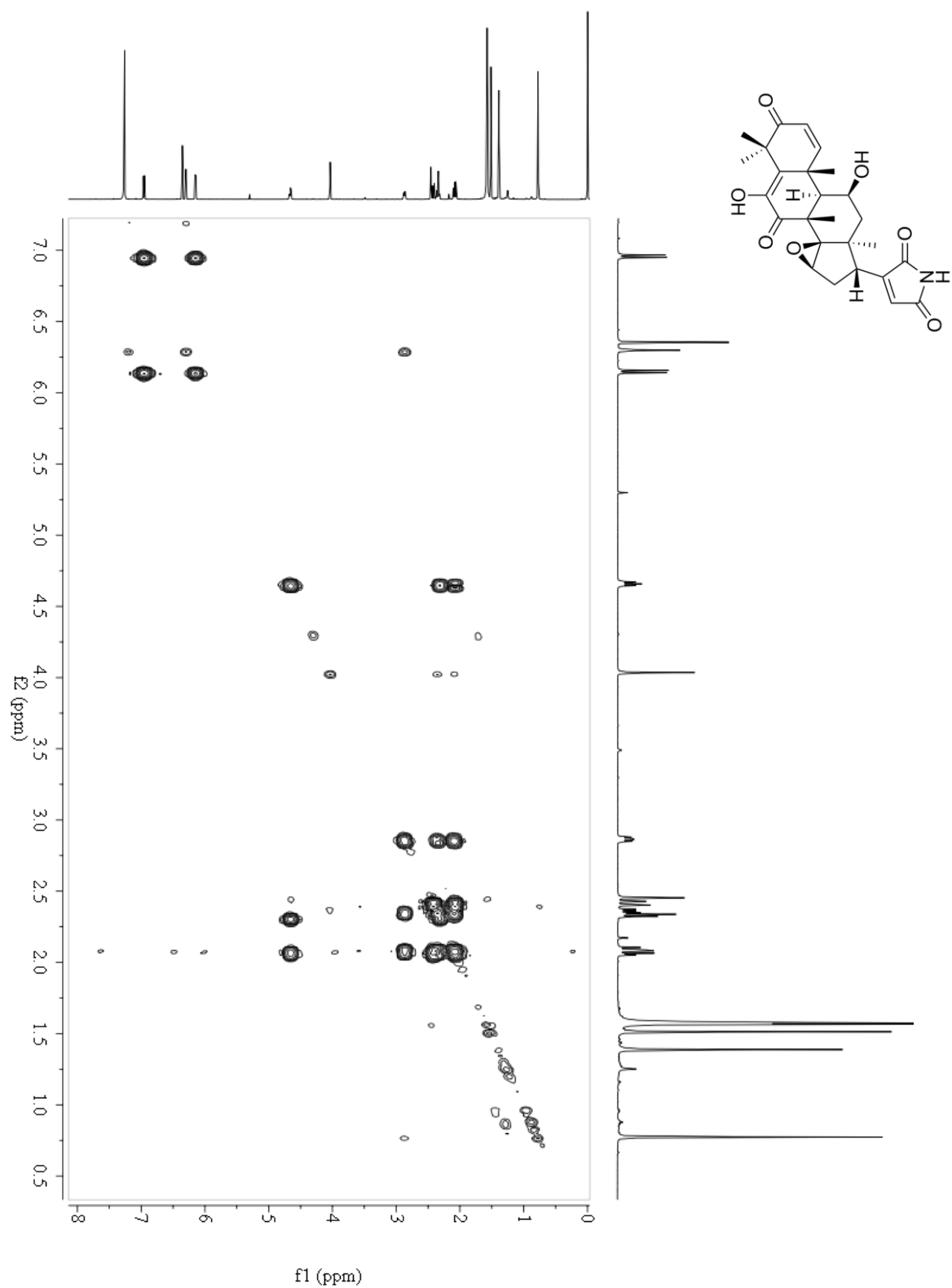


Figure S80. NOESY spectrum of walsunoid I (9) in CDCl₃

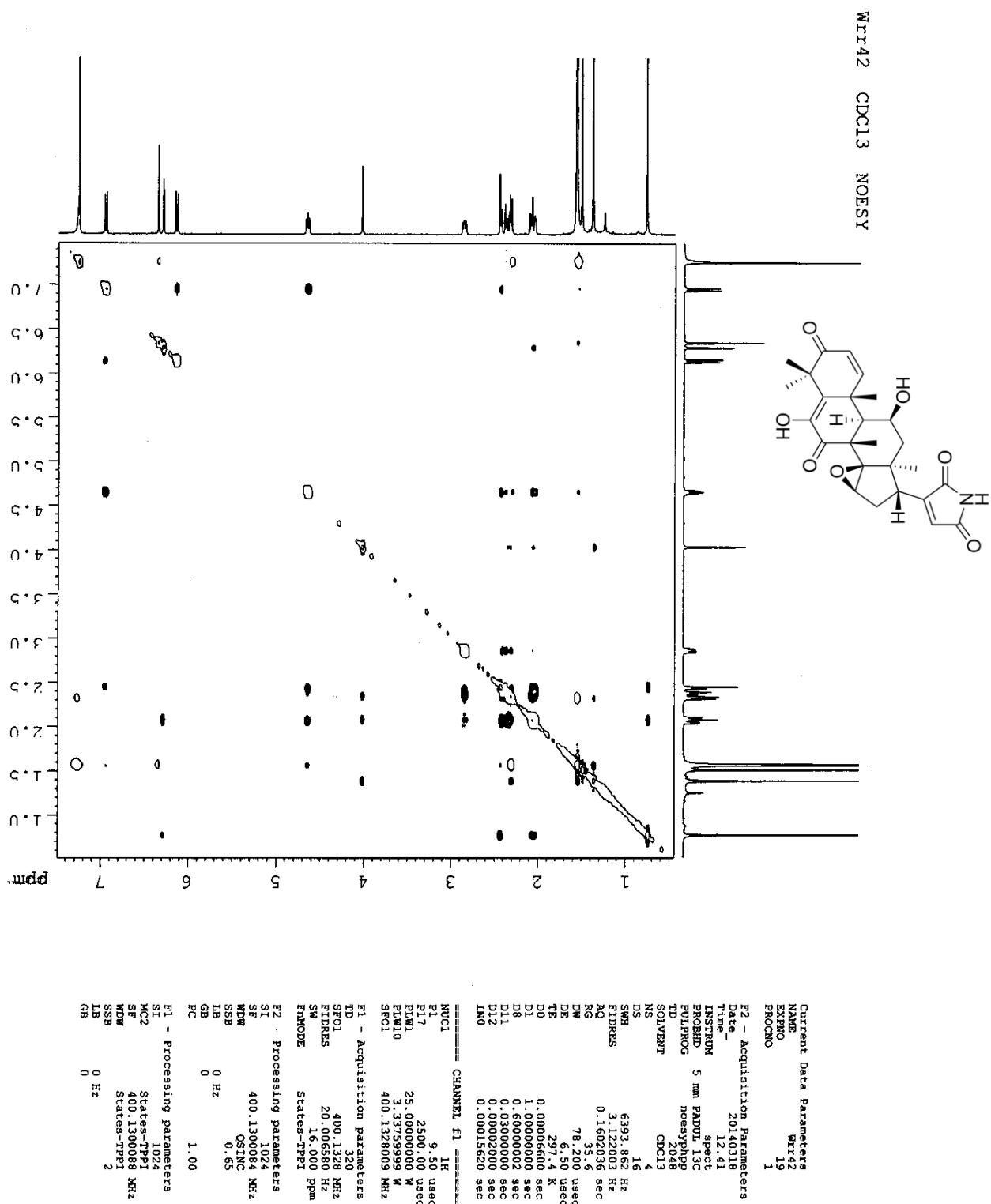


Figure S81. (+)-ESIMS spectrum of walsunoid I (**9**)

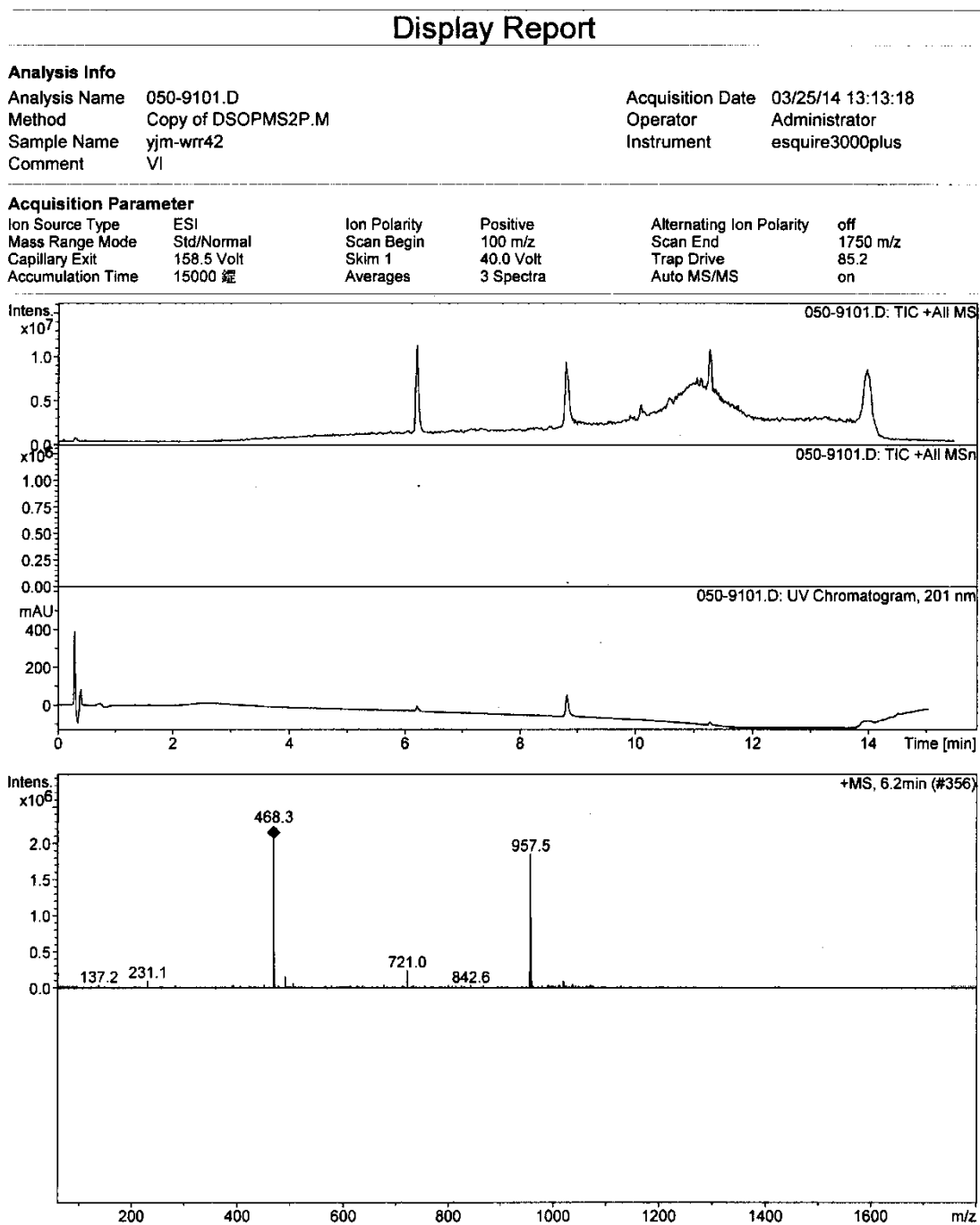


Figure S82. (-)-ESIMS spectrum of walsunoid I (9)

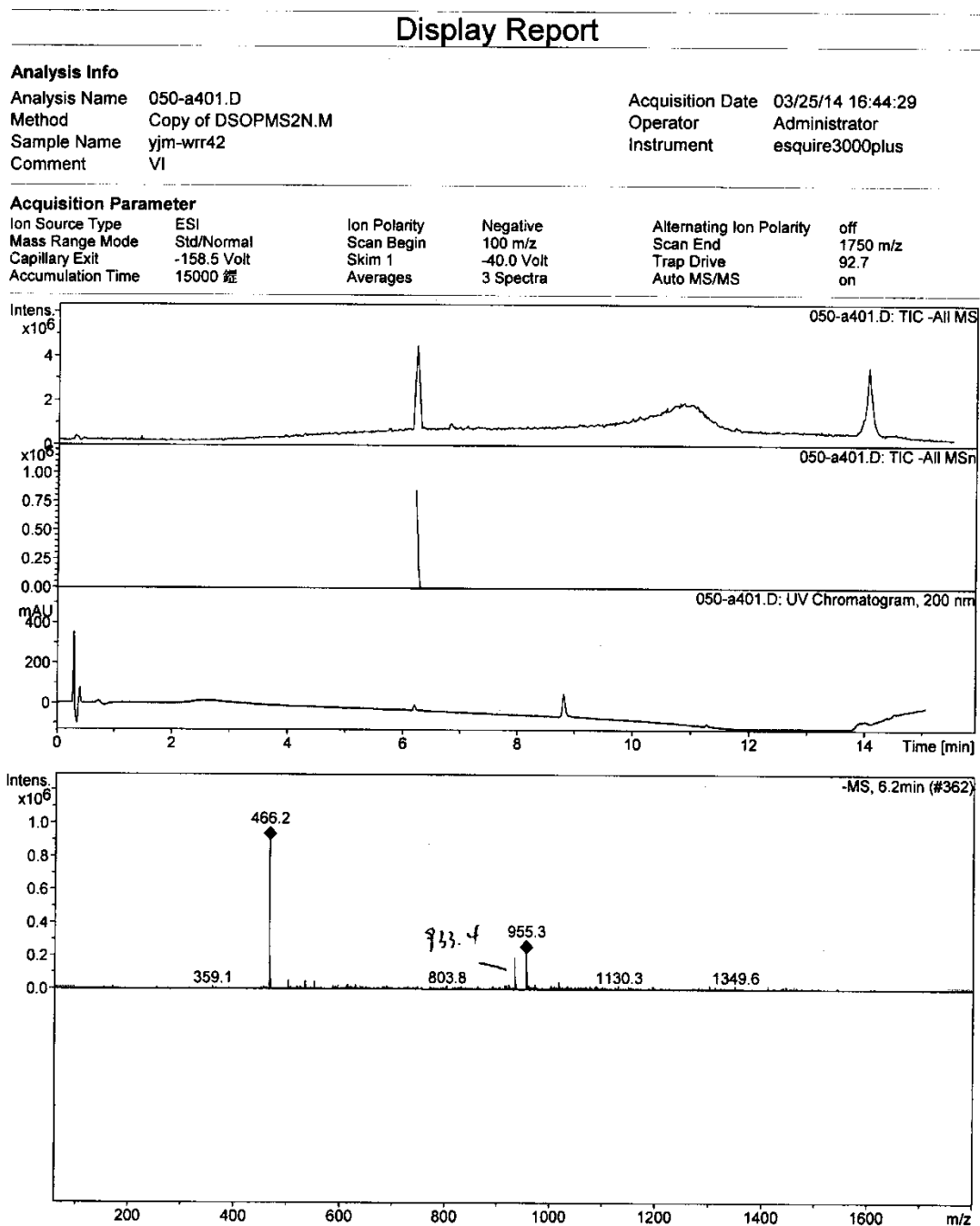


Figure S83. (-)-HRESIMS spectrum of walsunoid I (9)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

275 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 N: 0-2 O: 0-20

wrr42

LCT PXE KE324

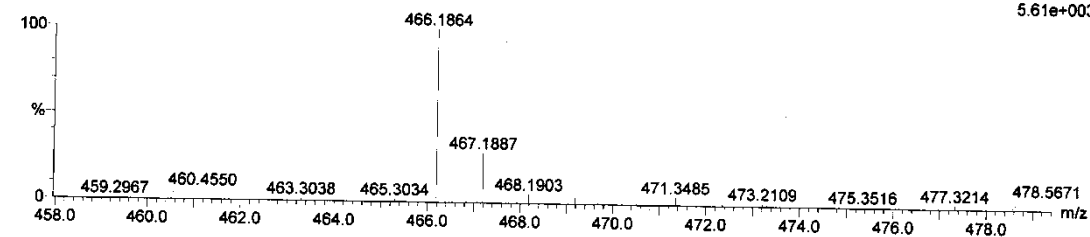
03-Apr-2014

15:02:37

1: TOF MS ES-

5.61e+003

wrr42_0403 25 (0.549) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (24:37)



Minimum:

Maximum: 5.0 5.0 -1.5

Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula

466.1864 466.1866 -0.2 -0.4 13.5 130.6 0.0 C26 H28 N O7

Figure S84. IR spectrum of walsunoid I (**9**)

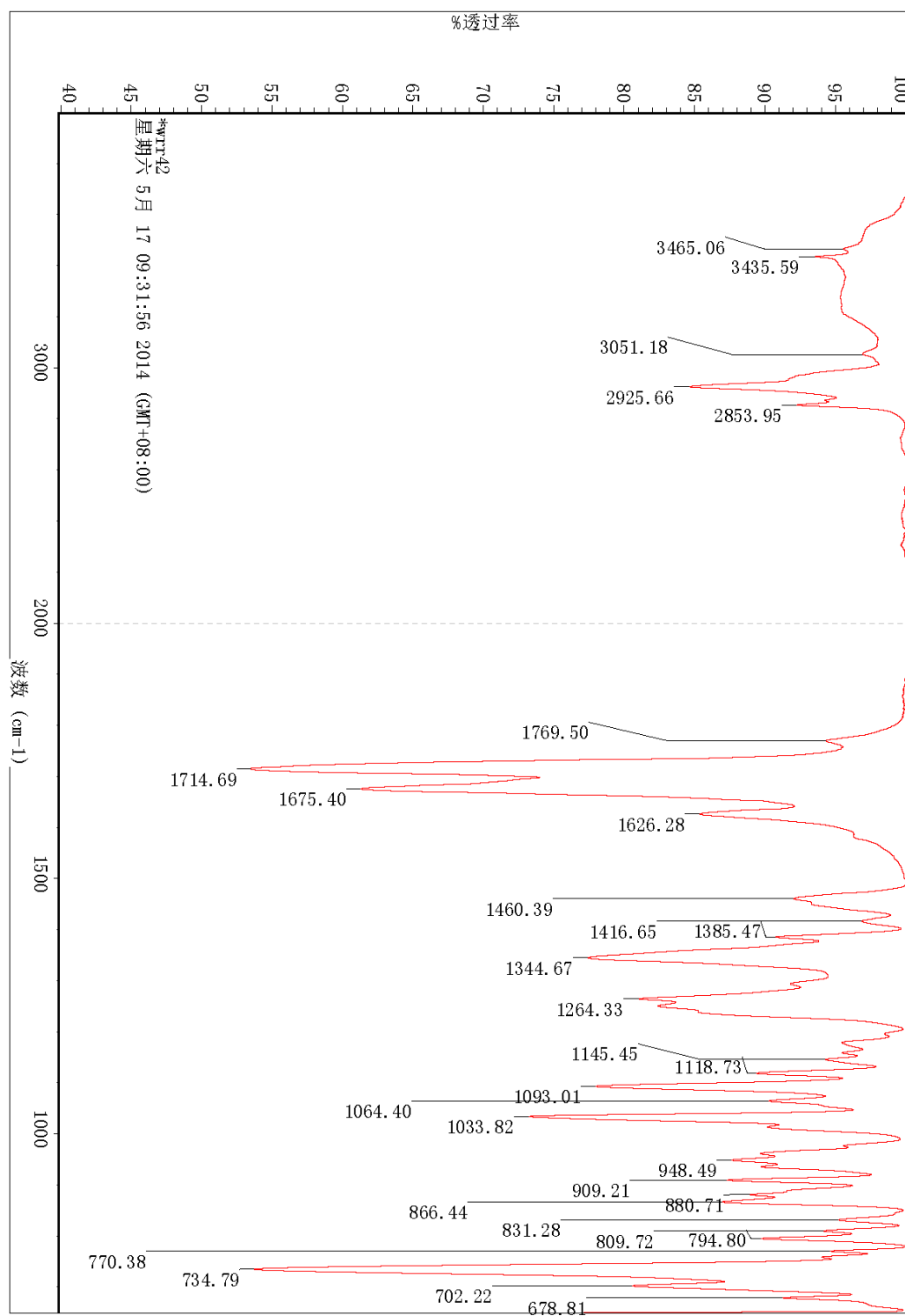


Figure S85. ^1H NMR spectrum of compound **10** in CDCl_3

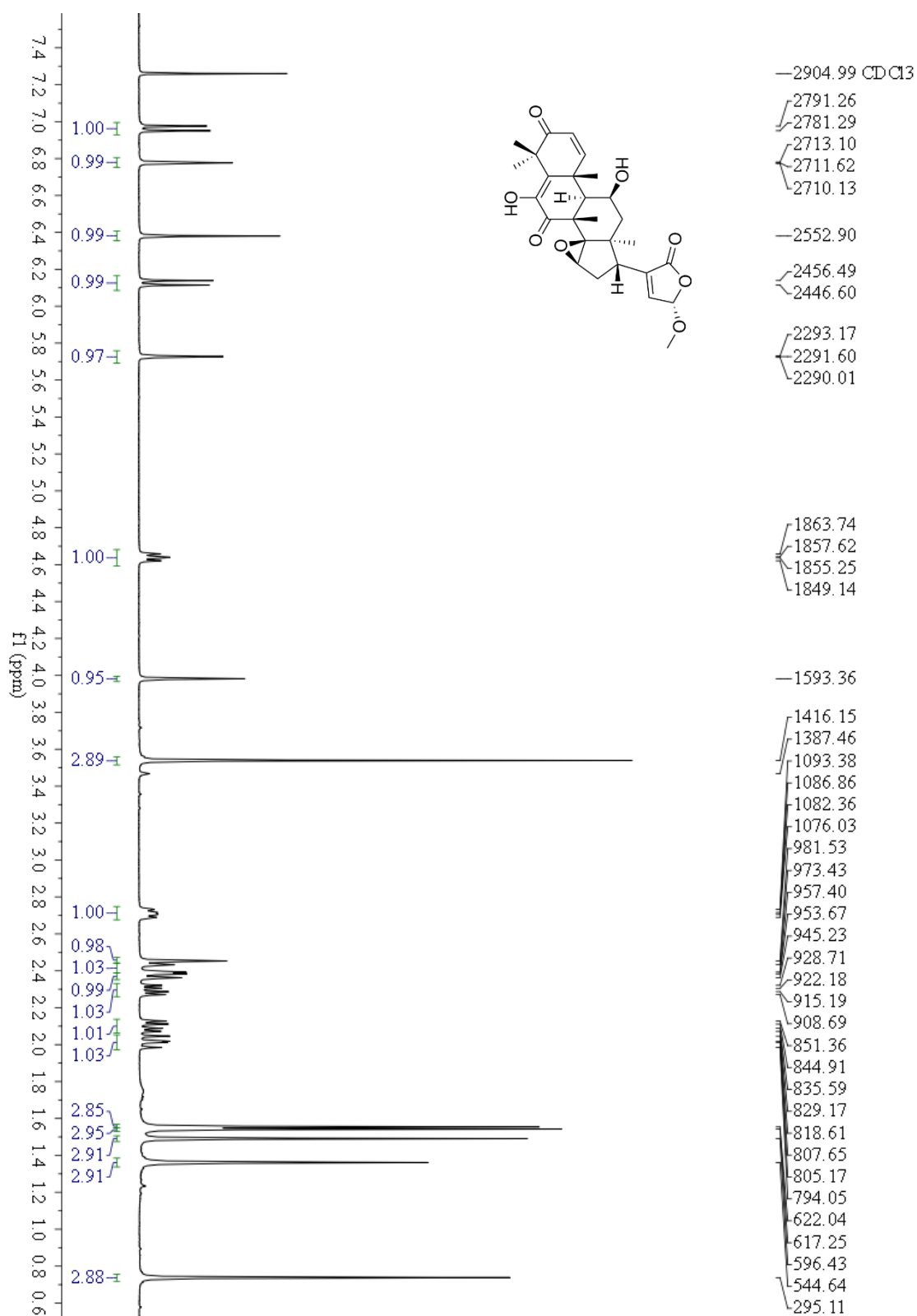


Figure S86. ^{13}C NMR spectrum of compound **10** in CDCl_3

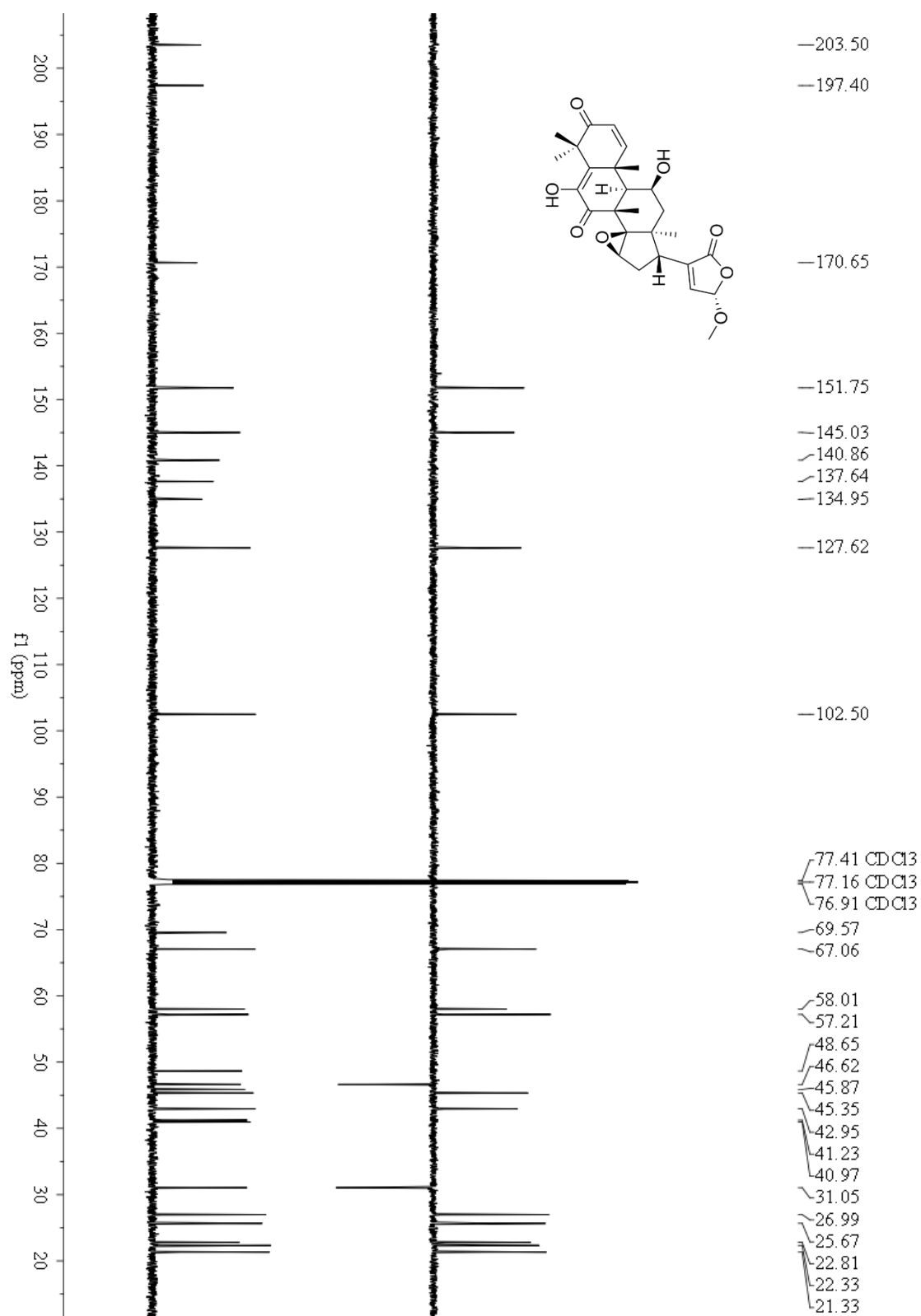


Figure S87. ^1H NMR spectrum of compound **10** in $\text{C}_5\text{D}_5\text{N}$

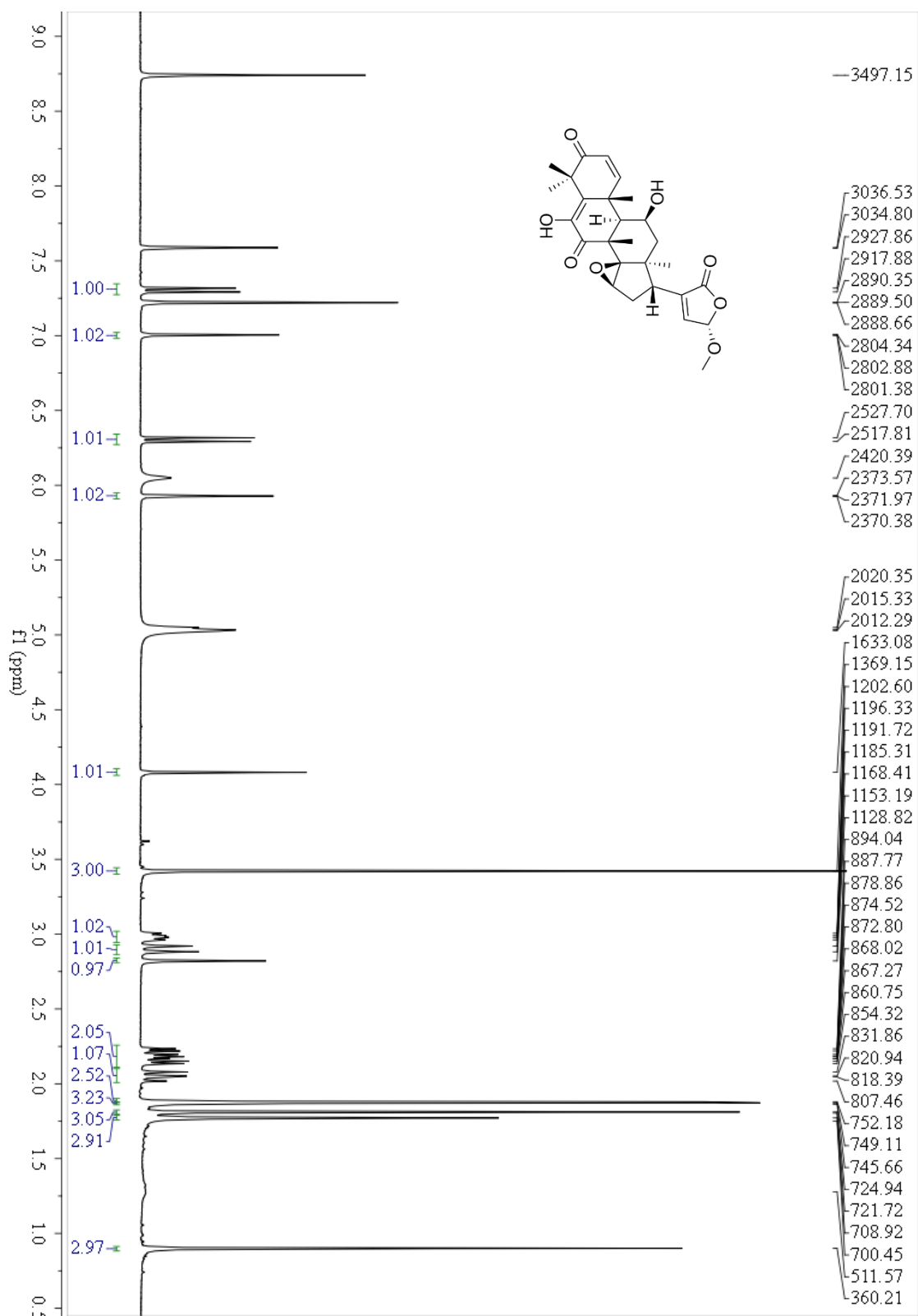


Figure S88. ^{13}C NMR spectrum of compound **10** in $\text{C}_5\text{D}_5\text{N}$

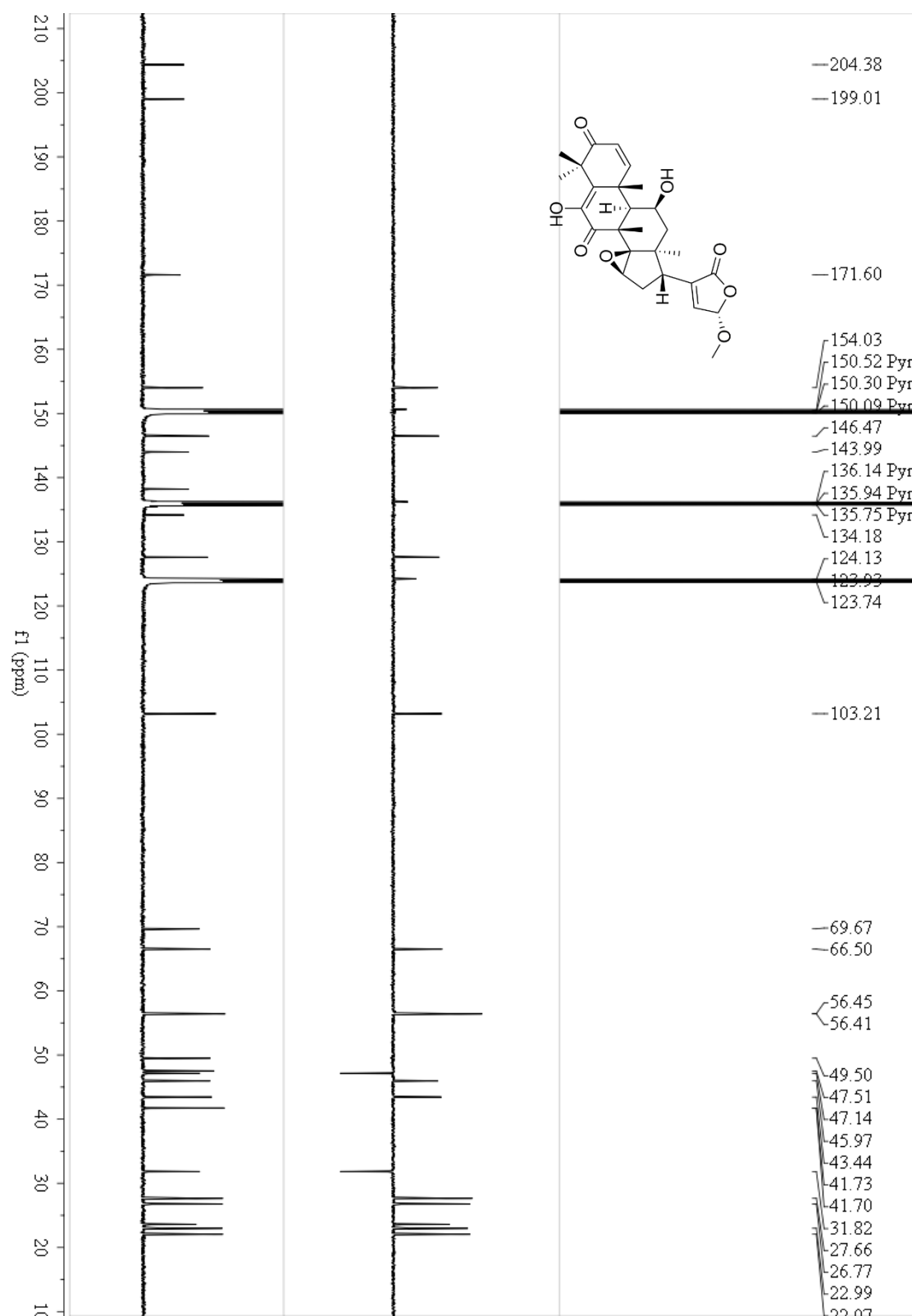


Figure S89. HSQC spectrum of compound **10** in CDCl₃

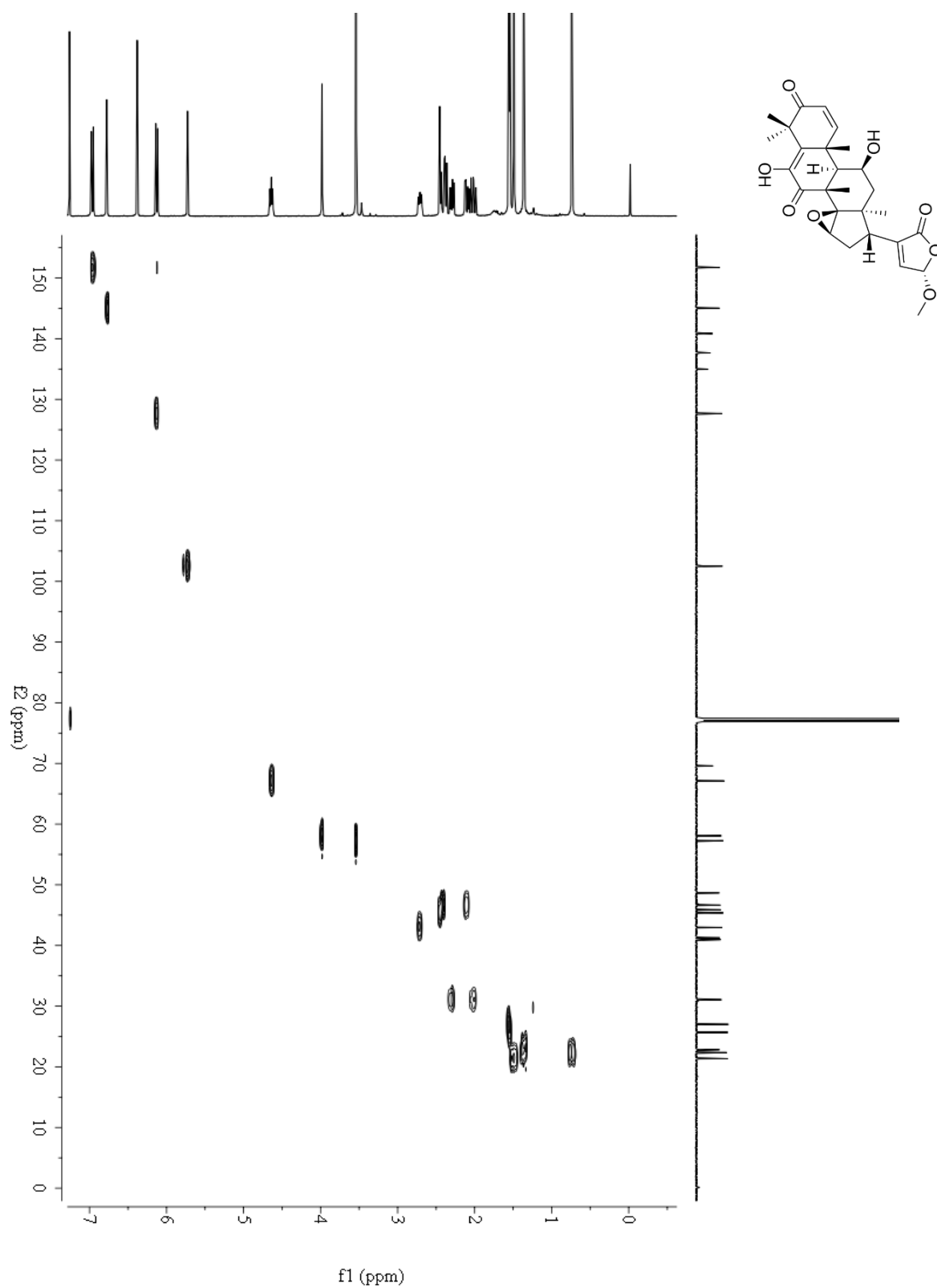


Figure S90. HMBC spectrum of compound **10** in CDCl₃

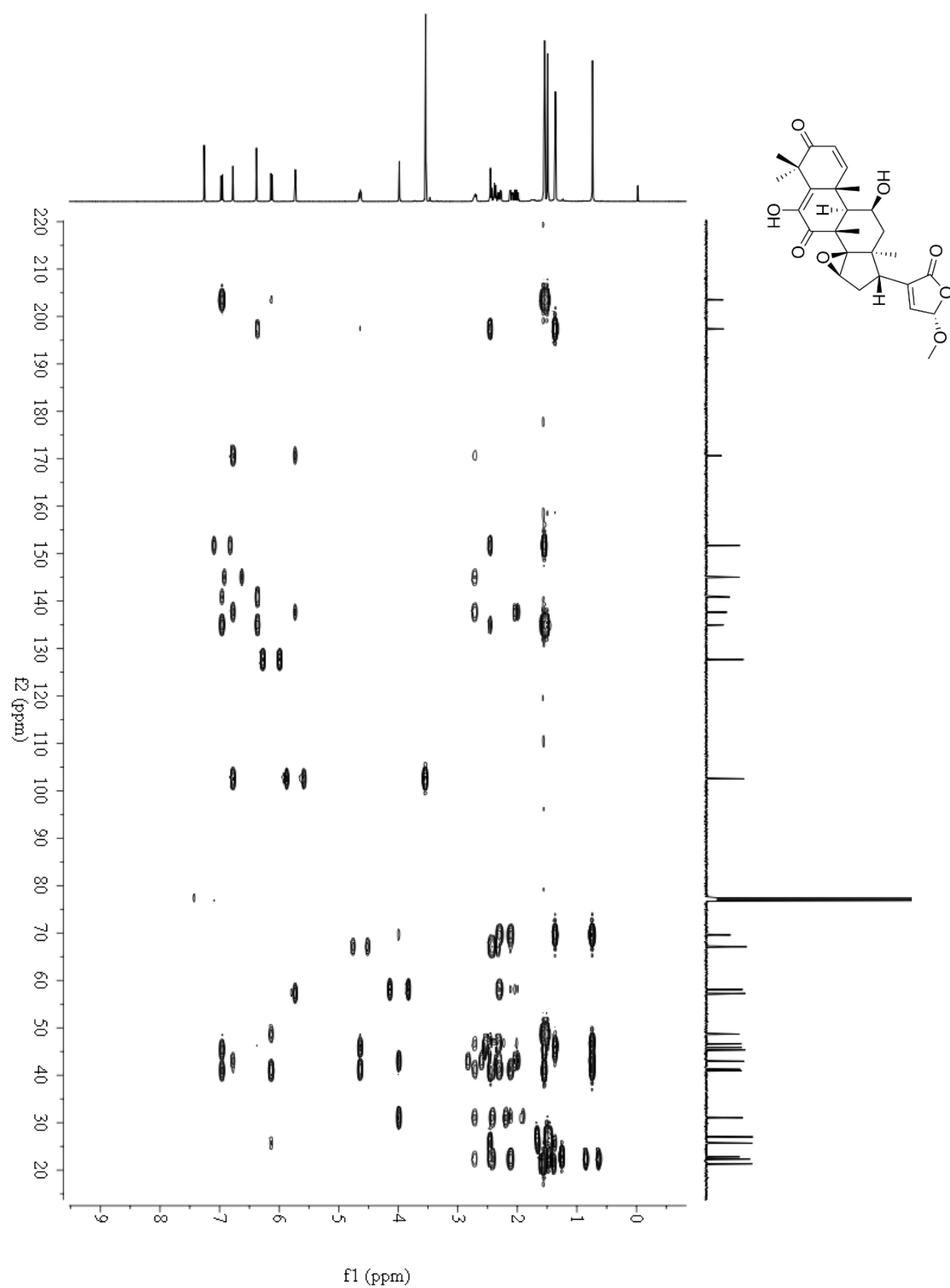


Figure S91. (-)-HRESIMS spectrum of 10

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

97 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 5-80 H: 2-120 O: 0-20

wrr32

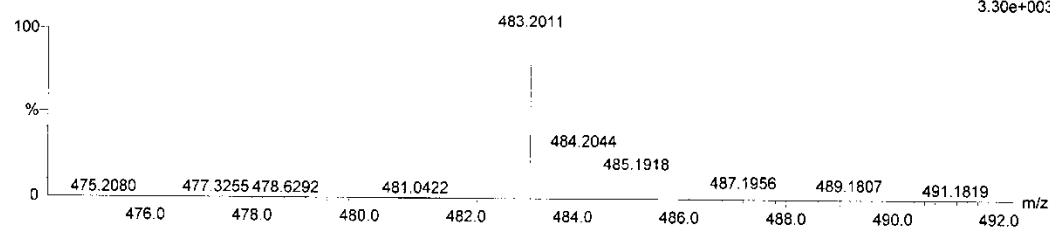
LCT PXE KE324

03-Apr-2014

15:38:10

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1: TOF MS ES-
3.30e+003



Minimum: -1.5
Maximum: 5.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
483.2011	483.2019	-0.6	-1.7	12.5	104.0	0.0	C27 H31 O8

Figure S92. LC-ESI(\pm)MS analysis of 2

==== Shimadzu LabSolutions Browser Report ====

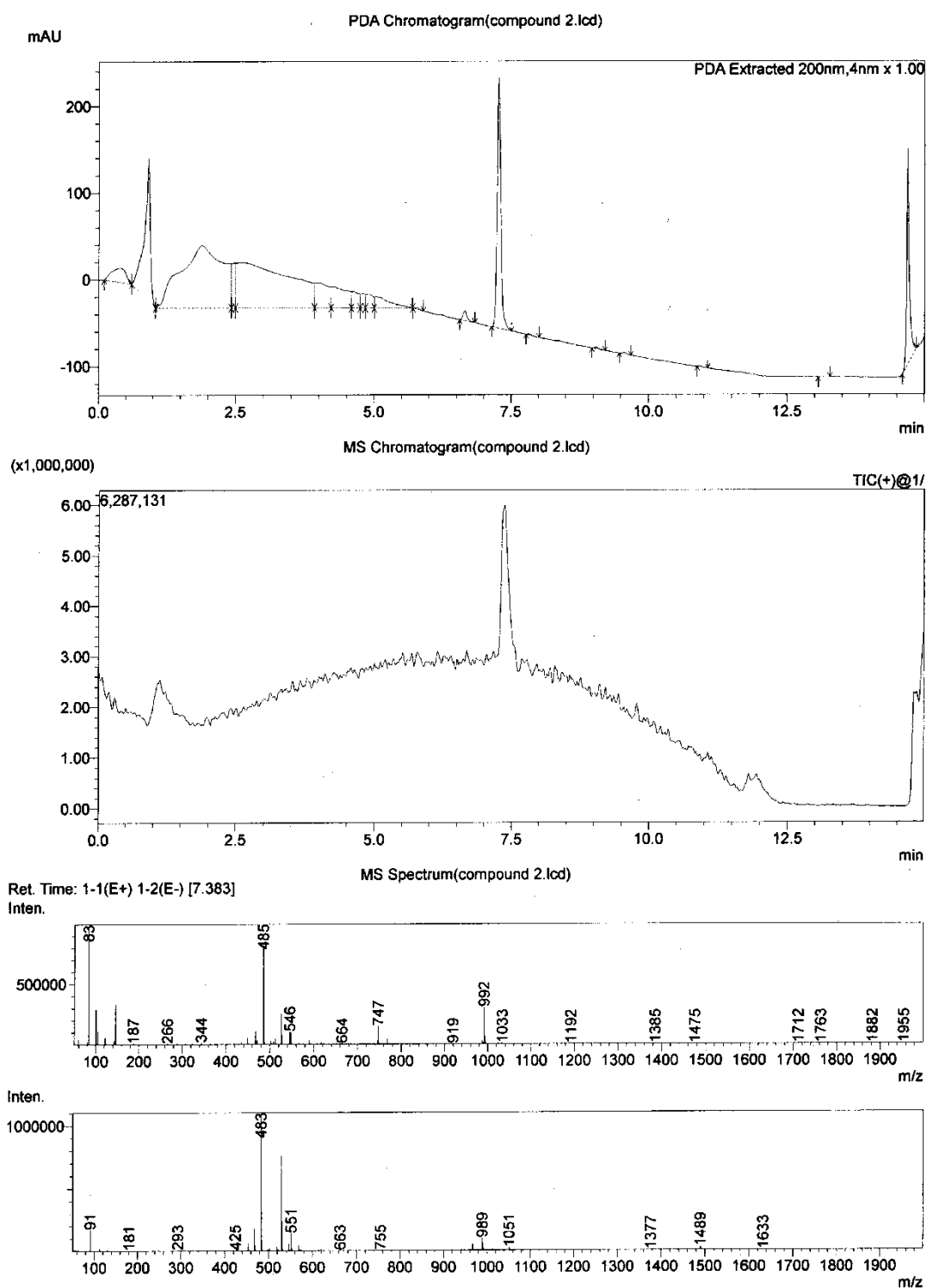


Figure S93. LC-ESI(±)MS analysis of 4

==== Shimadzu LabSolutions Browser Report ====

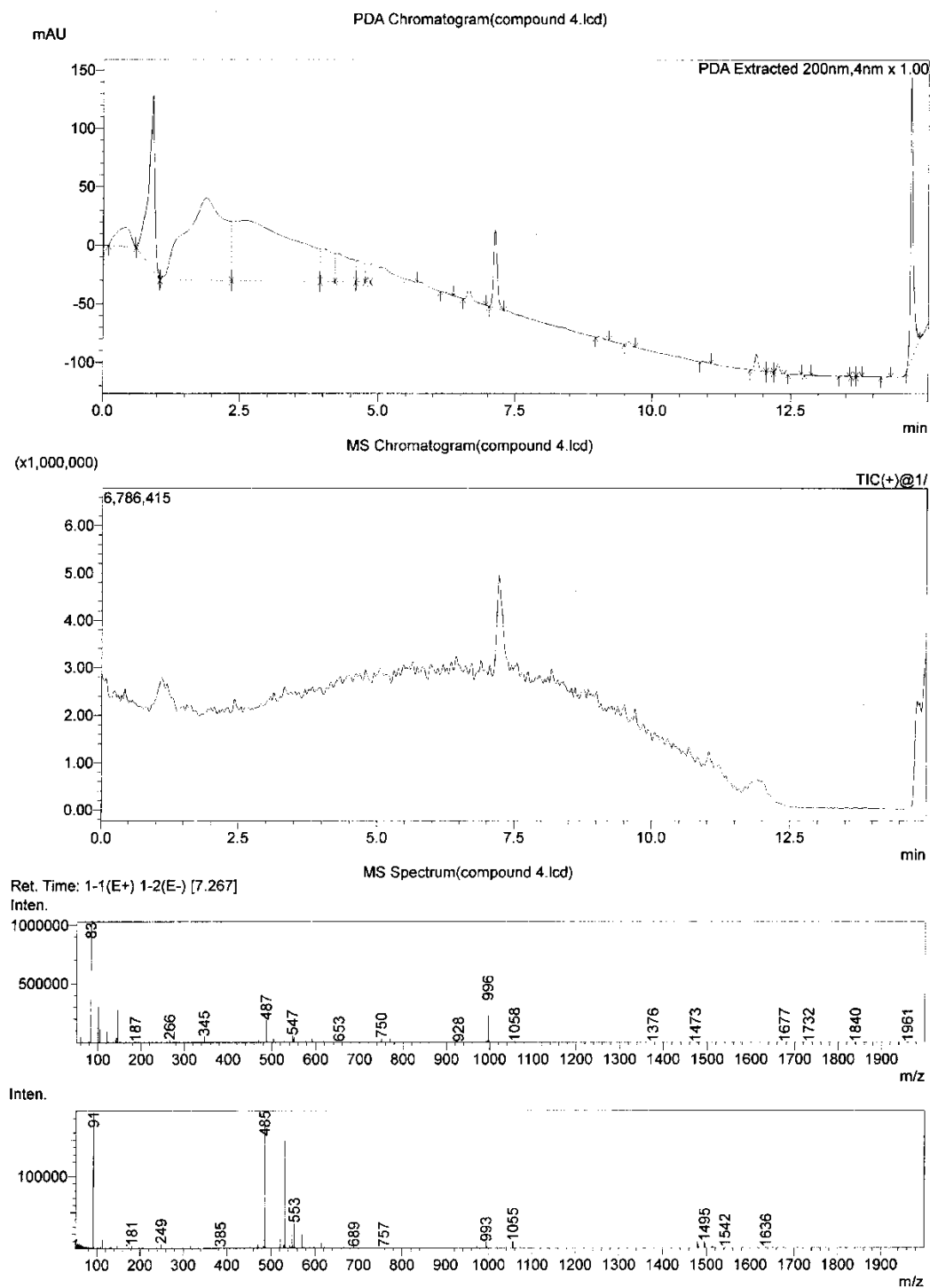


Figure S94. LC-ESI(\pm)MS analysis of 10

==== Shimadzu LabSolutions Browser Report ====

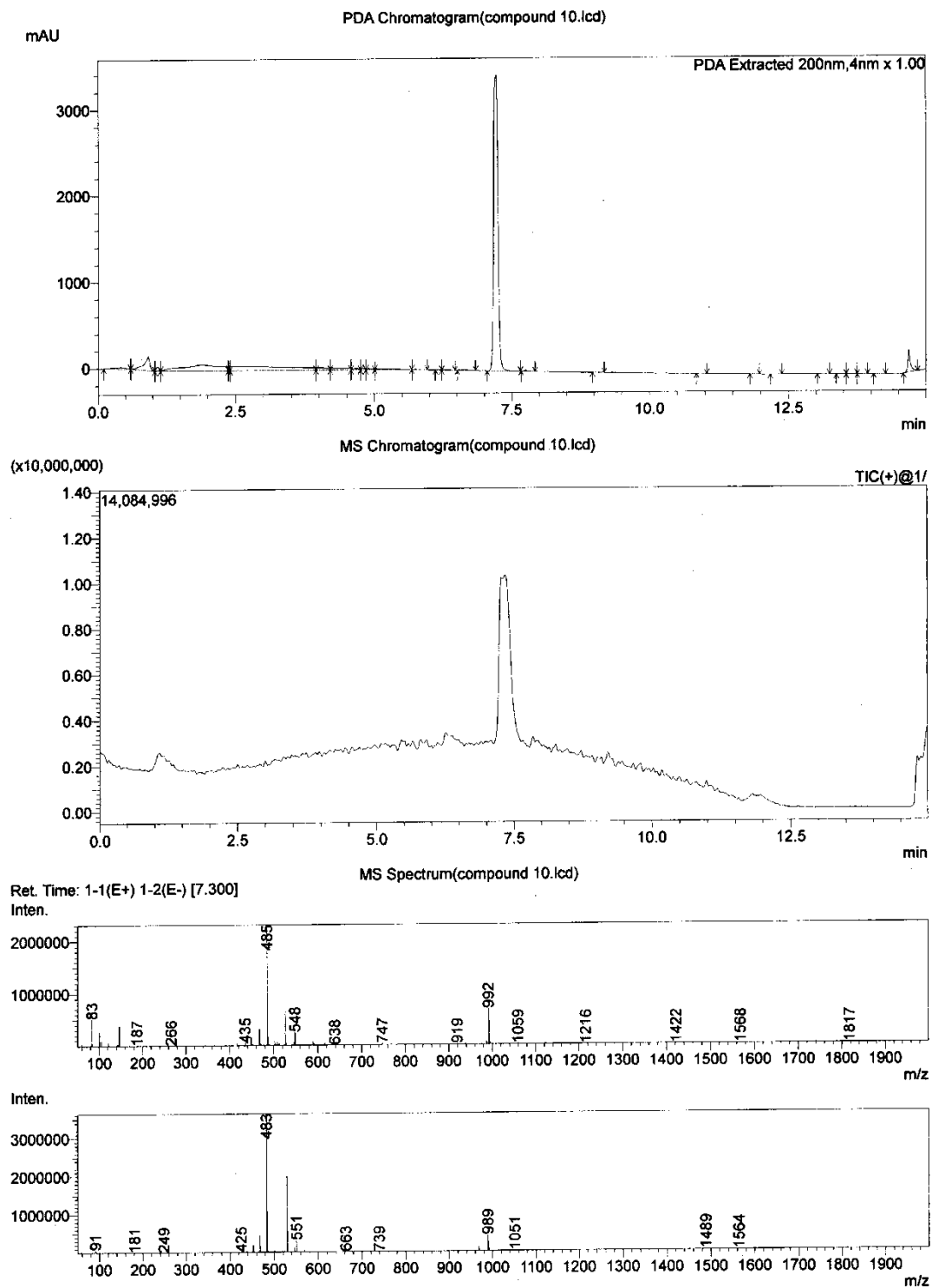


Figure S95. LC-ESI(±)MS analysis of ethanolic crude extract

==== Shimadzu LabSolutions Browser Report ====

