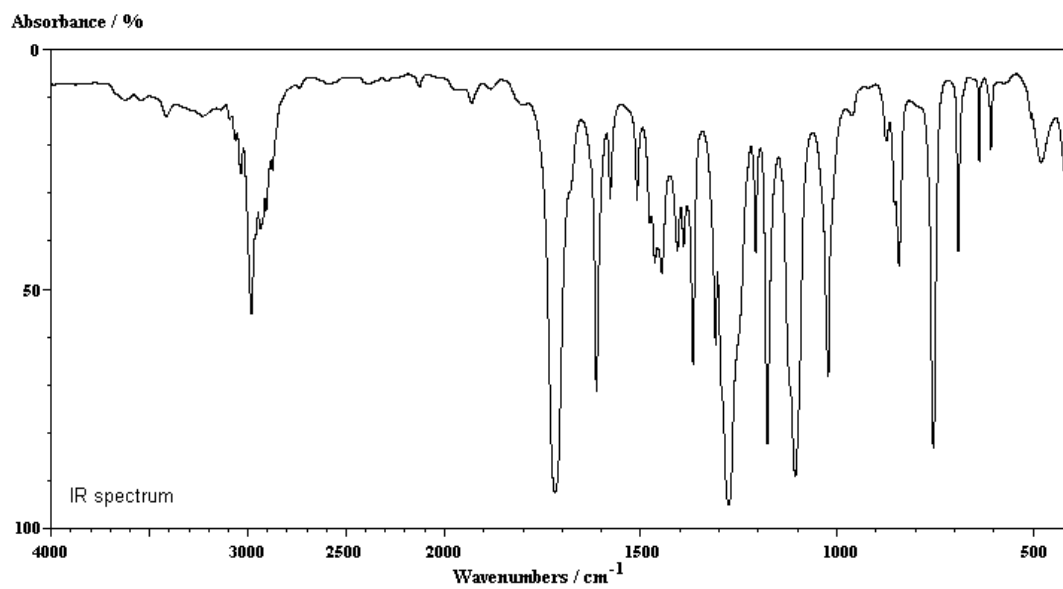
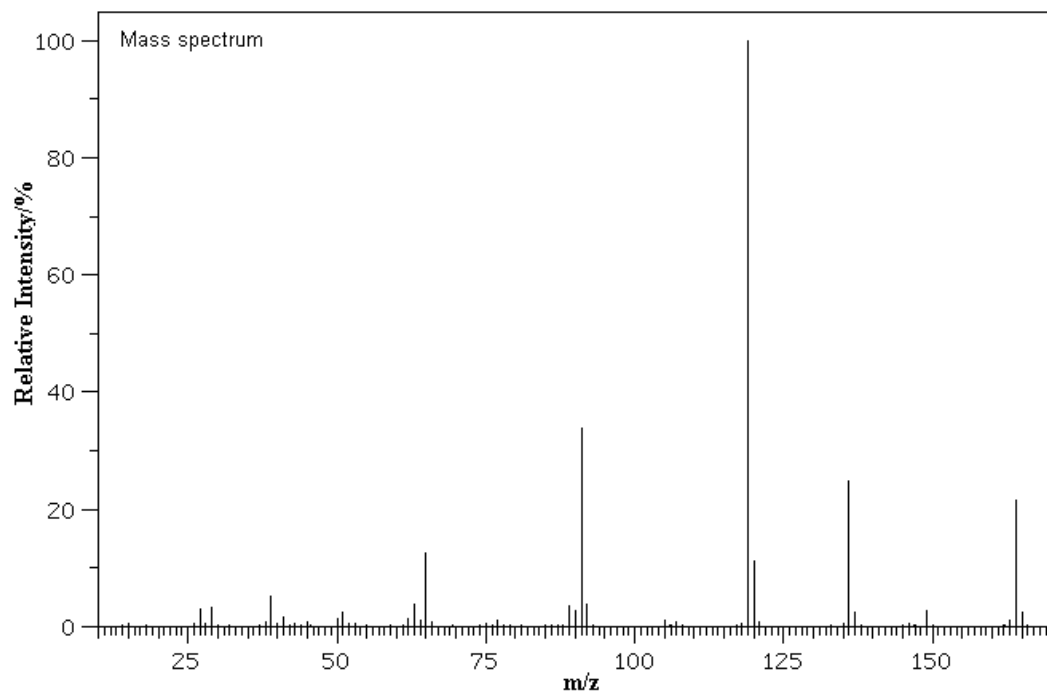
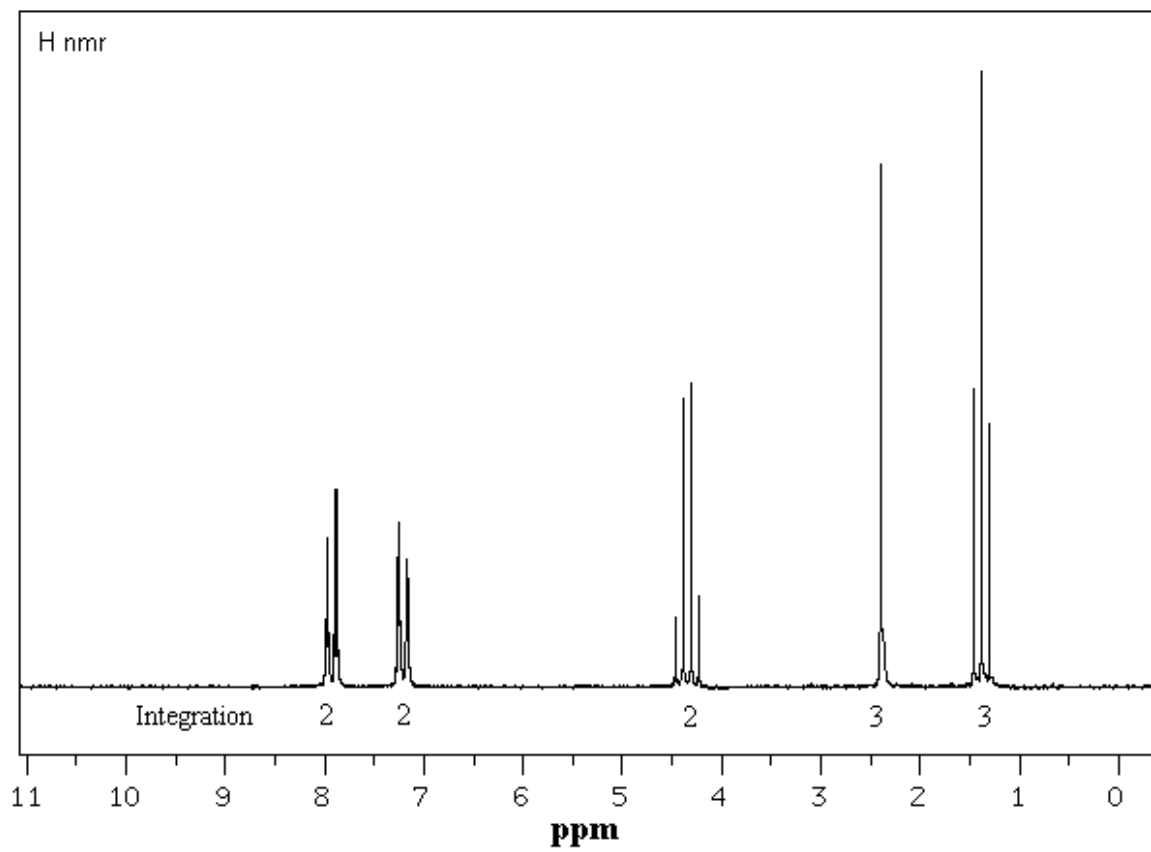
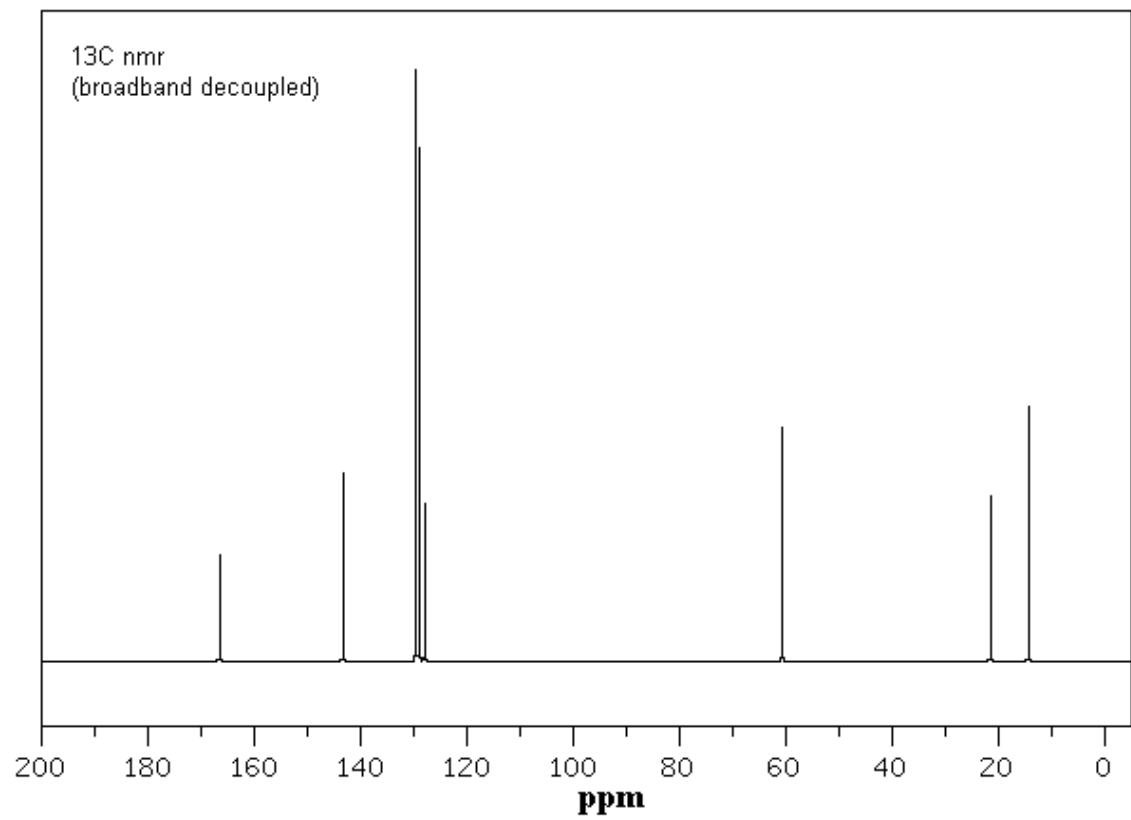


# SPECTROSCOPY PROBLEM WORKED EXAMPLE USING THE FRAGMENT APPROACH





## WORKED SOLUTION

### Mass spectrum:

M+ gives MW = 164 g/mol, no isotope pattern for Cl or Br. Even number implies even number of N atoms (so possibly none)

### IR:

1710cm<sup>-1</sup> C=O, 1600cm<sup>-1</sup> C=C, 1275 and 1100cm<sup>-1</sup> C-O possible.

No OH or NH (about 3500cm<sup>-1</sup>).

### <sup>13</sup>C nmr:

8 peaks = 8 types of C.

167 ppm C=O (probably an acid derivative)

4 types between 125-140 ppm = aromatic C

60 ppm is typical of a C bond to an electronegative atom

22 and 14 ppm most likely from alkyl C

### <sup>1</sup>H nmr:

5 peak sets = 5 types of H

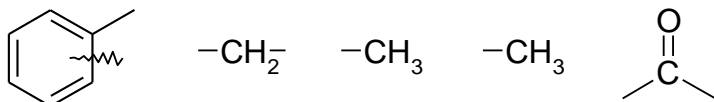
d/ppm	multiplicity	integration	Inference
7.8	"doublet"	2	Ar-H, must be disubstituted, most likely <i>para</i> ?
7.3	"doublet"	2	Ar-H, must be disubstituted, most likely <i>para</i> ?
4.3	quartet	2	CH <sub>2</sub> coupled to 3H, deshielded by O?
2.4	singlet	3	CH <sub>3</sub> with no adjacent H, slightly deshielded
1.4	triplet	3	CH <sub>3</sub> coupled to 2H

From the H nmr we have:

a disubstituted phenyl group, a -CH<sub>2</sub> and two -CH<sub>3</sub>

(note we will not worry about the details of the aromatic substitution pattern until later)

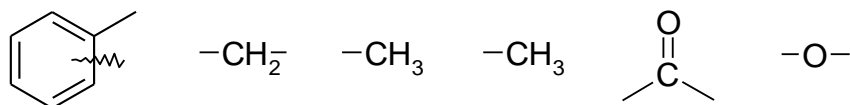
### List the fragments:



If we add up the masses of these fragments we get 76 + 14 + 15 + 15 + 28 = 148.

Compare this the MW :  $164 - 148 = 16$  (possibly missing an -O-, consistent with IR and C-NMR)

**Revised fragment list:**



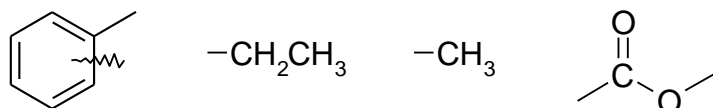
Hence the *molecular formula* =  $C_{10}H_{12}O_2 = 10 \times 12 + 12 \times 1 + 1 \times 16 = 164$  g/mol (a simple check for silly errors), and we get the IHD = 5 (i.e. 5 units of unsaturation (pi bonds and rings)).

Now start joining the fragments together....

The coupling in the H-NMR (the CH<sub>2</sub> is a quartet at 4.3ppm and the CH<sub>3</sub> a triplet at 1.4ppm) tells us that the CH<sub>2</sub> is connected to one of the CH<sub>3</sub> groups giving us an ethyl group: -CH<sub>2</sub>CH<sub>3</sub>

The IR gave us the C=O which the C-NMR suggests is an acid derivative, such as an ester rather than a aldehyde or ketone (typically > 190ppm), this is consistent with the other oxygen atom in the molecular formula.

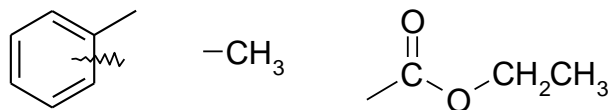
**Revised fragment list:**



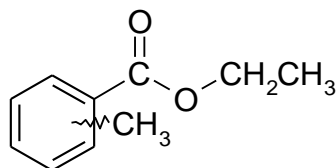
Notice that we now have a four piece puzzle, with two middles and two end pieces. Simple logic tells us that the two ends can't be directly connected to each other since that we prevent us from incorporating the other two pieces!

Looking at the H-NMR chemical shift for the -CH<sub>2</sub>- group at 4.3ppm, we can determine that it is most likely as an ethoxy group, i.e. -OCH<sub>2</sub>CH<sub>3</sub> this means we have an ethyl ester:

**Revised fragment list:** a three piece puzzle



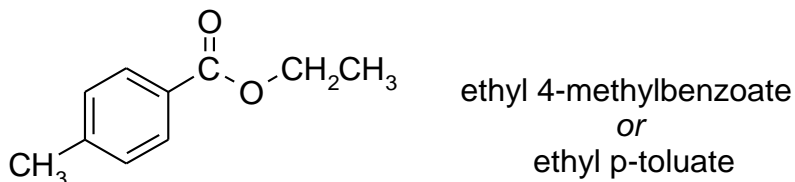
The ethyl ester group must be connected to the aromatic ring and so must the methyl group



So, what about the aromatic substitution pattern ?

The number of types of ArC (4 peaks between 125-140ppm) and the coupling in the Ar region of the H nmr (two 2H doublets between 7-8ppm) imply the *para* substitution pattern.

Altogether...



The final step should always be to check what you have drawn. The easiest thing to check is usually the coupling patterns you would expect to see, and the chemical shifts of each unit. You should be asking yourself: "Does my answer give me what the H-nmr shows?"

For more practice spectroscopy problems see the materials contained in Chapter 13 of our version of the Carey On-Line Learning Center.

<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-0.html>

especially the Interactive Spectroscopy Problems:

<http://www.chem.ucalgary.ca/courses/351/WebContent/spectroscopy/spectroscopy.html>