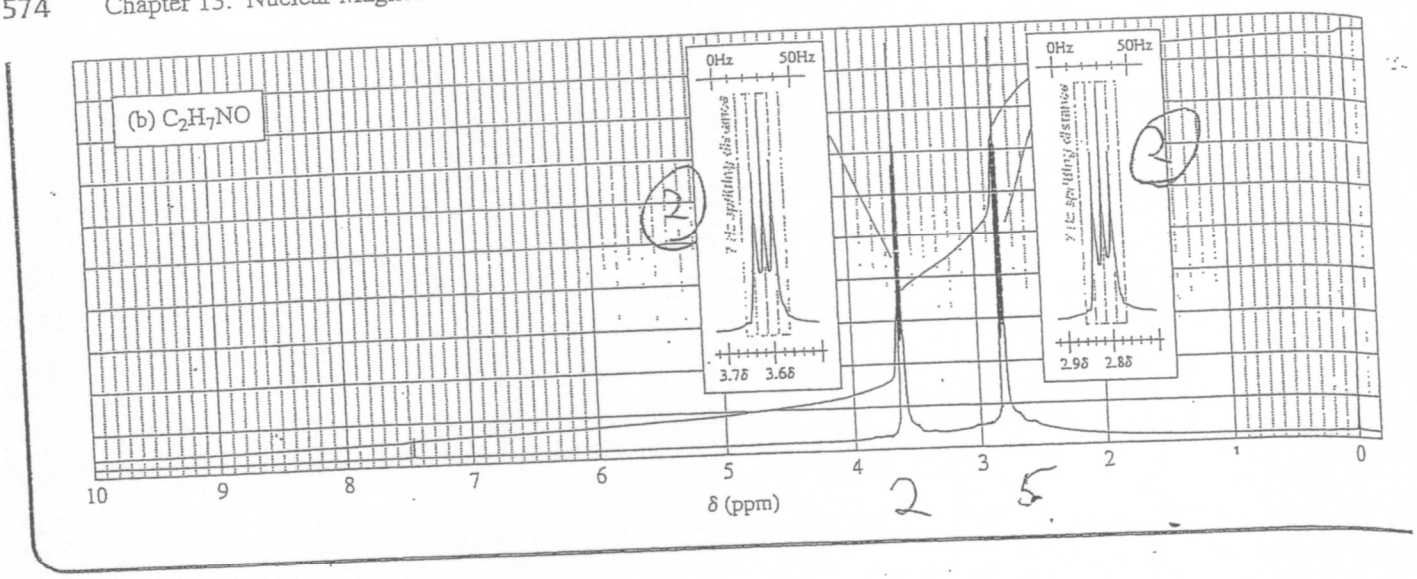
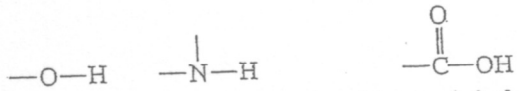


PROBLEM-SOLVING STRATEGY
Interpreting Proton NMR Spectra

Learning to interpret NMR spectra requires practice with a large number of examples and problems. The problems at the end of this chapter should help you gain confidence in your ability to assemble a structure from the NMR spectrum combined with other information. This section provides some hints that can help make spectral analysis a little easier.

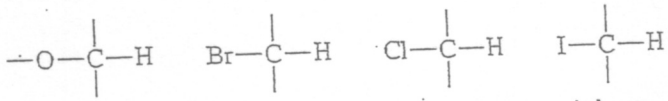
When you first look at a spectrum, consider the major features before getting bogged down in the minor details. Here are a few major characteristics you might watch for:

1. If the molecular formula is known, use it to determine the number of elements of unsaturation (see Section 7-3). The elements of unsaturation suggest rings, double bonds, or triple bonds. Matching the integrated peak areas with the number of protons in the formula gives the numbers of protons represented by the individual peaks.
2. Any broadened singlets in the spectrum might be due to —OH or —NH protons. If the broad singlet is deshielded past 10 ppm, an acid —OH group is likely.



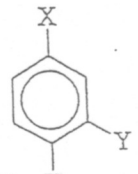
frequently broad singlets — broad (or sharp) singlet, $\delta > 10$

3. A signal around δ3 to δ4 suggests protons on a carbon bearing an electronegative element such as oxygen or a halogen. Protons that are more distant from the electronegative atom will be less strongly deshielded.



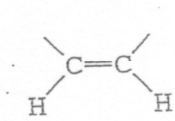
around δ3–δ4 for hydrogens on carbons bearing oxygen or halogen

4. Signals around δ7 to δ8 suggest the presence of an aromatic ring. If some of the aromatic absorptions are farther downfield than δ7.2, an electron-withdrawing substituent may be attached.

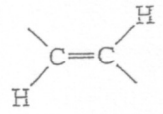


around δ7–δ8

gnals around δ5 to δ6 suggest vinyl protons. Splitting constants can differentiate cis and ans isomers.

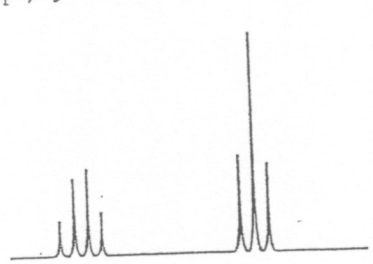


around δ5–δ6; J = 10 Hz



around δ5–δ6; J = 15 Hz

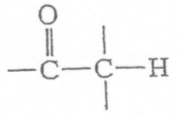
earn to recognize ethyl groups and isopropyl groups (and structures that resemble these groups) by their characteristic splitting patterns.



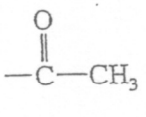
ethyl group

isopropyl group

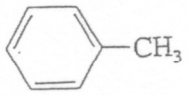
Signals around δ2.1 to δ2.5 may suggest protons adjacent to a carbonyl group or next to an aromatic ring. A singlet at δ2.1 often results from a methyl group bonded to a carbonyl group.



around δ2.1–δ2.5

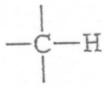


singlet, δ2.1



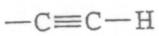
singlet, δ2.3

. Signals in the range δ9 to δ10 suggest an aldehyde.



aldehyde, δ9–δ10

9. A sharp singlet around δ2.5 suggests a terminal alkyne.



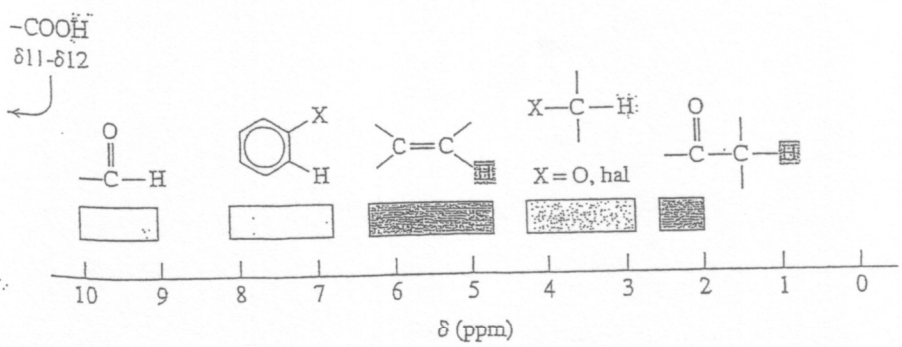
around δ2.5

These hints are neither exact nor complete. They are simple methods for making educated guesses about the major features of a compound from its NMR spectrum. The hints can be used to draw partial structures to examine all the possible ways they might be combined to give a molecule that corresponds with the spectrum. Figure 13-38 gives a graphic presentation of some of the most common chemical shifts. A more complete table of chemical shifts appears in Appendix 1.

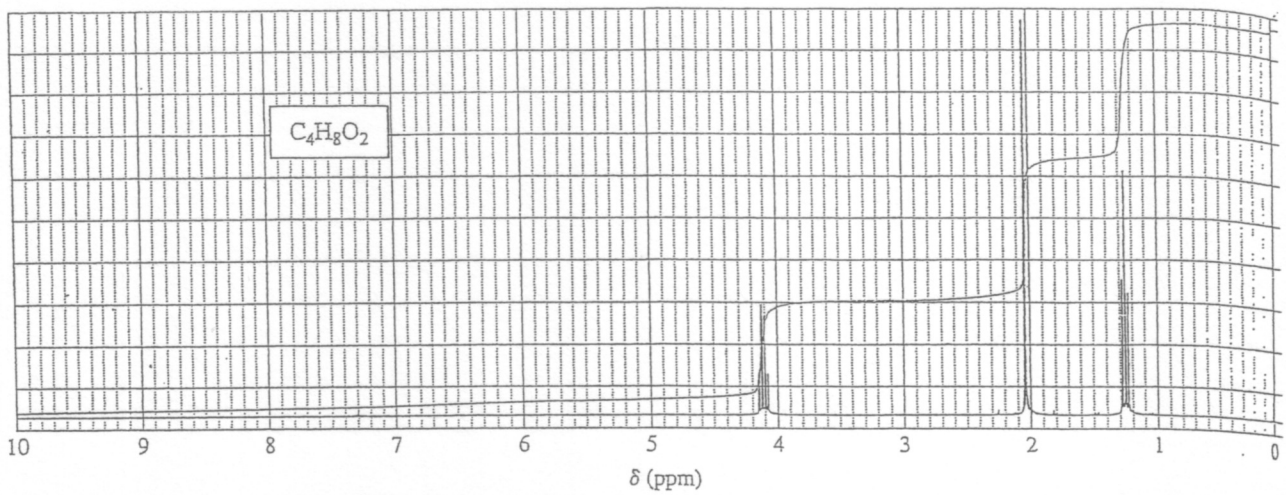
PROBLEM-SOLVING HINT

Remember to look for structural information based on

1. number of absorptions
2. chemical shifts
3. areas of peaks
4. spin-spin splitting



◀ **Figure 13-38**
Common chemical shifts in the ^{1}H NMR spectrum.



▲ **Figure 13-39**
Proton NMR spectrum for a compound of formula $C_4H_8O_2$.

SAMPLE PROBLEM

Consider how you might approach the NMR spectrum shown in Figure 13-39. The molecular formula is known to be $C_4H_8O_2$, implying one element of unsaturation (the saturated formula would be $C_4H_{10}O_2$). Three types of protons appear in this spectrum. The signals at δ4.1 and δ1.3 resemble an ethyl group—confirmed by the 2:3 ratio of the integrals.

partial structure: $-CH_2-CH_3$

The ethyl group is probably bonded to an electronegative element, since its methylene ($-CH_2-$) protons absorb close to δ4. The molecular formula contains oxygen, so an ethoxy group is suggested.

partial structure: $-O-CH_2-CH_3$

The singlet at δ2.1 (area = 3) might be a methyl group bonded to a carbonyl group. A carbonyl group would also account for the element of unsaturation.

partial structure: $-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

We have accounted for all eight hydrogen atoms in the spectrum. Putting together all the clues, we arrive at a proposed structure.

$$CH_3^a-CH_2^b-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3^c$$

ethyl acetate

At this point, the structure should be rechecked to make sure it is consistent with the molecular formula, the proton ratios given by the integrals, the chemical shifts of the signals, and the spin-spin splitting. In ethyl acetate, the H^a protons give a triplet (split by the adjacent CH_2 group, J = 7 Hz) of area 3 at δ1.3; the H^b protons give a quartet (split by the adjacent CH_3 group, J = 7 Hz) of area 2 at δ4.1; and the H^c protons give a singlet of area 3 at δ2.1.

T-107 Fig 13-15 Proton NMR Spectrum of acetic acid

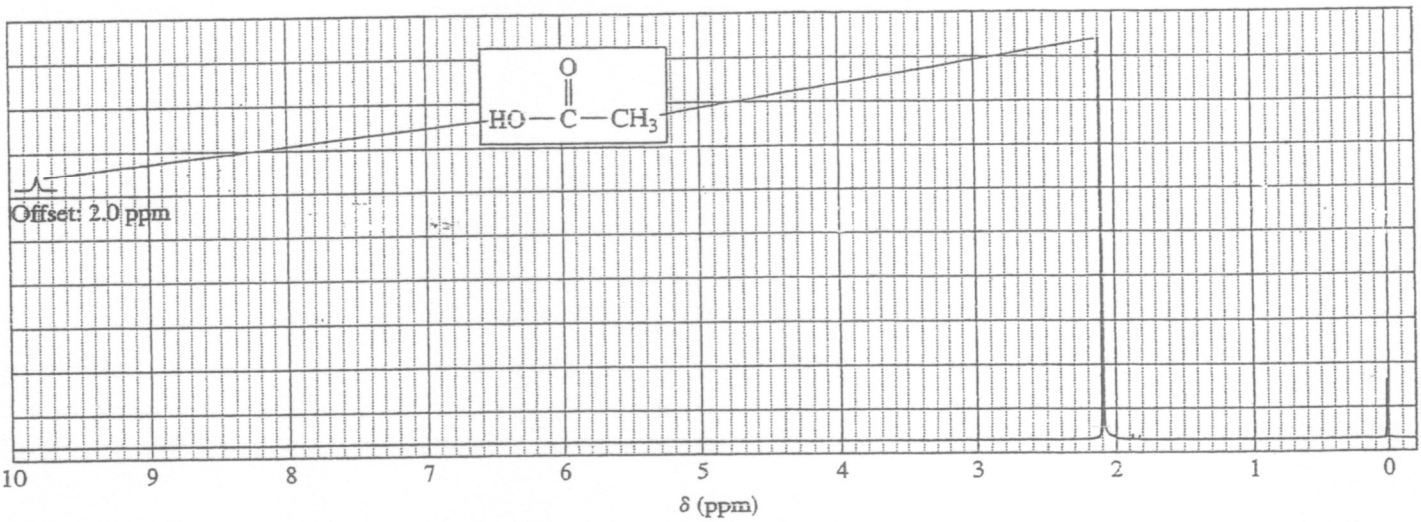


Fig 13-19 Proton NMR Spectrum of methyl t-butyl ether

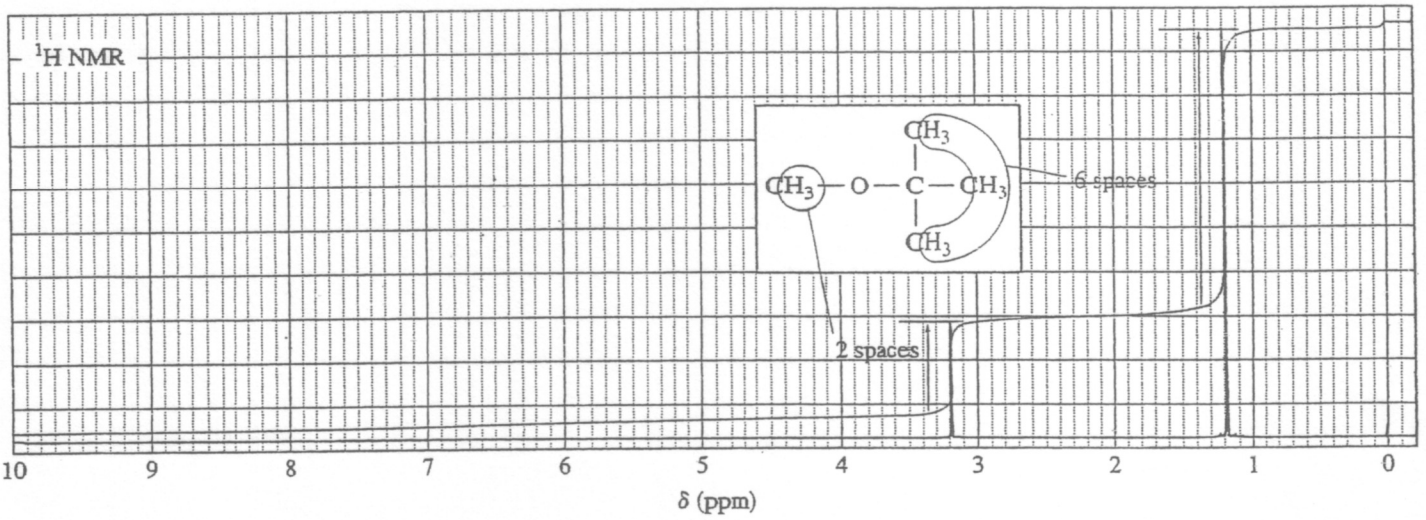
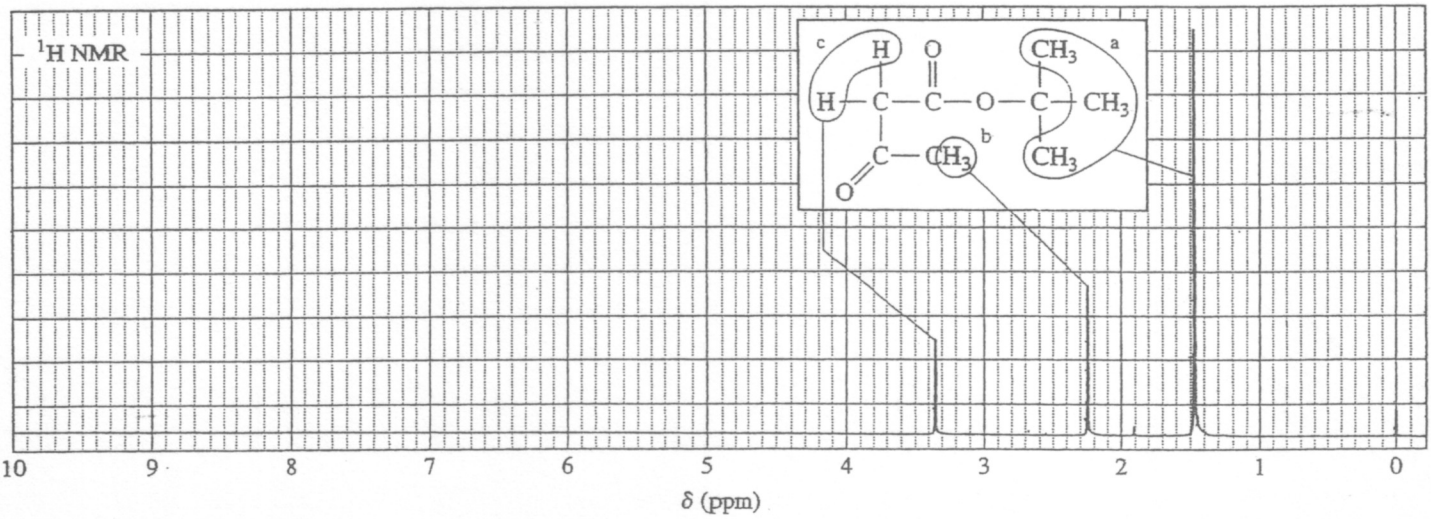
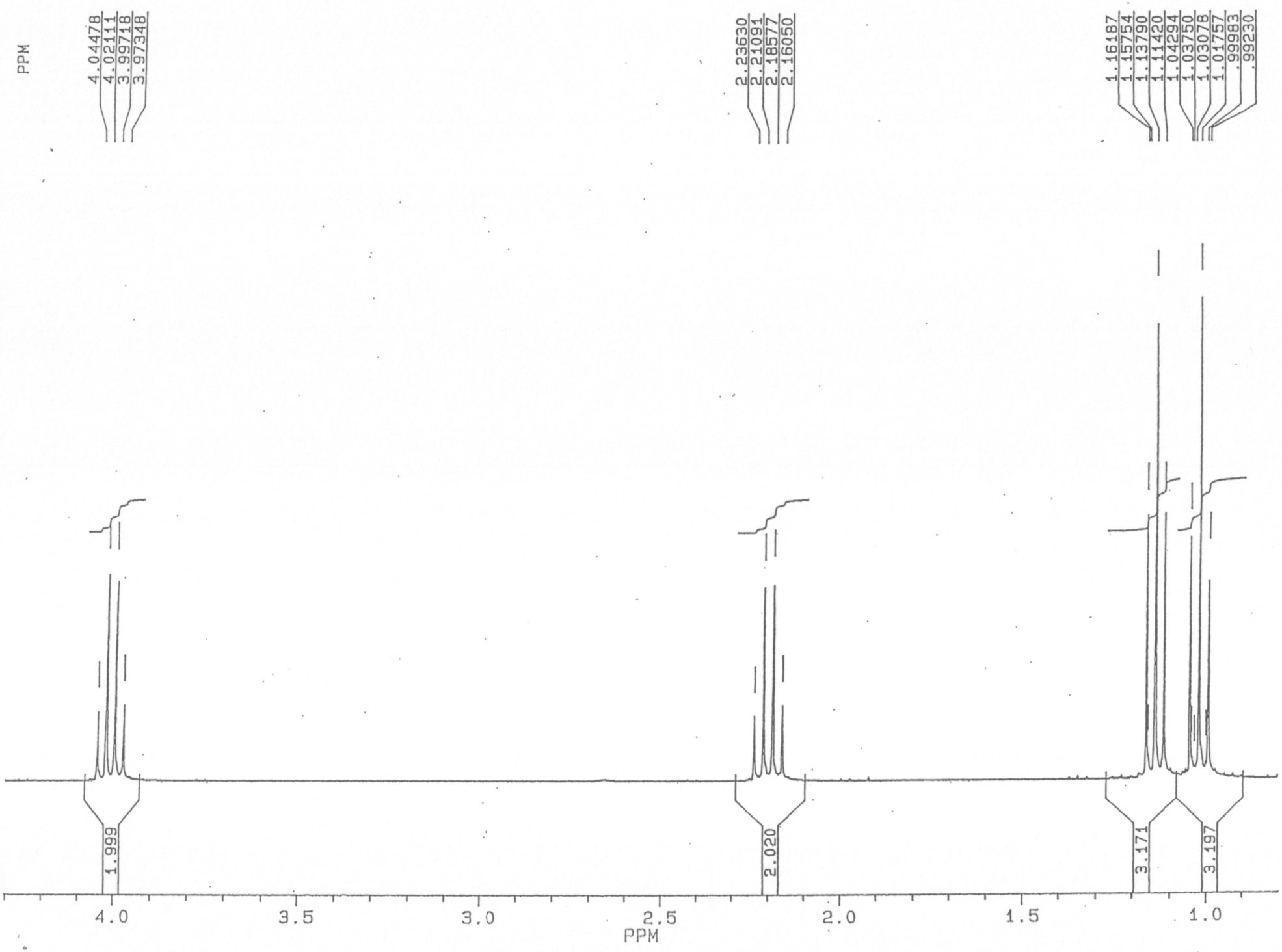


Fig 13-17 Proton NMR Spectrum of t-butyl acetoacetate

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4.02111
3.99718
3.97348
2.23630
2.21091
2.18577
2.16050
1.16187
1.15754
1.13790
1.11420
1.04294
1.03750
1.03078
1.01757
.99983
.99230
1.999
2.020
3.171
3.197
4.0
3.5
3.0
2.5
2.0
1.5
1.0
PPM