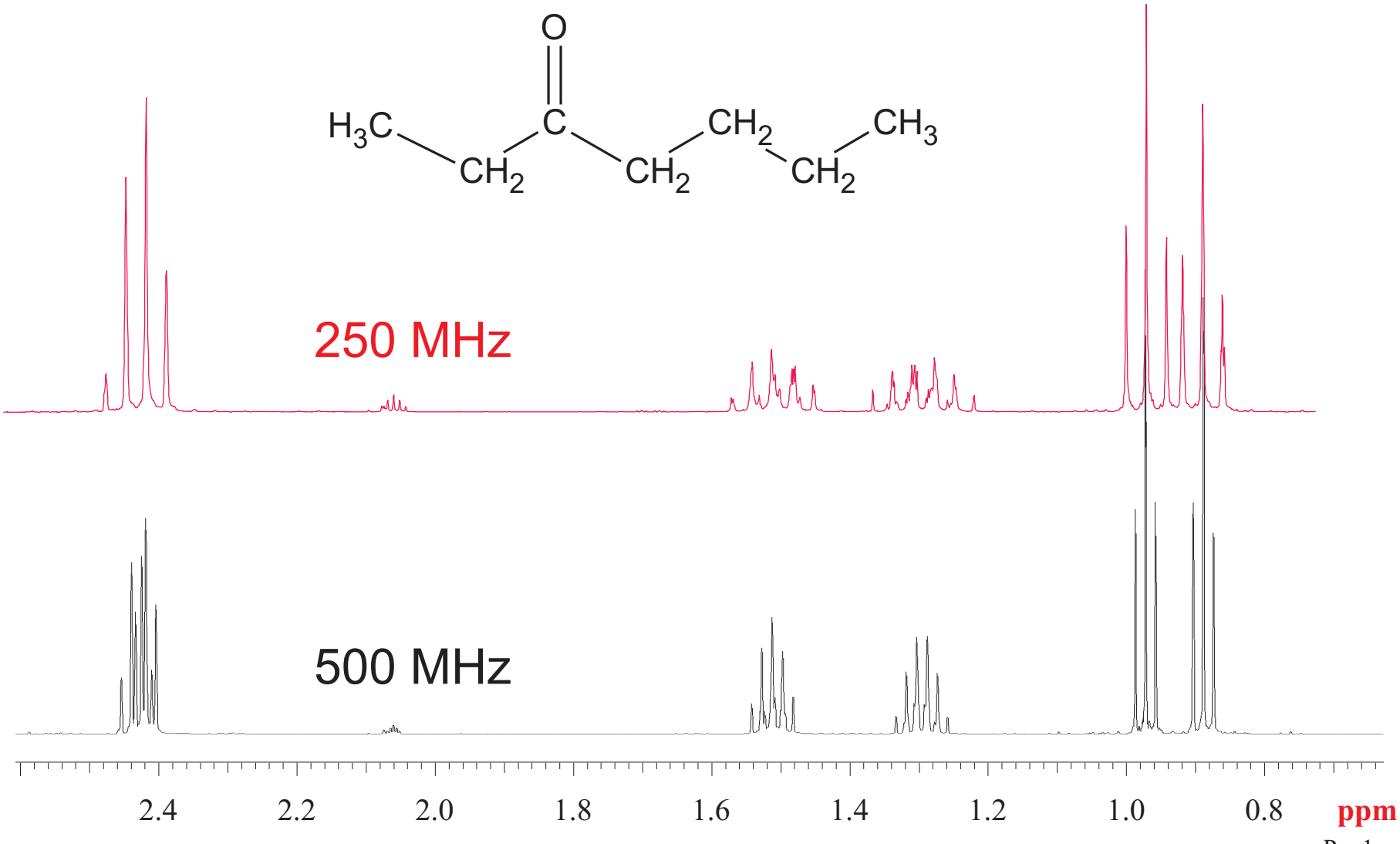
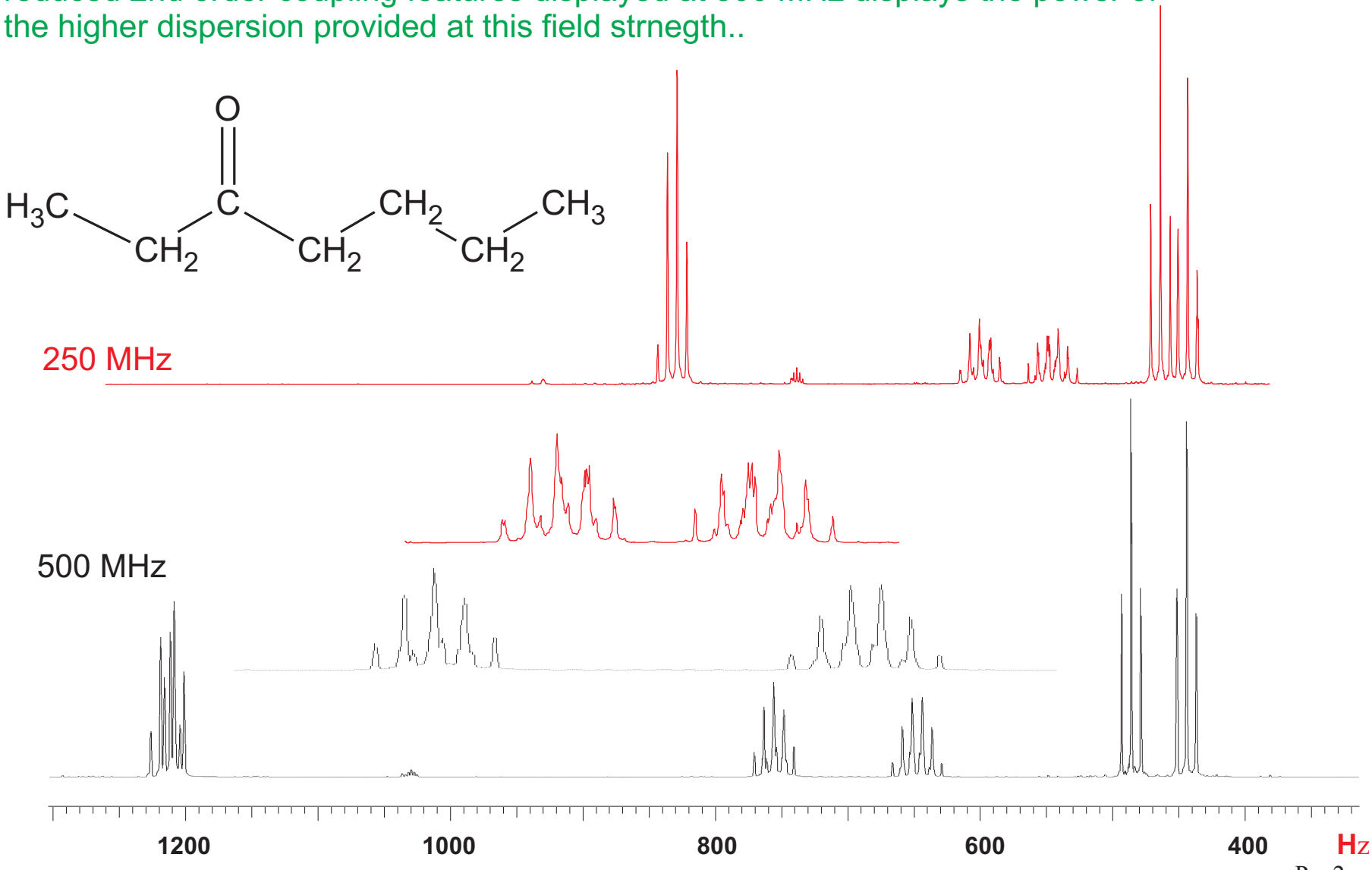
3-heptanone 1H 1d Spectra
acquired at 250MHz and 500MHz **plotted in ppm**.

Using a ppm scale, J-couplings (constant in Hz) on smaller magnets appear to be larger.



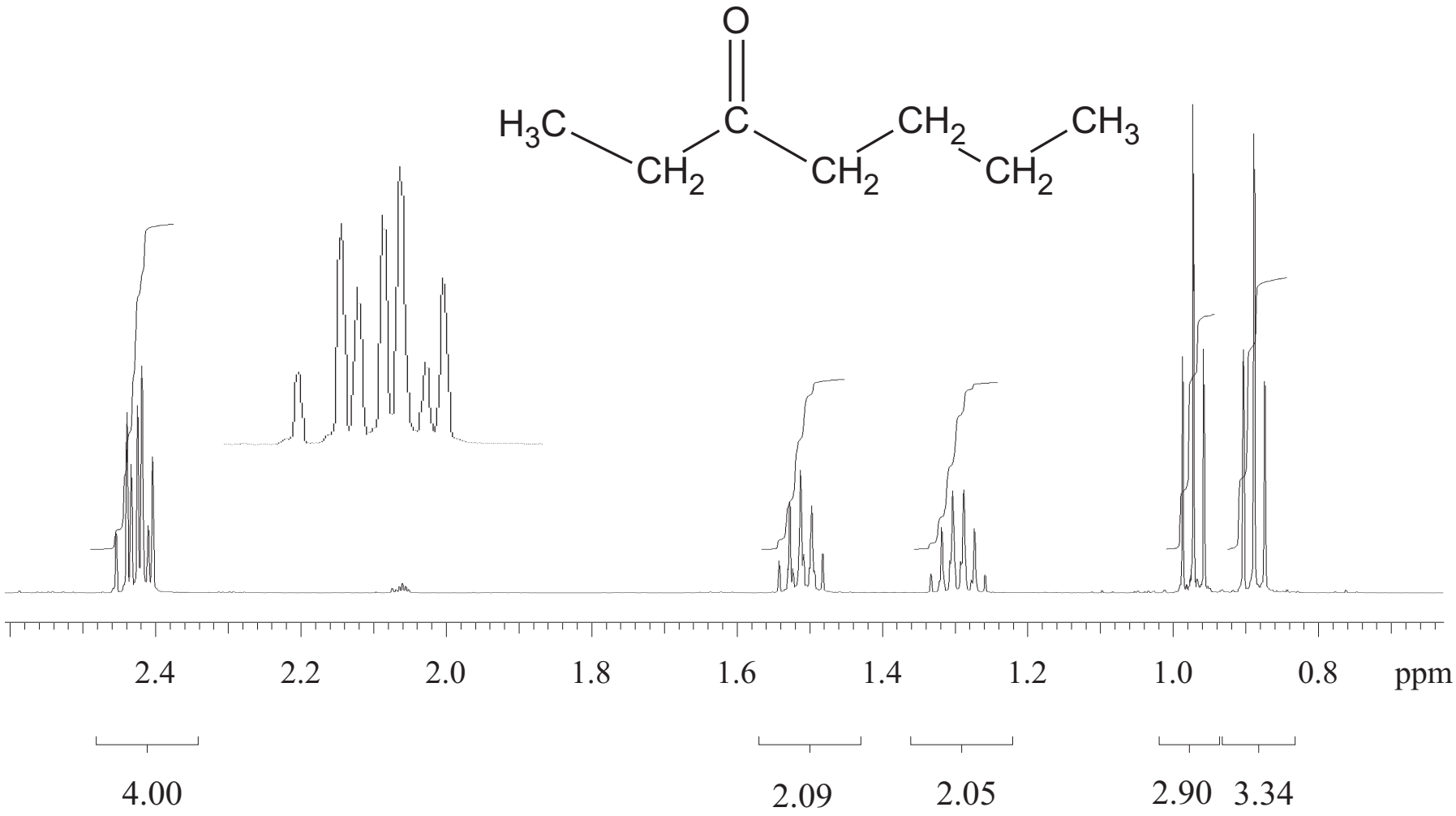
3-heptanone 1H 1d Spectra
acquired at 250MHz and 500MHz **plotted in Hz**.

Note the better resolution apparent in the 250 MHz spectrum; at the same time, reduced 2nd order coupling features displayed at 500 MHz displays the power of the higher dispersion provided at this field strnegth..



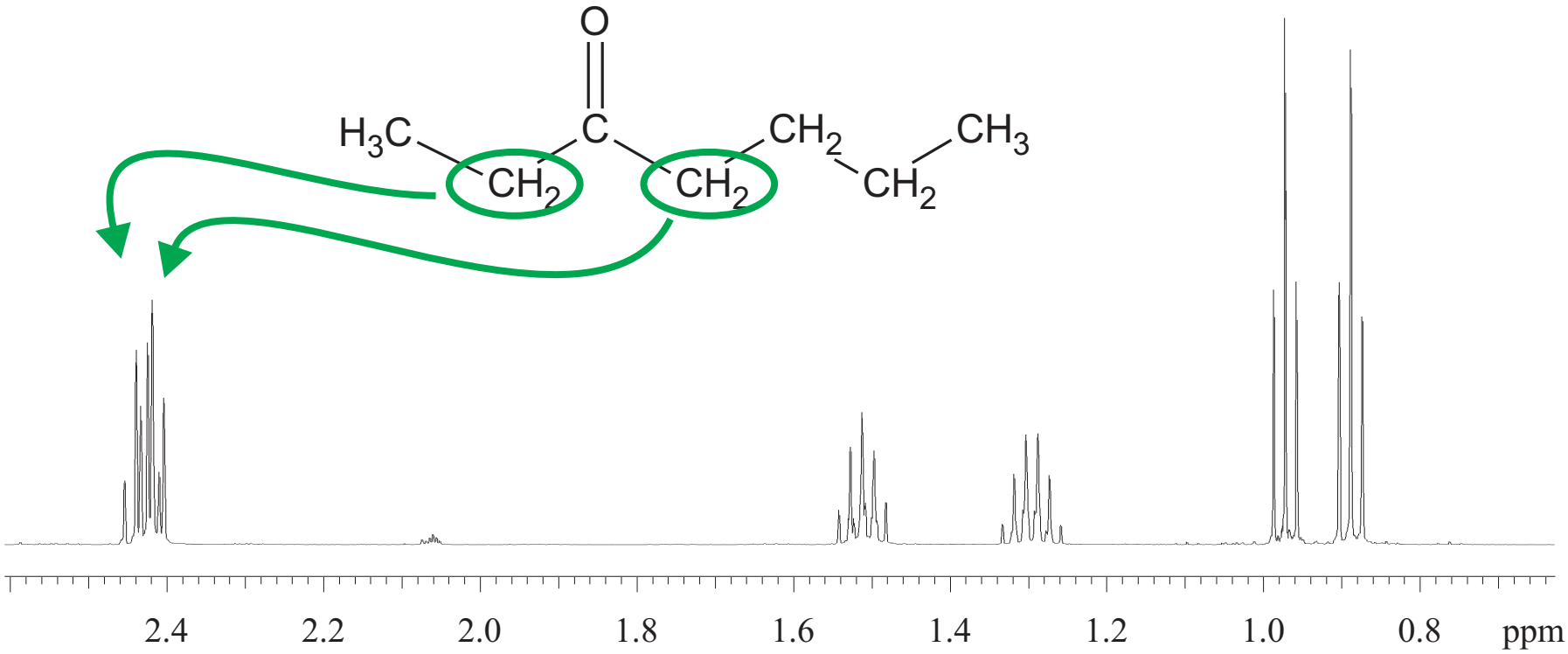
3-heptanone 1H 1d Spectra: 500MHz

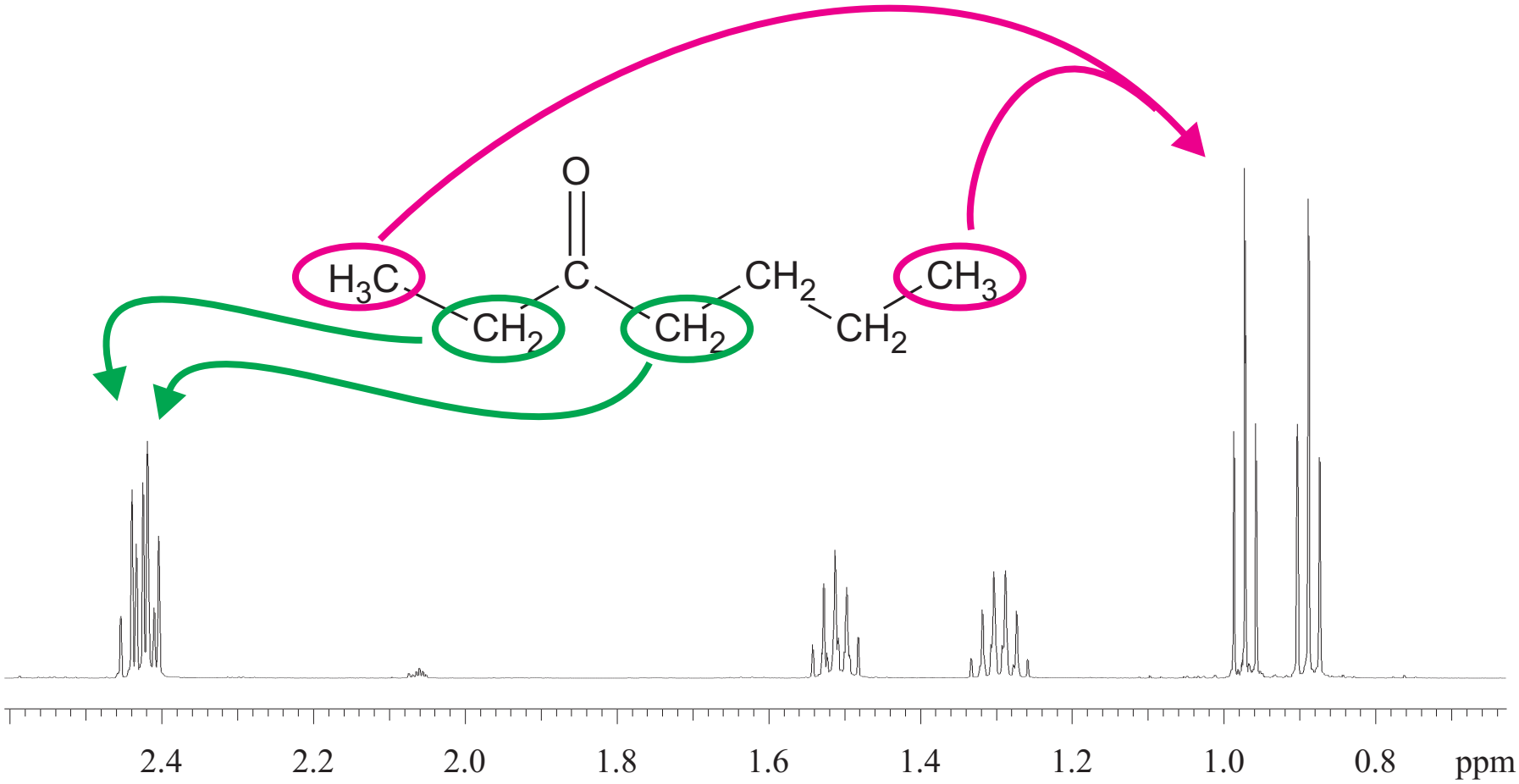
This simple compound can be easily assigned from the 1d spectrum (you should be able to identify the two overlapping multiplets). It is used here to provide an introduction—easy to follow—to more sophisticated experiments.



3-heptanone 1H 1d Spectra: 500MHz

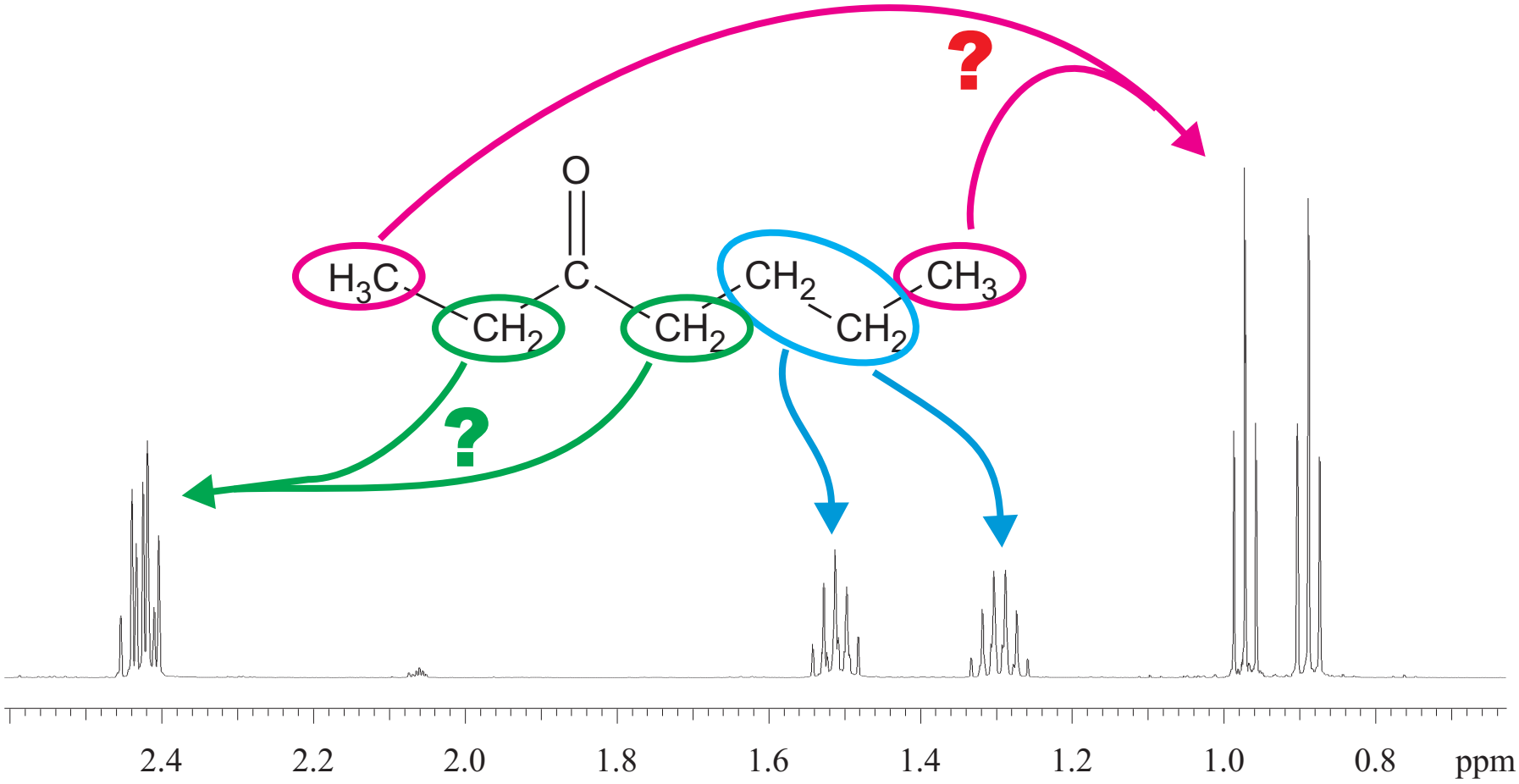
Chemical shift easily assigns these four protons to this region. J-coupling patterns can finish this assignment; in a more complex compound, the overlap may prevent final assignments, so pretend that that is the case here.




O
H3C
C
CH2
CH2
CH2
CH2
CH3
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm

3-heptanone 1H 1d Spectra: 500MHz

Again, pretend the compound is sufficiently complex that assignments cannot be made from the 1H 1d spectrum.

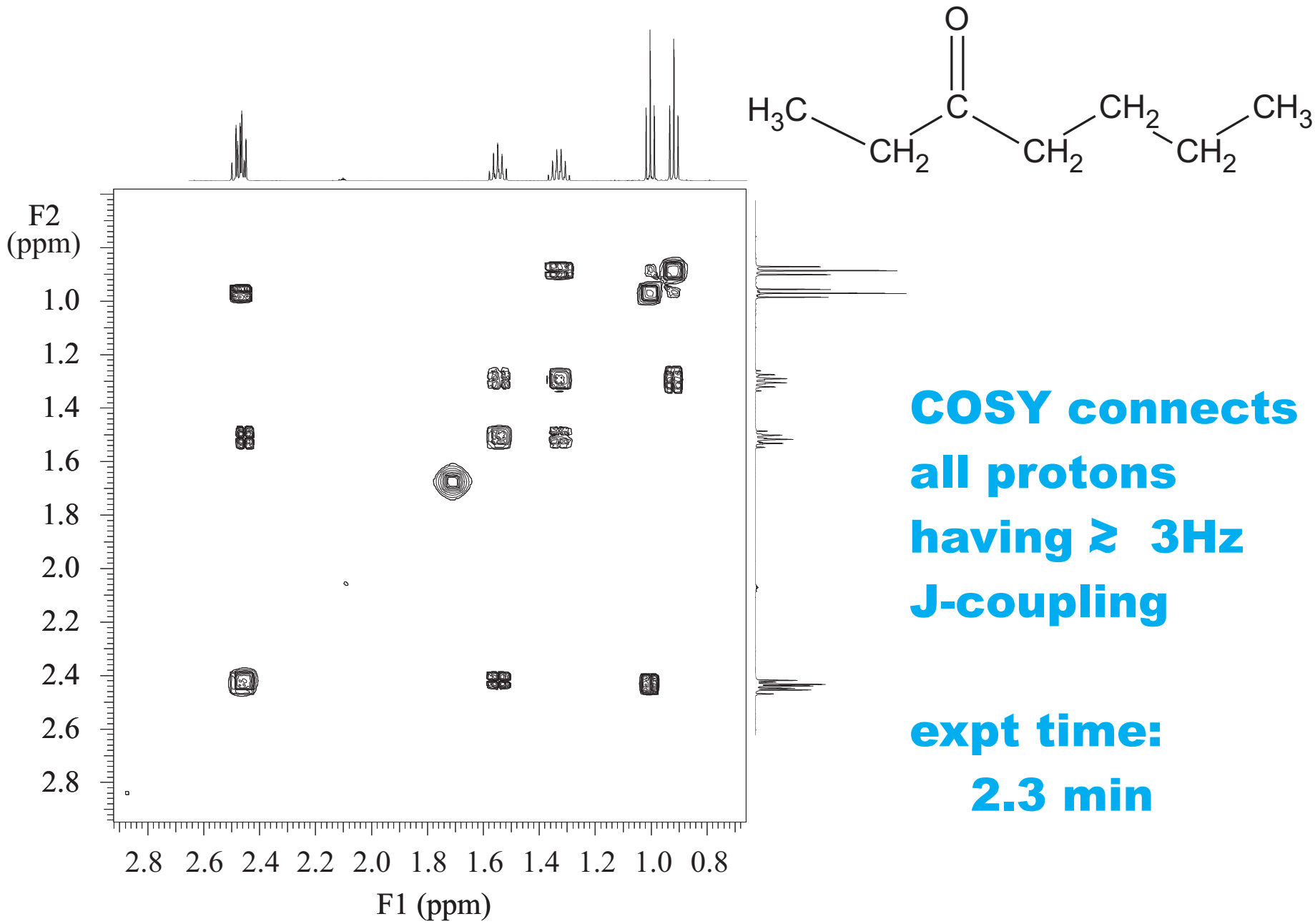


Modern NMR: Assignment Aids

Two basic classes of experiments:

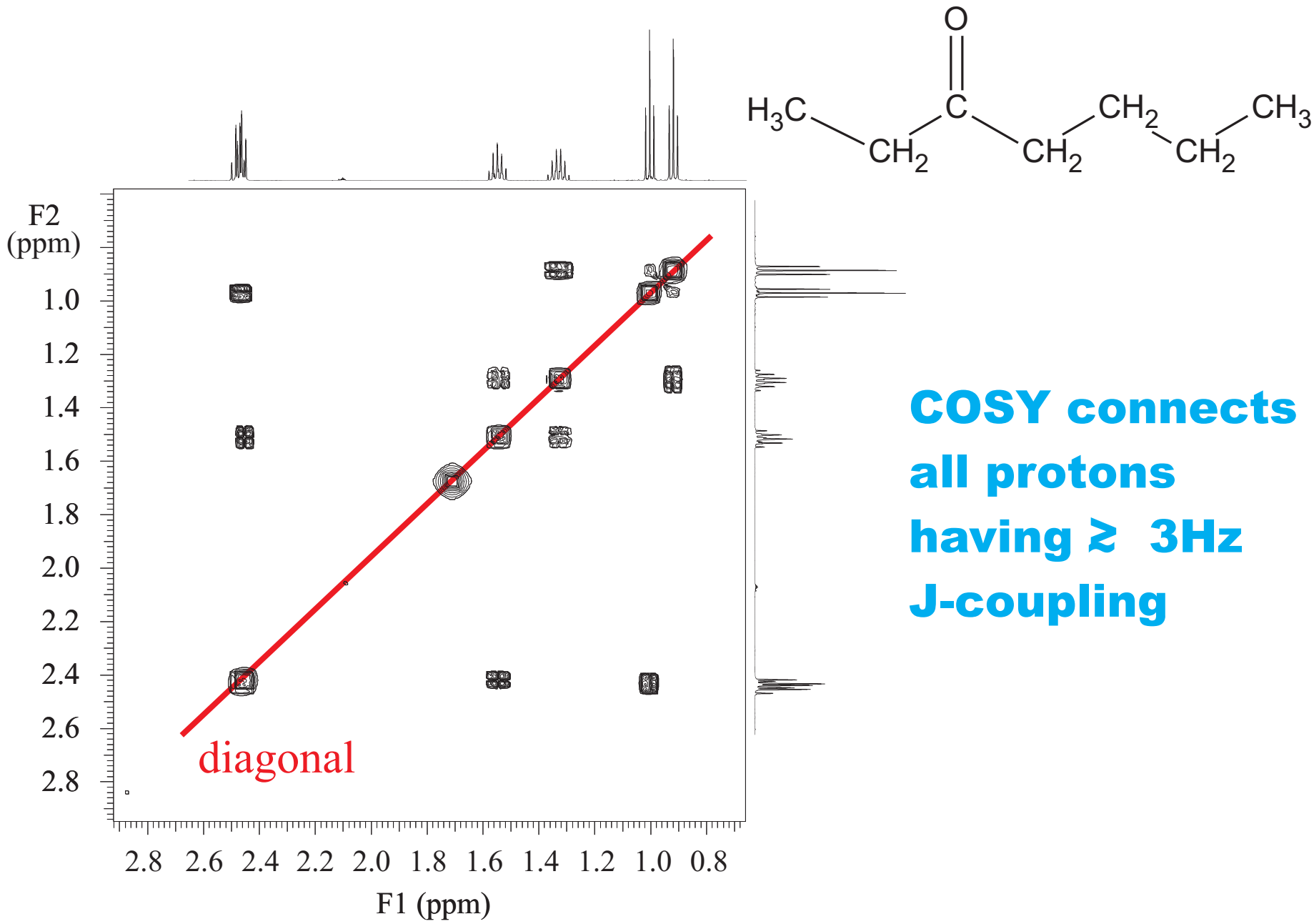
- **correlations via J-couplings**
  - homonuclear (usually 1H-1H)
    - direct 2 and 3 (sometimes >) bond
    - relayed (or total)
  - heteronuclear
    - 1-bond
    - n-bond
- **proximity (NOE or ROE)** **[examples next week]**

3rd and 4th classes, involving dynamics and diffusion, do not assist with assignments.

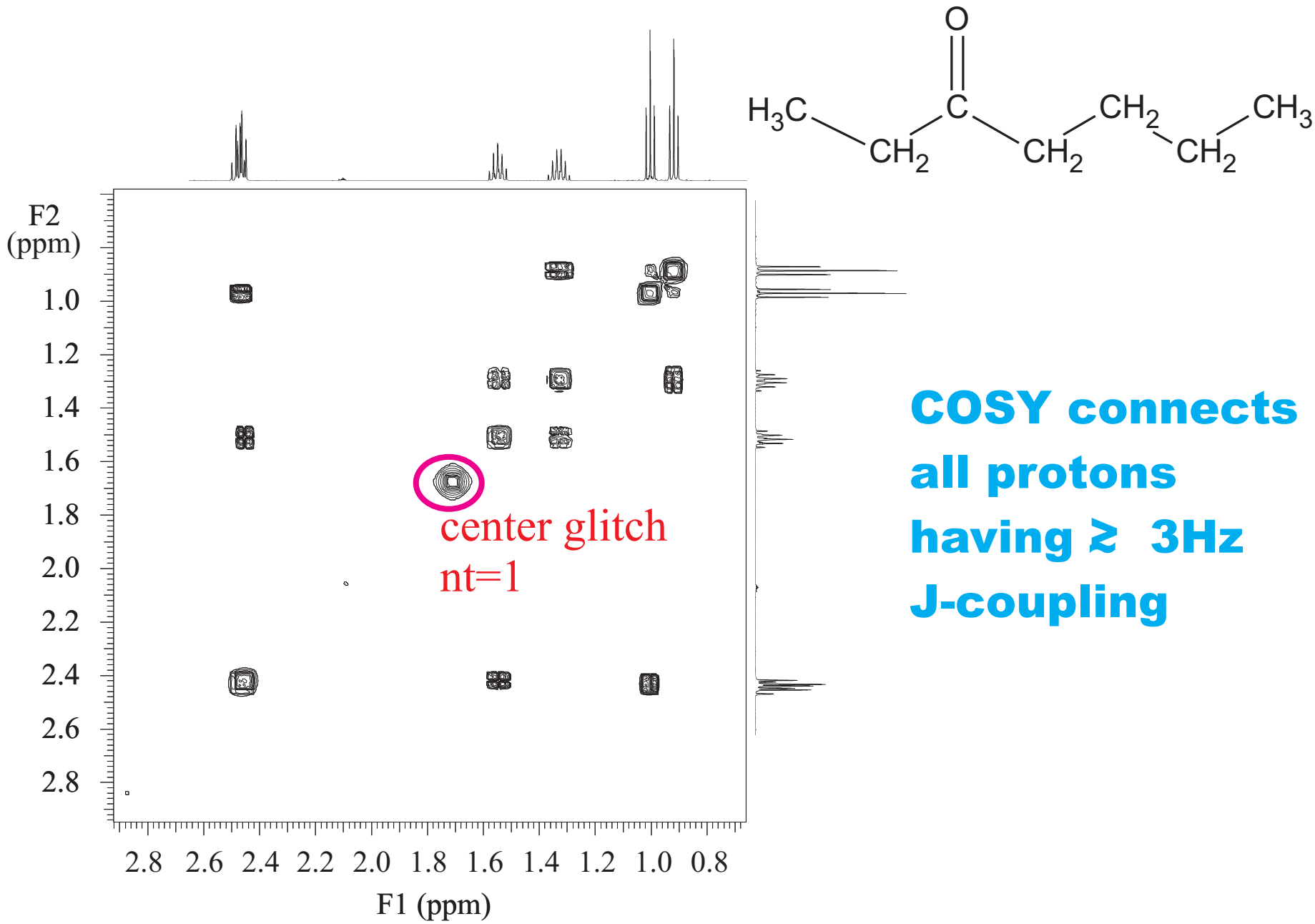


COSY connects all protons having ≥ 3Hz J-coupling

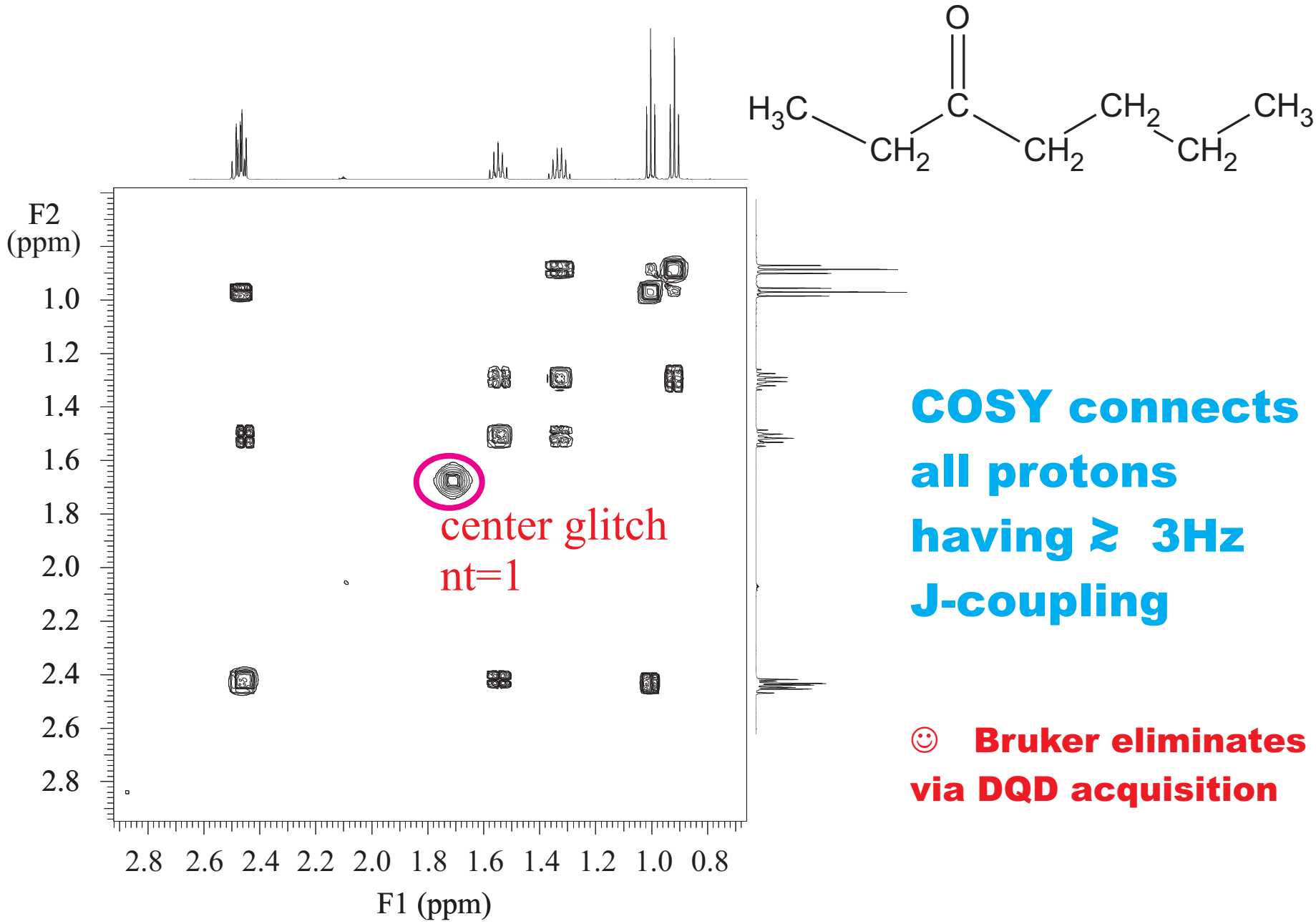
expt time: 2.3 min



COSY connects all protons having ≥ 3Hz J-coupling

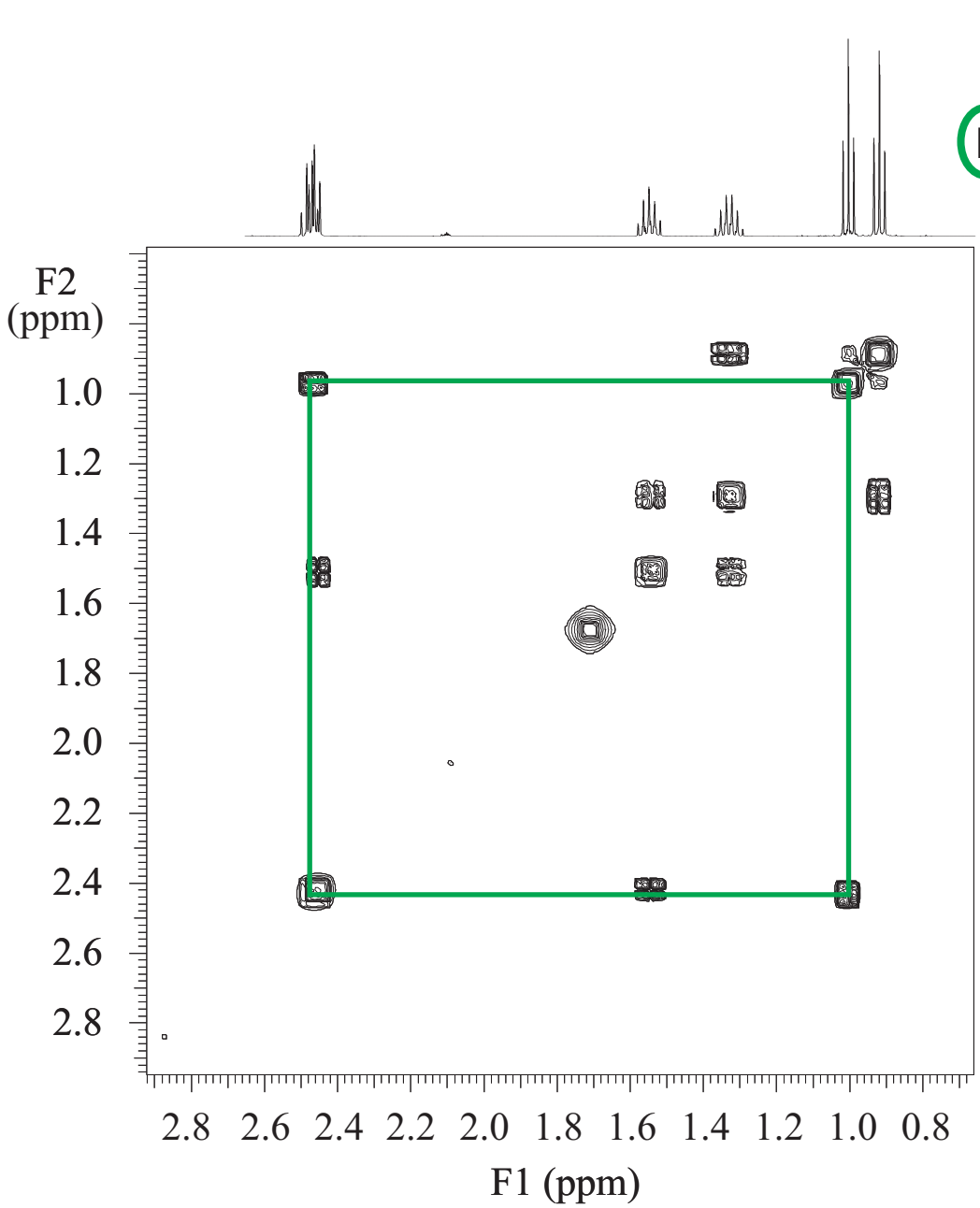


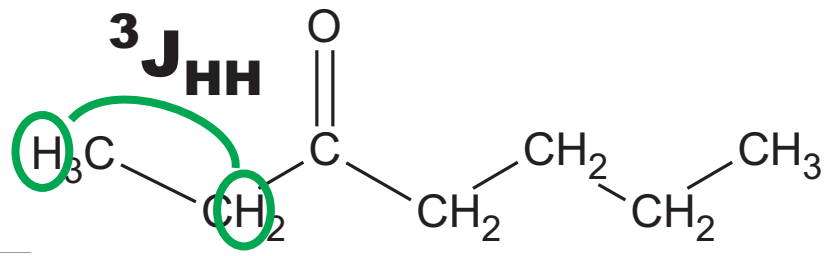
COSY connects all protons having ≥ 3Hz J-coupling



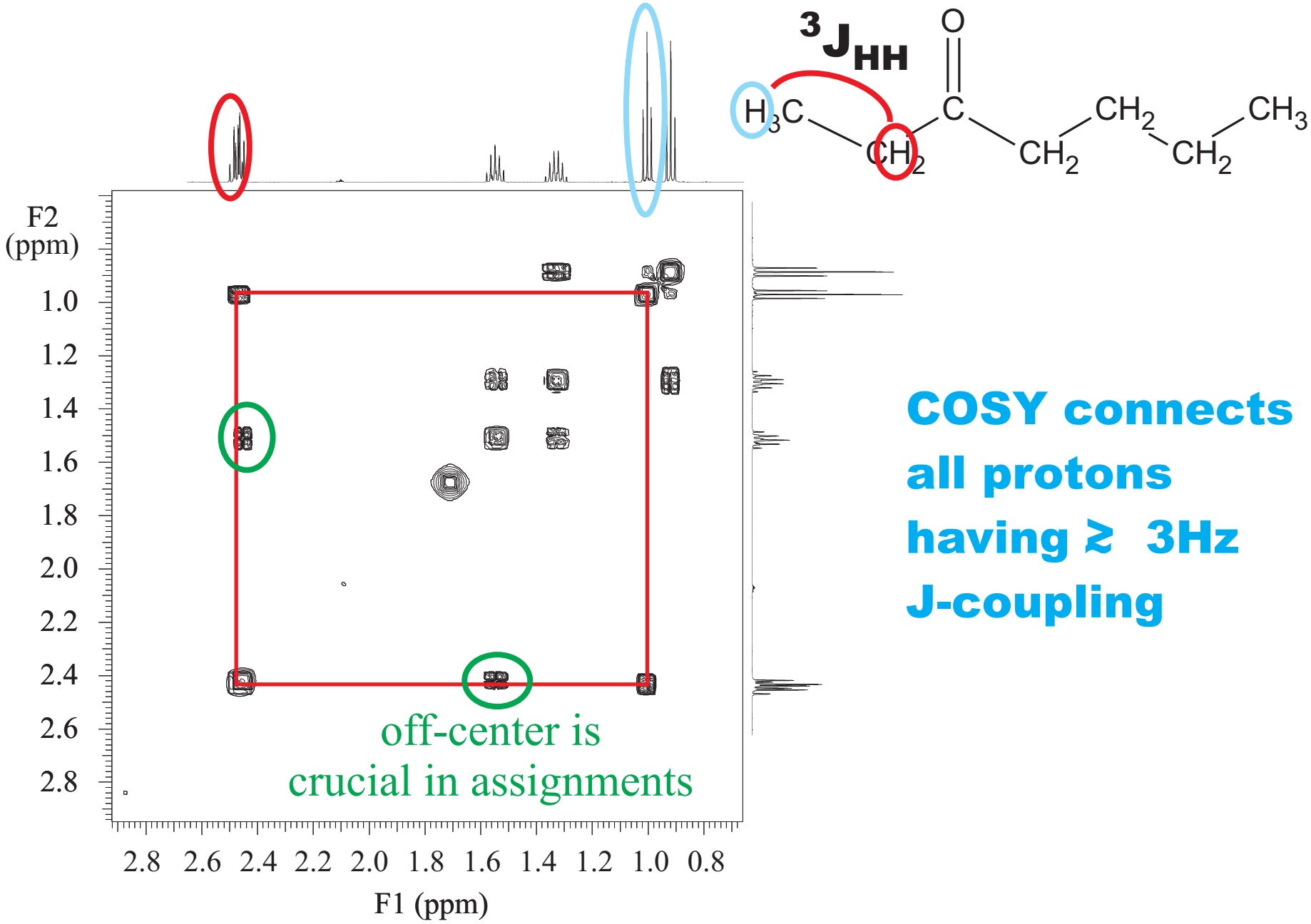
COSY connects all protons having ≥ 3Hz J-coupling

☺ **Bruker eliminates via DQD acquisition**





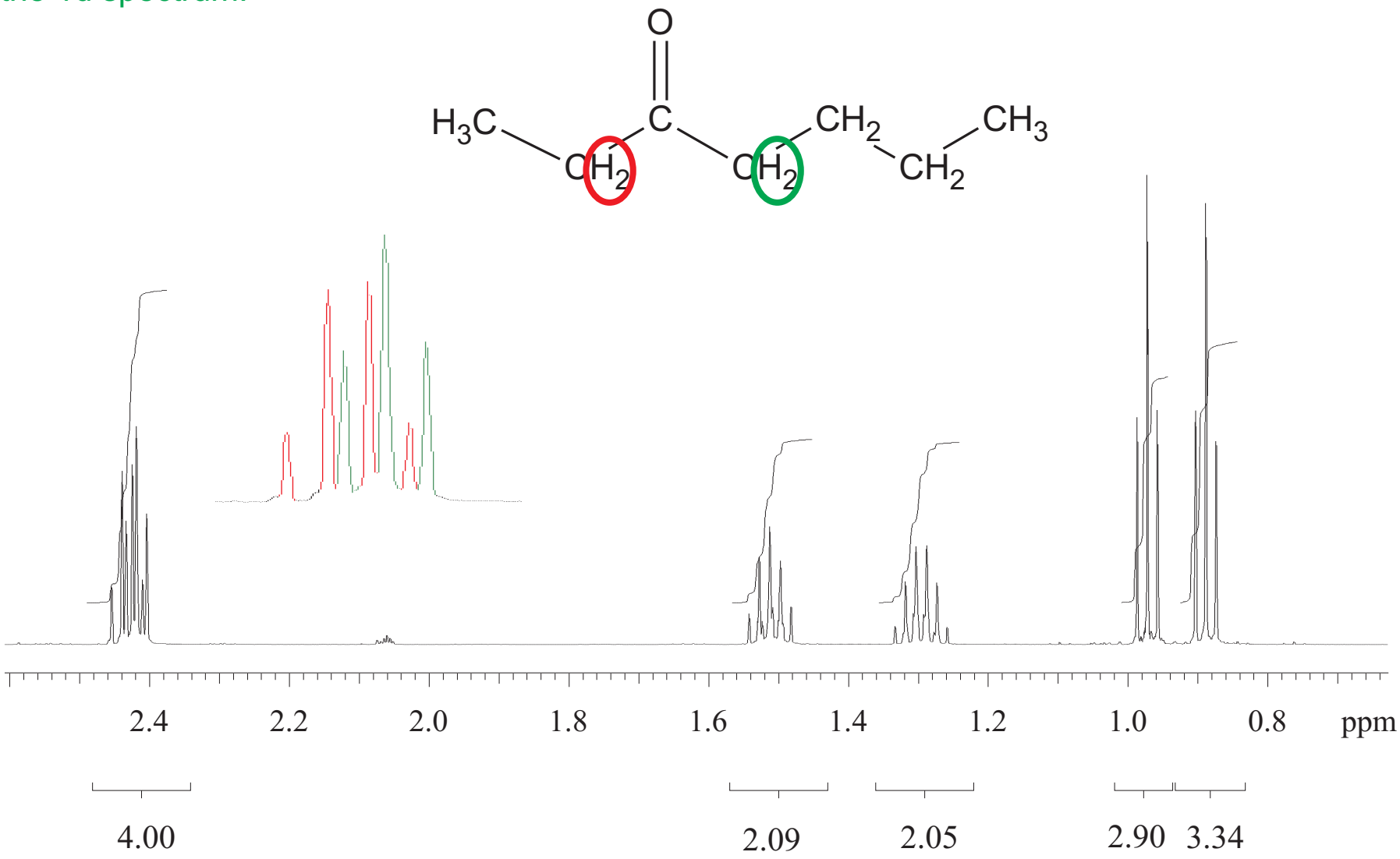
COSY connects all protons having ≥ 3Hz J-coupling

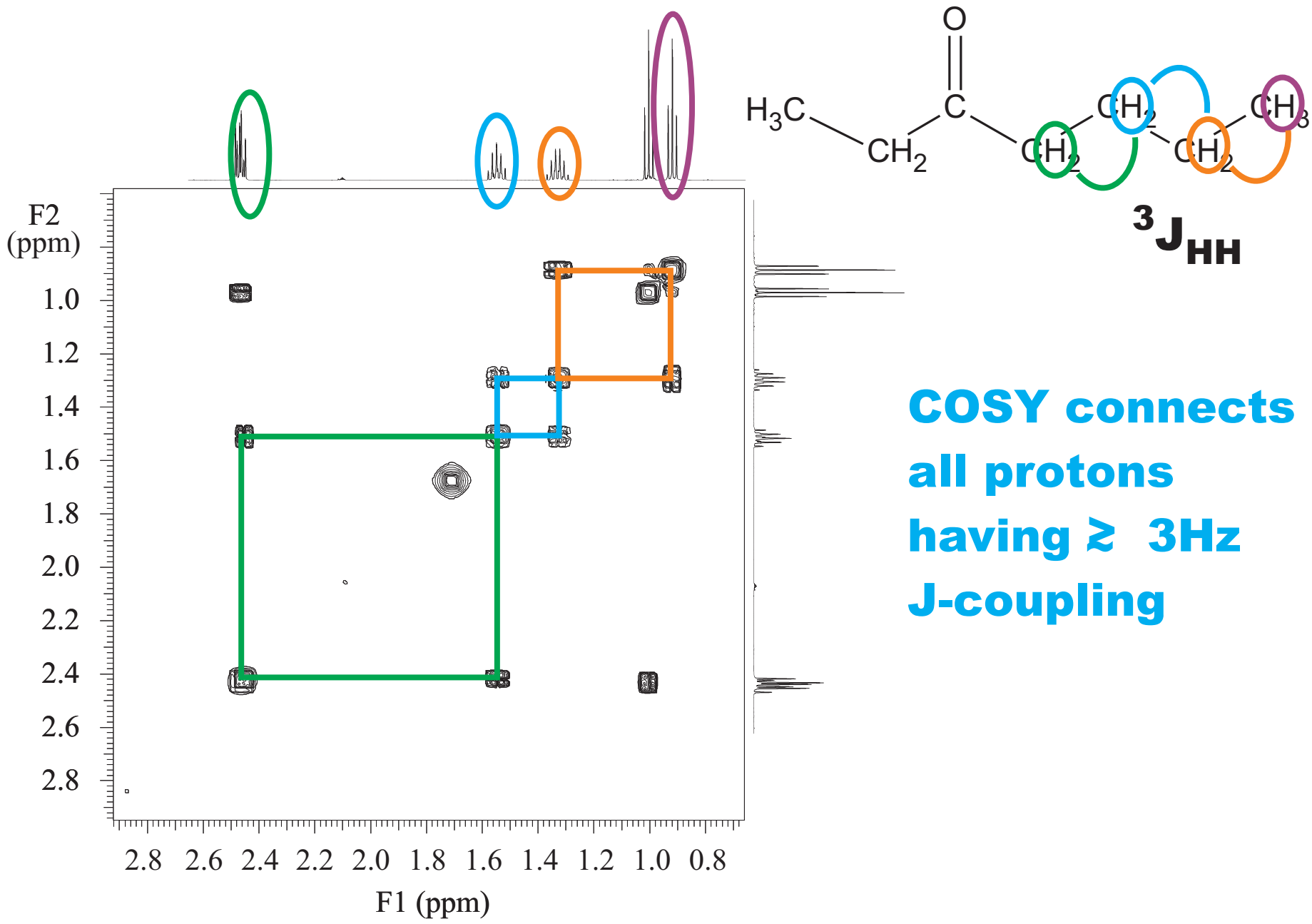


COSY connects all protons having ≥ 3Hz J-coupling

3-heptanone 1H 1d Spectra: 500MHz

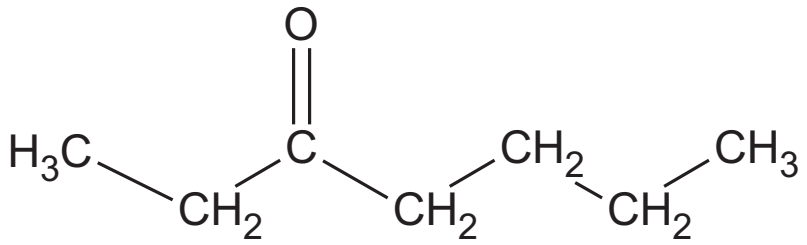
Here's sufficient detail such that a complete assignment can be made based off the 1d spectrum.





COSY connects all protons having ≥ 3Hz J-coupling

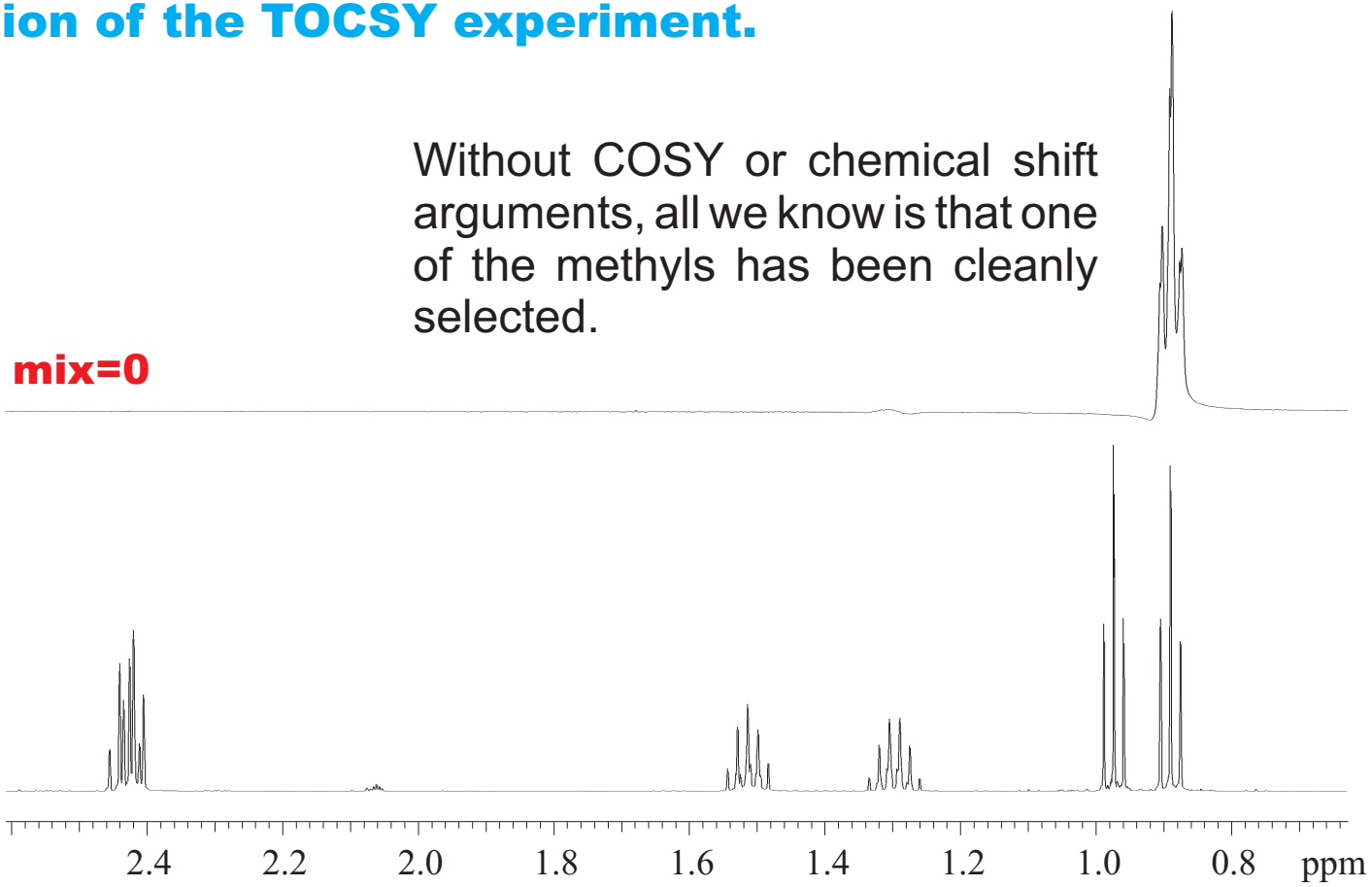
TOCSY-1D is similar to COSY: J-coupling larger than ~3 Hz "mix" coupled protons. [Note: COSY can observe smaller J; TOCSY cannot.]



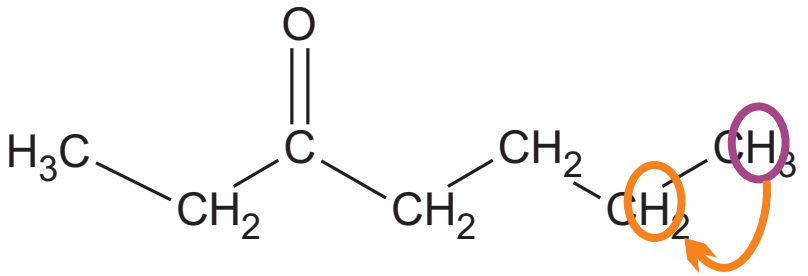
One multiplet is selected in the 1d vesion of the TOCSY experiment.

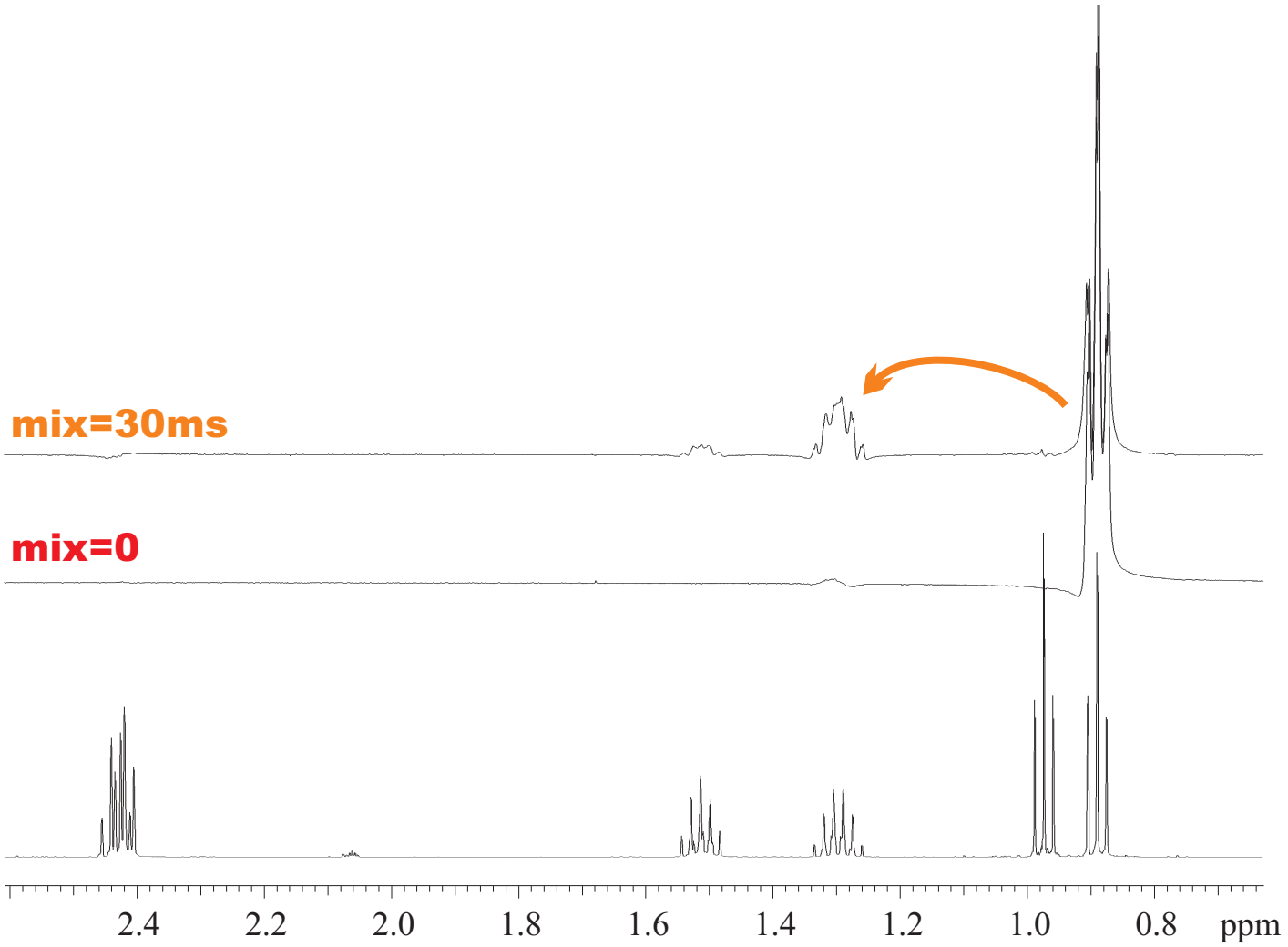
Without COSY or chemical shift arguments, all we know is that one of the methyls has been cleanly selected.

mix=0

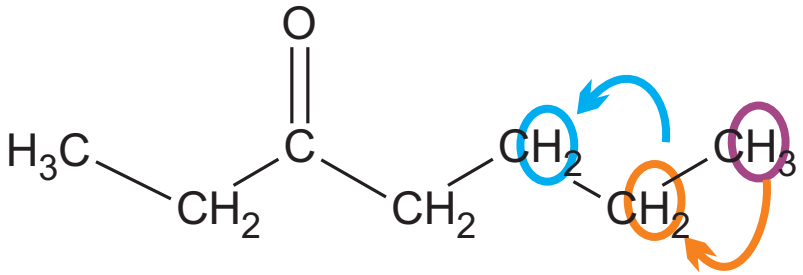


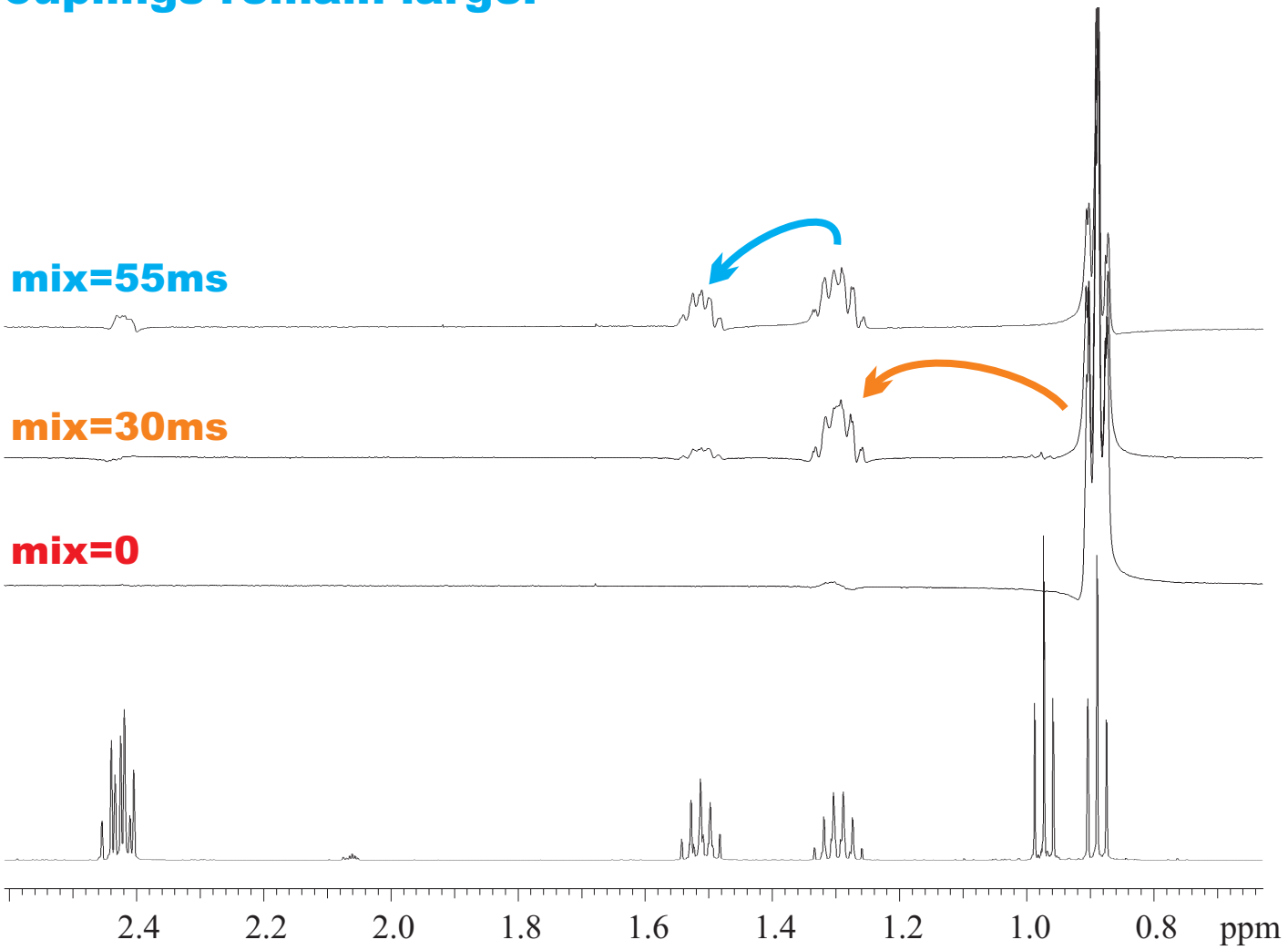
TOCSY-1D: short mix times show primarily 2- and 3-bond coupling, similar to COSY spectra.





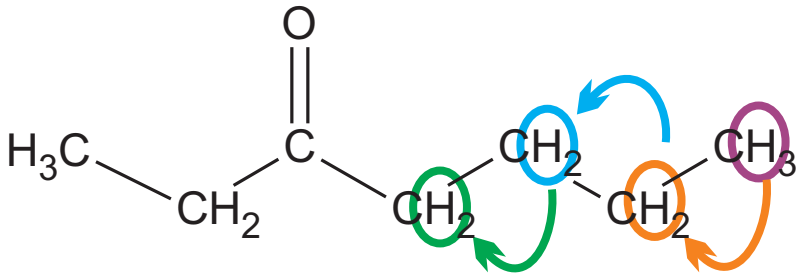
TOCSY-1D: with longer mix times, the coupling transfers magnetization to more distant protons, as long as J-couplings remain large.

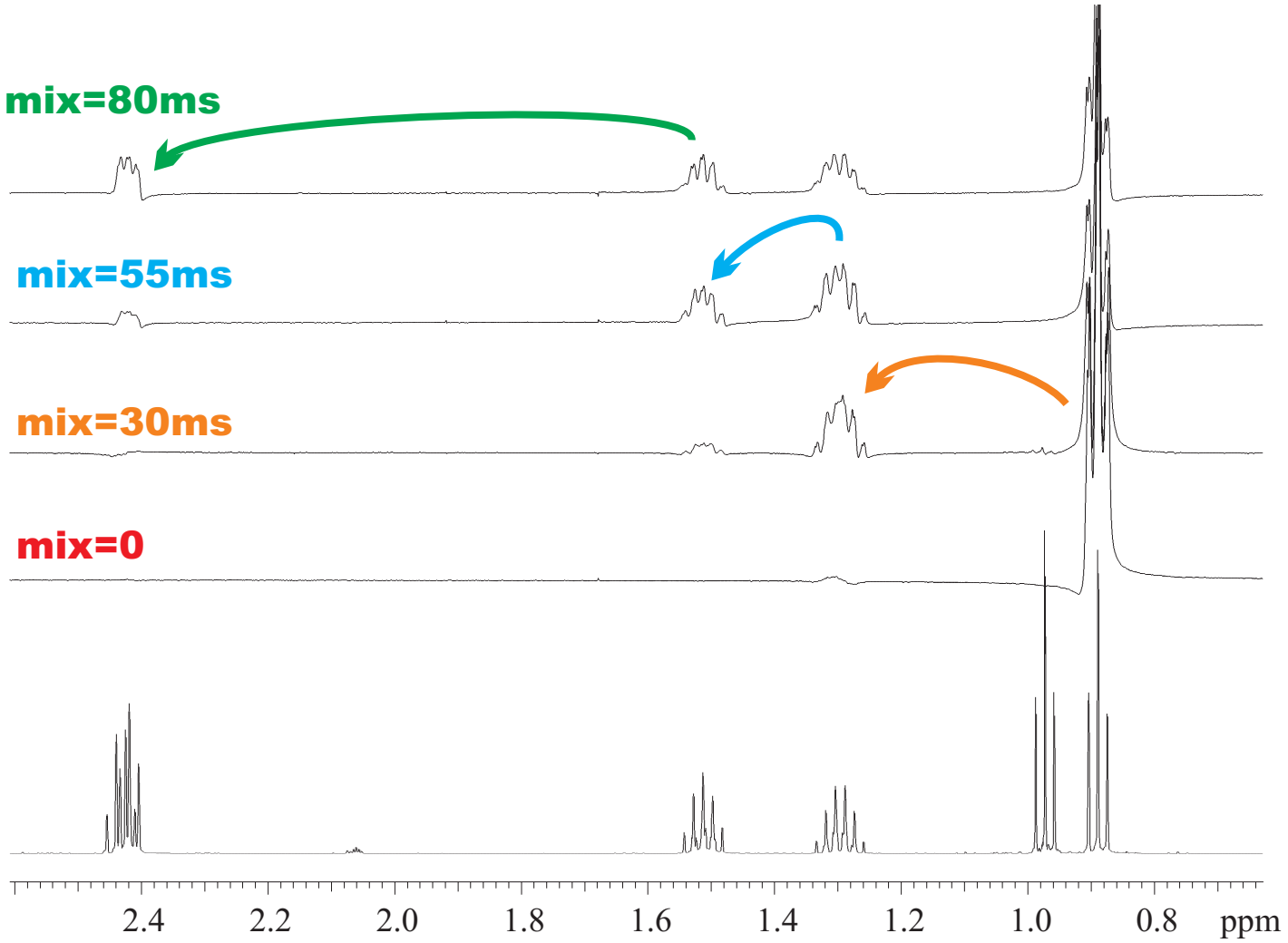




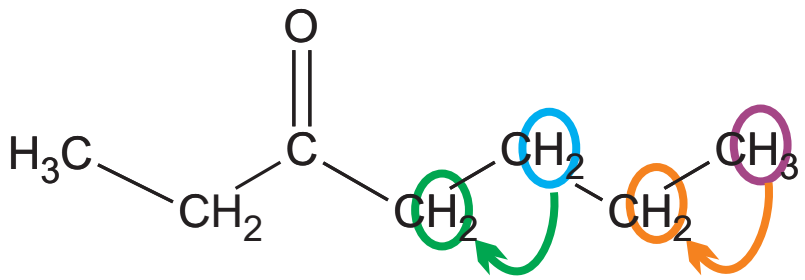
TOCSY-1D: with longer mix, the coupling transfers magnetization through the proton spin network, as long as J-couplings remain large.

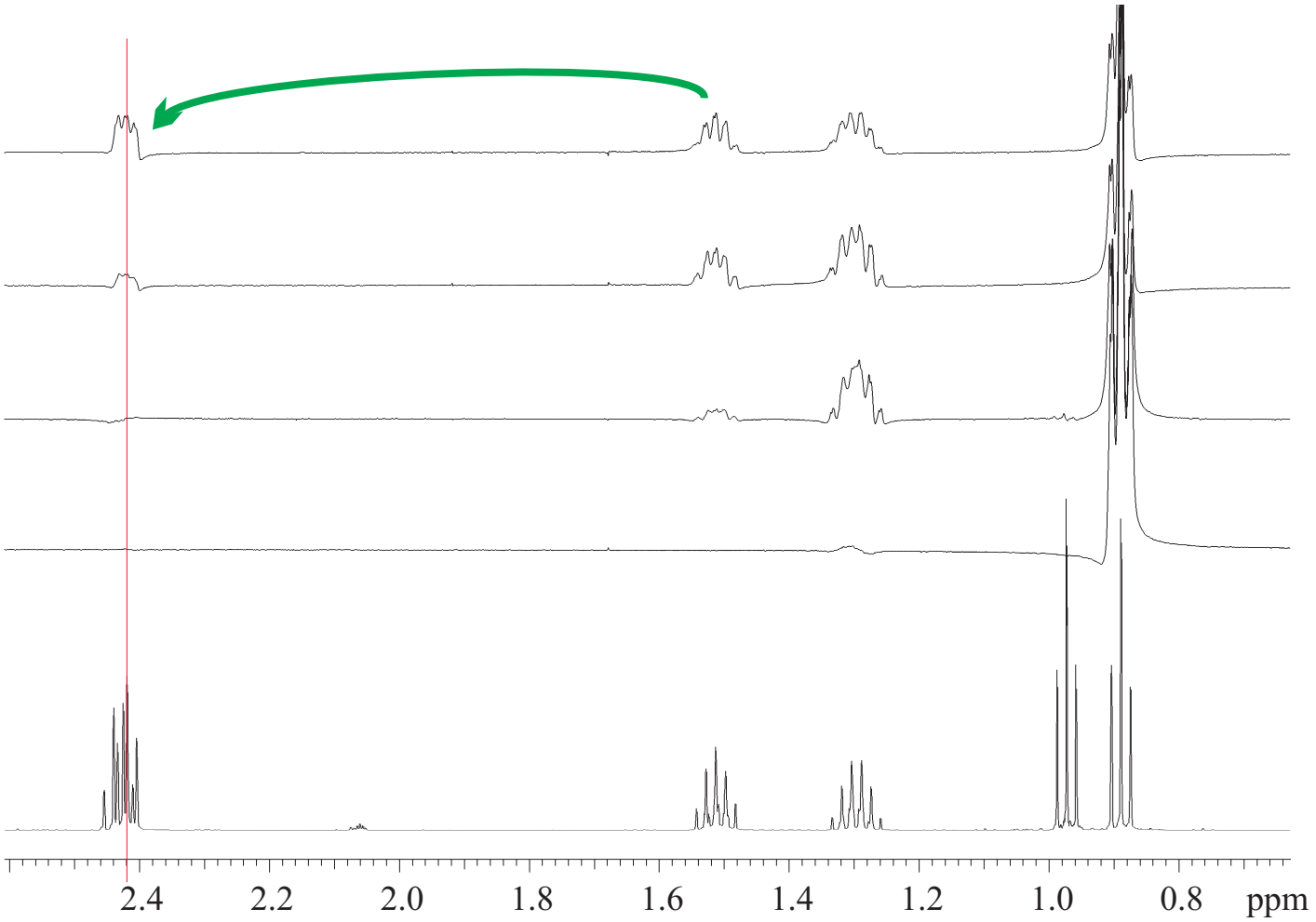
1D provides high-resolution.



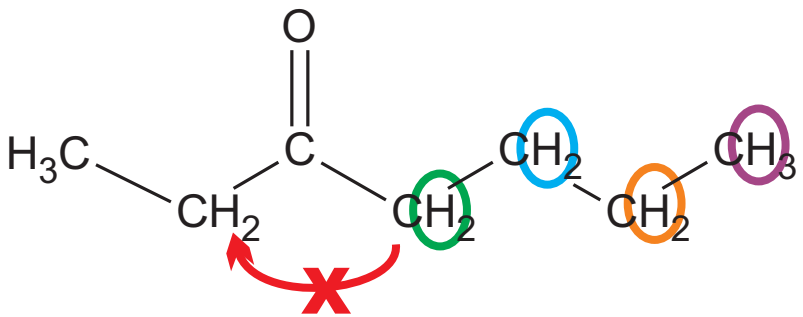


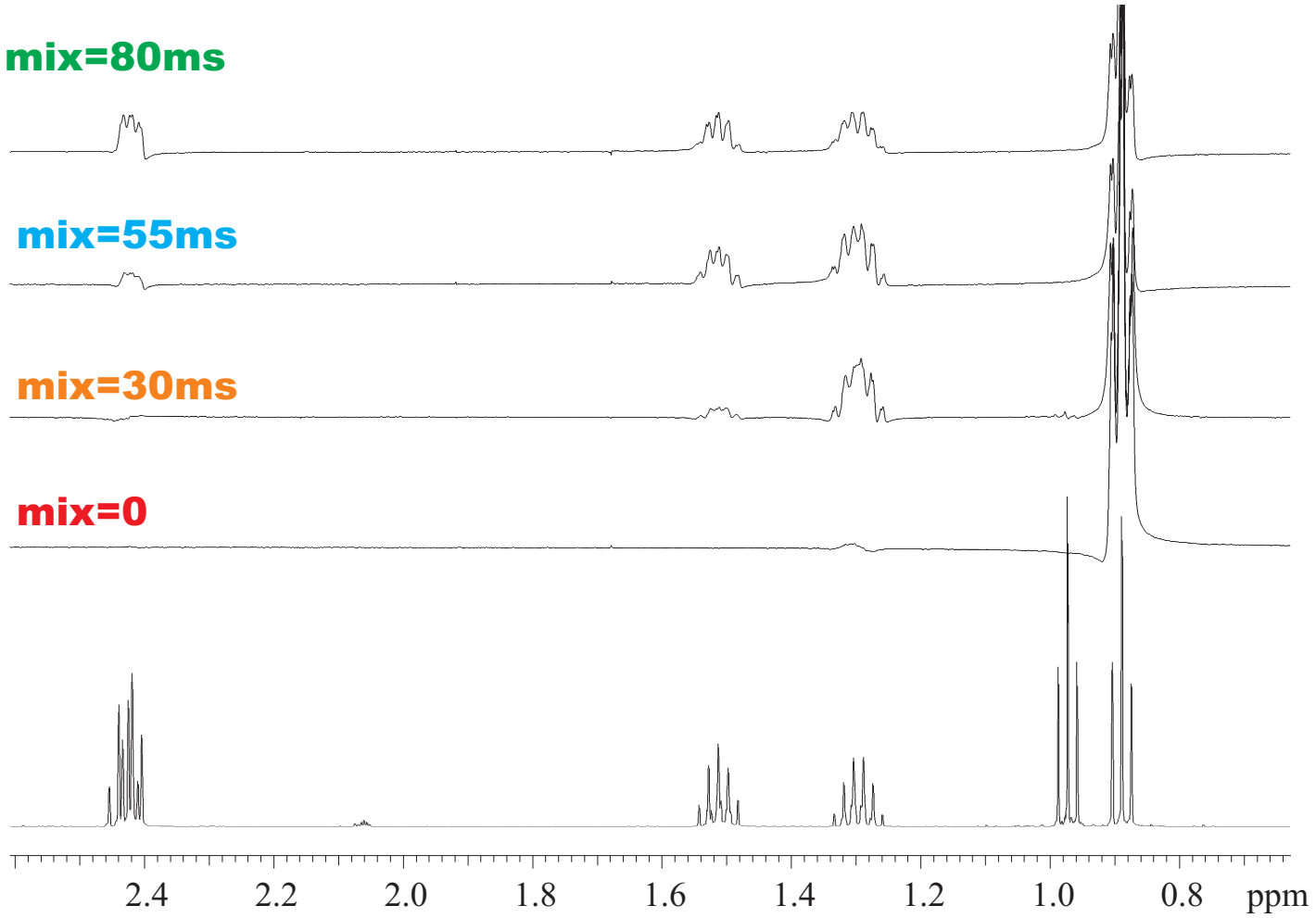
TOCSY-1D: we will see better examples later in the course, but note that the multiplet structure can be discerned, and compared properly to the 1d spectrum.





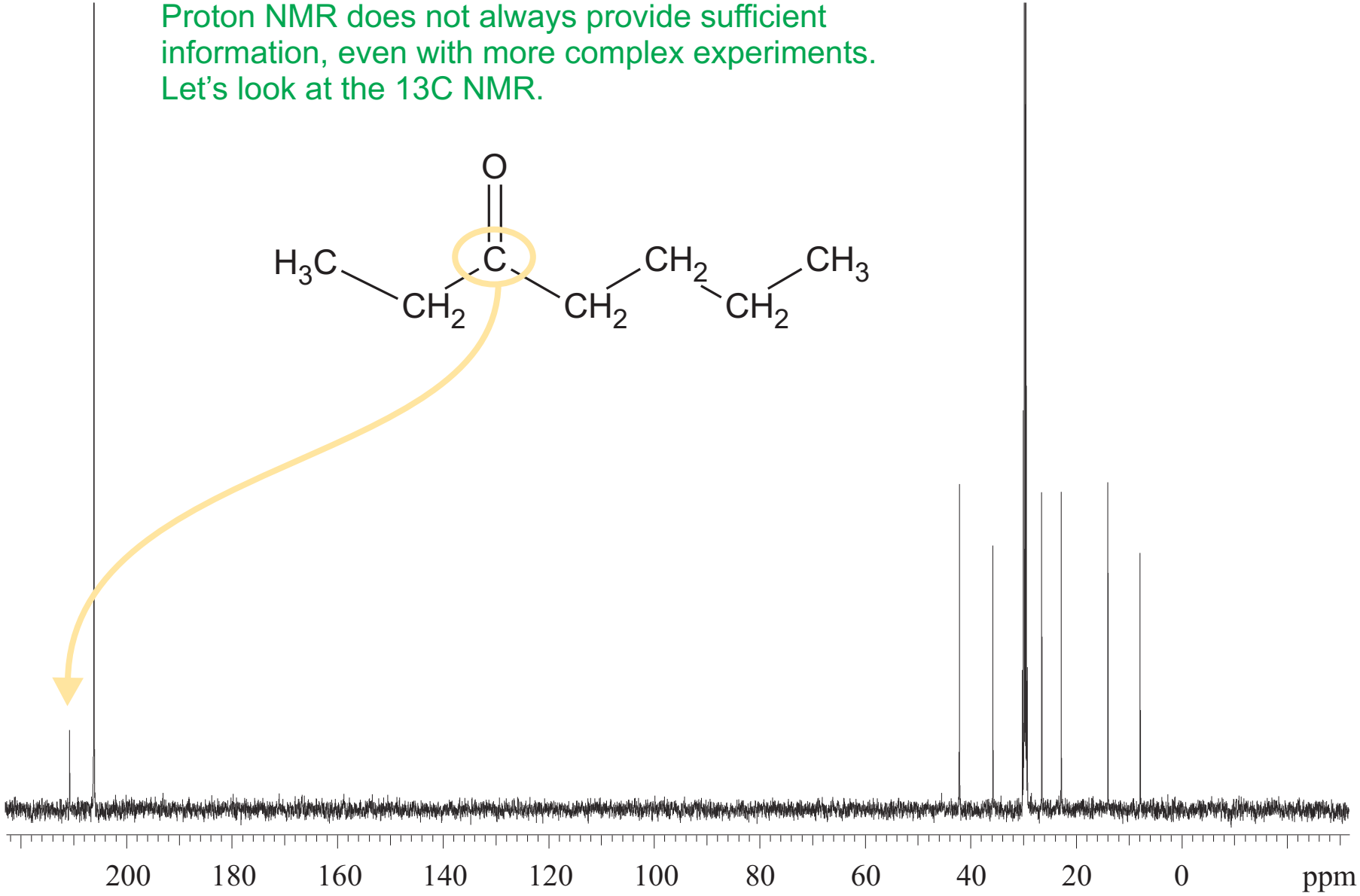
TOCSY-1D: this experiment separates protons into spin-coupling networks, very useful for mixture analysis and spin subsystems (e.g., peptides/proteins/oligosaccharides).





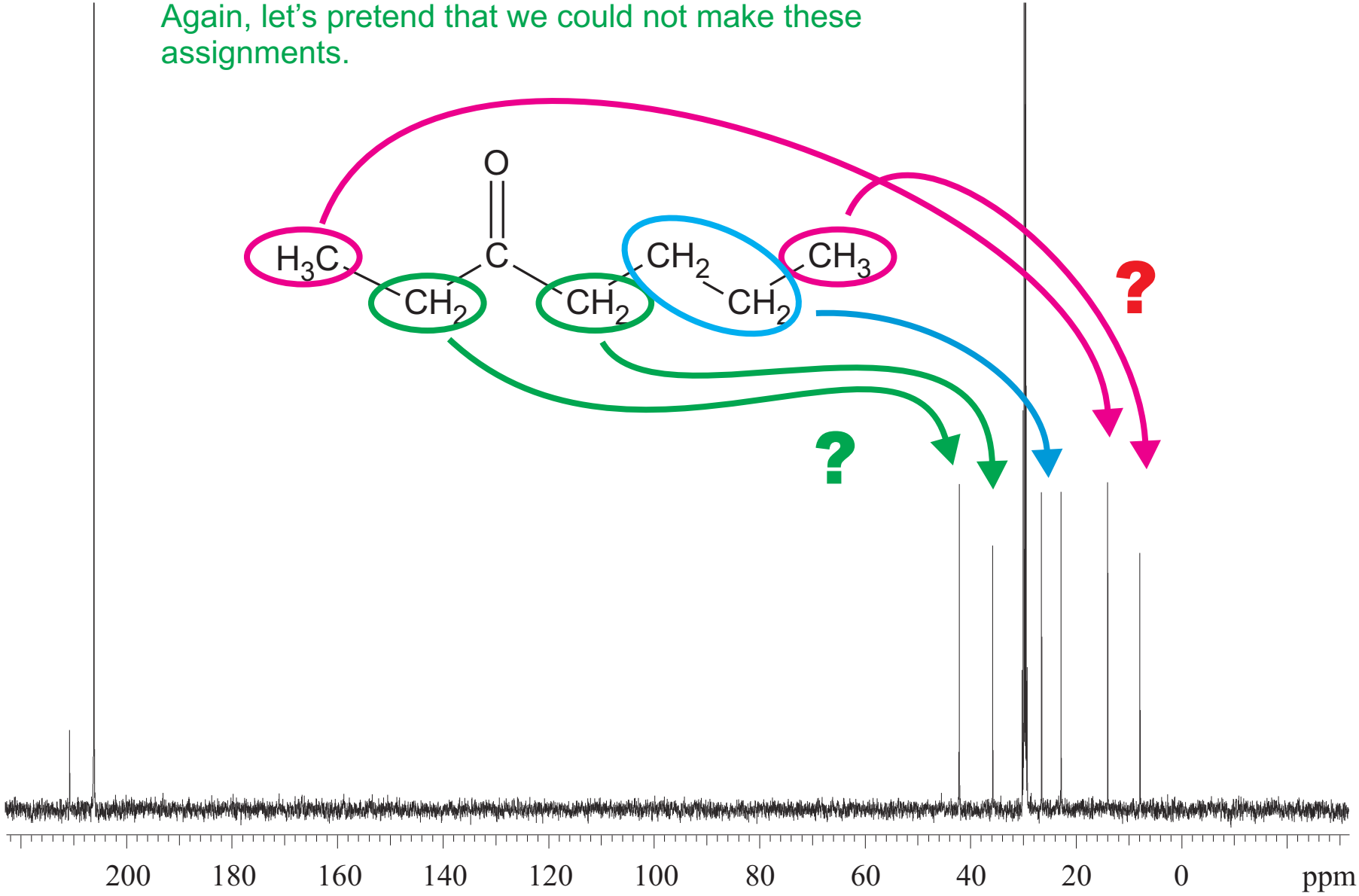
3-heptanone 13C 1d Spectra: 500MHz

Proton NMR does not always provide sufficient information, even with more complex experiments. Let's look at the 13C NMR.

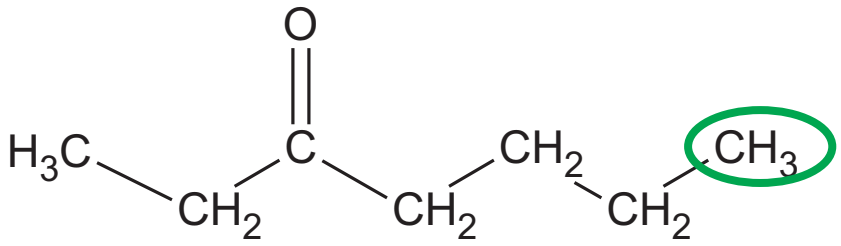


3-heptanone 13C 1d Spectra: 500MHz

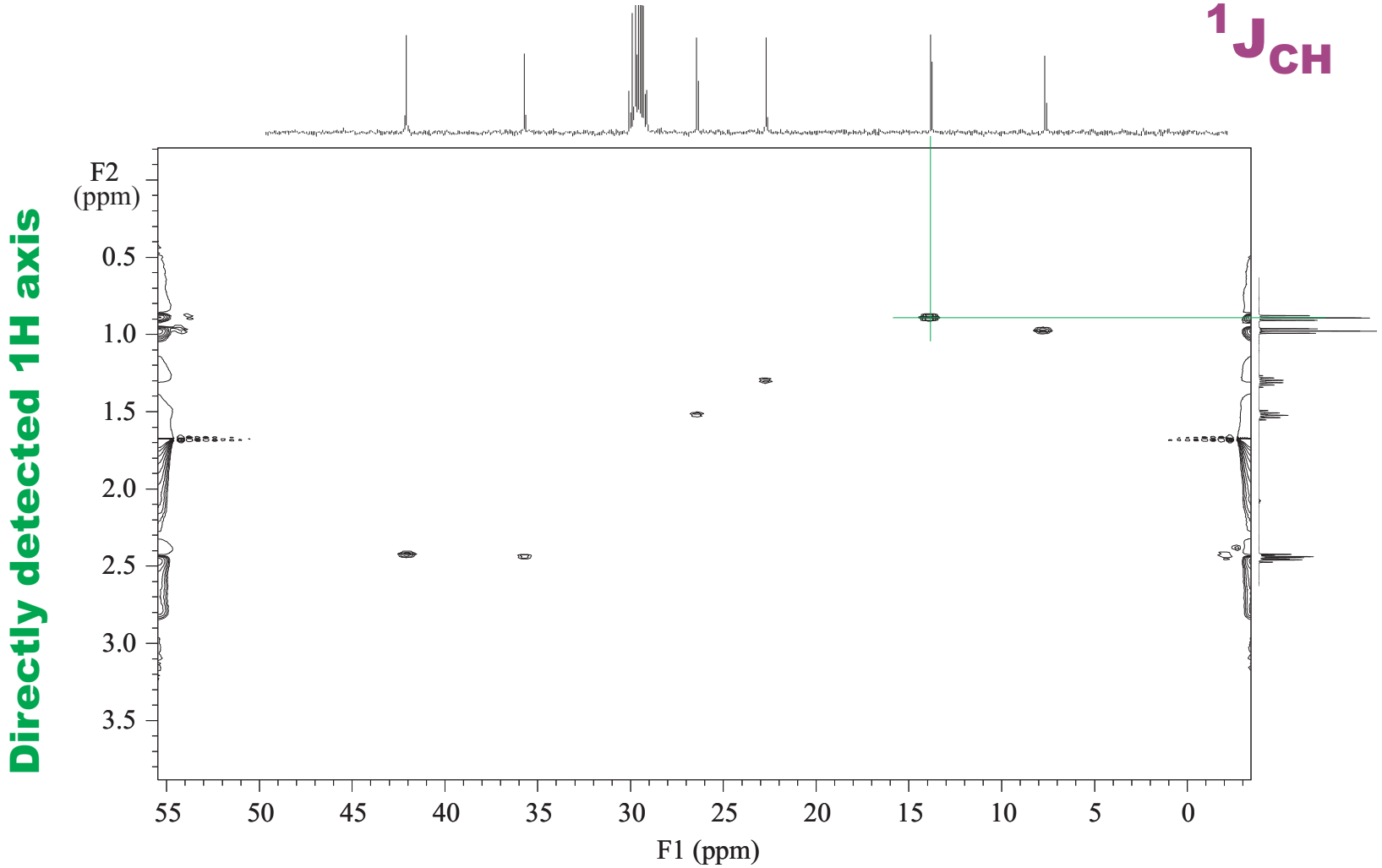
Again, let's pretend that we could not make these assignments.



HSQC: this experiment can provide 13C chemical shifts > 100× faster than normal 13C 1d.



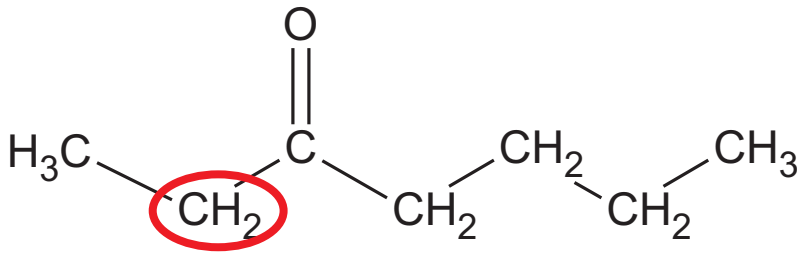
$^{1}J_{CH}$



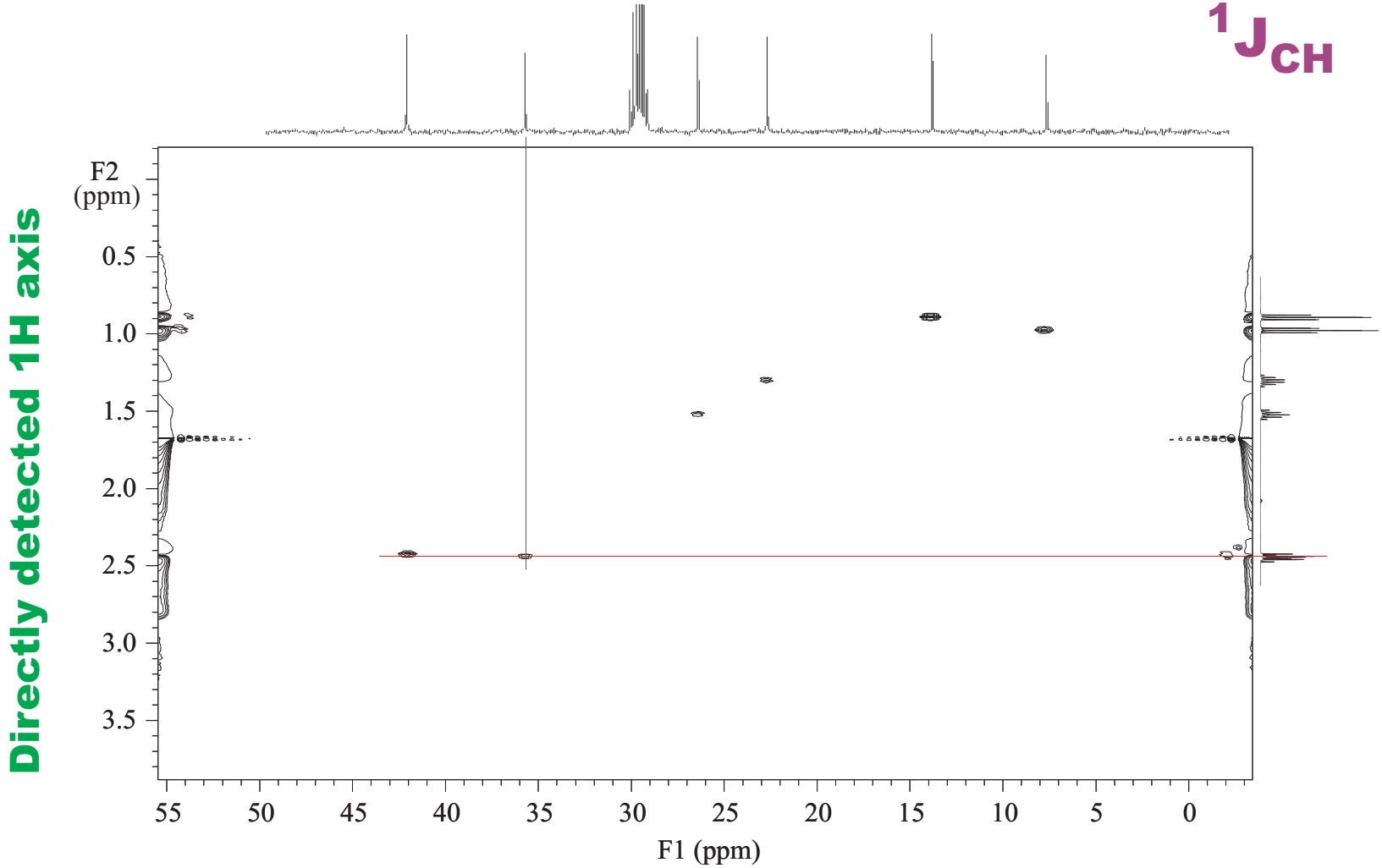
Directly detected 1H axis

Indirectly detected 13C axis

HSQC: a major utility of hetero-correlation is the dispersion provided by the X nucleus



$^{1}J_{CH}$



Directly detected 1H axis

Indirectly detected 13C axis