Doctoral Thesis

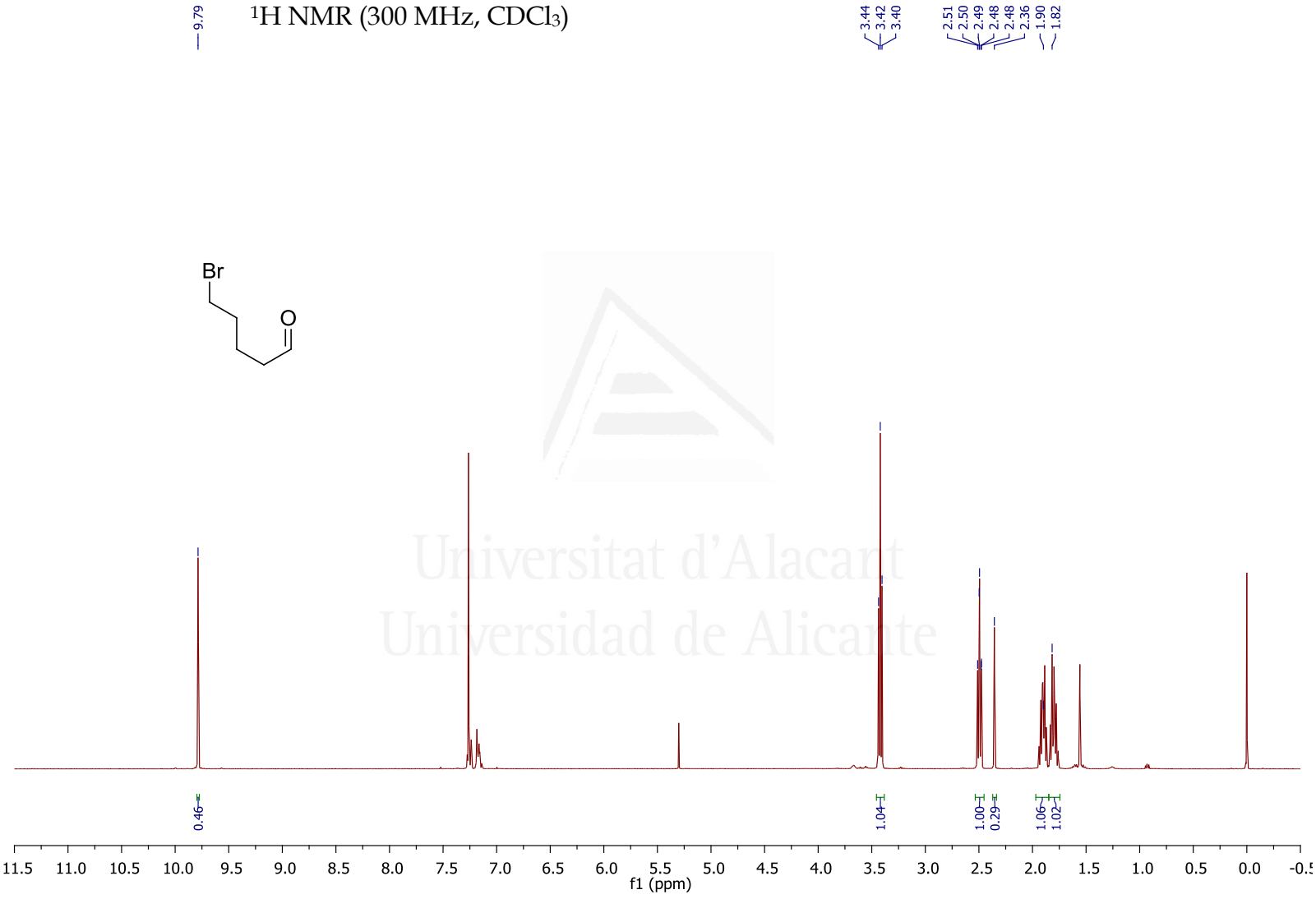
Irene Bosque Martínez

CHAPTER I.

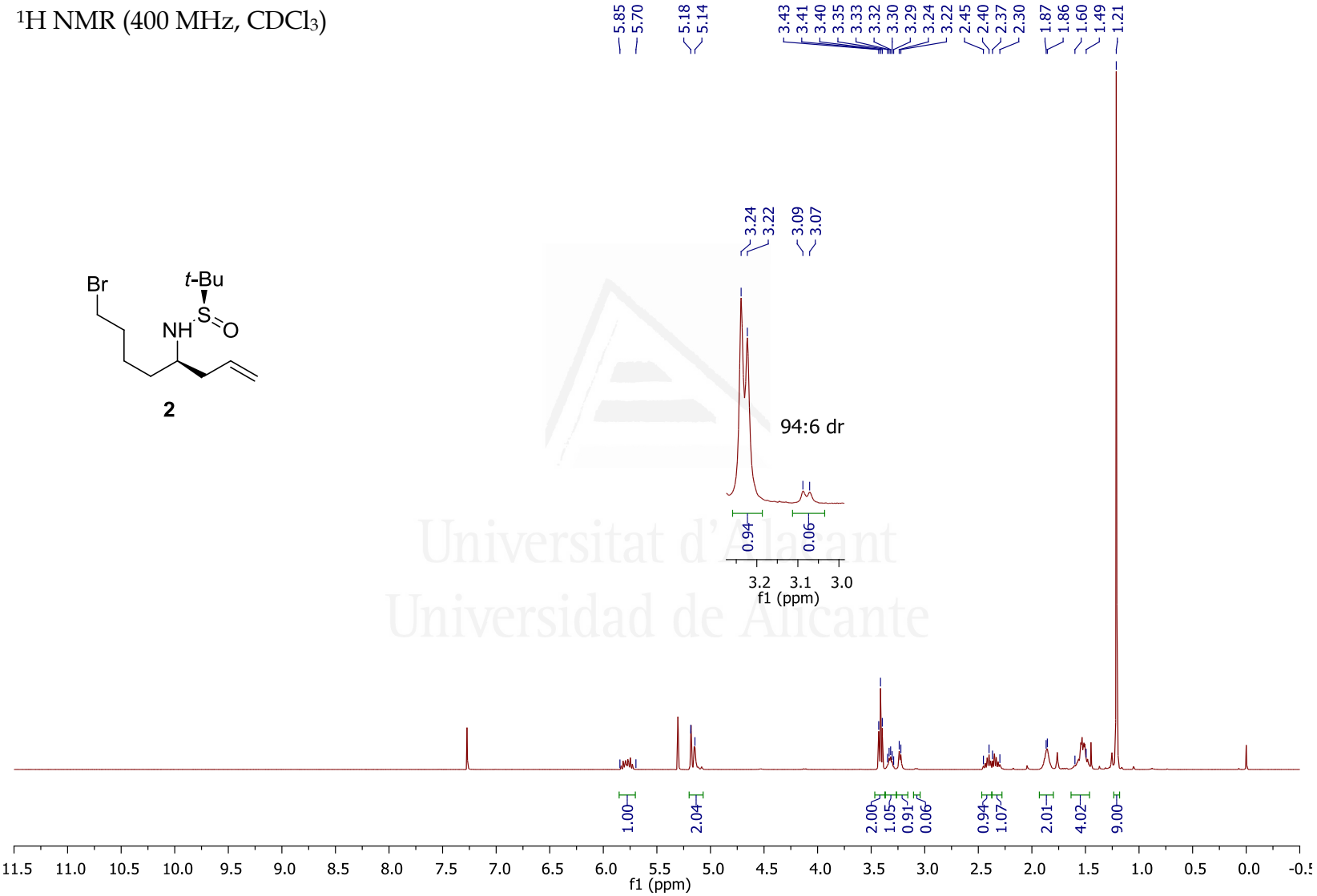
ENANTIOENRICHED 2-ALLYLPIPERIDINE: A VERY USEFUL PRECURSOR IN THE SYNTHESIS OF ALKALOIDS.

Supporting Information

^{1}H NMR (300 MHz, $CDCl_3$)

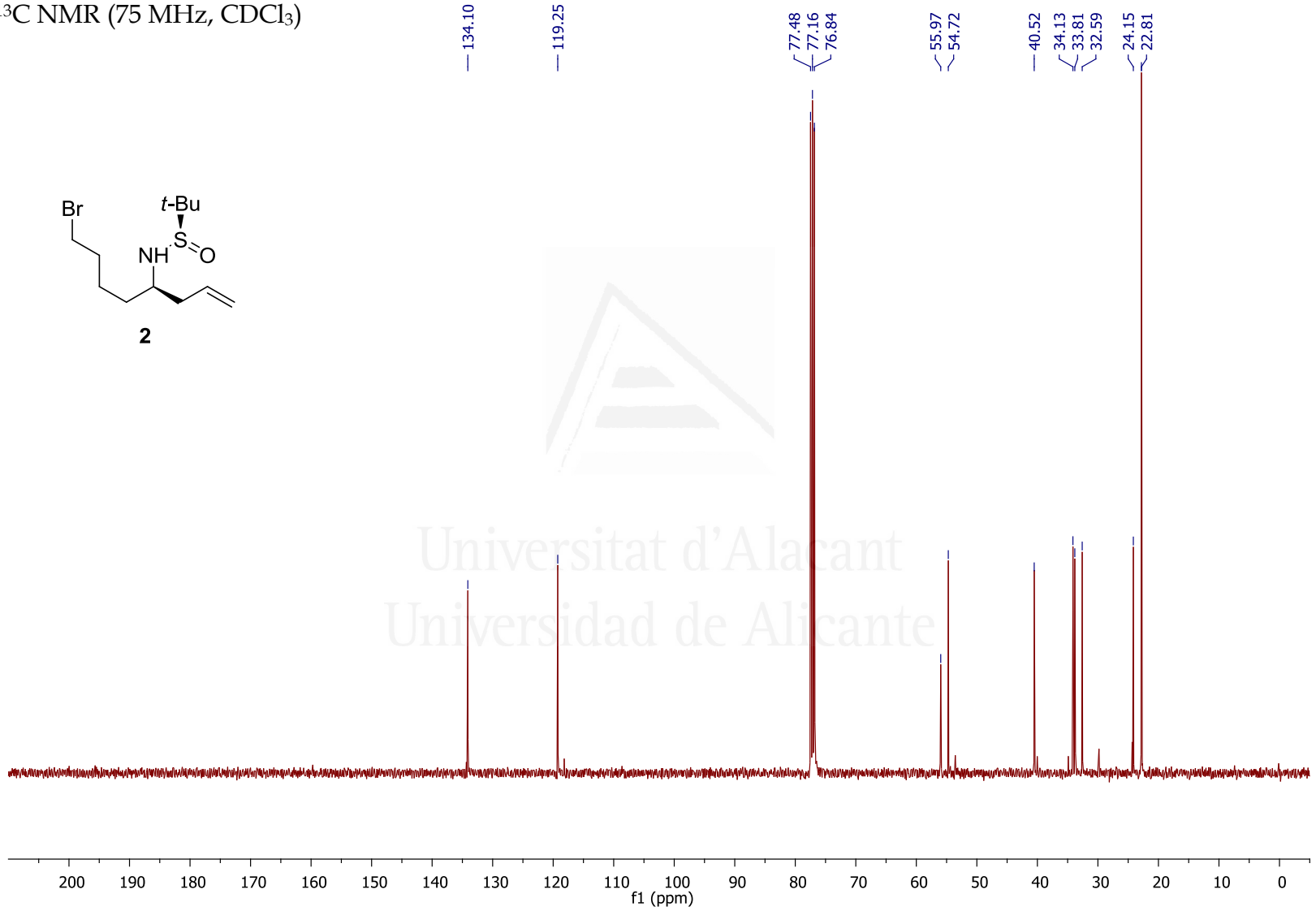


^{1}H NMR (400 MHz, $CDCl_3$)



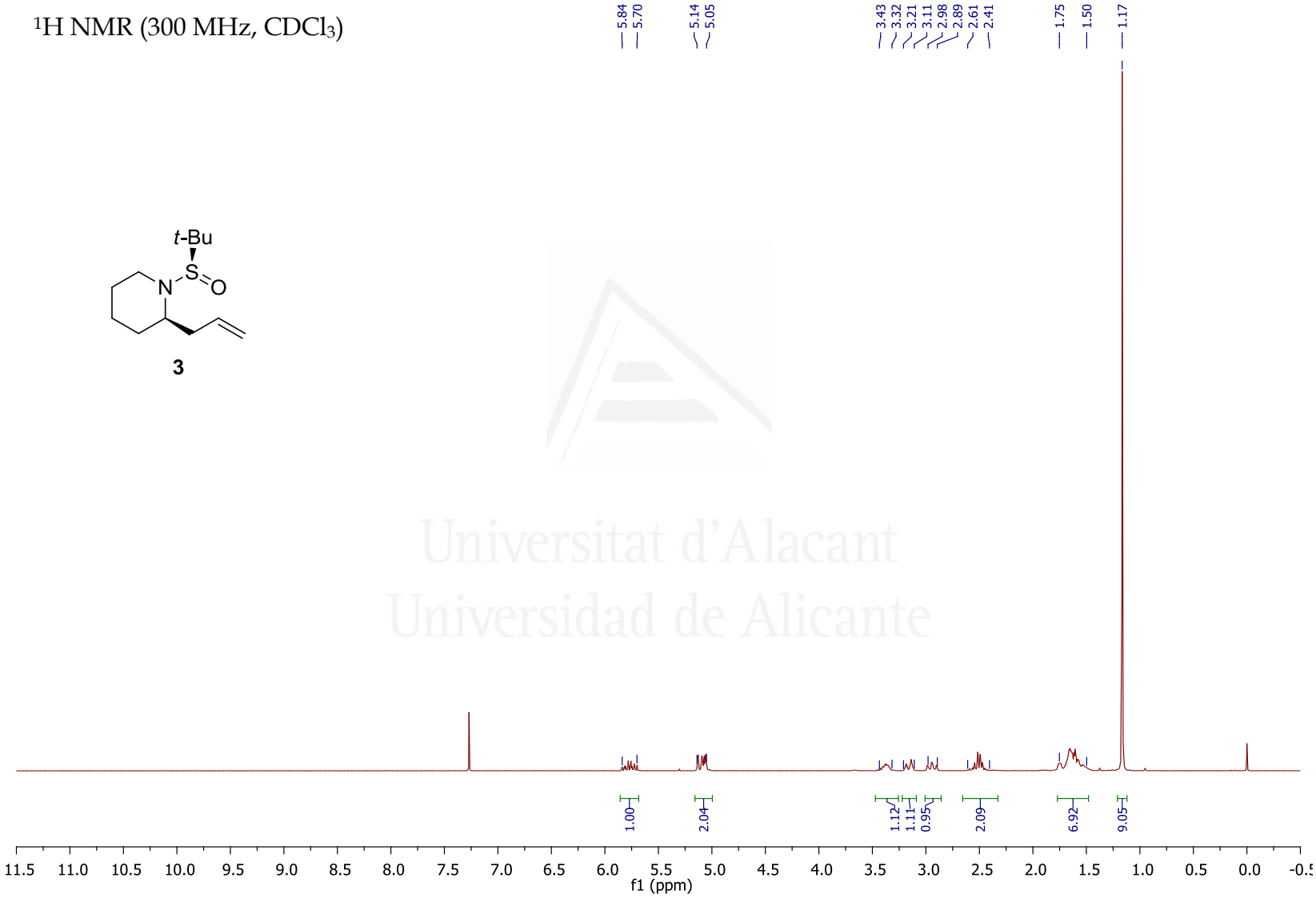
^{13}C NMR (75 MHz, $CDCl_3$)

2

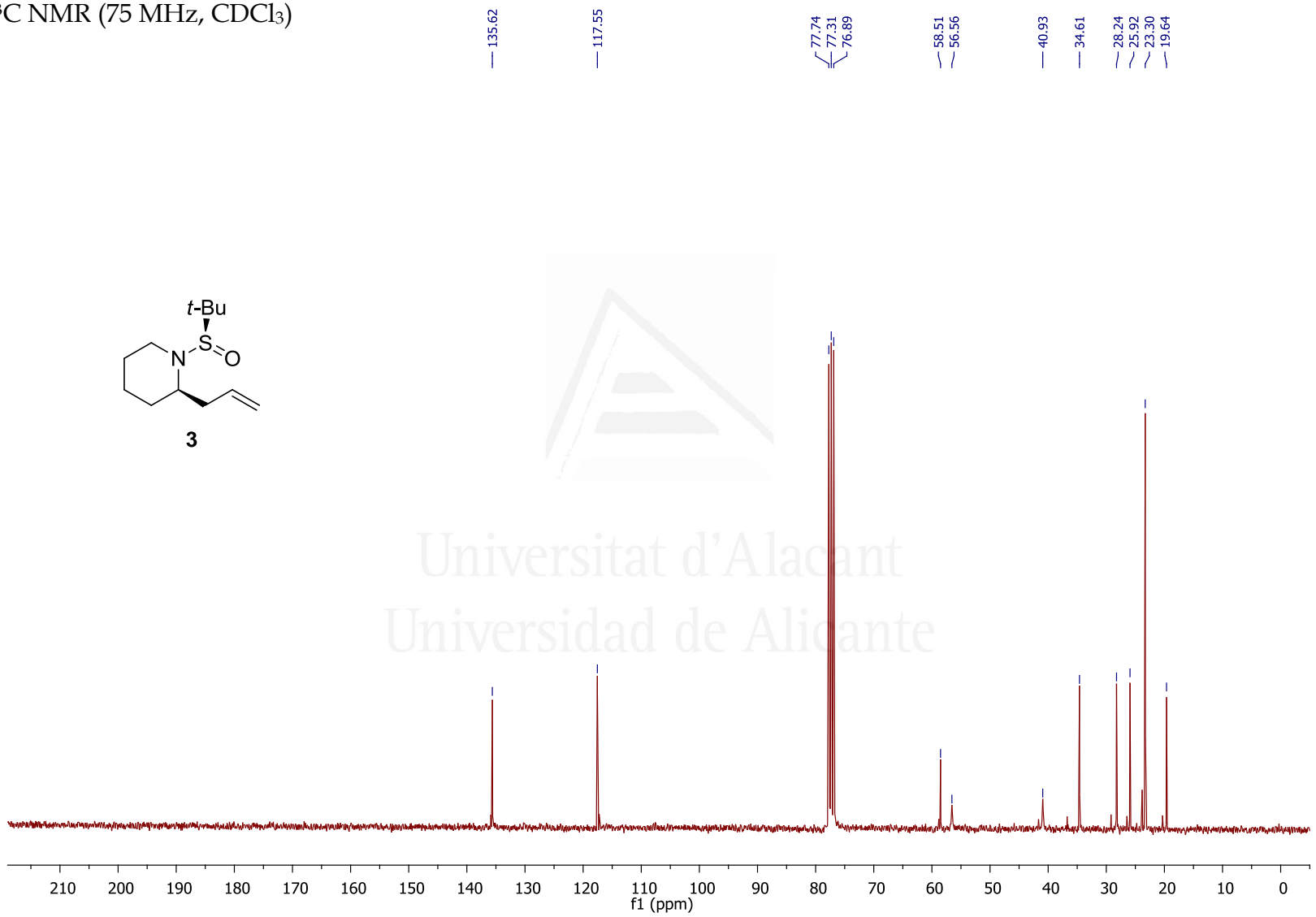


^{1}H NMR (300 MHz, $CDCl_3$)

3



^{13}C NMR (75 MHz, $CDCl_3$)



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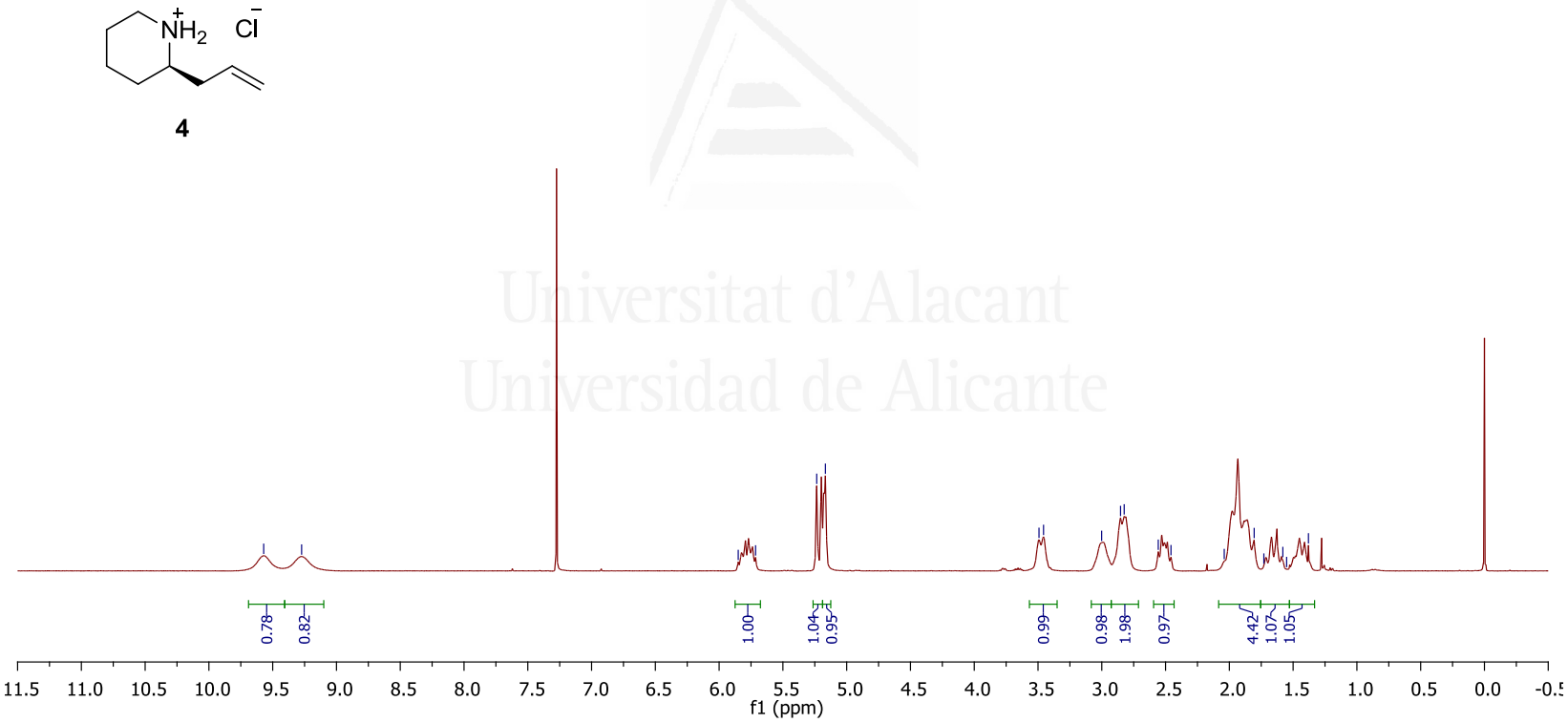
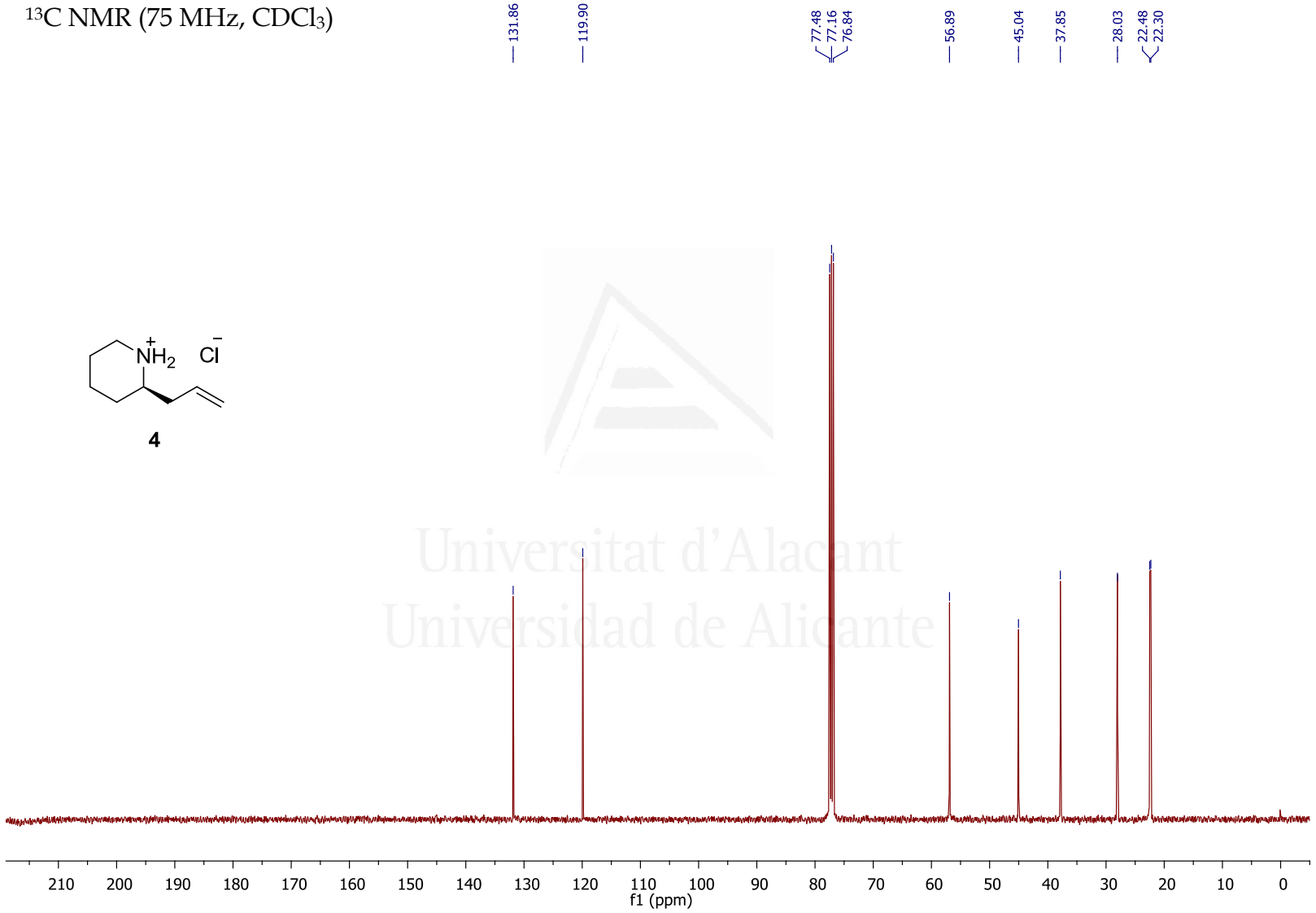


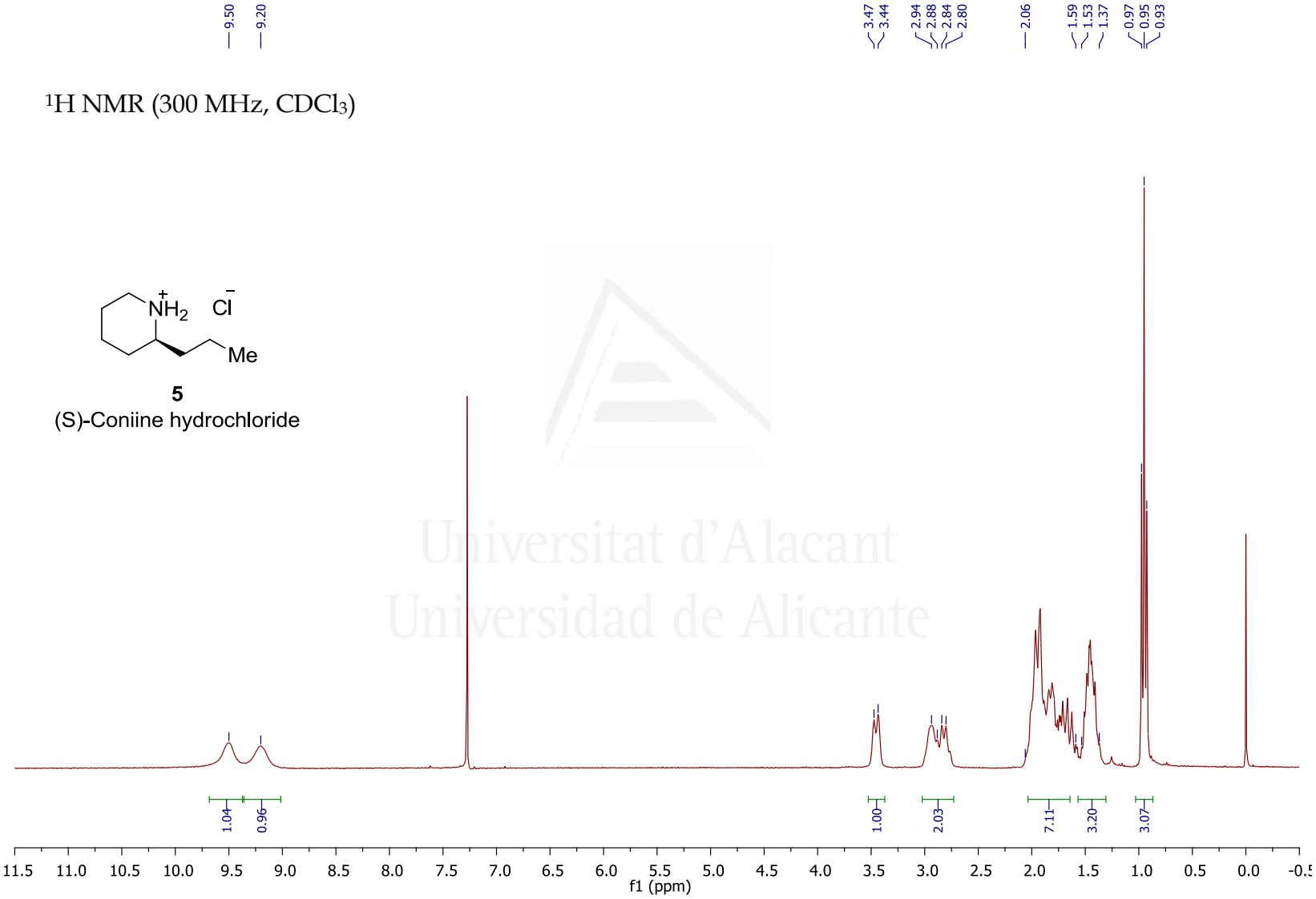
^{13}C NMR (75 MHz, $CDCl_3$)



4

^{1}H NMR (300 MHz, $CDCl_3$)

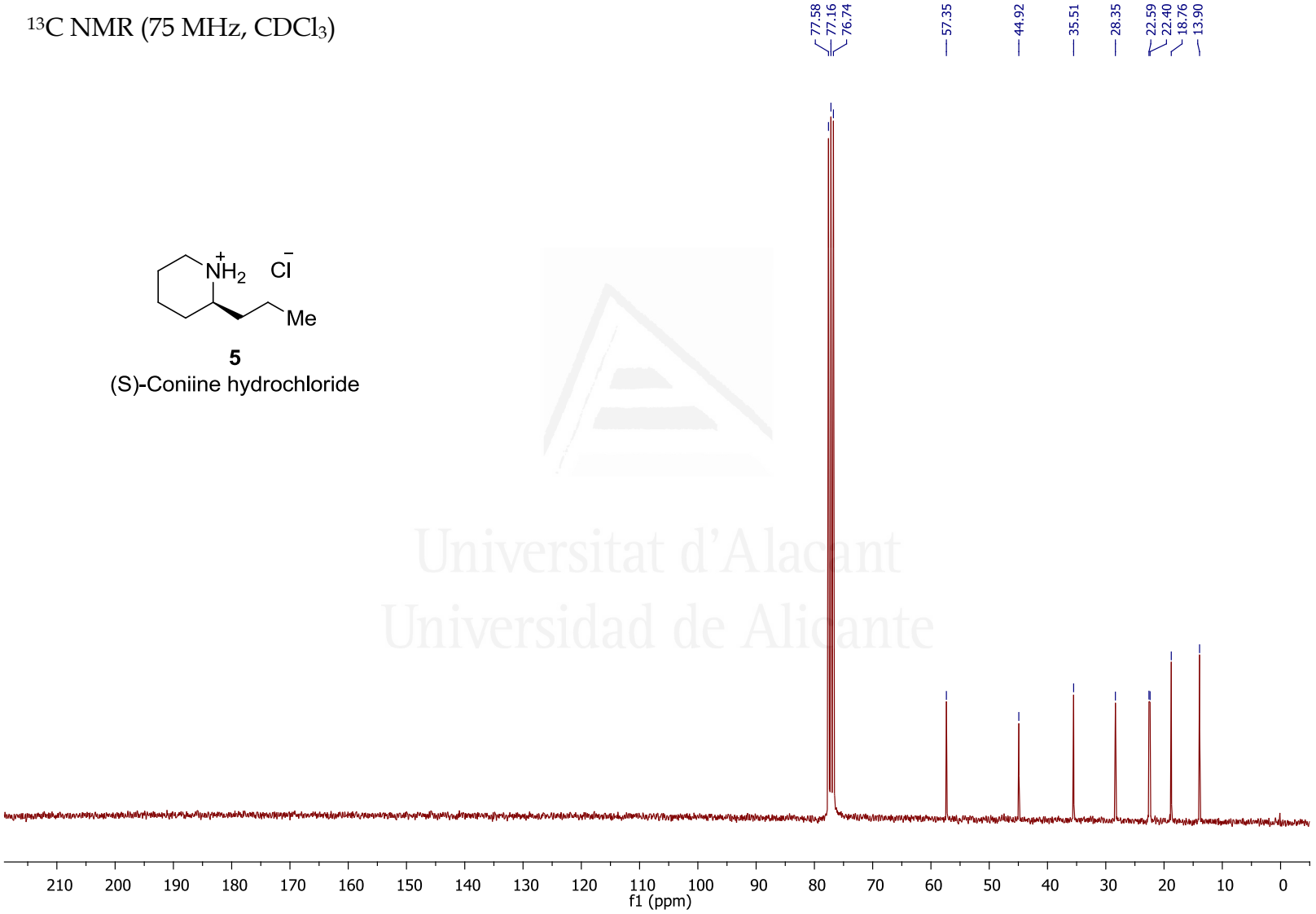
5
(S)-Coniine hydrochloride



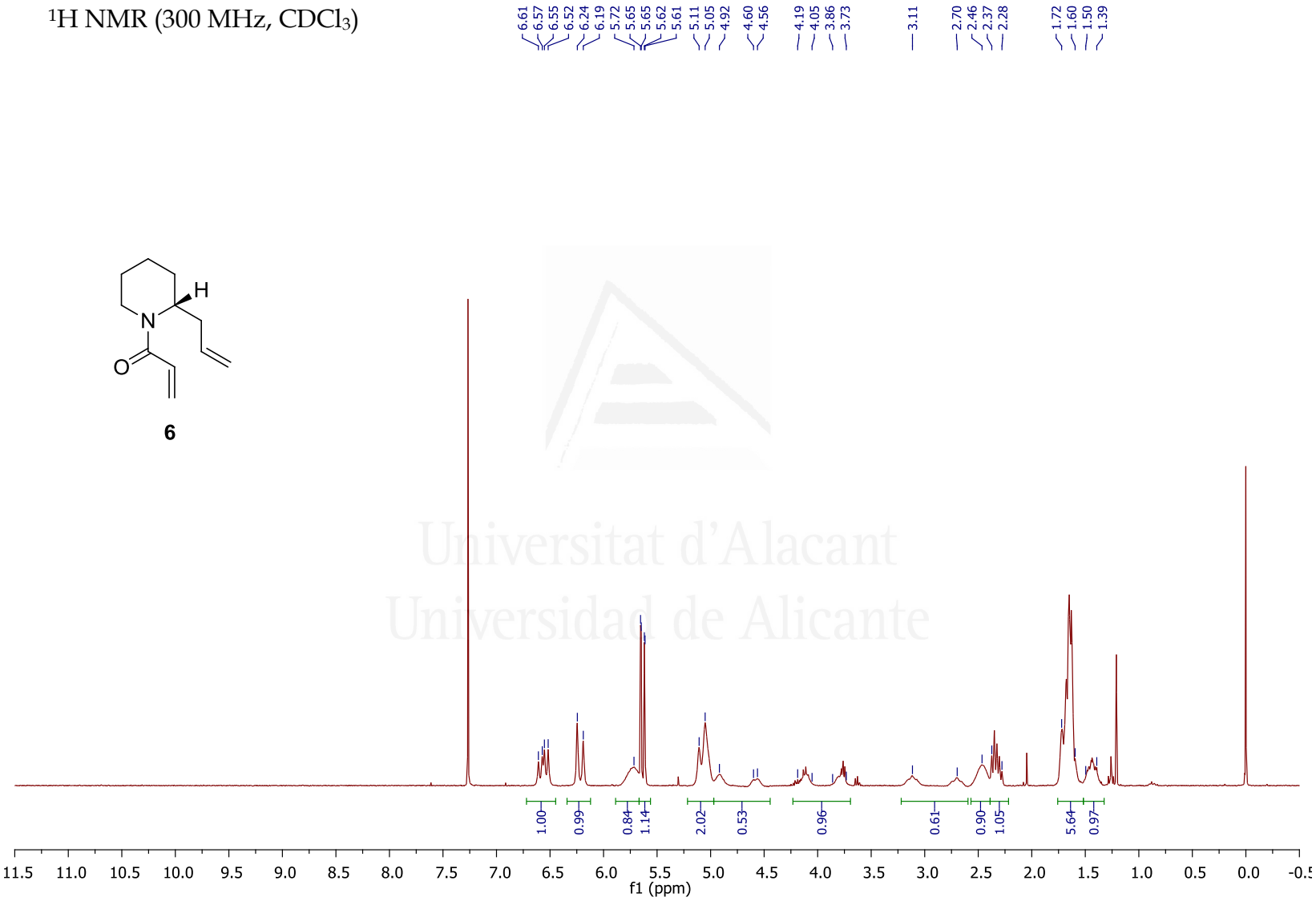
^{13}C NMR (75 MHz, $CDCl_3$)

5

(S)-Coniine hydrochloride



^{1}H NMR (300 MHz, $CDCl_3$)



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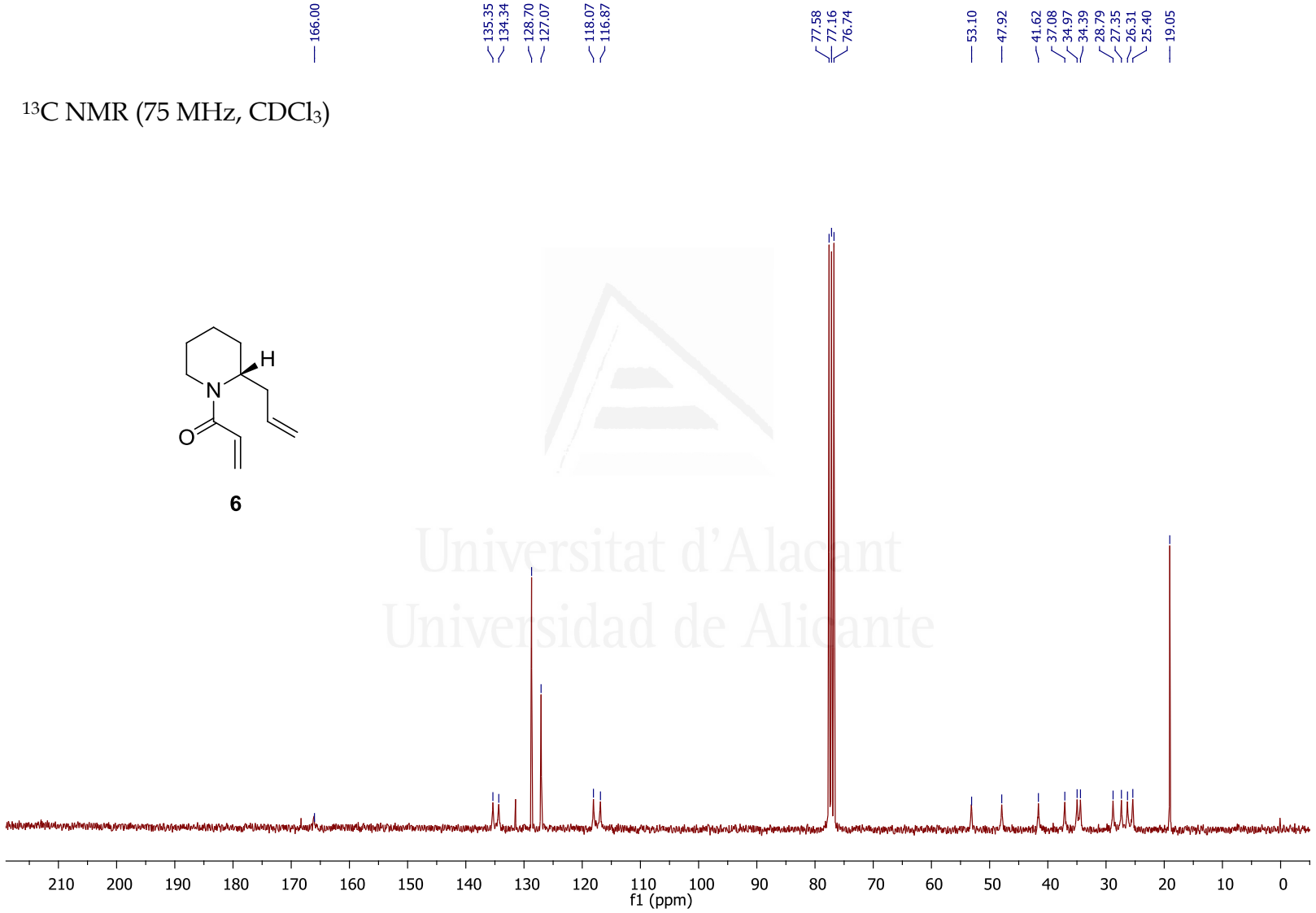
^{13}C NMR (75 MHz, $CDCl_3$)



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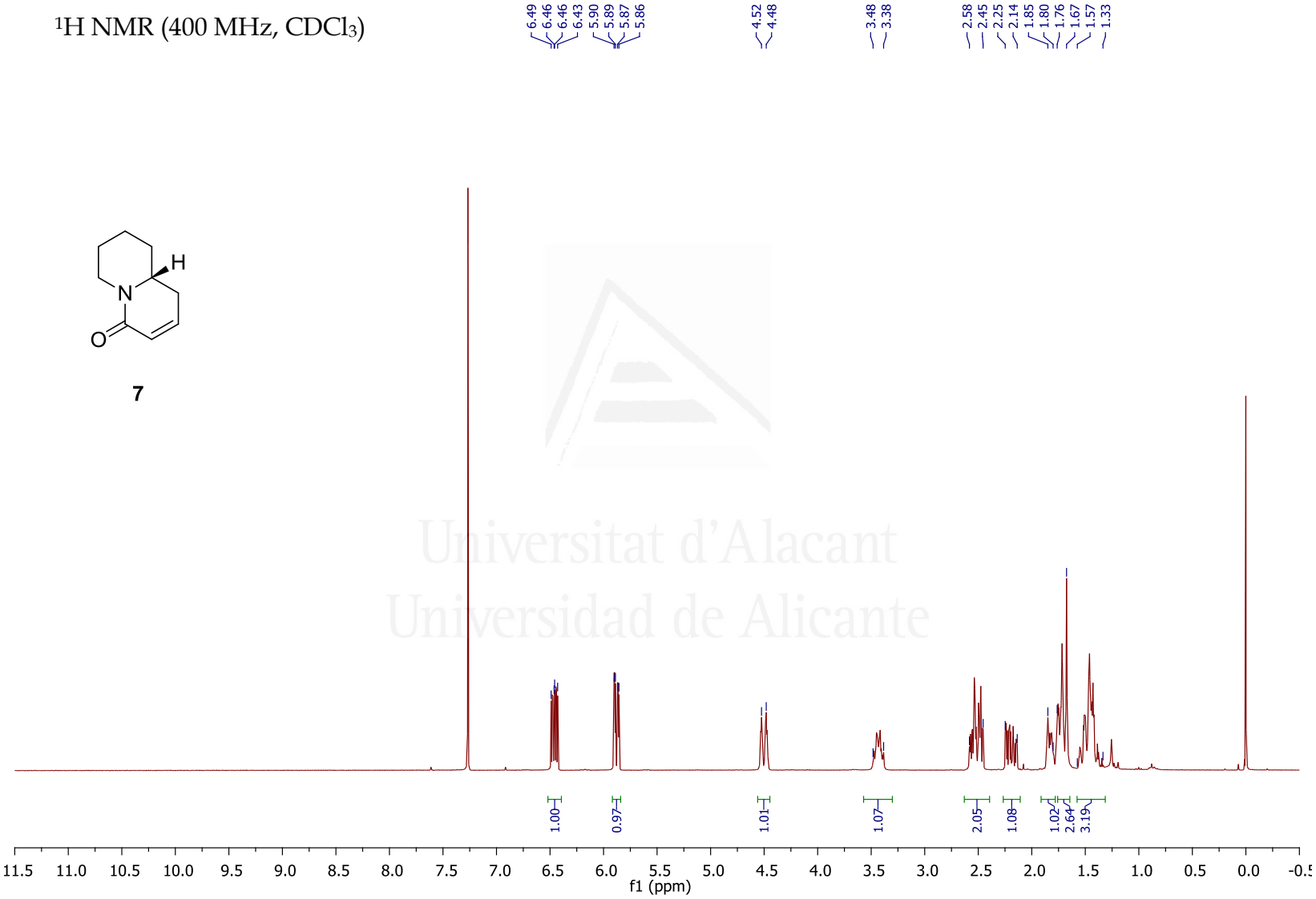
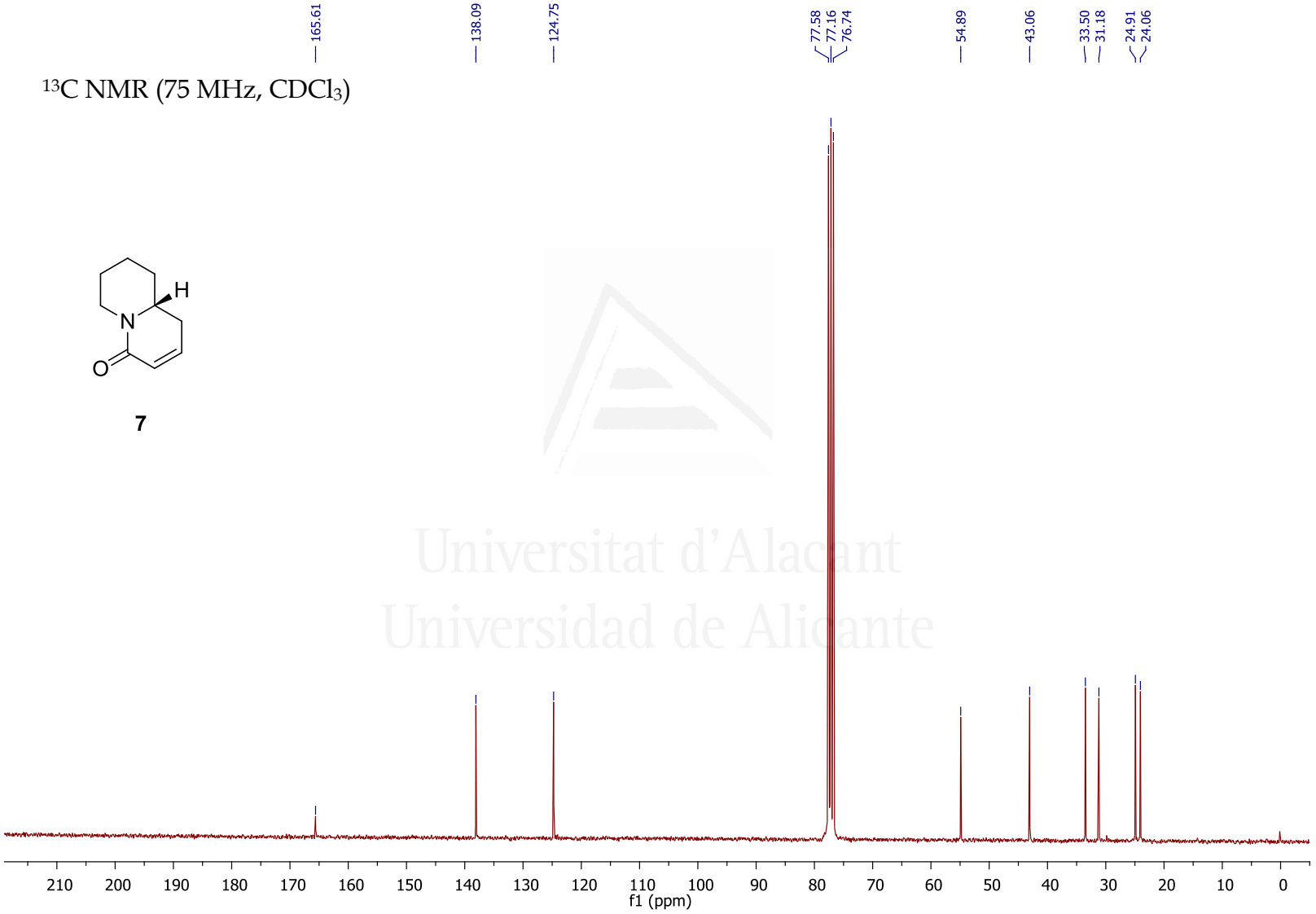
^{1}H NMR (400 MHz, $CDCl_3$)



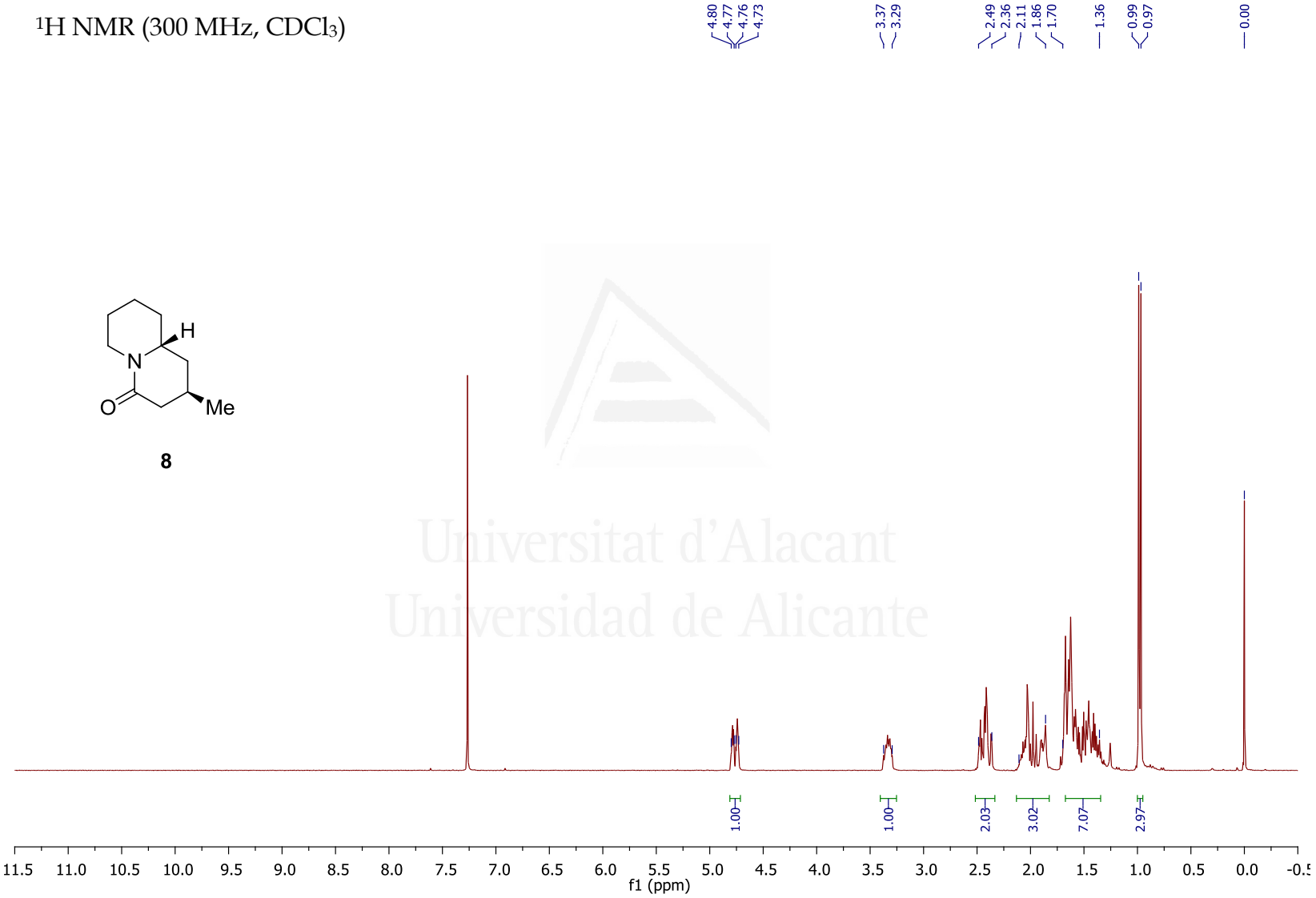
7

^{13}C NMR (75 MHz, $CDCl_3$)

7



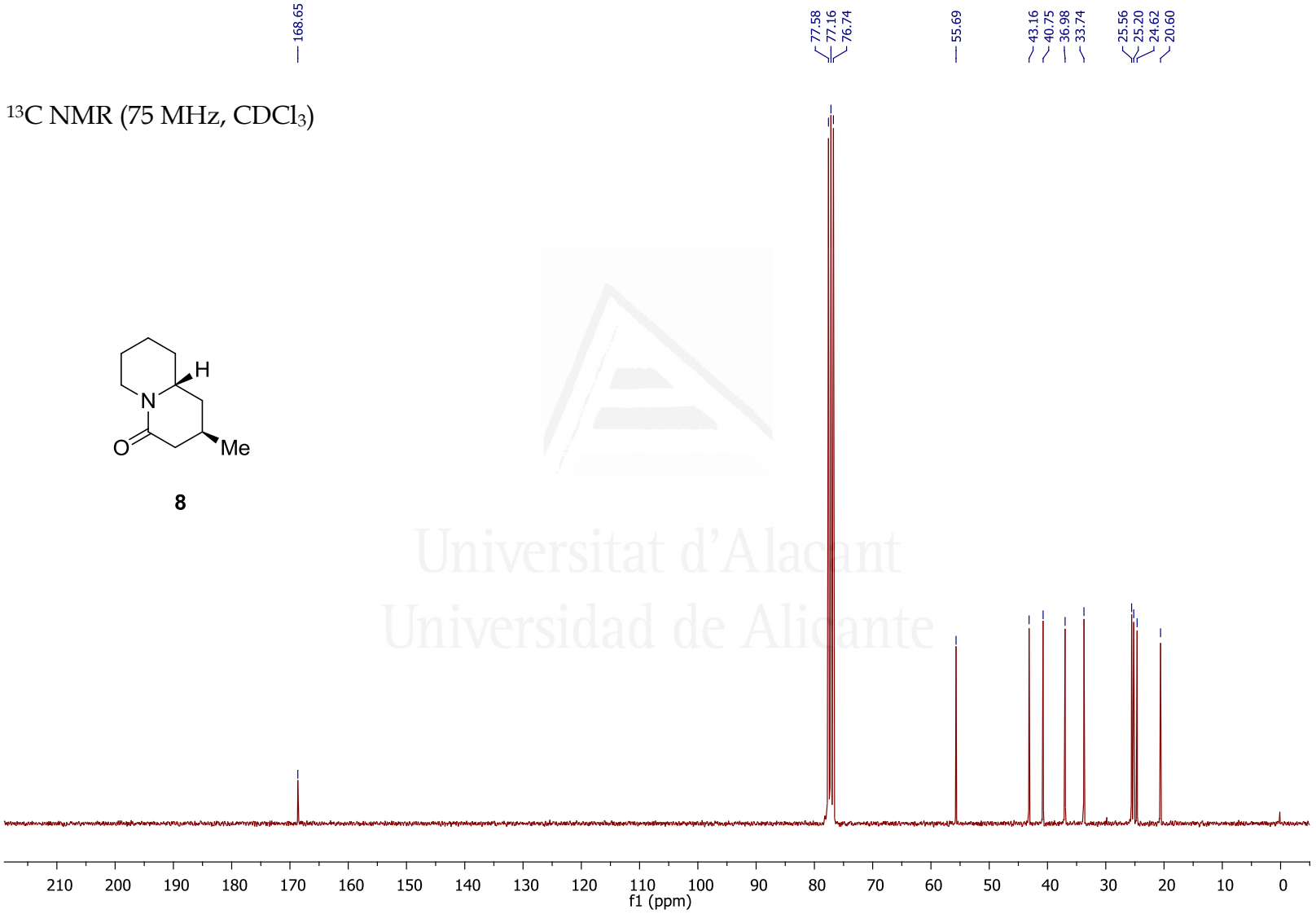
^{1}H NMR (300 MHz, $CDCl_3$)



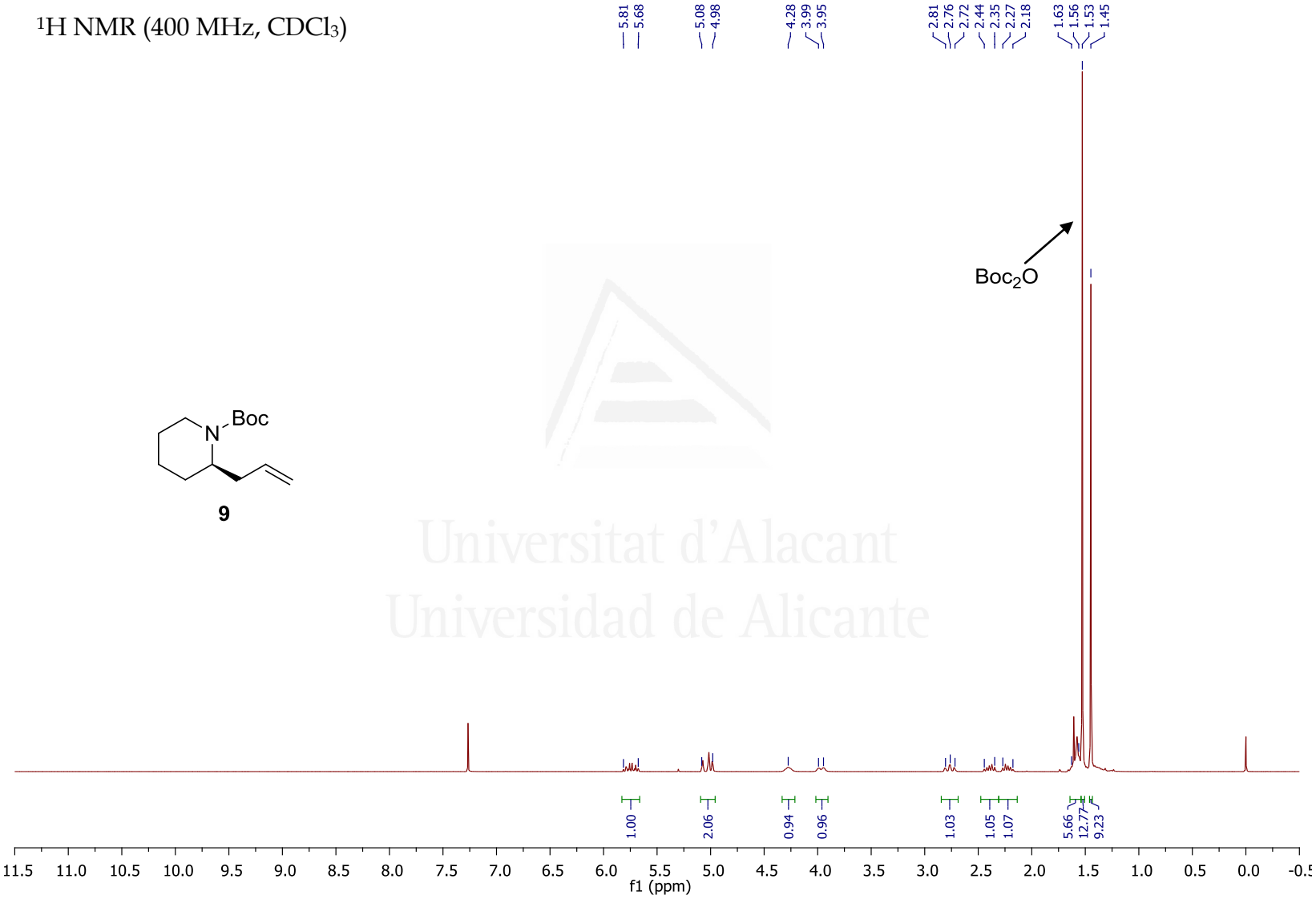
8

^{13}C NMR (75 MHz, $CDCl_3$)

8

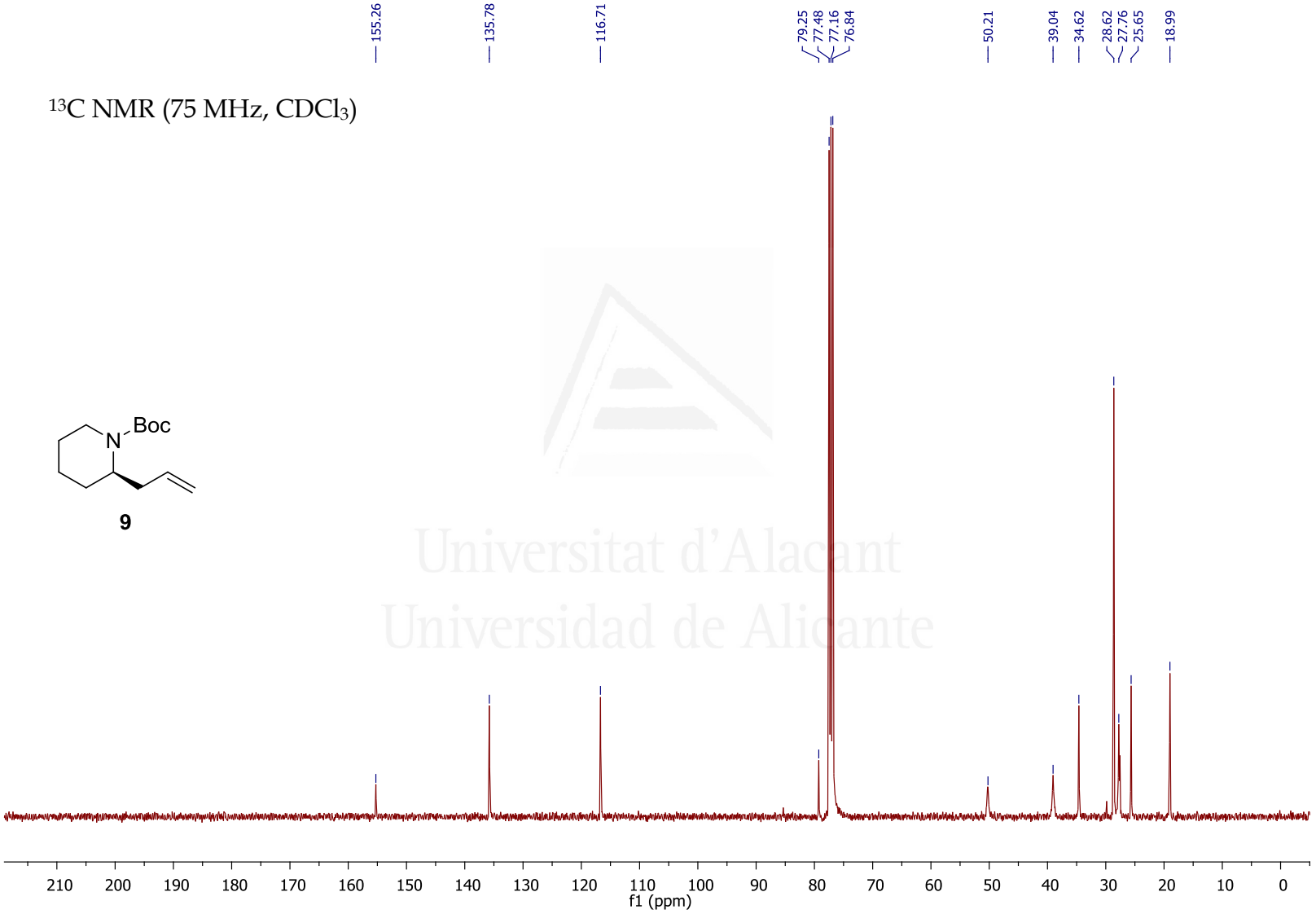


^{1}H NMR (400 MHz, $CDCl_3$)



9

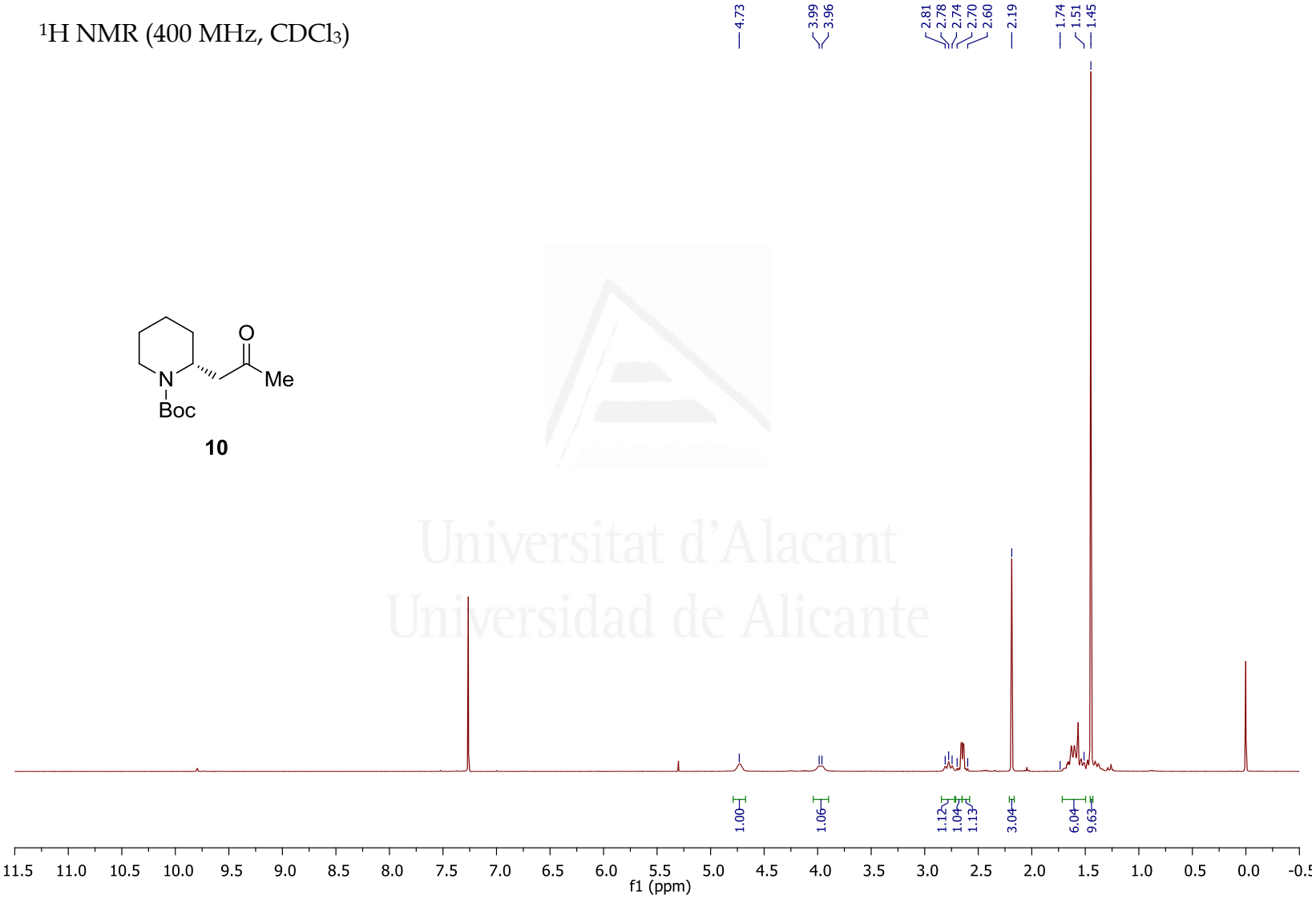
^{13}C NMR (75 MHz, $CDCl_3$)



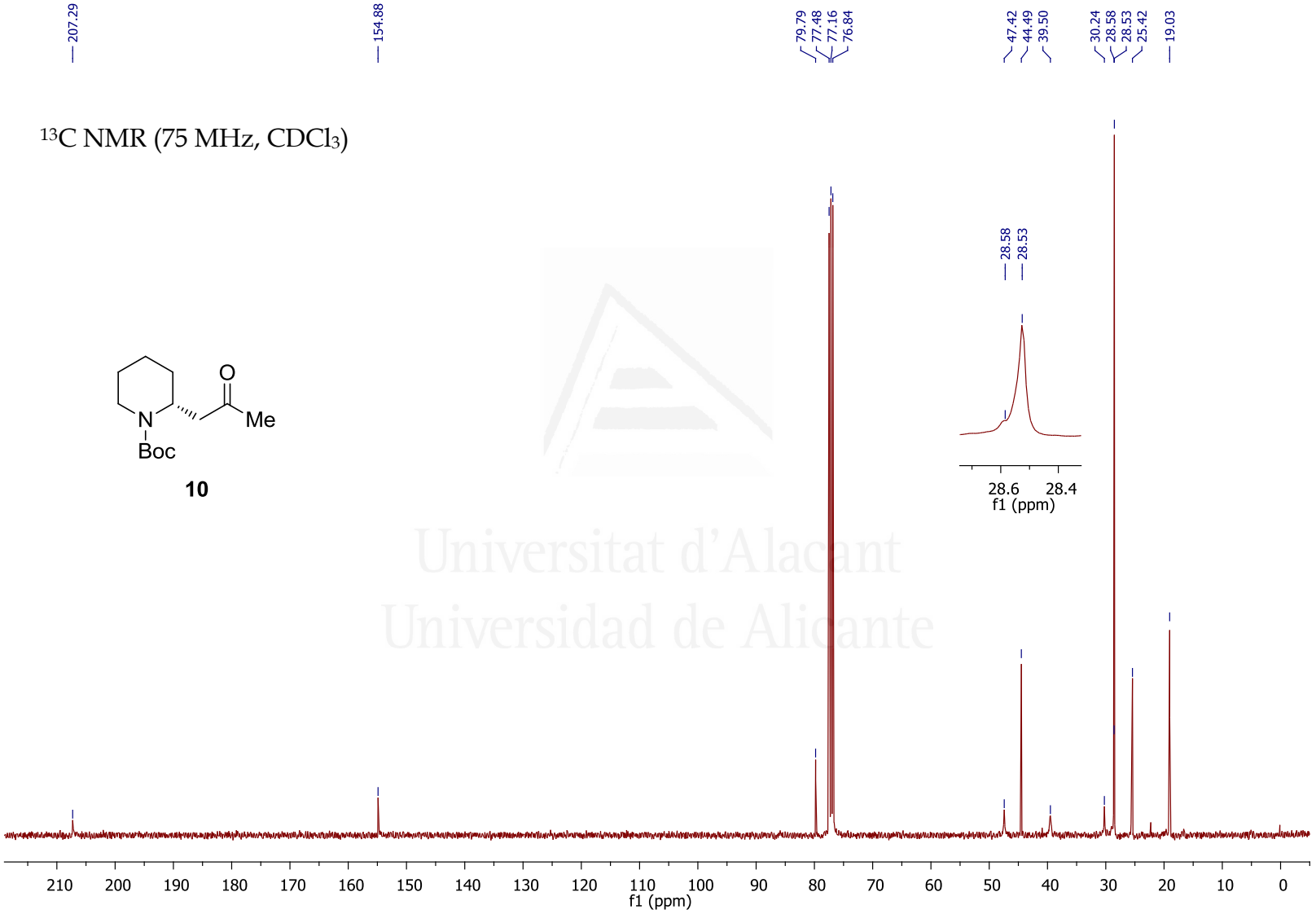
9

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

10

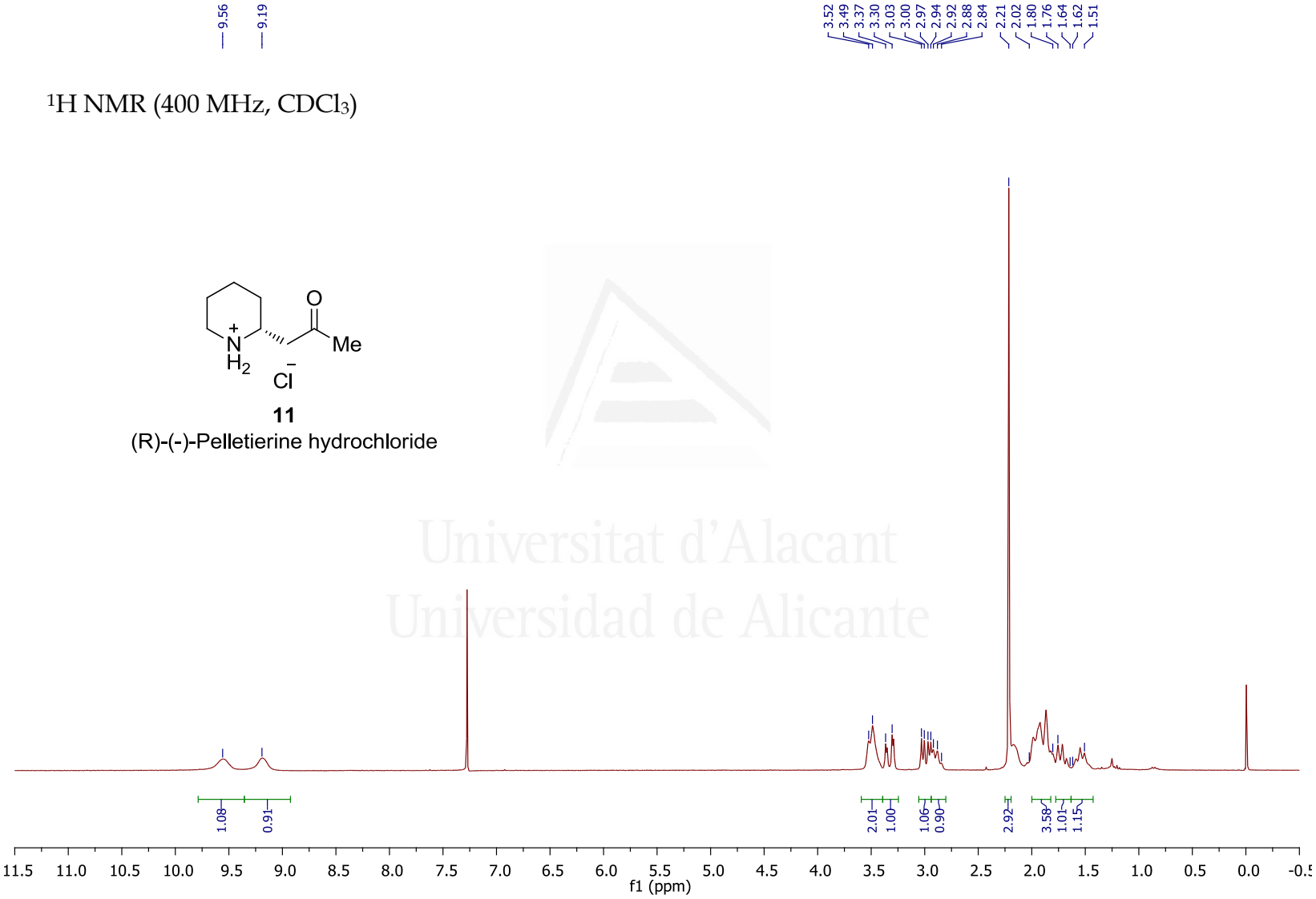


^{13}C NMR (75 MHz, $CDCl_3$)



10

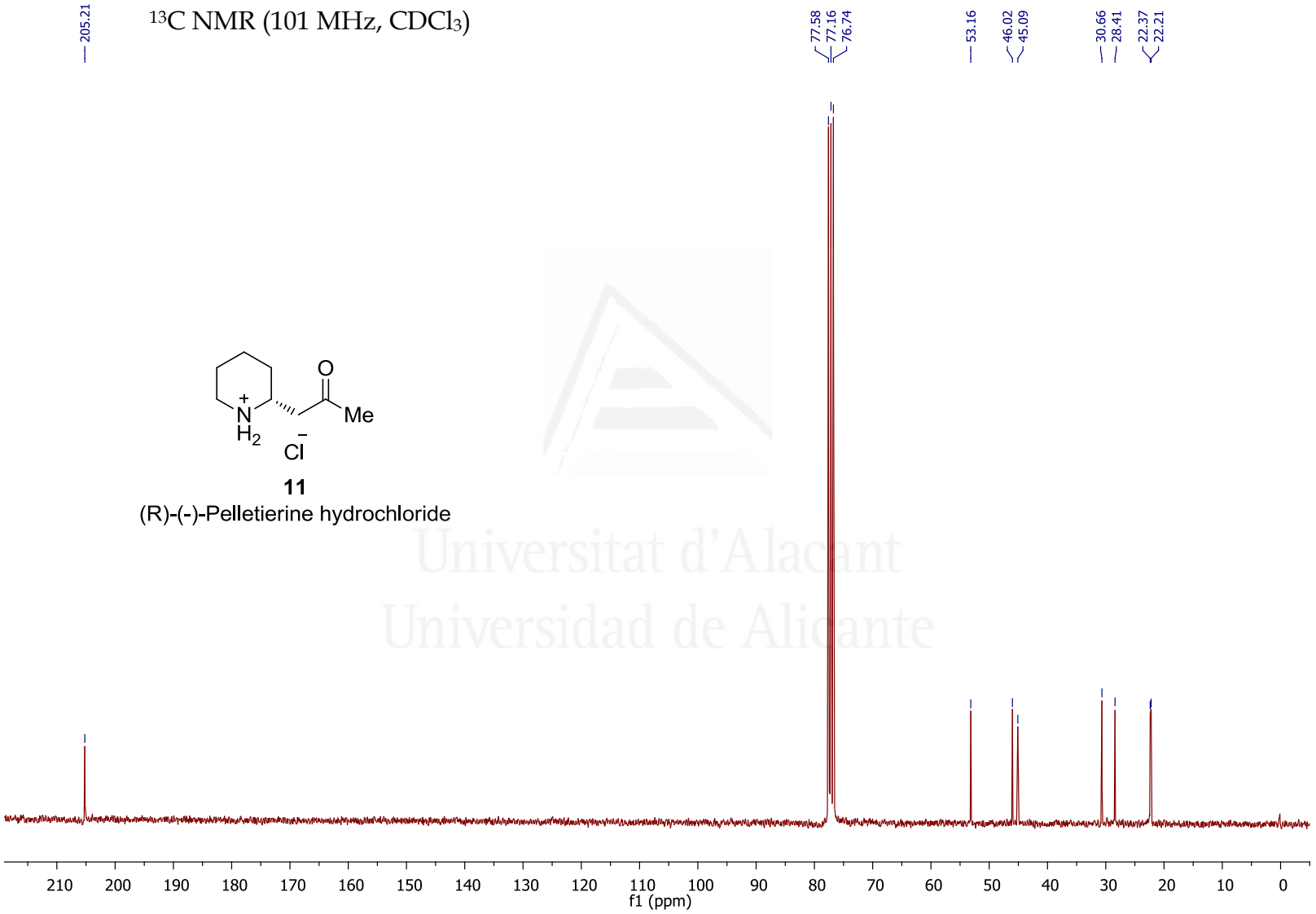
^{1}H NMR (400 MHz, $CDCl_3$)



11

(R)-(-)-Pelletierine hydrochloride

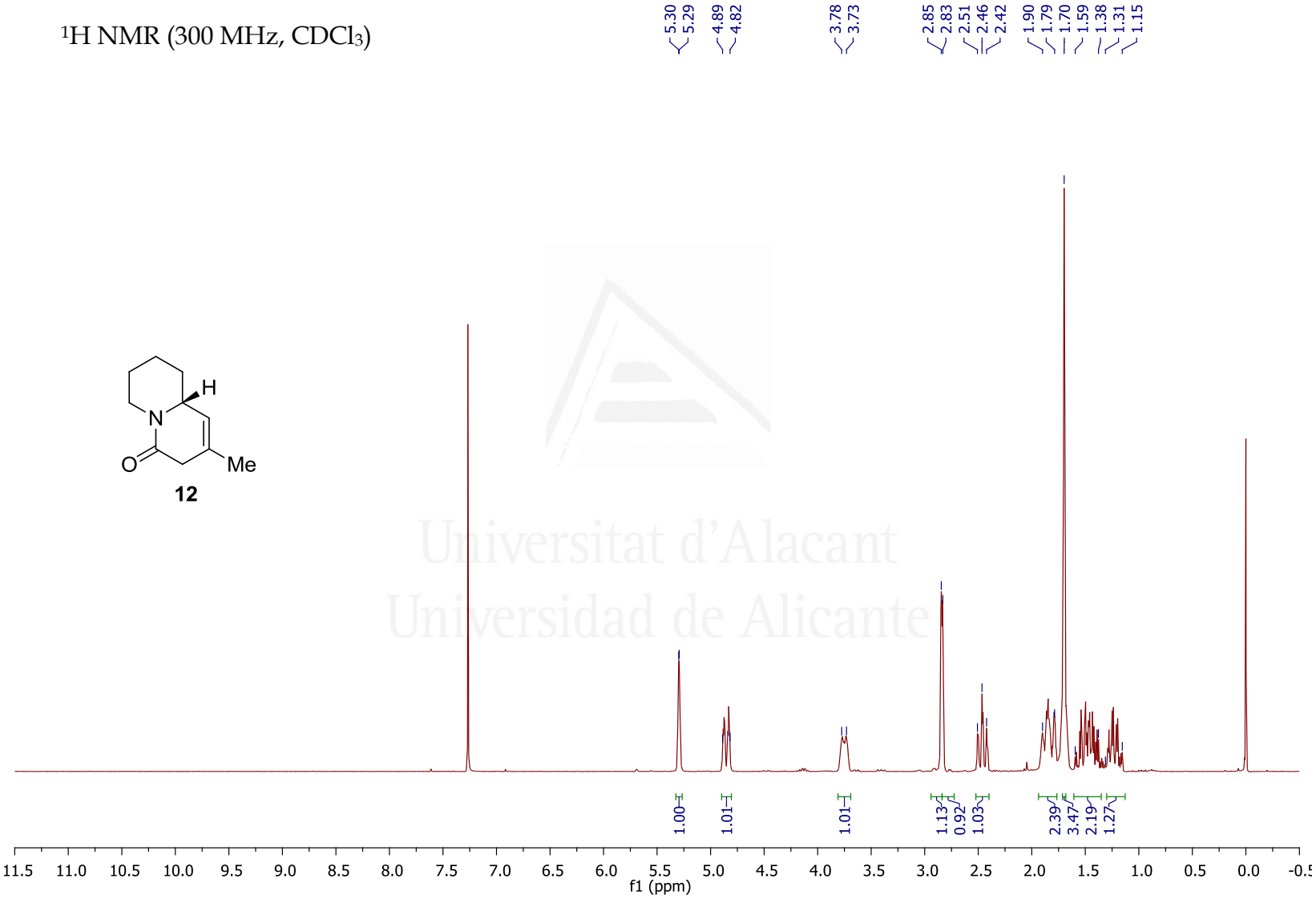
^{13}C NMR (101 MHz, $CDCl_3$)



11

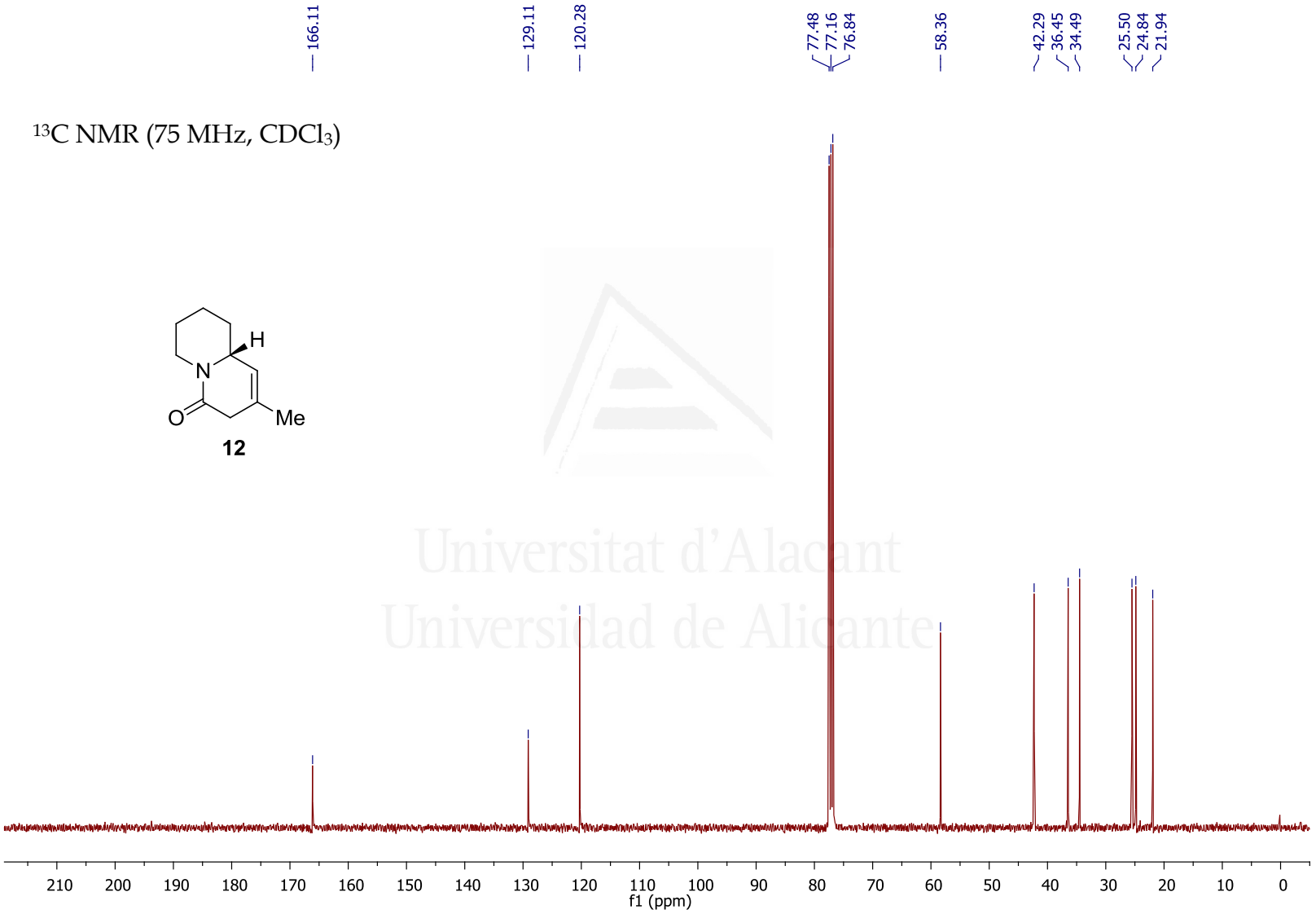
(R)-(-)-Pelletierine hydrochloride

^{1}H NMR (300 MHz, $CDCl_3$)

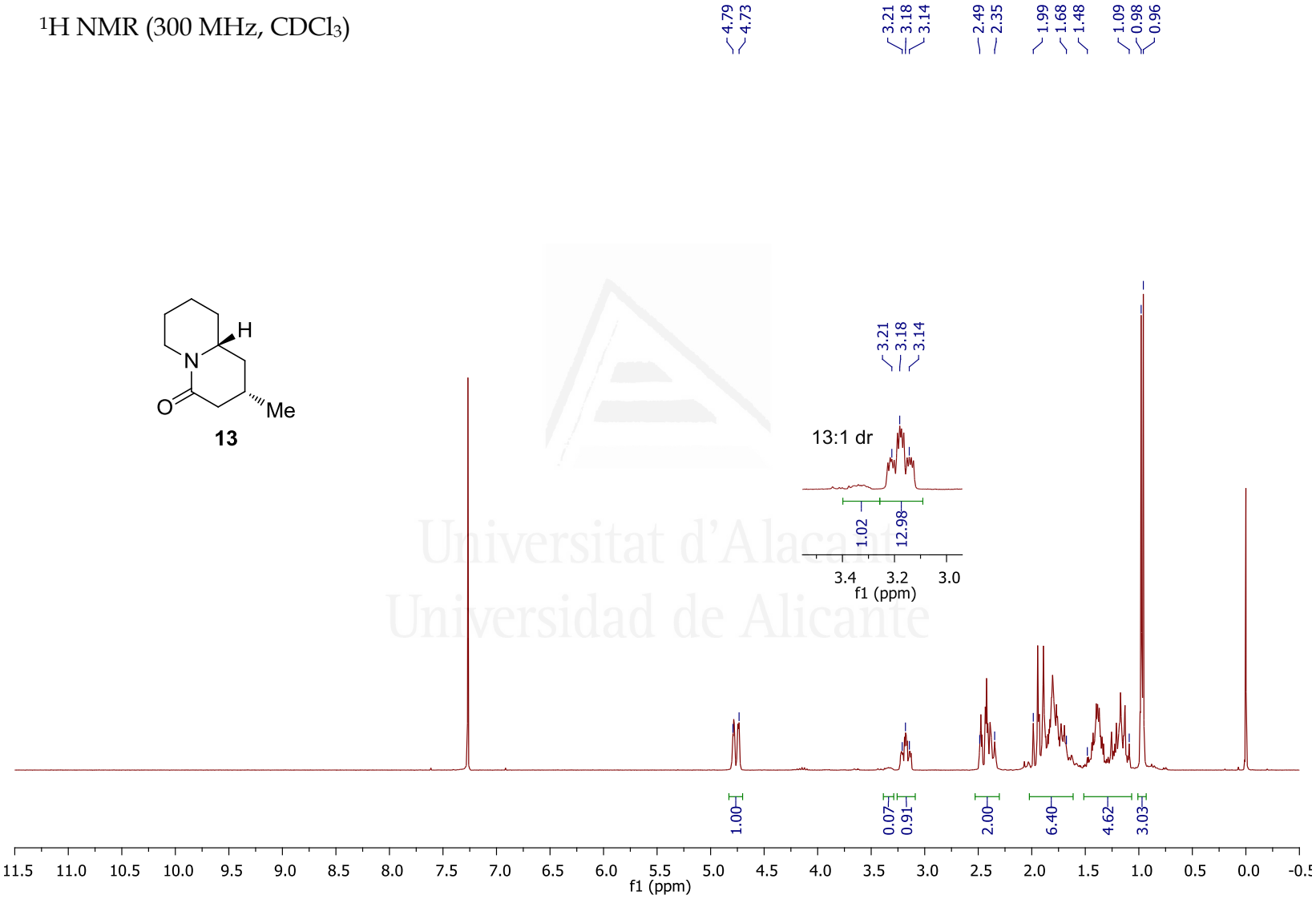


^{13}C NMR (75 MHz, $CDCl_3$)

12

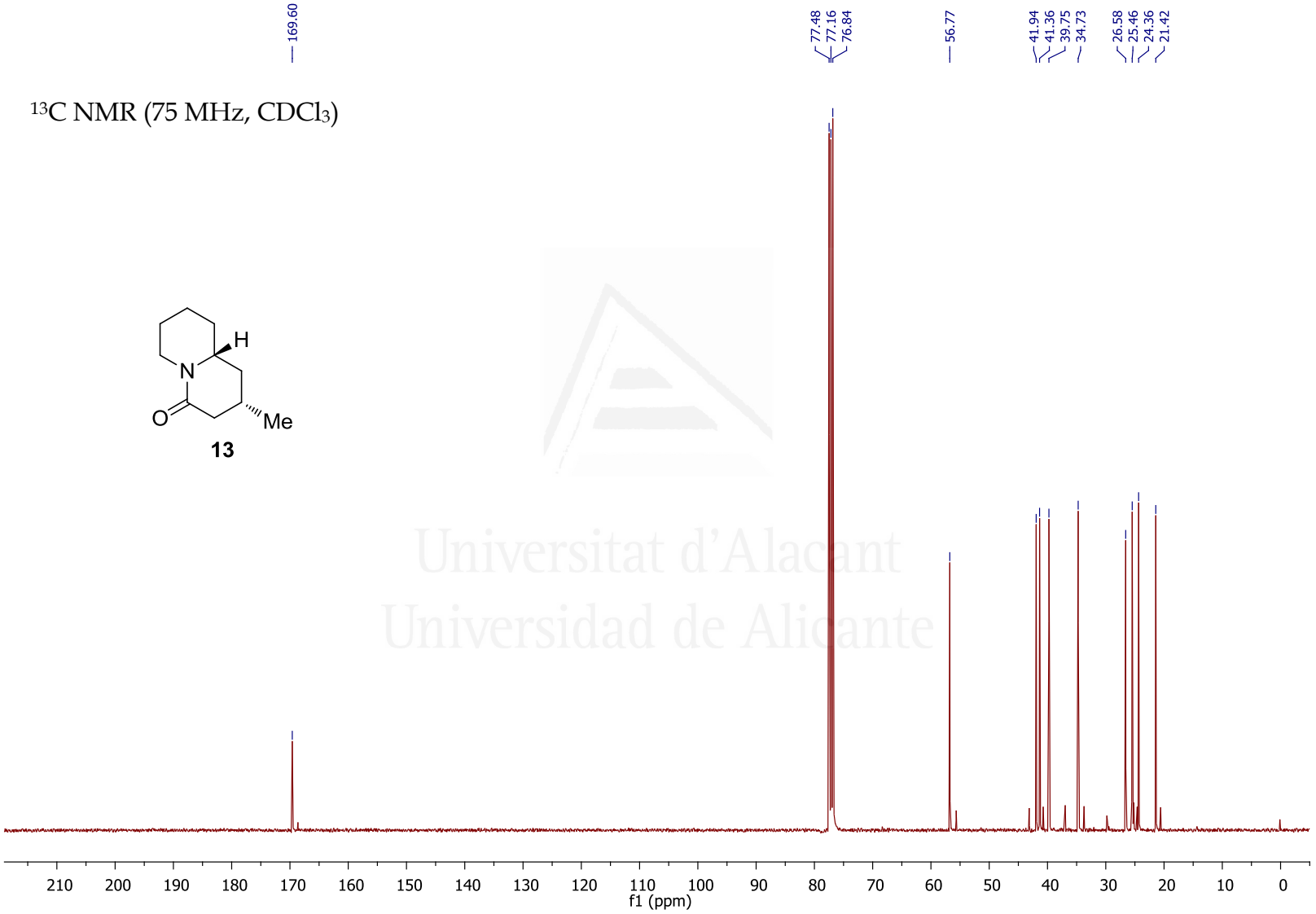


^{1}H NMR (300 MHz, $CDCl_3$)

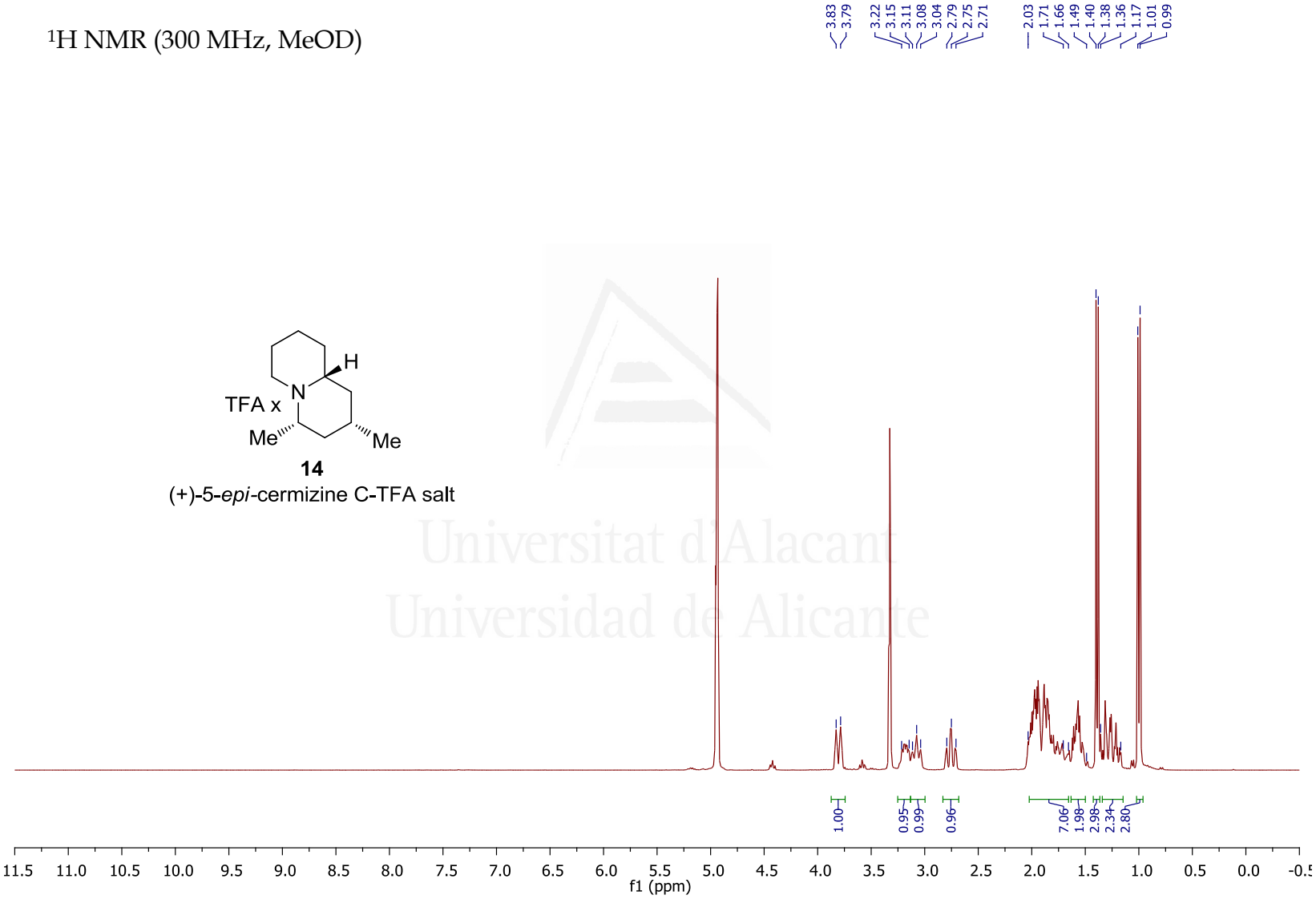


^{13}C NMR (75 MHz, $CDCl_3$)

13



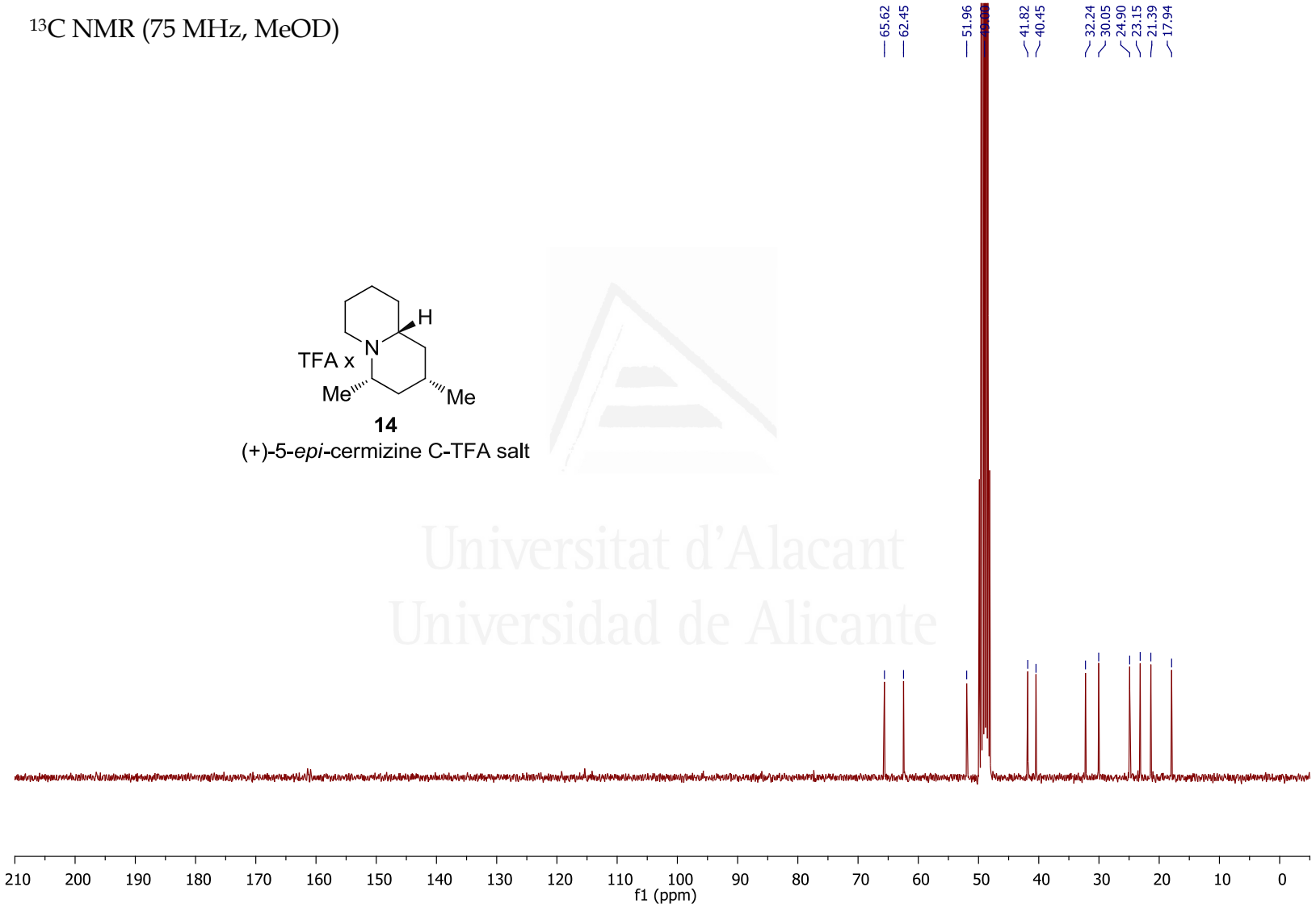
^{1}H NMR (300 MHz, MeOD)

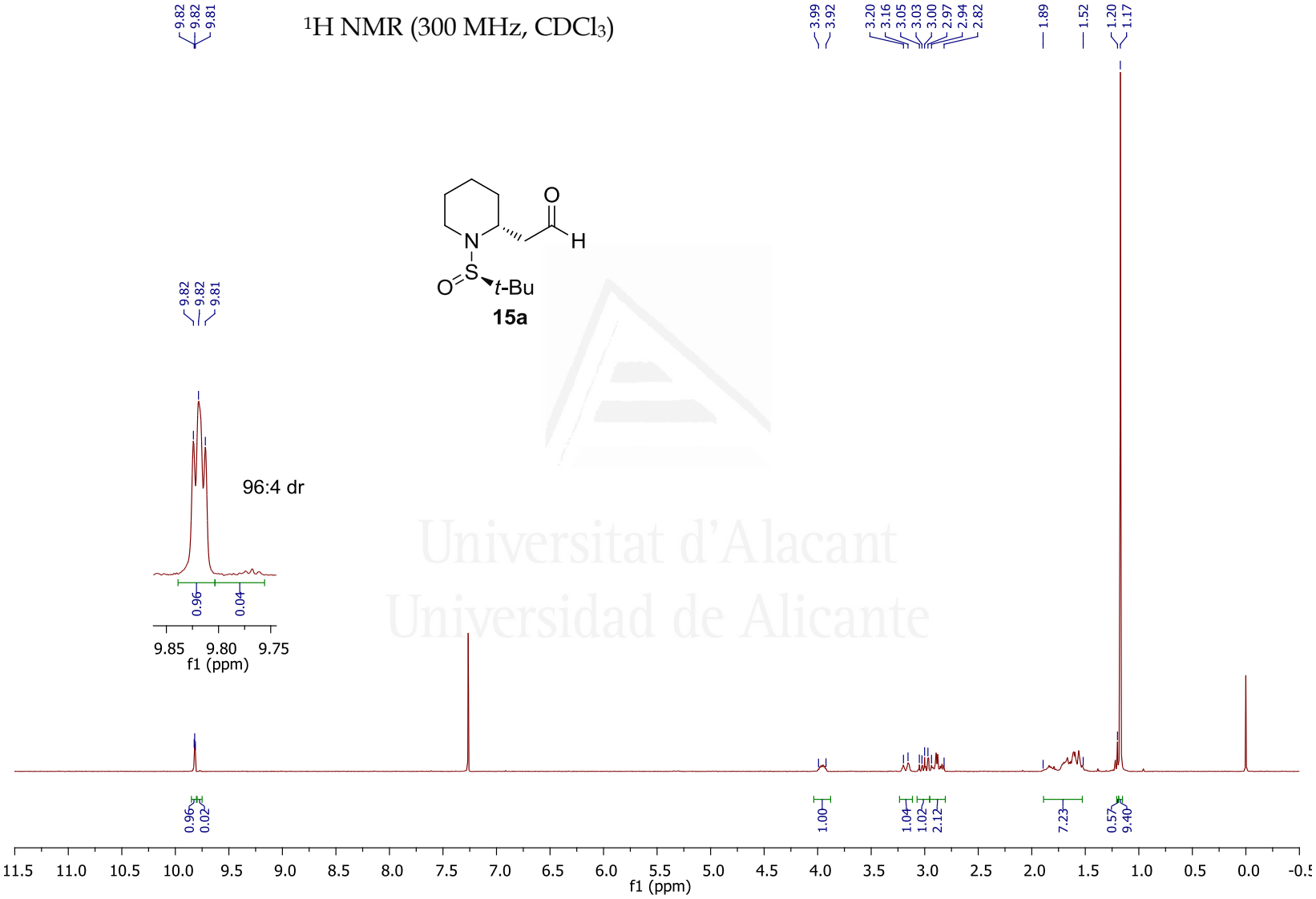


^{13}C NMR (75 MHz, MeOD)

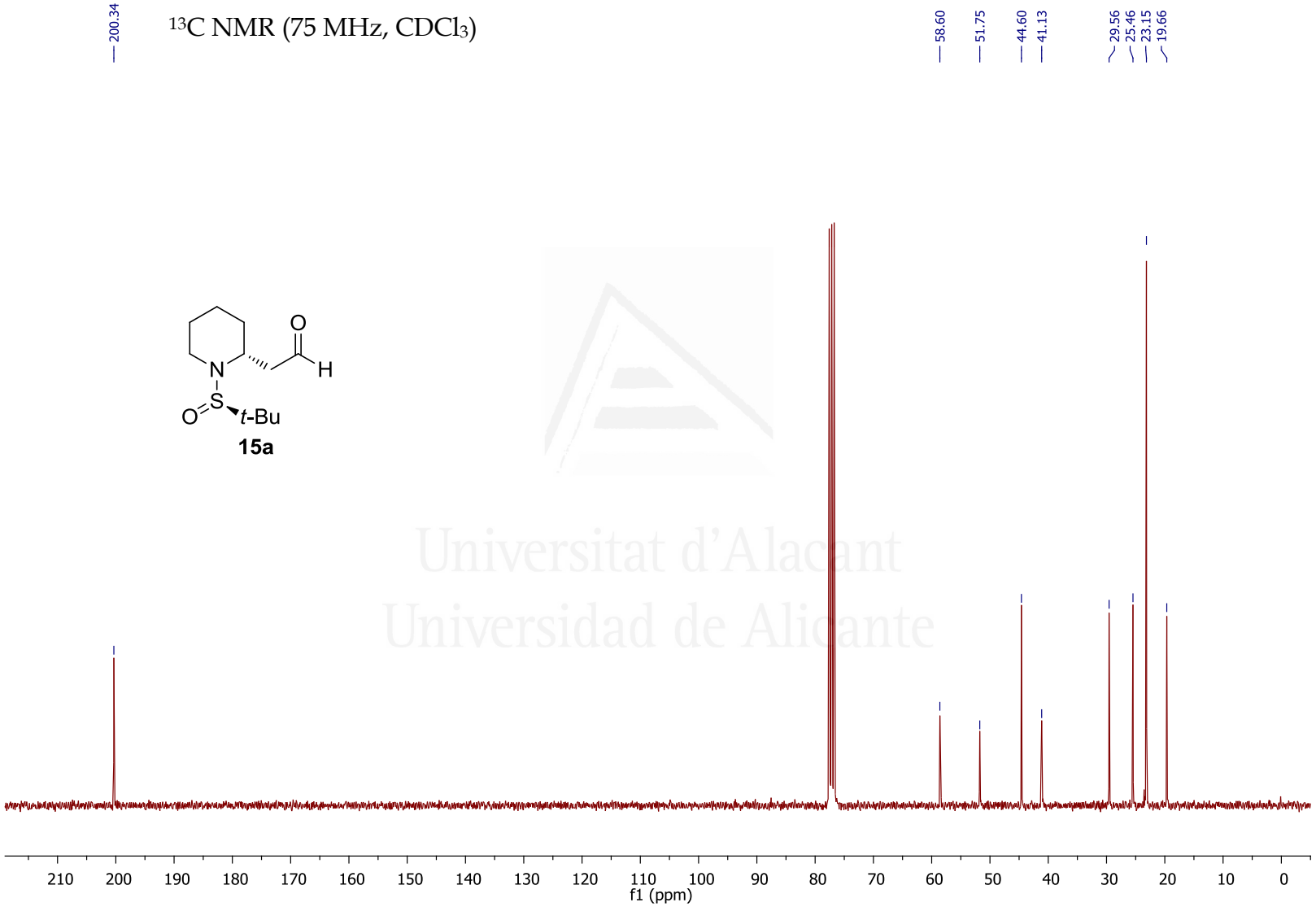
14

(+)-5-*epi*-cermizine C-TFA salt



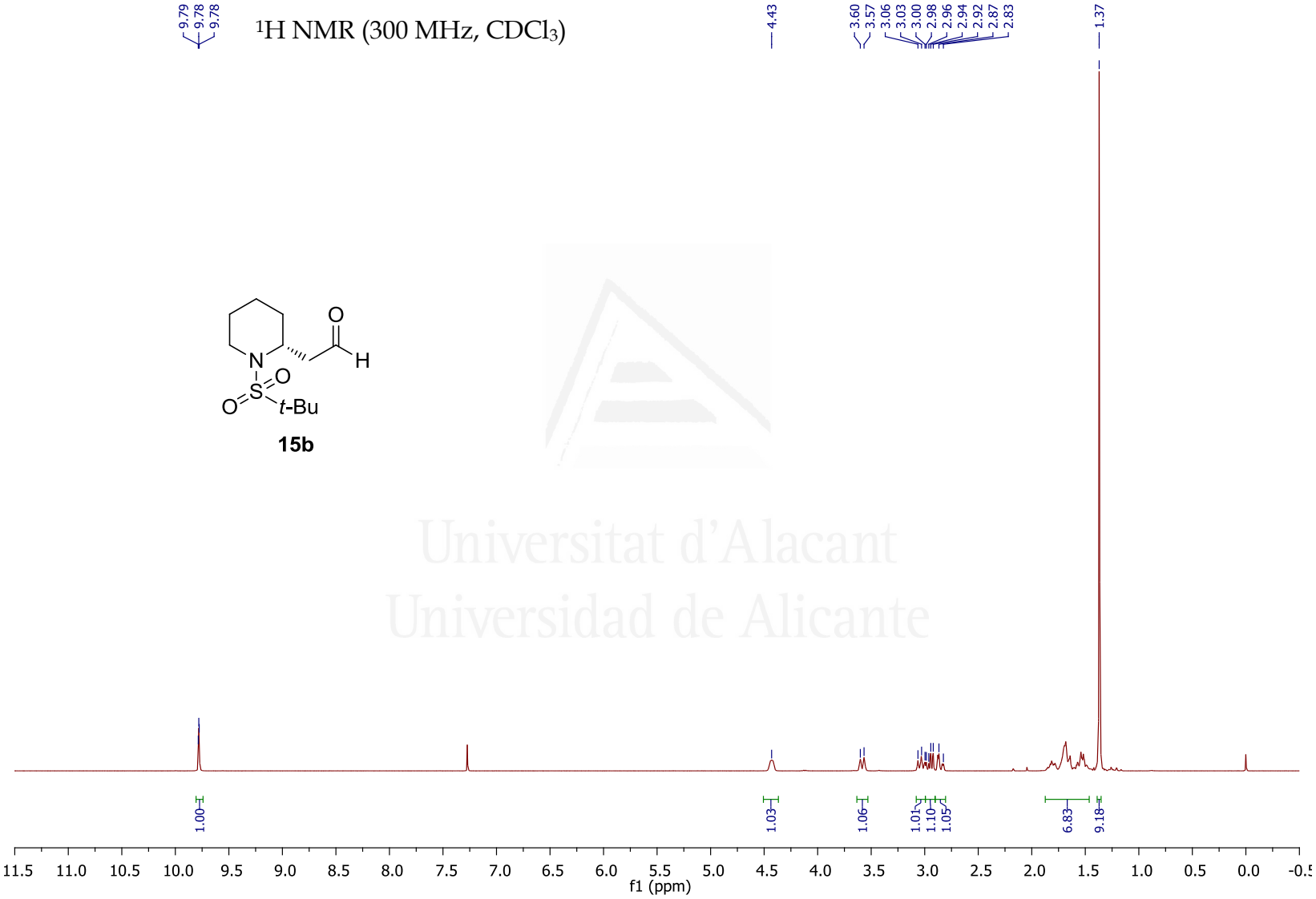


^{13}C NMR (75 MHz, $CDCl_3$)

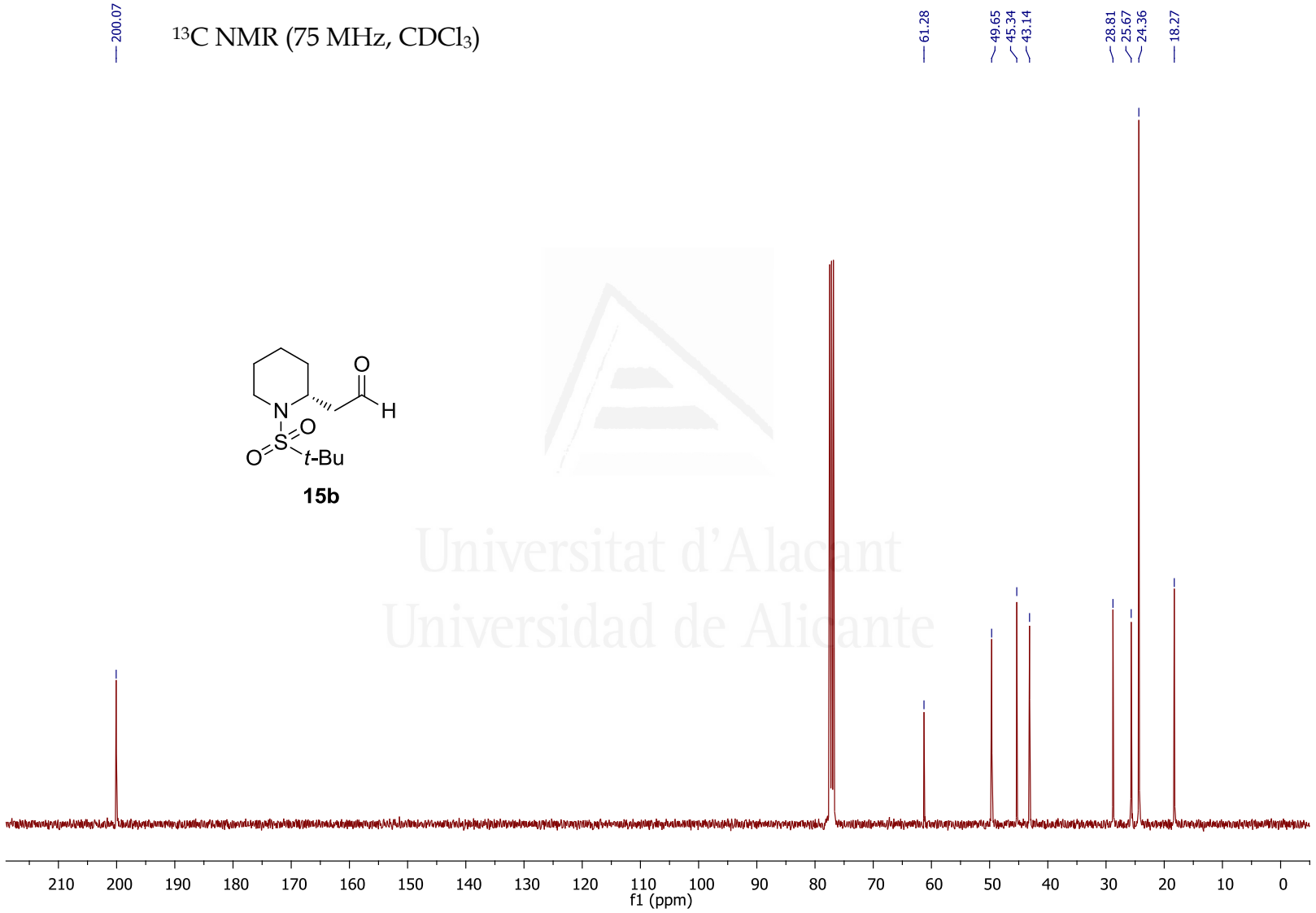


15a

^{1}H NMR (300 MHz, $CDCl_3$)



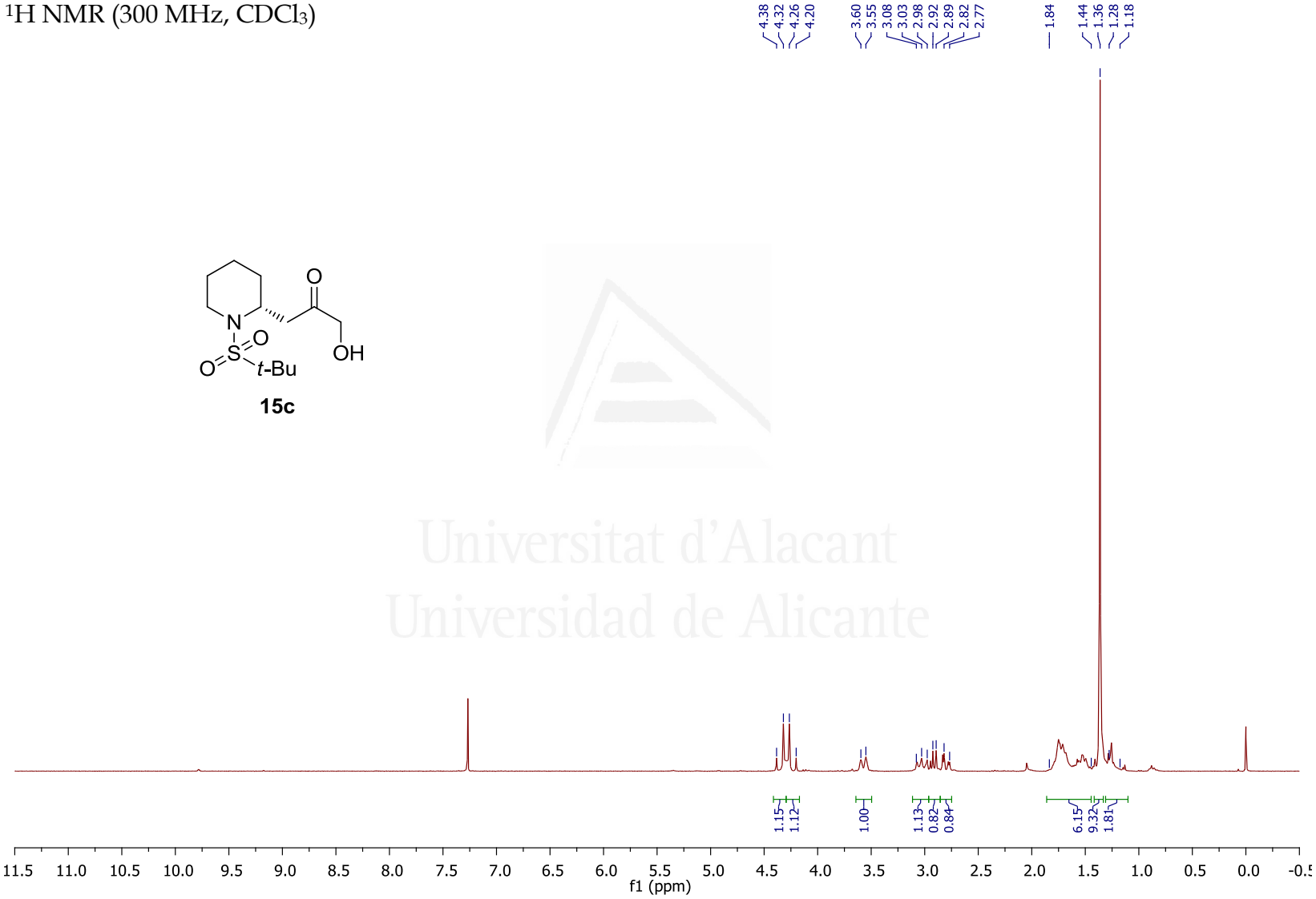
^{13}C NMR (75 MHz, $CDCl_3$)



15b

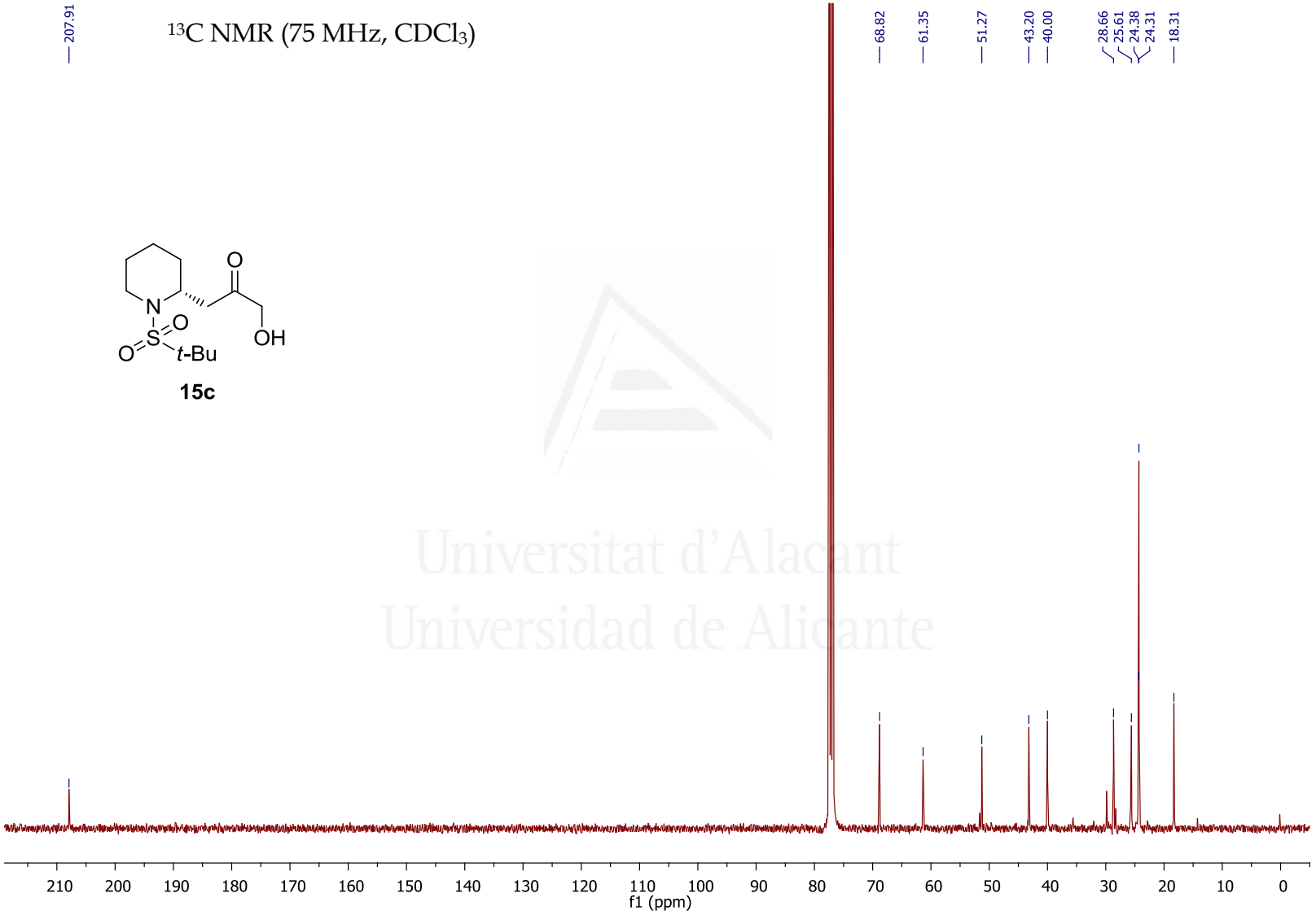
^{1}H NMR (300 MHz, $CDCl_3$)

15c



^{13}C NMR (75 MHz, $CDCl_3$)

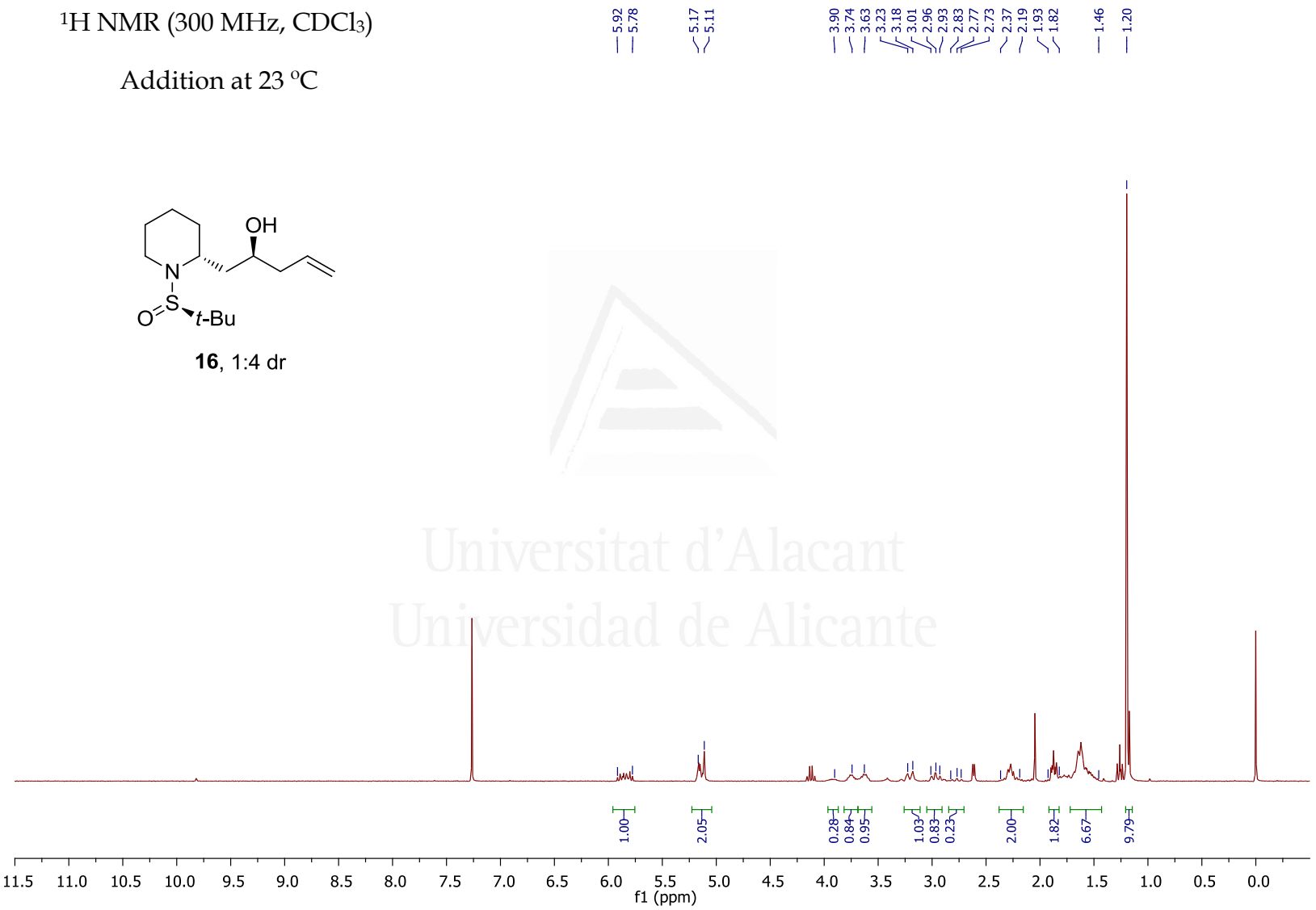
15c



^{1}H NMR (300 MHz, $CDCl_3$)

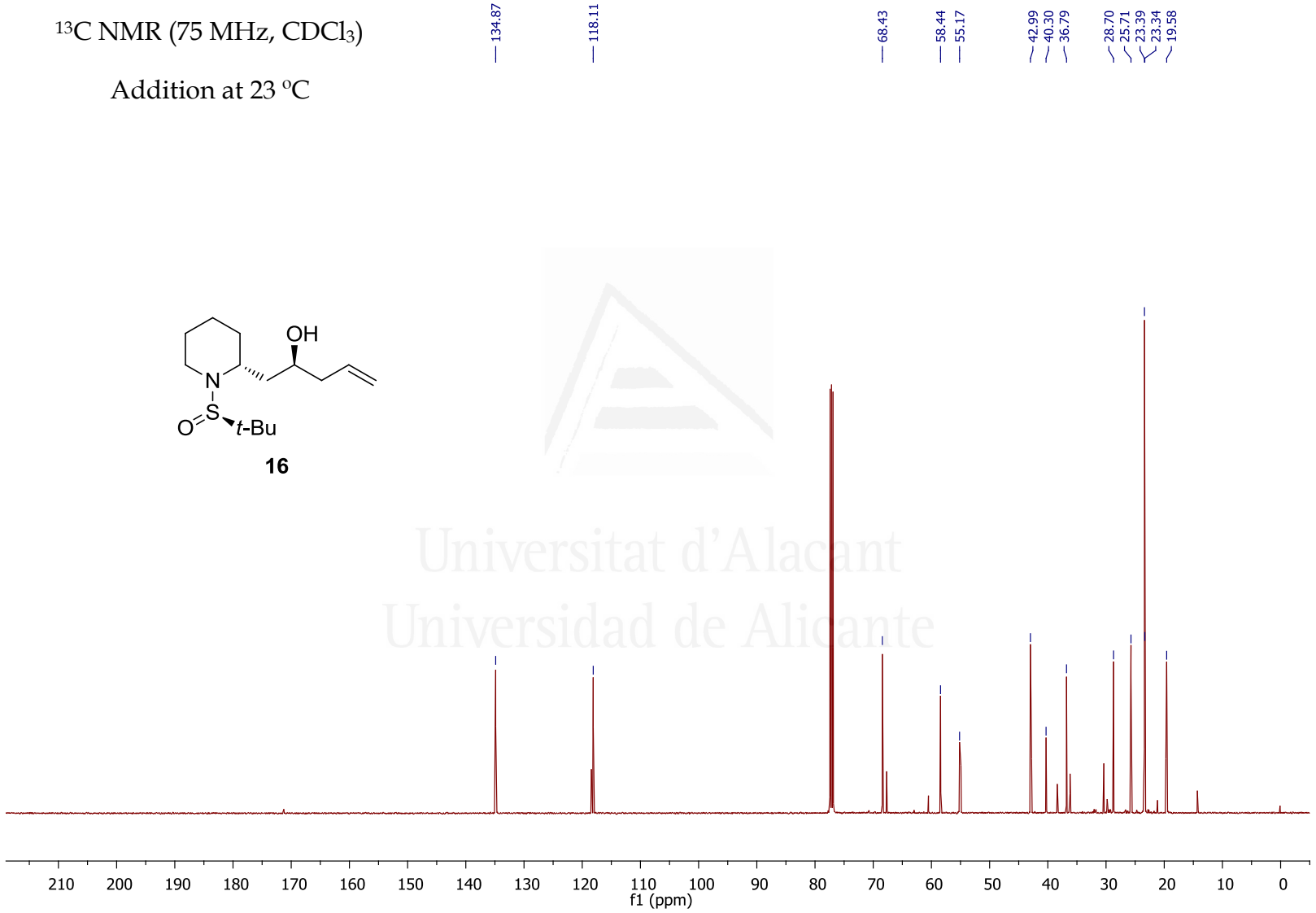
Addition at 23 ºC

16, 1:4 dr



^{13}C NMR (75 MHz, $CDCl_3$)

Addition at 23 ^{o}C

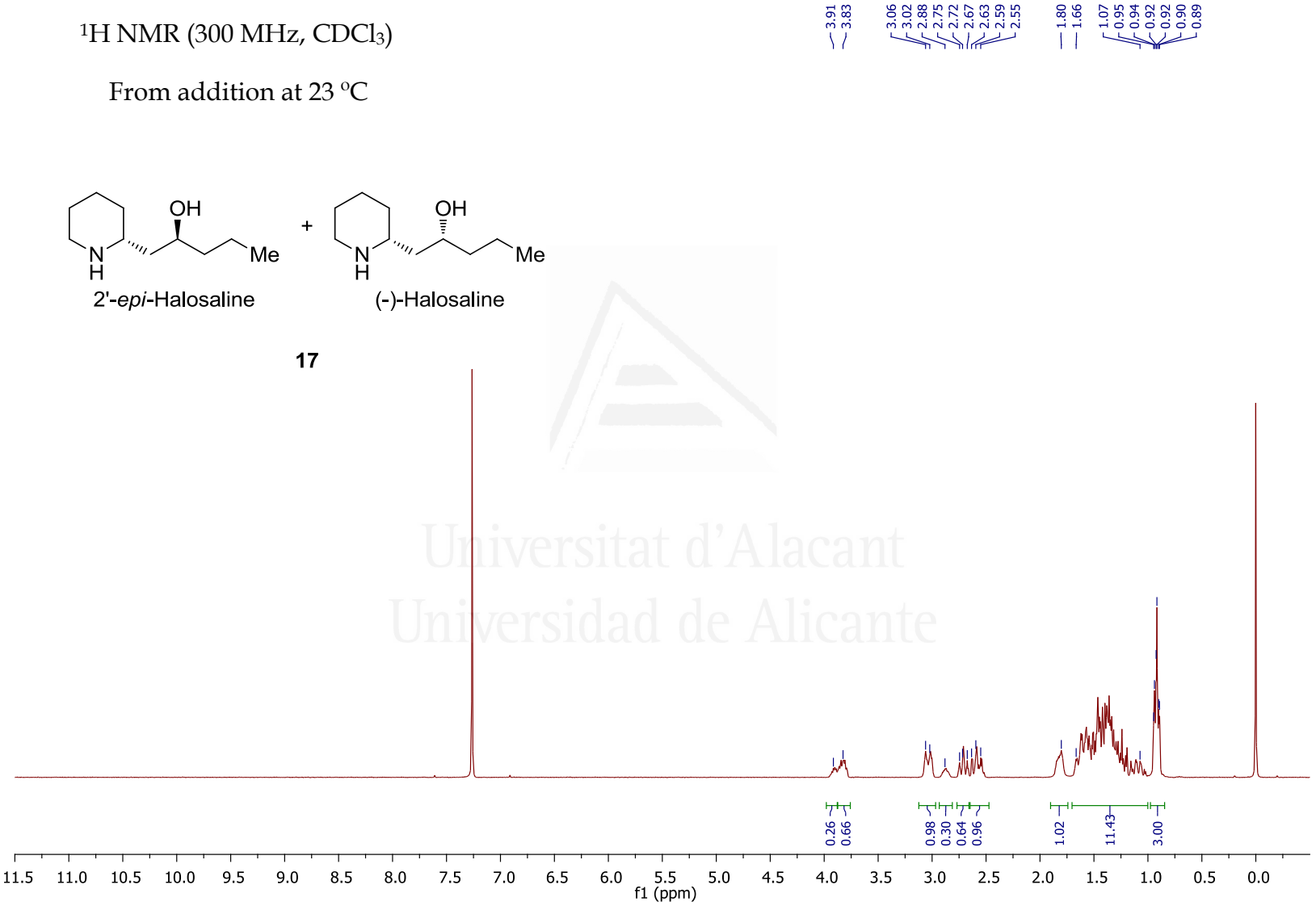


^{1}H NMR (300 MHz, $CDCl_3$)

From addition at 23 ^{o}C

2'-*epi*-Halosaline (-)-Halosaline

17



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Data File C:\CHEM32\1\DATA\IE\IE100-80-12-60B.D
Sample Name: IE100-80-12-60b

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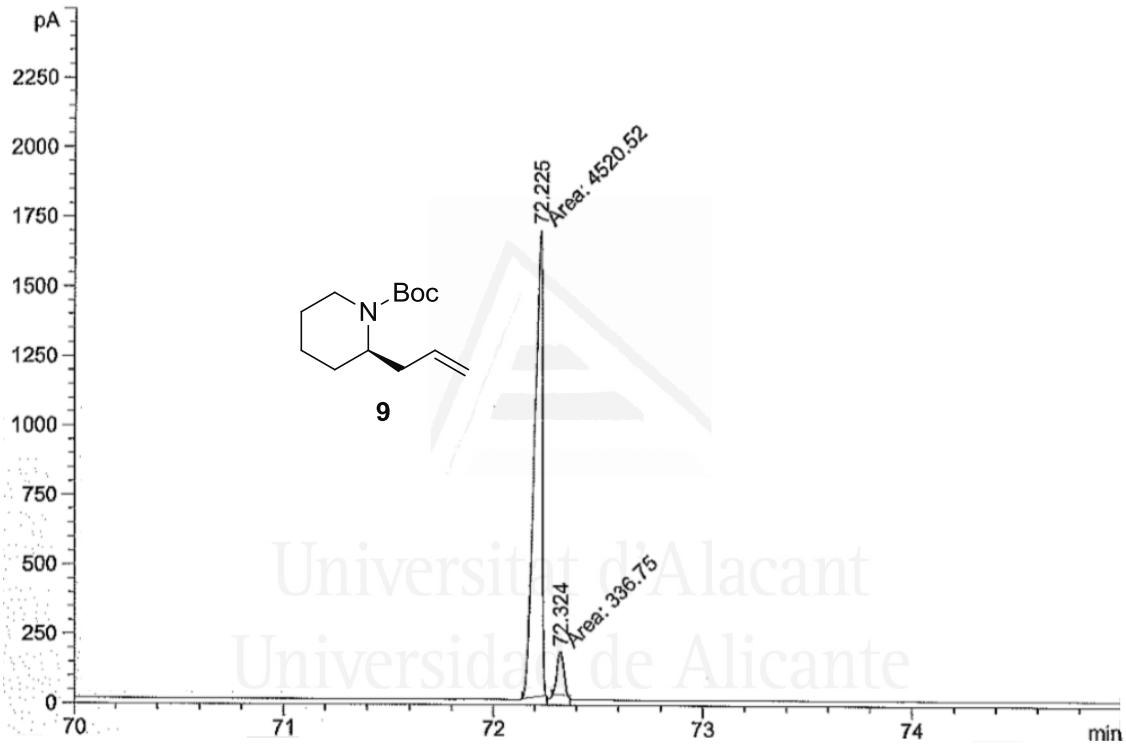
    Acq. Instrument : Instrument 1                       Location : Vial 206
    Injection Date  : 9/7/2011 1:58:08 PM                    Inj :   1
                                                       Inj Volume : 1 µl
    Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
    Acq. Method     : C:\CHEM32\1\METHODS\AUTO-BACK\80-12.0-60M_B.M
    Last changed    : 8/31/2011 5:56:16 PM by bea
    Analysis Method : C:\CHEM32\1\METHODS\MANUAL BOTH\120-14.3-100M_MAN_BOTH.M
    Last changed    : 11/22/2011 1:00:15 PM by EF
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

FID2 B, Back Signal (IE\IE100-80-12-60B.D)



9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======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  72.225 MM    0.0449 4520.51904 1676.48596 93.06708
   2  72.324 MM    0.0363  336.75043  154.55467  6.93292

Totals :                  4857.26947 1831.04063
```

```
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==========================================================================
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Acq. Instrument : Instrument 1                        Location : Vial 205
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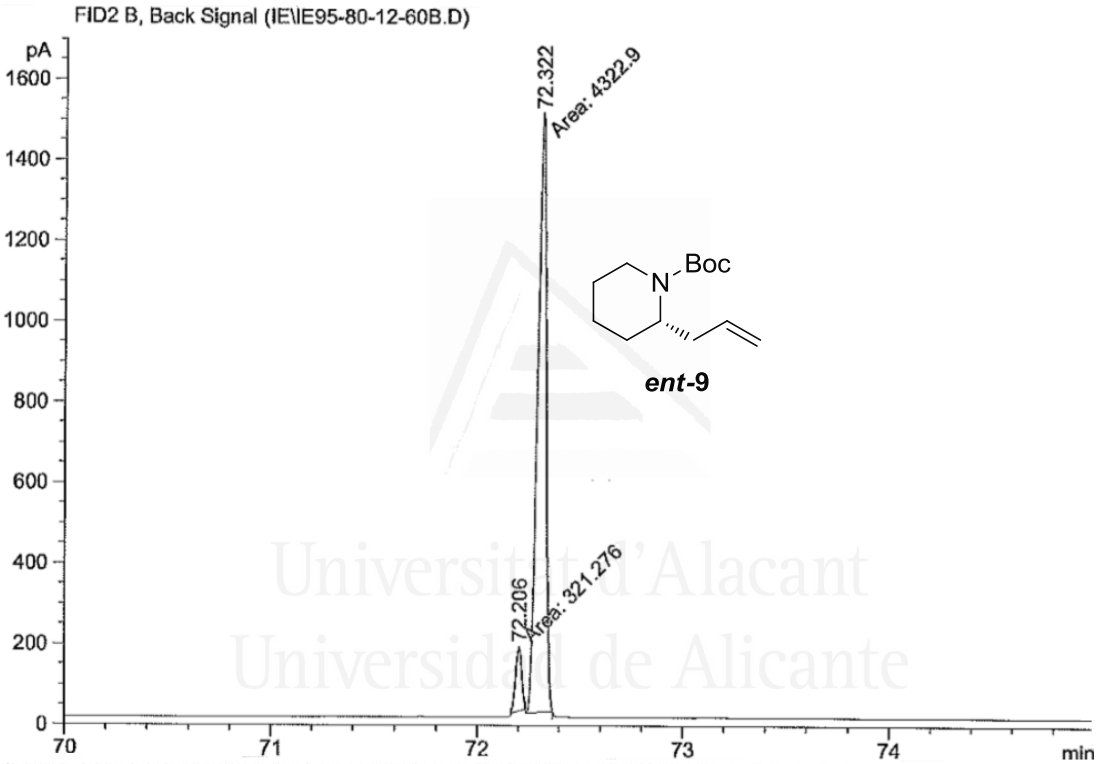
                                                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\1\METHODS\AUTO-BACK\80-12.0-60M_B.M
Last changed    : 8/31/2011 5:56:16 PM by bea
Analysis Method : C:\CHEM32\1\METHODS\MANUAL BOTH\120-14.3-100M_MAN_BOTH.M
Last changed    : 11/22/2011 1:00:15 PM by EF
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID2 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  72.206 MM    0.0339  321.27649  158.13979  6.91783
   2  72.322 MM    0.0486 4322.90186 1482.54736 93.08217

Totals :                  4644.17834 1640.68715
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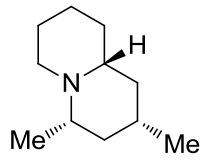
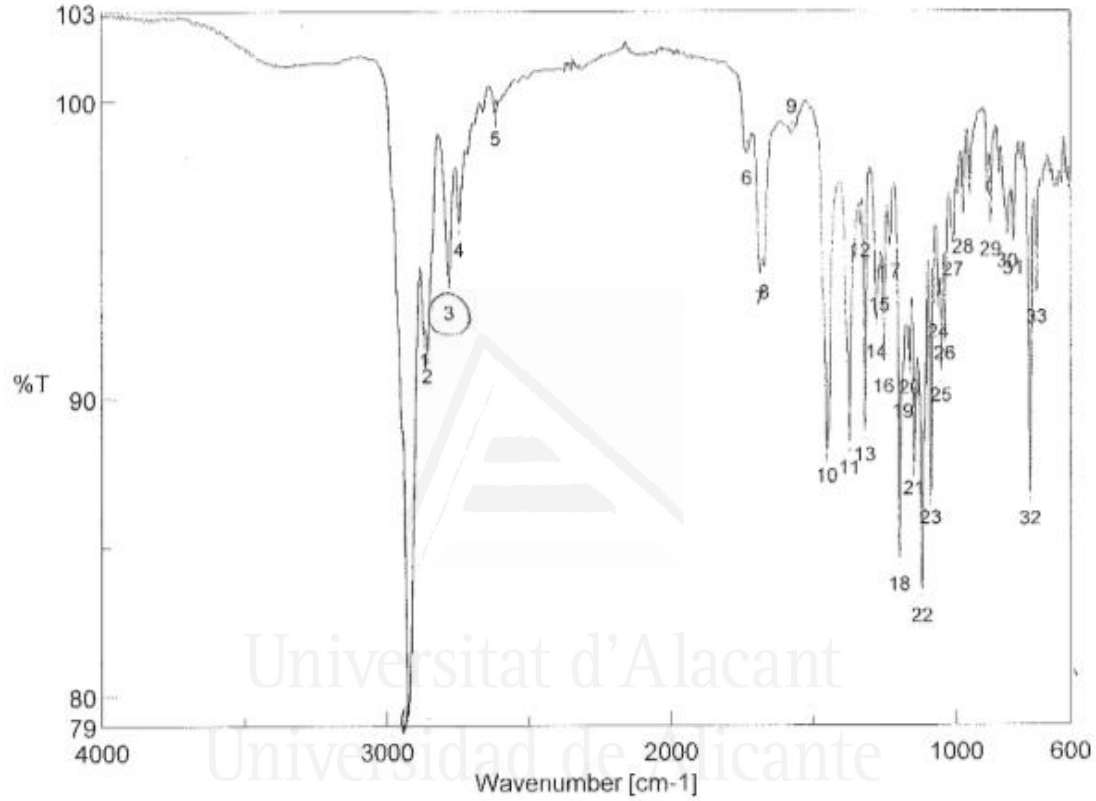
Free (+)-*epi*-Cermizine C: Bohlmann band is shown at 2781.81 cm^{-1}



free-14

free (+)-5-*epi*-cermizine C-TFA



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
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4	2745.17	95.84	5	2616.93	99.57	6	1731.76	98.23
7	1686.44	94.22	8	1671.98	94.41	9	1574.59	98.93
10	1453.1	88.22	11	1373.07	88.47	12	1336.43	95.80
13	1319.07	88.92	14	1279.54	92.39	15	1269.9	93.99
16	1253.5	91.23	17	1231.33	95.11	18	1198.54	84.57
19	1187.94	90.38	20	1162.87	91.19	21	1147.44	87.78
22	1119.48	83.51	23	1089.58	86.80	24	1062.59	93.07
25	1052.94	90.93	26	1040.41	92.34	27	1011.48	95.17
28	975.804	95.93	29	879.381	95.83	30	821.527	95.46
31	799.35	95.21	32	741.496	86.76	33	719.318	93.58