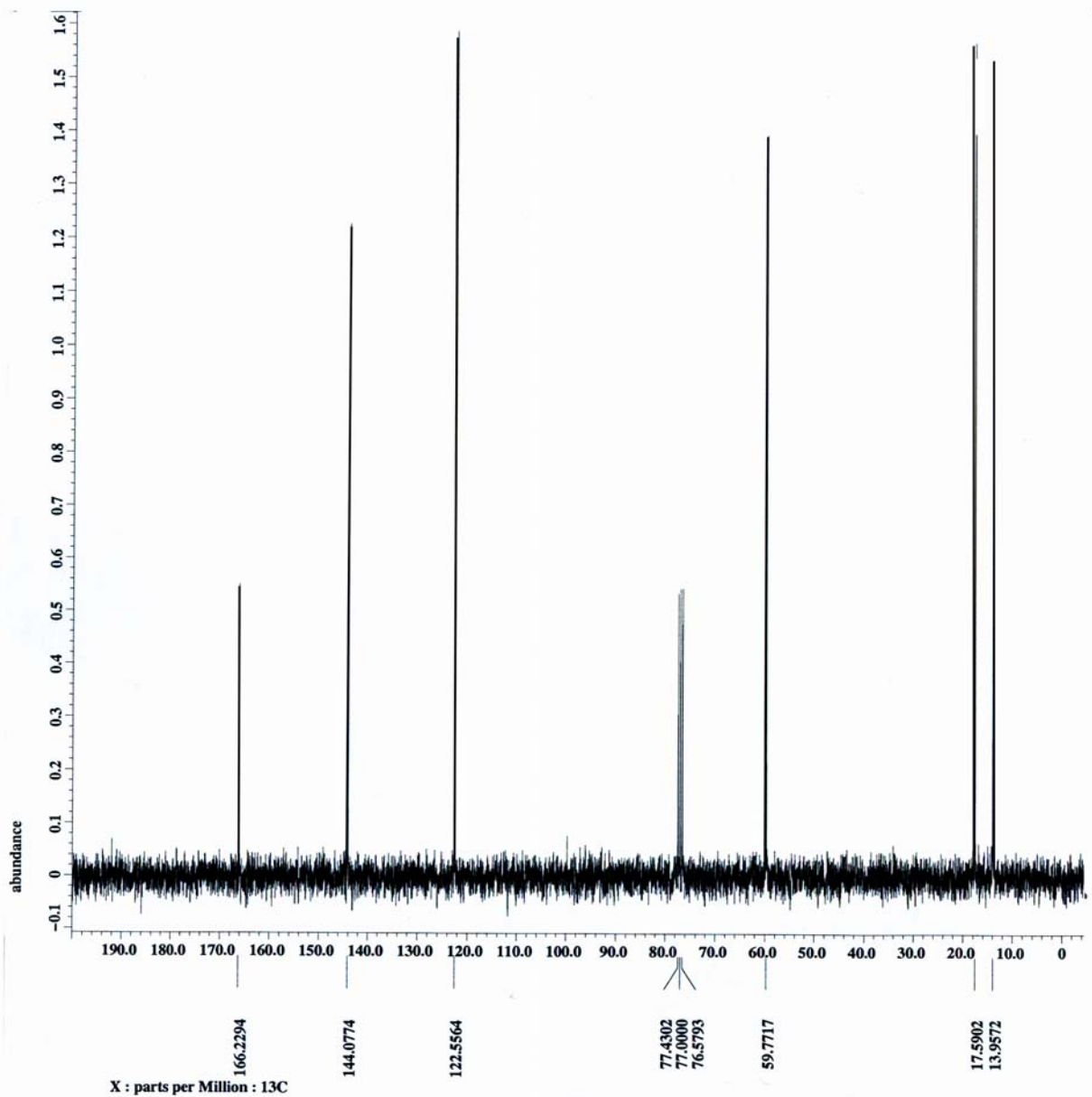


Analysis of NMR Spectra of a Compound: C-13, DEPT, Proton, COSY, and HETCOR

C-13 - Figure 1



The three signals centered at 77 ppm come from the solvent, CDCl_3 . The unknown compound gives rise to six signals: 14, 18, 60, 123, 144, and 166. This suggests that there are 6 different “kinds” of carbon in the compound. Each signal represents a set of one carbon atom or two or more equivalent carbon atoms. (In a C-13 spectrum it is unlikely that two non-equivalent carbon signals will fortuitously overlap, owing to the broad width of the spectrum.) We can get some idea of the nature of the carbons from the following table –

Typical C-13 Chemical Shifts, δ from TMS

“Type” of Carbon	Chemical Shift
$-\text{CH}_3$ (methyl)	10-40
$-\text{CH}_2-$ (methylene)	20-65
$\equiv\text{C}$	70-90
$=\text{C}$	100-150
aromatic	120-170
$\text{C}=\text{O}$, aldehydes/ketones	190-210
$\text{C}=\text{O}$, carboxylic acids, esters and amides	150-185

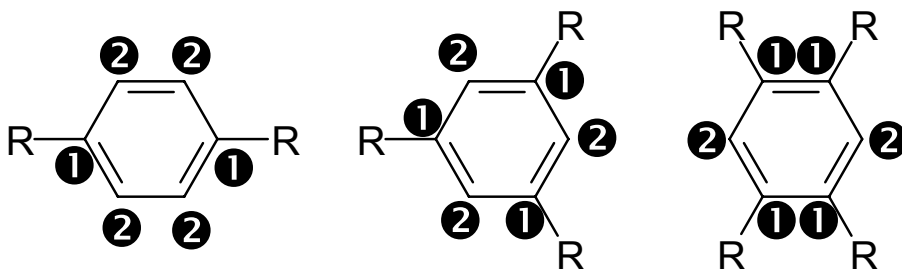
[To avoid somewhat tortured English, I'll refer to atoms in the singular, but remember that one signal may arise from more than one carbon, if they are equivalent.]

Our first guess, then, is that there are two methyl carbons (14, 18), one methylene carbon (60), one carbonyl carbon that is part of a carboxylic acid or related compound (166), and two carbons that are sp^2 hybridized (123, 144).

The sp^2 carbons could be vinylic or part of an aromatic ring:

(1) It is not reasonable that one of these signals comes from a vinylic carbon and the other from a benzene ring. This would require that all six carbons in the ring carry the very same substituent, making all of the carbons in the ring equivalent.

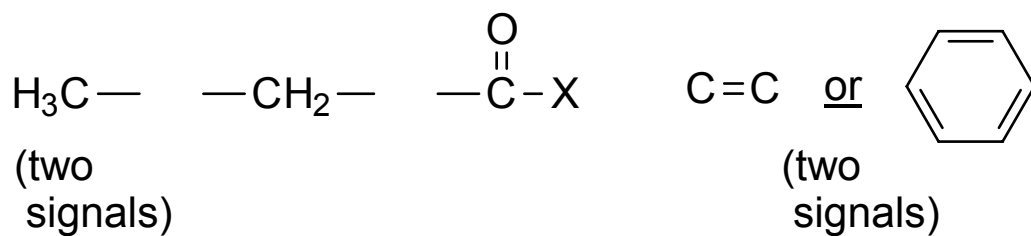
(2) If both of these signals come from an aromatic ring, the substitution pattern on the ring would have to be consistent with two signals. The possibilities follow –



The R groups must be identical.

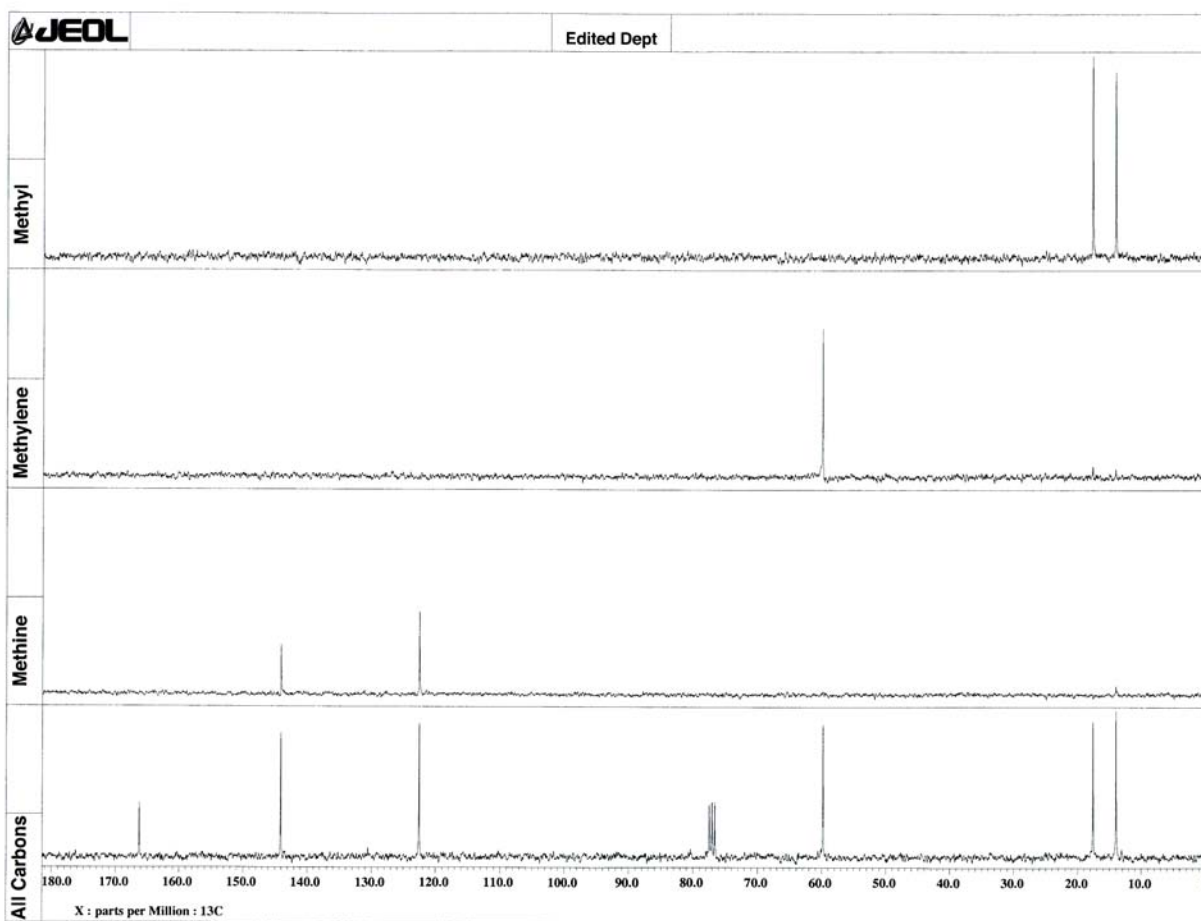
(3) Both of these signals may come from vinylic carbons. If the carbons joined by the double bond have different groups attached that would lead to two different signals; if not, there would have to be more than one double bond.

So, at this point it looks like the following features are present in the molecule –



where X = O, N, Cl

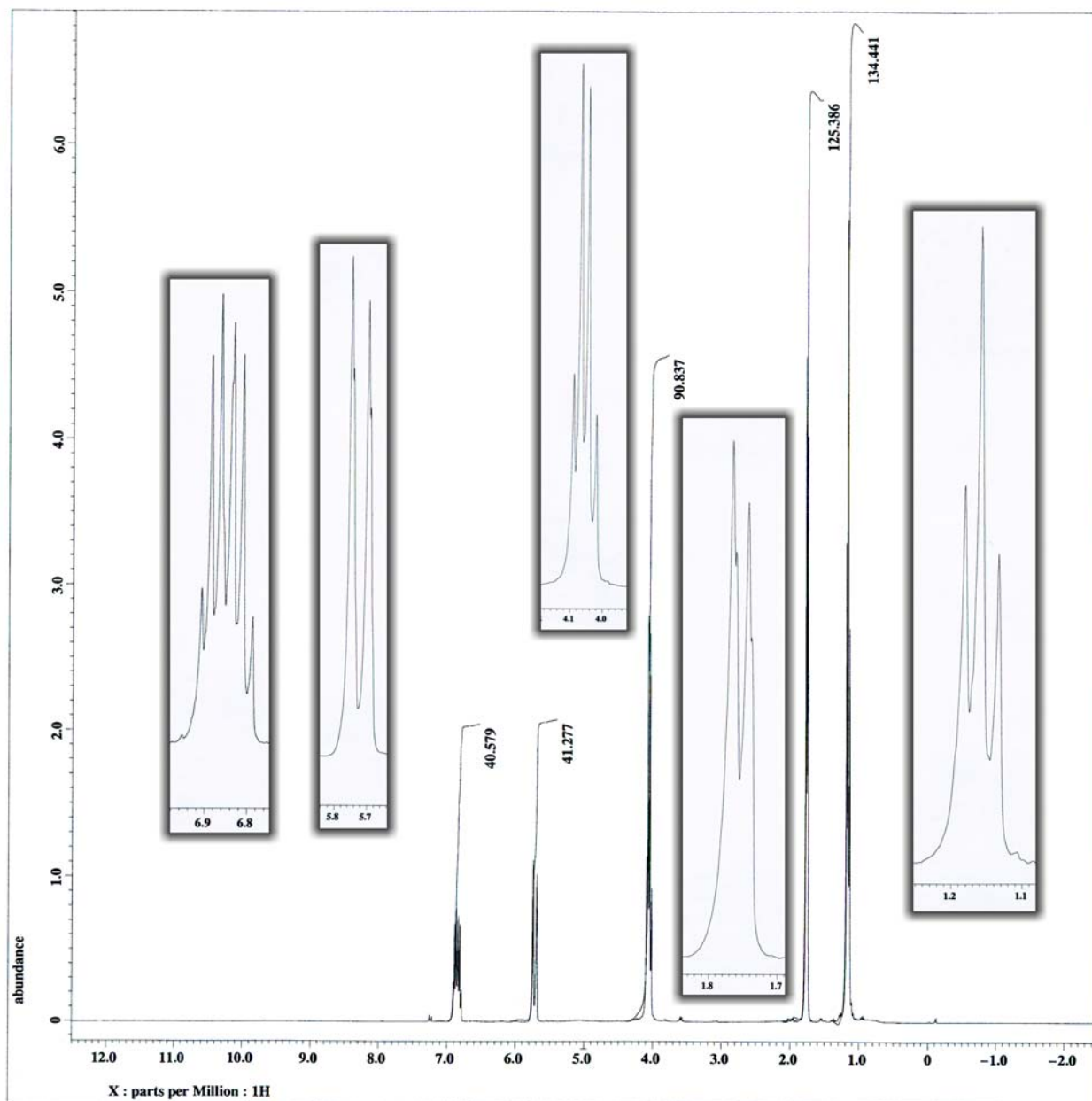
Edited DEPT Spectrum – Figure 2



This set of spectra confirms the assignments of the two methyl groups, the methylene group, and a carbon with no attached hydrogen (the carbonyl carbon).

In addition it tells us that the sp^2 carbons each hold one hydrogen. This rules out an aromatic ring because the only reasonable structures (*vide supra*) have one hydrogen on one of the sp^2 carbons and *no hydrogens* on the other.

Proton NMR – Figure 3



There are 5 proton signals. There are 6 carbon signals. One of the carbons (the carbonyl carbon) does not have an attached hydrogen. So, the C-13, DEPT, and proton spectra are consistent.

The methyl triplet at 1.2ppm suggests that there are two protons on adjacent carbons. The methylene quartet at 5.7ppm suggests that there are three protons on adjacent carbons. These two signals may correspond to an ethyl group; this is consistent with the integral values of these two signals (3:2).

The methyl signal at 1.8ppm (Fig. 4) appears to be a doublet (or a doublet of doublets, resulting from one proton on an adjacent carbon [doublet with larger coupling constant] and one proton further removed [doublet with smaller coupling constant]). One might not wish to bet the farm on the remote doublet since the coupling constant, J , is so small and it could be an artifact.

The vinylic proton signal at 6.8ppm is split into a sextet indicating 5 adjacent hydrogens. The vinylic proton signal at 5.7ppm is a doublet with some further splitting indicating one neighboring proton with small coupling to more distant proton(s).

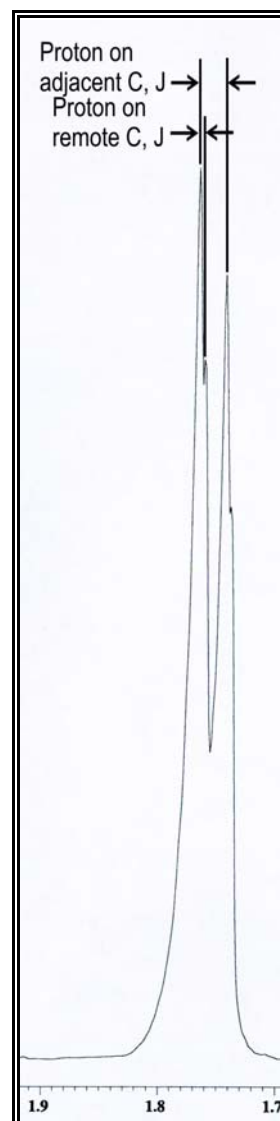
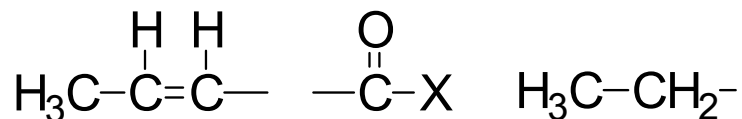


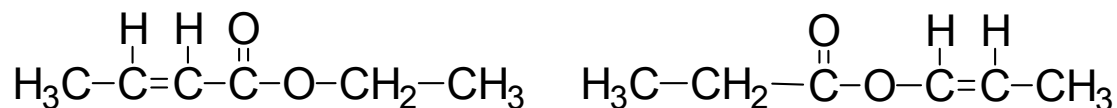
Figure 4

At this point it looks like we might have the following fragments –



X is unlikely to be the -NH- group of an amide; if it were we should see the NH hydrogen in the proton NMR. X cannot be a -Cl because Cl is univalent and it would not allow for the attachment *of both* of the other groups. This suggests that it is probably oxygen: we are dealing with an ester.

This ester could have either of the following structures –



– and the double bond could be *cis* or *trans*.

COSY and HETCOR 2-D Spectra

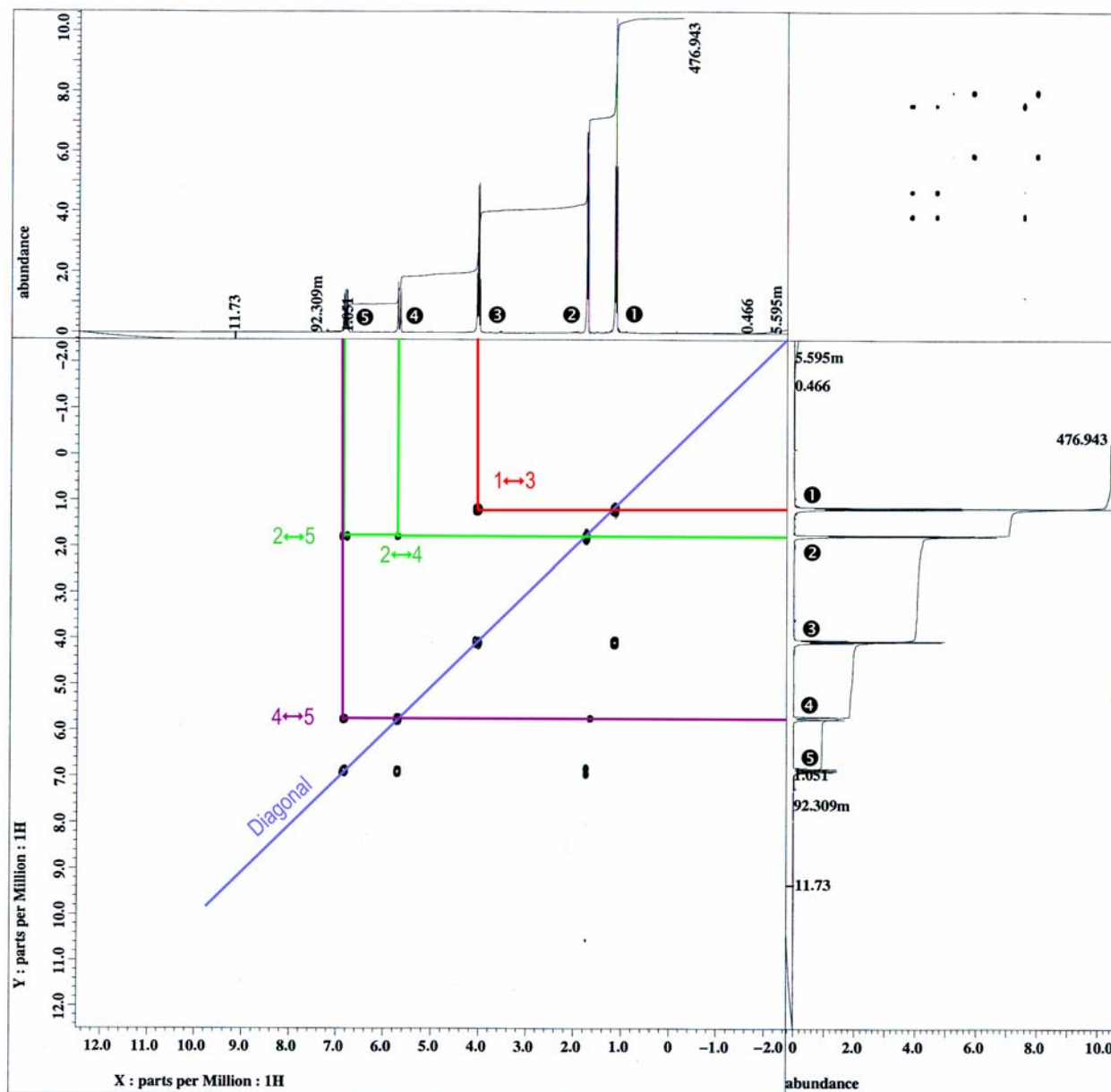
The spectra above are one-dimensional (1-D) in that the signals appear along the x-axis. The spectra we will consider now are two-dimensional (2-D); a 1-D spectrum appears along one axis (x-axis) and a second 1-D spectrum appears along the other axis (y-axis).

In COSY, the (1-D) proton spectrum is presented along both the x-axis and the y-axis. Signals in this case rise above the xy plane and are usually shown as a contour plot. Signals will appear where one set of protons couples with another set of protons. Thus, this type of spectrum indicates which protons are coupled in a molecule in a fairly unambiguous way.

HETCOR is similar to COSY, except that the x-axis is the C-13 spectrum and the y-axis is the proton spectrum. Signals result in the xy plane showing which protons are coupled (attached) to which carbon atoms.

COSY Spectrum – Figure 5

There are two common versions of the COSY spectrum: COSY and DQFCOSY, which is an improved version. We'll use the DQFCOSY.



The spectrum is mirror-imaged about the diagonal, so we can work on either side of the diagonal.

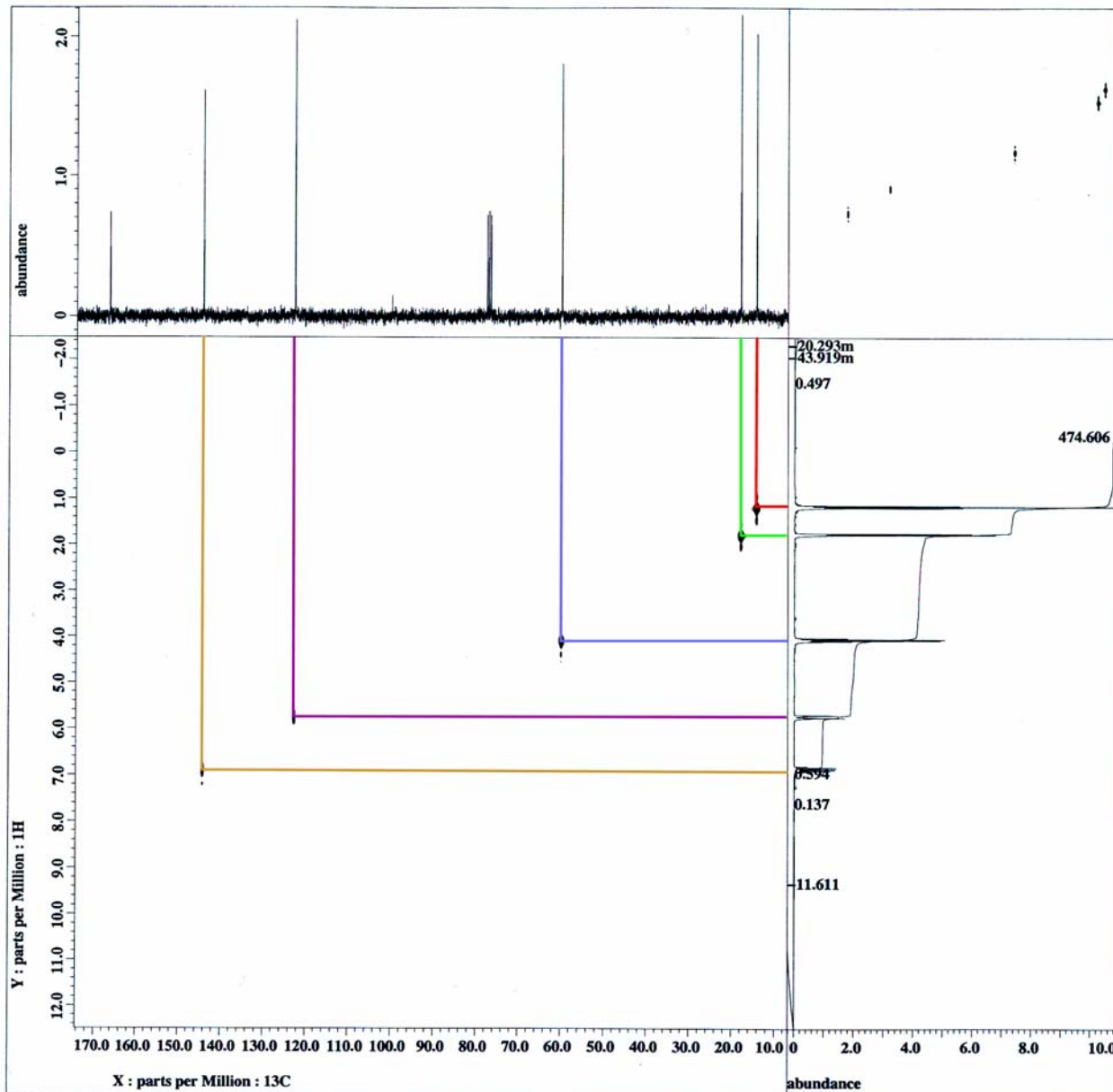
We can see that methyl protons 1 are coupled to methylene protons 3 (the ethyl group). Methyl protons 2 are coupled to vinyl protons 4 and 5. Vinylic proton 4 is coupled to vinylic proton 5.

In this case, we had more or less worked out the proton couplings from the 1-D proton spectrum. So, the information here serves as confirmation. In the case of a more complex spectrum it is likely that this spectrum would provide information we could not obtain from the 1-D proton spectrum.

HETCOR Spectrum – Figure 6

In this spectrum the x-axis is the C-13 spectrum and the y-axis is the proton spectrum. Signals appear in the spectrum that show which protons are attached to which carbons. Since there are 5 sets of protons, we will see 5 signals. There are 6 carbon signals, but one of the carbons does not hold a proton. Analysis is quite simple. If there is a “spot” where a horizontal line from a proton signal intersects a vertical line from a C-13 signal, those protons are attached to that carbon.

It should be noted that in this particular case C-13 signal 1 correlates with proton signal 1, C-13 signal 2 correlates with proton signal 2, etc. This is just fortuitous; in general we will not see this behavior.



At this point we still have 4 possible candidates. You may regard this as an abysmal failure or stunning success depending on whether you are inclined to view the glass as half empty or half full. Or maybe not. I'm a half empty kind of guy, and I think it is a stunning success that this one technique, NMR spectroscopy, has reduced our unknown from being one out of approximately 20 million known compounds to being one out of four possibilities. Moreover, careful analysis of chemical shifts and coupling constants, using the extensive tables that are available, might enable us to ascertain that the compound is ethyl crotonate:

