Spettroscopia IR e NMR: Esercizi

ESERCIZI DI GRUPPO

- Determinare l'analita corretto tra quelli proposti in base agli spettri NMR e/o IR
- Eventualmente verificare la presenza dei principali segnali IR e assegnare lo spettro NMR

NB
Nelle posizioni asteriscate i protoni apparentemente equivalenti non sono tali.

NB 2
Alcune di queste sostanze potrebbero essere ottenute per salificazione con HCl; quindi se presenti gruppi NH potrebbero non vedersi bene (o non vedersi proprio) all' IR.

Come procedere:

- Identificare quanti gruppi di segnali sono presenti sulla molecola (attenzione protoni equivalenti)
- Identificare i gruppi di segnali sullo spettro (potrebbero esserci sovrapposizioni)
- Guardare il valore del chemical shift del picco tenendo sotto occhio la tabella (guida) dei segnali tipici.
- Guardate il valore degli integrali e il numero di protoni totali
- Se possibile controllare la molteplicità
- Infine assegnare i protoni aromatici con le regole delle costanti additive

Come si calcola il grado di insaturazione?

C= atomi di carbonio
X= alogenuri
N= atomi di azoto
Ossigeno e Zolfo non si contano

$$\text{Anelli} + \text{Legami } \pi = C - \frac{H}{2} - \frac{X}{2} + \frac{N}{2} + 1$$

C_6H_6, Benzene

C_6H_{14}, saturated alkane

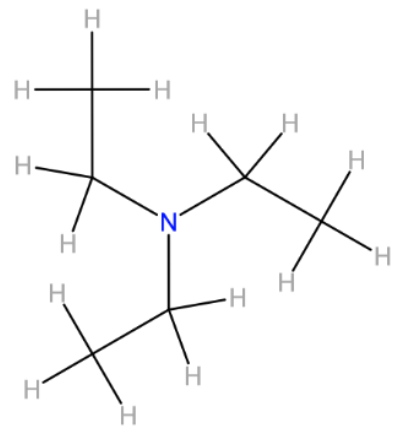
6-(6/2)+1=4

6-(14/2)+1=0

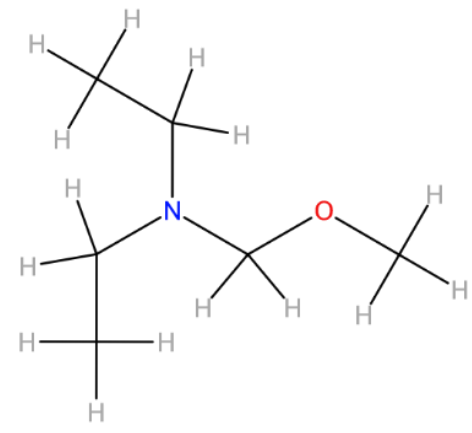
ESERCIZIO 1

Determinare l’analita corretto in base ai seguenti spettri NMR

a

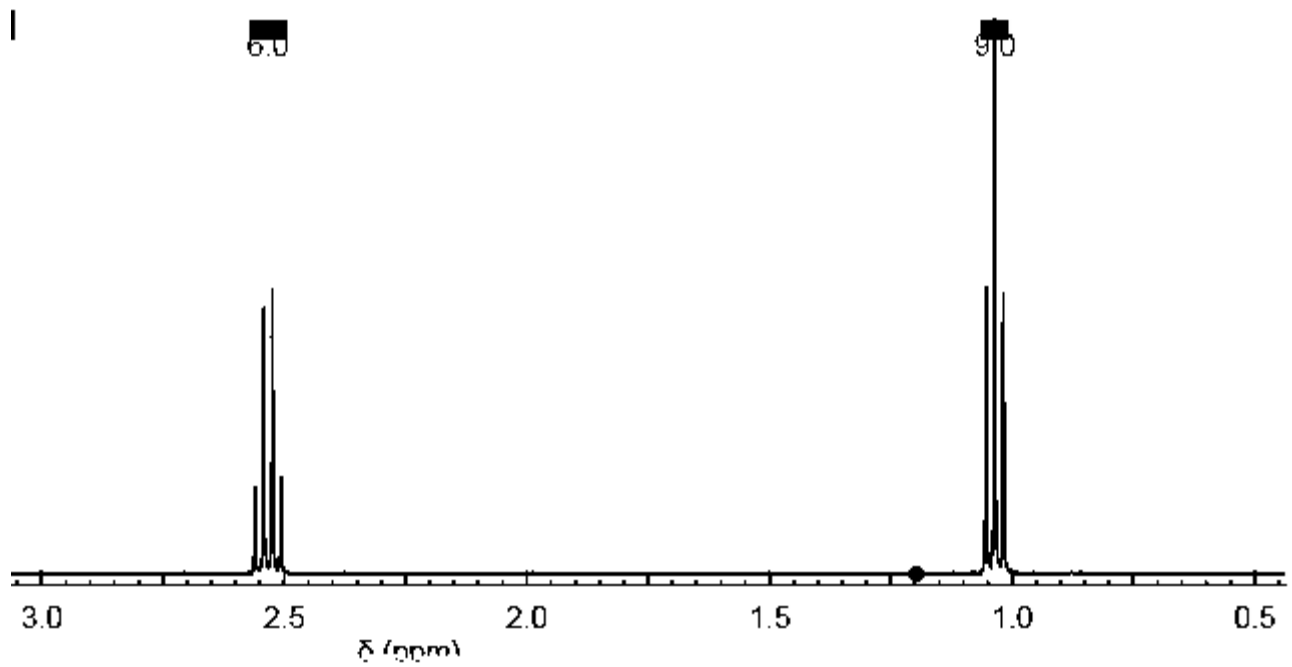


b



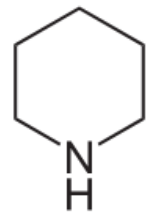
6, quartetto

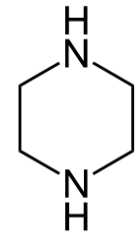
9, tripletto



ESERCIZIO 2

Prevedere grossolanamente lo spettro NMR per piperidina (a) e piperazine (b)

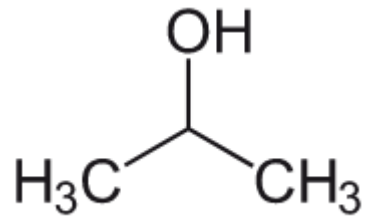
a 

b 

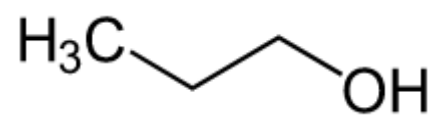
ESERCIZIO 3

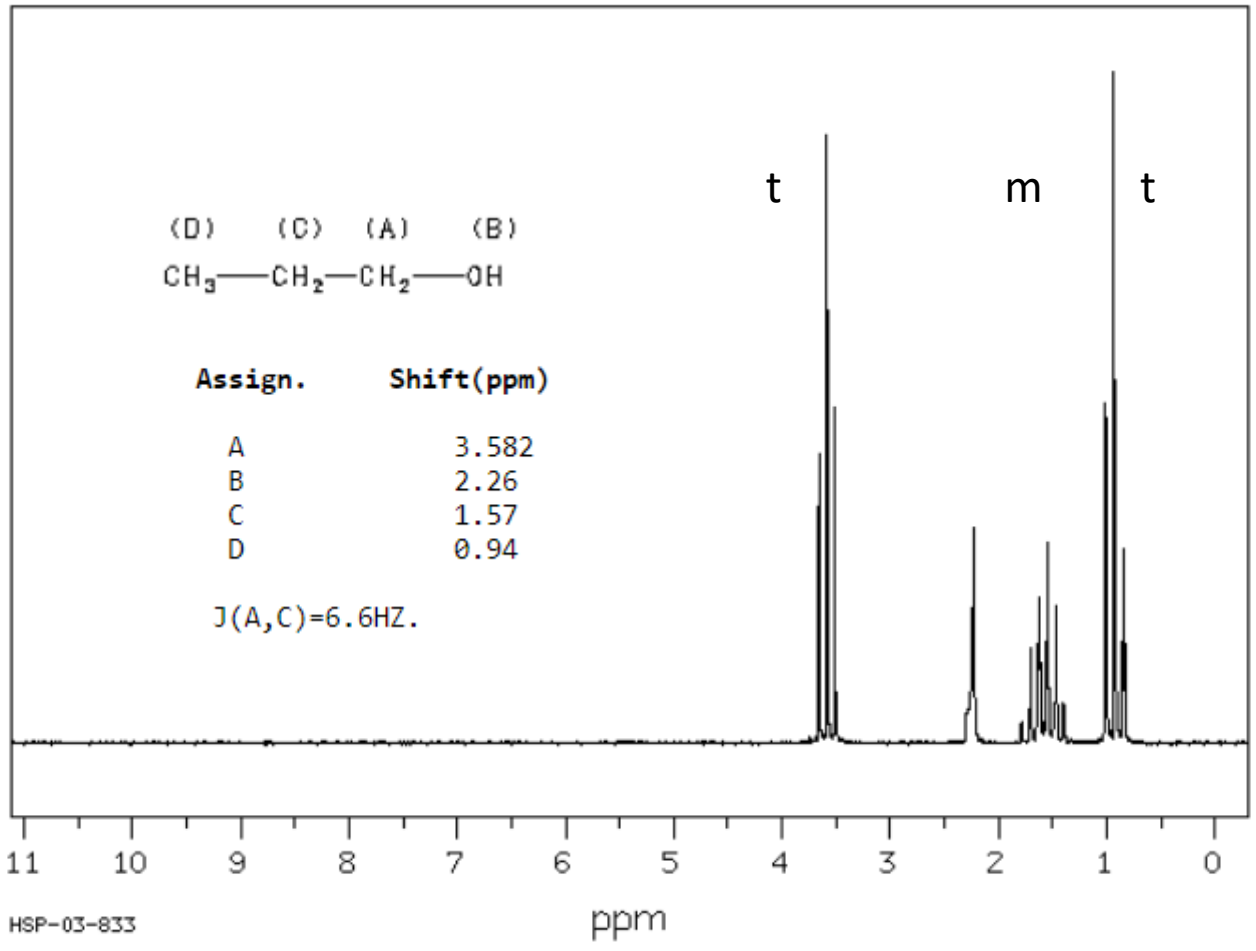
….1-propanolo o 2-propanolo?

a



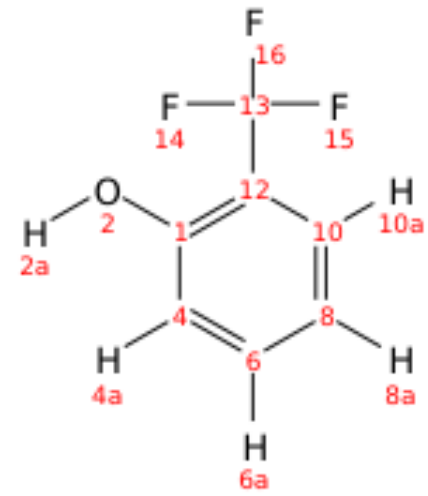
b



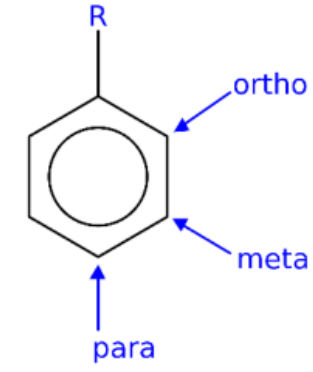


ESERCIZIO 3-bis

Calcola il chemical shift dei Protoni 4a, 6a, 8a e 10a con il metodo delle costanti additive per la seguente molecola?



Sostituente R	Z_{orto}	Z_{meta}	Z_{para}
H	0.0	0.0	0.0
CH_3[a]	-0.18	-0.11	-0.21
$C(CH_3)_3$	0.02	-0.08	-0.21
CH_2Cl	0.02	-0.01	-0.04
CH_2OH	-0.07	-0.07	-0.07
CF_3	0.32	0.14	0.20
CCl_3	0.64	0.13	0.10
$CH=CH_2$	0.04	-0.04	-0.12
CH=CHCOOH[a]	0.19	0.04	0.05
C C-H	0.15	-0.02	-0.01
C C-Ph[a]	0.17	-0.02	-0.03
Ph[a]	0.23	0.07	-0.02
COOH[a]	0.77	0.11	0.25
SH	-0.08	-0.16	-0.22
NH2	-0.71	-0.22	-0.62
NEt_2[a]	-0.68	-0.15	-0.73
$NHC(O)CH_3$[a]	0.14	-0.07	-0.27
NO_2[a]	0.87	0.20	0.35
I	0.39	-0.21	0.00
OH[a]	-0.53	-0.14	-0.43
OCH_3[a]	-0.45	-0.07	-0.41
$O-C(O)CH_3$[a]	-0.27	-0.02	-0.13
O-C(O)Ph[a]	-0.14	0.07	-0.09
OPh[a]	-0.36	-0.04	-0.28
$O-SO_2Me$	-0.05	0.07	-0.01

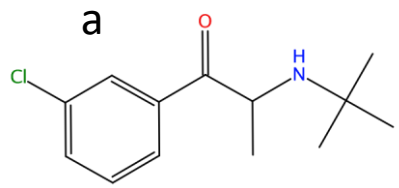


$$\delta_{Ar-H} = 7.36 + Z_{orto} + Z_{meta} + Z_{para}$$

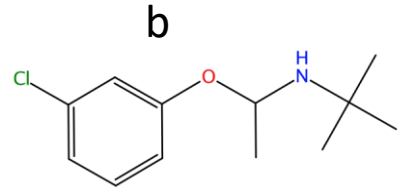
ESERCIZIO 4

Determinare l’analita corretto in base ai seguenti spettri IR e NMR

a



b



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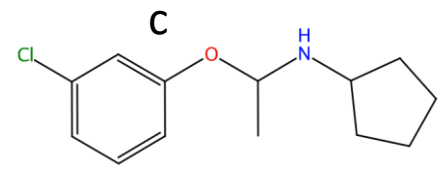
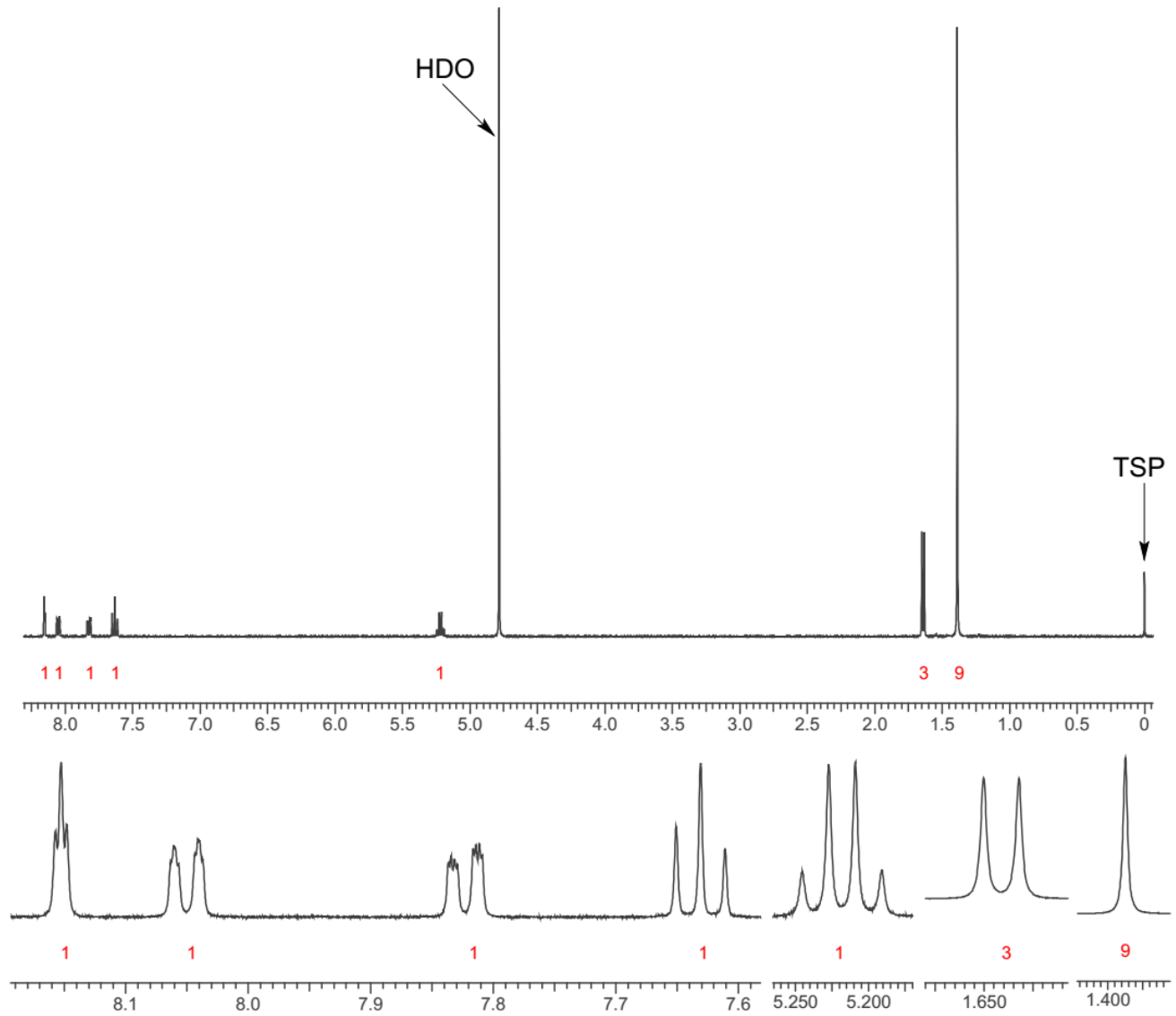
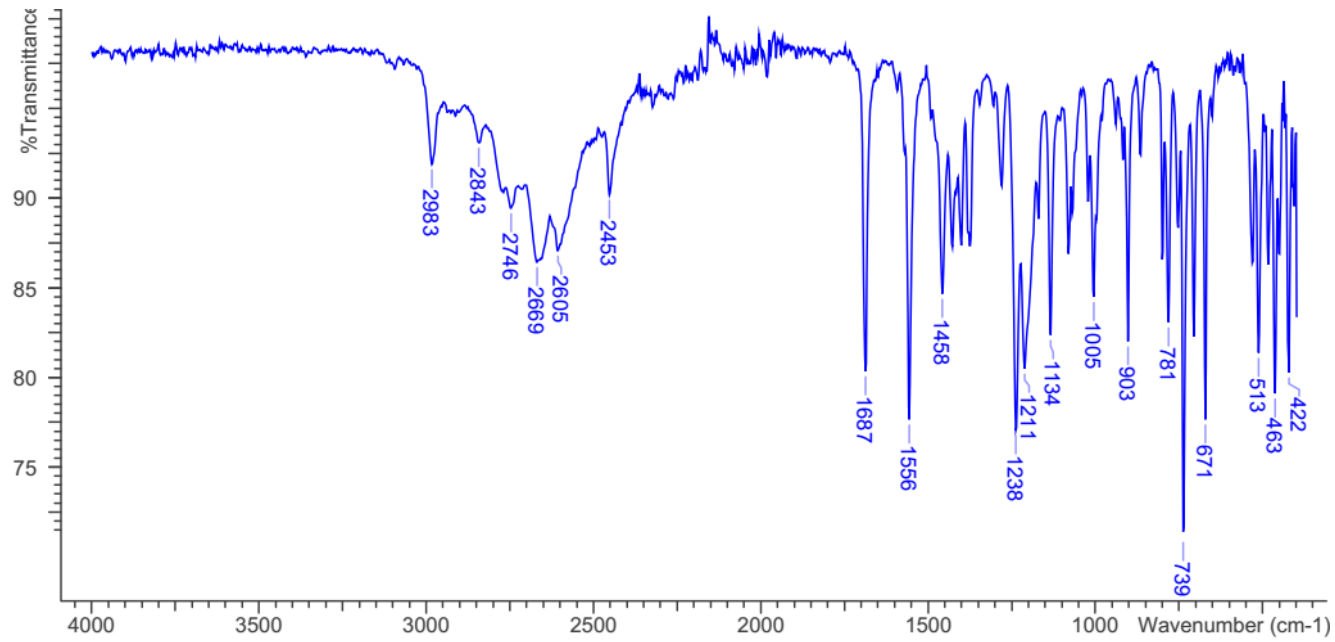
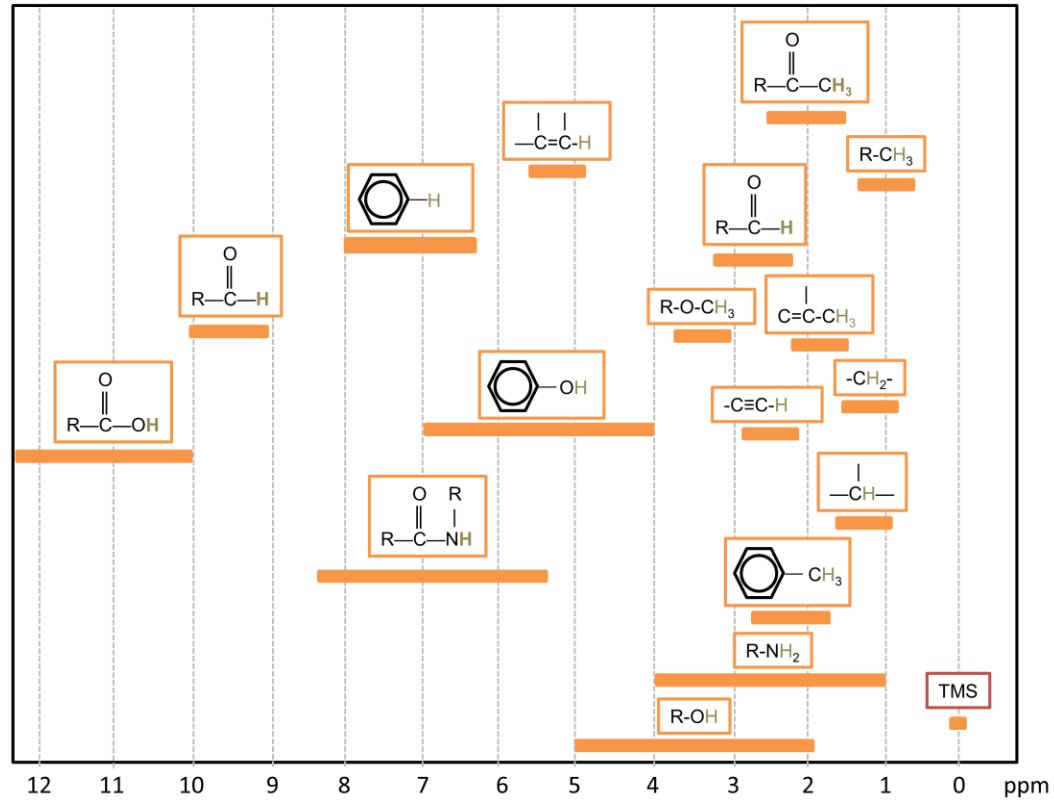






Spectra from www.swgdrug.org

Classical NMR chemical shifts



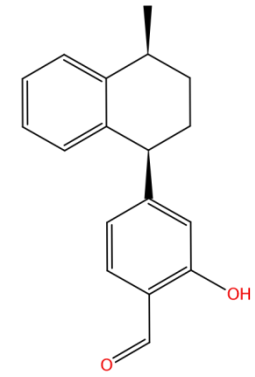
IR Freq. List

O-H	**≈3500**
N-H	**3100-3500**
C-H$_{alkanes}$	**3000-2850**
C-H$_{aromatics}$	**3150-3050**
C-H$_{alkenes}$	**3100-3000**
C=C$_{aromatic}$	**1600& 1475**
C=C$_{alkene}$	**1680-1600**
C=O$_{ketone}$	**1725-1700**
C=O$_{amide}$	**1670-1640**
C=O$_{ester}$	**1750-1730**

ESERCIZIO 5

Determinare l’analita corretto in base ai seguenti spettri NMR e IR

a



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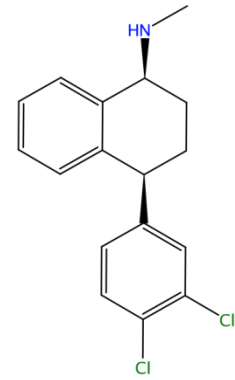

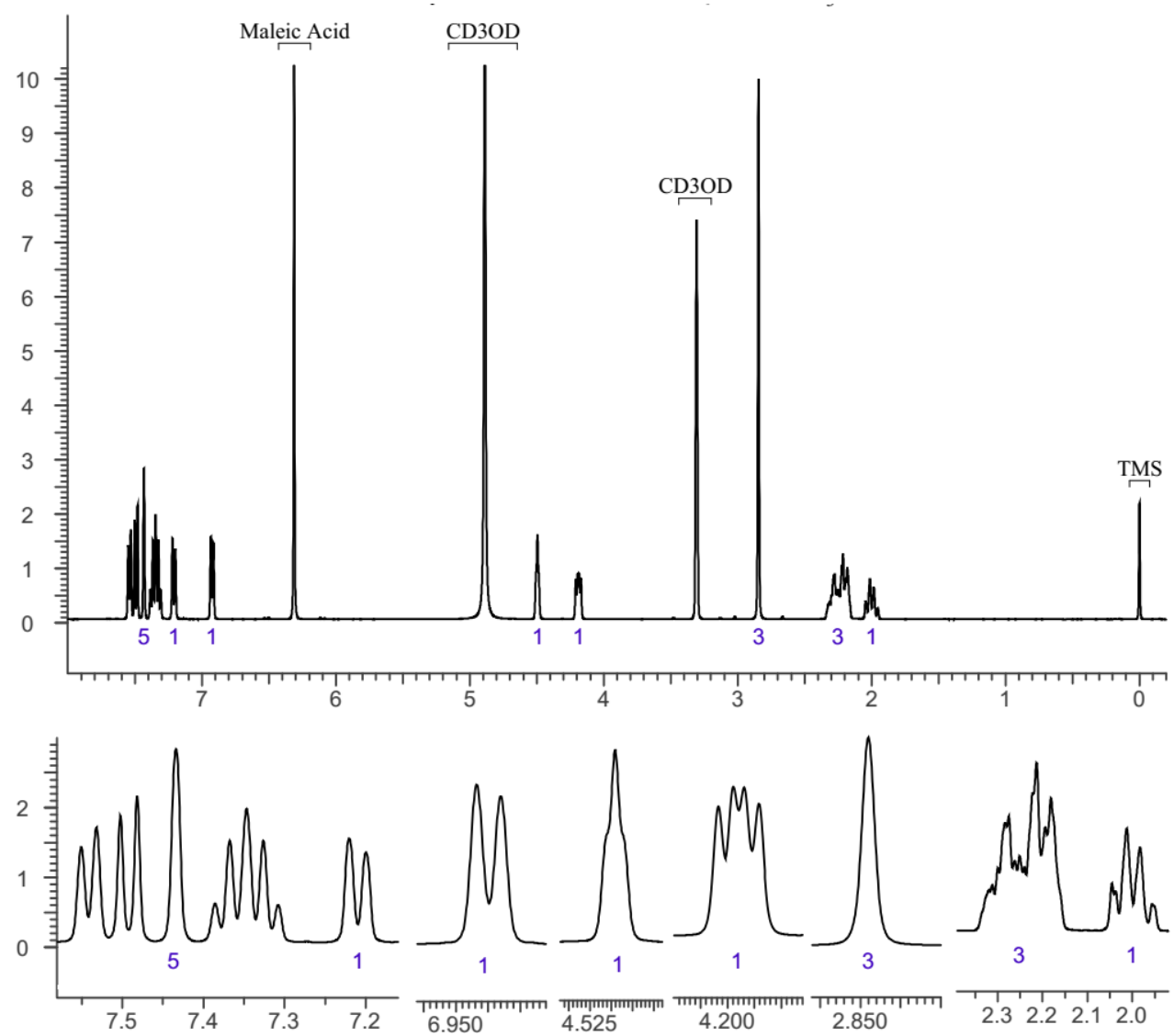

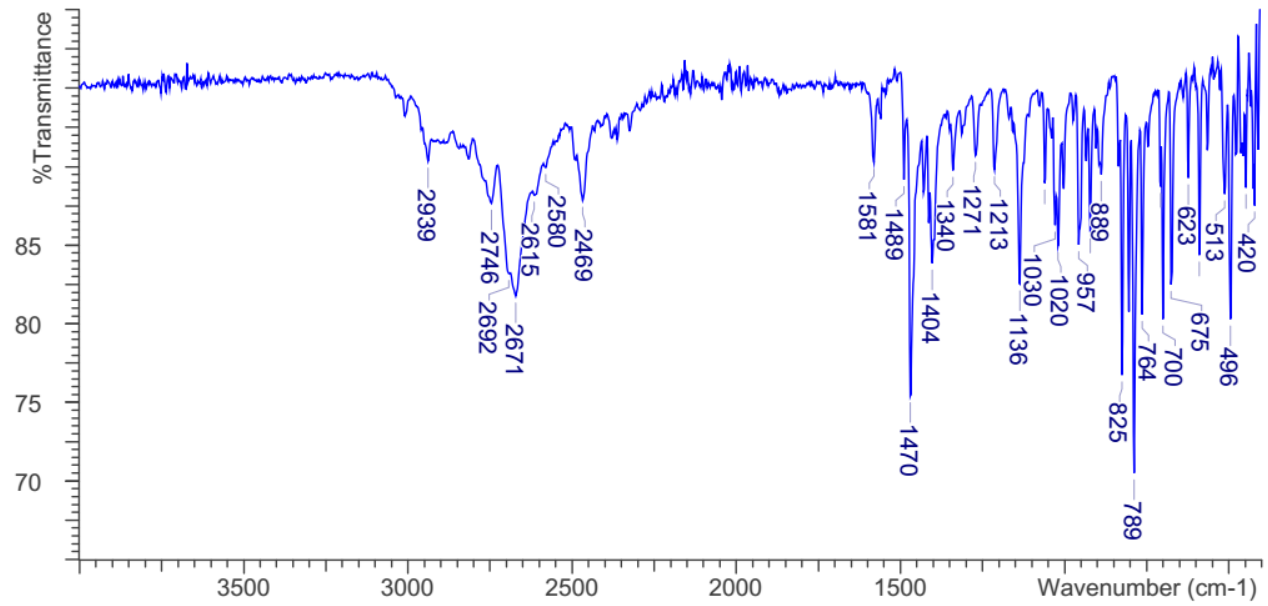

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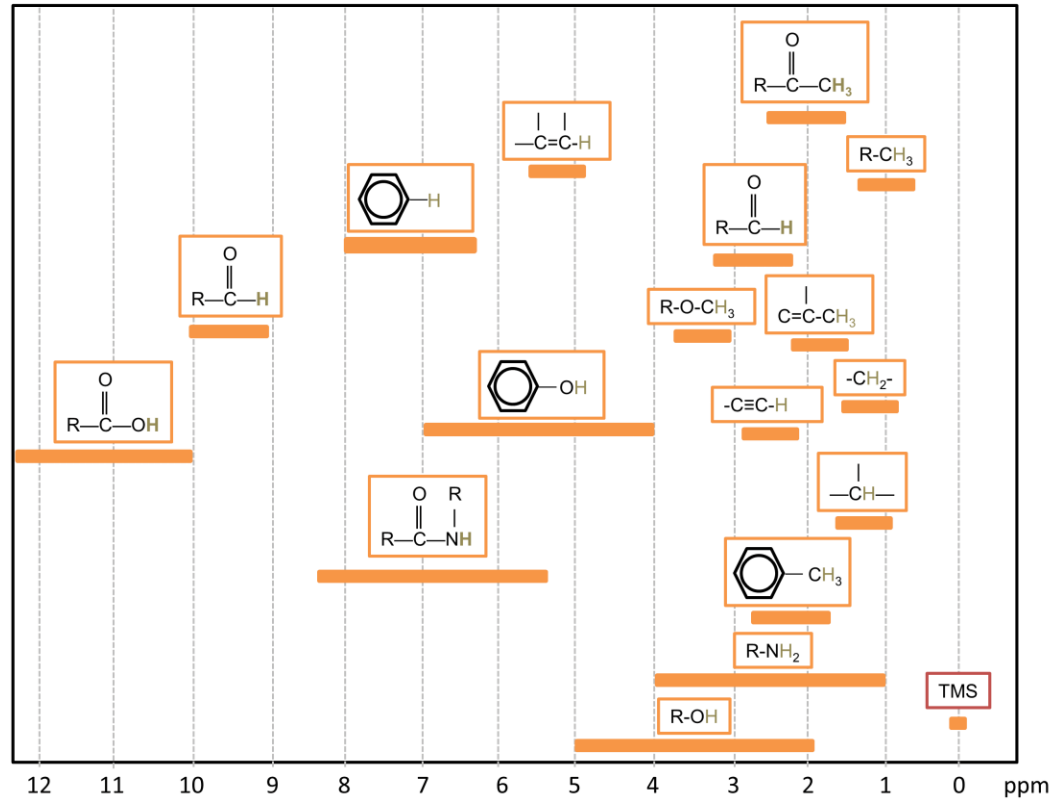
Classical NMR chemical shifts



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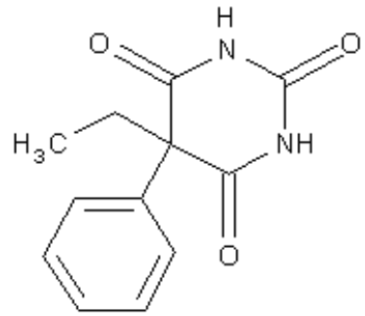
ESERCIZIO 6

Determinare l’analita corretto in base ai seguenti spettri

a



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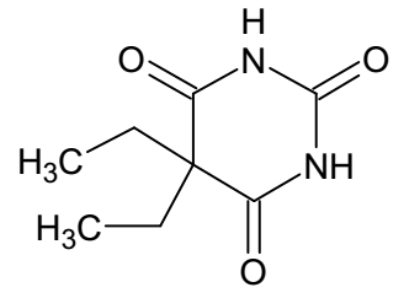
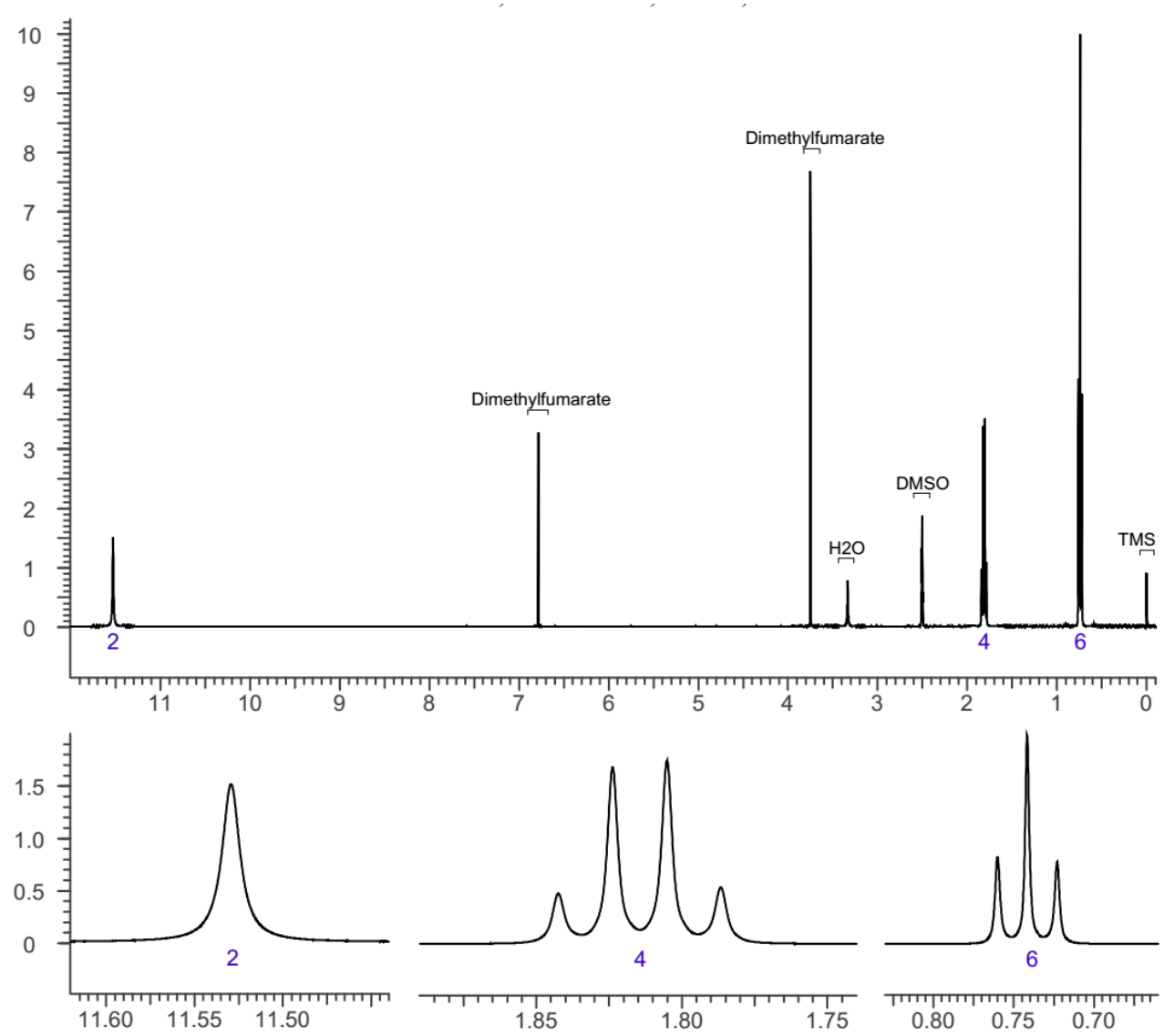
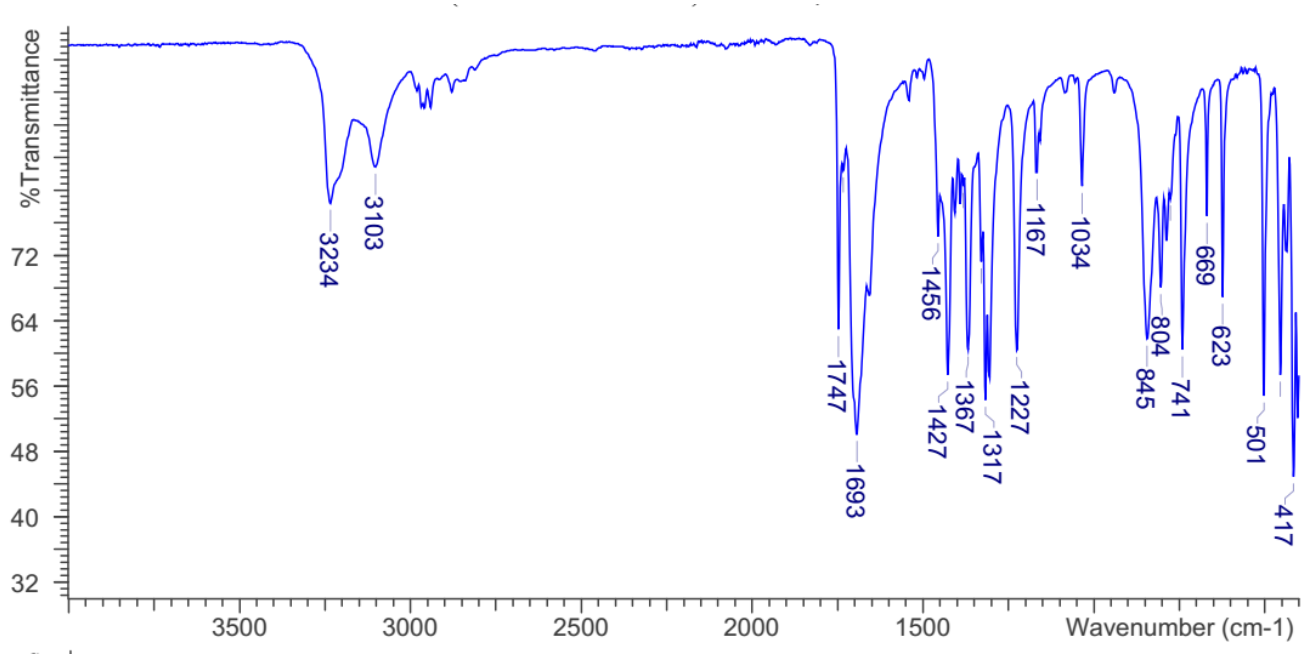
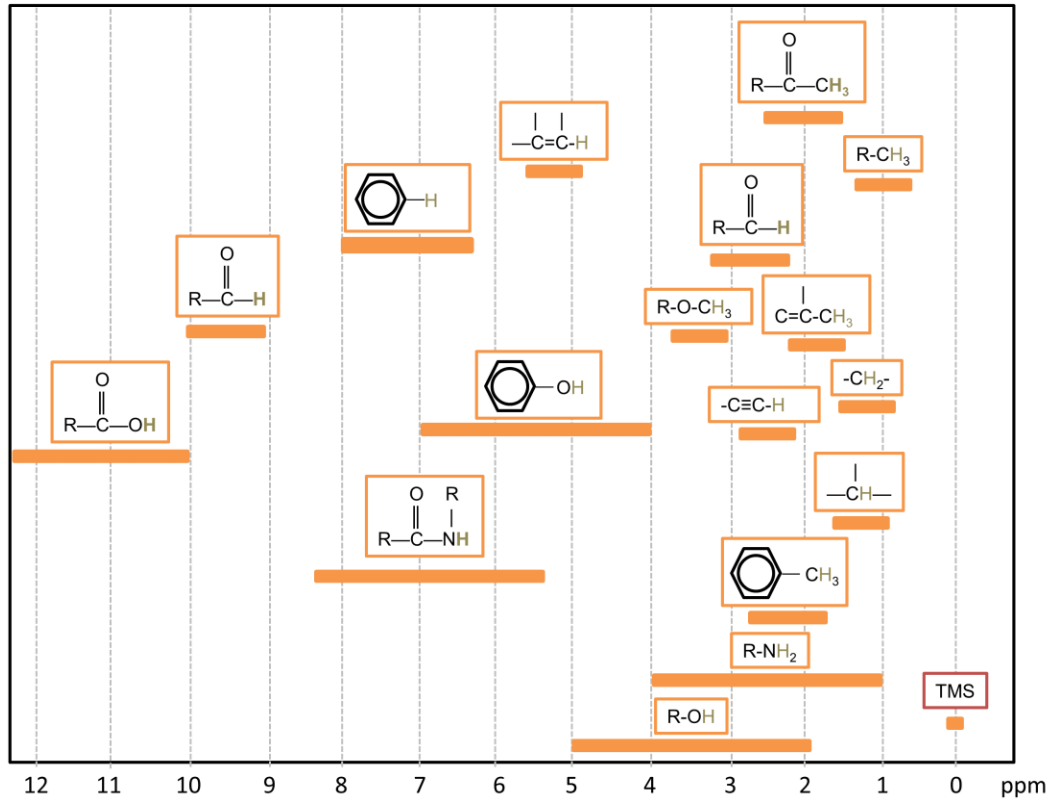






Spectra from www.swgdrug.org

Classical NMR chemical shifts



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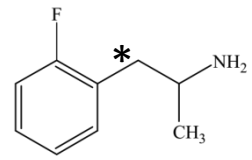
ESERCIZIO 7

Determinare l'analita corretto in base ai seguenti spettri NMR e IR.

a



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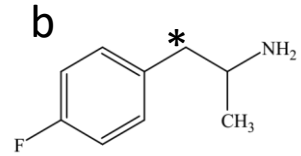

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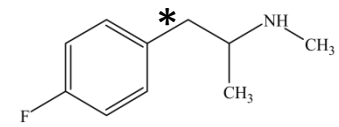
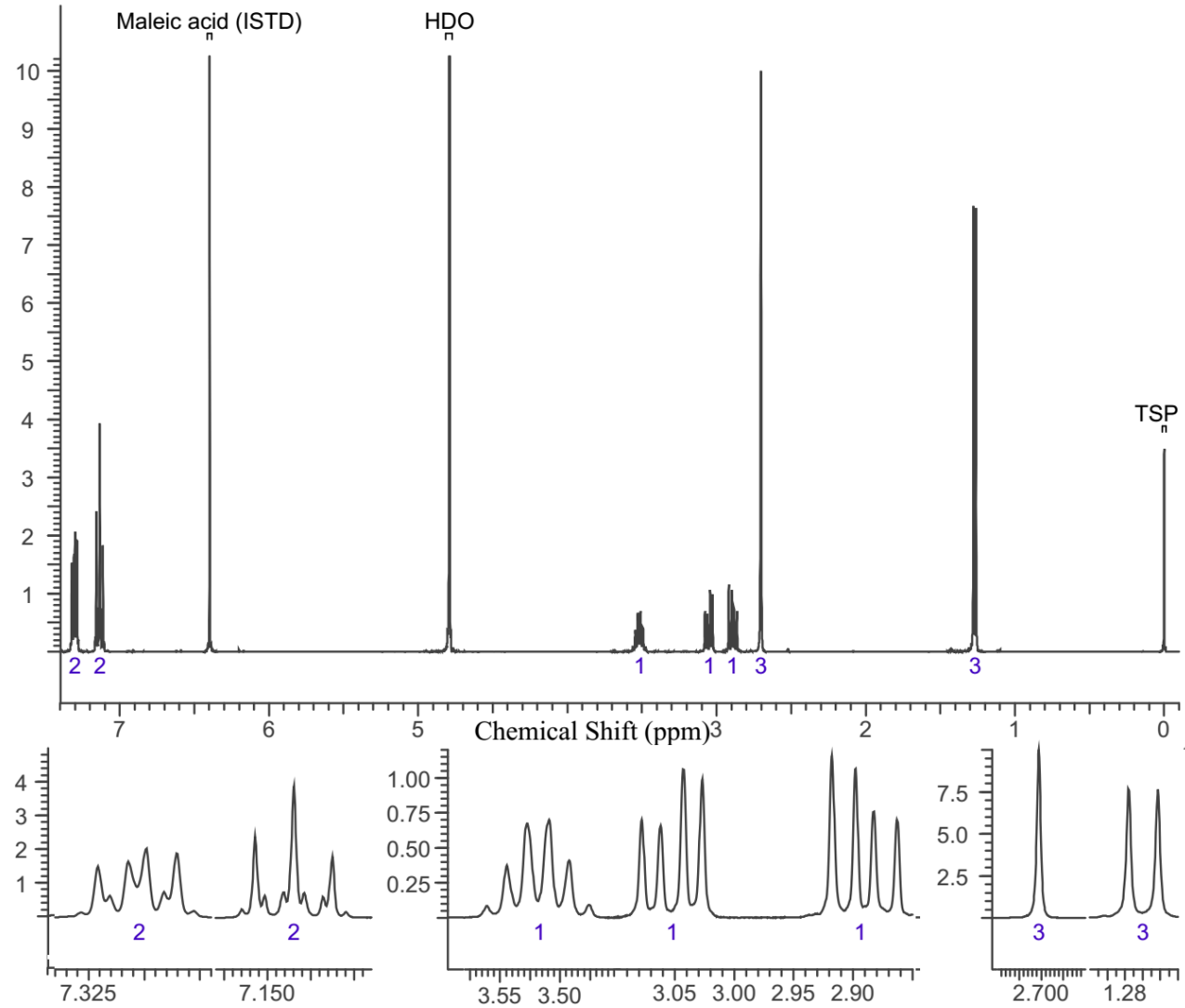
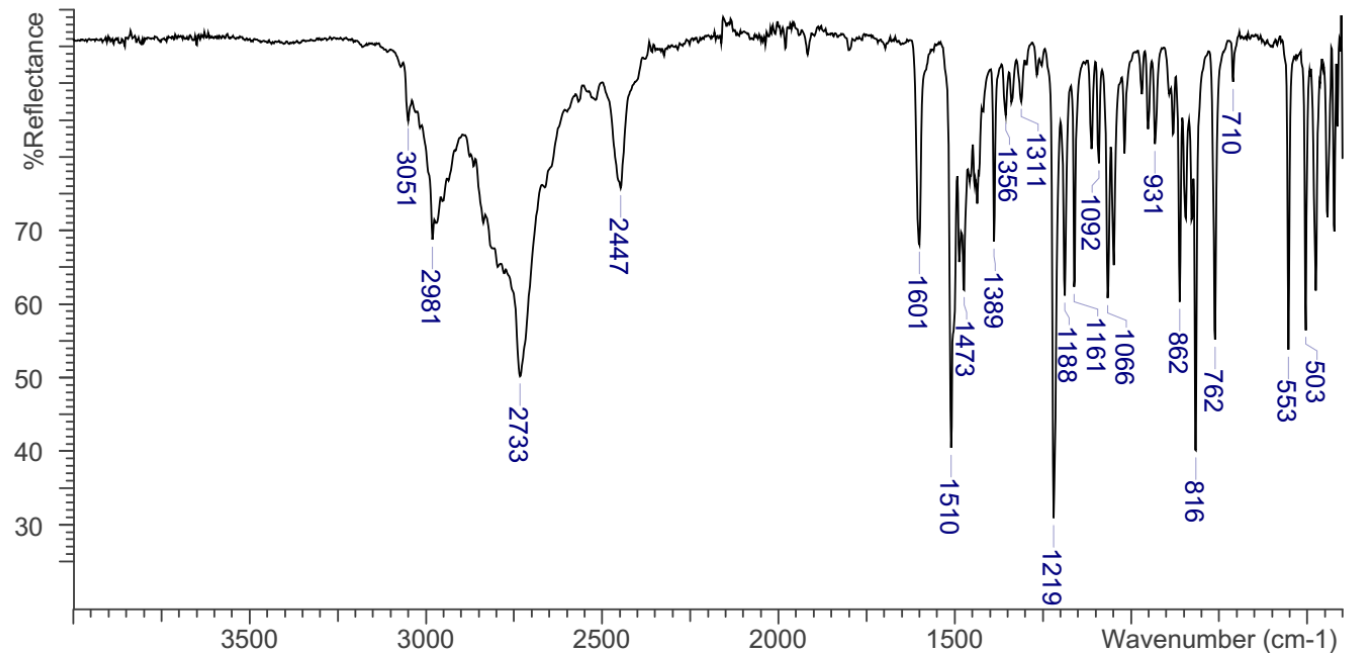




*Nelle posizioni asteriscate i protoni apparentemente equivalenti non sono tali.



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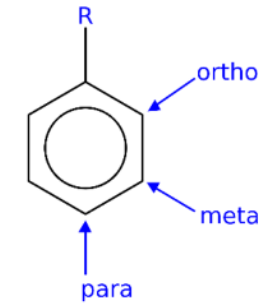
CH_2OH	-0.07	-0.07	-0.07
CF_3	0.32	0.14	0.20
CCl_3	0.64	0.13	0.10
$CH=CH_2$	0.04	-0.04	-0.12
CH=CHCOOH[a]	0.19	0.04	0.05
C C-H	0.15	-0.02	-0.01
C C-Ph[a]	0.17	-0.02	-0.03
Ph[a]	0.23	0.07	-0.02
COOH[a]	0.77	0.11	0.25
I	0.39	-0.21	0.00
OH[a]	-0.53	-0.14	-0.43
OCH_3[a]	-0.45	-0.07	-0.41
$O\text{-}C(O)CH_3$[a]	-0.27	-0.02	-0.13
O-C(O)Ph[a]	-0.14	0.07	-0.09
OPh[a]	-0.36	-0.04	-0.28
$O\text{-}SO_2Me$	-0.05	0.07	-0.01



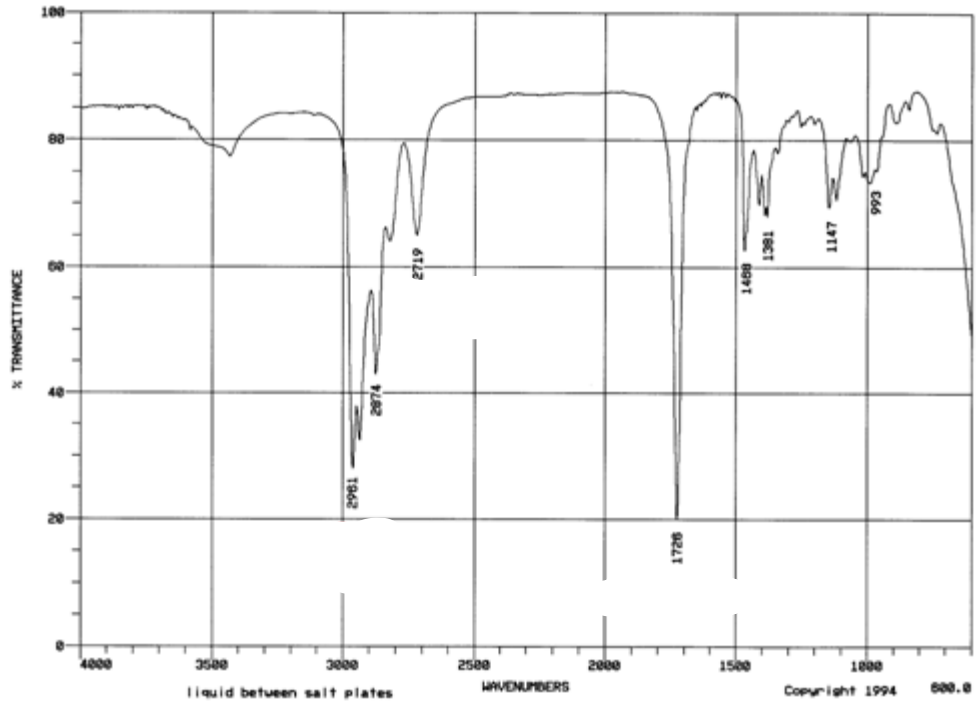
$$\delta_{Ar\text{-}H} = 7.36 + Z_{orto} + Z_{meta} + Z_{para}$$

SH	-0.08	-0.16	-0.22
NH2	-0.71	-0.22	-0.62
NEt_2[a]	-0.68	-0.15	-0.73
$NHC(O)CH_3$[a]	0.14	-0.07	-0.27
NO_2[a]	0.87	0.20	0.35

ESERCIZIO 8

Determinare l'analita

Dati: $C_5H_{10}O$; MM 86; grado di insaturazione 1: un C=C, o un anello o un C=O



IR Freq. List

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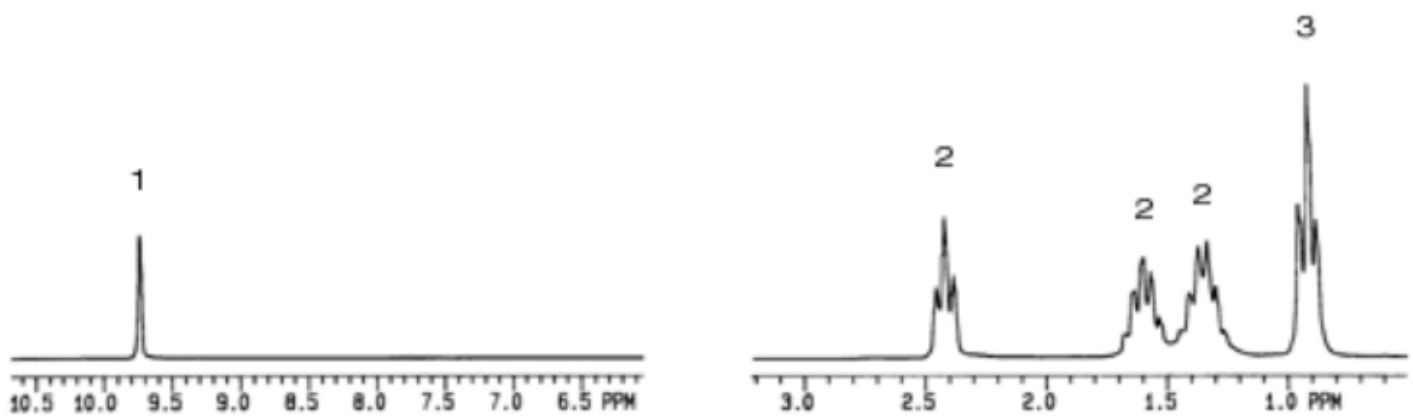


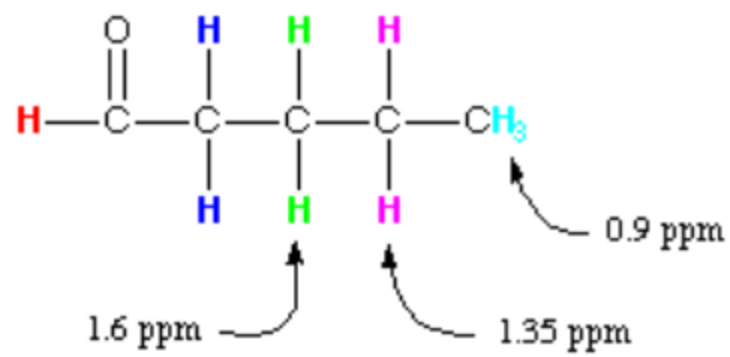
https://www.orgchemboulder.com/Spectroscopy/specttutor/tutorial.shtml

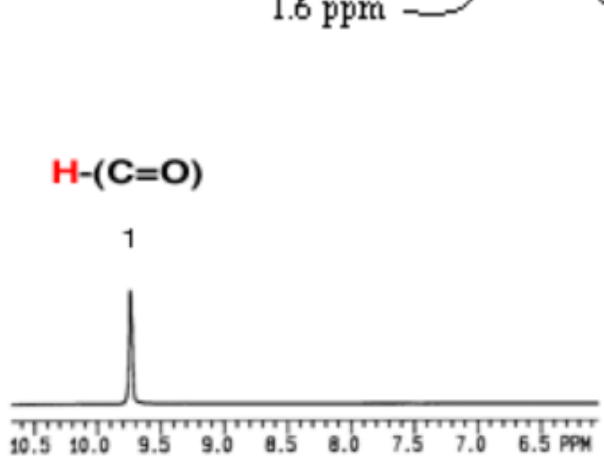
- Cerchiamo subito il C=O nello spettro IR
- Cerchiamo CH aromatici (sopra il 3000) e C=C (1680-1600)

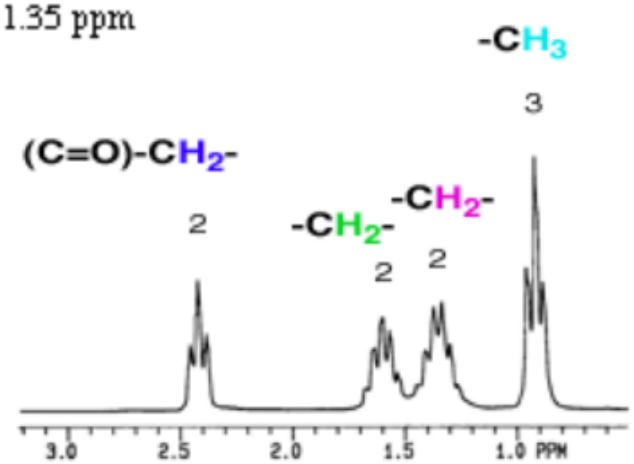
- Abbiamo un C=O

- Cerchiamo cerchiamo di capire che gruppi abbiamo dallo spettro NMR e cerchiamo di costruirla in base alla molteplicita

- Abbiamo dei gruppi metilici e metilenici tutti vicini



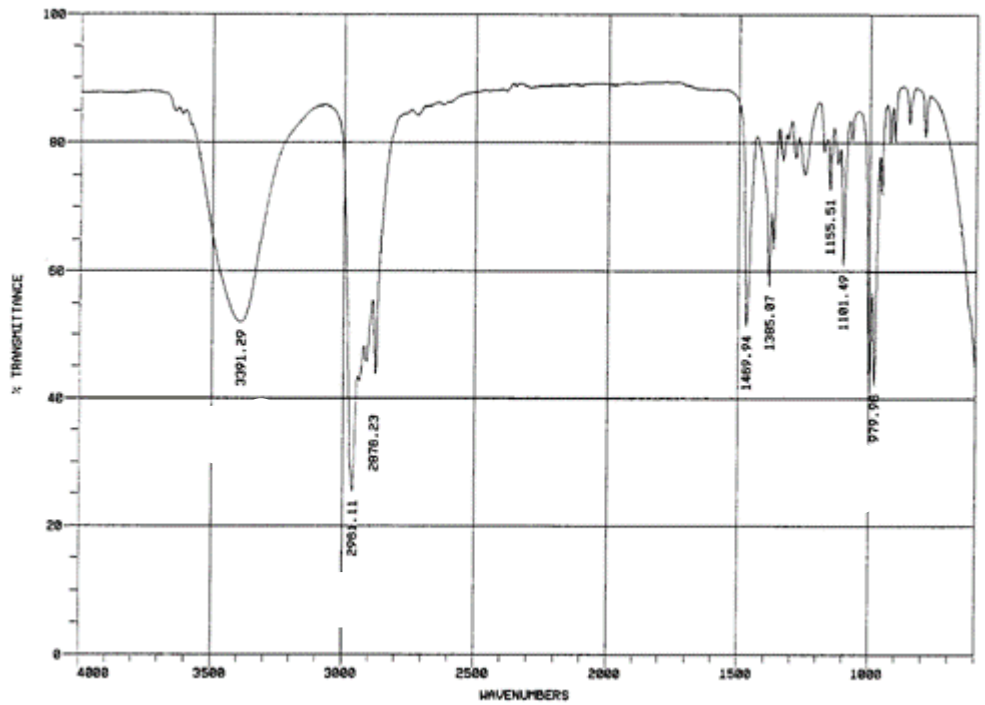




ESERCIZIO 9

Determinare l'analita

Dati: $C_7H_{16}O$; MM 116; grado di insaturazione= ?



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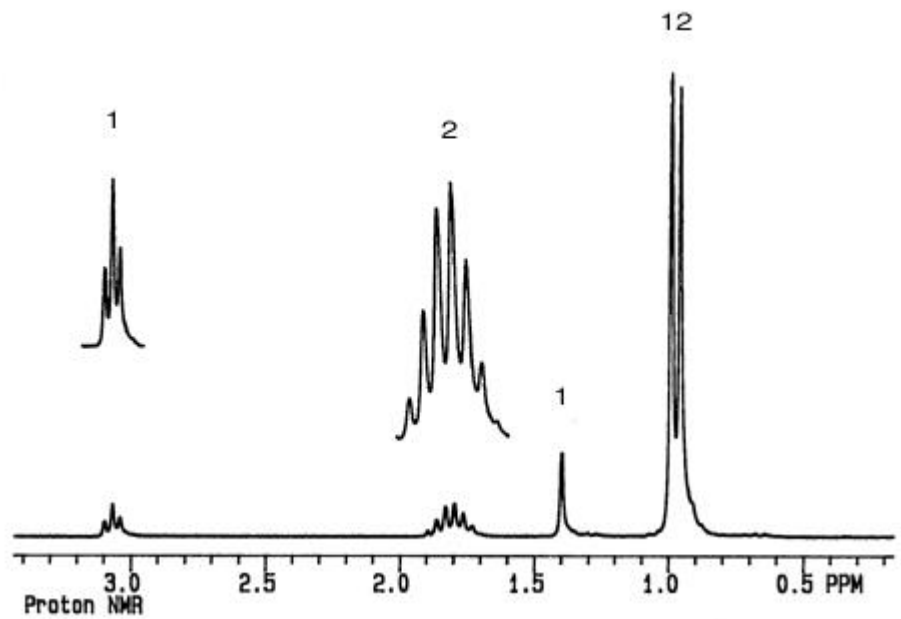


https://www.orgchemboulder.com/Spectroscopy/specttutor/tutorial.shtml

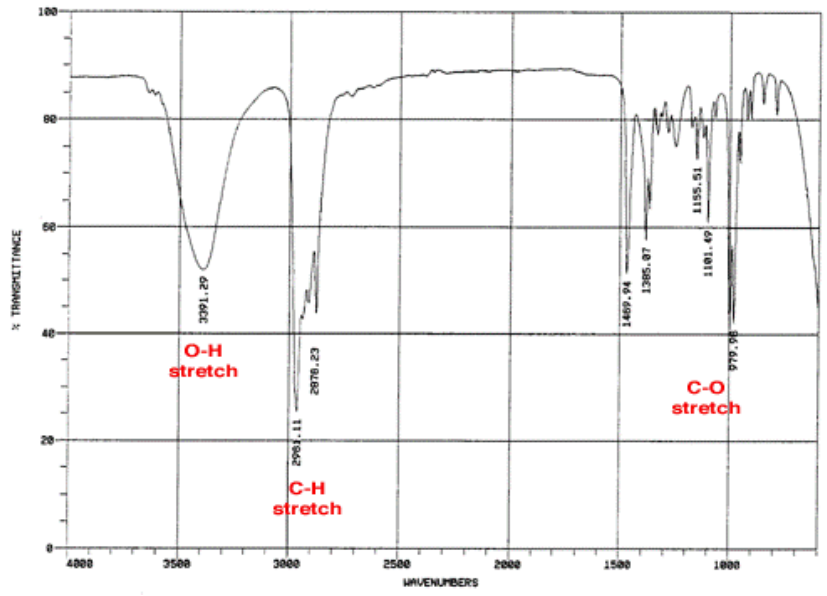
ESERCIZIO 9. Determinare l'analita

Dati: $C_7H_{16}O$; MM 116; grado di insaturazione ?

Grado di insaturazone:

7-(16/2)+1=0

No anelli o doppi legami



O-H	≈3500
N-H	3100-3500
C-H$_{alkanes}$	3000-2850
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C=C$_{aromatic}$	1600& 1475
C=C$_{alkene}$	1680-1600
C=O$_{ketone}$	1725-1700
C=O$_{amide}$	1670-1640
C=O$_{ester}$	1750-1730

Cosa ci dice l' IR?

Notiamo che c''e un segnale tipico del OH .

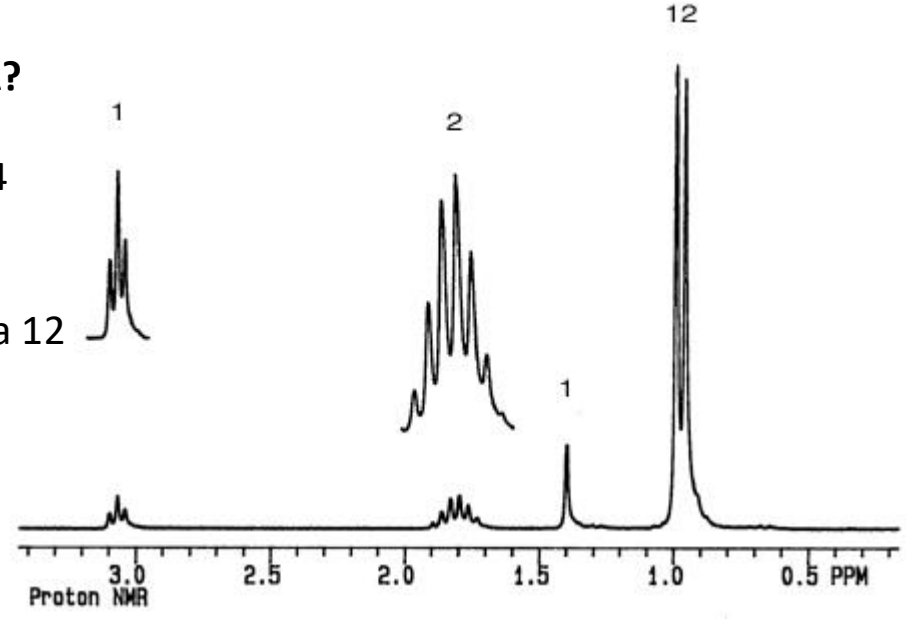
Presenza di segnali CH alifatici

Cosa ci dice l' NMR?

Solo alifatici e solo 4 gruppi di segnale

Ma soprattutto un Gruppo di segnali da 12

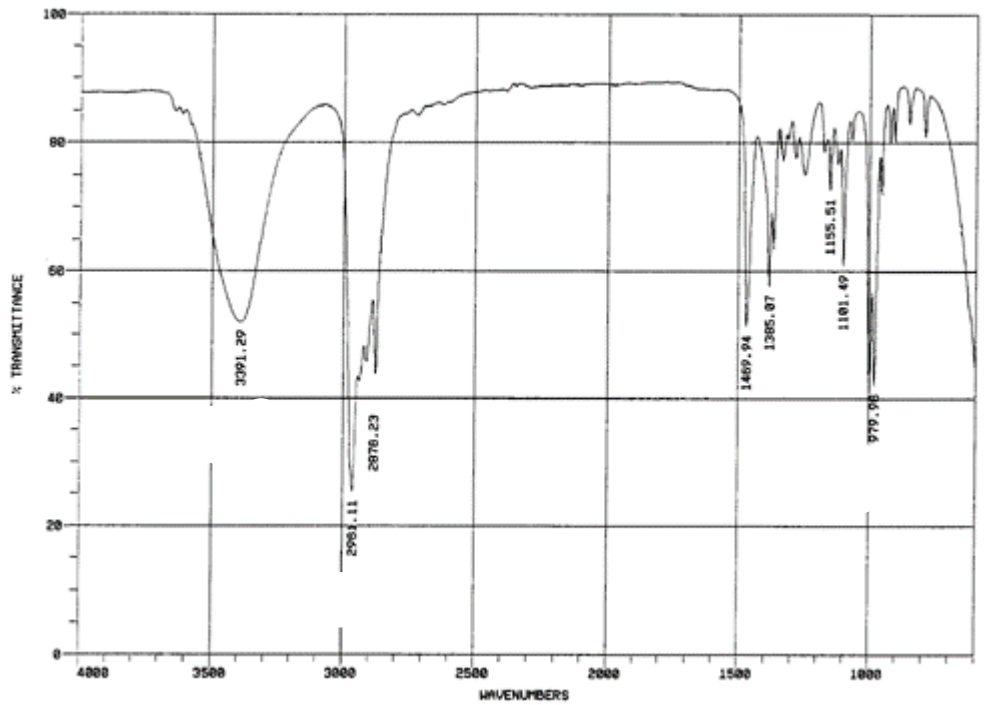
Guardiamo le molteplicità



ESERCIZIO 9

Determinare l'analita

Dati: $C_7H_{16}O$; MM 116; grado di insaturazione= ?



IR Freq. List

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N-H	3100-3500
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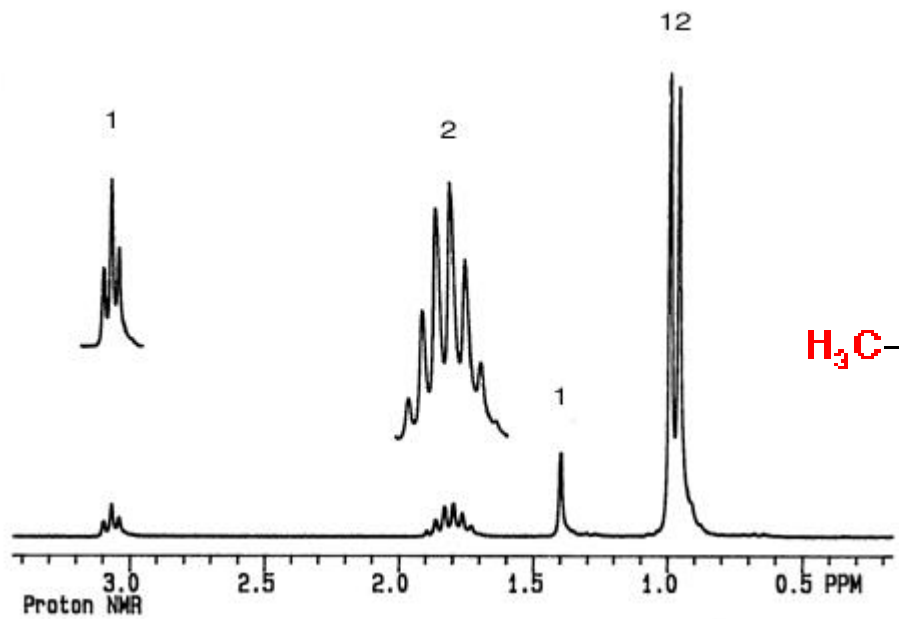
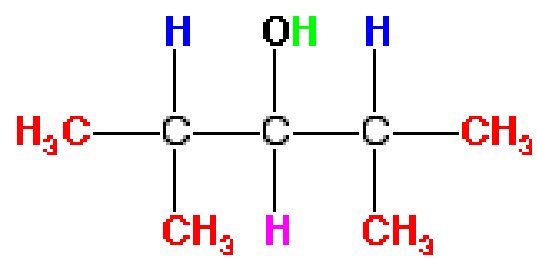
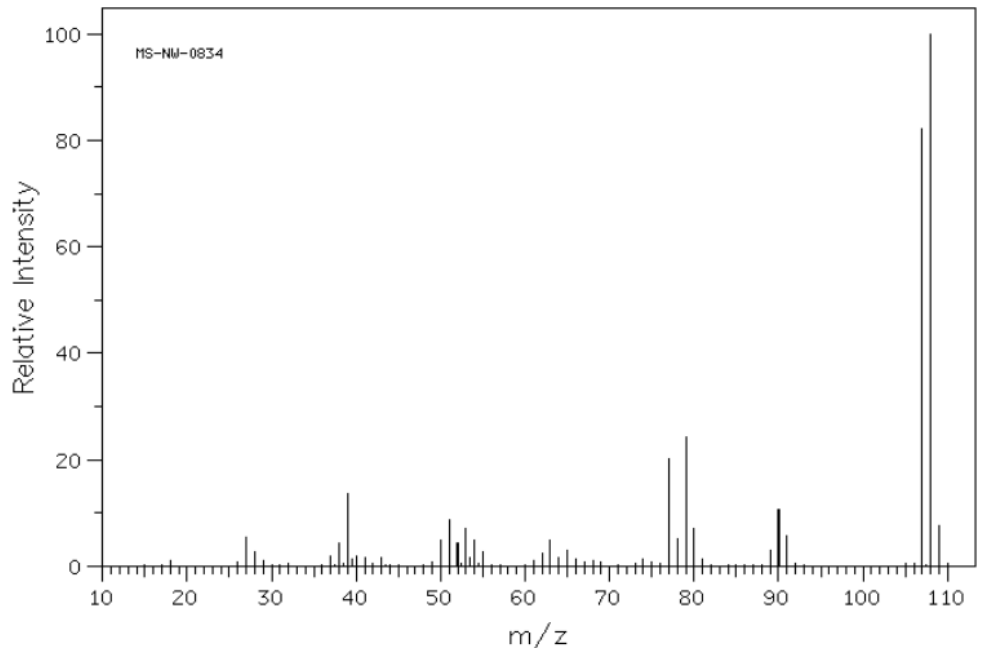


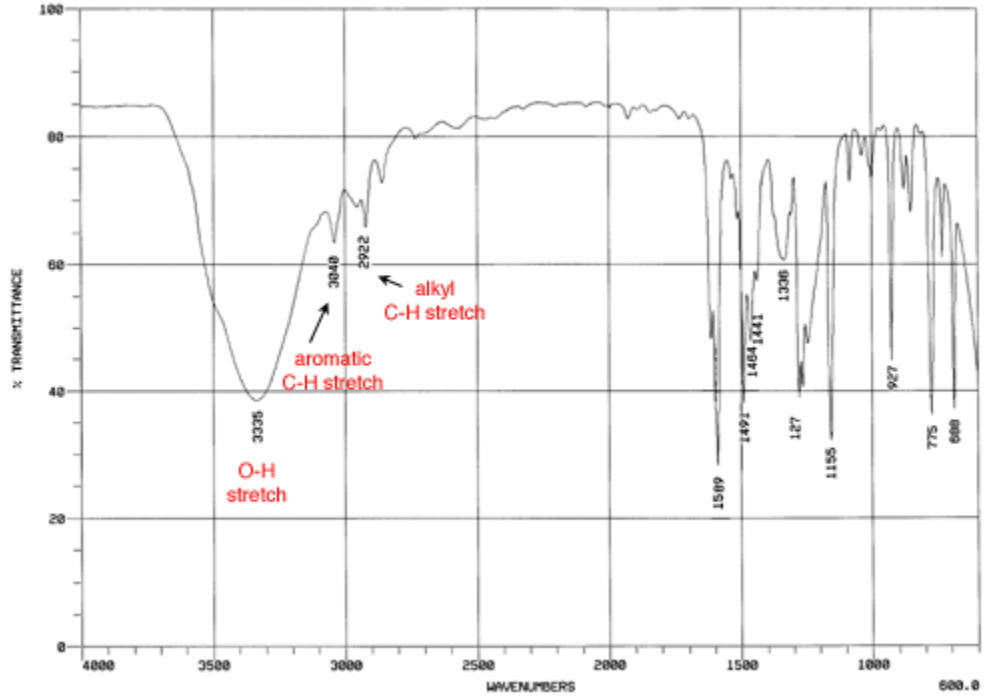


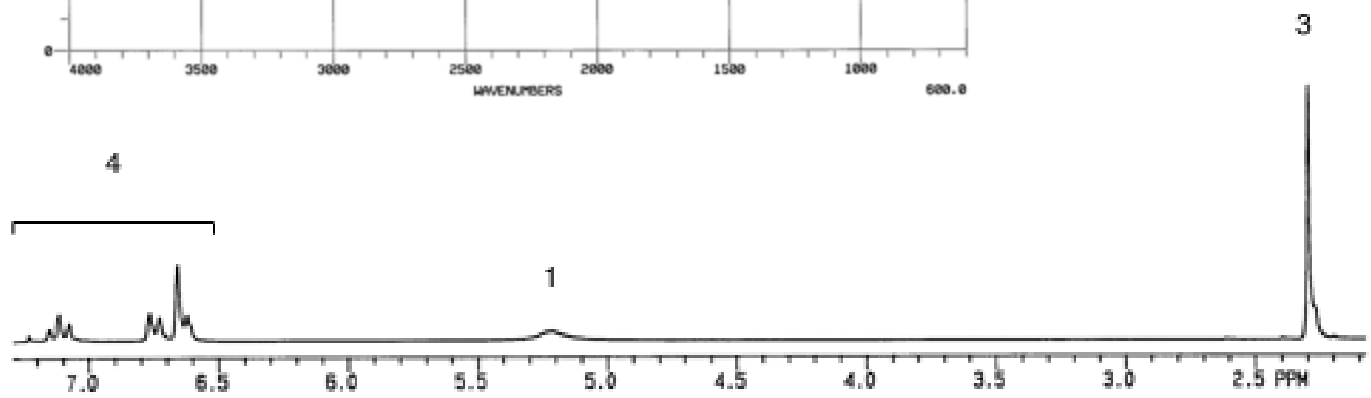
https://www.orgchemboulder.com/Spectroscopy/specttutor/tutorial.shtml

ESERCIZIO 10; Determinare l'analita

Formula: C_7H_8O ; MW =? ; grado di insaturazione: ?

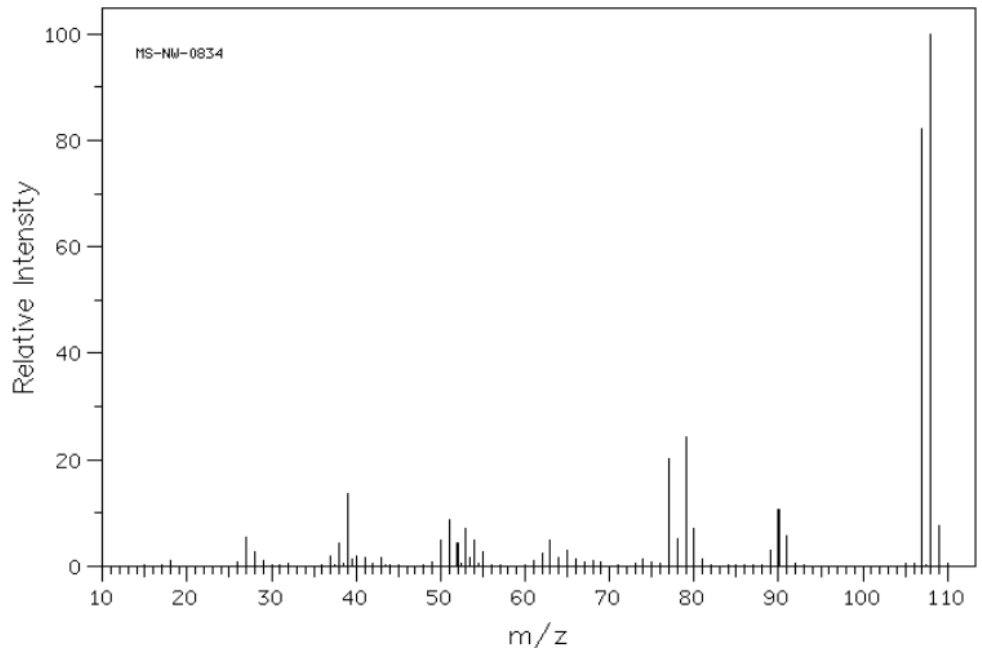






ESERCIZIO 10; Determinare l'analita

Formula: C_7H_8O ; MW=?; grado di insaturazione: ?

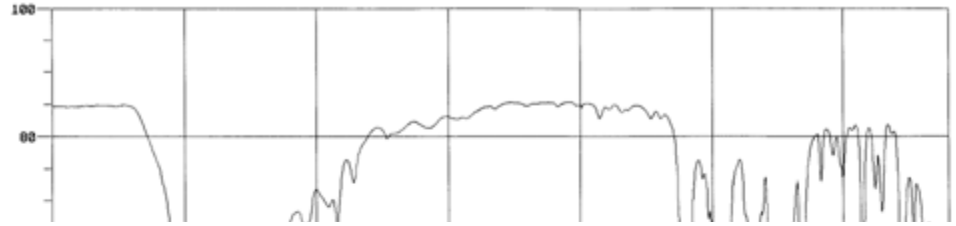


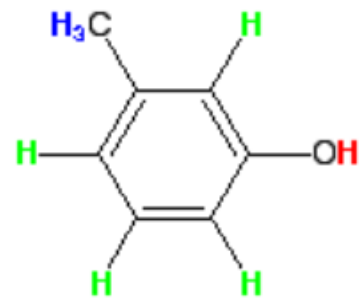
Grado di insaturazone:
7-(8/2)+1=4

Prob. Anello aromatico

Massa Molecolare?

Dallo spettro di massa
MM=108

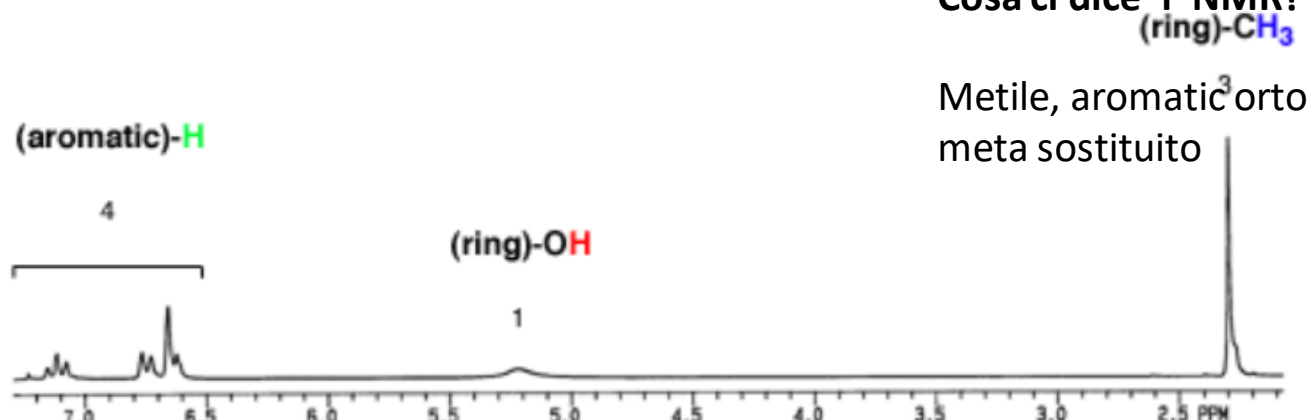




Cosa ci dice l' IR?

Notiamo che c''e un segnale tipico del OH .
Vediamo segnali CH Aromatici e alifatici

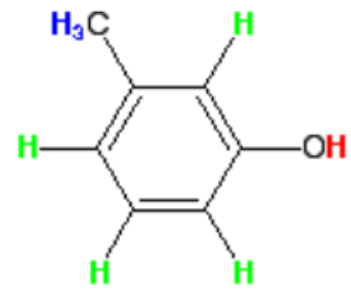
Cosa ci dice l' NMR?

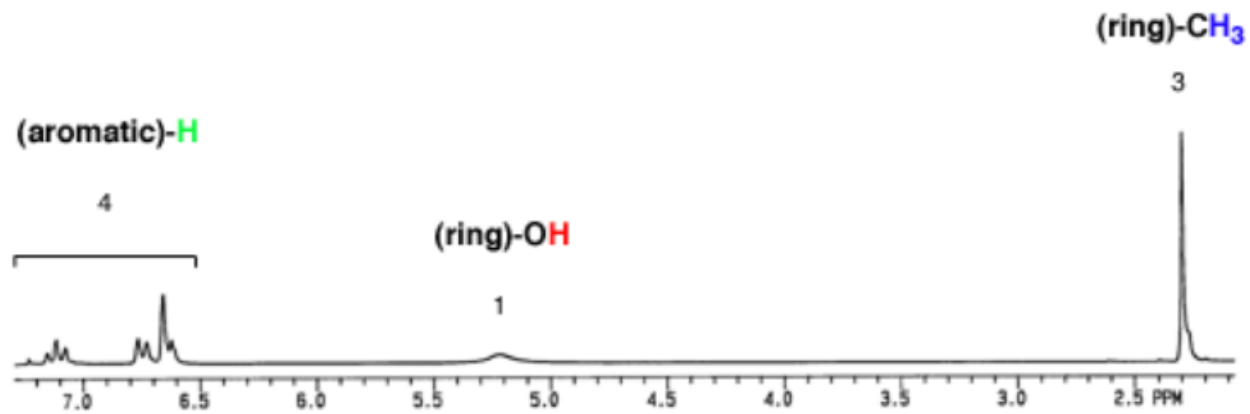


Metile, aromatic orto o meta sostituito

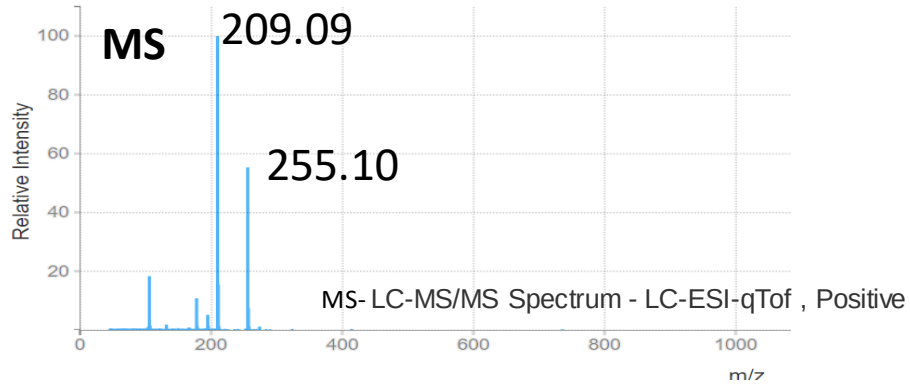
ESERCIZIO 10; Determinare l'analita
Formula: C_7H_8O ; MW 108;

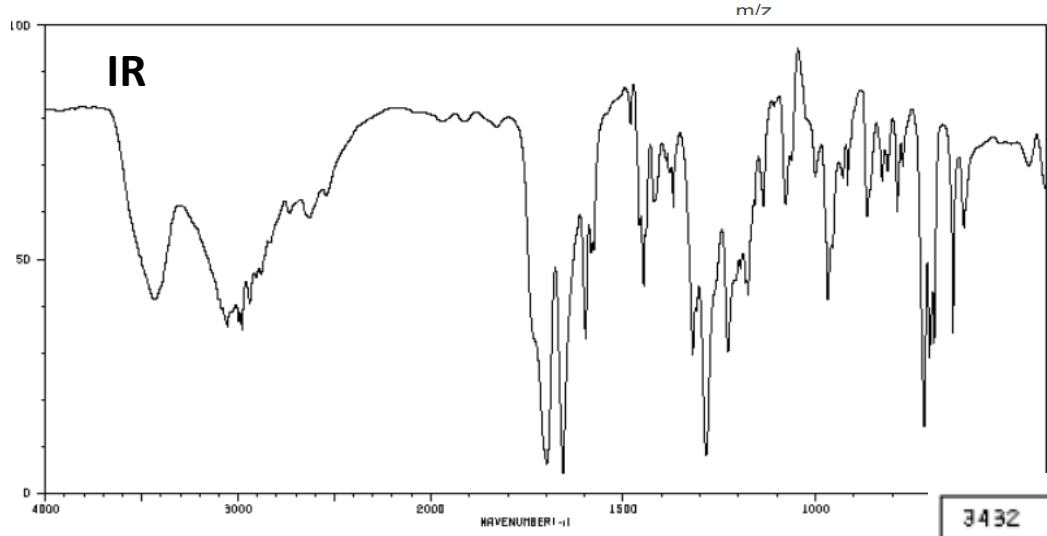
Grado di insaturazione: 4





ESERCIZIO 11; Determinare l'analita con Formula: $C_{16}H_{14}O_3$ dalla formula e seguenti spettri.





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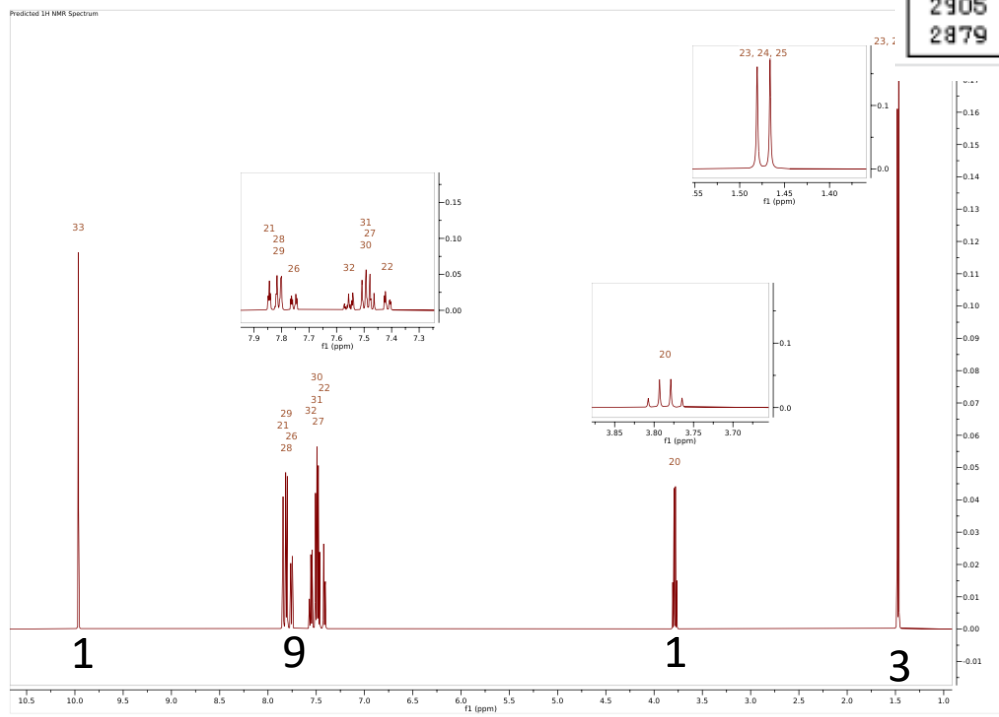
3432	42	2734	68	1676	62
3055	36	2645	58	1457	57
2997	37	2628	56	1447	44
2979	36	1698	6	1441	63
2940	41	1656	4	1320	30
2905	46	1598	35	1265	8
2879	46	1684	60	1228	31

IR peaks

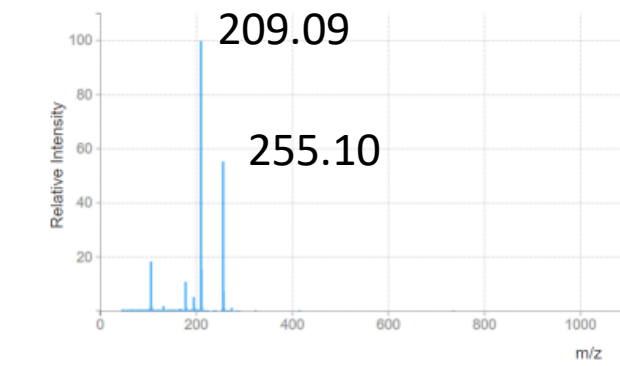
NMR

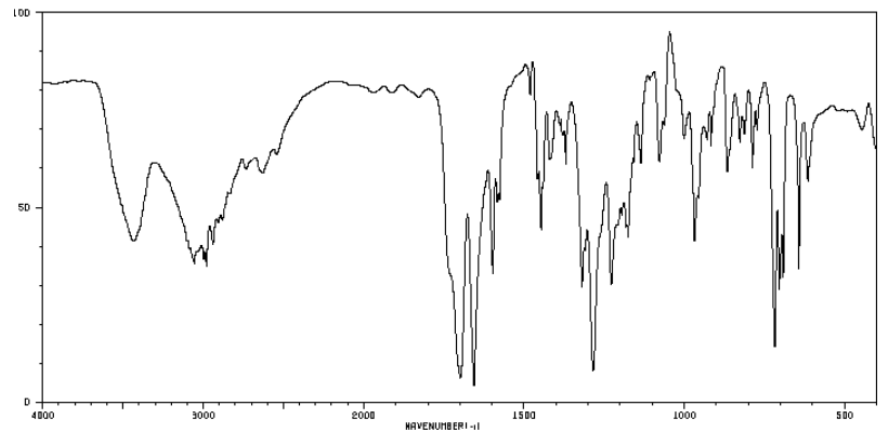


ESERCIZIO 11; Determinare l'analita

Formula: $C_{16}H_{14}O_3$;

MS- LC-MS/MS Spectrum - LC-ESI-qTof , Positive





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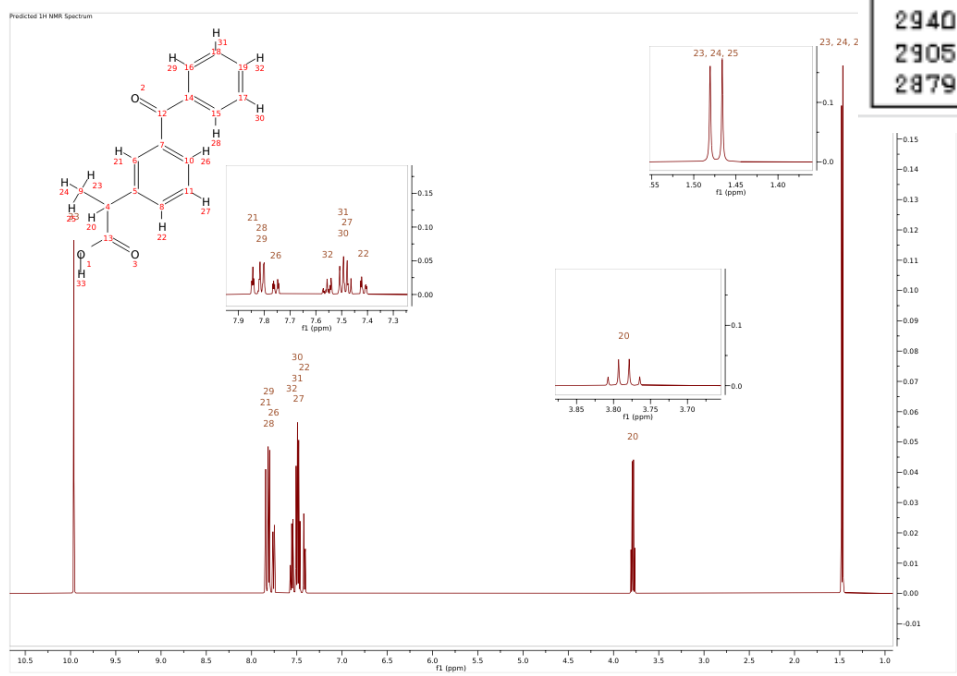
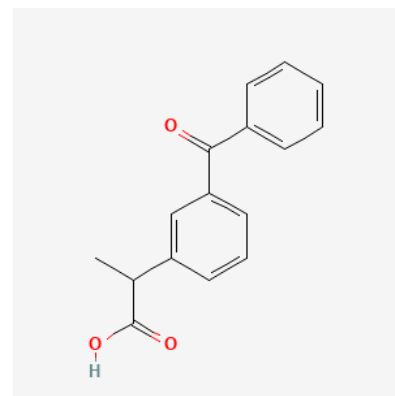
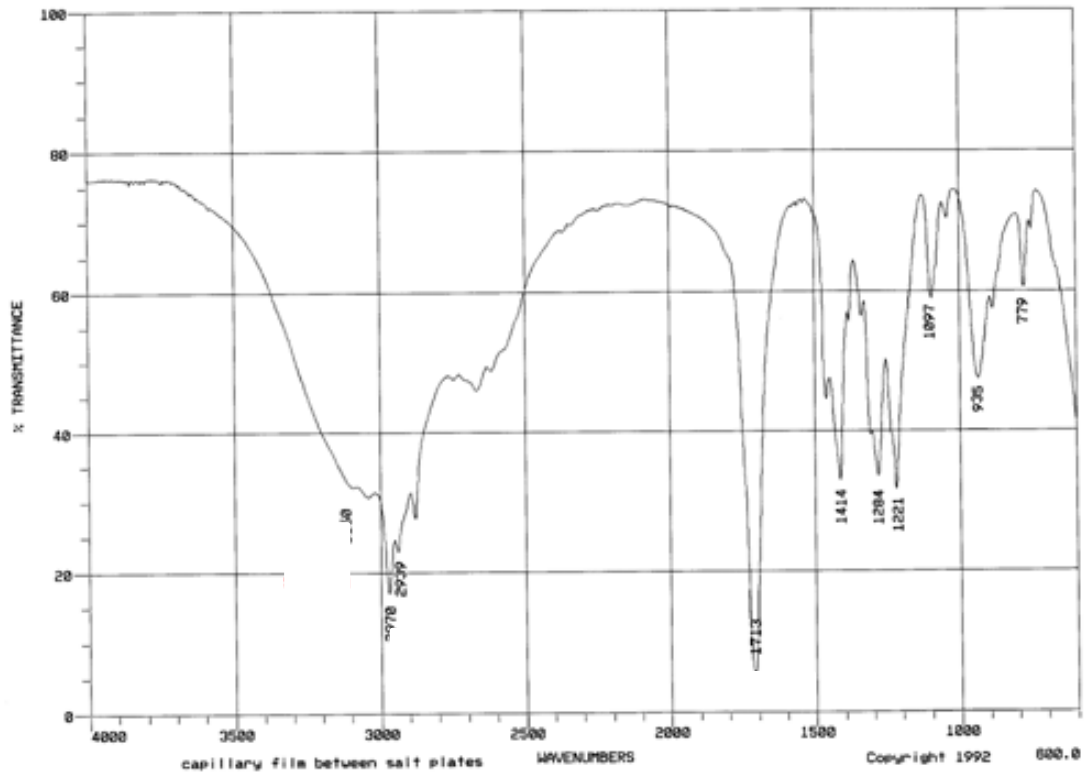




ESERCIZIO 12; Determinare l'analita con Formula: $C_4H_8O_2$ dalla formula e seguenti spettri.



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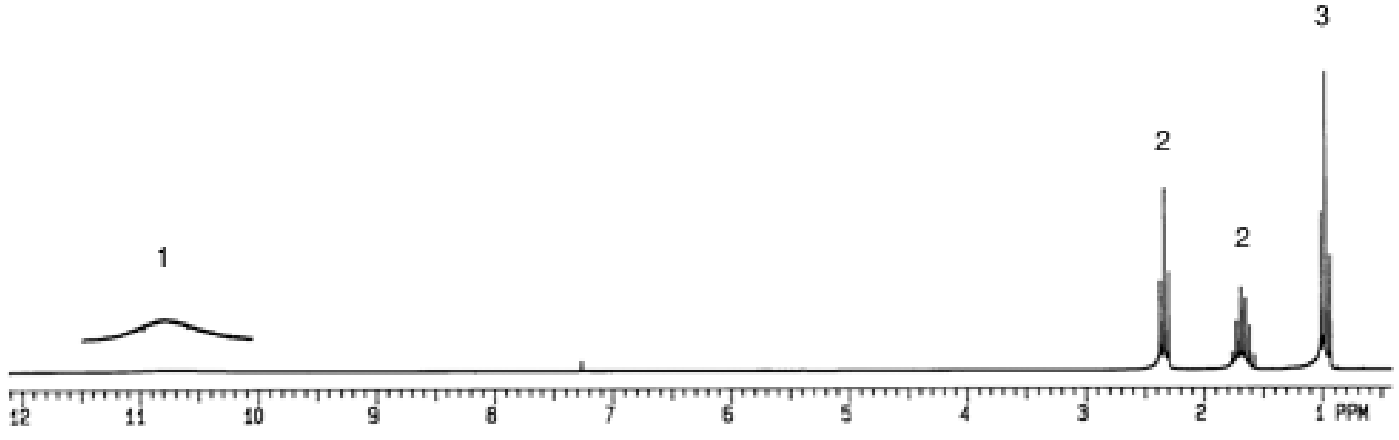

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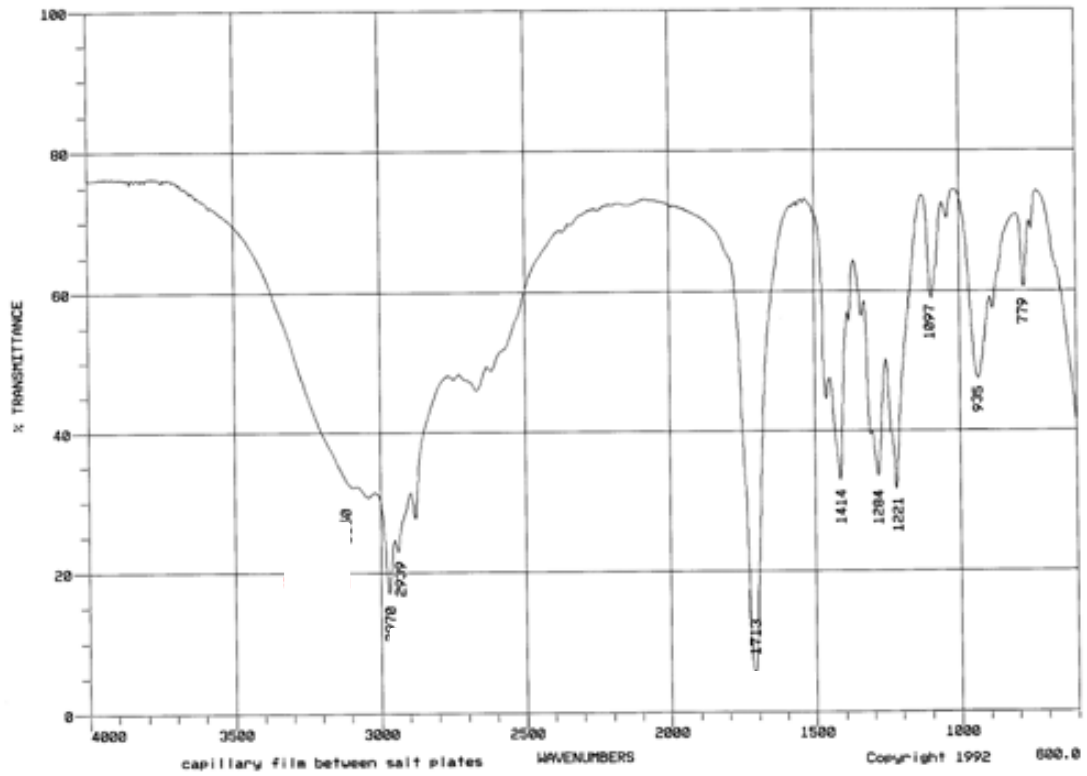

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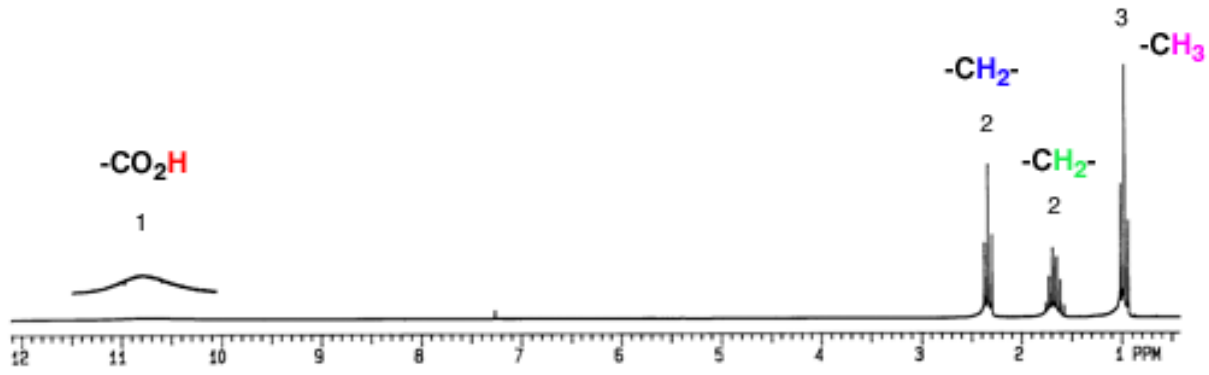
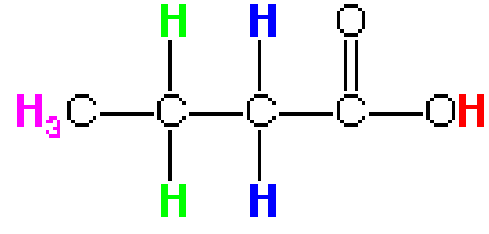
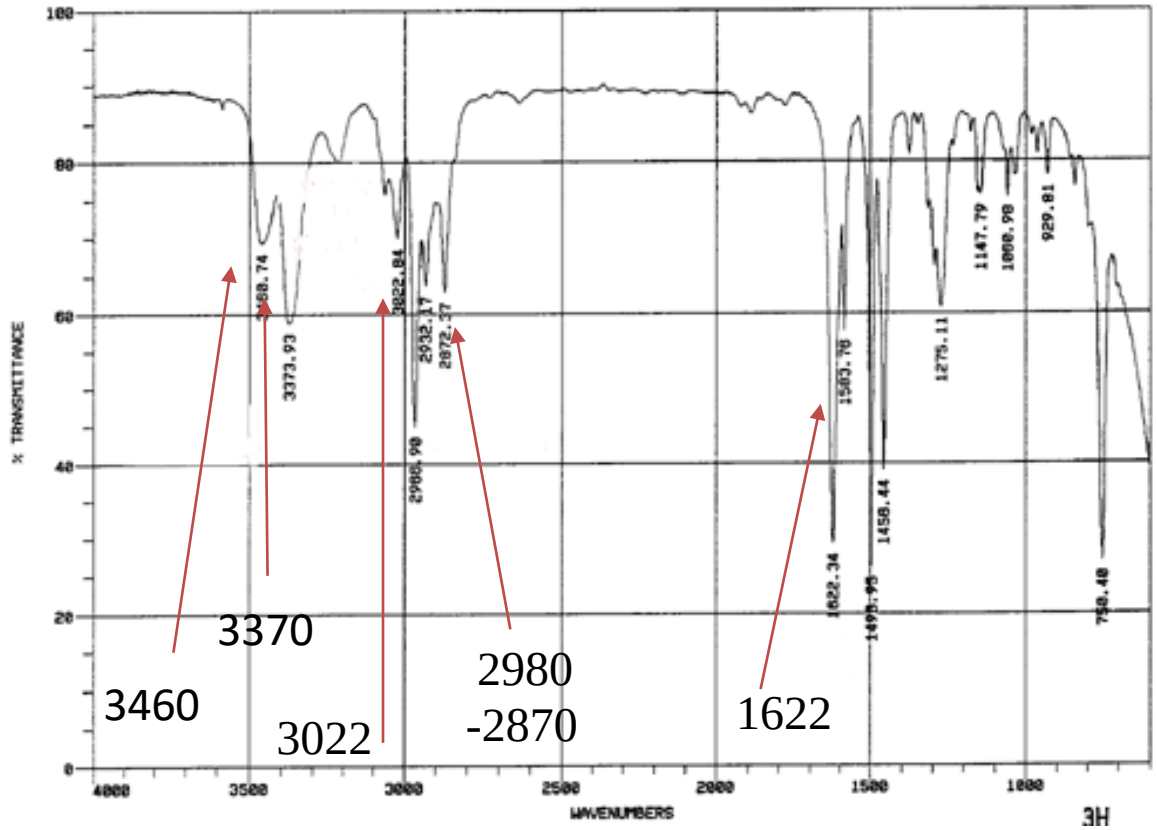




ESERCIZIO 13; Determinare l'analita con Formula: $C_8H_{11}N$ dalla formula e seguenti spettri.



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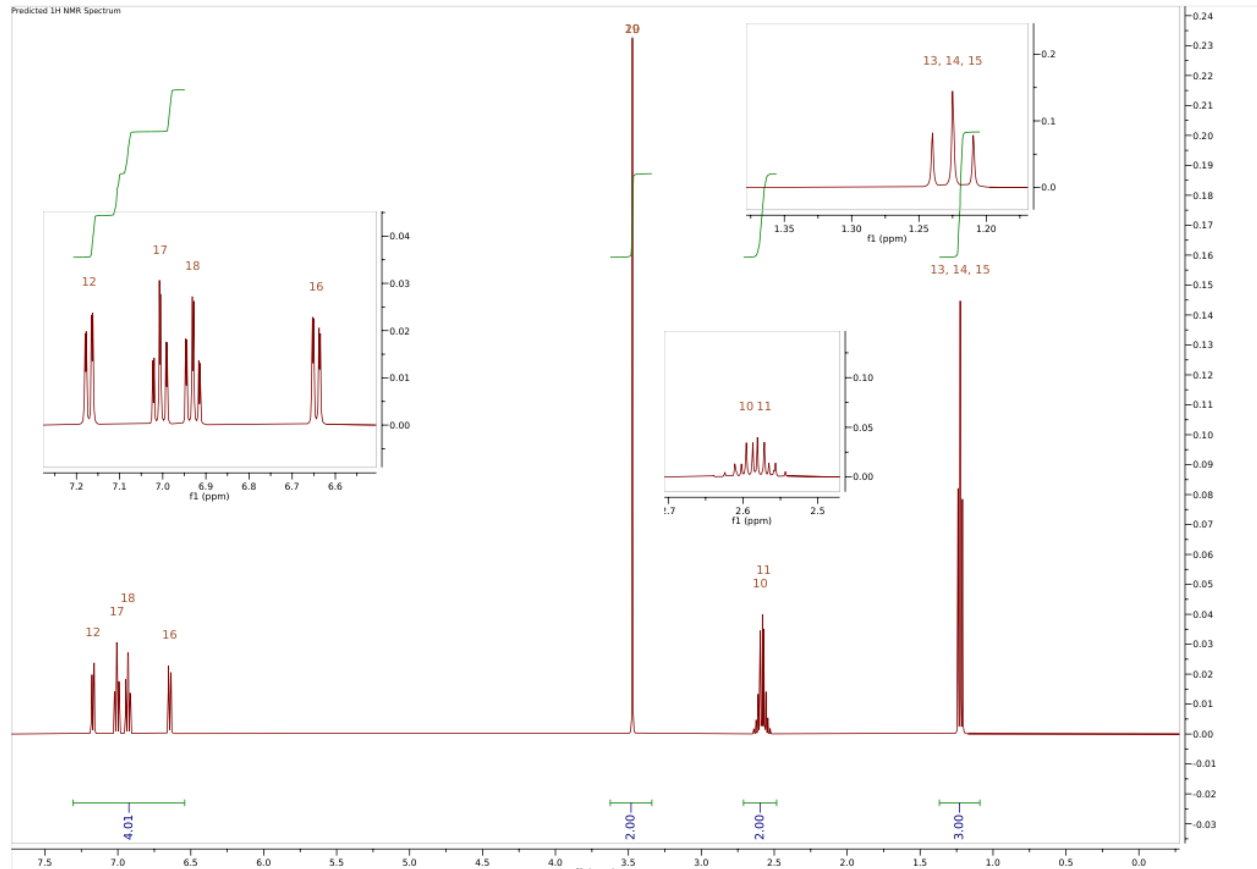
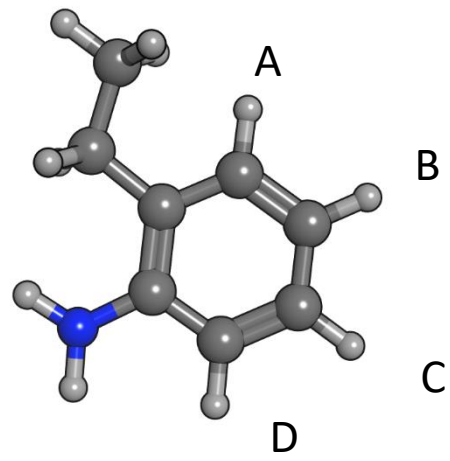
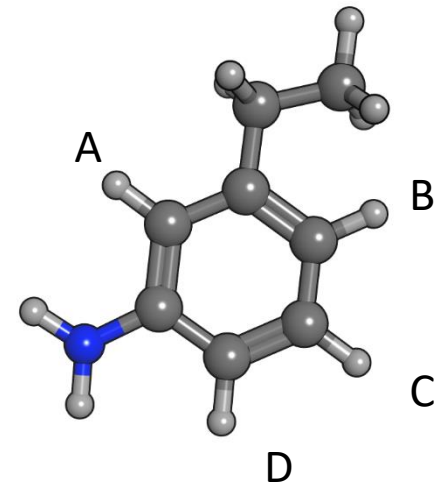
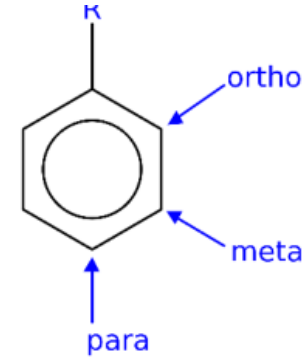






Sost	Z_{orto}	Z_{meta}	Z_{para}
NH2	-0.71	-0.22	-0.62
CH3	-0.18	-0.11	-0.21

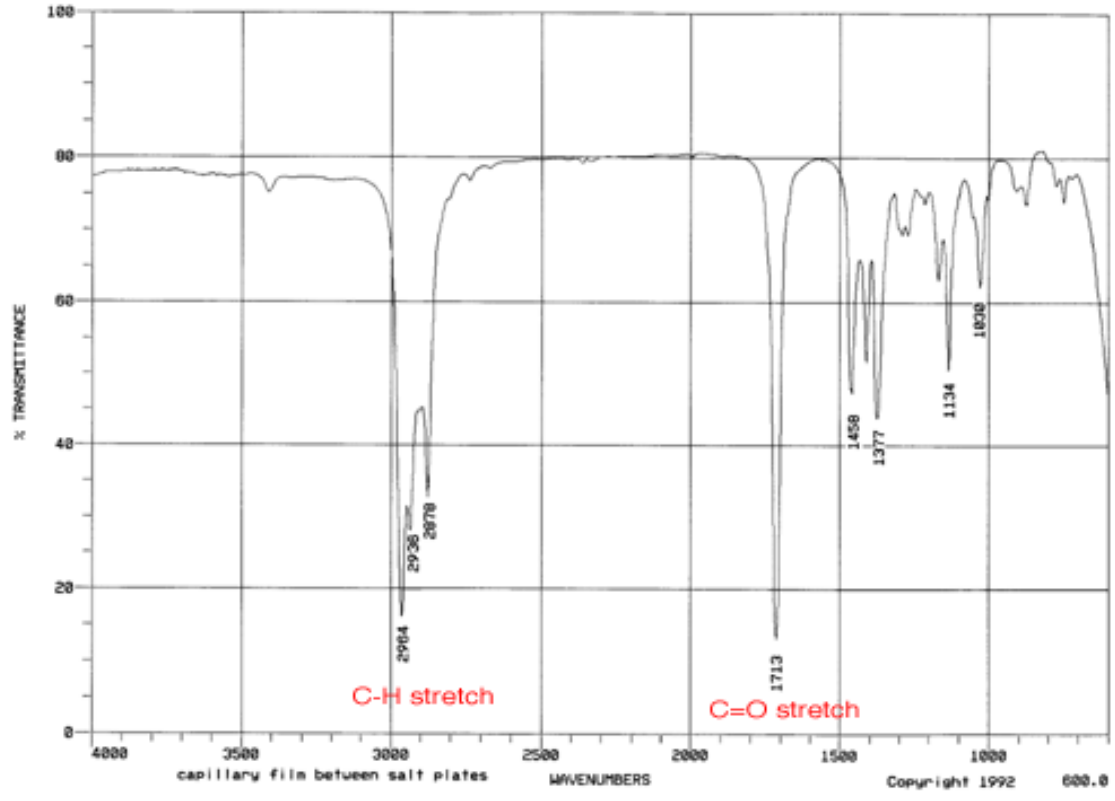


$$\delta_{Ar\text{-}H} = 7.36 + Z_{orto} + Z_{meta} + Z_{para}$$

A=7.36 - 0.18 (CH3orto)-0.22 (NHmeta)=6.96
B=7.36 - 0.11 (CH3meta)-0.62 (NHpara)=6.63
C=7.36 - 0.21 (CH3para)-0.22 (NHmeta)= 6.93
D=7.36 - 0.11 (CH3meta)-0.71 (NHorto)=6.54

A=7.36 - 0.18 (CH3orto)-0.71 (NHorto)=6.47
B=7.36 - 0.18 (CH3orto)-0.62 (NHpara)=6.56
C=7.36 - 0.11 (CH3meta)-0.22 (NHmeta)= 6.97
D=7.36 - 0.21 (CH3para)-0.71 (NHorto)=6.44

ESERCIZIO 14; Determinare l'analita con Formula: $C_7H_{14}O$ dalla formula bruta e seguenti spettri. MM=151 Da



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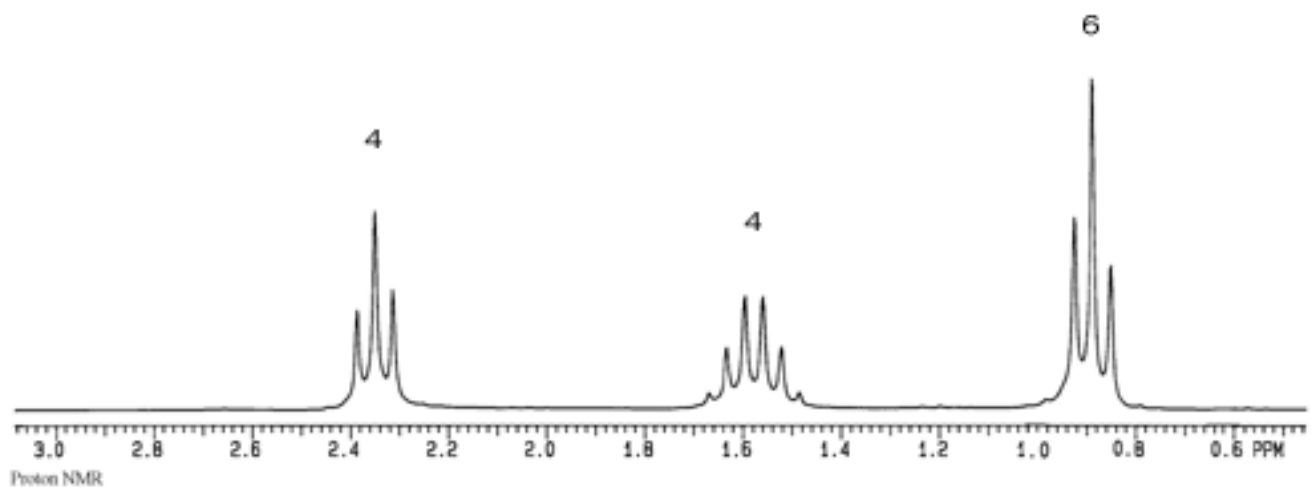
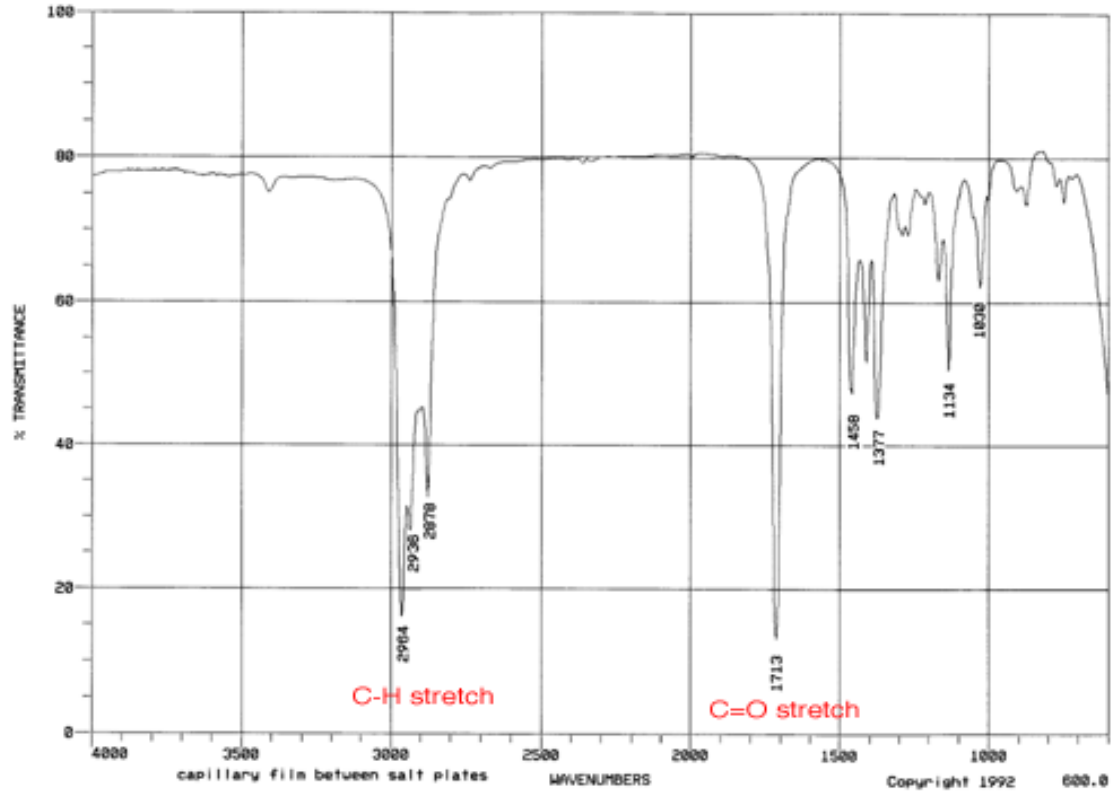


ESERCIZIO 14; Determinare l'analita con Formula: $C_7H_{14}O$ dalla formula bruta e seguenti spettri. MM=151 Da



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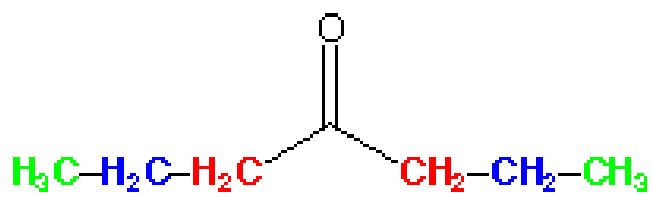
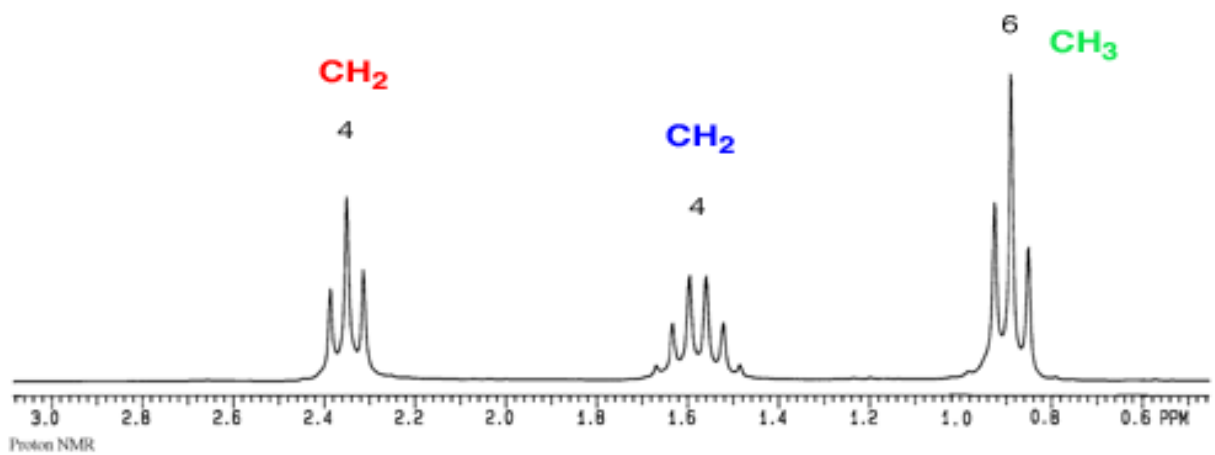




SOLUZIONI:

Esercizio 1: mol a

Esercizio 2: vedi spettro

Esercizio 3: mol b 2-propanolo

Esercizio 3-bis:

H-10a: 7.36 + 0.32 (CF3, orto) - 0.14 (OH meta) = 7.54

H-8a: 7.36 - 0.41 (OH para) + 0.14 (CF3 meta) = 7.09

H-6a: 7.36 + 0.20 (CF3, para) - 0.14 (OH meta) = 7.42

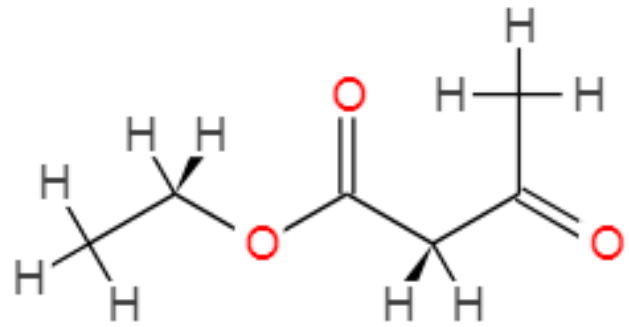
H-4a: 7.36 – 0.53 (OH orto) + 0.14 (CF3 meta) = 6.97

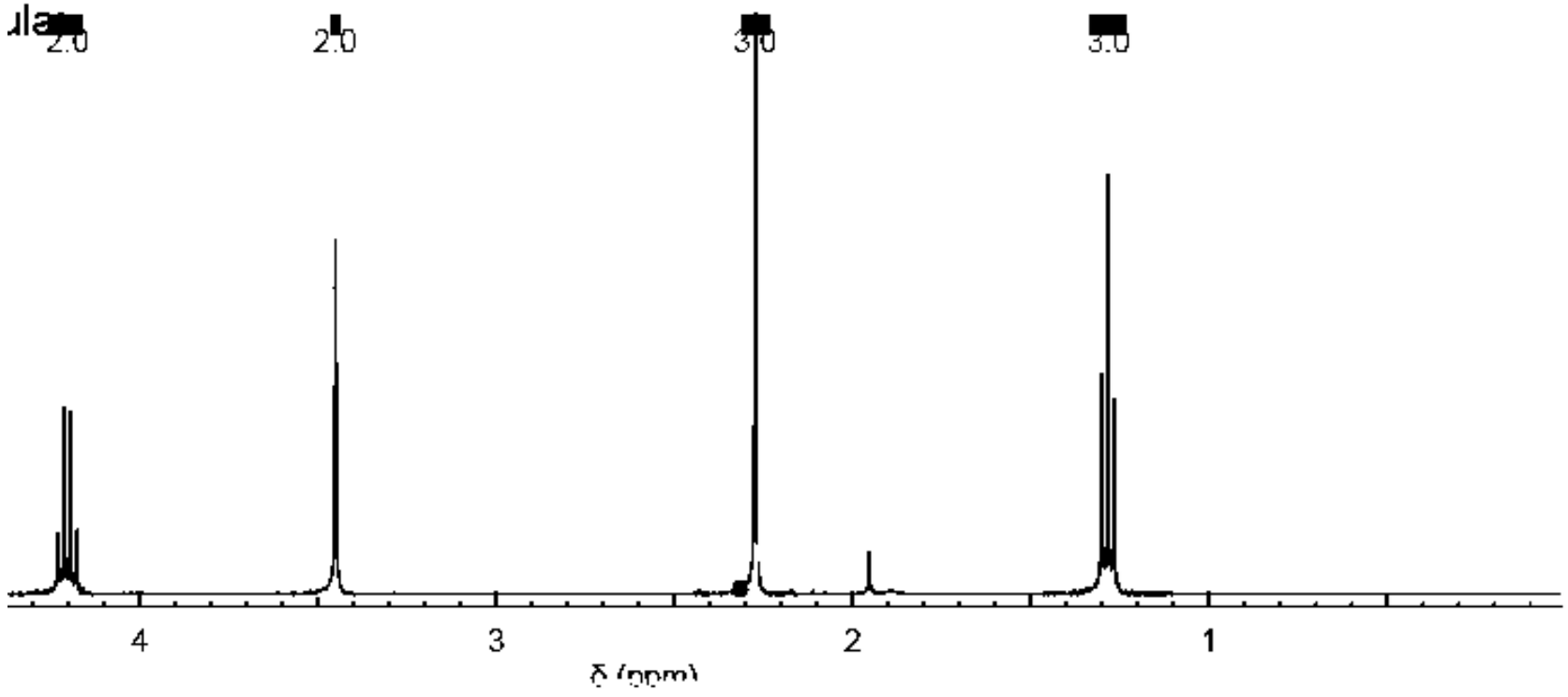
Esercizio 4: mol a Bupropione

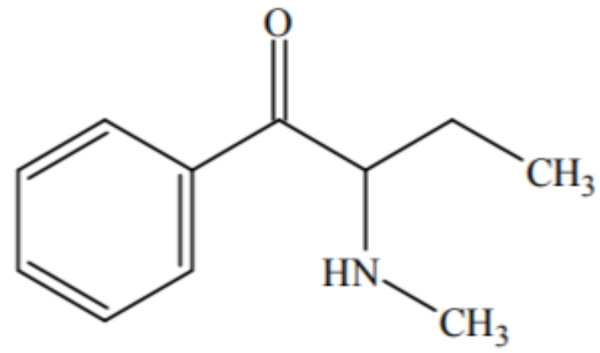
Esercizio 5: mol b Sertralina

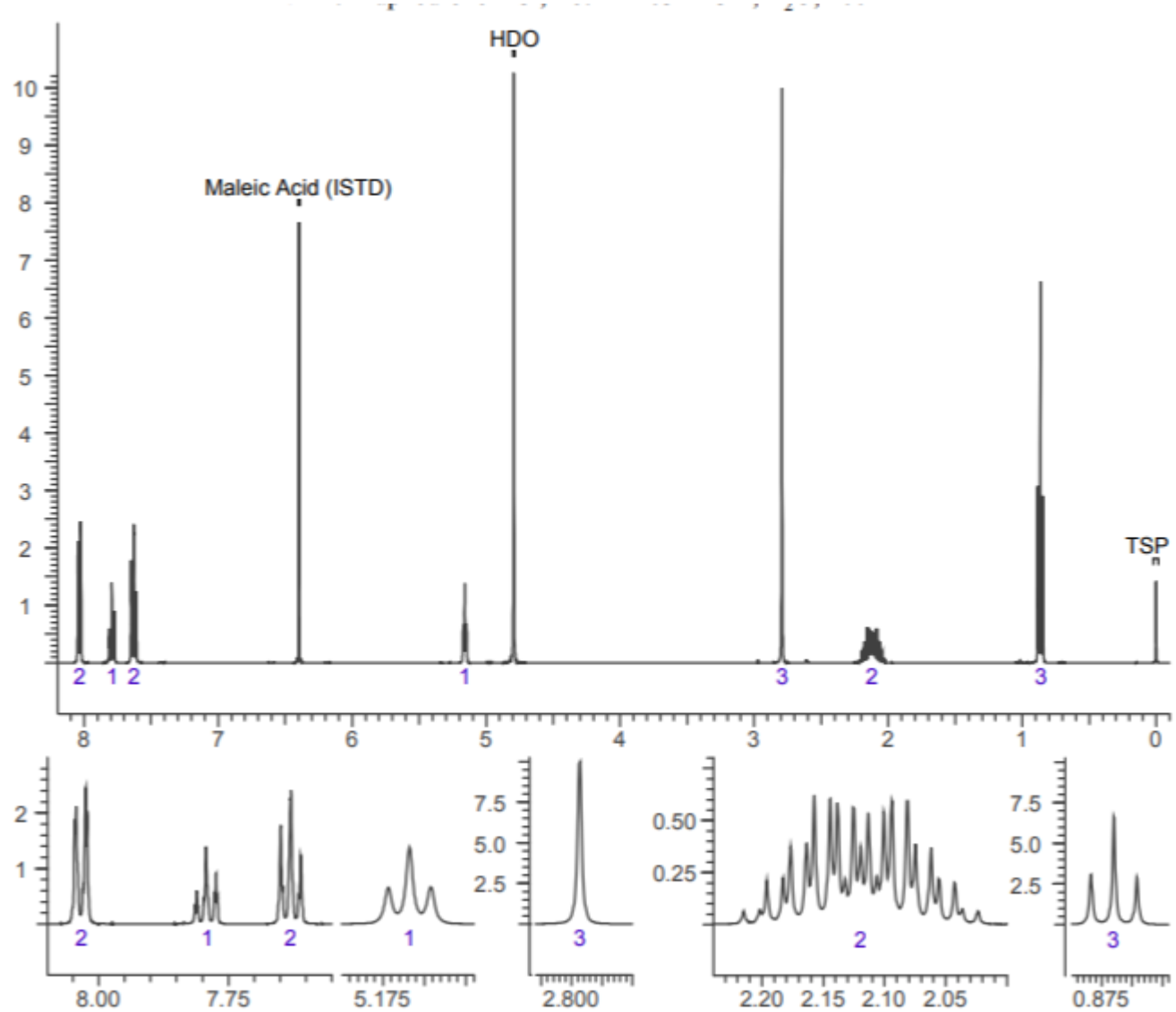
Esercizio 6: mol b Barbital

Esercizio 7: mol c p-fluorometaanfetamina


H
H
H
O
H
H
H
O
H
H
H
H


2.0
2.0
3.0
3.0
4
3
2
1
δ (ppm)


O
CH3
HN
CH3


HDO
Maleic Acid (ISTD)
TSP
2 1 2
1
3
2
3
8.00
7.75
5.175
2.800
2.20 2.15 2.10 2.05
0.875