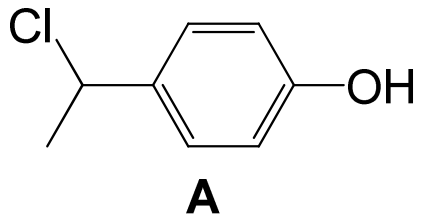
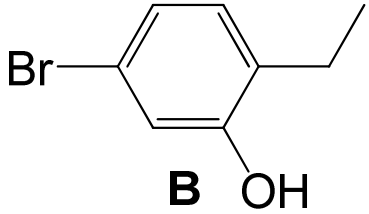
CHEM 266 - Homework 1 **Name_____Keys_____**

(Due on Thursday, September 14, 2017 at the beginning of the class, no late return, no exam under my office's door will be accepted)

1. Can IR be used to distinguish between the following compounds? Explain your answer (2 pts)



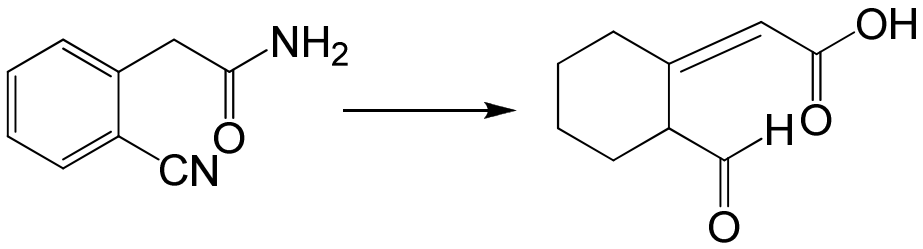
A



B

Both compounds will display the exact same signals including OH (3200 – 3500 cm^{-1}), $CHsp^2$ (3100 cm^{-1}), $CHsp^3$ (2960 cm^{-1}), C=C aromatic (1450 -1600 cm^{-1}). As such, they cannot be distinguish by IR.

2. You have performed the reaction below in the lab. List all the signals observed in the IR spectrum of the starting material and in the IR spectrum of the product. Explain how IR can be used to tell whether the reaction took place or not.



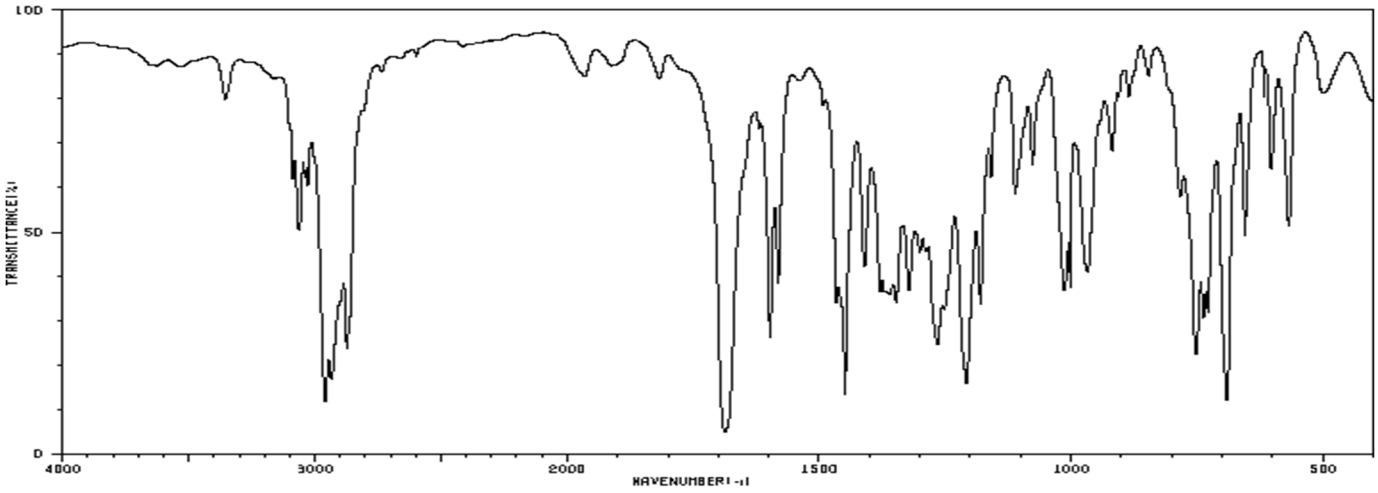
IR vibrational signals (5 pts)

Starting material	**Product**
$\bar{\upsilon}_{N-H}$ = 3200, 3300 cm^{-1}	$\bar{\upsilon}_{O-H}$ = 2500 – 3500 cm^{-1}
$\bar{\upsilon}_{C-Hsp2}$ = 3100 cm^{-1}	$\bar{\upsilon}_{C-Hsp2}$ = 3100 cm^{-1}
$\bar{\upsilon}_{C-Hsp3}$ = 2960 cm^{-1}	$\bar{\upsilon}_{C-Hsp3}$ = 2960 cm^{-1}
$\bar{\upsilon}_{CN}$ = 2250 cm^{-1}	$\bar{\upsilon}_{C-H\_aldehyde}$ = 2820, 2760 cm^{-1}
$\bar{\upsilon}_{C=O}$ = 1685 cm^{-1}	$\bar{\upsilon}_{C=O}$ = 1735 cm^{-1}
$\bar{\upsilon}_{c=c}$ = 1450 - 1600 cm^{-1}	$\bar{\upsilon}_{c=O}$ = 1680 cm^{-1}
$\bar{\upsilon}_{C-HAr\_bend}$ = 600 cm^{-1}	$\bar{\upsilon}_{c=c}$ = 1600 cm^{-1}

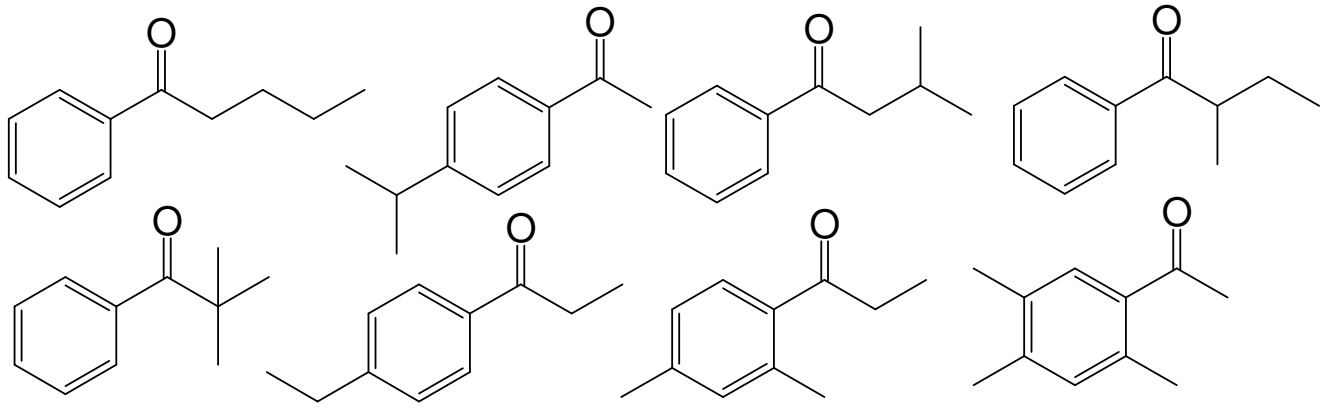
Explain (2 pts)

The bidented signal in the starting material due to NH_2 (3200, 3300 cm^{-1}), the signal due to CN (2250 cm^{-1}) and the signals due to C=C aromatic (1450 - 1600 cm^{-1}) in the starting material will disappear, and will be replaced in the product by a broad signal (2500 – 3500 cm^{-1}) due to the OH of the carboxylic acid. The signals due to the CH aldehyde (2820 and 2760 cm^{-1}) as well as and additional C=O signal (1735 cm^{-1}) will be observed in the product, and should be enough to distinguished between the product and the starting material. Otherwise both the starting material and the product should display similar signals for $CHsp^2$, $CHsp^3$ and conjugated C=O.

3. The compound with the IR spectrum below has a molecular formula of $C_{11}H_{14}O$. Propose **two** structures consistent with the IR spectrum and explain your answer



Structures (4 pts) – **Any two of the structures below will do.**



Explain (2 pts)

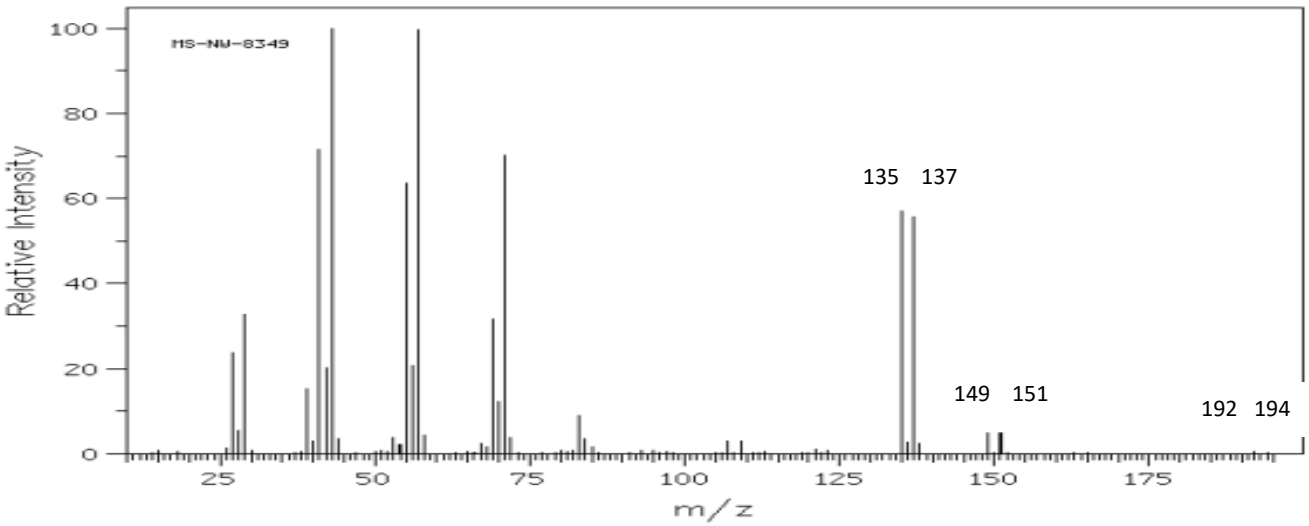
NI = 11 + 1 – ½ 14 = 5 element of isaturations.
The IR displays signals for CHsp^2 (3050 cm^{-1}), CHsp^3 (2960 cm^{-1}), C=O (1680 cm^{-1}) as well as C=C aromatic (1460 and 1600 cm^{-1}). So, the molecule contains an aromatic ring and a conjugated carbonyl. The lack of any signal due to the CH of aldehyde confirm that the compound is a ketone. So, any of the above structures, and any other structure that displays the exact same features will be accepted.

4. Both C_6H_9N and C_5H_5NO have the same nominal mass, namely 95. Show how these compounds can be distinguished by the *m/z* ratio of their molecular ions in high-resolution mass spectrometry (C 12.0107; O 15.9994; H 1. 00794; N 14.0067) (3 pts)

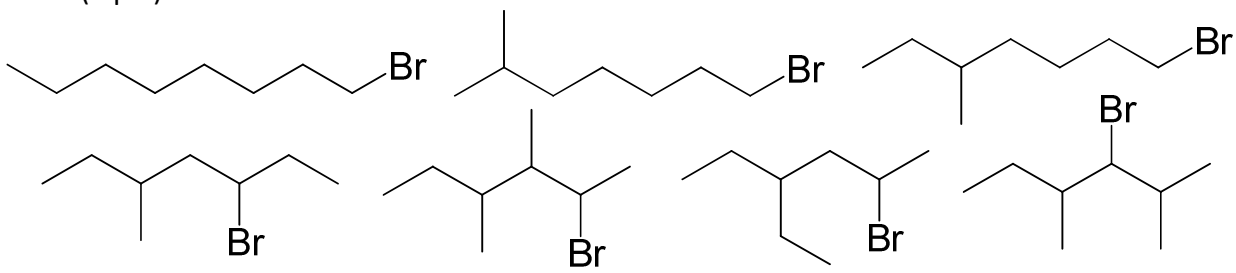
C_6H_9N = 6 x 12.0107 + 9 x 1. 00794 + 14.0067 = 95.14236
C_5H_5NO = 5 x 12.0107 + 5 x 1. 00794 + 14.0067 + 15.9994 = 95.0993
Difference 95.14236 – 95.0993 = 0.04306.

Although both compounds display the same nominal mass, at a high resolution they will display a difference in mass of about 0.04306.

5. Propose **three (03)** possible structures that can produce the mass spectrum given below and explain your answer (**beside carbon and hydrogen, this molecule contains only one other atom**)



Structures (3 pts)



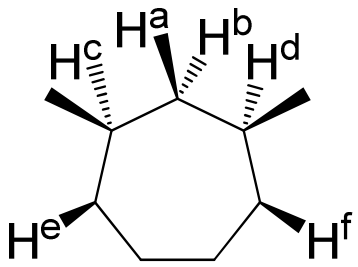
Explain (3 pts)

The molecular ion is always the highest value observed in the mass spectrum, in this case it should be either 192 or 194. Due to the two equal size signals for the molecular ion and other fragments, the molecule contains a bromine atom. Since the molecule contains only carbons and hydrogens in addition to this other atom, it can only be an alkane, alkene and alkyne.

An alkane will have a following general formula $CH_3(CH_2)_nBr$. As such, M = 192 = 15 + 79 + 14n, meaning that n = (192 -94) / 14 = 7.

So, the molecule has no insaturation, and must have a structural formula of $CH_3(CH_2)_7Br$. As such, any of the above formulas and any other structure displaying the exact same feature will be accepted. However, the most likely strcuture are those with a long chain of carbon as the mass spectrum shows a succession of loss of 14 units of mass.

6. State the relationship between the protons indicated in the structure below (as: equivalent, enantiotopic, diastereotopic, or unrelated). (1 x 5 = 5 pts)



H^a and H^b are_____**Equivalent**_____

H^b and H^c are _____**Unrelated** _____

H^c and H^d are _____ **Enantiotopic** _____

H^c and H^f are_____ **Unrelated** _____

H^f and H^e are _____**Enantiotopic**_____

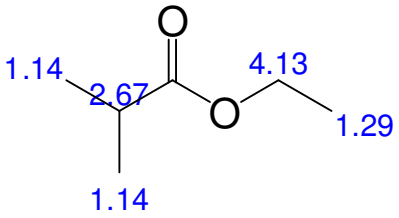
7. Two compounds A and B with the same molecular formula ($C_6H_{12}O_2$) have the ^{1}H-NMR data shown below. Both compounds have strong band around 2950 and 1710 cm^{-1} in their IR spectrum. Elucidate the structure of these two compounds and explain your answer.

Compound A: ^{1}H NMR (δ): 1.14 (6H, doublet), 1.29 (3H, triplet), 2.67 (1H, multiplet), 4.13 (2H, quartet)

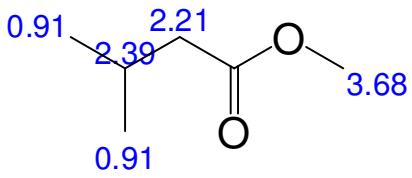
Compound B: ^{1}H NMR (δ): 0.91 (6H, doublet), 2.21 (2H, doublet), 2.39 (1H, multiplet), 3.68 (3H, singlet)

Structures (4 pts)

Compound A



Compound B

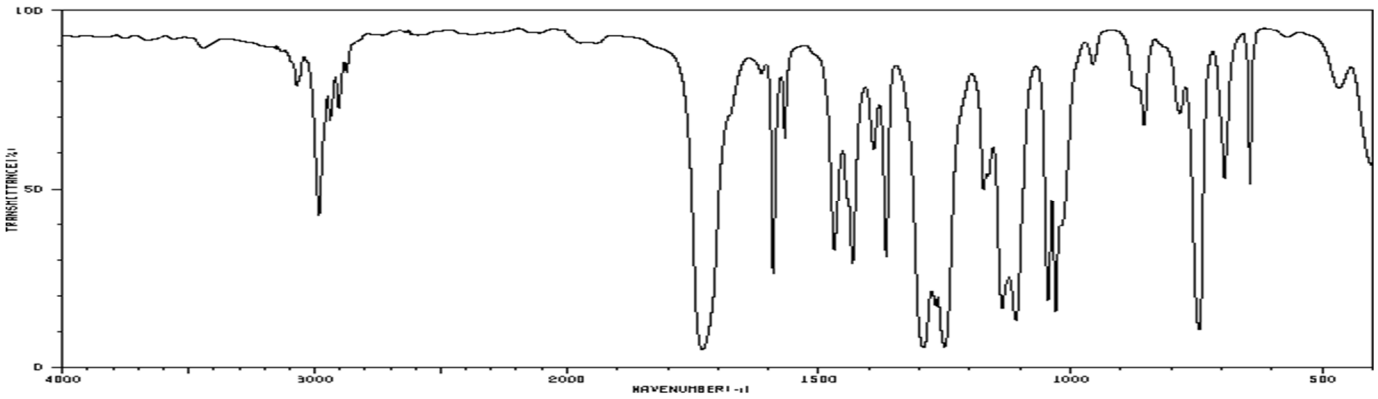


Explain (2 pts)

Both compounds have the same number of insaturation (NI = 6 + 1 – ½ 12 = 1 insaturation).
Compound A shows a doublet of 6H and a multiplet of 1H corresponding to an isopropyl group. It also displays a triplet of 3H and a quartet of 2H corresponding to an ethyl group CH_2CH_3. Obviously the insaturation correspond to a carbonyl of an ester with the ethyl group attached to the oxygen side as it is extremely deshielded, resulting in the structure shown for compound A.

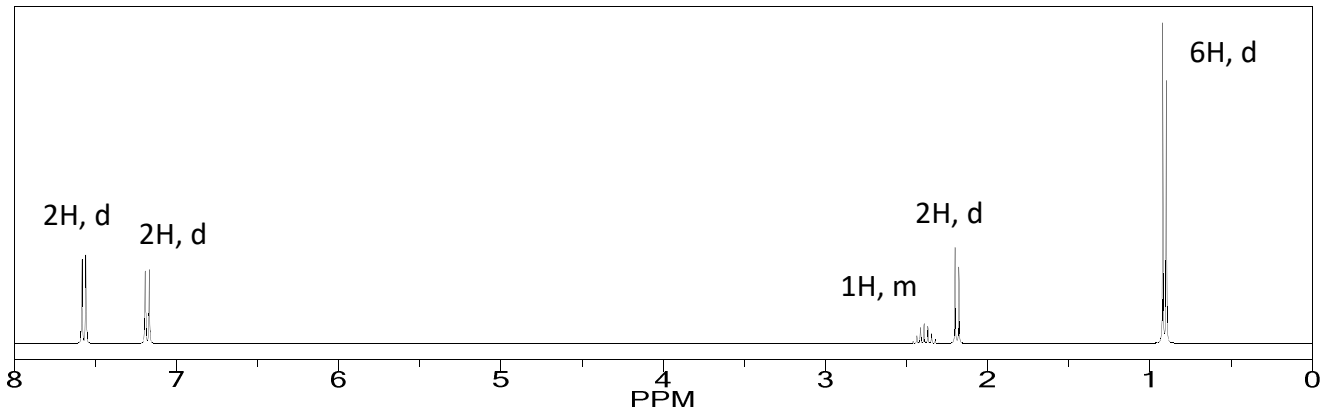
As for compound B, the proton NMR displays a doublet of 6H, a doublet of 2H and a multiplet of 1H corresponding to an isobutyl group. The one insaturation correspond to the carbonyl of the ester functional group while the 3H singlet corresponds to a CH_3 link to the carbonyl through the oxygen as these three protons appears to be very deshielded. These data are consistent with the above structure proposed for compound B.

8. (a) Identify the major signals and the corresponding bond types present in the compound having the following IR spectrum; Molecular formula **$C_{11}H_{13}BrO_2$** (3 pts)

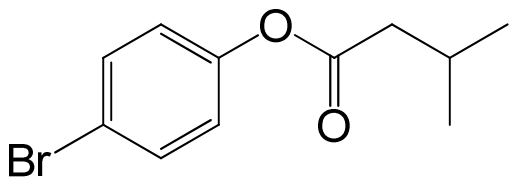


$\bar{\upsilon}_{C\text{-}Hsp2}$ = 3100 cm^{-1}, $\bar{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}, $\bar{\upsilon}_{C=O}$ = 1730 cm^{-1}, $\bar{\upsilon}_{C=C}$ = 1600, 1450 cm^{-1}, $\bar{\upsilon}_{C\text{-}0}$ = 1150 cm^{-1}, $\bar{\upsilon}_{C\text{-}HAr\_bend}$ = 600 - 700 cm^{-1}.

(b) The ^{1}H-NMR shown below is that of the same compound with the IR spectrum shown in (a). Determine its structure and explain your answer.



Structure (3 pts)

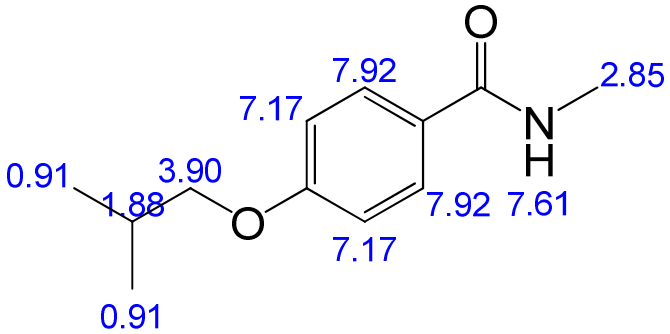


Explain (2 pts)

$C_{11}H_{13}BrO_2$, NI = 11 + 1 - ½ 14 = 5 elements of insaturation.

The IR indicated that this compound contains an aromatic ring and a carbonyl. The proton NMR shows two doublet of 2H in the aromatic area indicative of a para disubstituted benzene ring. The same spectrum also shows a doublet of 6H corresponding to two CH_3 connected to the same CH, a doublet of 2H corresponding to a CH_2 connected to a CH, and finally a multiplet of 1H corresponding to the CH connected to CH_2 and both CH_3s all characteristic of an isobutyl group. Since none of these proton is very deshielded, the remaining oxygen atom which should be part of the ester group is thus attached to the aromatic ring while the carbonyl connects the isobutyl group to the rest of the molecule. As for the bromine, it is attached at the other side of the para disubstituted benzene ring, resulting in the above shown structures.

9. Predict the number of signals expected, their chemical shifts, their multiplicity, and the number of protons under each signal in the ^{1}H NMR spectrum of the following compound (3 pts)



δ(ppm) = 0.91 (6H, d), 1.88 (1H, m), 2.85 (3H, s), 3.90 (2H, d), 7.17 (2H, d), 7.61 (1H, brs), 7.92 (2H, d).

10. The mass spectrum below is that of benzyl 3-methylbutanoate (see structure below). Provide a structure for the fragments at m/z 192, 150, 107, 101, 91, 85, 57 and 41 (**You must show the fragmentation pattern**) (0. 5 x 8 = 4 pts)