¹H

2   3   2   2   3

11   10   9   8   7   6   5   4   3   2   1   0
ppm

HSP-00-301

CDS-03-559

200   180   160   140   120   100   80   60   40   20   0
ppm
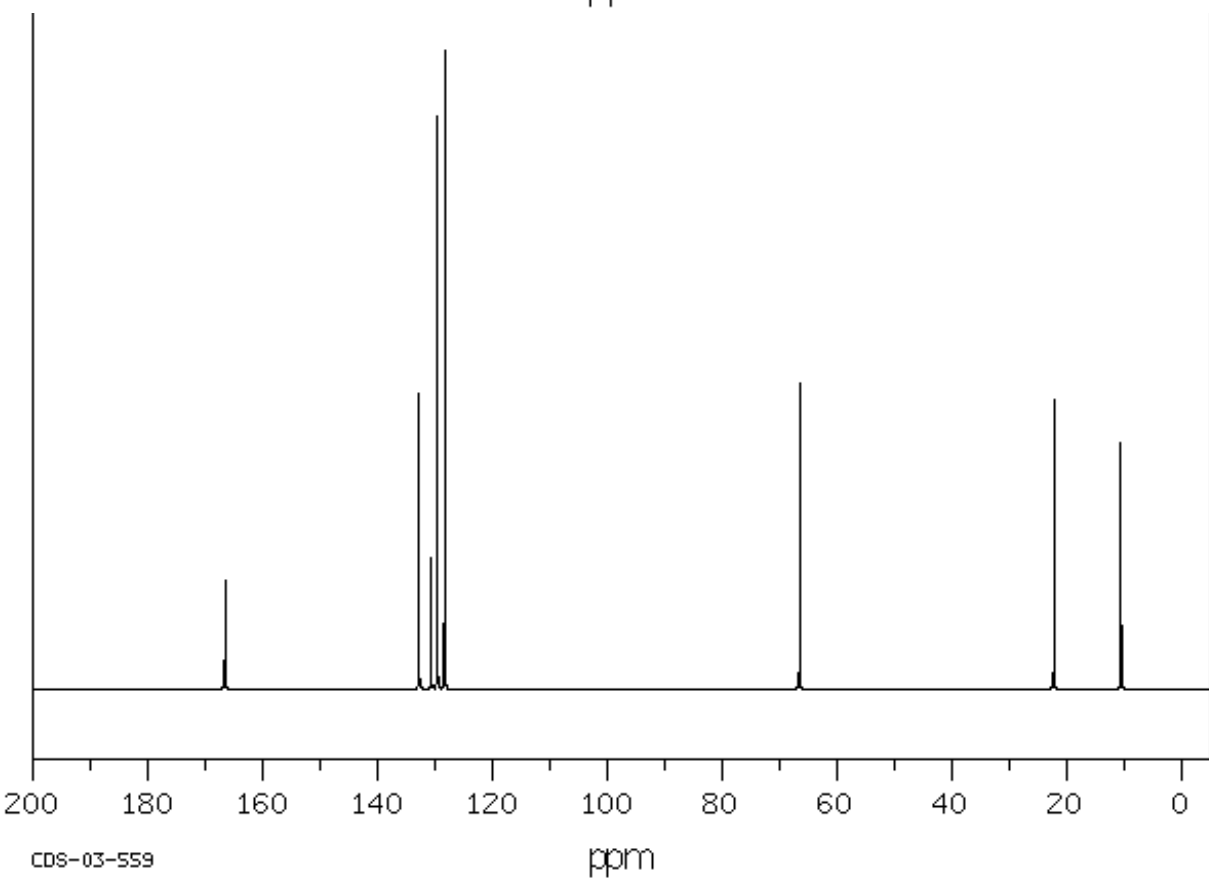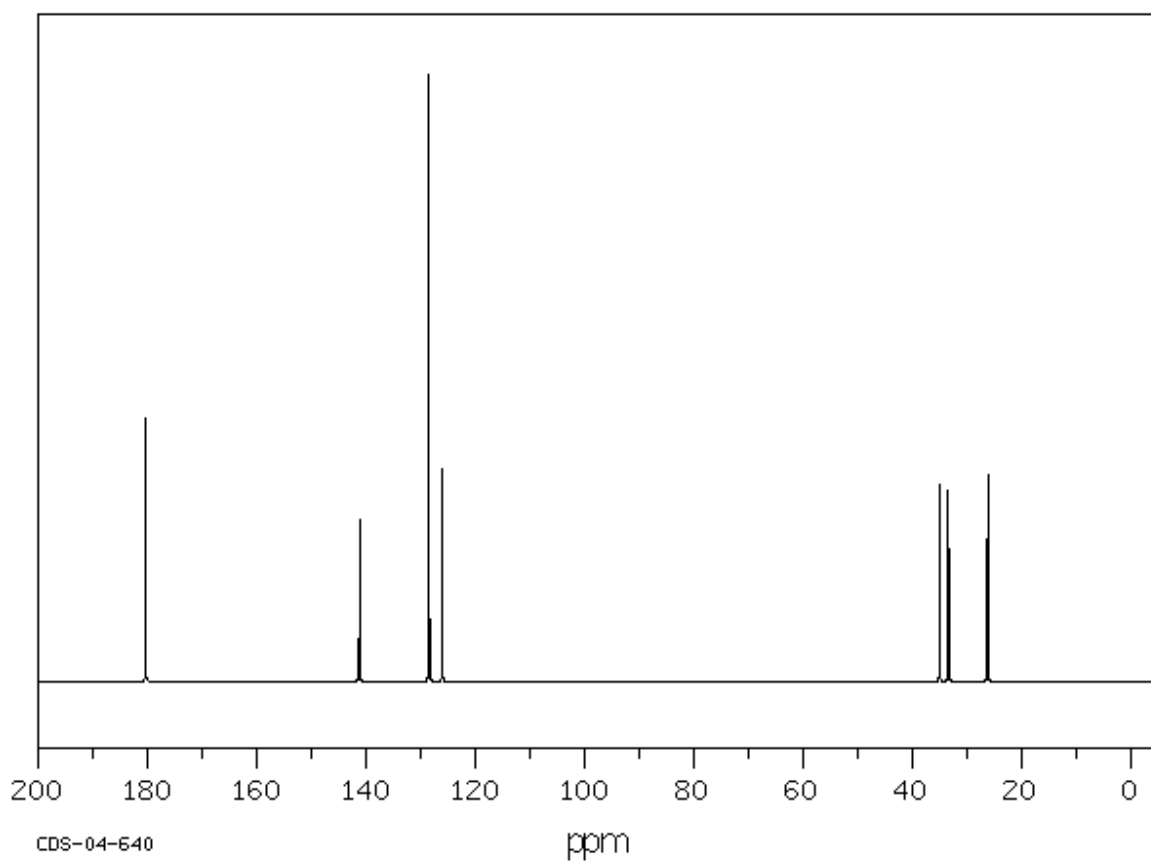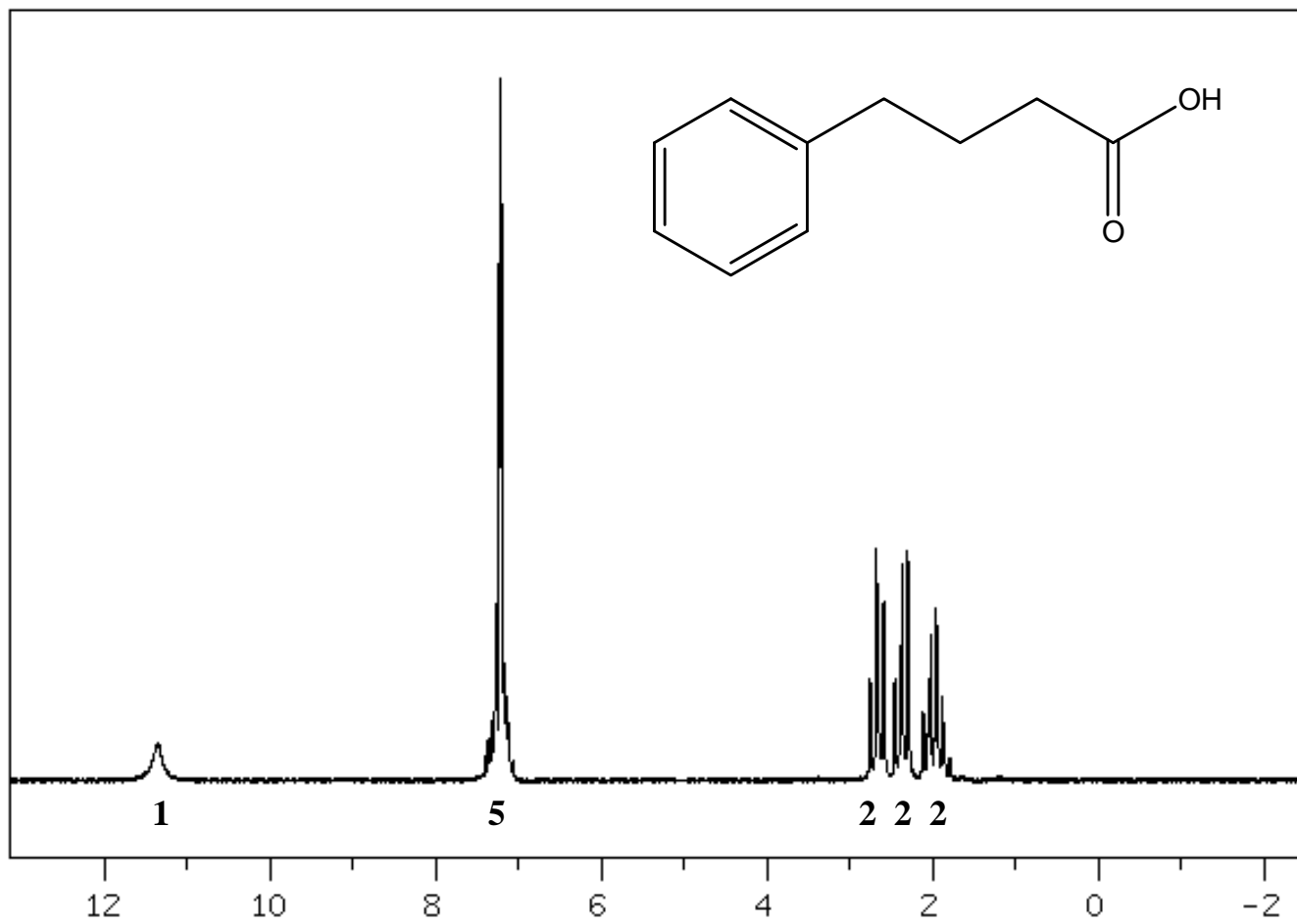
CDS-04-640

How spectra can be used:
- Confirm identity of a compound
     Match known spectrum
     Match signals/bands to atoms/groups present in the molecule

- Deduce a chemical structure
     Solve the structure by matching evidence from different types of spectra

- Follow a reaction
     As a molecular reaction takes place, some functional groups will be destroyed and others created;
     the spectra of the molecule/mixture must change accordingly.

Types of problems:
     Match a spectrum to a compound
     Assign bands/peaks in a spectrum to the corresponding atom or group in a molecule
     Given a structure, predict the spectrum
     Solve a structure given a set of spectra

Problem Solving Routine

Be sure to take all data into account! Don't focus on one type of spectra; don't try to "guess" a structure before you've thought of all the data – you'll then start looking for evidence that agrees with you and ignore evidence that doesn't. In the ^{1}H NMR, don't focus on one type of data. You must consider chemical shift, coupling and integration together. Any of these, by themselves will not solve the structure for you.

1. If you have a molecular formula, use it. Calculate the number of unsaturations (see p. 174). If at least 4, you may have an aromatic ring (look for signs in both IR and NMR). If less than 4 unsaturations, you can not have an aromatic ring.

$$\text{unsaturation} = (2*\#C + 2 - \#H - \#\text{halogen} + \#N) / 2 \quad \text{(each ring or } \pi \text{ bond counts as an unsaturation)}$$

2. If you have an IR, use it to identify functional groups – cross check with NMR. For example, say your IR shows an intense stretch at 1725 cm^{-1}. This suggests a C=O group. Therefore, there should be a signal between 160 and 220 ppm in the ^{13}C NMR.

3. Count the number of signals in the ^{13}C NMR. This is the number of magnetically different carbons in the molecule. This will also tell you which types of carbon you have. Always cross check with other spectra/data. If you have a molecular formula, the difference in number of carbons and number of ^{13}C signals will give you information about the symmetry of the molecule. Take benzene, C_6H_6. You know it has six carbons, but there is only one ^{13}C signal. Therefore, the molecule must be highly symmetric (to make all the different carbon atoms identical).

4. Move to the ^{1}H NMR. Prepare a table that lists each signal, its integration, its chemical shift and its splitting. For each signal, write down possibilities. For example, you have a triplet at 4.2 ppm that integrates for two protons. The protons responsible for this signal must be on a carbon bonded to something electronegative (X) and have two other protons within three bonds. So, possibilities are: CH$_2$-CH$_2$-X (bold are the protons causing the signal), X-CH(CH)-CH(CH)-X. Each piece must then be consistent with the rest of the ^{1}H NMR signals and evidence from the IR and ^{13}C.

5. Once you've proposed a structure, go back through the data and be sure that the structure is completely consistent with the data and that no piece of data contradicts your structure. If there is data that contradicts your structure, it is the wrong structure. You may be close, but there won't be random errors in the spectra (also, you may be wrong in how you're interpreting the data). Always be skeptical.

6. Be sure to check that your structure fits the molecular formula, if you have it. This is an easy thing to miss.