CHAPTER 9

COMBINED STRUCTURE PROBLEMS

In this chapter, you will employ jointly all of the spectroscopic methods we have discussed so far to solve structural problems in organic chemistry. Forty-three problems are provided to give you practice in applying the principles learned in earlier chapters. The problems involve analysis of the mass spectrum (MS), the infrared (IR) spectrum, and proton and carbon (^{1}H and ^{13}C) nuclear magnetic resonance (NMR). Ultraviolet (UV) spectral data, if provided in the problem, appear in a tabular form rather than as a spectrum. You will notice as you proceed through this chapter that the problems use different "mixes" of spectral information. Thus, you may be provided with a mass spectrum, an infrared spectrum, and a proton NMR spectrum in one problem, and in another you may have available the infrared spectrum and both proton and carbon NMR.

All ^{1}H (proton) NMR spectra were determined at 300 MHz, while the ^{13}C NMR spectra were obtained at 75 MHz. The ^{1}H and ^{13}C spectra were determined in $CDCl_3$ unless otherwise indicated. In some cases, the ^{13}C spectral data have been tabulated, along with the DEPT-135 and DEPT-90 data. Some of the proton NMR spectra have been expanded to show detail. Finally, all infrared spectra on *liquid* samples were obtained neat (with no solvent) on KBr salt plates. The infrared spectra of *solids* have either been melted (cast) onto the salt plate or else determined as a mull (suspension) in Nujol (mineral oil).

The compounds in these problems may contain the following elements: C, H, O, N, S, Cl, Br, and I. In most cases if halogens are present, the mass spectrum should provide you with information regarding which halogen atom is present and the number of halogen atoms (Section 8.7).

There are a number of possible approaches that you may take in solving the problems in this chapter. There are no "right" ways of solving them. In general, however, you should first try to gain an overall impression by looking at the gross features of the spectra provided in the problem. As you do so, you will observe evidence for pieces of the structure. Once you have identified pieces, you can assemble them and test against each of the spectra the validity of the structure you have assembled.

1. **Mass Spectrum.** You should be able to use the mass spectrum to obtain a molecular formula by performing the Rule of Thirteen calculation (p. 9) on the molecular ion peak (*M*) labeled on the spectrum. In most cases, you will need to convert the hydrocarbon formula to one containing a functional group. For example, you may observe a carbonyl group in the infrared spectrum or ^{13}C spectrum. Make appropriate adjustments to the hydrocarbon formula so that it fits the spectroscopic evidence. When the mass spectrum is not provided in the problem, you will be given the molecular formula. Some of the labeled fragment peaks may provide excellent evidence for the presence of a particular feature in the compound being analyzed.

2. **Infrared Spectrum.** The infrared spectrum provides some idea of the functional group or groups that are present or absent. Look first at the left-hand side of the spectrum to identify functional groups such as O−H, N−H, C≡N, C≡C, C=C, C=O, NO_2, and aromatic rings. See Chapter 2, Sections 2.8 and 2.9 (pp. 28–31) for tips on what to look for in the spectrum. Ignore C−H stretching bands during this first "glance" at the spectrum as well as the right-hand side of the spectrum. Determine the type of C=O group you have and also check to

see if there is conjugation with a double bond or aromatic ring. Remember that you can often determine the substitution patterns on alkenes (pp. 41–42) and aromatic rings (pp. 45–47) by using the out-of-plane bending bands (oops). A complete analysis of the infrared spectrum is seldom necessary.

3. **Proton NMR Spectrum.** The proton (^{1}H) NMR spectrum gives information on the numbers and types of hydrogen atoms attached to the carbon skeleton. Chapter 3, Section 3.19 (pp. 142–161) provides information on proton NMR spectra of various functional groups, especially expected chemical shift values. You will need to determine the integral ratios for the protons by using the integral traces shown. See Chapter 3, Section 3.9 (pp. 121–123) to see how you can obtain the numbers of protons attached to the carbon chain. In most cases, it is not easy to see the splitting patterns of multiplets in the full 300-MHz spectrum. We have therefore indicated the multiplicities of peaks as doublet, triplet, quartet, quintet, and sextet on the full spectrum. Singlets are usually easy to see, and they have not been labeled. Many problems have been provided with proton expansions. When expansions are provided, Hertz values have been shown so that you can calculate the coupling constants. Often, the magnitude of the proton coupling constants will help you to assign structural features to the compound such as the relative position of hydrogen atoms in alkenes (*cis*/*trans* isomers).

4. **Carbon NMR Spectra.** The carbon (^{13}C) NMR spectrum indicates the total number of nonequivalent carbon atoms in the molecule. In some cases, because of symmetry, carbon atoms may have identical chemical shifts. In this case, the total number of carbons is less than that found in the molecular formula. Chapter 4 contains important correlation charts that you should review. Figure 4.1 (p. 178) and Table 4.1 (p. 179) show the chemical shift ranges that you should expect for various structural features. Expected ranges for carbonyl groups are shown in Figure 4.2 (p. 180). In addition, you may find it useful to calculate approximate ^{13}C chemical shift values as shown in Appendix 8. Commonly, sp^3 carbon atoms appear to the upfield (right) side of the $CDCl_3$ solvent peak, while the sp^2 carbon atoms in an alkene or in an aromatic ring appear to the left of the solvent peak. Carbon atoms in a C=O group appear furthest to the left in a carbon spectrum. You should first look on the left-hand side of the carbon spectrum to see if you can identify potential carbonyl groups.

5. **DEPT-135 and DEPT-90 Spectra.** In some cases, the problems list information that can provide valuable information on the types of carbon atoms present in the unknown compound. Review Chapter 4, Section 4.10 (p. 192), A Quick Dip into DEPT, for information on how to determine the presence of CH_3, CH_2, CH, and C atoms in a carbon spectrum.

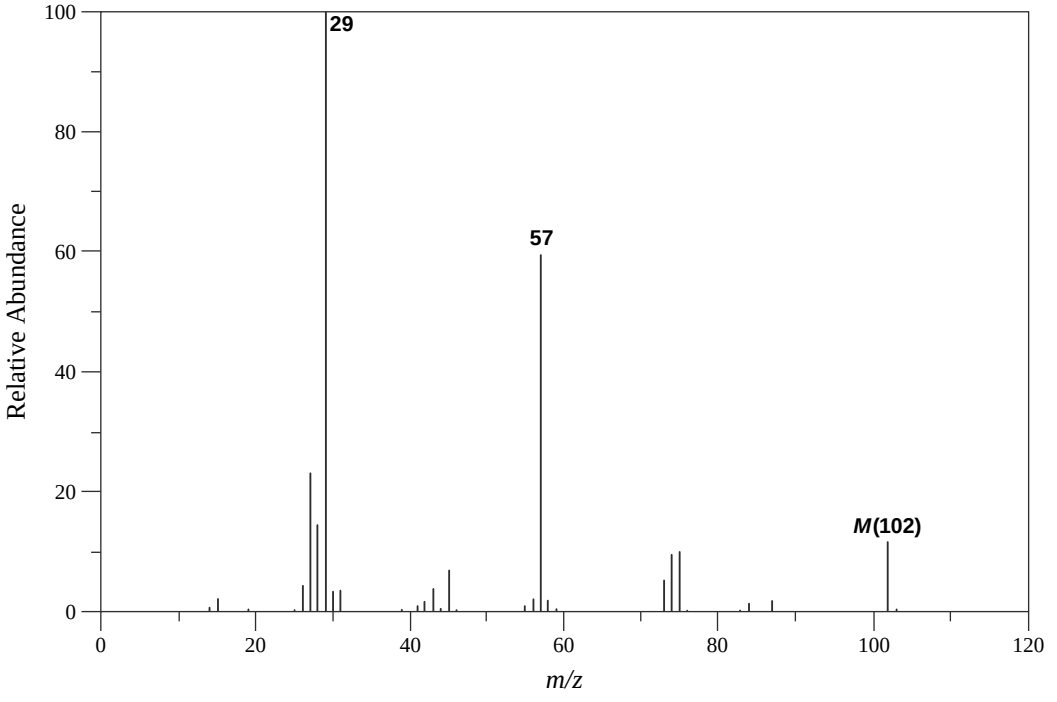
6. **Ultraviolet/Visible Spectrum.** The ultraviolet spectrum becomes useful when unsaturation is present in a molecule. See Chapter 7, Section 7.17 (p. 413) for information on how to interpret a UV spectrum.

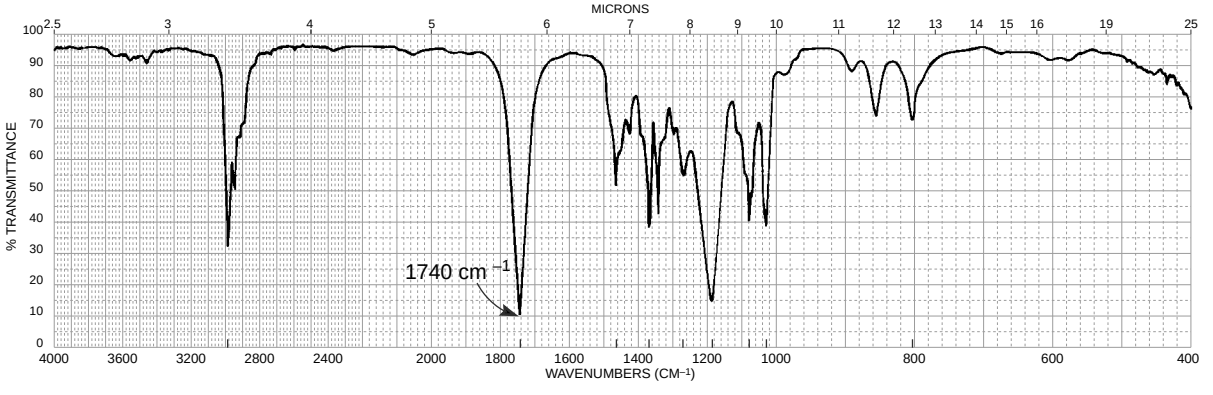
7. **Determining a Final Structure.** A complete analysis of the information provided in the problems should lead to a unique structure for the unknown compound. Four solved examples are presented first. Note that more than one approach may be taken to the solution of these example problems. Since the problems near the beginning of this chapter are easier, you should attempt them before you move on. Have fun (no kidding)! You may even find that you have as much fun as the authors of this book.

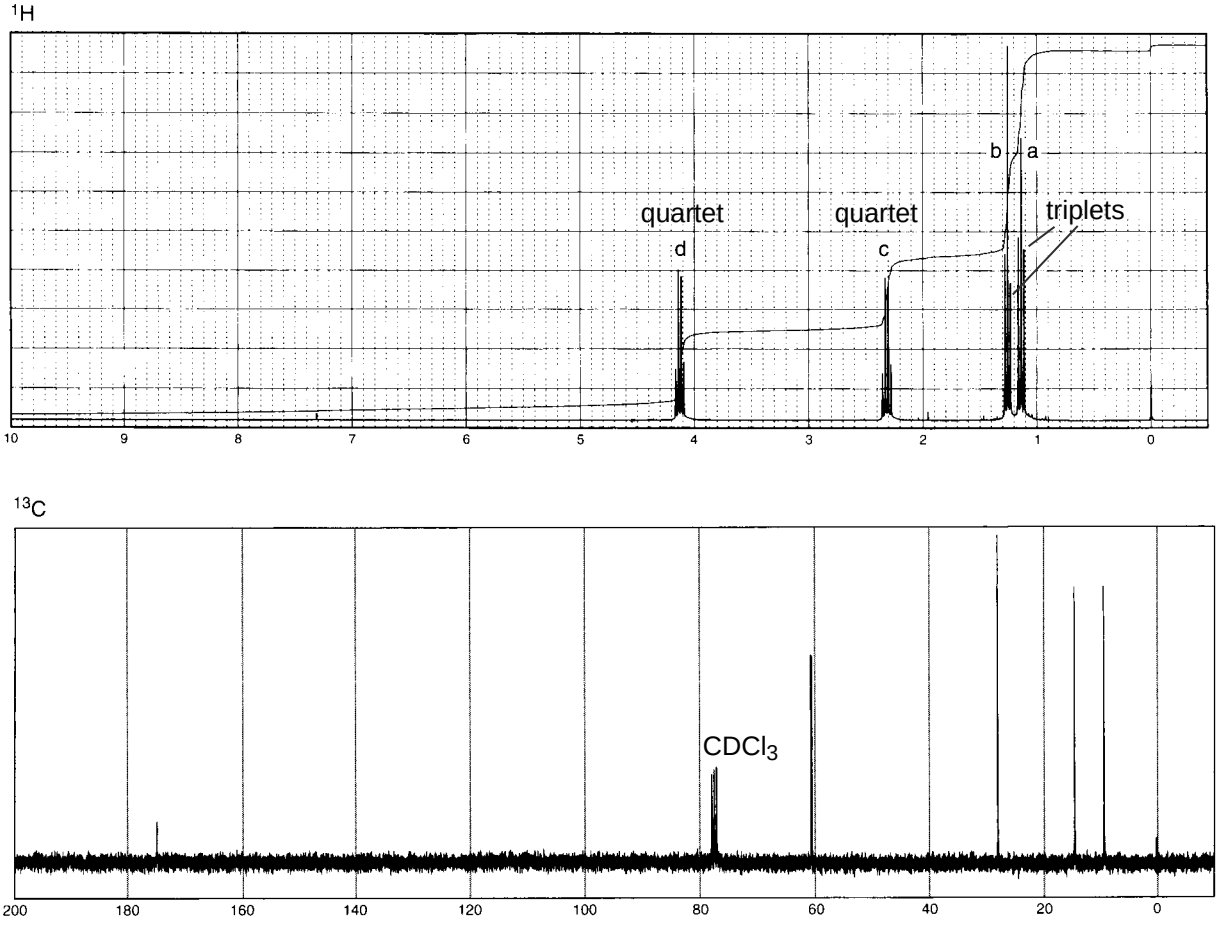
EXAMPLE 1

Problem

The UV spectrum of this compound shows only end absorption. Determine the structure of the compound.





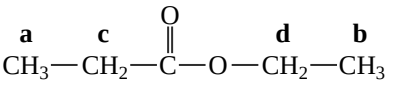


Solution

Notice that this problem does not provide a molecular formula. We need to obtain it from the spectral evidence. The molecular ion peak appears at $m/z = 102$. Using the Rule of Thirteen (p. 9), we can calculate a formula of C_7H_{18} for the peak at 102. The infrared spectrum shows a strong absorption at 1740 cm^{-1}, suggesting that a simple unconjugated ester is present in the compound. The presence of a C—O (strong and broad) at 1200 cm^{-1} confirms the ester. We now know that there are two oxygen atoms in the formula. Returning to the mass spectral evidence, the formula calculated via the Rule of Thirteen was C_7H_{18}. We can modify this formula by converting carbons and hydrogens (one carbon and four hydrogens per oxygen atom) to the two oxygen atoms, yielding the formula $C_5H_{10}O_2$. This is the molecular formula for the compound. We can now calculate the index of hydrogen deficiency for this compound, which equals one, and that corresponds to the unsaturation in the C=O group. The infrared spectrum also shows sp^3 (aliphatic) C—H absorption at less than 3000 cm^{-1}. We conclude that the compound is an aliphatic ester with formula $C_5H_{10}O_2$.

Notice that the ^{13}C NMR spectrum shows a total of five peaks, corresponding exactly to the number of carbons in the molecular formula! This is a nice check on our calculation of the formula via the Rule of Thirteen (five carbon atoms). The peak at 174 ppm corresponds to the ester C=O carbon. The peak at 60 ppm is a deshielded carbon atom caused by a neighboring single-bonded oxygen atom. The rest of the carbon atoms are relatively shielded. These three peaks correspond to the remaining part of the carbon chain in the ester.

We could probably derive a couple of possible structures at this point. The ^{1}H NMR spectrum should provide confirmation. Using the integral traces on the spectrum, we should conclude that the peaks shown have the ratio 2:2:3:3 (downfield to upfield). These numbers add up to the 10 total hydrogen atoms in the formula. Now, using the splitting patterns on the peaks, we can determine the structure of the compound. It is ethyl propanoate.



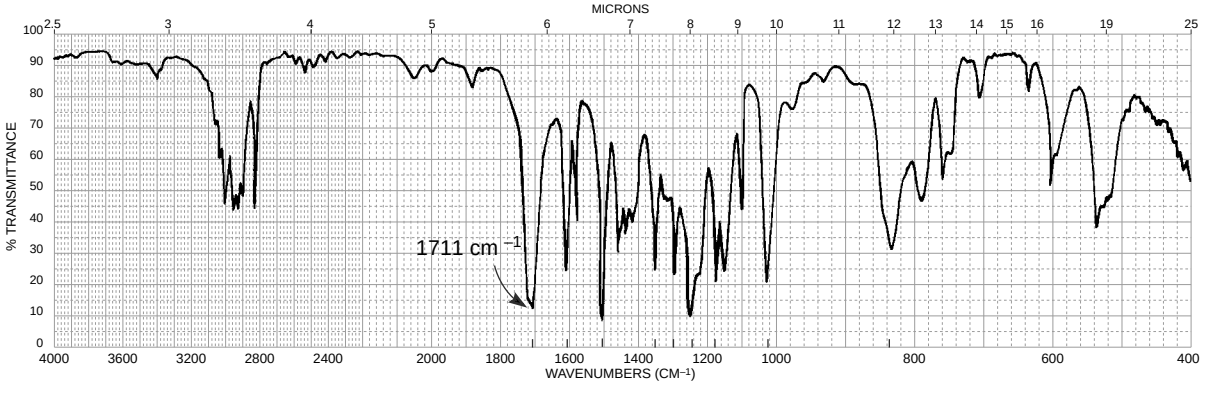
The downfield quartet at 4.1 ppm (**d** protons) results from splitting with the neighboring protons on carbon **b**, while the other quartet at 2.4 ppm (**c** protons) results from spin-spin splitting with the protons on carbon **a**. Thus, the proton NMR is consistent with the final structure.

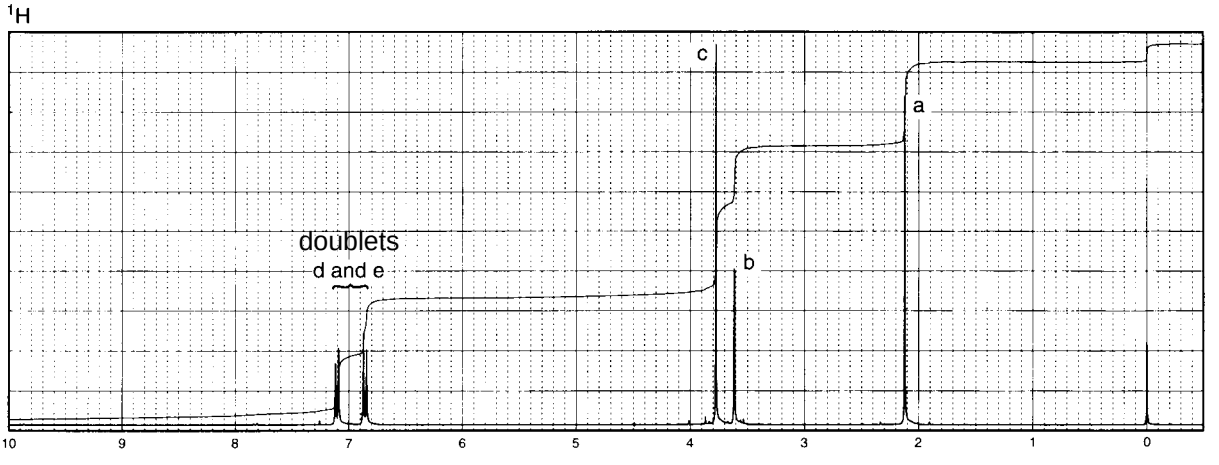
The UV spectrum is uninteresting but supports the identification of structure. Simple esters have weak $n \rightarrow \pi^*$ transitions (205 nm) near the solvent cutoff point. Returning to the mass spectrum, the strong peak at 57 mass units results from an α-cleavage of an alkoxy group to yield the acylium ion ($CH_3-CH_2-\overset{+}{C}=O$), which has a mass of 57.

EXAMPLE 2

Problem

Determine the structure of a compound with the formula $C_{10}H_{12}O_2$. In addition to the infrared spectrum and ^{1}H NMR, the problem includes tabulated data for the normal ^{13}C NMR, DEPT-135, and DEPT-90 spectral data.



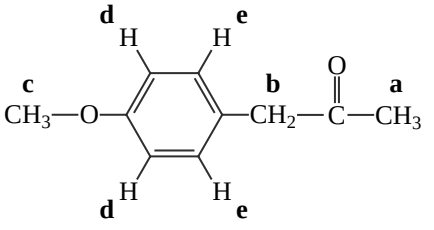


Normal Carbon	DEPT-135	DEPT-90
29 ppm	Positive	No peak
50	Negative	No peak
55	Positive	No peak
114	Positive	Positive
126	No peak	No peak
130	Positive	Positive
159	No peak	No peak
207	No peak	No peak

Solution

We calculate an index of hydrogen deficiency (p. 6) of five. The ^{1}H and ^{13}C NMR spectra, as well as the infrared spectrum, suggest an aromatic ring (unsaturation index = four). The remaining index of one is attributed to a C=O group found in the infrared spectrum at 1711 cm^{-1}. This value for the C=O is close to what you might expect for an unconjugated carbonyl group in a ketone and is too low for an ester. The ^{13}C NMR confirms the ketone C=O; the peak at 207 ppm is typical for a ketone. The ^{13}C NMR spectrum shows only 8 peaks, while 10 are present in the molecular formula. This suggests some symmetry that makes some of the carbon atoms equivalent.

When inspecting the ^{1}H NMR spectrum, notice the nice *para* substitution pattern between 6.8 and 7.2 ppm, which appears as a nominal "pair of doublets", integrating for two protons in each pair. The electron-donating nature of the methoxy (or ^{1}H chemical shift calculations) allow us to assign the more upfield resonance at 6.8 ppm to the protons (d) adjacent to the $-OCH_3$ group on the aromatic ring. Also notice in the ^{1}H NMR that the upfield portion of the spectrum has protons that integrate for 3:2:3 for a CH_3, a CH_2, and a CH_3, respectively. Also notice that these peaks are unsplit, indicating that there are no neighboring protons. The downfield methyl at 3.8 ppm is next to an oxygen atom, suggesting a methoxy group. The ^{13}C DEPT NMR spectra results confirm the presence of two methyl groups and one methylene group. The methyl group at 55 ppm is deshielded by the presence of an oxygen atom ($O-CH_3$). Keeping in mind the *para*-disubstituted pattern and the singlet peaks in the ^{1}H NMR, we derive the following structure for 4-methoxyphenylacetone:

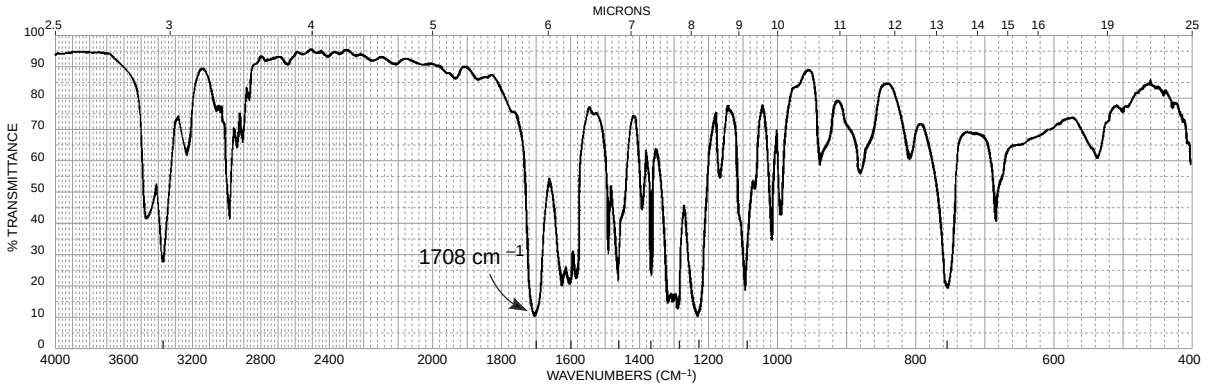


Further confirmation of the *para*-disubstituted ring is obtained from the carbon spectral results. Notice the presence of four peaks in the aromatic region of the ^{13}C NMR spectrum. Two of these peaks (126 and 159 ppm) are *ipso* carbon atoms (no attached protons) that do not appear in the DEPT-135 or DEPT-90 spectra. The remaining two peaks at 114 and 130 ppm are assigned to the remaining four carbons (two each equivalent by symmetry). The two carbon atoms **d** show peaks in both of the DEPT experiments, which confirms that they have attached protons (C−H). Likewise, the two carbon atoms **e** have peaks in both DEPT experiments confirming the presence of C−H. The infrared spectrum has a *para* substitution pattern in the out-of-plane region (835 cm^{-1}), which helps to confirm the 1,4-disubstitution on the aromatic ring.

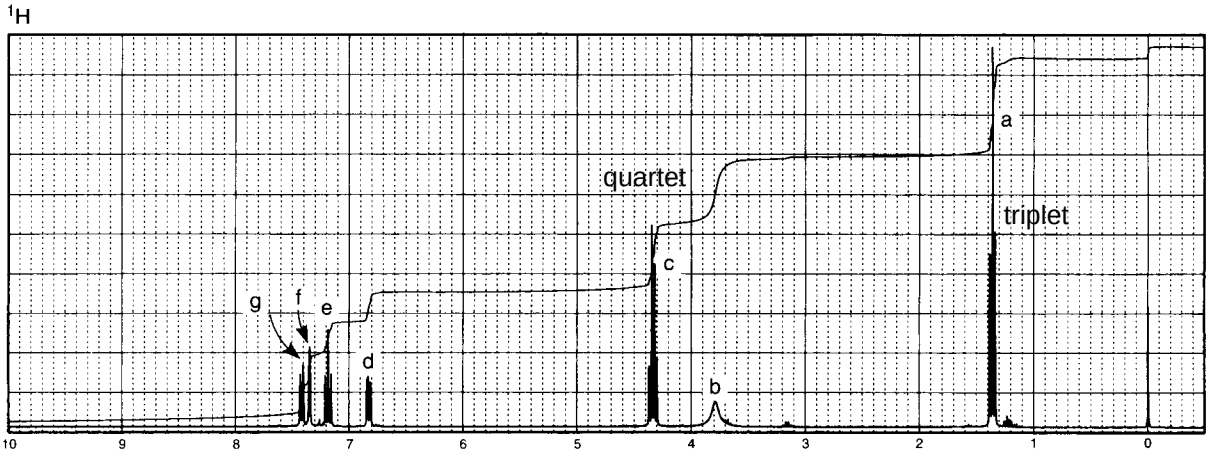
EXAMPLE 3

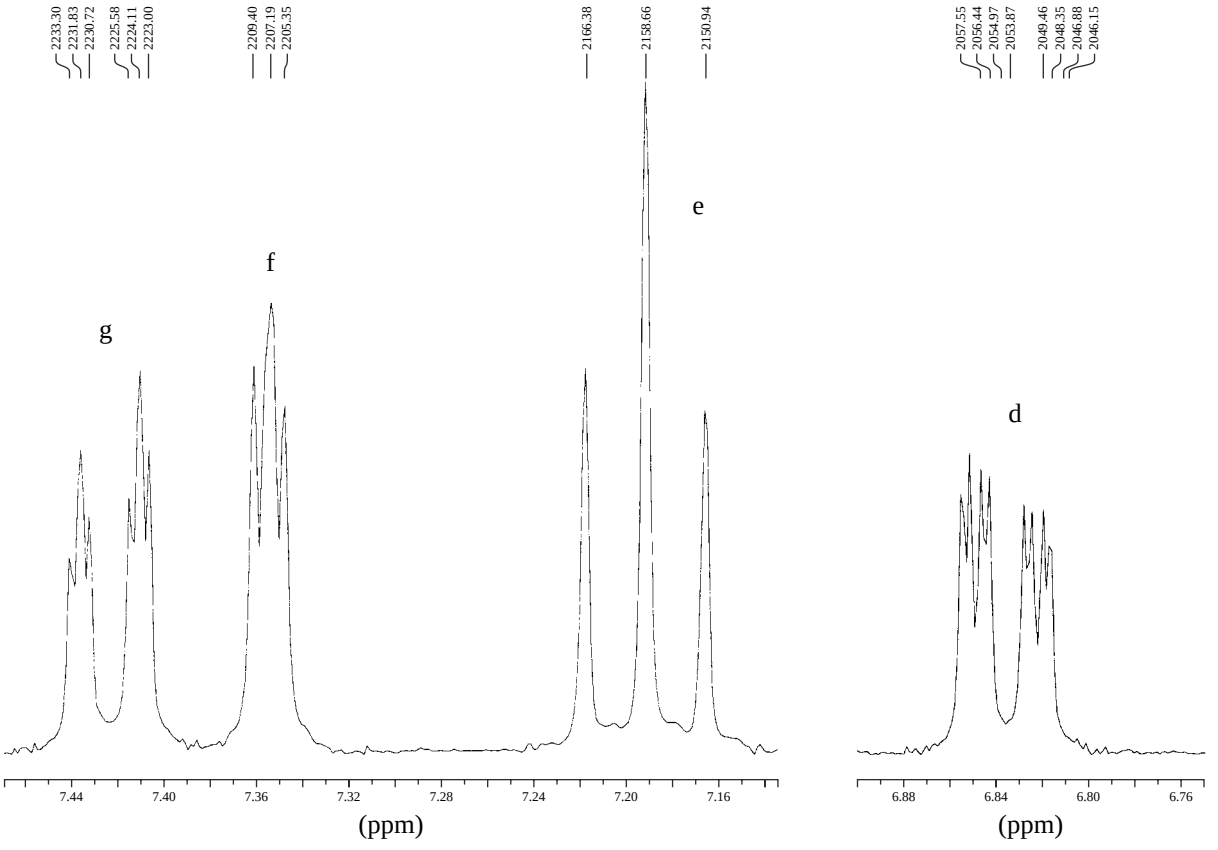
Problem

This compound has the molecular formula $C_9H_{11}NO_2$. Included in this problem are the infrared spectrum, ^1H NMR with expansions, and ^{13}C NMR spectra data.



Normal Carbon	DEPT-135	DEPT-90
14 ppm	Positive	No peak
61	Negative	No peak
116	Positive	Positive
119	Positive	Positive
120	Positive	Positive
129	Positive	Positive
131	No peak	No peak
147	No peak	No peak
167	No peak	No peak





Solution

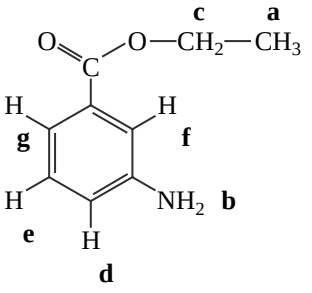
We calculate an index of hydrogen deficiency of five. All of the spectra shown in this problem suggest an aromatic ring (unsaturation index = four). The remaining index of one is assigned to the C=O group found at 1708 cm^{-1}. This value for the carbonyl group is too high for an amide. It is in a reasonable place for a conjugated ester. While the NO_2 present in the formula suggests a possible nitro group, this cannot be the case because we need the two oxygens for the ester functional group. The doublet at about 3400 cm^{-1} in the infrared spectrum is perfect for a primary amine.

The ^{13}C NMR spectrum has nine peaks, which correspond to the nine carbon atoms in the molecular formula. The ester C=O carbon atom appears at 167 ppm. The remaining downfield carbons are attributed to the six unique aromatic ring carbons. From this, we know that the ring is not symmetrically substituted. The DEPT results confirm the presence of two carbon atoms with no attached protons (131 and 147 ppm) and four carbon atoms with one attached proton (116, 199, 120, and 129). From this information, we now know that the ring is disubstituted.

We must look carefully at the aromatic region between 6.8 and 7.5 ppm in the ^1H spectrum shown on page 526. Notice that there are four protons on the aromatic ring with each integrating for one proton each (see integral lines drawn on the ^1H spectrum). Since it is difficult to determine the splitting pattern for the protons shown in the ^1H spectrum shown on page 526, an expansion of the 6.8 to 7.5 ppm region is shown in the spectrum, above. The ring must be disubstituted because four protons appear on the aromatic ring. The pattern suggests a 1,3 disubstituted pattern rather than 1,4- or 1,2-disubstitution (see p. 292). The key observation is that proton **f** is a narrowly spaced triplet (or dd), suggesting ^4J couplings, but with no ^3J couplings. In other words, that proton must not have any adjacent protons! It is "sandwiched" between two non-proton groups: amino ($-NH_2$) and carbonyl

(C=O). Protons **g** and **f** appear down field relative to protons **e** and **d** because of the deshielding effect of the anisotropy of the C=O group (see p. 288). Although not as reliable as the proton NMR evidence, the aromatic out-of-plane bending bands in the infrared spectrum suggests *meta*-disubstitution: 680, 760, and 880 cm^{-1}.

The ^1H NMR spectrum shows an ethyl group because of the quartet and triplet found upfield in the spectrum (4.3 and 1.4 ppm, respectively, for the CH_2 and CH_3 groups). Finally, a broad NH_2 peak, integrating for two protons, appears in the Proton NMR spectrum at 3.8 ppm. The compound is ethyl 3-aminobenzoate.



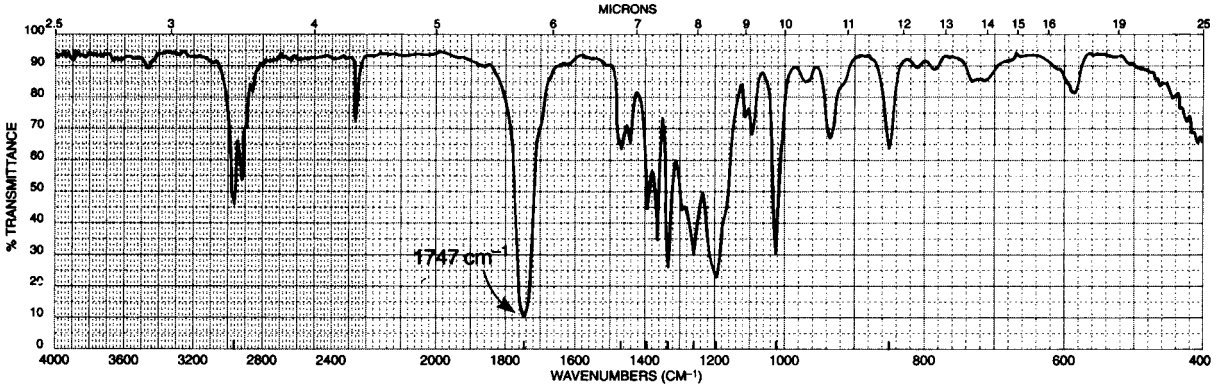
We need to look at the proton expansions provided in the problem to confirm the assignments made for the aromatic protons. The Hertz values shown on the expansions allow us the opportunity to obtain coupling constants that confirms the 1,3-disubstitution pattern. The splittings observed in the expansions can be explained by looking at the coupling constants ^3J and ^4J present in the compound. ^5J couplings are either zero or too small to be observed in the expansions.

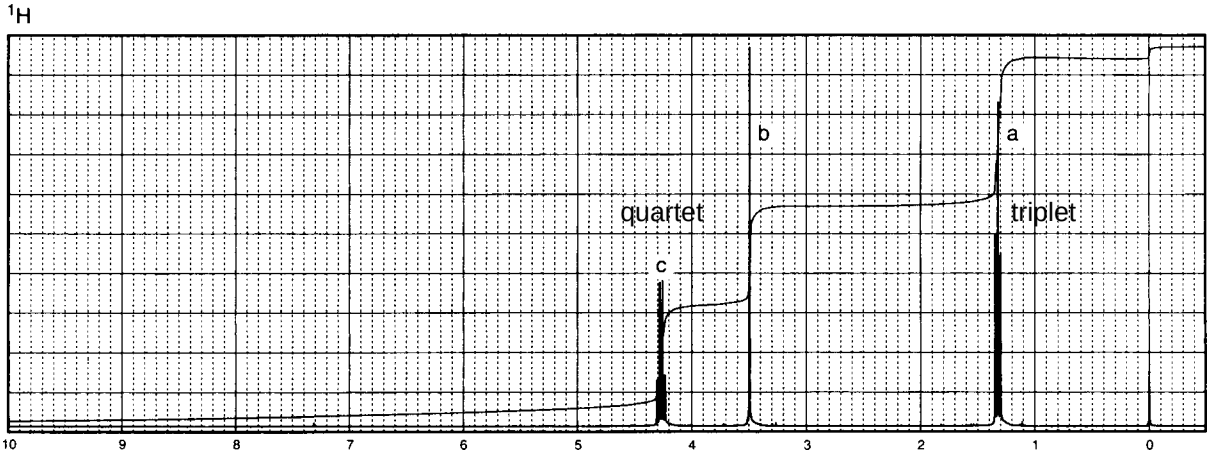
7.42 ppm (H_g)	Doublet of triplets (dt) or doublet of doublets of doublets (ddd); $^3J_{eg} = 7.8$ Hz, $^4J_{fg}$ and $^4J_{dg} \approx 1.5$ Hz.
7.35 ppm (H_f)	This proton is located between the two attached groups. The only proton couplings that are observed are small ^4J couplings that result in a closely spaced triplet or, more precisely, a doublet of doublets; $^4J_{fg}$ and $^4J_{df} \approx 1.5$ to 2 Hz.
7.19 ppm (H_e)	This proton appears as a widely spaced "triplet." One of the coupling constants, $^3J_{eg} = 7.8$ Hz, was obtained from the pattern at 7.42 ppm. The other coupling constant, $^3J_{de} = 8.1$ Hz, was obtained from the pattern at 6.84 ppm. The pattern appears as a triplet because the coupling constants are nearly equal, resulting in an accidental overlap of the center peak in the "triplet." More precisely, we should describe this "triplet" as a doublet of doublets (dd).
6.84 ppm (H_d)	Doublet of doublets of doublets (ddd); $^3J_{de} = 8.1$ Hz, $^4J_{dg} \neq {}^4J_{df}$.

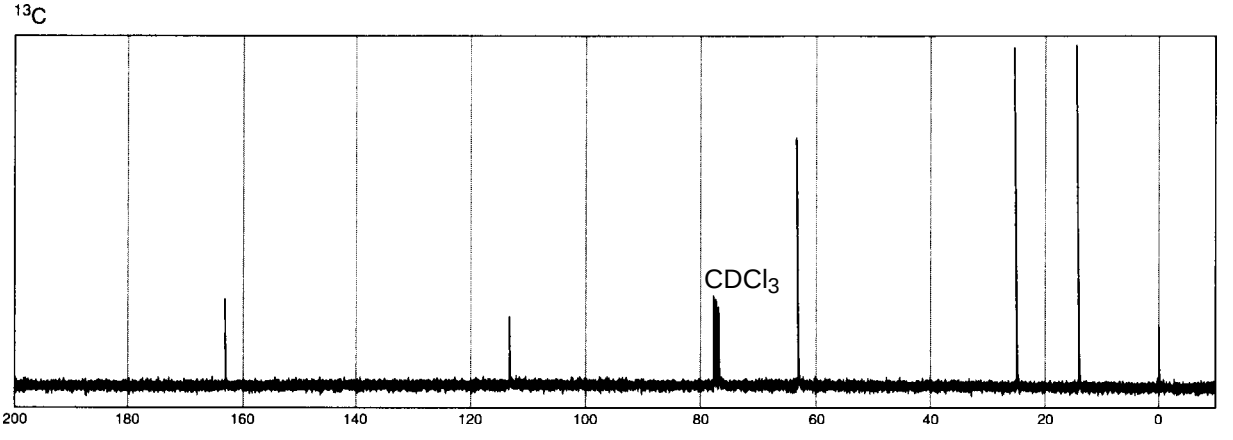
EXAMPLE 4

Problem

This compound has the molecular formula $C_5H_7NO_2$. Following are the infrared, ^1H NMR, and ^{13}C NMR spectra.



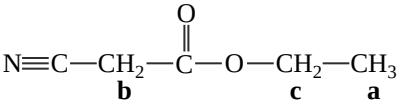




Solution

We calculate an index of hydrogen deficiency of three. A quick glance at the infrared spectrum reveals the source of unsaturation implied by an index of three: a nitrile group at 2260 cm^{-1} (unsaturation index = two) and a carbonyl group at 1747 cm^{-1} (unsaturation index = one). The frequency of the carbonyl absorption indicates an unconjugated ester. The appearance of several strong C−O bands near 1200 cm^{-1} confirms the presence of an ester functional group. We can rule out a C≡C bond because they usually absorb at a lower value (2150 cm^{-1}) and have a weaker intensity than compounds that contain C≡N.

The ^{13}C NMR spectrum shows five peaks and thus is consistent with the molecular formula, which contains five carbon atoms. Notice that the carbon atom in the C≡N group has a characteristic value of 113 ppm. In addition, the carbon atom in the ester C=O appears at 163 ppm. One of the remaining carbon atoms (63 ppm) probably lies next to an electronegative oxygen atom. The remaining two carbon atoms, which absorb at 25 and 14 ppm, are attributed to the remaining methylene and methyl carbons. The structure is

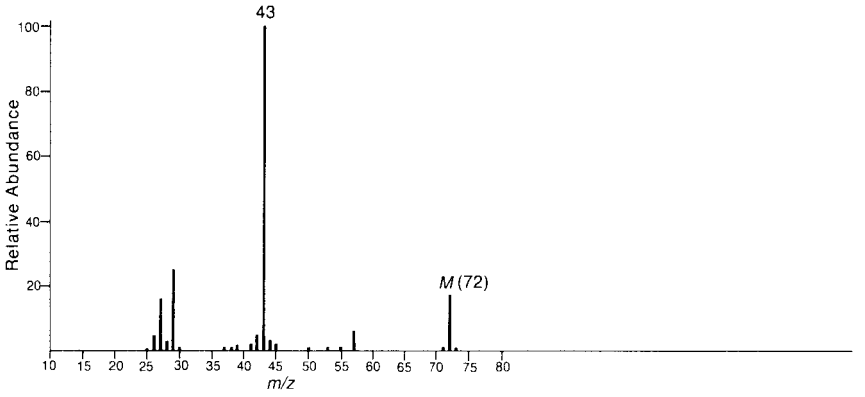


The ^{1}H NMR spectrum shows a classic ethyl pattern: a quartet (2 H) at 4.3 ppm and a triplet (3 H) at 1.3 ppm. The quartet is strongly influenced by the electronegative oxygen atom, which shifts it downfield. There is also a two-proton singlet at 3.5 ppm.

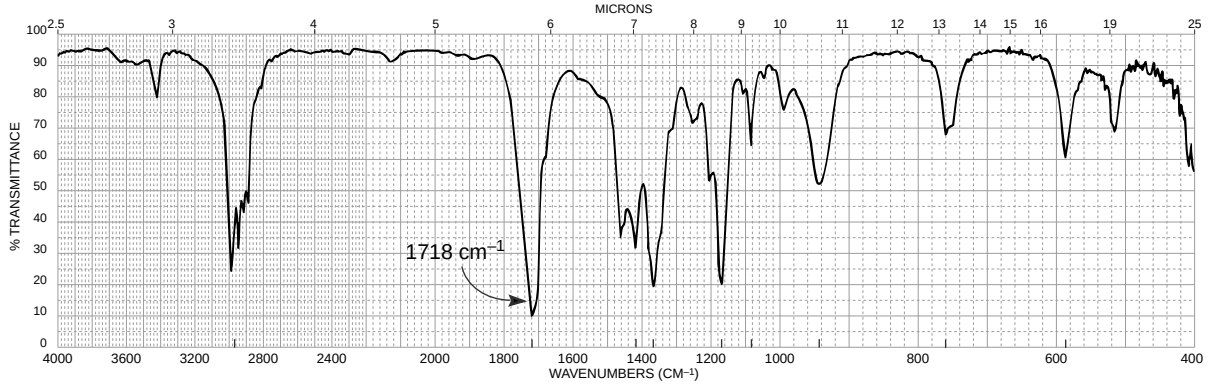
PROBLEMS

***1.** The UV spectrum of this compound is determined in 95% ethanol: λ_{max} 290 nm (log ε =1.3).

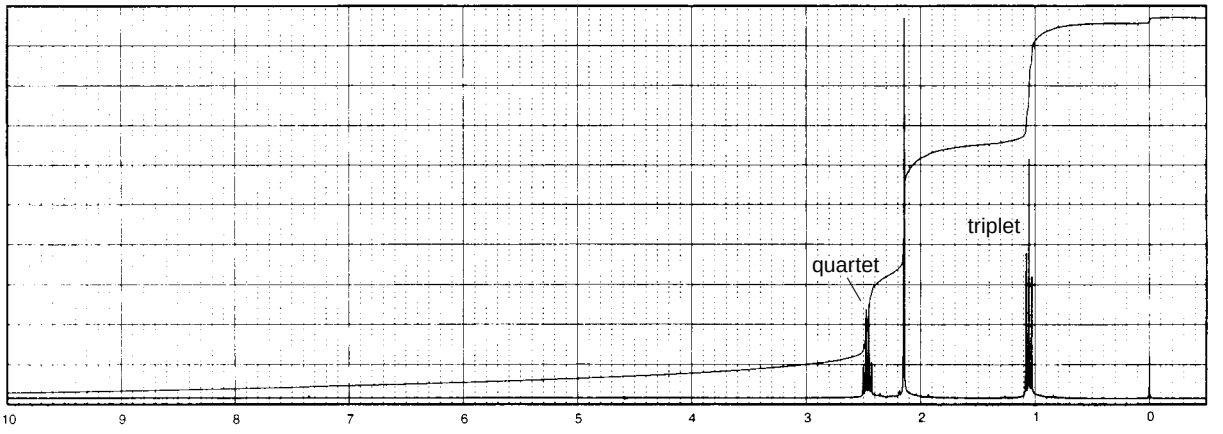
(a)



(b)

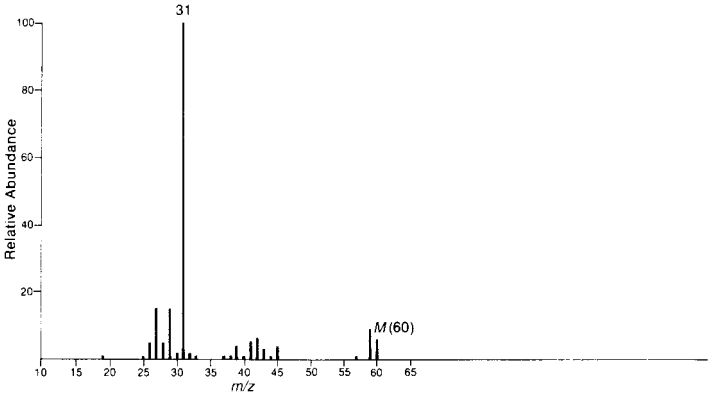


(c)

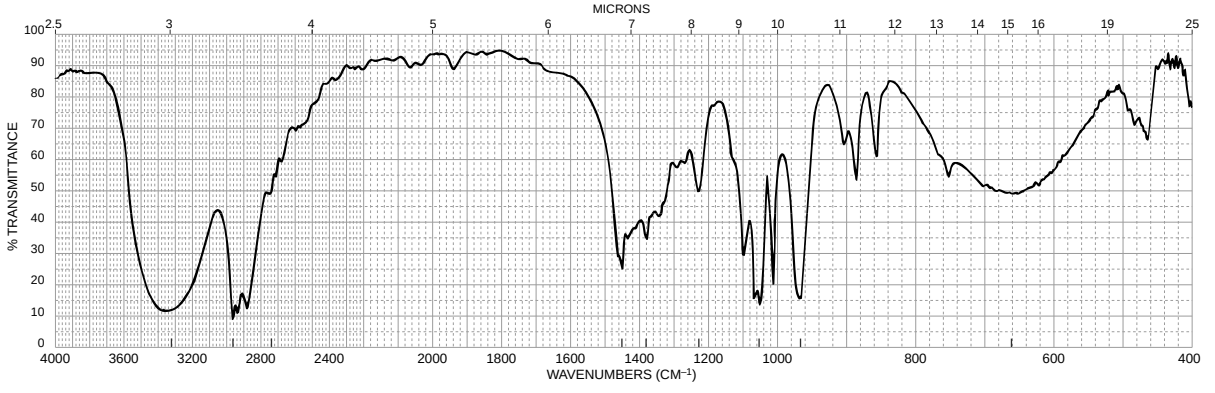


***2.** The UV spectrum of this compound shows no maximum above 205 nm. When a drop of aqueous acid is added to the sample, the pattern at 3.6 ppm in the ^{1}H NMR spectrum simplifies to a triplet, and the pattern at 3.2 ppm simplifies to a singlet.

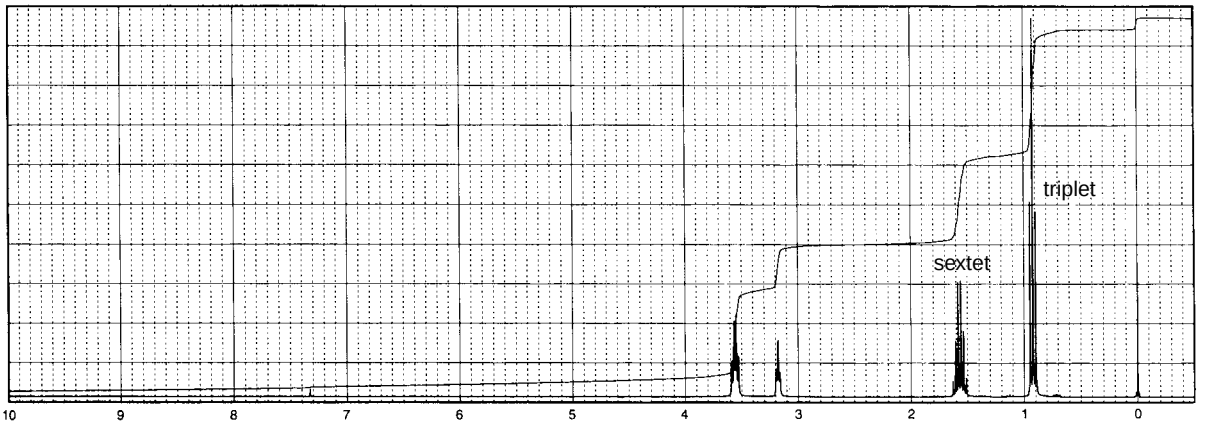
(a)



(b)

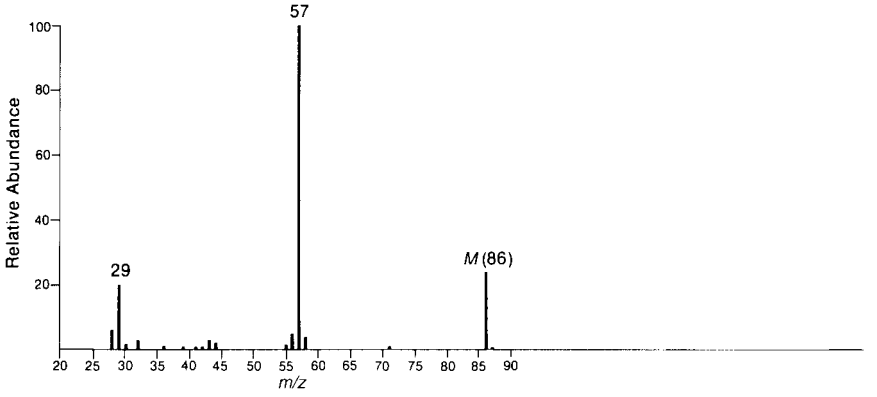


(c)



***3.** UV spectrum of this compound is determined in 95% ethanol: λ_{max} 280 nm (log $\varepsilon = 1.3$).

(a)



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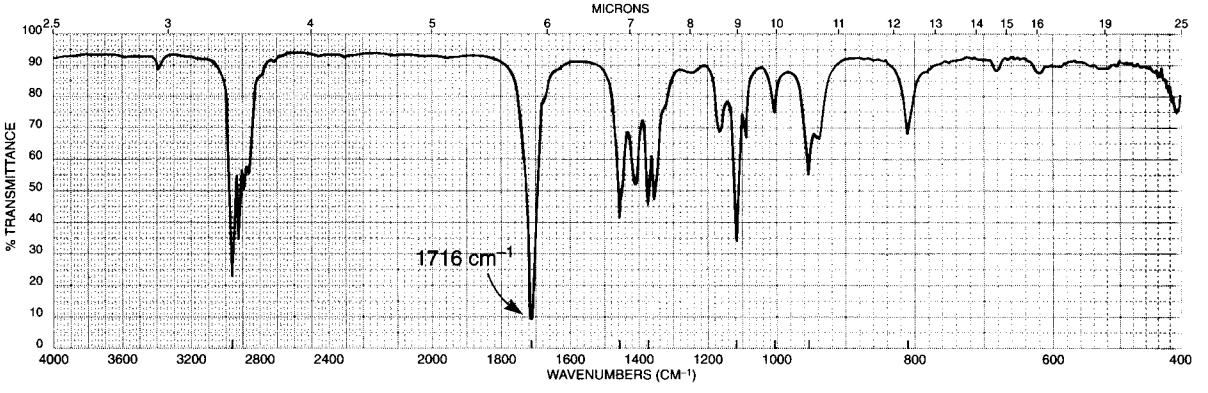
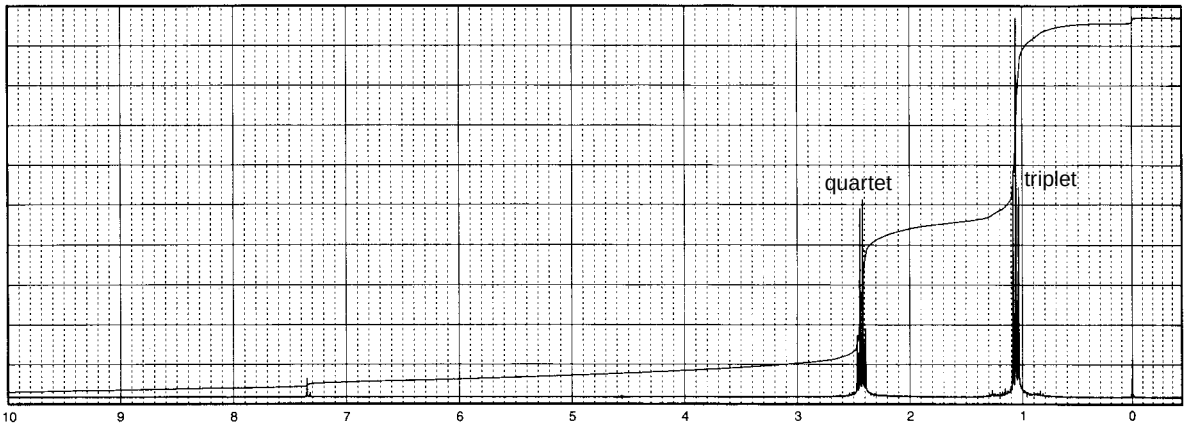
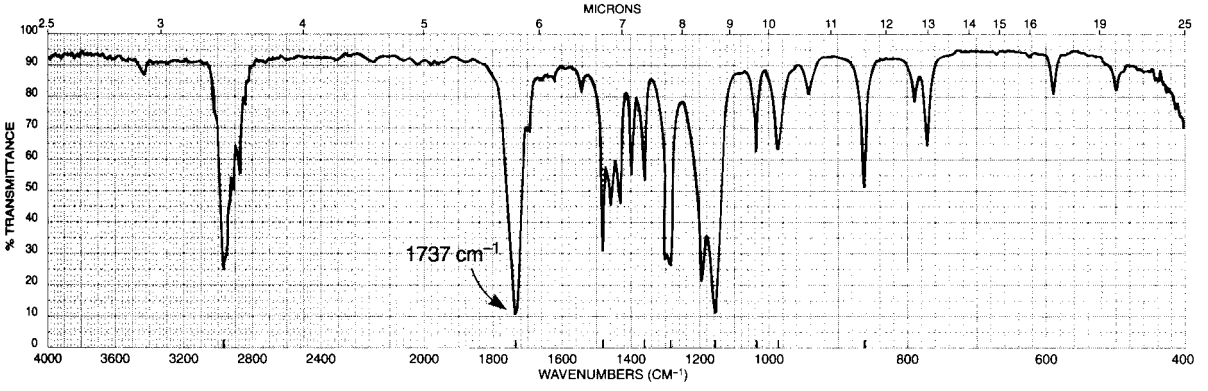


(c)

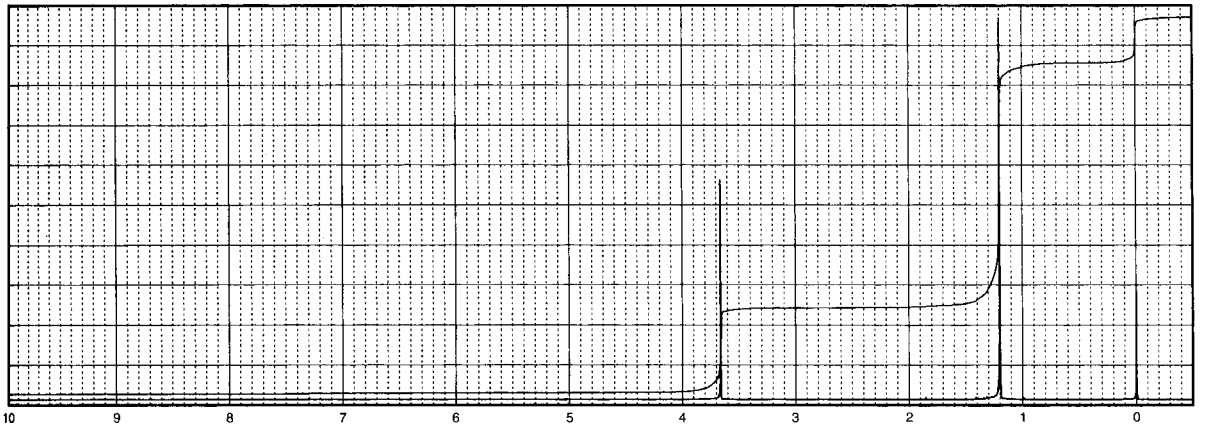


***4.** The formula for this compound is $C_6H_{12}O_2$.

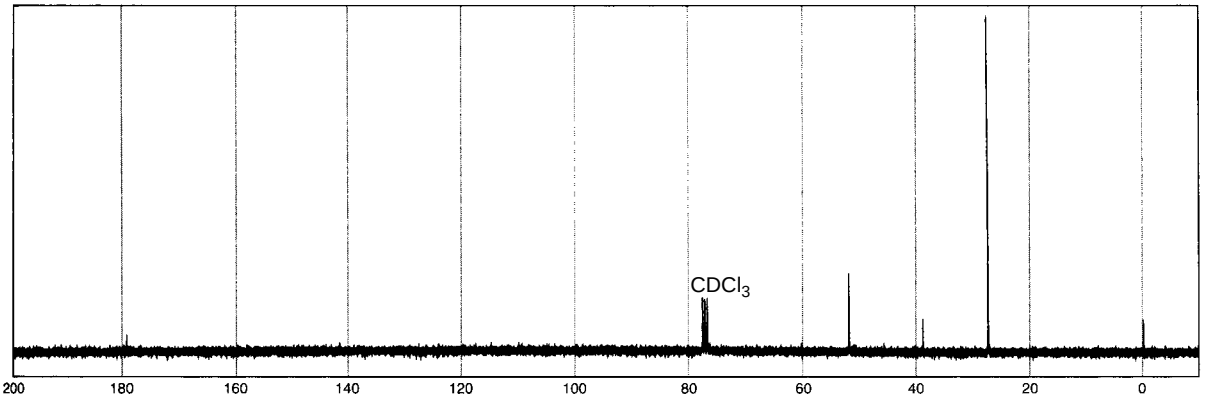
(a)



(b)

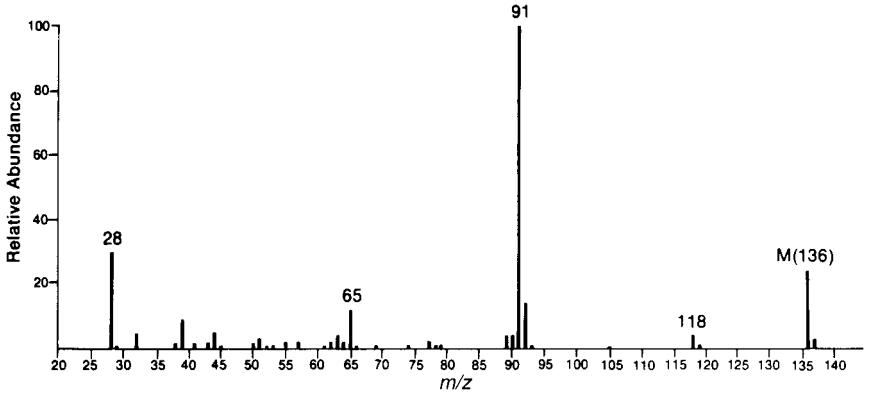


(c)

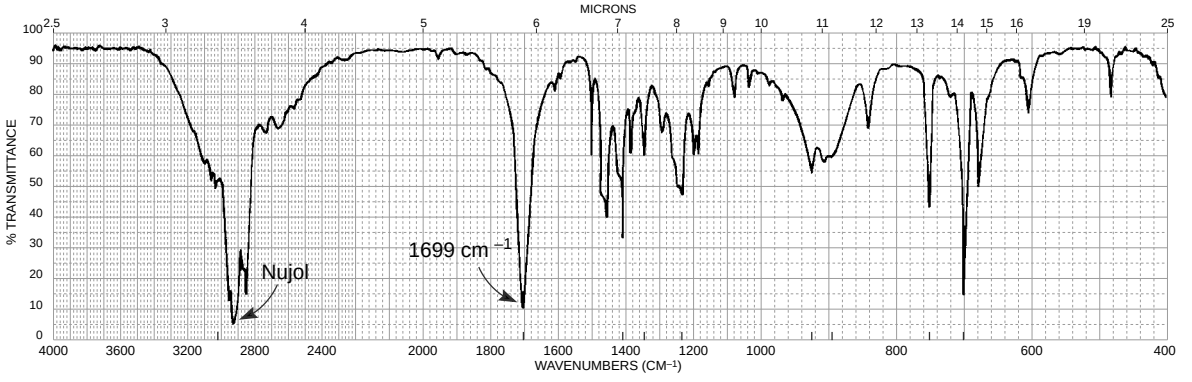


***5.** The UV spectrum of this compound is determined in 95% ethanol: strong end absorption and a band with fine structure appearing at λ_{max} 257 nm (log $\varepsilon = 2.4$). The IR spectrum was obtained as a Nujol mull. The strong bands at about 2920 and 2860 cm^{-1} from the C—H stretch in Nujol overlap the broad band that extends from 3300 to 2500 cm^{-1}.

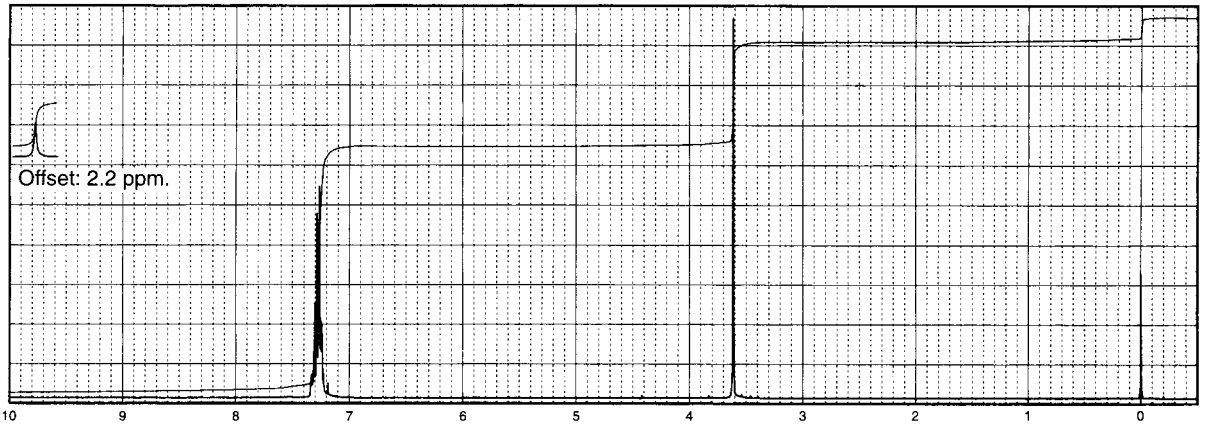
(a)



(b)

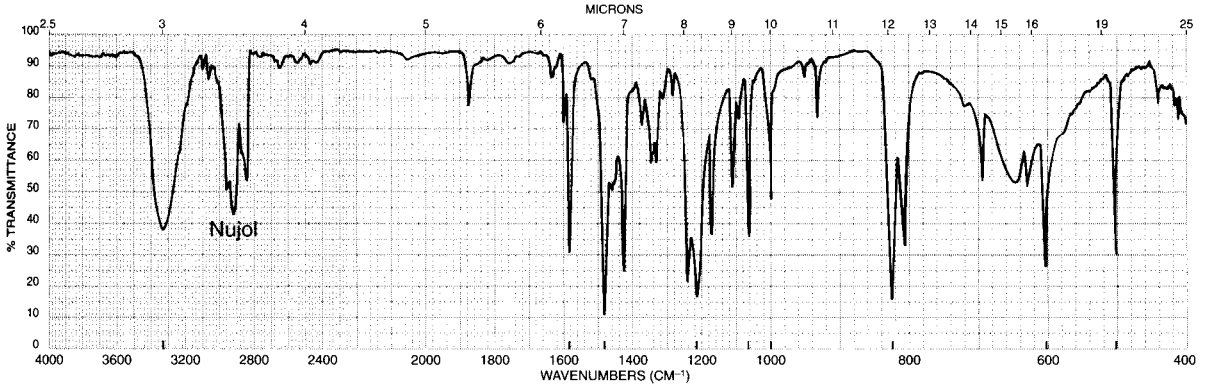


(c)

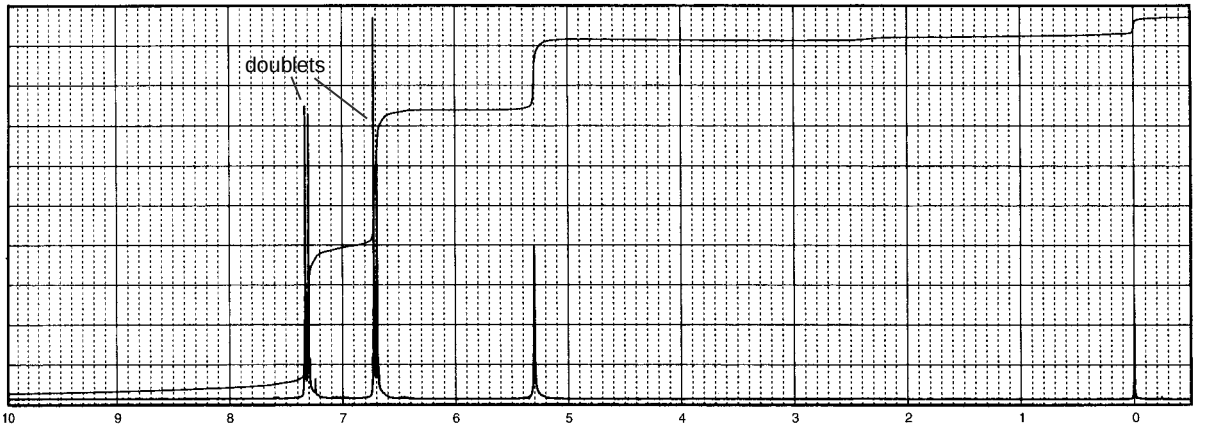


***6.** The mass spectrum of this compound shows an intense molecular ion at 172 mass units and an $M + 2$ peak of approximately the same size. The IR spectrum of this solid unknown was obtained in Nujol. The prominent C—H stretching bands centering on about 2900 cm^{-1} are derived from the Nujol and are not part of the unknown. The peak appearing at about 5.3 ppm in the ^1H NMR spectrum is solvent dependent. It shifts readily when the concentration is changed.

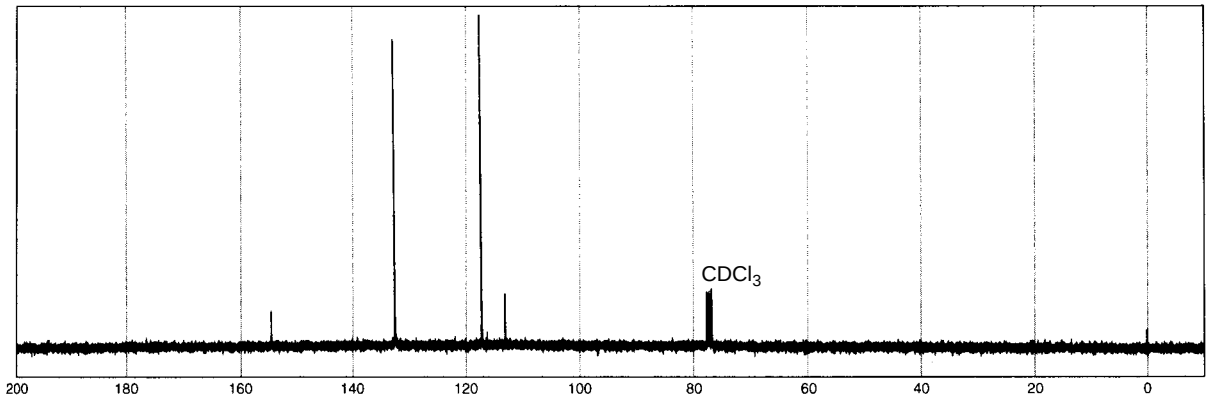
(a)



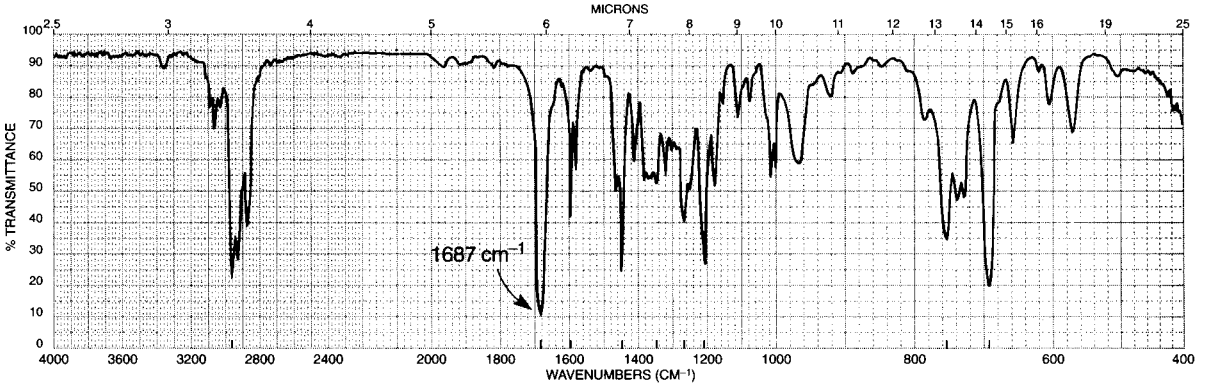
(b)



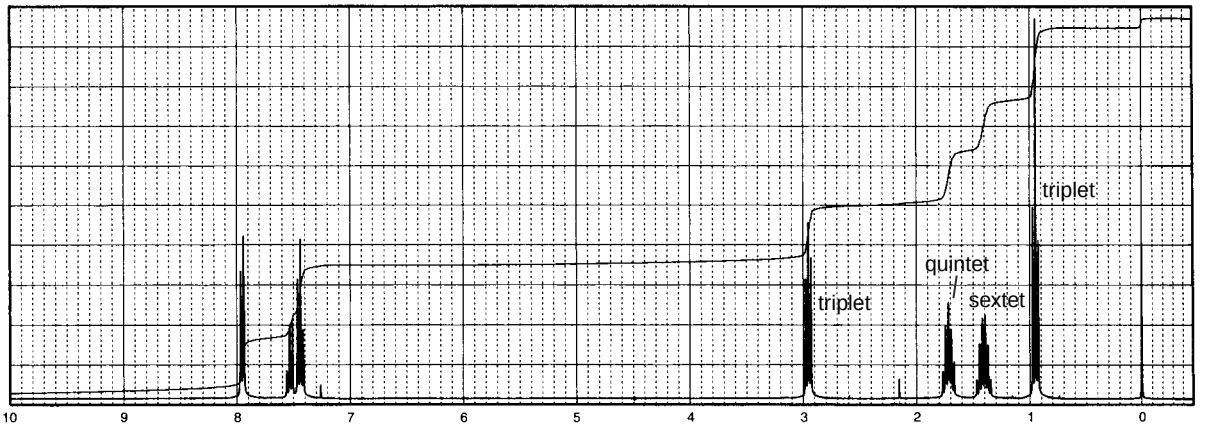
(c)

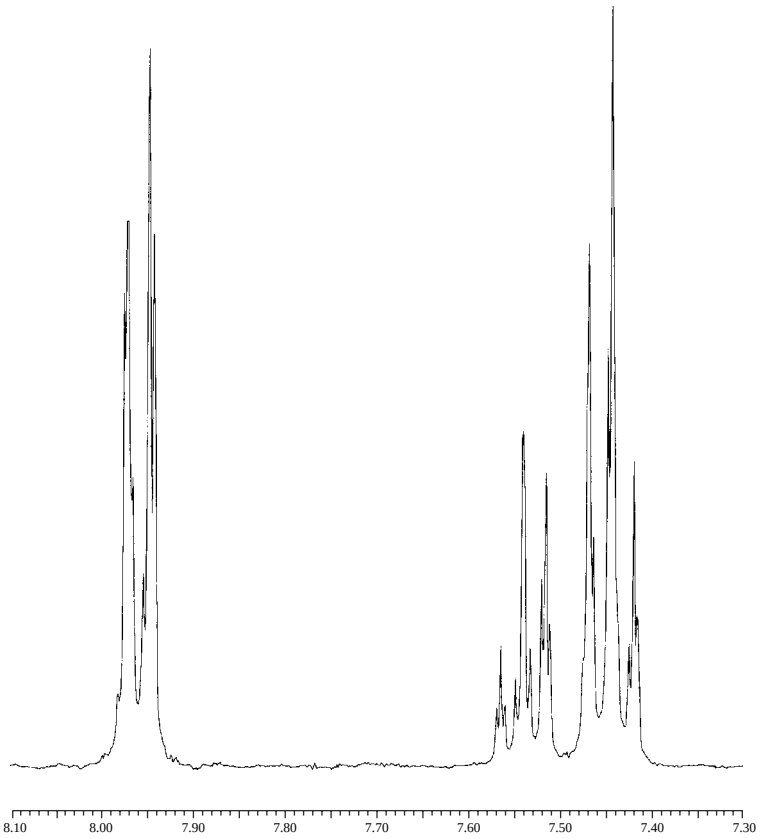


***7.** This compound has the molecular formula $C_{11}H_{14}O$.



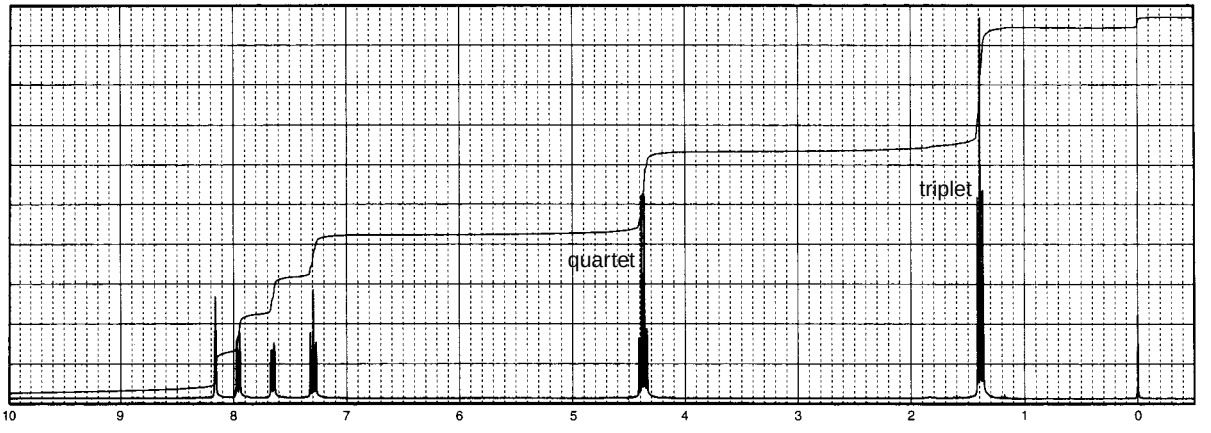
Normal Carbon	DEPT-135	DEPT-90
14 ppm	Positive	No peak
22	Negative	No peak
26	Negative	No peak
38	Negative	No peak
128	Positive	Positive
129	Positive	Positive
133	Positive	Positive
137	No peak	No peak
200	No peak	No peak

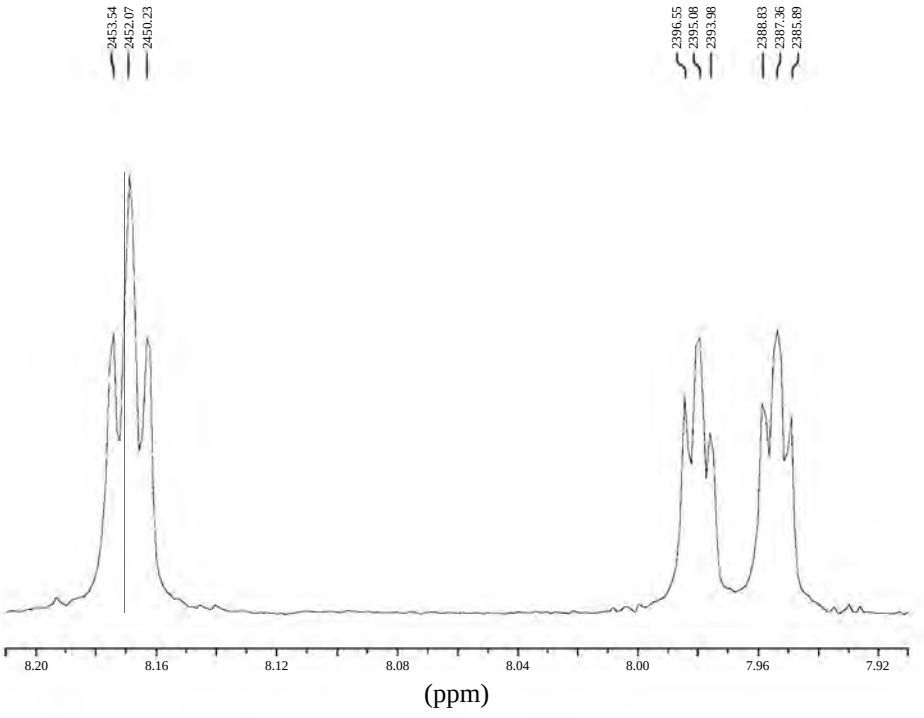


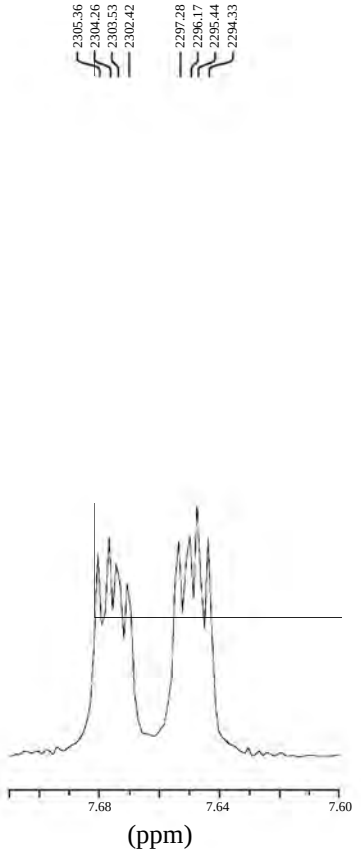


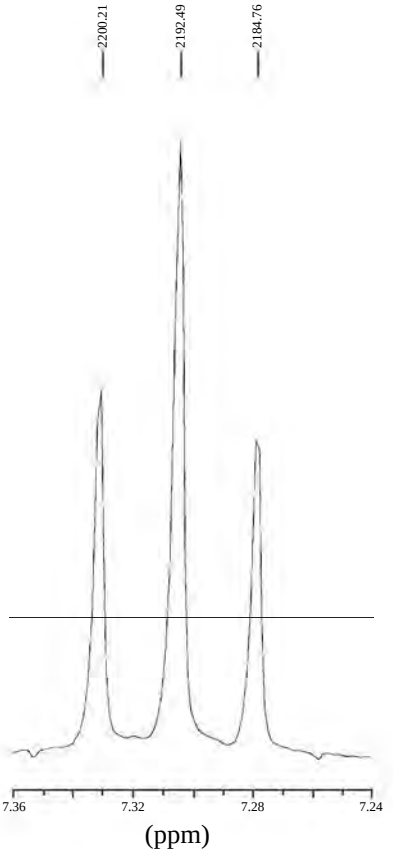
8.** Determine the structures of the isomeric compounds that show strong infrared bands at 1725 cm^{-1} and several strong bands in the range 1300–1200 cm^{-1}. Each isomer has the formula $C_9H_9BrO_2$. Following are the ^1H NMR spectra for both compounds, ***A and ***B***. Expansions have been included for the region from 8.2 to 7.2 ppm for compound ***A***.

A.

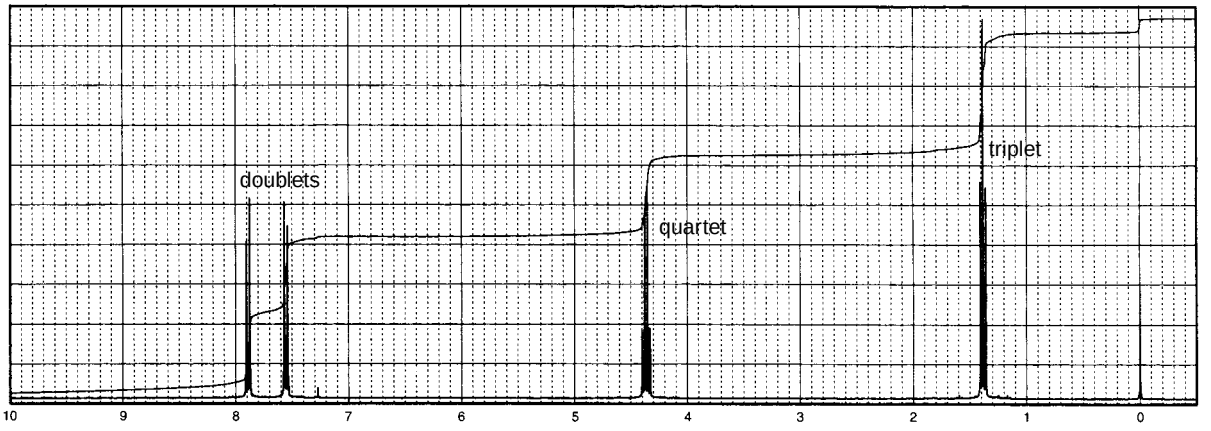



2453.54
2452.07
2450.23
2396.55
2395.08
2393.98
2388.83
2387.36
2385.89
8.20
8.16
8.12
8.08
8.04
8.00
7.96
7.92
(ppm)


2305.36
2304.26
2303.53
2302.42
2297.28
2296.17
2295.44
2294.33
7.68
7.64
7.60
(ppm)

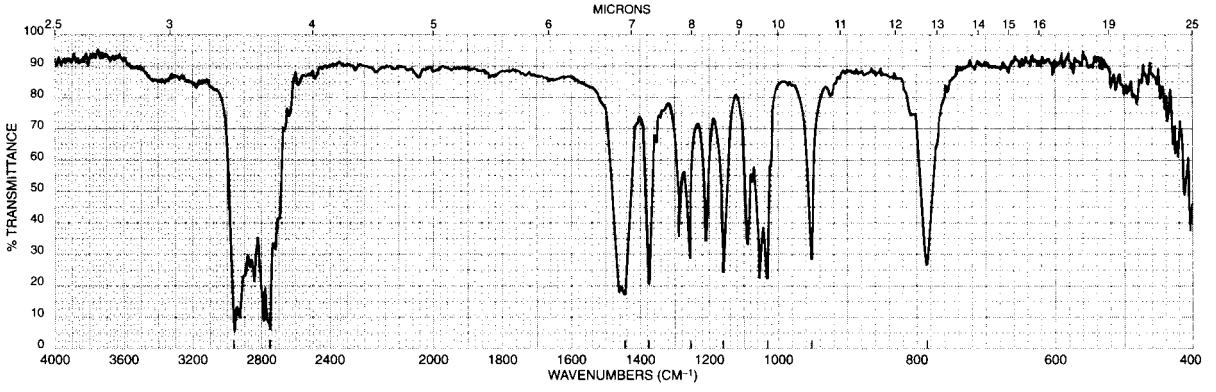

2200.21
2192.49
2184.76
7.36
7.32
7.28
7.24
(ppm)

B.

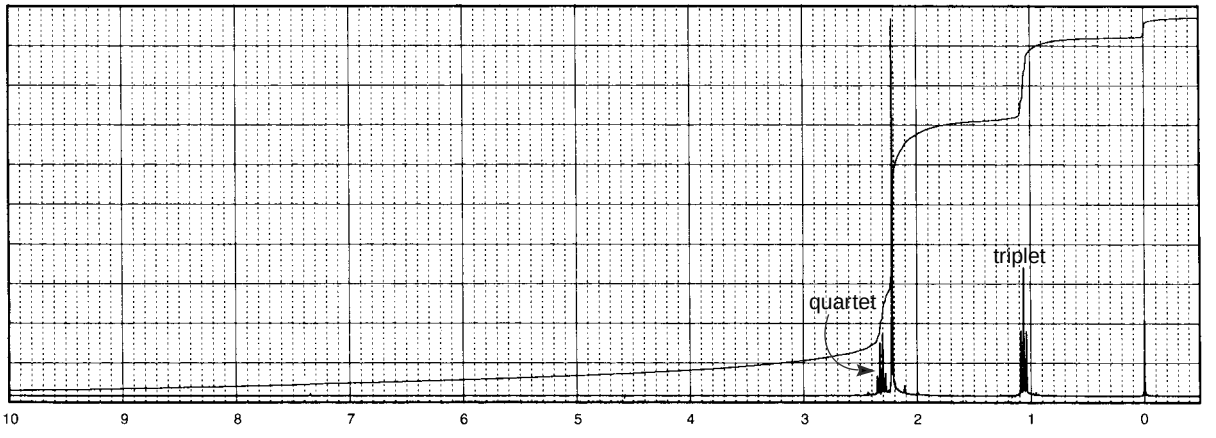


***9.** This compound has the molecular formula $C_4H_{11}N$.

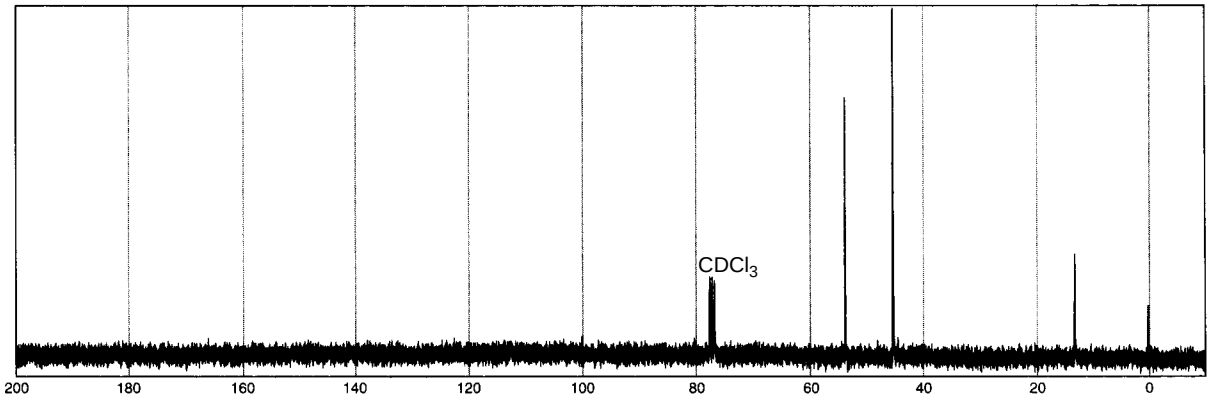
(a)



(b)

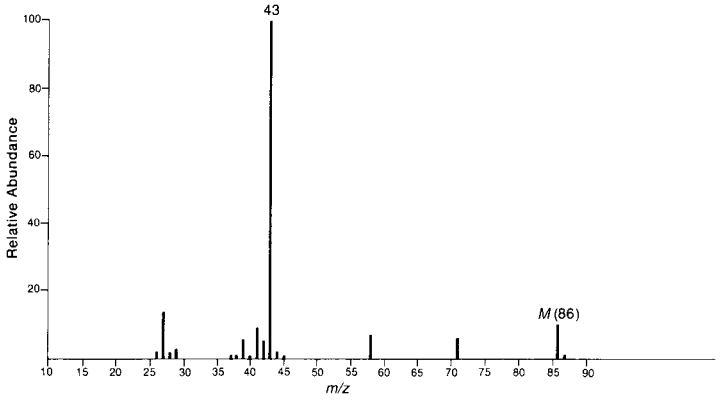


(c)

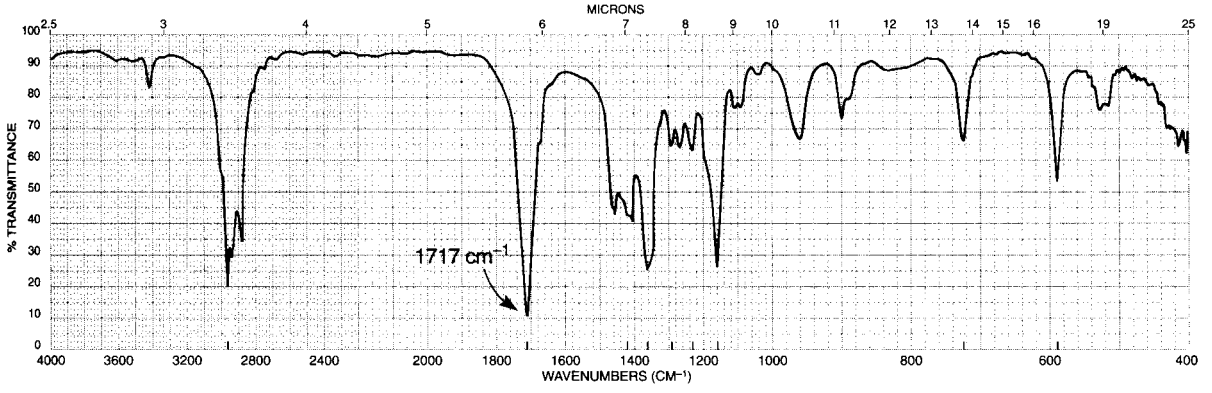


***10.** The UV spectrum of this compound is determined in 95% ethanol: λ_{max} 280 nm (log ε = 1.3). This compound has the formula $C_5H_{10}O$.

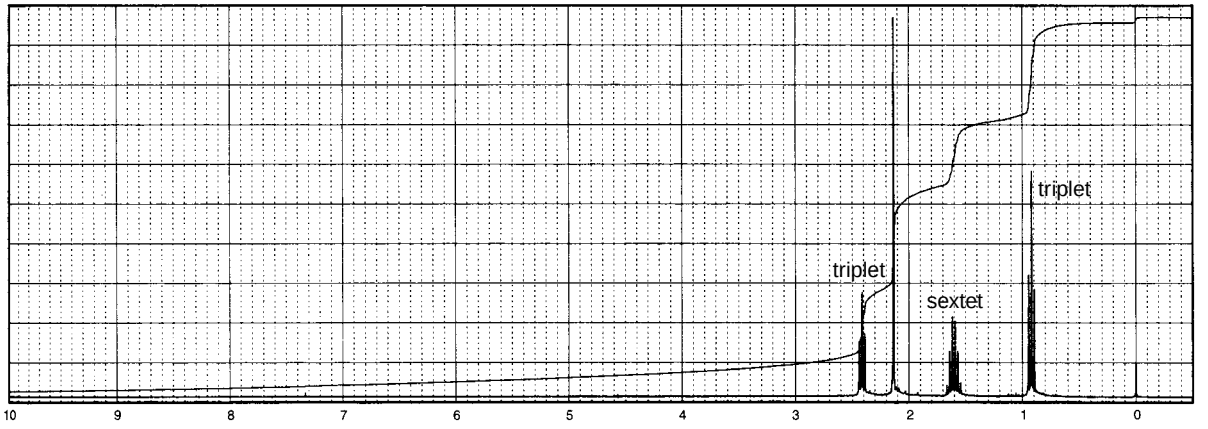
(a)



(b)

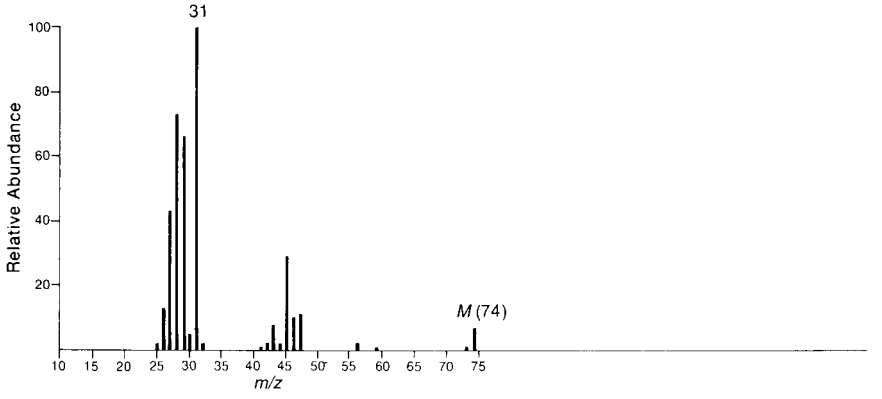


(c)

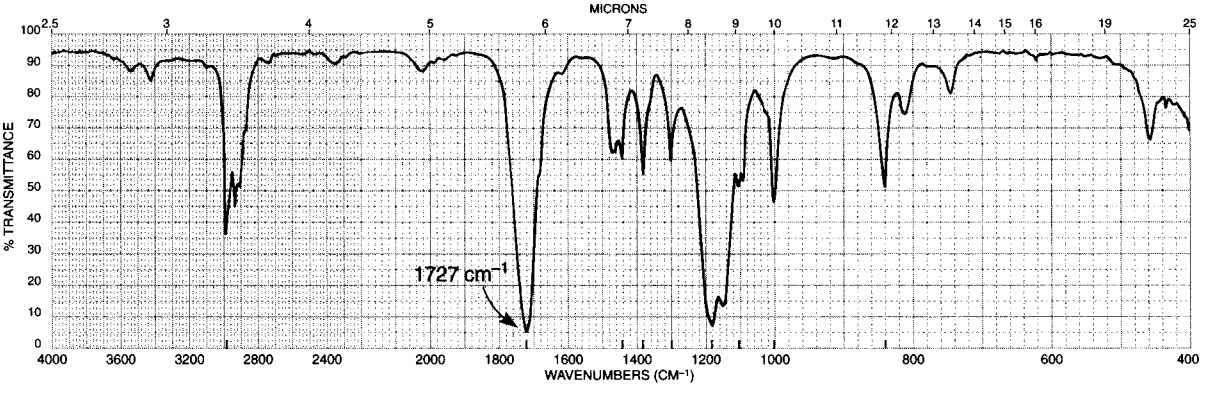


***11.** This compound has the formula $C_3H_6O_2$. The UV spectrum of this compound shows no maximum above 205 nm. The ^{13}C NMR spectrum shows peaks at 14, 60, and 161 ppm. The peak at 161 ppm appears as a positive peak in the DEPT-90 spectrum.

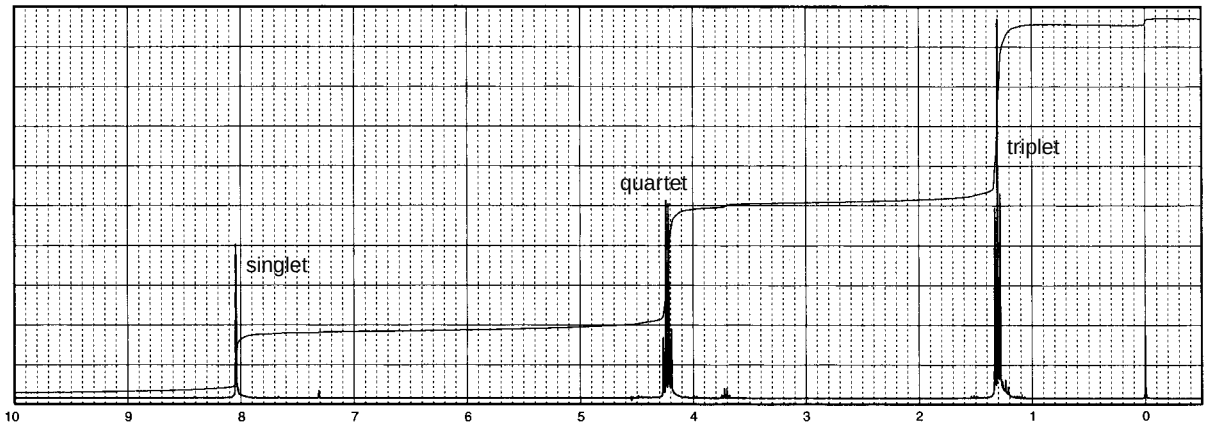
(a)



(b)

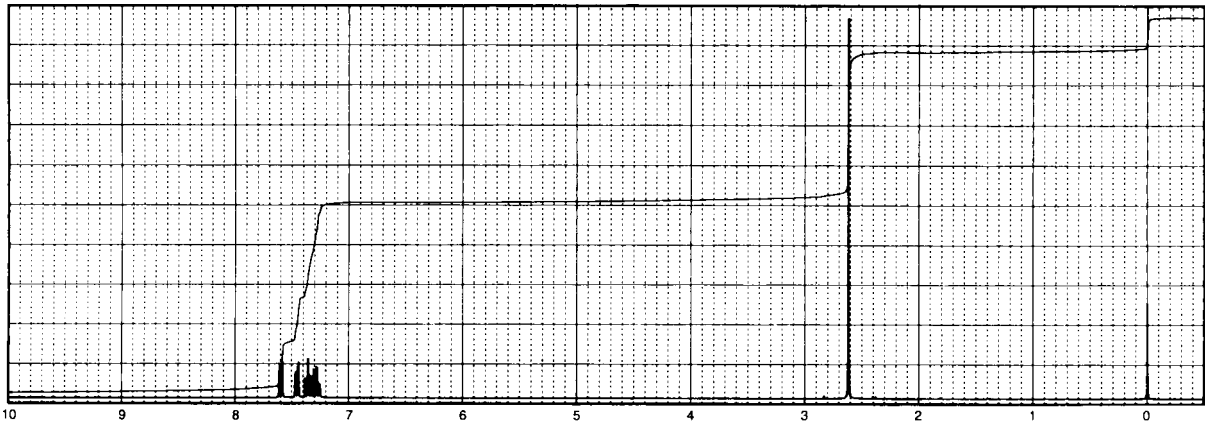


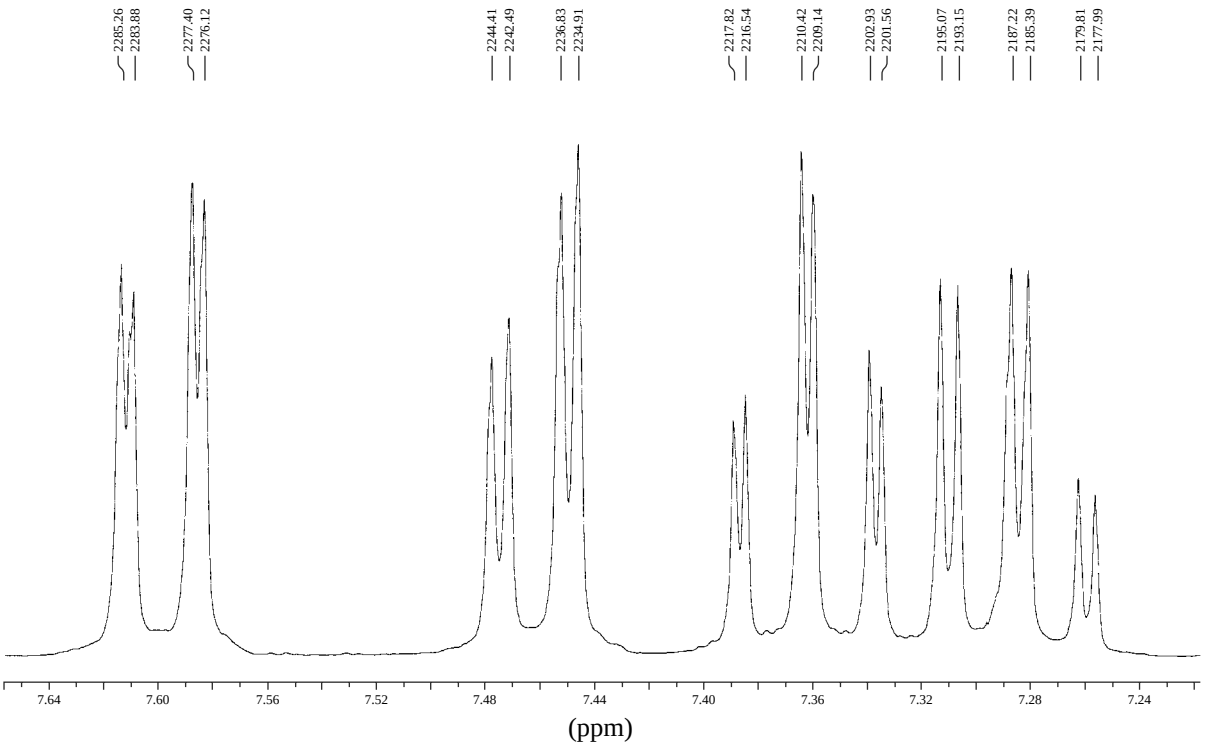
(c)



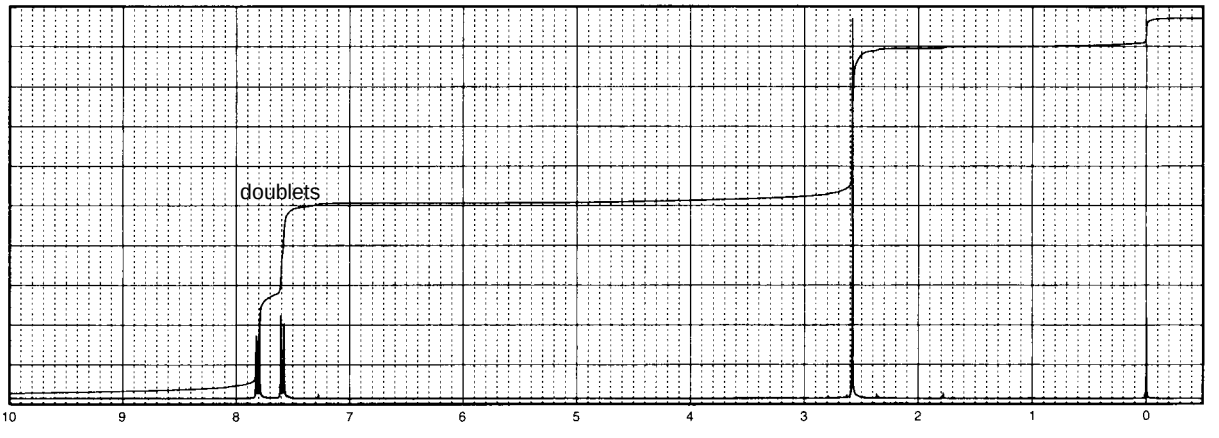
12.** Determine the structures of the isomeric compounds ***A and ***B***, each of which has the formula C_8H_7BrO. The infrared spectrum for compound ***A*** has a strong absorption band at 1698 cm^{-1}, while compound ***B*** has a strong band at 1688 cm^{-1}. The ^1H NMR spectrum for compound ***A*** is shown, along with expansions for the region from 7.7 to 7.2 ppm. The ^1H NMR spectrum of compound ***B*** is also shown.

A.

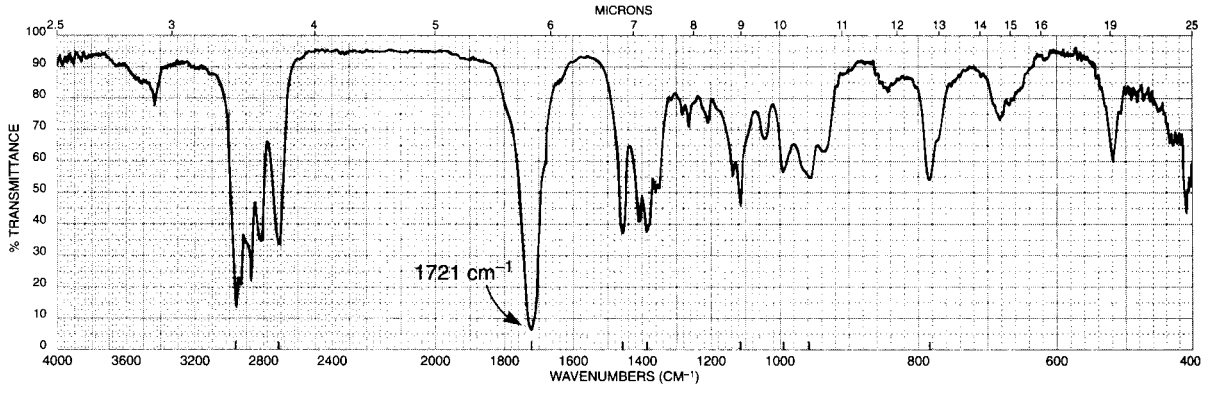


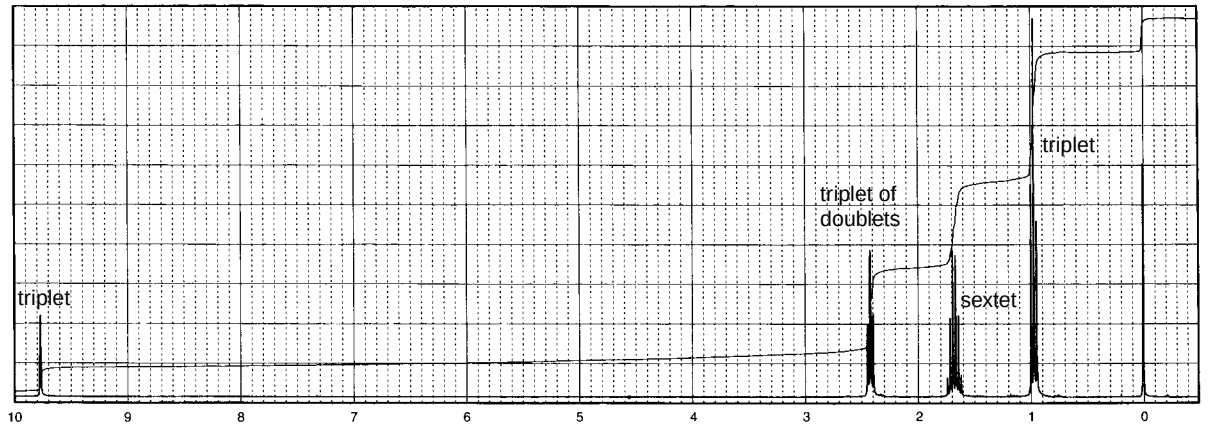

2285.26
2283.88
2277.40
2276.12
2244.41
2242.49
2236.83
2234.91
2217.82
2216.54
2210.42
2209.14
2202.93
2201.56
2195.07
2193.15
2187.22
2185.39
2179.81
2177.99
7.64
7.60
7.56
7.52
7.48
7.44
7.40
7.36
7.32
7.28
7.24
(ppm)

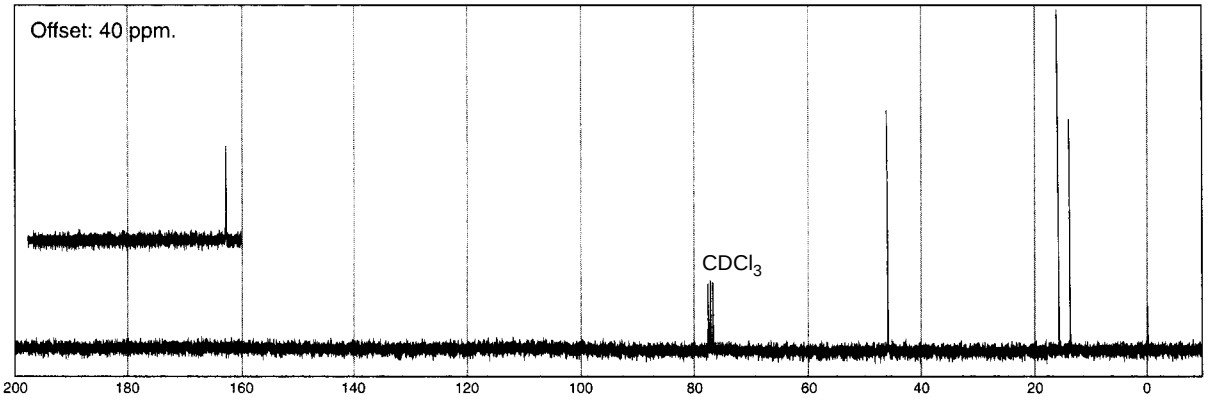
B.


doublets
10
9
8
7
6
5
4
3
2
1
0

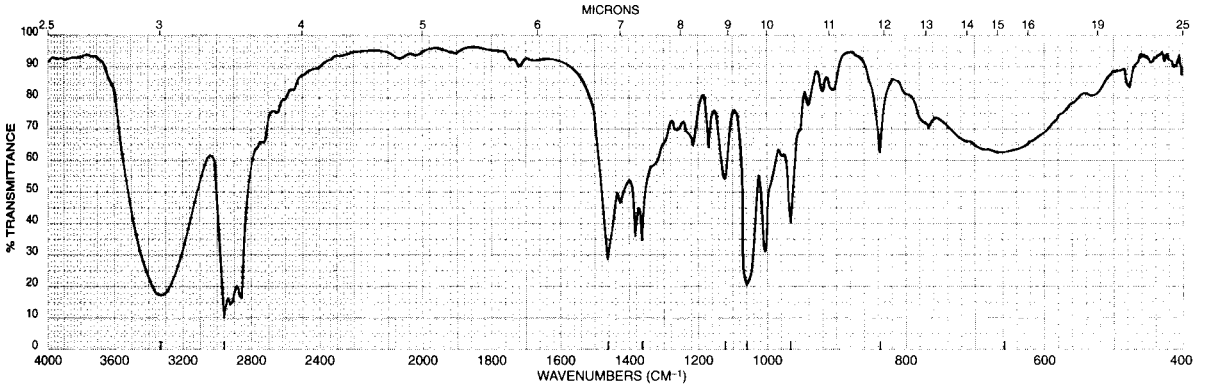
***13.** This compound has the formula C_4H_8O. When expanded, the singlet peak at 9.8 ppm in the ^1H NMR spectrum is actually a triplet. The triplet pattern at 2.4 ppm turns out to be a triplet of doublets when expanded.

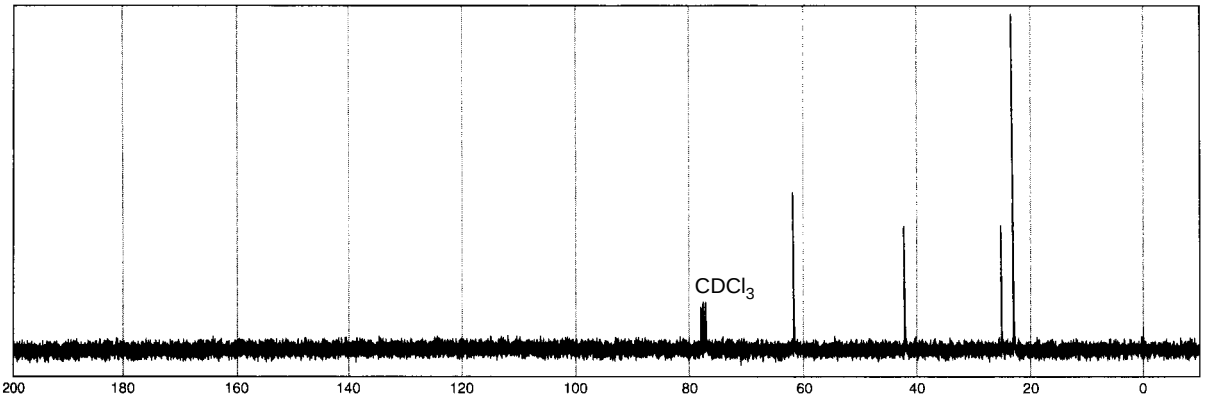




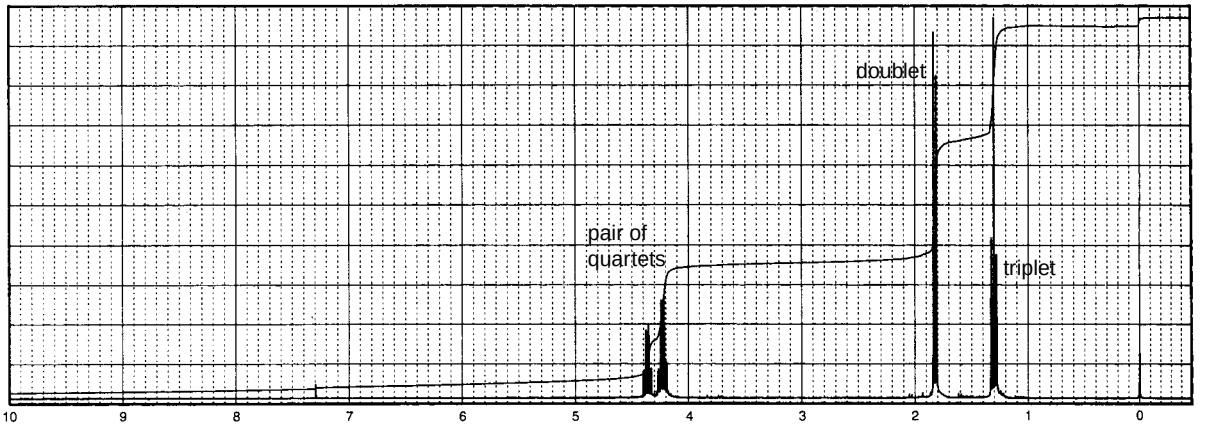


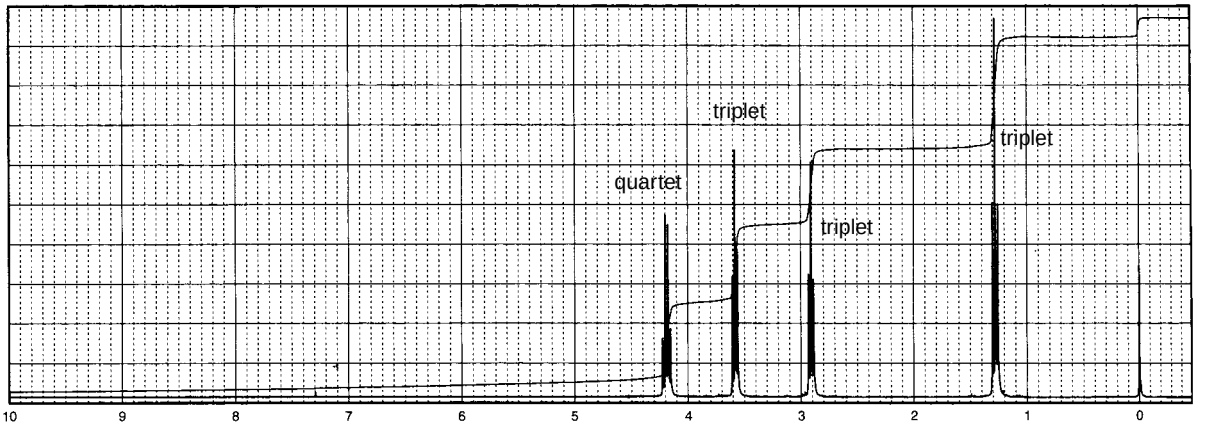
***14.** This compound has the formula $C_5H_{12}O$. When a trace of aqueous acid is added to the sample, the ^1H NMR spectrum resolves into a clean triplet at 3.6 ppm, and the broad peak at 2.2 ppm moves to 4.5 ppm.



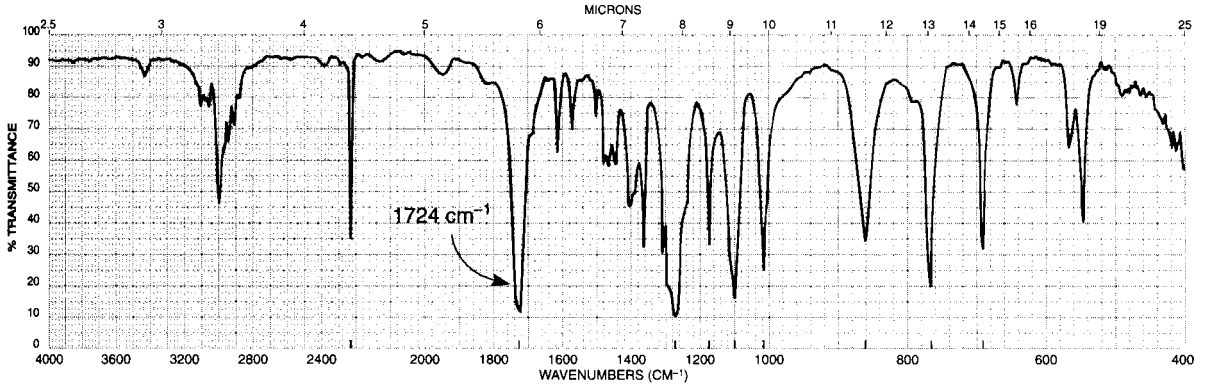


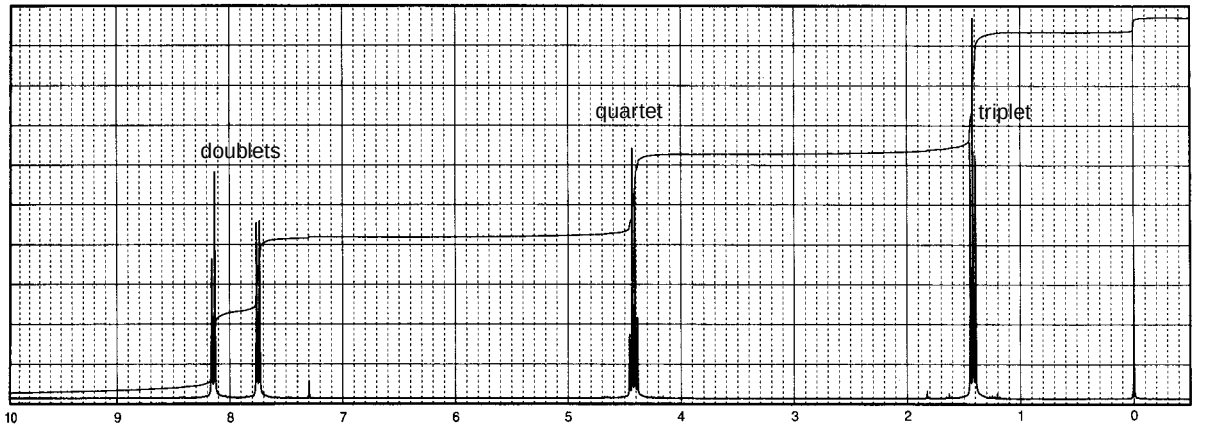
***15.** Determine the structures of the isomeric compounds with the formula $C_5H_9BrO_2$. The ^1H NMR spectra for both compounds follow. The IR spectrum corresponding to the first ^1H NMR spectrum has strong absorption bands at 1739, 1225, and 1158 cm^{-1}, and that corresponding to the second one has strong bands at 1735, 1237, and 1182 cm^{-1}.

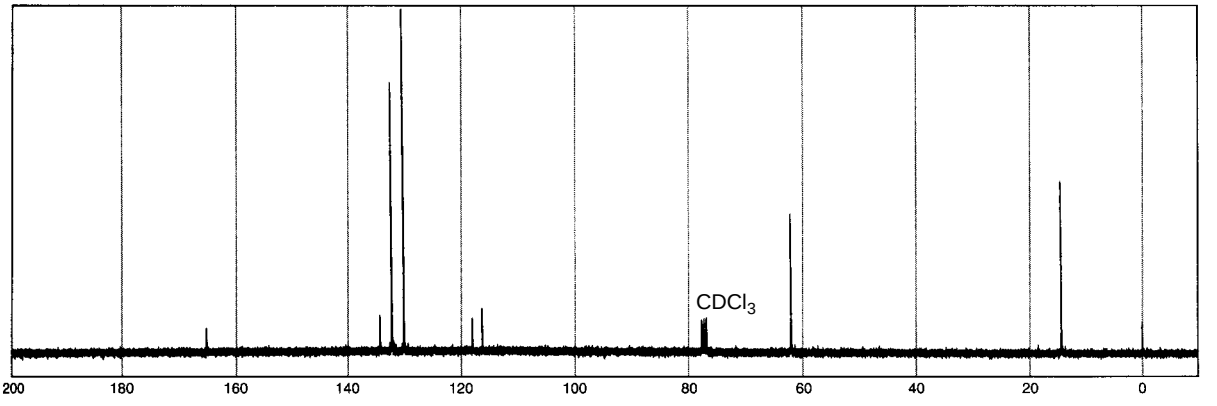




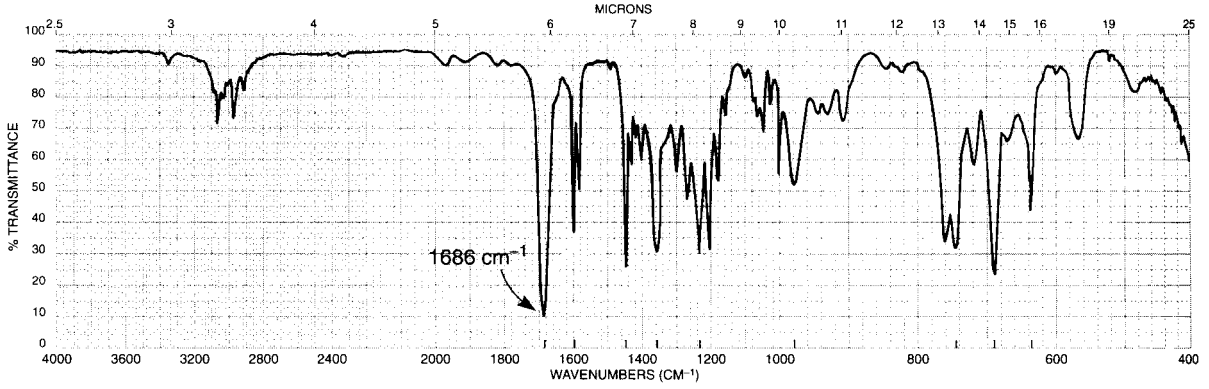
***16.** This compound has the molecular formula $C_{10}H_9NO_2$.

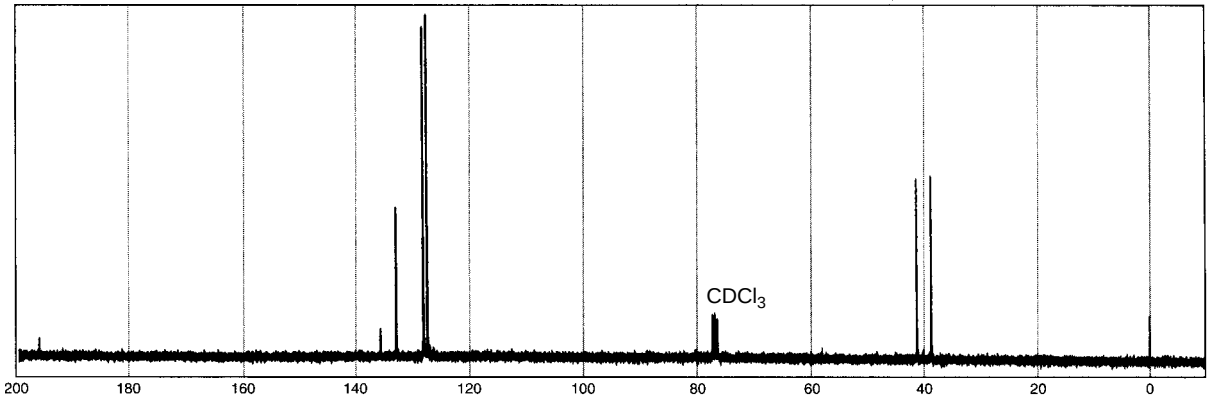


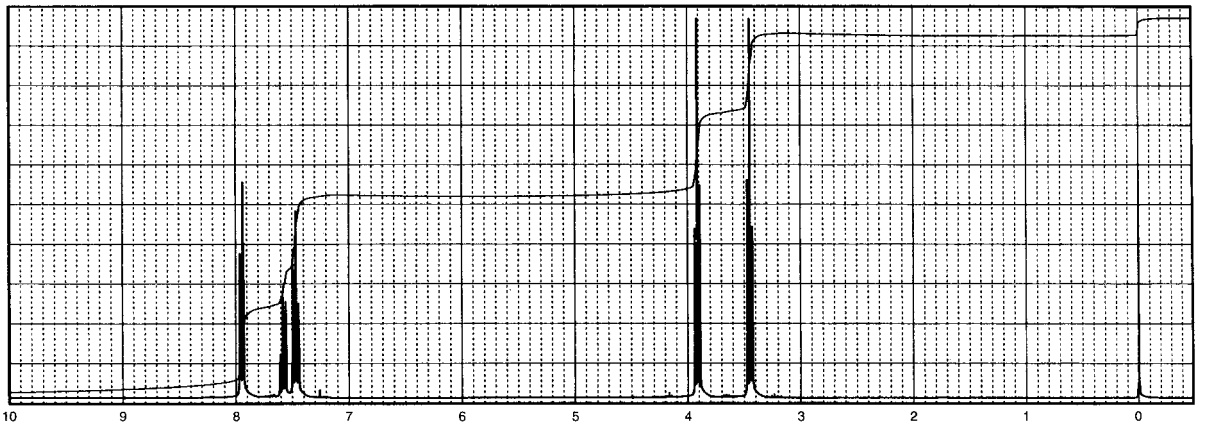


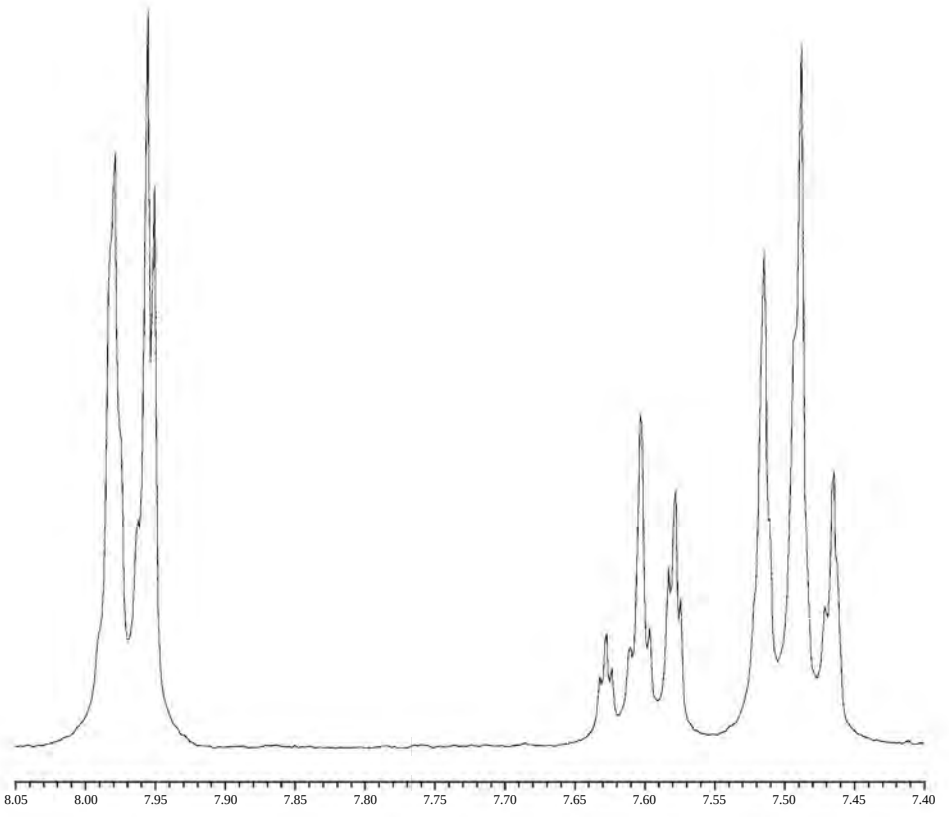


***17.** This compound has the formula C_9H_9ClO. The full ^1H NMR spectrum is shown along with expansions of individual patterns.

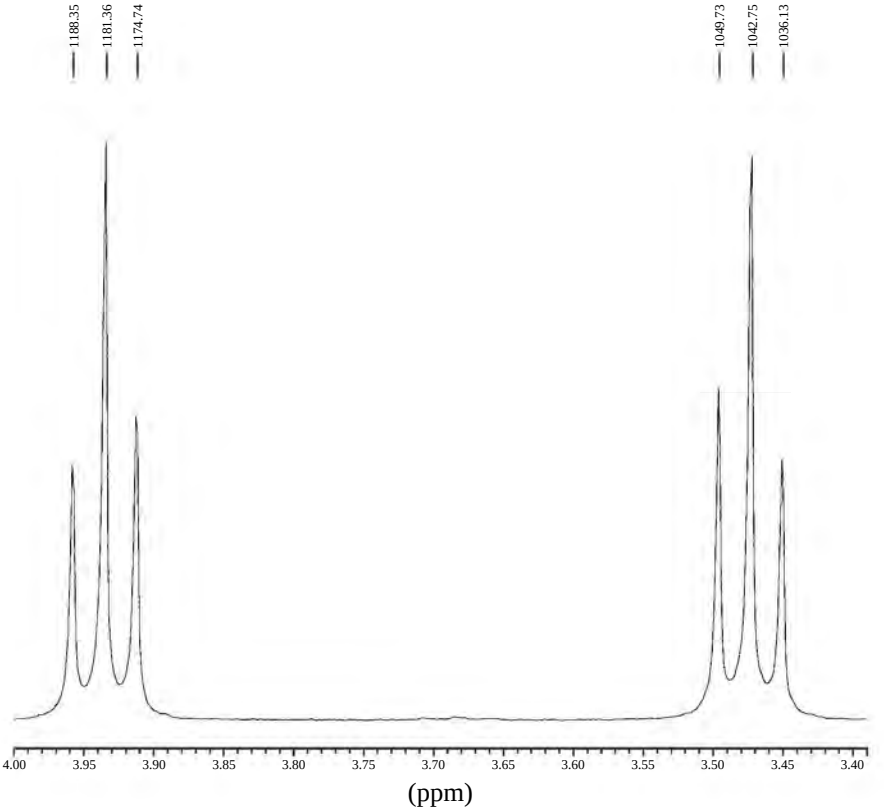






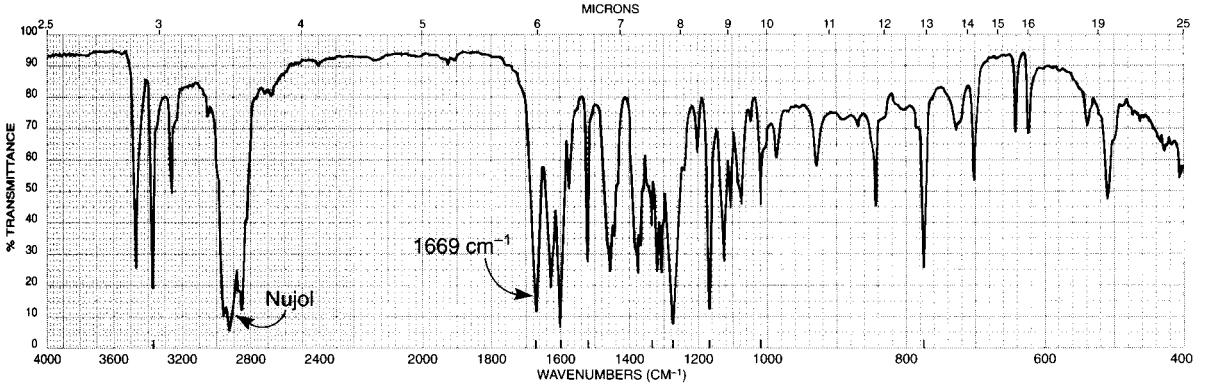

8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40

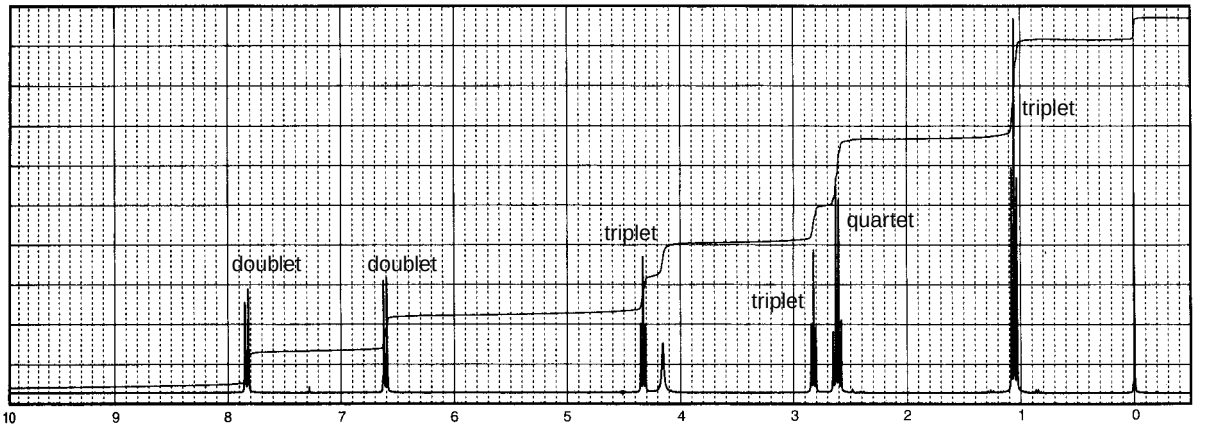
(ppm)


1188.35
1181.36
1174.74
1049.73
1042.75
1036.13
4.00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.40

(ppm)

18. The anesthetic procaine (Novocaine) has the formula $C_{13}H_{20}N_2O_2$. In the ^1H NMR spectrum, each pair of triplets at 2.8 and 4.3 ppm has a coupling constant of 6 Hz. The triplet at 1.1 and the quartet at 2.6 ppm have coupling constants of 7 Hz. The IR spectrum was determined in Nujol. The C−H absorption bands of Nujol at about 2920 cm^{-1} in the IR spectrum obscure the entire C−H stretch region. The carbonyl group appearing at 1669 cm^{-1} in the IR spectrum has an unusually low frequency. Why?

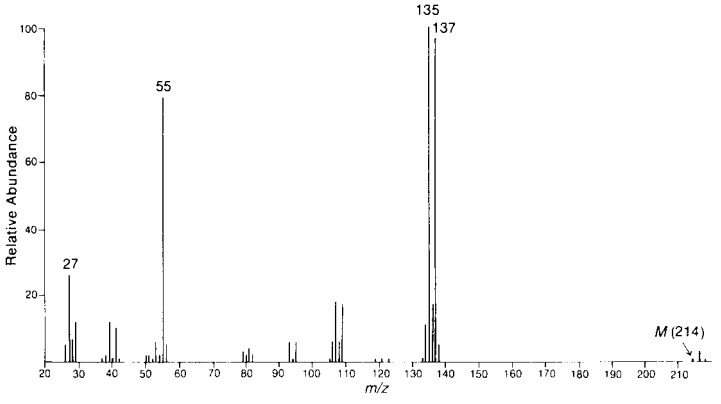




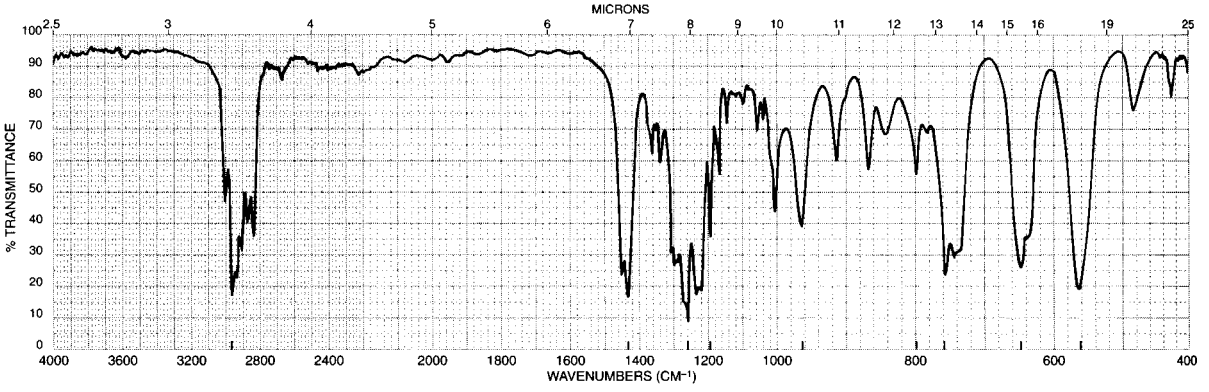
Normal Carbon	DEPT-135	DEPT-90
12 ppm	Positive	No peak
48	Negative	No peak
51	Negative	No peak
63	Negative	No peak
114	Positive	Positive
120	No peak	No peak
132	Positive	Positive
151	No peak	No peak
167	No peak	No peak

19. The UV spectrum of this compound shows no maximum above 250 nm. In the mass spectrum, notice that the patterns for the M, $M + 2$, and $M + 4$ peaks have a ratio of 1:2:1 (214, 216, and 218 m/z). Draw the structure of the compound and comment on the structures of the mass 135 and 137 fragments.

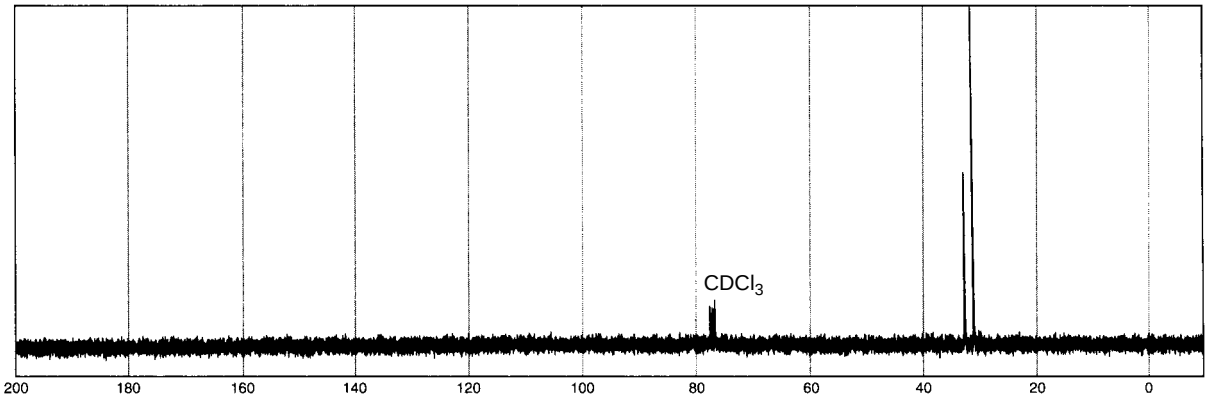
(a)



(b)

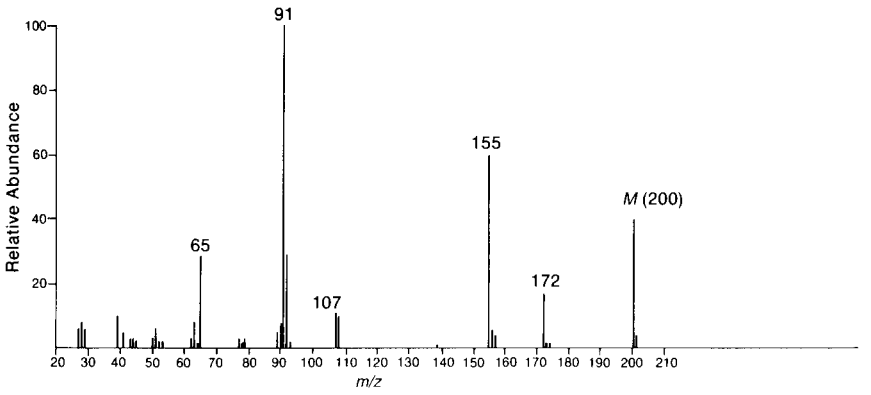


(c)

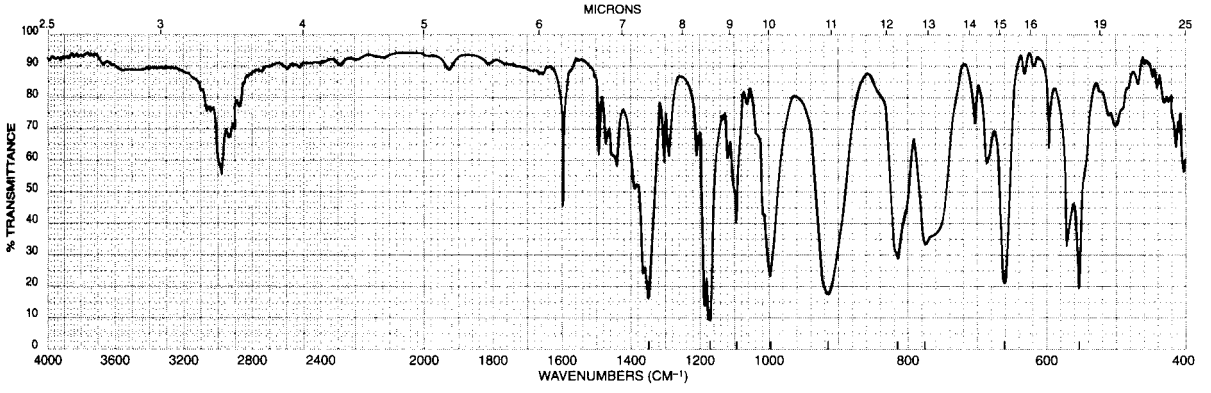


20. The UV spectrum of this compound is determined in 95% ethanol: λ_{max} 225 nm (log $\varepsilon = 4.0$) and 270 nm (log $\varepsilon = 2.8$). This compound has the formula $C_9H_{12}O_3S$.

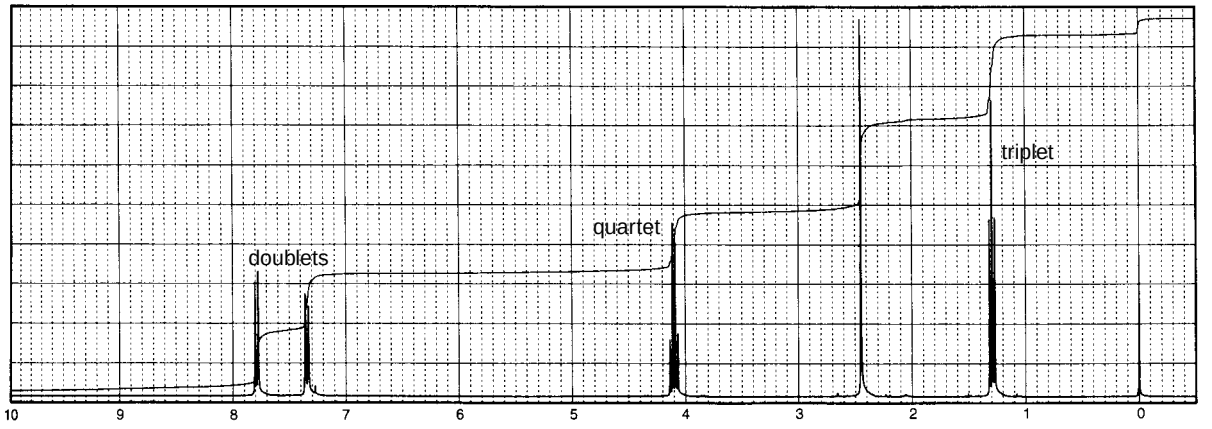
(a)



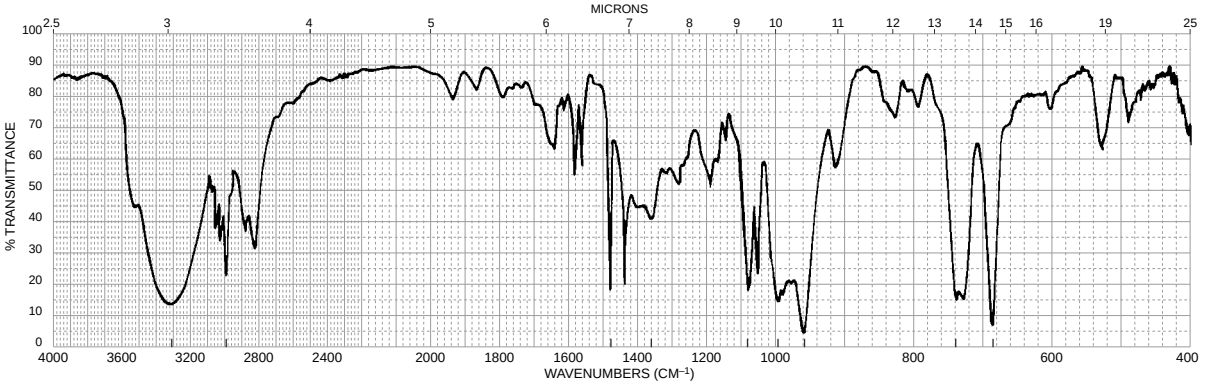
(b)

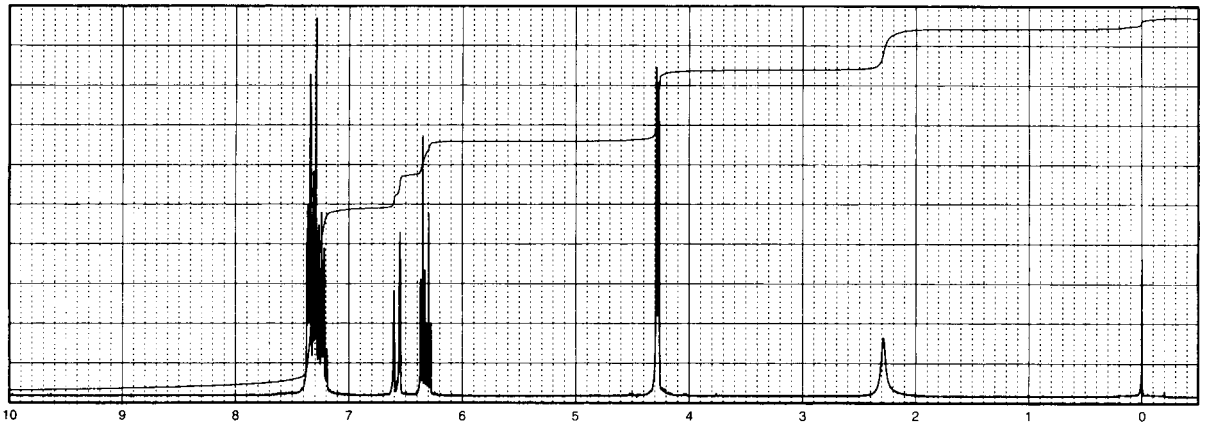


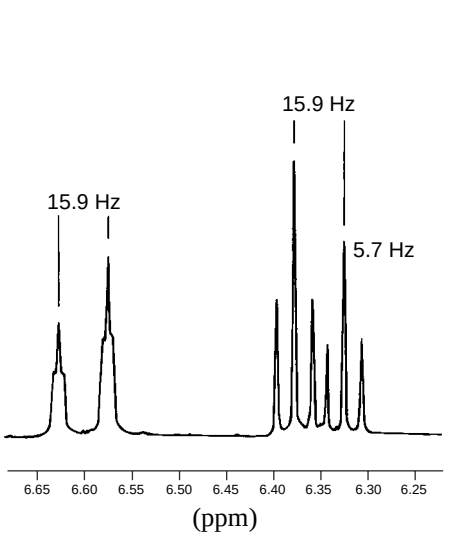
(c)

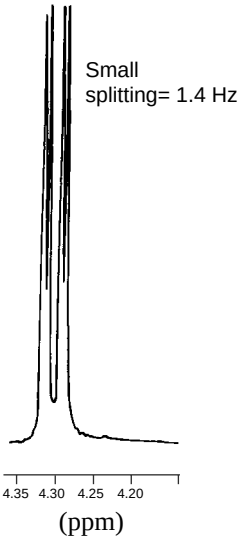


21. This compound has the molecular formula $C_9H_{10}O$. We have supplied you with the IR and ^1H NMR spectra. The expansions of the interesting sets of peaks centering near 4.3, 6.35, and 6.6 ppm in the ^1H NMR are provided as well. Do not attempt to interpret the messy pattern near 7.4 ppm for the aromatic protons. The broad peak at 2.3 ppm (one proton) is solvent and concentration dependent.

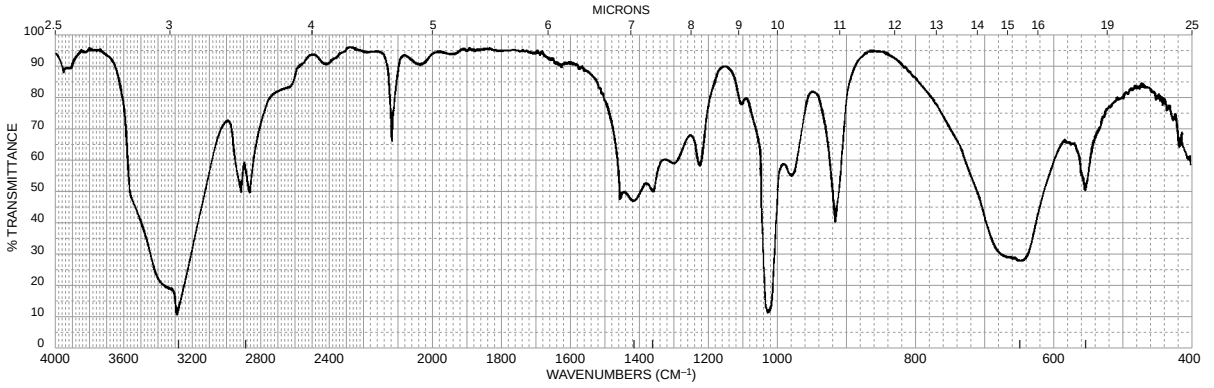


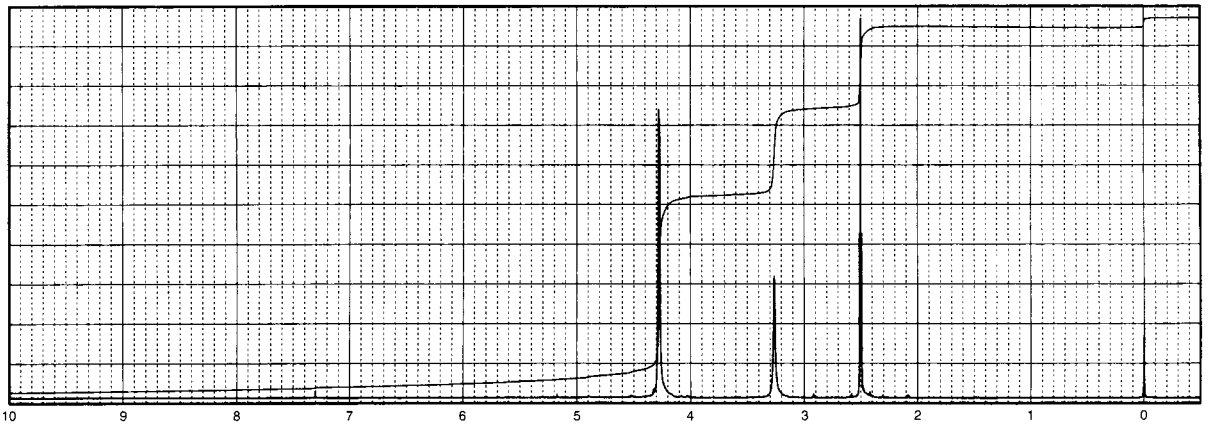


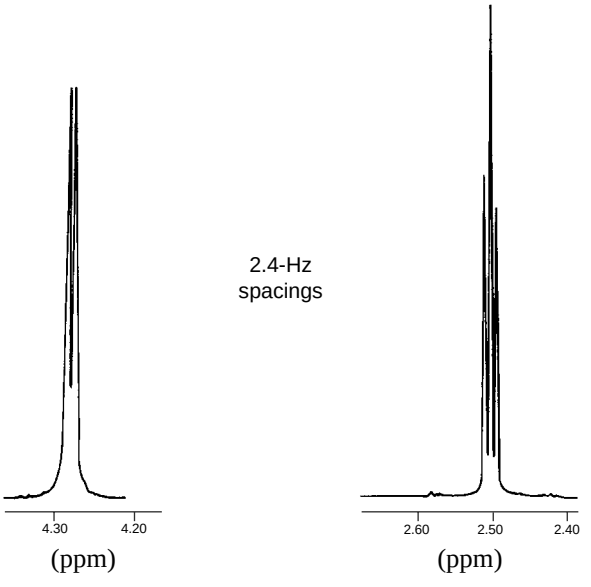




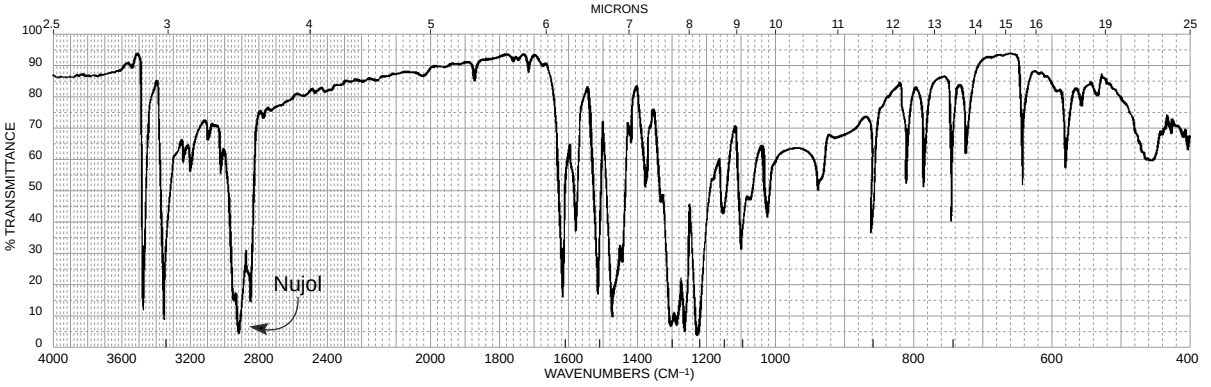
22. This compound has the formula C_3H_4O. We have supplied you with the IR and ^1H NMR spectra. Notice that a single peak at 3300 cm^{-1} overlaps the broad peak there. The expansions of the interesting sets of peaks centering near 2.5 and 4.3 ppm in the ^1H NMR are provided as well. The peak at 3.25 ppm (one proton) is solvent and concentration dependent.

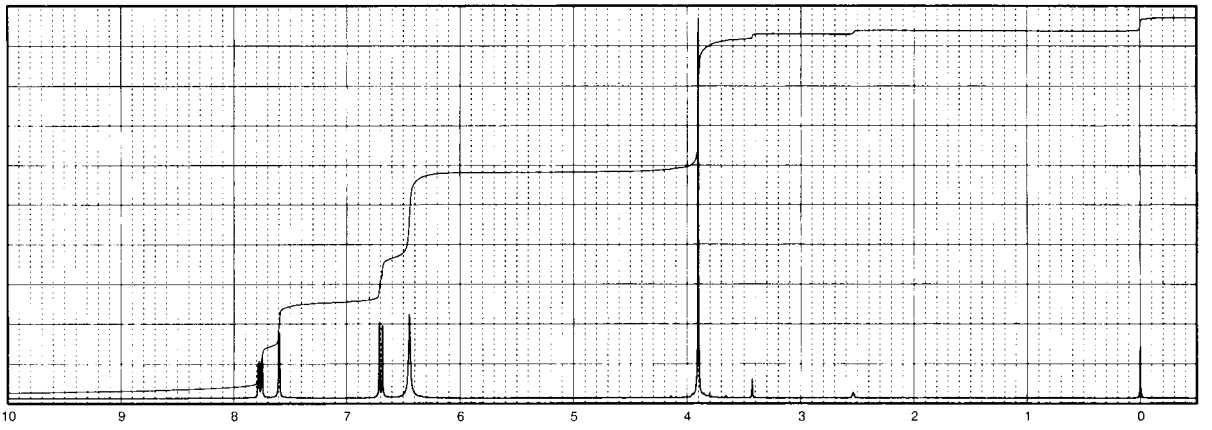


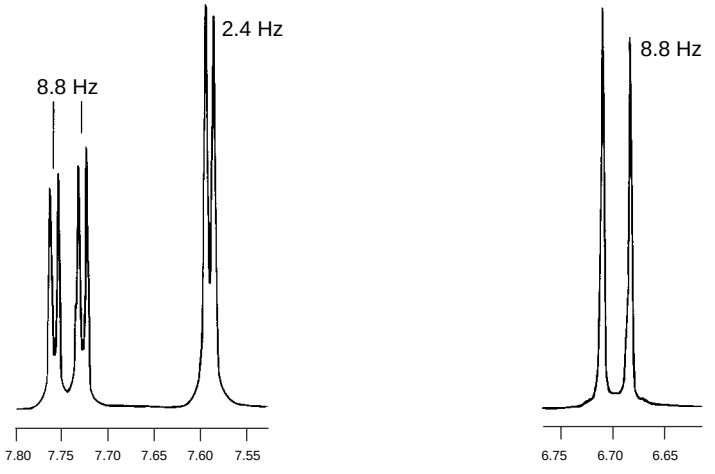




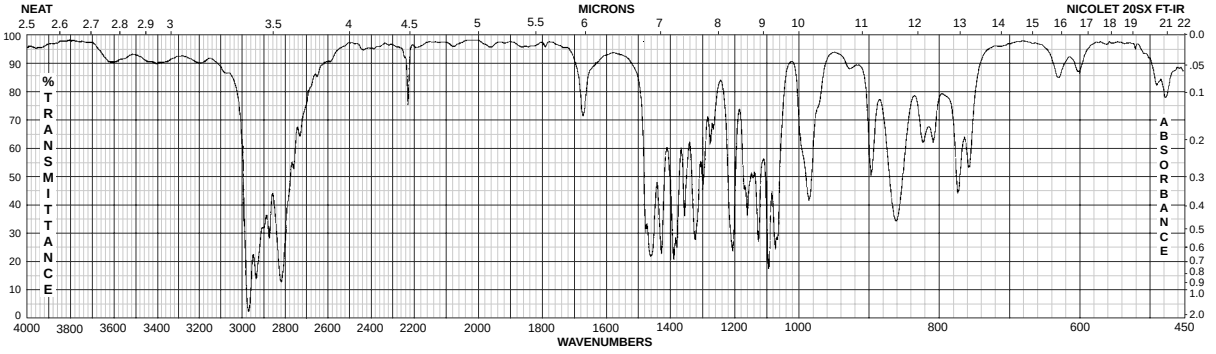
23. This compound has the molecular formula $C_7H_8N_2O_3$. We have supplied you with the IR and ^1H NMR spectra (run in DMSO-d_6). The expansions of the interesting sets of peaks centering near 7.75, 7.6, and 6.7 ppm in the ^1H NMR are provided as well. The peak at 6.45 ppm (two protons) is solvent and concentration dependent. The UV spectrum shows peaks at 204 nm ($\varepsilon = 1.68 \times 10^4$), 260 nm ($\varepsilon = 6.16 \times 10^3$), and 392 nm ($\varepsilon = 1.43 \times 10^4$). The presence of the intense band at 392 nm is an important clue regarding the positions of groups on the ring. This band moves to a lower wavelength when acidified. The IR spectrum was determined in Nujol. The C−H bands for Nujol at about 2920 cm^{-1} obscure the C−H bands in the unknown compound.

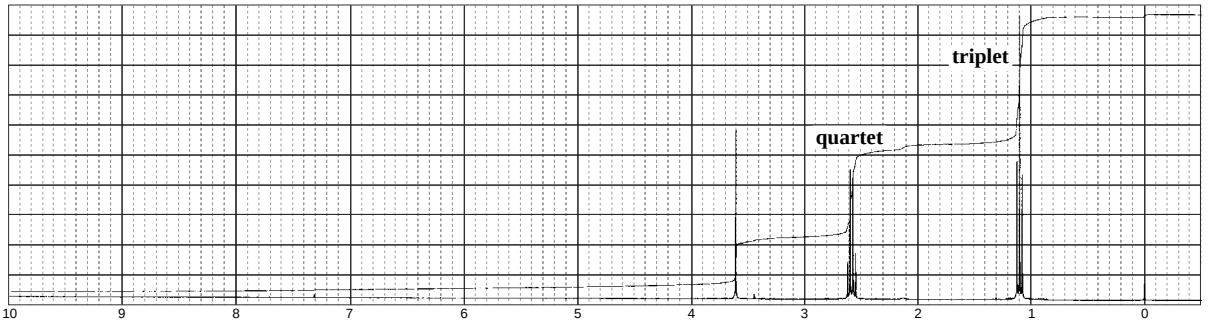






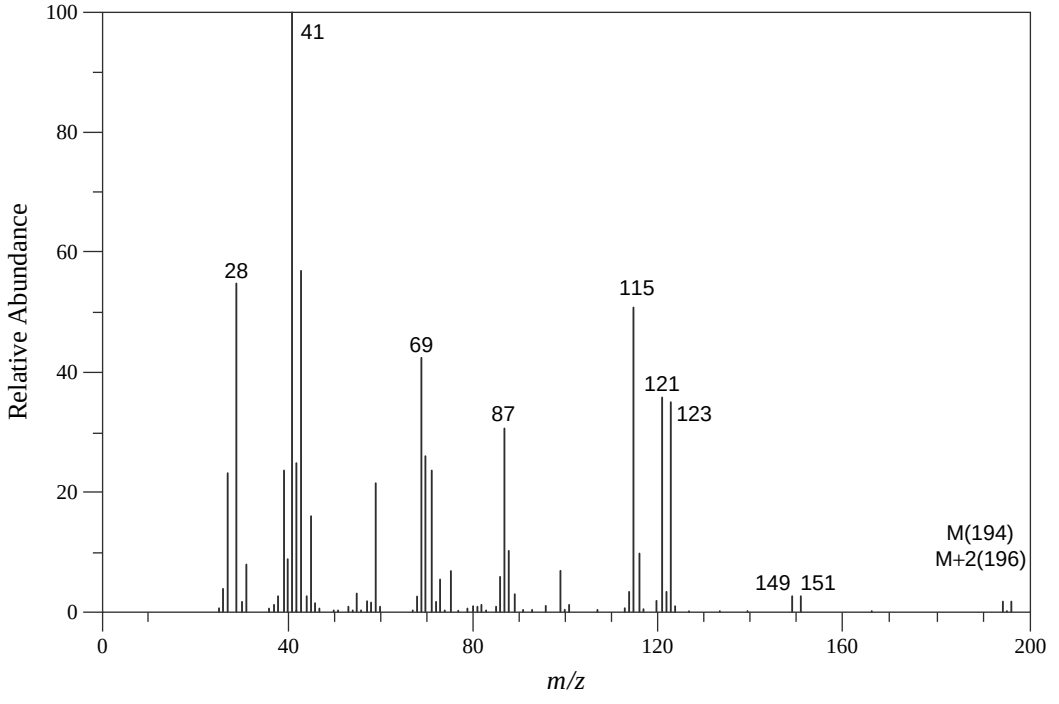
24. This compound has the formula $C_6H_{12}N_2$.

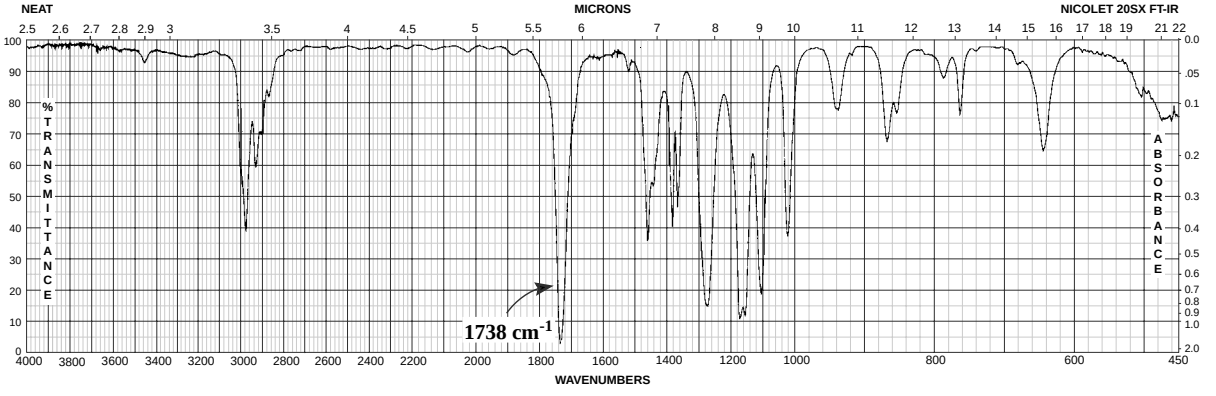


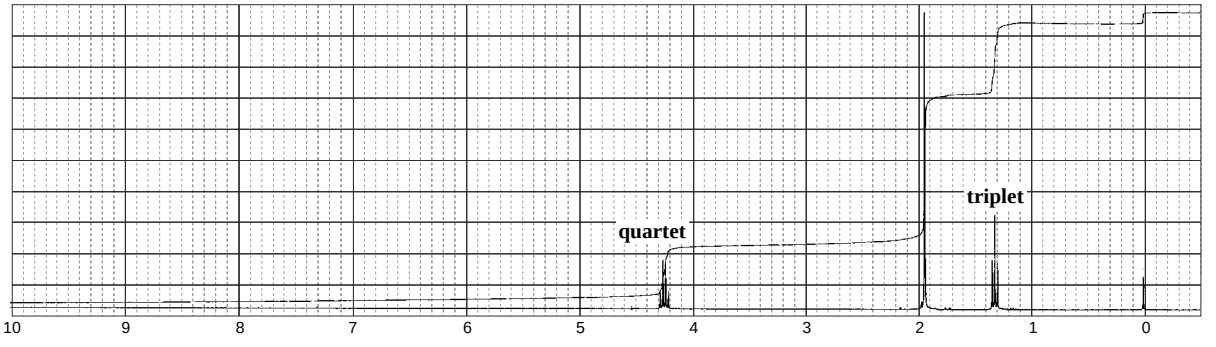


Normal Carbon	DEPT-135	DEPT-90
13 ppm	Positive	No peak
41	Negative	No peak
48	Negative	No peak
213	No peak	No peak

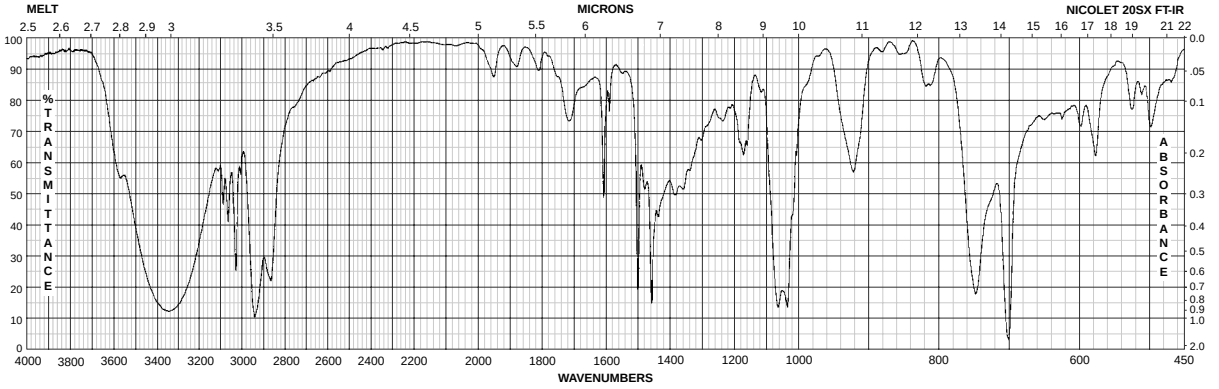
25. This compound has the formula $C_6H_{11}BrO_2$. Determine the structure of this compound. Draw the structures of the fragments observed in the mass spectrum at 121/123 and 149/151. The ^{13}C NMR spectrum shows peaks at 14, 31, 56, 62, and 172 ppm.

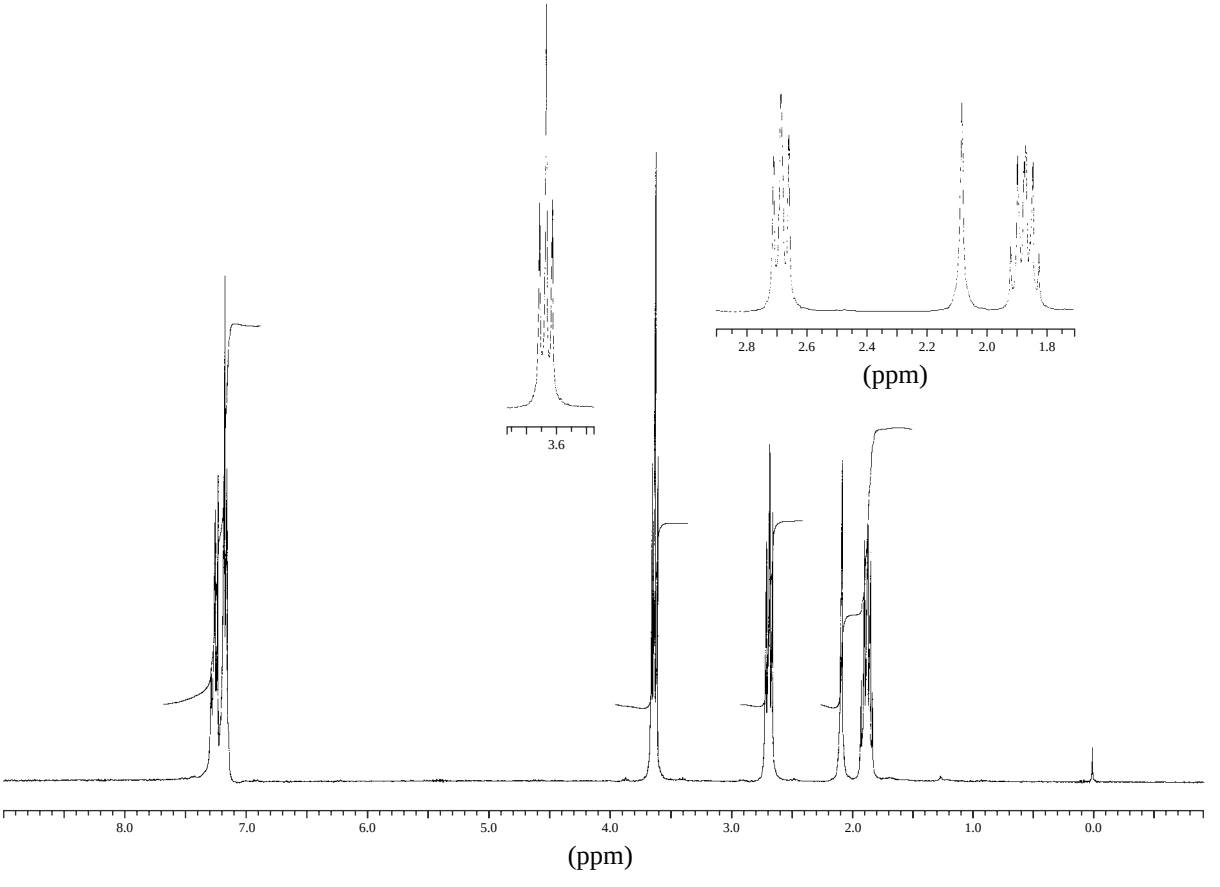




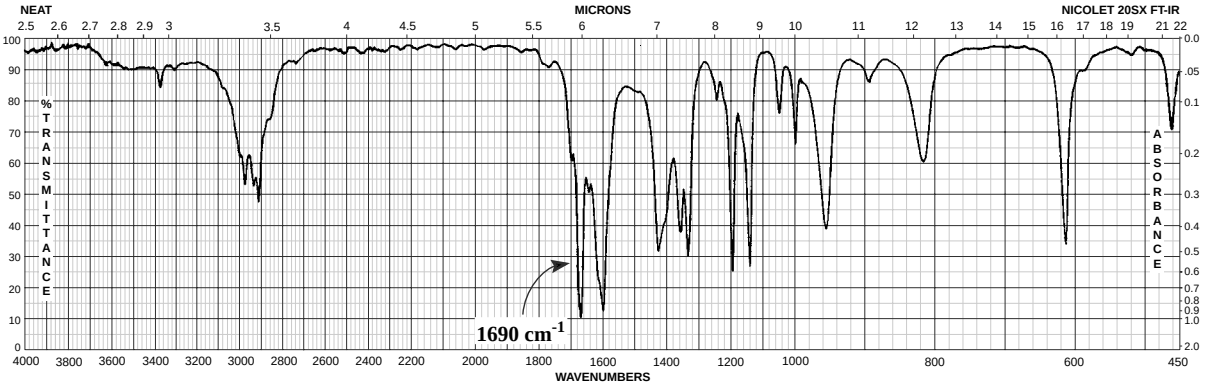


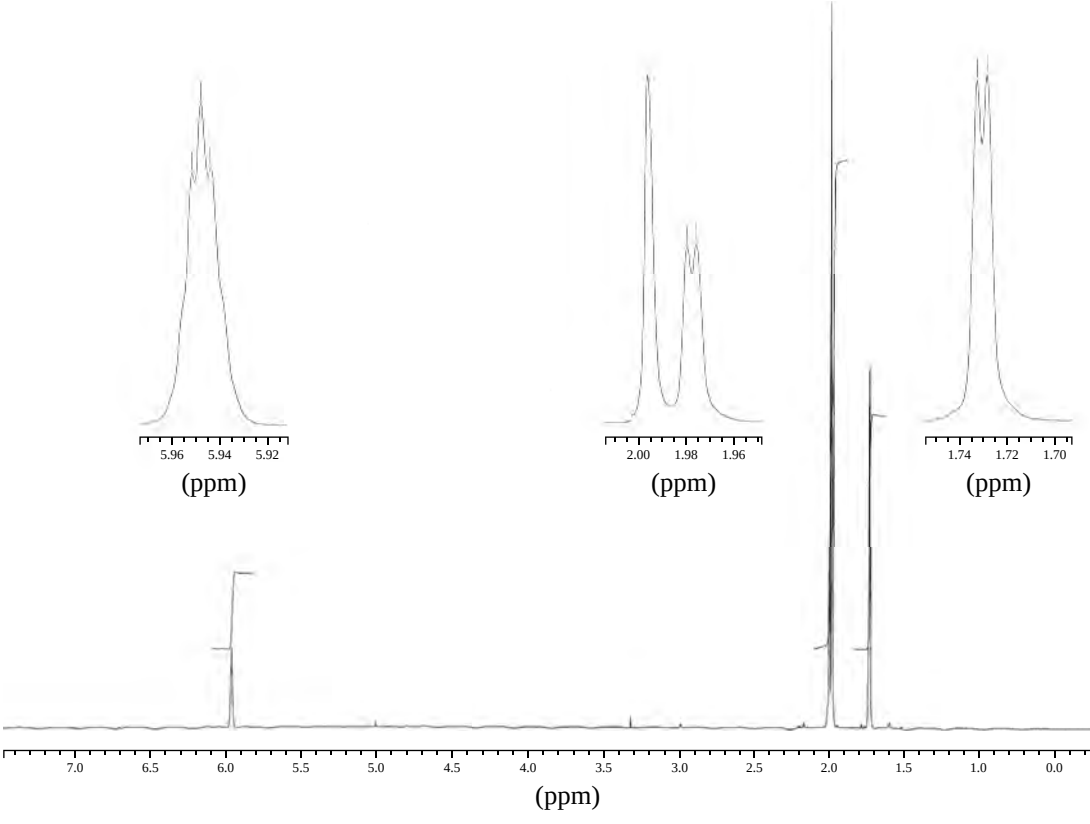
26. This compound has the formula $C_9H_{12}O$. The ^{13}C NMR spectrum shows peaks at 28, 31, 57, 122, 124, 125, and 139 ppm.



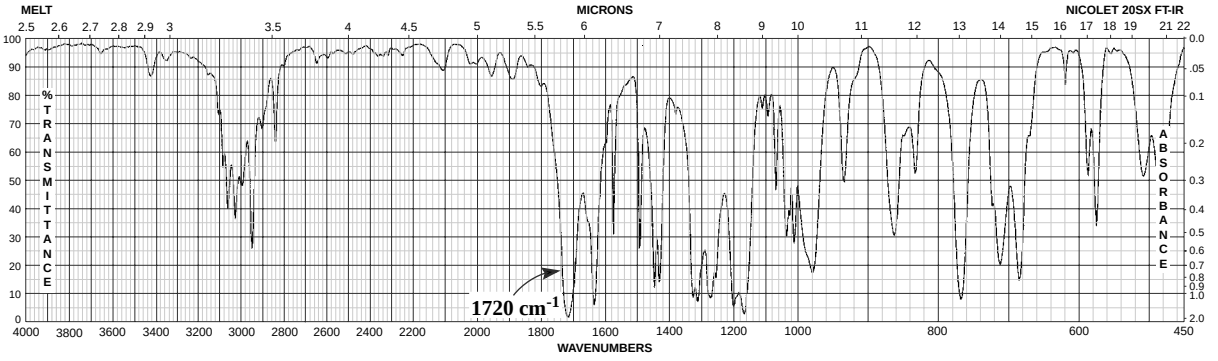


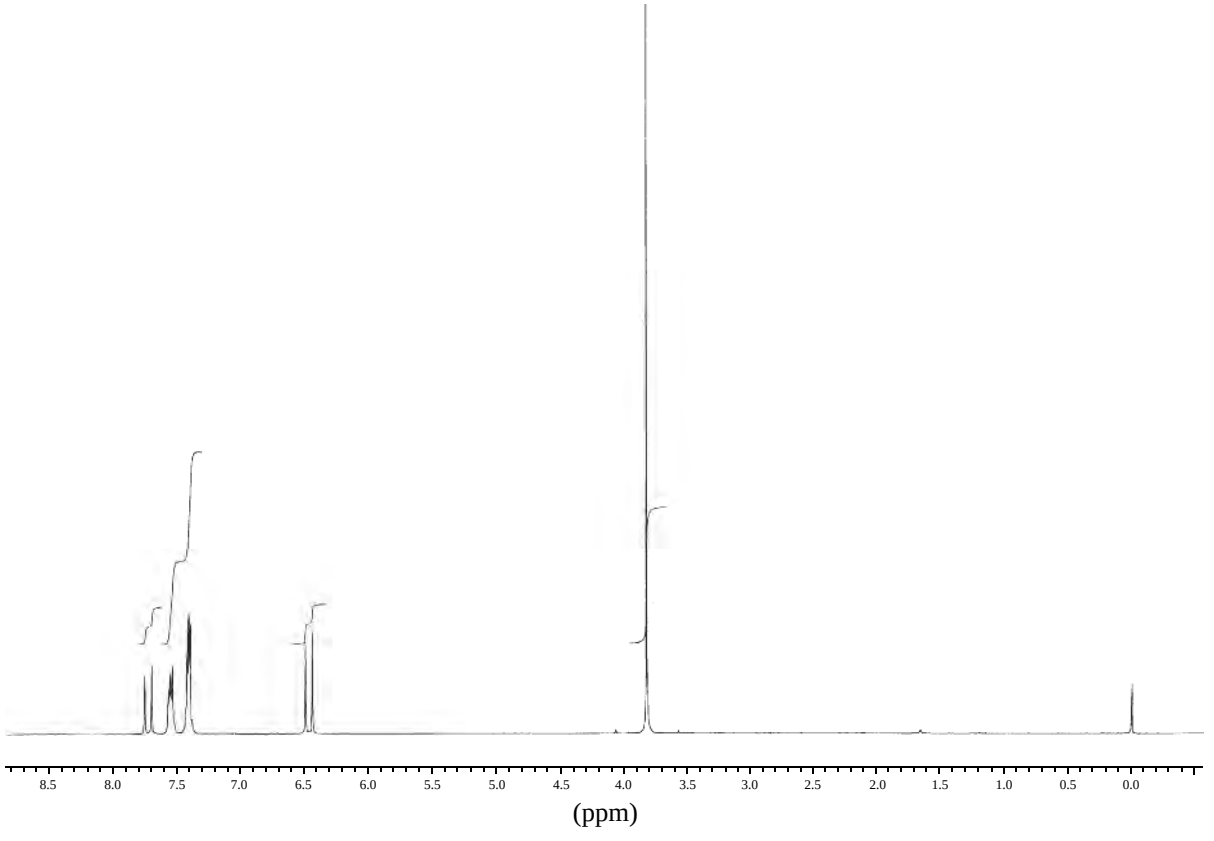
27. This compound has the formula $C_6H_{10}O$. The ^{13}C NMR spectrum shows peaks at 21, 27, 31, 124, 155, and 198 ppm.

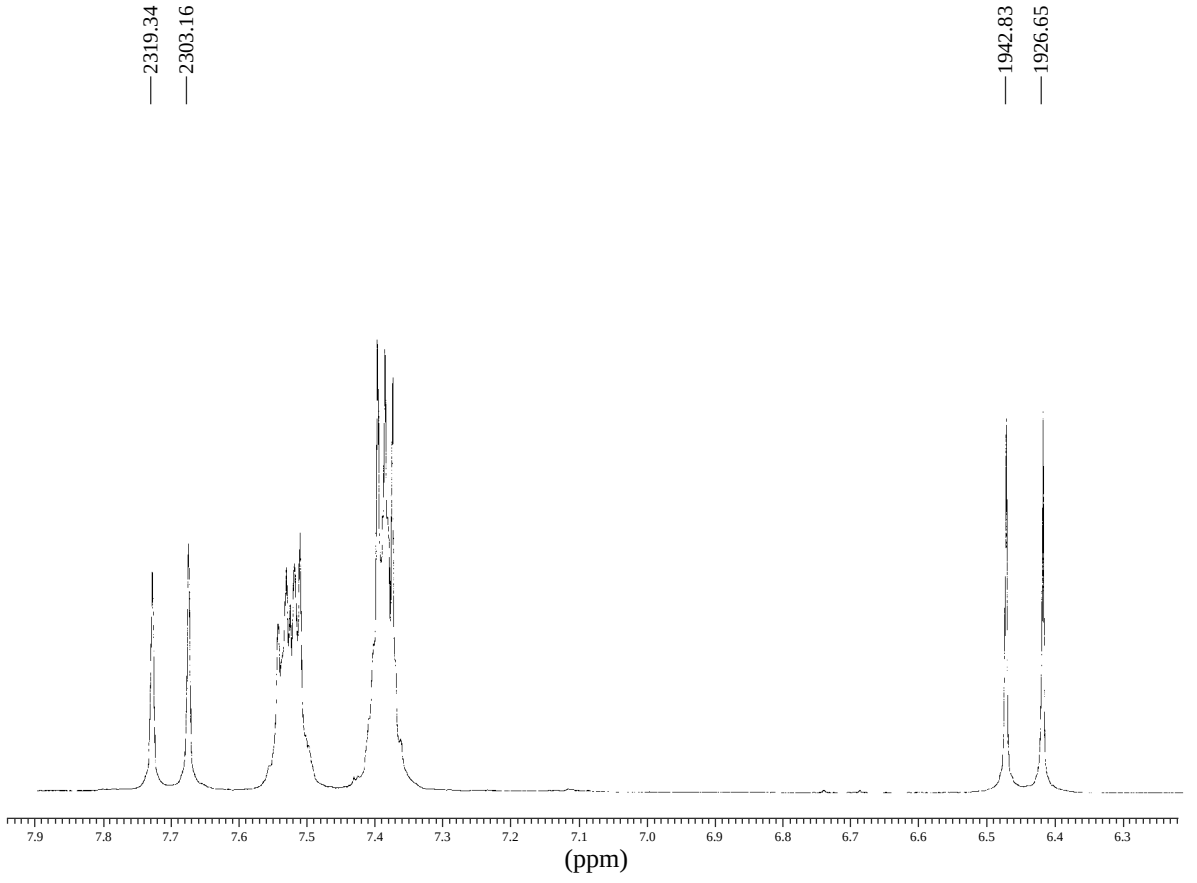




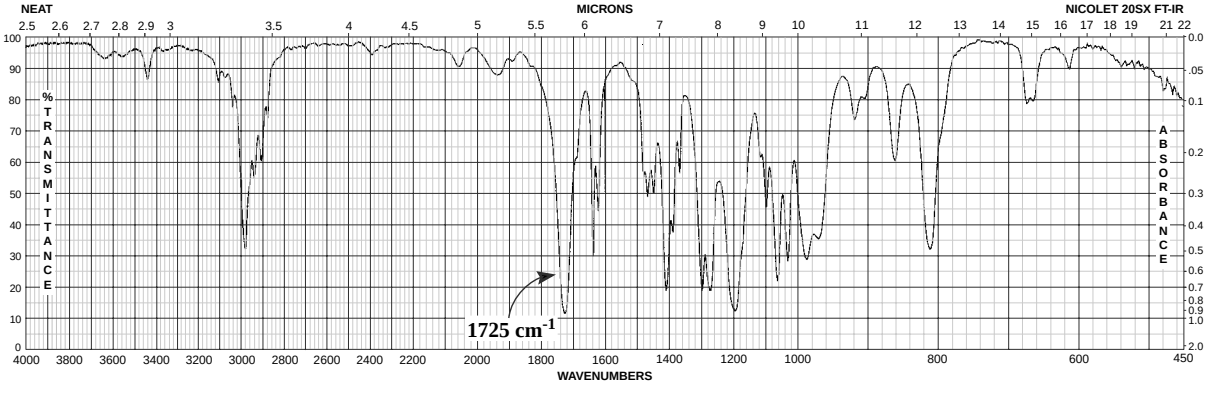
28. This compound has the formula $C_{10}H_{10}O_2$. The ^{13}C NMR spectrum shows peaks at 52, 118, 128, 129, 130, 134, 145, and 167 ppm.

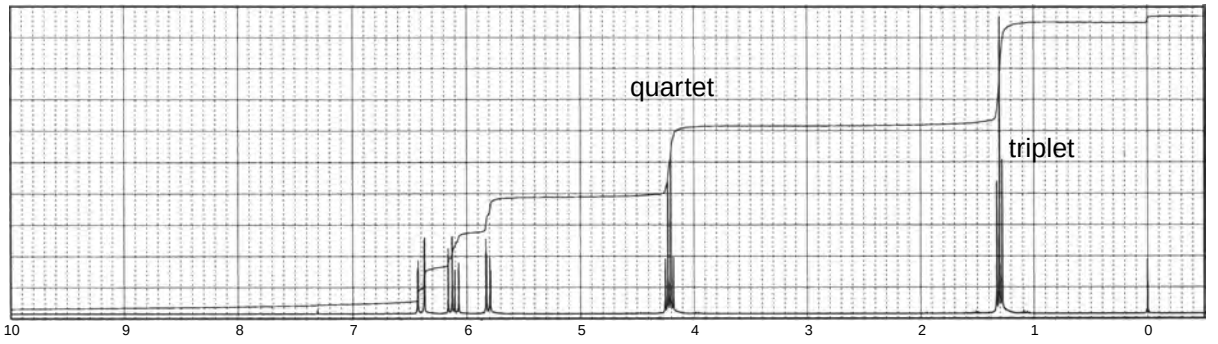


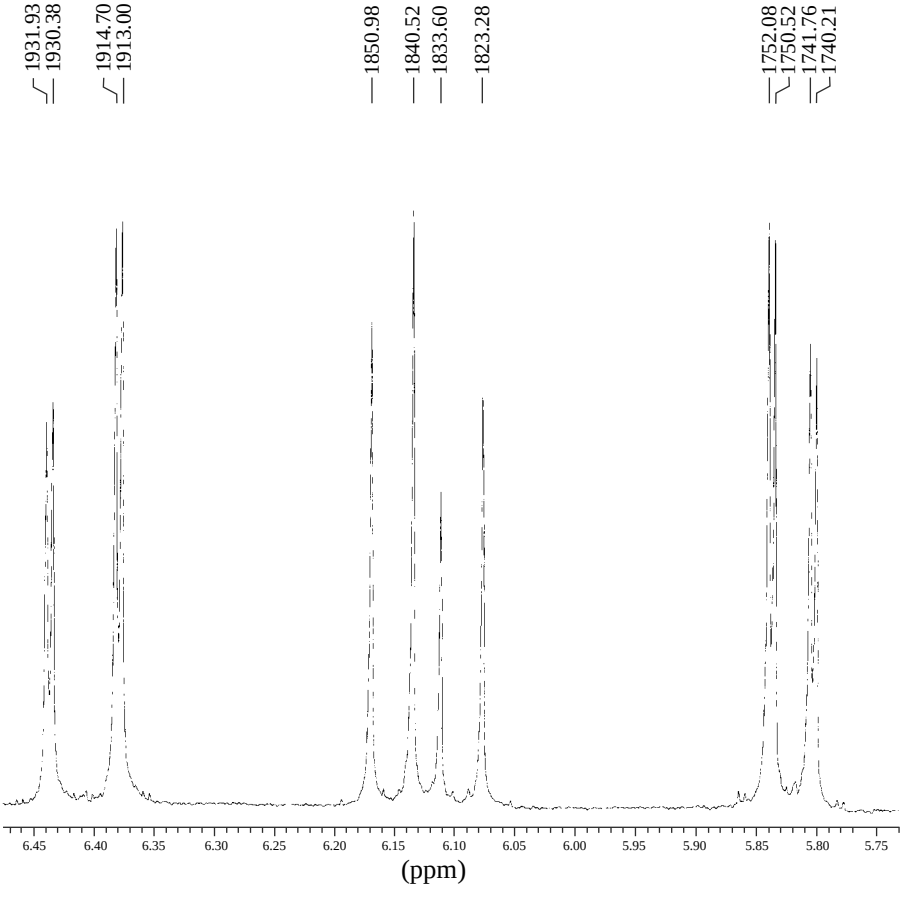


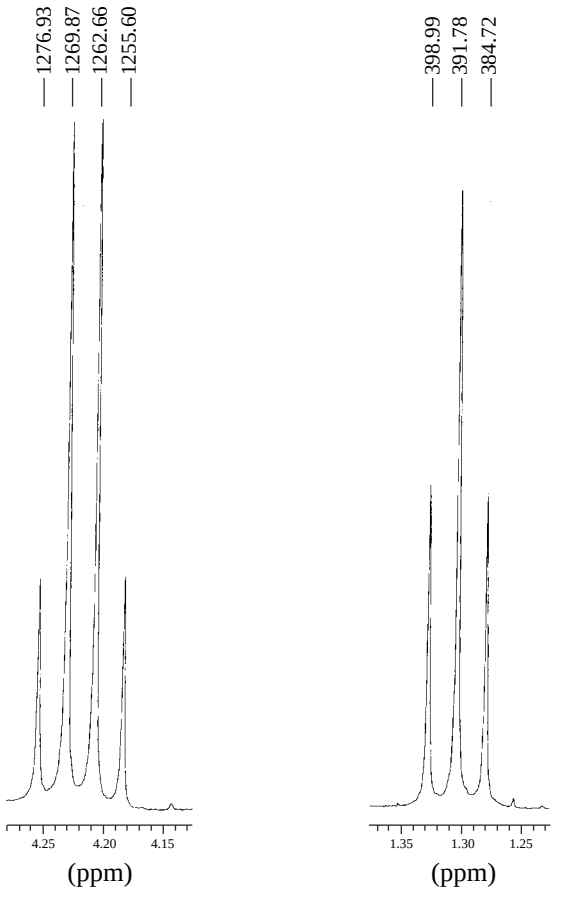


29. This compound has the formula $C_5H_8O_2$. The ^{13}C NMR spectrum shows peaks at 14, 60, 129, 130, and 166 ppm.

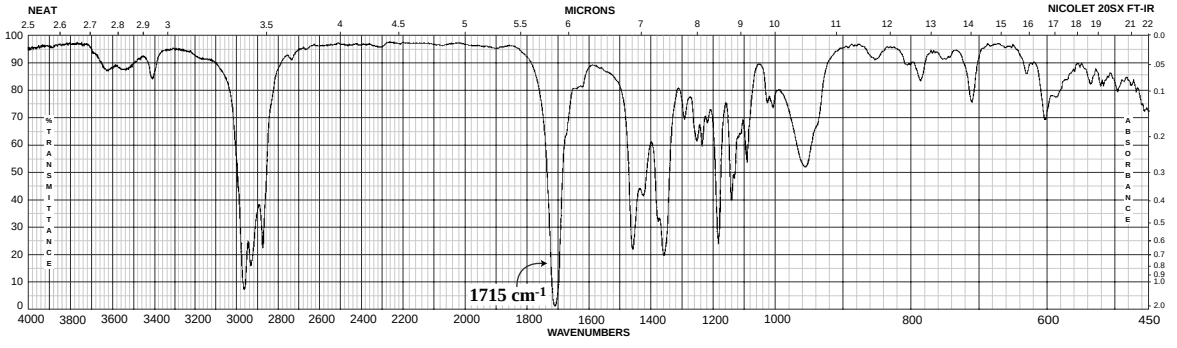


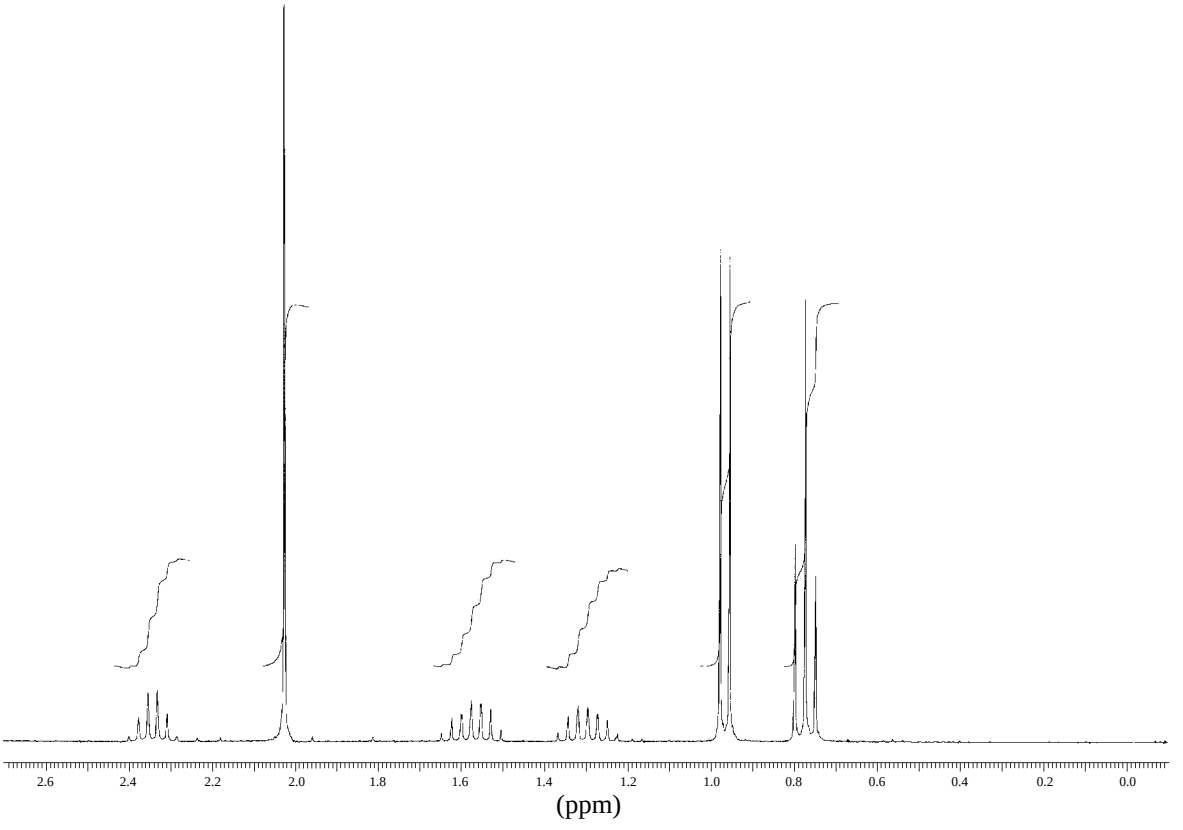

quartet
triplet
10
9
8
7
6
5
4
3
2
1
0


1931.93
1930.38
1914.70
1913.00
1850.98
1840.52
1833.60
1823.28
1752.08
1750.52
1741.76
1740.21
6.45
6.40
6.35
6.30
6.25
6.20
6.15
6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
(ppm)

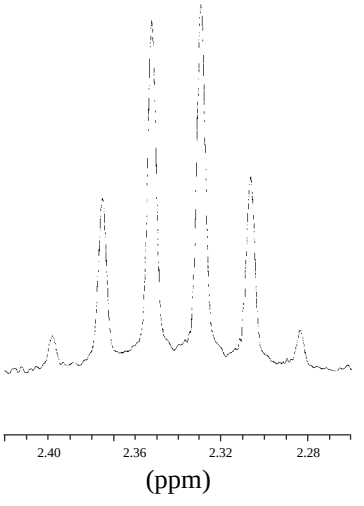


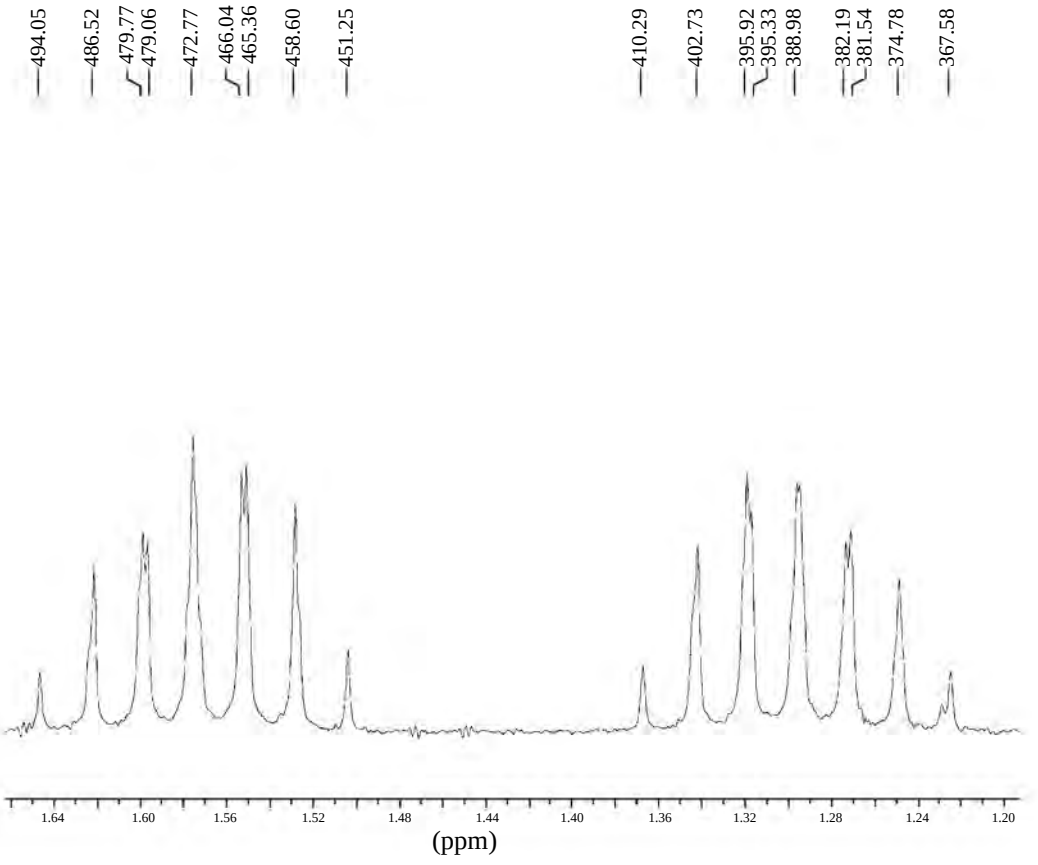
30. This compound has the formula $C_6H_{12}O$. Interpret the patterns centering on 1.3 and 1.58 ppm in the ^1H NMR spectrum.

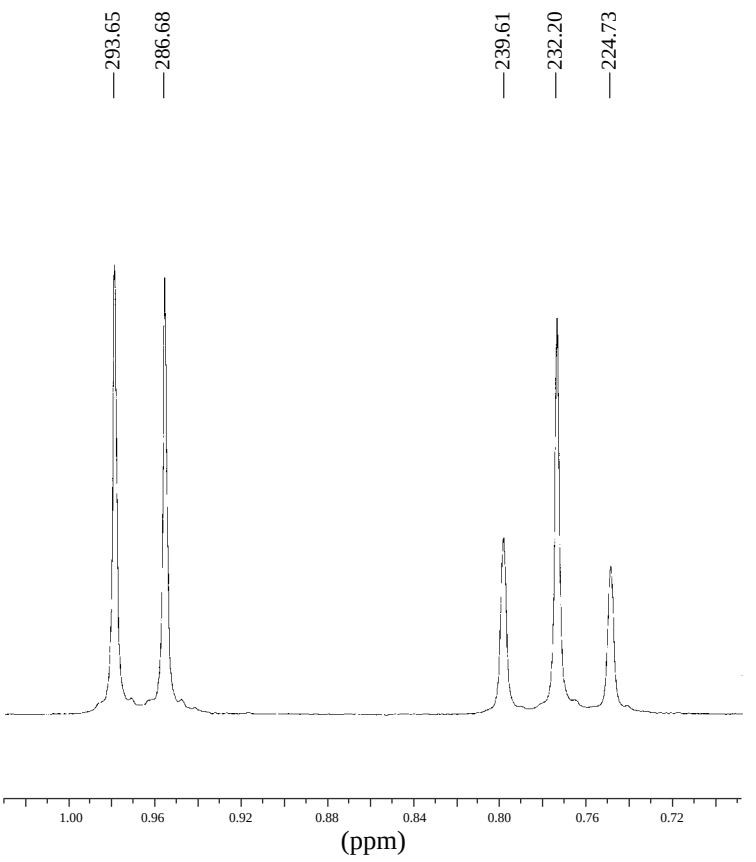




719.63
712.78
705.90
699.06
692.18
685.36

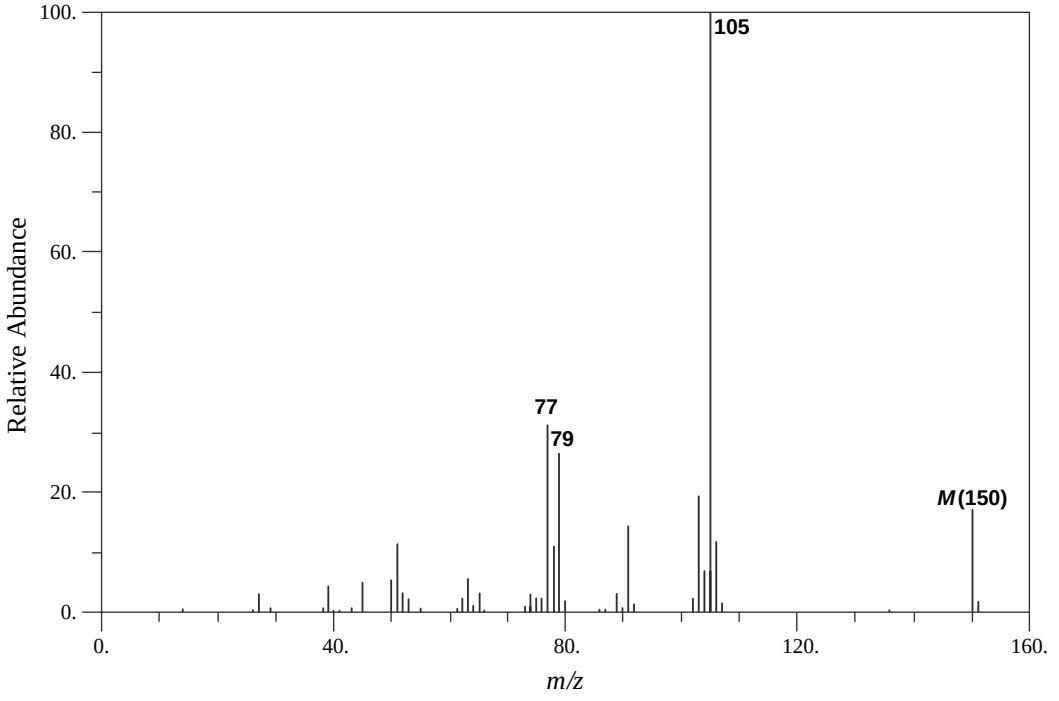


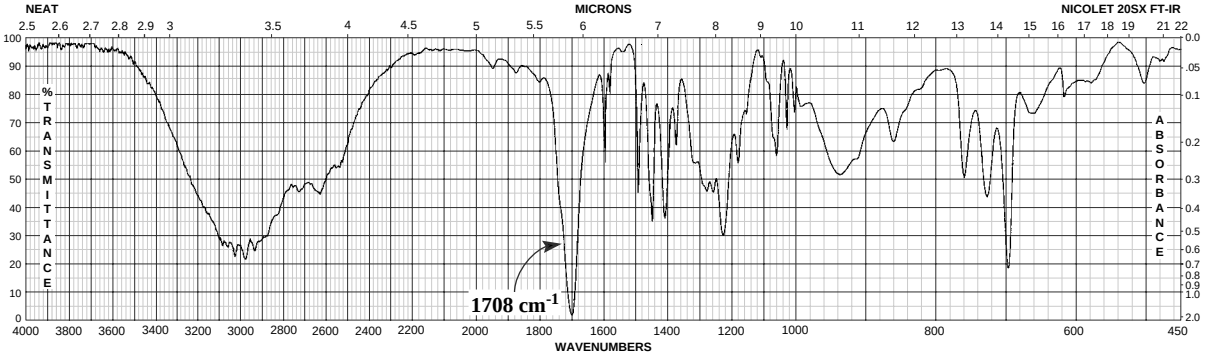

494.05
486.52
479.77
479.06
472.77
466.04
465.36
458.60
451.25
410.29
402.73
395.92
395.33
388.98
382.19
381.54
374.78
367.58
1.64
1.60
1.56
1.52
1.48
1.44
1.40
1.36
1.32
1.28
1.24
1.20
(ppm)

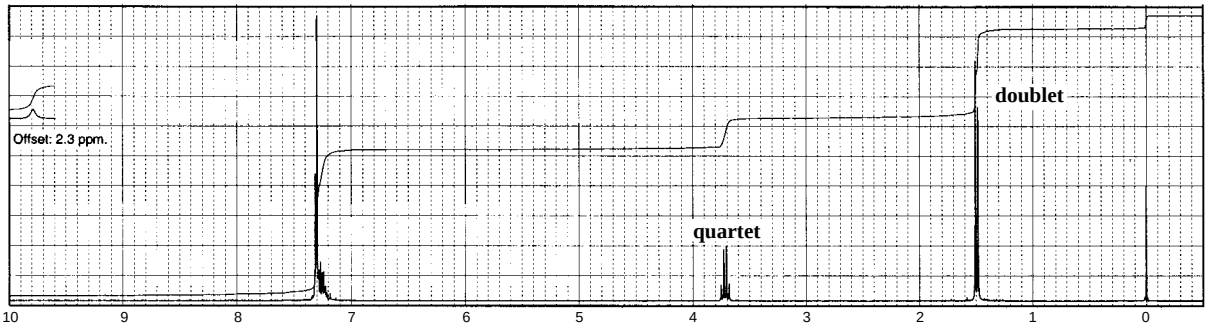


Normal Carbon	DEPT-135	DEPT-90
12 ppm	Positive	No peak
16	Positive	No peak
26	Negative	No peak
28	Positive	No peak
49	Positive	Positive
213	No peak	No peak

31. This compound has the formula $C_9H_{10}O_2$.

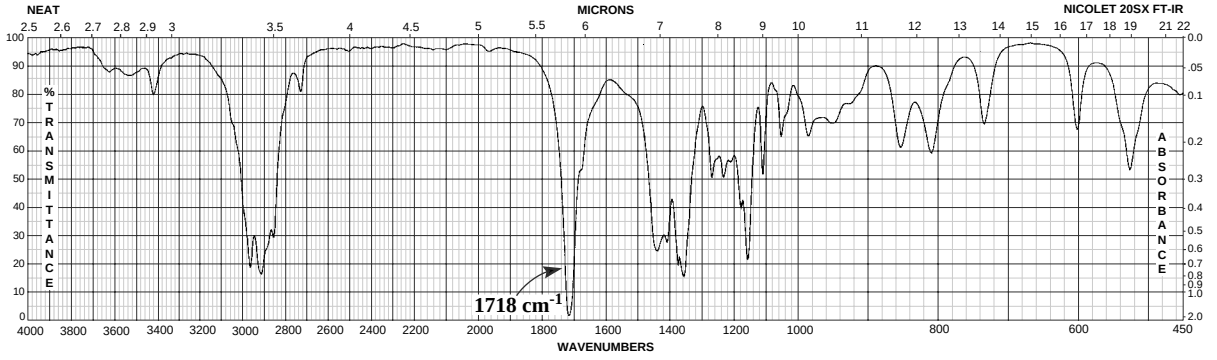




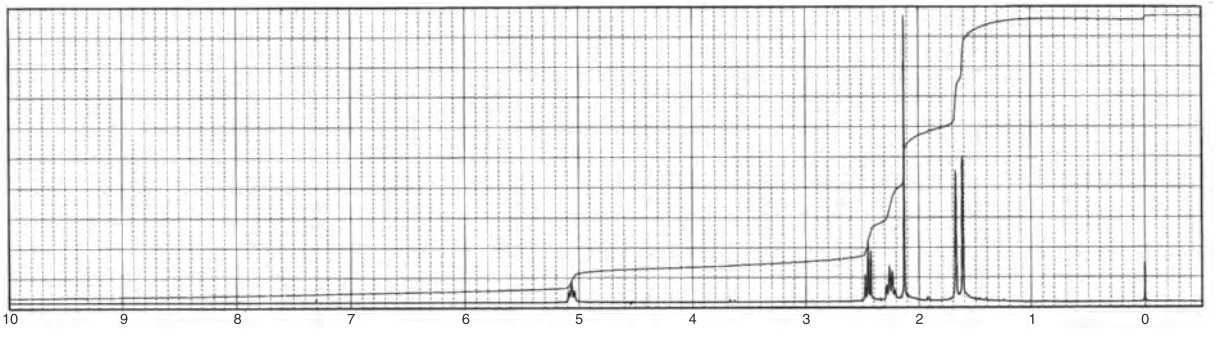


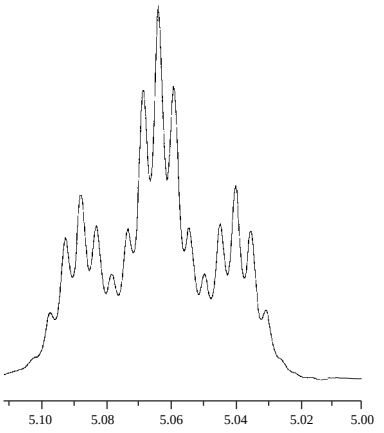
1690 cm^{-1}

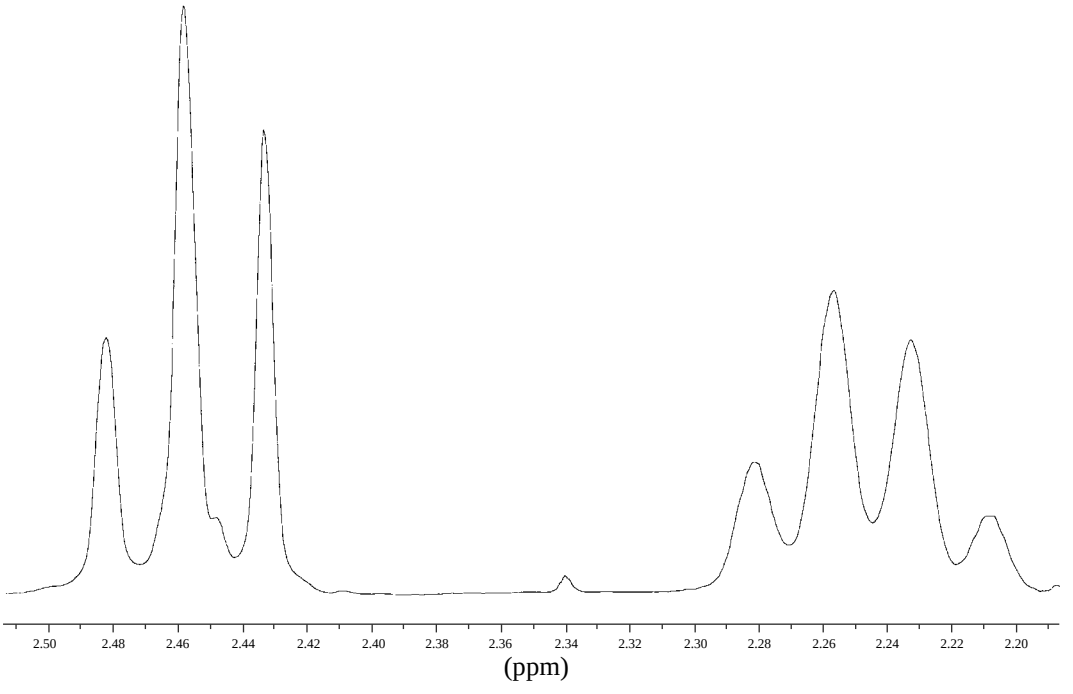
32. This compound has the formula $C_8H_{14}O$.



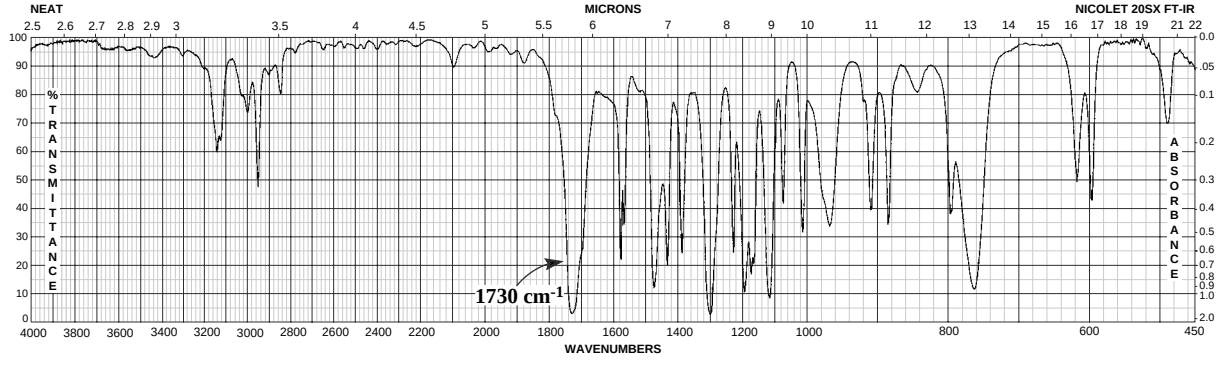
Normal Carbon	DEPT-135	DEPT-90
18 ppm	Positive	No peak
23	Negative	No peak
26	Positive	No peak
30	Positive	No peak
44	Negative	No peak
123	Positive	Positive
133	No peak	No peak
208	No peak	No peak

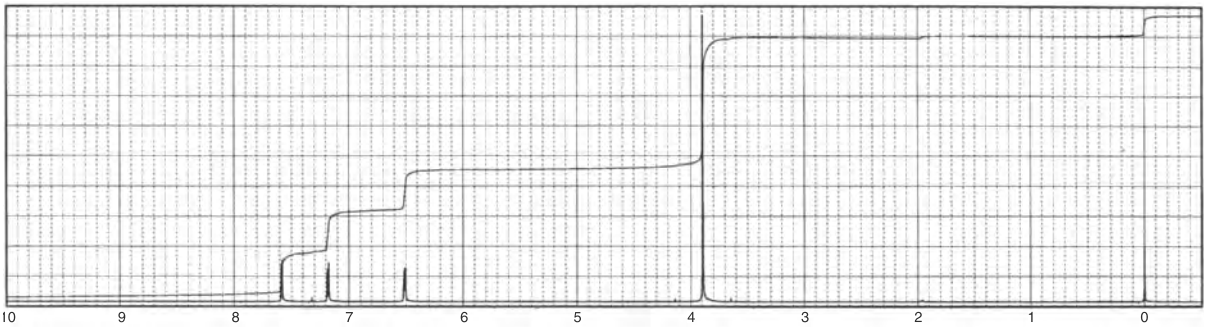






33. This compound has the formula $C_6H_6O_3$. The ^{13}C NMR spectrum shows peaks at 52, 112, 118, 145, 146, and 159 ppm.



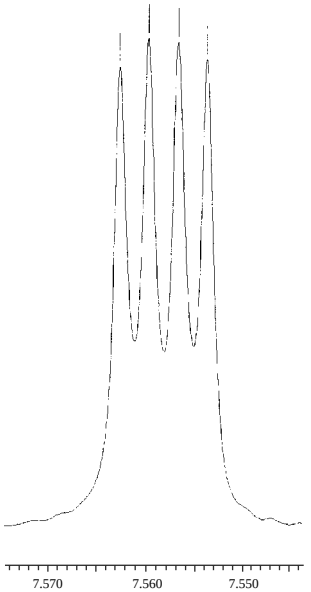


2269.77
2268.90
2268.01
2267.16

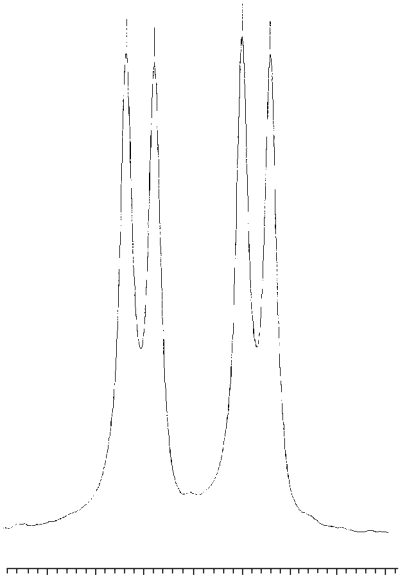
2152.55
2151.70

2149.05
2148.20

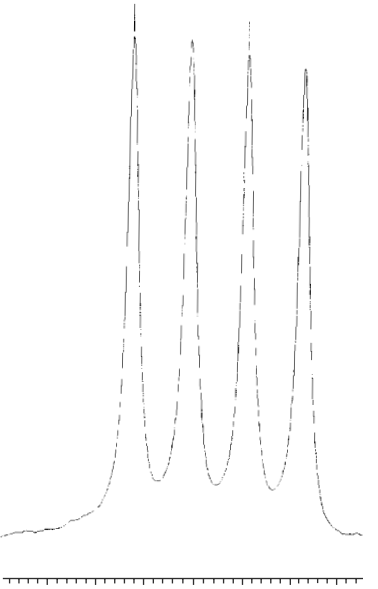
1951.15
1949.39
1947.65
1945.89



(ppm)

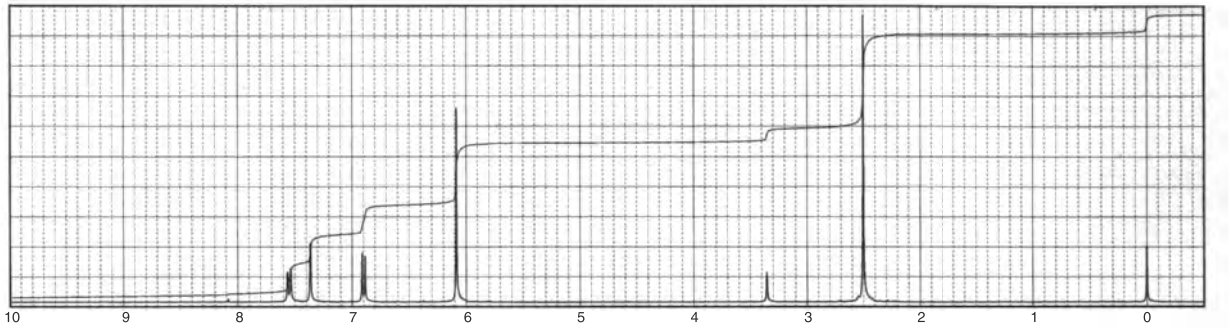


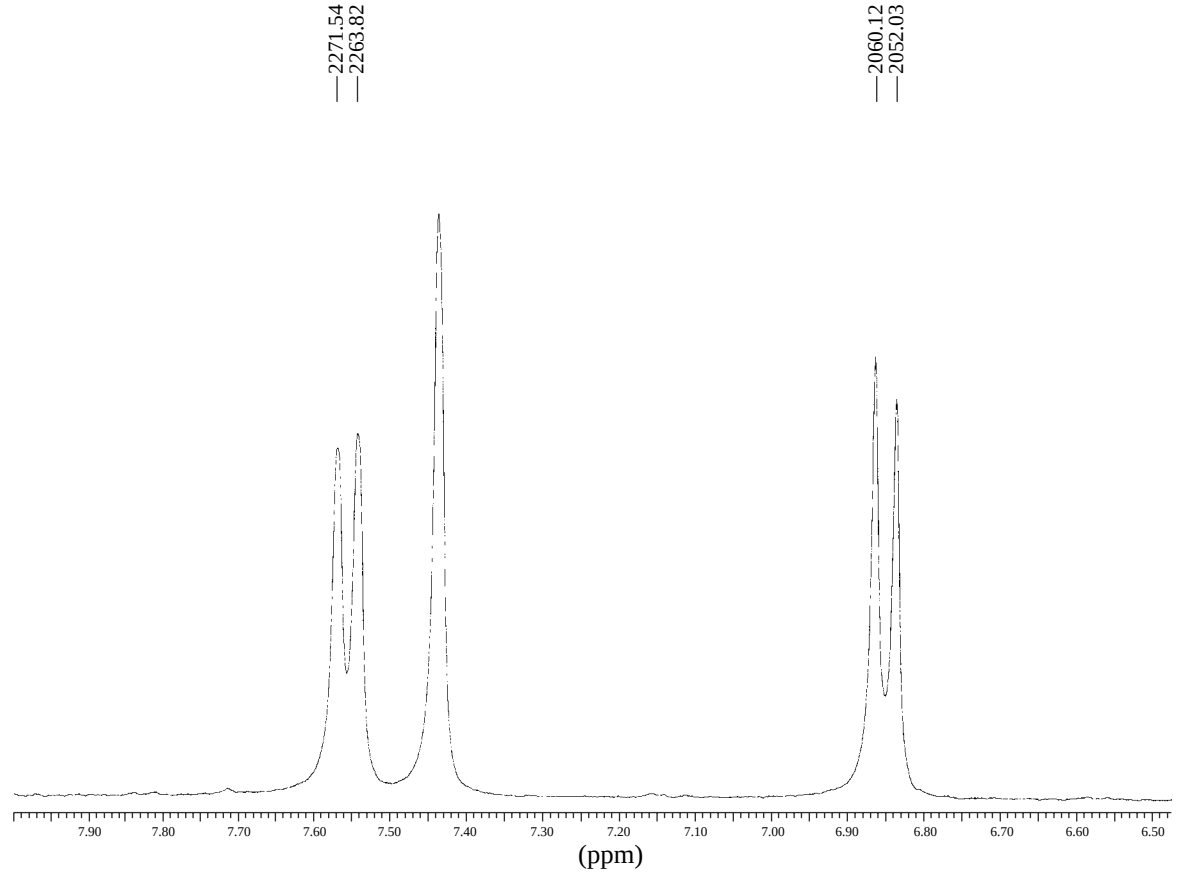
(ppm)



(ppm)

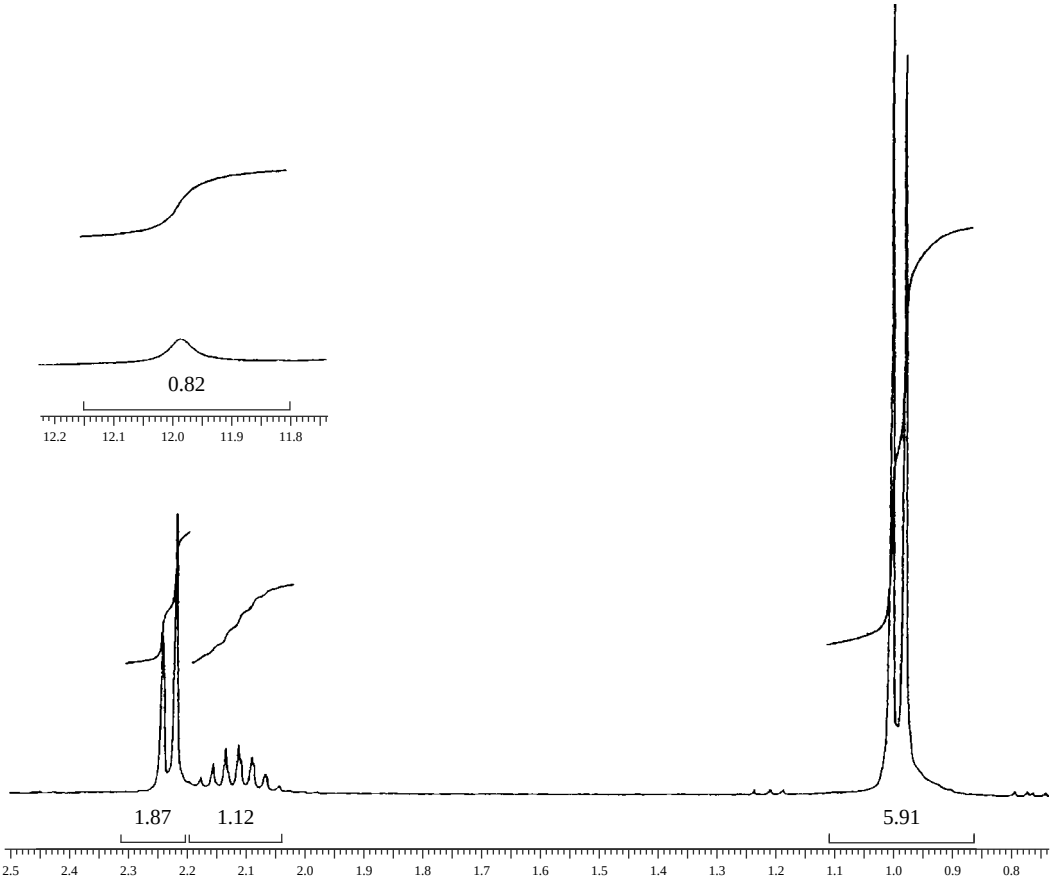
34. A compound with the formula $C_9H_8O_3$ shows a strong band at 1661 cm^{-1} in the infrared spectrum. The ^1H NMR spectrum is shown, but there is a small impurity peak at 3.35 ppm that should be ignored. Expansions are shown for the downfield protons. In addition, the normal ^{13}C NMR, DEPT-135, and DEPT-90 spectral results are tabulated.

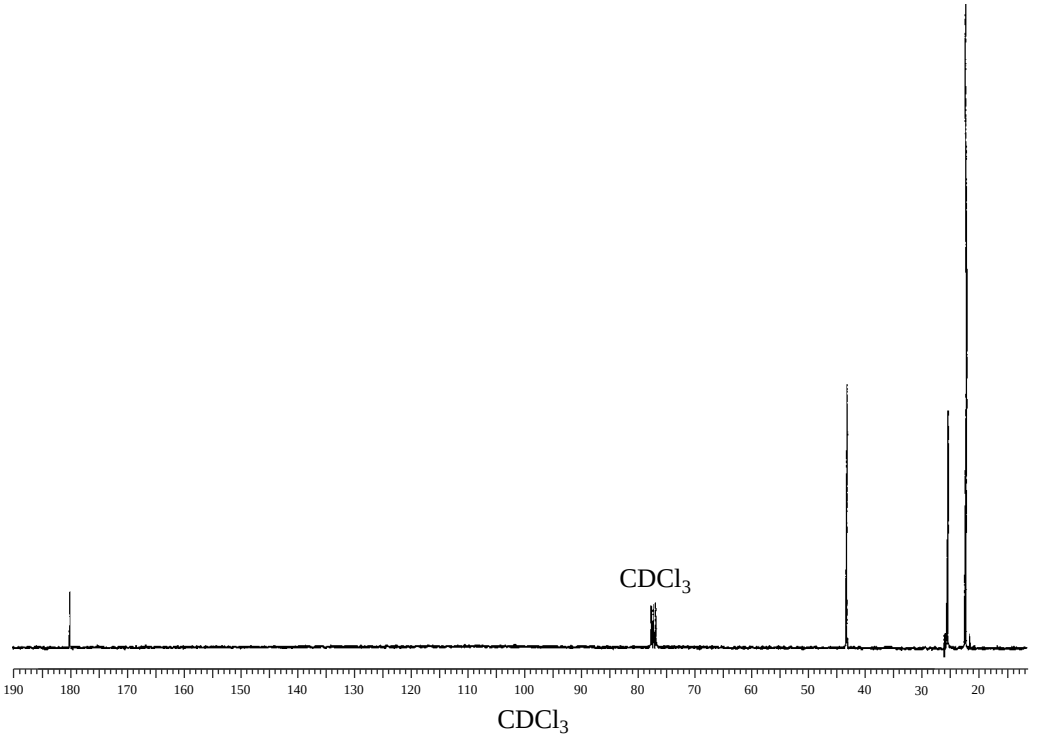




Normal Carbon	DEPT-135	DEPT-90
26 ppm	Positive	No peak
102	Negative	No peak
107	Positive	Positive
108	Positive	Positive
125	Positive	Positive
132	No peak	No peak
148	No peak	No peak
151	No peak	No peak
195	No peak	No peak

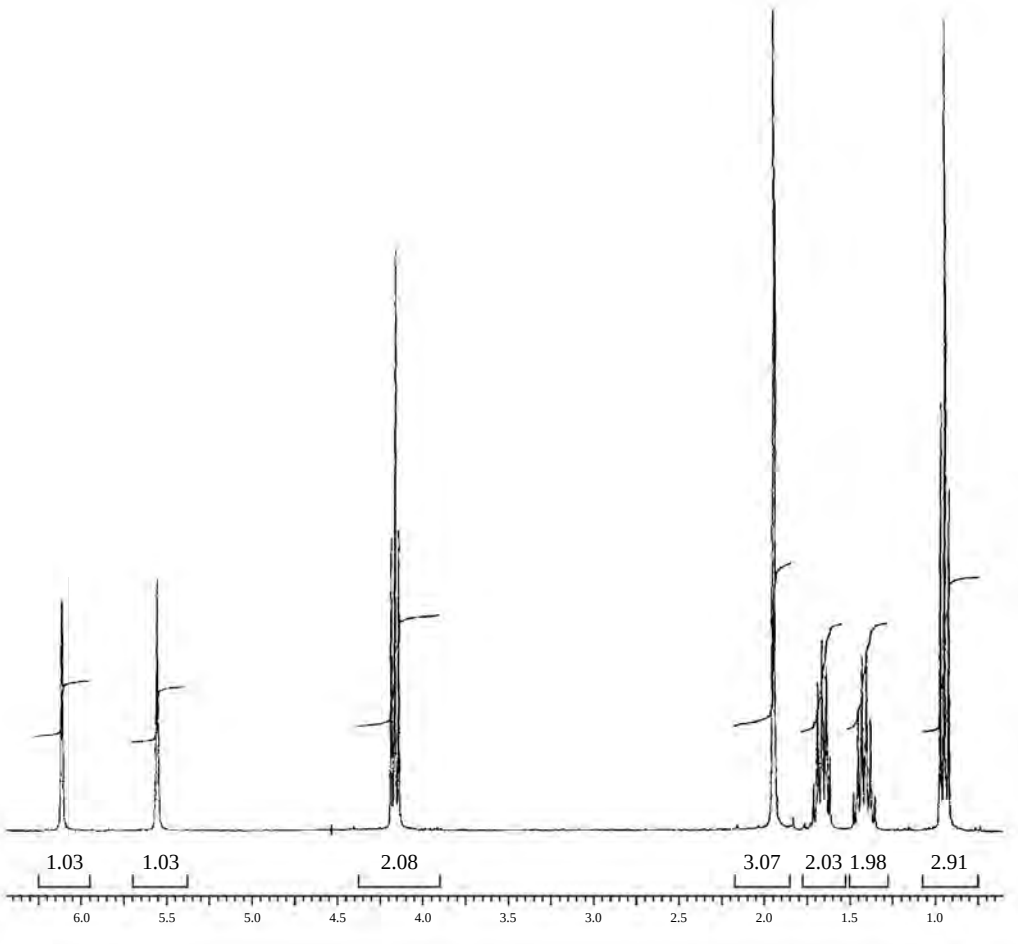
35. A compound with the formula $C_5H_{10}O_2$ shows a very broad band that extends from about 3500 to 2500 cm^{-1} in the infrared spectrum. Another prominent band appears at 1710 cm^{-1}. The ^1H and ^{13}C NMR spectra are shown. Draw the structure for this compound.

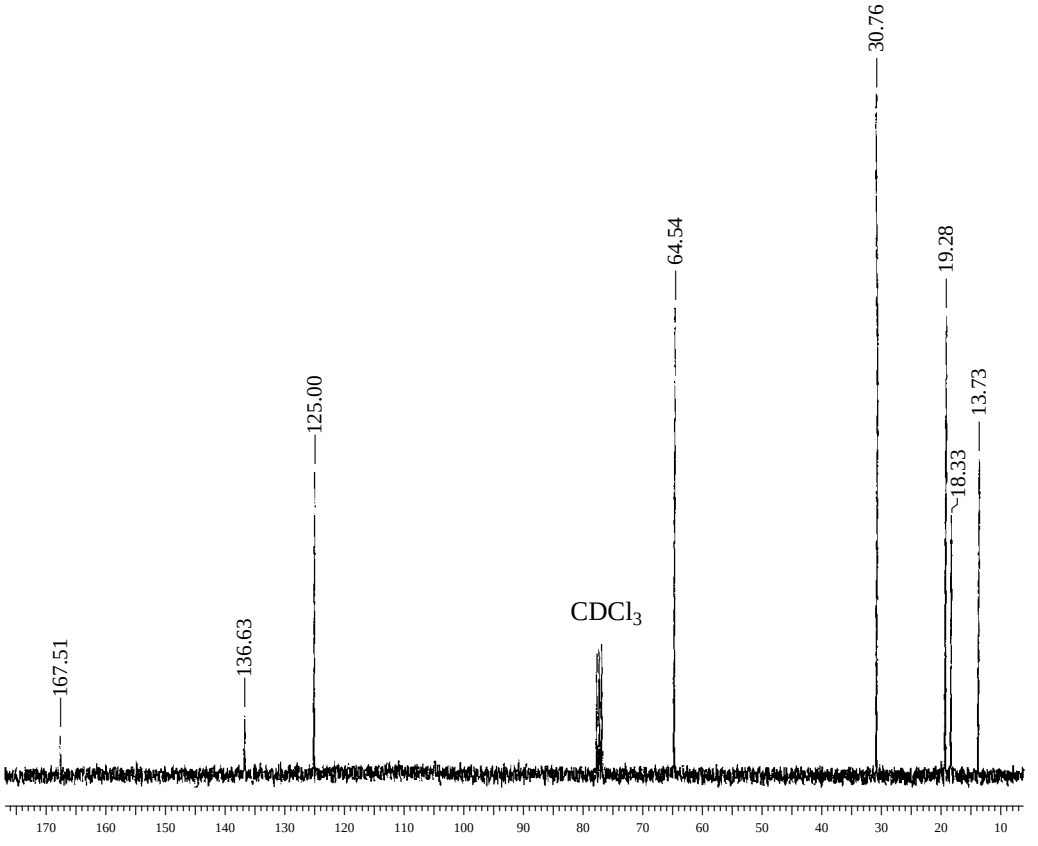




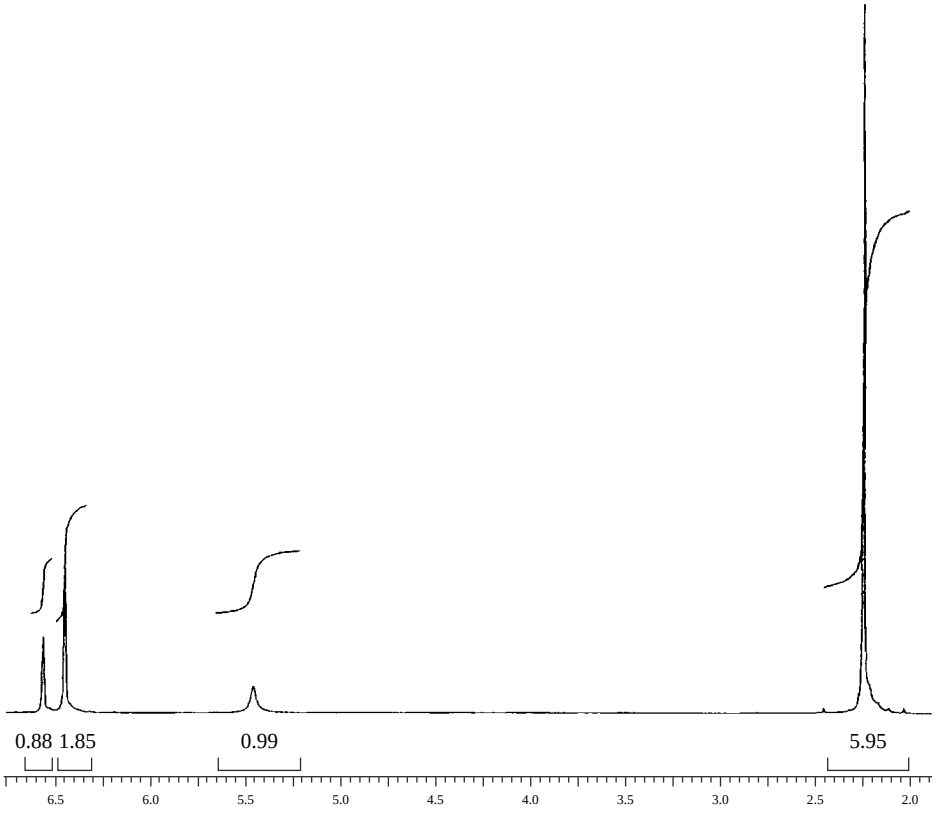
36. A compound with the formula $C_8H_{14}O_2$ shows several bands in the infrared spectrum in the region from 3106 to 2876 cm^{-1}. In addition there are strong peaks that appear at 1720 and 1170 cm^{-1}. A medium-sized peak appears at 1640 cm^{-1}. The ^1H and ^{13}C NMR spectra are shown along with the DEPT data. Draw the structure for this compound.

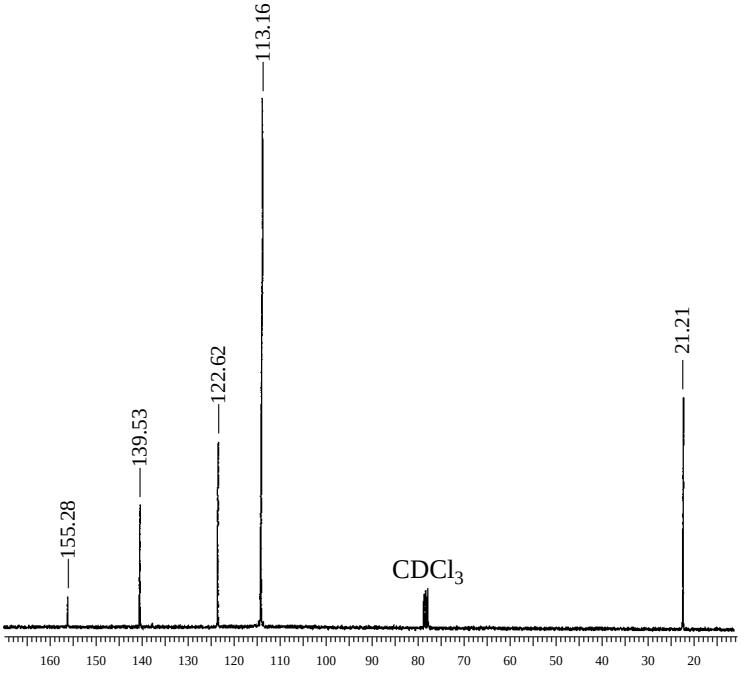
Normal Carbon	DEPT-135	DEPT-90
13.73 ppm	Positive	No peak
18.33	Positive	No peak
19.28	Negative	No peak
30.76	Negative	No peak
64.54	Negative	No peak
125.00	Negative	No peak
136.63	No peak	No peak
167.51	No peak	No peak


1.03
1.03
2.08
3.07
2.03
1.98
2.91
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


167.51
136.63
125.00
CDCl3
64.54
30.76
19.28
18.33
13.73
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

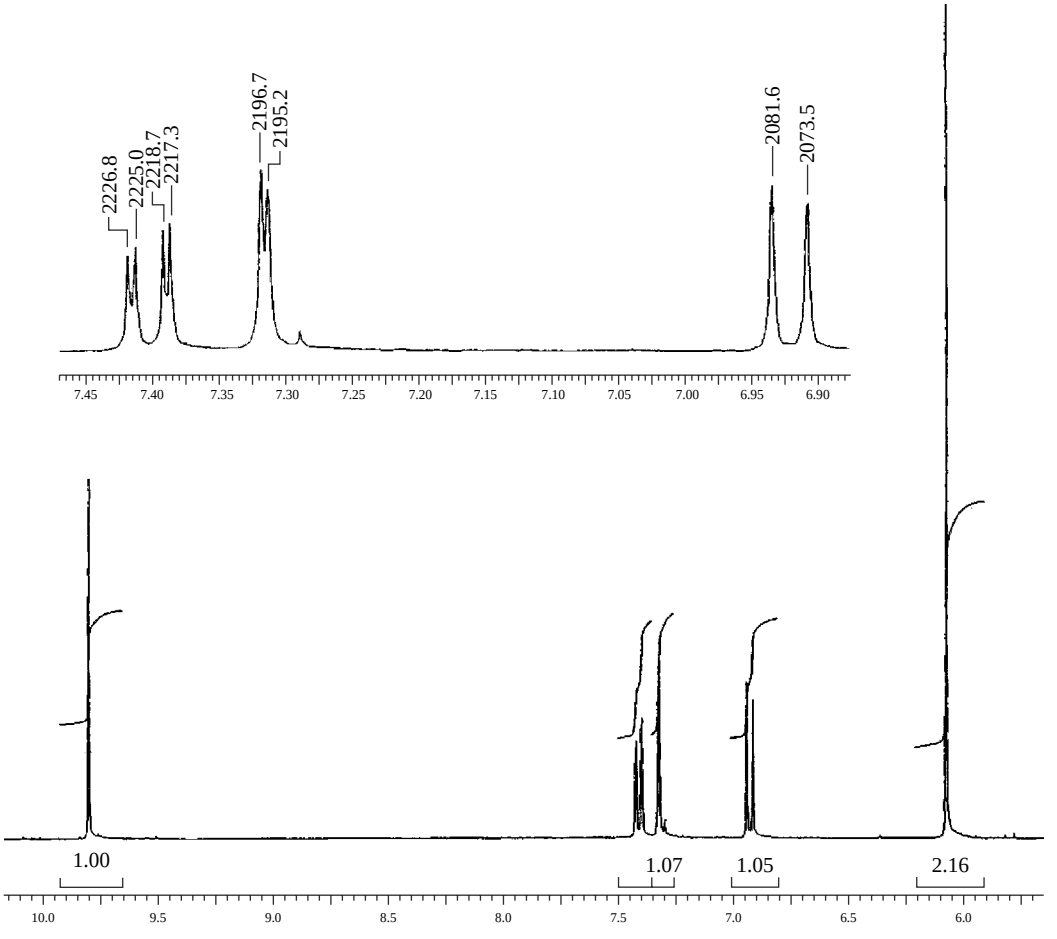
37. A compound with the formula $C_8H_{10}O$ shows a broad peak centering on about 3300 cm^{-1} in the infrared spectrum. In addition, there are several bands appearing in the region from 3035 to 2855 cm^{-1}. There are also medium-sized peaks appearing in the range of 1595 to 1445 cm^{-1}. The ^1H and ^{13}C NMR spectra are shown. Draw the structure for this compound.

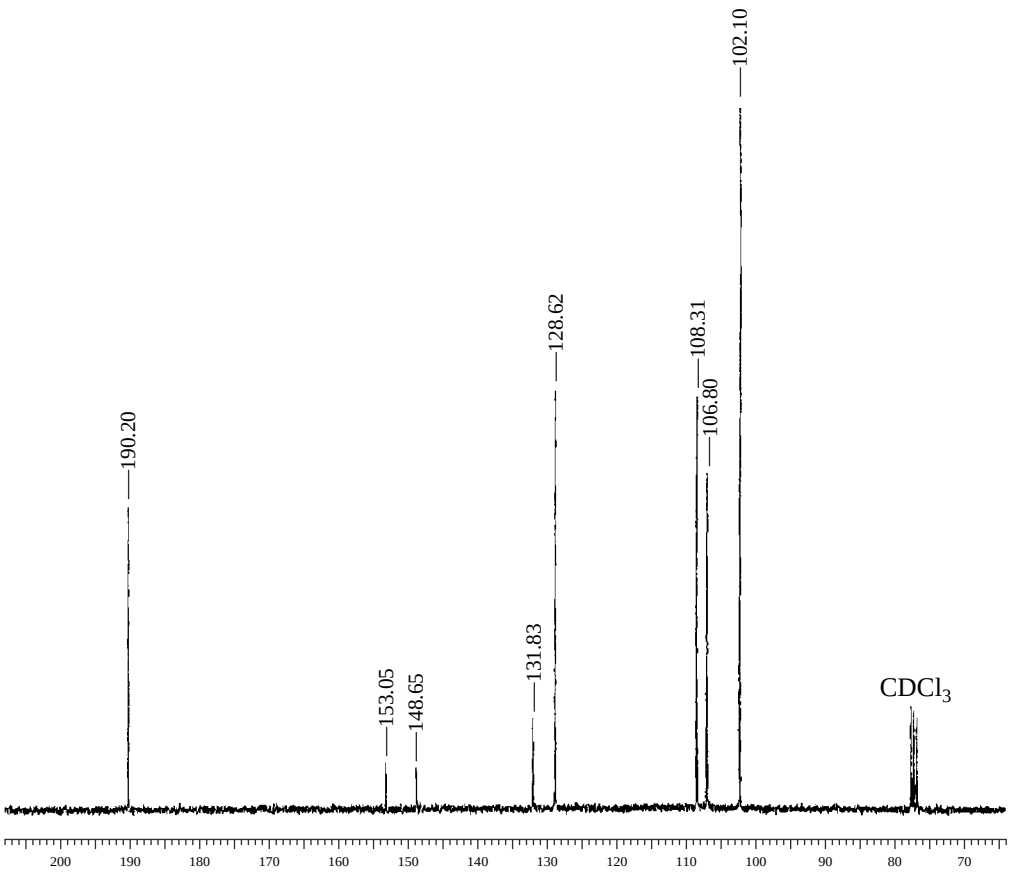




38. A compound with the formula $C_8H_6O_3$ shows weak peaks between 3100 and 2716 cm^{-1} in the infrared spectrum. Very strong peaks appear at 1697 and 1260 cm^{-1}. There are also several medium-sized peaks appearing in the range of 1605 to 1449 cm^{-1}. The ^1H and ^{13}C NMR spectra are shown. The DEPT results are tabulated. Draw the structure for this compound.

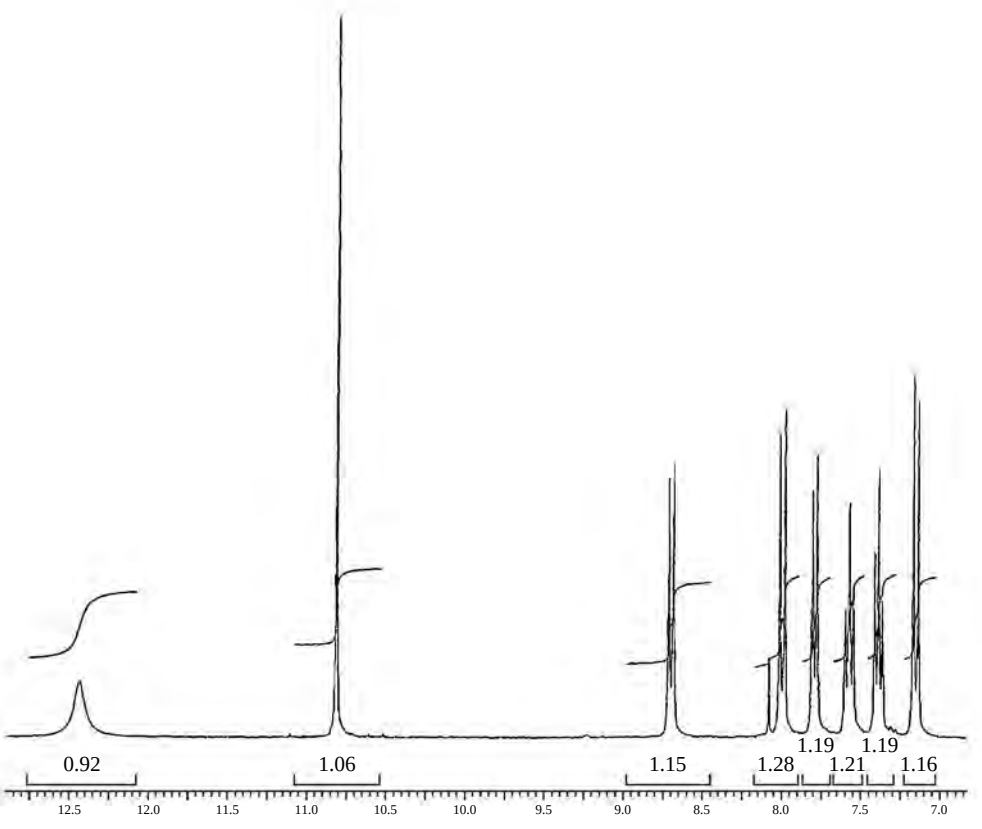
Normal Carbon	DEPT-135	DEPT-90
102.10 ppm	Negative	No peak
106.80	Positive	Positive
108.31	Positive	Positive
128.62	Positive	Positive
131.83	No peak	No peak
148.65	No peak	No peak
153.05	No peak	No peak
190.20	Positive	Positive (C=0)

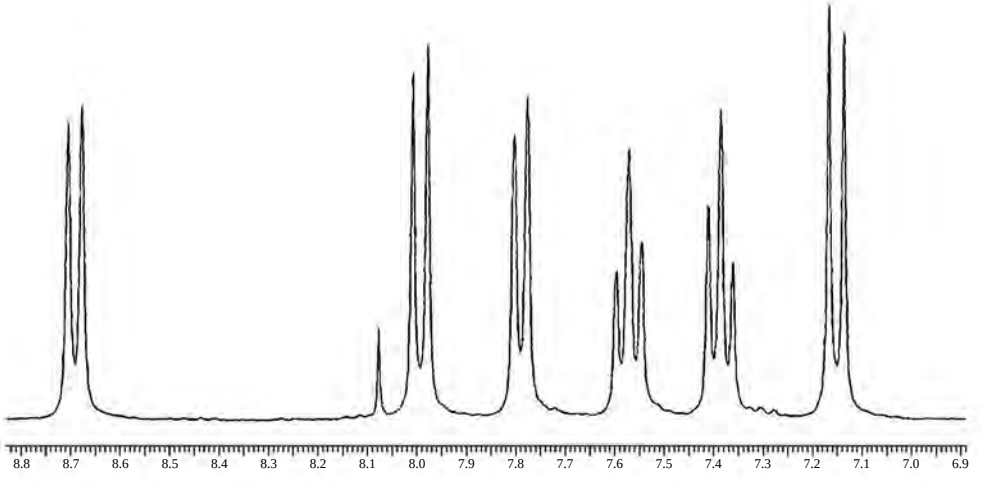


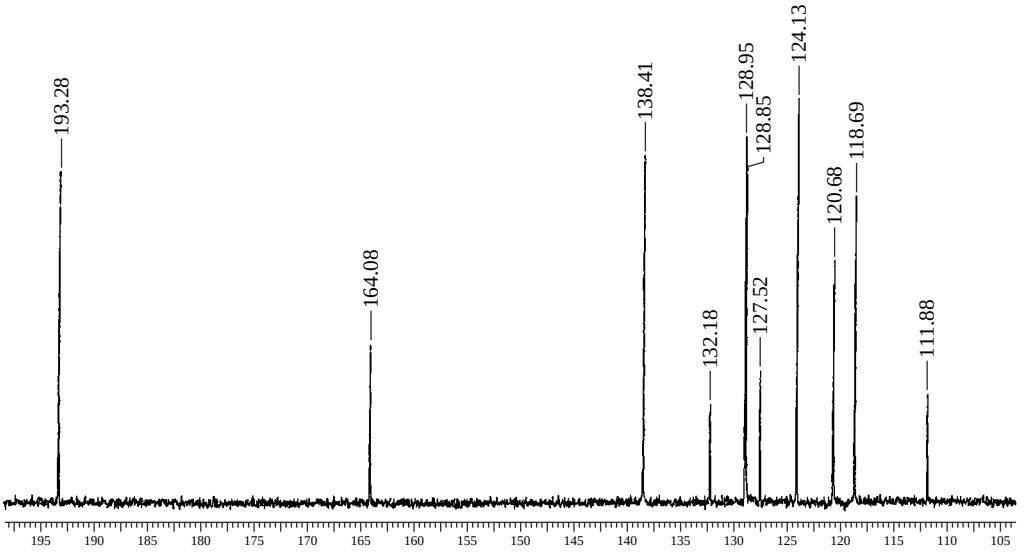


39. The ^{1}H and ^{13}C NMR spectra of a compound with formula $C_{11}H_8O_2$ are shown. The DEPT experimental results are tabulated. The infrared spectrum shows a broad peak centering on about 3300 cm^{-1} and a strong peak at 1670 cm^{-1}. Draw the structure of this compond. *Hint*: There are two substituents on the same ring of a naphthalene system.

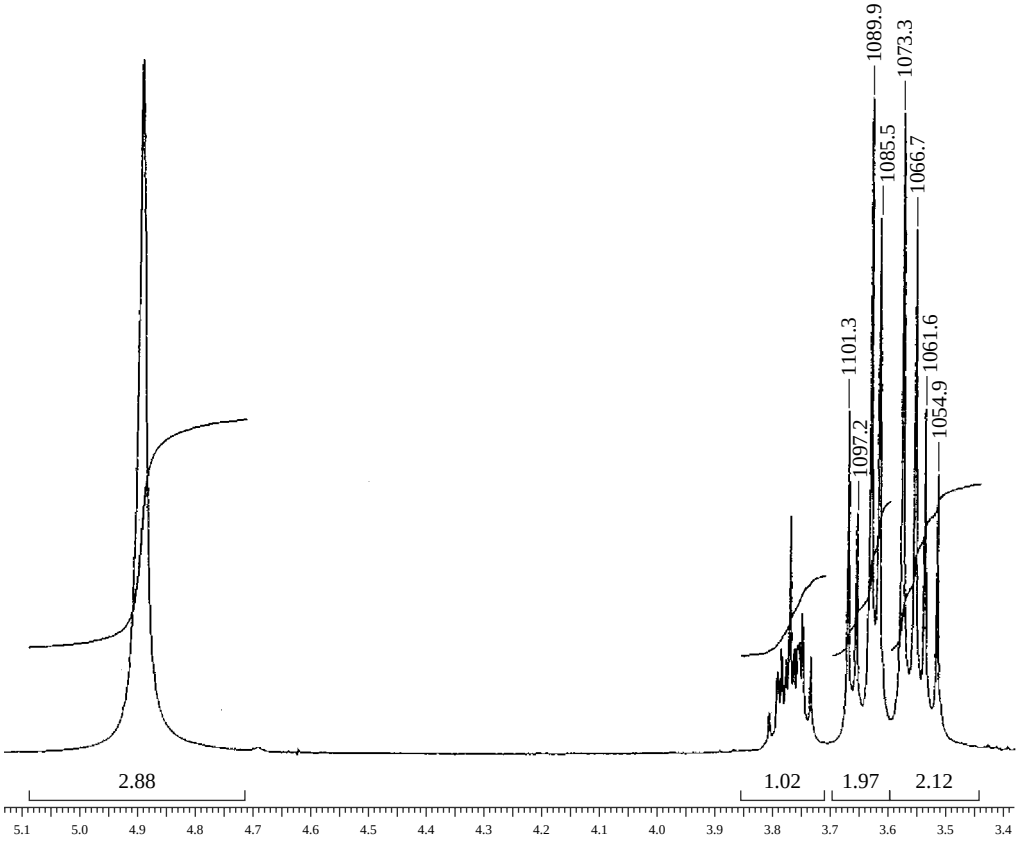
Normal Carbon	DEPT-135	DEPT-90
111.88 ppm	No peak	No peak
118.69	Positive	Positive
120.68	Positive	Positive
124.13	Positive	Positive
127.52	No peak	No peak
128.85	Positive	Positive
128.95	Positive	Positive
132.18	No peak	No peak
138.41	Positive	Positive
164.08	No peak	No peak
193.28	Positive	Positive (C=0)

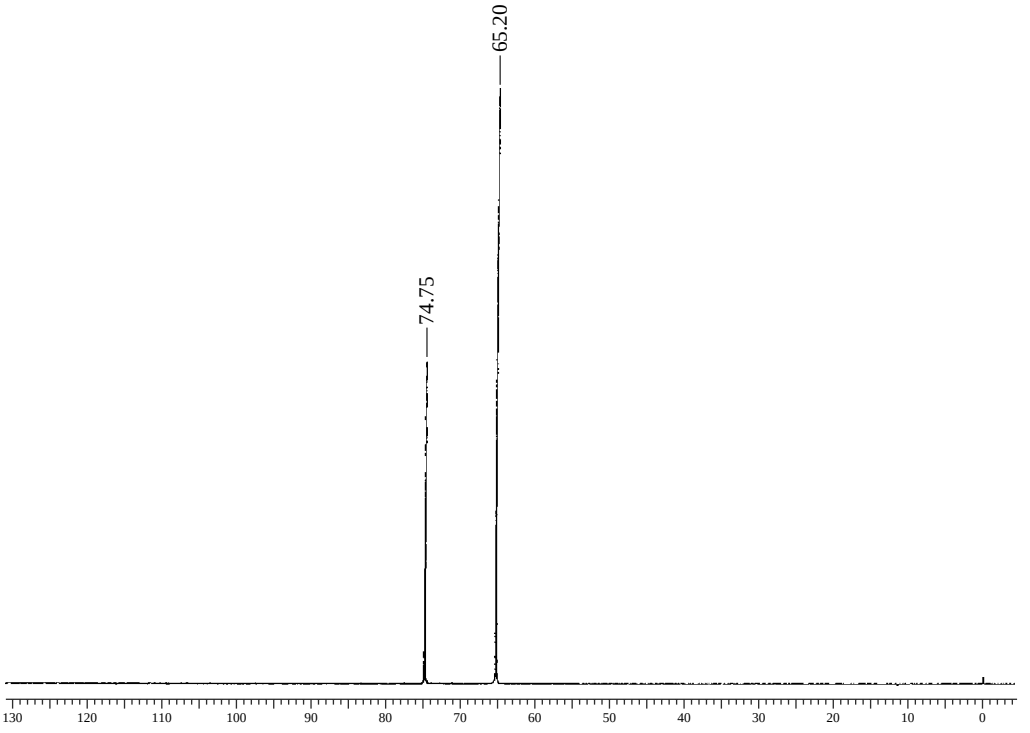

0.92
1.06
1.15
1.28
1.19
1.21
1.19
1.16
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0


8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9

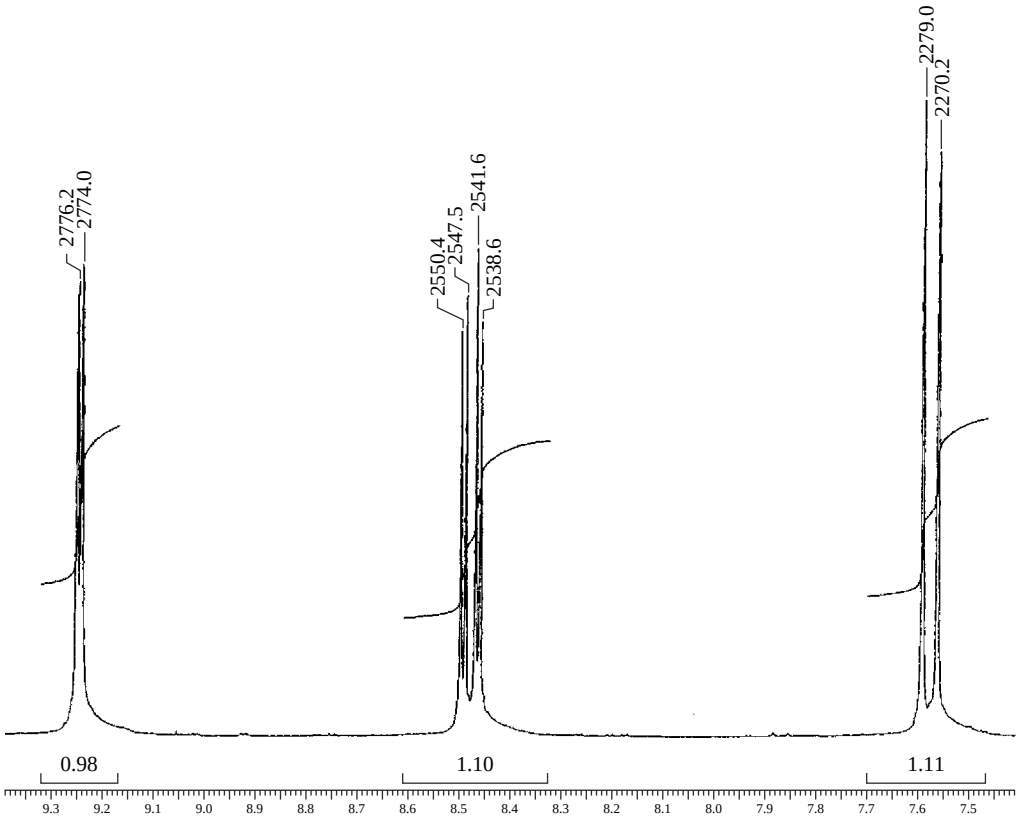


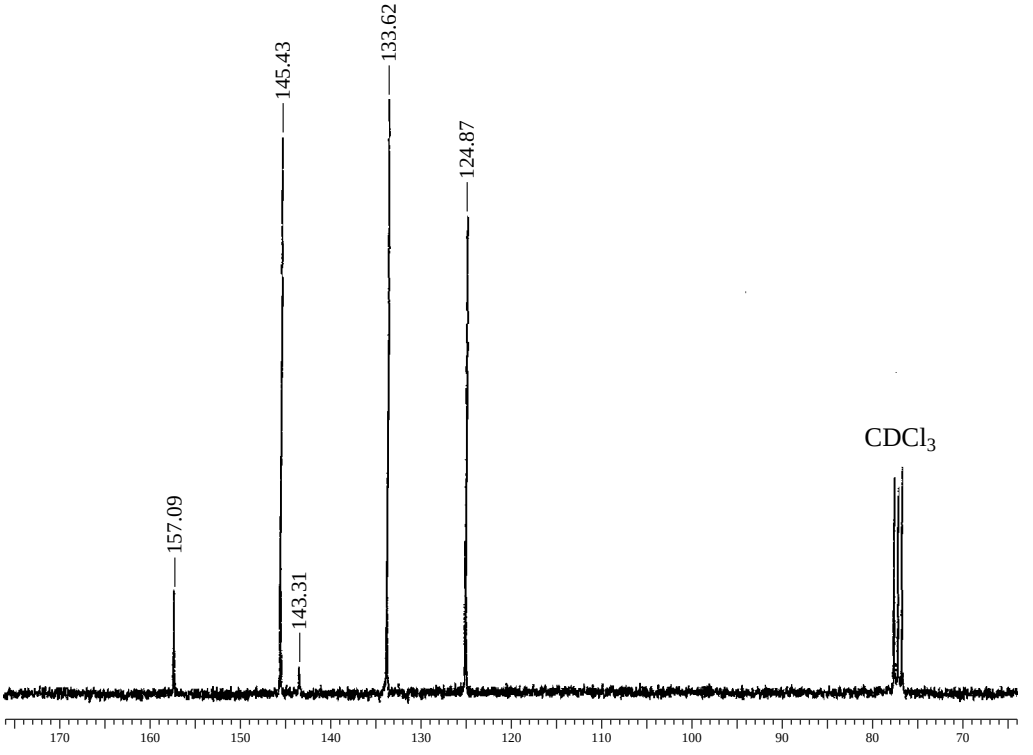
40. The ^{1}H and ^{13}C NMR spectra of a compound with formula $C_3H_8O_3$ are shown. The infrared spectrum shows a broad peak centering on about 3350 cm^{-1} and strong peaks at 1110 and 1040 cm^{-1}. Draw the structure of this compound and determine the coupling constants for pattern at 3.55 and 3.64 ppm to support the structure that you have drawn.





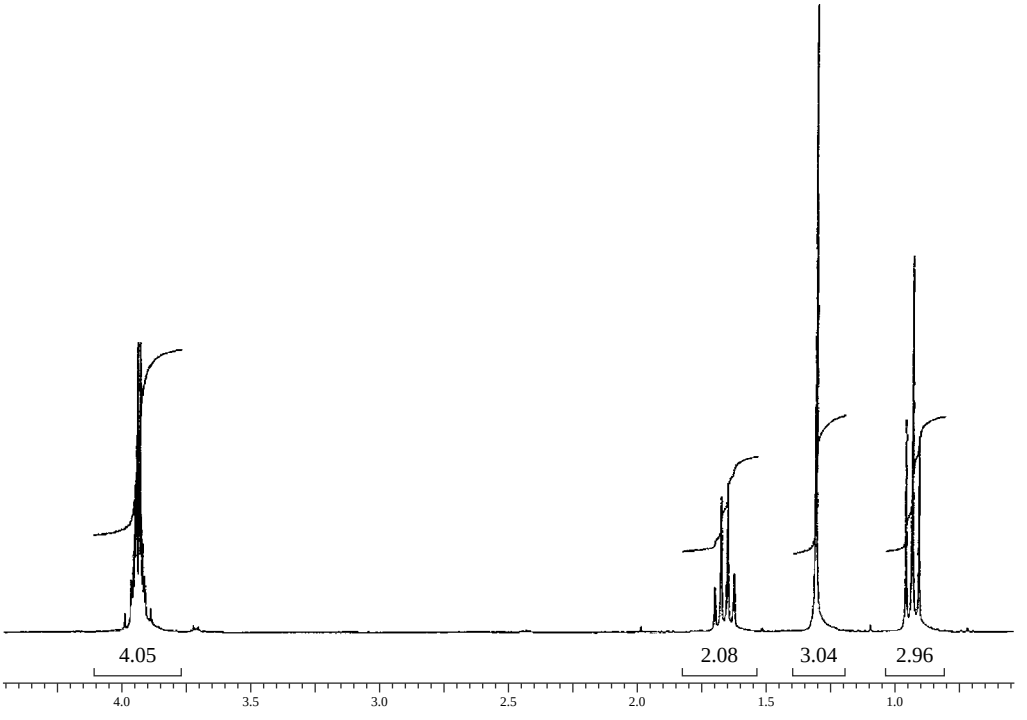
41. The ^{1}H and ^{13}C NMR spectra of a compound with formula $C_5H_3ClN_2O_2$ are shown. The infrared spectrum shows medium-sized peaks at 3095, 3050, 1590, 1564, and 1445 cm^{-1} and strong peaks at 1519 and 1355 cm^{-1}. Determine the coupling constants from the Hertz values printed on the ^{1}H NMR spectrum. The coupling constant data listed in Appendix 5 should allow you to determine the structure(s) of compounds that fit the data.

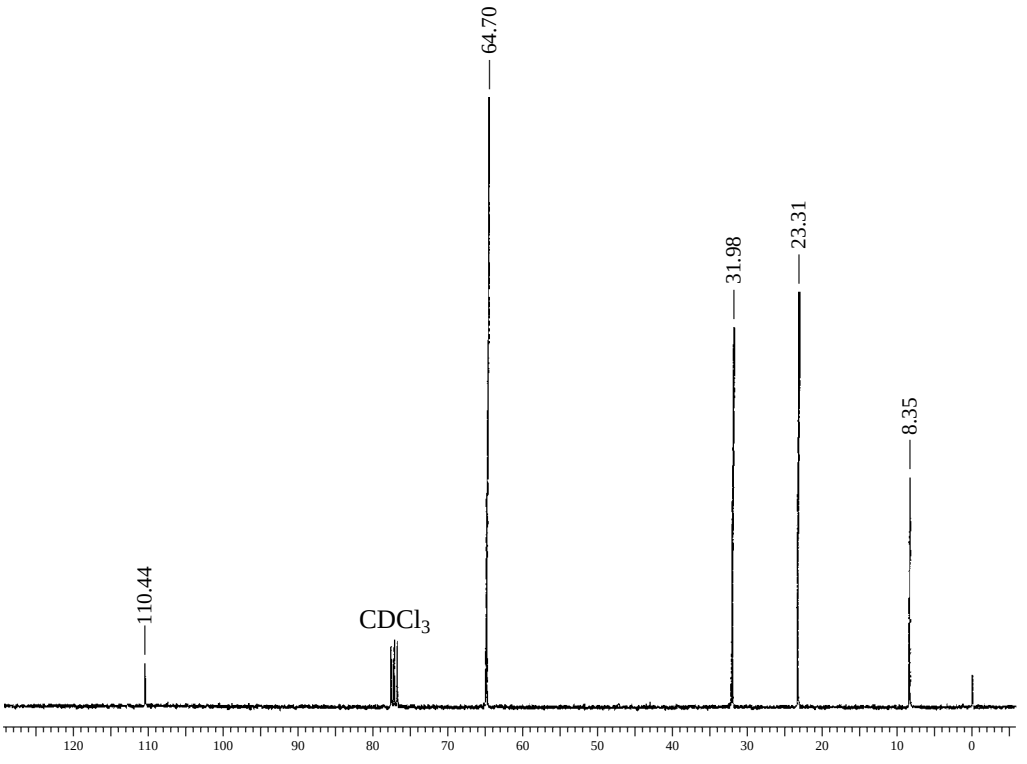

2776.2
2774.0
2550.4
2547.5
2541.6
2538.6
2279.0
2270.2
0.98
1.10
1.11
9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5


157.09
145.43
143.31
133.62
124.87
CDCl3
170 160 150 140 130 120 110 100 90 80 70

42. The ^{1}H NMR spectrum of a compound with formula $C_6H_{12}O_2$ is shown. The DEPT experimental results are tabulated. The infrared spectrum is rather uninteresting. There are four strong bands that appear in the range of 1200 to 1020 cm^{-1}. The compound is prepared from the reaction of 1,2-ethanediol and 2-butanone. Draw the structure of this compound.

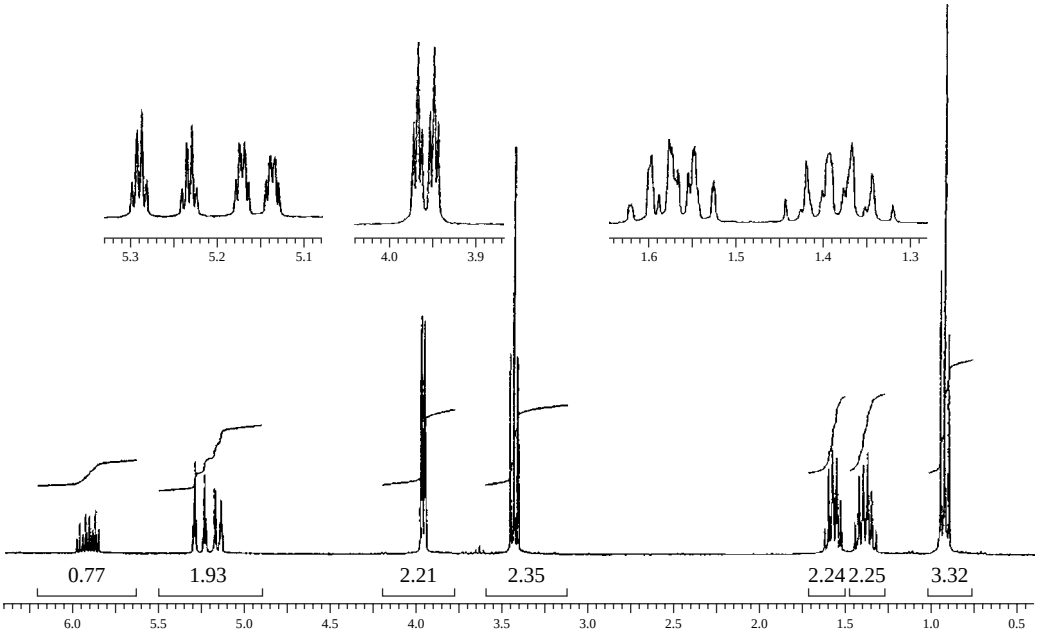
Normal Carbon	DEPT-135	DEPT-90
8.35 ppm	Positive	No peak
23.31	Positive	No peak
31.98	Negative	No peak
64.70	Negative	No peak
110.44	No peak	No peak





43. The ^{1}H NMR spectrum of a compound with formula $C_7H_{14}O$ is shown. The DEPT experimental results are tabulated. The infrared spectrum shows bands at 3080, 2960, 2865, and 1106 cm^{-1} and a medium-intensity band at 1647 cm^{-1}. Draw the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90
13.93 ppm	Positive	No peak
19.41	Negative	No peak
31.91	Negative	No peak
70.20	Negative	No peak
71.80	Negative	No peak
116.53	Negative	No peak
135.16	Positive	Positive



SOURCES OF ADDITIONAL PROBLEMS

Books that Contain Combined Spectral Problems

Ault, A., *Problems in Organic Structural Determination*, McGraw–Hill, New York, 1967.

Banks, R. C., E. R. Matjeka, and G. Mercer, *Introductory Problems in Spectroscopy*, Benjamin/Cummings, Menlo Park, CA, 1980.

Davis, R., and C. H. J. Wells, *Spectral Problems in Organic Chemistry*, Chapman and Hall, New York, 1984.

Field, L. D., S. Sternhell, and J. R. Kalman, *Organic Structures from Spectra*, 2nd ed., John Wiley and Sons, Chichester, England, 1995.

Fuchs, P. L., and C. A. Bunnell, *Carbon-13 NMR Based Organic Spectral Problems*, John Wiley and Sons, New York, 1979.

Shapiro, R. H., and C. H. DePuy, *Exercises in Organic Spectroscopy*, 2nd ed., Holt, Rinehart and Winston, New York, 1977.

Silverstein, R. M., F. X. Webster, and D. J. Kiemle, *Spectrometric Identification of Organic Compounds*, 7th ed., John Wiley and Sons, New York, 2005.

Sternhell, S., and J. R. Kalman, *Organic Structures from Spectra*, John Wiley and Sons, Chichester, England, 1986.

Tomasi, R. A., *A Spectrum of Spectra*, Sunbelt R&T, Inc., Tulsa, OK, 1992.

Williams, D. H., and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th ed., McGraw–Hill, London, 1987.

Websites that Have Combined Spectral Problems

http://www.nd.edu/~smithgrp/structure/workbook.html

The Smith group at the University of Notre Dame has a number of combined problems.

http://www.chem.ucla.edu/~webspectra/

The UCLA Department of Chemistry and Biochemistry in connection with Cambridge University Isotopes Laboratories maintains a website with combined problems. They provide links to other sites with problems.

Websites that Have Spectral Data

http://webbook.nist.gov/chemistry/

National Institute of Standards and Technology (NIST). The site includes gas phase infrared spectra and mass spectral data.

http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi

Integrated Spectral Data Base System for Organic Compounds, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan. This database includes infrared, mass spectra, and NMR data (proton and carbon-13).