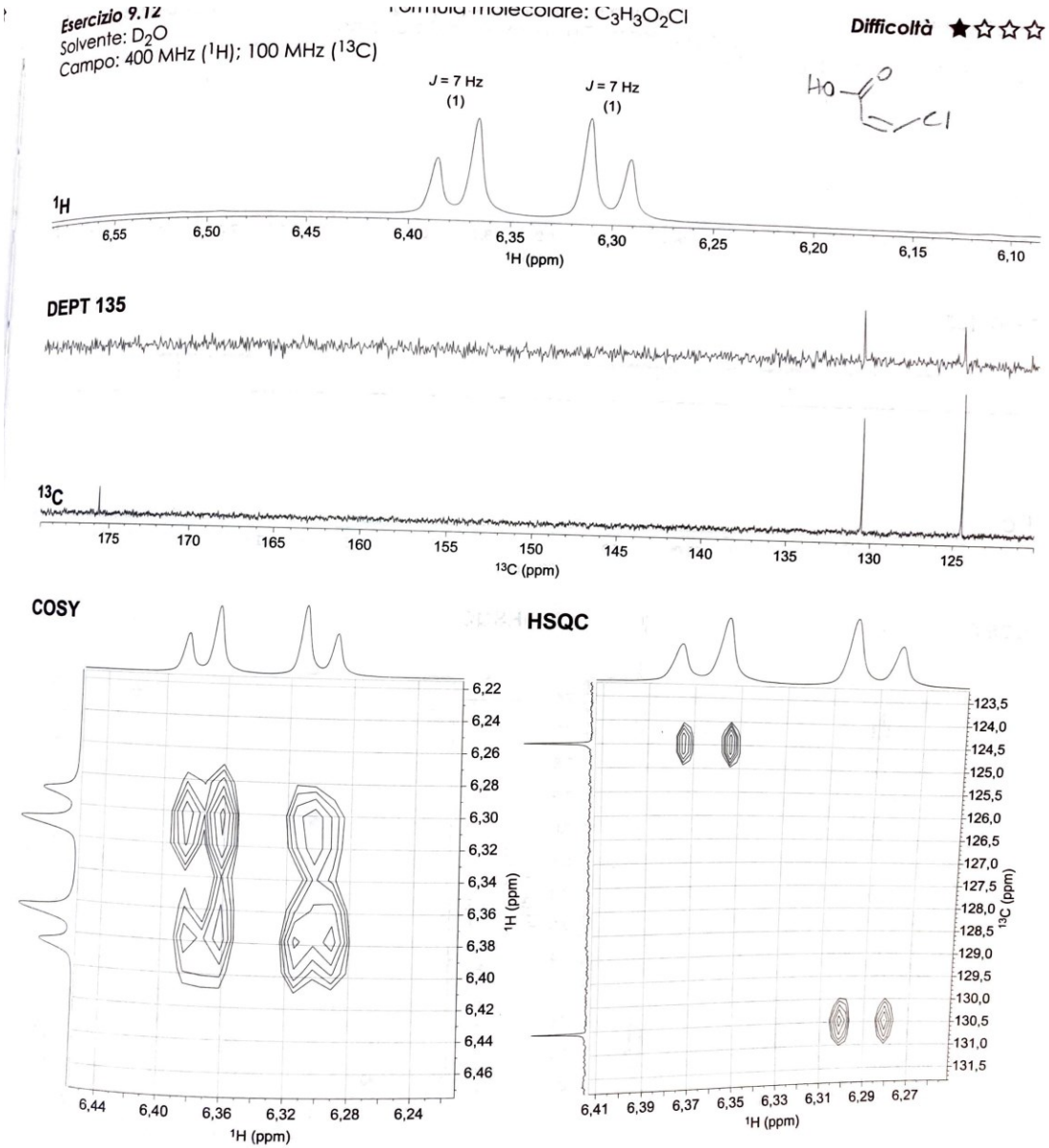
TABLE 10.1 Spectroscopic Techniques and Their Applications in Structure Elucidation of Organic Molecules

Spectroscopic Techniques	Radiation Absorbed	Effect on the Molecule	Structural Information Deduced
Ultraviolet/Visible spectrophotometry	Ultraviolet-visible λ, 190–400 nm and 400–800 nm	Changes in electronic energy levels within the molecule	Extent of π-electron systems. Presence of conjugated unsaturation, and conjugation with nonbonding electrons
Infrared spectrophotometry	Infrared (mid infrared) λ, 2.5–25 mm ν, 400–4000 cm^{-1}	Changes in the vibrational and rotational movements of the molecule	Detection of functional groups, which have specific vibration frequencies, for example, C═O, NH_2, OH, etc.
NMR spectroscopy	Radiofrequency λ, 25 cm	Nuclei placed under the static magnetic field change their spins after absorption of radiofrequency radiations	The electronic environment of nuclei, their numbers and number of neighboring atoms
Circular dichroism (CD)/Optical rotatory dispersion (ORD)	Ultraviolet/visible λ 200–600 nm	Changes in the electronic energy level of a molecule	Identification of absolute configurations of small molecules in solution
Mass spectrometry	High-speed electron beam and other ionization sources	Effects of ionization and fragmentation of charged particles	Relative masses of molecular ions and fragments

TECNICHE NMR PIU' USATE E LORO UTILIZZO

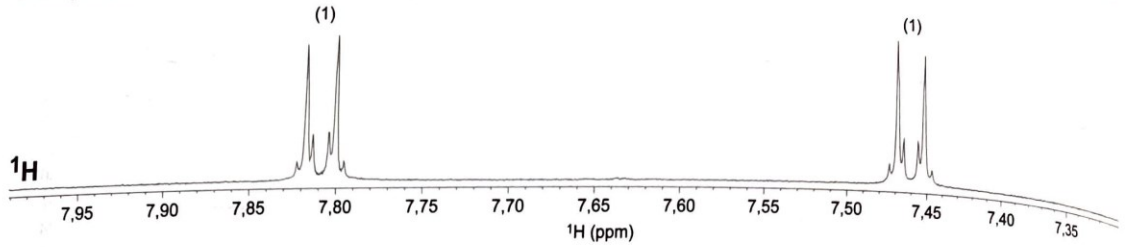
1. 1D-^{1}H NMR: informazioni su chemical shift, J e integrali.
2. 2D-COSY: identifica gli accoppiamenti H-H
3. 1D ^{13}C NMR (BBD) permette di identificare il numero di atomi di C e il loro chemical shift
4. 1D-DEPT: informazioni sulla molteplicità
5. 2D-HSQC (HMQC) identifica gli accoppiamenti C-H diretti (^{1}J)
6. 2D-HMBC identifica accoppiamenti C-H geminali (^{2}J) o vicinali (^{3}J)
7. 2D-NOESY, 1D DIFNOE o 1D NOESY: informazioni su relazioni spaziali.

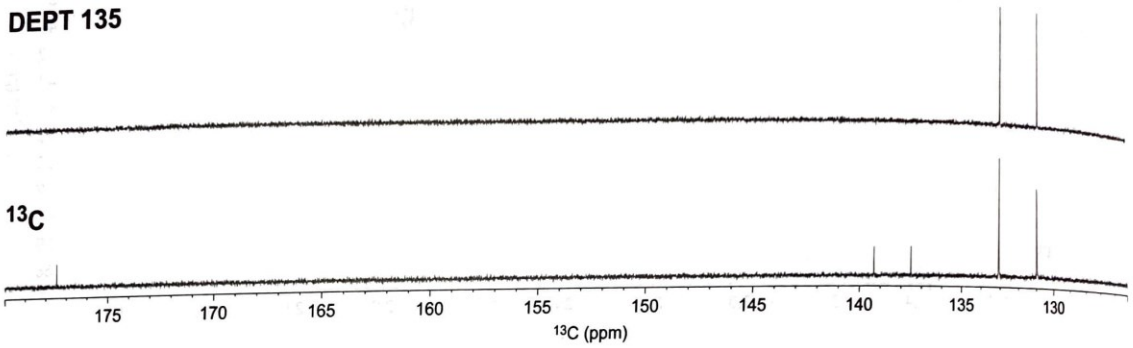


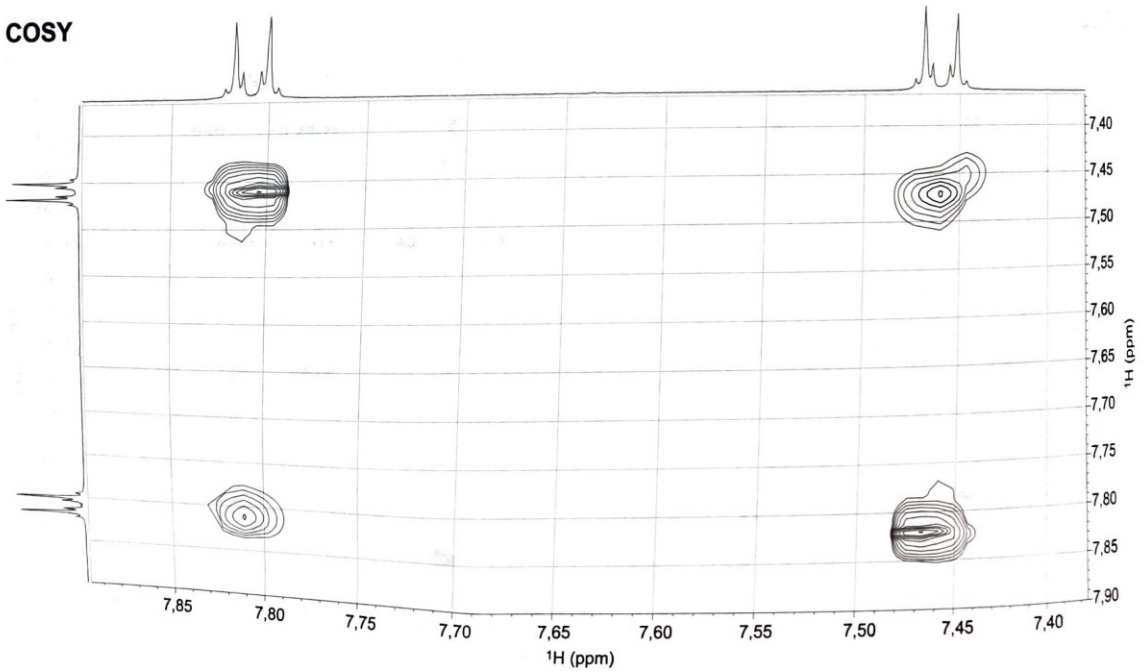
Sistema di spin?

Solvente: D_2O
Campo: 500 MHz (^1H); 125 MHz (^{13}C)

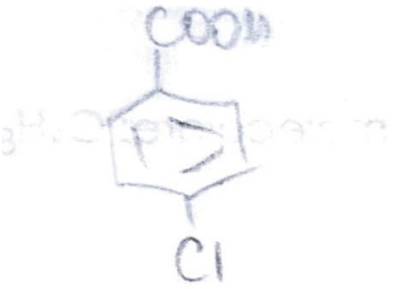
Difficoltà ★☆☆☆







Sistema di spin?

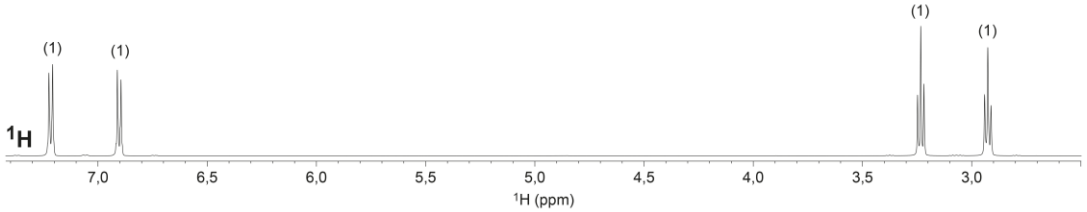


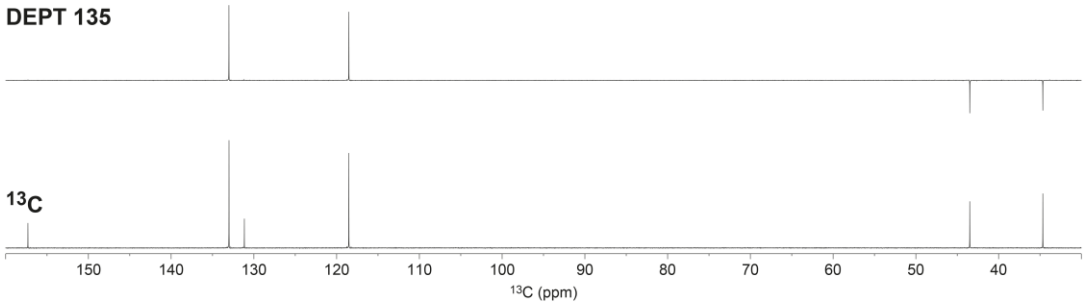
Acido p-clorobenzoico

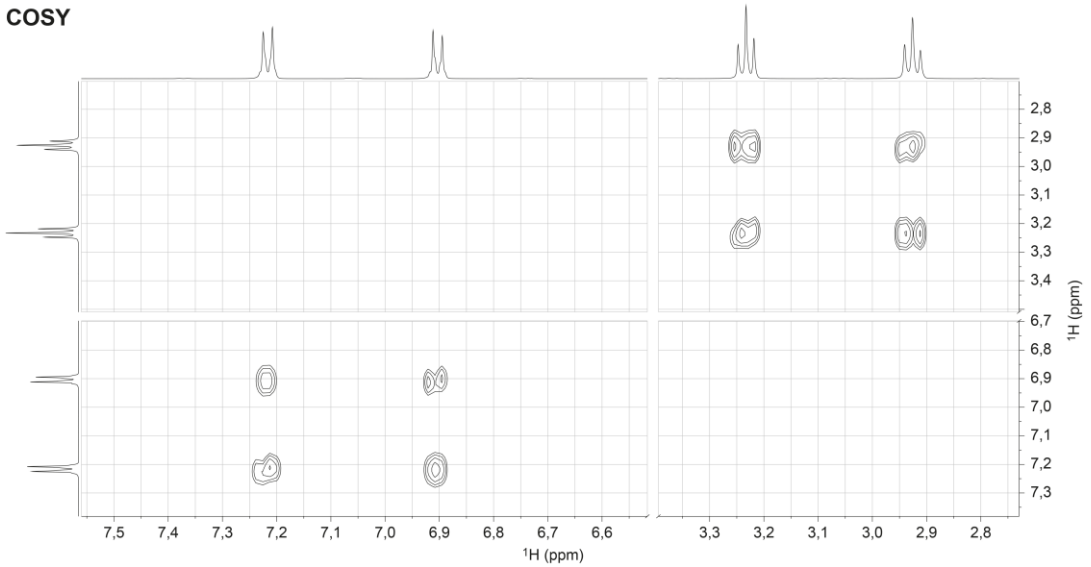
Esercizio 8.11 Formula molecolare: $C_8H_{11}NO$ ***Difficoltà*** ★★☆☆

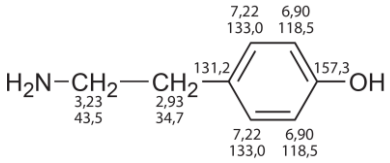
Solvente: D_2O

Campo: 500 MHz (^1H); 125 MHz (^{13}C)



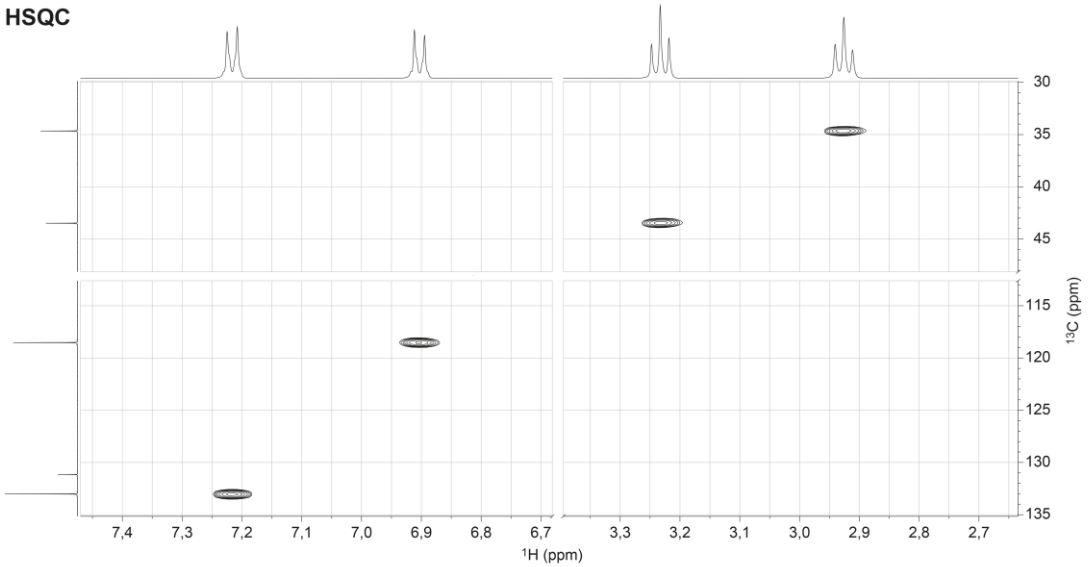


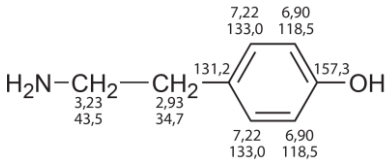




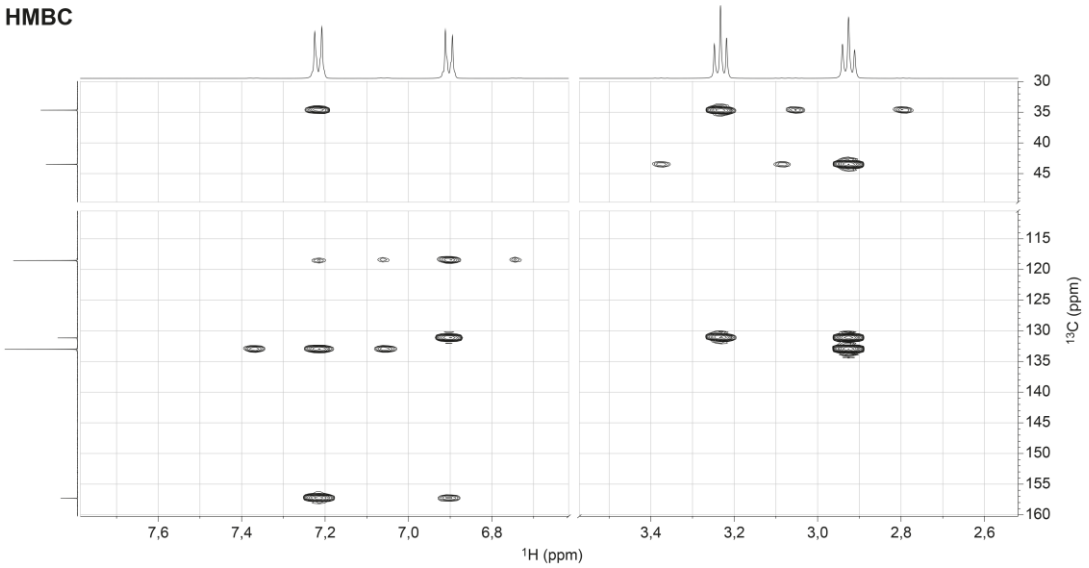
Sistemi di spin?

HSQC


30
35
40
45
115
120
125
130
135
7,4
7,3
7,2
7,1
7,0
6,9
6,8
6,7
3,3
3,2
3,1
3,0
2,9
2,8
2,7
^{1}H (ppm)
^{13}C (ppm)


7,22
133,0
6,90
118,5
131,2
157,3
$H_2N-CH_2-CH_2$
OH
3,23
43,5
2,93
34,7
7,22
133,0
6,90
118,5

HMBC


30
35
40
45
115
120
125
130
135
140
145
150
155
160
7,6
7,4
7,2
7,0
6,8
3,4
3,2
3,0
2,8
2,6
^{1}H (ppm)
^{13}C (ppm)

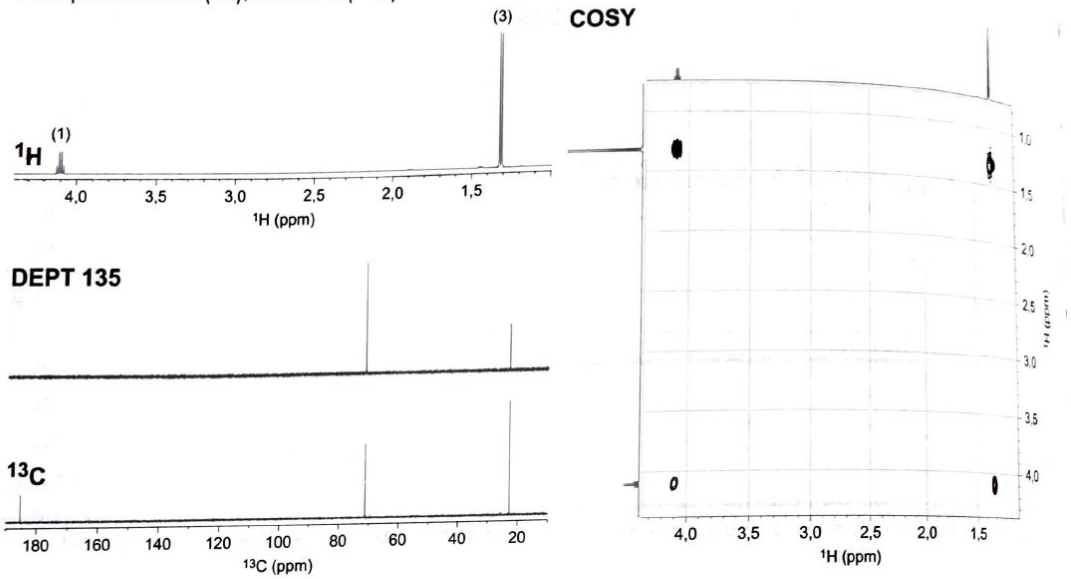
Esercizio 9.11

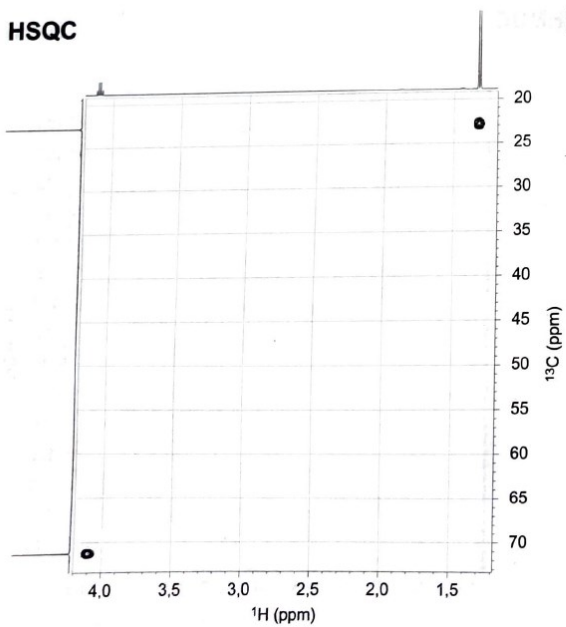
Solvente: D_2O

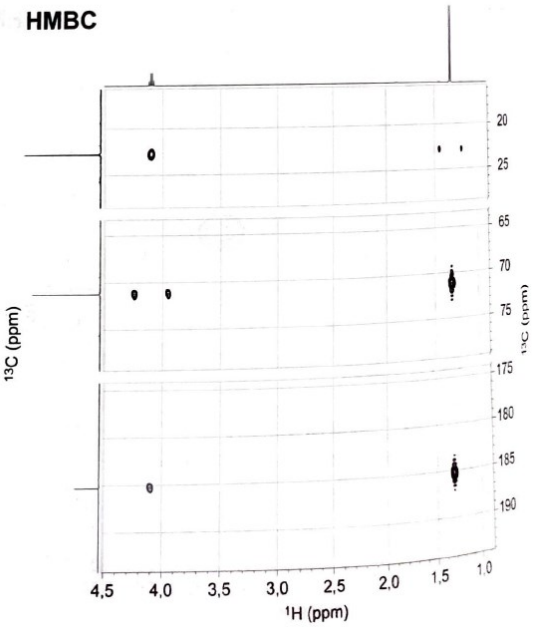
Campo: 500 MHz (^1H); 125 MHz (^{13}C)

Formula molecolare: $C_3H_6O_3$

Difficoltà ★☆☆☆





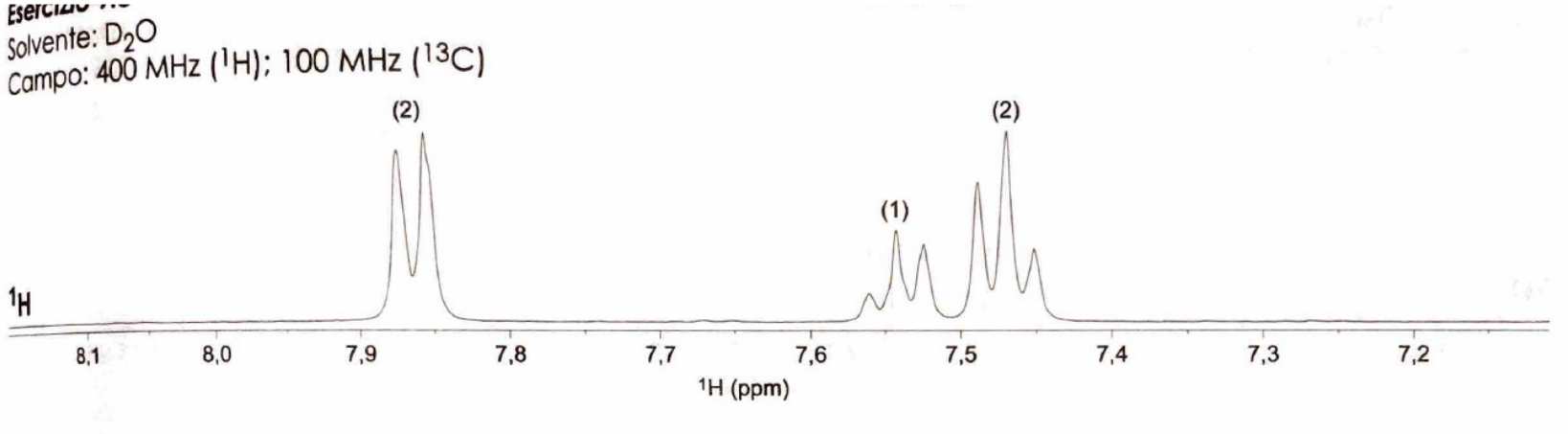


$CH_3CHCOOH$

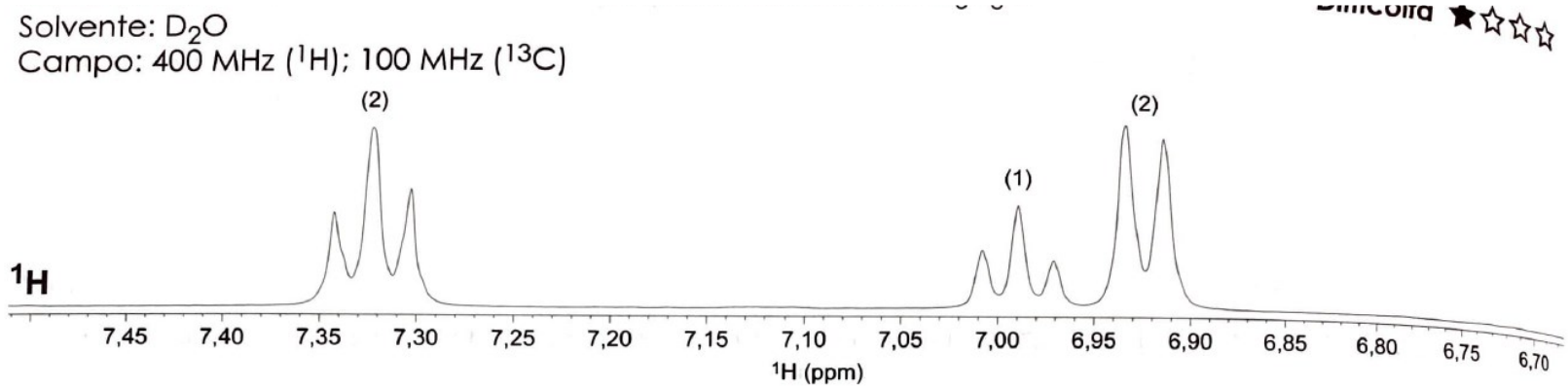
OH

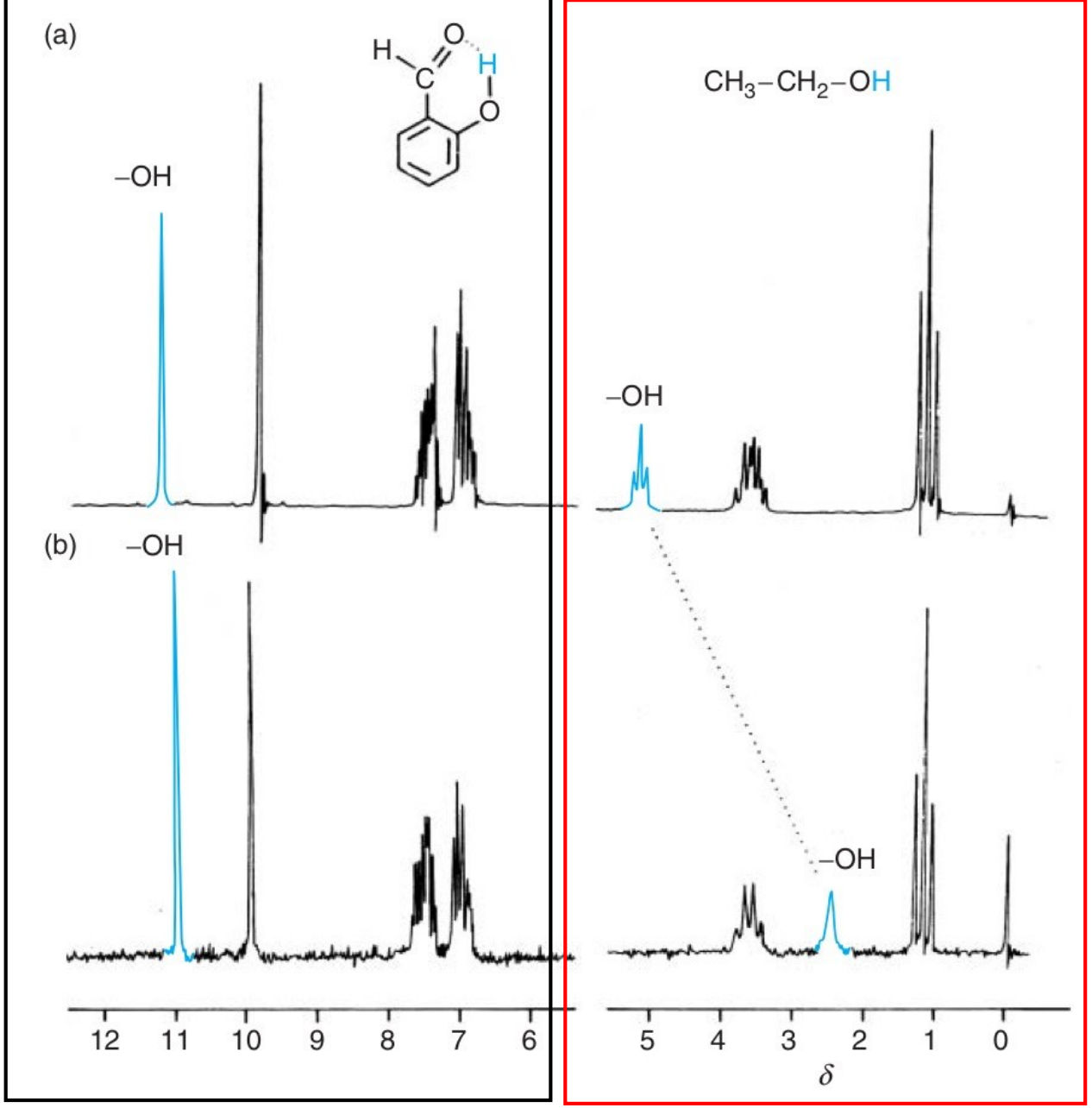
In D2O

Sistema di spin?



Fenolo o acido benzoico?



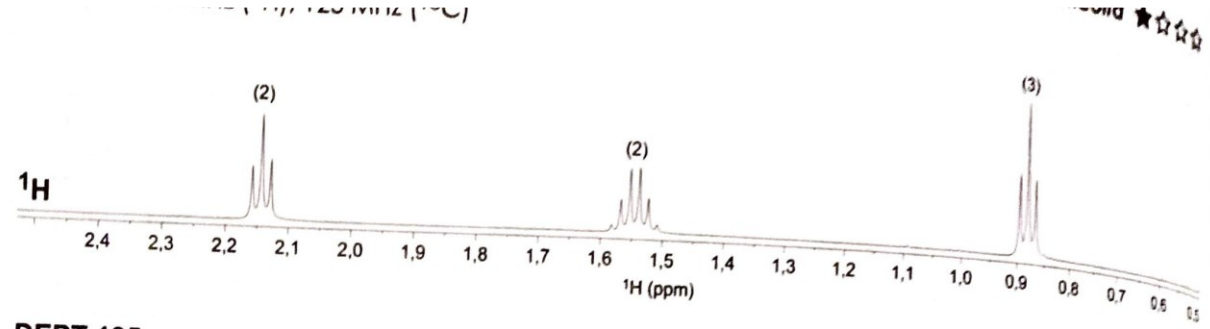


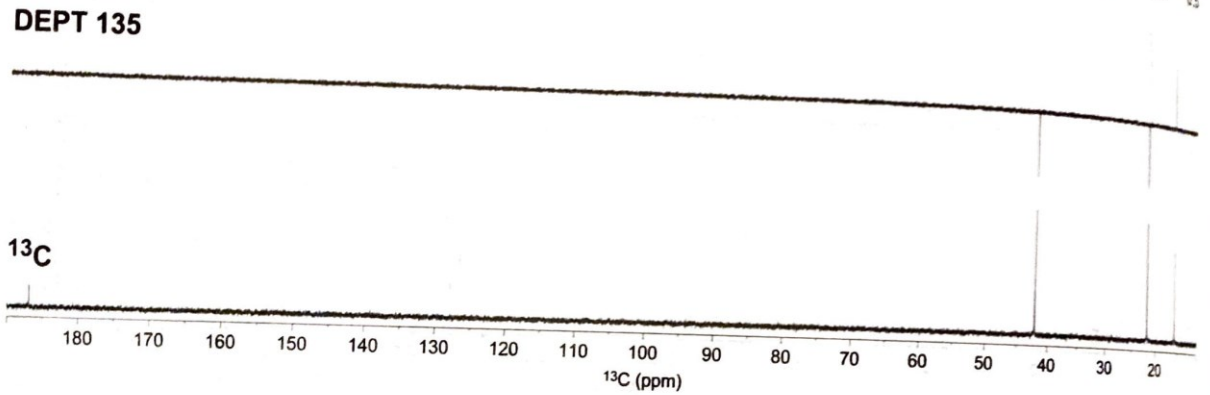
Spiegare le variazioni degli spettri con i solventi

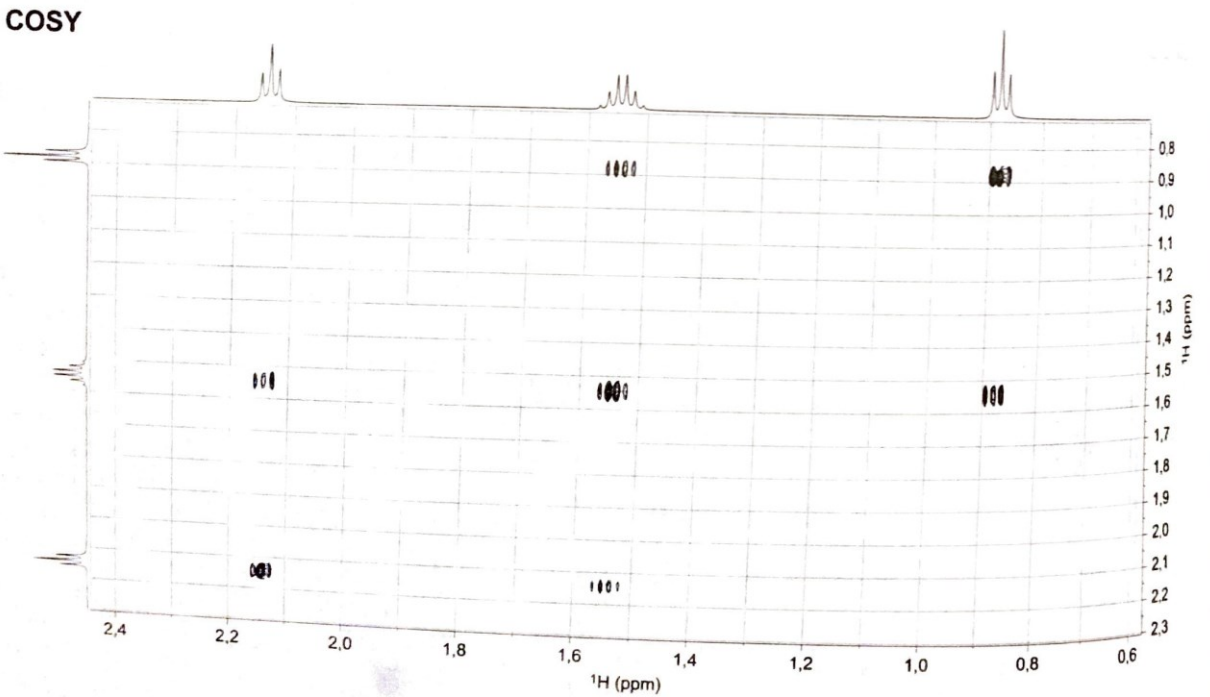
a) DMSO d6

b) CDCl3

Figure 5.21 Concentration dependence of the proton resonance frequency of the hydroxyl protons of salicylaldehyde and ethanol: (a) neat and (b) 5% by volume in CCl_4.



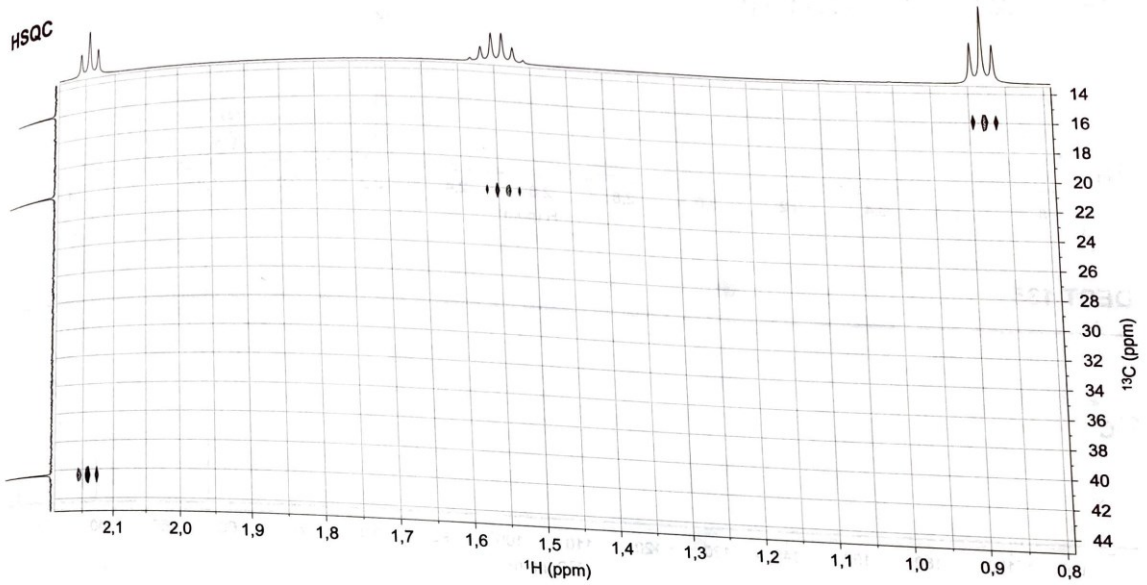




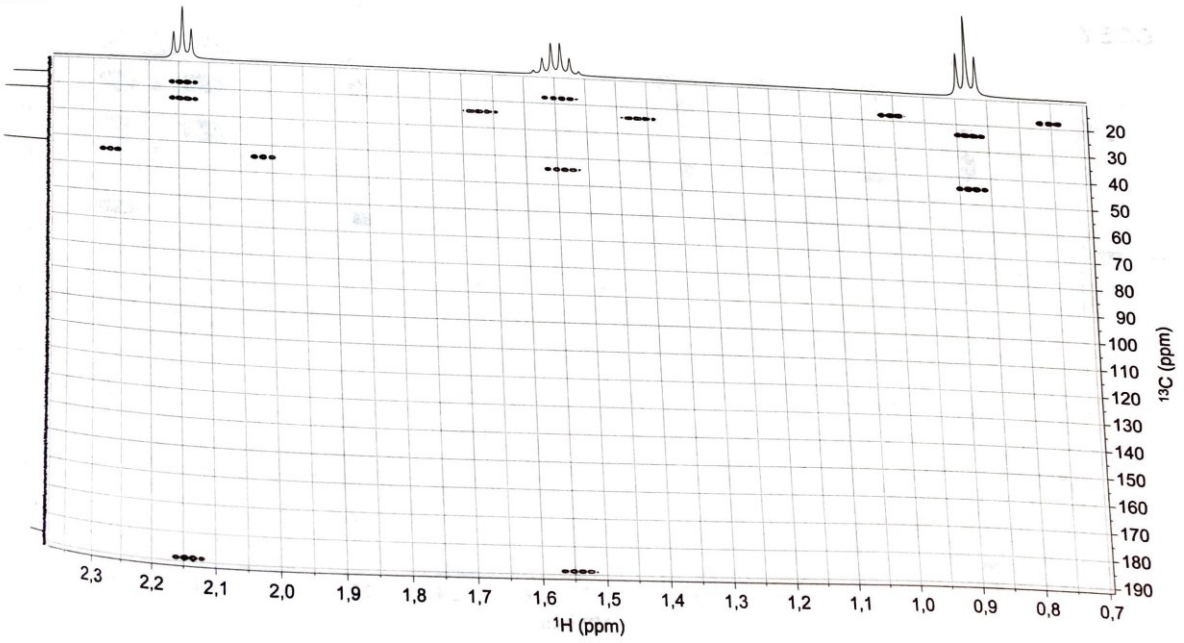
$CH_3CH_2CH_2COOH$

In D2O

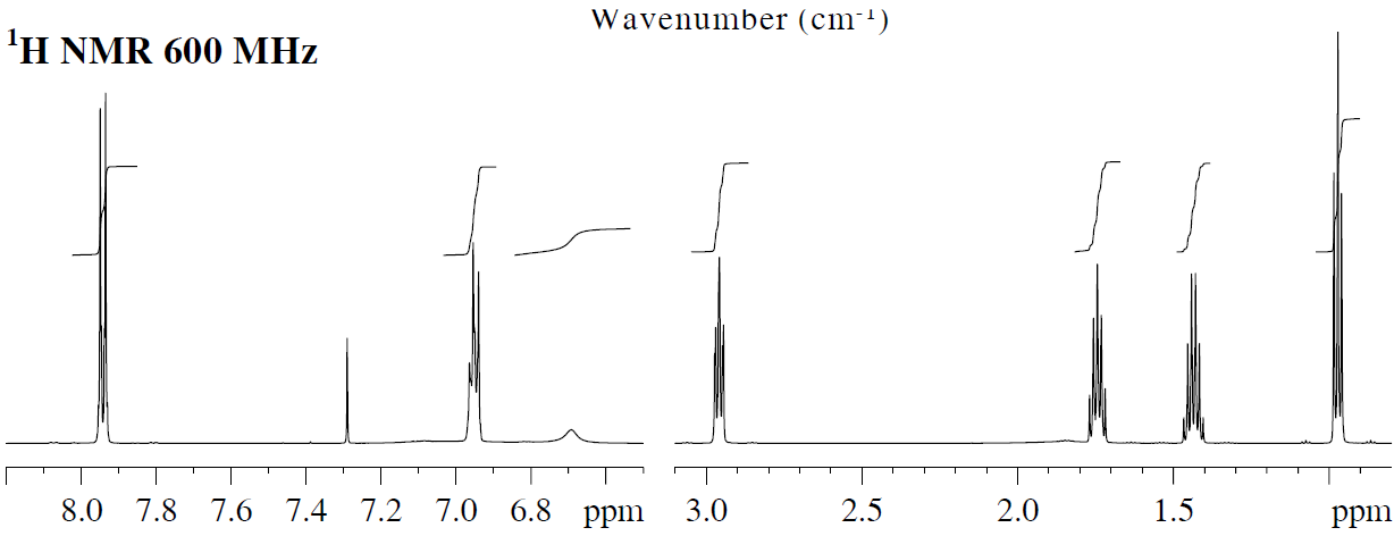
HSQC


14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
13C (ppm)
2,1
2,0
1,9
1,8
1,7
1,6
1,5
1,4
1,3
1,2
1,1
1,0
0,9
0,8
1H (ppm)

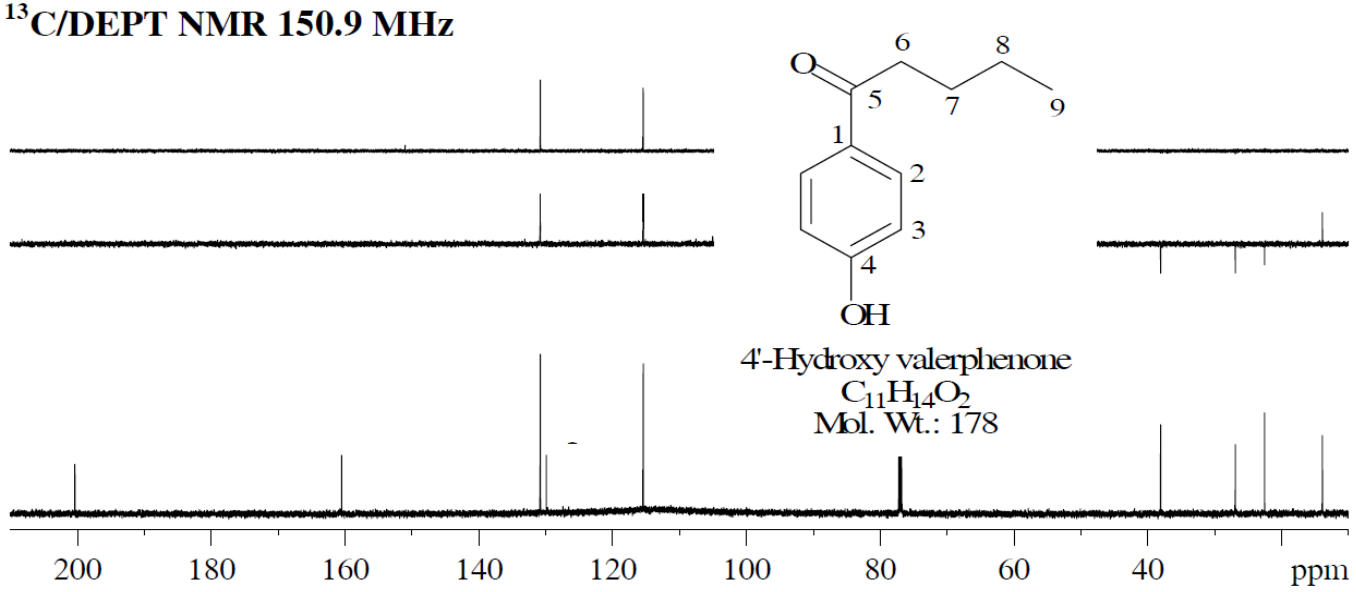
HMBC


20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
13C (ppm)
2,3
2,2
2,1
2,0
1,9
1,8
1,7
1,6
1,5
1,4
1,3
1,2
1,1
1,0
0,9
0,8
0,7
1H (ppm)

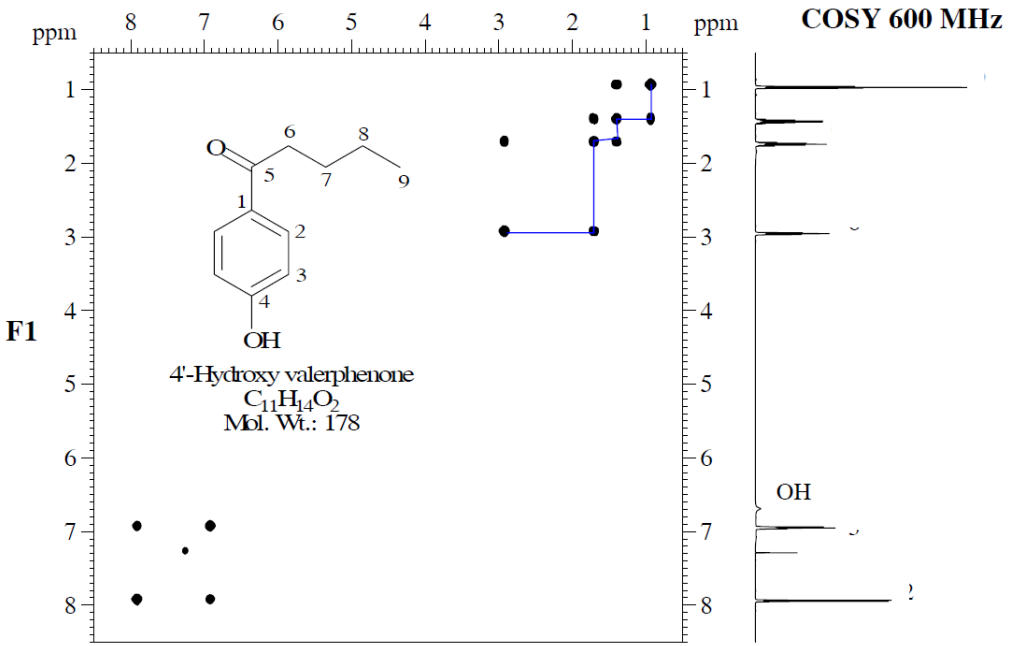
ES. 1

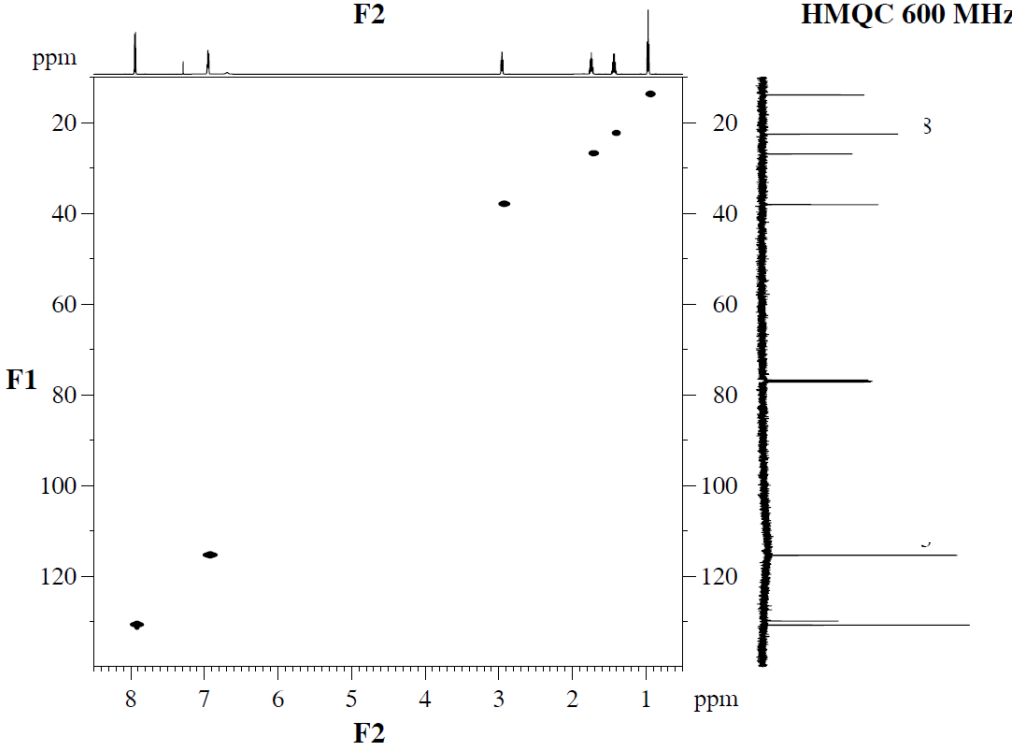

Wavenumber (cm⁻¹)
¹H NMR 600 MHz
8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
3.0 2.5 2.0 1.5 ppm

In CDCl3

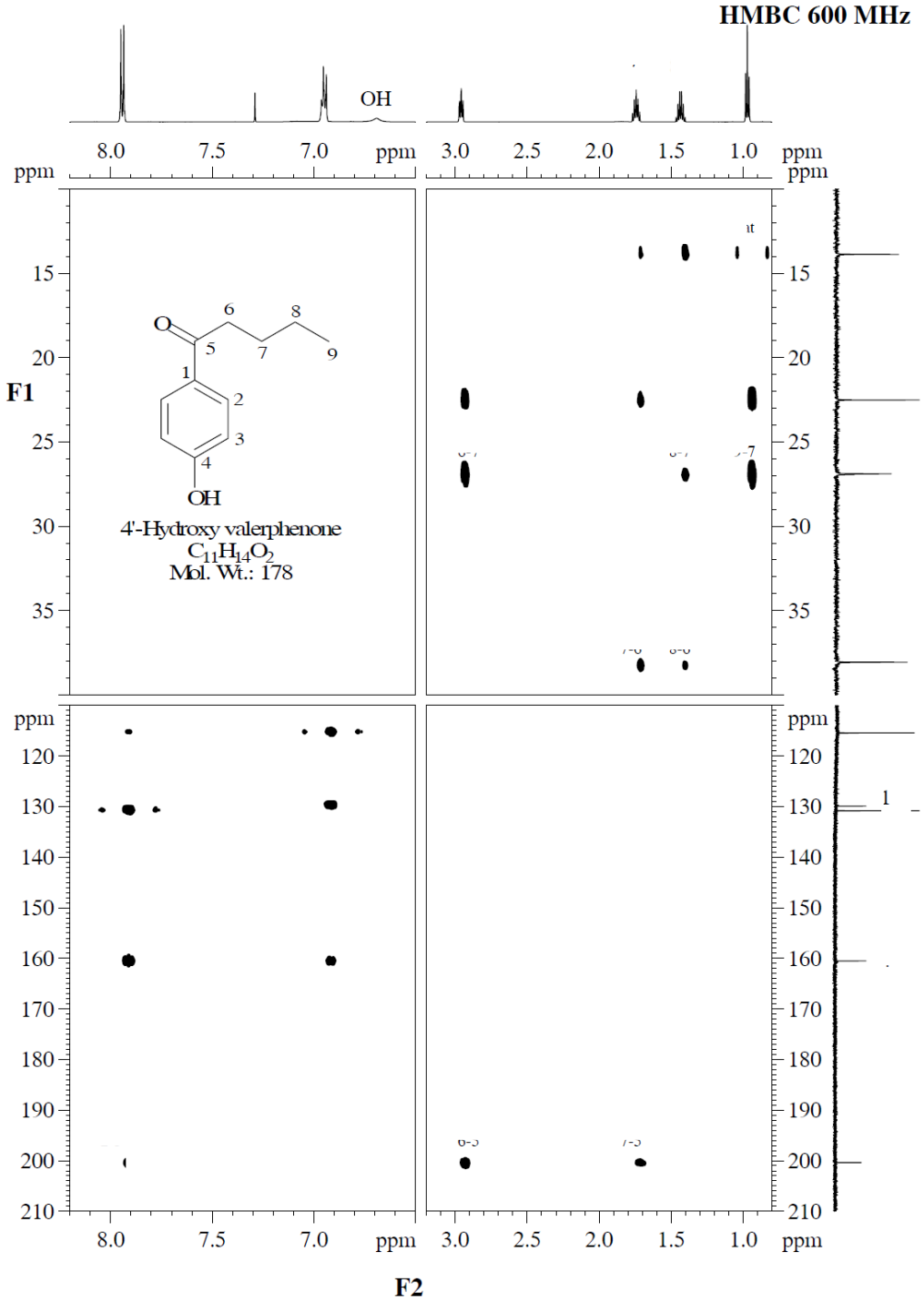

¹³C/DEPT NMR 150.9 MHz
O
OH
1 2 3 4 5 6 7 8 9
4'-Hydroxy valerphenone
C11H14O2
Mol. Wt.: 178
200 180 160 140 120 100 80 60 40 ppm

ES. 1


COSY 600 MHz
ppm
F1
F2
OH
4'-Hydroxy valerphenone
$C_{11}H_{14}O_2$
Mol. Wt.: 178


HMQC 600 MHz
ppm
F1
F2

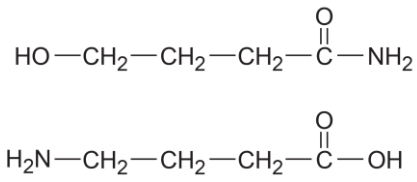
ES. 1


HMBC 600 MHz
OH
8.0
7.5
7.0
ppm
3.0
2.5
2.0
1.5
1.0
F1
F2
4'-Hydroxy valerphenone
$C_{11}H_{14}O_2$
Mol. Wt.: 178

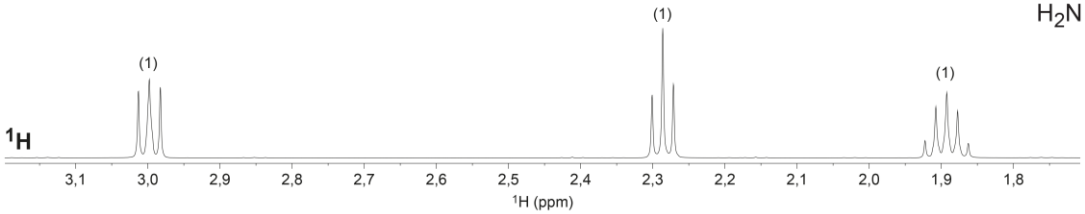
Esercizio 8.9 Formula molecolare: $C_4H_9NO_2$ ***Difficoltà*** ★

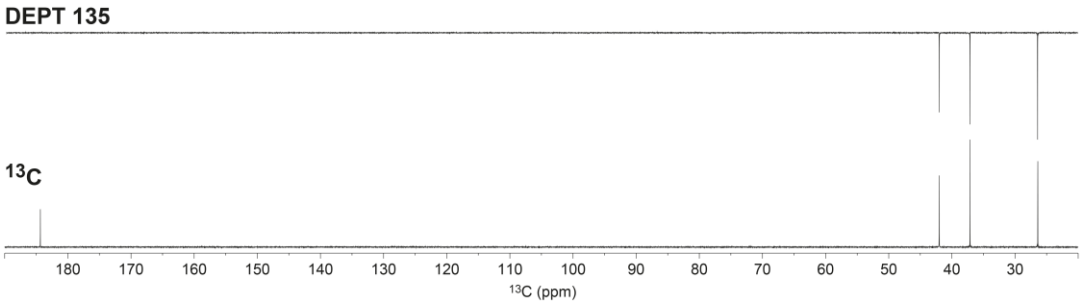
Solvente: D_2O

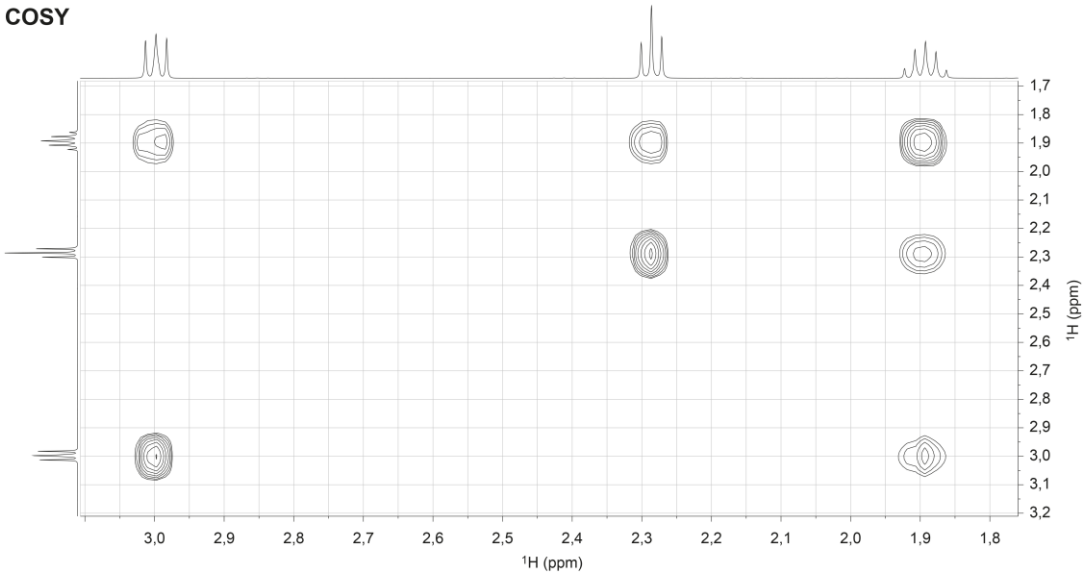
Campo: 500 MHz (^1H); 125 MHz (^{13}C)



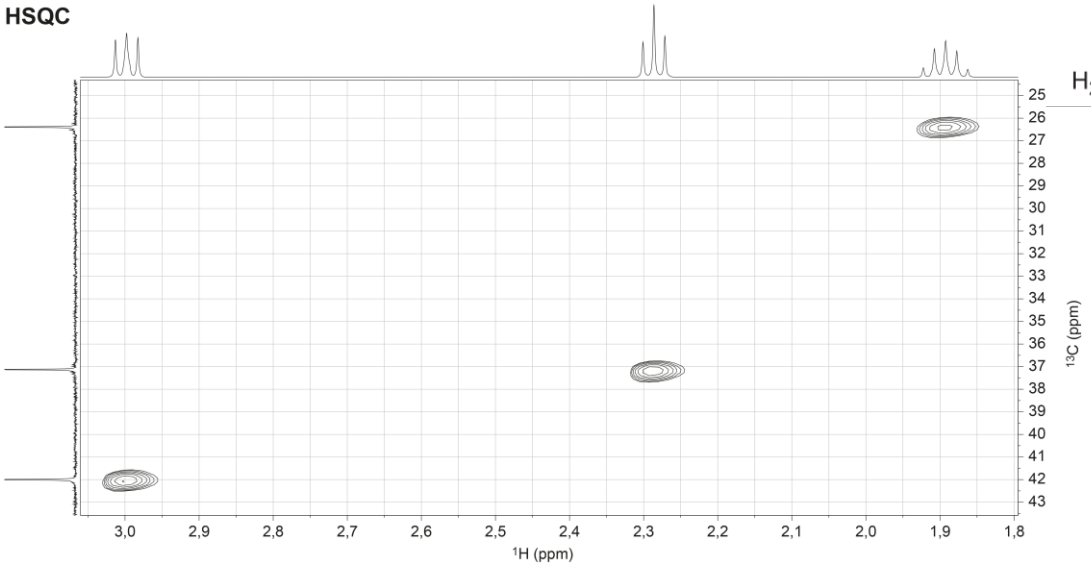
In D2O

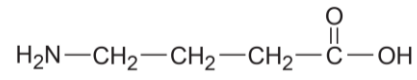




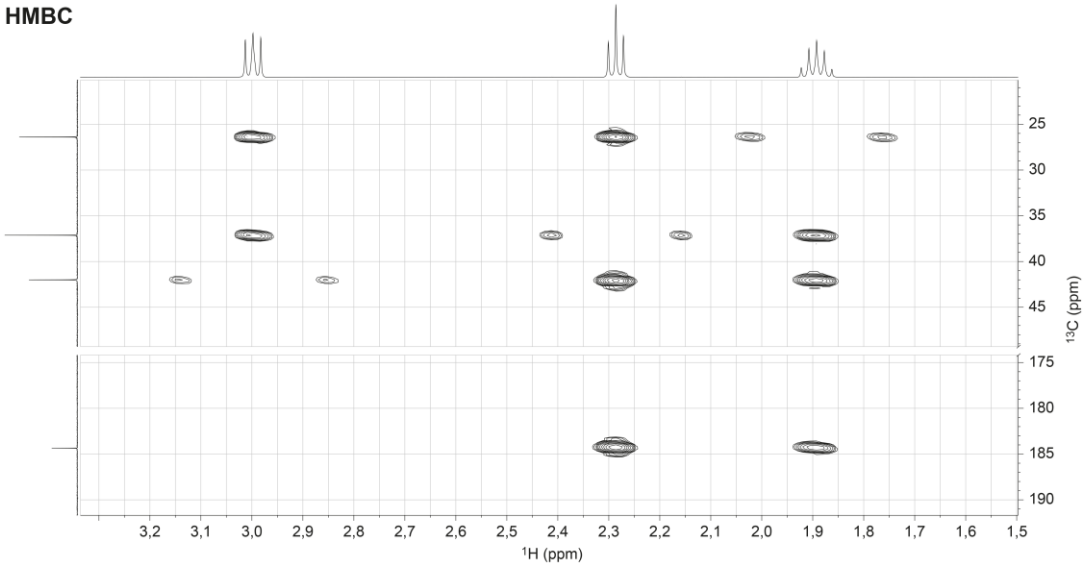


HSQC


25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
^{13}C (ppm)
3,0
2,9
2,8
2,7
2,6
2,5
2,4
2,3
2,2
2,1
2,0
1,9
1,8
^{1}H (ppm)

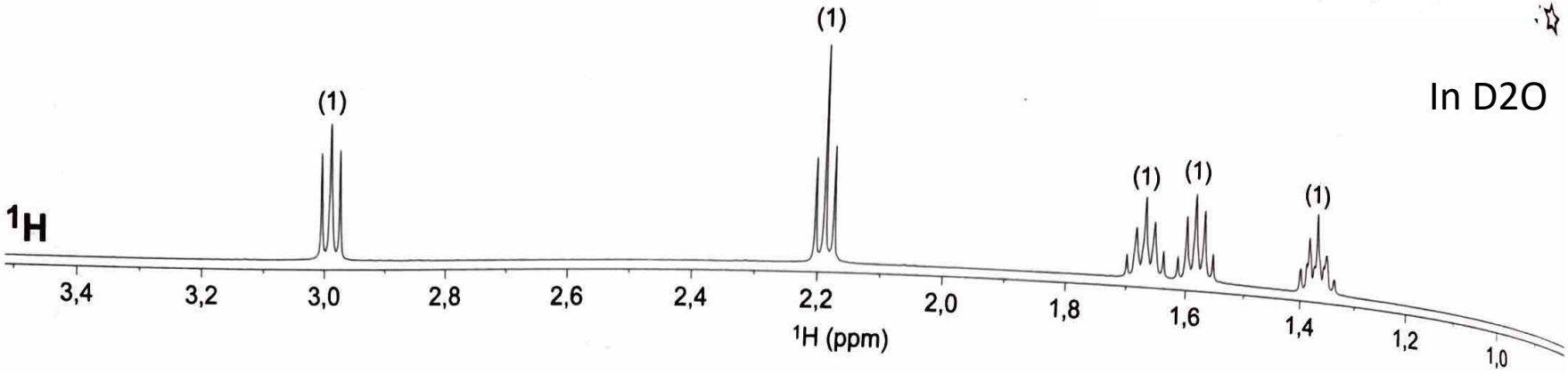

O
H_2N—CH_2—CH_2—CH_2—C—OH

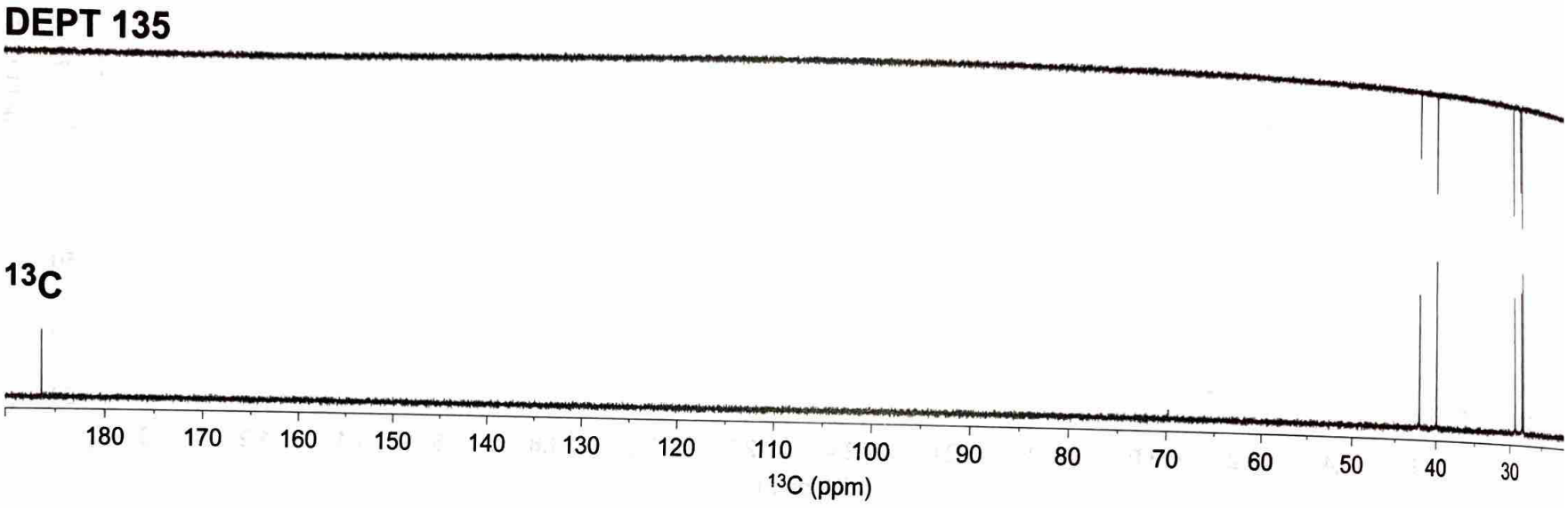
HMBC

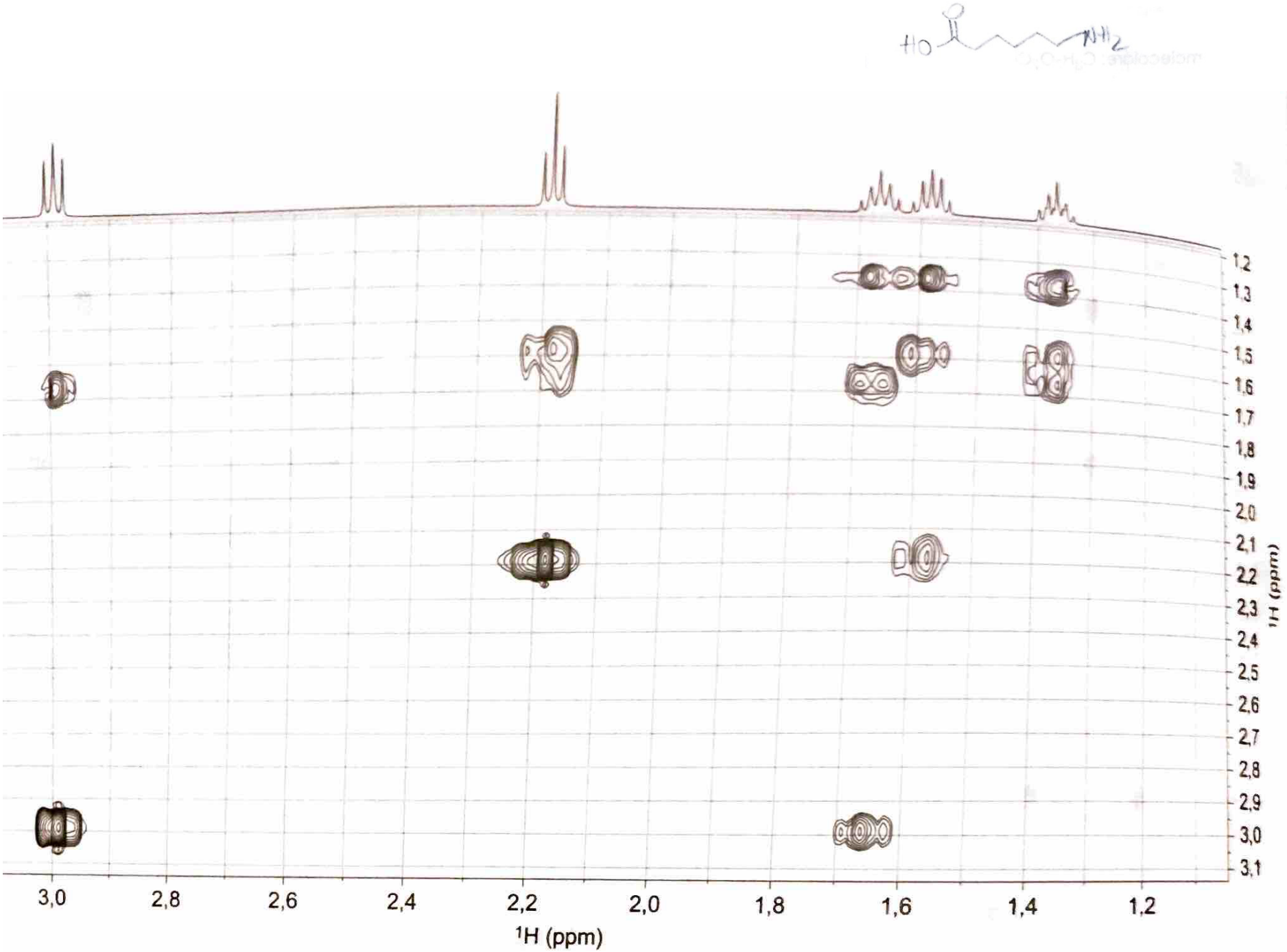

25
30
35
40
45
175
180
185
190
^{13}C (ppm)
3,2
3,1
3,0
2,9
2,8
2,7
2,6
2,5
2,4
2,3
2,2
2,1
2,0
1,9
1,8
1,7
1,6
1,5
^{1}H (ppm)

Campo: 500 MHz (^{1}H); 125 MHz (^{13}C)

In D2O

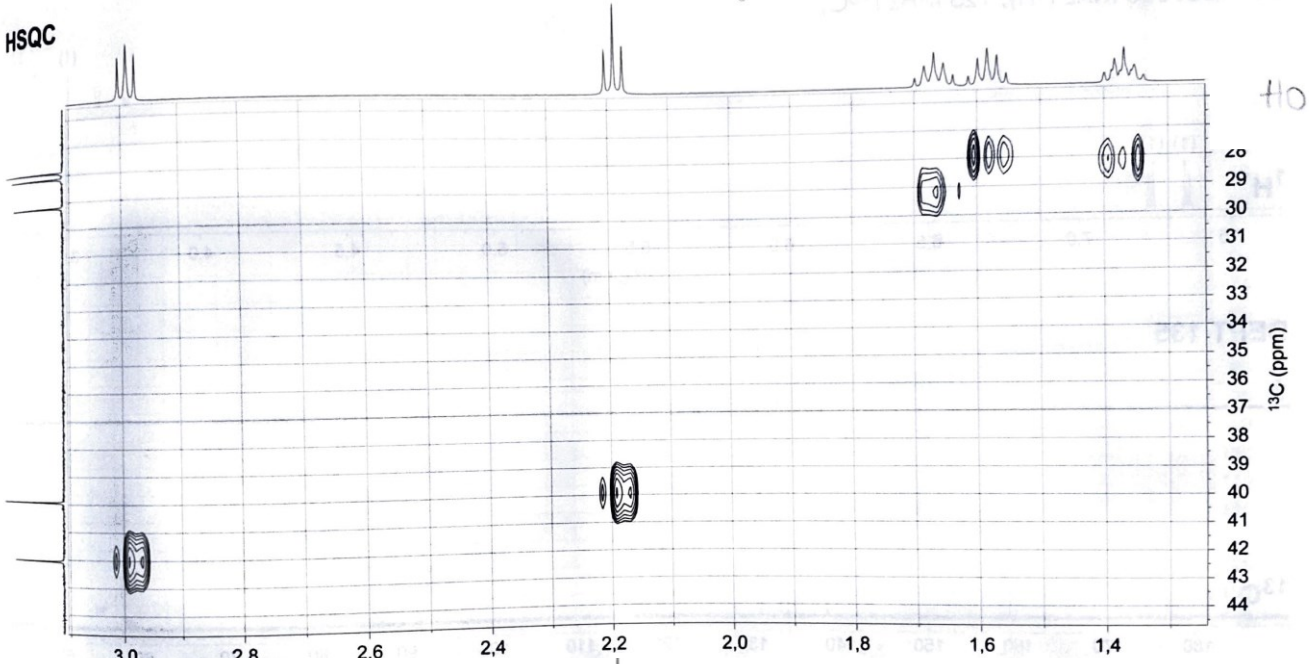




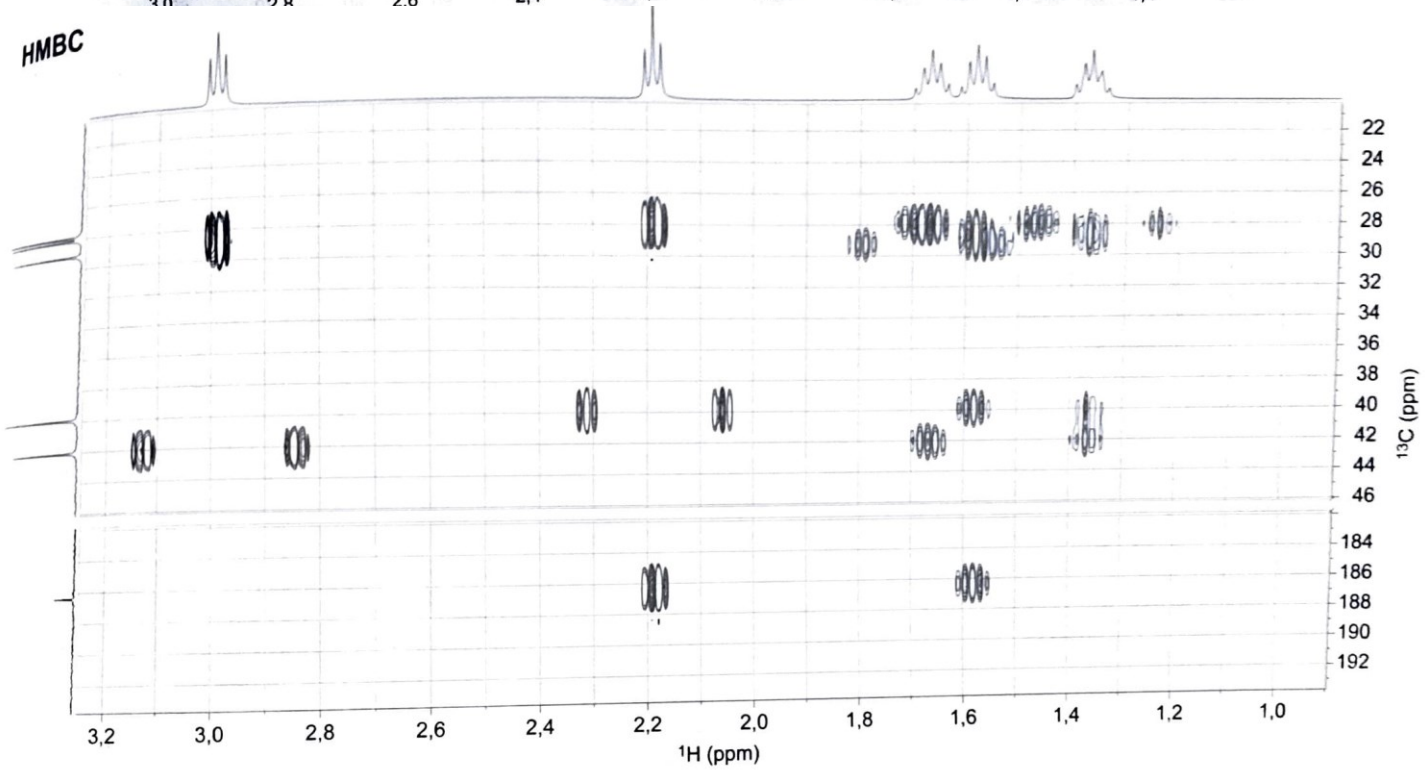

HO
NH2
1,2
1,3
1,4
1,5
1,6
1,7
1,8
1,9
2,0
2,1
2,2
2,3
2,4
2,5
2,6
2,7
2,8
2,9
3,0
3,1
1H (ppm)
3,0
2,8
2,6
2,4
2,2
2,0
1,8
1,6
1,4
1,2
1H (ppm)

HSQC


HO
NH2
1
6

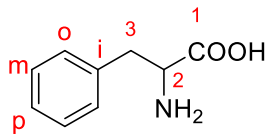

28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
13C (ppm)
3,0
2,8
2,6
2,4
2,2
2,0
1,8
1,6
1,4

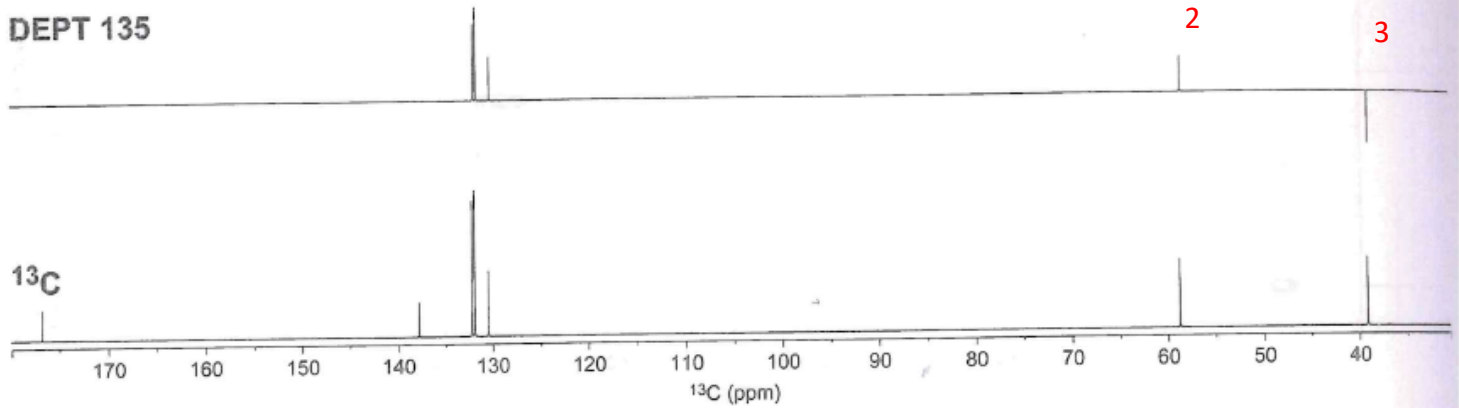
HMBC

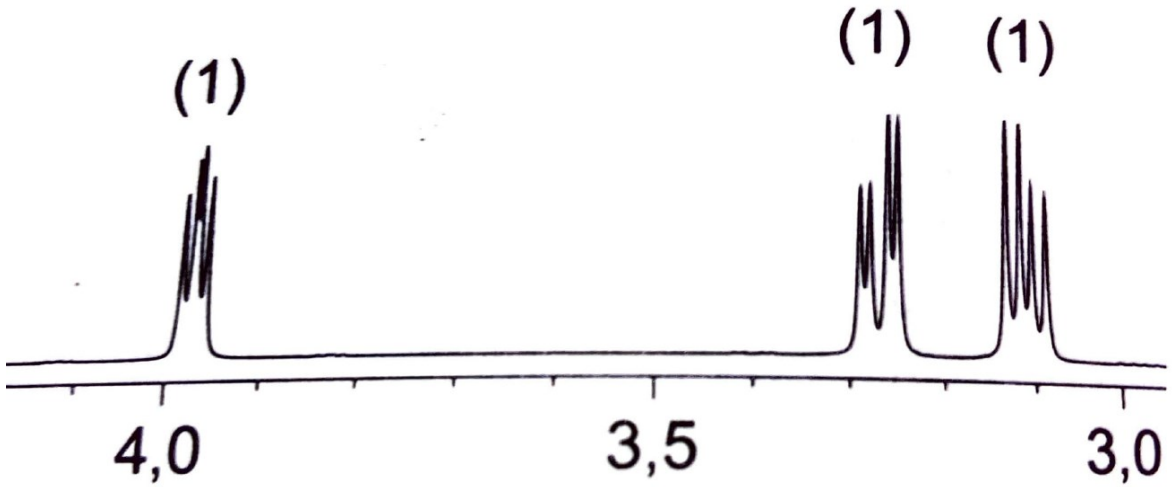

22
24
26
28
30
32
34
36
38
40
42
44
46
184
186
188
190
192
13C (ppm)
3,2
3,0
2,8
2,6
2,4
2,2
2,0
1,8
1,6
1,4
1,2
1,0
1H (ppm)

Solvente: D_2O Suggerimento: È un amminoacido naturale

Campo: 500 MHz (^1H); 125 MHz (^{13}C)



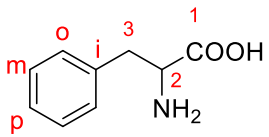


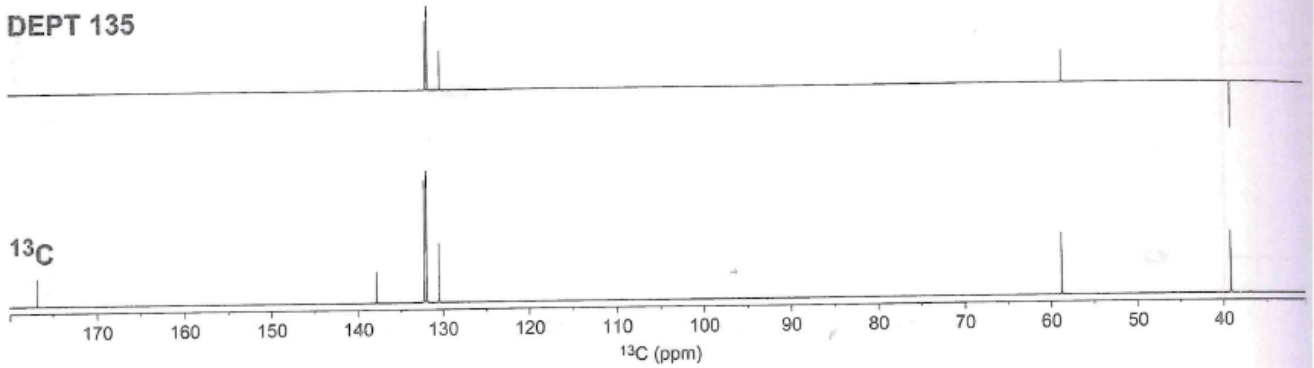


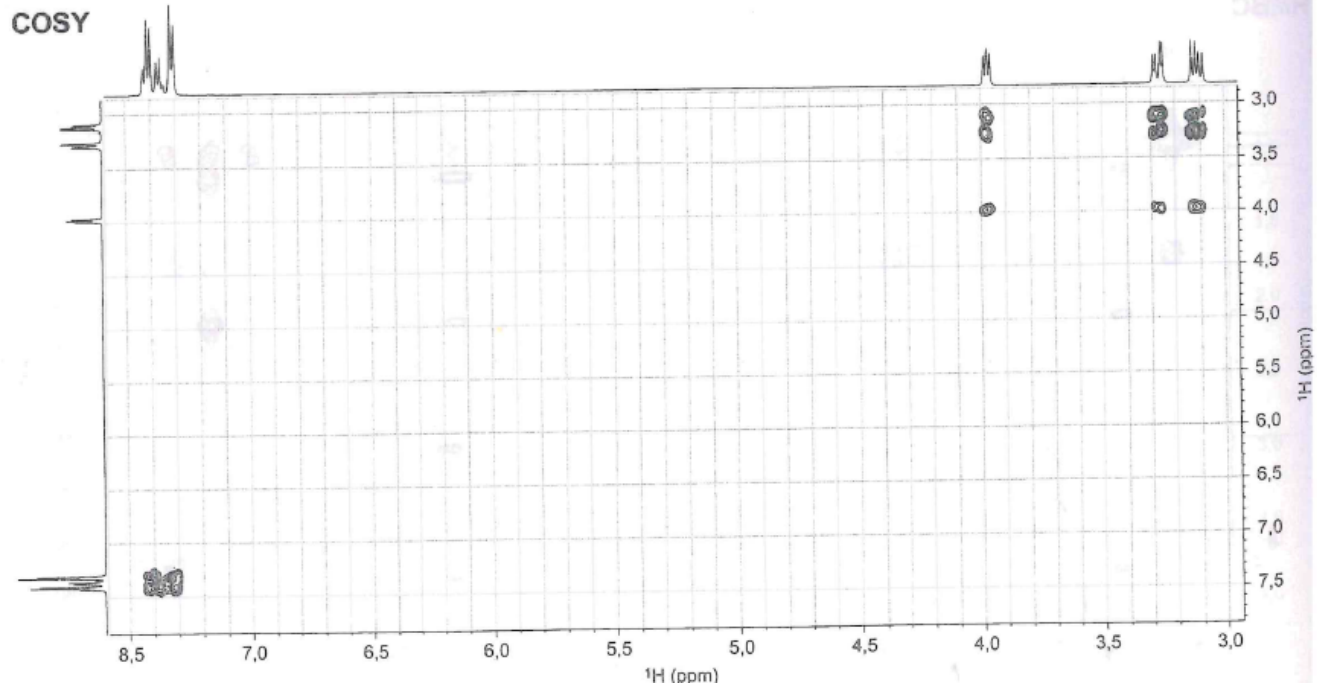
Sistema di spin?

Solvente: D_2O Suggerimento: È un amminoacido naturale

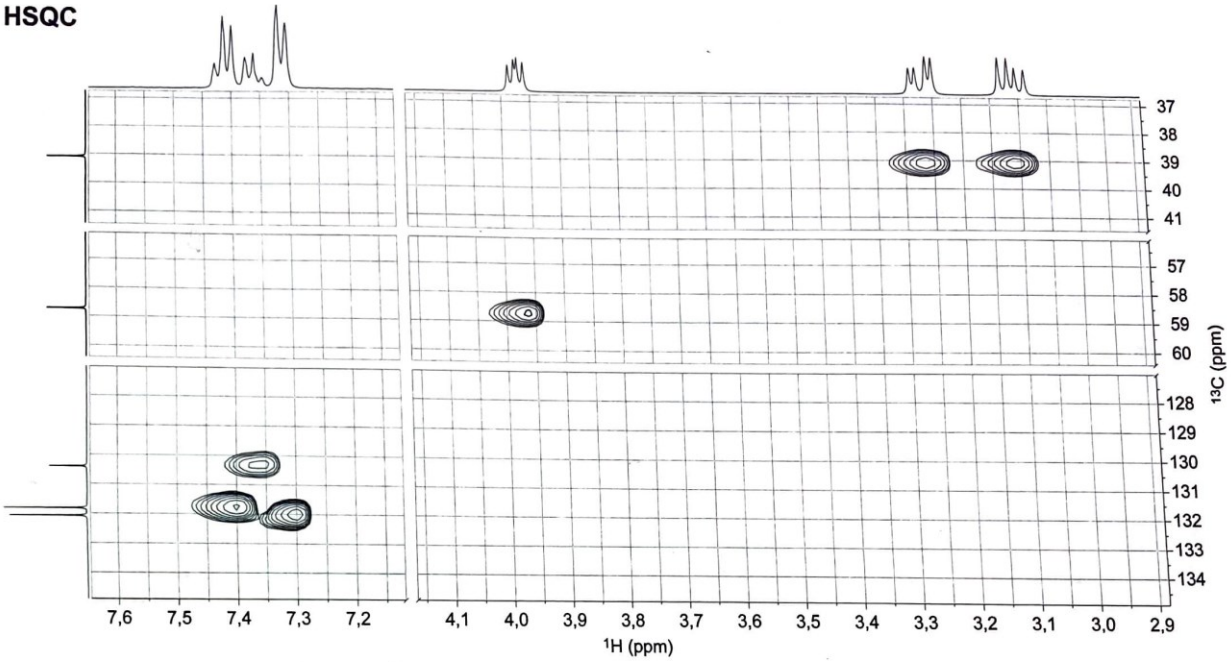
Campo: 500 MHz (^1H); 125 MHz (^{13}C)

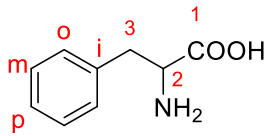




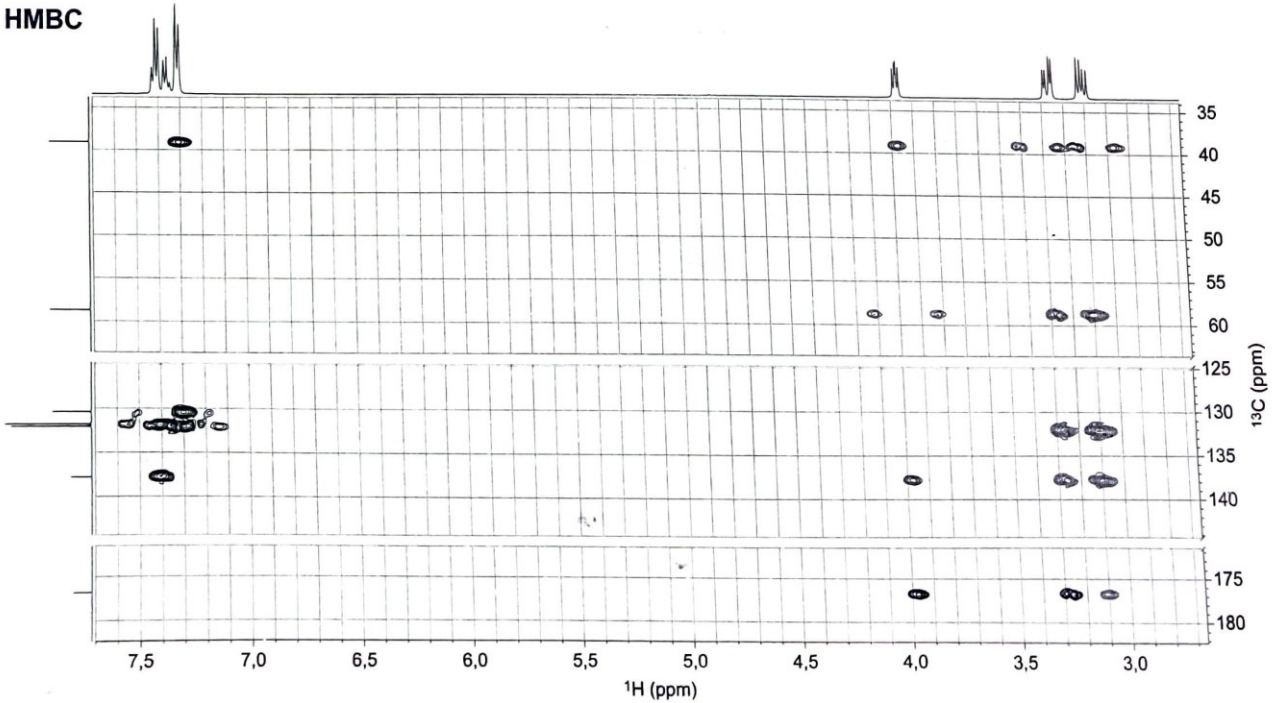


HSQC


37
38
39
40
41
57
58
59
60
128
129
130
131
132
133
134
13C (ppm)
7,6
7,5
7,4
7,3
7,2
4,1
4,0
3,9
3,8
3,7
3,6
3,5
3,4
3,3
3,2
3,1
3,0
2,9
1H (ppm)

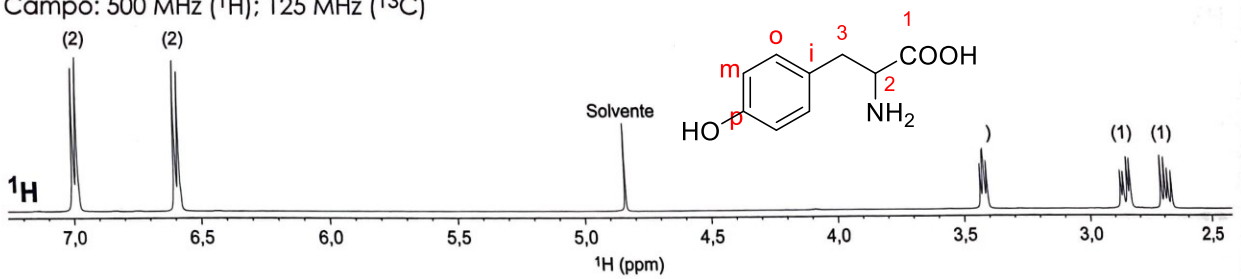

o
i
3
1
COOH
m
2
NH2
p

HMBC

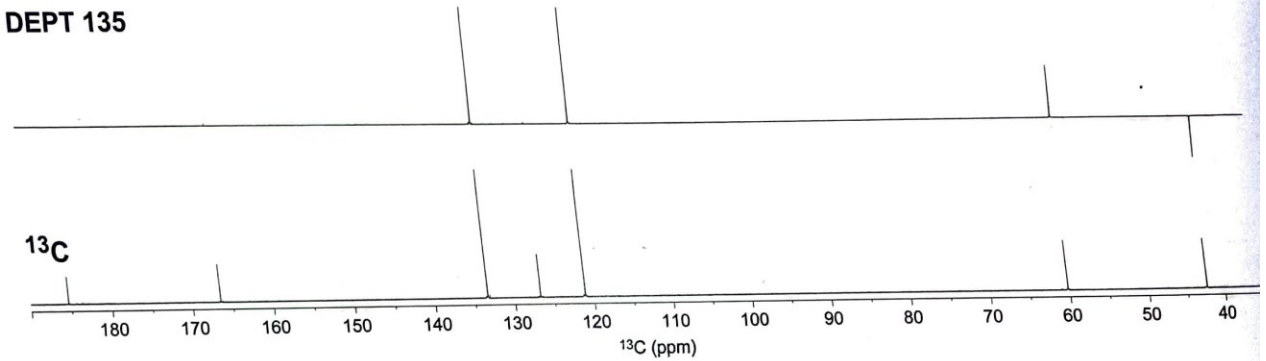

35
40
45
50
55
60
125
130
135
140
175
180
13C (ppm)
7,5
7,0
6,5
6,0
5,5
5,0
4,5
4,0
3,5
3,0
1H (ppm)

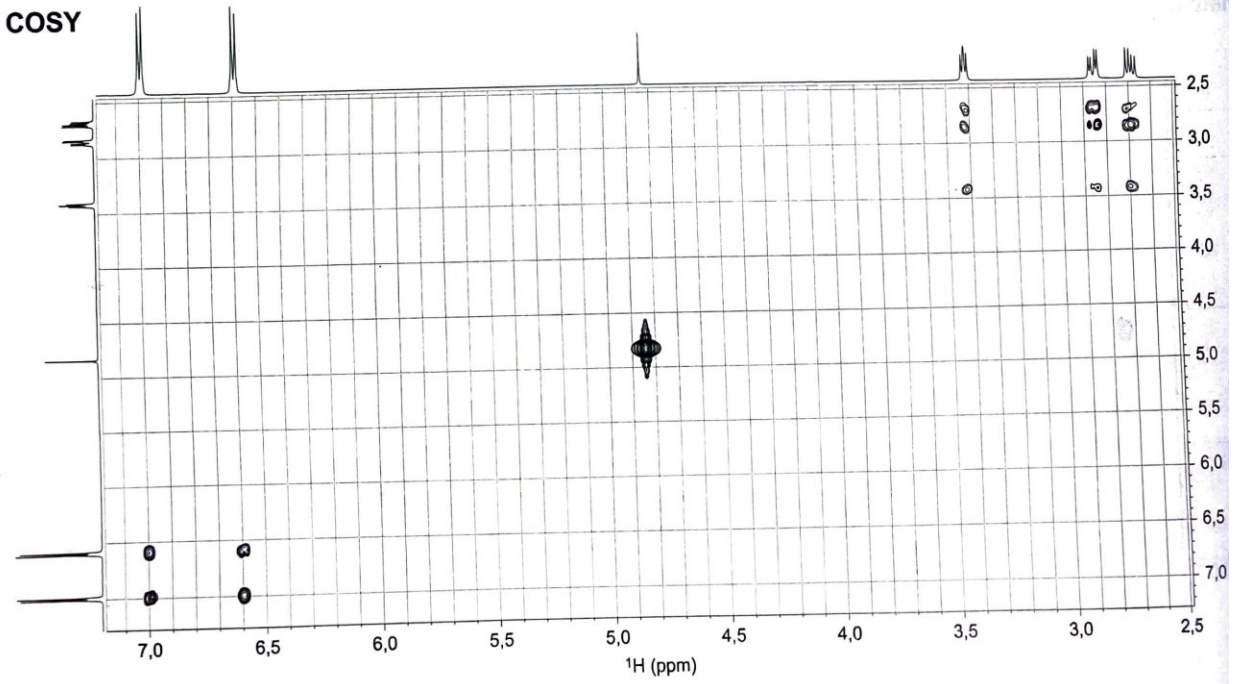
Solvente: D_2O Suggerimento: È un amminoacido naturale

Campo: 500 MHz (^1H); 125 MHz (^{13}C)

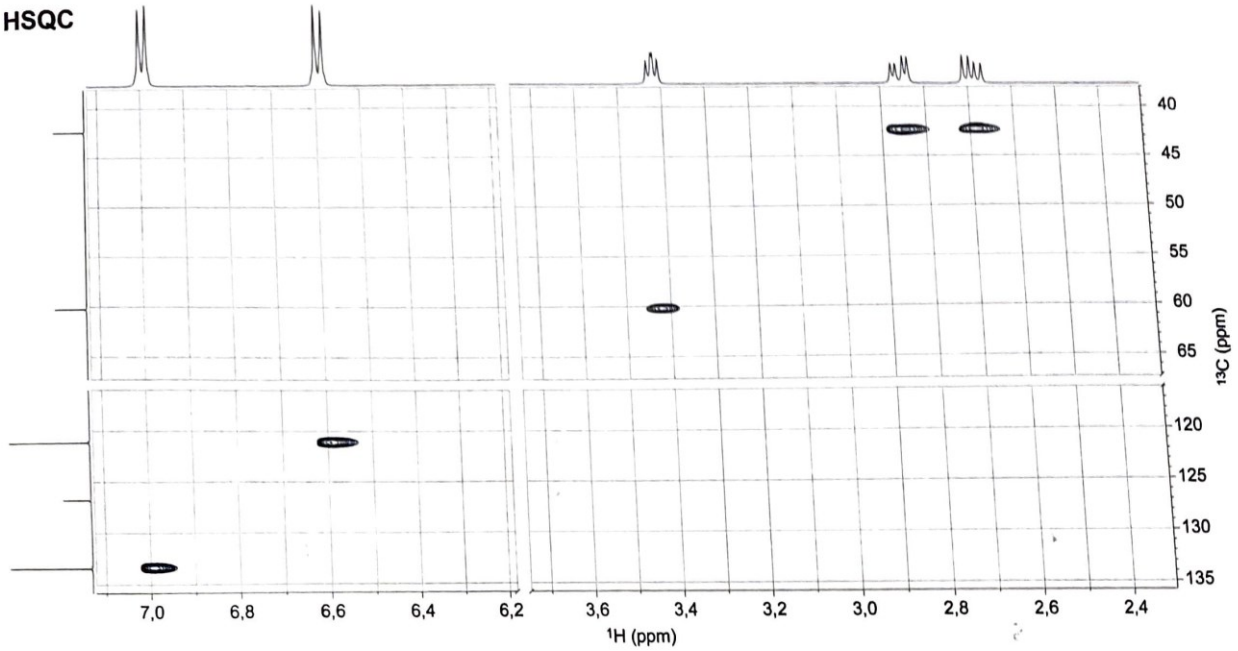


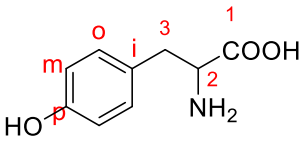
In D2O



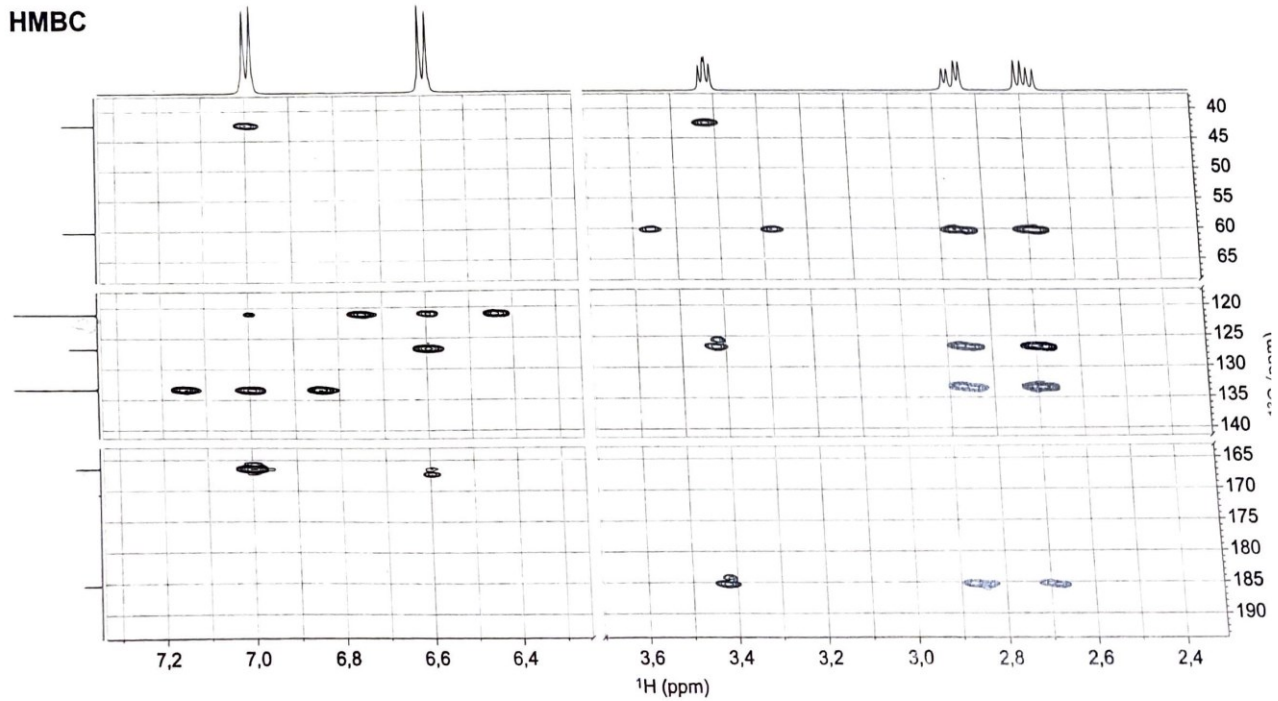


HSQC

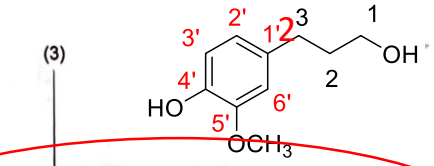

40
45
50
55
60
65
120
125
130
135
^{13}C (ppm)
7,0
6,8
6,6
6,4
6,2
3,6
3,4
3,2
3,0
2,8
2,6
2,4
^{1}H (ppm)

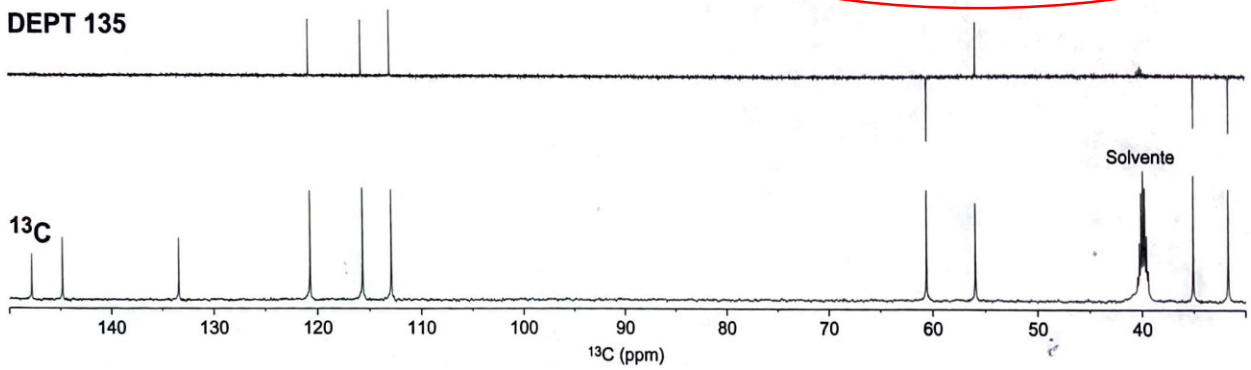

o
i
3
1
m
2
COOH
p
HO
NH_2

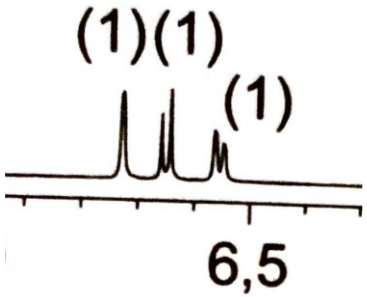
HMBC

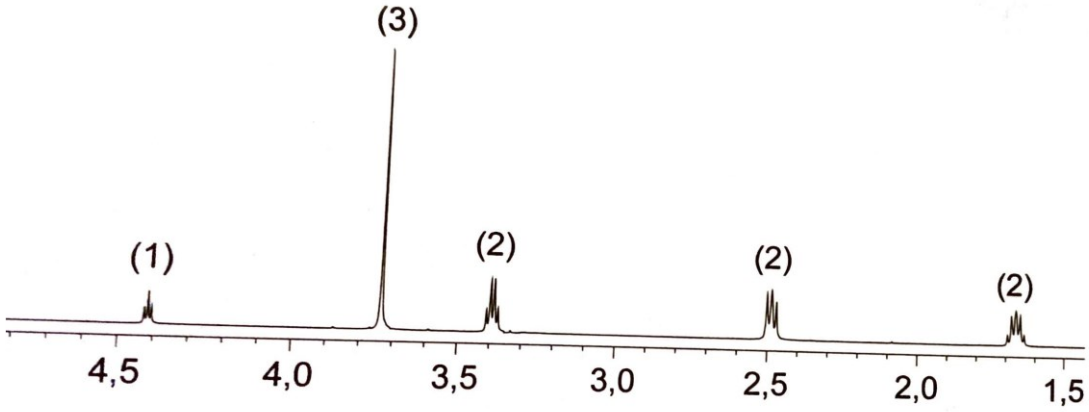

40
45
50
55
60
65
120
125
130
135
140
165
170
175
180
185
190
7,2
7,0
6,8
6,6
6,4
3,6
3,4
3,2
3,0
2,8
2,6
2,4
^{1}H (ppm)

Solvente: CD_3-SO-CD_3
Campo: 500 MHz (^1H); 125 MHz (^{13}C)

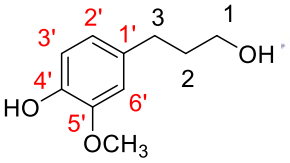






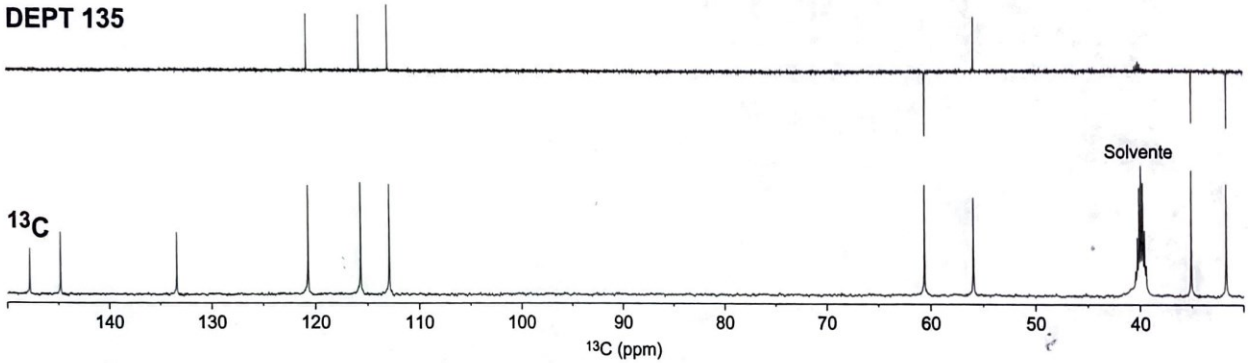


Solvente: CD_3-SO-CD_3
Campo: 500 MHz (^1H); 125 MHz (^{13}C)

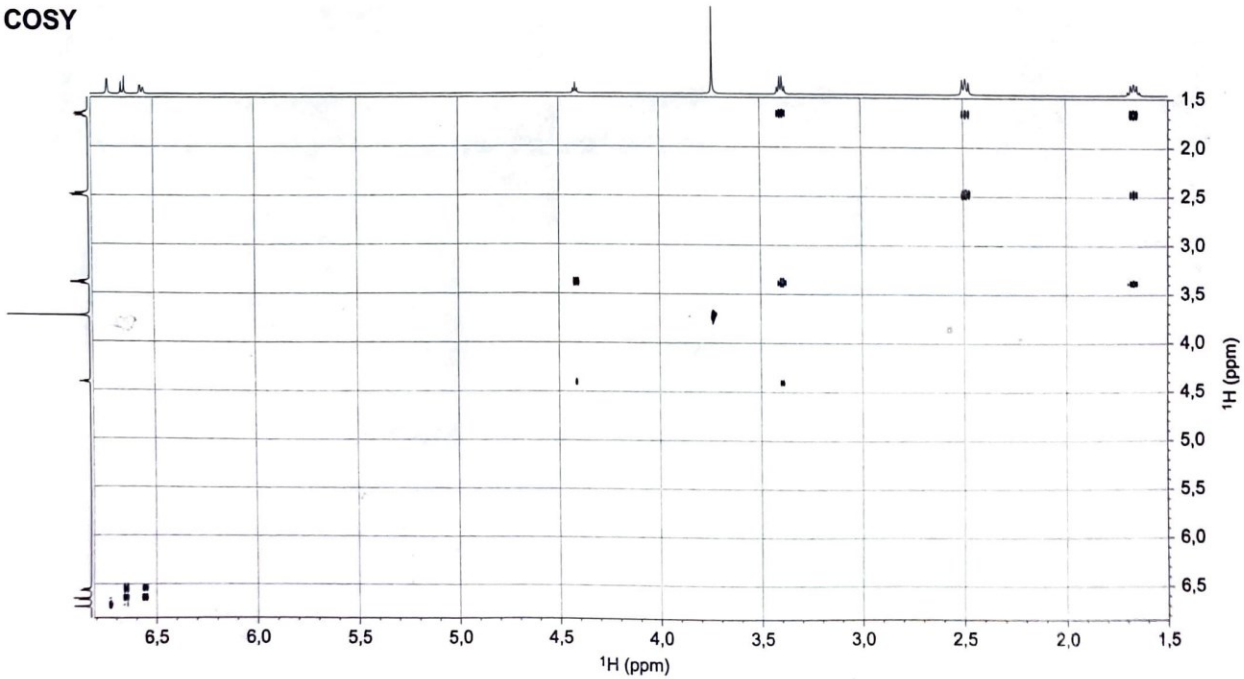


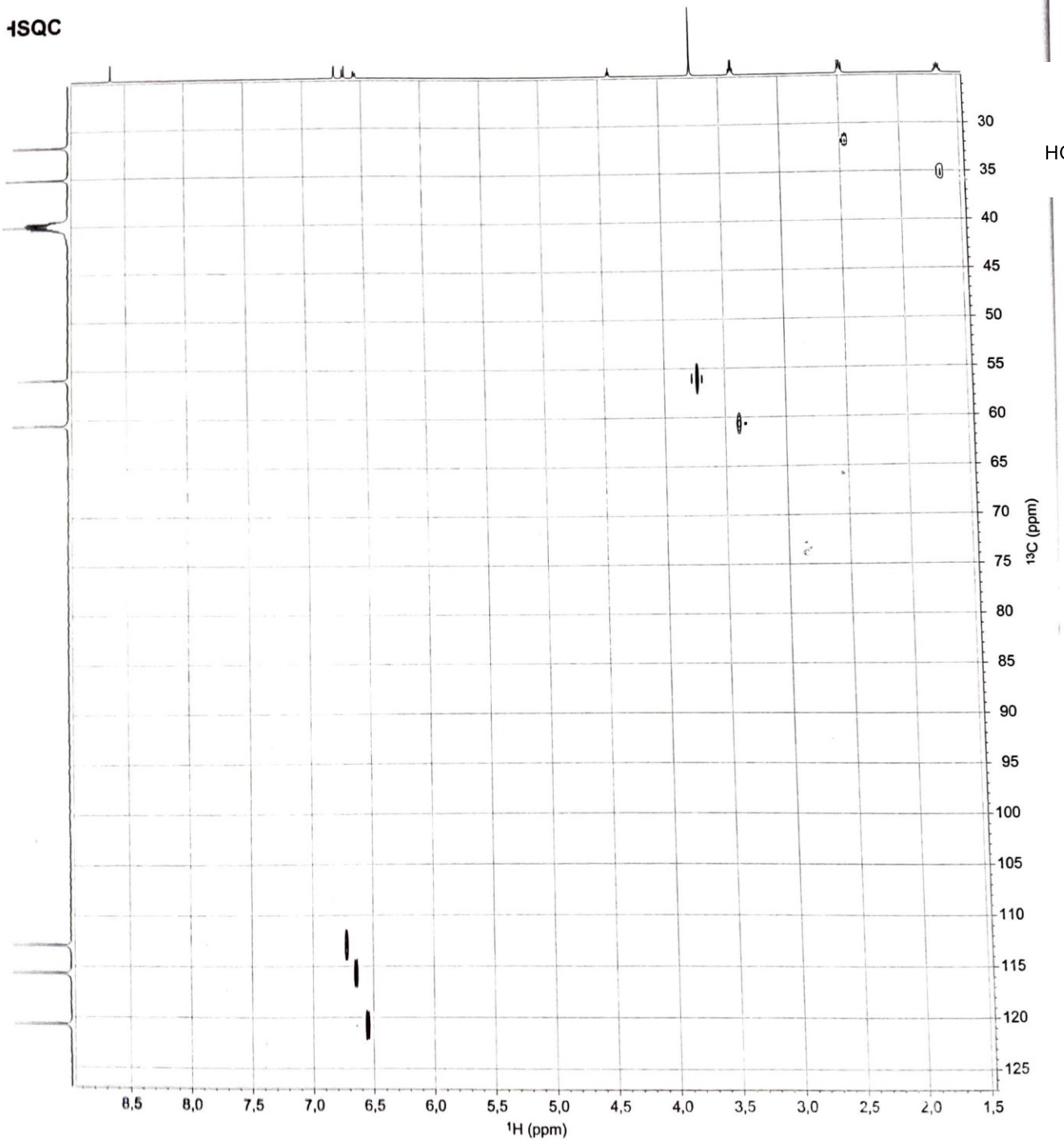
^1H

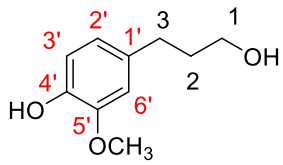
DEPT 135



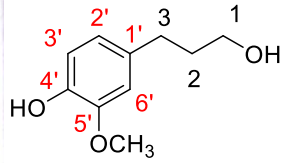
COSY

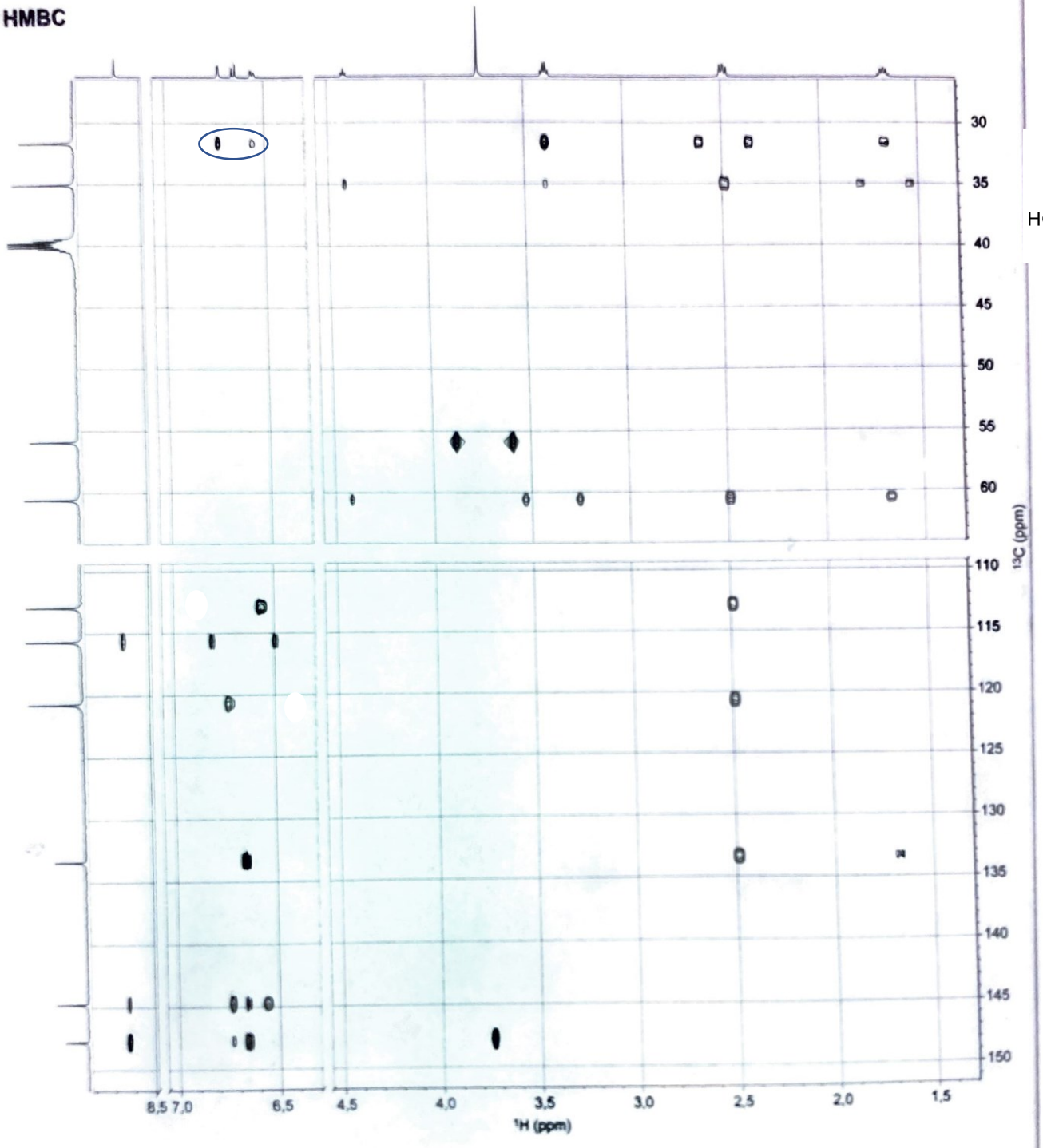



HSQC
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
13C (ppm)
8,5
8,0
7,5
7,0
6,5
6,0
5,5
5,0
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1H (ppm)


2'
3'
1'
3
1
OH
4'
2
HO
6'
5'
OCH3

HMBC


1
2
3
OH
1'
2'
3'
4'
5'
6'
HO
OCH3


30
35
40
45
50
55
60
110
115
120
125
130
135
140
145
150
13C (ppm)
8,5
7,0
6,5
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1H (ppm)

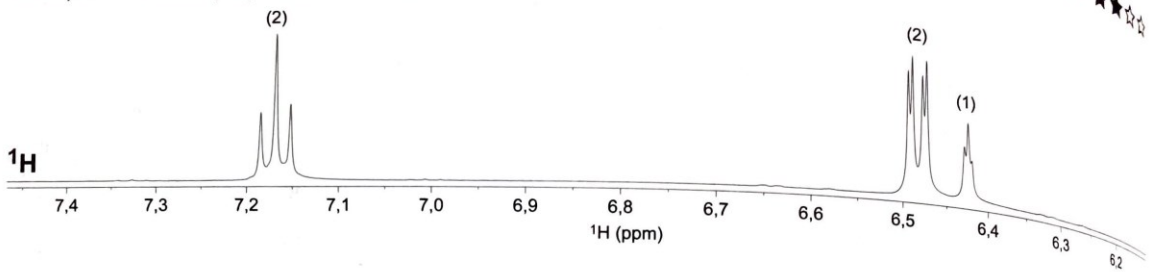
Esercizio 9.55

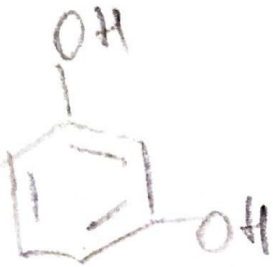
Solvente: D_2O

Campo: 500 MHz (^1H); 125 MHz (^{13}C)

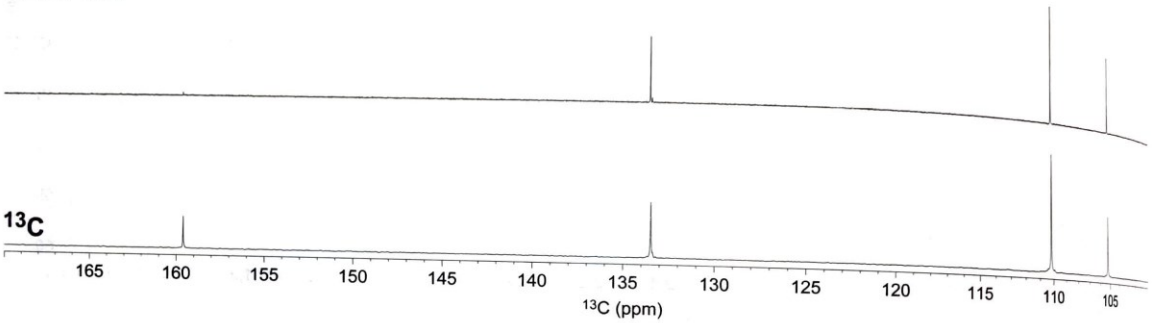
Formula molecolare: $C_6H_6O_2$

Difficoltà ★★☆☆

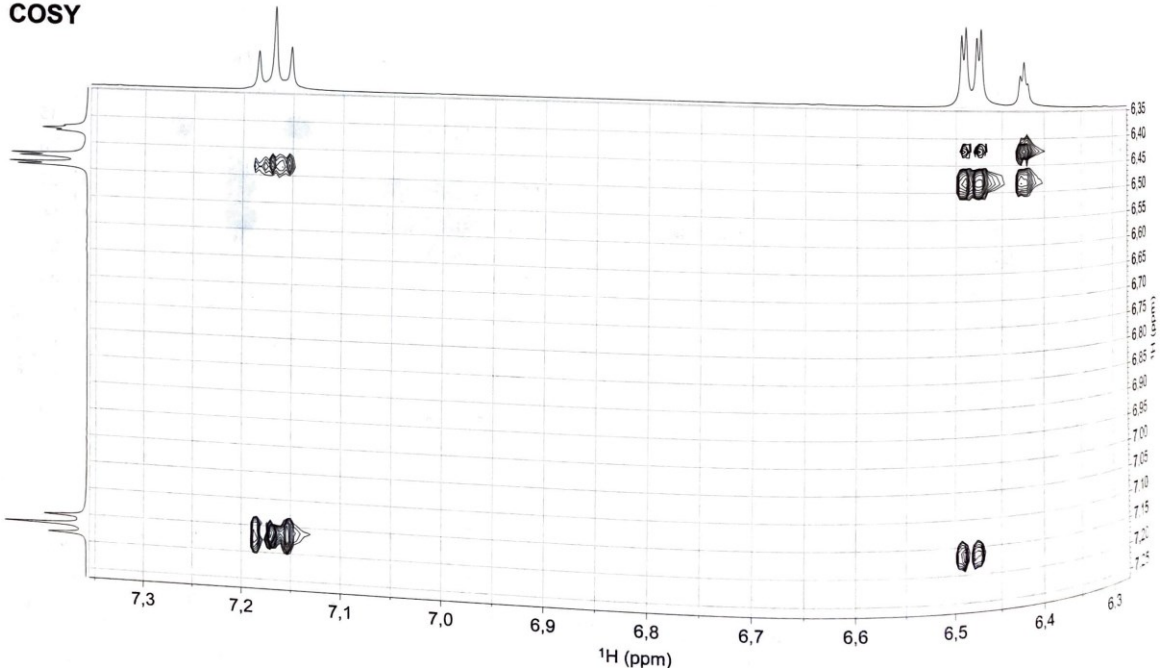


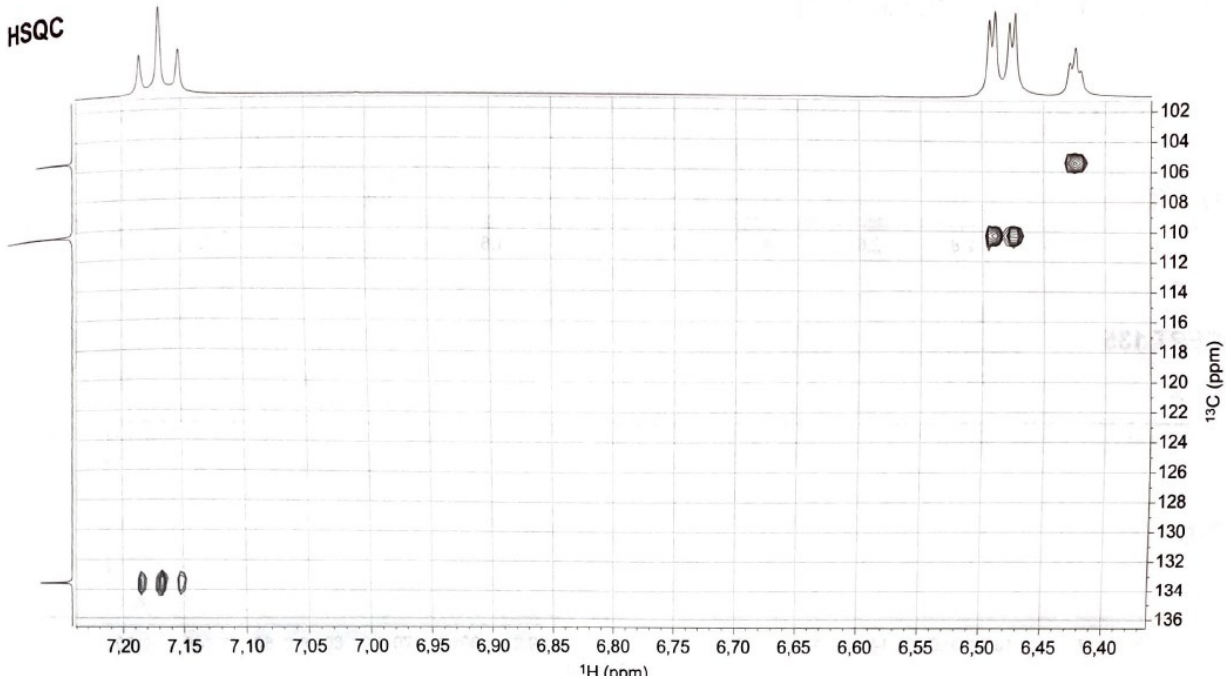


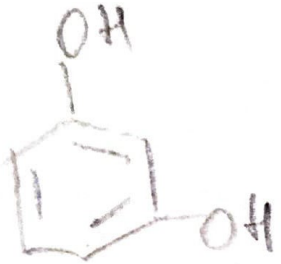
DEPT 135

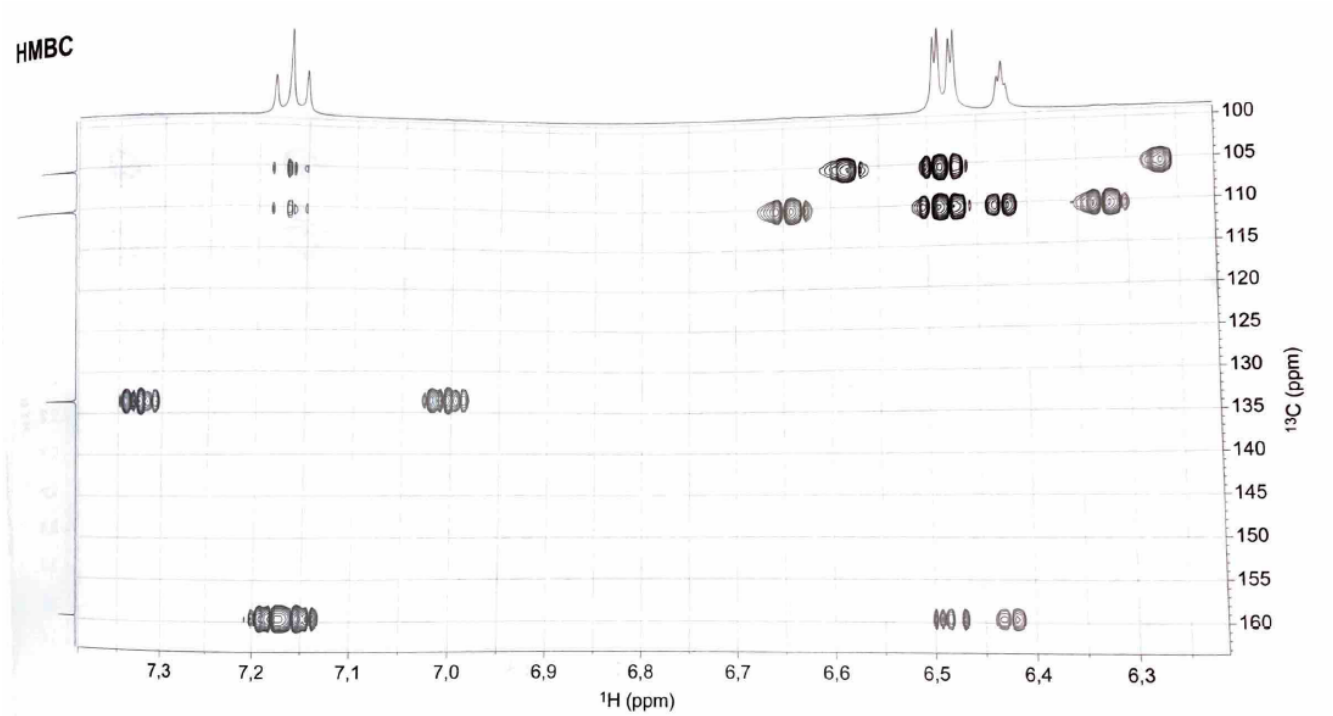


COSY

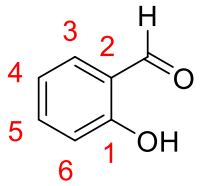


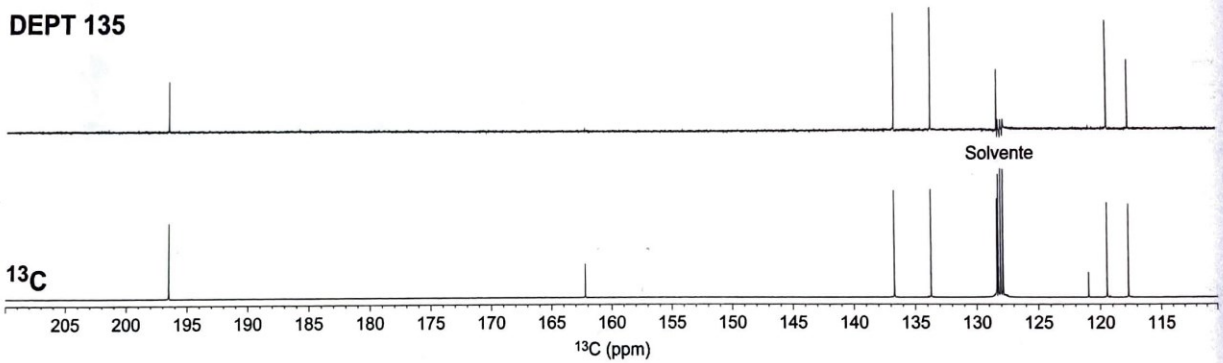

HSQC
102
104
106
108
110
112
114
116
118
120
122
124
126
128
130
132
134
136
13C (ppm)
7,20 7,15 7,10 7,05 7,00 6,95 6,90 6,85 6,80 6,75 6,70 6,65 6,60 6,55 6,50 6,45 6,40
1H (ppm)

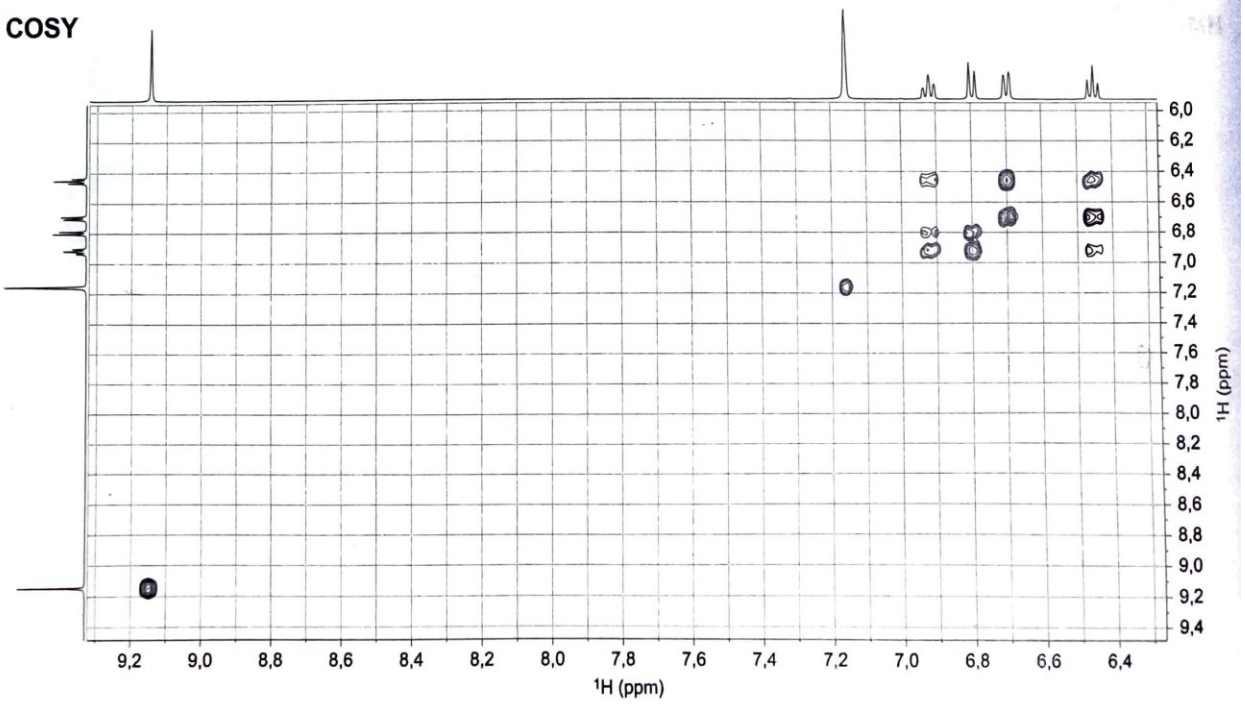

OH
OH


HMBC
100
105
110
115
120
125
130
135
140
145
150
155
160
13C (ppm)
7,3 7,2 7,1 7,0 6,9 6,8 6,7 6,6 6,5 6,4 6,3
1H (ppm)

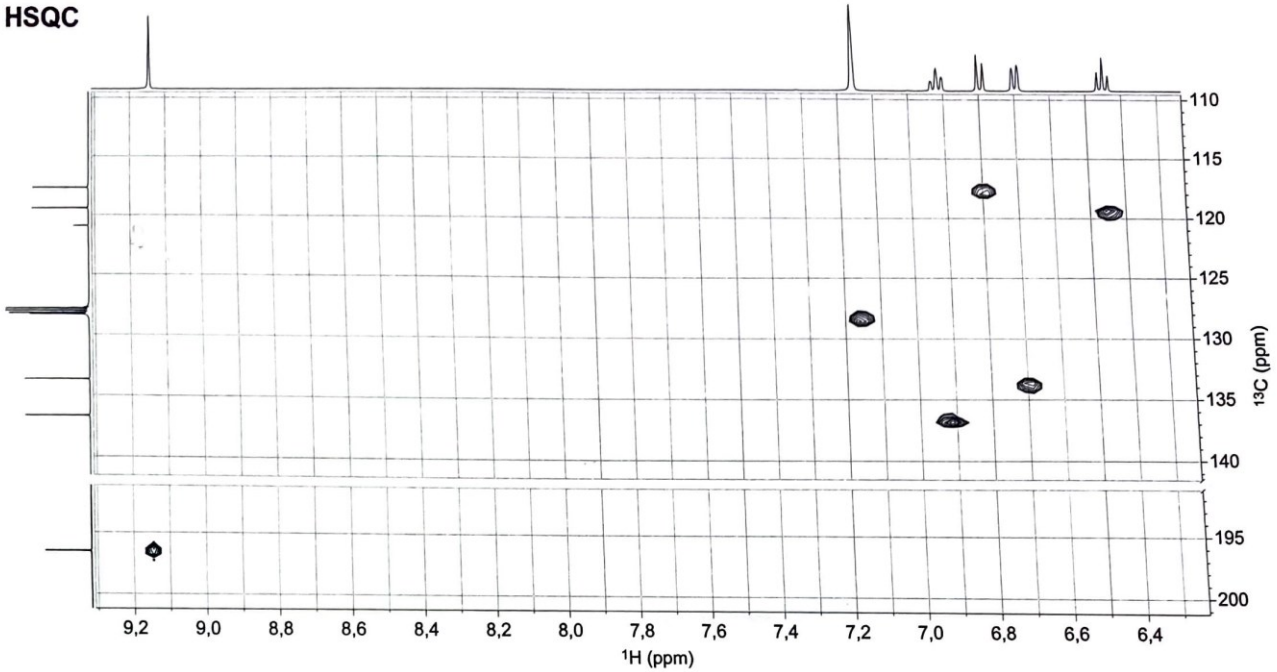
Solvente: C_6D_6
Campo: 500 MHz (^1H); 125 MHz (^{13}C)

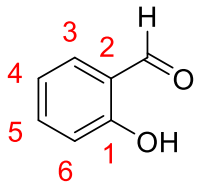




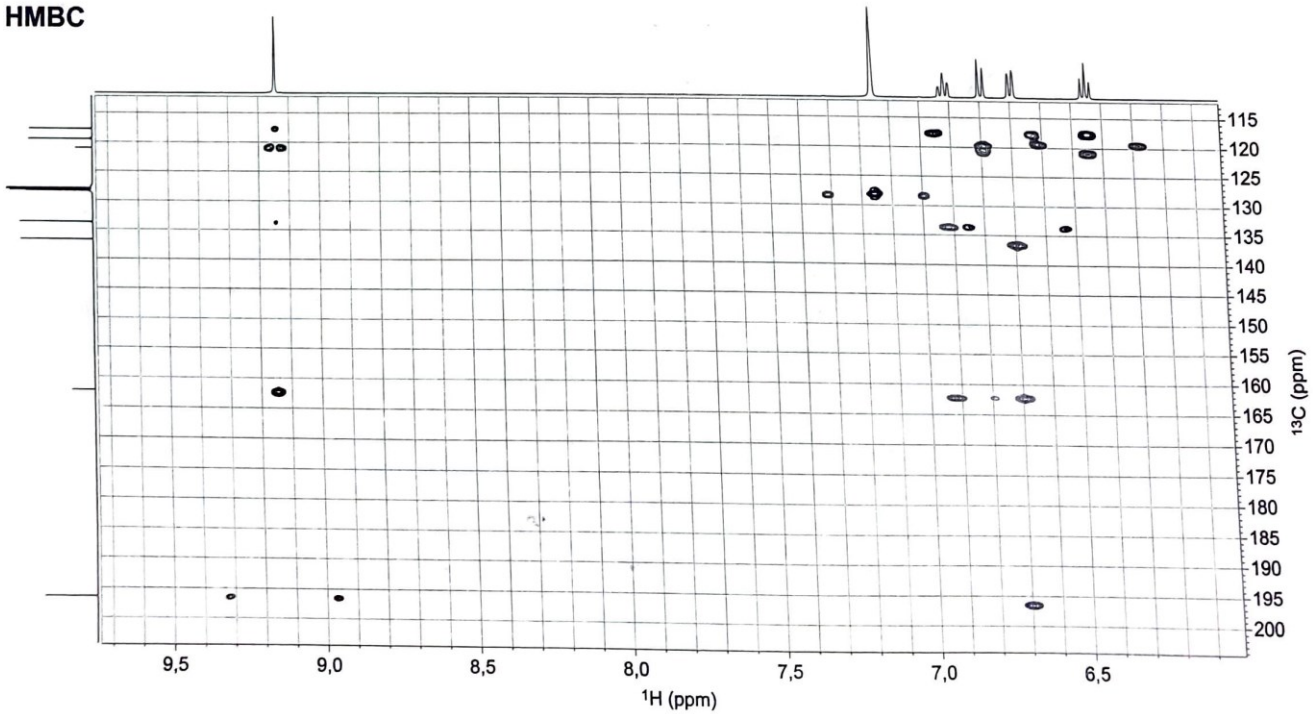


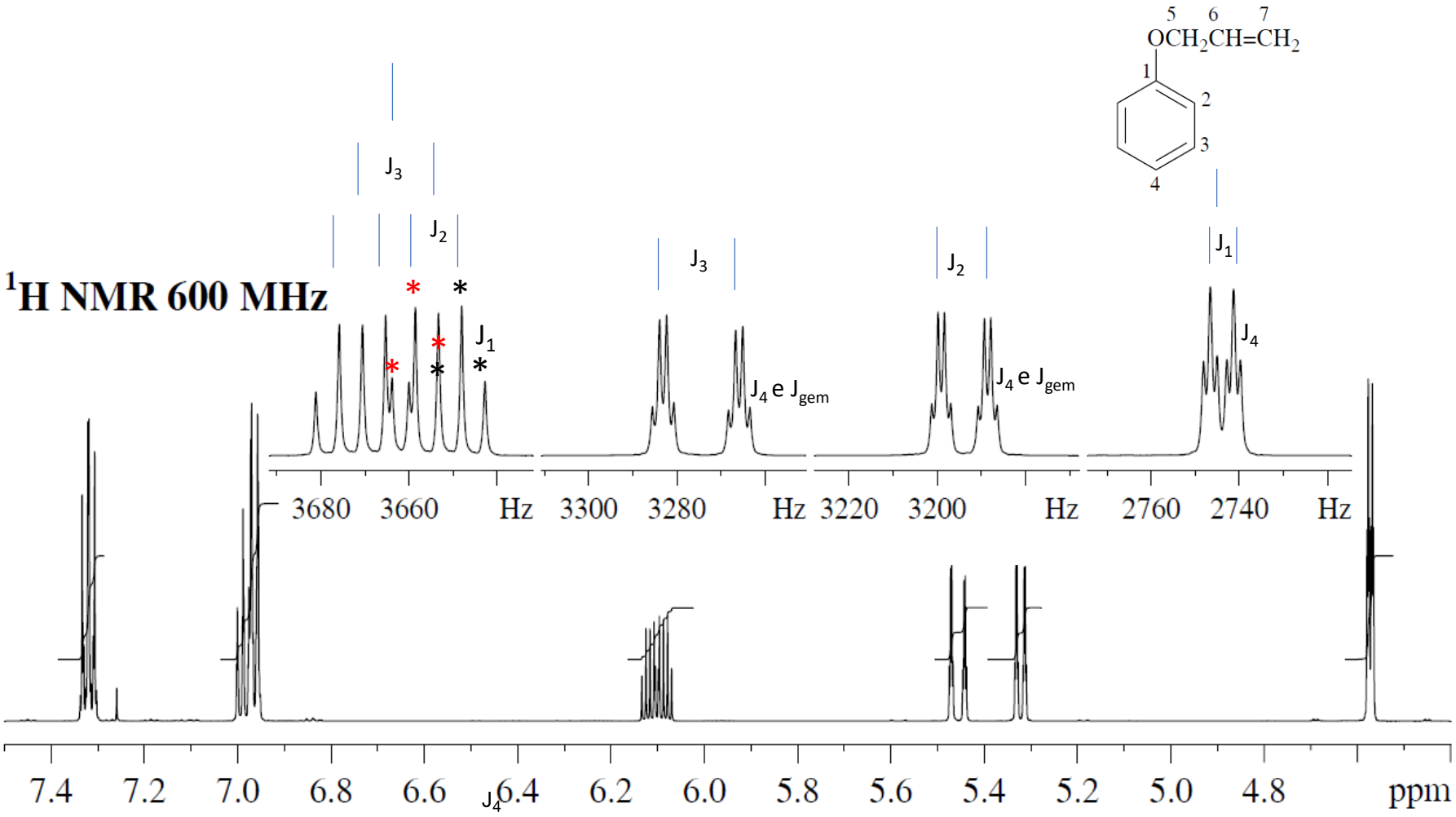
HSQC

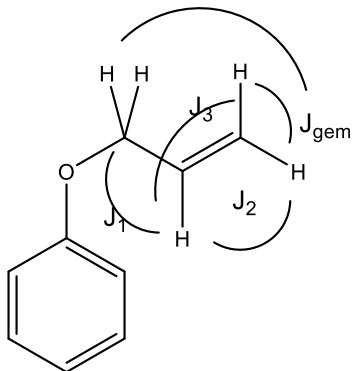

110
115
120
125
130
135
140
195
200
9,2
9,0
8,8
8,6
8,4
8,2
8,0
7,8
7,6
7,4
7,2
7,0
6,8
6,6
6,4
¹H (ppm)
¹³C (ppm)


H
O
OH
1
2
3
4
5
6

HMBC


115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
9,5
9,0
8,5
8,0
7,5
7,0
6,5
¹H (ppm)
¹³C (ppm)





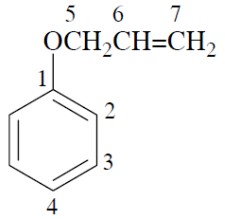
$J_1 = J_{5,6}$

$J_2 = J_{6,7\ cis}$

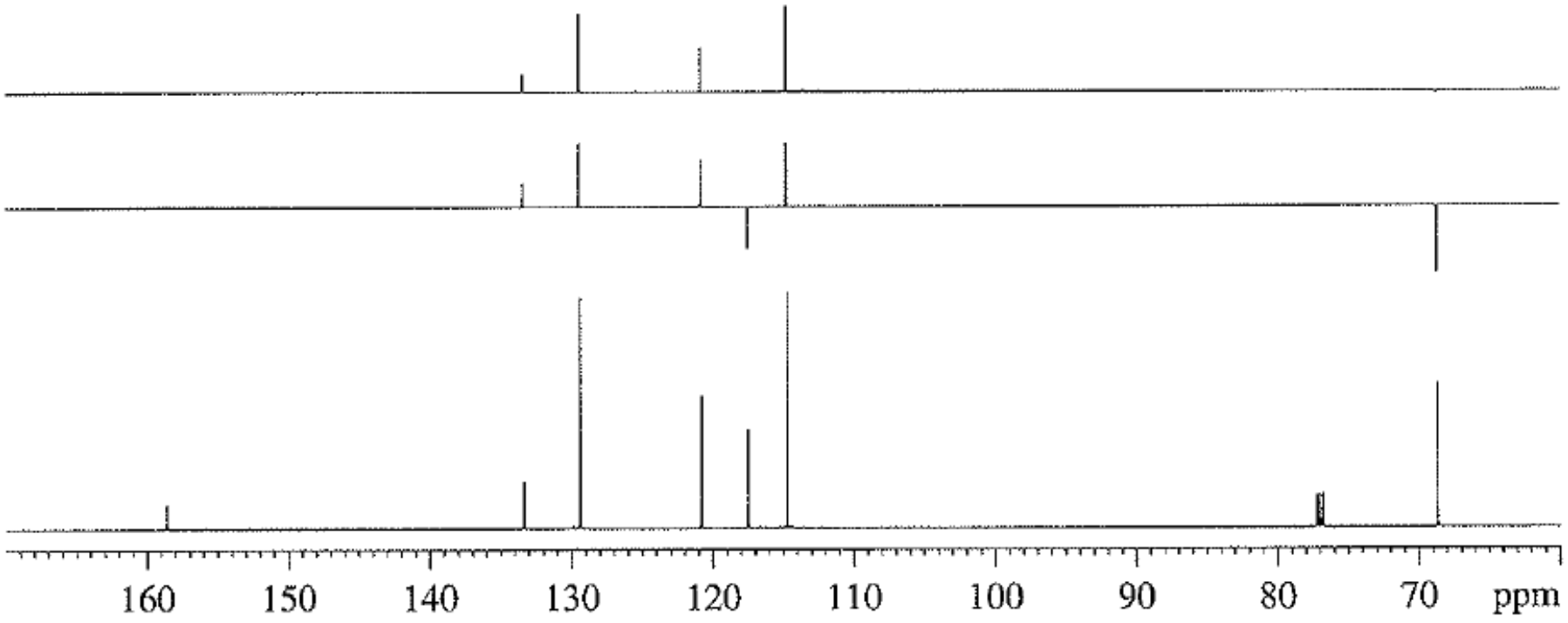
$J_3 = J_{6,7\ trans}$

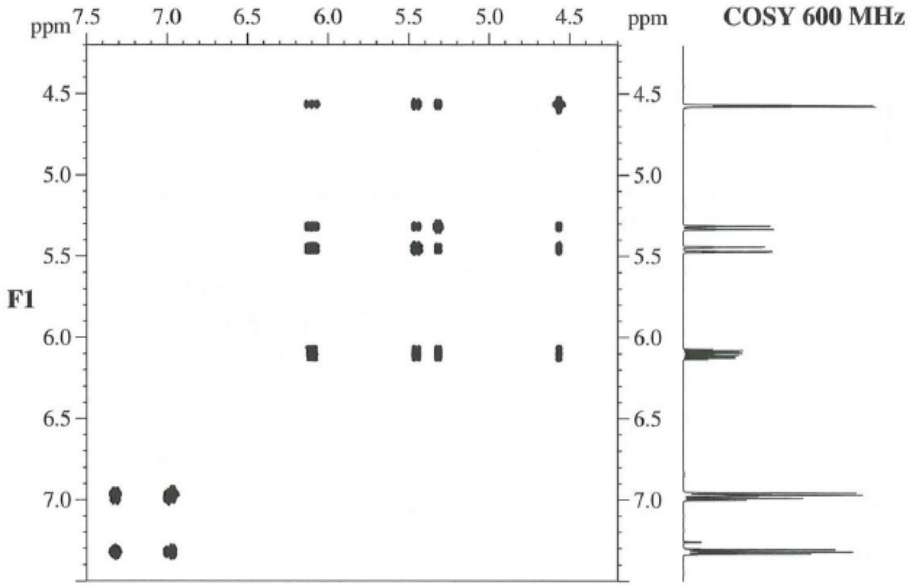
$J_4 = J_{5,7}$

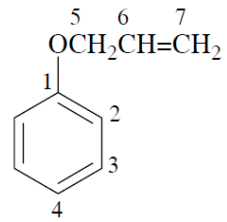
$J_5 = J_{gem}$

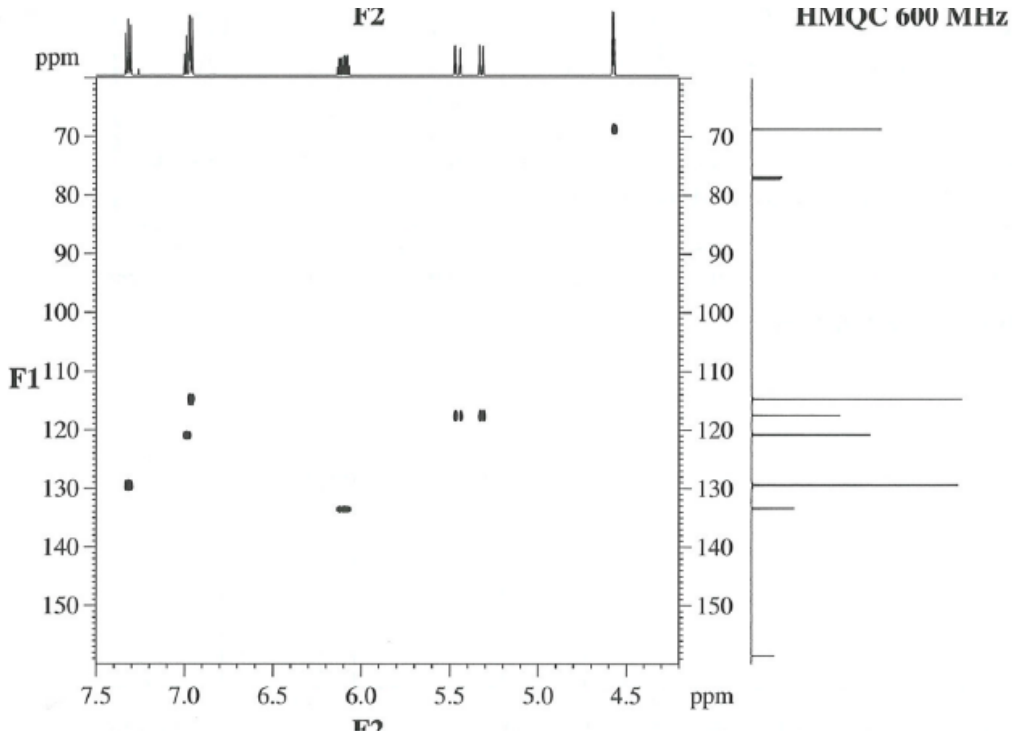


^{13}C/DEPT NMR 150.9 MHz




COSY 600 MHz
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
F1


5 6 7
OCH2CH=CH2
1
2
3
4


HMQC 600 MHz
F2
ppm
70
80
90
100
110
120
130
140
150
F1
7.5
7.0
6.5
6.0
5.5
5.0
4.5