Electronic Supplementary Information (ESI)

Diterpenoids from the shed trunk barks of the endangered plant *Pinus dabeshanensis* and their PTP1B inhibitory effects

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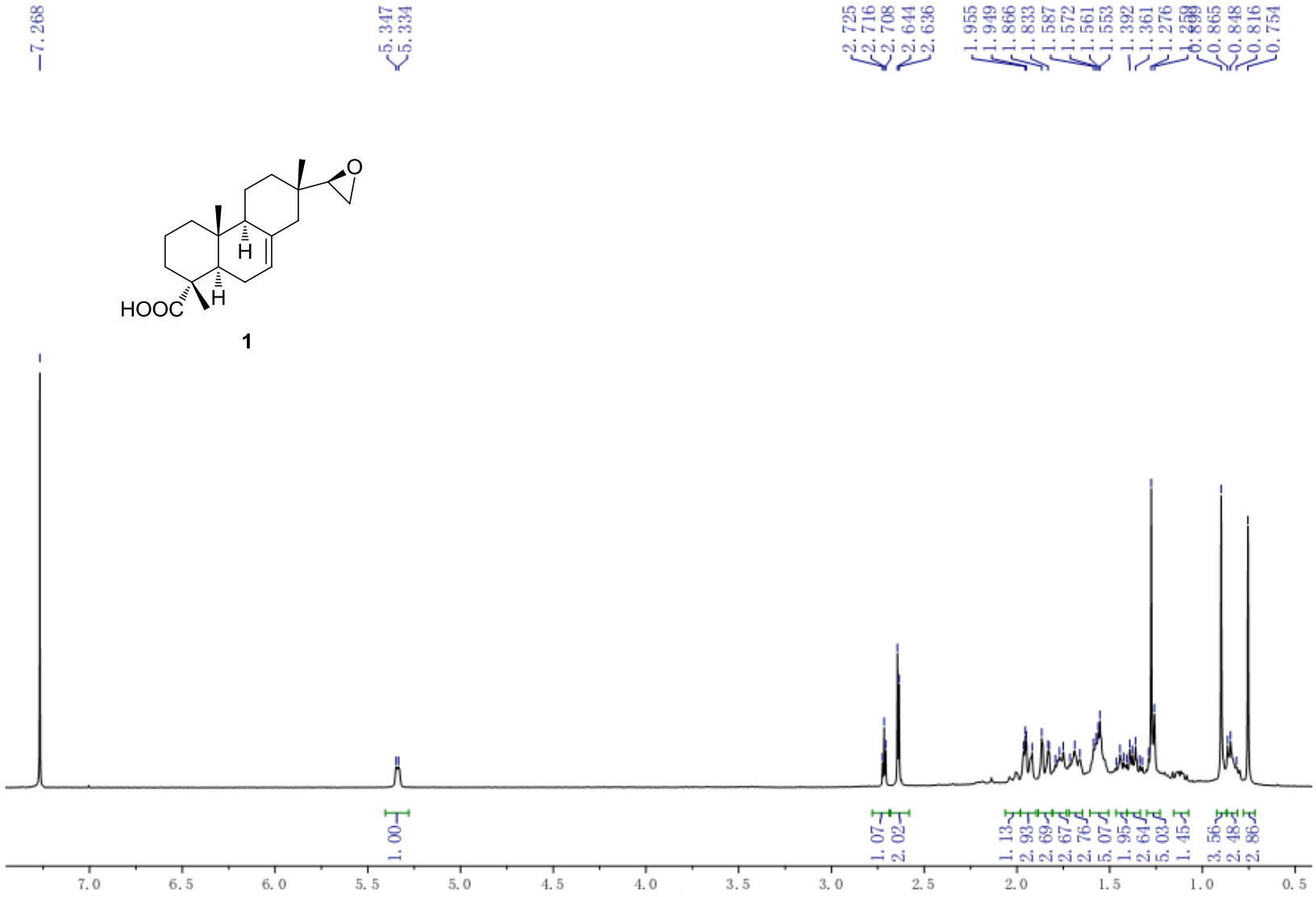
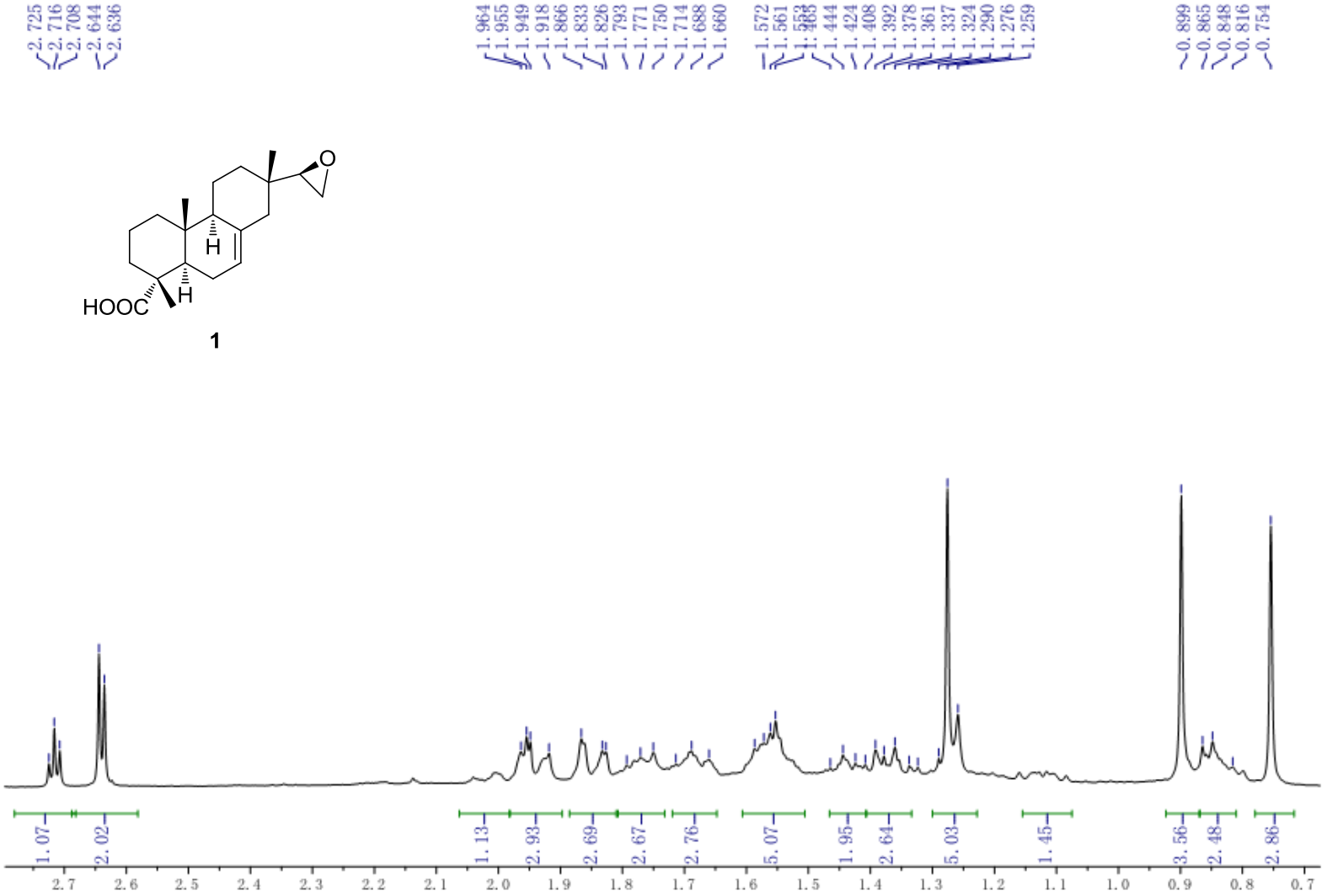
[‡] These authors have contributed equally to this work.

Contents

Compound 1: ^{1}H NMR ($CDCl_3$) spectrum



Compound 1: ^{1}H NMR ($CDCl_3$) spectrum-Expansion



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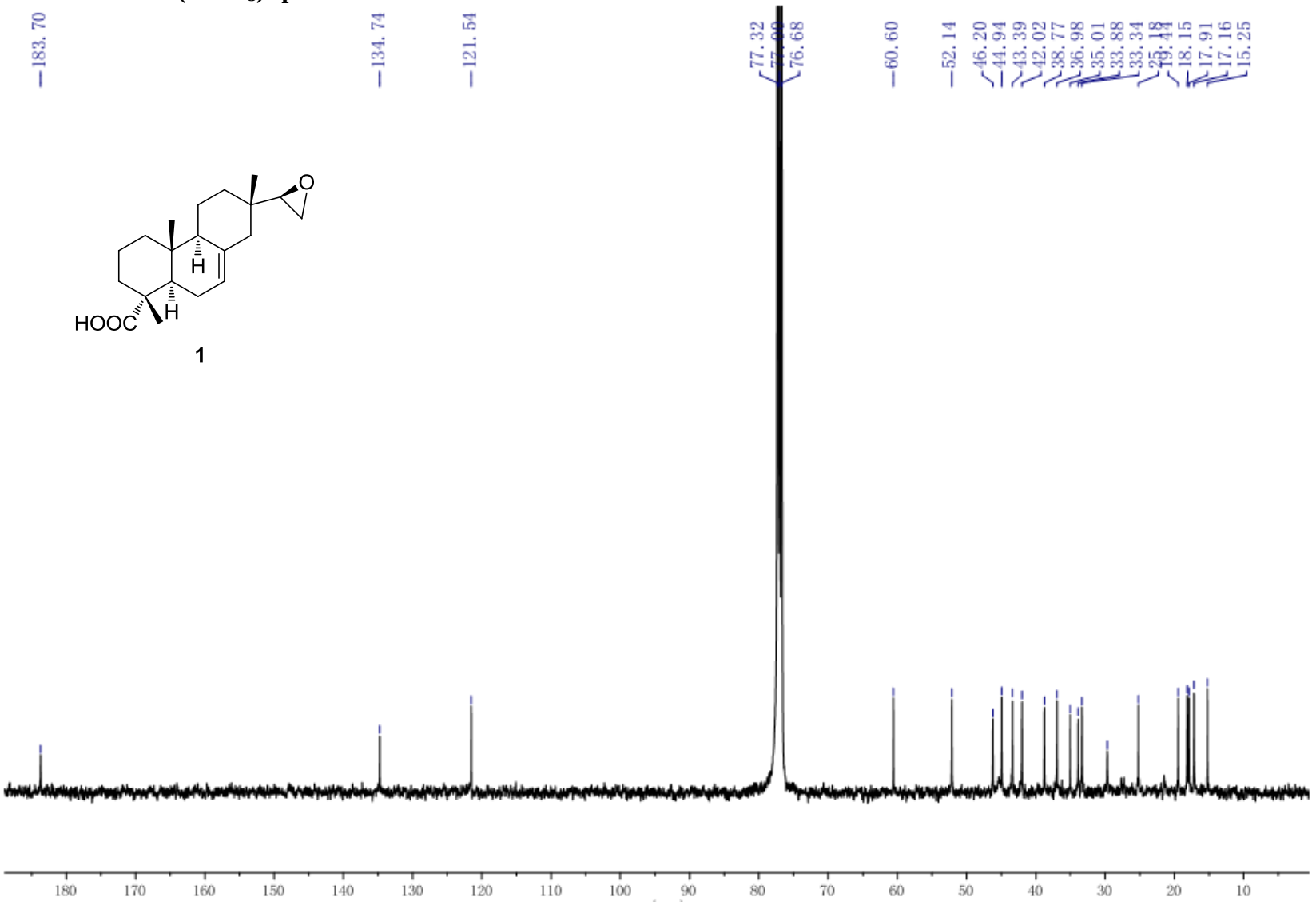
Compound 1: ^{13}C NMR ($CDCl_3$) spectrum



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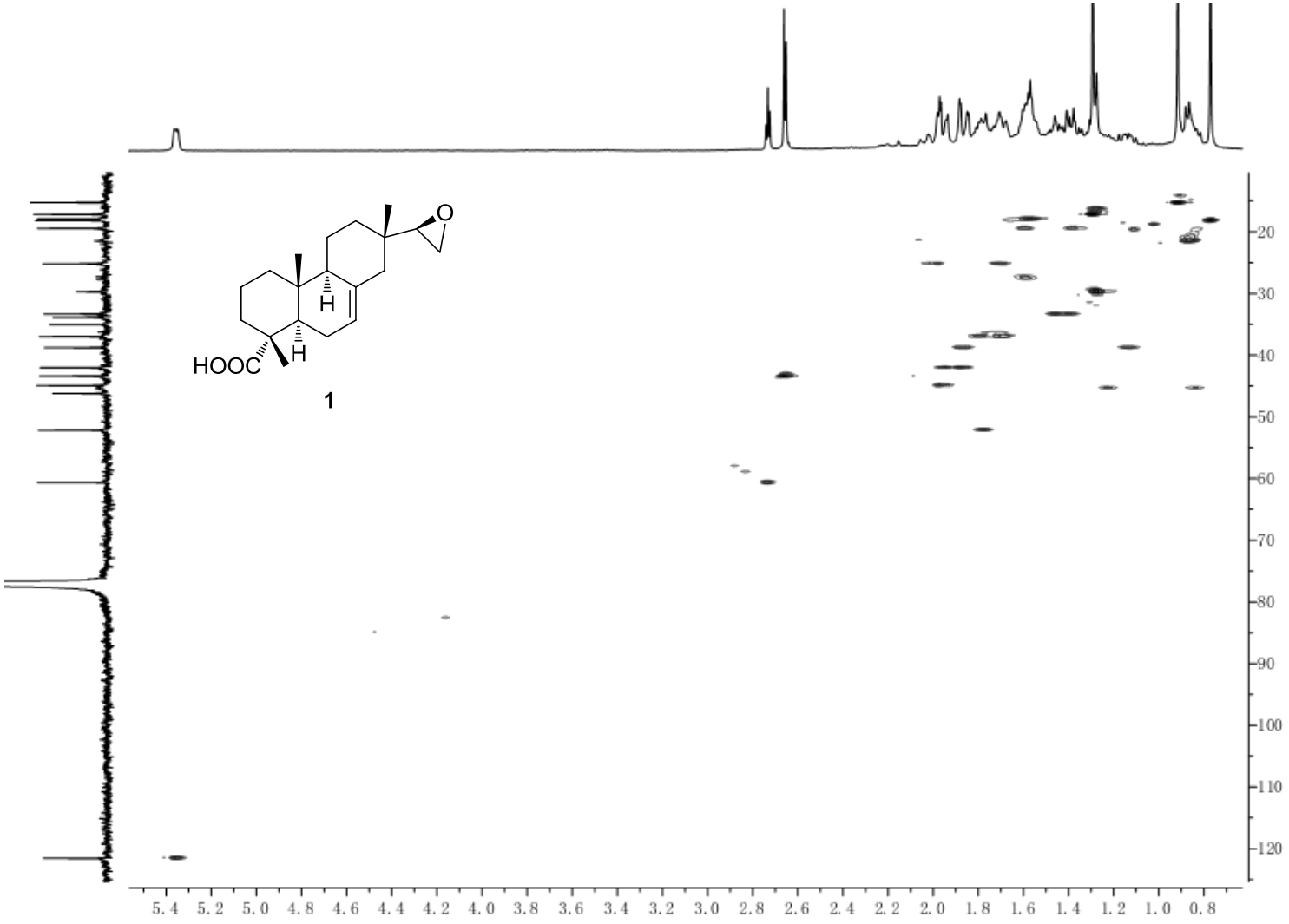
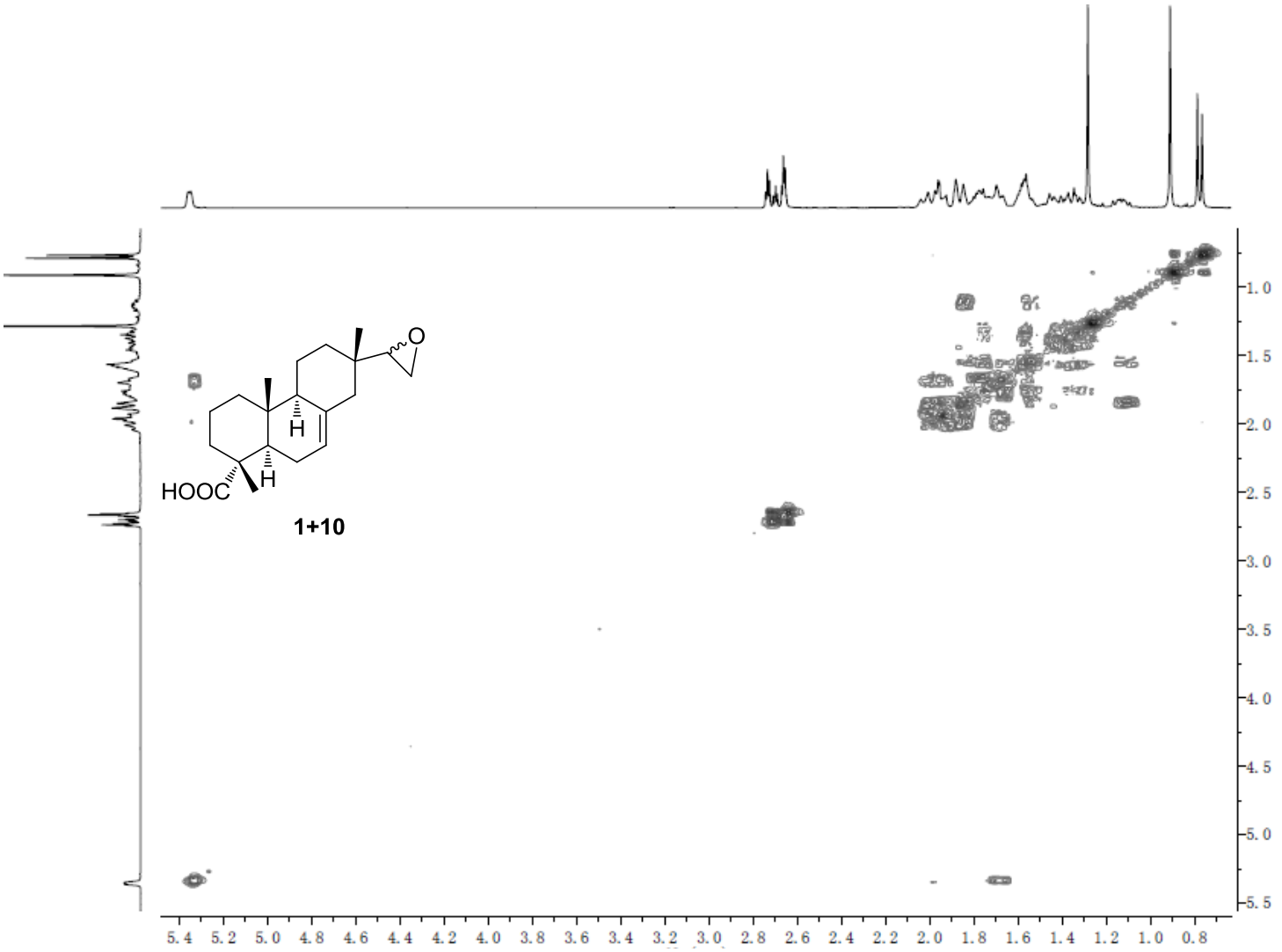
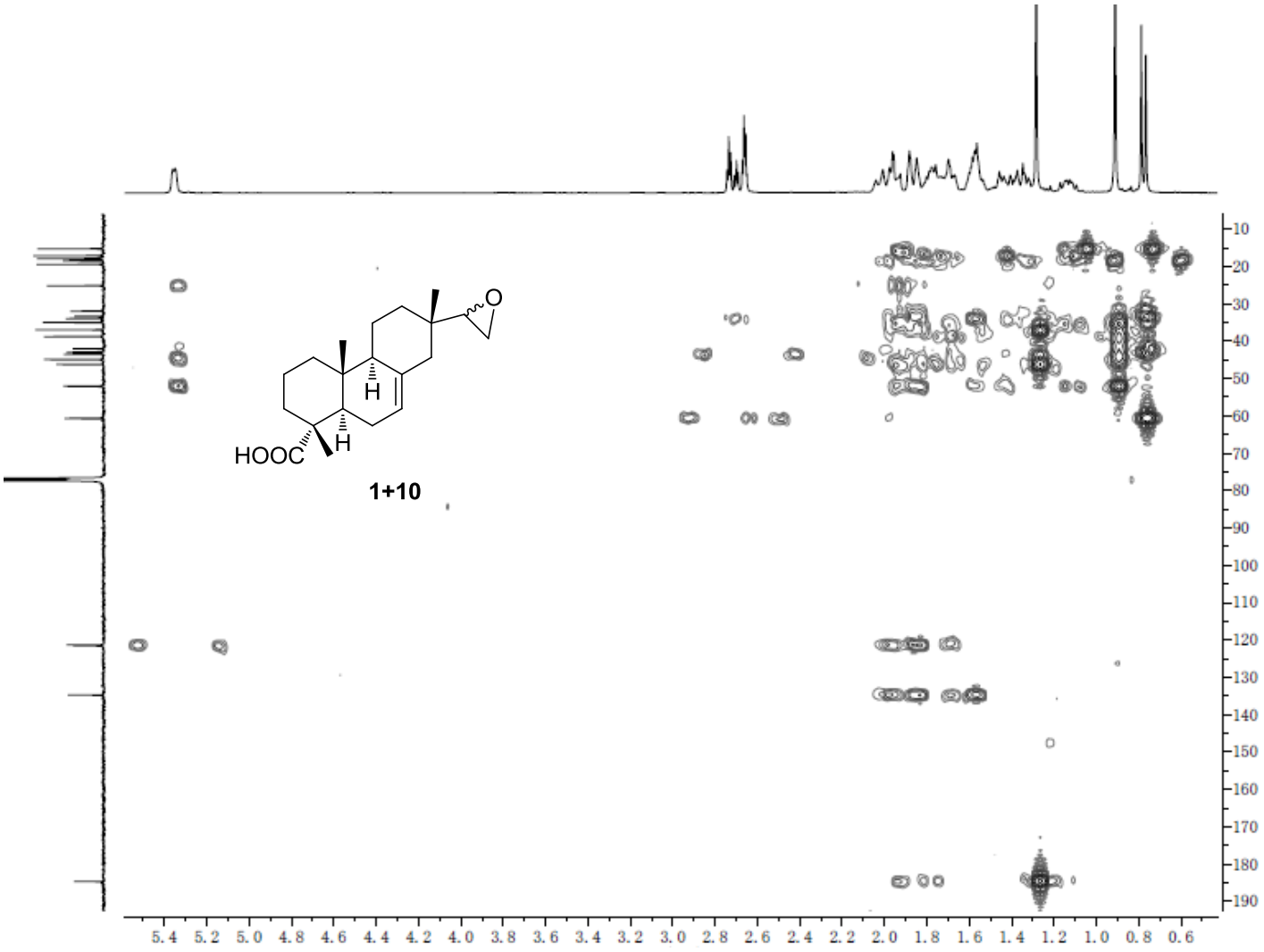
Compound 1: HSQC ($CDCl_3$) spectrum



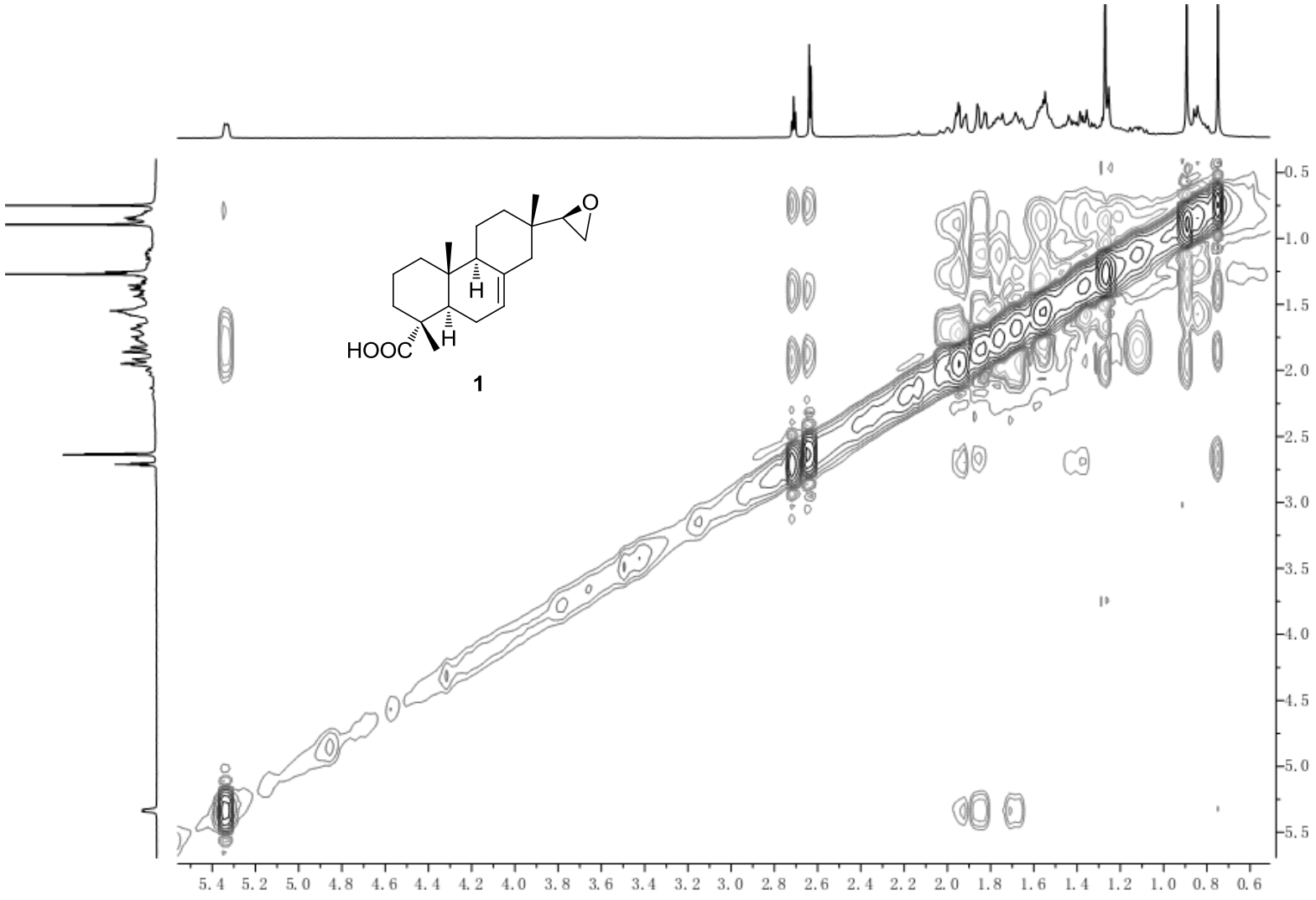
Mixture of compounds 1 and 10: ^{1}H-^{1}H COSY ($CDCl_3$) spectrum



Mixture of compounds 1 and 10: HMBC ($CDCl_3$) spectrum



Compound 1: NOESY ($CDCl_3$) spectrum



Compound 1: (+) HRESIMS

Qualitative Analysis Report

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Acq Method	general test 2.m	**Acquired Time**	12/19/2013 5:23:04 PM
IRM Calibration Status	Some Ions Missed	**DA Method**	Screening-Default.m
Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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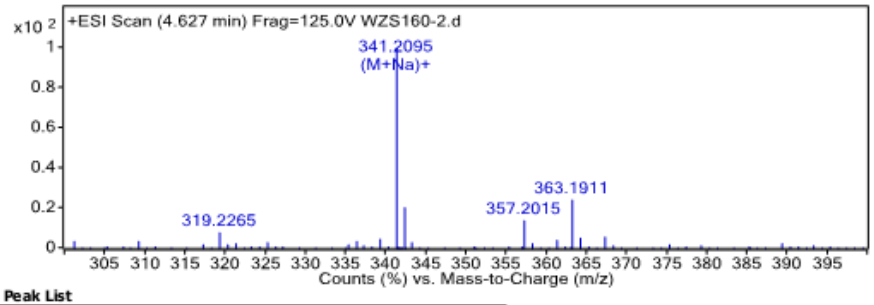


Peak List

m/z	z	Abund	Formula	Ion
341.2095	1	630460	C20 H30 Na O3	(M+Na)+

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H30 O3	TRUE	318.2203	318.2195	-2.46	C20 H30 Na O3	96.16

--- End Of Report ---

Figure S1 and Table S1. *Ab initio* density functional theory (DFT) calculations of compounds 1 and 10.

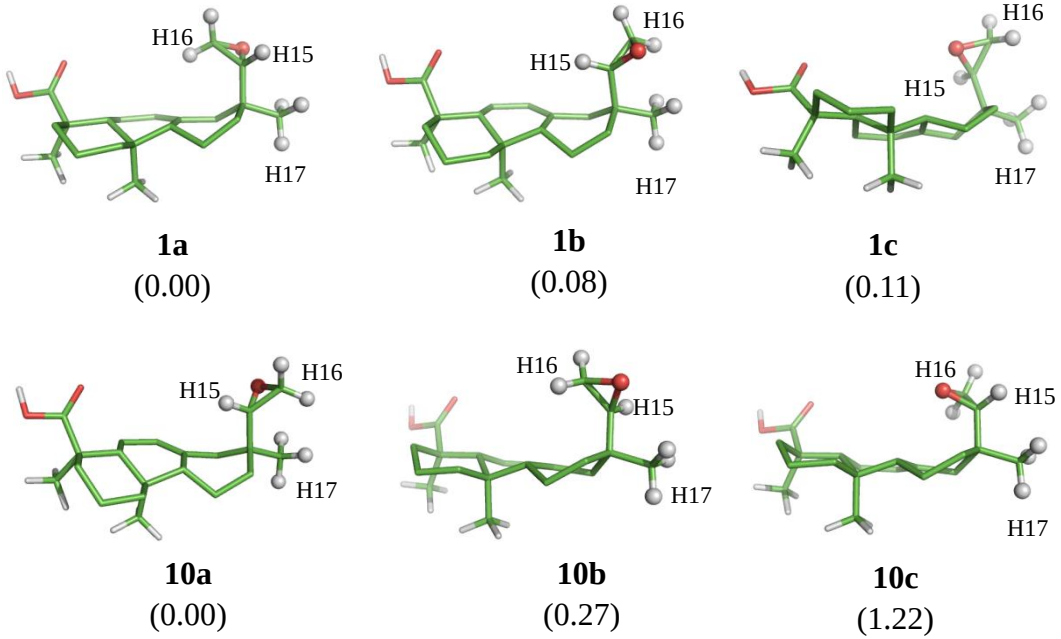


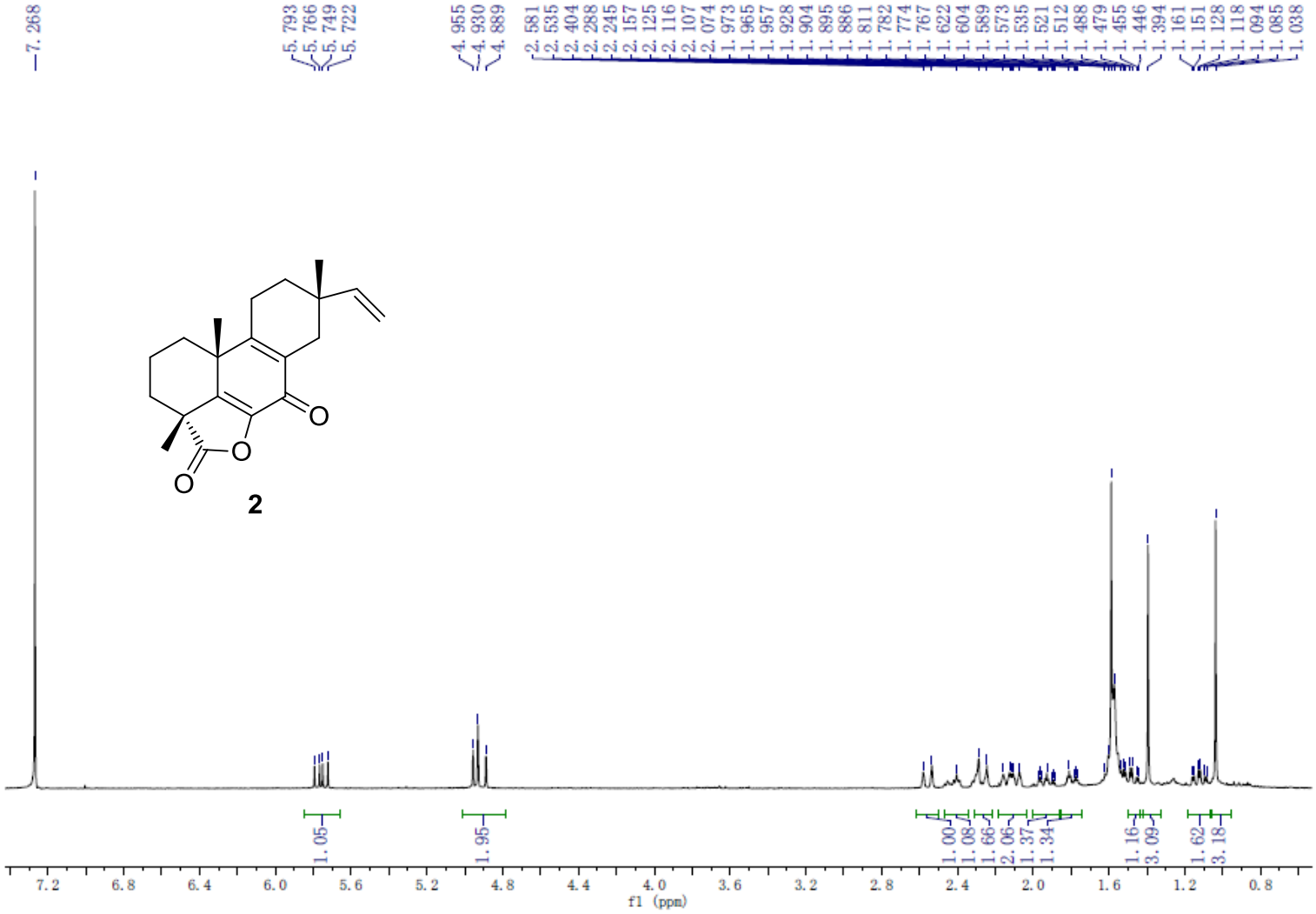
Figure S1. *Ab initio* (B3LYP/6-31G* level in the Gas Phase) optimized conformers (**1a**–**1c** and **10a**–**10c**) derived from compounds **1** and **10**. Highlighted as white spheres are those critical hydrogen atoms (H-15, H-16 and H-17) that allows us to confidently assign one of these six conformers (**1a**–**1c** and **10a**–**10c**). Shown in parenthesis is the calculated relative energy (kcal/mol) normalized against the most stable conformers **1a** and **10a**. Color code: green = carbon, white = hydrogen, red = oxygen.

Table S1. Conformation analysis of **1a**–**1c** and **10a**–**10c**.

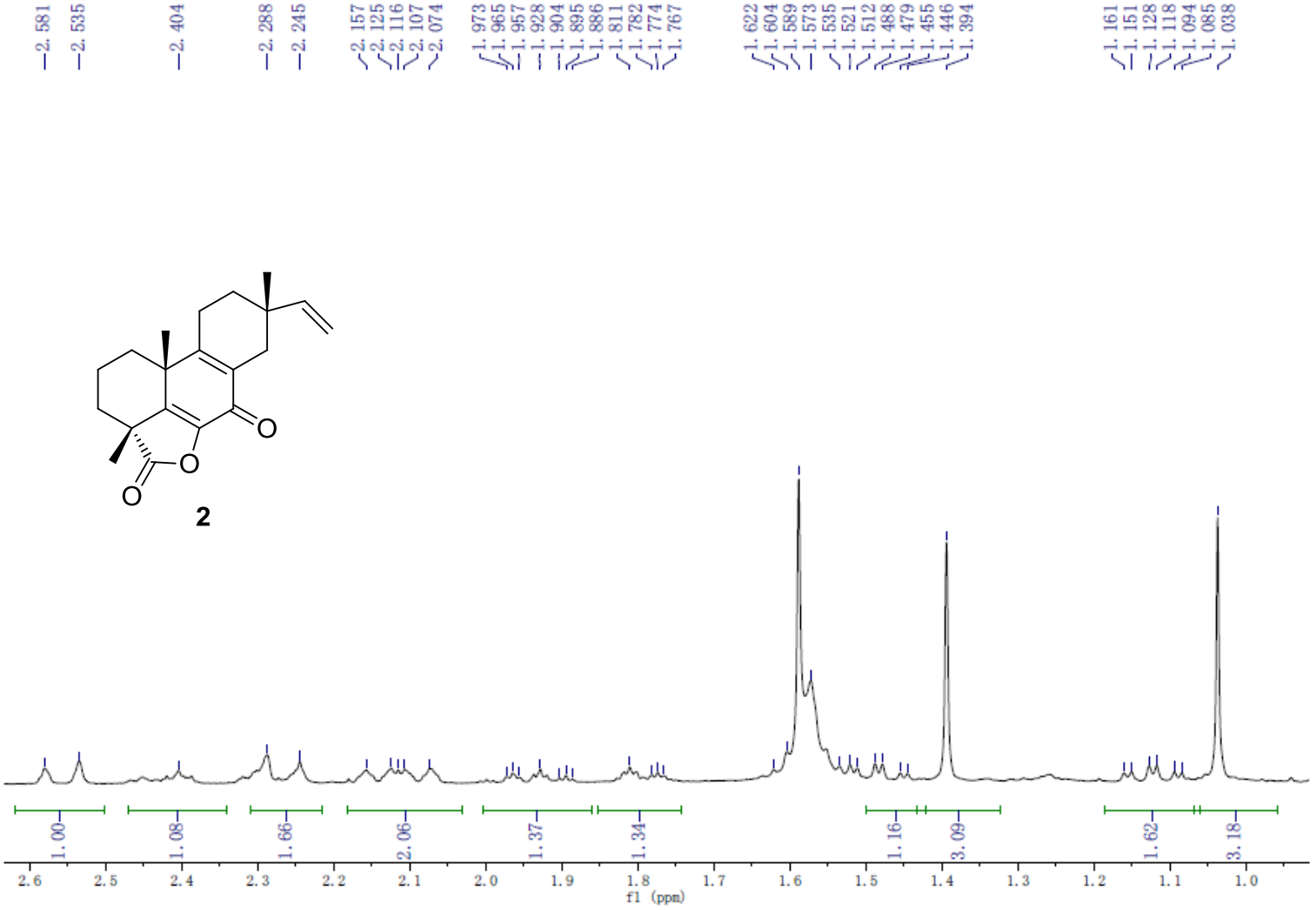
	1a	**1b**	**1c**	**10a**	**10b**	**10c**
Relative Energy (kcal/mol)	0.00	0.08	0.11	0.00	0.27	1.22
H15-H17 (Å)	2.52	3.78, 3.83	2.63	3.75	2.48, 3.08	2.40, 2.90
H16-H17 (Å)	4.24	2.27, 2.62	2.83	2.26, 2.75	4.30	3.56, 3.94

Relative energy, relative zero point energy, and relative Gibbs free energy at the B3LYP/6-31G* level in the Gas Phase. The calculated Boltzmann-averaged interproton distances (in Å) for all possible conformers (**1a**–**1c** and **10a**–**10c**).

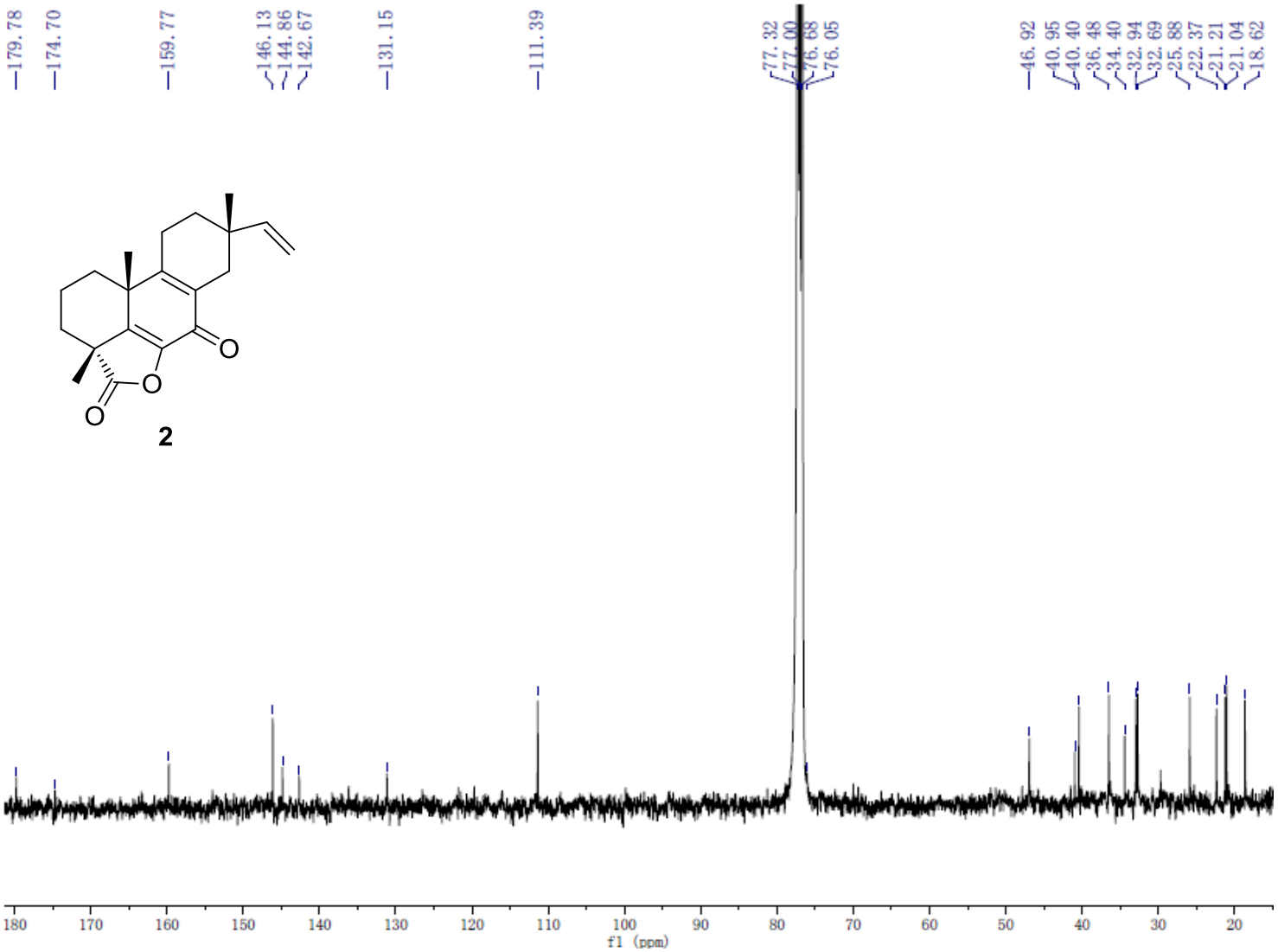
Compound 2: ^{1}H NMR ($CDCl_3$) spectrum



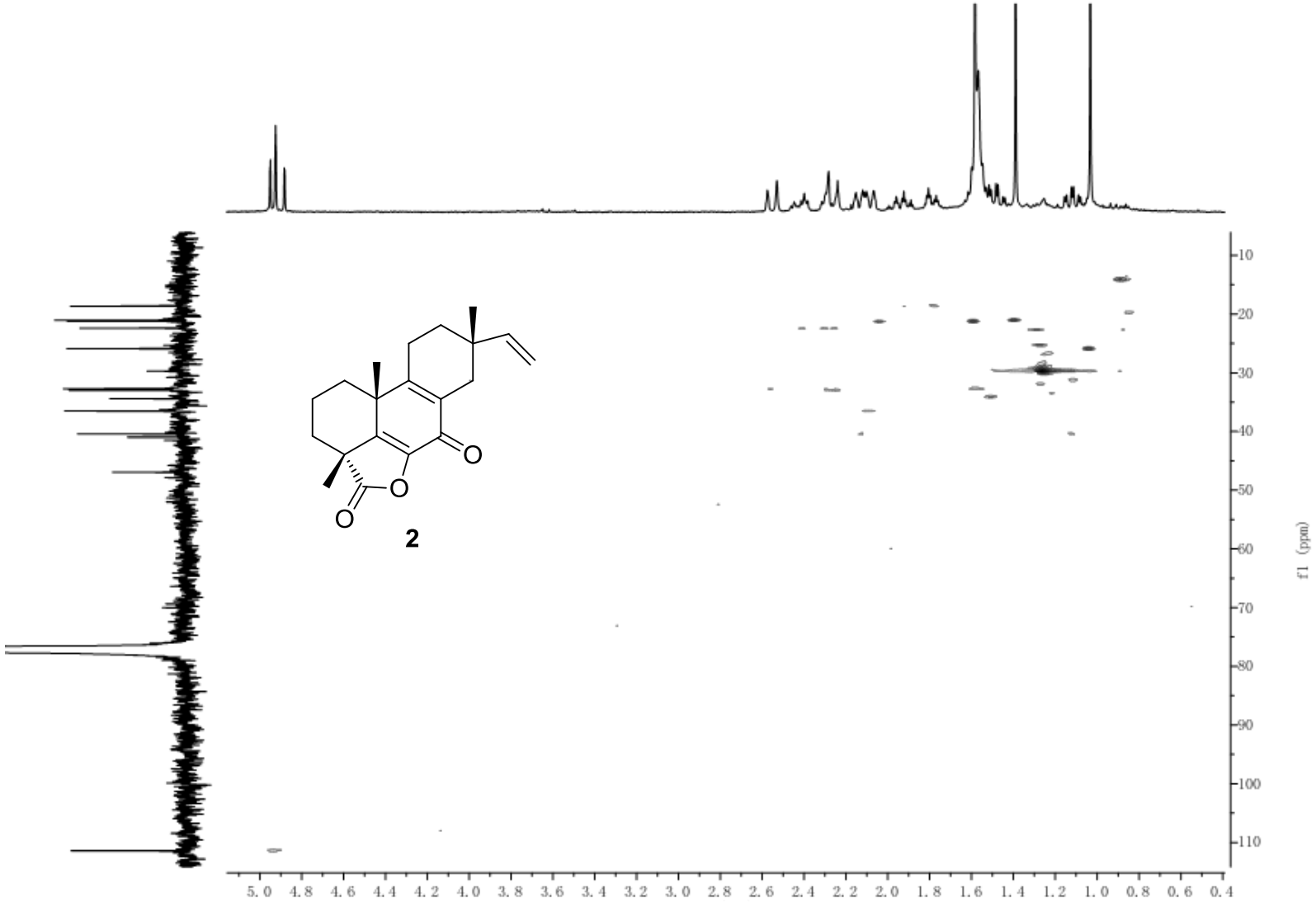
Compound 2: ^{1}H NMR ($CDCl_3$) spectrum-Expansion



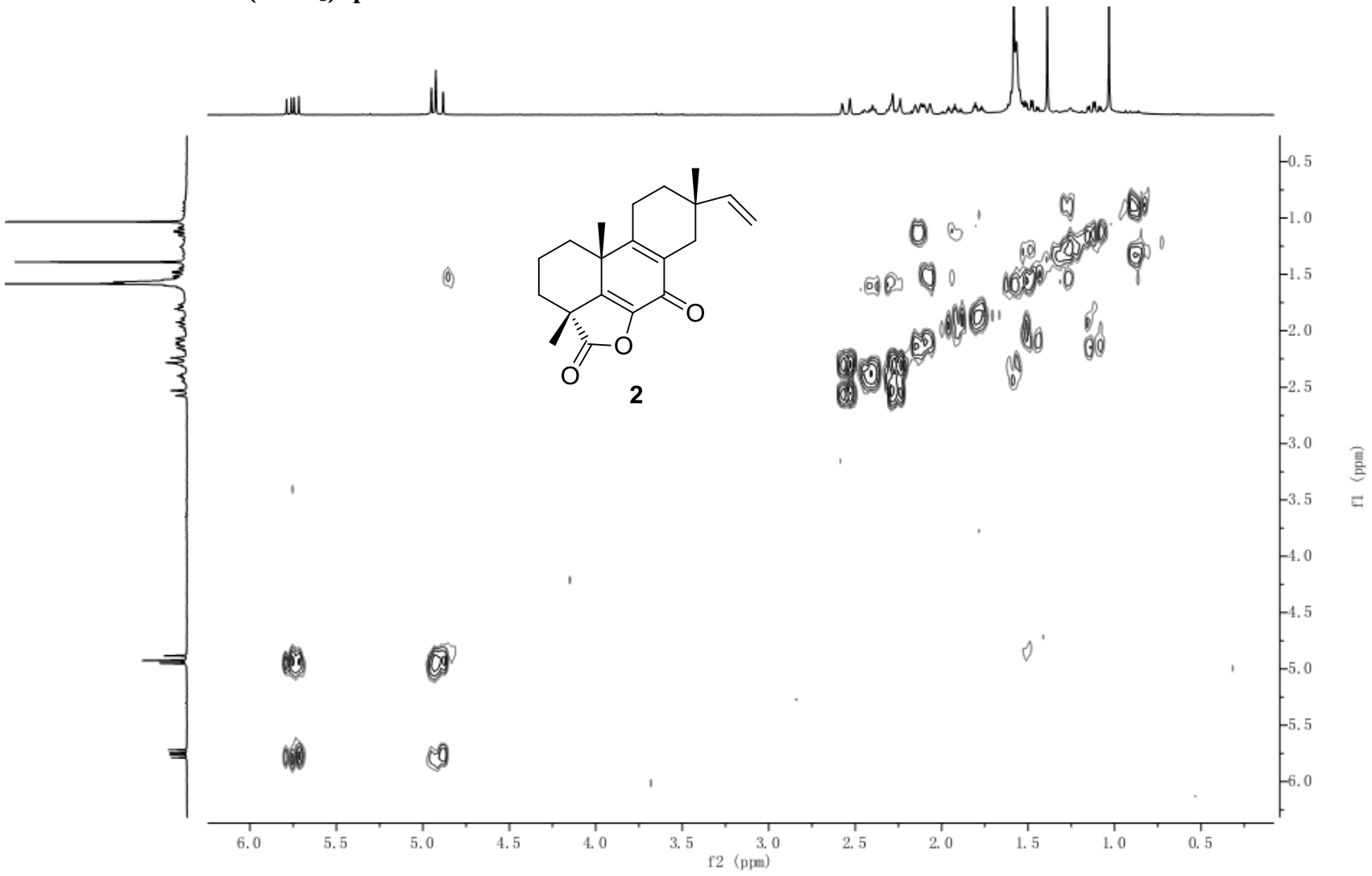
Compound 2: ^{13}C NMR ($CDCl_3$) spectrum



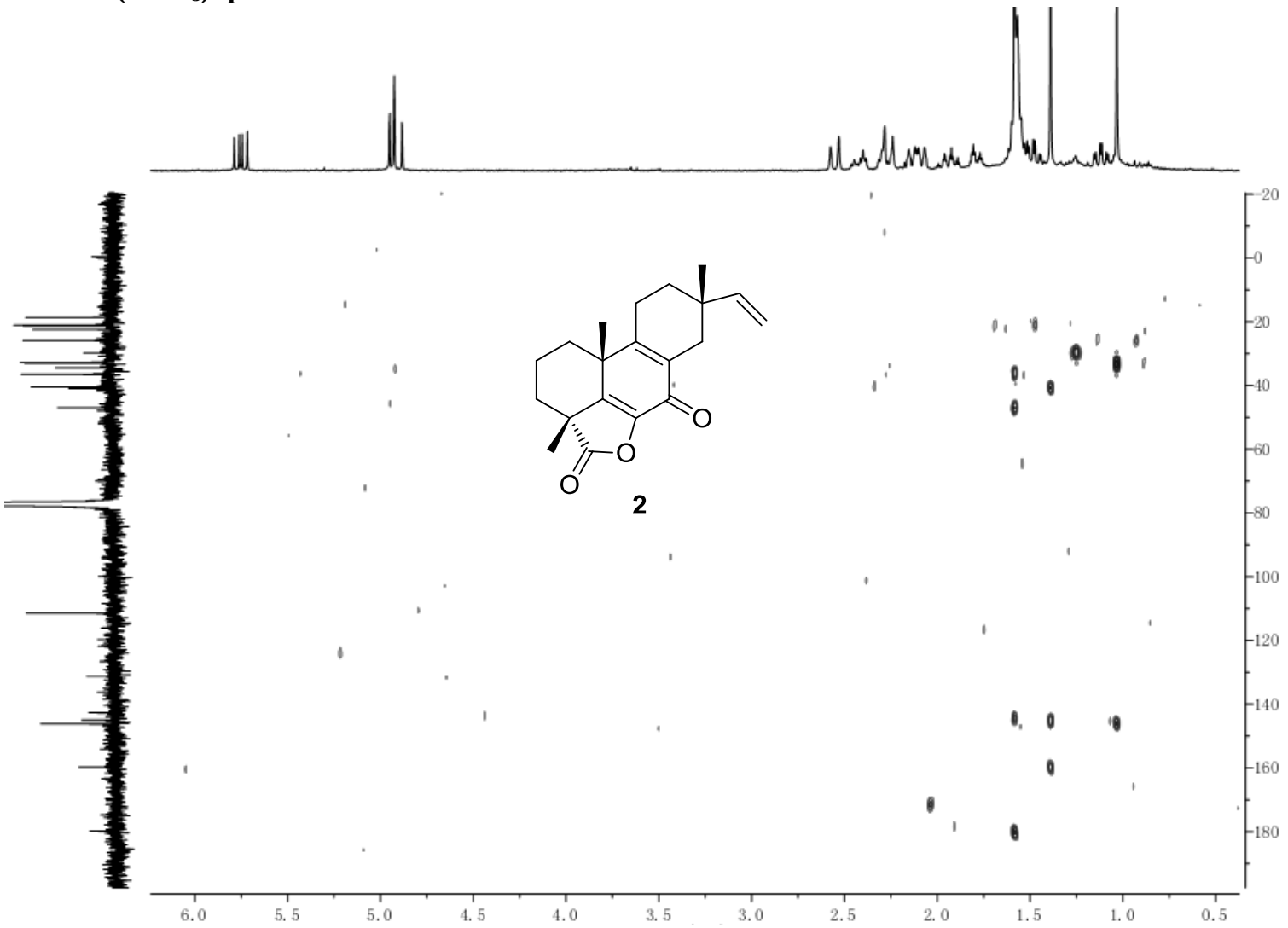
Compound 2: HSQC ($CDCl_3$) spectrum



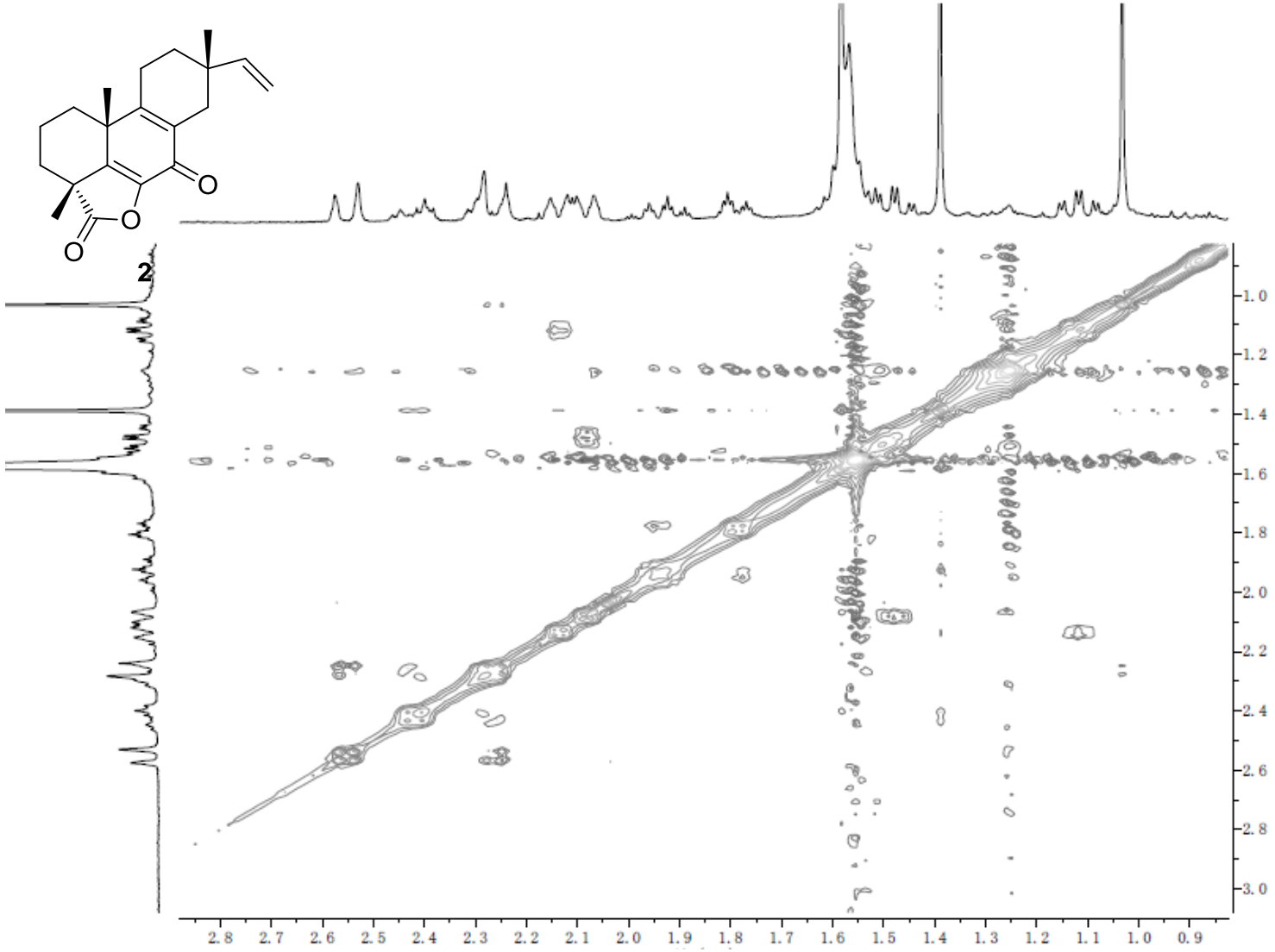
Compound 2: ^{1}H-^{1}H COSY ($CDCl_3$) spectrum



Compound 2: HMBC ($CDCl_3$) spectrum



Compound 2: NOESY ($CDCl_3$) spectrum



Compound 2: (+) HR-ESIMS

Qualitative Analysis Report

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IRM Calibration Status	Some Ions Missed	**DA Method**	Screening-Default.m
Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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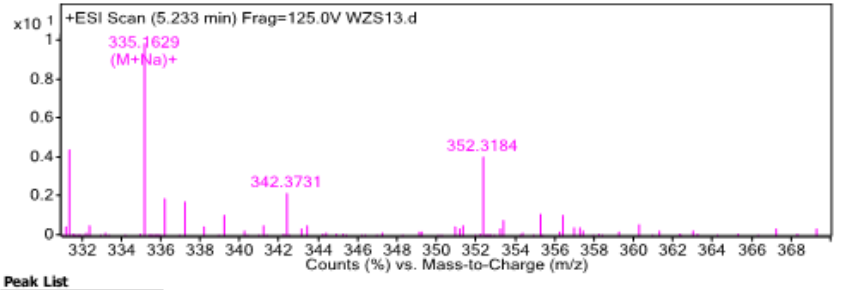


Peak List

m/z	z	Abund
330.338	1	569502

Formula Calculator Element Limits

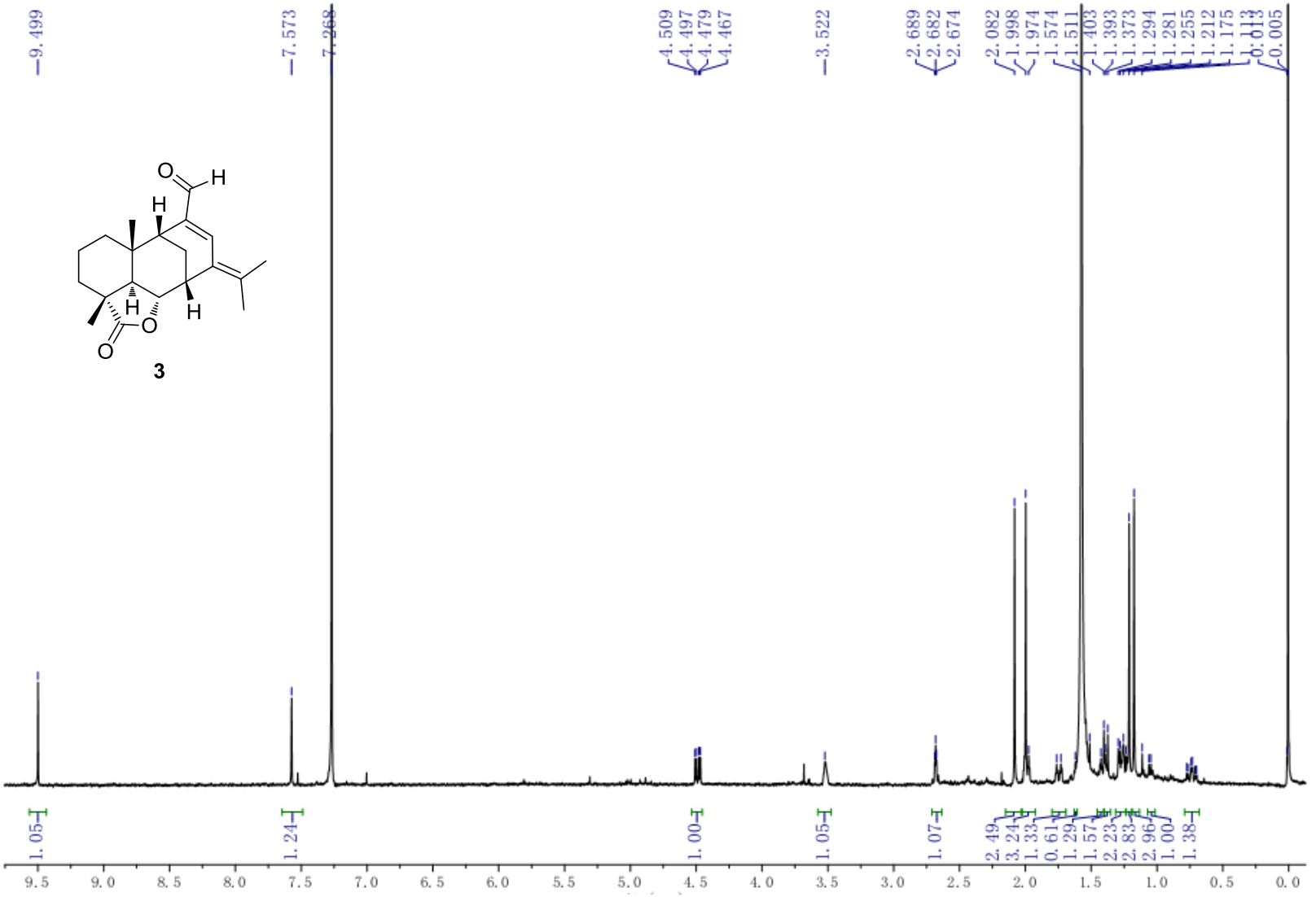
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

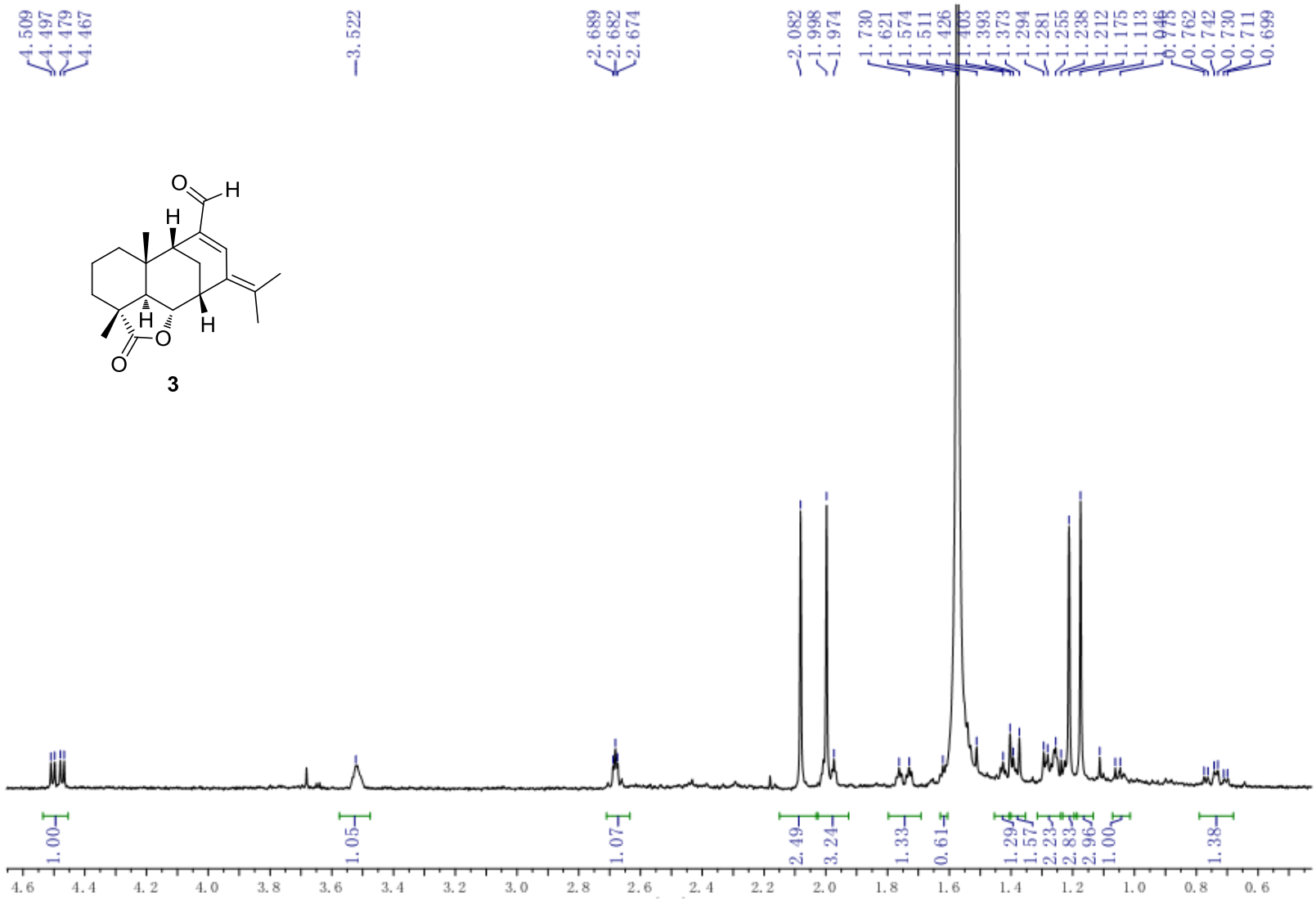
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H24 O3	TRUE	312.1738	312.1725	-3.9	C20 H24 Na O3	60.39

--- End Of Report ---

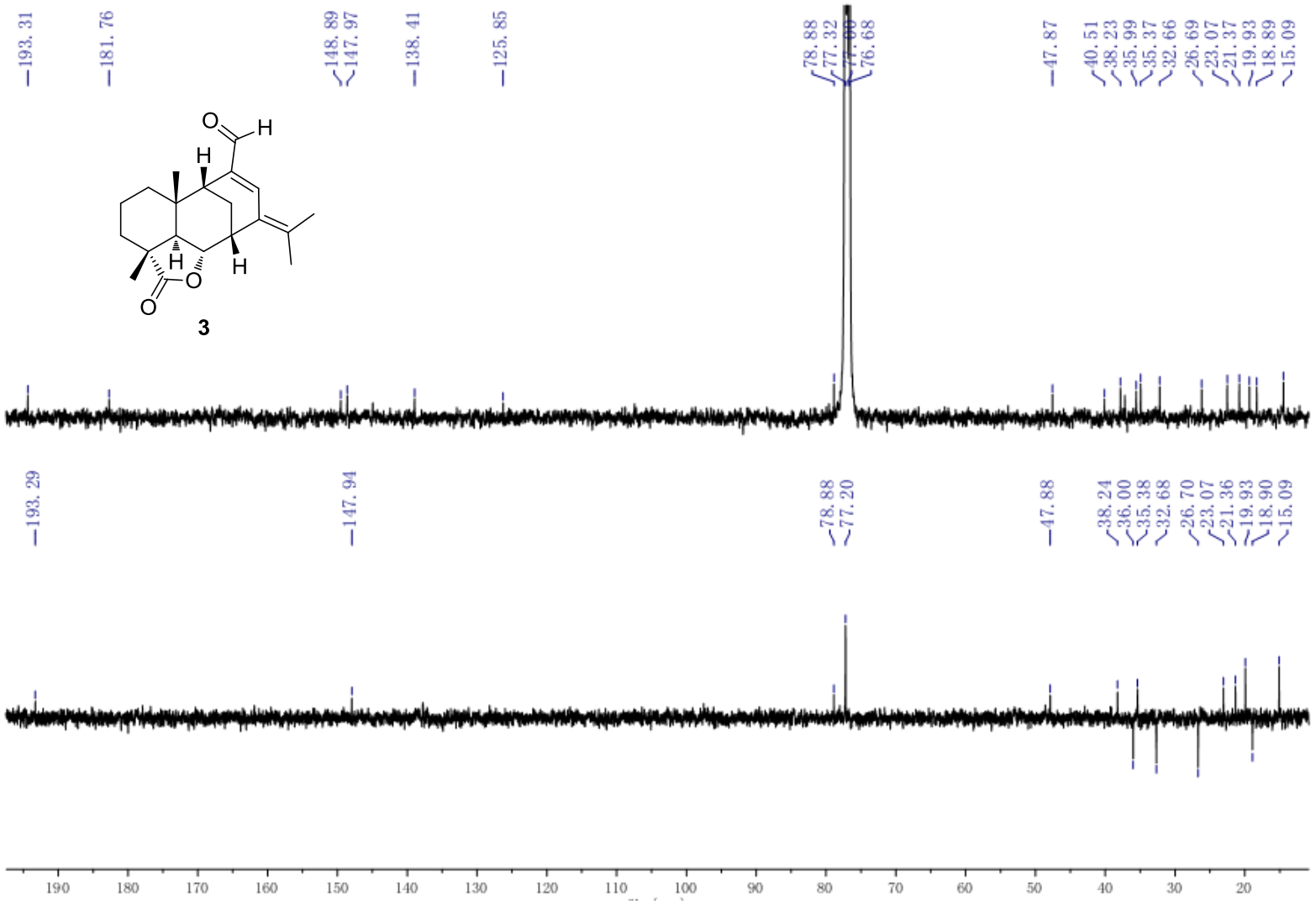
Compound 3: ^{1}H NMR ($CDCl_3$) spectrum



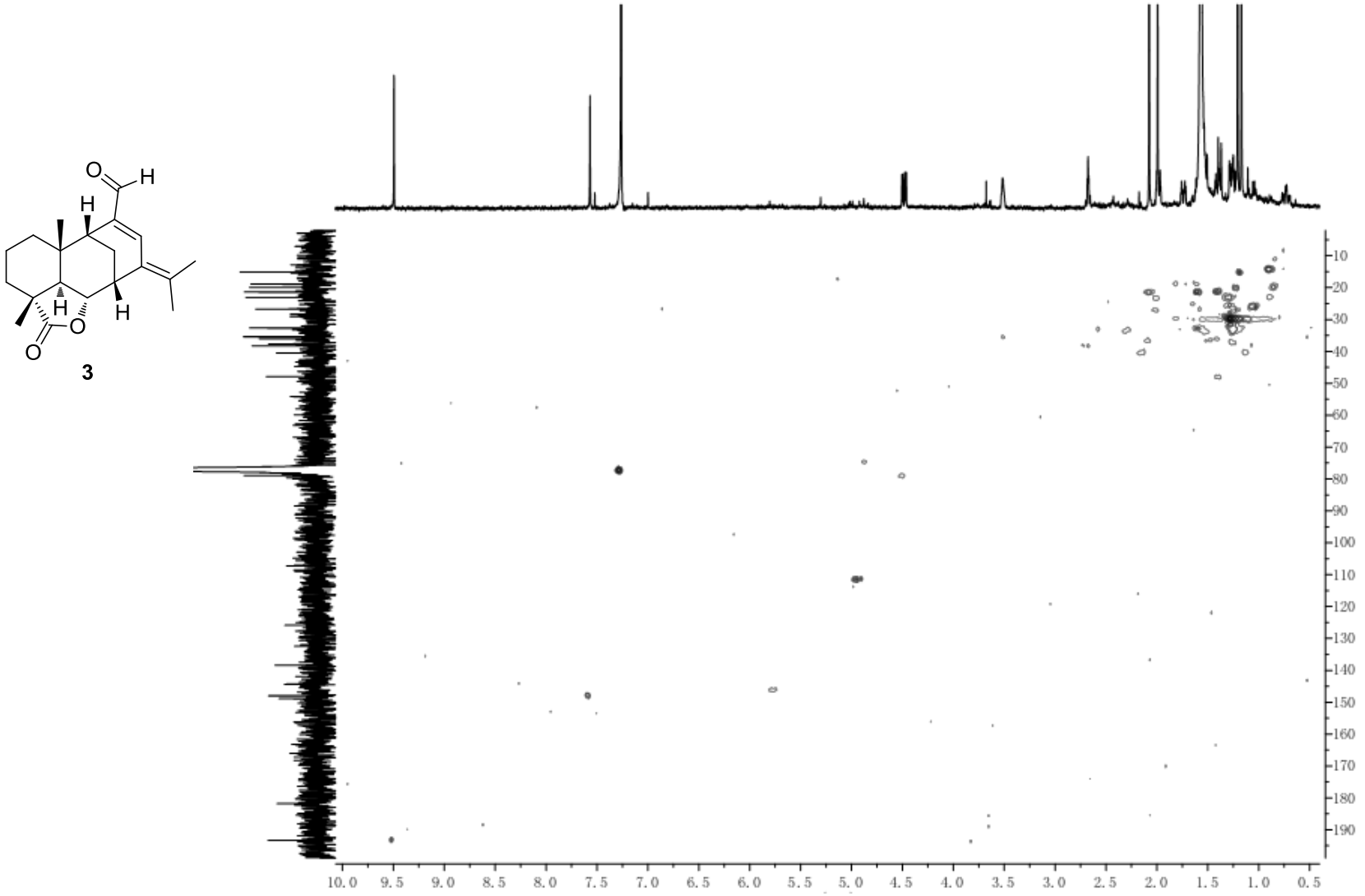
Compound 3: ^{1}H NMR ($CDCl_3$) spectrum-Expansion



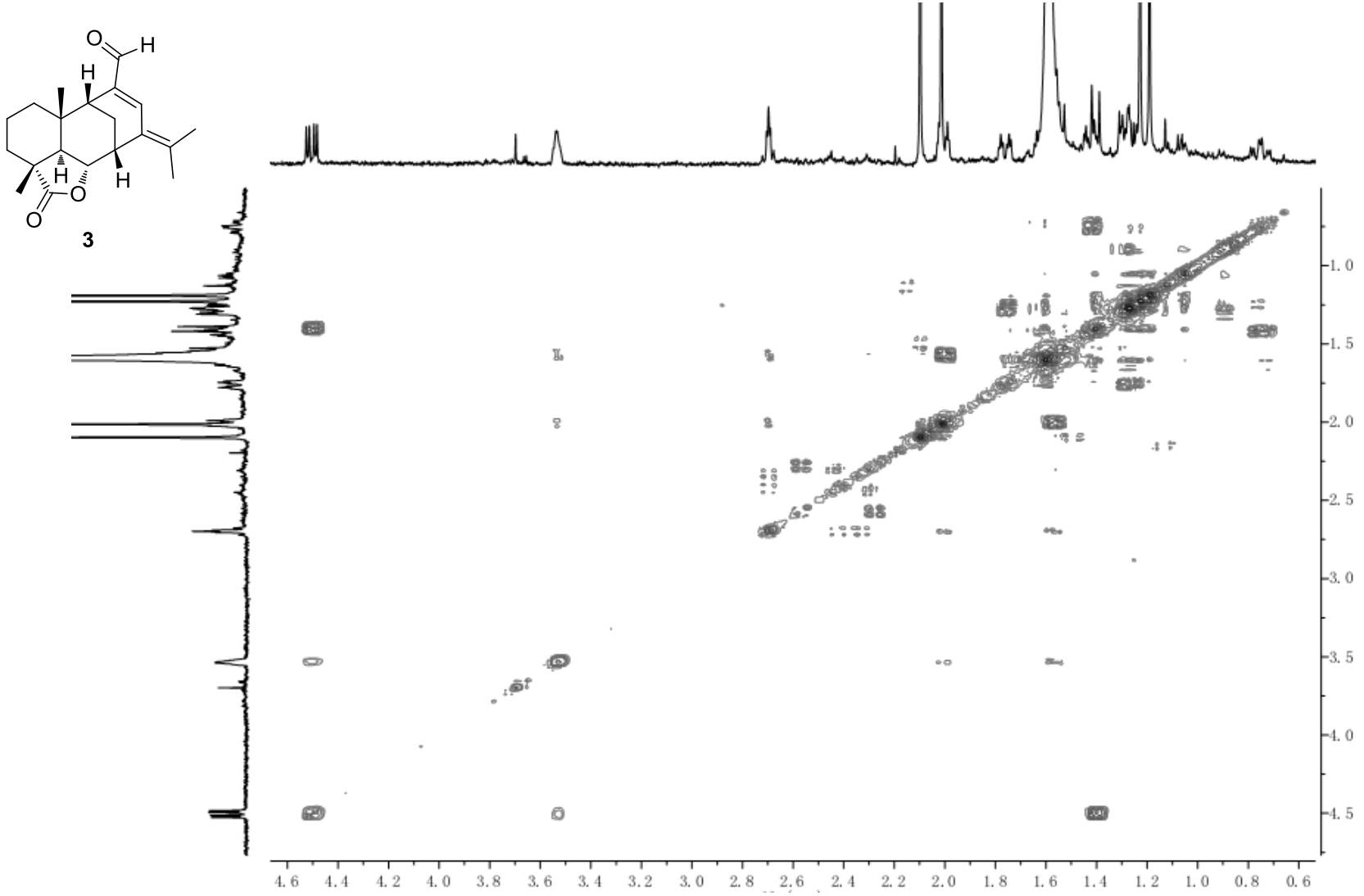
Compound 3: ^{13}C NMR and DEPT ($CDCl_3$) spectrum



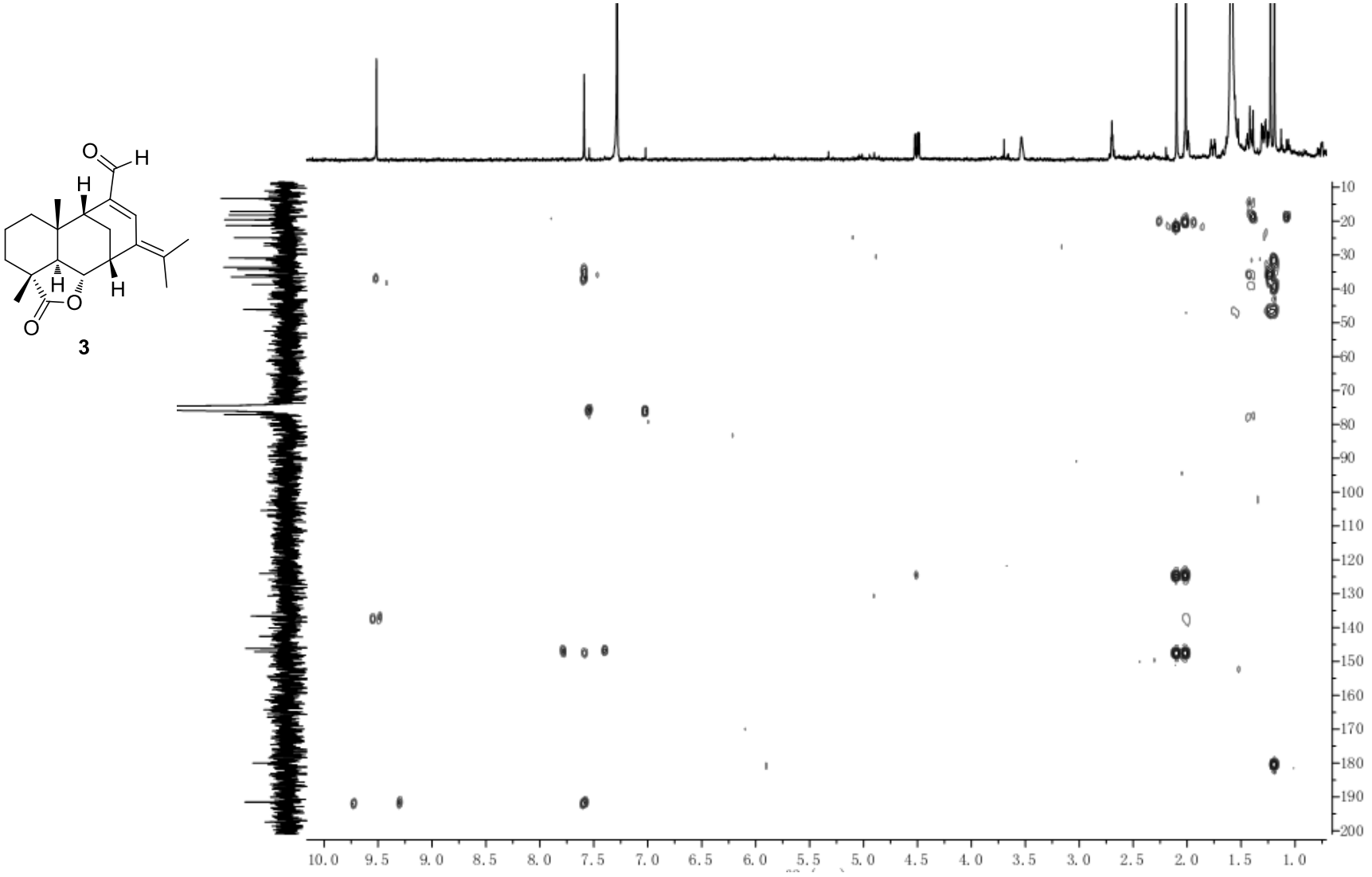
Compound 3: HSQC ($CDCl_3$) spectrum



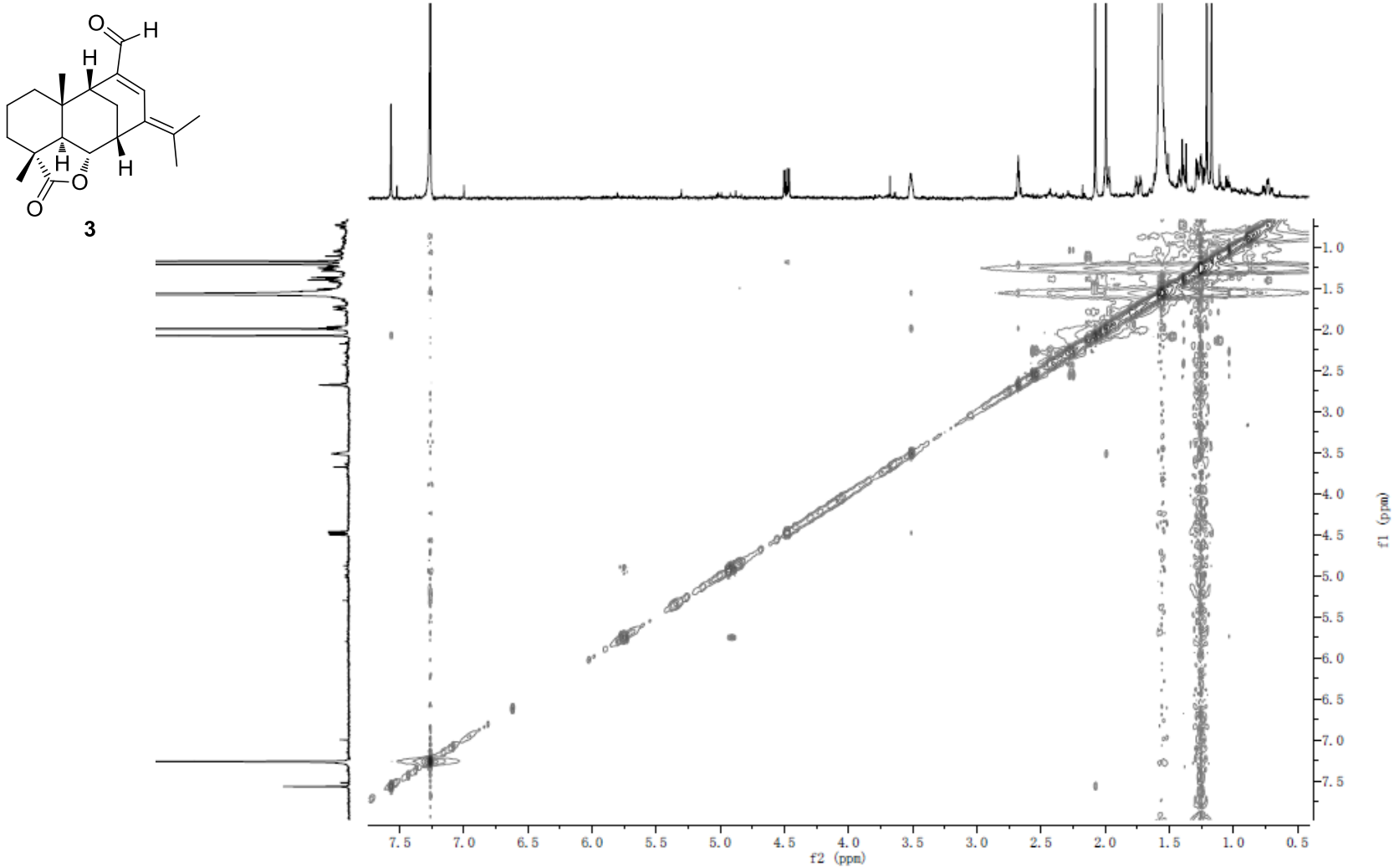
Compound 3: ^{1}H-^{1}H COSY ($CDCl_3$) spectrum



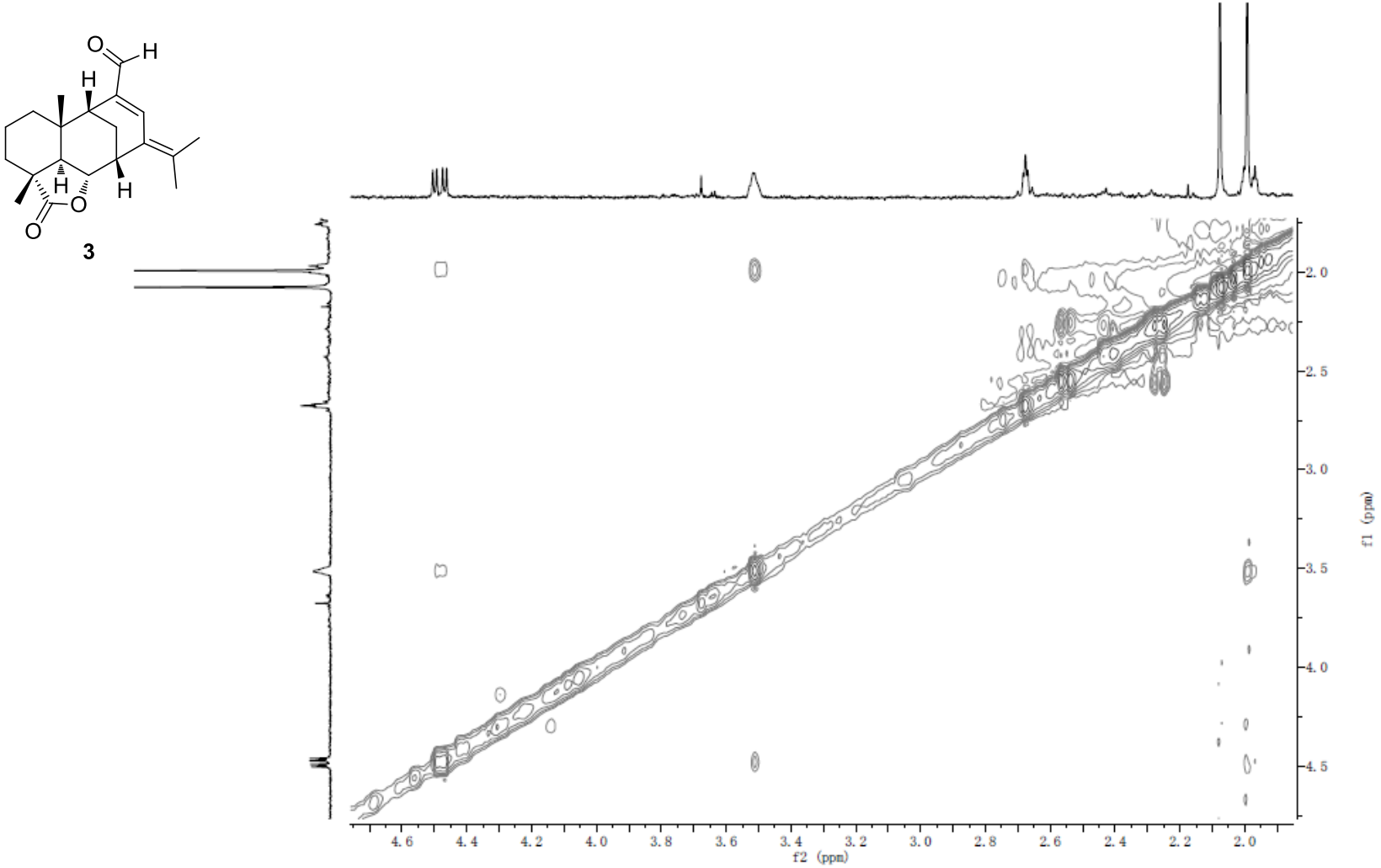
Compound 3: HMBC ($CDCl_3$) spectrum



Compound 3: NOESY ($CDCl_3$) spectrum



Compound 3: NOESY ($CDCl_3$) spectrum-Expansion



Compound 3: (+) HR-ESIMS

Qualitative Analysis Report

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Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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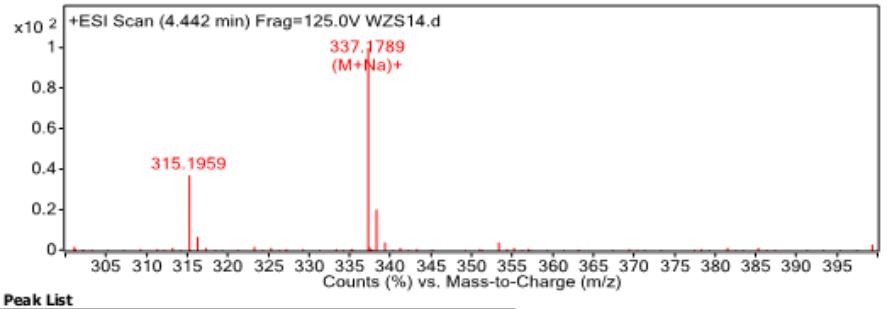


Peak List

m/z	z	Abund	Formula	Ion
337.1789	1	784110	C20 H26 Na O3	(M+Na)+

Formula Calculator Element Limits

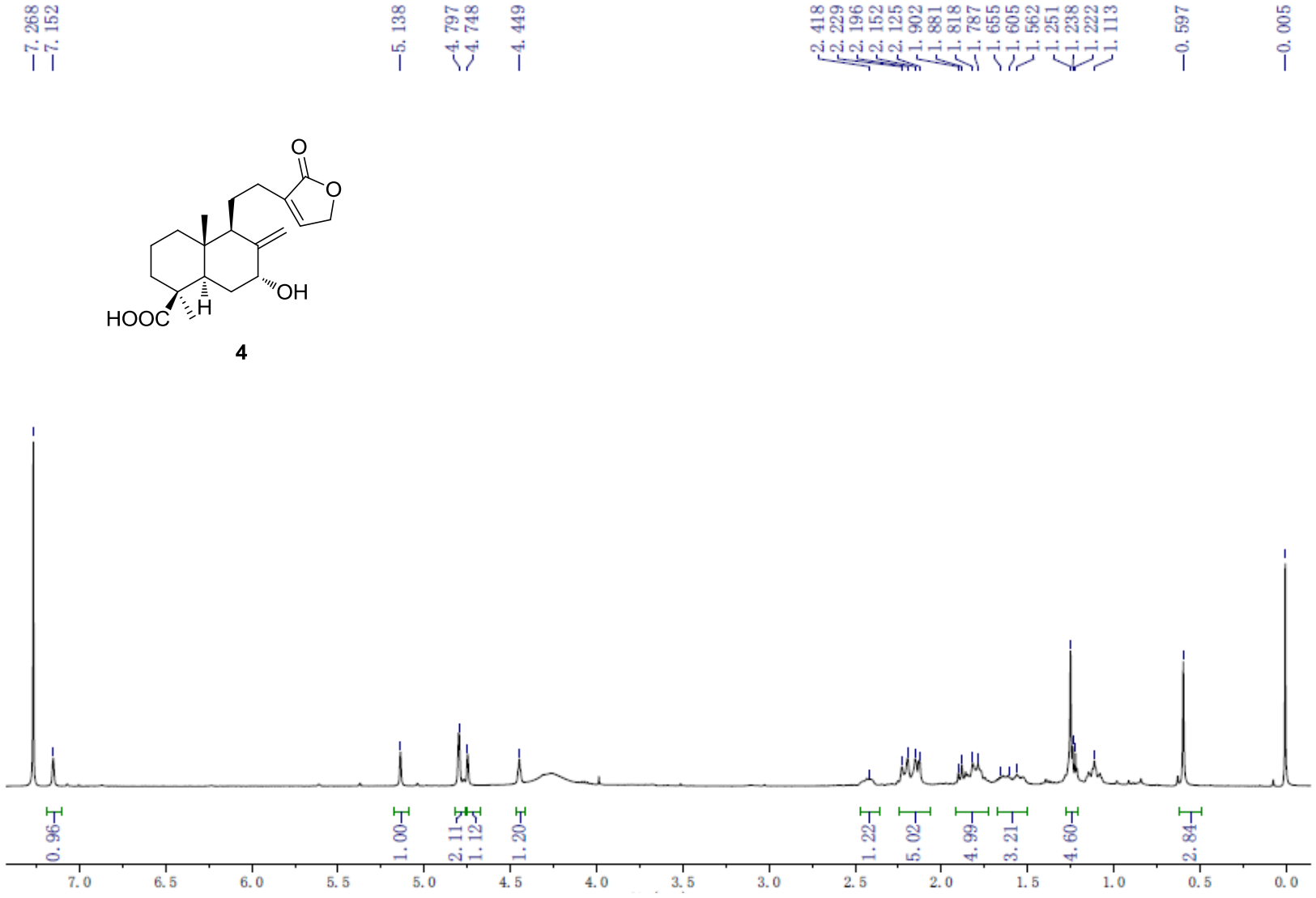
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H26 O3	TRUE	314.1897	314.1882	-4.64	C20 H26 Na O3	85.15

--- End Of Report ---

Compound 4: ^{1}H NMR ($CDCl_3$) spectrum



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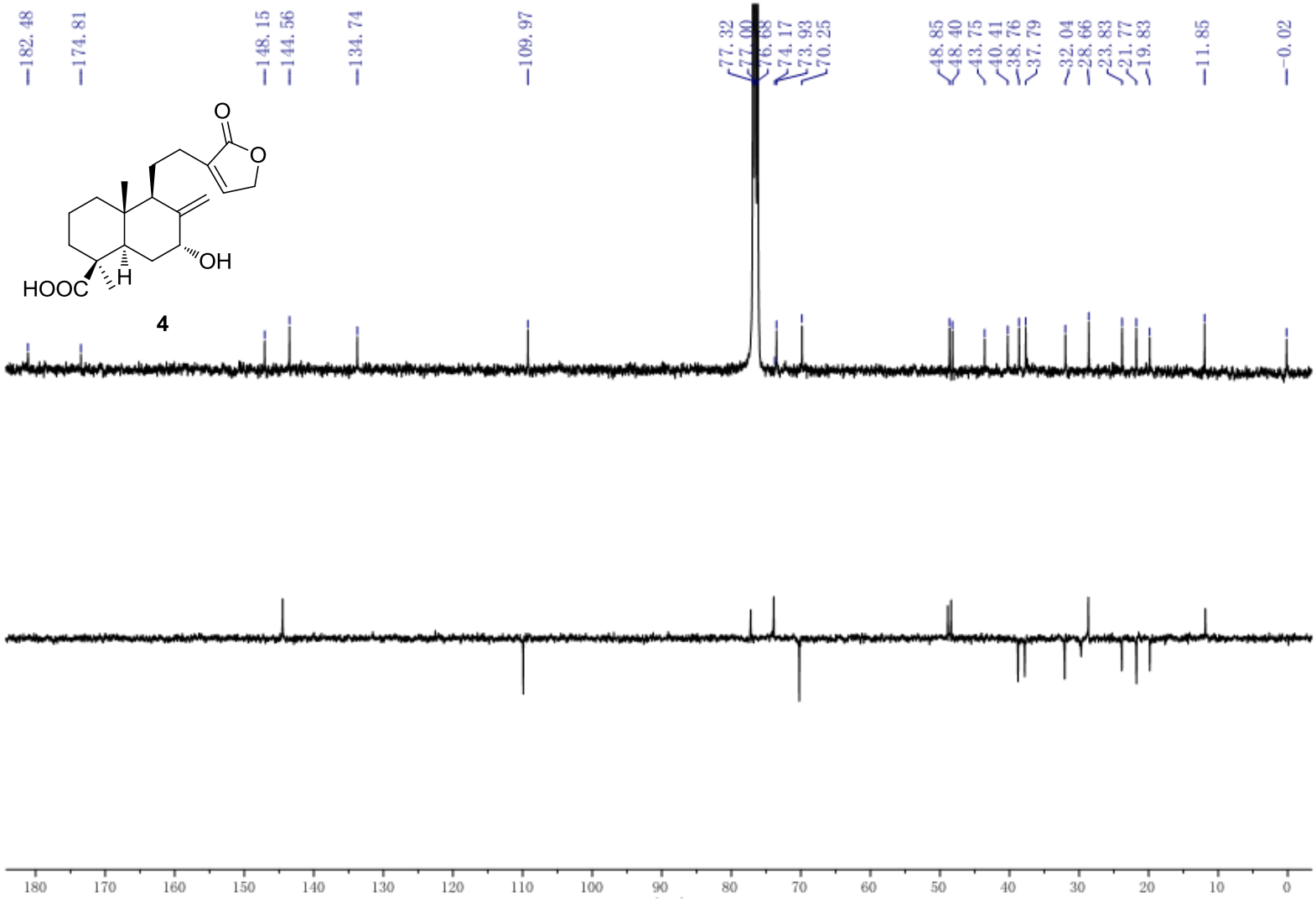
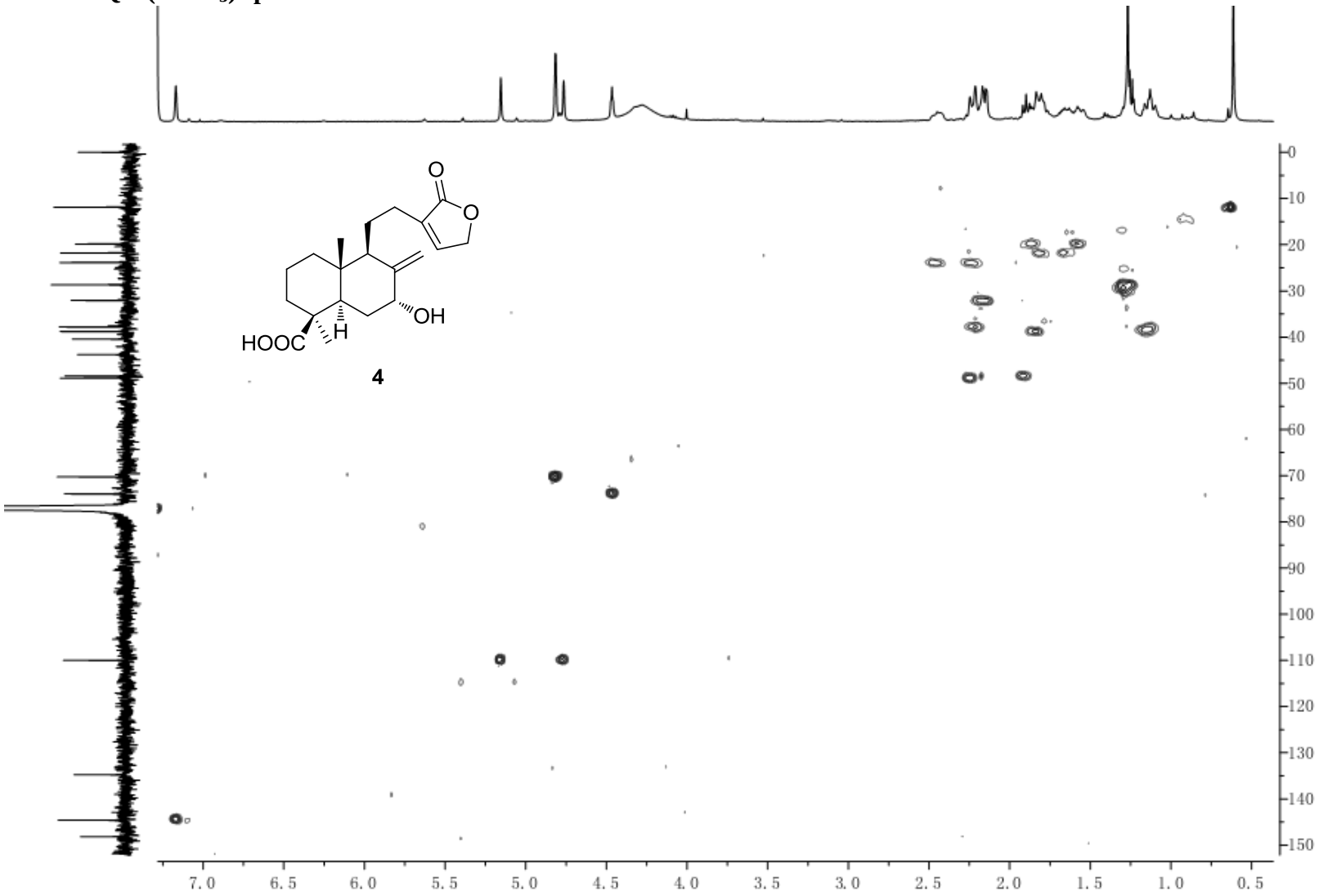
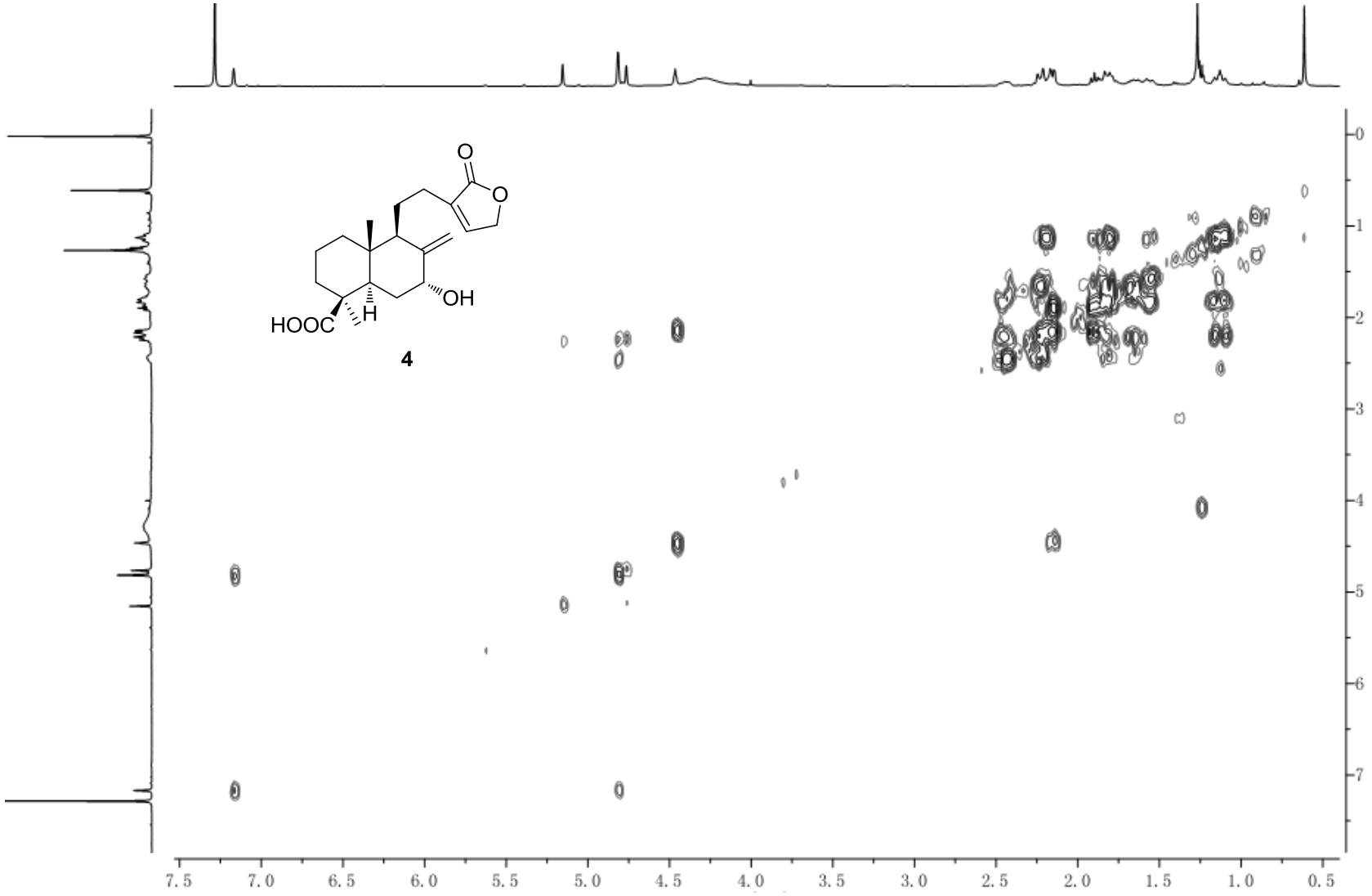
Compound 4: ^{13}C NMR and DEPT ($CDCl_3$) spectrum



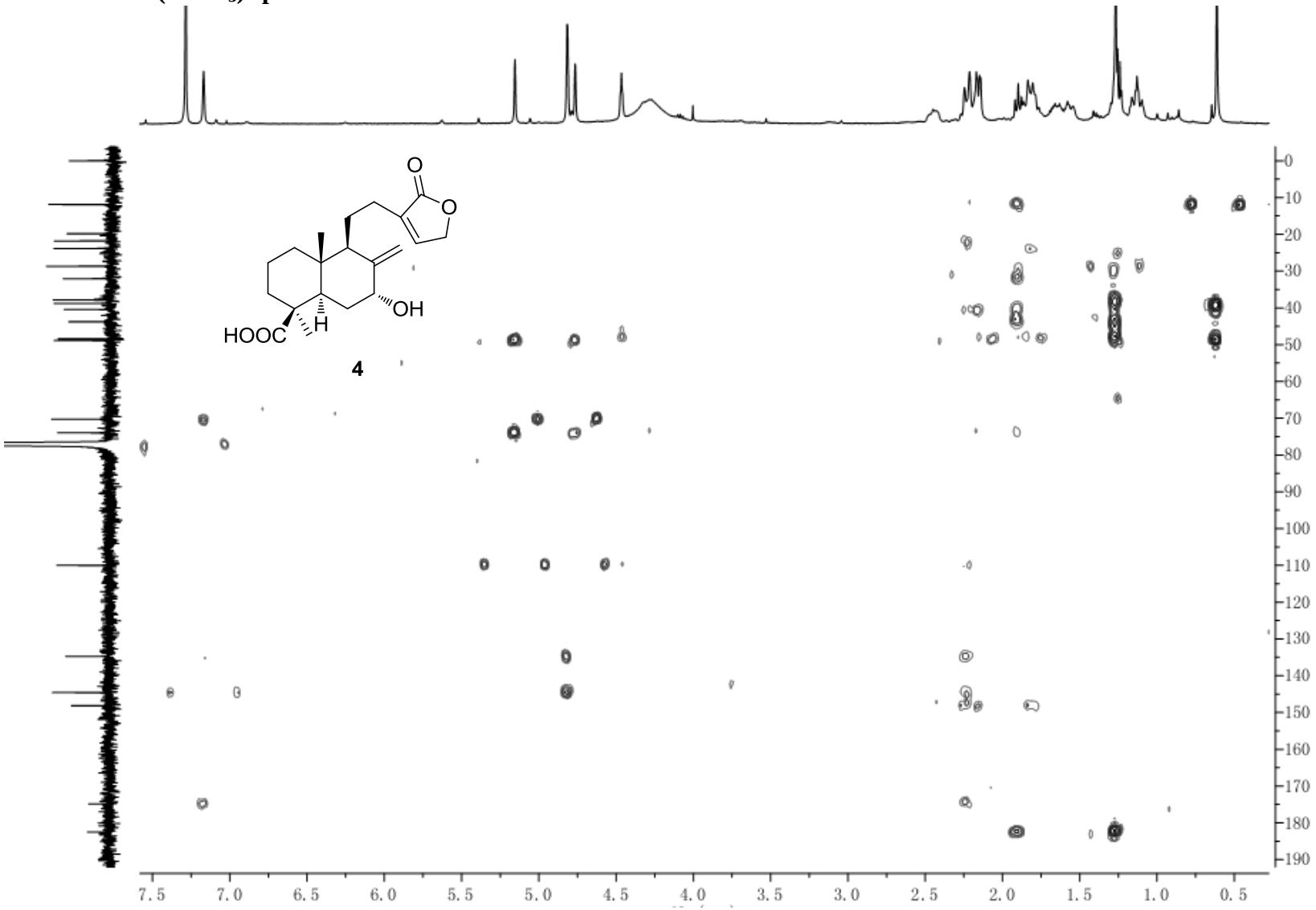
Compound 4: HSQC ($CDCl_3$) spectrum



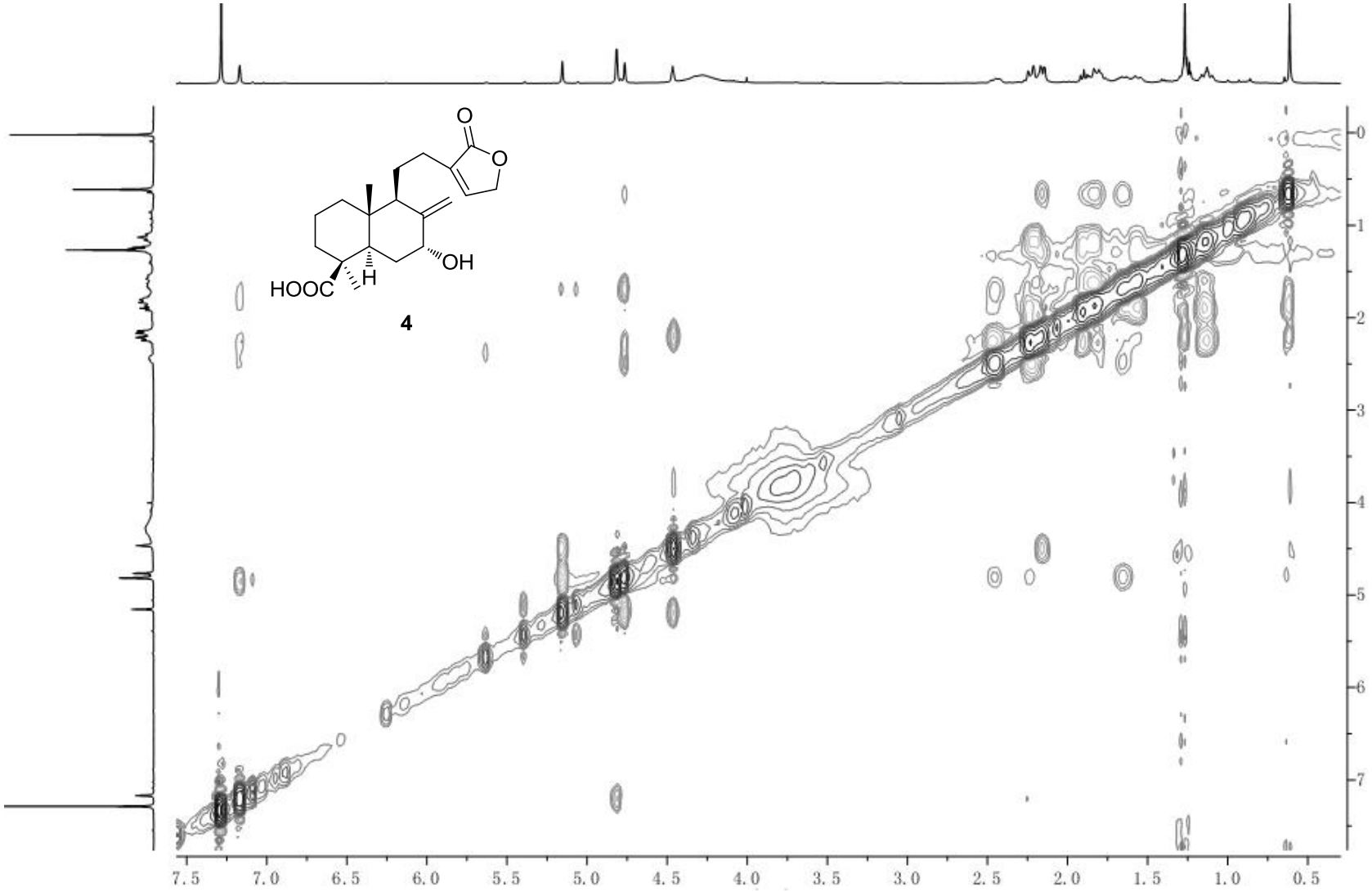
Compound 4: ^{1}H-^{1}H COSY ($CDCl_3$) spectrum



Compound 4: HMBC ($CDCl_3$) spectrum



Compound 4: NOESY ($CDCl_3$) spectrum



Compound 4: (+) HR-ESIMS

Qualitative Analysis Report

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Sample Type	Sample	**Position**	P1-D6
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Acq Method	general test 2.m	**Acquired Time**	12/19/2013 2:59:00 PM
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Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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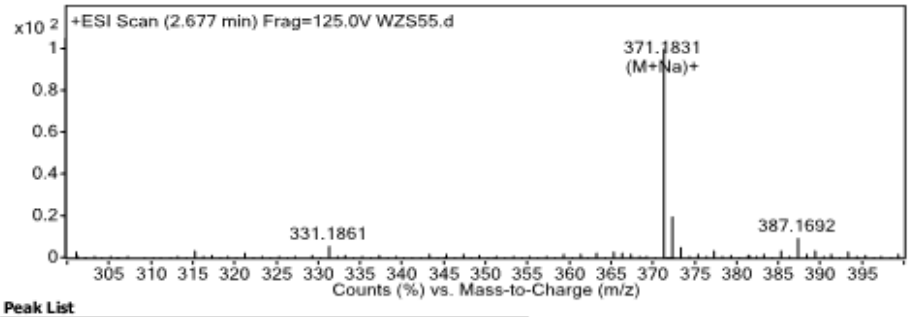


Peak List

m/z	z	Abund	Formula	Ion
371.1831	1	332967	C20 H28 Na O5	(M+Na)+

Formula Calculator Element Limits

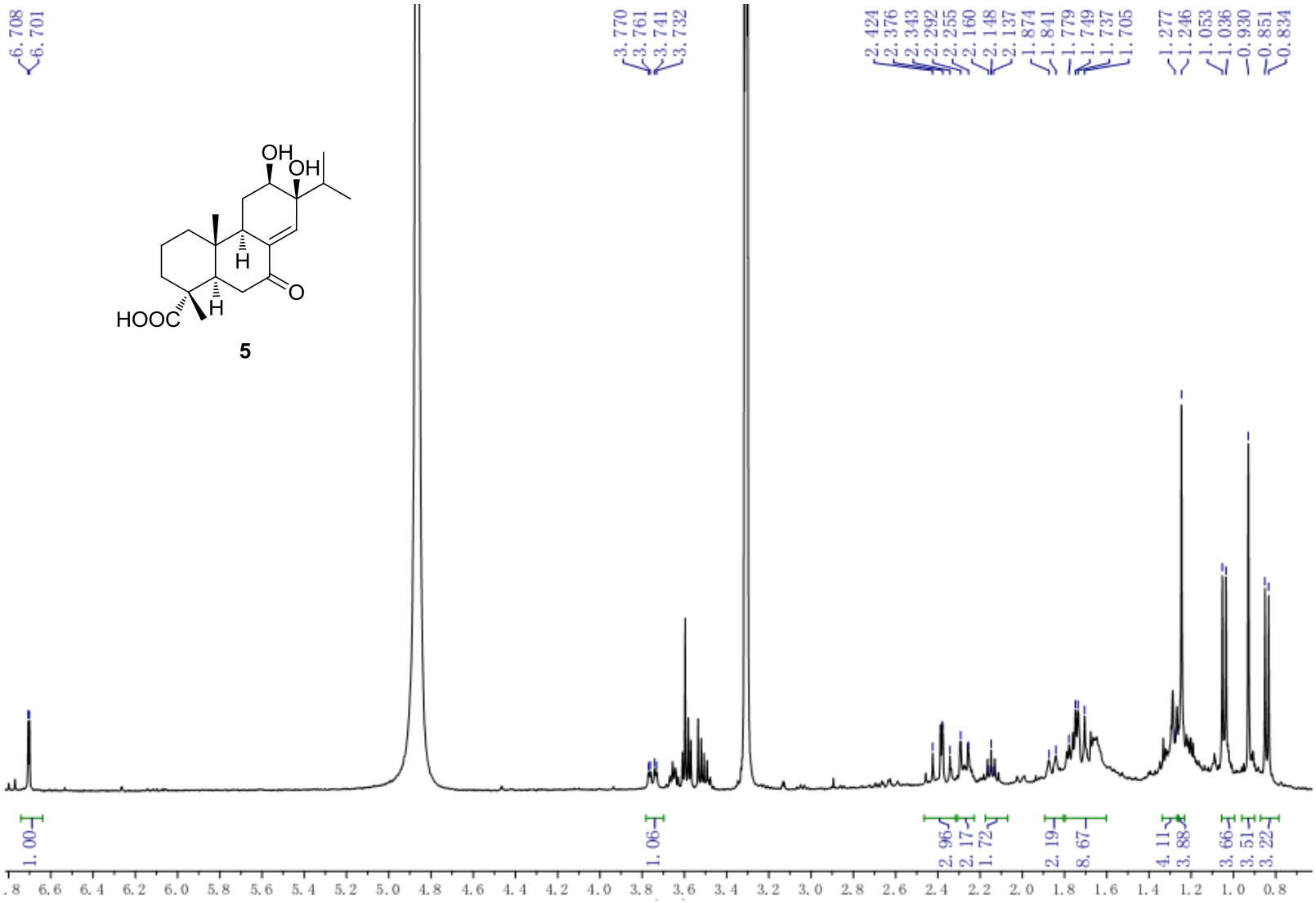
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

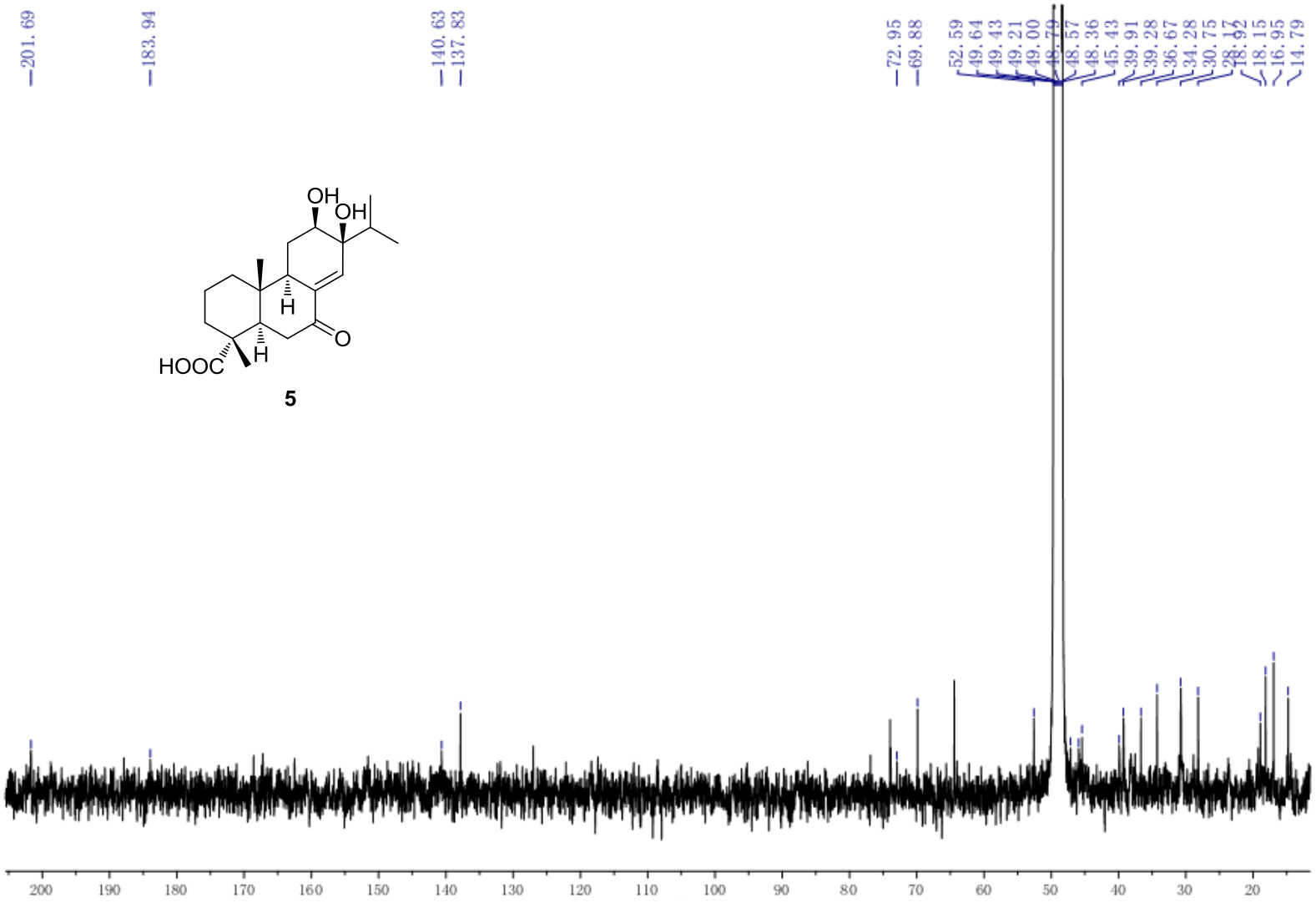
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H28 O5	TRUE	348.1938	348.1937	-0.47	C20 H28 Na O5	86.8

--- End Of Report ---

Compound 5: ^{1}H NMR (CD_3OD) spectrum

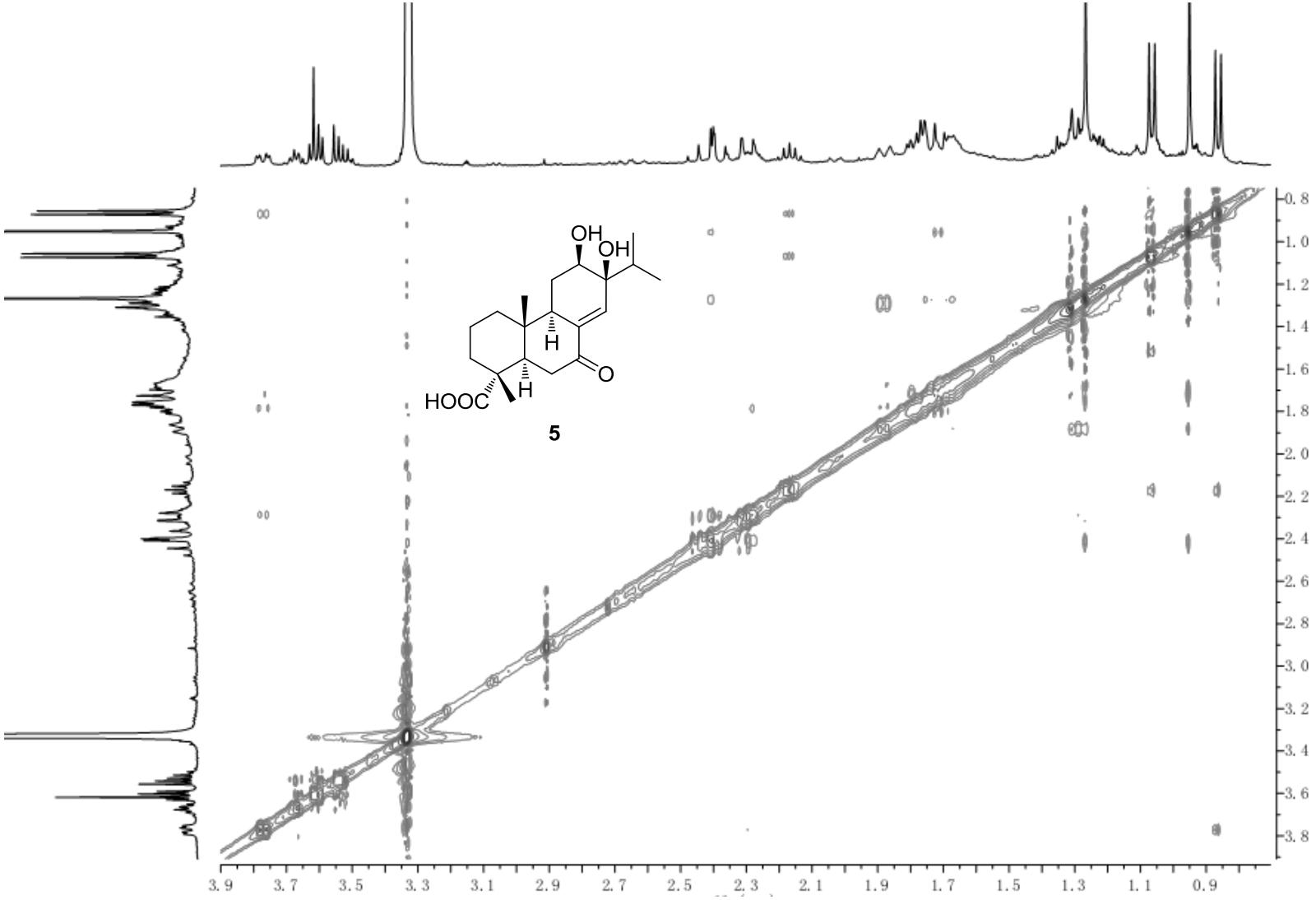


Compound 5: ^{13}C NMR (CD_3OD) spectrum



5

Compound 5: NOESY (CD_3OD) spectrum



Compound 5: (+) HR-ESIMS

Qualitative Analysis Report

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Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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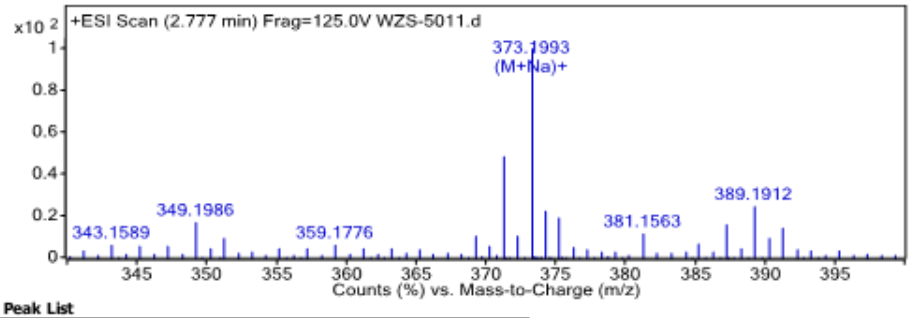


Peak List

m/z	z	Abund	Formula	Ion
373.1993	1	497468	C20 H30 Na O5	(M+Na)+

Formula Calculator Element Limits

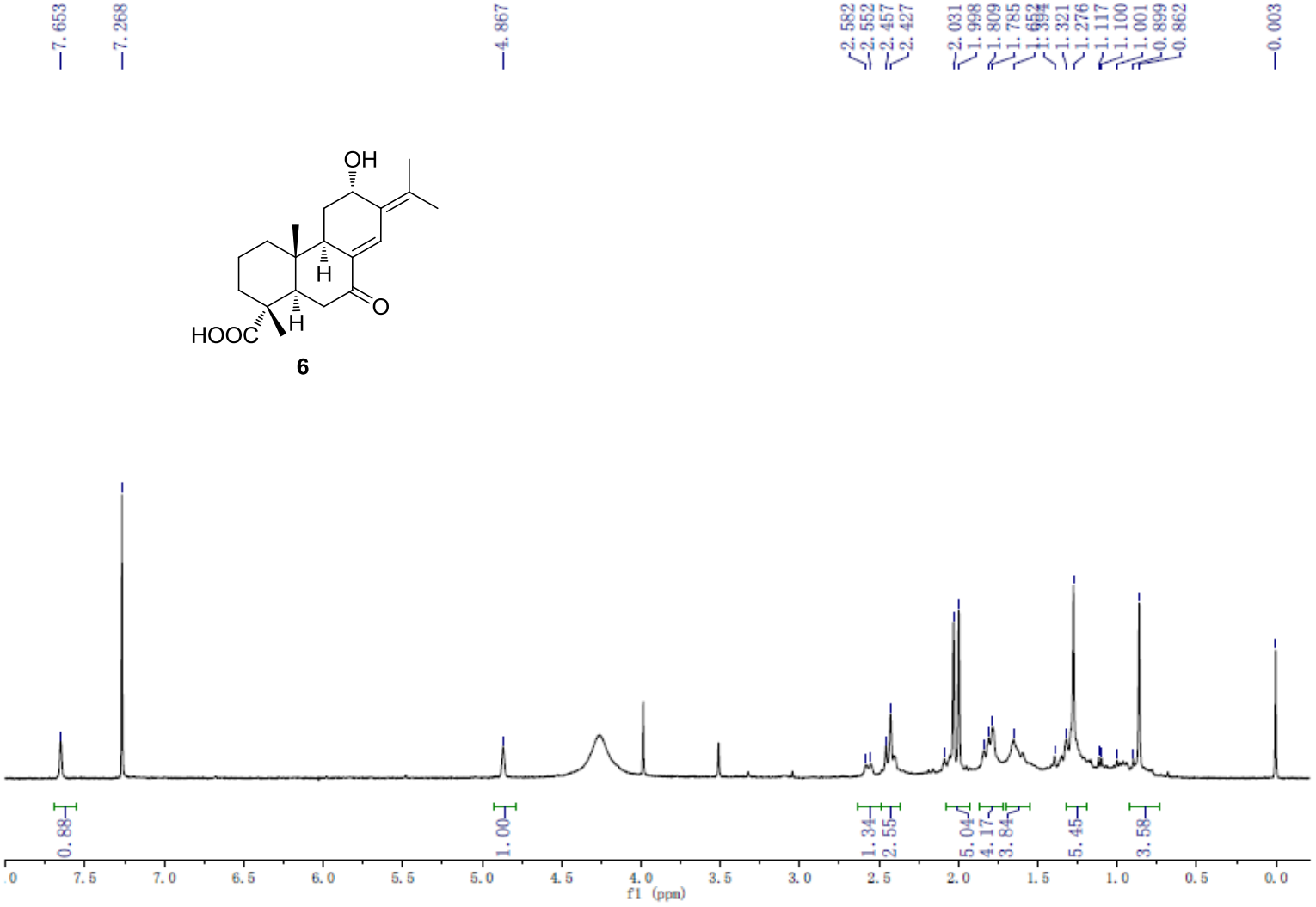
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

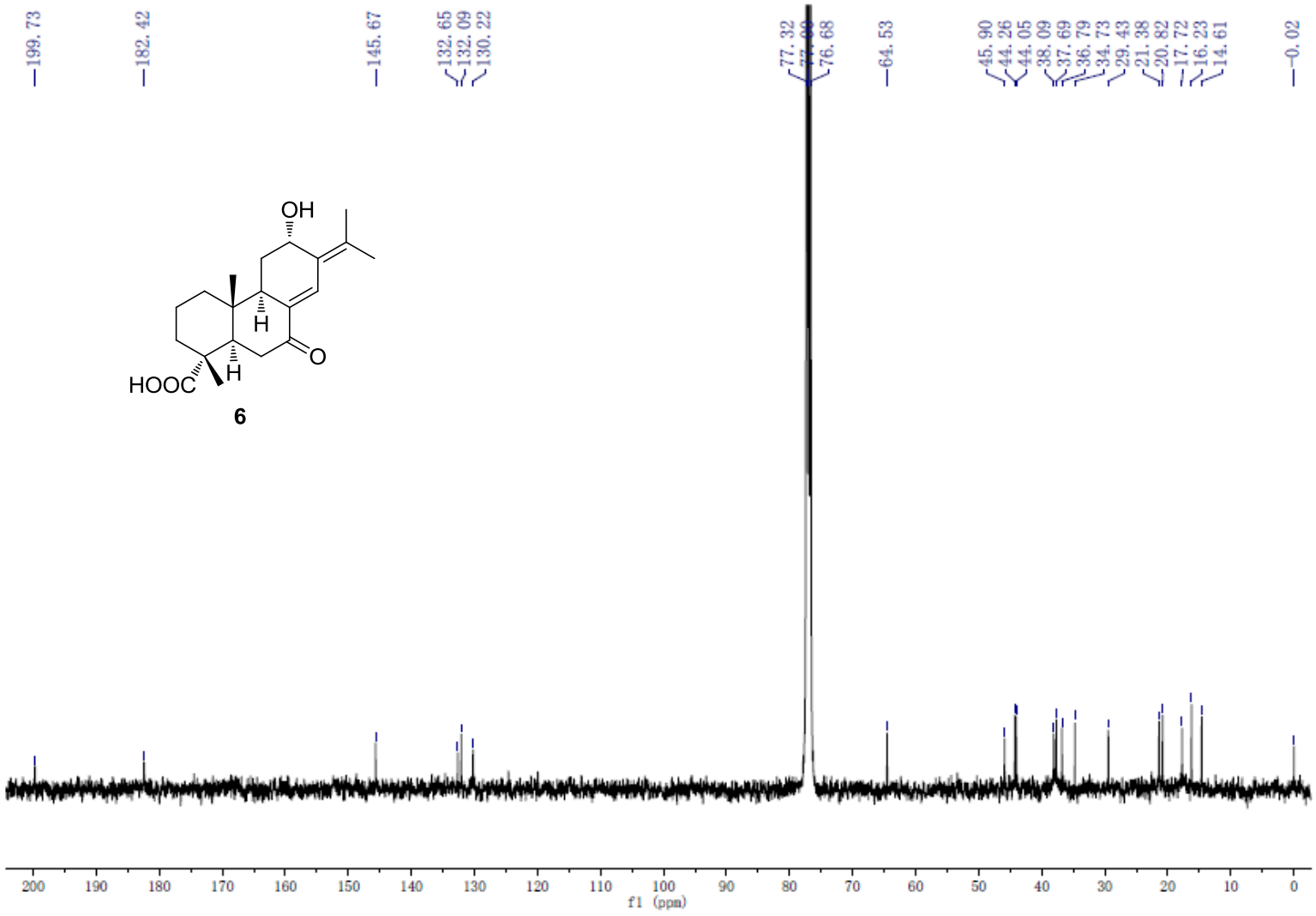
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H30 O5	TRUE	350.21	350.2093	-1.84	C20 H30 Na O5	61.85

--- End Of Report ---

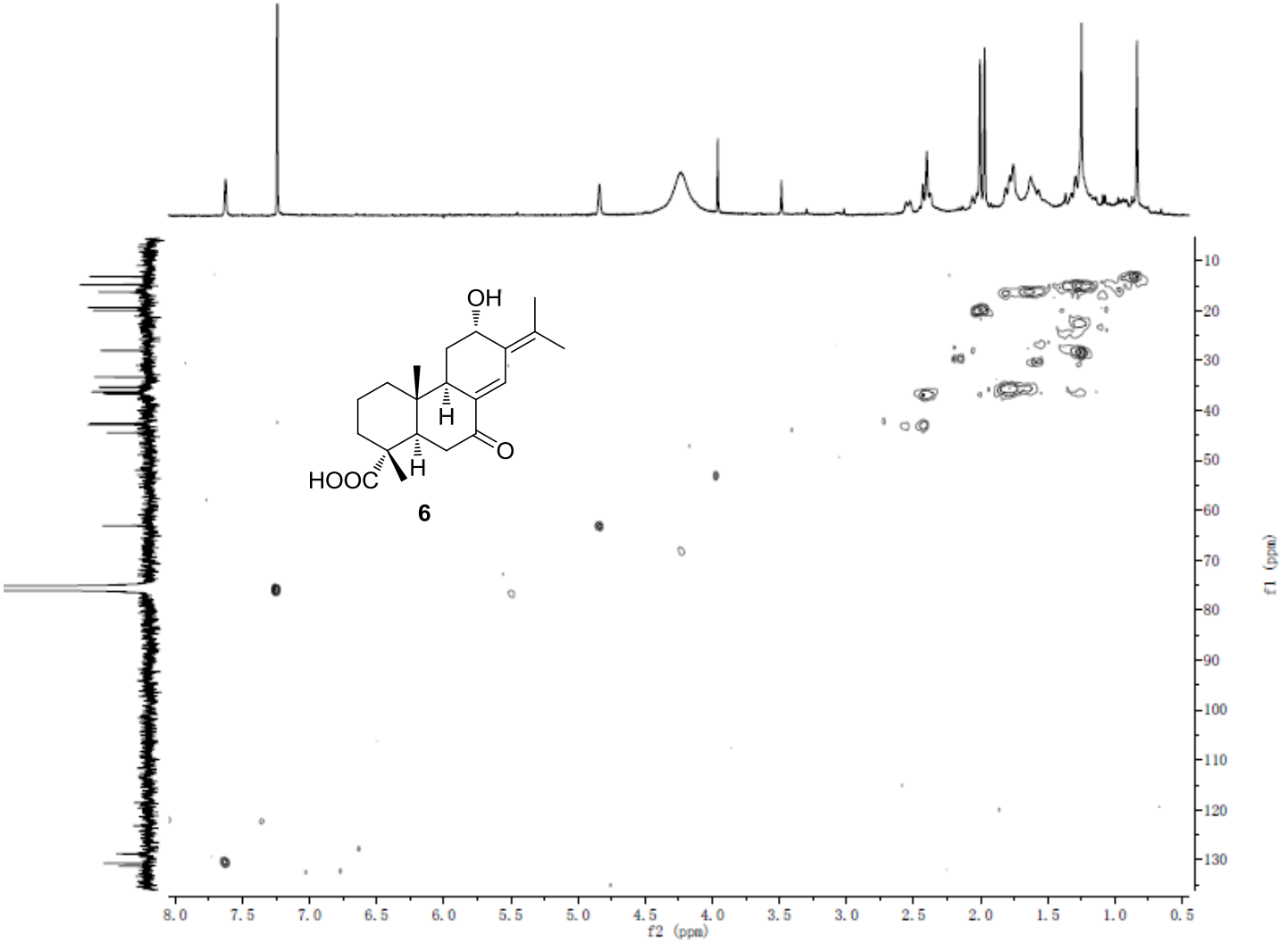
Compound 6: ^{1}H NMR ($CDCl_3$) spectrum



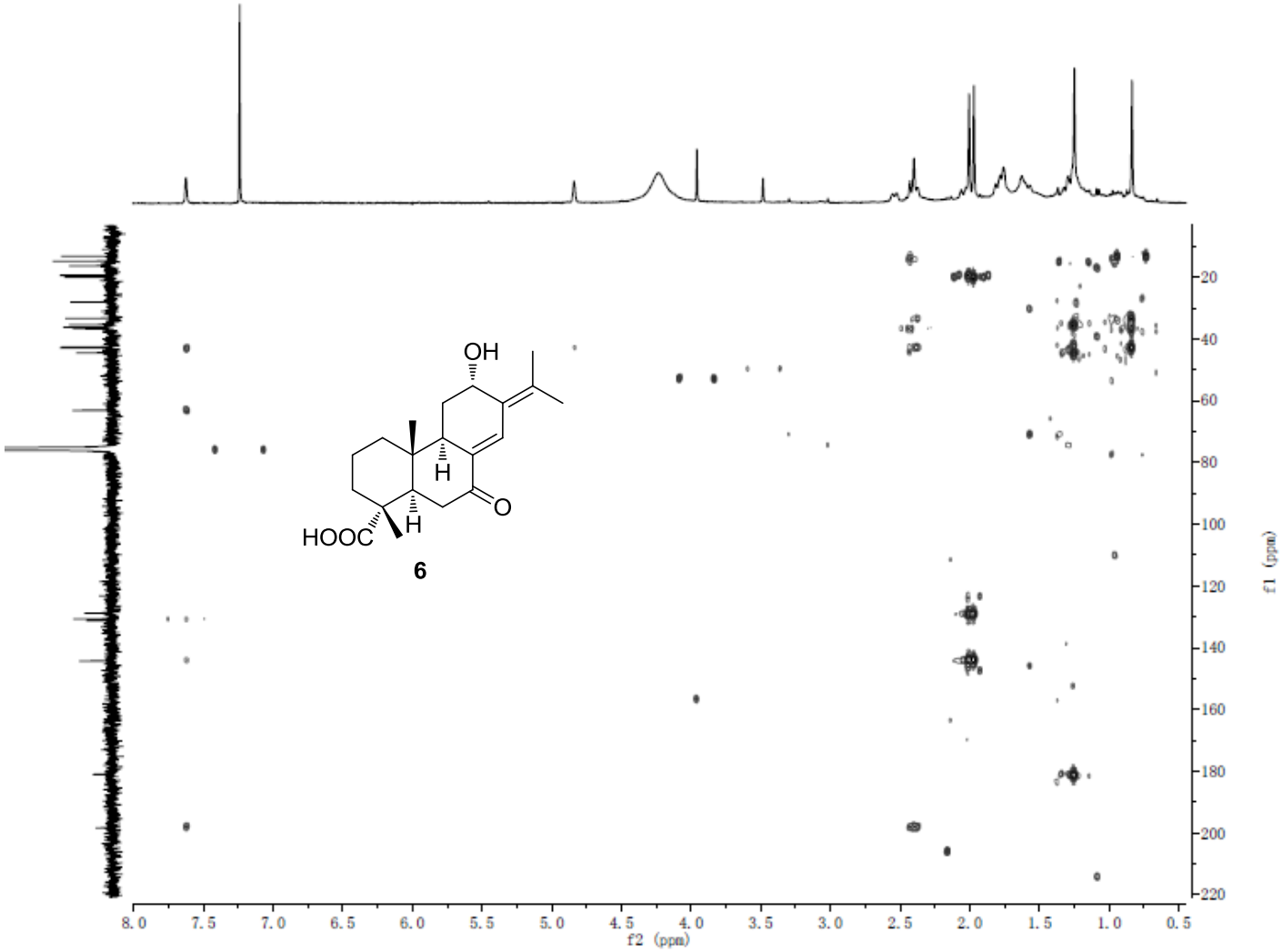
Compound 6: ^{13}C NMR ($CDCl_3$) spectrum



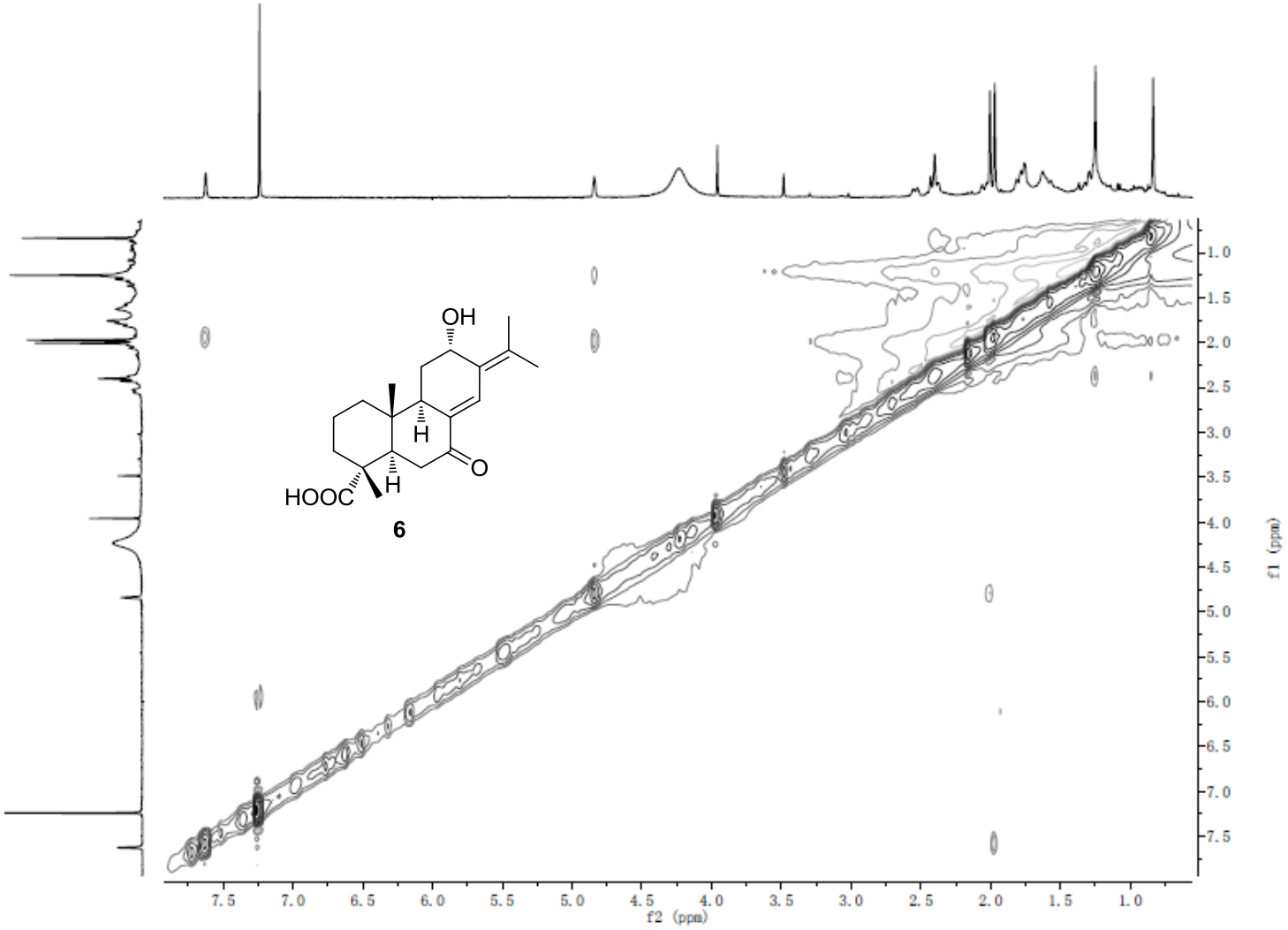
Compound 6: HSQC ($CDCl_3$) spectrum



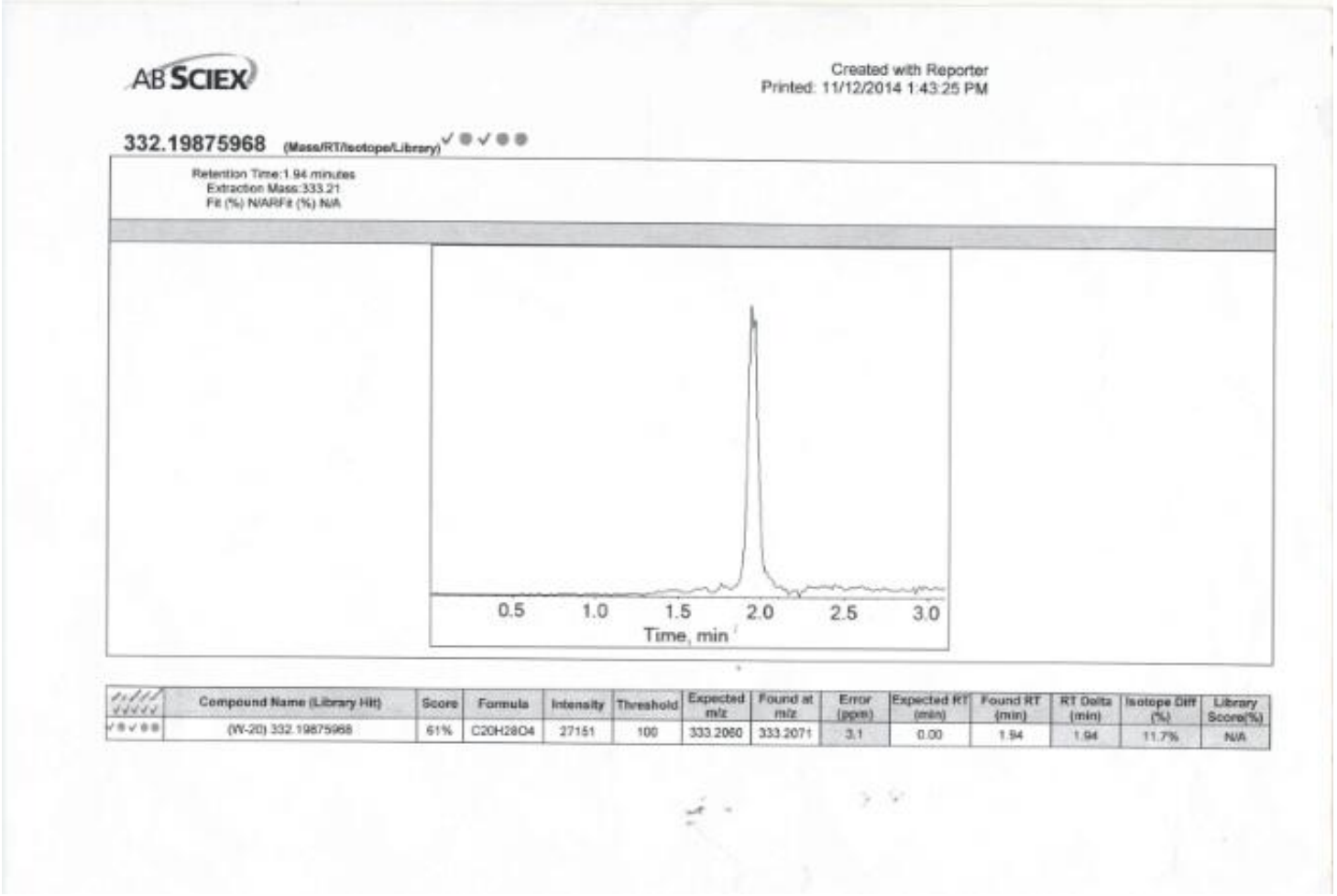
Compound 6: HMBC ($CDCl_3$) spectrum



Compound 6: NOESY ($CDCl_3$) spectrum

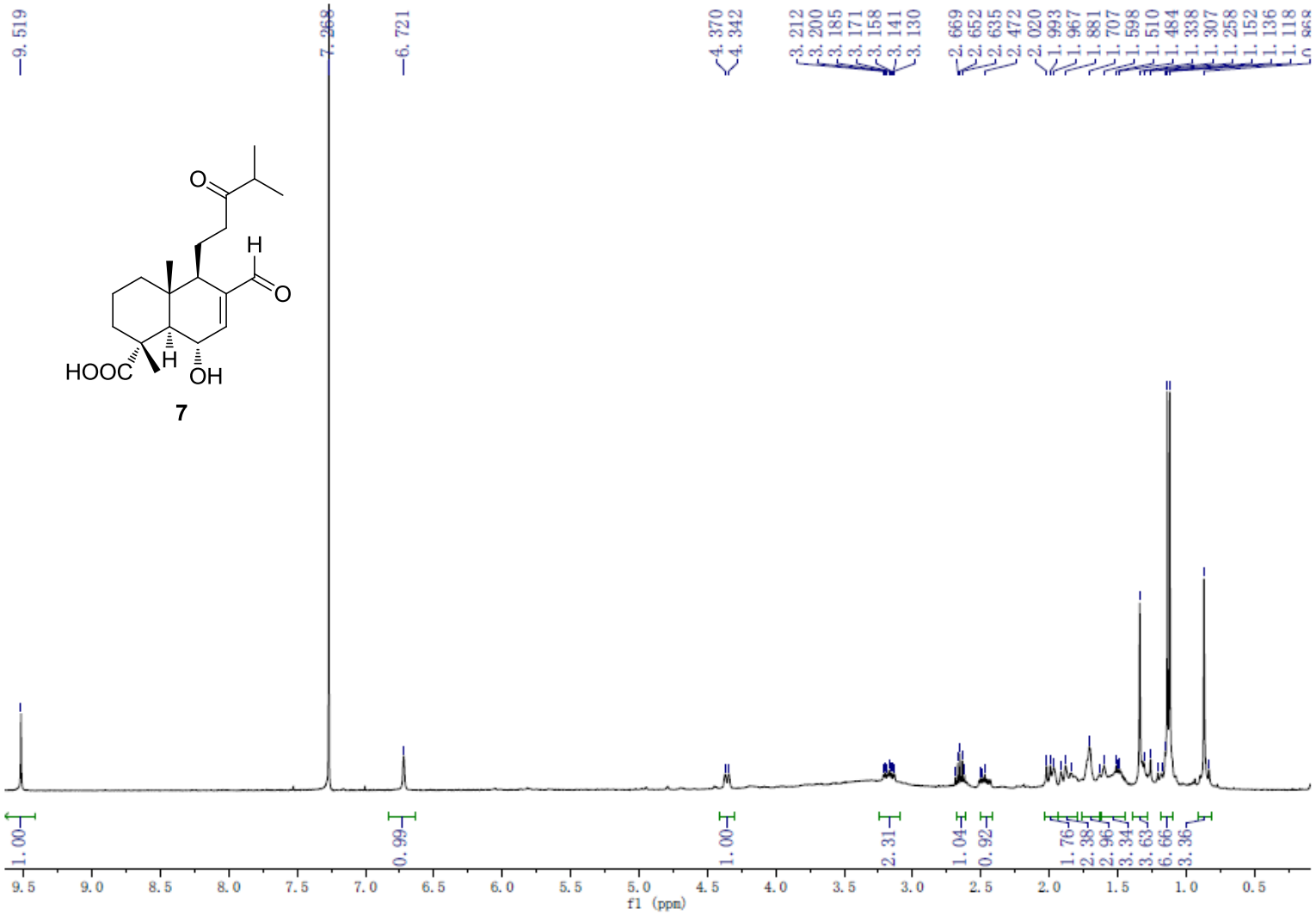


Compound 6: (+) HR-ESIMS

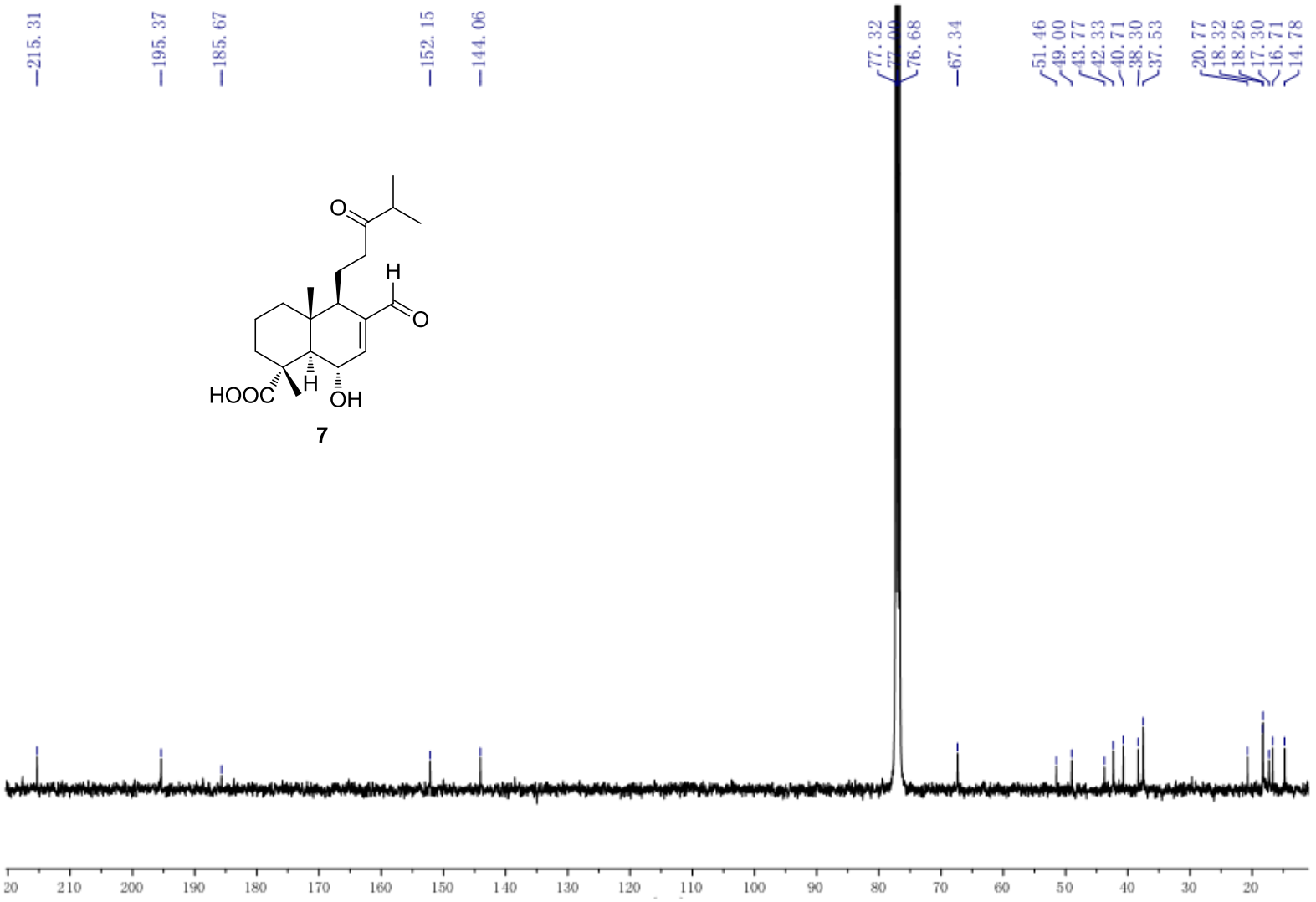


Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
(W-20) 332.19875968	61%	C20H28O4	27151	100	333.2060	333.2071	3.1	0.00	1.94	1.94	11.7%	N/A

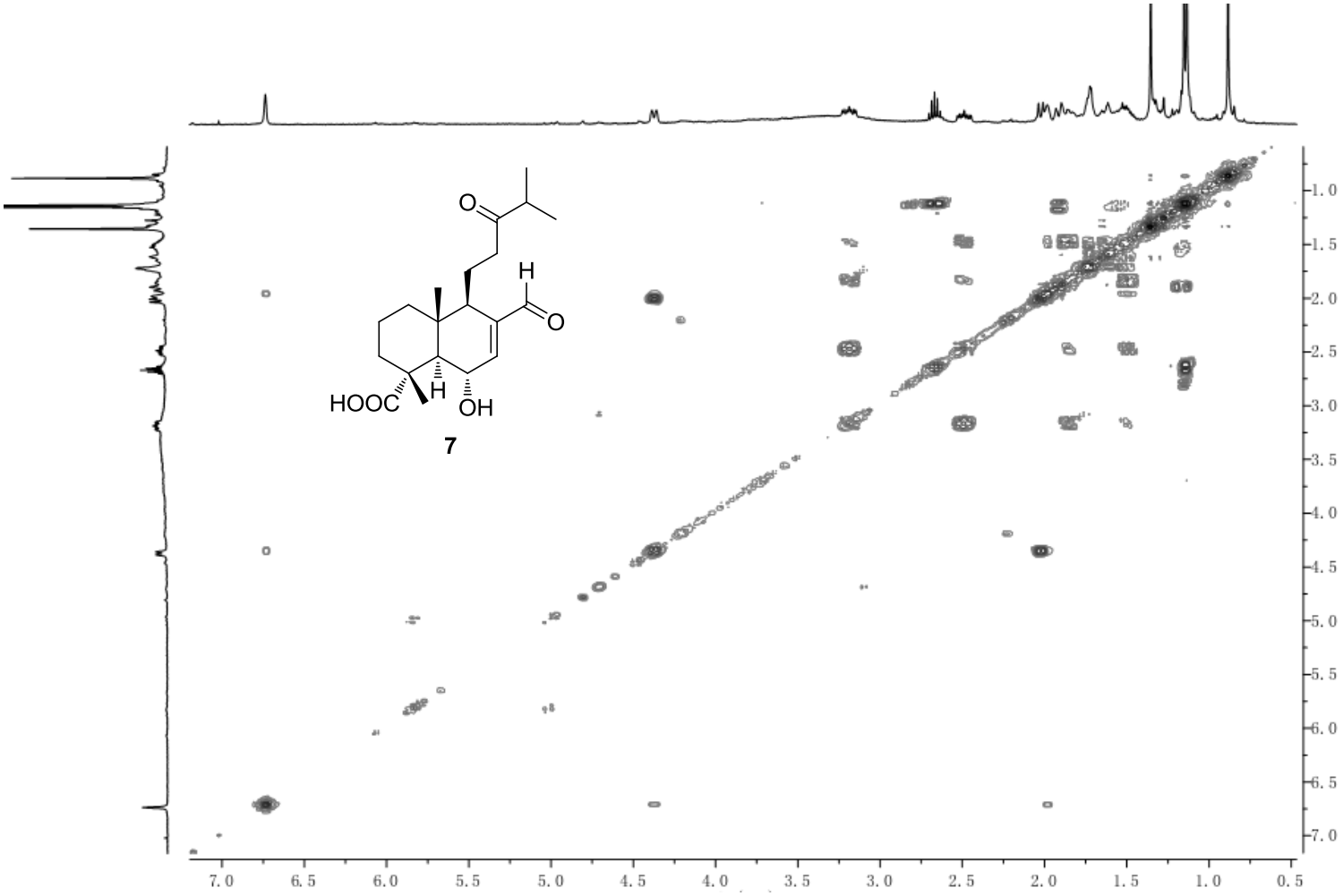
Compound 7: ^{1}H NMR ($CDCl_3$) spectrum



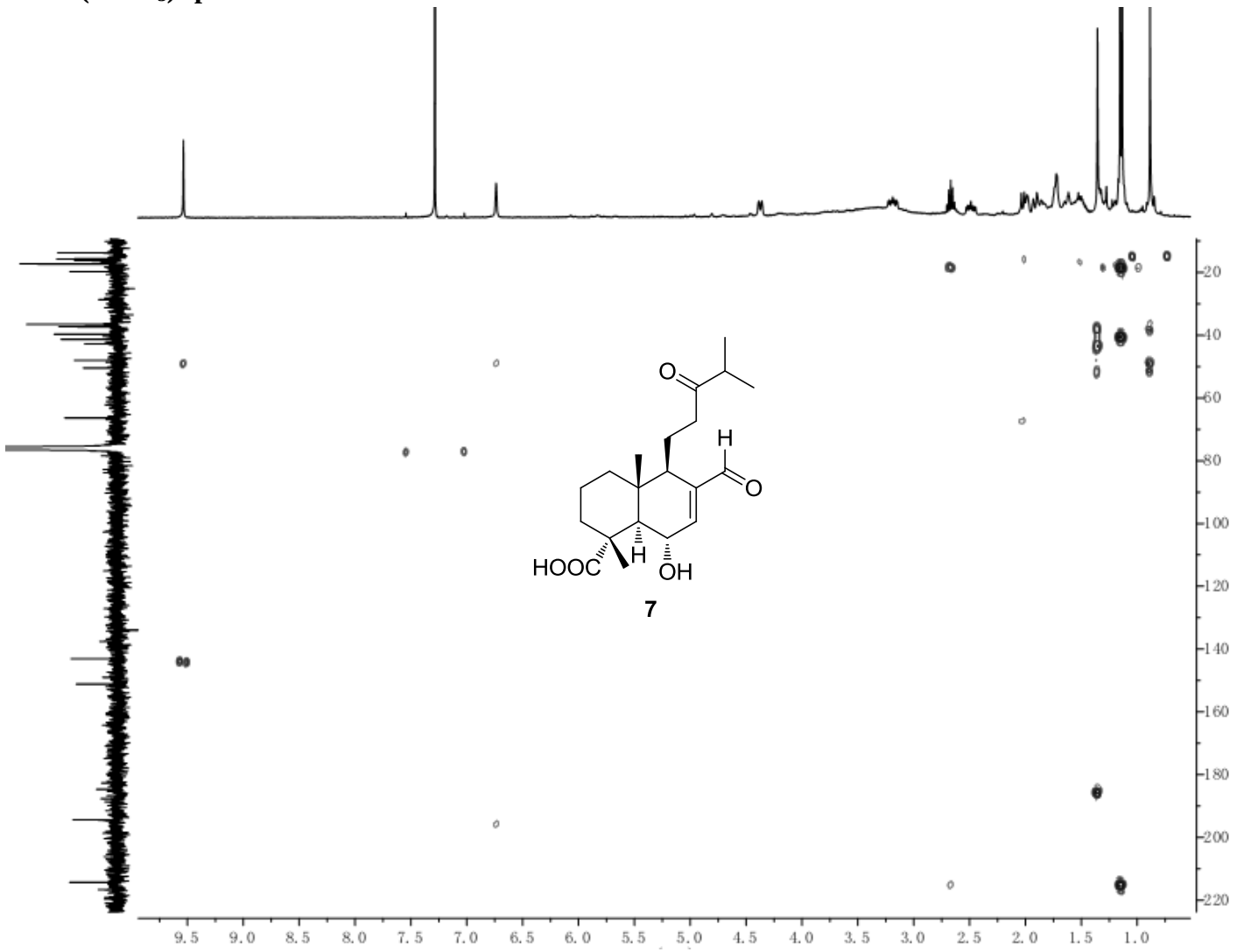
Compound 7: ^{13}C NMR ($CDCl_3$) spectrum



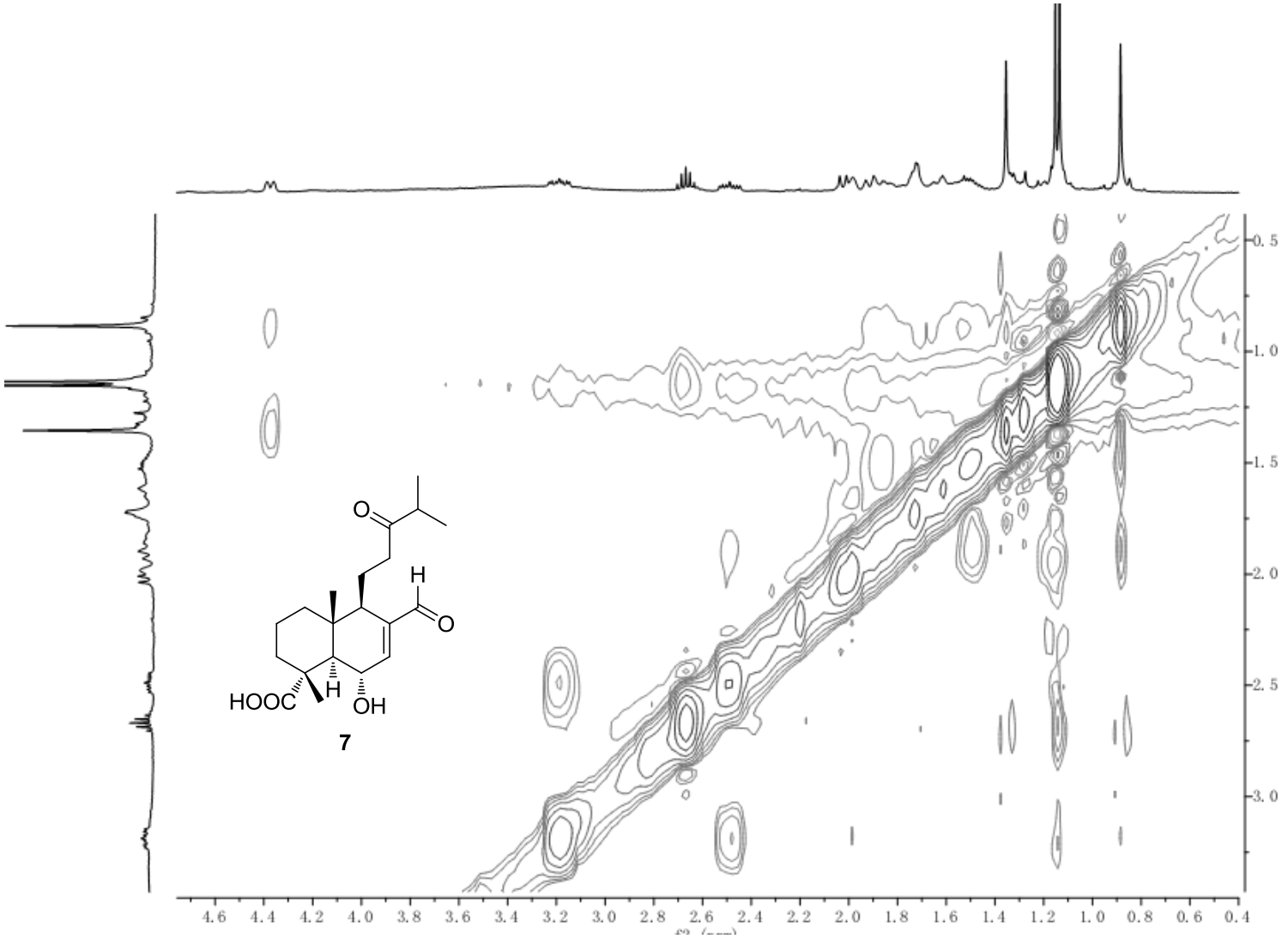
Compound 7: ^{1}H-^{1}H COSY ($CDCl_3$) spectrum



Compound 7: HMBC ($CDCl_3$) spectrum



Compound 7: NOESY ($CDCl_3$) spectrum



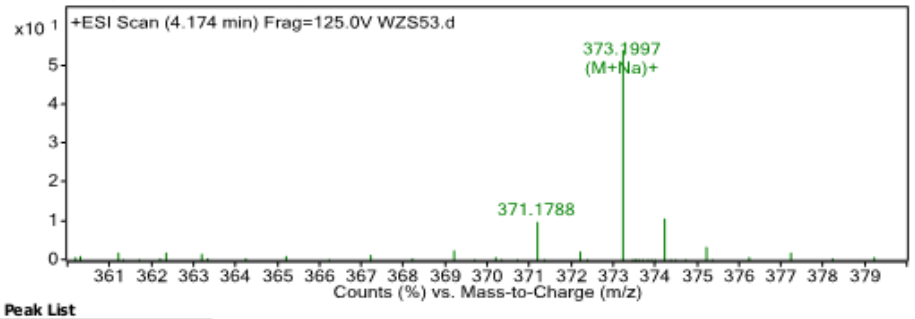
Compound 7: (+) HR-ESIMS

Qualitative Analysis Report

Data Filename	WZS53.d	**Sample Name**	WZS53
Sample Type	Sample	**Position**	P1-D5
Instrument Name	Instrument 1	**User Name**	
Acq Method	general test 2.m	**Acquired Time**	12/19/2013 2:51:11 PM
IRM Calibration Status	Some Ions Missed	**DA Method**	Screening-Default.m
Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	Esi



Peak List

m/z	z	Abund
355.1893	1	741171

Formula Calculator Element Limits

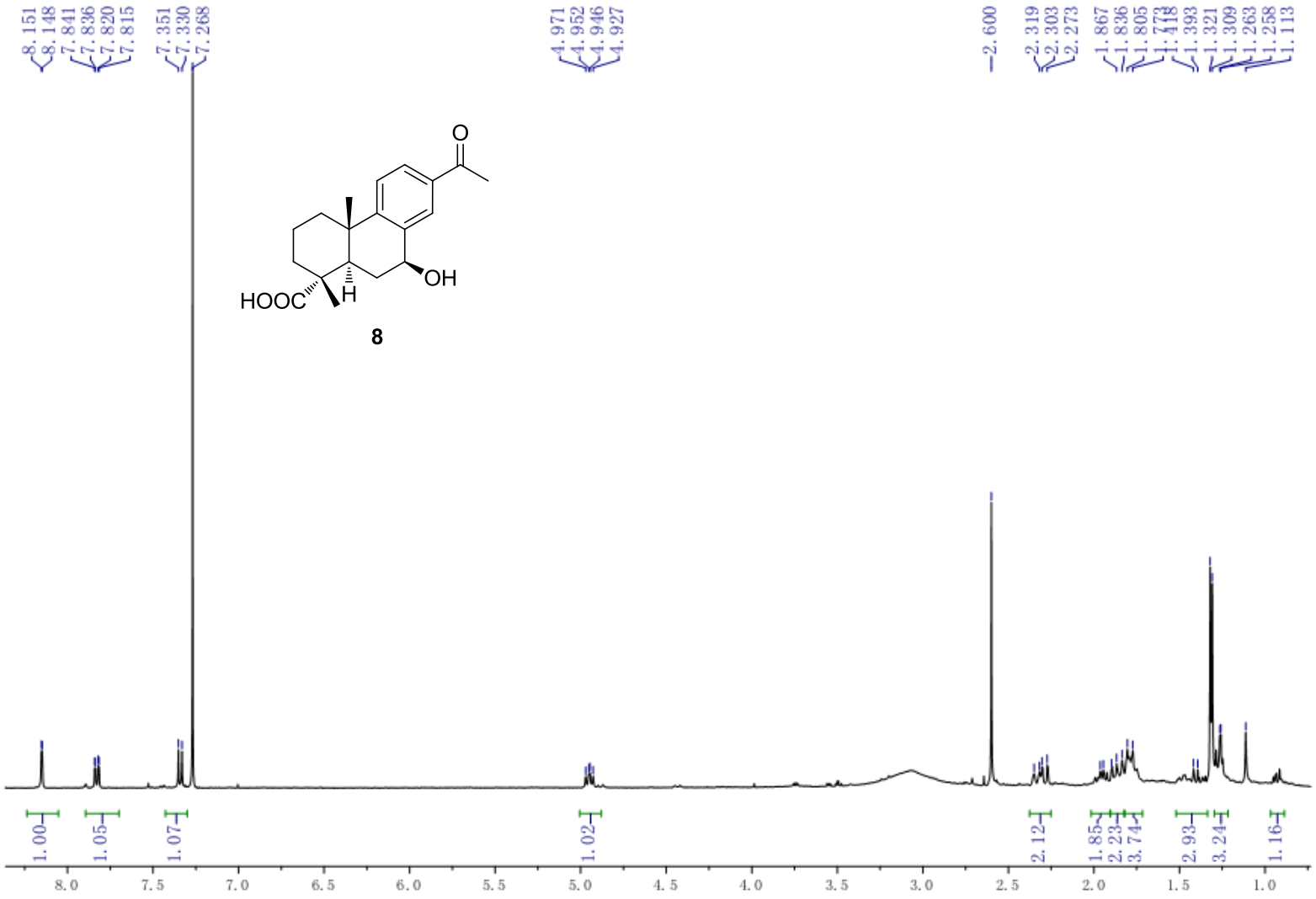
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

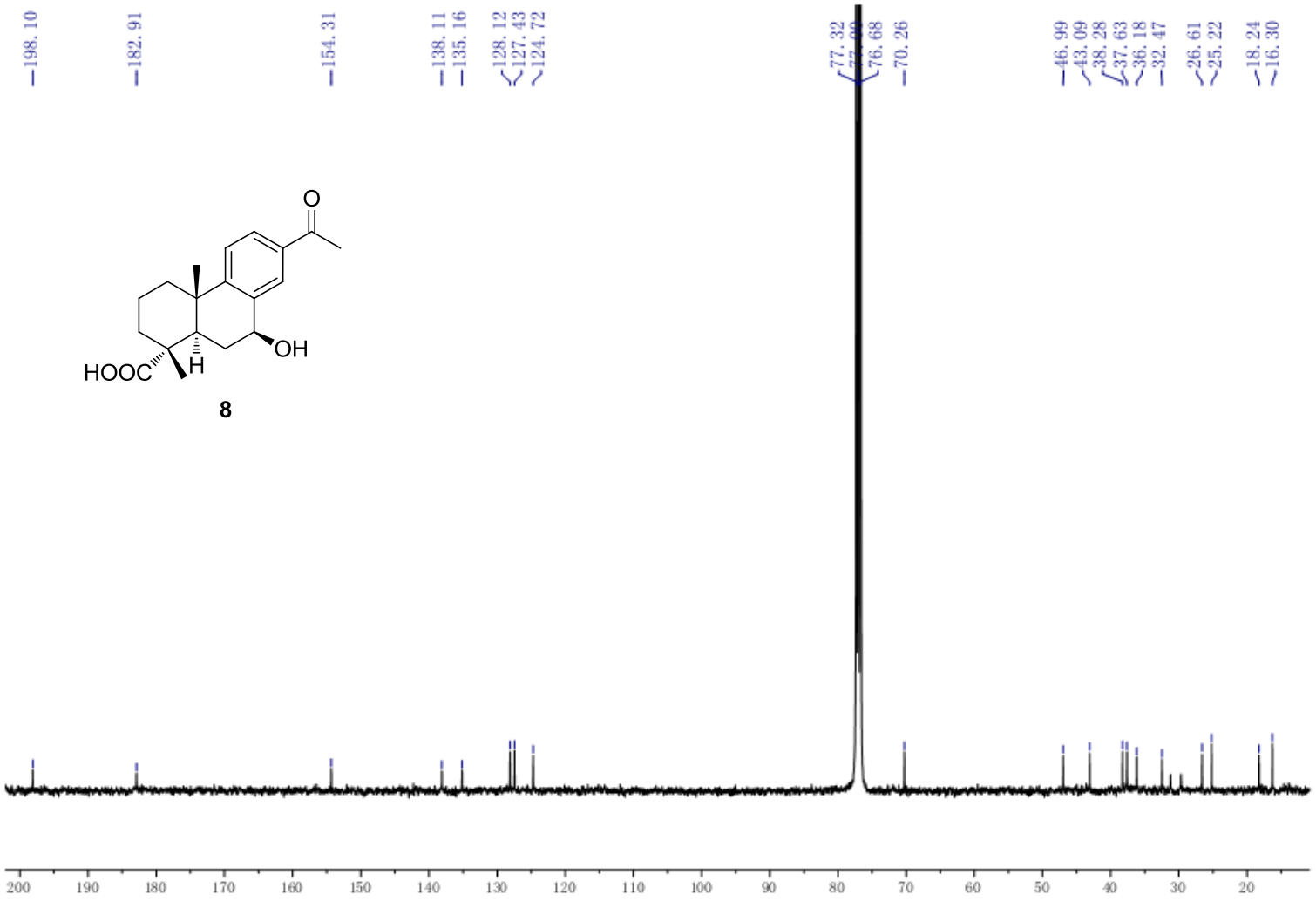
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H30 O5	TRUE	350.2105	350.2093	-3.33	C20 H30 Na O5	82.25

--- End Of Report ---

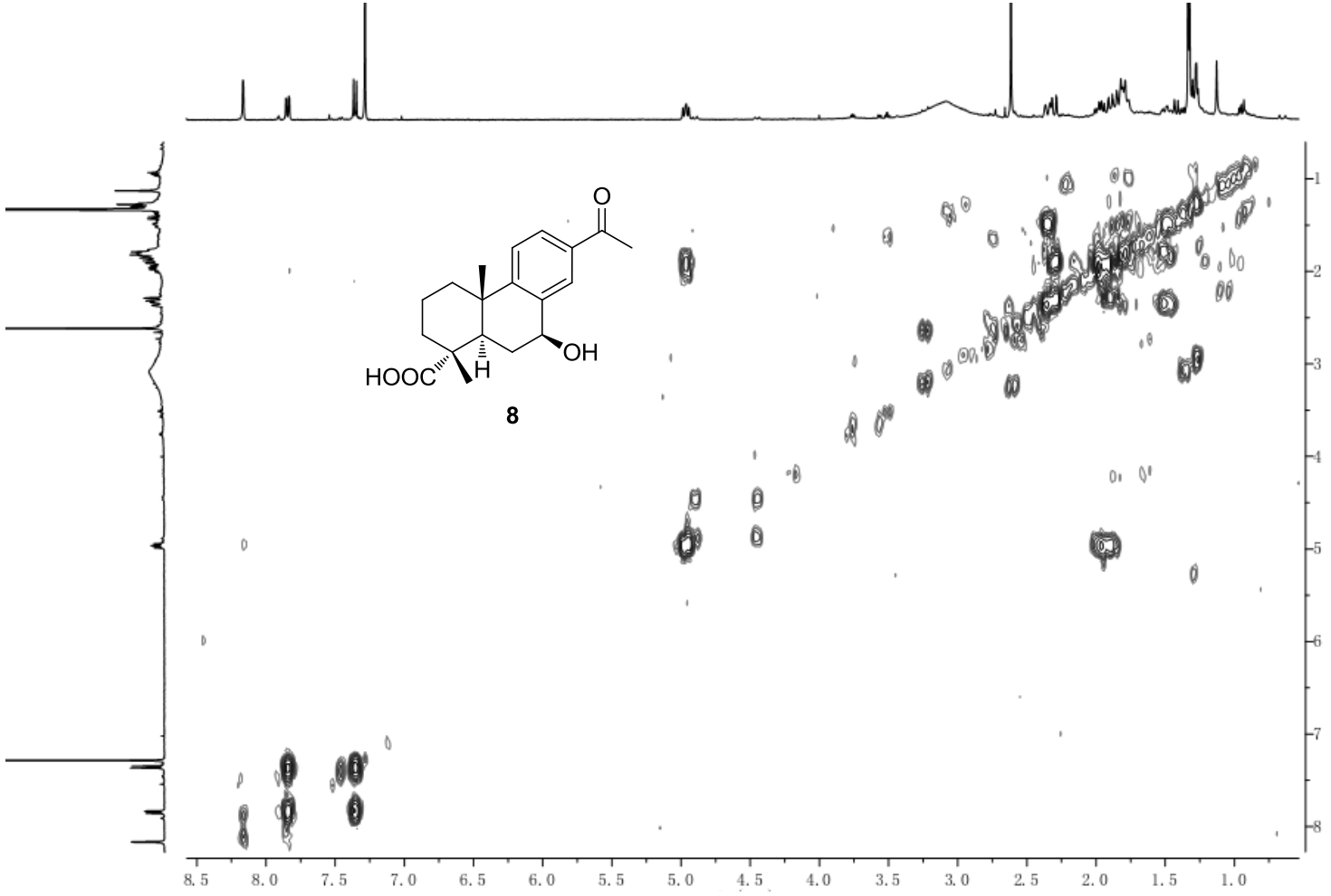
Compound 8: ^{1}H NMR ($CDCl_3$) spectrum



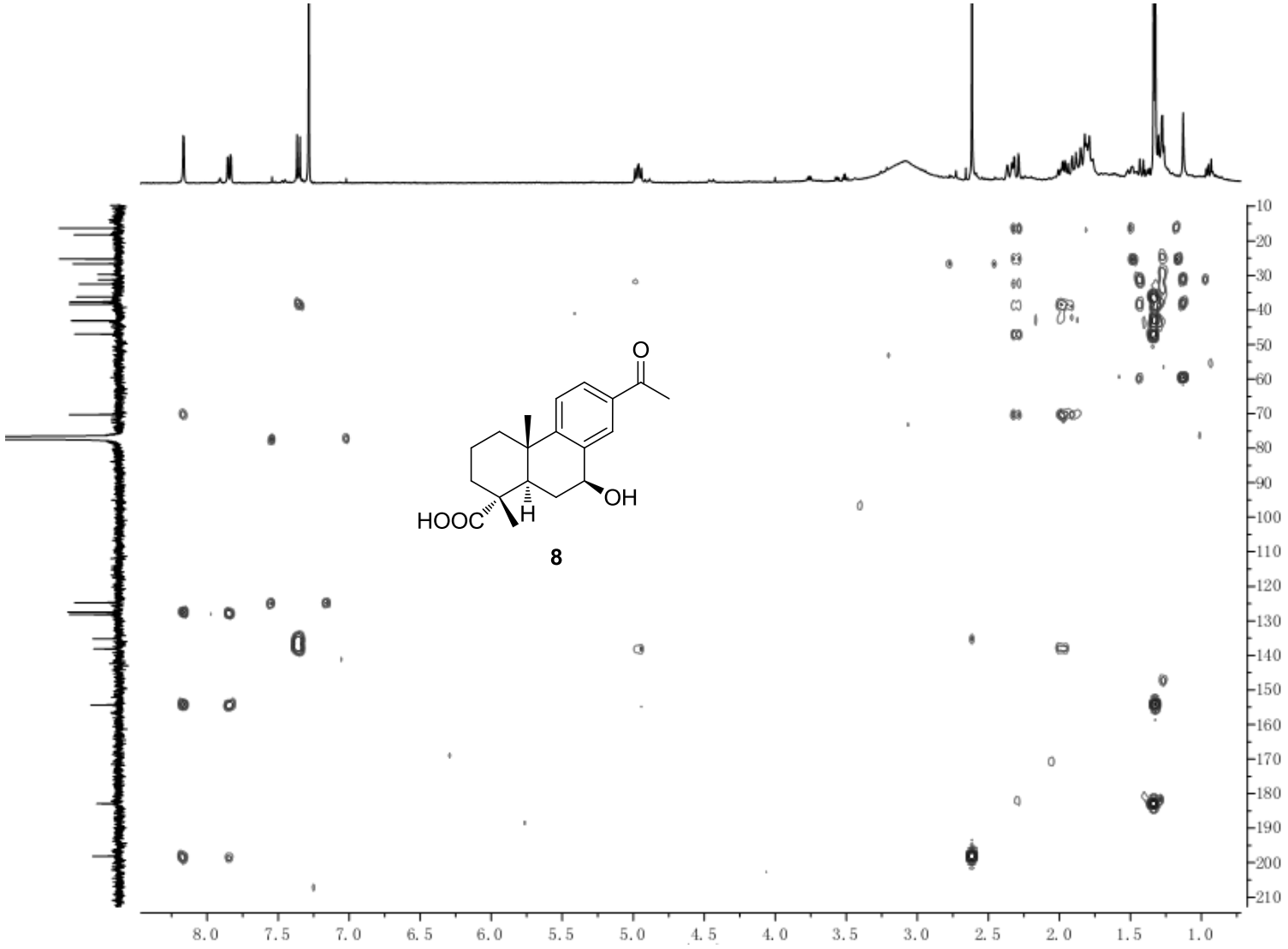
Compound 8: ^{13}C NMR ($CDCl_3$) spectrum



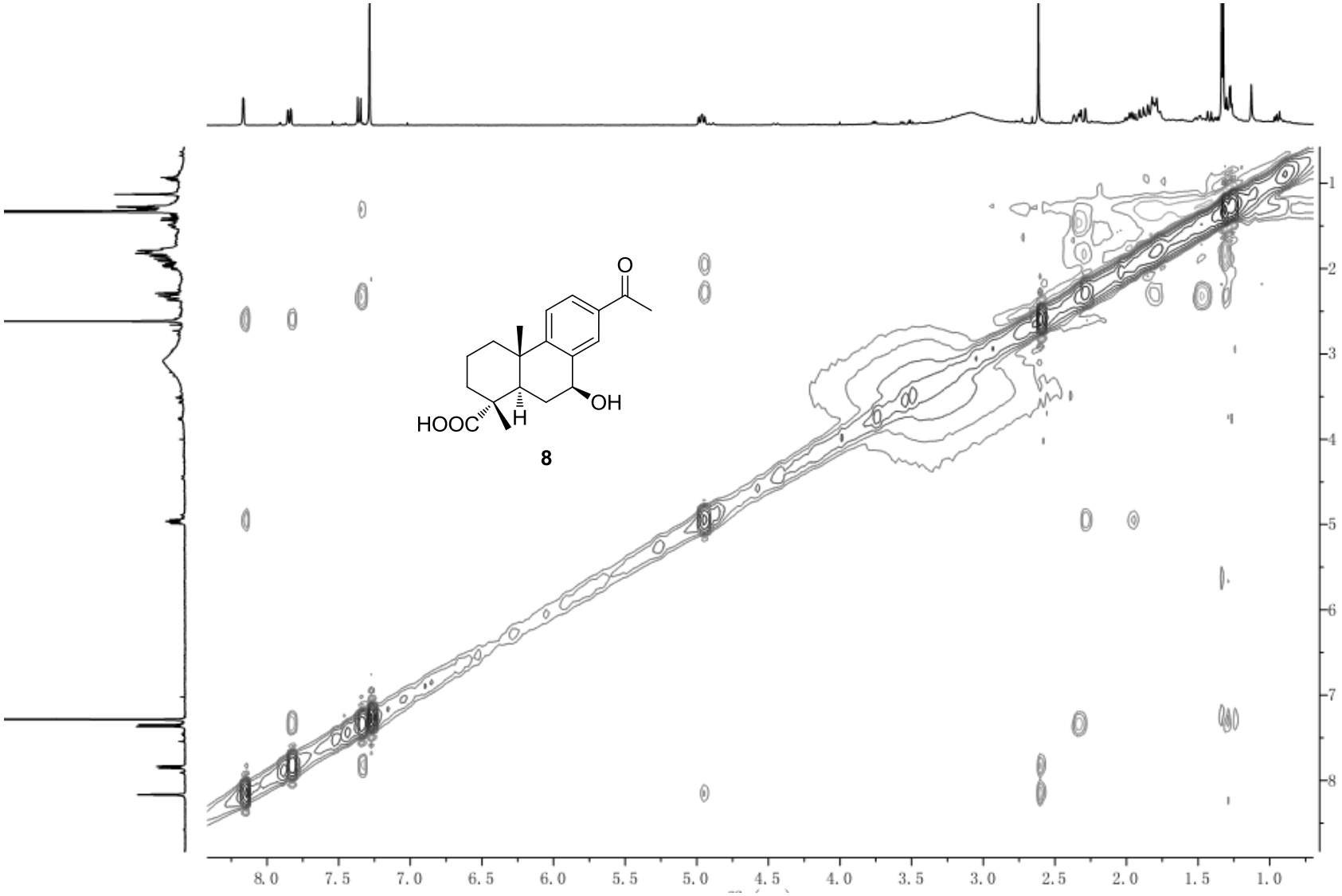
Compound 8: ^{1}H-^{1}H COSY ($CDCl_3$) spectrum



Compound 8: HMBC ($CDCl_3$) spectrum



Compound 8: NOESY ($CDCl_3$) spectrum



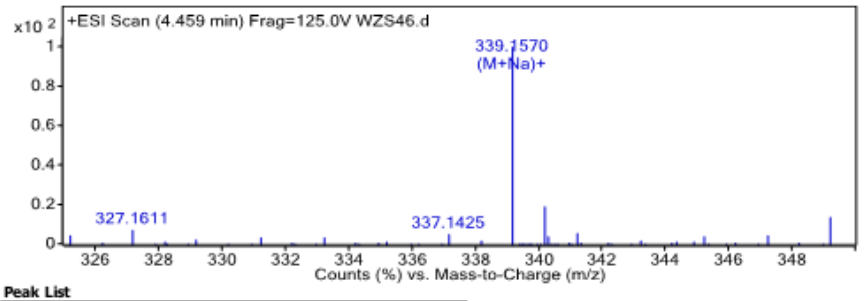
Compound 8: (+) HR-ESIMS

Qualitative Analysis Report

Data Filename	WZS46.d	**Sample Name**	WZS46
Sample Type	Sample	**Position**	P1-D4
Instrument Name	Instrument 1	**User Name**	
Acq Method	general test 2.m	**Acquired Time**	12/19/2013 2:43:21 PM
IRM Calibration Status	Some Ions Missed	**DA Method**	Screening-Default.m
Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
339.157	1	140530	C19 H24 Na O4	(M+Na)+

Formula Calculator Element Limits

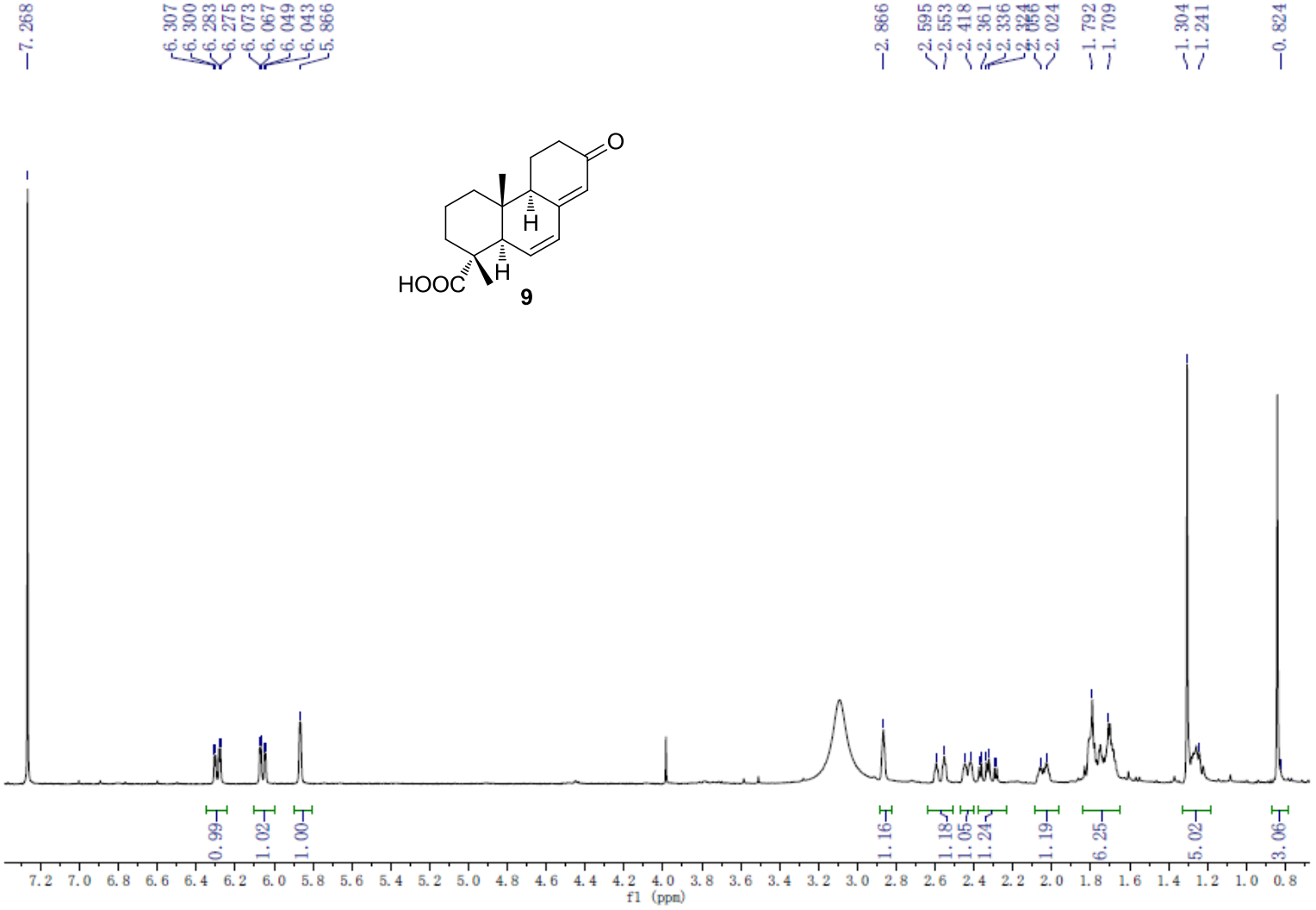
Element	Min	Max
C	3	19
H	0	24
O	0	4
N	0	0
S	0	0
Cl	0	0
Br	0	0
Si	0	0
I	0	0
P	0	0

Formula Calculator Results

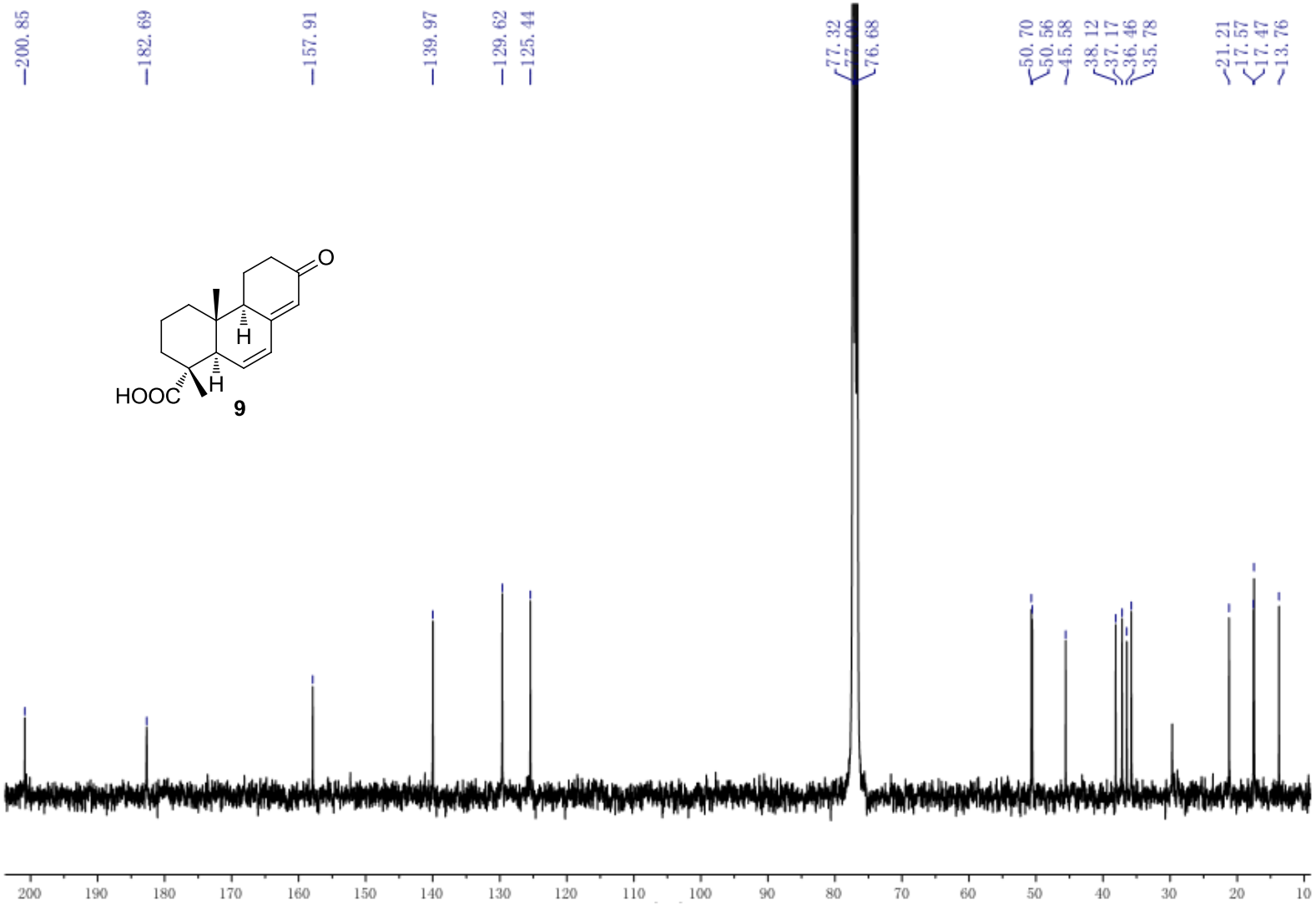
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C19 H24 O4	TRUE	316.1677	316.1675	-0.9	C19 H24 Na O4	90.29

--- End Of Report ---

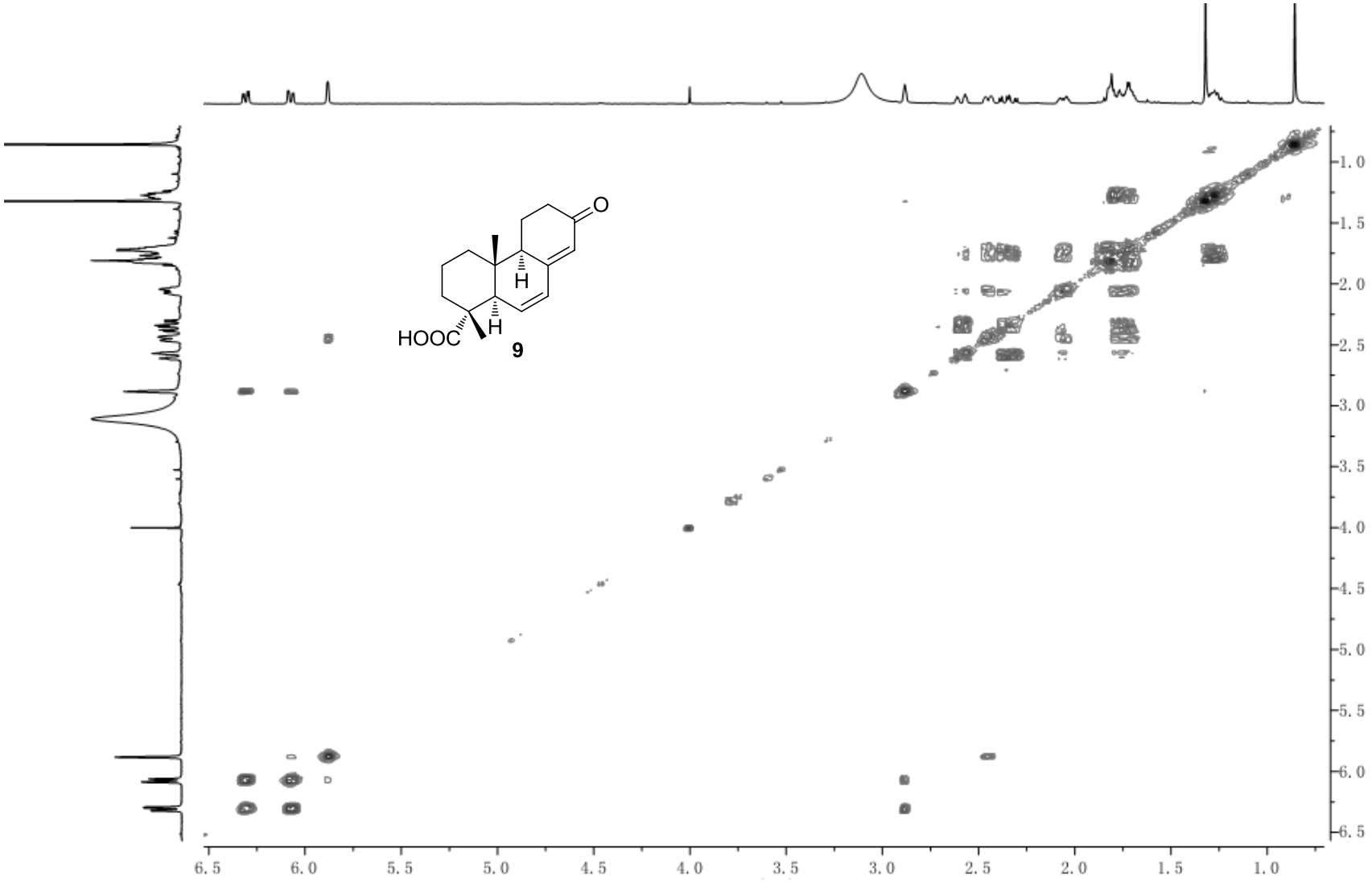
Compound 9: ^{1}H NMR ($CDCl_3$) spectrum



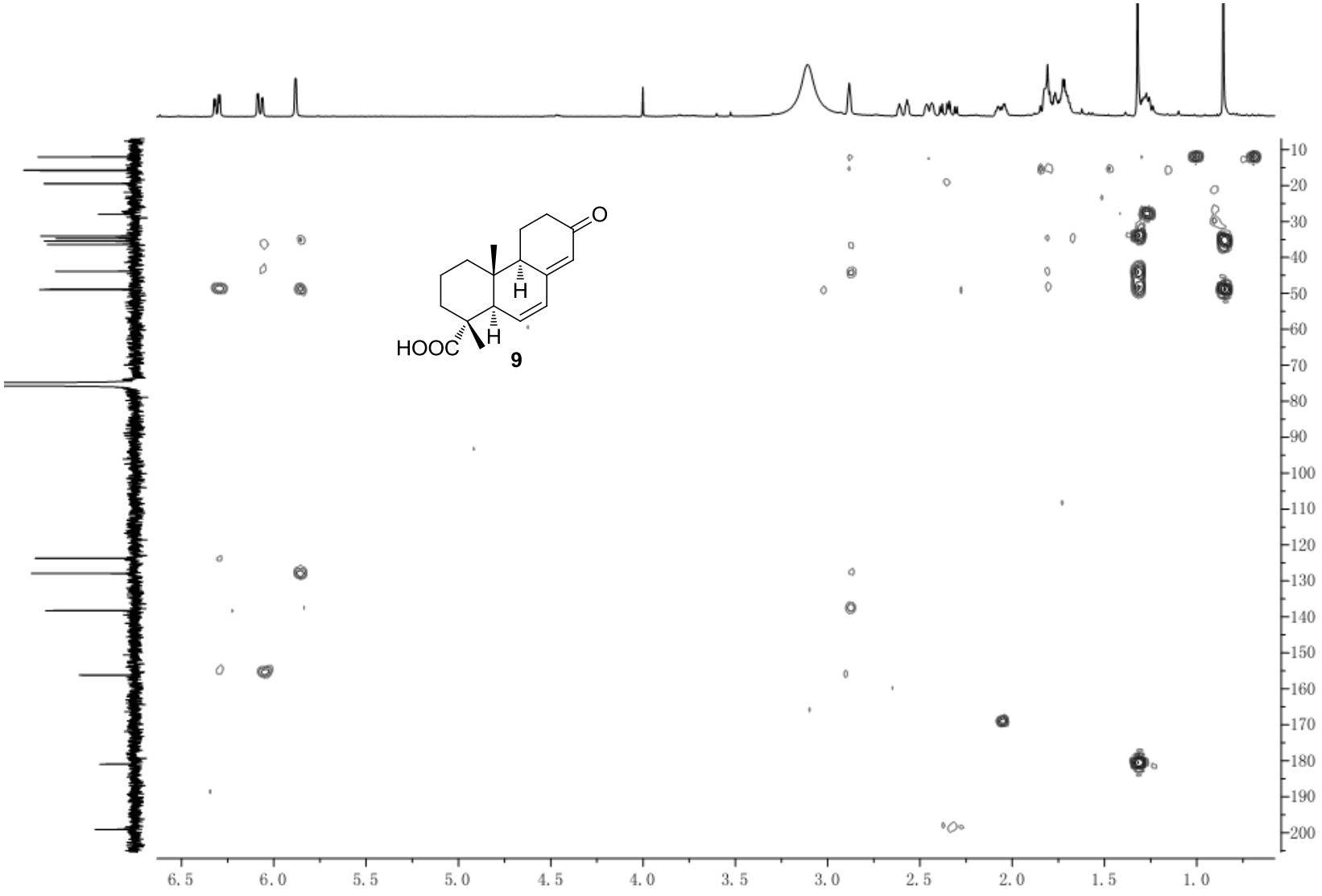
Compound 9: ^{13}C NMR ($CDCl_3$) spectrum



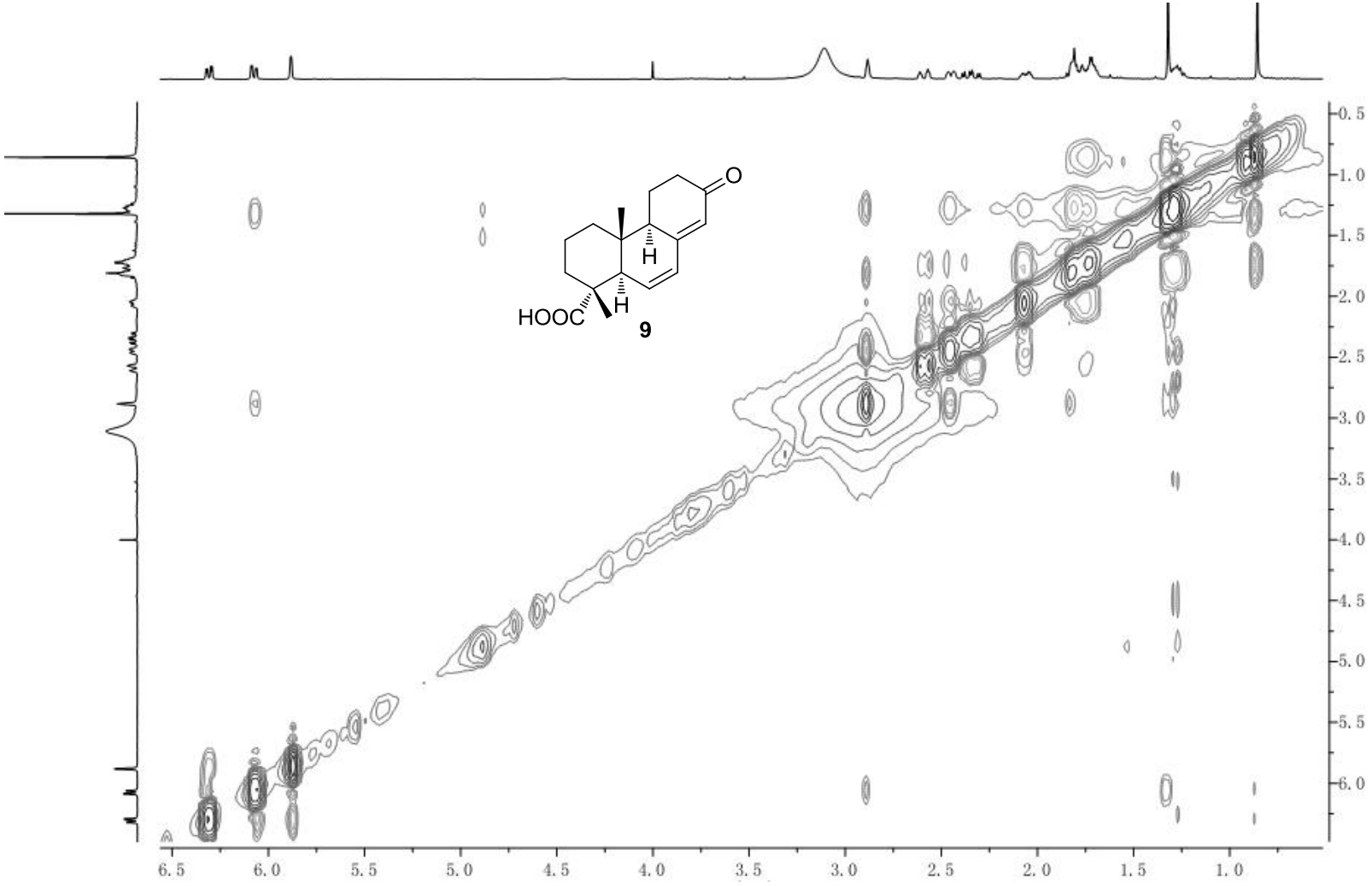
Compound 9: ^{1}H-^{1}H COSY ($CDCl_3$) spectrum



Compound 9: HMBC ($CDCl_3$) spectrum



Compound 9: NOESY ($CDCl_3$) spectrum



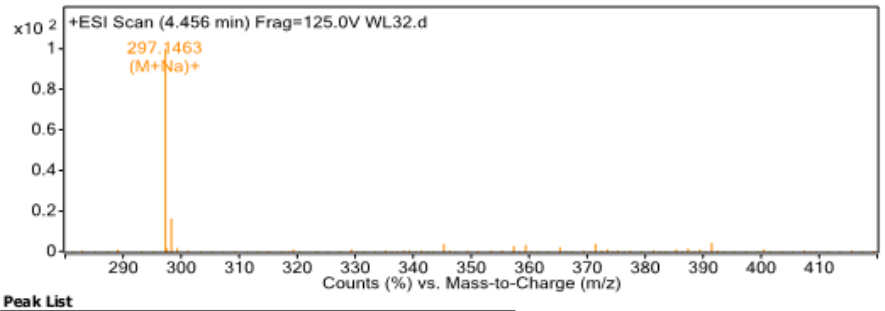
Compound 9: (+) HR-ESIMS

Qualitative Analysis Report

Data Filename	WL32.d	**Sample Name**	WL32
Sample Type	Sample	**Position**	P1-C6
Instrument Name	Instrument 1	**User Name**	
Acq Method	general test 2.m	**Acquired Time**	12/19/2013 4:09:22 PM
IRM Calibration Status	Some Ions Missed	**DA Method**	Screening-Default.m
Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	Esi



Peak List

m/z	z	Abund	Formula	Ion
297.1463	1	927320	C17 H22 Na O3	(M+Na)+

Formula Calculator Element Limits

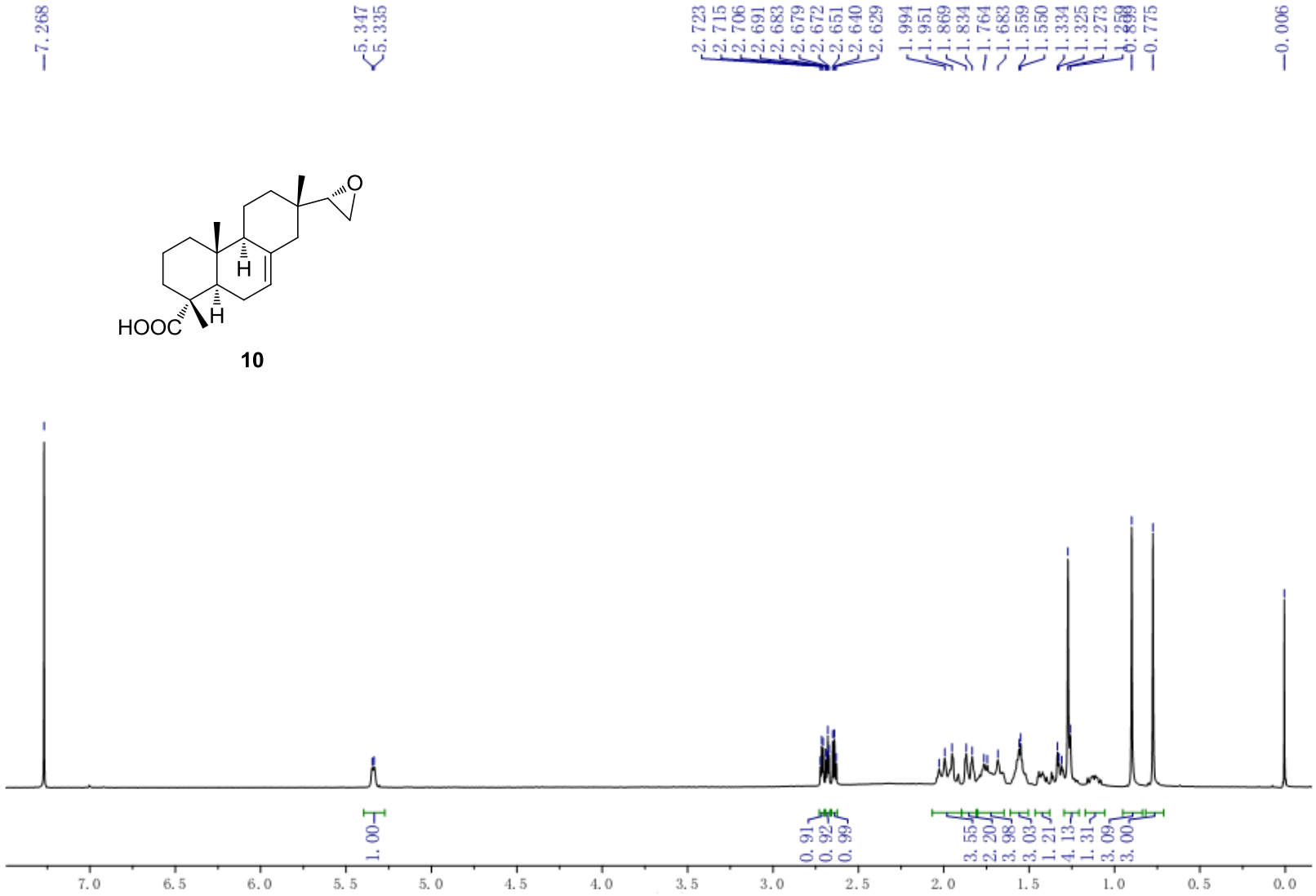
Element	Min	Max
C	3	60
H	0	120
O	0	90
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C17 H22 O3	TRUE	274.1571	274.1569	-0.79	C17 H22 Na O3	98.47

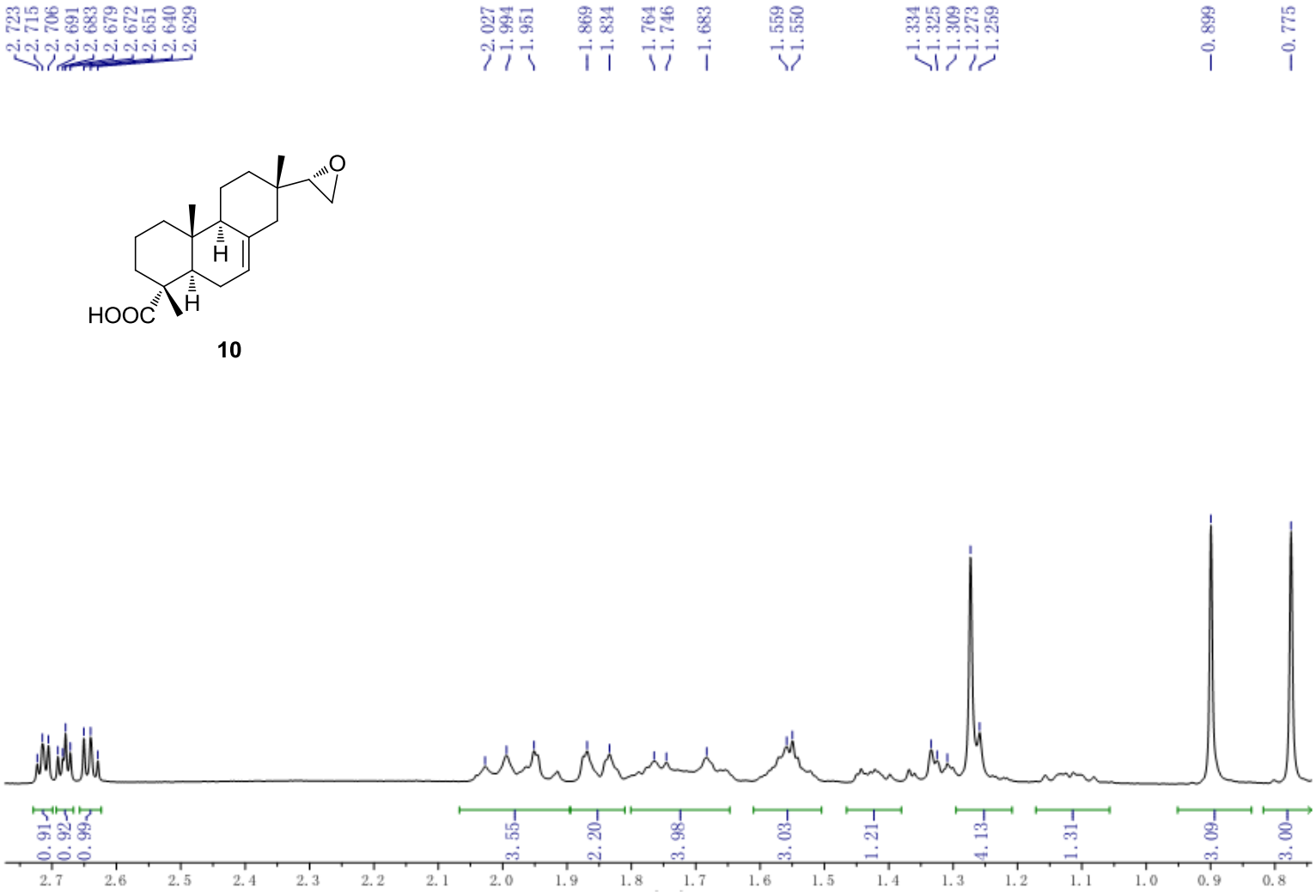
--- End Of Report ---

Compound 10: ^{1}H NMR ($CDCl_3$) spectrum



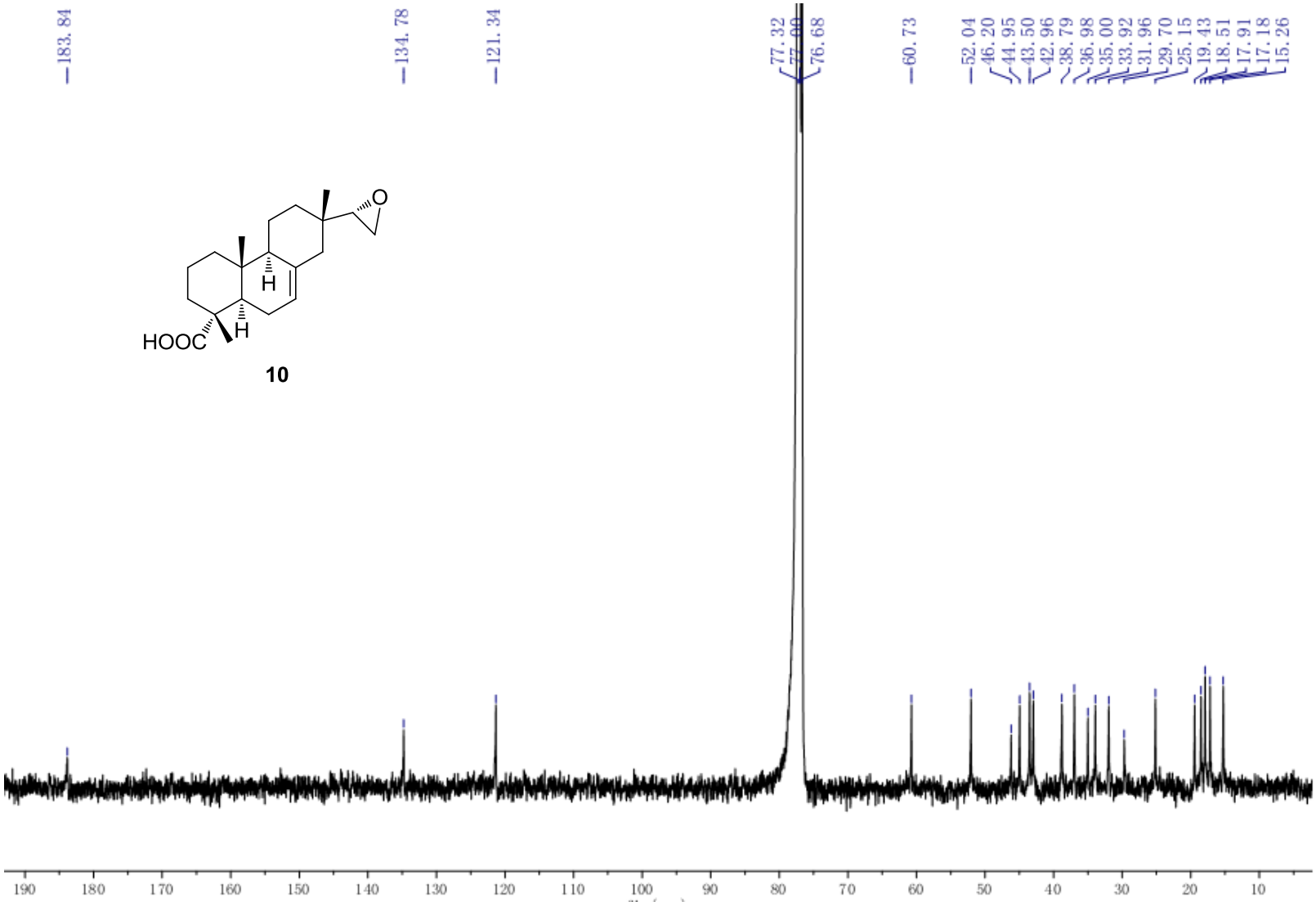
10

Compound 10: ^{1}H NMR ($CDCl_3$) spectrum-Expansion



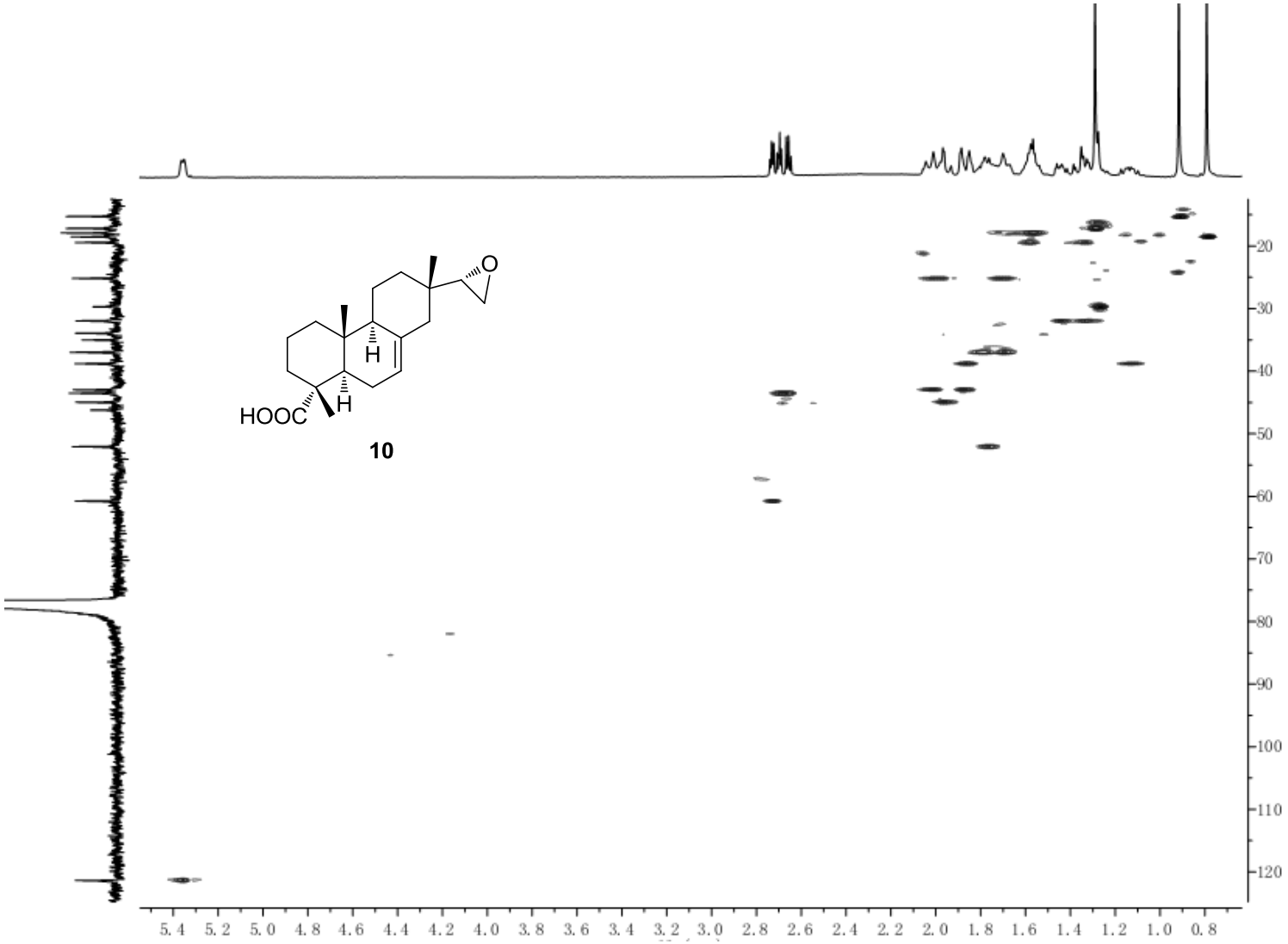
10

Compound 10: ^{13}C NMR ($CDCl_3$) spectrum

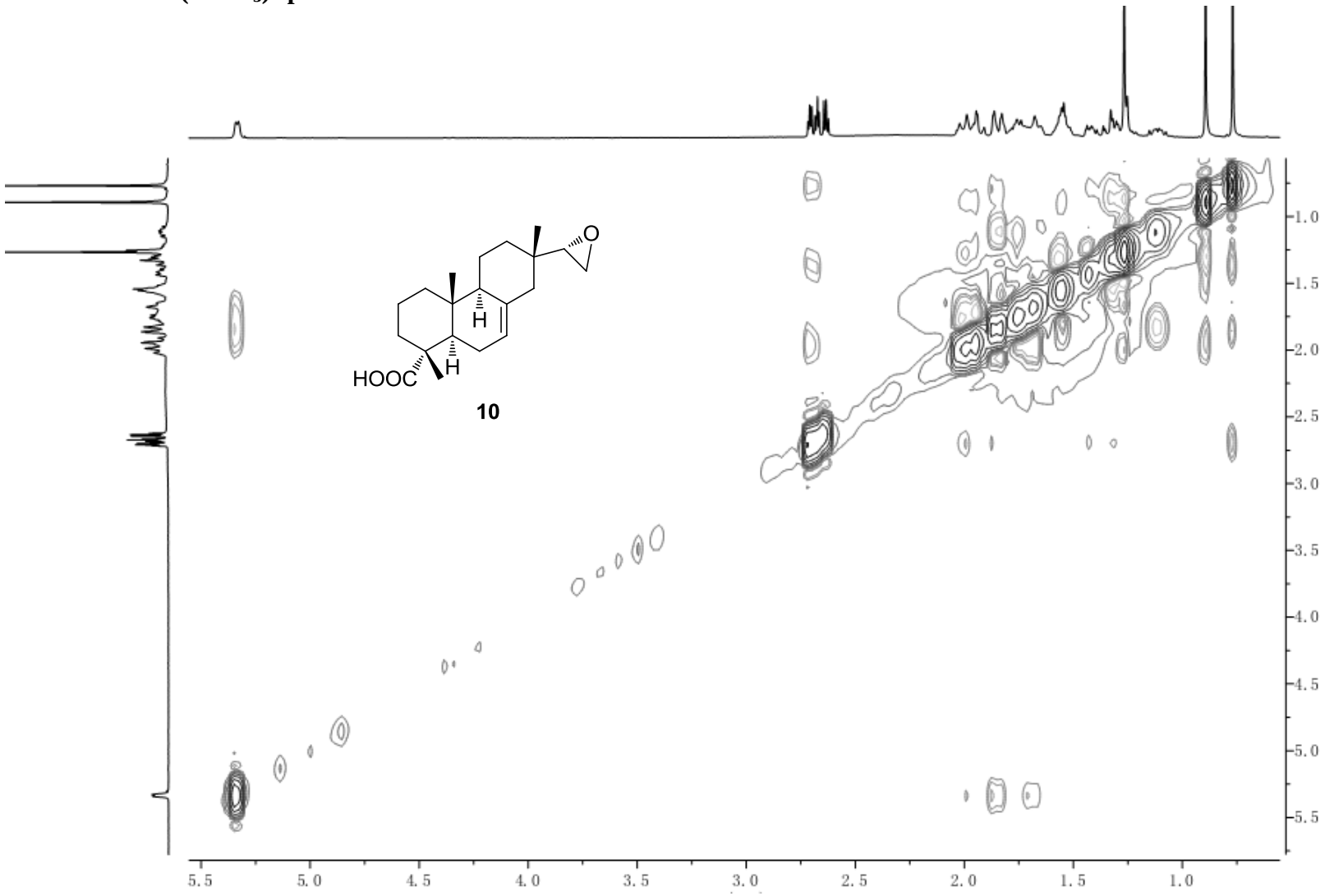


10

Compound 10: HSQC ($CDCl_3$) spectrum



Compound 10: NOESY ($CDCl_3$) spectrum



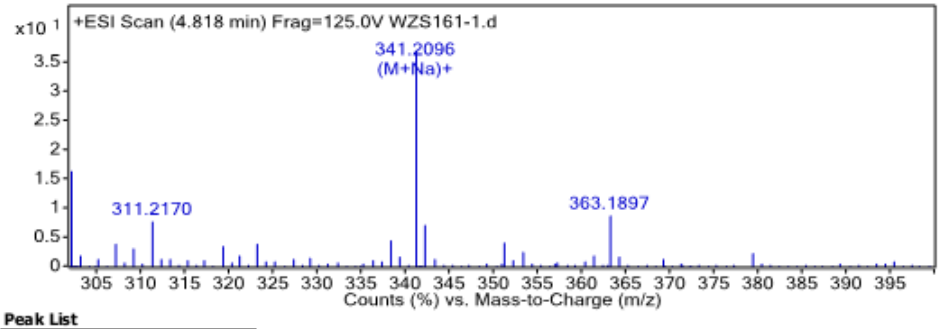
Compound 10: (+) HR-ESIMS

Qualitative Analysis Report

Data Filename	WZS161-1.d	**Sample Name**	WZS161
Sample Type	Sample	**Position**	P1-D8
Instrument Name	Instrument 1	**User Name**	
Acq Method	general test 2.m	**Acquired Time**	12/19/2013 5:29:53 PM
IRM Calibration Status	Some Ions Missed	**DA Method**	Screening-Default.m
Comment			

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
125	0	Esi



Peak List

m/z	z	Abund
301.1423	1	1587864

Formula Calculator Element Limits

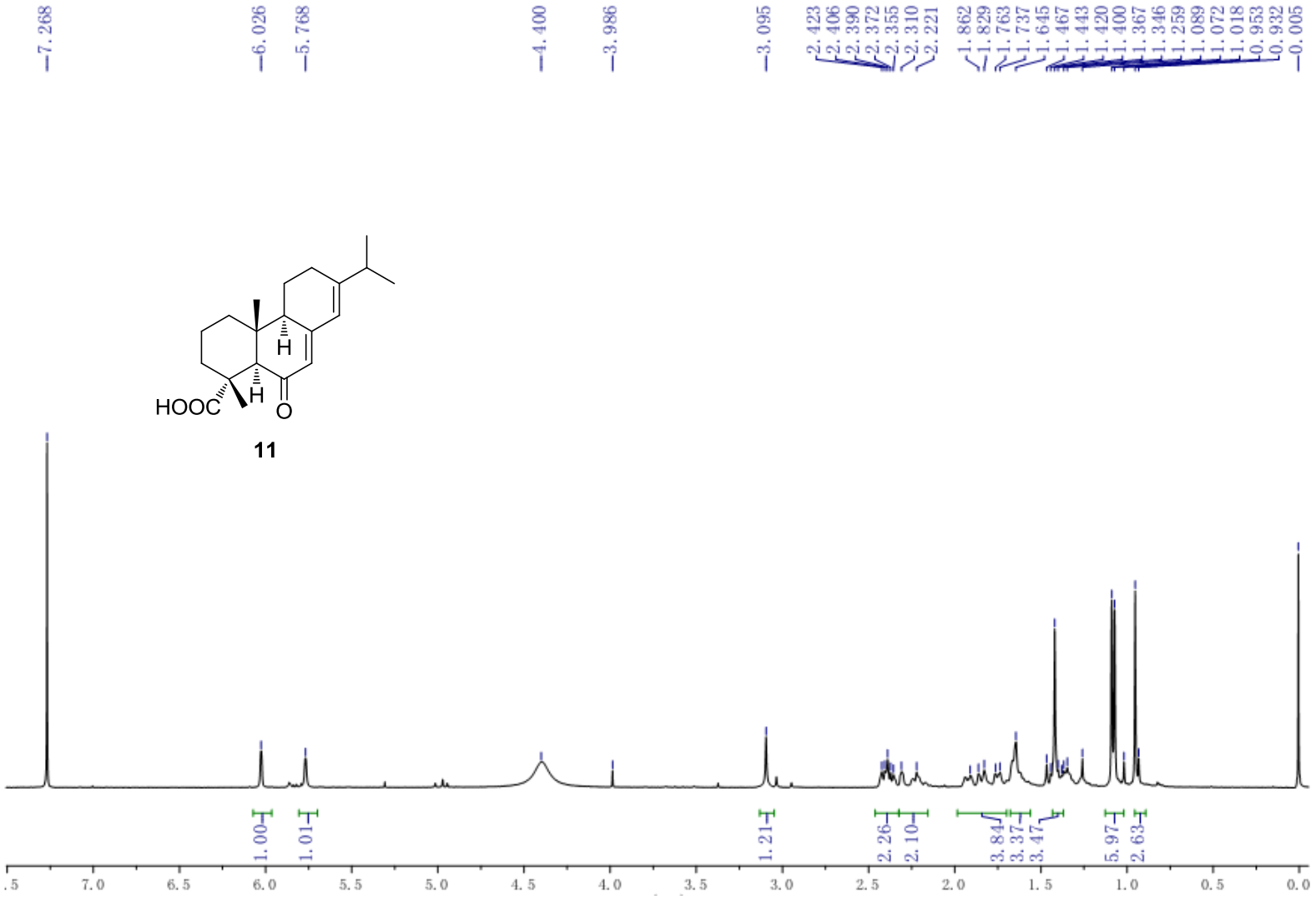
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	1
S	0	0
Cl	0	0
Br	0	0
Si	0	0

Formula Calculator Results

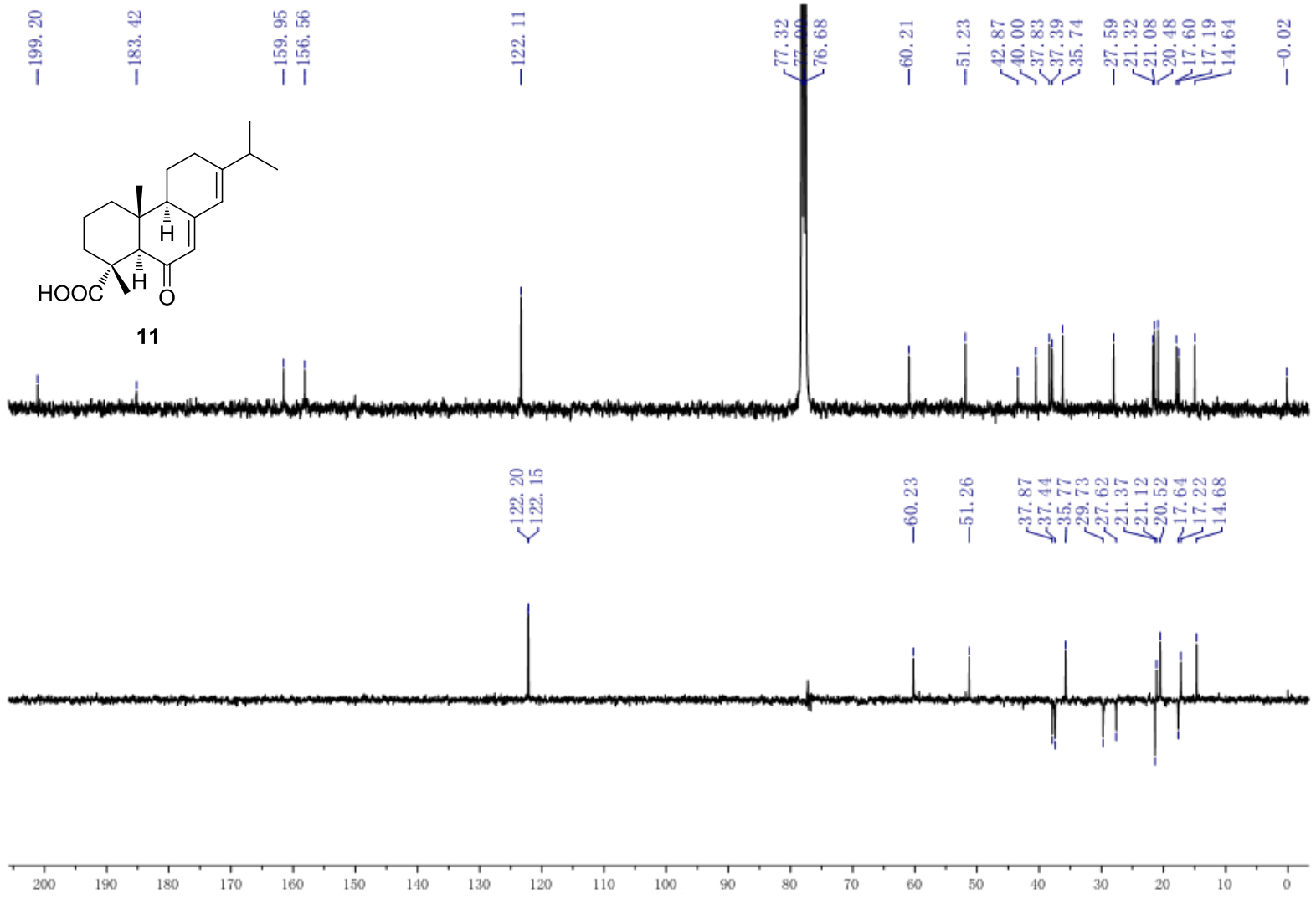
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C20 H30 O3	TRUE	318.2203	318.2195	-2.67	C20 H30 Na O3	96.09

--- End Of Report ---

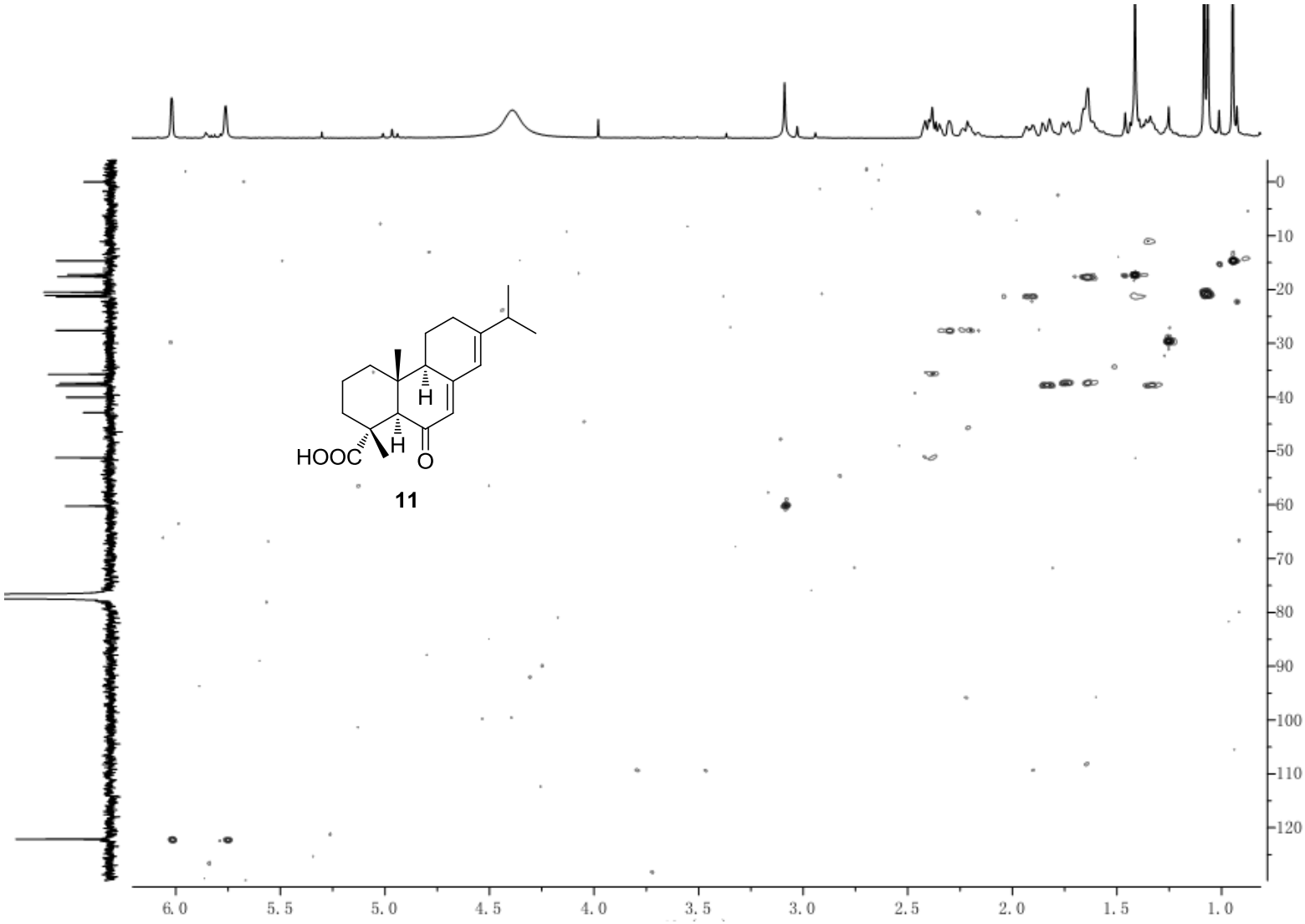
Compound 11: ^{1}H NMR ($CDCl_3$) spectrum



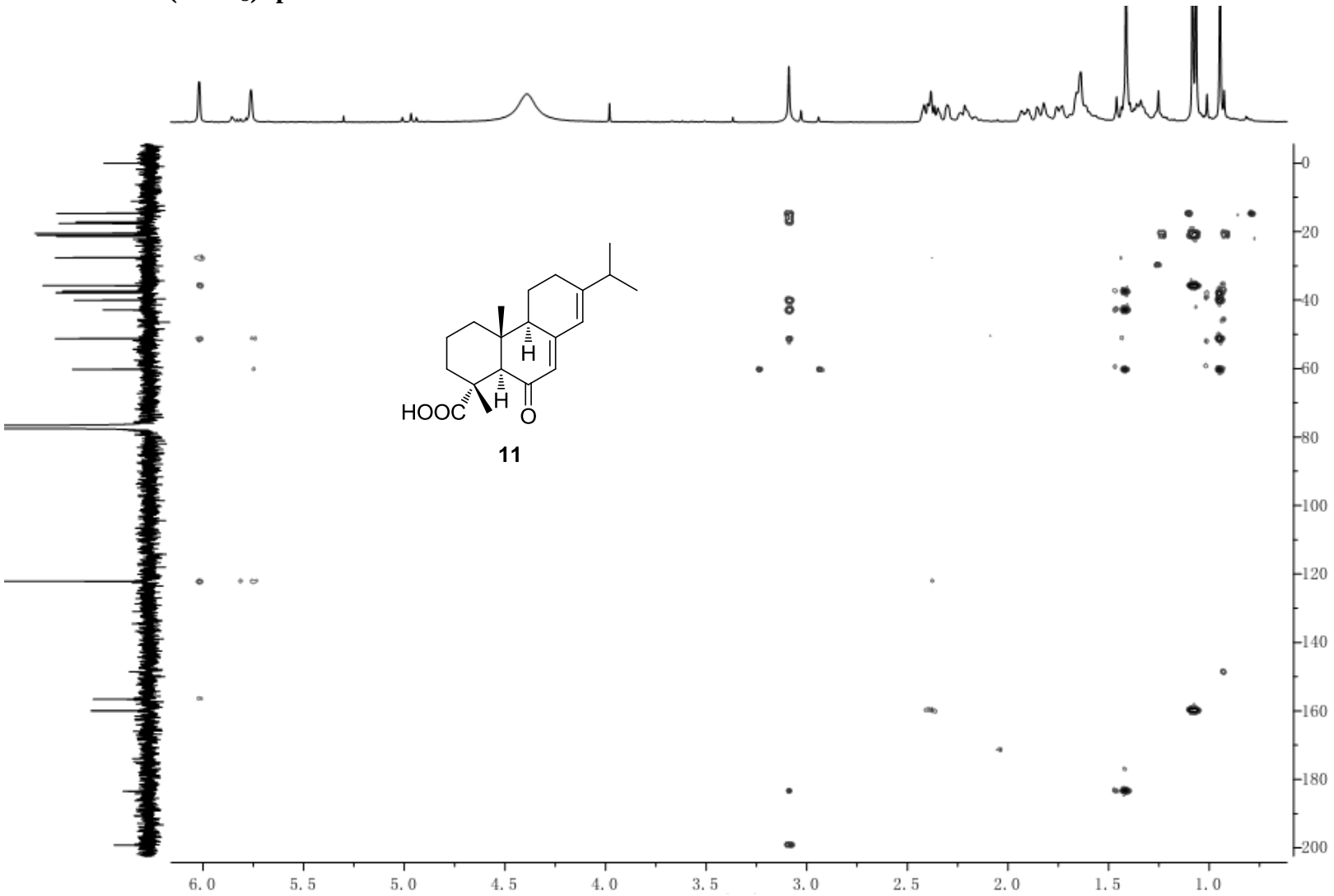
Compound 11: ^{13}C NMR and DEPT($CDCl_3$) spectrum



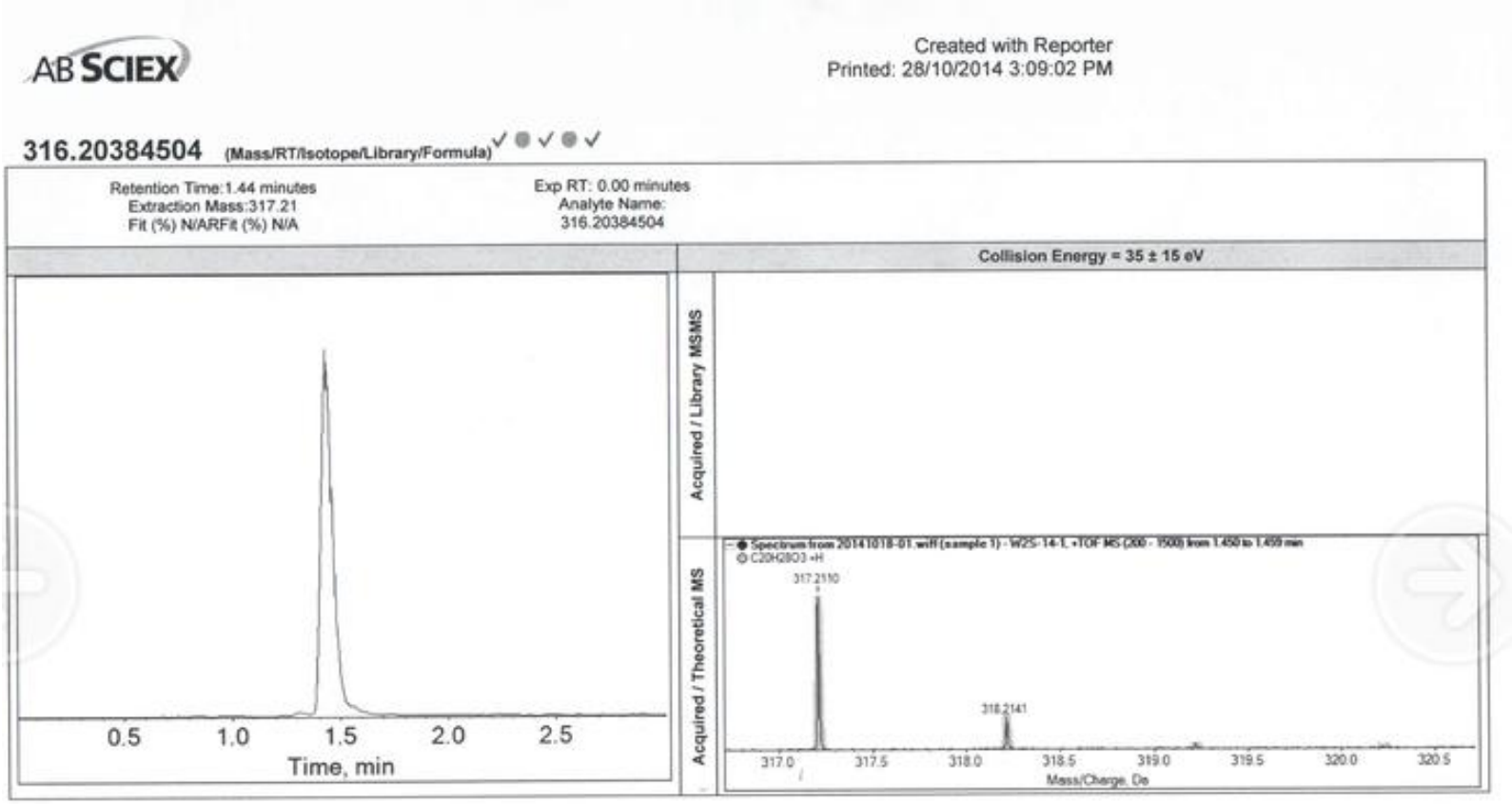
Compound 11: HSQC ($CDCl_3$) spectrum



Compound 11: HMBC ($CDCl_3$) spectrum



Compound 11: (+) HR-ESIMS



	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓●✓●✓	316.20384504	95%	C20H28O3	265580	100	317.2111	317.2110	-0.5	0.00	1.44	1.44	2.0%	N/A

Spectroscopic Data of the Known Compounds 12-39:

Pinusolide acid (12): pale yellow oil, $[\alpha]_D^{20}$ +45.0 ° (*c* 0.1, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.62 (3H, s, Me-20), 1.08 (1H, m, H-1a), 1.08 (1H, m, H-3a), 1.26 (3H, s, H-18), 1.32 (1H, dd, *J* = 13.4, 3.6 Hz, H-5), 1.56 (2H, m, H-2a, H-11a), 1.61 (1H, dd, *J* = 11.4, 3.5 Hz, H-9), 1.78 (1H, m, H-6a), 1.82 (1H, m, H-1b), 1.86 (1H, m, H-11b), 1.88 (1H, m, H-2b), 1.93 (1H, m, H-6b), 2.01 (1H, dd, *J* = 13.0, 4.0 Hz, H-8a), 2.13 (1H, m, H-12a), 2.19 (1H, m, H-3b), 2.45 (2H, m, H-8b, H-12b), 4.60 (1H, s, H-17a), 4.79 (2H, dd, *J* = 3.6, 1.6 Hz, H_2-15), 4.91 (1H, s, H-17b), 7.12 (1H, t, *J* = 1.6 Hz, H-14); (+) ESIMS *m*/*z* 333 $[M+H]^+$, 355 $[M+Na]^+$.

Pinusolide (13): pale yellow oil, $[\alpha]_D^{20}$ +36.0 ° (*c* 0.1, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.52 (3H, s, Me-20), 1.08 (2H, m, H-1a, H-3a), 1.20 (3H, s, H-18), 1.32 (1H, dd, *J* = 13.4, 3.6 Hz, H-5), 1.56 (1H, m, H-2a), 1.56 (1H, m, H-11a), 1.61 (1H, dd, *J* = 11.4, 3.5 Hz, H-9), 1.78 (1H, m, H-6a), 1.82 (1H, m, H-1b), 1.86 (1H, m, H-11b), 1.88 (1H, m, H-2b), 1.93 (1H, m, H-6b), 2.01 (1H, dd, *J* = 13.0, 4.0 Hz, H-8a), 2.13 (1H, m, H-12a), 2.19 (1H, m, H-3b), 2.45 (2H, m, H-8b, H-12b), 3.63 (3H, s, H-21), 4.60 (1H, s, H-17a), 4.79 (2H, dd, *J* = 3.6, 1.6 Hz, H_2-15), 4.91 (1H,s, H-17b), 7.12 (1H, t, *J* = 1.6 Hz, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.2 (C-1), 19.8 (C-2), 38.2 (C-3), 44.3 (C-4), 56.3 (C-5), 26.1 (C-6), 38.6 (C-7), 147.4 (C-8), 55.6 (C-9), 40.3 (C-10), 21.8 (C-11), 24.6 (C-12), 134.8 (C-13), 143.8 (C-14), 70.1 (C-15), 174.3 (C-16), 106.6 (C-17), 28.8 (C-18), 177.7 (C-19), 12.5 (C-20), 51.2 (OCH_3); (+) ESIMS *m*/*z* 347 $[M+H]^+$, 369 $[M+Na]^+$.

16-Hydroxy-labda-8(17),13-dien-15,19-dioic acid butenolide (14): colorless oil, $[\alpha]_D^{20}$ +42.0 ° (*c* 0.1, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.61 (3H, s, Me-20), 1.04 (2H, m, H-1a, H-3a), 1.26 (3H, s, H-18), 1.32 (1H, dd, *J* = 13.4, 3.6 Hz, H-5), 1.52 (2H, m, H-2a, H-11a), 1.57 (1H, dd, *J* = 12.4, 3.2 Hz, H-9), 1.72 (1H, m, H-6a), 1.78 (1H, m, H-1b), 1.82 (1H, m, H-11b), 1.83 (1H, m, H-2b), 1.85 (1H, m, H-6b), 2.01 (1H, dd, *J* = 13.0, 4.0 Hz, H-8a), 2.13 (1H, m, H-12a, H-3b), 2.40 (1H, m, H-12b), 2.45 (1H, m, H-8b), 4.52 (1H, s, H-17a), 4.92 (1H, s, H-17b), 5.88 (1H, s, H-14), 6.00 (1H, s, H-16), ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.2 (C-1), 19.8 (C-2), 37.8 (C-3), 44.5 (C-4), 56.2 (C-5), 26.1 (C-6), 38.6 (C-7),

147.2 (C-8), 55.7 (C-9), 40.6 (C-10), 21.0 (C-11), 26.8 (C-12), 170.2 (C-13), 117.3 (C-14), 171.5 (C-15), 99.3 (C-16), 106.8 (C-17), 28.9 (C-18), 183.2 (C-19), 12.7 (C-20); (+) ESIMS *m*/*z* 349 $[M+H]^+$, 371 $[M+Na]^+$.

7-Oxo-12*α*,13*β*-dihydroxyabiet-8(14)-en-18-oic acid (15): pale-yellow amorphous powder, $[\alpha]_D^{20}$ +12.5 (*c* 0.1, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 0.95 (3H, s, Me-20), 1.03 (3H, d, *J* = 6.8 Hz, Me-16), 1.07 (3H, d, *J* = 6.8 Hz, Me-17), 1.27 (3H, s, Me-19), 3.91 (1H, br s, H-12), 6.83 (1H, br s, H-14), ^{13}C NMR (100 MHz, CD_3OD): δ 38.9 (C-1), 18.7 (C-2), 38.0 (C-3), 47.1 (C-4), 46.9 (C-5), 39.9 (C-6), 202.3 (C-7), 137.6 (C-8), 46.2 (C-9), 36.4 (C-10), 26.6 (C-11), 71.0 (C-12), 72.2 (C-13), 139.6 (C-14), 33.1 (C-15), 16.6 (C-16), 16.3 (C-17), 181.3 (C-18), 16.7 (C-19), 14.6 (C-20); (+) ESIMS *m*/*z* 351 $[M+H]^+$, 373 $[M+Na]^+$.

7-Oxo-13*β*,15-dihydroxyabiet-8(14)-en-18-oic acid (16): pale-yellow amorphous powder, $[\alpha]_D^{20}$ +17.5 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (3H, s, Me-20), 1.19 (3H, s, Me-19), 1.28 (3H, s, Me-16), 1.32 (3H, s, Me-17), 7.05 (1H, br s, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.8 (C-1), 17.8 (C-2), 36.8 (C-3), 45.9 (C-4), 44.1 (C-5), 38.6 (C-6), 202.6 (C-7), 137.5 (C-8), 51.5 (C-9), 35.4 (C-10), 18.6 (C-11), 32.0 (C-12), 72.6 (C-13), 139.2 (C-14), 75.0 (C-15), 23.9 (C-16), 24.7 (C-17), 182.2 (C-18), 16.2 (C-19), 14.5 (C-20); (+) ESIMS *m*/*z* 335 $[M+H]^+$, 357 $[M+Na]^+$.

7-Oxo-13*α*,15-dihydroxyabiet-8(14)-en-18-oic acid (17): pale-yellow amorphous powder, $[\alpha]_D^{20}$ −17.5 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, s, Me-20), 0.94 (3H, d, *J* = 6.8 Hz, Me-16), 0.97 (3H, d, *J* = 6.8 Hz, Me-17), 1.24 (3H, s, Me-19); (+) ESIMS *m*/*z* 335 $[M+H]^+$, 357 $[M+Na]^+$.

Abiesadine E (18): colorless oil, $[\alpha]_D^{20}$ −27.0 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (3H, s, Me-20), 1.02 (3H, d, *J* = 6.8 Hz, Me-16), 1.05 (3H, d, *J* = 6.8 Hz, Me-17), 1.29 (3H, s, H-19), 1.58 (2H, m, H_2-2), 1.62 (1H, m, H-3a), 1.82 (1H, dd, *J* = 13.6, 3.6 Hz, H_2-1), 2.05

(2H, m, H_2-12), 2.11 (1H, dd, *J* = 14.1, 3.9 Hz, H-5), 2.22 (1H, dd, *J* = 12.8, 3.6 Hz, H-3b), 2.27 (1H, dd, *J* = 15.8, 14.1 Hz, H-6a), 2.42 (1H, dd, *J* = 15.8, 3.9 Hz, H-6b), 2.51 (1H, m, H-9), 2.86 (1H, sept., *J* = 6.8 Hz, H-15), 6.14 (1H, dd, *J* = 5.0, 2.4 Hz, H-12), 6.86 (1H, s, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.6 (C-1), 17.9 (C-2), 37.4 (C-3), 45.9 (C-4), 43.9 (C-5), 37.0 (C-6), 199.7 (C-7), 133.9 (C-8), 48.5 (C-9), 34.6 (C-10), 26.2 (C-11), 131.9 (C-12), 141.1 (C-13), 142.2 (C-14), 26.1 (C-15), 21.6 (C-16), 22.0 (C-17), 184.5 (C-18), 16.6 (C-19), 14.5 (C-20); (+) ESIMS *m*/*z* 317 $[M+H]^+$, 339 $[M+Na]^+$.

Abiesanordine K (19): white amorphous powder, $[\alpha]_D^{20}$ +8.0 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (3H, s, Me-20), 1.28 (3H, s, Me-20), 2.59 (3H, s, H-16), 4.85 (1H, br s, H-7), 7.38 (1H, d, *J* = 8.4 Hz, H-11), 7.86 (1H, dd, *J* = 8.4, 2.1 Hz, H-12), 7.94 (1H, d, *J* = 2.1 Hz, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.1 (C-1), 18.4 (C-2), 37.4 (C-3), 46.6 (C-4), 39.3 (C-5), 30.6 (C-6), 67.7 (C-7), 136.0 (C-8), 154.6 (C-9), 39.2 (C-10), 124.8 (C-11), 128.1 (C-12), 135.4 (C-13), 131.2 (C-14), 198.2 (C-15), 26.6 (C-16), 183.5 (C-18), 16.3 (C-19), 24.1 (C-20); (+) ESIMS *m*/*z* 317 $[M+H]^+$, 339 $[M+Na]^+$.

16-Nor-15-oxodehydroabietic acid (20): colorless oil, $[\alpha]_D^{20}$ +47.0 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (1H, m, H-3a), 1.25 (3H, s, Me-20), 1.29 (3H, s, Me-19), 1.33 (1H, m, H-1a), 1.54 (1H, m, H-1b), 1.56 (1H, m, H-6a), 1.75 (2H, m, H_2-2), 1.80 (1H, m, H-3b), 1.87 (1H, m, H-6b), 2.26 (1H, dd, *J* = 12.4, 2.4 Hz, H-5), 2.56 (3H, s, Me-16), 7.63 (1H, d, *J* = 8.4 Hz, H-11), 7.66 (1H, d, *J* = 2.0 Hz, H-14), 7.72 (1H, dd, *J* = 8.4, 2.0 Hz, H-12), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.7 (C-1), 18.4 (C-2), 36.6 (C-3), 47.3 (C-4), 44.2 (C-5), 21.5 (C-6), 29.9 (C-7), 135.4 (C-8), 155.5 (C-9), 37.6 (C-10), 124.6 (C-11), 125.8 (C-12), 134.5 (C-13), 129.2 (C-14), 198.2 (C-15), 26.6 (C-16), 183.2 (C-18), 16.3 (C-19), 24.8 (C-20); (+) ESIMS *m*/*z* 301 $[M+H]^+$, 323 $[M+Na]^+$.

17-Nor-7,15-dion-8,11,13-abietatrien-18-oic acid (21): colorless oil, $[\alpha]_D^{20}$ +28.0 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (1H, dd, *J* = 12.8, 4.0 Hz, H-3a), 1.29 (3H, s, Me-20), 1.32 (3H, s, Me-19), 1.54 (1H, br d, *J* = 13.4 Hz, H-1b), 1.75 (2H, m, H_2-2), 1.80 (1H, br d, *J* =

12.8 Hz, H-3b), 2.33 (1H, br d, *J* = 13.4 Hz, H-1a), 2.42 (1H, dd, *J* = 16.8, 3.2 Hz, H-6a), 2.63 (3H, s, Me-16), 2.68 (1H, dd, *J* = 14.0, 3.2 Hz, H-5), 2.86 (1H, dd, *J* = 16.8, 14.0 Hz, H-6b), 7.52 (1H, d, *J* = 8.4 Hz, H-11), 8.18 (1H, dd, *J* = 8.4, 2.0 Hz, H-12), 8.56 (1H, dd, *J* = 2.0 Hz, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.7 (C-1), 18.4 (C-2), 36.6 (C-3), 47.3 (C-4), 45.2 (C-5), 38.5 (C-6), 199.5 (C-7), 132.4 (C-8), 161.0 (C-9), 37.8 (C-10), 124.6 (C-11), 134.8 (C-12), 136.5 (C-13), 128.5 (C-14), 198.2 (C-15), 26.6 (C-16), 182.2 (C-18), 16.3 (C-19), 24.8 (C-20); (+) ESIMS *m*/*z* 315 $[M+H]^+$, 337 $[M+Na]^+$, 629 $[2M+H]^+$.

Methyl 13-acetyl-7-oxo-podocarpa-8,11,13-trien-15-oate (22): colorless oil, $[\alpha]_D^{20}$ +39.0 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (1H, dd, *J* = 12.8, 4.0 Hz, H-3a), 1.29 (3H, s, Me-20), 1.32 (3H, s, Me-19), 1.54 (1H, br d, *J* = 13.4 Hz, H-1b), 1.75 (2H, m, H_2-2), 1.80 (1H, br d, *J* = 12.8 Hz, H-3b), 2.33 (1H, br d, *J* = 13.4 Hz, H-1a), 2.42 (1H, dd, *J* = 16.8, 3.2 Hz, H-6a), 2.65 (3H, s, Me-16), 2.68 (1H, dd, *J* = 14.0, 3.2 Hz, H-5), 2.86 (1H, dd, *J* = 16.8, 14.0 Hz, H-6b), 3.69 (3H, s, OMe), 7.52 (1H, d, *J* = 8.4 Hz, H-11), 8.18 (1H, dd, *J* = 8.4, 2.0 Hz, H-12), 8.56 (1H, dd, *J* = 2.0 Hz, H-14); (+) ESIMS *m*/*z* 329 $[M+H]^+$, 327 $[M-H]^-$.

8(14)-Podocarpen-13-on-18-oic acid (23): pale yellow oil, $[\alpha]_D^{20}$ +12.0 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, s, Me-20), 1.26 (3H, s, Me-19), 6.01 (1H, br s, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4 (C-1), 17.8 (C-2), 36.8 (C-3), 47.1 (C-4), 47.7 (C-5), 24.0 (C-6), 35.3 (C-7), 168.7 (C-8), 51.7 (C-9), 38.1 (C-10), 20.0 (C-11), 36.1 (C-12), 202.6 (C-13), 125.7 (C-14), 184.6 (C-18), 16.7 (C-19), 15.6 (C-20); (+) ESIMS *m*/*z* 277 $[M+H]^+$, 299 $[M+Na]^+$.

Abiesanordine E (24): pale yellow oil, $[\alpha]_D^{20}$ +12.0 (*c* 0.1, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, s, Me-20), 1.26 (3H, s, Me-19), 2.35 (1H, m, H-12a), 2.42 (1H, s, H-12b), 2.58 (1H, dd, *J* = 14.0, 3.2 Hz, H-5), 2.64 (1H, dd, *J* = 12.8, 3.0 Hz, H-9), 4.39 (1H, br s, H-7), 6.01 (1H, br s, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.9 (C-1), 18.0 (C-2), 36.5 (C-3), 46.5 (C-4), 41.4 (C-5), 31.5 (C-6), 71.2 (C-7), 163.0 (C-8), 47.3 (C-9), 38.9 (C-10), 20.1 (C-11), 36.5 (C-12), 201.0 (C-13), 128.1 (C-14), 184.0 (C-18), 16.5 (C-19), 14.9 (C-20); (+) ESIMS *m*/*z* 293

$[M+H]^+$, 315 $[M+Na]^+$.

8(14)-Podocarpen-7,13-dion-18-oic acid (25): pale yellow oil, $[\alpha]_D^{20}$ +22.0 (*c* 0.1, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.97 (3H, s, Me-20), 1.30 (3H, s, Me-19), 2.37 (1H, m, H-12a), 2.50 (1H, dd, overlapped, H-5), 2.50 (1H, dd, overlapped, H-6a), 2.52 (1H, dd, *J* = 16.8, 14.0 Hz, H-5), 2.56 (1H, dd, *J* = 13.6, 3.6 Hz, H-9), 2.66 (1H, br d, *J* = 15.8 Hz, H-12b), 4.39 (1H, br s, H-7), 6.01 (1H, br s, H-14); (+) ESIMS *m*/*z* 291 $[M+H]^+$, 313 $[M+Na]^+$.

7-Oxo-13-Hydroxy-podocarpa-8,11,13-trien-18-oic acid (26): pale yellow oil, $[\alpha]_D^{20}$ +29.0 (*c* 0.1, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.25 (3H, s, Me-20), 1.31 (3H, s, Me-19), 2.48 (1H, dd, *J* = 17.2, 2.4 Hz, H-12a), 2.64 (1H, dd, *J* = 14.2, 2.4 Hz, H-5), 2.70 (1H, dd, *J* = 17.2, 14.0 Hz, H-9), 2.66 (1H, br d, *J* = 15.8 Hz, H-12b), 7.06 (1H, dd, *J* = 8.0, 2.0 Hz, H-12), 7.24 (1H, d, *J* = 8.0 Hz, H-11), 7.49 (1H, d, *J* = 2.0 Hz, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.2 (C-1), 18.1 (C-2), 36.9 (C-3), 46.1 (C-4), 43.6 (C-5), 36.5 (C-6), 199.4 (C-7), 131.4 (C-8), 148.0 (C-9), 37.7 (C-10), 125.1 (C-11), 112.8 (C-12), 154.5 (C-13), 122.3 (C-14), 182.7 (C-18), 16.1 (C-19), 23.6 (C-20); (+) ESIMS *m*/*z* 289 $[M+H]^+$, 311 $[M+Na]^+$, 577 $[2M+H]^+$, 599 $[2M+Na]^+$.

12*α*-Hydroxyabietic acid (27): pale-yellow amorphous powder, $[\alpha]_D^{20}$ +32.0 (*c* 0.1, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, s, Me-20), 1.02 (1H, m, H-1a), 1.08 (1H, m, H-3a), 1.09 (3H, d, *J* = 7.2 Hz, Me-16), 1.11 (3H, d, *J* = 7.2 Hz, Me-17), 1.27 (3H, s, Me-19), 1.50 (1H, m, H-2a), 1.82 (1H, m, H-11a), 1.92 (1H, m, H-1b), 1.94 (2H, m, H-2b, H-6a), 1.97 (1H, m, H-11b), 2.02 (1H, m, H-6b), 2.17 (1H, br d, *J* = 12.4 Hz, H-3b), 2.21 (1H, dd, *J* = 13.5, 3.6 Hz, H-9), 2.35 (1H, dd, *J* = 13.5, 3.6 Hz, H-5), 2.42 (1H, sept., *J* = 7.2 Hz, H-15), 4.25 (1H, br s, H-12), 4.52 (1H, br s, H-7), 5.86 (1H, br s, H-14); (+) ESIMS *m*/*z* 319 $[M+H]^+$, 331 $[M+Na]^+$.

7-Oxo-13-*epi*-pimara-8,15-dien-18-oic acid (28): white amorphous powder, $[\alpha]_D^{20}$ +65.0 (*c* 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.00

(3H, s, Me-20), 1.12 (3H, s, Me-17), 1.27 (3H, s, Me-19), 4.88 (1H, br d, *J* = 17.0 Hz, H-16a), 4.96 (1H, br d, *J* = 11.0 Hz, H-16b), 5.68 (1H, dd, *J* = 17.0, 11.0 Hz, H-15), ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.0 (C-1), 17.8 (C-2), 36.8 (C-3), 46.3 (C-4), 44.8 (C-5), 34.6 (C-6), 199.6 (C-7), 129.0 (C-8), 165.8 (C-9), 39.1 (C-10), 22.8 (C-11), 33.5 (C-12), 34.4 (C-13), 33.3 (C-14), 144.8 (C-15), 111.7 (C-16), 28.0 (C-17), 181.5 (C-18), 16.2 (C-19), 18.0 (C-20); (+) ESIMS *m*/*z* 317 $[M+H]^+$, 329 $[M+Na]^+$.

Piceanolactones A (29): white amorphous powder, $[\alpha]_D^{20}$ +15.0 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (3H, d, *J* = 7.2 Hz, Me-16), 1.31 (3H, d, *J* = 7.2 Hz, Me-17), 1.39 (1H, m, H-1a), 1.50 (1H, m, H-3a), 1.63 (3H, s, Me-20), 1.67 (3H, s, Me-19), 1.85 (2H, m, H_2-2), 2.18 (1H, m, H-3b), 2.34 (1H, br d, *J* = 12.4 Hz, H-5), 3.04 (1H, sept., *J* = 7.2 Hz, H-15), 7.48 (1H, d, *J* = 8.0 Hz, H-11), 7.52 (1H, dd, *J* = 8.0, 2.0 Hz, H-12), 8.18 (1H, d, *J* = 2.0 Hz, H-14); (+) ESIMS *m*/*z* 311 $[M+H]^+$, 621 $[2M+H]^+$.

Piceanolactones B (30): white amorphous powder, $[\alpha]_D^{20}$ +15.0 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (3H, s, Me-16), 1.61 (3H, s, Me-17), 1.63 (3H, s, Me-20), 1.65 (3H, s, Me-19), 7.50 (1H, d, *J* = 8.0 Hz, H-11), 7.82 (1H, dd, *J* = 8.0, 2.0 Hz, H-12), 8.32 (1H, d, *J* = 2.0 Hz, H-14); (+) ESIMS *m*/*z* 327 $[M+H]^+$, 653 $[2M+H]^+$.

Piceanolactones C (31): white amorphous powder, $[\alpha]_D^{20}$ +15.0 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.24 (3H, d, *J* = 7.2 Hz, Me-16), 1.24 (3H, d, *J* = 7.2 Hz, Me-17), 1.34 (1H, m, H-1a), 1.50 (1H, m, H-3a), 1.56 (3H, s, Me-20), 1.59 (3H, s, Me-19), 1.85 (2H, m, H_2-2), 2.11 (1H, m, H-3b), 2.22 (1H, br d, *J* = 12.4 Hz, H-5), 3.30 (1H, sept., *J* = 7.2 Hz, H-15), 7.06 (1H, s, H-11), 7.98 (1H, s, H-12), ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.7 (C-1), 20.4 (C-2), 37.7 (C-3), 48.4 (C-4), 147.6 (C-5), 143.9 (C-6), 175.7 (C-7), 124.4 (C-8), 153.8 (C-9), 44.2 (C-10), 113.0 (C-11), 162.0 (C-12), 137.0 (C-13), 126.6 (C-14), 28.5 (C-15), 23.2 (C-16), 23.2 (C-17), 182.1 (C-18), 22.0 (C-19), 25.4 (C-20); (+) ESIMS *m*/*z* 327 $[M+H]^+$, 349 $[M+Na]^+$.

Dehydroabietic acid (32): pale yellow oil, $[\alpha]_D^{20}$ +30.0 ° (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (1H, dd, *J* = 12.8, 4.0 Hz, H-3a), 1.23 (3H, d, *J* = 7.2 Hz, Me-16), 1.23 (3H, d, *J* = 7.2 Hz, Me-17), 1.25 (3H, s, Me-20), 1.29 (3H, s, H-19), 1.54 (2H, m, H-1a, H-6a), 1.75 (2H, m, H_2-2), 1.80 (1H, m, H-3b), 1.87 (1H, m, H-6b), 2.26 (1H, dd, *J* = 12.4, 2.4 Hz, H-5), 2.33 (1H, br d, *J* = 13.5 Hz, H-1b), 2.92 (2H, m, H_2-7), 2.94 (1H, sept., *J* = 7.2 Hz, H-15), 6.91 (1H, d, *J* = 2.0 Hz, H-14), 7.02 (1H, dd, *J* = 8.0, 2.0 Hz, H-12), 7.19 (1H, d, *J* = 8.0 Hz, H-11); (+) ESIMS *m*/*z* 301 $[M+H]^+$, 323 $[M+Na]^+$.

12-Hydroxydehydroabietic acid (33): pale yellow oil, $[\alpha]_D^{20}$ +35.0 ° (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (3H, s, Me-20), 1.25 (3H, d, *J* = 7.2 Hz, Me-16), 1.27 (3H, d, *J* = 7.2 Hz, Me-17), 1.29 (3H, s, H-19), 1.52 (1H, m, overlapped, H-6a), 1.52 (1H, dd, overlapped, H-1a), 1.70 (1H, m, H-3a), 1.74 (2H, m, H_2-2), 1.79 (1H, m, H-3b), 1.82 (1H, m, H-6b), 2.22 (1H, dd, *J* = 12.5, 2.2 Hz, H-5), 2.25 (1H, br d, *J* = 13.5 Hz, H-1b), 2.83 (2H, m, H_2-7), 3.12 (1H, sept., *J* = 7.2 Hz, H-15), 6.64 (1H, s, H-11), 6.85 (1H, s, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.9 (C-1), 18.5 (C-2), 36.7 (C-3), 47.4 (C-4), 44.5 (C-5), 21.9 (C-6), 29.2 (C-7), 127.0 (C-8), 147.8 (C-9), 36.8 (C-10), 110.8 (C-11), 150.7 (C-12), 131.8 (C-13), 126.7 (C-14), 26.8 (C-15), 22.7 (C-16), 22.5 (C-17), 184.5 (C-18), 16.2 (C-19), 25.0 (C-20); (+) ESIMS *m*/*z* 317 $[M+H]^+$, 339 $[M+Na]^+$.

15-Hydroxydehydroabietic acid (34): pale yellow powder, $[\alpha]_D^{20}$ +16.5 (*c* 0.1, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (3H, s, Me-20), 1.31 (3H, s, Me-19), 1.50 (1H, m, H-1a), 1.52 (1H, m, H-6a), 1.58 (6H, s, Me-16, 17), 1.60 (2H, m, H_2-2), 1.70 (1H, m, H-3a), 1.82 (1H, m, H-6b), 1.94 (1H, m, H-3b), 2.24 (1H, dd, *J* = 12.5, 2.2 Hz, H-5), 2.26 (1H, m, H-1b), 7.17 (1H, d, *J* = 2.0 Hz, H-14), 7.24 (1H, dd, *J* = 8.4, 2.0 Hz, H-12), 7.26 (1H, d, *J* = 8.4 Hz, H-11), ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.5 (C-1), 18.2 (C-2), 37.1 (C-3), 47.3 (C-4), 45.3 (C-5), 22.1 (C-6), 30.5 (C-7), 136.2 (C-8), 148.2 (C-9), 37.3 (C-10), 124.2 (C-11), 122.9 (C-12), 147.7 (C-13), 125.7 (C-14), 71.3 (C-15), 32.5 (C-16), 32.5 (C-17), 180.8 (C-18), 17.1 (C-19), 25.2 (C-20); (+) ESIMS *m*/*z* 317 $[M+H]^+$, 329 $[M+Na]^+$.

Abieta-8,11,13,15-tetraen-18-oic acid (35): white amorphous powder, $[\alpha]_D^{20}$ +55.0 (*c* 0.1, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (3H, s, Me-20), 1.29 (3H, s, Me-19), 1.50 (2H, m, H-1a, H-6a), 1.72 (1H, m, H-3a), 1.75 (2H, m, H_2-2), 1.80 (1H, m, H-3b), 1.84 (1H, m, H-6b), 2.14 (3H, br s, H-17), 2.25 (1H, dd, *J* = 12.4, 2.1 Hz, H-5), 2.33 (1H, br d, *J* = 13.5 Hz, H-1b), 2.94 (2H, m, H_2-7), 5.04 (1H, br s, H-16a), 5.34 (1H, br s, H-16b), 7.16 (1H, d, *J* = 2.0 Hz, H-14), 7.20 (1H, d, *J* = 8.0 Hz, H-11), 7.26 (1H, dd, *J* = 8.0, 2.0 Hz, H-12); (+) ESIMS *m*/*z* 299 $[M+H]^+$, 321 $[M+Na]^+$.

7-Oxocallitrisic acid (36): white amorphous powder, $[\alpha]_D^{20}$ +59.0 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (3H, d, *J* = 7.2 Hz, Me-16), 1.27 (3H, d, *J* = 7.2 Hz, Me-17), 1.29 (3H, s, H-19), 1.30 (3H, s, Me-20), 1.35 (3H, s, Me-19), 1.60 (1H, m, H-2a), 1.78 (1H, m, H-2b), 1.82 (1H, m, H-1a), 1.88 (1H, m, H-3a), 1.93 (1H, m, H-1b), 2.39 (1H, dd, *J* = 17.4, 2.8 Hz, H-6a), 2.45 (1H, br d, *J* = 13.5 Hz, H-3b), 2.67 (1H, dd, *J* = 14.0, 2.8 Hz, H-5), 2.82 (1H, dd, *J* = 17.4, 14.0 Hz, H-6b), 2.93 (1H, sept., *J* = 7.2 Hz, H-15), 7.41 (1H, d, *J* = 8.0 Hz, H-11), 7.51 (1H, dd, *J* = 8.0, 2.0 Hz, H-12), 7.83 (1H, d, *J* = 2.0 Hz, H-14); (+) ESIMS *m*/*z* 315 $[M+H]^+$, 629 $[2M+H]^+$.

15-Hydroxy-7-oxo-8,11,13-abietatrien-18-oic acid (37): pale yellow powder, $[\alpha]_D^{20}$ +16.5 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (3H, s, Me-20), 1.29 (3H, s, Me-19), 1.58 (6H, s, Me-16, 17), 1.68 (1H, m, H-1a), 1.80 (5H, m, H-1b, H_2-2, H_2-3), 2.42 (1H, dd, *J* = 17.0, 3.2 Hz, H-6a), 2.68 (1H, dd, *J* = 13.5, 3.2 Hz, H-5), 2.86 (1H, dd, *J* = 17.0, 13.5 Hz, H-6b), 7.38 (1H, d, *J* = 8.4 Hz, H-11), 7.76 (1H, dd, *J* = 8.4, 2.1 Hz, H-12), 8.06 (1H, d, *J* = 2.1 Hz, H-14), ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.7 (C-1), 18.1 (C-2), 37.0 (C-3), 46.3 (C-4), 43.5 (C-5), 36.4 (C-6), 198.8 (C-7), 130.4 (C-8), 153.8 (C-9), 37.3 (C-10), 123.6 (C-11), 130.7 (C-12), 147.3 (C-13), 123.3 (C-14), 72.4 (C-15), 31.7 (C-16), 31.5 (C-17), 182.5 (C-18), 16.1 (C-19), 23.6 (C-20); (+) ESIMS *m*/*z* 331 $[M+H]^+$, 353 $[M+Na]^+$.

Methyl 15-hydroxy-7-oxo-dehydroabietate (38): pale yellow powder, $[\alpha]_D^{20}$ +36.5 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (3H, s, Me-19), 1.37 (3H, s, Me-20), 1.61 (6H, s, Me-16, 17), 1.63 (1H, m, H-1a), 1.80 (5H, m, H-1b, H_2-2, H_2-3), 2.40 (1H, dd, *J* = 17.0, 3.2 Hz, H-6a),

2.42 (1H, dd, *J* = 13.5, 3.2 Hz, H-5), 2.75 (1H, dd, *J* = 17.0, 13.5 Hz, H-6b), 3.67 (3H, s, OMe-21), 7.38 (1H, d, *J* = 8.4 Hz, H-11), 7.75 (1H, dd, *J* = 8.4, 2.1 Hz, H-12), 8.08 (1H, d, *J* = 2.1 Hz, H-14); (+) ESIMS *m*/*z* 345 $[M+H]^+$, 367 $[M+Na]^+$, 689 $[2M+H]^+$.

Abiesadine O (39): pale yellow powder, $[\alpha]_D^{20}$ +26.0 (*c* 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.19 (3H, s, Me-20), 1.29 (3H, s, Me-19), 1.47 (1H, m, H-1a), 1.54 (6H, s, Me-16, 17), 1.66 (1H, m, H-6a), 1.68 (1H, m, H-3a), 1.72 (1H, m, H-2a), 1.80 (1H, m, H-2b), 1.92 (1H, m, H-3b), 2.16 (1H, br dd, *J* = 17.0, 13.2 Hz, H-6b), 2.39 (1H, m, H-1b), 2.56 (1H, dd, *J* = 13.2, 3.2 Hz, H-5), 3.07 (3H, s, OMe), 4.75 (1H, br s, H-7), 7.31 (1H, d, *J* = 8.4 Hz, H-11), 7.34 (1H, dd, *J* = 8.4, 2.0 Hz, H-12), 7.37 (1H, d, *J* = 2.0 Hz, H-14); (+) ESIMS *m*/*z* 347 $[M+H]^+$, 369 $[M+Na]^+$.