Supporting information

Synthesis of natural (–)-antrocin and its enantiomer *via* stereoselective aldol reaction

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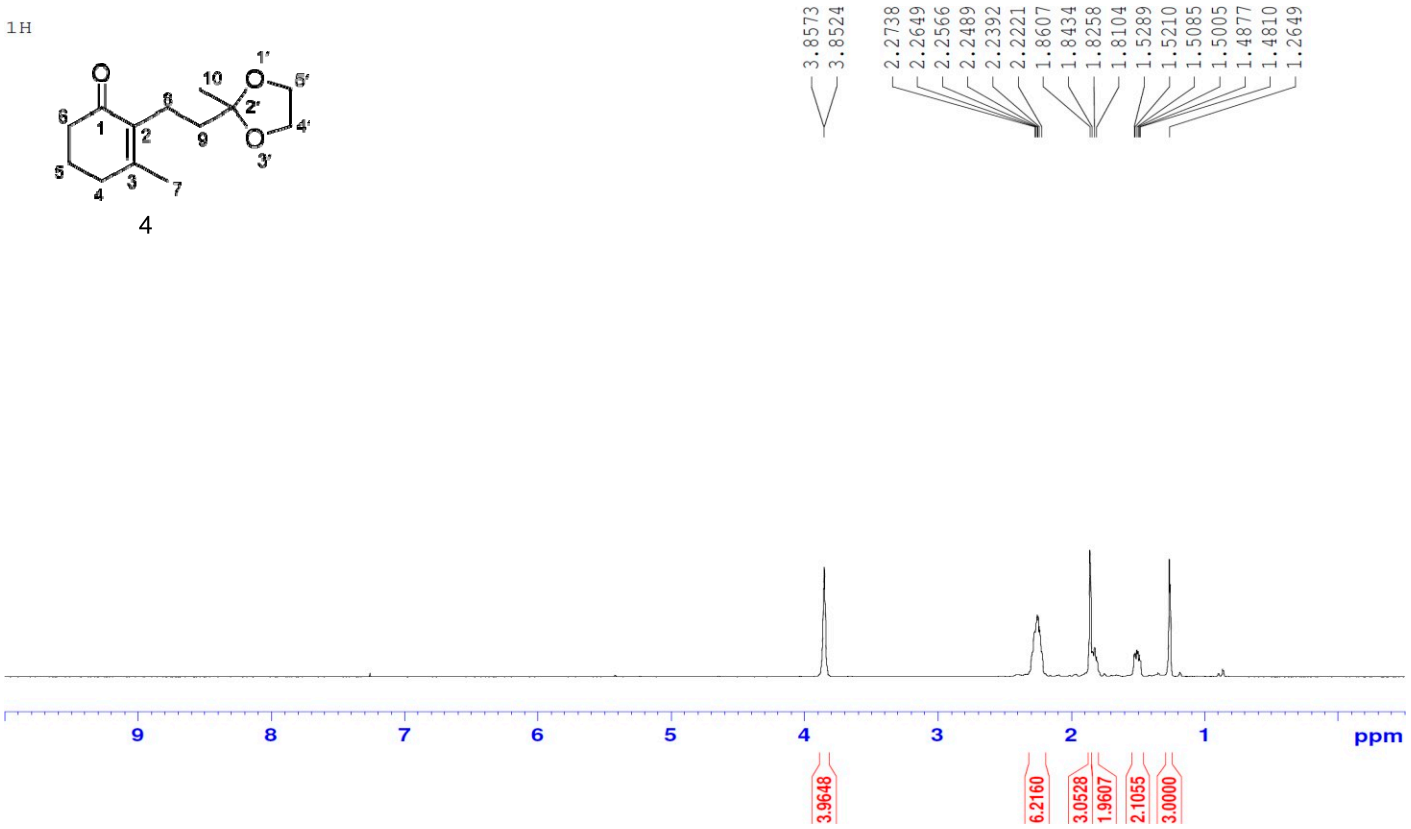
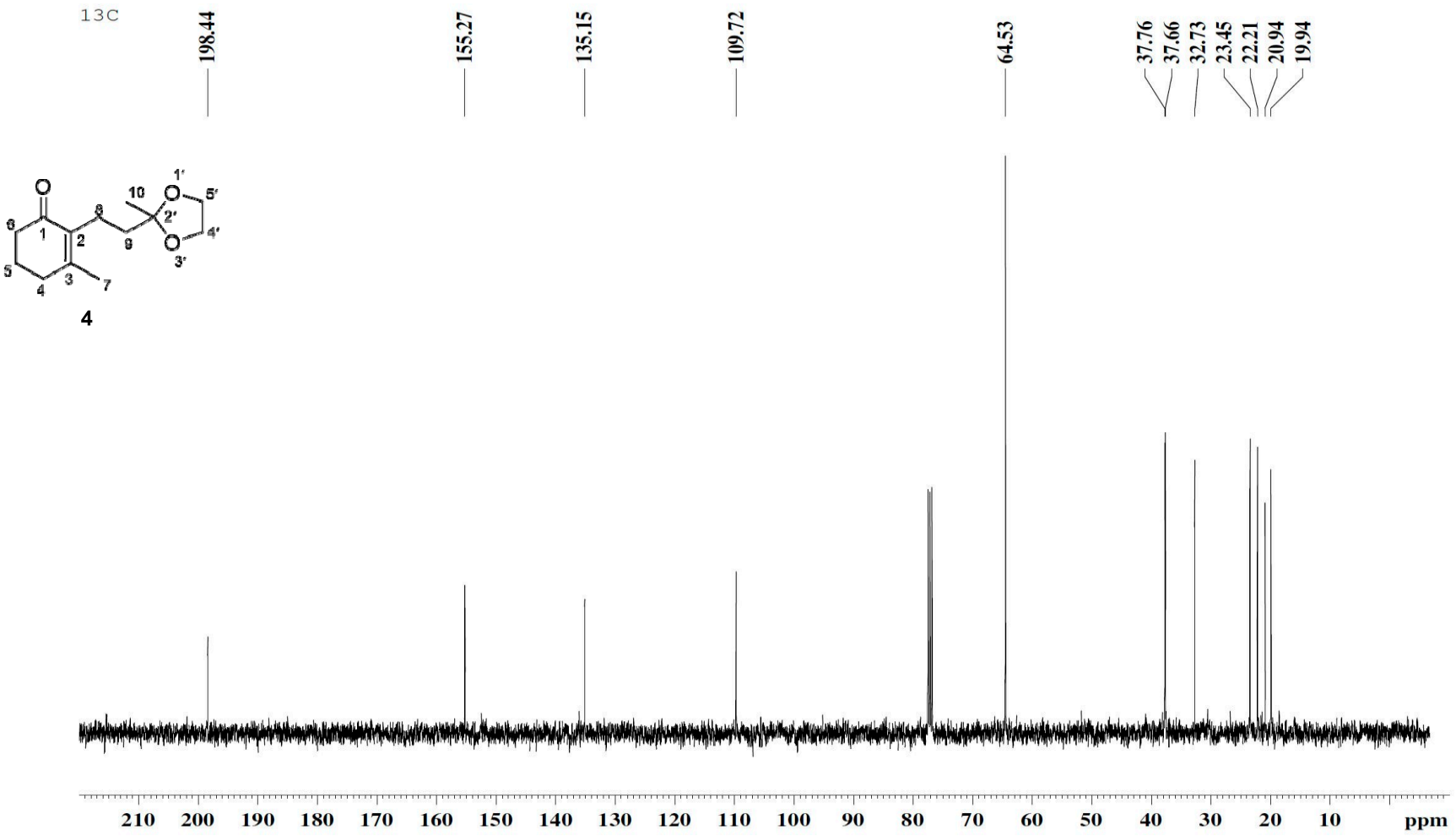
Figure S1



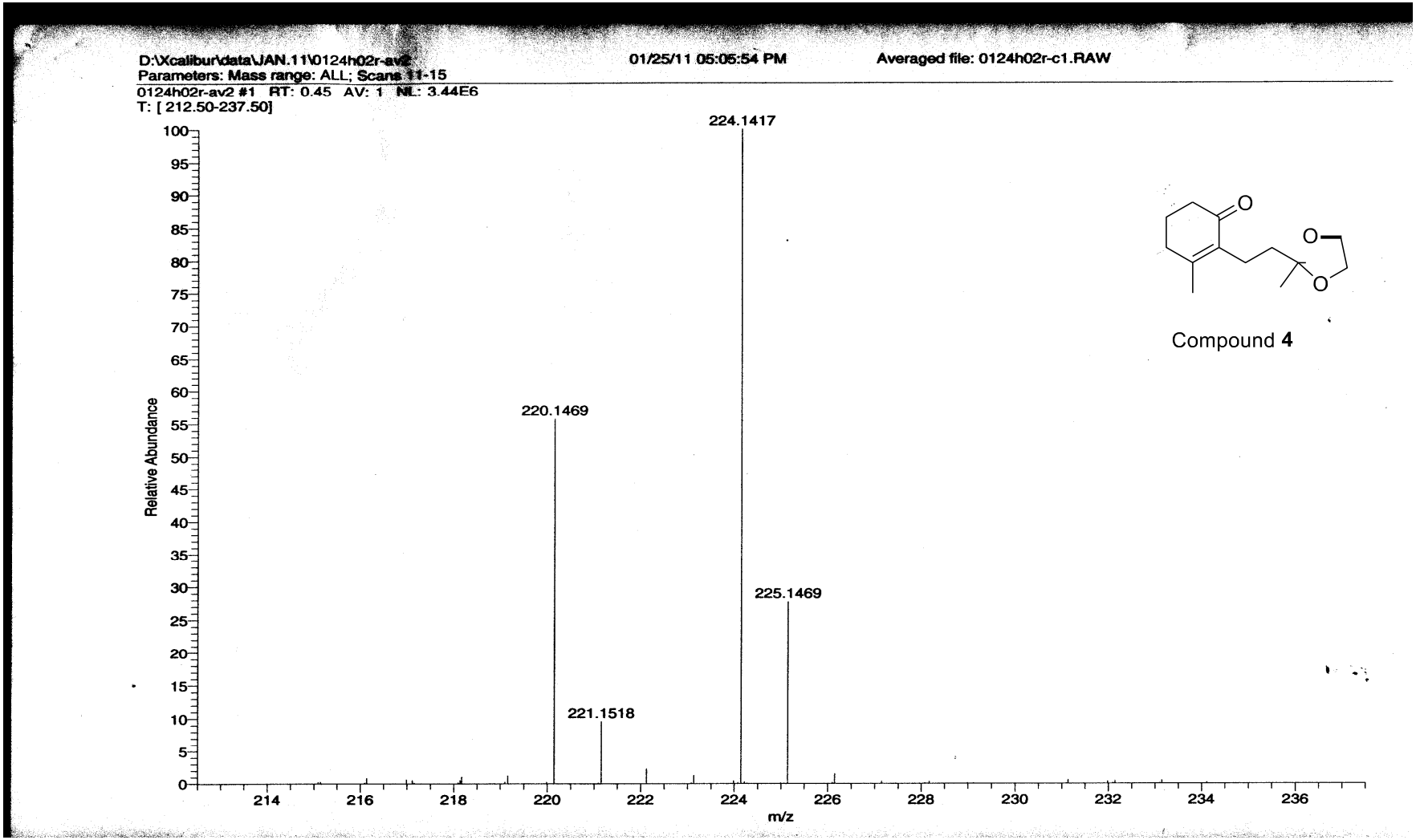
^{1}H NMR of compound **4** (400 MHz, $CDCl_3$)

Figure S2



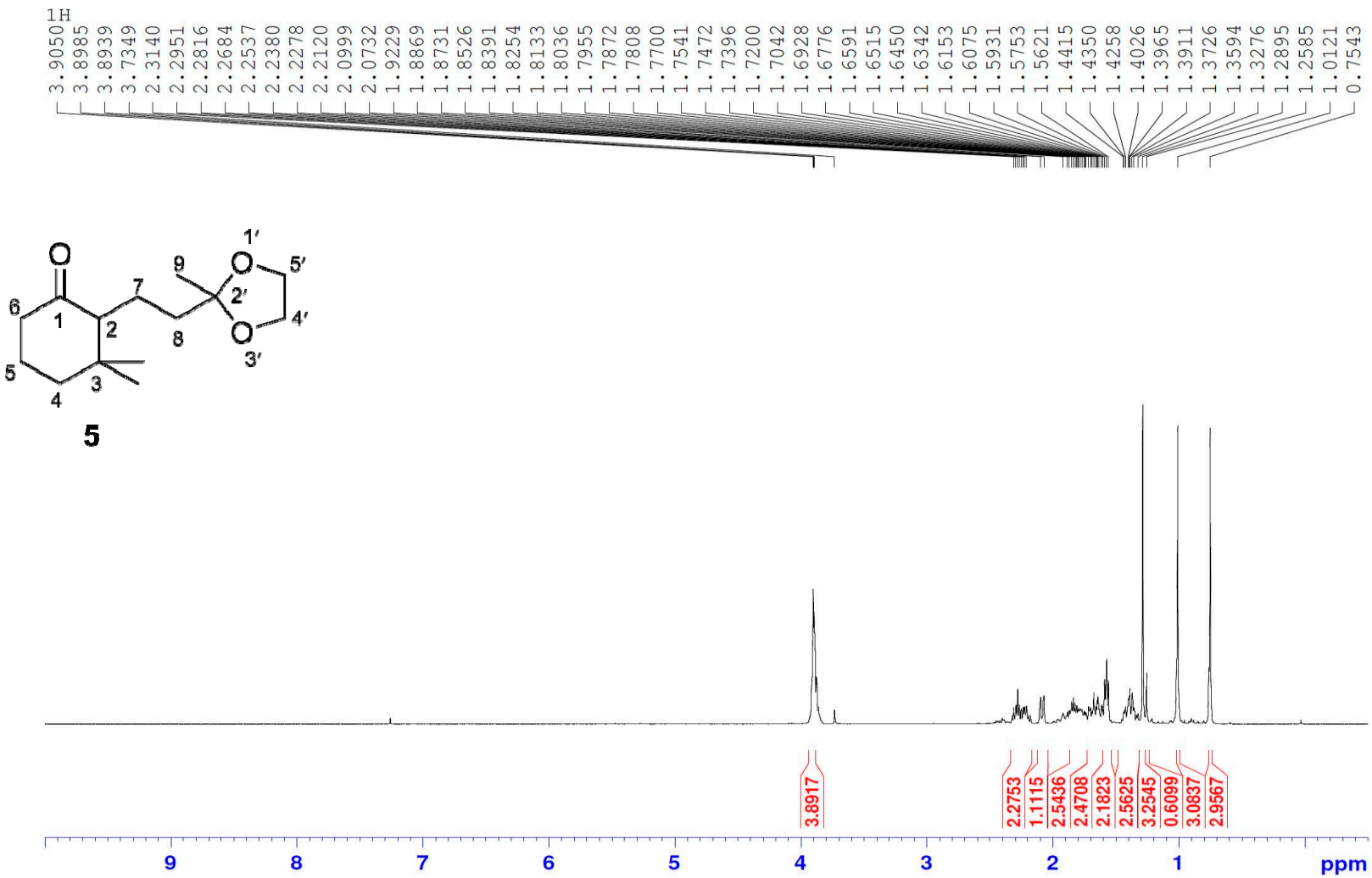
^{13}C NMR of compound **4** (100 MHz, $CDCl_3$)

Figure S3



HRMS (ESI) of compound **4**

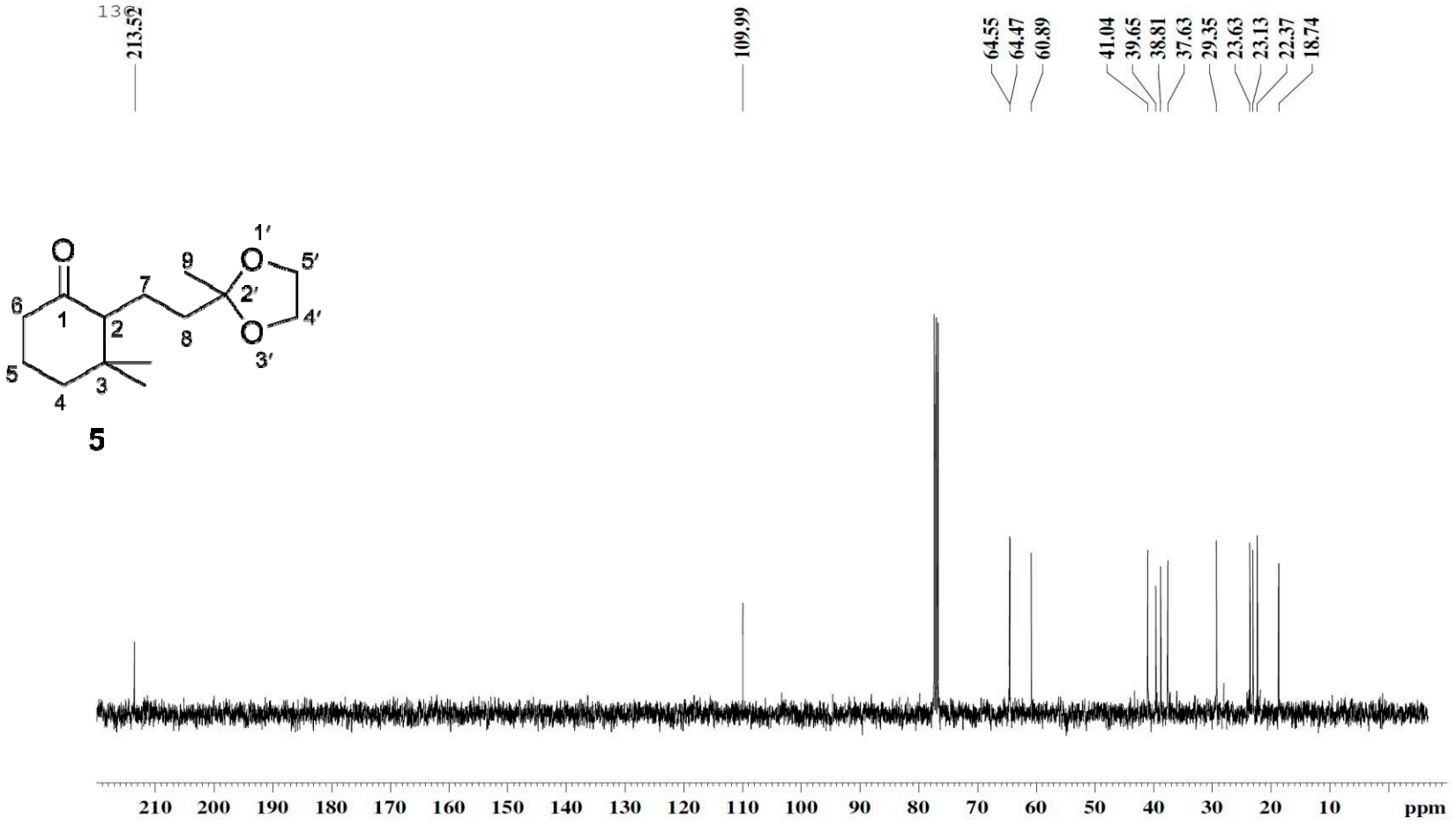
Figure S4



5

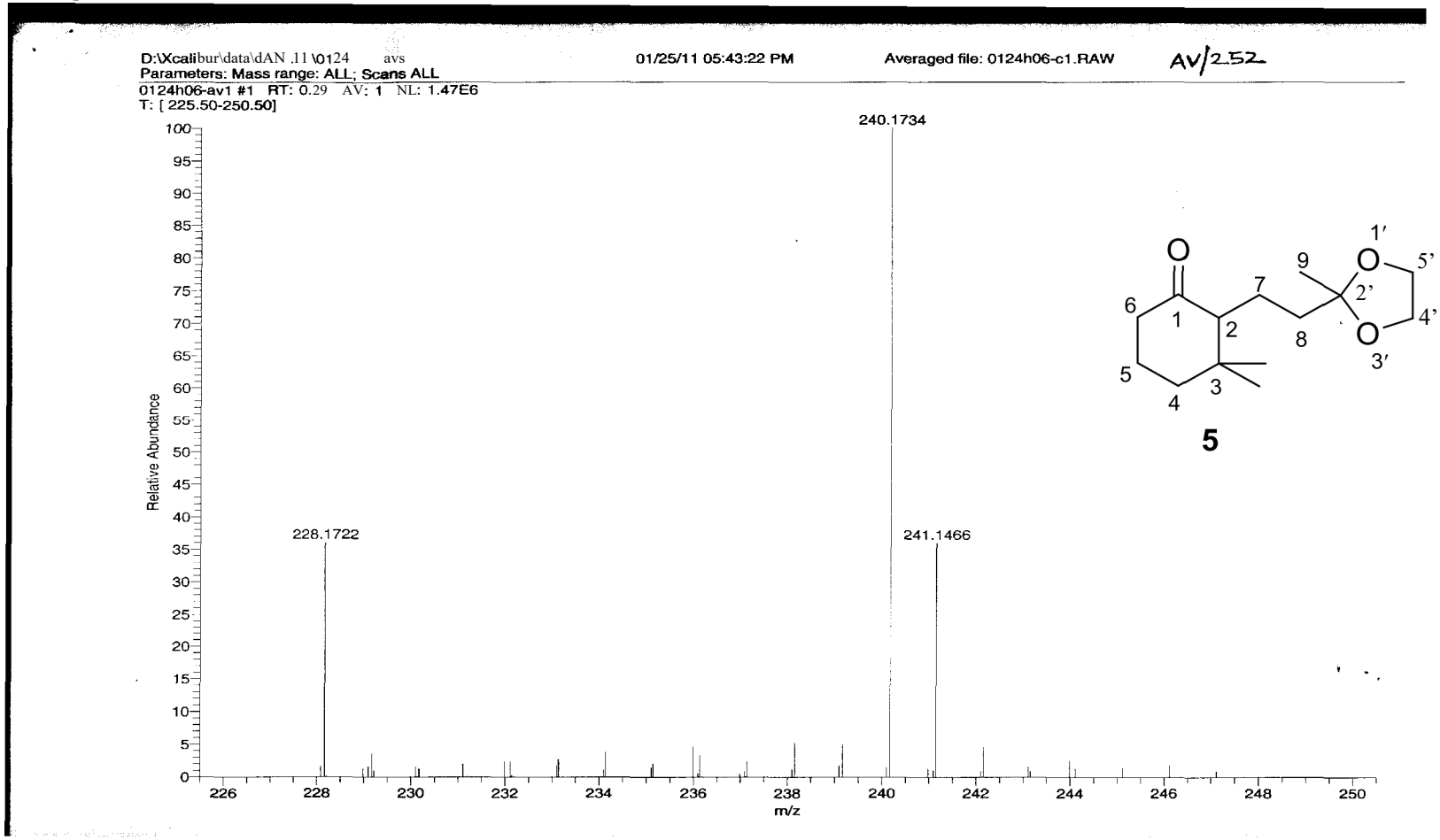
^{1}H NMR of compound **5** (400 MHz, $CDCl_3$)

Figure S5



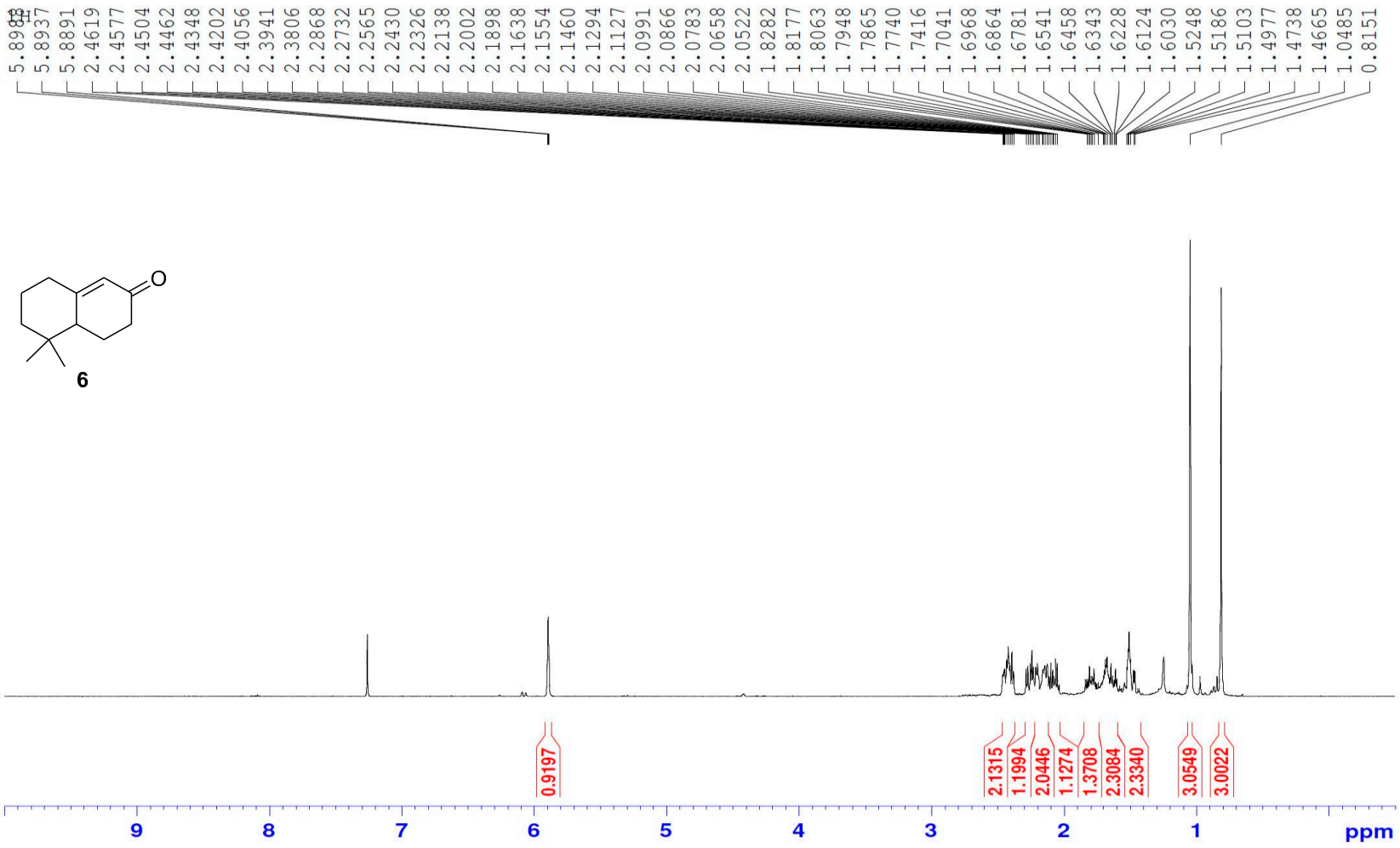
^{13}C NMR of compound **5** (100 MHz, $CDCl_3$)

Figure S5



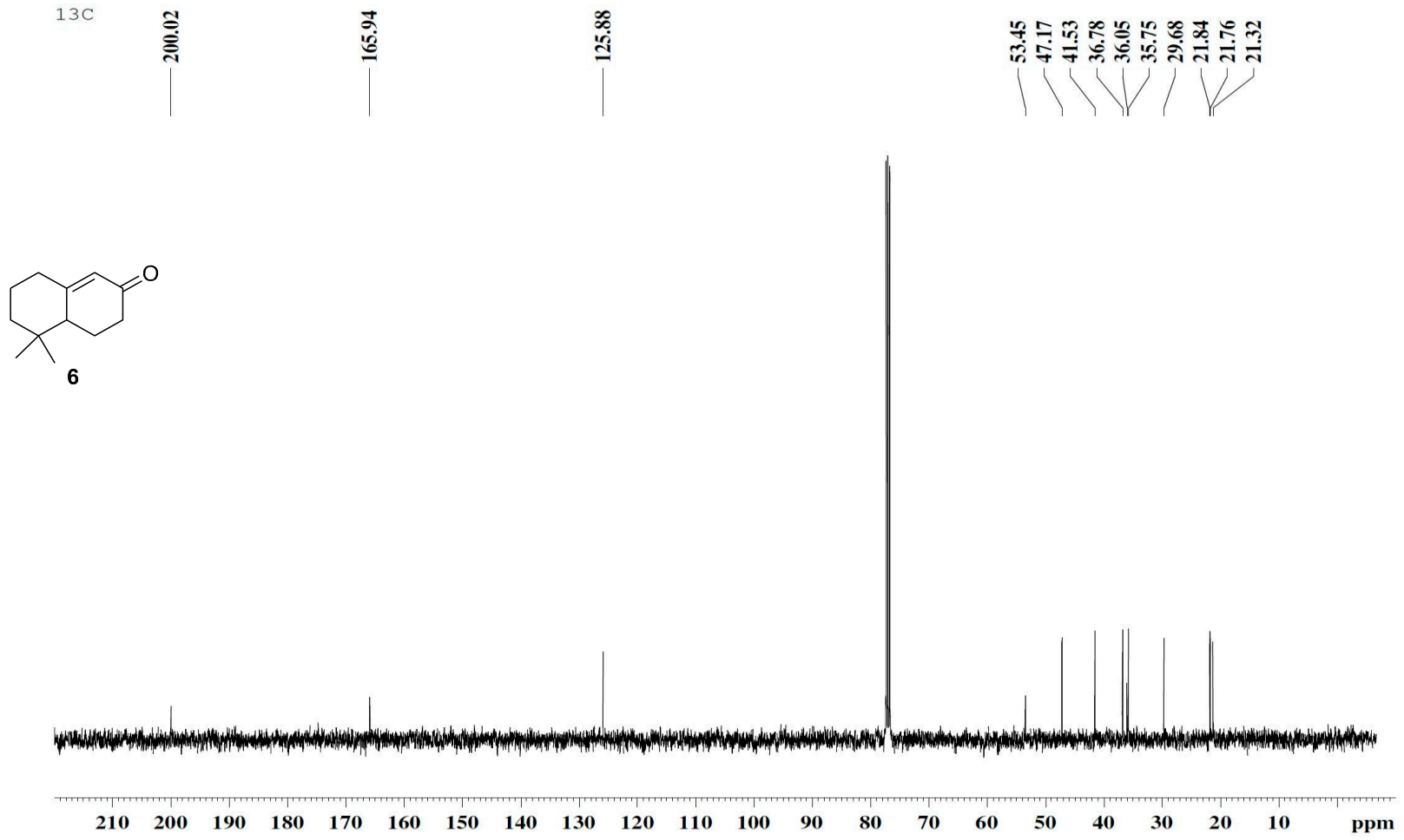
HRMS (ESI) of compound 5

Figure S7



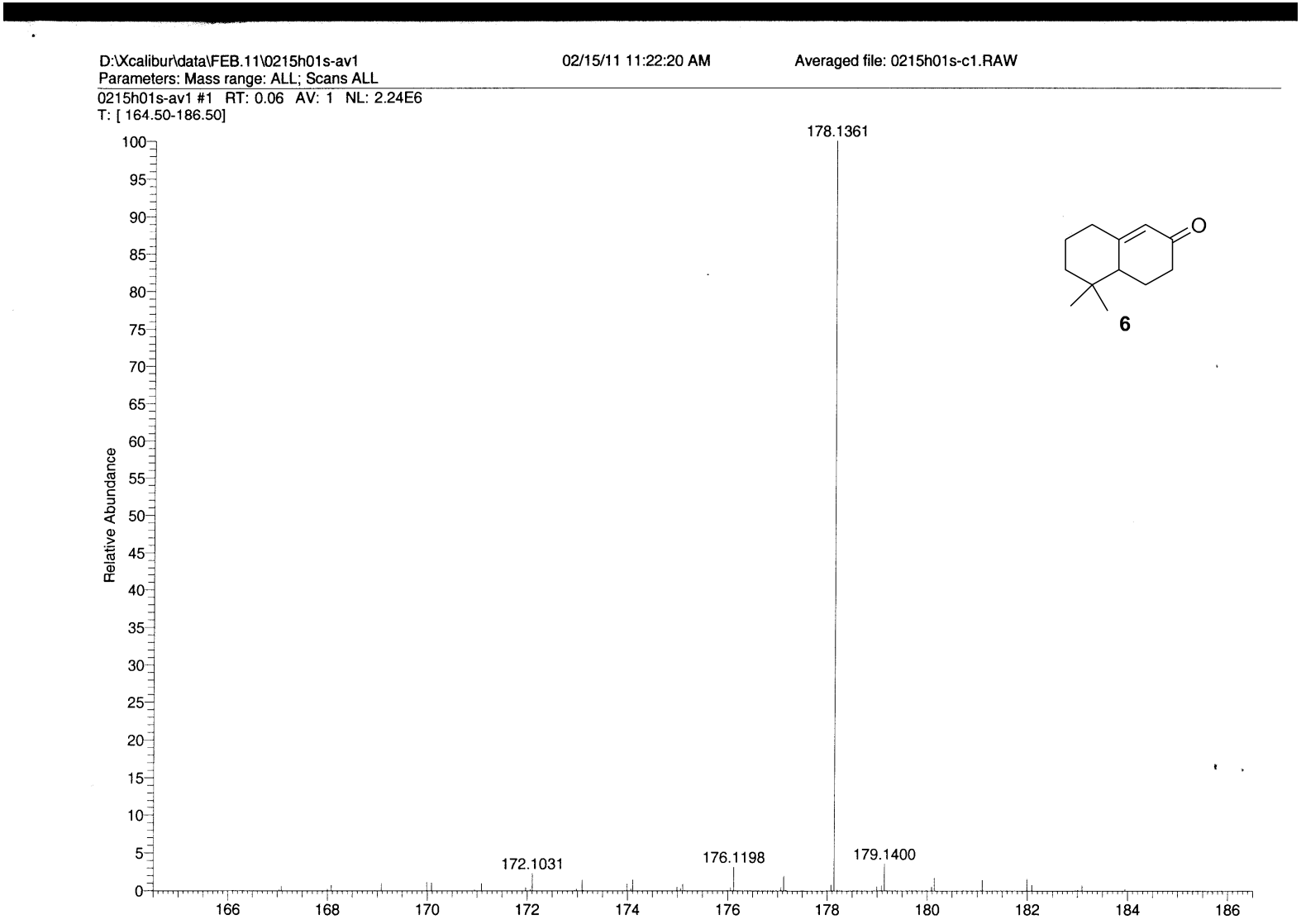
^{1}H NMR of compound **6** (400 MHz, $CDCl_3$)

Figure S8



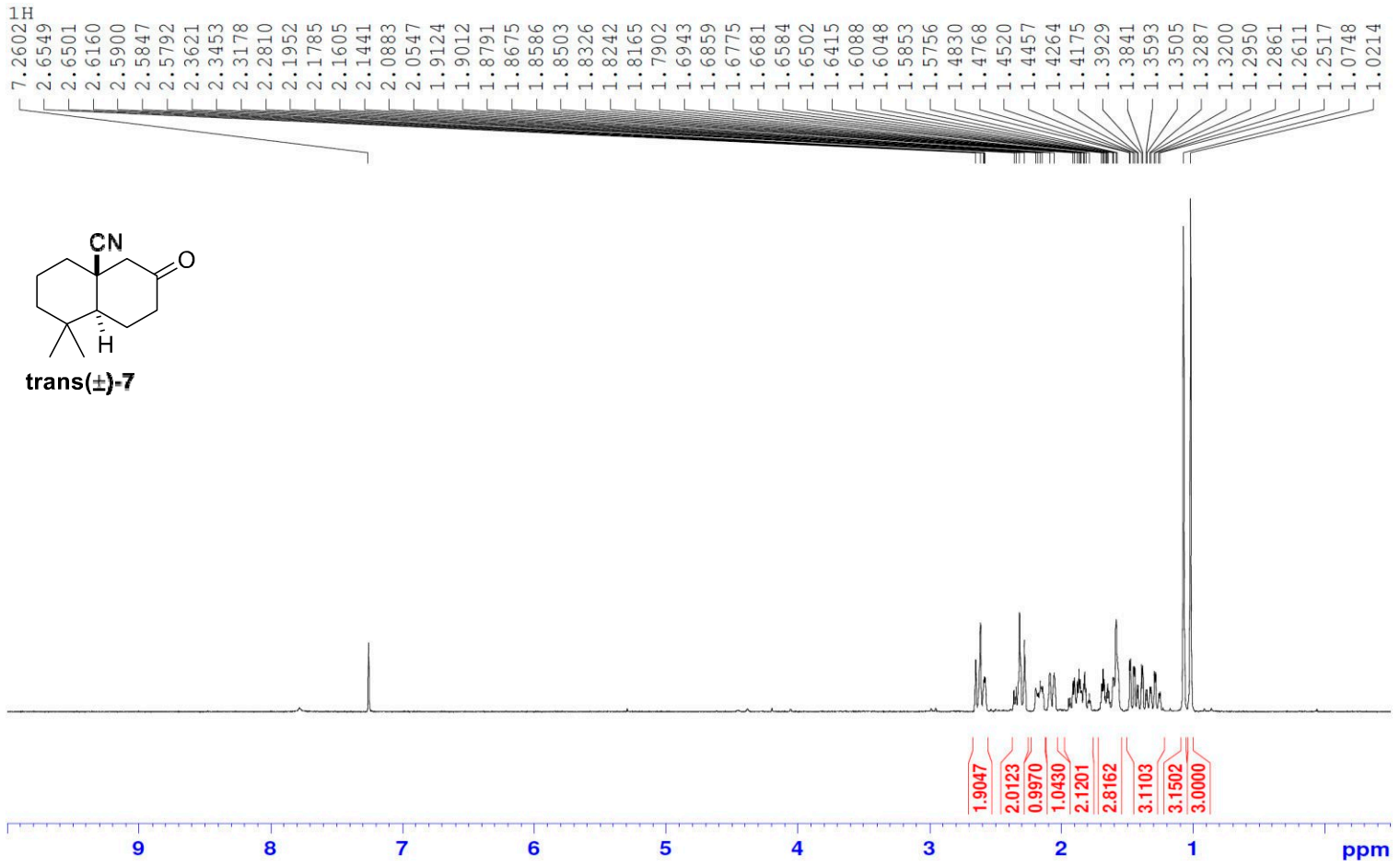
^{13}C NMR of compound **6** (100 MHz, $CDCl_3$)

Figure S9



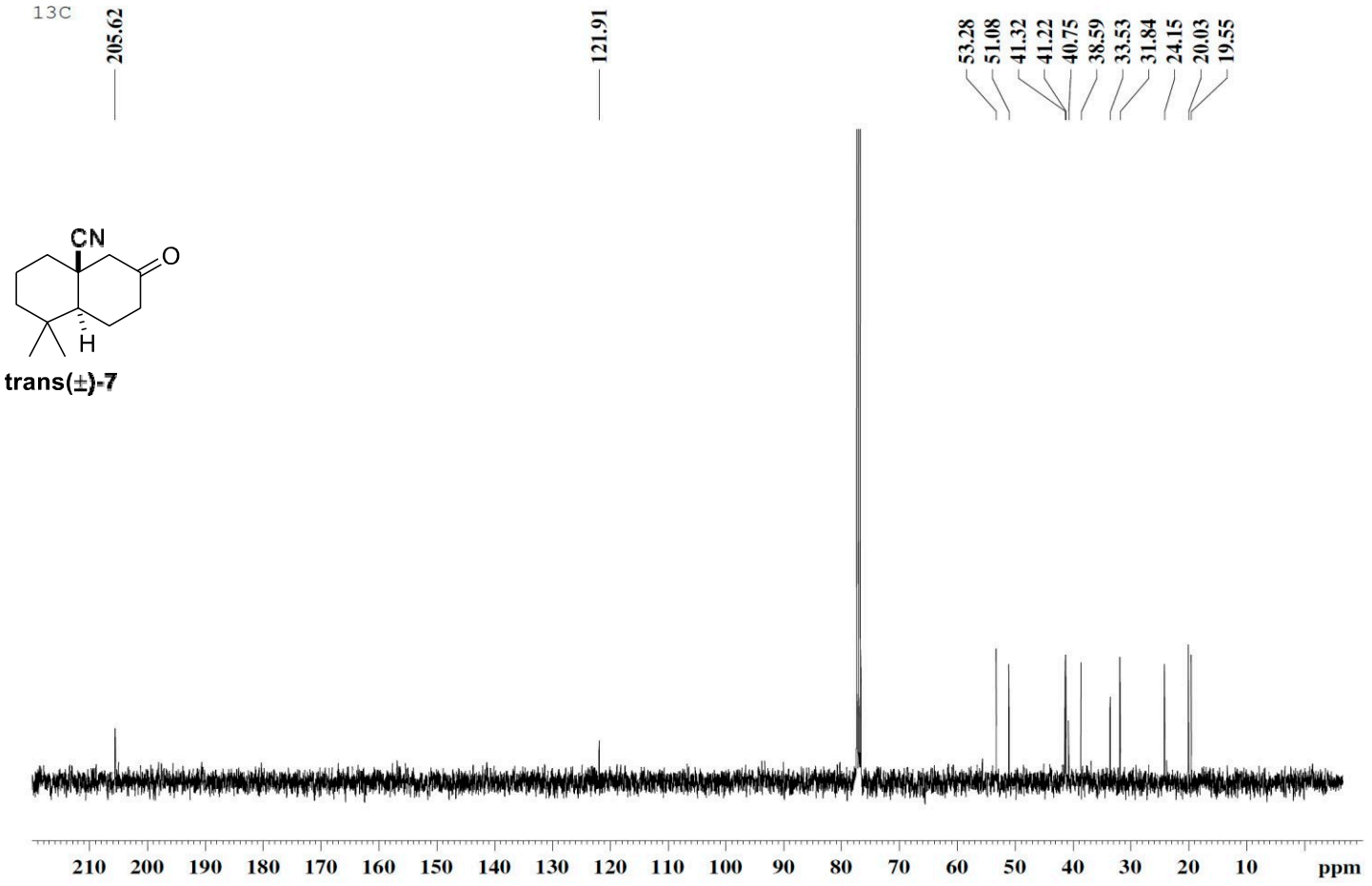
HRMS (ESI) of compound **6**

Figure S10



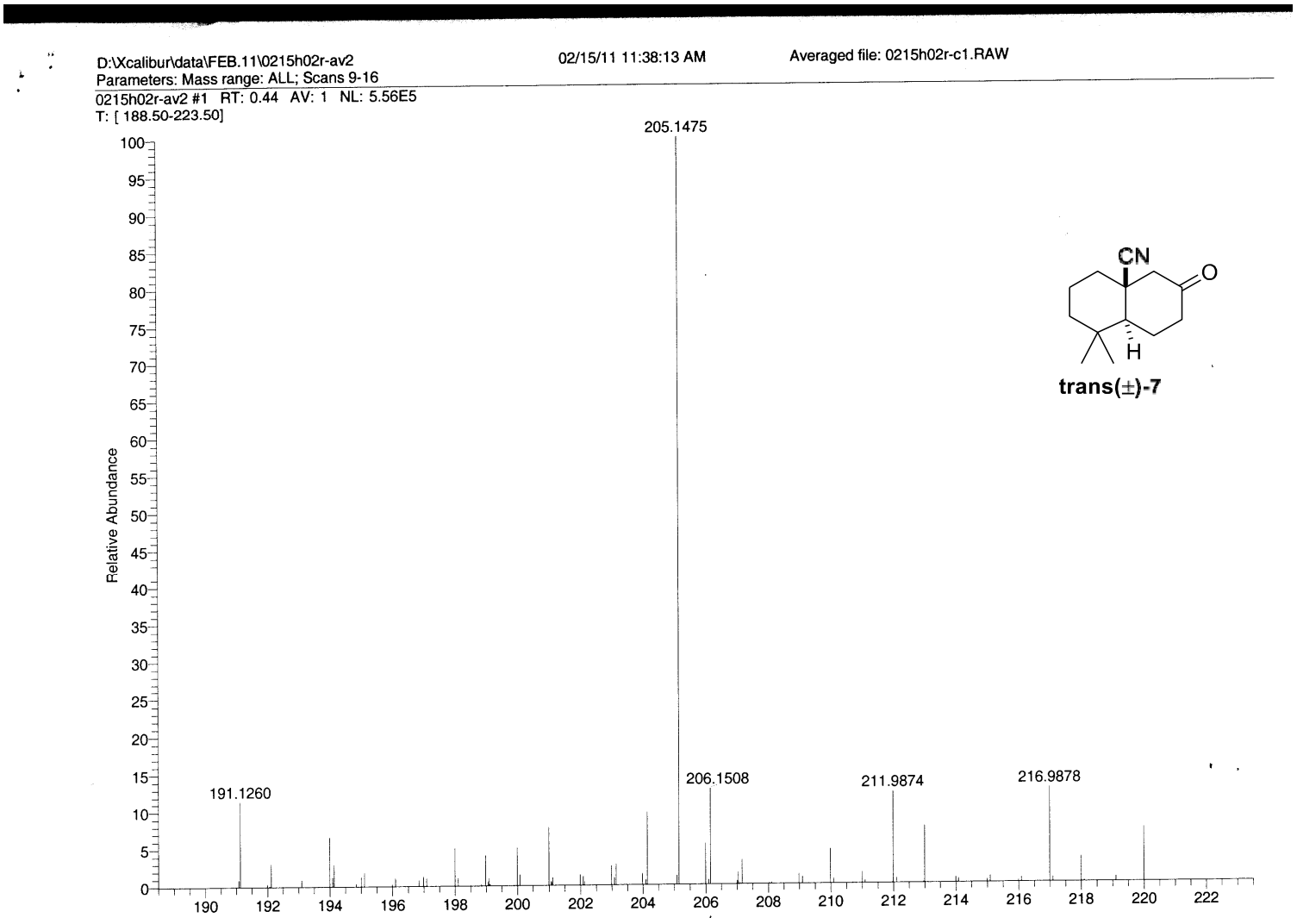
^{1}H NMR of compound trans-**(±)-7** (400 MHz, $CDCl_3$)

Figure S11



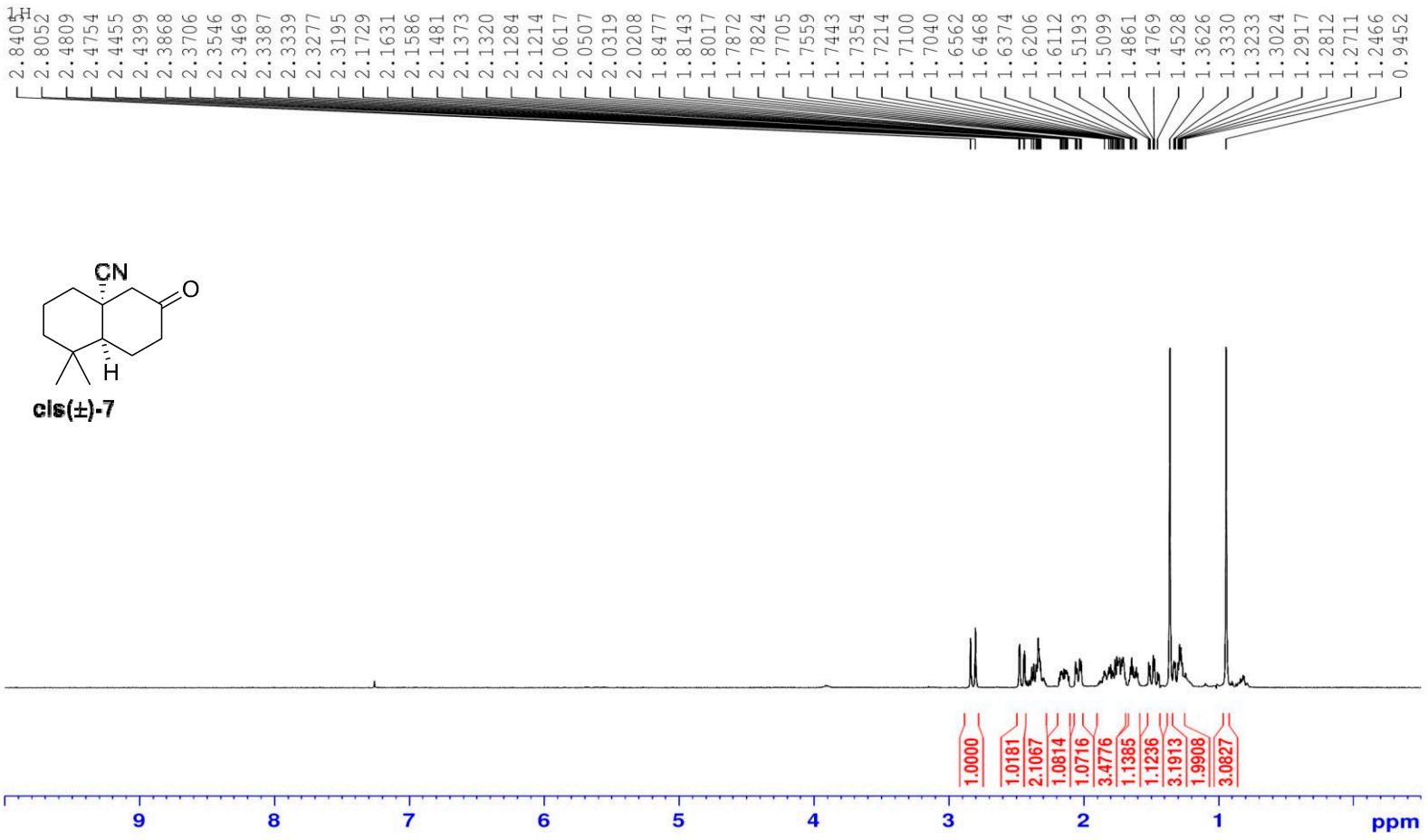
^{13}C NMR of compound trans-**(±)-7** (100 MHz, $CDCl_3$)

Figure S12



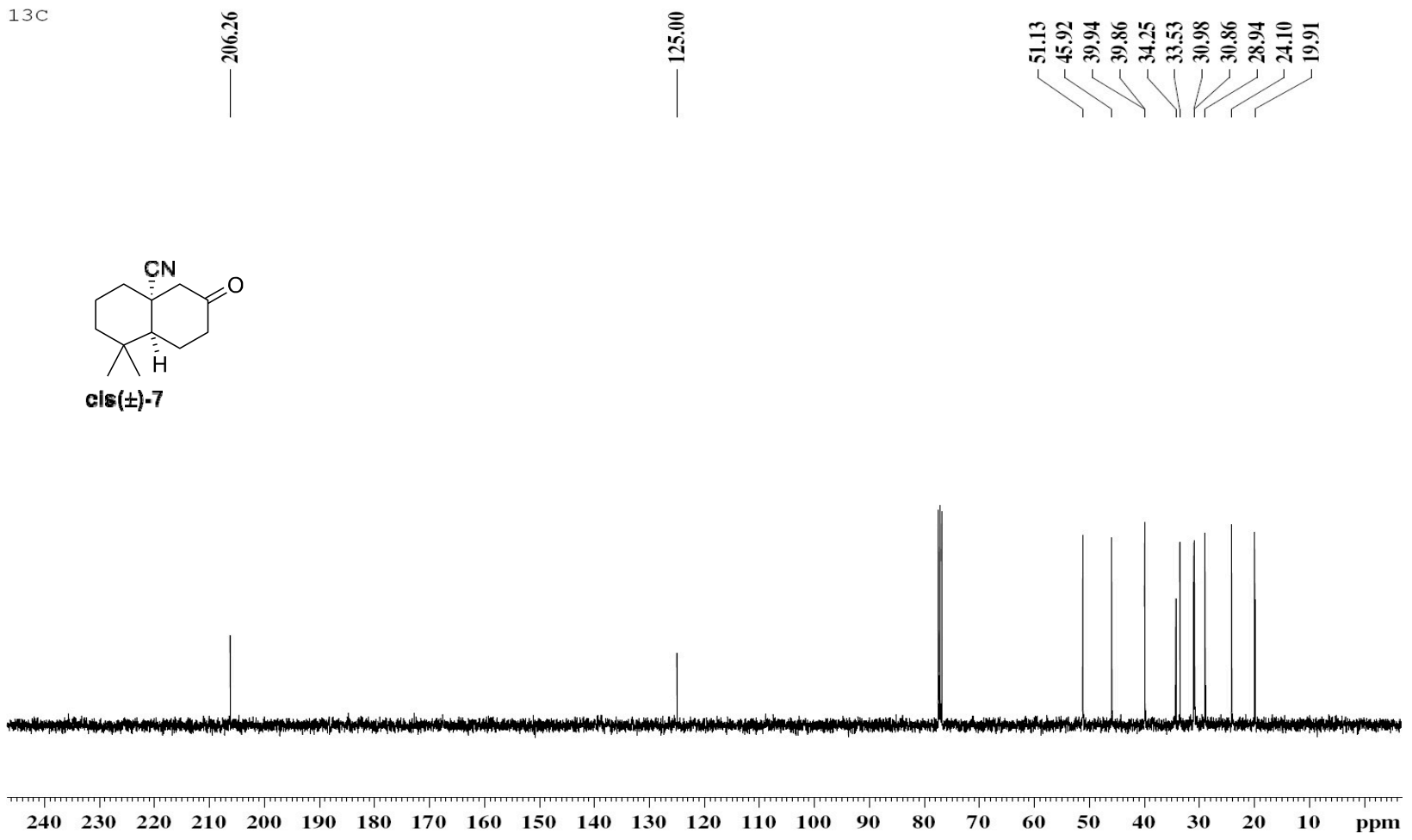
HRMS (ESI) of compound trans-**(±)-7**

Figure S13



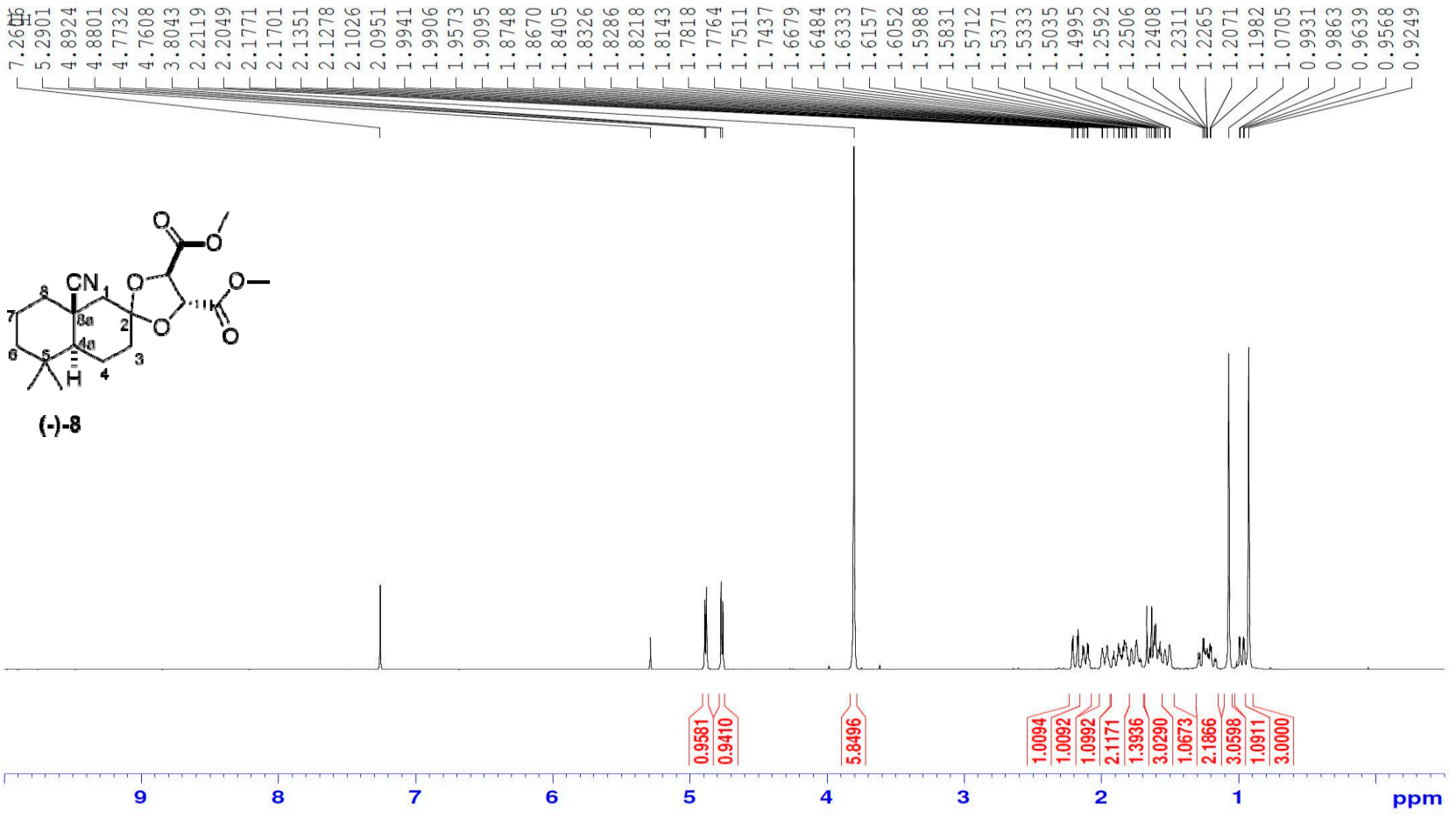
^{1}H NMR of compound cis-**(±)-7** (400 MHz, $CDCl_3$)

Figure S14



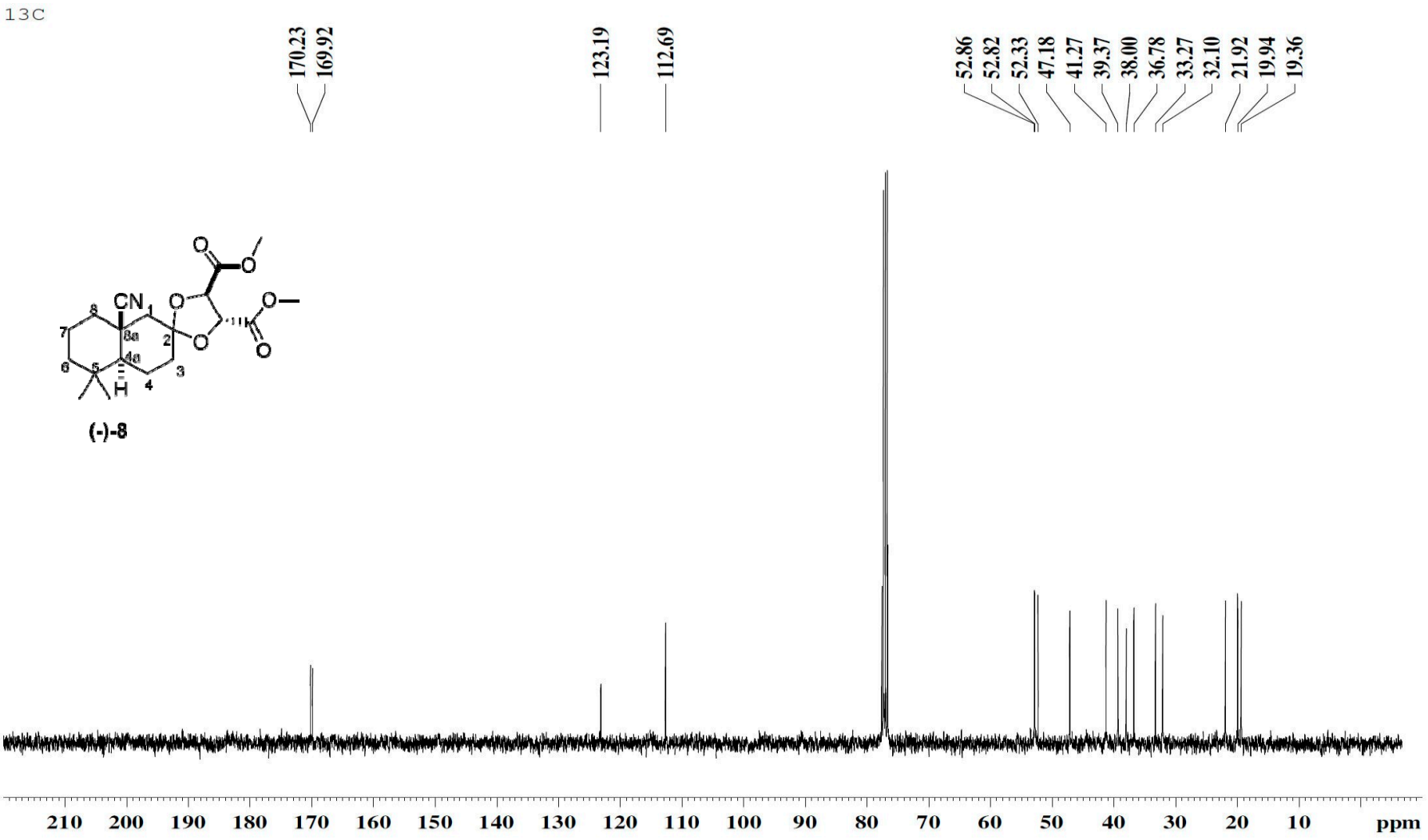
^{13}C NMR of compound cis-**(±)-7** (100 MHz, $CDCl_3$)

Figure S15



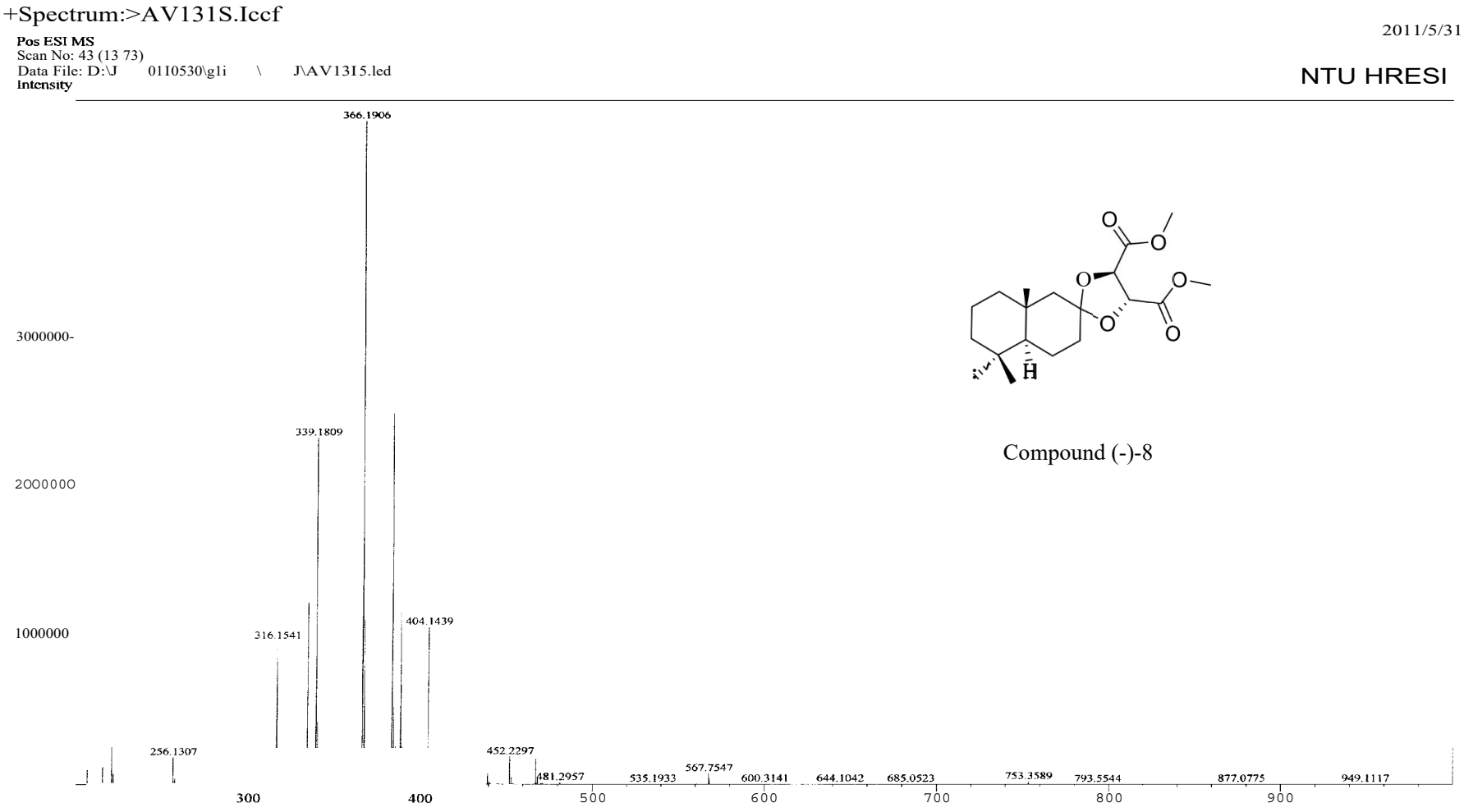
^{1}H NMR of compound (-)-**8** (400 MHz, $CDCl_3$)

Figure S16



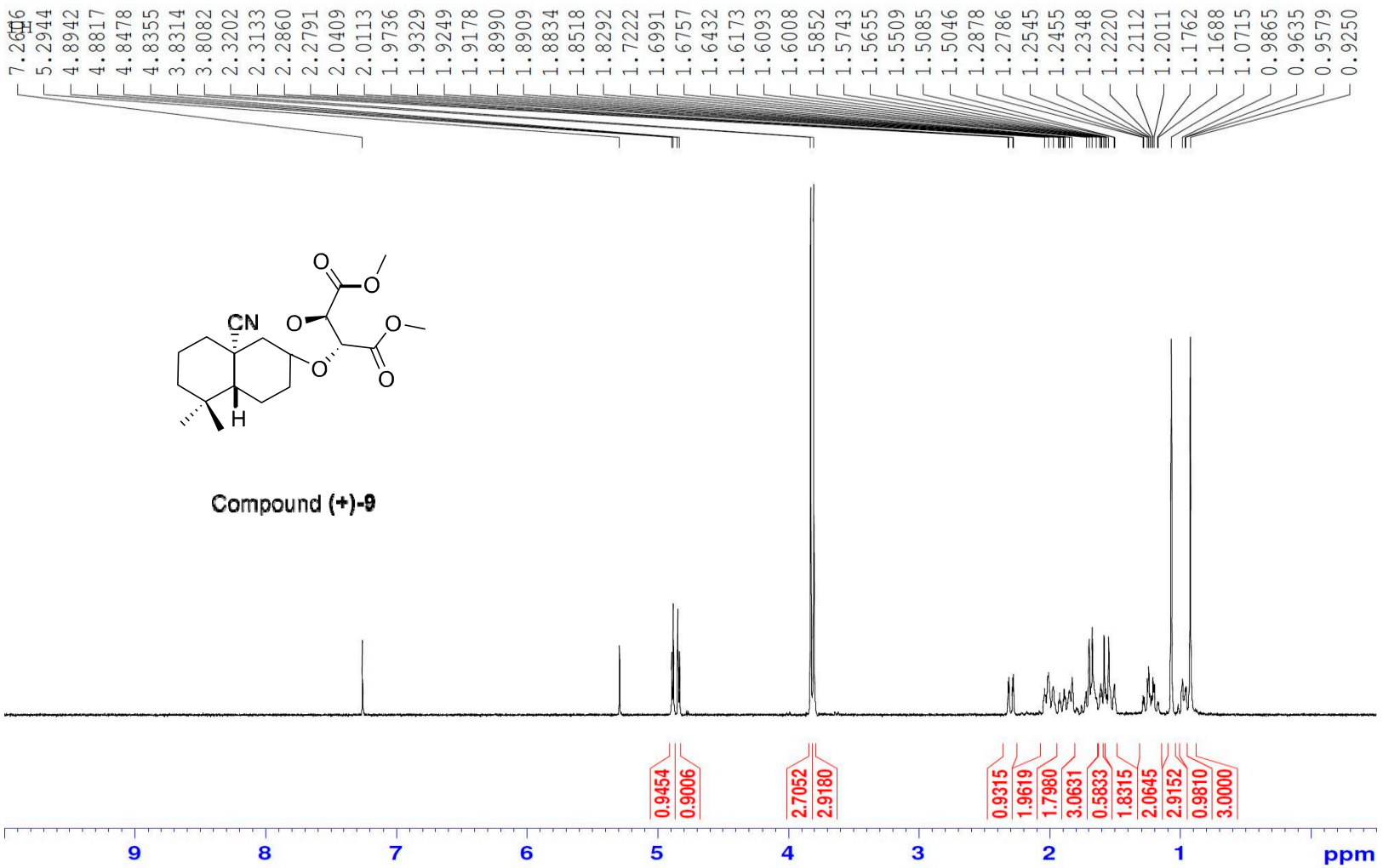
^{13}C NMR of compound **(-)-8** (100 MHz, $CDCl_3$)

Figure S17



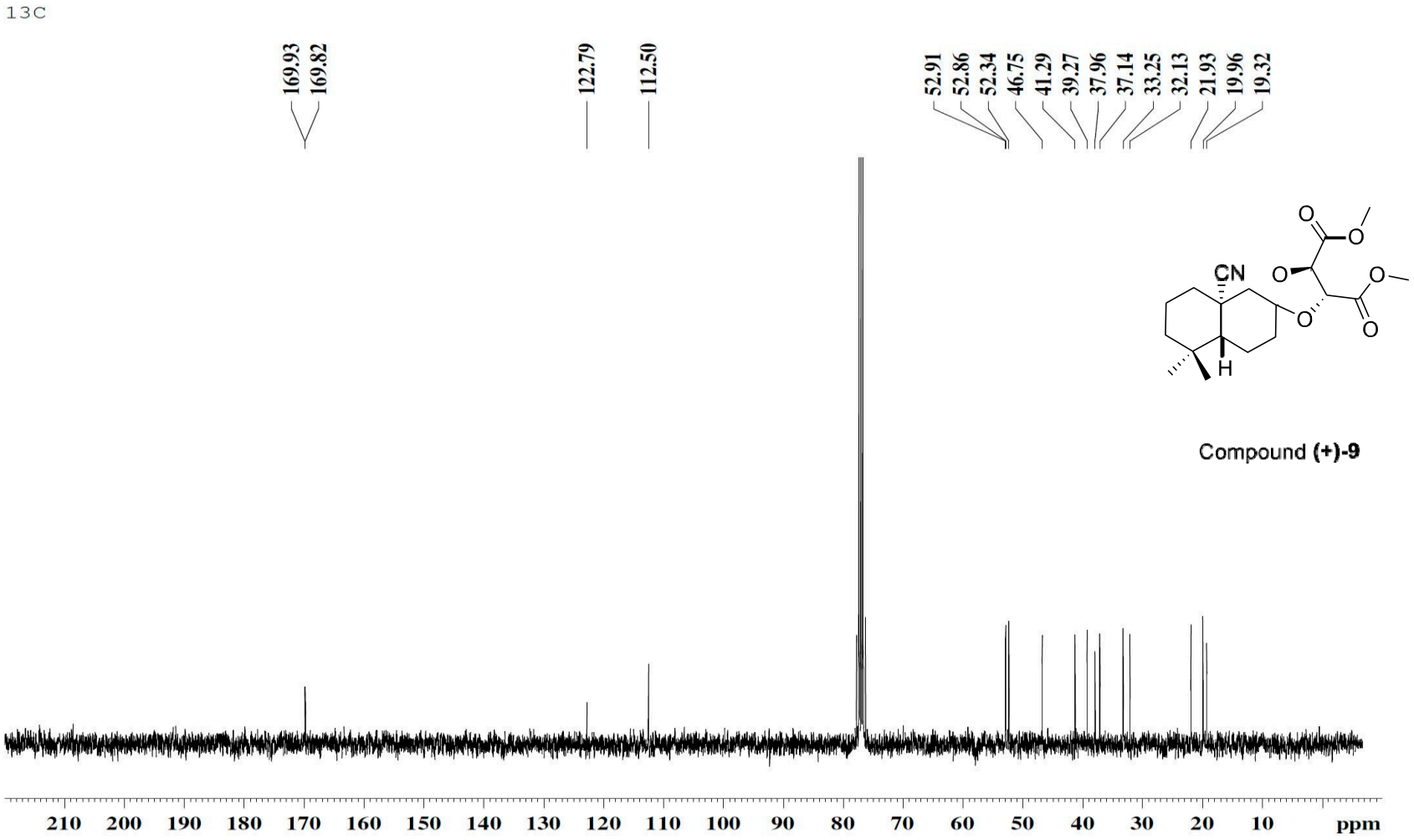
HRMS (ESI) of compound (-)-8

Figure S18



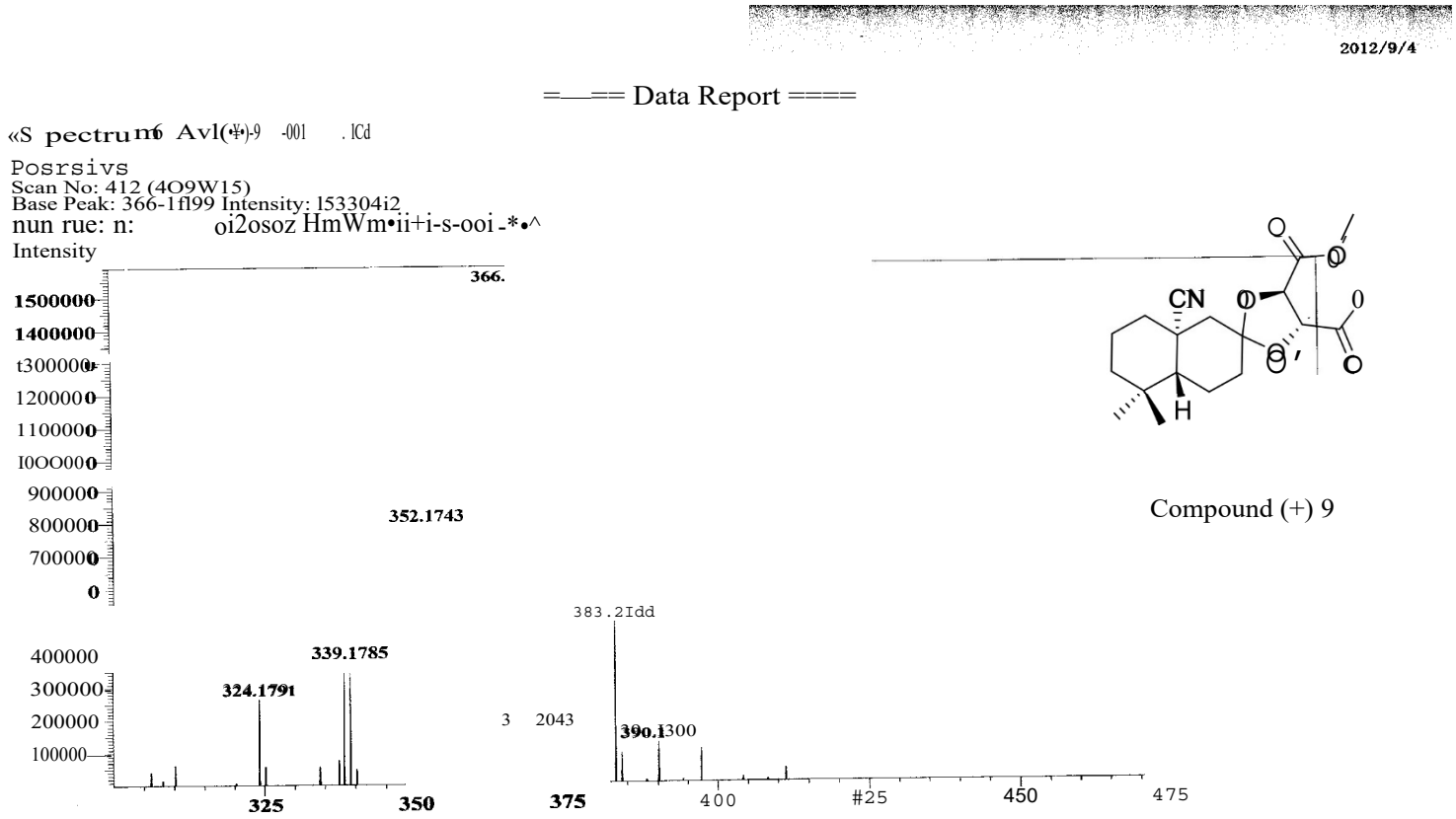
^{1}H NMR of compound (+)**-9** (400 MHz, $CDCl_3$)

Figure S19



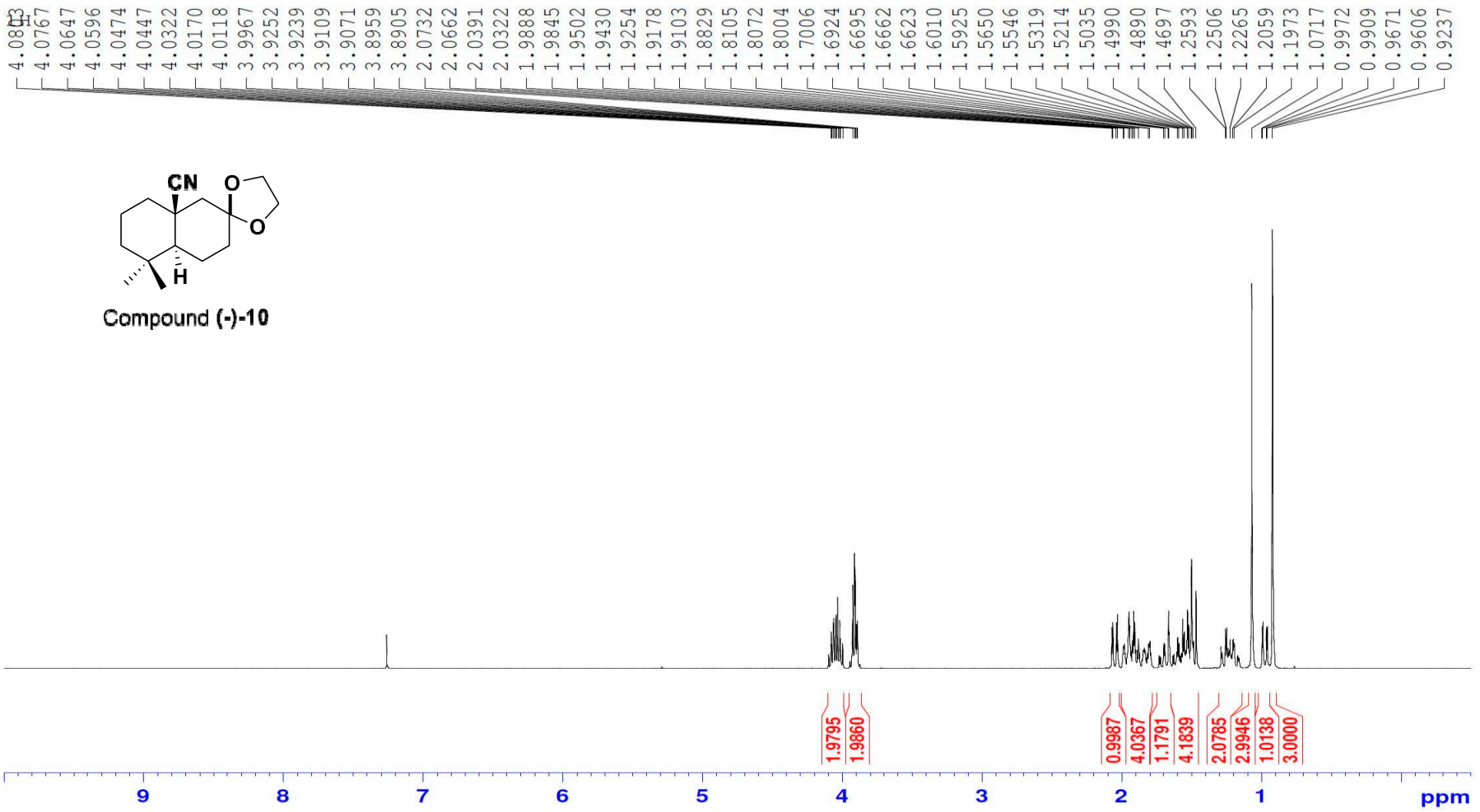
^{13} C NMR of compound (+)**-9** (100 MHz, $CDCl_3$)

Figure 520



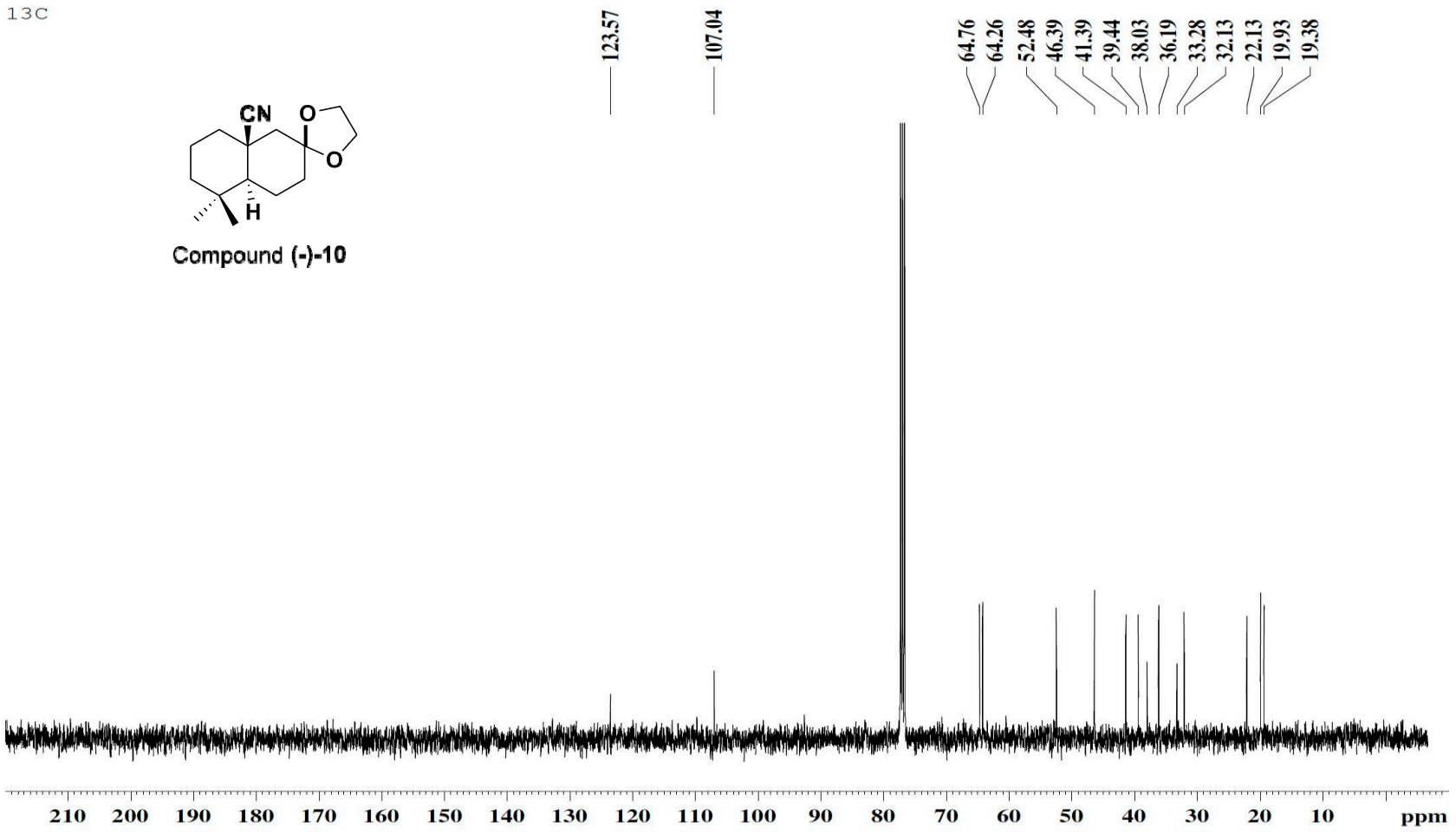
HRMS (ESI) of compound (+)-9

Figure S21



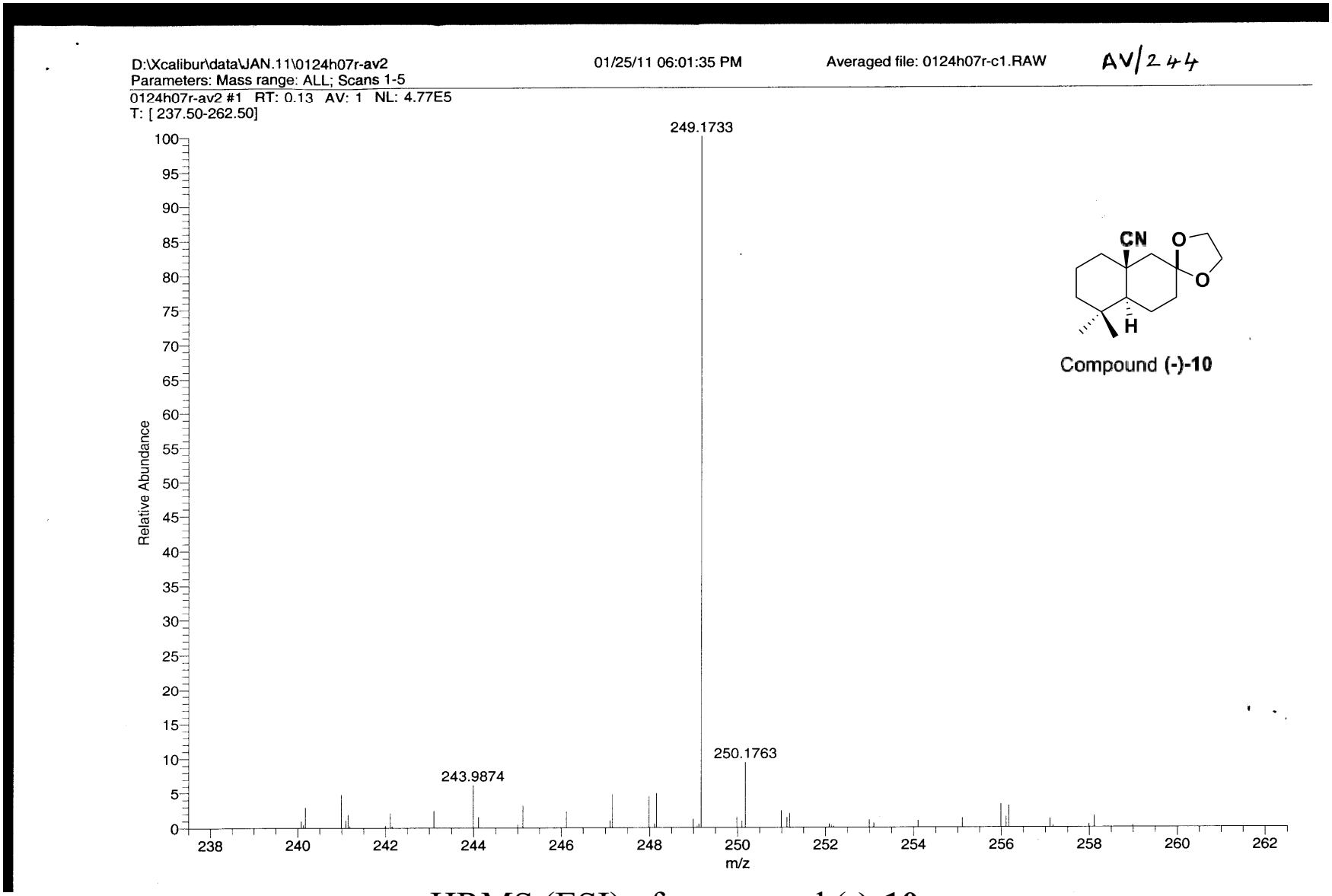
^{1}H NMR of compound (-)-**10** (400 MHz, $CDCl_3$)

Figure S22



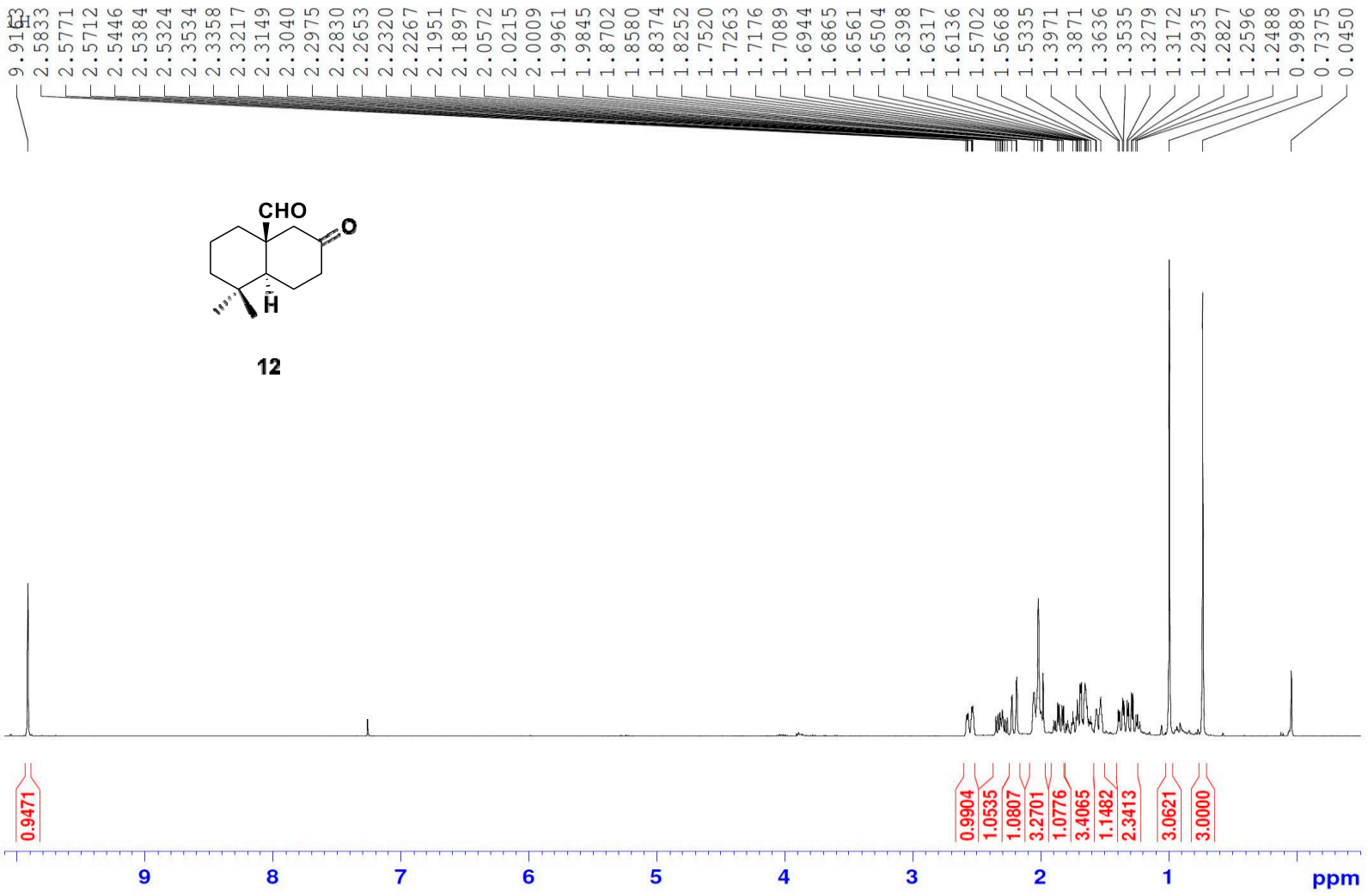
^{13} C NMR of compound **(-)-10** (100 MHz, $CDCl_3$)

Figure S23



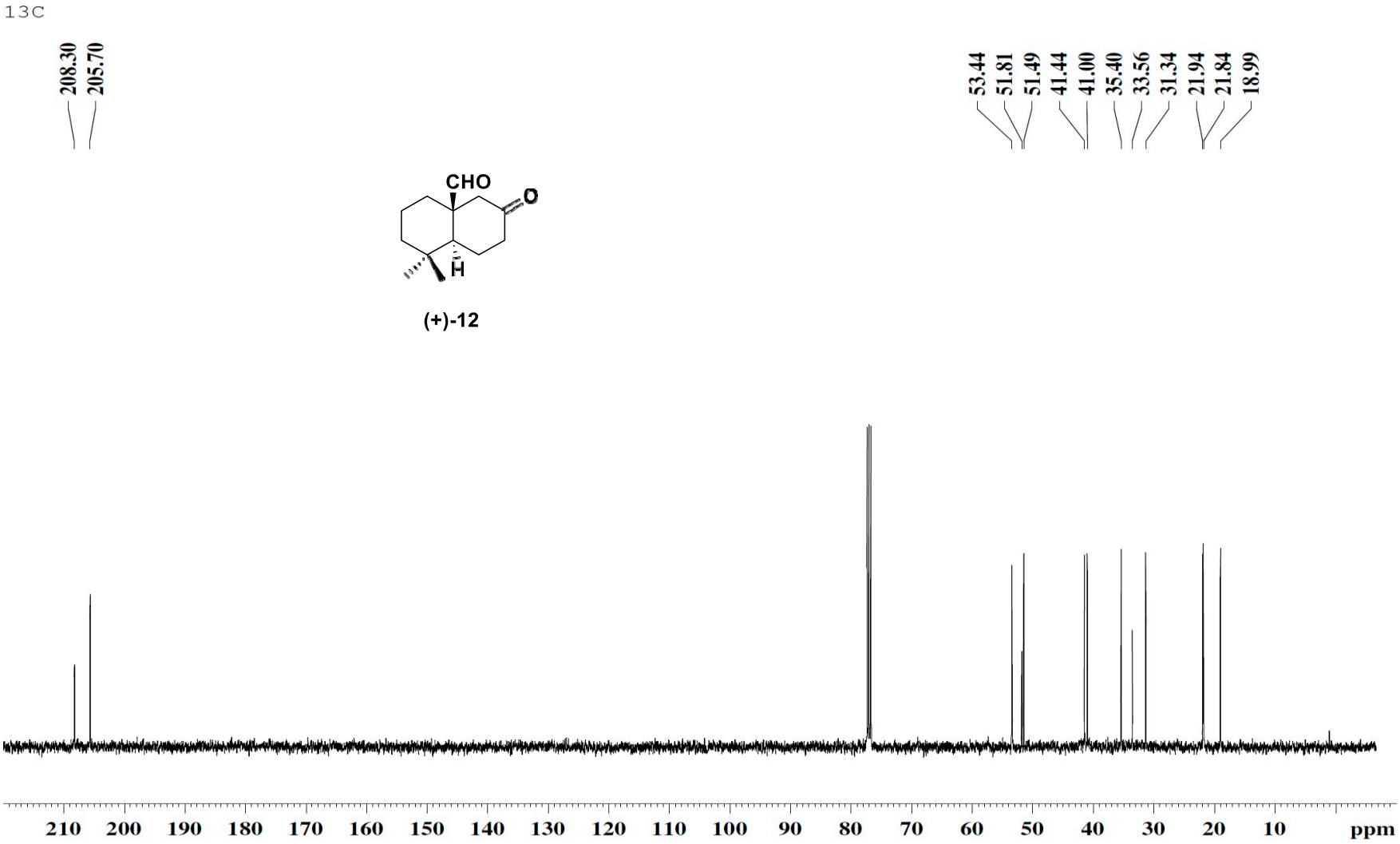
HRMS (ESI) of compound (-)-**10**

Figure S24



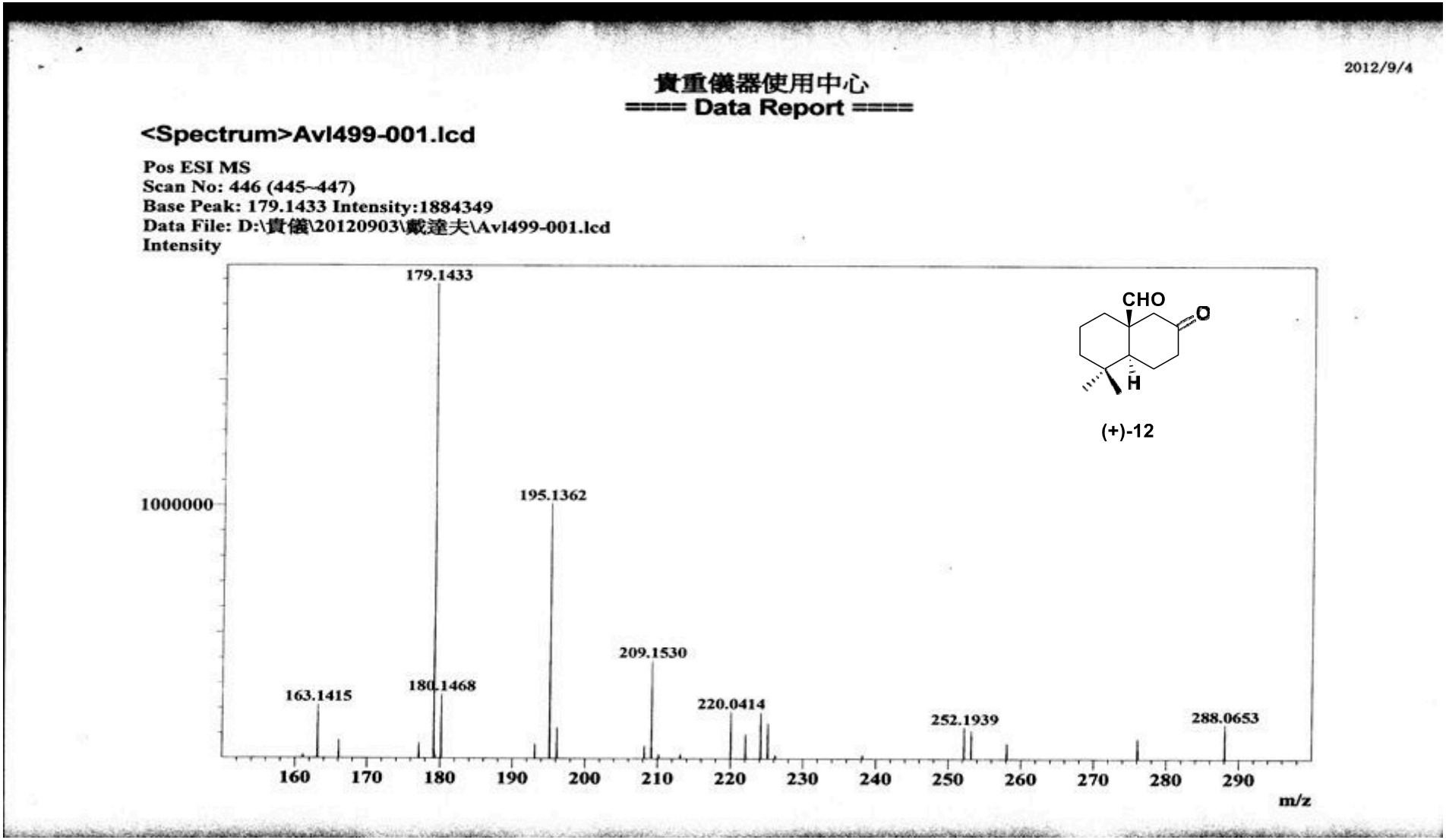
^{1}H NMR of compound 12 (400 MHz, $CDCl_3$)

Figure S25



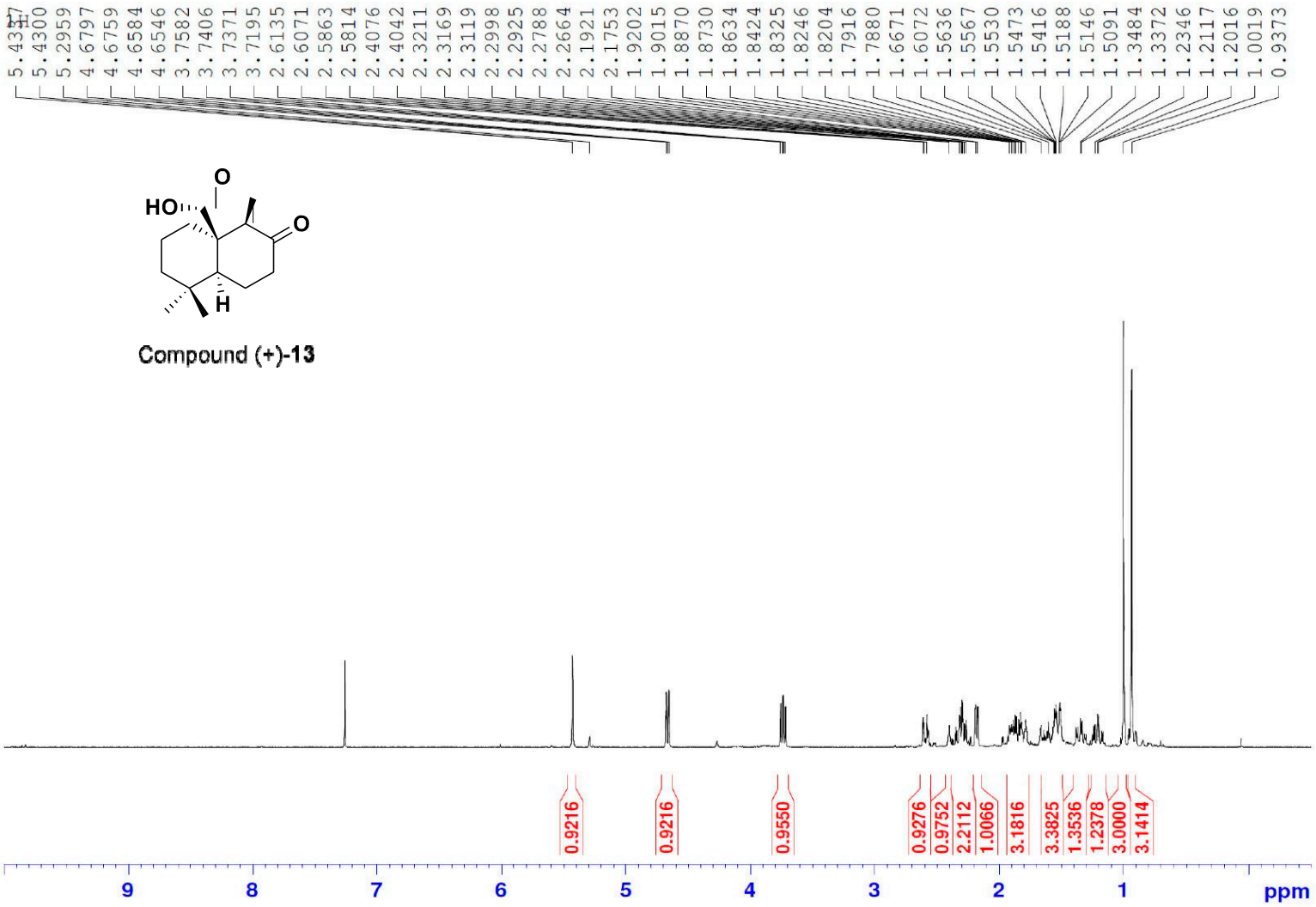
^{13}C NMR of compound (+)-**12** (100 MHz, $CDCl_3$)

Figure S26



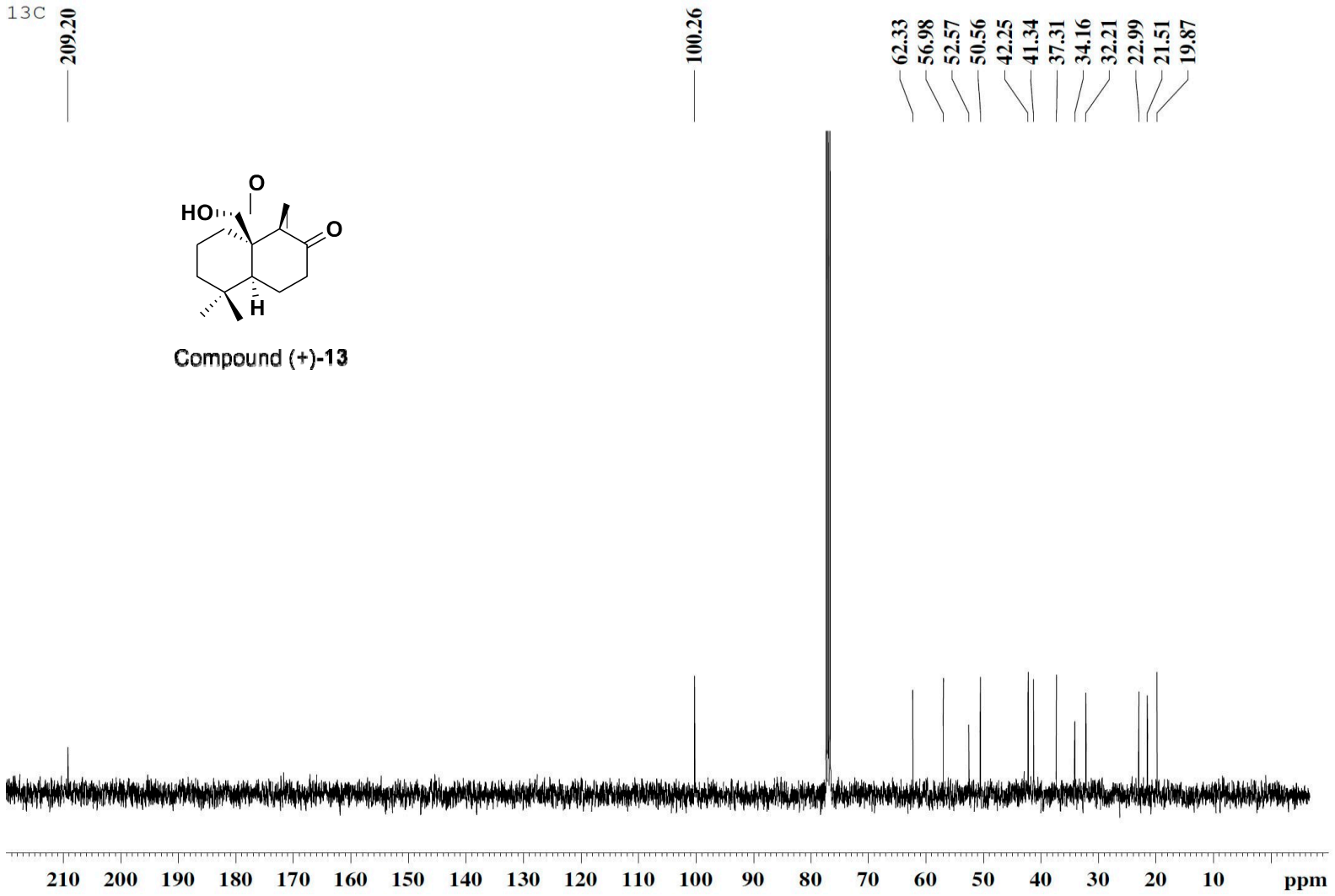
HRMS (ESI) of compound **12**

Figure S27



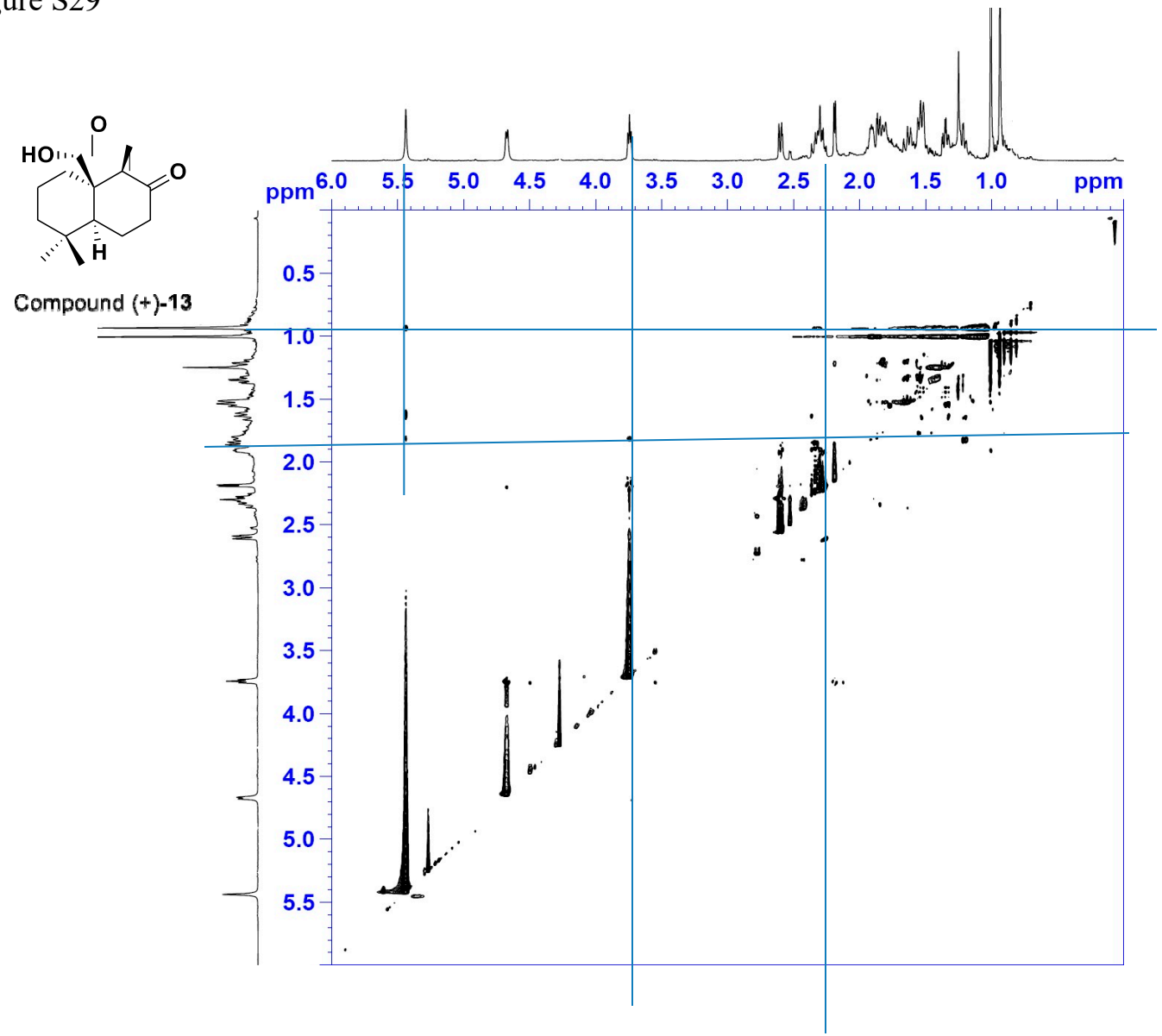
^{1}H NMR of compound (+)-**13** (400 MHz, $CDCl_3$)

Figure S28



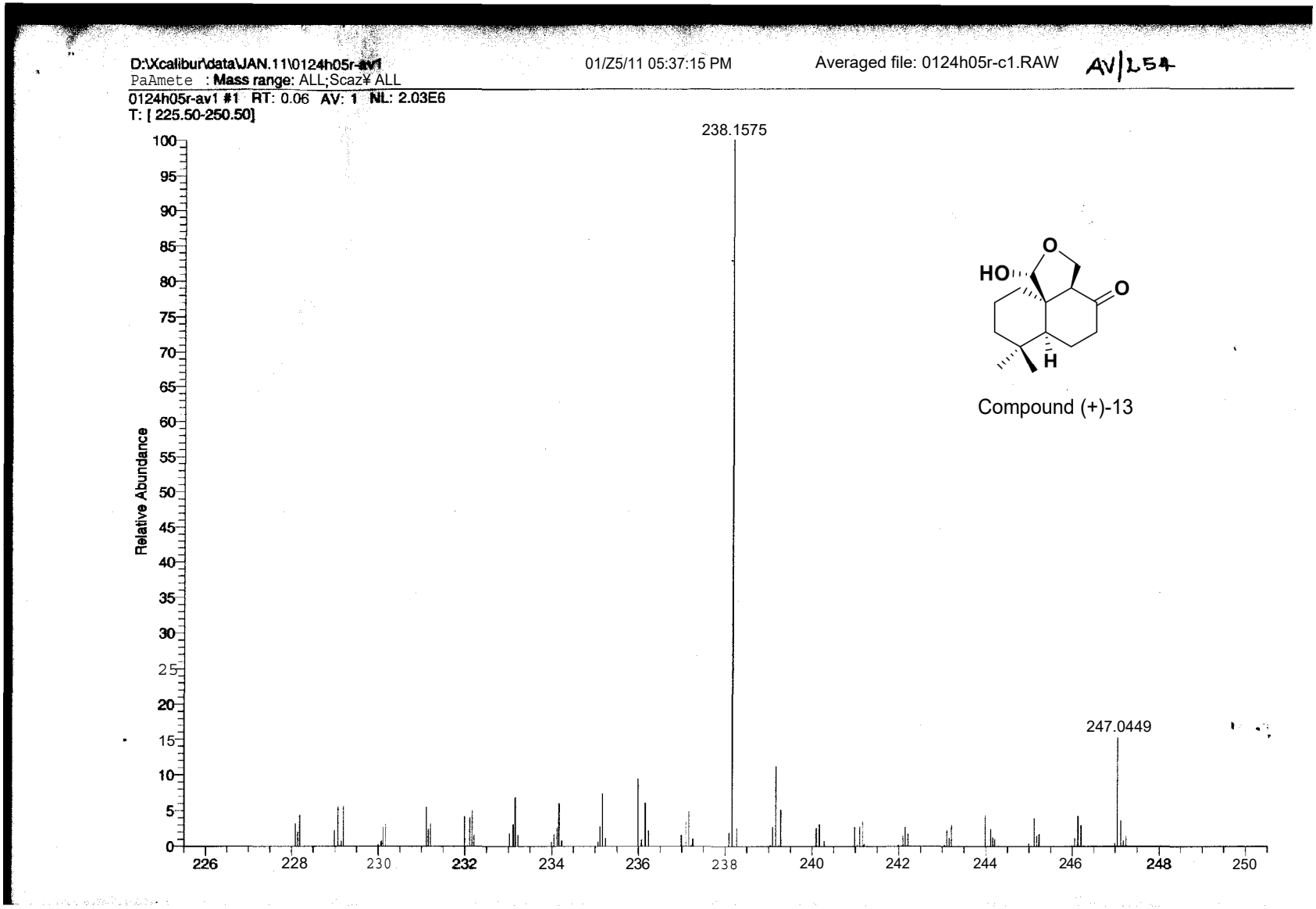
^{13} C NMR of compound (+)-**13** (100 MHz, $CDCl_3$)

Figure S29



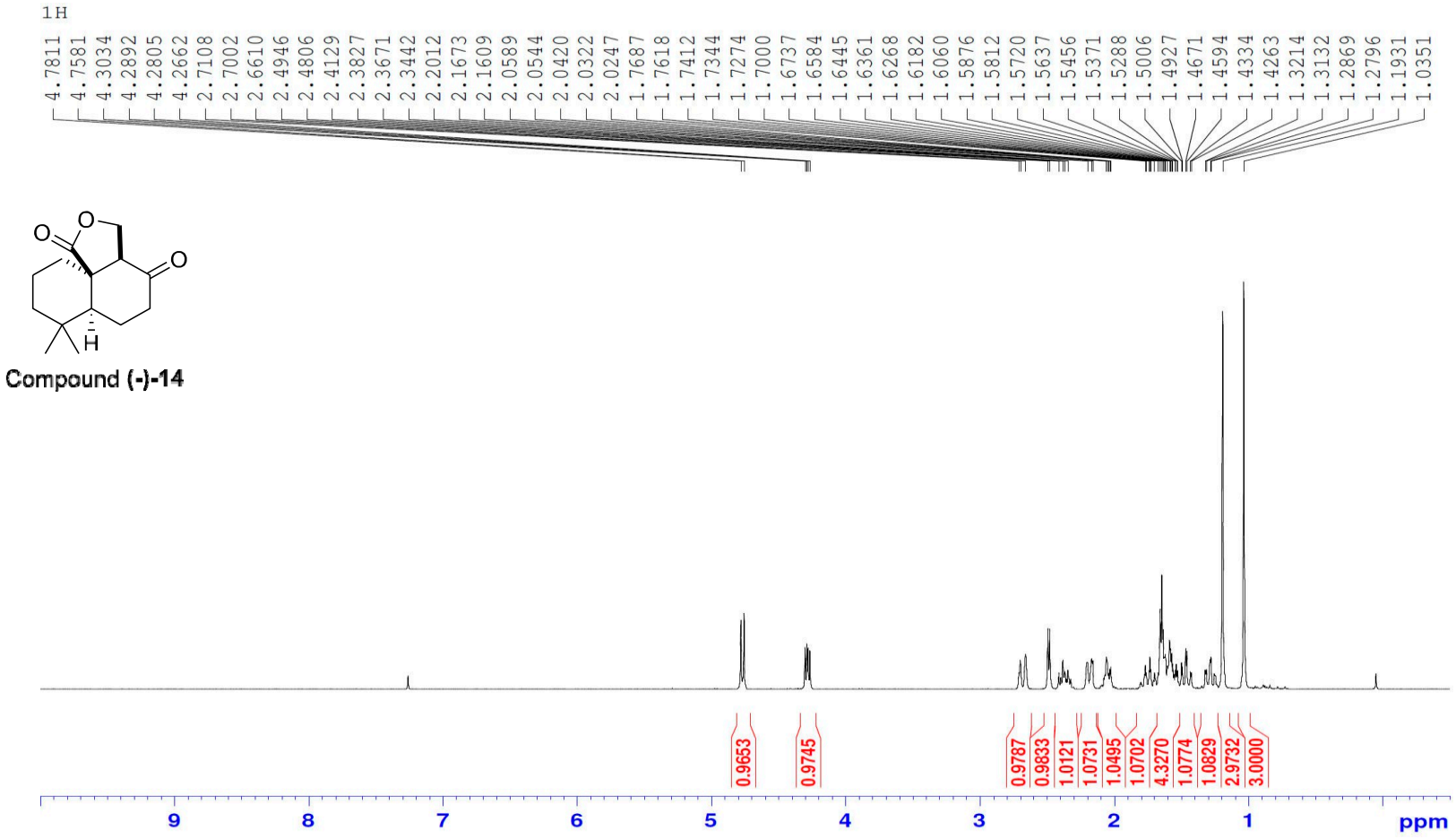
2D NOESY of compound (+)-13 (600 MHz, $CDCl_3$)

Figure 530



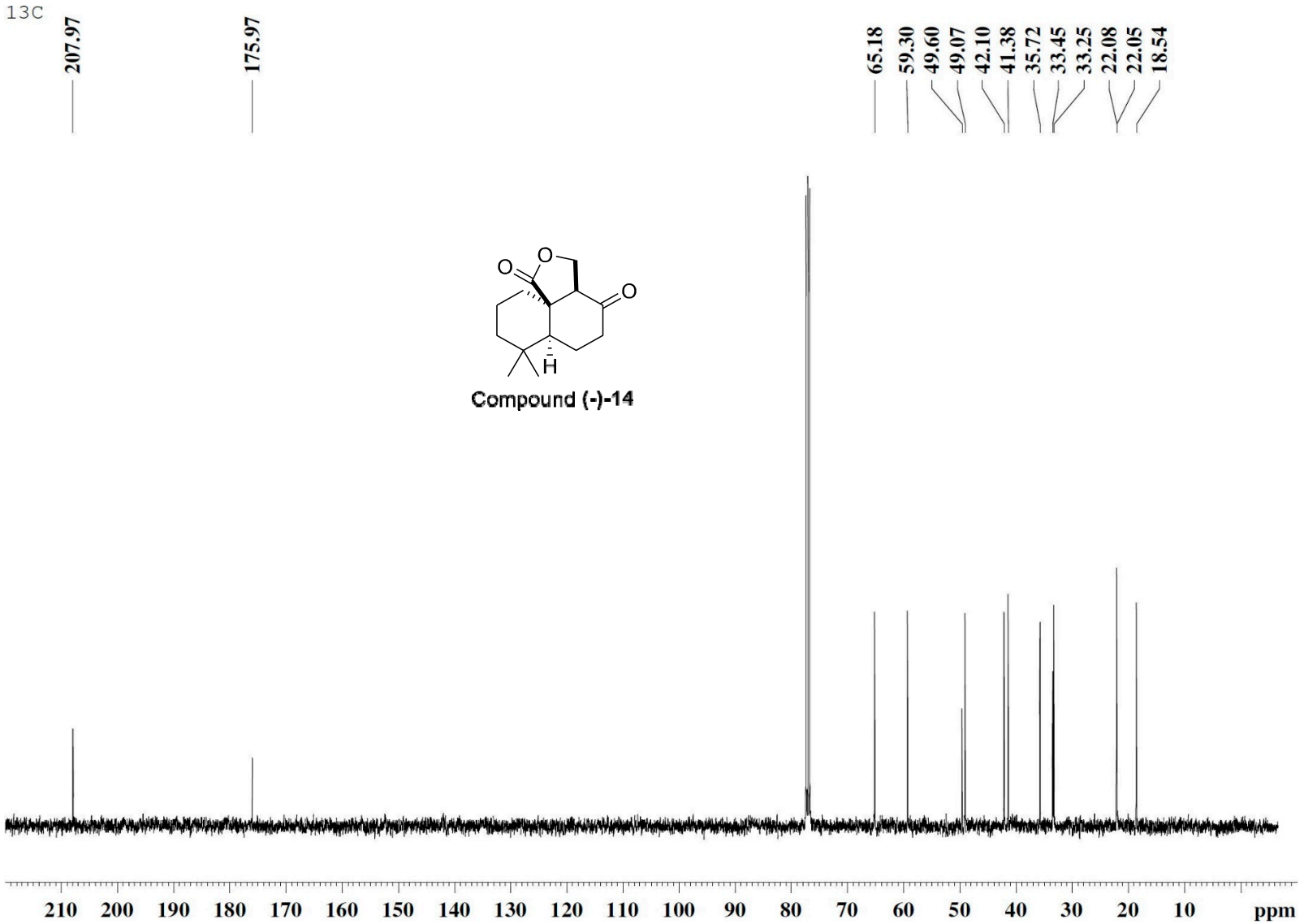
HRMS (ESI) of compound (+)-13

Figure S31



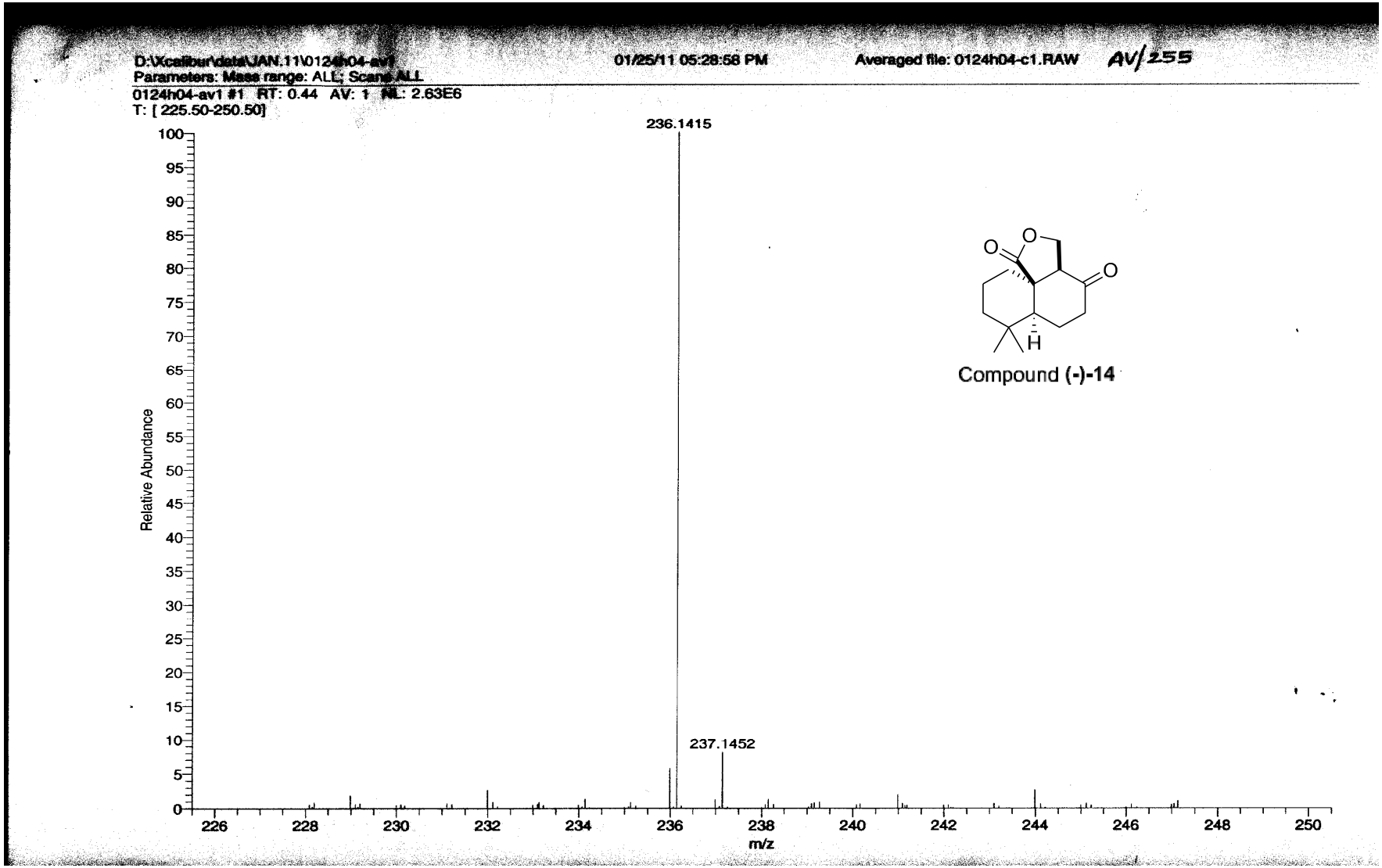
^{1}H NMR of compound **14** (400 MHz, $CDCl_3$)

Figure S32



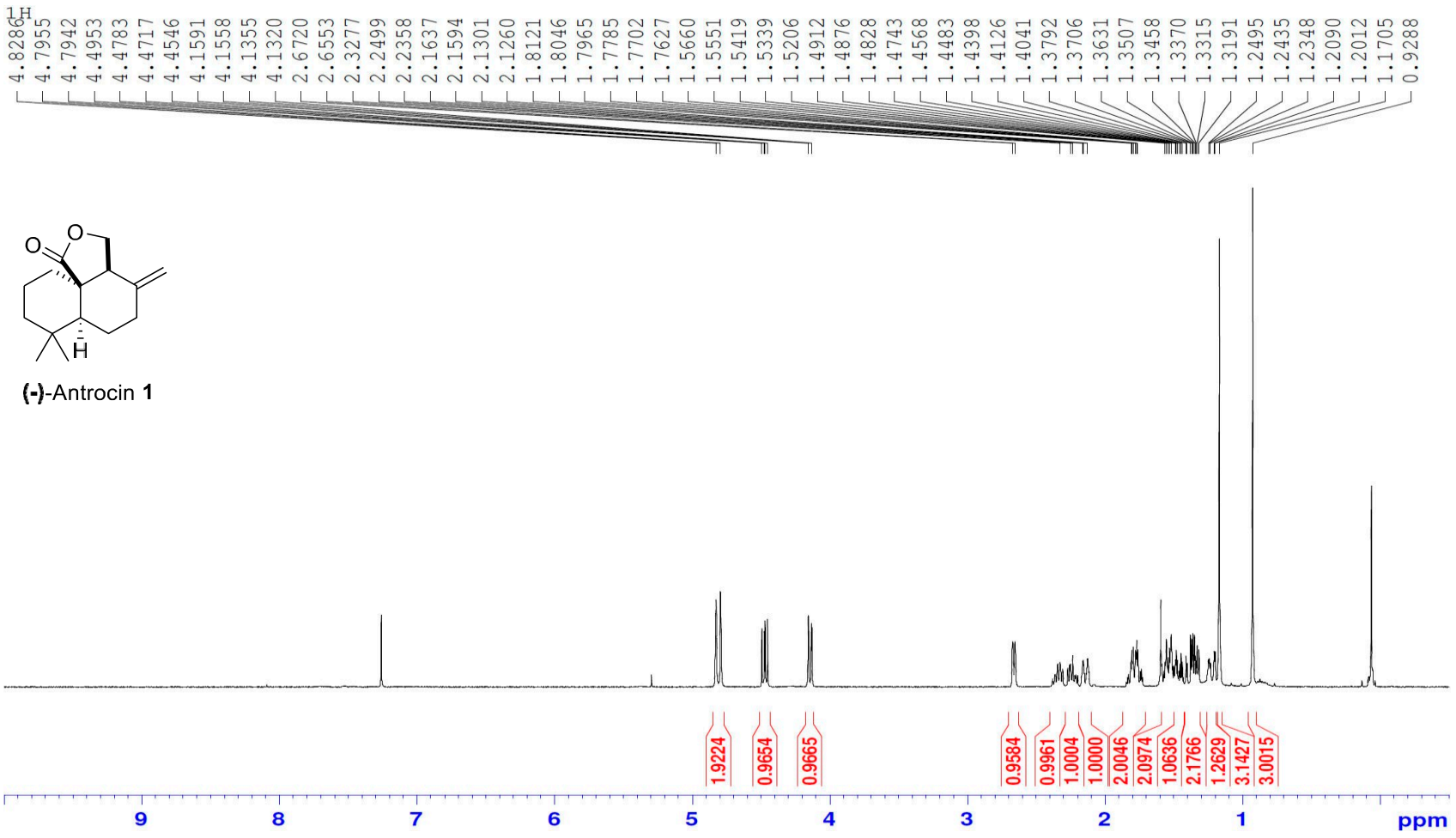
^{13}C NMR of compound **14** (100 MHz, $CDCl_3$)

Figure S33



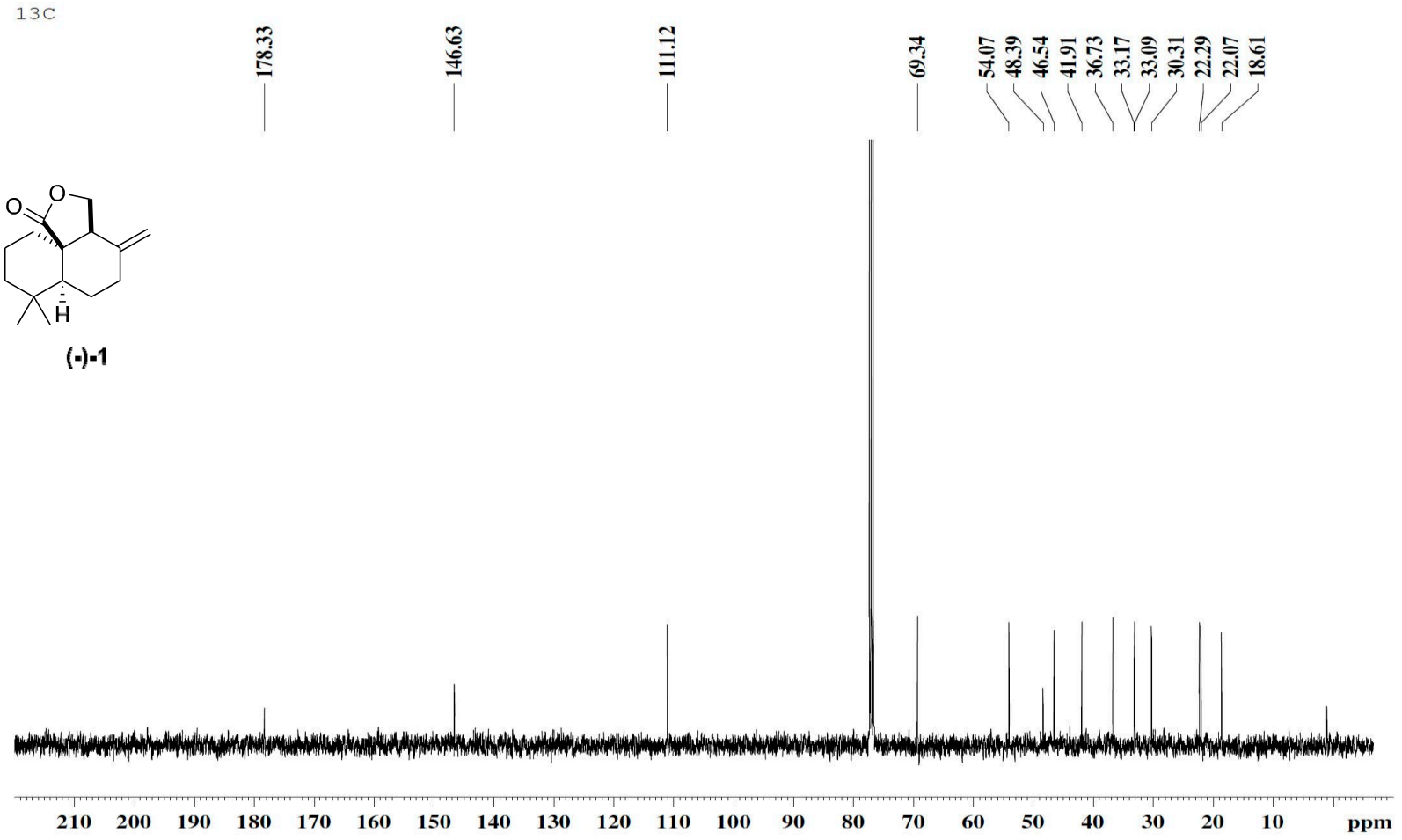
HRMS (ESI) of compound **14**

Figure S34



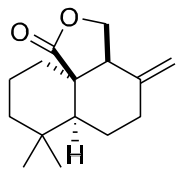
^{1}H NMR of (-)-antrocin **1a** (400 MHz, $CDCl_3$)

Figure S35

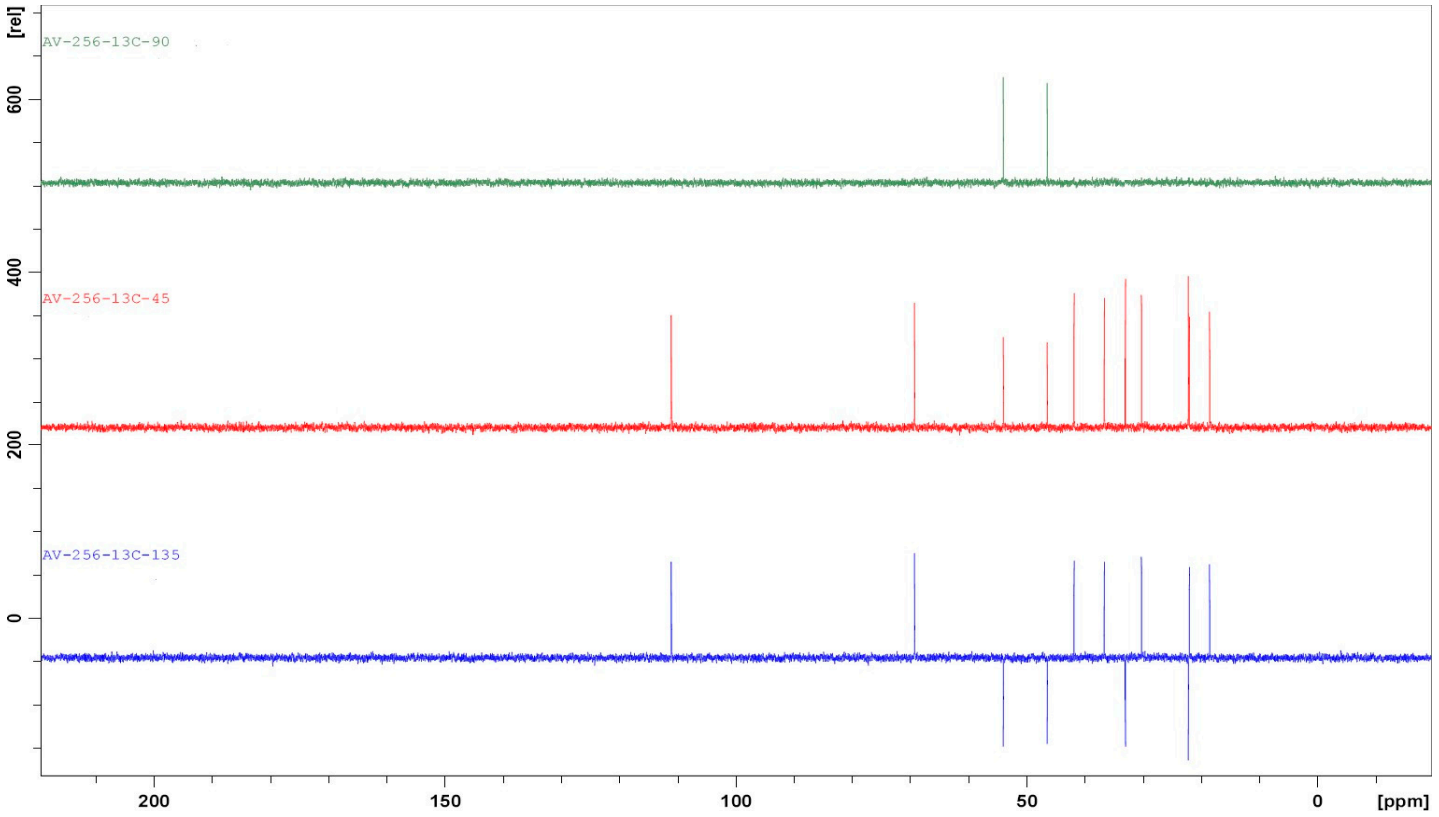


^{13}C NMR of (-)-antrocin **1**(100 MHz, $CDCl_3$)

Figure S36

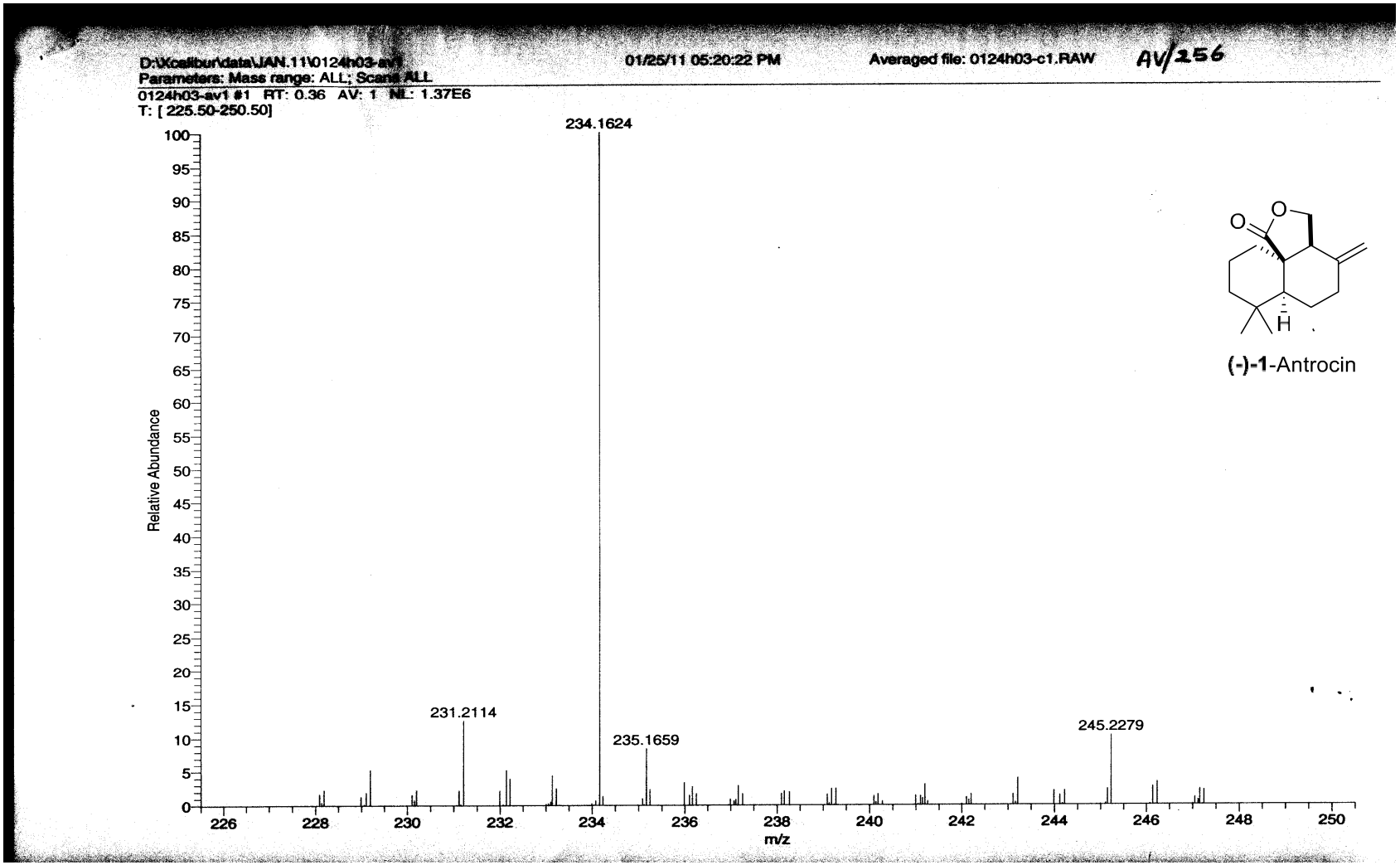


(-)-1



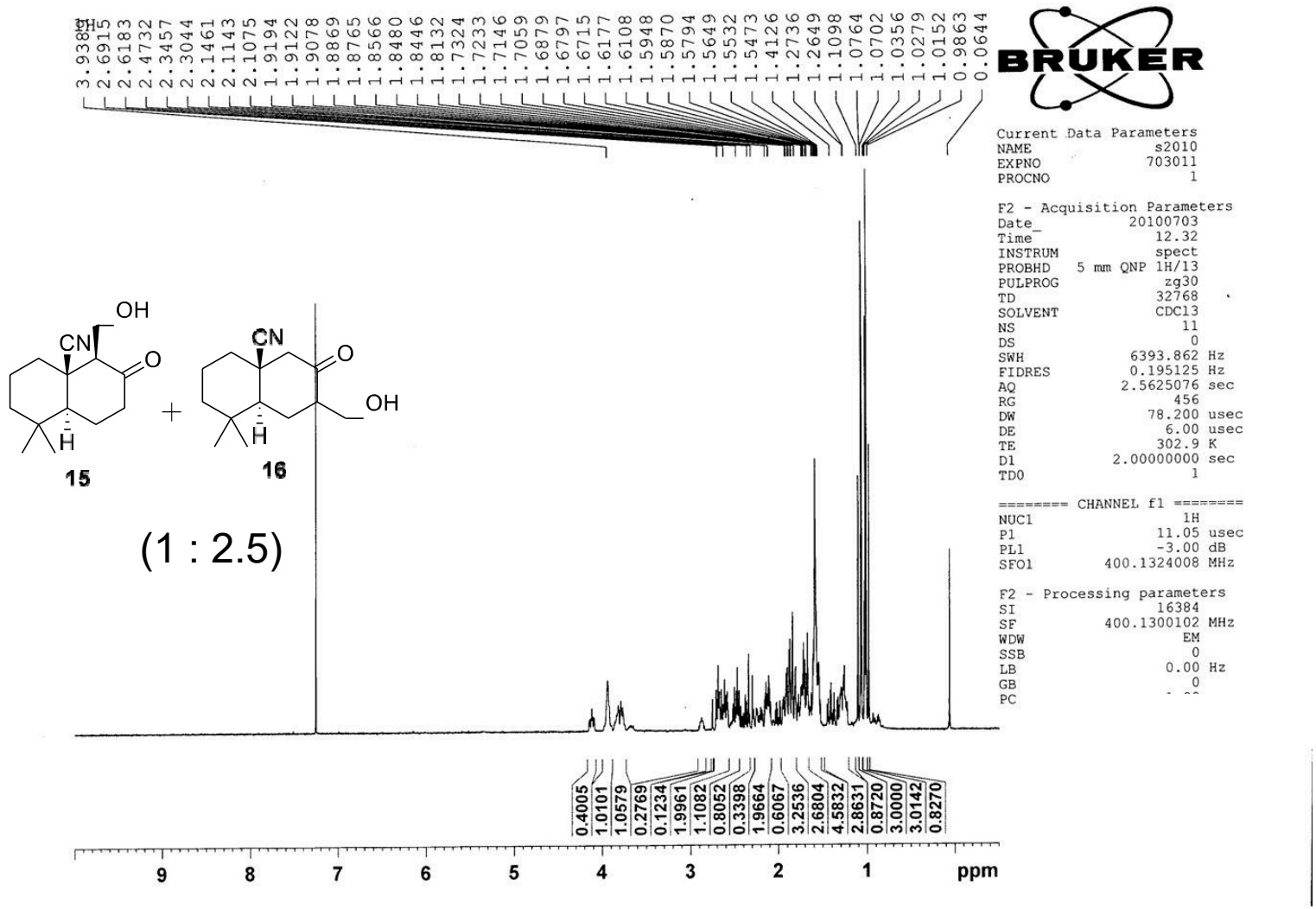
^{13}C, DEPT 135, DEPT 45 and DEPT 90 NMR Of (-)-antrocin **1** (100 MHz, $CDCl_3$)

Figure S37



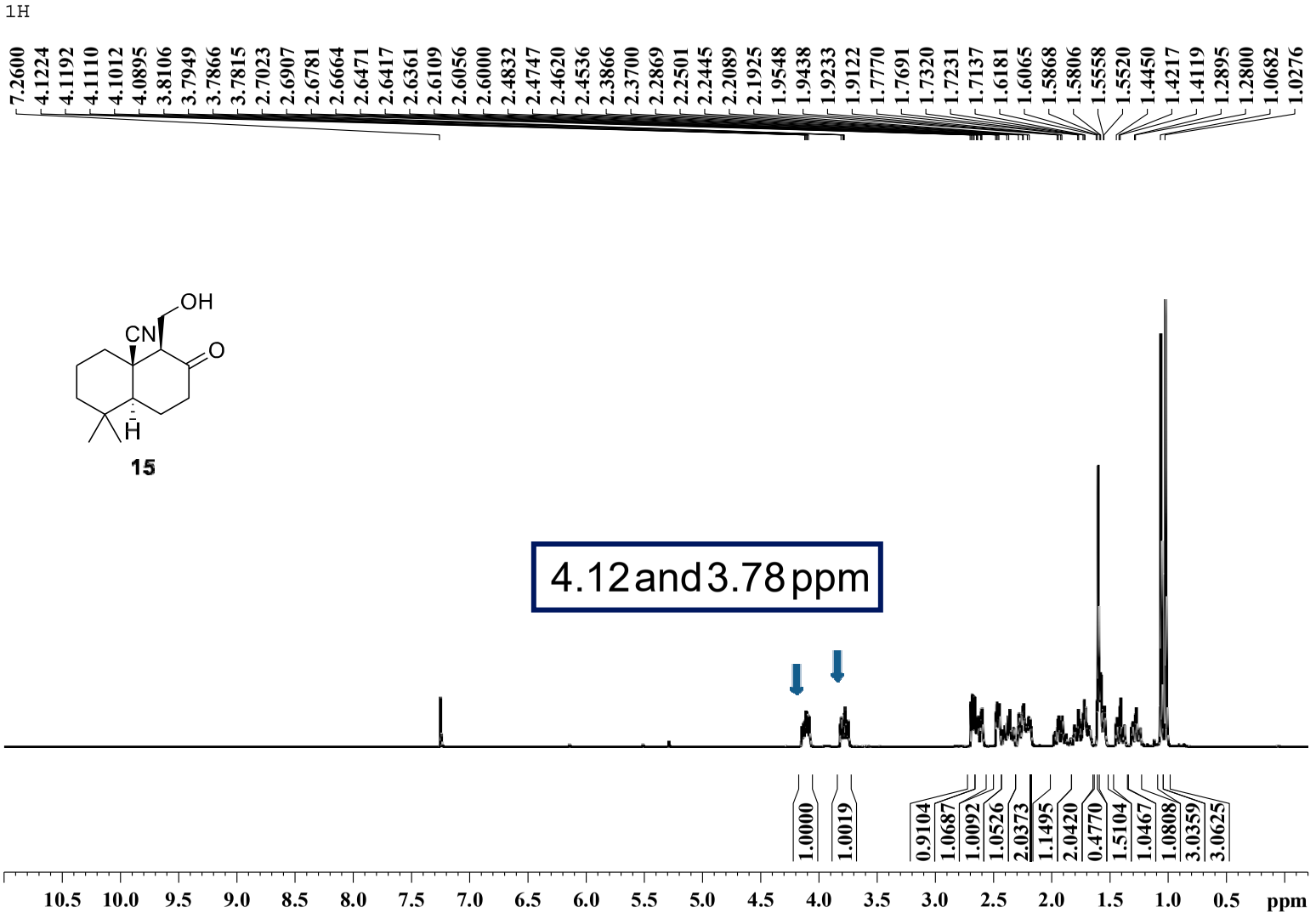
HRMS (ESI) of (-)-antrocin **1**

Figure S38



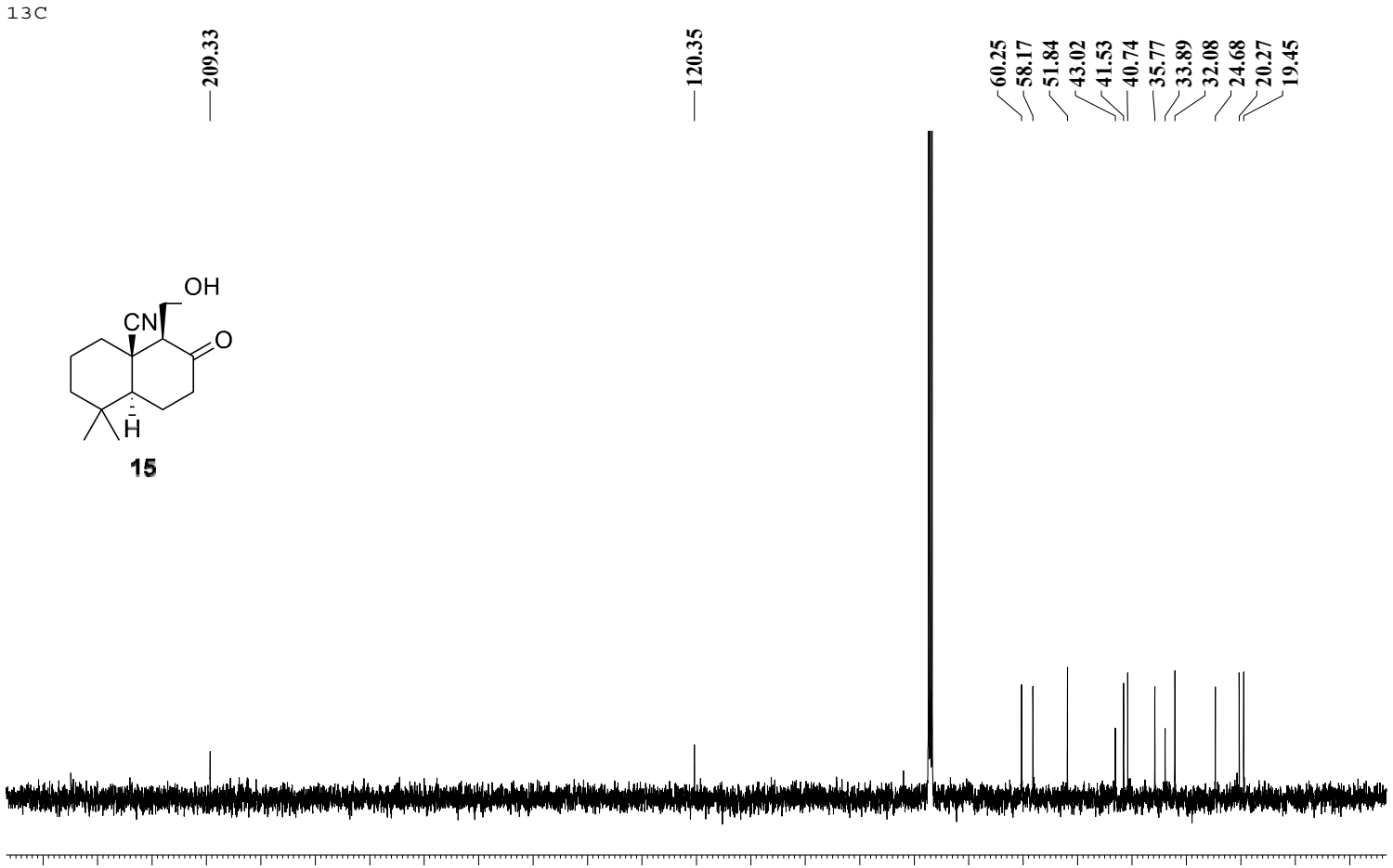
^{1}H NMR of compound 15 and 16 mixture (400 MHz, $CDCl_3$)

Figure S39



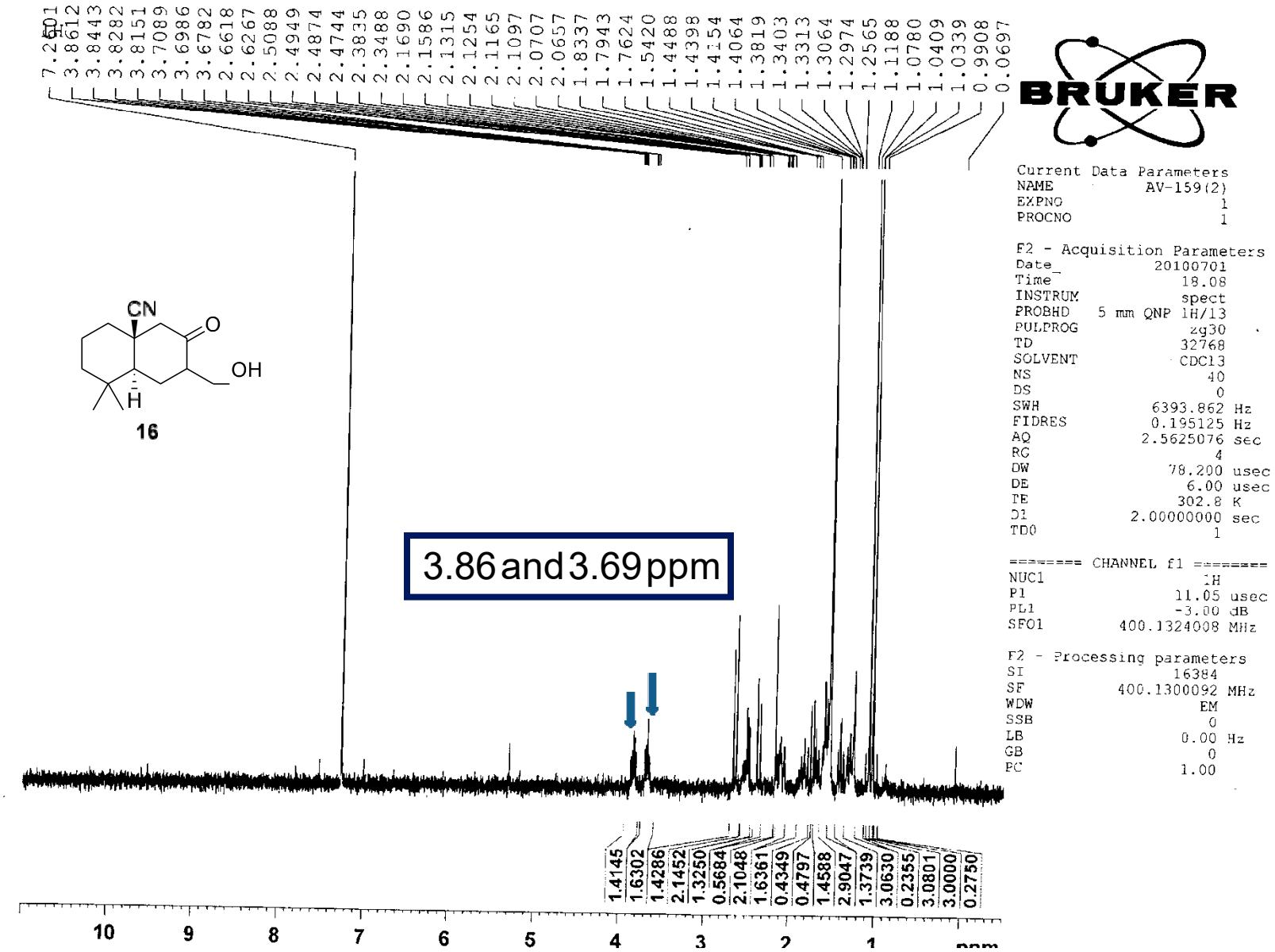
^{1}H NMR of compound **15** (400 MHz, $CDCl_3$)

Figure S40


13C
209.33
120.35
60.25
58.17
51.84
43.02
41.53
40.74
35.77
33.89
32.08
24.68
20.27
19.45
OH
CN
O
H
15

^{13}C NMR of compound **15** (100 MHz, $CDCl_3$)

Figure S41


7.2601
3.8612
3.8443
3.8282
3.8151
3.7089
3.6986
3.6782
3.6618
2.6267
2.5088
2.4949
2.4874
2.4744
2.3835
2.3488
2.1690
2.1586
2.1315
2.1254
2.1165
2.1097
2.0707
2.0657
1.8337
1.7943
1.7624
1.5420
1.4488
1.4398
1.4154
1.4064
1.3819
1.3403
1.3313
1.3064
1.2974
1.2565
1.1188
1.0780
1.0409
1.0339
0.9908
0.0697
CN
O
OH
H
16
3.86 and 3.69 ppm
1.4145
1.6302
1.4286
2.1452
1.3250
0.5684
2.1048
1.6361
0.4349
0.4797
1.4588
2.9047
1.3739
3.0630
0.2355
3.0801
3.0000
0.2750
10
9
8
7
6
5
4
3
2
1
ppm
BRUKER
Current Data Parameters
NAME AV-159(2)
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100701
Time 18.08
INSTRUM spect
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 40
DS 0
SWH 6393.862 Hz
FIDRES 0.195125 Hz
AQ 2.5625076 sec
RG 4
DW 78.200 usec
DE 6.00 usec
TE 302.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.05 usec
PL1 -3.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 16384
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

Crystallographic data for *trans* cyanobicyclic ketone, (–)-7

Table S1. Crystal data and structure refinement for *trans*-cyanobicyclicketone, **(–)7.**

Identification code	**(–)-7**
Empirical formula	$C_{13}H_{19}NO$
Formula weight	205.29
Temperature	296(2) K
Wavelength	0.626 Å
Crystal system, space group	Monoclinic
Unit cell dimensions	a = 8.7609 (7) Å $\alpha = 90°$.
	b = 9.3363 (8) Å $\beta = 90°$.
	c = 14.6484 (14) Å $\gamma = 90°$.
Volume	1198.16 (18) $Å^3$
Z, Calculated density	4
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8727, 2464, 1632
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.626
Crystal size (mm)	0.42 × 0.38 × 0.33
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8727, 2464, 1632
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.626
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.102, 1.02
No. of reflections	2464
No. of parameters	138
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.09, −0.13

Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
F(000)	448
Absolute structure parameter	2 (3)
Reflections	2464
Refinement method	Full-matrix least-squares on F^2

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *trans*-cyanobicycli ketone **(–)-7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	X	Y	Z	U
C(5)	2002 (2)	1074 (2)	6994 (14)	45 (5)
C(6)	1936 (2)	67.5 (19)	6224 (13)	44 (5)
C(1)	0666 (2)	316 (2)	5553 (14)	54 (5)
C(2)	893 (2)	421 (3)	6018 (16)	66 (7)
C(7)	3488 (2)	-443 (2)	5781 (15)	56 (6)
C(8)	4673 (3)	−678 (3)	6533 (16)	70 (7)
C(4)	445 (2)	1118 (2)	7480 (15)	62 (6)
C(9)	4797 (3)	539 (3)	7216 (16)	71 (7)
C(3)	854 (3)	1384 (2)	6832 (17)	63 (6)
C(10)	3276 (2)	747 (3)	7680 (14)	62 (6)
C(11)	2255 (2)	533 (3)	6621 (14)	53 (5)
N(1)	2396 (2)	3680 (2)	6370 (15)	77 (6)
O(1)	−1780 (18)	2315 (2)	6962 (15)	94 (6)
C(13)	3316 (3)	−1857 (3)	5258 (19)	84 (8)
C(12)	4050 (3)	712 (3)	5118 (16)	77 (8)

Table S3. Bond lengths [Å] and angles [°] for *trans*-cyanobicyclic ketone **(–)-7**

C(5)-C11	1.485 (3)
C(5)-C(10)	1.532 (3)
C(5)-C(4)	1.539 (3)
C(5)-C(6)	1.553 (3)
C(6)-C(1)	1.527 (3)
C(6)-C(7)	1.547 (3)
C(1)-C(2)	1.530 (3)
C(2)-C(3)	1.494 (3)
C(11)-C5-C(10)	108.37 (16)
C(11)-C(5)-C(4)	106.16 (16)
C(10)-C(5)-C(4)	110.38 (16)
C(11)-C(5)-C(6)	111.57 (16)
C(10)-C(5)-C(6)	111.51 (16)
C(4)-C(5)-C(6)	108.72 (15)
C(1)-C(6)-C(7)	115.00 (17)
C(1)-C(6)-C(5)	109.53 (15)
C(7)-C(6)-C(5)	115.31 (15)
C(6)-C(1)-C(2)	112.27 (17)
C(3)-C(2)-C(1)	111.91 (17)
C(8)-C(7)-C(12)	109.87 (19)
C(8)-C(7)-C(13)	107.63 (19)
C(7)-C(8)	1.530 (3)
C(7)-C(12)	1.532 (3)
C(7)-C(13)	1.534 (3)
C(8)-C(9)	1.517 (3)

C(4)-C(3)	1.502 (3)
C(9)-C(10)	1.509 (3)
C(3)-O(1)	1.204 (3)
C(11)-N(1)	1.139 (3)
C(12)-C(7)-C(13)	108.67 (19)
C(8)-C(7)-C(6)	109.06 (17)
C(12)-C(7)-C(6)	112.91 (17)
C(13)-C(7)-C(6)	108.56 (17)
C(9)-C(8)-C(7)	114.54 (19)
C(3)-C(4)-C(5)	112.55 (17)
C(10)-C(9)-C(8)	109.27 (18)
O(1)-C(3)-C(2)	123.0 (2)
O(1)-C(3)-C(4)	122.0 (2)
C(2)-C(3)-C(4)	114.99 (19)
C(9)-C(10)-C(5)	111.96 (17)
N(1)-C(11)-C(5)	176.3 (2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for *trans* bicyclicketone **(–)-7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C(5)	46 (12)	41(12)	48(11)	−4 (9)	4 (10)	−1 (9)
C(6)	46 (12)	35(11)	48 (11)	−6 (9)	6 (9)	3 (9)
C(1)	54 (13)	46 (12)	61 (13)	1 (10)	−11 (11)	−5 (10)
C(2)	45 (14)	57 (14)	94 (18)	-1 (11)	−14 (12)	−2 (14)
C(7)	50 (13)	53 (13)	64 (13)	8 (11)	7 (11)	3 (12)
C(8)	45 (13)	71 (16)	95 (18)	11 (12)	3 (13)	15 (15)
C(4)	63 (15)	59 (14)	63 (14)	−4 (12)	13 (12)	−14 (11)
C(9)	54 (15)	76 (17)	84 (17)	−3 (13)	−22 (13)	17 (15)
C(3)	47 (13)	51 (14)	90 (18)	−3 (11)	13 (12)	−2 (14)
C(10)	67 (15)	63 (15)	55 (13)	−8 (12)	−14 (12)	4 (11)
C(11)	49 (13)	46 (13)	64 (13)	−6 (11)	−9 (10)	−3 (11)
N(1)	85 (16)	47 (12)	10 (15)	−9 (11)	−22 (12)	6 (13)
O(1)	64 (11)	76 (12)	14 (16)	23 (10)	20 (11)	−13 (12)
C(13)	92 (2)	68 (17)	93 (18)	21 (15)	13 (17)	−19 (15)
C(12)	71 (17)	84 (18)	76 (17)	5 (14)	27 (13)	15 (15)

Crystallographic data for ketol diastreomer, (–)-8

Table S5. Crystal data and structure refinement for ketal diastreomer **(–)-8**

Identification code	**(–)-8**
Chemical formula	$C_{19}H_{27}NO_6$
M_r	365.42
Crystal system, space group	P2(1)
Temperature (K)	296
a, *b*, *c* (Å)	12.9504 (5), 11.5452 (5), 13.3239 (5)
α, β, γ (°)	90, 96.190 (1), 90
V (Å^3)	1980.51 (14)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.49 × 0.48 × 0.25
Data collection	
Diffractometer	–
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19868, 7836, 6201
R_{int}	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.131, 1.03
No. of reflections	7836

No. of parameters	477
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.19
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Absolute structure parameter	0.4 (9)

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ketol diastreomer **(–)-8.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8757 (19)	−2316 (2)	6866 (2)	50. (6)
C(2))	879 (2)	−2889 (2)	5843 (2)	55 (6)
C(3)	832 (2)	−2091 (2)	5008 (2)	58 (7)
C(4)	884 (19)	−904 (2)	9889 (17)	46 (5)
C(5)	889 (16)	−355 (18)	60565 (16)	36 (4)
C(6)	933 (15)	−1146 (18)	6933 (16)	35 (4)
C(7)	9198 (17)	−552 (2)	7951 (16)	42 (5)
C(8)	9647 (16)	655 (2)	8045 (15)	39 (5)
C(9)	9244 (2)	1410 (2)	7168 (17)	47 (5)
C(10)	9412 (2)	835 (19)	6162 (16)	44 (5)
C(11)	9921 (2)	–1021 (3)	4598 (2)	60 (7)
C(12)	8156 (3)	−151 (3)	4243 (2)	77 (9)
C(13)	10454 (17)	−1418 (2)	6915 (18)	43 (5)
C(14)	11569 (19)	2403 (2)	8744 (2)	48 (6)
C(15)	11184 (17)	1204 (2)	8996 (15)	42 (5)

C((16)	10286 (17)	1254 (2)	9660 (16)	44. (5)
C(170)	10345 (2)	243 (3)	10408(18)	53 (6)
C(18)	12521 (3)	3987 (3)	9491 (4)	106 (14)
C(19)	11024 (4)	−413 (3)	2004 (3)	95 (12)
C(20)	39820 (2)	7605 (2)	7045 (2)	54 (6)
C(21)	4174 (2)	6908 (2)	6118 (2)	61 (7)
C(22)	3559 (2)	7402 (2)	5184 (2)	61 (7)
C(23)	37976 (19)	8683 (2)	9763 (19)	51 (6)
C(24)	36761 (16)	9391 (2)	59474 (17)	41 (5)
C(25)	4262 (16)	8887 (2)	6932 (17)	42 (5)
C(26)	3957 (17)	9574 (2)	7847 (18)	46 (5)
C(27)	4108 (17)	10861(2)	7762 (17)	45 (5)
C(28)	3551 (19)	11330 (2)	6793 (17)	49 (5)
C(29)	3889 (19)	10692 (2)	5884 (18)	47 (5)
C(30)	4867 (2)	8798 (3)	4592 (2)	70 (8)
C(31)	2976 (3)	9108 (3)	4135 (2)	70 (8)
C(32)	5409 (17)	8957 (2)	6943 (2)	52 (6)
C(33)	4450 (2)	10826 (3)	10284 (2)	64 (7)
C(34)	4603 (2)	11591 (2)	9366 (19)	53 (6)
C(35	5547 (18)	11224 (2)	8839 (17)	50 (6)
C(36_	6448 (2)	12056 (3)	9011 (2)	55 (7)
C(37)	3737 (4)	10792 (5)	11812 (3)	114(16)
C(38)	7657 (3)	12791 (4)	10301 (3)	89 (11)
N(1)	11288 (17)	−1701 (2)	6934 (2)	69(7)
N(2)	6287 (18)	8958 (3)	7000 (2)	85 (8)
O(1)	10764 (12)	5894 (15)	8141 (11)	46 (4)

O(2)	9393 (11)	11883 (16)	8962 (11)	49 (4)
O(3)	12059 (15)	28564 (18)	9578 (15)	67 (5)
O(4)	11466 (17)	28518 (19)	7937 (16)	71 (6)
O(5)	10914 (2)	482 (2)	11237 (15)	87 (7)
O(6)	9979 (3)	−707 (2)	10259 (17)	103 (9)
O(7)	5167 (12)	11197 (16)	78095 (11)	48 (4)
O(8)	3741 (13)	11436 (17)	86203 (12)	56 (5)
O(9)	4017 (2)	11411 (3)	10951 (17)	93 (8)
O(10)	4698 (3)	9844 (3)	10366 (2)	125 (11)
O(11)	6795 (16)	12034 (2)	9989 (15)	74 (6)
O(12)	6796 (18)	12641 (2)	8398 (17)	80 (6)

Table S7. Bond lengths [Å] and angles [°] for ketol diastreomer **(–)-8**

C(1)-C(2)	1.522 (4)
C(1)-C(6)	1.538 (3)
C(2)-C(3)	1.522 (4)
C(3)-C(4)	1.531 (4)
C(4)-C(12)	1.534 (4)
C(4)-C(11)	1.544 (4)
C(4)-C(5)	1.552 (3)
C(5)-C(10)	1.529 (3)
C(5)-C(6)	1.541 (3)
C(6)-C(13)	1.491 (3)
C(6)-C(7)	1.545 (3)

C(7)-C(8)	1.511 (3)
C(8)-O(2)	1.438 (2)
C(8)-O(1)	1.440 (3)
C(8)-C(9)	1.505 (3)
C(9)-C(10)	1.532 (3)
C(13)-N(1)	1.127 (3)
C(14)-O(4)	1.187 (3)
C(14)-O(3)	1.327 (3)
C(14)-C(15)	1.521 (4)
C(15)-O(1)	1.401 (3)
C(15)-C(16)	1.537 (3)
C(16)-O(2)	1.405 (3)
C1(6)-C(17)	1.531 (4)
C(17)-O(6)	1.203 (4)
C(17)-O(5)	1.290 (3)
C(18)-O(3)	1.445 (4)
C(19)-O(5)	1.449 (4)

C(2)-C(1)-C(6)	111.75 (19)
C(3)-C(2)-C(1)	109.9 (2)
C(2)-C(3)-C(4)	114.1 (2)
C(3)-C(4)-C(12)	106.9 (2)
C(3)-C(4)-C(11)	110.1 (2)
C(12)-C(4)-C(11)	108.4 (2)
C(3)-C(4)-C(5)	109.0 (2)
C(12)-C(4)-C(5)	109.1 (2)

C(11)-C(4)-C(5)	113.23 (19)
C(10)-C(5)-C(6)	110.09 (17)
C(10)-C(5)-C(40	115.22 (18)
C(6)-C(5)-C(4)	115.44 (17)
C(13)-C(6)-C(1)	106.26 (18)
C(13)-C(6)-C(5)	112.87 (17)
C(1)-C(6)-C(5)	109.99 (18)
C(13)-C(6)-C(7)	107.91 (18)
C(1)-C(6)-C(7)	110.06 (17)
C(5)-C(6)-C(7)	109.67 (17)
C(8)-C(7)-C(6)	113.87 (17)
O(2)-C(8)-O(1)	105.43 (16)
O(2)-C(8)-C(9)	108.67 (18)
O(1)-C(8)-C(9)	111.20 (18)
O(2)-C(8)-C(7)	110.12 (17)
O(1)-C(8)-C(7)	109.43 (17)
C(9)-C(8)-C(7)	111.80 (18)
C(8)-C(9)-C(10)	111.00 (18)
C(9)-C(10)-C(5)	111.59 (18)
N(1)-C(13)-C(6)	174.8 (3)
O(4)-C(14)-O(30	125.7 (2)
O(4)-C(14)-C(15)	126.1 (2)
O(3)-C(14)-C(15)	108.1 (2)
O(1)-C(15)-C(14)	112.90 (19)
O(1)-C(15)-C(16)	103.59 (17)
C(14)-C(15)-C(16)	112.33 (19)

O(2)-C(16)-C(17)	111.6 (2)
O(2)-C(16)-C(15)	103.68 (17)
C(17)-C(16)-C(15)	111.0 (2)
O(6)-C(17)-O(5)	121.0 (3)
O(6)-C(17)-C(16)	126.7 (2)
O(5)-C(17)-C(16)	112.2 (2)
C(21)-C(20)-C(25)	111.8 (2)
C(22)-C(21)-C(20)	110.6 (2)
C(21)-C(22)-C(23)	114.3 (2)
C(30)-C(23)-C(31)	107.9 (2)
C(20)-C(21)	1.517 (4)
C(20)-C(25)	1.535 (4)
C(21)-C(22)	1.515 (4)
C(22)-C(23)	1.541 (4)
C(23)-C(30)	1.533 (4)
C(23)-C(31)	1.540 (4)
C(23)-C(24)	1.553 (3)
C(24)-C(29)	1.532 (3)
C(24)-C(25)	1.556 (3)
C(25)-C(32)	1.485 (3)
C(25)-C(26)	1.542 (3)
C(26)-C(27)	1.514 (4)
C(27)-O(7)	1.418 (3)
C((27)-O(8)	1.441 (3)
C(27)-C(28)	1.510 (3)
C(28)-C(29)	1.526 (3)

C(32)-N(2)	1.131 (3)
C(33)-O(10)	1.181 (4)
C(33)-O(9)	1.293 (4)
C(33)-C(34)	1.538 (4)
C(34)-O(8)	1.424 (3)
C(34)-C(35)	1.534 (3)
C(35)-O(7)	1.407 (3)
C(35)-C(36)	1.509 (4)
C(36)-O(12)	1.187 (3)
C(36)-O(11)	1.333 (3)
C(37)-O(9)	1.433 (4)
C(38)-O(11)	1.443 (4)

C(30)-C(23)-C(22)	110.4 (2)
C(31)-C(23)-C(22)	107.5 (2)
C(30)-C(23)-C(24)	114.1 (2)
C(31)-C(23)-C(24)	108.4 (2)
C(22)-C(23)-C(24)	108.4 (2)
C(29)-C(24)-C(23)	115.81 (19)
C(29)-C(24)-C(25)	109.79 (19)
C(23)-C(24)-C(25)	114.94 (18)
C(32)-C(25)-C(20)	107.37 (19)
C(32)-C(25)-C(26)	107.8 (2)
C(20)-C(25)-C(26)	109.58 (19)
C(32)-C(25)-C(24)	112.60 (19)
C(20)-C(25)-C(24)	110.1 (2)

C(26)-C(25)-C(24)	109.35 (17)
C2)(7)-C(26)-C(25)	113.78 (19)
O(7)-C(27)-O(8)	104.13 (18)
O(7)-C(27)-C(28)	108.20 (19)
O(8)-C(27)-C(28)	110.31 (18)
O(7)-C(7)-C(26)	113.11 (18)
O(8)-C(27)-C(26)	109.48 (19)
C(28)-C(27)-C(26)	111.4 (2)
C(27)-C(28)-C(29)	110.65 (19)
C(28)-C(29)-C(24)	111.50 (19)
N(2)-C(32)-C(25)	175.5 (3)
O(10)-C(33)-O(9)	125.1 (3)
O(10)-C(33)-C(34)	124.6 (3)
O(9)-C(33)-C(34)	110.3 (3)
O(8)-C(34)-C(35)	104.44 (19)
O(8)-C(34)-C(33)	108.9 (2)
C(35)-C(34)-C(33)	112.5 (2)
O(7)-C(35)-C(36)	110.2 (2)
O(7)-C(35)-C(34)	103.91 (18)
C(36)-C(35)-C(34)	113.3 (2)
O(12)-C(36)-O(11)	124.8 (3)
O(12)-C(36)-C(35)	127.1 (2)
O(11)-C(36)-C(35)	108.1 (2)
C(15)-O(1)-C(80)	110.15 (15)
C(16)-O(2)-C(8)	109.78 (16)
C(14)-O(3)-C(18)	116.9 (3)

C(17)-O(5)-C(19)	117.1 (3)
C(35)-O(7)-C(27)	106.47 (16)
C(34)-O(8)-C(27)	108.03 (18)
C(33)-O(9)-C(37)	116.9 (3)
C(36)-O(11)-C(38)	116.1 (3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y-1/2,-z+2 #2 x-1,y,z #3 x,y,z-1 #4 -x,y+1/2,-z+2
#5 x+1, y,z

Table S8. Anisotropic displacement parameters ($Å^2$ x 10^3) for ketol diastreomer, **(–)-8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C(1)	45 (12)	39 (13)	68 (16)	−5 (10)	11 (11)	5 (12)
C(2)	52 (14)	32 (13)	82 (18)	−8 (10)	5 (13)	−13 (12)
C(3)	55 (14)	51 (15)	64 (16)	−3 (12)	−5 (12)	−21 (13)
C(4)	54 (13)	40 (13)	43 (12)	4 (10)	−2 (10)	−10 (10)
C(5)	34 (10)	34 (11)	41 (11)	3 (8)	2 (8)	−11 (9)
C(6)	30 (9)	32 (10)	44 (11)	2 (8)	4 (8)	3 (9)
C(7)	39 (11)	47 (13)	40 (12)	3 (9)	7 (9)	5 (10)
C(8)	44 (11)	43 (12)	30 (10)	3 (9)	5 (8)	−6 (9)
C(9)	64 (14)	33 (12)	44 (12)	4 (10)	3 (10)	−6 (10)
C(10)	65 (14)	32 (11)	34 (11)	−1 (10)	4 (10)	2 (9)
C(11)	83 (19)	49 (15)	52 (15)	−0.000 (13)	4 (14)	−9 (12)
C(12)	107 (2)	68 (2)	51 (16)	2 (18)	−4 (16)	−11 (14)
C(13)	34 (11)	40 (12)	54 (13)	1 (9)	3 (9)	−12 (10)

C(14)	44 (12)	46 (13)	54 (15)	1 (10)	5 (11)	−6 (12)
C(15)	45 (11)	42 (12)	38 (11)	3 (10)	2 (9)	−5 (10)
C(16)	48 (12)	49 (13)	36 (11)	1 (11)	2 (9)	−6 (10)
C(17)	56 (14)	65 (17)	37 (12)	−3 (12)	4 (10)	−2 (12)
C(18)	90 (3)	68 (2)	15 (4)	−3 (2)	5 (3)	−37 (3)
C(19)	13 (3)	83 (2)	60 (19)	−2 (2)	−2 (2)	23 (18)
C(20)	46 (13)	44 (14)	71 (16)	3 (10)	5 (12)	12 (12)
C(21)	54 (15)	41 (14)	8 (2)	2 (11)	8 (14)	−6 (14)
C(22)	58 (15)	54 (15)	71 (18)	1 (12)	5 (13)	−11 (13)
C(23)	51 (14)	50 (15)	54 (14)	3 (11)	1 (11)	−2 (11)
C(24)	31 (10)	44 (13)	50 (13)	0 (9)	8 (9)	4 (10)
C(25)	30 (10)	45 (12)	52 (13)	1 (9)	6 (9)	8 (11)
C(26)	36 (10)	56 (15)	45 (13)	5 (10)	5 (9)	10 (11)
C(27)	37 (11)	55 (15)	45 (12)	2 (10)	7 (9)	1 (10)
C(28)	54 (13)	45 (13)	49 (13)	2 (11)	1 (10)	2 (11)
C(29)	51 (13)	44 (13)	46 (12)	3 (10)	7 (10)	9 (10)
C(30)	71 (18)	70 (19)	75 (19)	4 (15)	4 (16)	−6 (16)
C(31)	79 (2)	75 (2)	54 (16)	9 (15)	−2 (14)	−8 (14)
C(32)	34 (12)	49 (14)	72 (16)	6 (10)	5 (11)	−.2 (12)
C(33)	63 (16)	79 (2)	50 (15)	0 (15)	5 (12)	−1 (14)
C(34)	51 (13)	61 (17)	48 (14)	1 (11)	8 (11)	−8 (12)
C(35)	49 (13)	53 (14)	49 (13)	5 (11)	4 (10)	3 (12)
C(36)	47 (13)	64 (18)	55 (16)	0 (12)	4 (12)	−8 (13)
C(37)	13 (3)	141 (4)	7 (2)	−4 (3)	4 (2)	−5 (2)
C(38)	58 (18)	118 (3)	9 (2)	−1(19)	1 (16)	−41 (2)
N(1)	42 (12)	73 (16)	91 (18)	1 (11)	5 (11)	−9 (14)

N(2)	38 (12)	92 (2)	12 (2)	1 (12)	10 (13)	−3 (18)
O(1)	41 (8)	53 (10)	40 (9)	−4 (7)	9 (7)	−15 (7)
O(2)	45 (8)	67 (11)	39 (8)	8 (8)	4 (6)	−13 (8)
O(3)	65 (12)	60 (12)	72 (13)	−1 (10)	2 (10)	−23 (10)
O(4)	81 (14)	64 (12)	66 (13)	−2 (11)	6 (10)	14 (11)
O(5)	128 (2)	68 (14)	57 (12)	−3 (13)	−30 (12)	13 (11)
O(6)	159 (3)	82 (17)	62 (14)	−5 (17)	−20 (14)	15 (12)
O(7)	44 (8)	56 (10)	41 (8)	2 (8)	5 (6)	−3 (8)
O(8)	45 (9)	74 (12)	49 (9)	2 (8)	7 (7)	−8 (9)
O(9)	98 (17)	121 (2)	65 (14)	−5 (15)	30 (12)	−7 (14)
O(10)	186 (3)	105 (2)	9 (2)	2 (2)	5 (2)	31 (17)
O(11)	62 (12)	99 (17)	60 (12)	−1.0 (11)	−2 (9)	−8 (11)
O(12)	76 (14)	90 (16)	73 (14)	−3 (12)	6 (11)	5 (12)

Crystallographic data for lactone (–)-14

Table S9. Crystal data and structure refinement for compound **(-)-14 .**

Identification code	**(-)-14**	
Empirical formula	C14 H20 O3	
Formula weight	236.30	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 6.2642(2) Å	□= 90°.
	b = 20.3792(8) Å	□= 0.100(15)°.
	c = 9.5788(3) Å	□ = 90°.
Volume	1222.82(7) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	512	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.92 to 27.50°.	
Index ranges	-7<=h<=8, -25<=k<=25, -12<=l<=12	
Reflections collected	12454	
Independent reflections	2775 [R(int) = 0.0389]	
Completeness to theta = 27.50°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.96063	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2775 / 0 / 155	
Goodness-of-fit on F^2	5.709	
Final R indices [I>2sigma(I)]	R1 = 0.2837, wR2 = 0.6672	
R indices (all data)	R1 = 0.2964, wR2 = 0.6699	
Extinction coefficient	0.35(12)	
Largest diff. peak and hole	1.462 and -0.955 $e.Å^{-3}$	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement

parameters ($Å^2 x\ 10^3$) for lactone **(-)-14.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7511(11)	-234(4)	-33(8)	46(2)
O(2)	5125(11)	-176(3)	3219(7)	37(2)
O(3)	3118(10)	696(4)	3481(8)	43(2)
C(1)	7767(18)	275(5)	632(11)	39(3)
C(2)	8120(20)	293(5)	2189(11)	42(3)
C(3)	7423(19)	-330(5)	2902(13)	48(3)
C(4)	4857(16)	484(5)	3237(9)	31(2)
C(5)	7037(14)	827(5)	3063(10)	32(2)
C(6)	8011(17)	911(5)	4473(10)	36(2)
C(7)	6920(20)	1470(5)	5294(13)	46(3)
C(8)	7160(20)	2114(5)	4477(11)	43(3)
C(9)	6280(19)	2109(6)	3020(13)	47(3)
C(10)	6991(16)	1491(5)	2237(9)	32(2)
C(11)	6060(20)	1405(5)	761(13)	47(3)
C(12)	7381(18)	923(5)	-76(10)	41(3)
C(13)	3690(20)	2157(5)	3078(13)	46(3)
C(14)	7090(20)	2726(6)	2287(11)	47(3)

Table S11. Bond lengths [Å] and angles [°] for lactone **(-)-14.**

O(1)-C(1)	1.228(12)
O(2)-C(4)	1.355(12)
O(2)-C(3)	1.505(14)
O(3)-C(4)	1.195(12)
C(1)-C(12)	1.504(14)
C(1)-C(2)	1.508(15)
C(2)-C(3)	1.507(16)
C(2)-C(5)	1.531(14)
C(4)-C(5)	1.543(14)
C(5)-C(6)	1.492(14)
C(5)-C(10)	1.568(14)
C(6)-C(7)	1.546(16)
C(7)-C(8)	1.536(15)
C(8)-C(9)	1.501(15)
C(9)-C(14)	1.528(16)
C(9)-C(10)	1.533(15)
C(9)-C(13)	1.625(17)
C(10)-C(11)	1.538(15)
C(11)-C(12)	1.514(16)
C(4)-O(2)-C(3)	109.2(7)
O(1)-C(1)-C(12)	119.1(9)
O(1)-C(1)-C(2)	123.5(9)
C(12)-C(1)-C(2)	116.6(9)
C(3)-C(2)-C(1)	112.7(9)
C(3)-C(2)-C(5)	102.9(9)
C(1)-C(2)-C(5)	119.6(9)

O(2)-C(3)-C(2)	101.0(8)
O(3)-C(4)-O(2)	118.3(9)
O(3)-C(4)-C(5)	131.6(9)
O(2)-C(4)-C(5)	109.8(8)
C(6)-C(5)-C(2)	113.3(8)
C(6)-C(5)-C(4)	108.4(8)
C(2)-C(5)-C(4)	97.4(8)
C(6)-C(5)-C(10)	111.4(8)
C(2)-C(5)-C(10)	110.2(8)
C(4)-C(5)-C(10)	115.5(7)
C(5)-C(6)-C(7)	111.3(8)
C(8)-C(7)-C(6)	109.0(10)
C(9)-C(8)-C(7)	115.5(9)
C(8)-C(9)-C(14)	107.3(9)
C(8)-C(9)-C(10)	110.7(9)
C(14)-C(9)-C(10)	110.8(9)
C(8)-C(9)-C(13)	109.5(10)
C(14)-C(9)-C(13)	107.5(9)
C(10)-C(9)-C(13)	110.9(8)
C(9)-C(10)-C(11)	115.7(8)
C(9)-C(10)-C(5)	117.9(8)
C(11)-C(10)-C(5)	111.9(8)
C(12)-C(11)-C(10)	110.8(9)
C(1)-C(12)-C(11)	114.7(9)

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **(-)-14.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	40(4)	47(5)	50(5)	-16(4)	-17(4)	7(3)
O(2)	36(4)	29(4)	46(4)	5(3)	12(3)	-7(3)
O(3)	20(4)	43(5)	67(5)	-8(4)	4(3)	6(3)
C(1)	47(6)	34(6)	36(6)	2(4)	0(5)	10(4)
C(2)	59(7)	37(6)	29(5)	-6(4)	0(5)	1(5)
C(3)	60(8)	31(6)	52(7)	2(5)	-11(6)	13(5)
C(4)	39(6)	33(5)	22(4)	-1(4)	-11(4)	-6(4)
C(5)	23(5)	38(6)	36(5)	-2(4)	1(4)	10(4)
C(6)	38(5)	36(6)	33(5)	6(4)	4(4)	1(4)
C(7)	50(6)	40(7)	49(7)	-7(5)	-3(5)	4(5)
C(8)	67(8)	29(6)	33(5)	-7(4)	-11(5)	-2(5)
C(9)	52(7)	38(6)	49(6)	4(5)	-7(5)	-7(5)
C(10)	36(5)	35(6)	24(4)	3(4)	12(4)	-1(4)
C(11)	61(7)	25(5)	54(7)	4(5)	-7(6)	-3(5)
C(12)	58(7)	40(6)	25(5)	-1(4)	-8(5)	9(5)
C(13)	59(7)	30(6)	49(6)	-2(4)	0(5)	14(5)
C(14)	58(7)	53(7)	30(5)	0(5)	4(5)	-9(5)