^{1}H NMR Problem-Solving Strategies

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The goal of solving a ^{1}H NMR spectrum is to determine the structure that is consistent with ALL given data. Since the NMR provides a lot of information, we must develop a systematic approach. First, we determine what pieces are present. Next, we figure out how those pieces fit together. Finally, we confirm that our structure matches the spectral data given. Be sure to label every proton a/b/c/etc. to match NMR peaks a/b/c.

1) **If given an IR spectrum, what functional groups (FG) are present?** These are pieces to your puzzle. e.g.
   ~1700 cm^{-1} strong absorption indicates a carbonyl (**C=O** stretch)
   ~3300 cm^{-1} broad signal indicates an alcohol (**O—H** stretch)
   absorptions *just above* >3000 cm^{-1} indicate **sp^2 C—H**, and *just below* <3000 cm^{-1} indicate **sp^3 C—H**

2) If given molecular formula: **check for sites/degrees of unsaturation** (DU).
   If saturated, maximum # of H's = $C_nH_{2n+2+\#N}$
   every 2 missing H's = 1 DU
   each DU = a π bond or a ring
   4 DU = a possible benzene ring (3 π bonds, plus 1 ring)

3) **Using the peak integration, determine the pieces of your molecule.** *Ignore δ value for now, unless ~7 ppm!*
   3H signal = —CH_3
   2H signal = —CH_2—
   1H signal = CH or OH or NH (Note: OH and NH typically appear as broad singlets)

   6H signal = two equivalent —CH_3 groups
   4H signal = two CH_2's or a CH_3 + CH (overlapping signals are possible!)

   peaks around 7 ppm = aromatic H's (indicates presence of a benzene ring)
   may be grouped closely together (as a singlet or multiplet) or may be several signals in the region:
   a total of 5 H's around 7 ppm = monosubstituted benzene ring
   a total of 4 H's around 7 ppm = disubstituted benzene ring (groups can be *ortho*, *meta* or *para*)

4) **Do you have all your pieces?** "Add up" your pieces and compare to your molecular formula.
   have you accounted for the calculated DU?
   have you accounted for the functional groups in the IR?

5) **Put the pieces together!** Start with an end piece, such as a methyl (—CH_3).
   consider chemical shift (refer to a provided table https://www.chemistryconnected.com/NMR)
   is it next to an oxygen? (~3.8 ppm)
   is it next to a C=O or a benzene ring? (~2.2 ppm)
   consider splitting patterns (n+1 rule, where n = # of nonequivalent neighbors)
   is it a triplet? It might be attached to a CH_2 (2 neighbors → 3 peaks)
   is it a singlet? There must be no protons on neighboring carbon atoms (0 neighbors → 1 peak).

6) **Check your answer!** Final structure must match molecular formula, and IR and NMR spectra.
   Look for symmetry…how may peaks should be in the NMR? What would integration be for each?
   Calculate/estimate chemical shifts, predict splitting patterns, compare to NMR spectrum, label H's a/b/c.