Supporting Information for

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

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

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

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

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

	2		**10**	
position	^{1}H (*J* in Hz)	^{13}C	^{1}H (*J* 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
12α	2.11, dd (15.7,6.3)	46.8	2.10, dd (15.9,6.4)	46.6
12β	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
16α	2.02, dd (13.5,10.9)	30.9	2.02, dd (13.5,11.0)	31.1
16β	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 11β-HSD1 at 10 μM.

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%
Glycyrrhetinic acid 1 nM	15.45%	11.05%	8.86%	11.79%	3.36%
Glycyrrhetinic acid 10 nM	56.78%	51.97%	59.55%	56.10%	3.87%
Glycyrrhetinic acid 100 nM	94.66%	88.87%	89.99%	91.17%	3.07%
Activity of **15** was already reported in our previous article. (*J. Nat. Prod.* 2013, 76, 1319)					

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

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%
Glycyrrhetinic acid 1 nM	12.58%	11.04%	12.13%	11.91%	0.79%
Glycyrrhetinic acid 10 nM	58.83%	59.77%	66.01%	61.53%	3.90%
Glycyrrhetinic acid 100 nM	93.51%	105.80%	99.43%	99.58%	6.15%

Activity of **15** was already reported in our previous article. (*J. Nat. Prod.* 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) Å, α = 90 ° *b* = 12.0869 (4) Å, β = 90.180(2) ° *c* = 28.1295 (7) Å, γ = 90 °
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) Å, α = 90 ° *b* = 11.6919 (2) Å, β = 90 ° *c* = 14.6190 (2) Å, γ = 90 °
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. ^{1}H NMR spectrum of walsunoid A (**1**) in $CDCl_3$

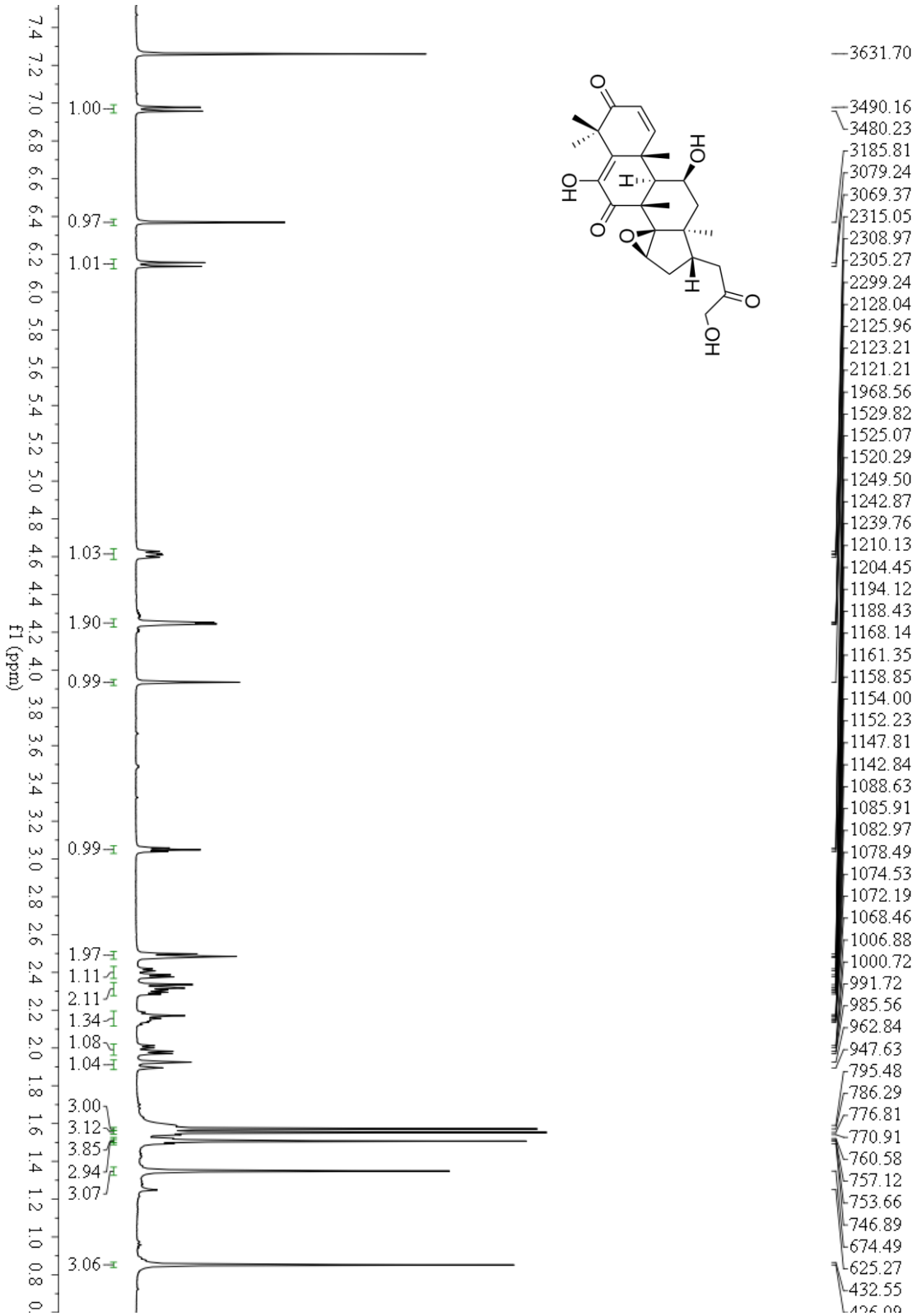


Figure S2. ^{13}C NMR spectrum of walsunoid A (**1**) in $CDCl_3$

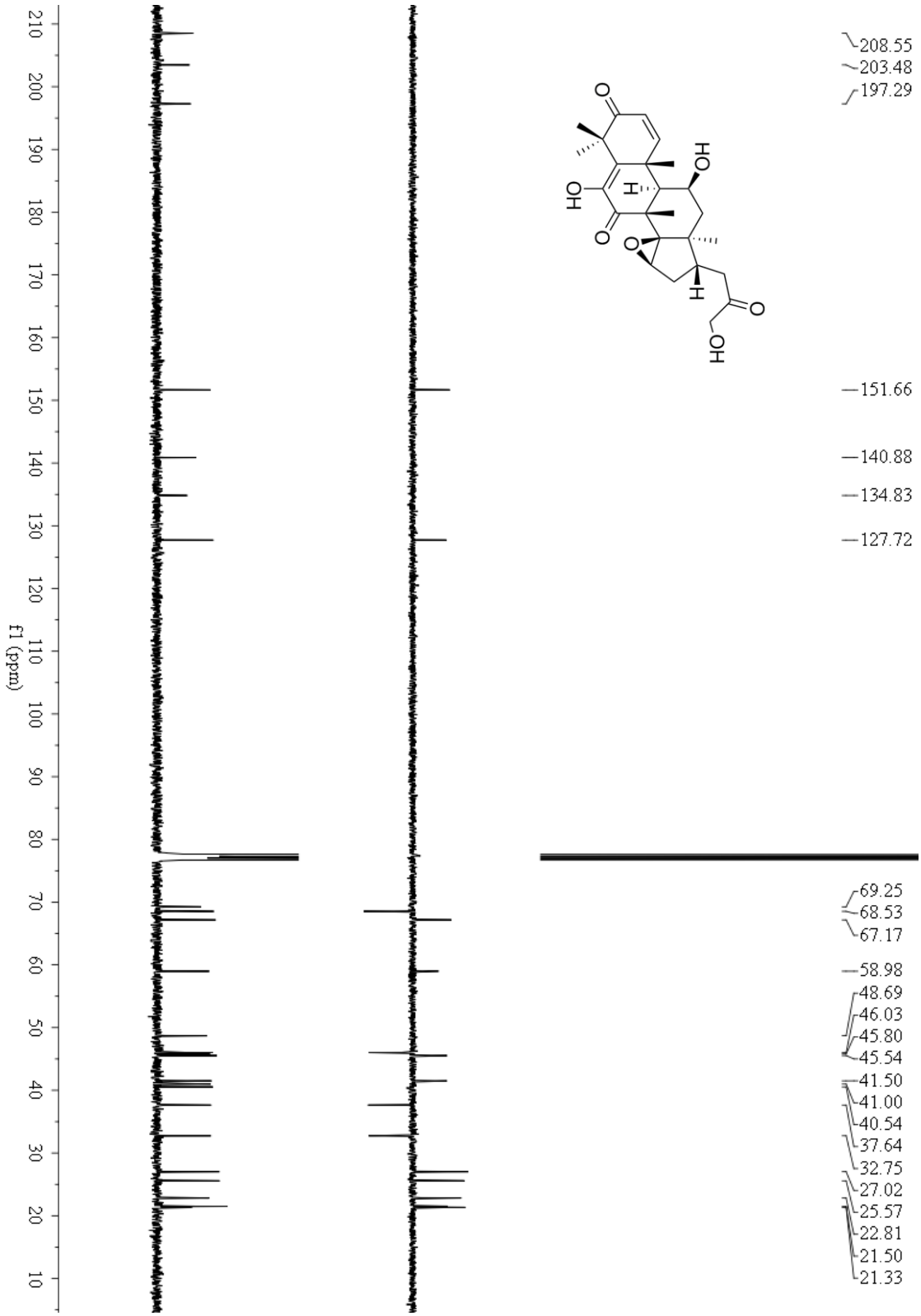


Figure S3. HSQC spectrum of walsunoid A (**1**) in $CDCl_3$

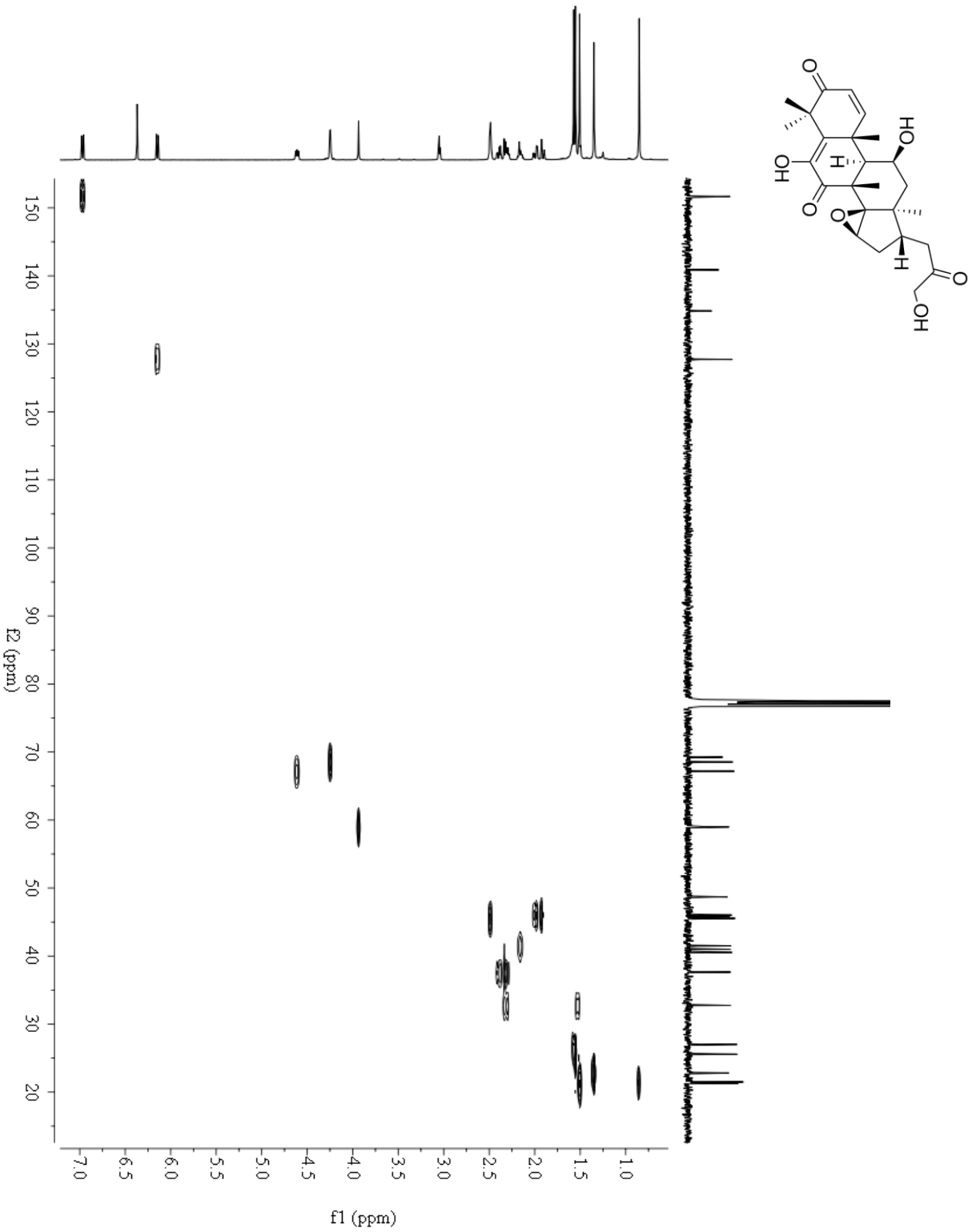


Figure S4. HMBC spectrum of walsunoid A (**1**) in $CDCl_3$

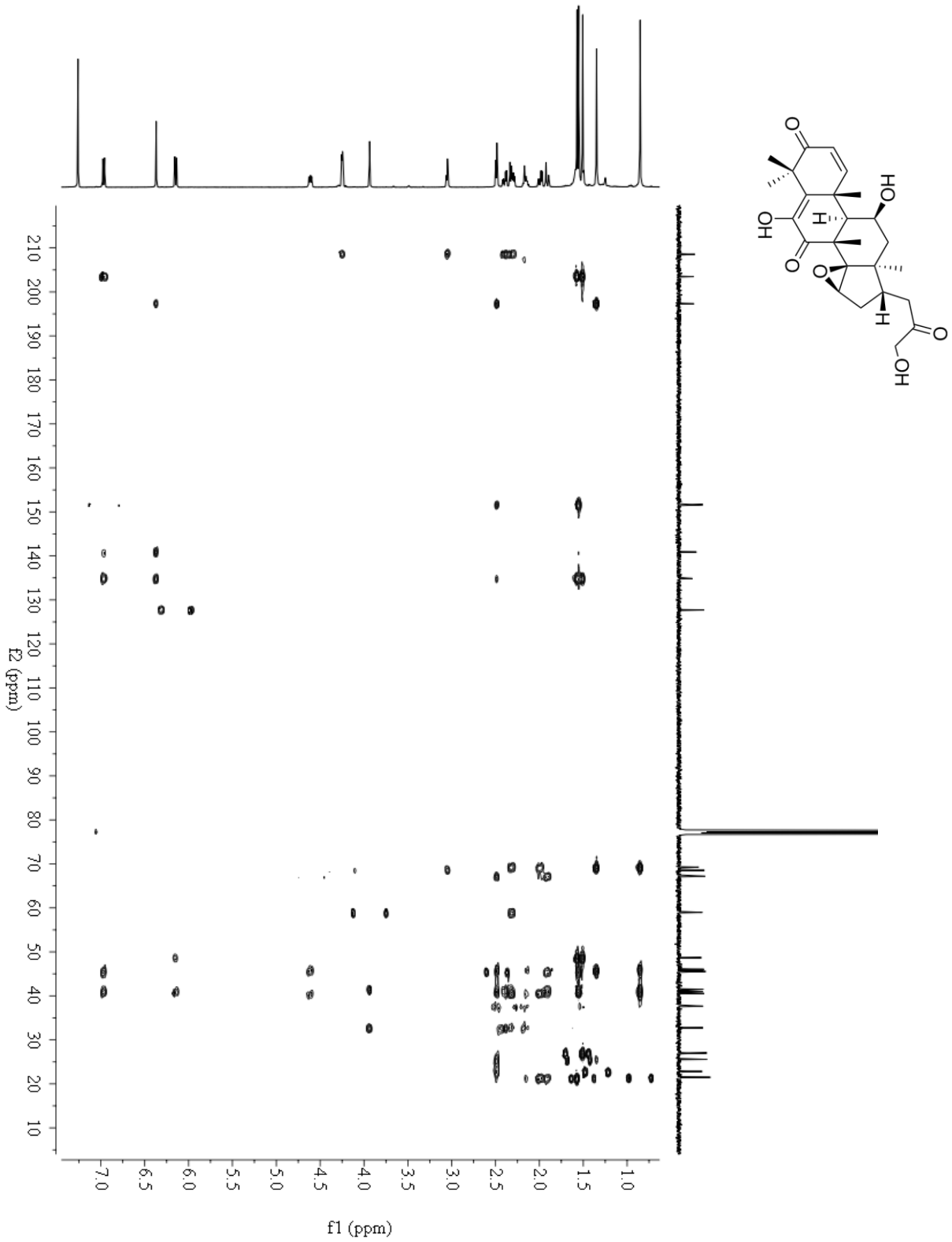


Figure S5. ^{1}H-^{1}H COSY spectrum of walsunoid A (**1**) in $CDCl_3$

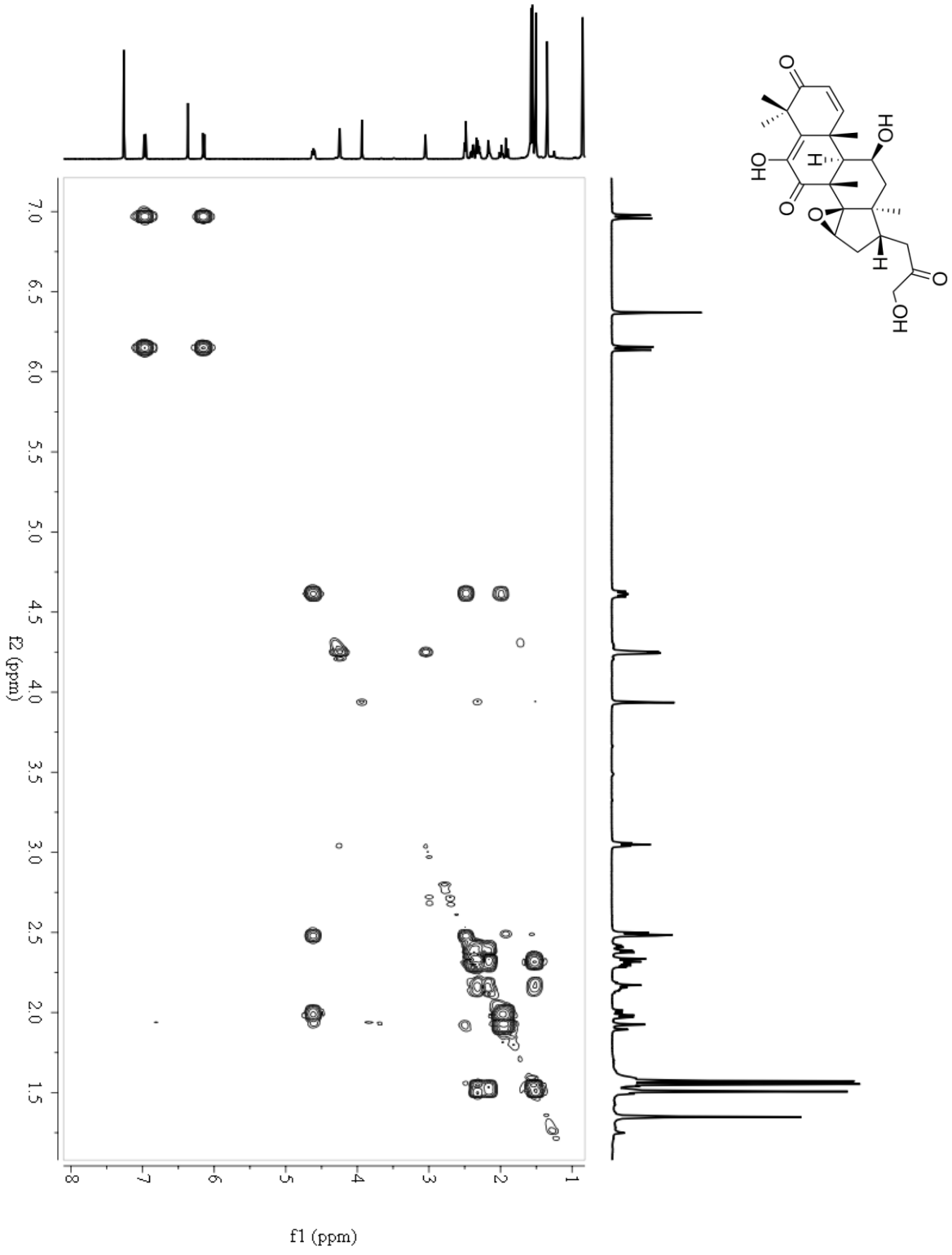


Figure S6. ROESY spectrum of walsunoid A (**1**) in $CDCl_3$

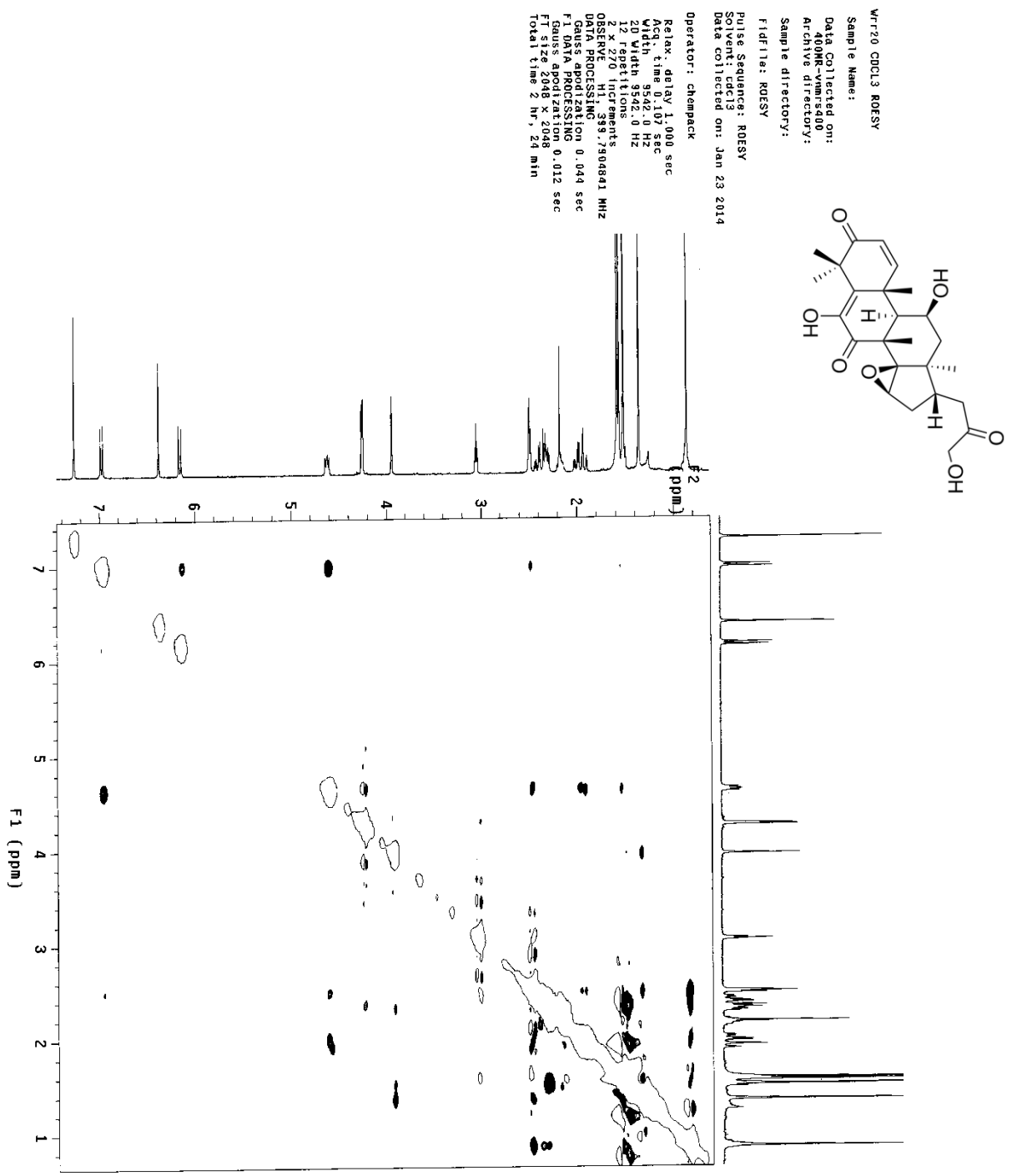


Figure S7. ESI(+)MS spectrum of walsunoid A (**1**)

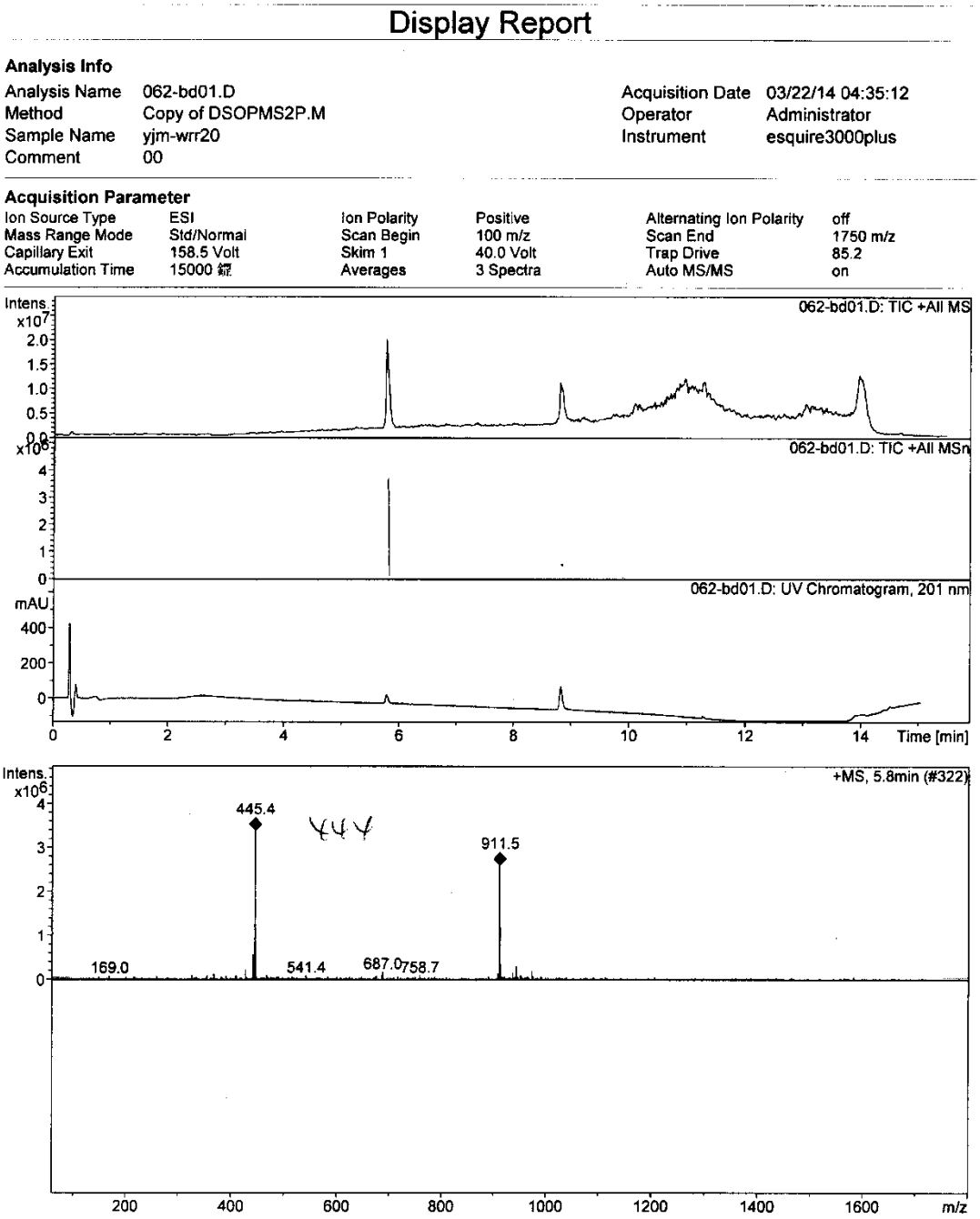


Figure S8. (–)-ESIMS spectrum of walsunoid A (**1**)

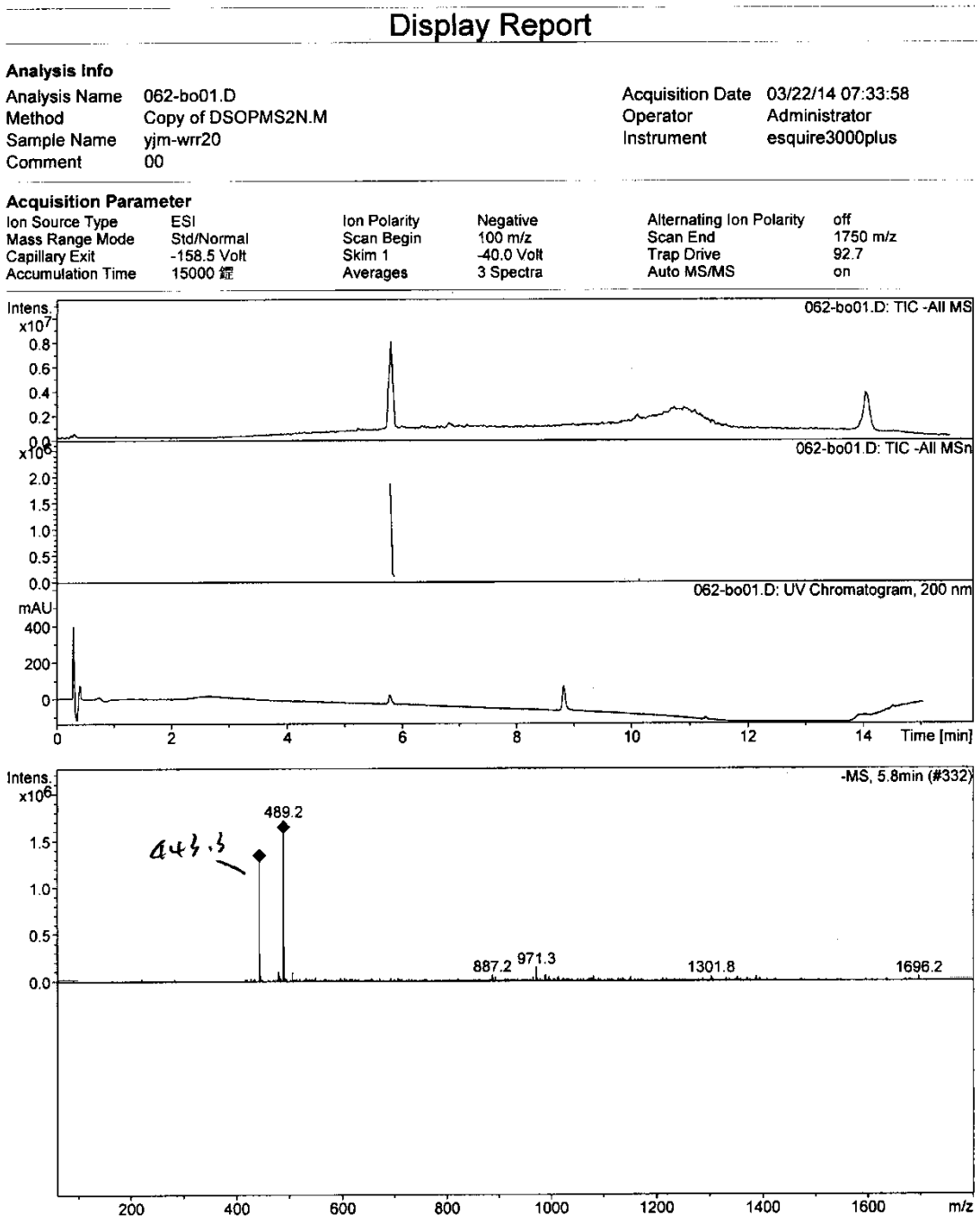
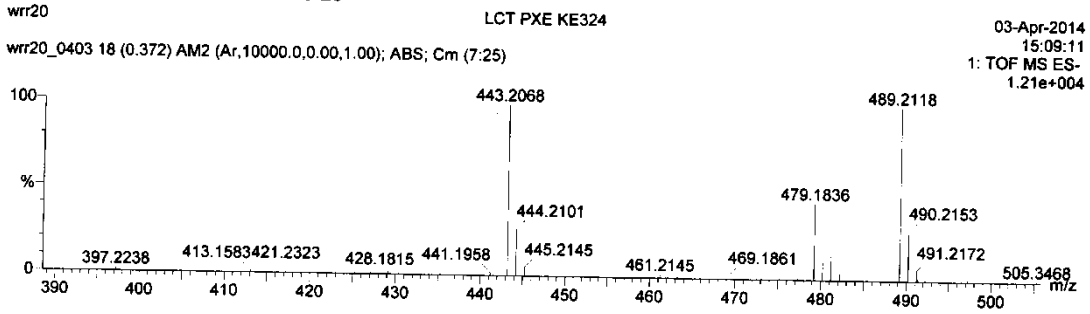


Figure S9. (–)-HRESIMS spectrum of walsunoid A (**1**)

Elemental Composition Report **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
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



Minimum:				-1.5			
Maximum:		5.0	5.0	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**)

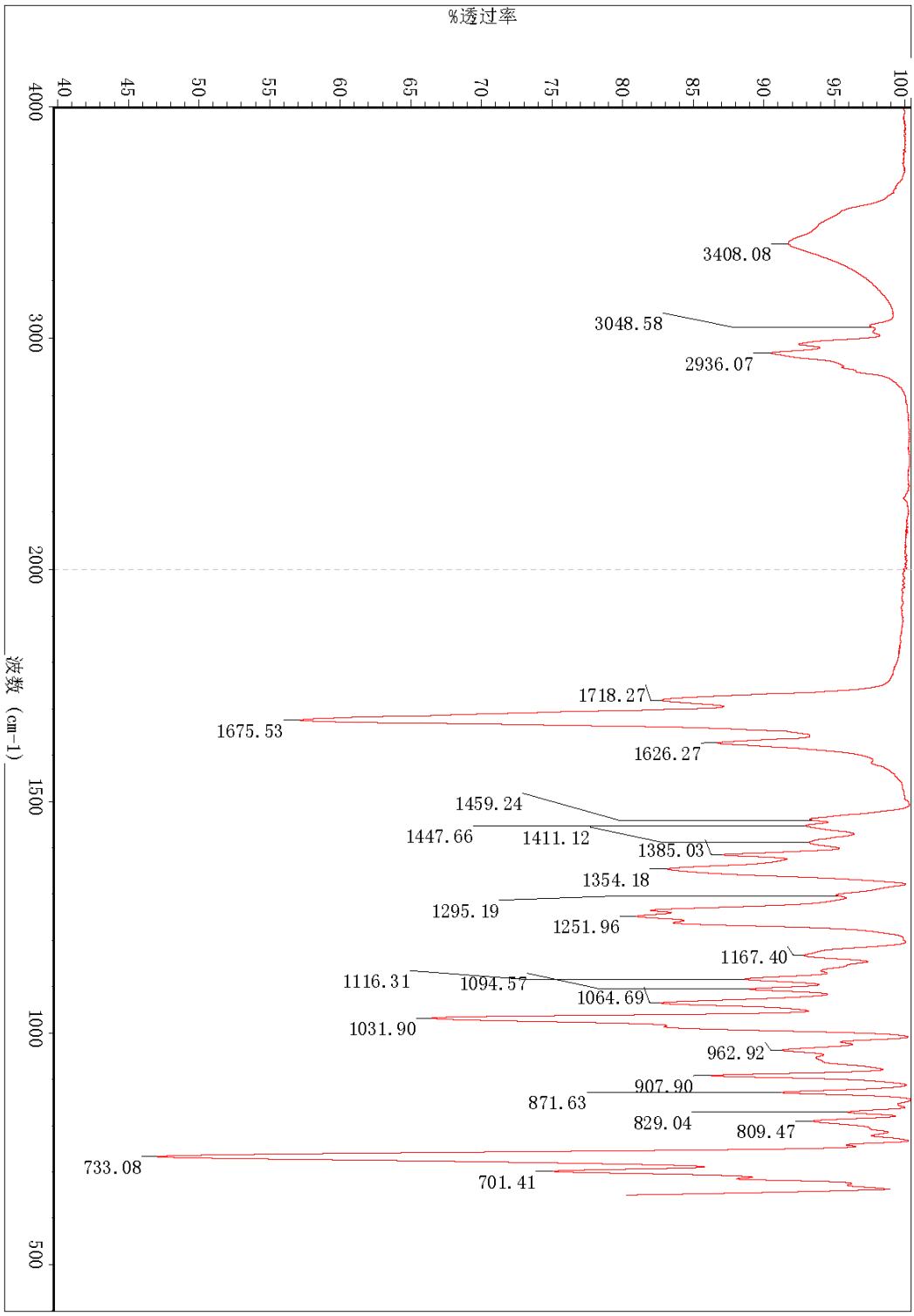


Figure S11. ^{1}H NMR spectrum of walsunoid B (**2**) in $CDCl_3$

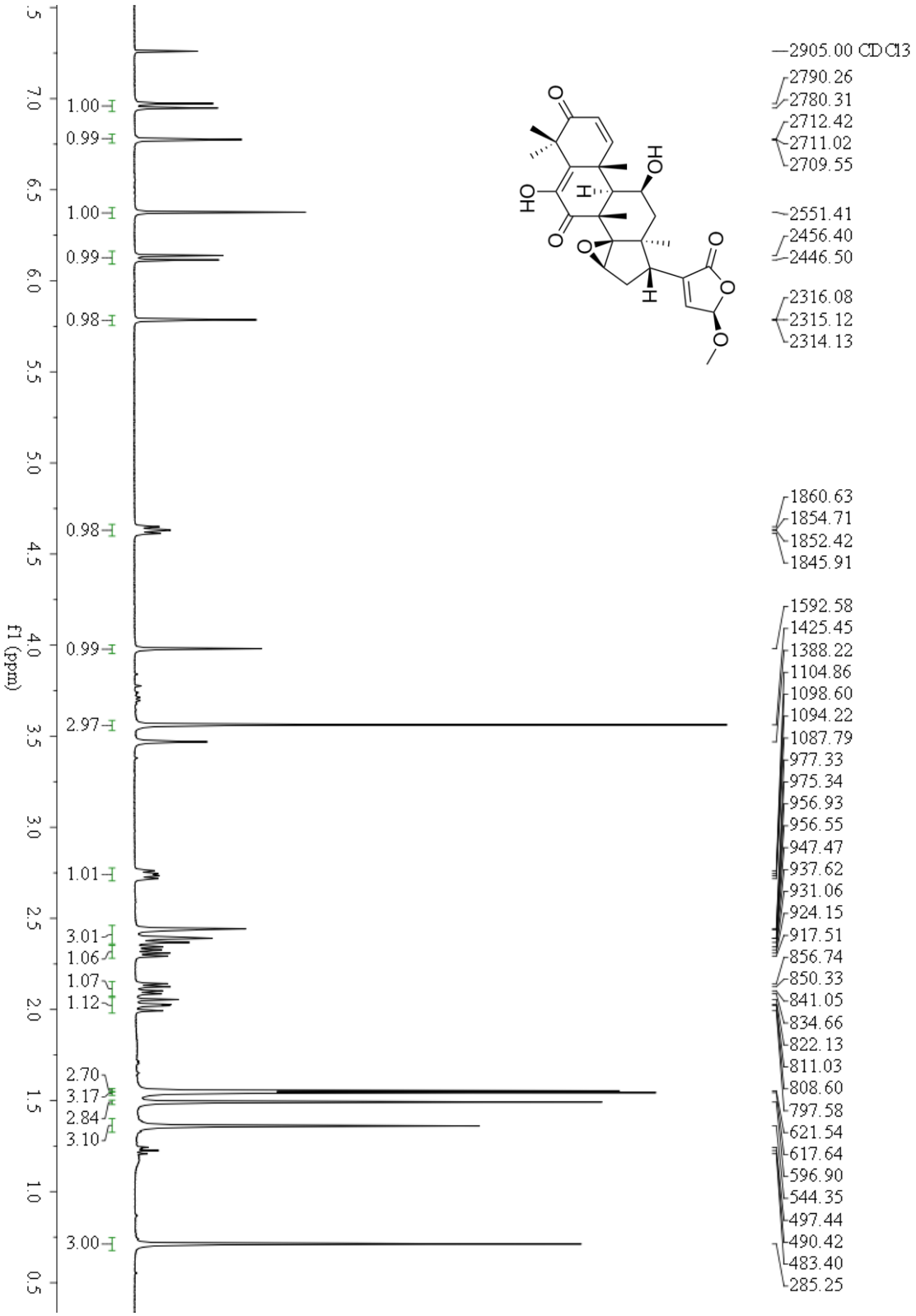


Figure S12. ^{13}C NMR spectrum of walsunoid B (**2**) in $CDCl_3$

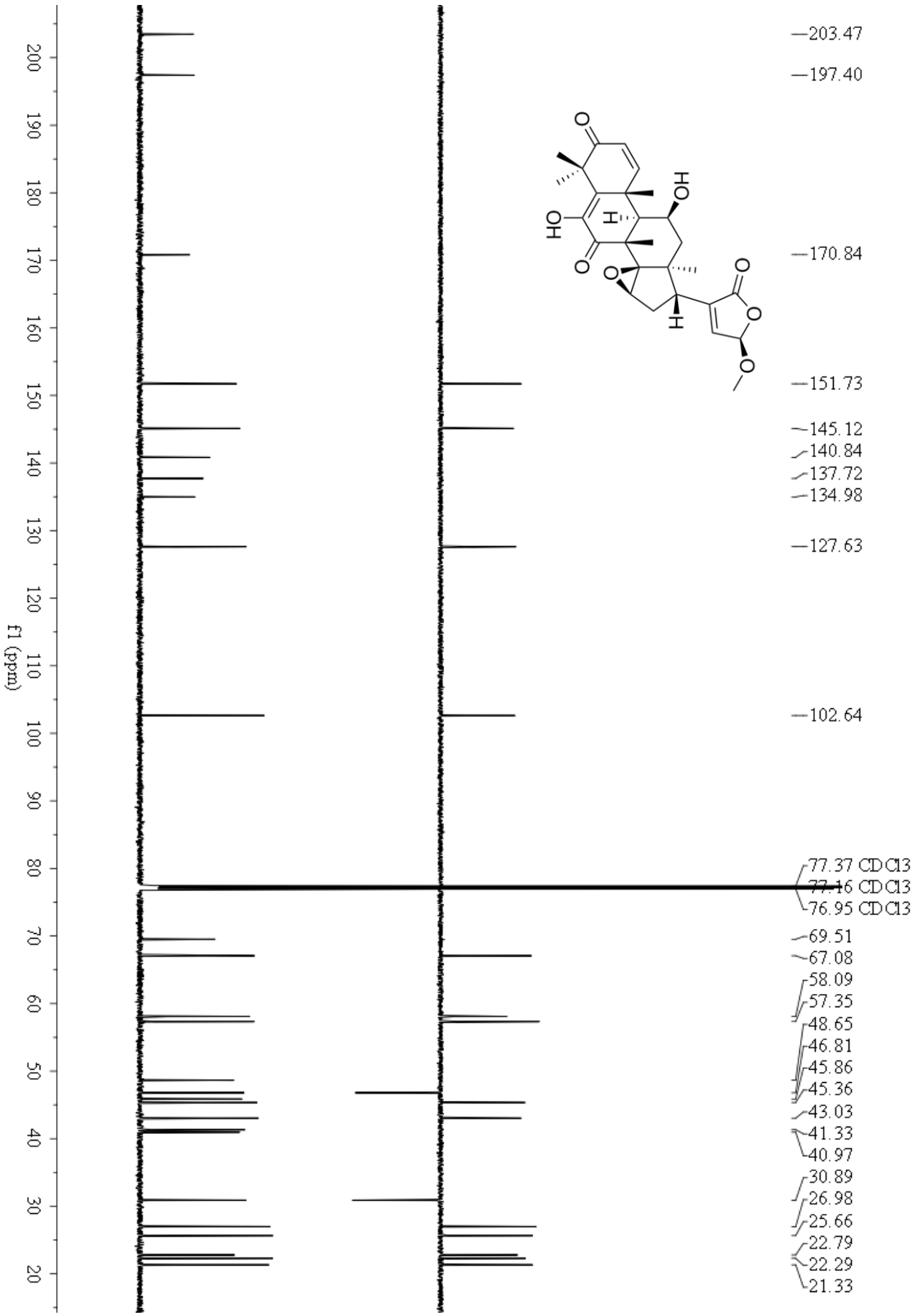


Figure S13. ^{1}H NMR spectrum of walsunoid B (**2**) in C_5D_5N

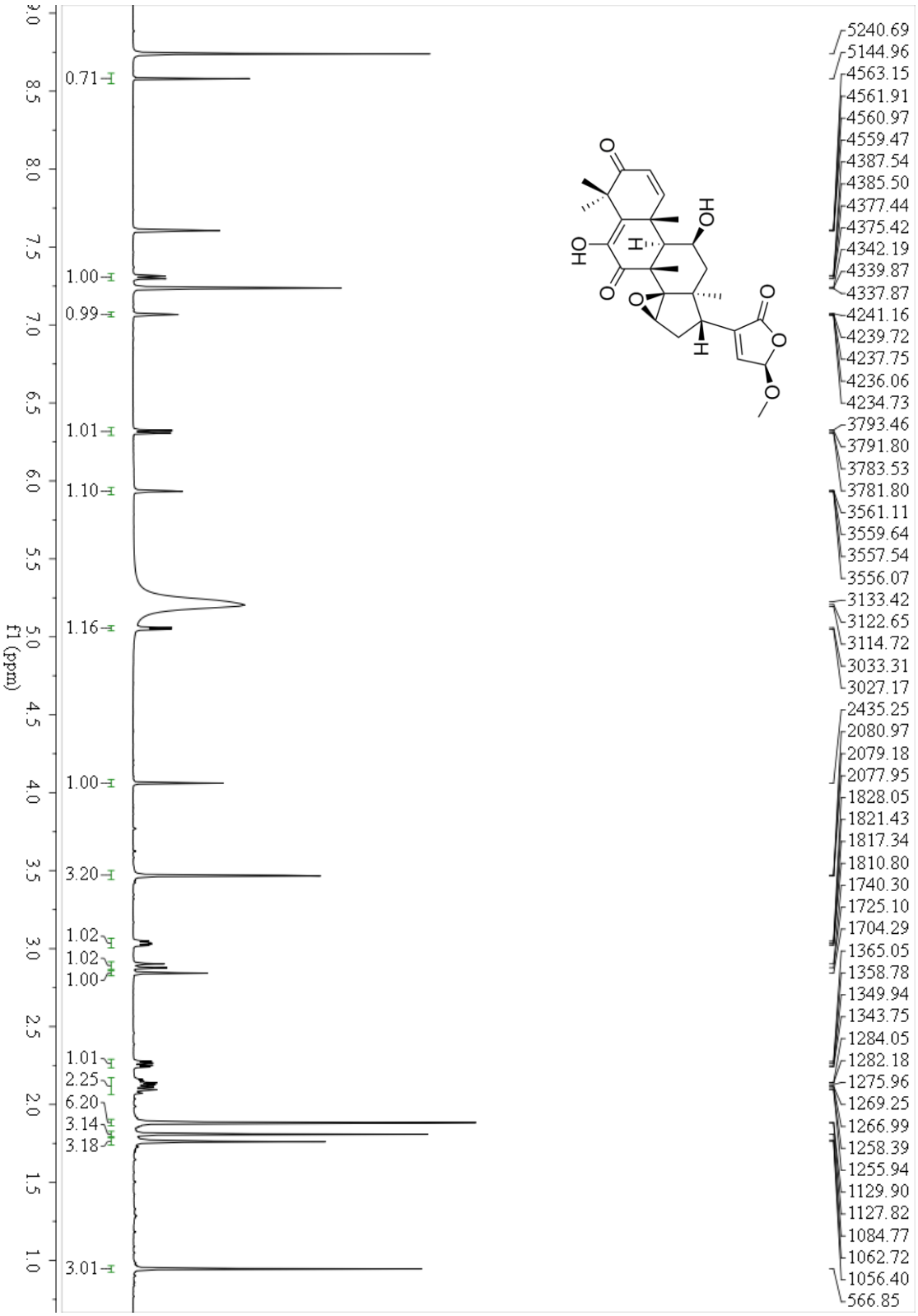


Figure S14. ^{13}C NMR spectrum of walsunoid B (**2**) in C_5D_5N

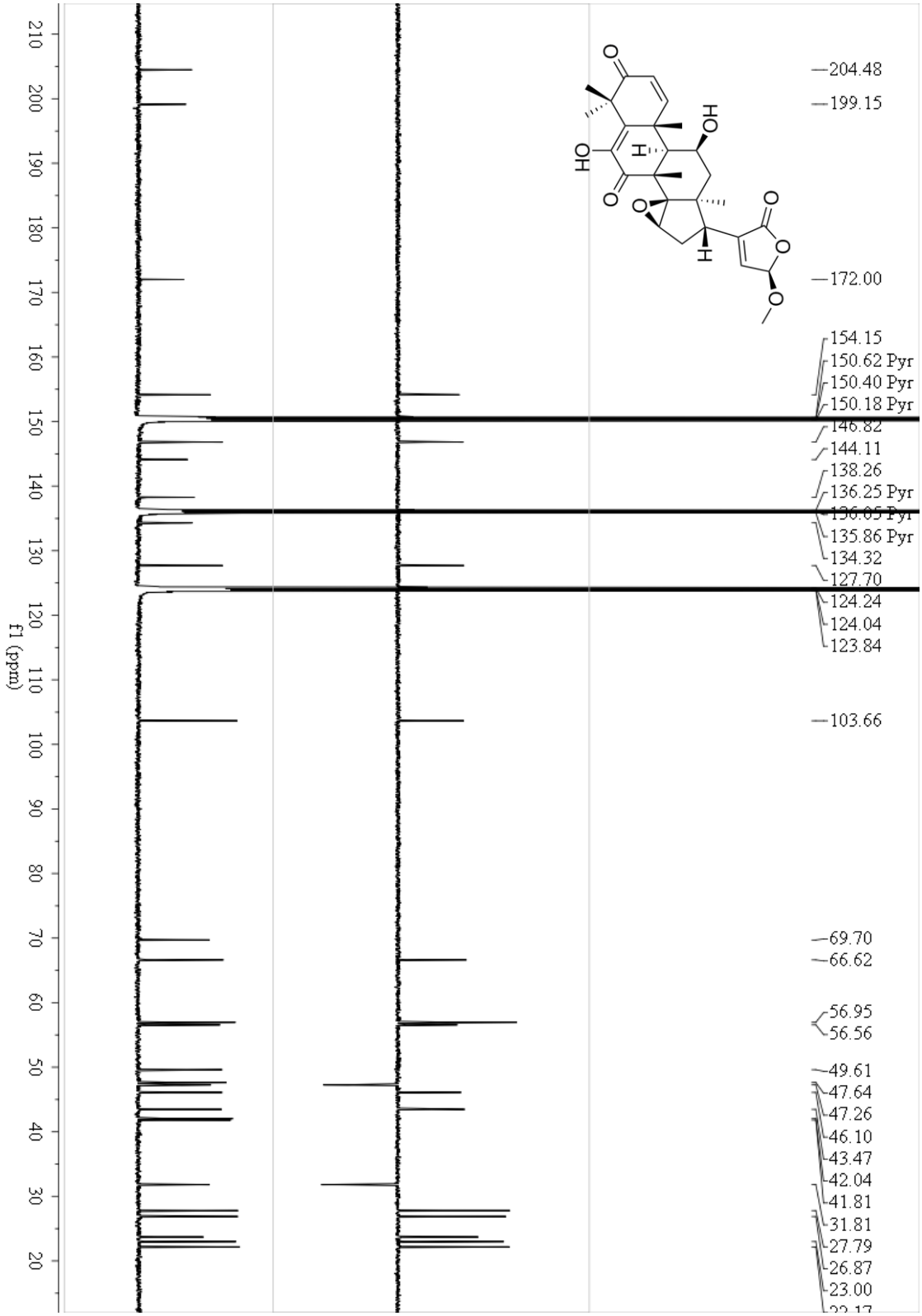


Figure S15. HSQC spectrum of walsunoid B (**2**) in C_5D_5N

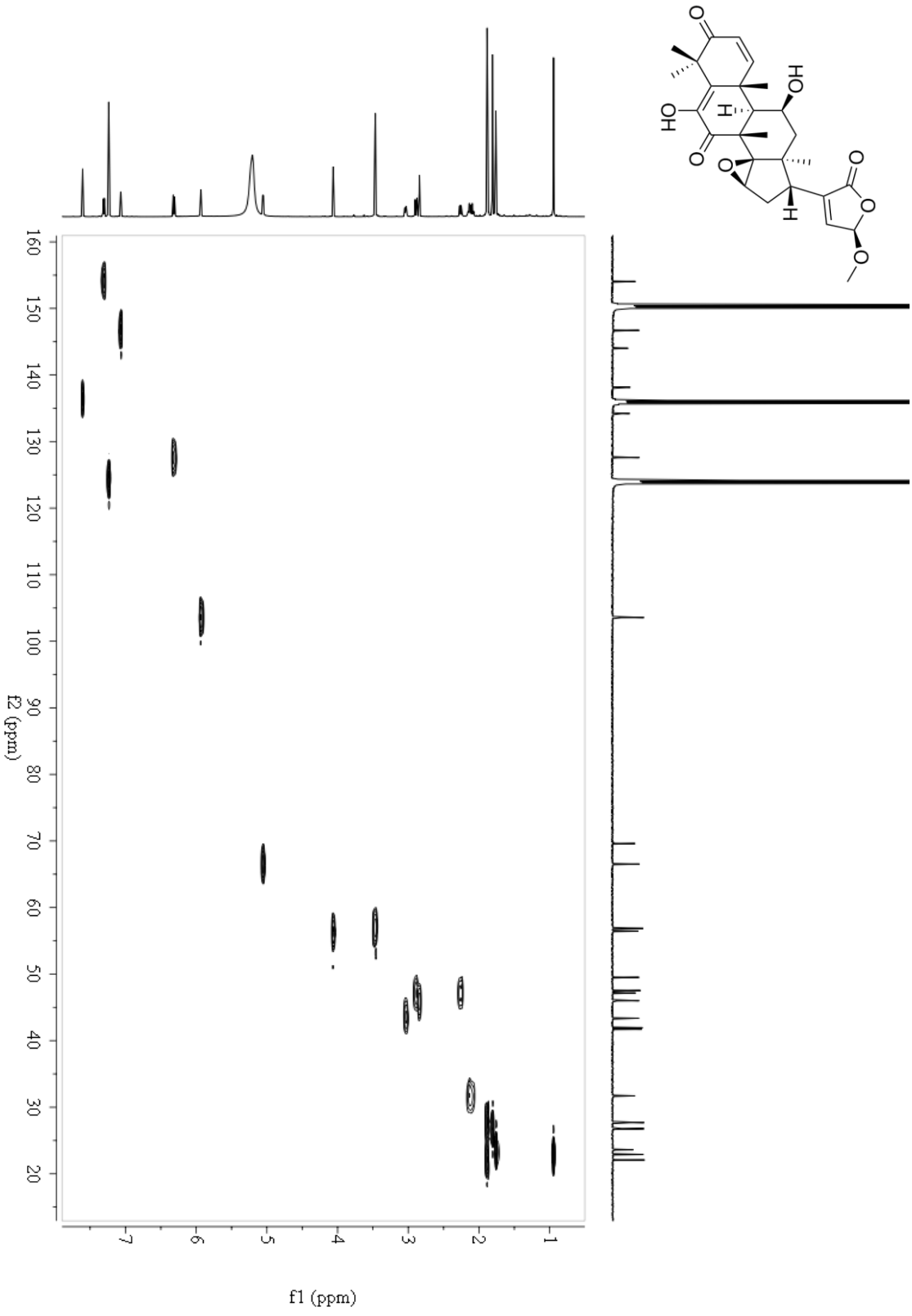


Figure S16. HMBC spectrum of walsunoid B (**2**) in C_5D_5N

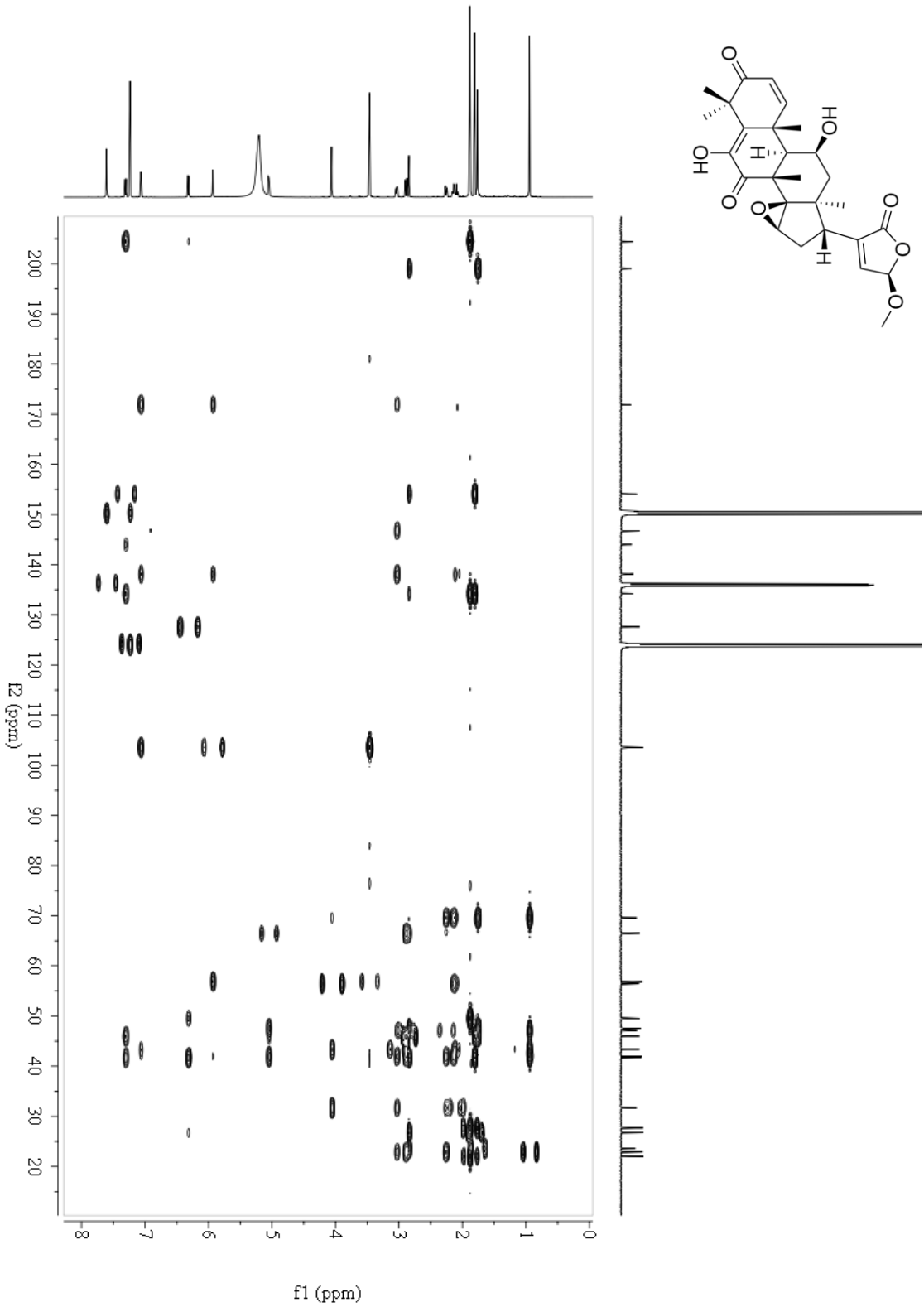


Figure S17. NOESY spectrum of walsunoid B (**2**) in C_5D_5N

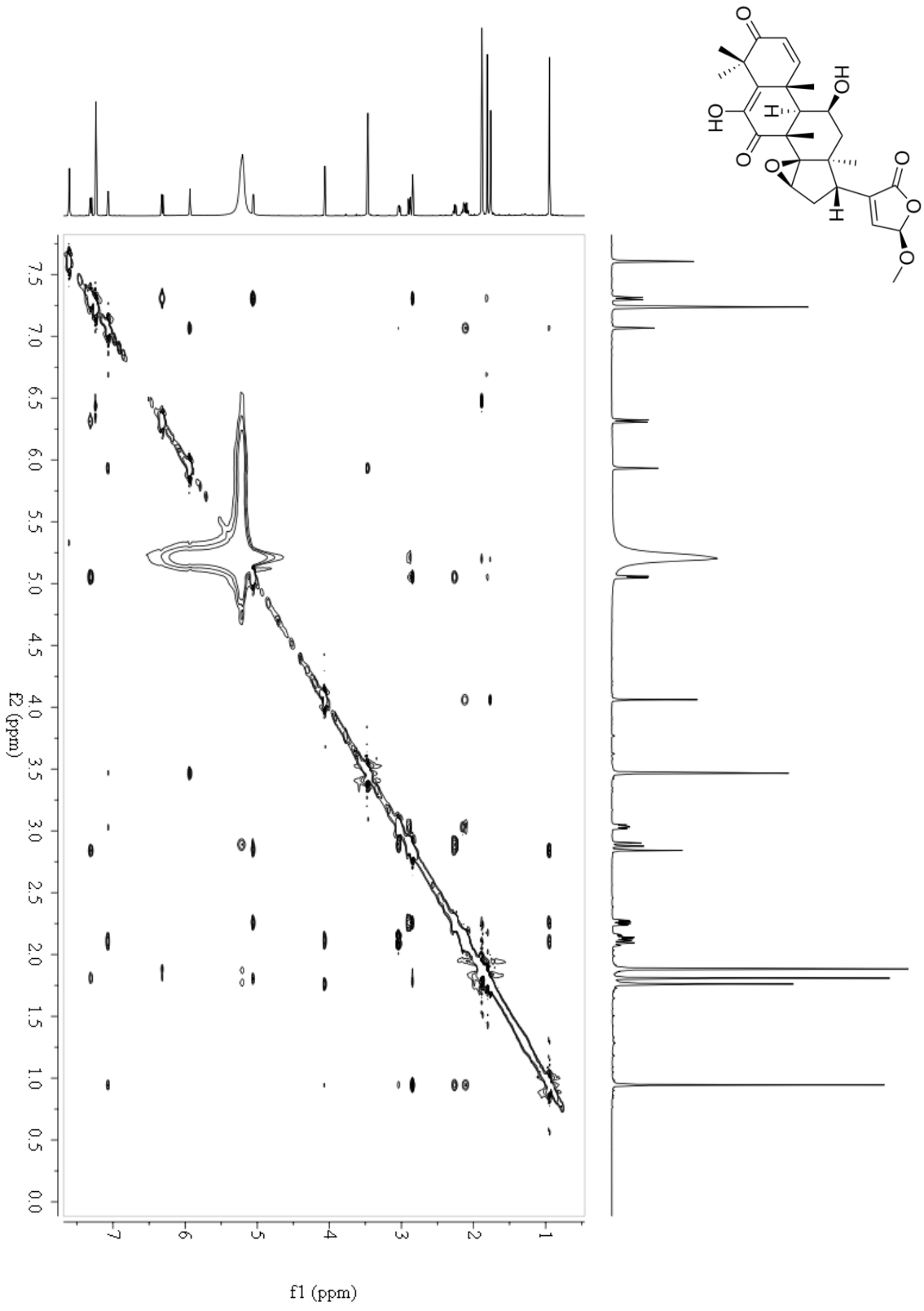


Figure S18. (+)-ESIMS spectrum of walsunoid B (**2**)

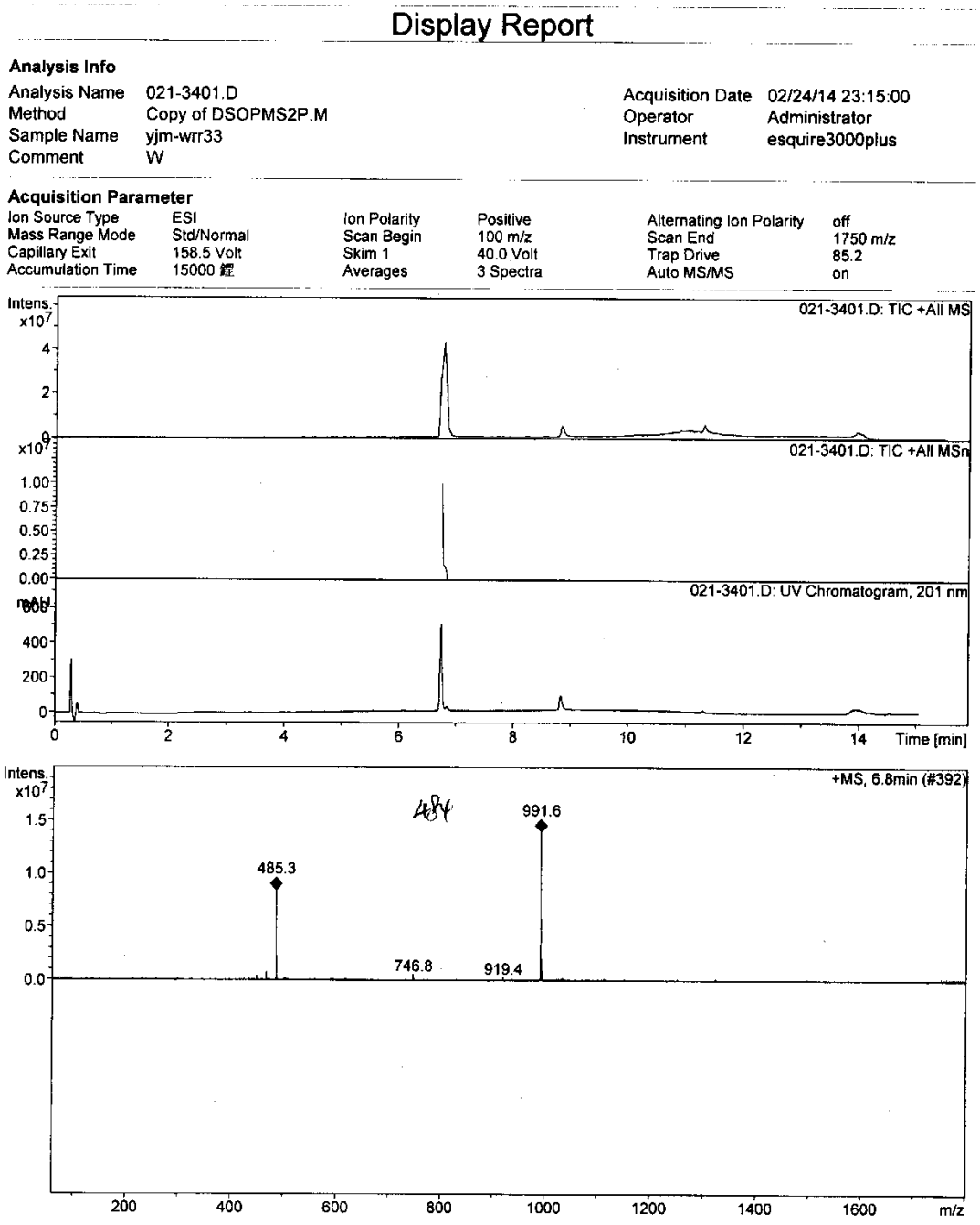


Figure S19. (–)-ESIMS spectrum of walsunoid B (**2**)

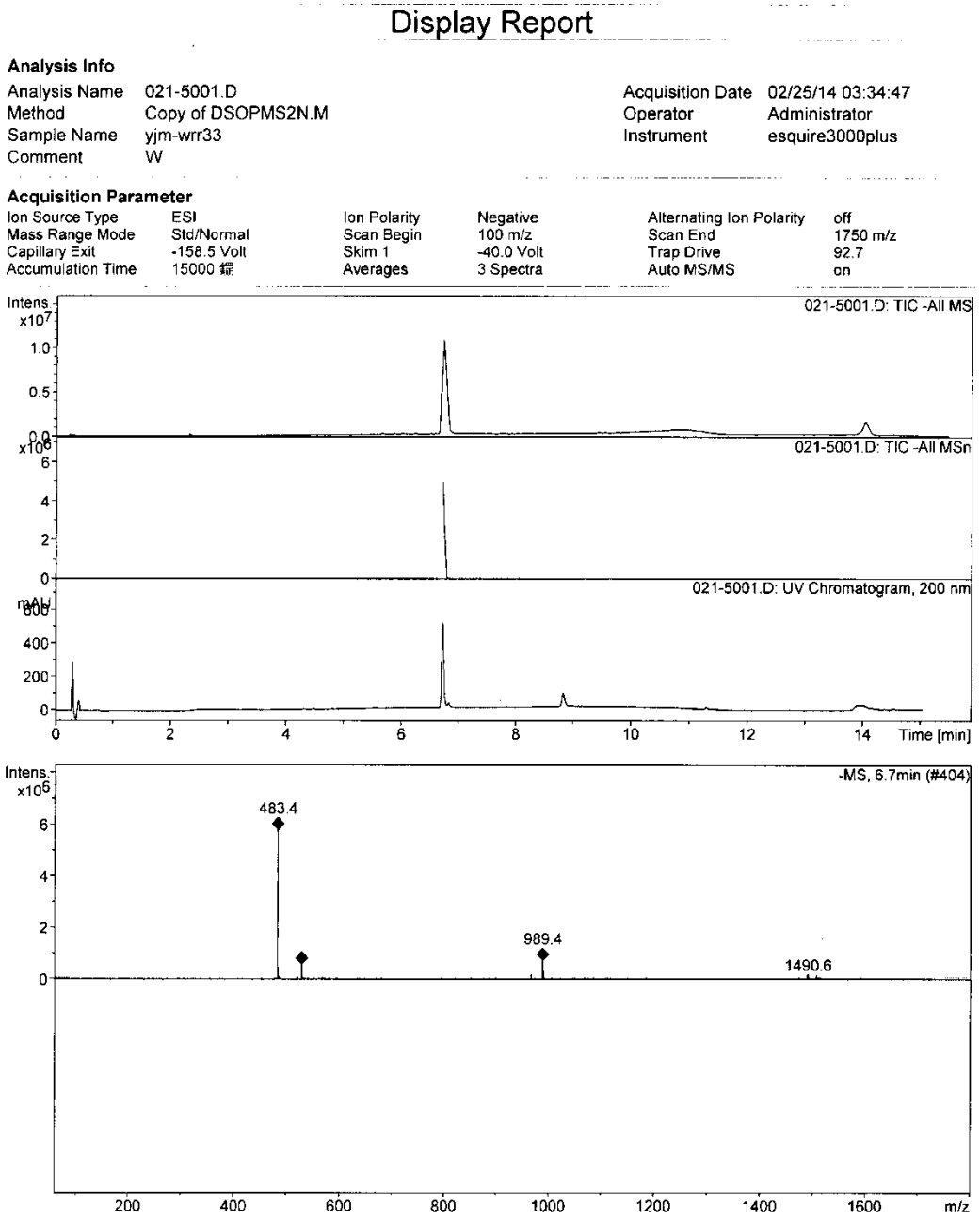
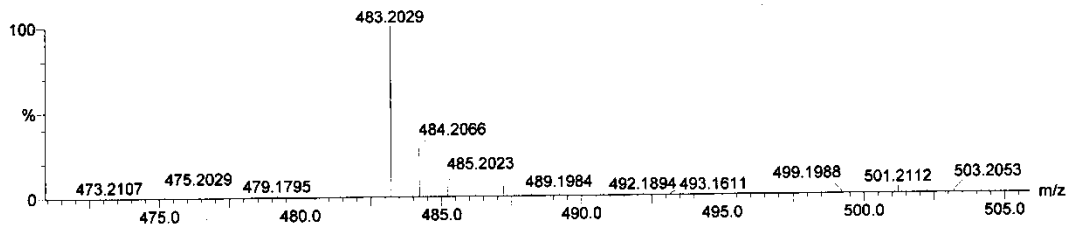


Figure S20. (–)-HRESIMS spectrum of walsunoid B (**2**)

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
wrr33_0403 13 (0.284) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (9:23) 1: TOF MS ES- 9.63e+003



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
483.2029	483.2019	1.0	2.1	12.5	125.0	0.0	C27 H31 O8

Figure S21. IR spectrum of walsunoid B (**2**)

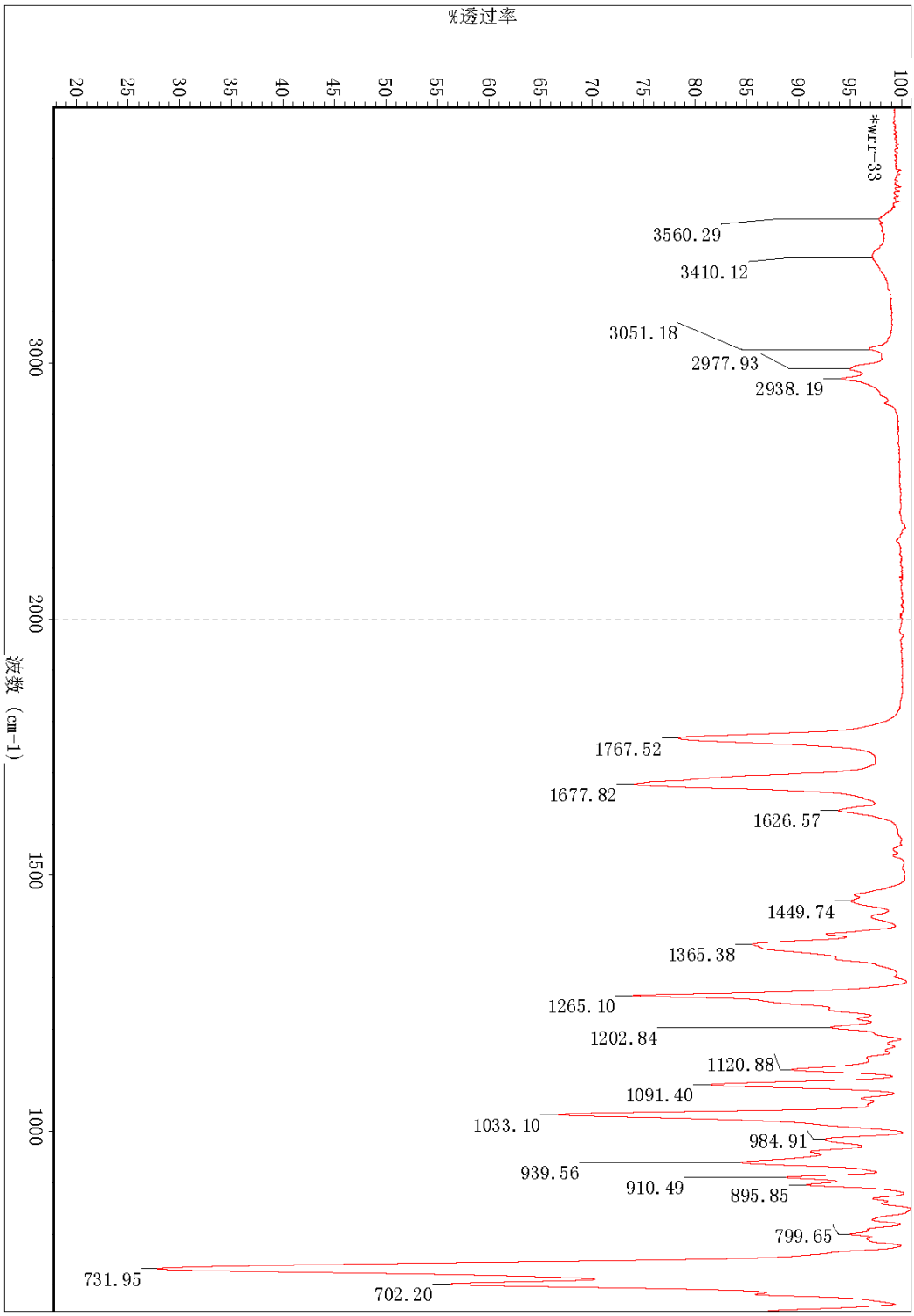


Figure S22. ^{1}H NMR spectrum of walsunoid C (**3**) in C_5D_5N

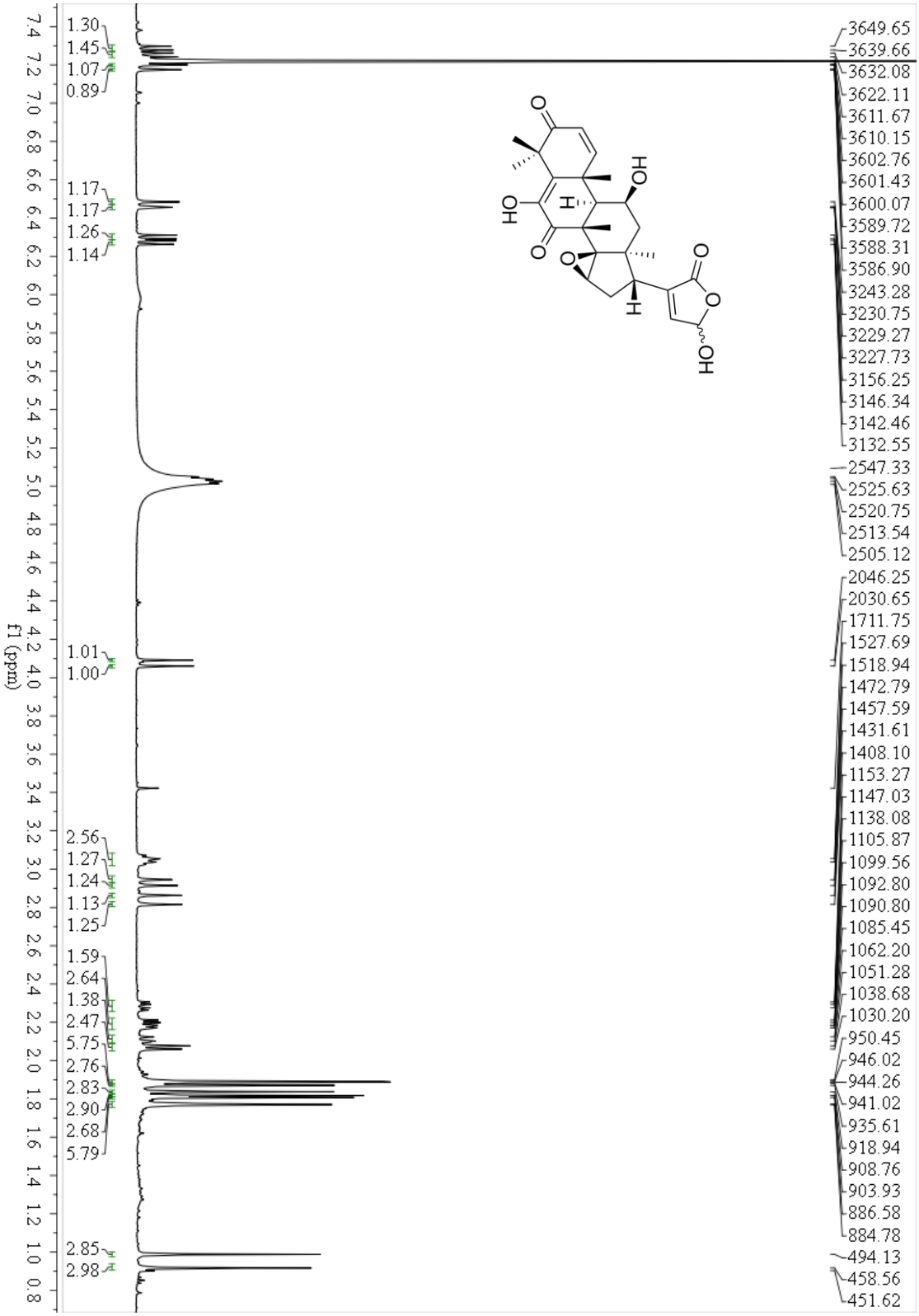


Figure S23. ^{13}C NMR spectrum of walsunoid C (**3**) in C_5D_5N

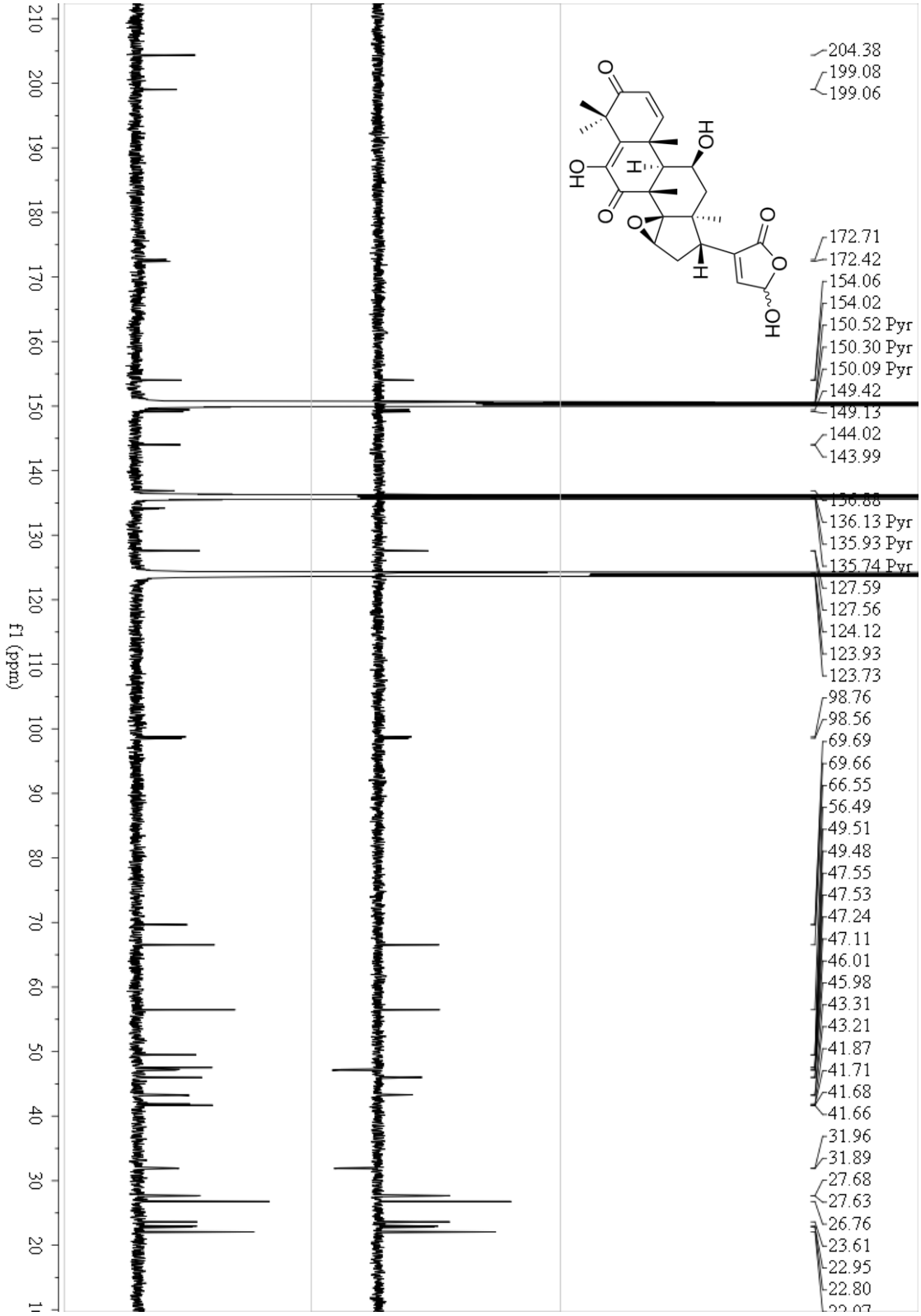


Figure S24. HSQC spectrum of walsunoid C (**3**) in C_5D_5N

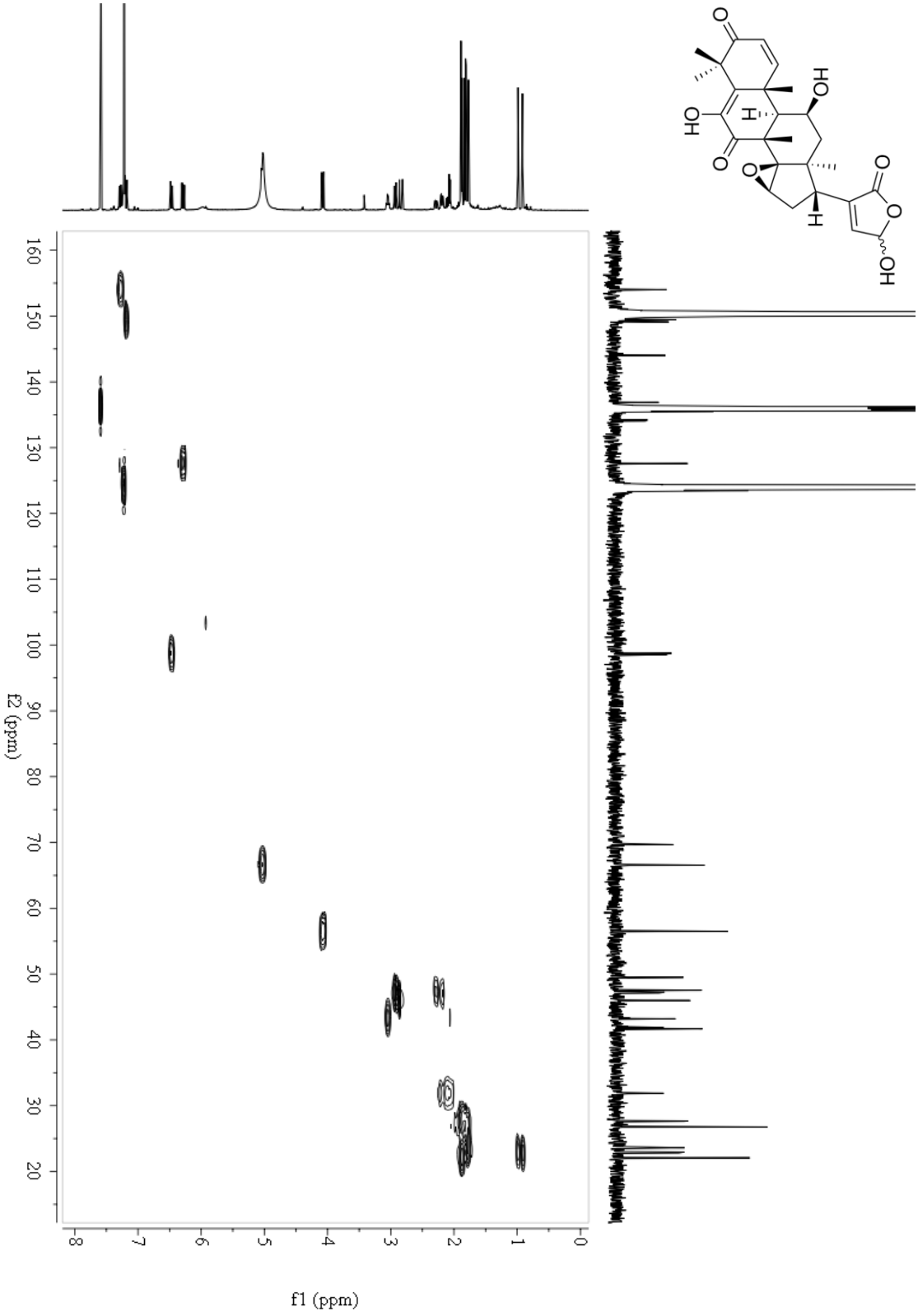


Figure S25. HMBC spectrum of walsunoid C (**3**) in C_5D_5N

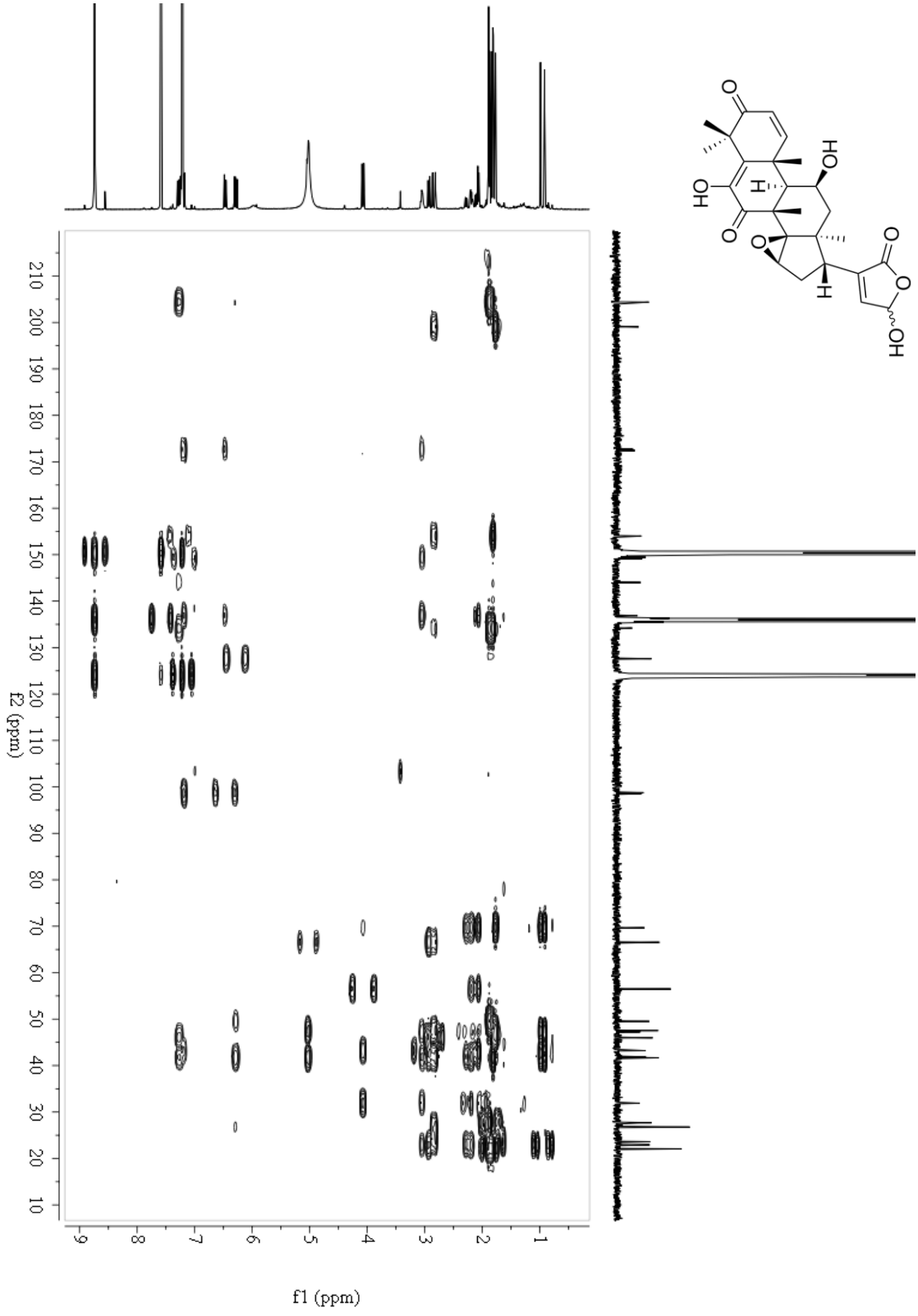


Figure S26. NOESY spectrum of walsunoid C (**3**) in C_5D_5N

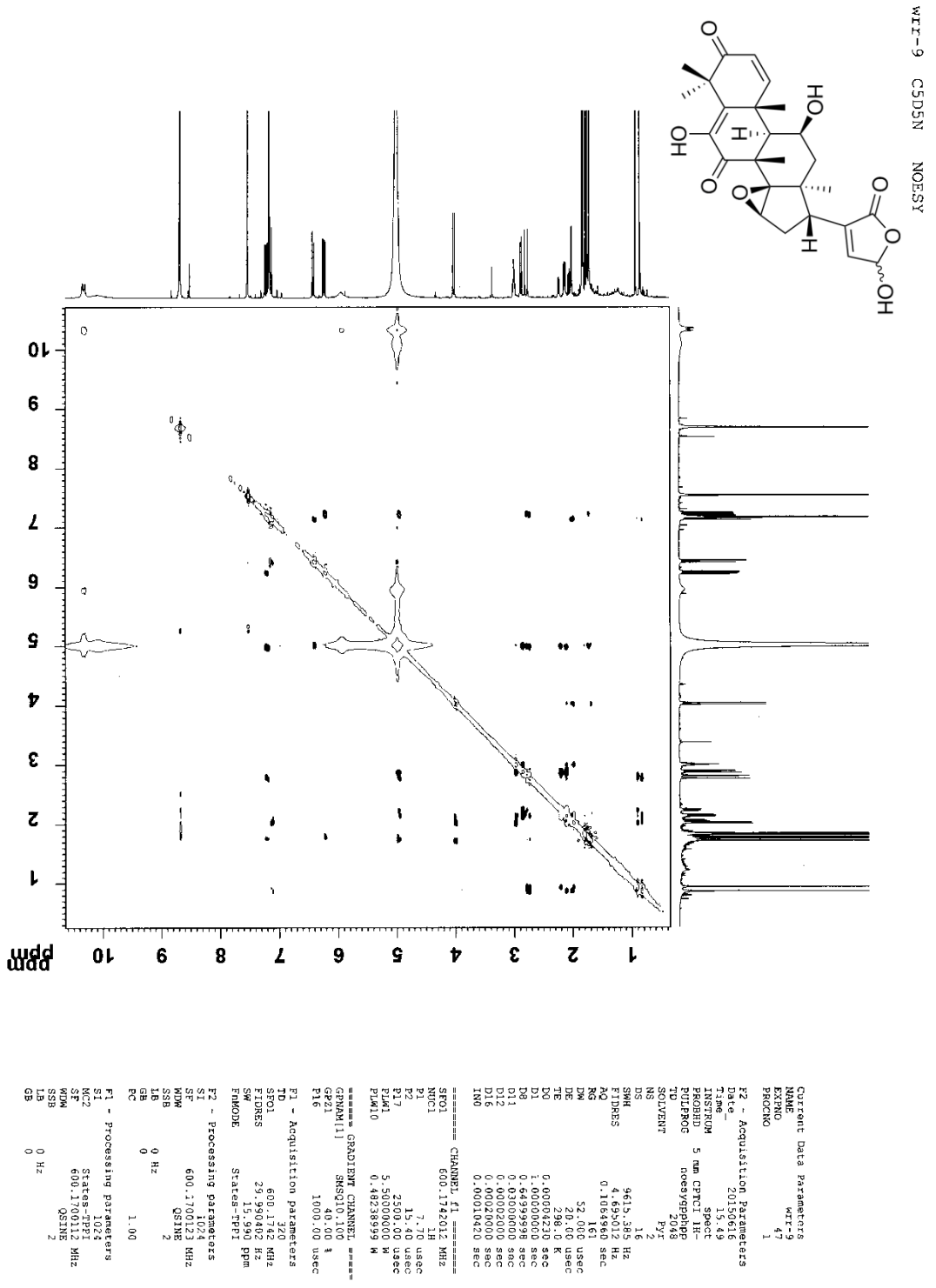


Figure S27. (+)-ESIMS spectrum of walsunoid C (**3**)

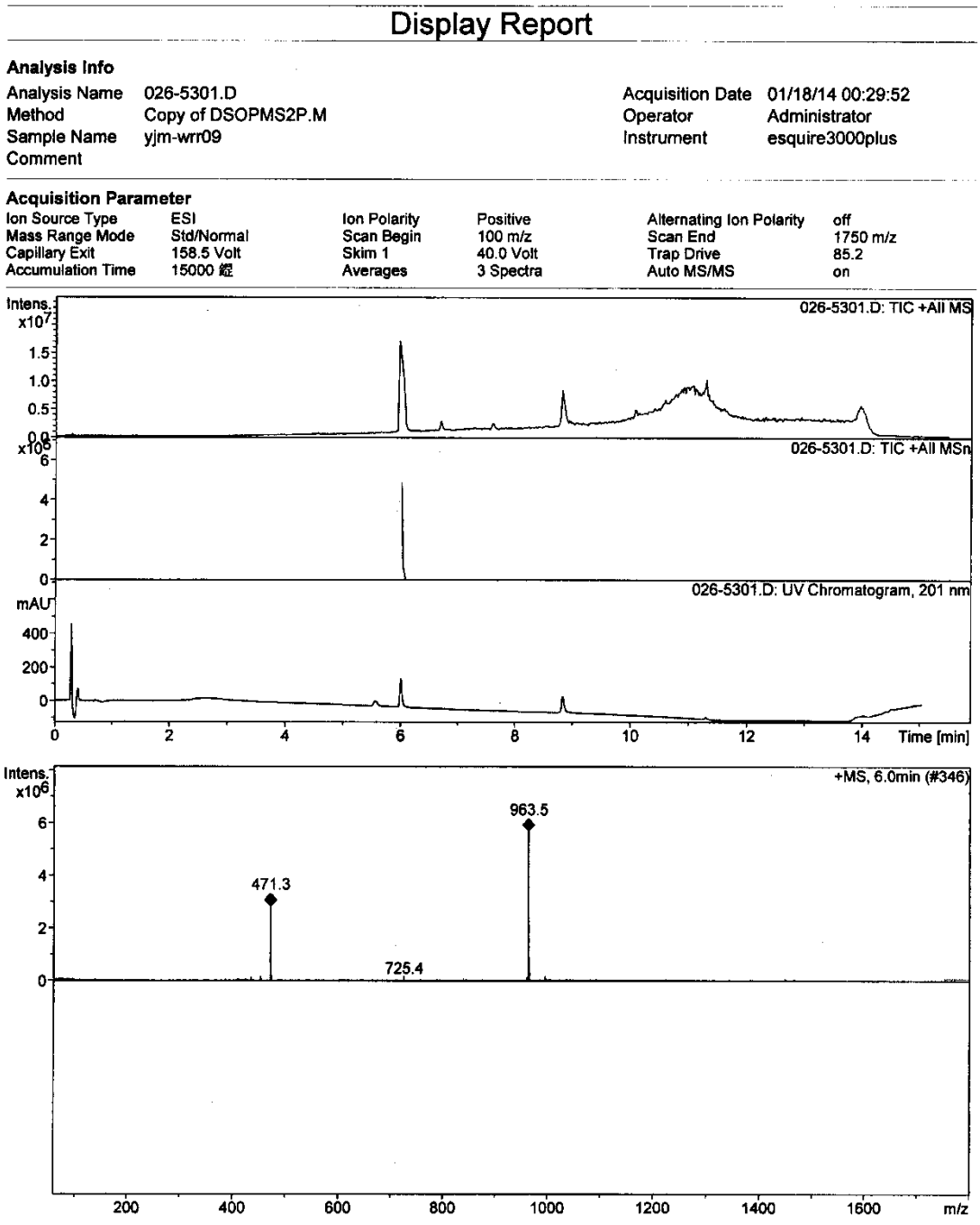


Figure S28. (–)-ESIMS spectrum of walsunoid C (**3**)

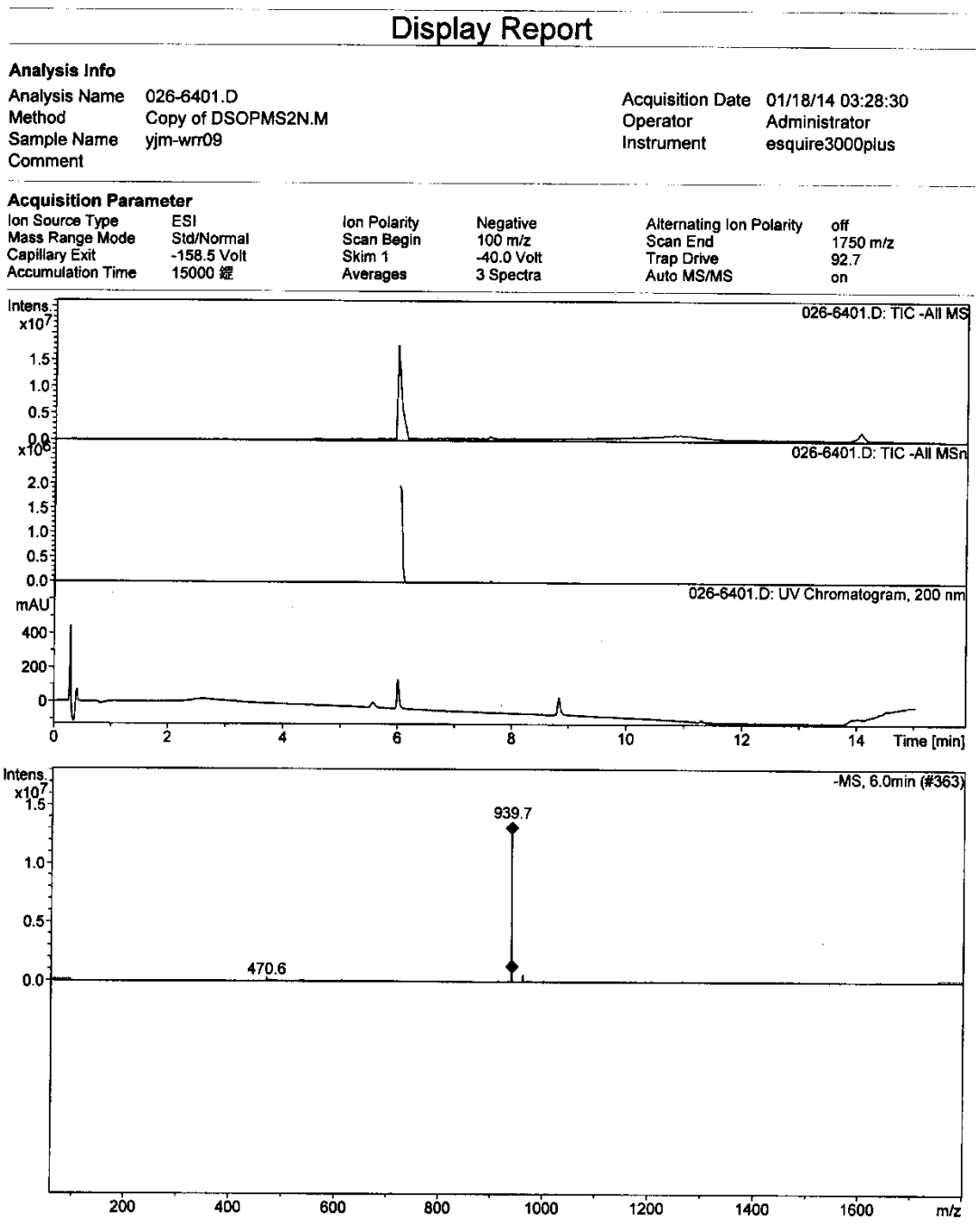


Figure S29. (–)-HRESIMS spectrum of walsunoid C (**3**)

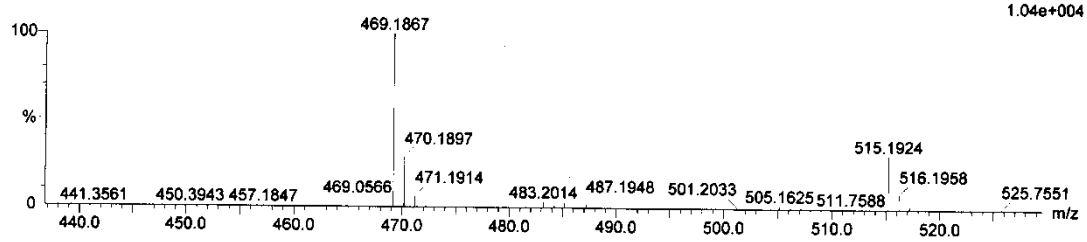
Elemental Composition Report **Page 1**

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:				-1.5			
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**)

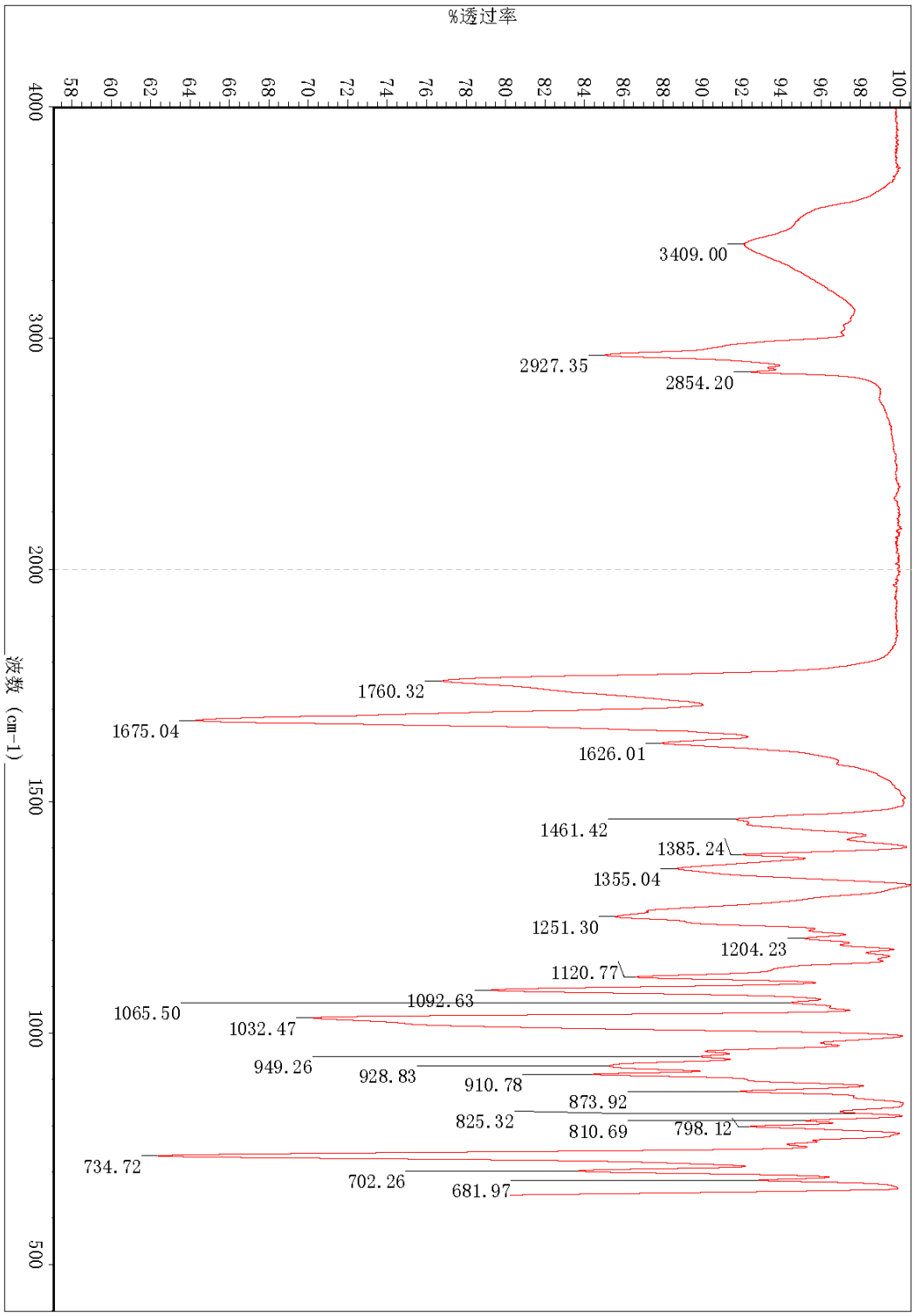


Figure S31. ^{1}H NMR spectrum of walsunoid D (**4**) in $CDCl_3$

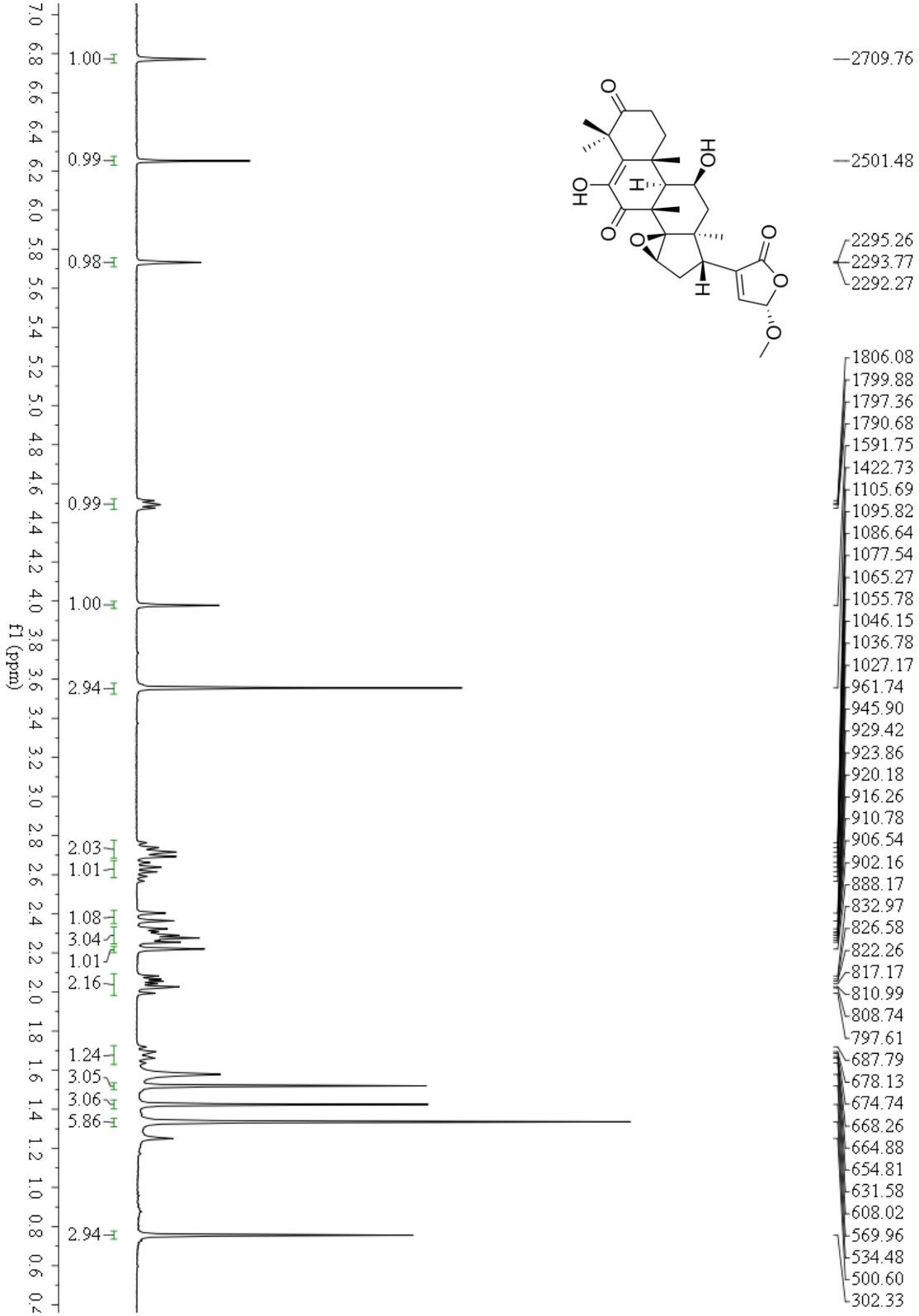


Figure S32. ^{13}C NMR spectrum of walsunoid D (**4**) in $CDCl_3$

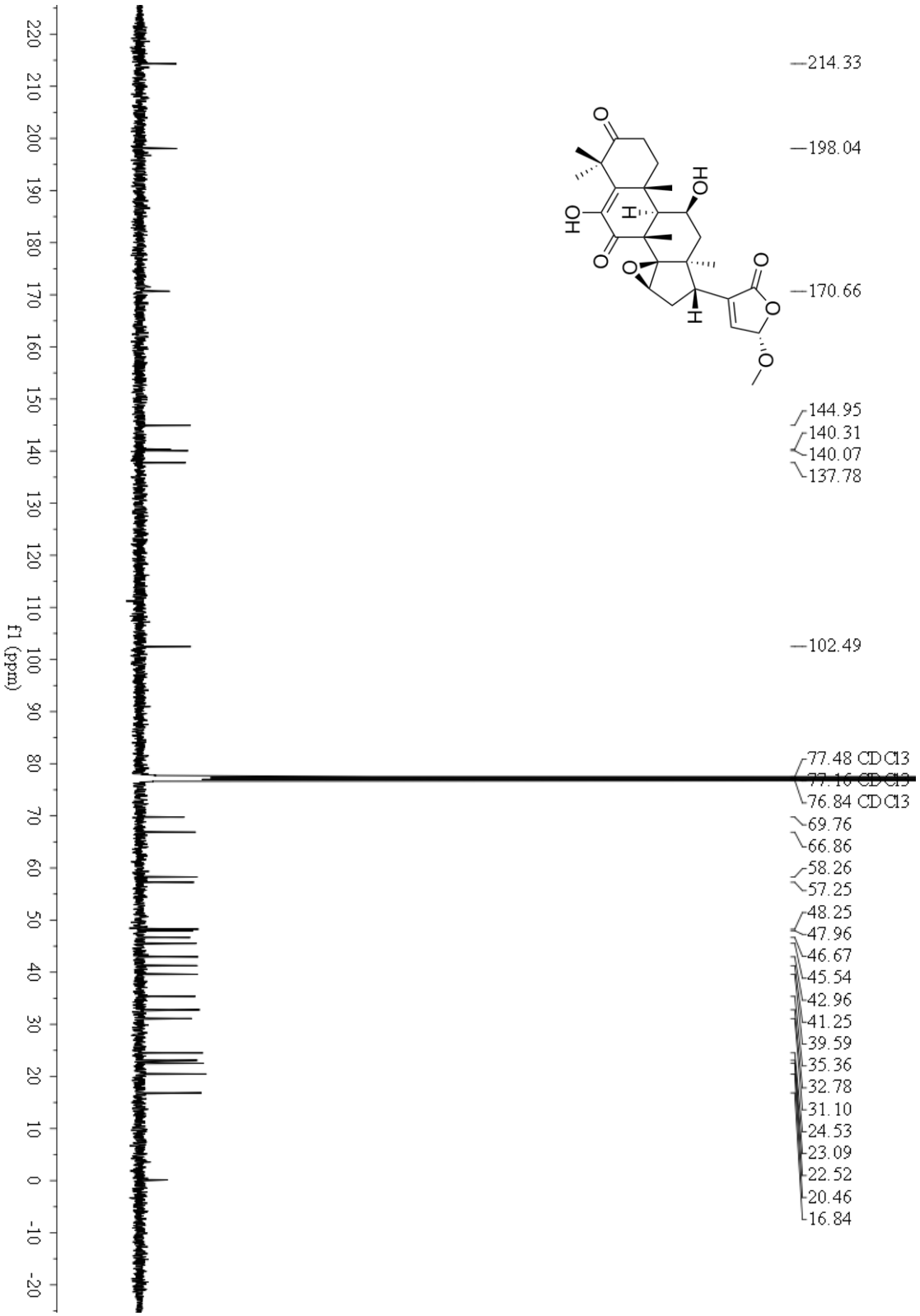


Figure S33. HSQC spectrum of walsunoid D (**4**) in $CDCl_3$

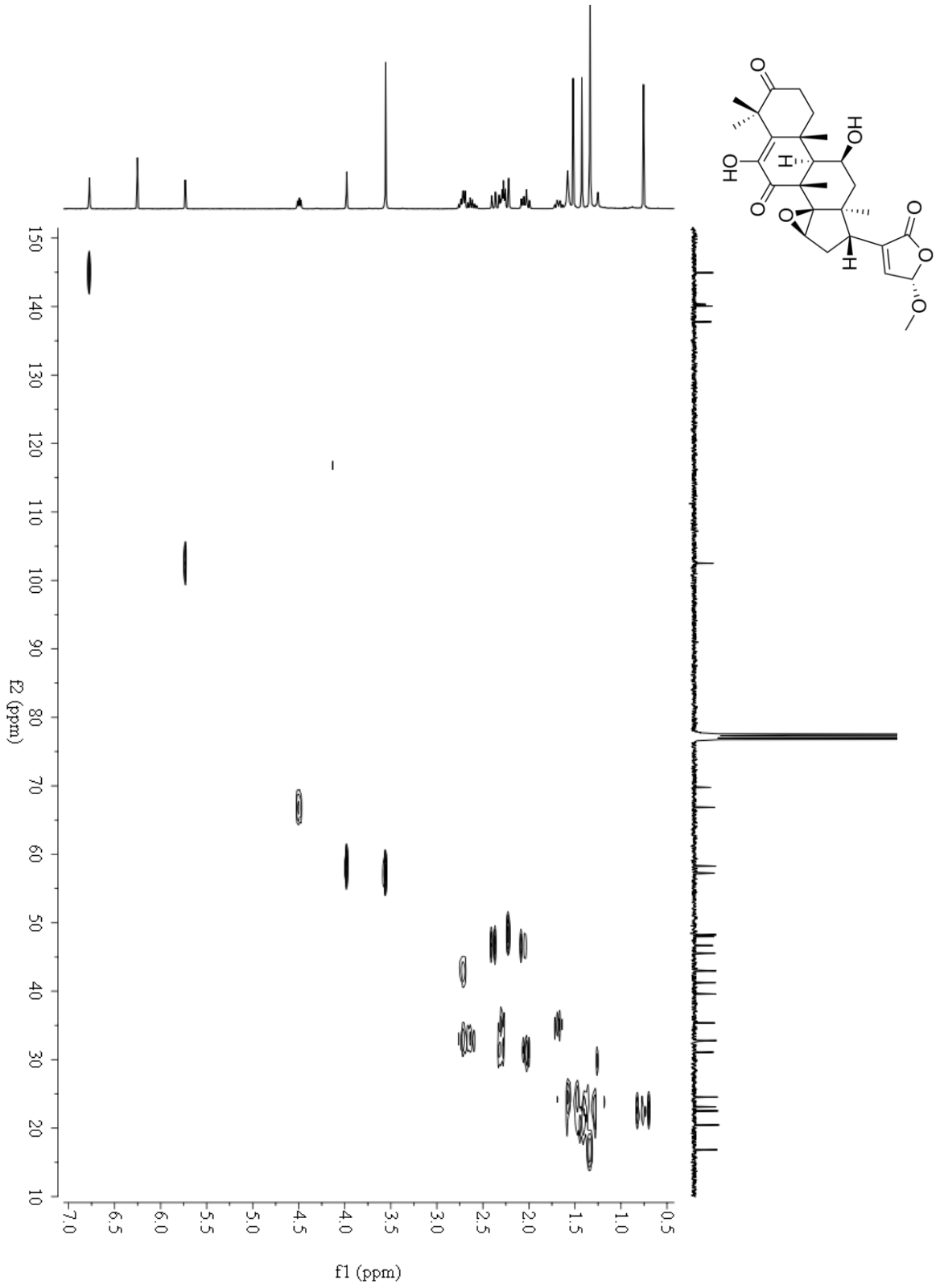


Figure S34. HMBC spectrum of walsunoid D (**4**) in $CDCl_3$

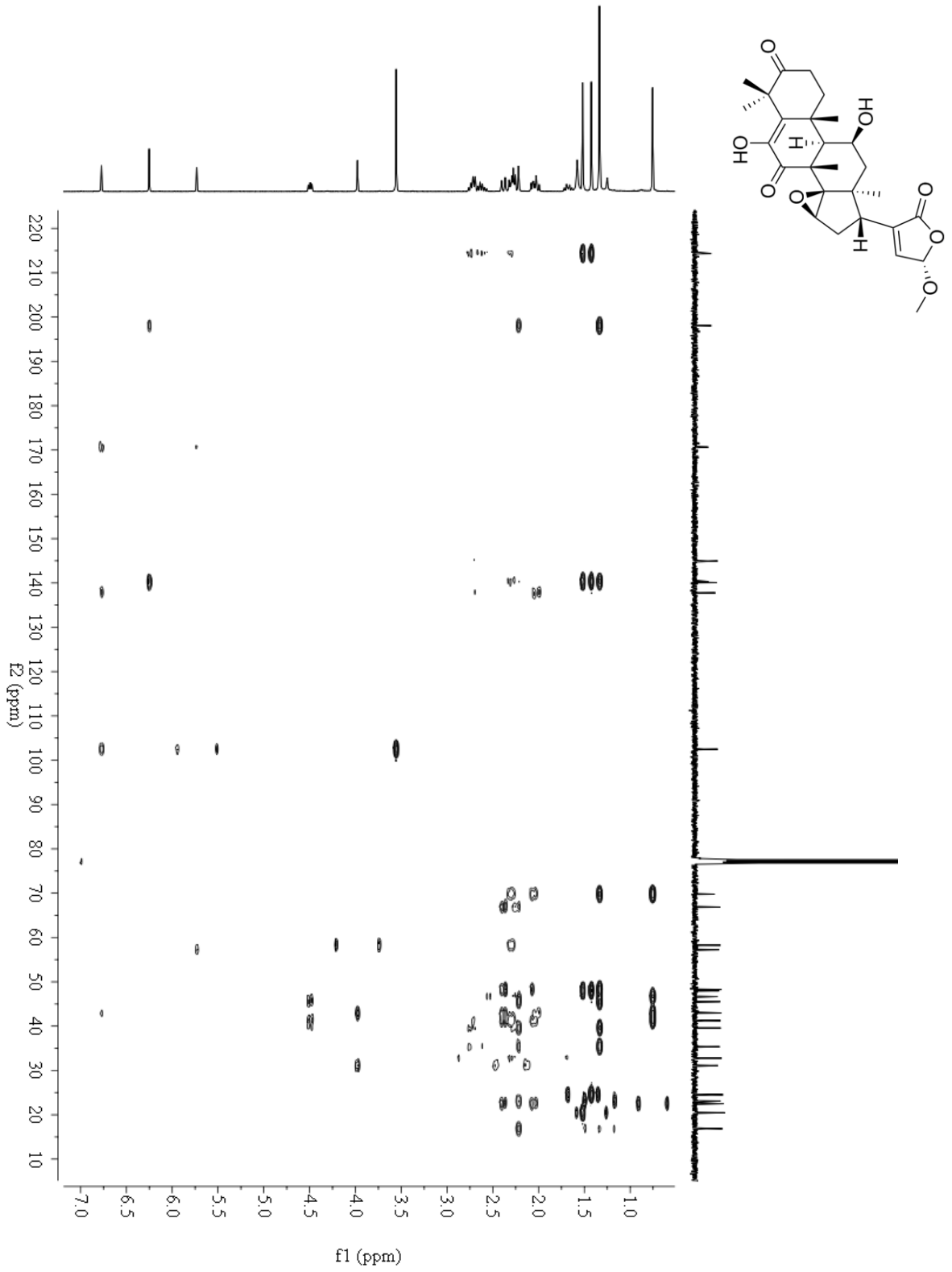
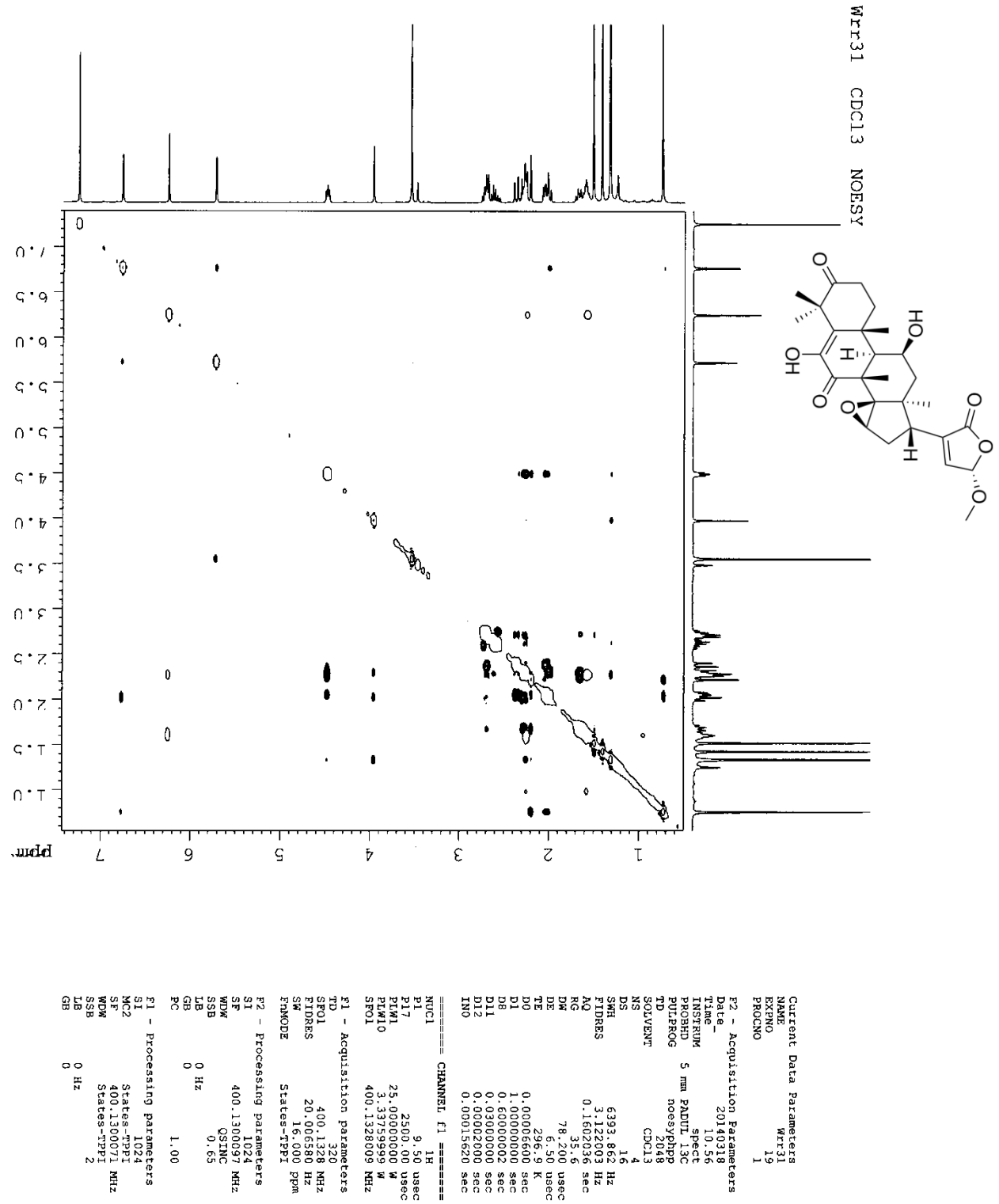


Figure S35. NOESY spectrum of walsunoid D (**4**) in $CDCl_3$

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PROCNO                    1

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PULPROG          noesyphpp
TD                    2048
SOLVENT               CDCl3
NS                       4
DS                      16
SWH               6393.862 Hz
FIDRES            3.122003 Hz
AQ                0.1602036 sec
RG                     35.6
DW                78.200 usec
DE                 6.50 usec
TE                 296.9 K
D0                0.00006600 sec
D1                1.00000000 sec
D8                0.60000002 sec
D11               0.03000000 sec
D12               0.00002000 sec
INO               0.00015620 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.50 usec
P17                 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
FnMODE          States-TPPI

F2 - Processing parameters
SI                     1024
SF            400.1300097 MHz
WDW                   QSINC
SSB                    0.65
LB                  0 Hz
GB                     0
PC                     1.00

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

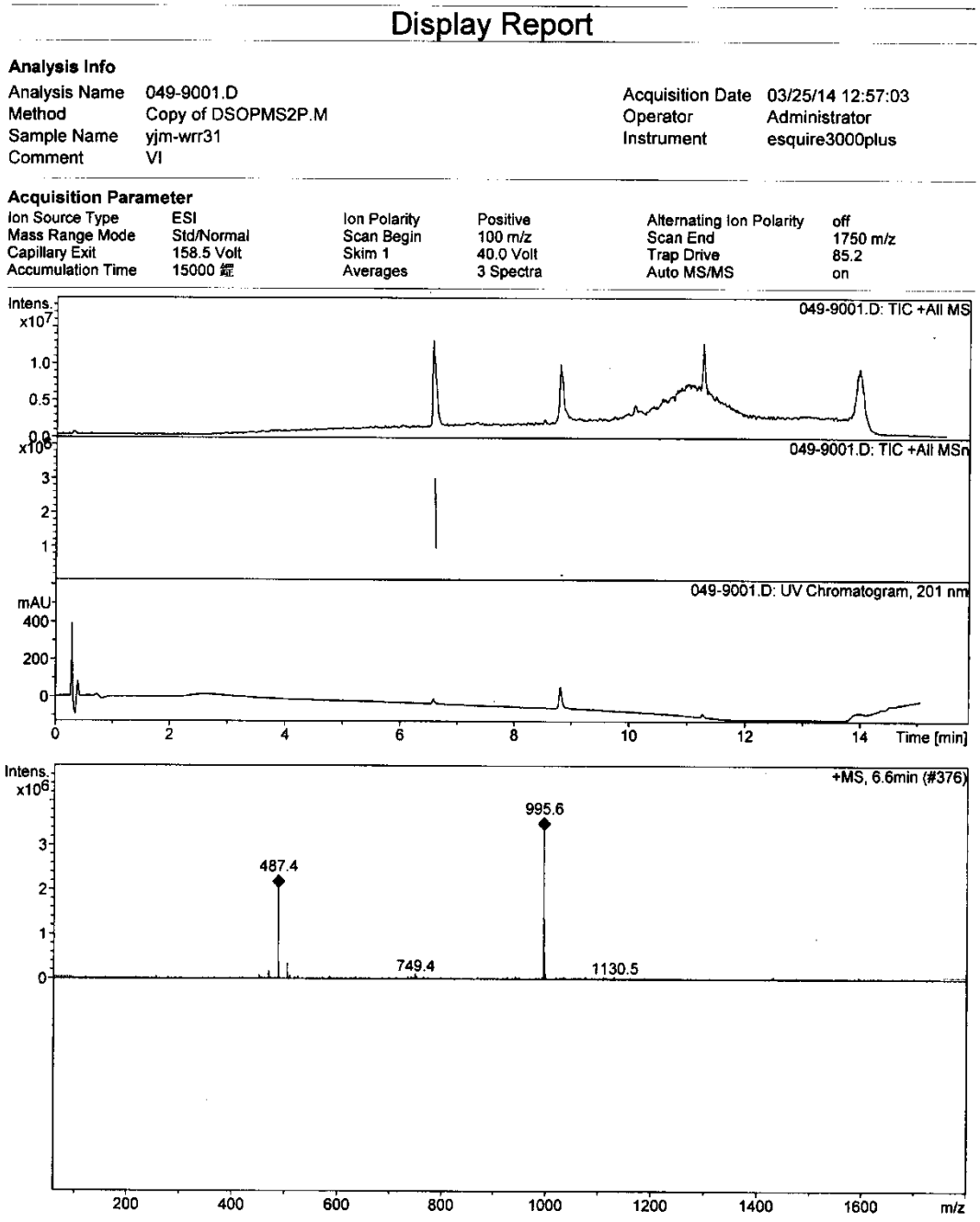


Figure S37. (–)-ESIMS spectrum of walsunoid D (**4**)

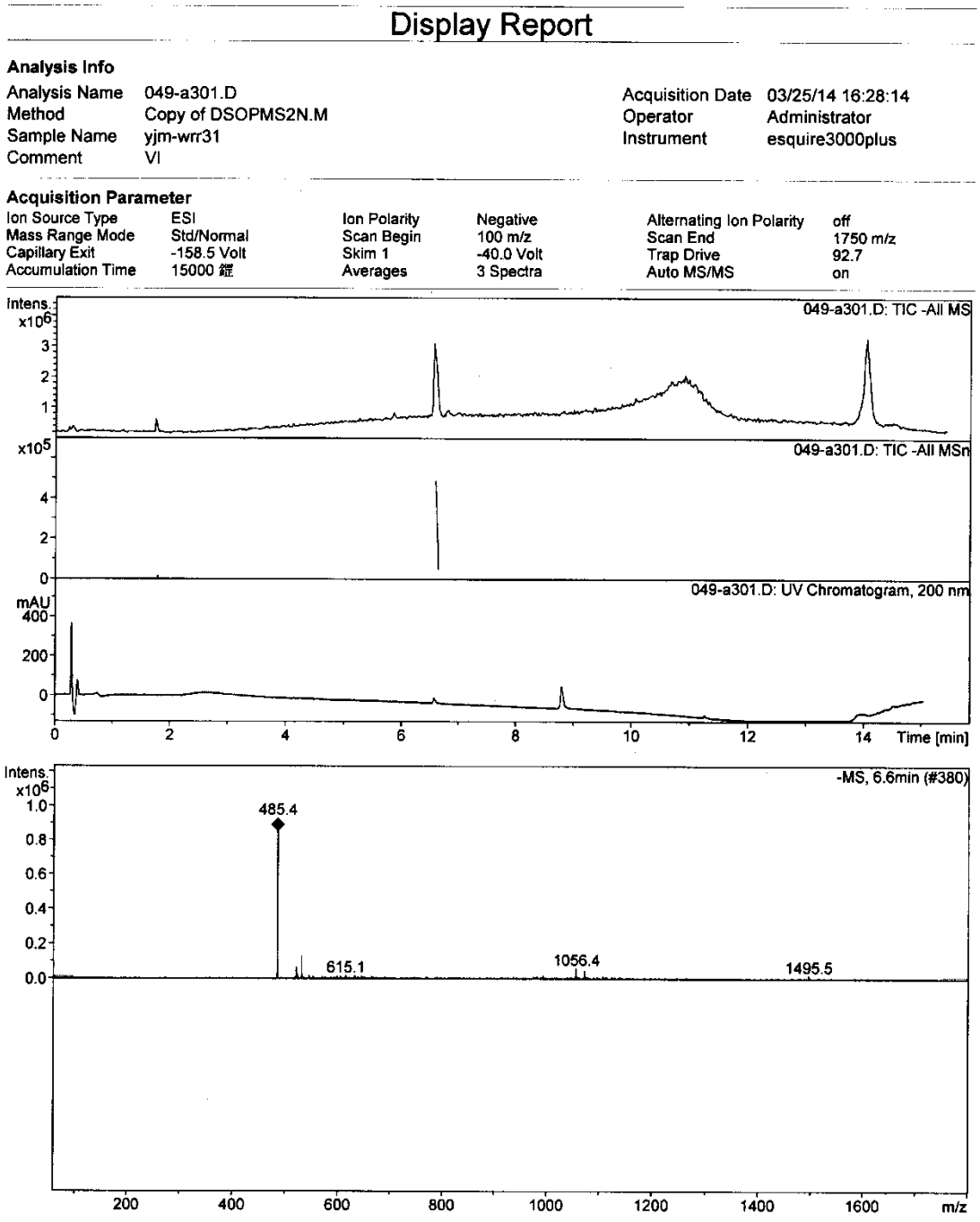


Figure S38. (+)-HRESIMS spectrum of walsunoid D (**4**)

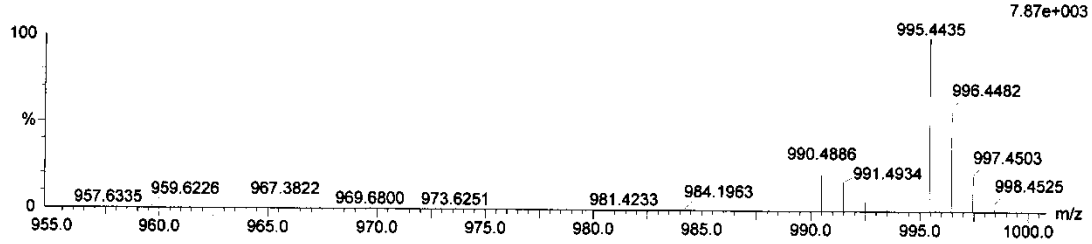
Elemental Composition Report **Page 1**

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

wrr31_0403 49 (1.078) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (49:62) 1: TOF MS ES+ 7.87e+003



Minimum:				-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**)

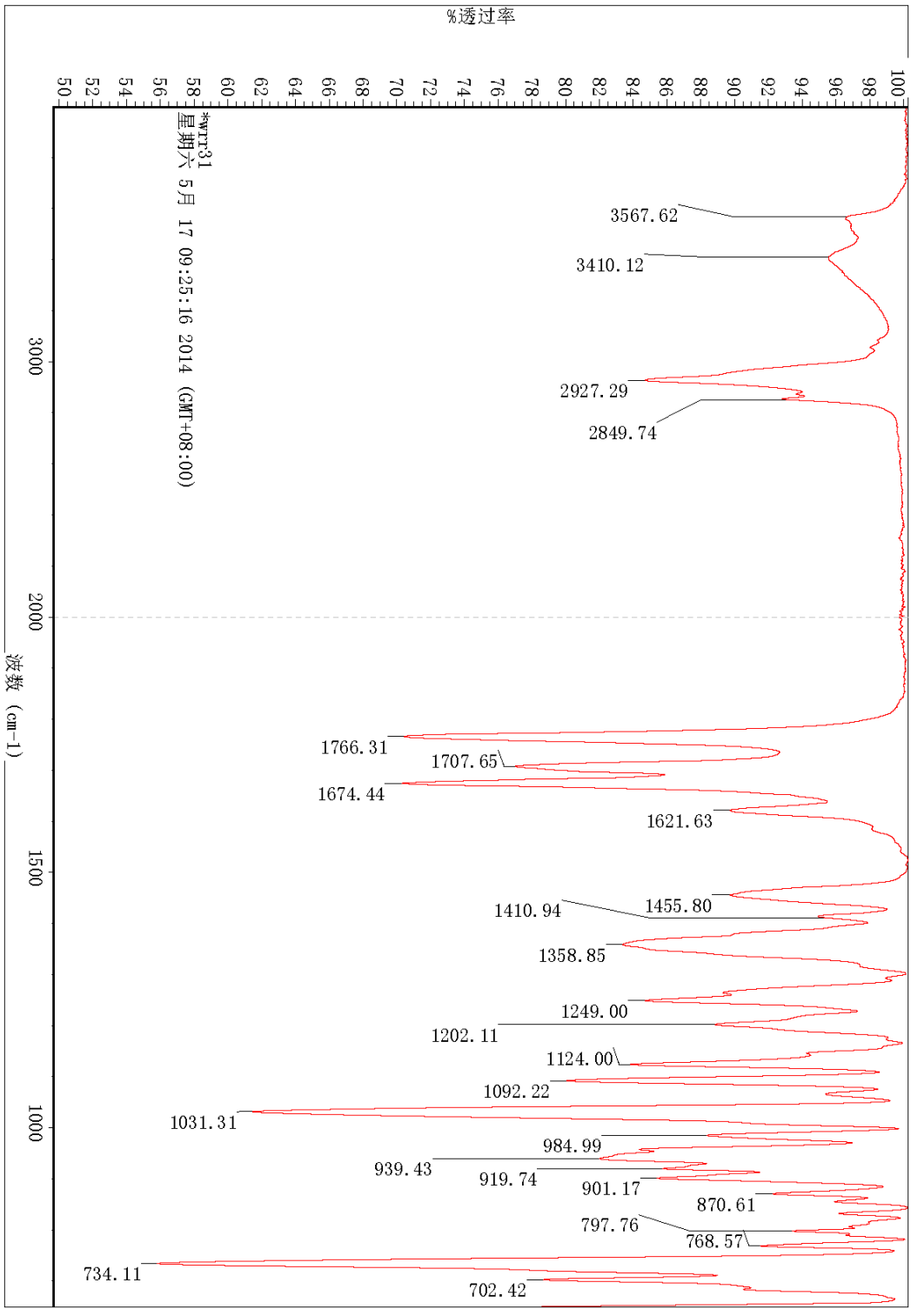


Figure S40. ^{1}H NMR spectrum of walsunoid E (**5**) in $CDCl_3$

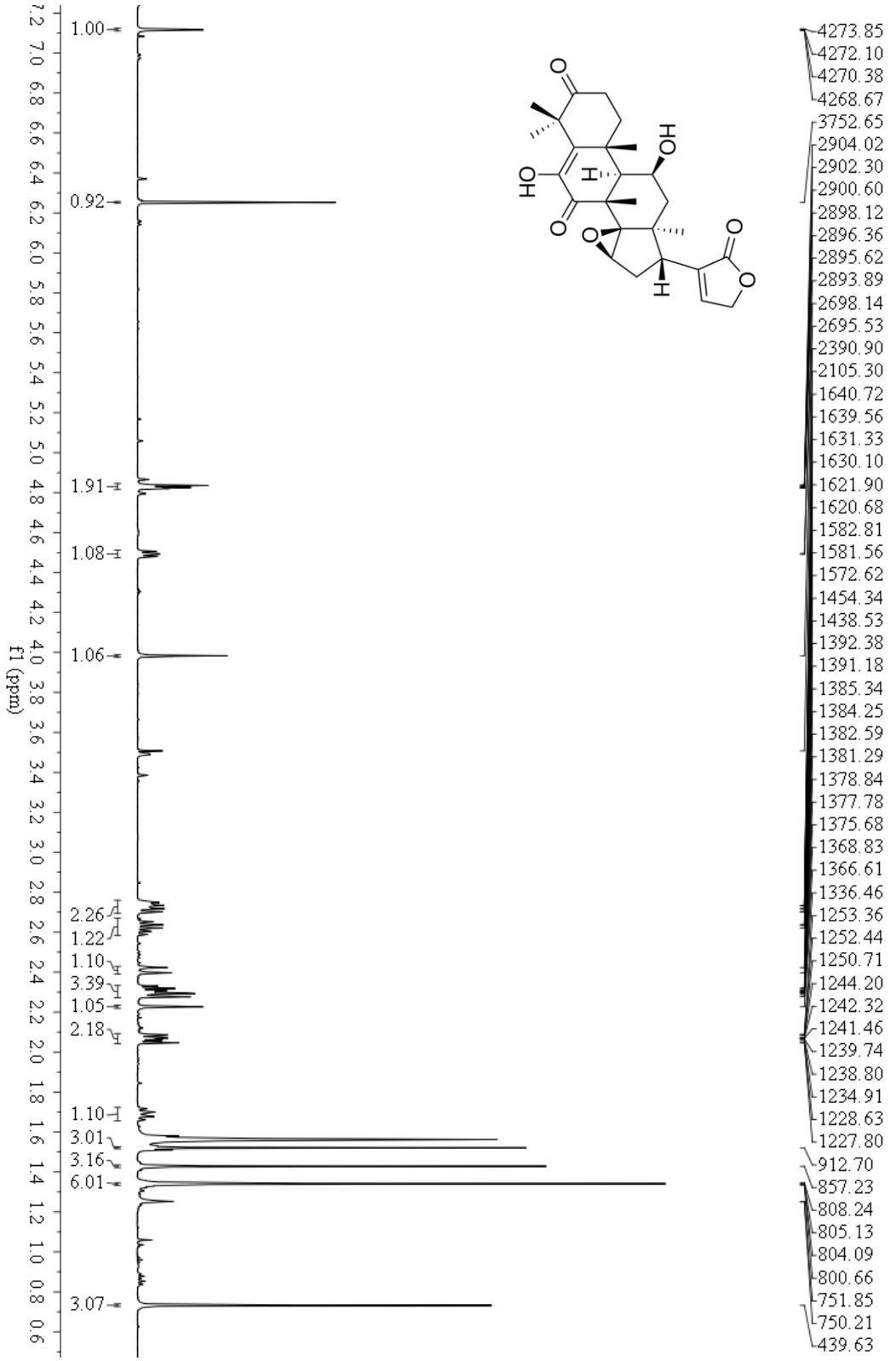


Figure S41. ^{13}C NMR spectrum of e walsunoid E (**5**) in $CDCl_3$

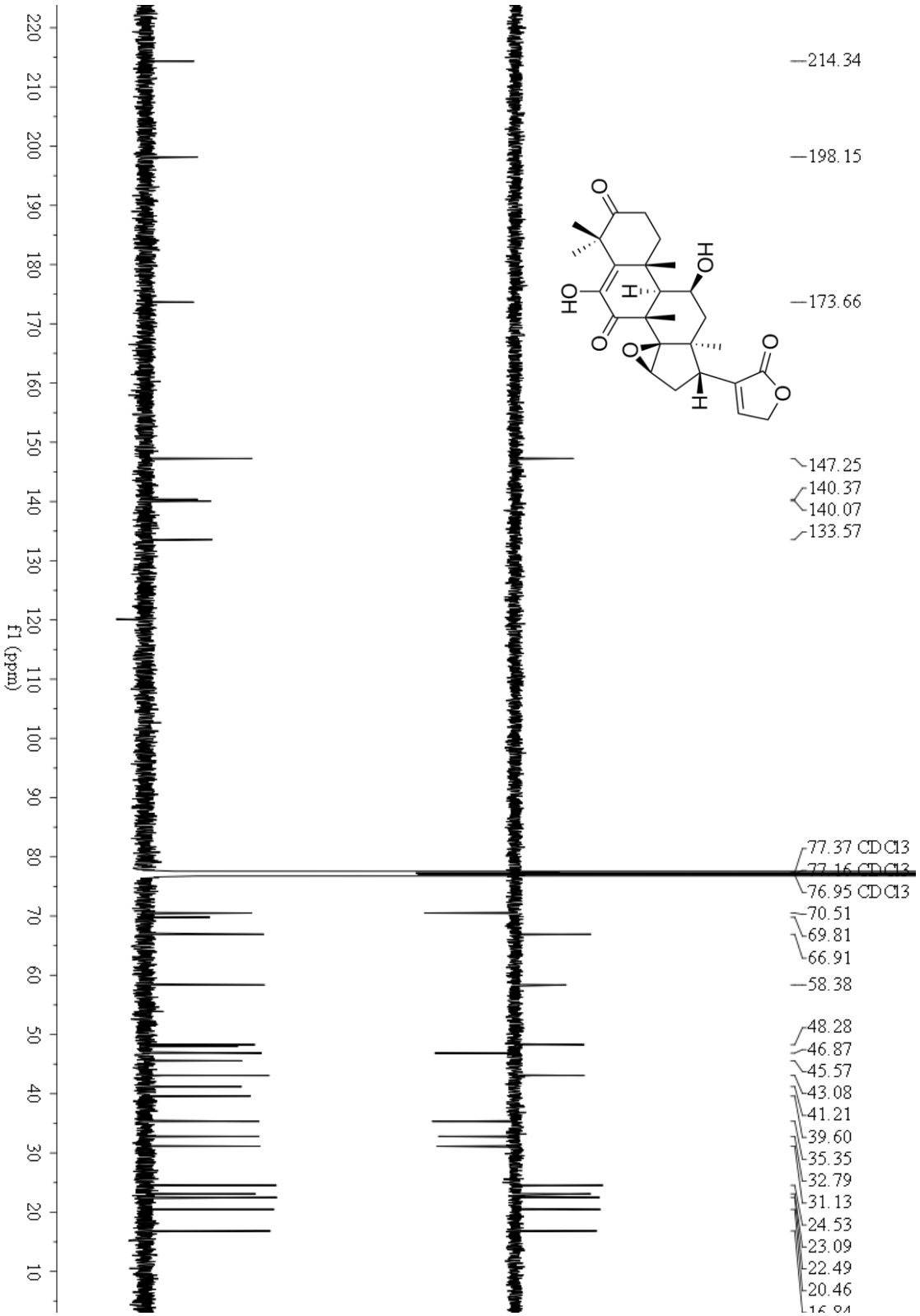


Figure S42. HSQC spectrum of walsunoid E (**5**) in $CDCl_3$

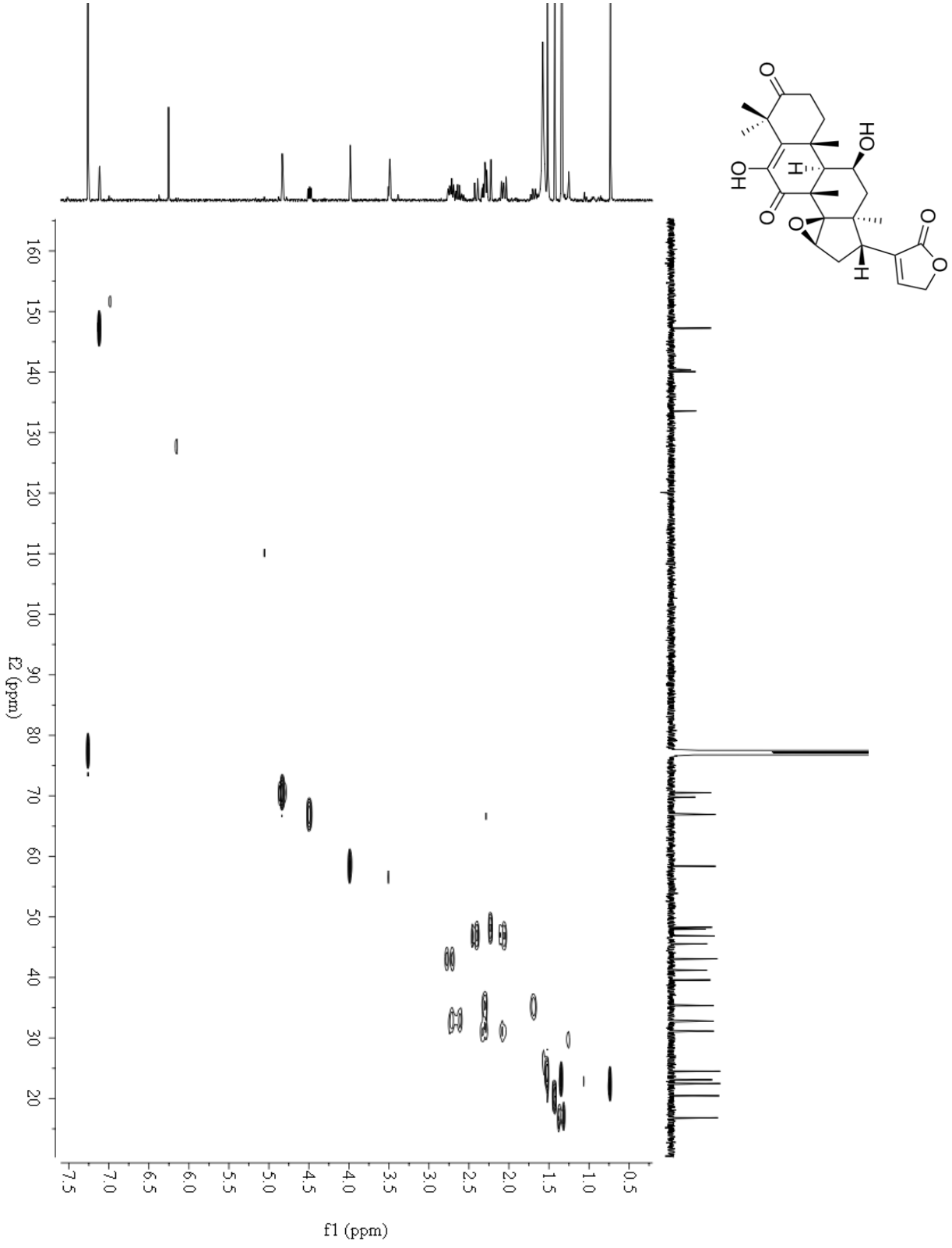


Figure S43. HMBC spectrum of walsunoid E (**5**) in $CDCl_3$

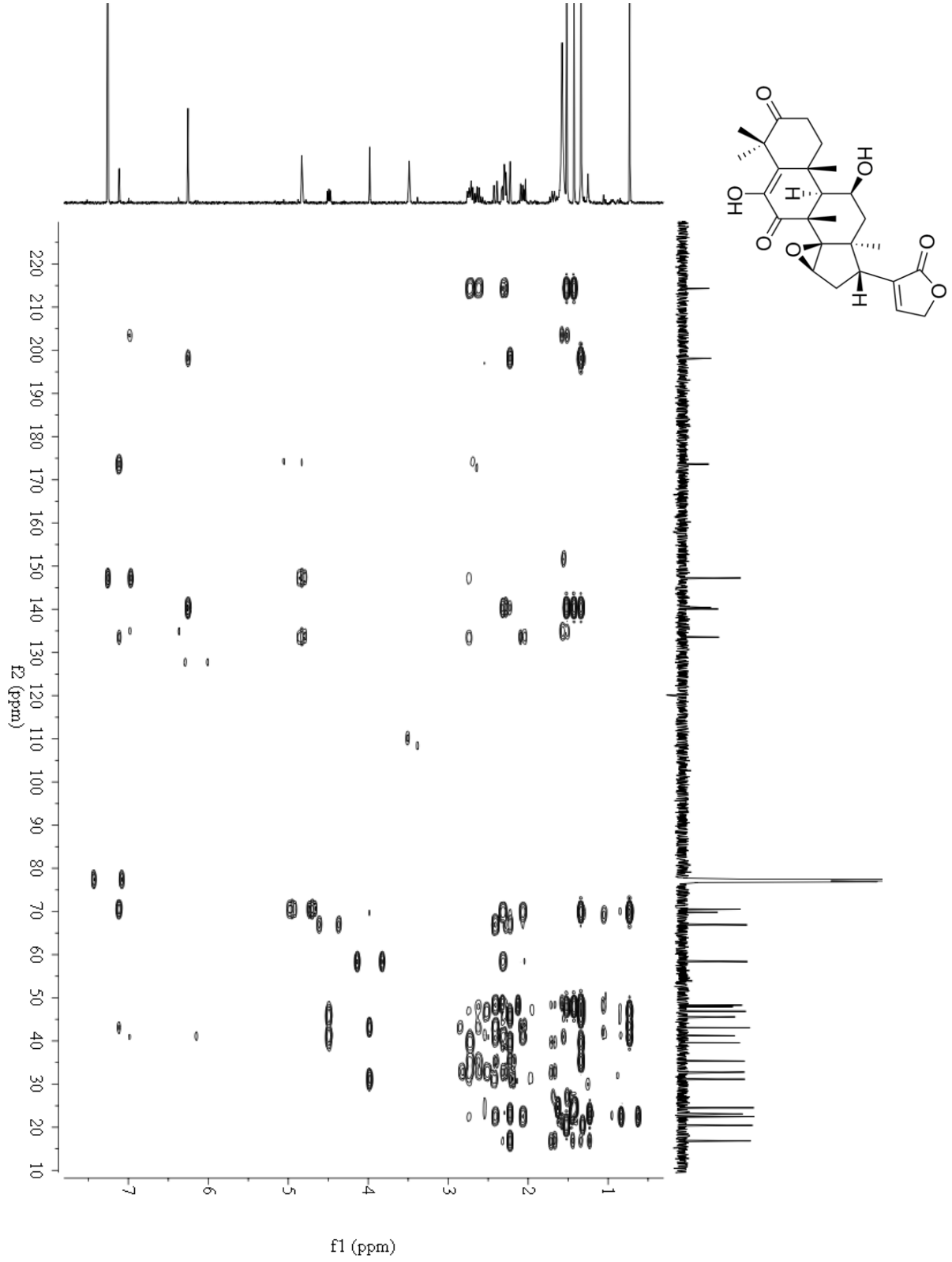


Figure S44. (+)-ESIMS spectrum of walsunoid E (**5**)

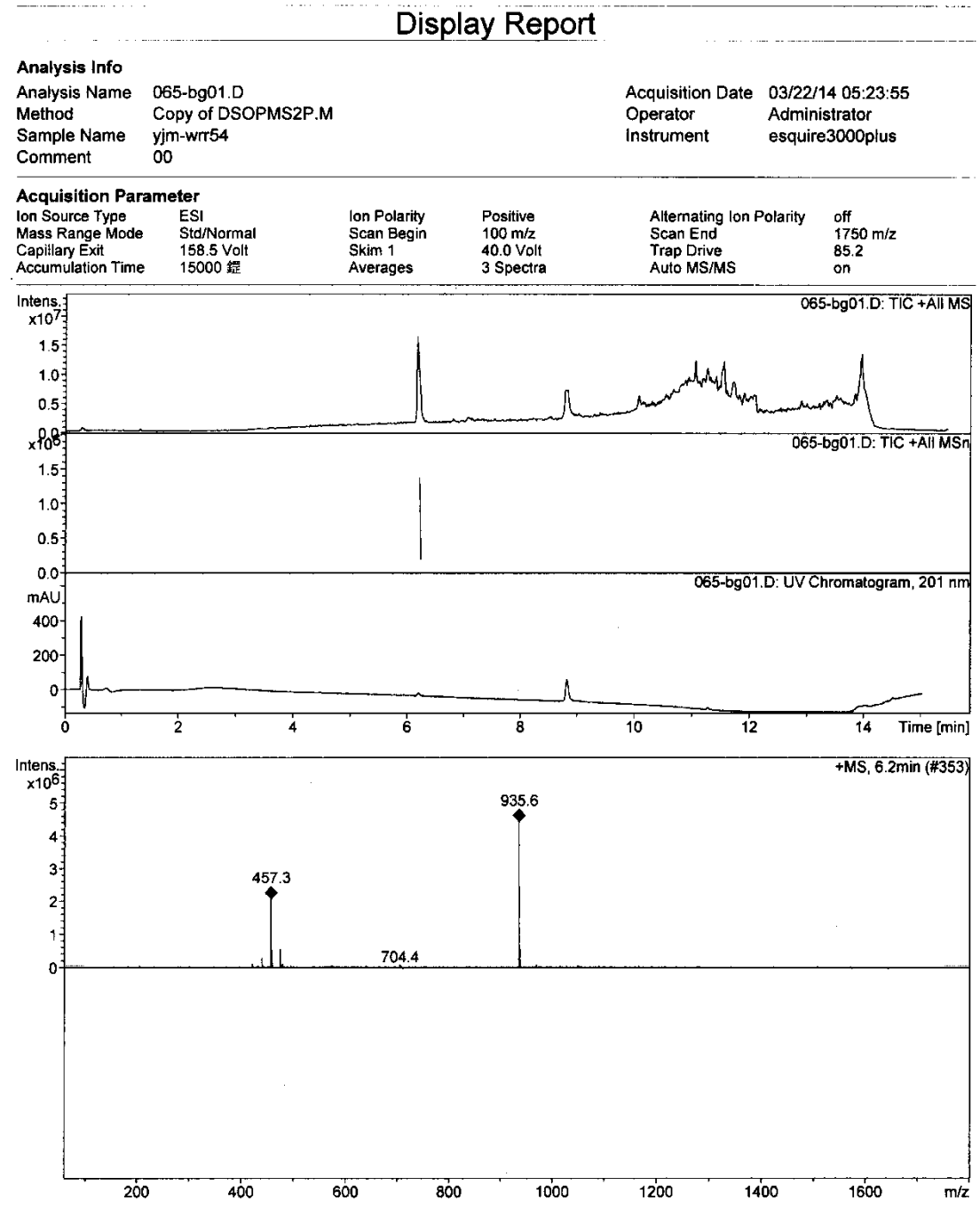


Figure S45. (–)-ESIMS spectrum of walsunoid E (**5**)

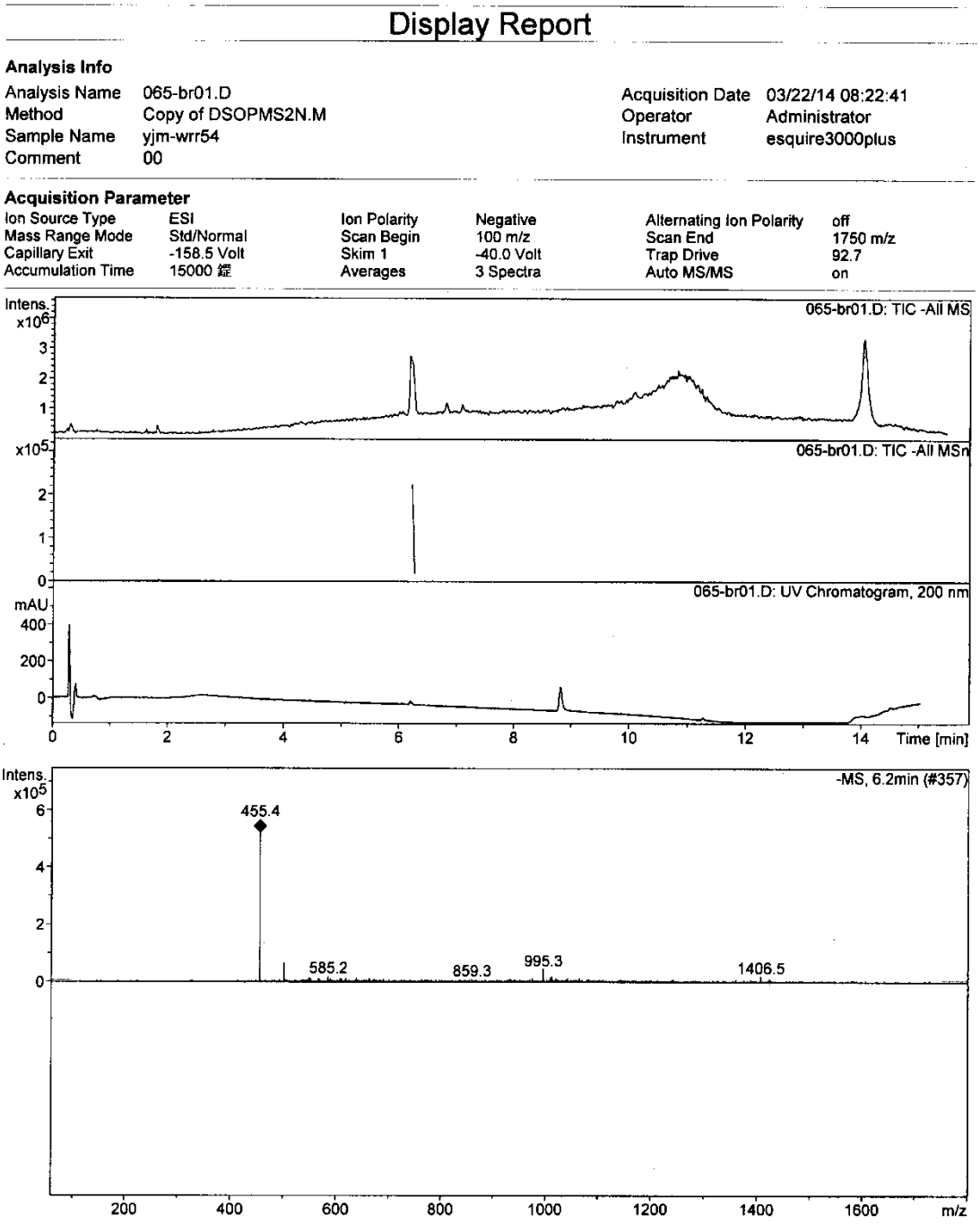
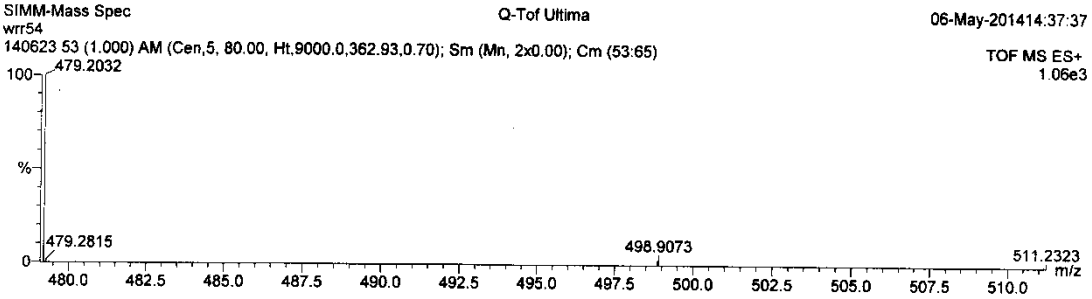


Figure S46. (+)-HRESIMS spectrum of walsunoid E (**5**)

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)



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**)

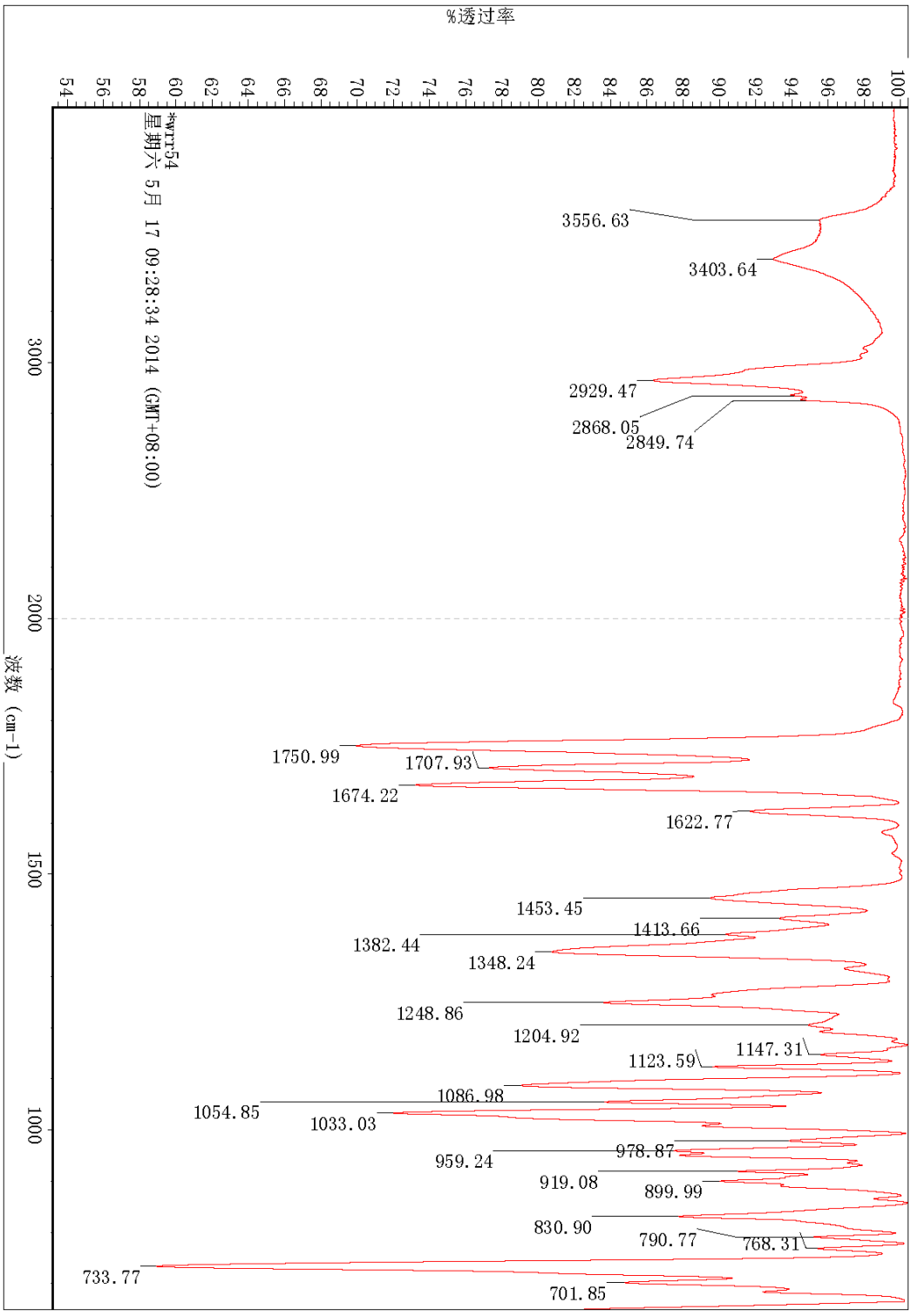


Figure S48. ^{1}H NMR spectrum of walsunoid F (**6**) in C_5D_5N

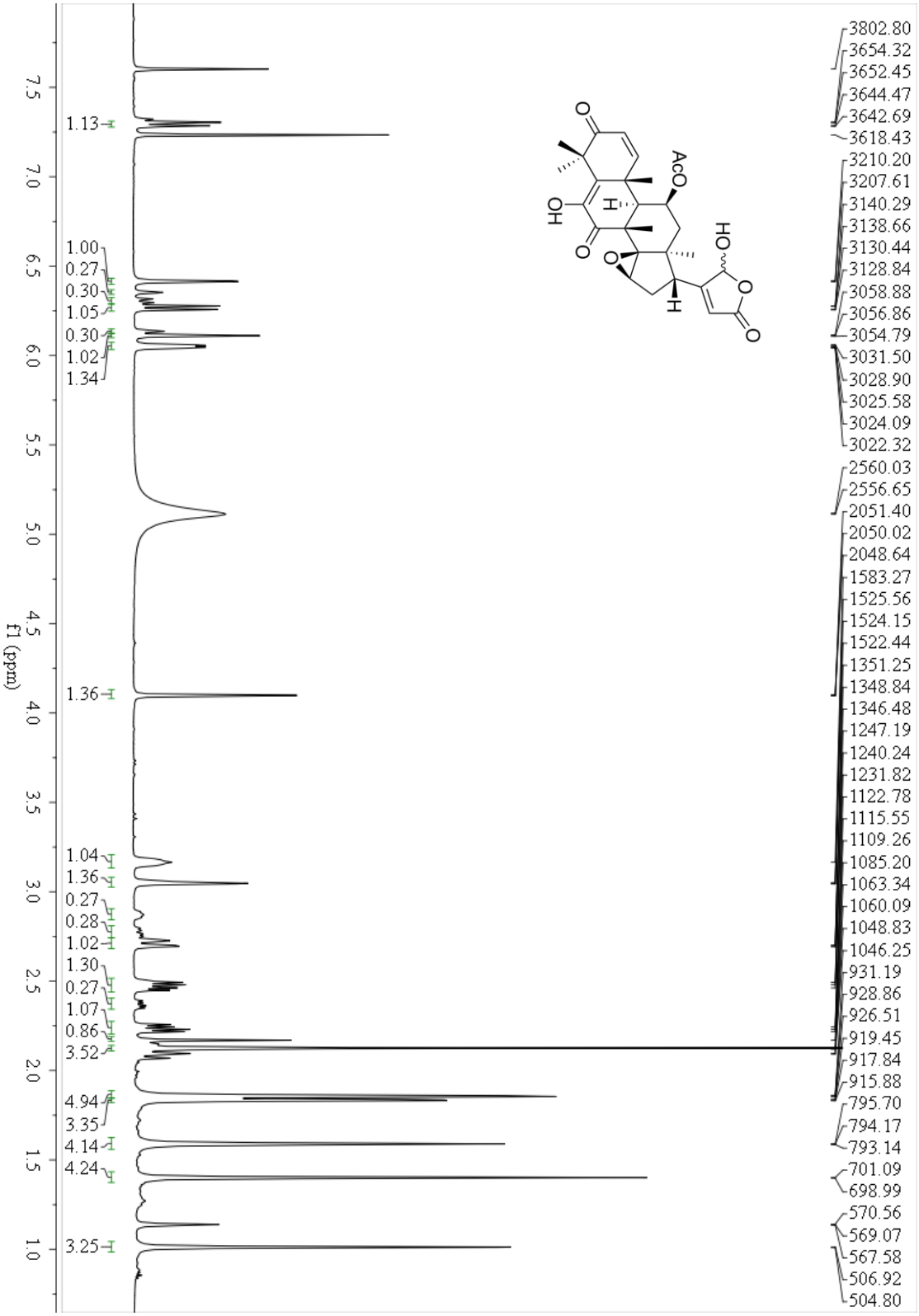


Figure S49. ^{13}C NMR spectrum of walsunoid F (**6**) in C_5D_5N

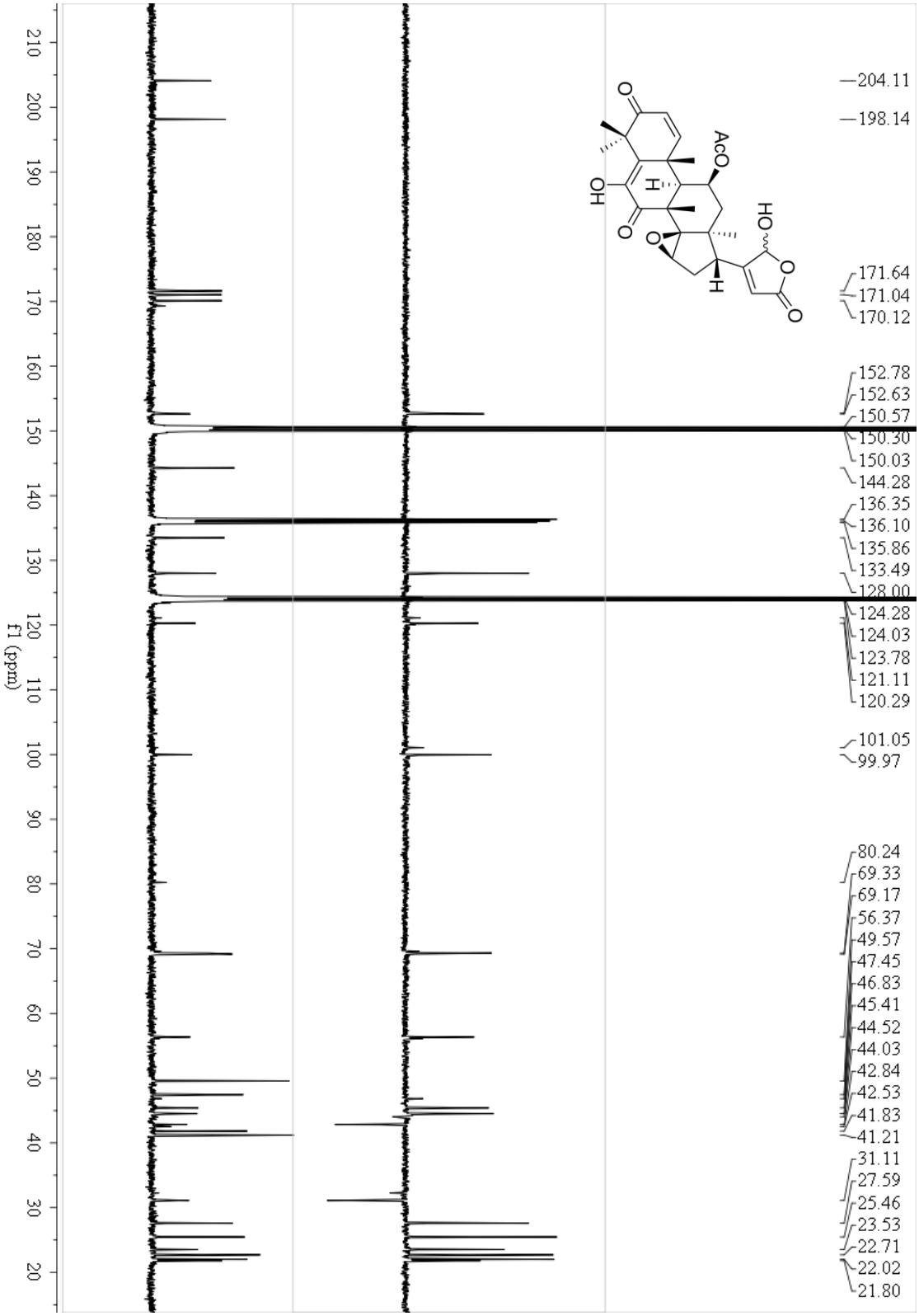


Figure S50. HSQC spectrum of walsunoid F (**6**) in C_5D_5N

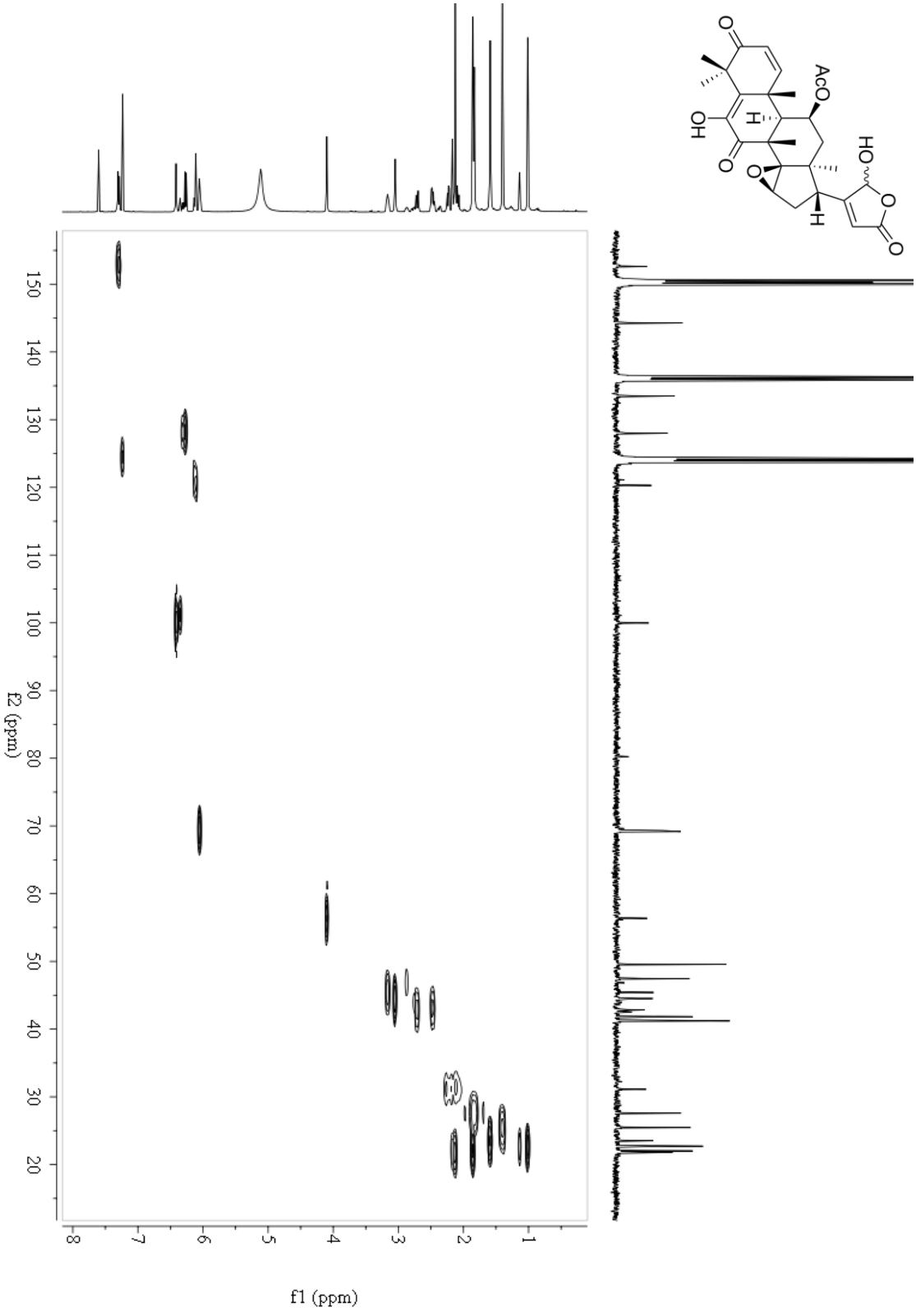


Figure S51. HMBC spectrum of walsunoid d F (**6**) in C_5D_5N

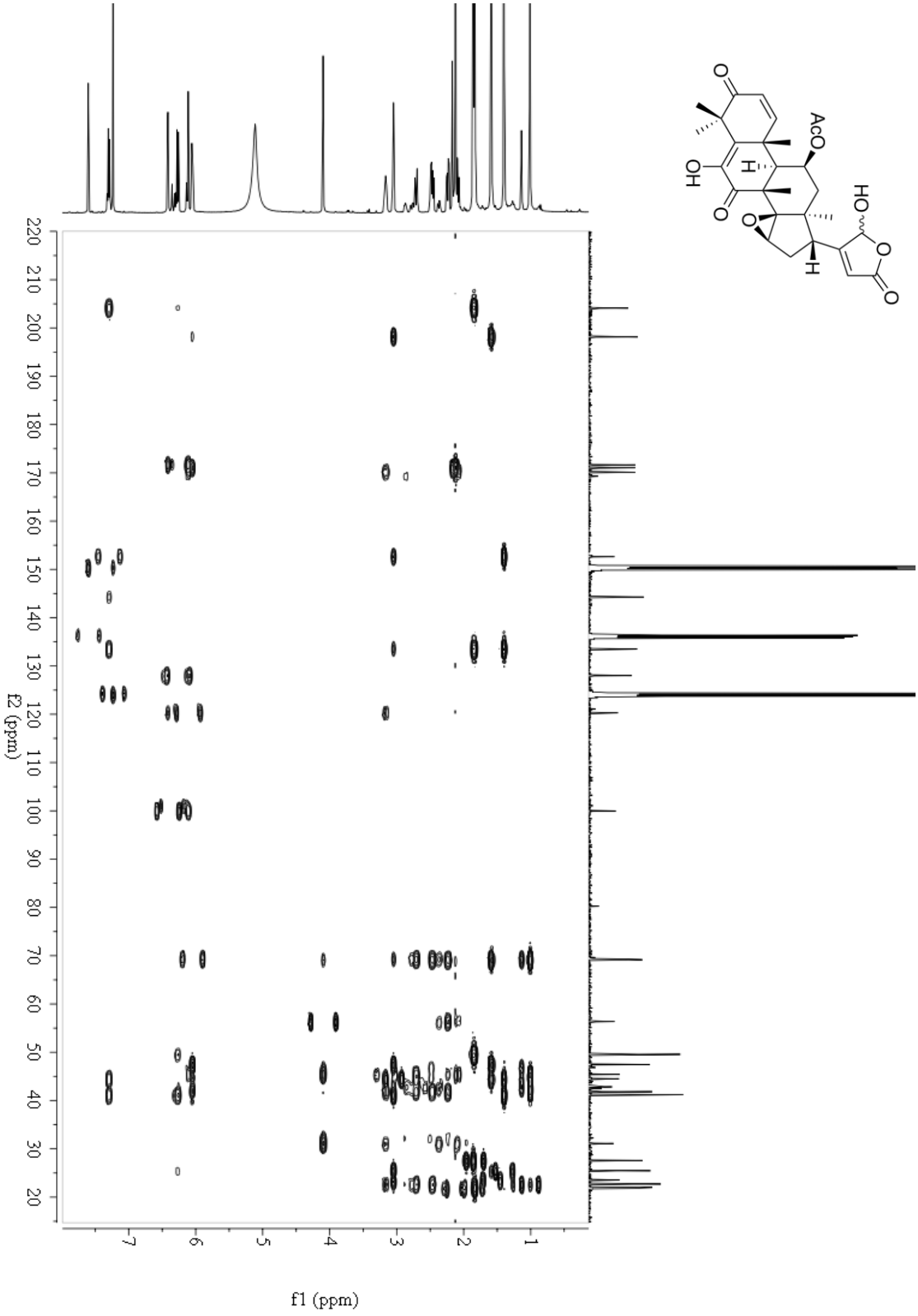
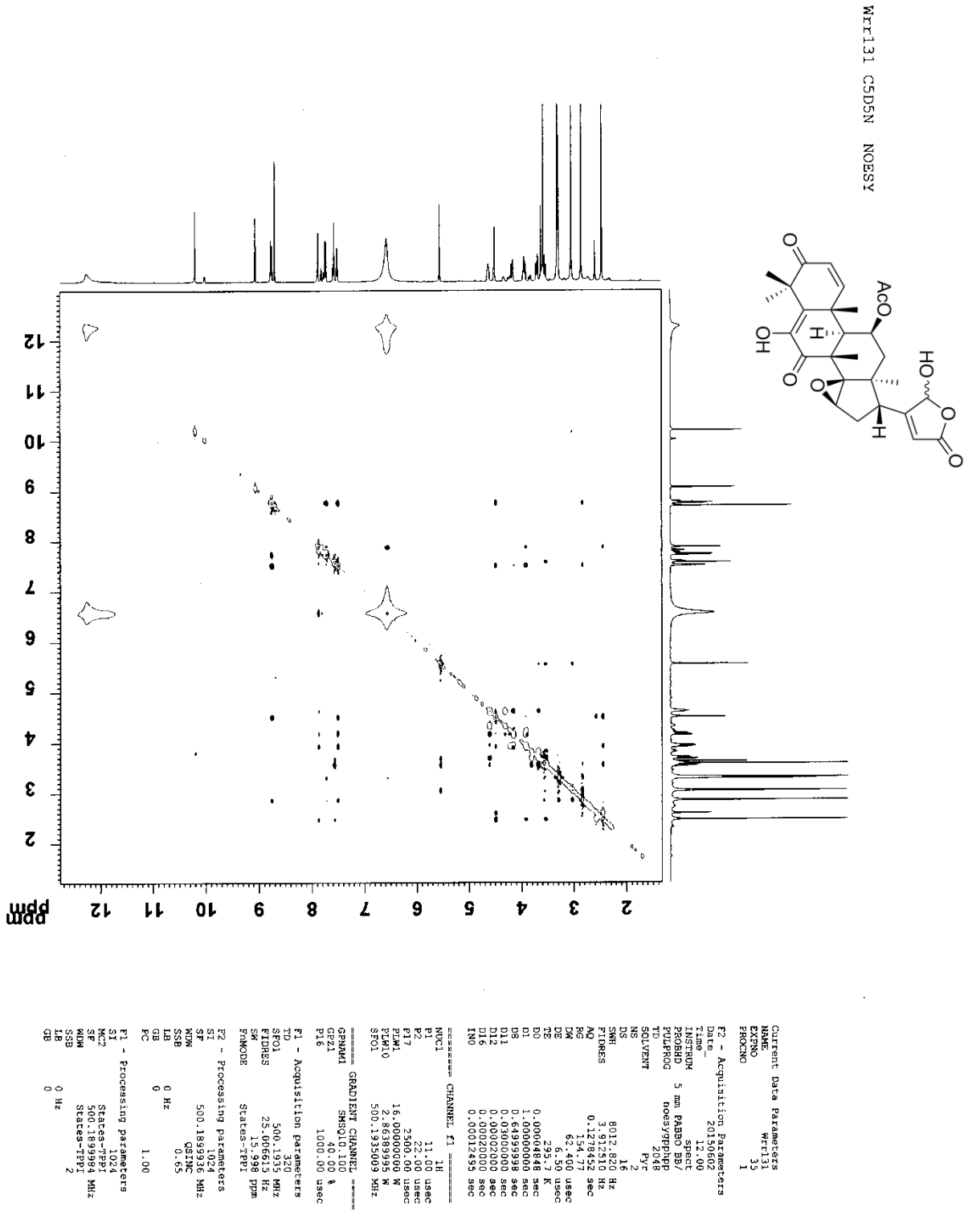


Figure S52. NOESY spectrum of walsunoid F (**6**) in C_5D_5N

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PROCNO             1

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PULPROG      noesygpphpp
TD                2048
SOLVENT            Pyr
NS                   2
DS                  16
SWH          8012.820 Hz
FIDRES       3.912510 Hz
AQ           0.12784452 sec
RG                154.77
DW               62.400 usec
DE                6.50 usec
TE               295.7 K
D0           0.00004848 sec
D1           1.00000000 sec
D8           0.64999998 sec
D11          0.03000000 sec
D12          0.00002000 sec
D16          0.00020000 sec
IN0          0.00012495 sec

======== CHANNEL f1 ========
NUC1               1H
P1               11.00 usec
P2               22.00 usec
PLW1        16.00000000 W
PLW10        2.86389995 W
SFO1       500.1935009 MHz

====== GRADIENT CHANNEL =====
GPNAM1     SMSQ10.100
GPZ1            40.00 %
P16           1000.00 usec

F1 - Acquisition parameters
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FIDRES       25.006615 Hz
SW           15.998 ppm
FnMODE       States-TPPI

F2 - Processing parameters
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SF         500.1899316 MHz
WDW               QSINC
SSB                0.65
LB           0 Hz
GB                 0.65
PC                 1.00

F1 - Processing parameters
SI                1024
MC2          States-TPPI
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WDW
SSB          States-TPPI 2
LB           0 Hz
GB           0
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Figure S53. (+)-ESIMS spectrum of walsunoid F (**6**)

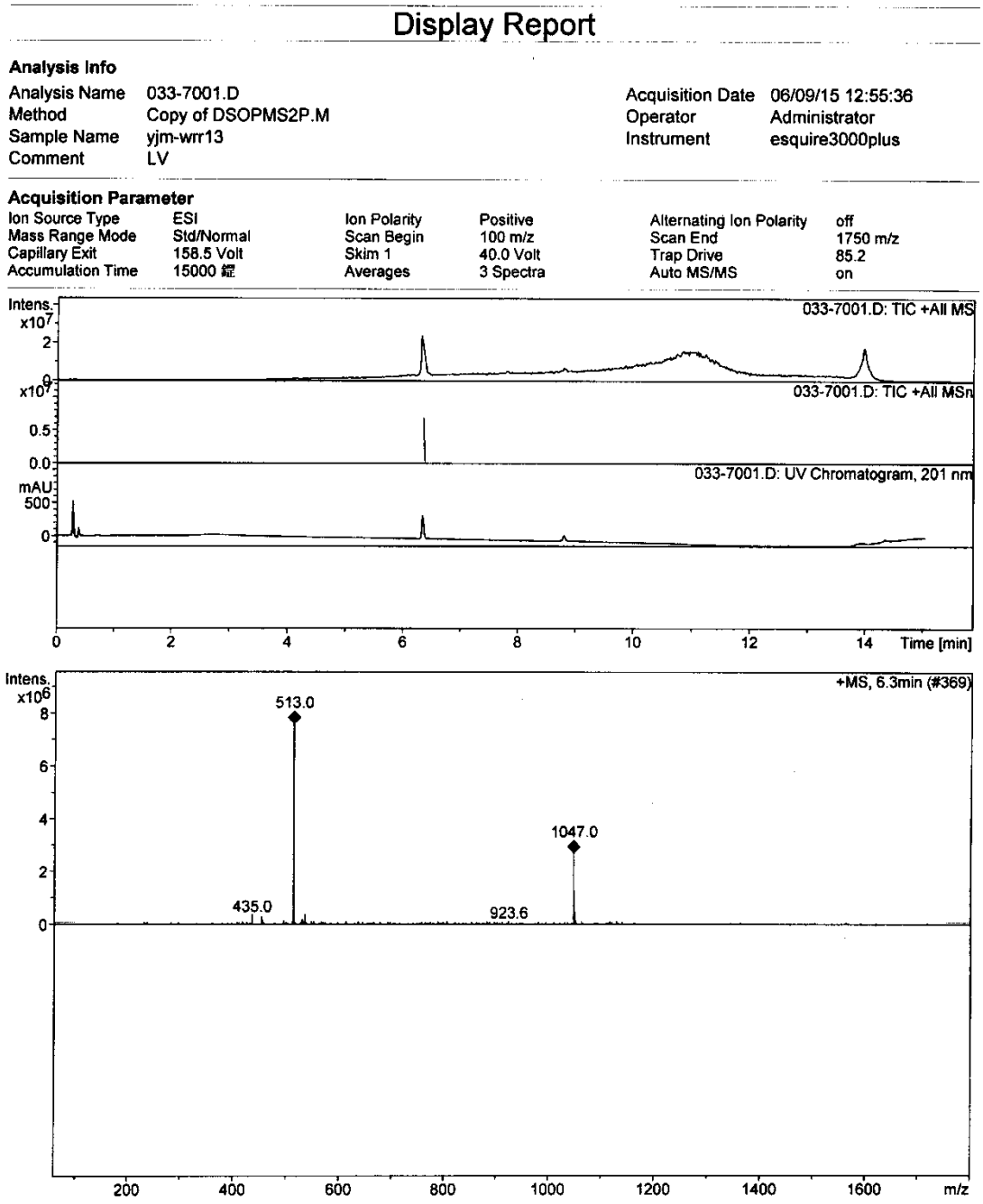


Figure S54. (–)-ESIMS spectrum of walsunoid F (**6**)

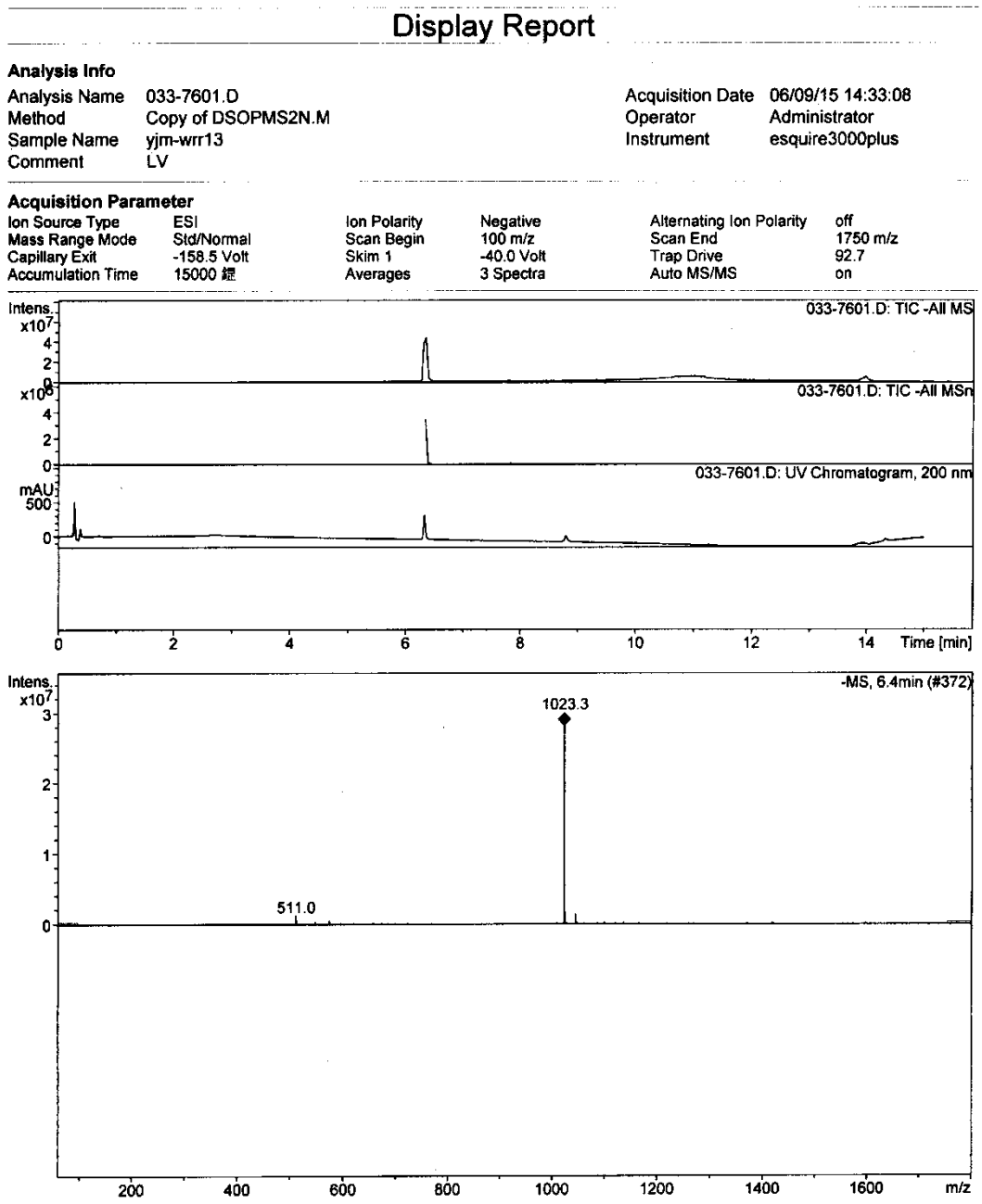


Figure S55. (–)-HRESIMS spectrum of walsunoid F (**6**)

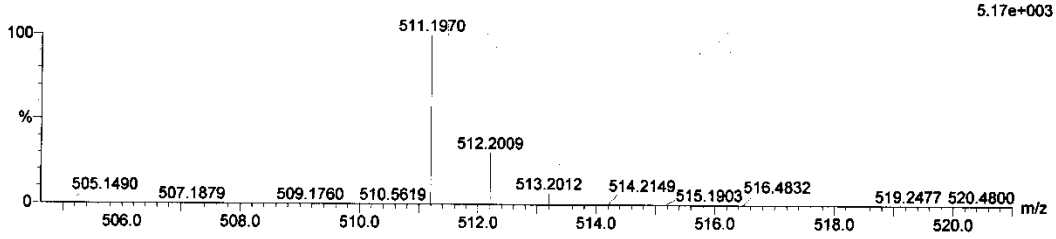
Elemental Composition Report **Page 1**

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

wrr13_20150611 12 (0.230) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (10:17) 1: TOF MS ES- 5.17e+003



Minimum:				-1.5			
Maximum:		5.0	5.0	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**)

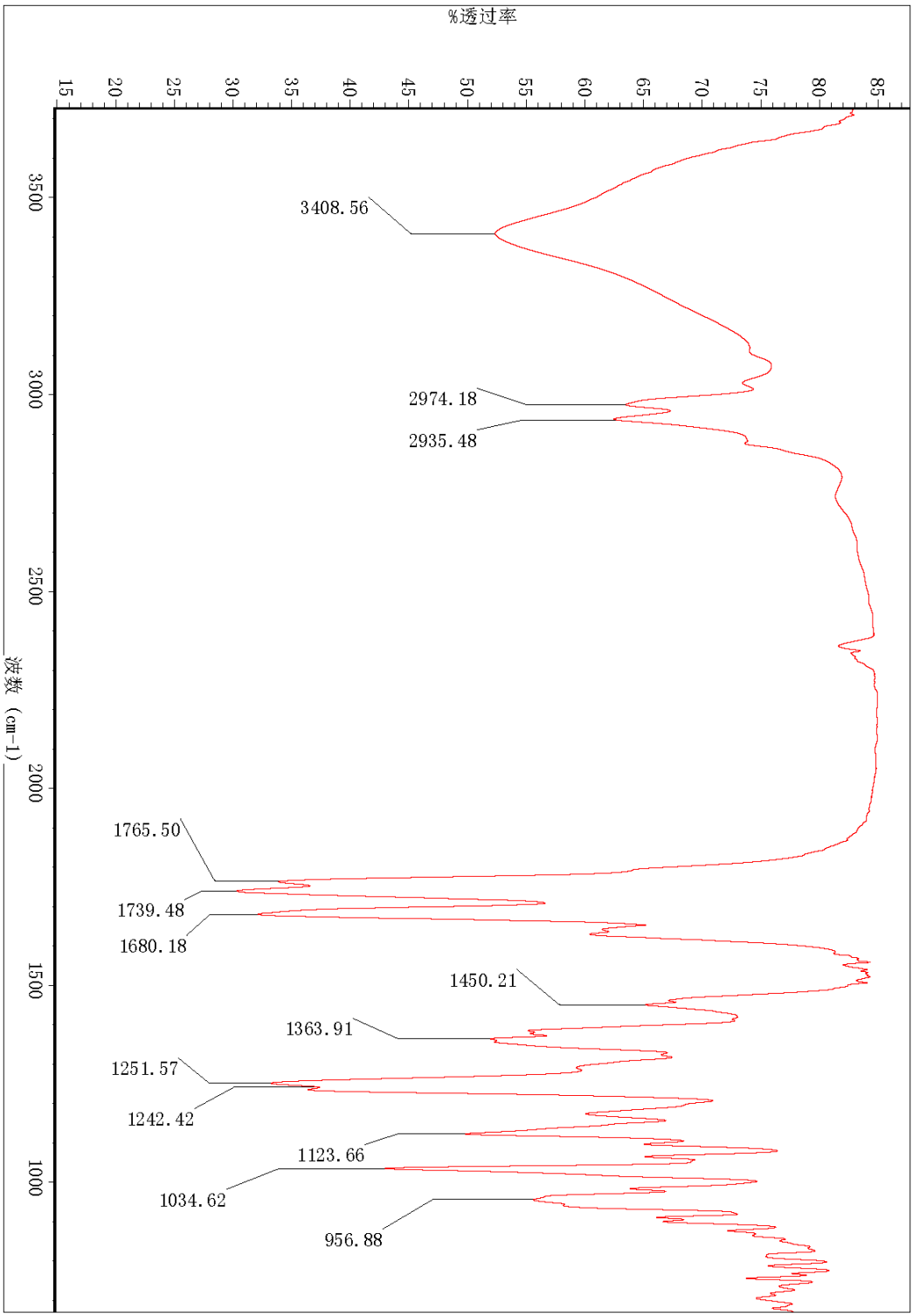


Figure S57. ^{1}H NMR spectrum of walsunoid G (**7**) in C_5D_5N

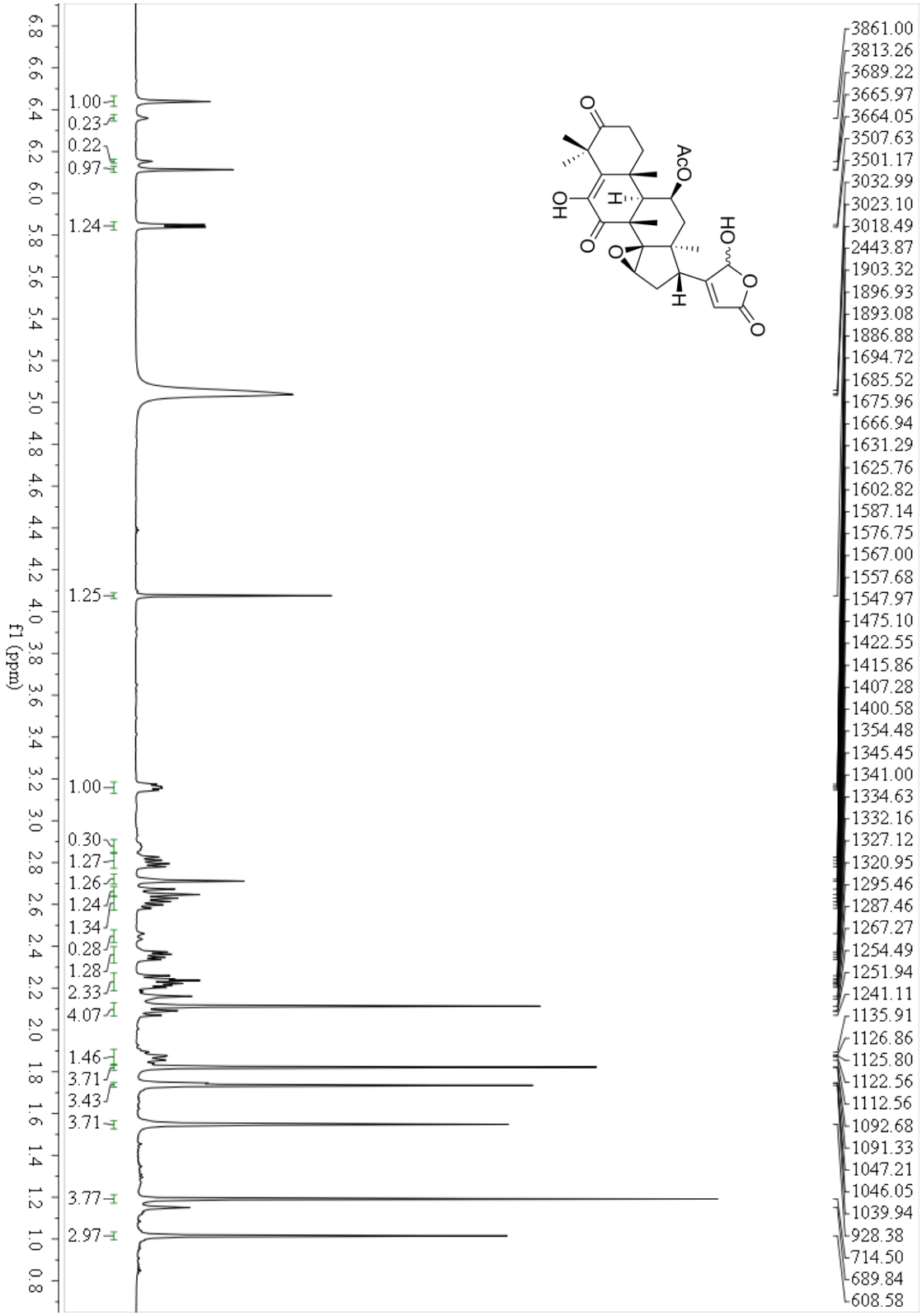


Figure S58. ^{13}C NMR spectrum of walsunoid G (**7**) in C_5D_5N

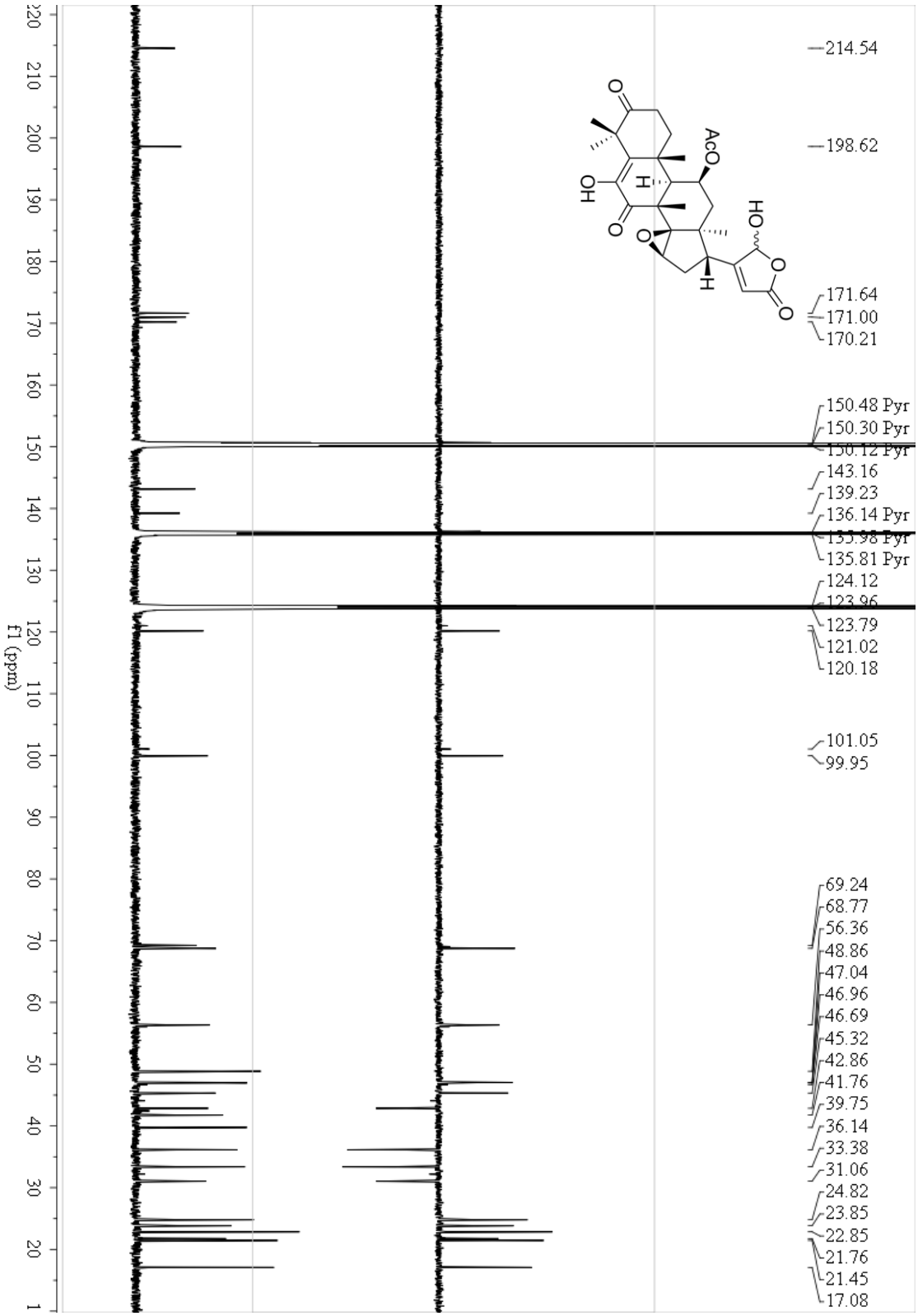


Figure S59. HSQC spectrum of walsunoid G (**7**) in C_5D_5N

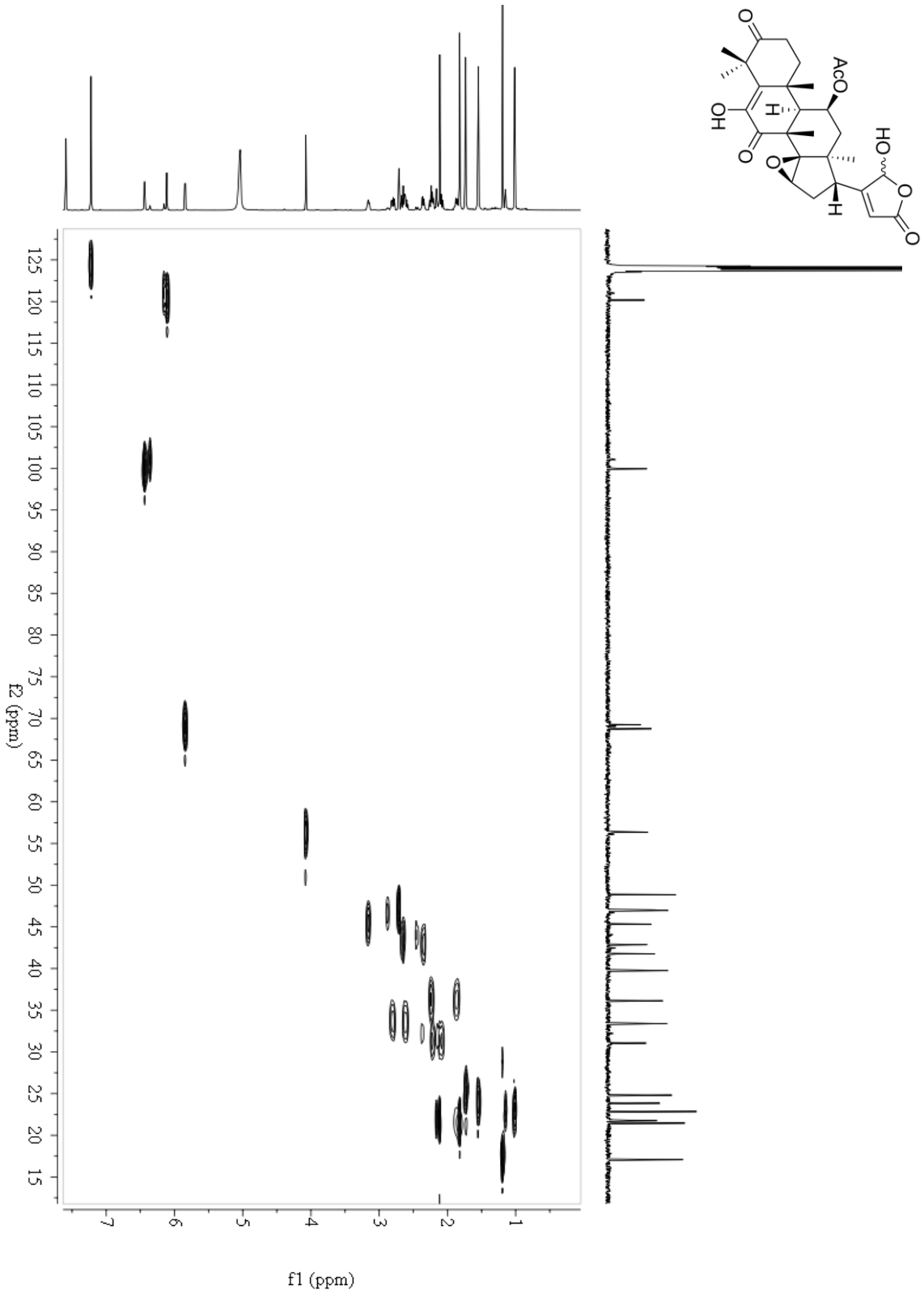


Figure S60. HMBC spectrum of walsunoid G (**7**) in C_5D_5N

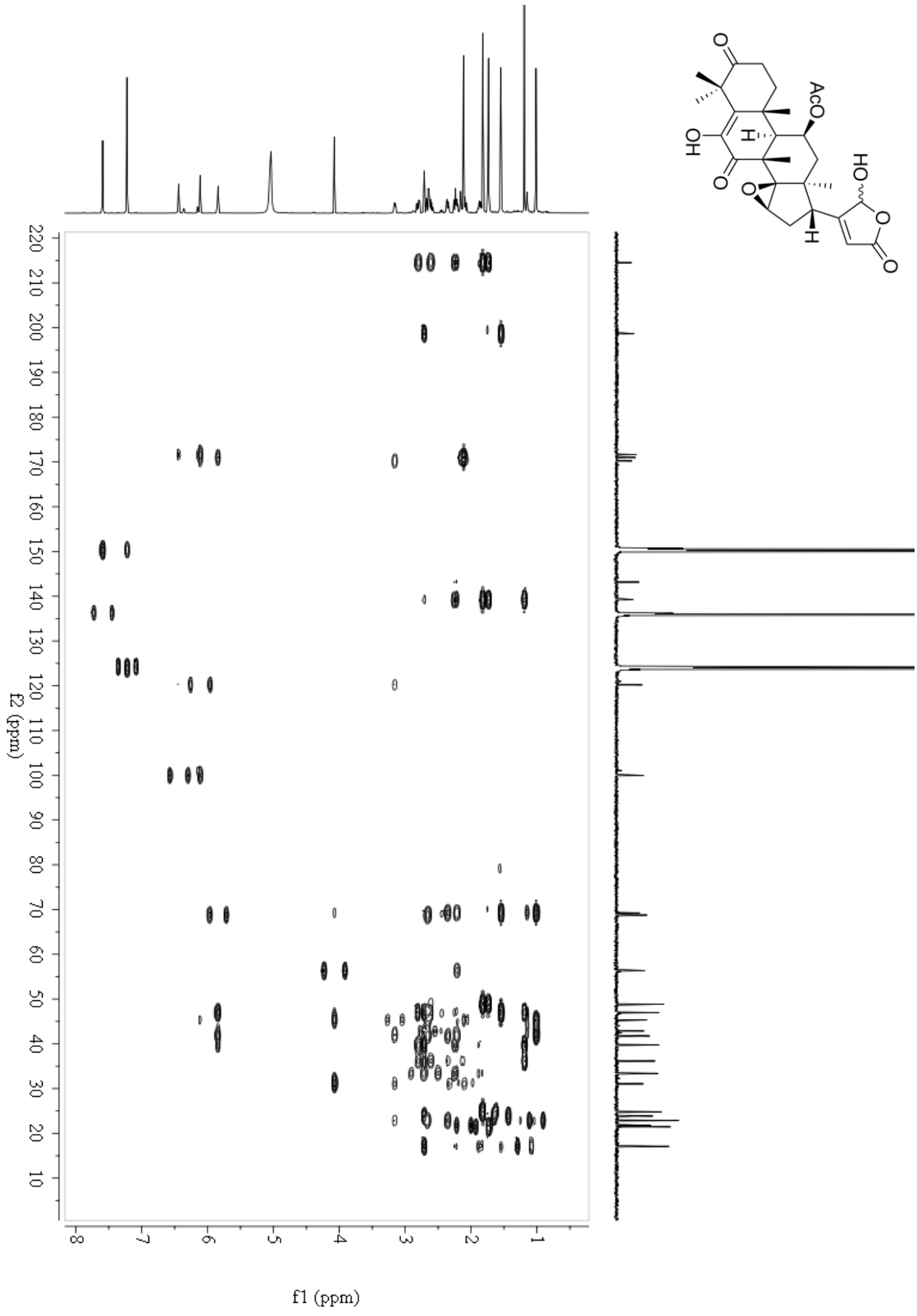


Figure S61. NOESY spectrum of walsunoid G (**7**) in C_5D_5N

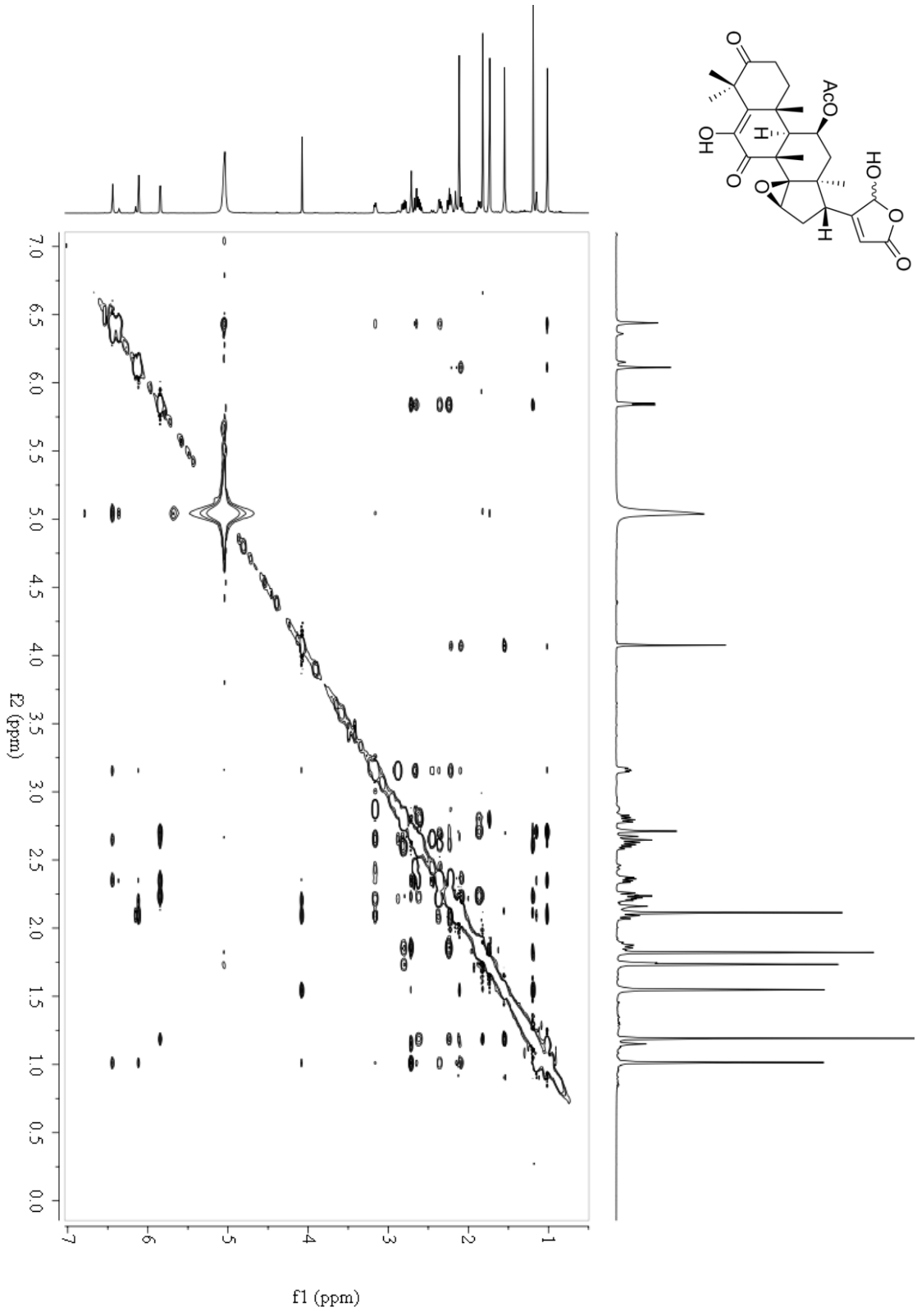


Figure S62. (+)-ESIMS spectrum of walsunoid G (**7**)

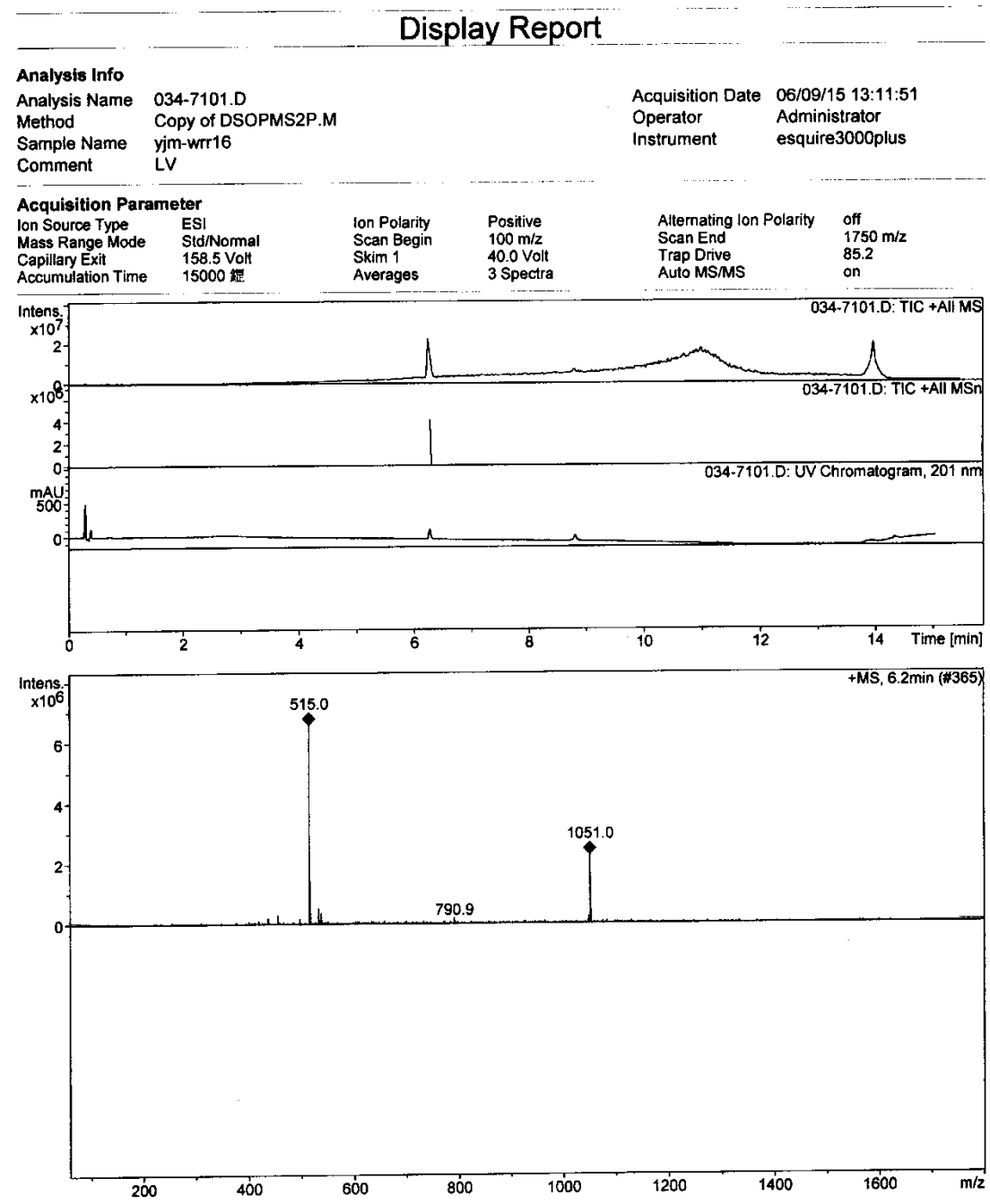


Figure S63. (–)-ESIMS spectrum of walsunoid G (**7**)

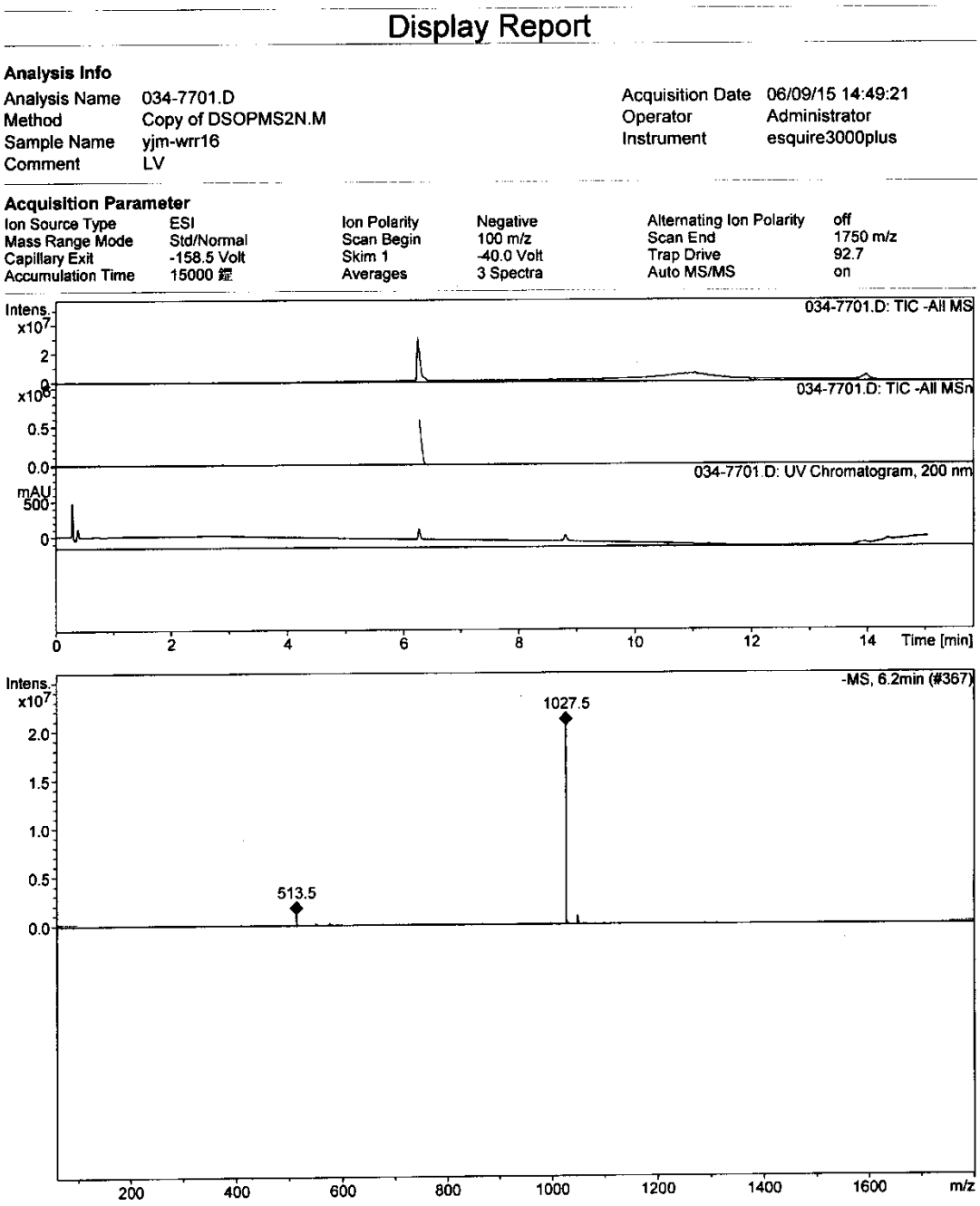


Figure S64. (–)-HRESIMS spectrum of walsunoid G (**7**)

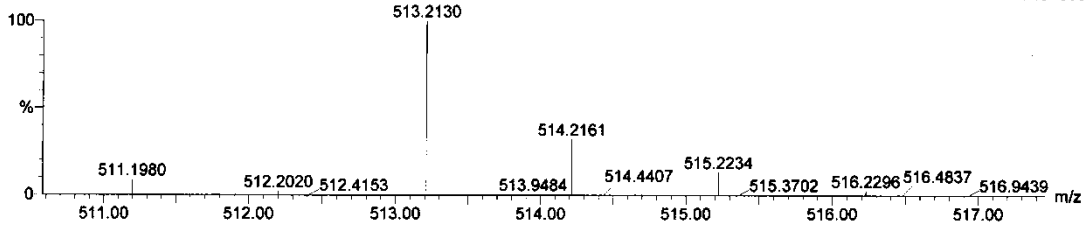
Elemental Composition Report **Page 1**

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

wrr16_20150611 11 (0.212) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (10:22) 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**)

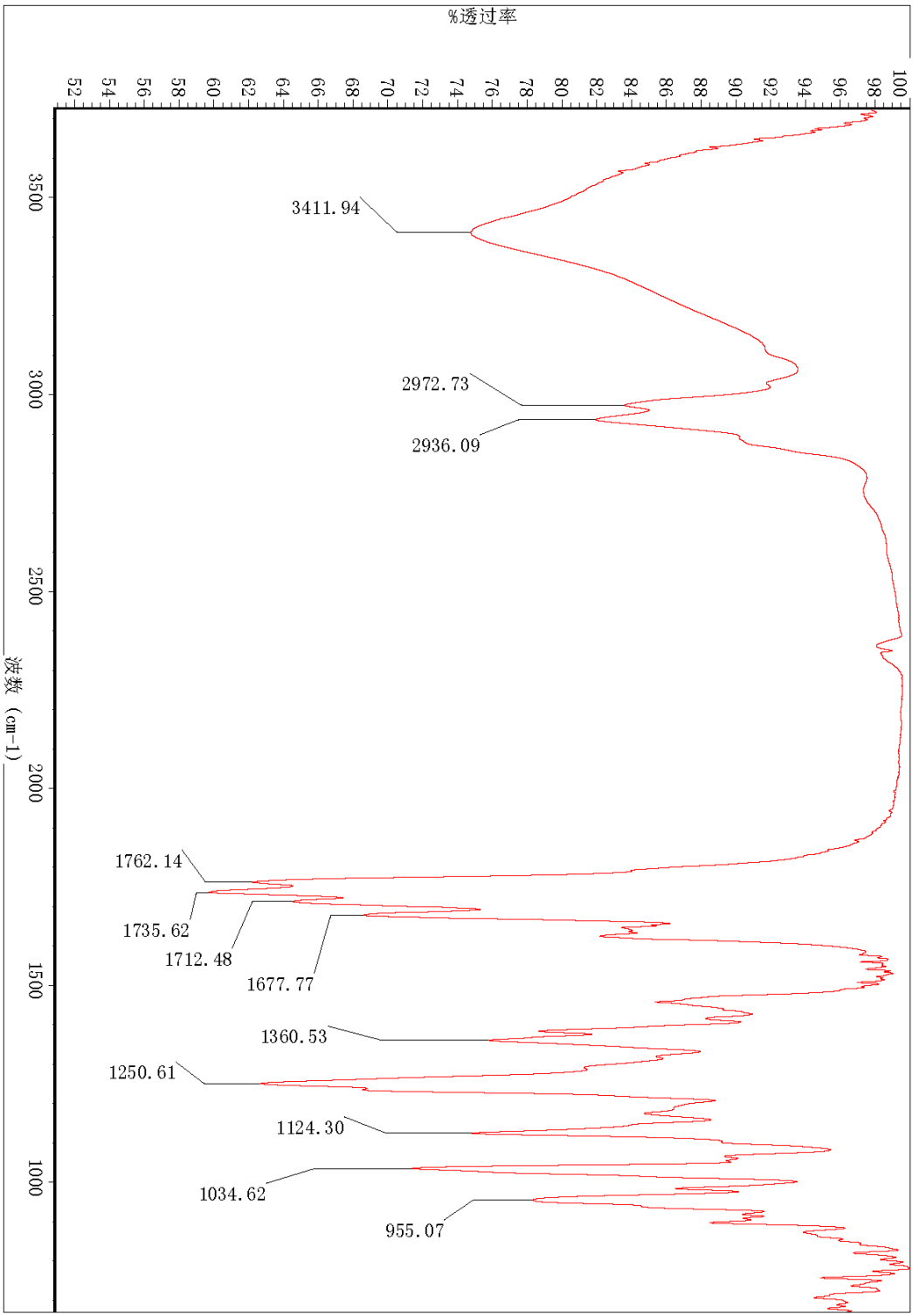


Figure S66. ^{1}H NMR spectrum of walsunoid H (**8**) in $CDCl_3$

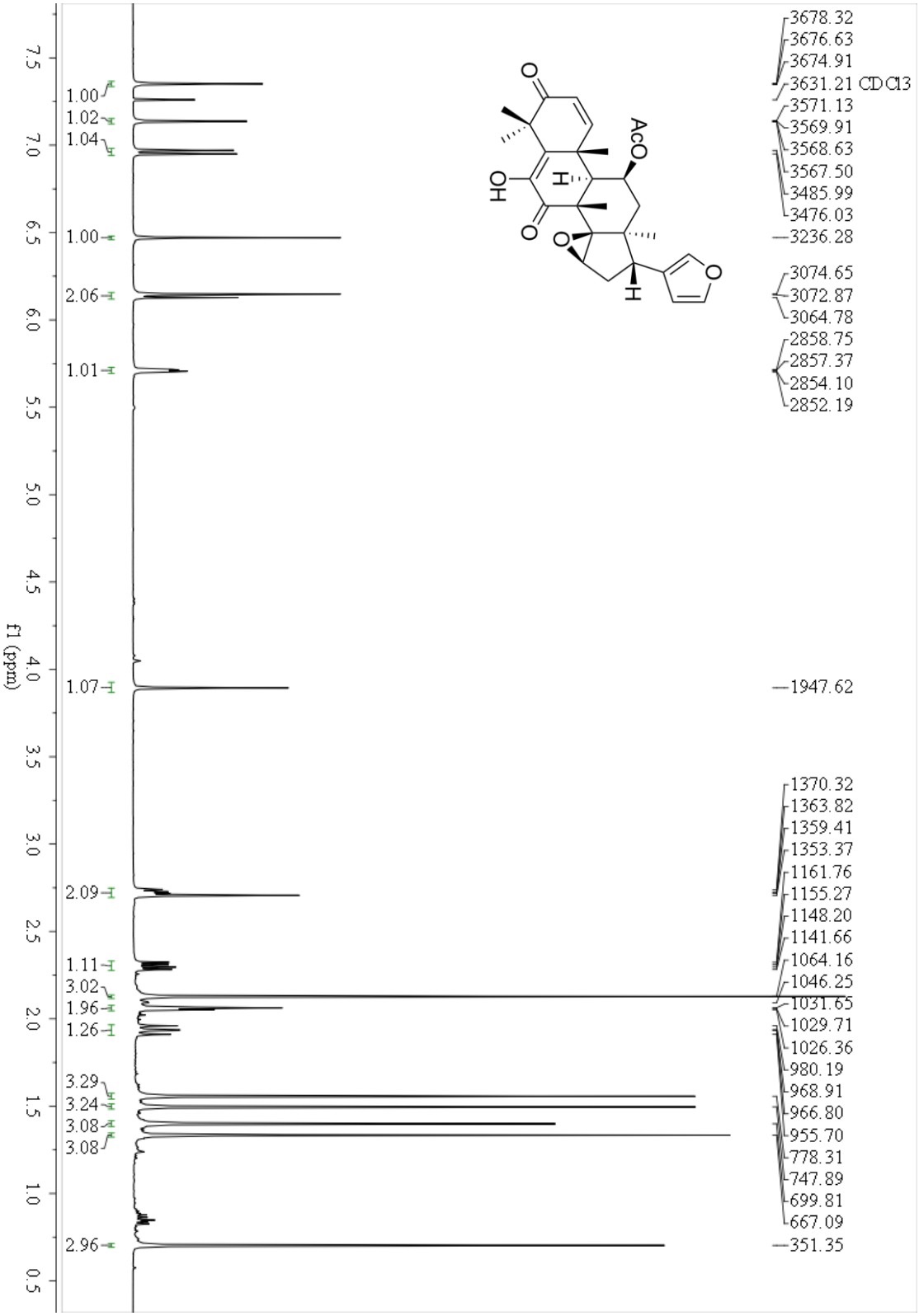


Figure S67. ^{13}C NMR spectrum of walsunoid H (**8**) in $CDCl_3$

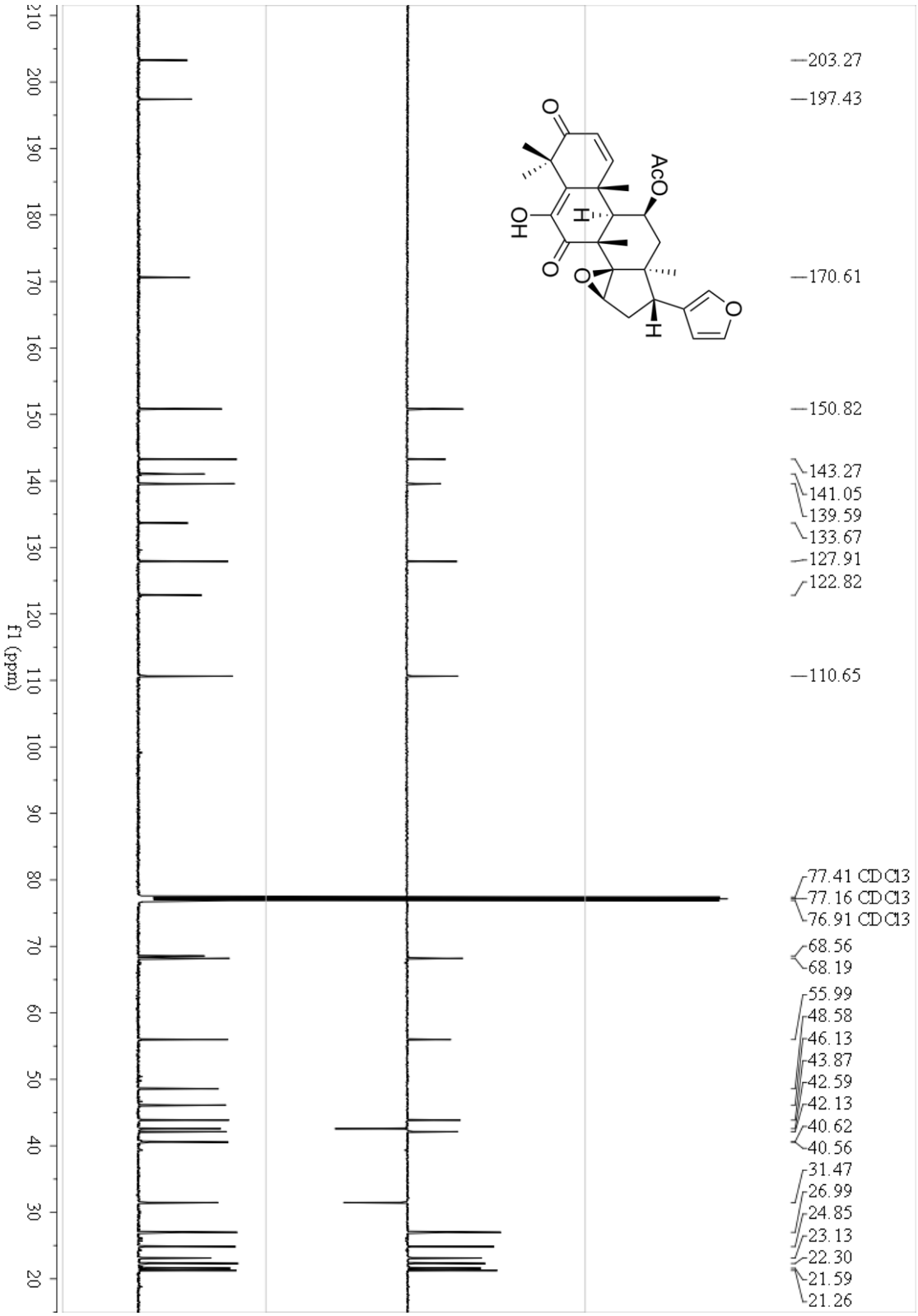


Figure S68. HSQC spectrum of walsunoid H (**8**) in $CDCl_3$

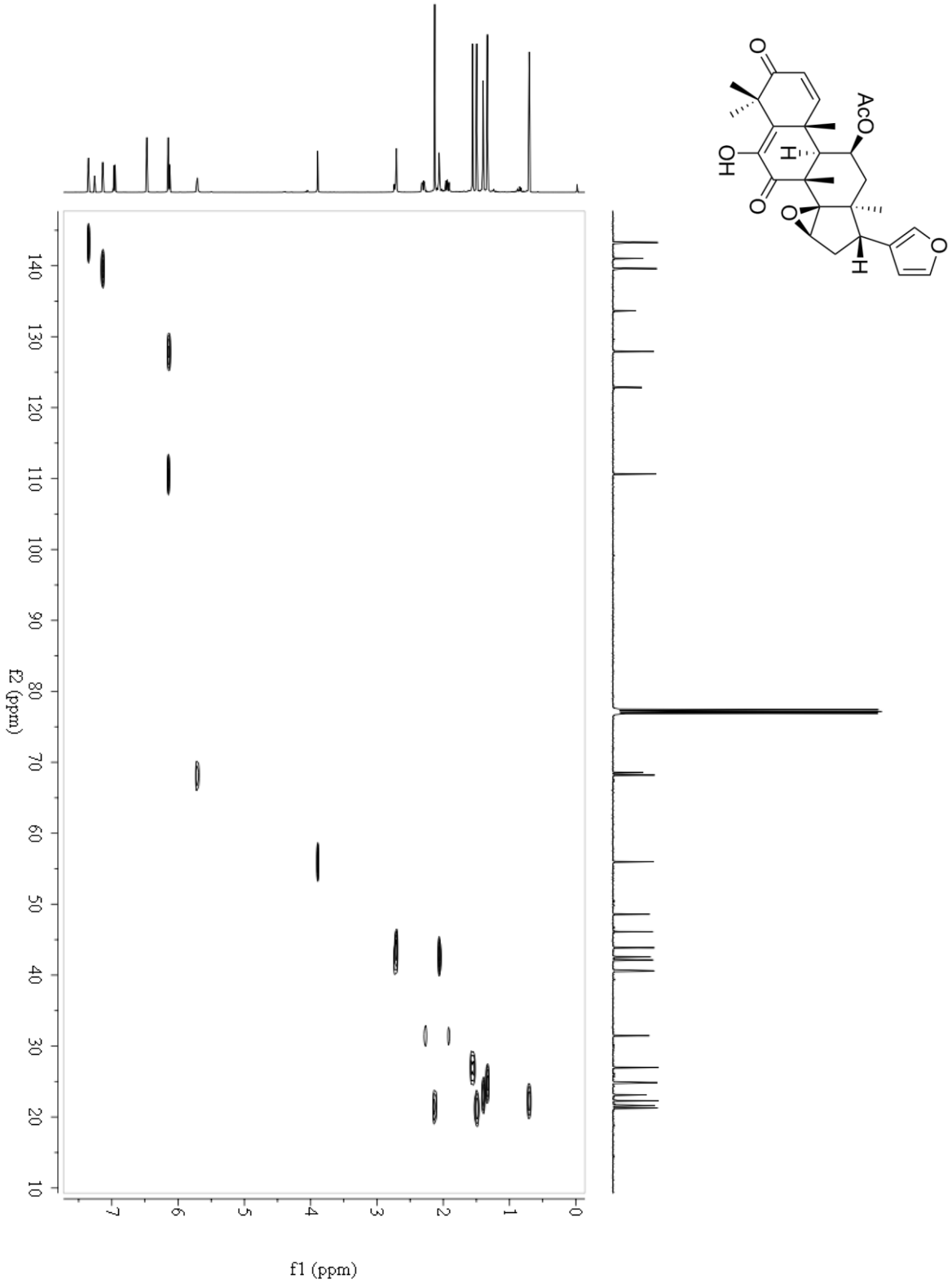


Figure S69. HMBC spectrum of walsunoid H (**8**) in $CDCl_3$

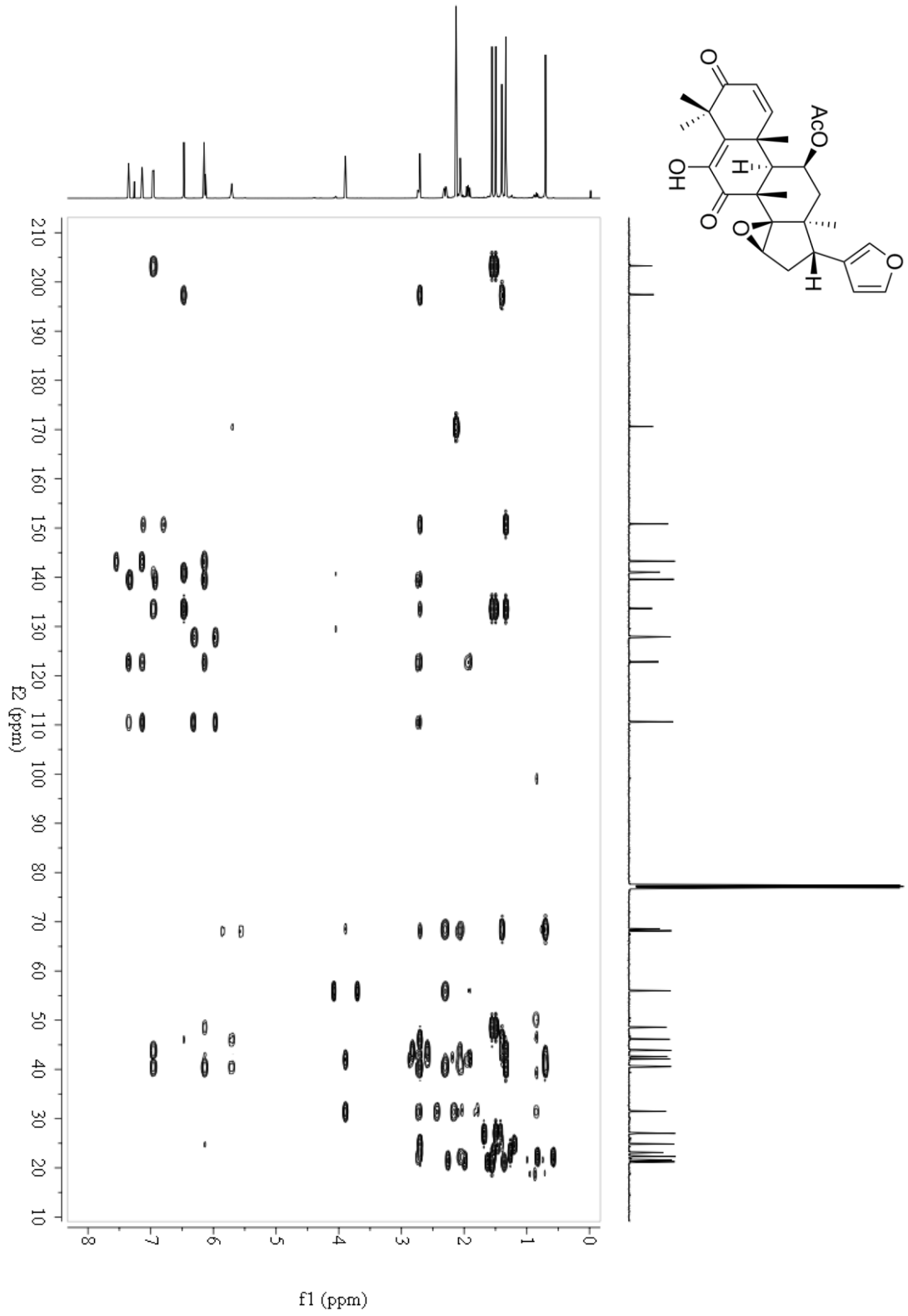
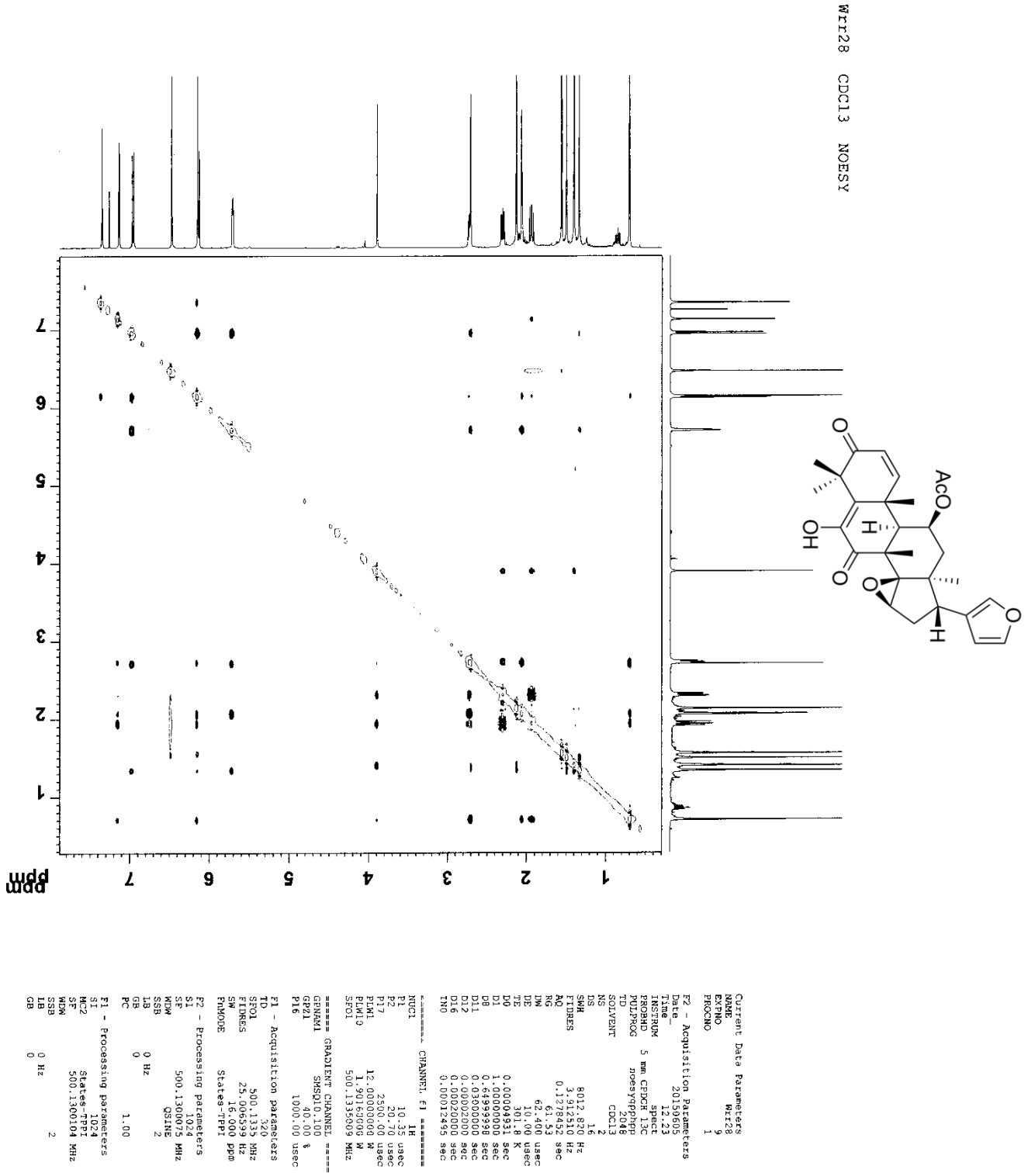


Figure S70. NOESY spectrum of walsunoid H (**8**) in $CDCl_3$



Current Data Parameters
NAME Wrr28
EXPNO 9
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150605
Time 12.23
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG noesygpphp
TD 2048
SOLVENT CDCl3
NS 16
DS 16
SWH 8012.820 Hz
FIDRES 3.912510 Hz
AQ 0.1278452 sec
RG 61.53
DW 62.400 usec
DE 10.00 usec
TE 301.8 K
D0 0.00004931 sec
D1 1.00000000 sec
D8 0.64999998 sec
D11 0.03000000 sec
D12 0.00002000 sec
D16 0.00020000 sec
IN0 0.00031495 sec

======== CHANNEL f1 ========
NUC1 1H
P1 10.15 usec
P2 20.30 usec
P17 2500.00 usec
PLW1 12.00000000 W
PLW10 1.90160009 W
SFO1 500.1335009 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 320
SFO1 500.1335 MHz
FIDRES 25.006599 Hz
SW 16.000 ppm
FnMODE States-TPPI

F2 - Processing parameters
SI 1024
SF 500.1300075 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 500.1300104 MHz
WDW
SSB 2
LB 0 Hz
GB 0

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

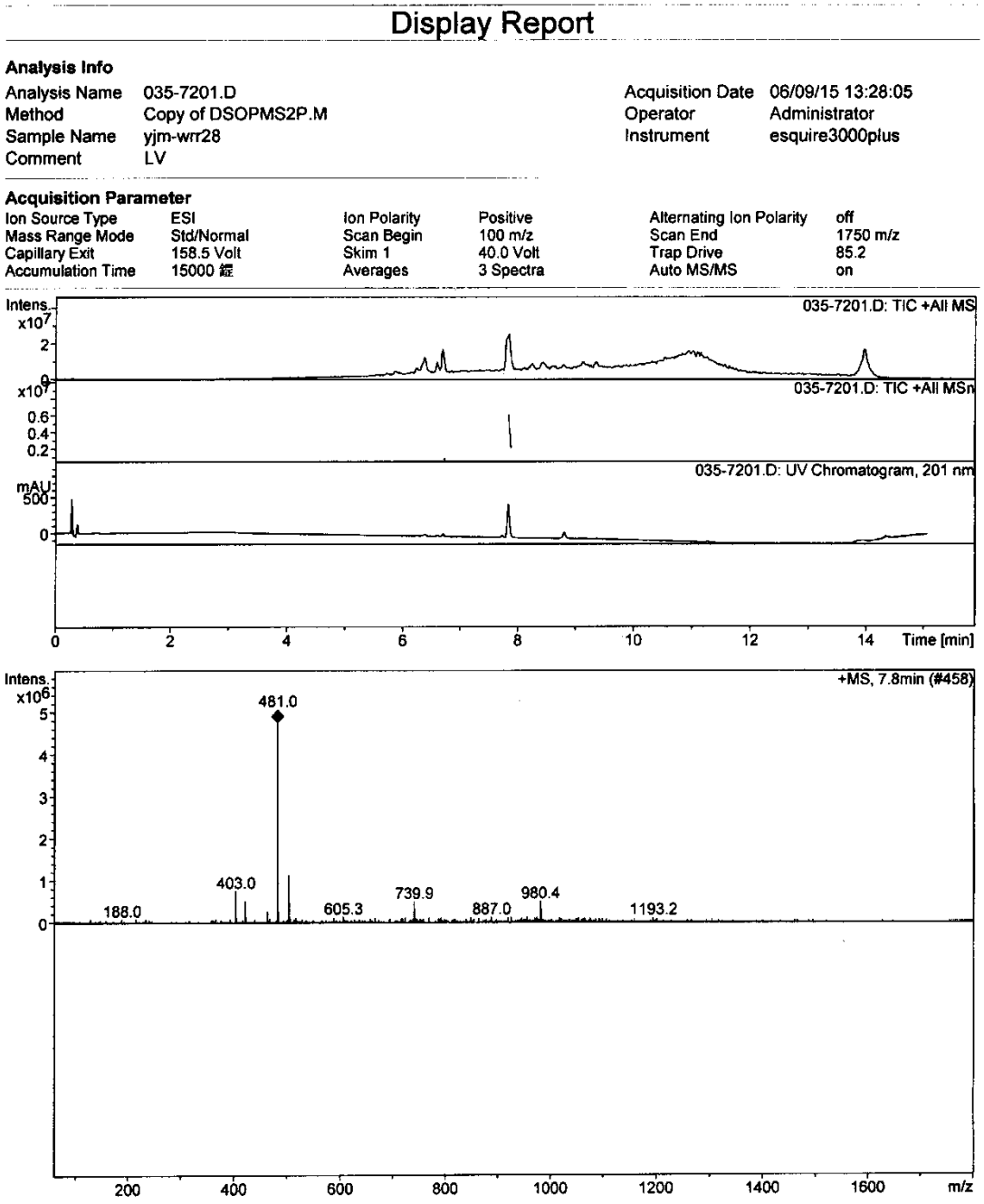


Figure S72. (–)-ESIMS spectrum of walsunoid H (**8**)

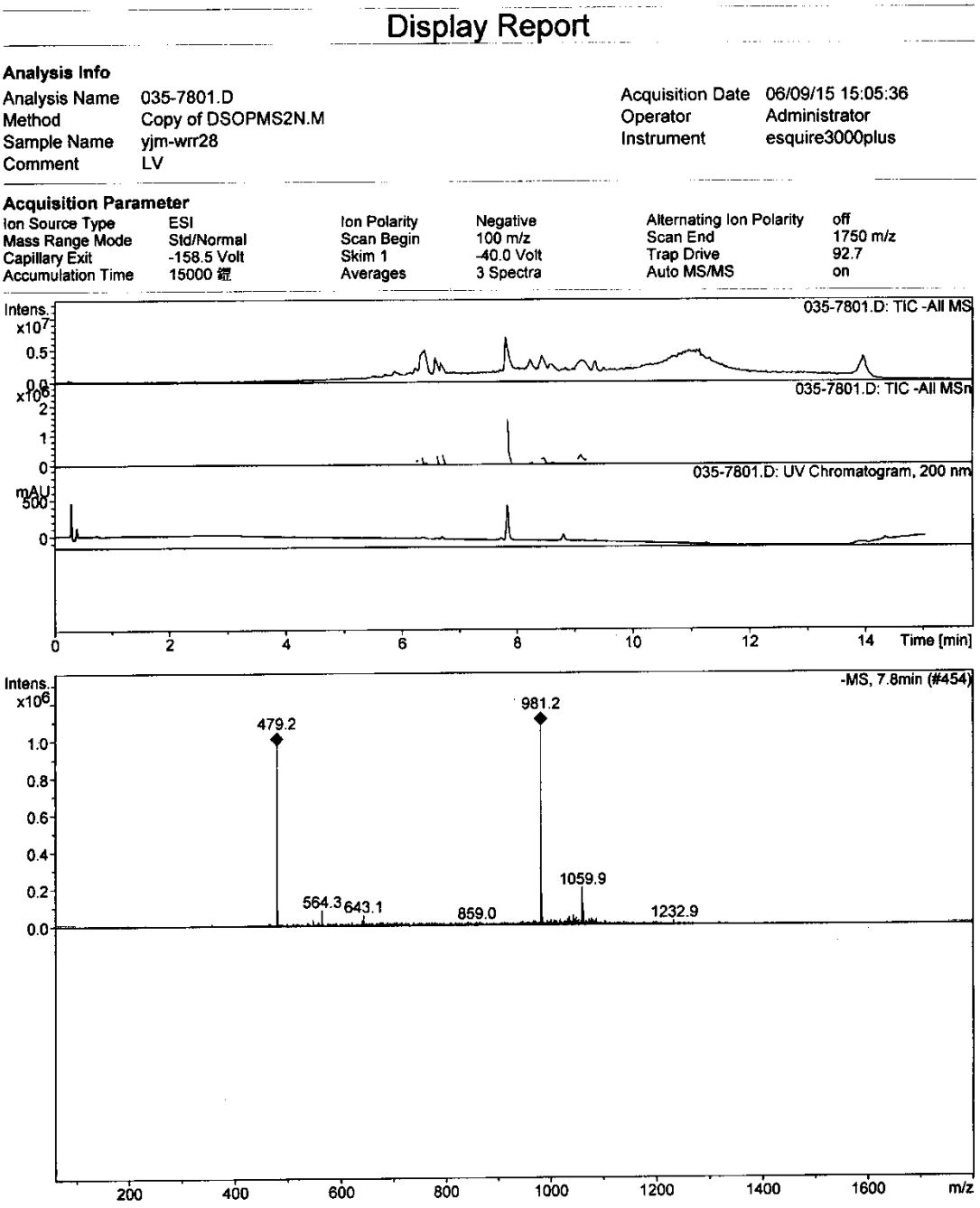


Figure S73. (–)-HRESIMS spectrum of walsunoid H (**8**)

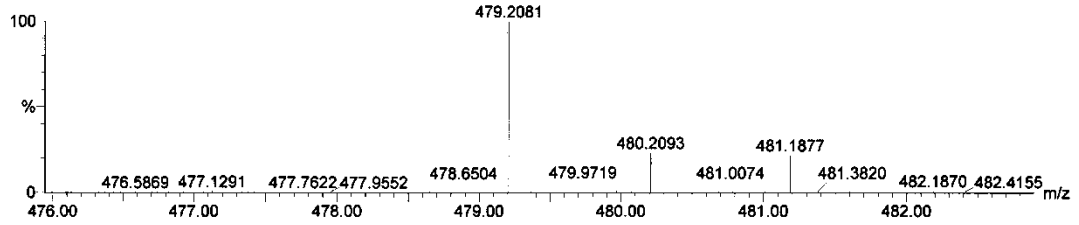
Elemental Composition Report **Page 1**

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

wrr28_20150611 15 (0.317) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (7:20) 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**)

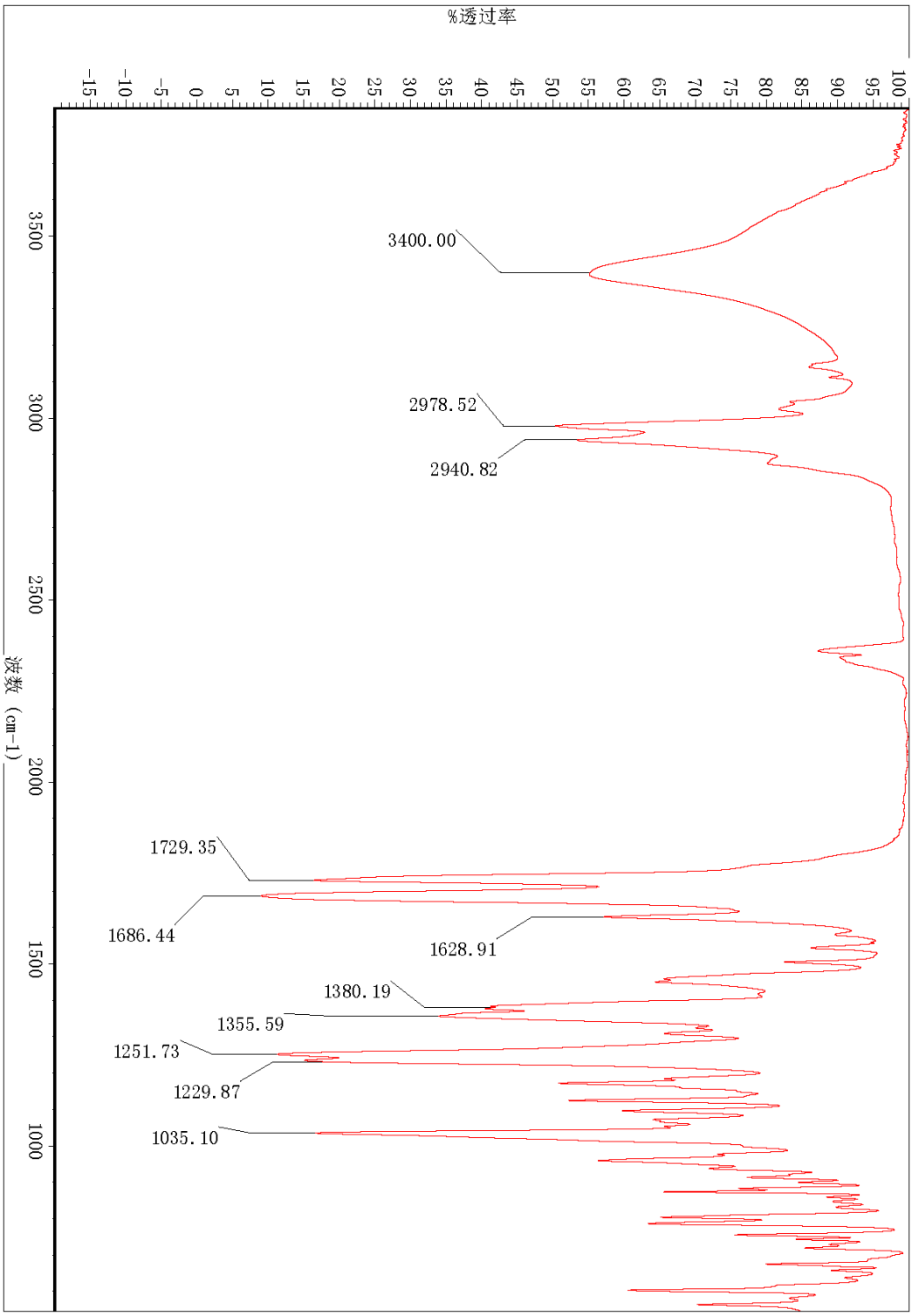


Figure S75. ^{1}H NMR spectrum of walsunoid I (**9**) in $CDCl_3$

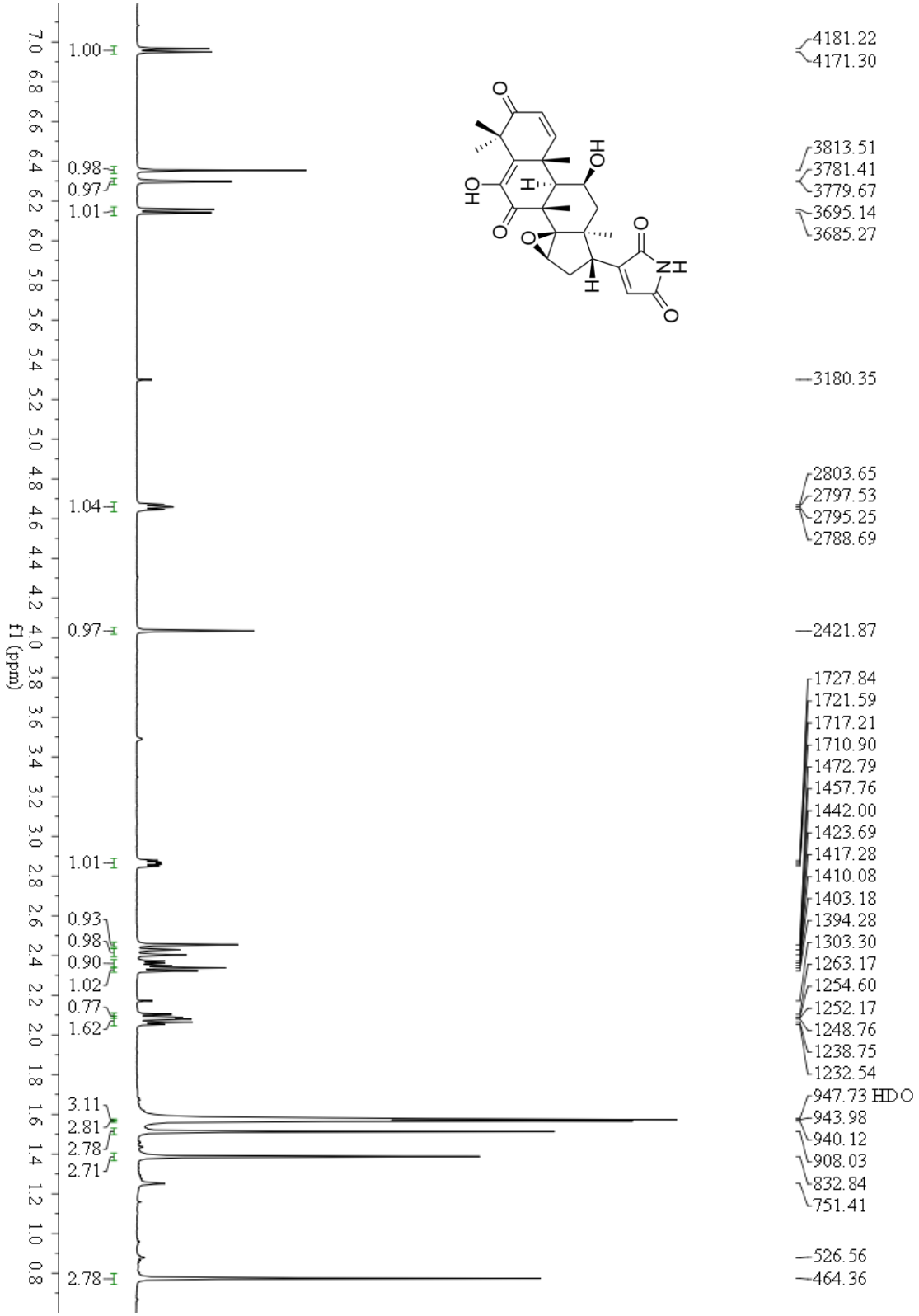


Figure S76. ^{13}C NMR spectrum of walsunoid I (**9**) in $CDCl_3$

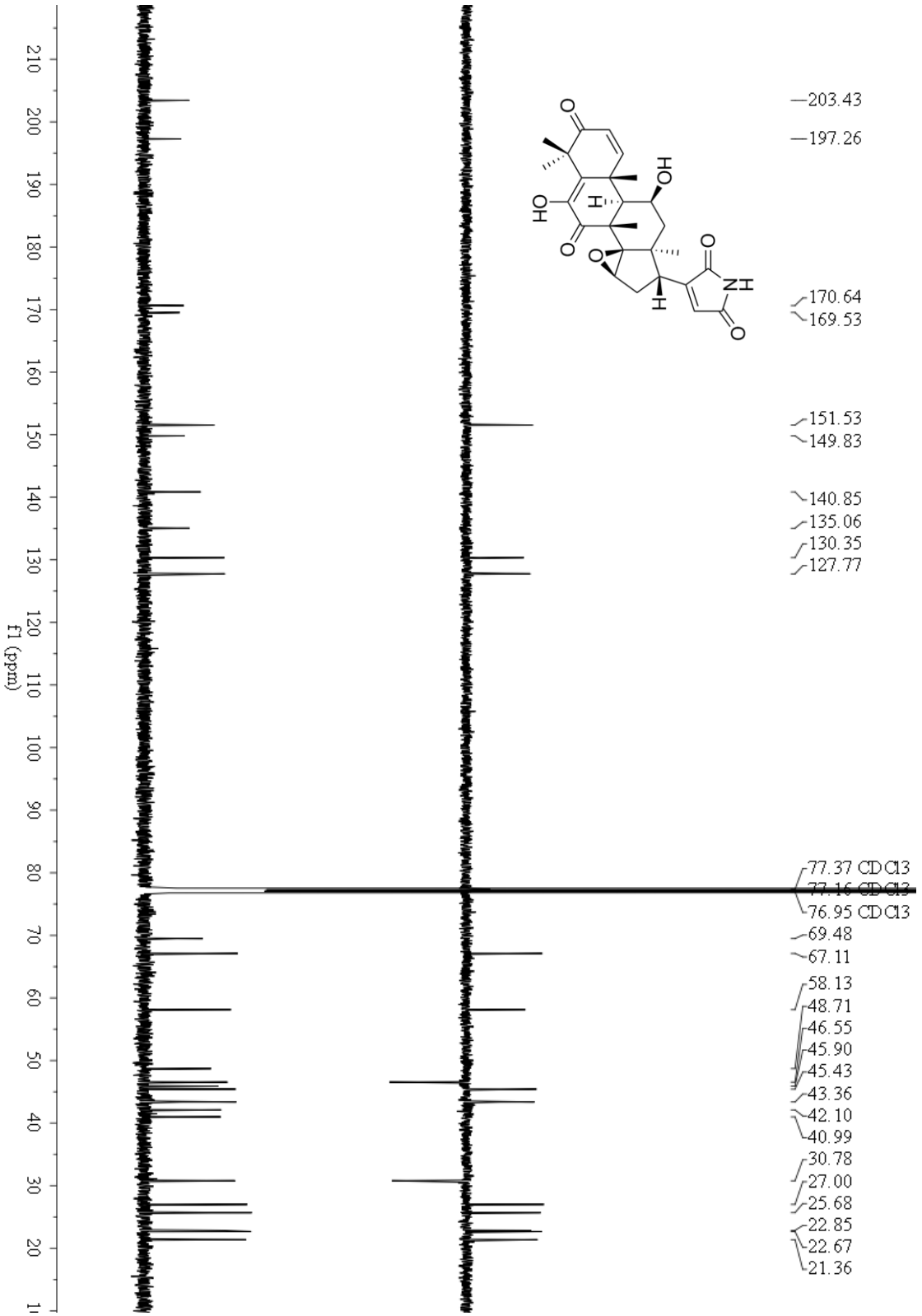


Figure S77. HSQC spectrum of walsunoid I (**9**) in $CDCl_3$

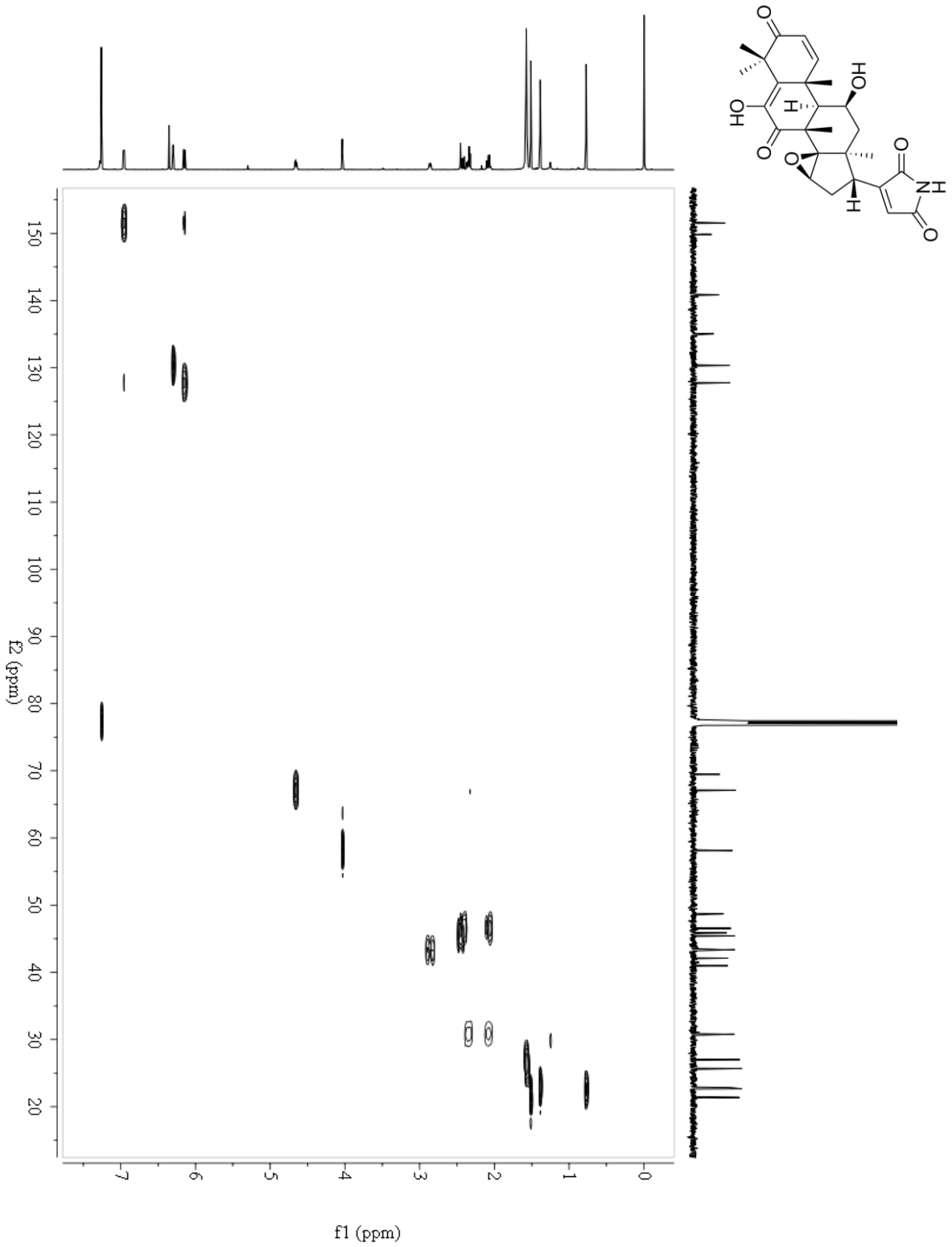


Figure S78. HMBC spectrum of walsunoid I (**9**) in $CDCl_3$

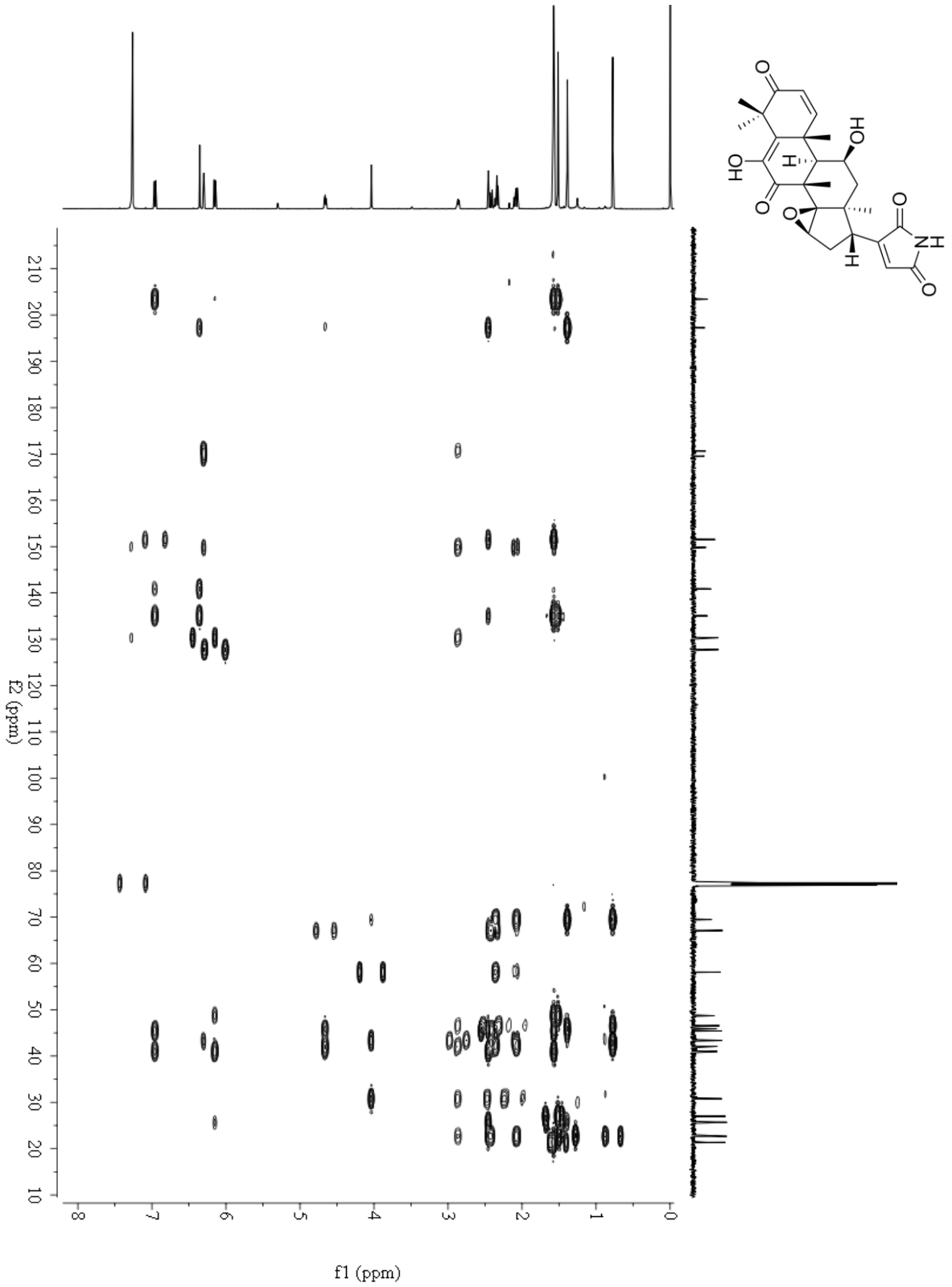


Figure S79. ^{1}H-^{1}H COSY spectrum of walsunoid I (**9**) in $CDCl_3$

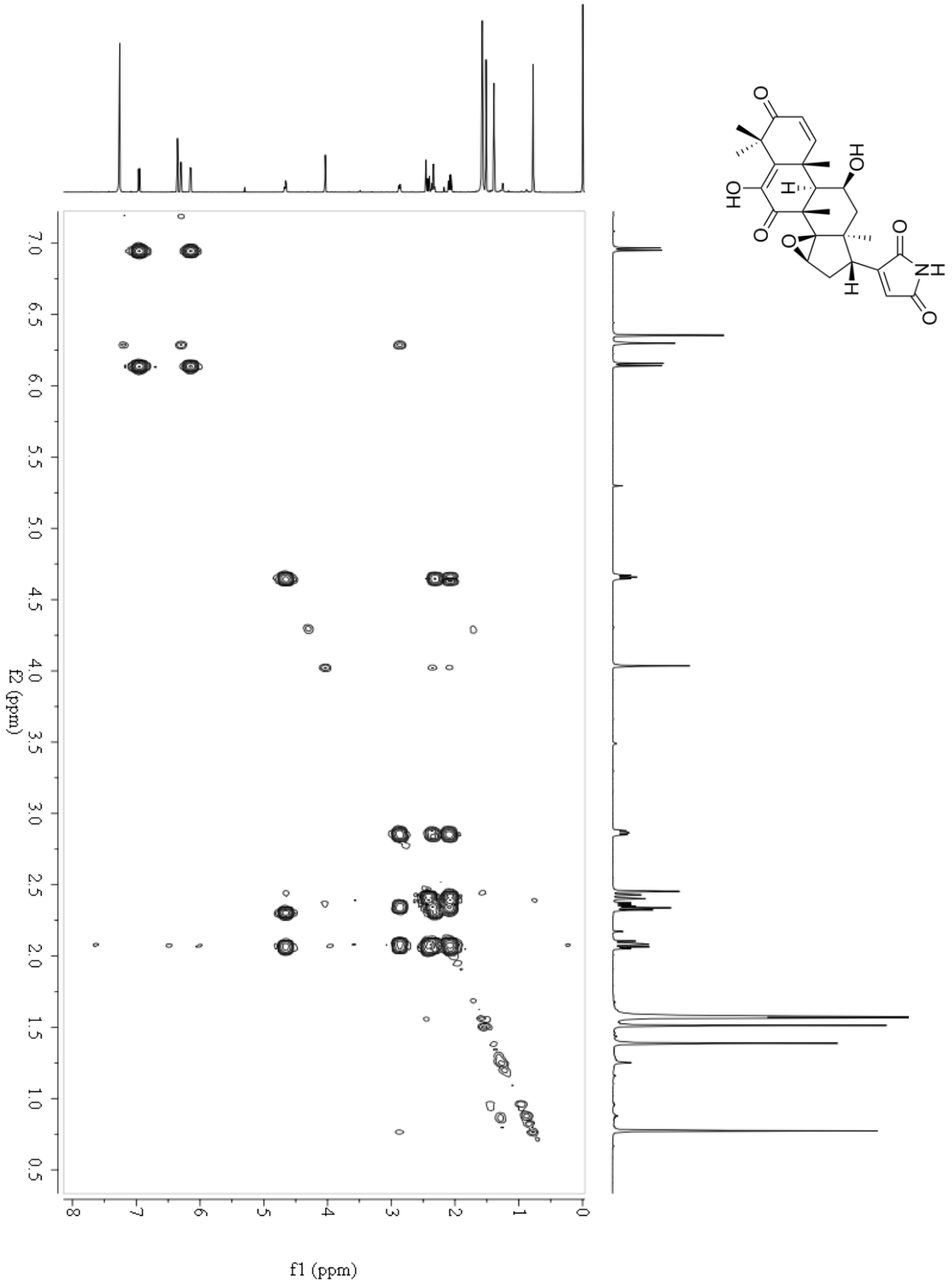


Figure S80. NOESY spectrum of walsunoid I (**9**) in $CDCl_3$

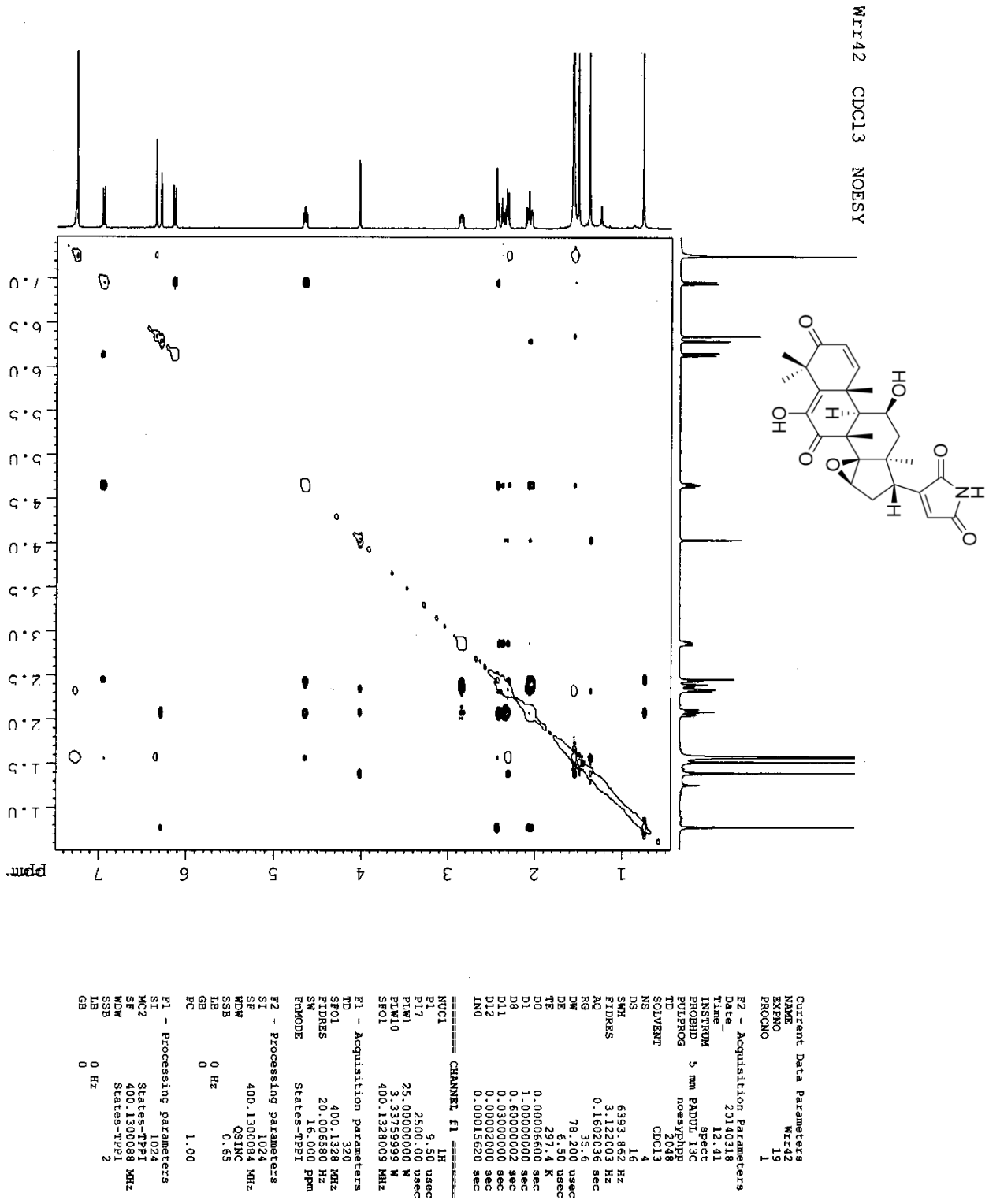


Figure S81. (+)-ESIMS spectrum of walsunoid I (**9**)

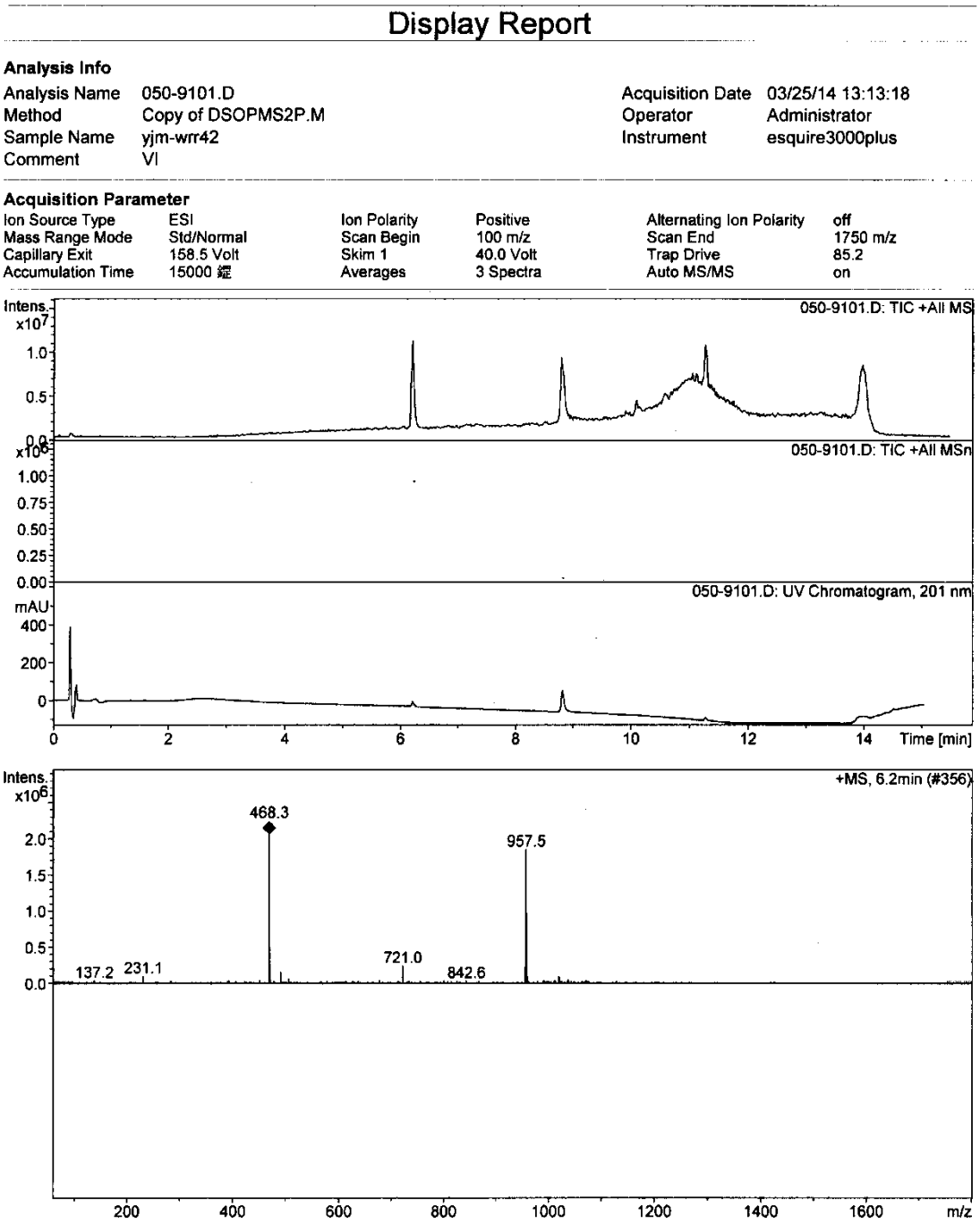


Figure S82. (–)-ESIMS spectrum of walsunoid I (**9**)

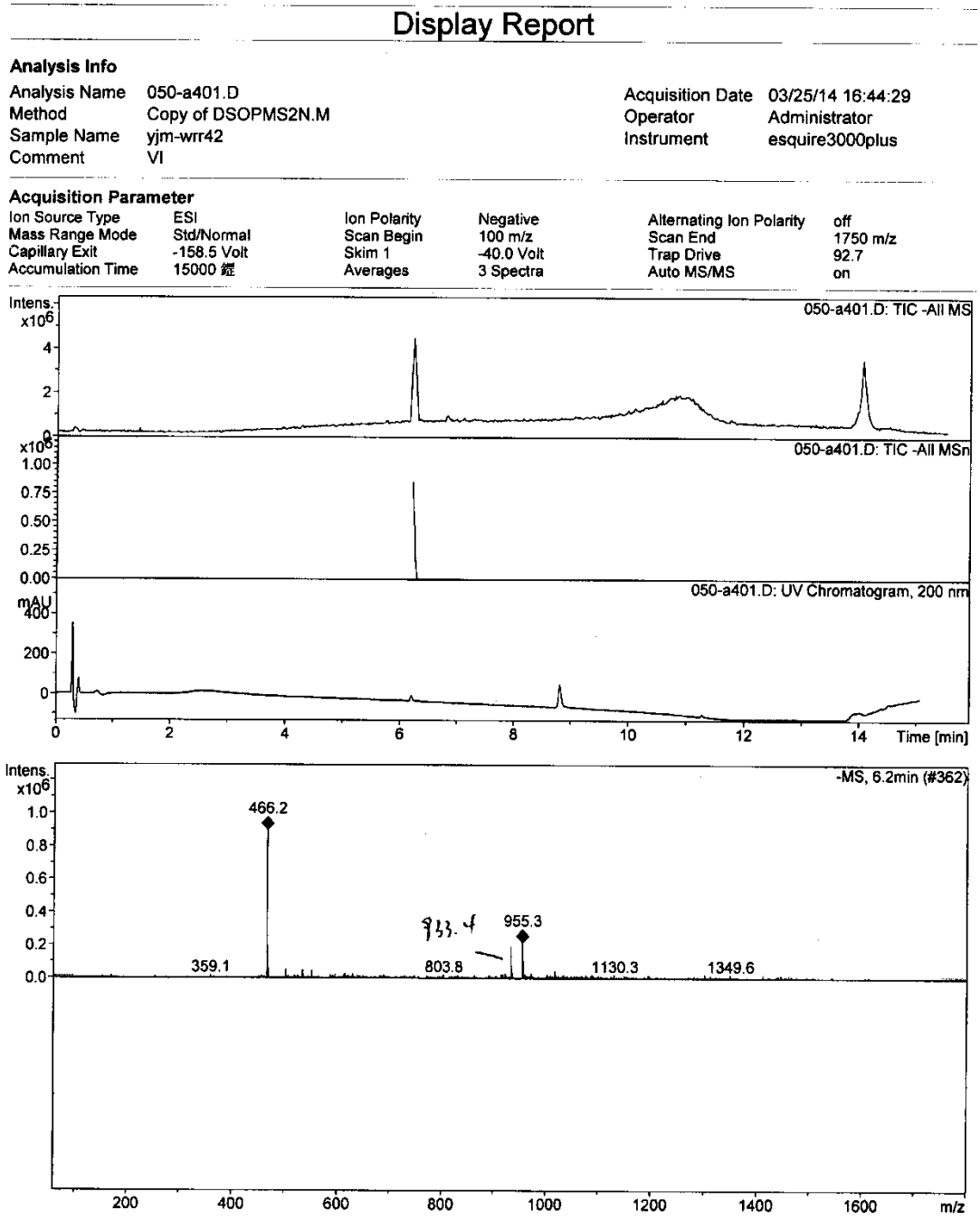


Figure S83. (–)-HRESIMS spectrum of walsunoid I (**9**)

Elemental Composition Report **Page 1**

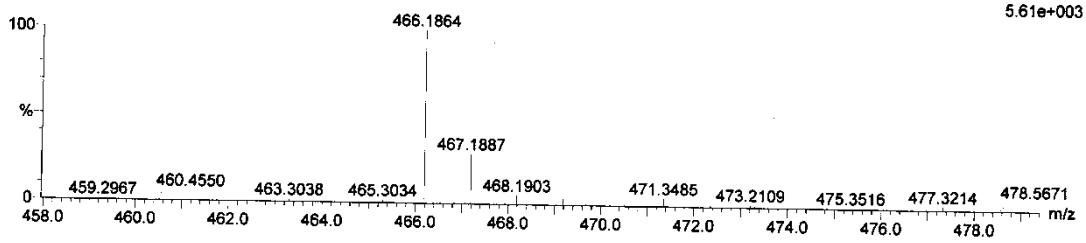
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

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:				-1.5			
Maximum:		5.0	5.0	50.0			
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**)

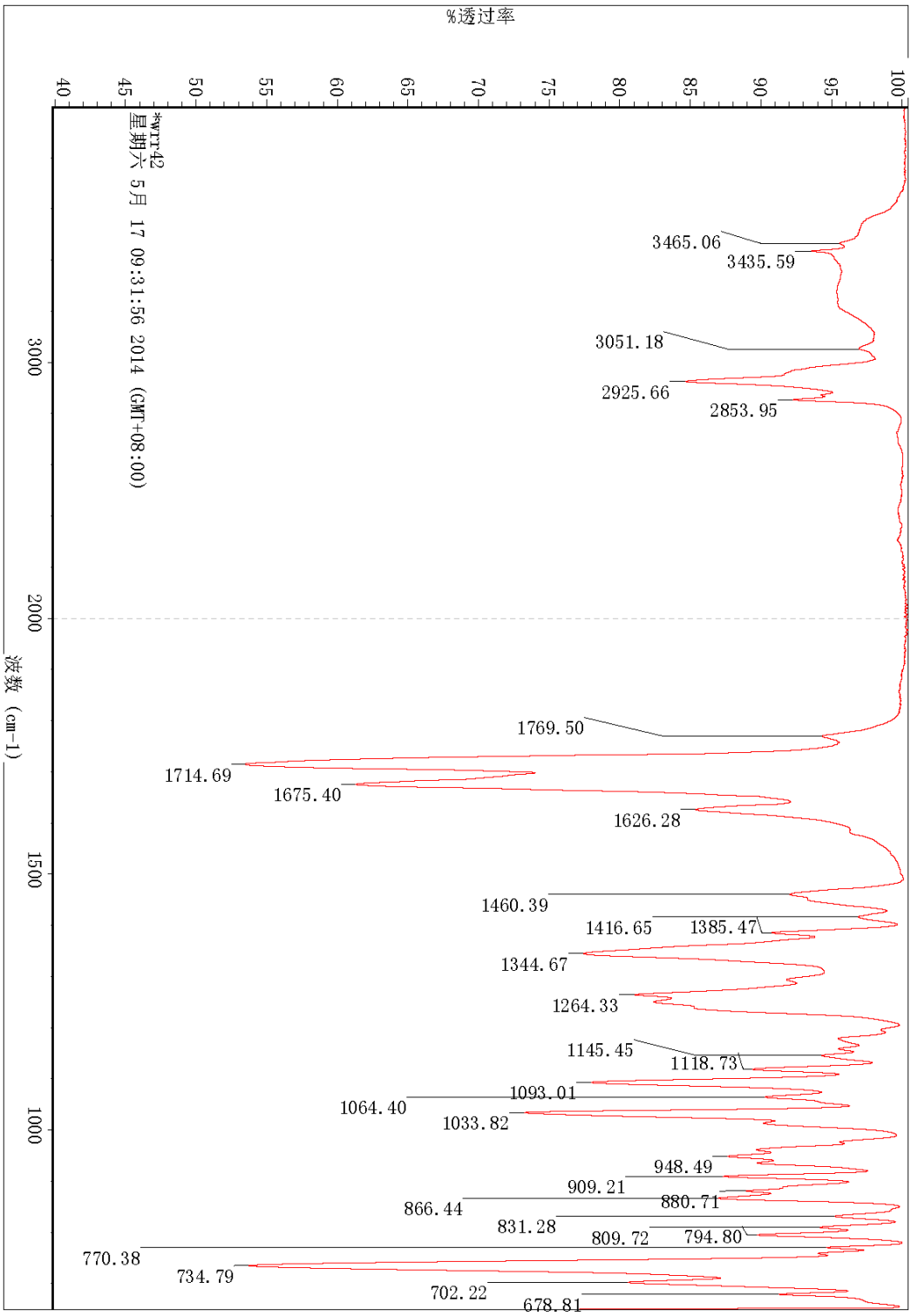


Figure S85. ^{1}H NMR spectrum of compound **10** in $CDCl_3$

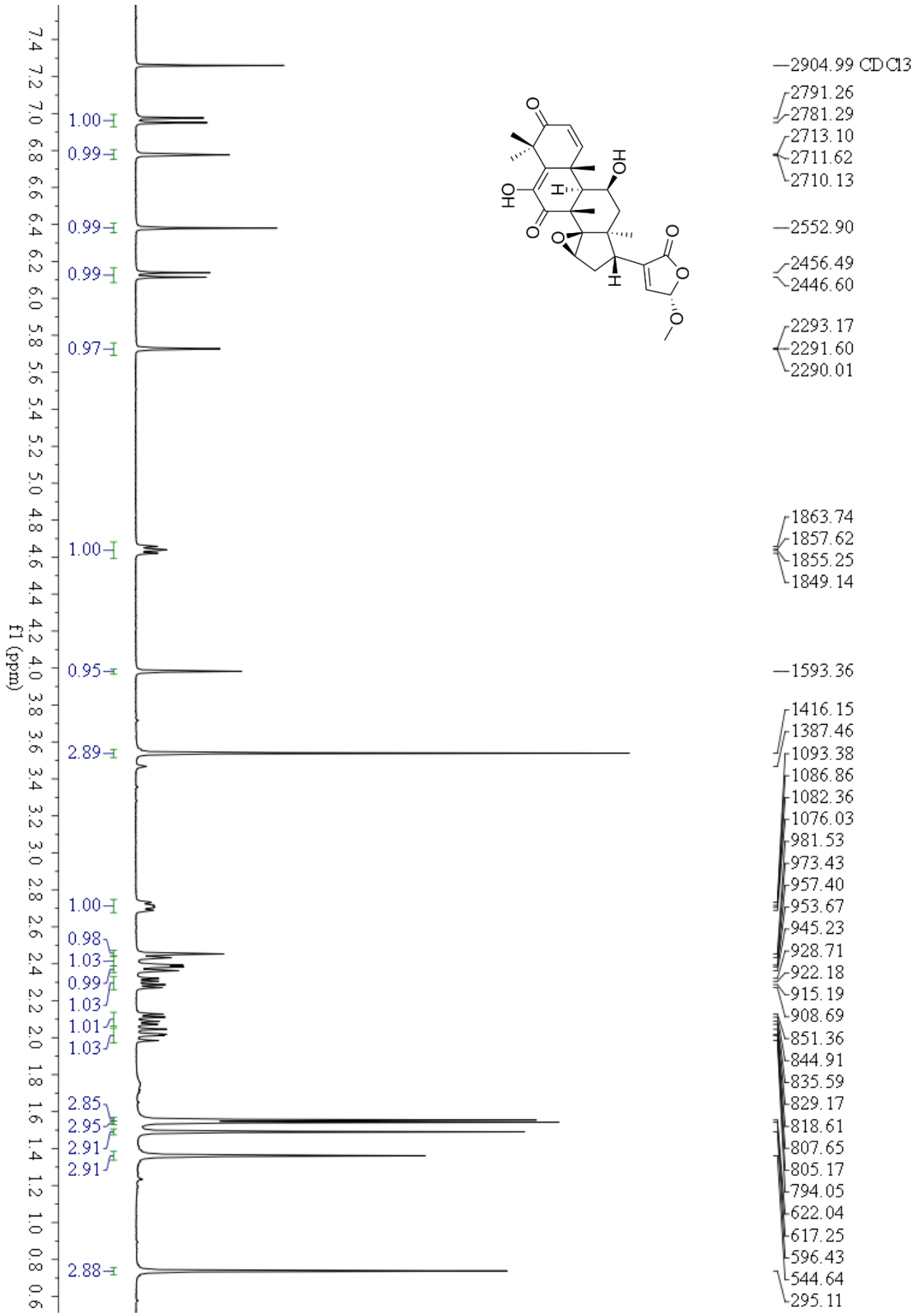


Figure S86. ^{13}C NMR spectrum of compound **10** in $CDCl_3$

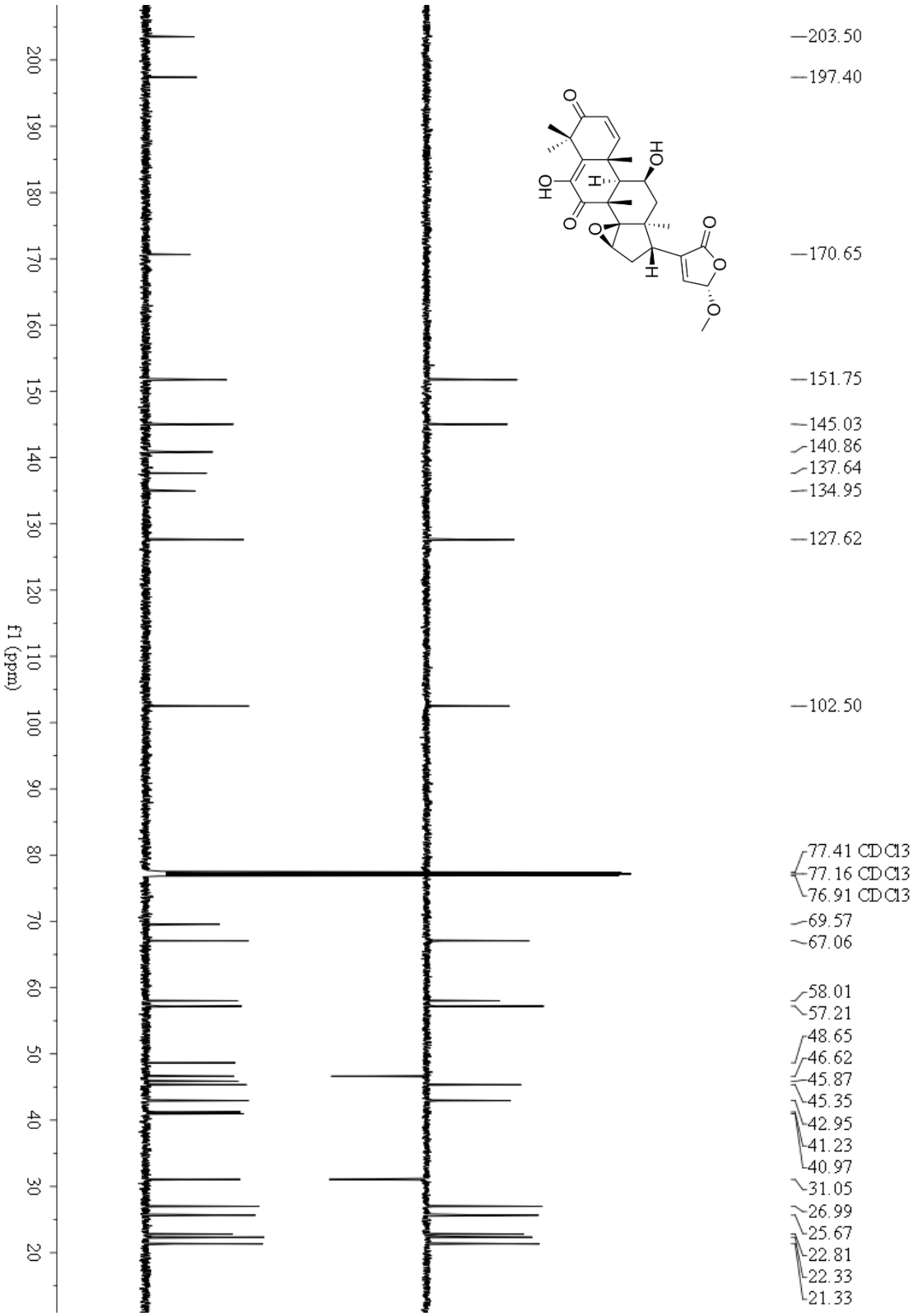


Figure S87. ^{1}H NMR spectrum of compound **10** in C_5D_5N

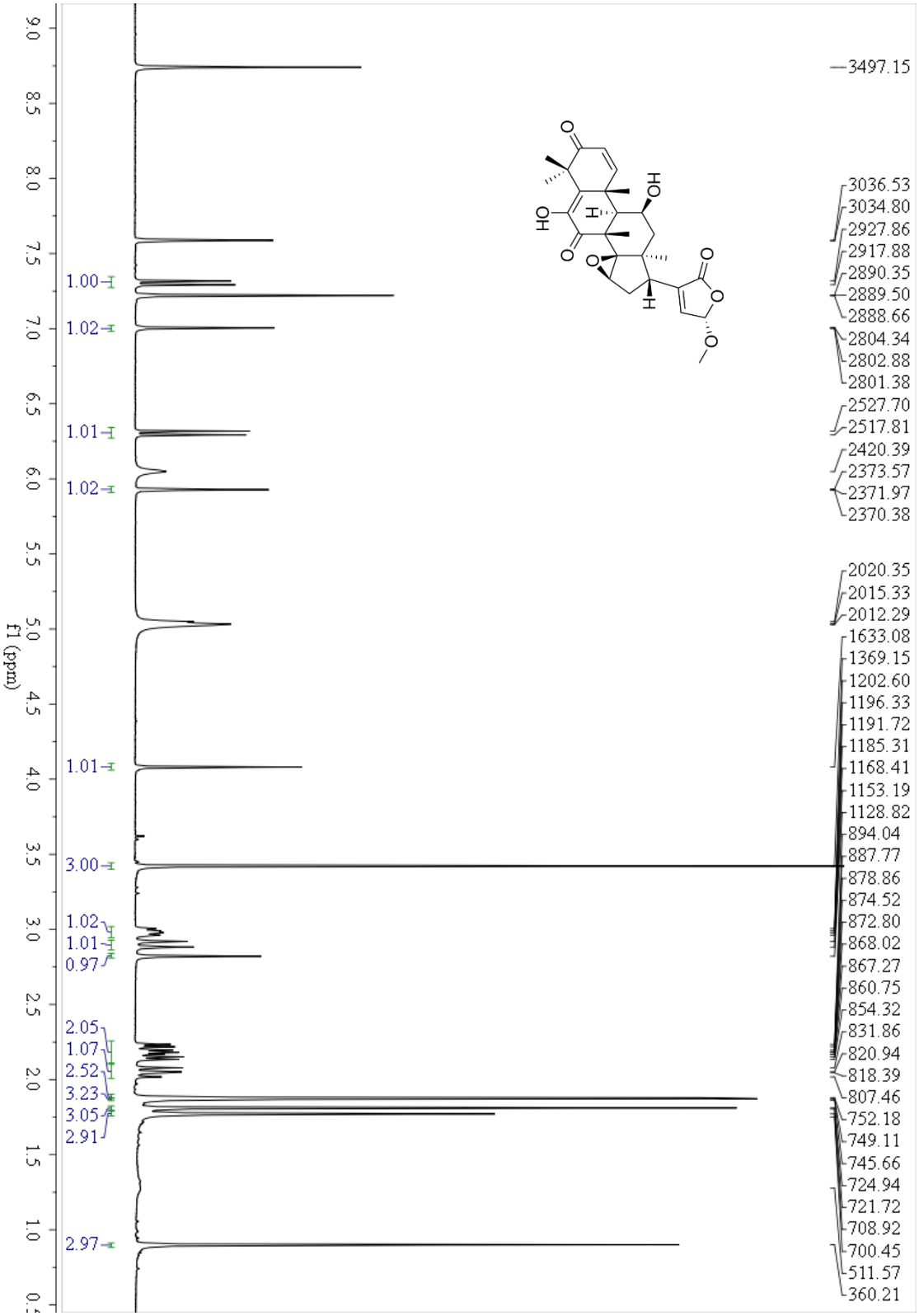


Figure S88. ^{13}C NMR spectrum of compound **10** in C_5D_5N

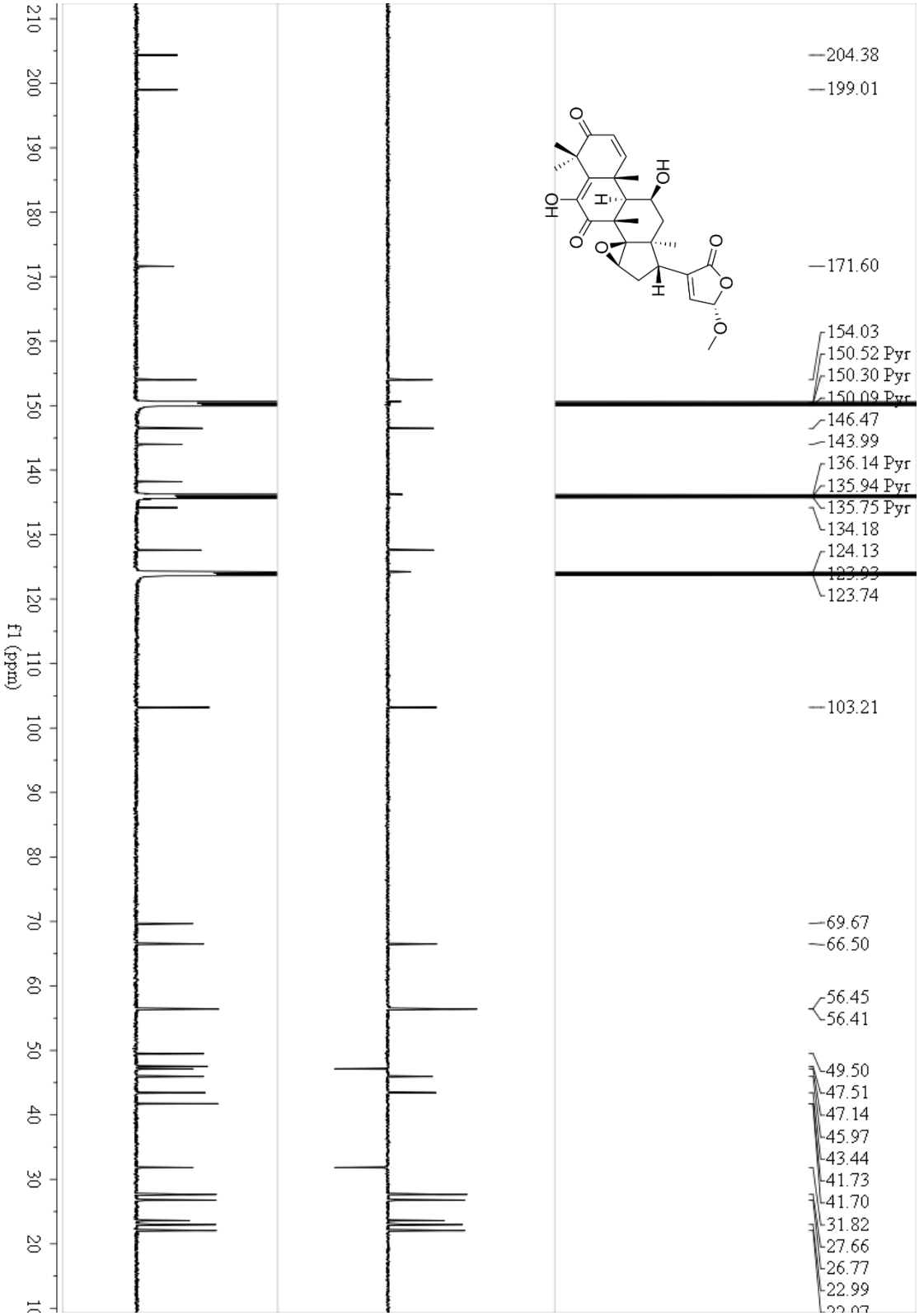


Figure S89. HSQC spectrum of compound **10** in $CDCl_3$

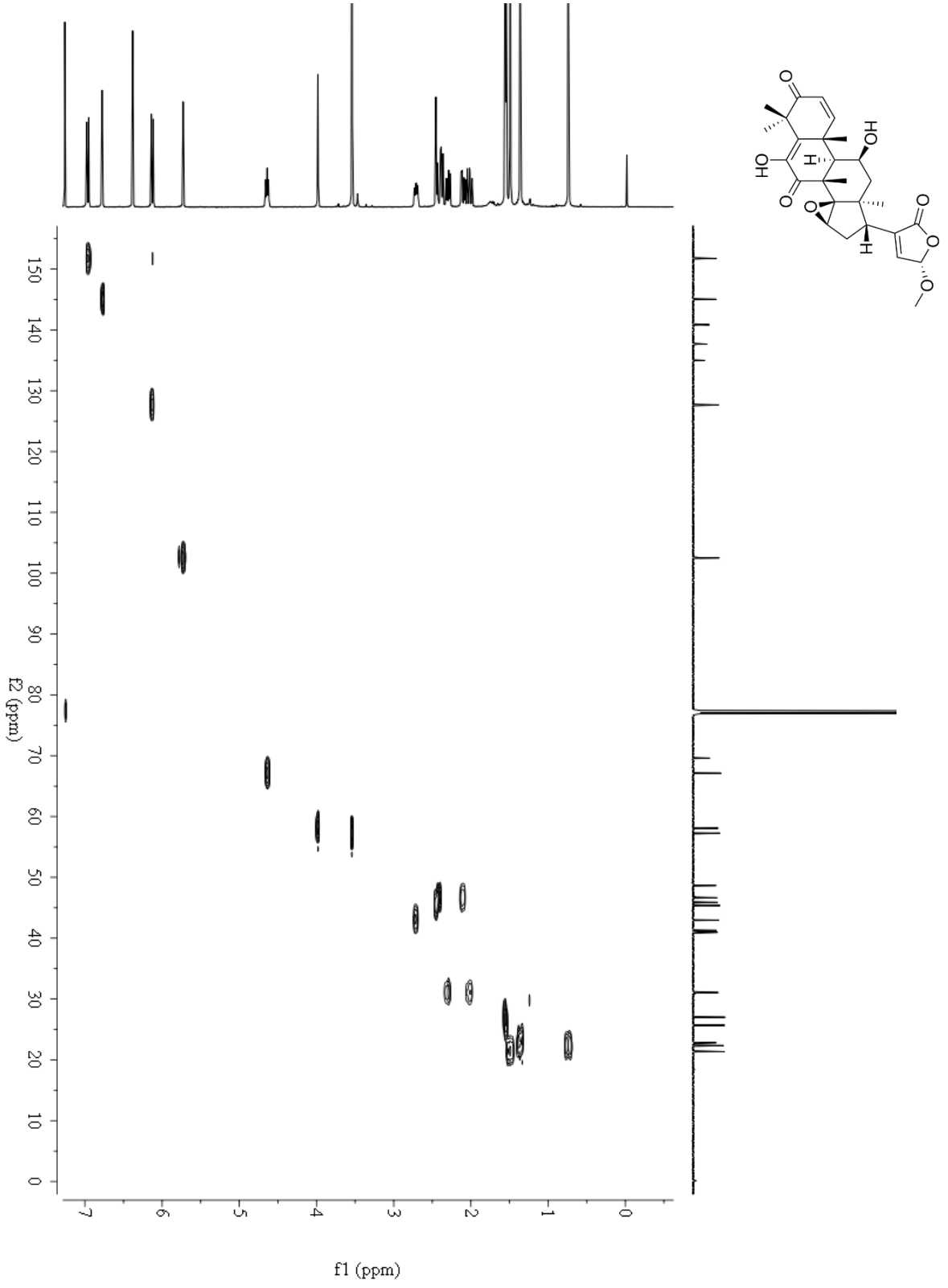


Figure S90. HMBC spectrum of compound **10** in $CDCl_3$

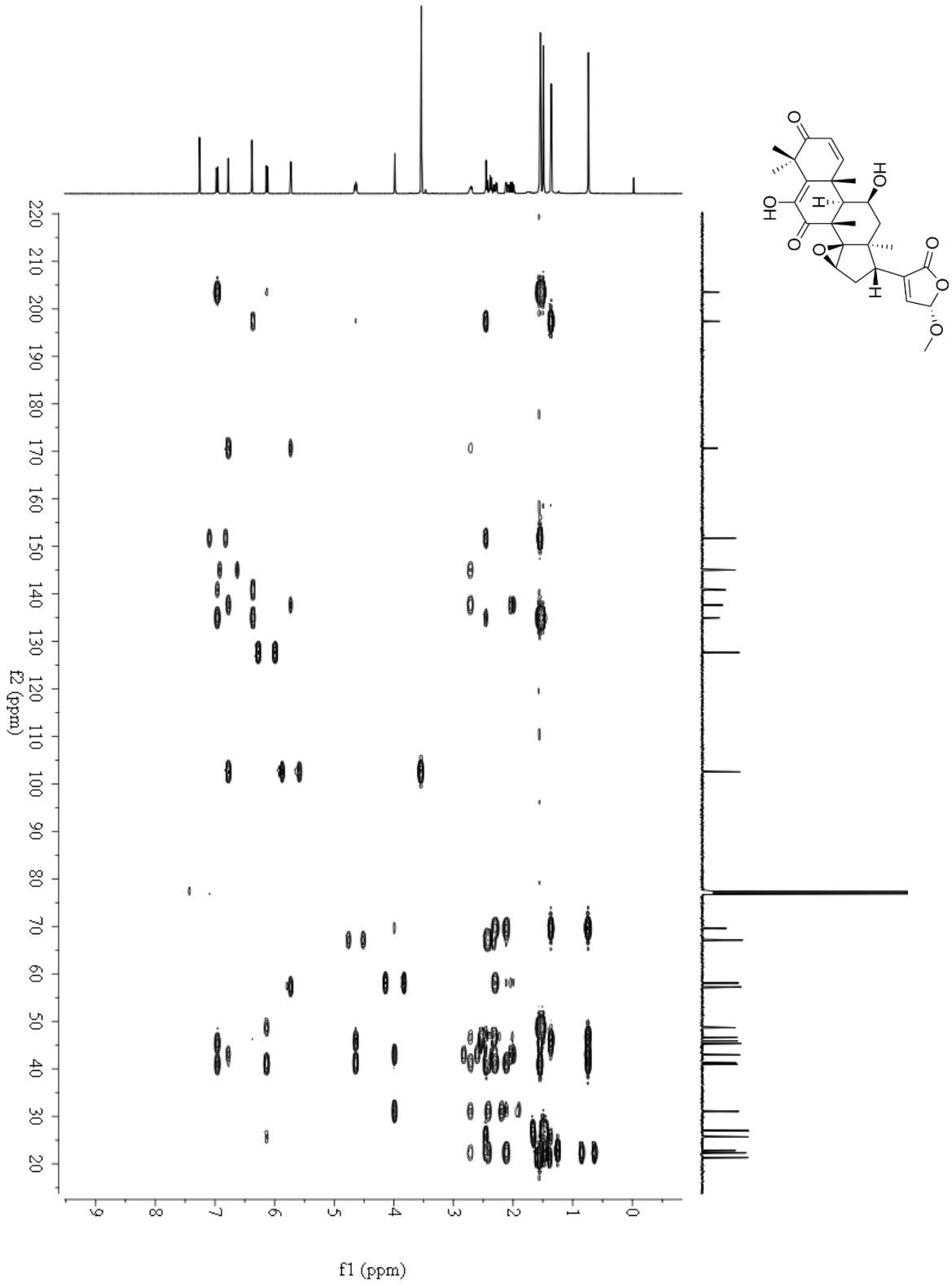


Figure S91. (–)-HRESIMS spectrum of **10**

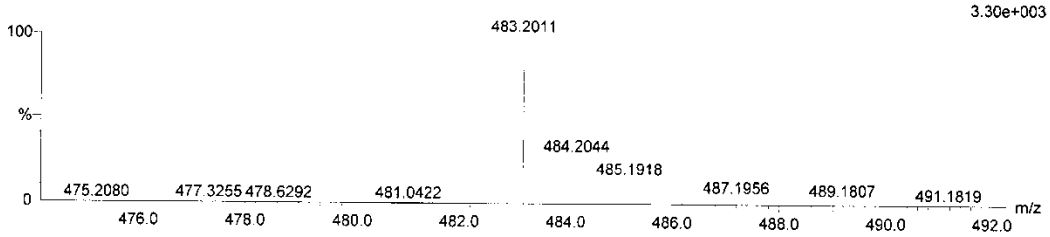
Elemental Composition Report **Page 1**

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

wrr32_0403 18 (0.372) AM2 (Ar,13000.0,0.00,0.70); ABS; Cm (14:24) 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	-0.8	-1.7	12.5	104.0	0.0	C27 H31 O8

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

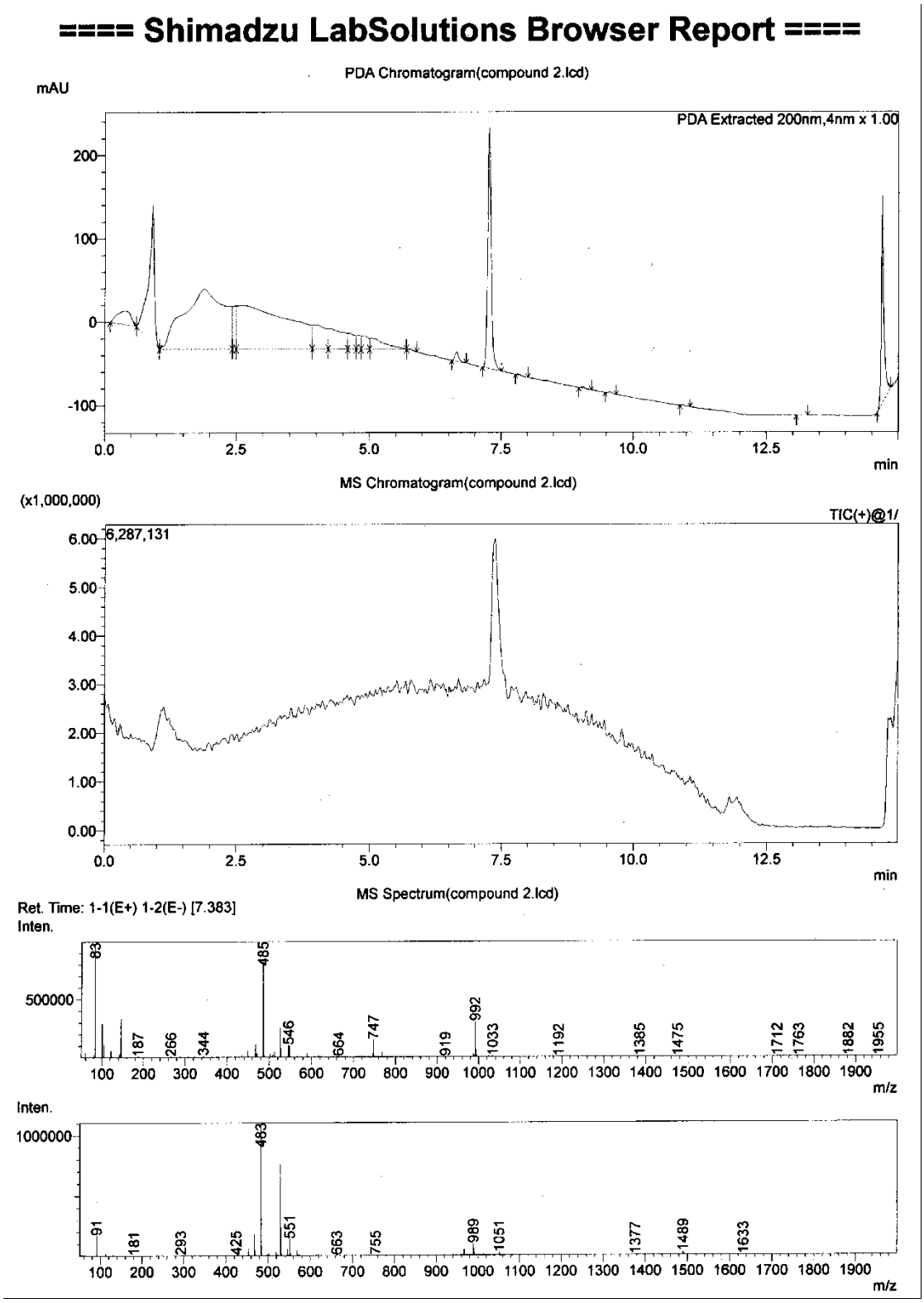


Figure S93. LC-ESI(±)MS analysis of **4**

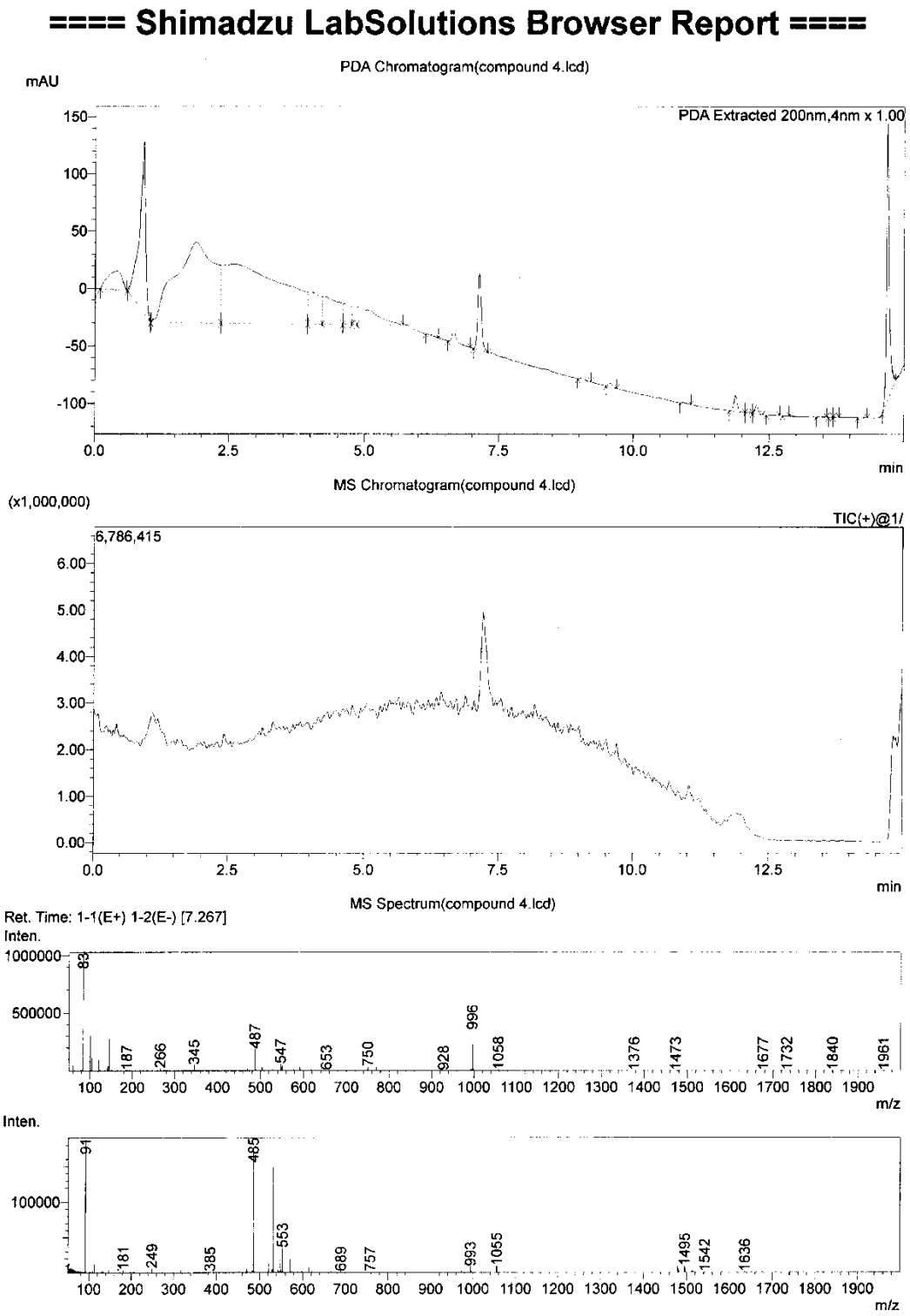


Figure S94. LC-ESI(±)MS analysis of **10**

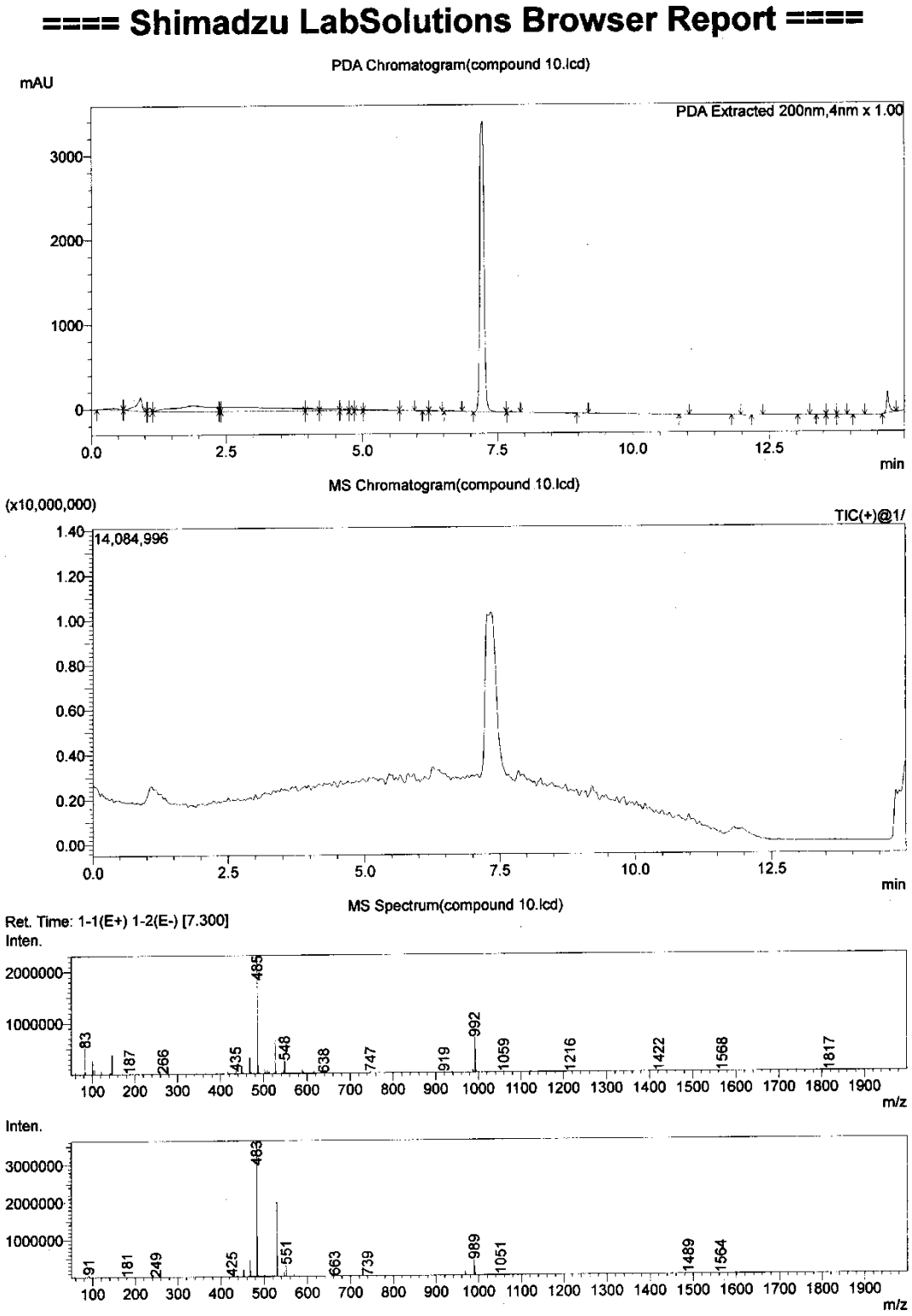


Figure S95. LC-ESI(±)MS analysis of ethanolic crude extract