CHM201 Spectroscopy and other Physical Methods

Spectral Problems

Nuclear Magnetic Resonance – Spectral Problems Solving

Information from ^{1}H-NMR Spectral Data:

1. **Number of signals** – Information on symmetry & types of protons
2. **Nature of the peak** – Information on relaxation/hydrogen bonding
3. **Chemical Shift** – Local environment around the proton

$$\nu_{\text{eff}} = (\gamma/2\pi)\, \boldsymbol{B}_0\, (1 - \sigma)$$

4. **Splitting pattern (multiplicity)** – Neighboring group & connectivity
5. **Integral values** – Number of protons or proton ratios
6. **Coupling constant** – Geometrical position of coupling partner

Solving structure of molecules

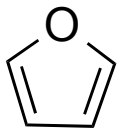
For a compound of molecular formula $C_aH_bN_cO_dS_eX_f$

$$\text{Double bond equivalent} = (a+1) - \frac{b-c+f}{2}$$

where
a = No. of carbon atoms (Tetravalent)
b = No. of hydrogen atoms (Monovalent)
c = No. of nitrogen atoms (Trivalent)
d = No. of oxygen atoms (Divalent)
e = No. of sulphur atoms (Divalent)
f = No. of halogen atoms (Monovalent)

Nuclear Magnetic Resonance – Spectral Problems Solving

Problem 1: Predict the number of signals in 1H-NMR for the following compounds.



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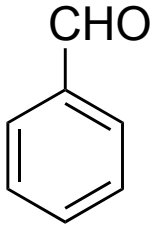

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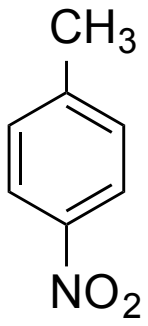

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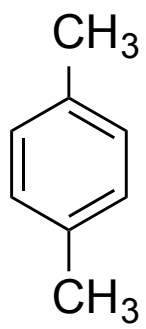

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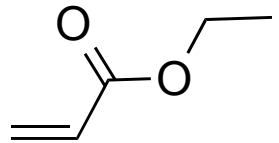
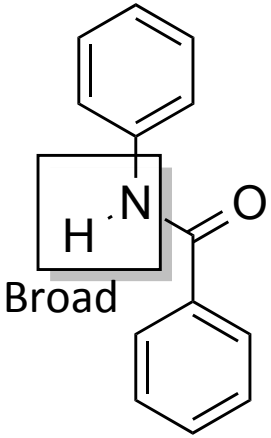
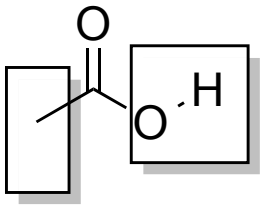


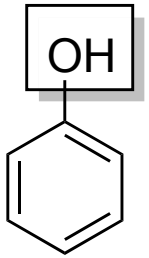
5

Problem 2: What will be the nature of the signals at the indicated protons?

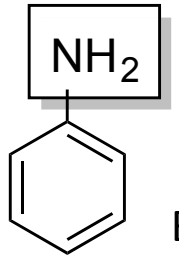


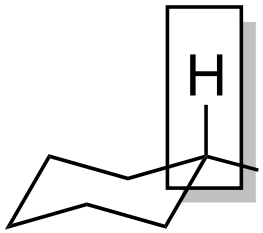


Broad



Broad





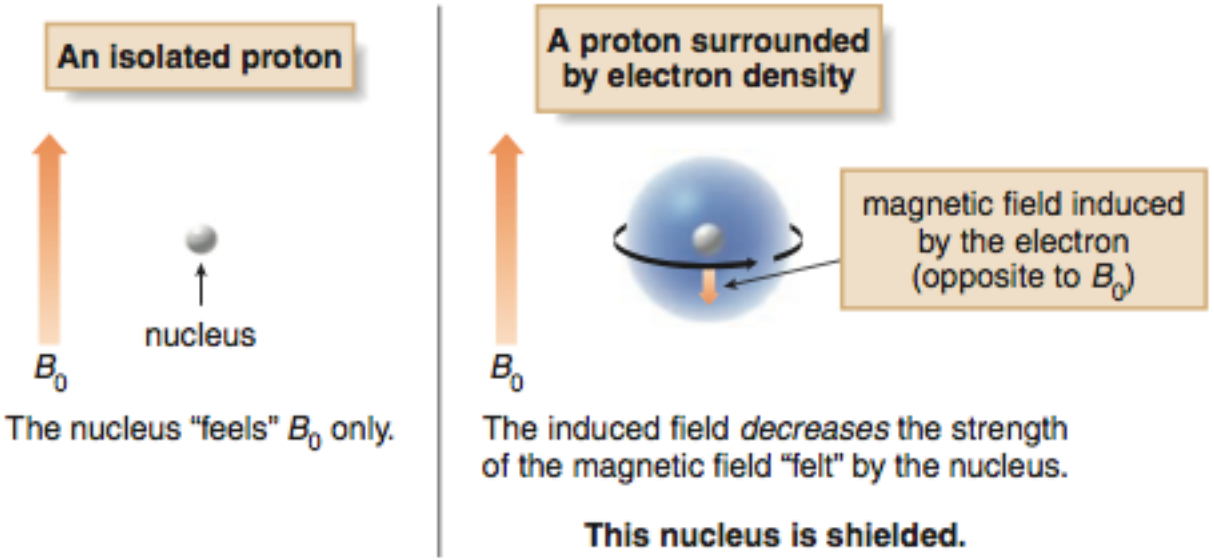
Broad

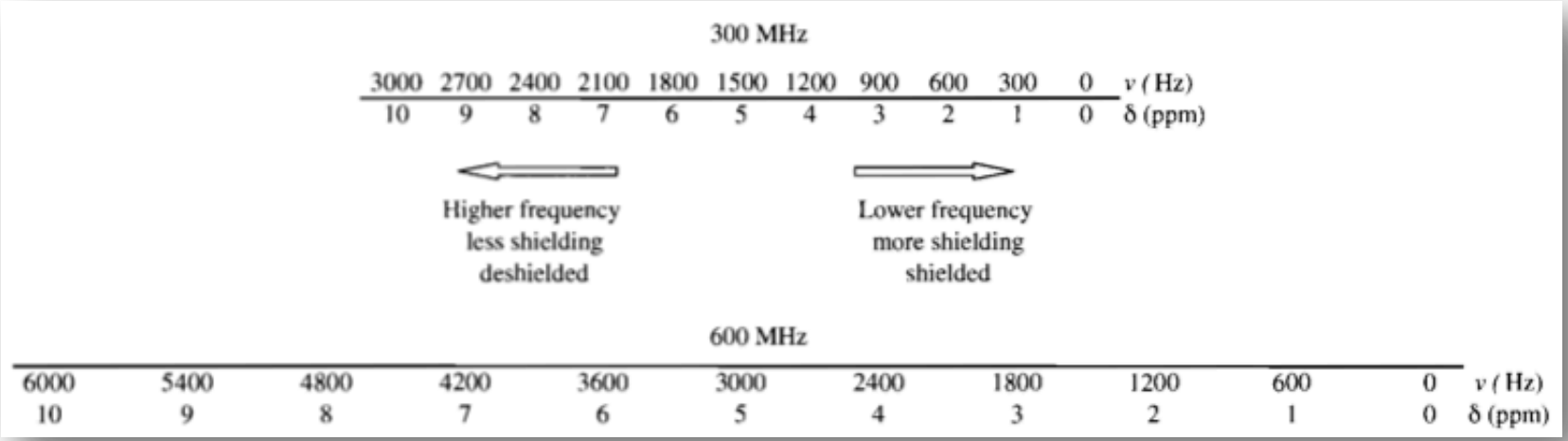
Broadness can be due to

1. Hydrogen bonding
2. Quadrupolar nuclei
3. Dynamics (conformational)

Nuclear Magnetic Resonance – Spectral Problems Solving

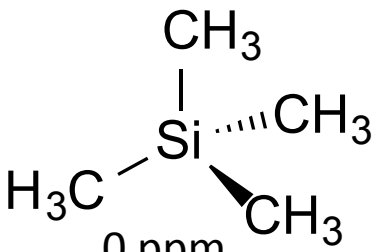
Chemical Shifts in terms of shielding and deshielding





Nuclear Magnetic Resonance – Spectral Problems Solving

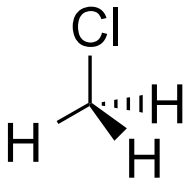
Factors affecting chemical shift



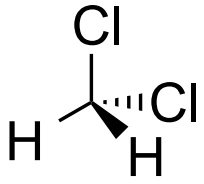
0 ppm
(Standard)

CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_3CH_3	CH_4	CH_3SiMe_3	CH_3Li
4.26	3.05	2.69	2.19	0.96	0.2	0.0	-2.1

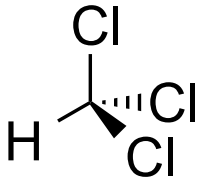
Electronegativity



3.05



5.33



7.26

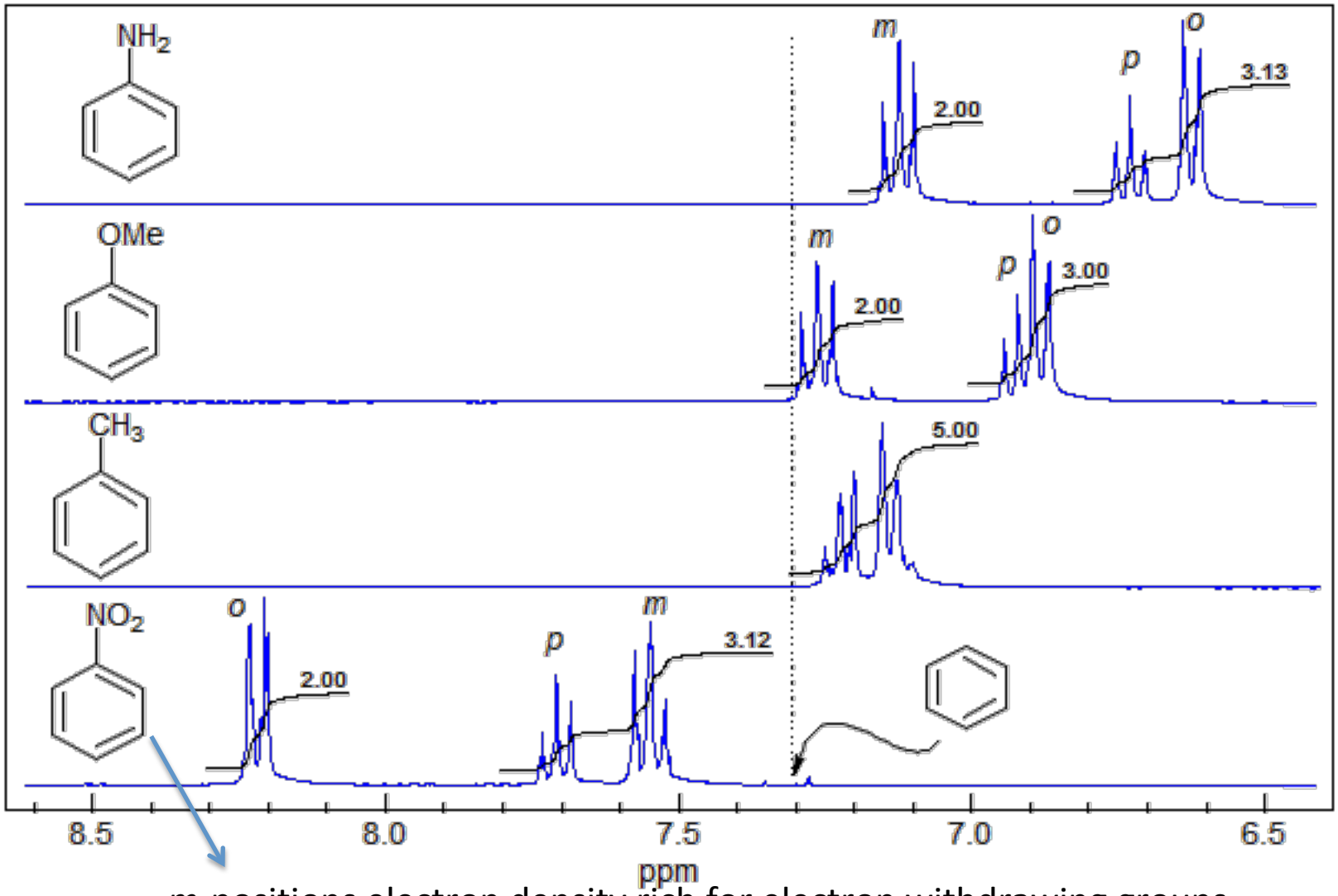
Number of electronegative atoms increase

Chemical Shift increase

Nuclear Magnetic Resonance – Spectral Problems Solving

Factors affecting chemical shift

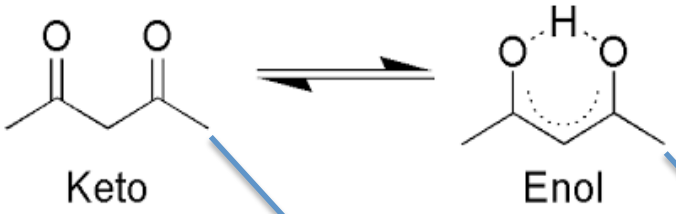
Electron donating and electron withdrawing groups



m-positions electron density rich for electron withdrawing groups

Nuclear Magnetic Resonance – Spectral Problems Solving

NMR spectrum of acetylacetone



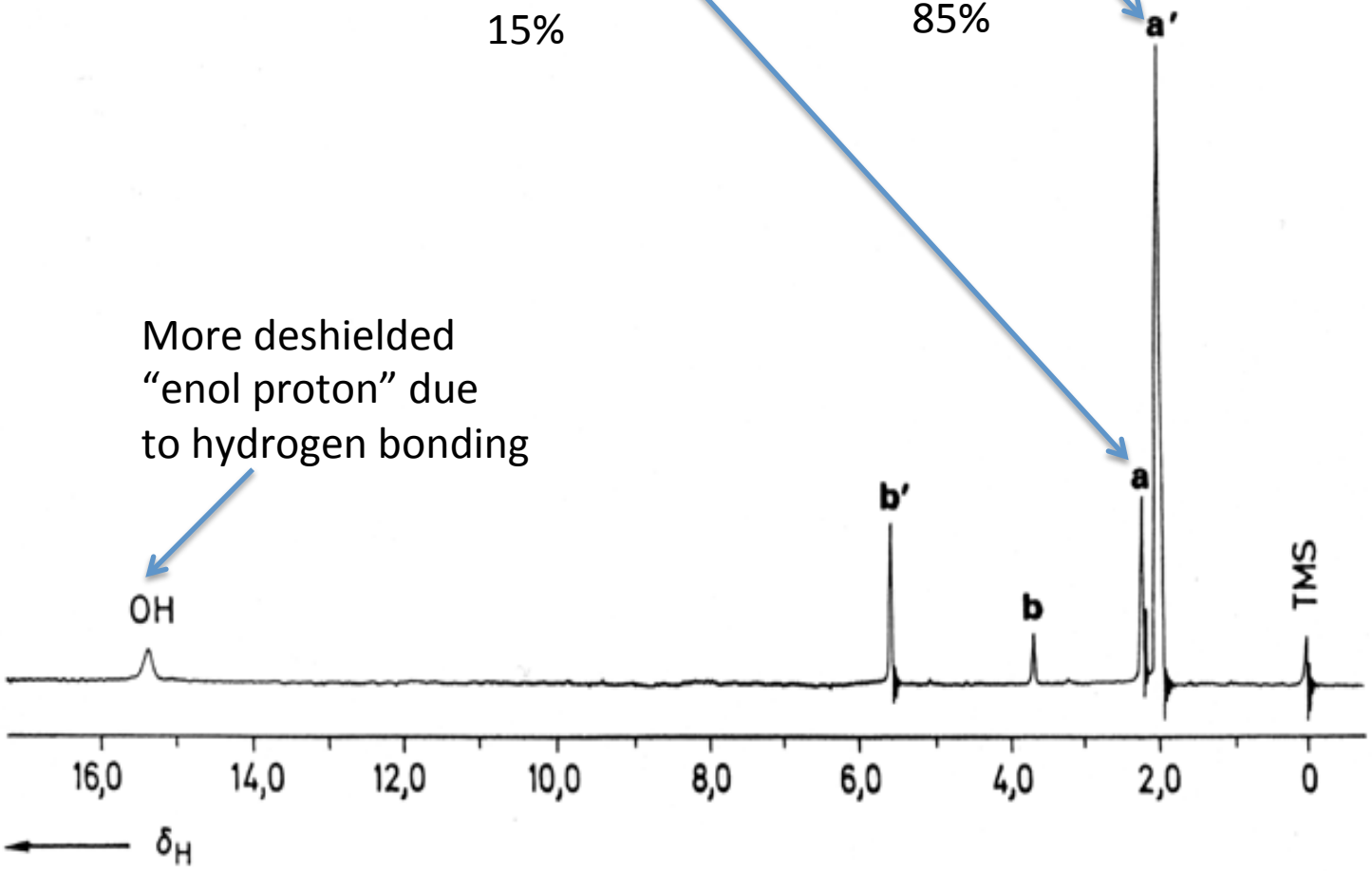
Keto

15%

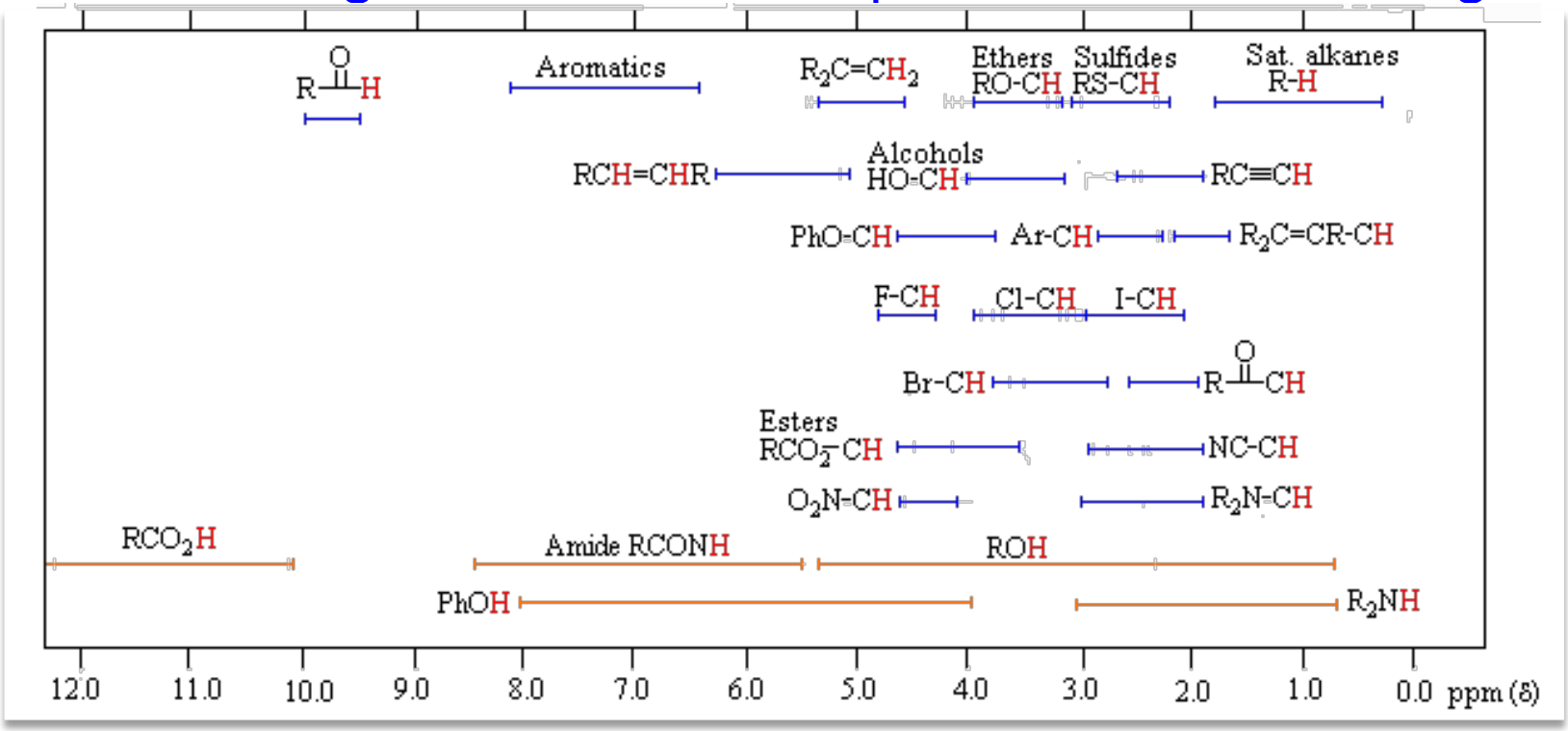
Enol

85%

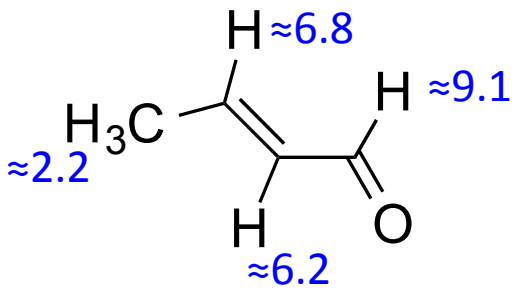
More deshielded
"enol proton" due
to hydrogen bonding



Nuclear Magnetic Resonance – Spectral Problems Solving

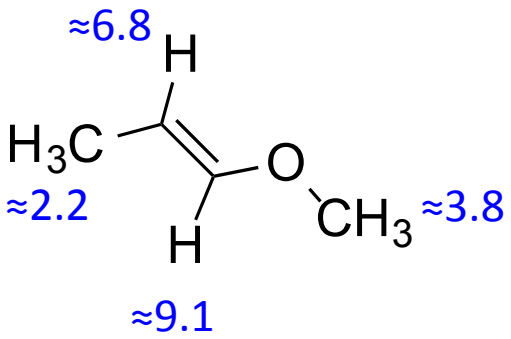


Problem 3: Predict the number of signals, and approximate chemical shifts.



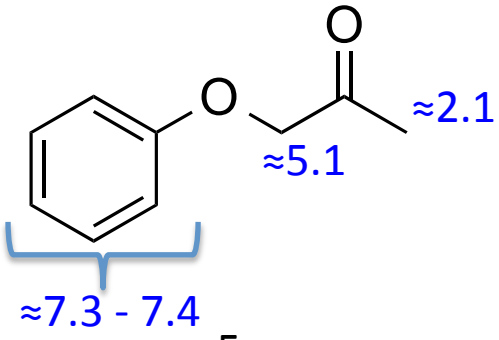
4

Reason: Resonance structure



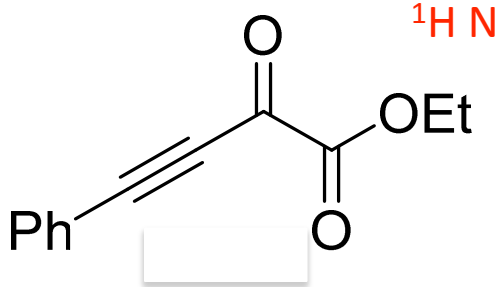
4

Reason: Inductive effect



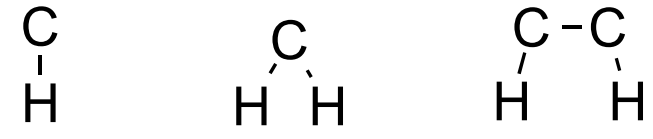
5

Nuclear Magnetic Resonance – Spectral Problems Solving



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.64 (m, 2H),
7.57-7.50 (m, 1H),
7.48-7.39 (m, 2H),
4.41 (q, *J* = 7.1 Hz, 2H),
1.43 (t, *J* = 7.1 Hz, 3H).

Spin – spin coupling



^{1}J Direct

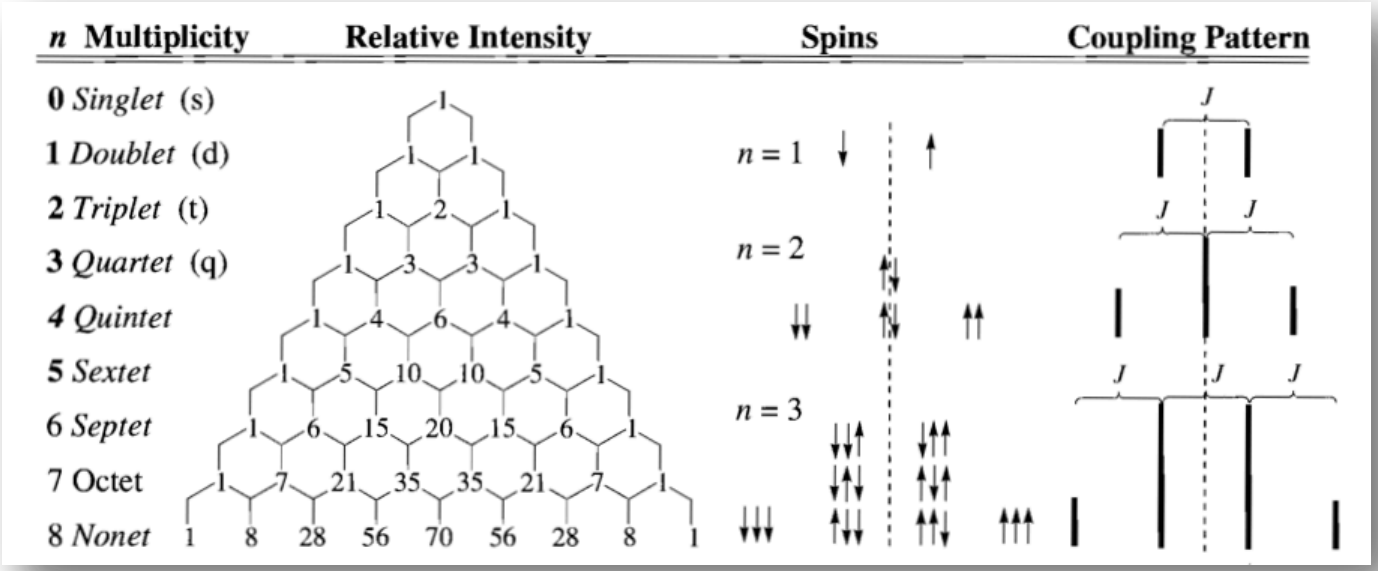
^{2}J Geminal

^{3}J Vicinal

^{x}J x = Number of intervening bonds

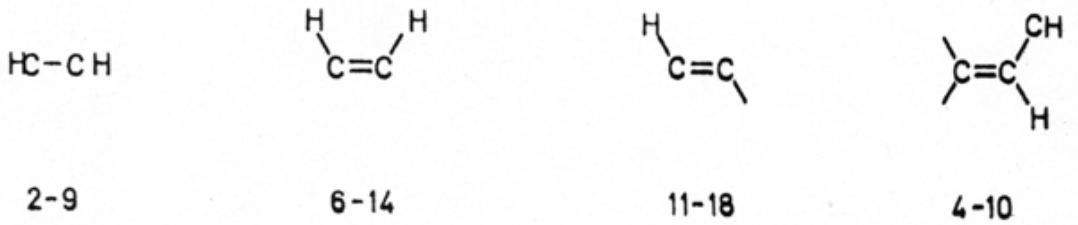
General formula for determining coupling = 2n*I* + 1

n = Number of nuclei at neighboring position

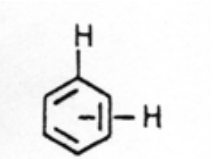


Nuclear Magnetic Resonance – Spectral Problems Solving

^3J (Vicinal) coupling



Ortho, meta and *para* coupling

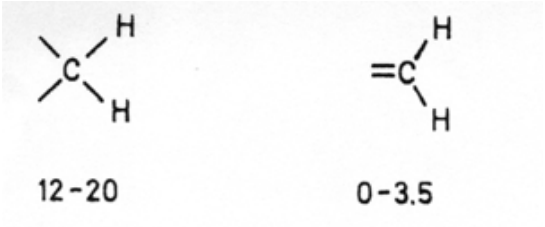


J_o = 7-10

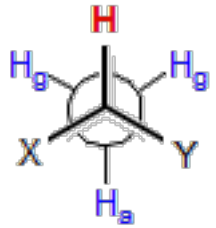
J_m = 2-3

J_p = 0.1-1

^2J (Geminal) coupling



Conformational influence in coupling



For a methyl group, the observed coupling is the average of the three couplings, since these will be fully averaged by methyl rotation:

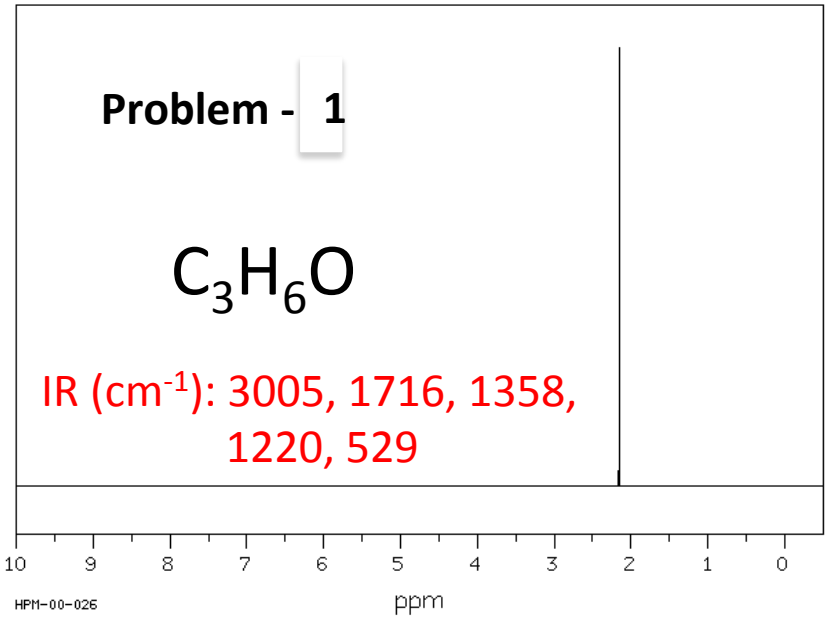
$$^3J_{obs} = \frac{J_g + J_g + J_a}{3} = \frac{4 + 4 + 13}{3} = 7$$

Nuclear Magnetic Resonance – Spectral Problems Solving

Problem - 1

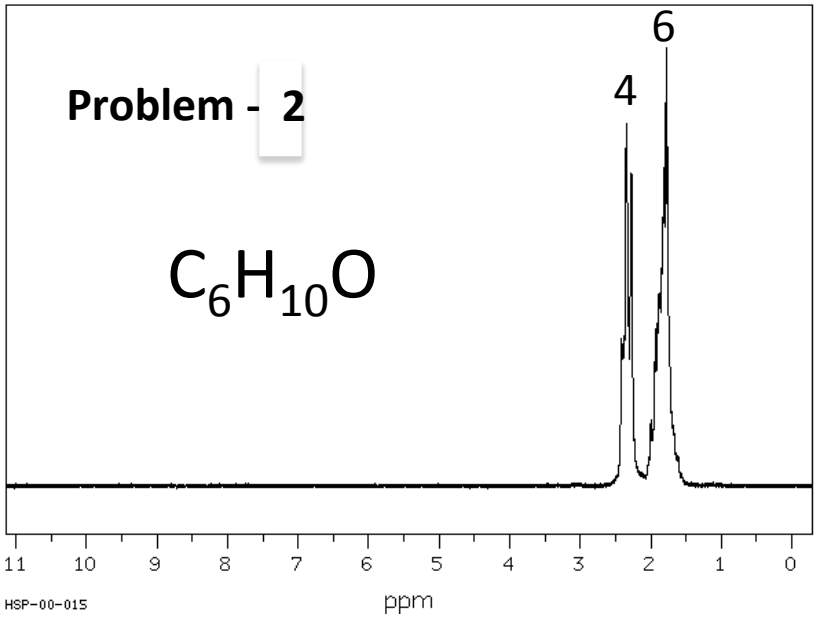
C_3H_6O

IR (cm^{-1}): 3005, 1716, 1358, 1220, 529



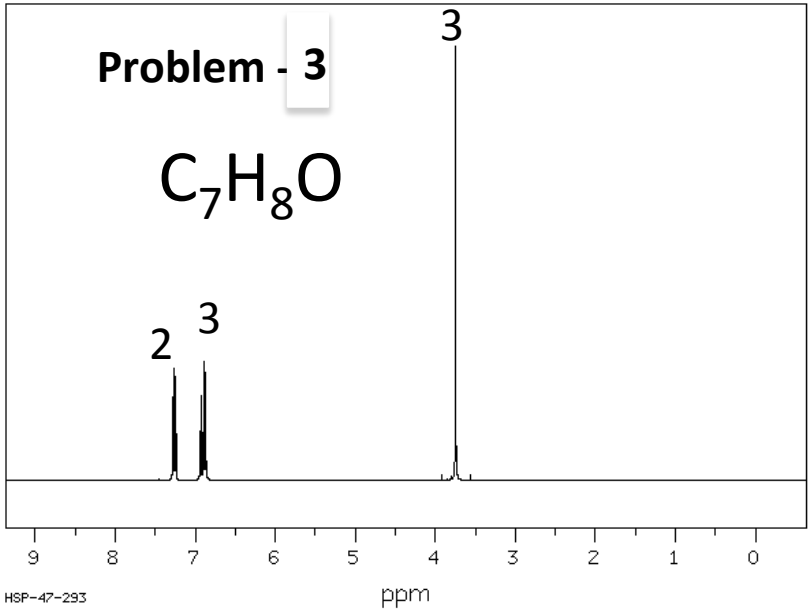
Problem - 2

$C_6H_{10}O$



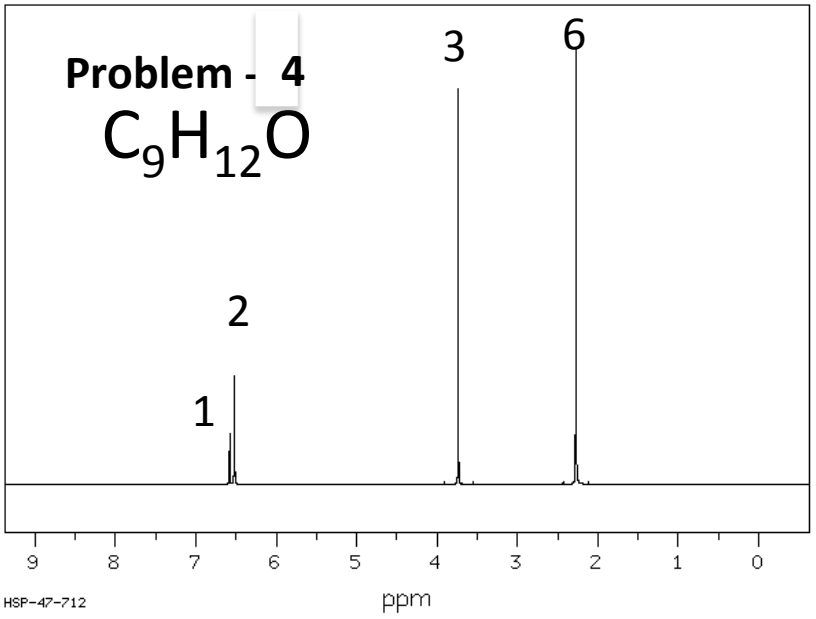
Problem - 3

C_7H_8O



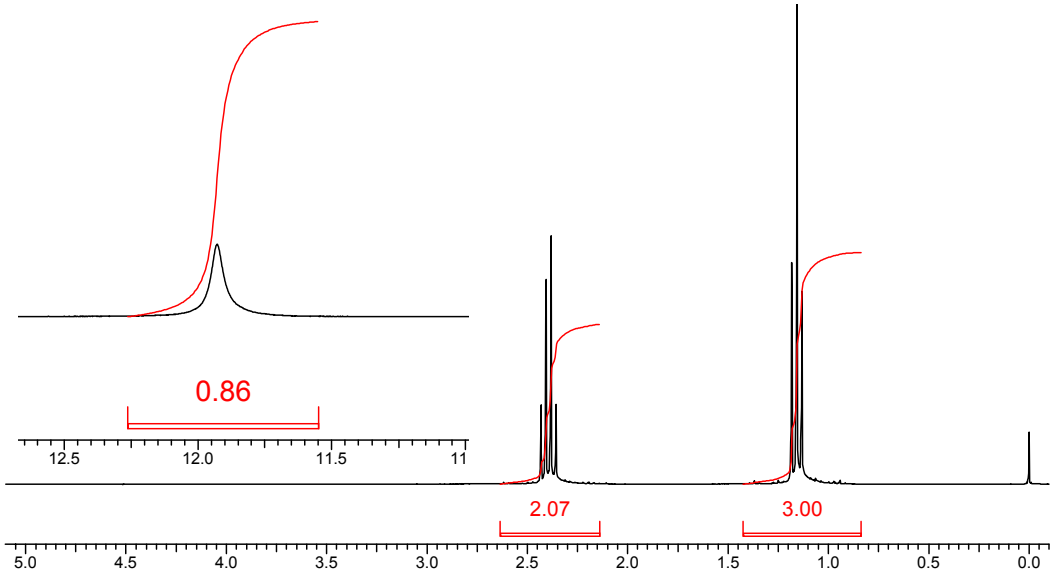
Problem - 4

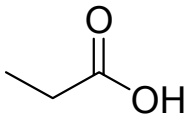
$C_9H_{12}O$



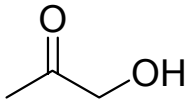
Nuclear Magnetic Resonance – Spectral Problems Solving

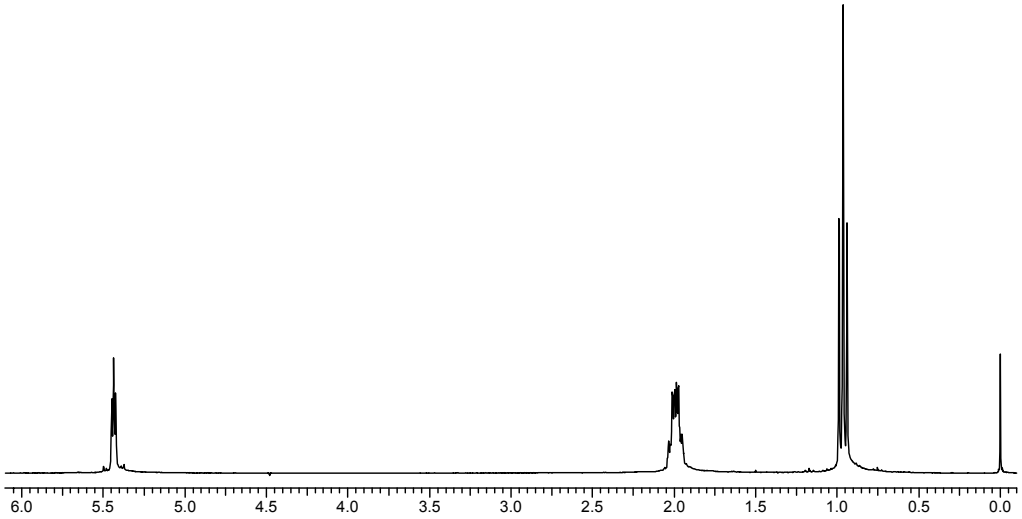
Problem 5: For each spectrum below, choose between the alternative compounds.





or





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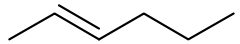
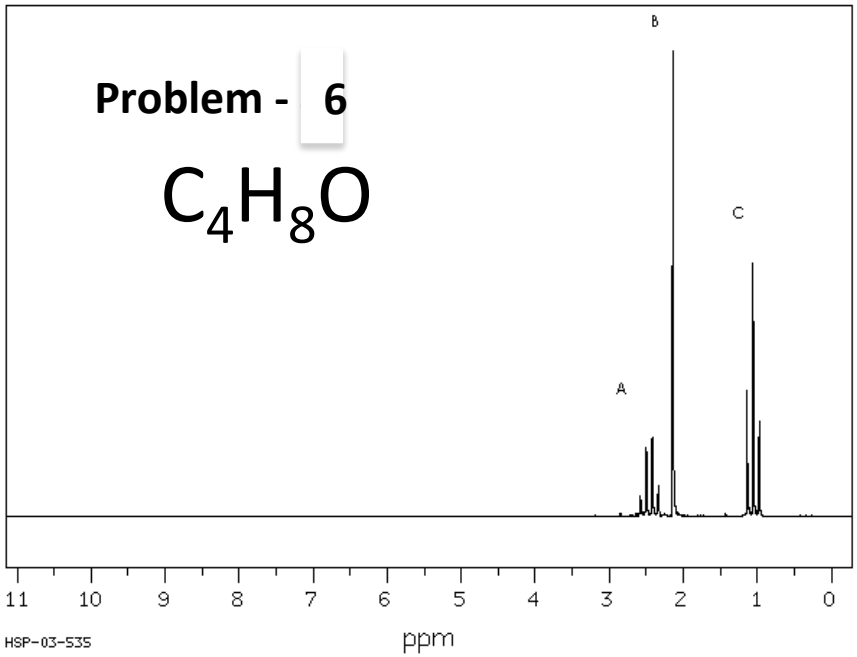


Nuclear Magnetic Resonance – Spectral Problems Solving

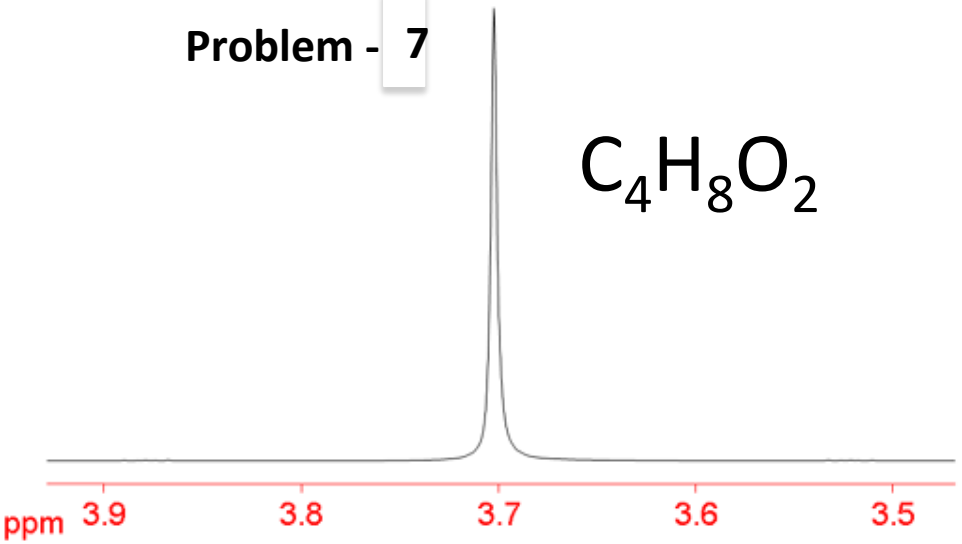
Problem - 6

C_4H_8O

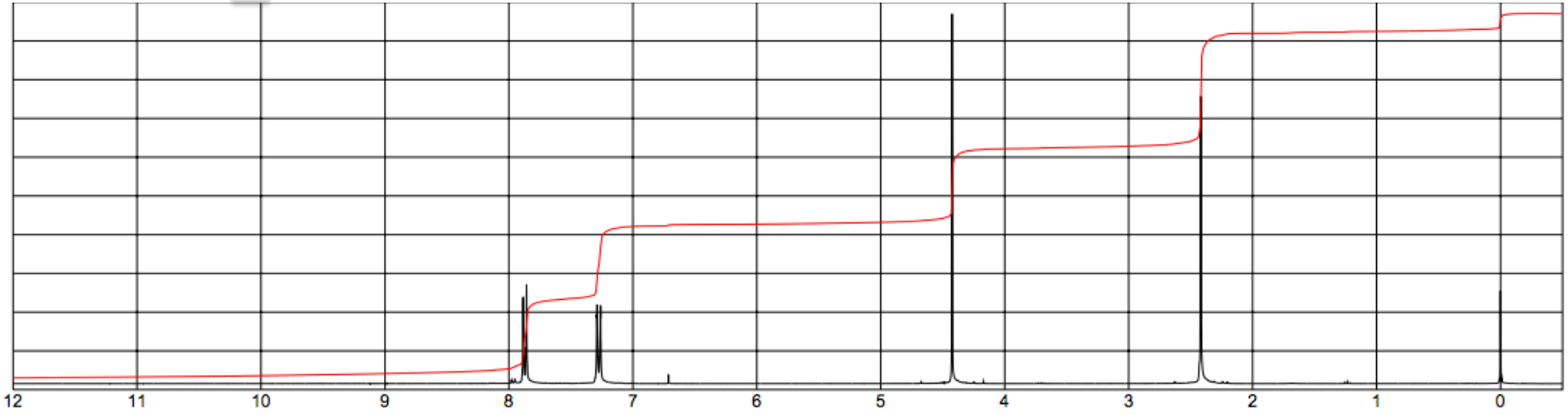


Problem - 7

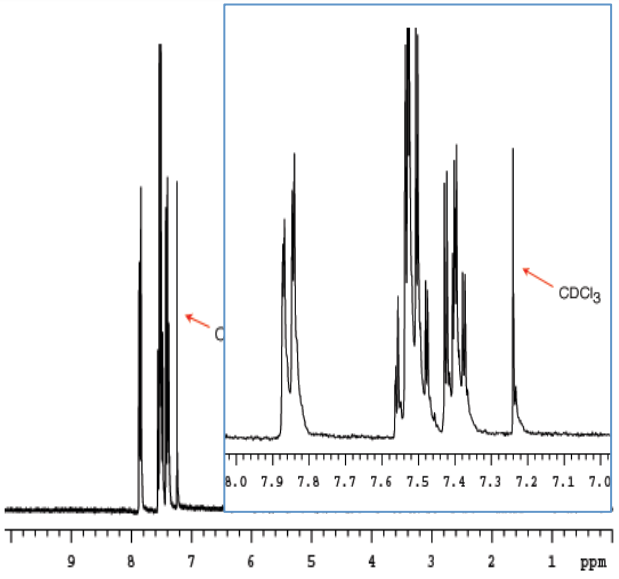
$C_4H_8O_2$

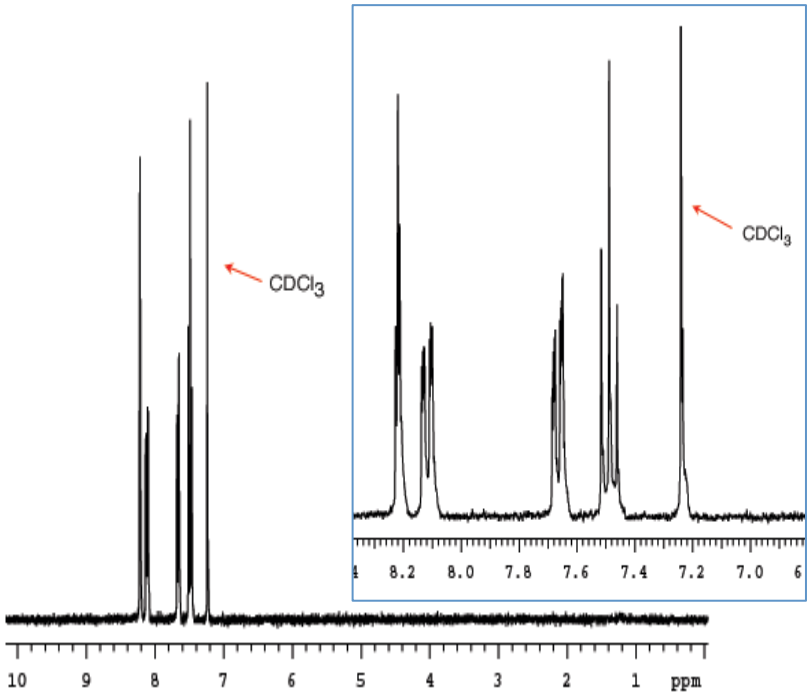


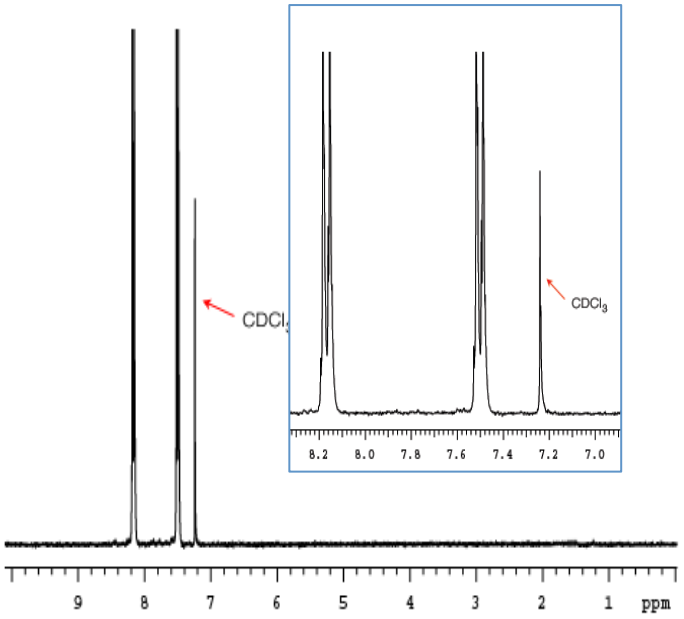
Problem - 8



Nuclear Magnetic Resonance – Spectral Problems Solving





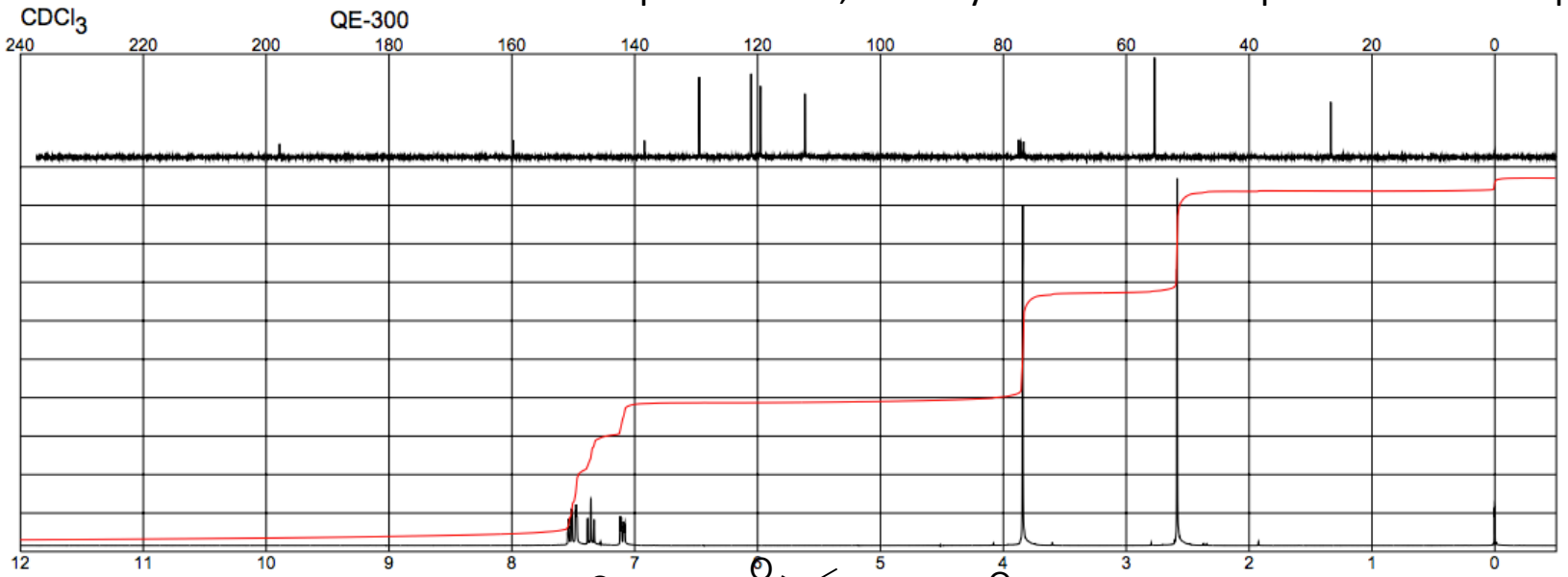


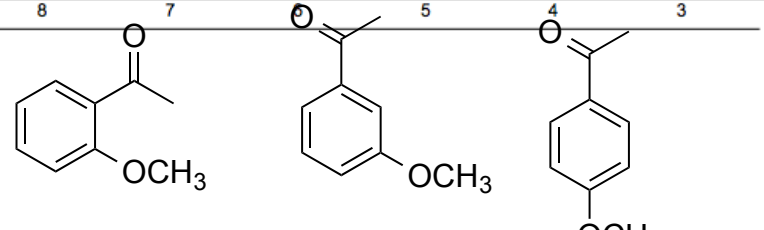
Problem - 9

$C_6H_4ClNO_2$

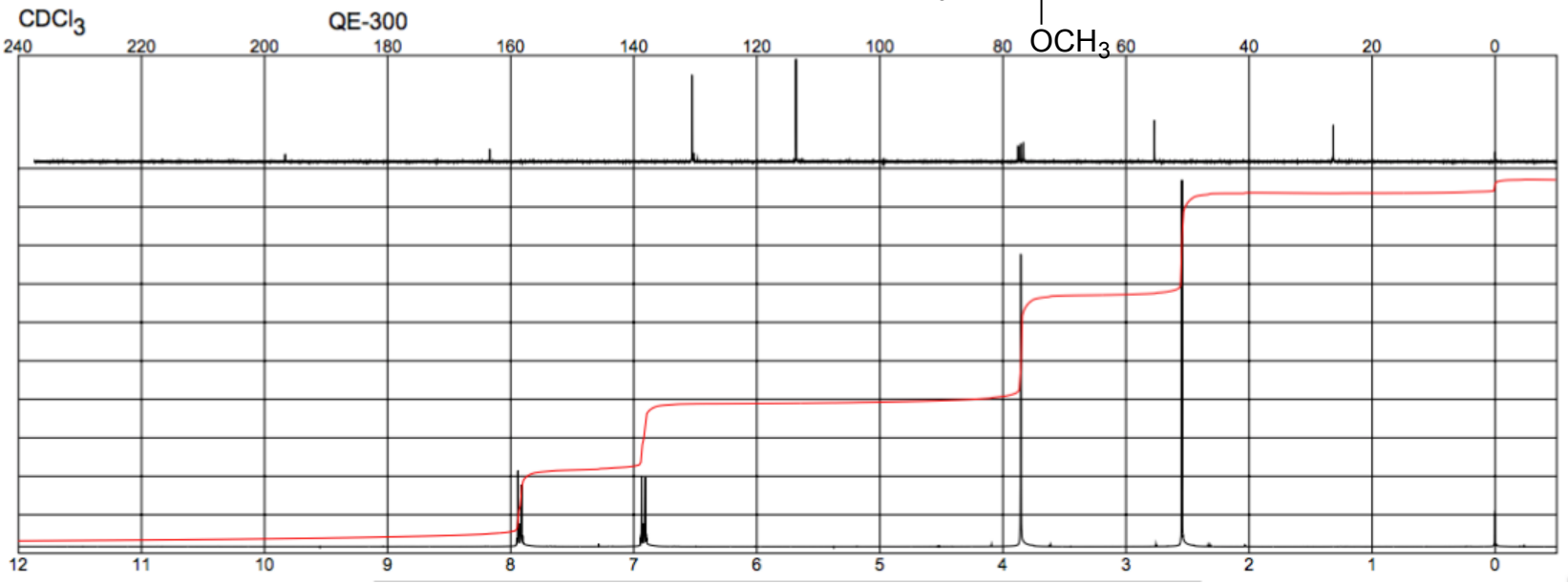
Problem 10: Based on the available ^{1}H & ^{13}C spectral data, identify the correct compound from the options:

A



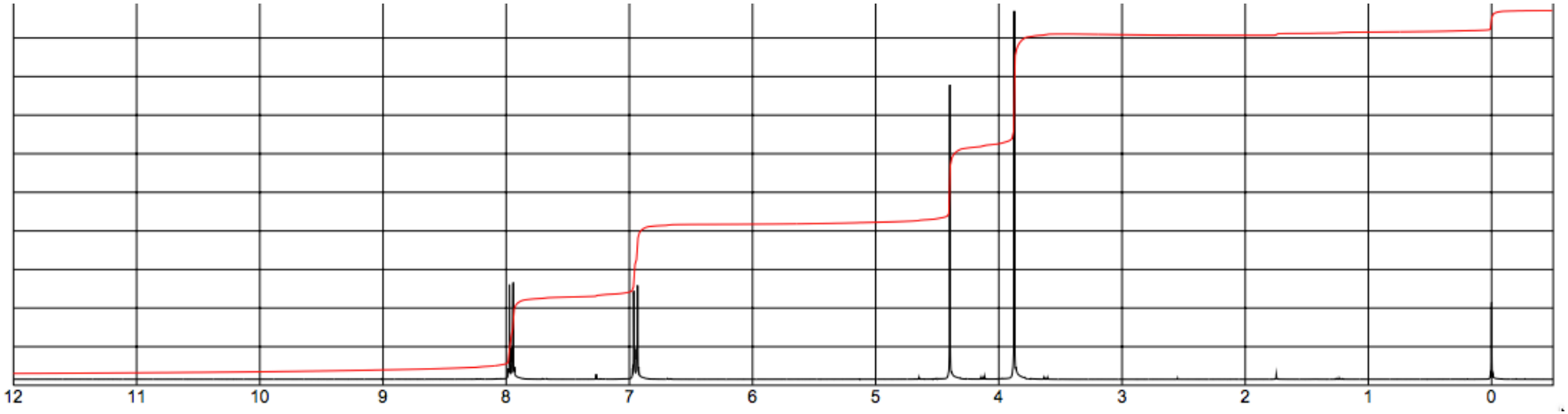


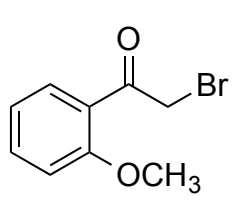
B

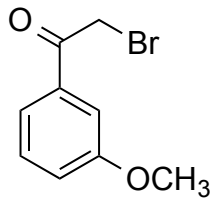


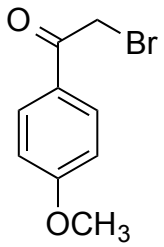
Problem 11: Based on the available ^{1}H spectral data, identify the correct compound from the options:

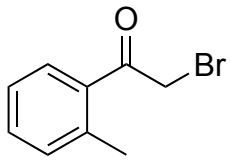
A

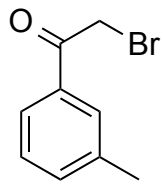












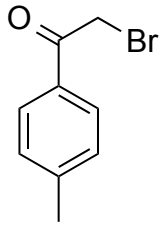
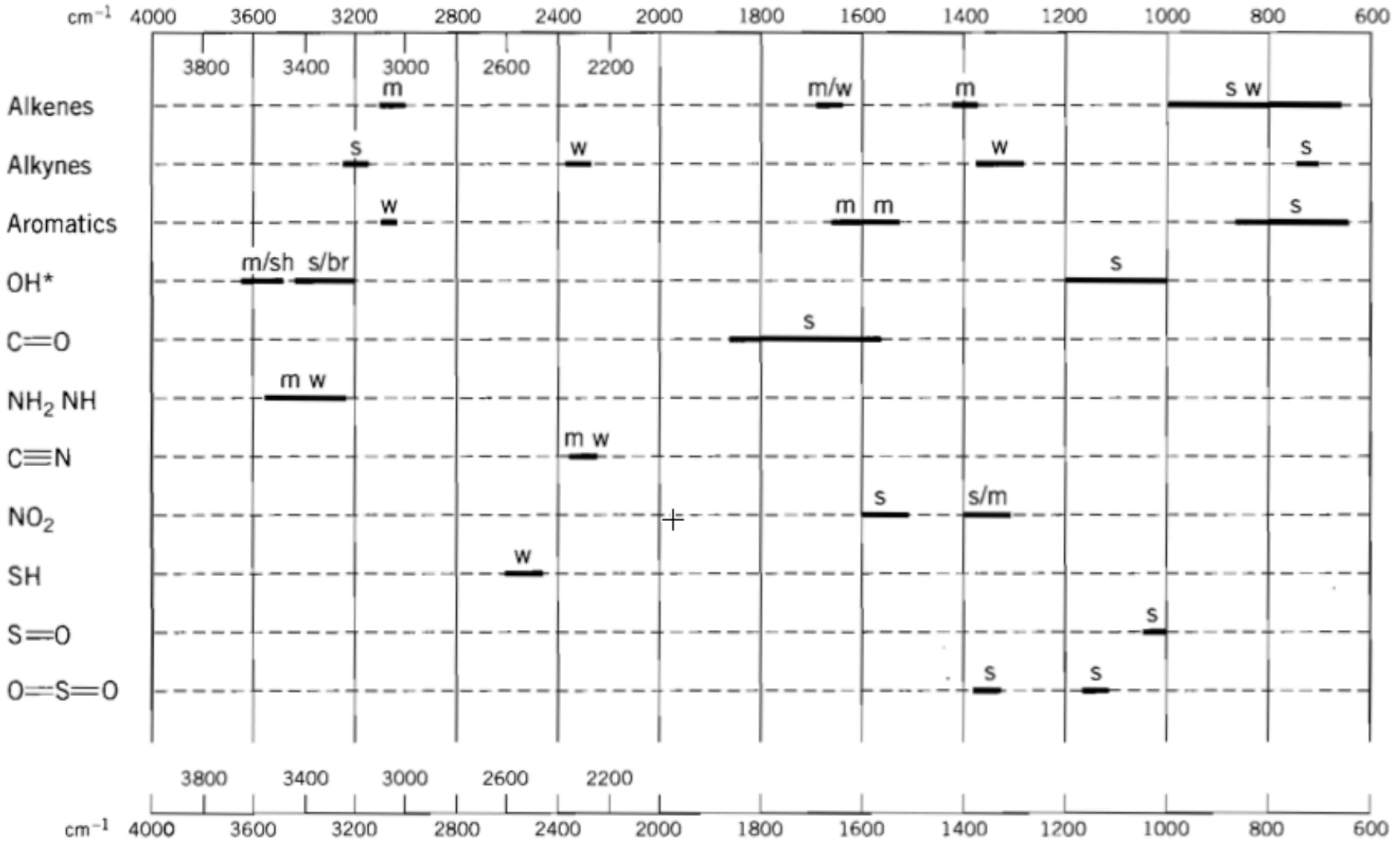


Table of characteristic IR absorptions

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1685 (s)	C=O stretch	α, β–unsaturated aldehydes
1685–1666 (s)	C=O stretch	α, β–unsaturated ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

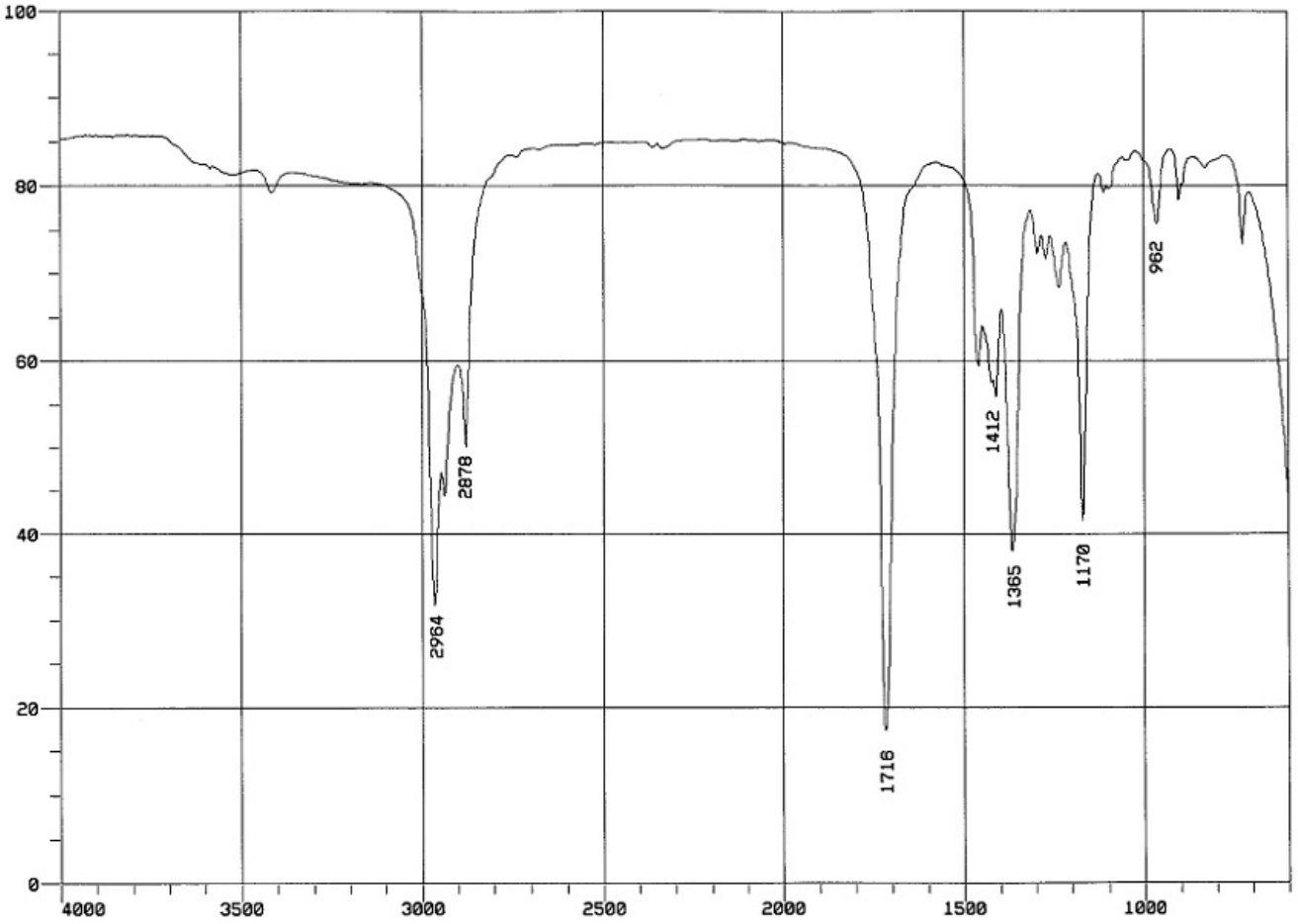
* m = medium, w = weak, s = strong, n = narrow, b = broad, s = sharp.

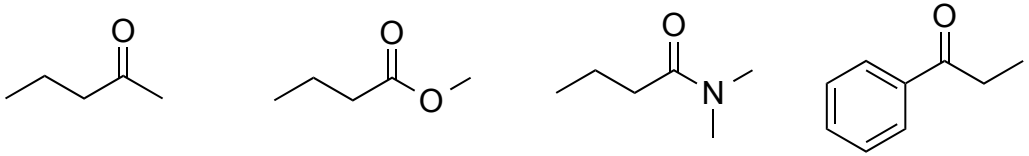
Useful infrared characteristic frequencies

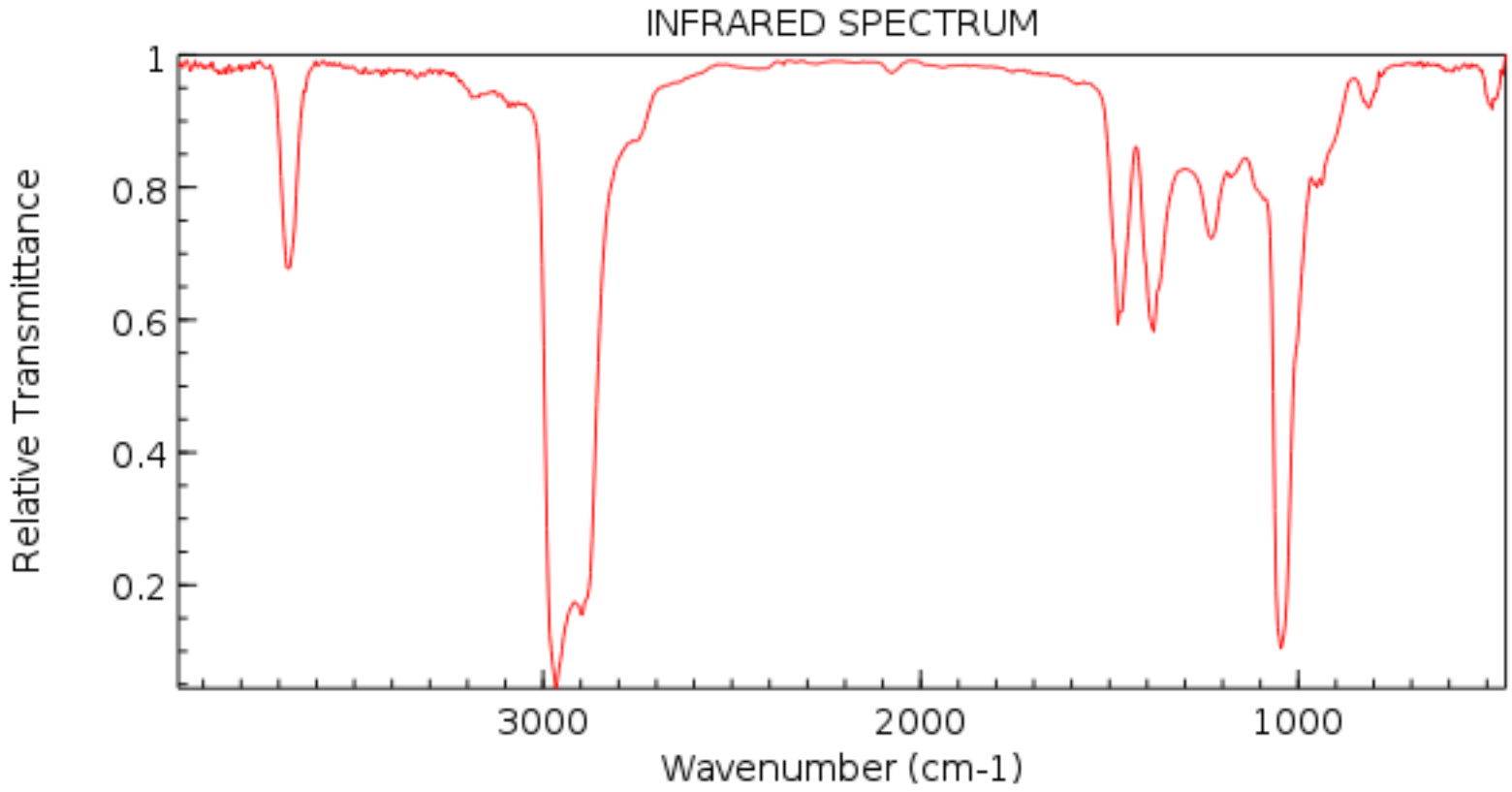


*Free OH, medium and sharp; bonded OH, strong and broad

1. Identify the compound from the given options based on the infrared signals. Assign the key and characteristic signals for identification.







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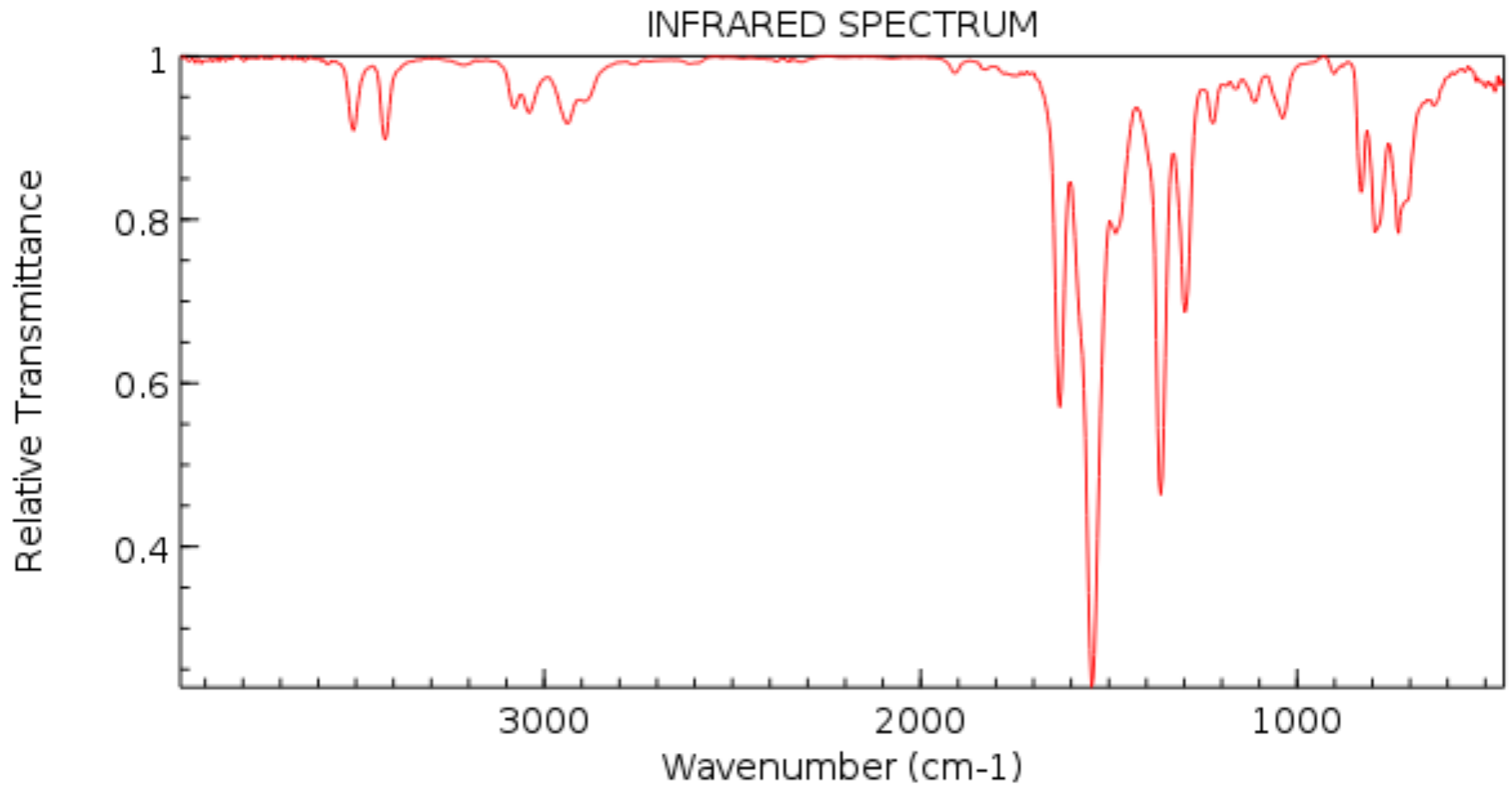

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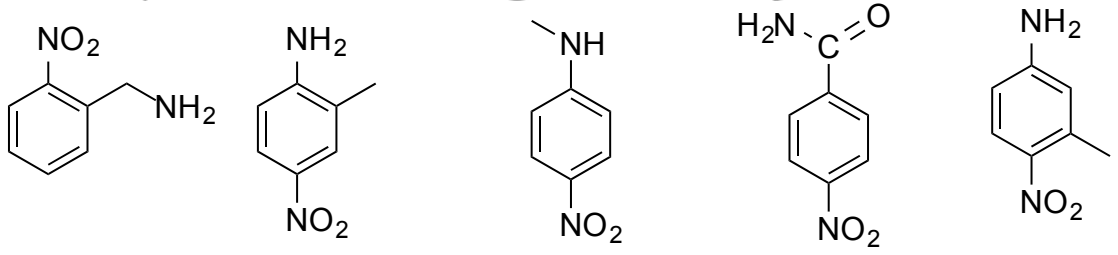
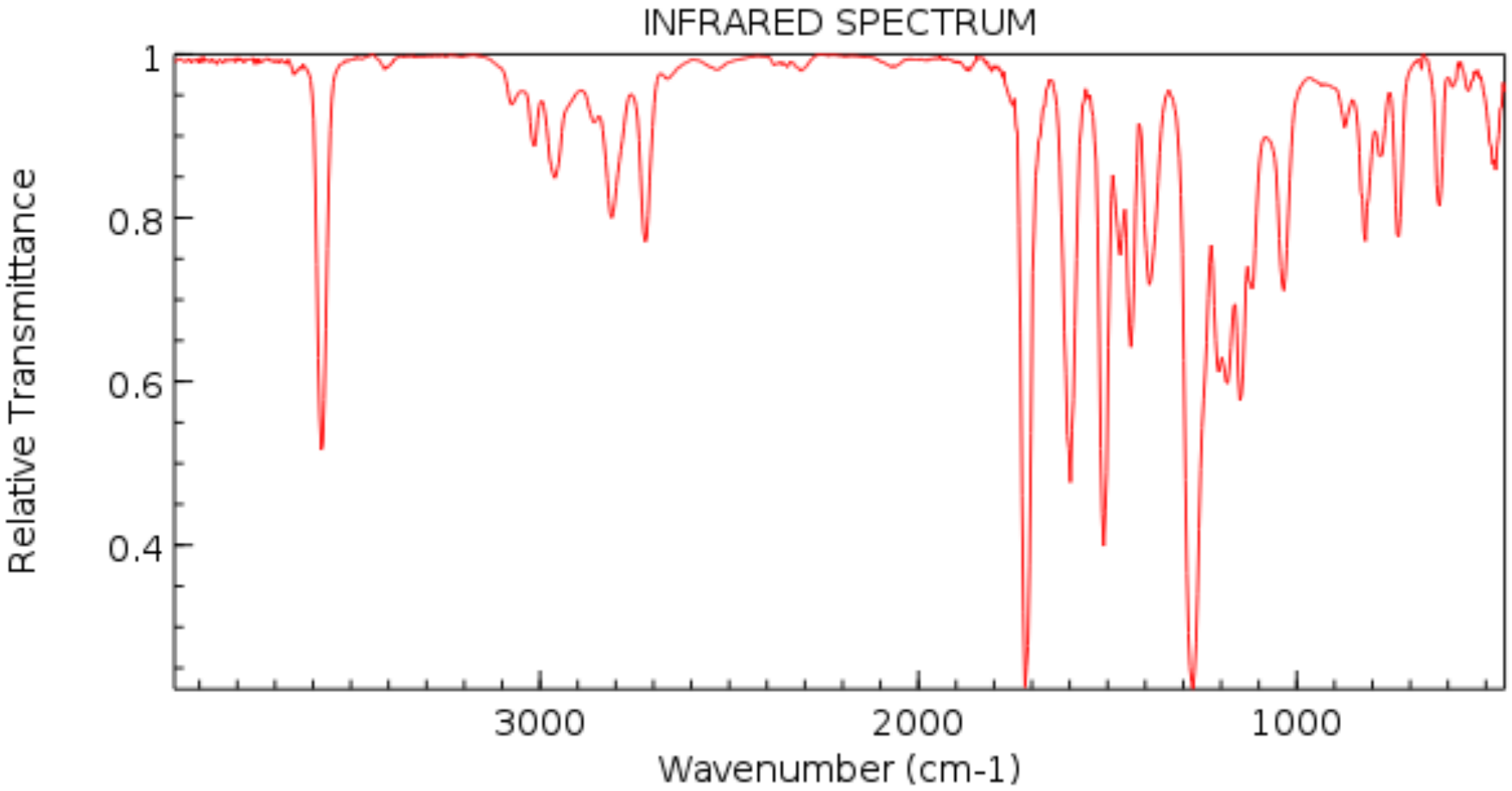
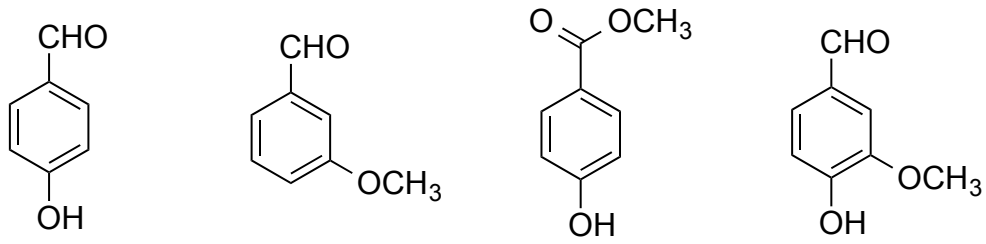
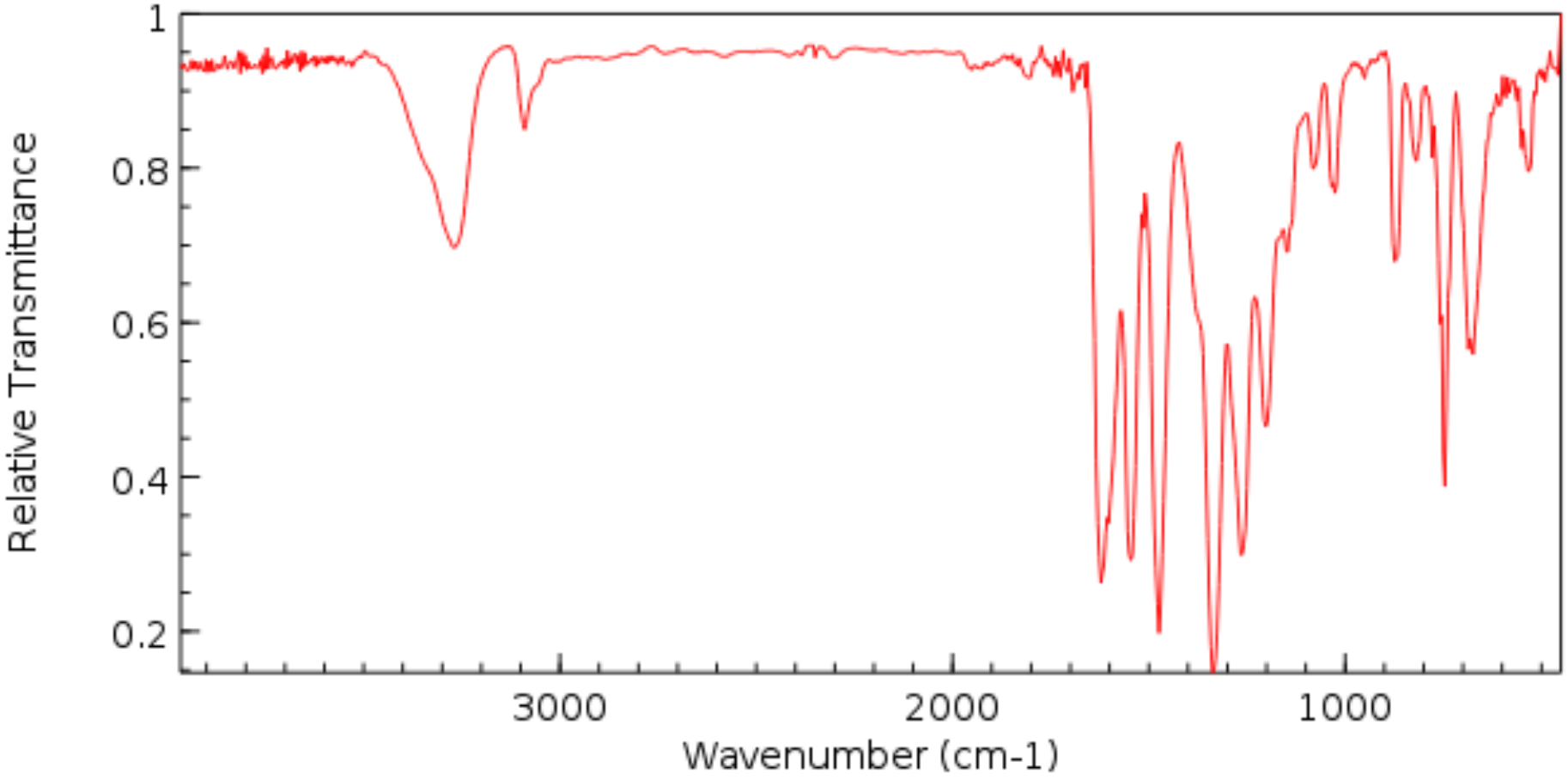
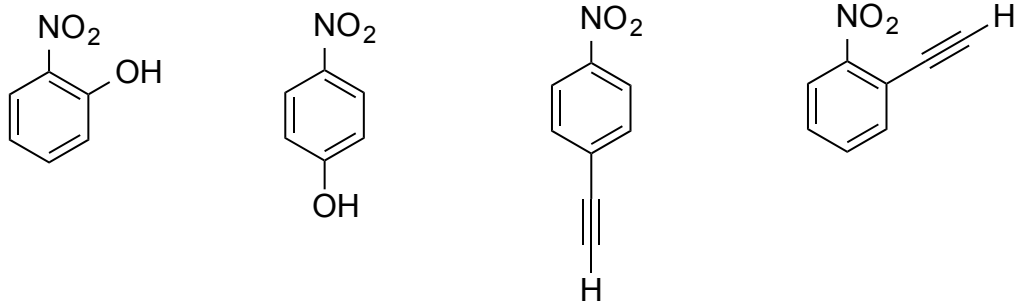


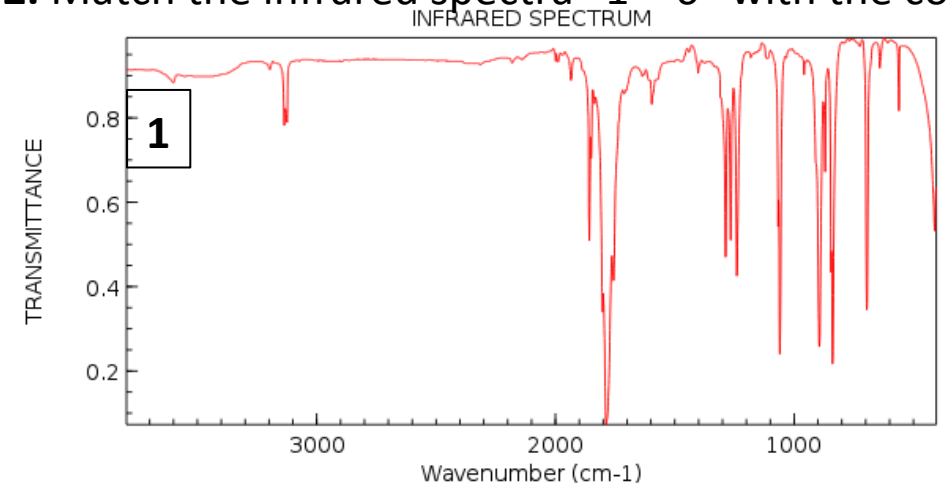

INFRARED SPECTRUM
Relative Transmittance
1
0.8
0.6
0.4
3000
2000
1000
Wavenumber (cm-1)


CHO
OH
CHO
OCH3
O
OCH3
OH
CHO
OCH3
OH


Relative Transmittance
1
0.8
0.6
0.4
0.2
3000
2000
1000
Wavenumber (cm-1)


NO2
OH
NO2
OH
NO2
H
NO2
H

2. Match the infrared spectra "1 – 6" with the correct molecules given:



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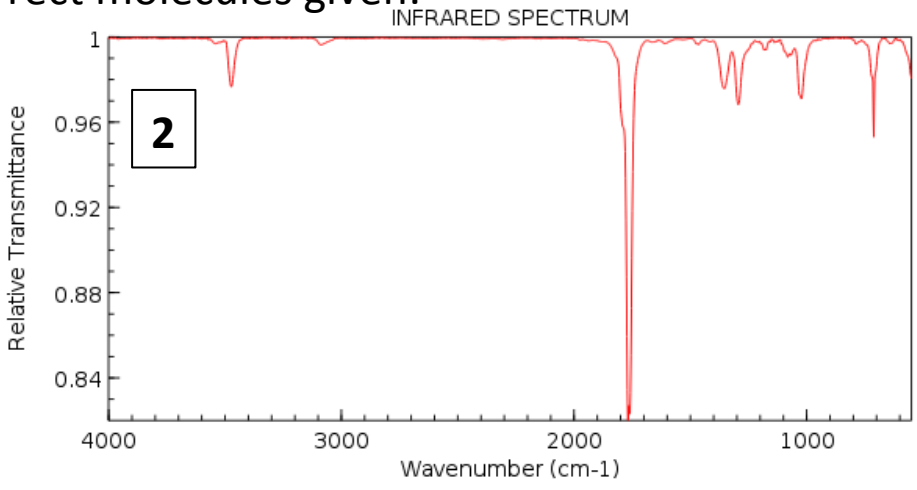

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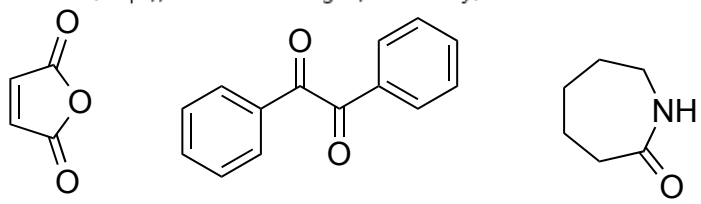

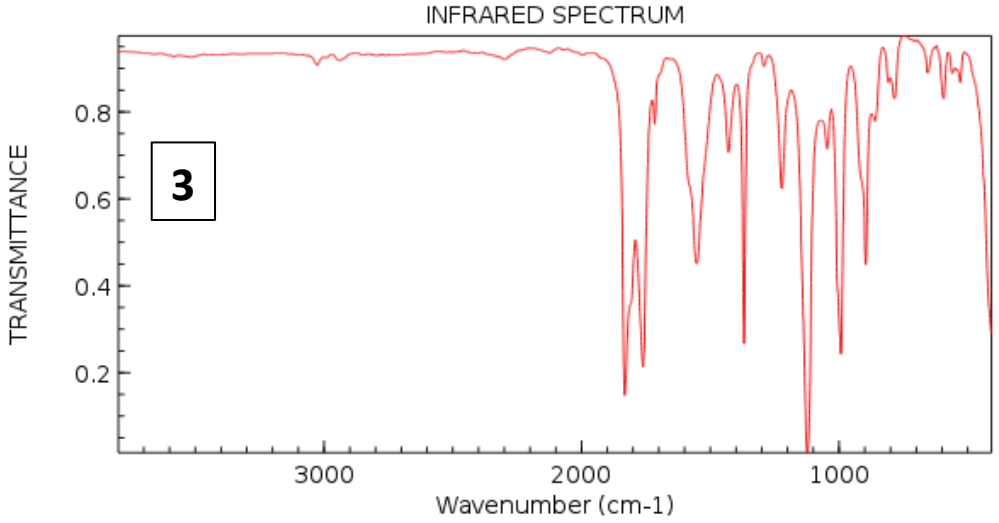

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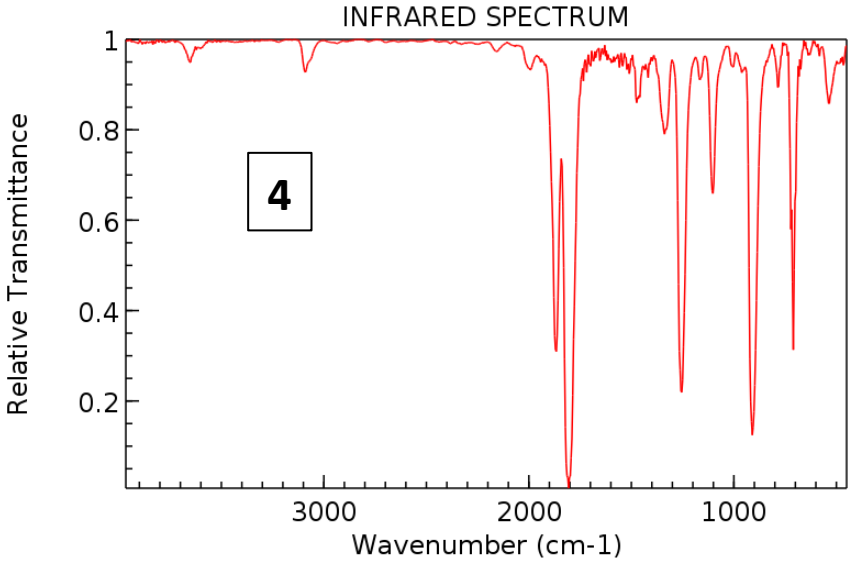

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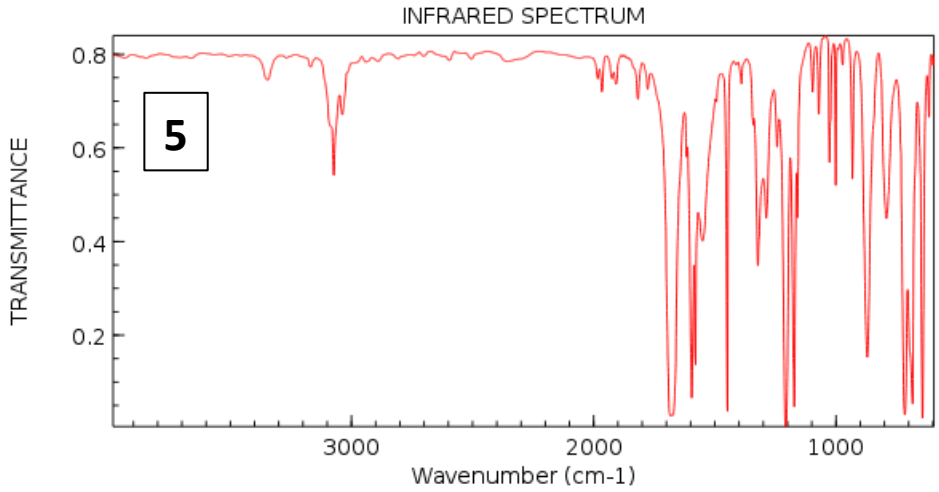

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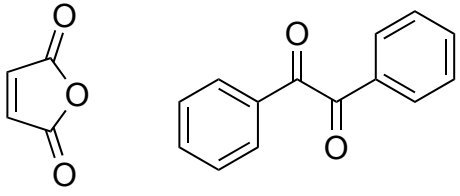

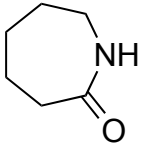

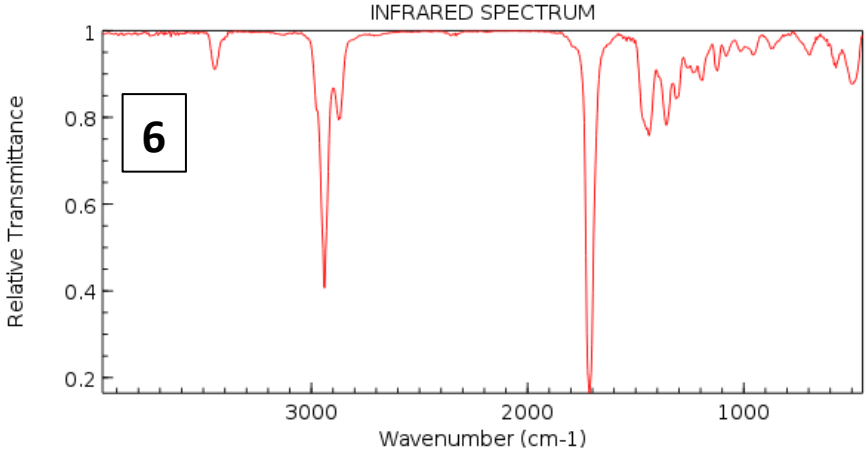

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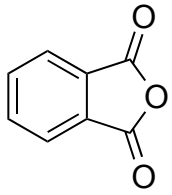
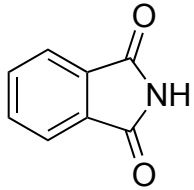
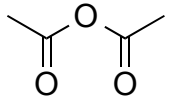






3. Identify the compounds "a − i" based on the spectral details and the structures given below:

a. 3080 (w), nothing 3000–2800, 2230 (s), 1450 (s), 760 (s), 688 (s)

b. 3380 (m), 3300 (m), nothing 3200–3000, 2980 (s), 2870 (m), 1610 (m), ~900–700 (b)

c. 3080 (w), nothing 3000–2800, 1315 (s), 1300 (s), 1155 (s)

d. 2955 (s), 2850 (5), 1120 (s)

e. 2946 (s), 2930 (m), 1550 (s), 1386 (m)

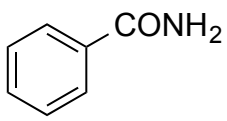
f. 2900 (b, s), 1720 (b, s)

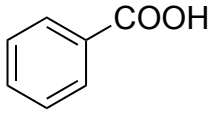
g. 3030 (m), 730 (s), 690 (s)

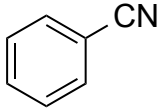
h. 3200–2400 (5), 1685 (b, s), 705 (s)

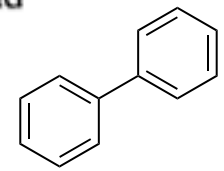
i. 3350 (s), 3060 (m), 1635 (s)

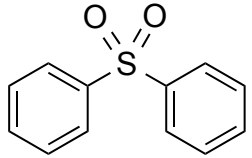
s = strong, m = medium, w = weak, b = broad











HCOOH