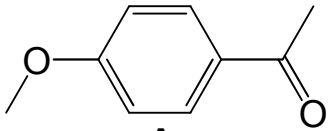
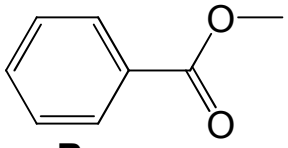
CHEM 266 - Homework 1 **Name**_____

(Due on Tuesday, September 12, 2016 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)



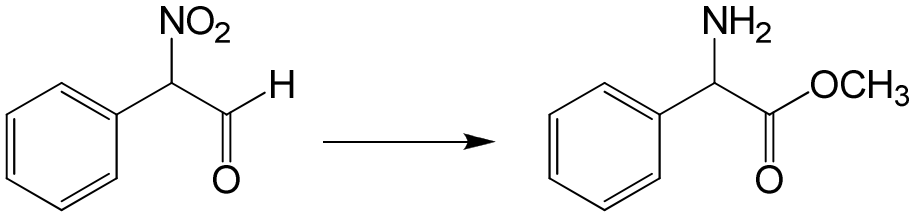
A



B

Both compounds will display the following signals: CH aromatic at 3050 cm^{-1}, CH_{sp3} at 2950 cm^{-1}, C=O at 1700 cm^{-1}, C=C around 1450 – 1600 cm^{-1} and CH aromatic bending around 600 – 800 cm^{-1}. So, it will not be possible to use IR to distinguish them.

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.



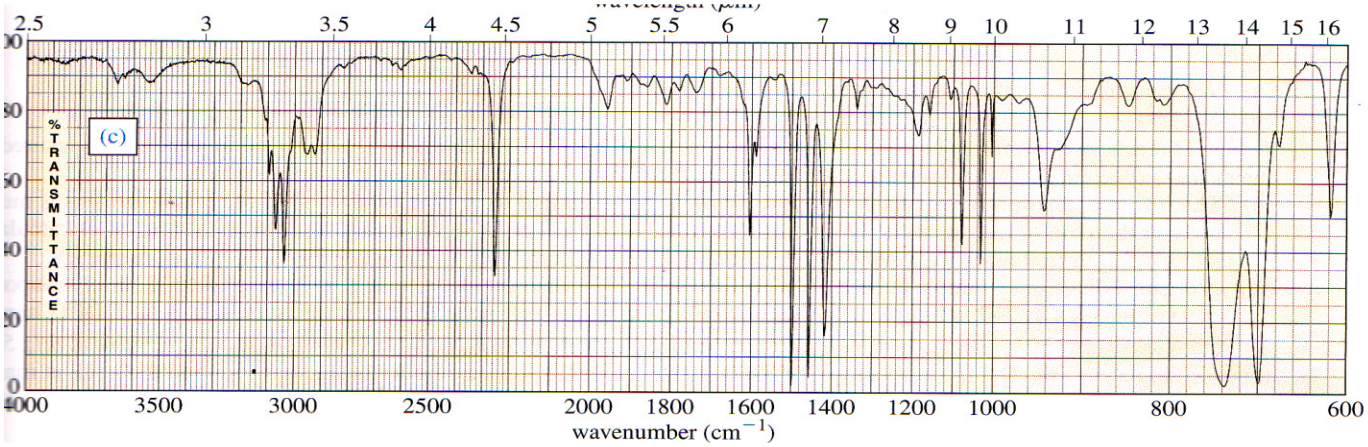
IR vibrational signals (5 pts)

Starting material		**Products**	
$\ddot{\upsilon}_{C\text{-}HAr}$	**= 3100 cm^{-1}**	$\ddot{\upsilon}_{NH2}$	**= 3300 and 3230 cm^{-1}**
$\ddot{\upsilon}_{C\text{-}Hsp3}$	**= 2950 cm^{-1}**	$\ddot{\upsilon}_{C\text{-}HAr}$	**= 3100 cm^{-1}**
$\ddot{\upsilon}_{C\text{-}HAldehyde}$	**= 2830 and 2760 cm^{-1}**	$\ddot{\upsilon}_{C\text{-}Hsp3}$	**= 2950 cm^{-1}**
$\ddot{\upsilon}_{C=O}$	**= 1750 cm^{-1}**	$\ddot{\upsilon}_{C=O}$	**= 1750 cm^{-1}**
$\ddot{\upsilon}_{C=C}$	**= 1450 - 1600 cm^{-1}**	$\ddot{\upsilon}_{C=C}$	**= 1450 - 1600 cm^{-1}**
$\ddot{\upsilon}_{NO2}$	**= 1355 and 1560 cm^{-1}**	$\ddot{\upsilon}_{C\text{-}N}$	**= 1200 cm^{-1}**
$\ddot{\upsilon}_{C\text{-}HAr\_bending}$	**= 600 - 800 cm^{-1}**	$\ddot{\upsilon}_{CO}$	**= 1050 cm^{-1}**
		$\ddot{\upsilon}_{CHAr\_bend}$	**= 600 - 800 cm^{-1}**

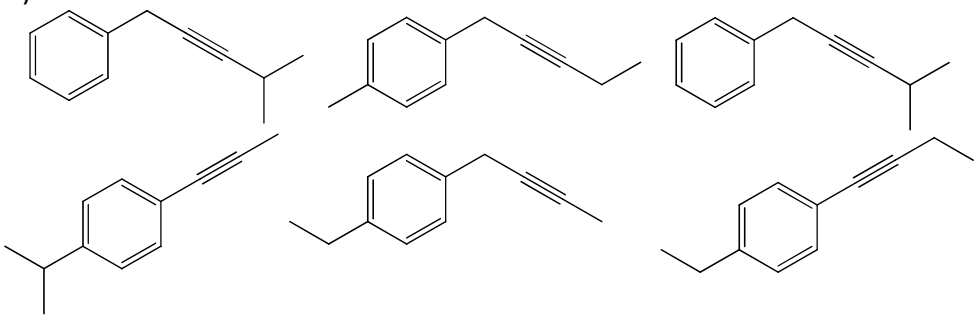
Explain (2 pts)

Although both compounds will keep the signature signals for the aromatic ring (CH aromatic at 3100 cm^{-1}, C=C at 1450-1600 cm^{-1} and CH aromatic bending around 600 – 800 cm^{-1}), CH_{sp3} signal around 2950 cm^{-1} and C=O at 1750 cm^{-1}, they will also exhibit some significant differences. In fact, the signals due to the CH aldehyde (2830 and 2760 cm^{-1}) and NO_2 (1355 and 1560 cm^{-1}) in the starting material will be replaced in the product by the signals for NH_2 at 3300 and 3230 cm^{-1}. The signals for C-N and C-O are in the fingerprint area and are thus not very noticeable.

3. The compound with the IR spectrum below has a molecular formula of **$C_{12}H_{14}$**. Propose **two** structures consistent with the IR spectrum and explain your answer.



Structures (4 pts)



Explain (2 pts)

nI = 12 + 1 – 14/2 = 6 elements of insaturations. The IR shows signal for CH aromatic around 3050 cm^{-1}, CHsp3 around 2950 cm^{-1}, CC triple bond around 2250 cm^{-1}, C=C aromatic around 1600 – 1450 cm^{-1} and the C-H aromatic bending around 600 – 800 cm^{-1}. Furthermore, the CC triple bond most be close enough to the aromatic ring (no more than two bonds away) to produce the change in dipole moment needed for the signal of the CC triple bond to be visible in the IR spectrum, and the triple bond is not terminal as indicated by the lack of a signal for CH sp.

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)

In high resolution, the mass of different fragments is displayed with more significant figures.

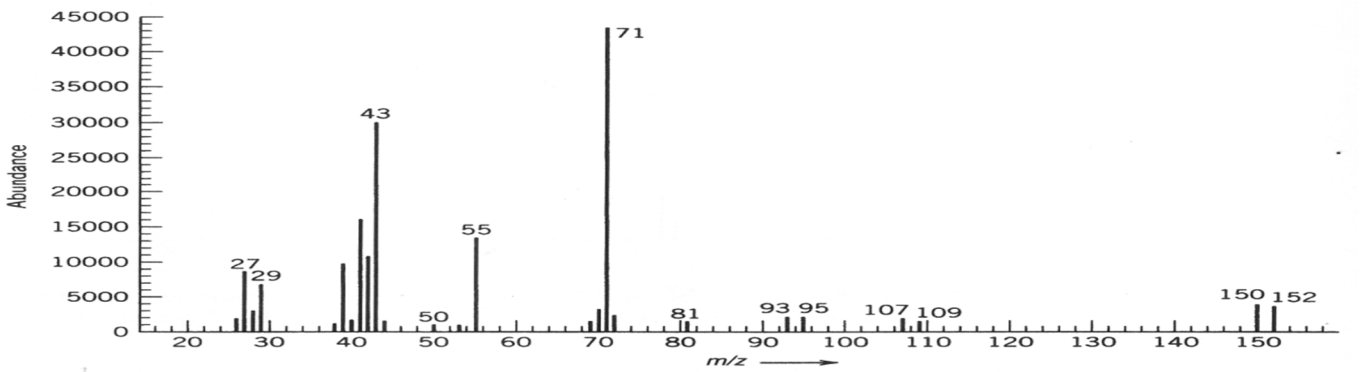
C_6H_9N = 6 (12.0107) + 9 (1.00794) + 14.0067 = 95.14236

C_5H_5NO = 5 (12.0107) + 5 (1.00794) + 14.0067 + 15.9994 = 95.0995

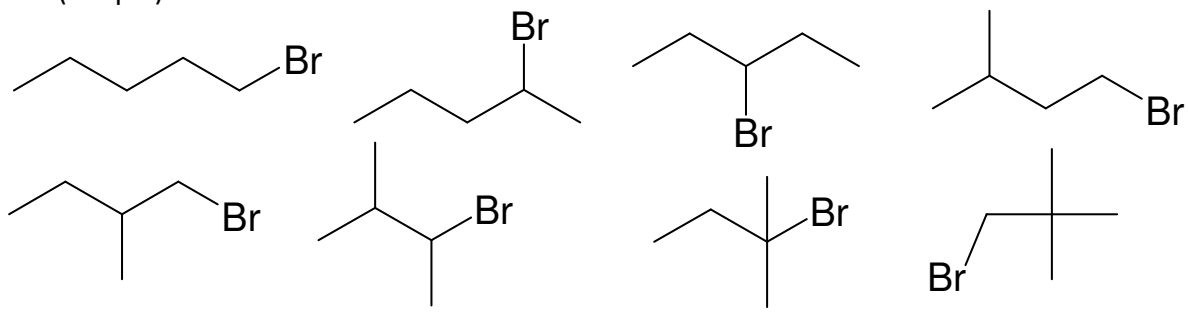
Although both compounds show the same nominal mass for their molecular ion, at high resolution they exhibit very different masses

95.14236 – 95.0995 = 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**)



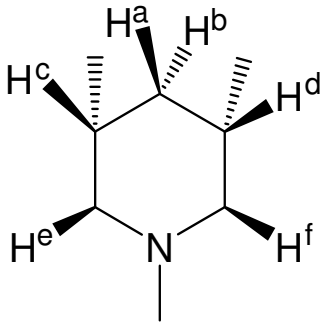
Structures (4.5 pts)



Explain (1.5 pts)

The molecule contains only carbon, hydrogen and another atom. The presence of two by two signals of a same size (M and M+2) in the mass spectrum indicates the presence of a bromine atom (79 and 81). The carbon chain has a mass of *m/z* 71 (150 – 79 = 71 or 152 – 81 = 71). So, the molecule should be $CH_3(CH_2)_nBr$, and all that needs to find is the value of n. The mass of $(CH_2)_n$ = 71 – 15 (with is a CH_3 group) = 56. Since CH_2 has a mass of 14, by dividing 56 by 14 I should obtained the value of n, which is 4. So, the molecule has no insaturation, and contains 5 carbons, 11 hydrogens and one bromine atom. So, any structure that has all these attributes is valid.

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



H^a and H^b are____**Equivalent or homotopic**_____

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**_____

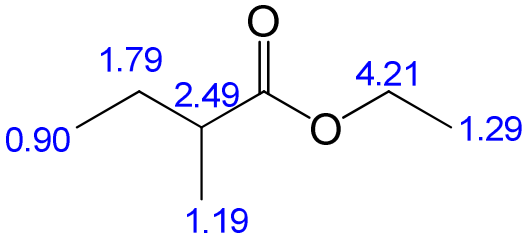
7. Two compounds A and B with the same molecular formula ($C_7H_{14}O_2$) have the ^{1}H-NMR data shown below. Both compounds have strong band around 2950, 1750 and 1075 cm^{-1} in their IR spectrum. Elucidate the structure of these two compounds and explain your answer.

Compound A: ^{1}H NMR (δ): 0.90 (3H, triplet), 1.19 (3H, doublet), 1.29 (3H, triplet), 1.79 (2H, quintet), 2.49 (1H, multiplet), 4.21 (2H, quartet).

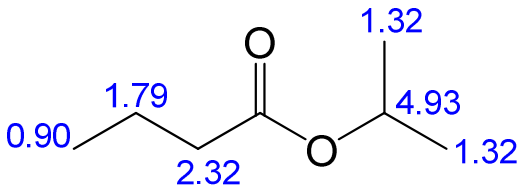
Compound B: ^{1}H NMR (δ): 0.90 (3H, triplet), 1.32 (6H, doublet), 1.79 (2H, multiplet), 2.32 (2H, triplet), 4.93 (1H, multiplet).

Structures (4 pts)

Compound A



Compound B



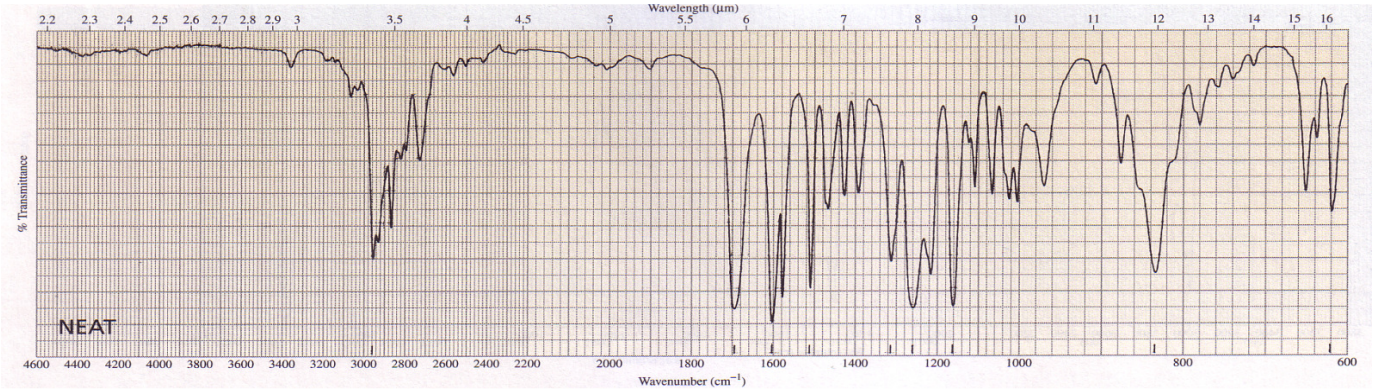
Explain (2 pts)

Both compound contain only one element of insaturation (7+ 1 – 14/2 =1)

Compound A displays a triplet of 3H at 1.29 ppm corresponding to a CH_3 close to a CH_2 (2H, quartet) at 4.21 ppm. These two signals form a deshielded isolated ethyl group (CH_3CH_2O) which is one side of the molecule. The other side of the molecule is made of a triplet of 3H (0.90 ppm) close to a quintet of 2H (1.79 ppm), which is a CH_2 with 4 neighbors. This CH_2 is of course between the CH_3 and the CH (1H, multiplet at 2.49 ppm). The CH is between the CH_2 at 1.79 and the CH_3 (3H, doublet) at 1.19 ppm. This explains why the CH appears as a multiplet (sextet), the CH_3 as a doublet because it has just one neighbor. The only insaturation correspond to the carbonyl, which with the other oxygen above mentioned form the ester functional group. All these data are consistent with the structure provided for compound A.

As for compound B, it displays a triplet of 3H (0.90 ppm), a multiplet of 2H (1.79 ppm) and a triplet of 2H (2.32 ppm) consistent with a propyl chain ($CH_3CH_2CH_2$). The other part of the molecule consists of 6H doublet (1.32 ppm) which corresponds to two CH_3 connected to the same CH group at 4.93 ppm (1H, multiplet). These two signals form an isopropyl group, which is very deshielded as indicated by the chemical shifts, forming an isopropoxy group. Just like in compound A, the insaturation correspond to a carbonyl group, which with the other oxygen, constitutes the ester group. These data are consistent with the structure provided for compound B.

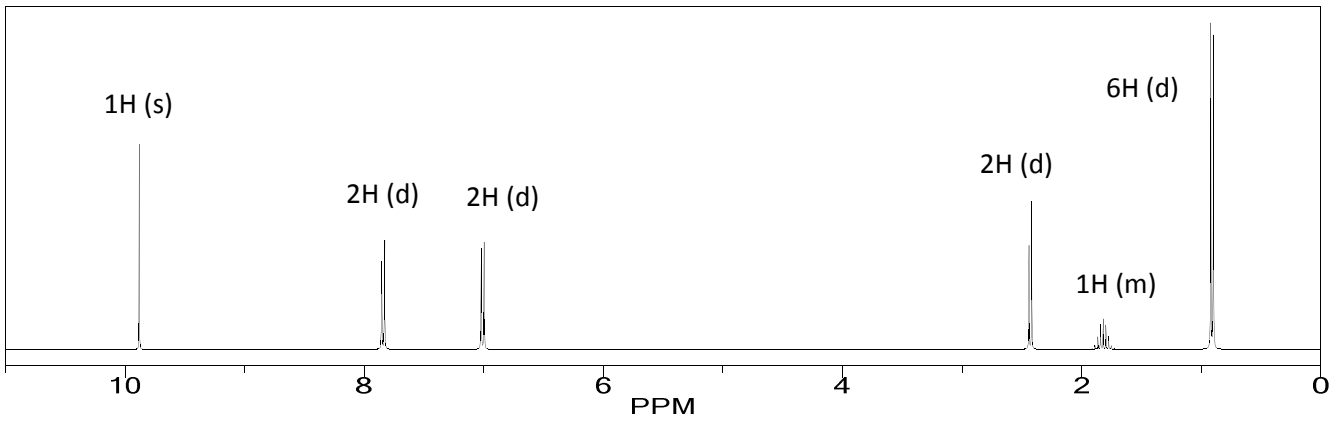
8. (a) Identify the major signals and the corresponding bond types present in the compound having the following IR spectrum; Molecular formula **$C_{11}H_{14}O$** (3 pts)



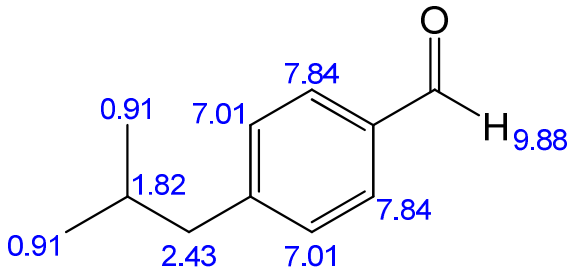
nI = 11 + 1 – 14/2 = 5 elements of insaturation

$\ddot{\upsilon}_{C\text{-}HAr}$	**= 3100 cm^{-1}**	**$\ddot{\upsilon}_{C\text{-}Hsp3}$**	**= 2950 cm^{-1}**
$\ddot{\upsilon}_{C\text{-}HAldehyde}$	**= 2840 and 2710 cm^{-1}**	**$\ddot{\upsilon}_{C=O}$**	**= 1700 cm^{-1}**
$\ddot{\upsilon}_{C=C}$	**= 1600 - 1450 cm^{-1}**	**$\ddot{\upsilon}_{C\text{-}HArbending}$**	**= 600 - 800cm^{-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)

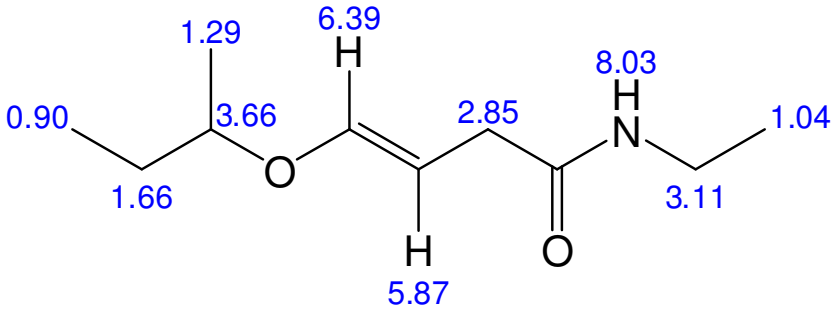


Explain (2 pts)

The IR spectrum suggested the presence of an aldehyde and a benzene ring, accounting for the observed 5 elements of insaturation. This observations are confirmed on the NMR spectrum by the doublet of 2H around 7.84 and 7.01 ppm corresponding to a para-disubstituted aromatic ring. The hydrogen of

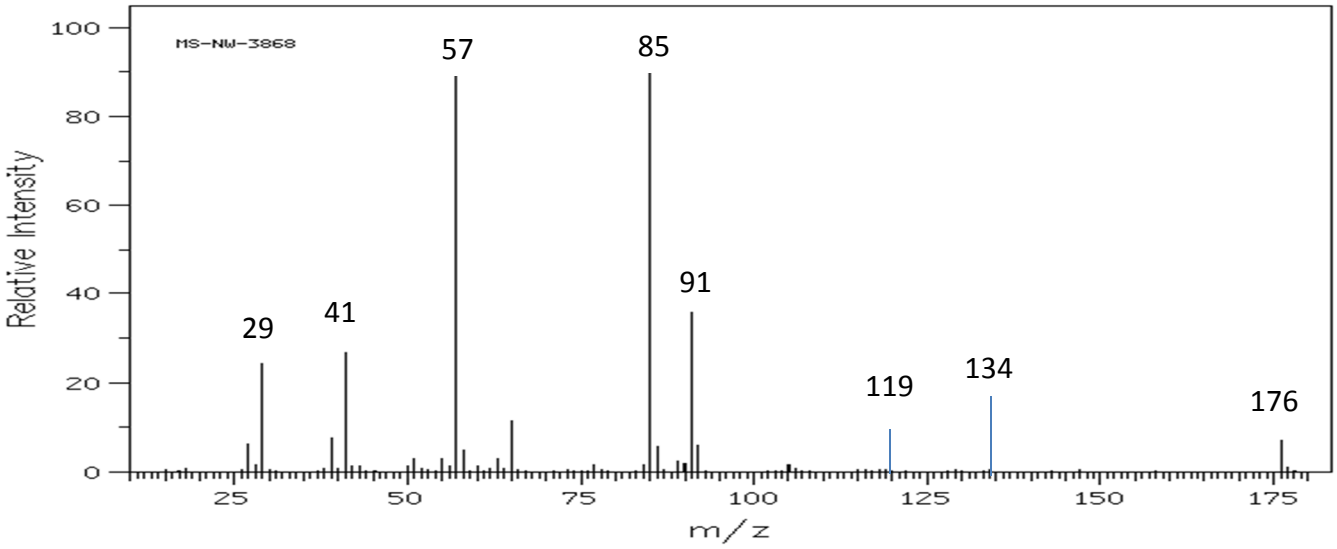
aldehyde is also observed around 9.88 ppm. The other part of the molecule is made of 6H doublet (0.91 ppm) corresponding to two CH_3 groups connected to the same carbon, confirm by the presence in the spectrum of a signal for 1H multiplet around 1.82 ppm. The last signal is that of 2H doublet at 2.43 corresponding to a CH_2 connected to the aforementioned CH, all forming and isobutyl group. So, the molecule is made of an aldehyde on one side of the para-disubstituted aromatic system, and the isobutyl group at the other end as illustrated in the above structure.

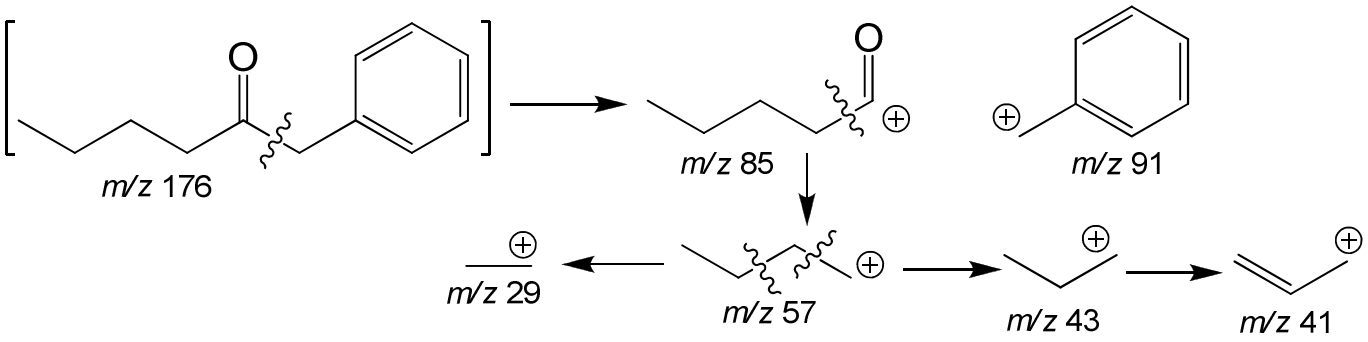
9. Predict the number of signals expected, their chemical shifts, their multiplicity, and the number of protons under each signal in the ^{1}H NMR spectrum of the following compound (3 pts)

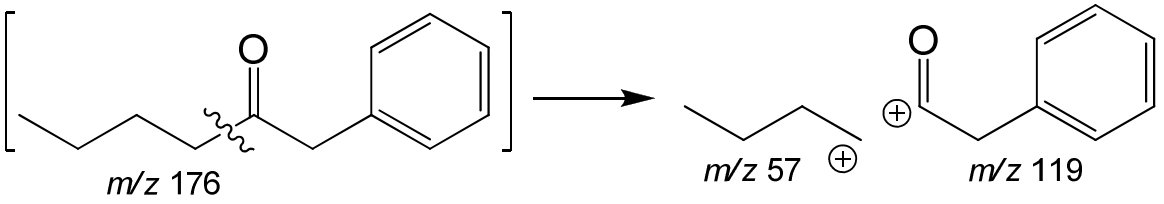


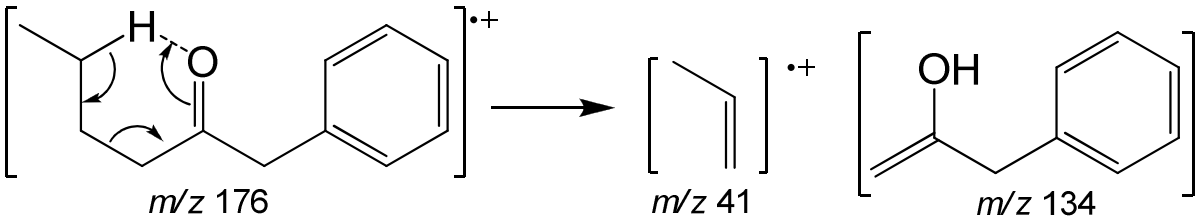
δ(ppm) = 0.90 (3H, triplet), 1.04 (3H, triplet), 1.29 (3H, doublet), 1.66 (2H, quintet), 2.85 (2H, doublet), 3.11 (2H, quartet), 3.66 (1H, multiplet), 5.87 (1H, multiplet or quartet), 6.39 (1H, doublet), 8.03 (1H, broad singlet).

10. The mass spectrum below is that of 1-phenylhexan-2-one (see structure below). Provide a structure for each of the fragments corresponding to the peaks indicated by the *m/z* 176, 134, 119, 91, 85, 57, 41 and 29 (you must show the fragmentation pattern to receive full credit) (4 pts)




O
m/z 176
O
m/z 85
m/z 91
m/z 29
m/z 57
m/z 43
m/z 41


O
m/z 176
m/z 57
O
m/z 119


H
O
•+
m/z 176
m/z 41
•+
OH
m/z 134