

Lecture # 12

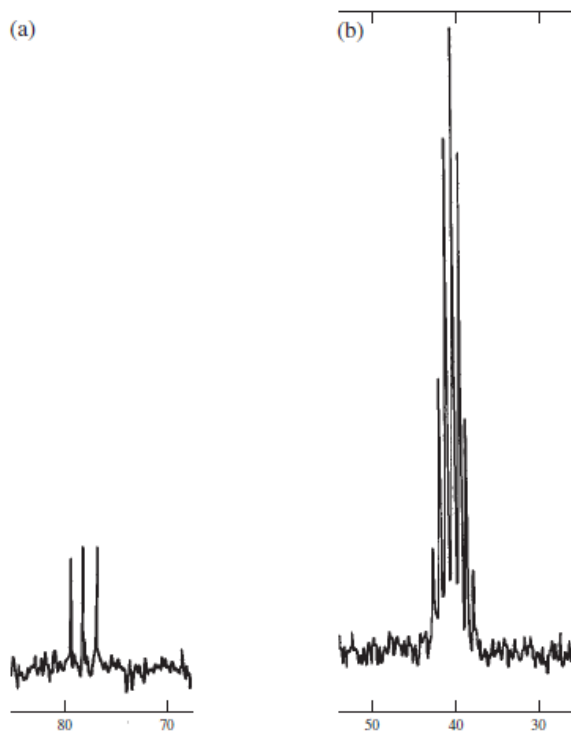


FIGURE 6.17 The ^{13}C NMR peaks of two common solvents. (a) Chloroform-d. (b) Dimethylsulfoxide-d₆.

6.15 HETERONUCLEAR COUPLING OF CARBON-13 TO FLUORINE-19

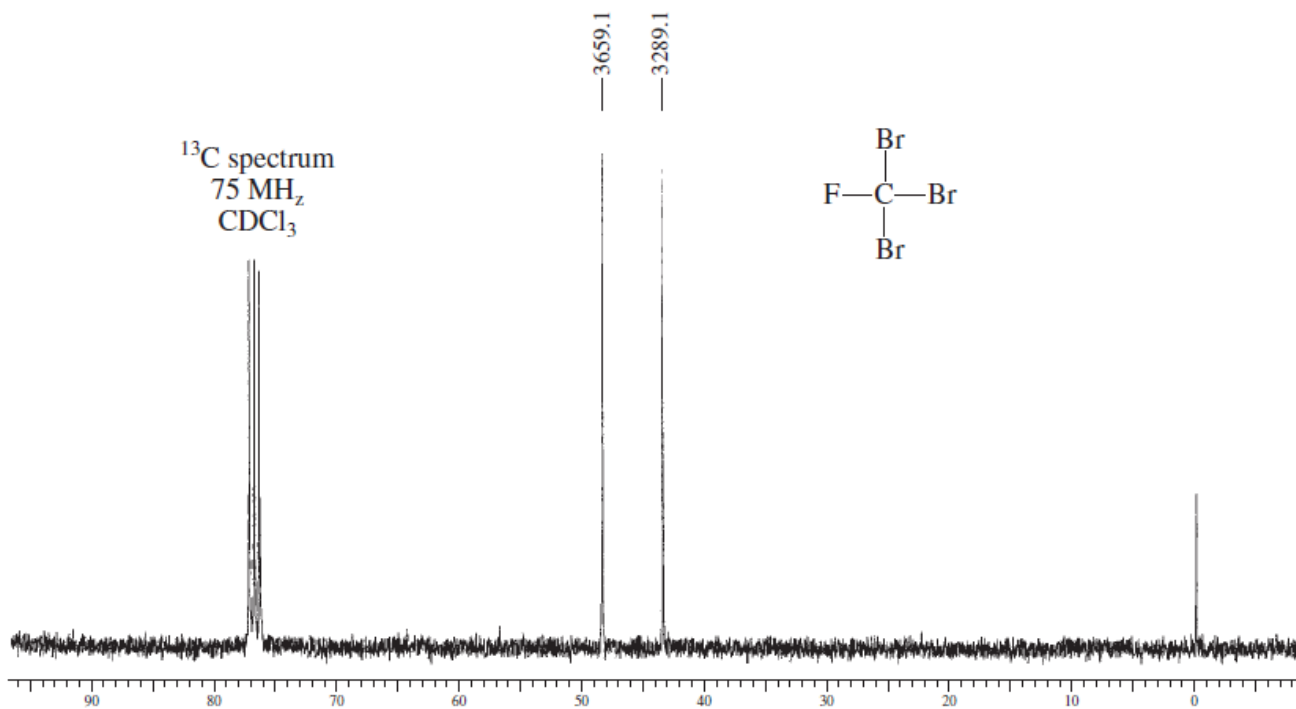


FIGURE 6.21 The ¹³C proton-decoupled spectrum of CBr₄ (75 MHz).

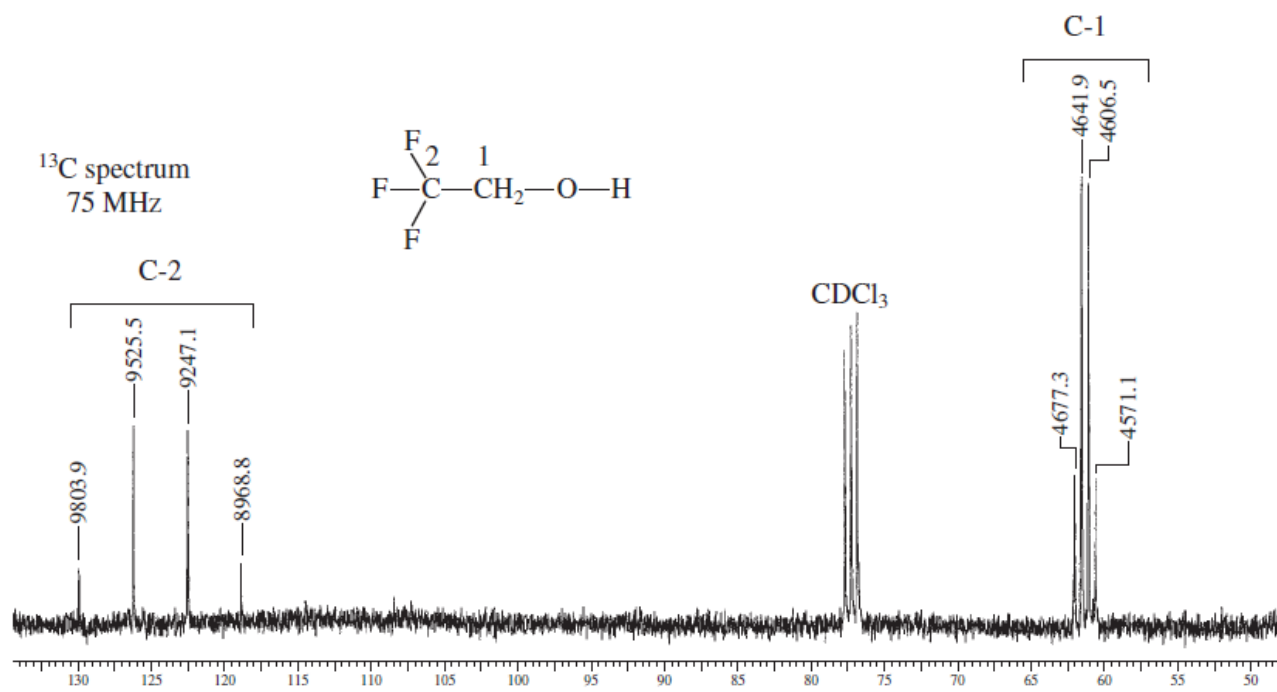


FIGURE 6.22 The ¹³C proton-decoupled spectrum of CF₃CH₂OH (75 MHz).

The spectrum of CFBr_3 shown in Figure 6.21 has Hertz (Hz) values recorded on top of each peak in the doublet rather than parts-per-million (ppm) values, which is more typical. The chemical shift values for each of the peaks can be calculated by dividing the Hertz values by the field strength of the NMR spectrometer (75 MHz), giving 43.85 and 48.79 ppm. The actual chemical shift for the carbon atom would be in the center of the doublet: 46.32 ppm. The ^{13}C – ^{19}F coupling constant in

Hertz is easily determined by subtracting the two Hertz values, yielding 370 Hz. This huge coupling constant is typical for direct one-bond coupling of the fluorine nucleus to a carbon-13 atom (1J).

The second example for fluorine coupling to ^{13}C is shown in Figure 4.21. This spectrum shows both one-bond and two-bond coupling of ^{13}C to ^{19}F . The large quartet centering on about 125 ppm for C-2 results from the one-bond coupling of three attached fluorine atoms (1J) to a ^{13}C atom ($n + 1 = 4$). Again, Hertz values are included on each peak in the large quartet. Subtracting the Hertz values on the center two peaks in the quartet yields 278 Hz. Also notice that there is another quartet centering on about 62 ppm for C-1. This quartet results from the three fluorine atoms that are further away from the ^{13}C . Notice that the spacings in that quartet are about 35 Hz. This is described as a two-bond coupling (2J). Notice that the coupling falls off with distance (see Appendix 9 for typical ^{13}C to ^{19}F coupling constants).

6.16 HETERONUCLEAR COUPLING OF CARBON-13 TO PHOSPHORUS-31

The two spectra in Figures 6.23 and 6.24 demonstrate coupling between ^{13}C and ^{31}P . In the first compound, shown in Figure 6.23, the carbon atom of the methyl group at about 12 ppm is split by one adjacent phosphorus atom into a doublet with a coupling constant equal to 56.1 Hz ($919.3 - 863.2 = 56.1$ Hz). Notice that the $n + 1$ Rule predicts how the pattern will appear (doublet). The nuclear spin number for phosphorus is the same as for a proton and for a fluorine atom ($\frac{1}{2}$). This interaction is an example of one-bond coupling (1J).

The second compound, shown in Figure 6.24, shows both one-bond and two-bond coupling of ^{13}C to ^{31}P . The one-bond coupling occurs between the phosphorus atom and the ^{13}C atom of the directly attached methyl group, ^{31}P – $^{13}\text{CH}_3$, has a value of 144 Hz ($819.2 - 675.2$). This doublet is found at about 10 ppm. The other CH_3 group, ^{31}P – O – $^{13}\text{CH}_3$, is two bonds away from the phosphorus atom, and it appears as a doublet about 52 ppm. This two-bond coupling constant equals about 6 Hz ($3949.6 - 3943.5$). One-bond coupling constants can vary because of the differences in hybridization of the phosphorus atom.

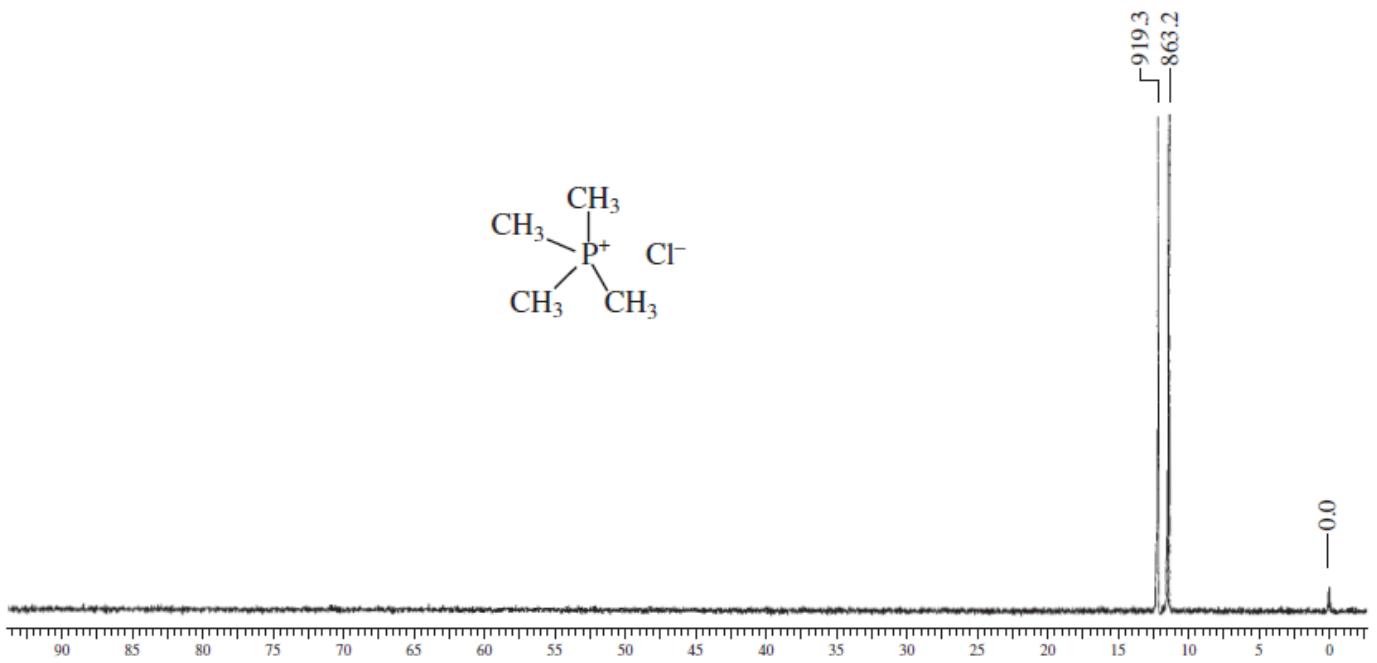


FIGURE 6.23 The ^{13}C proton-decoupled spectrum of tetramethylphosphonium chloride, $(\text{CH}_3)_4\text{P}^+\text{Cl}^-$ (75 MHz).

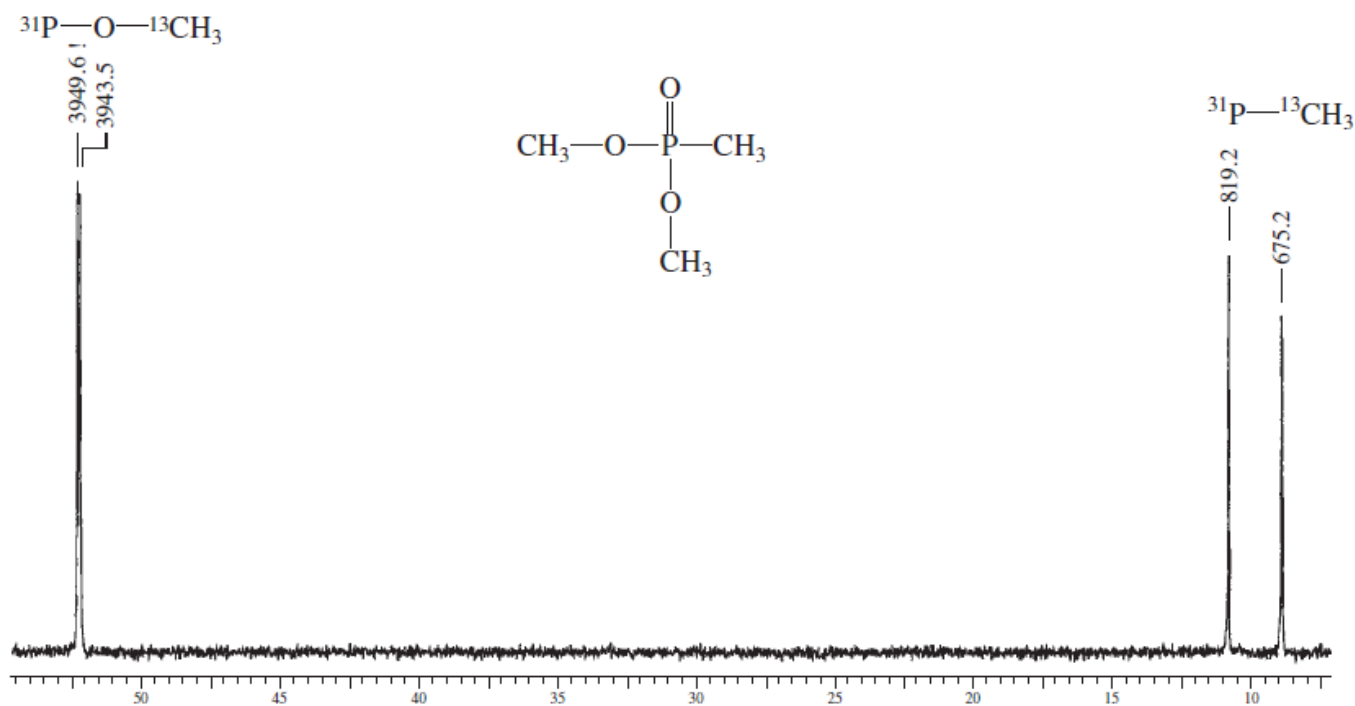
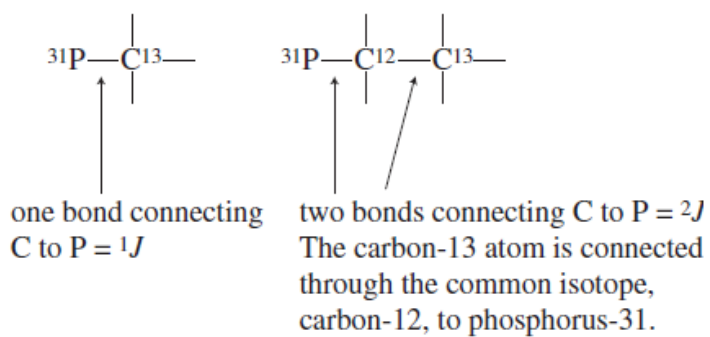


FIGURE 6.24 The ^{13}C proton-decoupled spectrum of $\text{CH}_3\text{PO}(\text{OCH}_3)_2$ (75 MHz).



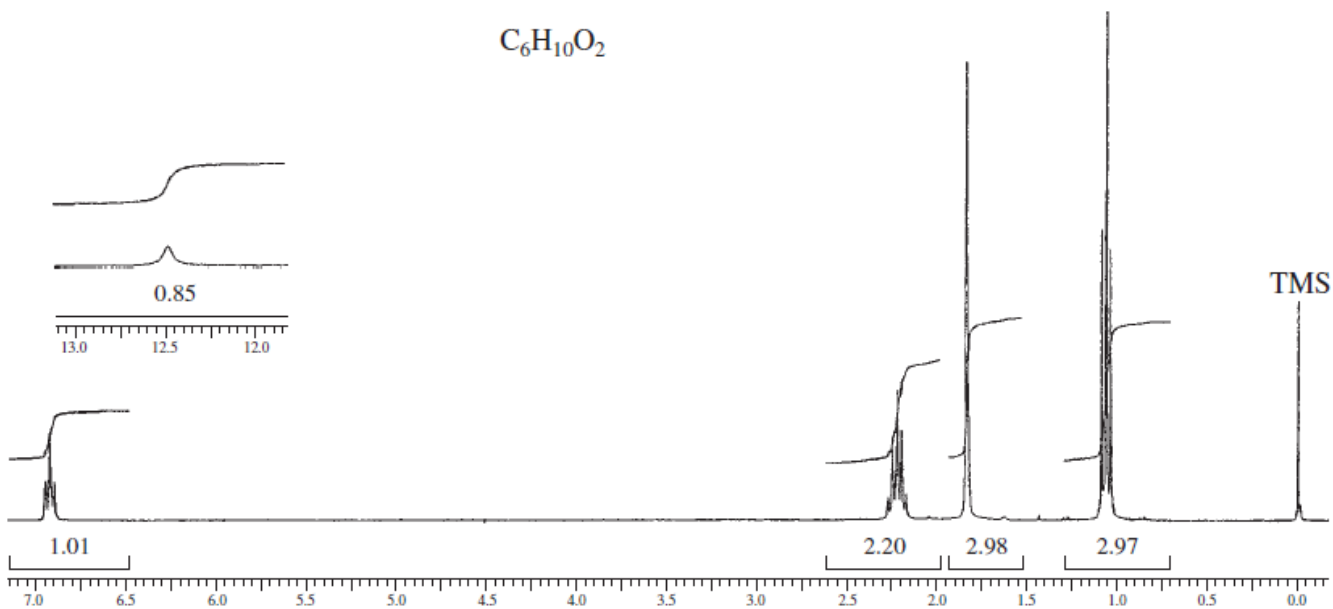


FIGURE 6.25 The proton NMR spectrum for an unknown compound.

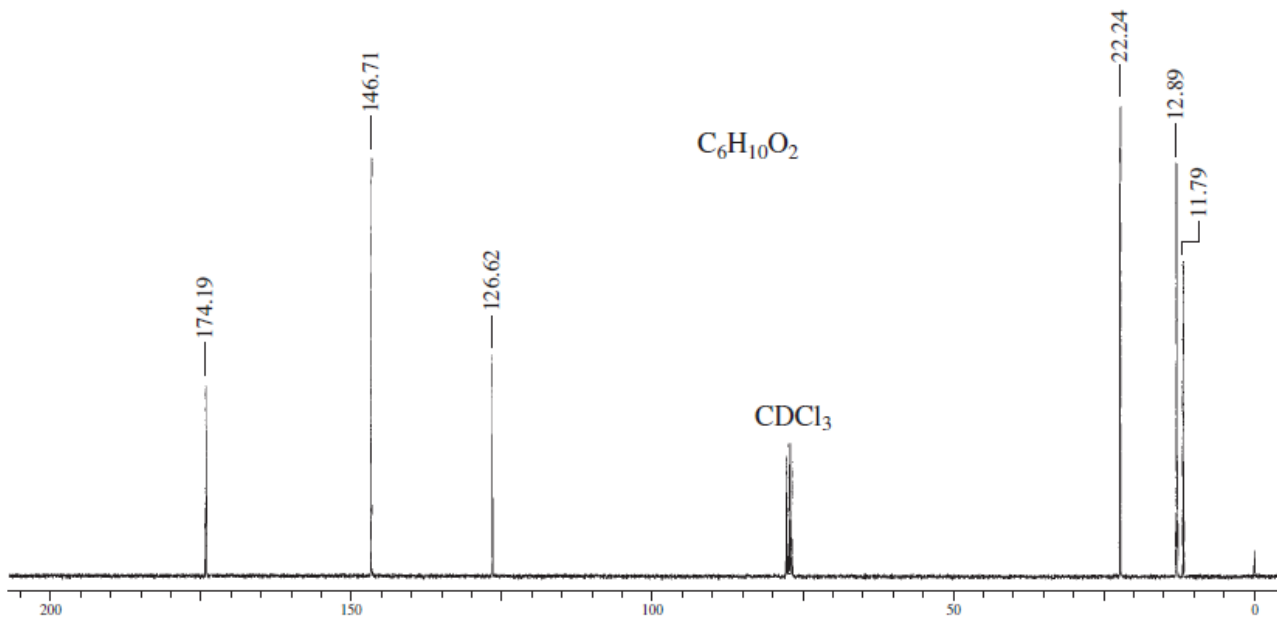
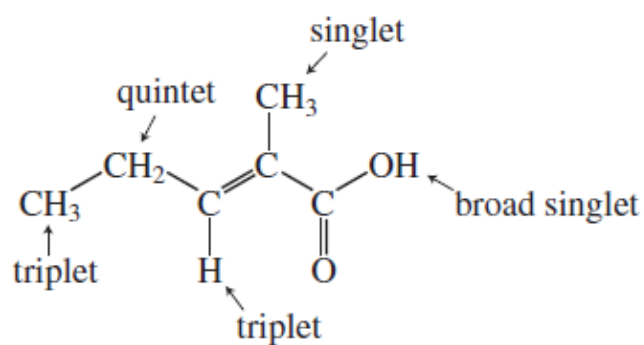


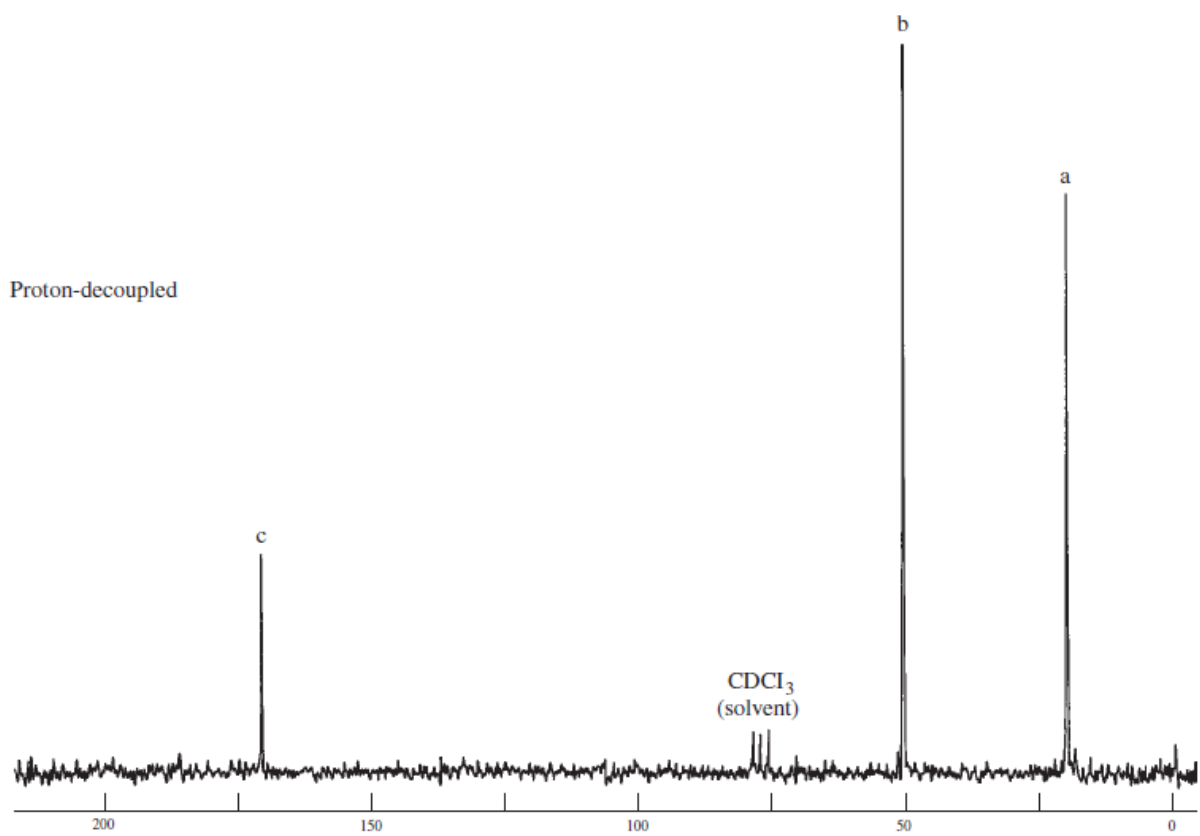
FIGURE 6.26 The carbon-13 spectrum for an unknown compound.

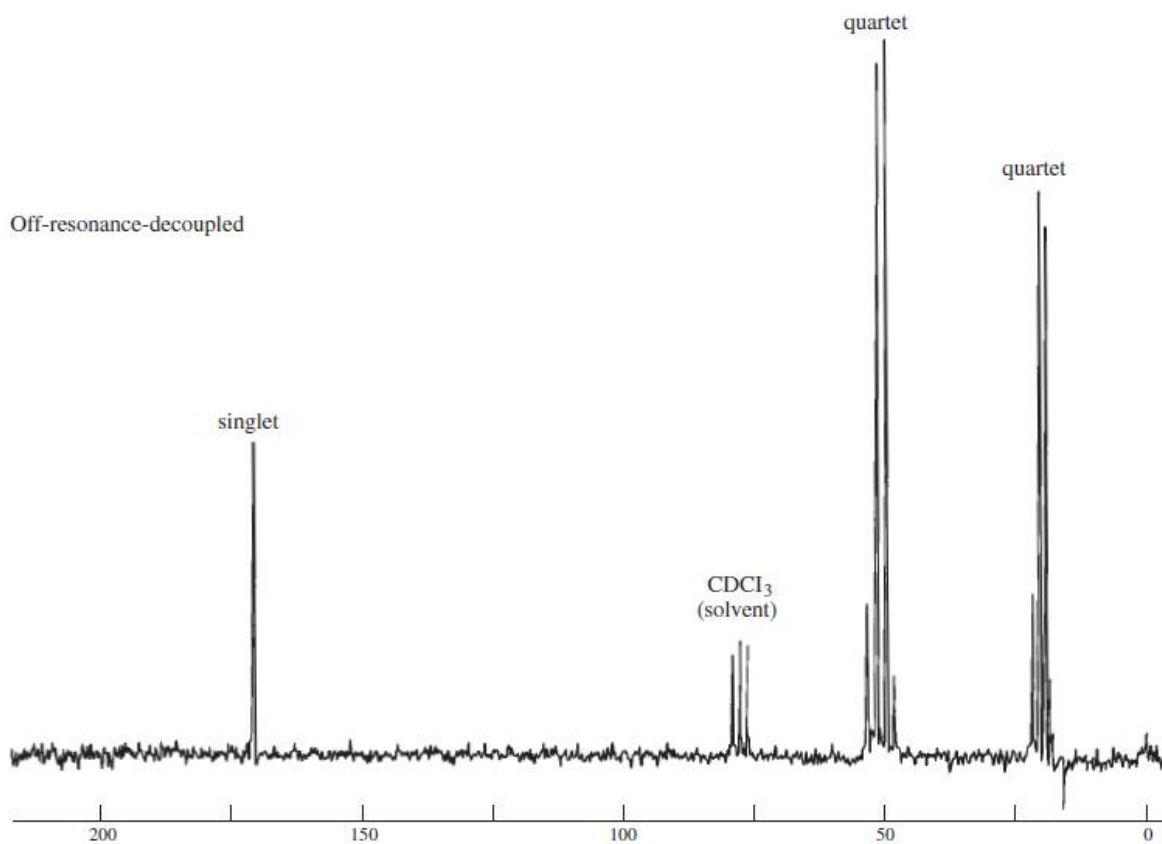
Normal Carbon	DEPT-135	DEPT-90	Conclusion
11.79 ppm	Positive	No peak	CH ₃
12.89	Positive	No peak	CH ₃
22.24	Negative	No peak	CH ₂
126.62	No peak	No peak	C
146.71	Positive	Positive	CH
174.19	No peak	No peak	C=O



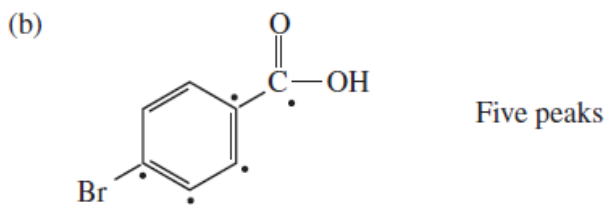
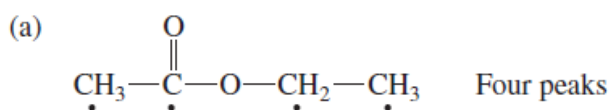
PROBLEMS

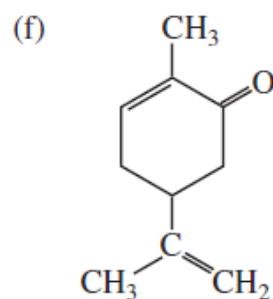
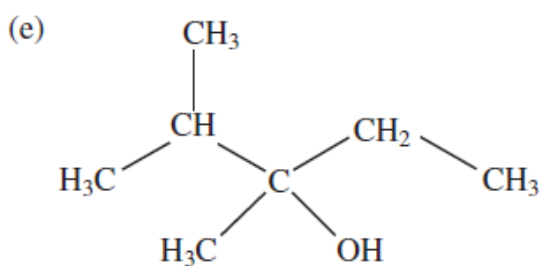
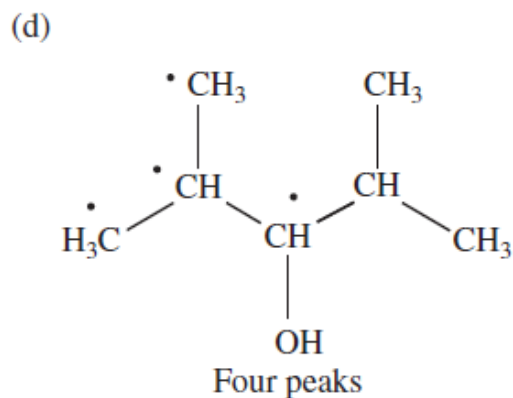
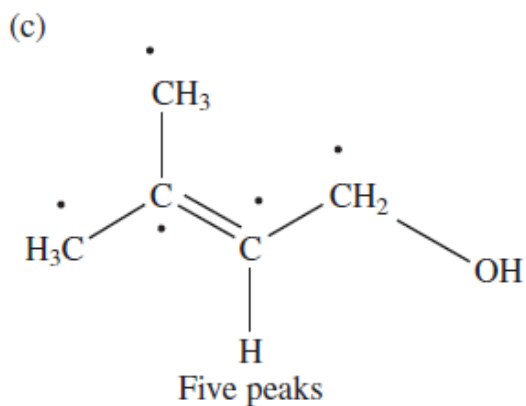
- *1. A compound with the formula $C_3H_6O_2$ gives the following proton-decoupled and off-resonance-decoupled spectra. Determine the structure of the compound.



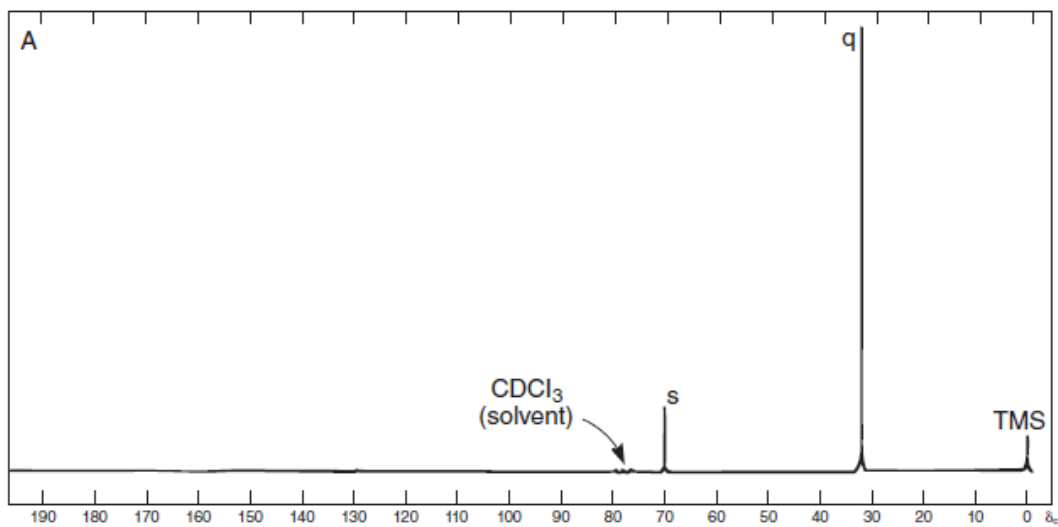


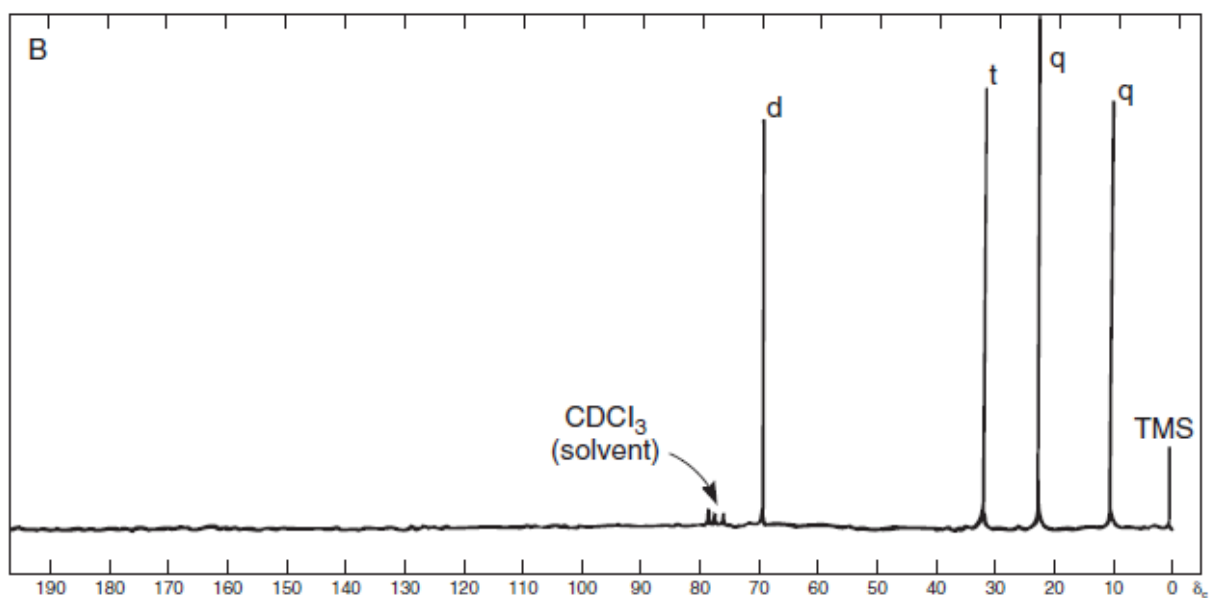
*2. Predict the number of peaks that you would expect in the proton-decoupled ¹³C spectrum of each of the following compounds. Problems 2a and 2b are provided as examples. Dots are used to show the nonequivalent carbon atoms in these two examples.



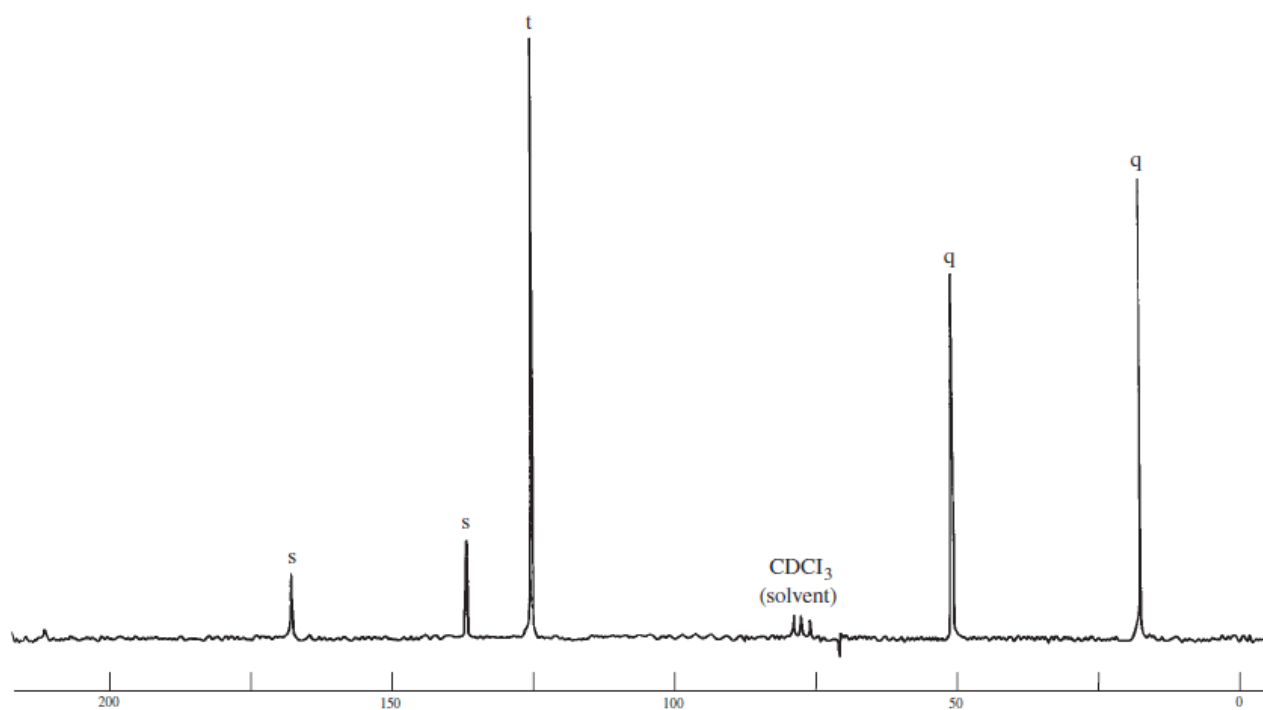


- *3. Following are proton-decoupled ^{13}C spectra for three isomeric alcohols with the formula $\text{C}_4\text{H}_{10}\text{O}$. A DEPT or an off-resonance analysis yields the multiplicities shown; s = singlet, d = doublet, t = triplet, and q = quartet. Identify the alcohol responsible for each spectrum and assign each peak to an appropriate carbon atom or atoms.

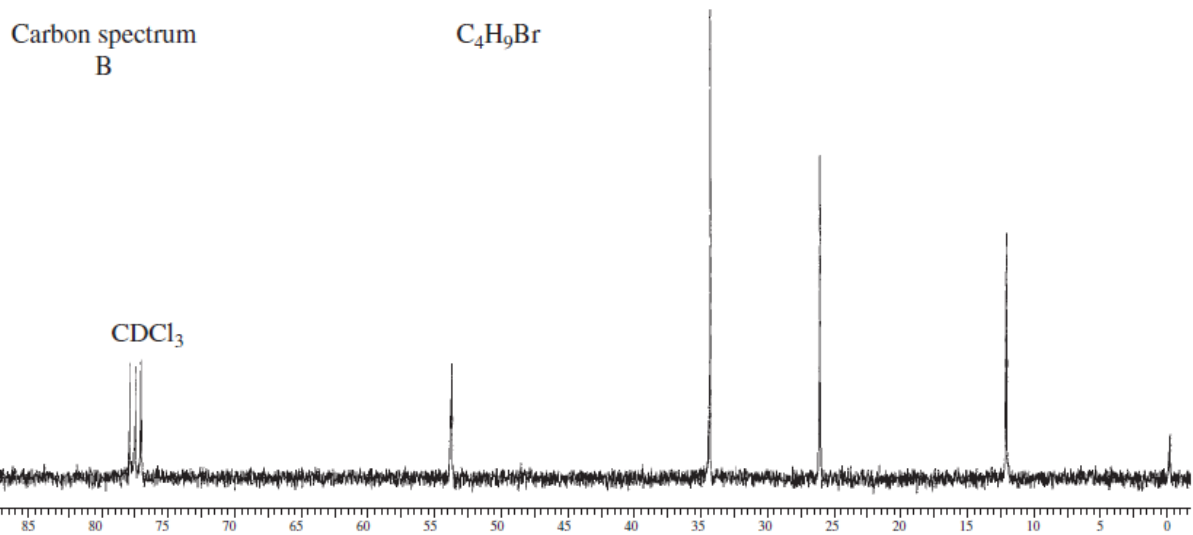
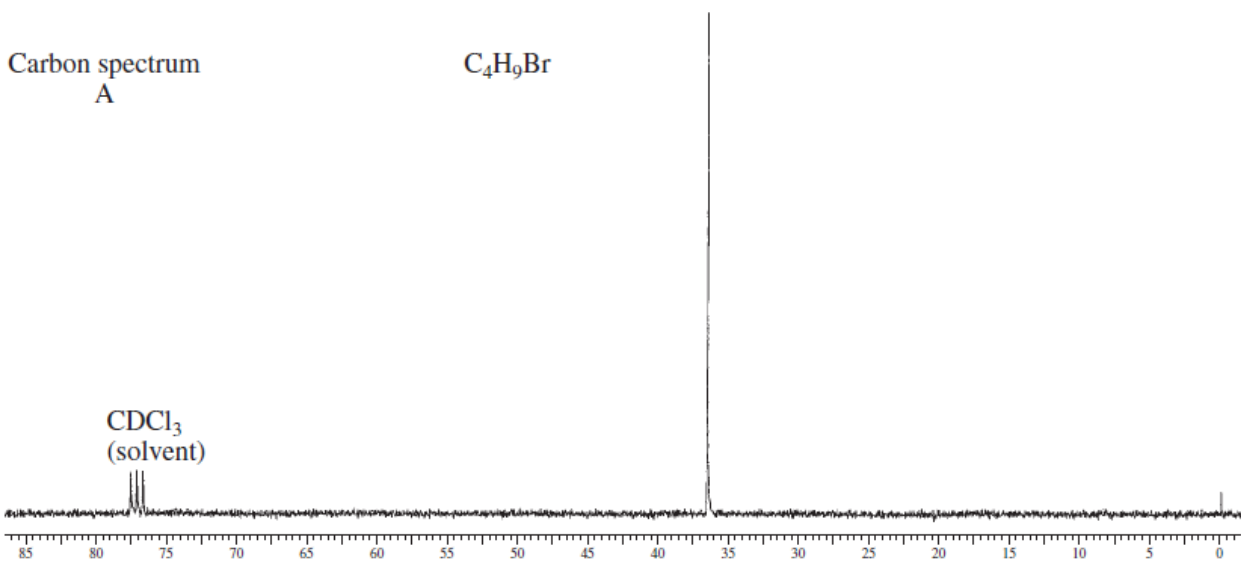




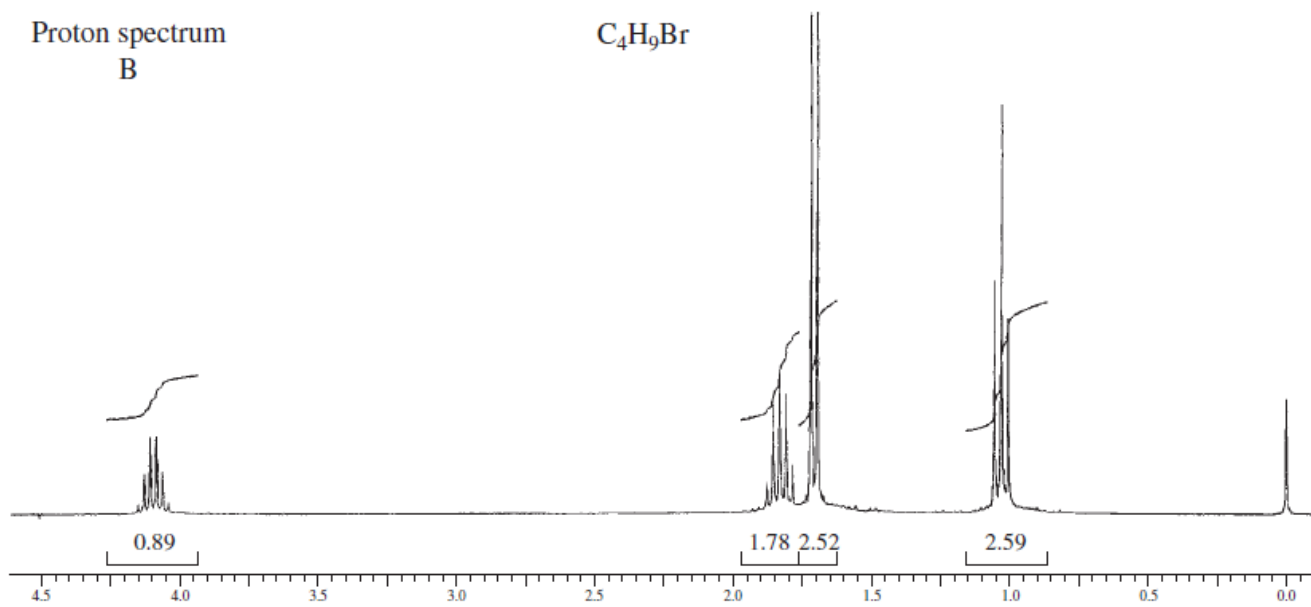
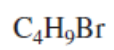
*4. The following spectrum is of an ester with formula C₅H₈O₂. Multiplicities are indicated. Draw the structure of the compound and assign each peak.



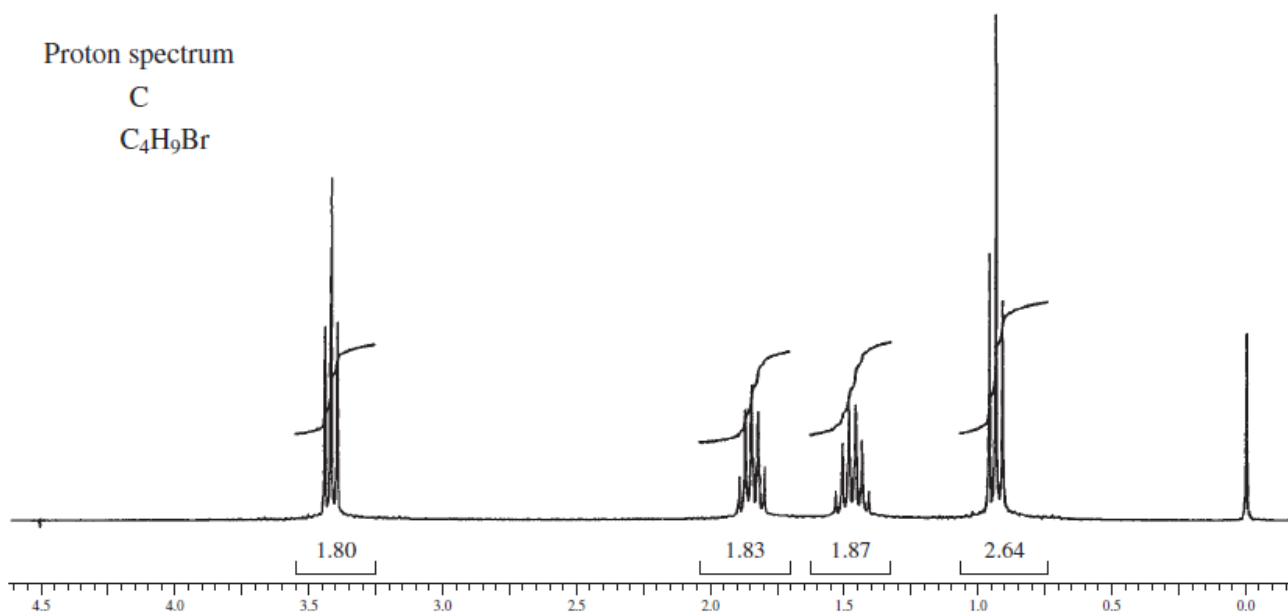
*5. Following are the ^1H and ^{13}C spectra for each of four isomeric bromoalkanes with formula $\text{C}_4\text{H}_9\text{Br}$. Assign a structure to each pair of spectra.



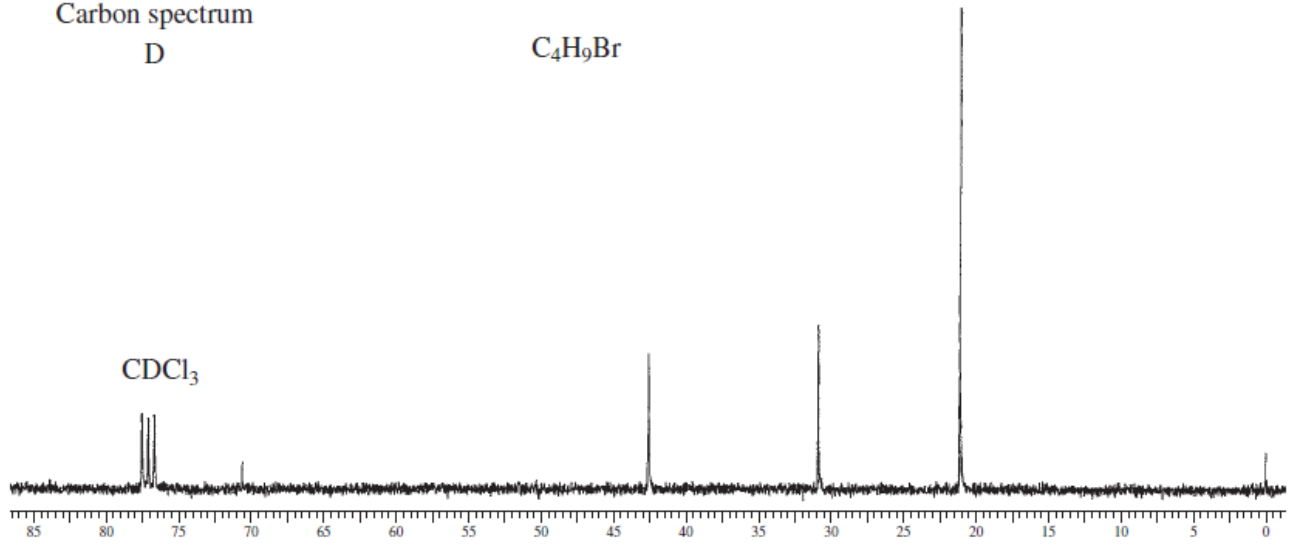
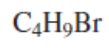
Proton spectrum
B



Proton spectrum
C
 C_4H_9Br



Carbon spectrum
D



Proton spectrum
D

